Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Organocatalytic Asymmetric Multicomponent Cascade Reaction *via* 1,3-Proton Shift and [3+2] Cycloaddition: An Efficient Strategy for the Synthesis of Oxindole Derivatives

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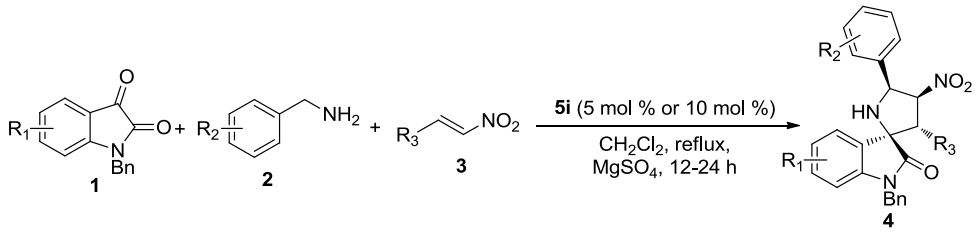
1. General information

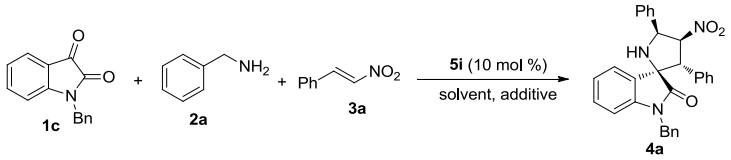
Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography (TLC) was performed on silicycle silica gel plates with F-254 indicator and the compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing silica gel 200-300 mesh. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C). The spectra were recorded in $CDCl_3$ as solvent at room temperature, ^{1}H and ^{13}CNMR chemical shifts are reported in ppm relative to either the residual solvent peak (^{13}C) (δ = 77.00 ppm) or TMS (^{1}H) (δ = 0 ppm) as an internal standard. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. IR spectra were recorded using Nicolet NEXUS 670 FT-IR instrument and are reported in wavenumbers (cm^{-1}). HRMS were performed on Thermo Scientific Orbitrap Elite mass instrument (ESI). Enantiomeric excess values were determined by HPLC employing a Daicel Chirapak AD-H on Waters 600 Delta or Agilent 1100 series and eluting with *i*-PrOH and *n*-hexane solution. Optical rotation was measured on the Perkin Elmer 341 polarimeter with $[\alpha]_D$ values reported in degrees; concentration (c) is reported in g/100 mL.

2. General procedure for the synthesis of spiro[indoline-3,2'-pyrrolidin]-2-one



To a solution of catalyst **5i** (0.01 mmol or 0.02 mmol), isatins **1** (0.2 mmol), nitroalkene **3** (1 mmol) and $MgSO_4$ (1 mmol) in dry CH_2Cl_2 (0.5 mL) was added freshly distilled benzylamine **2** (0.2 mmol) under stirring. After refluxing for 12–24 h, the reaction was completed. The rest of nitroalkene **3** could be recycled easily when purifying the crude mixture by flash chromatography on silica gel to afford product **4**.

3. Additional optimization for the cascade reaction [a]

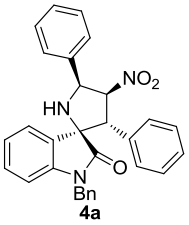


entry	**5i** (mol %)	solvent	T (^oC)	time (h)	yield (%)[b]	d.r.[c]	ee (%)[d]
1	10	$CHCl_3$	10	12	71	10:1	69
2	10	$C_2H_4Cl_2$	10	12	72	11:1	71
3	10	xylene	10	12	57	8:1	73
4	10	CH_2Cl_2	0	24	68	12:1	76
5	10	CH_2Cl_2	-10	36	70	n.d.	67
6	20	CH_2Cl_2	10	4	80	8:1	70
7	15	CH_2Cl_2	10	4	70	10:1	73
8	5	CH_2Cl_2	10	15	72	11:1	76
9	3	CH_2Cl_2	reflux	5	66	n.d.	72
10	1	CH_2Cl_2	reflux	12	<20	n.d.	n.d.
11[e]	10	CH_2Cl_2	10	4	74	12:1	60
12[f]	10	CH_2Cl_2	reflux	1.5	75	9:1	78
13[g,h]	5	CH_2Cl_2	reflux	12	78	9:1	82
14[g,h,i]	5	CH_2Cl_2	reflux	12	76	10:1	81

[a] Unless otherwise specified, the reaction was carried out with **1** (0.2 mmol), **2a** (0.2 mmol), **3a** (0.2mmol), and **5i** (10 mol %), in the indicated solvent (1.0 mL) at 10 ^oC. [b] The yields were the combined yields of the mixtures of diastereomers after flash chromatography. [c] Determined by ^1H NMR analysis of the crude products. [d] Determined by chiral-phase HPLC analysis (AD-H column). [e] 50 mg 4ÅMs was added. [f] 0.6mmol 3a was added. [g] 120 mg

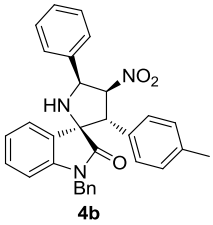
$MgSO_4$ was added. [h] 1mmol 3a was added. [i] By using of 2.0 mL CH_2Cl_2.

4. Characterization data of spiro[indoline-3,2'-pyrrolidin]-2-one



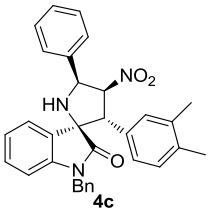
4a

(2'R, 3'S, 4'S, 5'S)-1-benzyl-4'-nitro-3',5'-diphenylspiro[indoline-3,2'-pyrrolidin]-2-one (4a): white solid; $[\alpha]_D^{20}$ = -29.2 (*c* 0.513, CH_2Cl_2); mp 166-168 °C; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 254 nm; $t_{R(major)}$ = 12.1 min, $t_{R(minor)}$ = 38.2 min, ee : 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6Hz, 2H), 7.55-7.53 (m, 1H), 7.45-7.36 (m, 3H), 7.24-7.02 (m, 10H), 6.89 (d, *J* = 6.8Hz, 2H), 6.50-6.48 (m, 1H), 6.24-6.18 (m, 1H), 5.55 (d, *J* = 9.2, 1H), 5.13 (d, *J* = 16.0Hz, 1H), 4.93 (d, *J* = 12.0Hz, 1H), 4.57 (d, *J* = 15.6Hz, 1H), 2.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 142.0, 137.3, 134.7, 131.7, 129.8, 129.5, 128.9, 128.6, 128.5, 128.3, 128.10, 128.05, 127.7, 127.4, 126.8, 124.1, 122.7, 109.8, 91.6, 71.2, 63.1, 56.3, 44.0; IR (KBr): 3440.6, 1958.1, 1703.7, 1612.4, 1550.5, 1468.5, 1370.8, 1179.9, 747.8, 697.1 cm^{-1}; HRMS (ESI) for $C_{30}H_{25}N_3O_3$ $[M+H]^+$ calcd 476.1969, found 476.1979.



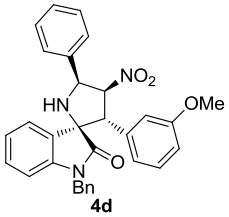
4b

(2'R, 3'S, 4'S, 5'S)-1-benzyl-4'-nitro-5'-phenyl-3'-(p-tolyl)spiro[indoline-3,2'-pyrrolidin]-2-one (4b): white solid; $[\alpha]_D^{20}$ = -45.0 (*c* 0.200, CH_2Cl_2); mp 172-174 °C; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 254 nm; $t_{R(major)}$ = 12.0 min, $t_{R(minor)}$ = 29.9 min, ee : 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.2Hz, 2H), 7.52-7.50 (m, 1H), 7.41-7.38 (m, 2H), 7.35-7.32 (m, 1H), 7.22-7.18 (m, 1H), 7.16-7.12 (m, 2H), 7.11-7.07 (m, 2H), 6.88-6.82 (m, 6H), 6.46-6.44 (m, 1H), 6.13 (dd, *J* = 10.0Hz, 12.0Hz, 1H), 5.50 (t, *J* = 7.6Hz, 1H), 5.12 (d, *J* = 16.0Hz, 1H), 4.84 (d, *J* = 12.0Hz, 1H), 4.52 (d, *J* = 16.0Hz, 1H), 2.91 (d, *J* = 7.2Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 142.1, 137.8, 137.4, 134.7, 130.0, 129.5, 129.1, 128.9, 128.6, 128.5, 128.1, 127.8, 127.4, 126.8, 124.1, 122.7, 109.9, 91.8, 71.2, 63.1, 56.1, 44.0, 21.0; IR (KBr): 3438.7, 1958.9, 1719.3, 1613.7, 1555.0, 1468.4, 1367.4, 1177.5, 754.2, 699.6 cm^{-1}; HRMS (ESI) for $C_{31}H_{27}N_3O_3$ $[M+H]^+$ calcd 490.2125, found 490.2138.



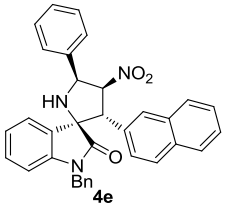
4c

(2'R, 3'S, 4'S, 5'S)-1-benzyl-3'-(3,4-dimethylphenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (4c): white solid; $[\alpha]_D^{20}$ = -78.6 (*c* 0.280, CH_2Cl_2); mp 168-170 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 254 nm; $t_{R(major)}$ = 10.6 min, $t_{R(minor)}$ = 36.8 min, ee : 86%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.2Hz, 2H), 7.53-7.51 (m, 1H), 7.40-7.37 (m, 2H), 7.34-7.31 (m, 1H), 7.20-7.16 (m, 1H), 7.13-7.06 (m, 4H), 6.80-6.77 (m, 4H), 6.69 (d, *J* = 8.0Hz, 1H), 6.43-6.41 (m, 1H), 6.12 (dd, *J* = 9.6Hz, 11.6Hz, 1H), 5.49 (t, *J* = 7.2Hz, 1H), 5.16 (d, *J* = 16.0Hz, 1H), 4.81 (d, *J* = 12.0Hz, 1H), 4.48 (d, *J* = 16.0Hz, 1H), 2.91 (d, *J* = 6.8Hz, 1H), 2.10 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 142.1, 137.4, 136.6, 136.4, 134.7, 130.1, 129.9, 129.5, 129.4, 129.0, 128.9, 128.5, 127.7, 127.3, 126.6, 125.2, 124.1, 122.6, 109.9, 91.9, 71.2, 63.0, 56.1, 44.0, 19.5, 19.3; IR (KBr): 3440.6, 1958.7, 1721.2, 1612.6, 1554.8, 1467.9, 1366.2, 1178.8, 750.7, 699.7 cm^{-1}; HRMS (ESI) for $C_{32}H_{29}N_3O_3$ $[M+H]^+$ calcd 504.2282, found 504.2296.



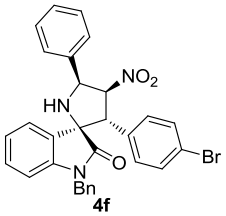
4d

(2'R, 3'S, 4'S, 5'S)-1-benzyl-3'-(3-methoxyphenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (4d): white solid; $[\alpha]_D^{20}$ = -40.5 (*c* 0.888, CH_2Cl_2); mp 160-162 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 230 nm; $t_{R(major)}$ = 16.1 min, $t_{R(minor)}$ = 54.9 min, ee : 87%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.2Hz, 2H), 7.52-7.50 (m, 1H), 7.41-7.38 (m, 2H), 7.35-7.32 (m, 1H), 7.19-7.14 (m, 3H), 7.11-7.08 (m, 2H), 6.95 (t, *J* = 8.0Hz 1H), 6.84 (d, *J* = 6.4Hz, 2H), 6.67 (dd, *J* = 2.0Hz, 8.4Hz, 1H), 6.60 (d, *J* = 7.6Hz, 1H), 6.53 (d, *J* = 1.6Hz, 1H), 6.47-6.45 (m, 1H), 6.13 (dd, *J* = 9.6Hz, 11.6Hz, 1H), 5.51 (d, *J* = 9.6Hz, 1H), 5.12 (d, *J* = 16.0Hz, 1H), 4.86 (d, *J* = 12.0Hz, 1H), 4.52 (d, *J* = 16.0Hz, 1H), 3.52 (s, 3H), 2.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 159.4, 142.2, 137.3, 134.6, 133.2, 129.9, 129.5, 129.4, 128.9, 128.6, 128.5, 127.7, 127.4, 126.6, 124.1, 122.7, 120.5, 114.3, 113.4, 109.9, 91.7, 71.2, 63.1, 56.3, 55.0, 44.0; IR (KBr): 3441.0, 1957.6, 1714.1, 1610.6, 1554.1, 1467.1, 1365.8, 1176.2, 744.4, 699.8 cm^{-1}; HRMS (ESI) for $C_{31}H_{27}N_3O_4$ $[M+H]^+$ calcd 506.2074, found 506.2093.



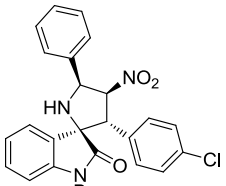
4e

(2'R, 3'S, 4'S, 5'S)-1-benzyl-3'-(naphthalen-2-yl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (4e): white solid; $[\alpha]_D^{20}$ = -58.3 (*c* 0.120, CH_2Cl_2); mp 120-122 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 254 nm; $t_{R(major)}$ = 12.8 min, $t_{R(minor)}$ = 27.8 min, ee : 85%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2Hz, 2H), 7.69-7.67 (m, 1H), 7.63-7.59 (m, 3H), 7.48-7.34 (m, 6H), 7.12-6.99 (m, 4H), 6.72 (t, *J* = 8.0Hz 2H), 6.62 (d, *J* = 7.6Hz, 2H), 6.35 (d, *J* = 7.2Hz, 1H), 6.28 (dd, *J* = 9.6Hz, 12.0Hz, 1H), 5.59 (t, *J* = 6.4Hz, 1H), 5.13 (d, *J* = 16.0Hz, 1H), 5.05 (d, *J* = 11.6Hz, 1H), 4.45 (d, *J* = 16.0Hz, 1H), 2.98 (d, *J* = 6.4Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 142.1, 137.3, 134.4, 133.0, 132.9, 129.9, 129.6, 129.2, 129.0, 128.6, 128.5, 128.4, 128.1, 128.0, 127.8, 127.4, 127.3, 126.4, 126.3, 126.2, 124.9, 124.2, 122.8, 110.0, 91.8, 71.4, 63.3, 56.6, 44.0; IR (KBr): 3438.8, 1958.5, 1718.3, 1613.1, 1554.9, 1468.2, 1367.4, 1177.7, 749.8, 699.6 cm^{-1}; HRMS (ESI) for $C_{34}H_{27}N_3O_3$ $[M+H]^+$ calcd 526.2125, found 526.2140.



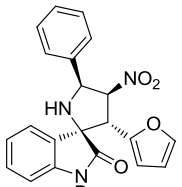
4f

(2'R, 3'S, 4'S, 5'S)-1-benzyl-3'-(4-bromophenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (4f): white solid; $[\alpha]_D^{20}$ = -20.0 (*c* 0.848, CH_2Cl_2); mp 158-160 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 230 nm; $t_{R(major)}$ = 18.1 min, $t_{R(minor)}$ = 22.2 min, ee : 82%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.8Hz, 2H), 7.51-7.49 (m, 1H), 7.42-7.33 (m, 3H), 7.24-7.19 (m, 3H), 7.16-7.08 (m, 4H), 6.84-6.80 (m, 4H), 6.51 (d, *J* = 7.2Hz, 1H), 6.08 (dd, *J* = 9.6Hz, 12.0Hz, 1H), 5.51 (d, *J* = 9.6Hz, 1H), 5.11 (d, *J* = 16.0Hz, 1H), 4.80 (d, *J* = 11.6Hz, 1H), 4.51 (d, *J* = 16.0Hz, 1H), 2.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 142.1, 137.2, 134.6, 131.5, 130.7, 129.9, 129.8, 129.5, 129.0, 128.6, 128.5, 127.8, 127.6, 126.8, 124.0, 122.9, 122.4, 110.0, 91.3, 70.9, 62.9, 55.7, 44.0; IR (KBr): 3439.0, 1958.2, 1717.4, 1612.6, 1554.5, 1489.4, 1366.0, 1176.6, 754.7, 700.0 cm^{-1}; HRMS (ESI) for $C_{30}H_{24}BrN_3O_3$ $[M+H]^+$ calcd 554.1074, found 554.1091.



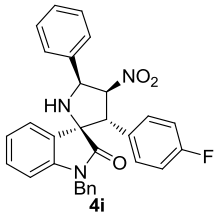
4g

(2'R, 3'S, 4'S, 5'S)-1-benzyl-3'-(4-chlorophenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyr -rolidin]-2-one (4g): white solid; $[\alpha]_D^{20}$ = -19.4 (*c* 0.412, CH_2Cl_2); mp 167-169 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 254 nm; $t_{R(major)}$ = 18.1 min, $t_{R(minor)}$ = 24.6 min, ee : 80%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.2Hz, 2H), 7.51-7.50 (m, 1H), 7.42-7.33 (m, 3H), 7.23-7.16 (m, 3H), 7.15-7.09 (m, 2H), 6.99 (d, *J* = 8.4Hz, 2H), 6.89 (d, *J* = 8.4Hz, 2H), 6.83 (d, *J* = 6.4Hz, 2H), 6.51 (d, *J* = 7.2Hz, 1H), 6.08 (dd, *J* = 9.6Hz, 12.0Hz, 1H), 5.51 (d, *J* = 9.2Hz, 1H), 5.10 (d, *J* = 16.0Hz, 1H), 4.82 (d, *J* = 12.0Hz, 1H), 4.52 (d, *J* = 16.0Hz, 1H), 2.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 142.1, 137.2, 134.6, 134.2, 130.2, 129.8, 129.6, 129.1, 128.6, 128.59, 128.58, 127.8, 127.6, 126.8, 124.0, 122.9, 110.0, 91.4, 71.0, 63.0, 55.6, 44.0; IR (KBr): 3440.7, 1957.8, 1721.5, 1613.0, 1554.7, 1468.3, 1366.9, 1178.6, 754.3, 699.6 cm^{-1}; HRMS (ESI) for $C_{30}H_{24}ClN_3O_3$ $[M+H]^+$ calcd 510.1579, found 510.1596.



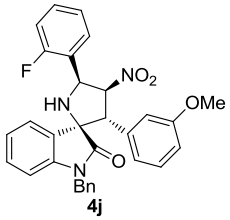
4h

(2'R, 3'S, 4'S, 5'S)-1-benzyl-3'-(furan-2-yl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin] -2-one (4h): white solid; $[\alpha]_D^{20}$ = -36.4 (*c* 0.834, CH_2Cl_2); mp 165-167 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 230 nm; $t_{R(major)}$ = 12.6 min, $t_{R(minor)}$ = 54.1 min, ee : 78%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.2Hz, 2H), 7.41-7.34 (m, 4H), 7.30-7.22 (m, 5H), 7.13 (t, *J* = 7.6Hz, 1H), 7.03-6.97 (m, 2H), 6.64 (d, *J* = 8.0Hz, 1H), 6.12 (t, *J* = 9.6Hz, 1H), 6.02 (dd, *J* = 2.0Hz, 2.8Hz, 1H), 5.90 (d, *J* = 3.2Hz, 1H), 5.46 (t, *J* = 8.8Hz, 1H), 5.16 (d, *J* = 16.0Hz, 1H), 5.01(d, *J* = 10.0Hz, 1H), 4.72 (d, *J* = 16.0Hz, 1H), 3.00 (d, *J* = 8.4Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 147.2, 142.4, 142.2, 136.3, 135.1, 129.5, 129.4, 129.0, 128.7, 128.6, 127.7, 127.5, 127.3, 124.3, 122.7, 110.1, 109.6, 108.1, 91.4, 70.4, 64.2, 50.9, 44.2; IR (KBr): 3440.4, 1957.9, 1713.3, 1612.4, 1555.2, 1468.4, 1370.3, 1180.6, 736.7, 698.3 cm^{-1}; HRMS (ESI) for $C_{28}H_{23}N_3O_4$ $[M+H]^+$ calcd 466.1761, found 466.1771.



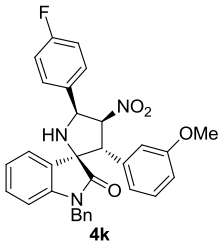
4i

(2'R, 3'S, 4'S, 5'S)-1-benzyl-3'-(4-fluorophenyl)-4'-nitro-5'-phenylspiro[indoline-3,2'-pyrrolidin]-2-one (4i): white solid; $[\alpha]_D^{20}$ = -31.1 (*c* 0.418, CH_2Cl_2); mp 173-175 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 254 nm; $t_{R(major)}$ = 14.5 min, $t_{R(minor)}$ = 30.5 min, ee : 80%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.2Hz, 2H), 7.50 (d, *J* = 6.8Hz, 1H), 7.43-7.33 (m, 3H), 7.23-7.16 (m, 3H), 7.14-7.08 (m, 2H), 6.94 (dd, *J* = 5.2Hz, 8.4Hz, 2H), 6.87 (d, *J* = 6.4Hz, 2H), 6.71 (t, *J* = 8.4Hz, 2H), 6.52 (d, *J* = 7.6Hz, 1H), 6.08 (dd, *J* = 9.6Hz, 12.0Hz, 1H), 5.51 (d, *J* = 9.2Hz, 1H), 5.08 (d, *J* = 16.0Hz, 1H), 4.84 (d, *J* = 12.0Hz, 1H), 4.55 (d, *J* = 16.0Hz, 1H), 2.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 163.7, 161.2, 142.1, 137.3, 134.7, 129.9, 129.84, 129.77, 129.7, 129.1, 128.7, 128.6, 127.8, 127.7, 127.59, 127.56, 126.9, 124.0, 122.9, 115.5, 115.3, 110.0, 91.7, 71.1, 63.1, 55.6, 44.1; IR (KBr): 3438.8, 1958.2, 1721.4, 1613.3, 1553.9, 1468.7, 1367.3, 1179.5, 755.2, 700.5 cm^{-1}; HRMS (ESI) for $C_{30}H_{24}FN_3O_3$ $[M+H]^+$ calcd 494.1874, found 494.1892.



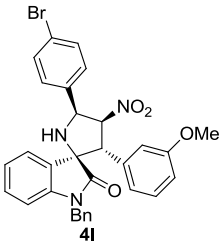
4j

(2'R, 3'S, 4'S, 5'S)-1-benzyl-5'-(2-fluorophenyl)-3'-(3-methoxyphenyl)-4'-nitrospiro[indoline-3,2'-pyrrolidin]-2-one (4j): white solid; $[\alpha]_D^{20}$ = -66.4 (*c* 0.256, CH_2Cl_2); mp 173-175 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 254 nm; $t_{R(major)}$ = 11.1 min, $t_{R(minor)}$ = 28.8 min, ee : 85%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12-8.08 (m, 1H), 7.54-7.52 (m, 1H), 7.35-7.27 (m, 2H), 7.23-7.14 (m, 3H), 7.12-7.03 (m, 3H), 6.98 (t, *J* = 8.0Hz, 1H), 6.89-6.87 (m, 2H), 6.69-6.67 (m, 1H), 6.62 (d, *J* = 7.6Hz 1H), 6.54-6.49 (m, 2H), 6.17 (dd, *J* = 9.2Hz, 10.8Hz, 1H), 5.90 (d, *J* = 9.2Hz, 1H), 5.14 (d, *J* = 16.0Hz, 1H), 4.87 (d, *J* = 10.8Hz, 1H), 4.57 (d, *J* = 16.0Hz, 1H), 3.55 (s, 3H), 2.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 161.5, 159.5, 159.1, 142.3, 134.7, 133.4, 130.43, 130.35, 129.7, 129.5, 129.33, 129.30, 128.7, 127.5, 126.7, 124.62, 124.58, 124.3, 124.2, 124.1, 122.8, 120.6, 115.2, 114.9, 114.3, 113.4, 110.0, 91.7, 71.4, 57.3, 56.61, 56.56, 55.1, 44.1; IR (KBr): 3442.4, 1957.7, 1711.4, 1607.1, 1553.1, 1465.3, 1364.7, 1174.9, 759.3, 700.2 cm^{-1}; HRMS (ESI) for $C_{31}H_{26}FN_3O_4$ $[M+H]^+$ calcd 524.1980, found 524.1999.



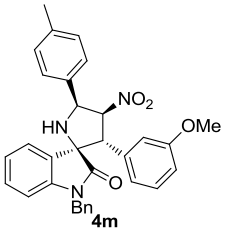
4k

(2'R, 3'S, 4'S, 5'S)-1-benzyl-5'-(4-fluorophenyl)-3'-(3-methoxyphenyl)-4'-nitrospiro[indoline-3,2'-pyrrolidin]-2-one (4k): white solid; $[\alpha]_D^{20}$ = -35.8 (*c* 0.614, CH_2Cl_2); mp 186-188 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 254 nm; $t_{R(major)}$ = 20.0 min, $t_{R(minor)}$ = 45.0 min, ee : 86%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2H), 7.51-7.49 (m, 1H), 7.20-7.13 (m, 3H), 7.12-7.05 (m, 4H), 6.95 (t, *J* = 8.0Hz, 1H), 6.85-6.83 (m, 2H), 6.67 (dd, *J* = 2.0Hz, 8.0Hz, 1H), 6.58 (d, *J* = 7.6Hz 1H), 6.51 (s, 1H), 6.48-6.46 (m, 1H), 6.11 (dd, *J* = 9.6Hz, 11.6Hz, 1H), 5.50 (d, *J* = 9.6Hz, 1H), 5.12 (d, *J* = 16.0Hz, 1H), 4.82 (d, *J* = 12.0Hz, 1H), 4.54 (d, *J* = 16.0Hz, 1H), 3.53 (s, 3H), 2.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 164.2, 161.8, 159.4, 142.2, 134.6, 133.4, 133.3, 133.0, 130.0, 129.66, 129.65, 129.6, 129.4, 128.7, 127.5, 126.6, 124.0, 122.8, 120.5, 115.6, 115.4, 114.3, 113.4, 110.0, 91.3, 71.0, 62.0, 55.7, 55.0, 44.1; IR (KBr): 3441.8, 1957.2, 1714.2, 1606.8, 1554.9, 1467.5, 1366.9, 1176.9, 755.5, 698.0 cm^{-1}; HRMS (ESI) for $C_{31}H_{26}FN_3O_4$ $[M+H]^+$ calcd 524.1980, found 524.1994.



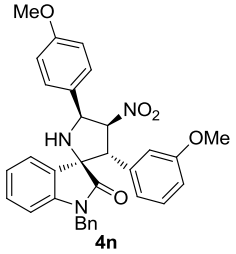
4l

(2'R, 3'S, 4'S, 5'S)-1-benzyl-5'-(4-bromophenyl)-3'-(3-methoxyphenyl)-4'-nitrospiro[indoline-3,2'-pyrrolidin]-2-one (4l): white solid; $[\alpha]_D^{20}$ = -35.1 (*c* 0.570, CH_2Cl_2); mp 190-192 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 254 nm; $t_{R(major)}$ = 23.6 min, $t_{R(minor)}$ = 61.5 min, ee : 86%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4Hz, 2H), 7.52-7.48 (m, 3H), 7.20-7.14 (m, 3H), 7.12-7.08 (m, 2H), 6.95 (t, *J* = 8.0Hz, 1H), 6.84-6.82 (m, 2H), 6.67 (dd, *J* = 2.0Hz, 8.0Hz, 1H), 6.58 (d, *J* = 8.0Hz, 1H), 6.51-6.46 (m, 2H), 6.12 (dd, *J* = 9.6Hz, 12.0Hz, 1H), 5.46 (d, *J* = 9.2Hz, 1H), 5.12 (d, *J* = 16.0Hz, 1H), 4.80 (d, *J* = 12.0Hz, 1H), 4.52 (d, *J* = 16.0Hz, 1H), 3.53 (s, 3H), 2.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 159.4, 142.2, 136.7, 134.6, 132.9, 131.6, 129.9, 129.7, 129.5, 129.4, 128.7, 127.5, 126.6, 124.0, 123.1, 122.8, 120.5, 114.4, 113.4, 110.0, 91.1, 70.9, 62.0, 55.7, 55.0, 44.0; IR (KBr): 3439.8, 1954.7, 1716.5, 1605.4, 1555.4, 1467.2, 1364.0, 1175.8, 755.7, 697.8 cm^{-1}; HRMS (ESI) for $C_{31}H_{26}BrN_3O_4$ $[M+H]^+$ calcd 584.1179, found 584.1203.



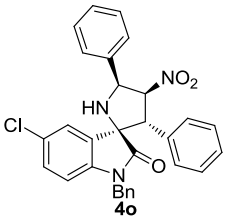
4m

(2'R, 3'S, 4'S, 5'S)-1-benzyl-3'-(3-methoxyphenyl)-4'-nitro-5'-(p-tolyl)spiro[indoline-3,2'-pyrrolidin]-2-one (4m): white solid; $[\alpha]_D^{20}$ = -40.6 (*c* 0.616, CH_2Cl_2); mp 188-190 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 254 nm; $t_{R(major)}$ = 17.7 min, $t_{R(minor)}$ = 56.2 min, ee : 81%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6Hz, 2H), 7.52-7.50 (m, 1H), 7.21-7.16 (m, 5H), 7.12-7.06 (m, 2H), 6.95 (t, *J* = 8.0Hz, 1H), 6.84 (d, *J* = 6.8Hz, 2H), 6.67 (dd, *J* = 2.4Hz, 8.4Hz, 1H), 6.59 (d, *J* = 7.6Hz 1H), 6.52 (s, 1H), 6.47-6.45 (m, 1H), 6.11 (dd, *J* = 9.6Hz, 11.6Hz, 1H), 5.48 (d, *J* = 9.2Hz, 1H), 5.13 (d, *J* = 16.0Hz, 1H), 4.84 (d, *J* = 12.0Hz, 1H), 4.53 (d, *J* = 16.0Hz, 1H), 3.53 (s, 3H), 2.95 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 159.4, 142.2, 138.8, 134.7, 134.1, 133.4, 130.0, 129.5, 129.34, 129.27, 128.7, 127.6, 127.4, 126.6, 124.1, 122.7, 120.6, 114.3, 113.4, 109.9, 92.1, 71.3, 63.3, 56.6, 55.0, 44.0, 21.2; IR (KBr): 3441.0, 1957.3, 1716.1, 1604.4, 1553.9, 1466.2, 1363.8, 1259.8, 1175.6, 740.8, 698.8 cm^{-1}; HRMS (ESI) for $C_{32}H_{29}N_3O_4$ $[M+H]^+$ calcd 520.2231, found 520.2246.



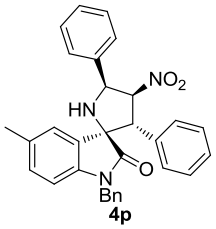
4n

(2'R, 3'S, 4'S, 5'S)-1-benzyl-3'-(3-methoxyphenyl)-5'-(4-methoxyphenyl)-4'-nitrospiro[indoline-3,2'-pyrrolidin]-2-one (4n): white solid, $[\alpha]_D^{20}$ = -32.6 (*c* 0.644, CH_2Cl_2); mp 162-164 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 254 nm; $t_{R(major)}$ = 22.2 min, $t_{R(minor)}$ = 75.2 min, ee : 77%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4Hz, 2H), 7.52-7.50 (m, 1H), 7.19-7.08 (m, 5H), 6.97-6.90 (m, 3H), 6.83 (d, *J* = 6.4Hz, 2H), 6.7 (d, *J* = 6.8Hz, 1H), 6.59 (d, *J* = 7.6Hz, 1H), 6.52 (s, 1H), 6.47-6.45 (m, 1H), 6.12-6.07 (m, 1H), 5.47 (d, *J* = 9.6Hz, 1H), 5.13 (d, *J* = 16.0Hz, 1H), 4.84 (d, *J* = 11.6Hz, 1H), 4.53 (d, *J* = 16.0Hz, 1H), 3.78 (s, 3H), 3.52 (s, 3H), 2.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 160.0, 159.4, 142.2, 134.6, 133.3, 130.0, 129.5, 129.3, 129.2, 129.0, 128.6, 127.4, 126.6, 124.1, 122.7, 120.1, 114.3, 113.9, 113.4, 109.9, 91.8, 71.1, 62.8, 56.3, 55.2, 55.0, 44.0; IR (KBr): 3442.7, 1957.4, 1719.4, 1610.7, 1554.2, 1467.2, 1367.2, 1176.5, 753.9, 697.5 cm^{-1}; HRMS (ESI) for $C_{32}H_{29}N_3O_5$ $[M+H]^+$ calcd 536.2180, found 536.2194.



