Supporting Information

Direct Construction of Chiral Quaternary Dihydropyranones through Highly Enantioselective Organocatalytic Hetero-Diels-Alder Reactions of Olefinic Azlactones

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contents

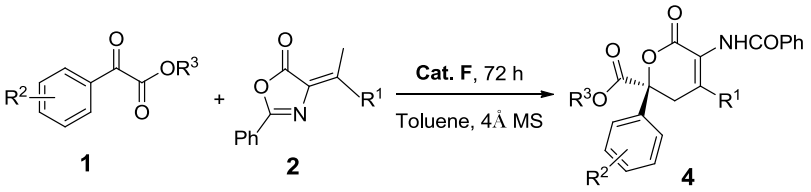
1. General information

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 $CDCl_3$ 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 ($CDCl_3$: δ_H = 7.27 ppm, δ_C = 77.00 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 Daicel Chirapak AD-H columns on Agilent 1100 eluting with EtOH and n-hexane or with Chiralcel ID-H and IA-H columns on Waters 1525/2998 eluting with DCM and n-hexane. α-keto esters **1**[1] and olefinic azalctones **2**[2] were prepared according to the literature procedures.

1 J. Zhuang, C. Wang, F. Xie, W. Zhang, *Tetrahedron*, 2009, **65**, 9797.

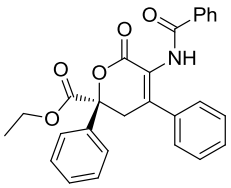
2 R. M. A. Motaleb, H. M. Bakeer, G. H. Tamam, W. A. A. Arafa, *J. Heterocyclic Chem.* 2012, **49**, 1071.

2. General procedure for the synthesis of products **4** and analytical data



To an oven-dried 25 ml Schlenk tube equipped with a stir bar was charged with catalyst **F** (0.01 mmol) and 4Å MS (100 mg). This tube was closed with a septum, evacuated, and backed-filled with N_2. To this mixture was added freshly distilled Toluene (1.0 mL), olefinic azlactones **2** (0.1 mmol) and α-keto esters **1** (0.3 mmol). The mixture was stirred at room temperature for 72 h under N_2 atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica gel, mixtures of petroleum/ethyl acetate) to afford the pure product **4**.

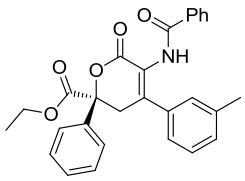
(S)-ethyl 5-benzamido-6-oxo-2,4-diphenyl-3,6-dihydro-2H-pyran-2-carboxylate (4a)



4a

White solid; 73% yield (32.2 mg); 95% ee; $[\alpha]_D^{20}$ = -169.8 (*c* 0.27, CH_2Cl_2); mp 108−112 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 65:35), 1.0 mL/min, λ = 230.16 nm, $t_{R(minor)}$ = 26.3 min, $t_{R(major)}$ = 14.1 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.67−7.01 (m, 4H), 7.42−7.49 (m, 4H), 7.35−7.41 (m, 6H), 7.29−7.32 (m, 1H), 4.24−4.33 (m, 2H), 3.98 (d, *J* = 18.0 Hz, 1H), 3.28 (d, *J* = 18.0 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 164.4, 163.5, 142.8, 140.0, 136.4, 133.8, 132.0, 129.3, 129.1, 128.8, 128.7, 128.6, 127.3, 126.9, 125.1, 120.9, 83.9, 63.2, 39.4, 14.0. IR (KBr, cm^{-1}): 3310, 2926, 2373, 1721, 1666, 1602, 1580, 1476, 1448, 1364, 1275, 1167, 1137, 1048, 715, 696, 585. HRMS (ESI) for $C_{27}H_{24}NO_5$ $[M+H]^+$ calcd. 442.1649, found 442.1642.

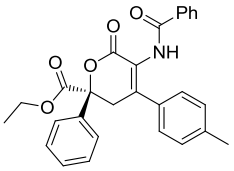
(S)-ethyl 5-benzamido-6-oxo-2-phenyl-4-(m-tolyl)-3,6-dihydro-2H-pyran-2-carboxylate (4b)



4b

White solid; 79% yield (35.9 mg); >99% ee; $[\alpha]_D^{20}$ = -68.7 (*c* 1.65, CH_2Cl_2); mp 123−128 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 70:30), 1.0 mL/min, λ = 280.16 nm, $t_{R(minor)}$ = 22.3 min, $t_{R(major)}$ = 55.3 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67−7.70 (m, 5H), 7.36−7.48 (m, 6H), 7.22−7.29 (m, 3H), 7.11 (d, *J* = 7.2 Hz, 1H), 4.28 (q, 2H), 3.97 (d, *J* = 18 Hz, 1H), 3.27 (d, *J* = 18 Hz, 1H), 2.32 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 164.6, 163.4, 143.2, 138.4, 136.8, 136.5, 133.9, 131.9, 130.2, 129.0, 128.8, 128.6, 128.5, 127.5, 127.3, 125.1, 124.0, 120.8, 83.8, 63.2, 39.7, 21.5, 14.0. IR (KBr, cm^{-1}): 3333, 2926, 2370, 1735, 1665, 1600, 1586, 1470, 1458, 1271, 1163, 1131, 787, 738, 703. HRMS (ESI) for $C_{28}H_{25}NO_5$ $[M+H]^+$ calcd. 456.1805, found 456.1802.

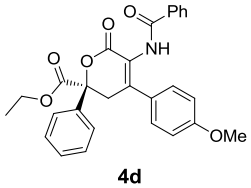
(S)-ethyl 5-benzamido-6-oxo-2-phenyl-4-(p-tolyl)-3,6-dihydro-2H-pyran-2-carboxylate (4c)



4c

White solid; 76% yield (34.6 mg); 95% ee; $[\alpha]_D^{20}$ = -18.8 (*c* 0.47, CH_2Cl_2); mp 81−84 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 280.16 nm, $t_{R(minor)}$ = 28.5 min, $t_{R(major)}$ = 12.9 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 4H), 7.37−7.50 (m, 6H), 7.17 (d, J = 8 Hz, 2H), 4.24−4.30 (m, 2H), 3.97 (d, *J* = 17.6 Hz, 2H), 3.26 (d, *J* = 17.6 Hz, 1H), 2.31 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 164.4, 163.4, 143.2, 138.3, 136.7, 136.4, 133.9, 131.9, 130.2, 129.0, 128.8, 128.6, 128.5, 127.6, 127.3, 125.1, 124.0, 120.8, 83.8, 63.1, 39.3, 21.5, 14.0. IR (KBr, cm^{-1}): 3346, 3061, 2961, 2925, 2855, 1736, 1670, 1604, 1581, 1510, 1478, 1450, 1358, 1269, 1165, 1136, 1117, 1099, 1049, 820, 734, 699, 663. HRMS (ESI) for $C_{28}H_{25}NO_5$ $[M+H]^+$ calcd. 456.1805, found 456.1797.

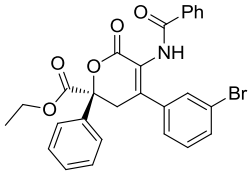
(S)-ethyl 5-benzamido-4-(4-methoxyphenyl)-6-oxo-2-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (4d)



4d

White solid; 83% yield (39.1 mg); 91.5% ee; $[\alpha]_D^{20}$ = -128.5 (*c* 0.90, CH_2Cl_2); mp 78−80 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 230.16 nm, $t_{R(minor)}$ = 40.2 min, $t_{R(major)}$ = 13.9 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 769−7.71 (m, 4H), 7.35−7.49 (m, 8H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.22−4.30 (m, 2H), 3.96 (d, *J* = 18 Hz, 1H), 3.76 (s, 3H), 3.24 (d, *J* = 18 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 164.5, 163.7, 160.2, 136.4, 133.7, 131.8, 128.9, 128.8, 128.7, 128.6, 128.5, 127.2, 125.0, 119.9, 114.1, 83.6, 63.1, 55.1, 39.1, 13.9. IR (KBr, cm^{-1}): 3347, 3062, 2925, 2853, 2373, 1736, 1686, 1665, 1605, 1510, 1477, 1359, 1268, 1164, 1131, 1075, 1101, 1049, 836, 772, 736, 703. HRMS (ESI) for $C_{28}H_{25}NO_6$ $[M+H]^+$ calcd. 472.1755, found 472.1747.

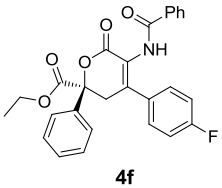
(S)-ethyl 5-benzamido-4-(3-bromophenyl)-6-oxo-2-phenyl-3,6-dihydro-2H-pyran-2-carboxylate **(4e)**



4e

White solid; 62% yield (32.2 mg); 97% ee; $[\alpha]_D^{20}$ = -100.6 (*c* 0.91, CH_2Cl_2); mp 80−85℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 280.16 nm, $t_{R(minor)}$ = 21.0 min, $t_{R(major)}$ = 14.9 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 767−7.71 (m, 4H), 7.62 (s, 1H), 7.38−7.51 (m, 8H), 7.24 (d, *J* = 9.0 Hz, 1H), 4.25−4.31 (m, 2H), 3.92 (d, *J* = 18 Hz, 1H), 3.26 (d, *J* = 18 Hz, 1H), 1.24 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 164.4, 163.3, 140.7, 139.0, 136.0, 133.6, 132.2, 132.0, 130.2, 129.8, 129.2, 128.8, 128.6, 127.2, 125.5, 125.0, 122.6, 121.4, 83.9, 63.2, 39.1, 14.0. IR (KBr, cm^{-1}): 3344, 3062, 2926, 2856, 2372, 1736, 1720, 1686, 1672, 1656, 1509, 1475, 1467, 1450, 1357, 1269, 1165, 1135, 1096, 1048, 791, 736, 703. HRMS (ESI) for $C_{27}H_{22}BrNO_5$ $[M+H]^+$ calcd. 520.0754, found 520.0748.

(S)-ethyl 5-benzamido-4-(4-fluorophenyl)-6-oxo-2-phenyl-3,6-dihydro-2H-pyran -2-carboxylate (4f)

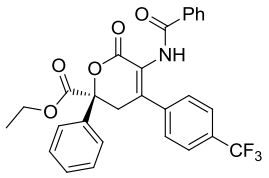


4f

White solid; 66% yield (30.3 mg); 96% ee; $[\alpha]_D^{20}$ = -72.1 (*c* 1.35, CH_2Cl_2); mp 123−126 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 230.16 nm, $t_{R(minor)}$ = 27.8 min, $t_{R(major)}$ = 15.5 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 768−7.70 (m, 4H), 746−7.50 (m, 4H), 7.37−7.44 (m, 4H), 7.05 (d, *J* = 8.8 Hz, 2H), 4.21−4.33 (m, 2H),

3.94 (d, *J* = 17.6 Hz, 1H), 3.26 (d, *J* = 17.6 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 164.3, 164.1, 163.5, 141.5, 136.2, 133.6, 133.0, 133.0, 132.1, 129.1, 129.0, 128.9, 128.8, 128.6, 127.2, 125.1, 120.9, 116.0, 115.8, 83.9, 63.2, 39.5, 14.0. IR (KBr, cm^{-1}): 3353, 3064, 2926, 2856, 2372, 1736, 1656, 1602, 1466, 1460, 1449, 1270, 1228, 1159, 1134, 841, 768, 738, 705, 662. HRMS (ESI) for $C_{27}H_{22}FNO_5$ $[M+H]^+$ calcd. 460.1555, found 460.1552.

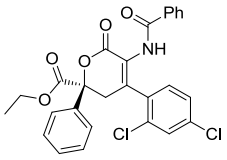
(S)-ethyl 5-benzamido-6-oxo-2-phenyl-4-(4-(trifluoromethyl)phenyl)-3,6-dihydro-2H-pyran-2-carboxylate (4g)



4g

White solid; 61% yield (31.0 mg); 96% ee; $[\alpha]_D^{20}$ = -17.8 (*c* 1.13, CH_2Cl_2); mp 116−118 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 230.16 nm, $t_{R(minor)}$ = 10.6 min, $t_{R(major)}$ = 7.05 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.67−7.71 (m, 4H), 7.58−7.63 (m, 4H), 7.49−7.53 (m, 1H), 7.39−7.47 (m, 5H), 4.22−4.34 (m, 2H), 3.96 (d, *J* = 18 Hz, 1H), 3.29 (d, *J* = 18 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 164.1, 163.3, 140.9, 140.1, 136.0, 133.3, 132.2, 129.2, 128.8, 128.7, 127.3, 127.2, 125.7, 125.7, 125.0, 121.6, 84.1, 63.3, 39.2, 14.0. IR (KBr, cm^{-1}): 3324, 3065, 2927, 2373, 1739, 1617, 1509, 1477, 1450, 1410, 1324, 1272, 1167, 1127, 1065, 1017, 845, 699, 608. HRMS (ESI) for $C_{28}H_{22}F_3NO_5$ $[M+H]^+$ calcd. 510.1523, found 510.1526.

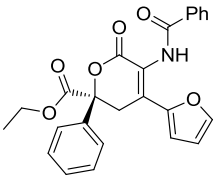
(S)-ethyl 5-benzamido-4-(2,4-dichlorophenyl)-6-oxo-2-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (4h)



4h

White solid; 67% yield (34.1 mg); 98% ee; $[\alpha]_D^{20}$ = -25.9 (*c* 0.39, CH_2Cl_2); mp 59−60 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 280.16 nm, $t_{R(minor)}$ = 20.6 min, $t_{R(major)}$ = 12.6 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.68−7.70 (m, 4H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.50−7.54 (m, 1H), 7.35−7.47 (m, 6H), 7.33 (d, *J* = 1.6 Hz, 1H), 4.21−4.33 (m, 2H), 3.91 (d, *J* = 18 Hz, 1H), 3.25 (d, *J* = 18 Hz, 1H), 1.23 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 164.3, 163.3, 138.7, 137.1, 135.9, 133.4, 133.3, 133.0, 132.3, 130.8, 129.3, 128.9, 128.9, 128.8, 127.2, 126.3, 125.0, 121.5, 84.0, 63.3, 39.0, 14.0. IR (KBr, cm^{-1}): 3349, 2925, 2855, 2373, 1737, 1656, 1601, 1581, 1510, 1475, 1383, 1271, 1199, 1165, 1133, 1097, 1049, 702. HRMS (ESI) for $C_{27}H_{21}Cl_2NO_5$ $[M+H]^+$ calcd. 510.0870, found 510.0867.

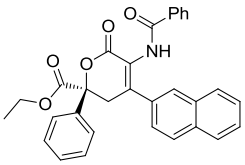
(S)-ethyl 5-benzamido-4-(furan-2-yl)-6-oxo-2-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (4i)



4i

White solid; 63% yield (27.2 mg); 91% ee; $[\alpha]_D^{20}$ = -67.9 (*c* 1.33, CH_2Cl_2); mp 82−85 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 230.16 nm, $t_{R(minor)}$ = 24.1 min, $t_{R(major)}$ = 8.0 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.91 (d, *J* = 7.2 Hz, 2H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.53−7.58 (m, 2H), 7.39−7.49 (m, 5H), 6.81 (d, *J* = 3.6 Hz, 1H), 6.51−6.52 (m, 1H), 4.20−4.25 (m, 2H), 4.14 (d, *J* = 17.6 Hz, 1H), 3.27 (d, *J* = 18 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 165.0, 163.3, 148.9, 145.2, 136.6, 133.7, 132.2, 129.5, 129.0, 128.7, 128.7, 127.5, 125.1, 117.3, 116.2, 112.8, 83.3, 63.1, 35.1, 13.9. IR (KBr, cm^{-1}): 3342, 3063, 2924, 2367, 1736, 1686, 1628, 1509, 1475, 1450, 1270, 1166, 1138, 1107, 1051, 737, 702. HRMS (ESI) for $C_{25}H_{21}NO_6$ $[M+H]^+$ calcd. 432.1442, found 432.1439.

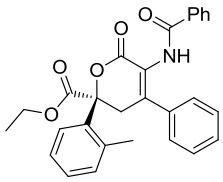
(S)-ethyl 5-benzamido-4-(naphthalen-2-yl)-6-oxo-2-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (4j)



4j

White solid; 63% yield (30.9 mg); 96% ee; $[\alpha]_D^{20}$ = -103.8 (*c* 0.11, CH_2Cl_2); mp 93−95 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 280.16 nm, $t_{R(minor)}$ = 38.4 min, $t_{R(major)}$ = 16.1 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 7.2 Hz, 3H), 7.54−7.58 (m, 2H), 7.38−7.50 (m, 6H), 7.07−7.09 (m, 1H), 4.26 (q, *J* = 6.8 Hz, 2H), 4.16 (d, *J* = 16.8 Hz, 1H), 3.36 (d, *J* = 16.8 Hz, 1H), 1.20 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 166.3, 163.6, 137.9, 136.9, 136.5, 133.7, 132.2, 131.8, 130.7, 129.1, 128.8, 128.7, 127.6, 127.2, 125.1, 117.8, 83.2, 63.2, 37.8, 13.9. IR (KBr, cm^{-1}): 3339, 3059, 2959, 2926, 2854, 1734, 1672, 1600, 1581, 1507, 1475, 1450, 1365, 1270, 1164, 1132, 1098, 1075, 1049, 738, 702. HRMS (ESI) for $C_{31}H_{25}NO_5$ $[M+H]^+$ calcd. 492.1805, found 492.1801.

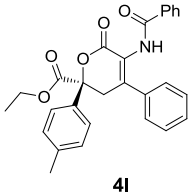
(S)-ethyl 5-benzamido-6-oxo-4-phenyl-2-(o-tolyl)-3,6-dihydro-2H-pyran-2-carboxylate (4k)



4k

White solid; 72% yield (32.7 mg); 93% ee; $[\alpha]_D^{20}$ = -92.4 (*c* 0.66, CH_2Cl_2); mp 116−118 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 280.16 nm, $t_{R(minor)}$ = 19.1 min, $t_{R(major)}$ = 9.9 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.54 (s, 1H), 7.46−7.50 (m, 4H), 7.35−7.40 (m, 4H), 7.28−7.34 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 4.24−4.32 (m, 2H), 3.97 (d, *J* = 17.6 Hz, 1H), 3.27 (d, *J* = 17.6 Hz, 1H), 2.39 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 164.4, 163.5, 142.9, 138.6, 136.9, 136.2, 133.7, 131.9, 129.8, 129.2, 128.6, 128.6, 128.5, 127.2, 126.9, 125.6, 122.0, 120.8, 83.9, 63.1, 39.3, 21.5, 14.0. IR (KBr, cm^{-1}): 3344, 3060, 2924, 2858, 2371, 1736, 1686, 1674, 1656, 1603, 1581, 1510, 1476, 1468, 1360, 1270, 1128, 1094, 1049, 702. HRMS (ESI) for $C_{28}H_{25}NO_5$ $[M+H]^+$ calcd. 456.1805, found 456.1808.

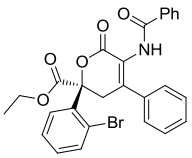
(S)-ethyl 5-benzamido-6-oxo-4-phenyl-2-(p-tolyl)-3,6-dihydro-2H-pyran-2-carboxylate (4l)



4l

White solid; 71% yield (32.2 mg); 91% ee; $[\alpha]_D^{20}$ = -250.9 (*c* 0.30, CH_2Cl_2); mp 120−122 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 230.16 nm, $t_{R(minor)}$ = 57.4 min, $t_{R(major)}$ = 13.2 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 4H), 7.43−7.48 (m, 2H), 7.38−7.41 (m, 6H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.23−4.31 (m, 2H), 3.97 (d, *J* = 17.6 Hz, 1H), 3.25 (d, *J* = 17.6 Hz, 1H), 2.31 (s, 1H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 164.4, 163.5, 142.7, 139.5, 136.4, 133.9, 133.9, 131.9, 129.4, 129.0, 128.7, 128.5, 127.3, 126.8, 125.1, 120.4, 83.8, 63.1, 39.3, 21.3, 14.0. IR (KBr, cm^{-1}): 3341, 3061, 2925, 2371, 1736, 1670, 1603, 1581, 1510, 1477, 1449, 1357, 1271, 1163, 1136, 1100, 820, 699. HRMS (ESI) for $C_{28}H_{25}NO_5$ $[M+H]^+$ calcd. 455.1805, found 455.1802.

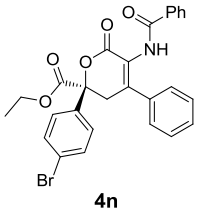
(S)-ethyl 5-benzamido-2-(2-bromophenyl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (4m)



4m

White solid; 62% yield (32.2 mg); 90.0% ee; $[\alpha]_D^{20}$ = -70.3 (*c* 0.56, CH_2Cl_2); mp 114−118 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 254.4 nm, $t_{R(minor)}$ = 49.2 min, $t_{R(major)}$ = 9.3 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.76−7.88 (m, 1H), 7.64−7.69 (m, 3H), 7.52−7.54 (m, 1H), 7.46−4.49 (m, 3H), 7.25−7.40 (m, 6H), 4.23−4.36 (m, 2H), 3.94 (d, *J* = 17.6 Hz, 1H), 3.24 (d, *J* = 17.6 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 164.4, 163.1, 142.9, 142.8, 138.5, 136.7, 133.6, 132.2, 132.0, 130.3, 129.4, 128.7, 128.6, 128.3, 127.2, 126.9, 123.7, 123.0, 120.9, 83.2, 63.5, 39.5, 14.0. IR (KBr, cm^{-1}): 3418, 2955, 2923, 2854, 2366, 1736, 1655, 1638, 1461, 1389, 1265, 1157, 1123, 1096, 740. HRMS (ESI) for $C_{27}H_{22}BrNO_5$ $[M+H]^+$ calcd. 520.0754, found 520.0751.

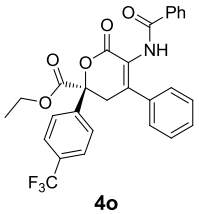
(S)-ethyl 5-benzamido-2-(4-bromophenyl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran -2-carboxylate (4n)



4n

White solid; 69% yield (35.8 mg); 95% ee; $[\alpha]_D^{20}$ = -101.6 (*c* 0.92, CH_2Cl_2); mp 78−83 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 230.16 nm, $t_{R(minor)}$ = 73.7 min, $t_{R(major)}$ = 13.5 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.55−7.61 (m, 4H), 7.46−7.50 (m, 3H), 7.31−7.40 (m, 4H), 7.29−7.31 (m, 1H), 4.22−4.34 (m, 2H), 3.94 (d, *J* = 18.0 Hz, 1H), 3.24 (d, *J* = 18.0 Hz, 1H), 1.25 (t, *J* = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 163.4, 162.1, 141.7, 135.7, 134.4, 132.6, 131.0, 130.9, 128.4, 127.7, 127.5, 126.2, 125.8, 125.8, 122.4, 119.9, 82.4, 62.4, 38.3, 12.9. IR (KBr, cm^{-1}): 3335, 2960, 2924, 2855, 1736, 1685, 1668, 1581, 1509, 1477, 1445, 1360, 1269, 1164, 1083, 1049, 1012, 765, 704. HRMS (ESI) for $C_{27}H_{22}BrNO_5$ $[M+H]^+$ calcd. 520.0754, found 520.0750.

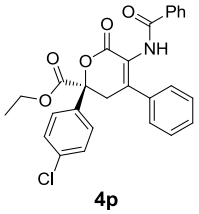
(S)-ethyl 5-benzamido-6-oxo-4-phenyl-2-(4-(trifluoromethyl)phenyl)-3,6-dihydro -2H-pyran-2-carboxylate (4o)



4o

White solid; 80% yield (40.7 mg); 97% ee; $[\alpha]_D^{20}$ = -52.9 (*c* 0.17, CH_2Cl_2); mp 118−120 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 230.16 nm, $t_{R(minor)}$ = 47.6 min, $t_{R(major)}$ = 8.5 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.75 (s, 1H), 7.67−7.71 (m, 4H), 7.47−7.51 (m, 3H), 7.36−7.41 (m, 4H), 7.30−7.33 (m, 1H), 4.23−4.36 (m, 2H), 3.99 (d, *J* = 17.6 Hz, 1H), 3.26 (d, *J* = 17.6 Hz, 1H), 1.25 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 164.5, 162.9, 142.8, 140.1, 136.6, 133.6, 132.0, 129.4, 128.7, 128.6, 127.2, 126.9, 125.8, 125.8, 125.7, 125.7, 125.6, 120.9, 83.3, 63.5, 39.5, 13.9. IR (KBr, cm^{-1}): 3394, 3307, 2956, 2925, 2854, 2376, 1725, 1668, 1509, 1477, 1413, 1328, 1164, 1130, 1108, 1071, 741, 716. HRMS (ESI) for $C_{28}H_{22}F_3NO_5$ $[M+H]^+$ calcd. 510.1523, found 510.1519.

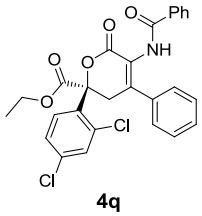
(S)-ethyl 5-benzamido-2-(4-chlorophenyl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran -2-carboxylate (4p)



4p

White solid; 73% yield (34.7 mg); 96% ee; $[\alpha]_D^{20}$ = -69.9 (*c* 0.27, CH_2Cl_2); mp 103−105 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 280.16 nm, $t_{R(minor)}$ = 64.7 min, $t_{R(major)}$ = 13.1 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.64−7.68 (m, 4H), 7.45−7.48 (m, 3H), 7.32−7.41 (m, 6H), 7.28−7.32 (m, 1H), 4.21−4.34 (m, 2H), 3.94 (d, *J* = 18.0 Hz, 1H), 3.24 (d, *J* = 18.0 Hz, 1H), 1.24 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 164.5, 163.1, 142.9, 136.7, 135.2, 135.0, 133.6, 131.9, 129.4, 129.0, 128.7, 128.6, 127.2, 126.9, 126.6, 121.0, 83.4, 63.4, 39.3, 14.0. IR (KBr, cm^{-1}): 3340, 2957, 2925, 2854, 1737, 1672, 1600, 1492, 1477, 1359, 1270, 1164, 1094, 1049, 1015, 765, 704, 594. HRMS (ESI) for $C_{27}H_{22}ClNO_5$ $[M+H]^+$ calcd. 476.1259, found 476.1262.

(S)-ethyl 5-benzamido-2-(2-bromo-4-chlorophenyl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (4q)

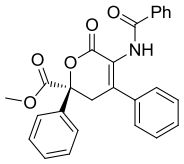


4q

White solid; 77% yield (39.2 mg); >99% ee; $[\alpha]_D^{20}$ = -89.4 (*c* 0.37, CH_2Cl_2); mp 116−119 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 254.4 nm, $t_{R(minor)}$ = 48.16 min, $t_{R(major)}$ = 12.4 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J*

= 7.2 Hz, 3H), 7.54−7.57 (m, 2H), 7.38−7.50 (m, 6H), 7.07−7.09 (m, 1H), 4.26 (q, *J* = 6.8 Hz, 2H), 4.16 (d, *J* = 16.8 Hz, 1H), 3.36 (d, *J* = 16.8 Hz, 1H), 1.20 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 164.2, 163.3, 138.7, 137.1, 135.9, 133.4, 133.3, 133.0, 132.3, 130.7, 129.2, 128.9, 128.9, 127.2, 126.2, 125.0, 121.5, 84.0, 63.3, 39.0, 14.0. IR (KBr, cm^{-1}): 3336, 2956, 2923, 2854, 2374, 1736, 1665, 1657, 1509, 1501, 1475, 1450, 1271, 1167, 1135, 1091, 1048, 702. HRMS (ESI) for $C_{27}H_{21}Cl_2NO_5$ $[M+H]^+$ calcd. 510.0870, found 510.0864.

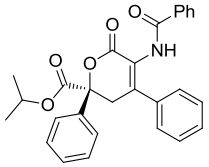
(S)-methyl 5-benzamido-6-oxo-2,4-diphenyl-3,6-dihydro-2H-pyran-2-carboxylate (4r).



4r

White solid; 70% yield (29.9 mg); 92% ee; $[\alpha]_D^{20}$ = -70.5 (*c* 1.39, CH_2Cl_2); mp 119−125 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 60:40), 1.0 mL/min, λ = 230.16 nm, $t_{R(minor)}$ = 22.5 min, $t_{R(major)}$ = 18.1 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67−7.71 (m, 5H), 7.43−7.49 (m, 4H), 7.37−7.42 (m, 7H), 7.30−7.35 (m, 1H), 3.96 (d, *J* = 18.0 Hz, 1H), 3.83 (s, 3H), 3.30 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 164.7, 163.2, 143.8, 136.7, 136.3, 133.6, 131.9, 129.4, 129.1, 128.8, 128.7, 128.5, 127.3, 126.9, 125.1, 121.0, 84.1, 53.9, 39.5. IR (KBr, cm^{-1}): 3317, 3062, 2954, 2924, 2854, 1727, 1507, 1475, 1449, 1275, 1166, 1136, 1047, 738, 715, 696. HRMS (ESI) for $C_{26}H_{21}NO_5$ $[M+H]^+$ calcd. 428.1492, found 428.1488.

(S)-isopropyl 5-benzamido-6-oxo-2,4-diphenyl-3,6-dihydro-2H-pyran-2-carboxylate (4s)

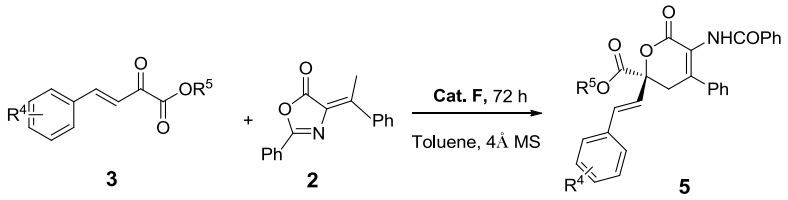


4s

White solid; 52% yield (23.6 mg); 96.7% ee; $[\alpha]_D^{20}$ = -11.7 (*c* 0.94, CH_2Cl_2); mp 114−120 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 50:50), 1.0 mL/min, λ = 280.16 nm, $t_{R(minor)}$ = 21.6 min, $t_{R(major)}$ = 10.7 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.67−7.72 (m, 4H), 7.44−7.50 (m, 5H), 7.32−7.42 (m, 5H), 7.28−7.30 (m, 2H), 5.08−5.15 (m, 2H), 3.99 (d, *J* = 18.0 Hz, 1H), 3.26 (d, *J* = 18.0 Hz, 1H), 1.25 (d, *J* = 6.0 Hz, 3H), 1.18 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 163.0, 162.6, 140.8, 136.1, 135.4, 132.8, 130.9, 128.2, 128.0, 127.7, 127.6, 127.6, 126.2, 125.9, 124.0, 119.7, 82.8, 70.2, 38.3, 20.5, 20.4. IR (KBr, cm^{-1}): 3350, 3061, 2924, 2856, 2374, 1737, 1672, 1602,

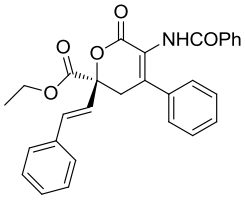
1580, 1477, 1376, 1359, 1271, 1168, 1135, 1101, 1046, 700. HRMS (ESI) for $C_{28}H_{25}NO_5$ $[M+H]^+$ calcd. 456.1805, found 456.1800.

3. General procedure for the synthesis of products **5** and analytical data



To an oven-dried 25 ml Schlenk tube equipped with a stir bar was charged with catalyst **F** (0.01 mmol) and 4Å MS (100 mg). This tube was closed with a septum, evacuated, and backed-filled with N_2. To this mixture was added freshly distilled Toluene (1.0 mL), olefinic azlactones **2** (0.1 mmol) and α-keto esters **3** (0.3 mmol). The mixture was stirred at room temperature for 72 h under N_2 atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica gel, mixtures of petroleum/ethyl acetate) to afford the pure product **5**.

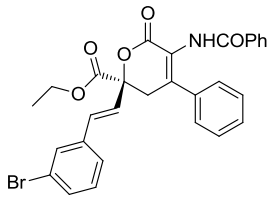
(S,E)-ethyl 5-benzamido-6-oxo-4-phenyl-2-styryl-3,6-dihydro-2H-pyran-2-carboxylate (5a)



5a

White solid; 88% yield (41.1 mg); 89% ee; $[\alpha]_D^{20}$ = -111.6 (*c* 0.83, CH_2Cl_2); mp 78−80 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 30:70), 1.0 mL/min, λ = 310.0 nm, $t_{R(minor)}$ = 7.5 min, $t_{R(major)}$ = 8.2 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.42−7.49 (m, 5H), 7.33−7.39 (m, 6H), 7.25−7.31 (m, 2H), 7.02 (d, *J* = 16.0 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 4.32 (q, *J* = 6.8 Hz, 2H), 3.70 (d, *J* = 18.0 Hz, 1H), 3.16 (d, *J* = 18.0 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 164.3, 163.5, 142.0, 136.8, 135.3, 133.7, 132.7, 131.9, 129.2, 128.7, 128.6, 128.6, 128.5, 127.2, 126.8, 124.0, 120.8, 83.0, 63.2, 38.9, 14.0. IR (KBr, cm^{-1}): 3344, 2926, 2854, 2371, 1732, 1671, 1647, 1474, 1447, 1358, 1265, 1174, 1094, 765, 739, 700. HRMS (ESI) for $C_{29}H_{25}NO_5$ $[M+H]^+$ calcd. 468.1805, found 468.1811.

