Supporting Information

Catalytic Asymmetric Hetero-Diels-Alder Reaction of Olefinic Azlactones and Isatins: Facile Access to Chiral Spirooxindole Dihydropyranones

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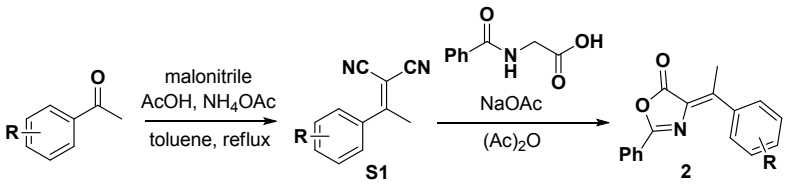
contents

1. General information

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400 MHz). The spectra were recorded in d_6-DMSO as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale (d_6-DMSO: δ_H = 2.50 ppm, δ_C = 39.52 ppm). 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}). 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. HRMS were performed on a Bruker Apex II mass instrument (ESI). Enantiomeric excess values were determined by HPLC with Chiralcel ID-H columns on Waters 1525/2998 eluting with DCM，MeOH and n-hexane.

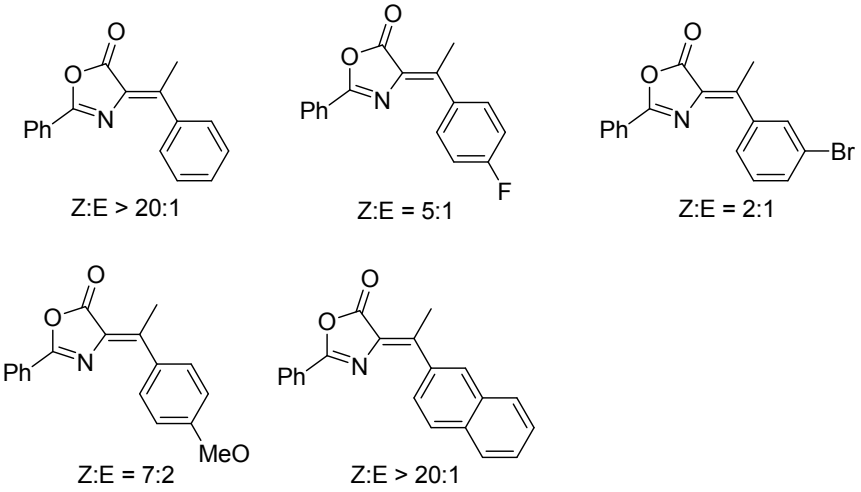
2. General procedure for the synthesis of olefinic azlactones[1]



Acetophenone (2.4 g, 20 mmol) and malonitrile (2.6 g, 40 mmol) were dissolved in

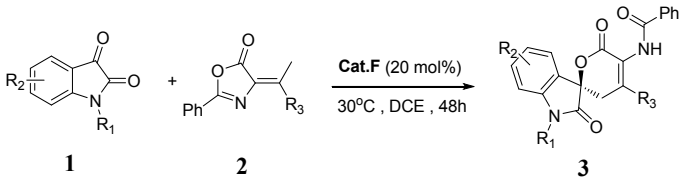
toluene, NH_4OAc (3.8 g, 50 mmol) dissolved in AcOH (5.5 mL, 100 mmol) was added. The flask was equipped with a Dean-Stark apparatus and the reaction mixture was heated to reflux and stirred for 2h. After cooling to room temperature, the reaction was diluted with diethyl ether (30 mL), washed with water (2×30 mL), brine (30 mL) and dried with $MgSO_4$. Evaporation of the solvents gave the crude product **S1** which was used without further purification.

A mixture of **S1** (10 mmol), hippuric acid (10 mmol), and acetic anhydride (20 mmol) was warmed for 3h. Excess acetic anhydride was decomposed with water and the solution was extracted with DCM for 3 times. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to give crude product which was purified by flash chromatography (silica gel, mixtures of petroleum/ethyl acetate) to afford the pure product **2**.



[1] R. M. A.-Motaleb, H. M. Bakeer, G. H. Tamam and W. A. A. Arafa, *J. Heterocyclic Chem.*, 2012, **49**, 1071.

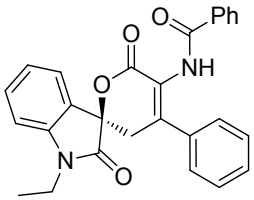
3. General procedure for the synthesis of product **3** and analytical data



1 **2** **3**

Isatins **1** (0.1 mmol) and olefinic azlactones **2** (0.1 mmol) was added to a solution of catalyst **F** (20 mol%) in dry DCE (1.0 mL). The mixture was stirred at 30°C for 48h, then the crude mixture was purified by flash chromatography (silica gel, mixtures of petroleum/ethyl acetate) to afford the pure product **3**.

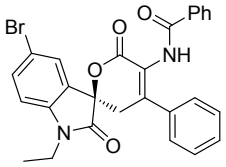
(R)-N-(1-ethyl-2,6'-dioxo-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3a)



3a

White solid; 82% yield; 98% ee; [α]20 D = 36.0 (*c* 0.25, CH_2Cl_2); mp 202−204℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 50:47.5:2.5), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 7.5 min, $t_{R(major)}$ = 11.8 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.93 (s, 1H), 8.29 (d, *J* = 7.2 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 2H), 7.43−7.60 (m, 6H), 7.35−7.41 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 3.71-3.79 (m, 3H), 3.13 (d, *J* = 18.0 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 171.0, 167.2, 160.9, 147.1, 142.0, 136.1, 133.2, 131.9, 131.1, 129.5, 128.4, 127.6, 127.5, 127.2, 124.6, 122.9, 122.1, 109.7, 79.1, 34.9, 34.6,12.3. IR (KBr, cm^{-1}): 3317, 2923, 2374, 1735, 1661, 1611, 1468, 1383, 1261, 1090, 748, 702, 583. HRMS (ESI) for $C_{27}H_{22}N_2O_4$ $[M+Na]^+$ calcd. 461.1472, found 461.1467.

(R)-N-(5-bromo-1-ethyl-2,6'-dioxo-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3b)

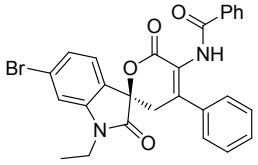


3b

White solid; 75% yield; 99% ee; [α]20 D = 80.0 (*c* 0.5, CH_2Cl_2); mp 204−207℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 60:38:2), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 13.2 min, $t_{R(major)}$ = 21.2 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.94 (s, 1H), 8.50 (s, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.49−7.65 (m, 5H), 7.36−7.44 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 1H), 3.69−3.79 (m, 3H), 3.25 (d, *J* = 18.0 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 170.6, 167.3, 160.7, 147.2, 141.4, 136.0, 133.7, 133.2, 131.9, 129.6, 129.5, 128.4, 128.4, 127.6, 127.5, 127.3, 122.1, 114.8, 111.7, 78.9, 34.7, 34.5, 12.1. IR (KBr, cm^{-1}): 3343, 2923, 2370, 1733, 1605, 1463, 1264, 1113, 741, 590. HRMS (ESI) for $C_{27}H_{21}BrN_2O_4$ $[M+Na]^+$ calcd. 539.0577, found

539.0568.

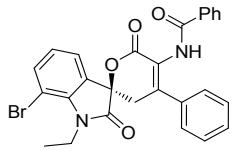
(R)-N-(6-bromo-1-ethyl-2,6'-dioxo-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3c)



3c

White solid; 83% yield; 99% ee; [α]20 D = 20.0 (*c* 0.5, CH_2Cl_2); mp 186−190℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 60: 38: 2), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 13.0 min, $t_{R(major)}$ = 22.2 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.93 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.48−7.60 (m, 6H), 3.74−3.80 (m, 2H), 3.70 (dd, *J* = 17.6 Hz, 2 Hz, 1H), 3.19 (d, *J* = 17.6 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 171.0, 167.2, 160.7, 147.1, 143.8, 136.0, 133.1, 131.9, 129.6, 128.4, 128.4, 127.6, 127.3, 126.7, 126.2, 125.4, 124.3, 122.1, 78.8, 34.8, 34.6, 12.2. IR (KBr, cm^{-1}): 3332, 2924, 2367, 1737, 1603, 1477, 1262, 1159, 1094, 738, 599. HRMS (ESI) for $C_{27}H_{21}BrN_2O_4$ $[M+Na]^+$ calcd. 539.0577, found 539.0569.

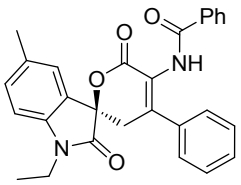
(R)-N-(7-bromo-1-ethyl-2,6'-dioxo-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3d)



3d

White solid; 79% yield; 75% ee; [α]20 D = 7.0 (*c* 1.0, CH_2Cl_2); mp 203−206℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 60: 38: 2), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 11.2 min, $t_{R(major)}$ = 25.2 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.92 (s, 1H), 8.33 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.49−7.59 (m, 5H), 7.33−7.41 (m, 3H), 7.08 (t, *J* = 7.6 Hz, 1H), 4.08−4.14 (m, 2H), 3.30 (d, *J* = 17.6 Hz, 1H), 1.27 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ172.6, 167.7, 161.1, 147.5, 140.0, 137.0, 136.4, 133.6, 132.3, 131.4, 130.0, 128.9, 128.8, 128.1, 127.8, 125.2, 124.4, 122.5, 102.6, 78.7, 36.8, 35.3, 14.9. IR (KBr, cm^{-1}): 3364, 2923, 2372, 1734, 1595, 1459, 1261, 1106, 794, 706. HRMS (ESI) for $C_{27}H_{21}BrN_2O_4$ $[M+Na]^+$ calcd. 539.0577, found 539.0566.

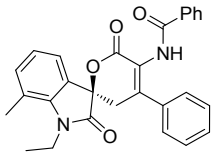
(R)-N-(1-ethyl-5-methyl-2,6'-dioxo-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3e)



3e

White solid; 75% yield; 99% ee; [α]20 D = 8.0 (*c* 0.5, CH_2Cl_2); mp190−194℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 60:38:2), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 12.0 min, $t_{R(major)}$ = 22.5 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.93 (s, 1H), 8.20 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.53−7.65 (m, 5H), 7.41−7.47 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8 Hz, 1H), 3.71-3.81 (m, 3H), 3.17 (d, *J* = 17.6 Hz, 1H), 2.35 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 171.4, 167.7, 161.5, 147.8, 140.0, 136.6, 133.8, 132.6, 132.3, 131.5, 130.0, 128.9, 128.1, 128.0, 127.7, 125.9, 122.6, 109.9, 79.7, 21.1, 12.8. IR (KBr, cm^{-1}):3299, 2961, 2925, 2371, 1728, 1663, 1494, 1264, 1088, 1026, 804, 700, 584. HRMS (ESI) for $C_{28}H_{24}N_2O_4$ $[M+Na]^+$ calcd. 475.1628, found 475.1624.

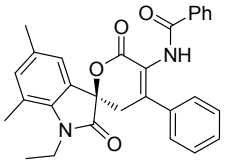
(R)-N-(1-ethyl-7-methyl-2,6'-dioxo-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3f)



3f

White solid; 82% yield; 94% ee; [α]20 D = 10.0 (*c* 0.5, CH_2Cl_2); mp 208−212℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 60:38:2), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 7.5 min, $t_{R(major)}$ = 11.8 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.90 (s, 1H), 8.14 (d, *J* = 7.2 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.47−7.59 (m, 5H), 7.24−7.40 (m, 3H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 3.91−3.96 (m, 2H), 3.68 (d, *J* = 17.6 Hz, 1H), 3.11 (d, J = 17.6 Hz, 1H), 2.52 (s, 3H), 1.22 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 172.7, 167.6, 161.4, 147.4, 140.3, 136.6, 135.3, 133.7, 132.3, 130.3, 130.0, 128.9, 128.9, 128.1, 127.7, 123.5, 122.9, 122.5, 122.7, 78.9, 37.0, 35.7, 18.8, 14.8. IR (KBr, cm^{-1}): 3306, 2921, 2364, 1733, 1666, 1463, 1262, 1098, 797, 742, 591. HRMS (ESI) for $C_{28}H_{24}N_2O_4$ $[M+Na]^+$ calcd. 475.1628, found 475.1623.

(R)-N-(1-ethyl-5,7-dimethyl-2,6'-dioxo-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3g)

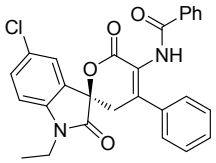


3g

White solid; 77% yield; 99% ee; [α]20 D = 15.0 (*c* 1.00, CH_2Cl_2); mp 218−220℃;

The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 60:38:2), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 10.9 min, $t_{R(major)}$ = 20.0 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.85 (s, 1H), 8.00 (s, 1H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.47−7.59 (m, 5H), 7.33−7.41 (m, 3H), 7.04 (s, 1H), 3.88−3.94 (m, 2H), 3.67 (d, *J* = 1.6 Hz, 2H), 3.62 (dd, *J* = 17.6 1.6 Hz, 1H), 3.11 (d, *J* = 17.6 Hz, 1H), 2.47 (s, 3H), 2.26 (s, 3H), 1.211 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 172.6, 167.6, 161.5, 147.6, 137.7, 136.7, 135.4, 133.8, 132.6, 132.2, 129.9, 128.9, 128.8, 128.1, 127.7, 123.7, 122.5, 120.3, 79.0, 36.9, 35.8, 20.8, 18.6, 14.7. IR (KBr, cm^{-1}): 3309, 2924, 1733, 1711, 1661, 1512, 1478, 1380, 1314, 1265, 1185, 1098, 869, 745, 701, 583. HRMS (ESI) for $C_{29}H_{26}N_2O_4$ $[M+Na]^+$ calcd. 489.1785, found 489.1782.

(R)-N-(5-chloro-1-ethyl-2,6'-dioxo-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3h)

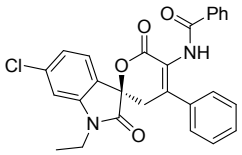


3h

White solid; 75% yield; 95% ee; [α]20 D = 15.0 (*c* 1.00, CH_2Cl_2); mp 208−210℃;

The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 60:38:2), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 10.7 min, $t_{R(major)}$ = 24.8 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.93 (s, 1H), 8.39 (s, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.48−7.60 (m, 6H), 7.37−7.44 (m, 3H), 7.24 (d, *J* = 8.4 Hz, 1H), 3.68−3.79 (m, 2H), 3.24 (d, *J* = 18.0 Hz, 2H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 170.6, 167.4, 160.7, 147.3, 141.0, 135.9, 135.7, 133.2, 132.8, 131.8, 130.8, 129.6, 129.2, 128.4, 128.4, 127.6, 127.3, 127.1, 124.9, 122.0, 111.3, 78.9, 34.7, 34.5, 12.1. IR (KBr, cm^{-1}): 3317, 2925, 1732, 1662, 1610, 1481, 1360, 1263, 1095, 800, 737, 548. HRMS (ESI) for $C_{27}H_{21}ClN_2O_4$ $[M+Na]^+$ calcd. 495.1062, found 495.1076.

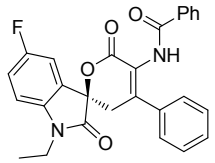
(R)-N-(6-chloro-1-ethyl-2,6'-dioxo-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3i)



3i

White solid; 73% yield; >99% ee; [α]20 D =38 (*c* 0.5, CH_2Cl_2); mp 188−190℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 50:47.5:2.5), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 11.7 min, $t_{R(major)}$ = 19.9 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.95 (s, 1H), 8.28 (d, *J* = 8.0, 1H), 7.89 (d, *J* = 7.2, 2H), 7.48−7.60 (m, 5H), 7.36−7.41 (m, 4H), 7.20 (dd, *J* = 8.2 Hz, 1.2 Hz, 1H), 3.69−3.80 (m, 3H), 3.19 (d, *J* = 18.0 Hz, 1H), 1.19 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 171.5, 167.7, 161.1, 147.6, 144.3, 136.4, 136.2, 133.6, 132.4, 130.0, 128.9, 128.9, 128.1, 127.7, 126.7, 126.4, 123.0, 122.6, 110.7, 79.2, 35.3, 35.2, 12.7. IR (KBr, cm^{-1}): 3275, 2961, 2925, 1731, 1608, 1485, 1356, 1262, 1075, 799, 702, 603. HRMS (ESI) for $C_{27}H_{21}ClN_2O_4$ $[M+Na]^+$ calcd. 495.1062, found 495.1077.

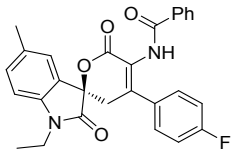
(R)-N-(1-ethyl-5-fluoro-2,6'-dioxo-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3j)



3j

White solid; 63% yield; 95% ee; [α]20 D = 10.0 (*c* 1.0, CH_2Cl_2); mp 162−168℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 50:47.5:2.5), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 13.3 min, $t_{R(major)}$ = 23.2 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.95 (s, 1H), 8.27 (d, *J* = 6.8 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.48−7.60 (m, 5H), 7.22−7.25 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 3.71−3.79 (m, 3H), 3.19 (d, *J* = 18.0 Hz, 1H), 1.19 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 171.2, 168.0, 161.2, 161.1, 160.1, 157.7, 147.9, 138.8, 136.4, 133.5, 132.4, 130.1, 129.3, 128.9, 128.1, 127.7, 122.5, 117.9, 117.6, 113.4, 113.1, 111.4, 111.3, 79.6, 35.2, 35.1, 12.7. IR (KBr, cm^{-1}): 3314, 2924, 1735, 1461, 1263, 1094, 740, 582. HRMS (ESI) for $C_{27}H_{21}FN_2O_4$ $[M+Na]^+$ calcd. 479.1378, found 479.1372.

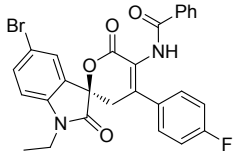
(R)-N-(1-ethyl-4'-(4-fluorophenyl)-5-methyl-2,6'-dioxo-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3k)



3k

White solid; 82% yield; >99% ee; [α]20 D = -10 (*c* 1.0, CH_2Cl_2); mp 218−220℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 50:47.5:2.5), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 11.8 min, $t_{R(major)}$ = 19.8 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.90 (s, 1H), 8.11 (s, 1H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.57−7.62 (m, 3H), 7.51 (t, J = 7.6, 2H), 7.25−7.29 (m, 3H), 7. 09 (d, *J* = 8.0 Hz, 1H), 3.67−3.76 (m, 3H), 3.15 (d, *J* = 18.0 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 171.3, 167.6, 161.7, 161.5, 146.9, 140.0, 133.7, 133.0, 133.0, 132.6, 132.3, 131.6, 130.3, 130.2, 128.9, 128.1, 127.9, 125.9, 122.6, 116.0, 115.8, 109.9, 79.6, 35.4, 35.0, 21.1, 12.8. IR (KBr, cm^{-1}): 3311, 2924, 1727, 1602, 1509, 1263, 1093, 1021, 805, 553. HRMS (ESI) for $C_{28}H_{23}FN_2O_4$ $[M+Na]^+$ calcd. 493.1534, found 493.1531.

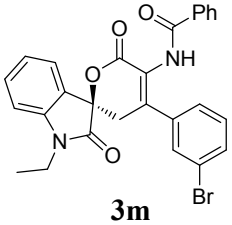
(R)-N-(5-bromo-1-ethyl-4'-(4-fluorophenyl)-2,6'-dioxo-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3l)



3l

White solid; 75% yield; 85% ee; [α]20 D = 9.0 (*c* 1.0, CH_2Cl_2); mp 212−214℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 60: 38:2), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 14.3 min, $t_{R(major)}$ = 22.9 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.93 (s, 1H), 8.45 (d, *J* = 1.6 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.70 (d, J = 4.0 Hz, 1H), 7.57−7.62 (m, 3H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 8.8 Hz, 2H), 7.19 (d, J = 8.4 Hz, 1H), 3.67−3.78 (m, 3H), 3. 27 (d, *J* = 18.0 Hz, 1H), 1.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 171.0, 167.8, 164.2, 161.8, 161.1, 146.7, 141.9, 134.2, 133.6, 132.8, 132.8, 132.4, 130.3, 130.2, 130.0, 128.9, 128.1, 128.0, 122.5, 116.1, 115.9, 115.3, 112.2, 79.3, 35.2, 34.9, 12.6. IR (KBr ,cm^{-1}): 3271, 2921, 1725, 1603, 1478, 1346, 1261, 1095, 1022, 802, 709, 575. HRMS (ESI) for $C_{27}H_{20}BrFN_2O_4$ $[M+Na]^+$ calcd. 557.0483, found 557.0481.

(R)-N-(4'-(3-bromophenyl)-1-ethyl-2,6'-dioxo-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3m)

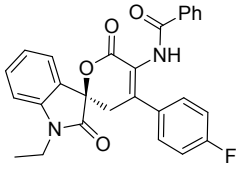


3m

White solid; 73% yield; 97% ee; [α]20 D = -15 (*c* 1.0, CH_2Cl_2); mp 200−204℃; The

enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 60:38:2), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 10.5 min, $t_{R(major)}$ = 17.7 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.94 (s, 1H), 8.23 (d, *J* = 7.3 Hz, 1H), 7.89 (d, *J* = 7.3 Hz, 2H), 7.57−7.63 (m, 2H), 7.33−7.53 (m, 6H), 7.20 (d, J = 7.9 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 3.71−3.80 (m, 3H), 3.23 (d, *J* = 18.0 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 170.9, 167.2, 160.7, 145.8, 142.1, 138.4, 138.1, 133.2, 132.2, 132.0, 131.2, 130.5, 130.3, 129.9, 129.3, 128.5, 127.6, 127.4, 127.2, 126.3, 126.0, 124.6, 123.0, 122.8, 121.7, 109.7, 79.2, 34.6, 12.3. IR (KBr, cm^{-1}): 3308, 2924, 1734, 1611, 1466, 1377, 1263, 1099, 741, 593. HRMS (ESI) for $C_{27}H_{21}BrN_2O_4$ $[M+Na]^+$ calcd. 539.0577, found 539.0577.

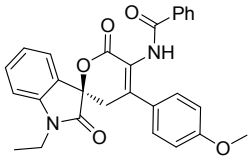
(R)-N-(1-ethyl-4'-(4-fluorophenyl)-2,6'-dioxo-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3n)



3n

White solid; 88% yield; 94% ee; [α]20 D = 8.0 (*c* 1.0, CH_2Cl_2); mp 195−198℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 60:38:2), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 12.2 min, $t_{R(major)}$ = 20.1 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.93 (s, 1H), 8.27 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 2H), 7.56−7.62 (m, 3H), 7.43−7.52 (m, 3H), 7.19−7.28 (m, 3H), 7.13 (t, *J* = 7.6 Hz, 1H), 3.70−3.79 (m, 3H), 3.16 (d, *J* = 18.0 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 171.0, 167.2, 163.7, 161.3, 160.9, 146.2, 142.1, 133.2, 132.5, 132.5, 131.9, 131.1, 129.8, 129.8, 128.5, 127.7, 127.5, 124.6, 123.0, 122.2, 115.6, 115.4, 109.7, 79.1, 34.9, 34.6, 12.3. IR (KBr, cm^{-1}): 3308, 2925, 1732, 1466, 1376, 1263, 1161, 1099, 1015, 840, 742, 572, 543. HRMS (ESI) for $C_{27}H_{21}FN_2O_4$ $[M+Na]^+$ calcd. 479.1378, found 479.1375.

(R)-N-(1-ethyl-4'-(4-methoxyphenyl)-2,6'-dioxo-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3o)

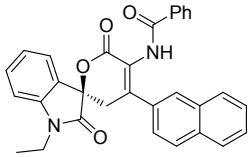


3o

White solid; 78% yield; 73% ee; [α]20 D = 13.0 (*c*1.0, CH_2Cl_2); mp 207−210℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 60:38:2), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 12.2 min, $t_{R(major)}$ = 27.7 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.89 (s, 1H), 8.28 (d, *J* = 6.8 Hz, 1H),

7.94 (d, *J* = 7.6 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 3.65−3.79 (m, 6H), 3.11 (d, *J* = 17.6 Hz, 1H), 1.21 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 171.0, 167.2, 161.1, 160.3, 146.6, 142.0, 133.3, 131.8, 131.0, 129.3, 128.4, 128.1, 127.7, 127.6, 124.7, 122.9, 120.9, 113.8, 109.6, 79.0, 55.2, 34.9, 34.6, 12.3. IR (KBr, cm^{-1}): 3313, 2924, 1729, 1606, 1466, 1358, 1260, 1108, 1023, 800, 738, 707, 575. HRMS (ESI) for $C_{28}H_{24}N_2O_4$ [M+Na]$^+$ calcd. 491.1577, found 491.1573.

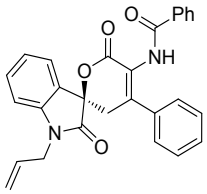
(R)-N-(1-ethyl-4'-(naphthalen-2-yl)-2,6'-dioxo-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3p)



3p

White solid; 76% yield; 76% ee; [α]20 D =8.0 (*c* 0.25, CH_2Cl_2); mp 203−206℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 60:38:2), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 14.2 min, $t_{R(major)}$ = 22.6 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.96 (s, 1H), 8.30 (d, *J* = 7.6 Hz, 1H), 8.12 (s, 1H), 7.85−7.96 (m, 5H), 7.67 (d, J = 8.4 Hz, 1H), 7.44−7.54 (m, 6H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 3.77−3.3 (m, 3H), 3.28 (s, 1H), 1.21 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 171.0, 167.1, 161.0, 146.8, 142.1, 133.6, 133.3, 133.0, 132.4, 131.9, 131.1, 129.2, 128.5, 128.4, 128.3, 127.7, 127.6, 127.5, 127.5, 127.3, 127.3, 126.7, 124.7, 124.6, 123.0, 122.3, 109.7, 79.2, 35.0, 34.6, 12.3. IR (KBr, cm^{-1}): 3305, 2922, 1727, 1612, 1376, 1263, 1088, 800, 755, 706, 593. HRMS (ESI) for $C_{31}H_{24}N_2O_4$ [M+Na]$^+$ calcd. 511.1628, found 511.1626.

(R)-N-(1-allyl-2,6'-dioxo-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3q)

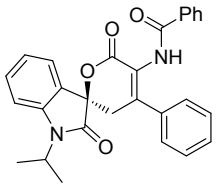


3q

White solid; 77% yield; 99% ee; [α]20 D = 22.0 (*c* 1.0, CH_2Cl_2); mp 188−190℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 60:38:2), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 12.8 min, $t_{R(major)}$ = 26.8 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.94 (s, 1H), 8.30 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.48−7.60 (m, 5H), 7.34−7.45 (m, 4H), 7.08−7.15 (m, 2H), 5.84−5.93 (m, 1H), 4.19−5.24 (m, 2H), 4.38 (d, *J* = 4.4 Hz, 2H), 3.76 (d, *J* = 17.6 Hz, 1H), 3.18 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 171.6, 167.7,

161.3, 147.6, 142.6, 136.6, 133.7, 132.3, 131.8, 131.5, 130.0, 128.9, 128.1, 127.8, 127.7, 125.0, 123.6, 122.6, 117.6, 110.7, 79.6, 42.3, 35.4. IR (KBr, cm^{-1}): 3315, 2924, 1730, 1662, 1612, 1468, 1361, 1262, 1186, 1093, 757, 698, 588. HRMS (ESI) for $C_{28}H_{22}N_2O_4$ $[M+Na]^+$ calcd. 473.1472, found 473.1467.

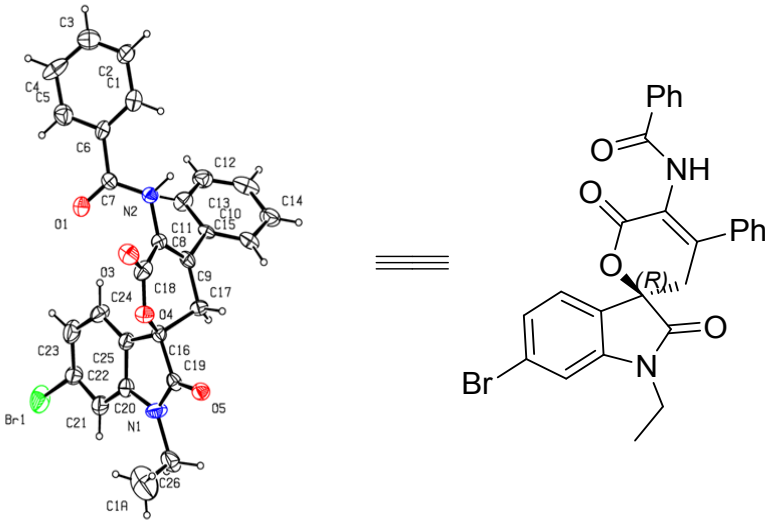
(R)-N-(1-isopropyl-2,6'-dioxo-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-5'-yl)benzamide (3r).