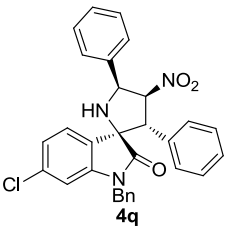
4o

(2'R, 3'S, 4'S, 5'S)-1-benzyl-5-chloro-4'-nitro-3',5'-diphenylspiro[indoline-3,2'-pyrrolidin] -2-one (4o): white solid; $[\alpha]_D^{20}$ = -67.6 (*c* 0.444, CH_2Cl_2); mp 98-100 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 267 nm; $t_{R(major)}$ = 10.2 min, $t_{R(minor)}$ = 38.7 min, ee : 80%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.2Hz, 2H), 7.46 (d, *J* = 2.0Hz, 1H), 7.43-7.40 (m, 2H), 7.38-7.34 (m, 1H), 7.22-7.13 (m, 4H), 7.10-7.05 (m, 3H), 7.00 (d, *J* = 7.2Hz, 2H), 6.86 (d, *J* = 6.8Hz, 2H), 6.37 (d, *J* = 8.4Hz, 1H), 6.13 (dd, *J* = 9.6Hz, 12.0Hz, 1H), 5.49 (d, *J* = 9.2Hz, 1H), 5.07 (d, *J* = 15.6Hz, 1H), 4.89 (d, *J* = 11.6Hz, 1H), 4.55 (d, *J* = 16.0Hz, 1H), 2.94 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 140.6, 137.0, 134.3, 131.7, 131.4, 129.4, 129.1, 128.8, 128.64, 128.58, 128.3, 128.2, 128.1, 127.73, 127.70, 126.9, 124.6, 110.8, 91.3, 71.4, 63.3, 56.4, 44.2; IR (KBr): 3442.9, 1955.7, 1712.6, 1609.6, 1553.6, 1455.7, 1357.1, 1174.6, 745.3, 698.4 cm^{-1}; HRMS (ESI) for $C_{30}H_{24}ClN_3O_3$ $[M+H]^+$ calcd 510.1579, found 510.1585.



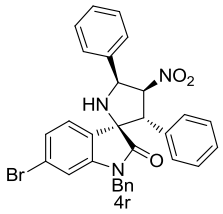
4p

(2'R, 3'S, 4'S, 5'S)-1-benzyl-5-methyl-4'-nitro-3',5'-diphenylspiro[indoline-3,2'-pyrrolidin] -2-one (4p): white solid; $[\alpha]_D^{20}$ = -72.3 (*c* 0.650, CH_2Cl_2); mp 176-178 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 254 nm; $t_{R(major)}$ = 15.5 min, $t_{R(minor)}$ = 46.6 min, ee : 82%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.2Hz, 2H), 7.45-7.35 (m, 4H), 7.20-7.14 (m, 4H), 7.09-7.02 (m, 4H), 6.94-6.86 (m, 3H), 6.37 (d, *J* = 8.0Hz, 1H), 6.21 (t, *J* = 10.8Hz, 1H), 5.55 (d, *J* = 9.2Hz, 1H), 5.11 (d, *J* = 16.0Hz, 1H), 4.91 (d, *J* = 12.0Hz, 1H), 4.55 (d, *J* = 16.0Hz, 1H), 2.97 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 139.7, 137.4, 134.8, 132.3, 131.8, 129.9, 129.7, 128.9, 128.6, 128.5, 128.3, 128.2, 128.0, 127.8, 127.4, 126.8, 124.8, 109.6, 91.6, 71.3, 63.1, 56.2, 44.0, 21.2; IR (KBr): 3445.2, 1958.3, 1709.3, 1615.5, 1553.4, 1494.3, 1367.4, 1165.7, 746.1, 698.9 cm^{-1}; HRMS (ESI) for $C_{31}H_{27}N_3O_3$ $[M+H]^+$ calcd 490.2125, found 490.2141.



4q

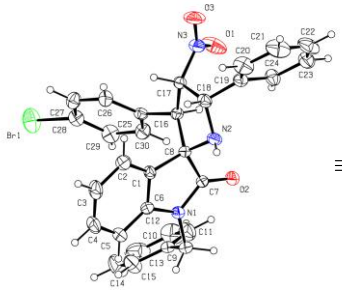
(2'R, 3'S, 4'S, 5'S)-1-benzyl-6-chloro-4'-nitro-3',5'-diphenylspiro[indoline-3,2'-pyrrolidin]-2-one (4q): white solid; $[\alpha]_D^{20}$ = -25.2 (*c* 0.220, CH_2Cl_2); mp 190-192 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 220 nm; $t_{R(major)}$ = 19.0 min, $t_{R(minor)}$ = 35.3 min, ee : 81%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.2Hz, 2H), 7.42-7.33 (m, 4H), 7.25-7.13 (m, 4H), 7.08-7.04 (m, 3H), 6.98 (d, *J* = 7.6Hz, 2H), 6.88-6.86 (m, 2H), 6.46 (d, *J* = 1.6Hz, 1H), 6.12 (dd, *J* = 9.6Hz, 12.0Hz, 1H), 5.47 (d, *J* = 9.6Hz, 1H), 5.07 (d, *J* = 16.0Hz, 1H), 4.88 (d, *J* = 11.6Hz, 1H), 4.52 (d, *J* = 16.0Hz, 1H), 2.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 143.4, 137.1, 135.2, 134.1, 131.5, 129.1, 128.8, 128.59, 128.56, 128.4, 128.3, 128.0, 127.72, 127.69, 126.8, 125.0, 122.6, 110.4, 91.4, 70.9, 63.2, 56.3, 44.2; IR (KBr): 3440.0, 1957.8, 1729.0, 1608.3, 1554.4, 1490.8, 1372.8, 1179.7, 744.7, 699.7 cm^{-1}; HRMS (ESI) for $C_{30}H_{24}ClN_3O_3$ $[M+H]^+$ calcd 510.1579, found 510.1596.

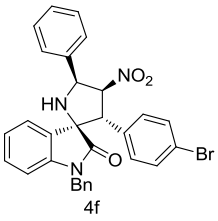


4r

(2'R, 3'S, 4'S, 5'S)-1-benzyl-6-bromo-4'-nitro-3',5'-diphenylspiro[indoline-3,2'-pyrrolidin]-2-one (4r): white solid; $[\alpha]_D^{20}$ = -24.2 (*c* 0.784, CH_2Cl_2); mp 194-196 ^oC; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: *i*-PrOH = 60:40), 1.0 mL/min, λ = 220 nm; $t_{R(major)}$ = 19.4 min, $t_{R(minor)}$ = 35.3 min, ee : 83%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.2Hz, 2H), 7.42-7.38 (m, 2H), 7.36-7.33 (m, 2H), 7.23-7.16 (m, 4H), 7.13 (d, *J* = 7.2Hz, 1H), 7.06 (t, *J* = 7.6Hz, 2H), 6.97 (d, *J* = 7.2Hz, 2H), 6.87 (d, *J* = 6.4Hz, 2H), 6.61 (d, *J* = 1.6Hz, 1H), 6.11 (dd, *J* = 9.6Hz, 11.6Hz, 1H), 5.46 (d, *J* = 9.2Hz, 1H), 5.06 (d, *J* = 16.0Hz, 1H), 4.87 (d, *J* = 11.6Hz, 1H), 4.51 (d, *J* = 16.0Hz, 1H), 2.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 143.5, 137.1, 134.1, 131.5, 129.0, 128.9, 128.8, 128.6, 128.3, 128.0, 127.72, 127.69, 126.8, 125.6, 125.3, 123.1, 113.1, 91.4, 91.0, 63.2, 56.2, 44.2; IR (KBr): 3440.1, 1956.0, 1726.9, 1604.3, 1554.2, 1487.0, 1372.0, 1179.1, 740.9, 699.5 cm^{-1}; HRMS (ESI) for $C_{30}H_{24}BrN_3O_3$ $[M+H]^+$ calcd 554.1074, found 554.1090.

5. X-ray Crystallographic data of 4f

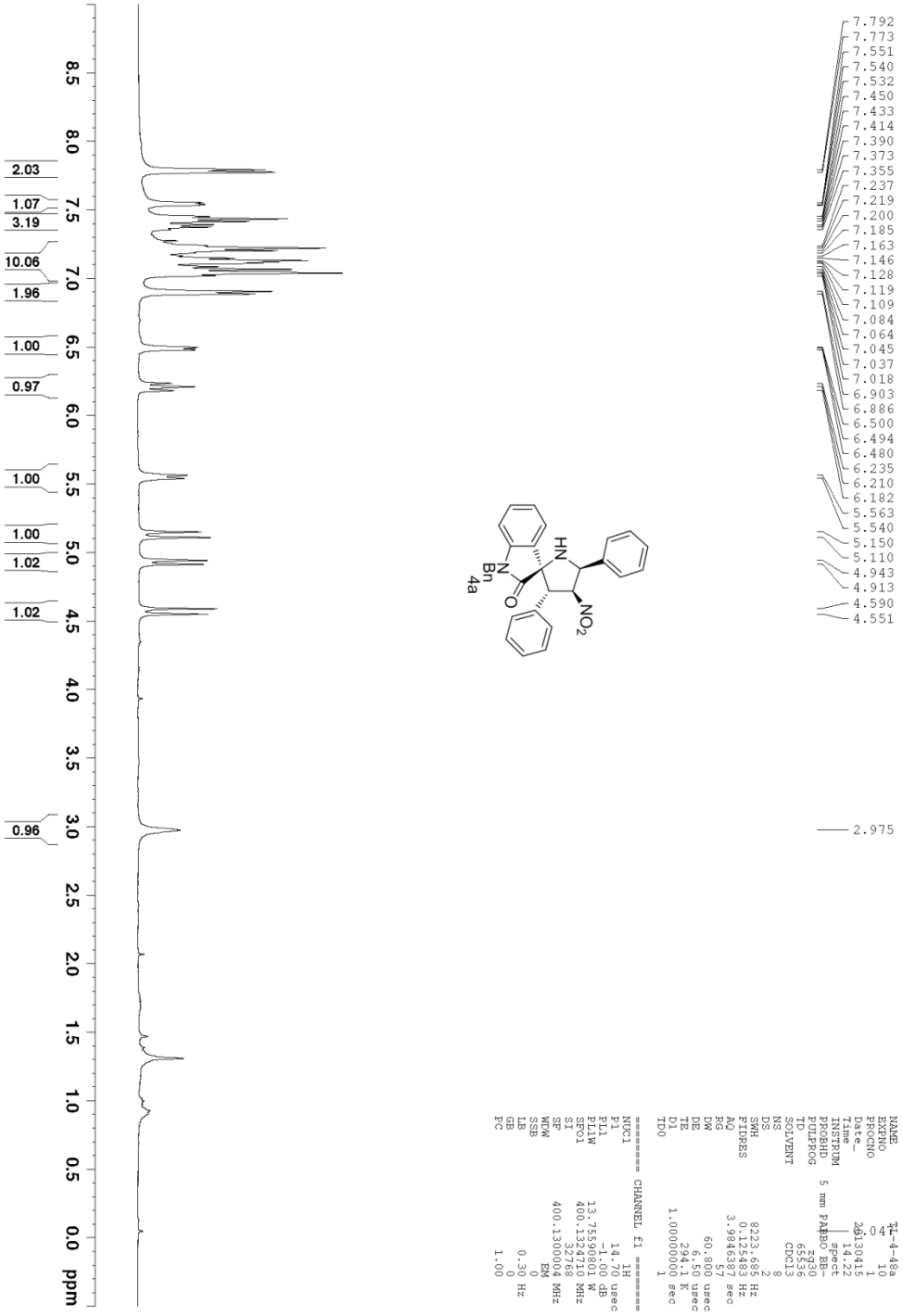


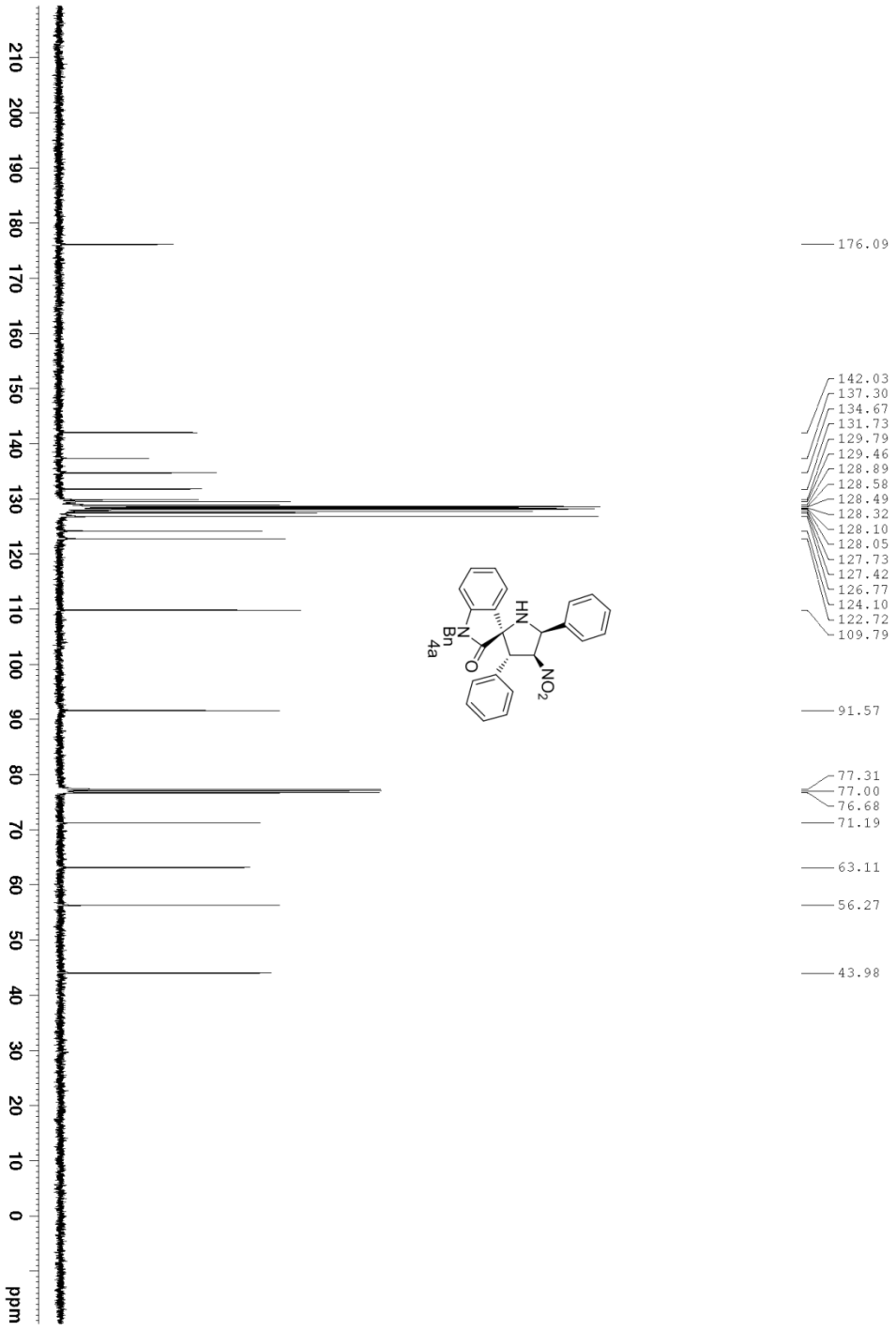


4f

Empirical formula	$C_{30}H_{24}N_3O_3Br$
Formula weight	554.43
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.4213(5)
b/Å	13.1929(4)
c/Å	17.2730(5)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2602.68(16)
Z	4
ρ_{calc}mg/mm^3	1.415
m/mm^{-1}	1.616
F(000)	1136.0
Crystal size/mm^3	0.28 × 0.16 × 0.11
2Θ range for data collection	5.92 to 52.74°
Index ranges	$-8 \leqslant h \leqslant 14$, $-16 \leqslant k \leqslant 16$, $-21 \leqslant l \leqslant 21$
Reflections collected	9098
Independent reflections	5296[R(int) = 0.0404]
Data/restraints/parameters	5296/0/338
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0530, wR_2 = 0.0731
Final R indexes [all data]	R_1 = 0.1025, wR_2 = 0.0883
Largest diff. peak/hole / e Å^{-3}	0.33/-0.37
Flack parameter	-0.005(8)

6. ^{1}H NMR and ^{13}C NMR spectra

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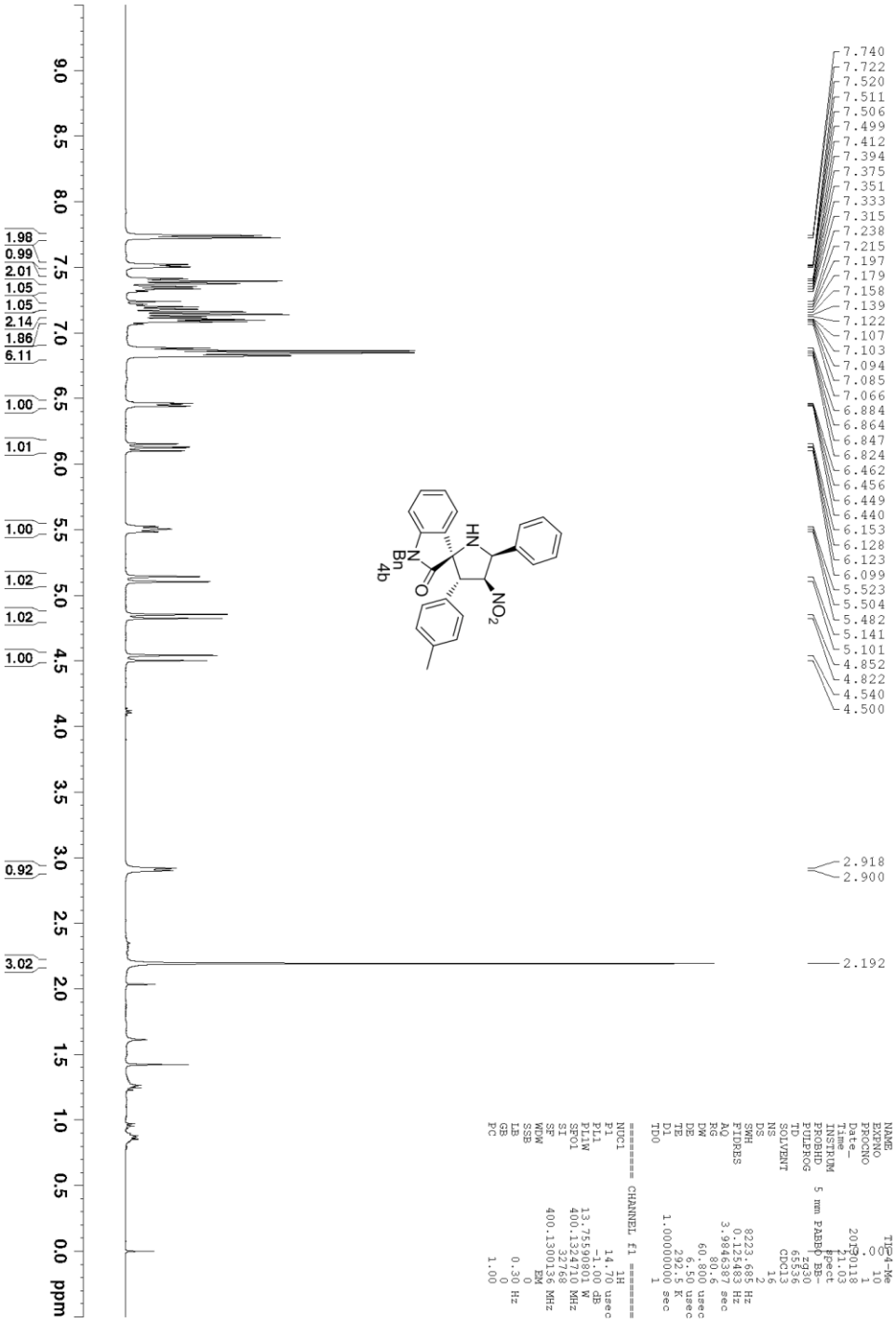
142.03
137.30
134.67
131.73
129.79
129.46
128.89
128.58
128.49
128.32
128.10
128.05
127.73
127.42
126.77
124.10
122.72
109.79
91.57
77.31
77.00
76.68
71.19
63.11
56.27
43.98
ppm
HN
N
Bn
O
NO2
4a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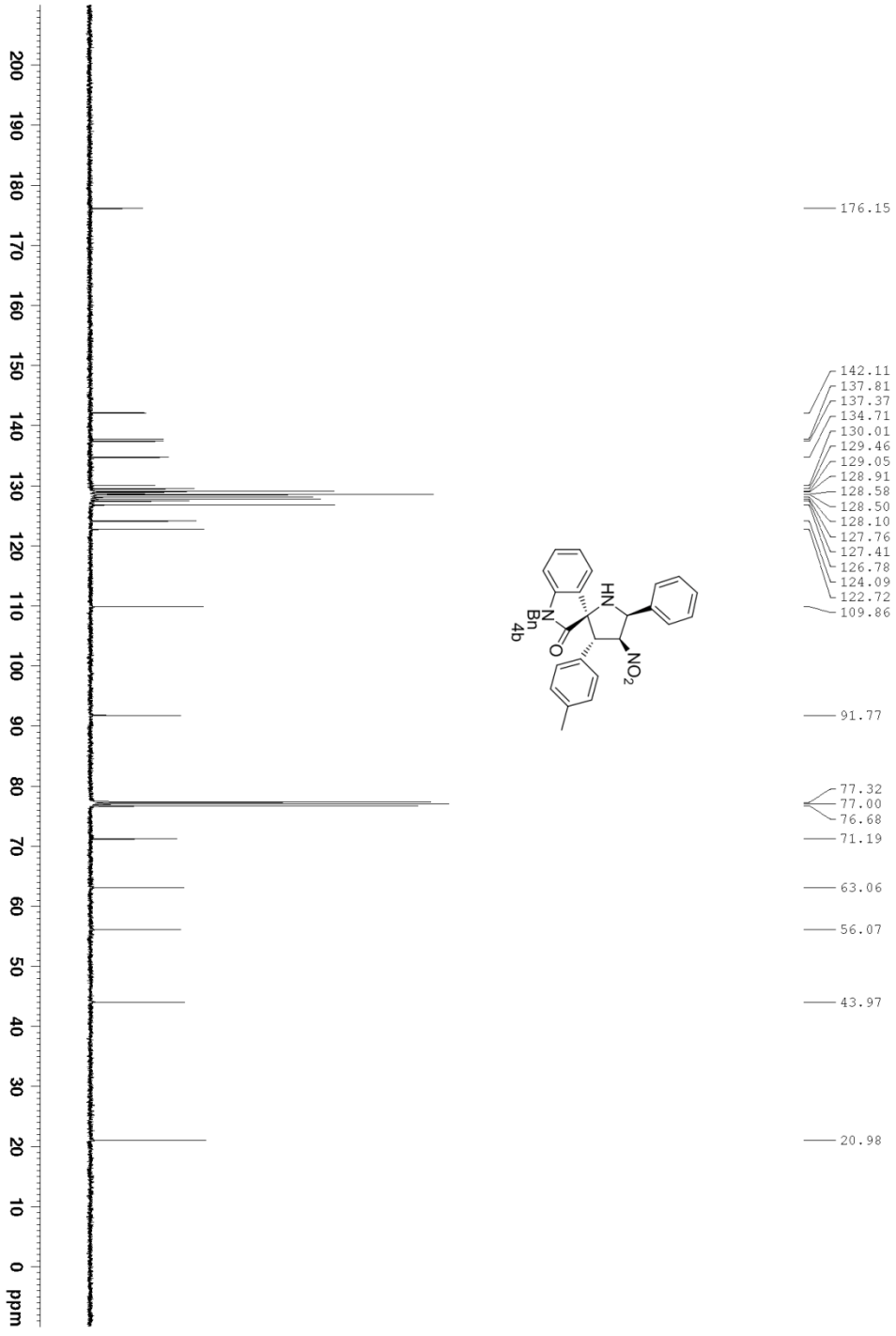
7.520
7.511
7.506
7.499
7.412
7.394
7.375
7.351
7.333
7.315
7.238
7.215
7.197
7.179
7.158
7.139
7.122
7.107
7.103
7.094
7.085
7.066
6.884
6.864
6.847
6.824
6.462
6.456
6.449
6.440
6.153
6.128
6.123
6.099
5.523
5.504
5.482
5.141
5.101
4.852
4.822
4.540
4.500
2.918
2.900
2.192
1.98
0.99
2.01
1.05
1.05
2.14
1.86
6.11
1.00
1.01
1.00
1.02
1.02
1.00
0.92
3.02
HN
N
Bn
4b
O
NO2
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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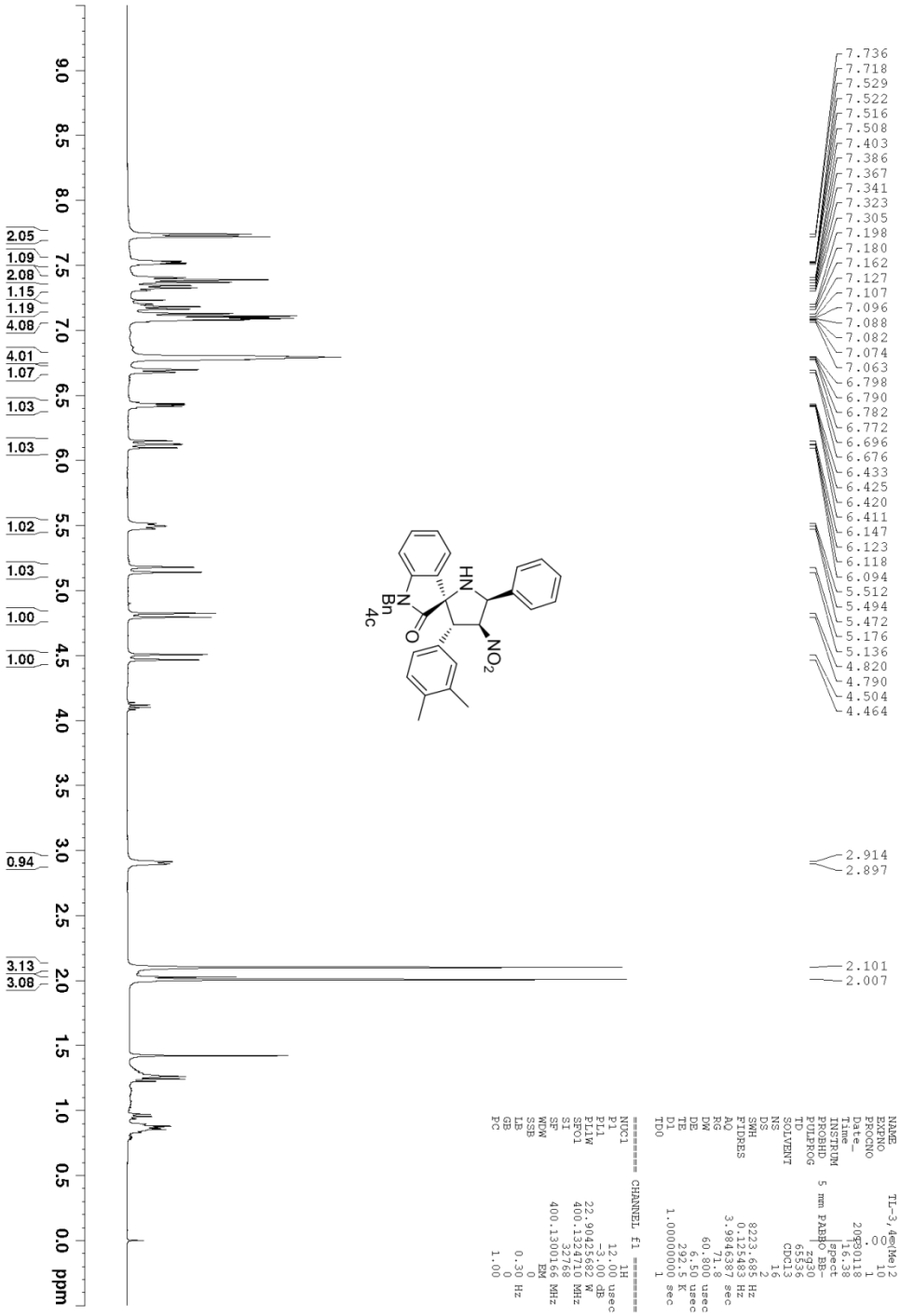
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
176.15
142.11
137.81
137.37
134.71
130.01
129.46
129.05
128.91
128.58
128.50
128.10
127.76
127.41
126.78
124.09
122.72
109.86
91.77
77.32
77.00
76.68
71.19
63.06
56.07
43.97
20.98
HN
N
Bn
O
NO2
4b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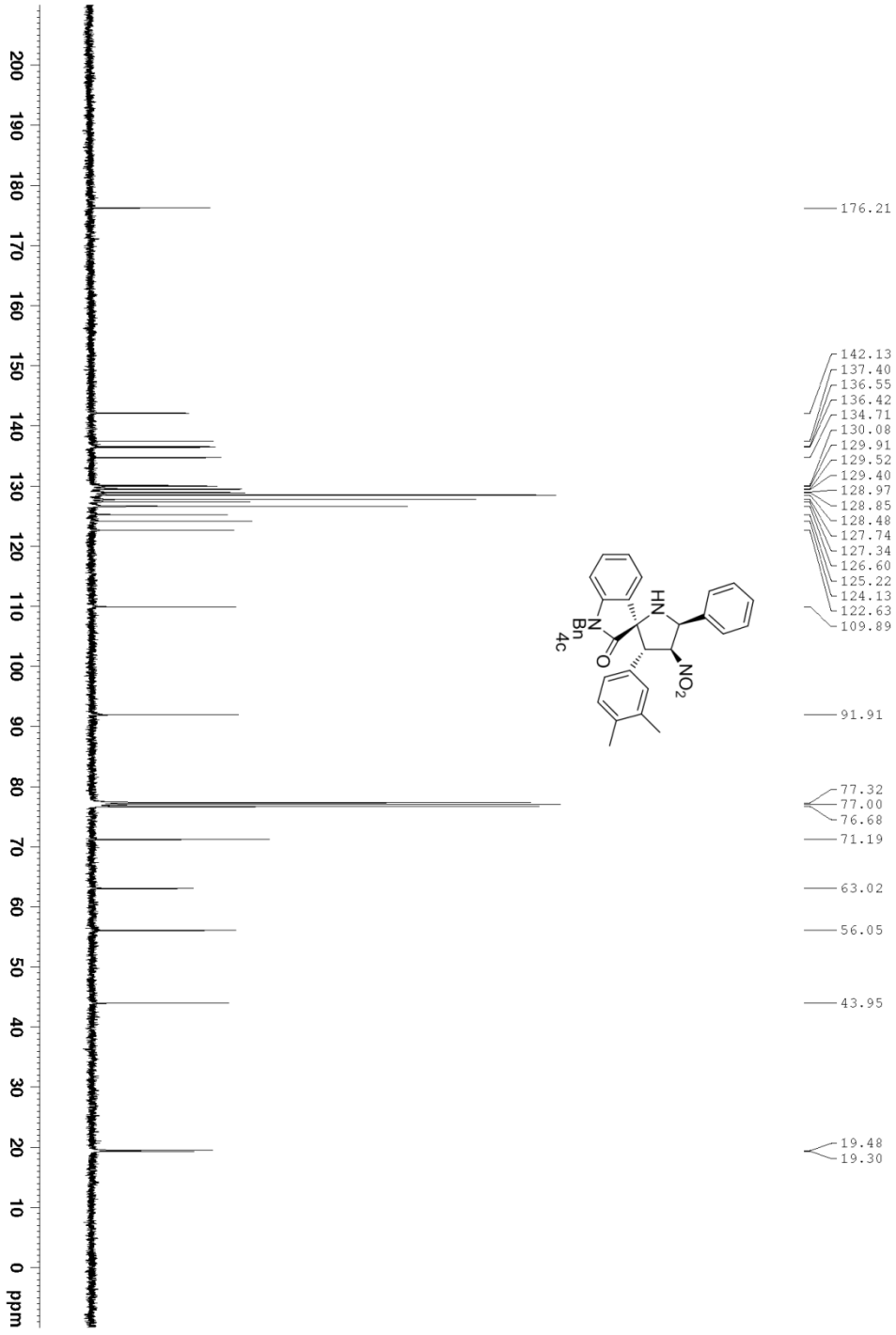
7.529
7.522
7.516
7.508
7.403
7.386
7.367
7.341
7.323
7.305
7.198
7.180
7.162
7.127
7.107
7.096
7.088
7.082
7.074
7.063
6.798
6.790
6.782
6.772
6.696
6.676
6.433
6.425
6.420
6.411
6.147
6.123
6.118
6.094
5.512
5.494
5.472
5.176
5.136
4.820
4.790
4.504
4.464
2.914
2.897
2.101
2.007
2.05
1.09
2.08
1.15
1.19
4.08
4.01
1.07
1.03
1.03
1.02
1.03
1.00
1.00
0.94
3.13
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
HN
N
Bn
O
NO2
4c
NAME TL-3,4c(Me)2
EXPNO 11
PROCNO 1
Date_ 20130118
Time_ 16.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 71.8
DW 60.800 usec
DE 6.50 usec
TE 292.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -3.00 dB
PL1W 22.90425682 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300166 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00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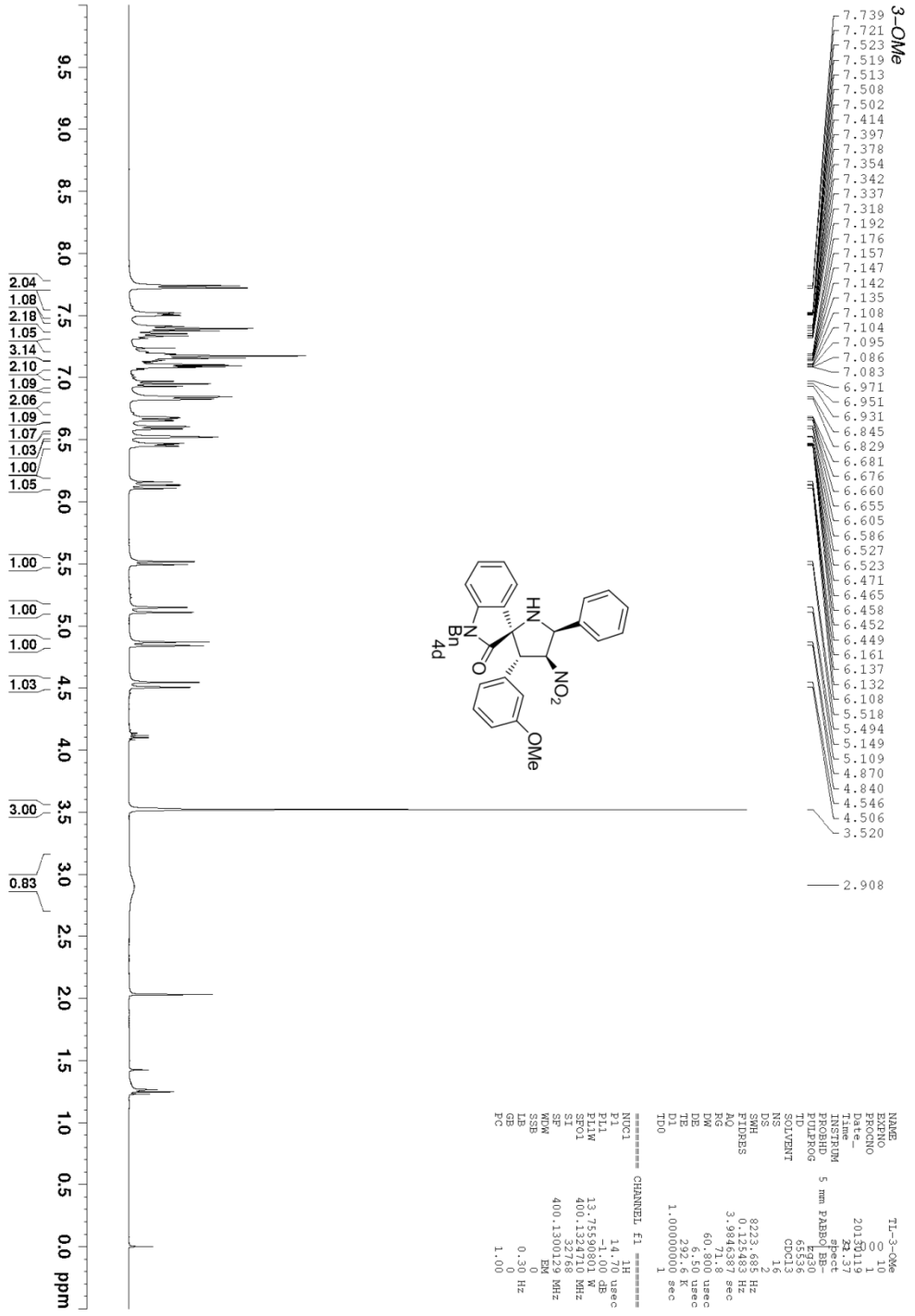
142.13
137.40
136.55
136.42
134.71
130.08
129.91
129.52
129.40
128.97
128.85
128.48
127.74
127.34
126.60
125.22
124.13
122.63
109.89
91.91
77.32
77.00
76.68
71.19
63.02
56.05
43.95
19.48
19.30
HN
N
Bn
O
NO2
4c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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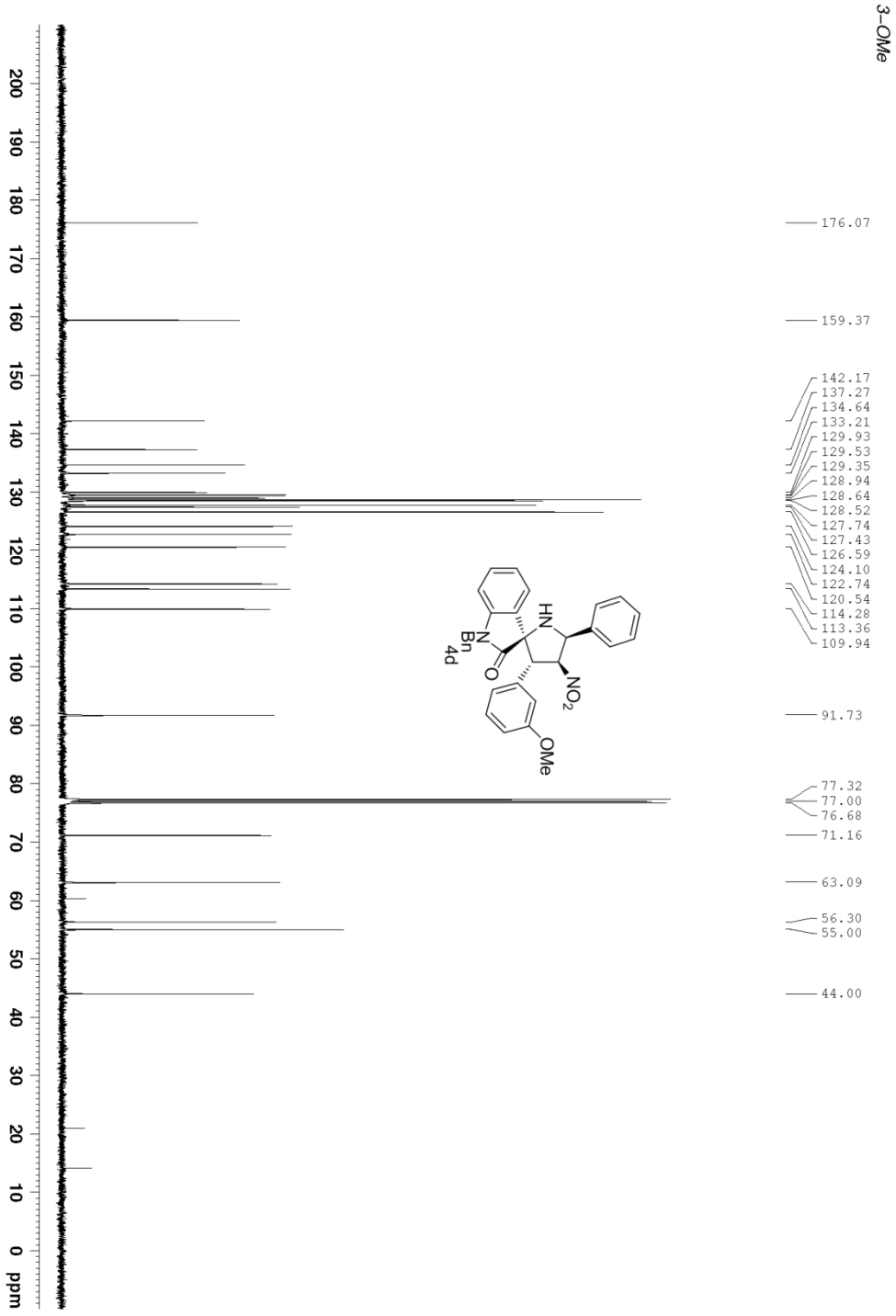
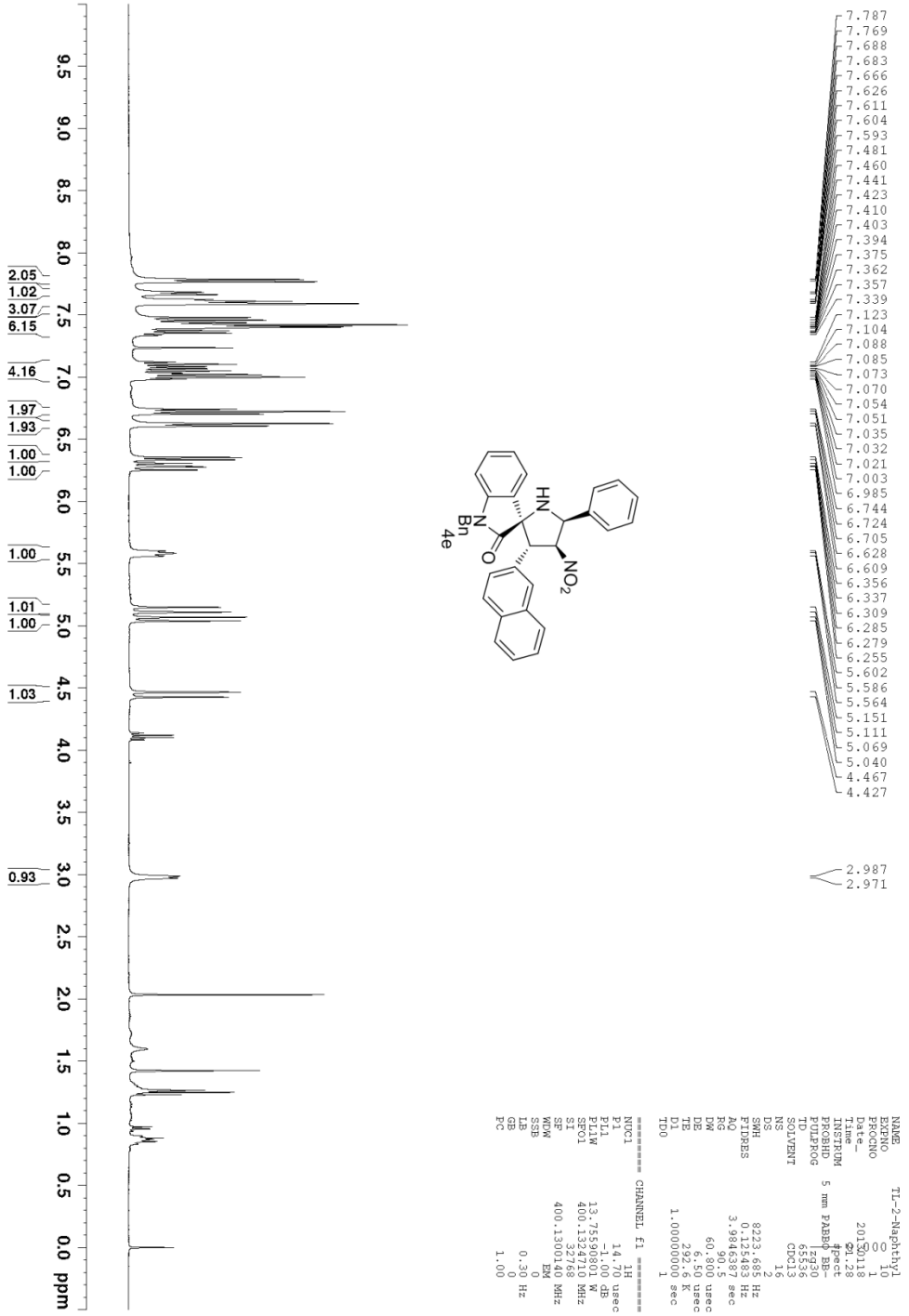
7.721
7.523
7.519
7.513
7.508
7.502
7.414
7.397
7.378
7.354
7.342
7.337
7.318
7.192
7.176
7.157
7.147
7.142
7.135
7.108
7.104
7.095
7.086
7.083
6.971
6.951
6.931
6.845
6.829
6.681
6.676
6.660
6.655
6.605
6.586
6.527
6.523
6.471
6.465
6.458
6.452
6.449
6.161
6.137
6.132
6.108
5.518
5.494
5.149
5.109
4.870
4.840
4.546
4.506
3.520
2.908
HN
N
Bn
O
NO2
OMe
4d
2.04
1.08
2.18
1.05
3.14
2.10
1.09
2.06
1.09
1.07
1.03
1.00
1.05
1.00
1.00
1.00
1.03
3.00
0.83
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
NAME TL-3-OMe
EXPNO 10
PROCNO 1
Date_ 20130119
Time 21.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9845387 sec
RG 71
DW 60.800 usec
DE 6.50 usec
TE 292.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 -1.00 dB
PL1W 13.75590801 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300129 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


