Supporting Information

Catalytic Asymmetric Construction of Spirocyclopentaneoxindoles by a Combined Ru-Catalyzed Cross-Metathesis/Double Michael Addition Sequence

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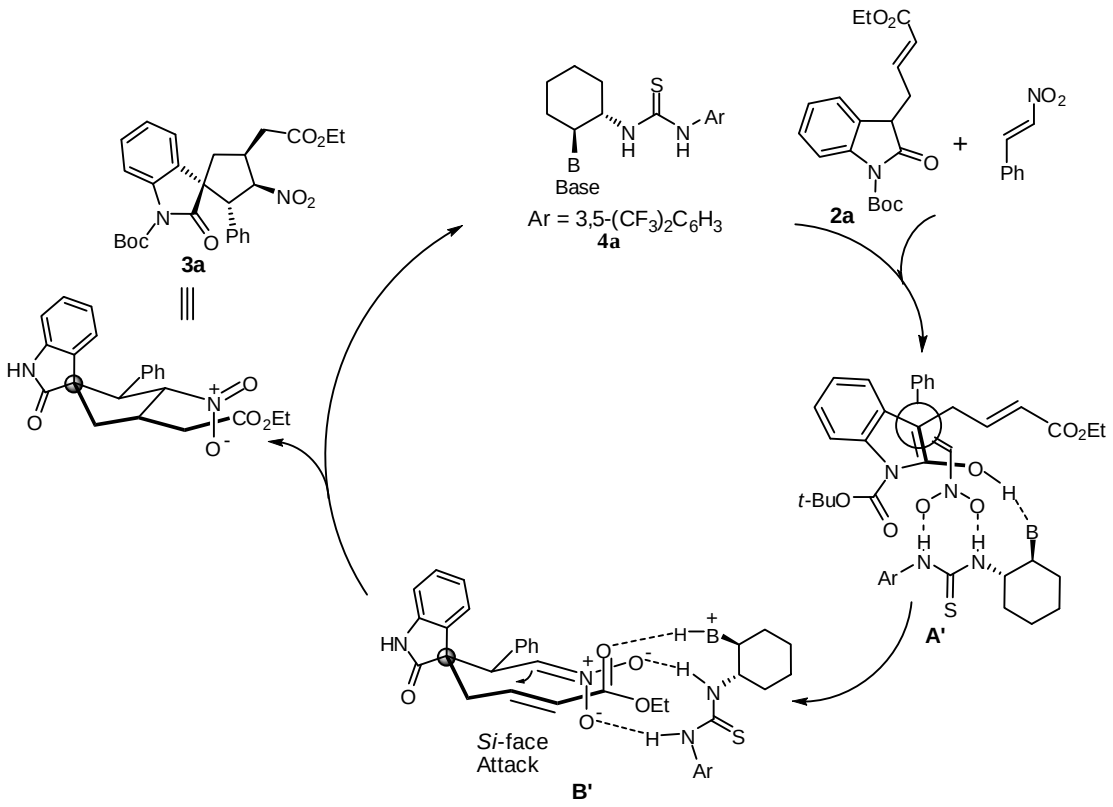
General Information

^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz spectrophotometer. Chemical shifts (δ) are expressed in ppm, and J values are given in Hz. The enantiomeric excess was determined by HPLC using Chiralpak AD-H, Chiralcel OD-H and Chiralcel OJ-H column with *n*-hexane and *i*-propanol as eluents. High resolution mass spectrometry (HRMS) was recorded on a VG Auto Spec-3000 spectrometer. Optical rotations were measured on a JASCO DIP-370 polarimeter. All chemicals and solvents were used as received without further purification unless otherwise stated. Flash column chromatography was performed on silica gel (230–400 mesh).

Racemic compounds were obtained by using 1.1 eq. DABCO or piperidine as catalyst.

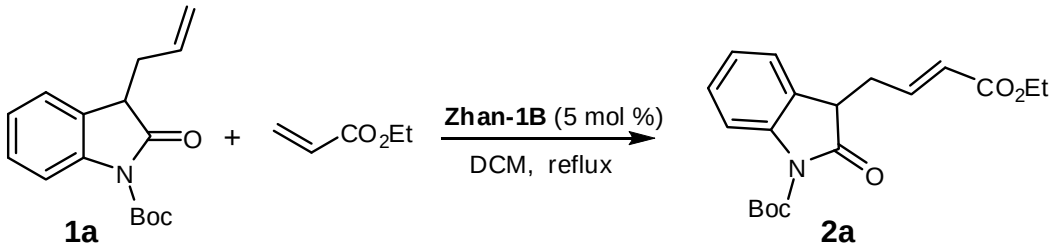
Proposed Catalytic Cycle for the Michael/Michael Addition:

A plausible catalytic cycle for the double Michael addition of 3-functionalzed oxindoles with nitroolefin enoates is outlined in Scheme 1. Firstly, The thiourea moiety of catalyst **4a** activates nitroolefin through a hydrogen-bonding interaction whereas the amino moiety serves as a base for deprotonation of the acidic proton of the oxindole **2a**, thereby forming the synclinal transition state **A'**, which undergoes the intermolecular Michael addition to provide the intermediate **B'**. Another intramolecular Michael addition to this intermediate generates a cyclized intermediate, and subsequent proton transfer leads to the corresponding spirocyclopentaneoxindole **3a** with the release of catalyst **4a**.

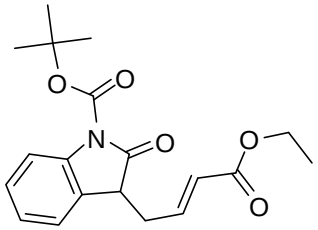


Scheme 1.

General Procedure for the Ru-Catalyzed Cross-Metathesis:



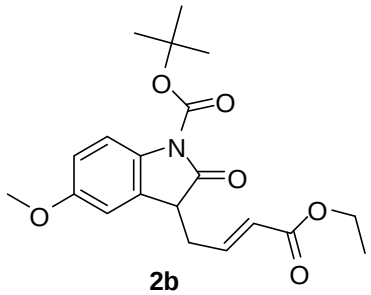
Under nitrogen atmosphere, to a solution of 3-allyl-oxindole **1a**[1] (200 mg, 0.73 mmol) and ethyl acrylate (366 mg, 3.66 mmol, 5 equiv) in CH_2Cl_2 (4 mL) was added **Zhan-1B** catalyst (26.8 mg, 5% mol %). The reaction mixture was stirred at reflux for 5 h before being filtered through 1.5 cm pad of Florisil/silica. The pad was washed with CH_2Cl_2, and the solvent was removed by evaporation. The residue was purified by flash column chromatography to yield the compound **2a** (179 mg, 71%) as a colorless oil.



2a

(*E*)-*tert*-butyl 3-(4-ethoxy-4-oxobut-2-enyl)-2-oxoindoline-1-carboxylate (2a):

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.1 Hz, 1H), 7.11-7.22 (m, 2H), 7.16 (m, 1H), 6.89 (m, 1H), 5.91 (d, J = 14.4 Hz, 1H), 4.17 (m, 2H), 3.69 (m, 1H), 2.99 (m, 1H), 2.77 (m, 1H), 1.65 (brs, 9H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.7, 165.8, 149.0, 143.5, 140.0, 128.5, 126.5, 124.6, 124.4, 123.8, 115.1, 84.4, 60.3, 45.0, 33.6, 28.0, 14.2.



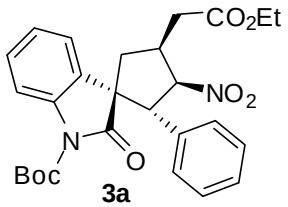
2b

(*E*)-*tert*-butyl 3-(4-ethoxy-4-oxobut-2-enyl)-5-methoxy-2-oxoindoline-1-carboxylate (**2b**):

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, J = 8.7 Hz, 1H), 6.80-6.94 (m, 3H), 5.91 (d, J = 15.6 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 3.79 (s, 3H), 3.66 (m, 1H), 2.95 (m, 1H), 2.75 (m, 1H), 1.64 (brs, 9H), 1.26 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.7, 165.8, 156.7, 149.1, 143.3, 133.4, 127.8, 124.7, 116.0, 113.1, 110.4, 84.2, 76.6, 60.3, 55.6, 45.3, 33.6, 28.1, 14.2.

General Procedure for the Organocatalytic Cascade Michael-Michael Addition Reactions:

To a solution of oxindole **2a** (35 mg, 0.1 mmol) and nitrostyrene (17 mg, 0.11 mmol, 1.1 equiv) in dry dichloromethane (0.5 mL) at room temperature was added the organocatalyst **4a** (6.6 mg, 10 mol %). The resulting solution was stirred at room temperature for 12 h. The reaction mixture was quenched with aqueous NH_4Cl, extracted with EtOAc and dried over Na_2SO_4. The crude product was purified by flash silica gel chromatography to give 43 mg (86% yield) of the adduct **3a**.

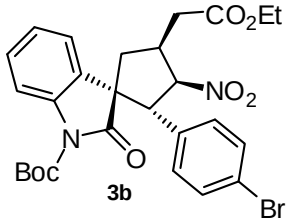


3a

(1*S*,2*R*,3*R*,4*S*)-*tert*-butyl 4-(2-ethoxy-2-oxoethyl)-3-nitro-2'-oxo-2-phenylspiro[cyclopentane-1,3'-indoline]-1'-carboxylate (3a):

A white solid; $[\alpha]_D^{20}$ = + 17.9 (c = 0.2 M, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, J = 7.2 Hz, 1H), 7.01-7.29 (m, 6H), 6.90 (d, J = 7.2 Hz, 2H), 5.82 (t, J = 10.2 Hz, 1H), 4.64 (d, J = 10.8 Hz, 1H), 4.17 (m, 2H), 3.64 (m, 1H), 2.65 (d, J = 7.5 Hz, 2H), 2.33-2.53 (m, 2H), 1.60 (brs, 9H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.1, 148.6, 139.0, 132.9, 128.8, 128.6, 128.3, 128.1, 127.3, 124.3, 123.6, 115.2, 90.4, 84.6, 61.1, 58.6, 58.5, 42.0, 36.5, 35.7, 28.0, 14.1; HPLC (Chiralpak AD-H, *i*-

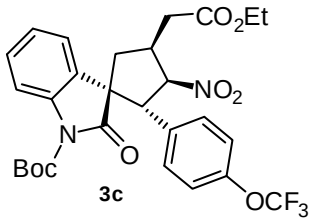
propanol/hexane = 3/97, flow rate 0.6 mL/min, λ = 254 nm): t_{minor} = 33.9 min, t_{major} = 36.2 min; HRMS calcd. for $C_{27}H_{30}N_2O_7Na$ $[M+Na]^+$: 517.1950, found 517.1949.



3b

(1*S*,2*R*,3*R*,4*S*)-*tert*-butyl 2-(4-bromophenyl)-4-(2-ethoxy-2-oxoethyl)-3-nitro-2'-oxospiro[cyclopentane-1,3'-indoline]-1'-carboxylate (3b):

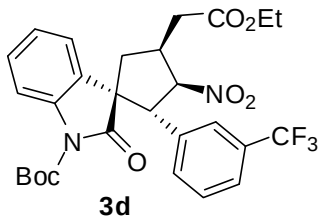
A white solid; $[\alpha]_D^{20}$ = + 6.5 (*c* = 0.2 M, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.2 Hz, 1H), 7.14-7.29 (m, 5H), 6.78 (d, *J* = 8.4 Hz, 2H), 5.76 (t, *J* = 10.5 Hz, 1H), 4.59 (d, *J* = 10.8 Hz, 1H), 4.16 (m, 2H), 3.65 (m, 1H), 2.64 (d, *J* = 7.5 Hz, 2H), 2.33-2.51 (m, 2H), 1.61 (brs, 9H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.8, 170.9, 148.4, 139.1, 132.0, 131.6, 129.1, 128.2, 124.5, 123.5, 122.3, 115.4, 90.4, 84.9, 61.1, 58.4, 57.9, 42.2, 36.4, 35.6, 28.0, 14.1; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 3/97, flow rate 0.6 mL/min, λ = 254 nm): t_{minor} = 46.8 min, t_{major} = 57.9 min; HRMS calcd. for $C_{27}H_{29}N_2O_7BrNa$ $[M+Na]^+$: 595.1055, found 5951045.



3c

(1*S*,2*R*,3*R*,4*S*)-*tert*-butyl 4-(2-ethoxy-2-oxoethyl)-3-nitro-2'-oxo-2-(4-(trifluoromethoxy)phenyl)spiro[cyclopentane-1,3'-indoline]-1'-carboxylate (3c):

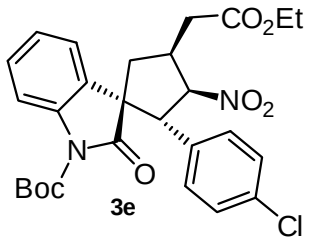
A yellow oil; $[\alpha]_D^{20}$ = + 23.8 (*c* = 0.2 M, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 7.8 Hz, 1H), 7.17-7.30 (m, 3H), 6.92 (m, 4H), 5.77 (t, *J* = 10.5 Hz, 1H), 4.62 (d, *J* = 11.1 Hz, 1H), 4.15 (m, 2H), 3.67(m, 1H), 2.65 (d, *J* = 7.5 Hz, 2H), 2.43 (m, 2H), 1.60 (brs, 9H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.8, 170.9, 148.9, 148.4, 139.0, 131.6, 129.1, 128.9, 128.2, 124.5, 123.5, 121.9, 120.6, 118.5, 115.4, 90.4, 84.8, 61.1, 58.5, 57.8, 41.8, 36.4, 35.6, 28.0, 14.1; HPLC (Chiralcel OD-H, *i*-propanol/hexane = 10/90, flow rate 0.7 mL/min, λ = 254 nm): t_{major} = 16.4 min, t_{minor} (not found); HRMS calcd. for $C_{28}H_{29}N_2O_8F_3Na$ $[M+Na]^+$: 601.1773, found 601.1764.



3d

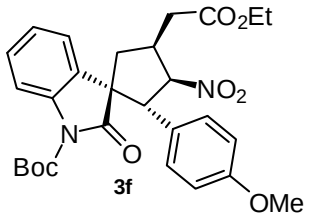
(1*S*,2*R*,3*R*,4*S*)-*tert*-butyl 4-(2-ethoxy-2-oxoethyl)-3-nitro-2'-oxo-2-(3-(trifluoromethyl)phenyl)spiro[cyclopentane-1,3'-indoline]-1'-carboxylate (3d):

A colorless oil; $[\alpha]_D^{20}$ = + 167.9 (*c* = 0.2 M, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 0.9 Hz, 1H), 7.08-7.61 (m, 7H), 5.81 (t, *J* = 10.5 Hz, 1H), 4.67 (d, *J* = 10.8 Hz, 1H), 4.18 (m, 2H), 3.71 (m, 1H), 2.69 (d, *J* = 5.4 Hz, 2H), 2.45 (m, 2H), 1.65 (brs, 9H), 1.27 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.7, 170.9, 148.4, 139.0, 134.1, 130.6, 129.2, 128.9, 128.0, 125.0, 124.5, 124.2, 123.5, 115.3, 90.0, 84.9, 61.1, 58.5, 58.3, 41.5, 36.6, 35.6, 27.9, 14.1; HPLC (Chiralcel OD-H, *i*-propanol/hexane = 10/90, flow rate 0.7 mL/min, λ = 254 nm): t_{major} = 9.9 min, t_{minor} = 21.7 min; HRMS calcd. for $C_{28}H_{29}N_2O_7F_3Na$ $[M+Na]^+$: 585.1824, found 585.1814.



(1*S*,2*R*,3*R*,4*S*)-*tert*-butyl 2-(4-chlorophenyl)-4-(2-ethoxy-2-oxoethyl)-3-nitro-2'-oxospiro[cyclopentane-1,3'-indoline]-1'-carboxylate (3e):

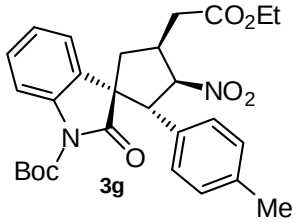
A white solid; $[\alpha]_D^{20}$ = + 13.9 (*c* = 0.2 M, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.8 Hz, 1H), 7.16-7.29 (m, 3H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.76 (t, *J* = 10.5 Hz, 1H), 4.60 (d, *J* = 10.8 Hz, 1H), 4.16 (m, 2H), 3.65 (m, 1H), 2.64 (d, *J* = 7.5 Hz, 2H), 2.42 (m, 2H), 1.60 (brs, 9H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.9, 170.9, 148.5, 139.0, 134.1, 131.5, 129.1, 128.8, 128.6, 128.2, 124.4, 123.5, 115.4, 90.5, 84.8, 61.1, 58.5, 57.8, 42.1, 36.4, 35.6, 28.0, 14.1; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 3/97, flow rate 0.6 mL/min, λ = 254 nm): t_{minor} = 39.6 min t_{major} = 51.8 min; HRMS calcd. for $C_{27}H_{29}N_2O_7ClNa$ $[M+Na]^+$: 551.1560, found 551.1564.



(1*S*,2*R*,3*R*,4*S*)-*tert*-butyl 4-(2-ethoxy-2-oxoethyl)-2-(4-methoxyphenyl)-3-nitro-2'-oxospiro[cyclopentane-1,3'-indoline]-1'-carboxylate (3f):

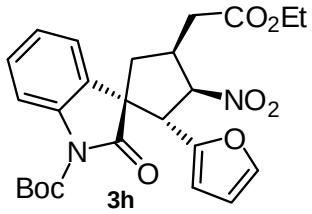
A white solid; $[\alpha]_D^{20}$ = -2.7 (*c* = 0.2 M, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.8 Hz, 1H), 7.16-7.31 (m, 3H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 5.75 (t, *J* = 10.5 Hz, 1H), 4.57 (d, *J* = 11.1 Hz, 1H), 4.15 (m, 2H), 3.65 (s, 3H), 2.64 (d, *J* = 7.5 Hz, 2H), 2.34-2.50 (m, 2H), 1.60 (brs, 9H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.1, 171.1, 159.3, 148.6, 139.1, 128.8, 128.6, 124.8, 124.3, 123.6, 115.3, 113.8, 90.8, 84.6, 61.0, 58.6, 58.1, 55.0, 42.0, 36.2, 35.7, 28.0, 14.1; HPLC

(Chiralpak AD-H, *i*-propanol/hexane = 3/97, flow rate 0.6 mL/min, λ = 254 nm): t_{minor} = 61.2 min, min, t_{major} = 64.5 min; HRMS calcd. for $C_{28}H_{32}N_2O_8Na$ $[M+Na]^+$: 547.2056, found 547.2065.



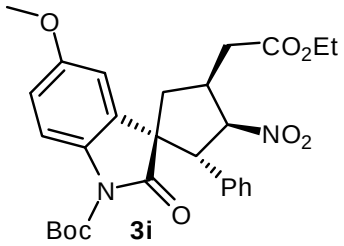
(1*S*,2*R*,3*R*,4*S*)-*tert*-butyl 4-(2-ethoxy-2-oxoethyl)-3-nitro-2'-oxo-2-p-tolylspiro[cyclopentane-1,3'-indoline]-1'-carboxylate (3g):

A white solid; $[\alpha]_D^{20}$ = + 11.9 (*c* = 0.2 M, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 7.8 Hz, 1H), 7.12-7.29 (m, 3H), 6.81 (dd, *J* = 8.1, 8.1 Hz, 4H), 5.80 (t, *J* = 10.5 Hz, 1H), 4.60 (d, *J* = 10.8 Hz, 1H), 4.15(m, 2H), 3.63 (m, 1H), 2.64 (d, *J* = 7.5 Hz, 2H), 2.31-2.51 (m, 2H), 2.15 (brs, 3H), 1.60 (brs, 9H), 0.86 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.2, 171.1, 148.7, 139.1, 137.8, 129.8, 129.1, 128.8, 127.3, 124.3, 123.6, 115.2, 90.7, 84.5, 61.0, 58.6, 58.2, 42.2, 36.4, 35.7, 28.0, 20.9, 14.1; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 3/97, flow rate 0.6 mL/min, λ = 254 nm): t_{minor} = 34.7 min, t_{major} = 37.9 min; HRMS calcd. for $C_{28}H_{32}N_2O_7Na$ $[M+Na]^+$: 531.2107, found 531.2102.



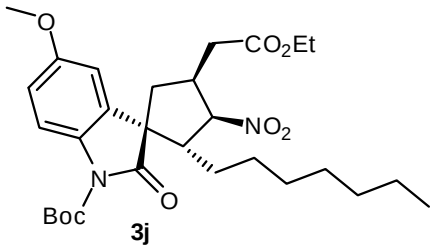
(1*S*,2*R*,3*R*,4*S*)-*tert*-butyl 4-(2-ethoxy-2-oxoethyl)-2-(furan-2-yl)-3-nitro-2'-oxospiro[cyclopentane-1,3'-indoline]-1'-carboxylate (3h):

A white solid; $[\alpha]_D^{20}$ = + 34.4 (*c* = 0.2 M, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 11.4 Hz, 1H), 7.03-7.31 (m, 4H), 6.03 (d, *J* =1.8 Hz, 1H), 5.89 (d, *J* = 2.7 Hz, 1H), 5.77 (t, *J* = 9.3 Hz, 1H), 4.82 (d, *J* = 9.0 Hz, 1H), 4.16 (m, 2H), 3.58 (m, 1H), 2.60 (d, *J* = 3.3 Hz, 2H), 2.50 (t, *J* = 12.0 Hz, 1H), 2.25 (m, 1H), 1.65 (brs, 9H), 1.26 (t, *J* = 6.9 Hz, 3H); 175.9, 170.9, 148.9, 148.4, 142.5, 139.1, 128.8, 128.7, 124.2, 123.7, 115.1, 110.1, 107.4, 90.4, 84.7, 61.1, 57.7, 52.1, 43.2, 37.6, 34.8, 28.1, 14.1; HPLC (Chiralcel OD-H, *i*-propanol/hexane = 5/95, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 13.1 min, t_{minor} = 15.2 min; HRMS calcd. for $C_{25}H_{28}N_2O_8Na$ $[M+Na]^+$: 507.1743, found 507.1738.



(1*S*,2*R*,3*R*,4*S*)-*tert*-butyl 4-(2-ethoxy-2-oxoethyl)-5'-methoxy-3-nitro-2'-oxo-2-phenylspiro[cyclopentane-1,3'-indoline]-1'-carboxylate (3i):

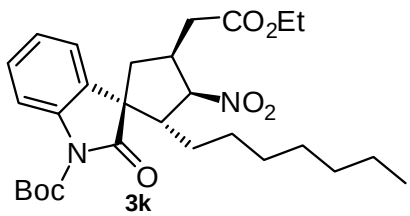
A white solid; $[\alpha]_D^{20}$ = - 36.9 (*c* = 0.2 M, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 9.0 Hz, 1H), 7.07 (m, 3H), 6.92 (m, 2H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.71 (dd, *J* = 2.4, 2.4 Hz, 1H), 5.81 (t, *J* = 10.5 Hz, 1H), 4.63 (t, *J* = 10.5 Hz, 1H), 4.15 (q, *J* = 6.9 Hz, 2H), 3.81 (s, 3H), 3.63 (m, 1H), 2.64 (d, *J* = 7.2 Hz, 2H), 2.41 (m, 2H), 1.59 (brs, 9H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.1, 171.0, 156.6, 148.6, 132.9, 132.5, 130.0, 128.4, 128.1, 127.3, 116.0, 112.4, 111.1, 90.3, 84.4, 61.1, 58.8, 58.3, 55.8, 42.0, 36.4, 35.7, 28.0, 14.1; HPLC (Chiralcel OD-H, *i*-propanol/hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 12.6 min, t_{minor} (not found); HRMS calcd. for $C_{28}H_{32}N_2O_8Na$ $[M+Na]^+$: 547.2056, found 547.2040.



3j

(1*S*,2*R*,3*R*,4*S*)-*tert*-butyl 4-(2-ethoxy-2-oxoethyl)-2-heptyl-5'-methoxy-3-nitro-2'-oxospiro[cyclopentane-1,3'-indoline]-1'-carboxylate (3j):

A white solid; $[\alpha]_D^{20}$ = - 51.9 (*c* = 0.2 M, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 9.0 Hz, 1H), 6.86 (d, *J* = 6.6 Hz, 1H), 6.70 (d, *J* = 2.4 Hz, 1H), 5.10 (t, *J* = 9.0 Hz, 1H), 4.15(m, 2H), 3.84 (s, 3H), 3.33-2.51 (m, 2H), 2.50 (m, 2H), 2.37 (t, *J* = 12.3 Hz, 1H), 2.07 (m, 1H), 1.64 (brs, 9H), 1.06-1.32 (m, 15H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.5, 171.1, 156.7, 149.1, 132.7, 130.2, 116.2, 112.2, 111.2, 94.0, 84.5, 61.0, 57.6, 55.7, 53.5, 44.0, 38.1, 34.7, 31.4, 30.2, 29.1, 28.7, 28.1, 27.1, 22.5, 14.1, 13.9; HPLC (Chiralcel OD-H, *i*-propanol/hexane = 5/95, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 8.8 min, t_{minor} (not found); HRMS calcd. for $C_{29}H_{42}N_2O_8Na$ $[M+Na]^+$: 569.2838, found 569.2839.