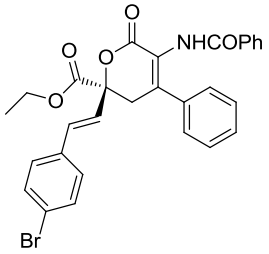
(S,E)-ethyl 5-benzamido-2-(3-bromostyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (5b)



5b

White solid; 76% yield (41.4 mg); 93% ee; $[\alpha]_D^{20}$ = -190.8 (*c* 2.51, CH_2Cl_2); mp 90−92 ℃; The enantiomeric excess was determined by HPLC with an IA-H column. (*n*-hexane: DCM = 50:50), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 8.6 min, $t_{R(major)}$ = 9.2 min.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.57 (s, 1H), 7.43−7.49 (m, 3H), 7.25−7.40 (m, 7H), 7.19−7.23 (m, 1H), 6.96 (d, *J* = 16.0 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.68 (d, *J* = 18.0 Hz, 1H), 3.15 (d, *J* = 18.0 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 164.4, 163.3, 141.9, 137.4, 136.7, 133.7, 131.9, 131.4, 131.3, 130.2, 129.5, 129.3, 128.6, 128.5, 127.2, 126.8, 125.6, 125.5, 122.8, 120.8, 82.8, 63.3, 38.9, 14.0. IR (KBr, cm^{-1}): 3346, 2923, 2854, 2372, 1736, 1668, 1510, 1467, 1377, 1265, 1169, 1095, 766, 738, 702. HRMS (ESI) for $C_{29}H_{24}BrNO_5$ $[M+H]^+$ calcd. 546.0911, found 546.0924.

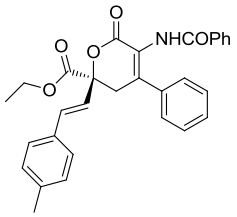
(S,E)-ethyl 5-benzamido-2-(4-bromostyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (5c)



5c

White solid; 74% yield (40.3 mg); 91% ee; $[\alpha]_D^{20}$ = -182.2 (*c* 1.29, CH_2Cl_2); mp 82−84 ℃; The enantiomeric excess was determined by HPLC with an IA-H column. (*n*-hexane: DCM = 50:50), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 9.2 min, $t_{R(major)}$ = 10.2 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.43−7.48 (m, 5H), 7.33−7.39 (m, 4H), 7.25−7.30 (m, 3H), 6.96 (d, *J* = 16.0 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 4.29−4.35 (m, 2H), 3.68 (d, *J* = 18.0 Hz, 1H), 3.14 (d, *J* = 18.0 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 164.3, 163.4, 141.9, 136.7, 134.2, 133.7, 131.9, 131.8, 131.5, 129.3, 128.6, 128.5, 128.3, 127.2, 126.8, 124.7, 122.6, 120.8, 82.8, 63.2, 38.9, 14.0. IR (KBr, cm^{-1}): 3347, 3057, 2924, 2854, 2372, 1736, 1581, 1465, 1377, 1363, 1264, 1169, 1072, 1010, 970, 856, 808, 742. HRMS (ESI) for $C_{29}H_{24}BrNO_5$ $[M+H]^+$ calcd. 546.0911, found 546.0925.

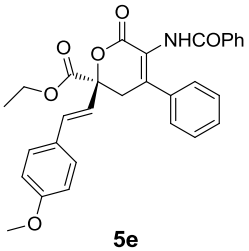
(S,E)-ethyl 5-benzamido-2-(4-methylstyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (5d)



5d

White solid; 83% yield (39.9 mg); 86% ee; $[\alpha]_D^{20}$ = -72.7 (*c* 1.57, CH_2Cl_2); mp 69−70 ℃; The enantiomeric excess was determined by HPLC with an IA-H column. (*n*-hexane: DCM = 50:50), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 7.9 min, $t_{R(major)}$ = 8.6 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.43−7.49 (m, 3H), 7.25−7.39 (m, 7H), 7.14−7.16 (m, 2H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.69 (d, *J* = 18.0 Hz, 1H), 3.15 (d, *J* = 18.0 Hz, 1H), 2.34 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 164.3, 163.6, 141.9, 138.6, 136.9, 133.8, 132.6, 132.5, 131.9, 129.4, 129.2, 128.6, 128.5, 127.2, 126.8, 126.8, 122.9, 120.7, 83.1, 63.1, 39.0, 21.2, 14.0. IR (KBr, cm^{-1}): 3394, 2924, 2854, 2371, 1735, 16743, 1464, 1377, 1265, 1172, 1093, 1019, 740. HRMS (ESI) for $C_{30}H_{27}NO_5$ $[M+H]^+$ calcd. 482.1962, found 482.1973.

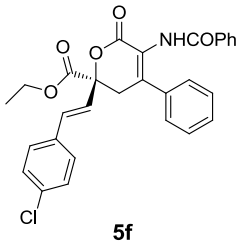
(S,E)-ethyl 5-benzamido-2-(4-methoxystyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (5e)



5e

White solid; 88% yield (43.7 mg); 87% ee; $[\alpha]_D^{20}$ = -57.9 (*c* 1.07, CH_2Cl_2); mp 67−70 ℃; The enantiomeric excess was determined by HPLC with an IA-H column. (*n*-hexane: DCM = 50:50), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 9.1 min, $t_{R(major)}$ = 10.1 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.43−7.49 (m, 3H), 7.30−7.39 (m, 6H), 7.25−7.29 (m, 1H), 6.94 (d, *J* = 16.0 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.24 (d, *J* = 16.0 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 3.69 (d, *J* = 17.6 Hz, 1H), 3.15 (d, *J* = 18.0 Hz, 1H), 1.28 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 164.3, 163.6, 160.0, 142.0, 136.9, 133.8, 132.2, 131.9, 129.2, 128.6, 128.5, 128.2, 128.0, 127.2, 126.8, 121.7, 120.7, 114.1, 83.1, 63.1, 55.3, 39.0, 14.1. IR (KBr, cm^{-1}): 3390, 2959, 2927, 1735, 1664, 1512, 1465, 1264, 1174, 1029, 742, 706. HRMS (ESI) for $C_{30}H_{27}NO_6$ $[M+H]^+$ calcd. 498.1911, found 498.1922.

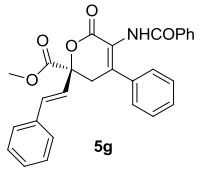
(S,E)-ethyl 5-benzamido-2-(4-chlorostyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (5f)



5f

White solid; 80% yield (40.1 mg); 93% ee; $[\alpha]_D^{20}$ = -156.6 (*c* 1.17, CH_2Cl_2); mp 77−80 ℃; The enantiomeric excess was determined by HPLC with an IA-H column. (*n*-hexane: DCM = 50:50), 1.0 mL/min, λ = 280.0 nm, $t_{R(minor)}$ = 14.5 min, $t_{R(major)}$ = 12.6 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.43−7.49 (m, 3H), 7.25−7.39 (m, 9H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.68 (d, *J* = 18.0 Hz, 1H), 3.15 (d, *J* = 18.0 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 64.3, 163.4, 141.9, 136.7, 134.4, 133.8, 133.7, 131.9, 131.5, 129.3, 128.9, 128.6, 128.5, 128.1, 127.2, 126.8, 124.6, 120.8, 82.8, 63.2, 38.9, 14.0. IR (KBr, cm^{-1}): 3400, 3058, 2958, 2927, 2854, 2371, 1733, 1685, 1467, 1265, 1173, 1092, 1014, 740, 704. HRMS (ESI) for $C_{29}H_{24}ClNO_5$ $[M+H]^+$ calcd. 502.1416, found 502.1430.

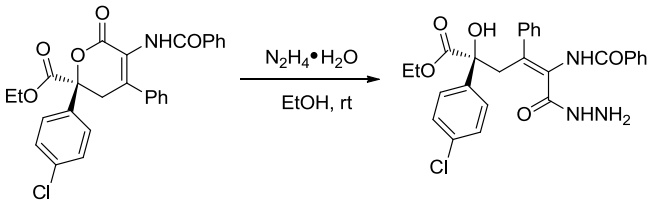
(S,E)-methyl 5-benzamido-6-oxo-4-phenyl-2-styryl-3,6-dihydro-2H-pyran-2-carboxylate (5g)



5g

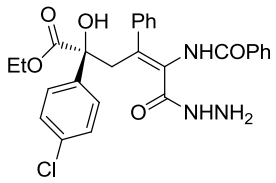
White solid; 79% yield (35.8 mg); 84% ee; $[\alpha]_D^{20}$ = -128.7 (*c* 1.15, CH_2Cl_2); mp 196−200 ℃; The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane: EtOH = 30:70), 1.0 mL/min, λ = 254.4 nm, $t_{R(minor)}$ = 69.0 min, $t_{R(major)}$ = 9.5 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67−7.71 (m, 3H), 7.40−7.50 (m, 5H), 7.32−7.38 (m, 6H), 7.25−7.30 (m, 2H), 7.02 (d, *J* = 16.0 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 3.87 (s, 3H), 3.70 (d, *J* = 18.0 Hz, 1H), 3.18 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 163.6, 162.3, 141.9, 135.6, 134.2, 132.6, 131.8, 130.9, 128.3, 127.7, 127.7, 127.5, 126.2, 125.9, 122.8, 119.9, 82.2, 52.8, 37.9. IR (KBr, cm^{-1}): 3360, 2955, 2927, 2367, 1737, 1666, 1474, 1265, 1167, 1047, 969, 739, 704. HRMS (ESI) for $C_{28}H_{24}NO_5$ $[M+H]^+$ calcd. 454.1649, found 454.1653.

4. General procedure for the synthesis of product **6** and analytical data



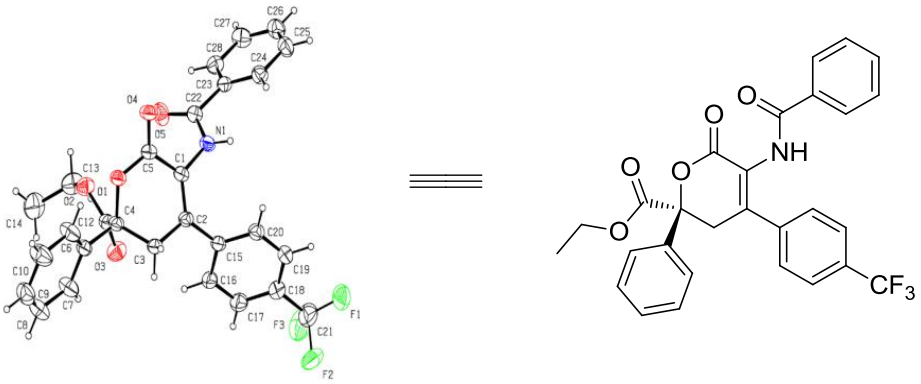
A solution of **4p** (47.6 mg, 0.1 mmol), EtOH (2 mL) and hydrazine hydrate (52.3 mg, 1.6 mmol) was stirred at room temperature for 3 h and monitored by TLC. After the reaction was completed, the volatile components were evaporated in vacuo to give the product **6**.

(S,Z)-ethyl 5-benzamido-2-(4-chlorophenyl)-6-hydrazinyl-2-hydroxy-6-oxo-4-phenylhex-4-enoate (6)



White solid; 98% yield (49.7 mg); mp 125−128 ℃; ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.73 (s, 1H), 9.32 (s, 1H), 7.87 (s, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.44−7.50 (m, 3H), 7.33−7.37 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.10 (s, 5H), 4.54 (br, 2H), 3.73 (d, *J* = 13.2 Hz, 1H), 3.54 (m, 1H), 3.35 (d, *J* = 10.4 Hz, 1H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 172.9, 166.4, 165.7, 142.9, 139.1, 138.7, 134.2, 132.3, 131.8, 129.8, 129.1, 128.4, 128.3, 128.0, 127.9, 127.7, 127.6, 76.5, 61.0, 43.7, 14.0. IR (KBr, cm^{-1}): 3268, 2926, 2370, 1739, 1655, 1647, 1639, 1510, 1476, 1278, 1249, 1212, 1093, 727, 703. HRMS (ESI) for $C_{27}H_{27}ClN_3O_5$ $[M+H]^+$ calcd. 508.1634, found 508.1646.

5. X-ray crystallographic data of compound **4g**



Datablock:

Bond precision: **C-C = 0.0065 A** **Wavelength=1.54184**

Cell: **a=9.1158(3)** **b=9.8126(3)** **c=28.3116(9)**
alpha=90 **beta=90** **gamma=90**

Temperature: **294 K**

	Calculated	Reported
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Space group	**P 21 21 21**	**P 21 21 21**
Hall group	**P 2ac 2ab**	**P 2ac 2ab**
Moiety formula	**C28 H22 F3 N O5**	**C28 H22 F3 N O5**
Sum formula	**C28 H22 F3 N O5**	**C28 H22 F3 N O5**
Mr	**509.47**	**509.47**
Dx,g cm-3	**1.336**	**1.336**
Z	**4**	**4**
Mu (mm-1)	**0.903**	**0.903**
F000	**1056.0**	**1056.0**
F000'	**1059.87**	
h,k,lmax	**11,11,34**	**10,11,34**
Nref	**4772[2733]**	**4094**
Tmin,Tmax	**0.788,0.939**	**0.737,1.000**
Tmin'	**0.770**	

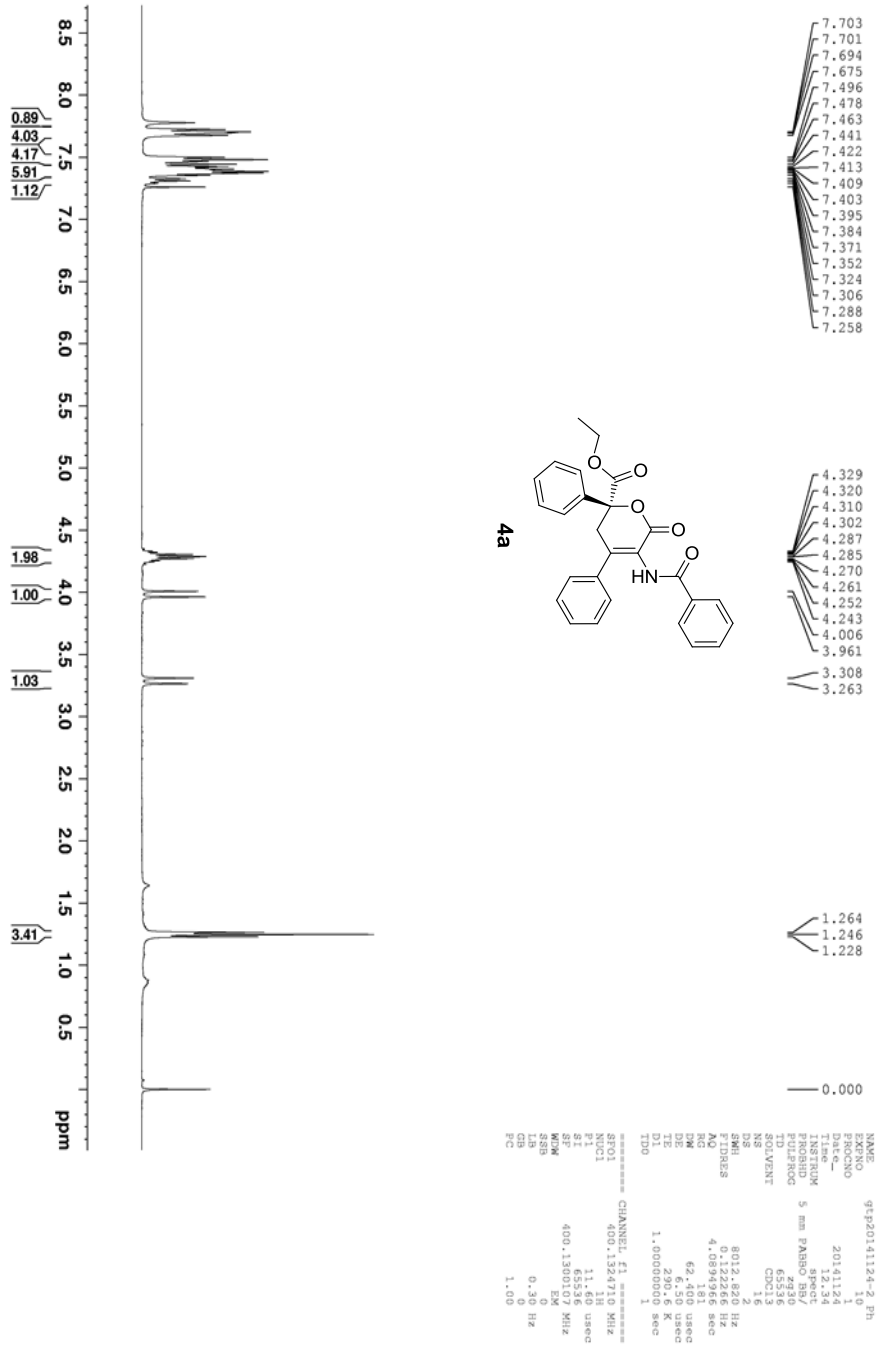
Correction method= MULTI-SCAN

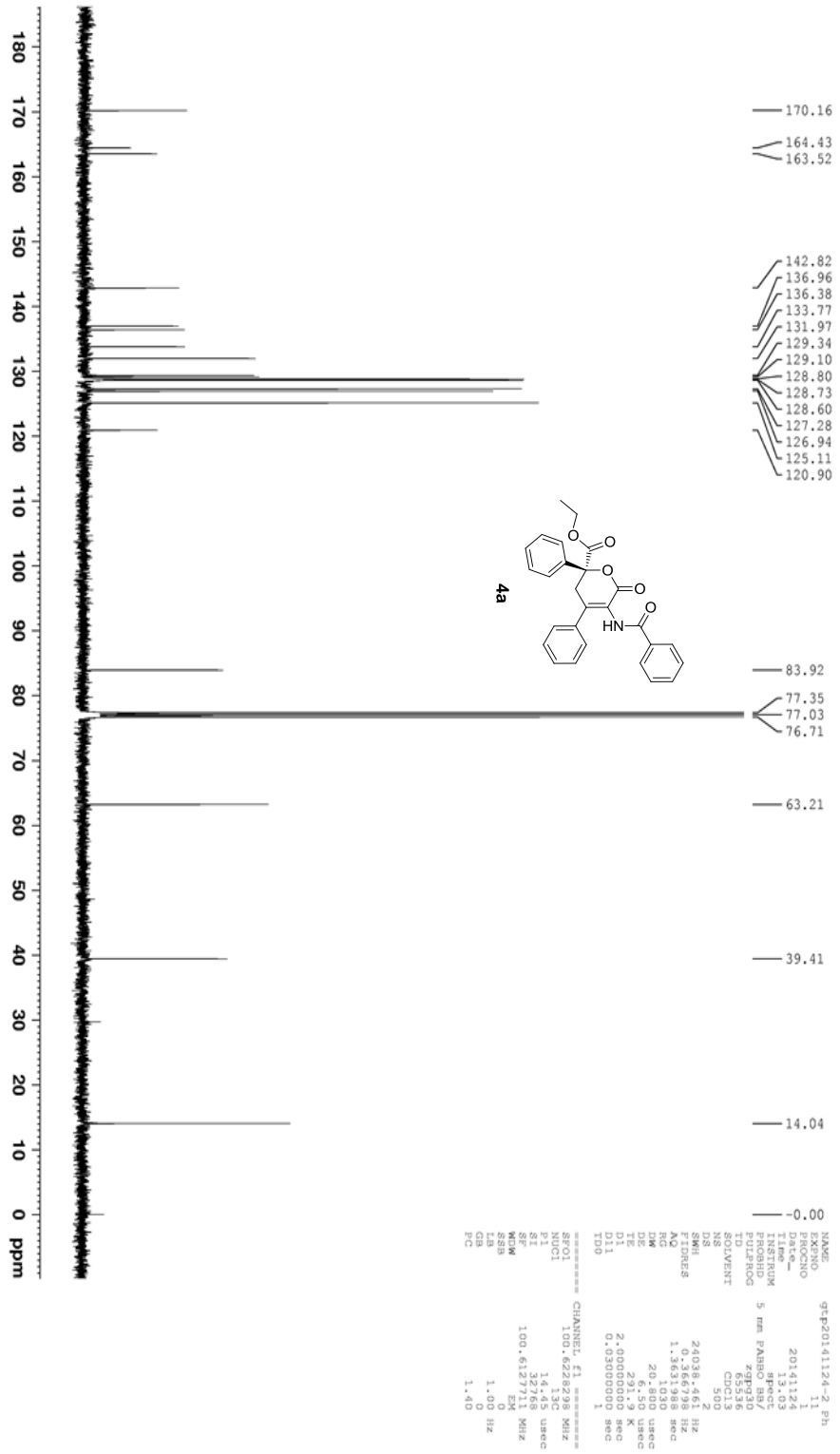
Data completeness= 1.50/0.86 **Theta(max)= 69.720**

R(reflections)= 0.0533(2681) **wR2(reflections)= 0.1481(4094)**

S = 1.013 **Npar= 367**

6. NMR spectra of compounds **4**

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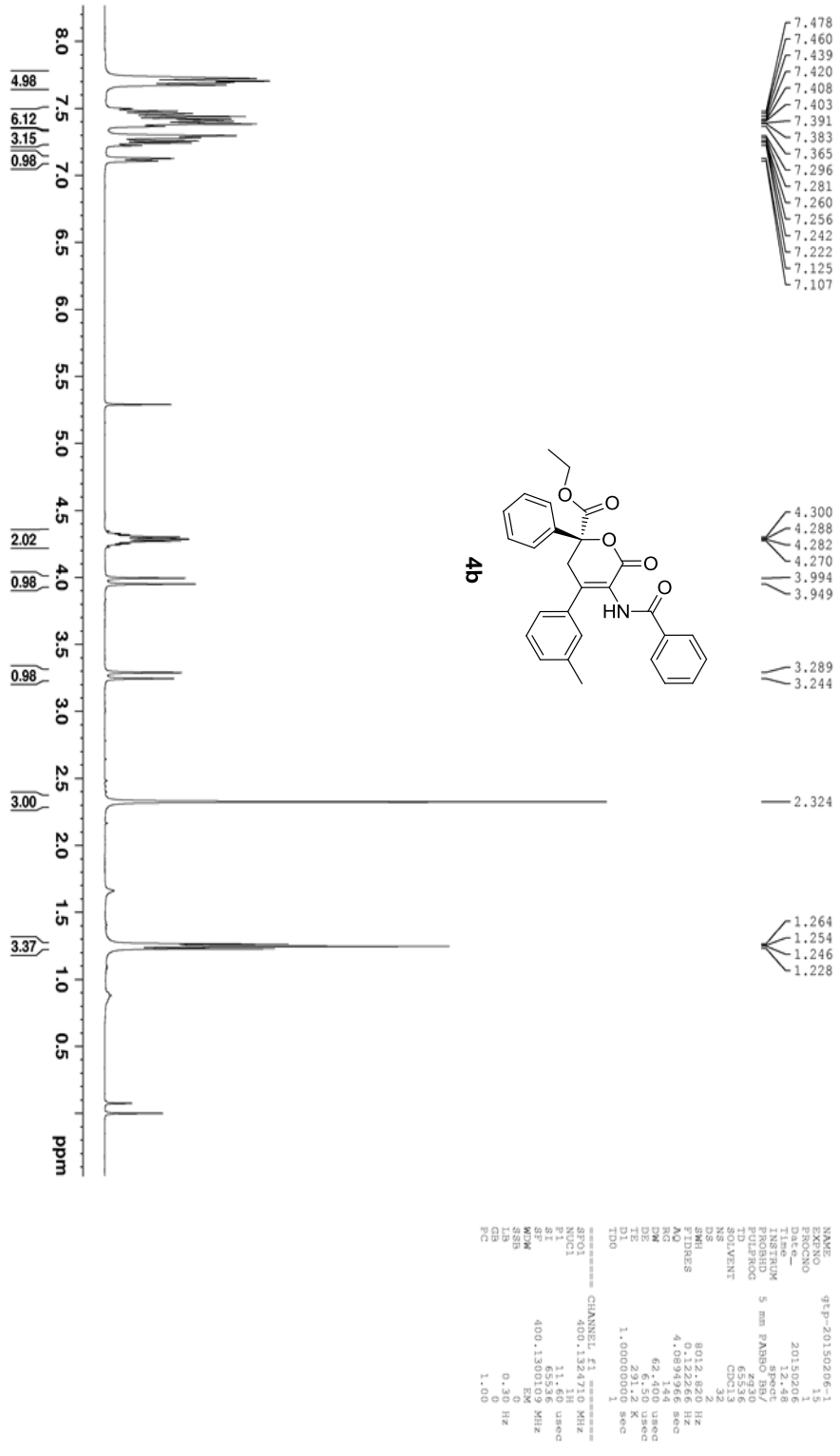
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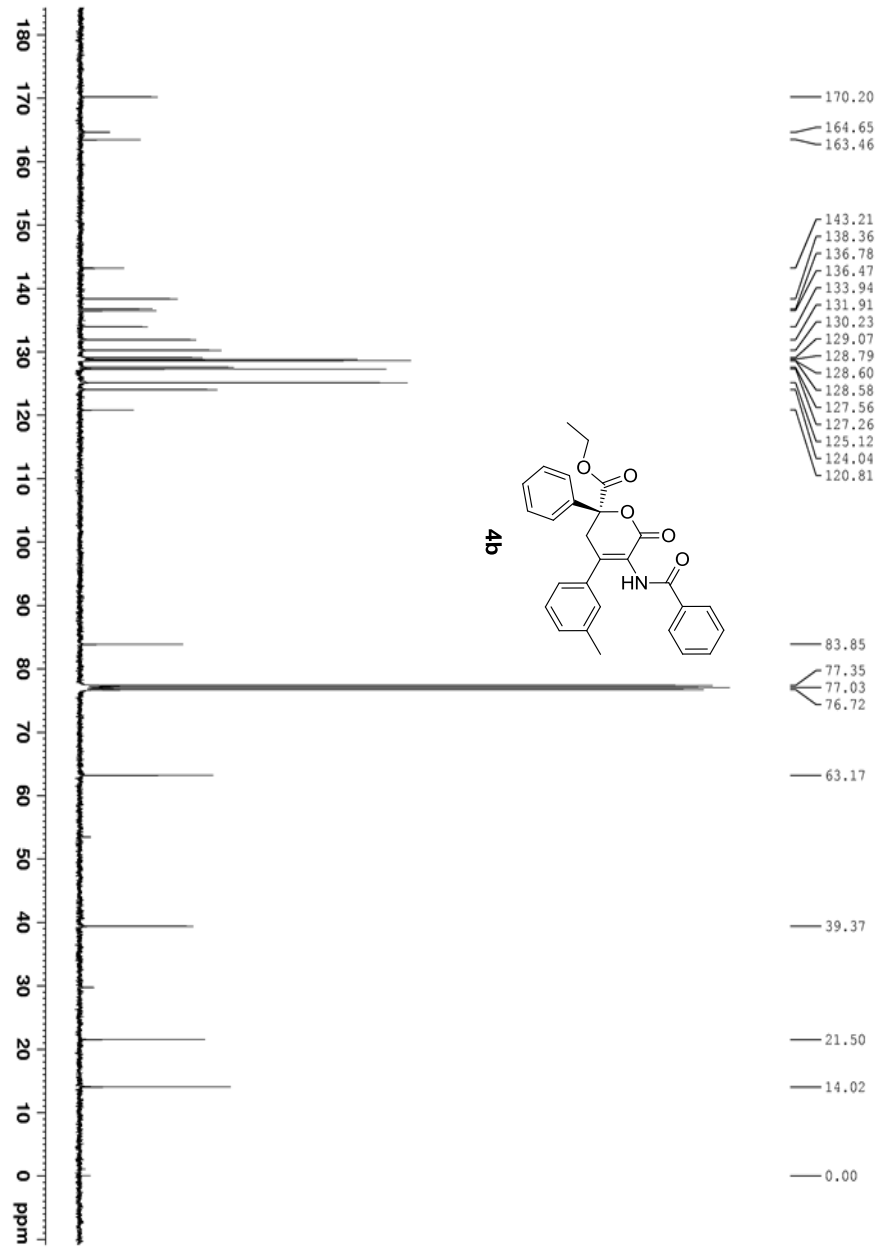