3r

White solid; 82% yield; 93% ee; [α]20 D = 38.0 (*c* 1.0, CH_2Cl_2); mp 192−196℃; The enantiomeric excess was determined by HPLC with an ID-H column. (*n*-hexane: DCM: MeOH = 60:38:2), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 10.2 min, $t_{R(major)}$ = 17.2 min. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.89 (s, 1H), 8.28 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 2H),7.58(t, *J* = 7.6 Hz, 1H), 7.47−7.53 (m, 4H), 7.35−7.44 (m, 4H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 4.48−4.55 (m, 1H), 3.69 (dd, *J* = 17.6 Hz, 1.6 Hz, 2H), 3.13 (d, *J* = 17.6 Hz, 1H), 1.45 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 171.1, 167.2, 160.9, 147.1, 141.8, 136.2, 133.2, 131.9, 131.0, 129.5, 128.4, 127.6, 127.3, 124.7, 122.6, 122.1, 110.7, 79.2, 44.0, 35.1, 18.86, 18.83. IR (KBr, cm^{-1}): 3302, 2921, 1734, 1662, 1476, 1262, 1190, 1157, 1084, 740, 700, 590. HRMS (ESI) for $C_{28}H_{24}N_2O_4$ $[M+Na]^+$ calcd. 475.1628, found 475.1624.

4. X-ray crystallographic data of compound **3c**.



Datablock:

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alpha=90 beta=90 gamma=90
Temperature: 293 K
Crystal system orthorhombic

	Calculated	Reported
Volume	**2817.2(3)**	**2817.2(3)**
Space group	**P 21 21 21**	**P 21 21 21**
Hall group	**P 2ac 2ab**	**P 2ac 2ab**

Moiety formula	**C27 H21 Br N2 O4**	**C27 H21 Br N2 O4**
Sum formula	**C27 H21 Br N2 O4**	**C27 H21 Br N2 O4**
Mr	**517.36**	**517.37**
Dx,g cm^{-3}	**1.220**	**1.220**
Z	**4**	**4**
Mu (mm-1)	**1.490**	**1.490**
F000	**1056.0**	**1056.0**
F000'	**1055.29**	
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Nref	**5555[3154]**	**5465**
Tmin,Tmax	**0.627,0.640**	**0.127,1.000**
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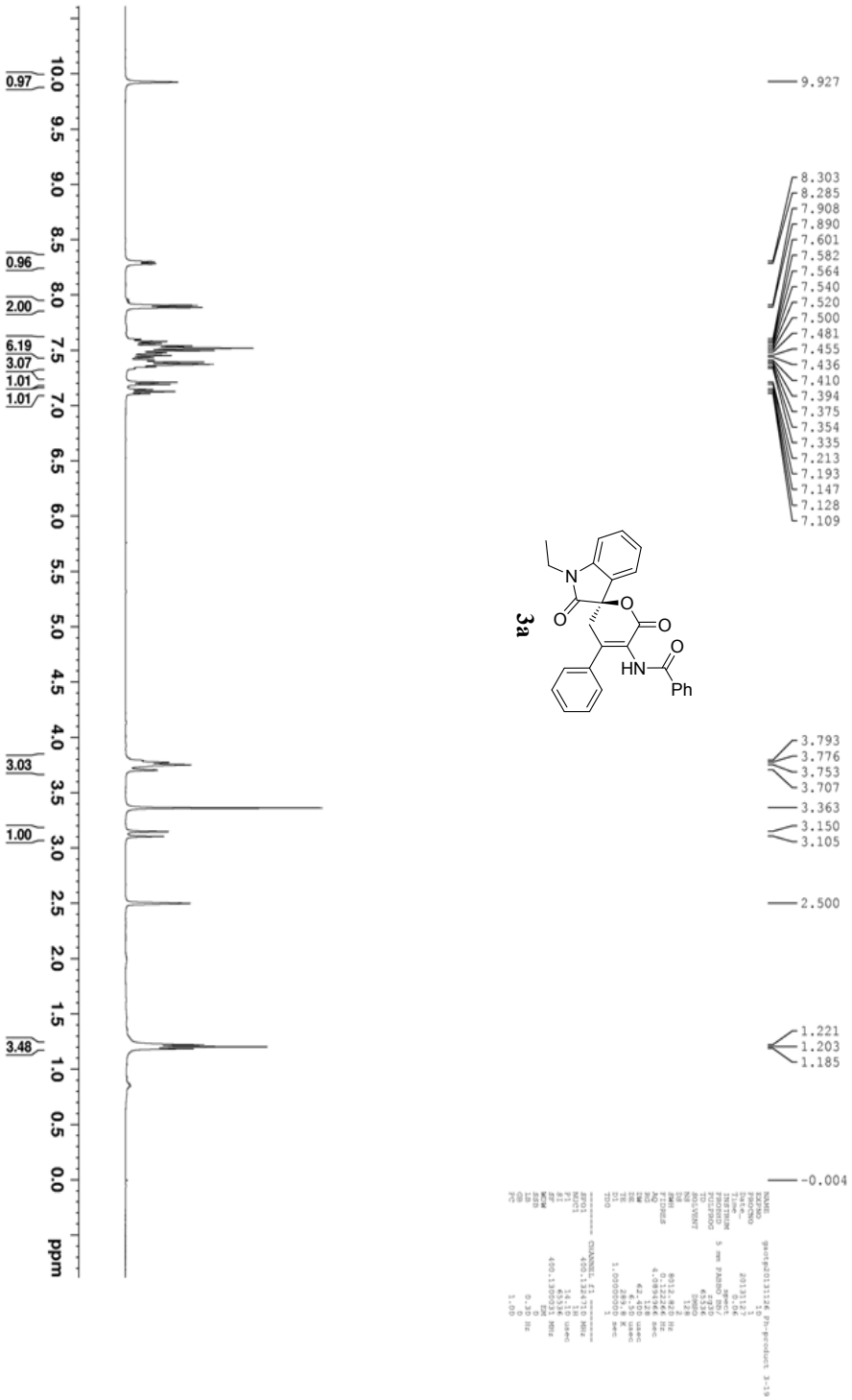
Correction method= MULTI-SCAN

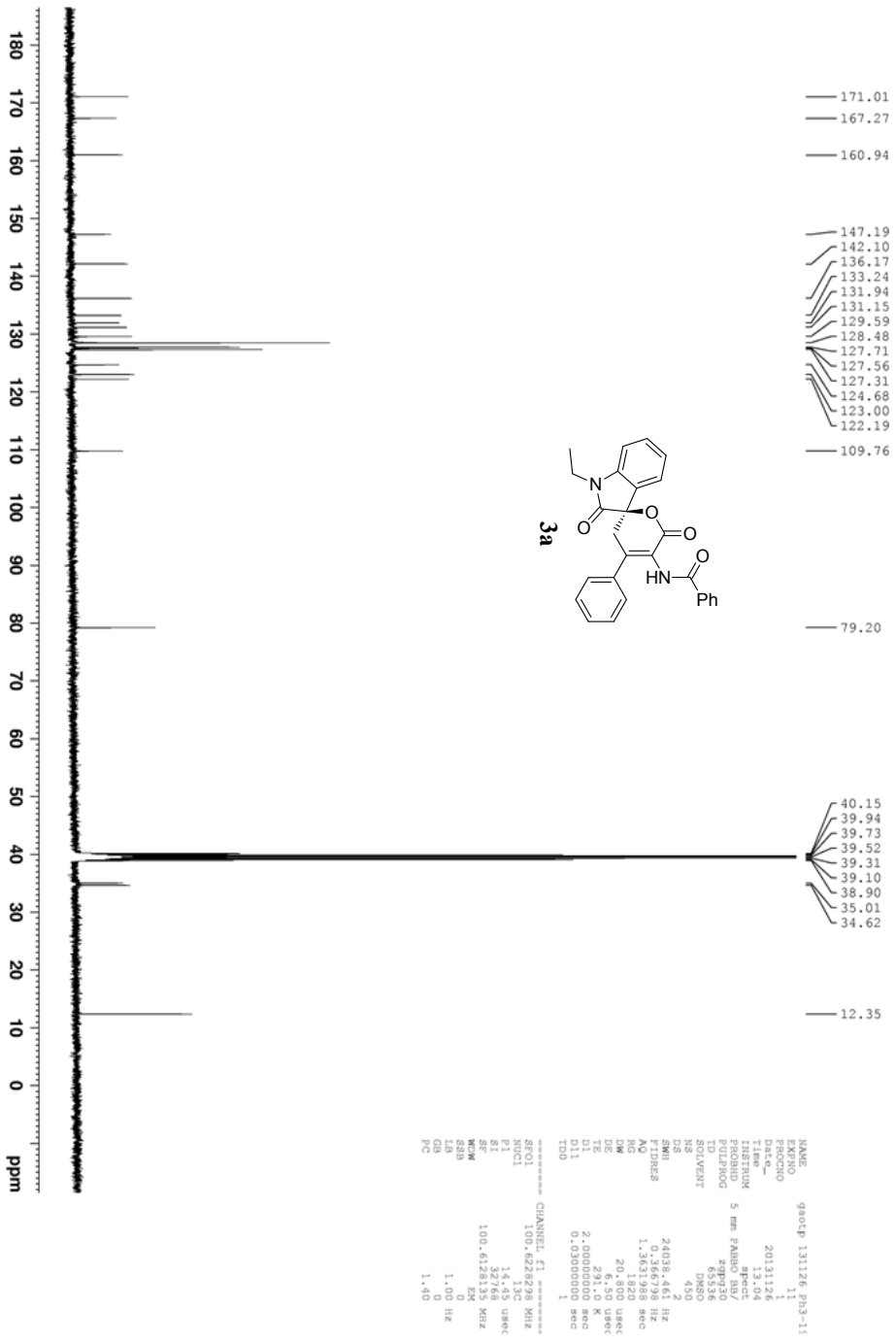
Data completeness= 1.73/0.98 **Theta(max)= 25.994**

R(reflections)= 0.0668(2028) **wR2(reflections)= 0.1732(5465)**

S = 0.796 **Npar= Npar = 308**

5. NMR spectra of compound **3**.

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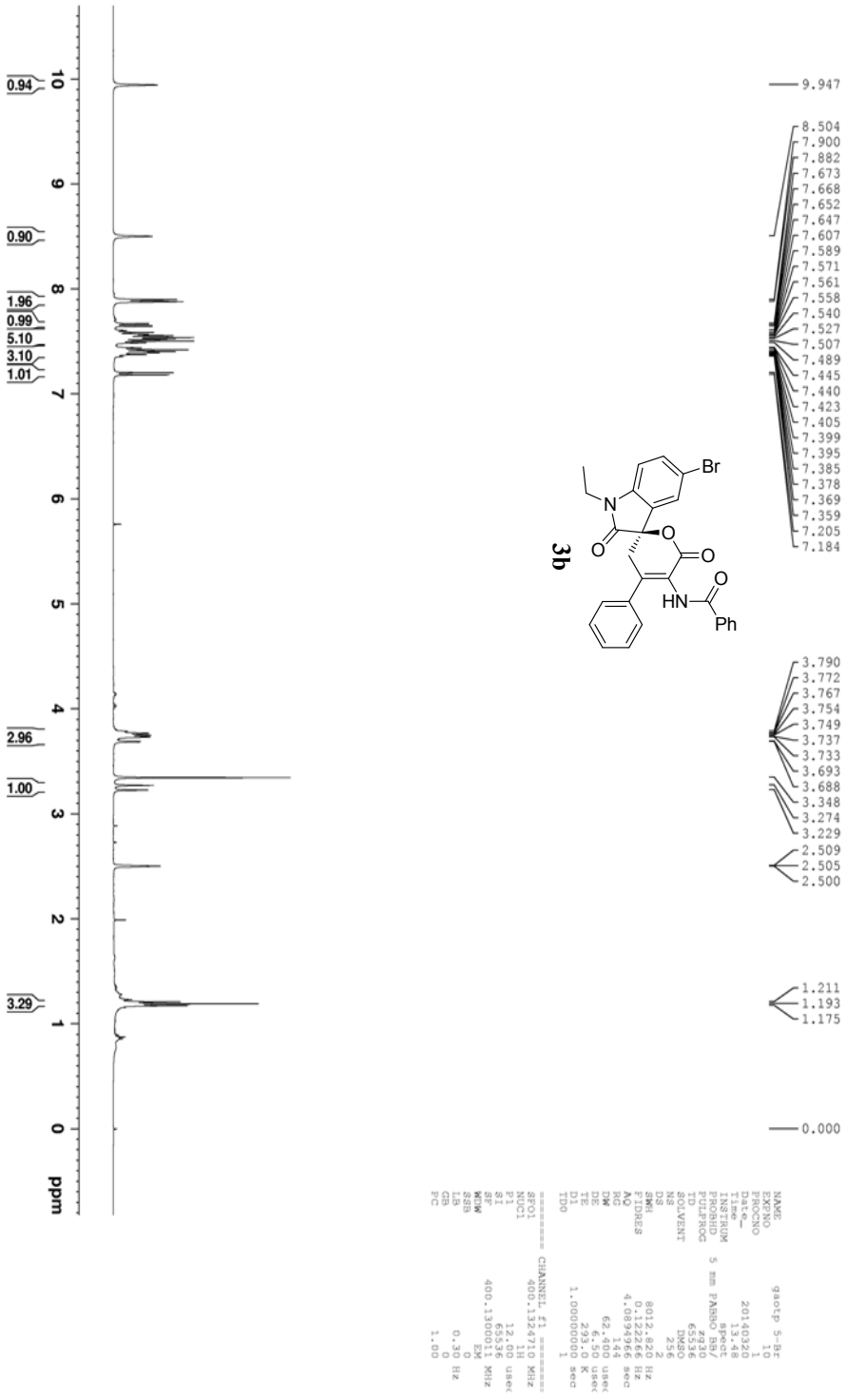
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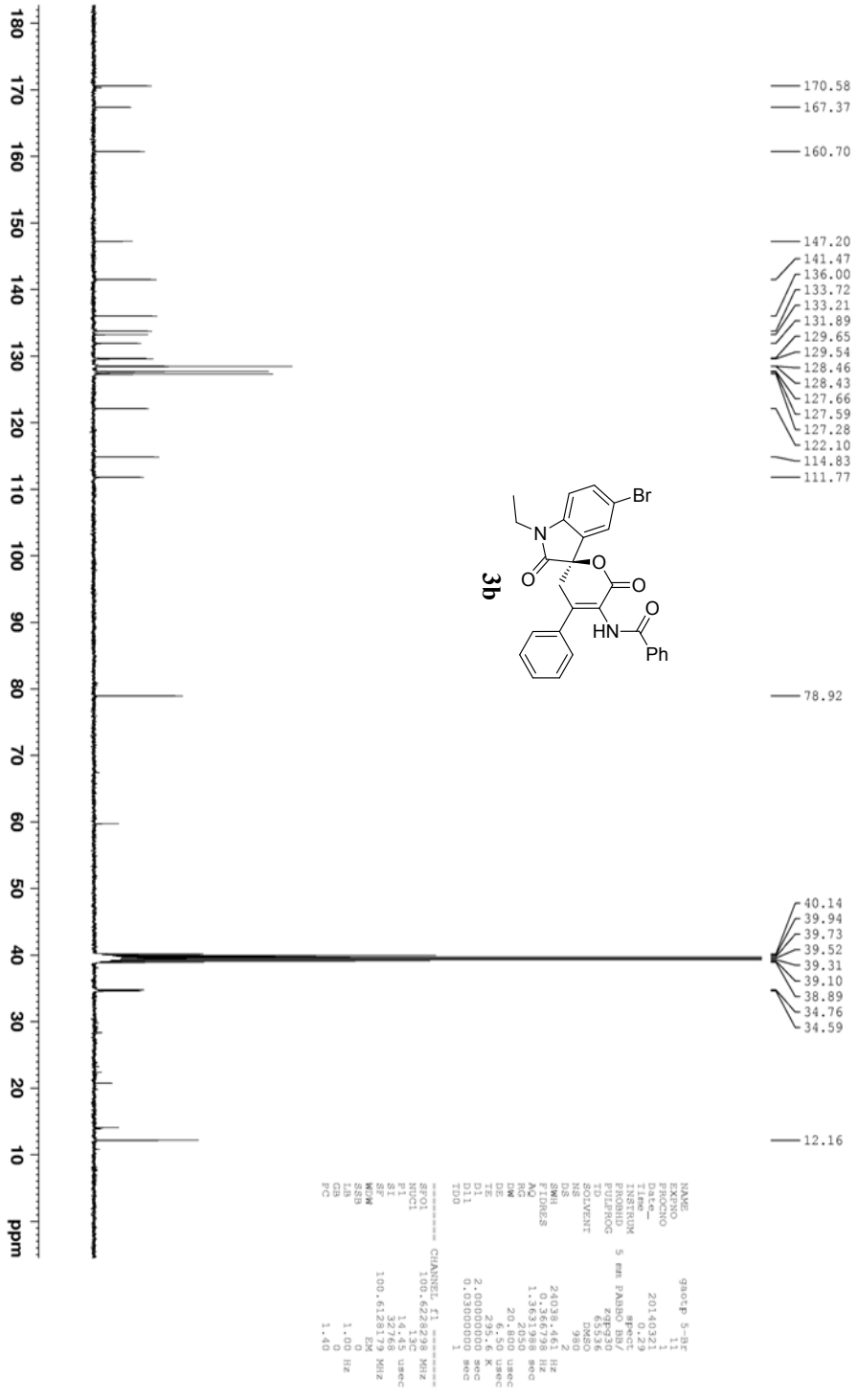
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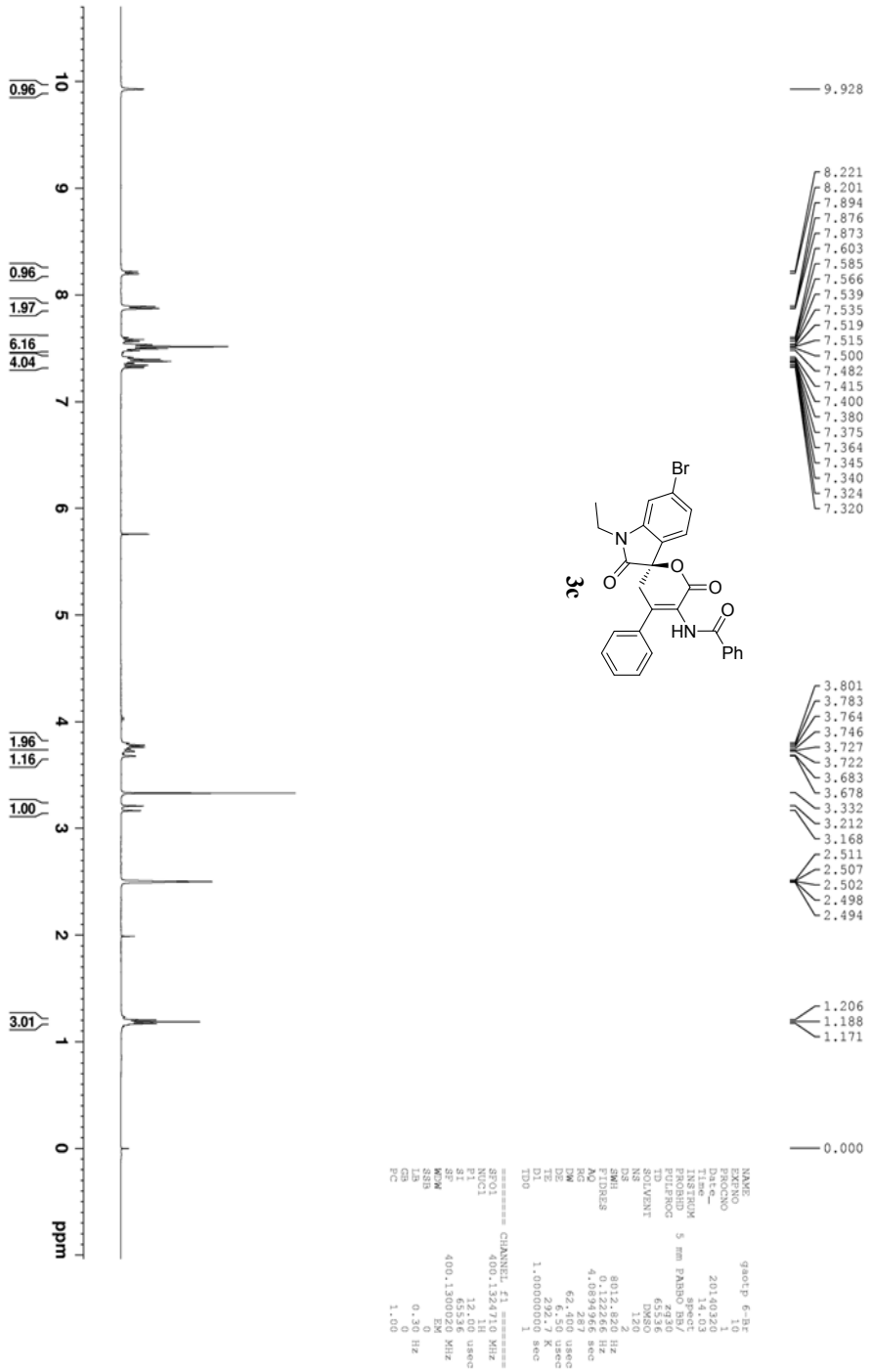
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7.539
7.535
7.519
7.515
7.500
7.482
7.415
7.400
7.380
7.375
7.364
7.345
7.340
7.324
7.320
3.801
3.783
3.764
3.746
3.727
3.722
3.683
3.678
3.332
3.212
3.168
2.511
2.507
2.502
2.498
2.494
1.206
1.188
1.171
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N
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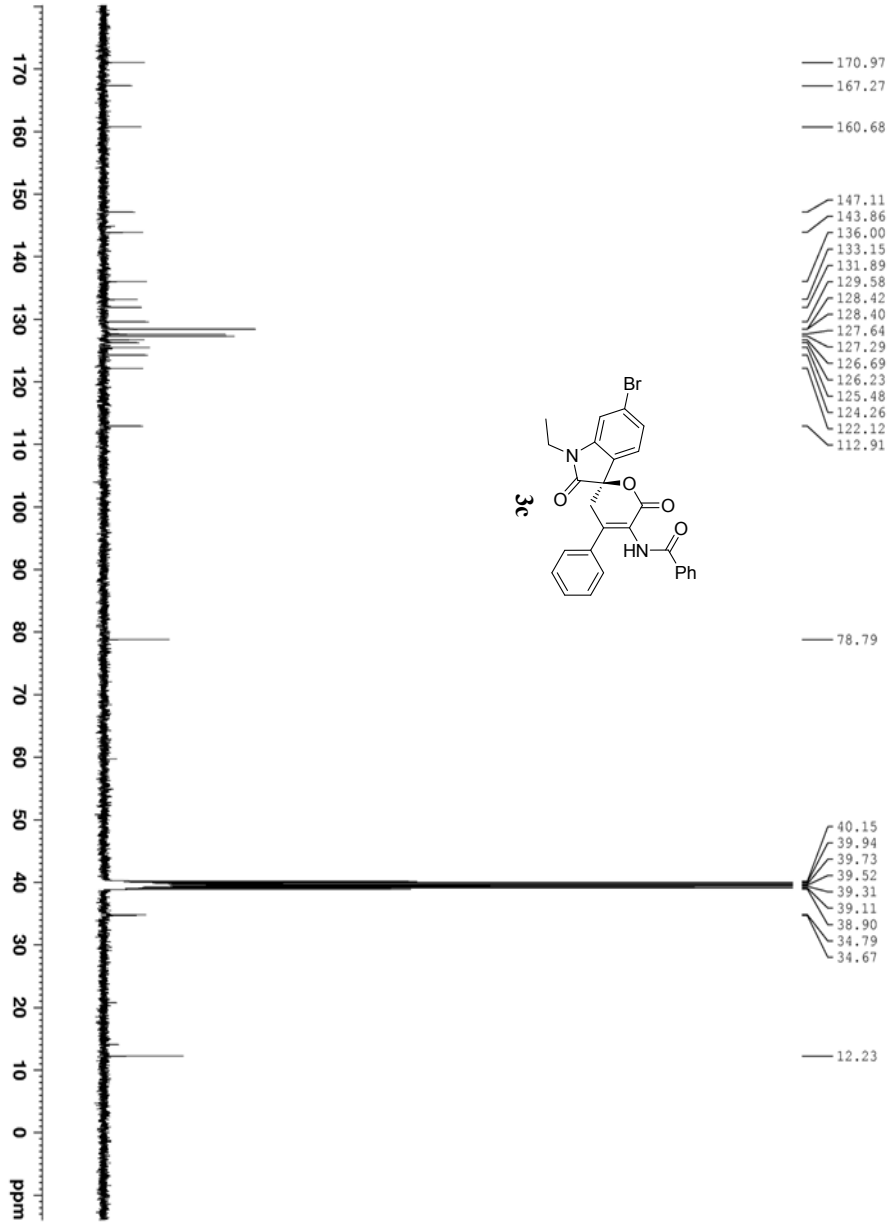
O
O
HN
O
Ph
3c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167.27
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147.11
143.86
136.00
133.15
131.89
129.58
128.42
128.40
127.64
127.29
126.69
126.23
125.48
124.26
122.12
112.91
78.79
40.15
39.94
39.73
39.52
39.31
39.11
38.90
34.79
34.67
12.23
Br
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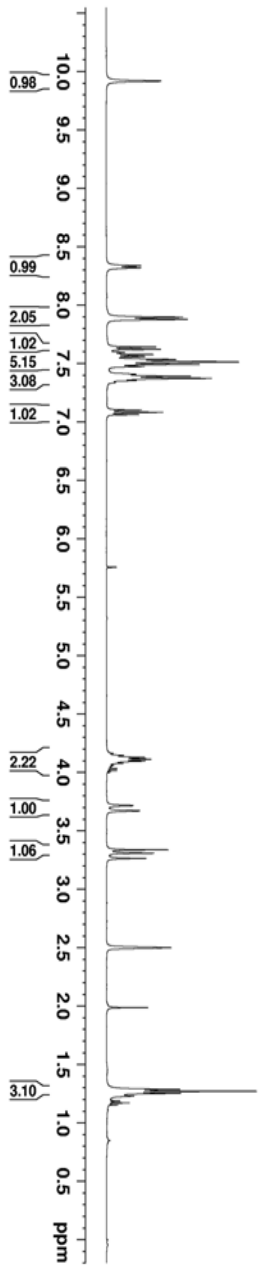
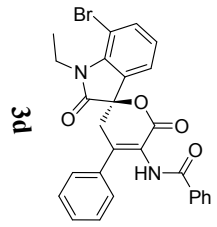
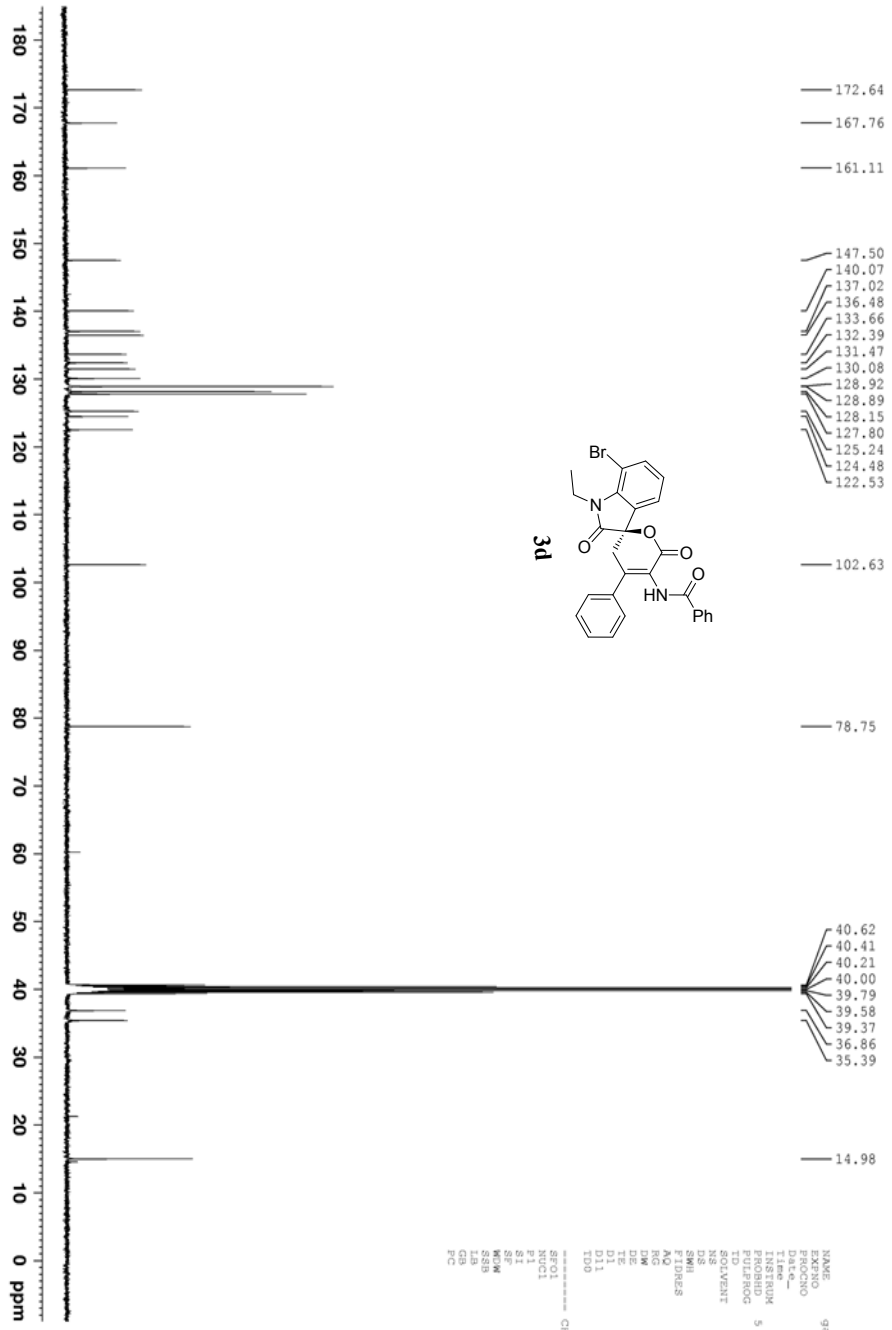
O
O
O
O
HN
Ph
3c
ppm

