Concise Total Synthesis of (+)-Bionectins A and C

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Supporting Material

General Procedures. All reactions were performed in oven-dried or flame-dried round-bottom flasks. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Cannulae or gas-tight syringes with stainless steel needles were used to transfer air- or moisture-sensitive liquids. Where necessary (so noted), solutions were deoxygenated by sparging with argon for a minimum of 10 min. Flash column chromatography was performed as described by Still et al. using granular silica gel (60-Å pore size, 40–63 μm, 4–6% H_2O content, Zeochem).[1] Analytical thin layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) and an aqueous solution of ceric ammonium molybdate (CAM) followed by heating on a hot plate (~ 250 ºC). Organic solutions were concentrated at 29–30 °C on rotary evaporators capable of achieving a minimum pressure of ~2 torr. The benzenesulfonyl photodeprotection was accomplished by irradiation in a Rayonet RMR-200 photochemical reactor (Southern New England Ultraviolet Company, Branford, CT, USA) equipped with 16 lamps (RPR-3500, 24 W, λ_{max} = 350 nm, bandwidth ~ 20 nm).

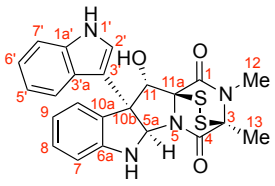
Materials. Commercial reagents and solvents were used as received with the following exceptions: dichloromethane, acetonitrile, tetrahydrofuran, methanol, pyridine, toluene, and triethylamine were purchased from J.T. Baker (Cycletainer™) and were purified by the method of Grubbs *et al*. under positive argon pressure.[2] Nitromethane and nitroethane (from Sigma–Aldrich) were purified by fractional distillation over calcium hydride and were stored over Linde 4Å molecular sieves in Schlenk flasks sealed with septa and teflon tape under argon atmosphere.[3] Titanium (IV) ethoxide (99.99%-Ti) PURATREM and bromine were purchased from Strem Chemicals, Inc.; *N*-Boc-L-sarcosine, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride, *N*-hydroxybenzotriazole, *tert*-butyldimethylsilyl trifluoromethanesulfonate, trifluoroacetic acid, 4-(dimethylamino)pyridine, silver nitrate were purchased from Chem-Impex; 1,4-dimethoxynaphthalene and iodomethane were purchased from Alfa Aesar; di-*tert*-butyl dicarbonate was purchased from Oakwood Products, Inc.; 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) was purchased from OChem Incorporation. All other solvents and chemicals were purchased from Sigma–Aldrich. 1,4-Dimethoxynaphthalene was purified by crystallization from absolute ethanol.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Bruker AVANCE-600 NMR spectrometer (with a Magnex Scientific superconducting actively-shielded magnet) or with a Varian inverse probe 500 INOVA spectrometer, are reported in parts per million on the δ scale, and are referenced from the residual protium in the NMR solvent ($CDCl_3$: δ 7.26 ($CHCl_3$) or DMSO-d_6: δ 2.50 (DMSO-d_5)).[4] Data are reported as follows: chemical shift [multiplicity (br = broad, s = singlet, d = doublet, t = triplet, sp = septet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Bruker AVANCE-600 NMR Spectrometer (with a Magnex Scientific superconducting actively-shielded magnet) or a Bruker AVANCE-400 NMR Spectrometer (with a Magnex Scientific superconducting magnet) or with a Varian 500 INOVA spectrometer, are reported in parts per million on the δ scale, and are referenced from the carbon resonances of the solvent ($CDCl_3$: δ 77.23 or DMSO-d_6: δ 39.52). Data are reported as follows: chemical shift (multiplicity,

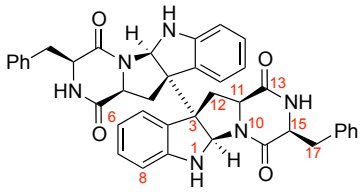
[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
[3] Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth–Heinemann: London, 2003.
[4] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.

coupling constant(s) in Hertz, assignment). Infrared data (IR) were obtained with a Perkin-Elmer 2000 FTIR and are reported as follows: frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad). Optical rotations were measured on a Jasco-1010 polarimeter with a sodium lamp and are reported as follows: $[\alpha]_{\lambda}^{T\,^{\circ}C}$ (c = g/100 mL, solvent). We are grateful to Dr. Li Li and Deborah Bass for obtaining the mass spectrometric data at the Department of Chemistry's Instrumentation Facility, Massachusetts Institute of Technology. High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics APEXIV 4.7 Tesla FT-ICR-MS using an electrospray (ESI) ionization source.

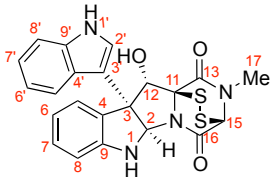
Positional Numbering System. At least three numbering systems for dimeric diketopiperazine alkaloids exist in the literature.[5] In assigning the ^{1}H and ^{13}C NMR data of all intermediates en route to our total syntheses of (+)-bionectins A (**1**) and C (**2**), we wished to employ a uniform numbering scheme. For ease of direct comparison, particularly between early intermediates, non-thiolated diketopiperazines, and advanced compounds, the numbering system used by Barrow for (+)-WIN-64821 (using positional numbers 1–21) is optimal and used throughout this report. In key instances, the products are accompanied by the numbering system as shown below.



(+)-bionectin A (**1**)
Kim's isolation report
Overman's reports



(+)-WIN-64821
Barrow's numbering for the simpler diketopiperazine framework



(+)-bionectin A (**1**)
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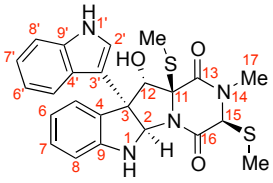

(+)-bionectin C (**2**)
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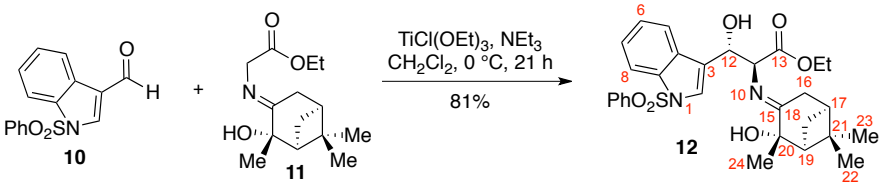
[5] (a) Von Hauser, D.; Weber, H. P.; Sigg, H. P. *Helv. Chim. Acta* **1970**, *53*, 1061. (b) Barrow, C. J.; Cai, P.; Snyder, J. K.; Sedlock, D. M.; Sun, H. H.; Cooper, R. *J. Org. Chem.* **1993**, *58*, 6016. (c) Springer, J. P.; Büchi, G.; Kobbe, B.; Demain, A. L.; Clardy, J. *Tetrahedron Lett.* **1977**, *28*, 2403. (d) Zheng, C.-J. ; Kim, C.-J. ; Bae, K. S. ; Kim, Y.-H. ; Kim, W.-G *J. Nat. Prod.* **2006**, *69*, 1816. (e) DeLorbe, J. E. ; Jabri, S. Y. ; Mennen, S. M. ; Overman, L. E. ; Zhang, F.-L. *J. Am. Chem. Soc.* **2011**, *133*, 6549.



12-Hydroxytryptophan Alcohol 12:

A solution of chlorotitanium (IV) triethoxide[6] (22.5 g, 103 mmol, 1.05 equiv) in dichloromethane (69 mL) was added via cannula to a solution of ethyl 2-((1*S*,2*S*,5*S*)-2-hydroxypinan-3-imino)glycinate[7] (**11**, 24.8 g, 97.8 mmol, 1 equiv) in dichloromethane (300 mL) at 0 °C. A fine powder of 1-(phenylsulfonyl)-1*H*-indole-3-carbaldehyde[8] (**10**, 29.3 g, 103 mmol, 1.05 equiv) was then added as a solid to the reaction mixture. Triethylamine (27.3 mL, 196 mmol, 2.00 equiv) was subsequently added dropwise via syringe and the reaction mixture was stirred at 0 °C. After 21 h, brine (1 L) at 0 °C was added to the reaction mixture and the resulting bilayer suspension was filtered through Celite. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 × 300 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting orange foam was purified by flash column chromatography on silica gel (eluent: gradient, 30→50% ethyl acetate in hexanes) to provide an inseparable mixture of diastereomeric aldol products (42.5 g, 80.6%) as a yellow foam.[9] Structural assignments were made using additional information from gCOSY, HSQC, and gHMBC experiments.

^{1}H NMR (600 MHz, $CDCl_3$, 20 °C):[10]

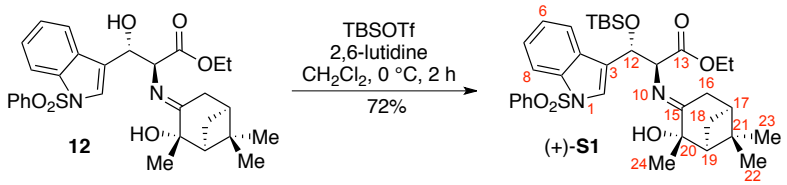
δ 7.96 (d, *J* = 8.3, 1H, C_8**H**), 7.86 (d, *J* = 8.6, 2H, SO_2Ph-*o*-**H**), 7.71 (s, 1H, C_2**H**), 7.67 (d, *J* = 7.8, 1H, C_5**H**), 7.49 (t, *J* = 7.6, 1H, SO_2Ph-*p*-**H**), 7.39 (app-t, *J* = 8.1, 2H, SO_2Ph-*m*-**H**), 7.29 (app-t, *J* = 7.3, 1H, C_7**H**), 7.23 (app-t, *J* = 7.2, 1H, C_6**H**), 5.49 (d, *J* = 6.9, 1H, C_{12}**H**), 4.46 (d, *J* = 6.9, 1H, C_{11}**H**), 4.11–3.99 (m, 2H, CO_2C**H**$_2CH_3$), 3.90 (br-s, 1H, $C_{12}O$**H**), 2.42 (dd, *J* = 2.0, 17.7, 1H, C_{16}**H**$_a$), 2.19 (dd, *J* = 2.7, 18.0, 1H, C_{16}**H**$_b$), 2.11–2.05 (m, 1H, C_{18}**H**$_a$), 2.00 (br-s, 1H, $C_{20}O$**H**), 1.89 (app-t, *J* = 5.8, 1H, C_{19}**H**), 1.87–1.83 (m, 1H, C_{17}**H**), 1.42 (s, 3H, C_{24}**H**), 1.23 (s, 3H, $C_{22/23}$**H**), 1.06 (app-t, *J* = 7.4, 3H, CO_2CH_2C**H**$_3$), 1.02 (d, *J* = 4.7, 1H, C_{18}**H**$_b$), 0.80 (s, 3H, $C_{22/23}$**H**).

^{13}C NMR (150 MHz, $CDCl_3$, 20 °C):[10]

δ 180.6 (**C**$_{15}$), 169.5 (**C**$_{13}$), 138.0 (SO_2Ph-*ipso*-**C**), 134.5 (**C**$_9$), 133.6 (SO_2Ph-*p*-**C**), 129.9 (**C**$_4$), 129.2 (SO_2Ph-*m*-**C**), 126.7 (SO_2Ph-*o*-**C**), 124.9 (**C**$_7$), 124.7 (**C**$_2$), 123.1 (**C**$_6$), 122.3 (**C**$_3$), 120.2 (**C**$_5$), 113.5 (**C**$_8$), 76.8 (**C**$_{20}$), 67.7 (**C**$_{12}$), 67.4 (**C**$_{11}$), 61.1

[6] Holoway, H. *Chem. Ind.* **1962**, *3*, 214.
[7] (a) Oguri, T.; Kaway, N.; Yamada, S. *Chem. Pharm. Bull.* **1978**, *26*, 803. (b) Solladiè-Cavallo, A.; Simon, M. C. *Tetrahedron Lett.***1989**, *30*, 6011. (c) Solladiè-Cavallo, A.; Simon-Wermeister, M. C.; Schwarz, J. *Organometallics* **1993**, *12*, 3743.
[8] Wenkert, E.; Moeller, P. D. R.; Piettre,S. R. *J. Am. Chem. Soc.* **1988**, *110*, 7188.
[9] The aldol products were highly prone to degradation through a retro-aldol pathway; thus, the mixture of diastereomers was quickly isolated and immediately used in the subsequent reaction.
[10] Only the peaks corresponding to the major diastereomer are tabulated.

	($CO_2\mathbf{C}H_2CH_3$), 50.3 ($\mathbf{C}_{19}$), 38.5 ($\mathbf{C}_{21}$), 38.2 ($\mathbf{C}_{17}$), 33.8 ($\mathbf{C}_{16}$), 28.1 ($\mathbf{C}_{24}$), 27.8 ($\mathbf{C}_{18}$), 27.1 ($\mathbf{C}_{22/23}$), 22.6 ($\mathbf{C}_{22/23}$), 13.7 ($CO_2CH_2\mathbf{C}H_3$).
FTIR (thin film) cm^{-1}:	3422 (br-m), 2926 (s), 1734 (s), 1649 (m), 1557 (w), 1448 (s), 1373 (s), 1273 (m), 1181 (s), 1126 (m), 1089 (m), 1022 (w), 978 (w), 920 (w), 751 (m).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{29}H_{35}N_2O_6S$ $[M+H]^+$: 539.2210, found: 539.2198.
TLC (50% ethyl acetate in hexanes), R*f*:	0.49 (UV, CAM, $KMnO_4$).



12-Hydroxytryptophan Silyl Ether (+)-S1:

t-Butyldimethylsilyl trifluoromethanesulfonate (21.8 mL, 94.7 mmol, 1.20 equiv) was added via syringe to a solution of 12-hydroxytryptophan alcohol **12** (42.5 g, 78.9 mmol, 1 equiv) and 2,6-lutidine (18.7 mL, 161 mmol, 2.04 equiv) in dichloromethane (900 mL) at 0 °C. After 2 h, saturated aqueous ammonium chloride solution (750 mL) was added to the reaction mixture and the resulting solution was allowed to warm to 23 °C. After 10 min, the layers were separated and the aqueous layer was further extracted with dichloromethane (2 × 200 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting orange foam was purified by flash column chromatography on silica gel (eluent: 20% ethyl acetate in hexanes) to provide the 12-hydroxytryptophan silyl ether (+)**-S1** (37.1 g, 72.0%) as a yellow oil. Structural assignments were made using additional information from gCOSY, HSQC, and gHMBC experiments.

^{1}H NMR (600 MHz, $CDCl_3$, 20 ºC):

δ 7.97 (d, *J* = 8.3, 1H, C_8**H**), 7.84 (d, *J* = 7.4, 2H, SO_2Ph-*o*-**H**), 7.77 (d, *J* = 7.8, 1H, C_5**H**), 7.52 (s, 1H, C_2**H**), 7.50 (t, *J* = 7.9, 1H, SO_2Ph-*p*-**H**), 7.39 (app-t, *J* = 8.2, 2H, SO_2Ph-*m*-**H**), 7.30 (app-t, *J* = 7.3, 1H, C_7**H**), 7.24 (app-t, *J* = 7.1, 1H, C_6**H**), 5.53 (d, *J* = 8.5, 1H, C_{12}**H**), 4.41 (d, *J* = 8.6, 1H, C_{11}**H**), 4.23–4.14 (m, 2H, CO_2C**H**$_2CH_3$), 2.42 (app-dt, *J* = 2.5, 18.1, 1H, C_{16}**H**$_a$), 2.00 (dd, *J* = 2.9, 18.1, 1H, C_{16}**H**$_b$), 1.93–1.90 (m, 1H, C_{18}**H**$_a$), 1.80 (app-t, *J* = 5.8, 1H, C_{19}**H**), 1.75–1.71 (m, 1H, C_{17}**H**), 1.42 (br-s, 1H, C_{20}O**H**), 1.31 (s, 3H, C_{24}**H**), 1.06 (app-t, *J* = 7.2, 3H, CO_2CH_2C**H**$_3$), 1.18 (s, 3H, $C_{22/23}$**H**), 0.82 (s, 9H, $Si(CH_3)_2C(C$**H**$_3)_3$), 0.70 (d, *J* = 5.2, 1H, C_{18}**H**$_b$), 0.69 (s, 3H, $C_{22/23}$**H**), 0.03 (s, 3H, $Si(C$**H**$_3)_2C(CH_3)_3$), –0.30 (s, 3H, $Si(C$**H**$_3)_2C(CH_3)_3$).

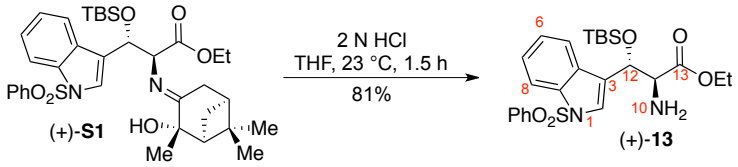
^{13}C NMR (150 MHz, $CDCl_3$, 20 ºC):

δ 180.2 (**C**$_{15}$), 170.0 (**C**$_{13}$), 138.3 (SO_2Ph-*ipso*-**C**), 135.2 (**C**$_9$), 133.9 (SO_2Ph-*p*-**C**), 129.5 (**C**$_4$), 129.4 (SO_2Ph-*m*-**C**), 126.8 (SO_2Ph-*o*-**C**), 125.2 (**C**$_7$), 124.6 (**C**$_3$), 124.0 (**C**$_2$), 123.3 (**C**$_6$), 121.0 (**C**$_5$), 114.1 (**C**$_8$), 76.4 (**C**$_{20}$), 70.7 (**C**$_{11}$), 70.0 (**C**$_{12}$), 61.1 (CO_2**C**H_2CH_3), 49.8 (**C**$_{19}$), 38.4 (**C**$_{21}$), 38.1 (**C**$_{17}$), 33.4 (**C**$_{16}$), 28.3 (**C**$_{24}$), 27.8 (**C**$_{18}$), 27.3 (**C**$_{22/23}$), 25.7 ($Si(CH_3)_2C($**C**$H_3)_3$)), 22.8 (**C**$_{22/23}$), 18.1 ($Si(CH_3)_2$**C**$(CH_3)_3$), 14.4 (CO_2CH_2**C**H_3), –4.6 ($Si($**C**$H_3)_2C(CH_3)_3$), –5.3 ($Si($**C**$H_3)_2C(CH_3)_3$).

FTIR (thin film) cm^{-1}:

2929 (s), 1735 (s), 1652 (m), 1559 (w), 1494 (w), 1448 (s), 1372 (s), 1259 (m), 1179 (s), 1088 (s), 977 (w), 837 (m), 780 (m), 750 (m), 686 (m).

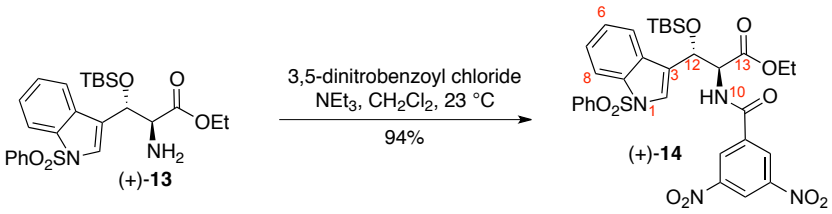
HRMS (ESI) (*m*/*z*):	calc'd for $C_{35}H_{49}N_2O_6SSi$ $[M+H]^+$: 653.3075, found: 653.3063.
$[\alpha]_D^{24}$:	+3.1 (*c* = 0.30, $CHCl_3$).
TLC (33% ethyl acetate in hexanes), R*f*:	0.42 (UV, CAM).



12-Hydroxytryptophan Amine (+)-13:

Aqueous hydrogen chloride solution (2 N, 520 mL) was added to a solution of 12-hydroxytryptophan silyl ether (+)-**S1** (37.1 g, 56.8 mmol, 1 equiv) in tetrahydrofuran (520 mL) at 23 °C. After 1.5 h, the mixture was concentrated to remove the organic solvent. The resulting mixture was extracted with ethyl acetate (3 × 500 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting orange foam was purified by flash column chromatography on silica gel (eluent: gradient, 20→30→100% ethyl acetate in hexanes) to provide 12-hydroxytryptophan amine (+)**-13** (23.0 g, 80.5%) as a yellow foam. Structural assignments were made using additional information from gCOSY, HSQC, and gHMBC experiments.

^{1}H NMR (600 MHz, $CDCl_3$, 20 ºC):	δ 8.00 (d, *J* = 8.3, 1H, C_8**H**), 7.83 (d, *J* = 7.4, 2H, SO_2Ph-*o*-**H**), 7.64 (d, *J* = 7.9, 1H, C_5**H**), 7.52 (t, *J* = 7.4, 1H, SO_2Ph-*p*-**H**), 7.49 (s, 1H, C_2**H**), 7.41 (app-t, *J* = 8.2, 2H, SO_2Ph-*m*-**H**), 7.32 (app-t, *J* = 7.4, 1H, C_7**H**), 7.22 (app-t, *J* = 7.3, 1H, C_6**H**), 5.01 (d, *J* = 6.5, 1H, C_{12}**H**), 4.10–3.98 (m, 2H, CO_2C**H**$_2CH_3$), 3.78 (d, *J* = 6.5, 1H, C_{11}**H**), 1.13 (app-t, *J* = 7.1, 3H, CO_2CH_2C**H**$_3$), 0.80 (s, 9H, $Si(CH_3)_2C(C$**H**$_3)_3$), 0.00 (s, 3H, $Si(C$**H**$_3)_2C(CH_3)_3$), –0.33 (s, 3H, $Si(C$**H**$_3)_2C(CH_3)_3$).
^{13}C NMR (150 MHz, $CDCl_3$, 20 ºC):	δ 172.9 (**C**$_{13}$), 138.1 (SO_2Ph-*ipso*-**C**), 135.2 (**C**$_9$), 134.0 (SO_2Ph-*p*-**C**), 129.4 (SO_2Ph-*m*-**C**), 129.0 (**C**$_4$), 126.8 (SO_2Ph-*o*-**C**), 125.2 (**C**$_7$), 124.6 (**C**$_2$), 123.5 (**C**$_6$), 122.9 (**C**$_3$), 121.1 (**C**$_5$), 114.0 (**C**$_8$), 72.0 (**C**$_{12}$), 61.1 (CO_2**C**H_2CH_3), 60.8 (**C**$_{11}$), 25.7 ($Si(CH_3)_2C($**C**$H_3)_3$), 18.2 ($Si(CH_3)_2$**C**$(CH_3)_3$), 14.1 (CO_2CH_2**C**H_3), –4.8 ($Si($**C**$H_3)_2C(CH_3)_3$), –5.3 ($Si($**C**$H_3)_2C(CH_3)_3$).
FTIR (thin film) cm^{-1}:	2931 (s), 2858 (s), 1735 (s), 1560 (w), 1448 (m), 1372 (s), 1258 (m), 1180 (s), 1088 (m), 1023 (w), 976 (w), 838 (s), 751 (s), 686 (m).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{25}H_{35}N_2O_5SSi$ $[M+H]^+$: 503.2030, found: 503.2016.
$[\alpha]_D^{24}$:	+31 (*c* = 0.45, $CHCl_3$).
TLC (50% ethyl acetate in hexanes), R*f*:	0.47 (UV, CAM, $KMnO_4$).



12-Hydroxytryptophan 3,5-Dinitrobenzamide (+)-14:

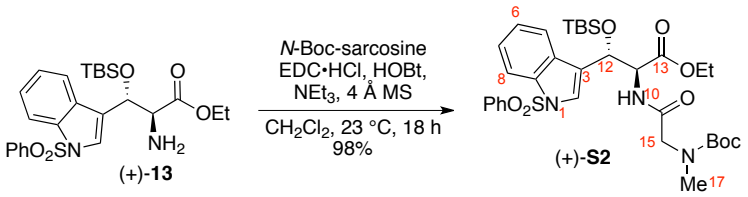
Triethylamine (83.1 μL, 596 μmol, 2.00 equiv) was added to a solution of 12-hydroxytryptophan amine (+)-**13** (100 mg, 198 μmol, 1 equiv) and 3,5-dinitrobenzoyl chloride (68.7 mg, 298 μmol, 1.50 mmol) in dichloromethane (10 mL) at 23 °C. After 1 h, saturated aqueous ammonium chloride solution was added (5 mL) to the reaction mixture. After 5 min, the layers were separated, and the aqueous layer was further extracted with ethyl acetate (2 × 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting orange foam was purified by flash column chromatography on silica gel (eluent: gradient, 20→40 % ethyl acetate in hexanes) to provide 12-hydroxytryptophan 3,5-dinitrobenzamide (+)-**14** (129 mg, 93.9%) as a yellow solid. Structural assignments were made using additional information from gCOSY, HSQC, and gHMBC experiments.

^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ 9.20 (s, 1H, Bz-*p*-**H**), 8.95 (s, 2H, Bz-*o*-**H**), 8.05 (d, J = 8.1, 1H, C_8**H**), 7.98 (d, J = 7.6, 1H, C_5**H**), 7.86 (d, J = 7.7, 2H, SO_2Ph-*o*-**H**), 7.54 (t, J = 7.2, 1H, SO_2Ph-*p*-**H**), 7.47 (s, 1H, C_2**H**), 7.43 (app-t, J = 7.5, 2H, SO_2Ph-*m*-**H**), 7.39 (app-t, J = 7.7, 1H, C_7**H**), 7.35 (app-t, J = 7.2, 1H, C_6**H**), 7.31 (d, J = 6.5, 1H, N_{10}**H**), 5.48 (app-s, 1H, C_{12}**H**), 5.10 (d, J = 5.0, 1H, C_{11}**H**), 4.16 (m, 1H, $COCH_{2a}CH_3$), 4.06 (m, 1H, $CO_2CH_{2b}CH_3$), 1.14 (app-t, J = 7.0, 3H, $CO_2CH_2CH_3$), 0.93 (s, 9H, $Si(CH_3)_2C(CH_3)_3$), 0.00 (s, 3H, $Si(CH_3)_2C(CH_3)_3$), –0.15 (s, 3H, $Si(CH_3)_2C(CH_3)_3$).

^{13}C NMR (150 MHz, $CDCl_3$, 20 °C): δ 168.8 (C_{13}), 162.4 ($C{=}O_{Bz}$), 148.9 (Bz-*m*-**C**), 138.2 (SO_2Ph-*ipso*-**C**), 137.2 (Bz-*ipso*-**C**), 135.5 (C_9), 134.1 (SO_2Ph-*p*-**C**), 129.4 (SO_2Ph-*m*-**C**), 128.6 (C_4), 127.3 (Bz-*o*-**C**), 126.8 (SO_2Ph-*o*-**C**), 125.4 (C_7), 124.2 (C_2), 123.9 (C_6), 122.7 (C_3), 121.7 (Bz-*p*-**C**), 120.5 (C_5), 114.0 (C_8), 70.1 (C_{12}), 62.3 ($CO_2CH_2CH_3$), 59.3 (C_{11}), 25.7 ($Si(CH_3)_2C(CH_3)_3$), 18.3 ($Si(CH_3)_2C(CH_3)_3$), 14.2 ($CO_2CH_2CH_3$), –4.6 ($Si(CH_3)_2C(CH_3)_3$), –5.1 ($Si(CH_3)_2C(CH_3)_3$).

FTIR (thin film) cm^{-1}: 3394 (br), 2932 (w), 2362 (m), 1736 (m), 1674 (m), 1545 (s), 1448 (m), 1345 (s), 1253 (m), 1180 (s), 1119 (m), 1093 (m), 977 (w), 920 (w), 838 (m), 726 (m).

HRMS (ESI) (*m*/*z*):	calc'd for $C_{32}H_{40}N_5O_{10}SSi$ $[M+NH_4]^+$: 714.2260, found: 714.2251.
$[\alpha]_D^{24}$:	+20 (*c* = 0.37, $CHCl_3$).
TLC (20% ethyl acetate in hexanes), R*f*:	0.21 (UV, CAM).



Dipeptide (+)-S2:

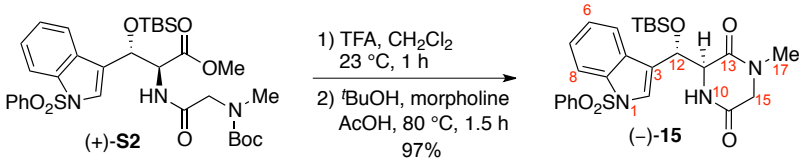
A round-bottom flask was charged sequentially with 12-hydroxytryptophan amine (+)-**13** (7.05 g, 14.0 mmol, 1 equiv), *N*-Boc-sarcosine (3.45 g, 18.2 mmol, 1.30 equiv), *N*-hydroxybenzotriazole (2.84 g, 21.0 mmol, 1.50 equiv), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrogen chloride (5.37 g, 28.0 mmol, 2.00 equiv), and powdered 4 Å molecular sieves (4.00 g), and the contents were placed under an atmosphere of argon. Dichloromethane (100 mL) was introduced via cannula and the resulting solution was cooled to 0 °C. Triethylamine (5.86 mL, 42.0 mmol, 3.00 equiv) was subsequently added dropwise via syringe and the reaction mixture was allowed to warm slowly to 23 °C. After 18 h, saturated aqueous sodium bicarbonate solution (200 mL) was added, and the aqueous layer was extracted with ethyl acetate (3 × 250 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting orange foam was purified by flash column chromatography on silica gel (eluent: 50% ethyl acetate in hexanes) to provide dipeptide (+)-**S2** (9.05 g, 98%) as a yellow foam. Structural assignments were made using additional information from gCOSY, HSQC, and gHMBC experiments.

^{1}H NMR (500 MHz, DMSO-d_6, 60 °C): δ 7.97 (d, J = 7.7, 1H, N_{10}**H**), 7.89 (d, J = 8.3, 1H, C_8**H**), 7.87 (d, J = 7.7, 2H, SO_2Ph-*o*-**H**), 7.76 (d, J = 7.7, 1H, C_5**H**), 7.67 (t, J = 7.3, 1H, SO_2Ph-*p*-**H**), 7.64 (s, 1H, C_2**H**), 7.55 (app-t, J = 7.7, 2H, SO_2Ph-*m*-**H**), 7.33 (app-t, J = 7.7, 1H, C_7**H**), 7.26 (app-t, J = 7.7, 1H, C_6**H**), 5.16 (d, J = 7.7, 1H, C_{12}**H**), 4.75 (app-t, J = 7.8, 1H, C_{11}**H**), 4.08 (q, J = 7.1, 2H, CO_2C**H**$_2CH_3$), 3.85–3.65 (m, 1H, C_{15}**H**$_a$), 3.44 (d, J = 17.0, 1H, C_{15}**H**$_b$), 3.14 (s, 3H, C_{17}**H**), 1.24 (br-s, 9H, $CO_2C(C$**H**$_3)_3$), 1.17 (t, J = 7.1, 3H, CO_2CH_2C**H**$_3$), 0.74 (s, 9H, $Si(CH_3)_2C(C$**H**$_3)_3$), –0.04 (s, 3H, $Si(C$**H**$_3)_2C(CH_3)_3$), –0.39 (s, 3H, $Si(C$**H**$_3)_2C(CH_3)_3$).

^{13}C NMR (125.8 MHz, DMSO-d_6, 60 °C): δ 171.0 (**C**$_{13}$), 169.4 (**C**$_{16}$), 156.2 ($CO_2C(CH_3)_3$), 138.5 (SO_2Ph-*ipso*-**C**), 136.1 (**C**$_9$), 135.6 (SO_2Ph-*p*-**C**), 130.9 (SO_2Ph-*m*-**C**), 129.6 (**C**$_4$), 127.6 (SO_2Ph-*o*-**C**), 126.1 (**C**$_7$), 126.1 (**C**$_2$), 124.5 (**C**$_6$), 123.6 (**C**$_3$), 122.1 (**C**$_5$), 114.4 (**C**$_8$), 80.3 (CO_2**C**$(CH_3)_3$), 70.2 (**C**$_{12}$), 61.8 (CO_2**C**H_2CH_3), 58.6 (**C**$_{11}$), 52.1 (**C**$_{15}$), 35.9 (**C**$_{17}$), 29.1 ($CO_2C($**C**$H_3)_3$), 26.5 ($Si(CH_3)_2C($**C**$H_3)_3$), 18.8 ($Si(CH_3)_2$**C**$(CH_3)_3$), 15.0 (CO_2CH_2**C**H_3), –4.1 ($Si($**C**$H_3)_2C(CH_3)_3$), –4.4 ($Si($**C**$H_3)_2C(CH_3)_3$).

FTIR (thin film) cm^{-1}: 3414 (br-m), 2933 (s), 2859 (m), 1739 (m), 1699 (s), 1510 (m), 1450 (m), 1374 (s), 1252 (m), 1179

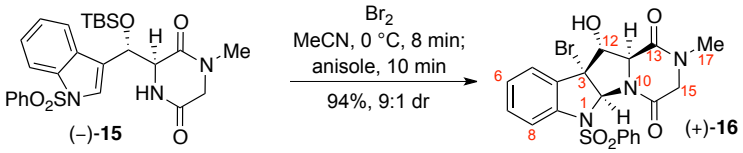
	(s), 1120 (m), 1024 (w), 975 (w), 840 (w), 753 (w), 685 (w).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{33}H_{48}N_3O_8SSi$ $[M+H]^+$: 674.2926, found: 674.2926.
$[\alpha]_D^{24}$:	+69 ($c = 0.24$, $CHCl_3$).
TLC (50% ethyl acetate in hexanes), R*f*:	0.45 (UV, CAM).



Diketopiperazine (–)-15:

Trifluoroacetic acid (27 mL) was introduced dropwise to a solution of dipeptide (+)-**S2** (14.6 g, 21.7 mmol, 1 equiv) in dichloromethane (140 mL) at 23 °C. After 1 h, the reaction mixture was concentrated to dryness under reduced pressure. The crude residue was dissolved in *tert*-butanol (210 mL). Acetic acid (32 mL) and morpholine (32 mL) were successively added to the solution, and the resulting reaction mixture was warmed to 80 °C. After 1.5 h, the reaction mixture was concentrated under reduced pressure and the solids were removed by vacuum filtration over a sintered funnel. The solids were extracted with ethyl acetate and the combined organic filtrates were concentrated under reduced pressure. The resulting orange oil was purified by flash column chromatography on silica gel (eluent: gradient, 50→100% ethyl acetate in hexanes) to provide diketopiperazine (–)-**15** (11.1 g, 97.0%) as a yellow foam. Structural assignments were made using additional information from gCOSY, HSQC, and gHMBC experiments.

^{1}H NMR (600 MHz, $CDCl_3$, 20 °C):	δ 7.97 (d, *J* = 8.4, 1H, C_8**H**), 7.89 (d, *J* = 7.8, 2H, SO_2Ph-*o*-**H**), 7.55 (s, 1H, C_2**H**), 7.54 (t, *J* = 7.4, 1H, SO_2Ph-*p*-**H**), 7.51 (d, *J* = 7.9, 1H, C_5**H**), 7.47 (app-t, *J* = 7.7, 2H, SO_2Ph-*m*-**H**), 7.31 (app-t, *J* = 7.6, 1H, C_7**H**), 7.22 (app-t, *J* = 7.8, 1H, C_6**H**), 6.39 (br-s, 1H, N**H**), 5.51 (d, *J* = 3.4, 1H, C_{12}**H**), 4.31 (app-s, 1H, C_{11}**H**), 3.19 (d, *J* = 17.6, 1H, C_{15}**H**$_a$), 2.32 (s, 3H, C_{14}**H**), 2.17 (d, *J* = 17.6, 1H, C_{15}**H**$_b$), 0.89 (s, 9H, $Si(CH_3)_2C(CH_3)_3$), 0.06 (s, 3H, $Si(CH_3)_2C(CH_3)_3$), –0.07 (s, 3H, $Si(CH_3)_2C(CH_3)_3$).
^{13}C NMR (150 MHz, $CDCl_3$, 20 °C):	δ 164.9 (**C**$_{13}$), 162.6 (**C**$_{16}$), 138.0 (SO_2Ph-*ipso*-**C**), 134.7 (**C**$_9$), 134.1 (SO_2Ph-*p*-**C**), 129.6 (SO_2Ph-*m*-**C**), 127.9 (**C**$_4$), 127.1 (SO_2Ph-*o*-**C**), 126.0 (**C**$_2$), 125.4 (**C**$_7$), 123.6 (**C**$_6$), 120.6 (**C**$_3$), 120.5 (**C**$_5$), 113.6 (**C**$_8$), 70.4 (**C**$_{12}$), 61.7 (**C**$_{11}$), 50.5 (**C**$_{15}$), 33.3 (**C**$_{17}$), 25.9 ($Si(CH_3)_2C(\mathbf{C}H_3)_3$), 18.3 ($Si(CH_3)_2\mathbf{C}(CH_3)_3$), –4.7 ($Si(\mathbf{C}H_3)_2C(CH_3)_3$), –5.1 ($Si(\mathbf{C}H_3)_2C(CH_3)_3$).
FTIR (thin film) cm^{-1}:	3251 (br m), 2932 (m), 1676 (s), 1448 (m), 1371 (m), 1179 (s), 1122 (m), 979 (w), 838 (w), 751 (w), 686 (w).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{26}H_{34}N_3O_5SSi$ $[M+H]^+$: 528.1983, found: 528.1982.
$[\alpha]_D^{24}$:	–21 (*c* = 0.17, $CHCl_3$).
TLC (50% ethyl acetate in hexanes), R*f*:	0.32 (UV, CAM).

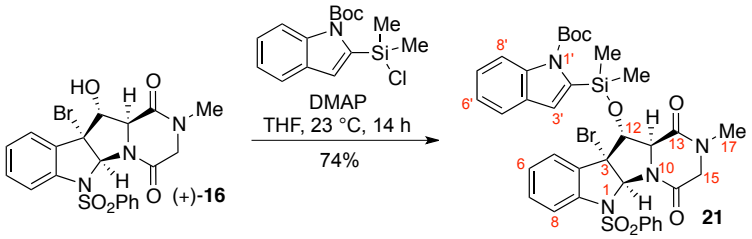


Tetracyclic Bromide (+)-16:

A solution of bromine (2 M, 61.0 mL, 122 mmol, 4.00 equiv) in acetonitrile that was pre-cooled to 0 °C was poured in one portion into a solution of diketopiperazine (–)-**15** (16.1 g, 30.5 mmol, 1 equiv) in acetonitrile (268 mL) at 0 °C. The reaction progress was monitored by TLC analysis in 2 min interval. After 8 min, upon complete consumption of starting material, anisole (19.9 mL, 183 mmol, 6.00 equiv) that was pre-cooled to 0 °C was poured in one portion into the reaction mixture. After 10 min, a mixture of saturated aqueous sodium thiosulfate solution and saturated aqueous sodium bicarbonate solution (1:1, 500 mL) was added to the red solution. The reaction mixture was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: gradient, 20→50% acetone in dichloromethane) to afford a mixture of the *endo*-tetracyclic bromide (+)-**16** and its minor *exo*-diastereomer (14.2 g, 94.5%, 8.7:1 dr) as a white foam.[11] Structural assignments were made with additional information using gCOSY, HSQC, gHMBC, and NOESY experiments.

^{1}H NMR (600 MHz, $CDCl_3$, 20 ºC):	δ 7.98 (d, *J* = 8.0, 2H, SO_2Ph-*o*-**H**), 7.54 (d, *J* = 8.3, 1H, C_8**H**), 7.52 (t, *J* = 7.6, 1H, SO_2Ph-*p*-**H**), 7.42 (app-t, *J* = 7.8, 2H, SO_2Ph-*m*-**H**), 7.33 (d, *J* = 7.6, 1H, C_5**H**), 7.28 (app-t, *J* = 7.9, 1H, C_7**H**), 7.11 (app-t, *J* = 7.6, 1H, C_6**H**), 6.25 (s, 1H, C_2**H**), 4.62 (d, *J* = 5.9, 1H, C_{12}**H**), 4.23 (d, *J* = 5.8, 1H, C_{11}**H**), 4.16 (d, *J* = 17.6, 1H, C_{15}**H**$_a$), 3.91 (br-s, 1H, O**H**), 3.84 (d, *J* = 17.5, 1H, C_{15}**H**$_b$), 2.88 (s, 3H, C_{17}**H**).
^{13}C NMR (150 MHz, $CDCl_3$, 20 ºC):	δ 165.8 (**C**$_{13}$), 164.9 (**C**$_{16}$), 139.2 (**C**$_9$), 137.4 (SO_2Ph-*ipso*-**C**), 134.0 (SO_2Ph-*p*-**C**), 131.8 (**C**$_4$), 131.2 (**C**$_7$), 129.1 (SO_2Ph-*m*-**C**), 128.4 (SO_2Ph-*o*-**C**), 125.9 (**C**$_6$), 125.3 (**C**$_5$), 116.8 (**C**$_8$), 85.1 (**C**$_2$), 74.2 (**C**$_{12}$), 68.0 (**C**$_3$), 63.4 (**C**$_{11}$), 54.0 (**C**$_{15}$), 33.5 (**C**$_{17}$).
FTIR (thin film) cm^{-1}:	3367 (br s), 2958 (s), 1677 (s), 1458 (m), 1399 (m), 1364 (m), 1170 (m), 1089 (w), 729 (w), 688 (w).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{20}H_{19}BrN_3O_5S$ $[M+H]^+$: 492.0223, found: 492.0222.
$[\alpha]_D^{24}$:	+56 (*c* = 0.30, $CHCl_3$).
TLC (33% acetone in dichloromethane), R*f*:	0.35 (UV, CAM).

[11] The mixture of diastereomers can be separated easily on smaller scales using the same purification conditions reported here. However, on decagram scales, it was more practical to carry the diastereomeric mixture to next step.



Indole-Tethered Tetracycle 21:

A solution of *n*-butyllithium (1.57 M, 18.3 mL, 28.7 mmol, 1.61 equiv) in hexanes was added dropwise to a solution of freshly distilled diisopropylamine (4.02 mL, 28.7 mmol, 1.61 equiv) in tetrahydrofuran (4.28 mL) at –78 °C. After 5 min, the solution was allowed to warm to 0 °C. After 35 min, the solution of lithium diisopropylamide was transferred via cannula to a solution of *N*-Boc-indole (6.24 g, 28.7 mmol, 1.61 equiv) and dimethyldichlorosilane (3.25 mL, 26.8 mmol, 1.50 equiv) in tetrahydrofuran (47.3 mL) at 0 °C. After 8 h, the reaction mixture was transferred via cannula to a solution of tetracyclic bromide (+)-**16** (8.78 g, 17.83 mmol, 1 equiv) and 4-dimethylaminopyridine (4.68 g, 38.28 mmol, 2.15 equiv) in tetrahydrofuran (63.3 mL) at 23 °C. After 14 h, the reaction mixture was diluted with ethyl acetate (300 mL) and washed with saturated aqueous sodium bicarbonate solution (500 mL). The aqueous layer was further extracted with ethyl acetate (2 × 200 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting orange foam was purified by flash column chromatography on silica gel (eluent: gradient, 33→50% ethyl acetate in hexanes) to provide the indole-tethered tetracycle **21** (10.1 g, 74.3%) as a white foam. Structural assignments were made using additional information from gCOSY, HSQC, and gHMBC experiments.

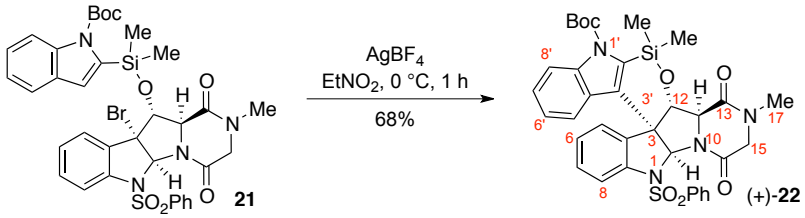
^{1}H NMR (600 MHz, $CDCl_3$, 20 °C):

δ 8.03 (d, *J* = 7.6, 2H, SO_2Ph-*o*-**H**), 7.96 (d, *J* = 8.3, 1H, $C_{8'}$**H**), 7.63 (d, *J* = 7.7, 1H, C_5**H**), 7.57 (d, *J* = 8.1, 1H, C_8**H**), 7.53 (t, *J* = 7.4, 1H, SO_2Ph-*p*-**H**), 7.44 (app-t, *J* = 7.9, 2H, SO_2Ph-*m*-**H**), 7.31 (app-t, *J* = 7.4, 1H, C_7**H**), 7.27 (app-t, *J* = 7.9, 1H, C_7**H**), 7.26–7.21 (m, 1H, C_5**H**), 7.26–7.21 (m, 1H, $C_{6'}$**H**), 7.26–7.21 (m, 1H, $C_{3'}$**H**), 7.00 (app-t, *J* = 7.5, 1H, C_6**H**), 6.33 (s, 1H, C_2**H**), 5.13 (d, *J* = 3.7, 1H, C_{12}**H**), 4.30 (d, *J* = 3.6, 1H, C_{11}**H**), 4.11 (d, *J* = 17.2, 1H, C_{15}**H**$_a$), 3.79 (d, *J* = 17.2, 1H, C_{15}**H**$_b$), 2.82 (s, 3H, C_{17}**H**), 1.69 (s, 9H, $CO_2C(C$**H**$_3)_3$), 0.54 (s, 3H, $Si(C$**H**$_3)_2$), 0.50 (s, 3H, $Si(C$**H**$_3)_2$).

^{13}C NMR (150 MHz, $CDCl_3$, 20 °C):

δ 165.5 (**C**$_{13}$), 165.2 (**C**$_{16}$), 151.7 (**C**=$O_{carbamate}$), 139.1 (**C**$_{2'}$), 138.9 (**C**$_9$), 137.8 (SO_2Ph-*ipso*-**C**), 137.3 (**C**$_{9'}$), 133.8 (SO_2Ph-*p*-**C**), 131.4 (**C**$_{4'}$), 131.3 (**C**$_4$), 131.0 (**C**$_7$), 129.0 (SO_2Ph-*m*-**C**), 128.4 (SO_2Ph-*o*-**C**), 125.6 (**C**$_6$), 125.4 (**C**$_5$), 124.9 (**C**$_{7'}$), 122.7 (**C**$_{6'}$), 121.5 (**C**$_{5'}$), 121.1 (**C**$_{3'}$), 116.5 (**C**$_8$), 115.4 (**C**$_{8'}$), 85.5 (**C**$_2$), 84.6 (CO_2**C**$(CH_3)_3$), 74.6 (**C**$_{12}$), 69.6 (**C**$_3$), 66.5 (**C**$_{11}$), 54.3 (**C**$_{15}$), 33.6 (**C**$_{17}$), 28.3 ($CO_2C($**C**$H_3)_3$), 0.5 ($Si($**C**$H_3)_2$), –0.4 ($Si($**C**$H_3)_2$).

FTIR (thin film) cm^{-1}:	2957 (w), 1715 (s), 1466 (w), 1447 (w), 1373 (s), 1335 (m), 1251 (m), 1169 (s), 1072 (w), 922 (w), 834 (w), 751 (m), 689 (w).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{35}H_{38}BrN_4O_7SSi$ $[M+H]^+$: 765.1408, found: 765.1441.
TLC (50% ethyl acetate in hexanes), R*f*:	0.44 (UV, CAM).



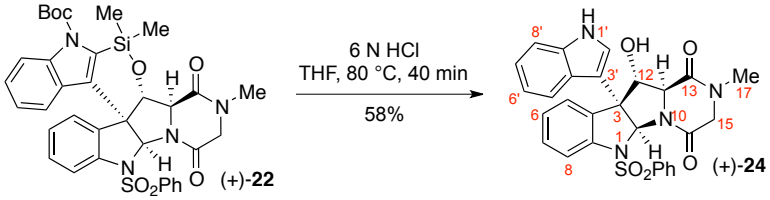
Silacyclic Tetracycle (+)-22:

A round-bottom flask was charged with indole-tethered tetracycle **21** (6.85 g, 8.95 mmol, 1 equiv) and 2,6-di-*tert*-butyl-4-methylpyridine (3.69 g, 17.9 mmol, 2.00 equiv) and azeotropically dried with benzene (3 × 50 mL) under reduced pressure. The flask was left under reduced pressure for 12 h to ensure the complete removal of benzene then returned to atmospheric pressure by backfilling with argon. Anhydrous nitroethane (200 mL, distilled over CaH_2 and stored over 4Å molecular sieves) was then introduced via cannula and the resulting solution was cooled to 0 °C. A solution of silver (I) tetrafluoroborate (8.69 g, 44.8 mmol, 5.00 equiv) in nitroethane (30 mL) at 0 °C was introduced via cannula to the solution containing the indole-tethered tetracycle **21** over 1 min. The reaction mixture immediately changed color to a dark red then to brown. After 1 h, brine (150 mL) was added and the resulting biphasic mixture was vigorously stirred at 23 °C. After 10 min, the reaction mixture was extracted with ethyl acetate (3 × 150 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting white residue was purified by flash column chromatography (eluent: gradient, 40→100% ethyl acetate in hexanes) to afford the silacyclic tetracycle (+)**-22** (4.20 g, 68.5%) as a white foam. Structural assignments were made using additional information from gCOSY, HSQC, gHMBC, and NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 8.25 (d, J = 8.3, 2H, SO_2Ph-*o*-**H**), 7.96 (d, J = 8.2, 1H, C_8**H**), 7.87 (d, J = 8.4, 1H, $C_{8'}$**H**), 7.74 (t, J = 7.5, 1H, SO_2Ph-*p*-**H**), 7.59 (app-t, J = 7.8, 2H, SO_2Ph-*m*-**H**), 7.30 (app-t, J = 7.6, 1H, C_7**H**), 7.15 (app-t, J = 7.5, 1H, $C_{7'}$**H**), 6.91 (app-t, J = 7.5, 1H, C_6**H**), 6.71 (d, J = 7.4, 1H, C_5**H**), 6.50 (app-t, J = 7.4, 1H, $C_{6'}$**H**), 6.39 (s, 1H, C_2**H**), 5.51 (d, J = 8.0, 1H, $C_{5'}$**H**), 4.91 (d, J = 9.5, 1H, C_{12}**H**), 4.32 (d, J = 9.5, 1H, C_{11}**H**), 4.02 (d, J = 18.2, 1H, C_{15}**H**$_a$), 3.95 (d, J = 18.1, 1H, C_{15}**H**$_b$), 3.05 (s, 3H, C_{17}**H**), 1.70 (s, 9H, $CO_2C(CH_3)_3$), 0.54 (s, 3H, $Si(CH_3)_2$), 0.48 (s, 3H, $Si(CH_3)_2$).

^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C): δ 167.7 (**C**$_{13}$), 166.5 (**C**$_{16}$), 151.6 (**C**=O$_{carbamate}$), 139.8 (**C**$_9$), 136.8 (**C**$_{9'}$), 136.3 (SO_2Ph-*ipso*-**C**), 136.0 (**C**$_{2'}$), 133.8 (SO_2Ph-*p*-**C**), 132.0 (**C**$_4$), 129.8 (**C**$_7$), 129.6 (SO_2Ph-*m*-**C**), 129.5 (**C**$_{4'}$), 128.4 (SO_2Ph-*o*-**C**), 125.3 (**C**$_{7'}$), 125.1 (**C**$_{3'}$), 124.5 (**C**$_6$), 123.5 (**C**$_5$), 122.7 (**C**$_{6'}$), 119.3 (**C**$_{5'}$), 115.5 (**C**$_{8'}$), 115.2 (**C**$_8$), 85.6 (CO_2**C**$(CH_3)_3$), 80.5 (**C**$_{12}$), 79.1 (**C**$_2$), 61.4 (**C**$_{11}$), 56.6 (**C**$_3$), 54.2 (**C**$_{15}$), 33.5 (**C**$_{17}$), 28.3 ($CO_2C(CH_3)_3$), 1.7 ($Si(CH_3)_2$), 0.6 ($Si(CH_3)_2$).

FTIR (thin film) cm^{-1}:	2927 (s), 1700 (m), 1652 (w), 1558 (m), 1494 (m), 1454 (w), 1373 (m), 1328 (w), 1258 (w), 1159 (w), 1050 (w), 876 (m), 825 (m), 751 (w).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{35}H_{36}N_4NaO_7SSi$ $[M+Na]^+$: 707.1966, found: 707.1986.
$[\alpha]_D^{24}$:	+203 (*c* = 0.22, $CHCl_3$).
TLC (33% acetone in hexanes), R*f*:	0.25 (UV, CAM).



3-Indolylated Tetracycle (+)-24:

Aqueous hydrogen chloride solution (6 N, 20 mL) was added in one portion to a sealed tube charged with a solution of silacyclic tetracycle (+)**-22** (1.02 g, 1.49 mmol, 1 equiv) in tetrahydrofuran (20 mL) at 23 °C. The reaction flask was then sealed and heated to 80 °C. After 40 min, the sealed tube was immediately immersed in an ice-water bath and rapidly cooled to 0 °C. The cold solution was slowly poured into a saturated aqueous sodium bicarbonate solution (250 mL) at 0 °C and extracted with ethyl acetate (200 mL). The aqueous layer was further extracted with ethyl acetate (2 × 100 mL), and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (eluent: gradient, 25→50% acetone in dichloromethane) to afford the 3-indolylated tetracycle (+)**-24** (456 mg, 57.9%) as a white solid. Structural assignments were made using additional information from gCOSY, HSQC, gHMBC, and NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC):

δ 7.94 (br-s, 1H, $N_{1'}$**H**), 7.75 (d, *J* = 8.1, 1H, C_8**H**), 7.44 (dd, *J* = 1.2, 8.6, 2H, SO_2Ph-*o*-**H**), 7.37–7.27 (m, 1H, SO_2Ph-*p*-**H**), 7.37–7.27 (m, 1H, $C_{8'}$**H**), 7.37–7.27 (m, 1H, C_7**H**), 7.18–7.13 (m, 1H, C_5**H**), 7.18–7.13 (m, 1H, $C_{7'}$**H**), 7.09–7.01 (m, 2H, SO_2Ph-*m*-**C**), 7.09–7.01 (m, 1H, C_6**H**), 6.91–6.84 (m, 1H, $C_{5'}$**H**), 6.91–6.84 (m, 1H, $C_{6'}$**H**), 6.64 (d, *J* = 2.7, 1H, $C_{2'}$**H**), 6.49 (s, 1H, C_2**H**), 4.92 (dd, *J* = 3.3, 6.0, 1H, C_{12}**H**), 4.42 (d, *J* = 5.7, 1H, C_{11}**H**), 4.09 (d, *J* = 17.1, 1H, C_{15}**H**$_a$), 3.84 (d, *J* = 17.5, 1H, C_{15}**H**$_b$), 2.88 (s, 3H, C_{17}**H**), 2.71 (d, *J* = 3.2, 1H, O**H**).

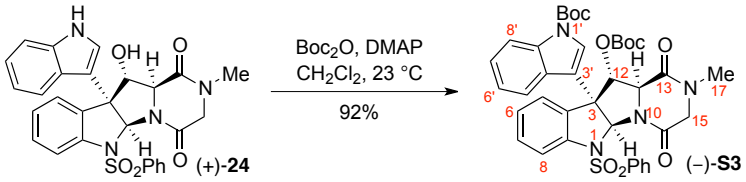
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 ºC):

δ 166.9 (**C**$_{13}$), 165.4 (**C**$_{16}$), 139.6 (**C**$_9$), 137.4 (SO_2Ph-*ipso*-**C**), 136.9 (**C**$_{9'}$), 134.5 (**C**$_4$), 133.0 (SO_2Ph-*p*-**C**), 129.6 (**C**$_7$), 128.6 (SO_2Ph-*m*-**C**), 127.5 (SO_2Ph-*o*-**C**), 126.2 (**C**$_{4'}$), 125.8 (**C**$_{2'}$), 125.3 (**C**$_5$), 125.2 (**C**$_6$), 122.8 (**C**$_{7'}$), 120.5 (**C**$_{5'}$), 120.5 (**C**$_{6'}$), 117.3 (**C**$_8$), 111.7 (**C**$_{8'}$), 110.6 (**C**$_{3'}$), 82.3 (**C**$_2$), 77.4 (**C**$_{12}$), 64.6 (**C**$_{11}$), 59.8 (**C**$_3$), 54.3 (**C**$_{15}$), 33.5 (**C**$_{17}$).

FTIR (thin film) cm^{-1}:

3388 (br-s), 3061 (m), 2923 (m), 1673 (s), 1458 (m), 1427 (m), 1402 (m), 1357 (m), 1260 (w), 1168 (m), 1109 (m), 735 (m), 687 (w).

HRMS (ESI) (*m*/*z*):	calc'd for $C_{28}H_{25}N_4O_5S$ $[M+H]^+$: 529.1540, found: 529.1545.
$[\alpha]_D^{24}$:	+11 (*c* = 0.05, $CHCl_3$).
TLC (50% acetone in dichloromethane), R*f*:	0.41 (UV, CAM).



Bis(*tert*-butoxycarbonyl) Tetracycle (–)-S3:

Di-*tert*-butyl dicarbonate (783 μL, 3.41 mmol, 4.00 equiv) was added via syringe to a solution of 3-indolylated tetracycle (+)-**24** (450 mg, 852 μmol, 1 equiv) and 4-dimethylaminopyridine (52.1 mg, 426 μmol, 0.500 equiv) in dichloromethane (10.0 mL) at 23 °C. After 30 min, the crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 8% acetone in dichloromethane) to afford bis(*tert*-butoxycarbonyl) tetracycle (–)-**S3** (568 mg, 91.5%) as a white solid. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 7.98 (d, J = 7.3, 1H, $C_{8'}$**H**), 7.73 (d, J = 7.6, 1H, C_8**H**), 7.67 (d, J = 8.1, 1H, C_5**H**), 7.58 (d, J = 7.7, 1H, $C_{5'}$**H**), 7.33 (app-t, J = 7.9, 1H, C_6**H**), 7.30 (app-t, J = 7.3, 1H, $C_{7'}$**H**), 7.25 (app-t, J = 8.0, 1H, $C_{6'}$**H**), 7.20 (app-t, J = 7.5, 1H, C_7**H**), 7.02 (t, J = 7.4, 1H, SO_2Ph-*p*-**H**), 6.88 (d, J = 7.3, 2H, SO_2Ph-*o*-**H**), 6.64 (app-t, J = 7.5, 2H, SO_2Ph-*m*-**H**), 6.58 (s, 1H, C_2**H**), 5.99 (s, 1H, $C_{2'}$**H**), 5.92 (d, J = 4.0, 1H, C_{12}**H**), 4.53 (d, J = 3.9, 1H, C_{11}**H**), 4.18 (d, J = 17.4, 1H, C_{15}**H**$_a$), 3.79 (d, J = 17.4, 1H, C_{15}**H**$_b$), 2.81 (s, 3H, C_{17}**H**), 1.50 (s, 9H, C(C**H**$_3$)$_{3carbamate}$), 0.80 (s, 9H, C(C**H**$_3$)$_{3carbonate}$).

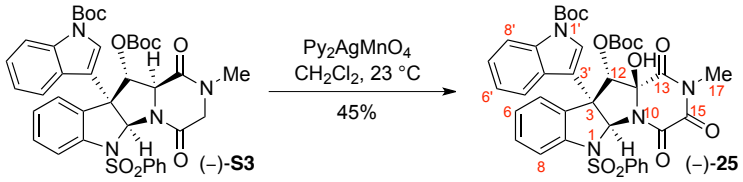
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C): δ 164.8 (**C**$_{13}$), 164.5 (**C**$_{16}$), 151.4 (**C**=O$_{carbonate}$), 148.6 (**C**=O$_{carbamate}$), 139.2 (**C**$_4$), 137.8 (SO_2Ph-*ipso*-**C**), 135.8 (**C**$_{9'}$), 133.8 (**C**$_9$), 132.2 (SO_2Ph-*p*-**C**), 130.1 (**C**$_6$), 128.1 (**C**$_{4'}$), 127.7 (SO_2Ph-*o*-**C**), 127.5 (**C**$_{2'}$), 126.8 (**C**$_8$), 126.5 (SO_2Ph-*o*-**C**), 126.2 (**C**$_7$), 124.7 (**C**$_{7'}$), 122.9 (**C**$_{6'}$), 121.5 (**C**$_{5'}$), 118.8 (**C**$_5$), 115.9 (**C**$_{3'}$), 115.1 (**C**$_{8'}$), 84.0 (**C**(CH$_3$)$_{3carbamate}$), 82.4 (**C**(CH$_3$)$_{3carbonate}$), 82.3 (**C**$_2$), 78.3 (**C**$_{12}$), 63.4 (**C**$_{11}$), 59.6 (**C**$_3$), 54.1 (**C**$_{15}$), 33.6 (**C**$_{17}$), 28.0 (C(**C**H$_3$)$_{3carbamate}$), 26.6 (C(**C**H$_3$)$_{3carbonate}$).

FTIR (thin film) cm^{-1}: 2979 (w), 1740 (s), 1708 (s), 1686 (s), 1453 (m), 1371 (s), 1280 (s), 1258 (s), 1156 (s), 1100 (m), 750 (m).

HRMS (ESI) (*m*/*z*): calc'd for $C_{38}H_{40}N_4NaO_9S$ [M+Na]$^+$: 751.2408, found 751.2405.

$[\alpha]_D^{24}$: –22 (c = 0.31, $CHCl_3$).

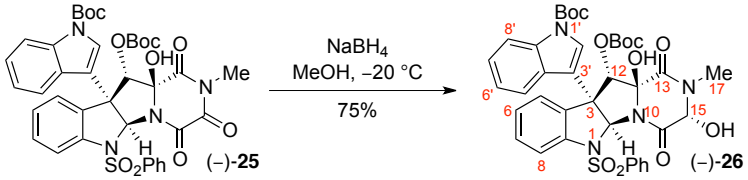
TLC (8% acetone in dichloromethane), R*f*: 0.28 (UV, CAM).



Triketopiperazine (–)-25:

Bis(pyridine)silver permanganate (945 mg, 2.45 mmol, 8.00 equiv) was added as a solid to a solution of bis(*tert*-butoxycarbonyl) tetracycle (–)-**S3** (224 mg, 307 μmol, 1 equiv) in dichloromethane (10.0 mL) at 23 °C. After 1 h, the reaction mixture was diluted with dichloromethane (100 mL) and washed with aqueous sodium bisulfite solution (1 M, 125 mL). The resulting aqueous layer was extracted with dichloromethane (2 × 50 mL) and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 50% ethyl acetate in hexanes) to afford triketopiperazine (–)-**25** (105 mg, 45.1%) as a white solid. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C):	δ 7.97 (d, *J* = 8.2, 1H, $C_{8'}$**H**), 7.86 (d, *J* = 8.0, 1H, C_8**H**), 7.59–7.52 (m, 1H, C_5**H**), 7.59–7.52 (m, 1H, C_7**H**), 7.33 (app-t, *J* = 7.6, 1H, C_6**H**), 7.32–7.26 (m, 1H, $C_{7'}$**H**), 7.32–7.26 (m, 1H, $C_{5'}$**H**), 7.22 (app-t, *J* = 7.1, 1H, $C_{6'}$**H**), 7.10 (d, *J* = 7.5, 2H, SO_2Ph-*o*-**H**), 6.98 (t, *J* = 7.5, 1H, SO_2Ph-*p*-**H**), 6.93 (s, 1H, C_2**H**), 6.61 (app-t, *J* = 7.9, 2H, SO_2Ph-*m*-**H**), 6.53 (s, 1H, $C_{2'}$**H**), 5.69 (s, 1H, C_{12}**H**), 4.45 (s, 1H, C_{11}O**H**), 3.34 (s, 3H, C_{17}**H**), 1.61 (s, 9H, C(C**H**$_3$)$_{3carbamate}$), 0.78 (s, 9H, C(C**H**$_3$)$_{3carbonate}$).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C):	δ 165.5 (**C**$_{15}$), 157.0 (**C**$_{13}$), 151.3 (**C**$_{16}$), 150.7 (**C**=O$_{carbonate}$), 149.0 (**C**=O$_{carbamate}$), 140.9 (**C**$_9$), 136.3 (**C**$_{9'}$), 136.2 (SO_2Ph-*ipso*-**C**), 133.7 (**C**$_4$), 132.7 (SO_2Ph-*p*-**C**), 130.5 (**C**$_7$), 128.0 (SO_2Ph-*m*-**C**), 127.4 (**C**$_{2'}$), 127.4 (**C**$_{4'}$), 127.0 (SO_2Ph-*o*-**C**), 126.5 (**C**$_6$), 125.3 (**C**$_5$), 124.9 (**C**$_{5'}$), 123.3 (**C**$_{6'}$), 121.8 (**C**$_{7'}$), 120.0 (**C**$_8$), 115.7 (**C**$_{3'}$), 115.2 (**C**$_{8'}$), 90.5 (**C**$_{11}$), 85.3 (**C**$_{12}$), 84.4 (**C**(CH$_3$)$_{3carbamate}$), 83.5 (**C**(CH$_3$)$_{3carbonate}$), 82.2 (**C**$_2$), 57.8 (**C**$_3$), 28.3 (C(**C**H$_3$)$_{3carbamate}$), 28.1 (**C**$_{17}$), 26.8 (C(**C**H$_3$)$_{3carbonate}$).
FTIR (thin film) cm^{-1}:	3386 (br-s), 2981 (w), 1738 (s), 1703 (s), 1453 (m), 1371 (s), 1274 (m), 1252 (m), 1156 (m), 751 (m).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{38}H_{39}N_4O_{11}S$ $[M+H]^+$: 759.2331, found 759.2302.
$[\alpha]_D^{24}$:	–69 (*c* = 0.15, $CHCl_3$).
TLC (40% ethyl acetate in hexanes), R*f*:	0.20 (UV, CAM).