3-OMe
176.07
159.37
142.17
137.27
134.64
133.21
129.93
129.53
129.35
128.94
128.64
128.52
127.74
127.43
126.59
124.10
122.74
120.54
114.28
113.36
109.94
91.73
77.32
77.00
76.68
71.16
63.09
56.30
55.00
44.00
HN
N
Bn
O
NO2
OMe
4d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.604
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7.423
7.410
7.403
7.394
7.375
7.362
7.357
7.339
7.123
7.104
7.088
7.085
7.073
7.070
7.054
7.051
7.035
7.032
7.021
7.003
6.985
6.744
6.724
6.705
6.628
6.609
6.356
6.337
6.309
6.285
6.279
6.255
5.602
5.586
5.564
5.151
5.111
5.069
5.040
4.467
4.427
2.987
2.971
2.05
1.02
3.07
6.15
4.16
1.97
1.93
1.00
1.00
1.00
1.01
1.00
1.03
0.93
HN
N
Bn
O
NO2
4e
NAME TL-2-Naphthyl
EXPNO 10
PROCNO 1
Date_ 20130118
Time 21.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 90.5
DW 60.800 usec
DE 6.50 usec
TE 292.6 K
D1 1.00000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 1H
P1 14.70 usec
PL1 -1.00 dB
PL1W 13.75590801 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300140 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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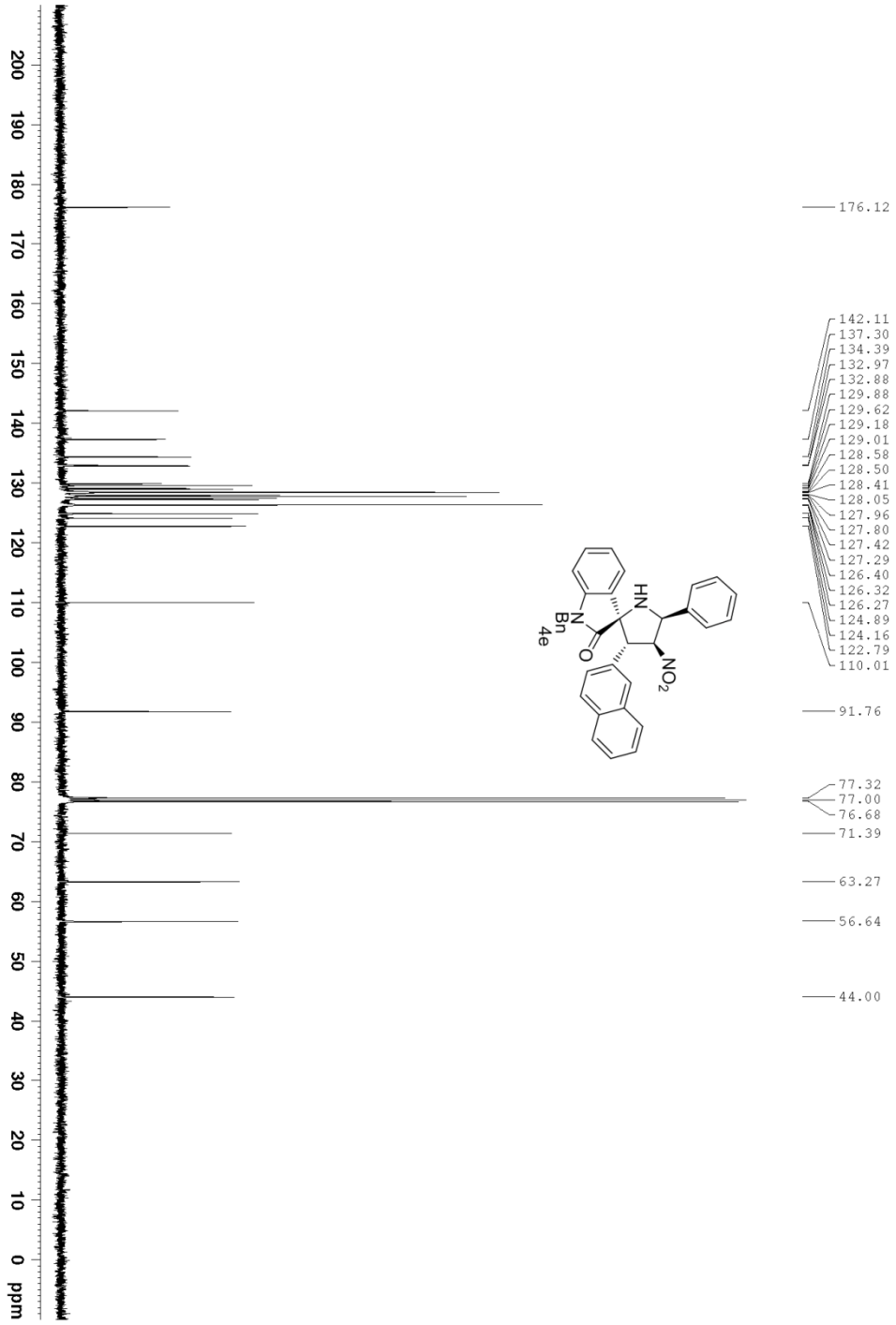
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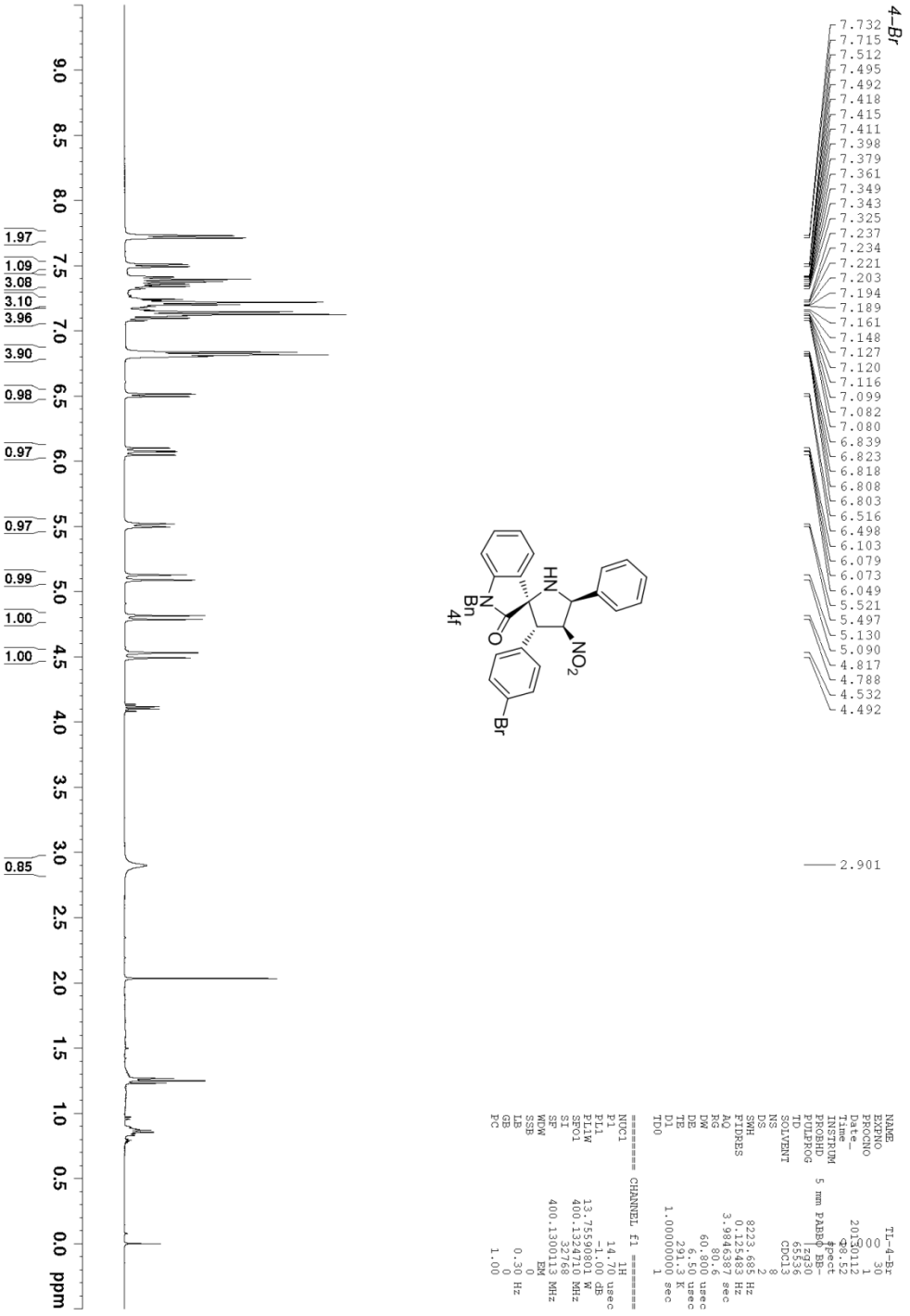
128.41
128.05
127.96
127.80
127.42
127.29
126.40
126.32
126.27
124.89
124.16
122.79
110.01
91.76
77.32
77.00
76.68
71.39
63.27
56.64
44.00
HN
N
Bn
O
NO2
4e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



NAME TL-4-Br
EXPNO 30
PROCNO 1
Date_ 20130112
Time_ 18.52
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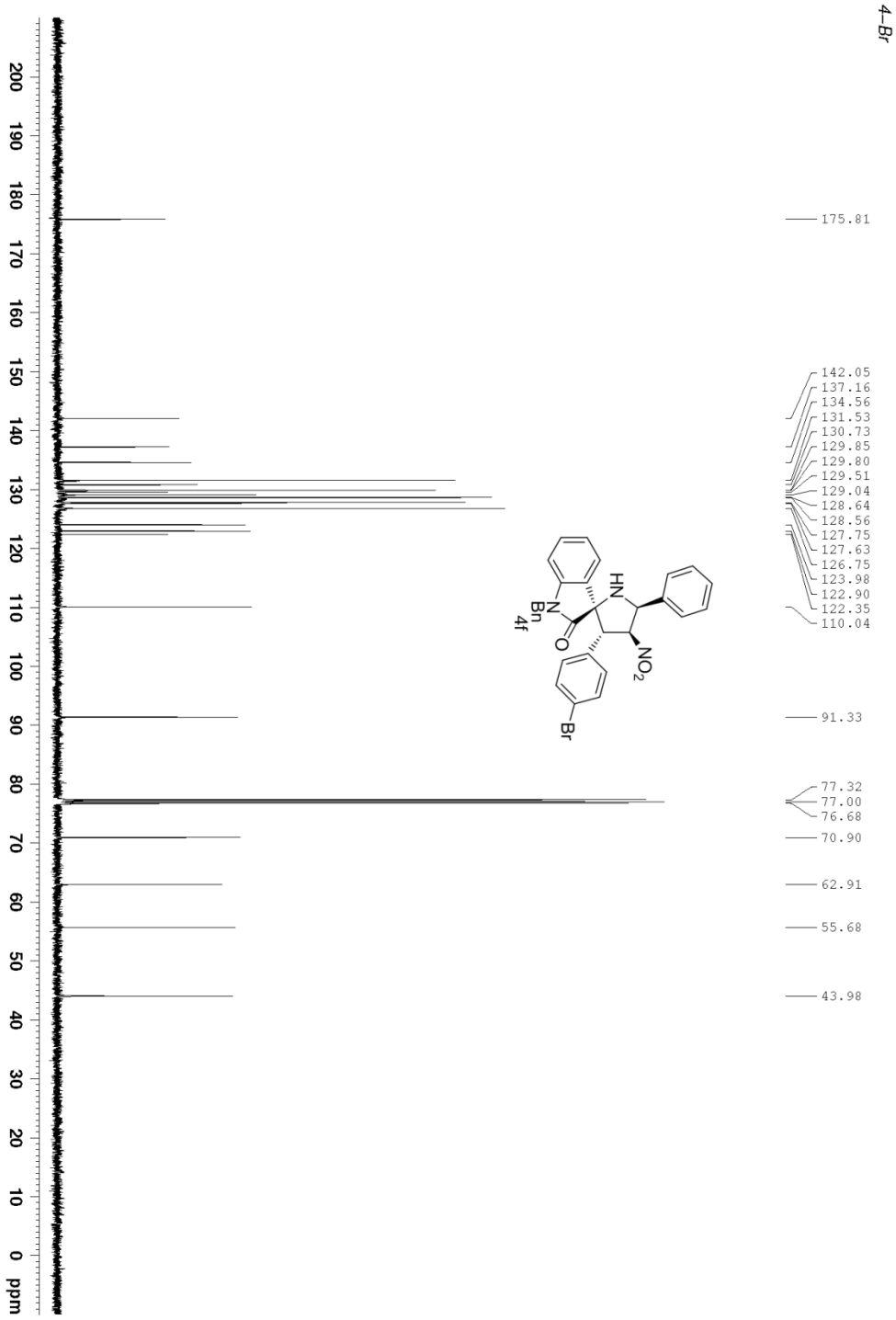
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 80.6
DW 60.800 usec
DE 6.50 usec
TE 291.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 -1.00 dB
PLIW 13.75590801 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300113 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00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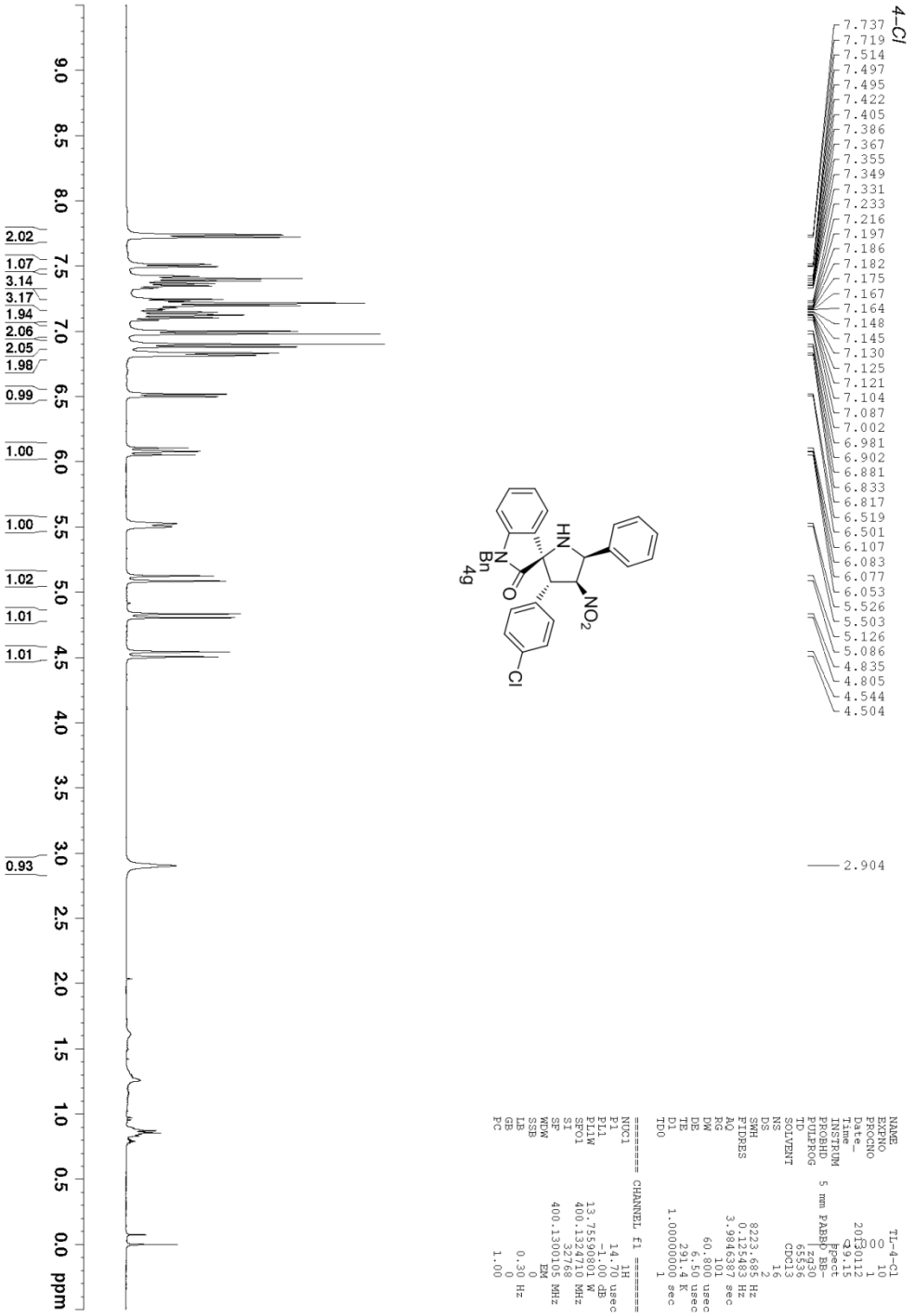
137.16
134.56
131.53
130.73
129.85
129.80
129.51
129.04
128.64
128.56
127.75
127.63
126.75
123.98
122.90
122.35
110.04
91.33
77.32
77.00
76.68
70.90
62.91
55.68
43.98
HN
N
Bn
4f
O
NO2
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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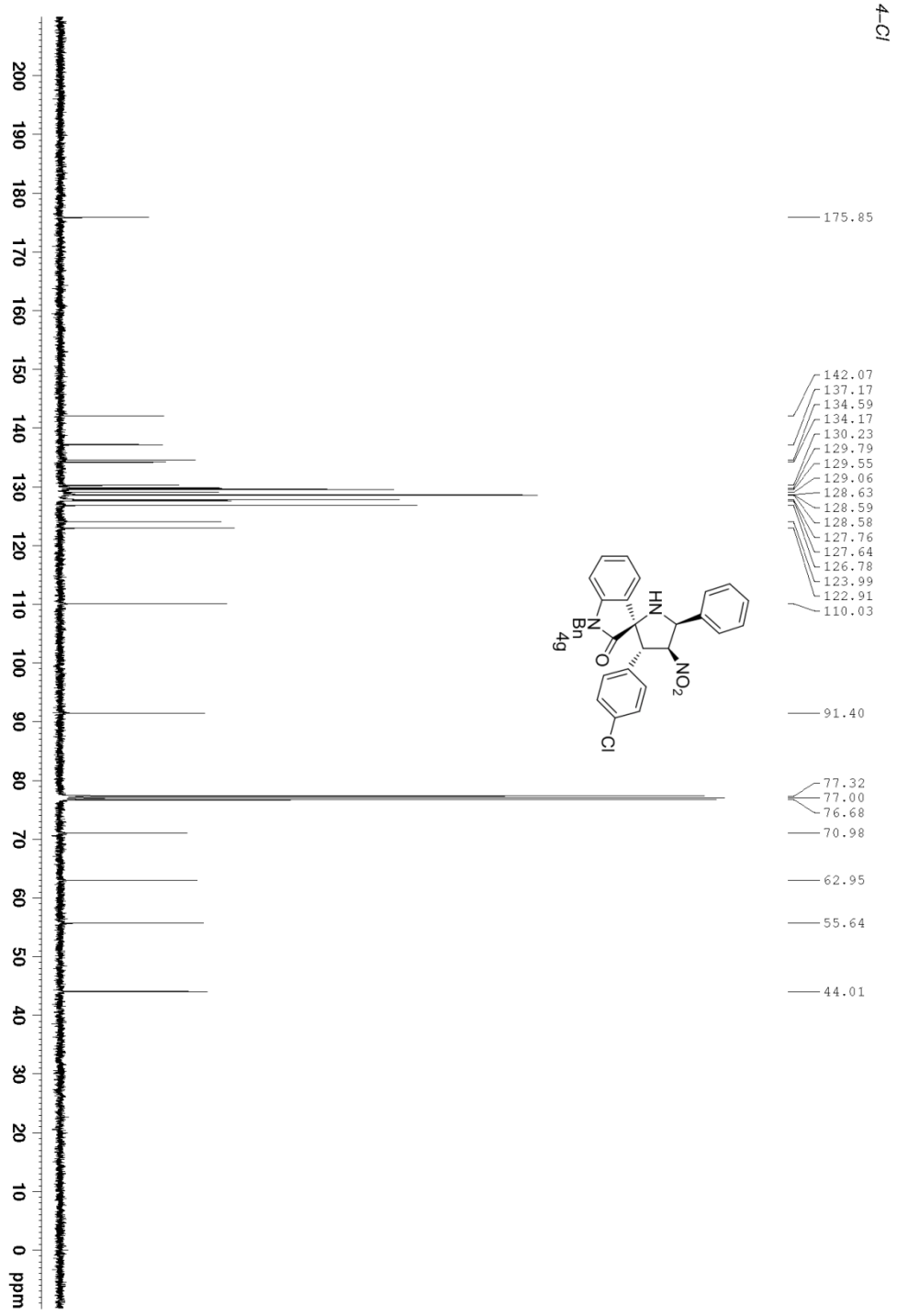
7.719
7.514
7.497
7.495
7.422
7.405
7.386
7.367
7.355
7.349
7.331
7.233
7.216
7.197
7.186
7.182
7.175
7.167
7.164
7.148
7.145
7.130
7.125
7.121
7.104
7.087
7.002
6.981
6.902
6.881
6.833
6.817
6.519
6.501
6.107
6.083
6.077
6.053
5.526
5.503
5.126
5.086
4.835
4.805
4.544
4.504
2.904
HN
N
Bn
O
NO2
Cl
4g
NAME TI-4-Cl
EXPNO 10
PROCNO 1
Date_ 20130112
Time 9.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 101
DW 60.800 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 1.00 dB
PL1W 13.75590801 W
SFO1 400.1332768 MHz
SI 32768
SF 400.1300105 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.02
1.07
3.14
3.17
1.94
2.06
2.05
1.98
0.99
1.00
1.00
1.02
1.01
1.01
0.93
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