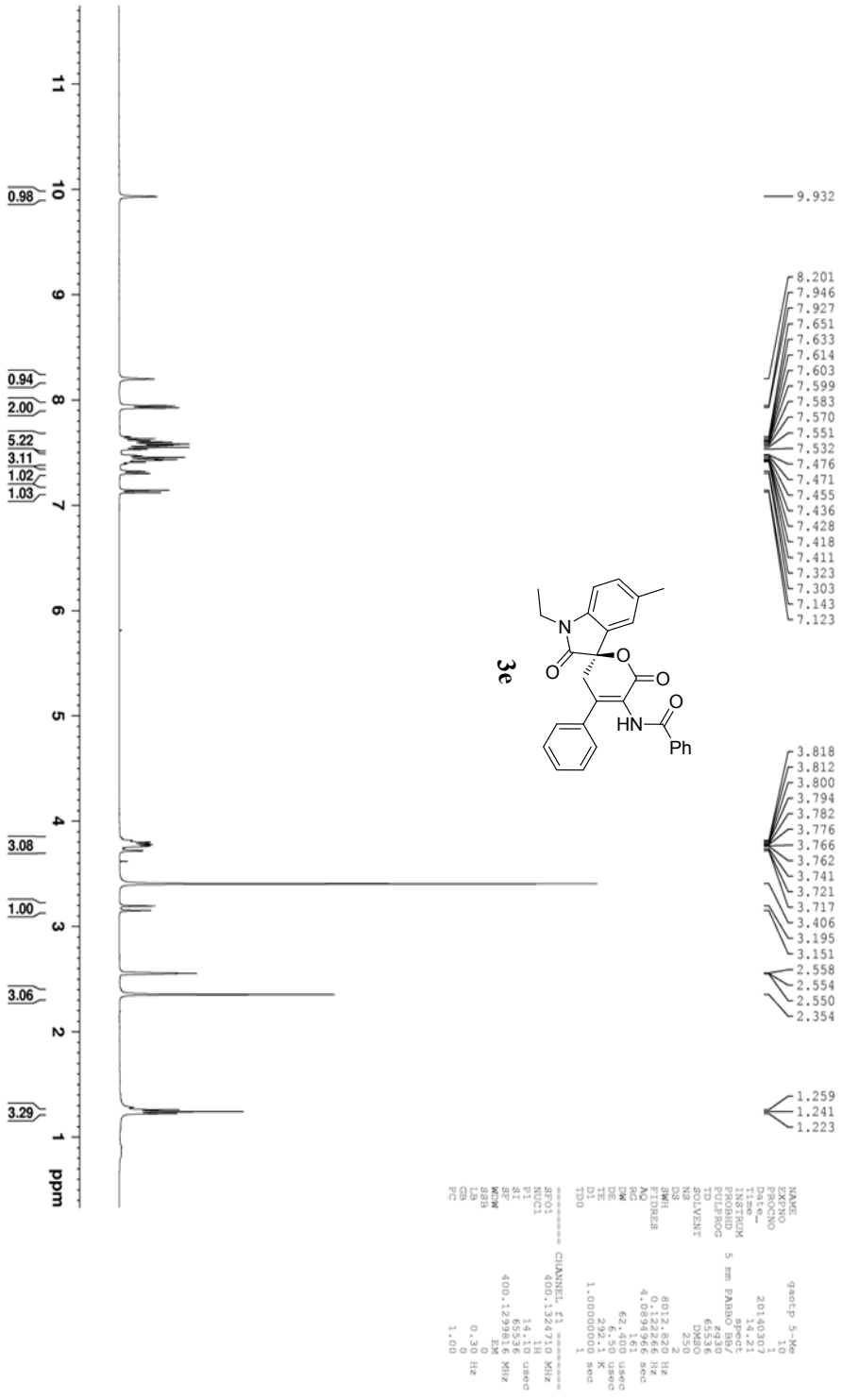




3d

NAME gaccp 7-Br
EXPNO 10
PROCNO 1
Date_ 20140311
Time 22:01
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 256
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894144 sec
RG 144
DW 62.400 usec
DE 6.50 usec
TE 293.8 K
D1 1.00000001 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUCL1 1H
P1 14.10 usec
SI 65536
SF 400.1300031 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


3d
Br
N
O
O
O
O
HN
Ph
172.64
167.76
161.11
147.50
140.07
137.02
136.48
133.66
132.39
131.47
130.08
128.92
128.89
128.15
127.80
125.24
124.48
122.53
102.63
78.75
40.62
40.41
40.21
40.00
39.79
39.58
39.37
36.86
35.39
14.98
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


3e
N
O
O
O
HN
O
Ph
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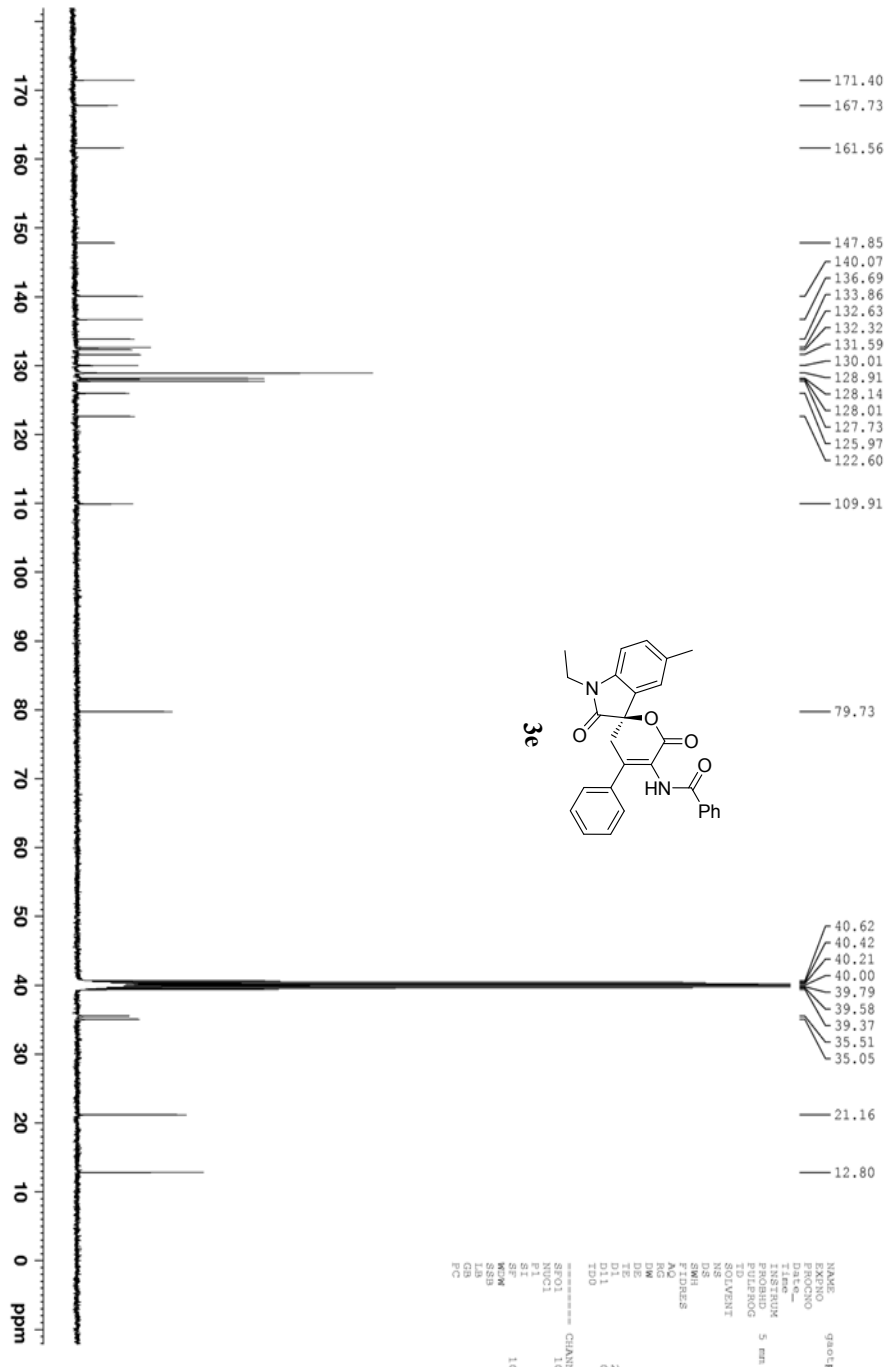
8.201
7.946
7.927
7.651
7.633
7.614
7.603
7.599
7.583
7.570
7.551
7.532
7.476
7.471
7.455
7.436
7.428
7.418
7.411
7.323
7.303
7.143
7.123
3.818
3.812
3.800
3.794
3.782
3.776
3.766
3.762
3.741
3.721
3.717
3.406
3.195
3.151
2.558
2.554
2.550
2.354
1.259
1.241
1.223
0.98
0.94
2.00
5.22
3.11
1.02
1.03
3.08
1.00
3.06
3.29
ppm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161.56
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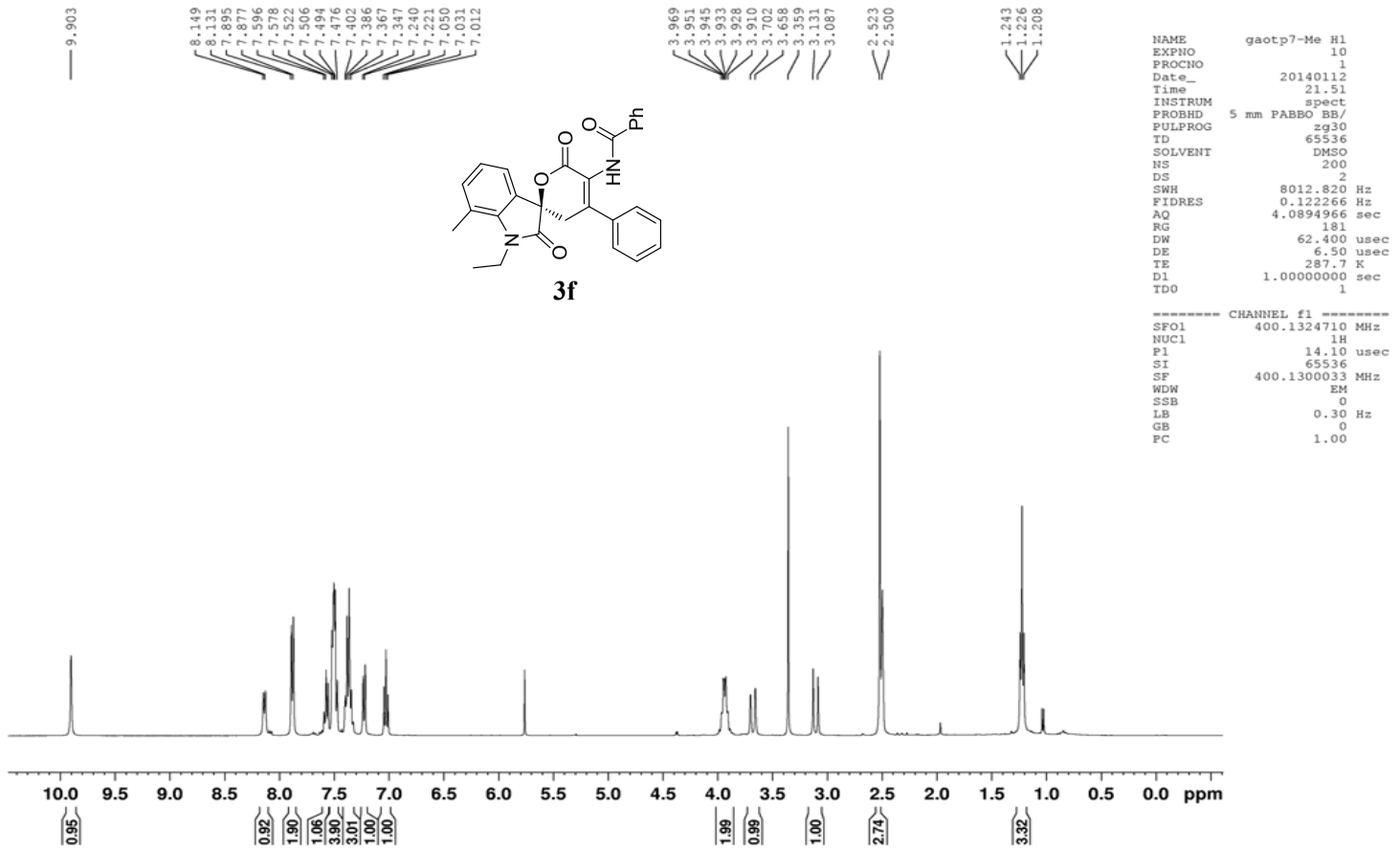
140.07
136.69
133.86
132.63
132.32
131.59
130.01
128.91
128.14
128.01
127.73
125.97
122.60
109.91
79.73
40.62
40.42
40.21
40.00
39.79
39.58
39.37
35.51
35.05
21.16
12.80
3e
N
O
O
O
O
HN
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.895
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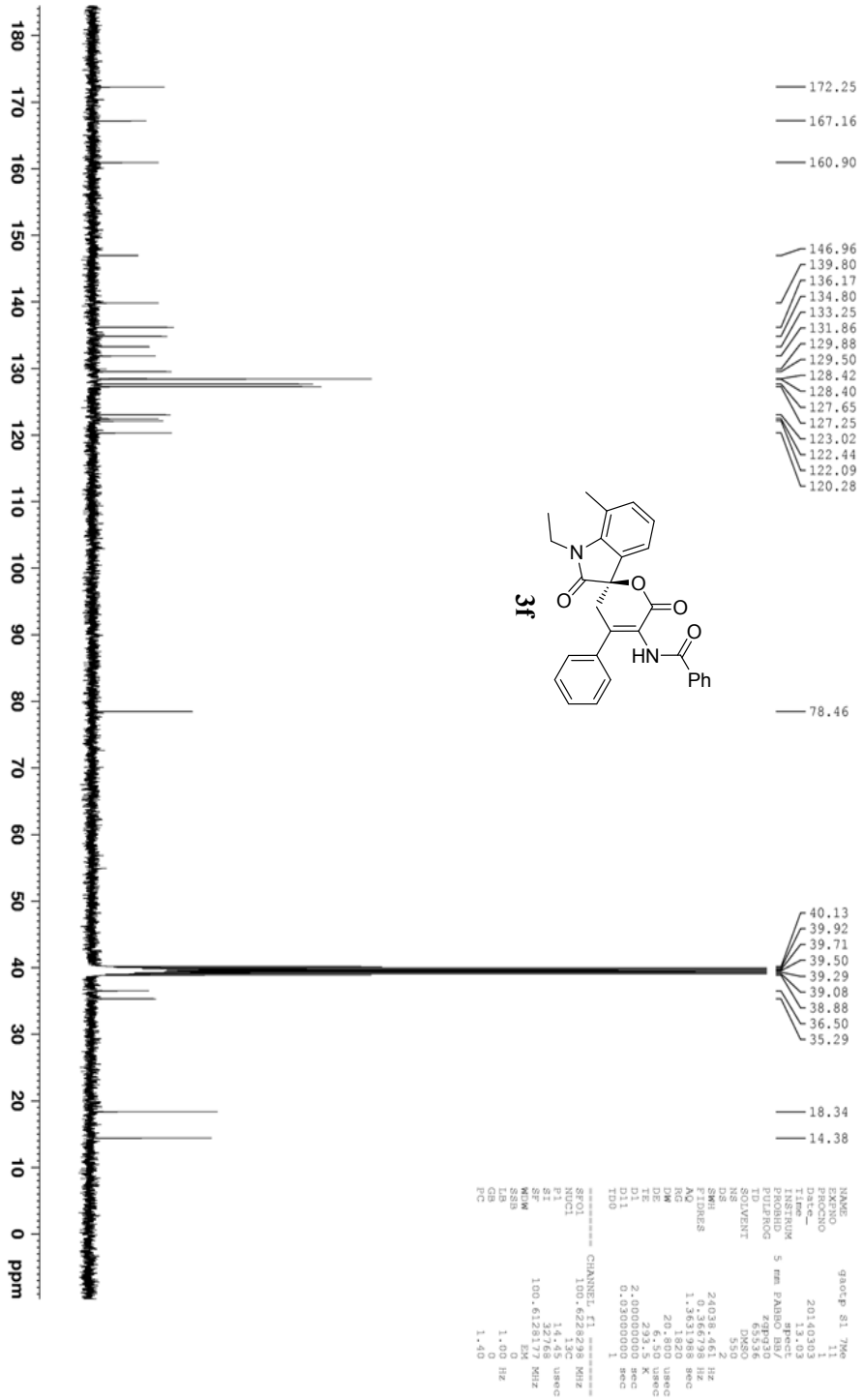
7.596
7.578
7.522
7.506
7.494
7.476
7.402
7.386
7.367
7.347
7.240
7.221
7.050
7.031
7.012
3.969
3.951
3.945
3.933
3.928
3.910
3.702
3.658
3.359
3.131
3.087
2.523
2.500
1.243
1.226
1.208
NAME gaotp7-Me H1
EXPNO 10
PROCNO 1
Date_ 20140112
Time 21.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 200
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 181
DW 62.400 usec
DE 6.50 usec
TE 287.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 14.10 usec
SI 65536
SF 400.1300033 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.95
0.92
1.90
1.06
3.90
3.01
1.00
1.00
1.99
0.99
1.00
2.74
3.32

3f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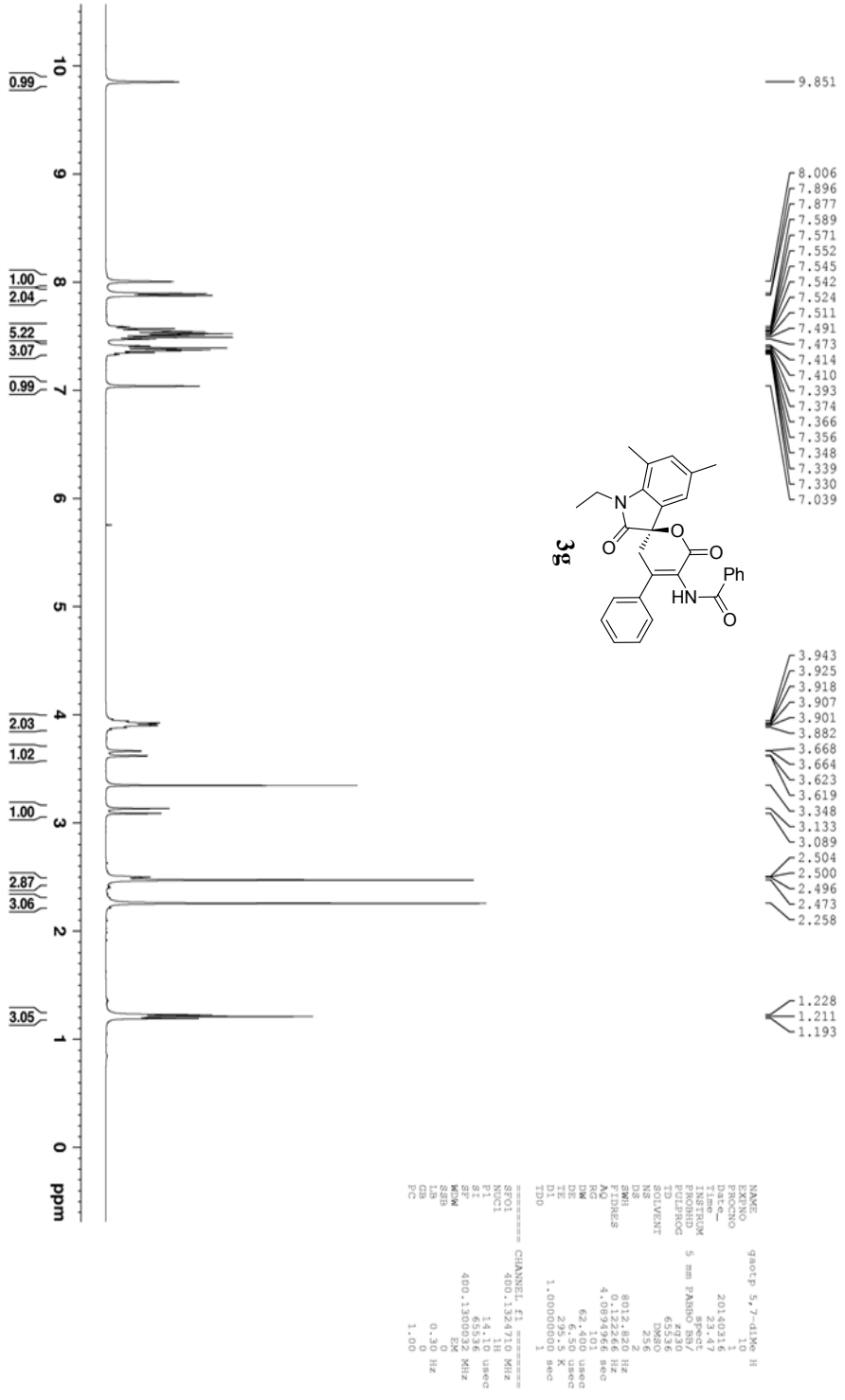
167.16
160.90
146.96
139.80
136.17
134.80
133.25
131.86
129.88
129.50
128.42
128.40
127.65
127.25
123.02
122.44
122.09
120.28
78.46
40.13
39.92
39.71
39.50
39.29
39.08
38.88
36.50
35.29
18.34
14.38
3f
N
O
O
O
O
HN
Ph
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


3g
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7.589
7.571
7.552
7.545
7.542
7.524
7.511
7.491
7.473
7.414
7.410
7.393
7.374
7.366
7.356
7.348
7.339
7.330
7.039
3.943
3.925
3.918
3.907
3.901
3.882
3.668
3.664
3.623
3.619
3.348
3.133
3.089
2.504
2.500
2.496
2.473
2.258
1.228
1.211
1.193
0.99
1.00
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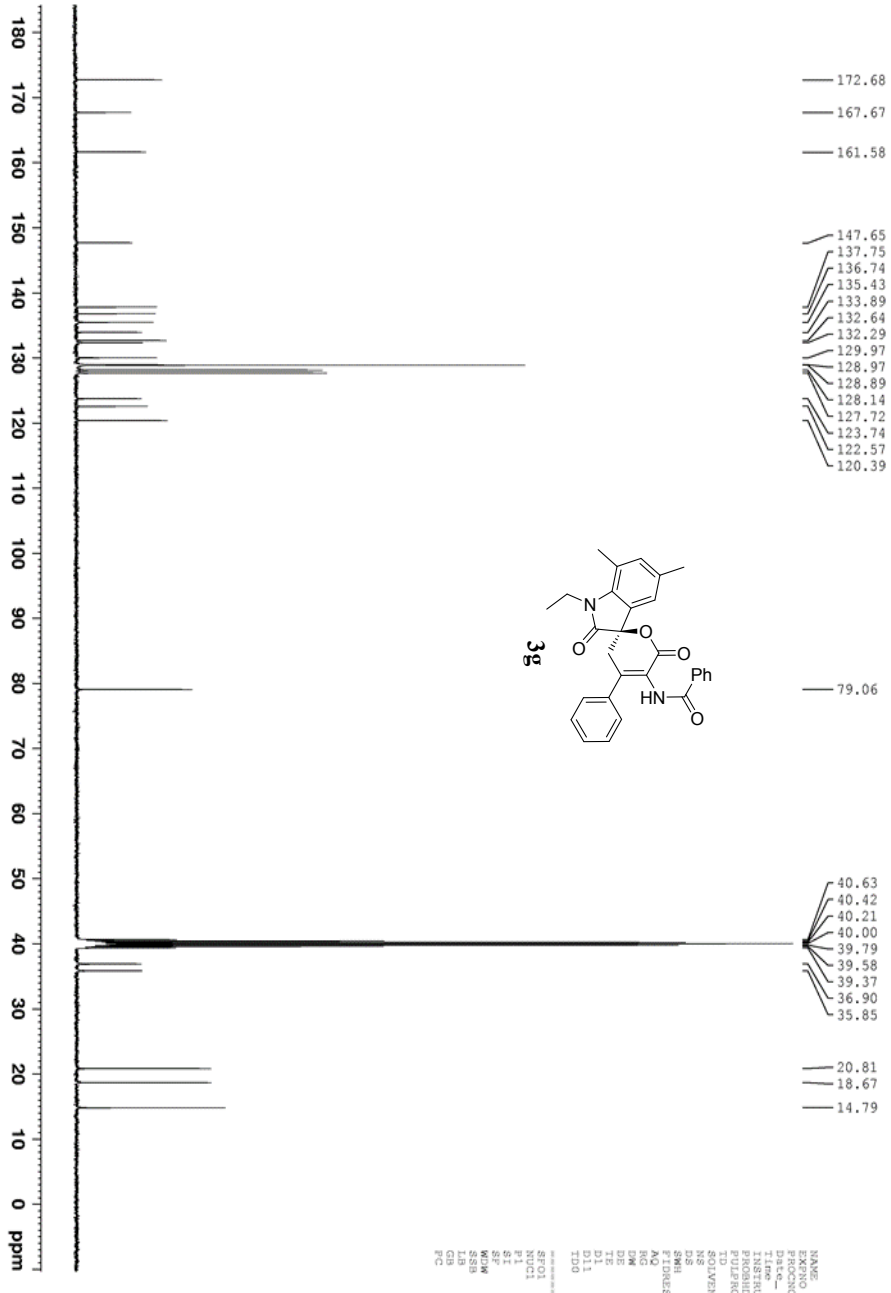
5.22
3.07
0.99
2.03
1.02
1.00
2.87
3.06
3.05
ppm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161.58
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137.75
136.74
135.43
133.89
132.64
132.29
129.97
128.97
128.89
128.14
127.72
123.74
122.57
120.39
79.06
40.63
40.42
40.21
40.00
39.79
39.58
39.37
36.90
35.85
20.81
18.67
14.79
3g
Ph
HN
O
N
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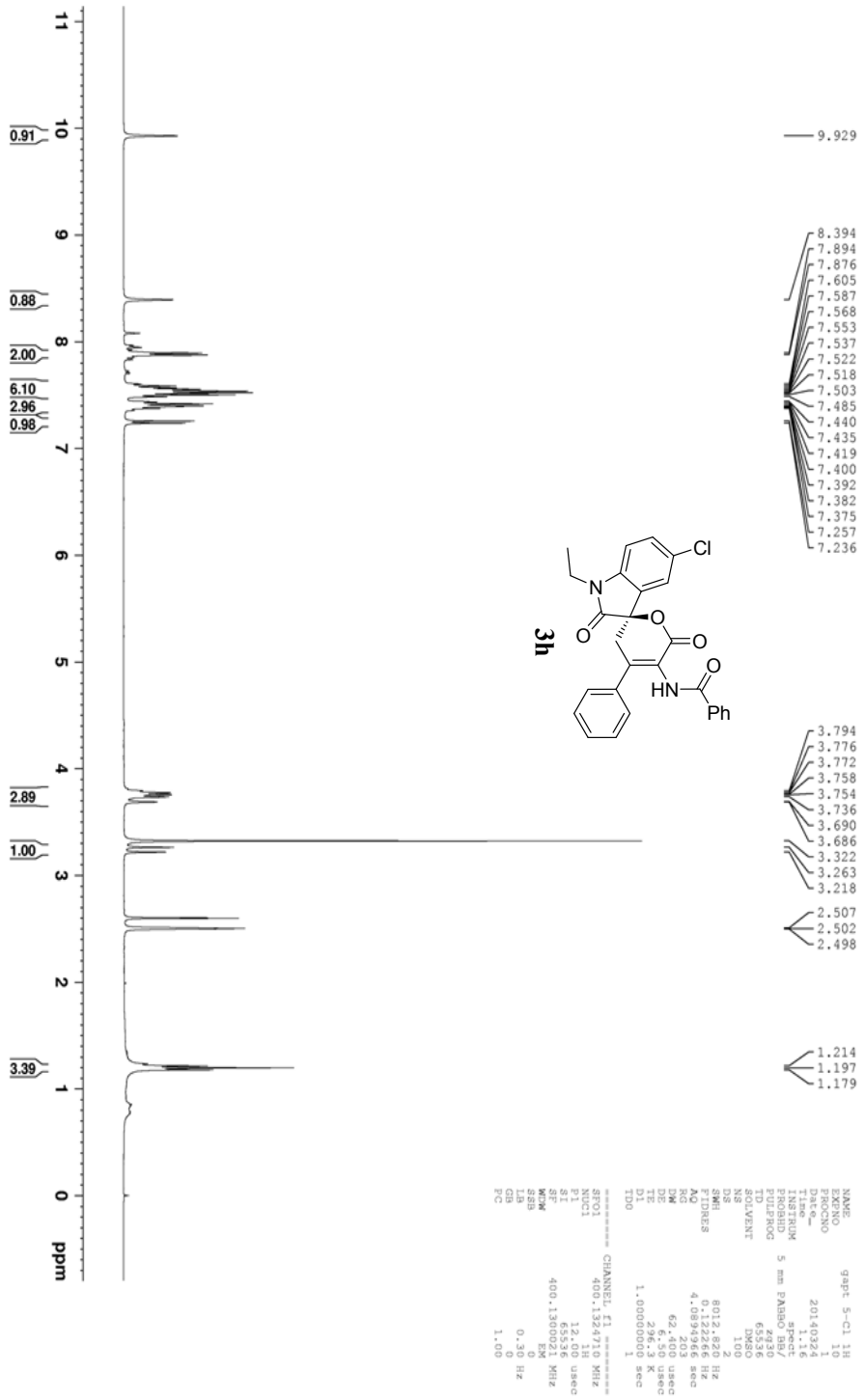
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