Tetracyclic Diol (–)-26:

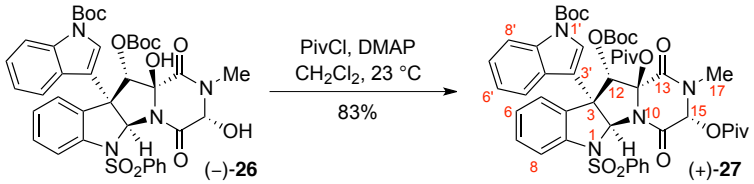
Sodium borohydride (17.3 mg, 457 μmol, 2.00 equiv) was added as a solid to a solution of triketopiperazine (–)-**25** (174 mg, 229 μmol, 1 equiv) in methanol at –20 °C. After 20 min, saturated aqueous sodium bicarbonate solution (5 mL) was added to the reaction mixture. The solution was diluted with dichloromethane (60 mL) and washed with saturated aqueous sodium bicarbonate solution (60 mL). The mixture was extracted with dichloromethane (2 × 60 mL), and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 20% acetone in dichloromethane) to afford tetracyclic diol (–)-**26** (130 mg, 74.9%) as a white solid. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 7.97 (d, *J* = 7.6, 1H, $C_{8'}$**H**), 7.75 (d, *J* = 8.1, 1H, C_8**H**), 7.52 (d, *J* = 7.1, 1H, C_5**H**), 7.45 (d, *J* = 7.9, 1H, $C_{5'}$**H**), 7.36 (app-t, *J* = 7.8, 1H, C_7**H**), 7.31 (app-t, *J* = 7.3, 1H, $C_{7'}$**H**), 7.26 (app-t, *J* = 7.6, 1H, $C_{6'}$**H**), 7.23 (app-t, *J* = 7.5, 1H, C_6**H**), 7.01 (d, *J* = 7.4, 2H, SO_2Ph-*o*-**H**), 6.97 (t, *J* = 7.5, 1H, SO_2Ph-*p*-**H**), 6.94 (s, 1H, C_2**H**), 6.58 (app-t, *J* = 8.1, 2H, SO_2Ph-*m*-**H**), 6.43 (s, 1H, $C_{2'}$**H**), 5.66 (s, 1H, C_{12}**H**), 5.39 (d, *J* = 3.0, 1H, C_{15}**H**), 4.92 (d, *J* = 2.8, 1H, C_{15}O**H**), 4.38 (br-s, 1H, C_{11}O**H**), 2.99 (s, 3H, C_{17}**H**), 1.59 (s, 9H, C(C**H**$_3$)$_{3carbamate}$), 0.80 (s, 9H, C(C**H**$_3$)$_{3carbonate}$).

^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C): δ 165.4 (**C**$_{16}$), 163.7 (**C**$_{13}$), 151.2 (**C**=O$_{carbonate}$), 149.0 (**C**=O$_{carbamate}$), 140.7 (**C**$_9$), 136.8 (SO_2Ph-*ipso*-**C**), 136.3 (**C**$_{9'}$), 134.0 (**C**$_4$), 132.4 (SO_2Ph-*p*-**C**), 129.8 (**C**$_7$), 127.8 (SO_2Ph-*m*-**C**), 127.7 (**C**$_{4'}$), 127.3 (**C**$_{2'}$), 126.8 (SO_2Ph-*o*-**C**), 126.2 (**C**$_6$), 125.4 (**C**$_5$), 124.8 (**C**$_{7'}$), 123.1 (**C**$_{6'}$), 122.3 (**C**$_{5'}$), 119.7 (**C**$_8$), 116.0 (**C**$_{3'}$), 115.1 (**C**$_{8'}$), 90.5 (**C**$_{11}$), 84.9 (**C**$_{12}$), 84.2 (**C**(CH$_3$)$_{3carbamate}$), 83.0 (**C**(CH$_3$)$_{3carbonate}$), 81.4 (**C**$_2$), 77.1 (**C**$_{15}$), 57.3 (**C**$_3$), 29.6 (**C**$_{17}$), 28.3 (C(**C**H$_3$)$_{3carbamate}$), 26.9 (C(**C**H$_3$)$_{3carbonate}$).

FTIR (thin film) cm^{-1}: 3417 (br-s), 2980 (w), 1738 (s), 1687 (s), 1454 (m), 1371 (s), 1276 (m), 1252 (m), 1156 (s), 749 (w).

HRMS (ESI) (*m*/*z*):	calc'd for $C_{38}H_{41}N_4O_{11}S$ $[M+H]^+$: 761.2487, found 761.2481.
$[\alpha]_D^{24}$:	–19 (*c* = 0.16, $CHCl_3$).
TLC (20% acetone in dichloromethane), R*f*:	0.23 (UV, CAM).



Tetracyclic Dipivaloate (+)-27:

Pivaloyl chloride (75.8 µL, 616 µmol, 4.00 equiv) was added via syringe to a solution of tetracyclic diol (–)-**26** (117 mg, 154 µmol, 1 equiv) and 4-dimethylaminopyridine (94.1 mg, 771 µmol, 5.00 equiv) in dichloromethane (4 mL) at 23 °C. After 1 h 45 min, methanol (50 µL) was added to the reaction mixture, and the crude solution was purified by flash column chromatography on silica gel (eluent: 1% acetone in dichloromethane) to afford tetracyclic dipivaloate (+)-**27** (119 mg, 83.0%) as a white solid. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC): δ 7.96 (d, J = 7.9, 1H, $C_{8'}$**H**), 7.81 (d, J = 8.1, 1H, C_8**H**), 7.60 (dd, J = 0.7, 7.5, 1H, C_5**H**), 7.45 (br-s, 1H, $C_{5'}$**H**), 7.39 (app-dt, J = 1.2, 7.7, 1H, C_7**H**), 7.32–7.25 (m, 1H, C_6**H**), 7.32–7.25 (m, 1H, $C_{7'}$**H**), 7.20–7.13 (m, 2H, SO_2Ph-*o*-**H**), 7.20–7.13 (m, 1H, $C_{6'}$**H**), 6.99 (t, J = 7.5, SO_2Ph-*p*-**H**), 6.91 (s, 1H, C_2**H**), 6.63 (app-t, J = 7.9, 2H, SO_2Ph-*m*-**H**), 6.52 (br-s, 1H, C_{15}**H**), 6.44 (s, 1H, $C_{2'}$**H**), 5.70 (s, 1H, C_{12}**H**), 2.91 (s, 3H, C_{17}**H**), 1.59 (s, 9H, C(C**H**$_3$)$_{3carbamate}$), 1.40 (s, 9H, C(C**H**$_3$)$_{3pivaloate}$), 0.79 (s, 9H, C(C**H**$_3$)$_{3carbonate}$), 0.68 (s, 9H, C(C**H**$_3$)$_{3pivaloate}$).

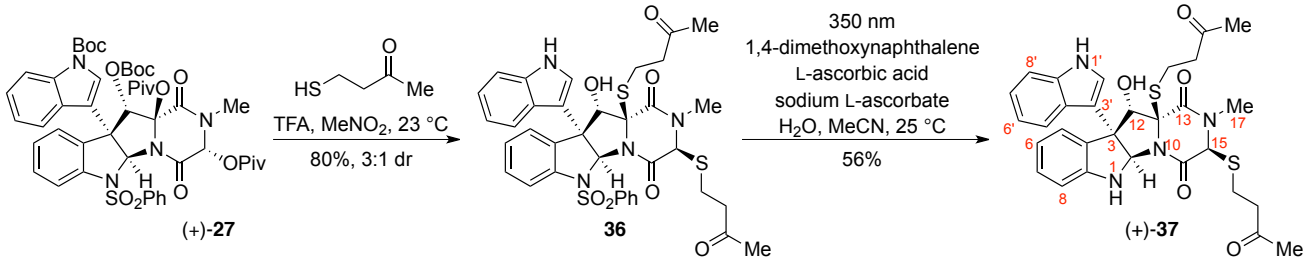
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 ºC): δ 177.3 (**C**=O$_{pivaloate}$), 176.3 (**C**=O$_{pivaloate}$), 161.3 (**C**$_{16}$), 160.8 (**C**$_{13}$), 151.0 (**C**=O$_{carbonate}$), 149.0 (**C**=O$_{carbamate}$), 141.5 (**C**$_9$), 136.6 (SO_2Ph-*ipso*-**C**), 136.3 (**C**$_{9'}$), 133.1 (**C**$_4$), 132.6 (SO_2Ph-*p*-**C**), 130.0 (**C**$_7$), 127.9 (SO_2Ph-*m*-**C**), 127.5 (**C**$_{4'}$), 127.3 (**C**$_{2'}$), 127.0 (SO_2Ph-*o*-**C**), 126.0 (**C**$_6$), 125.7 (**C**$_5$), 124.7 (**C**$_{7'}$), 123.0 (**C**$_{6'}$), 122.3 (**C**$_{5'}$), 119.4 (**C**$_8$), 116.6 (**C**$_{3'}$), 115.0 (**C**$_{8'}$), 92.2 (**C**$_{11}$), 85.2 (**C**$_{12}$), 84.2 (**C**(CH$_3$)$_{3carbamate}$), 83.2 (**C**$_2$), 82.8 (**C**(CH$_3$)$_{3carbonate}$), 78.3 (**C**$_{15}$), 57.9 (**C**$_3$), 39.3 (**C**(CH$_3$)$_{3pivaloate}$), 38.7 (**C**(CH$_3$)$_{3pivaloate}$), 30.7 (**C**$_{17}$), 28.3 (C(**C**H$_3$)$_{3carbamate}$), 27.2 (C(**C**H$_3$)$_{3pivaloate}$), 26.8 (C(**C**H$_3$)$_{3carbonate}$), 26.3 (C(**C**H$_3$)$_{3pivaloate}$).

FTIR (thin film) cm^{-1}: 2978 (m), 1742 (s), 1699 (m), 1454 (m), 1371 (s), 1276 (m), 1252 (m), 1155 (m), 1123 (s), 750 (m).

HRMS (ESI) (*m*/*z*): calc'd for $C_{48}H_{56}N_4NaO_{13}S$ [M+Na]$^+$: 951.3457, found 951.3451.

$[\alpha]_D^{24}$: +5.3 (*c* = 0.095, $CHCl_3$).

TLC (1% acetone in dichloromethane), R*f*: 0.27 (UV, CAM).



Tetracyclic Bisthioether (+)-37:

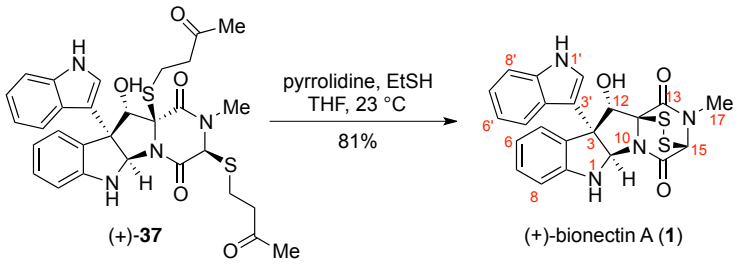
Trifluoroacetic acid (3 mL) was added via syringe to a solution of tetracyclic dipivaloate (+)-**27** (109 mg, 117 μmol, 1 equiv) and 3-mercapto-2-butanone[12] (366 mg, 3.51 mmol, 30.0 equiv) in nitromethane (3 mL) at 23 °C. After 45 min, the reaction mixture was diluted with dichloromethane (60 mL) and washed with saturated aqueous sodium bicarbonate solution (100 mL). The aqueous layer was extracted with dichloromethane (2 × 30 mL), and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 20% acetone in dichloromethane) to afford a diastereomeric mixture of bisthioethers (68.8 mg, 80.2%, 3:1 dr, major:minor) as a beige solid.

A 25–mL Pyrex pear-shaped flask was sequentially charged with the diastereomeric mixture of bisthioethers (68.8 mg, 93.9 μmol, 1 equiv), L-ascorbic acid (165 mg, 939 μmol, 10.0 equiv), sodium L-ascorbate (186 mg, 939 μmol, 10.0 equiv), and 1,4-dimethoxynaphthalene (1.06 g, 5.63 mmol, 60.0 equiv), and the mixture was placed under an argon atmosphere. Acetonitrile (8 mL) and water (2 mL) were then sequentially introduced via syringe and the resulting solution was sparged with argon for 5 min at 23 °C. The system was stirred vigorously and irradiated in a Rayonet photoreactor equipped with 16 radially distributed (r=12.7 cm) 25 W black light phosphor lamps (λ_{max}=350 nm) at 25 °C. After 1.5 h, the lamps were turned off and the reaction mixture was diluted with dichloromethane (60 mL). The resulting solution was washed with saturated aqueous sodium bicarbonate solution (60 mL). The aqueous layer was extracted with dichloromethane (2 × 10 mL), and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: gradient, 20→25% acetone in dichloromethane) to afford tetracyclic bisthioether (+)-**37** (31.0 mg, 55.7%) as a single diastereomer and as a clear film. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 8.00 (s, 1H, N_1**H**), 7.85 (d, *J* = 7.4, 1H, C_5**H**), 7.37 (d, *J* = 7.3, 1H, C_5**H**), 7.31 (d, *J* = 7.5, 1H, $C_{8'}$**H**), 7.17 (app-t, *J* = 7.2, 1H, C_7**H**), 7.14 (app-t, *J* = 7.2, 1H, C_6**H**), 7.09 (d, *J* = 2.5, 1H, C_2**H**), 7.05 (app-t, *J* = 7.5, 1H, C_7**H**), 6.69 (app-t, *J* = 7.3, 1H, C_6**H**), 6.62 (d, *J* = 7.7, 1H, C_8**H**), 6.29 (s, 1H, C_2**H**), 5.30 (d, *J* = 1.8, 1H, C_{12}**H**), 5.07 (s, 1H, N_1**H**), 4.76 (s, 1H, C_{15}**H**), 3.34 (d, *J* = 2.0, 1H, C_{12}O**H**), 3.10–3.02 (m, 2H, C_{22}**H**), 3.08 (s, 3H, C_{17}**H**), 2.98–2.86 (m, 2H, C_{23}**H**), 2.86–2.77 (m, 1H, C_{18}**H**$_a$), 2.75–2.67 (m, 1H, C_{18}**H**$_b$), 2.47–2.32

[12] Ross, N. C.; Levine, R. *J. Org. Chem.* **1964**, *29*, 2346.

	(m, 2H, C_{19}**H**), 2.20 (s, 3H, C_{25}**H**), 2.04 (s, 3H, C_{21}**H**).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 ºC):	δ 206.9 (**C**$_{24}$), 206.3 (**C**$_{20}$), 165.4 (**C**$_{16}$), 165.1 (**C**$_{13}$), 147.5 (**C**$_{9}$), 137.1 (**C**$_{9'}$), 132.2 (**C**$_{4}$), 128.8 (**C**$_{7}$), 125.8 (**C**$_{4'}$), 123.7 (**C**$_{5}$), 123.2 (**C**$_{2'}$), 122.4 (**C**$_{7'}$), 121.2 (**C**$_{5'}$), 120.0 (**C**$_{6'}$), 119.3 (**C**$_{6}$), 114.9 (**C**$_{3'}$), 111.8 (**C**$_{8'}$), 110.2 (**C**$_{8}$), 81.6 (**C**$_{2}$), 81.5 (**C**$_{12}$), 73.5 (**C**$_{11}$), 66.9 (**C**$_{15}$), 59.3 (**C**$_{3}$), 44.1 (**C**$_{23}$), 42.6 (**C**$_{19}$), 32.0 (**C**$_{17}$), 30.3 (**C**$_{25}$), 30.1 (**C**$_{21}$), 28.6 (**C**$_{22}$), 25.7 (**C**$_{18}$).
FTIR (thin film) cm^{-1}:	3371 (br-s), 2930 (w), 1711 (m), 1661 (s), 1423 (m), 1397 (m), 1364 (w), 1238 (w), 743 (m).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{30}H_{32}N_4NaO_5S_2$ $[M+Na]^+$: 615.1706, found 615.1693.
$[\alpha]_D^{24}$:	+179 (*c* = 0.075, $CHCl_3$).
TLC (25% acetone in dichloromethane), R*f*:	0.23 (UV, CAM).

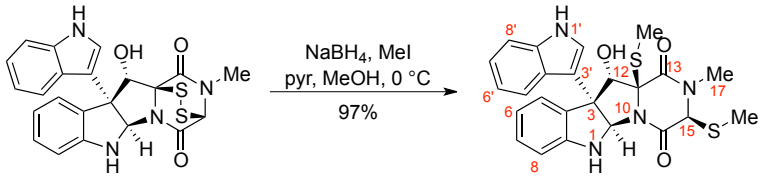


(+)-Bionectin A (1):

Pyrrolidine (20 µL, 242 µmol, 27.6 equiv) was added via syringe to a solution of tetracyclic bisthioether (+)-**37** (5.2 mg, 8.77 µmol, 1 equiv) and ethanethiol (20 µL, 270 µmol, 30.8 equiv) in tetrahydrofuran (1 mL) at 23 °C. After 2 h, the reaction mixture was diluted with dichloromethane (10 mL) and washed with aqueous hydrochloric acid (1N, 10 mL). The aqueous layer was extracted with dichloromethane (2 × 5 mL), and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 10% acetone in dichloromethane) to afford (+)-bionectin A (**1**) (3.2 mg, 81%) as a beige solid. Structural assignments were made using additional information from gCOSY, HSQC, HMBC, and NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C):	δ 8.11 (br-s, 1H, $N_{1'}$**H**), 7.91 (d, *J* = 7.8, 1H, $C_{5'}$**H**), 7.44 (d, *J* = 7.5, 1H, C_5**H**), 7.32 (d, *J* = 8.1, 1H, $C_{8'}$**H**), 7.18 (app-t, *J* = 6.9, 1H, $C_{7'}$**H**), 7.16–7.11 (m, 1H, $C_{6'}$**H**), 7.16–7.11 (m, 1H, C_7**H**), 7.06 (d, *J* = 2.6, 1H, C_2**H**), 6.83 (app-t, *J* = 7.5, 1H, C_6**H**), 6.69 (d, *J* = 7.8, 1H, C_8**H**), 6.30 (s, 1H, C_2**H**), 5.36 (br-s, 1H, N_1**H**),[13] 5.32 (s, 1H, C_{12}**H**), 5.19 (s, 1H, C_{12}O**H**), 5.17 (s, 1H, C_{15}**H**), 3.11 (s, 3H, C_{17}**H**).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C):	δ 166.2 (**C**$_{13}$), 161.9 (**C**$_{16}$), 147.3 (**C**$_9$), 137.1 (**C**$_{9'}$), 130.9 (**C**$_4$), 129.6 (**C**$_7$), 126.3 (**C**$_{4'}$), 124.7 (**C**$_5$), 123.5 (**C**$_{2'}$), 122.6 (**C**$_{7'}$), 121.6 (**C**$_{5'}$), 120.1 (**C**$_{6'}$), 120.1 (**C**$_6$), 113.4 (**C**$_{3'}$), 111.7 (**C**$_{8'}$), 110.9 (**C**$_8$), 82.5 (**C**$_2$), 81.0 (**C**$_{12}$), 77.0 (**C**$_{11}$), 67.7 (**C**$_{15}$), 61.6 (**C**$_3$), 32.0 (**C**$_{17}$).
FTIR (thin film) cm^{-1}:	3402 (br-s), 2922 (w), 1677 (s), 1482 (w), 1458 (w), 1377 (m), 1237 (m), 1093 (w), 747 (m).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{22}H_{19}N_4O_3S_2$ $[M+H]^+$: 451.0893, found 451.0891.
$[\alpha]_D^{24}$:	+284 (*c* = 0.11, $CHCl_3$).
TLC (10% acetone in dichloromethane), R*f*:	0.25 (UV, CAM).

[13] The N_1**H** proton was too broad for observation at high concentrations.

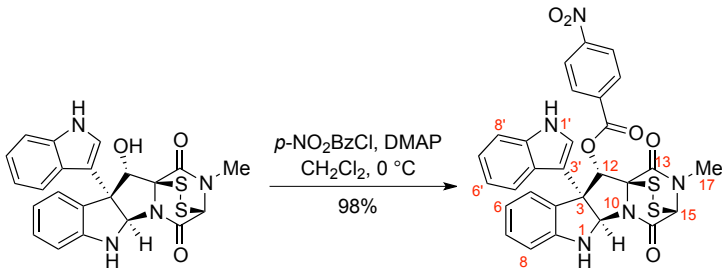


(+)-bionectin A (**1**) (+)-bionectin C (**2**)

(+)-Bionectin C (2):

Sodium borohydride (2.2 mg, 57.7 μmol, 10.0 equiv) was added as a solid to a solution of (+)-bionectin A (**1**) (2.6 mg, 5.77 μmol, 1 equiv) and methyl iodide (35.9 μL, 577 μmol, 100 equiv) in pyridine (100 μL) and methanol (200 μL) at 0 °C. After 1 h, the reaction mixture was diluted with ethyl acetate (10 mL) and washed with saturated aqueous ammonium chloride solution (10 mL). The aqueous layer was extracted with ethyl acetate (2 × 10 mL), and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: gradient, 10→15% acetone in dichloromethane) to afford (+)-bionectin C (**2**) (2.7 mg, 97%) as a white solid. Structural assignments were made using additional information from gCOSY, HSQC, HMBC, and NOESY experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C):	δ 8.00 (br-s, 1H, $N_{1'}$**H**), 7.85 (d, *J* = 7.9, 1H, $C_{5'}$**H**), 7.41 (d, *J* = 7.5, 1H, C_5**H**), 7.31 (d, *J* = 7.6, 1H, $C_{8'}$**H**), 7.17 (app-dt, *J* = 1.0, 7.1, 1H, $C_{7'}$**H**), 7.13 (app-dt, *J* = 1.0, 7.1, 1H, $C_{6'}$**H**), 7.10 (d, *J* = 2.7, 1H, $C_{2'}$**H**), 7.08 (app-dt, *J* = 1.1, 7.6, 1H, C_7**H**), 6.71 (ap-dt, *J* = 0.7, 7.5, 1H, C_6**H**), 6.63 (d, *J* = 7.8, 1H, C_8**H**), 6.34 (s, 1H, C_2**H**), 5.30 (d, *J* = 2.1, 1H, C_{12}**H**), 5.09 (s, 1H, N_1**H**), 4.59 (s, 1H, C_{15}**H**), 3.24 (d, *J* = 2.2, 1H, C_{12}O**H**), 3.10 (s, 3H, C_{17}**H**), 2.45 (s, 3H, C_{15}SC**H**$_3$), 2.06 (s, 3H, C_{11}SC**H**$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C):	δ 165.0 (**C**$_{16}$), 164.8 (**C**$_{13}$), 147.6 (**C**$_9$), 137.1 (**C**$_{9'}$), 131.9 (**C**$_4$), 129.0 (**C**$_7$), 126.0 (**C**$_{4'}$), 123.4 (**C**$_5$), 123.1 (**C**$_{2'}$), 122.6 (**C**$_{7'}$), 121.3 (**C**$_{5'}$), 120.1 (**C**$_{6'}$), 119.3 (**C**$_6$), 115.1 (**C**$_{3'}$), 111.8 (**C**$_{8'}$), 110.1 (**C**$_8$), 81.8 (**C**$_2$), 80.5 (**C**$_{12}$), 73.4 (**C**$_{11}$), 67.8 (**C**$_{15}$), 59.1 (**C**$_3$), 32.4 (**C**$_{17}$), 18.3 (C_{15}S**C**H$_3$), 15.7 (C_{11}S**C**H$_3$).
FTIR (thin film) cm^{-1}:	3399 (br-s), 2921 (w), 1661 (s), 1608 (w), 1483 (w), 1458 (w), 1424 (m), 1397 (m), 1238 (m), 1087 (w), 741 (m).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{24}H_{25}N_4O_3S_2$ $[M+H]^+$: 481.1363, found 481.1355.
$[\alpha]_D^{24}$:	+270 (*c* = 0.09, $CHCl_3$).
TLC (10% acetone in dichloromethane), R*f*:	0.08 (UV, CAM).



(+)-bionectin A (**1**) (+)-**38**

Bionectin A *p*-Nitrobenzoate (38):

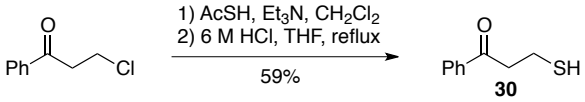
p-Nitrobenzoyl chloride (1.6 mg, 8.67 μmol, 1.50 equiv) was added to a solution of (+)-bionectin A (**1**) (2.6 mg, 5.78 μmol, 1 equiv) and 4-dimethylaminopyridine (3.5 mg, 28.9 μmol, 5.00 equiv) in dichloromethane (1 mL) at 0 °C. After 1 h, another portion of *p*-nitrobenzoyl chloride (1.5 mg, 8.08 μmol, 1.40 equiv) was added to the reaction. After 1 h 10 min, another portion of *p*-nitrobenzoyl chloride (2.2 mg, 11.9 μmol, 2.05 equiv) was added to the reaction. After 1 h 20 min, another portion of 4-dimethylaminopyridine (0.7 mg, 5.73 μmol, 0.99 equiv) was added to the reaction. After 1 h 10 min, *p*-nitrobenzoyl chloride (5.0 mg, 26.9 μmol, 4.66 equiv) was added to the reaction. After 38 min, methanol (50 μL) was added to the reaction. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 2% acetone in dichloromethane) to afford (+)-bionectin A *p*-nitrobenzoate (**38**) (3.4 mg, 98%) as a yellow solid. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of (+)-**38** in chloroform at 23 °C. Structural assignments were made using additional information from gCOSY, HSQC, and HMBC experiments.

^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC): δ 8.05 (br-s, 1H, $N_{1'}$**H**), 8.04 (d, *J* = 8.8, 2H, *p*-NO_2Bz-*m*-**H**), 7.75 (d, *J* = 8.2, 1H, $C_{5'}$**H**), 7.72 (d, *J* = 8.9, 2H, *p*-NO_2Bz-*o*-**H**), 7.66 (d, *J* = 7.4, C_5**H**), 7.21 (app-t, *J* = 7.7, 1H, C_7**H**), 7.19 (d, *J* = 8.1, 1H, $C_{8'}$**H**), 7.04 (d, *J* = 2.7, 1H, $C_{2'}$**H**), 7.00 (app-t, *J* = 7.9, 1H, $C_{7'}$**H**), 6.95 (app-t, *J* = 7.6, 1H, C_6**H**), 6.91 (app-t, *J* = 7.3, 1H, $C_{6'}$**H**), 6.73 (d, *J* = 7.8, 1H, C_8**H**), 6.65 (s, 1H, C_{12}**H**), 6.55 (s, 1H, C_2**H**), 5.40 (br-s, 1H, N_1**H**), 5.26 (s, 1H, C_{15}**H**), 3.03 (s, 3H, C_{17}**H**).

^{13}C NMR (125.8 MHz, $CDCl_3$, 20 ºC): δ 163.7 (**C**=O_{Bz}), 163.1 (**C**$_{13}$), 161.7 (**C**$_{16}$), 150.4 (*p*-NO_2Bz-*p*-**C**), 147.7 (**C**$_9$), 137.1 (**C**$_{9'}$), 134.9 (*p*-NO_2Bz-*ipso*-**C**), 130.9 (*p*-NO_2Bz-*m*-**C**), 130.1 (**C**$_7$), 129.5 (**C**$_4$), 125.7 (**C**$_{4'}$), 125.0 (**C**$_5$), 124.7 (**C**$_{2'}$), 123.3 (*p*-NO_2Bz-*o*-**C**), 122.7 (**C**$_{7'}$), 121.1 (**C**$_{5'}$), 120.2 (**C**$_6$), 120.1 (**C**$_{6'}$), 111.8 (**C**$_{8'}$), 111.8 (**C**$_{3'}$), 110.9 (**C**$_8$), 81.3 (**C**$_2$), 80.6 (**C**$_{12}$), 75.8 (**C**$_{11}$), 68.7 (**C**$_{15}$), 60.9 (**C**$_3$), 32.3 (**C**$_{17}$).

FTIR (thin film) cm^{-1}: 3406 (br-s), 1738 (w), 1691 (s), 1608 (w), 1526 (m), 1346 (w), 1263 (m), 1099 (m), 749 (m), 715 (w).

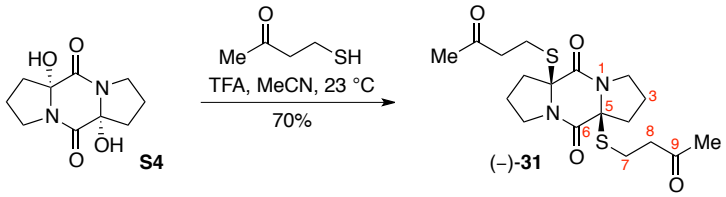
HRMS (ESI) (*m*/*z*):	calc'd for $C_{29}H_{21}N_5NaO_6S_2$ $[M+Na]^+$: 622.0825, found 622.0820.
$[\alpha]_D^{24}$:	+17 (*c* = 0.12, $CHCl_3$).
TLC (2% acetone in dichloromethane), R*f*:	0.28 (UV, CAM).



3-Mercaptopropiophenone (30):

Triethylamine (1.49 mL, 10.7 mmol, 1.50 equiv) was added to a solution of 3-chloropropiophenone (1.20 g, 7.12 mmol, 1 equiv) in dichloromethane (100 mL) at 23 °C. Thioacetic acid (602 μL, 8.54 mmol, 1.20 equiv) was then added dropwise to the solution. After 1 h, the reaction mixture was concentrated in vacuo. The crude residue was dissolved in tetrahydrofuran (50 mL) and aqueous hydrochloric acid (6 N, 50 mL) was added to the solution. Thee reaction mixture was then heated to reflux. After 36 h, the reaction was diluted with ethyl acetate (200 mL) and washed with saturated aqueous sodium bicarbonate solution (400 mL). The aqueous layer was extracted with ethyl acetate (3 × 200 mL), and the combined organic layers were dried over sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 20% ethyl acetate in hexanes) to afford 3-mercaptopropiophenone (**30**, 703 mg, 59.4%) as a colorless oil.

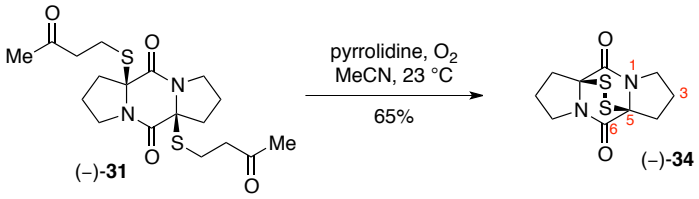
^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC):	δ 7.93 (d, *J* = 7.5, 2H, COPh-*o*-**H**), 7.55 (t, *J* = 7.5, 1H, COPh-*p*-**H**), 7.45 (app-t, *J* = 7.5, 2H, COPh-*m*-**H**), 3.31 (t, *J* = 7, 2H, C**H**$_2$CH$_2$SH, 2.89 (dt, *J* = 8.5, 6.0, 2H, CH$_2$C**H**$_2$SH), 1.74 (t, *J* = 8.5, 1H, S**H**).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 ºC):	δ 198.2 (**C**=O), 136.8 (COPh-*ipso*-**C**), 133.6 (COPh-*p*-**C**), 128.9 (COPh-*m*-**C**), 128.2 (COPh-*o*-**C**), 42.7 (**C**H$_2$CH$_2$SH), 19.1 (CH$_2$**C**H$_2$SH).
FTIR (thin film) cm^{-1}:	3061 (w), 2941 (w), 1683 (s), 1597 (m), 1580 (m) 1448 (m).
HRMS (ESI) (*m*/*z*):	calc'd for $C_9H_{11}OS$ $[M+H]^+$: 167.0525, found 167.0526
TLC (20% ethyl acetate in hexanes), R*f*:	0.28 (UV, CAM).



Bisproline Bis(ethylmethylketone thioether) (–)-31:

Trifluoroacetic acid (15 mL) was added via syringe to a solution of bisproline diol **S4** (397 mg, 1.76 mmol, 1 equiv) and 3-mercaptobutan-2-one[12] (**29**, 928 μL, 8.77 mmol, 5.00 equiv) in acetonitrile (15 mL) at 23 °C. The clear solution immediately turned yellow. After 30 min, the reaction was diluted with ethyl acetate (50 mL) and washed with saturated aqueous sodium bicarbonate solution (50 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL), and the combined organic layers were dried over sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 3% acetone in dichloromethane) to afford the bisproline bis(ethylmethylketone thioether) (–)-**31** (490 mg, 70.2%) as a white solid.

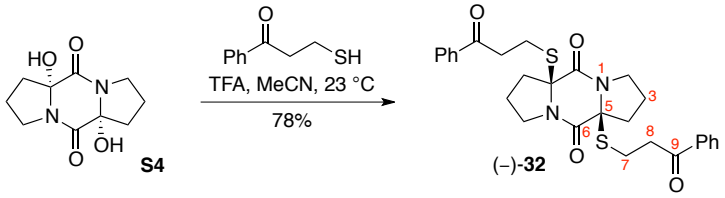
^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC):	δ 3.68–3.62 (m, 2H, C_2**H**), 3.56–3.51 (m, 2H, C_2**H**), 2.90–2.87 (m, 4H, C_8**H**), 2.75–2.61 (m, 4H, C_7**H**), 2.46–2.42 (m, 2H, C_4H_a), 2.33–2.22 (m, 2H, C_3H_a), 2.12–2.04 (m, 2H, C_4H_b), 2.10 (s, 6H, CO**C**H_3), 2.01–1.95 (m, 2H, C_3H_b).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 ºC):	δ 206.4 (**C**$_9$), 165.3 (**C**$_6$), 71.7 (**C**$_5$), 45.4 (**C**$_2$), 43.2 (**C**$_7$), 35.4 (**C**$_4$), 30.0 (CO**C**H_3), 25.2 (**C**$_8$), 20.0 (**C**$_3$).
FTIR (thin film) cm^{-1}:	1715 (m), 1660 (s), 1409 (s), 1363 (w), 1158 (w)
HRMS (ESI) (*m*/*z*):	calc'd for $C_{18}H_{30}N_3O_4S_2$ $[M+NH_4]^+$: 416.1672, found: 416.1679.
$[\alpha]_D^{24}$:	–33 (*c* = 0.28, CH_2Cl_2).
TLC (10% acetone in dichloromethane), R*f*:	0.39 (UV, CAM).



Bisproline Epidithiodiketopiperazine (–)-34:

Pyrrolidine (70.0 μL, 852 μmol, 4.07 equiv) was added to a solution of bis(ethylmethylketone thioether) (–)-**31** (83.5 mg, 210 μmol, 1 equiv) in acetonitrile (250 μL) at 23 °C, and the reaction was placed under a balloon of oxygen. The clear solution immediately turned orange. After 1 h, the reaction was diluted with dichloromethane (5 mL) and washed with saturated aqueous ammonium chloride solution (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 3 mL), and the combined organic layers were dried over sodium sulfate, were filtered, and were concentrated under reduced pressure. The orange residue was purified by flash column chromatography on silica gel (eluent: 3% acetone in dichloromethane) to afford the bisproline epidithiodiketopiperazine (–)-**34** (34.8 mg, 64.8%) as a white solid.

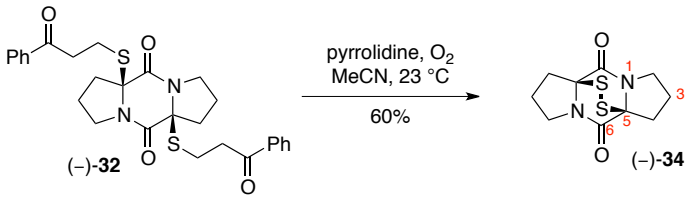
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C):	δ 3.88–3.84 (m, 2H, $C_2\mathbf{H}_a$), 3.58–3.52 (m, 2H, $C_2\mathbf{H}_b$), 3.02–2.94 (m, 2H, $C_4\mathbf{H}_a$), 2.35–2.27 (m, 2H, $C_4\mathbf{H}_b$), 2.35–2.27 (m, 2H, $C_3\mathbf{H}_a$), 2.25–2.18 (m, 2H, $C_3\mathbf{H}_b$).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C):	δ 164.1 ($\mathbf{C}_6$), δ 78.1 ($\mathbf{C}_5$), δ 46.6 ($\mathbf{C}_2$), δ 32.9 ($\mathbf{C}_4$), δ 24.4 ($\mathbf{C}_3$).
FTIR (thin film) cm^{-1}:	2921 (m), 1660 (s), 1405 (m), 1338 (w), 1097 (m),
HRMS (ESI) (*m*/*z*):	calc'd for $C_{10}H_{12}N_2NaO_2S_2$ $[M+Na]^+$: 279.0323, found: 279.0314.
$[\alpha]_D^{24}$:	–144 (c = 0.11, CH_2Cl_2).
TLC (10% acetone in dichloromethane), R*f*:	0.44 (UV, CAM).



Bisproline bis(ethylphenylketone thioether) (–)-32:

Trifluoroacetic acid (1 mL) was added via syringe to a solution of bisproline diol **S4** (36.6 mg, 0.162 mmol, 1 equiv) and 3-mercaptopropiophenone (**30**, 76.2 μL, 801 μmol, 5.00 equiv) in acetonitrile (1 mL) at 23 °C. The clear solution immediately turned yellow. After 30 min, the reaction was diluted with ethyl acetate (5 mL) and washed with saturated aqueous sodium bicarbonate solution (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 5 mL), and the combined organic layers were dried over sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 3% acetone in dichloromethane) to afford the bisproline bis(ethylmethylketone thioether) (–)-**32** (65.9 mg, 77.5%) as a white solid.

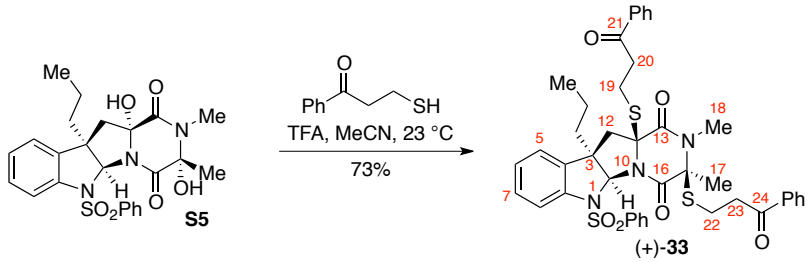
^{1}H NMR (500 MHz, $CDCl_3$, 20 ºC):	δ 7.89 (d, *J* = 7.5, 4H, COPh-*o*-**H**), 7.53 (t, *J* = 7.5, 2H, COPh-*p*-**H**), 7.42 (app-t, *J* = 8.0, 4H, COPh-*m*-**H**), 3.73–3.67 (m, 2H, $C_2\mathbf{H}_a$), 3.61–3.56 (m, 2H, $C_2\mathbf{H}_b$), 3.33–3.27 (m, 2H, $C_7\mathbf{H}_a$), 3.23–3.26 (m, 2H, $C_7\mathbf{H}_b$), 3.12–3.09 (m, 4H, $C_8\mathbf{H}$), 2.55–2.51 (m, 2H, $C_4\mathbf{H}_a$), 2.38–2.28 (m, 2H, $C_3\mathbf{H}_a$), 2.17–2.10 (m, 2H, $C_4\mathbf{H}_b$), 2.05–1.99 (m, 2H, $C_3\mathbf{H}_b$).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 ºC):	δ 198.7 (**C**$_9$), 166.2 (**C**$_6$), 137.2 (COPh-*ipso*-**C**), 133.6 (COPh-*p*-**C**), 128.9 (COPh-*m*-**C**), 128.2 (COPh-*o*-**C**), 72.5 (**C**$_5$), 45.7 (**C**$_2$), 38.9 (**C**$_7$), 35.7 (**C**$_4$), 25.7 (**C**$_8$), 20.1 (**C**$_3$).
FTIR (thin film) cm^{-1}:	2956 (w), 1683 (m), 1660 (m), 1597 (w), 1448 (w), 1406 (m), 1350 (w).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{28}H_{34}N_3O_4S_2$ $[M+NH_4]^+$: 540.1925, found: 540.1925.
$[\alpha]_D^{24}$:	–54 (*c* = 0.17, CH_2Cl_2).
TLC (10% acetone in dichloromethane), R*f*:	0.43 (UV, CAM).



Bisproline Epidithiodiketopiperazine (–)-34:

Pyrrolidine (24.3 μL, 284 μmol, 3.79 equiv) was added to a solution of bis(ethylmethylketone thioether) (–)-**32** (39.2 mg, 75.0 μmol, 1 equiv) in acetonitrile (250 μL) at 23 °C, and the reaction was placed under a balloon of oxygen. The clear solution immediately turned orange. After 1 h, the reaction was diluted with dichloromethane (5 mL) and washed with saturated aqueous ammonium chloride solution (5 mL). The aqueous layer was extracted with dichloromethane (3 × 3 mL), and the combined organic layers were dried over sodium sulfate, were filtered, and were concentrated under reduced pressure. The orange residue was purified by flash column chromatography on silica gel (eluent: 3% acetone in dichloromethane) to afford the bisproline epidithiodiketopiperazine (–)-**34** (11.5 mg, 59.8%) as a white solid.

Please see page S34 for the full characterization data for bisproline epidithiodiketopiperazine (–)-**34**.



3-Propyl Tetracyclic Bis(ethylphenylketone thioether) (+)-33:

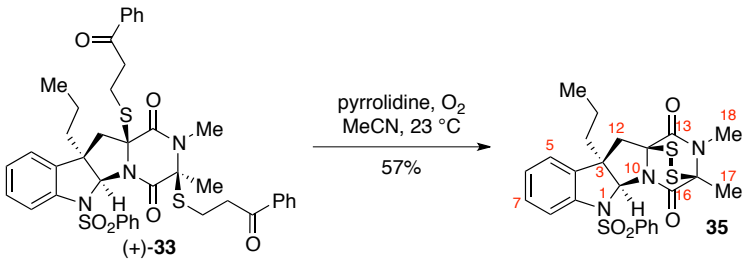
Trifluoroacetic acid (1 mL) was added via syringe to a solution of 3-propyl tetracyclic diol **S5** (46.3 mg, 95.4 μmol, 1 equiv) and 3-mercaptopropiophenone (**30**, 72.3 μL, 477 μmol, 5.00 equiv) in acetonitrile (1 mL) at 23 °C. The clear solution immediately turned yellow. After 30 min, the reaction was diluted with ethyl acetate (5 mL) and washed with saturated aqueous sodium bicarbonate solution (2 mL). The aqueous layer was extracted with ethyl acetate (3 × 5 mL), and the combined organic layers were dried over sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 3% acetone in dichloromethane) to afford the 3-propyl tetracyclic bis(ethylphenylketone thioether) (+)-**33** (54.5 mg, 73.1%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 8.00–7.97 (m, 4H, COPh-*m*-**H**), 7.81 (d, *J* = 8.5, 2H, SO_2Ph-*o*-**H**), 7.67 (d, 1H, C_8**H**), (7.53–7.48, (m, 1H, SO_2Ph-*p*-**H**), 7.53–7.48 (m, 2H, SO_2Ph-*m*-**H**), 7.47–7.53 (m, 4H, COPh-*o*-**H**), 7.47–7.35 (m, 2H, COPh-*p*-**H**), 7.53–7.48 (m, 1H, SO_2Ph-*p*-**H**), 7.17 (app-dt, *J* = 1.3, 7.0, 1H, C_7**H**), 7.06 (d, *J* = 7.5, 1H, C_5**H**), 7.00 (app-t, *J* = 7.5, 1H, C_6**H**), 6.26 (s, 1H, C_2**H**), 3.45–3.38 (m, 1H, C_{19}**H**$_a$), 3.30–3.23 (m, 1H, C_{19}**H**$_b$), 3.12–3.02 (m, 2H, C_{20}**H**), 3.07 (s, 3H, C_{18}**H**), 2.99–2.92 (m, 2H, C_{22}**H**), 2.81 (d, *J* = 14, 1H, C_{12}**H**$_a$), 2.61–2.68 (m, 2H, C_{23}**H**), 2.30 (d, *J* = 14, 1H, C_{12}**H**$_b$), 1.92 (s, 3H, C_{17}**H**), 1.44–1.37 (m, 2H, CH_2**H**$_2$$CH_2CH_3$), 1.31–1.22 (m, 2H, CH_2CH_2**H**$_2$$CH_3$), 0.56–0.52 (m, 3H, $CH_2CH_2CH_3$**H**$_3$).

^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): δ 199.1 (**C**$_{21}$), 198.4 (**C**$_{24}$), 166.7 (**C**$_{16}$), 164.8 (**C**$_{13}$), 143.6 (**C**$_9$), 138.9 (SO_2Ph-*ipso*-**C**), 137.2 (COPh-*ipso*-**C**), 137.1 (COPh-*ipso*-**C**), 136.3 (**C**$_4$), 133.9 (SO_2Ph-*p*-**C**), 133.9 (COPh-*p*-**C**), 133.8 (COPh-*p*-**C**), 129.9 (**C**$_7$), 129.4 (SO_2Ph-*o*-**C**), 129.3 (SO_2Ph-*m*-**C**), 129.2 (COPh-*o*-**C**), 129.0 (COPh-*o*-**C**), 128.8 (COPh-*m*-**C**), 128.1 (COPh-*m*-**C**), 125.3 (**C**$_6$), 123.5 (**C**$_5$), 116.6 (**C**$_8$), 83.0 (**C**$_2$), 71.7 (**C**$_{11}$), 68.8 (**C**$_{15}$), 54.1 (**C**$_3$), 50.0 (**C**$_{12}$), 42.5 (**C**$H_2CH_2CH_3$), 39.6 (**C**$_{20}$), 38.8 (**C**$_{23}$), 30.1 (**C**$_{18}$), 27.1 (**C**$_{17}$), 25.9 (**C**$_{19}$), 25.3 (**C**$_{22}$), 38.4 (CH_2**C**H_2CH_3), 14.7 (CH_2CH_2**C**H_3).

FTIR (thin film) cm^{-1}: 2924 (m), 2851 (m), 1682 (s), 1597 (w), 1448 (m), 1372 (m).

HRMS (ESI) (*m*/*z*):	calc'd for $C_{42}H_{47}N_4O_6S_3$ $[M+NH_4]^+$: 799.2652, found: 799.2658
$[\alpha]_D^{24}$:	+124 (c = 0.075)
TLC (5% acetone in dichloromethane), R*f*:	0.25 (UV, CAM)



3-Propyl Pentacyclic Epidithiodiketopiperazine 35:

Pyrrolidine (6.8 μL, 82.8 μmol, 4.16 equiv) was added to a solution of 3-propyl tetracyclic bis(ethylphenylketone thioether) (+)-**33** (15.6 mg, 19.9 μmol, 1 equiv) in acetonitrile (150 μL) at 23 °C, and the reaction was placed under a balloon of oxygen. The clear solution immediately turned orange. After 1 h, the reaction was diluted with dichloromethane (3 mL) and washed with saturated aqueous ammonium chloride solution (3 mL). The aqueous layer was extracted with ethyl acetate (3 × 2 mL), and the combined organic layers were dried over sodium sulfate, were filtered, and were concentrated under reduced pressure. The orange residue was purified by flash column chromatography on silica gel (eluent: 3% acetone in dichloromethane) to afford the 3-propyl pentacyclic epidithiodiketopiperazine **35** (5.9 mg, 57.4%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C):	δ 7.80 (d, *J* = 7.0, 2H, SO_2Ph-*o*-**H**), 7.53 (app-t, *J* = 7.0, 1H, SO_2Ph-*p*-**H**), 7.46–7.37 (m, 1H, C_8**H**), 7.46–7.37 (m, 2H, SO_2Ph-*m*-**H**), 7.29, (app-dt, *J* = 1.1, 7.7, 1H, C_7**H**), 7.16 (app-t, *J* = 7.7, 1H, C_6**H**), 7.12 (d, *J* = 7.6, 1H, C_5**H**), 6.09 (s, 1H, C_2**H**), 3.19 (d, *J* = 15.2, 1H, C_{12}**H**$_a$), 2.98 (s, 2H, C_{18}**H**), 2.57 (d, *J* = 15.2, 1H, C_{12}**H**$_b$), 1.87 (s, 3H, C_{17}**H**), 1.43–1.30 (m, 1H, CH_2C**H**$_2CH_3$), 1.22–1.04 (m, 2H, C**H**$_2CH_2CH_3$), 0.77–0.68 (m, 2H, CH_2CH_2C**H**$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$, 20 °C):	δ 165.9 (**C**$_{13}$), 161.6 (**C**$_{16}$), 142.1 (**C**$_9$), 139.8 (SO_2Ph-*ipso*-**C**), 137.6 (**C**$_4$), 133.4 (SO_2Ph-*p*-**C**), 129.3 (**C**$_7$), 129.2 (SO_2Ph-*m*-**C**), 127.4 (SO_2Ph-*o*-**C**), 125.9 (**C**$_6$), 123.6 (**C**$_5$), 118.4 (**C**$_8$), 83.7 (**C**$_2$), 73.7 (**C**$_{11}$), 73.5 (**C**$_{15}$), 55.9 (**C**$_3$), 41.8 (**C**$_{12}$), 40.0 (**C**$H_2CH_2CH_3$), 27.7 (**C**$_{18}$), 18.3 (CH_2**C**H_2CH_3), 18.0 (**C**$_{17}$), 14.3 (CH_2CH_2**C**H_3).
FTIR (thin film) cm^{-1}:	2960 (w), 1713 (s), 1688 (s), 1478 (w), 1460 (w), 1341 (m), 1172 (m), 1092 (w).
HRMS (ESI) (*m*/*z*):	calc'd for $C_{24}H_{25}NaN_3O_4S_3$ $[M+Na]^+$: 538.0899, found: 538.0923.
TLC (1% acetone in dichloromethane), R*f*:	0.21 (UV, CAM).

Table S1. Comparison of our data for (+)-Bionectin A (1) with literature:

Assignment[17]	This Work (+)-Bionectin A (**1**) ^{1}H NMR, 500 MHz, $CDCl_3$, 20 °C	Kim's Report[16] (+)-Bionectin A (**1**) ^{1}H NMR, 500 MHz, $CDCl_3$	$\Delta\delta$[14] (ppm)	Overman's Report[15] (+)-Bionectin A (**1**) ^{1}H NMR, 500 MHz, $CDCl_3$	$\Delta\delta$[14] (ppm)
N1	5.36 (br-s)	5.63 (s)	–0.27	5.40 (br-s)	–0.04
C2	6.30 (s)	6.54 (s)	–0.24	6.33 (s)	–0.03
C3	–	–	–	–	–
C4	–	–	–	–	–
C5	7.44 (d, J = 7.5)	7.32 (dd, J = 7.5, 1.0)	+0.12	7.46 (d, J = 7.5)	–0.02
C6	6.83 (app-t, J = 7.5)	6.75 (td, J = 7.5, 1.0)	+0.08	6.85 (t, J = 7.5)	–0.02
C7	7.16–7.11 (m)	7.07 (td, J = 7.5, 1.0)	+0.07	7.19–7.13 (m)	–0.03
C8	6.69 (d, J = 7.8)	6.68 (dd, J = 7.5, 1.0)	+0.01	6.72 (d, J = 7.8)	–0.03
C9	–	–	–	–	–
N10	–	–	–	–	–
C11	–	–	–	–	–
C12	5.32 (s)	5.28 (s)	+0.04	5.35 (s)	–0.03
$C_{12}OH$	5.19 (s)	–	–	5.22 (s)	–0.03
C13		–	–	–	–
N14	–	–	–	–	–
C15	5.17 (s)	5.19 (s)	–0.02	5.20 (s)	–0.03
C16	–	–	–	–	–
C17	3.11 (s)	3.02 (s)	+0.09	3.14 (s)	–0.03
N1'	8.11 (br-s)	8.08 (br-s)	+0.03	8.06 (br-s)	+0.05
C2'	7.06 (d, J = 2.6)	7.11 (d, J = 2.4 Hz)	–0.05	7.09 (d, J = 2.5)	–0.03
C3'	–	–	–	–	–
C4'	–	–	–	–	–
C5'	7.91 (d, J = 7.8)	7.93 (dd, J = 7.8, 1.0)	–0.02	7.94 (d, J = 7.8)	–0.03
C6'	7.16–7.11 (m)	7.15 (td, J = 7.8, 1.0)	–0.02	7.19–7.13 (m)	–0.03
C7'	7.18 (app-t, J = 6.9)	7.20 (td, J = 7.8, 1.0)	–0.02	7.21 (t, J = 7.1)	–0.03
C8'	7.32 (d, J = 8.1)	7.33 (dd, J = 7.8, 1.0)	–0.01	7.34 (d, J = 8.0)	–0.02
C9'	–	–	–	–	–

[14] $\Delta\delta$ = δ (this work) – δ (reference cited in preceding column)
[15] Delorbe, J. E.; Horne, D.; Jove, R.; Mennen, S. M.; Nam, S.; Zhang, F.-L.; Overman, L. E. *J. Am. Chem. Soc.* **2013**, *135*, 4117.
[16] Zheng, C.-J.; Kim, C.-J.; Bae, K. S.; Kim, Y.-H.; Kim, W.-G. *J. Nat. Prod.* **2006**, *86*, 1816.
[17] Please see page S3 for the positional numbering system used in this report.

Table S2. Comparison of our data for (+)-Bionectin A (1) with literature:

Assignment[17]	This Work (+)-Bionectin A (1) ^{13}C NMR, 125 MHz, $CDCl_3$, 20 °C	Kim's Report[16] (+)-Bionectin A (1) ^{13}C NMR, 125 MHz, $CDCl_3$	$\Delta\delta^{14}$ (ppm)	Overman's Report[15] (+)-Bionectin A (1) ^{13}C NMR, 125 MHz, $CDCl_3$	$\Delta\delta^{14}$ (ppm)
N1	–	–	–	–	–
C2	82.5	83.1	–0.6	82.3	+0.2
C3	61.6	59.1	+2.5	61.4	+0.2
C4	130.9	131.5	–0.6	130.7	+0.2
C5	124.7	125.3	–0.6	124.5	+0.2
C6	120.1	120.3	–0.2	119.8	+0.3
C7	129.6	129.3	+0.3	129.2	+0.4
C8	110.9	110.5	+0.4	110.7	+0.2
C9	147.3	147.0	+0.3	147.1	+0.2
N10	–	–	–	–	–
C11	77.0	79.1	–2.1	76.7	+0.3
C12	81.0	80.1	+0.9	80.8	+0.2
C13	166.2	167.0	–0.8	165.9	+0.3
N14	–	–	–	–	–
C15	67.7	70.6	–2.9	67.5	+0.2
C16	161.9	163.1	–1.2	161.7	+0.2
C17	32.0	33.1	–1.1	31.8	+0.2
N1'	–	–	–	–	–
C2'	123.5	123.3	+0.2	123.3	+0.2
C3'	113.4	113.6	–0.2	113.2	+0.2
C4'	126.3	126.1	+0.2	126.1	+0.2
C5'	121.6	121.4	+0.2	121.4	+0.2
C6'	120.1	120.1	0	119.9	+0.2
C7'	122.6	122.4	+0.2	122.4	+0.2
C8'	111.7	111.7	0	111.5	+0.2
C9'	137.1	137.1	0	136.9	+0.2

Table S3. Comparison of our data for (+)-Bionectin C (2) with literature:

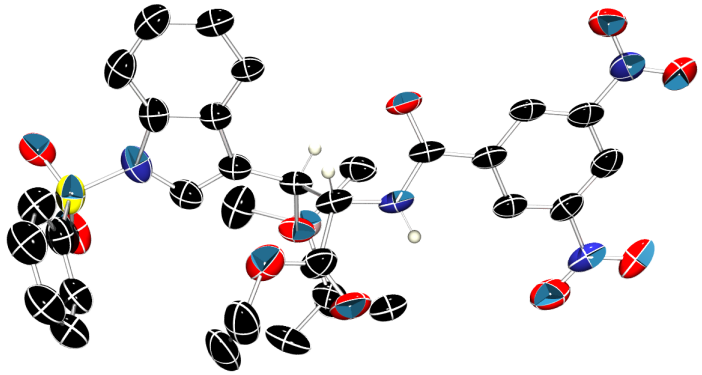
Assignment[17]	This Work (+)-Bionectin C (**2**) ^{1}H NMR, 500 MHz, $CDCl_3$, 20 ºC	Kim's Report[16] (+)-Bionectin C (**2**) ^{1}H NMR, 500 MHz, $CDCl_3$	Δδ (ppm)	Usami's Report[18] (+)-Gliocladin A (**2**) ^{1}H NMR, 500 MHz, $CDCl_3$	$\Delta\delta^{14}$ (ppm)	Overman's Report[15] (+)-Bionectin C (**2**) ^{1}H NMR, 500 MHz, $CDCl_3$	$\Delta\delta^{14}$ (ppm)
N1	5.09 (s)	5.12 (s)	–0.03	5.12 (br-s)	–0.03	5.12 (br-s)	–0.03
C2	6.34 (s)	6.35 (s)	–0.01	6.35 (s)	–0.01	6.36 (s)	–0.02
C3	–	–	–	–	–	–	–
C4	–	–	–	–	–	–	–
C5	7.41 (d, J = 7.5)	7.42 (dd, J = 7.5, 1.0)	–0.01	7.32 (br-d, J = 7.8)	+0.09	7.43 (d, J = 7.6)	–0.02
C6	6.71 (app-dt, J = 0.7, 7.5)	6.73 (td, J = 7.5, 1.0)	–0.02	6.73 (td, J = 7.8, 0.9)	–0.02	6.74 (t, J = 7.4)	–0.03
C7	7.08 (app-dt, J = 1.1, 7.6)	7.09 (td, J = 7.5, 1.0)	–0.01	7.09 (td, J = 7.8, 1.1)	–0.01	7.09 (t, J = 7.8)	–0.01
C8	6.63 (d, J = 7.8)	6.65 (dd, J = 7.5, 1.0)	–0.02	6.65 (br-d, J = 7.8)	–0.02	6.65 (d, J = 7.7)	–0.02
C9	–	–	–	–	–	–	–
N10	–	–	–	–	–	–	–
C11	–	–	–	–	–	–	–
C12	5.30 (d, J = 2.1)	5.32 (s)	–0.02	5.32 (br-d, J = 3.9)	–0.02	5.32 (br-d, J = 2.0)	–0.02
$C_{12}OH$	3.24 (d, J = 2.2)	–	–	3.28 (d, J = 3.9)	–0.04	3.28 (br-d, J = 2.0)	–0.04
C13	–	–	–	–	–	–	–
N14	–	–	–	–	–	–	–
C15	4.59 (s)	4.60 (s)	–0.01	4.60 (s)	–0.01	4.61 (s)	–0.02
C16	–	–	–	–	–	–	–
C17	3.10 (s)	3.11 (s)	–0.01	3.11 (s)	–0.01	3.12 (s)	–0.02
N1'	8.00 (br-s)	8.06 (br-s)	–0.06	8.04 (br-s)	–0.04	8.05 (br-s)	–0.05
C2'	7.10 (d, J = 2.7)	7.11 (d, J = 2.5)	–0.01	7.11 (d, J = 2.5)	–0.01	7.11 (d, J = 2.4)	–0.01
C3'	–	–	–	–	–	–	–
C4'	–	–	–	–	–	–	–
C5'	7.85 (d, J = 7.9)	7.87 (dd, J = 7.8, 1.0)	–0.02	7.87 (br-d, J = 7.8)	–0.02	7.87 (d, J = 7.8)	–0.02
C6'	7.13 (dt, J = 1.0, 7.1)	7.15 (td, J = 7.8, 1.0)	–0.02	7.15 (td, J = 7.8, 1.4)	–0.02	7.15 (t, J = 7.5)	–0.02
C7'	7.17 (dt, J = 1.0, 7.1)	7.19 (td, J = 7.8, 1.0)	–0.02	7.19 (td, J = 7.8, 1.4)	–0.02	7.20 (t, J = 7.5)	–0.03
C8'	7.31 (d, J = 7.6)	7.32 (dd, J = 7.8, 1.0)	–0.01	7.32 (br-d, J = 7.8)	–0.01	7.32 (d, J = 7.6)	–0.01
C9'	–	–	–	–	–	–	–
$C_{11}SCH_3$	2.06 (s)	2.08 (s)	–0.02	2.08 (s)	–0.02	2.09 (s)	–0.03
$C_{15}SCH_3$	2.45 (s)	2.47 (s)	–0.02	2.47 (s)	–0.02	2.48 (s)	–0.03

[18] Usami, Y.; Yamaguchi, J.; Numata, A. *Heterocycles* **2004**, *63*, 1123.

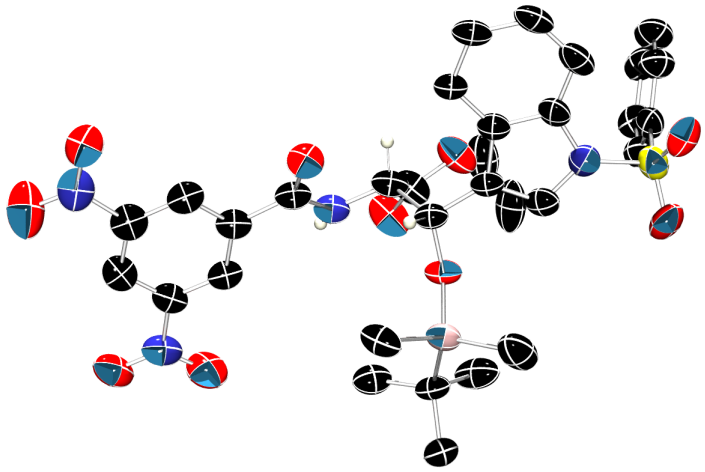
Table S4. Comparison of our data for (+)-Bionectin C (2) with literature:

Assignment[17]	This Work (+)-Bionectin C (**2**) ^{13}C NMR, 125 MHz, $CDCl_3$, 20 °C	Kim's Report[16] (+)-Bionectin C (**2**) ^{13}C NMR, 125 MHz, $CDCl_3$	$\Delta\delta^{14}$ (ppm)	Usami's Report[18] (+)-Gliocladin A (**2**) ^{13}C NMR, 125 MHz, $CDCl_3$	$\Delta\delta^{14}$ (ppm)	Overman's Report[15] (+)-Bionectin C (**2**) ^{13}C NMR, 125 MHz, $CDCl_3$	$\Delta\delta^{14}$ (ppm)
N1	–	–	–	–	–	–	–
C2	81.8	81.8	0	81.55	+0.25	81.5	+0.3
C3	59.1	59.1	0	58.94	+0.16	58.9	+0.3
C4	131.9	131.9	0	131.65	+0.25	131.6	+0.3
C5	123.4	123.5	–0.1	123.21	+0.19	123.2	+0.2
C6	119.3	119.3	0	119.10	+0.20	119.1	+0.2
C7	129.0	129.0	0	128.74	+0.26	128.7	+0.3
C8	110.1	110.1	0	109.89	+0.21	109.9	+0.2
C9	147.6	147.6	0	147.42	+0.18	147.4	+0.2
N10	–	–	–	–	–	–	–
C11	73.4	73.3	+0.1	73.15	+0.25	73.1	+0.3
C12	80.5	80.6	–0.1	80.26	+0.24	80.2	+0.3
C13	164.8	164.9	–0.1	164.6	+0.2	164.6	+0.2
N14	–	–	–	–	–	–	–
C15	67.8	60.8	**+7.0**	67.59	+0.21	67.6	+0.2
C16	165.0	165.0	0	164.78	+0.22	164.8	+0.2
C17	32.4	32.2	+0.2	32.13	+0.27	32.1	+0.3
N1'	–	–	–	–	–	–	–
C2'	123.1	123.3	–0.2	122.91	+0.19	122.9	+0.2
C3'	115.1	115.0	+0.1	114.89	+0.21	114.9	+0.2
C4'	126.0	125.9	+0.1	125.78	+0.22	125.8	+0.2
C5'	121.3	121.3	0	121.08	+0.22	121.1	+0.2
C6'	120.1	120.2	–0.1	119.90	+0.20	119.9	+0.2
C7'	122.6	122.6	0	122.34	+0.26	122.3	+0.3
C8'	111.8	111.8	0	111.53	+0.27	111.5	+0.3
C9'	137.1	137.1	0	136.91	+0.19	136.9	+0.2
$C_{11}SCH_3$	15.7	15.7	0	15.42	+0.28	15.4	+0.3
$C_{15}SCH_3$	18.3	18.2	+0.1	18.06	+0.24	18.1	+0.2

Crystal Structure of 12-Hydroxytryptophan 3,5-Dinitrobenzamide (+)-14.



View 1:



View 2:

Table S5. Crystal data and structure refinement for 12-hydroxytryptophan 3,5-dinitrobenzamide (+)-**14**.