3k

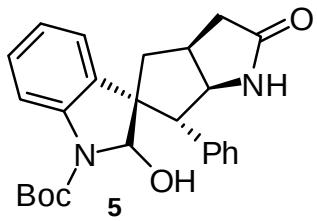
(1*S*,2*R*,3*R*,4*S*)-*tert*-butyl 4-(2-ethoxy-2-oxoethyl)-2-heptyl-3-nitro-2'-oxospiro[cyclopentane-1,3'-indoline]-1'-carboxylate (3k):

A colorless oil; $[\alpha]_D^{20}$ = -12.6 (*c* = 0.2 M, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.1 Hz, 1H), 7.36 (m, 1H), 7.17 (m, 2H), 5.12 (t, *J* = 9.3 Hz, 1H), 4.13 (m, 2H), 3.42 (m, 2H), 2.50 (dd, *J* = 2.7, 3.0 Hz, 2H), 2.39 (t, *J* = 12.6 Hz, 1H), 2.06 (m, 1H), 1.65 (brs, 9H), 0.88-1.27 (m, 14H), 0.81 (t, *J* = 7.2

Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.5, 171.1, 149.0, 139.3, 128.8, 124.4, 123.7, 115.5, 94.1, 84.7, 61.0, 57.3, 53.5, 44.1, 38.2, 34.7, 31.4, 30.3, 29.0, 28.7, 28.0, 27.1, 22.4, 14.0, 13.9; HPLC (Chiralcel OD-H, *i*-propanol/hexane = 5/95, flow rate 0.7 mL/min, λ = 254 nm): t_{major} = 8.1 min, t_{minor} = 12.5 min; HRMS calcd. for $C_{28}H_{40}N_2O_7Na$ $[M+Na]^+$: 539.2733, found 539.2738.

Procedure for the Reduction of Compound 3a:

Under nitrogen atmosphere, to the suspension of **3a** (49 mg, 0.1 mmol) and $NiCl_2{\cdot}6H_2O$ (24 mg, 0.1 mmol) in MeOH (2 mL) was added $NaBH_4$ (46 mg, 12 equiv)at 0 °C. After the reaction mixture was stirred for 30 min at room temperature, the reaction was quenched with sat. NH_4Cl aq and diluted with CH_2Cl_2. The organic layer was separated and dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired product **5** as a white solid (36 mg, 73% yield). $[\alpha]_D^{20}$ = + 84.5 (*c* = 0.2 M, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (brs, 1H), 6.91-7.09 (m, 4H), 6.78 (brs, 1H), 6.62 (brs, 2H), 6.35 (brs, 1H), 5.98 (brs, 1H), 4.54 (brs, 1H), 3.47 (m, 2H), 286 (m, 1H), 2.57 (m, 3H), 1.48 (brs, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.3, 153.0, 140.0, 139.1, 133.3, 127.9, 127.8, 126.7, 124.2, 122.1, 114.6, 89.3, 82.0, 75.6, 65.7, 60.8, 56.0, 38.4, 36.9, 28.4; HRMS calcd. for $C_{25}H_{28}N_2O_4Na$ $[M+Na]^+$: 443.1946, found 443.1952.



X-ray data

Structure of Compound **3i**

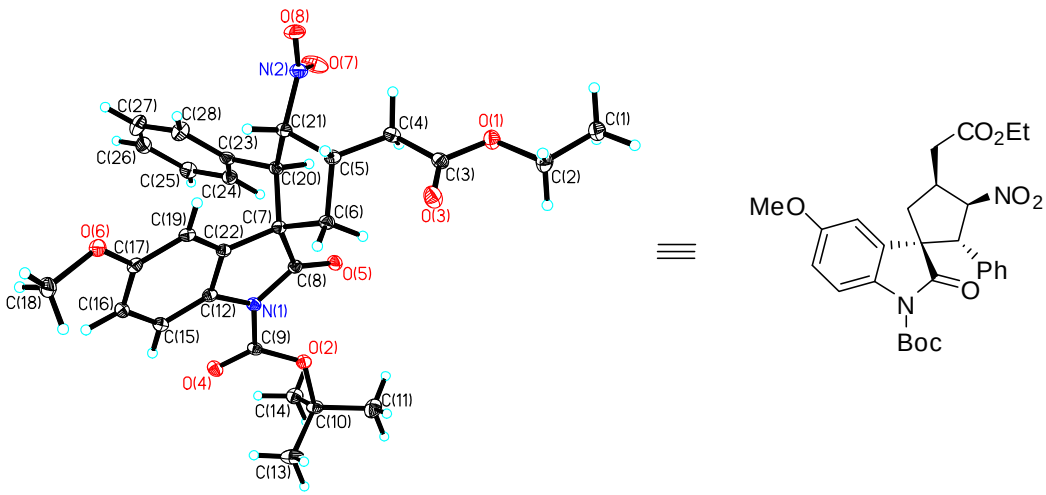


Table 1. Crystal data and structure refinement for aj3000.

Identification code	aj3000
Empirical formula	C28 H32 N2 O8
Formula weight	524.56
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Hexagonal, P 61
Unit cell dimensions	a = 12.5407(2) A alpha = 90 deg. b = 12.5407(2) A beta = 90 deg. c = 29.5324(5) A gamma = 120 deg.
Volume	4022.28(11) A^3
Z, Calculated density	6, 1.299 Mg/m^3
Absorption coefficient	0.793 mm^-1
F(000)	1668
Crystal size	0.55 x 0.35 x 0.35 mm
Theta range for data collection	4.07 to 69.38 deg.
Limiting indices	-14<=h<=12, -14<=k<=15, -34<=l<=34
Reflections collected / unique	26202 / 4831 [R(int) = 0.0351]
Completeness to theta = 69.38	98.4 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4831 / 1 / 349
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0248, wR2 = 0.0631
R indices (all data)	R1 = 0.0248, wR2 = 0.0631
Absolute structure parameter	0.04(10)

Extinction coefficient	0.00162(12)
Largest diff. peak and hole	0.175 and -0.143 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for aj3000.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	5314(1)	-890(1)	149(1)	29(1)
O(2)	9771(1)	6111(1)	954(1)	24(1)
O(3)	4656(1)	-26(1)	657(1)	37(1)
O(4)	10378(1)	6778(1)	1672(1)	26(1)
O(5)	9232(1)	3748(1)	849(1)	25(1)
O(6)	6352(1)	2459(1)	3026(1)	25(1)
O(7)	8657(1)	-352(1)	1299(1)	46(1)
O(8)	6998(1)	-1583(1)	1661(1)	39(1)
N(1)	9178(1)	4725(1)	1513(1)	20(1)
C(22)	7856(1)	3039(1)	1939(1)	18(1)
C(1)	4397(1)	-1725(1)	-565(1)	32(1)
C(2)	4317(1)	-1077(2)	-152(1)	32(1)
C(3)	5364(1)	-355(1)	543(1)	24(1)
C(4)	6421(1)	-221(1)	828(1)	25(1)
C(5)	6466(1)	366(1)	1284(1)	22(1)
C(6)	6789(1)	1730(1)	1230(1)	24(1)
C(7)	7998(1)	2548(1)	1492(1)	20(1)
C(8)	8867(1)	3722(1)	1228(1)	20(1)
C(9)	9863(1)	5992(1)	1391(1)	20(1)
C(10)	10336(1)	7355(1)	741(1)	25(1)
C(11)	9945(2)	7034(2)	254(1)	39(1)
C(12)	8601(1)	4319(1)	1944(1)	19(1)
C(13)	9782(2)	8074(2)	948(1)	41(1)
C(14)	11724(1)	8000(1)	790(1)	30(1)
C(15)	8645(1)	5006(1)	2316(1)	22(1)
C(16)	7910(1)	4391(1)	2689(1)	22(1)
C(17)	7132(1)	3118(1)	2681(1)	21(1)
C(18)	6166(1)	3146(1)	3370(1)	31(1)
C(19)	7105(1)	2434(1)	2304(1)	20(1)
C(20)	8604(1)	1724(1)	1522(1)	20(1)
C(21)	7488(1)	461(1)	1603(1)	22(1)
N(2)	7754(1)	-564(1)	1517(1)	29(1)
C(23)	9664(1)	2165(1)	1853(1)	21(1)
C(24)	10820(1)	3093(1)	1716(1)	25(1)
C(25)	11815(1)	3548(1)	2011(1)	30(1)
C(26)	11667(1)	3083(1)	2443(1)	30(1)
C(27)	10519(1)	2161(2)	2584(1)	36(1)
C(28)	9527(1)	1702(1)	2287(1)	30(1)

Table 3. Bond lengths [A] and angles [deg] for aj3000.

O(1)-C(3)	1.3298(17)
O(1)-C(2)	1.4538(17)
O(2)-C(9)	1.3105(16)
O(2)-C(10)	1.4906(15)
O(3)-C(3)	1.1986(17)
O(4)-C(9)	1.1999(16)
O(5)-C(8)	1.2042(16)
O(6)-C(17)	1.3686(15)
O(6)-C(18)	1.4232(17)
O(7)-N(2)	1.2117(17)
O(8)-N(2)	1.2250(16)
N(1)-C(8)	1.3966(16)
N(1)-C(12)	1.4250(17)
N(1)-C(9)	1.4250(16)
C(22)-C(19)	1.3817(18)
C(22)-C(12)	1.3962(17)
C(22)-C(7)	1.5044(17)
C(1)-C(2)	1.497(2)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.5076(19)
C(4)-C(5)	1.5202(18)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(21)	1.5470(18)
C(5)-C(6)	1.5565(17)
C(5)-H(5)	1.0000
C(6)-C(7)	1.5494(17)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.5361(17)
C(7)-C(20)	1.5615(17)
C(10)-C(11)	1.508(2)
C(10)-C(13)	1.515(2)
C(10)-C(14)	1.5161(19)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(15)	1.3808(18)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800

C(14)-H(14C)	0.9800
C(15)-C(16)	1.3961(18)
C(15)-H(15)	0.9500
C(16)-C(17)	1.3944(18)
C(16)-H(16)	0.9500
C(17)-C(19)	1.3946(18)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19)	0.9500
C(20)-C(23)	1.5133(17)
C(20)-C(21)	1.5190(17)
C(20)-H(20)	1.0000
C(21)-N(2)	1.5017(17)
C(21)-H(21)	1.0000
C(23)-C(28)	1.384(2)
C(23)-C(24)	1.3896(19)
C(24)-C(25)	1.390(2)
C(24)-H(24)	0.9500
C(25)-C(26)	1.376(2)
C(25)-H(25)	0.9500
C(26)-C(27)	1.385(2)
C(26)-H(26)	0.9500
C(27)-C(28)	1.389(2)
C(27)-H(27)	0.9500
C(28)-H(28)	0.9500

C(3)-O(1)-C(2)	115.84(11)
C(9)-O(2)-C(10)	120.70(10)
C(17)-O(6)-C(18)	116.69(10)
C(8)-N(1)-C(12)	110.66(10)
C(8)-N(1)-C(9)	126.35(11)
C(12)-N(1)-C(9)	122.67(10)
C(19)-C(22)-C(12)	120.32(11)
C(19)-C(22)-C(7)	130.30(11)
C(12)-C(22)-C(7)	109.33(10)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(1)-C(2)-C(1)	107.40(12)
O(1)-C(2)-H(2A)	110.2
C(1)-C(2)-H(2A)	110.2
O(1)-C(2)-H(2B)	110.2
C(1)-C(2)-H(2B)	110.2
H(2A)-C(2)-H(2B)	108.5
O(3)-C(3)-O(1)	124.29(13)
O(3)-C(3)-C(4)	124.48(12)
O(1)-C(3)-C(4)	111.23(11)
C(3)-C(4)-C(5)	111.45(11)

C(3)-C(4)-H(4A)	109.3
C(5)-C(4)-H(4A)	109.3
C(3)-C(4)-H(4B)	109.3
C(5)-C(4)-H(4B)	109.3
H(4A)-C(4)-H(4B)	108.0
C(4)-C(5)-C(21)	113.89(10)
C(4)-C(5)-C(6)	111.57(11)
C(21)-C(5)-C(6)	103.15(10)
C(4)-C(5)-H(5)	109.3
C(21)-C(5)-H(5)	109.3
C(6)-C(5)-H(5)	109.3
C(7)-C(6)-C(5)	107.87(10)
C(7)-C(6)-H(6A)	110.1
C(5)-C(6)-H(6A)	110.1
C(7)-C(6)-H(6B)	110.1
C(5)-C(6)-H(6B)	110.1
H(6A)-C(6)-H(6B)	108.4
C(22)-C(7)-C(8)	103.01(10)
C(22)-C(7)-C(6)	115.69(10)
C(8)-C(7)-C(6)	111.74(10)
C(22)-C(7)-C(20)	114.76(10)
C(8)-C(7)-C(20)	108.45(10)
C(6)-C(7)-C(20)	103.26(10)
O(5)-C(8)-N(1)	127.19(12)
O(5)-C(8)-C(7)	125.19(11)
N(1)-C(8)-C(7)	107.58(10)
O(4)-C(9)-O(2)	129.01(12)
O(4)-C(9)-N(1)	121.14(12)
O(2)-C(9)-N(1)	109.78(11)
O(2)-C(10)-C(11)	101.62(11)
O(2)-C(10)-C(13)	109.45(11)
C(11)-C(10)-C(13)	111.05(14)
O(2)-C(10)-C(14)	109.68(10)
C(11)-C(10)-C(14)	111.51(12)
C(13)-C(10)-C(14)	112.94(13)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(15)-C(12)-C(22)	121.31(11)
C(15)-C(12)-N(1)	129.28(11)
C(22)-C(12)-N(1)	109.29(11)
C(10)-C(13)-H(13A)	109.5
C(10)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(10)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(10)-C(14)-H(14A)	109.5
C(10)-C(14)-H(14B)	109.5

H(14A)-C(14)-H(14B)	109.5
C(10)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(12)-C(15)-C(16)	118.37(12)
C(12)-C(15)-H(15)	120.8
C(16)-C(15)-H(15)	120.8
C(17)-C(16)-C(15)	120.54(12)
C(17)-C(16)-H(16)	119.7
C(15)-C(16)-H(16)	119.7
O(6)-C(17)-C(16)	123.89(12)
O(6)-C(17)-C(19)	115.63(11)
C(16)-C(17)-C(19)	120.48(11)
O(6)-C(18)-H(18A)	109.5
O(6)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
O(6)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(22)-C(19)-C(17)	118.92(11)
C(22)-C(19)-H(19)	120.5
C(17)-C(19)-H(19)	120.5
C(23)-C(20)-C(21)	117.61(11)
C(23)-C(20)-C(7)	115.05(10)
C(21)-C(20)-C(7)	101.49(9)
C(23)-C(20)-H(20)	107.4
C(21)-C(20)-H(20)	107.4
C(7)-C(20)-H(20)	107.4
N(2)-C(21)-C(20)	112.54(10)
N(2)-C(21)-C(5)	111.17(10)
C(20)-C(21)-C(5)	106.34(10)
N(2)-C(21)-H(21)	108.9
C(20)-C(21)-H(21)	108.9
C(5)-C(21)-H(21)	108.9
O(7)-N(2)-O(8)	124.38(12)
O(7)-N(2)-C(21)	119.01(12)
O(8)-N(2)-C(21)	116.55(12)
C(28)-C(23)-C(24)	118.67(12)
C(28)-C(23)-C(20)	122.86(12)
C(24)-C(23)-C(20)	118.46(12)
C(23)-C(24)-C(25)	120.52(13)
C(23)-C(24)-H(24)	119.7
C(25)-C(24)-H(24)	119.7
C(26)-C(25)-C(24)	120.31(14)
C(26)-C(25)-H(25)	119.8
C(24)-C(25)-H(25)	119.8
C(25)-C(26)-C(27)	119.67(13)
C(25)-C(26)-H(26)	120.2
C(27)-C(26)-H(26)	120.2
C(26)-C(27)-C(28)	119.98(14)
C(26)-C(27)-H(27)	120.0
C(28)-C(27)-H(27)	120.0

C(23)-C(28)-C(27)	120.85(13)
C(23)-C(28)-H(28)	119.6
C(27)-C(28)-H(28)	119.6

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for aj3000. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	28(1)	33(1)	27(1)	-5(1)	-4(1)	16(1)
O(2)	26(1)	17(1)	24(1)	3(1)	2(1)	7(1)
O(3)	31(1)	46(1)	39(1)	-14(1)	-9(1)	24(1)
O(4)	29(1)	18(1)	26(1)	0(1)	5(1)	7(1)
O(5)	31(1)	23(1)	21(1)	1(1)	4(1)	14(1)
O(6)	28(1)	26(1)	22(1)	4(1)	7(1)	14(1)
O(7)	40(1)	35(1)	73(1)	-5(1)	9(1)	26(1)
O(8)	49(1)	19(1)	46(1)	3(1)	-8(1)	15(1)
N(1)	20(1)	18(1)	21(1)	1(1)	2(1)	9(1)
C(22)	16(1)	20(1)	21(1)	0(1)	-1(1)	11(1)
C(1)	33(1)	30(1)	30(1)	-4(1)	-6(1)	14(1)
C(2)	28(1)	39(1)	29(1)	-4(1)	-7(1)	16(1)
C(3)	23(1)	18(1)	27(1)	-1(1)	1(1)	7(1)
C(4)	26(1)	21(1)	28(1)	-2(1)	0(1)	12(1)
C(5)	20(1)	18(1)	25(1)	2(1)	1(1)	8(1)
C(6)	25(1)	20(1)	28(1)	-3(1)	-6(1)	11(1)
C(7)	20(1)	19(1)	21(1)	0(1)	0(1)	11(1)
C(8)	20(1)	20(1)	22(1)	0(1)	-1(1)	12(1)
C(9)	20(1)	18(1)	24(1)	1(1)	4(1)	10(1)
C(10)	26(1)	17(1)	30(1)	6(1)	5(1)	9(1)
C(11)	44(1)	29(1)	32(1)	9(1)	-2(1)	10(1)
C(12)	17(1)	19(1)	22(1)	2(1)	0(1)	10(1)
C(13)	46(1)	33(1)	53(1)	15(1)	18(1)	26(1)
C(14)	28(1)	24(1)	32(1)	5(1)	5(1)	9(1)
C(15)	22(1)	20(1)	25(1)	-1(1)	0(1)	11(1)
C(16)	26(1)	24(1)	20(1)	-1(1)	1(1)	15(1)
C(17)	20(1)	24(1)	20(1)	5(1)	2(1)	13(1)
C(18)	37(1)	34(1)	23(1)	3(1)	9(1)	18(1)
C(19)	20(1)	18(1)	25(1)	2(1)	0(1)	11(1)
C(20)	21(1)	19(1)	21(1)	-1(1)	1(1)	12(1)
C(21)	24(1)	18(1)	25(1)	0(1)	1(1)	11(1)
N(2)	32(1)	23(1)	35(1)	-2(1)	-7(1)	16(1)
C(23)	23(1)	21(1)	25(1)	-2(1)	0(1)	15(1)
C(24)	25(1)	26(1)	26(1)	0(1)	1(1)	13(1)
C(25)	22(1)	28(1)	37(1)	-2(1)	-2(1)	11(1)

C(26)	27(1)	36(1)	32(1)	-7(1)	-8(1)	20(1)
C(27)	32(1)	49(1)	28(1)	7(1)	-2(1)	22(1)
C(28)	23(1)	35(1)	31(1)	6(1)	2(1)	13(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for aj3000.

	x	y	z	U(eq)
H(1A)	5200	-1222	-710	48
H(1B)	3743	-1855	-777	48
H(1C)	4302	-2522	-478	48
H(2A)	4398	-275	-236	39
H(2B)	3512	-1581	0	39
H(4A)	7204	293	665	30
H(4B)	6331	-1043	878	30
H(5)	5649	-113	1437	26
H(6A)	6898	1962	905	28
H(6B)	6116	1840	1353	28
H(11A)	10280	6534	133	58
H(11B)	10257	7792	77	58
H(11C)	9044	6567	237	58
H(13A)	8882	7575	938	62
H(13B)	10053	8835	777	62
H(13C)	10053	8275	1264	62
H(14A)	11948	8199	1110	44
H(14B)	12100	8760	612	44
H(14C)	12023	7457	682	44
H(15)	9163	5875	2318	26
H(16)	7940	4844	2952	27
H(18A)	6929	3620	3543	47
H(18B)	5508	2581	3573	47
H(18C)	5935	3710	3230	47
H(19)	6580	1566	2299	25
H(20)	8932	1712	1215	24
H(21)	7211	410	1923	27
H(24)	10931	3419	1418	30
H(25)	12601	4183	1914	35
H(26)	12349	3394	2644	36
H(27)	10410	1842	2882	43
H(28)	8744	1062	2384	37

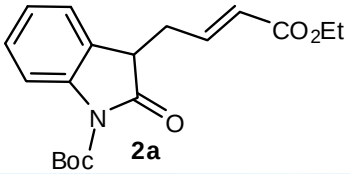
Table 6. Torsion angles [deg] for aj3000.

C(3)-O(1)-C(2)-C(1)	-178.02(12)
C(2)-O(1)-C(3)-O(3)	-0.4(2)

C(2)-O(1)-C(3)-C(4)	179.35(11)
O(3)-C(3)-C(4)-C(5)	0.94(19)
O(1)-C(3)-C(4)-C(5)	-178.80(11)
C(3)-C(4)-C(5)-C(21)	176.77(11)
C(3)-C(4)-C(5)-C(6)	-66.96(13)
C(4)-C(5)-C(6)-C(7)	-119.69(11)
C(21)-C(5)-C(6)-C(7)	2.96(13)
C(19)-C(22)-C(7)-C(8)	173.94(12)
C(12)-C(22)-C(7)-C(8)	-3.24(13)
C(19)-C(22)-C(7)-C(6)	51.74(18)
C(12)-C(22)-C(7)-C(6)	-125.44(11)
C(19)-C(22)-C(7)-C(20)	-68.40(16)
C(12)-C(22)-C(7)-C(20)	114.42(12)
C(5)-C(6)-C(7)-C(22)	-104.07(12)
C(5)-C(6)-C(7)-C(8)	138.50(11)
C(5)-C(6)-C(7)-C(20)	22.15(13)
C(12)-N(1)-C(8)-O(5)	-177.42(12)
C(9)-N(1)-C(8)-O(5)	9.0(2)
C(12)-N(1)-C(8)-C(7)	0.43(13)
C(9)-N(1)-C(8)-C(7)	-173.18(11)
C(22)-C(7)-C(8)-O(5)	179.57(12)
C(6)-C(7)-C(8)-O(5)	-55.61(16)
C(20)-C(7)-C(8)-O(5)	57.55(16)
C(22)-C(7)-C(8)-N(1)	1.67(12)
C(6)-C(7)-C(8)-N(1)	126.50(11)
C(20)-C(7)-C(8)-N(1)	-120.35(11)
C(10)-O(2)-C(9)-O(4)	-0.9(2)
C(10)-O(2)-C(9)-N(1)	176.01(10)
C(8)-N(1)-C(9)-O(4)	-158.78(12)
C(12)-N(1)-C(9)-O(4)	28.34(18)
C(8)-N(1)-C(9)-O(2)	23.99(16)
C(12)-N(1)-C(9)-O(2)	-148.90(11)
C(9)-O(2)-C(10)-C(11)	-177.35(12)
C(9)-O(2)-C(10)-C(13)	-59.88(16)
C(9)-O(2)-C(10)-C(14)	64.54(15)
C(19)-C(22)-C(12)-C(15)	2.55(18)
C(7)-C(22)-C(12)-C(15)	-179.94(11)
C(19)-C(22)-C(12)-N(1)	-173.84(11)
C(7)-C(22)-C(12)-N(1)	3.67(13)
C(8)-N(1)-C(12)-C(15)	-178.61(12)
C(9)-N(1)-C(12)-C(15)	-4.72(19)
C(8)-N(1)-C(12)-C(22)	-2.58(13)
C(9)-N(1)-C(12)-C(22)	171.30(11)
C(22)-C(12)-C(15)-C(16)	-0.92(18)
N(1)-C(12)-C(15)-C(16)	174.68(12)
C(12)-C(15)-C(16)-C(17)	-1.39(18)
C(18)-O(6)-C(17)-C(16)	12.37(18)
C(18)-O(6)-C(17)-C(19)	-167.22(11)
C(15)-C(16)-C(17)-O(6)	-177.46(11)
C(15)-C(16)-C(17)-C(19)	2.11(19)
C(12)-C(22)-C(19)-C(17)	-1.81(18)
C(7)-C(22)-C(19)-C(17)	-178.73(12)

O(6)-C(17)-C(19)-C(22)	179.12(10)
C(16)-C(17)-C(19)-C(22)	-0.48(18)
C(22)-C(7)-C(20)-C(23)	-40.00(15)
C(8)-C(7)-C(20)-C(23)	74.53(13)
C(6)-C(7)-C(20)-C(23)	-166.81(11)
C(22)-C(7)-C(20)-C(21)	88.10(12)
C(8)-C(7)-C(20)-C(21)	-157.37(10)
C(6)-C(7)-C(20)-C(21)	-38.71(12)
C(23)-C(20)-C(21)-N(2)	-69.54(14)
C(7)-C(20)-C(21)-N(2)	164.02(10)
C(23)-C(20)-C(21)-C(5)	168.51(10)
C(7)-C(20)-C(21)-C(5)	42.08(12)
C(4)-C(5)-C(21)-N(2)	-29.91(15)
C(6)-C(5)-C(21)-N(2)	-150.99(11)
C(4)-C(5)-C(21)-C(20)	92.91(12)
C(6)-C(5)-C(21)-C(20)	-28.18(13)
C(20)-C(21)-N(2)-O(7)	-17.38(18)
C(5)-C(21)-N(2)-O(7)	101.78(14)
C(20)-C(21)-N(2)-O(8)	165.40(11)
C(5)-C(21)-N(2)-O(8)	-75.44(14)
C(21)-C(20)-C(23)-C(28)	-21.92(18)
C(7)-C(20)-C(23)-C(28)	97.59(15)
C(21)-C(20)-C(23)-C(24)	159.40(11)
C(7)-C(20)-C(23)-C(24)	-81.09(14)
C(28)-C(23)-C(24)-C(25)	-0.2(2)
C(20)-C(23)-C(24)-C(25)	178.50(12)
C(23)-C(24)-C(25)-C(26)	0.0(2)
C(24)-C(25)-C(26)-C(27)	-0.2(2)
C(25)-C(26)-C(27)-C(28)	0.6(2)
C(24)-C(23)-C(28)-C(27)	0.6(2)
C(20)-C(23)-C(28)-C(27)	-178.05(13)
C(26)-C(27)-C(28)-C(23)	-0.8(2)