3h
Cl
N
O
O
O
O
HN
Ph
9.929
8.394
7.894
7.876
7.605
7.587
7.568
7.553
7.537
7.522
7.518
7.503
7.485
7.440
7.435
7.419
7.400
7.392
7.382
7.375
7.257
7.236
3.794
3.776
3.772
3.758
3.754
3.736
3.690
3.686
3.322
3.263
3.218
2.507
2.502
2.498
1.214
1.197
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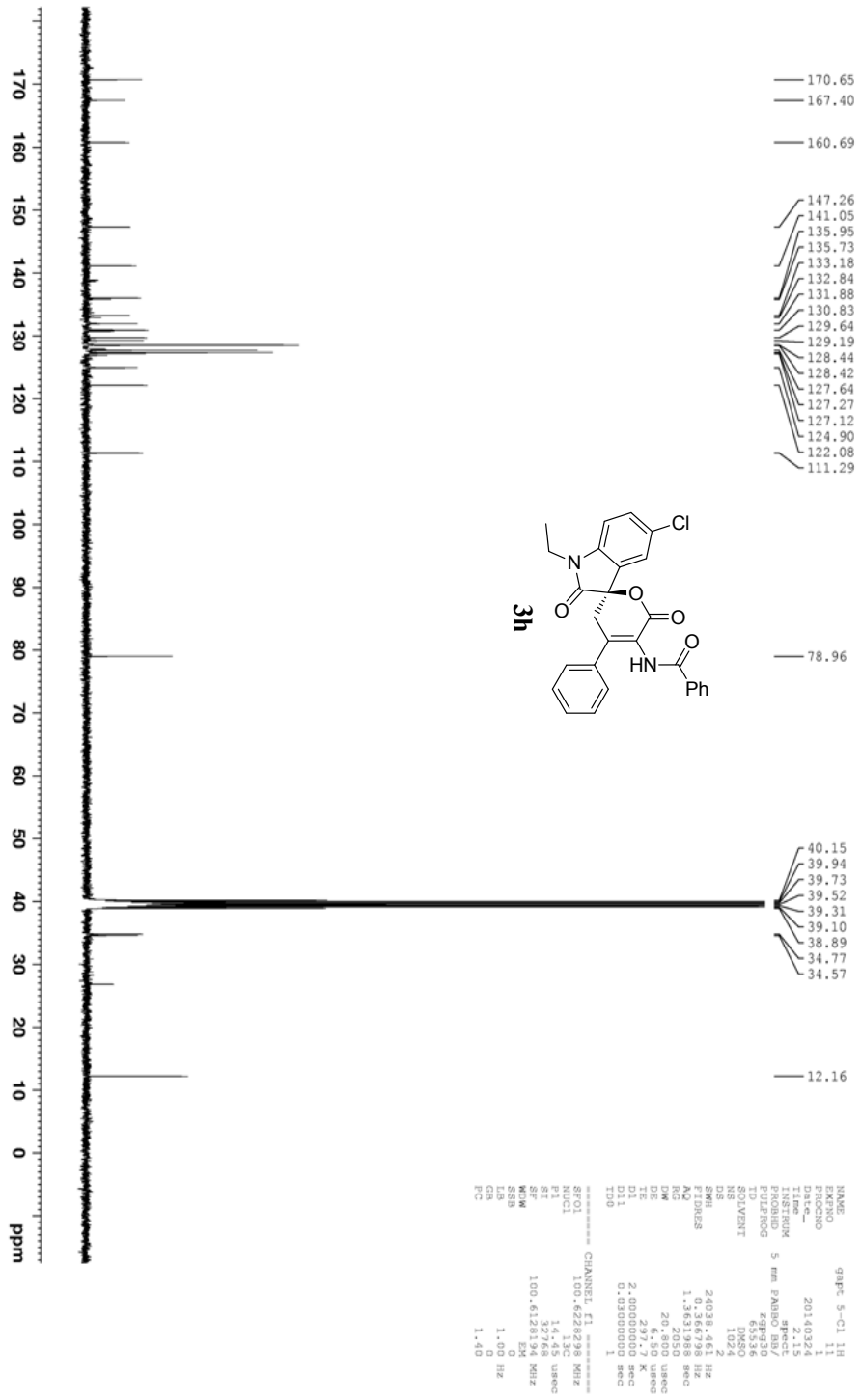
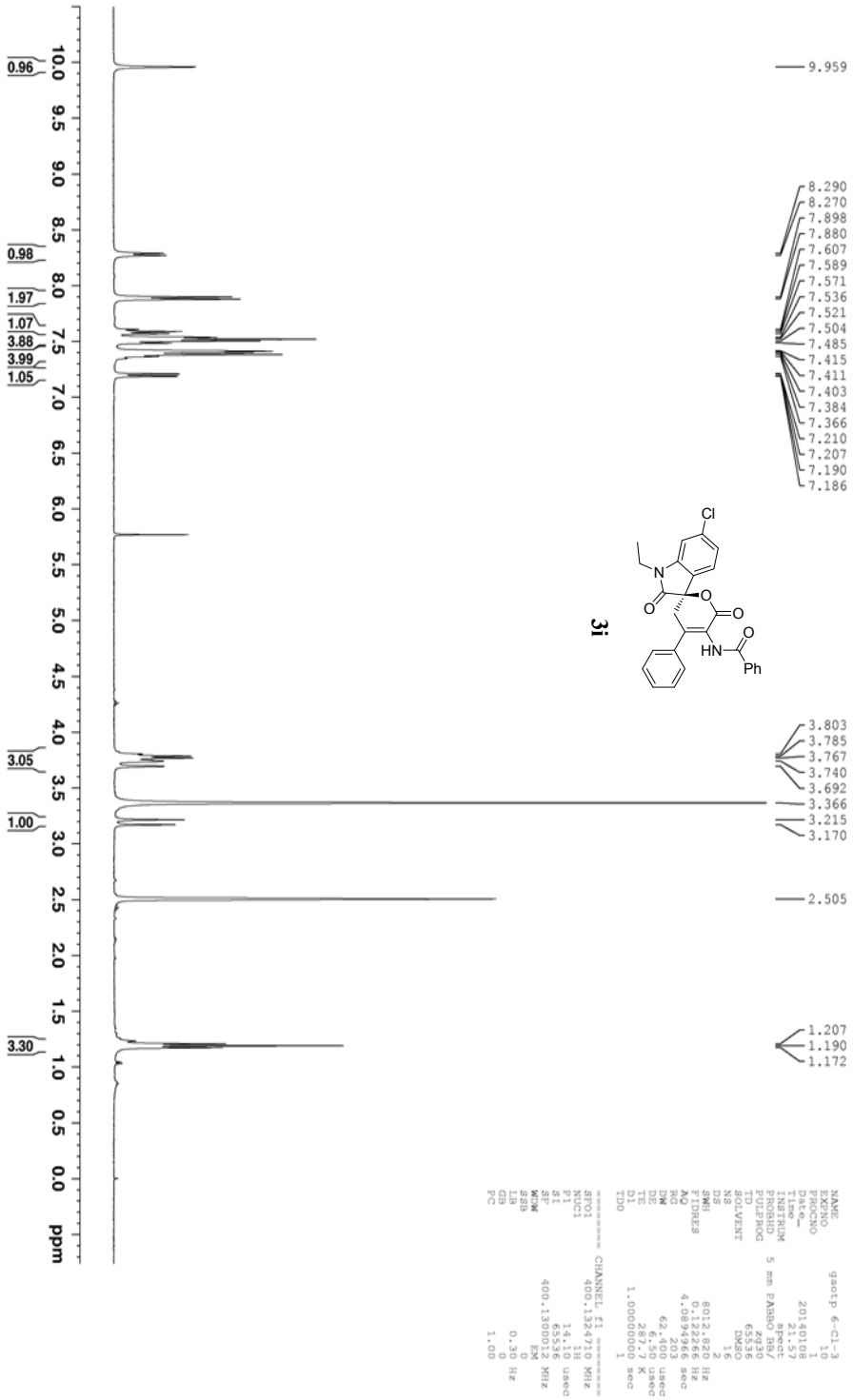
0.91
0.88
2.00
6.10
2.96
0.98
2.89
1.00
3.39
ppm


170.65
167.40
160.69
147.26
141.05
135.95
135.73
133.18
132.84
131.88
130.83
129.64
129.19
128.44
128.42
127.64
127.27
127.12
124.90
122.08
111.29
78.96
40.15
39.94
39.73
39.52
39.31
39.10
38.89
34.77
34.57
12.16
3h
Cl
N
O
O
O
O
HN
Ph
ppm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7.607
7.589
7.571
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7.521
7.504
7.485
7.415
7.411
7.403
7.384
7.366
7.210
7.207
7.190
7.186
3.803
3.785
3.767
3.740
3.692
3.366
3.215
3.170
2.505
1.207
1.190
1.172
0.96
0.98
1.97
1.07
3.88
3.99
1.05
3.05
1.00
3.30
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
Cl
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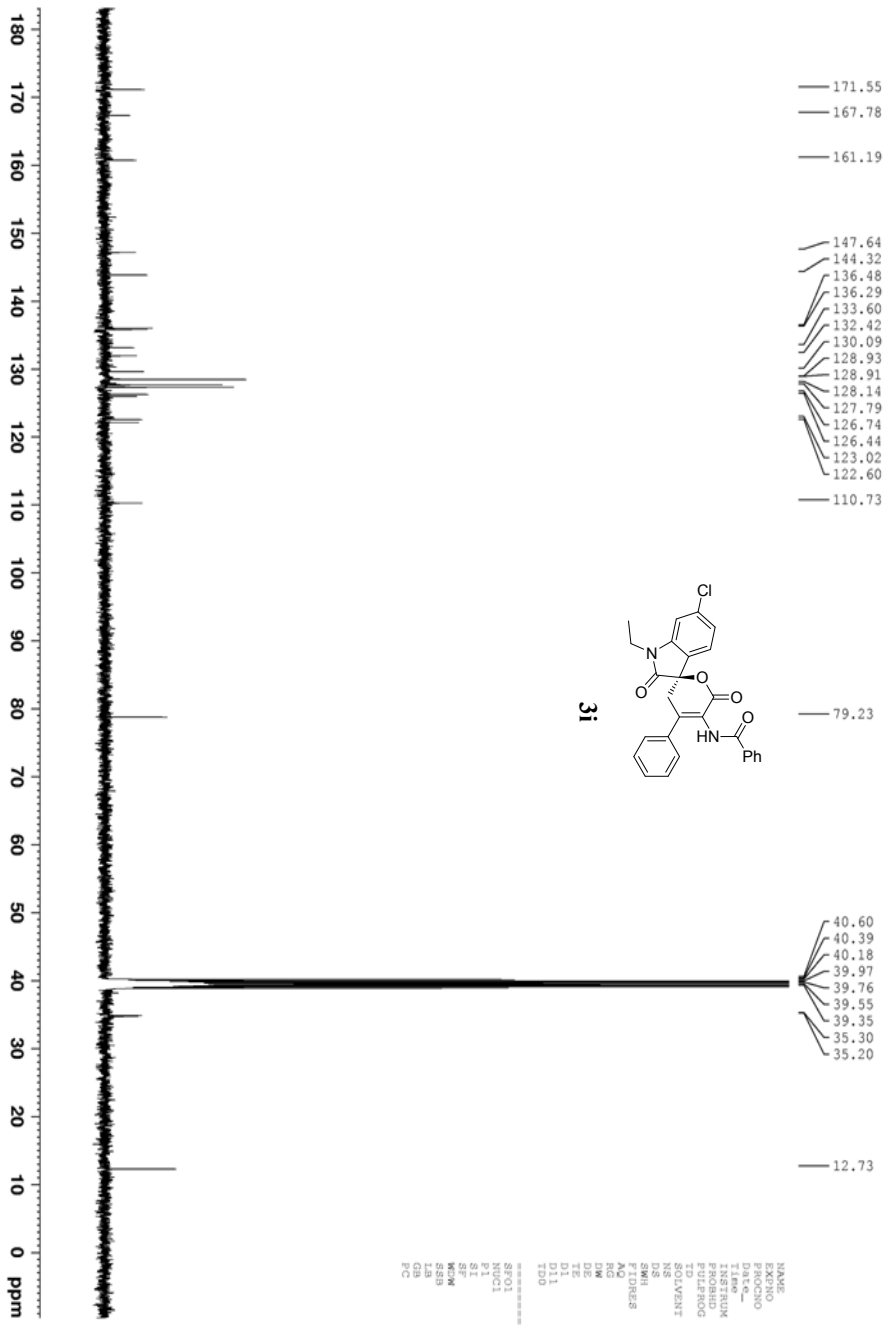
O
O
O
HN
O
Ph
3i
NAME gaotp 6-Cl-3
EXPNO 10
PROCNO 1
Date_ 20140108
Time 21.57
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122766 Hz
AQ 4.0894966 sec
RG 203
DW 62.400 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 14.10 usec
SI 65536
SF 400.1300012 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00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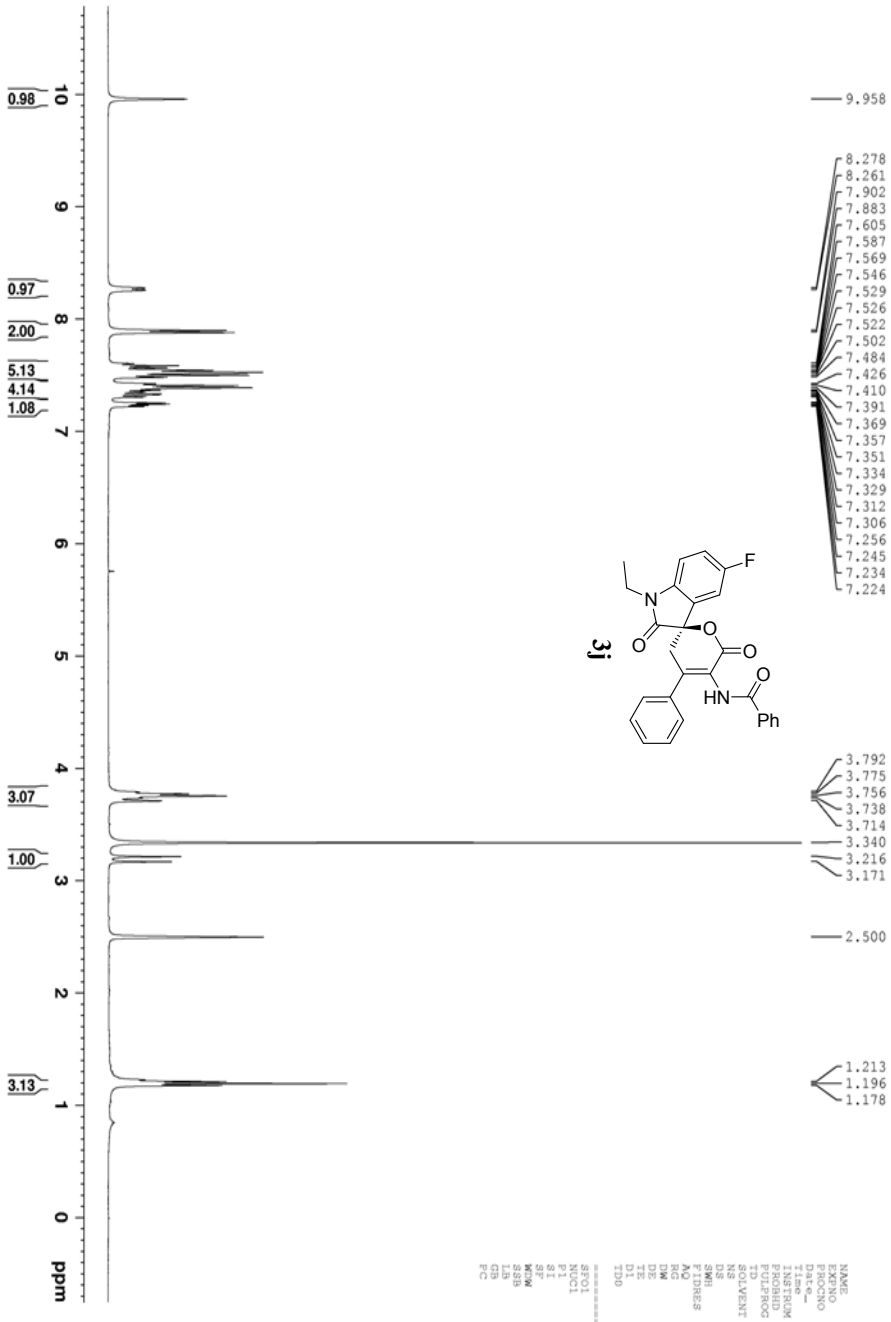
161.19
147.64
144.32
136.48
136.29
133.60
132.42
130.09
128.93
128.91
128.14
127.79
126.74
126.44
123.02
122.60
110.73
79.23
40.60
40.39
40.18
39.97
39.76
39.55
39.35
35.30
35.20
12.73
Cl
N
O
O
O
HN
O
Ph
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

3i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7.587
7.569
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7.529
7.526
7.522
7.502
7.484
7.426
7.410
7.391
7.369
7.357
7.351
7.334
7.329
7.312
7.306
7.256
7.245
7.234
7.224
3.792
3.775
3.756
3.738
3.714
3.340
3.216
3.171
2.500
1.213
1.196
1.178
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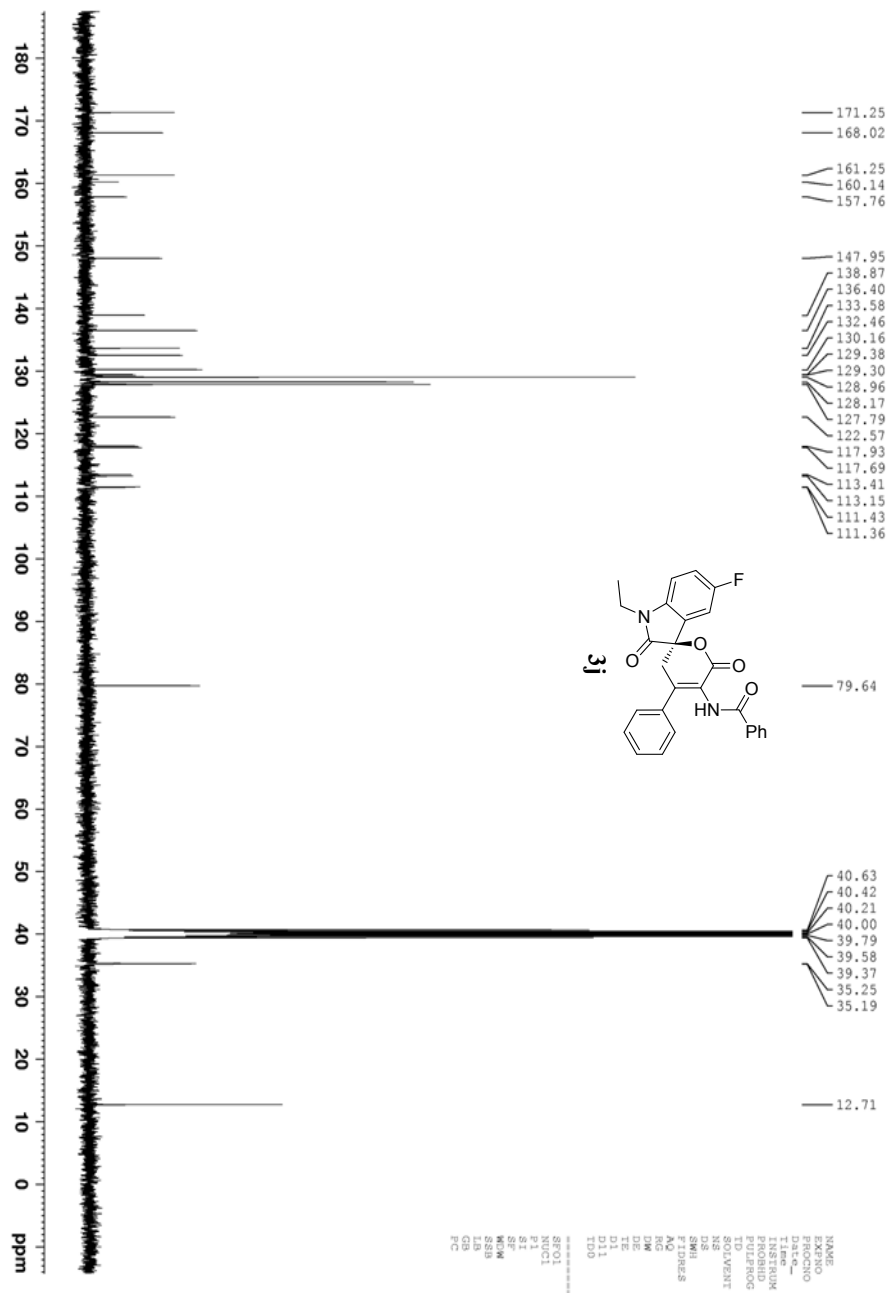
0.97
2.00
5.13
4.14
1.08
3.07
1.00
3.13
10
9
8
7
6
5
4
3
2
1
0
ppm
F
N
O
O
O
HN
O
Ph
3j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157.76
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138.87
136.40
133.58
132.46
130.16
129.38
129.30
128.96
128.17
127.79
122.57
117.93
117.69
113.41
113.15
111.43
111.36
79.64
40.63
40.42
40.21
40.00
39.79
39.58
39.37
35.25
35.19
12.71
3j
F
N
O
O
O
O
HN
Ph
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170
160
150
140
130
120
110
100
90
80
70
60
50
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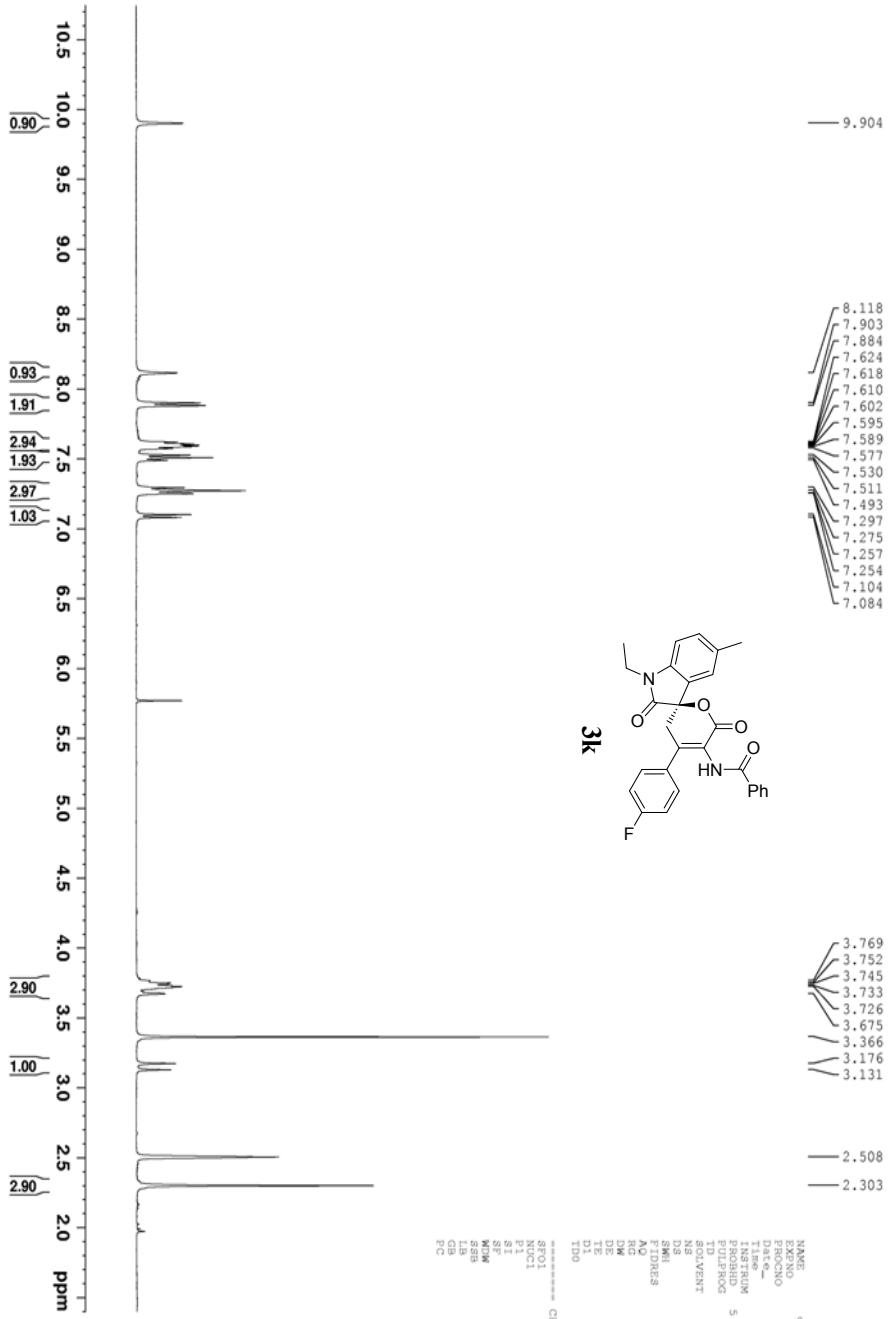
30
20
10
0
ppm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7.602
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7.589
7.577
7.530
7.511
7.493
7.297
7.275
7.257
7.254
7.104
7.084
3.769
3.752
3.745
3.733
3.726
3.675
3.366
3.176
3.131
2.508
2.303
0.90
0.93
1.91
2.94
1.93
2.97
1.03
2.90
1.00
2.90
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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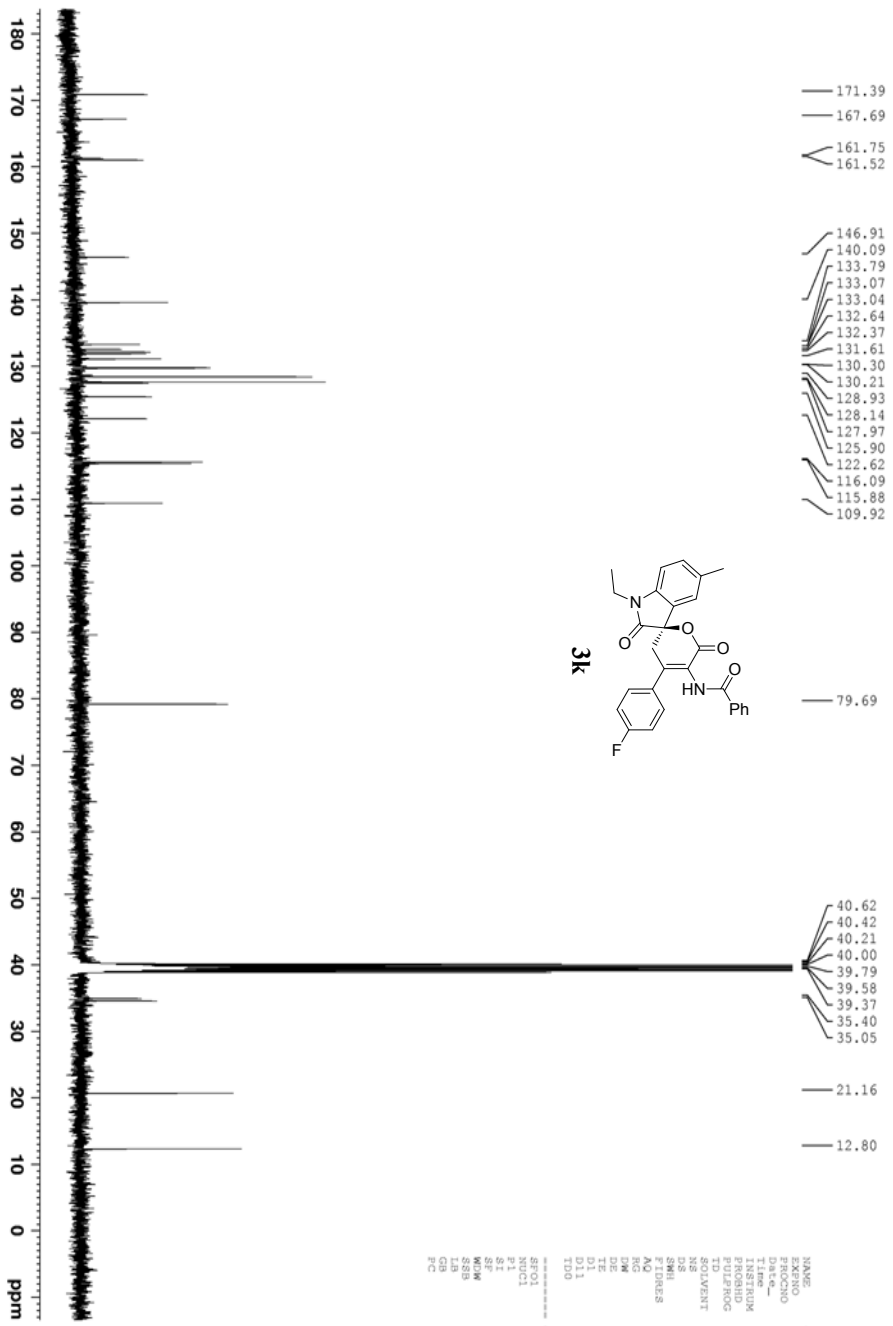
3.0
2.5
2.0
ppm
3k
N
O
O
O
O
HN
Ph
F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133.07
133.04
132.64
132.37
131.61
130.30
130.21
128.93
128.14
127.97
125.90
122.62
116.09
115.88
109.92
79.69
40.62
40.42
40.21
40.00
39.79
39.58
39.37
35.40
35.05
21.16
12.80
3k
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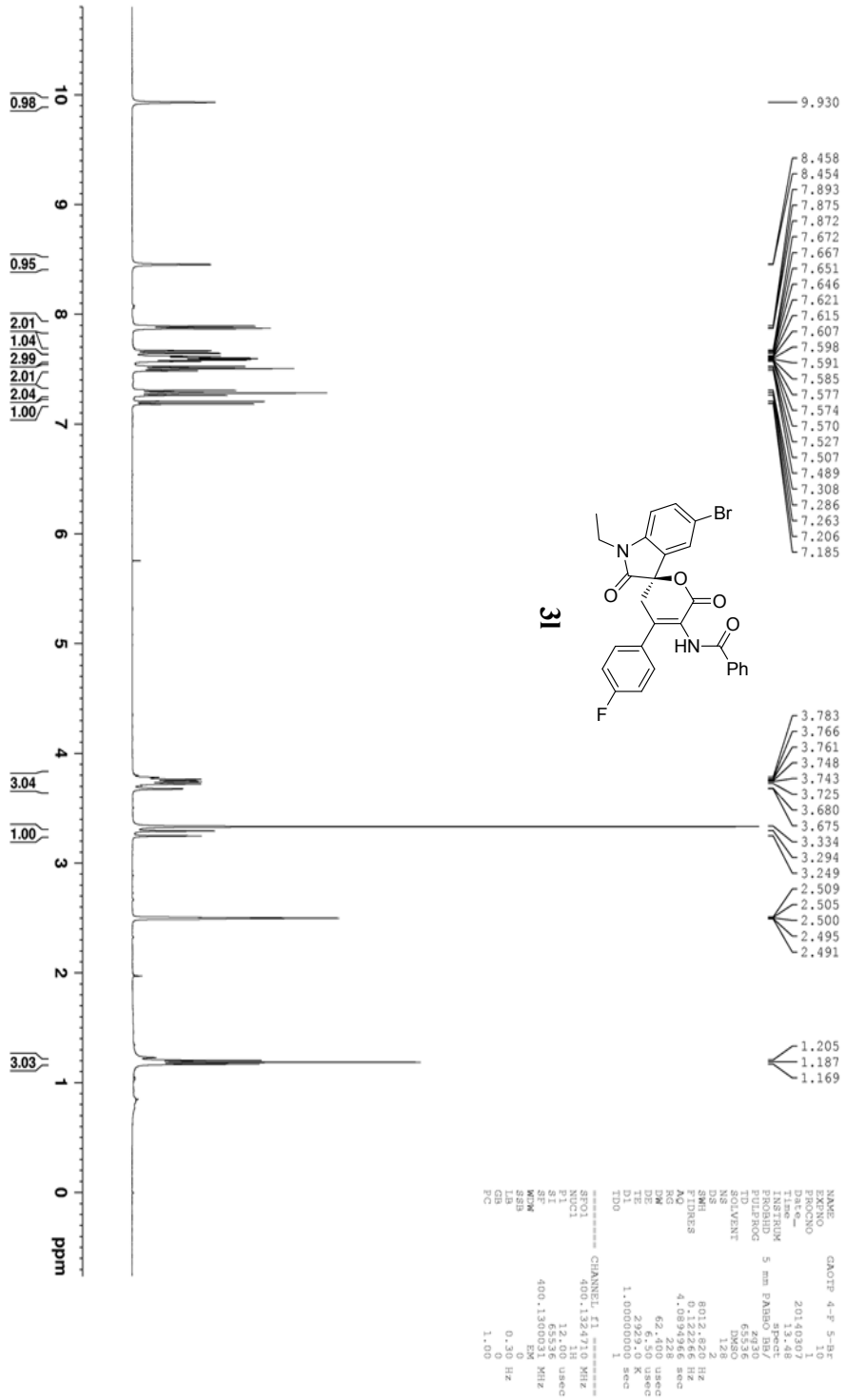
O
O
HN
O
Ph
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