4-Cl
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134.59
134.17
130.23
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129.06
128.63
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127.76
127.64
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122.91
110.03
91.40
77.32
77.00
76.68
70.98
62.95
55.64
44.01
HN
N
Bn
O
NO2
Cl
4g
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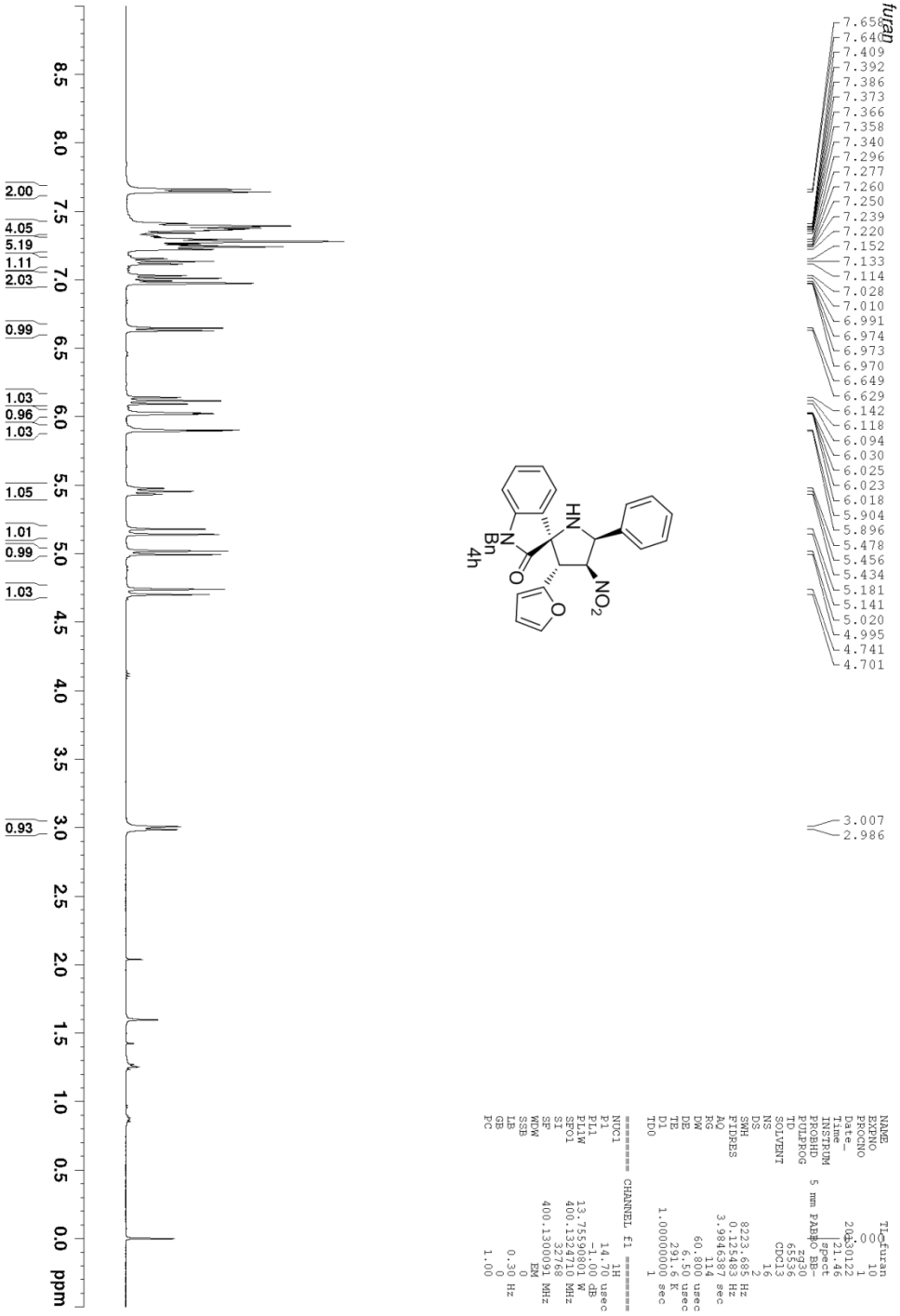
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7.386
7.373
7.366
7.358
7.340
7.296
7.277
7.260
7.250
7.239
7.220
7.152
7.133
7.114
7.028
7.010
6.991
6.974
6.973
6.970
6.649
6.629
6.142
6.118
6.094
6.030
6.025
6.023
6.018
5.904
5.896
5.478
5.456
5.434
5.181
5.141
5.020
4.995
4.741
4.701
3.007
2.986
HN
N
Bn
4h
O
NO2
O
NAME furan
EXPNO 10
PROCNO 1
Date_ 20130122
Time 21.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 114
DW 60.800 usec
DE 6.00 usec
TE 291.6 K
D1 1.00000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 1H
P1 14.70 usec
PL1 -1.00 dB
PL1W 13.75590038 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.00
4.05
5.19
1.11
2.03
0.99
1.03
0.96
1.03
1.05
1.01
0.99
1.03
0.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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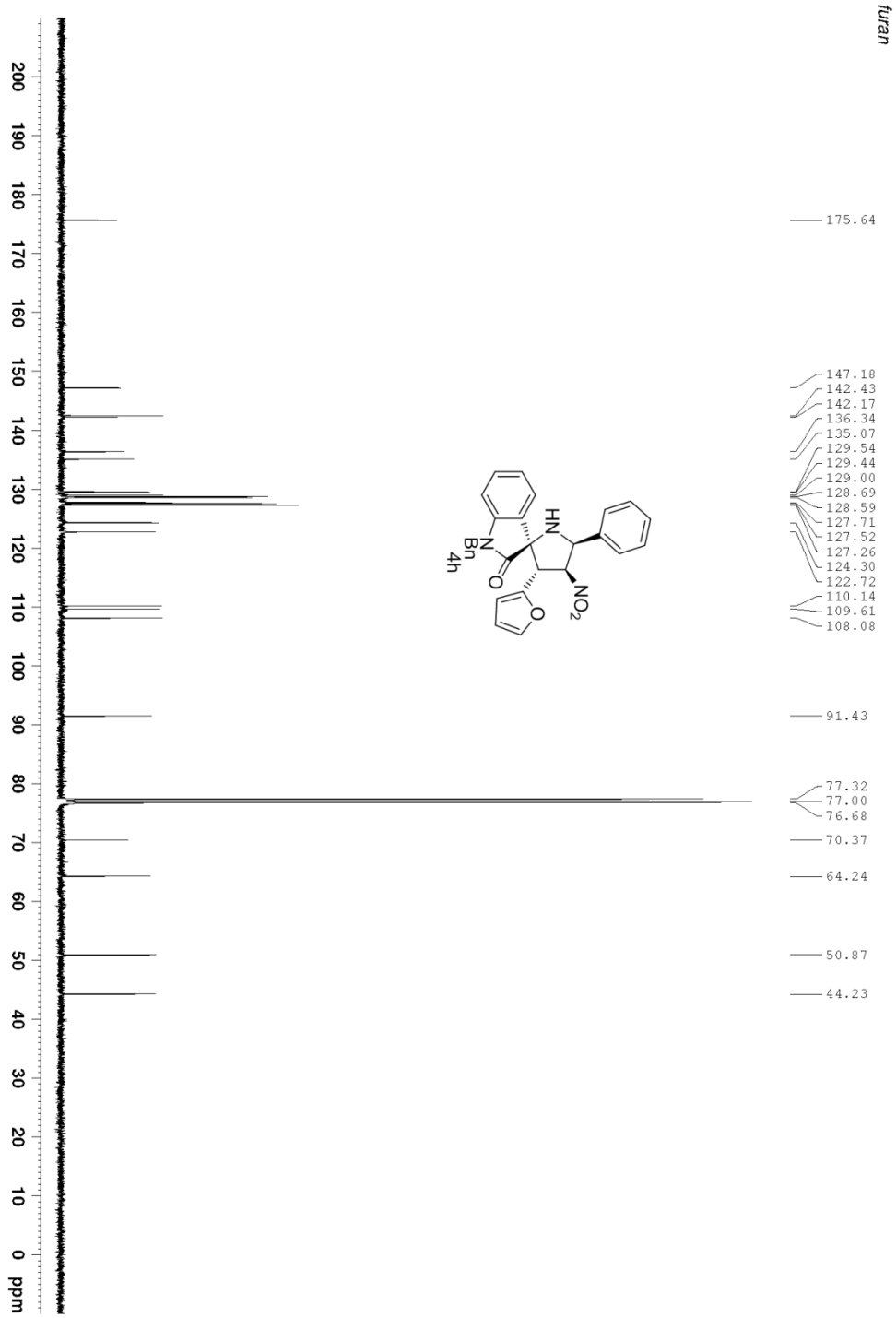
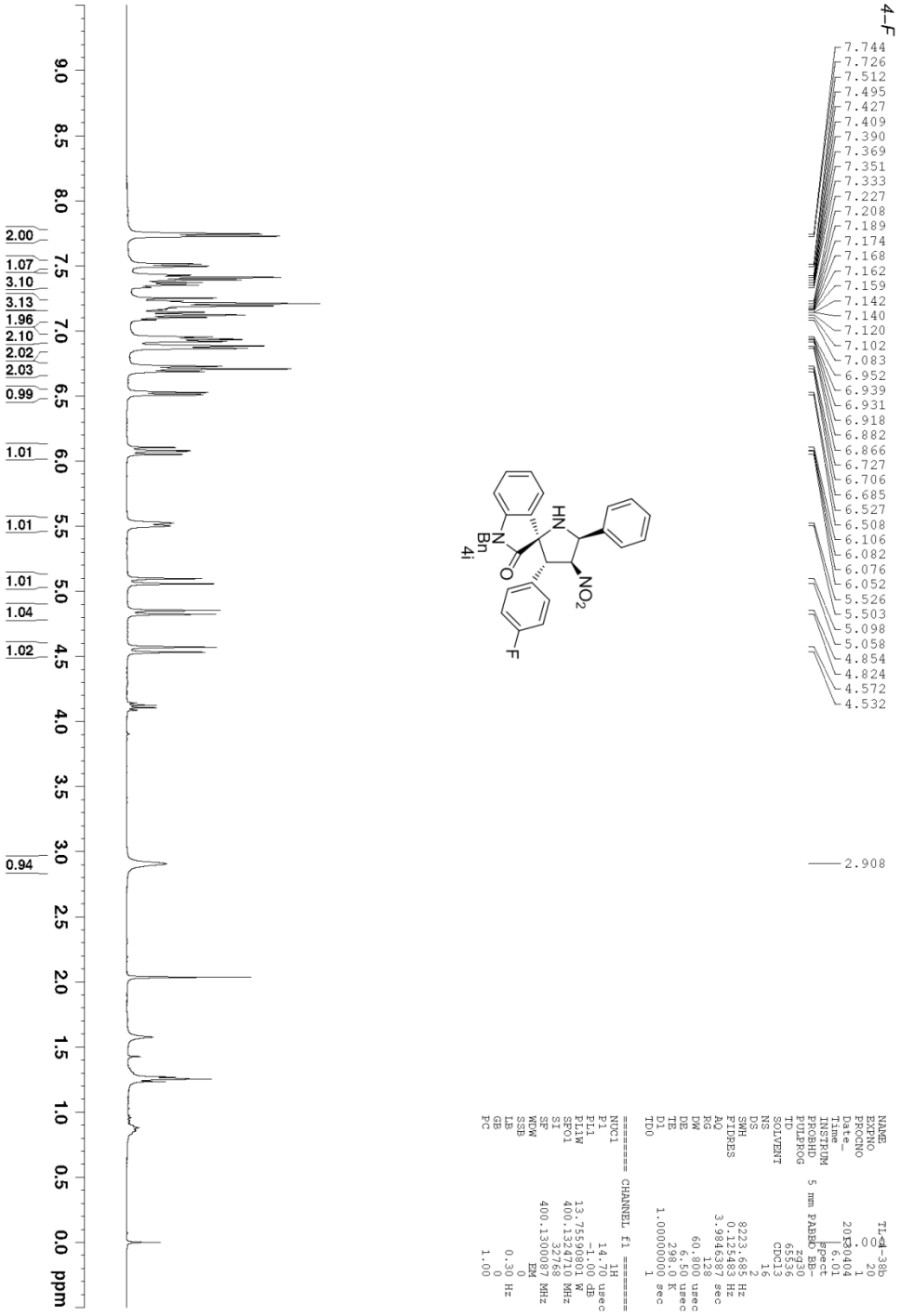
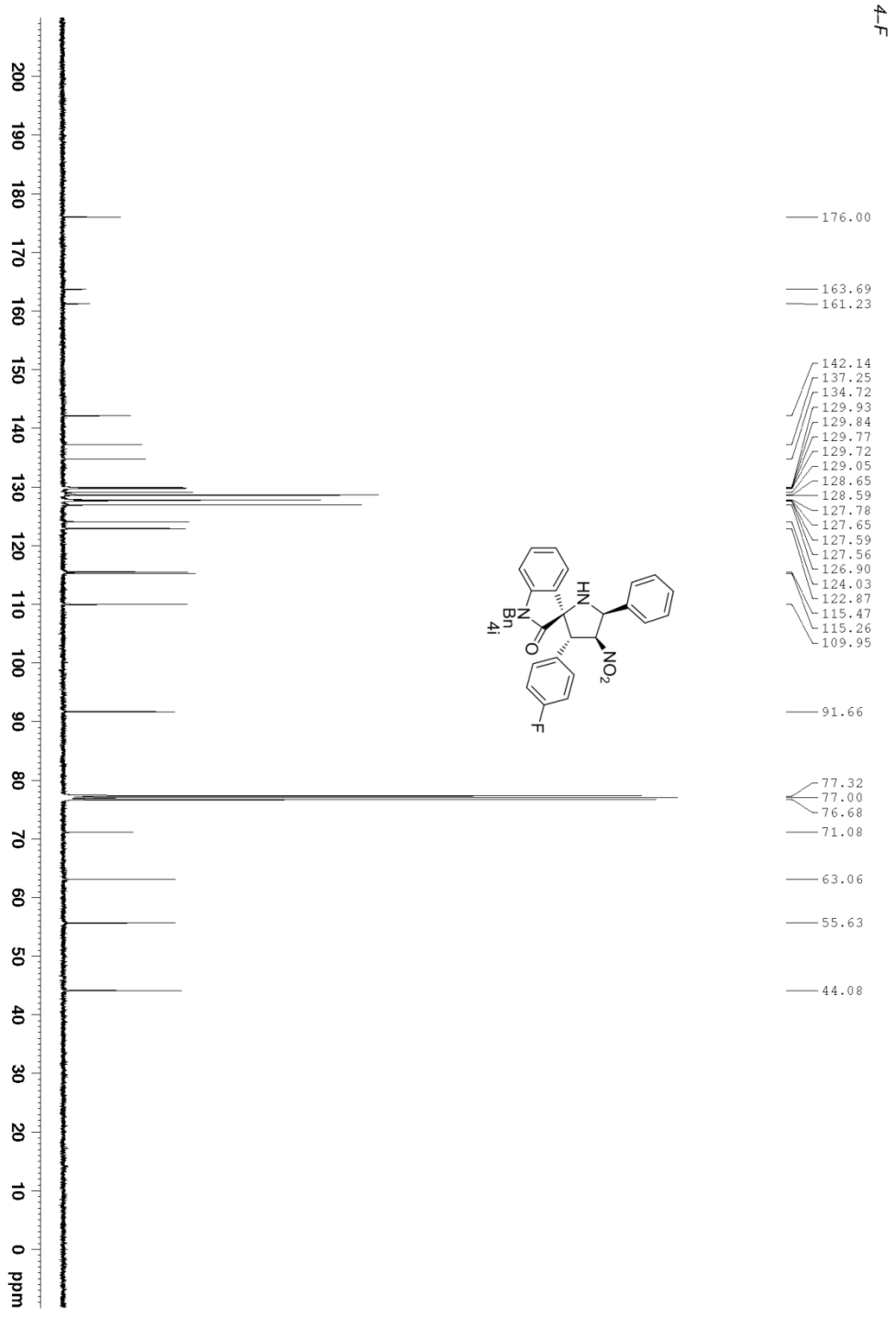
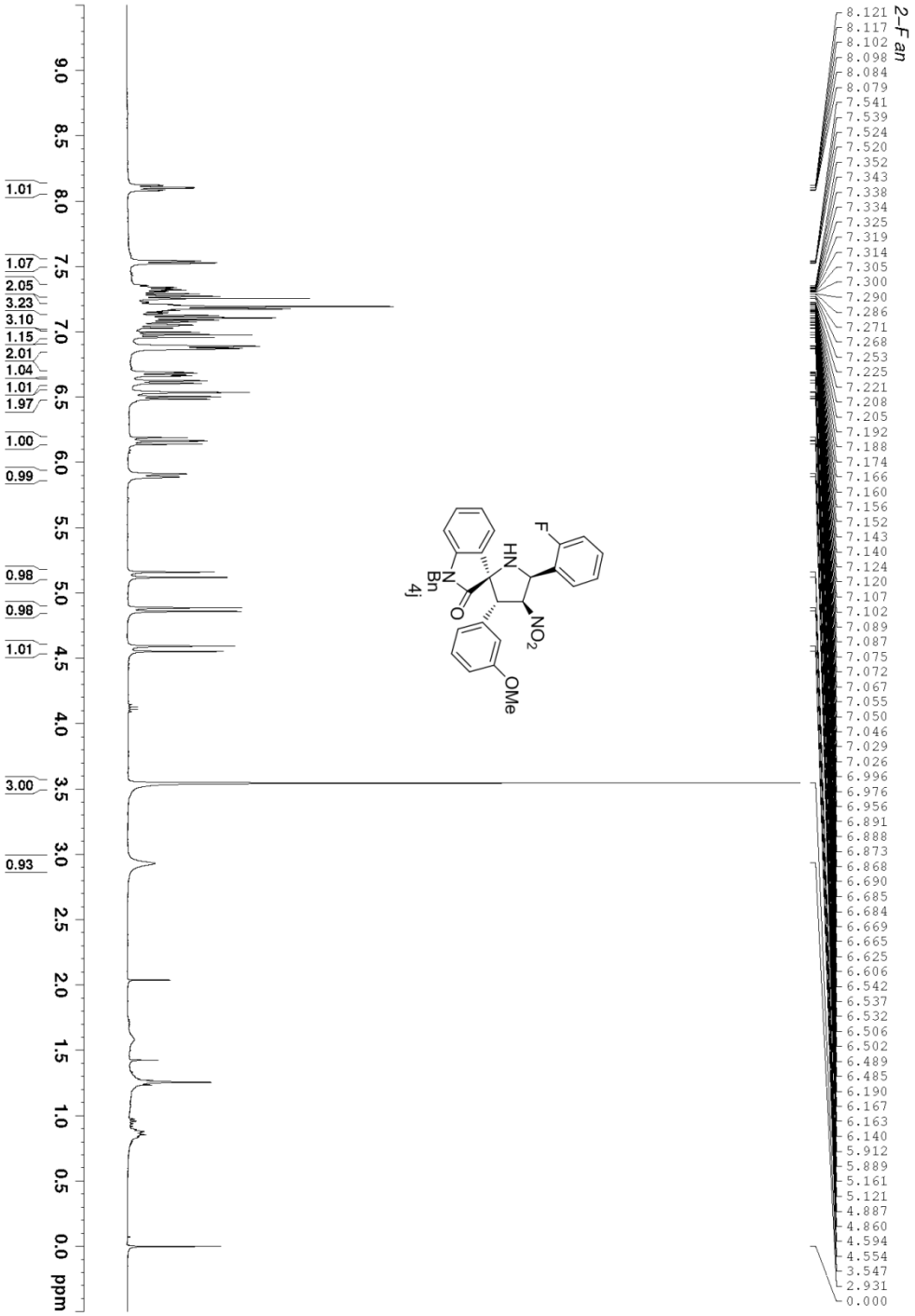
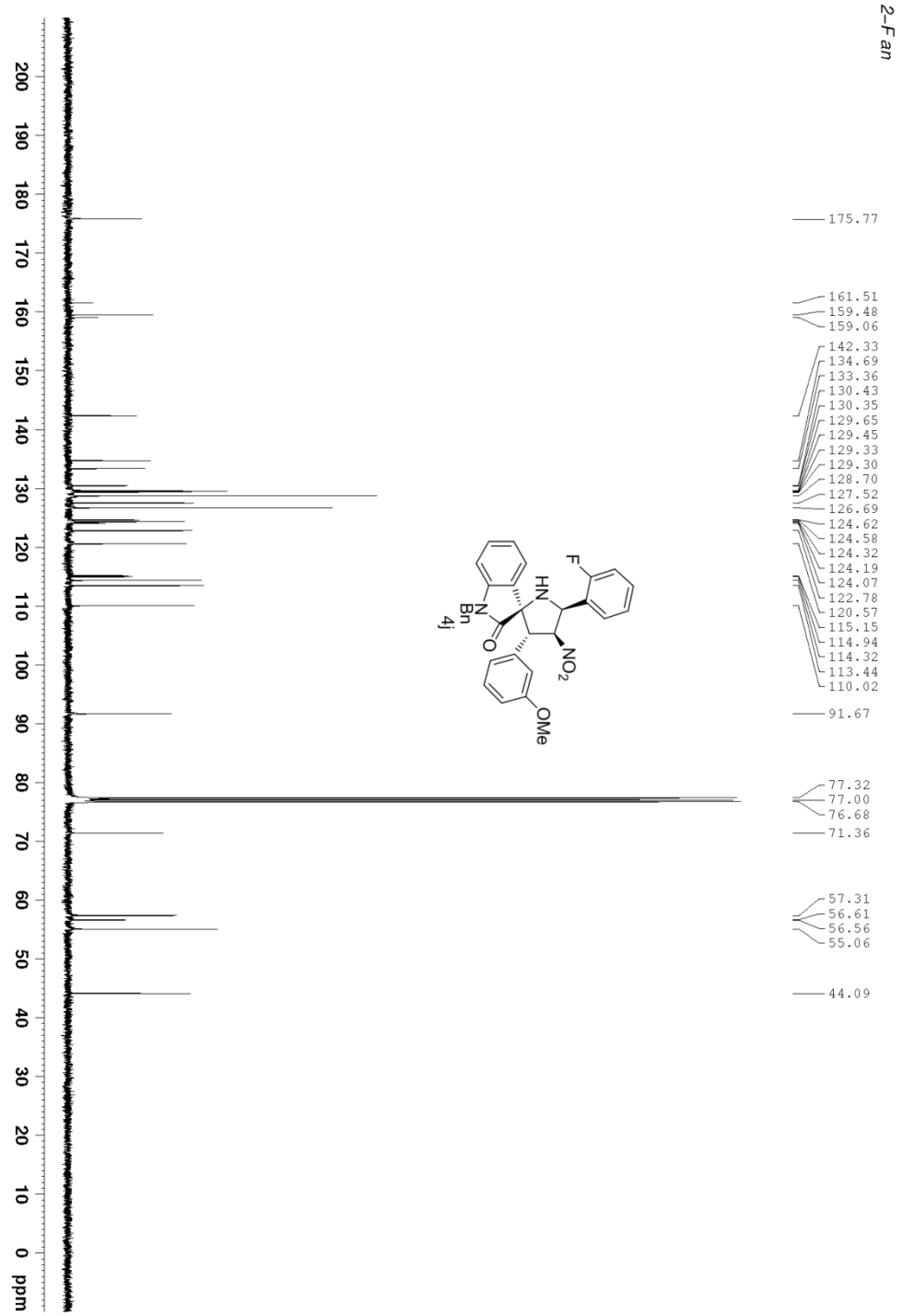
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

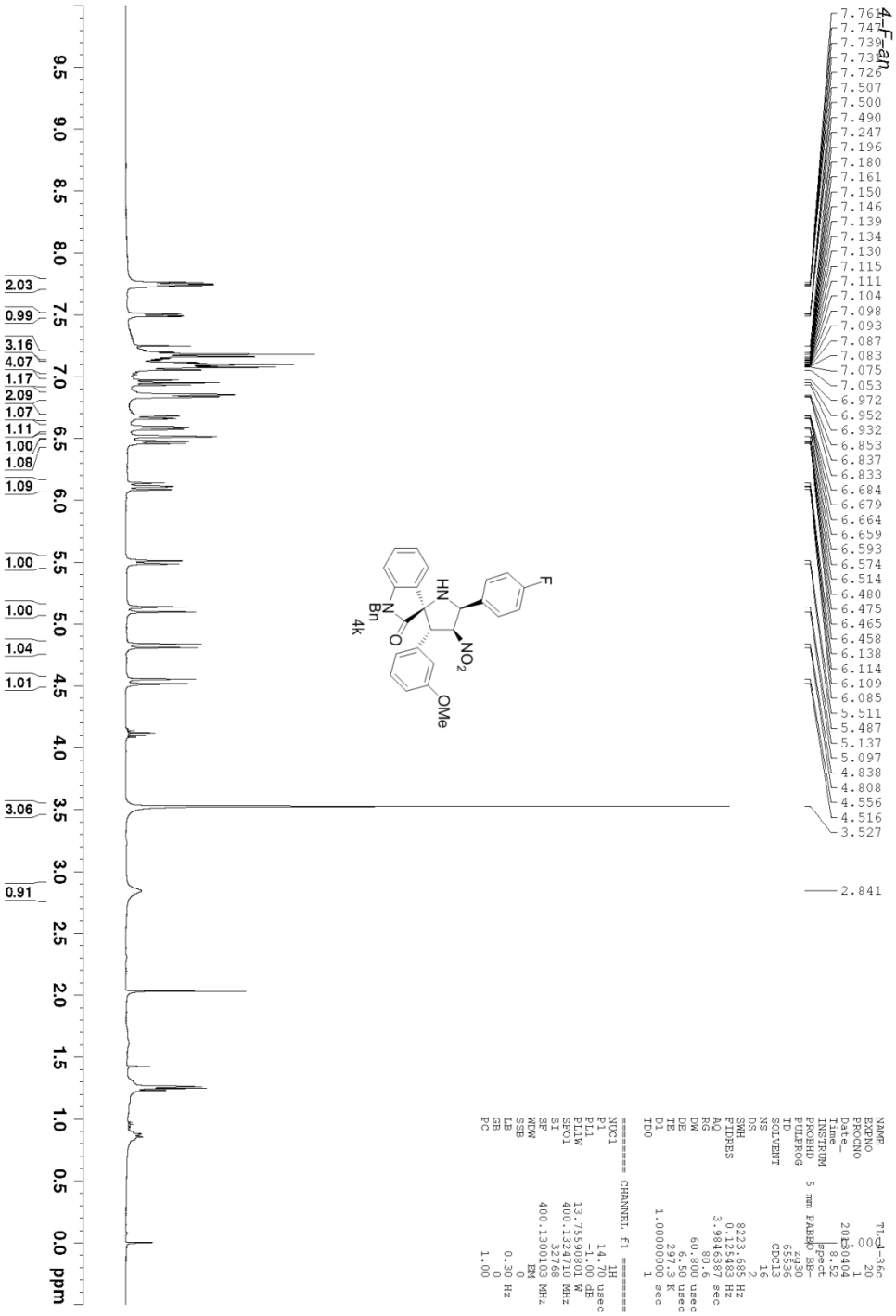

furan
175.64
147.18
142.43
142.17
136.34
135.07
129.54
129.44
129.00
128.69
128.59
127.71
127.52
127.26
124.30
122.72
110.14
109.61
108.08
91.43
77.32
77.00
76.68
70.37
64.24
50.87
44.23
HN
N
Bn
O
O
NO2
4h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

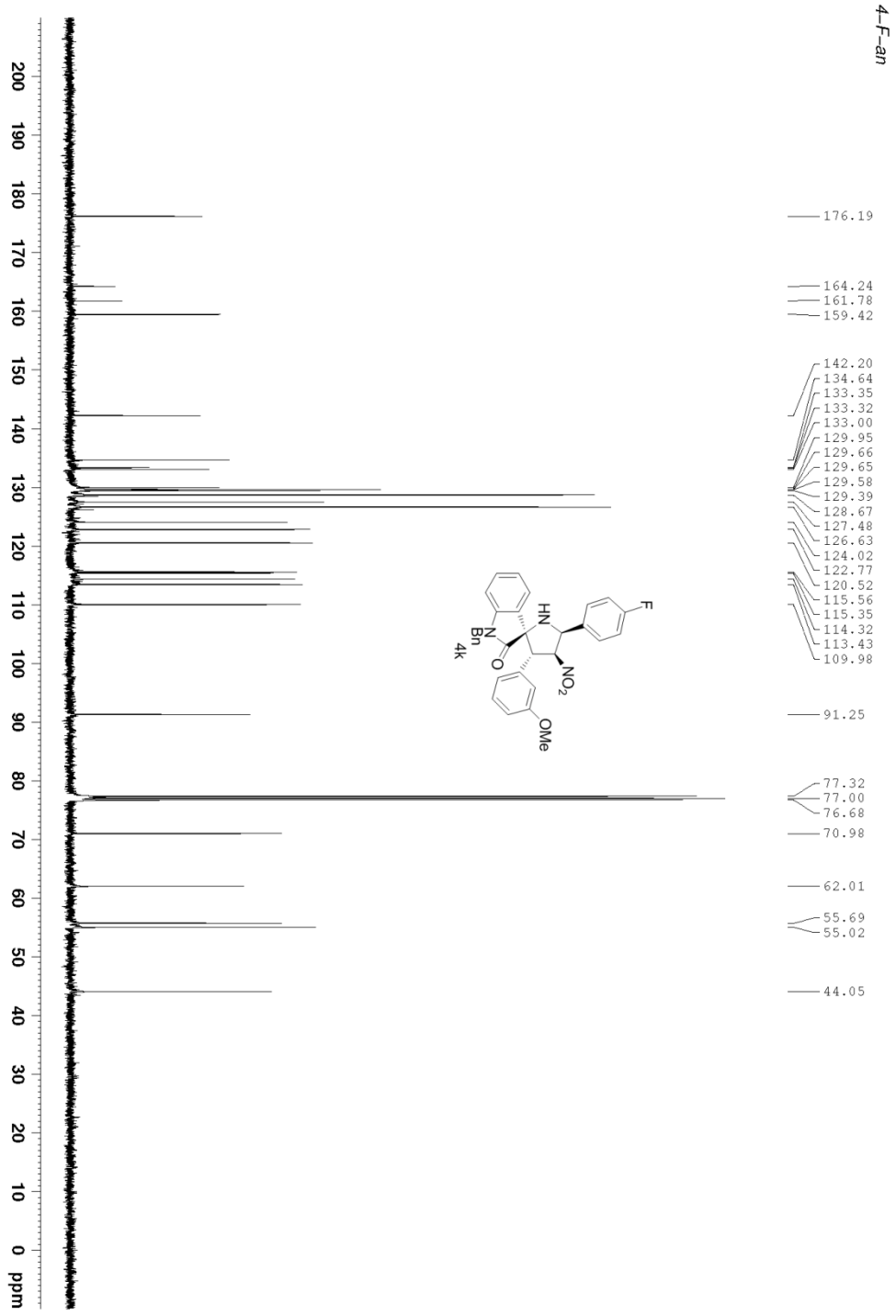

4-F
7.744
7.726
7.512
7.495
7.427
7.409
7.390
7.369
7.351
7.333
7.227
7.208
7.189
7.174
7.168
7.162
7.159
7.142
7.140
7.120
7.102
7.083
6.952
6.939
6.931
6.918
6.882
6.866
6.727
6.706
6.685
6.527
6.508
6.106
6.082
6.076
6.052
5.526
5.503
5.098
5.058
4.854
4.824
4.572
4.532
2.908
HN
N
Bn
4i
O
NO2
F
2.00
1.07
3.10
3.13
1.96
2.10
2.02
2.03
0.99
1.01
1.01
1.01
1.04
1.02
0.94
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