Symmetry transformations used to generate equivalent atoms: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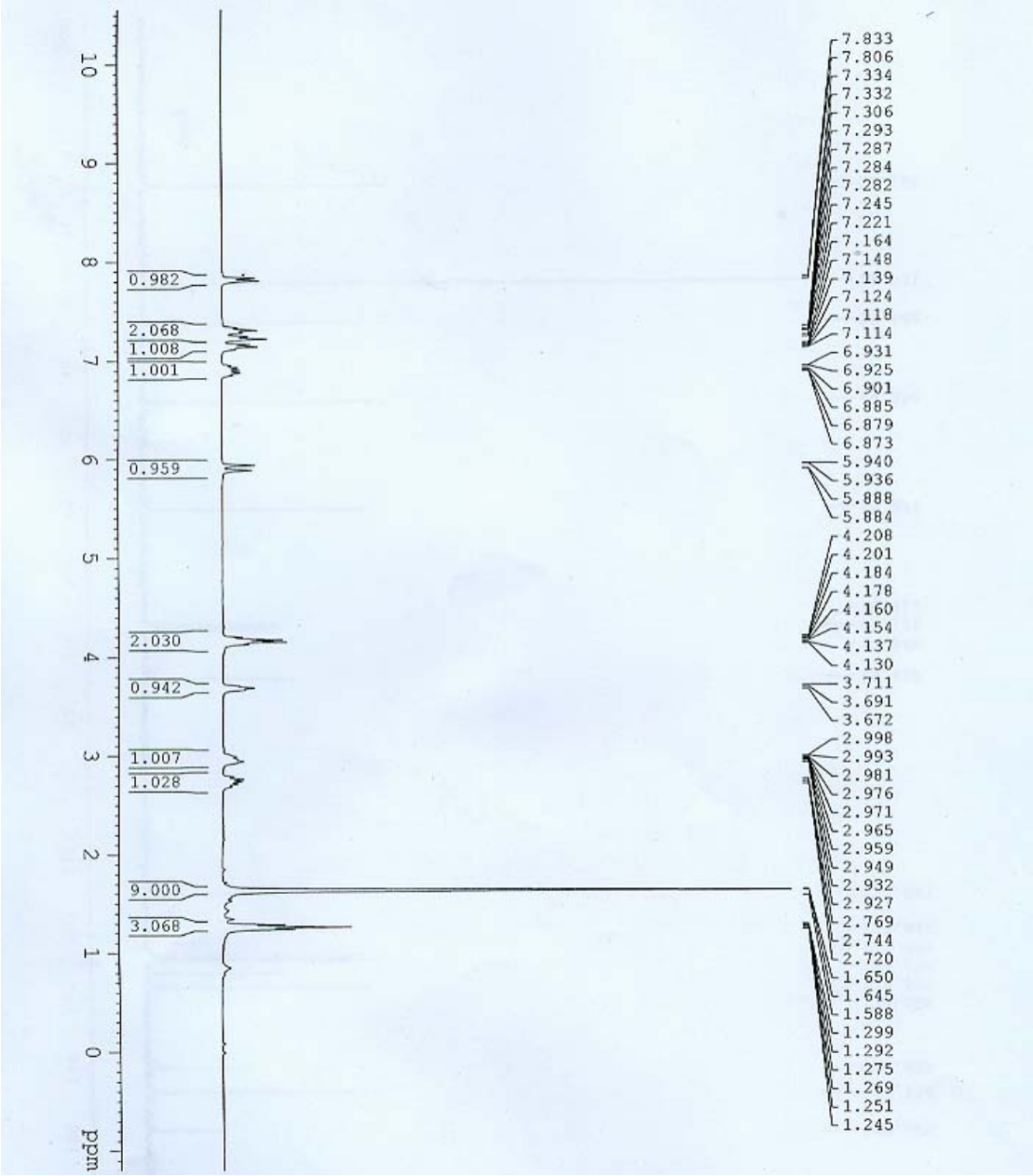
O
Boc

2a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7.332
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7.282
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5.884
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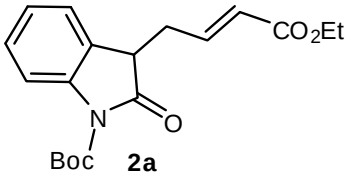
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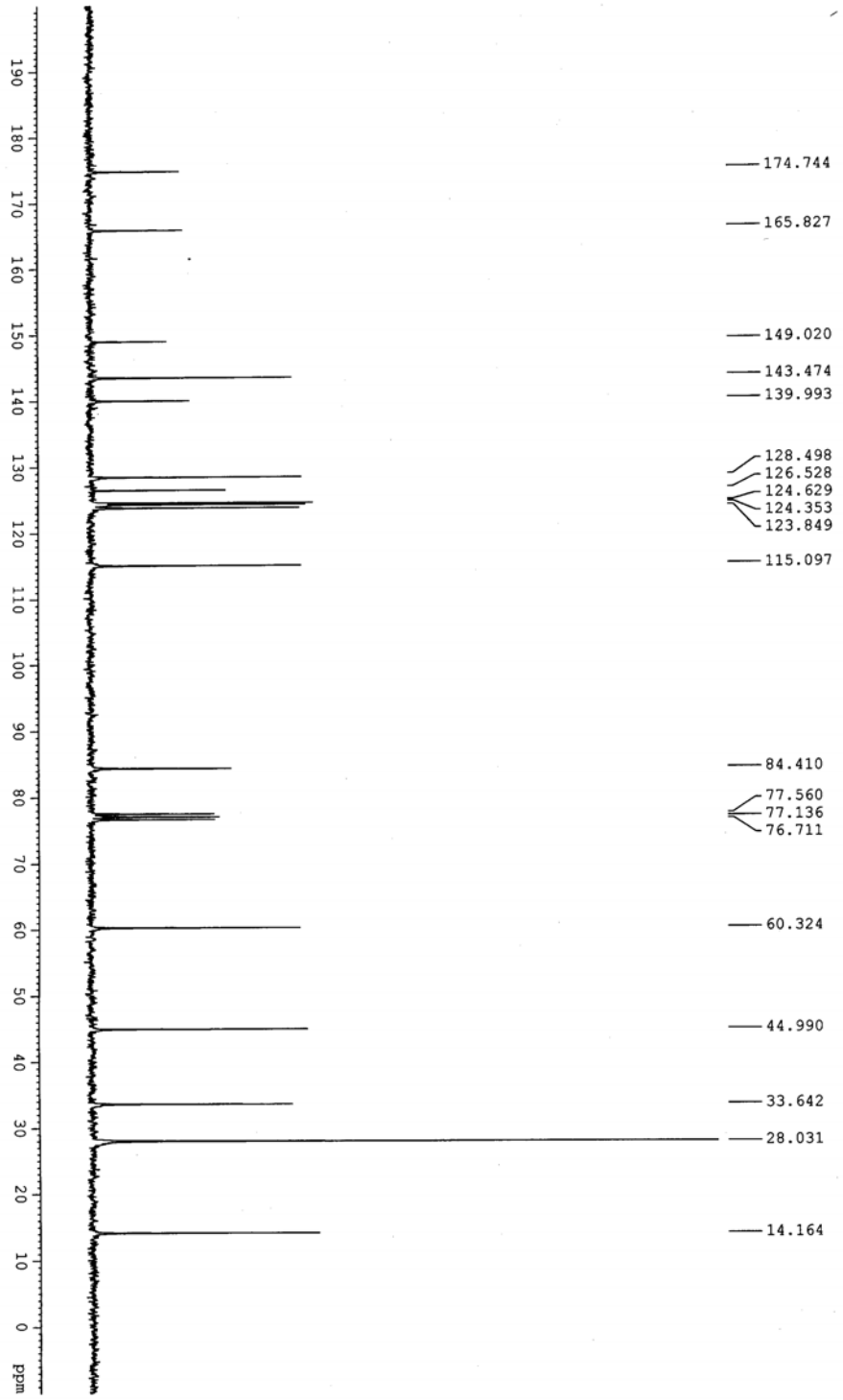
O
Boc

2a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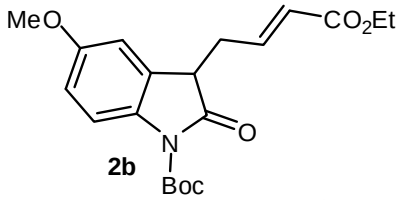
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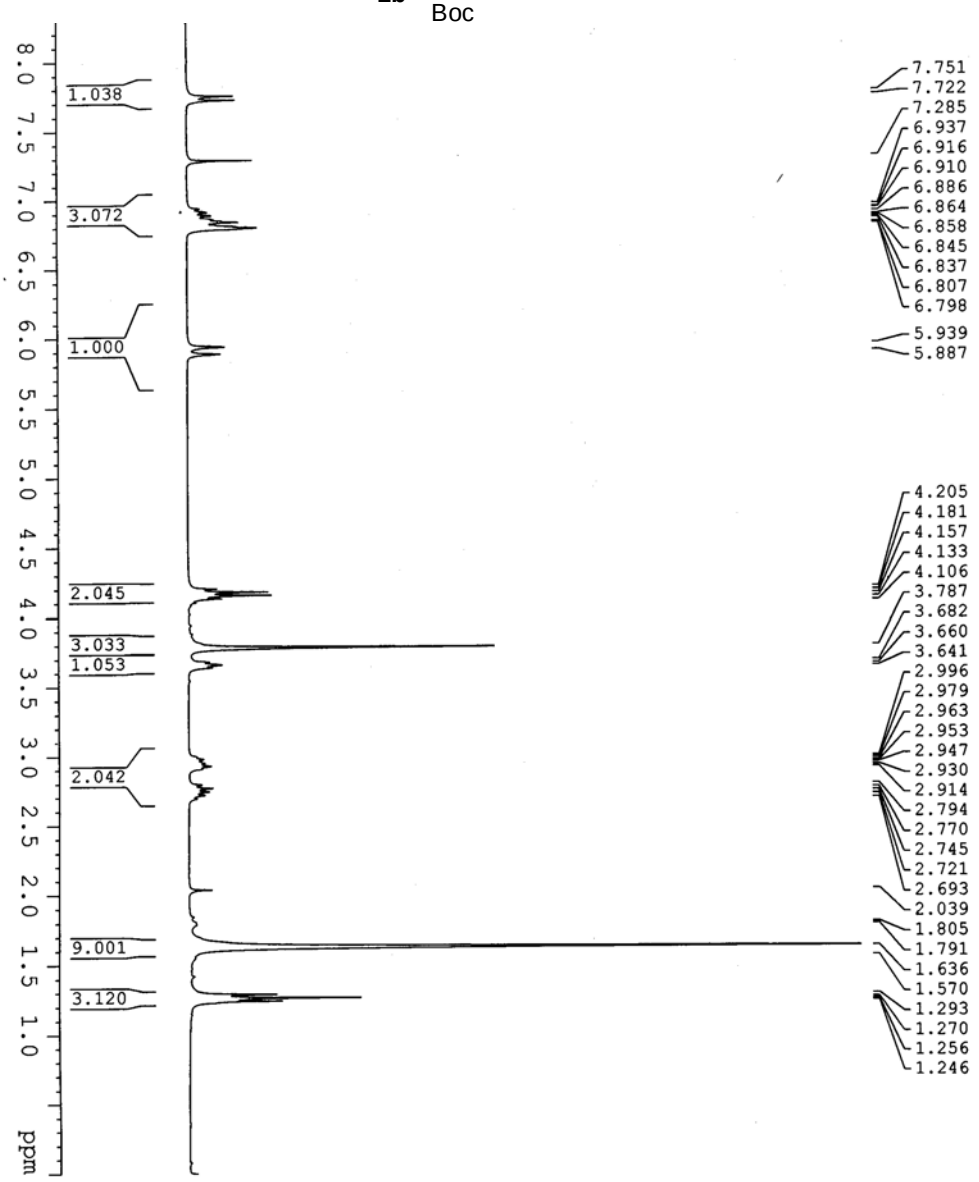
O
N
Boc

2b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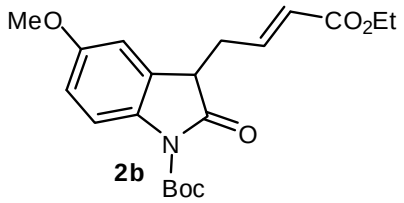
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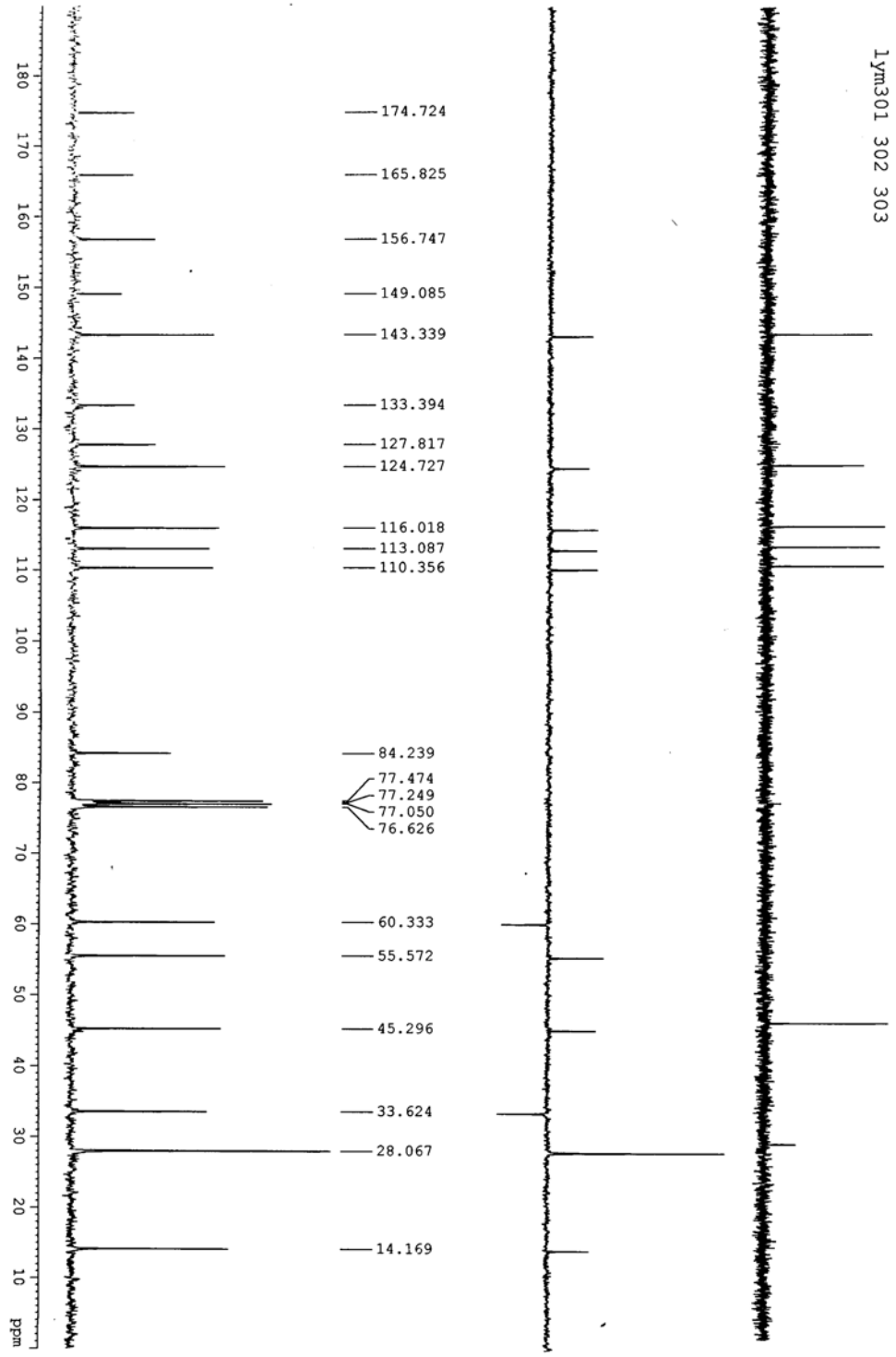
CO2Et
O
N
Boc

2b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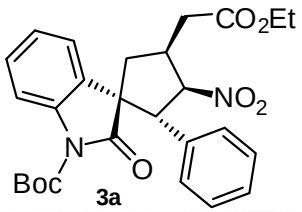
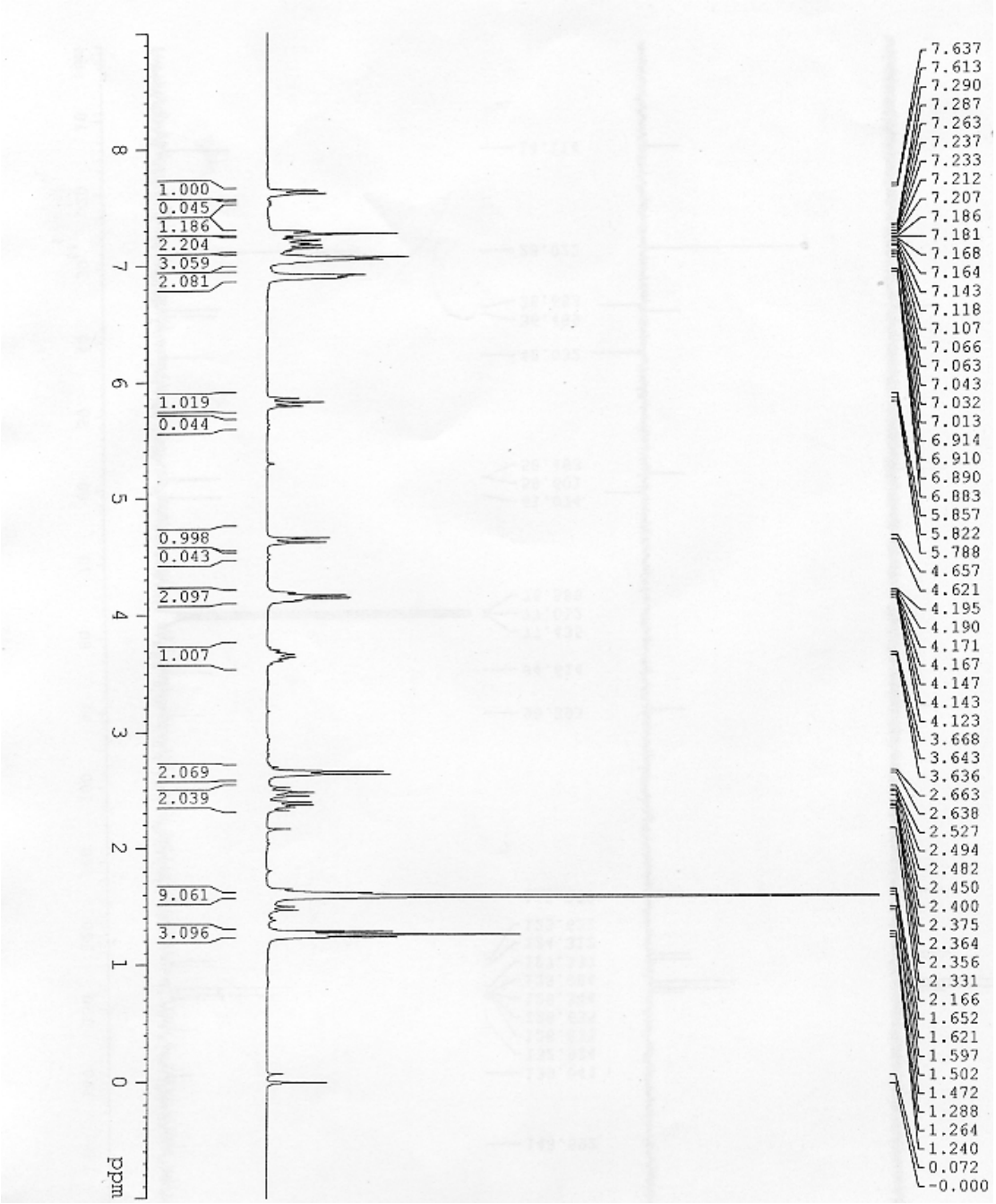

CO2Et
NO2
N
O
Boc

3a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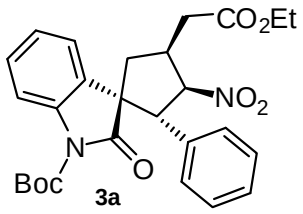
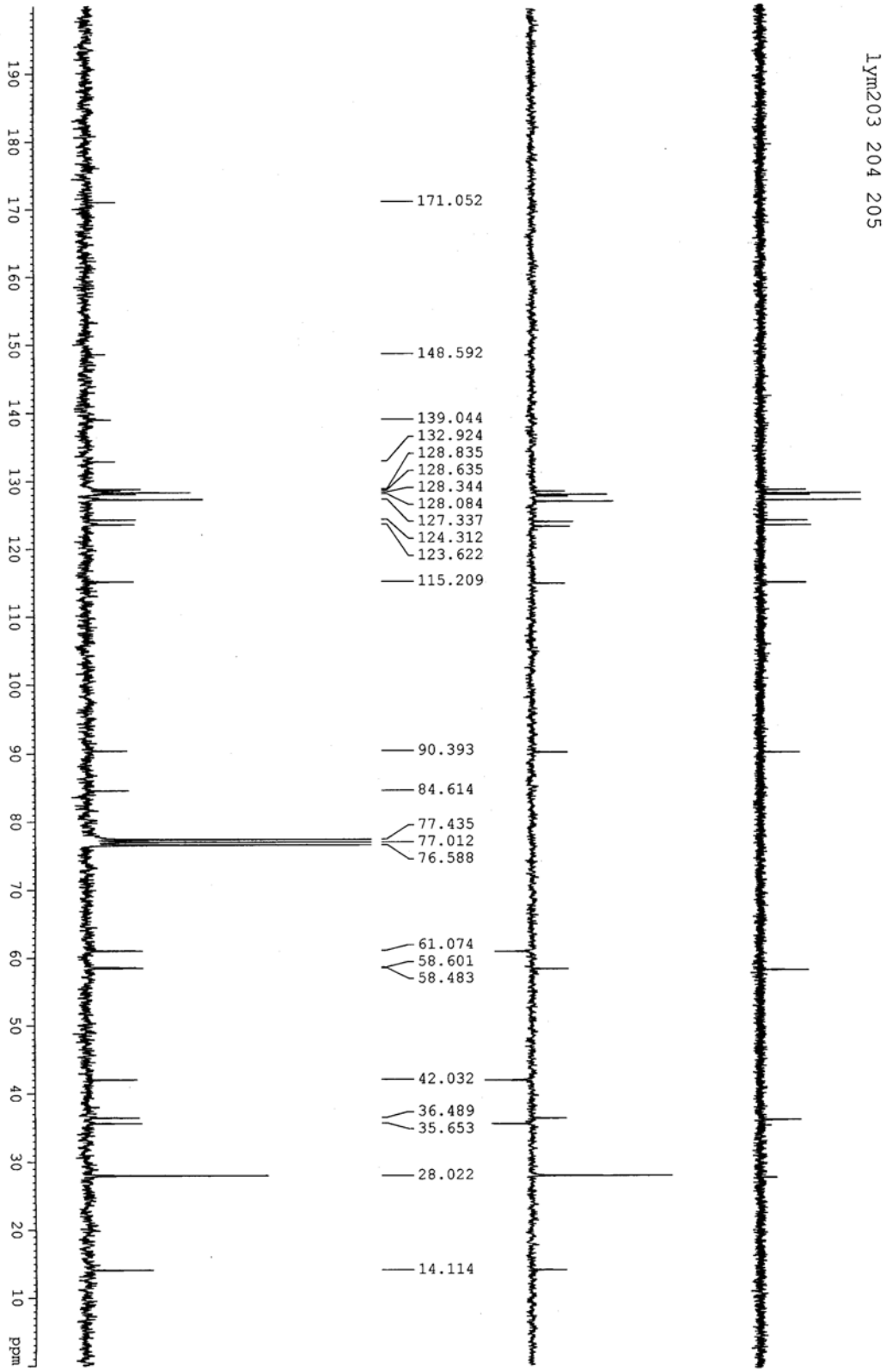