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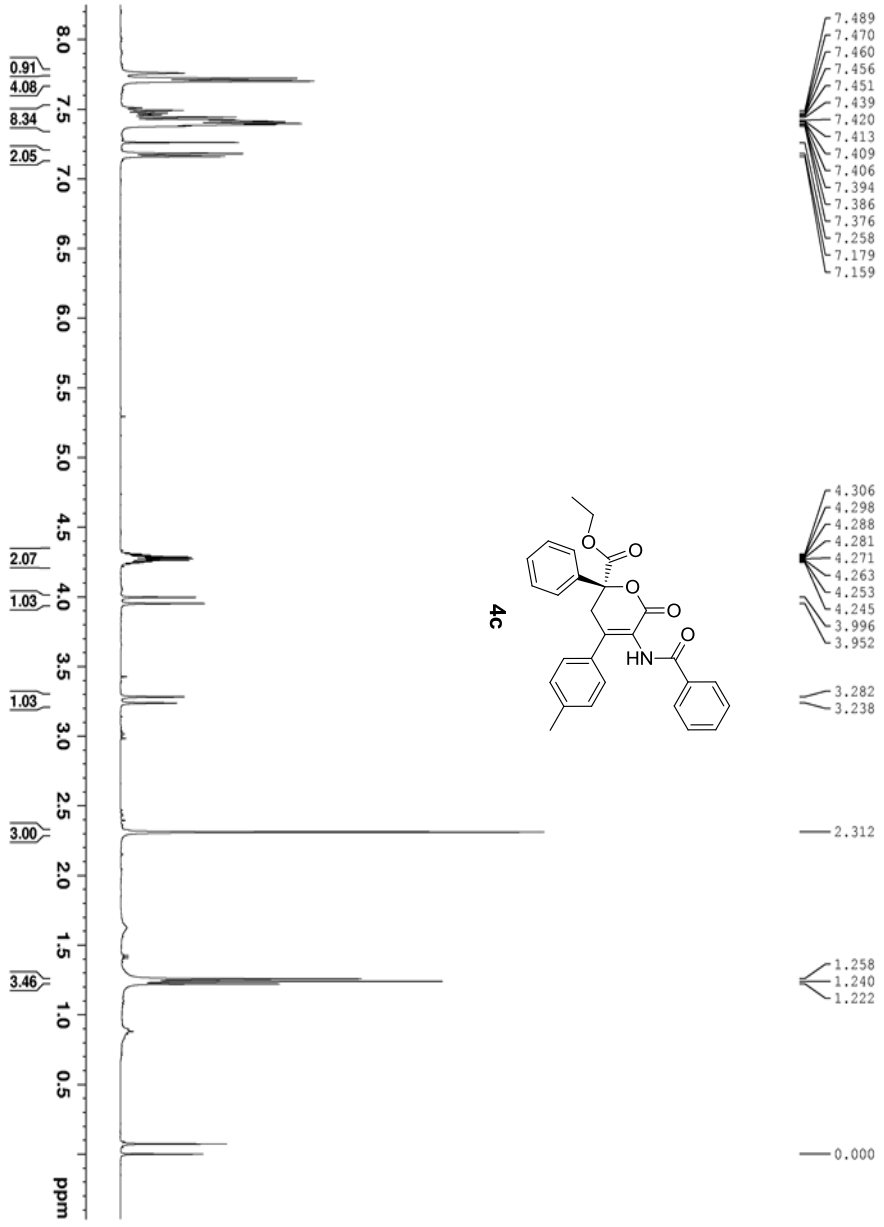
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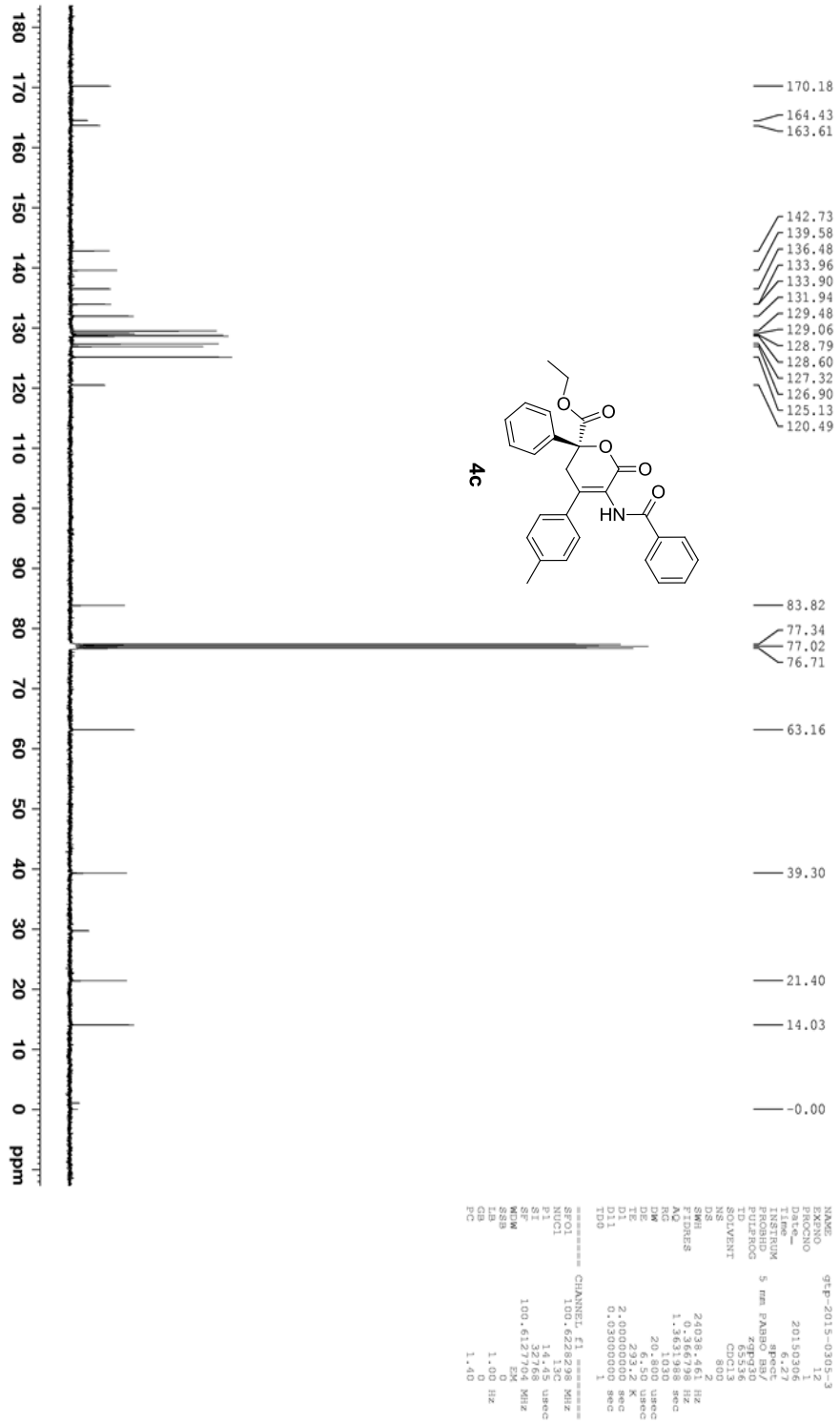
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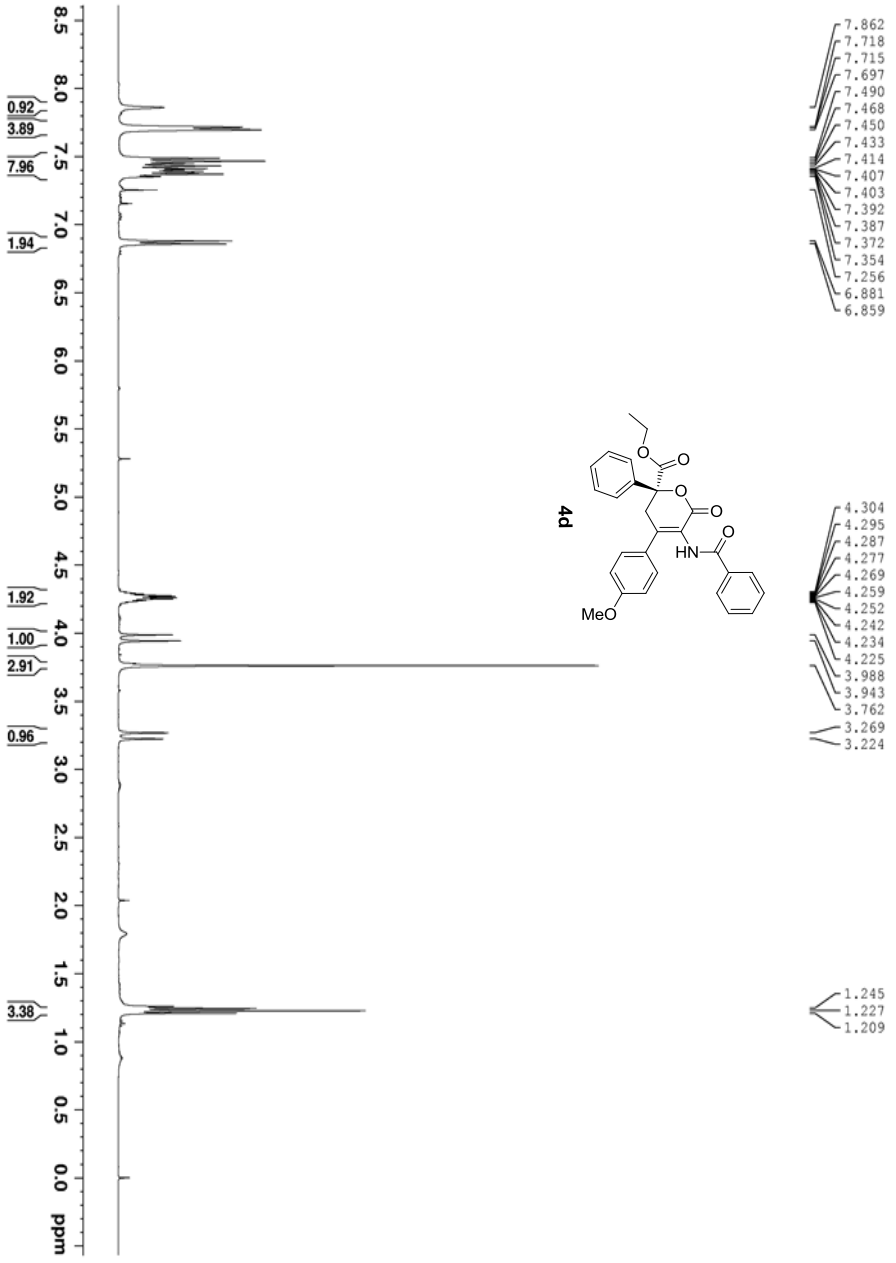
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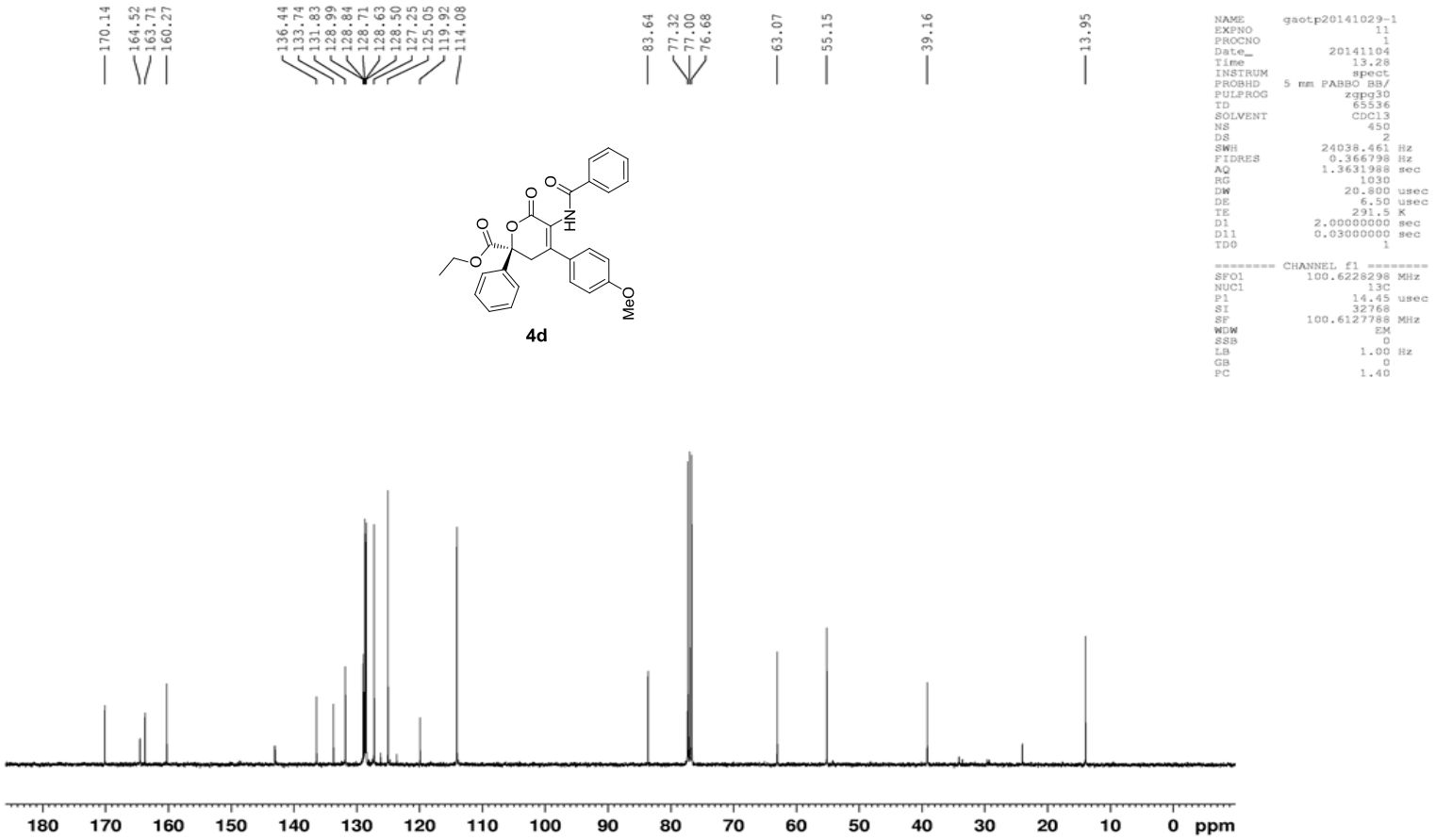

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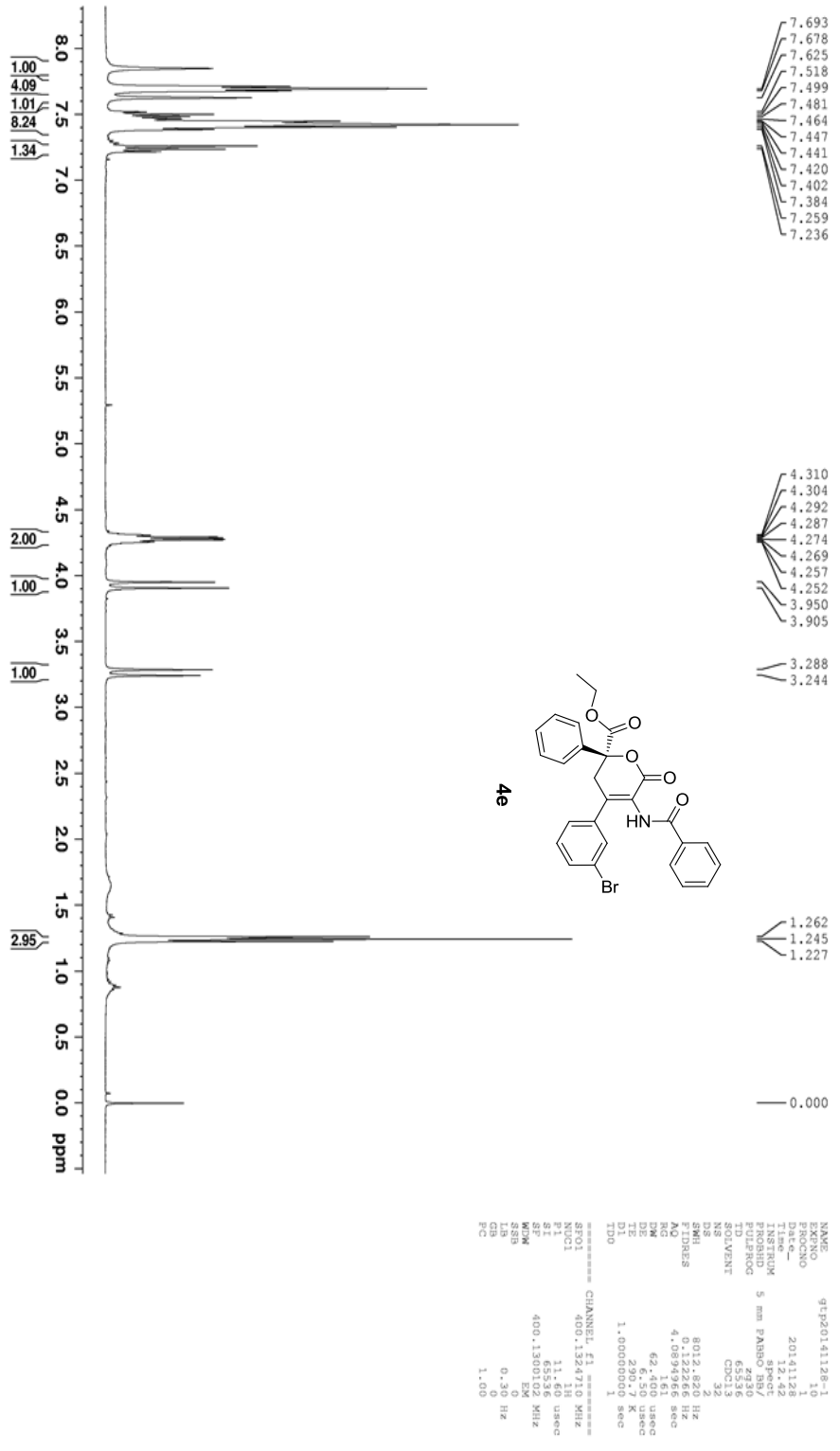
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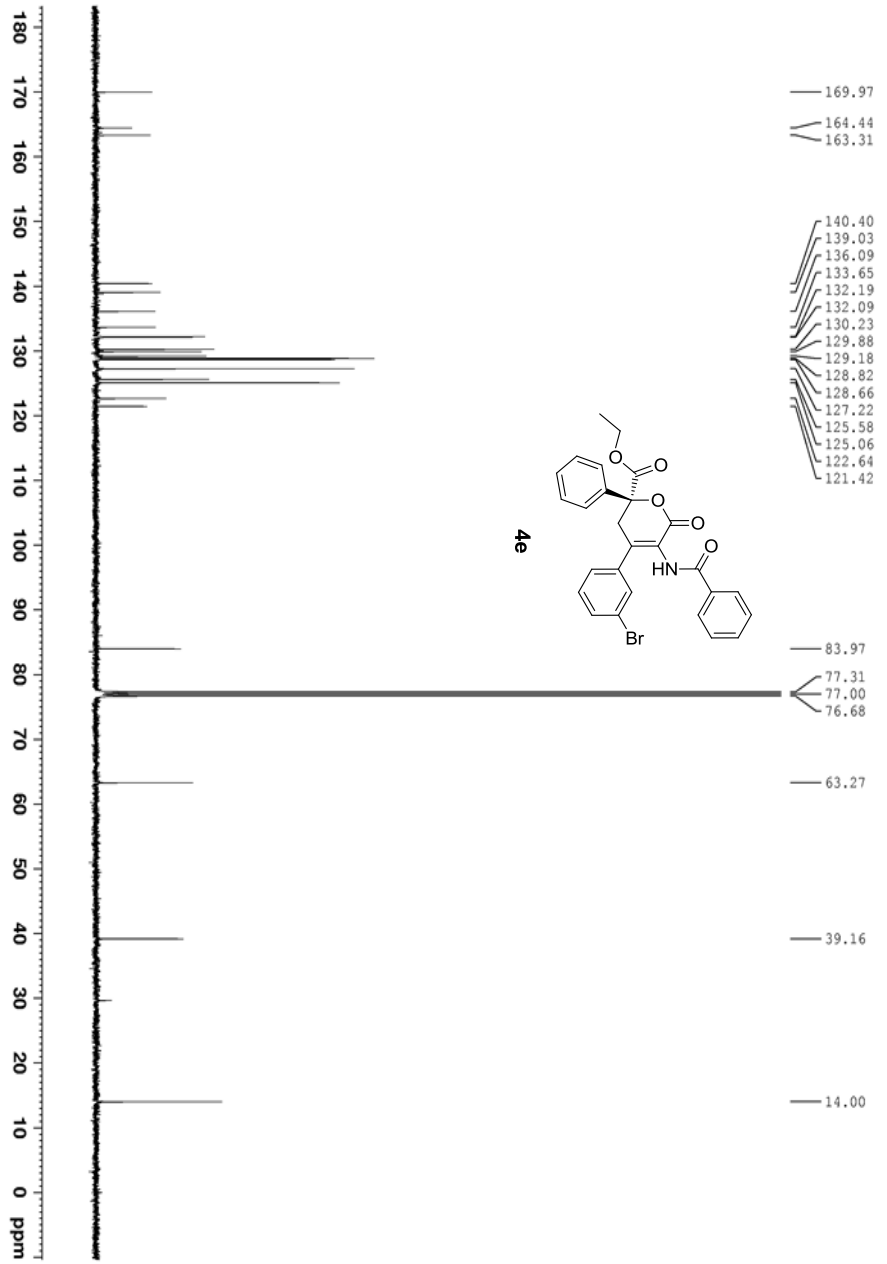
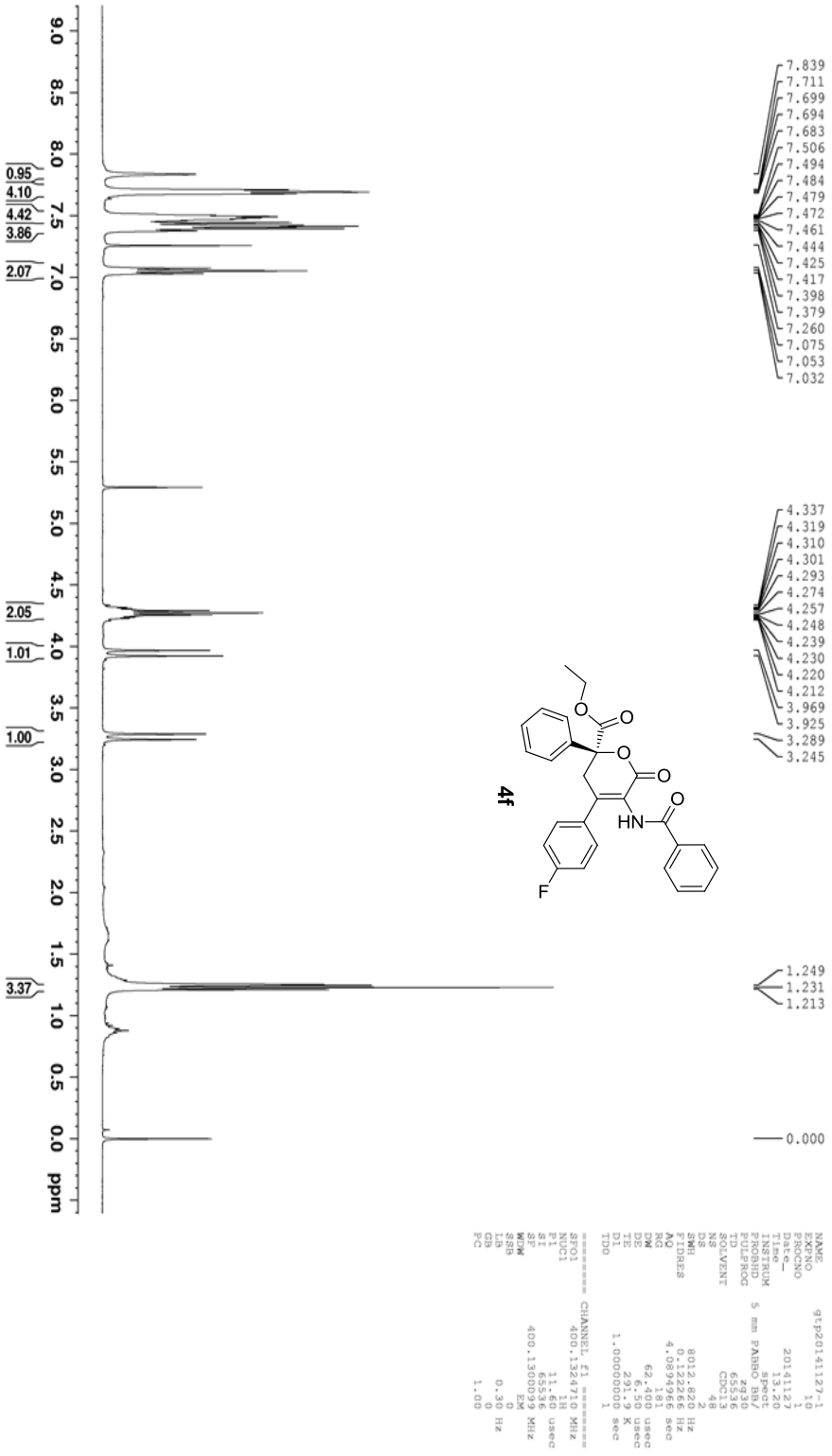
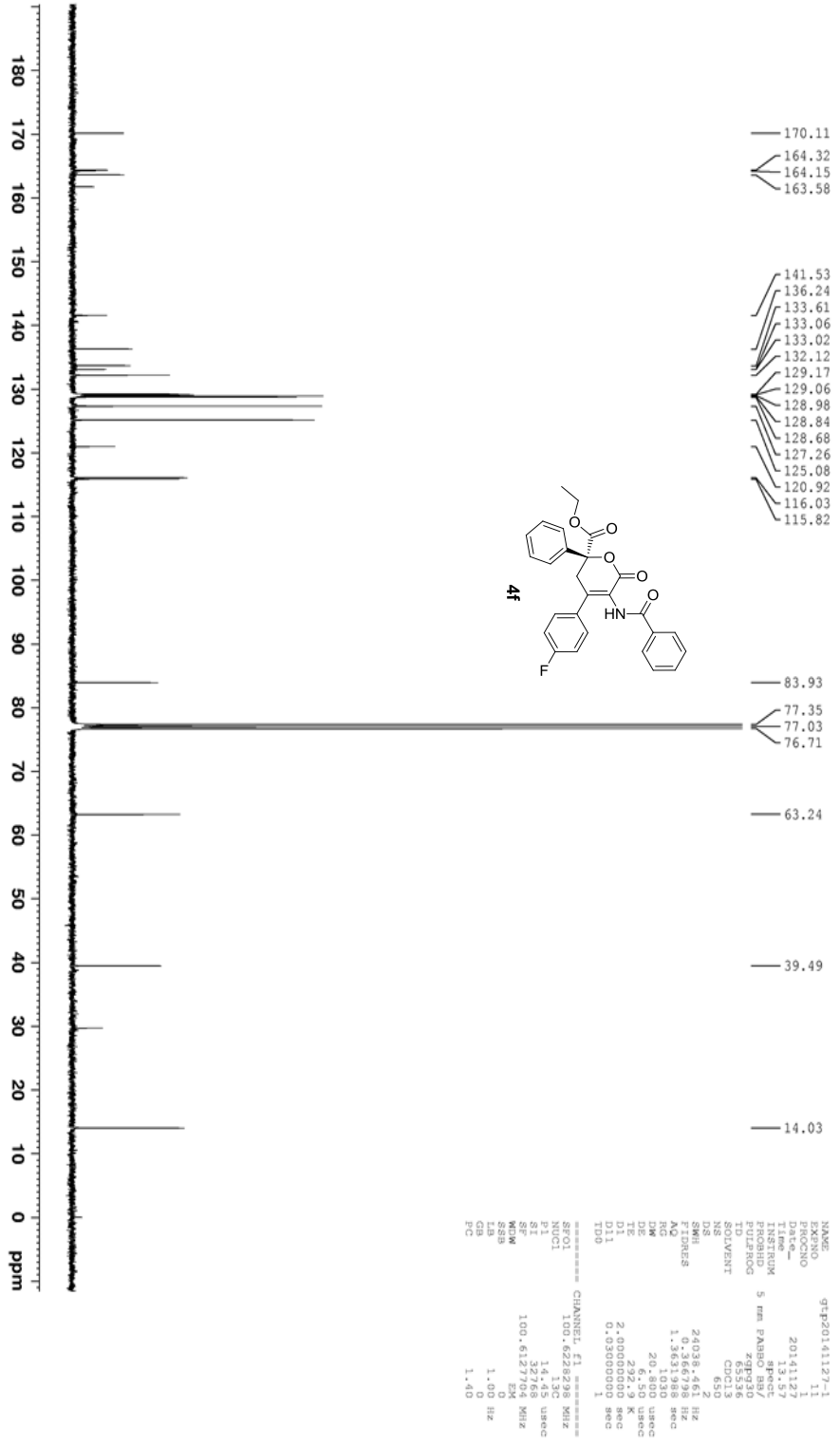
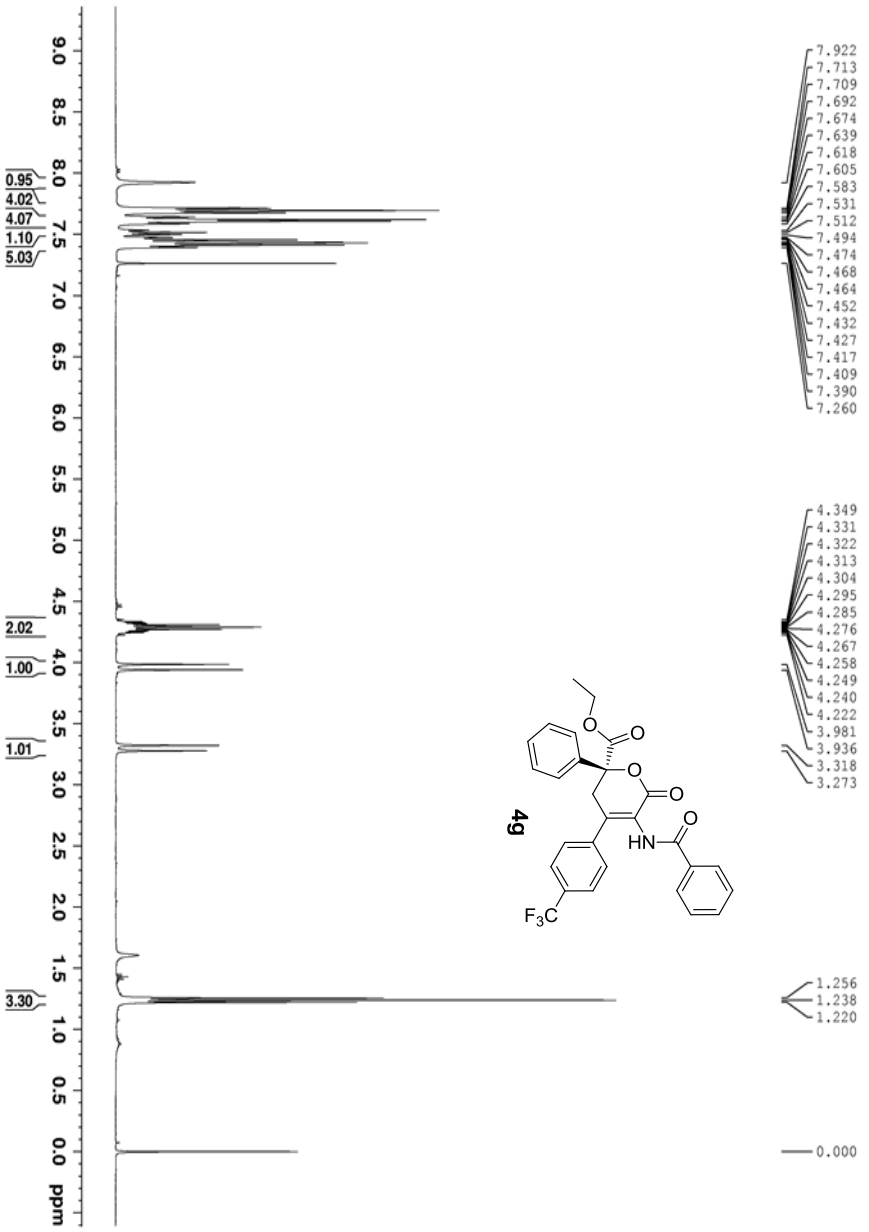
4.274
4.269
4.257
4.252
3.950
3.905
3.288
3.244
1.262
1.245
1.227
0.000
1.00
4.09
1.01
8.24
1.34
2.00
1.00
1.00
2.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4e
HN
Br
O
O
O
O
O
NAME
EXPNO
PROCNO
Date_
Time
INSTRUM
PROBHD
PULPROG
TD
SOLVENT
NS
DS
SWH
FIDRES
AQ
RG
DW
DE
TE
D1
TD0
SFO1
NUC1
P1
SI
SF
WDW
SSB
LB
GB
PC
gtp20141128-1
10
20141123
12.42
spect
5 mm PABBO BB/
65536
CDCl3
32
2
6012.820 Hz
0.183066 Hz
4.089496 sec
161
62.400 usec
6.50 usec
298.7 K
1.0000000 sec
1
CHANNEL f1
400.1324710 MHz
11.60 usec
65536
400.1300102 MHz
EM
0.30 Hz
0
1.00

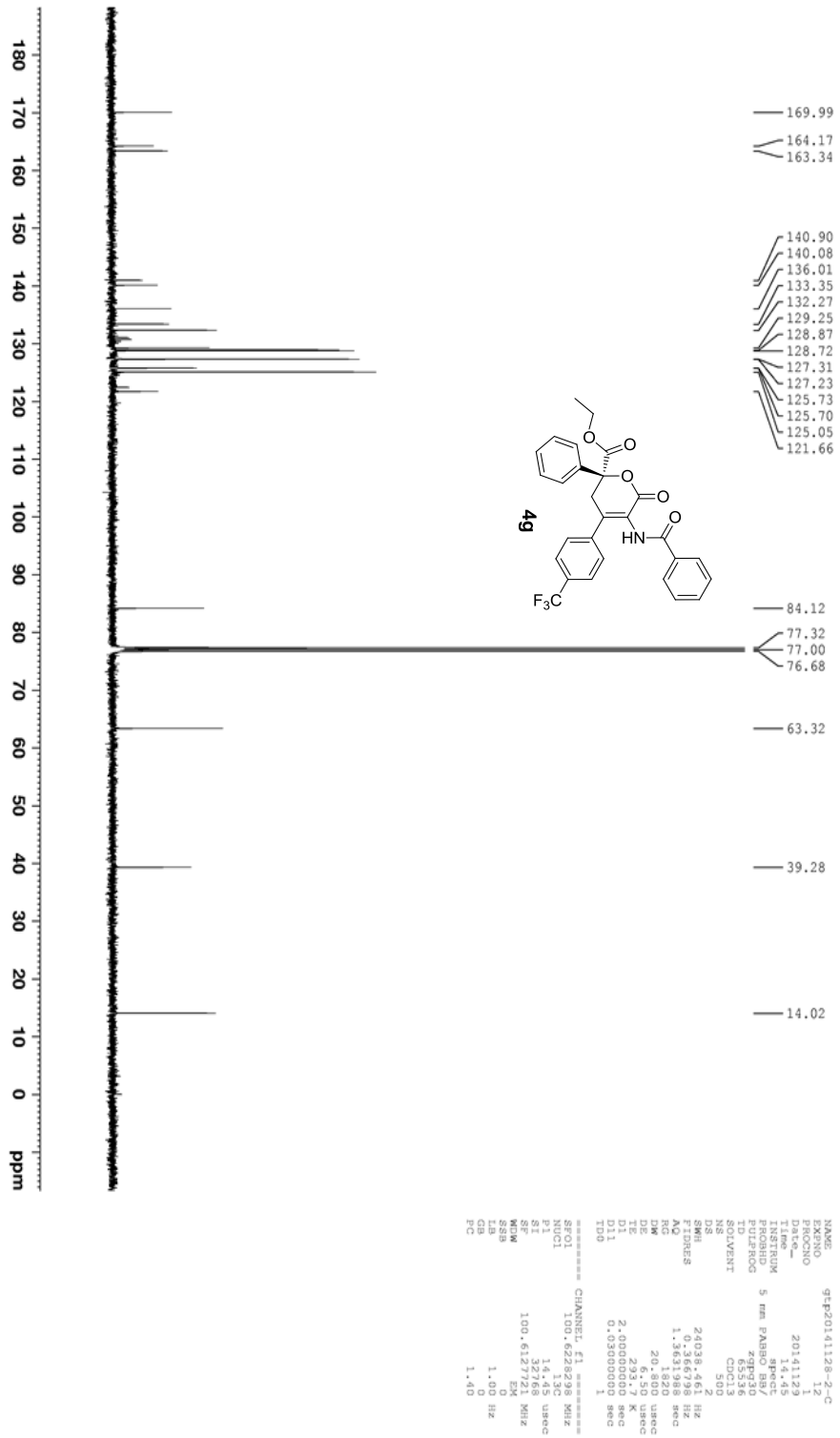

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
169.97
164.44
163.31
140.40
139.03
136.09
133.65
132.19
132.09
130.23
129.88
129.18
128.82
128.66
127.22
125.58
125.06
122.64
121.42
83.97
77.31
77.00
76.68
63.27
39.16
14.00
4e
O
O
O
O
HN
O
Br
NAME gtp20141128-1-C
EXPNO 12
PROCNO 1
Date_ 20141129
Time 1.44
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631038 sec
RG 20.800
DW 6.50 usec
DE 233.6 K
TE 2.00000000 sec
D1 0.03000001 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 14.45 usec
SI 32768
SF 100.6127744 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


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
4.10
4.42
3.86
2.07
2.05
1.01
1.00
3.37
7.839
7.711
7.699
7.694
7.683
7.506
7.494
7.484
7.479
7.472
7.461
7.444
7.425
7.417
7.398
7.379
7.260
7.075
7.053
7.032
4.337
4.319
4.310
4.301
4.293
4.274
4.257
4.248
4.239
4.230
4.220
4.212
3.969
3.925
3.289
3.245
1.249
1.231
1.213
0.000
4f
O
O
O
O
HN
O
F