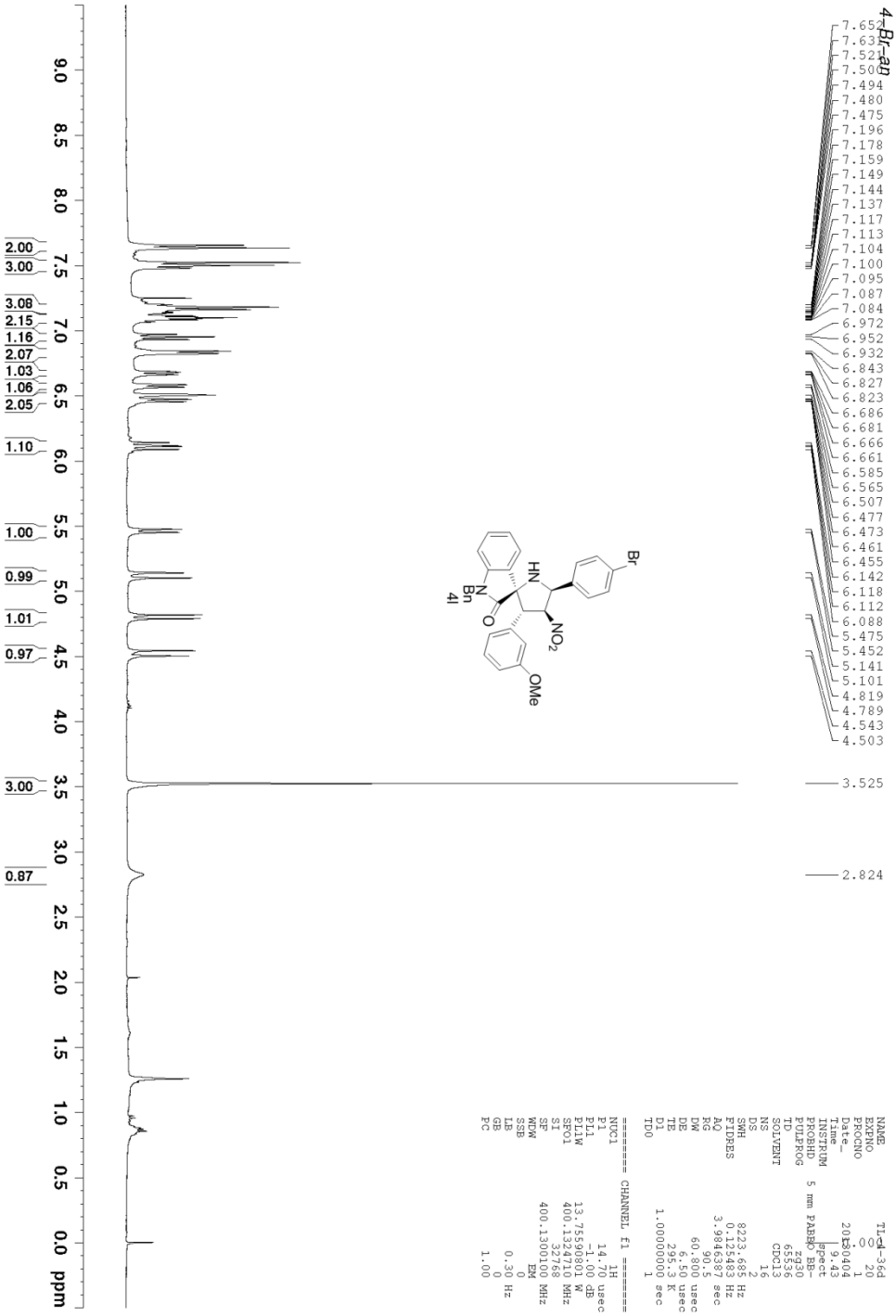

4-F
176.00
163.69
161.23
142.14
137.25
134.72
129.93
129.84
129.77
129.72
129.05
128.65
128.59
127.78
127.65
127.59
127.56
126.90
124.03
122.87
115.47
115.26
109.95
91.66
77.32
77.00
76.68
71.08
63.06
55.63
44.08
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
HN
N
Bn
4i
O
NO2
F

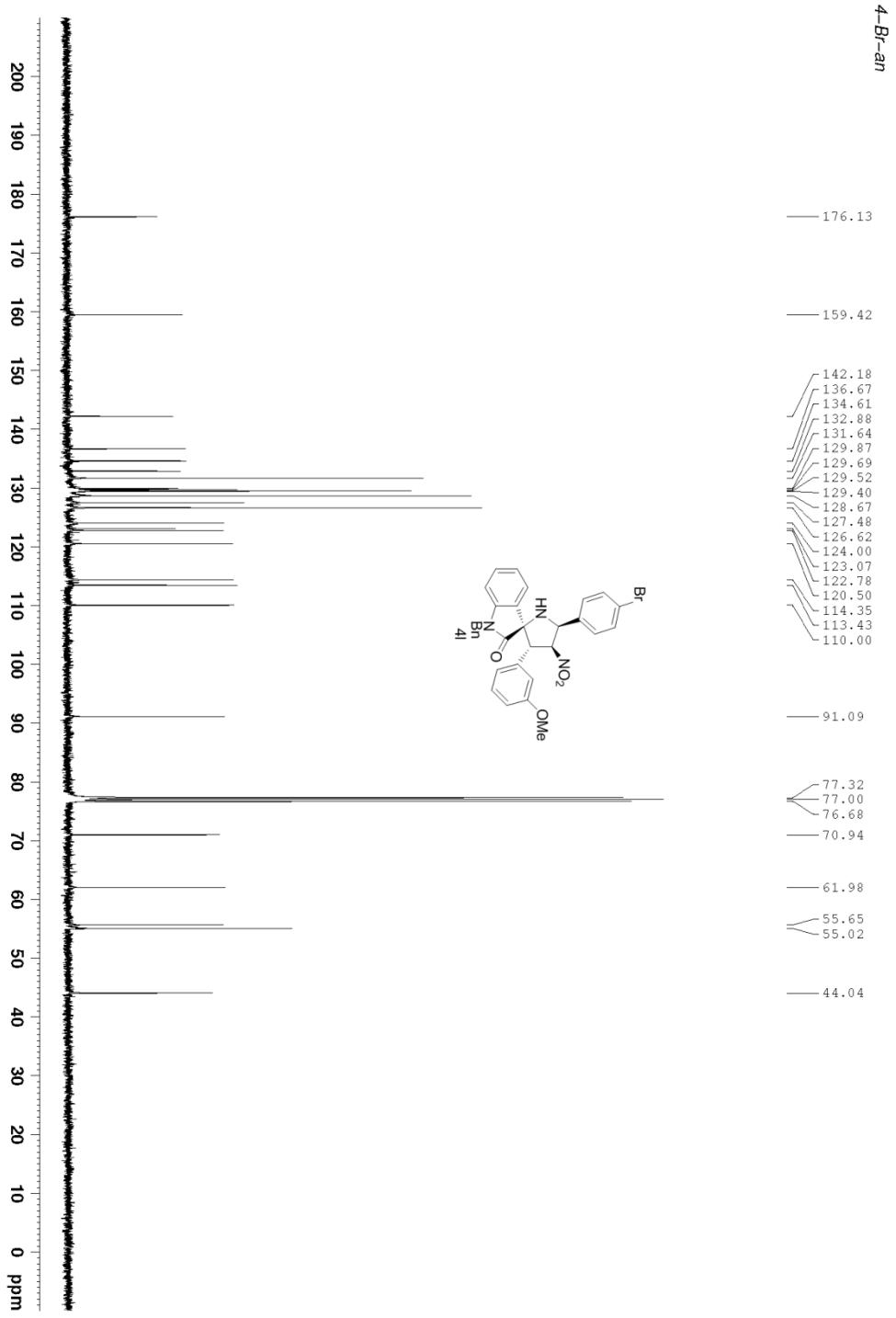

2-F an
8.121
8.117
8.102
8.098
8.084
8.079
7.541
7.539
7.524
7.520
7.352
7.343
7.338
7.334
7.325
7.319
7.314
7.305
7.300
7.290
7.286
7.271
7.268
7.253
7.225
7.221
7.208
7.205
7.192
7.188
7.174
7.166
7.160
7.156
7.152
7.143
7.140
7.124
7.120
7.107
7.102
7.089
7.087
7.075
7.072
7.067
7.055
7.050
7.046
7.029
7.026
6.996
6.976
6.956
6.891
6.888
6.873
6.868
6.690
6.685
6.684
6.669
6.665
6.625
6.606
6.542
6.537
6.532
6.506
6.502
6.489
6.485
6.190
6.167
6.163
6.140
5.912
5.889
5.161
5.121
4.887
4.860
4.594
4.554
3.547
2.931
0.000
1.01
1.07
2.05
3.23
3.10
1.15
2.01
1.04
1.01
1.97
1.00
0.99
0.98
0.98
1.01
3.00
0.93
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
HN
N
Bn
O
F
NO2
OMe
4j

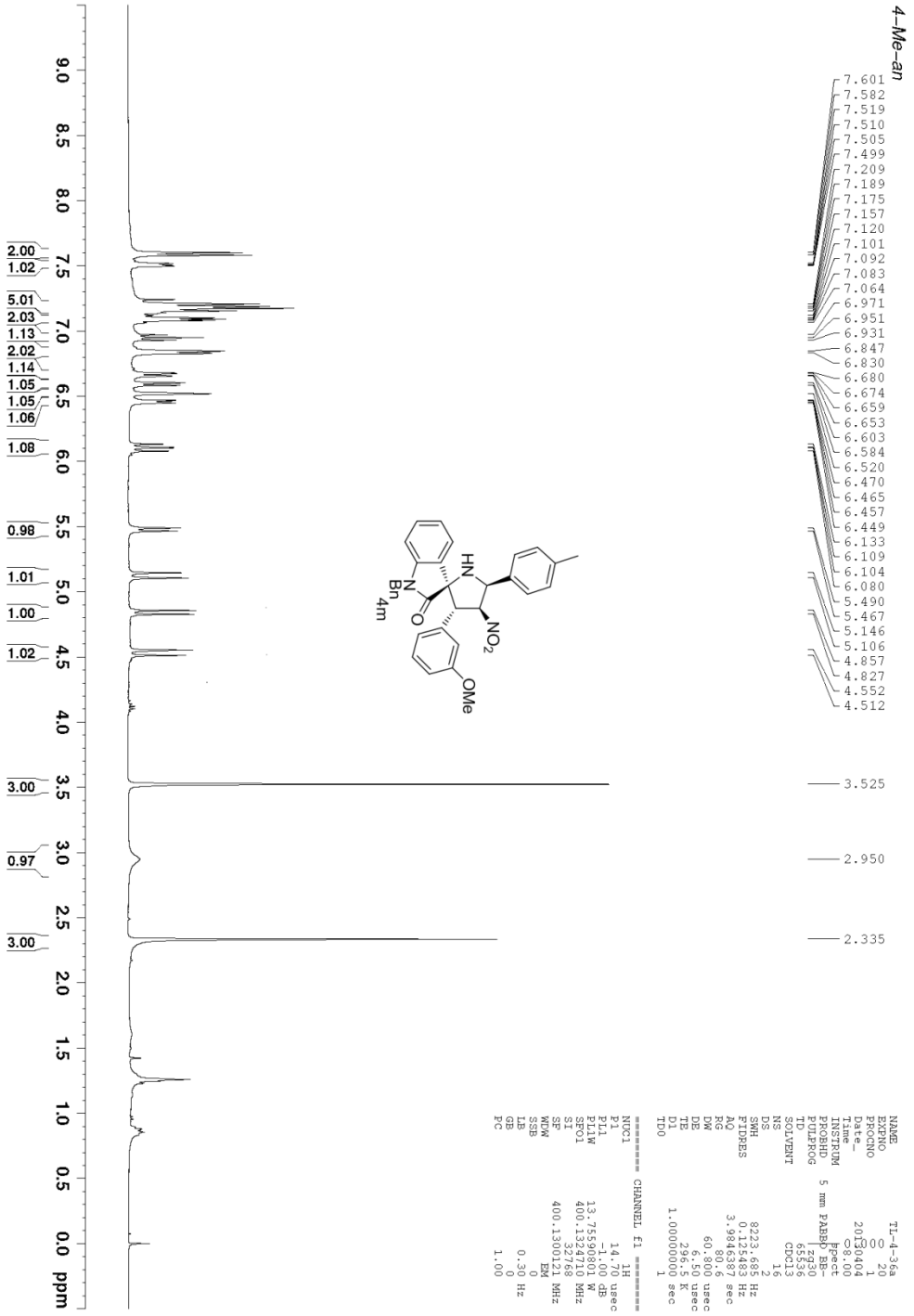

2-F an
175.77
161.51
159.48
159.06
142.33
134.69
133.36
130.43
130.35
129.65
129.45
129.33
129.30
128.70
127.52
126.69
124.62
124.58
124.32
124.19
124.07
122.78
120.57
115.15
114.94
114.32
113.44
110.02
91.67
77.32
77.00
76.68
71.36
57.31
56.61
56.56
55.06
44.09
HN
N
Bn
O
F
NO2
OMe
4j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

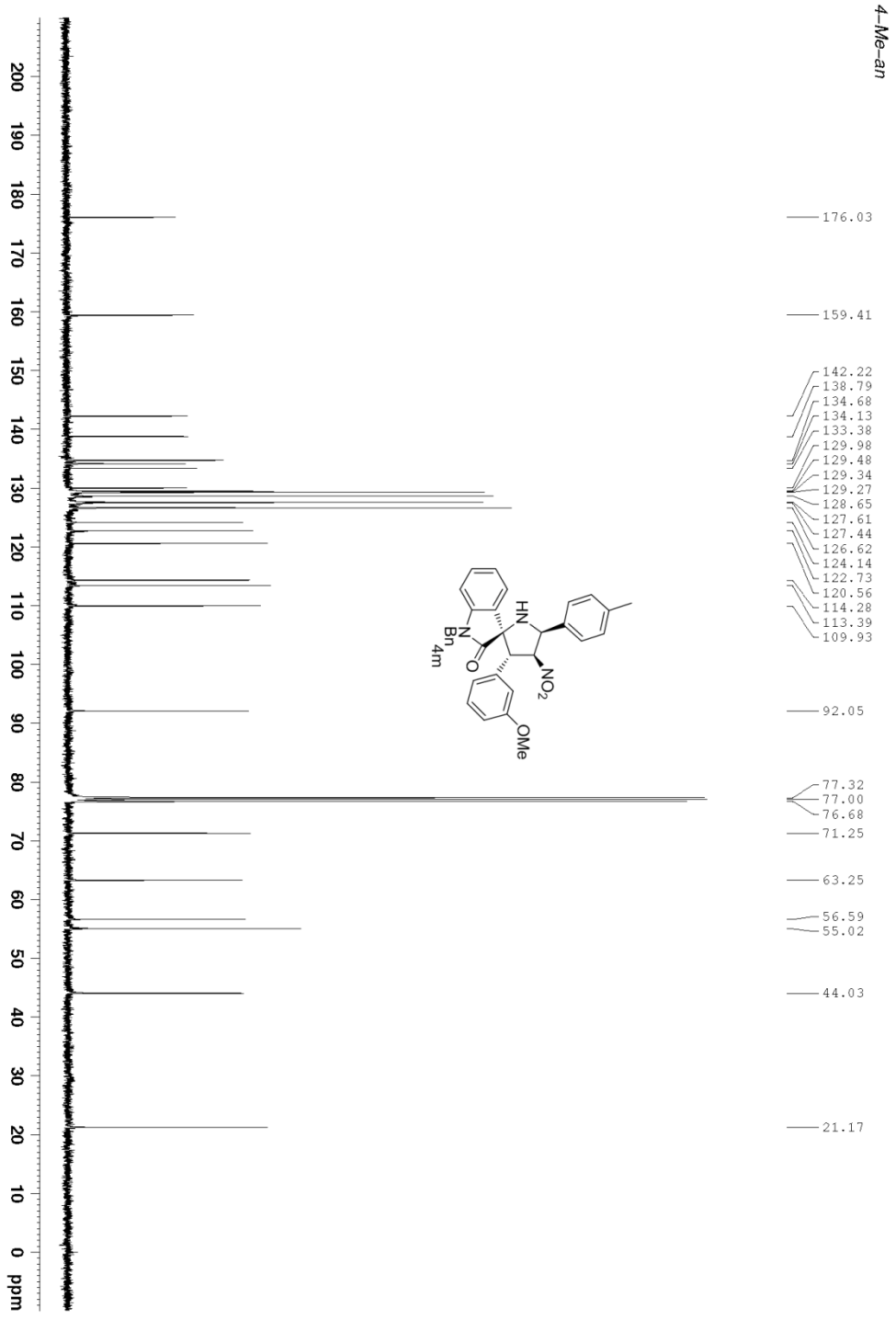

4-F-an
7.761
7.747
7.739
7.731
7.726
7.507
7.500
7.490
7.247
7.196
7.180
7.161
7.150
7.146
7.139
7.134
7.130
7.115
7.111
7.104
7.098
7.093
7.087
7.083
7.075
7.053
6.972
6.952
6.932
6.853
6.837
6.833
6.684
6.679
6.664
6.659
6.593
6.574
6.514
6.480
6.475
6.465
6.458
6.138
6.114
6.109
6.085
5.511
5.487
5.137
5.097
4.838
4.808
4.556
4.516
3.527
2.841
2.03
0.99
3.16
4.07
1.17
2.09
1.07
1.11
1.00
1.08
1.09
1.00
1.00
1.04
1.01
3.06
0.91
HN
N
Bn
O
NO2
F
OMe
4k
NAME TL-4-36c
EXPNO 20
PROCNO 1
Date_ 20130404
Time 8.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 80.6
DW 60.800 usec
DE 6.00 usec
TE 297.3 K
D1 1.00000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 1H
P1 14.70 usec
PL1 -1.00 dB
PL1W 13.75590038 W
SFO1 400.1330910 MHz
SI 32768
SF 400.1300103 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

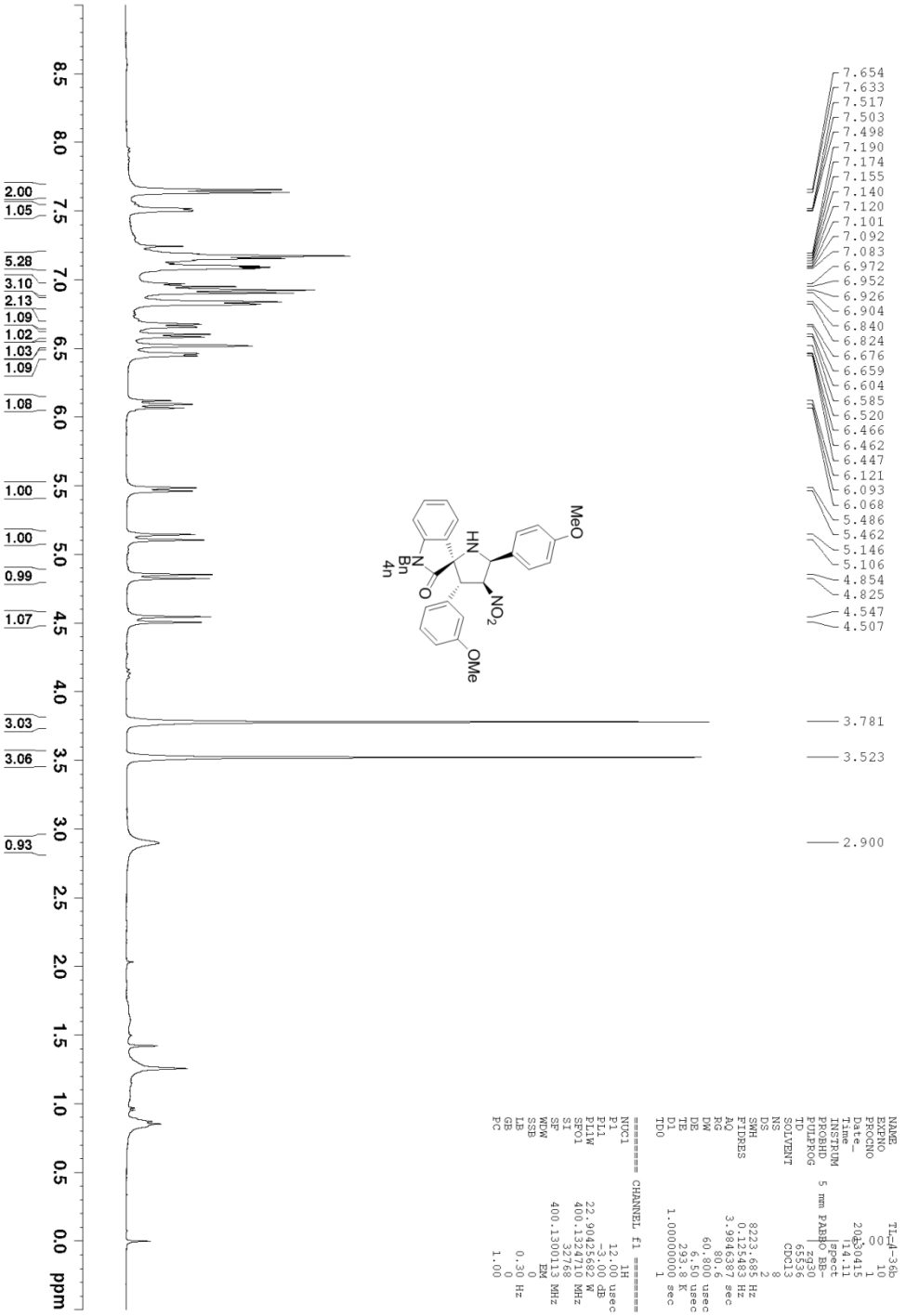

4-F-an
176.19
164.24
161.78
159.42
142.20
134.64
133.35
133.32
133.00
129.95
129.66
129.65
129.58
129.39
128.67
127.48
126.63
124.02
122.77
120.52
115.56
115.35
114.32
113.43
109.98
91.25
77.32
77.00
76.68
70.98
62.01
55.69
55.02
44.05
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
HN
N
Bn
O
NO2
F
OMe
4k

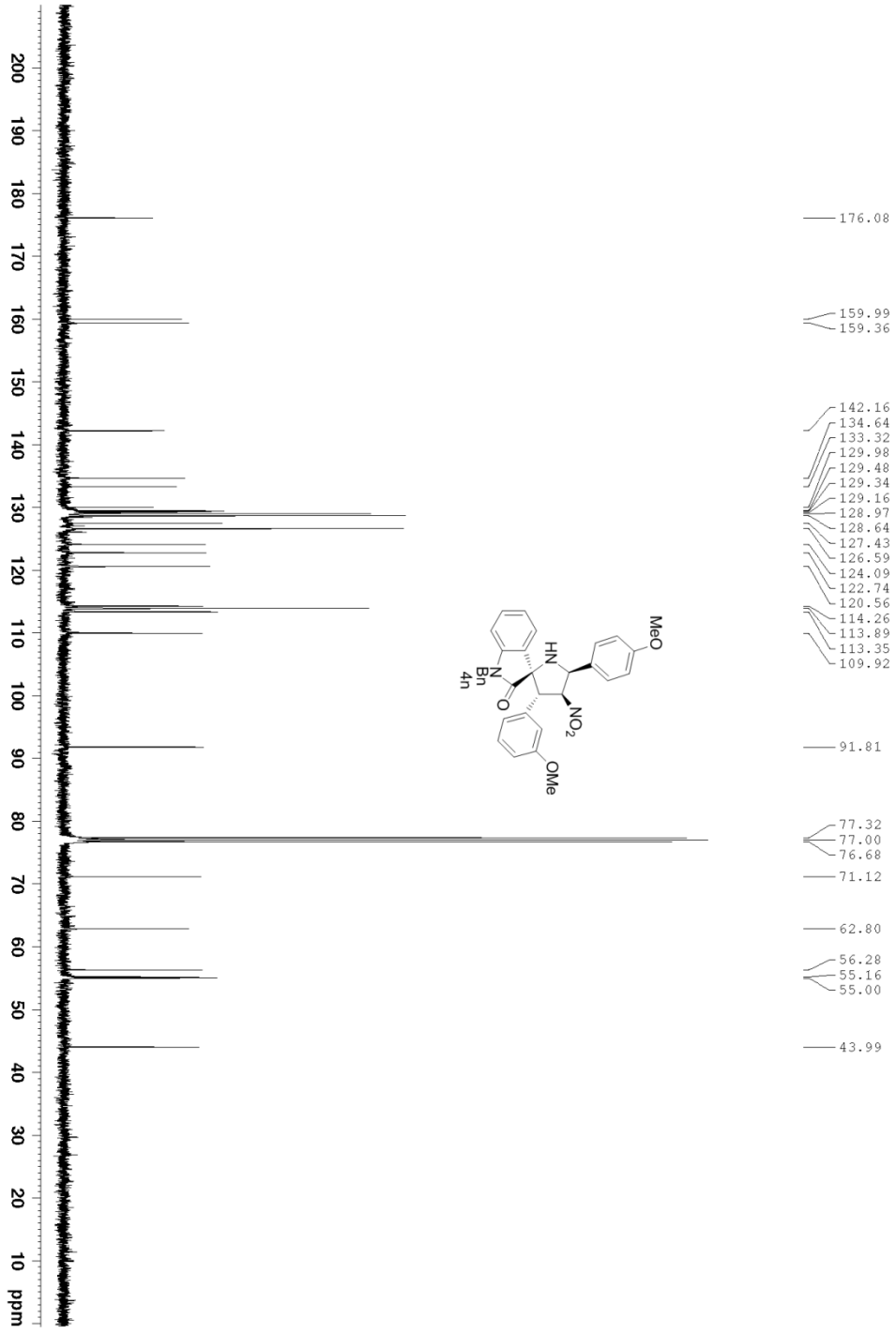

4-Br-ap
7.652
7.634
7.523
7.505
7.494
7.480
7.475
7.196
7.178
7.159
7.149
7.144
7.137
7.117
7.113
7.104
7.100
7.095
7.087
7.084
6.972
6.952
6.932
6.843
6.827
6.823
6.686
6.681
6.666
6.661
6.585
6.565
6.507
6.477
6.473
6.461
6.455
6.142
6.118
6.112
6.088
5.475
5.452
5.141
5.101
4.819
4.789
4.543
4.503
3.525
2.824
Br
HN
N
Bn
4l
O
NO2
OMe
2.00
3.00
3.08
2.15
1.16
2.07
1.03
1.06
2.05
1.10
1.00
0.99
1.01
0.97
3.00
0.87
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
NAME TL-4-36d
EXPNO 20
PROCNO 1
Date_ 20130404
Time 9.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846797 sec
RG 90.5
DW 60.800 usec
DE 6.50 usec
TE 295.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 -1.00 dB
PL1W 13.75590801 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

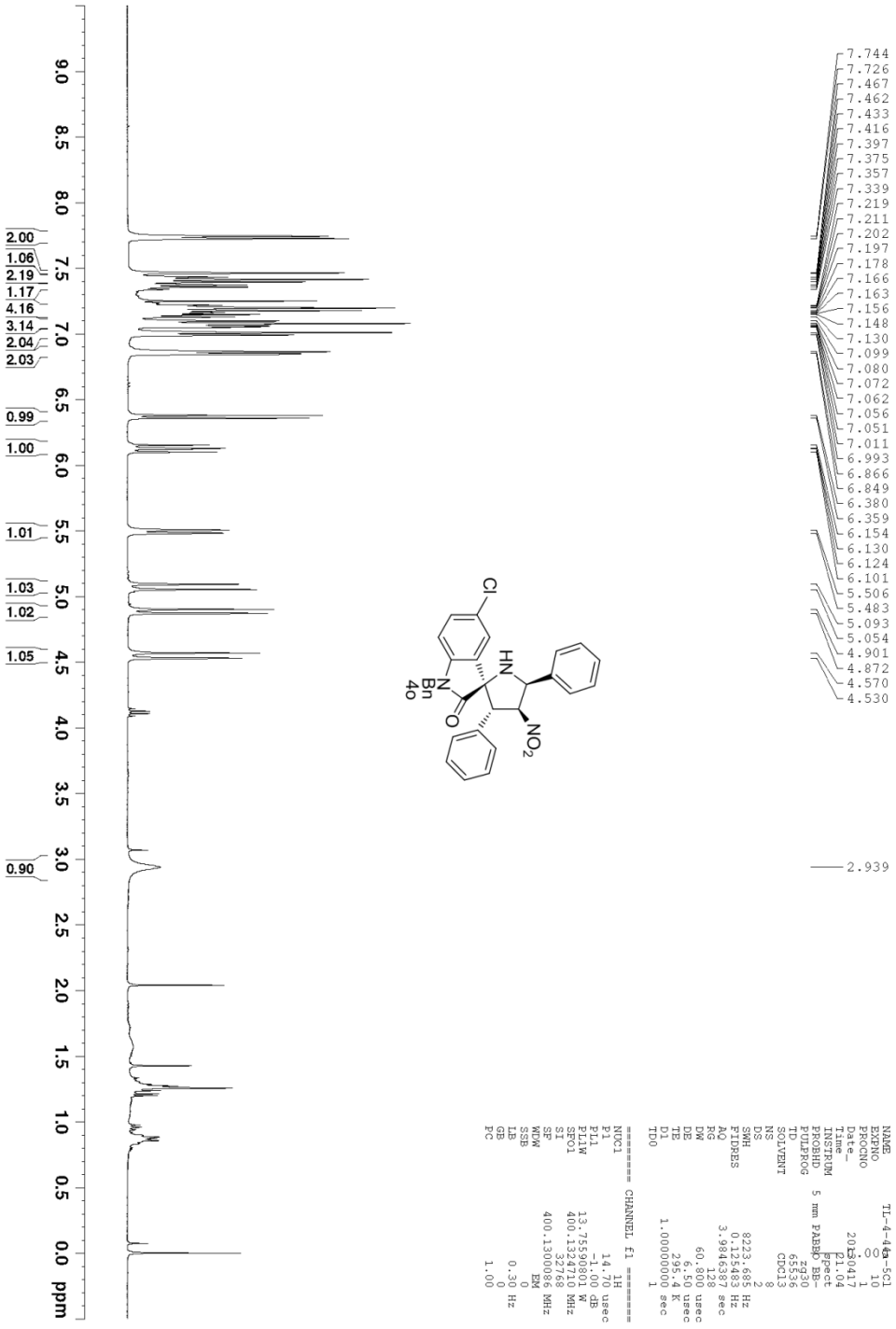

4-Br-an
176.13
159.42
142.18
136.67
134.61
132.88
131.64
129.87
129.69
129.52
129.40
128.67
127.48
126.62
124.00
123.07
122.78
120.50
114.35
113.43
110.00
91.09
77.32
77.00
76.68
70.94
61.98
55.65
55.02
44.04
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
HN
N
Bn
O
NO2
Br
OMe
4l


4-Me-an
7.601
7.582
7.519
7.510
7.505
7.499
7.209
7.189
7.175
7.157
7.120
7.101
7.092
7.083
7.064
6.971
6.951
6.931
6.847
6.830
6.680
6.674
6.659
6.653
6.603
6.584
6.520
6.470
6.465
6.457
6.449
6.133
6.109
6.104
6.080
5.490
5.467
5.146
5.106
4.857
4.827
4.552
4.512
3.525
2.950
2.335
HN
N
Bn
4m
O
NO2
OMe
2.00
1.02
5.01
2.03
1.13
2.02
1.14
1.05
1.05
1.06
1.08
0.98
1.01
1.00
1.02
3.00
0.97
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
NAME TL-4-36a
EXPNO 20
PROCNO 1
Date_ 20130404
Time 08.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 80.6
DW 60.800 usec
DE 6.00 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 1H
P1 14.70 usec
PL1 -1.00 dB
PL1W 13.75590038 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


4-Me-an
176.03
159.41
142.22
138.79
134.68
134.13
133.38
129.98
129.48
129.34
129.27
128.65
127.61
127.44
126.62
124.14
122.73
120.56
114.28
113.39
109.93
92.05
77.32
77.00
76.68
71.25
63.25
56.59
55.02
44.03
21.17
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
HN
N
Bn
O
NO2
OMe
4m


7.654
7.633
7.517
7.503
7.498
7.190
7.174
7.155
7.140
7.120
7.101
7.092
7.083
6.972
6.952
6.926
6.904
6.840
6.824
6.676
6.659
6.604
6.585
6.520
6.466
6.462
6.447
6.121
6.093
6.068
5.486
5.462
5.146
5.106
4.854
4.825
4.547
4.507
3.781
3.523
2.900
2.00
1.05
5.28
3.10
2.13
1.09
1.02
1.03
1.09
1.08
1.00
1.00
0.99
1.07
3.03
3.06
0.93
MeO
HN
Bn
4n
N
O
NO2
OMe
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
NAME TL-4-36b
EXPNO 10
PROCNO 1
Date_ 20130415
Time 14.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 80.6
DW 60.800 usec
DE 6.50 usec
TE 293.0 K
D1 1.00000008 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -3.00 dB
PL1W 22.90425682 W
SFO1 400.1327470 MHz
SI 32768
SF 400.1300113 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