CO2Et
NO2
N
O
Boc

3a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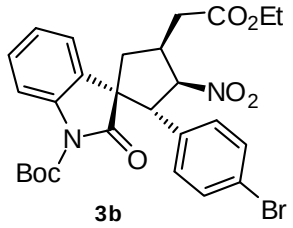
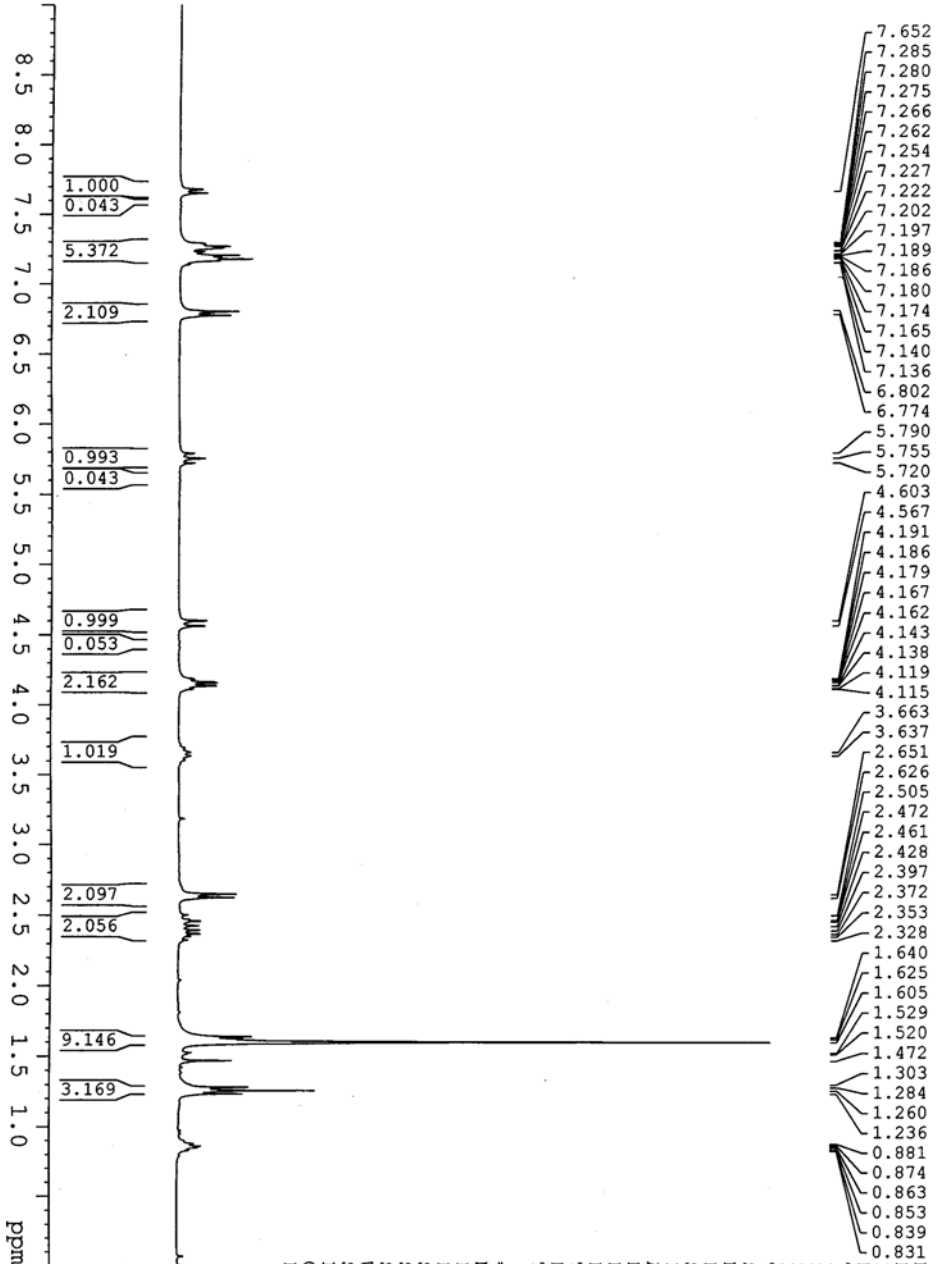

CO2Et
NO2
N
O
Boc
Br

3b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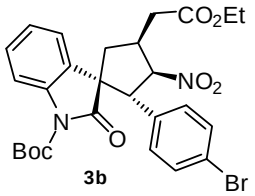
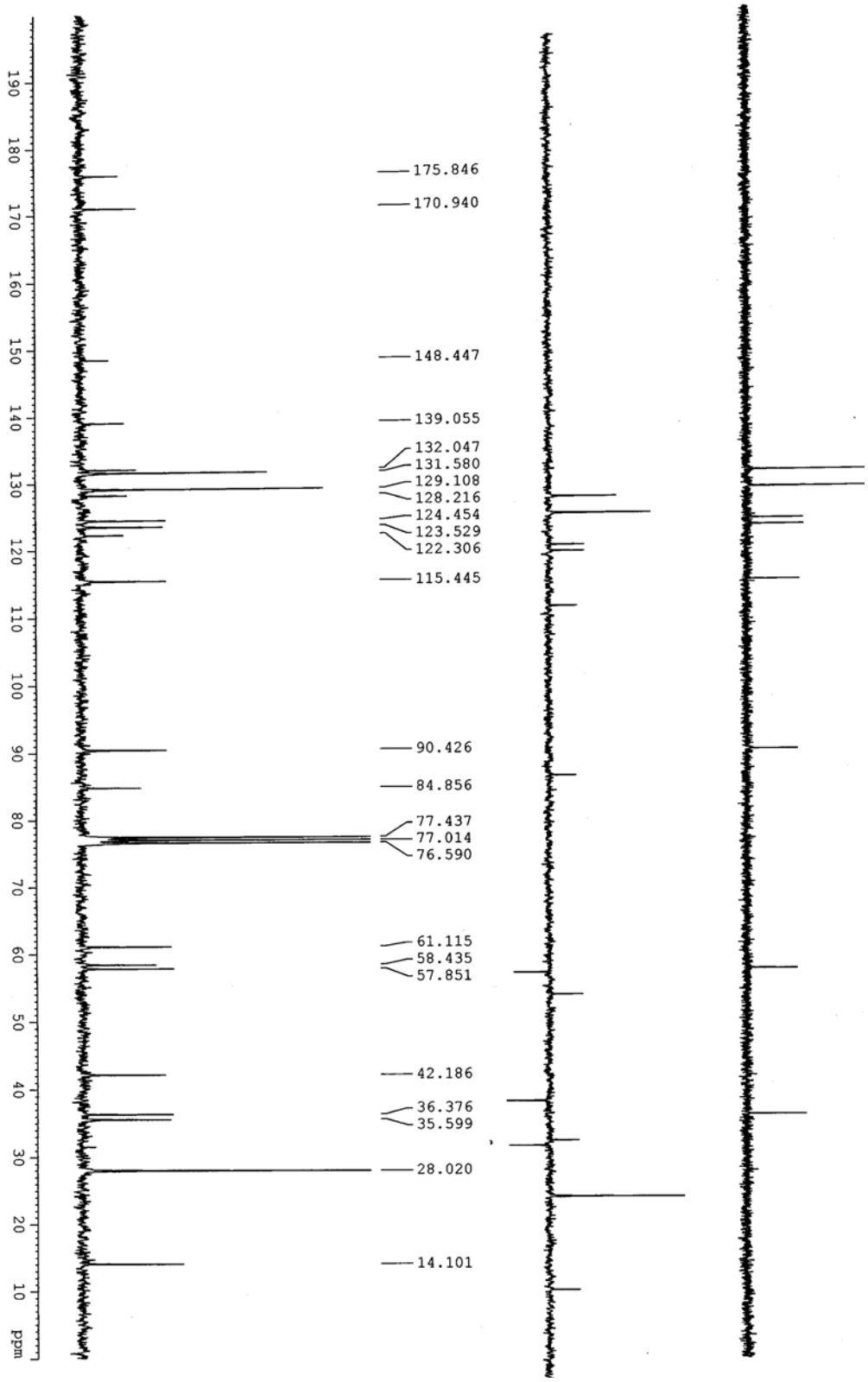

CO2Et
NO2
N
O
Boc
Br

3b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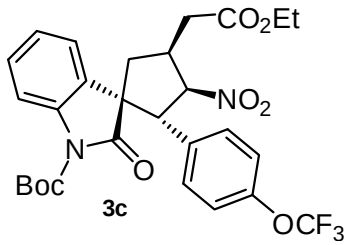
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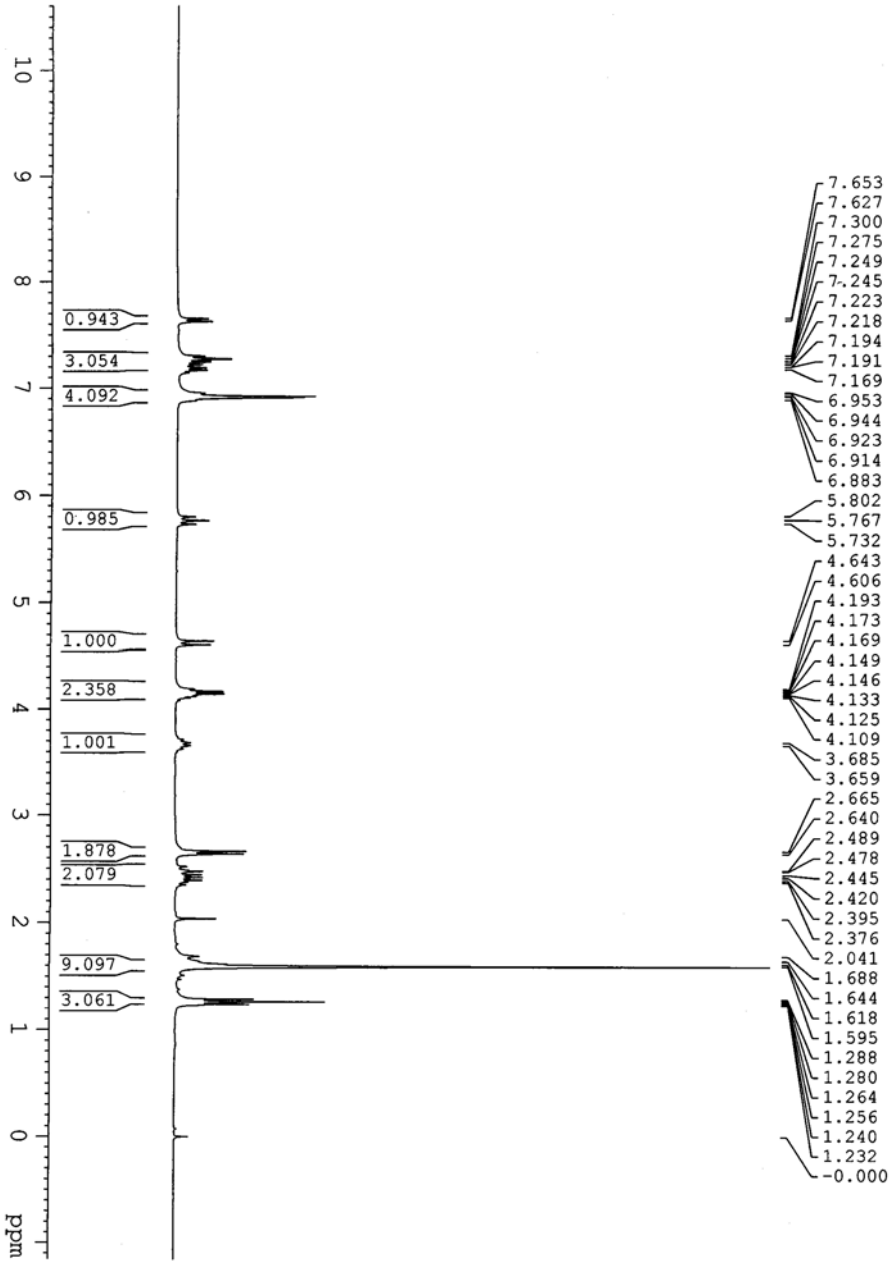
Boc
OCF3

3c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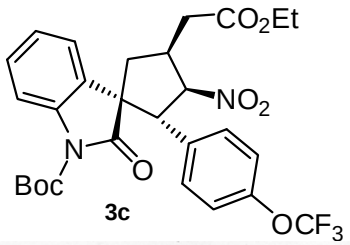
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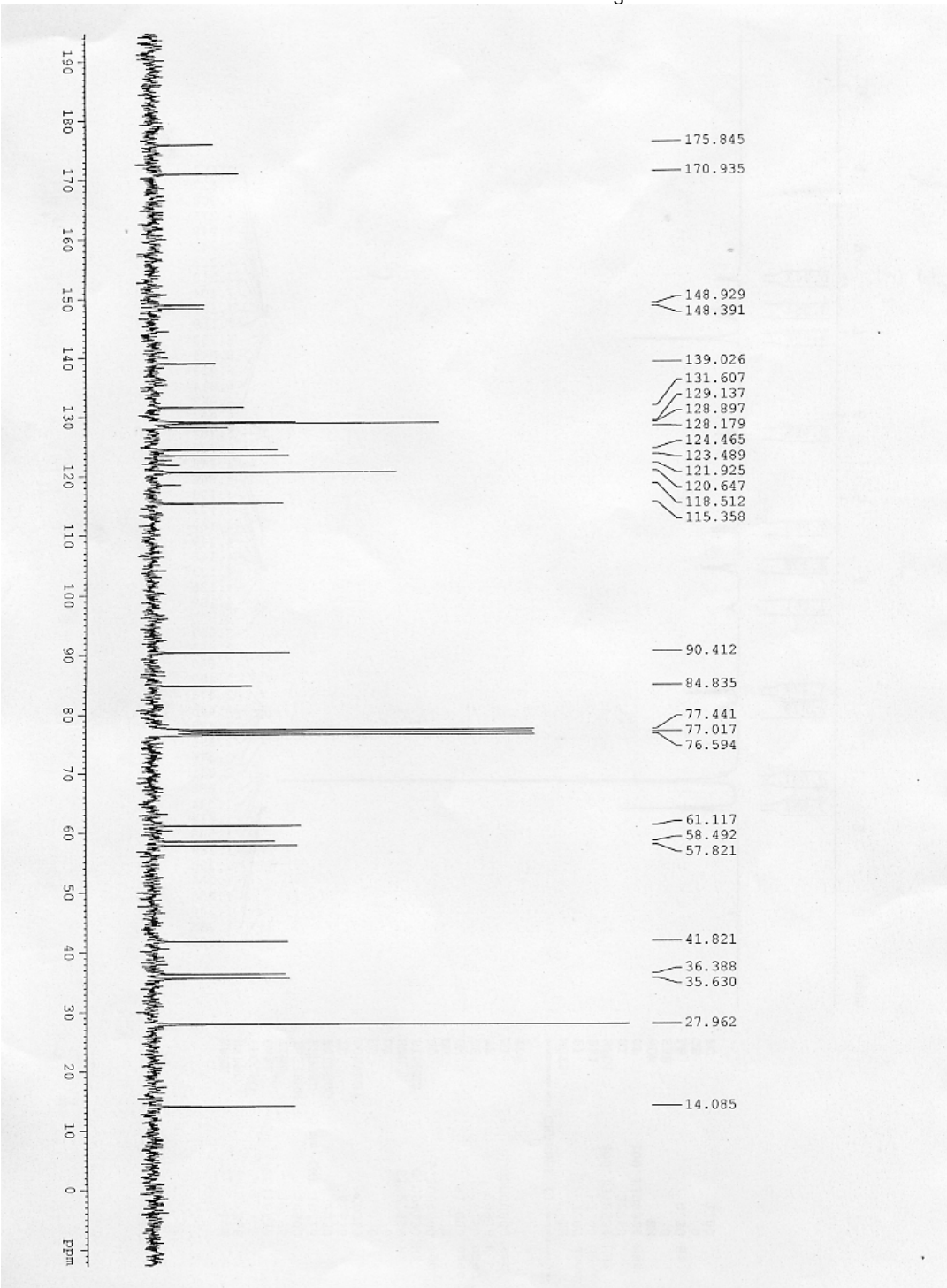
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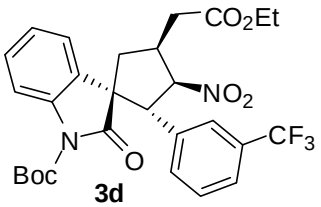
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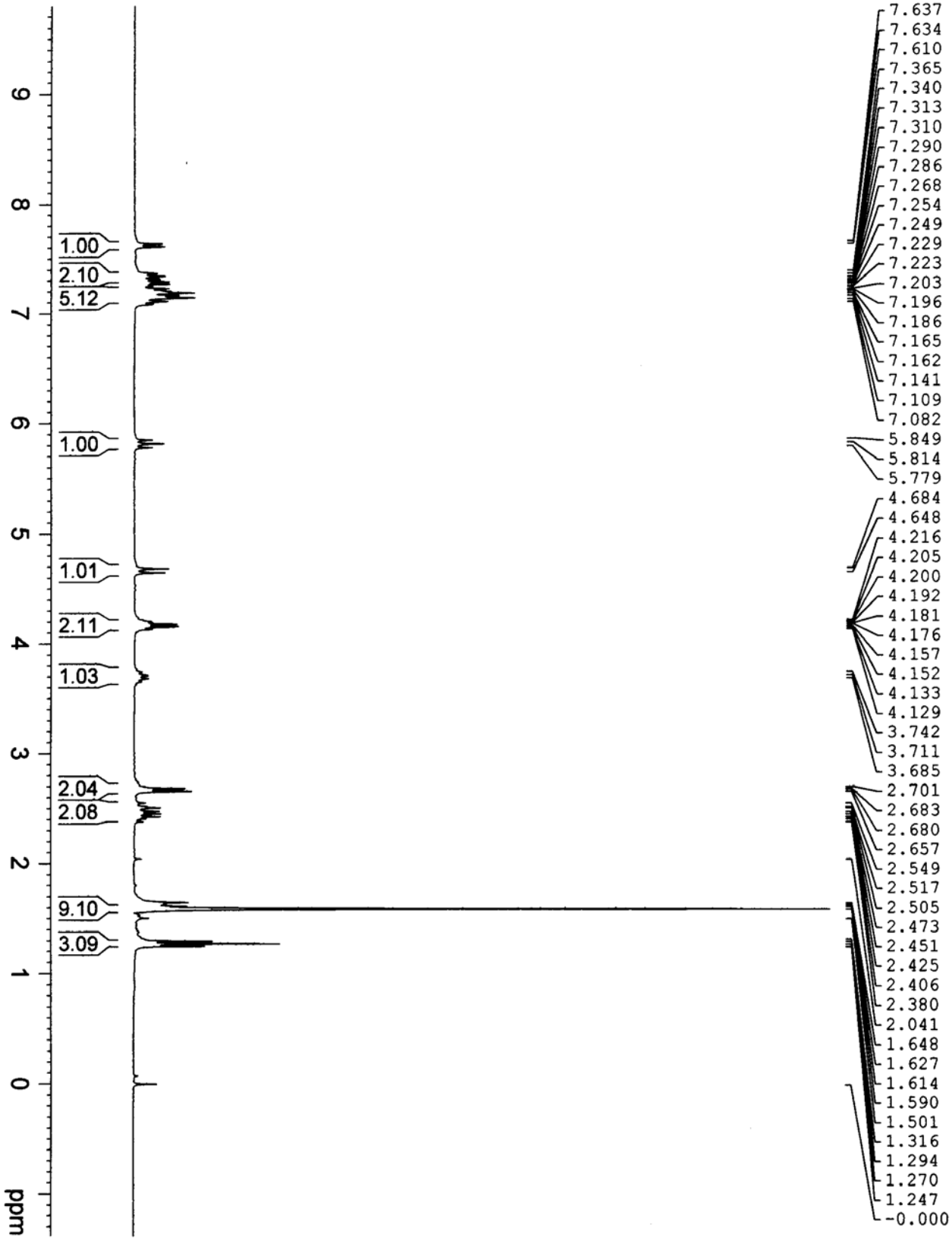
O
Boc