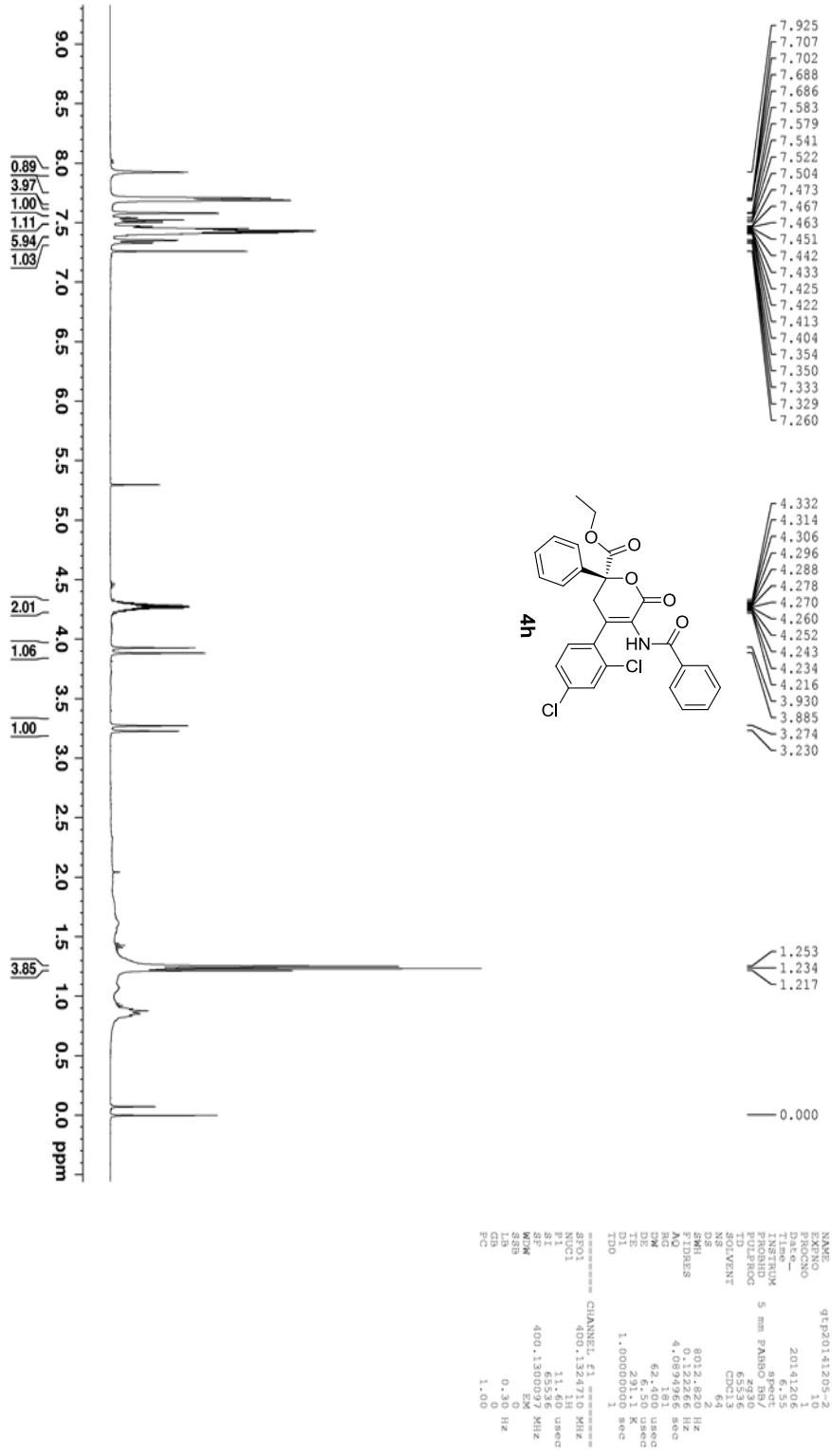

170.11
164.32
164.15
163.58
141.53
136.24
133.61
133.06
133.02
132.12
129.17
129.06
128.98
128.84
128.68
127.26
125.08
120.92
116.03
115.82
83.93
77.35
77.03
76.71
63.24
39.49
14.03
4f
O
O
O
O
HN
O
F
NAME gt-p20141127-1
EXPNO 11
PROCNO 1
Date_ 20141127
Time 13.27
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631008 sec
RG 1024
DW 20.800 usec
DE 6.50 usec
TE 292.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 14.45 usec
SI 32768
SF 100.6127704 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



NAME gtp20141128-2
EXPNO 10
PROCNO 1
Date_ 20141121
Time 12.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
SOLVENT CDCl3
NS 64
DS 2
SWH 8012.820 Hz
FIDRES 4.089496 Hz
AQ 4.089496 sec
RG 228
DW 62.400 usec
DE 6.50 usec
TE 296.0 K
D1 2.0000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1
P1 11.60 usec
SI 65536
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

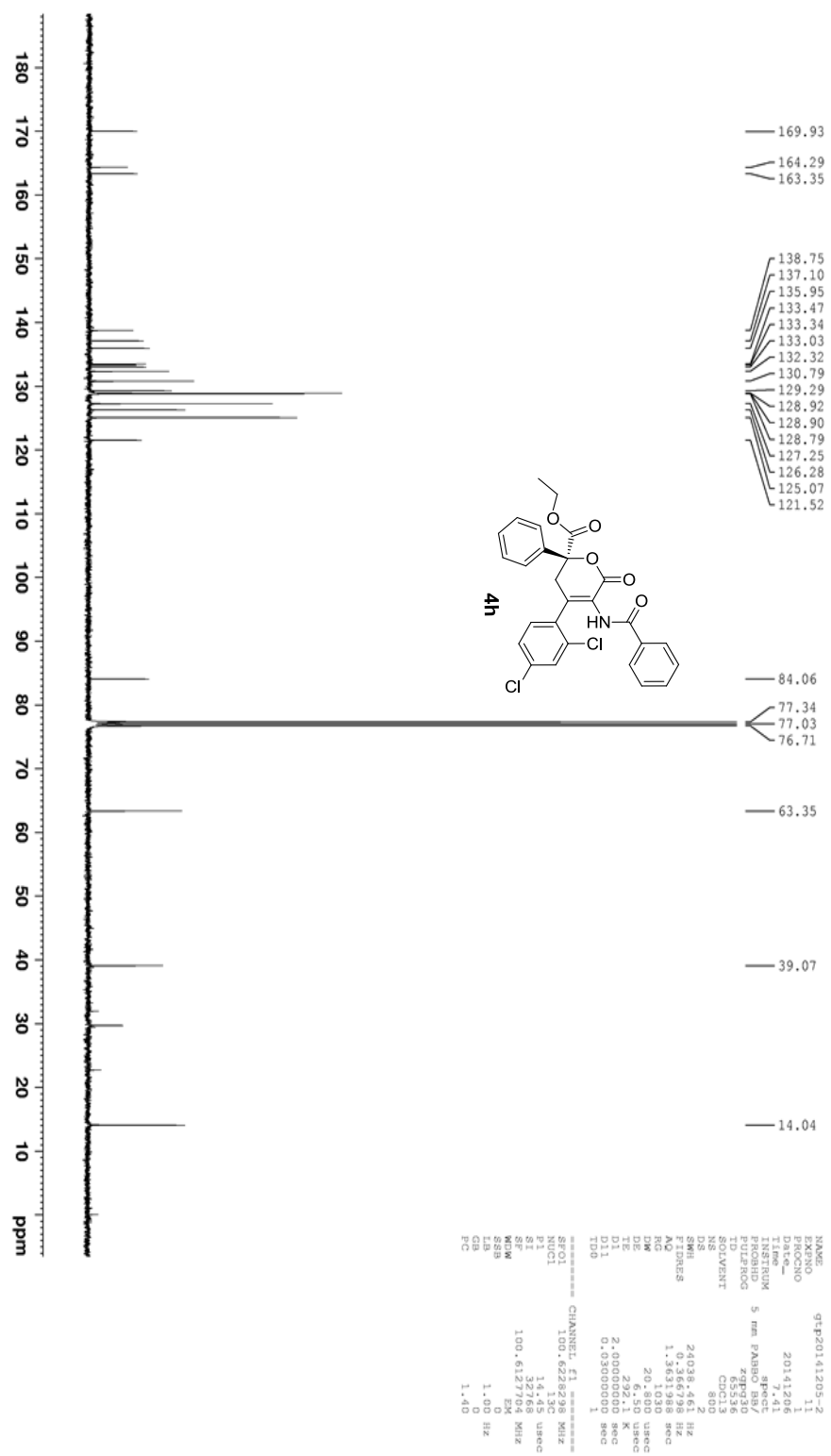


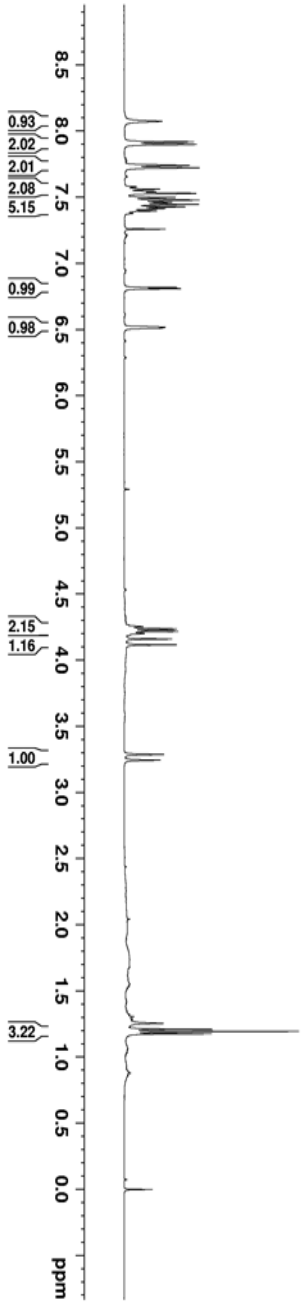
NAME qtf20141128-2-C
EXPNO 12
PROCNO 1
Date_ 20141129
Time 14.43
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631928 sec
RG 181.02
DW 20.800 usec
DE 6.50 usec
TE 293.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 14.45 usec
SI 32768
SF 100.6127721 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

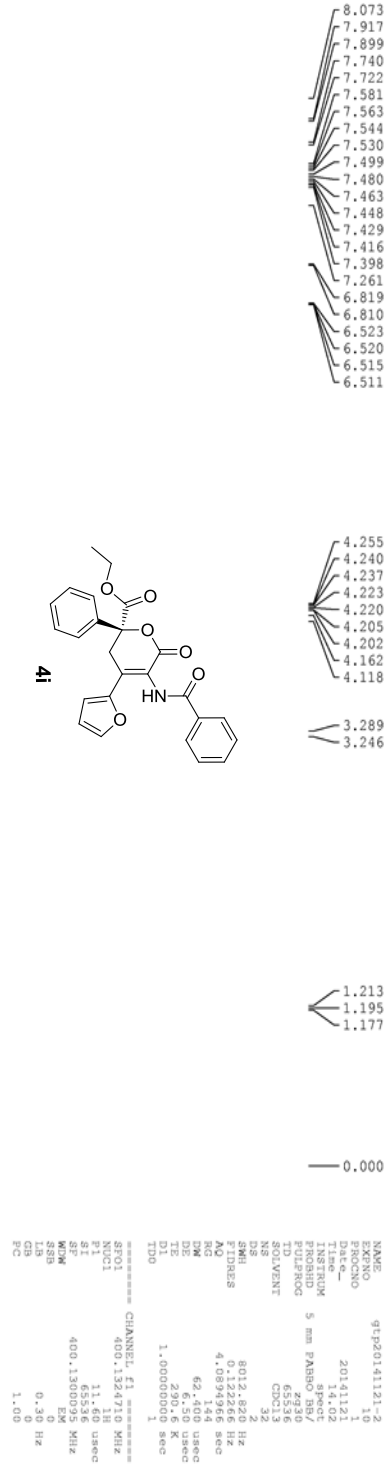


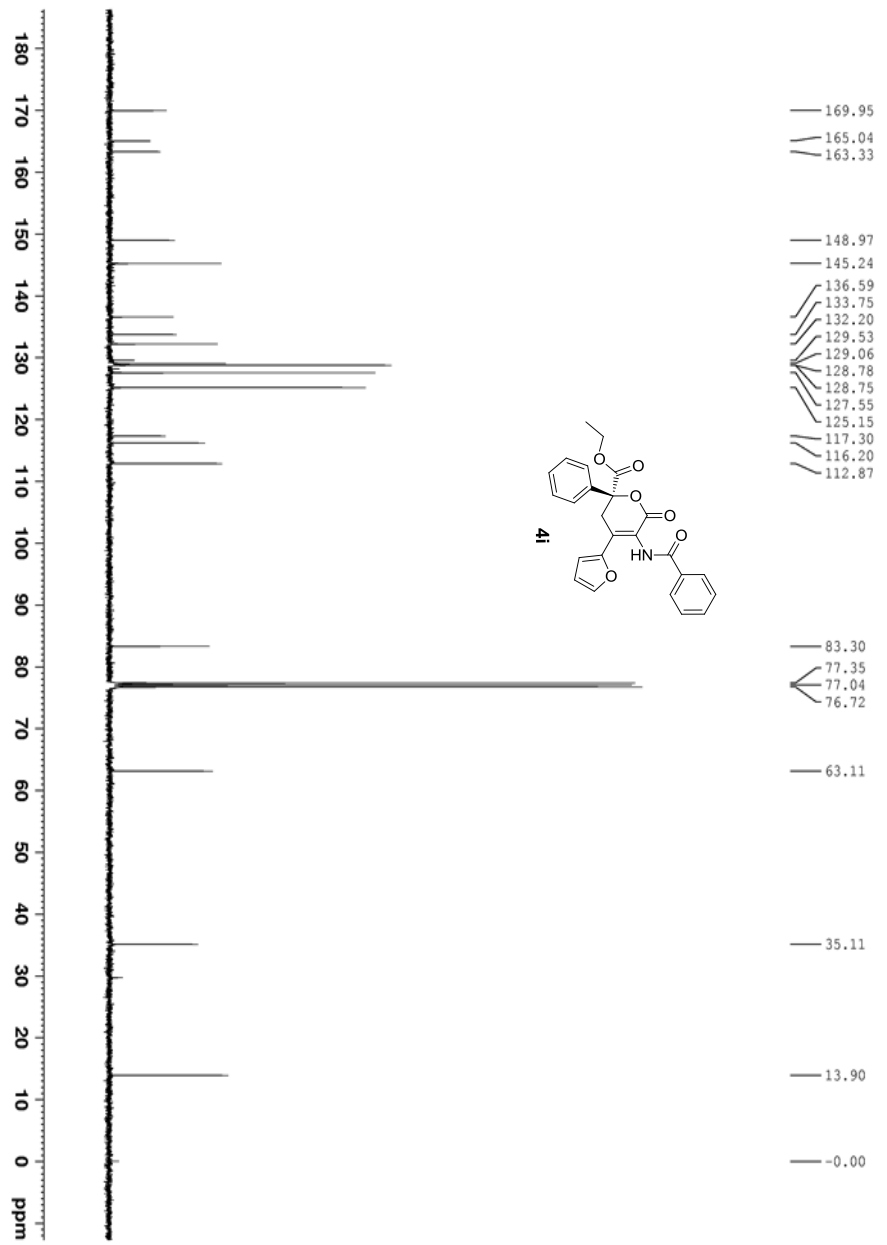
NAME qtp20141205-2
EXPNO 10
PROCNO 1
Date_ 20141205
Time_ 6.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 8012.820 Hz
FIDRES 0.122676 Hz
AQ 4.0894966 sec
RG 181
DW 62.400 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 11.60 usec
SI 65536
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


169.93
164.29
163.35
138.75
137.10
135.95
133.47
133.34
133.03
132.32
130.79
129.29
128.92
128.90
128.79
127.25
126.28
125.07
121.52
84.06
77.34
77.03
76.71
63.35
39.07
14.04
4h
O
O
O
O
HN
O
Cl
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


0.93
2.02
2.01
2.08
5.15
0.99
0.98
2.15
1.16
1.00
3.22
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

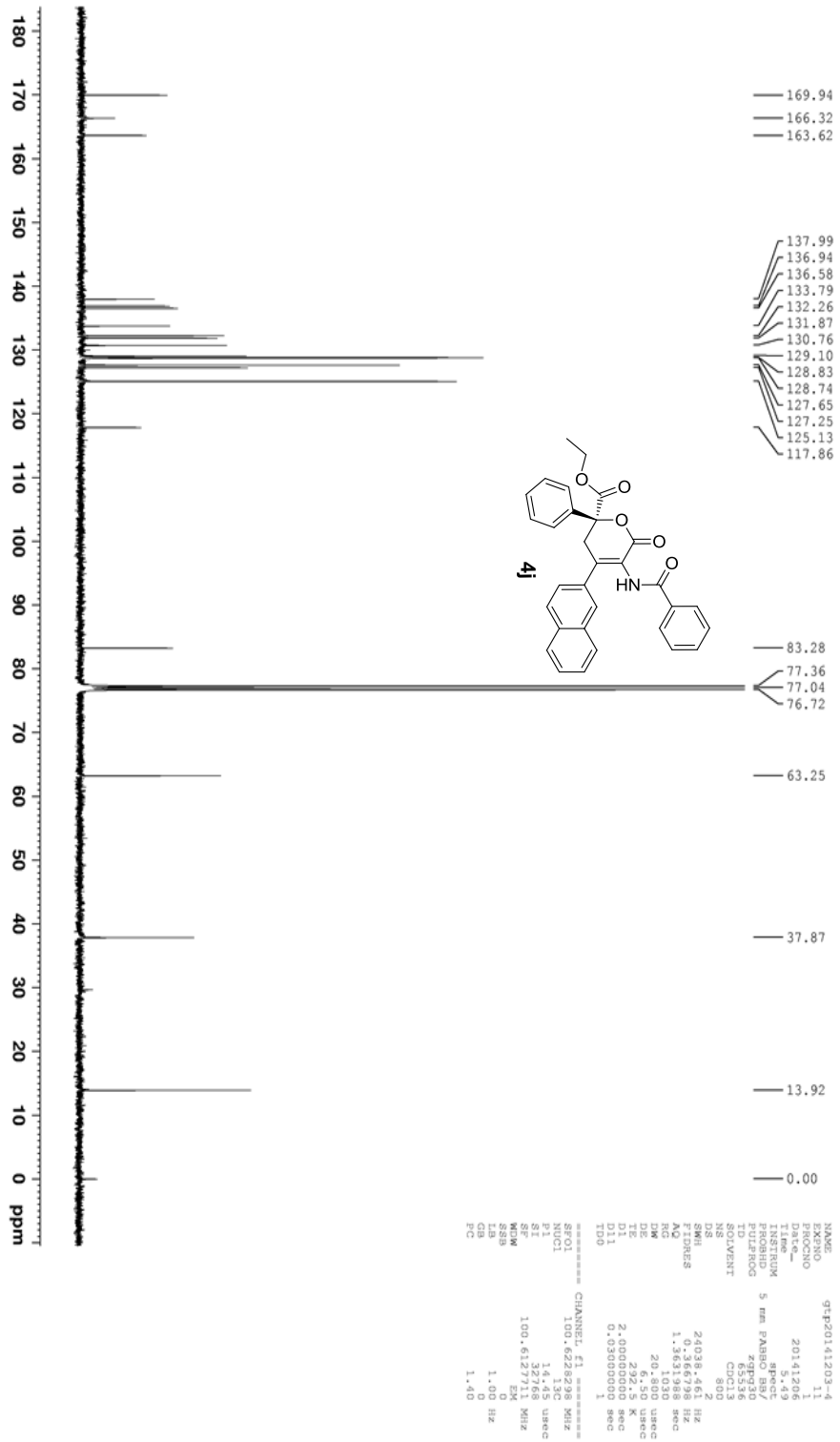

8.073
7.917
7.899
7.740
7.722
7.581
7.563
7.544
7.530
7.499
7.480
7.463
7.448
7.429
7.416
7.398
7.261
6.819
6.810
6.523
6.520
6.515
6.511
4.255
4.240
4.237
4.223
4.220
4.205
4.202
4.162
4.118
3.289
3.246
1.213
1.195
1.177
0.000
4i
O
O
O
O
HN
O
O
NAME gtp20141121-2
EXPNO 10
PROCNO 1
Date_ 20141121
Time 14.02
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
SOLVENT CDCl3
NS 32
DS 2
SWH 8012.820 Hz
FIDRES 0.122986 Hz
AQ 4.089996 sec
RG 144
DW 62.400 usec
DE 6.50 usec
TE 298.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1
P1 11.60 usec
SI 65536
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

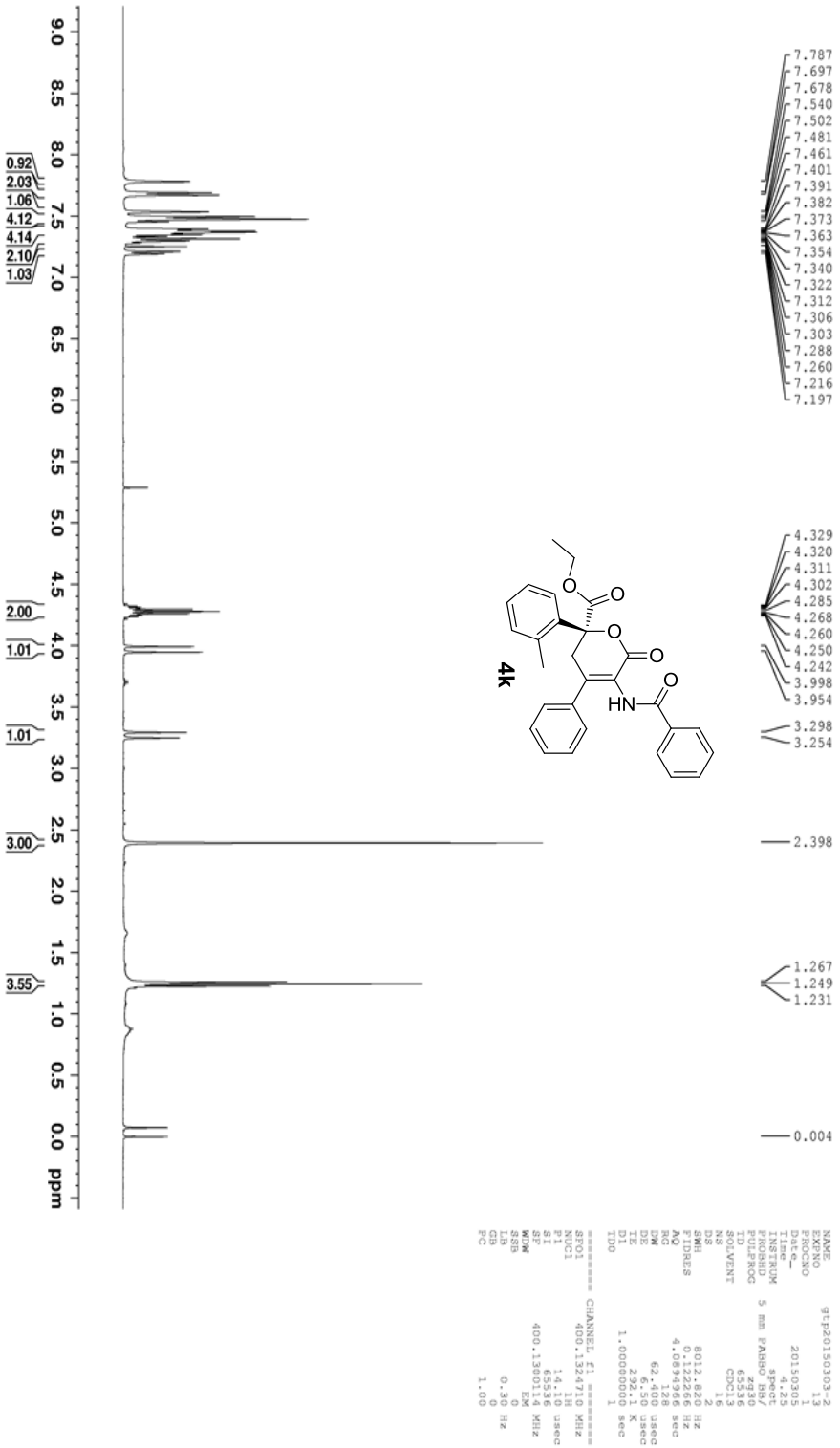


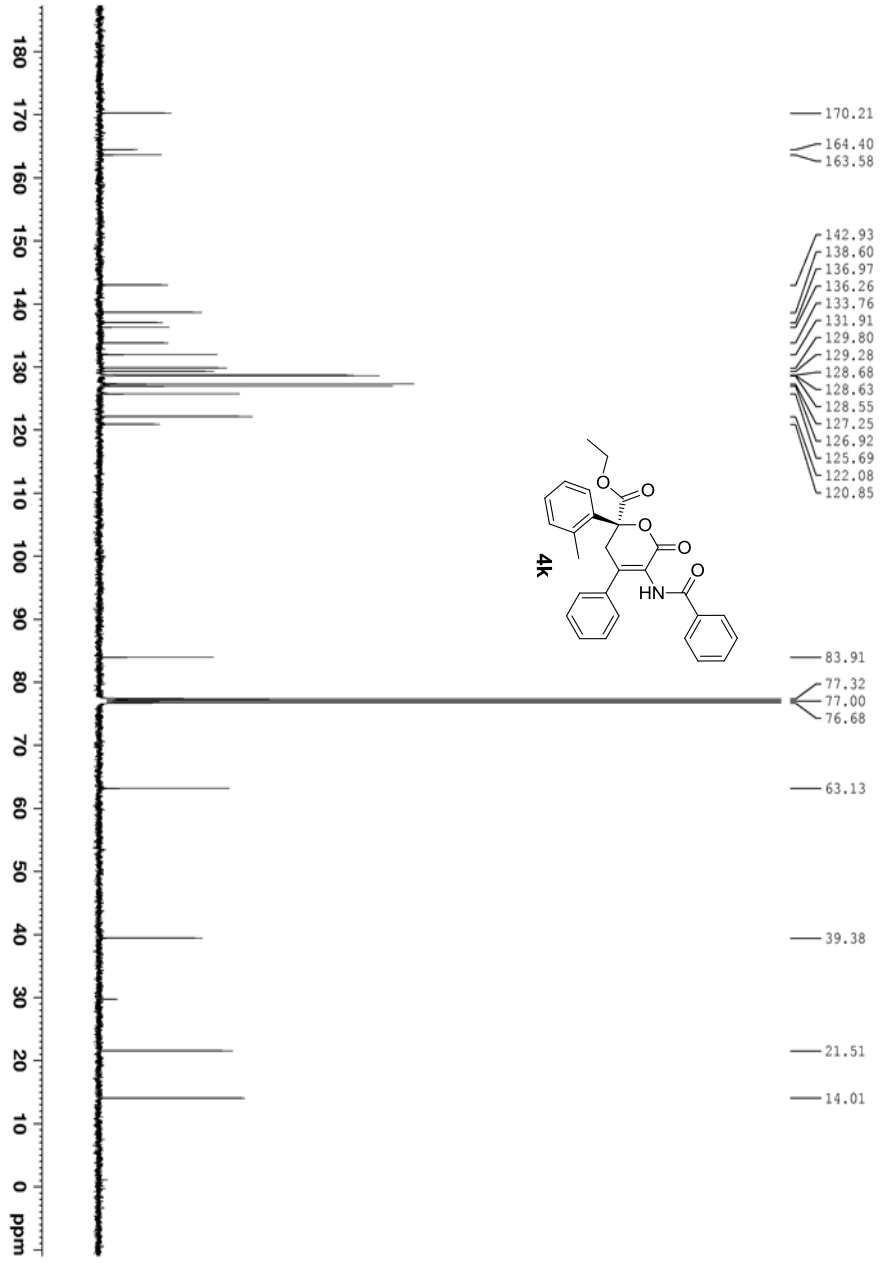

```
NAME                                    qtp20141121-2
EXPNO                                             11
PROCNO                                             1
Date_                                       20141121
Time                                            14:41
INSTRUM                                      spect
PROBHD                                5 mm PABBO BB/
PULPROG                                     zgpg30
TD                                           65536
SOLVENT                                      CDCl3
NS                                              450
DS                                                2
SWH                                       24038.461 Hz
FIDRES                                     0.366798 Hz
AQ                                        1.3631030 sec
RG                                             1030
DW                                          20.800 usec
DE                                           6.50 usec
TE                                         291.8 K
D1                                        2.00000000 sec
D11                                       0.03000000 sec
TD0                                               1

======== CHANNEL f1 ========
SFO1                                    100.6228298 MHz
NUC1                                               13C
P1                                              14.45 usec
SF                                      100.6127711 MHz
WDW                                               EM
SSB                                                0
LB                                              1.00 Hz
GB                                                 0
PC                                              1.40
```

7.932
7.913
7.742
7.724
7.579
7.561
7.542
7.503
7.492
7.477
7.454
7.435
7.423
7.405
7.387
7.258
7.098
7.088
7.077
4.285
4.268
4.251
4.233
4.187
4.145
3.387
3.345
1.221
1.204
1.186
0.000
4j
HN
O
1.99
2.96
2.08
6.26
1.02
2.03
1.05
1.00
3.11
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

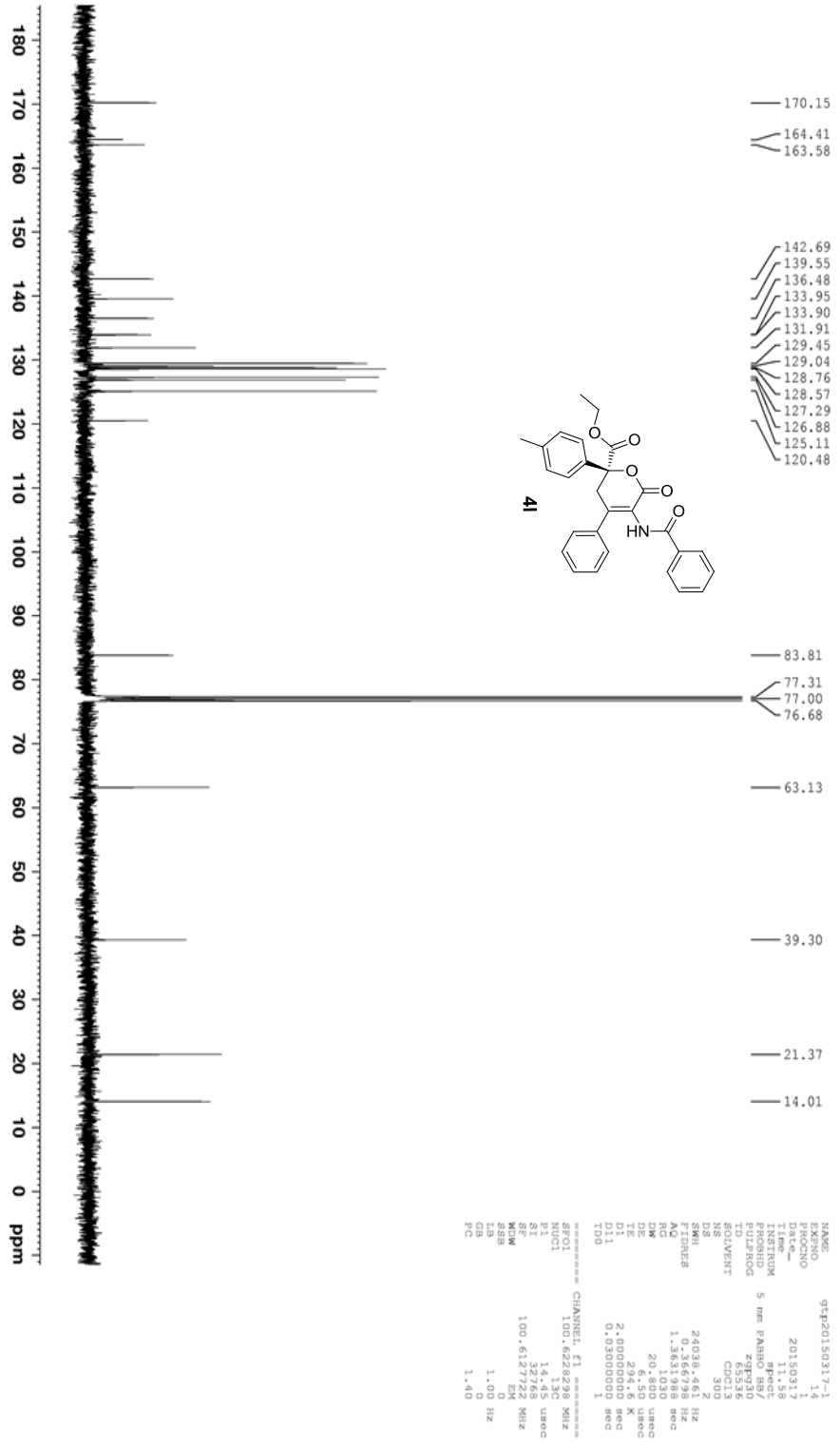

169.94
166.32
163.62
137.99
136.94
136.58
133.79
132.26
131.87
130.76
129.10
128.83
128.74
127.65
127.25
125.13
117.86
83.28
77.36
77.04
76.72
63.25
37.87
13.92
0.00
4j
O
O
O
O
HN
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

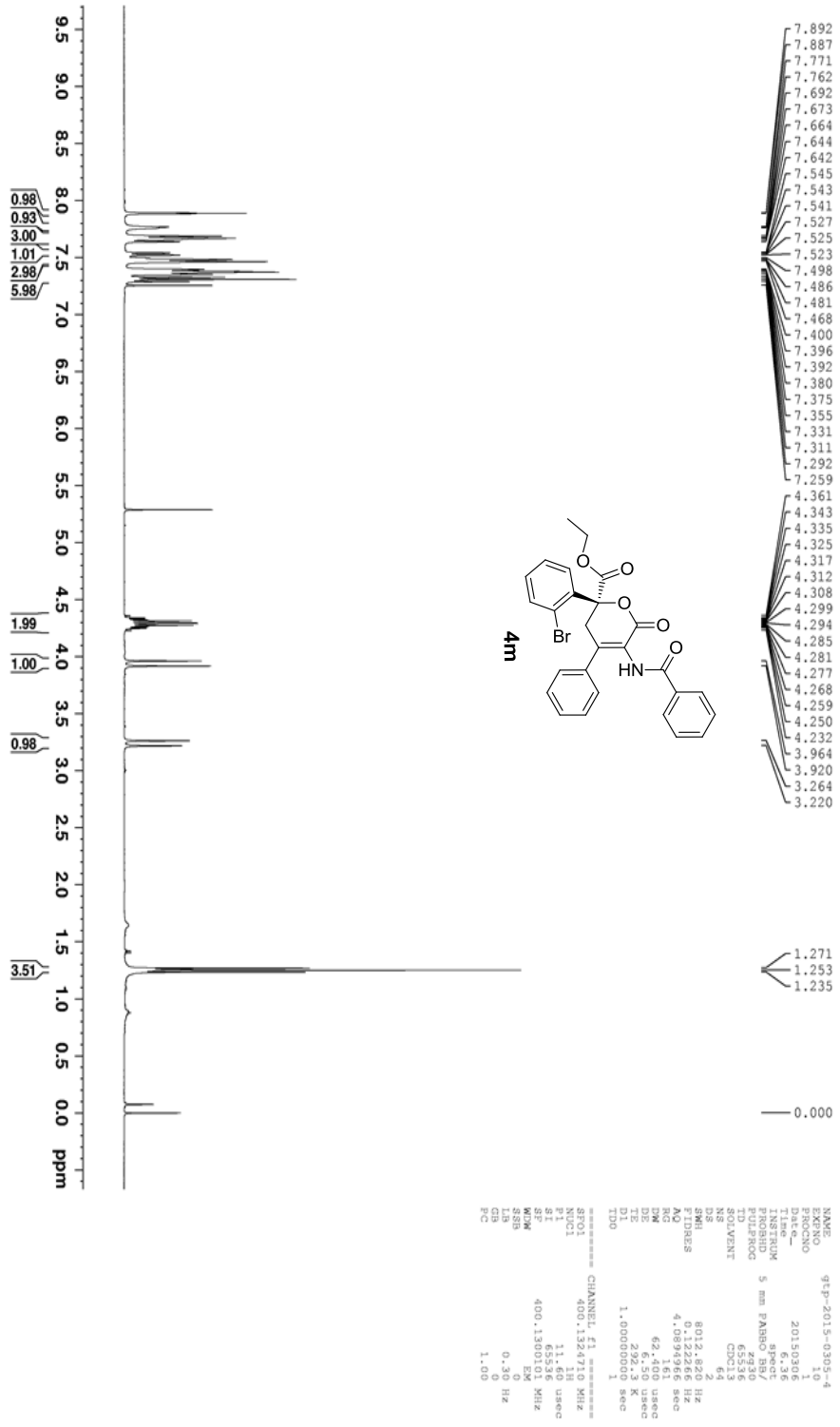

4k
7.787
7.697
7.678
7.540
7.502
7.481
7.461
7.401
7.391
7.382
7.373
7.363
7.354
7.340
7.322
7.312
7.306
7.303
7.288
7.260
7.216
7.197
4.329
4.320
4.311
4.302
4.285
4.268
4.260
4.250
4.242
3.998
3.954
3.298
3.254
2.398
1.267
1.249
1.231
0.004
0.92
2.03
1.06
4.12
4.14
2.10
1.03
2.00
1.01
1.01
3.00
3.55
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