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7.416
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7.375
7.357
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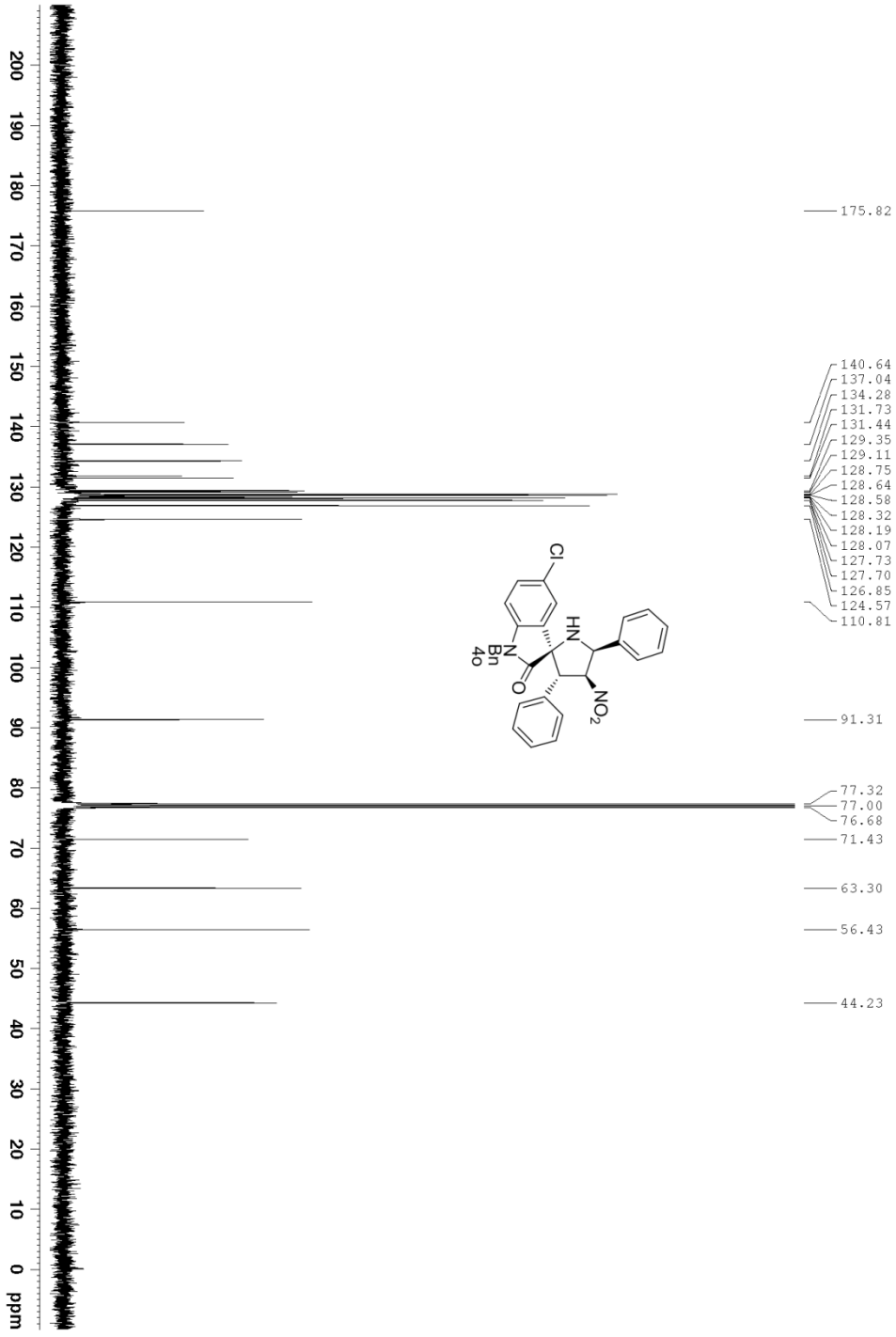
7.219
7.211
7.202
7.197
7.178
7.166
7.163
7.156
7.148
7.130
7.099
7.080
7.072
7.062
7.056
7.051
7.011
6.993
6.866
6.849
6.380
6.359
6.154
6.130
6.124
6.101
5.506
5.483
5.093
5.054
4.901
4.872
4.570
4.530
2.939
2.00
1.06
2.19
1.17
4.16
3.14
2.04
2.03
0.99
1.00
1.01
1.03
1.02
1.05
0.90
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
Cl
HN
N
Bn
O
NO2
4o
NAME TL-4-44a-5Cl
EXPNO 10
PROCNO 1
Date_ 20150417
Time 21.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 128
DW 60.800 usec
DE 6.50 usec
TE 295.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 -1.00 dB
PL1W 13.75590801 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300086 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


175.82
140.64
137.04
134.28
131.73
131.44
129.35
129.11
128.75
128.64
128.58
128.32
128.19
128.07
127.73
127.70
126.85
124.57
110.81
91.31
77.32
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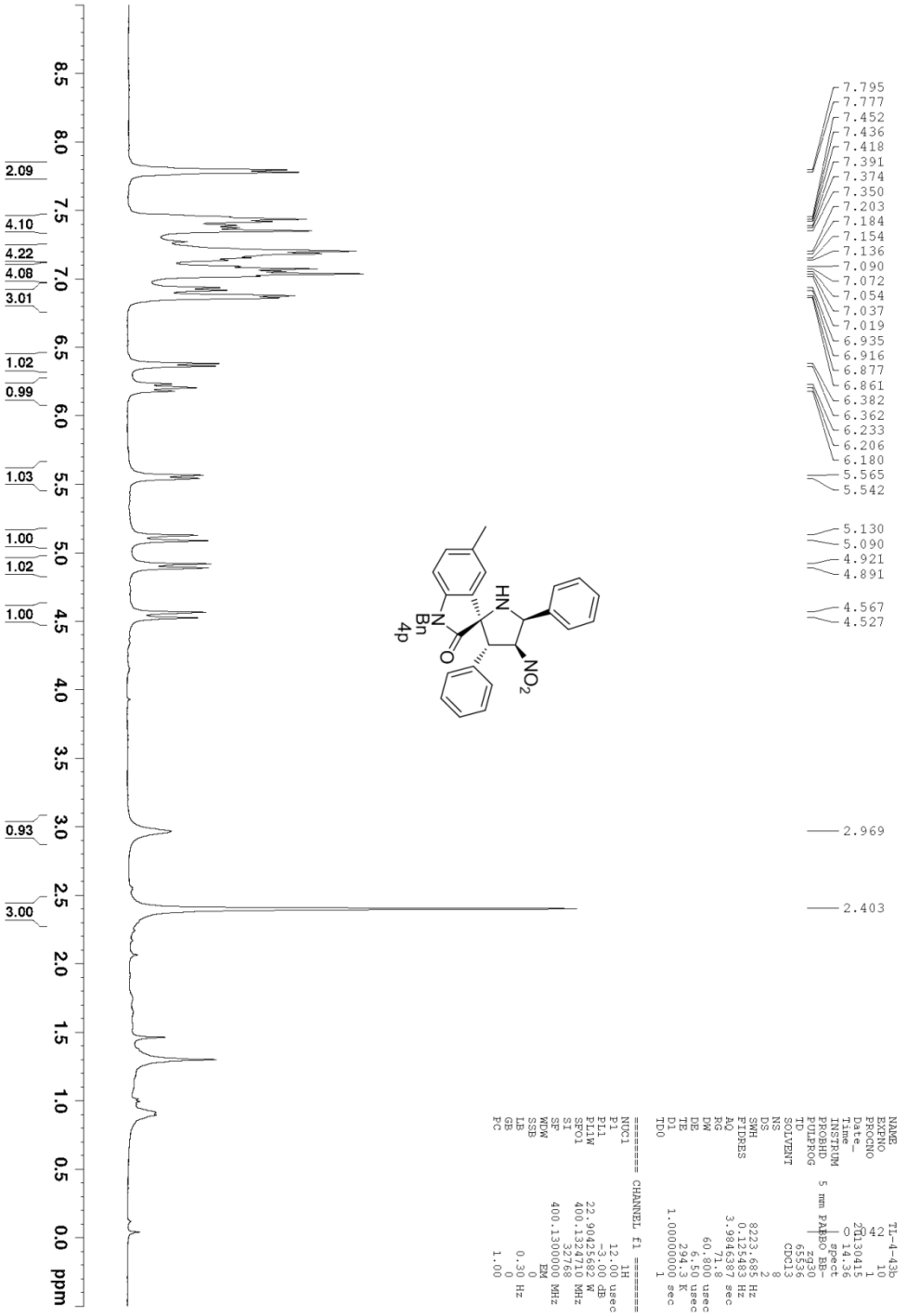
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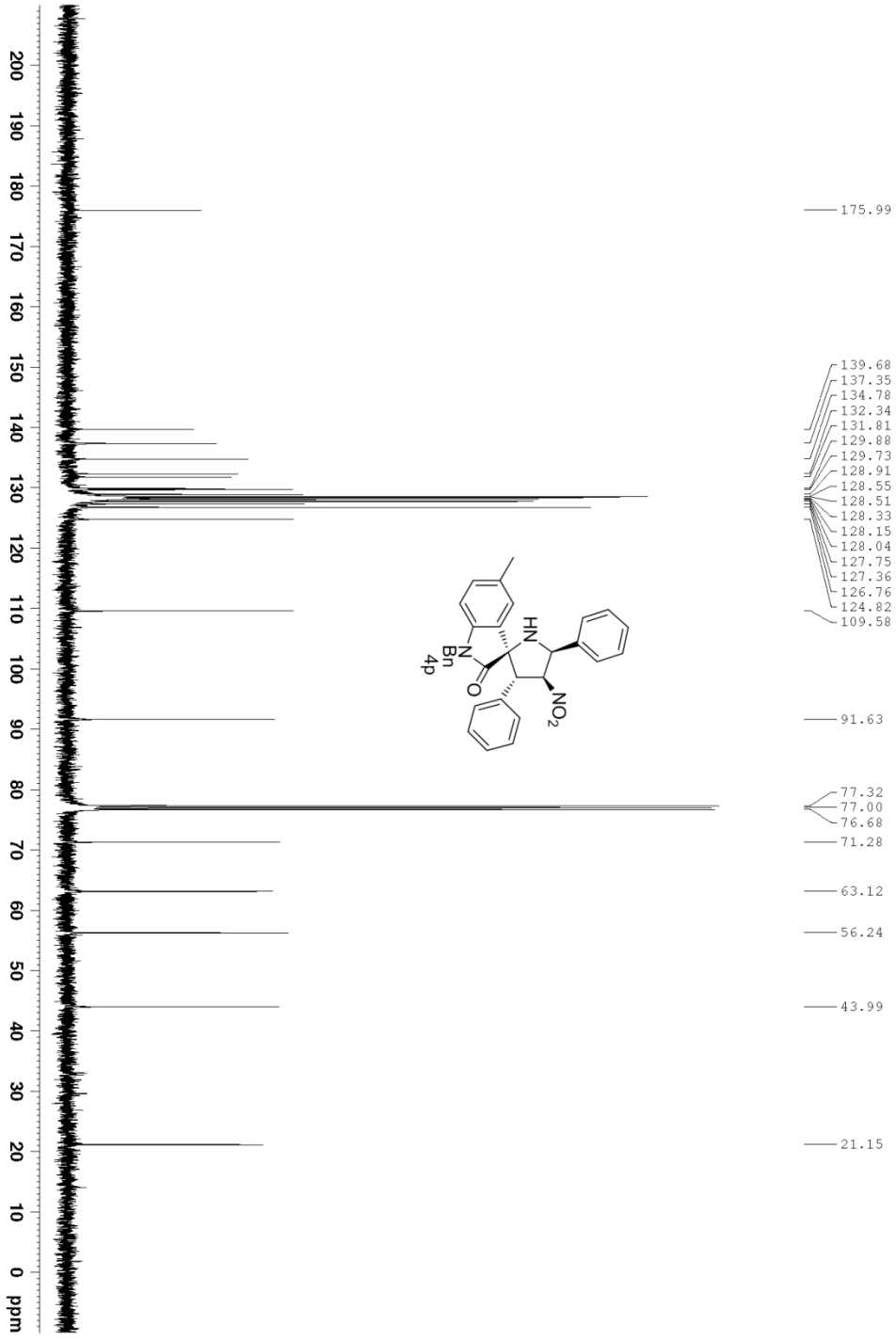

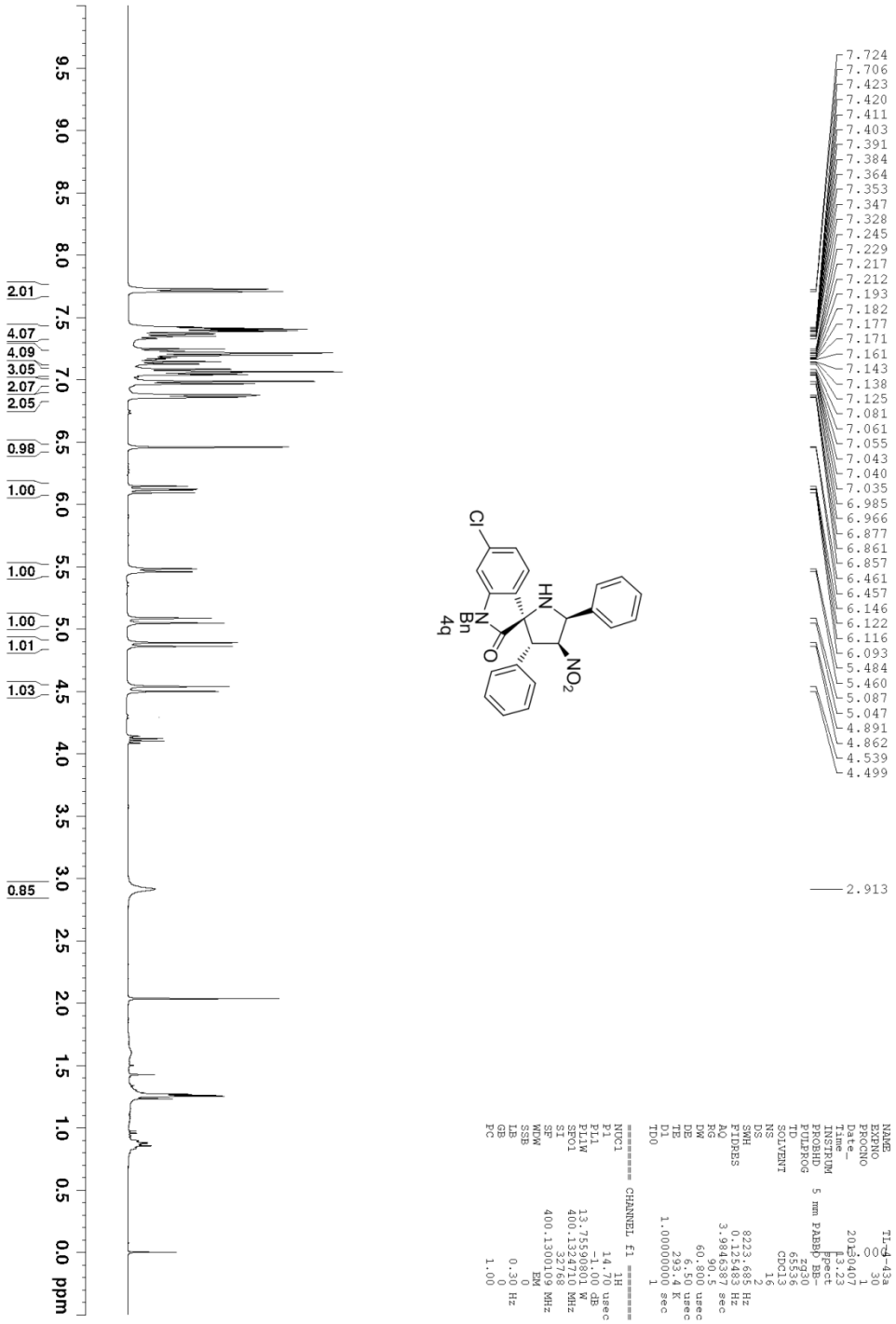
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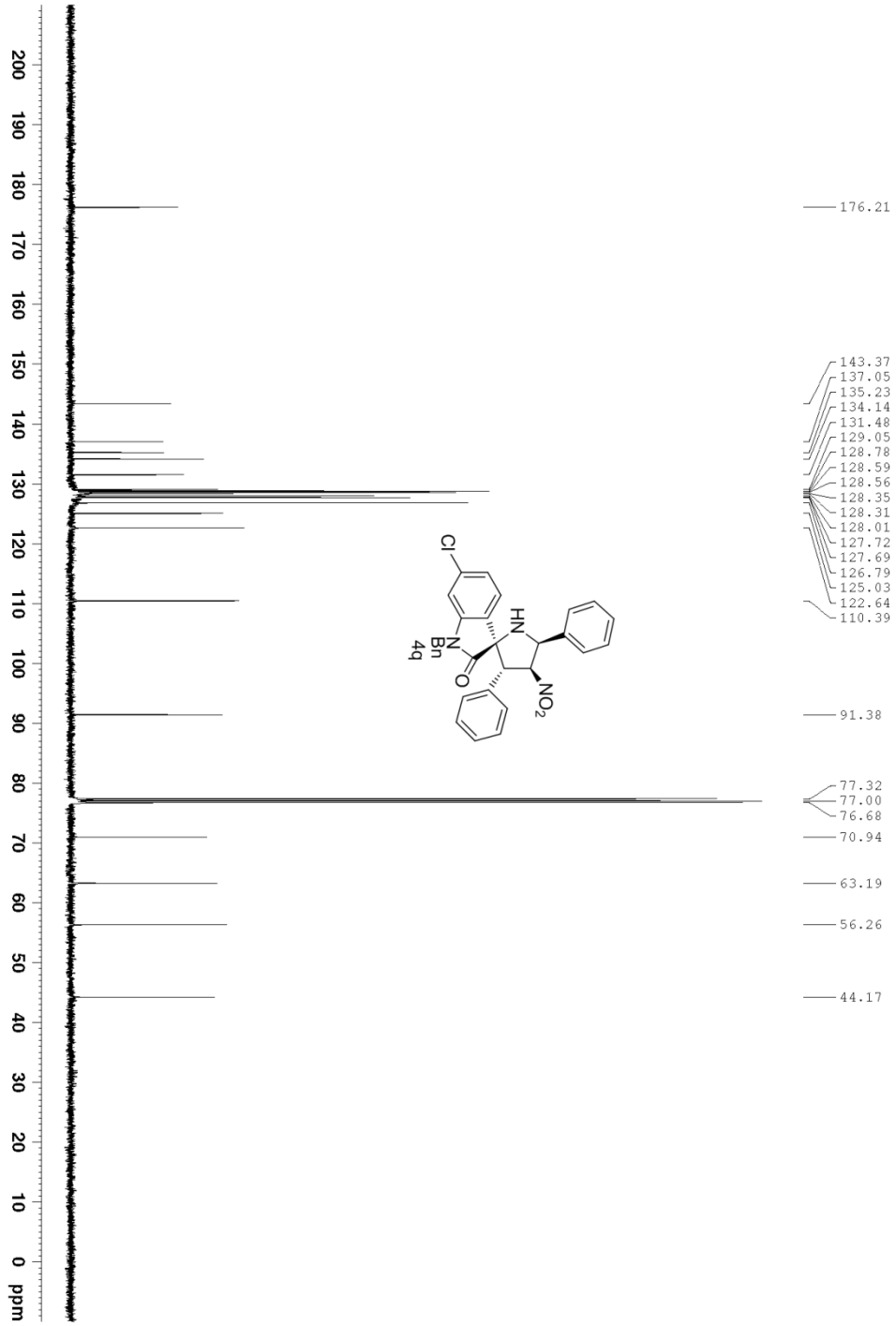

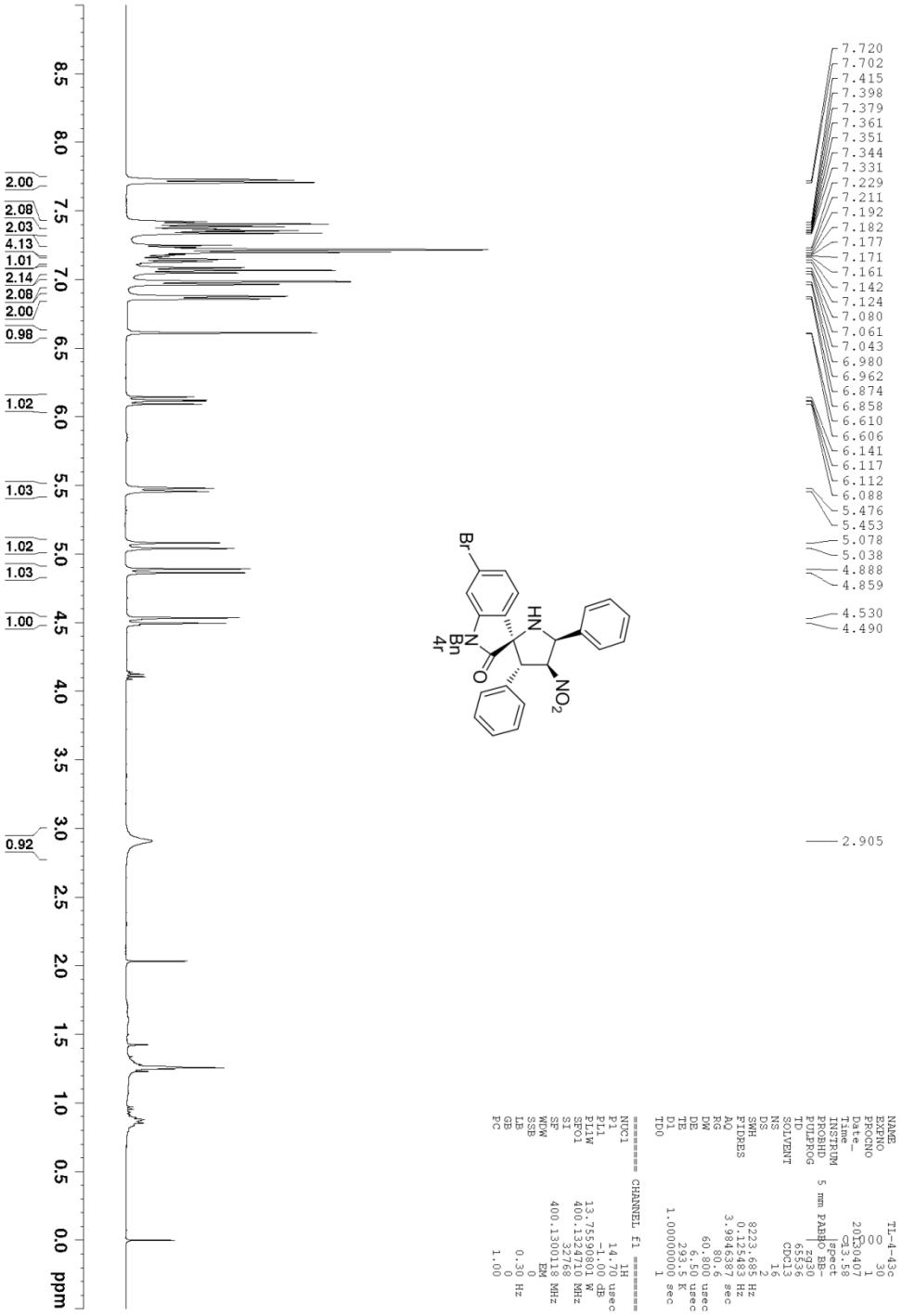
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RG 80.6
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DE 6.50 usec
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D1 1.00000000 sec
TD0 1
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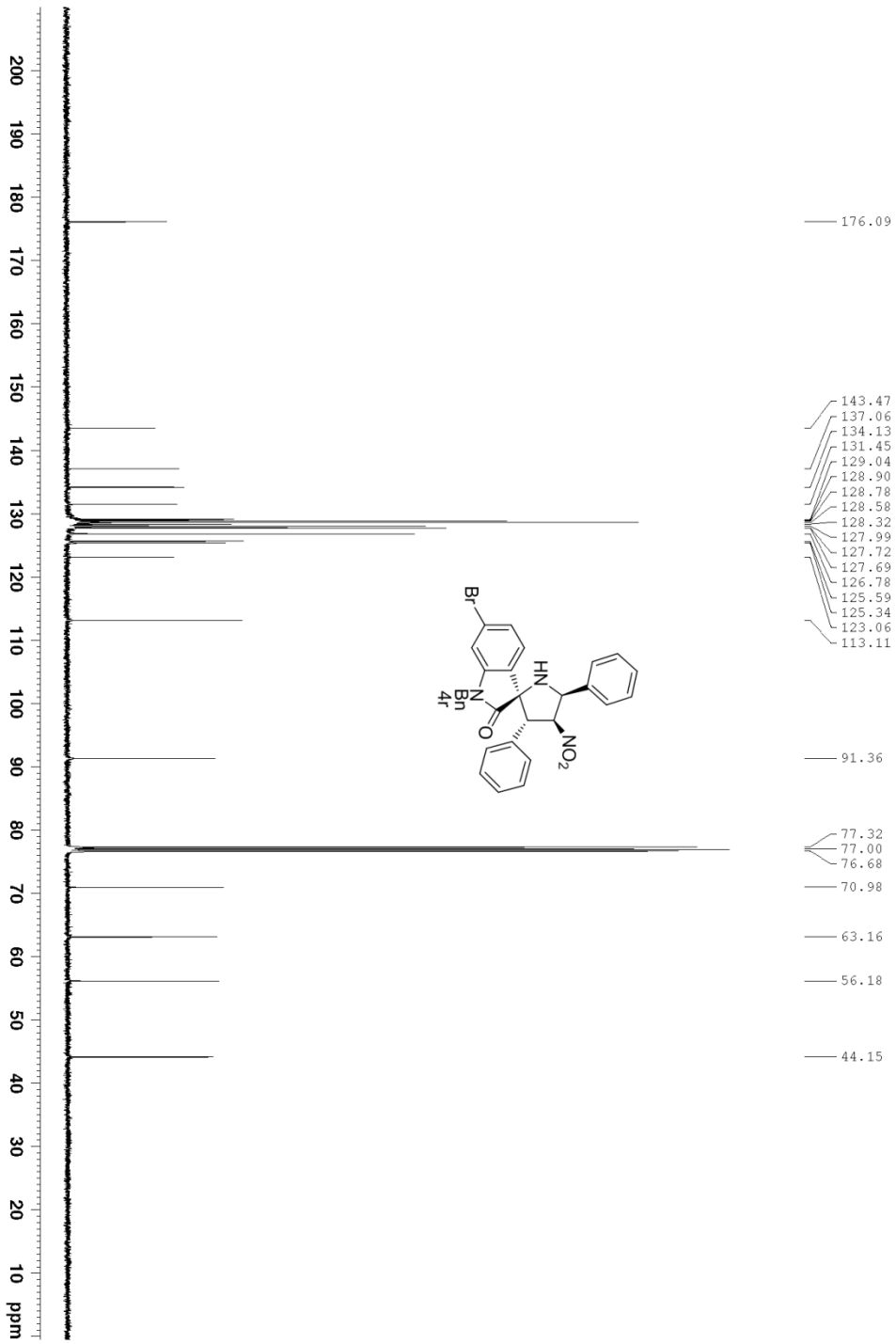
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ppm
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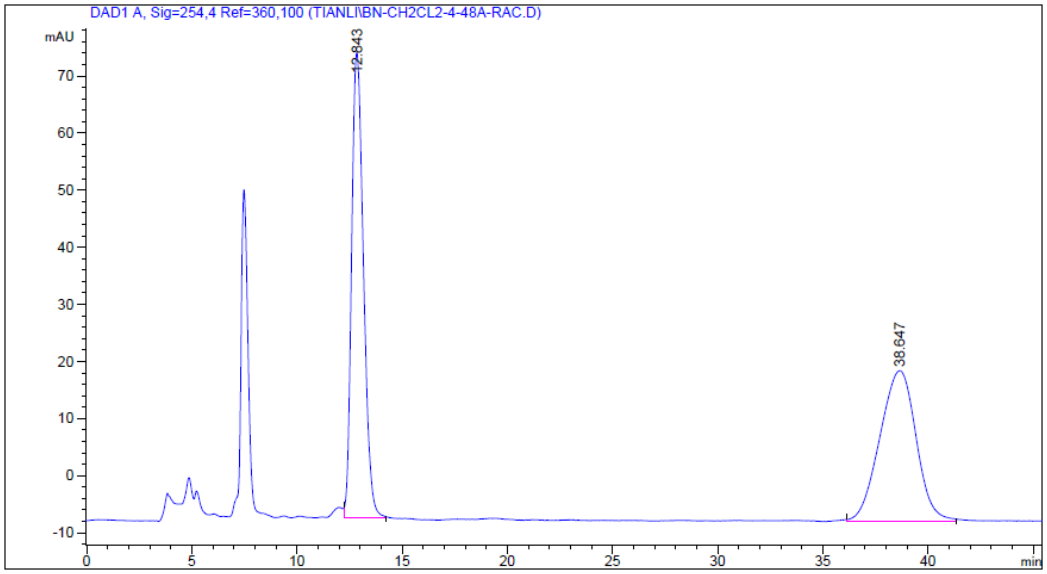
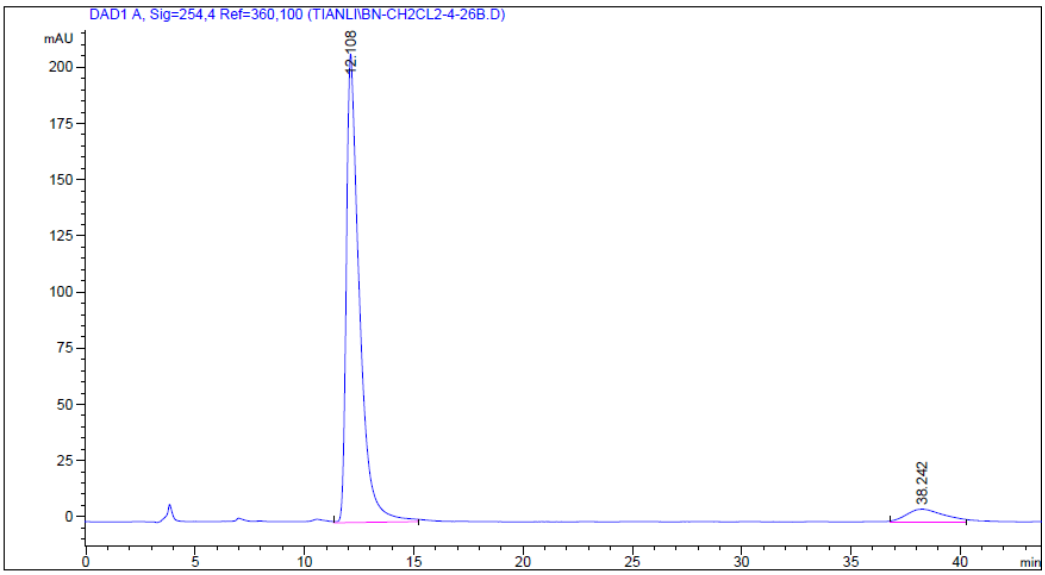
NO2

7. HPLC spectra

4a: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

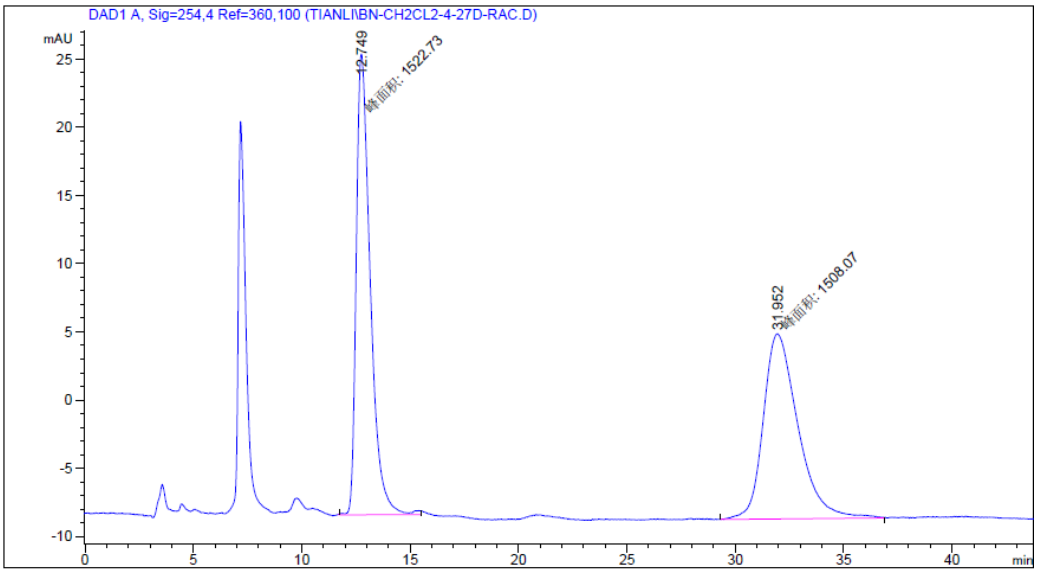


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	12.843	3195.95630	81.59977	50.4861
2	DAD 254.4 nm	38.647	3134.40820	26.27629	49.5139