3d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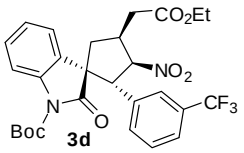
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O
Boc
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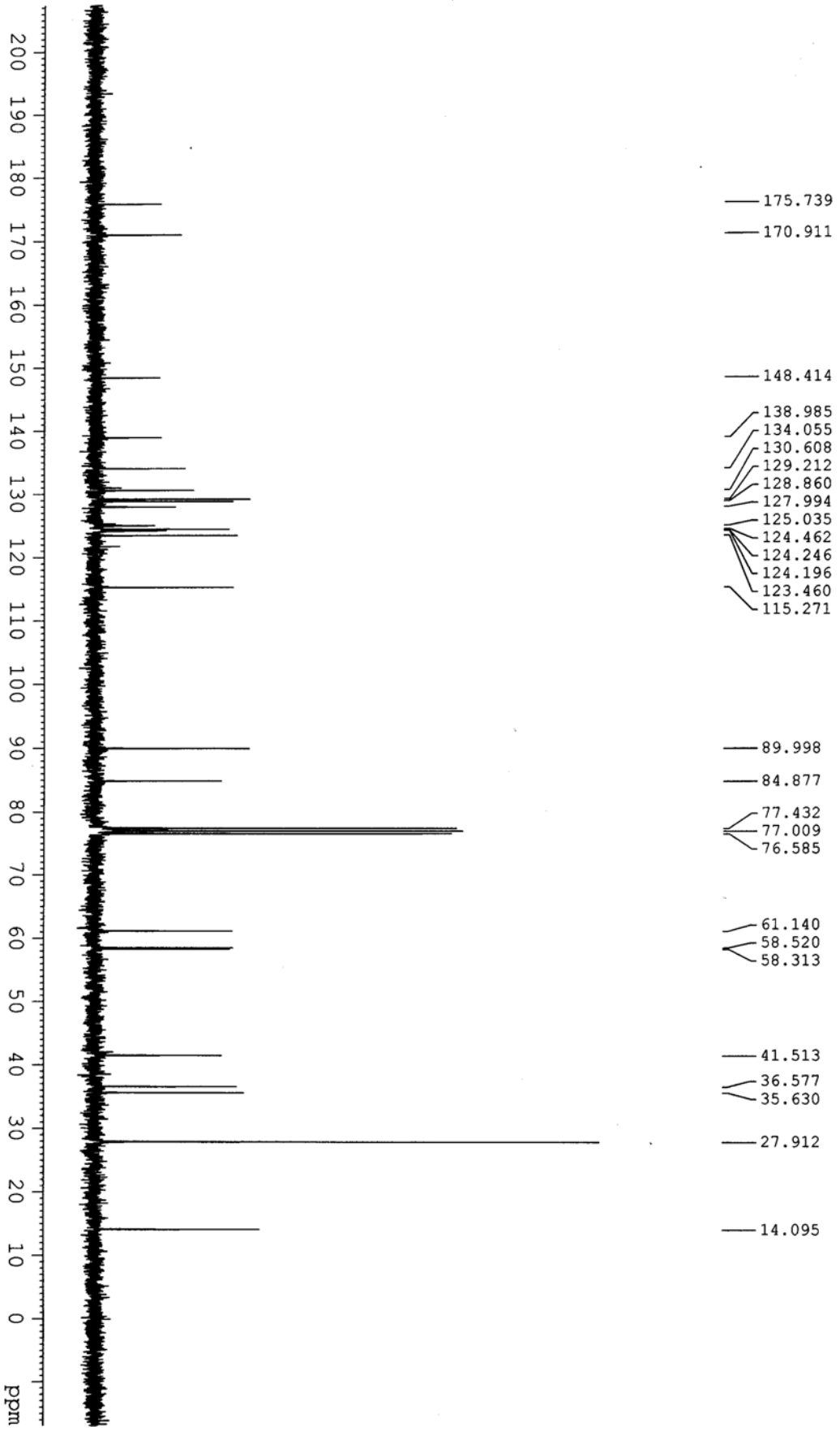
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89.998
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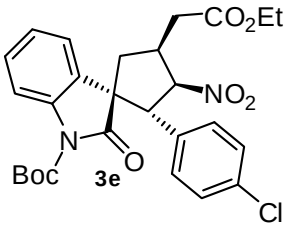
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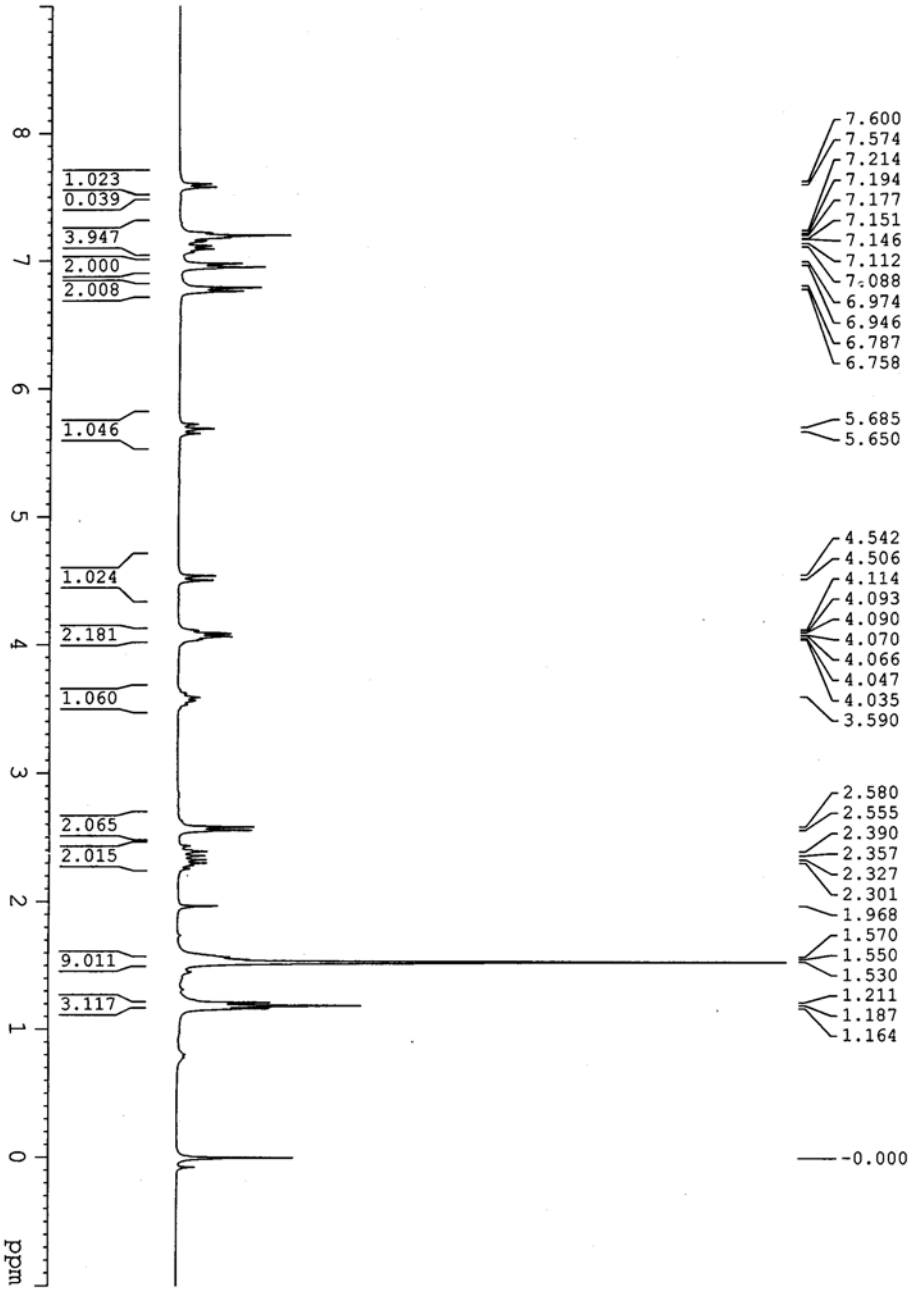
NO2
N
O
Boc
3e
Cl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3.117
7.600
7.574
7.214
7.194
7.177
7.151
7.146
7.112
7.088
6.974
6.946
6.787
6.758
5.685
5.650
4.542
4.506
4.114
4.093
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4.047
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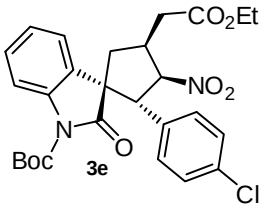
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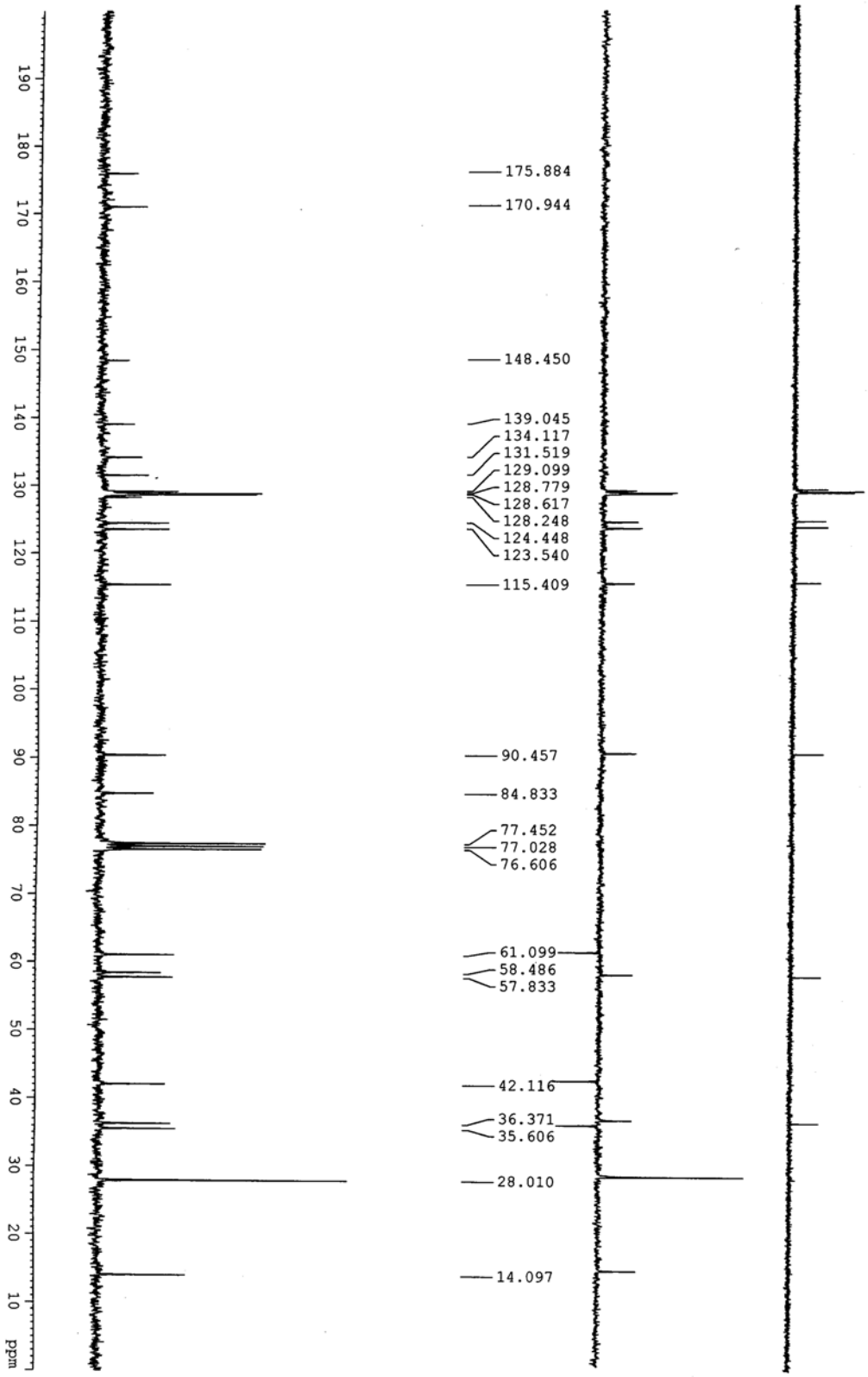
N
O
Boc
3e
Cl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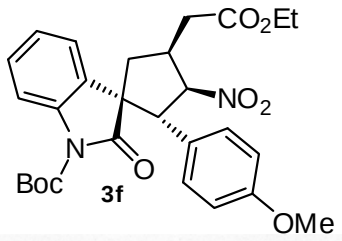
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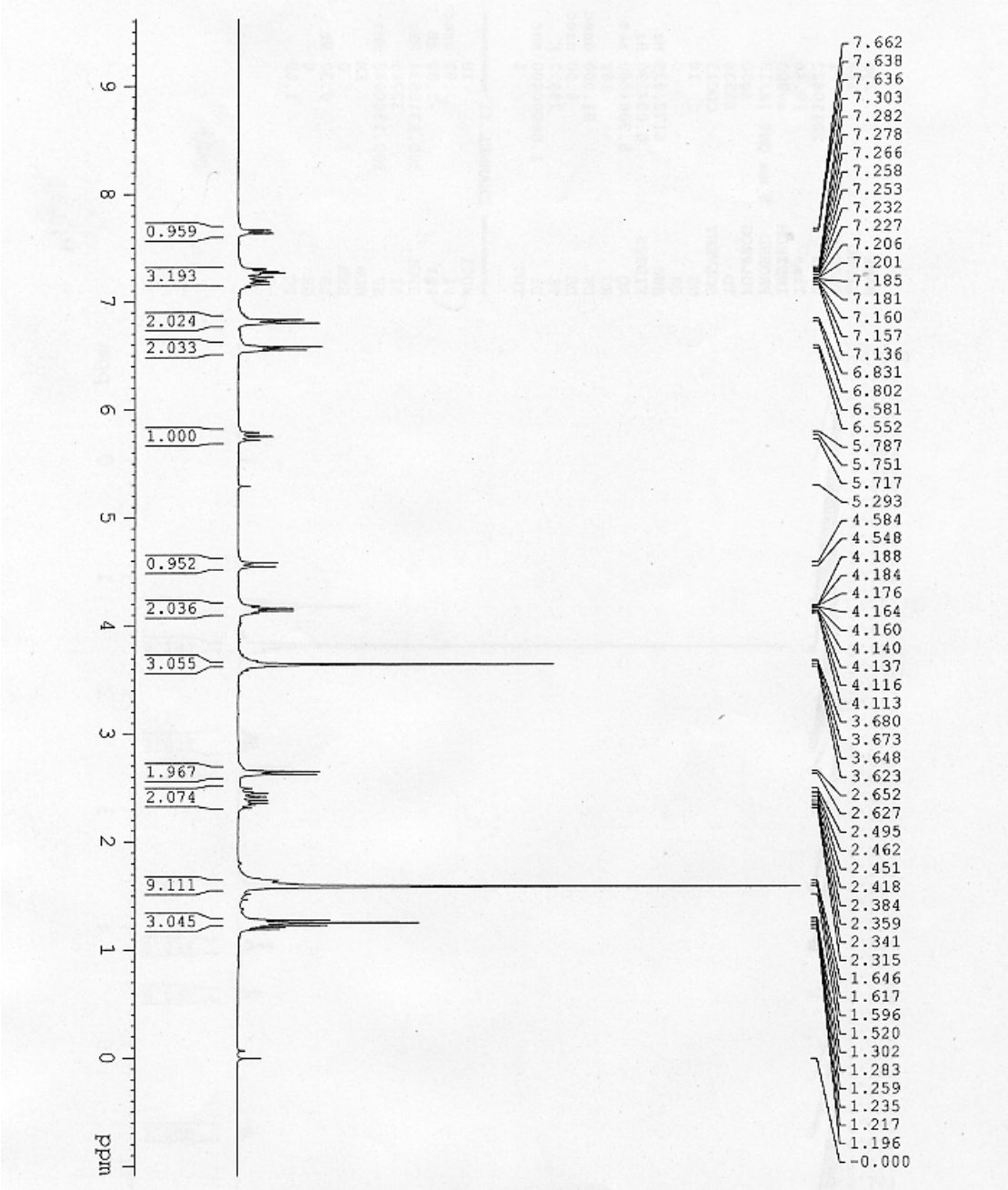
N
O
Boc
3f
OMe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7.636
7.303
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7.266
7.258
7.253
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7.181
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5.751
5.717
5.293
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4.548
4.188
4.184
4.176
4.164
4.160
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4.137
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3.673
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2.341
2.315
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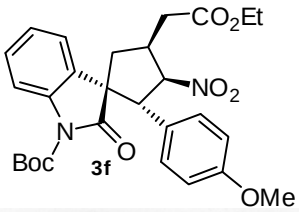
ppm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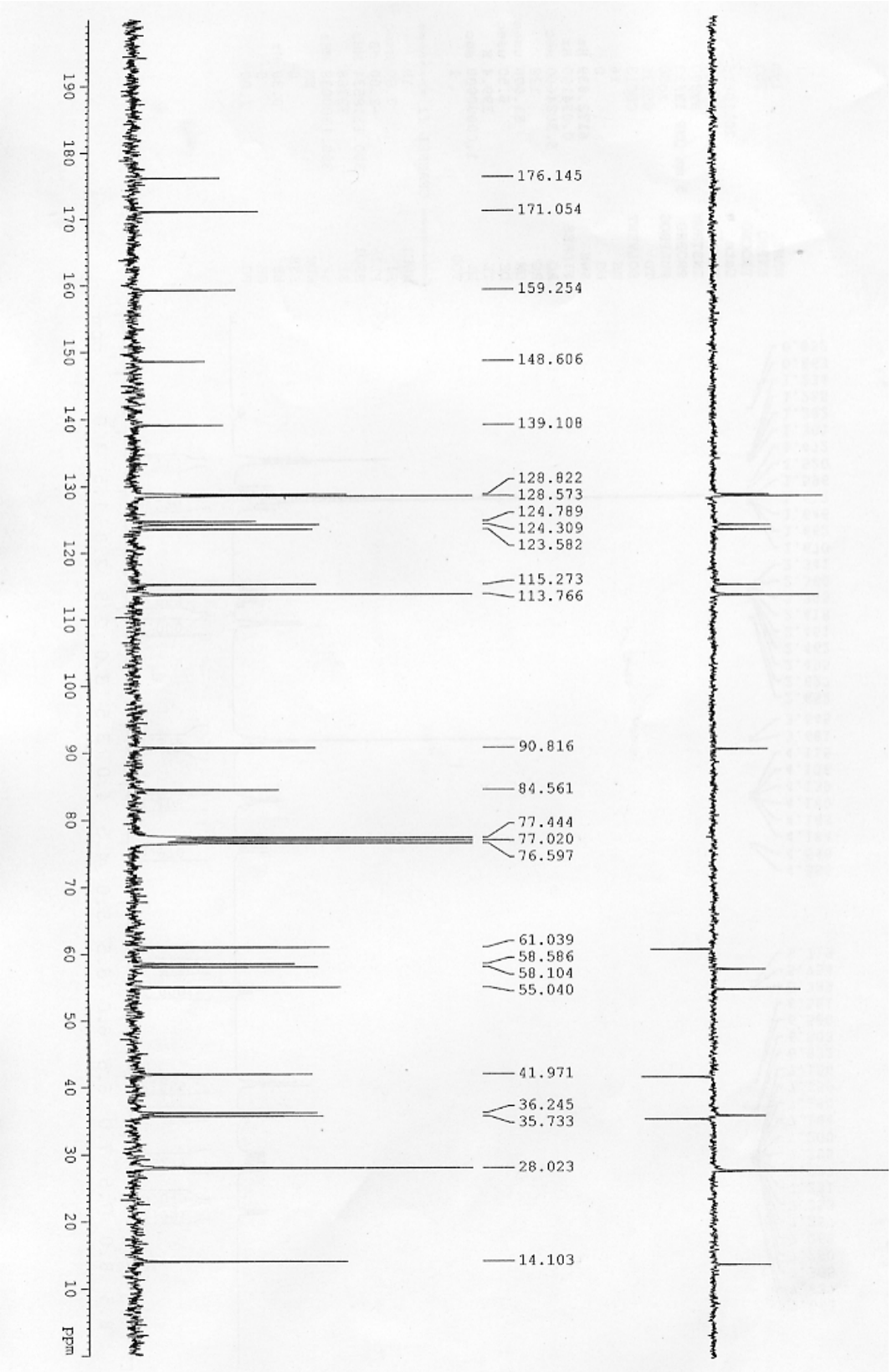
N
O
Boc
3f
OMe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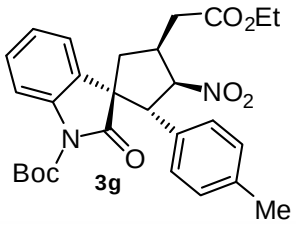
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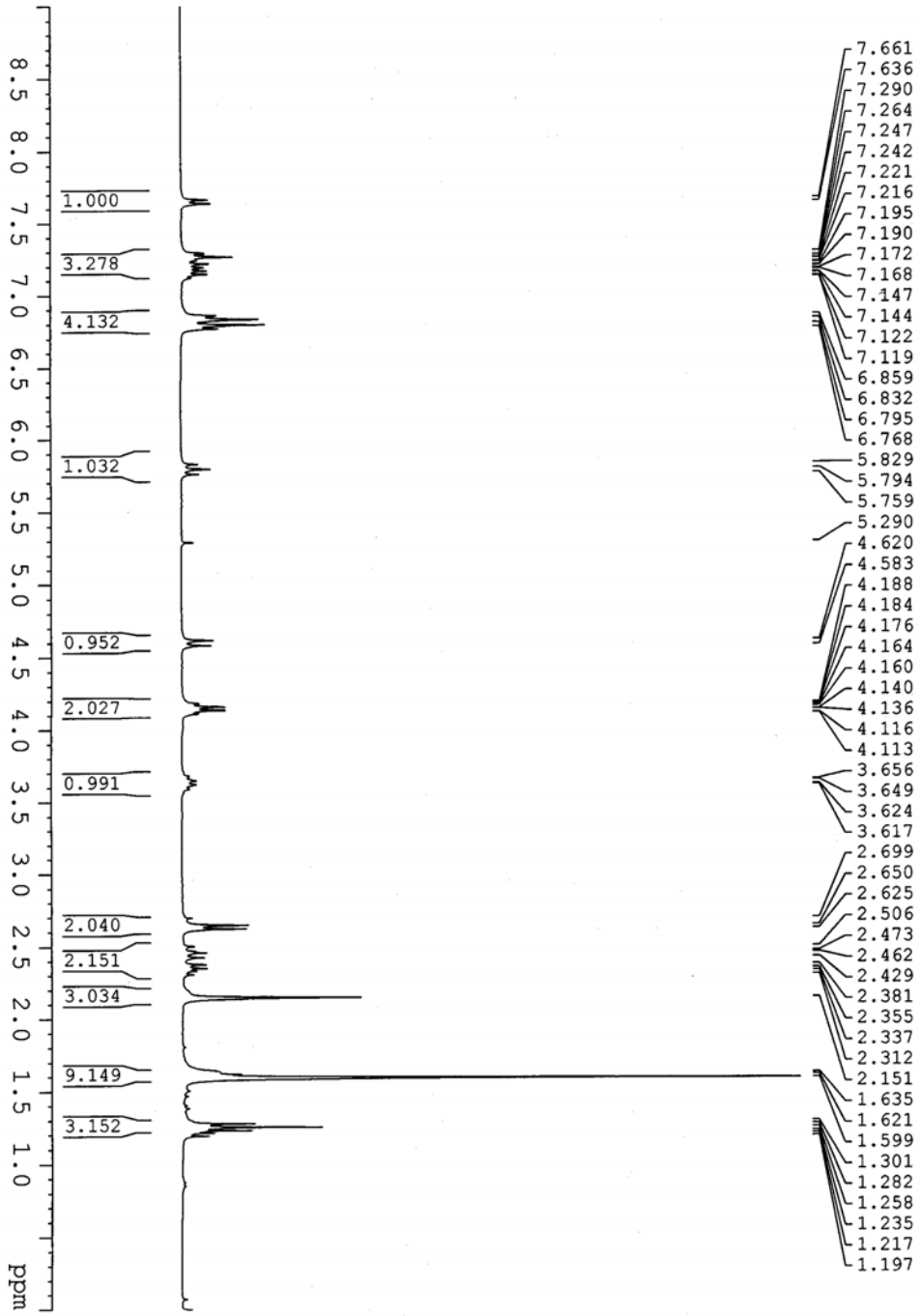
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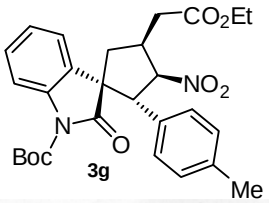
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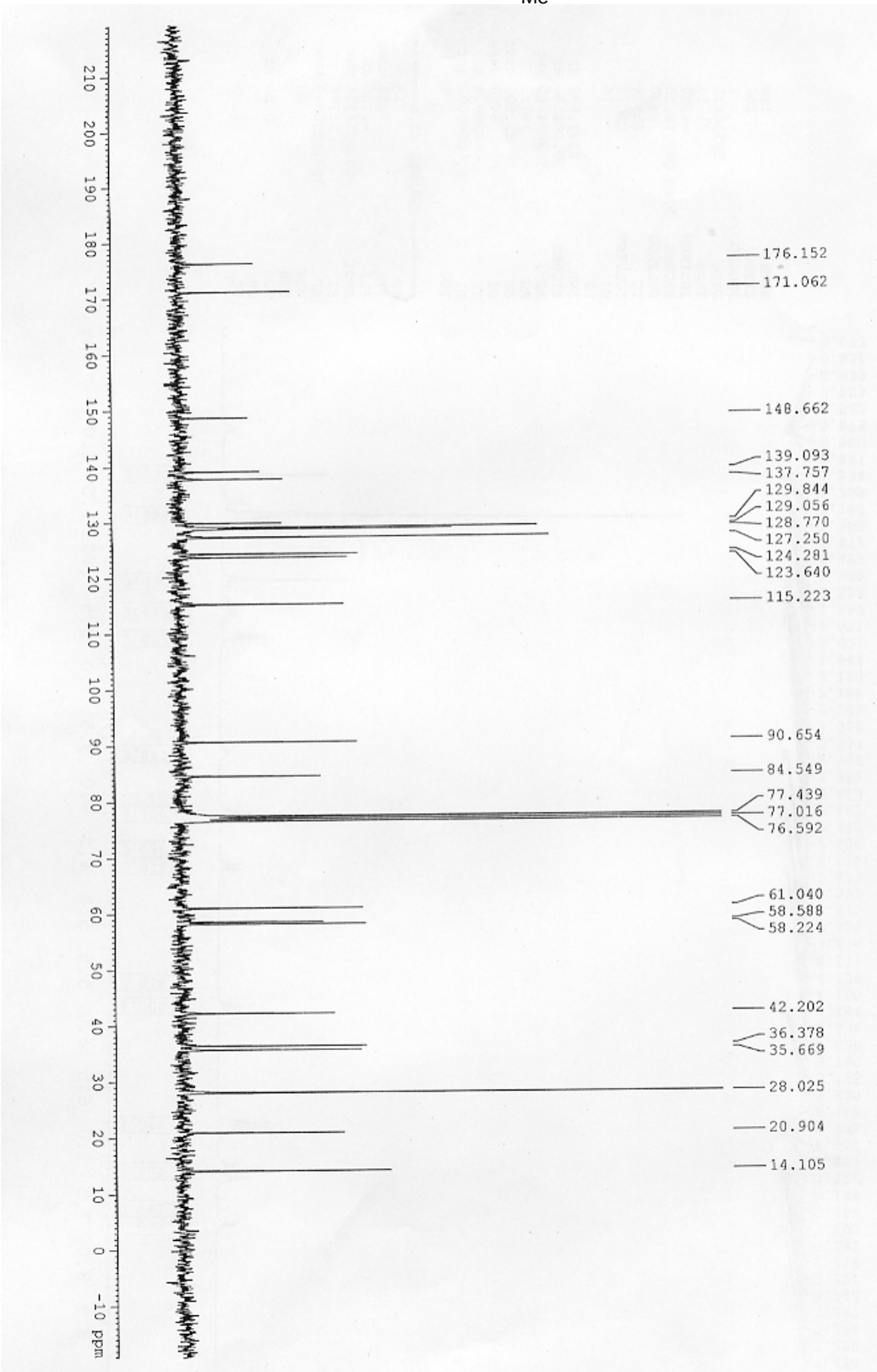
O
Boc
Me

3g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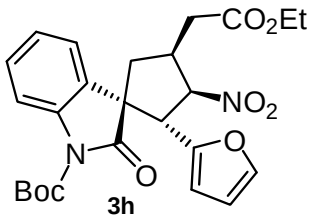
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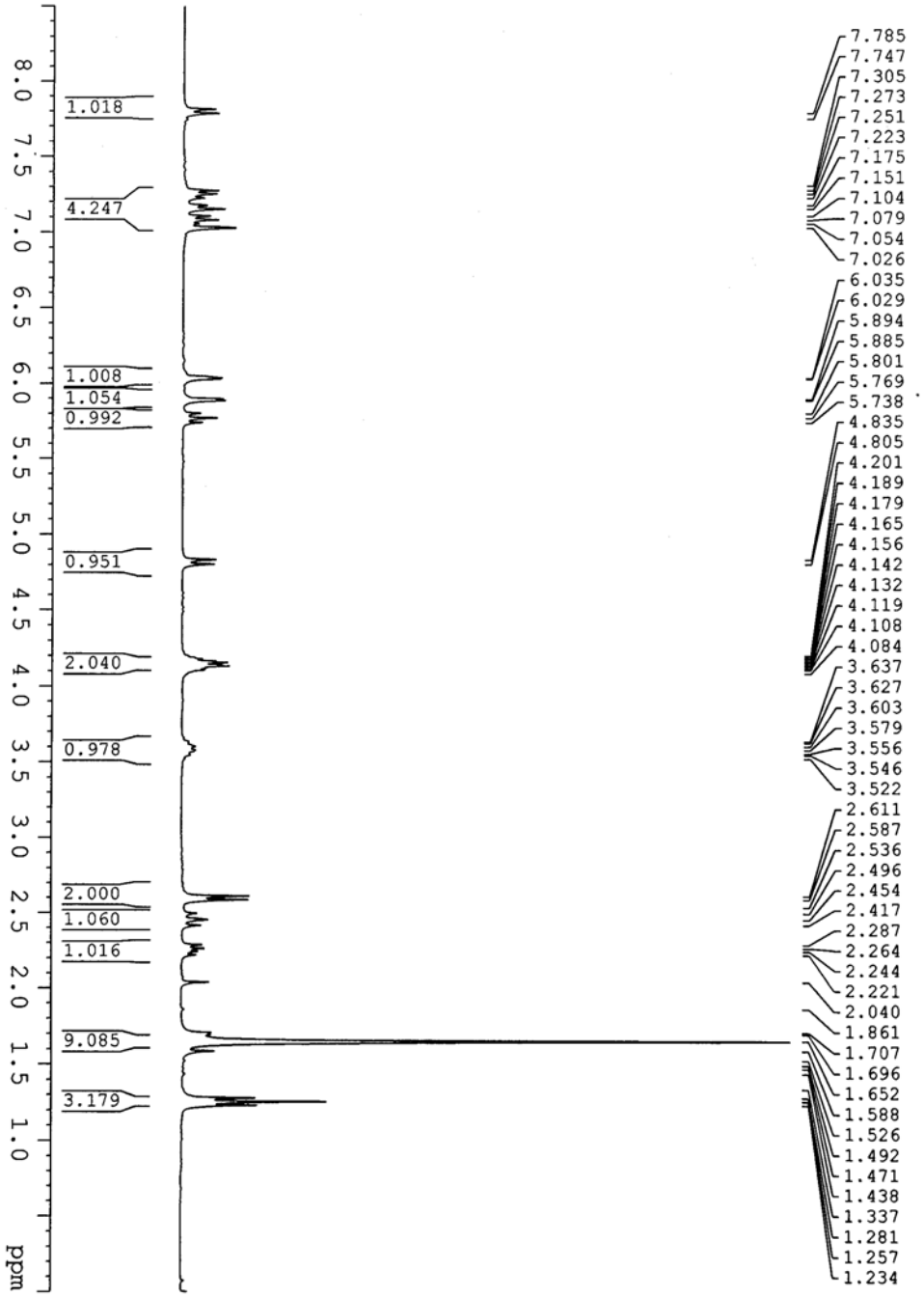
O
Boc

3h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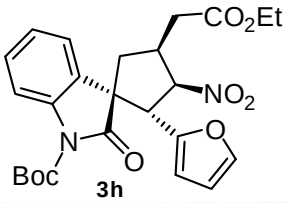
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Boc