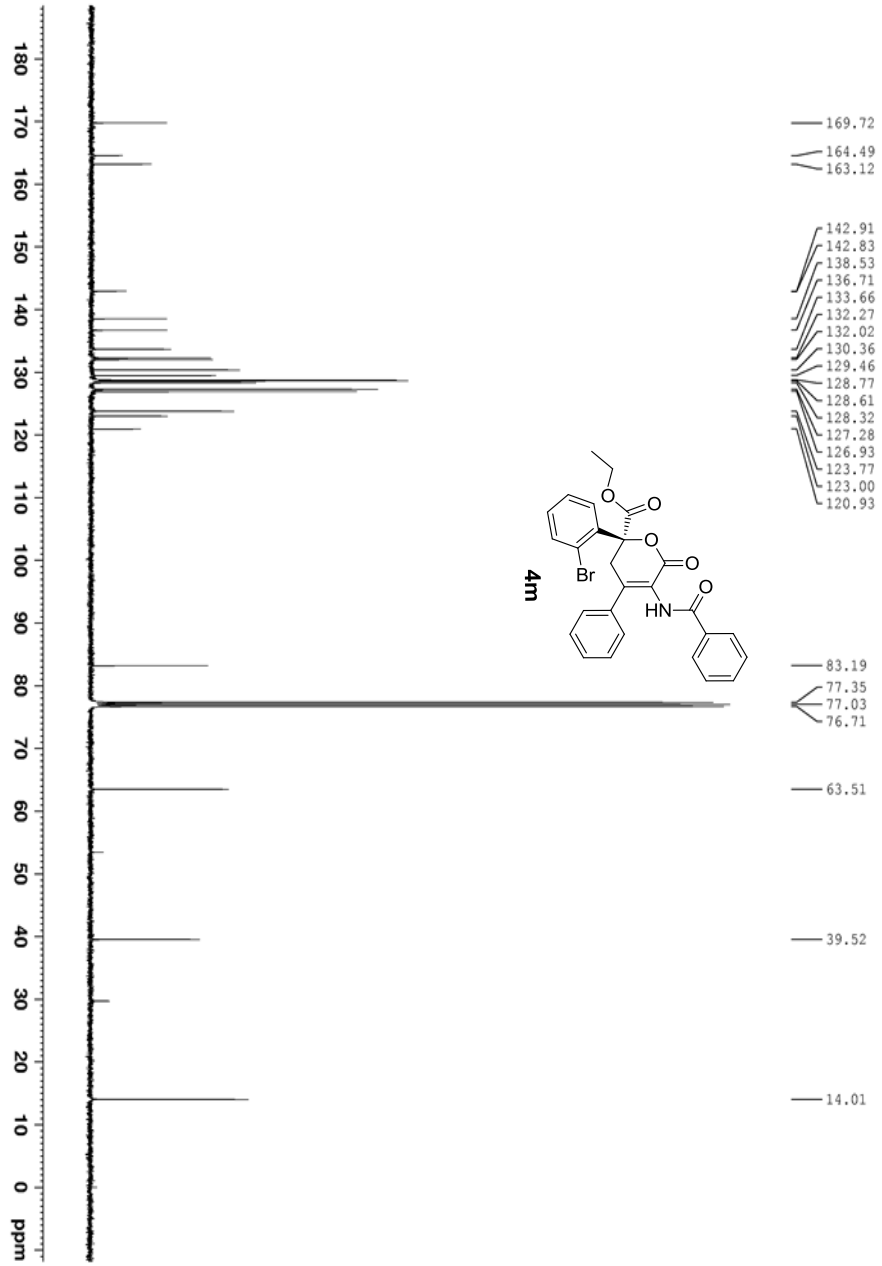


NAME gt-p20150303-2
EXPNO 14
PROCNO 1
1 20150305
Date_
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631258 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 293.0 K
D1 2.00000000 sec
D11 0.03000001 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 12.00 usec
SI 32768
SF 100.6127743 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1.06
4.23
2.35
5.94
2.00
2.16
1.09
1.10
3.00
3.51
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
7.747
7.717
7.698
7.489
7.470
7.455
7.438
7.413
7.405
7.394
7.384
7.258
7.178
7.158
4.316
4.307
4.298
4.290
4.281
4.272
4.263
4.254
4.245
4.237
3.995
3.951
3.279
3.235
2.311
1.258
1.240
1.222
0.000
4l
O
O
O
O
HN
O
NAME gtp20150317-1
EXPNO 13
PROCNO 1
Date_ 20150317
Time 11.40
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 8012.820 Hz
FIDRES 0.122776 Hz
AQ 4.0894366 sec
RG 228
DW 62.400 usec
DE 6.50 usec
TE 295.0 K
D1 1.0000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1
P1 11.60 usec
SI 65536
SF 400.1300107 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


170.15
164.41
163.58
142.69
139.55
136.48
133.95
133.90
131.91
129.45
129.04
128.76
128.57
127.29
126.88
125.11
120.48
83.81
77.31
77.00
76.68
63.13
39.30
21.37
14.01
41
HN
O
ppm


4m
Br
O
HN
7.892
7.887
7.771
7.762
7.692
7.673
7.664
7.644
7.642
7.545
7.543
7.541
7.527
7.525
7.523
7.498
7.486
7.481
7.468
7.400
7.396
7.392
7.380
7.375
7.355
7.331
7.311
7.292
7.259
4.361
4.343
4.335
4.325
4.317
4.312
4.308
4.299
4.294
4.285
4.281
4.277
4.268
4.259
4.250
4.232
3.964
3.920
3.264
3.220
1.271
1.253
1.235
0.000
0.98
0.93
3.00
1.01
2.98
5.98
1.99
1.00
0.98
3.51
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


169.72
164.49
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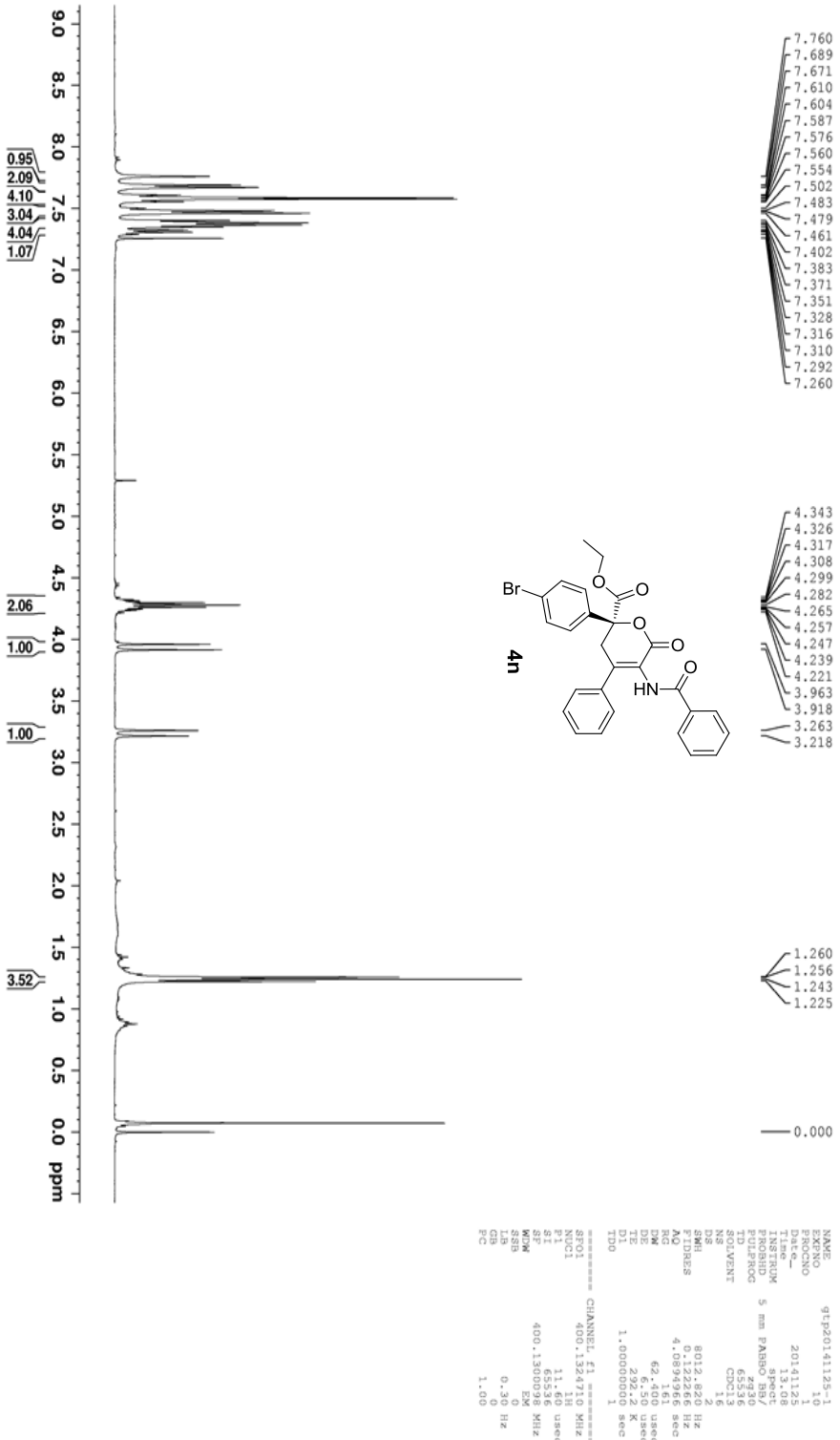
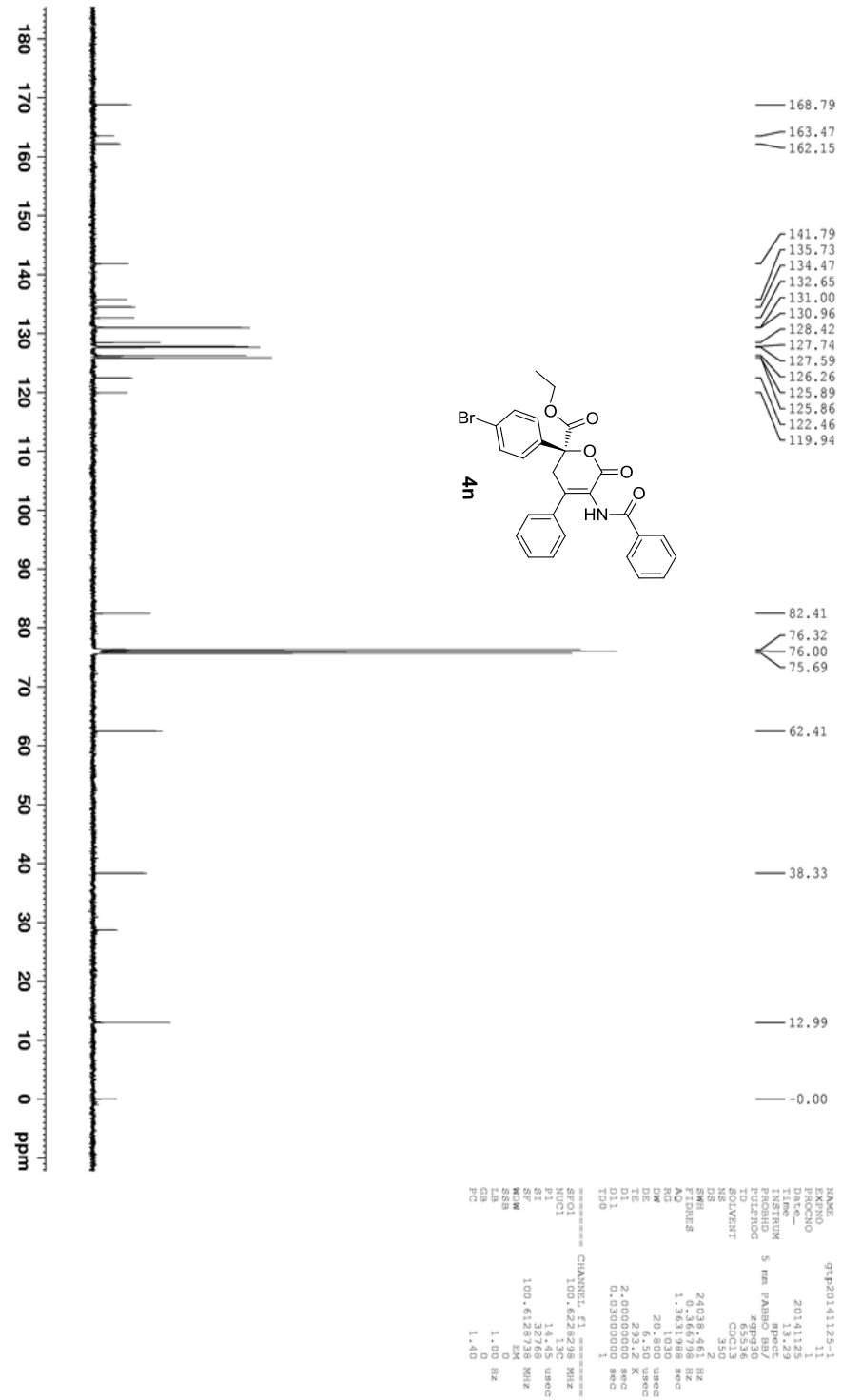
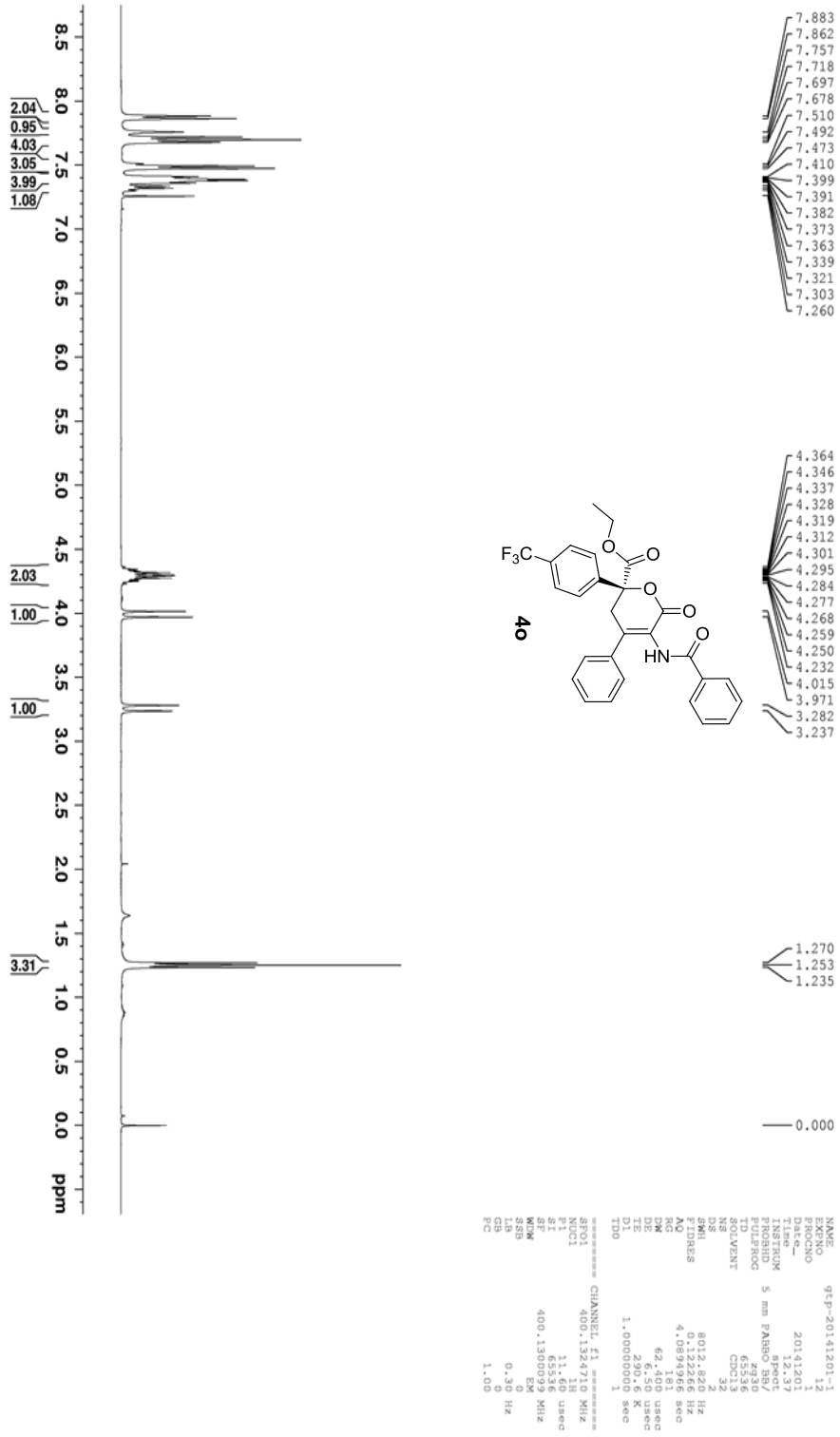
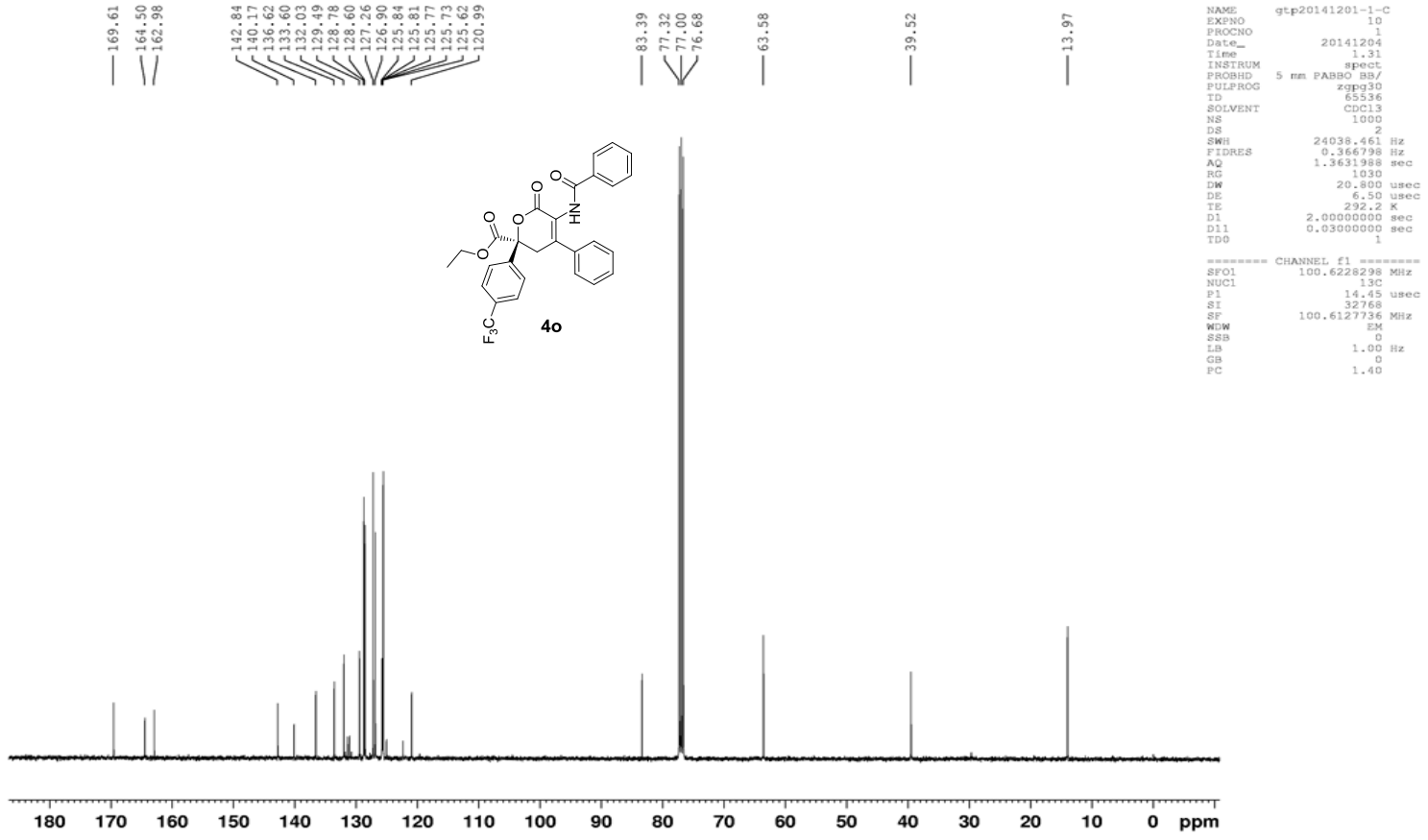
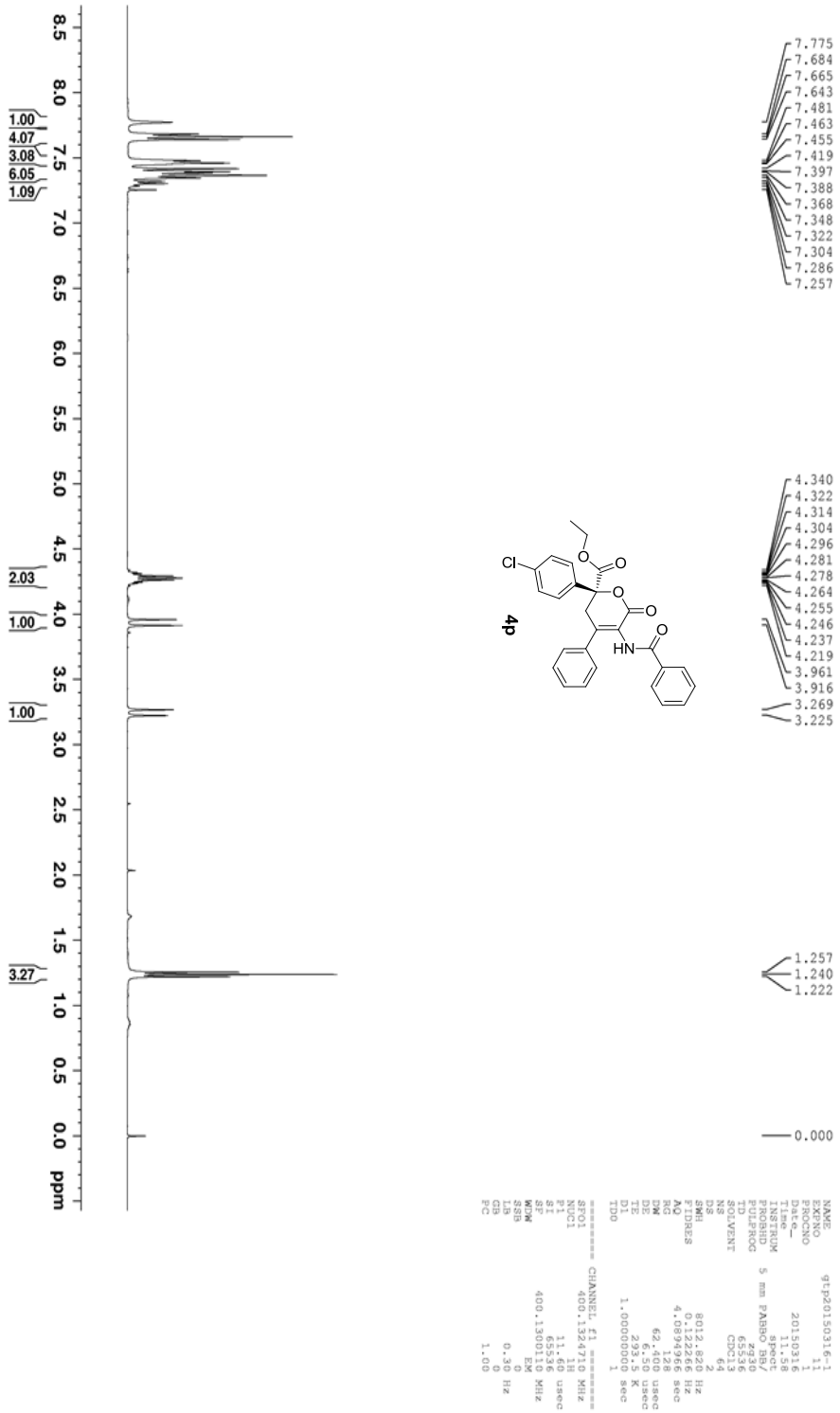
142.91
142.83
138.53
136.71
133.66
132.27
132.02
130.36
129.46
128.77
128.61
128.32
127.28
126.93
123.77
123.00
120.93
83.19
77.35
77.03
76.71
63.51
39.52
14.01
4m
Br
HN
O
ppm

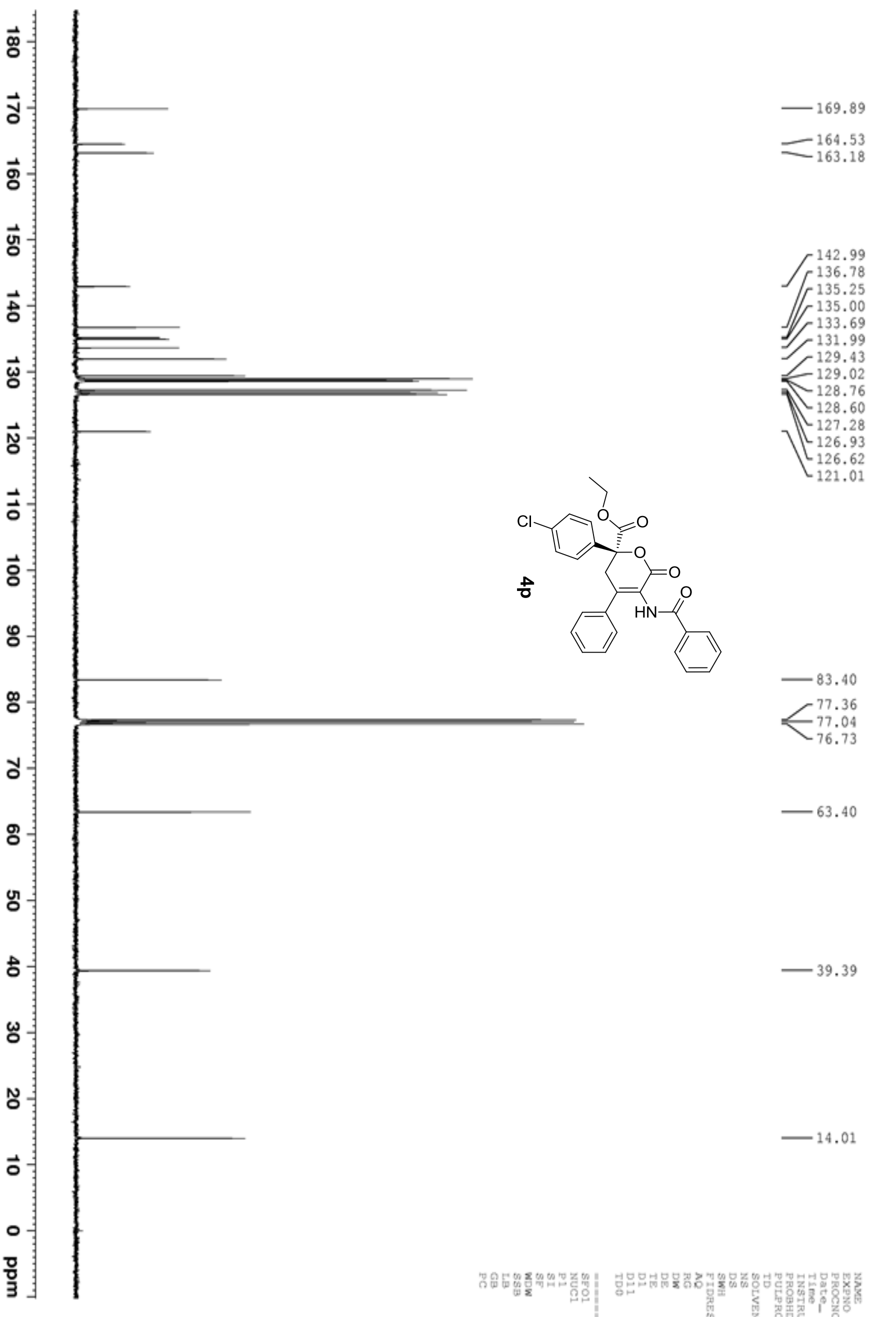

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.95
2.09
4.10
3.04
4.04
1.07
2.06
1.00
1.00
3.52
7.760
7.689
7.671
7.610
7.604
7.587
7.576
7.560
7.554
7.502
7.483
7.479
7.461
7.402
7.383
7.371
7.351
7.328
7.316
7.310
7.292
7.260
4.343
4.326
4.317
4.308
4.299
4.282
4.265
4.257
4.247
4.239
4.221
3.963
3.918
3.263
3.218
1.260
1.256
1.243
1.225
0.000
Br
O
O
O
O
HN
O
4n
NAME gtp20141125-1
EXPNO 10
PROCNO 1
Date_ 20141121
Time_ 13:08
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
SOLVENT CDCl3
NS 16
DS 2
SWH 6012.820 Hz
FIDRES 0.183496 Hz
AQ 4.0894966 sec
RG 161
DW 62.400 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000002 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1
P1 11.60 usec
SI 65536
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


168.79
163.47
162.15
141.79
135.73
134.47
132.65
131.00
130.96
128.42
127.74
127.59
126.26
125.89
125.86
122.46
119.94
82.41
76.32
76.00
75.69
62.41
38.33
12.99
-0.00
Br
O
O
O
O
HN
4n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

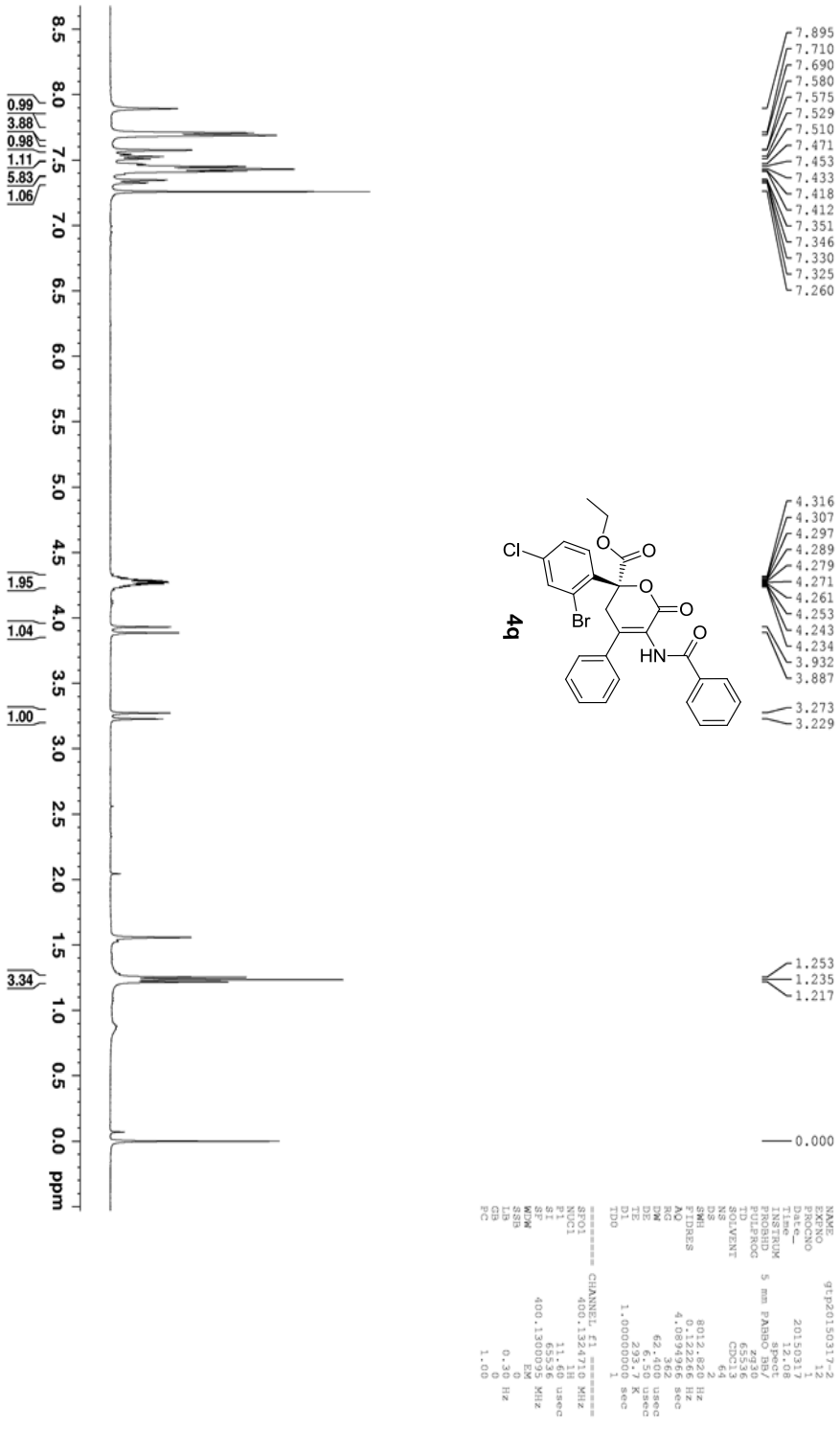

7.883
7.862
7.757
7.718
7.697
7.678
7.510
7.492
7.473
7.410
7.399
7.391
7.382
7.373
7.363
7.339
7.321
7.303
7.260
4.364
4.346
4.337
4.328
4.319
4.312
4.301
4.295
4.284
4.277
4.268
4.259
4.250
4.232
4.015
3.971
3.282
3.237
1.270
1.253
1.235
0.000
2.04
0.95
4.03
3.05
3.99
1.08
2.03
1.00
1.00
3.31
8.5
8.0
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
F3C
O
O
O
O
HN
4o
NAME qtp-20141201-1
EXPNO 12
PROCNO 1
Date_ 20141201
Time 12:37
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
SOLVENT CDCl3
NS 32
DS 2
SWH 8012.820 Hz
FIDRES 0.122988 Hz
AQ 4.089946 sec
RG 181
DW 62.400 usec
DE 20.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1
P1 11.60 usec
SI 65536
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