Identification code	x8_12215	
Empirical formula	C32.33 H36.66 Cl0.66 N4 O10 S Si	
Formula weight	724.82	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 13.7346(10) Å	a= 100.0100(10)°.
	b = 16.0038(11) Å	b= 92.2140(10)°.
	c = 17.3585(13) Å	g = 108.5900(10)°.
Volume	3543.2(4) $Å^3$	
Z	4	
Density (calculated)	1.359 Mg/m^3	
Absorption coefficient	0.236 mm^{-1}	
F(000)	1519	
Crystal size	0.25 x 0.25 x 0.17 mm^3	
Theta range for data collection	1.37 to 28.70°.	
Index ranges	-18<=h<=18, -21<=k<=21, -23<=l<=23	
Reflections collected	106332	
Independent reflections	36113 [R(int) = 0.0283]	
Completeness to theta = 28.70°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9610 and 0.9434	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	36113 / 2892 / 2057	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0751, wR2 = 0.2013	
R indices (all data)	R1 = 0.0940, wR2 = 0.2202	
Absolute structure parameter	0.03(6)	
Largest diff. peak and hole	1.234 and -0.691 $e.Å^{-3}$	

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 12-hydroxytryptophan 3,5-dinitrobenzamide (+)-**14**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1A)	4358(1)	9734(1)	9480(1)	49(1)
N(1A)	4962(3)	10019(2)	8696(2)	44(1)
C(2A)	5998(3)	10065(2)	8601(3)	46(1)
C(3A)	6318(3)	10495(2)	7995(2)	39(1)
C(4A)	5472(3)	10744(2)	7696(2)	38(1)
C(5A)	5338(3)	11151(2)	7073(2)	38(1)

C(6A)	4392(3)	11263(3)	6923(2)	44(1)
C(7A)	3591(3)	10984(3)	7395(2)	48(1)
C(8A)	3705(3)	10582(3)	8015(2)	45(1)
C(9A)	4649(3)	10453(2)	8152(2)	39(1)
N(10A)	8730(2)	11756(2)	7173(2)	40(1)
C(11A)	7953(3)	11648(2)	7720(2)	40(1)
C(12A)	7346(3)	10640(3)	7670(3)	45(1)
O(13A)	7955(2)	10270(2)	8089(2)	53(1)
C(14A)	8492(3)	12069(2)	8529(2)	43(1)
C(15A)	8465(3)	11700(2)	6399(2)	42(1)
C(16A)	9297(3)	11745(2)	5864(2)	42(1)
C(17A)	10259(3)	11704(3)	6092(3)	44(1)
C(18A)	10961(3)	11734(3)	5559(3)	49(1)
C(19A)	10782(3)	11821(3)	4789(3)	51(1)
C(20A)	9821(3)	11874(3)	4584(3)	48(1)
C(21A)	9082(3)	11839(2)	5094(2)	43(1)
N(22A)	9619(3)	12036(3)	3794(2)	62(1)
O(23A)	8796(3)	12119(3)	3622(2)	70(1)
O(24A)	10301(3)	12095(4)	3353(3)	92(2)
N(25A)	11984(3)	11698(3)	5813(3)	67(1)
O(26A)	12181(3)	11771(5)	6518(3)	105(2)
O(27A)	12582(3)	11648(3)	5336(3)	69(1)
O(28A)	7811(2)	12194(2)	9036(2)	54(1)
C(29A)	8186(4)	12504(4)	9860(3)	69(1)
C(30A)	8447(17)	13525(10)	10035(11)	94(3)
C(30E)	7737(11)	13190(10)	10278(7)	94(3)
Si(1A)	8282(2)	9356(1)	7842(1)	55(1)
C(31A)	8406(7)	9186(5)	6762(4)	73(2)
C(32A)	7327(9)	8333(5)	8058(7)	97(2)
C(33A)	9530(7)	9617(6)	8473(5)	82(2)
C(34A)	10419(7)	10296(7)	8140(8)	101(3)
C(35A)	9792(10)	8749(8)	8500(6)	101(3)
C(36A)	9452(10)	10045(8)	9324(5)	106(3)
Si(1E)	8494(5)	9494(4)	7585(4)	55(1)
C(31E)	9388(17)	9910(14)	6890(12)	73(2)
C(32E)	7422(16)	8481(10)	7076(14)	97(2)
C(33E)	9080(16)	9253(14)	8469(10)	82(2)
C(34E)	10119(17)	10027(18)	8720(20)	101(3)
C(35E)	8390(20)	9230(20)	9154(14)	101(3)
C(36E)	9280(30)	8348(18)	8218(17)	106(3)
C(37A)	4675(4)	10740(3)	10173(3)	53(1)
C(38A)	4039(6)	11290(4)	10193(4)	77(2)
C(39A)	4299(7)	12088(4)	10717(4)	86(2)
C(40A)	5195(6)	12343(4)	11248(3)	79(2)
C(41A)	5777(6)	11839(4)	11232(4)	84(2)
C(42A)	5554(5)	11026(3)	10678(3)	66(1)
O(43A)	4837(3)	9174(2)	9768(2)	62(1)
O(44A)	3278(3)	9426(2)	9224(2)	58(1)
O(45A)	9401(2)	12264(2)	8700(2)	48(1)

O(46A)	7577(2)	11573(2)	6146(2)	51(1)
Si(1B)	5434(1)	5969(1)	4970(1)	50(1)
S(1B)	1413(1)	5288(1)	2906(1)	61(1)
N(1B)	1743(3)	5089(3)	3763(2)	57(1)
C(2B)	2725(3)	5060(3)	3943(2)	51(1)
C(3B)	2732(3)	4698(2)	4589(2)	43(1)
C(4B)	1696(3)	4479(2)	4830(2)	43(1)
C(5B)	1257(3)	4108(2)	5471(2)	40(1)
C(6B)	228(3)	4013(3)	5560(3)	49(1)
C(7B)	-358(3)	4261(3)	5041(3)	57(1)
C(8B)	53(4)	4614(3)	4401(3)	61(1)
C(9B)	1087(3)	4718(3)	4316(3)	50(1)
N(10B)	4303(3)	3544(3)	5559(2)	50(1)
C(11B)	3536(3)	3599(3)	4992(3)	50(1)
C(12B)	3639(3)	4593(3)	4999(2)	43(1)
O(13B)	4550(2)	4972(2)	4643(2)	50(1)
C(14B)	3683(4)	3119(4)	4196(3)	62(1)
C(15B)	4163(3)	3634(3)	6318(3)	47(1)
C(16B)	4994(3)	3564(3)	6854(3)	48(1)
C(17B)	6001(3)	3691(3)	6647(3)	47(1)
C(18B)	6720(3)	3617(3)	7176(3)	51(1)
C(19B)	6492(4)	3393(3)	7904(3)	54(1)
C(20B)	5483(4)	3270(3)	8084(3)	56(1)
C(21B)	4739(4)	3369(3)	7586(3)	51(1)
N(22B)	5173(4)	2982(3)	8828(3)	64(1)
O(23B)	4313(3)	2919(3)	8996(2)	68(1)
O(24B)	5816(5)	2827(4)	9236(3)	103(2)
N(25B)	7784(3)	3762(3)	6955(3)	62(1)
O(26B)	7953(3)	3965(4)	6299(3)	83(1)
O(27B)	8426(3)	3686(2)	7419(3)	74(1)
O(28B)	2876(3)	2983(3)	3692(2)	73(1)
C(29B)	2958(6)	2579(5)	2885(4)	90(2)
C(30B)	3581(10)	3207(7)	2557(4)	98(3)
C(30F)	2120(20)	1958(16)	2501(11)	98(3)
C(31B)	5043(5)	6879(4)	4643(5)	82(2)
C(32B)	5623(4)	6184(4)	6064(3)	64(1)
C(33B)	6589(3)	5843(3)	4493(3)	53(1)
C(34B)	7465(4)	6756(4)	4627(4)	66(1)
C(35B)	6968(4)	5165(3)	4831(3)	62(1)
C(36B)	6296(5)	5500(4)	3605(3)	79(2)
C(37B)	976(4)	4227(3)	2276(3)	54(1)
C(38B)	-41(4)	3722(3)	2284(3)	64(1)
C(39B)	-388(5)	2856(4)	1763(4)	74(1)
C(40B)	296(5)	2556(4)	1332(3)	71(1)
C(41B)	1321(5)	3092(4)	1360(3)	67(1)
C(42B)	1658(4)	3934(4)	1837(3)	60(1)
O(43B)	2306(4)	5825(2)	2644(2)	76(1)
O(44B)	699(3)	5613(2)	3064(2)	60(1)
O(45B)	4432(3)	2909(3)	4065(2)	79(1)

O(46B)	3388(3)	3778(2)	6566(2)	59(1)
N(1C)	4585(3)	4847(2)	-4(2)	46(1)
C(2C)	3631(3)	4928(3)	-224(2)	43(1)
C(3C)	3668(3)	5238(3)	-891(2)	40(1)
C(4C)	4704(3)	5395(3)	-1121(2)	38(1)
C(5C)	5194(3)	5706(3)	-1757(2)	42(1)
C(7C)	6763(3)	5537(3)	-1224(3)	47(1)
C(6C)	6218(3)	5778(3)	-1809(2)	44(1)
C(8C)	6306(3)	5225(3)	-593(2)	45(1)
C(9C)	5272(3)	5151(3)	-550(2)	41(1)
N(10C)	1752(2)	5104(2)	-2582(2)	36(1)
C(11C)	2425(3)	4774(2)	-2147(2)	35(1)
C(12C)	2787(3)	5395(3)	-1333(2)	37(1)
O(13C)	1929(2)	5268(2)	-888(2)	42(1)
C(14C)	1824(3)	3800(3)	-2110(2)	39(1)
C(15C)	2113(3)	5707(2)	-3041(2)	33(1)
C(16C)	1302(3)	6014(2)	-3417(2)	33(1)
C(17C)	354(2)	5949(2)	-3106(2)	35(1)
C(18C)	-312(3)	6292(2)	-3451(2)	39(1)
C(19C)	-114(3)	6664(3)	-4111(3)	49(1)
C(20C)	821(3)	6699(3)	-4408(2)	44(1)
C(21C)	1540(3)	6400(2)	-4067(2)	38(1)
N(22C)	1034(4)	7058(4)	-5121(3)	69(1)
O(23C)	1909(3)	7180(3)	-5333(2)	82(1)
O(24C)	355(4)	7222(4)	-5470(3)	96(2)
N(25C)	-1282(3)	6256(3)	-3102(2)	51(1)
O(26C)	-1498(3)	5823(3)	-2580(3)	74(1)
O(27C)	-1787(3)	6657(3)	-3340(2)	74(1)
O(28C)	2402(2)	3455(2)	-1725(2)	43(1)
C(29C)	1918(4)	2557(3)	-1564(2)	47(1)
C(30C)	1842(4)	2638(4)	-689(2)	58(1)
C(31C)	1331(10)	6808(7)	-1063(6)	79(2)
C(32C)	2479(7)	6731(7)	431(5)	68(2)
Si(1C)	1515(4)	6014(4)	-379(3)	56(1)
C(33C)	252(7)	5429(6)	-96(5)	73(2)
C(34C)	-306(8)	6124(8)	180(7)	84(2)
C(35C)	405(10)	4880(8)	497(6)	98(3)
C(36C)	-451(7)	4781(8)	-860(6)	87(2)
C(31G)	2909(10)	6997(8)	134(8)	79(2)
C(32G)	1327(10)	5426(8)	653(6)	68(2)
Si(1G)	1727(5)	6050(6)	-168(4)	56(1)
C(33G)	647(8)	6362(7)	-572(6)	73(2)
C(34G)	1059(11)	6990(10)	-1160(8)	84(2)
C(35G)	260(13)	6900(11)	117(8)	98(3)
C(36G)	-226(8)	5505(9)	-971(9)	87(2)
S(1C)	4894(1)	4698(1)	884(1)	41(1)
O(43C)	3940(3)	4147(2)	1110(2)	51(1)
O(44C)	5749(4)	4392(4)	838(5)	53(1)
C(37C)	5227(3)	5765(3)	1482(2)	44(1)

C(38C)	6251(4)	6302(4)	1611(3)	54(1)
C(39C)	6498(5)	7164(3)	2109(3)	66(1)
C(40C)	5747(6)	7426(4)	2429(4)	83(2)
C(41C)	4725(6)	6882(4)	2308(5)	86(2)
C(42C)	4454(5)	6030(3)	1821(3)	63(1)
S(1G)	5286(13)	4977(10)	1100(9)	41(1)
O(43G)	4323(19)	4660(20)	1430(20)	51(1)
O(44G)	5840(40)	4380(40)	860(70)	53(1)
C(37G)	6010(20)	5890(20)	1824(19)	44(1)
C(38G)	6980(20)	6480(20)	1820(20)	54(1)
C(39G)	7330(30)	7310(20)	2390(20)	66(1)
C(40G)	6680(40)	7500(30)	2900(30)	83(2)
C(41G)	5710(40)	6940(30)	2910(30)	86(2)
C(42G)	5410(30)	6070(30)	2420(20)	63(1)
O(45C)	957(2)	3413(2)	-2412(2)	49(1)
O(46C)	3013(2)	6024(2)	-3146(2)	43(1)
S(1D)	8134(1)	10291(1)	1735(1)	50(1)
N(1D)	7800(3)	10173(2)	2623(2)	48(1)
C(2D)	6832(3)	10178(3)	2861(3)	48(1)
C(3D)	6698(3)	9890(3)	3554(2)	48(1)
C(4D)	7593(3)	9687(3)	3776(2)	45(1)
C(5D)	7881(4)	9366(3)	4429(3)	54(1)
C(6D)	8821(4)	9222(4)	4470(3)	64(1)
C(7D)	9476(4)	9390(4)	3868(3)	67(1)
C(8D)	9223(4)	9707(4)	3222(3)	58(1)
C(9D)	8272(3)	9847(3)	3195(3)	46(1)
C(11D)	5965(3)	10380(3)	4816(3)	53(1)
C(12D)	5752(3)	9781(3)	3987(3)	54(1)
O(13D)	4974(2)	9955(2)	3565(2)	62(1)
C(14D)	5951(3)	11317(3)	4802(2)	51(1)
N(10D)	5228(7)	9909(7)	5380(6)	40(2)
C(15D)	5350(7)	9262(8)	5768(7)	42(2)
O(46D)	6093(7)	9016(8)	5736(6)	50(2)
C(16D)	4501(7)	8891(7)	6278(7)	53(2)
C(17D)	4738(8)	8475(6)	6858(6)	55(2)
C(18D)	4002(7)	8161(6)	7365(6)	57(2)
C(19D)	3054(7)	8242(6)	7324(6)	62(2)
C(20D)	2826(7)	8642(7)	6728(6)	57(2)
C(21D)	3535(6)	8968(6)	6201(5)	50(2)
N(22D)	1793(6)	8731(6)	6634(5)	66(2)
O(23D)	1197(6)	8487(7)	7109(6)	86(3)
O(24D)	1573(8)	9014(8)	6057(5)	78(3)
N(25D)	4229(10)	7705(8)	7972(9)	73(3)
O(26D)	3637(8)	7524(5)	8461(5)	81(2)
O(27D)	5072(8)	7570(7)	7986(7)	93(3)
N(10H)	5081(10)	10058(10)	5194(8)	40(2)
C(15H)	5167(10)	9432(11)	5618(10)	42(2)
O(46H)	5861(10)	9114(11)	5575(9)	50(2)
C(16H)	4280(9)	9089(9)	6086(8)	56(3)

C(17H)	4413(11)	8576(9)	6618(9)	64(3)
C(18H)	3611(12)	8269(8)	7084(8)	69(3)
C(19H)	2707(12)	8436(10)	7005(10)	74(3)
C(20H)	2602(10)	8917(9)	6463(9)	72(3)
C(21H)	3377(10)	9257(9)	5987(9)	61(3)
N(22H)	1640(12)	9151(12)	6387(10)	86(4)
O(23H)	913(12)	8738(9)	6708(12)	124(6)
O(24H)	1588(9)	9631(12)	5930(10)	127(6)
N(25H)	3776(12)	7801(10)	7704(9)	90(4)
O(26H)	3062(13)	7493(6)	8081(7)	95(4)
O(27H)	4614(12)	7695(13)	7788(11)	109(5)
O(28D)	6664(2)	11721(2)	4376(2)	51(1)
C(29D)	6715(4)	12617(3)	4250(3)	59(1)
C(30D)	6538(6)	12572(5)	3409(4)	85(2)
C(31D)	3327(12)	8399(10)	3588(11)	81(2)
C(32D)	4261(17)	8900(20)	2076(9)	91(3)
Si(1D)	3822(5)	9388(5)	3172(6)	106(2)
C(33D)	2939(8)	9938(10)	2903(8)	97(2)
C(34D)	3485(16)	10533(12)	2323(10)	114(3)
C(35D)	2004(11)	9174(16)	2396(12)	138(5)
C(36D)	2763(14)	10376(14)	3751(11)	119(4)
C(31H)	3624(9)	8146(8)	3607(8)	81(2)
C(32H)	4003(12)	8951(14)	1970(6)	91(3)
Si(1H)	3902(3)	9101(3)	3120(3)	76(1)
C(33H)	2801(6)	9492(8)	3422(6)	97(2)
C(34H)	2983(13)	10432(10)	3234(9)	114(3)
C(35H)	1805(9)	8803(13)	2928(9)	138(5)
C(36H)	2648(10)	9574(12)	4303(7)	119(4)
C(37D)	7612(3)	9213(3)	1125(2)	45(1)
C(38D)	6600(4)	8918(3)	811(2)	49(1)
C(39D)	6207(5)	8094(3)	300(3)	59(1)
C(40D)	6822(5)	7571(3)	128(3)	65(1)
C(41D)	7812(5)	7859(4)	438(4)	72(1)
C(42D)	8248(5)	8697(4)	952(4)	67(1)
O(43D)	9237(3)	10563(3)	1793(2)	70(1)
O(44D)	7605(3)	10848(2)	1490(2)	61(1)
O(45D)	5369(2)	11637(3)	5147(2)	60(1)
Cl(1S)	-1630(2)	5448(1)	2030(1)	74(1)
Cl(2S)	-675(2)	7370(2)	2079(1)	88(1)
C(1S)	-1015(8)	6491(6)	2584(5)	78(2)
Cl(3S)	-9115(3)	-1357(3)	612(3)	127(2)
Cl(4S)	-8676(4)	525(3)	1030(3)	142(2)
C(2S)	-8234(12)	-331(10)	567(10)	114(4)

Table S7. Bond lengths [Å] and angles [°] for 12-hydroxytryptophan 3,5-dinitrobenzamide (+)-**14**.

S(1A)-O(43A)	1.411(3)	S(1A)-N(1A)	1.676(4)
S(1A)-O(44A)	1.431(4)	S(1A)-C(37A)	1.751(4)

N(1A)-C(9A)	1.394(5)	C(37A)-C(42A)	1.365(8)
N(1A)-C(2A)	1.418(5)	C(37A)-C(38A)	1.421(7)
C(2A)-C(3A)	1.368(6)	C(38A)-C(39A)	1.366(8)
C(3A)-C(4A)	1.448(5)	C(39A)-C(40A)	1.412(10)
C(3A)-C(12A)	1.505(5)	C(40A)-C(41A)	1.302(9)
C(4A)-C(5A)	1.389(6)	C(41A)-C(42A)	1.414(7)
C(4A)-C(9A)	1.409(5)	Si(1B)-O(13B)	1.654(3)
C(5A)-C(6A)	1.389(5)	Si(1B)-C(32B)	1.863(5)
C(6A)-C(7A)	1.402(6)	Si(1B)-C(33B)	1.868(5)
C(7A)-C(8A)	1.374(7)	Si(1B)-C(31B)	1.870(6)
C(8A)-C(9A)	1.394(5)	S(1B)-O(44B)	1.266(4)
N(10A)-C(15A)	1.359(5)	S(1B)-O(43B)	1.399(4)
N(10A)-C(11A)	1.445(5)	S(1B)-N(1B)	1.650(4)
C(11A)-C(14A)	1.499(6)	S(1B)-C(37B)	1.758(5)
C(11A)-C(12A)	1.547(5)	N(1B)-C(2B)	1.390(6)
C(12A)-O(13A)	1.414(5)	N(1B)-C(9B)	1.419(6)
O(13A)-Si(1A)	1.655(3)	C(2B)-C(3B)	1.349(6)
O(13A)-Si(1E)	1.764(6)	C(3B)-C(4B)	1.449(5)
C(14A)-O(45A)	1.198(5)	C(3B)-C(12B)	1.481(6)
C(14A)-O(28A)	1.345(5)	C(4B)-C(9B)	1.380(6)
C(15A)-O(46A)	1.221(4)	C(4B)-C(5B)	1.418(6)
C(15A)-C(16A)	1.492(6)	C(5B)-C(6B)	1.390(5)
C(16A)-C(17A)	1.389(5)	C(6B)-C(7B)	1.374(7)
C(16A)-C(21A)	1.401(6)	C(7B)-C(8B)	1.391(8)
C(17A)-C(18A)	1.356(6)	C(8B)-C(9B)	1.392(7)
C(18A)-C(19A)	1.389(6)	N(10B)-C(15B)	1.328(6)
C(18A)-N(25A)	1.478(6)	N(10B)-C(11B)	1.448(6)
C(19A)-C(20A)	1.386(6)	C(11B)-C(14B)	1.513(6)
C(20A)-C(21A)	1.367(6)	C(11B)-C(12B)	1.548(6)
C(20A)-N(22A)	1.471(6)	C(12B)-O(13B)	1.421(5)
N(22A)-O(23A)	1.212(6)	C(14B)-O(45B)	1.198(6)
N(22A)-O(24A)	1.223(6)	C(14B)-O(28B)	1.322(6)
N(25A)-O(27A)	1.199(6)	C(15B)-O(46B)	1.236(5)
N(25A)-O(26A)	1.220(7)	C(15B)-C(16B)	1.488(7)
O(28A)-C(29A)	1.446(6)	C(16B)-C(21B)	1.392(6)
C(29A)-C(30E)	1.516(11)	C(16B)-C(17B)	1.403(6)
C(29A)-C(30A)	1.528(15)	C(17B)-C(18B)	1.368(7)
Si(1A)-C(32A)	1.850(7)	C(18B)-C(19B)	1.394(7)
Si(1A)-C(31A)	1.869(7)	C(18B)-N(25B)	1.481(6)
Si(1A)-C(33A)	1.885(10)	C(19B)-C(20B)	1.392(7)
C(33A)-C(36A)	1.538(10)	C(20B)-C(21B)	1.379(7)
C(33A)-C(35A)	1.549(9)	C(20B)-N(22B)	1.479(7)
C(33A)-C(34A)	1.559(11)	N(22B)-O(23B)	1.205(6)
Si(1E)-C(31E)	1.810(13)	N(22B)-O(24B)	1.223(6)
Si(1E)-C(32E)	1.859(14)	N(25B)-O(27B)	1.221(6)
Si(1E)-C(33E)	1.860(16)	N(25B)-O(26B)	1.248(7)
C(33E)-C(35E)	1.544(14)	O(28B)-C(29B)	1.463(7)
C(33E)-C(34E)	1.550(15)	C(29B)-C(30F)	1.318(19)
C(33E)-C(36E)	1.553(14)	C(29B)-C(30B)	1.325(12)

C(33B)-C(35B)	1.533(7)	Si(1C)-C(33C)	1.821(10)
C(33B)-C(36B)	1.535(7)	C(33C)-C(35C)	1.513(11)
C(33B)-C(34B)	1.542(6)	C(33C)-C(34C)	1.564(9)
C(37B)-C(38B)	1.374(7)	C(33C)-C(36C)	1.597(11)
C(37B)-C(42B)	1.375(8)	C(31G)-Si(1G)	1.815(11)
C(38B)-C(39B)	1.441(8)	C(32G)-Si(1G)	1.881(11)
C(39B)-C(40B)	1.375(9)	Si(1G)-C(33G)	1.859(12)
C(40B)-C(41B)	1.390(8)	C(33G)-C(36G)	1.534(12)
C(41B)-C(42B)	1.378(8)	C(33G)-C(34G)	1.553(12)
N(1C)-C(9C)	1.402(5)	C(33G)-C(35G)	1.560(11)
N(1C)-C(2C)	1.402(5)	S(1C)-O(44C)	1.407(4)
N(1C)-S(1C)	1.659(4)	S(1C)-O(43C)	1.441(4)
N(1C)-S(1G)	2.058(16)	S(1C)-C(37C)	1.748(4)
C(2C)-C(3C)	1.332(6)	C(37C)-C(42C)	1.379(7)
C(3C)-C(4C)	1.449(5)	C(37C)-C(38C)	1.380(6)
C(3C)-C(12C)	1.519(5)	C(38C)-C(39C)	1.425(7)
C(4C)-C(5C)	1.398(5)	C(39C)-C(40C)	1.337(9)
C(4C)-C(9C)	1.419(5)	C(40C)-C(41C)	1.381(9)
C(5C)-C(6C)	1.383(5)	C(41C)-C(42C)	1.402(7)
C(7C)-C(8C)	1.375(7)	S(1G)-O(44G)	1.420(17)
C(7C)-C(6C)	1.414(6)	S(1G)-O(43G)	1.436(16)
C(8C)-C(9C)	1.392(5)	S(1G)-C(37G)	1.743(17)
N(10C)-C(15C)	1.343(5)	C(37G)-C(38G)	1.373(16)
N(10C)-C(11C)	1.450(4)	C(37G)-C(42G)	1.394(16)
C(11C)-C(14C)	1.527(5)	C(38G)-C(39G)	1.433(17)
C(11C)-C(12C)	1.540(5)	C(39G)-C(40G)	1.352(17)
C(12C)-O(13C)	1.414(4)	C(40G)-C(41G)	1.359(17)
O(13C)-Si(1C)	1.623(5)	C(41G)-C(42G)	1.413(17)
O(13C)-Si(1G)	1.706(7)	S(1D)-O(44D)	1.422(4)
C(14C)-O(45C)	1.202(5)	S(1D)-O(43D)	1.431(4)
C(14C)-O(28C)	1.322(4)	S(1D)-N(1D)	1.650(4)
C(15C)-O(46C)	1.213(4)	S(1D)-C(37D)	1.769(4)
C(15C)-C(16C)	1.521(5)	N(1D)-C(2D)	1.409(5)
C(16C)-C(21C)	1.379(5)	N(1D)-C(9D)	1.423(6)
C(16C)-C(17C)	1.409(5)	C(2D)-C(3D)	1.360(7)
C(17C)-C(18C)	1.375(5)	C(3D)-C(4D)	1.422(6)
C(18C)-C(19C)	1.378(6)	C(3D)-C(12D)	1.504(5)
C(18C)-N(25C)	1.474(5)	C(4D)-C(9D)	1.401(6)
C(19C)-C(20C)	1.391(6)	C(4D)-C(5D)	1.415(7)
C(20C)-C(21C)	1.381(5)	C(5D)-C(6D)	1.383(7)
C(20C)-N(22C)	1.455(5)	C(6D)-C(7D)	1.411(7)
N(22C)-O(24C)	1.214(6)	C(7D)-C(8D)	1.383(8)
N(22C)-O(23C)	1.235(6)	C(8D)-C(9D)	1.394(6)
N(25C)-O(27C)	1.190(5)	C(11D)-N(10H)	1.396(14)
N(25C)-O(26C)	1.223(6)	C(11D)-C(14D)	1.511(7)
O(28C)-C(29C)	1.460(5)	C(11D)-C(12D)	1.545(5)
C(29C)-C(30C)	1.512(6)	C(11D)-N(10D)	1.547(10)
C(31C)-Si(1C)	1.948(11)	C(12D)-O(13D)	1.400(6)
C(32C)-Si(1C)	1.836(9)	O(13D)-Si(1D)	1.605(7)

O(13D)-Si(1H)	1.701(5)	C(38D)-C(39D)	1.386(6)
C(14D)-O(45D)	1.205(5)	C(39D)-C(40D)	1.373(8)
C(14D)-O(28D)	1.319(6)	C(40D)-C(41D)	1.345(9)
N(10D)-C(15D)	1.377(10)	C(41D)-C(42D)	1.409(9)
C(15D)-O(46D)	1.206(9)	Cl(1S)-C(1S)	1.704(9)
C(15D)-C(16D)	1.522(10)	Cl(2S)-C(1S)	1.733(9)
C(16D)-C(21D)	1.375(10)	Cl(3S)-C(2S)	1.718(18)
C(16D)-C(17D)	1.382(11)	Cl(4S)-C(2S)	1.753(12)
C(17D)-C(18D)	1.396(10)	O(43A)-S(1A)-O(44A)	121.7(2)
C(18D)-C(19D)	1.350(11)	O(43A)-S(1A)-N(1A)	105.6(2)
C(18D)-N(25D)	1.458(15)	O(44A)-S(1A)-N(1A)	105.8(2)
C(19D)-C(20D)	1.381(12)	O(43A)-S(1A)-C(37A)	107.9(2)
C(20D)-C(21D)	1.403(10)	O(44A)-S(1A)-C(37A)	109.6(2)
C(20D)-N(22D)	1.475(12)	N(1A)-S(1A)-C(37A)	105.0(2)
N(22D)-O(23D)	1.209(9)	C(9A)-N(1A)-C(2A)	108.6(3)
N(22D)-O(24D)	1.234(11)	C(9A)-N(1A)-S(1A)	125.8(3)
N(25D)-O(26D)	1.207(10)	C(2A)-N(1A)-S(1A)	123.8(3)
N(25D)-O(27D)	1.243(12)	C(3A)-C(2A)-N(1A)	108.6(3)
N(10H)-C(15H)	1.373(13)	C(2A)-C(3A)-C(4A)	107.8(3)
C(15H)-O(46H)	1.214(12)	C(2A)-C(3A)-C(12A)	125.9(3)
C(15H)-C(16H)	1.500(13)	C(4A)-C(3A)-C(12A)	126.2(4)
C(16H)-C(21H)	1.362(13)	C(5A)-C(4A)-C(9A)	119.5(3)
C(16H)-C(17H)	1.381(13)	C(5A)-C(4A)-C(3A)	133.3(4)
C(17H)-C(18H)	1.405(13)	C(9A)-C(4A)-C(3A)	107.2(3)
C(18H)-C(19H)	1.358(14)	C(6A)-C(5A)-C(4A)	118.6(4)
C(18H)-N(25H)	1.462(16)	C(5A)-C(6A)-C(7A)	120.8(4)
C(19H)-C(20H)	1.346(14)	C(8A)-C(7A)-C(6A)	121.6(4)
C(20H)-C(21H)	1.403(12)	C(7A)-C(8A)-C(9A)	117.3(4)
C(20H)-N(22H)	1.490(17)	N(1A)-C(9A)-C(8A)	130.2(4)
N(22H)-O(24H)	1.211(13)	N(1A)-C(9A)-C(4A)	107.8(3)
N(22H)-O(23H)	1.222(12)	C(8A)-C(9A)-C(4A)	122.0(4)
N(25H)-O(26H)	1.220(12)	C(15A)-N(10A)-C(11A)	120.4(3)
N(25H)-O(27H)	1.223(13)	N(10A)-C(11A)-C(14A)	107.8(3)
O(28D)-C(29D)	1.468(6)	N(10A)-C(11A)-C(12A)	110.5(3)
C(29D)-C(30D)	1.456(8)	C(14A)-C(11A)-C(12A)	110.6(3)
C(31D)-Si(1D)	1.799(14)	O(13A)-C(12A)-C(3A)	110.1(4)
C(32D)-Si(1D)	2.116(14)	O(13A)-C(12A)-C(11A)	108.3(3)
Si(1D)-C(33D)	1.802(14)	C(3A)-C(12A)-C(11A)	112.3(3)
C(33D)-C(34D)	1.556(14)	C(12A)-O(13A)-Si(1A)	131.4(3)
C(33D)-C(35D)	1.567(13)	C(12A)-O(13A)-Si(1E)	120.4(4)
C(33D)-C(36D)	1.580(13)	Si(1A)-O(13A)-Si(1E)	19.24(17)
C(31H)-Si(1H)	1.818(12)	O(45A)-C(14A)-O(28A)	124.9(4)
C(32H)-Si(1H)	1.984(11)	O(45A)-C(14A)-C(11A)	124.6(4)
Si(1H)-C(33H)	1.871(10)	O(28A)-C(14A)-C(11A)	110.5(3)
C(33H)-C(36H)	1.539(12)	O(46A)-C(15A)-N(10A)	121.6(4)
C(33H)-C(34H)	1.540(13)	O(46A)-C(15A)-C(16A)	121.5(4)
C(33H)-C(35H)	1.563(11)	N(10A)-C(15A)-C(16A)	116.8(3)
C(37D)-C(38D)	1.374(6)	C(17A)-C(16A)-C(21A)	119.2(4)
C(37D)-C(42D)	1.390(6)	C(17A)-C(16A)-C(15A)	123.6(4)

C(21A)-C(16A)-C(15A)	117.2(3)
C(18A)-C(17A)-C(16A)	119.3(4)
C(17A)-C(18A)-C(19A)	123.6(4)
C(17A)-C(18A)-N(25A)	118.7(4)
C(19A)-C(18A)-N(25A)	117.8(4)
C(20A)-C(19A)-C(18A)	115.7(4)
C(21A)-C(20A)-C(19A)	123.2(4)
C(21A)-C(20A)-N(22A)	118.7(4)
C(19A)-C(20A)-N(22A)	117.9(4)
C(20A)-C(21A)-C(16A)	119.0(4)
O(23A)-N(22A)-O(24A)	123.8(4)
O(23A)-N(22A)-C(20A)	118.3(4)
O(24A)-N(22A)-C(20A)	117.9(4)
O(27A)-N(25A)-O(26A)	124.1(4)
O(27A)-N(25A)-C(18A)	119.6(4)
O(26A)-N(25A)-C(18A)	116.2(4)
C(14A)-O(28A)-C(29A)	117.6(4)
O(28A)-C(29A)-C(30E)	113.3(6)
O(28A)-C(29A)-C(30A)	107.0(8)
C(30E)-C(29A)-C(30A)	42.0(9)
O(13A)-Si(1A)-C(32A)	113.4(3)
O(13A)-Si(1A)-C(31A)	107.5(3)
C(32A)-Si(1A)-C(31A)	108.9(5)
O(13A)-Si(1A)-C(33A)	103.9(3)
C(32A)-Si(1A)-C(33A)	109.0(5)
C(31A)-Si(1A)-C(33A)	114.2(4)
C(36A)-C(33A)-C(35A)	107.5(7)
C(36A)-C(33A)-C(34A)	108.3(9)
C(35A)-C(33A)-C(34A)	110.0(7)
C(36A)-C(33A)-Si(1A)	110.8(6)
C(35A)-C(33A)-Si(1A)	110.9(7)
C(34A)-C(33A)-Si(1A)	109.4(6)
O(13A)-Si(1E)-C(31E)	115.7(6)
O(13A)-Si(1E)-C(32E)	108.4(7)
C(31E)-Si(1E)-C(32E)	109.8(11)
O(13A)-Si(1E)-C(33E)	97.0(7)
C(31E)-Si(1E)-C(33E)	115.2(10)
C(32E)-Si(1E)-C(33E)	110.1(11)
C(35E)-C(33E)-C(34E)	109.0(16)
C(35E)-C(33E)-C(36E)	111.7(15)
C(34E)-C(33E)-C(36E)	109.8(16)
C(35E)-C(33E)-Si(1E)	112.2(13)
C(34E)-C(33E)-Si(1E)	106.3(14)
C(36E)-C(33E)-Si(1E)	107.7(14)
C(42A)-C(37A)-C(38A)	119.0(5)
C(42A)-C(37A)-S(1A)	120.8(4)
C(38A)-C(37A)-S(1A)	120.2(4)
C(39A)-C(38A)-C(37A)	120.4(6)
C(38A)-C(39A)-C(40A)	118.7(6)
C(41A)-C(40A)-C(39A)	121.0(5)
C(40A)-C(41A)-C(42A)	121.8(6)
C(37A)-C(42A)-C(41A)	119.0(6)
O(13B)-Si(1B)-C(32B)	109.3(2)
O(13B)-Si(1B)-C(33B)	102.37(17)
C(32B)-Si(1B)-C(33B)	113.4(2)
O(13B)-Si(1B)-C(31B)	111.1(2)
C(32B)-Si(1B)-C(31B)	109.7(3)
C(33B)-Si(1B)-C(31B)	110.8(3)
O(44B)-S(1B)-O(43B)	118.5(3)
O(44B)-S(1B)-N(1B)	102.2(2)
O(43B)-S(1B)-N(1B)	107.7(2)
O(44B)-S(1B)-C(37B)	113.3(2)
O(43B)-S(1B)-C(37B)	109.0(3)
N(1B)-S(1B)-C(37B)	104.8(2)
C(2B)-N(1B)-C(9B)	109.0(4)
C(2B)-N(1B)-S(1B)	121.1(3)
C(9B)-N(1B)-S(1B)	128.1(3)
C(3B)-C(2B)-N(1B)	109.4(4)
C(2B)-C(3B)-C(4B)	106.9(4)
C(2B)-C(3B)-C(12B)	126.5(4)
C(4B)-C(3B)-C(12B)	126.6(4)
C(9B)-C(4B)-C(5B)	119.0(4)
C(9B)-C(4B)-C(3B)	108.9(4)
C(5B)-C(4B)-C(3B)	132.1(4)
C(6B)-C(5B)-C(4B)	118.1(4)
C(7B)-C(6B)-C(5B)	121.5(4)
C(6B)-C(7B)-C(8B)	121.3(4)
C(7B)-C(8B)-C(9B)	117.1(4)
C(4B)-C(9B)-C(8B)	122.9(5)
C(4B)-C(9B)-N(1B)	105.8(4)
C(8B)-C(9B)-N(1B)	131.3(4)
C(15B)-N(10B)-C(11B)	120.6(3)
N(10B)-C(11B)-C(14B)	107.4(3)
N(10B)-C(11B)-C(12B)	110.6(3)
C(14B)-C(11B)-C(12B)	112.2(4)
O(13B)-C(12B)-C(3B)	110.7(3)
O(13B)-C(12B)-C(11B)	107.1(3)
C(3B)-C(12B)-C(11B)	113.3(3)
C(12B)-O(13B)-Si(1B)	125.9(2)
O(45B)-C(14B)-O(28B)	126.9(5)
O(45B)-C(14B)-C(11B)	123.5(5)
O(28B)-C(14B)-C(11B)	109.6(4)
O(46B)-C(15B)-N(10B)	121.7(4)
O(46B)-C(15B)-C(16B)	121.8(4)
N(10B)-C(15B)-C(16B)	116.5(3)
C(21B)-C(16B)-C(17B)	120.1(4)
C(21B)-C(16B)-C(15B)	117.3(4)
C(17B)-C(16B)-C(15B)	122.6(4)

C(18B)-C(17B)-C(16B)	118.9(4)	C(7C)-C(8C)-C(9C)	117.1(4)
C(17B)-C(18B)-C(19B)	123.1(4)	C(8C)-C(9C)-N(1C)	131.5(4)
C(17B)-C(18B)-N(25B)	118.4(4)	C(8C)-C(9C)-C(4C)	122.4(4)
C(19B)-C(18B)-N(25B)	118.5(4)	N(1C)-C(9C)-C(4C)	106.1(3)
C(20B)-C(19B)-C(18B)	116.2(4)	C(15C)-N(10C)-C(11C)	122.3(3)
C(21B)-C(20B)-C(19B)	123.1(5)	N(10C)-C(11C)-C(14C)	107.4(3)
C(21B)-C(20B)-N(22B)	117.8(4)	N(10C)-C(11C)-C(12C)	109.0(3)
C(19B)-C(20B)-N(22B)	119.0(5)	C(14C)-C(11C)-C(12C)	113.7(3)
C(20B)-C(21B)-C(16B)	118.6(4)	O(13C)-C(12C)-C(3C)	110.1(3)
O(23B)-N(22B)-O(24B)	124.3(5)	O(13C)-C(12C)-C(11C)	108.0(3)
O(23B)-N(22B)-C(20B)	118.4(4)	C(3C)-C(12C)-C(11C)	113.7(3)
O(24B)-N(22B)-C(20B)	117.3(5)	C(12C)-O(13C)-Si(1C)	129.2(3)
O(27B)-N(25B)-O(26B)	124.9(4)	C(12C)-O(13C)-Si(1G)	126.4(4)
O(27B)-N(25B)-C(18B)	118.8(5)	Si(1C)-O(13C)-Si(1G)	15.0(3)
O(26B)-N(25B)-C(18B)	116.3(4)	O(45C)-C(14C)-O(28C)	126.2(4)
C(14B)-O(28B)-C(29B)	114.9(5)	O(45C)-C(14C)-C(11C)	123.4(3)
C(30F)-C(29B)-C(30B)	122.9(13)	O(28C)-C(14C)-C(11C)	110.4(3)
C(30F)-C(29B)-O(28B)	116.8(12)	O(46C)-C(15C)-N(10C)	124.8(3)
C(30B)-C(29B)-O(28B)	108.5(6)	O(46C)-C(15C)-C(16C)	120.1(3)
C(35B)-C(33B)-C(36B)	108.9(5)	N(10C)-C(15C)-C(16C)	115.0(3)
C(35B)-C(33B)-C(34B)	109.4(4)	C(21C)-C(16C)-C(17C)	120.1(3)
C(36B)-C(33B)-C(34B)	108.7(4)	C(21C)-C(16C)-C(15C)	117.6(3)
C(35B)-C(33B)-Si(1B)	110.1(3)	C(17C)-C(16C)-C(15C)	122.3(3)
C(36B)-C(33B)-Si(1B)	109.3(4)	C(18C)-C(17C)-C(16C)	118.9(3)
C(34B)-C(33B)-Si(1B)	110.4(4)	C(17C)-C(18C)-C(19C)	122.8(3)
C(38B)-C(37B)-C(42B)	123.9(5)	C(17C)-C(18C)-N(25C)	118.6(3)
C(38B)-C(37B)-S(1B)	116.5(4)	C(19C)-C(18C)-N(25C)	118.6(4)
C(42B)-C(37B)-S(1B)	119.5(4)	C(18C)-C(19C)-C(20C)	116.3(4)
C(37B)-C(38B)-C(39B)	115.8(5)	C(21C)-C(20C)-C(19C)	123.4(4)
C(40B)-C(39B)-C(38B)	120.3(5)	C(21C)-C(20C)-N(22C)	119.1(4)
C(39B)-C(40B)-C(41B)	121.1(5)	C(19C)-C(20C)-N(22C)	117.5(4)
C(42B)-C(41B)-C(40B)	119.2(6)	C(16C)-C(21C)-C(20C)	118.4(3)
C(37B)-C(42B)-C(41B)	119.6(5)	O(24C)-N(22C)-O(23C)	124.0(4)
C(9C)-N(1C)-C(2C)	108.6(3)	O(24C)-N(22C)-C(20C)	118.9(4)
C(9C)-N(1C)-S(1C)	126.4(3)	O(23C)-N(22C)-C(20C)	117.1(4)
C(2C)-N(1C)-S(1C)	122.8(3)	O(27C)-N(25C)-O(26C)	125.1(4)
C(9C)-N(1C)-S(1G)	114.2(5)	O(27C)-N(25C)-C(18C)	117.9(4)
C(2C)-N(1C)-S(1G)	129.6(5)	O(26C)-N(25C)-C(18C)	117.1(3)
S(1C)-N(1C)-S(1G)	15.4(4)	C(14C)-O(28C)-C(29C)	117.9(3)
C(3C)-C(2C)-N(1C)	110.3(3)	O(28C)-C(29C)-C(30C)	108.6(4)
C(2C)-C(3C)-C(4C)	107.4(3)	O(13C)-Si(1C)-C(33C)	107.8(4)
C(2C)-C(3C)-C(12C)	126.5(3)	O(13C)-Si(1C)-C(32C)	111.3(4)
C(4C)-C(3C)-C(12C)	126.0(3)	C(33C)-Si(1C)-C(32C)	115.7(5)
C(5C)-C(4C)-C(9C)	118.9(3)	O(13C)-Si(1C)-C(31C)	107.9(4)
C(5C)-C(4C)-C(3C)	133.6(3)	C(33C)-Si(1C)-C(31C)	107.8(5)
C(9C)-C(4C)-C(3C)	107.5(3)	C(32C)-Si(1C)-C(31C)	106.1(6)
C(6C)-C(5C)-C(4C)	119.3(4)	C(35C)-C(33C)-C(34C)	115.8(7)
C(8C)-C(7C)-C(6C)	122.1(4)	C(35C)-C(33C)-C(36C)	110.0(8)
C(5C)-C(6C)-C(7C)	120.2(4)	C(34C)-C(33C)-C(36C)	104.8(7)

C(35C)-C(33C)-Si(1C)	108.0(7)	C(2D)-N(1D)-C(9D)	107.5(4)
C(34C)-C(33C)-Si(1C)	109.3(7)	C(2D)-N(1D)-S(1D)	122.9(3)
C(36C)-C(33C)-Si(1C)	108.8(6)	C(9D)-N(1D)-S(1D)	128.0(3)
O(13C)-Si(1G)-C(31G)	110.3(5)	C(3D)-C(2D)-N(1D)	109.4(4)
O(13C)-Si(1G)-C(33G)	106.5(4)	C(2D)-C(3D)-C(4D)	107.9(3)
C(31G)-Si(1G)-C(33G)	113.6(7)	C(2D)-C(3D)-C(12D)	125.4(4)
O(13C)-Si(1G)-C(32G)	103.8(5)	C(4D)-C(3D)-C(12D)	126.7(4)
C(31G)-Si(1G)-C(32G)	111.3(7)	C(9D)-C(4D)-C(5D)	118.7(4)
C(33G)-Si(1G)-C(32G)	110.8(5)	C(9D)-C(4D)-C(3D)	108.4(4)
C(36G)-C(33G)-C(34G)	111.5(9)	C(5D)-C(4D)-C(3D)	132.9(4)
C(36G)-C(33G)-C(35G)	110.7(8)	C(6D)-C(5D)-C(4D)	118.9(4)
C(34G)-C(33G)-C(35G)	107.8(8)	C(5D)-C(6D)-C(7D)	120.3(5)
C(36G)-C(33G)-Si(1G)	109.3(7)	C(8D)-C(7D)-C(6D)	122.5(4)
C(34G)-C(33G)-Si(1G)	108.8(7)	C(7D)-C(8D)-C(9D)	116.1(4)
C(35G)-C(33G)-Si(1G)	108.7(8)	C(8D)-C(9D)-C(4D)	123.6(4)
O(44C)-S(1C)-O(43C)	120.0(4)	C(8D)-C(9D)-N(1D)	129.7(4)
O(44C)-S(1C)-N(1C)	107.6(4)	C(4D)-C(9D)-N(1D)	106.7(3)
O(43C)-S(1C)-N(1C)	104.6(2)	N(10H)-C(11D)-C(14D)	99.9(6)
O(44C)-S(1C)-C(37C)	111.0(3)	N(10H)-C(11D)-C(12D)	106.0(7)
O(43C)-S(1C)-C(37C)	107.7(2)	C(14D)-C(11D)-C(12D)	112.5(4)
N(1C)-S(1C)-C(37C)	104.57(19)	N(10H)-C(11D)-N(10D)	18.9(5)
C(42C)-C(37C)-C(38C)	122.5(5)	C(14D)-C(11D)-N(10D)	113.1(5)
C(42C)-C(37C)-S(1C)	118.4(4)	C(12D)-C(11D)-N(10D)	110.6(5)
C(38C)-C(37C)-S(1C)	119.1(4)	O(13D)-C(12D)-C(3D)	111.8(4)
C(37C)-C(38C)-C(39C)	117.7(5)	O(13D)-C(12D)-C(11D)	108.3(3)
C(40C)-C(39C)-C(38C)	119.8(5)	C(3D)-C(12D)-C(11D)	113.7(3)
C(39C)-C(40C)-C(41C)	122.5(6)	C(12D)-O(13D)-Si(1D)	135.9(4)
C(40C)-C(41C)-C(42C)	119.2(6)	C(12D)-O(13D)-Si(1H)	120.7(4)
C(37C)-C(42C)-C(41C)	118.3(6)	Si(1D)-O(13D)-Si(1H)	17.0(3)
O(44G)-S(1G)-O(43G)	120(3)	O(45D)-C(14D)-O(28D)	126.1(5)
O(44G)-S(1G)-C(37G)	112(3)	O(45D)-C(14D)-C(11D)	123.3(4)
O(43G)-S(1G)-C(37G)	102.9(17)	O(28D)-C(14D)-C(11D)	110.6(3)
O(44G)-S(1G)-N(1C)	95(5)	C(15D)-N(10D)-C(11D)	126.2(7)
O(43G)-S(1G)-N(1C)	93.5(17)	O(46D)-C(15D)-N(10D)	123.2(8)
C(37G)-S(1G)-N(1C)	134.2(16)	O(46D)-C(15D)-C(16D)	120.9(8)
C(38G)-C(37G)-C(42G)	119(2)	N(10D)-C(15D)-C(16D)	115.9(7)
C(38G)-C(37G)-S(1G)	129(2)	C(21D)-C(16D)-C(17D)	119.2(8)
C(42G)-C(37G)-S(1G)	111.1(18)	C(21D)-C(16D)-C(15D)	123.6(9)
C(37G)-C(38G)-C(39G)	119.8(19)	C(17D)-C(16D)-C(15D)	117.2(7)
C(40G)-C(39G)-C(38G)	119(2)	C(16D)-C(17D)-C(18D)	119.5(9)
C(39G)-C(40G)-C(41G)	122(2)	C(19D)-C(18D)-C(17D)	123.4(10)
C(40G)-C(41G)-C(42G)	118(2)	C(19D)-C(18D)-N(25D)	116.3(8)
C(37G)-C(42G)-C(41G)	120(2)	C(17D)-C(18D)-N(25D)	120.3(9)
O(44D)-S(1D)-O(43D)	120.8(2)	C(18D)-C(19D)-C(20D)	116.2(9)
O(44D)-S(1D)-N(1D)	105.3(2)	C(19D)-C(20D)-C(21D)	122.9(9)
O(43D)-S(1D)-N(1D)	106.5(2)	C(19D)-C(20D)-N(22D)	119.1(7)
O(44D)-S(1D)-C(37D)	107.8(2)	C(21D)-C(20D)-N(22D)	118.0(9)
O(43D)-S(1D)-C(37D)	109.3(2)	C(16D)-C(21D)-C(20D)	118.9(9)
N(1D)-S(1D)-C(37D)	106.32(18)	O(23D)-N(22D)-O(24D)	123.8(10)

O(23D)-N(22D)-C(20D)	118.1(9)	O(13D)-Si(1D)-C(32D)	95.7(7)
O(24D)-N(22D)-C(20D)	118.0(8)	C(31D)-Si(1D)-C(32D)	103.6(10)
O(26D)-N(25D)-O(27D)	122.7(12)	C(33D)-Si(1D)-C(32D)	103.0(8)
O(26D)-N(25D)-C(18D)	119.8(10)	C(34D)-C(33D)-C(35D)	105.5(13)
O(27D)-N(25D)-C(18D)	117.3(8)	C(34D)-C(33D)-C(36D)	121.0(13)
C(15H)-N(10H)-C(11D)	111.3(10)	C(35D)-C(33D)-C(36D)	118.1(12)
O(46H)-C(15H)-N(10H)	123.5(11)	C(34D)-C(33D)-Si(1D)	105.6(8)
O(46H)-C(15H)-C(16H)	121.1(13)	C(35D)-C(33D)-Si(1D)	105.4(10)
N(10H)-C(15H)-C(16H)	115.2(11)	C(36D)-C(33D)-Si(1D)	99.2(9)
C(21H)-C(16H)-C(17H)	121.0(11)	O(13D)-Si(1H)-C(31H)	111.7(5)
C(21H)-C(16H)-C(15H)	122.2(10)	O(13D)-Si(1H)-C(33H)	104.5(4)
C(17H)-C(16H)-C(15H)	116.8(10)	C(31H)-Si(1H)-C(33H)	98.3(6)
C(16H)-C(17H)-C(18H)	118.3(13)	O(13D)-Si(1H)-C(32H)	107.2(6)
C(19H)-C(18H)-C(17H)	121.9(13)	C(31H)-Si(1H)-C(32H)	121.1(7)
C(19H)-C(18H)-N(25H)	118.9(10)	C(33H)-Si(1H)-C(32H)	112.7(6)
C(17H)-C(18H)-N(25H)	119.1(12)	C(36H)-C(33H)-C(34H)	106.5(11)
C(20H)-C(19H)-C(18H)	117.7(12)	C(36H)-C(33H)-C(35H)	109.4(9)
C(19H)-C(20H)-C(21H)	123.4(13)	C(34H)-C(33H)-C(35H)	110.0(11)
C(19H)-C(20H)-N(22H)	119.1(10)	C(36H)-C(33H)-Si(1H)	115.2(9)
C(21H)-C(20H)-N(22H)	117.4(11)	C(34H)-C(33H)-Si(1H)	109.1(8)
C(16H)-C(21H)-C(20H)	117.7(12)	C(35H)-C(33H)-Si(1H)	106.7(9)
O(24H)-N(22H)-O(23H)	124.7(16)	C(38D)-C(37D)-C(42D)	121.4(4)
O(24H)-N(22H)-C(20H)	118.0(10)	C(38D)-C(37D)-S(1D)	119.4(3)
O(23H)-N(22H)-C(20H)	116.4(12)	C(42D)-C(37D)-S(1D)	119.1(4)
O(26H)-N(25H)-O(27H)	123.1(16)	C(37D)-C(38D)-C(39D)	119.4(4)
O(26H)-N(25H)-C(18H)	119.0(12)	C(40D)-C(39D)-C(38D)	120.0(5)
O(27H)-N(25H)-C(18H)	117.8(11)	C(41D)-C(40D)-C(39D)	120.6(5)
C(14D)-O(28D)-C(29D)	118.2(3)	C(40D)-C(41D)-C(42D)	121.5(5)
C(30D)-C(29D)-O(28D)	108.5(4)	C(37D)-C(42D)-C(41D)	117.1(5)
O(13D)-Si(1D)-C(31D)	109.8(7)	Cl(1S)-C(1S)-Cl(2S)	116.2(5)
O(13D)-Si(1D)-C(33D)	121.3(6)	Cl(3S)-C(2S)-Cl(4S)	109.2(9)
C(31D)-Si(1D)-C(33D)	118.5(8)		

Table S8. Anisotropic displacement parameters ($Å^2$ x 10^3) for 12-hydroxytryptophan 3,5-dinitrobenzamide (+)-**14**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1A)	54(1)	33(1)	60(1)	9(1)	8(1)	14(1)
N(1A)	44(2)	39(2)	51(2)	2(1)	5(1)	18(1)
C(2A)	42(2)	30(2)	67(2)	5(2)	1(2)	15(1)
C(3A)	37(2)	28(2)	52(2)	-3(1)	0(1)	14(1)
C(4A)	37(2)	27(1)	44(2)	-8(1)	-2(1)	13(1)
C(5A)	38(2)	35(2)	35(2)	-10(1)	0(1)	14(1)
C(6A)	46(2)	50(2)	36(2)	-8(2)	-7(1)	25(2)
C(7A)	43(2)	54(2)	48(2)	-4(2)	-2(2)	27(2)

C(8A)	43(2)	46(2)	45(2)	-6(2)	5(2)	20(2)
C(9A)	40(2)	36(2)	41(2)	-6(1)	1(1)	18(1)
N(10A)	32(1)	38(2)	51(2)	5(1)	-5(1)	12(1)
C(11A)	31(2)	32(2)	57(2)	6(1)	-3(1)	13(1)
C(12A)	36(2)	34(2)	68(2)	7(2)	0(2)	18(1)
O(13A)	44(1)	40(1)	83(2)	14(1)	3(1)	24(1)
C(14A)	43(2)	34(2)	51(2)	9(1)	-1(2)	11(1)
C(15A)	35(2)	32(2)	51(2)	0(1)	-8(1)	10(1)
C(16A)	32(2)	33(2)	52(2)	3(1)	-6(1)	5(1)
C(17A)	37(2)	42(2)	53(2)	14(2)	-4(2)	12(2)
C(18A)	36(2)	46(2)	64(2)	18(2)	2(2)	10(2)
C(19A)	39(2)	49(2)	58(2)	17(2)	0(2)	2(2)
C(20A)	41(2)	40(2)	49(2)	10(2)	-10(2)	-6(2)
C(21A)	32(2)	35(2)	52(2)	9(2)	-12(1)	-3(1)
N(22A)	44(2)	71(3)	52(2)	17(2)	-10(2)	-9(2)
O(23A)	54(2)	83(2)	57(2)	16(2)	-17(2)	0(2)
O(24A)	58(2)	141(4)	67(2)	49(3)	1(2)	2(2)
N(25A)	49(2)	89(3)	84(3)	48(3)	16(2)	33(2)
O(26A)	56(2)	196(6)	100(3)	89(4)	18(2)	62(3)
O(27A)	50(2)	80(2)	94(3)	43(2)	27(2)	28(2)
O(28A)	47(2)	62(2)	52(2)	1(1)	4(1)	21(1)
C(29A)	63(3)	85(4)	54(2)	5(2)	11(2)	21(3)
C(30A)	99(8)	104(6)	73(6)	-24(5)	-14(5)	49(6)
C(30E)	99(8)	104(6)	73(6)	-24(5)	-14(5)	49(6)
Si(1A)	60(1)	42(1)	85(1)	35(1)	43(1)	32(1)
C(31A)	93(5)	69(4)	85(4)	27(3)	40(4)	55(4)
C(32A)	122(6)	41(3)	131(6)	23(3)	59(5)	23(3)
C(33A)	99(5)	86(5)	105(4)	50(4)	38(4)	71(4)
C(34A)	68(4)	115(6)	142(8)	40(6)	11(4)	53(4)
C(35A)	149(7)	125(7)	93(6)	60(5)	40(5)	109(6)
C(36A)	158(9)	133(6)	73(4)	24(4)	-4(4)	112(7)
Si(1E)	60(1)	42(1)	85(1)	35(1)	43(1)	32(1)
C(31E)	93(5)	69(4)	85(4)	27(3)	40(4)	55(4)
C(32E)	122(6)	41(3)	131(6)	23(3)	59(5)	23(3)
C(33E)	99(5)	86(5)	105(4)	50(4)	38(4)	71(4)
C(34E)	68(4)	115(6)	142(8)	40(6)	11(4)	53(4)
C(35E)	149(7)	125(7)	93(6)	60(5)	40(5)	109(6)
C(36E)	158(9)	133(6)	73(4)	24(4)	-4(4)	112(7)
C(37A)	69(3)	40(2)	48(2)	8(2)	9(2)	17(2)
C(38A)	123(5)	55(3)	65(3)	5(2)	2(3)	49(3)
C(39A)	146(6)	61(3)	68(3)	6(2)	7(3)	63(4)
C(40A)	122(5)	53(3)	61(3)	-1(2)	10(3)	35(3)
C(41A)	121(5)	48(3)	67(3)	-3(2)	-18(3)	19(3)
C(42A)	88(3)	49(2)	64(3)	8(2)	15(2)	27(2)
O(43A)	71(2)	44(2)	78(2)	20(2)	11(2)	24(2)
O(44A)	52(2)	40(2)	76(2)	9(1)	10(2)	9(1)
O(45A)	39(1)	52(2)	52(2)	9(1)	-2(1)	13(1)
O(46A)	34(1)	54(2)	58(2)	-3(1)	-10(1)	13(1)
Si(1B)	44(1)	42(1)	53(1)	-3(1)	2(1)	7(1)

S(1B)	62(1)	48(1)	65(1)	4(1)	-18(1)	12(1)
N(1B)	64(2)	44(2)	46(2)	3(1)	-12(2)	2(2)
C(2B)	49(2)	49(2)	41(2)	-3(2)	0(2)	3(2)
C(3B)	42(2)	35(2)	42(2)	-3(1)	6(1)	5(1)
C(4B)	41(2)	35(2)	42(2)	-5(1)	2(1)	6(1)
C(5B)	39(2)	32(2)	44(2)	-5(1)	7(1)	9(1)
C(6B)	38(2)	34(2)	60(2)	-11(2)	8(2)	3(1)
C(7B)	35(2)	47(2)	75(3)	-8(2)	-7(2)	5(2)
C(8B)	45(2)	52(2)	73(3)	-5(2)	-19(2)	10(2)
C(9B)	44(2)	44(2)	49(2)	-1(2)	-12(2)	2(2)
N(10B)	42(2)	53(2)	55(2)	0(2)	19(1)	22(2)
C(11B)	40(2)	48(2)	58(2)	-4(2)	15(2)	15(2)
C(12B)	40(2)	42(2)	42(2)	0(1)	12(1)	8(1)
O(13B)	41(1)	49(2)	46(2)	-4(1)	12(1)	2(1)
C(14B)	58(3)	62(3)	61(3)	-14(2)	-1(2)	28(2)
C(15B)	43(2)	46(2)	54(2)	1(2)	22(2)	18(2)
C(16B)	48(2)	41(2)	54(2)	-4(2)	16(2)	20(2)
C(17B)	51(2)	36(2)	55(2)	0(2)	17(2)	18(2)
C(18B)	47(2)	38(2)	67(2)	-6(2)	6(2)	21(2)
C(19B)	65(2)	41(2)	60(2)	-8(2)	3(2)	31(2)
C(20B)	70(3)	46(2)	54(2)	-8(2)	17(2)	32(2)
C(21B)	59(2)	43(2)	53(2)	-2(2)	22(2)	25(2)
N(22B)	89(3)	55(2)	58(2)	-2(2)	15(2)	45(2)
O(23B)	90(3)	69(2)	54(2)	5(2)	24(2)	41(2)
O(24B)	132(4)	146(5)	79(3)	27(3)	28(3)	111(4)
N(25B)	49(2)	51(2)	88(3)	1(2)	17(2)	24(2)
O(26B)	55(2)	113(4)	90(3)	16(3)	24(2)	38(2)
O(27B)	51(2)	55(2)	116(3)	6(2)	-4(2)	26(2)
O(28B)	66(2)	67(2)	74(2)	-23(2)	-14(2)	28(2)
C(29B)	132(6)	78(4)	60(3)	-9(3)	-23(3)	50(4)
C(30B)	167(8)	100(6)	38(3)	3(3)	-12(4)	67(5)
C(30F)	167(8)	100(6)	38(3)	3(3)	-12(4)	67(5)
C(31B)	71(3)	55(3)	108(5)	-1(3)	-24(3)	15(3)
C(32B)	47(2)	80(3)	48(2)	-11(2)	6(2)	14(2)
C(33B)	44(2)	49(2)	56(2)	11(2)	15(2)	1(2)
C(34B)	57(3)	58(3)	74(3)	24(2)	6(2)	3(2)
C(35B)	52(2)	56(2)	77(3)	7(2)	23(2)	19(2)
C(36B)	78(4)	83(4)	48(2)	-1(2)	24(2)	-4(3)
C(37B)	60(2)	46(2)	47(2)	6(2)	-14(2)	8(2)
C(38B)	55(2)	51(2)	75(3)	9(2)	4(2)	7(2)
C(39B)	67(3)	60(3)	69(3)	-1(2)	-12(2)	-4(2)
C(40B)	88(4)	53(3)	55(3)	7(2)	1(2)	5(2)
C(41B)	77(3)	64(3)	49(2)	6(2)	7(2)	12(2)
C(42B)	64(3)	60(3)	48(2)	15(2)	2(2)	9(2)
O(43B)	100(3)	42(2)	67(2)	18(2)	-11(2)	-4(2)
O(44B)	100(2)	29(1)	48(2)	-1(1)	7(2)	23(1)
O(45B)	73(2)	100(3)	65(2)	-23(2)	5(2)	51(2)
O(46B)	56(2)	71(2)	64(2)	11(2)	29(2)	39(2)
N(1C)	46(2)	56(2)	40(2)	3(1)	2(1)	28(2)

C(2C)	39(2)	55(2)	39(2)	5(2)	5(1)	22(2)
C(3C)	35(2)	54(2)	36(2)	3(2)	8(1)	21(2)
C(4C)	35(2)	44(2)	35(2)	-4(1)	5(1)	21(1)
C(5C)	40(2)	47(2)	40(2)	0(2)	8(1)	20(2)
C(7C)	33(2)	43(2)	62(2)	-7(2)	5(2)	16(2)
C(6C)	38(2)	44(2)	46(2)	-3(2)	12(2)	14(2)
C(8C)	41(2)	45(2)	49(2)	-8(2)	1(2)	22(2)
C(9C)	42(2)	39(2)	40(2)	-7(1)	2(1)	20(2)
N(10C)	28(1)	47(2)	36(1)	11(1)	10(1)	14(1)
C(11C)	34(2)	47(2)	32(2)	6(1)	11(1)	23(1)
C(12C)	36(2)	50(2)	31(2)	6(1)	11(1)	22(2)
O(13C)	38(1)	62(2)	38(1)	9(1)	15(1)	29(1)
C(14C)	48(2)	52(2)	26(2)	7(1)	11(1)	26(2)
C(15C)	32(2)	33(2)	32(2)	1(1)	6(1)	8(1)
C(16C)	31(1)	27(1)	36(2)	3(1)	4(1)	4(1)
C(17C)	27(1)	34(2)	43(2)	8(1)	5(1)	7(1)
C(18C)	33(2)	33(2)	48(2)	4(1)	8(1)	10(1)
C(19C)	41(2)	54(2)	52(2)	15(2)	-2(2)	14(2)
C(20C)	43(2)	47(2)	40(2)	15(2)	3(1)	10(2)
C(21C)	34(2)	38(2)	36(2)	6(1)	2(1)	4(1)
N(22C)	61(2)	86(3)	61(2)	39(2)	3(2)	15(2)
O(23C)	67(2)	117(3)	67(2)	59(2)	14(2)	16(2)
O(24C)	91(3)	142(4)	83(3)	66(3)	10(2)	53(3)
N(25C)	35(2)	53(2)	67(2)	6(2)	7(2)	19(2)
O(26C)	55(2)	82(3)	111(3)	44(2)	50(2)	39(2)
O(27C)	54(2)	114(3)	73(2)	18(2)	6(2)	56(2)
O(28C)	53(2)	45(1)	35(1)	5(1)	3(1)	24(1)
C(29C)	62(2)	50(2)	37(2)	15(2)	11(2)	28(2)
C(30C)	54(2)	82(3)	38(2)	18(2)	7(2)	19(2)
C(31C)	101(6)	79(5)	56(4)	-11(3)	8(4)	42(4)
C(32C)	69(4)	78(5)	62(4)	1(3)	9(3)	38(3)
Si(1C)	55(2)	70(1)	48(2)	-6(2)	19(2)	33(1)
C(33C)	70(4)	102(5)	66(4)	11(3)	29(3)	53(3)
C(34C)	84(5)	95(5)	95(6)	16(4)	46(5)	56(5)
C(35C)	129(8)	132(8)	65(4)	29(4)	41(5)	76(6)
C(36C)	53(4)	114(6)	99(6)	10(5)	11(4)	39(4)
C(31G)	101(6)	79(5)	56(4)	-11(3)	8(4)	42(4)
C(32G)	69(4)	78(5)	62(4)	1(3)	9(3)	38(3)
Si(1G)	55(2)	70(1)	48(2)	-6(2)	19(2)	33(1)
C(33G)	70(4)	102(5)	66(4)	11(3)	29(3)	53(3)
C(34G)	84(5)	95(5)	95(6)	16(4)	46(5)	56(5)
C(35G)	129(8)	132(8)	65(4)	29(4)	41(5)	76(6)
C(36G)	53(4)	114(6)	99(6)	10(5)	11(4)	39(4)
S(1C)	48(1)	36(1)	40(1)	3(1)	-4(1)	18(1)
O(43C)	51(2)	42(2)	56(2)	6(1)	-5(1)	13(1)
O(44C)	54(2)	46(2)	63(2)	7(1)	-8(2)	24(1)
C(37C)	61(2)	34(2)	36(2)	7(1)	-4(2)	15(2)
C(38C)	60(2)	63(3)	33(2)	13(2)	-12(2)	11(2)
C(39C)	83(3)	47(2)	51(3)	13(2)	-9(2)	-3(2)