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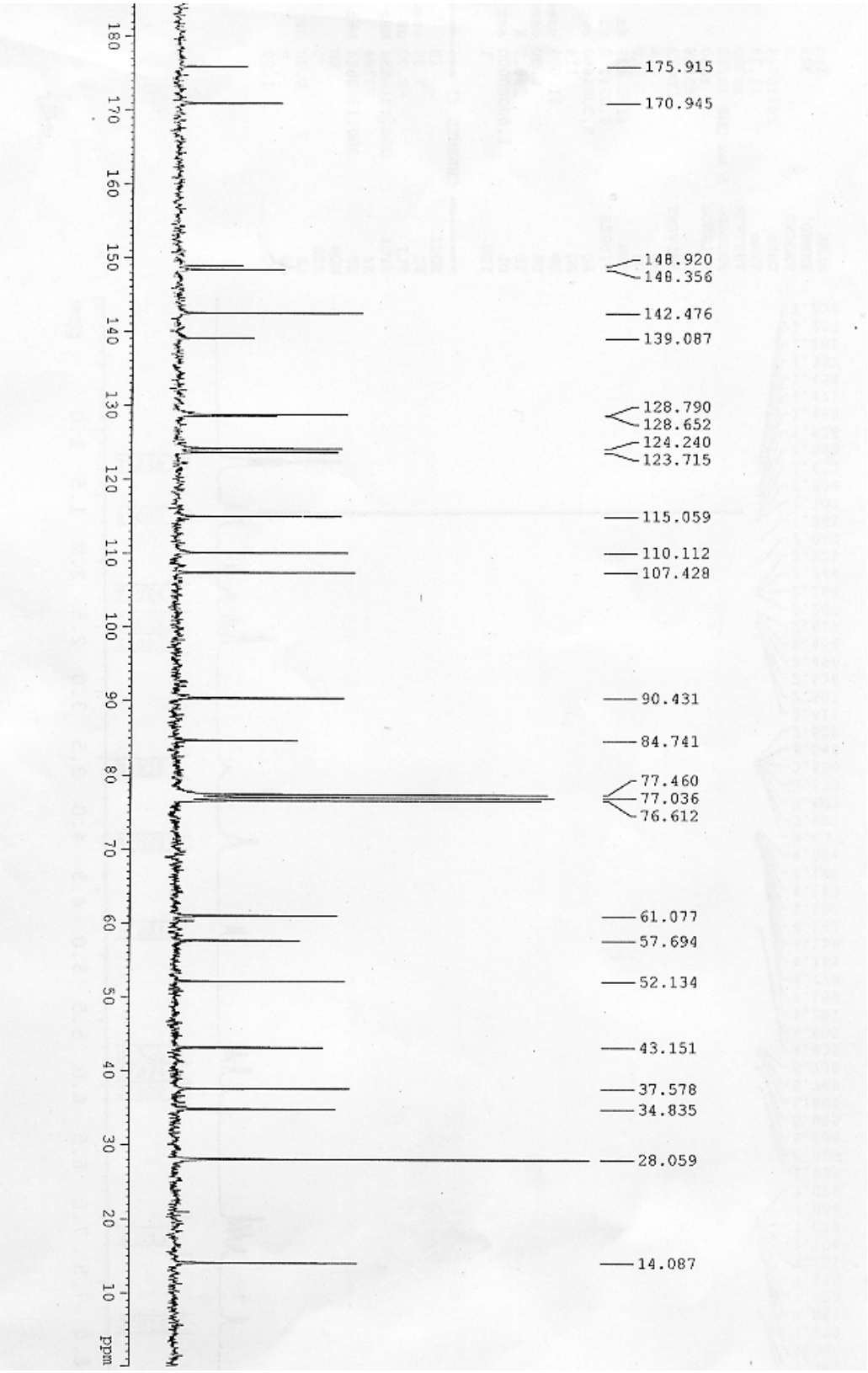
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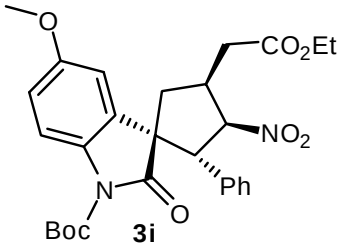
ppm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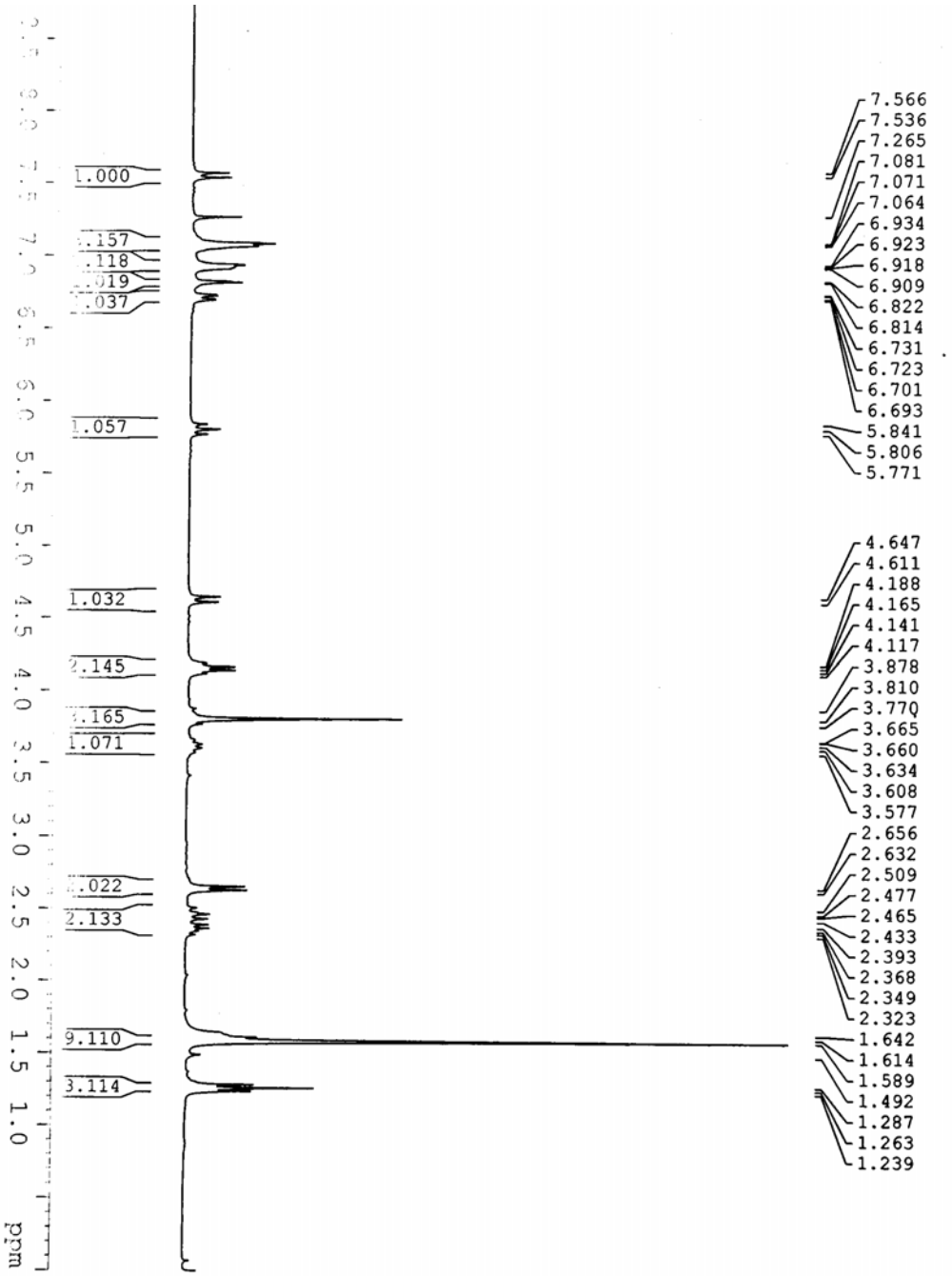
CO2Et
NO2
Ph
N
O
Boc

3i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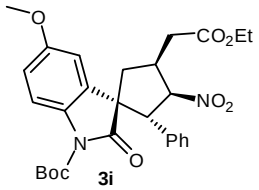
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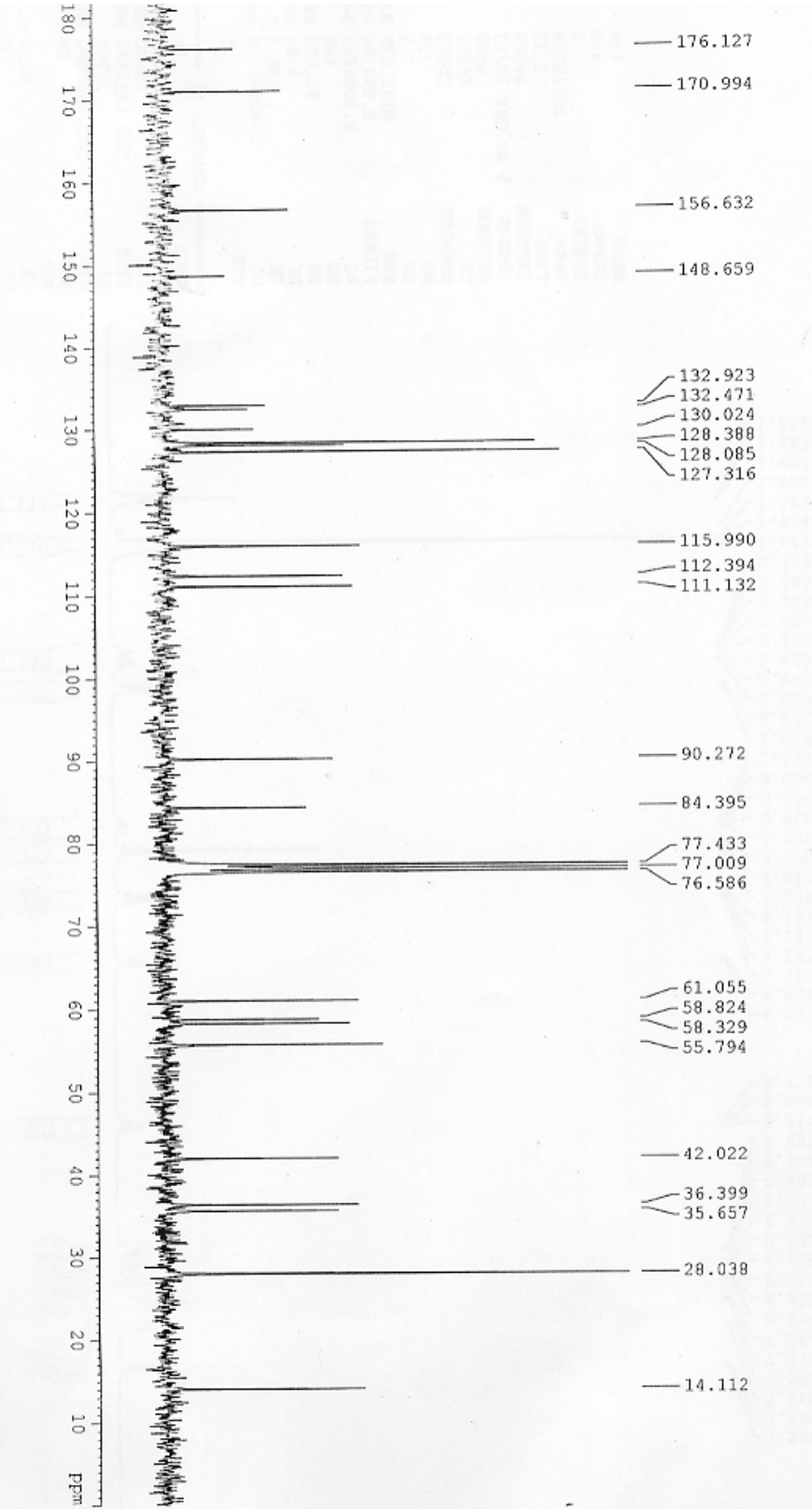
CO2Et
NO2
Ph
N
O
Boc

3i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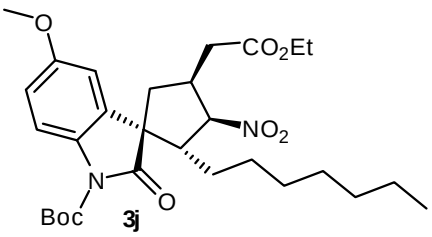
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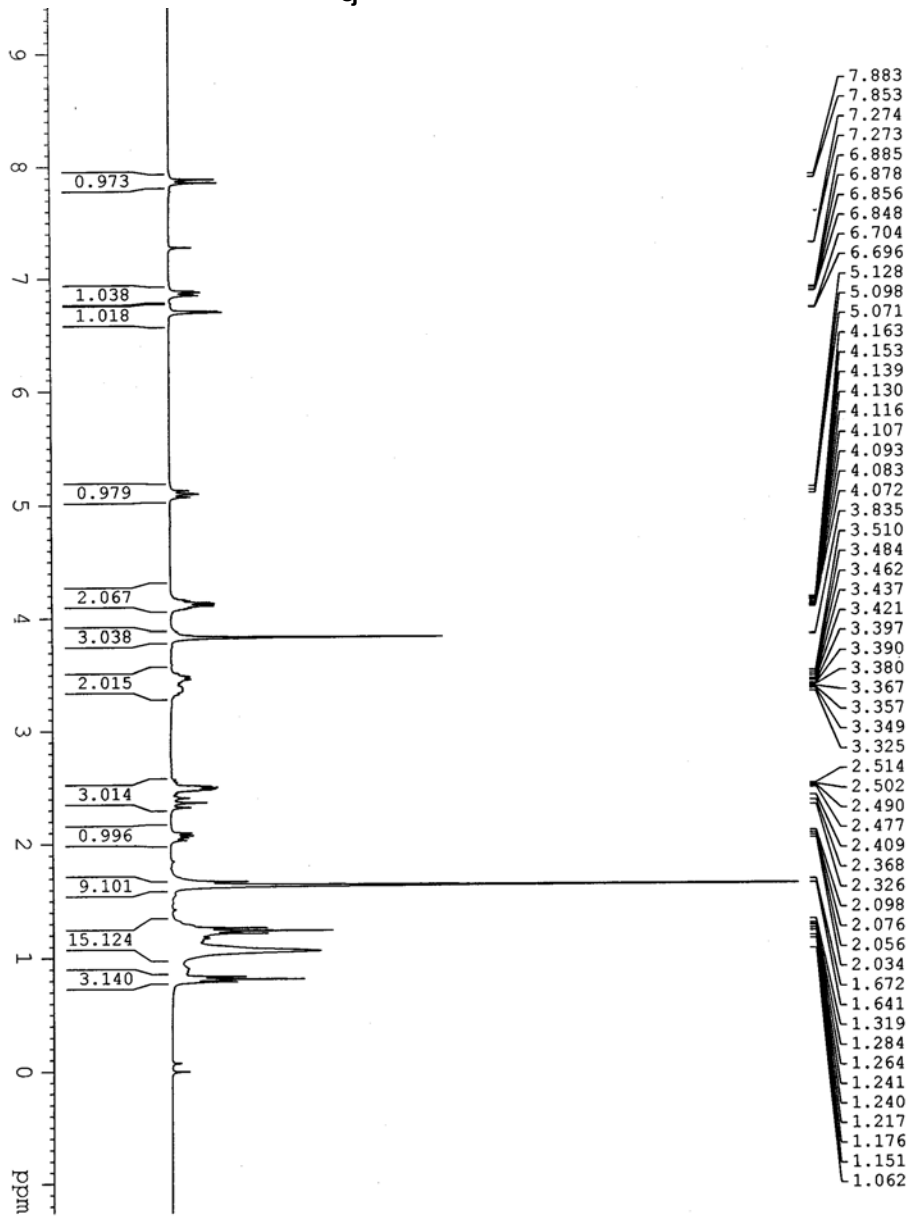
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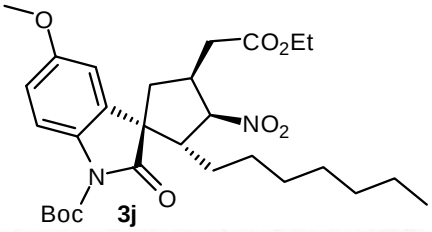
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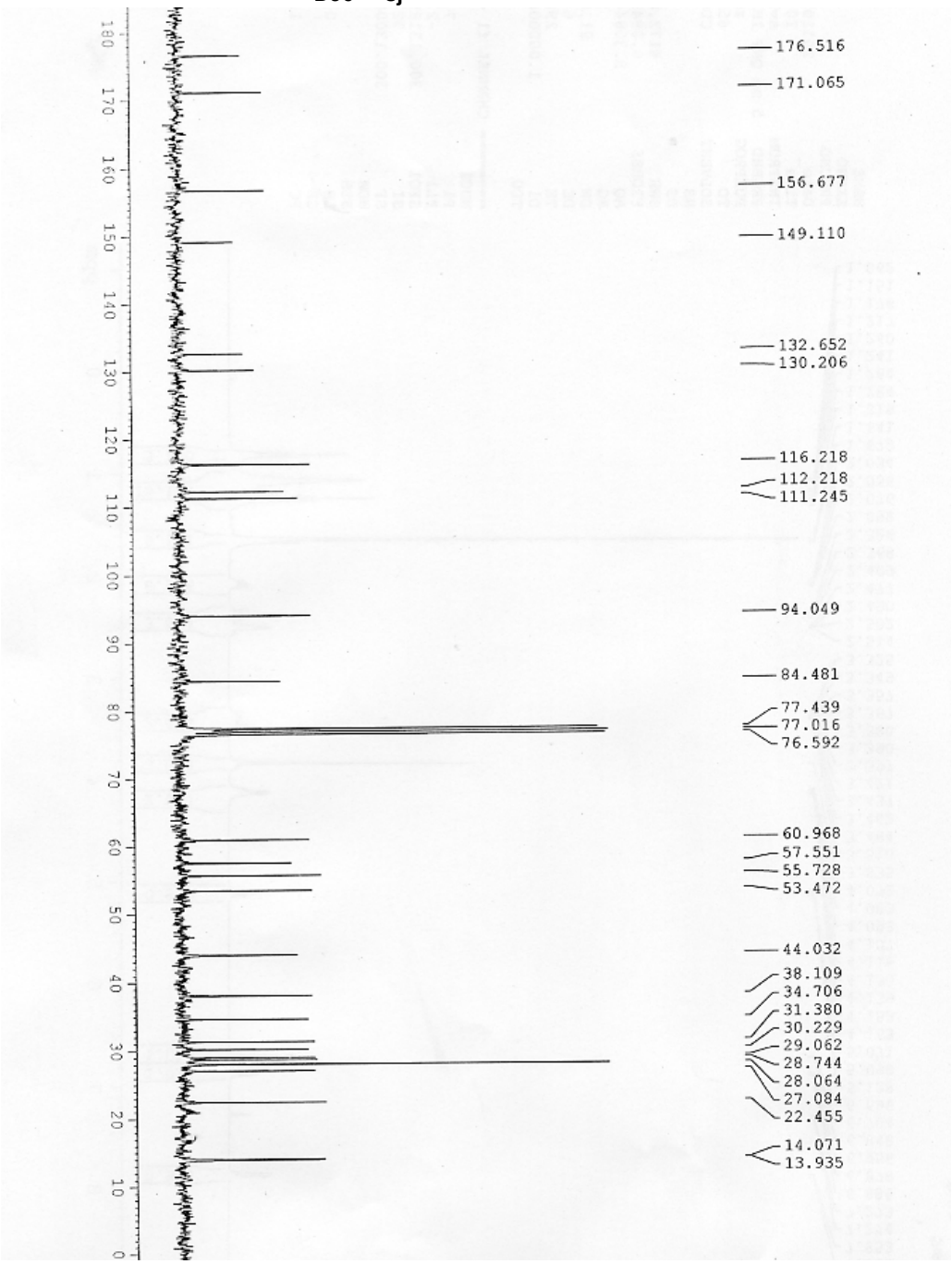
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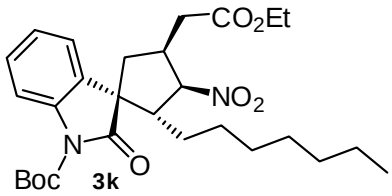
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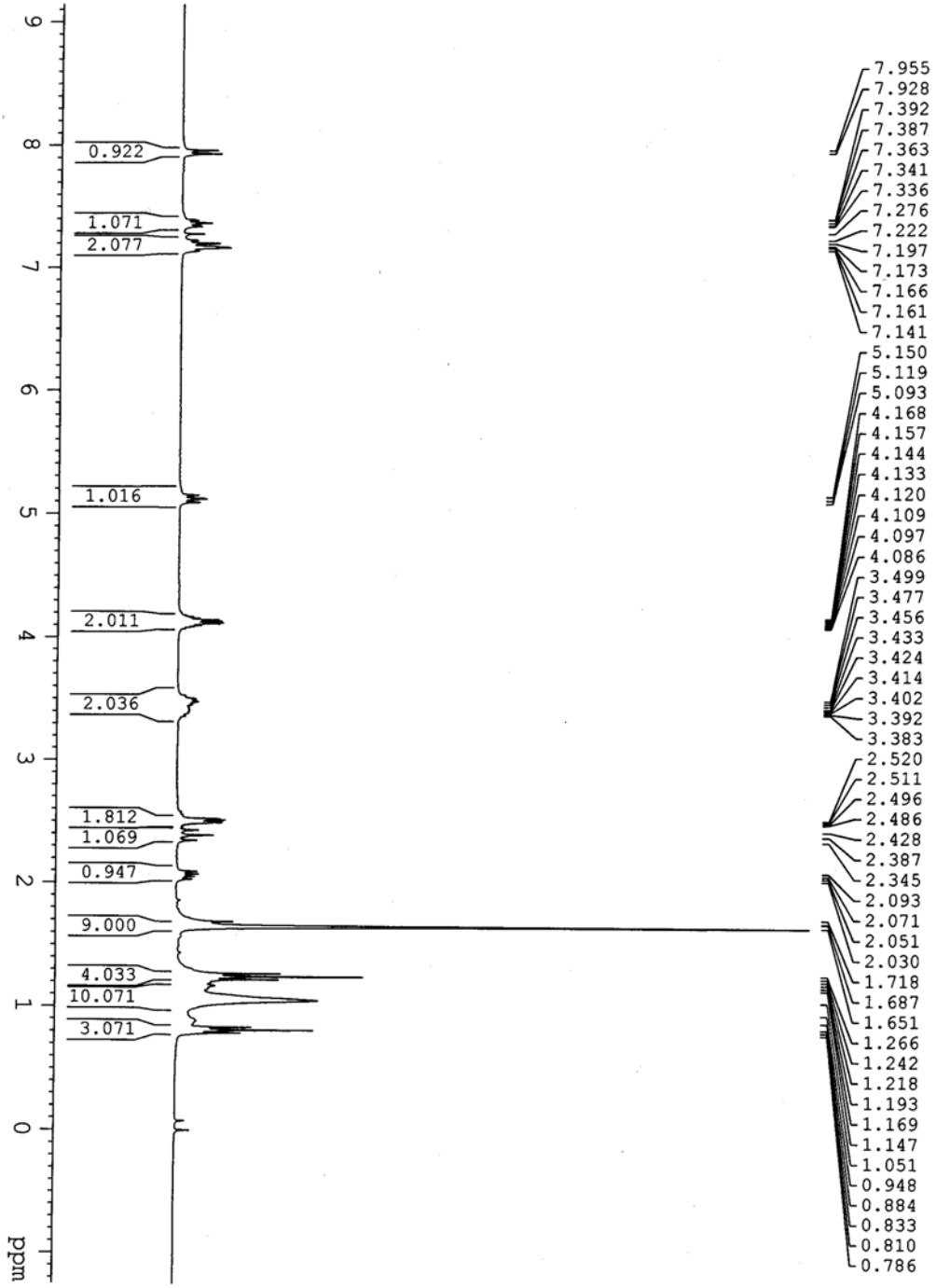
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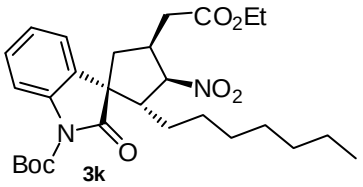
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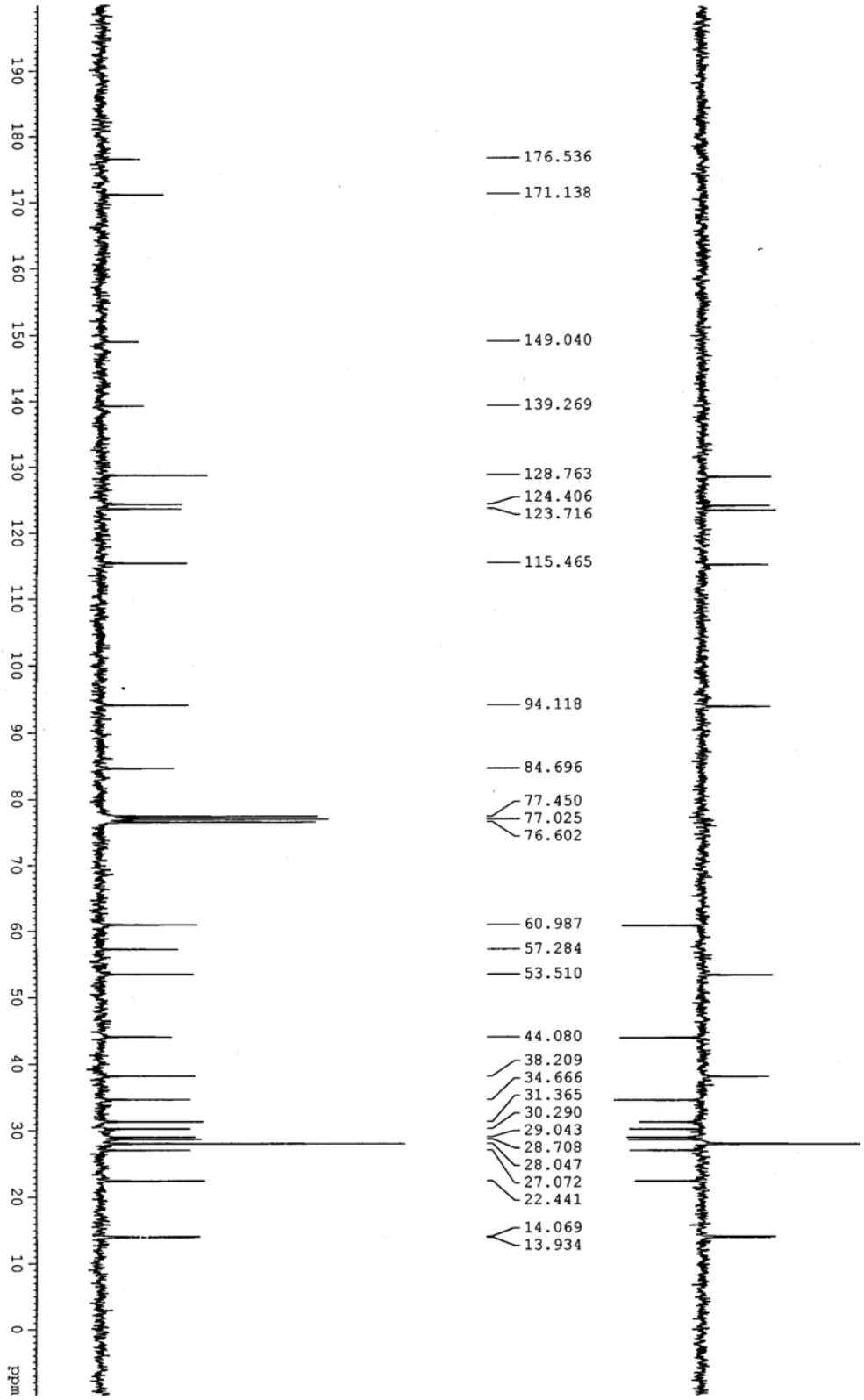
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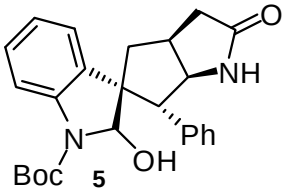
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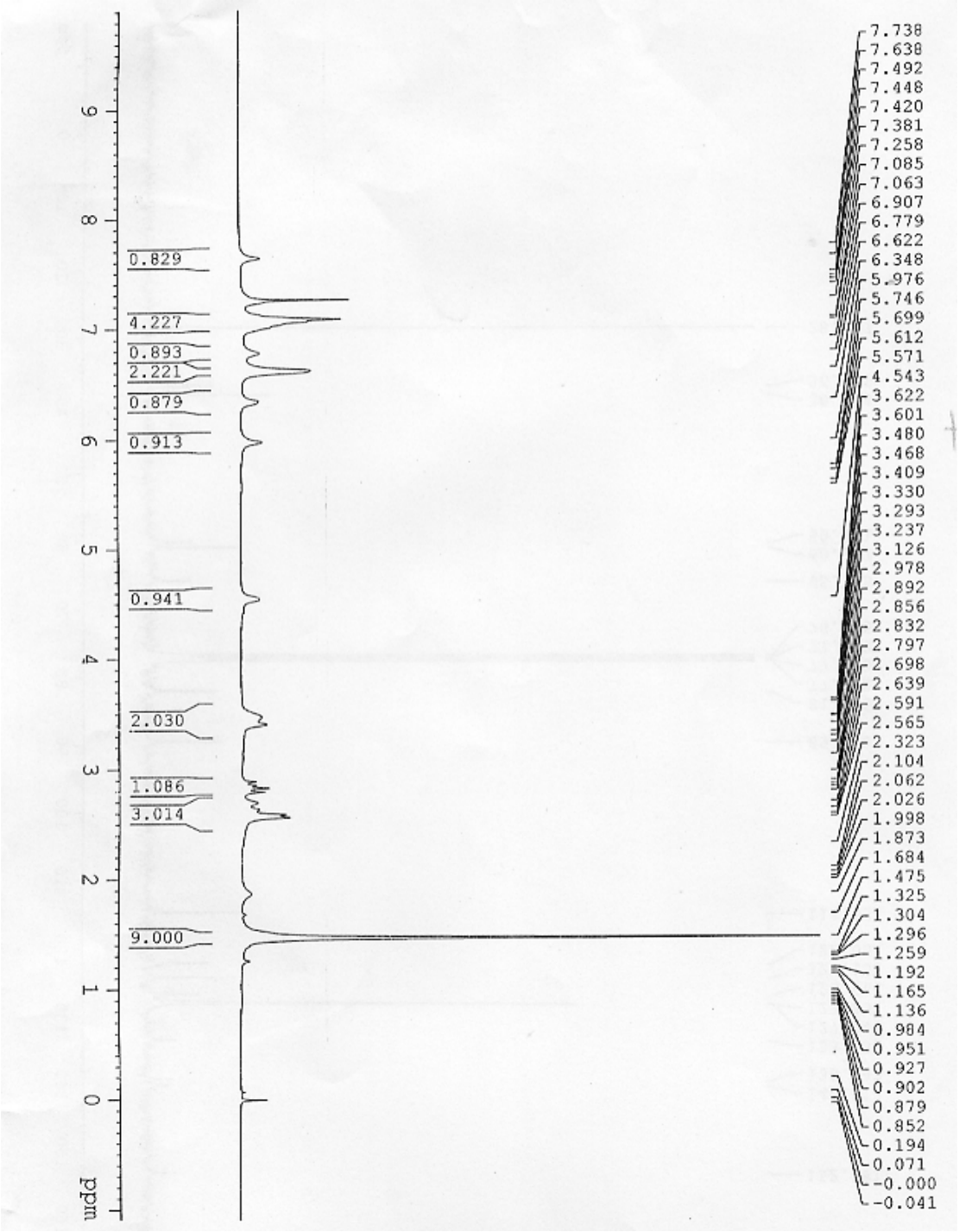
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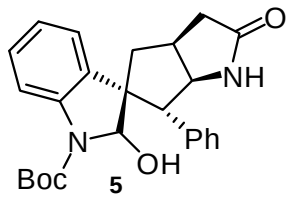
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Ph
N
OH
Boc