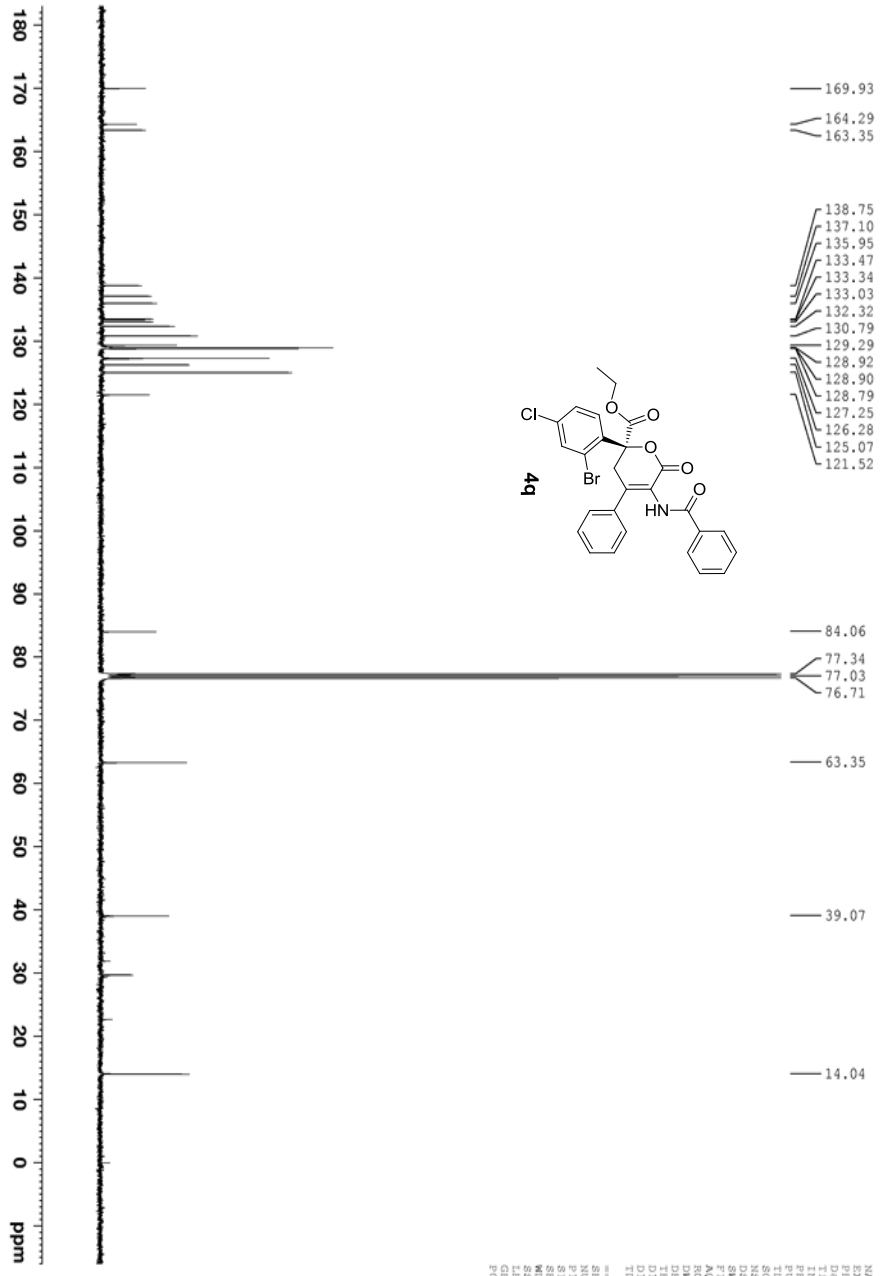

169.61
164.50
162.98
142.84
140.17
136.62
133.60
132.03
129.49
128.78
128.60
127.26
126.90
125.84
125.81
125.77
125.73
125.62
120.99
83.39
77.32
77.00
76.68
63.58
39.52
13.97
4o
NAME gtp20141201-1-C
EXPNO 10
PROCNO 1
Date_ 20141204
Time 1.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1000
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1030
DW 20.800 usec
DE 6.50 usec
TE 292.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 14.45 usec
SI 32768
SF 100.6127936 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

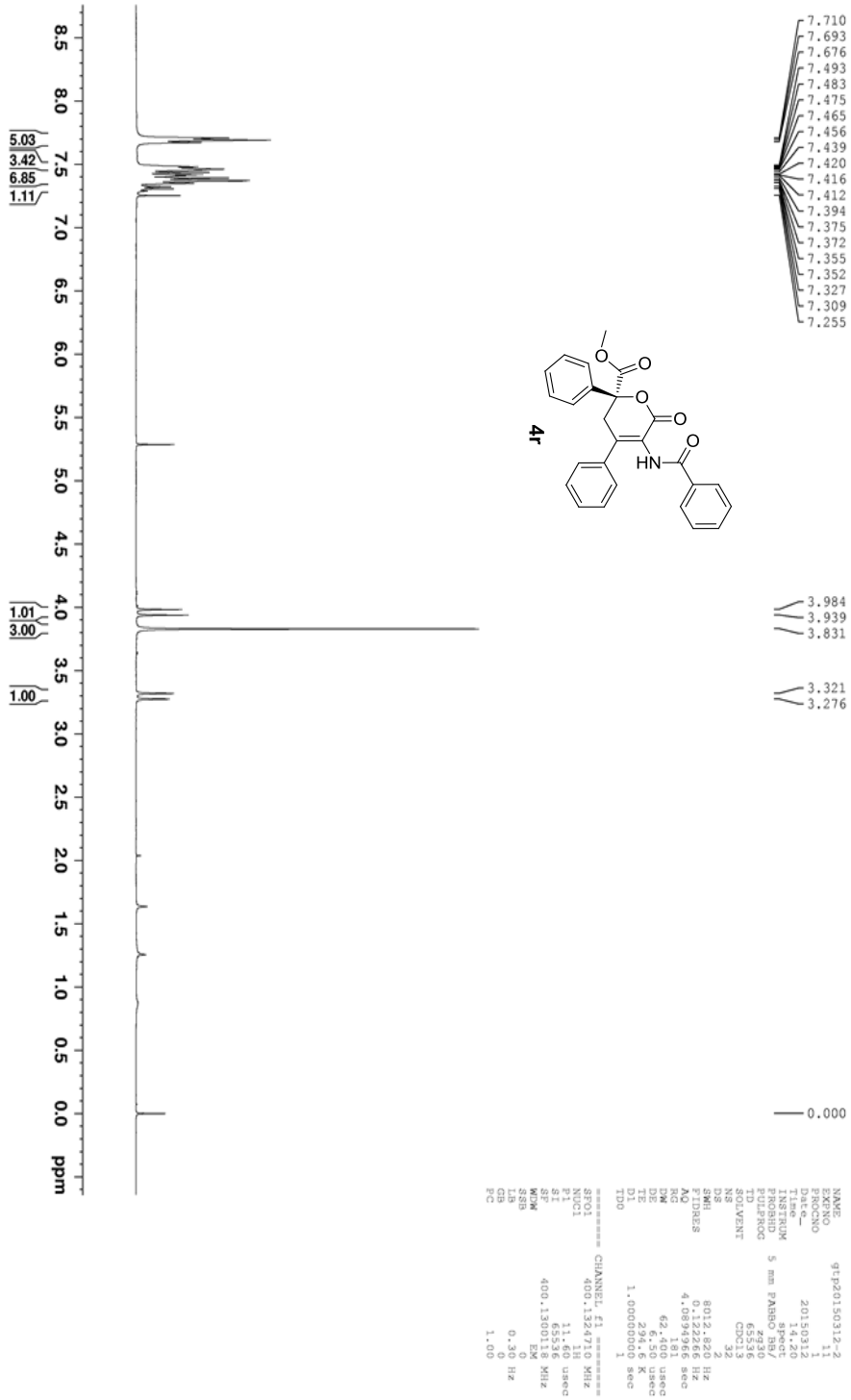

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
4.07
3.08
6.05
1.09
2.03
1.00
1.00
3.27
7.775
7.684
7.665
7.643
7.481
7.463
7.455
7.419
7.397
7.388
7.368
7.348
7.322
7.304
7.286
7.257
4.340
4.322
4.314
4.304
4.296
4.281
4.278
4.264
4.255
4.246
4.237
4.219
3.961
3.916
3.269
3.225
1.257
1.240
1.222
0.000
Cl
O
O
O
O
HN
4p

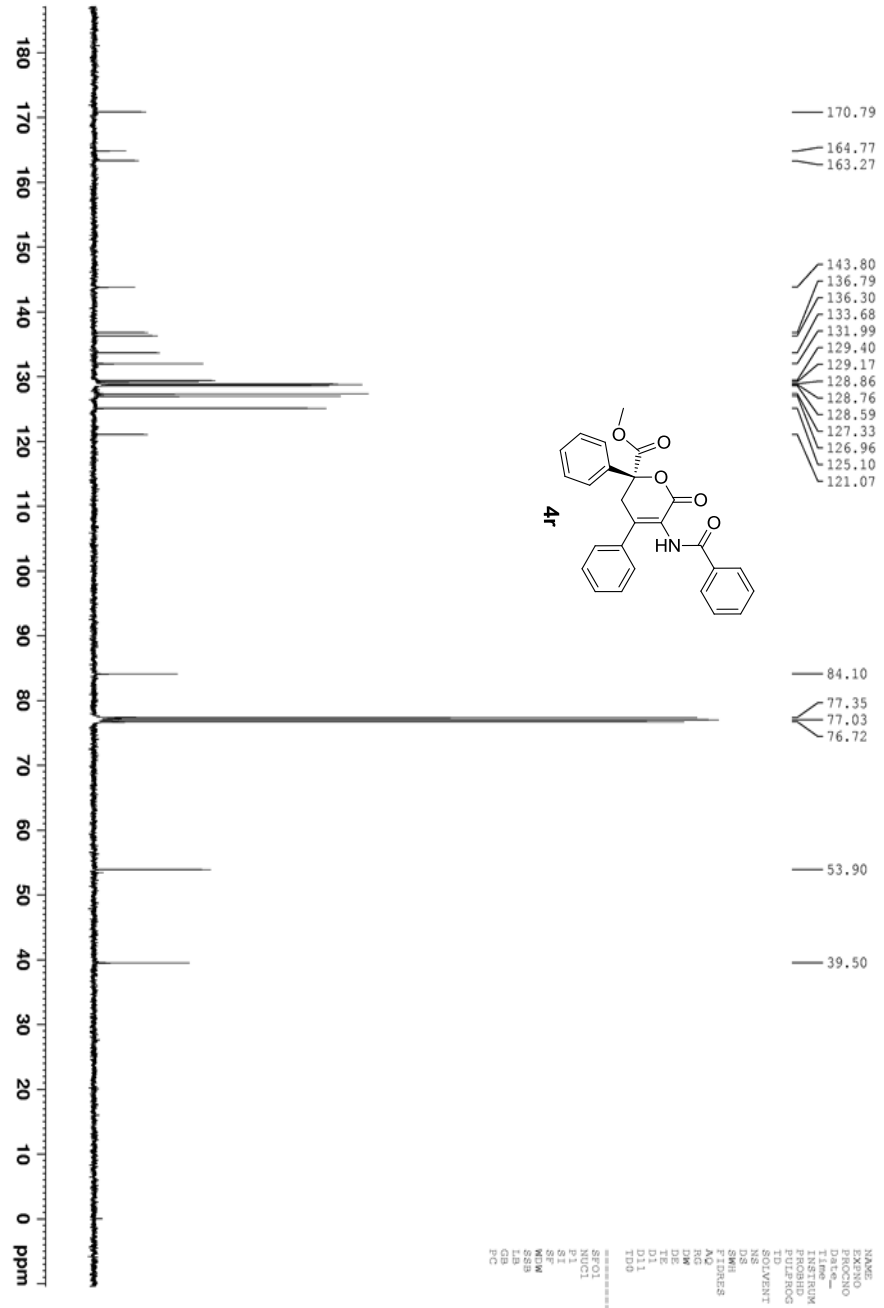


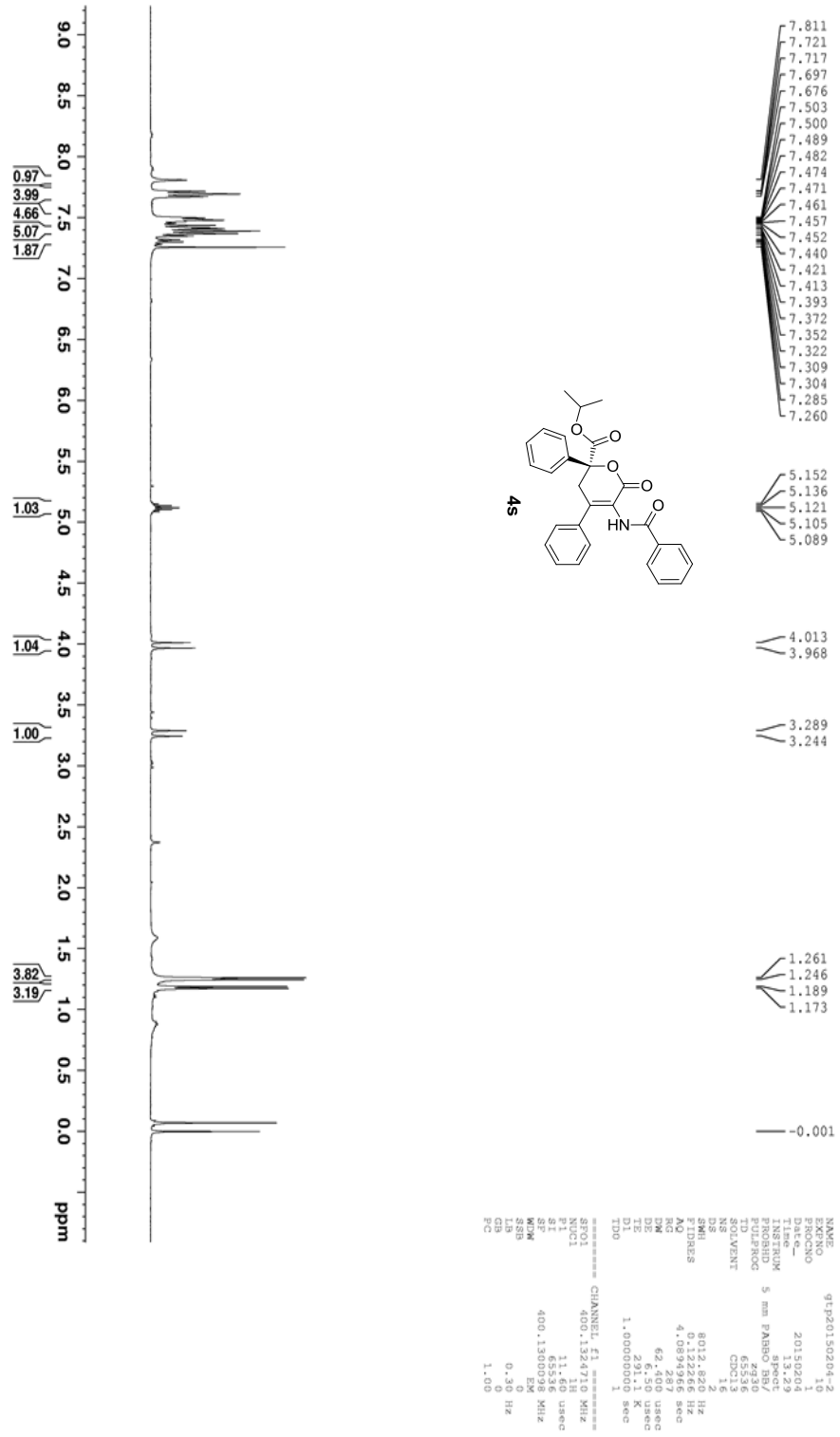
169.89
164.53
163.18
142.99
136.78
135.25
135.00
133.69
131.99
129.43
129.02
128.76
128.60
127.28
126.93
126.62
121.01
83.40
77.36
77.04
76.73
63.40
39.39
14.01
4p
Cl
O
HN
ppm

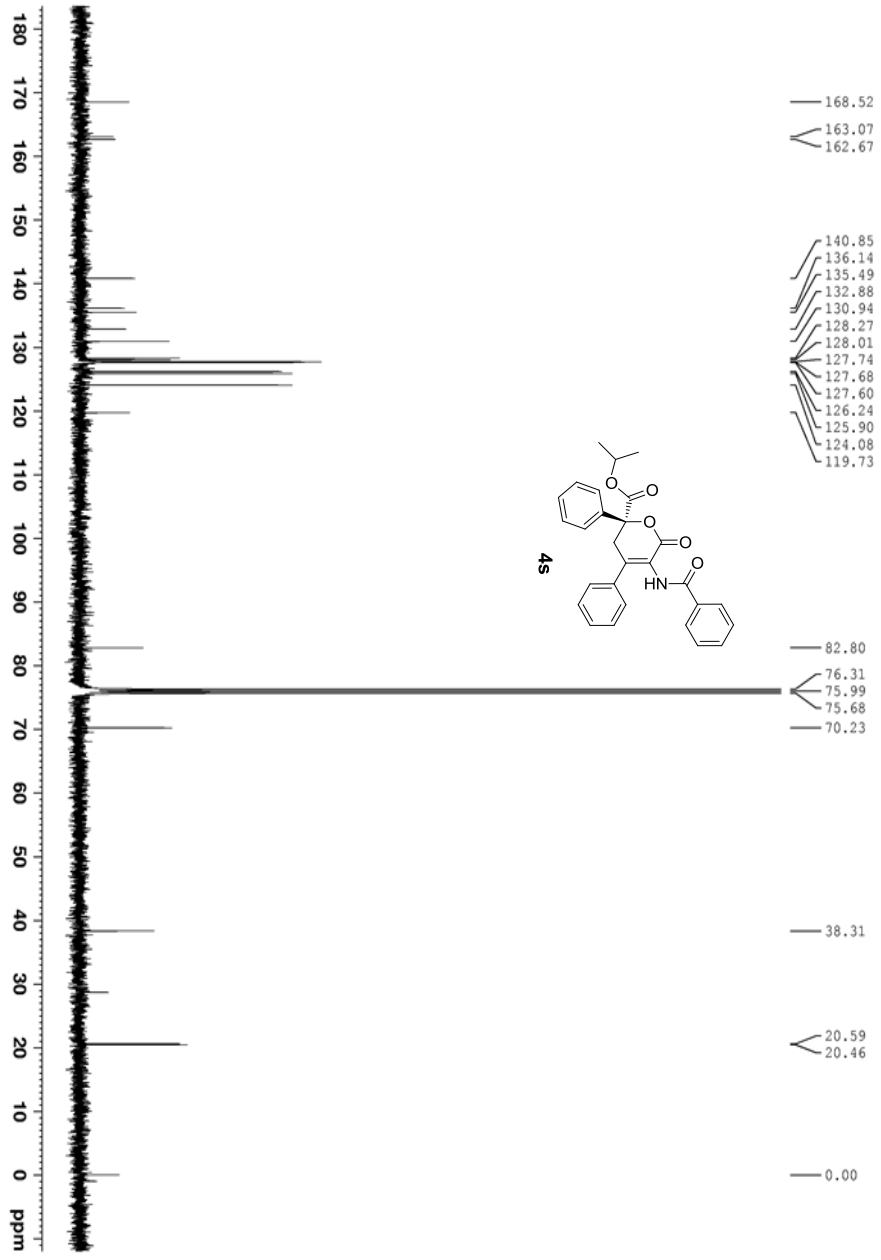

7.895
7.710
7.690
7.580
7.575
7.529
7.510
7.471
7.453
7.433
7.418
7.412
7.351
7.346
7.330
7.325
7.260
4.316
4.307
4.297
4.289
4.279
4.271
4.261
4.253
4.243
4.234
3.932
3.887
3.273
3.229
1.253
1.235
1.217
0.000
0.99
3.88
0.98
1.11
5.83
1.06
1.95
1.04
1.00
3.34
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
Cl
Br
O
O
O
O
HN
O
4q
NAME grp20150317-2
EXPNO 12
PROCNO 1
Date_ 20150317
Time 12.08
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 8012.820 Hz
FIDRES 0.122966 Hz
AQ 4.089496 sec
RG 62.400
DW 62.400 usec
DE 6.50 usec
TE 295.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 11.60 usec
SI 65536
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


169.93
164.29
163.35
138.75
137.10
135.95
133.47
133.34
133.03
132.32
130.79
129.29
128.92
128.90
128.79
127.25
126.28
125.07
121.52
84.06
77.34
77.03
76.71
63.35
39.07
14.04
4q
Cl
Br
O
HN
ppm

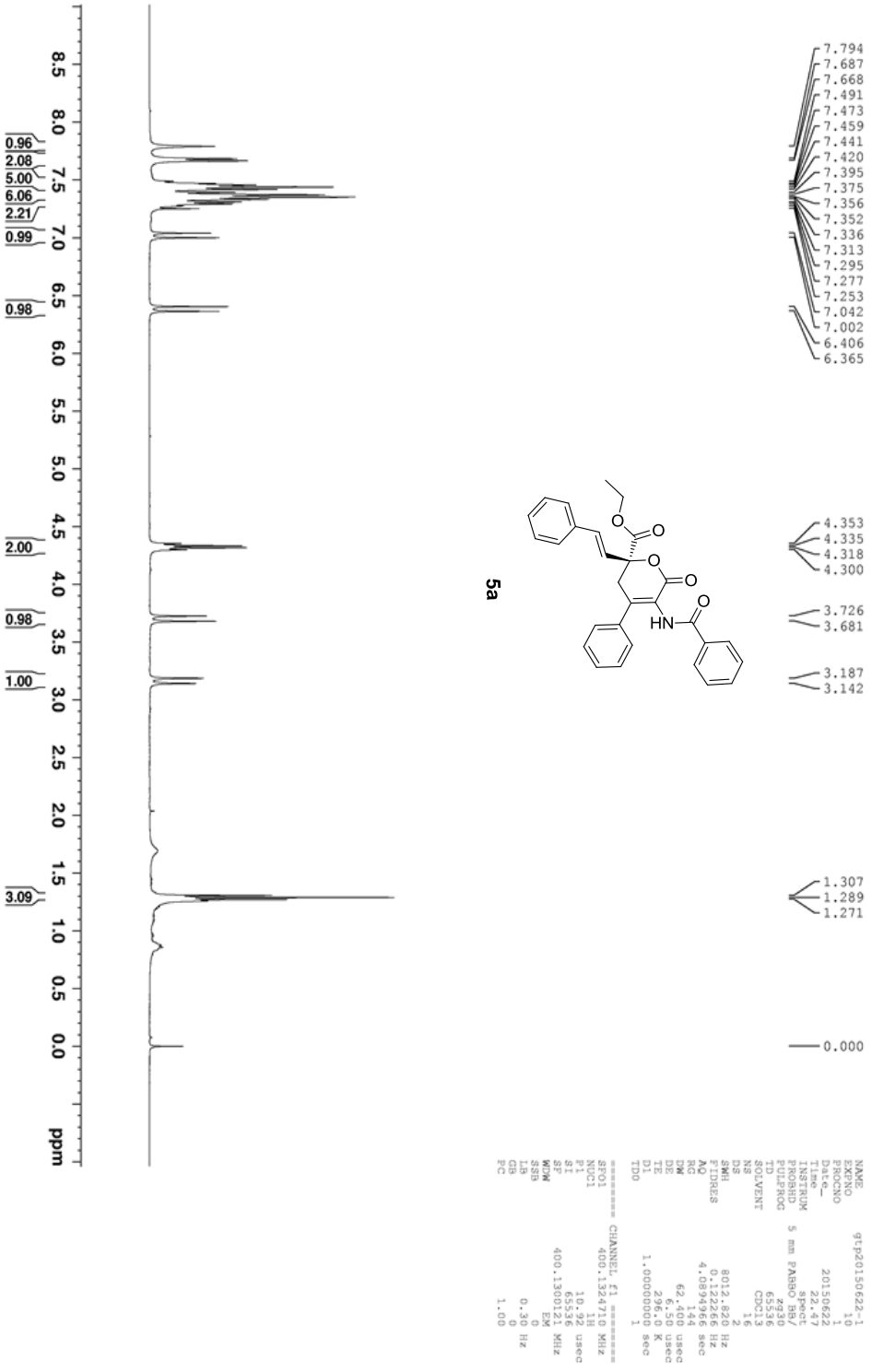

7.710
7.693
7.676
7.493
7.483
7.475
7.465
7.456
7.439
7.420
7.416
7.412
7.394
7.375
7.372
7.355
7.352
7.327
7.309
7.255
4r
3.984
3.939
3.831
3.321
3.276
0.000
5.03
3.42
6.85
1.11
1.01
3.00
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

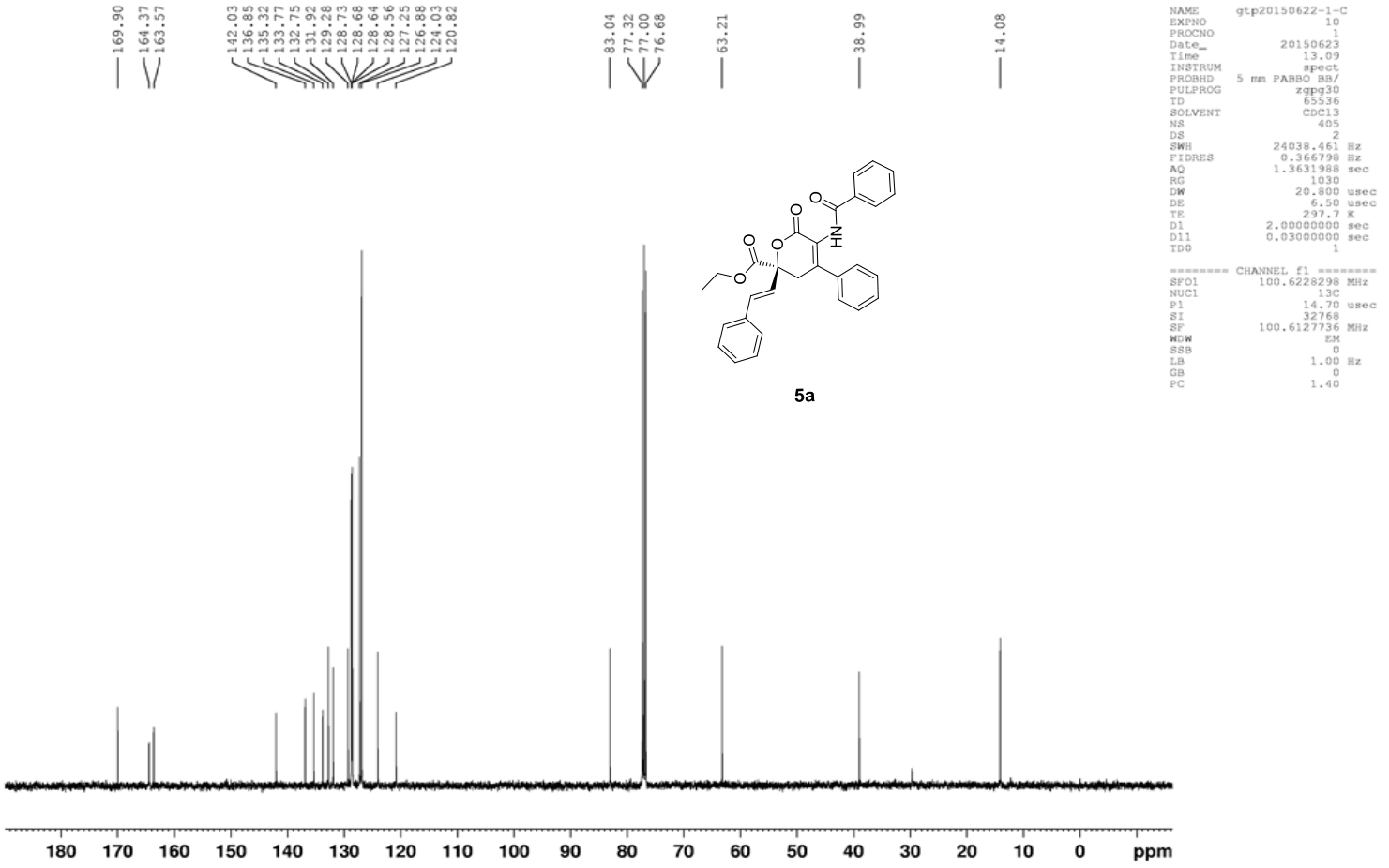

170.79
164.77
163.27
143.80
136.79
136.30
133.68
131.99
129.40
129.17
128.86
128.76
128.59
127.33
126.96
125.10
121.07
84.10
77.35
77.03
76.72
53.90
39.50
4r
O
O
O
O
HN
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

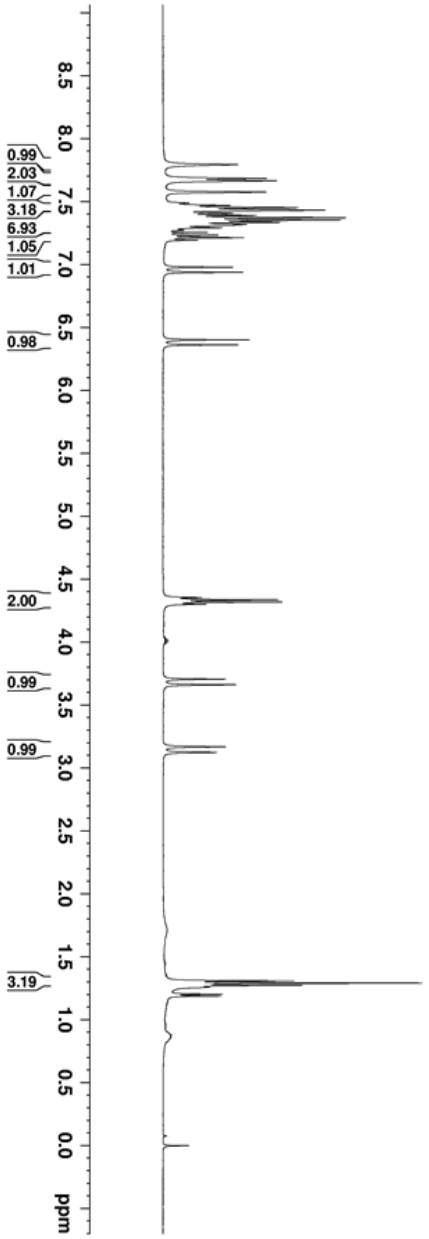

4s
HN
O
7.811
7.721
7.717
7.697
7.676
7.503
7.500
7.489
7.482
7.474
7.471
7.461
7.457
7.452
7.440
7.421
7.413
7.393
7.372
7.352
7.322
7.309
7.304
7.285
7.260
5.152
5.136
5.121
5.105
5.089
4.013
3.968
3.289
3.244
1.261
1.246
1.189
1.173
-0.001
0.97
3.99
4.66
5.07
1.87
1.03
1.04
1.00
3.82
3.19
9.0
8.5
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

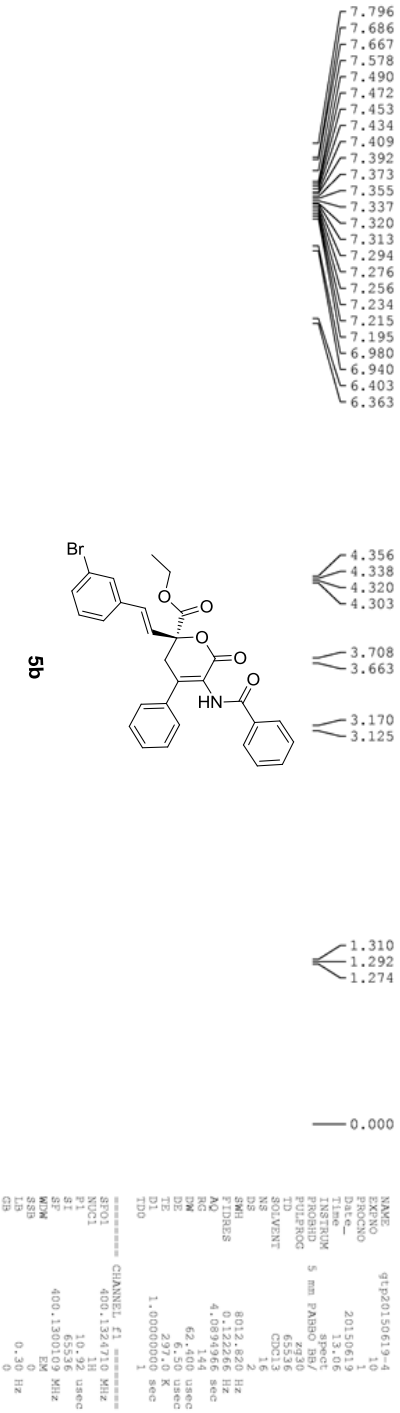

168.52
163.07
162.67
140.85
136.14
135.49
132.88
130.94
128.27
128.01
127.74
127.68
127.60
126.24
125.90
124.08
119.73
82.80
76.31
75.99
75.68
70.23
38.31
20.59
20.46
0.00
4s
HN
O
O
O
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