31
Br
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O
O
HN
O
Ph
F
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7.872
7.672
7.667
7.651
7.646
7.621
7.615
7.607
7.598
7.591
7.585
7.577
7.574
7.570
7.527
7.507
7.489
7.308
7.286
7.263
7.206
7.185
3.783
3.766
3.761
3.748
3.743
3.725
3.680
3.675
3.334
3.294
3.249
2.509
2.505
2.500
2.495
2.491
1.205
1.187
1.169
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0.95
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1.04
2.99
2.01
2.04
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1.00
3.03
10
9
8
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6
5
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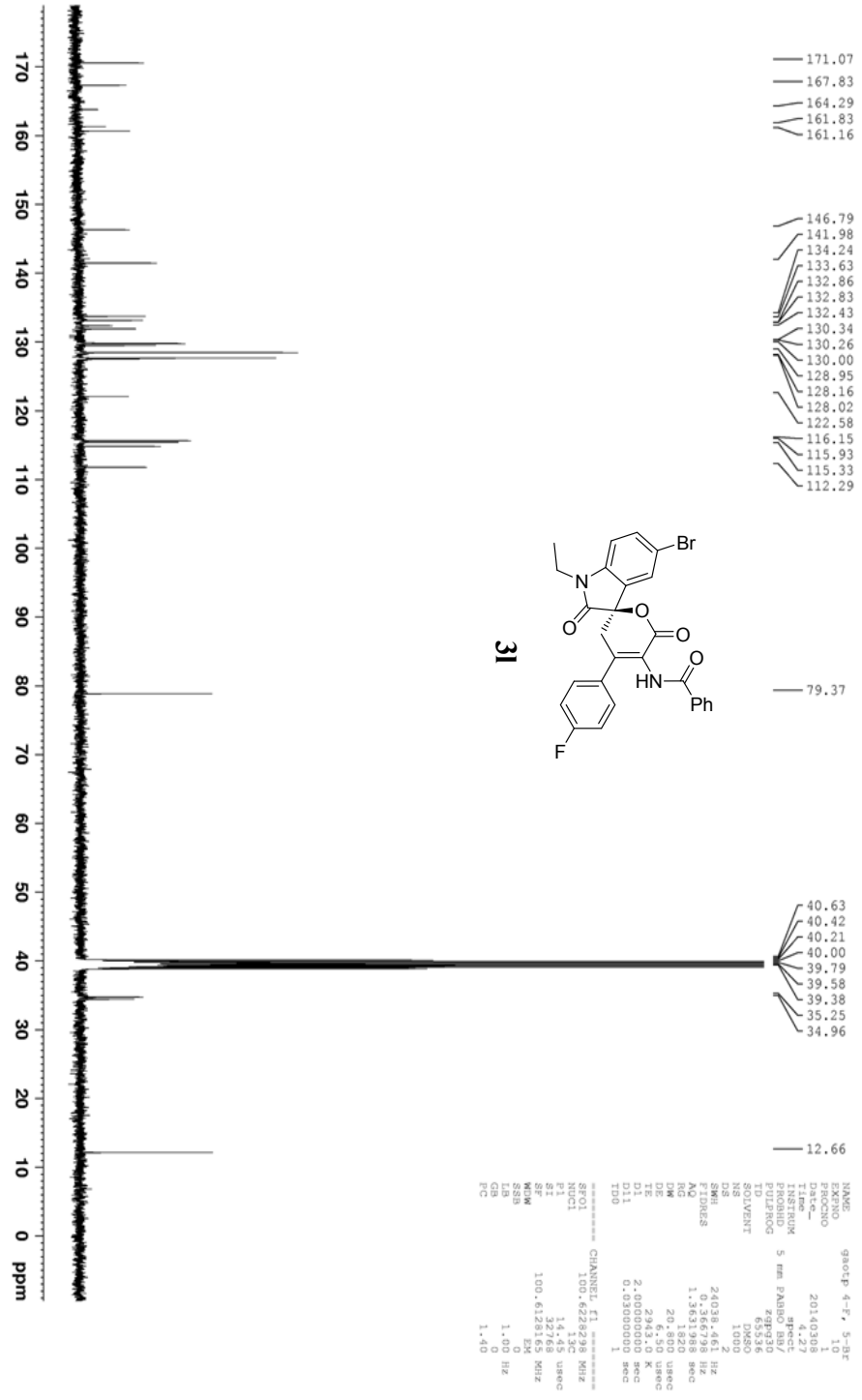
3
2
1
0
ppm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141.98
134.24
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132.86
132.83
132.43
130.34
130.26
130.00
128.95
128.16
128.02
122.58
116.15
115.93
115.33
112.29
79.37
40.63
40.42
40.21
40.00
39.79
39.58
39.38
35.25
34.96
12.66
31
Br
N
O
O
O
HN
O
Ph
F
170
160
150
140
130
120
110
100
90
80
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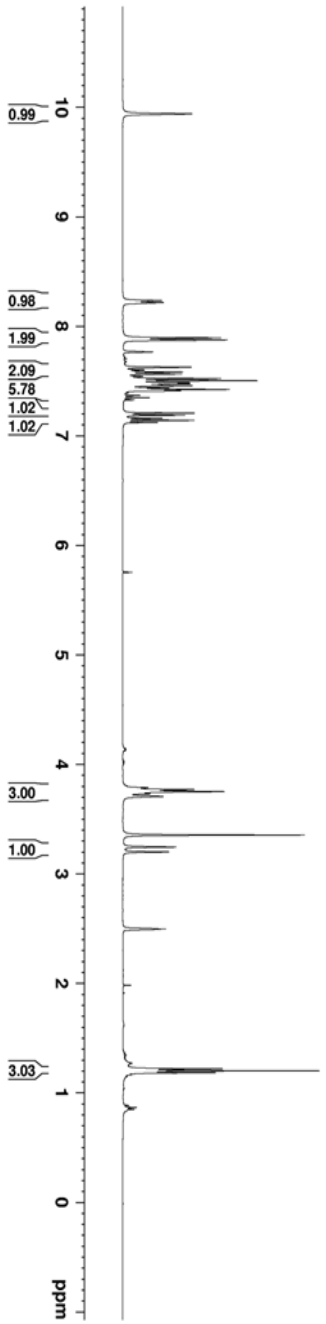

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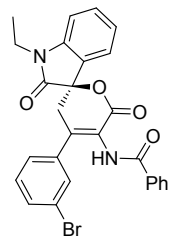

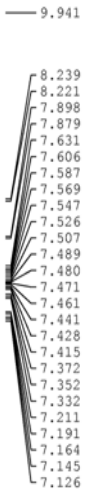

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PROCNO 1
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Time 11.02
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PULPROG zg30
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SOLVENT CDCl3
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FIDRES 0.122960 Hz
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RG 114
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DE 6.00 usec
TE 292.5 K
D1 1.00000000 sec
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P1 14.10 usec
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SI 65536
SF 400.1300000 MHz
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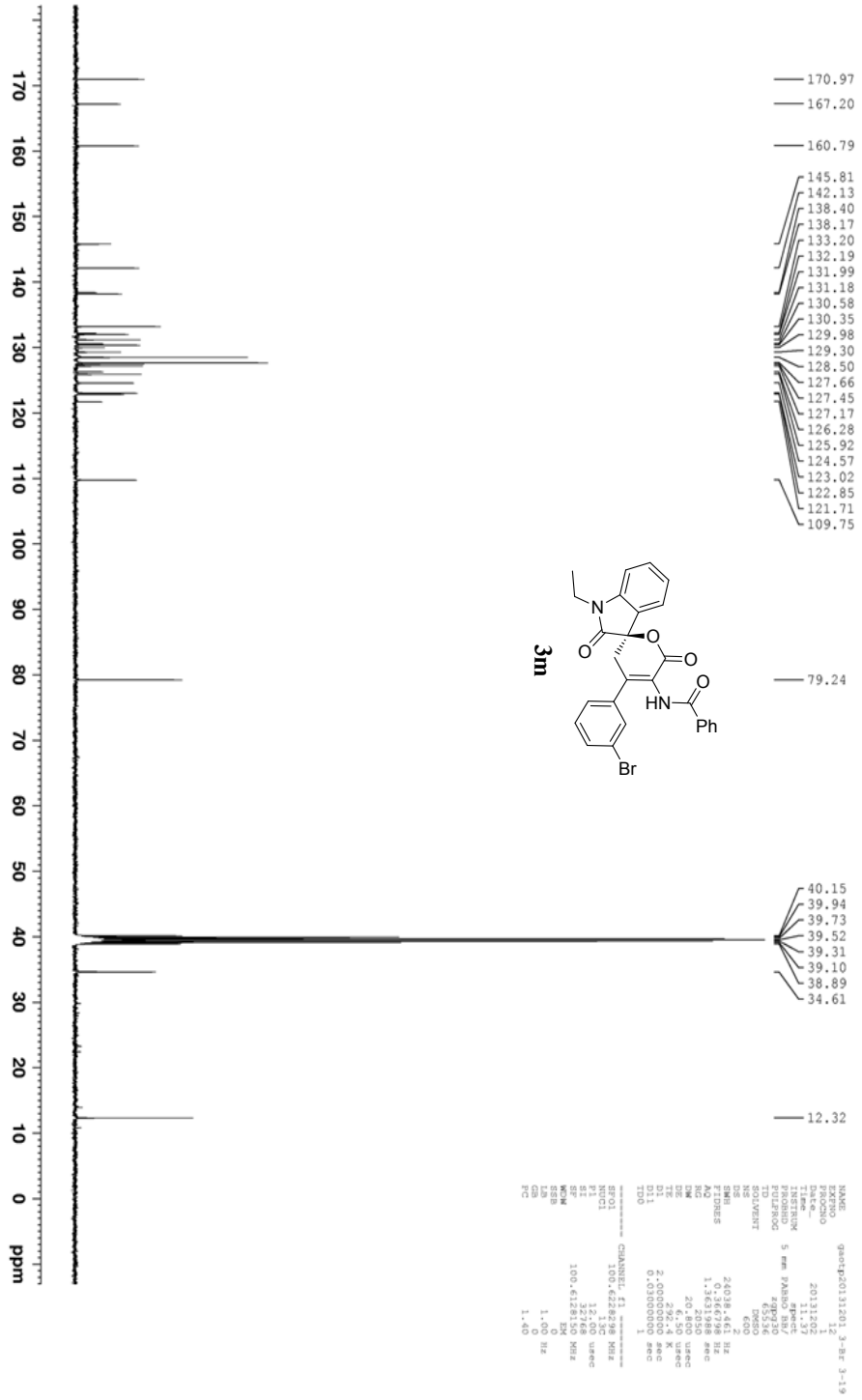
GB 0
PC 1.00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12.32
3m
N
O
O
O
HN
O
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Br
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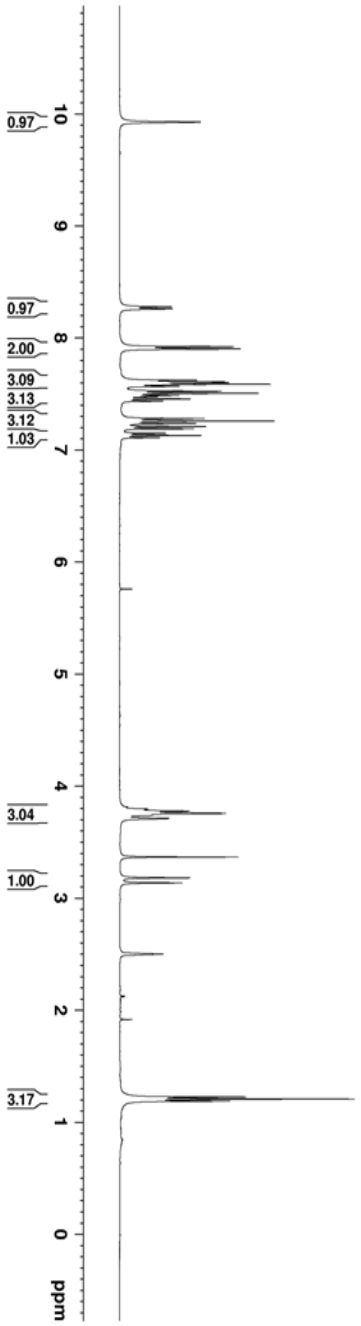
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2
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0
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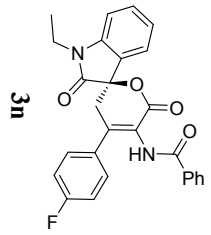
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Ph
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3n