C(40C)	122(5)	44(3)	68(3)	2(2)	6(3)	13(3)
C(41C)	111(4)	49(3)	95(4)	-3(3)	29(4)	29(3)
C(42C)	75(3)	45(2)	68(3)	-1(2)	4(2)	26(2)
S(1G)	48(1)	36(1)	40(1)	3(1)	-4(1)	18(1)
O(43G)	51(2)	42(2)	56(2)	6(1)	-5(1)	13(1)
O(44G)	54(2)	46(2)	63(2)	7(1)	-8(2)	24(1)
C(37G)	61(2)	34(2)	36(2)	7(1)	-4(2)	15(2)
C(38G)	60(2)	63(3)	33(2)	13(2)	-12(2)	11(2)
C(39G)	83(3)	47(2)	51(3)	13(2)	-9(2)	-3(2)
C(40G)	122(5)	44(3)	68(3)	2(2)	6(3)	13(3)
C(41G)	111(4)	49(3)	95(4)	-3(3)	29(4)	29(3)
C(42G)	75(3)	45(2)	68(3)	-1(2)	4(2)	26(2)
O(45C)	42(1)	59(2)	51(2)	24(1)	5(1)	17(1)
O(46C)	29(1)	50(2)	50(1)	15(1)	10(1)	10(1)
S(1D)	46(1)	43(1)	58(1)	10(1)	9(1)	12(1)
N(1D)	41(2)	48(2)	54(2)	2(1)	10(1)	20(1)
C(2D)	36(2)	46(2)	51(2)	-14(2)	0(2)	13(2)
C(3D)	32(2)	45(2)	50(2)	-17(2)	6(1)	6(1)
C(4D)	38(2)	37(2)	52(2)	-6(2)	13(2)	7(1)
C(5D)	52(2)	46(2)	59(2)	6(2)	17(2)	12(2)
C(6D)	68(3)	71(3)	65(3)	20(2)	18(2)	35(3)
C(7D)	57(3)	90(4)	73(3)	23(3)	23(2)	45(3)
C(8D)	45(2)	67(3)	75(3)	22(2)	21(2)	28(2)
C(9D)	37(2)	44(2)	57(2)	5(2)	10(2)	16(2)
C(11D)	36(2)	58(2)	46(2)	-20(2)	10(2)	3(2)
C(12D)	31(2)	53(2)	56(2)	-26(2)	7(2)	2(2)
O(13D)	31(1)	70(2)	60(2)	-34(2)	2(1)	10(1)
C(14D)	30(2)	64(2)	42(2)	-22(2)	-5(1)	10(2)
N(10D)	30(3)	51(4)	35(4)	-9(2)	-4(3)	15(2)
C(15D)	41(4)	33(4)	43(4)	-8(2)	1(3)	8(2)
O(46D)	40(4)	52(3)	56(4)	5(3)	-2(3)	16(2)
C(16D)	51(4)	33(5)	69(6)	-5(3)	14(4)	15(3)
C(17D)	64(5)	32(4)	56(5)	-9(3)	11(4)	9(4)
C(18D)	63(5)	28(3)	63(5)	-12(3)	15(4)	1(3)
C(19D)	61(4)	29(4)	72(6)	-12(3)	18(4)	-8(3)
C(20D)	56(4)	35(6)	63(6)	-6(4)	21(4)	-1(3)
C(21D)	48(4)	32(4)	54(4)	-14(3)	9(3)	3(3)
N(22D)	55(4)	53(5)	68(4)	-11(3)	19(3)	-1(3)
O(23D)	72(5)	79(6)	89(6)	1(4)	48(4)	6(4)
O(24D)	61(4)	94(7)	77(6)	4(5)	28(4)	26(4)
N(25D)	92(7)	24(4)	84(7)	2(4)	15(5)	-4(5)
O(26D)	131(7)	48(3)	60(4)	6(3)	14(4)	27(4)
O(27D)	95(6)	74(5)	103(7)	21(5)	-3(5)	15(5)
N(10H)	30(3)	51(4)	35(4)	-9(2)	-4(3)	15(2)
C(15H)	41(4)	33(4)	43(4)	-8(2)	1(3)	8(2)
O(46H)	40(4)	52(3)	56(4)	5(3)	-2(3)	16(2)
C(16H)	63(6)	26(5)	60(6)	-10(4)	18(5)	-2(5)
C(17H)	72(7)	31(6)	54(7)	-5(4)	4(6)	-22(5)
C(18H)	93(8)	32(5)	54(6)	-1(4)	15(6)	-14(5)

C(19H)	102(8)	29(7)	76(10)	0(5)	50(7)	1(6)
C(20H)	84(6)	40(6)	81(8)	2(5)	48(6)	7(5)
C(21H)	61(6)	34(6)	76(8)	4(5)	33(6)	0(4)
N(22H)	69(7)	77(10)	99(11)	3(8)	55(8)	9(6)
O(23H)	131(10)	78(7)	181(15)	37(8)	128(11)	40(7)
O(24H)	72(7)	130(12)	209(16)	84(11)	84(9)	41(7)
N(25H)	123(9)	50(7)	70(8)	17(5)	13(7)	-12(7)
O(26H)	173(11)	37(4)	62(6)	8(4)	36(7)	13(6)
O(27H)	103(9)	72(9)	104(11)	43(8)	-34(8)	-45(8)
O(28D)	30(1)	53(2)	56(2)	-21(1)	2(1)	9(1)
C(29D)	50(2)	58(2)	56(2)	-16(2)	-2(2)	16(2)
C(30D)	108(5)	100(5)	60(3)	2(3)	5(3)	62(4)
C(31D)	43(5)	78(5)	89(4)	-29(4)	15(4)	-5(3)
C(32D)	63(8)	111(6)	82(4)	-1(4)	-31(4)	21(6)
Si(1D)	44(3)	62(4)	190(6)	46(4)	-37(3)	-21(2)
C(33D)	30(3)	153(7)	105(6)	13(5)	12(3)	31(4)
C(34D)	141(9)	135(7)	94(7)	7(5)	9(6)	92(7)
C(35D)	51(4)	222(12)	109(8)	6(8)	-37(6)	21(6)
C(36D)	71(6)	154(10)	104(6)	1(6)	24(5)	11(6)
C(31H)	43(5)	78(5)	89(4)	-29(4)	15(4)	-5(3)
C(32H)	63(8)	111(6)	82(4)	-1(4)	-31(4)	21(6)
Si(1H)	40(1)	52(2)	110(2)	-44(2)	-21(2)	13(2)
C(33H)	30(3)	153(7)	105(6)	13(5)	12(3)	31(4)
C(34H)	141(9)	135(7)	94(7)	7(5)	9(6)	92(7)
C(35H)	51(4)	222(12)	109(8)	6(8)	-37(6)	21(6)
C(36H)	71(6)	154(10)	104(6)	1(6)	24(5)	11(6)
C(37D)	57(2)	44(2)	41(2)	14(2)	23(2)	20(2)
C(38D)	65(2)	41(2)	43(2)	10(2)	9(2)	20(2)
C(39D)	85(3)	41(2)	49(2)	7(2)	4(2)	19(2)
C(40D)	107(4)	44(2)	48(2)	2(2)	19(2)	33(2)
C(41D)	93(4)	55(3)	84(4)	12(2)	42(3)	43(3)
C(42D)	69(3)	67(3)	80(3)	21(2)	31(2)	37(2)
O(43D)	53(2)	74(2)	82(2)	32(2)	18(2)	9(2)
O(44D)	66(2)	36(1)	73(2)	4(1)	-6(2)	11(1)
O(45D)	44(2)	87(2)	44(2)	-19(2)	4(1)	31(2)
Cl(1S)	60(1)	68(1)	92(2)	7(1)	-7(1)	27(1)
Cl(2S)	124(2)	67(1)	62(1)	13(1)	18(1)	15(1)
C(1S)	109(7)	76(5)	53(4)	10(3)	-19(4)	39(5)
Cl(3S)	117(3)	166(4)	139(3)	62(3)	66(2)	82(3)
Cl(4S)	179(4)	155(4)	139(3)	29(3)	70(3)	115(4)
C(2S)	124(10)	119(8)	123(10)	8(8)	17(8)	81(7)

Table S9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 12-hydroxytryptophan 3,5-dinitrobenzamide (+)-**14**.

	x	y	z	U(eq)
H(2A)	6402	9835	8908	56

H(5A)	5883	11347	6756	46
H(6A)	4287	11533	6495	53
H(7A)	2953	11074	7283	57
H(8A)	3163	10401	8337	54
H(10A)	9350(20)	11960(30)	7440(30)	48
H(11A)	7465	11965	7593	48
H(12A)	7227	10329	7106	54
H(17A)	10424	11656	6615	53
H(19A)	11285	11842	4426	61
H(21A)	8433	11877	4930	52
H(29A)	8808	12343	9974	83
H(29B)	7649	12225	10189	83
H(29I)	8947	12775	9909	83
H(29J)	8013	11981	10123	83
H(30A)	8962	13791	9694	141
H(30B)	8724	13764	10586	141
H(30C)	7820	13674	9935	141
H(30D)	8058	13770	10124	141
H(30E)	7874	13259	10848	141
H(30F)	6990	12985	10133	141
H(31A)	7776	8730	6481	109
H(31B)	8999	8985	6655	109
H(31C)	8507	9754	6585	109
H(32A)	7358	8364	8627	146
H(32B)	7486	7801	7803	146
H(32C)	6633	8291	7857	146
H(34A)	10241	10838	8115	152
H(34B)	10513	10019	7612	152
H(34C)	11060	10459	8485	152
H(35A)	10471	8906	8792	152
H(35B)	9801	8438	7963	152
H(35C)	9268	8354	8763	152
H(36A)	8888	9632	9540	159
H(36B)	9315	10610	9329	159
H(36C)	10103	10164	9643	159
H(31D)	9029	9717	6358	109
H(31E)	9959	9669	6913	109
H(31F)	9661	10568	7022	109
H(32D)	6941	8259	7455	146
H(32E)	7704	8012	6850	146
H(32F)	7057	8638	6657	146
H(32G)	7527	8347	6519	146
H(32H)	6764	8593	7124	146
H(32I)	7411	7968	7317	146
H(34D)	10559	10047	8292	152
H(34E)	10467	9924	9185	152
H(34F)	9989	10600	8857	152
H(34G)	10117	10334	9264	152
H(34H)	10210	10456	8371	152

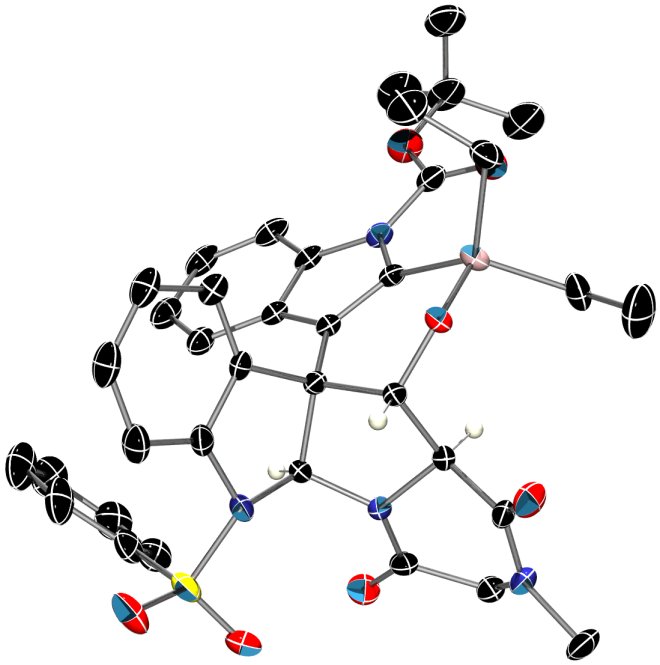
H(34I)	10688	9781	8699	152
H(35D)	7666	9001	8943	152
H(35E)	8557	9837	9467	152
H(35F)	8524	8833	9487	152
H(36D)	9801	8416	7840	159
H(36E)	8639	7880	7974	159
H(36F)	9536	8177	8682	159
H(38A)	3429	11101	9840	93
H(39A)	3885	12464	10724	103
H(40A)	5376	12890	11623	95
H(41A)	6369	12023	11603	100
H(42A)	6008	10684	10659	79
H(2B)	3301	5262	3656	61
H(5B)	1654	3928	5829	49
H(6B)	-77	3772	5990	59
H(7B)	-1058	4189	5121	69
H(8B)	-354	4777	4037	73
H(10B)	4740(30)	3280(30)	5360(30)	59
H(11B)	2833	3281	5133	60
H(12B)	3728	4916	5558	52
H(17B)	6181	3827	6149	57
H(19B)	6996	3328	8258	65
H(21B)	4066	3306	7739	61
H(29C)	3237	2080	2884	108
H(29D)	2267	2334	2584	108
H(29K)	3176	3066	2582	108
H(29L)	3514	2311	2896	108
H(30G)	3483	3007	1984	147
H(30H)	4299	3312	2747	147
H(30I)	3421	3766	2696	147
H(30J)	2270	1732	1973	147
H(30K)	1568	2218	2460	147
H(30L)	1899	1461	2785	147
H(30M)	1555	1876	2839	147
H(30N)	2256	1389	2352	147
H(30O)	1926	2146	2027	147
H(31G)	4997	6789	4068	123
H(31H)	5558	7465	4869	123
H(31I)	4369	6862	4821	123
H(32J)	5000	6260	6279	95
H(32K)	6213	6732	6255	95
H(32L)	5755	5674	6234	95
H(34J)	7610	7013	5191	99
H(34K)	7255	7167	4353	99
H(34L)	8088	6670	4422	99
H(35G)	7501	5031	4521	93
H(35H)	6388	4611	4810	93
H(35I)	7259	5421	5378	93
H(36G)	6881	5380	3361	118

H(36H)	6118	5956	3374	118
H(36I)	5701	4945	3513	118
H(38B)	-487	3931	2612	76
H(39B)	-1093	2490	1718	88
H(40B)	63	1972	1009	85
H(41B)	1785	2881	1055	80
H(42B)	2356	4309	1863	71
H(2C)	3043	4782	61	51
H(5C)	4826	5866	-2150	50
H(7C)	7467	5593	-1270	57
H(6C)	6557	5990	-2239	53
H(8C)	6680	5067	-202	54
H(10C)	1099(18)	4760(30)	-2650(30)	44
H(11C)	3042	4788	-2438	42
H(12C)	3023	6032	-1408	45
H(17C)	179	5673	-2665	42
H(19C)	-590	6886	-4350	59
H(21C)	2183	6459	-4275	46
H(29E)	2336	2171	-1739	56
H(29F)	1221	2281	-1852	56
H(30P)	2537	2884	-409	87
H(30Q)	1490	2043	-574	87
H(30R)	1450	3040	-517	87
H(31J)	1530	6622	-1585	118
H(31K)	1765	7427	-840	118
H(31L)	605	6774	-1110	118
H(32M)	2795	6360	676	102
H(32N)	2143	7032	823	102
H(32O)	3014	7183	226	102
H(34M)	50	6515	677	127
H(34N)	-1023	5804	256	127
H(34O)	-297	6489	-220	127
H(35J)	862	5280	953	147
H(35K)	715	4438	255	147
H(35L)	-265	4568	666	147
H(36J)	-210	4269	-1020	131
H(36K)	-405	5114	-1288	131
H(36L)	-1170	4563	-741	131
H(31M)	3410	6808	416	118
H(31N)	2759	7483	481	118
H(31O)	3197	7210	-331	118
H(32P)	962	5738	1011	102
H(32Q)	1941	5402	943	102
H(32R)	869	4813	434	102
H(34P)	478	7082	-1438	127
H(34Q)	1431	6714	-1540	127
H(34R)	1528	7571	-872	127
H(35M)	787	7121	568	147
H(35N)	-380	6506	267	147

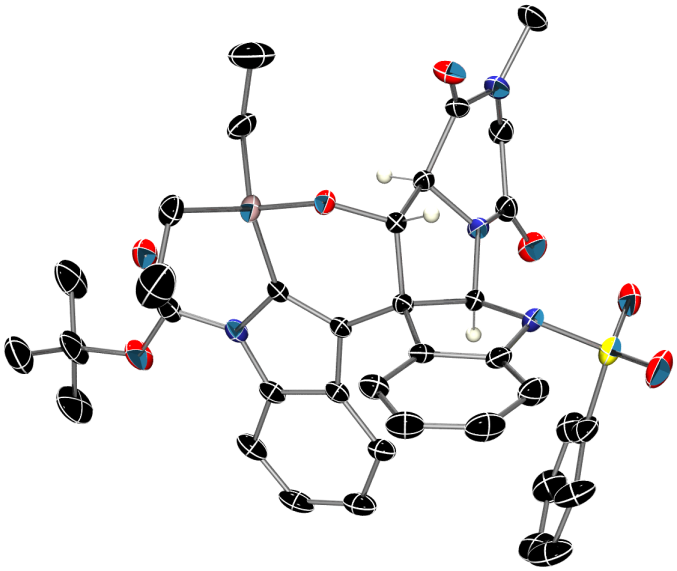
H(35O)	129	7410	-54	147
H(36M)	-809	5666	-1163	131
H(36N)	-450	5113	-591	131
H(36O)	24	5189	-1414	131
H(38C)	6773	6104	1377	65
H(39C)	7195	7553	2212	79
H(40C)	5923	8007	2752	99
H(41C)	4211	7084	2551	103
H(42C)	3756	5644	1726	75
H(38G)	7426	6344	1451	65
H(39G)	8010	7723	2397	79
H(40G)	6917	8055	3273	99
H(41G)	5241	7113	3233	103
H(42G)	4800	5618	2497	75
H(2D)	6347	10355	2580	57
H(5D)	7437	9252	4832	64
H(6D)	9026	9009	4906	77
H(7D)	10115	9281	3907	80
H(8D)	9671	9822	2821	70
H(11D)	6680	10444	5022	64
H(12D)	5480	9140	4050	65
H(10D)	4679	10070	5461	49
H(17D)	5396	8402	6911	66
H(19D)	2571	8037	7684	74
H(21D)	3350	9237	5797	60
H(10H)	4538	10234	5165	49
H(17H)	5031	8434	6667	77
H(19H)	2168	8221	7321	89
H(21H)	3275	9594	5610	73
H(29G)	6184	12810	4528	71
H(29H)	7402	13058	4459	71
H(30S)	7122	12470	3148	127
H(30T)	6470	13140	3319	127
H(30U)	5902	12077	3193	127
H(31P)	3673	7967	3392	122
H(31Q)	2582	8127	3437	122
H(31R)	3457	8566	4163	122
H(32S)	3687	8751	1667	136
H(32T)	4435	8354	2106	136
H(32U)	4863	9357	1947	136
H(34S)	2971	10681	2015	171
H(34T)	3835	10204	1967	171
H(34U)	3993	11088	2620	171
H(35P)	1619	8779	2733	207
H(35Q)	2260	8824	1981	207
H(35R)	1548	9442	2157	207
H(35S)	1999	9251	1848	207
H(35T)	1358	9206	2599	207
H(35U)	2070	8588	2424	207

H(36P)	3139	11024	3855	178
H(36Q)	3016	10102	4144	178
H(36R)	2024	10273	3782	178
H(31S)	4146	7852	3510	122
H(31T)	2940	7717	3400	122
H(31U)	3637	8353	4174	122
H(32V)	3867	9447	1777	136
H(32W)	3494	8379	1702	136
H(32X)	4698	8951	1861	136
H(34V)	2318	10526	3156	171
H(34W)	3333	10479	2754	171
H(34X)	3413	10890	3672	171
H(35V)	1195	8907	3140	207
H(35W)	1783	8190	2953	207
H(35X)	1814	8878	2379	207
H(36S)	2810	10209	4546	178
H(36T)	3108	9323	4559	178
H(36U)	1930	9243	4364	178
H(38D)	6173	9276	942	58
H(39D)	5514	7890	69	71
H(40D)	6546	7000	-214	78
H(41D)	8226	7489	308	87
H(42D)	8948	8900	1171	80
H(1S1)	-381	6479	2865	94
H(1S2)	-1468	6620	2986	94
H(2S1)	-8146	-283	11	137
H(2S2)	-7557	-269	832	137

Crystal Structure of Silacyclic Tetracycle 23.



View 1:



View 2:

Table S10. Crystal data and structure refinement for silacyclic tetracycle **23**.

Identification code	x8_11120	
Empirical formula	C38 H42 Cl2 N4 O7 S Si	
Formula weight	797.81	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.7839(4) Å	a= 90°.
	b = 16.5231(8) Å	b= 90°.
	c = 24.2524(12) Å	g = 90°.
Volume	3920.7(3) $Å^3$	
Z	4	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	0.303 mm^{-1}	
F(000)	1672	
Crystal size	0.25 x 0.10 x 0.10 mm^3	
Theta range for data collection	1.49 to 29.80°.	
Index ranges	-13<=h<=13, -23<=k<=22, -33<=l<=33	
Reflections collected	84425	
Independent reflections	11230 [R(int) = 0.0486]	
Completeness to theta = 29.80°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9704 and 0.9282	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11230 / 146 / 536	
Goodness-of-fit on F^2	1.100	
Final R indices [I>2sigma(I)]	R1 = 0.0485, wR2 = 0.1186	
R indices (all data)	R1 = 0.0544, wR2 = 0.1218	
Absolute structure parameter	-0.04(6)	
Largest diff. peak and hole	0.359 and -0.658 $e.Å^{-3}$	

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for silacyclic tetracycle **23**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	-1466(1)	-1668(1)	-2182(1)	29(1)
N(1)	-1489(2)	-1377(1)	-1526(1)	21(1)
O(1)	1958(2)	-2332(1)	-1679(1)	34(1)
O(2)	-945(2)	-2942(1)	119(1)	31(1)
C(2)	-117(2)	-1238(1)	-1258(1)	18(1)
O(3)	-700(2)	-971(1)	240(1)	19(1)
C(3)	-469(2)	-666(1)	-765(1)	16(1)
O(4)	-575(2)	-2347(1)	-2207(1)	37(1)

C(4)	-1800(2)	-290(1)	-934(1)	19(1)
O(5)	-2866(2)	-1742(1)	-2351(1)	43(1)
C(5)	-2480(2)	355(1)	-698(1)	25(1)
C(6)	-3806(2)	525(2)	-873(1)	32(1)
C(7)	-4419(3)	49(2)	-1268(1)	36(1)
C(8)	-3749(2)	-606(2)	-1510(1)	30(1)
C(9)	-2405(2)	-747(1)	-1347(1)	22(1)
N(10)	459(2)	-1948(1)	-1006(1)	20(1)
C(11)	328(2)	-1949(1)	-401(1)	18(1)
C(12)	-727(2)	-1298(1)	-294(1)	17(1)
C(13)	-37(2)	-2799(1)	-212(1)	22(1)
N(14)	747(2)	-3360(1)	-464(1)	27(1)
C(15)	1821(2)	-3127(1)	-851(1)	27(1)
C(16)	1431(2)	-2430(1)	-1230(1)	24(1)
C(17)	587(3)	-4221(1)	-331(1)	37(1)
C(18)	-727(3)	-853(2)	-2540(1)	32(1)
C(19)	651(3)	-872(2)	-2678(1)	36(1)
C(20)	1223(3)	-205(2)	-2933(1)	43(1)
C(21)	445(4)	480(2)	-3034(1)	48(1)
C(22)	-926(3)	496(2)	-2894(1)	50(1)
C(23)	-1532(3)	-168(2)	-2651(1)	44(1)
N(1')	2254(2)	621(1)	-174(1)	21(1)
C(2')	1253(2)	13(1)	-125(1)	18(1)
C(3')	663(2)	-85(1)	-632(1)	16(1)
C(4')	1264(2)	490(1)	-1013(1)	19(1)
C(5')	978(2)	701(1)	-1558(1)	25(1)
C(6')	1707(3)	1332(1)	-1796(1)	33(1)
O(6')	2793(2)	565(1)	736(1)	34(1)
C(7')	2706(2)	1742(1)	-1499(1)	32(1)
C(8')	3008(2)	1554(1)	-961(1)	28(1)
C(9')	2268(2)	921(1)	-719(1)	21(1)
C(10')	2955(2)	885(1)	292(1)	27(1)
O(7')	3735(2)	1504(1)	171(1)	40(1)
C(11')	4826(17)	1885(10)	522(8)	44(1)
C(12')	5640(20)	2422(12)	139(9)	60(2)
C(13')	5660(30)	1248(16)	814(14)	55(1)
C(14')	3950(20)	2358(12)	926(9)	51(1)
C(11B)	4426(5)	1969(2)	627(2)	44(1)
C(12B)	4999(6)	2668(3)	307(2)	60(2)
C(13B)	5554(7)	1422(3)	866(3)	55(1)
C(14B)	3435(6)	2251(3)	1063(2)	51(1)
C(15')	1815(3)	-1222(2)	851(1)	32(1)
C(16')	1070(4)	-1851(2)	1203(2)	58(1)
Si(1)	632(1)	-483(1)	519(1)	22(1)
C(17')	-150(4)	131(2)	1076(1)	30(1)
C(18')	-803(6)	897(3)	882(2)	63(1)
C(17A)	-264(12)	405(7)	892(4)	30(1)
C(18A)	-915(16)	168(10)	1423(5)	63(1)
C(1S)	-4328(7)	2453(3)	-2496(2)	25(1)

Cl(1)	-4158(2)	3380(1)	-2128(1)	51(1)
Cl(2)	-3764(2)	1638(2)	-2107(1)	62(1)
C(2S)	-4340(20)	2325(8)	-2531(6)	128(5)
Cl(3)	-3980(5)	2860(7)	-1903(2)	235(5)
Cl(4)	-4296(9)	1266(5)	-2433(3)	239(5)

Table S12. Bond lengths [Å] and angles [°] for silacyclic tetracycle **23**.

S(1)-O(4)	1.422(2)	C(3')-C(4')	1.450(3)
S(1)-O(5)	1.4342(19)	C(4')-C(5')	1.395(3)
S(1)-N(1)	1.6636(18)	C(4')-C(9')	1.406(3)
S(1)-C(18)	1.758(3)	C(5')-C(6')	1.389(3)
N(1)-C(9)	1.441(3)	C(6')-C(7')	1.390(4)
N(1)-C(2)	1.509(3)	O(6')-C(10')	1.211(3)
O(1)-C(16)	1.215(3)	C(7')-C(8')	1.374(4)
O(2)-C(13)	1.220(3)	C(8')-C(9')	1.401(3)
C(2)-N(10)	1.439(2)	C(10')-O(7')	1.310(3)
C(2)-C(3)	1.561(3)	O(7')-C(11')	1.503(14)
O(3)-C(12)	1.404(2)	O(7')-C(11B)	1.506(4)
O(3)-Si(1)	1.6743(15)	C(11')-C(12')	1.510(13)
C(3)-C(4)	1.499(3)	C(11')-C(13')	1.510(14)
C(3)-C(3')	1.500(3)	C(11')-C(14')	1.518(13)
C(3)-C(12)	1.570(3)	C(11B)-C(12B)	1.498(6)
C(4)-C(5)	1.380(3)	C(11B)-C(14B)	1.509(6)
C(4)-C(9)	1.388(3)	C(11B)-C(13B)	1.540(6)
C(5)-C(6)	1.394(3)	C(15')-C(16')	1.530(4)
C(6)-C(7)	1.377(4)	C(15')-Si(1)	1.864(3)
C(7)-C(8)	1.395(4)	Si(1)-C(17')	1.854(3)
C(8)-C(9)	1.392(3)	Si(1)-C(17A)	1.934(10)
N(10)-C(16)	1.354(3)	C(17')-C(18')	1.493(6)
N(10)-C(11)	1.471(2)	C(17A)-C(18A)	1.489(14)
C(11)-C(12)	1.514(3)	C(1S)-Cl(2)	1.736(7)
C(11)-C(13)	1.521(3)	C(1S)-Cl(1)	1.781(5)
C(13)-N(14)	1.349(3)	C(2S)-Cl(4)	1.765(13)
N(14)-C(15)	1.460(3)	C(2S)-Cl(3)	1.796(13)
N(14)-C(17)	1.467(3)	O(4)-S(1)-O(5)	120.43(12)
C(15)-C(16)	1.523(3)	O(4)-S(1)-N(1)	106.07(10)
C(18)-C(19)	1.390(4)	O(5)-S(1)-N(1)	106.53(11)
C(18)-C(23)	1.405(4)	O(4)-S(1)-C(18)	109.29(13)
C(19)-C(20)	1.382(4)	O(5)-S(1)-C(18)	108.49(12)
C(20)-C(21)	1.385(4)	N(1)-S(1)-C(18)	104.92(10)
C(21)-C(22)	1.384(5)	C(9)-N(1)-C(2)	108.30(16)
C(22)-C(23)	1.380(4)	C(9)-N(1)-S(1)	120.31(14)
N(1')-C(10')	1.392(3)	C(2)-N(1)-S(1)	116.37(13)
N(1')-C(2')	1.408(2)	N(10)-C(2)-N(1)	113.99(16)
N(1')-C(9')	1.411(3)	N(10)-C(2)-C(3)	104.77(15)
C(2')-C(3')	1.369(3)	N(1)-C(2)-C(3)	103.03(15)
C(2')-Si(1)	1.866(2)	C(12)-O(3)-Si(1)	124.93(13)

C(4)-C(3)-C(3')	115.76(15)	N(1')-C(2')-Si(1)	127.73(15)
C(4)-C(3)-C(2)	103.51(15)	C(2')-C(3')-C(4')	108.86(17)
C(3')-C(3)-C(2)	112.92(15)	C(2')-C(3')-C(3)	125.53(17)
C(4)-C(3)-C(12)	109.53(15)	C(4')-C(3')-C(3)	125.55(17)
C(3')-C(3)-C(12)	112.80(15)	C(5')-C(4')-C(9')	119.58(19)
C(2)-C(3)-C(12)	100.95(14)	C(5')-C(4')-C(3')	133.27(19)
C(5)-C(4)-C(9)	120.87(19)	C(9')-C(4')-C(3')	107.00(17)
C(5)-C(4)-C(3)	128.73(19)	C(6')-C(5')-C(4')	118.6(2)
C(9)-C(4)-C(3)	110.03(17)	C(5')-C(6')-C(7')	120.7(2)
C(4)-C(5)-C(6)	118.6(2)	C(8')-C(7')-C(6')	122.3(2)
C(7)-C(6)-C(5)	120.1(2)	C(7')-C(8')-C(9')	117.1(2)
C(6)-C(7)-C(8)	122.1(2)	C(8')-C(9')-C(4')	121.8(2)
C(9)-C(8)-C(7)	117.0(2)	C(8')-C(9')-N(1')	131.2(2)
C(4)-C(9)-C(8)	121.1(2)	C(4')-C(9')-N(1')	106.88(17)
C(4)-C(9)-N(1)	110.15(18)	O(6')-C(10')-O(7')	128.0(2)
C(8)-C(9)-N(1)	128.6(2)	O(6')-C(10')-N(1')	121.5(2)
C(16)-N(10)-C(2)	125.69(18)	O(7')-C(10')-N(1')	110.5(2)
C(16)-N(10)-C(11)	117.45(17)	C(10')-O(7')-C(11')	127.9(7)
C(2)-N(10)-C(11)	112.98(15)	C(10')-O(7')-C(11B)	119.8(3)
N(10)-C(11)-C(12)	103.33(15)	C(11')-O(7')-C(11B)	18.6(7)
N(10)-C(11)-C(13)	108.84(16)	O(7')-C(11')-C(12')	105.8(12)
C(12)-C(11)-C(13)	116.33(17)	O(7')-C(11')-C(13')	111.0(16)
O(3)-C(12)-C(11)	114.86(16)	C(12')-C(11')-C(13')	114.4(16)
O(3)-C(12)-C(3)	114.35(15)	O(7')-C(11')-C(14')	100.4(12)
C(11)-C(12)-C(3)	103.72(15)	C(12')-C(11')-C(14')	113.0(14)
O(2)-C(13)-N(14)	125.5(2)	C(13')-C(11')-C(14')	111.2(16)
O(2)-C(13)-C(11)	123.23(19)	C(12B)-C(11B)-O(7')	100.5(3)
N(14)-C(13)-C(11)	111.28(19)	C(12B)-C(11B)-C(14B)	111.4(4)
C(13)-N(14)-C(15)	121.34(18)	O(7')-C(11B)-C(14B)	112.5(3)
C(13)-N(14)-C(17)	120.3(2)	C(12B)-C(11B)-C(13B)	112.3(4)
C(15)-N(14)-C(17)	118.3(2)	O(7')-C(11B)-C(13B)	107.3(3)
N(14)-C(15)-C(16)	114.02(18)	C(14B)-C(11B)-C(13B)	112.2(4)
O(1)-C(16)-N(10)	125.5(2)	C(16')-C(15')-Si(1)	113.0(2)
O(1)-C(16)-C(15)	122.3(2)	O(3)-Si(1)-C(17')	103.68(13)
N(10)-C(16)-C(15)	112.21(19)	O(3)-Si(1)-C(15')	110.03(10)
C(19)-C(18)-C(23)	121.1(3)	C(17')-Si(1)-C(15')	107.48(15)
C(19)-C(18)-S(1)	120.1(2)	O(3)-Si(1)-C(2')	97.33(8)
C(23)-C(18)-S(1)	118.7(2)	C(17')-Si(1)-C(2')	120.19(14)
C(20)-C(19)-C(18)	118.8(3)	C(15')-Si(1)-C(2')	116.51(10)
C(19)-C(20)-C(21)	120.6(3)	O(3)-Si(1)-C(17A)	101.6(4)
C(22)-C(21)-C(20)	120.3(3)	C(17')-Si(1)-C(17A)	19.4(3)
C(23)-C(22)-C(21)	120.4(3)	C(15')-Si(1)-C(17A)	125.2(4)
C(22)-C(23)-C(18)	118.8(3)	C(2')-Si(1)-C(17A)	101.9(3)
C(10')-N(1')-C(2')	119.75(18)	C(18')-C(17')-Si(1)	114.3(3)
C(10')-N(1')-C(9')	130.27(18)	C(18A)-C(17A)-Si(1)	113.6(8)
C(2')-N(1')-C(9')	109.67(17)	Cl(2)-C(1S)-Cl(1)	111.4(3)
C(3')-C(2')-N(1')	107.55(17)	Cl(4)-C(2S)-Cl(3)	111.7(9)
C(3')-C(2')-Si(1)	124.22(15)		

Table S13. Anisotropic displacement parameters ($Å^2$ x 10^3) for silacyclic tetracycle **23**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	36(1)	33(1)	19(1)	-4(1)	-7(1)	-3(1)
N(1)	23(1)	23(1)	17(1)	0(1)	-6(1)	-1(1)
O(1)	40(1)	37(1)	25(1)	-5(1)	5(1)	11(1)
O(2)	36(1)	22(1)	35(1)	8(1)	4(1)	-3(1)
C(2)	21(1)	17(1)	15(1)	-1(1)	-2(1)	0(1)
O(3)	20(1)	22(1)	16(1)	-2(1)	0(1)	-3(1)
C(3)	17(1)	15(1)	18(1)	0(1)	-1(1)	0(1)
O(4)	53(1)	32(1)	28(1)	-12(1)	-6(1)	2(1)
C(4)	18(1)	17(1)	21(1)	6(1)	-1(1)	0(1)
O(5)	41(1)	60(1)	27(1)	-2(1)	-13(1)	-12(1)
C(5)	23(1)	21(1)	30(1)	3(1)	0(1)	2(1)
C(6)	26(1)	31(1)	40(1)	9(1)	2(1)	10(1)
C(7)	23(1)	41(1)	44(1)	13(1)	-6(1)	8(1)
C(8)	23(1)	35(1)	33(1)	6(1)	-9(1)	-1(1)
C(9)	25(1)	24(1)	19(1)	5(1)	-4(1)	1(1)
N(10)	26(1)	17(1)	16(1)	-1(1)	-1(1)	4(1)
C(11)	18(1)	18(1)	17(1)	0(1)	-2(1)	2(1)
C(12)	19(1)	15(1)	16(1)	0(1)	-1(1)	-1(1)
C(13)	27(1)	16(1)	24(1)	4(1)	-7(1)	1(1)
N(14)	34(1)	16(1)	30(1)	1(1)	-6(1)	4(1)
C(15)	32(1)	23(1)	27(1)	-4(1)	-3(1)	10(1)
C(16)	27(1)	22(1)	23(1)	-6(1)	-2(1)	6(1)
C(17)	47(2)	14(1)	50(1)	2(1)	-12(1)	4(1)
C(18)	40(1)	40(1)	16(1)	2(1)	-2(1)	1(1)
C(19)	44(1)	43(1)	22(1)	-2(1)	6(1)	5(1)
C(20)	47(2)	54(2)	28(1)	2(1)	12(1)	1(1)
C(21)	65(2)	51(2)	27(1)	12(1)	15(1)	2(2)
C(22)	61(2)	60(2)	31(1)	21(1)	8(1)	15(2)
C(23)	45(2)	57(2)	29(1)	18(1)	2(1)	10(1)
N(1')	18(1)	16(1)	28(1)	-1(1)	-2(1)	-2(1)
C(2')	18(1)	13(1)	24(1)	-1(1)	0(1)	0(1)
C(3')	16(1)	14(1)	19(1)	0(1)	2(1)	0(1)
C(4')	18(1)	15(1)	25(1)	0(1)	3(1)	2(1)
C(5')	30(1)	20(1)	26(1)	4(1)	5(1)	2(1)
C(6')	44(1)	24(1)	32(1)	8(1)	12(1)	4(1)
O(6')	36(1)	30(1)	35(1)	-4(1)	-12(1)	-4(1)
C(7')	29(1)	19(1)	47(1)	10(1)	16(1)	1(1)
C(8')	19(1)	18(1)	47(1)	0(1)	8(1)	0(1)
C(9')	17(1)	15(1)	32(1)	1(1)	5(1)	2(1)
C(10')	23(1)	18(1)	40(1)	-3(1)	-9(1)	2(1)
O(7')	40(1)	25(1)	53(1)	0(1)	-15(1)	-17(1)
C(11')	38(2)	24(2)	70(3)	-9(2)	-22(2)	-10(2)

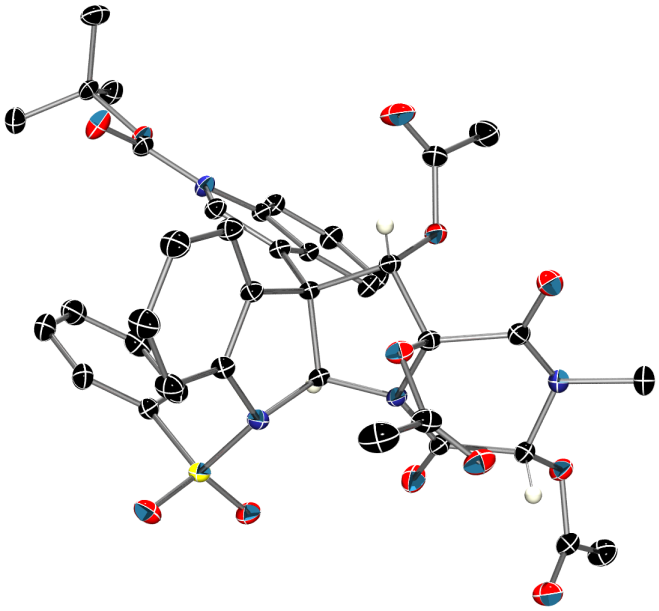
C(12')	54(3)	38(2)	87(3)	-1(2)	-16(2)	-27(2)
C(13')	42(2)	37(3)	87(3)	-11(2)	-31(2)	-7(2)
C(14')	56(3)	32(2)	66(3)	-16(2)	-21(2)	0(2)
C(11B)	38(2)	24(2)	70(3)	-9(2)	-22(2)	-10(2)
C(12B)	54(3)	38(2)	87(3)	-1(2)	-16(2)	-27(2)
C(13B)	42(2)	37(3)	87(3)	-11(2)	-31(2)	-7(2)
C(14B)	56(3)	32(2)	66(3)	-16(2)	-21(2)	0(2)
C(15')	33(1)	40(1)	24(1)	8(1)	-9(1)	-6(1)
C(16')	63(2)	50(2)	60(2)	30(2)	-9(2)	-8(2)
Si(1)	22(1)	26(1)	17(1)	-4(1)	1(1)	-3(1)
C(17')	35(2)	34(2)	21(2)	-6(1)	1(1)	1(1)
C(18')	69(3)	70(3)	50(2)	-16(2)	-7(2)	45(2)
C(17A)	35(2)	34(2)	21(2)	-6(1)	1(1)	1(1)
C(18A)	69(3)	70(3)	50(2)	-16(2)	-7(2)	45(2)
C(1S)	18(2)	37(2)	21(2)	-8(2)	10(2)	2(2)
Cl(1)	37(1)	57(1)	58(1)	-30(1)	-14(1)	5(1)
Cl(2)	60(1)	66(1)	60(1)	22(1)	10(1)	15(1)
C(2S)	123(12)	177(9)	85(9)	2(8)	-14(9)	63(11)
Cl(3)	106(3)	510(13)	88(3)	-55(5)	5(2)	-129(6)
Cl(4)	292(8)	210(5)	214(6)	155(5)	180(6)	197(5)

Table S14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for silacyclic tetracycle **23**.

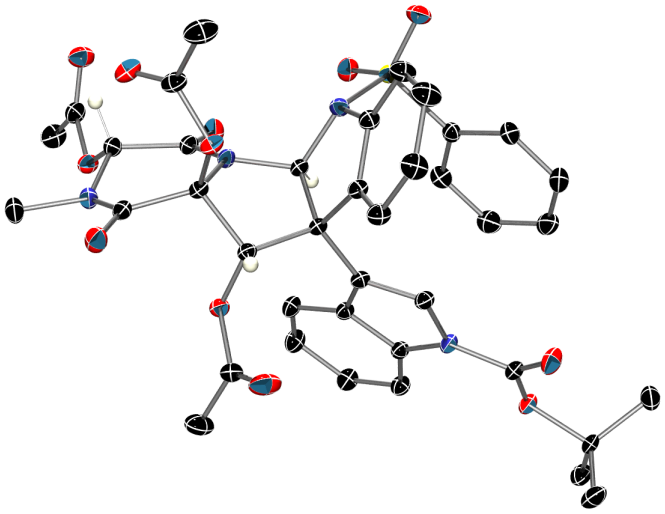
	x	y	z	U(eq)
H(2)	542	-978	-1519	21
H(5)	-2052	676	-423	30
H(6)	-4289	969	-719	39
H(7)	-5327	171	-1379	43
H(8)	-4189	-940	-1775	36
H(11)	1219	-1785	-233	21
H(12)	-1651	-1541	-354	20
H(15A)	2060	-3603	-1080	33
H(15B)	2646	-2973	-640	33
H(17A)	-44	-4280	-20	56
H(17B)	1477	-4450	-232	56
H(17C)	220	-4507	-652	56
H(19)	1191	-1336	-2599	44
H(20)	2157	-216	-3040	52
H(21)	855	941	-3200	57
H(22)	-1453	967	-2966	61
H(23)	-2477	-163	-2561	53
H(5')	298	420	-1761	30
H(6')	1521	1485	-2166	39
H(7')	3196	2166	-1674	38
H(8')	3690	1840	-761	34
H(12A)	6368	2105	-34	90

H(12B)	6038	2869	350	90
H(12C)	5033	2640	-147	90
H(13A)	5952	835	549	83
H(13B)	5106	994	1103	83
H(13C)	6468	1500	981	83
H(14A)	4492	2800	1085	77
H(14B)	3640	1998	1222	77
H(14C)	3158	2583	733	77
H(12D)	5699	2471	51	90
H(12E)	5408	3058	563	90
H(12F)	4264	2931	99	90
H(13D)	5134	975	1070	83
H(13E)	6134	1739	1115	83
H(13F)	6111	1204	565	83
H(14D)	2744	2602	894	77
H(14E)	3930	2554	1347	77
H(14F)	2988	1781	1230	77
H(15C)	2343	-1504	560	39
H(15D)	2471	-923	1086	39
H(16A)	508	-1576	1480	87
H(16B)	1742	-2197	1388	87
H(16C)	485	-2184	966	87
H(17D)	-848	-201	1266	36
H(17E)	566	268	1349	36
H(18A)	-107	1249	717	95
H(18B)	-1227	1174	1195	95
H(18C)	-1503	770	606	95
H(17F)	417	835	965	36
H(17G)	-972	633	646	36
H(18D)	-1457	-324	1369	95
H(18E)	-1512	606	1551	95
H(18F)	-205	66	1700	95
H(1S1)	-5299	2371	-2596	30
H(1S2)	-3791	2484	-2842	30
H(1S3)	-5251	2484	-2668	154
H(1S4)	-3654	2478	-2813	154

Crystal Structure of Tetracyclic Triacetate 28.



View 1:



View 2:

Table S15. Crystal data and structure refinement for tetracyclic triacetate **28**.

Identification code	x8_12224	
Empirical formula	C45 H50 N4 O14 S	
Formula weight	902.95	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 12.8803(7) Å	a= 90°.
	b = 10.3954(6) Å	b= 90.0630(10)°.
	c = 16.5478(9) Å	g = 90°.
Volume	2215.7(2) Å^3	
Z	2	
Density (calculated)	1.353 Mg/m^3	
Absorption coefficient	0.146 mm^{-1}	
F(000)	952	
Crystal size	0.45 x 0.36 x 0.16 mm^3	
Theta range for data collection	1.58 to 30.51°.	
Index ranges	-18<=h<=18, -14<=k<=14, -23<=l<=23	
Reflections collected	179249	
Independent reflections	13500 [R(int) = 0.0307]	
Completeness to theta = 30.51°	100.0 %	
Absorption correction	None	
Max. and min. transmission	0.9771 and 0.9373	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13500 / 1 / 588	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0301, wR2 = 0.0833	
R indices (all data)	R1 = 0.0311, wR2 = 0.0843	
Absolute structure parameter	-0.01(3)	
Largest diff. peak and hole	0.382 and -0.214 e.Å^{-3}	

Table S16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for tetracyclic triacetate **28**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	-1181(1)	-8803(1)	-1963(1)	15(1)
C(2)	-786(1)	-7511(1)	-2192(1)	14(1)
C(3)	123(1)	-7754(1)	-2805(1)	13(1)
C(4)	9(1)	-9171(1)	-2995(1)	15(1)
C(5)	487(1)	-9871(1)	-3605(1)	18(1)
C(6)	215(1)	-11159(1)	-3700(1)	23(1)
C(7)	-527(1)	-11724(1)	-3197(1)	25(1)
C(8)	-1021(1)	-11016(1)	-2596(1)	21(1)

C(9)	-736(1)	-9735(1)	-2504(1)	16(1)
N(10)	-1544(1)	-6752(1)	-2646(1)	14(1)
C(11)	-1363(1)	-6811(1)	-3502(1)	15(1)
C(12)	-176(1)	-6974(1)	-3575(1)	14(1)
C(13)	-1765(1)	-5674(1)	-4000(1)	17(1)
N(14)	-2253(1)	-4698(1)	-3609(1)	18(1)
C(15)	-2736(1)	-4922(1)	-2829(1)	16(1)
C(16)	-2089(1)	-5788(1)	-2272(1)	16(1)
C(17)	-2746(1)	-3713(1)	-4120(1)	24(1)
O(1)	-1590(1)	-5686(1)	-4723(1)	24(1)
O(2)	-2078(1)	-5620(1)	-1550(1)	24(1)
N(1')	2757(1)	-7671(1)	-1899(1)	15(1)
C(2')	1961(1)	-8254(1)	-2335(1)	16(1)
C(3')	1154(1)	-7424(1)	-2426(1)	14(1)
C(4')	1436(1)	-6245(1)	-2007(1)	14(1)
C(5')	913(1)	-5085(1)	-1857(1)	18(1)
C(6')	1411(1)	-4141(1)	-1411(1)	21(1)
C(7')	2426(1)	-4322(1)	-1125(1)	20(1)
C(8')	2960(1)	-5460(1)	-1257(1)	17(1)
C(9')	2445(1)	-6423(1)	-1690(1)	14(1)
O(3)	-2810(1)	-3705(1)	-2438(1)	19(1)
O(4)	-4296(1)	-4371(1)	-1842(1)	25(1)
C(18)	-3646(1)	-3560(1)	-1934(1)	20(1)
C(19)	-3627(1)	-2269(1)	-1538(1)	27(1)
O(5)	-1755(1)	-8006(1)	-3827(1)	17(1)
O(6)	-3387(1)	-7268(1)	-3694(1)	24(1)
C(20)	-2810(1)	-8142(1)	-3844(1)	20(1)
C(21)	-3118(1)	-9486(1)	-4051(1)	30(1)
O(7)	4285(1)	-7668(1)	-1244(1)	18(1)
O(8)	3813(1)	-9425(1)	-1977(1)	24(1)
C(22)	3667(1)	-8356(1)	-1718(1)	17(1)
C(23)	5358(1)	-8131(1)	-1060(1)	17(1)
C(24)	5948(1)	-8305(1)	-1847(1)	25(1)
C(25)	5799(1)	-7027(1)	-569(1)	22(1)
C(26)	5305(1)	-9355(1)	-560(1)	23(1)
S(1)	-1196(1)	-9148(1)	-974(1)	16(1)
O(9)	-1659(1)	-10397(1)	-910(1)	23(1)
O(10)	-1659(1)	-8058(1)	-590(1)	22(1)
C(27)	108(1)	-9250(1)	-670(1)	16(1)
C(28)	592(1)	-8161(1)	-357(1)	21(1)
C(29)	1628(1)	-8242(1)	-124(1)	25(1)
C(30)	2162(1)	-9396(1)	-209(1)	26(1)
C(31)	1675(1)	-10471(1)	-535(1)	27(1)
C(32)	641(1)	-10405(1)	-772(1)	21(1)
O(11)	266(1)	-5713(1)	-3584(1)	16(1)
O(12)	1576(1)	-6484(1)	-4348(1)	30(1)
C(33)	1167(1)	-5598(1)	-4014(1)	20(1)
C(34)	1544(1)	-4239(1)	-4007(1)	29(1)
O(1S)	-5266(1)	-4815(1)	-4353(1)	47(1)

C(1S)	-5717(1)	-6965(2)	-4670(1)	33(1)
C(2S)	-5562(1)	-5848(1)	-4114(1)	26(1)
C(3S)	-5814(1)	-6075(2)	-3246(1)	41(1)
O(2S)	-4818(1)	-1583(2)	-3213(1)	46(1)
C(4S)	-6380(1)	-2337(2)	-2629(1)	39(1)
C(5S)	-5758(1)	-1585(2)	-3232(1)	33(1)
C(6S)	-6346(2)	-821(3)	-3851(1)	57(1)

Table S17. Bond lengths [Å] and angles [°] for tetracyclic triacetate **28**.

N(1)-C(9)	1.4384(13)	O(3)-C(18)	1.3710(13)
N(1)-C(2)	1.4858(13)	O(4)-C(18)	1.1983(15)
N(1)-S(1)	1.6755(9)	C(18)-C(19)	1.4939(17)
C(2)-N(10)	1.4614(13)	O(5)-C(20)	1.3669(13)
C(2)-C(3)	1.5699(14)	O(6)-C(20)	1.1994(15)
C(3)-C(3')	1.5077(14)	C(20)-C(21)	1.4917(18)
C(3)-C(4)	1.5126(15)	O(7)-C(22)	1.3264(13)
C(3)-C(12)	1.5583(14)	O(7)-C(23)	1.4942(12)
C(4)-C(5)	1.3885(14)	O(8)-C(22)	1.2062(14)
C(4)-C(9)	1.3886(14)	C(23)-C(25)	1.5159(16)
C(5)-C(6)	1.3937(16)	C(23)-C(24)	1.5193(16)
C(6)-C(7)	1.3974(17)	C(23)-C(26)	1.5196(16)
C(7)-C(8)	1.3915(17)	S(1)-O(10)	1.4300(9)
C(8)-C(9)	1.3894(15)	S(1)-O(9)	1.4331(9)
N(10)-C(16)	1.3715(13)	S(1)-C(27)	1.7551(11)
N(10)-C(11)	1.4370(13)	C(27)-C(28)	1.3922(16)
C(11)-O(5)	1.4446(13)	C(27)-C(32)	1.3937(15)
C(11)-C(13)	1.5316(15)	C(28)-C(29)	1.3905(17)
C(11)-C(12)	1.5431(14)	C(29)-C(30)	1.3900(19)
C(12)-O(11)	1.4291(12)	C(30)-C(31)	1.390(2)
C(13)-O(1)	1.2180(14)	C(31)-C(32)	1.3888(17)
C(13)-N(14)	1.3574(14)	O(11)-C(33)	1.3676(13)
N(14)-C(15)	1.4530(14)	O(12)-C(33)	1.1962(15)
N(14)-C(17)	1.4714(15)	C(33)-C(34)	1.4936(17)
C(15)-O(3)	1.4236(13)	O(1S)-C(2S)	1.2056(18)
C(15)-C(16)	1.5335(15)	C(1S)-C(2S)	1.4948(19)
C(16)-O(2)	1.2086(14)	C(2S)-C(3S)	1.4915(19)
N(1')-C(2')	1.3921(13)	O(2S)-C(5S)	1.2110(19)
N(1')-C(9')	1.4020(13)	C(4S)-C(5S)	1.499(2)
N(1')-C(22)	1.4033(13)	C(5S)-C(6S)	1.501(2)
C(2')-C(3')	1.3595(14)	C(9)-N(1)-C(2)	108.25(8)
C(3')-C(4')	1.4537(14)	C(9)-N(1)-S(1)	117.91(7)
C(4')-C(5')	1.4039(14)	C(2)-N(1)-S(1)	116.55(7)
C(4')-C(9')	1.4124(14)	N(10)-C(2)-N(1)	112.99(8)
C(5')-C(6')	1.3857(15)	N(10)-C(2)-C(3)	104.71(8)
C(6')-C(7')	1.4015(15)	N(1)-C(2)-C(3)	105.98(8)
C(7')-C(8')	1.3863(15)	C(3')-C(3)-C(4)	113.15(8)
C(8')-C(9')	1.3983(14)	C(3')-C(3)-C(12)	116.02(8)

C(4)-C(3)-C(12)	108.23(8)	C(5')-C(6')-C(7')	121.03(10)
C(3')-C(3)-C(2)	110.60(8)	C(8')-C(7')-C(6')	121.62(10)
C(4)-C(3)-C(2)	102.64(8)	C(7')-C(8')-C(9')	117.15(10)
C(12)-C(3)-C(2)	105.07(8)	C(8')-C(9')-N(1')	130.76(9)
C(5)-C(4)-C(9)	120.75(10)	C(8')-C(9')-C(4')	122.18(9)
C(5)-C(4)-C(3)	128.18(9)	N(1')-C(9')-C(4')	107.05(9)
C(9)-C(4)-C(3)	110.89(9)	C(18)-O(3)-C(15)	115.26(9)
C(4)-C(5)-C(6)	118.31(10)	O(4)-C(18)-O(3)	123.37(11)
C(5)-C(6)-C(7)	120.54(11)	O(4)-C(18)-C(19)	125.94(11)
C(8)-C(7)-C(6)	121.17(11)	O(3)-C(18)-C(19)	110.69(10)
C(9)-C(8)-C(7)	117.65(11)	C(20)-O(5)-C(11)	116.34(8)
C(4)-C(9)-C(8)	121.56(10)	O(6)-C(20)-O(5)	122.21(11)
C(4)-C(9)-N(1)	110.84(9)	O(6)-C(20)-C(21)	126.36(11)
C(8)-C(9)-N(1)	127.46(10)	O(5)-C(20)-C(21)	111.42(10)
C(16)-N(10)-C(11)	123.96(9)	C(22)-O(7)-C(23)	120.09(9)
C(16)-N(10)-C(2)	120.38(9)	O(8)-C(22)-O(7)	127.84(10)
C(11)-N(10)-C(2)	111.95(8)	O(8)-C(22)-N(1')	121.46(10)
N(10)-C(11)-O(5)	110.31(8)	O(7)-C(22)-N(1')	110.70(9)
N(10)-C(11)-C(13)	116.29(9)	O(7)-C(23)-C(25)	102.20(8)
O(5)-C(11)-C(13)	110.19(8)	O(7)-C(23)-C(24)	109.10(9)
N(10)-C(11)-C(12)	104.11(8)	C(25)-C(23)-C(24)	111.25(10)
O(5)-C(11)-C(12)	102.85(8)	O(7)-C(23)-C(26)	109.78(9)
C(13)-C(11)-C(12)	112.14(8)	C(25)-C(23)-C(26)	111.02(9)
O(11)-C(12)-C(11)	107.16(8)	C(24)-C(23)-C(26)	112.94(10)
O(11)-C(12)-C(3)	112.80(8)	O(10)-S(1)-O(9)	120.75(5)
C(11)-C(12)-C(3)	103.70(8)	O(10)-S(1)-N(1)	105.62(5)
O(1)-C(13)-N(14)	124.21(11)	O(9)-S(1)-N(1)	105.68(5)
O(1)-C(13)-C(11)	117.27(10)	O(10)-S(1)-C(27)	108.69(5)
N(14)-C(13)-C(11)	118.47(9)	O(9)-S(1)-C(27)	108.84(5)
C(13)-N(14)-C(15)	120.19(9)	N(1)-S(1)-C(27)	106.32(5)
C(13)-N(14)-C(17)	116.49(10)	C(28)-C(27)-C(32)	121.64(10)
C(15)-N(14)-C(17)	115.88(9)	C(28)-C(27)-S(1)	119.04(9)
O(3)-C(15)-N(14)	106.89(9)	C(32)-C(27)-S(1)	119.29(9)
O(3)-C(15)-C(16)	106.58(9)	C(29)-C(28)-C(27)	118.92(11)
N(14)-C(15)-C(16)	113.22(9)	C(30)-C(29)-C(28)	119.91(12)
O(2)-C(16)-N(10)	123.04(10)	C(29)-C(30)-C(31)	120.64(11)
O(2)-C(16)-C(15)	121.03(10)	C(32)-C(31)-C(30)	120.13(12)
N(10)-C(16)-C(15)	115.92(9)	C(31)-C(32)-C(27)	118.74(11)
C(2')-N(1')-C(9')	108.65(8)	C(33)-O(11)-C(12)	115.11(8)
C(2')-N(1')-C(22)	120.27(9)	O(12)-C(33)-O(11)	123.16(11)
C(9')-N(1')-C(22)	131.04(9)	O(12)-C(33)-C(34)	126.08(10)
C(3')-C(2')-N(1')	110.07(9)	O(11)-C(33)-C(34)	110.76(10)
C(2')-C(3')-C(4')	106.96(9)	O(1S)-C(2S)-C(3S)	121.72(14)
C(2')-C(3')-C(3)	125.07(9)	O(1S)-C(2S)-C(1S)	122.17(13)
C(4')-C(3')-C(3)	127.60(9)	C(3S)-C(2S)-C(1S)	116.09(13)
C(5')-C(4')-C(9')	119.21(9)	O(2S)-C(5S)-C(4S)	121.25(15)
C(5')-C(4')-C(3')	133.52(9)	O(2S)-C(5S)-C(6S)	121.31(16)
C(9')-C(4')-C(3')	107.24(9)	C(4S)-C(5S)-C(6S)	117.44(15)
C(6')-C(5')-C(4')	118.75(10)		

Table S18. Anisotropic displacement parameters ($Å^2$ x 10^3) for tetracyclic triacetate **28**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	15(1)	16(1)	15(1)	0(1)	2(1)	0(1)
C(2)	11(1)	16(1)	15(1)	0(1)	1(1)	1(1)
C(3)	11(1)	15(1)	14(1)	-1(1)	1(1)	0(1)
C(4)	13(1)	15(1)	16(1)	-2(1)	0(1)	0(1)
C(5)	18(1)	18(1)	19(1)	-3(1)	3(1)	0(1)
C(6)	27(1)	19(1)	23(1)	-6(1)	4(1)	0(1)
C(7)	30(1)	18(1)	27(1)	-5(1)	4(1)	-5(1)
C(8)	22(1)	18(1)	24(1)	-1(1)	3(1)	-5(1)
C(9)	16(1)	16(1)	17(1)	-1(1)	0(1)	-1(1)
N(10)	12(1)	18(1)	13(1)	0(1)	1(1)	3(1)
C(11)	12(1)	18(1)	14(1)	-1(1)	0(1)	0(1)
C(12)	12(1)	16(1)	15(1)	0(1)	1(1)	0(1)
C(13)	13(1)	22(1)	18(1)	3(1)	-1(1)	1(1)
N(14)	17(1)	20(1)	18(1)	4(1)	1(1)	3(1)
C(15)	15(1)	15(1)	19(1)	1(1)	1(1)	2(1)
C(16)	14(1)	16(1)	19(1)	0(1)	2(1)	2(1)
C(17)	25(1)	24(1)	24(1)	7(1)	-3(1)	5(1)
O(1)	23(1)	32(1)	16(1)	4(1)	0(1)	4(1)
O(2)	28(1)	26(1)	17(1)	-2(1)	0(1)	9(1)
N(1')	11(1)	15(1)	20(1)	-1(1)	-2(1)	2(1)
C(2')	13(1)	14(1)	19(1)	-1(1)	0(1)	0(1)
C(3')	12(1)	15(1)	15(1)	-1(1)	1(1)	0(1)
C(4')	13(1)	15(1)	15(1)	-1(1)	1(1)	1(1)
C(5')	15(1)	18(1)	21(1)	-3(1)	-1(1)	4(1)
C(6')	20(1)	18(1)	24(1)	-5(1)	-1(1)	4(1)
C(7')	20(1)	18(1)	21(1)	-6(1)	-2(1)	1(1)
C(8')	16(1)	17(1)	19(1)	-3(1)	-2(1)	0(1)
C(9')	13(1)	15(1)	16(1)	0(1)	1(1)	1(1)
O(3)	16(1)	16(1)	25(1)	-1(1)	2(1)	1(1)
O(4)	21(1)	24(1)	31(1)	-2(1)	6(1)	-1(1)
C(18)	18(1)	20(1)	23(1)	0(1)	2(1)	4(1)
C(19)	26(1)	22(1)	31(1)	-7(1)	2(1)	1(1)
O(5)	14(1)	21(1)	18(1)	-4(1)	-1(1)	-2(1)
O(6)	15(1)	31(1)	26(1)	-4(1)	-1(1)	0(1)
C(20)	16(1)	28(1)	16(1)	-2(1)	0(1)	-4(1)
C(21)	24(1)	30(1)	36(1)	-12(1)	1(1)	-8(1)
O(7)	12(1)	18(1)	24(1)	-1(1)	-2(1)	2(1)
O(8)	19(1)	20(1)	32(1)	-6(1)	-5(1)	6(1)
C(22)	12(1)	18(1)	20(1)	1(1)	-1(1)	2(1)
C(23)	10(1)	20(1)	21(1)	2(1)	-2(1)	3(1)
C(24)	15(1)	39(1)	22(1)	0(1)	2(1)	3(1)

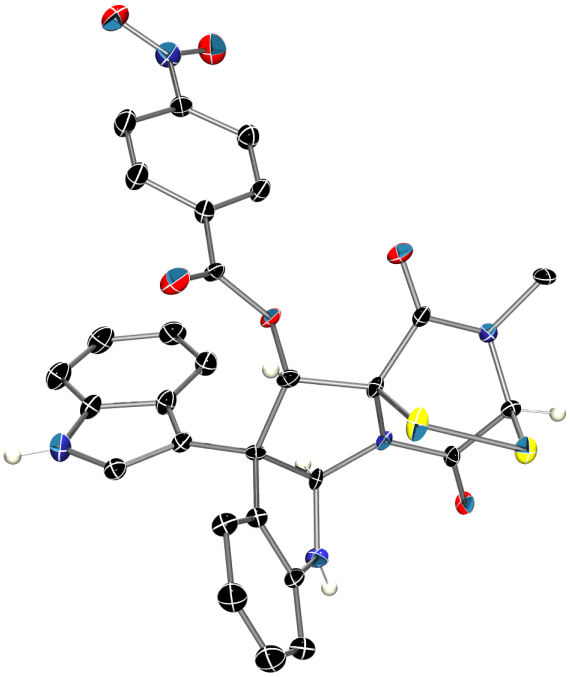
C(25)	16(1)	22(1)	29(1)	-1(1)	-4(1)	0(1)
C(26)	24(1)	20(1)	25(1)	4(1)	-3(1)	3(1)
S(1)	15(1)	18(1)	15(1)	2(1)	3(1)	1(1)
O(9)	22(1)	23(1)	23(1)	4(1)	3(1)	-6(1)
O(10)	21(1)	26(1)	18(1)	0(1)	6(1)	7(1)
C(27)	17(1)	18(1)	14(1)	2(1)	0(1)	1(1)
C(28)	25(1)	20(1)	18(1)	-1(1)	0(1)	0(1)
C(29)	26(1)	29(1)	20(1)	0(1)	-4(1)	-5(1)
C(30)	19(1)	35(1)	25(1)	9(1)	-4(1)	-1(1)
C(31)	23(1)	25(1)	32(1)	8(1)	-1(1)	6(1)
C(32)	22(1)	16(1)	26(1)	3(1)	0(1)	2(1)
O(11)	14(1)	16(1)	18(1)	0(1)	1(1)	0(1)
O(12)	23(1)	26(1)	40(1)	-5(1)	14(1)	-2(1)
C(33)	16(1)	22(1)	22(1)	3(1)	3(1)	-2(1)
C(34)	27(1)	20(1)	39(1)	1(1)	8(1)	-6(1)
O(1S)	58(1)	34(1)	48(1)	5(1)	-4(1)	-16(1)
C(1S)	30(1)	32(1)	36(1)	-7(1)	-5(1)	-2(1)
C(2S)	21(1)	31(1)	24(1)	0(1)	-3(1)	-2(1)
C(3S)	30(1)	70(1)	23(1)	0(1)	0(1)	-1(1)
O(2S)	29(1)	72(1)	37(1)	10(1)	0(1)	-3(1)
C(4S)	34(1)	34(1)	50(1)	-2(1)	3(1)	-10(1)
C(5S)	30(1)	41(1)	29(1)	-4(1)	0(1)	-2(1)
C(6S)	42(1)	95(2)	36(1)	10(1)	1(1)	17(1)

Table S19. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for tetracyclic triacetate **28**.