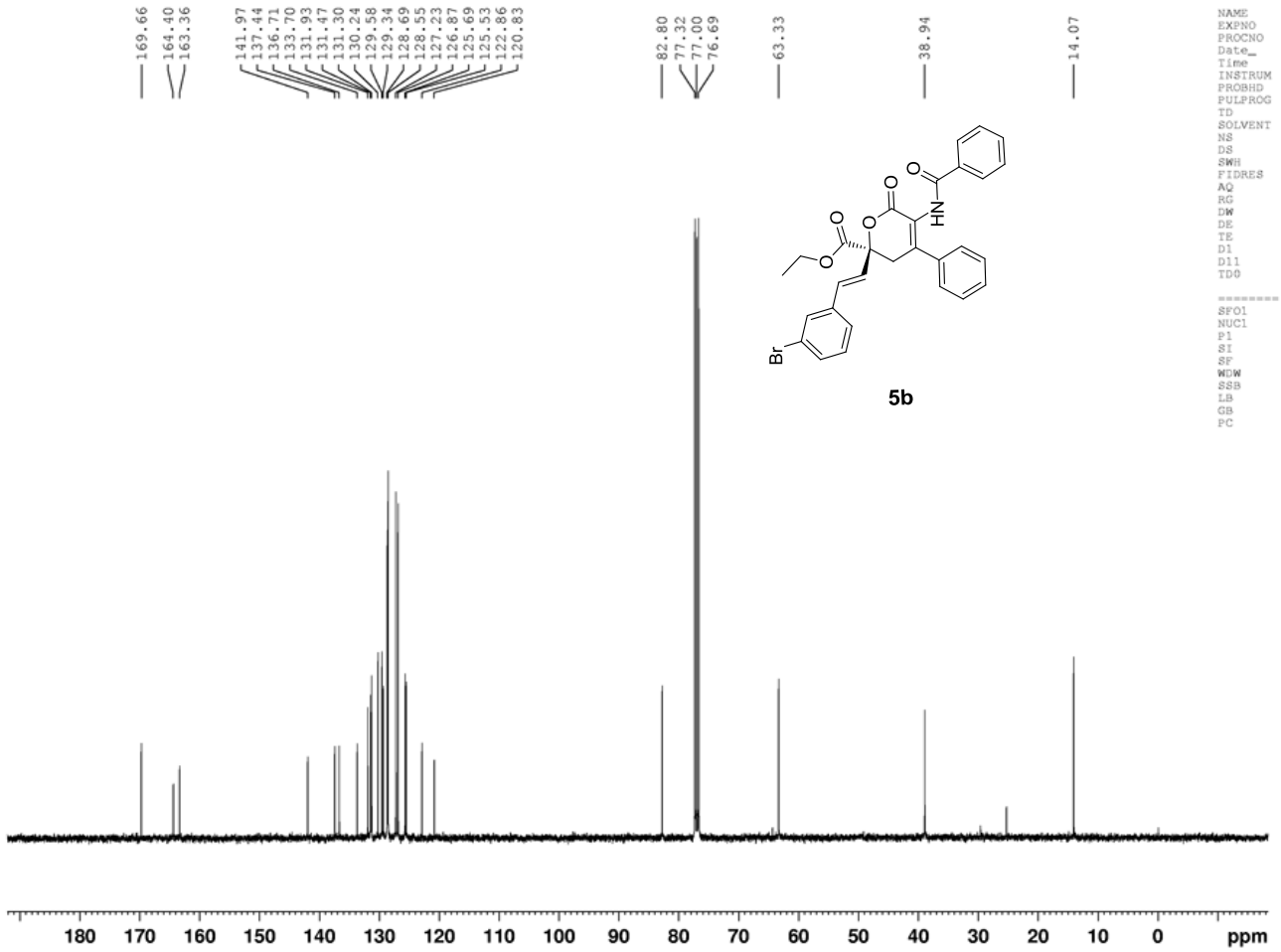
7. NMR spectra of compounds **5**




169.90
164.37
163.57
142.03
136.85
135.32
133.77
132.75
131.92
129.28
128.73
128.68
128.64
128.56
127.25
126.88
124.03
120.82
83.04
77.32
77.00
76.68
63.21
38.99
14.08
NAME gtp20150622-1-C
EXPNO 10
PROCNO 1
Date_ 20150623
Time 13.09
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 405
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1030
DW 20.800 usec
DE 6.50 usec
TE 297.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 14.70 usec
SI 32768
SF 100.6127736 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
HN
5a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

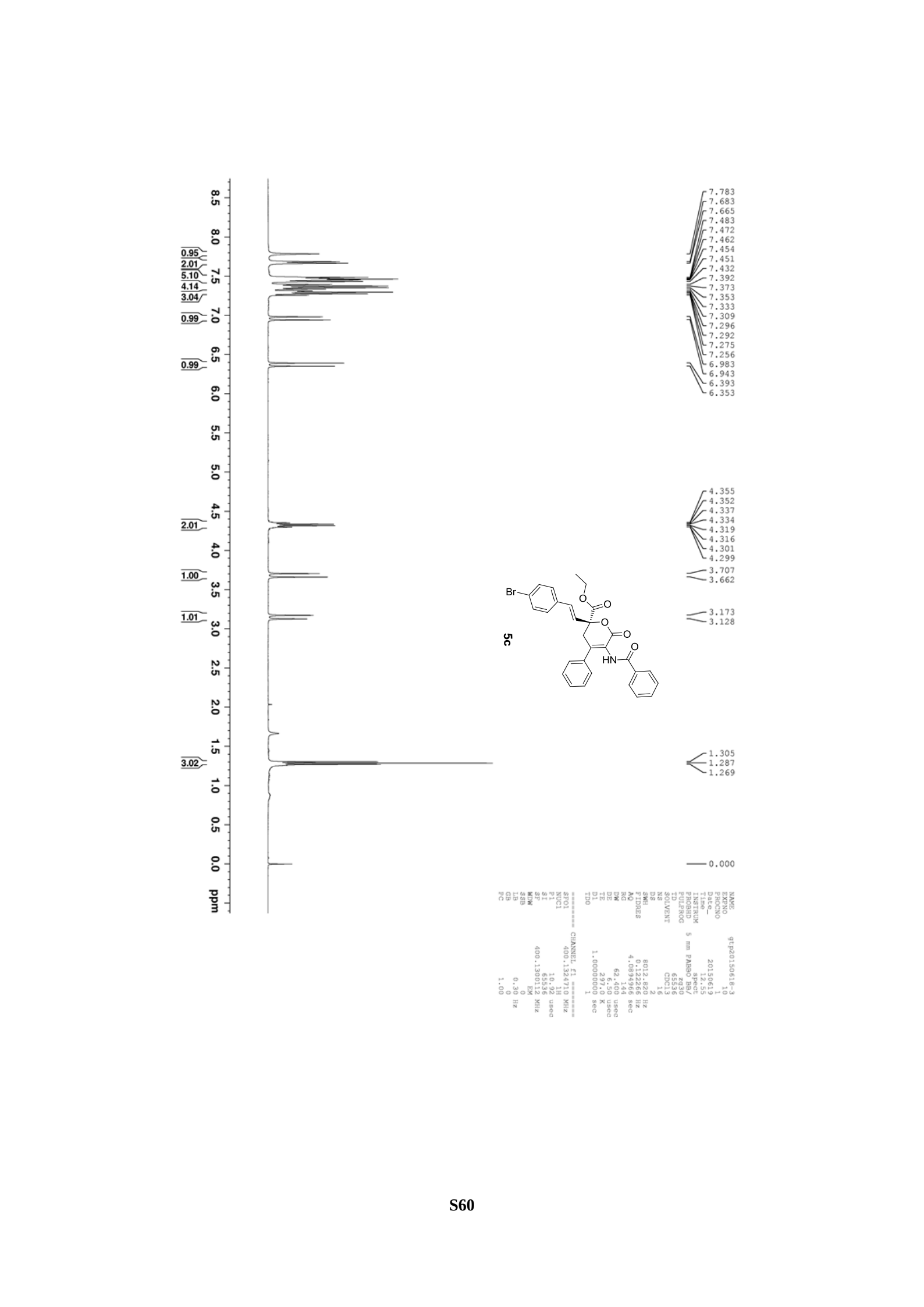

0.99
2.03
1.07
3.18
6.93
1.05
1.01
0.98
2.00
0.99
0.99
3.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


7.796
7.686
7.667
7.578
7.490
7.472
7.453
7.434
7.409
7.392
7.373
7.355
7.337
7.320
7.313
7.294
7.276
7.256
7.234
7.215
7.195
6.980
6.940
6.403
6.363
4.356
4.338
4.320
4.303
3.708
3.663
3.170
3.125
1.310
1.292
1.274
0.000
Br
O
O
O
O
HN
O
5b
NAME gtp20150619-4
EXPNO 1
PROCNO 1
Date_ 20150619
Time 13.06
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 144
DW 62.400 usec
DE 6.00 usec
TE 297.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 10.90 usec
SI 65536
SF 400.1300109 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



5b

NAME	gtp20150619-4
EXPNO	20
PROCNO	1
Date_	20150622
Time	23.17
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	450
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	1030
DW	20.800 usec
DE	6.50 usec
TE	296.9 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	14.70 usec
SI	32768
SF	100.6127751 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40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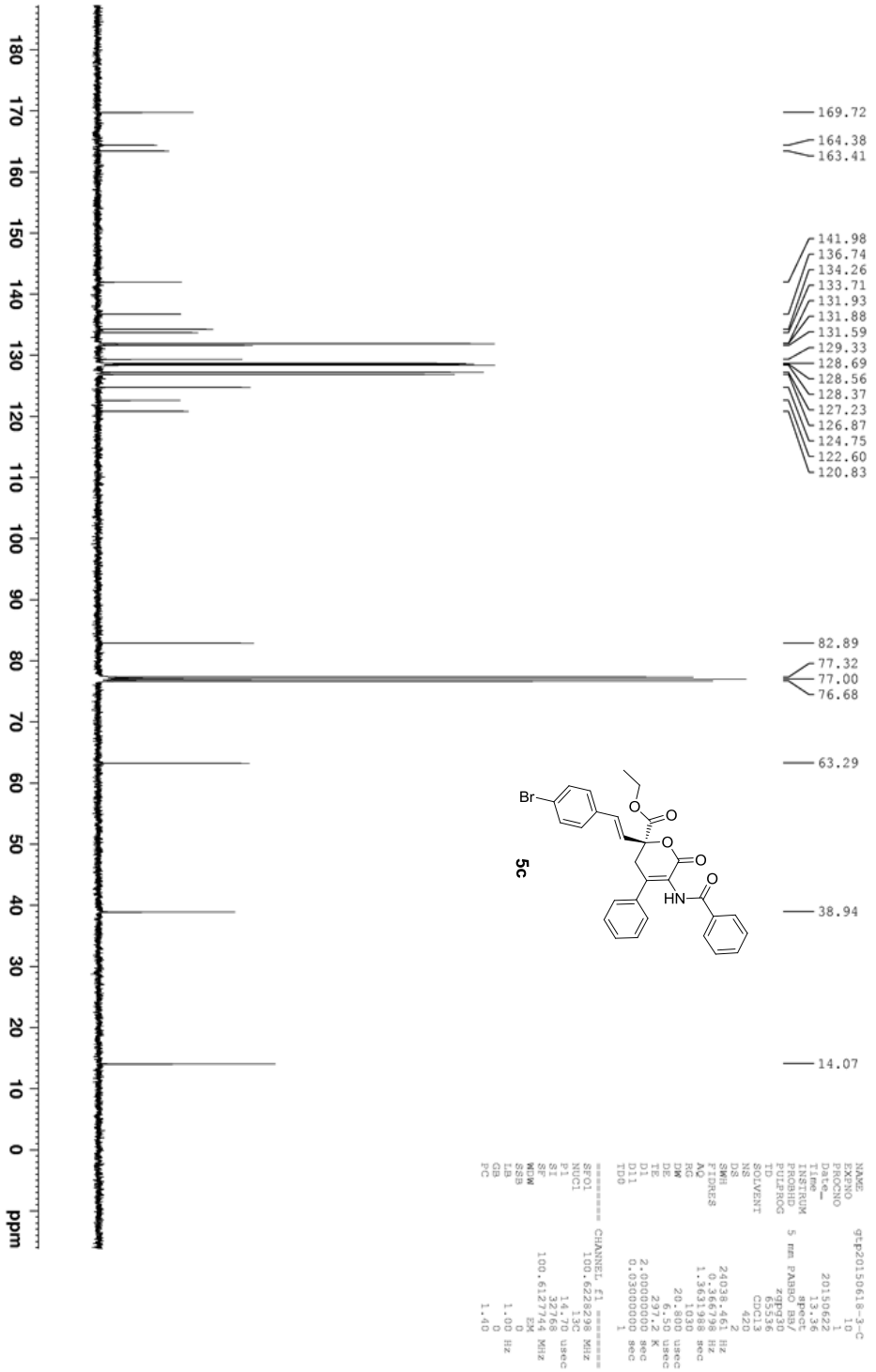
7.472
7.462
7.454
7.451
7.432
7.392
7.373
7.353
7.333
7.309
7.296
7.292
7.275
7.256
6.983
6.943
6.393
6.353
4.355
4.352
4.337
4.334
4.319
4.316
4.301
4.299
3.707
3.662
3.173
3.128
1.305
1.287
1.269
0.000
Br
O
O
O
O
HN
O
5c
0.95
2.01
5.10
4.14
3.04
0.99
0.99
2.01
1.00
1.01
3.02
8.5
8.0
7.5
7.0
6.5
6.0
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


169.72
164.38
163.41
141.98
136.74
134.26
133.71
131.93
131.88
131.59
129.33
128.69
128.56
128.37
127.23
126.87
124.75
122.60
120.83
82.89
77.32
77.00
76.68
63.29
38.94
14.07
Br
O
O
O
O
HN
5c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

7.772
7.686
7.668
7.492
7.474
7.455
7.437
7.397
7.377
7.354
7.333
7.311
7.290
7.272
7.254
7.165
7.146
6.999
6.959
6.349
6.309
4.347
4.330
4.312
4.295
3.717
3.672
3.179
3.134
2.348
1.302
1.284
1.267
0.000
5d
HN
O
O
O
O
O
NAME gtp20150618-2
EXPNO 10
PROCNO 1
Date_ 20150619
Time 12.50
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
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NUC1 1H
P1 10.90 usec
PL1 65536
SF 400.1300118 MHz
WDW EM
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LB 0.30 Hz
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PC 1.00
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3.14
7.34
2.18
1.06
1.01
2.11
1.06
1.05
3.00
3.33
8.5
8.0
7.5
7.0
6.5
6.0
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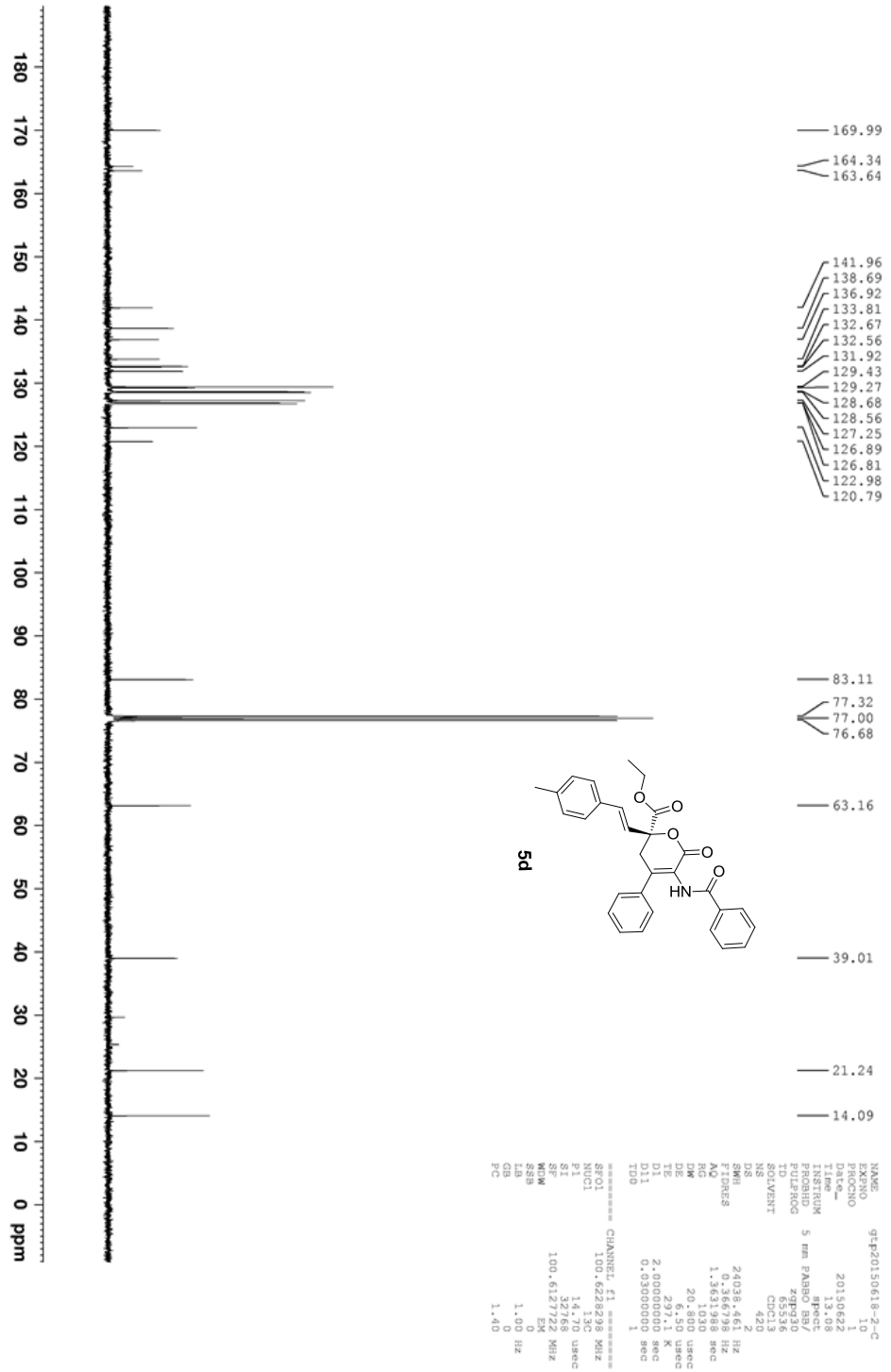
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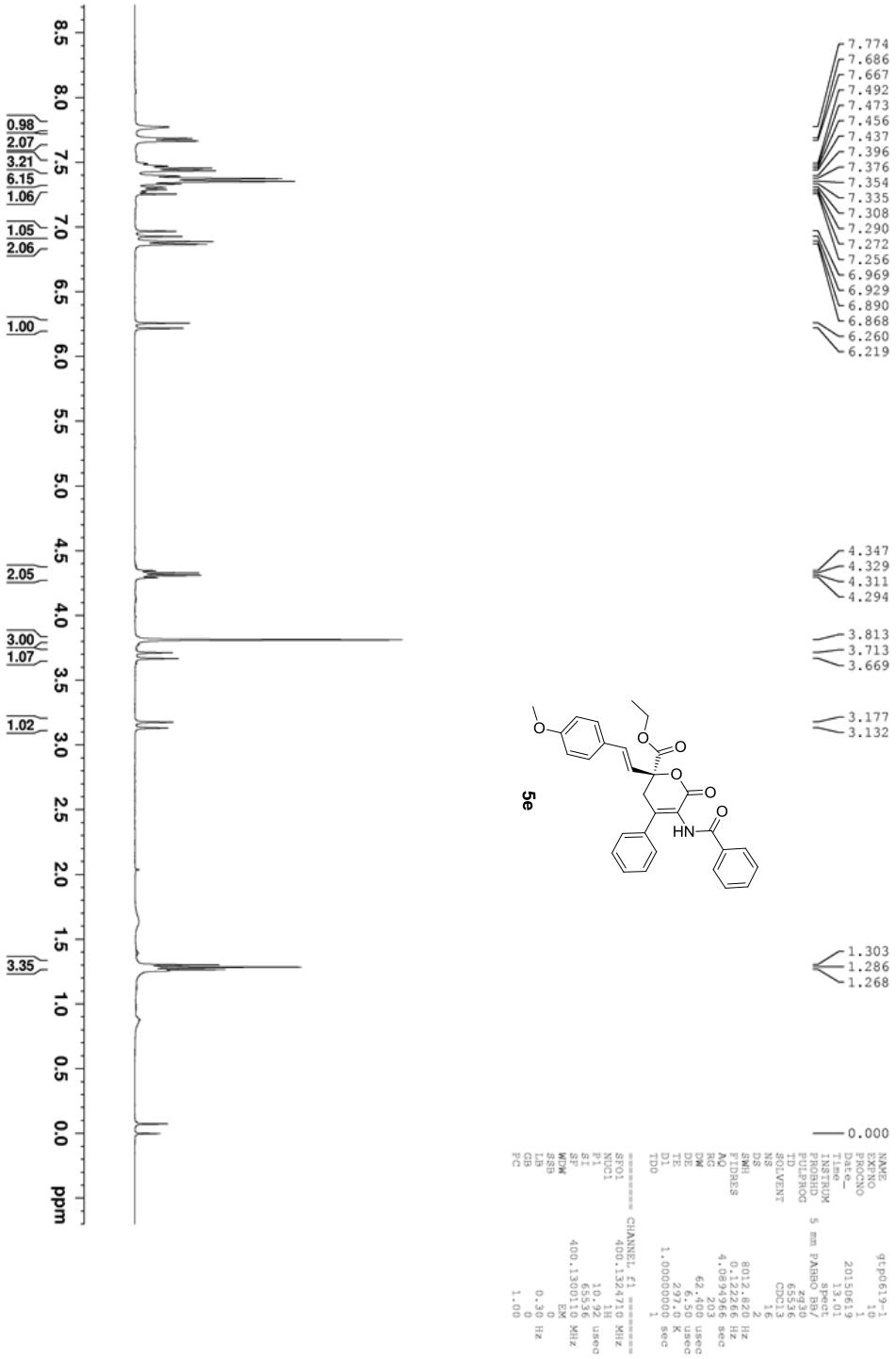
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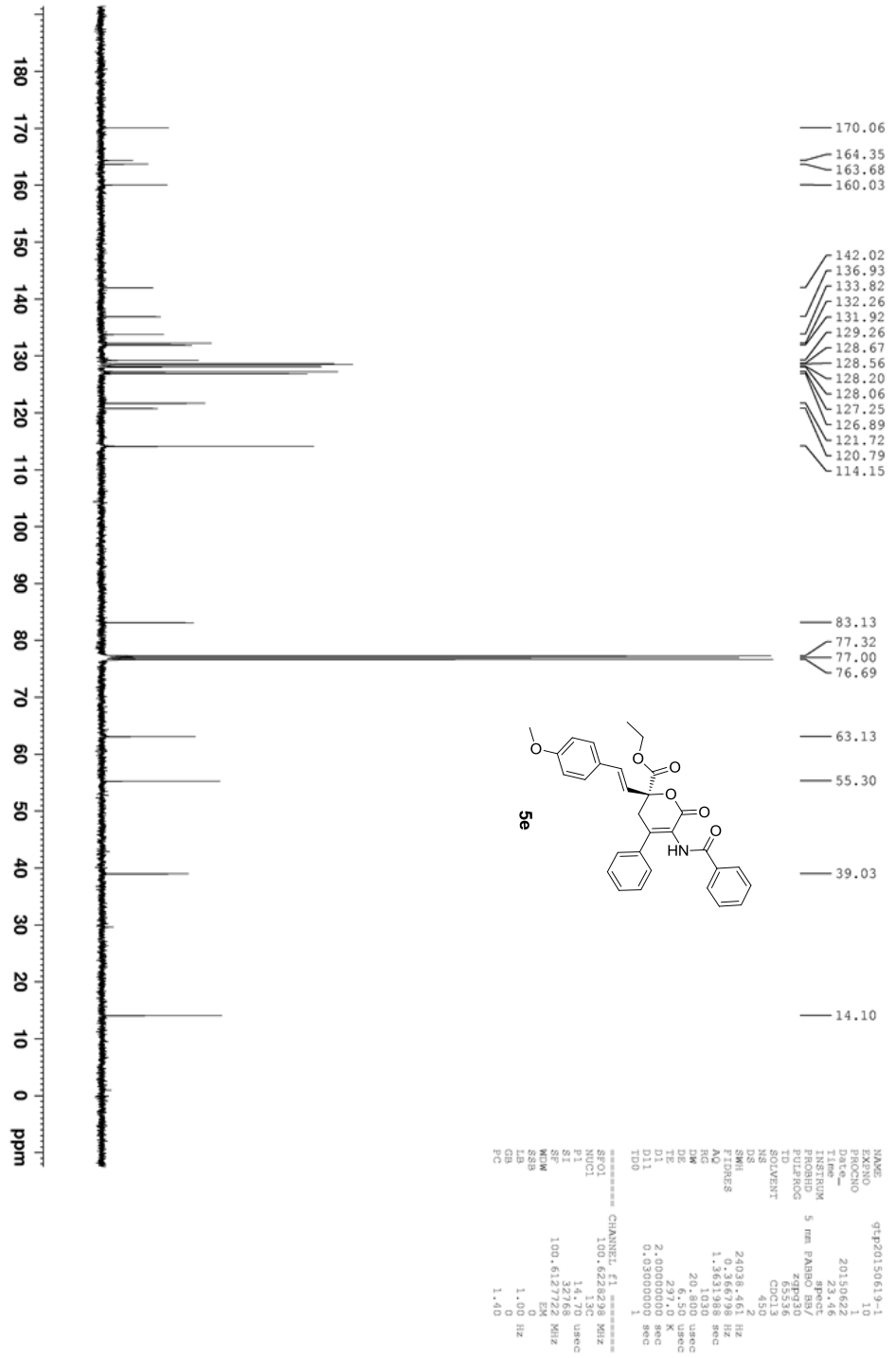
PC 1.00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114.15
83.13
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39.03
14.10
5e
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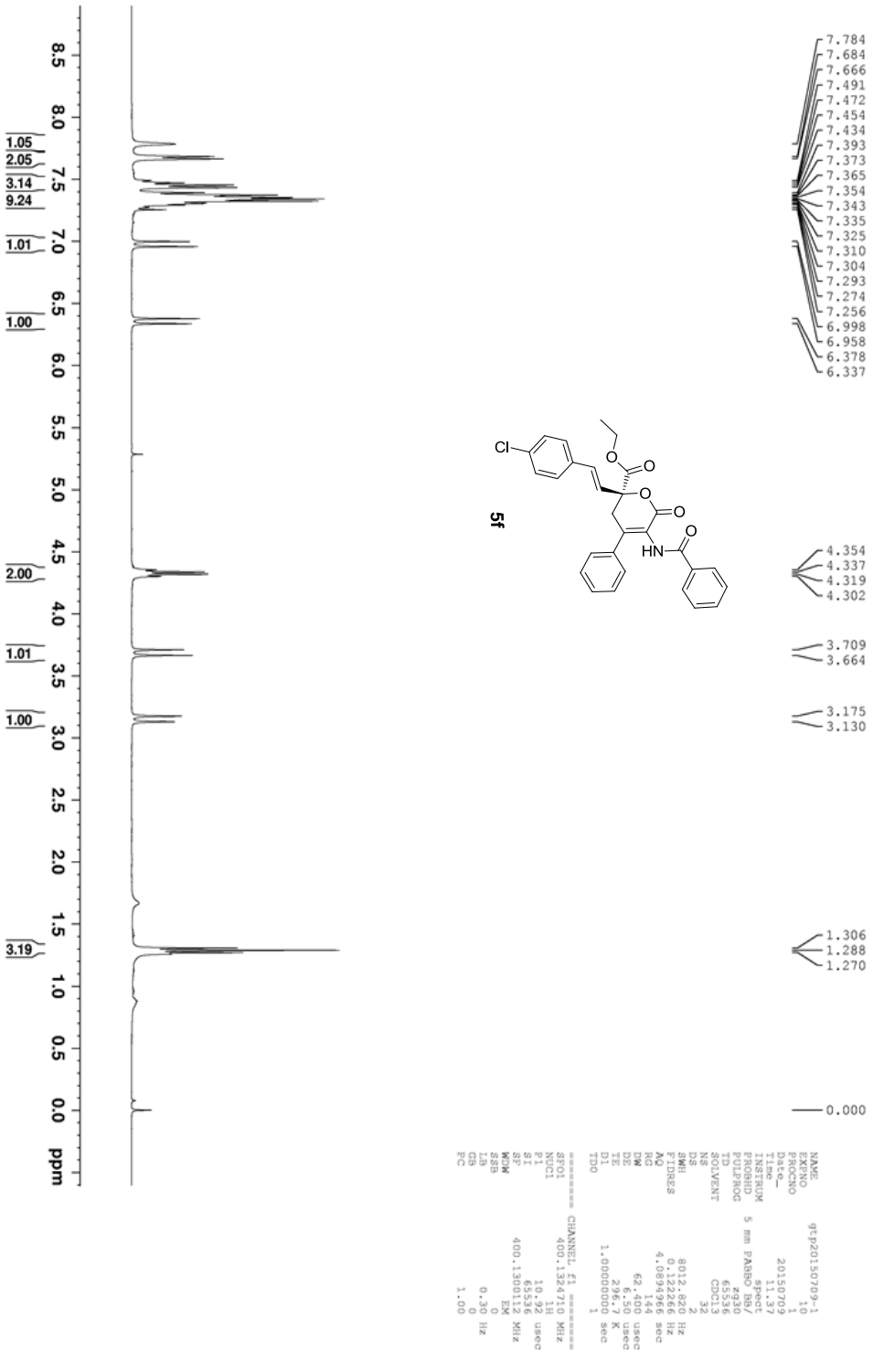
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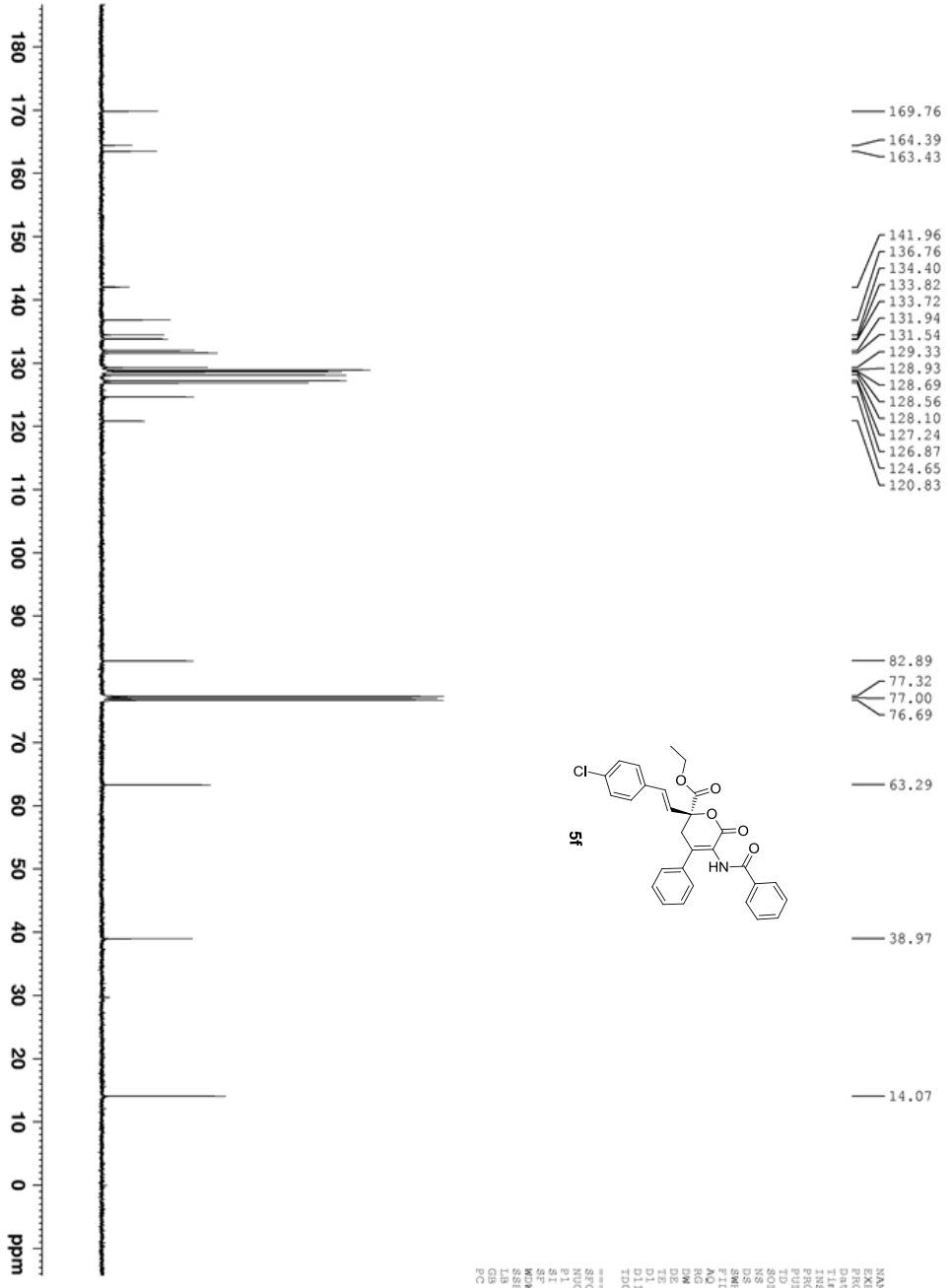
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5f
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DE 6.50 usec
TE 294.5 K
D1 1.00000000 sec
TD0 1
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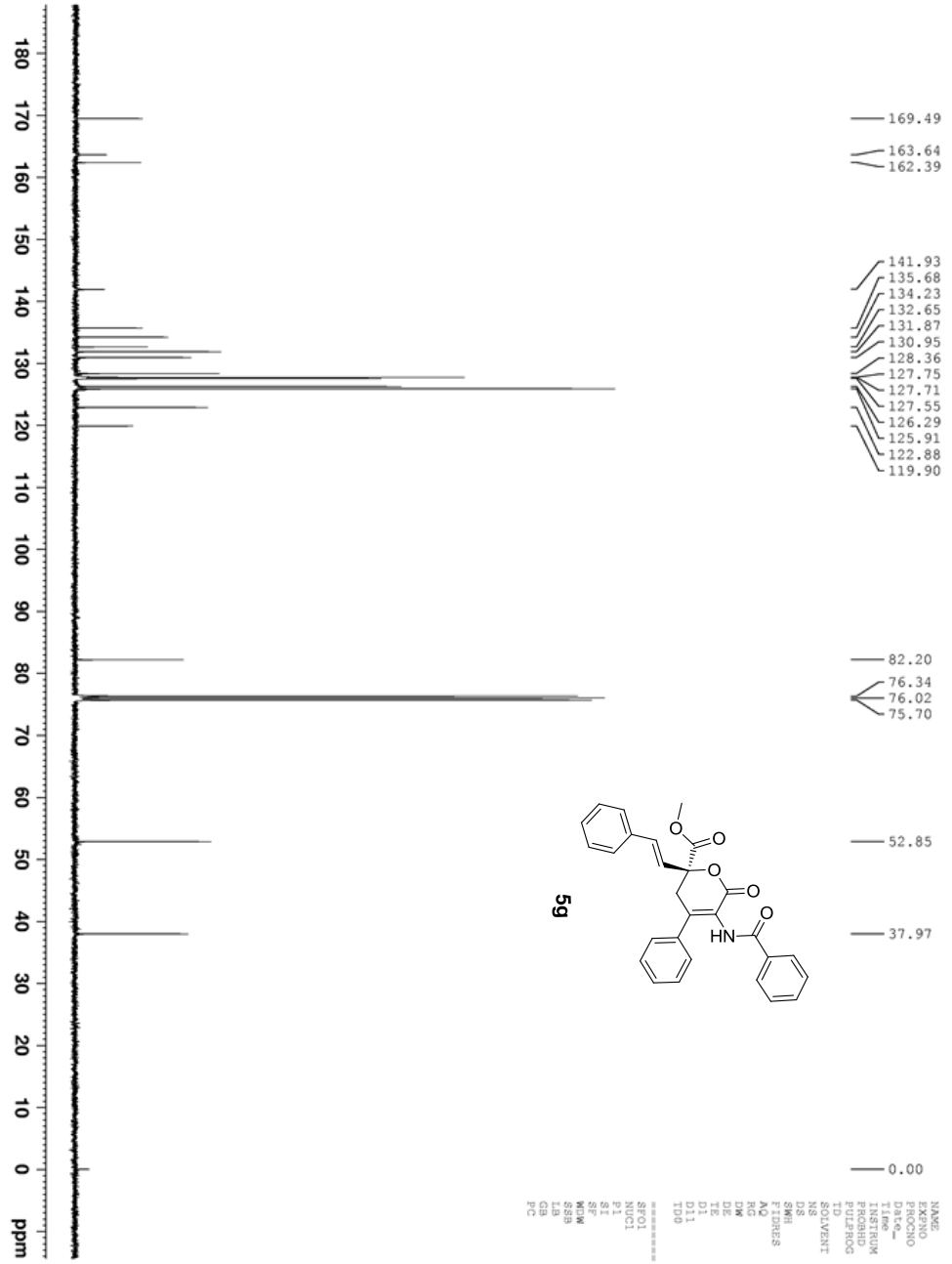
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TE 296.0 K
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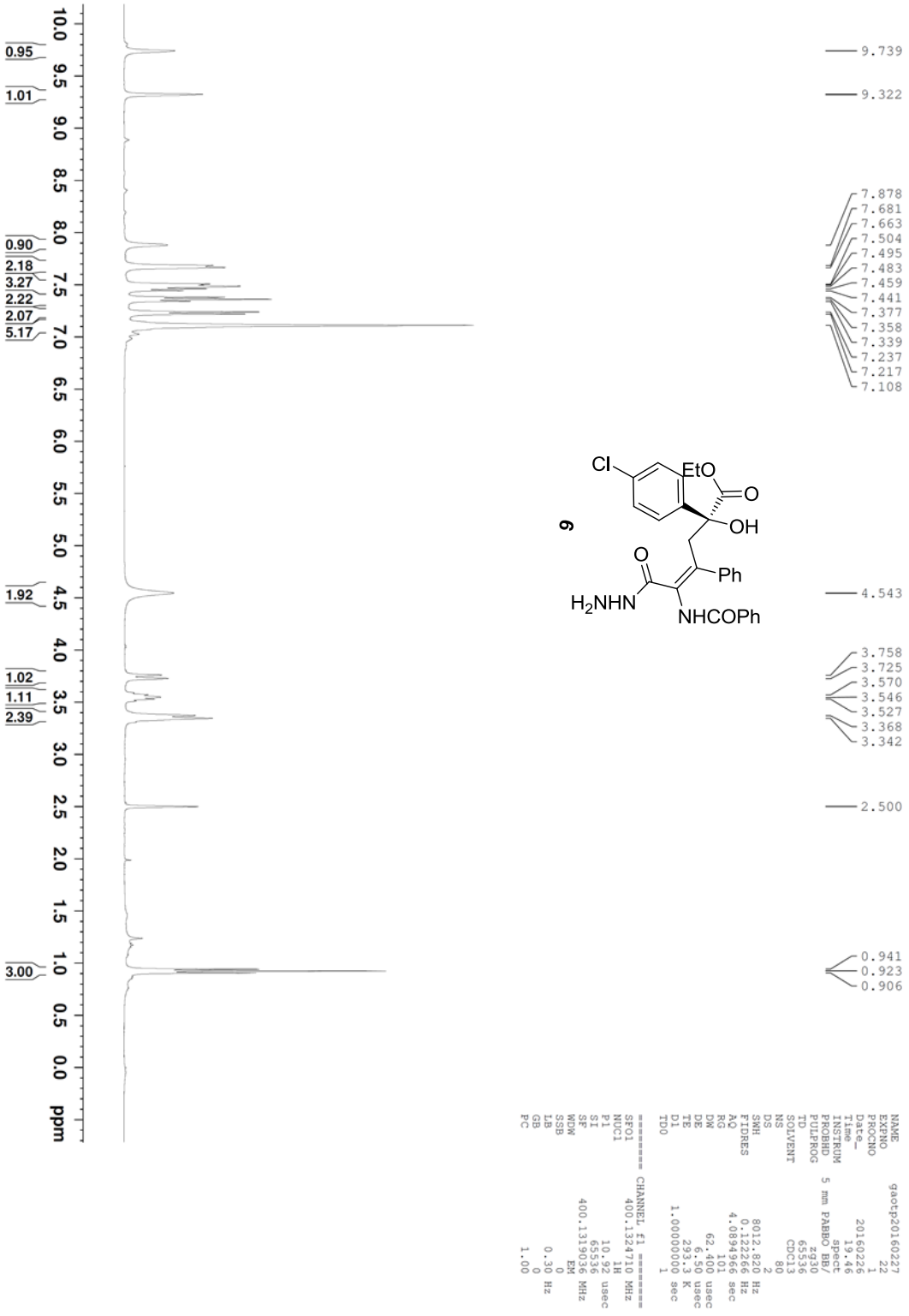
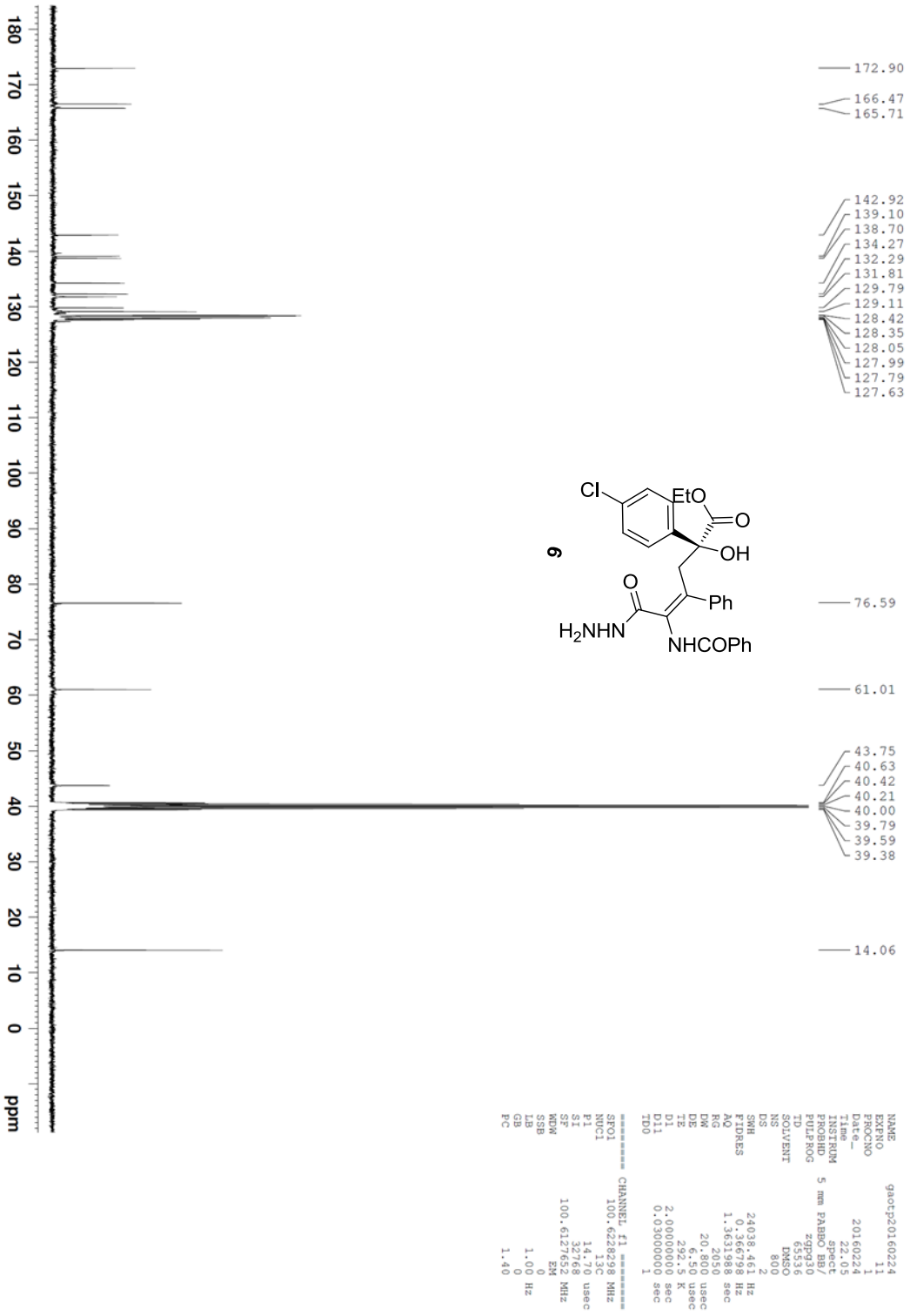
8. NMR spectra of compound **6**