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7.475
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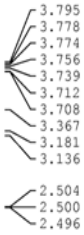
7.149
7.130
7.111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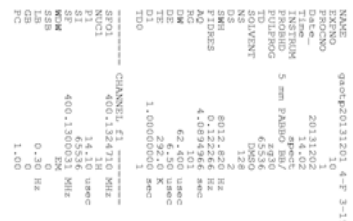
1.188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FIDRES 0.122826 Hz
AQ 4.0894966 sec
RG 101
DW 62.400 usec
DE 6.50 usec
TE 292.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
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NUC1 1H
P1 14.10 usec
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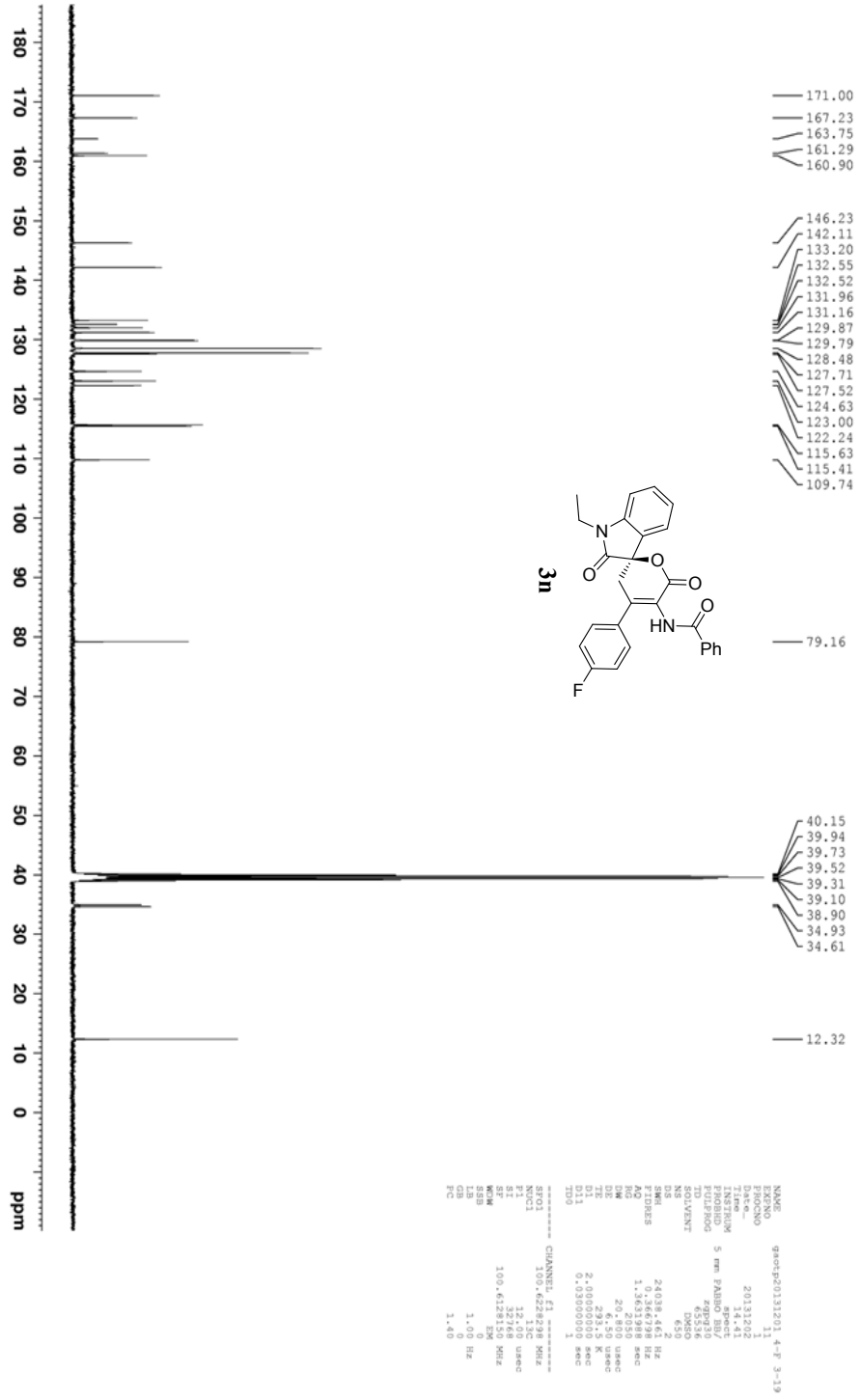
PC 1.00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127.52
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39.52
39.31
39.10
38.90
34.93
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O
O
HN
O
Ph
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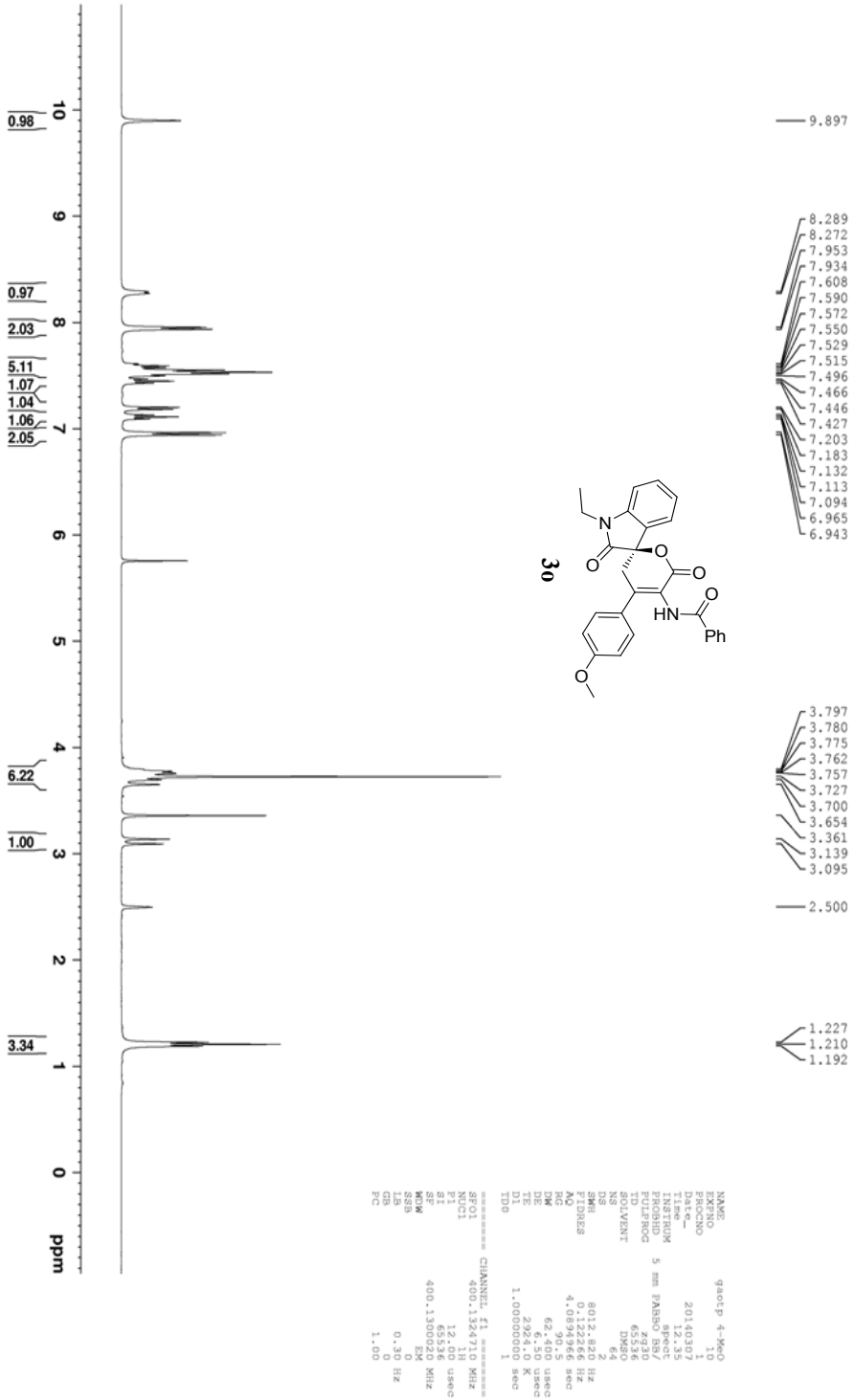
ppm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7.427
7.203
7.183
7.132
7.113
7.094
6.965
6.943
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3.780
3.775
3.762
3.757
3.727
3.700
3.654
3.361
3.139
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1.210
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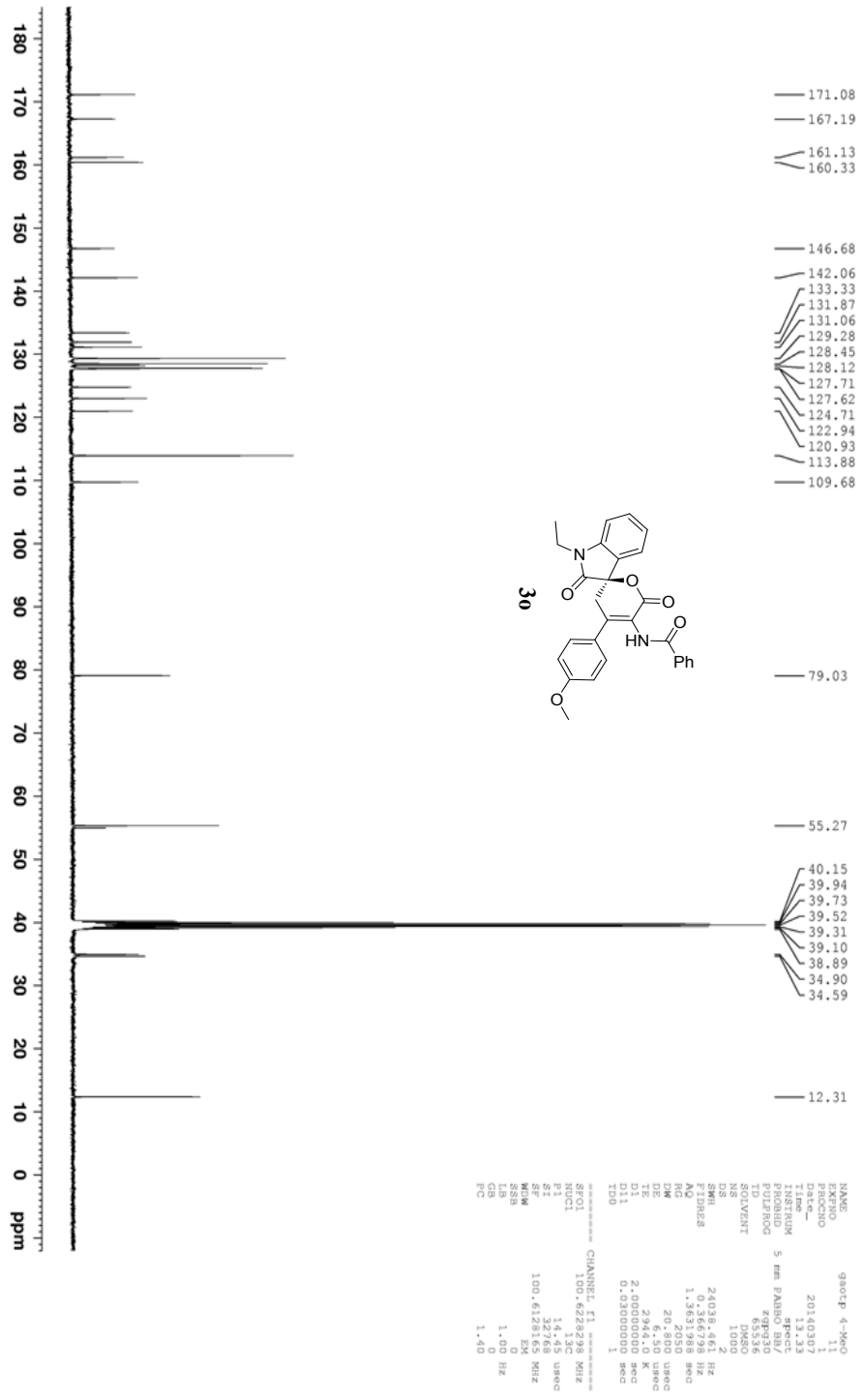
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39.94
39.73
39.52
39.31
39.10
38.89
34.90
34.59
12.31
30
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O
O
HN
O
Ph
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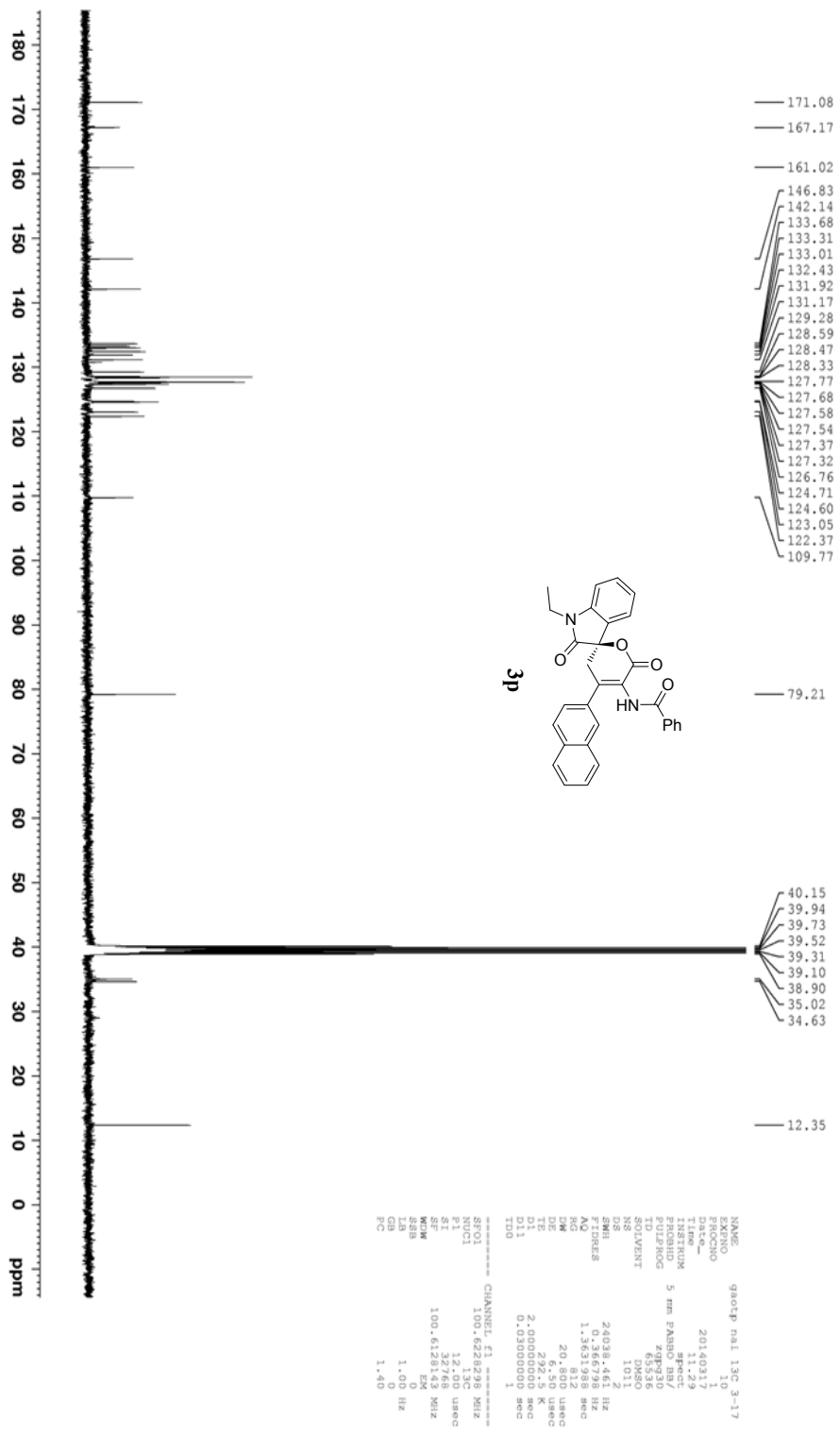
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127.32
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39.94
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39.31
39.10
38.90
35.02
34.63
12.35
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O
O
HN
O
Ph
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2.08
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2.11
2.04
1.05
1.00
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8.5
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7.5
7.0
6.5
6.0
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4.0
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3.0
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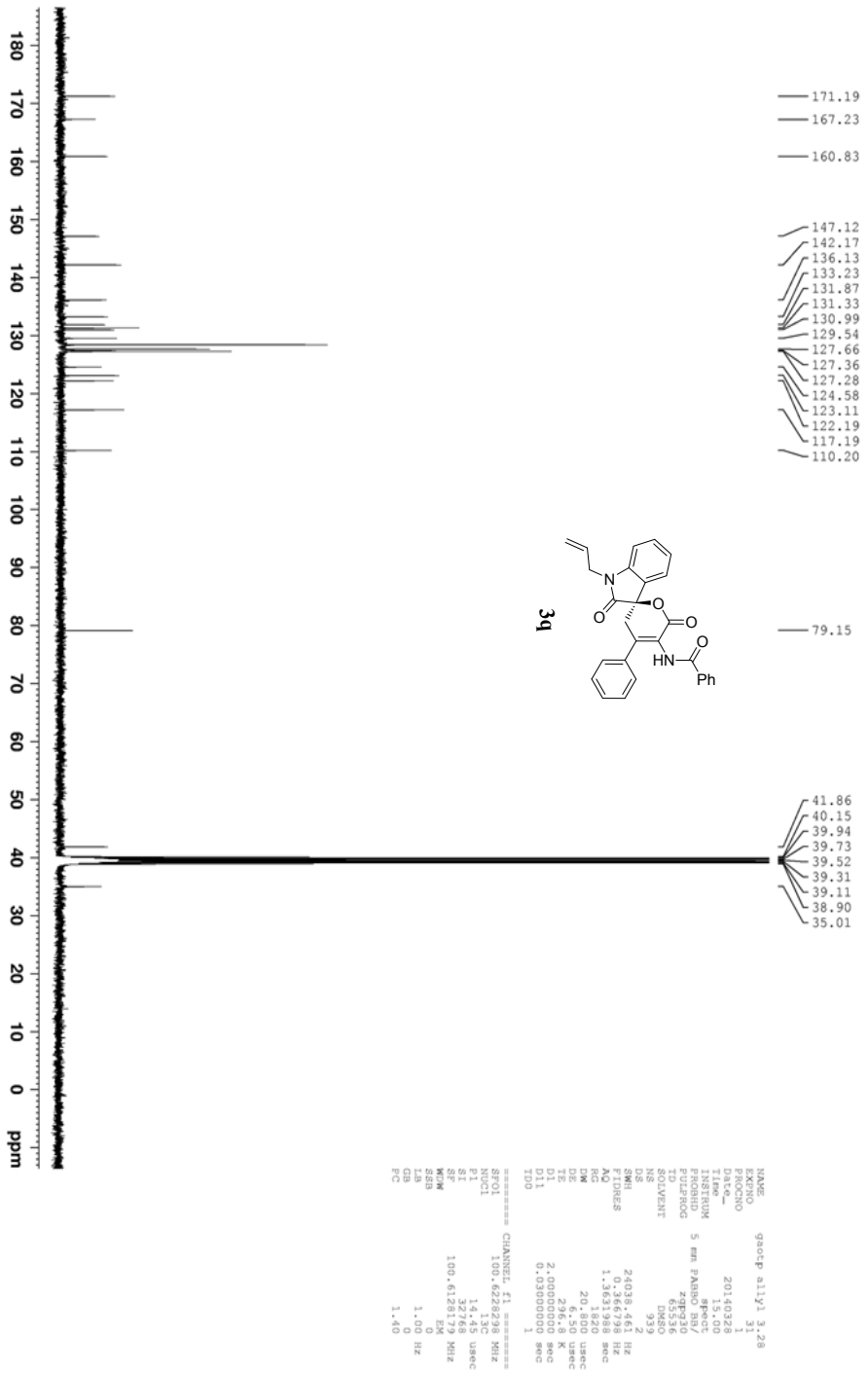
ppm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110.20
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39.94
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39.52
39.31
39.11
38.90
35.01
3q
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O
O
O
HN
O
Ph
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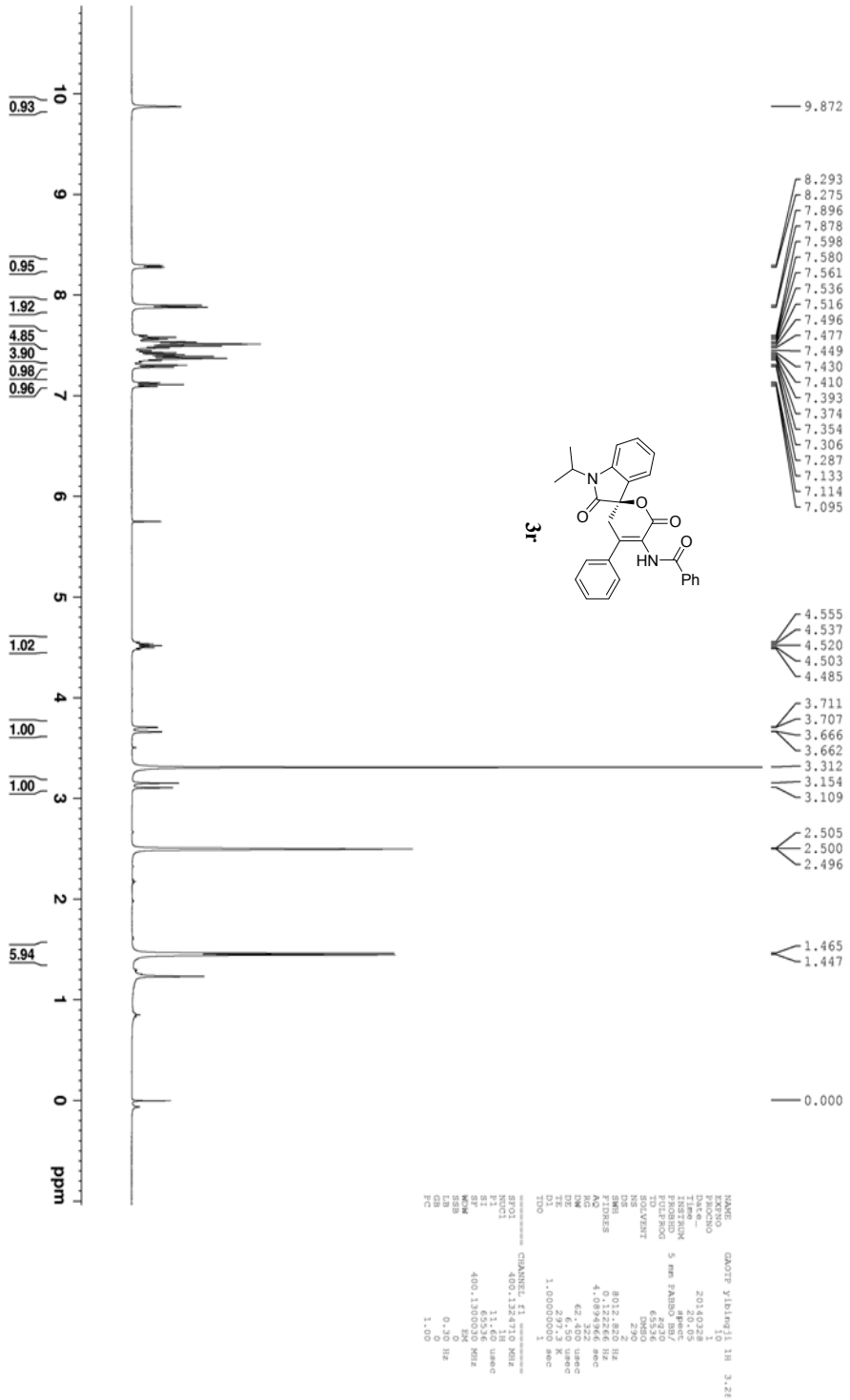
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1.447
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1.02
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1.00
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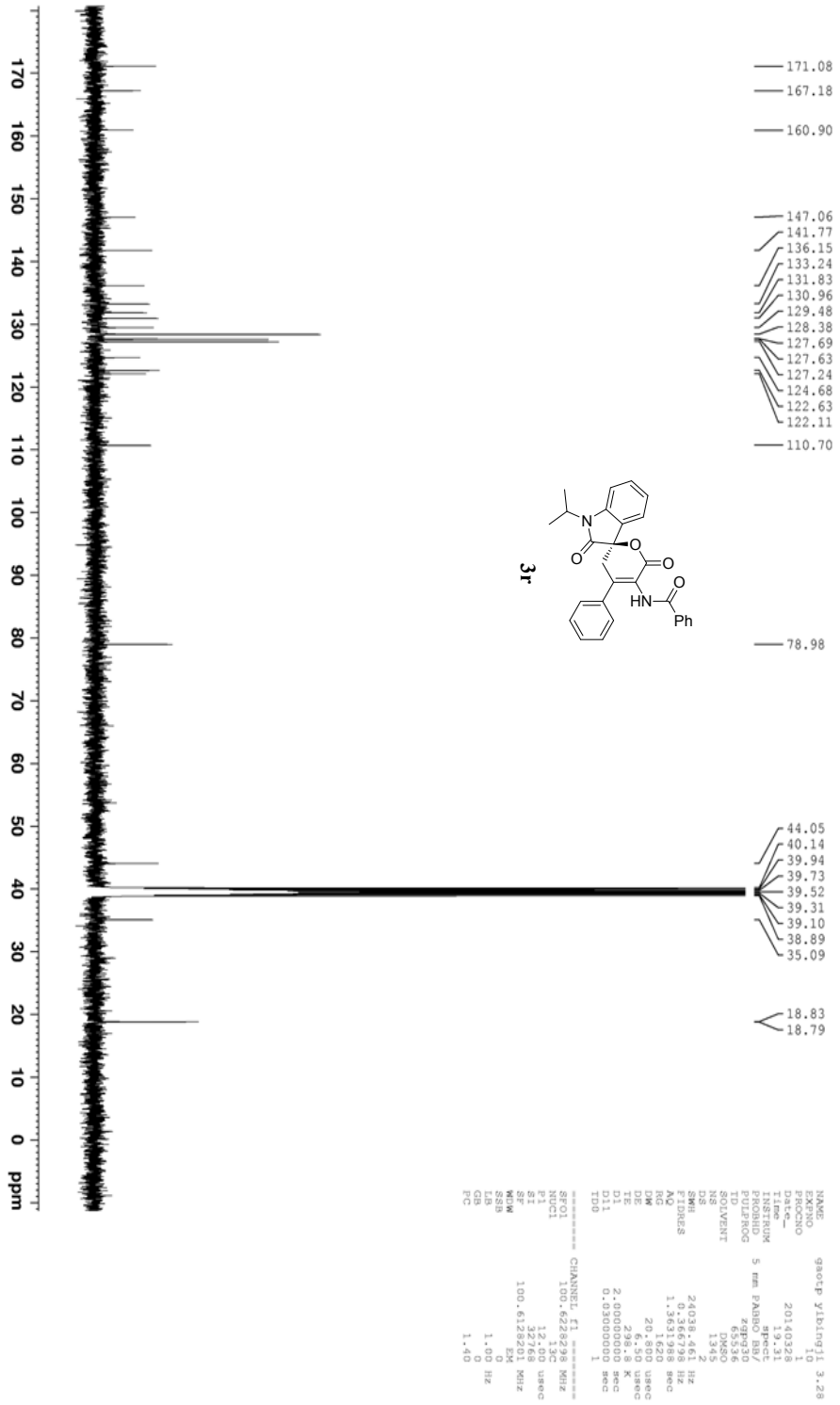
ppm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O
HN
Ph
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EXPNO 10
PROCNO 1
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Time_ 19.31
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DE 6.50 usec
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TD0 1
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SI 32768
SF 100.6128201 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
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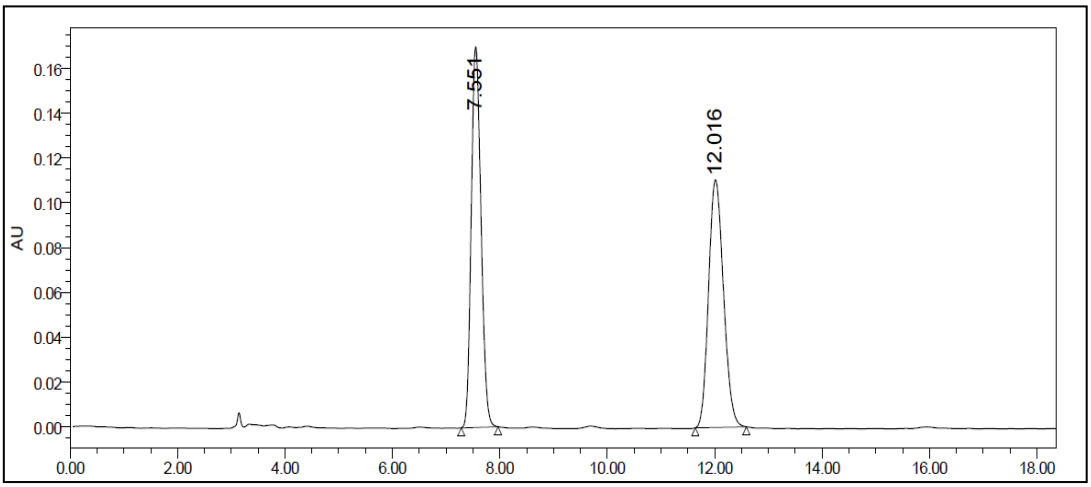
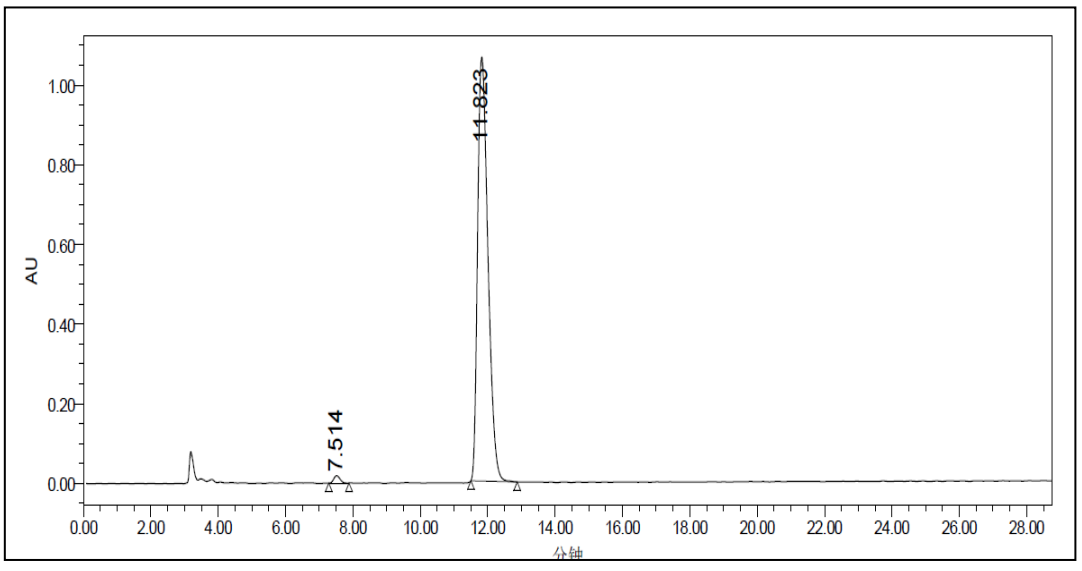
6. HPLC spectra of compound **3**.

3a HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 50:47.5:2.5, 1.0 mL/min)

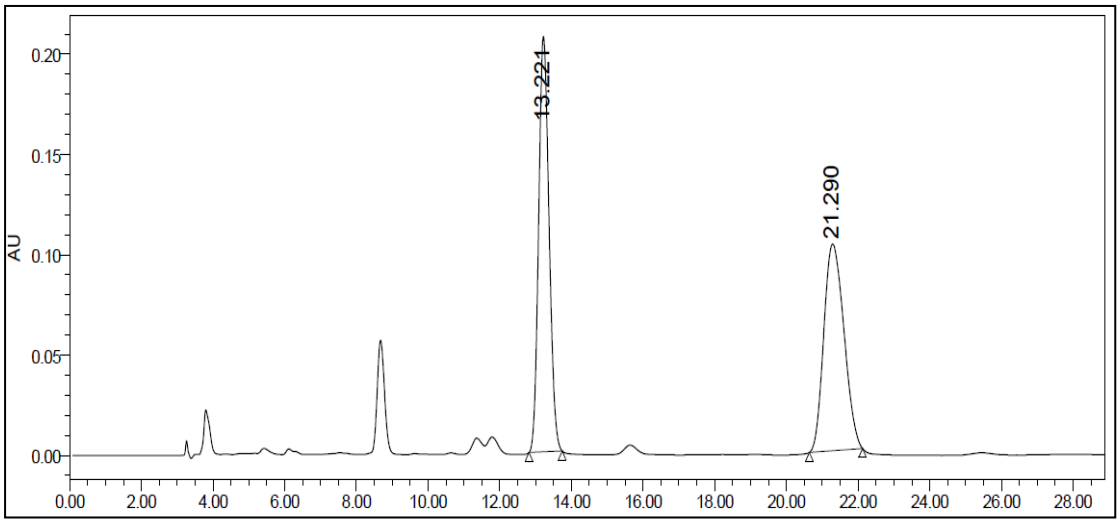


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	7.551	2143515	169895	50.18
2	PDA 280.0 nm	12.016	2127990	110494	49.82

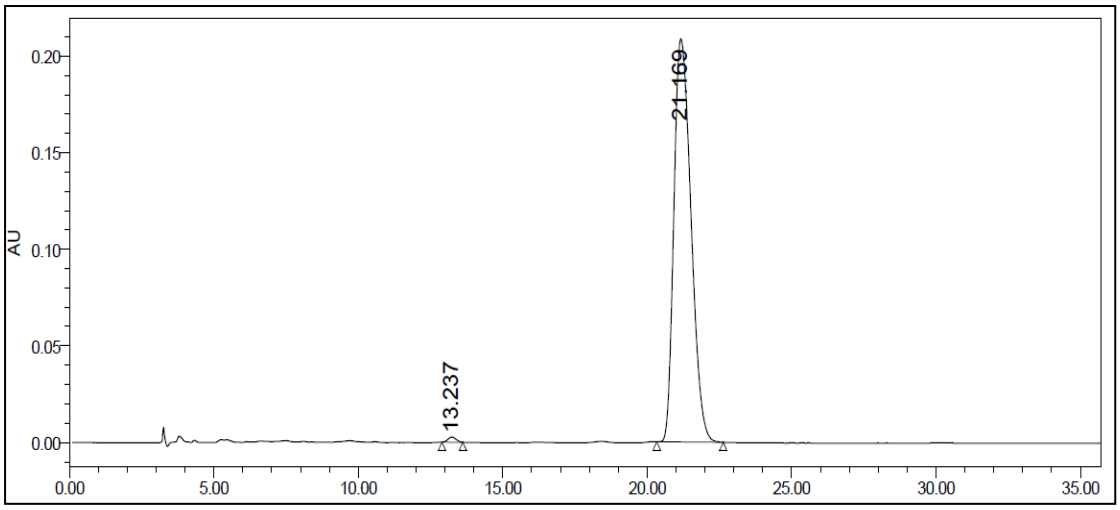


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	7.514	234573	18464	1.02
2	PDA 280.0 nm	12.823	22689357	1064158	98.98

3b HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)

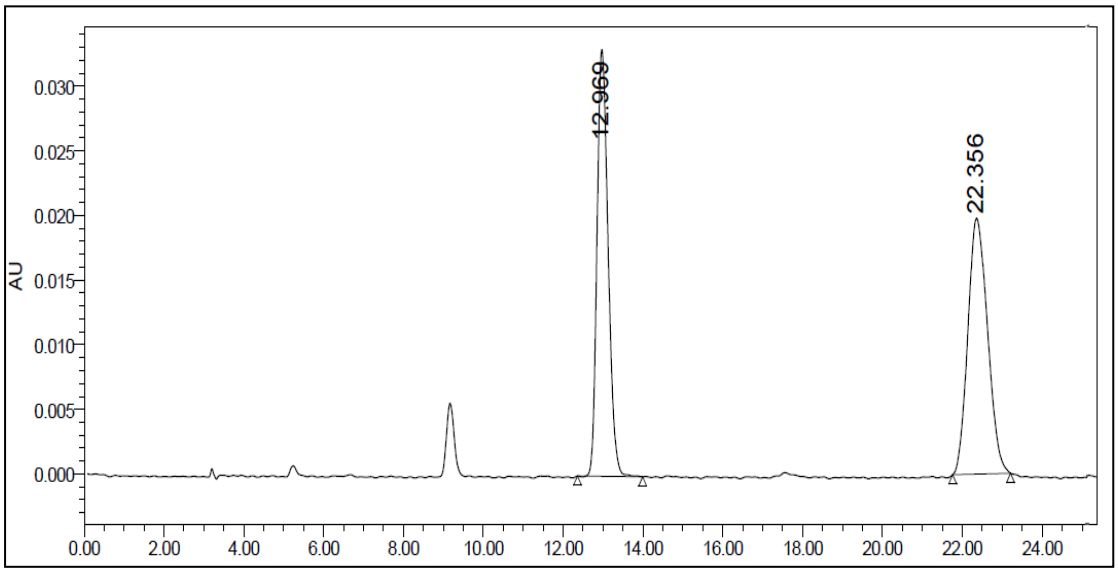


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	13.221	4175859	207119	50.94
2	PDA 280.0 nm	21.290	4021118	103039	49.06

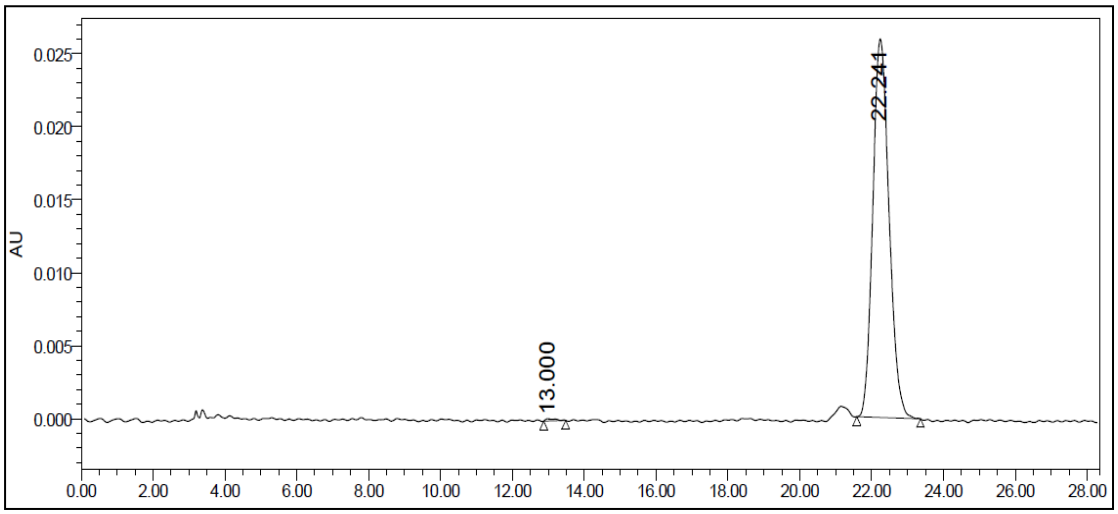


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	13.237	5226	2706	0.60
2	PDA 280.0 nm	21.196	8590460	208613	99.40

3c HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)

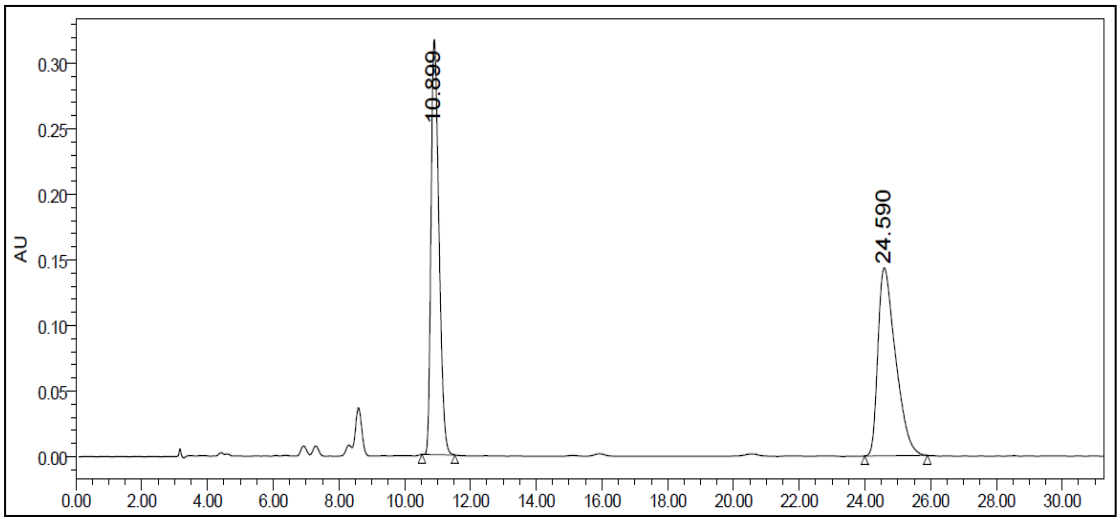


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	12.969	637493	33032	48.41
2	PDA 280.0 nm	22.356	679244	19786	51.59