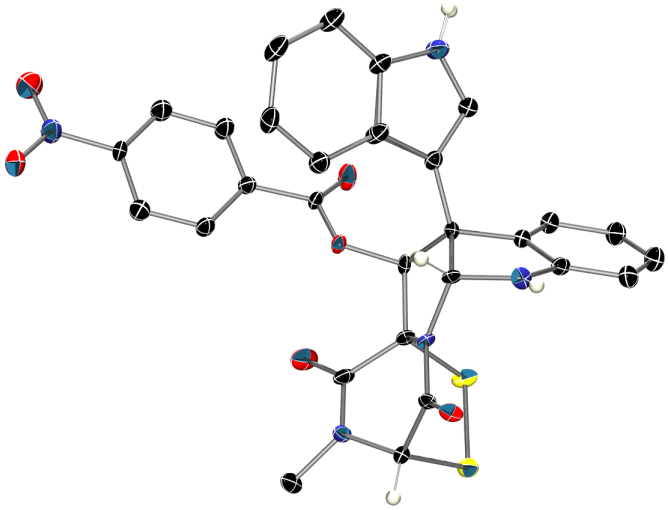
	x	y	z	U(eq)
H(2)	-535	-7030	-1707	17
H(5)	988	-9481	-3948	22
H(6)	536	-11658	-4111	28
H(7)	-697	-12606	-3266	30
H(8)	-1534	-11396	-2260	26
H(12)	9	-7458	-4076	17
H(15)	-3445	-5297	-2905	20
H(17A)	-2307	-3544	-4592	37
H(17B)	-2832	-2919	-3809	37
H(17C)	-3427	-4021	-4300	37
H(2')	1980	-9108	-2540	19
H(5')	231	-4950	-2058	21
H(6')	1060	-3358	-1296	25
H(7')	2755	-3648	-834	24
H(8')	3647	-5581	-1061	21
H(19A)	-3831	-1610	-1931	40
H(19B)	-2925	-2087	-1341	40
H(19C)	-4114	-2262	-1084	40

H(21A)	-3382	-9917	-3567	45
H(21B)	-2513	-9953	-4257	45
H(21C)	-3661	-9469	-4466	45
H(24A)	5623	-8991	-2165	38
H(24B)	6670	-8536	-1728	38
H(24C)	5931	-7500	-2155	38
H(25A)	5764	-6233	-886	34
H(25B)	6524	-7212	-430	34
H(25C)	5394	-6924	-72	34
H(26A)	4910	-9191	-65	35
H(26B)	6010	-9632	-419	35
H(26C)	4961	-10032	-874	35
H(28)	221	-7376	-303	25
H(29)	1970	-7509	93	30
H(30)	2866	-9451	-42	32
H(31)	2050	-11252	-597	32
H(32)	304	-11134	-998	26
H(34A)	2295	-4225	-4096	43
H(34B)	1386	-3846	-3483	43
H(34C)	1196	-3754	-4437	43
H(1S1)	-5585	-6695	-5228	49
H(1S2)	-6432	-7277	-4623	49
H(1S3)	-5235	-7656	-4523	49
H(3S1)	-5599	-5328	-2926	62
H(3S2)	-5446	-6842	-3056	62
H(3S3)	-6564	-6204	-3188	62
H(4S1)	-5910	-2761	-2247	59
H(4S2)	-6795	-2987	-2912	59
H(4S3)	-6843	-1753	-2335	59
H(6S1)	-5855	-331	-4183	86
H(6S2)	-6821	-227	-3579	86
H(6S3)	-6744	-1406	-4197	86

Crystal Structure of (+)-Bionectin A *p*-Nitrobenzoate (38).



View 1:



View 2:

Table S20. Crystal data and structure refinement for (+)-bionectin A *p*-nitrobenzoate (**38**).

Identification code	x8_13026	
Empirical formula	C29 H21 N5 O6 S2	
Formula weight	599.63	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 11.6928(7) Å	a= 90°.
	b = 11.2669(6) Å	b= 96.6760(10)°.
	c = 20.6483(11) Å	g = 90°.
Volume	2701.8(3) $Å^3$	
Z	4	
Density (calculated)	1.474 Mg/m^3	
Absorption coefficient	0.252 mm^{-1}	
F(000)	1240	
Crystal size	0.18 x 0.16 x 0.11 mm^3	
Theta range for data collection	0.99 to 31.00°.	
Index ranges	-16<=h<=16, -16<=k<=15, -29<=l<=29	
Reflections collected	97606	
Independent reflections	17143 [R(int) = 0.0361]	
Completeness to theta = 31.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9728 and 0.9560	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17143 / 3313 / 1207	
Goodness-of-fit on F^2	1.231	
Final R indices [I>2sigma(I)]	R1 = 0.0465, wR2 = 0.1452	
R indices (all data)	R1 = 0.0512, wR2 = 0.1496	
Absolute structure parameter	0.01(4)	
Largest diff. peak and hole	1.032 and -0.389 $e.Å^{-3}$	

Table S21. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for (+)-bionectin A *p*-nitrobenzoate (**38**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	-7440(1)	-4943(1)	-4207(1)	18(1)
S(2)	-7041(1)	-6351(1)	-4787(1)	21(1)
N(1)	-6408(2)	-4014(2)	-6291(2)	16(1)
C(2)	-7465(4)	-4684(4)	-6343(4)	13(1)
C(3)	-7110(2)	-5971(2)	-6504(2)	11(1)
C(4)	-5854(2)	-5962(2)	-6204(2)	14(1)
C(5)	-5090(2)	-6889(2)	-6058(1)	17(1)

C(6)	-3949(3)	-6632(4)	-5796(2)	24(1)
C(7)	-3614(3)	-5457(4)	-5705(2)	27(1)
C(8)	-4379(3)	-4521(3)	-5843(2)	22(1)
C(9)	-5502(3)	-4794(3)	-6093(2)	15(1)
C(12)	-7848(2)	-6788(3)	-6096(2)	14(1)
N(10)	-7996(3)	-4815(3)	-5727(2)	12(1)
C(11)	-8111(3)	-6024(3)	-5507(1)	13(1)
C(13)	-9257(3)	-6228(3)	-5232(1)	18(1)
N(14)	-9562(3)	-5283(4)	-4886(2)	15(1)
C(15)	-8714(5)	-4370(5)	-4730(2)	13(1)
C(16)	-8260(4)	-3904(2)	-5343(2)	12(1)
C(17)	-10554(4)	-5319(5)	-4513(3)	21(1)
O(18)	-9784(3)	-7165(3)	-5299(1)	32(1)
O(19)	-8088(3)	-2855(2)	-5451(2)	16(1)
O(20)	-8952(4)	-7004(5)	-6463(2)	15(1)
C(21)	-9094(3)	-8091(3)	-6747(2)	14(1)
O(22)	-8342(2)	-8830(3)	-6733(2)	26(1)
C(23)	-10279(3)	-8256(4)	-7079(2)	16(1)
C(24)	-11206(2)	-7584(3)	-6917(2)	18(1)
C(25)	-12301(2)	-7758(3)	-7248(2)	22(1)
C(26)	-12424(2)	-8591(4)	-7746(2)	19(1)
C(27)	-11518(4)	-9299(5)	-7903(3)	25(1)
C(28)	-10444(3)	-9122(5)	-7561(3)	24(1)
N(29)	-13566(3)	-8745(3)	-8119(1)	24(1)
O(30)	-13768(3)	-9602(3)	-8490(2)	38(1)
O(31)	-14317(2)	-8010(3)	-8042(1)	32(1)
N(1')	-6849(5)	-6933(7)	-8191(3)	21(1)
C(2')	-6434(4)	-6775(4)	-7548(3)	16(1)
C(3')	-7252(4)	-6247(4)	-7220(2)	15(1)
C(4')	-8256(6)	-6070(10)	-7692(3)	18(1)
C(5')	-9370(3)	-5610(3)	-7671(2)	20(1)
C(6')	-10136(2)	-5594(3)	-8236(1)	24(1)
C(7')	-9811(2)	-6027(3)	-8829(1)	27(1)
C(8')	-8729(3)	-6504(3)	-8865(2)	25(1)
C(9')	-7962(3)	-6527(4)	-8290(2)	19(1)
S(1B)	-7687(7)	-5010(9)	-4185(4)	63(3)
S(2B)	-7234(11)	-6609(8)	-4864(4)	73(3)
N(1B)	-6351(12)	-4281(11)	-6211(8)	16(1)
C(2B)	-7450(14)	-4843(16)	-6389(17)	13(3)
C(3B)	-7257(12)	-6186(13)	-6454(8)	11(1)
C(4B)	-5986(11)	-6219(12)	-6184(8)	15(1)
C(5B)	-5281(11)	-7175(12)	-6052(7)	17(1)
C(6B)	-4145(14)	-6972(17)	-5772(10)	31(4)
C(7B)	-3726(13)	-5868(16)	-5635(9)	31(3)
C(8B)	-4407(13)	-4866(15)	-5746(10)	29(3)
C(9B)	-5537(11)	-5139(13)	-6037(10)	22(3)
C(12B)	-8105(13)	-6850(18)	-6161(9)	14(1)
N(10B)	-8109(18)	-4973(13)	-5811(8)	12(1)
C(11B)	-8256(15)	-6208(14)	-5624(9)	29(2)

C(13B)	-9423(13)	-6285(15)	-5374(7)	18(1)
N(14B)	-9670(20)	-5400(20)	-4982(13)	27(4)
C(15B)	-8840(30)	-4480(20)	-4814(11)	19(3)
C(16B)	-8180(20)	-4112(13)	-5393(11)	12(1)
C(17B)	-10630(30)	-5560(30)	-4595(17)	35(6)
O(18B)	-10016(14)	-7163(14)	-5467(7)	32(1)
O(19B)	-7975(18)	-3058(12)	-5482(10)	16(1)
O(20B)	-9120(20)	-7100(30)	-6562(13)	26(3)
C(21B)	-9401(17)	-8181(18)	-6851(11)	25(3)
O(22B)	-8637(11)	-8919(16)	-6715(9)	26(1)
C(23B)	-10454(16)	-8200(18)	-7216(10)	26(3)
C(24B)	-11315(13)	-7380(15)	-7121(8)	37(4)
C(25B)	-12378(11)	-7567(12)	-7453(6)	22(1)
C(26B)	-12632(16)	-8492(16)	-7889(9)	29(3)
C(27B)	-11754(18)	-9280(30)	-7981(16)	34(4)
C(28B)	-10703(17)	-9170(20)	-7626(14)	33(4)
N(29B)	-13725(14)	-8544(15)	-8259(8)	24(1)
O(30B)	-13559(14)	-9377(16)	-8618(8)	38(1)
O(31B)	-14440(11)	-7850(14)	-8248(6)	32(1)
N(1'B)	-6850(20)	-6960(30)	-8185(13)	21(1)
C(2'B)	-6510(20)	-6960(20)	-7524(13)	16(1)
C(3'B)	-7330(20)	-6400(20)	-7211(11)	15(1)
C(4'B)	-8220(30)	-6020(50)	-7708(11)	18(1)
C(5'B)	-9257(17)	-5390(20)	-7708(9)	20(1)
C(6'B)	-9938(12)	-5248(13)	-8280(6)	24(1)
C(7'B)	-9629(11)	-5625(14)	-8877(6)	27(1)
C(8'B)	-8586(13)	-6195(15)	-8903(8)	25(1)
C(9'B)	-7859(18)	-6340(20)	-8318(9)	19(1)
S(1A)	-6988(1)	-373(1)	-679(1)	31(1)
S(2A)	-7280(1)	-1843(1)	-106(1)	27(1)
N(1A)	-8768(2)	321(3)	1061(2)	27(1)
C(2A)	-7620(2)	-29(2)	1318(1)	16(1)
C(3A)	-7733(2)	-1349(2)	1538(1)	15(1)
C(4A)	-8913(2)	-1675(3)	1206(1)	20(1)
C(5A)	-9432(2)	-2773(3)	1148(1)	27(1)
C(6A)	-10570(2)	-2843(3)	845(1)	37(1)
C(7A)	-11138(2)	-1822(4)	611(1)	37(1)
C(8A)	-10604(2)	-728(3)	651(1)	33(1)
C(9A)	-9469(2)	-659(3)	949(1)	23(1)
C(12A)	-6768(2)	-2065(2)	1238(2)	15(1)
N(10A)	-6781(3)	-116(3)	832(1)	19(1)
C(11A)	-6456(2)	-1292(2)	674(1)	16(1)
C(13A)	-5202(2)	-1350(2)	515(1)	20(1)
N(14A)	-4952(2)	-442(2)	127(1)	22(1)
C(15A)	-5856(3)	368(2)	-94(1)	22(1)
C(16A)	-6506(3)	797(3)	457(1)	23(1)
C(17A)	-3861(3)	-397(3)	-152(2)	34(1)
O(18A)	-4542(2)	-2153(2)	688(1)	25(1)
O(19A)	-6760(4)	1831(3)	548(2)	32(1)

O(20A)	-5773(2)	-2170(2)	1718(1)	16(1)
C(21A)	-5350(2)	-3278(2)	1814(1)	21(1)
O(22A)	-5821(2)	-4158(2)	1580(1)	38(1)
C(23A)	-4233(2)	-3297(3)	2250(2)	20(1)
C(24A)	-3640(2)	-2259(2)	2431(2)	36(1)
C(25A)	-2595(2)	-2327(3)	2830(2)	40(1)
C(26A)	-2186(3)	-3425(2)	3023(1)	22(1)
C(27A)	-2757(3)	-4460(3)	2850(2)	38(1)
C(28A)	-3795(3)	-4396(3)	2444(2)	36(1)
N(29A)	-1066(2)	-3514(2)	3437(1)	29(1)
O(30A)	-502(2)	-2608(3)	3531(2)	50(1)
O(31A)	-764(2)	-4484(3)	3666(2)	43(1)
N(1'A)	-8160(2)	-1823(2)	3273(1)	15(1)
C(2'A)	-8479(2)	-1962(3)	2618(1)	16(1)
C(3'A)	-7693(3)	-1428(4)	2277(1)	15(1)
C(4'A)	-6827(3)	-915(4)	2749(2)	15(1)
C(5'A)	-5834(2)	-215(2)	2715(1)	17(1)
C(6'A)	-5213(2)	153(2)	3288(1)	21(1)
C(7'A)	-5535(2)	-175(3)	3897(2)	20(1)
C(8'A)	-6513(3)	-838(3)	3949(1)	19(1)
C(9'A)	-7154(2)	-1190(2)	3367(1)	14(1)
S(1C)	-7375(6)	-225(6)	-752(3)	31(1)
S(2C)	-7752(7)	-1701(8)	-132(3)	40(2)
N(1C)	-8583(14)	714(15)	1122(11)	27(3)
C(2C)	-7444(15)	222(17)	1325(13)	16(1)
C(3C)	-7756(15)	-1063(16)	1510(10)	15(1)
C(4C)	-8970(13)	-1253(14)	1164(7)	24(3)
C(5C)	-9583(13)	-2270(16)	1068(8)	27(1)
C(6C)	-10708(16)	-2240(20)	731(9)	37(1)
C(7C)	-11068(15)	-1130(20)	538(9)	37(1)
C(8C)	-10491(13)	-70(20)	621(9)	42(4)
C(9C)	-9370(13)	-175(16)	948(9)	31(4)
C(12C)	-6970(20)	-1870(30)	1257(14)	15(1)
N(10C)	-6900(30)	-40(19)	757(14)	19(1)
C(11C)	-6772(14)	-1232(16)	529(11)	22(2)
C(13C)	-5539(14)	-1400(13)	367(9)	20(1)
N(14C)	-5269(14)	-422(15)	12(9)	22(1)
C(15C)	-6182(19)	380(20)	-225(10)	31(3)
C(16C)	-6700(30)	885(19)	370(13)	23(1)
C(17C)	-4326(17)	-520(20)	-399(10)	36(4)
O(18C)	-4982(14)	-2310(12)	475(9)	32(3)
O(19C)	-6930(40)	1920(20)	459(16)	32(1)
O(20C)	-5859(16)	-2135(15)	1558(7)	16(1)
C(21C)	-5605(15)	-3184(16)	1805(6)	21(1)
O(22C)	-6284(14)	-3991(13)	1722(9)	38(1)
C(23C)	-4442(18)	-3320(20)	2173(15)	20(1)
C(24C)	-3626(17)	-2496(18)	2166(12)	36(1)
C(25C)	-2558(18)	-2580(20)	2503(12)	42(4)
C(26C)	-2250(20)	-3591(16)	2863(10)	22(1)

C(27C)	-3135(19)	-4410(20)	2895(15)	38(1)
C(28C)	-4193(15)	-4232(18)	2584(9)	23(3)
N(29C)	-1344(15)	-3574(16)	3273(9)	29(1)
O(30C)	-515(14)	-2900(20)	3220(11)	50(1)
O(31C)	-1020(20)	-4500(30)	3583(14)	43(1)
N(1'C)	-8124(18)	-1950(20)	3149(9)	15(1)
C(2'C)	-8400(20)	-1950(20)	2492(10)	16(1)
C(3'C)	-7610(20)	-1400(30)	2192(10)	15(1)
C(4'C)	-6740(20)	-1030(40)	2709(11)	15(1)
C(5'C)	-5677(18)	-460(20)	2713(10)	17(1)
C(6'C)	-5070(20)	-110(20)	3289(10)	21(1)
C(7'C)	-5380(20)	-540(20)	3887(10)	28(5)
C(8'C)	-6450(20)	-1050(30)	3901(11)	19(1)
C(9'C)	-7085(19)	-1390(20)	3309(10)	14(1)

Table S22. Bond lengths [Å] and angles [°] for (+)-bionectin A *p*-nitrobenzoate (**38**).

S(1)-C(15)	1.851(6)	C(23)-C(24)	1.396(4)
S(1)-S(2)	2.0727(15)	C(24)-C(25)	1.393(3)
S(2)-C(11)	1.866(3)	C(25)-C(26)	1.389(4)
N(1)-C(9)	1.401(4)	C(26)-C(27)	1.394(4)
N(1)-C(2)	1.441(5)	C(26)-N(29)	1.472(4)
C(2)-N(10)	1.486(8)	C(27)-C(28)	1.382(3)
C(2)-C(3)	1.555(4)	N(29)-O(31)	1.232(4)
C(3)-C(3')	1.502(6)	N(29)-O(30)	1.237(4)
C(3)-C(4)	1.527(3)	N(1')-C(2')	1.371(4)
C(3)-C(12)	1.572(4)	N(1')-C(9')	1.372(4)
C(4)-C(5)	1.384(3)	C(2')-C(3')	1.370(4)
C(4)-C(9)	1.390(4)	C(3')-C(4')	1.450(4)
C(5)-C(6)	1.410(4)	C(4')-C(5')	1.407(4)
C(6)-C(7)	1.387(5)	C(4')-C(9')	1.418(4)
C(7)-C(8)	1.391(5)	C(5')-C(6')	1.385(4)
C(8)-C(9)	1.388(4)	C(6')-C(7')	1.411(4)
C(12)-O(20)	1.440(4)	C(7')-C(8')	1.384(4)
C(12)-C(11)	1.550(4)	C(8')-C(9')	1.402(3)
N(10)-C(16)	1.355(3)	S(1B)-C(15B)	1.85(4)
N(10)-C(11)	1.447(4)	S(1B)-S(2B)	2.379(13)
C(11)-C(13)	1.532(3)	S(2B)-C(11B)	1.91(2)
C(13)-O(18)	1.222(3)	N(1B)-C(9B)	1.374(13)
C(13)-N(14)	1.353(4)	N(1B)-C(2B)	1.441(14)
N(14)-C(15)	1.439(4)	C(2B)-N(10B)	1.50(4)
N(14)-C(17)	1.465(3)	C(2B)-C(3B)	1.538(15)
C(15)-C(16)	1.523(4)	C(3B)-C(12B)	1.43(2)
C(16)-O(19)	1.223(3)	C(3B)-C(4B)	1.525(13)
O(20)-C(21)	1.358(5)	C(3B)-C(3'B)	1.57(3)
C(21)-O(22)	1.209(4)	C(4B)-C(9B)	1.347(13)
C(21)-C(23)	1.484(4)	C(4B)-C(5B)	1.365(12)
C(23)-C(28)	1.391(4)	C(5B)-C(6B)	1.405(14)

C(6B)-C(7B)	1.354(15)	C(6A)-C(7A)	1.387(5)
C(7B)-C(8B)	1.386(15)	C(7A)-C(8A)	1.379(5)
C(8B)-C(9B)	1.420(13)	C(8A)-C(9A)	1.399(3)
C(12B)-C(11B)	1.35(3)	C(12A)-O(20A)	1.443(3)
C(12B)-O(20B)	1.40(2)	C(12A)-C(11A)	1.532(4)
N(10B)-C(16B)	1.308(13)	N(10A)-C(16A)	1.349(3)
N(10B)-C(11B)	1.460(14)	N(10A)-C(11A)	1.427(3)
C(11B)-C(13B)	1.516(14)	C(11A)-C(13A)	1.540(3)
C(13B)-O(18B)	1.210(13)	C(13A)-O(18A)	1.216(3)
C(13B)-N(14B)	1.339(14)	C(13A)-N(14A)	1.351(3)
N(14B)-C(15B)	1.436(14)	N(14A)-C(15A)	1.431(3)
N(14B)-C(17B)	1.459(15)	N(14A)-C(17A)	1.460(3)
C(15B)-C(16B)	1.549(14)	C(15A)-C(16A)	1.518(3)
C(16B)-O(19B)	1.230(14)	C(16A)-O(19A)	1.223(3)
O(20B)-C(21B)	1.37(3)	O(20A)-C(21A)	1.348(3)
C(21B)-O(22B)	1.23(3)	C(21A)-O(22A)	1.206(3)
C(21B)-C(23B)	1.37(2)	C(21A)-C(23A)	1.498(3)
C(23B)-C(28B)	1.395(13)	C(23A)-C(28A)	1.382(4)
C(23B)-C(24B)	1.397(13)	C(23A)-C(24A)	1.389(4)
C(24B)-C(25B)	1.364(12)	C(24A)-C(25A)	1.394(3)
C(25B)-C(26B)	1.387(12)	C(25A)-C(26A)	1.368(4)
C(26B)-C(27B)	1.387(13)	C(26A)-C(27A)	1.371(4)
C(26B)-N(29B)	1.41(2)	C(26A)-N(29A)	1.482(3)
C(27B)-C(28B)	1.361(13)	C(27A)-C(28A)	1.394(3)
N(29B)-O(31B)	1.15(2)	N(29A)-O(30A)	1.218(4)
N(29B)-O(30B)	1.23(2)	N(29A)-O(31A)	1.227(4)
N(1'B)-C(9'B)	1.374(14)	N(1'A)-C(2'A)	1.370(2)
N(1'B)-C(2'B)	1.377(15)	N(1'A)-C(9'A)	1.370(3)
C(2'B)-C(3'B)	1.363(15)	C(2'A)-C(3'A)	1.361(3)
C(3'B)-C(4'B)	1.443(14)	C(3'A)-C(4'A)	1.442(3)
C(4'B)-C(5'B)	1.404(14)	C(4'A)-C(9'A)	1.408(3)
C(4'B)-C(9'B)	1.420(14)	C(4'A)-C(5'A)	1.411(3)
C(5'B)-C(6'B)	1.356(14)	C(5'A)-C(6'A)	1.379(3)
C(6'B)-C(7'B)	1.390(13)	C(6'A)-C(7'A)	1.403(3)
C(7'B)-C(8'B)	1.384(14)	C(7'A)-C(8'A)	1.380(3)
C(8'B)-C(9'B)	1.403(13)	C(8'A)-C(9'A)	1.398(3)
S(1A)-C(15A)	1.881(3)	S(1C)-C(15C)	1.80(3)
S(1A)-S(2A)	2.0862(11)	S(1C)-S(2C)	2.175(10)
S(2A)-C(11A)	1.883(2)	S(2C)-C(11C)	1.76(2)
N(1A)-C(9A)	1.378(4)	N(1C)-C(9C)	1.380(15)
N(1A)-C(2A)	1.440(3)	N(1C)-C(2C)	1.459(15)
C(2A)-N(10A)	1.486(4)	C(2C)-N(10C)	1.43(4)
C(2A)-C(3A)	1.565(3)	C(2C)-C(3C)	1.552(16)
C(3A)-C(4A)	1.513(3)	C(3C)-C(12C)	1.44(3)
C(3A)-C(3'A)	1.525(4)	C(3C)-C(3'C)	1.45(3)
C(3A)-C(12A)	1.571(3)	C(3C)-C(4C)	1.528(15)
C(4A)-C(5A)	1.377(4)	C(4C)-C(5C)	1.353(15)
C(4A)-C(9A)	1.391(4)	C(4C)-C(9C)	1.359(15)
C(5A)-C(6A)	1.406(3)	C(5C)-C(6C)	1.416(15)

C(6C)-C(7C)	1.358(17)
C(7C)-C(8C)	1.379(17)
C(8C)-C(9C)	1.408(14)
C(12C)-O(20C)	1.40(3)
C(12C)-C(11C)	1.71(4)
N(10C)-C(16C)	1.351(16)
N(10C)-C(11C)	1.438(16)
C(11C)-C(13C)	1.530(15)
C(13C)-O(18C)	1.220(14)
C(13C)-N(14C)	1.380(14)
N(14C)-C(15C)	1.442(15)
N(14C)-C(17C)	1.472(15)
C(15C)-C(16C)	1.540(16)
C(16C)-O(19C)	1.216(15)
O(20C)-C(21C)	1.308(15)
C(21C)-O(22C)	1.207(15)
C(21C)-C(23C)	1.486(16)
C(23C)-C(24C)	1.33(2)
C(23C)-C(28C)	1.34(2)
C(24C)-C(25C)	1.36(2)
C(25C)-C(26C)	1.38(2)
C(26C)-N(29C)	1.28(3)
C(26C)-C(27C)	1.39(2)
C(27C)-C(28C)	1.34(2)
N(29C)-O(30C)	1.25(2)
N(29C)-O(31C)	1.26(2)
N(1'C)-C(2'C)	1.358(15)
N(1'C)-C(9'C)	1.371(15)
C(2'C)-C(3'C)	1.327(16)
C(3'C)-C(4'C)	1.446(15)
C(4'C)-C(5'C)	1.398(15)
C(4'C)-C(9'C)	1.409(15)
C(5'C)-C(6'C)	1.371(16)
C(6'C)-C(7'C)	1.415(16)
C(7'C)-C(8'C)	1.383(16)
C(8'C)-C(9'C)	1.406(15)

C(15)-S(1)-S(2)	98.62(16)
C(11)-S(2)-S(1)	97.68(10)
C(9)-N(1)-C(2)	107.8(3)
N(1)-C(2)-N(10)	115.4(4)
N(1)-C(2)-C(3)	104.9(3)
N(10)-C(2)-C(3)	103.8(4)
C(3')-C(3)-C(4)	113.0(3)
C(3')-C(3)-C(2)	113.7(4)
C(4)-C(3)-C(2)	100.1(2)
C(3')-C(3)-C(12)	113.7(3)
C(4)-C(3)-C(12)	110.4(2)
C(2)-C(3)-C(12)	104.7(4)
C(5)-C(4)-C(9)	120.5(2)
C(5)-C(4)-C(3)	130.5(2)
C(9)-C(4)-C(3)	109.0(2)
C(4)-C(5)-C(6)	119.1(3)
C(7)-C(6)-C(5)	119.2(3)
C(6)-C(7)-C(8)	122.0(3)
C(9)-C(8)-C(7)	117.8(3)
C(8)-C(9)-C(4)	121.3(3)
C(8)-C(9)-N(1)	128.3(3)
C(4)-C(9)-N(1)	110.3(2)
O(20)-C(12)-C(11)	105.1(3)
O(20)-C(12)-C(3)	109.3(3)
C(11)-C(12)-C(3)	105.5(3)
C(16)-N(10)-C(11)	119.6(3)
C(16)-N(10)-C(2)	124.8(3)
C(11)-N(10)-C(2)	115.2(3)
N(10)-C(11)-C(13)	112.1(3)
N(10)-C(11)-C(12)	104.0(3)
C(13)-C(11)-C(12)	118.0(2)
N(10)-C(11)-S(2)	110.99(19)
C(13)-C(11)-S(2)	102.1(2)
C(12)-C(11)-S(2)	109.8(2)
O(18)-C(13)-N(14)	125.4(3)
O(18)-C(13)-C(11)	122.6(3)
N(14)-C(13)-C(11)	111.9(2)
C(13)-N(14)-C(15)	117.6(3)
C(13)-N(14)-C(17)	121.9(3)
C(15)-N(14)-C(17)	118.0(3)
N(14)-C(15)-C(16)	111.0(3)
N(14)-C(15)-S(1)	111.6(4)
C(16)-C(15)-S(1)	105.7(3)
O(19)-C(16)-N(10)	124.9(3)
O(19)-C(16)-C(15)	124.4(3)
N(10)-C(16)-C(15)	110.5(3)
C(21)-O(20)-C(12)	115.9(4)
O(22)-C(21)-O(20)	123.9(3)
O(22)-C(21)-C(23)	124.1(3)
O(20)-C(21)-C(23)	111.9(3)
C(28)-C(23)-C(24)	120.4(3)
C(28)-C(23)-C(21)	117.6(3)
C(24)-C(23)-C(21)	122.0(3)
C(25)-C(24)-C(23)	120.1(3)
C(26)-C(25)-C(24)	118.0(2)
C(25)-C(26)-C(27)	122.9(3)
C(25)-C(26)-N(29)	118.5(3)
C(27)-C(26)-N(29)	118.6(3)
C(28)-C(27)-C(26)	117.9(3)
C(27)-C(28)-C(23)	120.6(3)
O(31)-N(29)-O(30)	121.2(3)

O(31)-N(29)-C(26)	118.0(3)
O(30)-N(29)-C(26)	120.8(3)
C(2')-N(1')-C(9')	108.9(4)
C(3')-C(2')-N(1')	110.3(3)
C(2')-C(3')-C(4')	106.6(3)
C(2')-C(3')-C(3)	125.0(4)
C(4')-C(3')-C(3)	128.4(4)
C(5')-C(4')-C(9')	118.7(4)
C(5')-C(4')-C(3')	135.3(4)
C(9')-C(4')-C(3')	106.0(3)
C(6')-C(5')-C(4')	119.3(3)
C(5')-C(6')-C(7')	120.8(3)
C(8')-C(7')-C(6')	121.4(2)
C(7')-C(8')-C(9')	117.5(3)
N(1')-C(9')-C(8')	129.5(4)
N(1')-C(9')-C(4')	108.3(3)
C(8')-C(9')-C(4')	122.3(3)
C(15B)-S(1B)-S(2B)	91.3(9)
C(11B)-S(2B)-S(1B)	98.3(6)
C(9B)-N(1B)-C(2B)	109.1(12)
N(1B)-C(2B)-N(10B)	111(2)
N(1B)-C(2B)-C(3B)	108.6(11)
N(10B)-C(2B)-C(3B)	93.9(18)
C(12B)-C(3B)-C(4B)	121.7(13)
C(12B)-C(3B)-C(2B)	111.2(17)
C(4B)-C(3B)-C(2B)	97.9(10)
C(12B)-C(3B)-C(3'B)	112.4(15)
C(4B)-C(3B)-C(3'B)	107.1(14)
C(2B)-C(3B)-C(3'B)	104.4(18)
C(9B)-C(4B)-C(5B)	117.2(11)
C(9B)-C(4B)-C(3B)	113.5(10)
C(5B)-C(4B)-C(3B)	129.2(11)
C(4B)-C(5B)-C(6B)	118.3(12)
C(7B)-C(6B)-C(5B)	122.5(15)
C(6B)-C(7B)-C(8B)	121.8(13)
C(7B)-C(8B)-C(9B)	112.5(13)
C(4B)-C(9B)-N(1B)	109.7(10)
C(4B)-C(9B)-C(8B)	127.6(12)
N(1B)-C(9B)-C(8B)	122.7(13)
C(11B)-C(12B)-O(20B)	114.2(18)
C(11B)-C(12B)-C(3B)	103.3(15)
O(20B)-C(12B)-C(3B)	116.2(19)
C(16B)-N(10B)-C(11B)	120.9(14)
C(16B)-N(10B)-C(2B)	122.1(14)
C(11B)-N(10B)-C(2B)	113.0(14)
C(12B)-C(11B)-N(10B)	105.2(15)
C(12B)-C(11B)-C(13B)	117.2(14)
N(10B)-C(11B)-C(13B)	106.4(13)
C(12B)-C(11B)-S(2B)	114.7(13)
N(10B)-C(11B)-S(2B)	111.2(13)
C(13B)-C(11B)-S(2B)	102.1(12)
O(18B)-C(13B)-N(14B)	123.0(14)
O(18B)-C(13B)-C(11B)	121.0(14)
N(14B)-C(13B)-C(11B)	115.5(12)
C(13B)-N(14B)-C(15B)	119.4(16)
C(13B)-N(14B)-C(17B)	118.4(15)
C(15B)-N(14B)-C(17B)	119.9(16)
N(14B)-C(15B)-C(16B)	113.0(15)
N(14B)-C(15B)-S(1B)	111(2)
C(16B)-C(15B)-S(1B)	104.2(19)
O(19B)-C(16B)-N(10B)	126.0(17)
O(19B)-C(16B)-C(15B)	120.0(16)
N(10B)-C(16B)-C(15B)	112.7(14)
C(21B)-O(20B)-C(12B)	125(2)
O(22B)-C(21B)-C(23B)	134.4(17)
O(22B)-C(21B)-O(20B)	111.8(17)
C(23B)-C(21B)-O(20B)	113.9(18)
C(21B)-C(23B)-C(28B)	117.3(15)
C(21B)-C(23B)-C(24B)	122.0(15)
C(28B)-C(23B)-C(24B)	120.1(14)
C(25B)-C(24B)-C(23B)	117.1(12)
C(24B)-C(25B)-C(26B)	123.8(12)
C(27B)-C(26B)-C(25B)	117.6(14)
C(27B)-C(26B)-N(29B)	122.5(14)
C(25B)-C(26B)-N(29B)	119.6(14)
C(28B)-C(27B)-C(26B)	120.4(14)
C(27B)-C(28B)-C(23B)	120.6(14)
O(31B)-N(29B)-O(30B)	134.5(17)
O(31B)-N(29B)-C(26B)	125.3(17)
O(30B)-N(29B)-C(26B)	99.3(15)
C(9'B)-N(1'B)-C(2'B)	109.7(15)
C(3'B)-C(2'B)-N(1'B)	109.7(15)
C(2'B)-C(3'B)-C(4'B)	106.6(14)
C(2'B)-C(3'B)-C(3B)	125.8(17)
C(4'B)-C(3'B)-C(3B)	127.6(18)
C(5'B)-C(4'B)-C(9'B)	118.2(15)
C(5'B)-C(4'B)-C(3'B)	134.7(16)
C(9'B)-C(4'B)-C(3'B)	107.0(12)
C(6'B)-C(5'B)-C(4'B)	118.7(16)
C(5'B)-C(6'B)-C(7'B)	123.2(13)
C(8'B)-C(7'B)-C(6'B)	119.9(12)
C(7'B)-C(8'B)-C(9'B)	117.9(14)
N(1'B)-C(9'B)-C(8'B)	130.6(17)
N(1'B)-C(9'B)-C(4'B)	106.8(13)
C(8'B)-C(9'B)-C(4'B)	121.5(15)
C(15A)-S(1A)-S(2A)	97.86(9)
C(11A)-S(2A)-S(1A)	97.04(9)
C(9A)-N(1A)-C(2A)	110.7(2)

N(1A)-C(2A)-N(10A)	115.5(3)	C(24A)-C(23A)-C(21A)	121.6(2)
N(1A)-C(2A)-C(3A)	105.12(19)	C(23A)-C(24A)-C(25A)	119.2(2)
N(10A)-C(2A)-C(3A)	102.6(2)	C(26A)-C(25A)-C(24A)	118.3(3)
C(4A)-C(3A)-C(3'A)	111.0(2)	C(25A)-C(26A)-C(27A)	123.4(3)
C(4A)-C(3A)-C(2A)	101.69(18)	C(25A)-C(26A)-N(29A)	119.0(2)
C(3'A)-C(3A)-C(2A)	110.6(2)	C(27A)-C(26A)-N(29A)	117.7(2)
C(4A)-C(3A)-C(12A)	110.86(19)	C(26A)-C(27A)-C(28A)	118.5(3)
C(3'A)-C(3A)-C(12A)	115.1(2)	C(23A)-C(28A)-C(27A)	119.2(3)
C(2A)-C(3A)-C(12A)	106.5(2)	O(30A)-N(29A)-O(31A)	124.1(2)
C(5A)-C(4A)-C(9A)	121.7(2)	O(30A)-N(29A)-C(26A)	117.4(2)
C(5A)-C(4A)-C(3A)	128.8(2)	O(31A)-N(29A)-C(26A)	118.5(2)
C(9A)-C(4A)-C(3A)	109.5(2)	C(2'A)-N(1'A)-C(9'A)	109.23(19)
C(4A)-C(5A)-C(6A)	118.3(3)	C(3'A)-C(2'A)-N(1'A)	109.7(2)
C(7A)-C(6A)-C(5A)	119.9(3)	C(2'A)-C(3'A)-C(4'A)	107.0(2)
C(8A)-C(7A)-C(6A)	121.7(2)	C(2'A)-C(3'A)-C(3A)	126.8(2)
C(7A)-C(8A)-C(9A)	118.5(3)	C(4'A)-C(3'A)-C(3A)	126.2(2)
N(1A)-C(9A)-C(4A)	110.68(19)	C(9'A)-C(4'A)-C(5'A)	118.6(2)
N(1A)-C(9A)-C(8A)	129.3(3)	C(9'A)-C(4'A)-C(3'A)	106.3(2)
C(4A)-C(9A)-C(8A)	119.9(3)	C(5'A)-C(4'A)-C(3'A)	135.0(3)
O(20A)-C(12A)-C(11A)	108.9(2)	C(6'A)-C(5'A)-C(4'A)	118.7(2)
O(20A)-C(12A)-C(3A)	109.3(2)	C(5'A)-C(6'A)-C(7'A)	121.4(2)
C(11A)-C(12A)-C(3A)	104.67(19)	C(8'A)-C(7'A)-C(6'A)	121.6(3)
C(16A)-N(10A)-C(11A)	119.3(3)	C(7'A)-C(8'A)-C(9'A)	116.9(3)
C(16A)-N(10A)-C(2A)	123.9(2)	N(1'A)-C(9'A)-C(8'A)	129.4(2)
C(11A)-N(10A)-C(2A)	115.5(3)	N(1'A)-C(9'A)-C(4'A)	107.83(19)
N(10A)-C(11A)-C(12A)	105.1(2)	C(8'A)-C(9'A)-C(4'A)	122.8(2)
N(10A)-C(11A)-C(13A)	111.9(2)	C(15C)-S(1C)-S(2C)	97.6(7)
C(12A)-C(11A)-C(13A)	117.03(18)	C(11C)-S(2C)-S(1C)	93.9(7)
N(10A)-C(11A)-S(2A)	112.2(2)	C(9C)-N(1C)-C(2C)	111.0(13)
C(12A)-C(11A)-S(2A)	108.65(19)	N(10C)-C(2C)-N(1C)	109(2)
C(13A)-C(11A)-S(2A)	102.05(14)	N(10C)-C(2C)-C(3C)	98.6(18)
O(18A)-C(13A)-N(14A)	124.3(2)	N(1C)-C(2C)-C(3C)	101.1(12)
O(18A)-C(13A)-C(11A)	123.8(2)	C(12C)-C(3C)-C(3'C)	100(2)
N(14A)-C(13A)-C(11A)	111.79(19)	C(12C)-C(3C)-C(4C)	109.9(16)
C(13A)-N(14A)-C(15A)	117.9(2)	C(3'C)-C(3C)-C(4C)	114.8(15)
C(13A)-N(14A)-C(17A)	121.3(2)	C(12C)-C(3C)-C(2C)	109(2)
C(15A)-N(14A)-C(17A)	119.9(2)	C(3'C)-C(3C)-C(2C)	119(2)
N(14A)-C(15A)-C(16A)	112.3(2)	C(4C)-C(3C)-C(2C)	104.4(12)
N(14A)-C(15A)-S(1A)	111.13(18)	C(5C)-C(4C)-C(9C)	123.6(13)
C(16A)-C(15A)-S(1A)	104.3(2)	C(5C)-C(4C)-C(3C)	129.4(14)
O(19A)-C(16A)-N(10A)	124.1(3)	C(9C)-C(4C)-C(3C)	107.1(11)
O(19A)-C(16A)-C(15A)	124.7(3)	C(4C)-C(5C)-C(6C)	119.7(15)
N(10A)-C(16A)-C(15A)	111.1(2)	C(7C)-C(6C)-C(5C)	114.0(15)
C(21A)-O(20A)-C(12A)	115.44(19)	C(6C)-C(7C)-C(8C)	129.1(15)
O(22A)-C(21A)-O(20A)	124.01(19)	C(7C)-C(8C)-C(9C)	113.5(16)
O(22A)-C(21A)-C(23A)	123.7(2)	C(4C)-C(9C)-N(1C)	111.7(11)
O(20A)-C(21A)-C(23A)	112.3(2)	C(4C)-C(9C)-C(8C)	120.0(15)
C(28A)-C(23A)-C(24A)	121.3(2)	N(1C)-C(9C)-C(8C)	128.2(15)
C(28A)-C(23A)-C(21A)	117.0(2)	O(20C)-C(12C)-C(3C)	125(2)

O(20C)-C(12C)-C(11C)	105.6(19)	C(24C)-C(23C)-C(21C)	122.6(16)
C(3C)-C(12C)-C(11C)	102.1(18)	C(28C)-C(23C)-C(21C)	121.3(16)
C(16C)-N(10C)-C(2C)	116.8(17)	C(23C)-C(24C)-C(25C)	124.2(18)
C(16C)-N(10C)-C(11C)	119.7(18)	C(24C)-C(25C)-C(26C)	119.8(19)
C(2C)-N(10C)-C(11C)	122.4(19)	N(29C)-C(26C)-C(25C)	119.0(16)
N(10C)-C(11C)-C(13C)	109.0(17)	N(29C)-C(26C)-C(27C)	122.9(17)
N(10C)-C(11C)-C(12C)	94.4(17)	C(25C)-C(26C)-C(27C)	115(2)
C(13C)-C(11C)-C(12C)	111.6(15)	C(28C)-C(27C)-C(26C)	122(2)
N(10C)-C(11C)-S(2C)	117(2)	C(27C)-C(28C)-C(23C)	122.5(19)
C(13C)-C(11C)-S(2C)	109.8(13)	O(30C)-N(29C)-O(31C)	111(2)
C(12C)-C(11C)-S(2C)	114.5(14)	O(30C)-N(29C)-C(26C)	123.1(15)
O(18C)-C(13C)-N(14C)	128.2(14)	O(31C)-N(29C)-C(26C)	120.0(15)
O(18C)-C(13C)-C(11C)	124.0(14)	C(2'C)-N(1'C)-C(9'C)	110.0(15)
N(14C)-C(13C)-C(11C)	107.3(12)	C(3'C)-C(2'C)-N(1'C)	111.6(16)
C(13C)-N(14C)-C(15C)	118.5(15)	C(2'C)-C(3'C)-C(4'C)	104.9(15)
C(13C)-N(14C)-C(17C)	118.6(14)	C(2'C)-C(3'C)-C(3C)	124.2(18)
C(15C)-N(14C)-C(17C)	115.2(15)	C(4'C)-C(3'C)-C(3C)	130(2)
N(14C)-C(15C)-C(16C)	107.8(15)	C(5'C)-C(4'C)-C(9'C)	118.4(16)
N(14C)-C(15C)-S(1C)	117.1(17)	C(5'C)-C(4'C)-C(3'C)	133.0(18)
C(16C)-C(15C)-S(1C)	105.8(18)	C(9'C)-C(4'C)-C(3'C)	108.5(13)
O(19C)-C(16C)-N(10C)	126(2)	C(6'C)-C(5'C)-C(4'C)	120.5(18)
O(19C)-C(16C)-C(15C)	126(2)	C(5'C)-C(6'C)-C(7'C)	119.9(18)
N(10C)-C(16C)-C(15C)	107.5(15)	C(8'C)-C(7'C)-C(6'C)	119.2(17)
C(21C)-O(20C)-C(12C)	121(2)	C(7'C)-C(8'C)-C(9'C)	118.8(17)
O(22C)-C(21C)-O(20C)	120.7(16)	N(1'C)-C(9'C)-C(8'C)	134.1(17)
O(22C)-C(21C)-C(23C)	122.9(16)	N(1'C)-C(9'C)-C(4'C)	104.9(13)
O(20C)-C(21C)-C(23C)	116.4(15)	C(8'C)-C(9'C)-C(4'C)	120.6(16)
C(24C)-C(23C)-C(28C)	115.9(18)		

Table S23. Anisotropic displacement parameters ($Å^2$ x 10^3) for (+)-bionectin A *p*-nitrobenzoate (**38**). The anisotropic displacement factor exponent takes the form: $-2p^2[h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	18(1)	21(1)	15(1)	0(1)	-1(1)	5(1)
S(2)	30(1)	17(1)	16(1)	-1(1)	-3(1)	10(1)
N(1)	18(1)	8(1)	23(1)	2(1)	4(1)	-1(1)
C(2)	17(1)	11(1)	12(2)	-5(1)	2(1)	2(1)
C(3)	11(1)	9(1)	13(1)	3(1)	1(1)	-2(1)
C(4)	14(1)	14(1)	15(1)	0(1)	1(1)	-1(1)
C(5)	17(1)	14(1)	20(1)	2(1)	-1(1)	1(1)
C(6)	15(1)	33(2)	23(1)	0(2)	-4(1)	5(1)
C(7)	18(1)	36(2)	25(1)	-2(1)	-3(1)	-1(1)
C(8)	18(1)	23(2)	25(1)	-3(1)	5(1)	-4(1)
C(9)	18(1)	11(1)	16(1)	-2(1)	4(1)	-3(1)
C(12)	8(1)	14(1)	19(1)	-1(1)	-2(1)	0(1)
N(10)	16(1)	10(1)	10(1)	-2(1)	-1(1)	-2(1)

C(11)	18(1)	8(1)	14(1)	-4(1)	1(1)	0(1)
C(13)	25(1)	17(1)	14(1)	-6(1)	5(1)	-8(1)
N(14)	16(1)	13(1)	16(1)	-3(1)	5(1)	-2(1)
C(15)	12(1)	13(2)	13(2)	0(1)	0(1)	-1(1)
C(16)	12(1)	11(1)	14(1)	-3(1)	2(1)	4(1)
C(17)	22(1)	14(2)	28(2)	-4(2)	13(1)	-8(1)
O(18)	42(2)	24(1)	33(2)	-12(1)	15(1)	-20(1)
O(19)	22(1)	7(1)	20(1)	-1(1)	6(1)	4(1)
O(20)	11(1)	12(1)	21(1)	-6(1)	-1(1)	0(1)
C(21)	12(1)	13(1)	16(1)	-3(1)	-2(1)	-2(1)
O(22)	16(1)	20(1)	42(1)	-8(1)	-3(1)	4(1)
C(23)	15(1)	18(1)	16(2)	-2(1)	-1(1)	3(1)
C(24)	17(1)	17(1)	21(1)	-7(1)	-1(1)	1(1)
C(25)	19(1)	23(1)	22(1)	-4(1)	2(1)	2(1)
C(26)	11(1)	25(1)	18(1)	-4(1)	-2(1)	-2(1)
C(27)	22(2)	26(1)	28(2)	-12(1)	1(1)	2(1)
C(28)	18(1)	26(1)	28(2)	-11(1)	-1(1)	3(1)
N(29)	19(1)	25(1)	26(2)	0(1)	0(1)	3(1)
O(30)	35(1)	37(2)	43(2)	-18(1)	6(1)	-13(1)
O(31)	17(1)	47(1)	32(1)	-6(1)	-3(1)	6(1)
N(1')	22(1)	23(1)	18(1)	-4(1)	1(1)	5(1)
C(2')	17(1)	13(2)	18(1)	0(1)	1(1)	1(1)
C(3')	15(1)	12(2)	16(1)	-2(1)	-1(1)	0(1)
C(4')	19(1)	18(1)	16(1)	-3(1)	-3(1)	4(1)
C(5')	18(1)	21(2)	20(1)	-2(1)	-1(1)	4(1)
C(6')	16(1)	28(2)	26(1)	0(1)	-5(1)	1(1)
C(7')	26(1)	29(2)	23(1)	-4(1)	-10(1)	1(1)
C(8')	28(1)	25(2)	20(1)	-3(1)	-7(1)	2(1)
C(9')	23(1)	17(2)	17(1)	-3(1)	-2(1)	0(1)
S(1B)	26(3)	117(6)	49(3)	49(3)	13(2)	13(3)
S(2B)	151(7)	37(4)	23(2)	1(2)	-20(3)	39(4)
N(1B)	18(1)	8(1)	23(1)	2(1)	4(1)	-1(1)
C(2B)	9(5)	21(5)	10(5)	-4(5)	-1(4)	-10(4)
C(3B)	11(1)	9(1)	13(1)	3(1)	1(1)	-2(1)
C(4B)	14(1)	12(2)	17(1)	2(2)	0(1)	-2(1)
C(5B)	17(1)	14(1)	20(1)	2(1)	-1(1)	1(1)
C(6B)	23(6)	37(8)	31(7)	-17(7)	-6(5)	0(5)
C(7B)	17(5)	40(9)	36(7)	9(7)	-6(4)	-1(5)
C(8B)	26(5)	28(7)	33(7)	7(6)	-3(4)	-16(5)
C(9B)	8(4)	26(5)	29(6)	7(6)	-5(3)	-3(4)
C(12B)	8(1)	14(1)	19(1)	-1(1)	-2(1)	0(1)
N(10B)	16(1)	10(1)	10(1)	-2(1)	-1(1)	-2(1)
C(11B)	39(6)	15(5)	33(5)	17(4)	3(4)	4(4)
C(13B)	25(1)	17(1)	14(1)	-6(1)	5(1)	-8(1)
N(14B)	38(6)	20(6)	24(8)	-5(4)	0(5)	-13(4)
C(15B)	31(8)	16(6)	9(5)	-7(4)	-1(4)	-2(4)
C(16B)	12(1)	11(1)	14(1)	-3(1)	2(1)	4(1)
C(17B)	47(9)	9(9)	53(12)	-12(7)	21(9)	-5(6)
O(18B)	42(2)	24(1)	33(2)	-12(1)	15(1)	-20(1)

O(19B)	22(1)	7(1)	20(1)	-1(1)	6(1)	4(1)
O(20B)	19(6)	18(5)	40(9)	-1(5)	-2(5)	-10(4)
C(21B)	28(7)	17(5)	28(7)	-9(4)	-6(5)	-1(5)
O(22B)	16(1)	20(1)	42(1)	-8(1)	-3(1)	4(1)
C(23B)	26(5)	30(6)	19(8)	5(5)	-8(4)	-3(4)
C(24B)	38(6)	33(8)	37(9)	-15(6)	-9(6)	8(5)
C(25B)	19(1)	23(1)	22(1)	-4(1)	2(1)	2(1)
C(26B)	39(6)	18(5)	28(8)	-9(5)	-3(5)	9(5)
C(27B)	37(7)	32(6)	30(6)	-18(4)	-10(6)	6(6)
C(28B)	38(7)	31(5)	29(6)	-25(4)	-6(6)	8(6)
N(29B)	19(1)	25(1)	26(2)	0(1)	0(1)	3(1)
O(30B)	35(1)	37(2)	43(2)	-18(1)	6(1)	-13(1)
O(31B)	17(1)	47(1)	32(1)	-6(1)	-3(1)	6(1)
N(1'B)	22(1)	23(1)	18(1)	-4(1)	1(1)	5(1)
C(2'B)	17(1)	13(2)	18(1)	0(1)	1(1)	1(1)
C(3'B)	15(1)	12(2)	16(1)	-2(1)	-1(1)	0(1)
C(4'B)	19(1)	18(1)	16(1)	-3(1)	-3(1)	4(1)
C(5'B)	18(1)	21(2)	20(1)	-2(1)	-1(1)	4(1)
C(6'B)	16(1)	28(2)	26(1)	0(1)	-5(1)	1(1)
C(7'B)	26(1)	29(2)	23(1)	-4(1)	-10(1)	1(1)
C(8'B)	28(1)	25(2)	20(1)	-3(1)	-7(1)	2(1)
C(9'B)	23(1)	17(2)	17(1)	-3(1)	-2(1)	0(1)
S(1A)	36(1)	40(1)	17(1)	4(1)	-3(1)	11(1)
S(2A)	33(1)	31(1)	15(1)	-4(1)	-4(1)	0(1)
N(1A)	22(1)	24(1)	33(1)	4(1)	-1(1)	8(1)
C(2A)	20(1)	14(1)	12(1)	2(1)	1(1)	3(1)
C(3A)	18(1)	13(1)	14(1)	0(1)	-2(1)	2(1)
C(4A)	16(1)	30(1)	13(1)	-1(1)	-4(1)	3(1)
C(5A)	26(1)	32(1)	22(1)	-2(1)	-6(1)	-1(1)
C(6A)	30(1)	47(2)	30(1)	-3(1)	-9(1)	-12(1)
C(7A)	21(1)	57(2)	31(1)	-2(1)	-10(1)	-1(1)
C(8A)	22(1)	48(2)	25(1)	6(1)	-10(1)	8(1)
C(9A)	20(1)	31(1)	16(1)	0(1)	-2(1)	5(1)
C(12A)	17(1)	15(1)	14(1)	-3(1)	0(1)	6(1)
N(10A)	26(1)	15(1)	15(1)	0(1)	3(1)	7(1)
C(11A)	22(1)	15(1)	10(1)	0(1)	-2(1)	5(1)
C(13A)	25(1)	18(1)	17(1)	-2(1)	2(1)	4(1)
N(14A)	25(1)	19(1)	23(1)	4(1)	6(1)	7(1)
C(15A)	34(1)	18(1)	16(1)	2(1)	7(1)	9(1)
C(16A)	35(2)	19(1)	17(1)	5(1)	7(1)	12(1)
C(17A)	33(1)	31(1)	43(2)	11(1)	20(1)	10(1)
O(18A)	28(1)	22(1)	26(1)	1(1)	7(1)	9(1)
O(19A)	55(2)	18(1)	25(1)	6(1)	14(1)	14(1)
O(20A)	20(1)	15(1)	12(1)	-1(1)	-3(1)	3(1)
C(21A)	25(1)	17(1)	18(1)	0(1)	-5(1)	4(1)
O(22A)	45(1)	12(1)	50(1)	-1(1)	-26(1)	3(1)
C(23A)	20(1)	20(1)	18(1)	2(1)	-3(1)	2(1)
C(24A)	31(1)	14(1)	59(2)	-6(1)	-16(1)	3(1)
C(25A)	26(1)	23(1)	67(2)	-4(1)	-15(1)	0(1)

C(26A)	20(1)	27(1)	20(1)	-2(1)	2(1)	2(1)
C(27A)	33(2)	26(1)	50(2)	10(1)	-22(2)	2(1)
C(28A)	32(2)	19(1)	51(2)	8(1)	-21(1)	2(1)
N(29A)	13(1)	42(1)	30(1)	5(1)	-3(1)	4(1)
O(30A)	20(1)	59(2)	68(2)	10(1)	-11(1)	-9(1)
O(31A)	34(2)	48(1)	40(1)	4(1)	-19(1)	13(1)
N(1'A)	18(1)	17(1)	10(1)	-2(1)	0(1)	-1(1)
C(2'A)	17(1)	18(1)	13(1)	-2(1)	1(1)	1(1)
C(3'A)	16(1)	16(1)	12(1)	-1(1)	1(1)	0(1)
C(4'A)	16(1)	13(1)	14(1)	0(1)	-1(1)	1(1)
C(5'A)	18(1)	15(1)	18(1)	1(1)	2(1)	2(1)
C(6'A)	22(1)	19(1)	20(1)	-2(1)	-1(1)	-1(1)
C(7'A)	20(1)	19(1)	19(1)	-2(1)	-4(1)	-1(1)
C(8'A)	24(1)	20(2)	12(1)	-2(1)	-1(1)	-2(1)
C(9'A)	17(1)	11(1)	14(1)	-2(1)	0(1)	2(1)
S(1C)	36(1)	40(1)	17(1)	4(1)	-3(1)	11(1)
S(2C)	30(3)	65(4)	22(2)	-18(2)	-6(2)	-8(3)
N(1C)	15(5)	20(7)	42(9)	15(7)	-9(5)	0(5)
C(2C)	20(1)	14(1)	12(1)	2(1)	1(1)	3(1)
C(3C)	18(1)	13(1)	14(1)	0(1)	-2(1)	2(1)
C(4C)	35(5)	14(6)	19(6)	6(6)	-13(5)	-3(5)
C(5C)	26(1)	32(1)	22(1)	-2(1)	-6(1)	-1(1)
C(6C)	30(1)	47(2)	30(1)	-3(1)	-9(1)	-12(1)
C(7C)	21(1)	57(2)	31(1)	-2(1)	-10(1)	-1(1)
C(8C)	24(7)	59(7)	39(9)	12(10)	-14(6)	-5(7)
C(9C)	35(6)	24(7)	30(8)	13(8)	-15(6)	0(6)
C(12C)	17(1)	15(1)	14(1)	-3(1)	0(1)	6(1)
N(10C)	26(1)	15(1)	15(1)	0(1)	3(1)	7(1)
C(11C)	26(6)	13(5)	27(5)	2(4)	2(4)	-5(5)
C(13C)	25(1)	18(1)	17(1)	-2(1)	2(1)	4(1)
N(14C)	25(1)	19(1)	23(1)	4(1)	6(1)	7(1)
C(15C)	35(8)	35(7)	24(7)	9(5)	7(6)	8(5)
C(16C)	35(2)	19(1)	17(1)	5(1)	7(1)	12(1)
C(17C)	31(8)	41(11)	36(9)	-9(8)	3(6)	-8(7)
O(18C)	30(7)	23(6)	47(9)	-4(6)	21(7)	-1(5)
O(19C)	55(2)	18(1)	25(1)	6(1)	14(1)	14(1)
O(20C)	20(1)	15(1)	12(1)	-1(1)	-3(1)	3(1)
C(21C)	25(1)	17(1)	18(1)	0(1)	-5(1)	4(1)
O(22C)	45(1)	12(1)	50(1)	-1(1)	-26(1)	3(1)
C(23C)	20(1)	20(1)	18(1)	2(1)	-3(1)	2(1)
C(24C)	31(1)	14(1)	59(2)	-6(1)	-16(1)	3(1)
C(25C)	36(7)	38(9)	49(10)	18(8)	-7(7)	-13(7)
C(26C)	20(1)	27(1)	20(1)	-2(1)	2(1)	2(1)
C(27C)	33(2)	26(1)	50(2)	10(1)	-22(2)	2(1)
C(28C)	16(6)	23(7)	30(7)	2(5)	2(5)	10(5)
N(29C)	13(1)	42(1)	30(1)	5(1)	-3(1)	4(1)
O(30C)	20(1)	59(2)	68(2)	10(1)	-11(1)	-9(1)
O(31C)	34(2)	48(1)	40(1)	4(1)	-19(1)	13(1)
N(1'C)	18(1)	17(1)	10(1)	-2(1)	0(1)	-1(1)

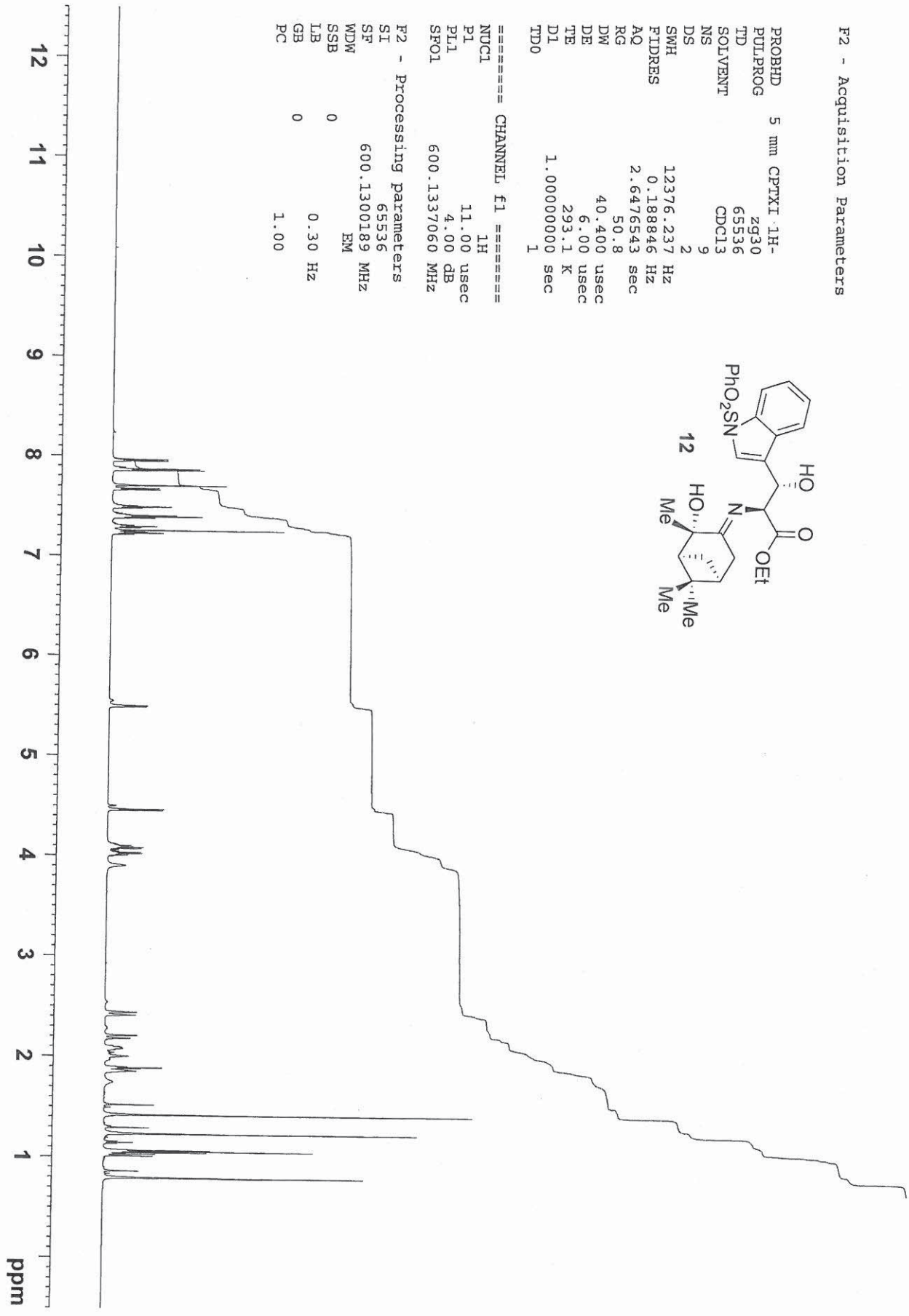
C(2'C)	17(1)	18(1)	13(1)	-2(1)	1(1)	1(1)
C(3'C)	16(1)	16(1)	12(1)	-1(1)	1(1)	0(1)
C(4'C)	16(1)	13(1)	14(1)	0(1)	-1(1)	1(1)
C(5'C)	18(1)	15(1)	18(1)	1(1)	2(1)	2(1)
C(6'C)	22(1)	19(1)	20(1)	-2(1)	-1(1)	-1(1)
C(7'C)	41(9)	25(11)	13(5)	8(7)	-14(6)	-3(8)
C(8'C)	24(1)	20(2)	12(1)	-2(1)	-1(1)	-2(1)
C(9'C)	17(1)	11(1)	14(1)	-2(1)	0(1)	2(1)

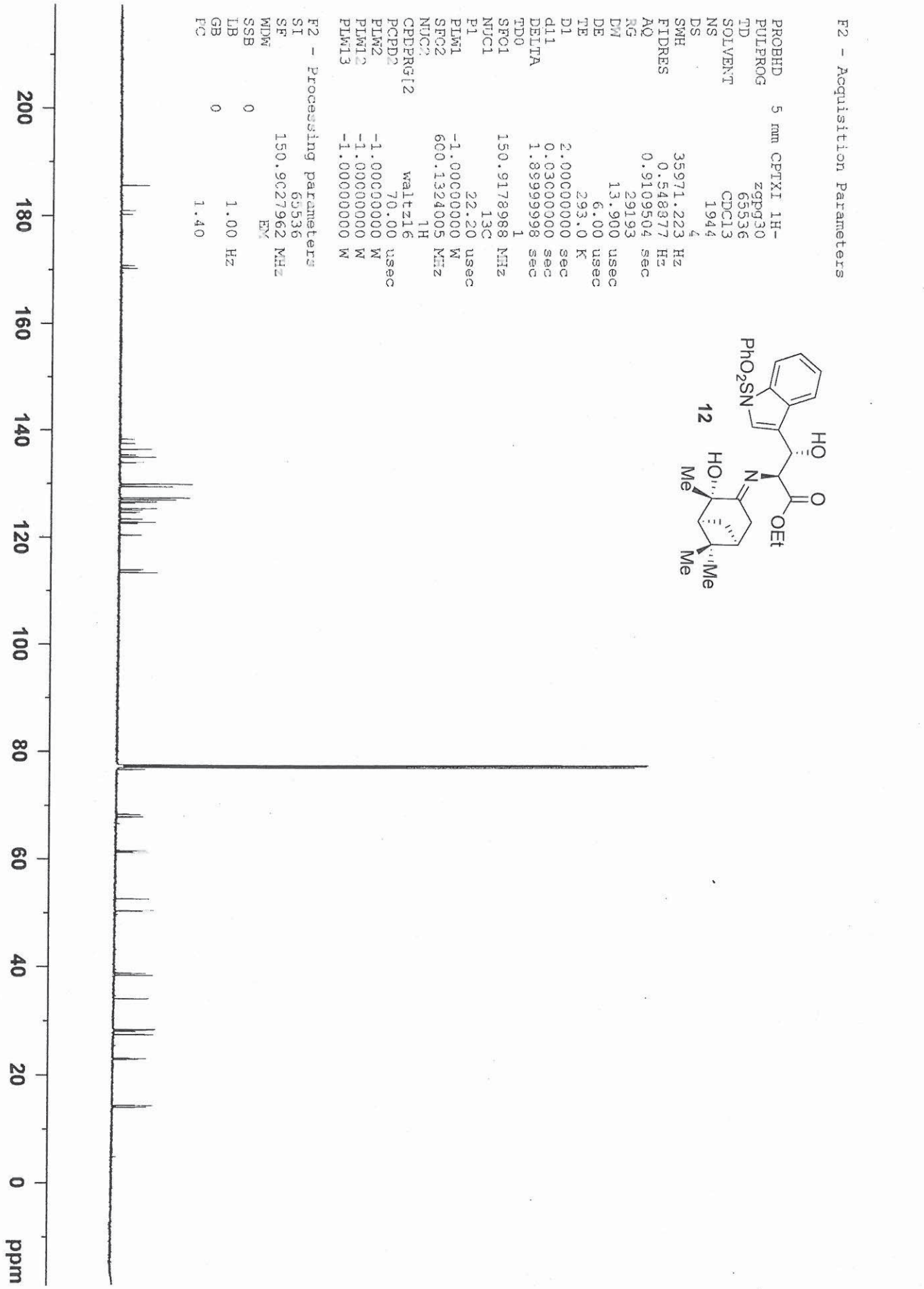
Table S24. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for (+)-bionectin A *p*-nitrobenzoate (**38**).