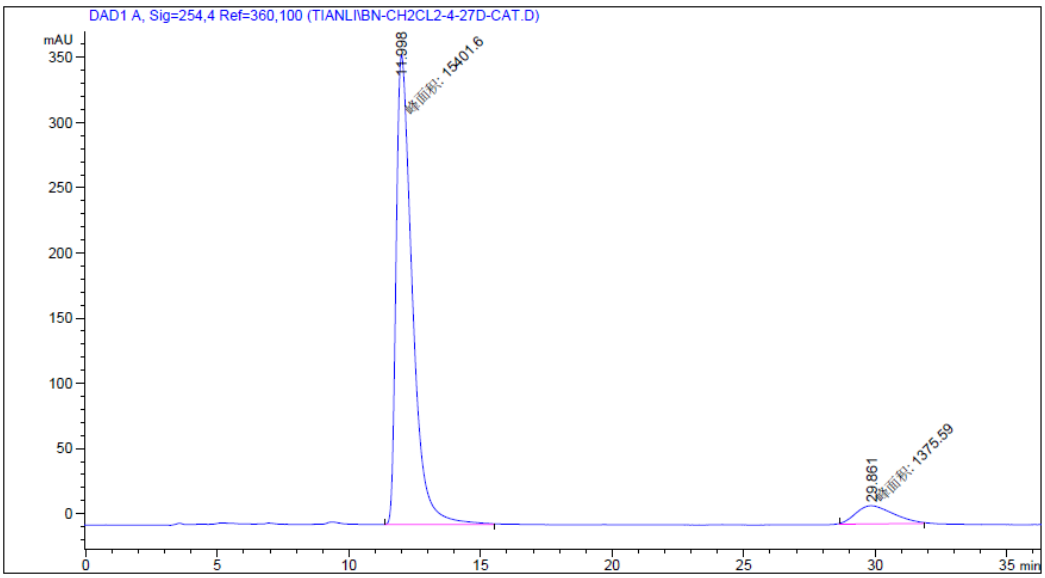


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	12.108	8669.92383	208.48779	93.0355
2	DAD 254.4 nm	38.242	649.01294	5.57843	6.9645

4b： HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

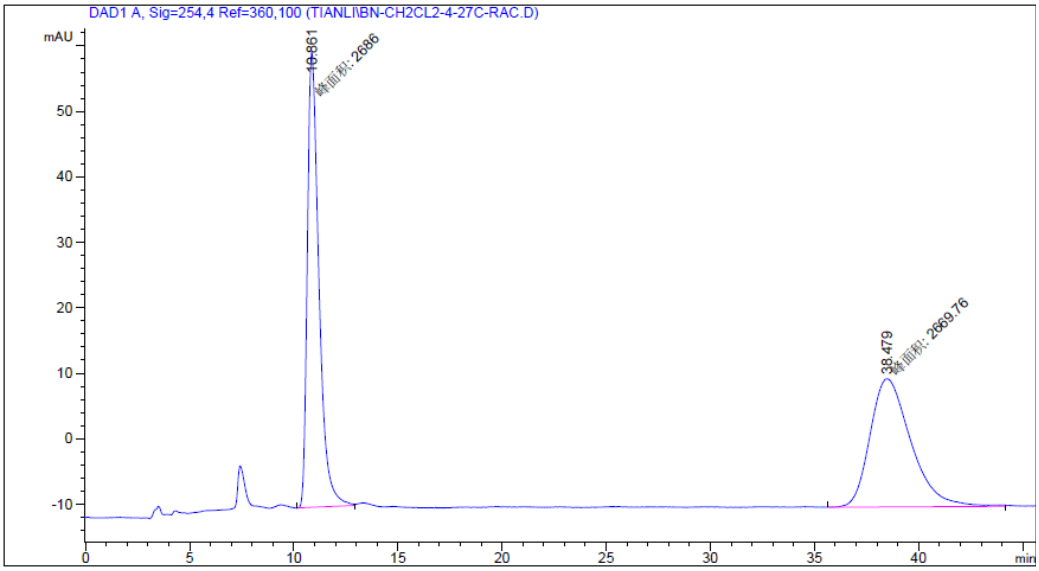


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	12.749	1522.72510	33.80012	50.2419
2	DAD 254.4 nm	31.952	1508.06506	13.58678	49.7581

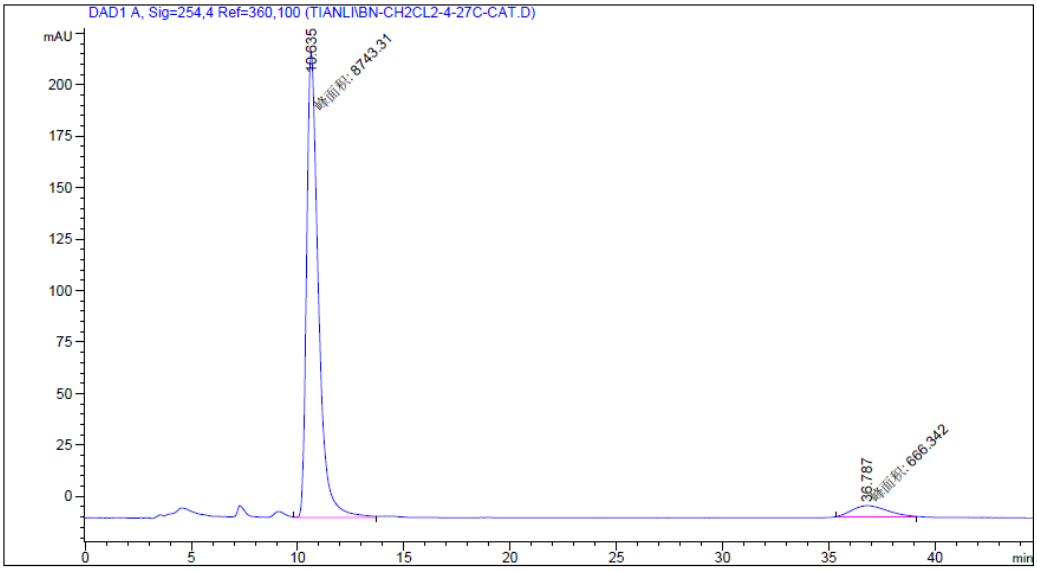


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	11.998	1.54016e4	360.24243	91.8008
2	DAD 254.4 nm	29.861	1375.59473	13.87683	8.1992

4c: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

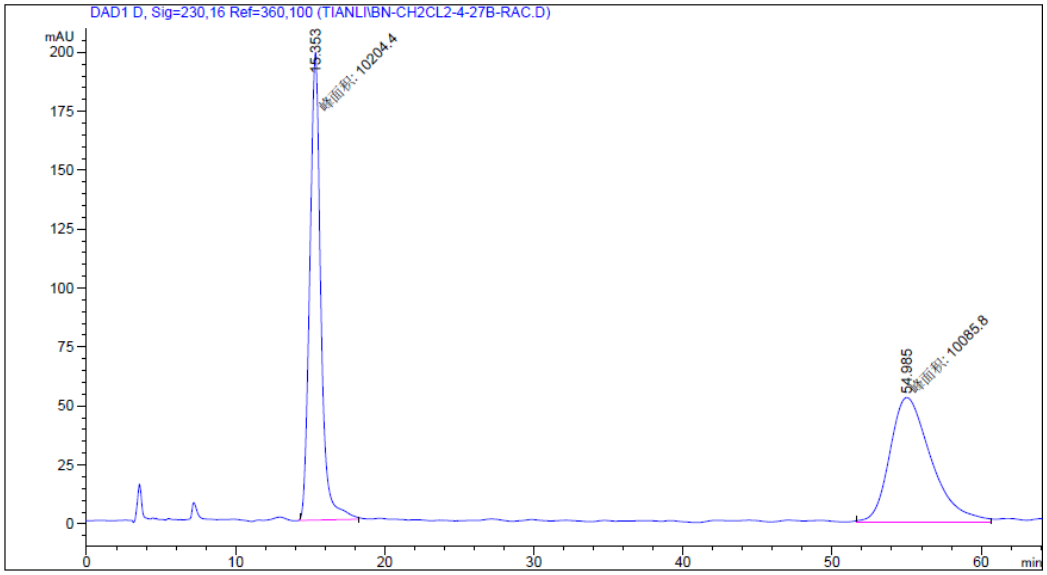


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	10.861	2685.99707	69.51553	50.1515
2	DAD 254.4 nm	38.479	2669.76489	19.57716	49.8485

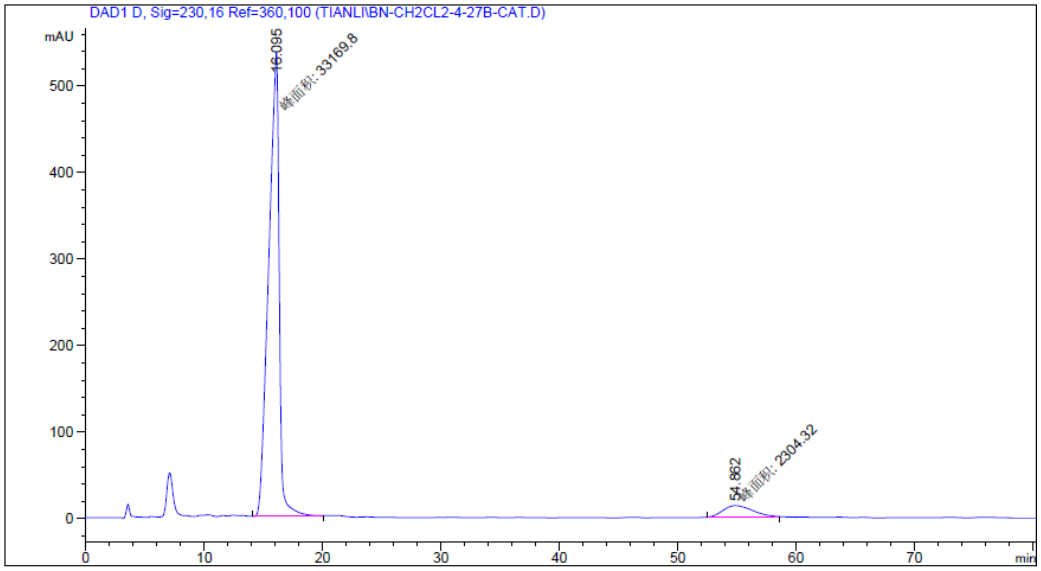


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	10.635	8743.30957	226.07661	92.9185
2	DAD 254.4 nm	36.787	666.34174	5.56928	7.0815

4d: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

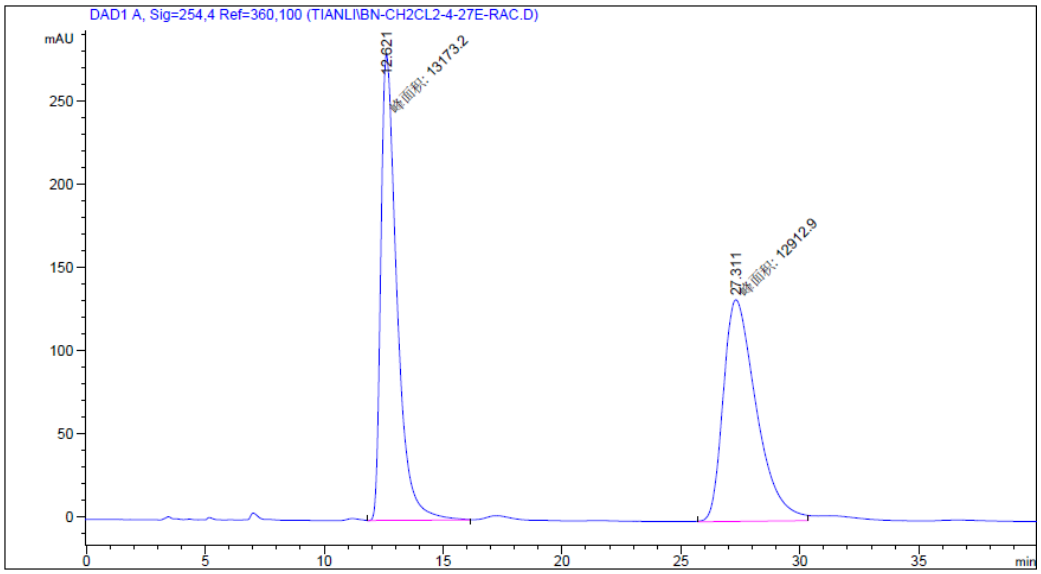


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	15.353	1.02044e4	198.39664	50.2924
2	DAD 230.16 nm	54.985	1.00858e4	52.63747	49.7076

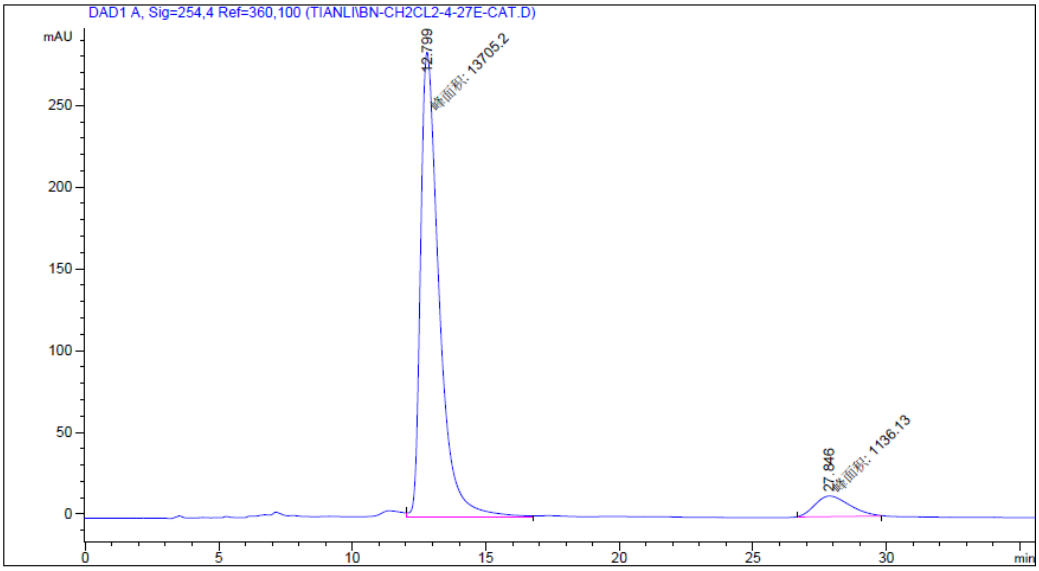


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	16.095	3.31698e4	536.61200	93.5042
2	DAD 230.16 nm	54.862	2304.31787	13.19223	6.4958

4e: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

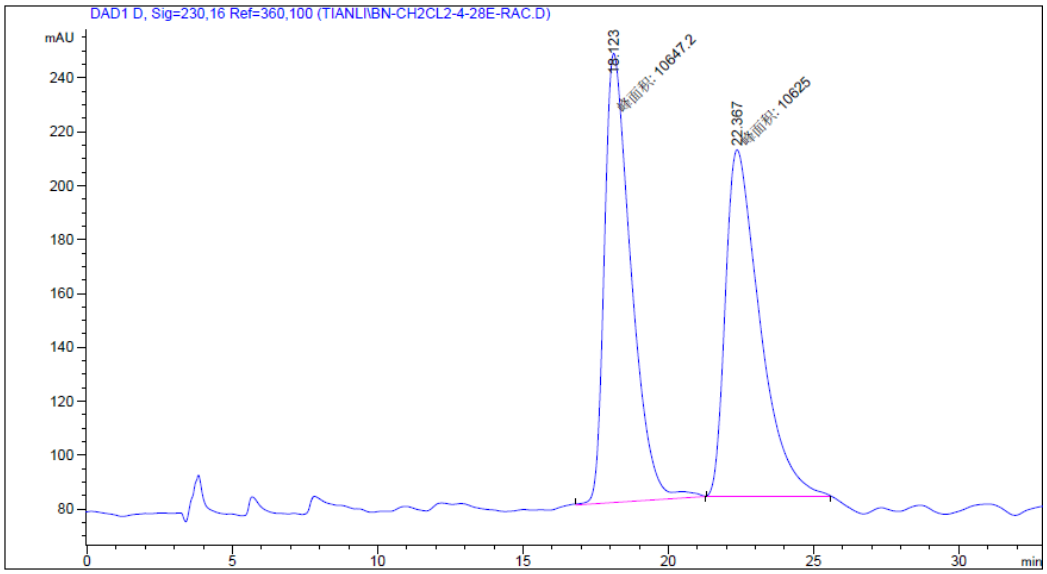


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	12.621	1.31732e4	280.42871	50.4989
2	DAD 254.4 nm	27.311	1.29129e4	133.31358	49.5011

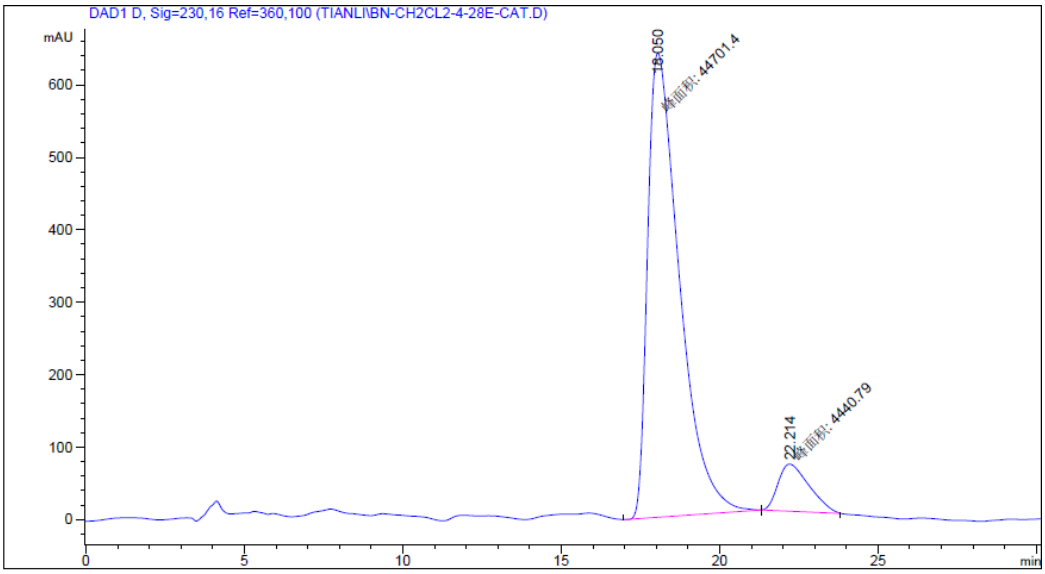


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	12.799	1.37052e4	284.27423	92.3448
2	DAD 254.4 nm	27.846	1136.13110	12.59568	7.6552

4f: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

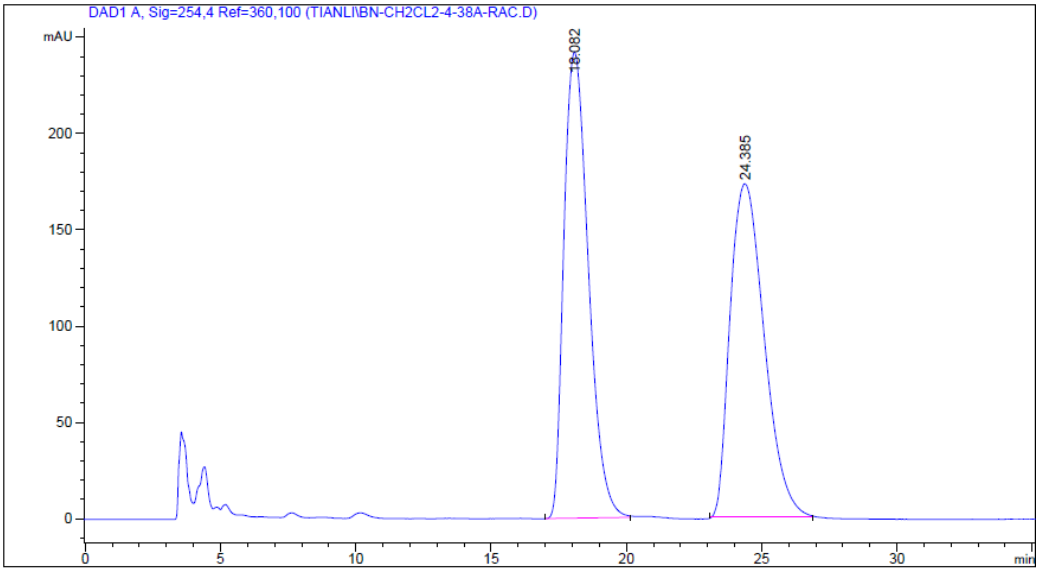


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	18.123	1.06472e4	166.62332	50.0522
2	DAD 230.16 nm	22.367	1.06250e4	128.65326	49.9478

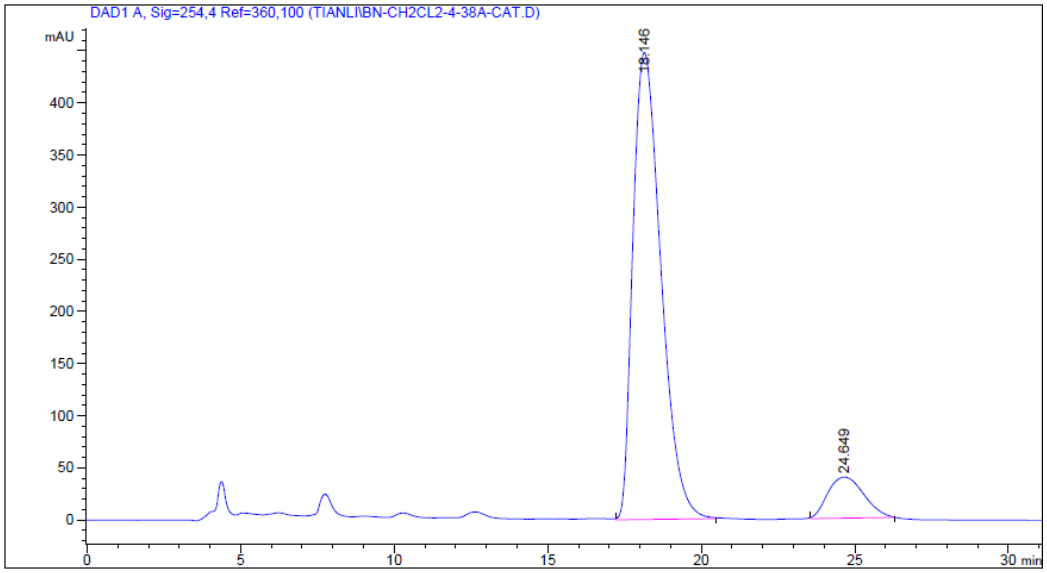


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	18.050	4.47014e4	640.77966	90.9634
2	DAD 230.16 nm	22.214	4440.78760	65.06643	9.0366

4g: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

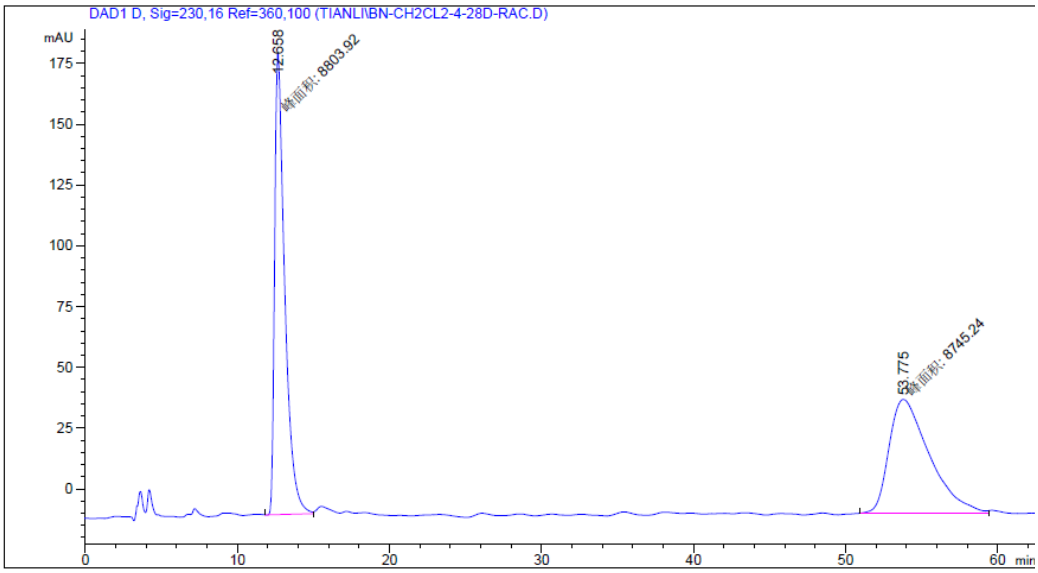


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	18.082	1.52096e4	242.02370	50.0342
2	DAD 254.4 nm	24.385	1.51889e4	173.27881	49.9658

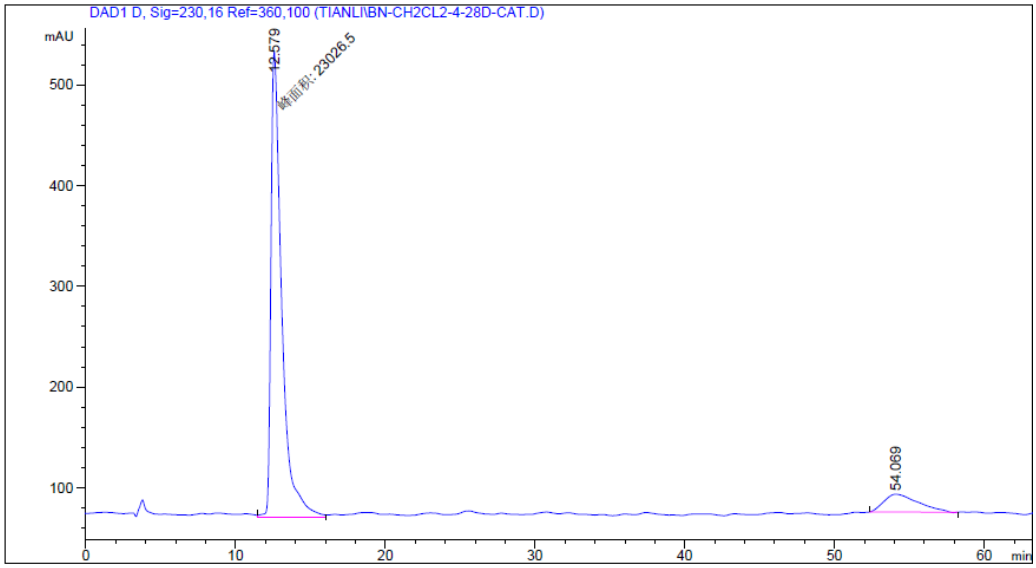


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	18.146	2.84083e4	447.97845	89.8264
2	DAD 254.4 nm	24.649	3217.46436	39.35492	10.1736

4h： HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

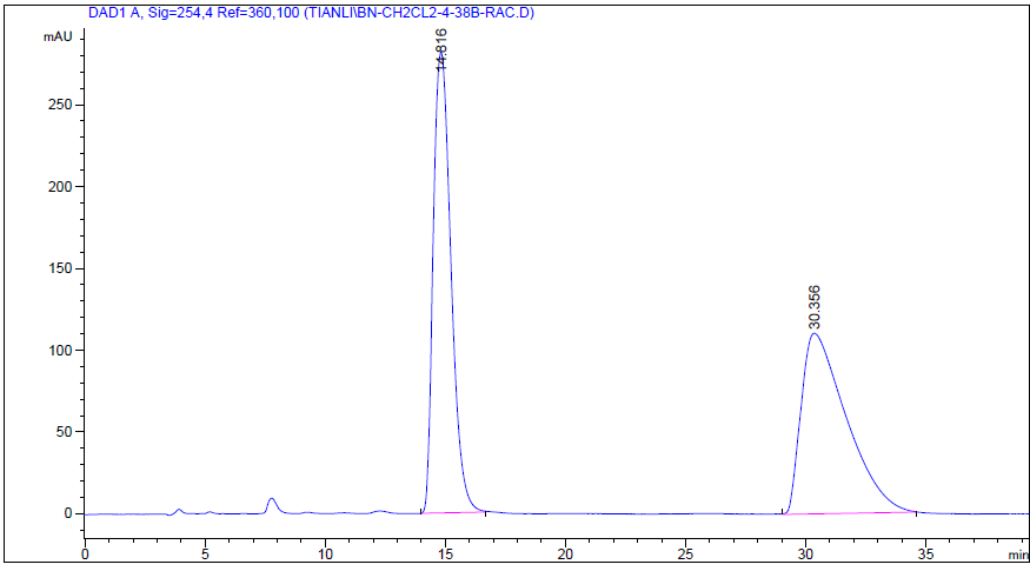


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	12.658	8803.91992	189.74937	50.1672
2	DAD 230.16 nm	53.775	8745.24121	46.97268	49.8328

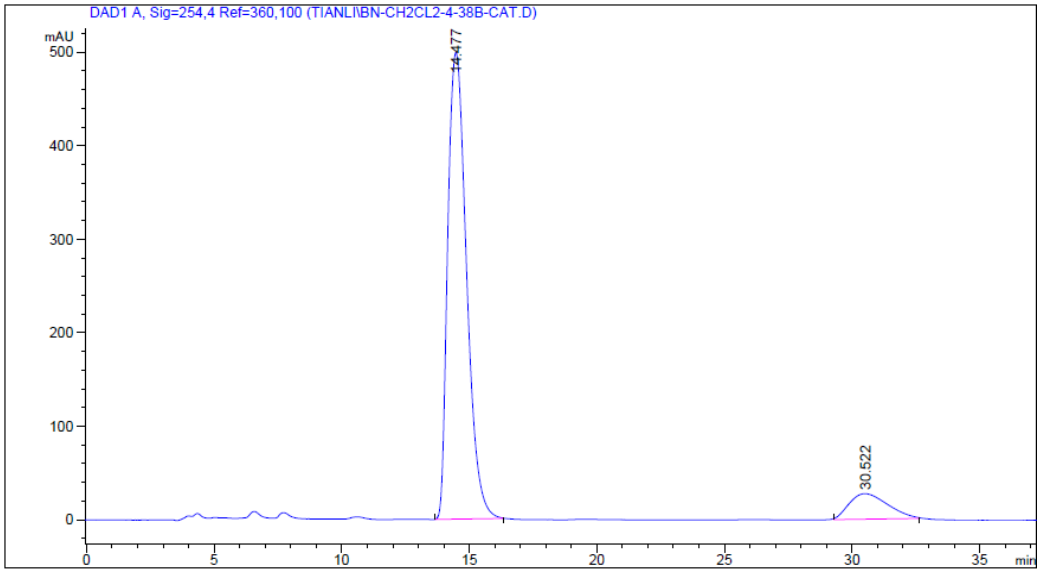


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	12.579	2.30265e4	461.59174	89.1013
2	DAD 230.16 nm	54.069	2816.54028	17.76291	10.8987

4i: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

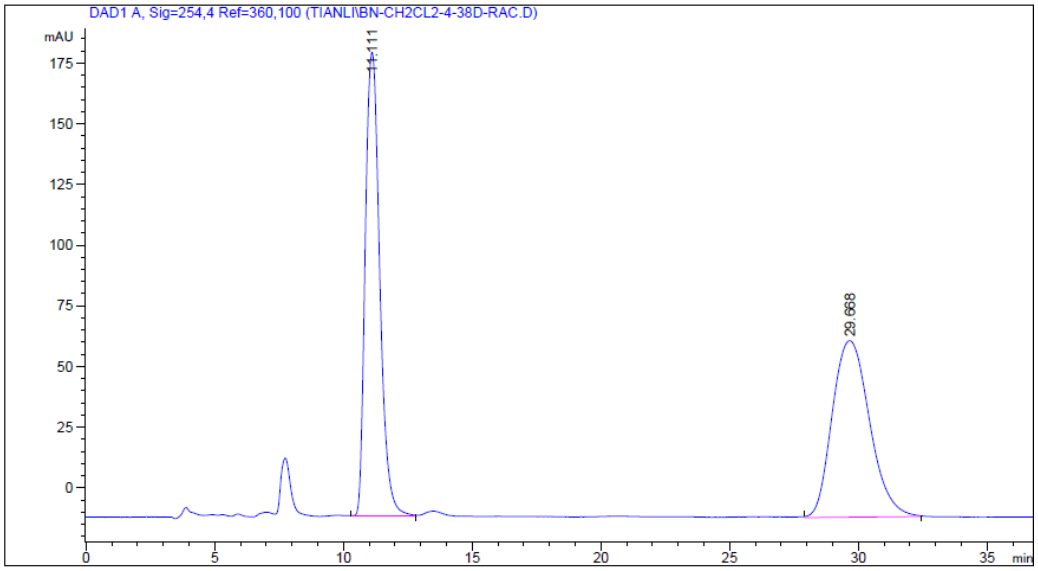


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	14.816	1.44427e4	281.72571	50.0805
2	DAD 254.4 nm	30.356	1.43963e4	110.44415	49.9195