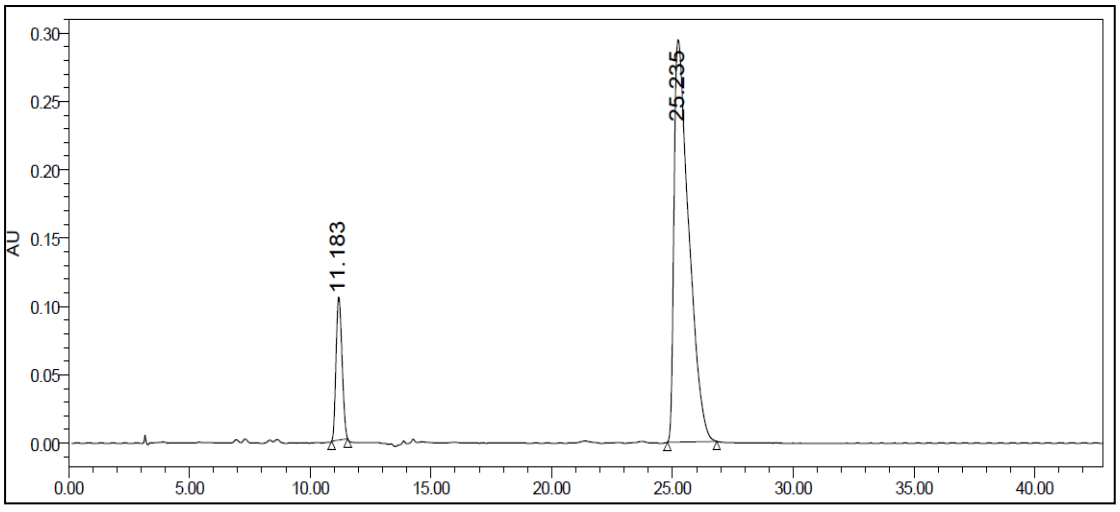


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	13.000	2796	158	0.34
2	PDA 280.0 nm	22.241	815878	25923	99.66

3d HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60: 38: 2, 1.0 mL/min)

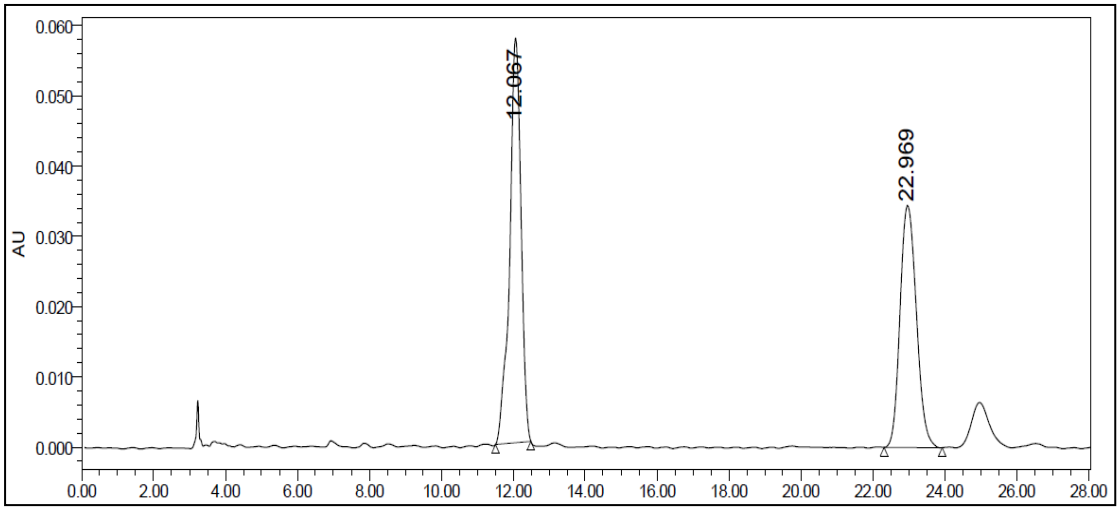


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	10.899	5289590	316620	49.76
2	PDA 280.0 nm	24.590	5340889	143342	50.24

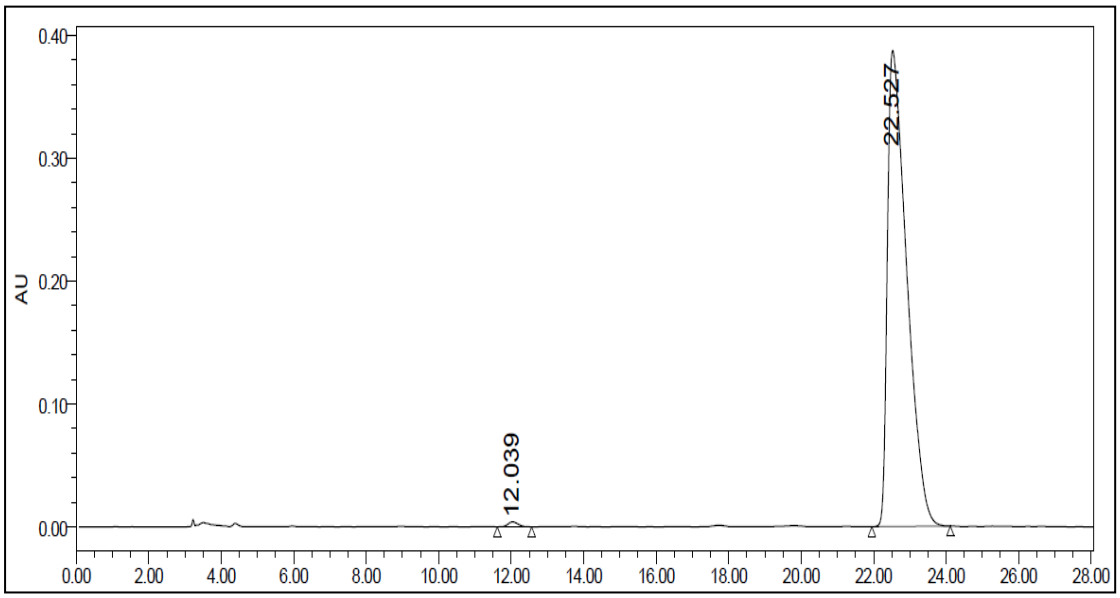


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	11.183	1803973	104413	12.64
2	PDA 280.0 nm	25.235	12468343	294297	87.36

3e HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60: 38: 2, 1.0 mL/min)

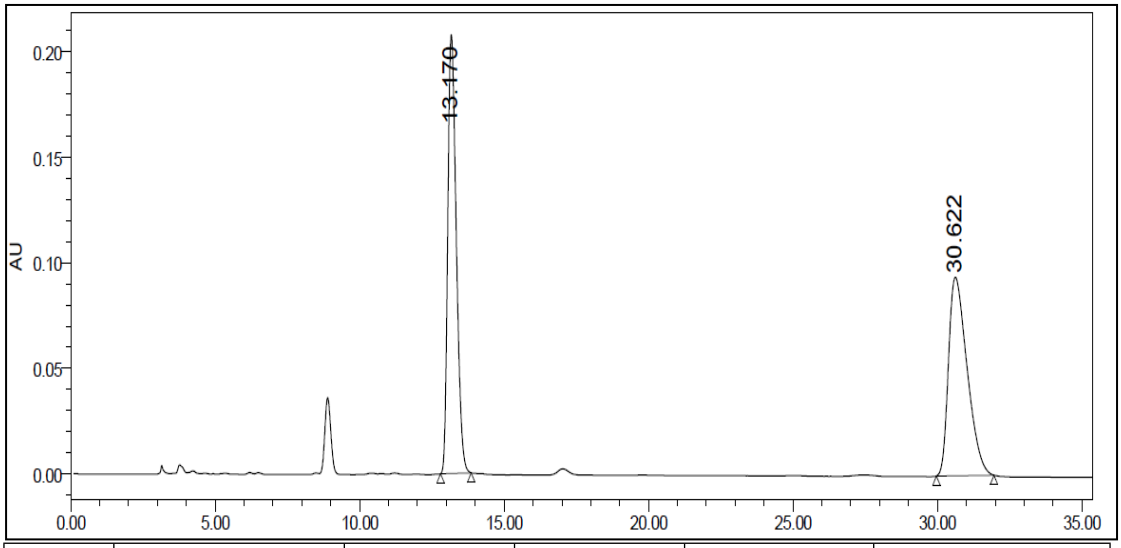


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	12.067	1265283	57574	53.79
2	PDA 280.0 nm	22.969	1086991	34404	46.21

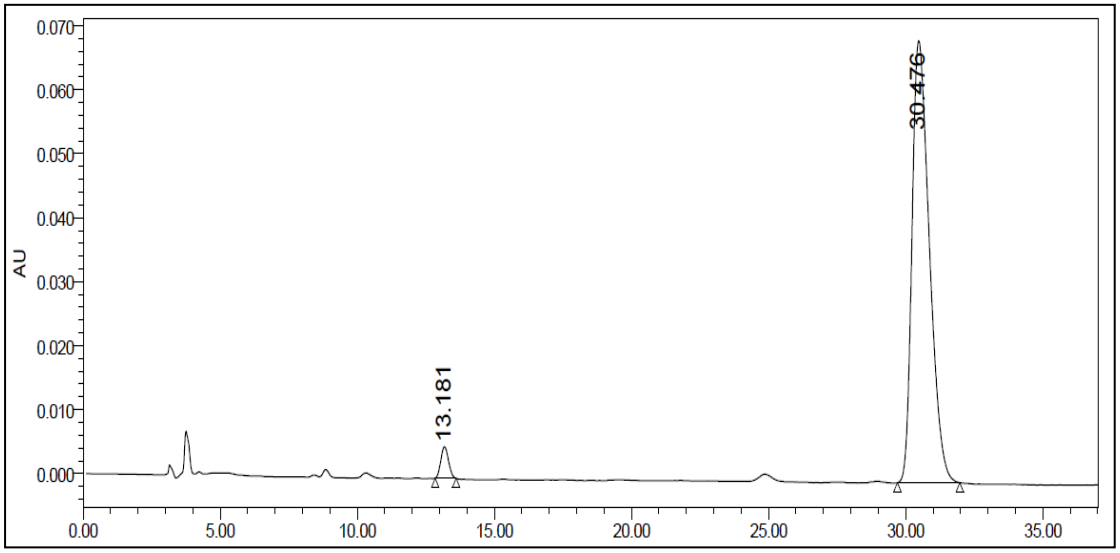


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	12.039	77647	4051	0.54
2	PDA 280.0 nm	22.527	14339781	387485	99.46

3f HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)

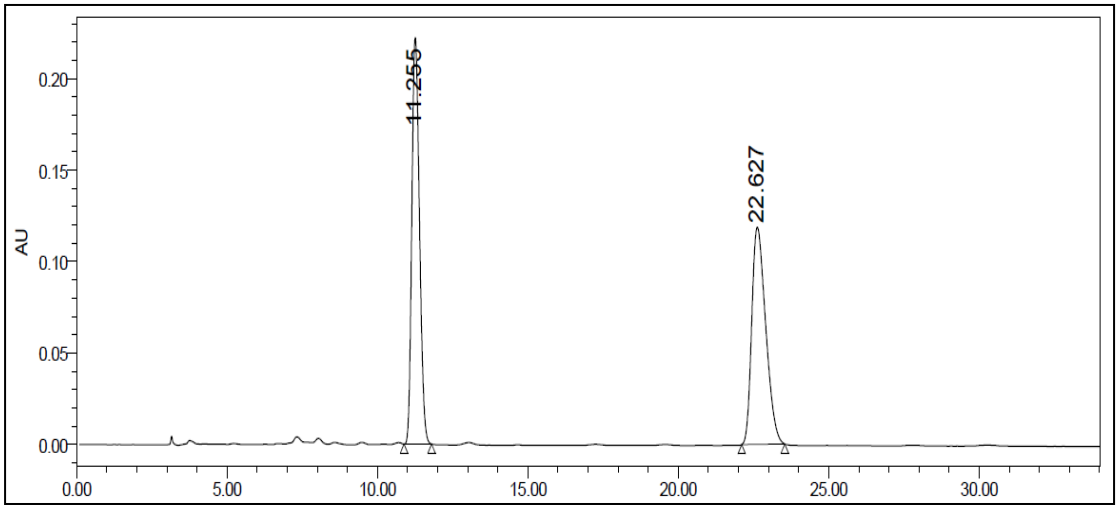


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	13.170	4263845	207980	50.30
2	PDA 280.0 nm	30.622	4213492	94090	49.70

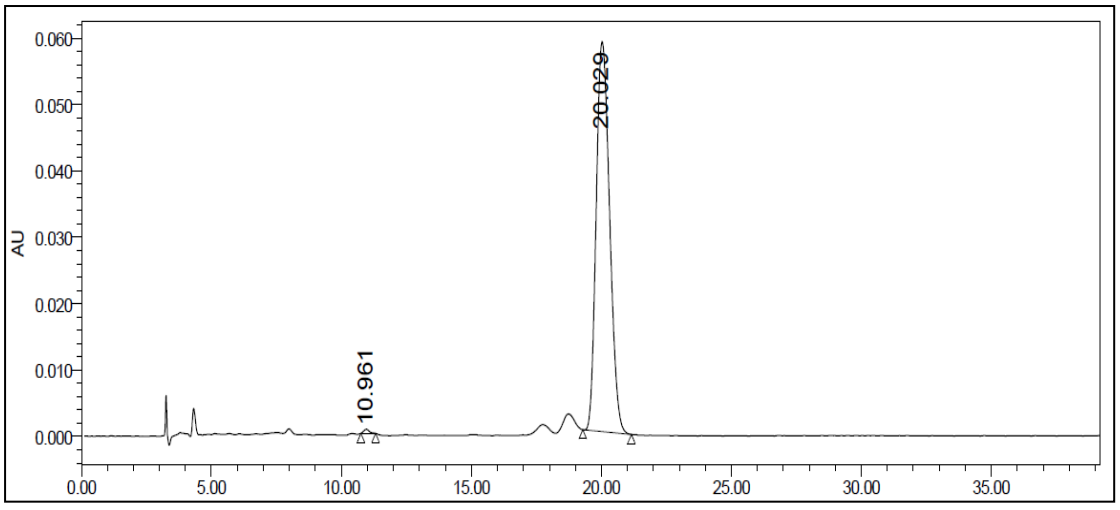


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	13.181	96638	4939	3.09
2	PDA 280.0 nm	30.476	3030669	69058	96.91

3g HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)

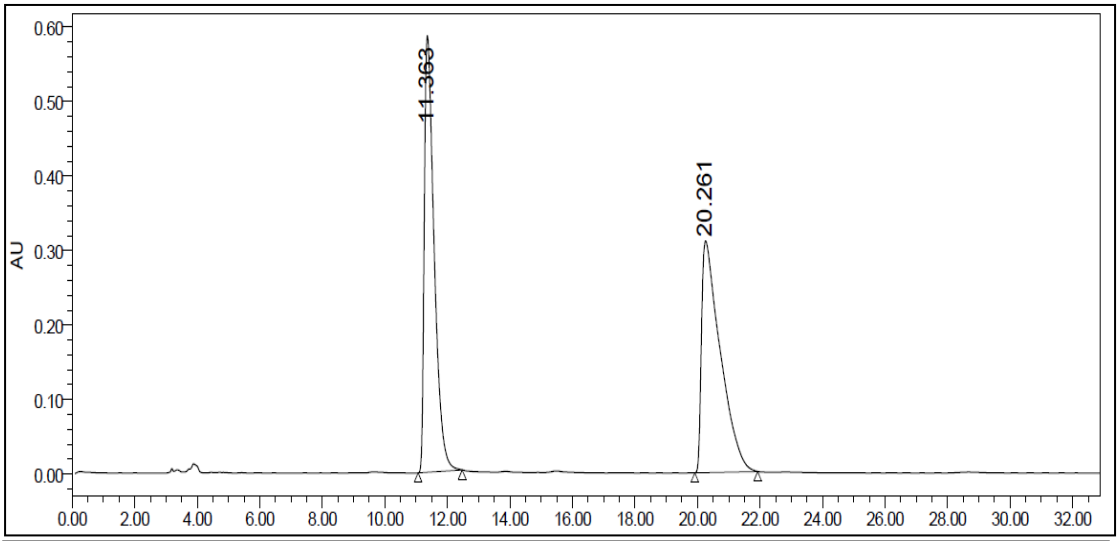


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	11.255	3923952	222300	50.59
2	PDA 280.0 nm	22.627	3832811	118784	49.41

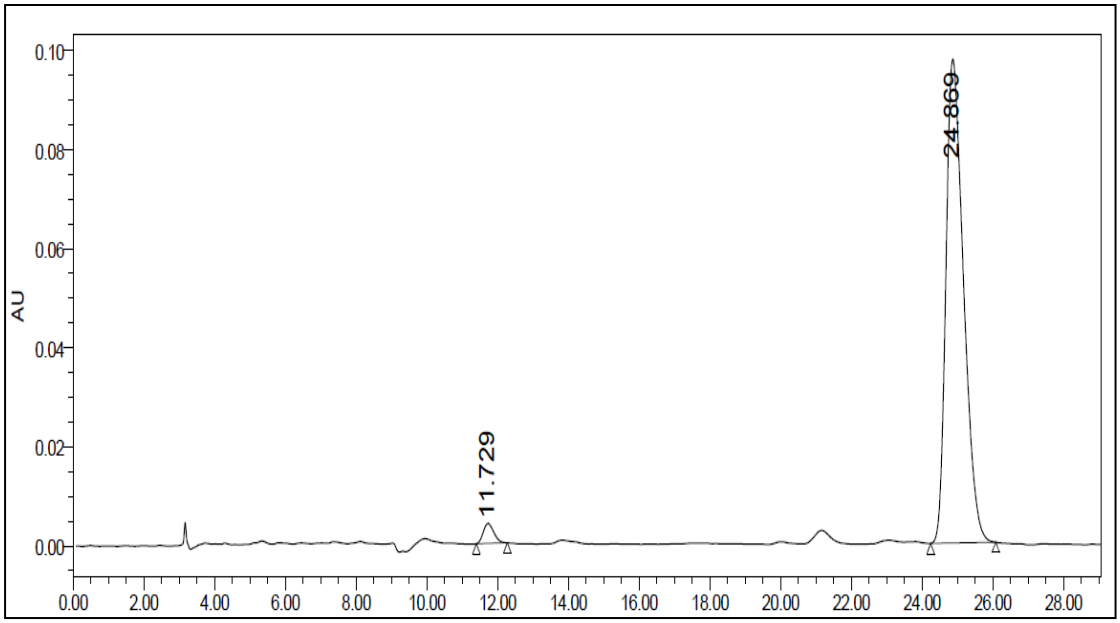


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	10.961	8913	598	0.42
2	PDA 280.0 nm	20.029	2106031	58763	99.58

3h HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)

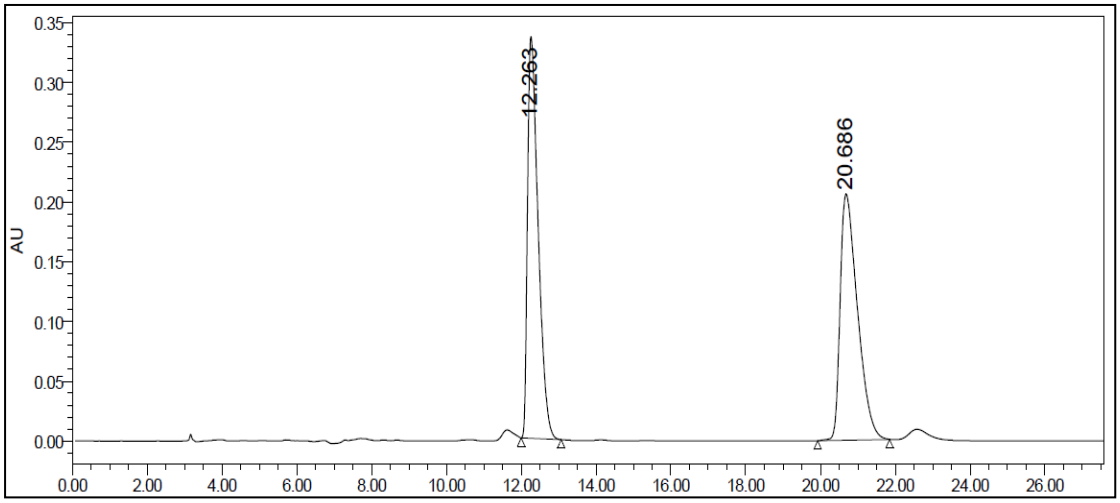


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	11.363	12809902	586308	49.70
2	PDA 280.0 nm	20.261	12962092	310824	50.30

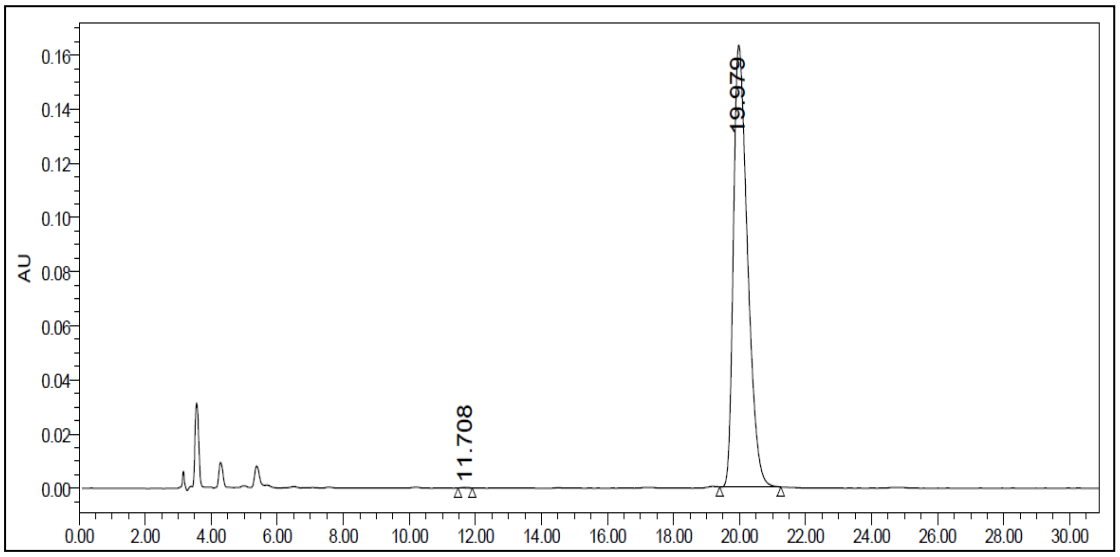


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	11.729	82658	4004	2.39
2	PDA 280.0 nm	24.869	3369952	97687	97.61

3i HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)

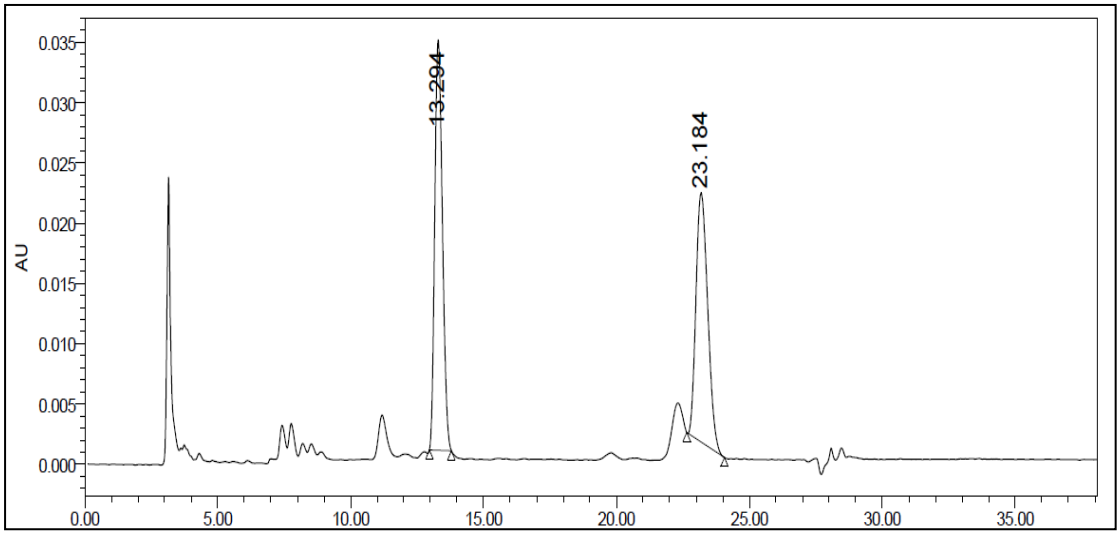


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	12.263	6606968	336103	49.94
2	PDA 280.0 nm	20.686	6623710	205914	50.06

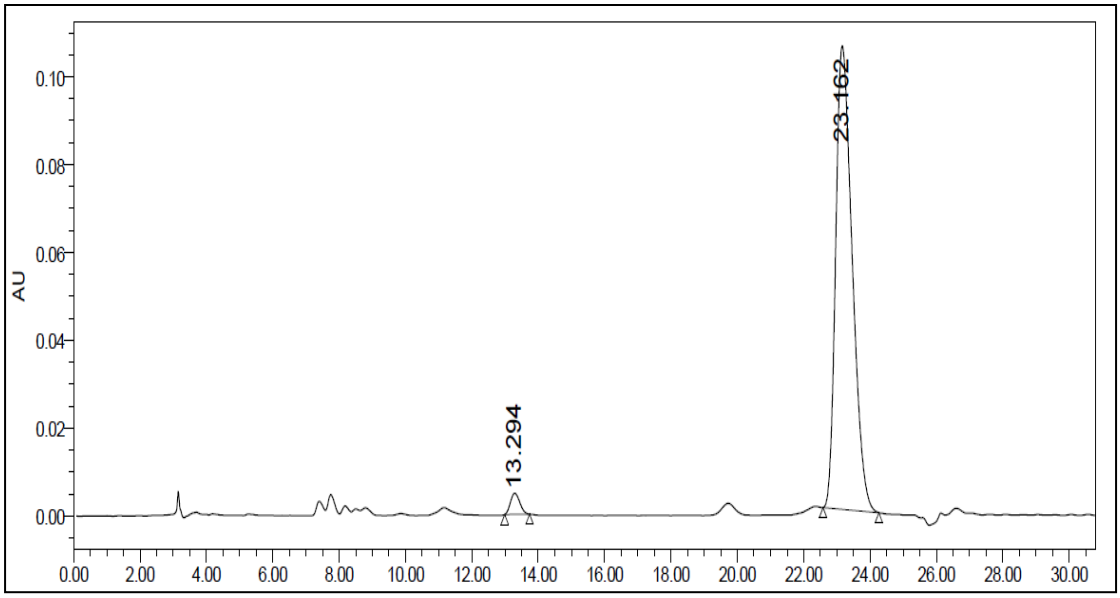


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	11.708	2893	199	0.06
2	PDA 280.0 nm	19.979	4835411	163205	99.94

3j HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)

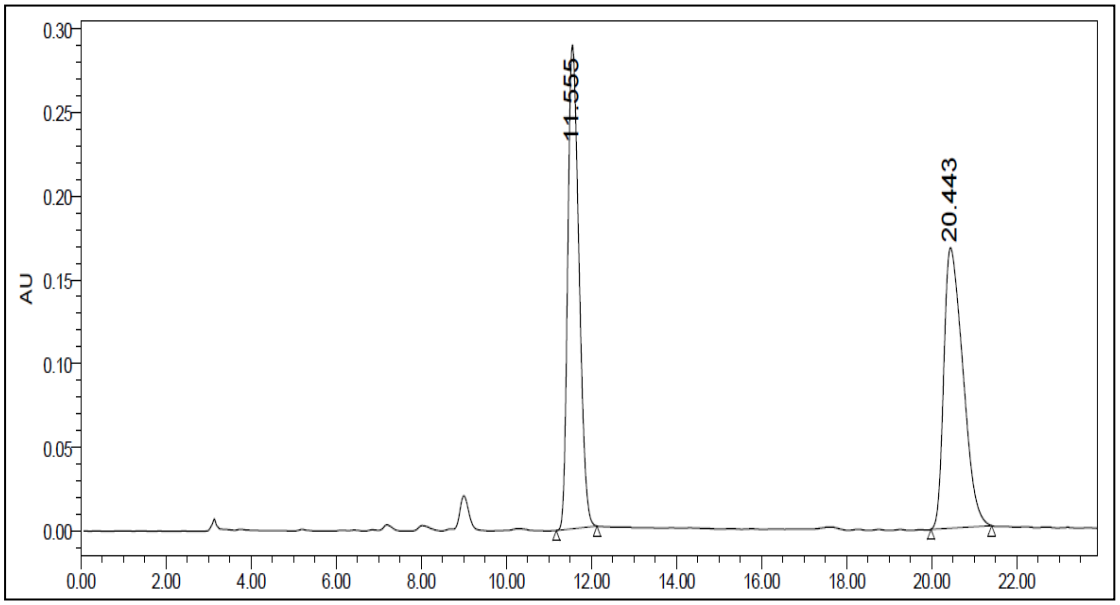


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	13.294	681462	34039	51.75
2	PDA 280.0 nm	23.184	635419	20671	48.25