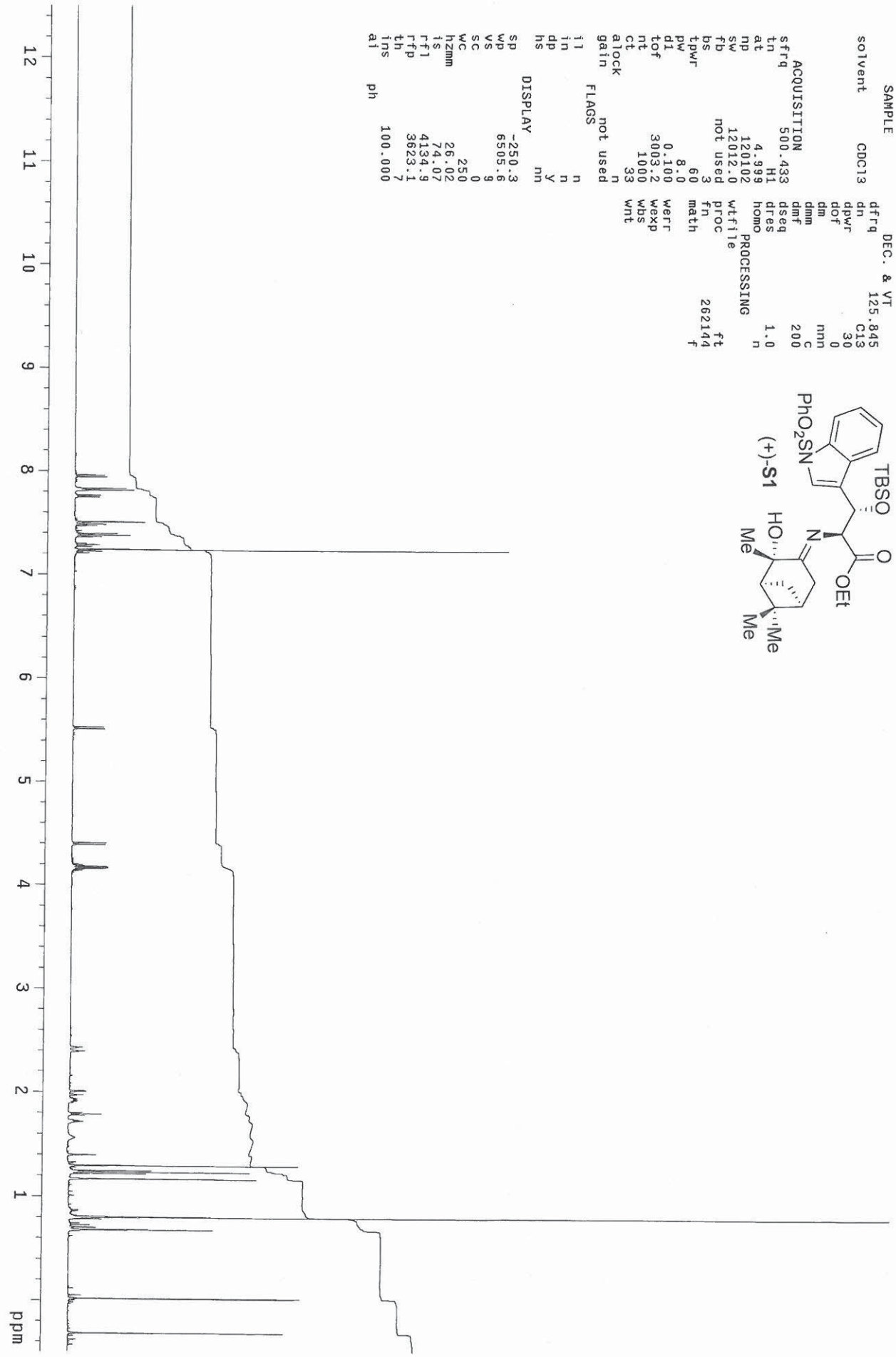
	x	y	z	U(eq)
H(1)	-6344	-3251	-6370	19
H(2)	-8034	-4360	-6698	16
H(5)	-5331	-7687	-6134	21
H(6)	-3416	-7255	-5683	29
H(7)	-2837	-5286	-5543	32
H(8)	-4141	-3721	-5770	26
H(12)	-7439	-7541	-5956	17
H(15)	-9064	-3703	-4502	16
H(17A)	-11077	-5956	-4682	31
H(17B)	-10961	-4557	-4556	31
H(17C)	-10289	-5467	-4053	31
H(24)	-11091	-7007	-6580	22
H(25)	-12944	-7320	-7135	26
H(27)	-11635	-9885	-8235	30
H(28)	-9813	-9597	-7656	29
H(2N)	-6510(30)	-7290(30)	-8508(17)	25
H(2')	-5686	-6999	-7358	19
H(5')	-9594	-5313	-7274	24
H(6')	-10890	-5287	-8223	28
H(7')	-10346	-5992	-9211	32
H(8')	-8515	-6803	-9263	30
H(1B)	-6222	-3512	-6214	19
H(2B)	-7907	-4480	-6778	16
H(5B)	-5552	-7958	-6147	21
H(6B)	-3652	-7634	-5674	37
H(7B)	-2944	-5779	-5458	38
H(8B)	-4147	-4084	-5640	35
H(12B)	-7747	-7624	-6011	17
H(15B)	-9224	-3774	-4647	23
H(17D)	-10690	-6395	-4479	52
H(17E)	-11347	-5300	-4849	52
H(17F)	-10493	-5078	-4197	52
H(24B)	-11167	-6720	-6838	44

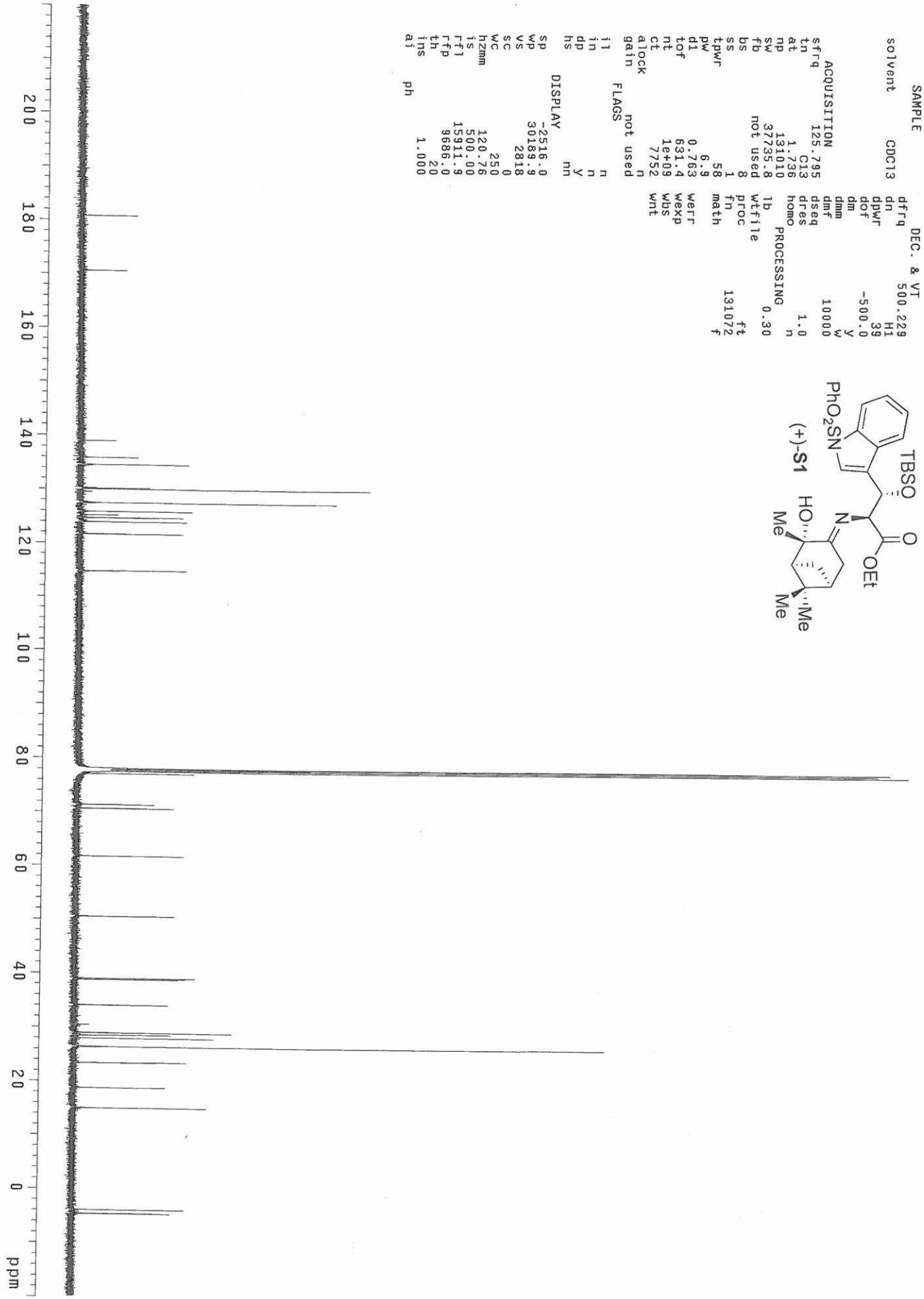
H(25B)	-12979	-7033	-7382	26
H(27B)	-11887	-9899	-8294	41
H(28B)	-10134	-9765	-7659	40
H(1'B)	-6477	-7314	-8478	25
H(2'B)	-5821	-7297	-7317	19
H(5'B)	-9476	-5074	-7314	24
H(6'B)	-10663	-4870	-8273	28
H(7'B)	-10131	-5492	-9265	32
H(8'B)	-8370	-6480	-9304	30
H(1A)	-8991	1059	986	32
H(2A)	-7316	485	1694	19
H(5A)	-9030	-3466	1308	33
H(6A)	-10950	-3589	800	44
H(7A)	-11915	-1876	418	45
H(8A)	-10998	-39	481	39
H(12A)	-7054	-2862	1080	18
H(15A)	-5530	1063	-311	27
H(17J)	-3322	121	115	52
H(17K)	-3993	-83	-597	52
H(17L)	-3537	-1197	-161	52
H(24A)	-3943	-1510	2285	44
H(25A)	-2177	-1630	2964	48
H(27A)	-2452	-5204	3002	46
H(28A)	-4197	-5100	2303	43
H(2NA)	-8550(20)	-2130(30)	3580(14)	18
H(2'A)	-9148	-2369	2430	19
H(5'A)	-5599	-2	2305	21
H(6'A)	-4553	638	3271	25
H(7'A)	-5070	65	4282	24
H(8'A)	-6739	-1047	4361	23
H(1C)	-8746	1477	1113	32
H(2C)	-6963	676	1672	19
H(5C)	-9259	-3003	1227	33
H(6C)	-11170	-2927	647	44
H(7C)	-11824	-1090	314	45
H(8C)	-10818	669	472	51
H(12C)	-7381	-2641	1162	18
H(15C)	-5843	1054	-457	37
H(17G)	-4070	-1348	-408	54
H(17H)	-3682	-18	-220	54
H(17I)	-4599	-261	-843	54
H(24C)	-3800	-1806	1909	44
H(25C)	-2023	-1950	2490	50
H(27C)	-2984	-5114	3143	46
H(28C)	-4789	-4772	2657	28
H(1'C)	-8549	-2255	3430	18
H(2'C)	-9077	-2296	2273	19
H(5'C)	-5374	-310	2313	21
H(6'C)	-4442	429	3286	25

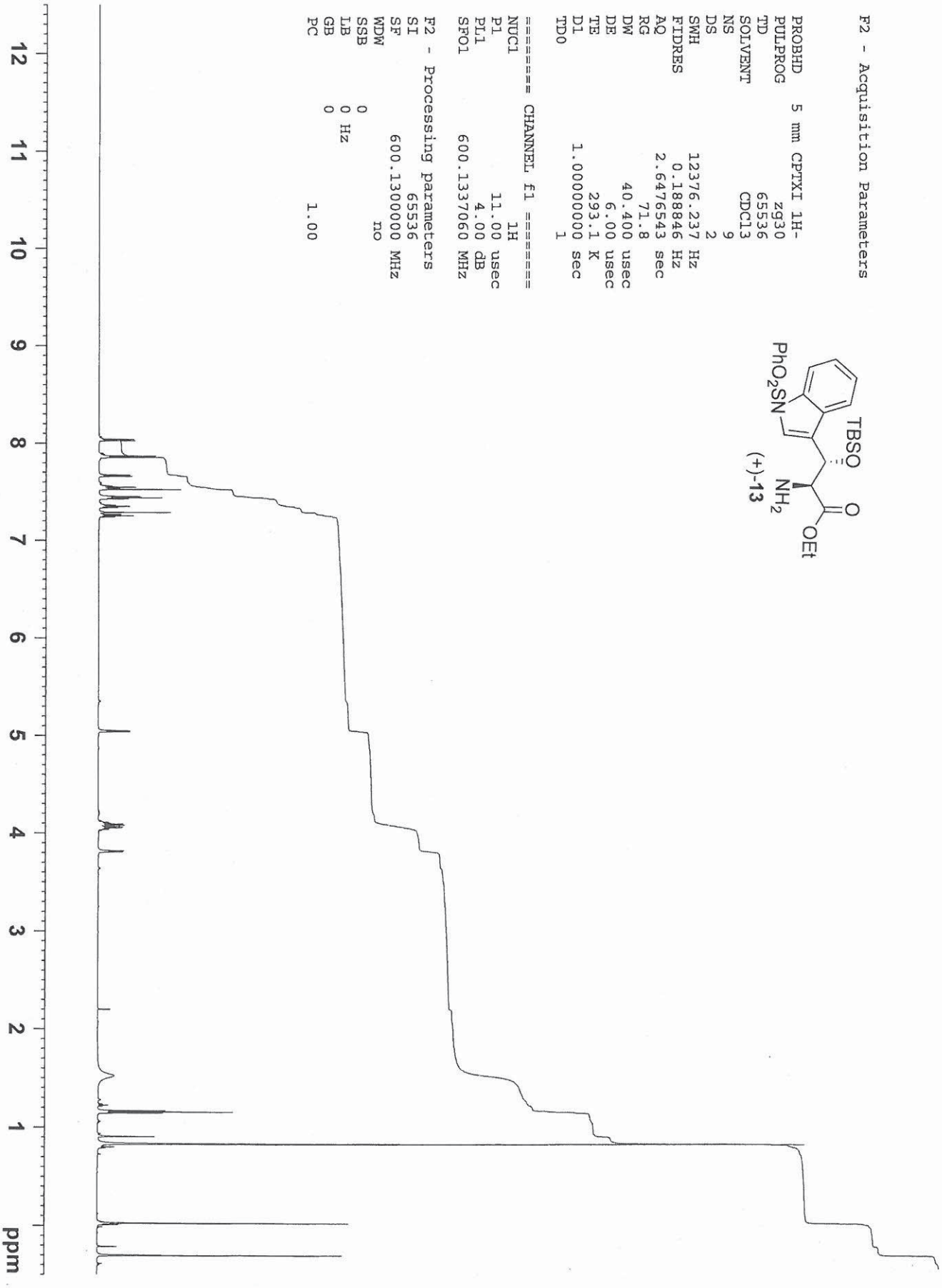
H(7'C)	-4859	-483	4274	33
H(8'C)	-6756	-1172	4304	23

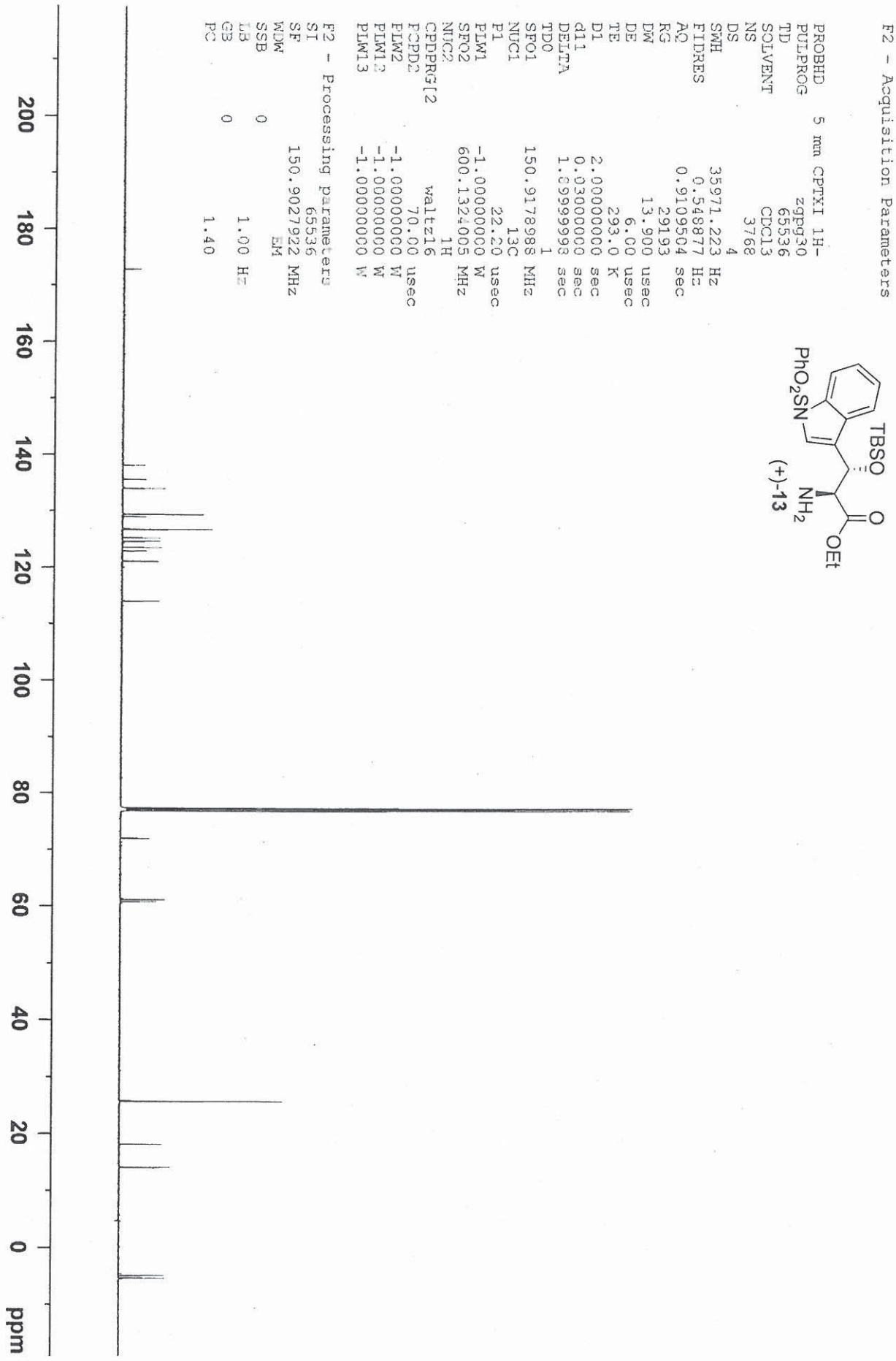

F2 - Acquisition Parameters
PROBHD 5 mm CPTXI 1H-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 9
DS 2
SWH 12376.237 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 50.8
DW 40.400 usec
DE 6.00 usec
TE 293.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 4.00 dB
SFO1 600.1337060 MHz
F2 - Processing parameters
SI 65536
SF 600.1300189 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
PhO2SN
HO
O
OEt
N
HO
Me
Me
Me
12
12
11
10
9
8
7
6
5
4
3
2
1
ppm

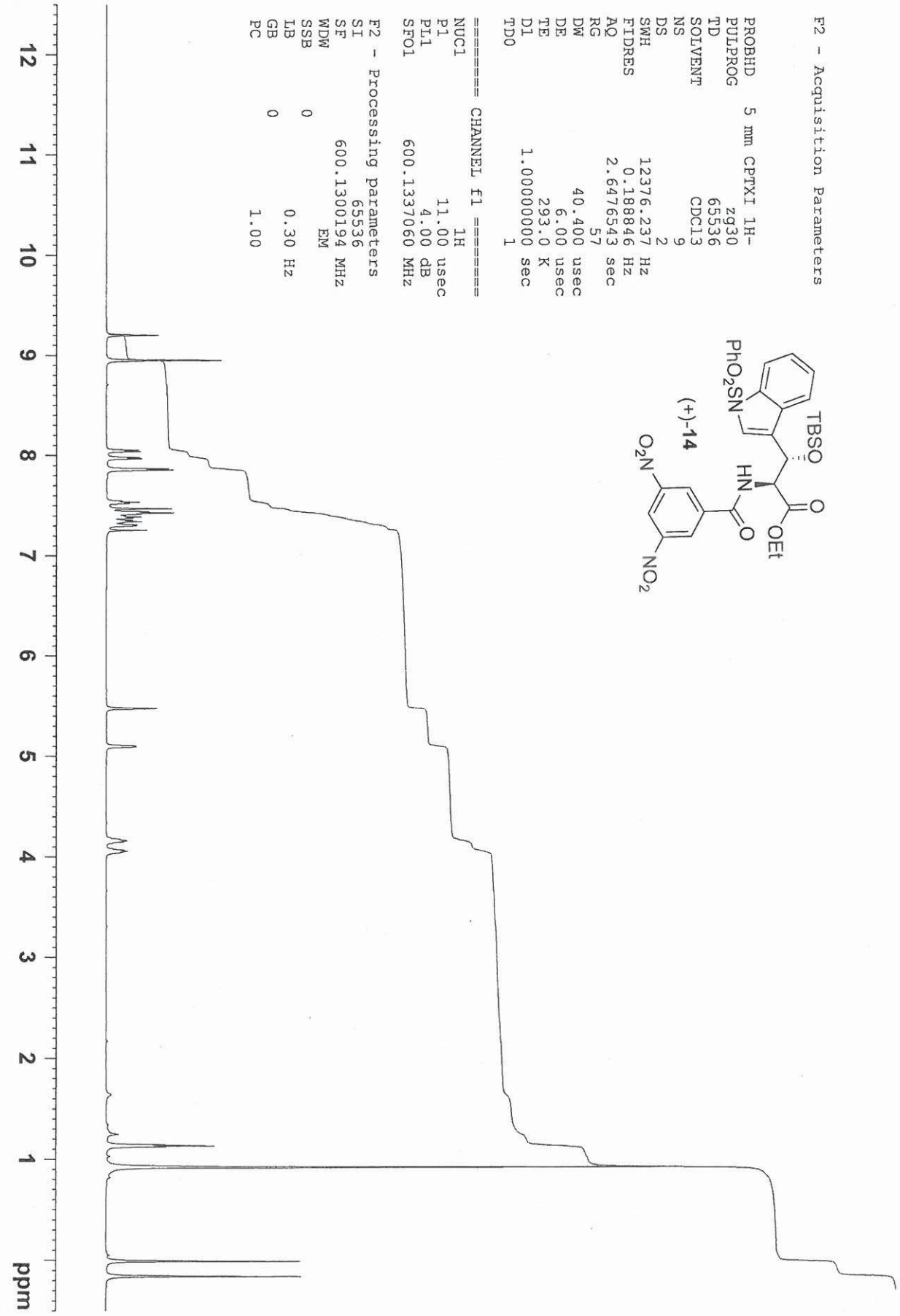

F2 - Acquisition Parameters
PROBHD 5 mm CPTXI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1944
DS 4
SWH 35971.223 Hz
FIDRES 0.548877 Hz
AQ 0.9109504 sec
RG 29193
DW 13.900 usec
DE 6.00 usec
TE 293.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P1 22.20 usec
PLW1 -1.00000000 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W
F2 - Processing parameters
SI 65536
SF 150.9027962 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
12
PhO2SN
HO
O
OEt
N
HO
Me
Me
Me
200
180
160
140
120
100
80
60
40
20
0
ppm

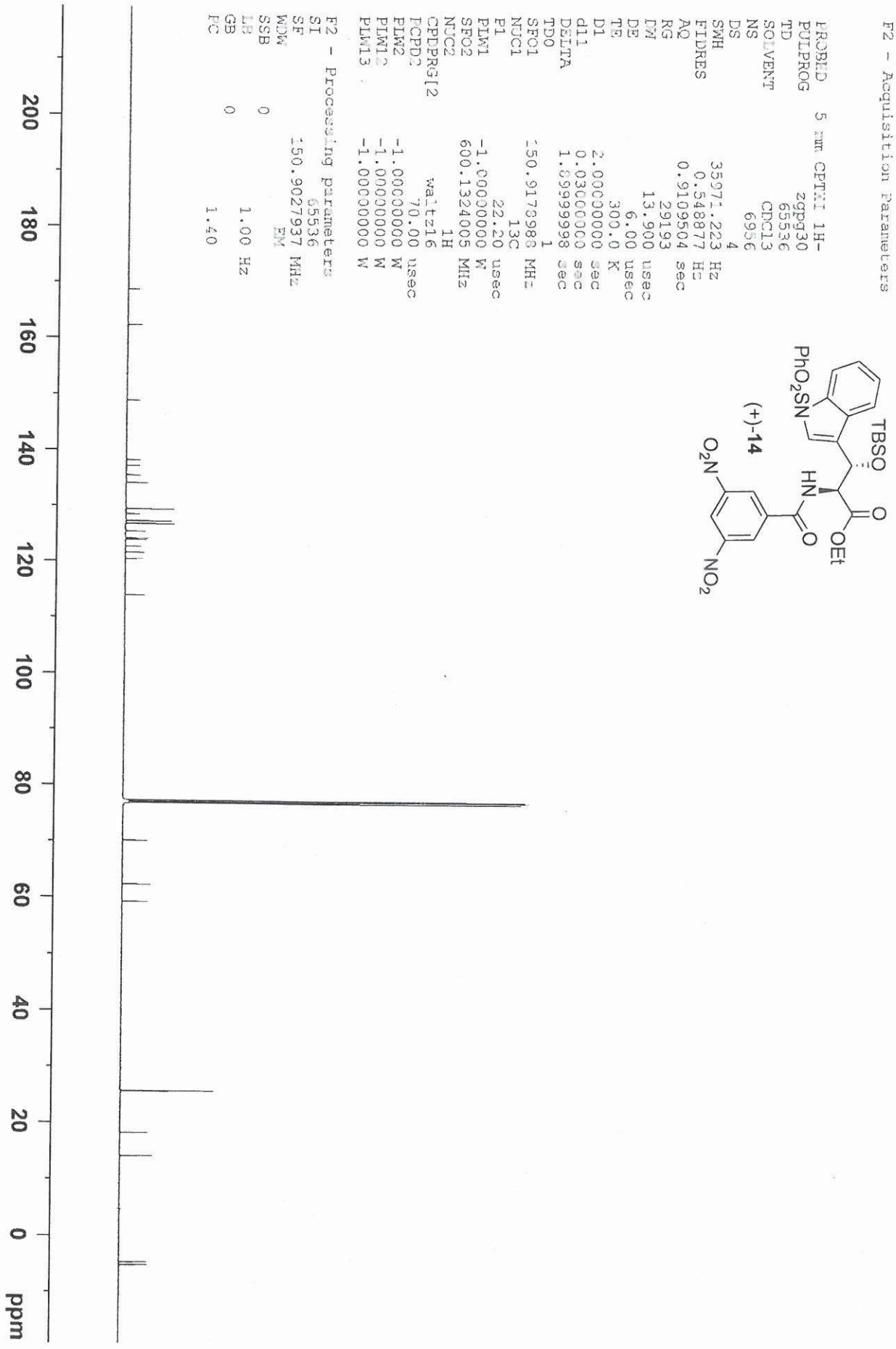

SAMPLE
solvent CDCl3
ACQUISITION
sfrq 500.433
tn H1
at 4.999
np 120102
sw 12012.0
fb not used
bs
tpwr 60
pw 8.0
d1 0.100
tof 3003.2
nt 1000
ct 33
alock wnt
gain n
FLAGS
not used
il n
in n
dp y
hs nn
DISPLAY
sp -250.3
wp 6505.6
vs 9
sc 0
wc 250
hzmm 26.02
is 74.07
rfl 4134.9
rfp 3623.1
th 7
ins 100.000
ai ph
DEC. & VT
dfrq 125.845
dn C13
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 262144
math f
wrr
wexp
wbs
wnt
PhO2SN
TBSO
O
OEt
N
(+)-S1
HO
Me
Me
Me
12
11
10
9
8
7
6
5
4
3
2
1
ppm

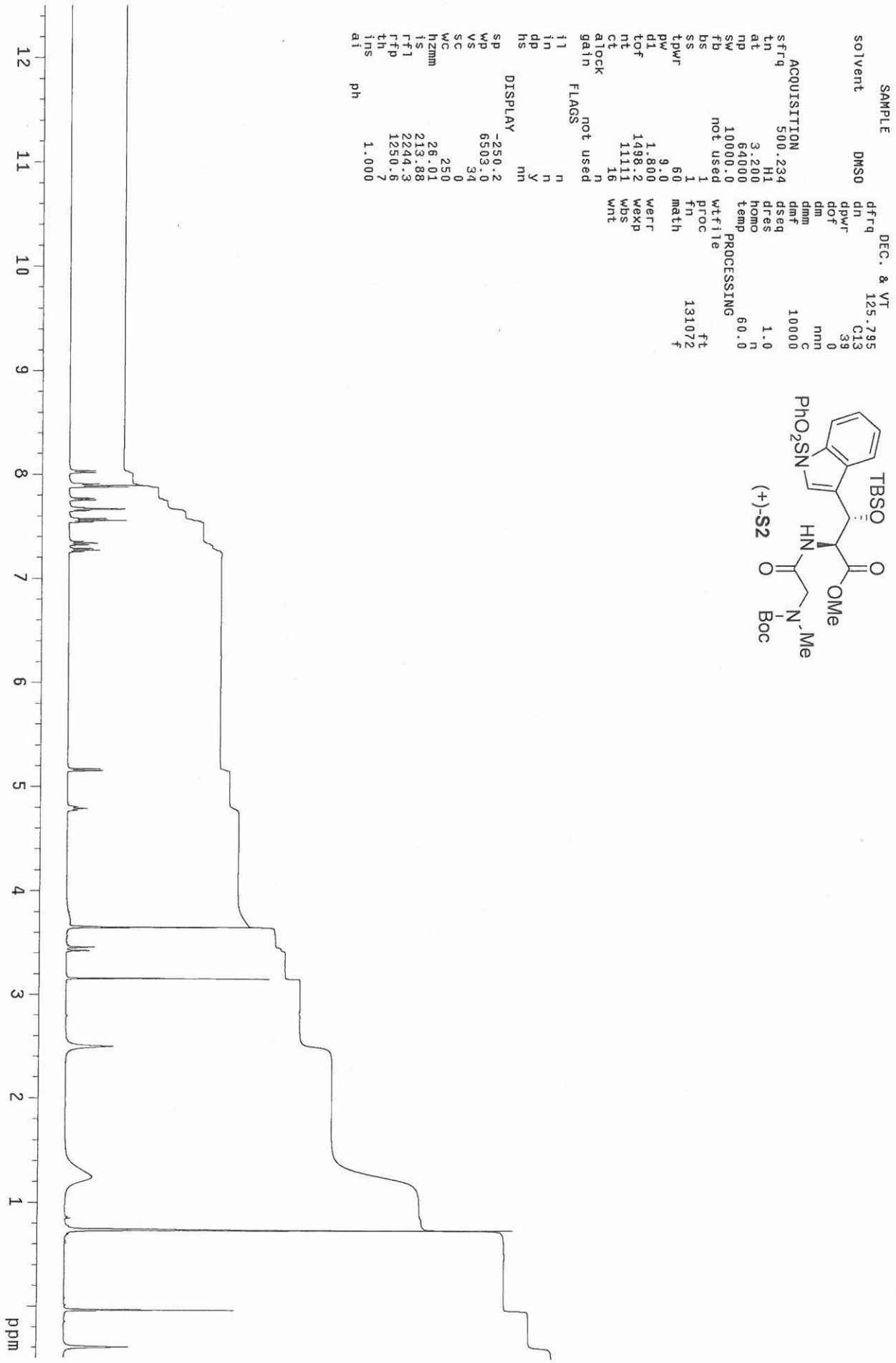

SAMPLE
solvent CDCl3
ACQUISITION
sfrq 125.795
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 58
pw 6.9
d1 0.763
tof 631.4
nt 1e+09
ct 7752
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2516.0
wp 30189.9
vs 2818
sc 0
wc 250
hzmm 120.76
is 500.00
rfl 15911.9
rfp 9686.0
th 20
ins 1.000
ai ph
DEC. & VT
dfrq 500.229
dn H1
dpwr 39
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
wexp
wbs
wnt
PhO2SN
TBSO
O
OEt
N
HO
Me
Me
Me
(+)-S1
200
180
160
140
120
100
80
60
40
20
0
ppm

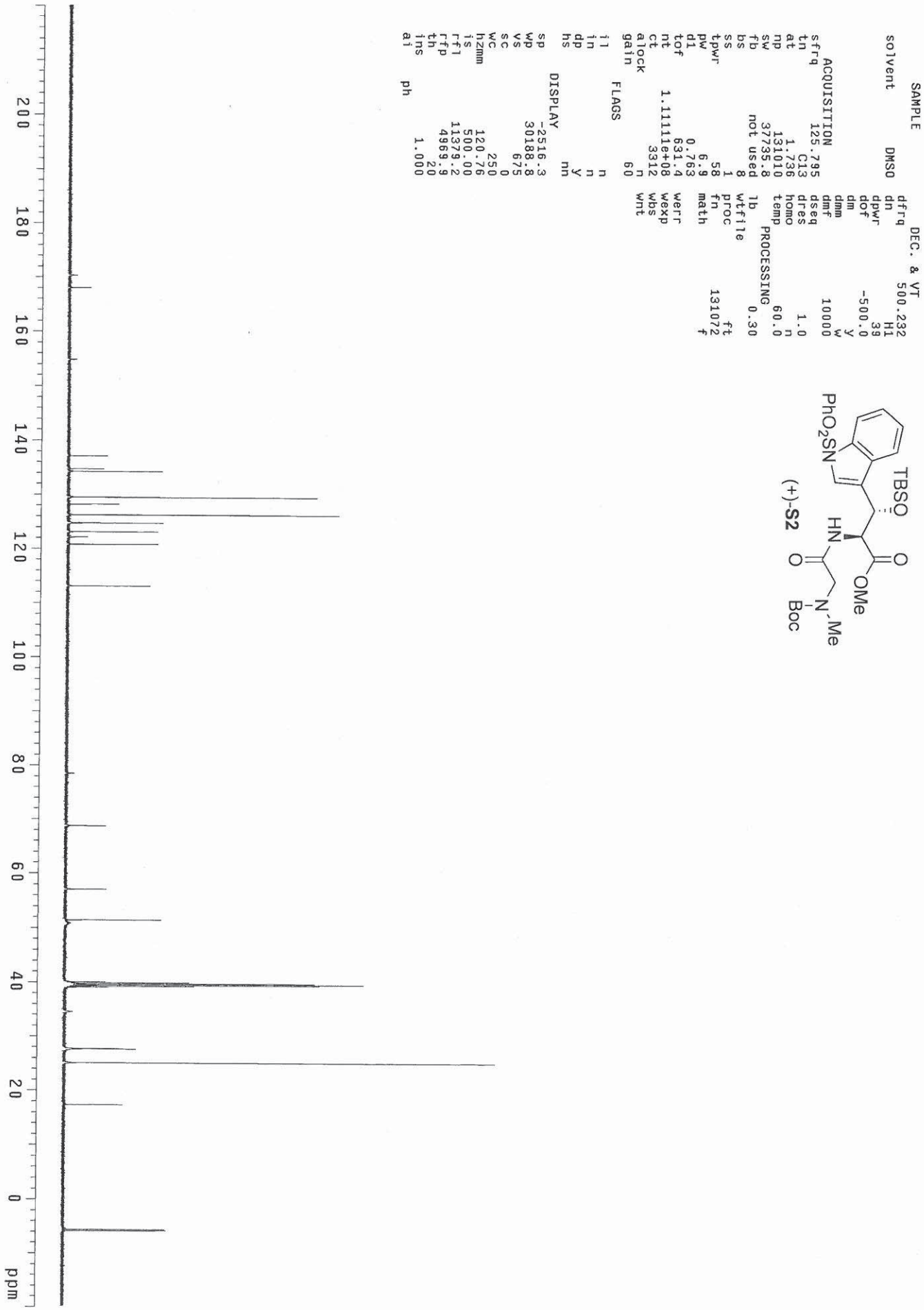

F2 - Acquisition Parameters
PROBHD 5 mm CPTXI 1H-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 9
DS 2
SWH 12376.237 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 71.8
DW 40.400 usec
DE 6.00 usec
TE 293.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 4.00 dB
SFO1 600.1337060 MHz
F2 - Processing parameters
SI 65536
SF 600.1300000 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00
PhO2SN
TBSO
NH2
OEt
(+)-13
12
11
10
9
8
7
6
5
4
3
2
1
ppm

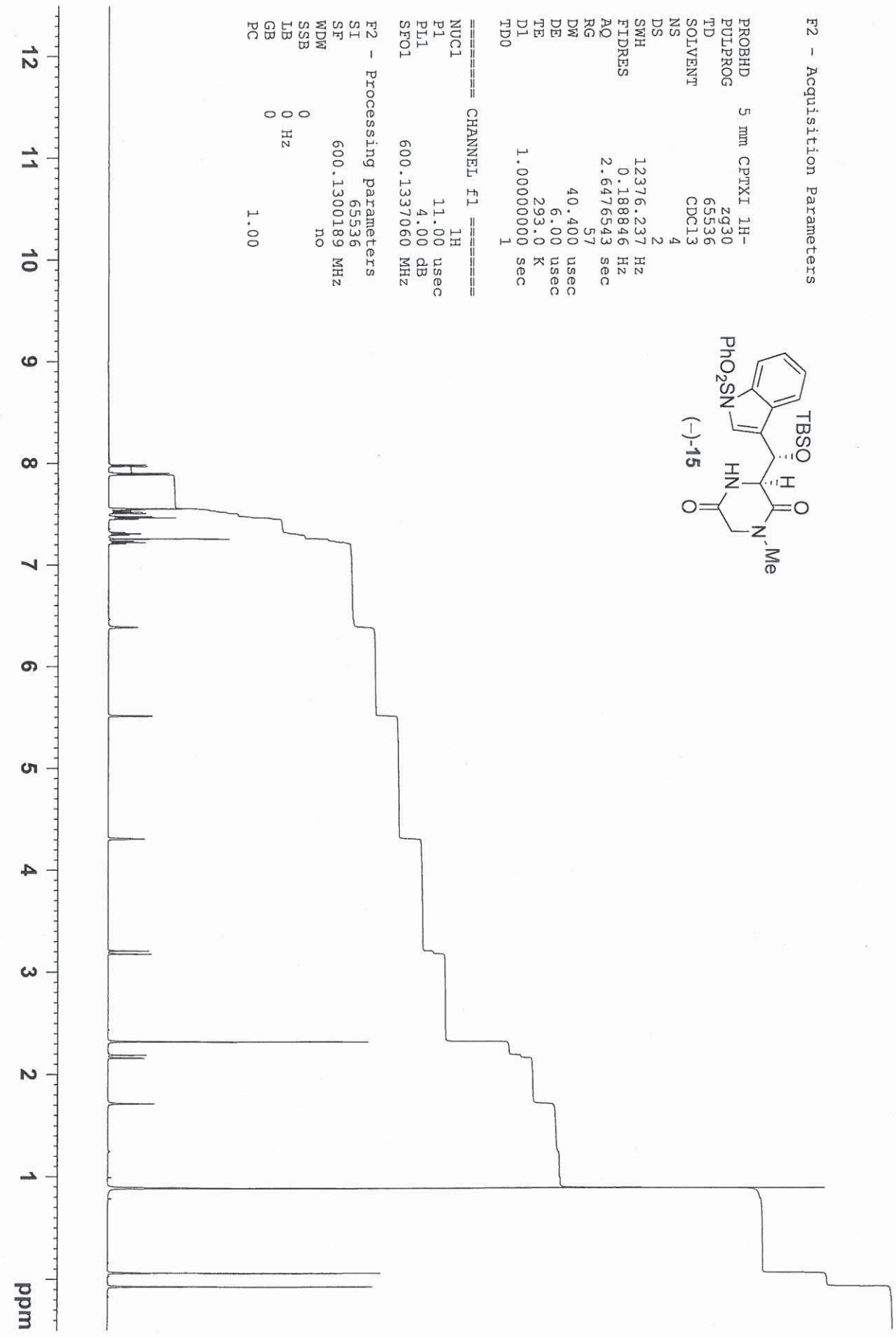

F2 - Acquisition Parameters
PROBHD 5 mm CPTXI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3768
DS 4
SWH 35971.223 Hz
FIDRES 0.548877 Hz
AQ 0.9109504 sec
RG 29193
DW 13.900 usec
DE 6.00 usec
TE 293.0 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999993 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P1 22.20 usec
PLW1 -1.00000000 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W
F2 - Processing parameters
SI 65536
SF 150.9027922 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
TBSO
O
OEt
PhO2SN
NH2
(+)-13
200
180
160
140
120
100
80
60
40
20
0
ppm


F2 - Acquisition Parameters
PROBHD 5 mm CPTXI 1H-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 9
DS 2
SWH 12376.237 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 57
DW 40.400 usec
DE 6.00 usec
TE 293.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 4.00 dB
SFO1 600.1337060 MHz
F2 - Processing parameters
SI 65536
SF 600.1300194 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
(+)-14
TBSO
OEt
HN
PhO2SN
O2N
NO2
12
11
10
9
8
7
6
5
4
3
2
1
ppm


F2 - Acquisition Parameters
PROBHD 5 mm CPTXI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 696
DS 4
SWH 35971.223 Hz
FIDRES 0.548877 Hz
AQ 0.9109504 sec
RG 29193
DW 13.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P1 22.20 usec
PLW1 -1.00000000 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W
F2 - Processing parameters
SI 65536
SF 150.9027937 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
(+)-14
TBSO
PhO2SN
HN
O
OEt
O2N
NO2
200
180
160
140
120
100
80
60
40
20
0
ppm

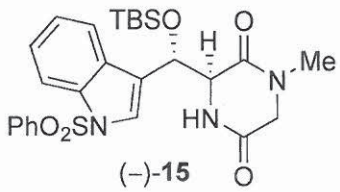

SAMPLE
solvent DMSO
ACQUISITION
sfrq 500.234
tn H1
at 3.200
np 64000
sw 10000.0
fb not used
bs 1
ss 1
tpwr 60
pw 9.0
d1 1.800
tof 1498.2
nt 11111
ct 16
alock wnt
gain n
FLAGS
not used
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 6503.0
vs 34
sc 0
wc 250
hzmm 26.01
is 213.88
rfl 2244.3
rfp 1250.6
th 7
ins 1.000
ai ph
dfrq DEC. & VT
dn C13 125.795
dpwr 39
dof 0
dm nnn
dmm c 10000
dmf
dseq
dres 1.0
homo n
temp 60.0
PROCESSING
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
PhO2SN
TBSO
HN
OMe
N
Me
Boc
(+)-S2
12
11
10
9
8
7
6
5
4
3
2
1
ppm





Concise Total Synthesis of (+)-Bionectins A and C
Alexis Coste, Justin Kim, Timothy C. Adams, and Mohammad Movassaghi*

F2 - Acquisition Parameters

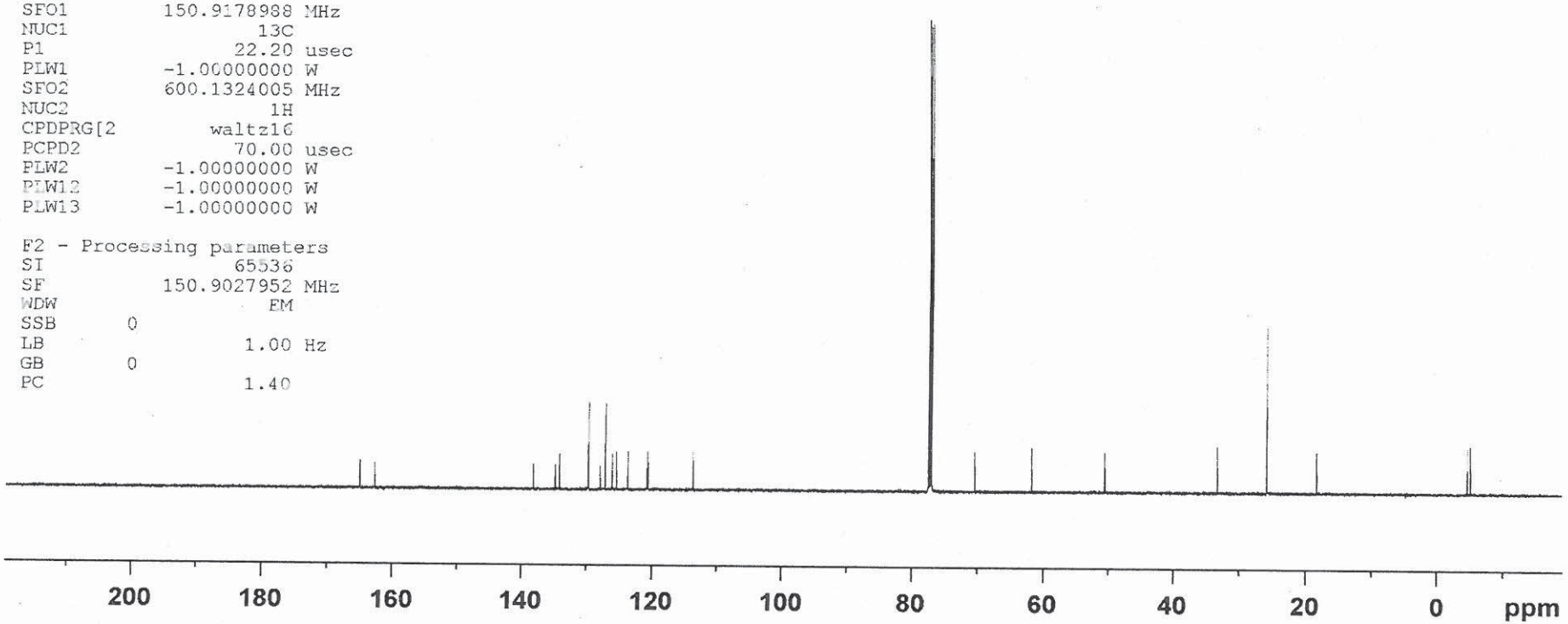


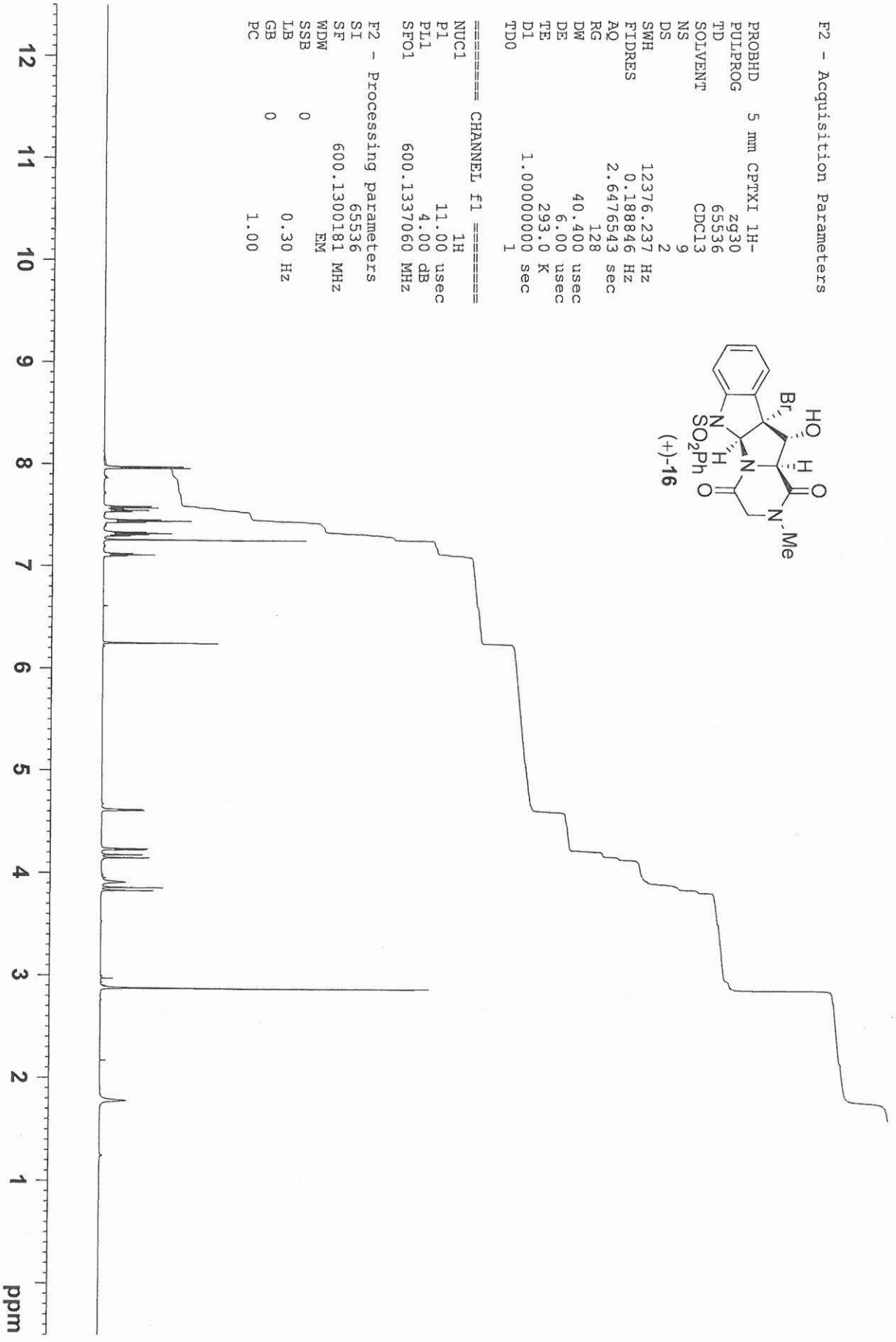
(–)-**15**

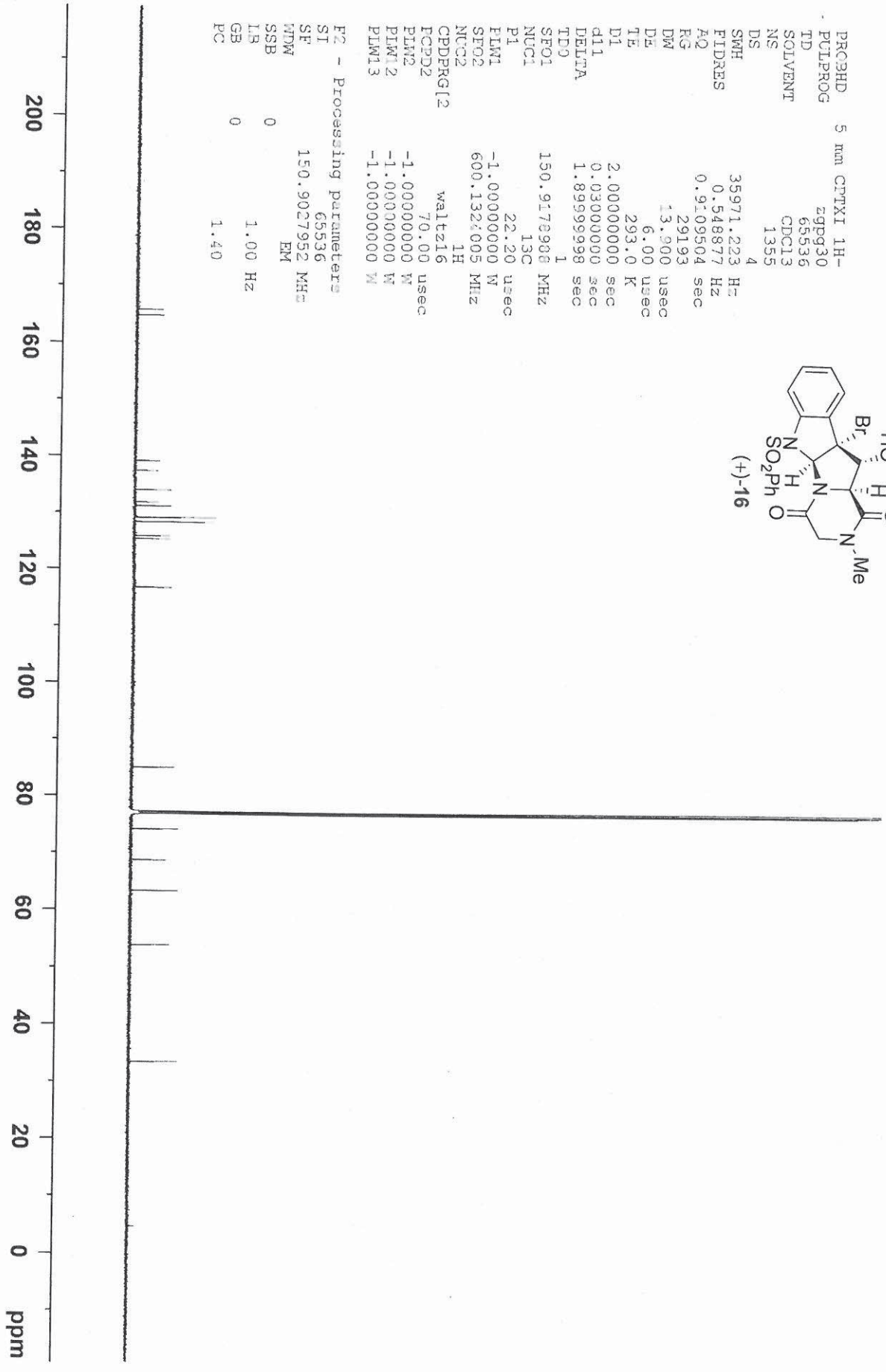
PROBHD	5 mm CPTXI 1H-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	776	
DS	4	
SWH	35971.223	Hz
FIDRES	0.548877	Hz
AQ	0.9109504	sec
RG	29193	
DW	13.900	usec
DE	6.00	usec
TE	293.0	K
D1	2.00000000	sec
d11	0.03000000	sec
DELTA	1.89999998	sec
TD0	1	
SFO1	150.9178988	MHz
NUC1	13C	
P1	22.20	usec
PLW1	-1.00000000	W
SFO2	600.1324005	MHz
NUC2	1H	
CPDPRG[2	waltz16	
PCPD2	70.00	usec
PLW2	-1.00000000	W
PLW12	-1.00000000	W
PLW13	-1.00000000	W

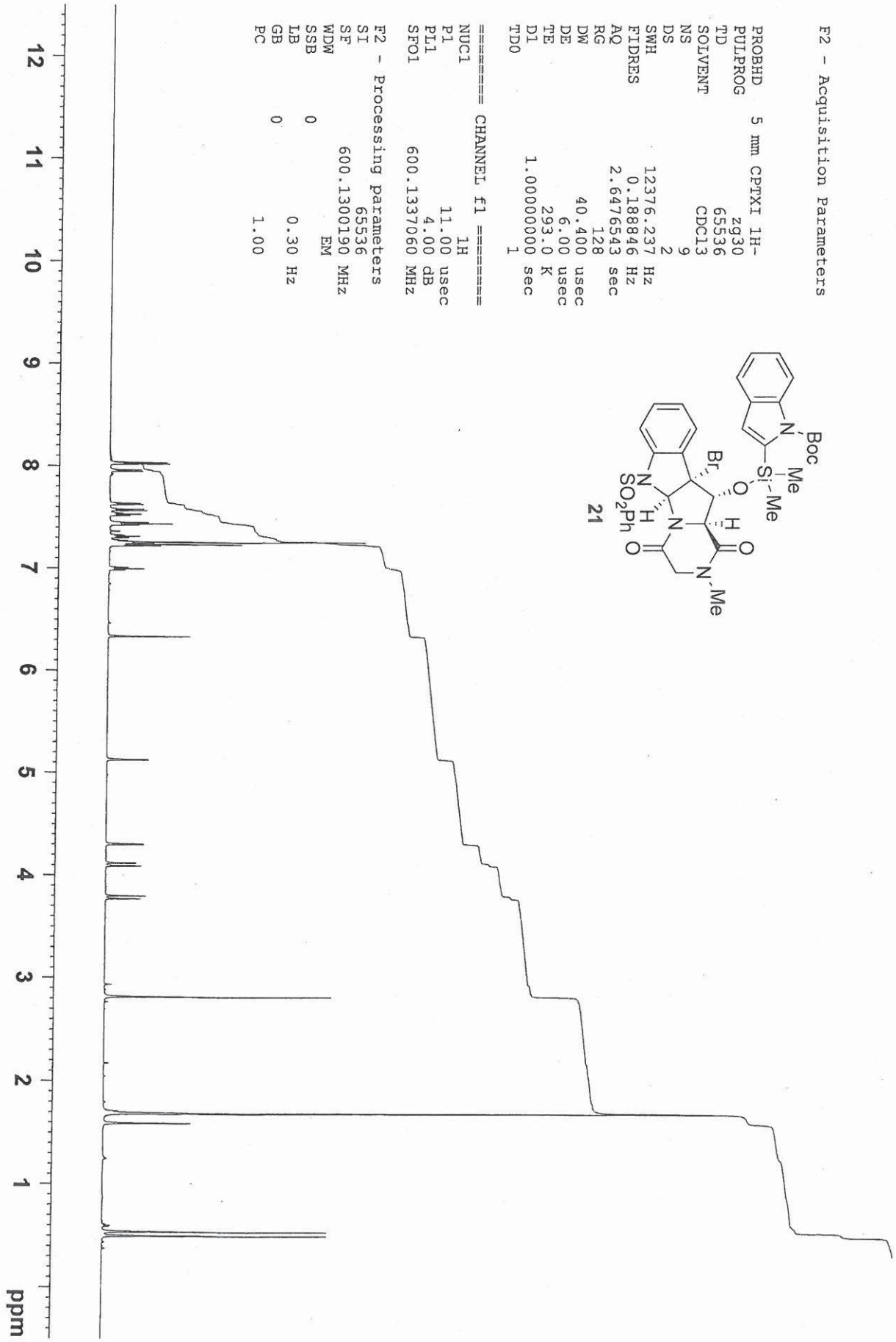
F2 - Processing parameters

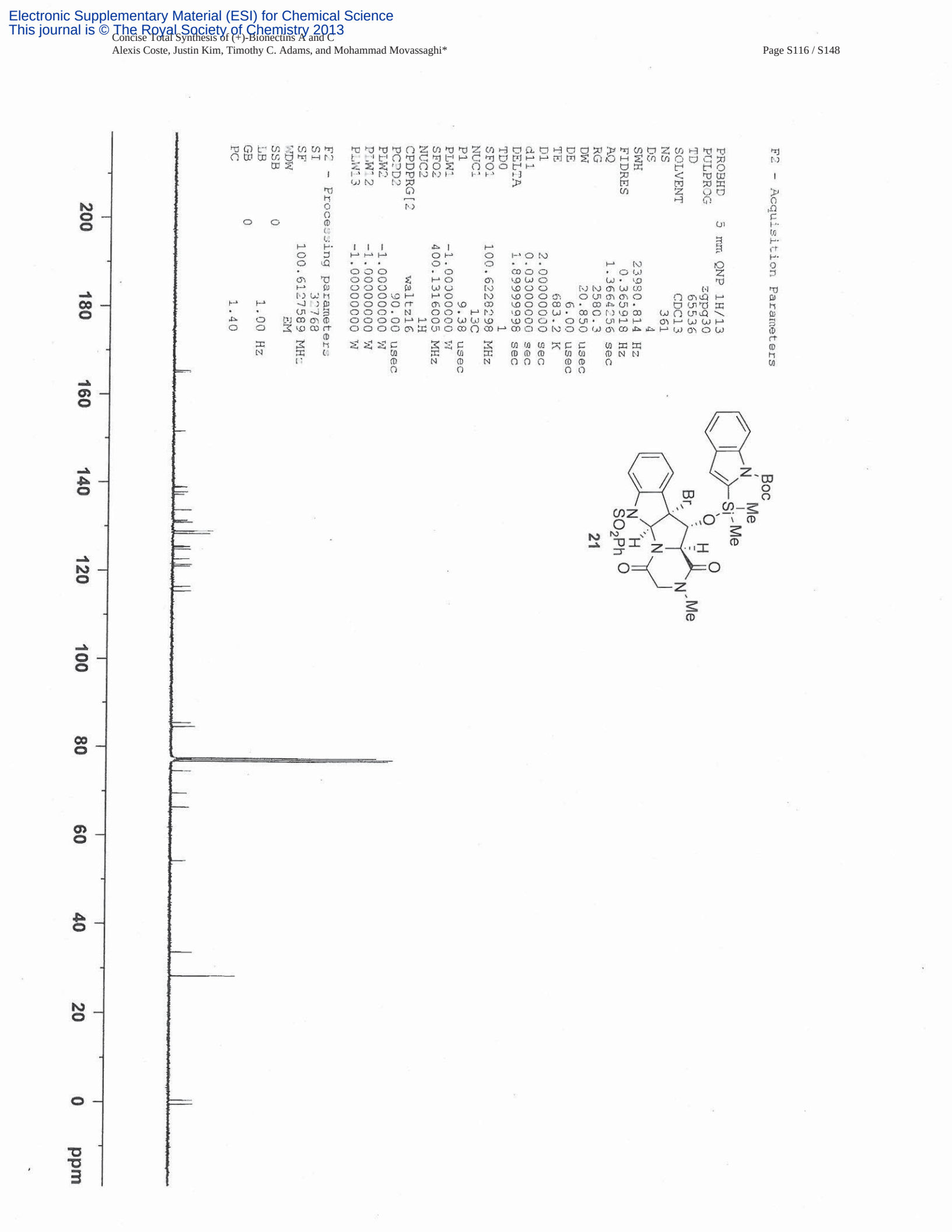
SI	65536	
SF	150.9027952	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	




F2 - Acquisition Parameters
PROBHD 5 mm CPTXI 1H-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 9
DS 2
SWH 12376.237 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 128
DW 40.400 usec
DE 6.00 usec
TE 293.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 4.00 dB
SFO1 600.1337060 MHz
F2 - Processing parameters
SI 65536
SF 600.1300181 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
(+)-16
ppm


F2 - Acquisition Parameters
PRCHD 5 mm CPTXI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1355
DS 4
SWH 35971.223 Hz
FIDRES 0.548877 Hz
AQ 0.910504 sec
RG 29193
DW 13.900 usec
DE 6.00 usec
TE 293.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 150.9178908 MHz
NUC1 13C
P1 22.20 usec
PLW1 -1.00000000 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W
F2 - Processing parameters
SI 65536
SF 150.9027952 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
HO
Br
H
O
N
H
N
SO2Ph
O
N
Me
(+)-16
200
180
160
140
120
100
80
60
40
20
0
ppm


F2 - Acquisition Parameters
PROBHD 5 mm CPTXI 1H-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 9
DS 2
SWH 12376.237 Hz
FIDRES 0.188846 Hz
AQ 2.6476543 sec
RG 128
DW 40.400 usec
DE 6.00 usec
TE 293.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 4.00 dB
SFO1 600.1337060 MHz
F2 - Processing parameters
SI 65536
SF 600.1300190 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Boc
Me
Si
Me
Br
O
H
N
H
SO2Ph
O
N
Me
21
12
11
10
9
8
7
6
5
4
3
2
1
ppm