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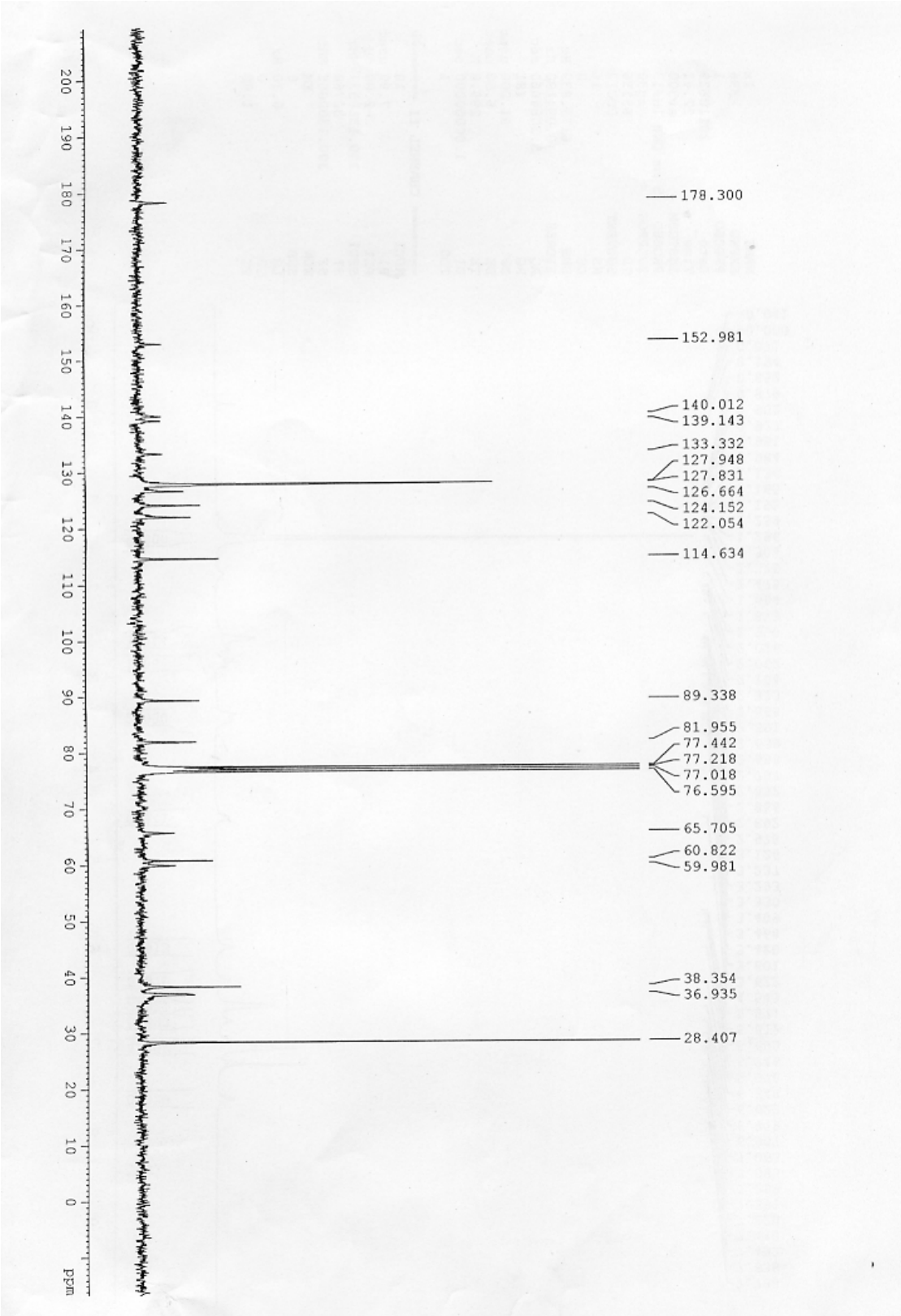
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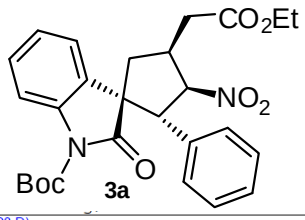
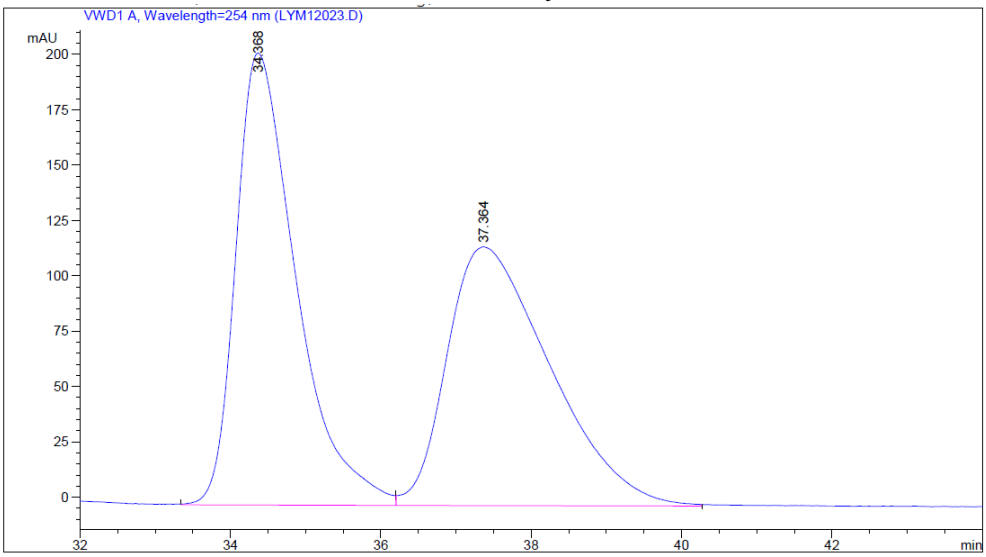
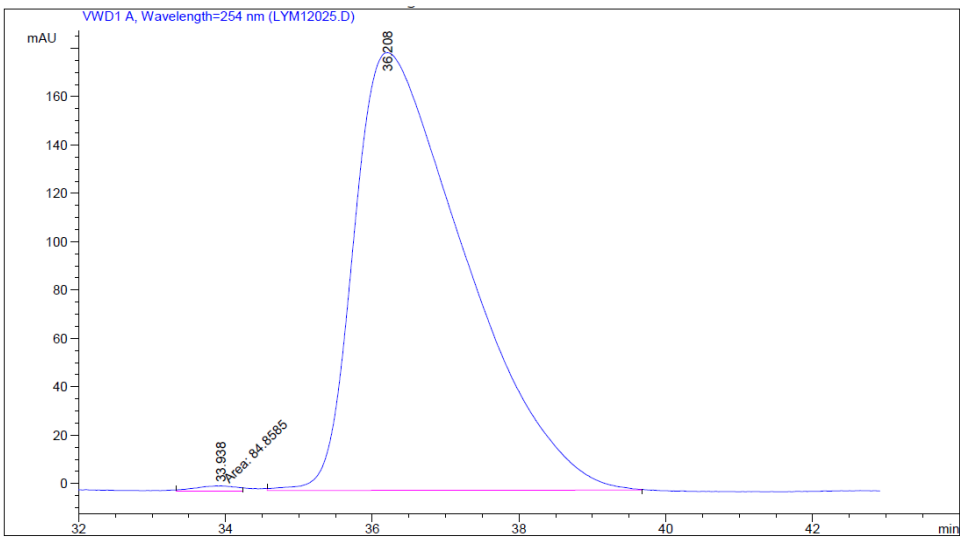
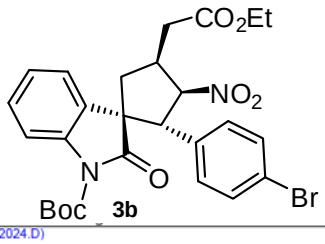




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.368	VV	0.8221	1.13520e4	204.12029	50.5140
2	37.364	VB	1.2630	1.11210e4	116.87505	49.4860



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.938	MM	0.6436	84.85847	2.19733	0.4445
2	36.208	VB	1.4333	1.90040e4	180.97624	99.5555



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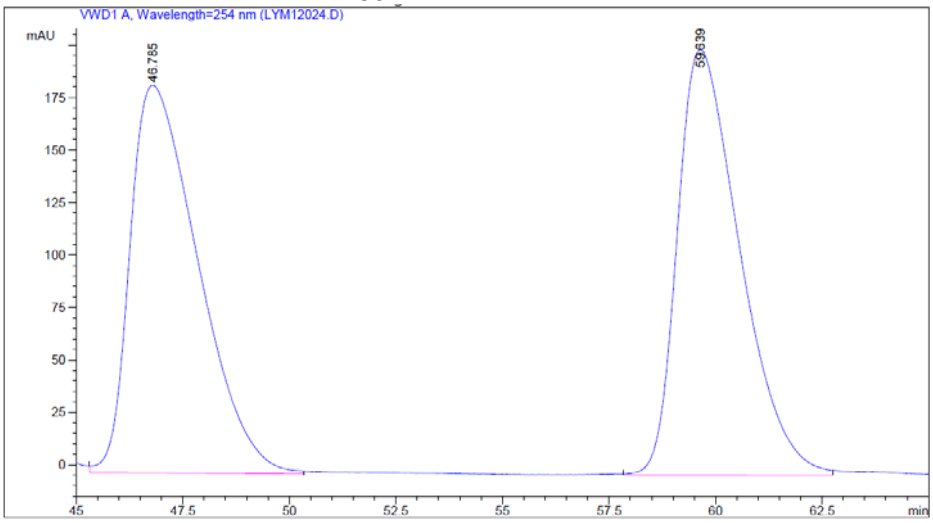
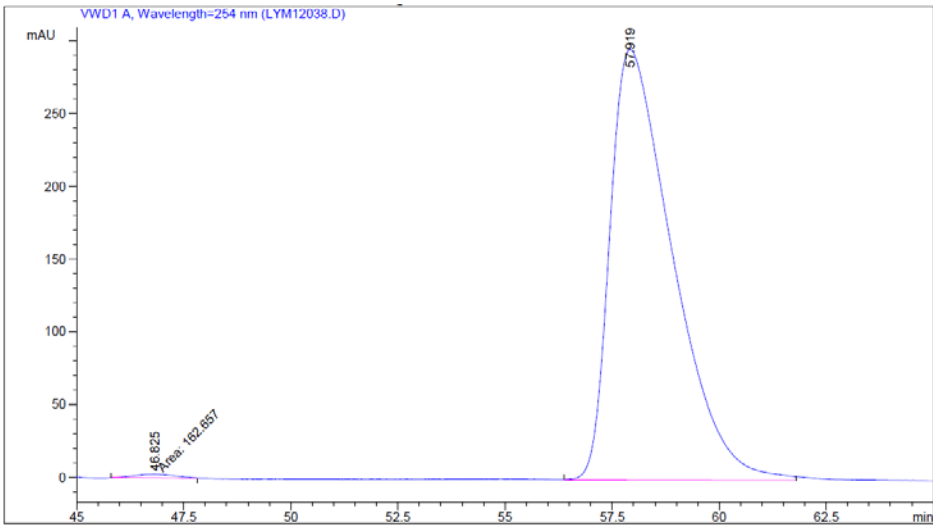
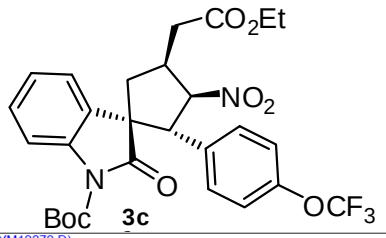


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	46.785	VV	1.4837	2.05086e4	184.64377	49.7874
2	59.639	VV	1.3265	2.06838e4	202.84113	50.2126



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	46.825	MM	1.0904	162.65747	2.48630	0.5375
2	57.919	VV	1.4070	3.00979e4	296.14636	99.4625



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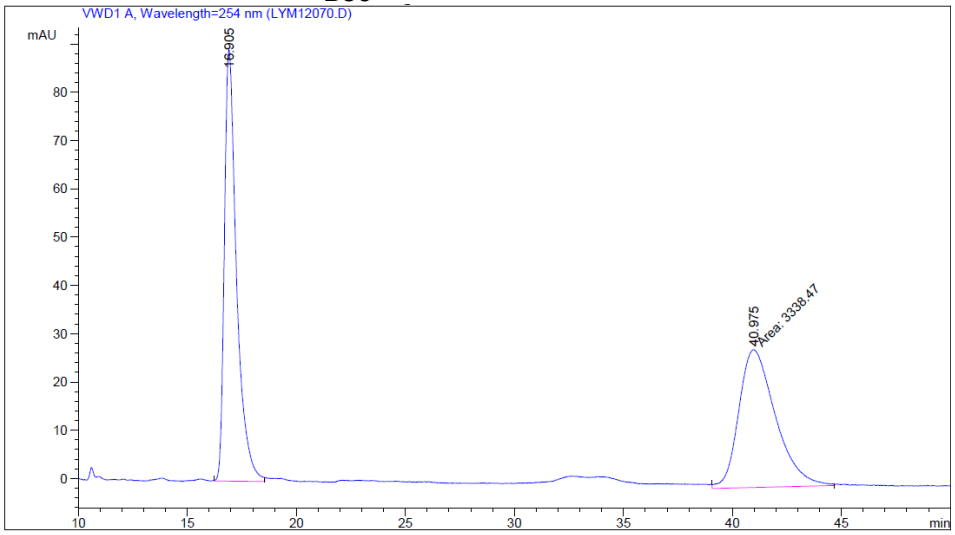
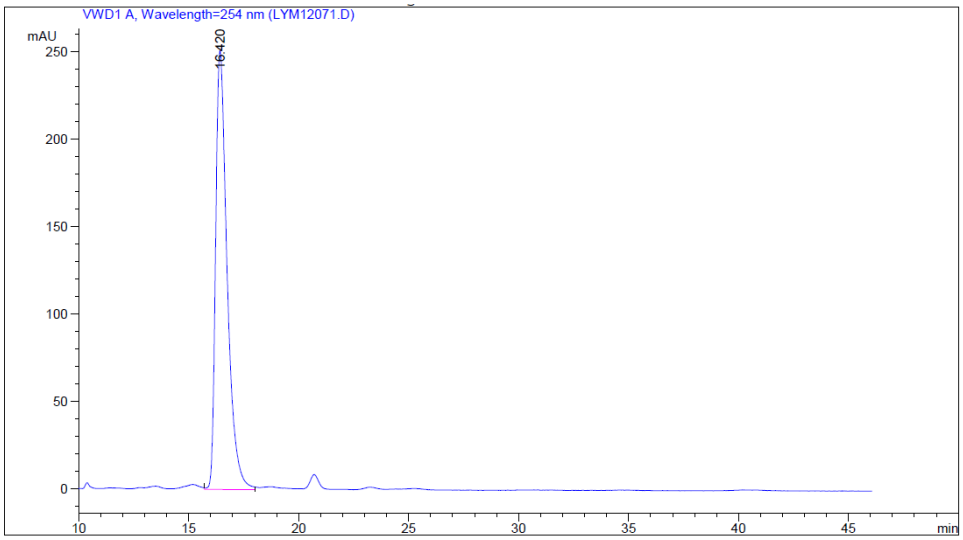


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.905	VV	0.5728	3473.56396	89.38020	50.9915
2	40.975	MM	1.9489	3338.47485	28.54996	49.0085



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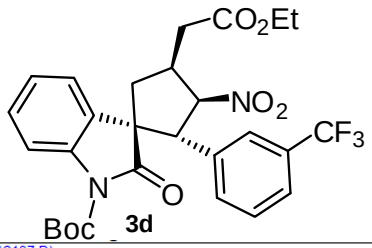
1	16.420	VB	0.5493	9121.99609	250.95786	100.0000



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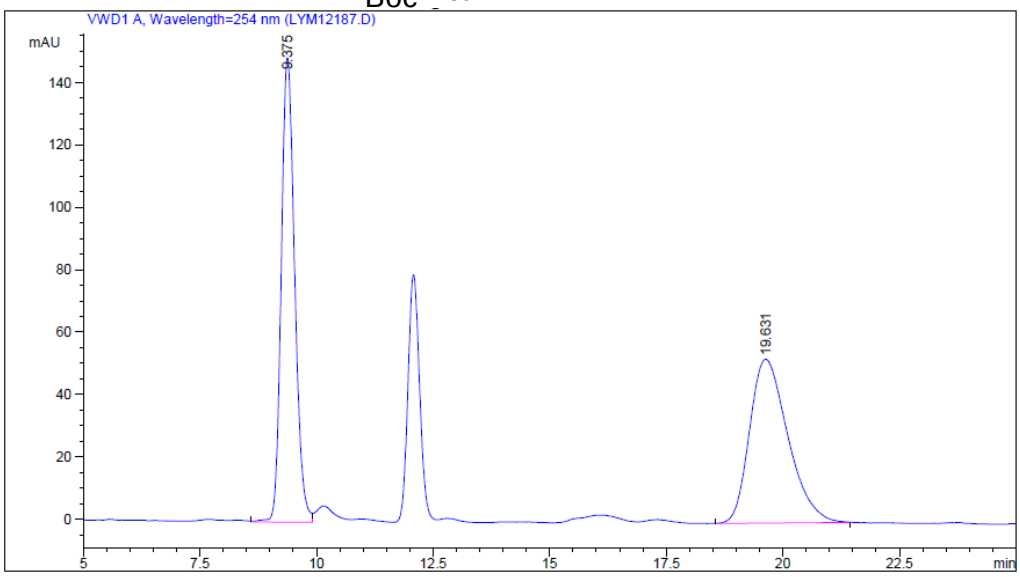
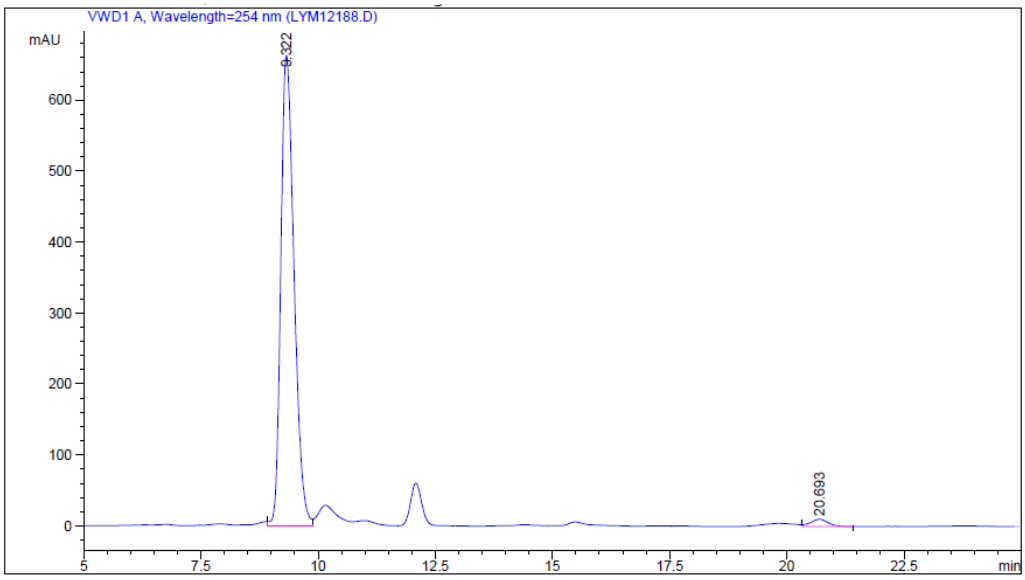
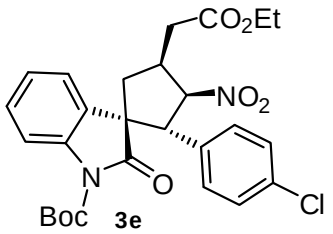


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.375	VV	0.3094	2981.36621	148.84688	49.8316
2	19.631	VB	0.8337	3001.51758	52.55554	50.1684



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.322	VV	0.3046	1.30148e4	663.25342	97.9610
2	20.693	VV	0.3774	270.89246	10.22787	2.0390