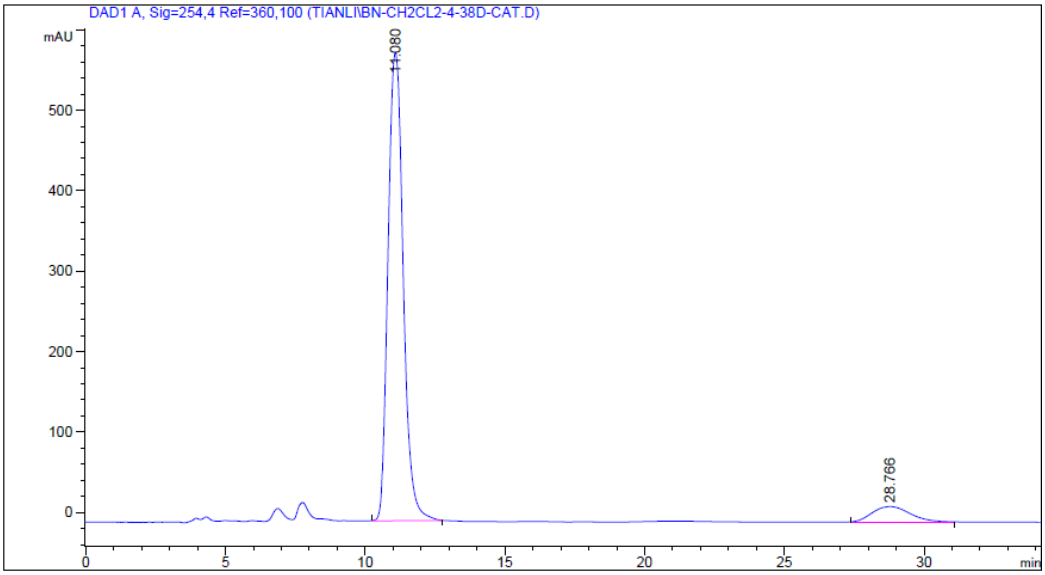


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	14.477	2.54708e4	499.27457	89.8593
2	DAD 254.4 nm	30.522	2874.40967	27.36990	10.1407

4j: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

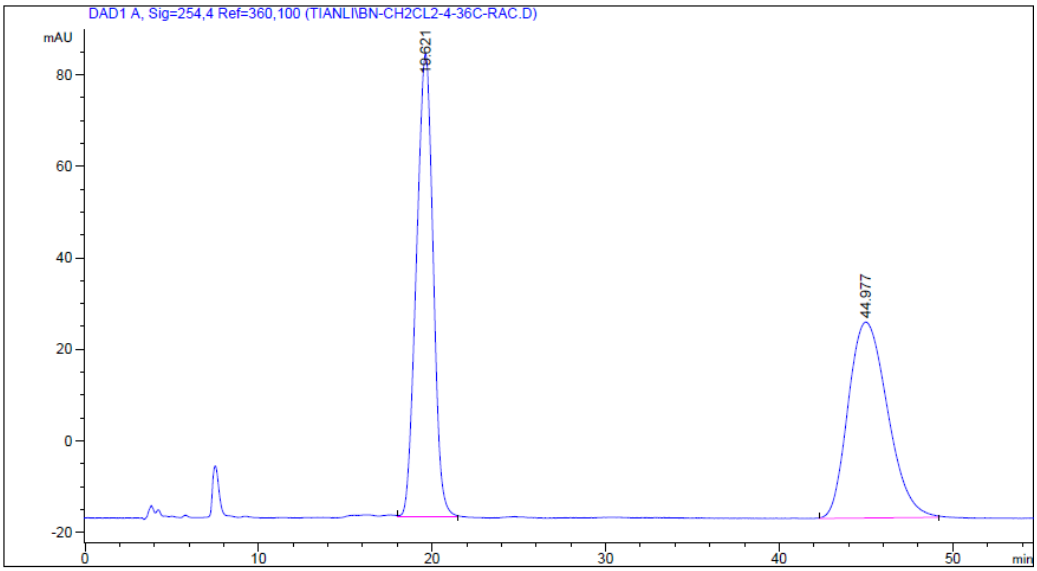


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	11.111	7481.87598	191.18770	50.4671
2	DAD 254.4 nm	29.668	7343.38672	72.71382	49.5329

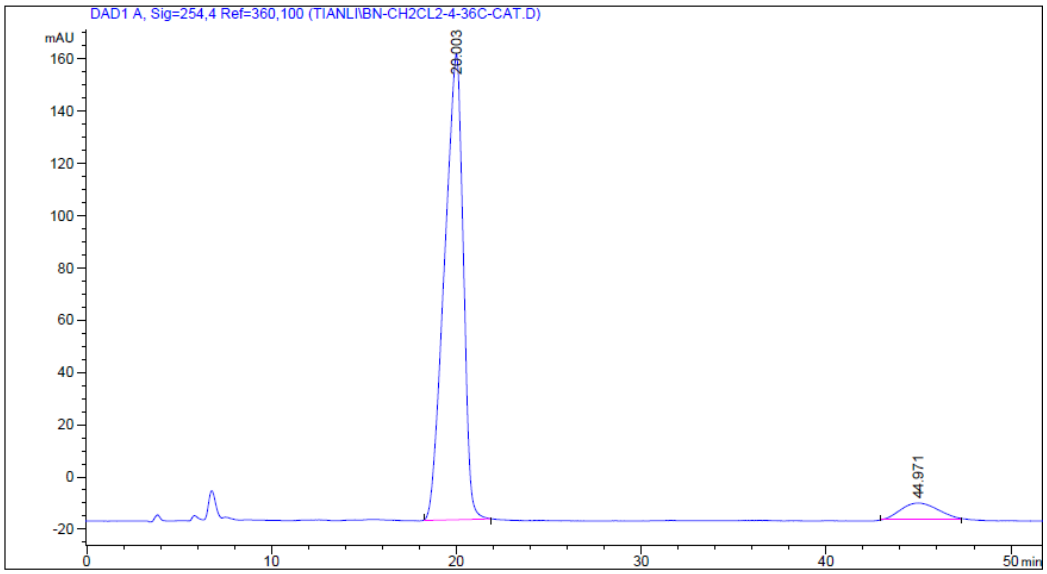


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	11.080	2.19934e4	581.75720	92.5055
2	DAD 254.4 nm	28.766	1781.82935	18.99689	7.4945

4k： HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

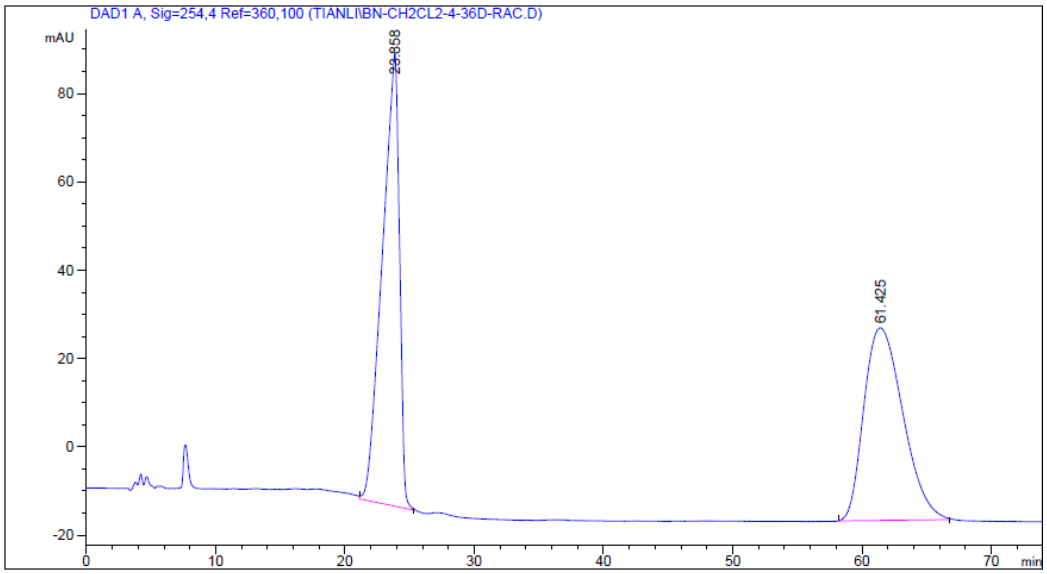


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	19.621	6780.57422	101.40557	50.1132
2	DAD 254.4 nm	44.977	6749.95410	42.80612	49.8868

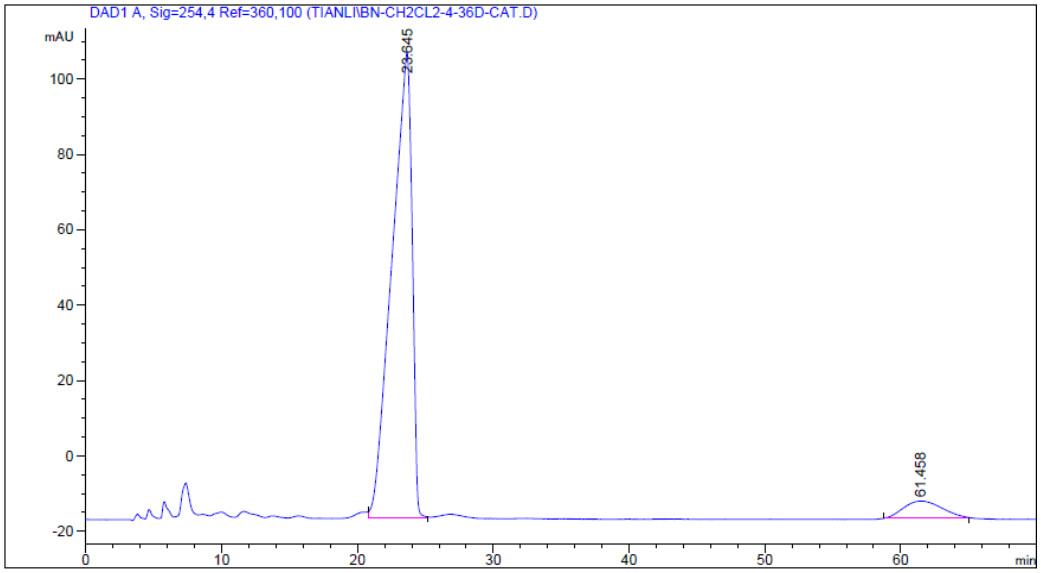


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	20.003	1.25229e4	178.46996	93.2013
2	DAD 254.4 nm	44.971	913.49902	6.43178	6.7987

4l: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

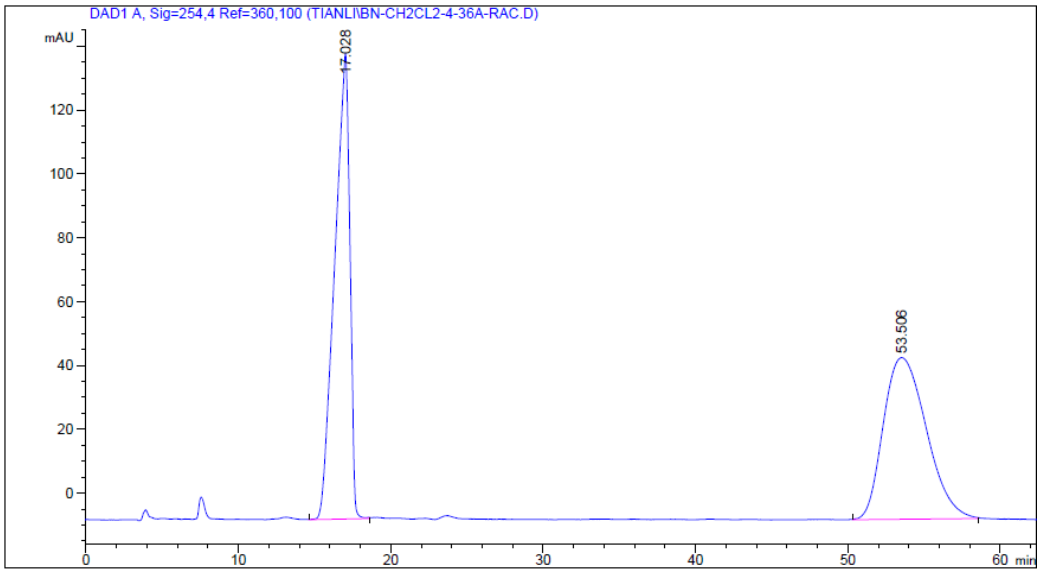


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	23.858	9390.08301	102.50266	50.6322
2	DAD 254.4 nm	61.425	9155.60156	43.59221	49.3678

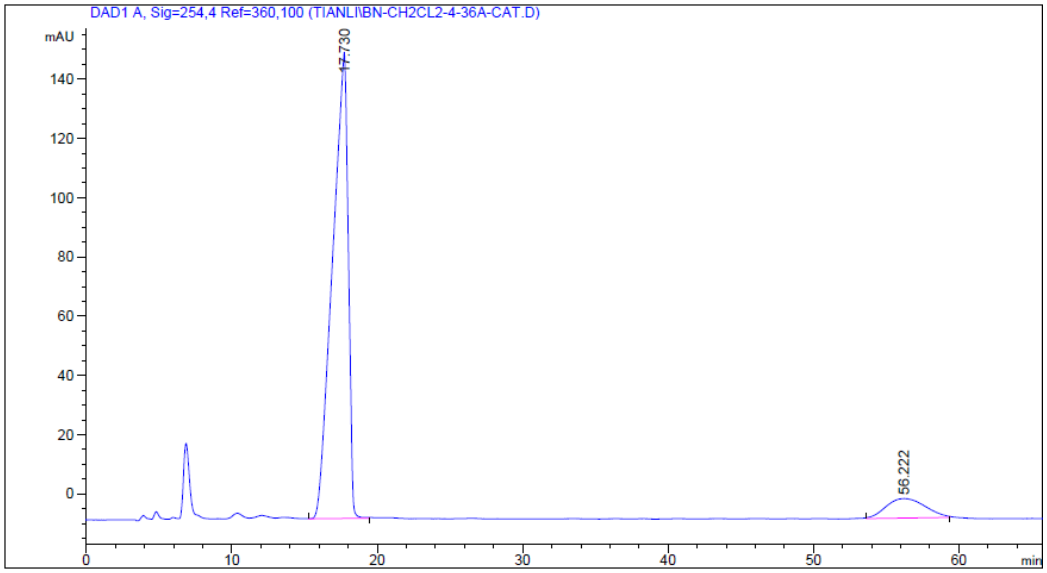


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	23.645	1.27410e4	123.69031	93.2364
2	DAD 254.4 nm	61.458	924.26617	4.63887	6.7636

4m: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

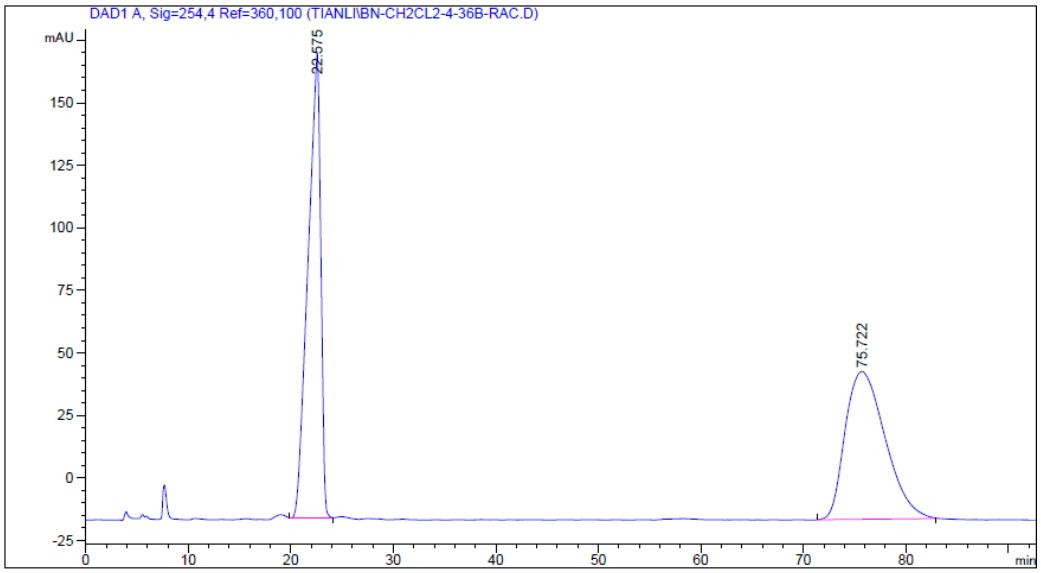


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	17.028	1.00423e4	145.92395	50.2292
2	DAD 254.4 nm	53.506	9950.67871	50.67793	49.7708

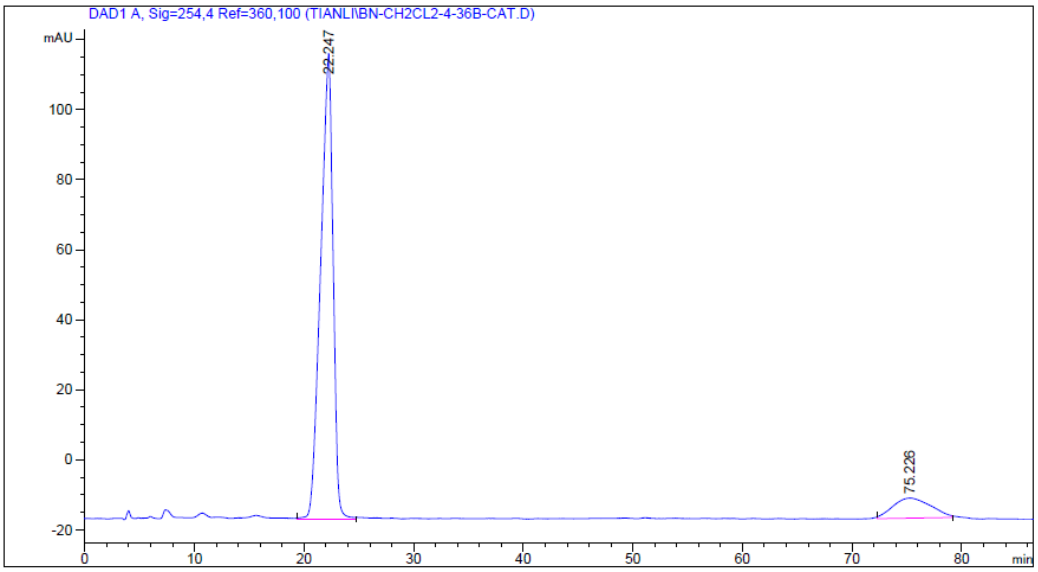


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	17.730	1.17703e4	157.30537	90.5352
2	DAD 254.4 nm	56.222	1230.50574	6.61603	9.4648

4n： HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

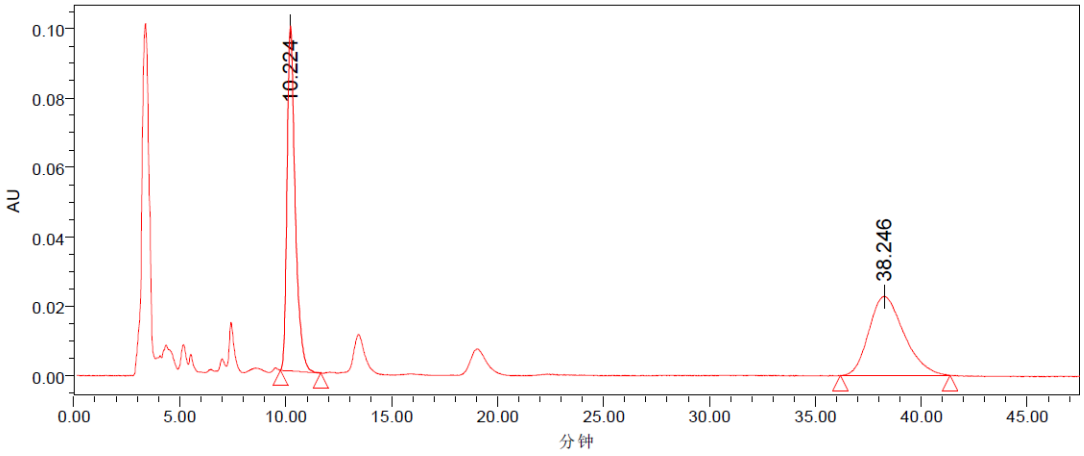


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	22.575	1.60481e4	186.05151	50.0300
2	DAD 254.4 nm	75.722	1.60289e4	59.13835	49.9700

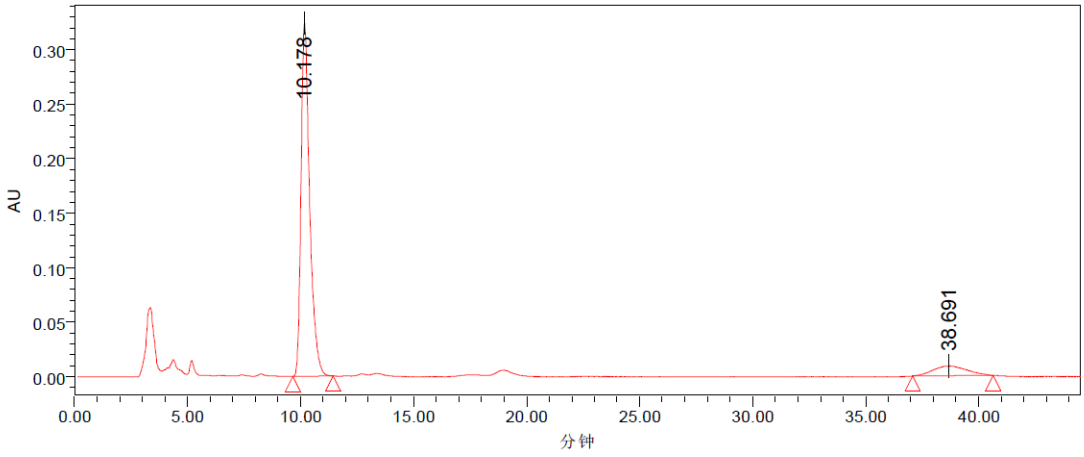


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	22.247	1.04265e4	132.90323	88.3326
2	DAD 254.4 nm	75.226	1377.18970	5.76975	11.6674

4o: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

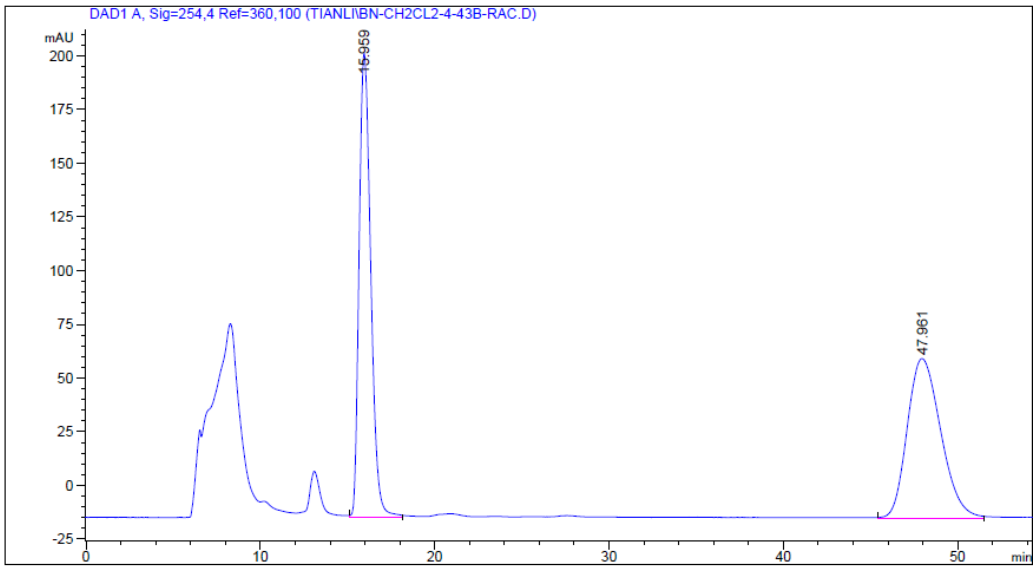


Peak	Processed Channel	Retention Time (min)	Peak Area	Peak Height	Peak Area (%)
1	DAD 267.0 nm	10.224	2653916	99482	50.29
2	DAD 267.0 nm	38.246	2623623	22777	49.71

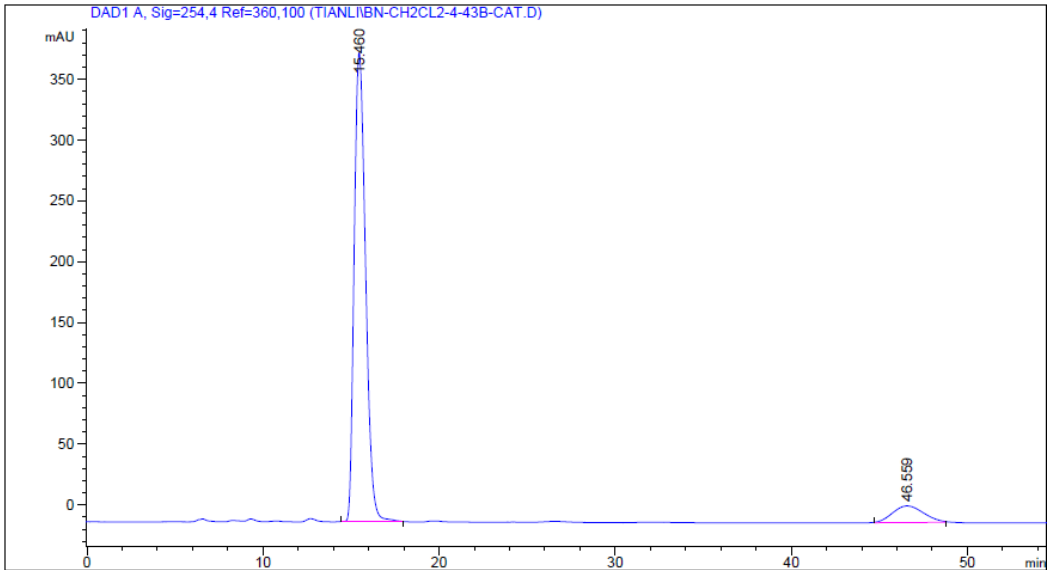


Peak	Processed Channel	Retention Time (min)	Peak Area	Peak Height	Peak Area (%)
1	DAD 267.0 nm	10.178	8577802	324371	90.15
2	DAD 267.0 nm	38.691	937612	8975	9.85

4p： HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

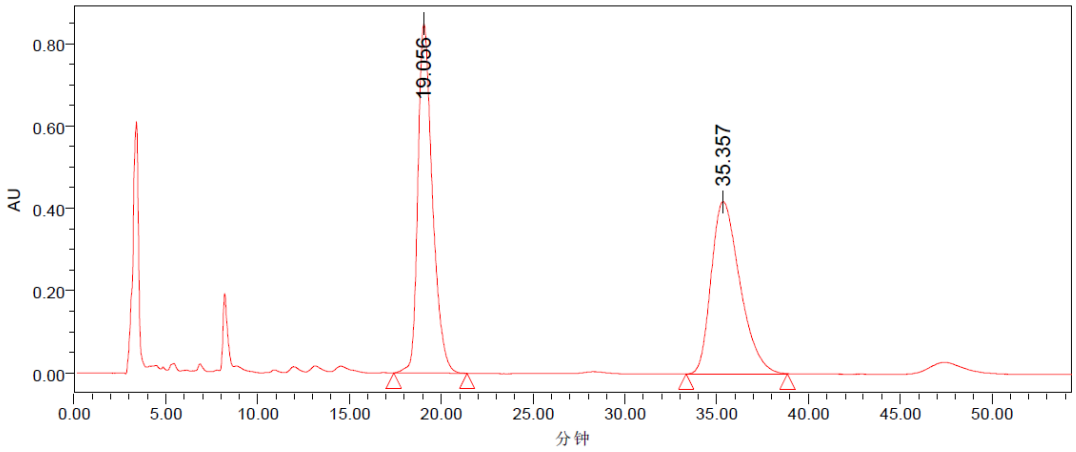


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	15.959	9986.24219	215.77444	50.2583
2	DAD 254.4 nm	47.961	9883.59473	74.17407	49.7417

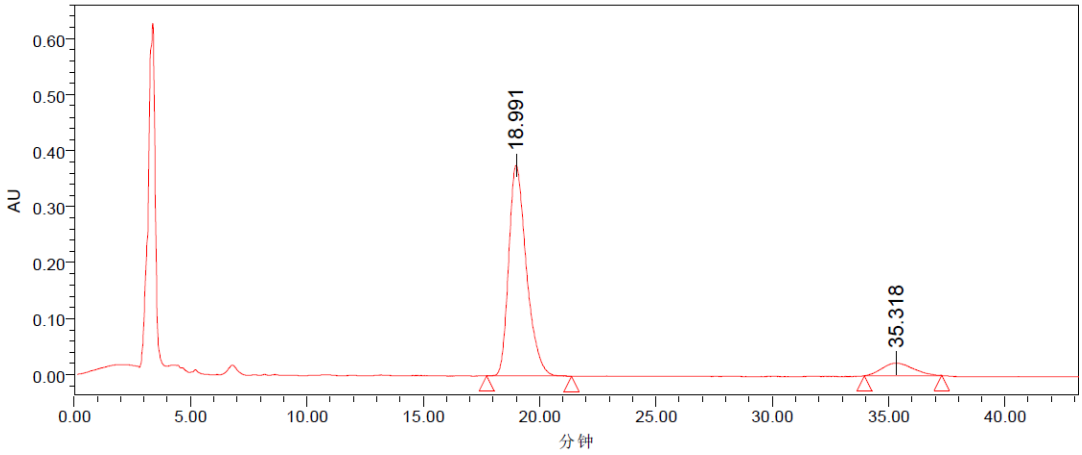


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	15.460	1.73079e4	385.86047	91.1533
2	DAD 254.4 nm	46.559	1679.77783	13.66537	8.8467

4q: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)

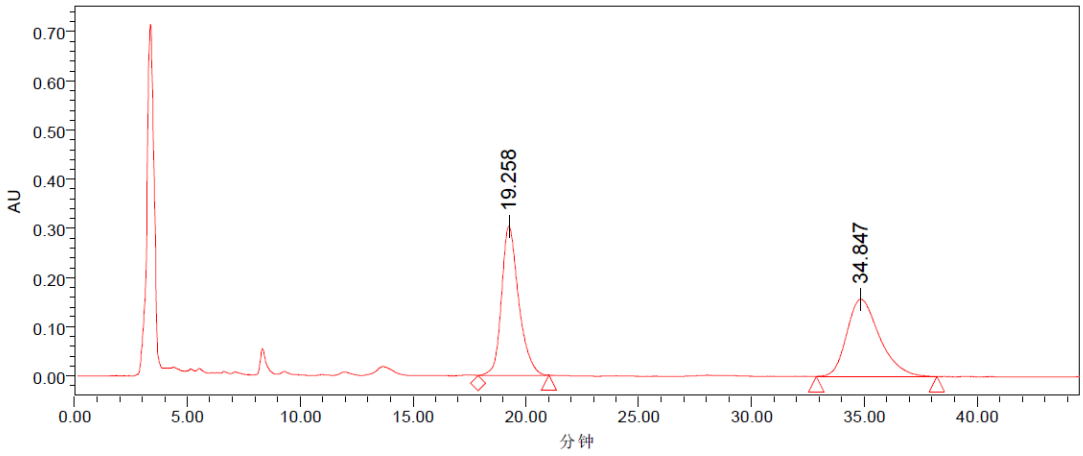


Peak	Processed Channel	Retention Time (min)	Peak Area	Peak Height	Peak Area (%)
1	DAD 220.0 nm	19.056	46567278	849449	50.50
2	DAD 220.0 nm	35.357	45654100	418713	49.50

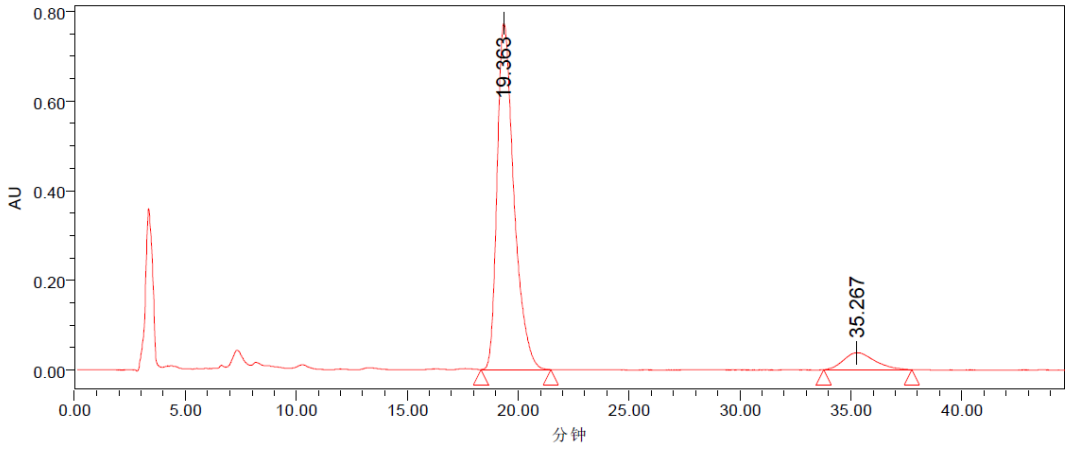


Peak	Processed Channel	Retention Time (min)	Peak Area	Peak Height	Peak Area (%)
1	DAD 220.0 nm	18.991	19842084	375894	90.37
2	DAD 220.0 nm	35.318	2114554	22573	9.63

4r: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =60:40, 1.0 mL/min)



Peak	Processed Channel	Retention Time (min)	Peak Area	Peak Height	Peak Area (%)
1	DAD 220.0 nm	19.258	16030804	303396	50.33
2	DAD 220.0 nm	34.847	15821678	157327	49.67



Peak	Processed Channel	Retention Time (min)	Peak Area	Peak Height	Peak Area (%)
1	DAD 220.0 nm	19.363	40797263	772608	91.64
2	DAD 220.0 nm	35.267	3723816	38152	8.36