F2 - Acquisition Parameters
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 361
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 2580.3
DW 20.850 usec
DE 6.00 usec
TE 683.2 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999936 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 9.38 usec
PLW1 -1.00000000 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W
F2 - Processing parameters
SI 32768
SF 100.6127589 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Boc
N
Me
Si
Me
Br
O
H
N
O
N
H
SO2Ph
O
N
Me
21
200
180
160
140
120
100
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60
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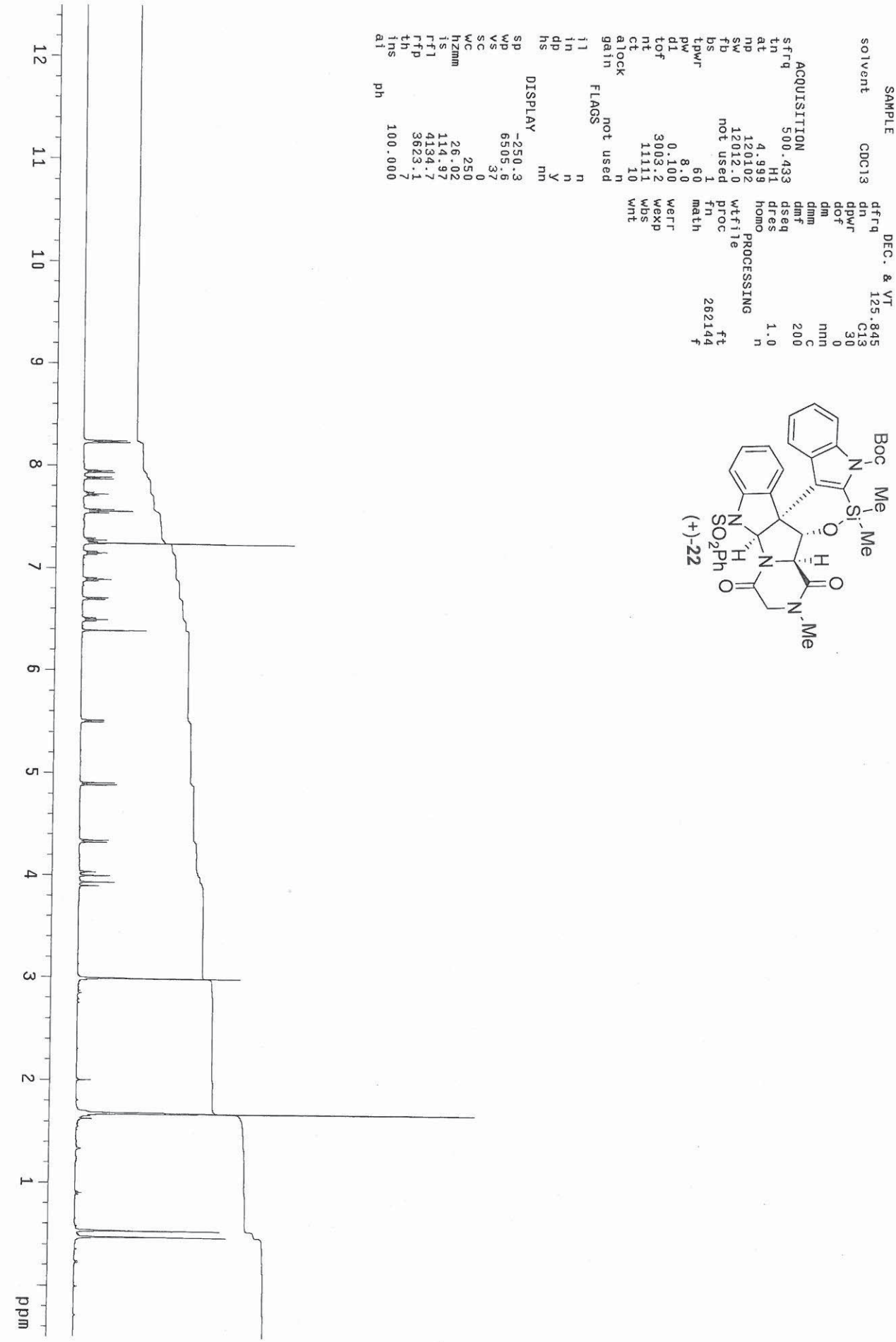
20
0
ppm


SAMPLE
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ACQUISITION
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at 4.999
np 120102
sw 12012.0
fb not used
bs 1
tpwr 60
pw 8.0
d1 0.100
tof 3003.2
nt 11111
ct 10
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.3
wp 6505.6
vs 37
sc 0
wc 250
hzmm 26.02
is 114.97
rfl 4134.7
rfp 3623.1
th 7
ins 100.000
ai ph
DEC. & VT
dfrq 125.845
dn C13
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc
fn 262144
math f
wexp
wbs
wnt
Boc
Me
Si
Me
N
O
H
N
N
SO2Ph
O
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N
Me
(+)-22
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11
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7
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5
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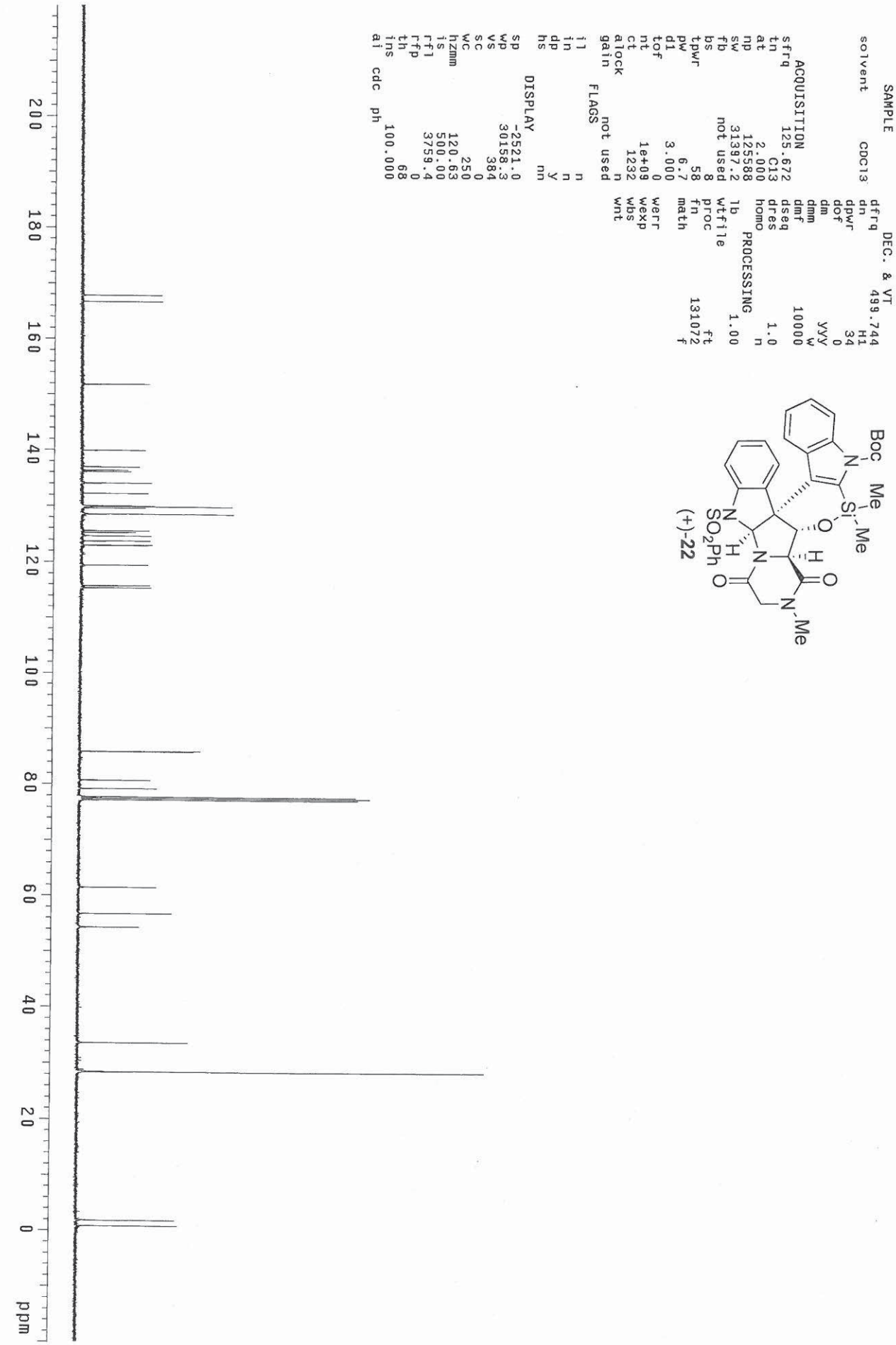
3
2
1
ppm


SAMPLE
solvent CDCl3
ACQUISITION
sfrq 125.672
tn C13
at 2.000
np 125588
sw 31397.2
fb not used
bs 8
tpwr 58
pw 6.7
d1 3.000
tof 0
nt 1e+09
ct 1232
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2521.0
wp 30158.3
vs 384
sc 0
wc 250
hzmm 120.63
is 500.00
rfl 3759.4
rfp 0
th 68
ins 100.000
ai cdc ph
dfrq
dn
dpwr
dof
dm
dmm
dmf
dseq
dres
homo
PROCESSING
lb
wtfile
proc
fn
math
werr
wexp
wbs
wnt
DEC. & VT
499.744
H1
34
0
yyy
w
10000
1.0
n
1.00
ft
131072
f
Boc
Me
Si
Me
N
O
H
O
N
H
SO2Ph
O
N
Me
(+)-22
200
180
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120
100
80
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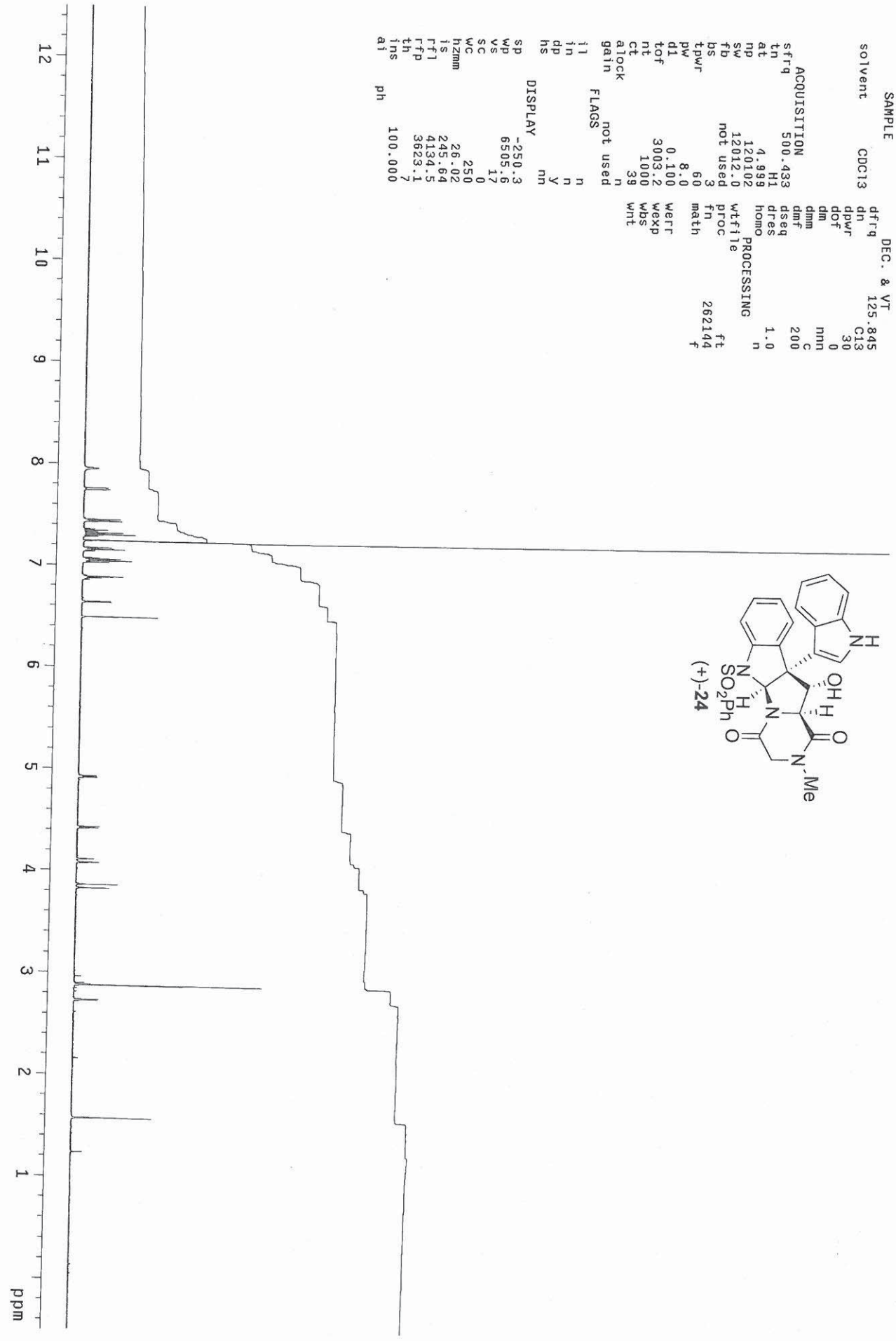
40
20
0
ppm


SAMPLE
solvent CDCl3
ACQUISITION
sfrq 500.433
tn H1
at 4.999
np 120102
sw 12012.0
fb not used
bs 3
tpwr 60
pw 8.0
d1 0.100
tof 3003.2
nt 1000
ct 39
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.3
wp 6505.6
vs 17
sc 0
wc 250
hzmm 26.02
is 245.64
rfl 4134.5
rfp 3623.1
th 7
ins 100.000
ai ph
dfrq DEC. & VT
dn 125.845
dpwr C13
dof 30
dm 0
dmm nnn
dmf c
dseq 200
dres
homo 1.0
n
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt
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10
9
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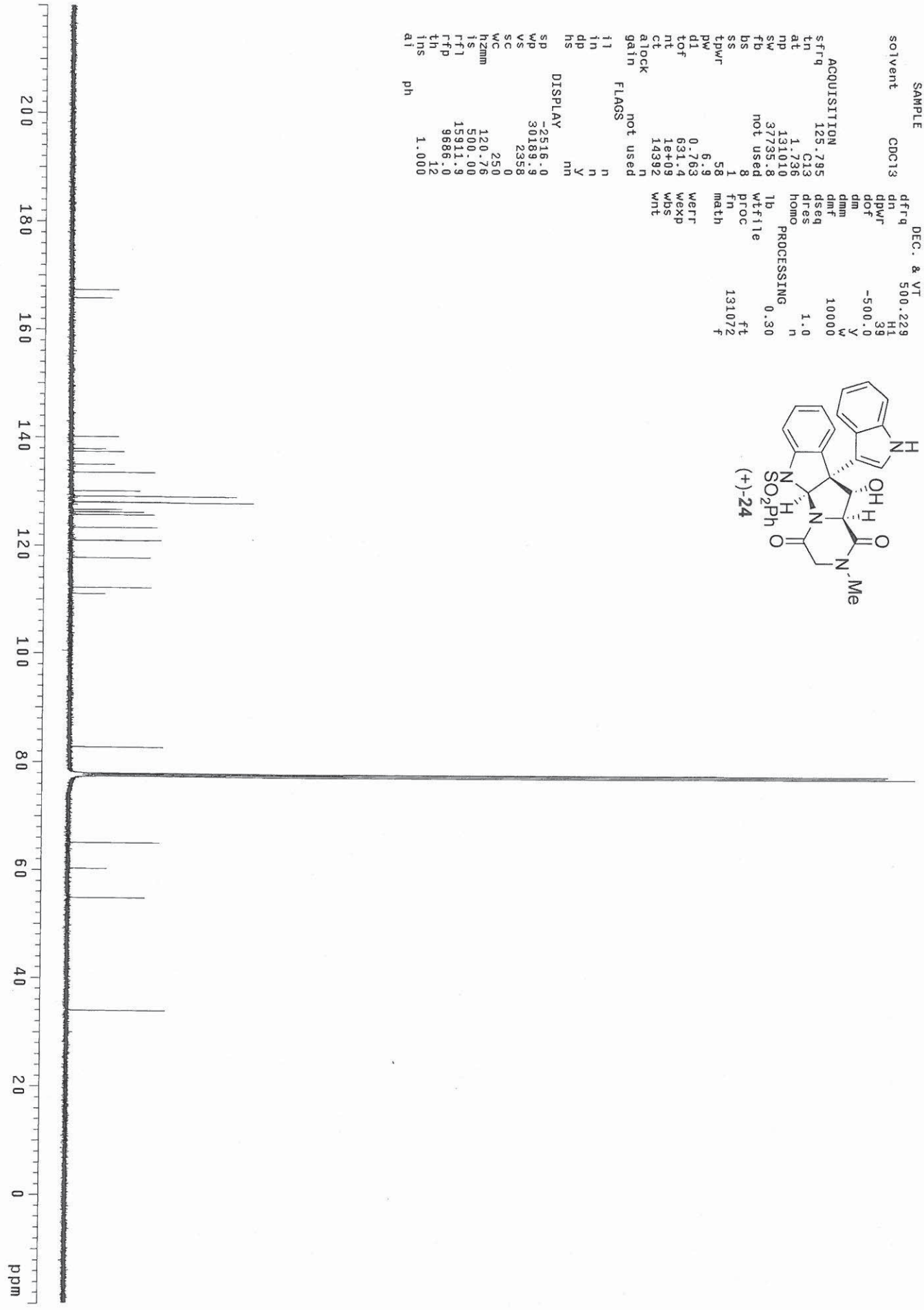
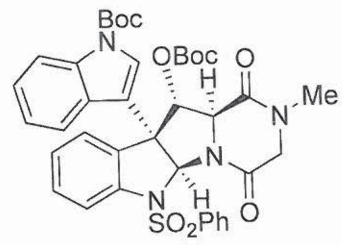
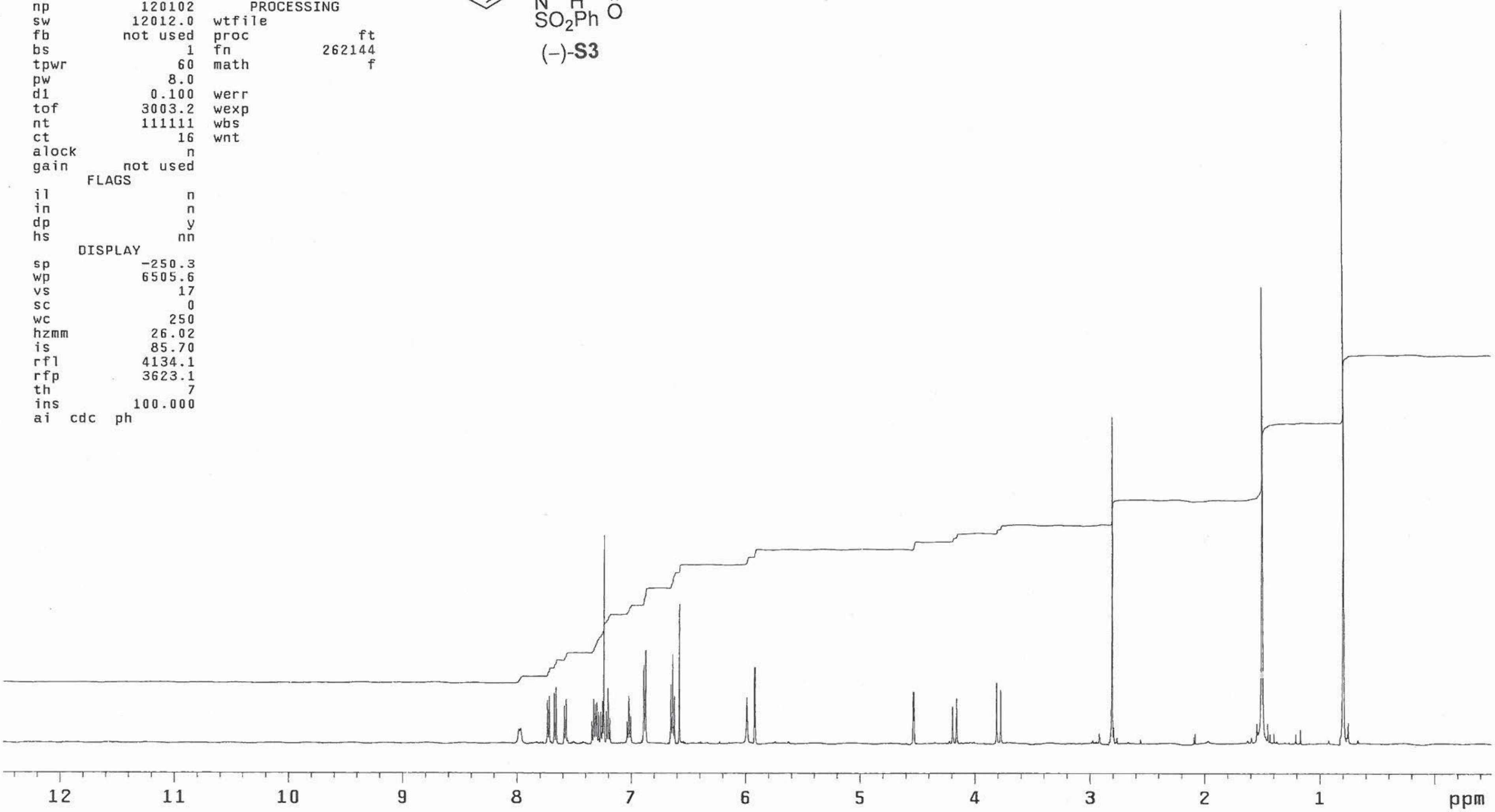
5
4
3
2
1
ppm
(+)-24

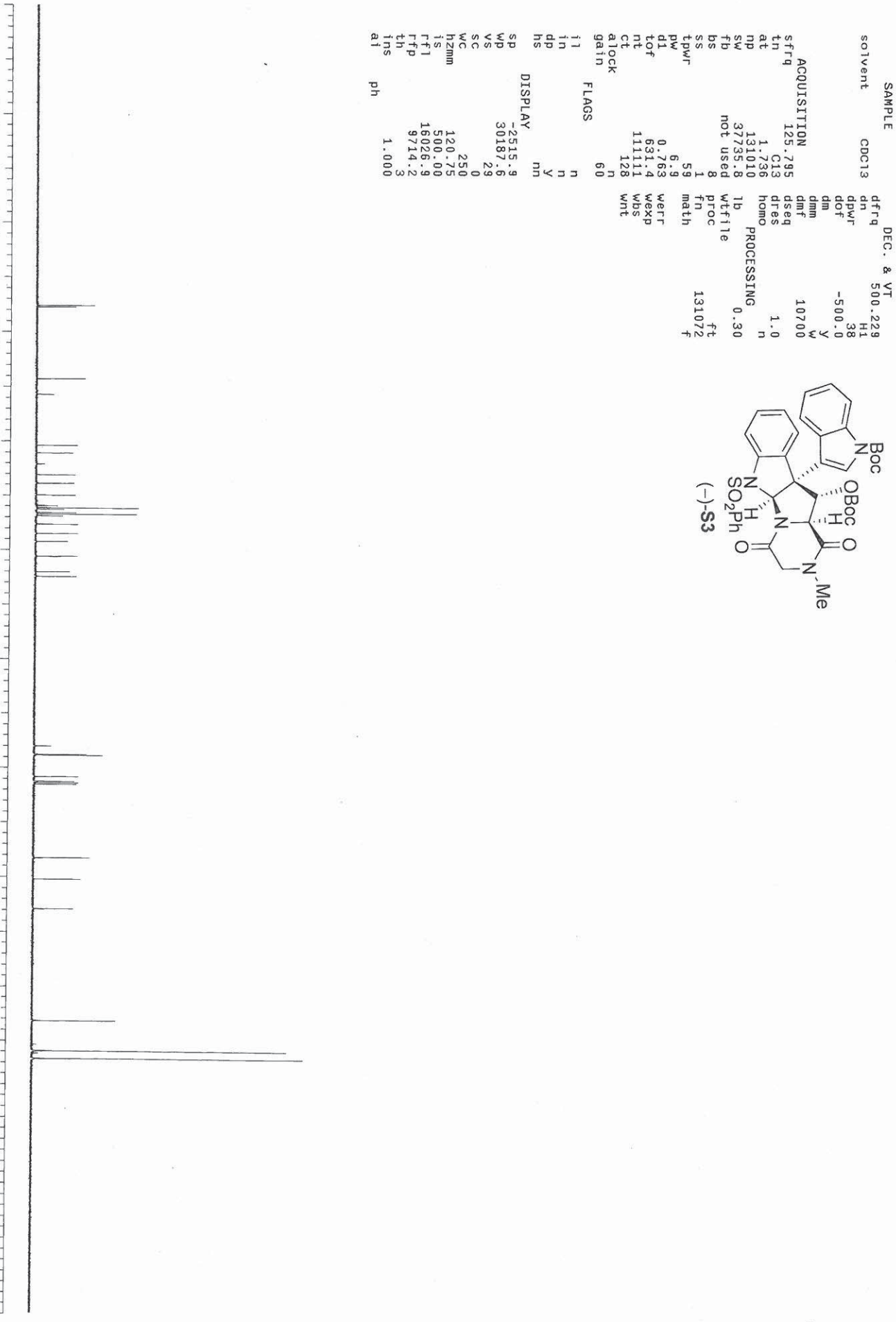

SAMPLE
solvent CDCl3
ACQUISITION
sfrq 125.795
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs
ss 1
tpwr 58
pw 6.9
d1 0.763
tof 631.4
nt 1e+09
ct 14392
alock wnt
gain n
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2516.0
wp 30189.9
vs 2358
sc 0
wc 250
hzmm 120.76
is 500.00
rfl 15911.9
rfp 9686.0
th 12
ins 1.000
ai
ph
DEC. & VT
dfrq 500.229
dn H1
dpwr 39
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
(+)-24
200
180
160
140
120
100
80
60
40
20
0
ppm

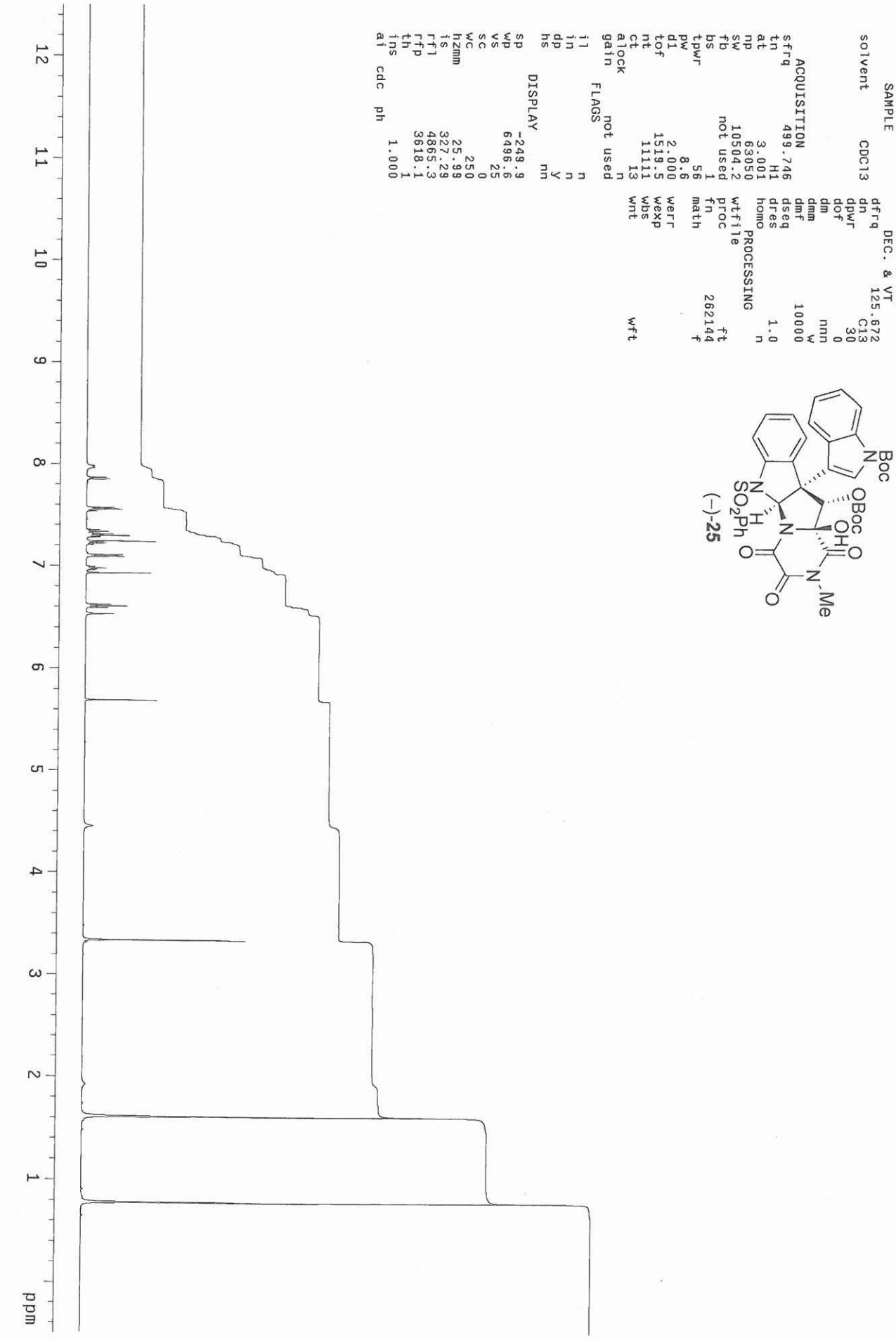
SAMPLE		DEC. & VT	
solvent	CDCl3	dfrq	125.845
		dn	C13
		dpwr	30
		dof	0
		dm	nnn
		dmm	c
ACQUISITION		dmf	200
sfrq	500.433	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	1	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	111111	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.3		
wp	6505.6		
vs	17		
sc	0		
wc	250		
hzmm	26.02		
is	85.70		
rfl	4134.1		
rfp	3623.1		
th	7		
ins	100.000		
ai cdc ph			

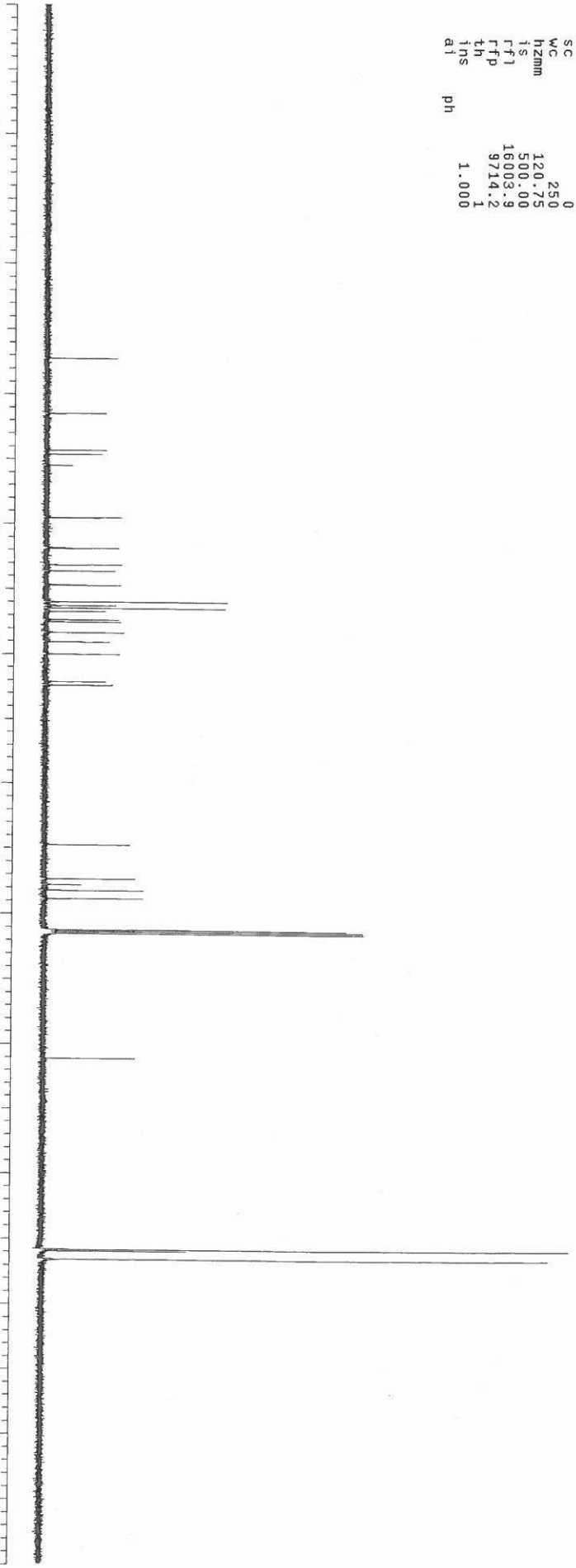


(−)-**S3**

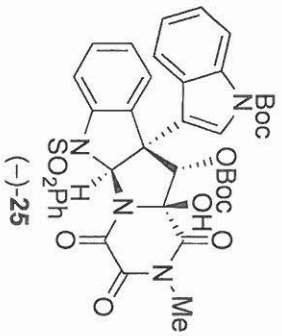



SAMPLE
solvent CDCl3
ACQUISITION
sfrq 125.795
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 59
pw 6.9
d1 0.763
tof 631.4
nt 111111
ct 128
alock wnt
gain n
60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2515.9
wp 30187.6
vs 29
sc 0
wc 250
hzmm 120.75
is 500.00
rfl 16026.9
rfp 9714.2
th 3
ins 1.000
al ph
dfrq DEC. & VT
dn 500.229
H1
dpwr 38
dof -500.0
dm y
dmm y
dmf 10700
dseq w
dres
homo 1.0
n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Boc
N
OBoc
H
O
N
N
H
SO2Ph
O
N
Me
(−)-S3
200
180
160
140
120
100
80
60
40
20
0
ppm

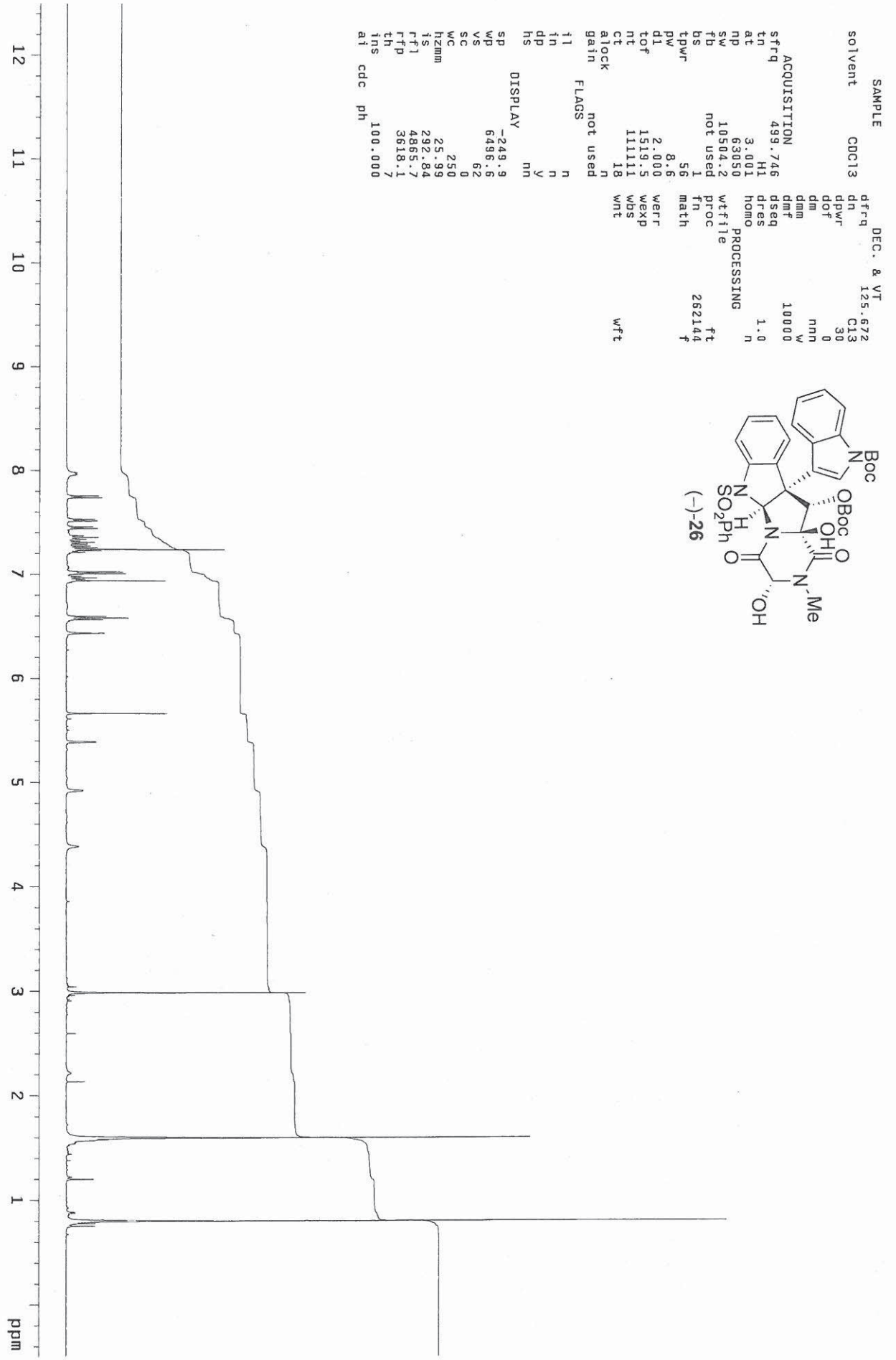


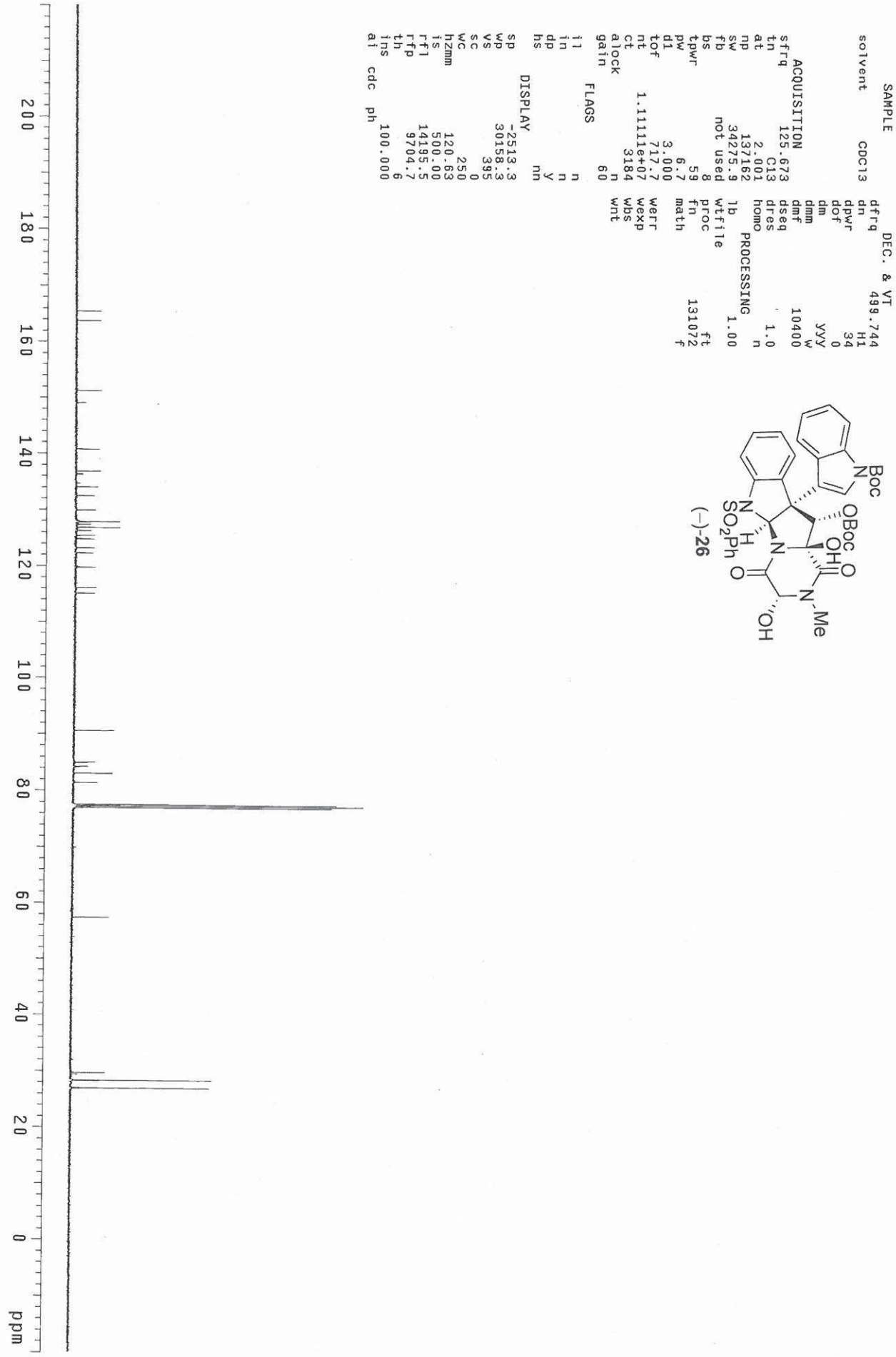



```
SAMPLE
solvent      CDC13
ACQUISITION
sfrq       125.795
tn             C13
at           1.736
np          131010
sw        37735.8
fb       not used
bs              8
ss              1
tpwr           59
pw            6.9
d1          0.763
tof         631.4
nt      1.11111e+07
ct             1784
alock             n
gain             60
FLAGS
il                n
in                n
dp                y
hs               nn
DISPLAY
sp          -2515.9
wp          30187.6
vs              315
sc                0
wc              250
hzmm         120.75
is           500.00
rfl         16003.9
rfp          9714.2
th                1
ins               1
ai            1.000
ph
DEC. & VT
dfrq       500.229
dn              H1
dpwr            38
dof          -500.0
dm                y
dmm               w
dmf           10700
dseq
dres            1.0
homo              n
PROCESSING
lb             0.30
wtfile
proc             ft
fn           131072
math              f
wexp
wbs
wnt
```



(−)-**25**

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ACQUISITION
sfrq 125.673
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at 2.001
np 137162
sw 34275.9
fb not used
bs 8
tpwr 59
pw 6.7
d1 3.000
tof 717.7
nt 1.11111e+07
ct 3184
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2513.3
wp 30158.3
vs 395
sc 0
wc 250
hzmm 120.63
is 500.00
rfl 14195.5
rfp 9704.7
th 6
ins 6
ai cdc ph 100.000
dfrq DEC. & VT
dn 499.744
dpwr H1
dof 34
dm 0
dmm yyy
dmf w
dseq 10400
dres 1.0
homo n
PROCESSING
lb 1.00
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Boc
N
OBoc
O
OH
N
N
H
SO2Ph
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N
Me
OH
(−)-26
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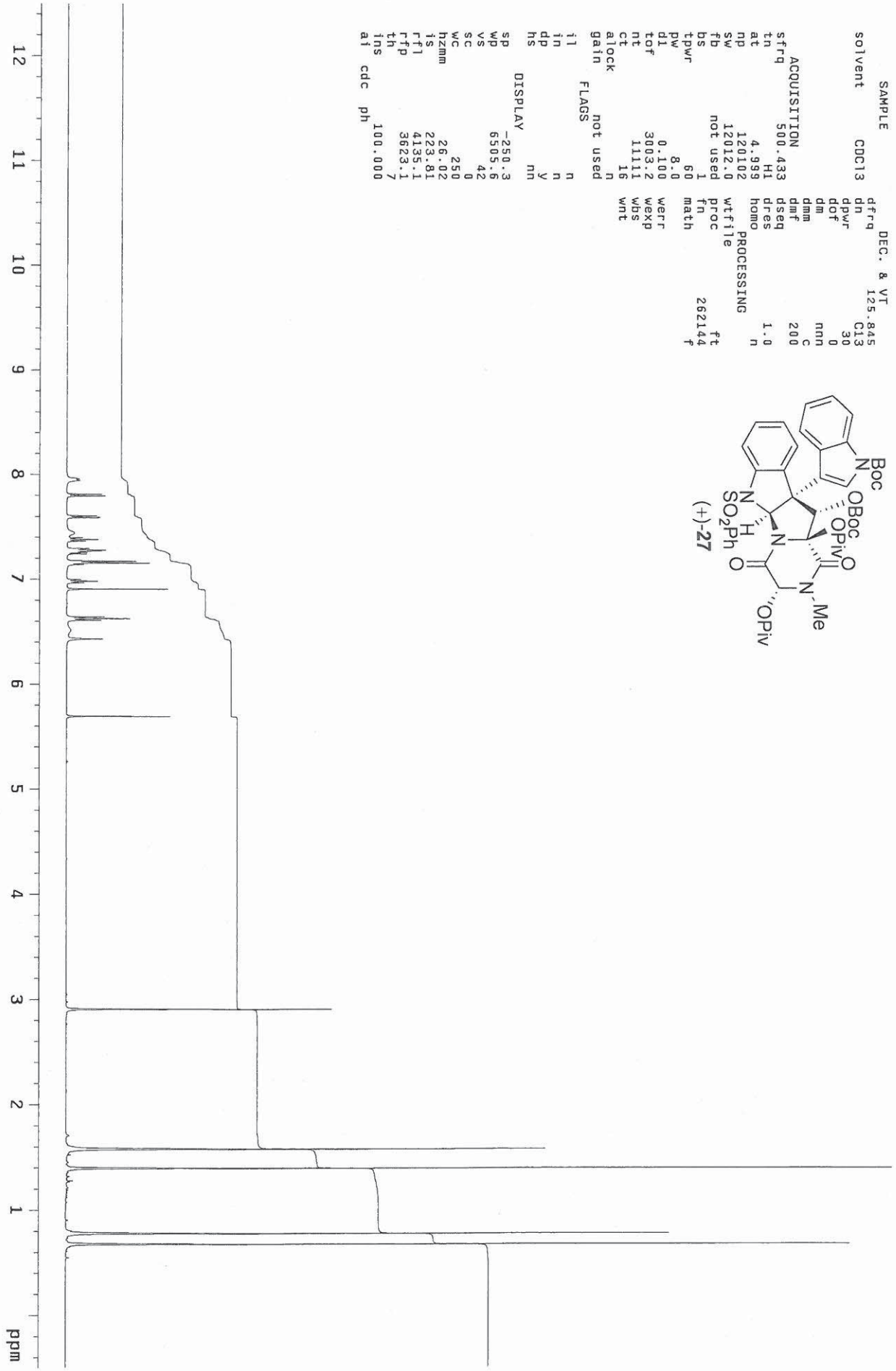
0
ppm


SAMPLE
solvent CDCl3
ACQUISITION
sfrq 500.433
tn H1
at 4.999
np 120102
sw 12012.0
fb not used
bs 1
tpwr 60
pw 8.0
d1 0.100
tof 3003.2
nt 11111
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.3
wp 6505.6
vs 42
sc 0
wc 250
hzmm 26.02
is 223.81
rfl 4135.1
rfp 3623.1
th 7
ins 100.000
ai cdc ph
dfrq
dn C13
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc
ft
fn 262144
math f
werr
wexp
wbs
wnt
DEC. & VT
125.845
Boc
OBoc
OPiv
N
N
H
SO2Ph
O
N
Me
OPiv
(+)-27
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7
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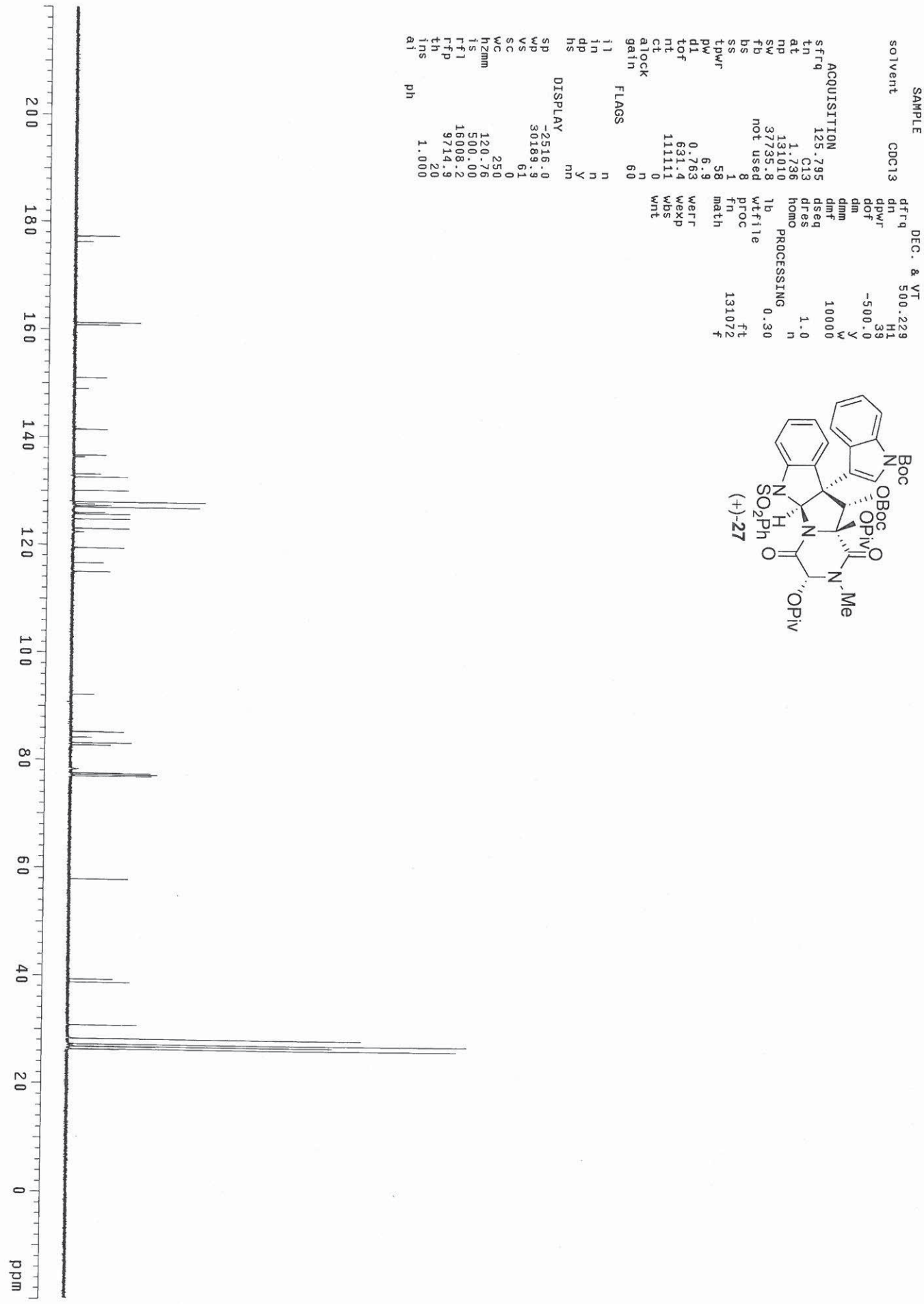
5
4
3
2
1
ppm


SAMPLE
solvent CDCl3
ACQUISITION
sfrq 125.795
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 58
pw 6.9
d1 0.763
tof 631.4
nt 111111
ct 0
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2516.0
wp 30189.9
vs 61
sc 0
wc 250
hzmm 120.76
is 500.00
rfl 16008.2
rfp 9714.9
th 20
ins 1.000
ai ph
dfrq
dn
dpwr
dof
dm
dmm
dmf
dseq
dres
homo
PROCESSING
lb
wtfile
proc
fn
math
werr
wexp
wbs
wnt
DEC. & VT
500.229
H1
39
-500.0
y
w
10000
1.0
n
0.30
ft
131072
f
Boc
N
OBoc
OPiv
O
N
H
SO2Ph
O
N
N
Me
OPiv
(+)-27
200
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120
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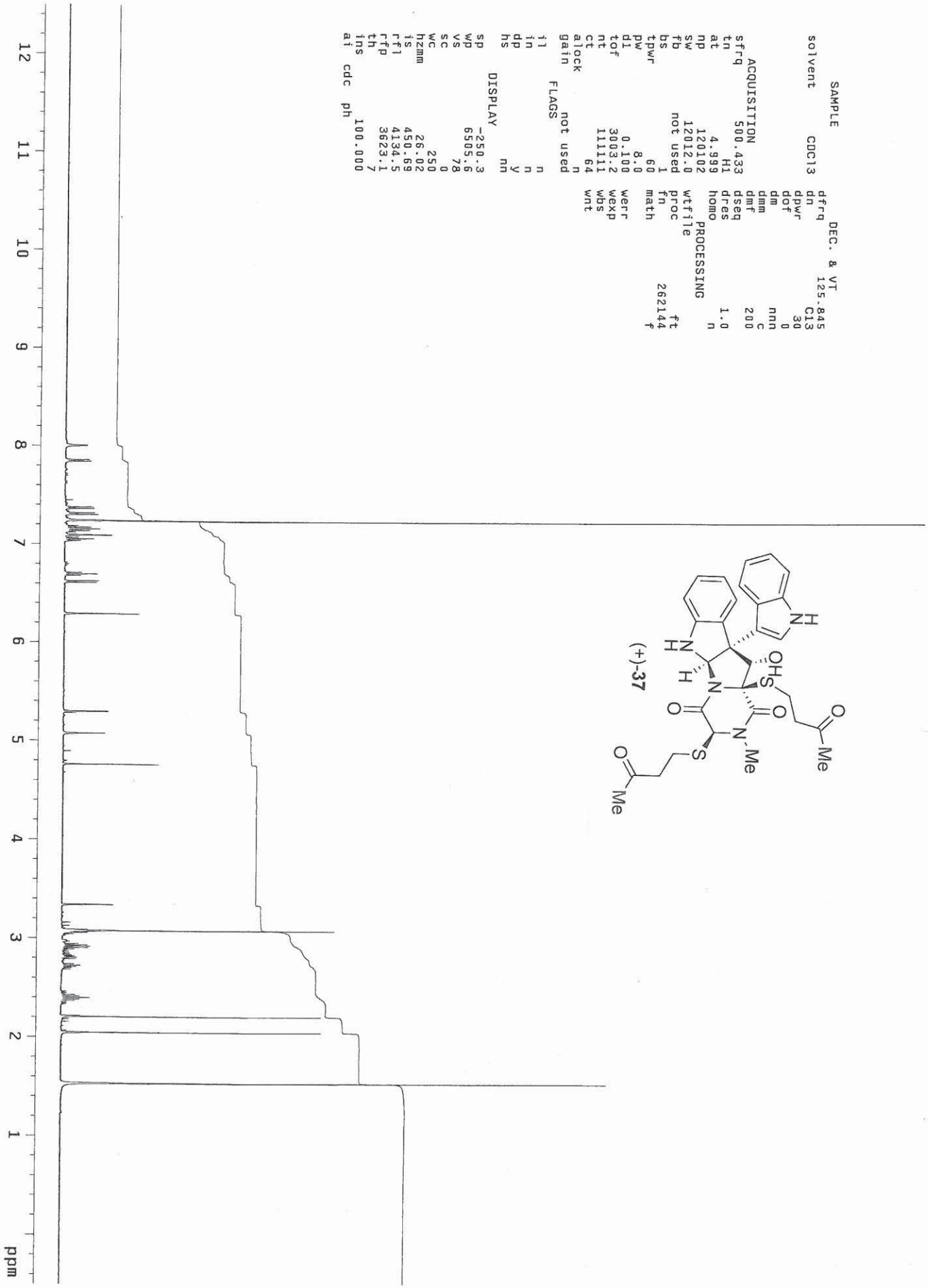
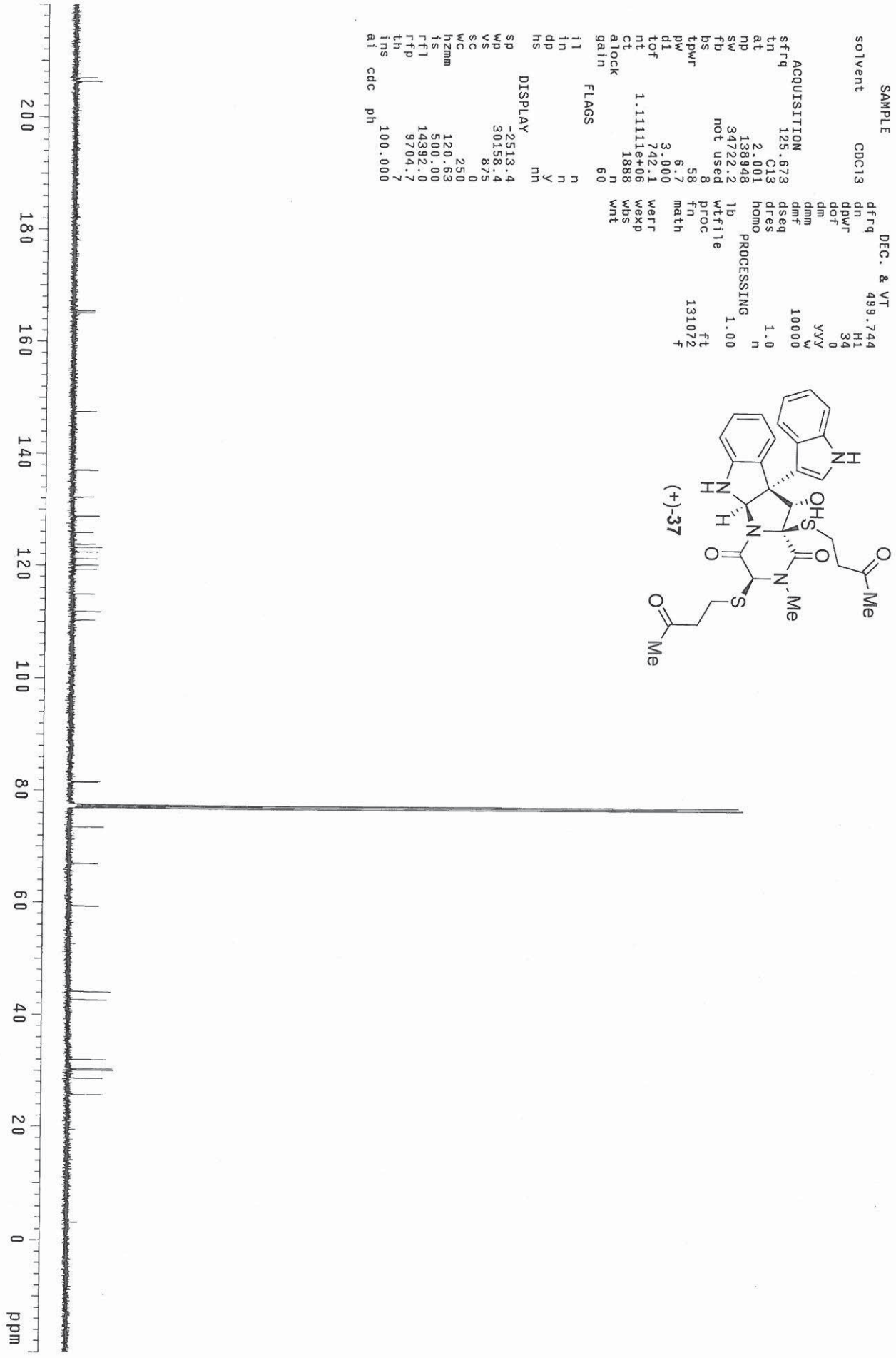
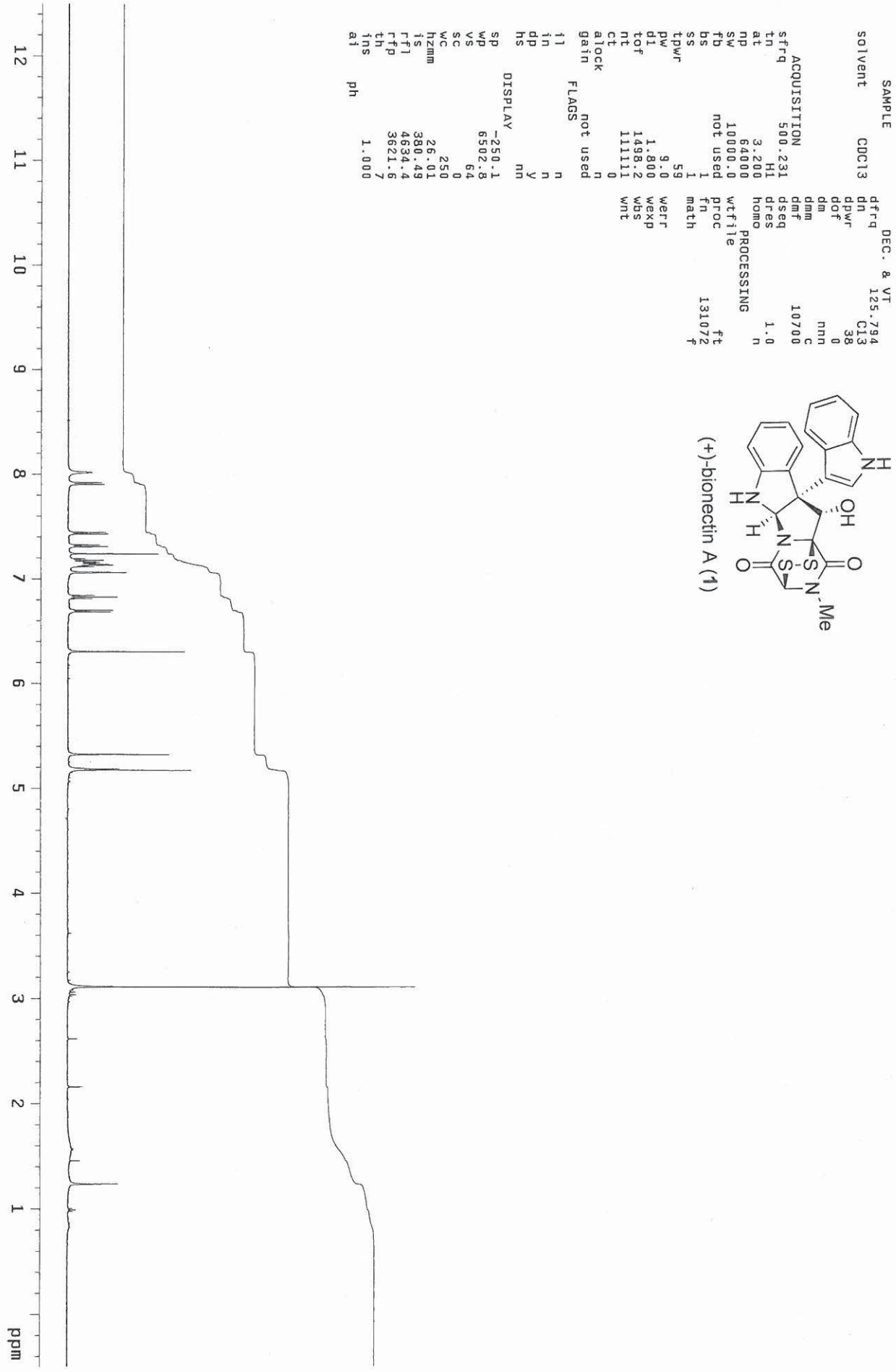
20
0
ppm


SAMPLE
solvent CDCl3
ACQUISITION
sfrq 500.433
tn H1
at 4.999
np 120102
sw 12012.0
fb not used
bs 1
tpwr 60
pw 8.0
d1 0.100
tof 3003.2
nt 111111
ct 64
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.3
wp 6505.6
vs 78
sc 0
wc 250
hzmm 26.02
is 450.69
rfl 4134.5
rfp 3623.1
th 7
ins
ai cdc ph 100.000
dfrq DEC. & VT
dn 125.845
C13
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt
(+)-37
ppm


SAMPLE
solvent CDCl3
ACQUISITION
sfrq 125.673
tn C13
at 2.001
np 138948
sw 34722.2
fb not used
bs 8
tpwr 58
pw 6.7
d1 3.000
tof 742.1
nt 1.11111e+06
ct 1888
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2513.4
wp 30158.4
vs 875
sc 0
wc 250
hzmm 120.63
is 500.00
rfl 14392.0
rfp 9704.7
th 7
ins 100.000
ai cdc ph
DEC. & VT
dfrq 499.744
dn H1
dpwr 34
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 1.00
wtfile
proc
ft
fn 131072
math f
werr
wexp
wbs
wnt
(+)-37
200
180
160
140
120
100
80
60
40
20
0
ppm