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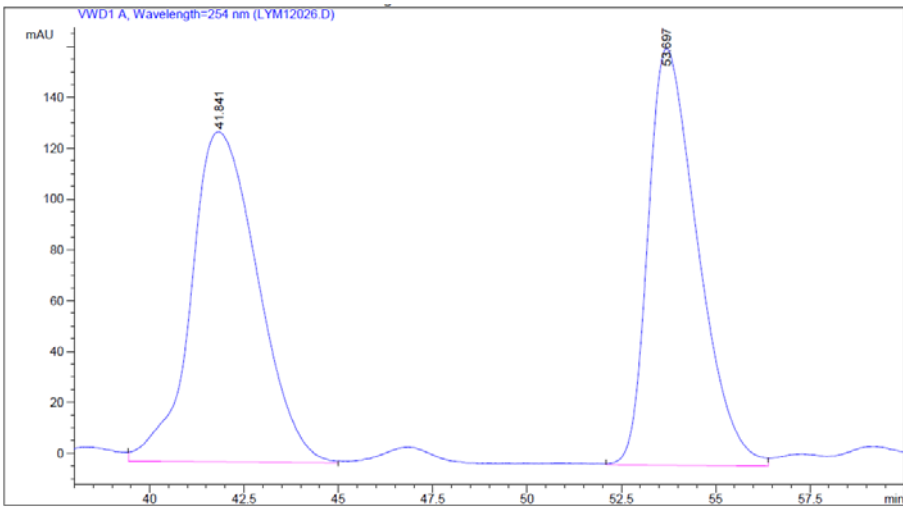
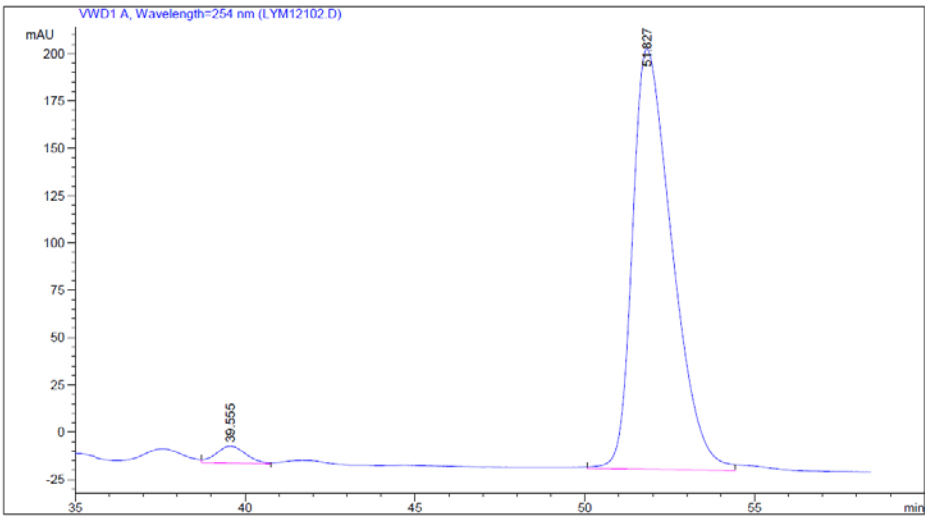
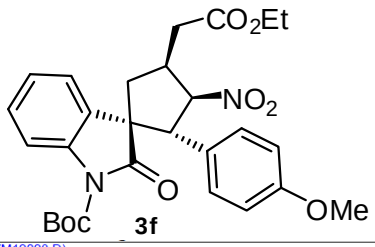


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	41.841	VV	1.4536	1.60547e4	129.90018	51.7230
2	53.697	BB	1.2583	1.49851e4	163.99263	48.2770



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	39.555	VV	0.7174	548.26233	9.08212	2.9594
2	51.827	VV	1.1830	1.79780e4	222.14259	97.0406



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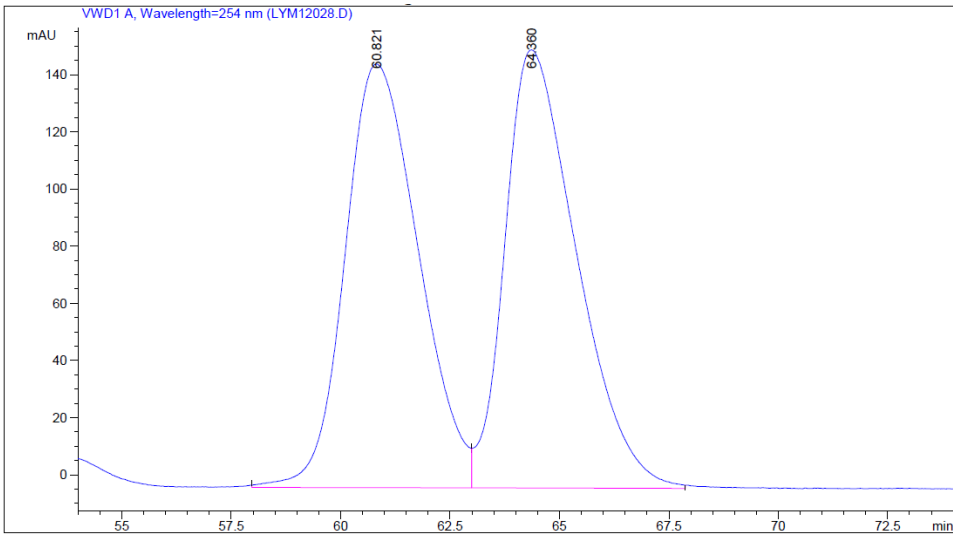
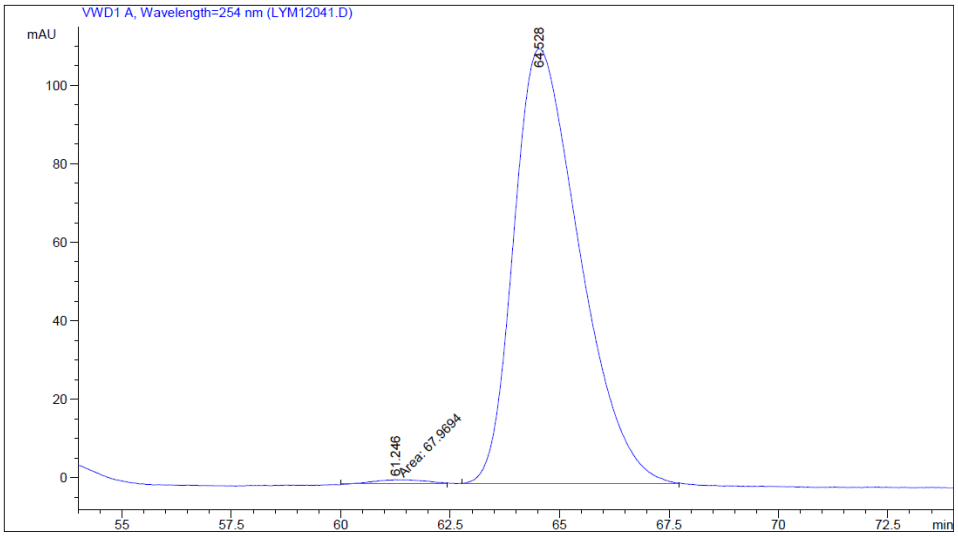
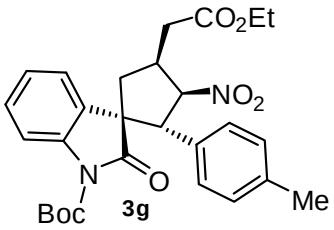


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	60.821	VV	1.4047	1.72900e4	148.21097	49.7084
2	64.360	VV	1.3792	1.74929e4	153.31371	50.2916



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	61.246	MM	1.2114	67.96942	9.35131e-1	0.5837
2	64.528	VB	1.4655	1.15763e4	110.75022	99.4163



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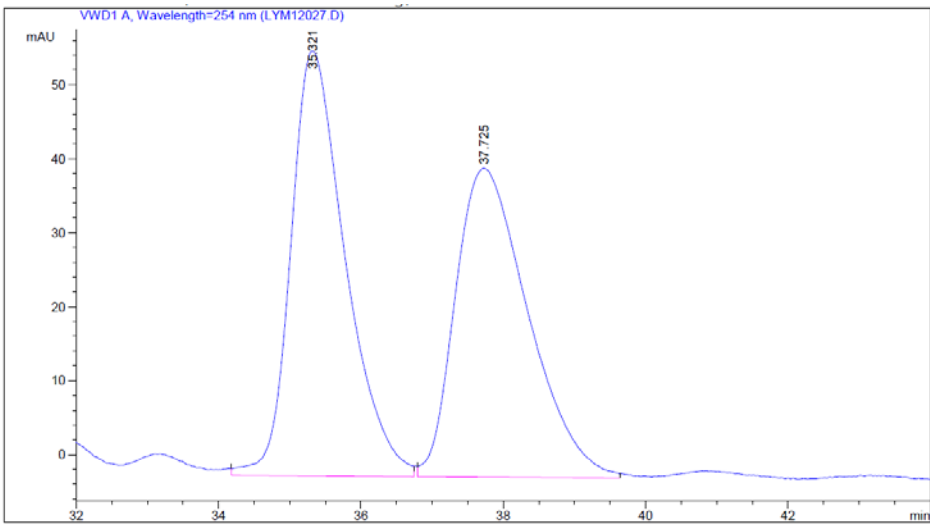
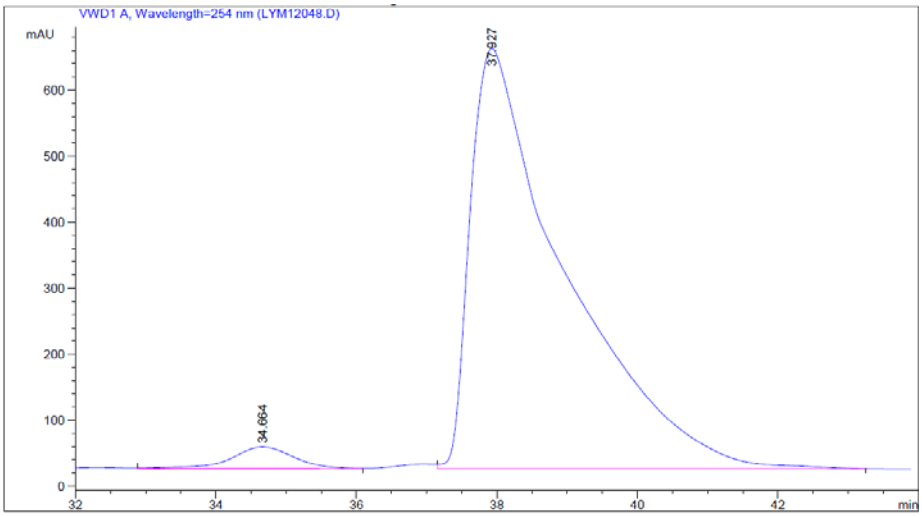
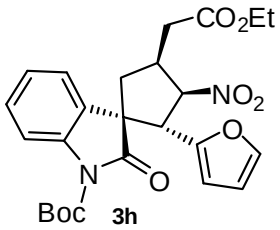


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	35.321	VV	0.7499	3056.13062	57.48086	50.7581
2	37.725	VV	0.9236	2964.84424	41.79984	49.2419



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.664	VV	0.8052	2050.40063	32.85813	3.3184
2	37.927	VB	1.2614	5.97388e4	637.07129	96.6816



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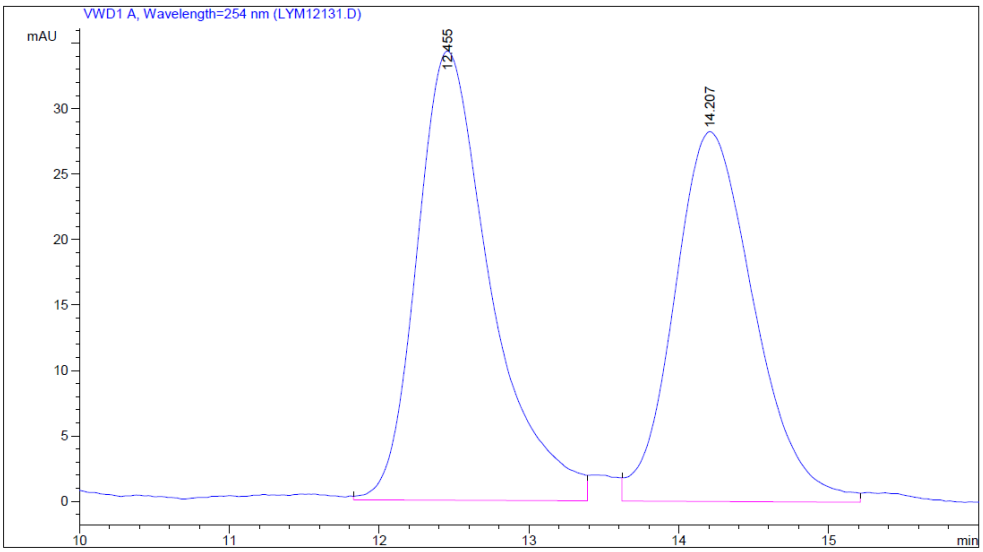
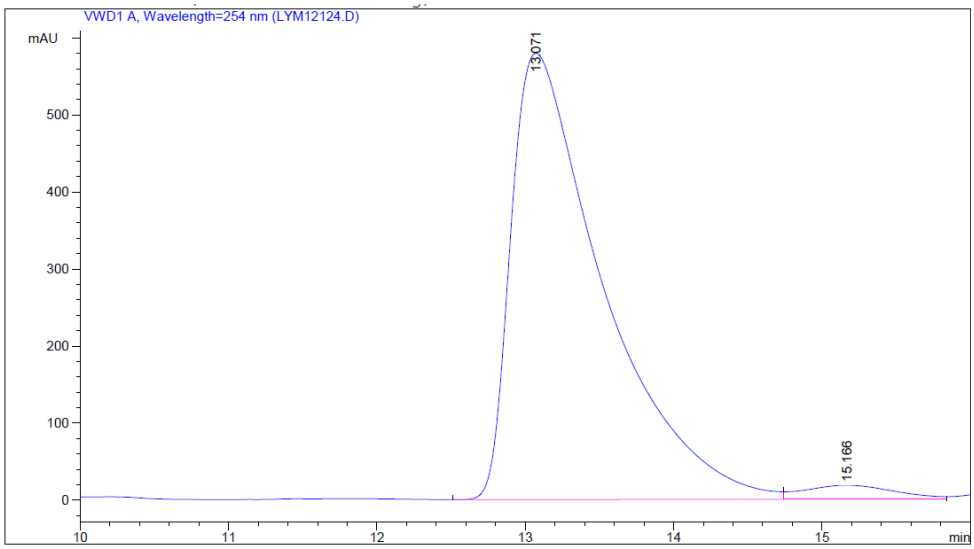
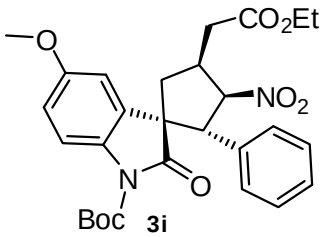


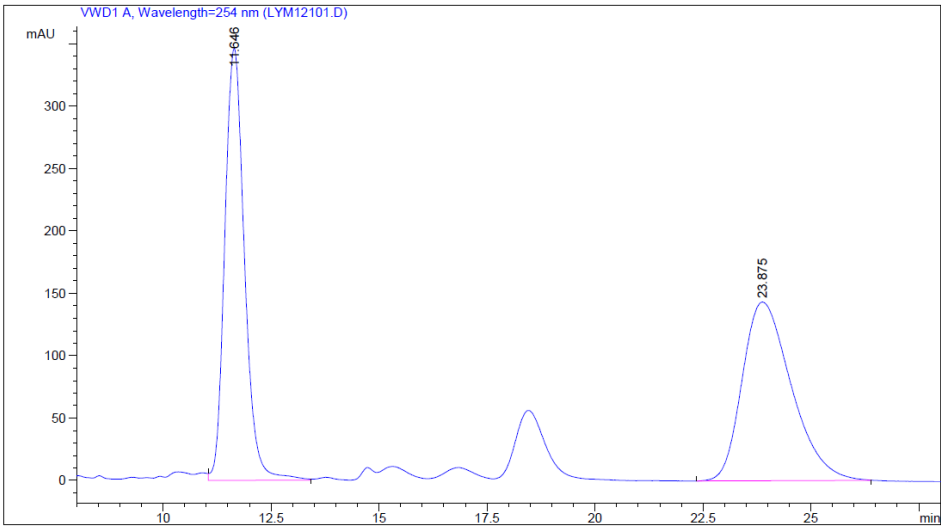
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.455	VV	0.5043	1170.28857	34.30368	52.7378
2	14.207	VV	0.5511	1048.78064	28.24846	47.2622



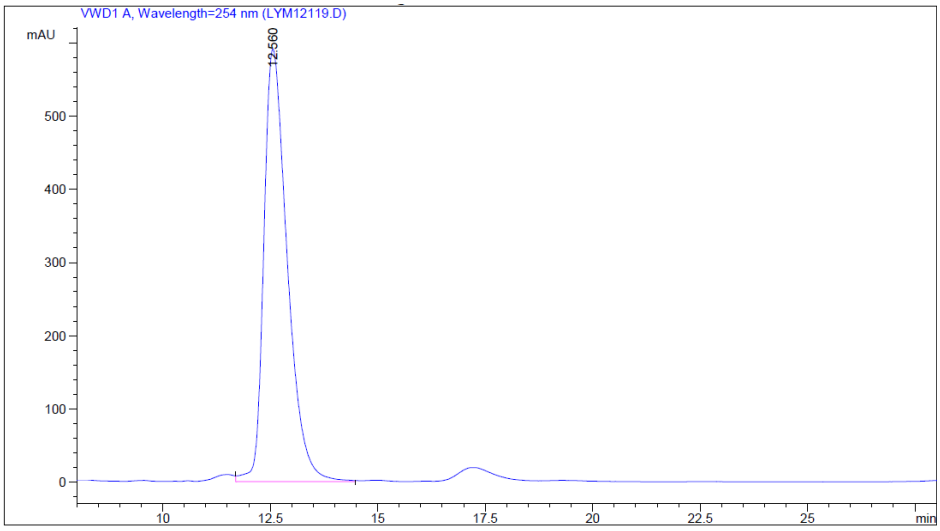
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.071	VV	0.6293	2.49567e4	579.27808	96.9667
2	15.166	VV	0.5152	780.68652	18.29882	3.0333



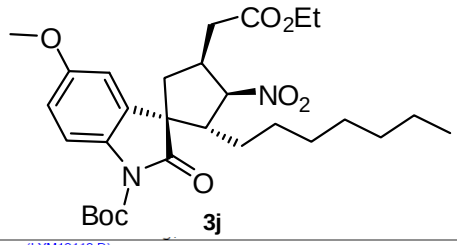
3i



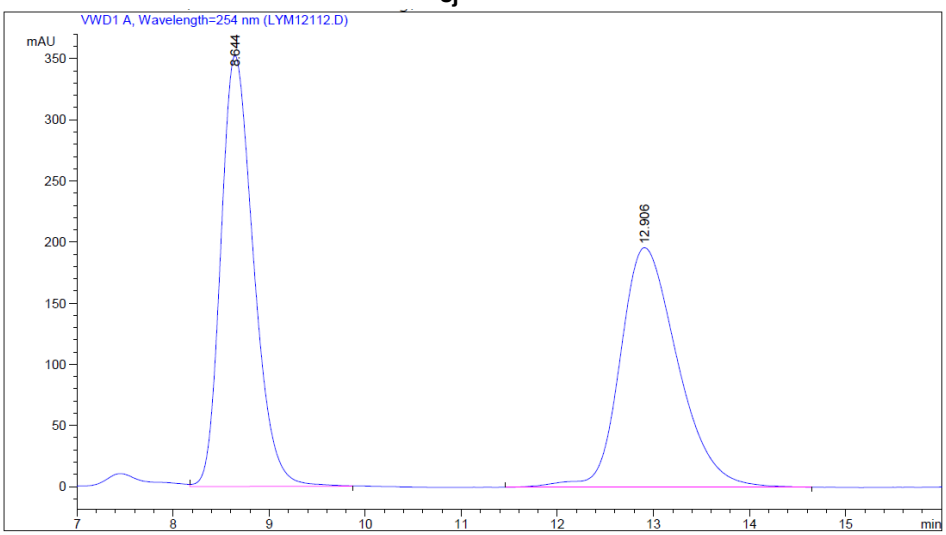
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.646	VB	0.4928	1.09995e4	346.38080	49.2557
2	23.875	VB	1.1400	1.13319e4	143.23021	50.7443



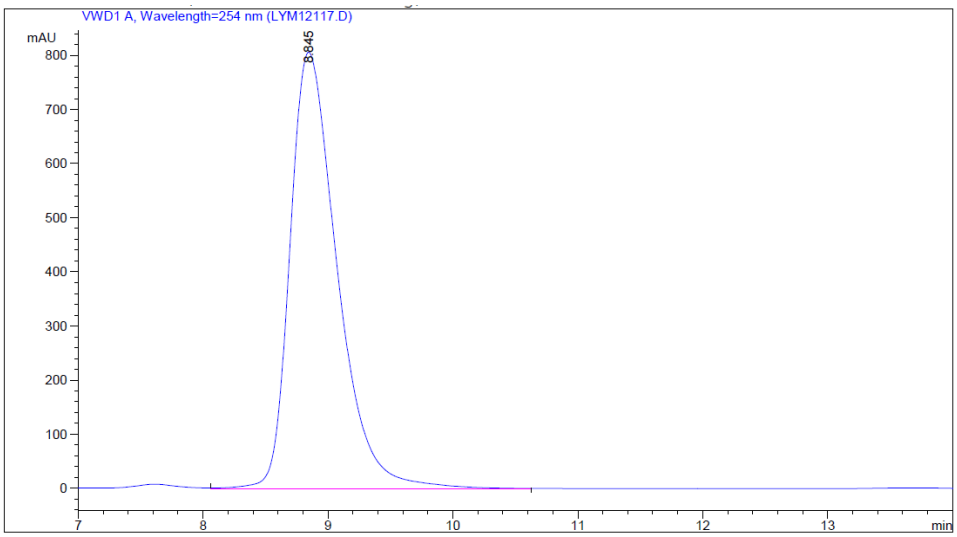
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.560	VV	0.5813	2.24274e4	590.62683	100.0000



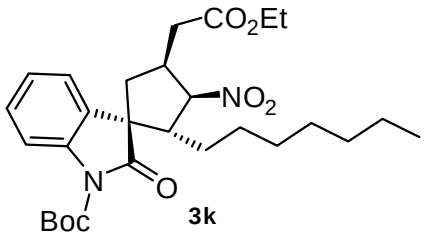
3j



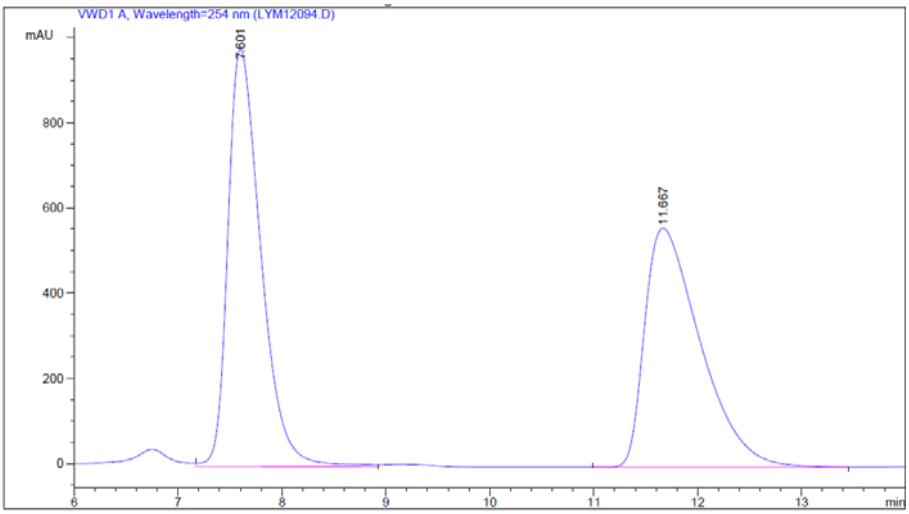
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.644	VB	0.3661	8330.99512	352.42691	50.4984
2	12.906	VB	0.6359	8166.55322	196.08170	49.5016



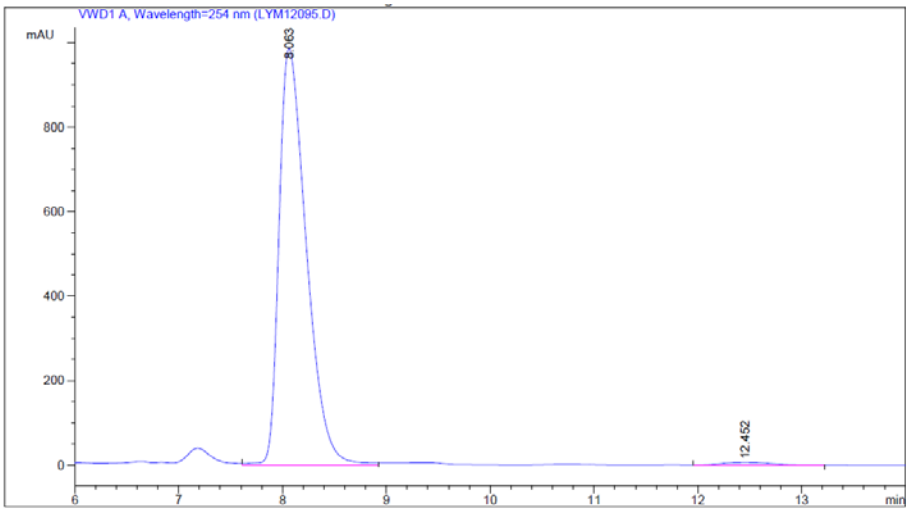
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.845	VB	0.3994	2.11608e4	806.16229	100.0000



3k



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.601	VV	0.3370	2.15796e4	979.84998	50.9193
2	11.667	BB	0.5582	2.08003e4	560.43176	49.0807



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.063	VV	0.2803	1.80412e4	986.78424	98.6921
2	12.452	VV	0.4441	239.08499	6.79266	1.3079

References:

(1) Bui, T.; Syed, S.; Barbas C. F. III. *J. Am. Chem. Soc.* **2009**, *131*, 8758.