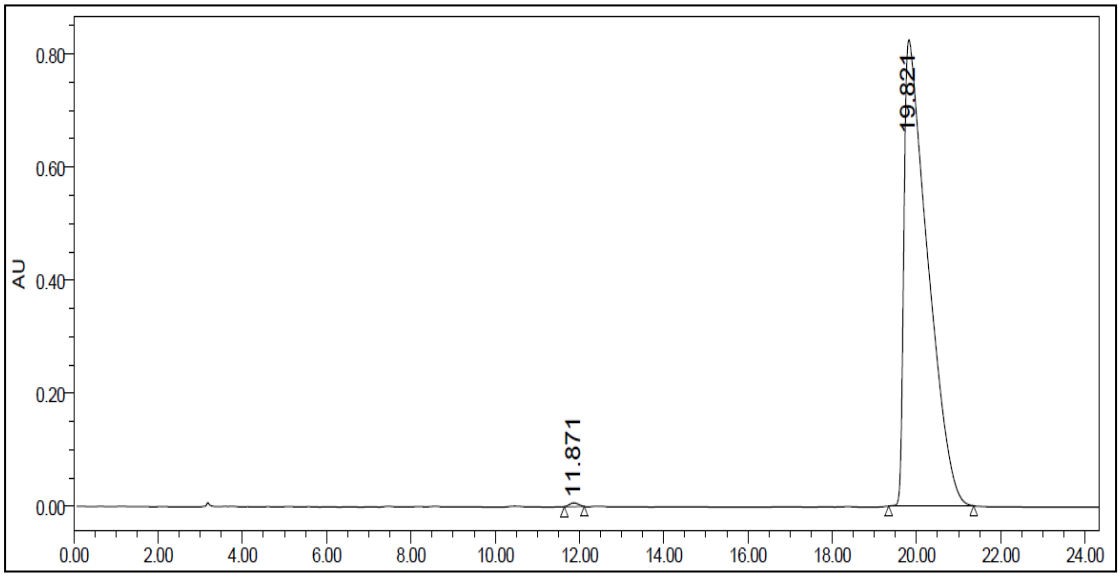


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	13.294	94317	4826	2.52
2	PDA 280.0 nm	23.162	3645939	105526	97.48

3k HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)

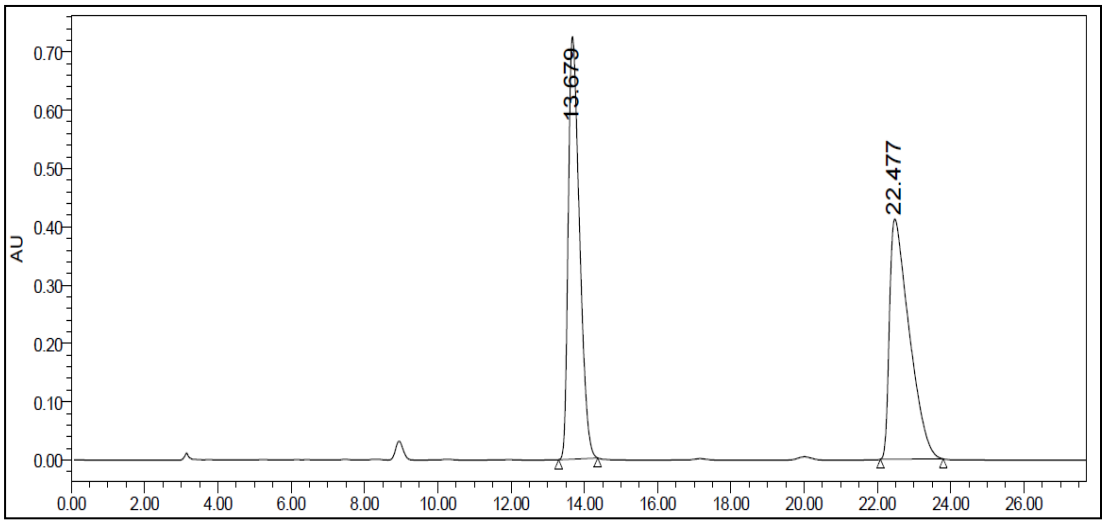


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	11.555	5283308	288836	50.28
2	PDA 280.0 nm	20.443	5224194	167406	49.72

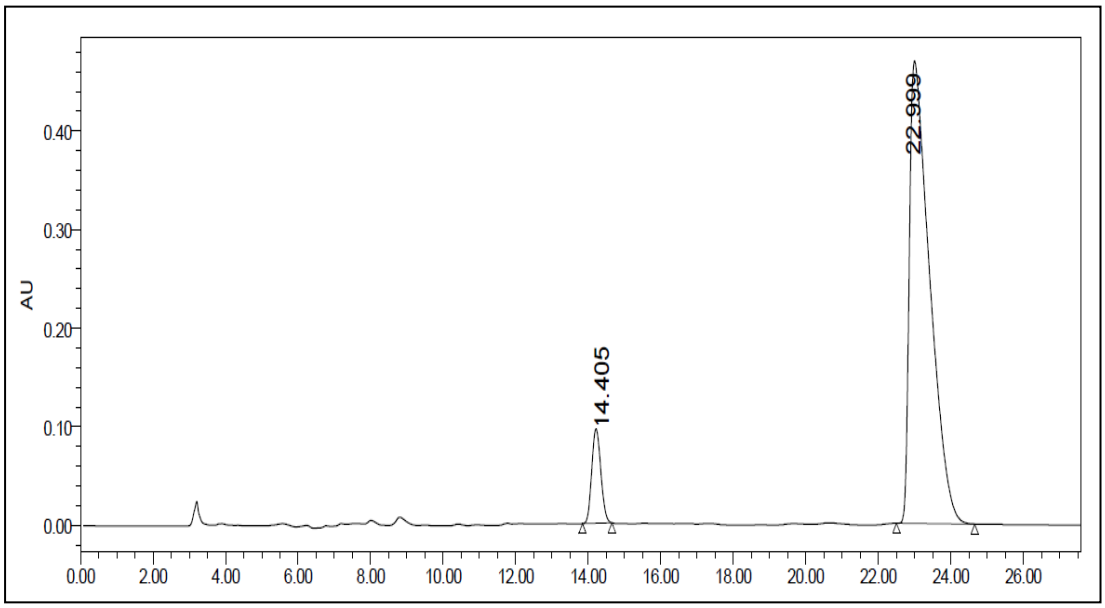


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	11.871	94577	6307	0.29
2	PDA 280.0 nm	19.821	32109368	824476	99.71

3l HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)

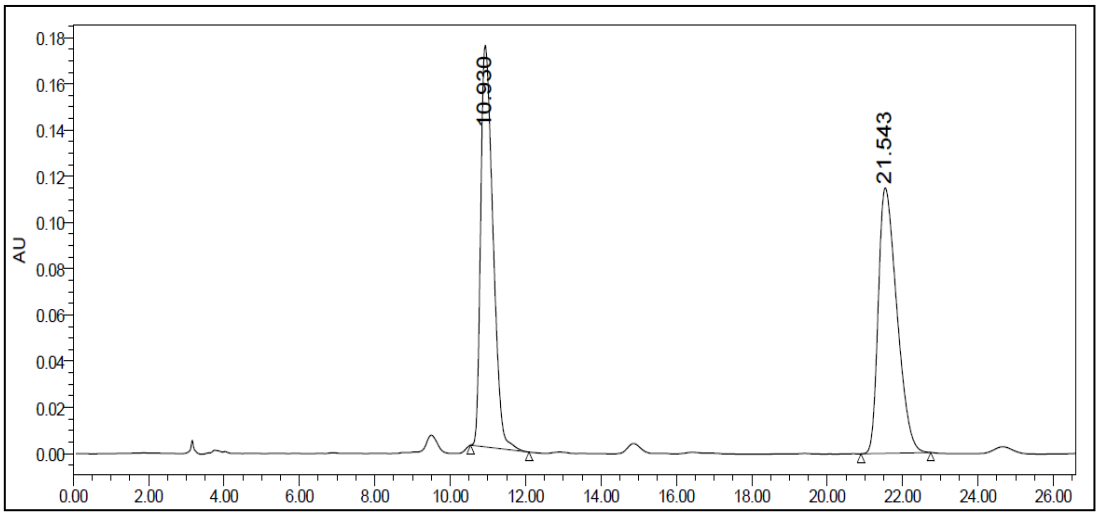


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	13.679	15445553	724835	50.06
2	PDA 280.0 nm	22.477	15409819	411828	49.94

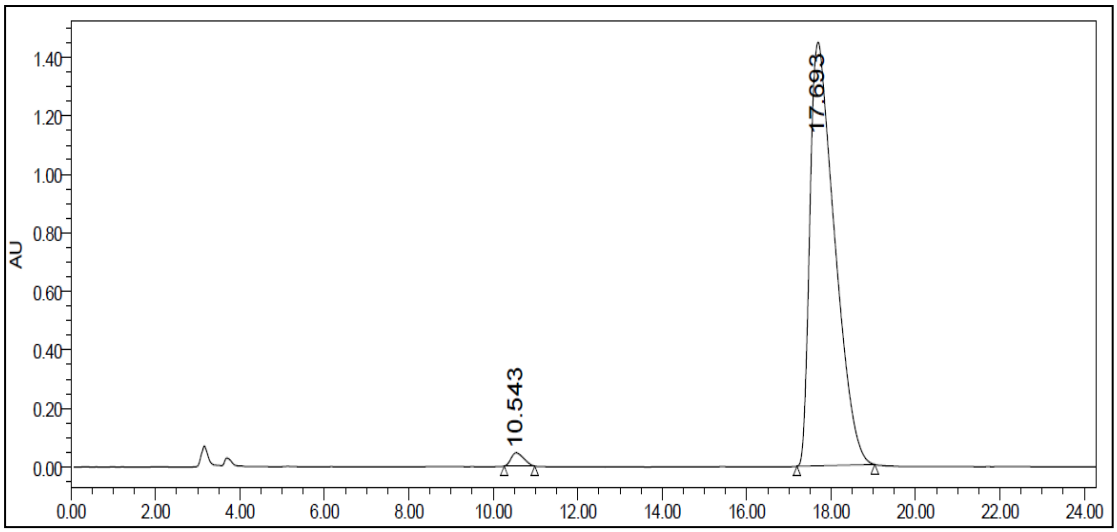


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	14.295	1500889	91418	7.70
2	PDA 280.0 nm	22.999	18238155	469266	92.40

3m HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)

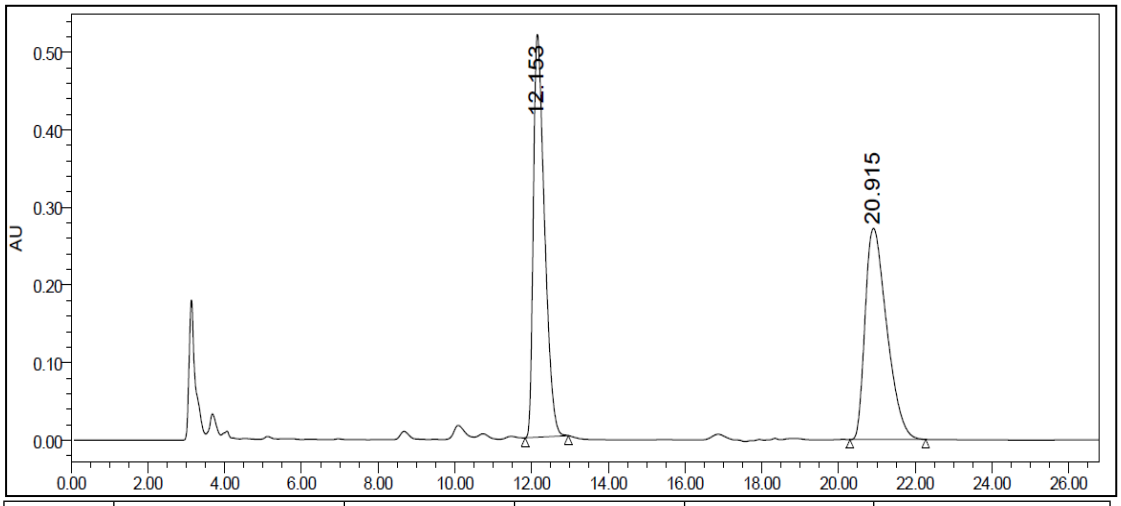


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	10.930	3921957	173757	49.96
2	PDA 280.0 nm	21.543	3928659	114847	50.04

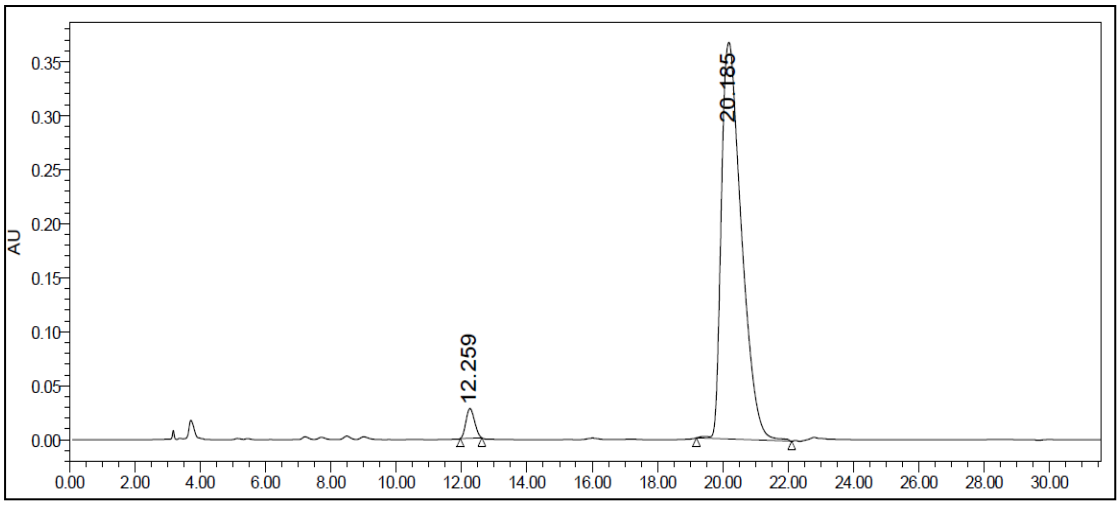


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	10.543	941017	45109	1.57
2	PDA 280.0 nm	17.693	58827390	1447939	98.43

3n HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)

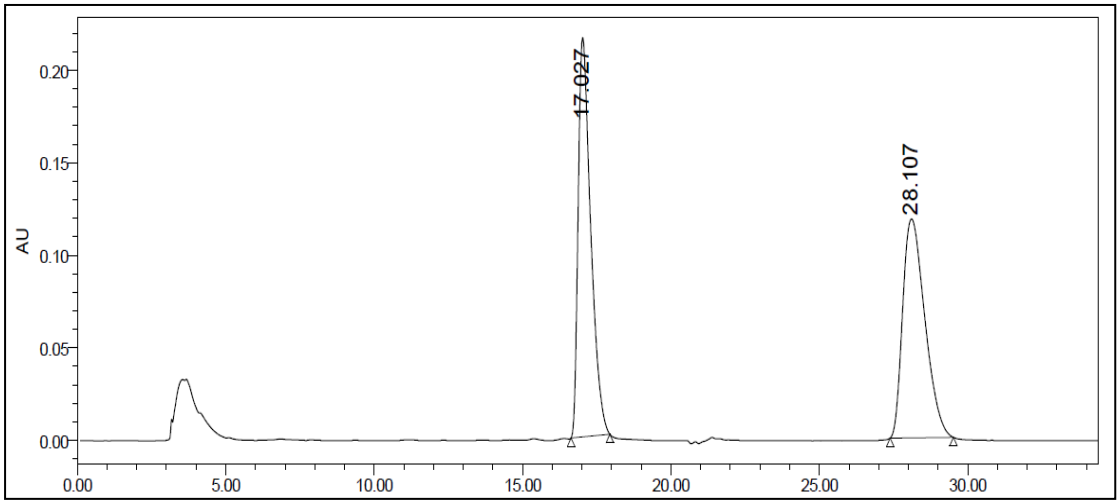


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	12.153	10501833	519135	49.55
2	PDA 280.0 nm	20.915	10691268	272025	50.45

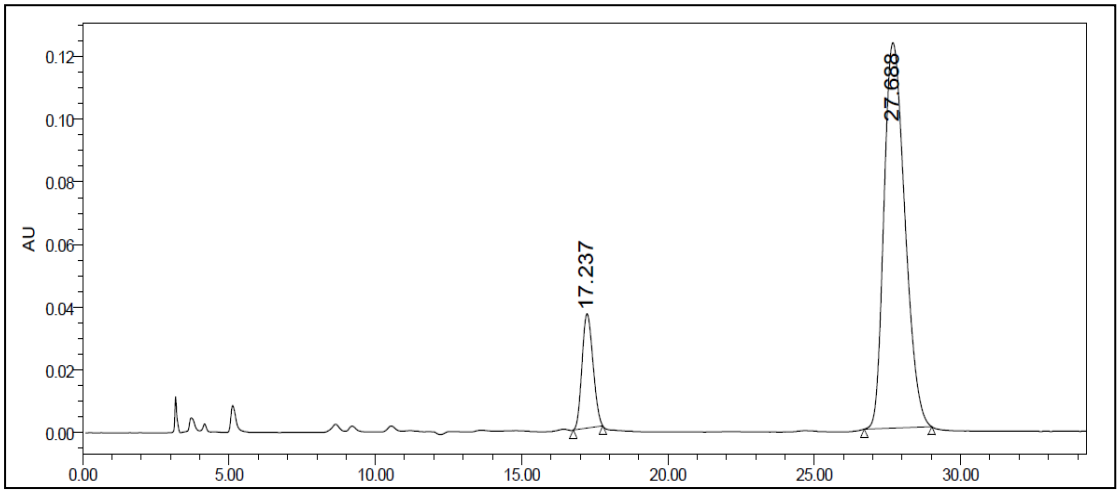


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	12.259	503249	27530	3.11
2	PDA 280.0 nm	20.185	15652579	367213	96.89

3o HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)

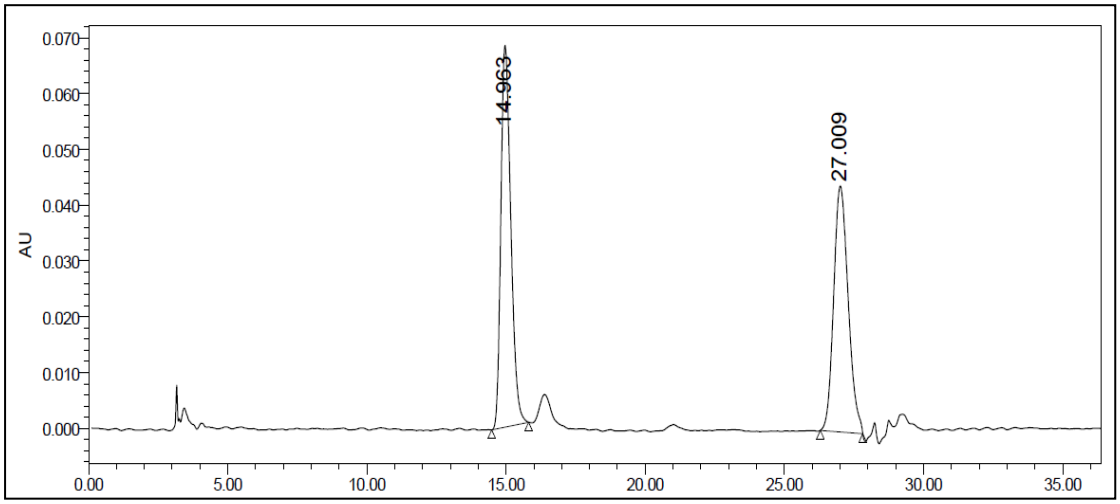


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	17.027	6318617	215650	50.69
2	PDA 280.0 nm	28.107	6146477	118210	49.31

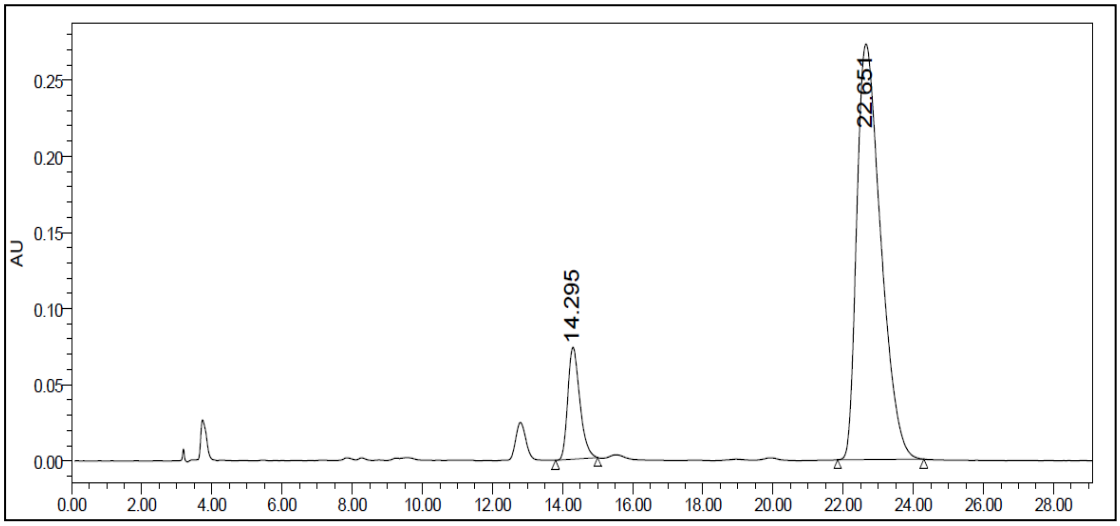


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	17.237	948154	36464	13.42
2	PDA 280.0 nm	27.688	6116222	122896	86.58

3p HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)

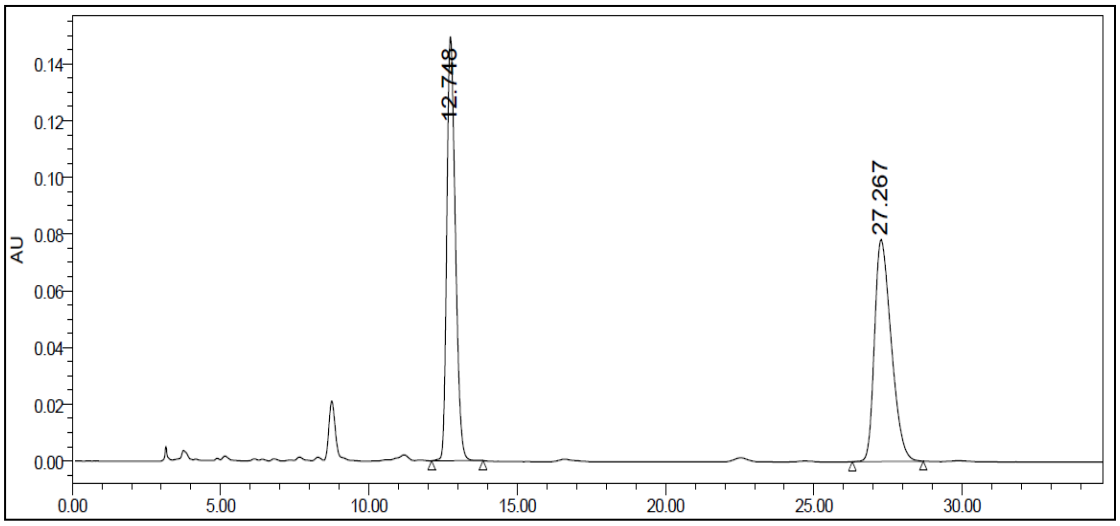


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	14.963	1698446	68456	51.52
2	PDA 280.0 nm	27.009	1598261	44088	48.48

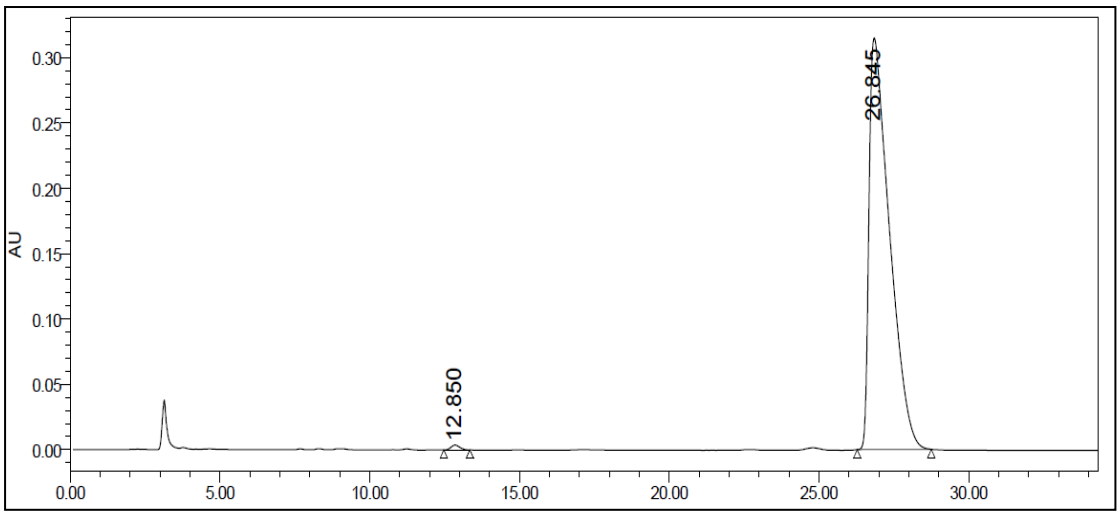


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	14.295	1751849	73489	11.91
2	PDA 280.0 nm	22.651	12953519	272819	88.09

3q HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)

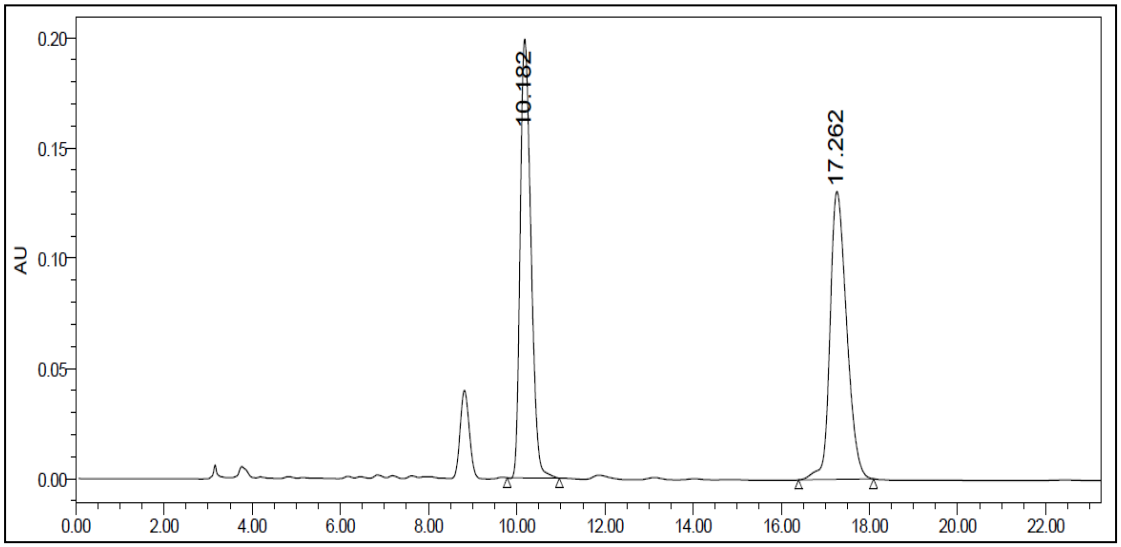


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	12.748	2988063	149488	49.37
2	PDA 280.0 nm	27.267	3064428	78172	50.63

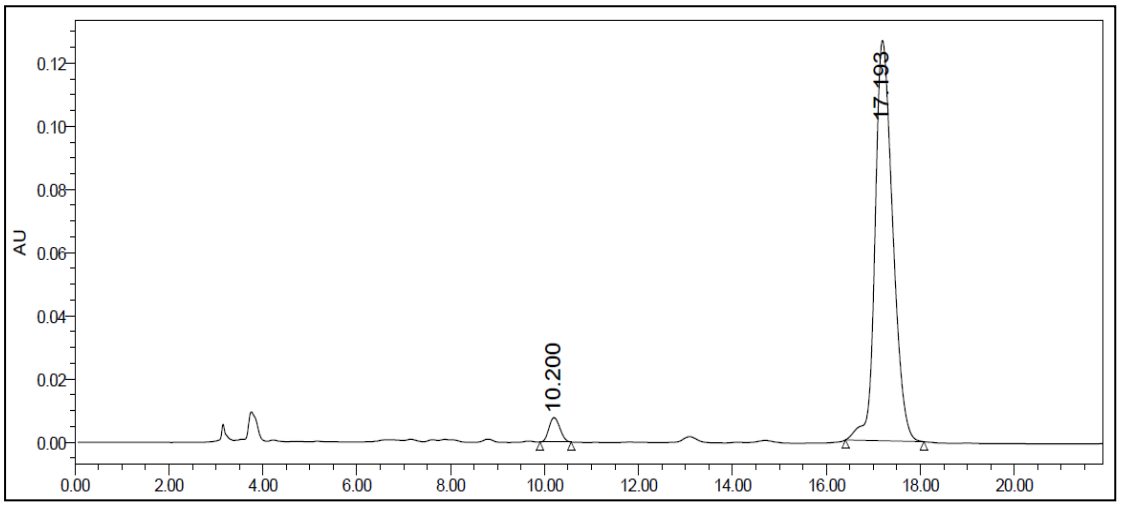


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	12.850	73211	3683	0.49
2	PDA 280.0 nm	26.845	14932253	315187	99.51

3r HPLC analysis using chiral ID-H Column (*n*-hexane: DCM: MeOH = 60:38:2, 1.0 mL/min)



Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	10.182	3361260	198936	49.52
2	PDA 280.0 nm	17.262	3426681	130570	50.48



Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.0 nm	10.200	126283	7784	3.67
2	PDA 280.0 nm	17.193	3313354	126659	96.33