SAMPLE
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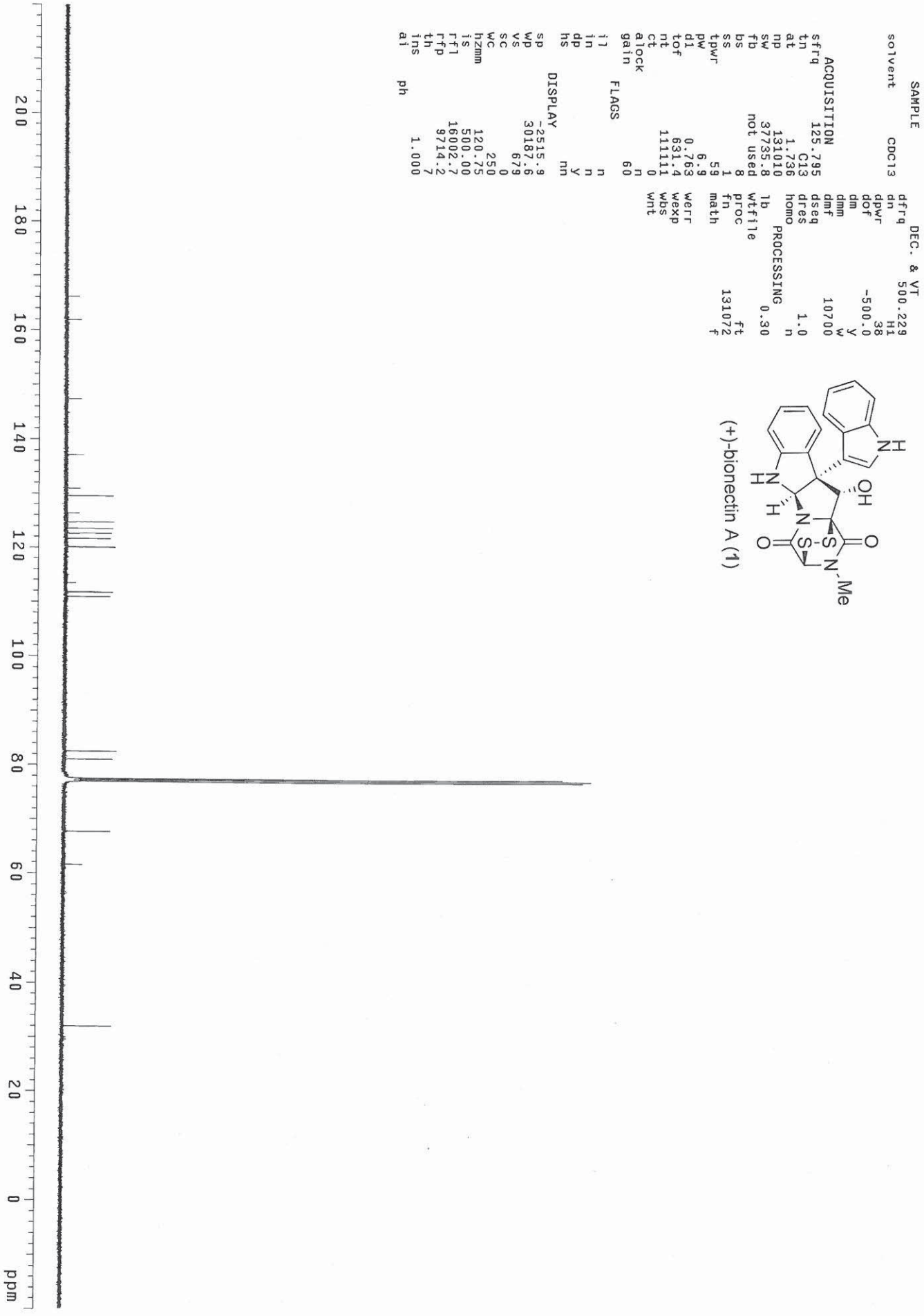
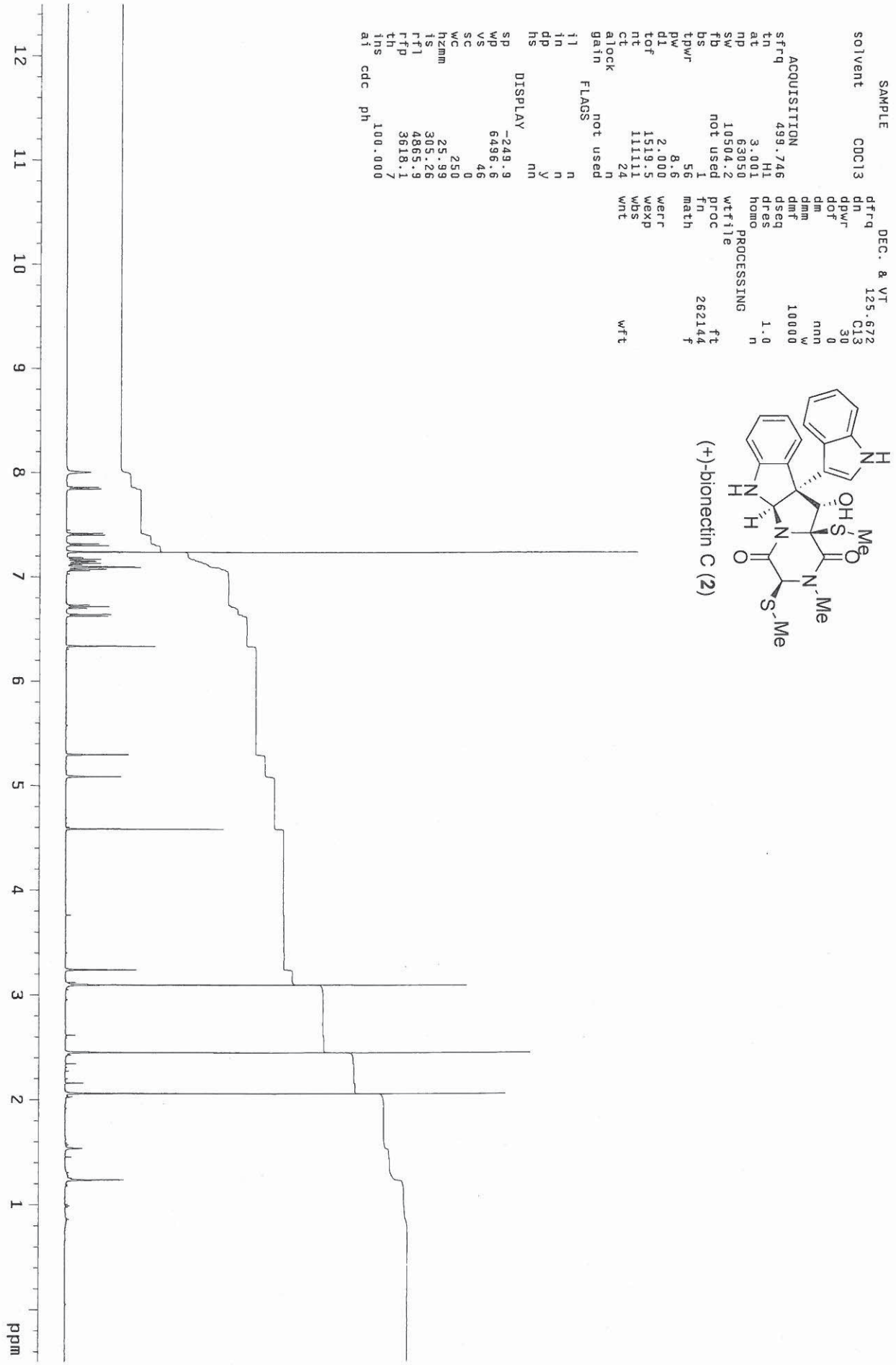
ACQUISITION
sfrq 500.231
tn H1
at 3.200
np 64000
sw 10000.0
fb not used
bs 1
ss 1
tpwr 59
pw 9.0
d1 1.800
tof 1498.2
nt 111111
ct 0
alock n
gain n
FLAGS
not used
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 6502.8
vs 64
sc 0
wc 250
hzmm 26.01
is 380.49
rfl 4634.4
rfp 3621.6
th 7
ins 1.000
ai ph
DEC. & VT
dfrq 125.794
dn C13
dpwr 38
dof 0
dm nnn
dmm c
dmf 10700
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
(+)-bionectin A (1)
12
11
10
9
8
7
6
5
4
3
2
1
ppm


SAMPLE
solvent CDCl3
ACQUISITION
sfrq 125.795
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 59
pw 6.9
d1 0.763
tof 631.4
nt 111111
ct 0
alock wnt
gain n
60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2515.9
wp 30187.6
vs 679
sc 0
wc 250
hzmm 120.75
is 500.00
rfl 16002.7
rfp 9714.2
th 7
ins 1.000
al ph
DEC. & VT
dfrq 500.229
dn H1
dpwr 38
dof -500.0
dm y
dmm y
dmf 10700
dseq w
dres
homo 1.0
n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
OH
N
H
O
S
Me
(+)-bionectin A (1)
200
180
160
140
120
100
80
60
40
20
0
ppm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solvent CDCl3
ACQUISITION
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at 3.001
np 63050
sw 10504.2
fb not used
bs 1
tpwr 56
pw 8.6
d1 2.000
tof 1519.5
nt 111111
ct 24
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -249.9
wp 6496.6
vs 46
sc 0
wc 250
hzmm 25.99
is 305.26
rfl 4865.9
rfp 3618.1
th 7
ins 100.000
ai cdc ph
DEC. & VT
dfrq 125.672
dn C13
dpwr 30
dof 0
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
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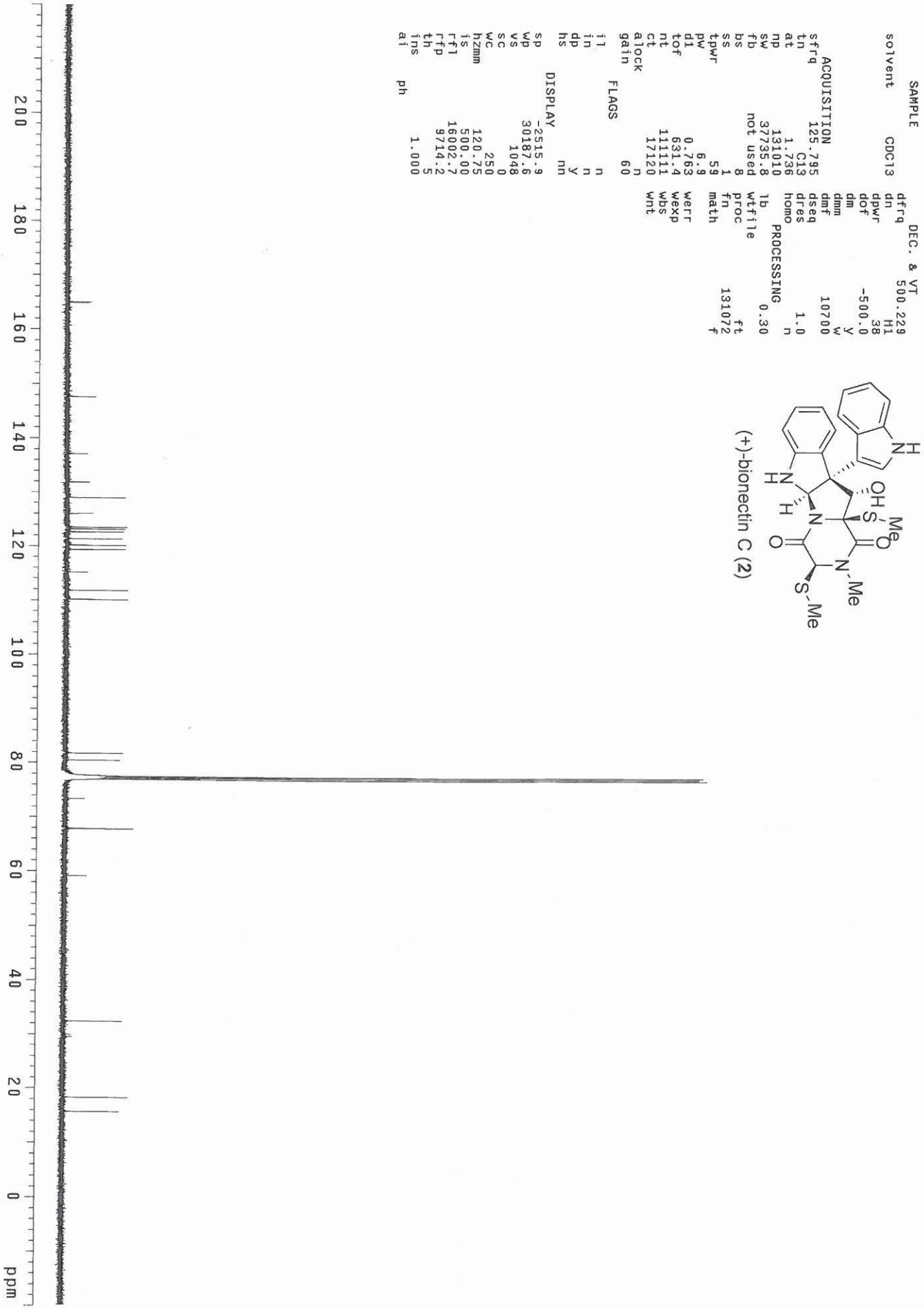
proc ft
fn 262144
math f
wnt
wft
(+)-bionectin C (2)
ppm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solvent CDCl3
ACQUISITION
sfrq 125.795
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 59
pw 6.9
d1 0.763
tof 631.4
nt 111111
ct 17120
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2515.9
wp 30187.6
vs 1048
sc 0
wc 250
hzmm 120.75
is 500.00
rfl 16002.7
rfp 9714.2
th 5
ins 1.000
ai
ph
DEC. & VT
dfrq 500.229
dn H1
dpwr 38
dof -500.0
dm y
dmm w
dmf 10700
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
(+)-bionectin C (2)
200
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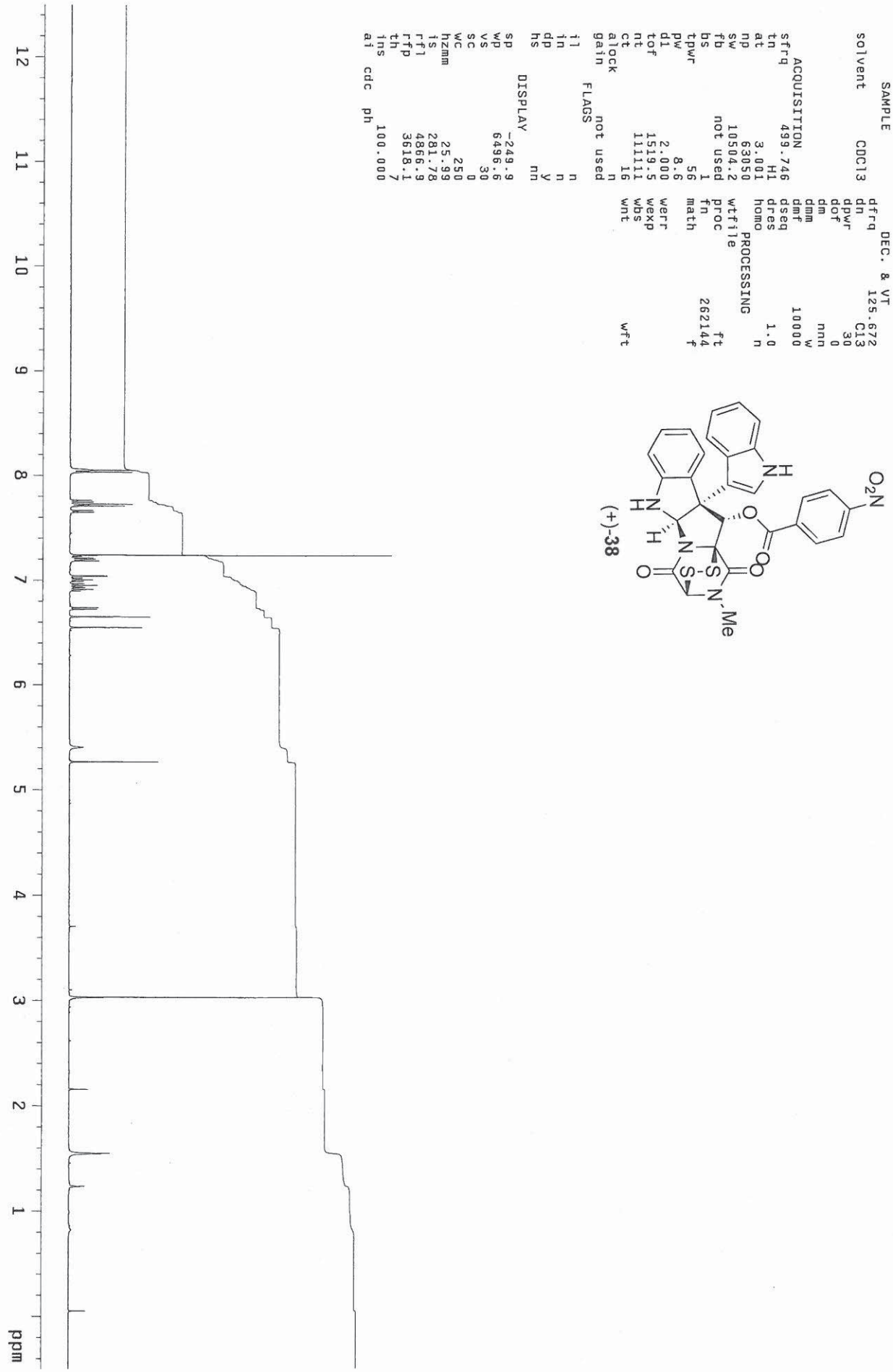
160
140
120
100
80
60
40
20
0
ppm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solvent CDCl3
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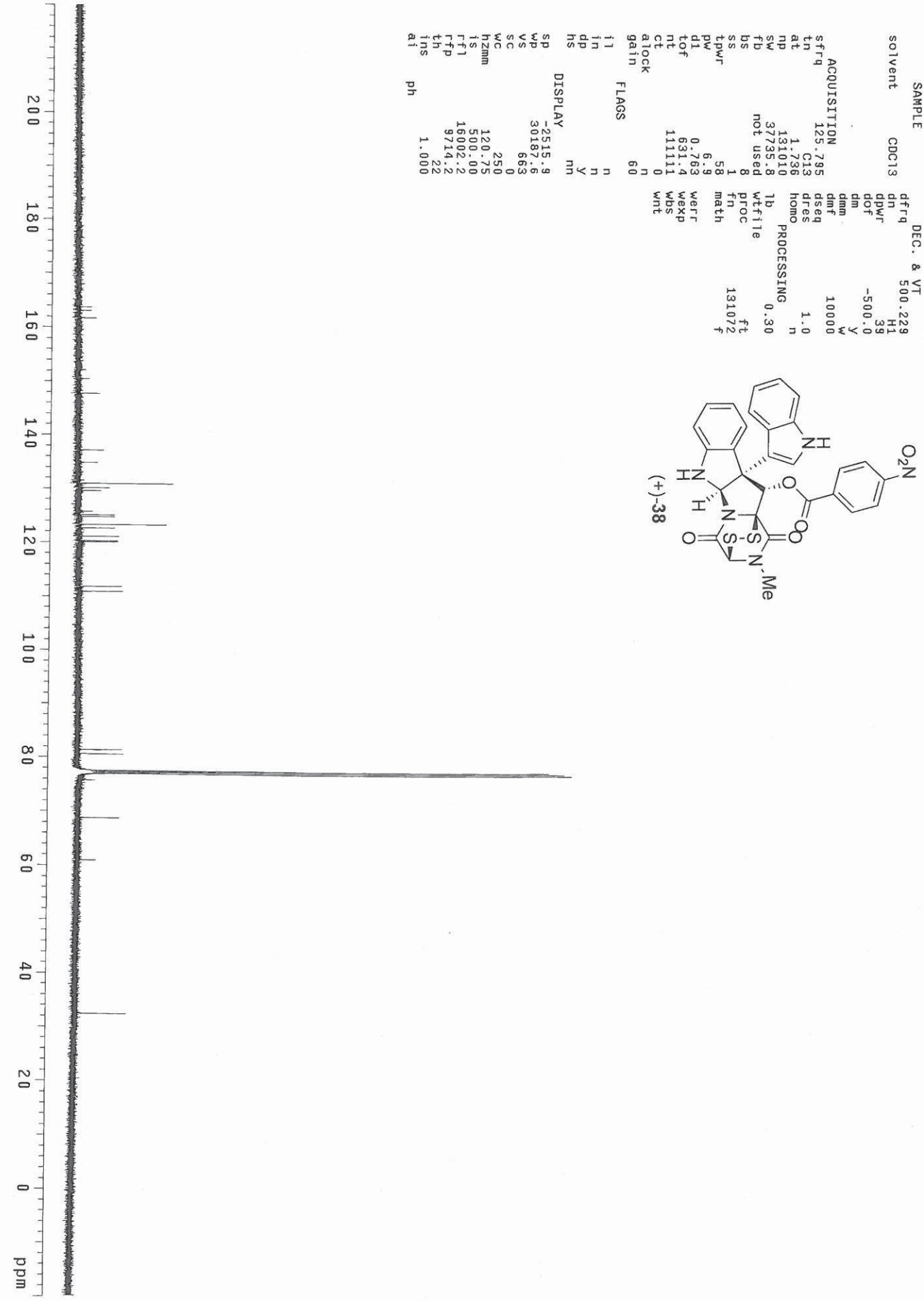
sfrq 499.746
tn H1
at 3.001
np 63050
sw 10504.2
fb not used
bs 1
tpwr 56
pw 8.6
d1 2.000
tof 1519.5
nt 111111
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -249.9
wp 6496.6
vs 30
sc 0
wc 250
hzmm 25.99
is 281.78
rfl 4866.9
rfp 3618.1
th 7
ins
ai cdc ph 100.000
DEC. & VT
dfrq 125.672
dn C13
dpwr 30
dof 0
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt wft
(+)-38
ppm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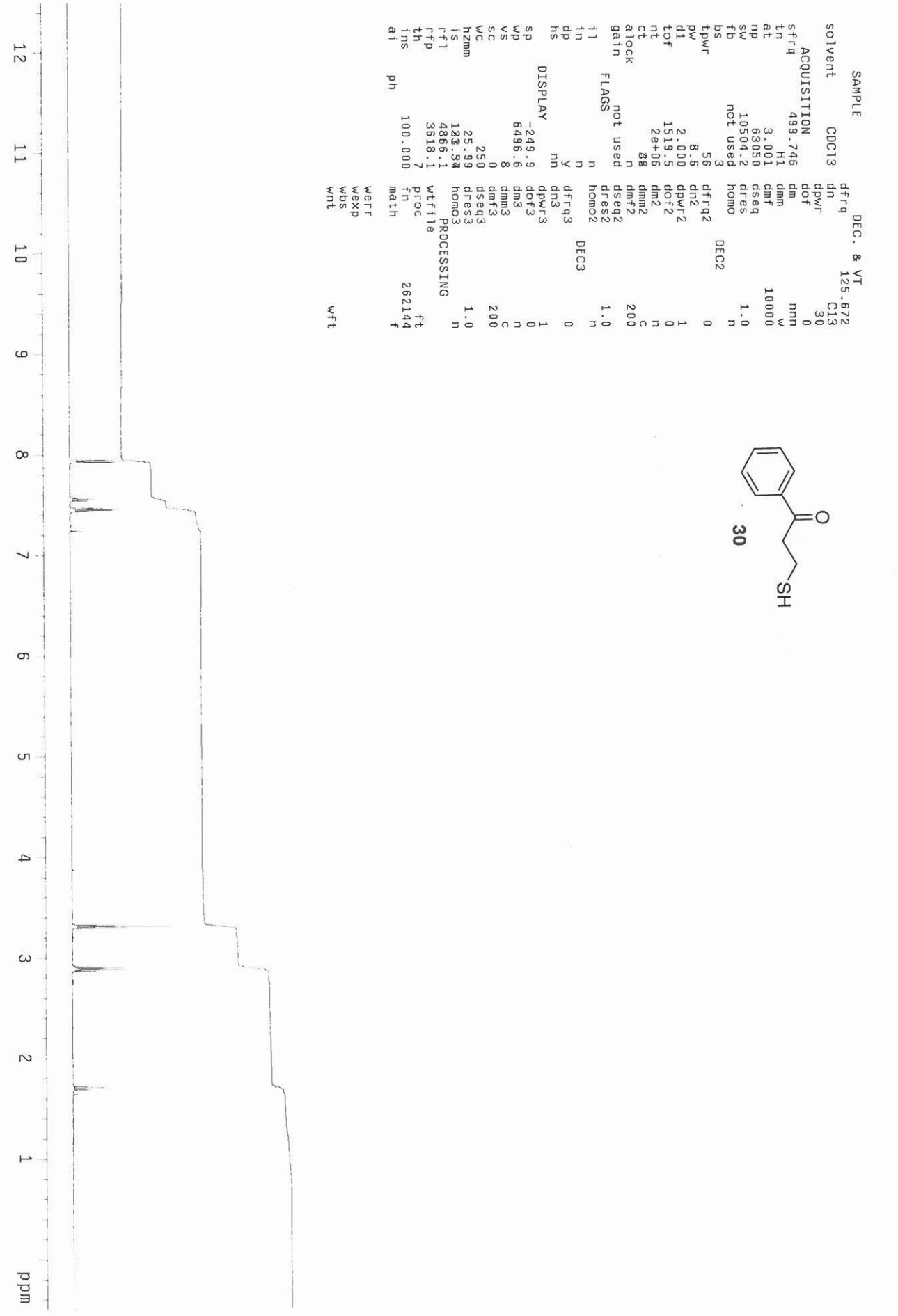
np 131010
sw 37735.8
fb not used
bs
ss 1
tpwr 58
pw 6.9
d1 0.763
tof 631.4
nt 111111
ct 0
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2515.9
wp 30187.6
vs 663
sc 0
wc 250
hzmm 120.75
is 500.00
rfl 16002.2
rfp 9714.2
th 22
ins 1.000
ai
ph
DEC. & VT
dfrq 500.229
dn H1
dpwr 39
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc
fn ft
math 131072 f
werr
wexp
wbs
wnt
(+)-38
ppm
200
180
160
140
120
100
80
60
40
20
0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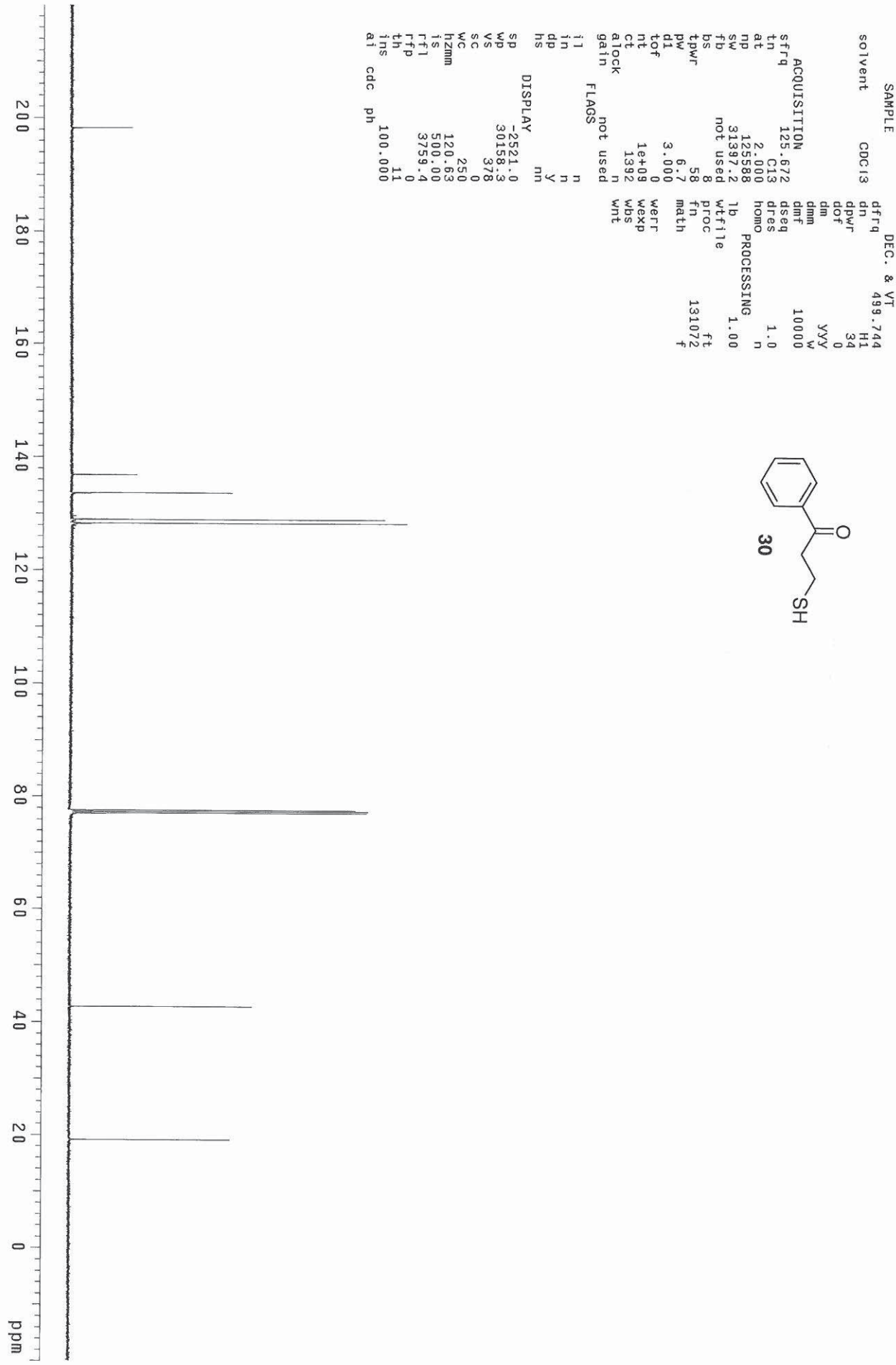
sfrq 499.746
tn H1
at 3.001
np 63050
sw 10504.2
fb not used
bs 3
tpwr 56
pw 8.6
d1 2.000
tof 1519.5
nt 2e+06
ct 28
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -249.9
wp 6496.6
vs 8
sc 0
wc 250
hzmm 25.99
is 133.32
rfl 4866.1
rfp 3618.1
th 7
ins 100.000
ai ph
DEC. & VT
dfrq 125.672
dn C13
dpwr 30
dof 0
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt wft
O
SH
30
12
11
10
9
8
7
6
5
4
3
2
1
ppm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solvent CDCl3
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np 125588
sw 31397.2
fb not used
bs 8
tpwr 58
pw 6.7
d1 3.000
tof 0
nt 1e+09
ct 1392
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2521.0
wp 30158.3
vs 378
sc 0
wc 250
hzmm 120.63
is 500.00
rfl 3759.4
rfp 0
th 11
ins 100.000
ai cdc ph
dfrq DEC. & VT
dn 499.744
dpwr H1
dof 34
dm 0
dmm yyy
dmf w
dseq 10000
dres 1.0
homo n
PROCESSING
lb 1.00
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
O
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SH
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120
100
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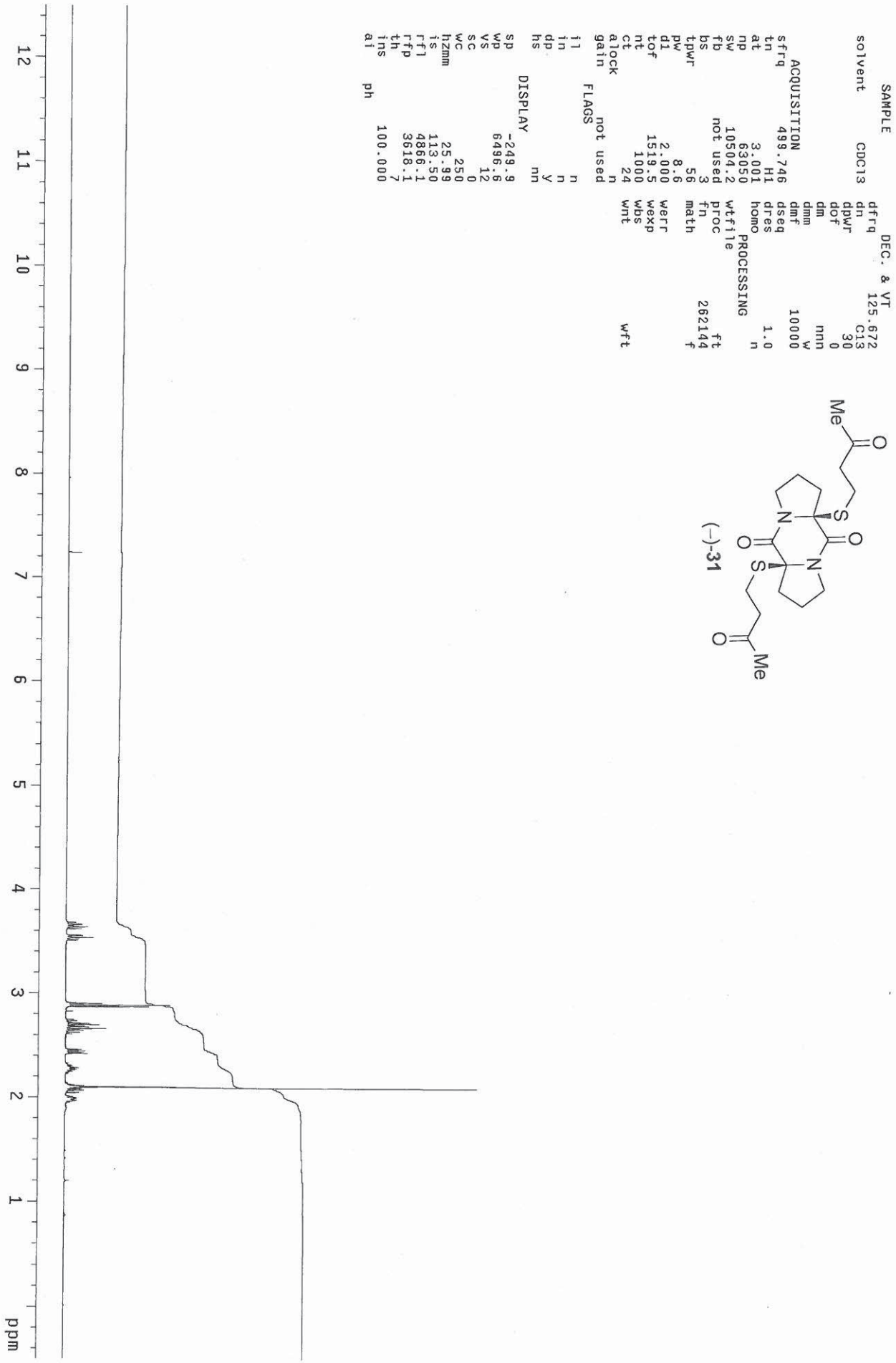
60
40
20
0
ppm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ACQUISITION
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at 3.001
np 63050
sw 10504.2
fb not used
bs 3
tpwr 56
pw 8.6
d1 2.000
tof 1519.5
nt 1000
ct 24
alock n
gain n
FLAGS
not used
il n
in n
dp y
hs nn
DISPLAY
sp -249.9
wp 6496.6
vs 12
sc 0
wc 250
hzmm 25.99
is 113.50
rfl 4866.1
rfp 3618.1
th 7
ins 100.000
ai ph
DEC. & VT
dfrq 125.672
dn C13
dpwr 30
dof 0
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
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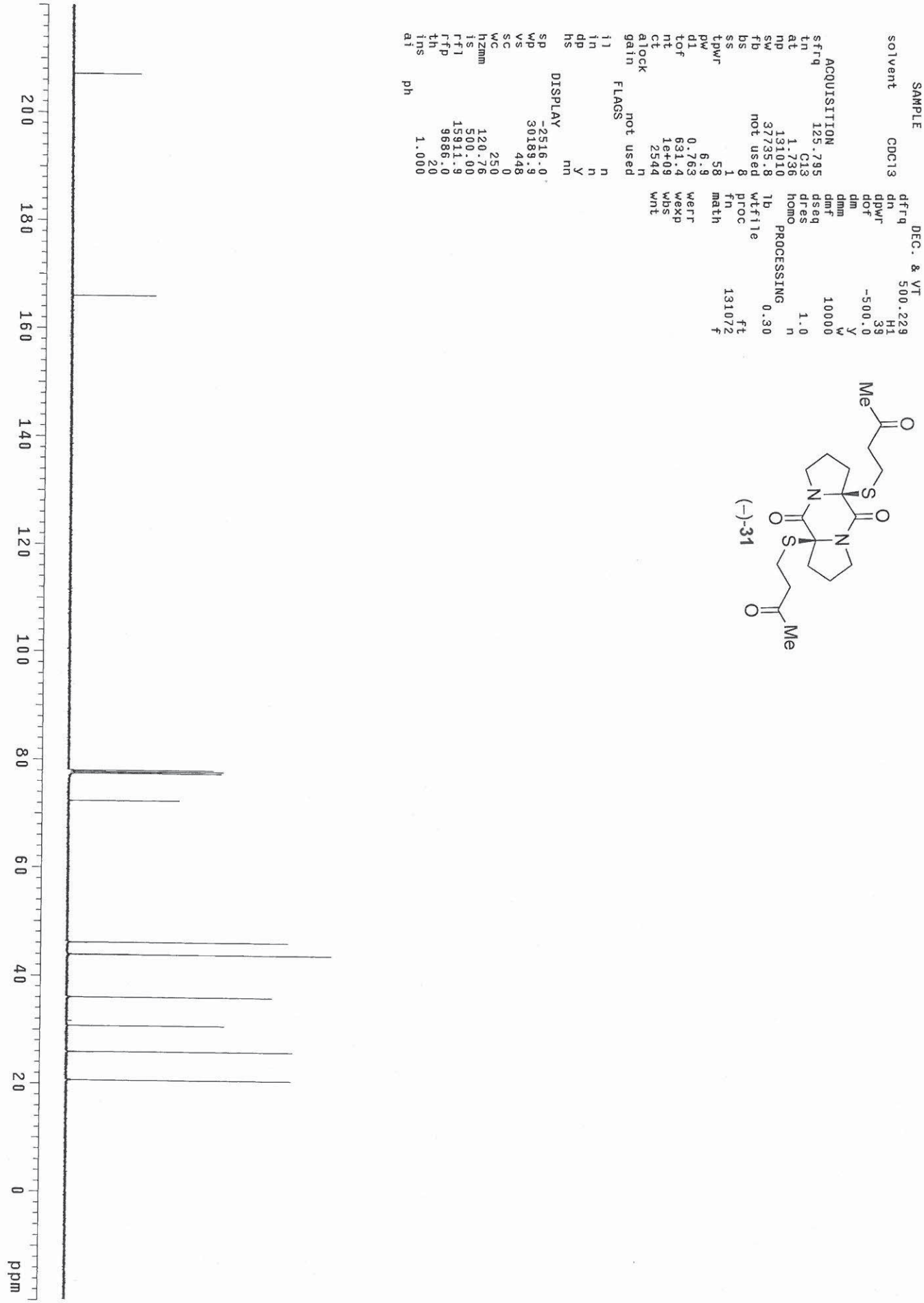
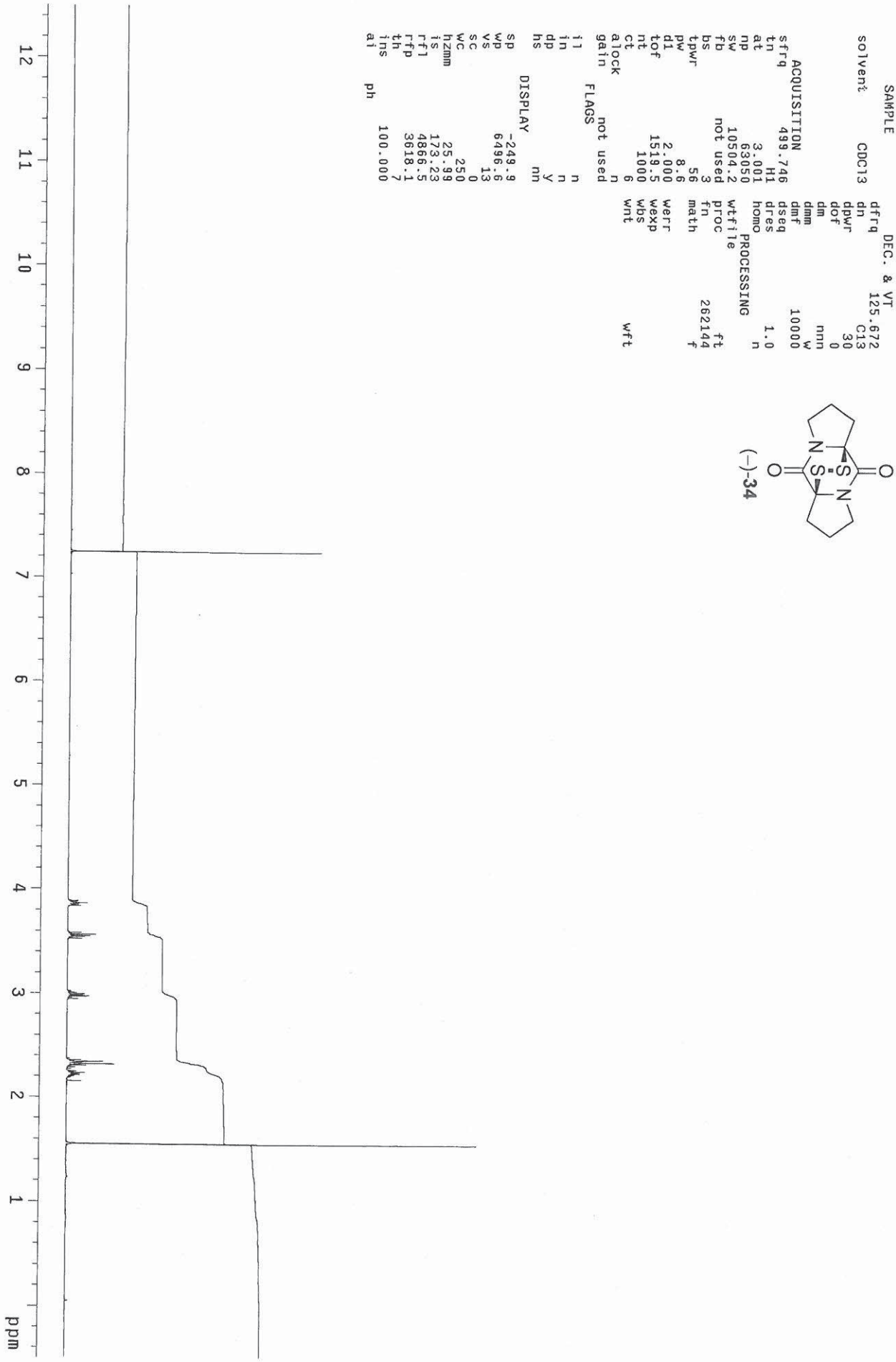
10
9
8
7
6
5
4
3
2
1

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np 63050
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fb not used
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pw 8.6
d1 2.000
tof 1519.5
nt 1000
ct 6
alock n
gain n
FLAGS not used
il n
in n
dp y
hs nn
DISPLAY
sp -249.9
wp 6496.6
vs 13
sc 0
wc 250
hzmm 25.99
is 173.23
rfl 4866.5
rfp 3618.1
th 7
ins 100.000
ai ph
DEC. & VT
dfrq 125.672
dn C13
dpwr 30
dof 0
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt wft
(−)-34
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11
10
9
8
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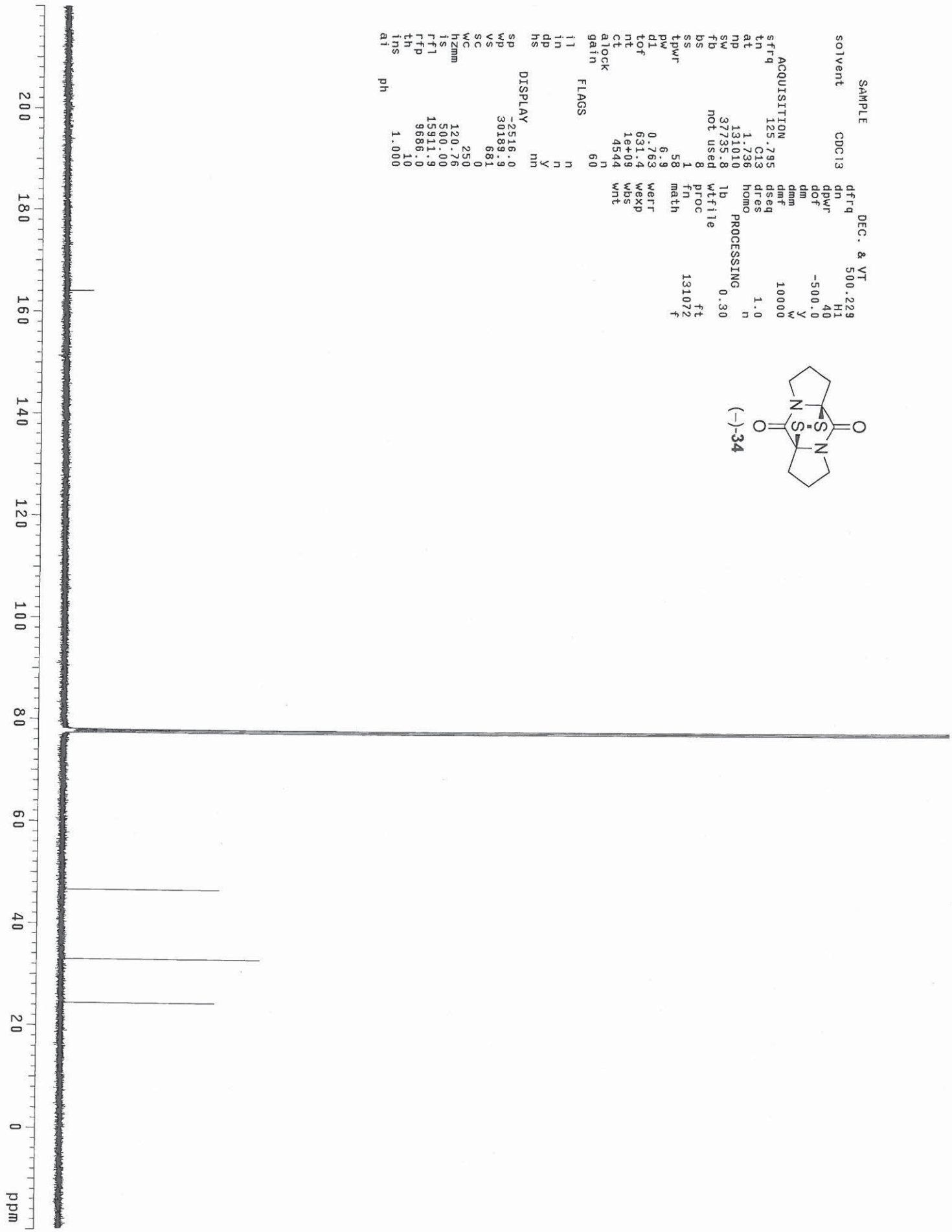
6
5
4
3
2
1
ppm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solvent CDCl3
ACQUISITION
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tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 58
pw 6.9
d1 0.763
tof 631.4
nt 1e+09
ct 4544
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2516.0
wp 30189.9
vs 681
sc 0
wc 250
hzmm 120.76
is 500.00
rfl 15911.9
rfp 9686.0
th 10
ins 1.000
ai ph
DEC. & VT
dfrq 500.229
dn H1
dpwr 40
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
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wbs
wnt
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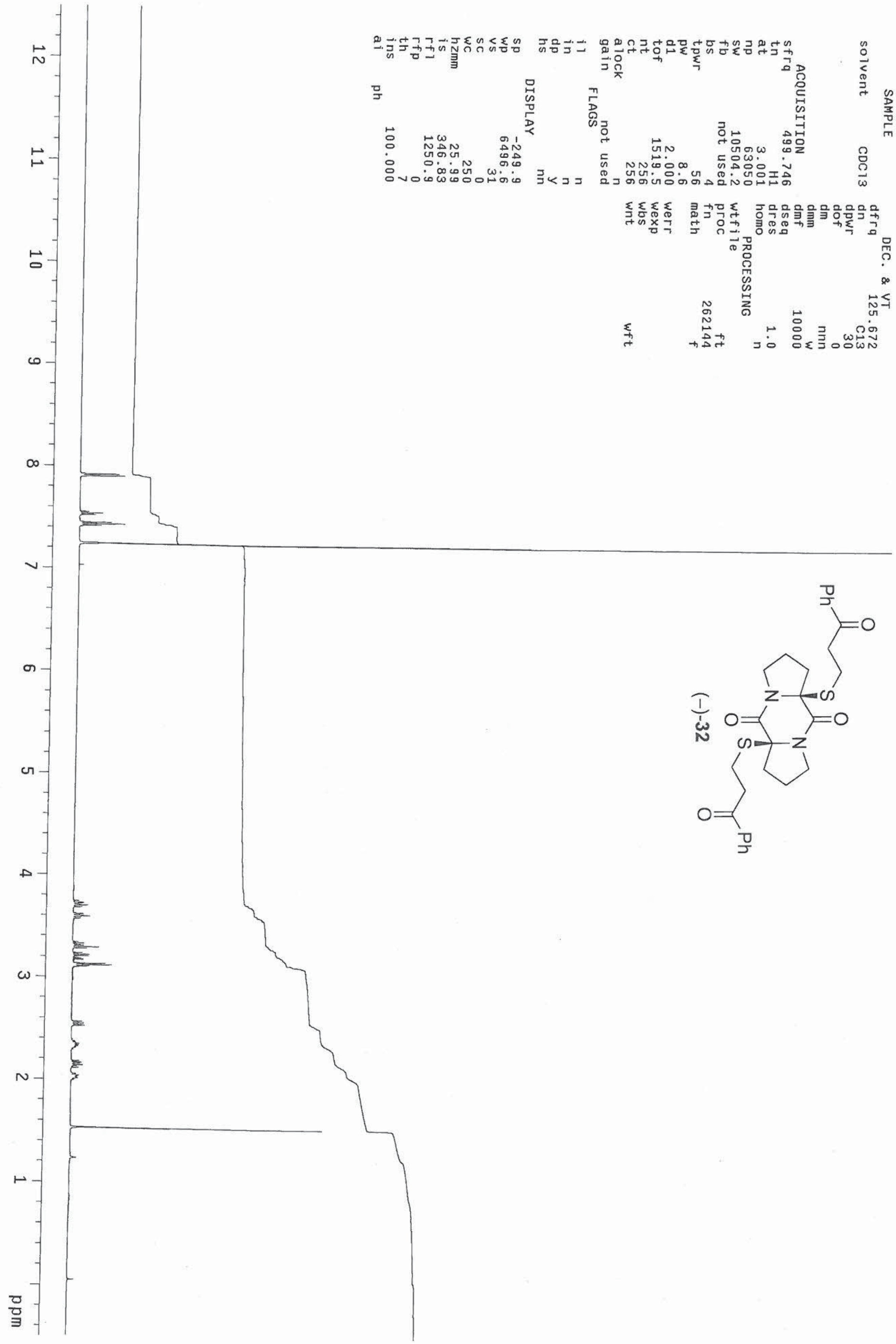
ppm



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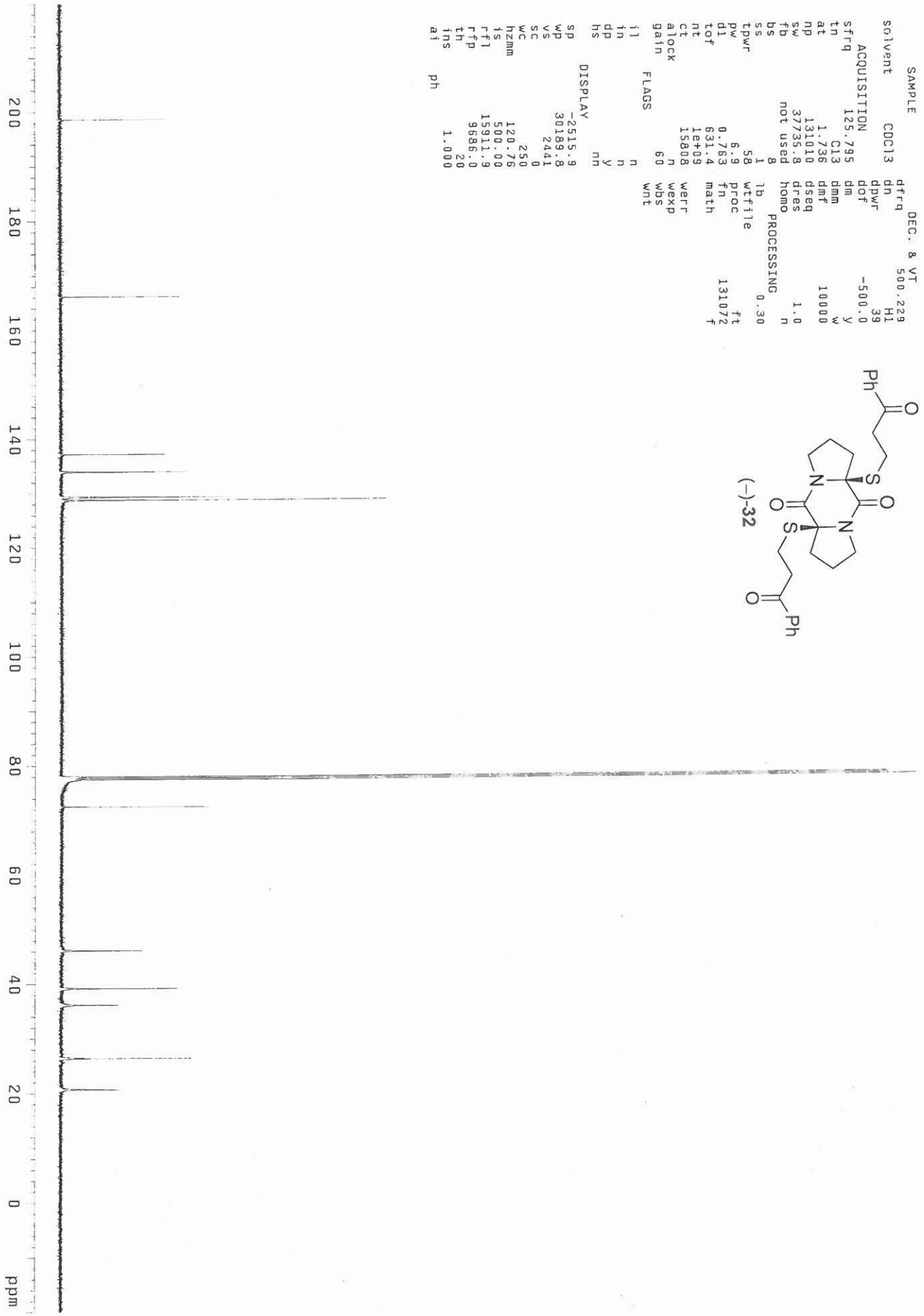
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np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 58
pw 6.9
d1 0.763
tof 631.4
nt 1e+09
ct 15808
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2515.9
wp 30189.8
vs 2441
sc 0
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hzmm 120.76
is 500.00
rfl 15911.9
rfp 9686.0
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ins 1.000
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dfrq
dn
dpwr
dof
dm
dmm
dmf
dseq
dres
homo
PROCESSING
lb
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proc
fn
math
werr
wexp
wbs
wnt
DEC. & VT
500.229
H1
39
-500.0
y
w
10000
1.0
n
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131072
f
(−)-32
200
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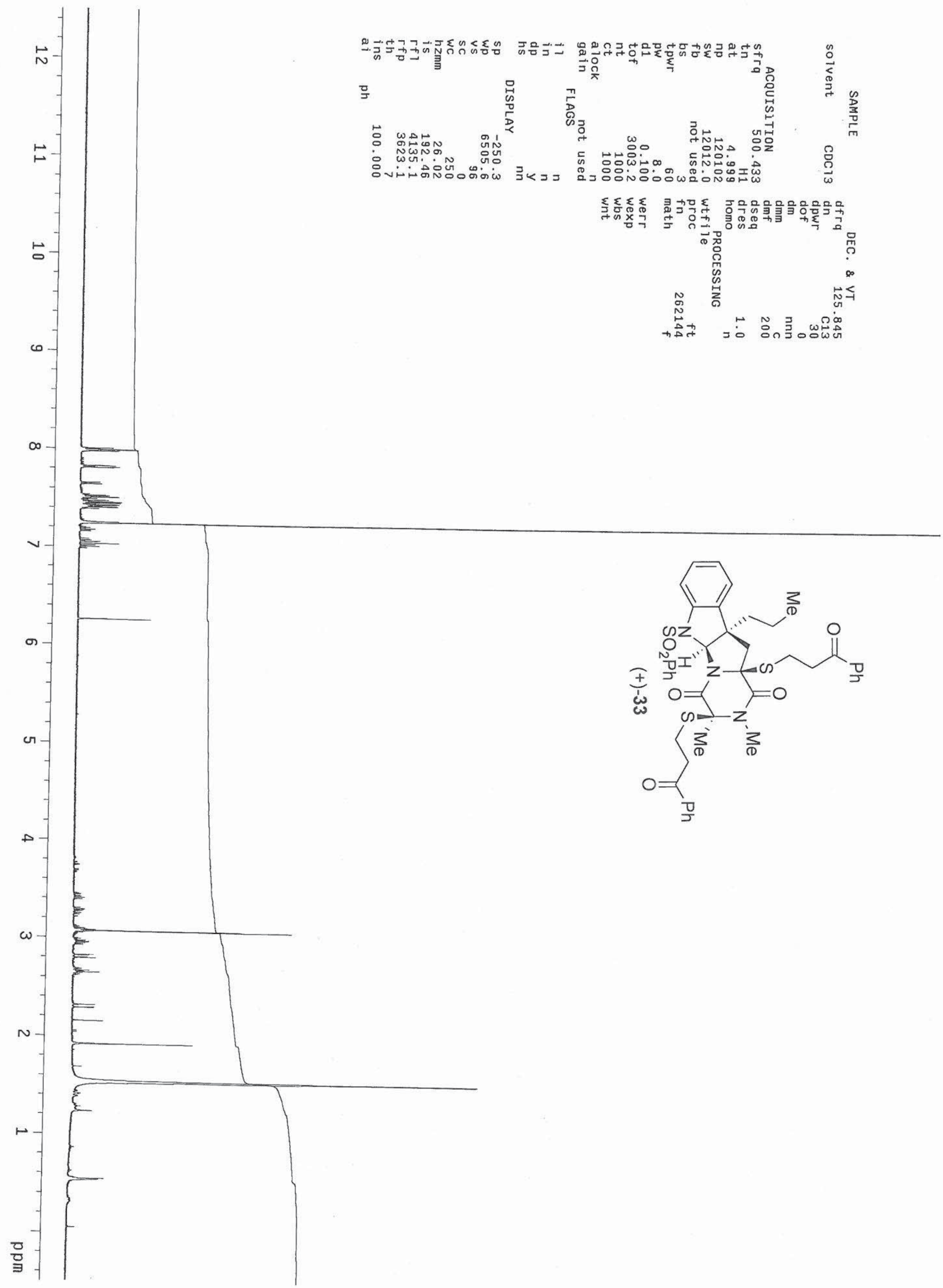
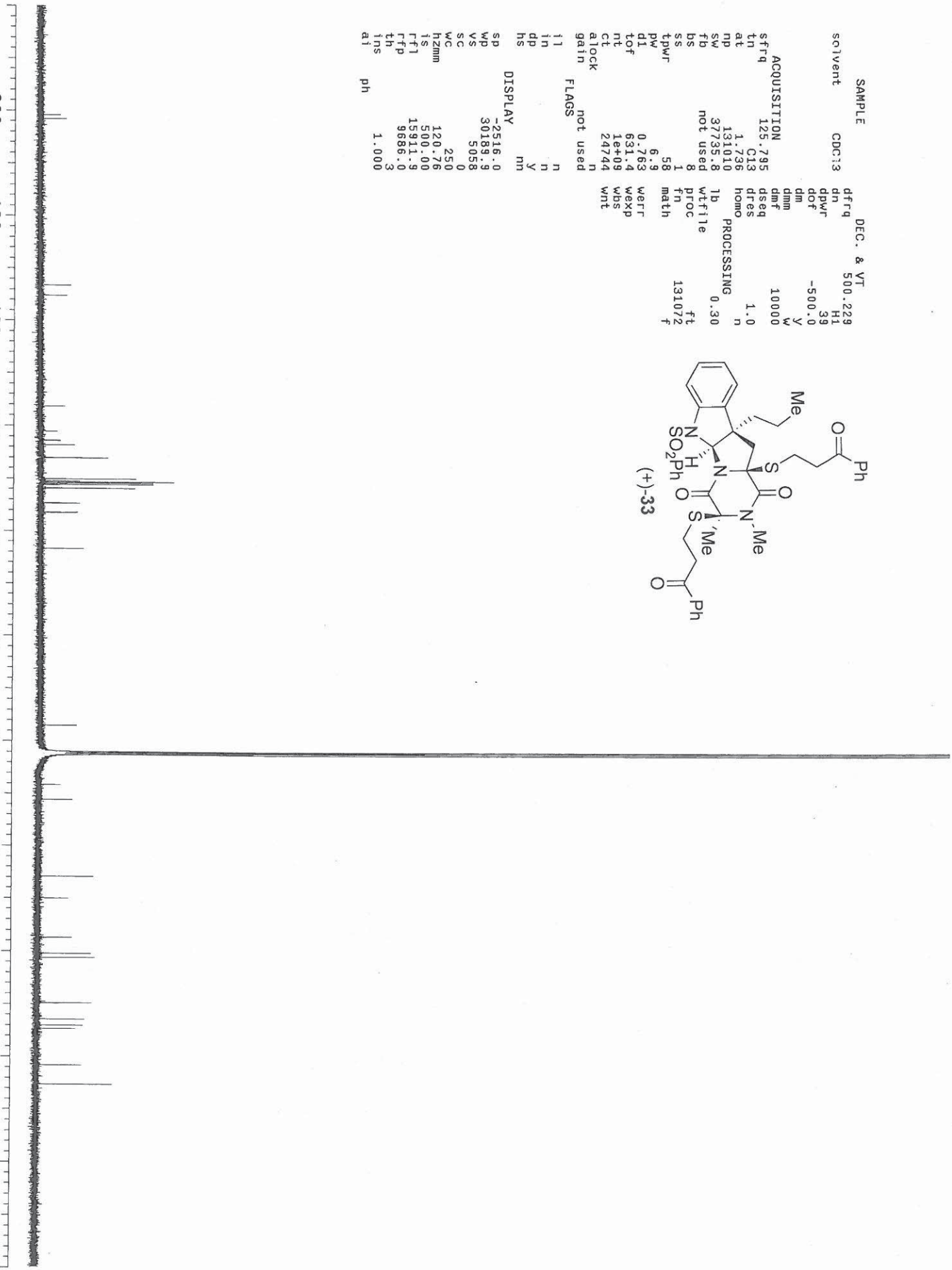
140
120
100
80
60
40
20
0
ppm

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np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 58
pw 6.9
d1 0.763
tof 631.4
nt 24744
ct
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2516.0
wp 30189.9
vs 5058
sc 0
wc 250
hzmm 120.76
is 500.00
rfl 15911.9
rfp 9686.0
th 3
ins 1.000
ai
ph
DEC. & VT
dfrq 500.229
dn H1
dpwr 39
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
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wbs
wnt
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120
100
80
60
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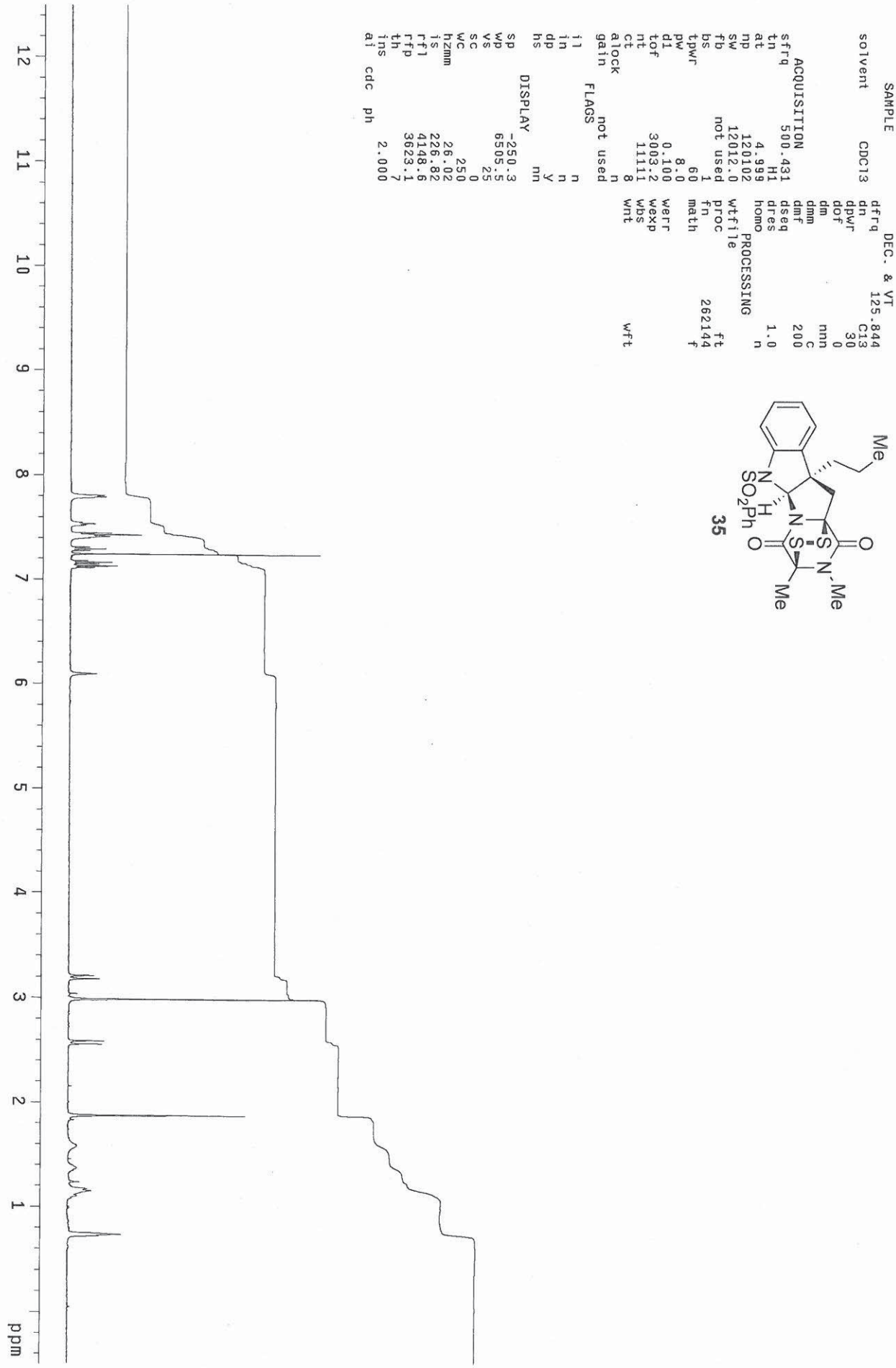
20
0
ppm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tpwr 60
pw 8.0
d1 0.100
tof 3003.2
nt 11111
ct 8
alock n
gain n
FLAGS
not used
il n
in n
dp y
hs nn
DISPLAY
sp -250.3
wp 6505.5
vs 25
sc 0
wc 250
hzmm 26.02
is 226.82
rfl 4148.6
rfp 3623.1
th 7
ins
ai cdc ph 2.000
DEC. & VT
dfrq 125.844
dn C13
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt wft
Me
N
SO2Ph
H
N
S
S
O
O
N
Me
Me
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12
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8
7
6
5
4
3
2
1
ppm