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SF 100.612752 MHz
WDW EM
SSB 0
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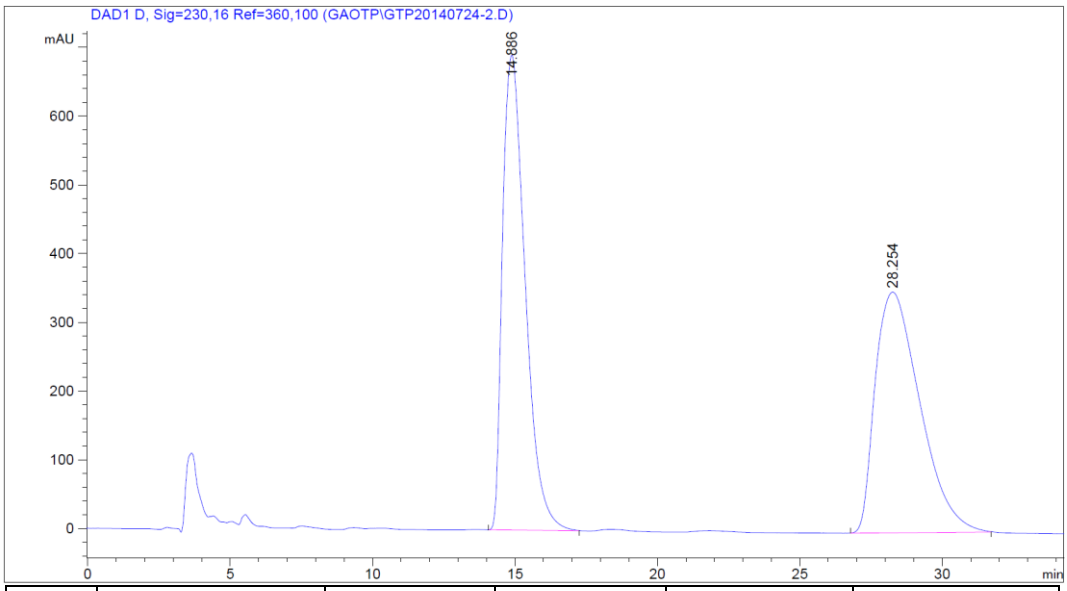
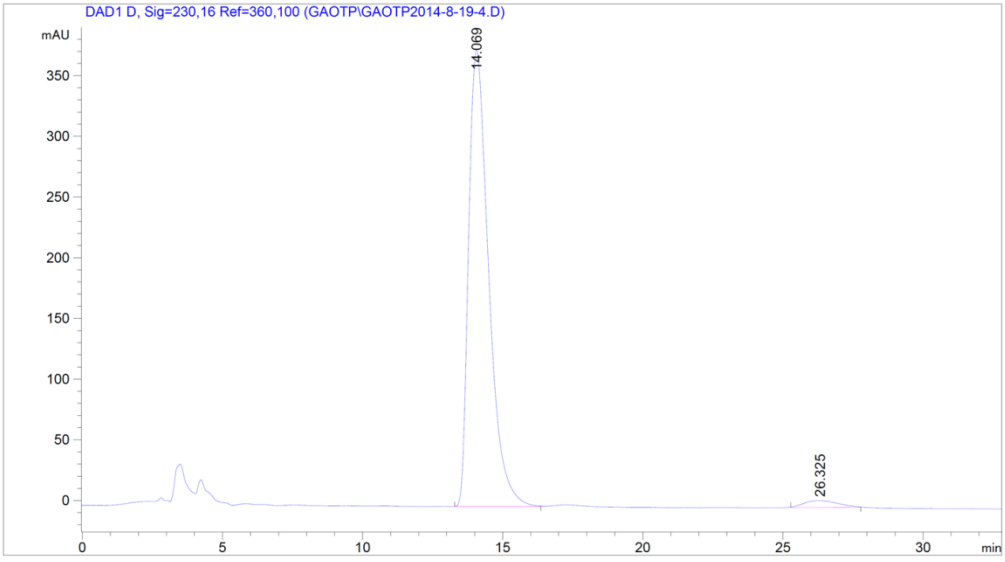
PC 1.40

9. HPLC spectra of compounds **4**

4a HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 65:35, 1.0 mL/min)

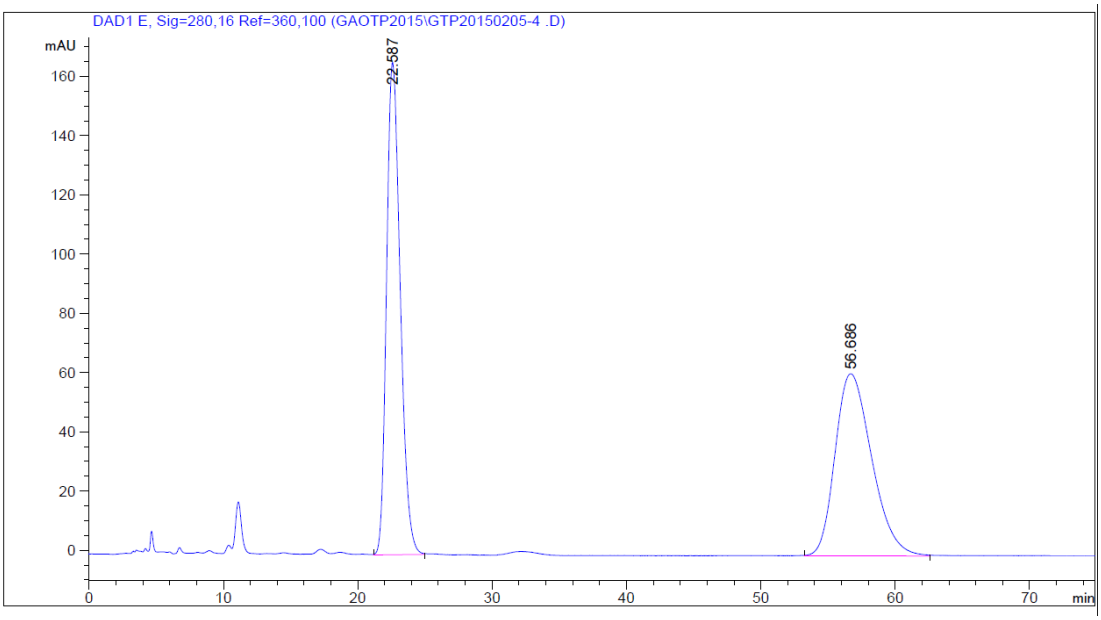


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	230.16 nm	14.884	3.81421e4	691.07147	49.9397
2	230.16 nm	28.254	3.82341e4	350.22070	50.0603

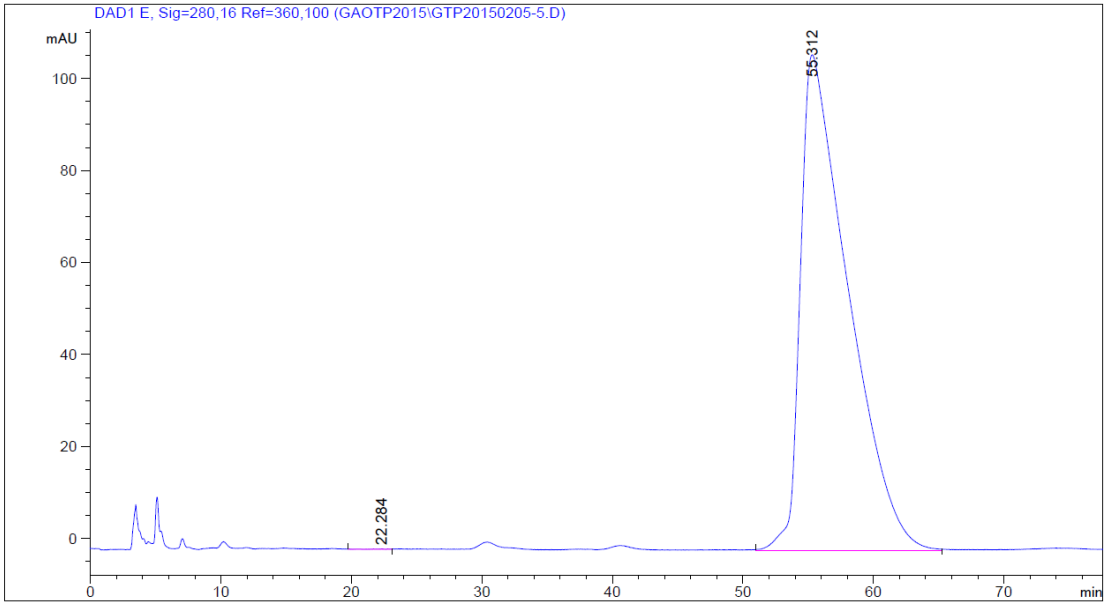


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	230.16 nm	14.069	1.86349e4	375.74661	97.5214
2	230.16 nm	26.325	473.62268	5.66661	2.4786

4b HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 70:30, 1.0 mL/min)

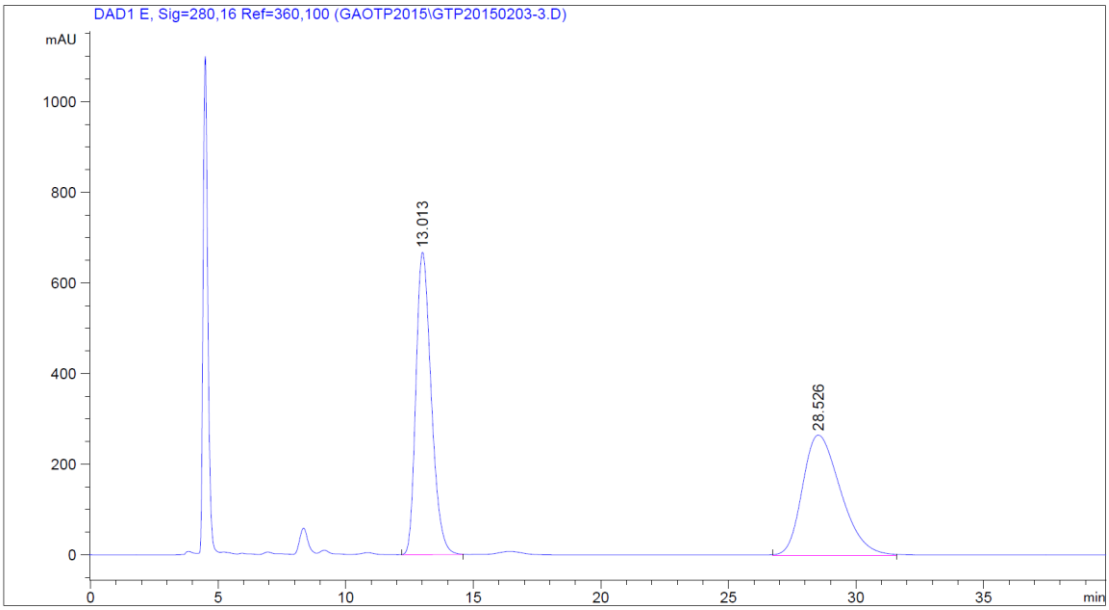


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	22.587	1.17552e4	166.25552	50.2197
2	PDA 280.16 nm	56.686	1.16524e4	61.50541	49.7803

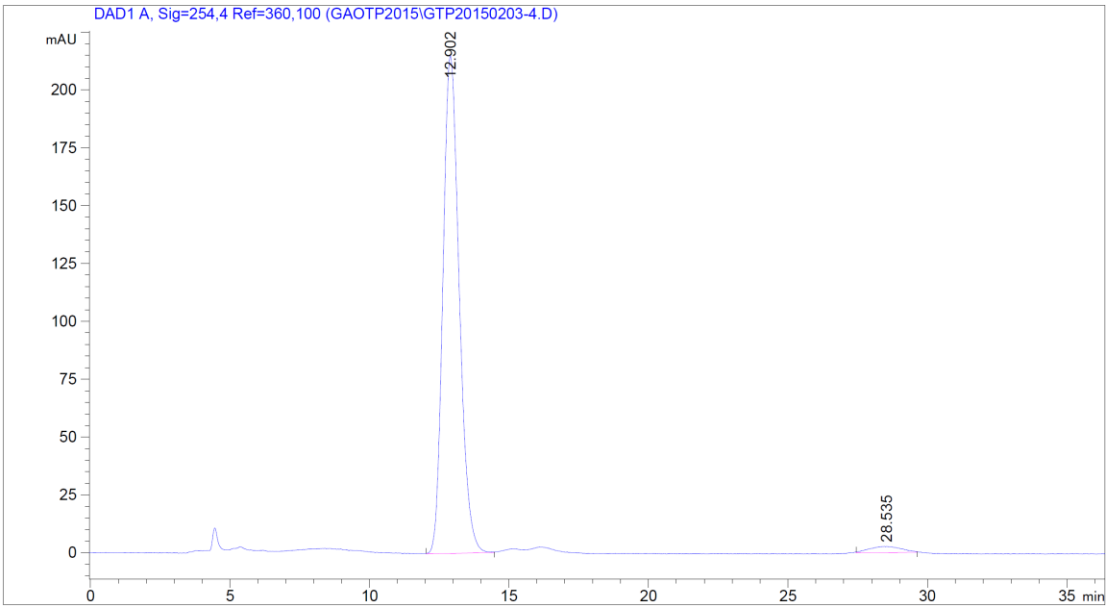


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	22.284	10.73880	1.16856e-1	0.0391
2	PDA 280.16 nm	55.312	2.74521e4	107.78524	99.9609

4c HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)

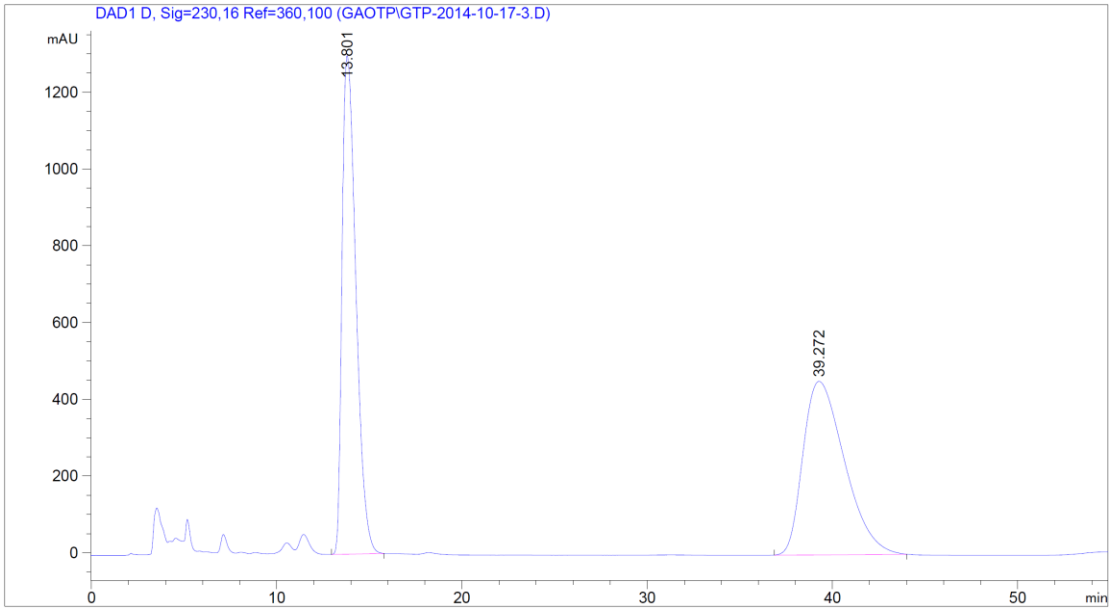


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	13.013	2.78419e4	667.63483	50.2931
2	PDA 280.16 nm	28.526	2.75173e4	265.12363	49.7069

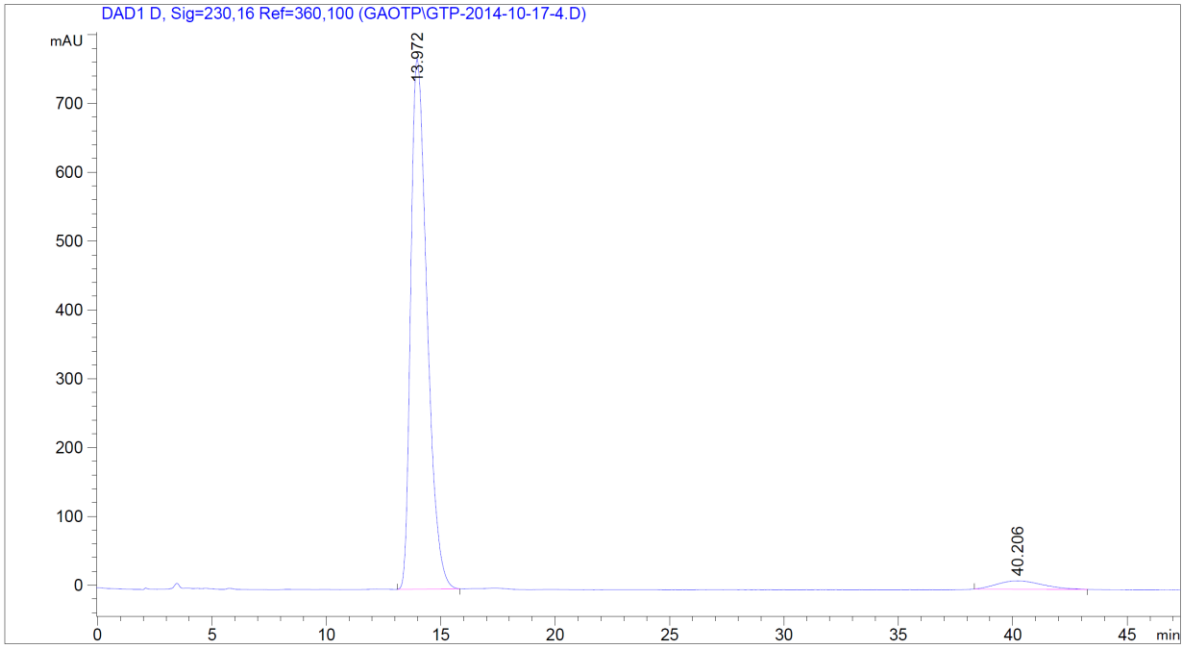


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	12.902	8693.22754	214.92070	97.5926
2	PDA 280.16 nm	28.535	214.44049	2.70033	2.4074

4d HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)

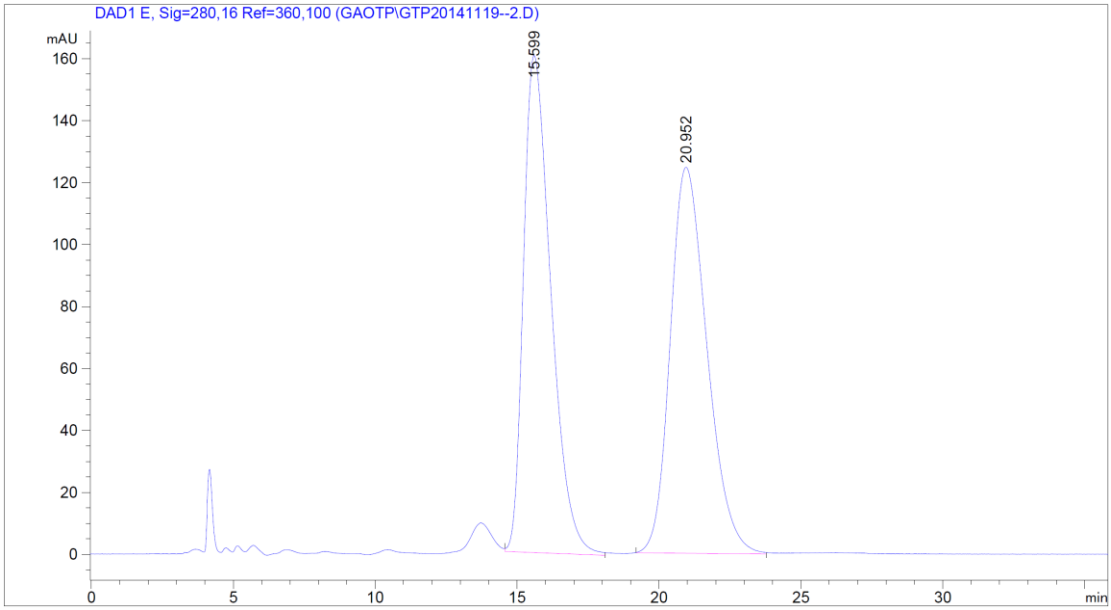


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	13.801	6.73970e4	1298.55298	48.8801
2	PDA 230.16 nm	39.272	7.04854e4	452.23926	51.1199

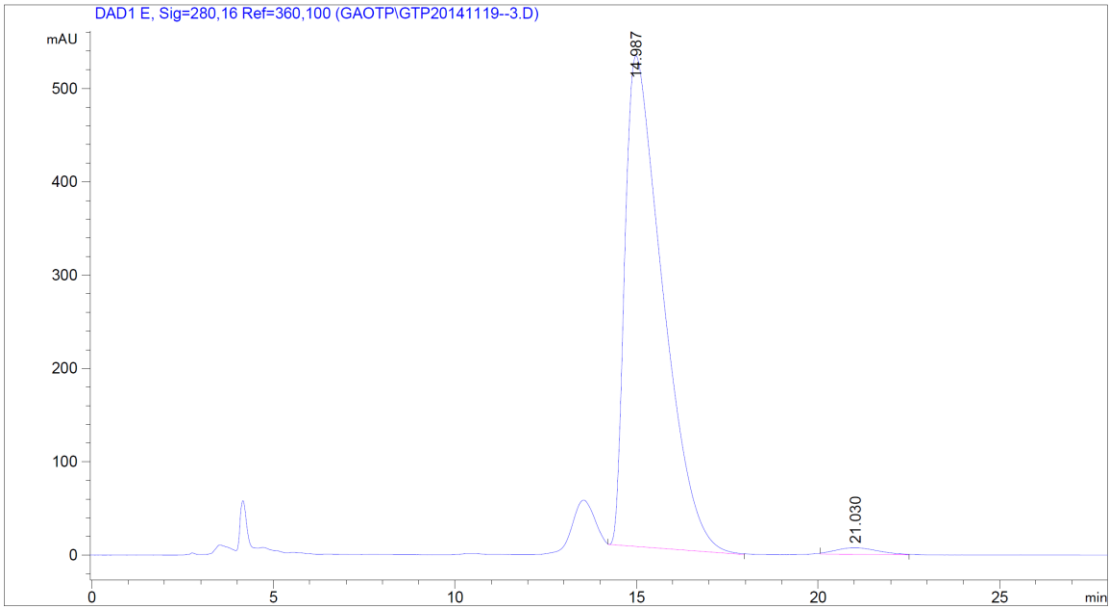


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	13.972	3.81448e4	770.85284	95.7869
2	PDA 230.16 nm	40.206	1677.75623	12.18955	4.2131

4e HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)

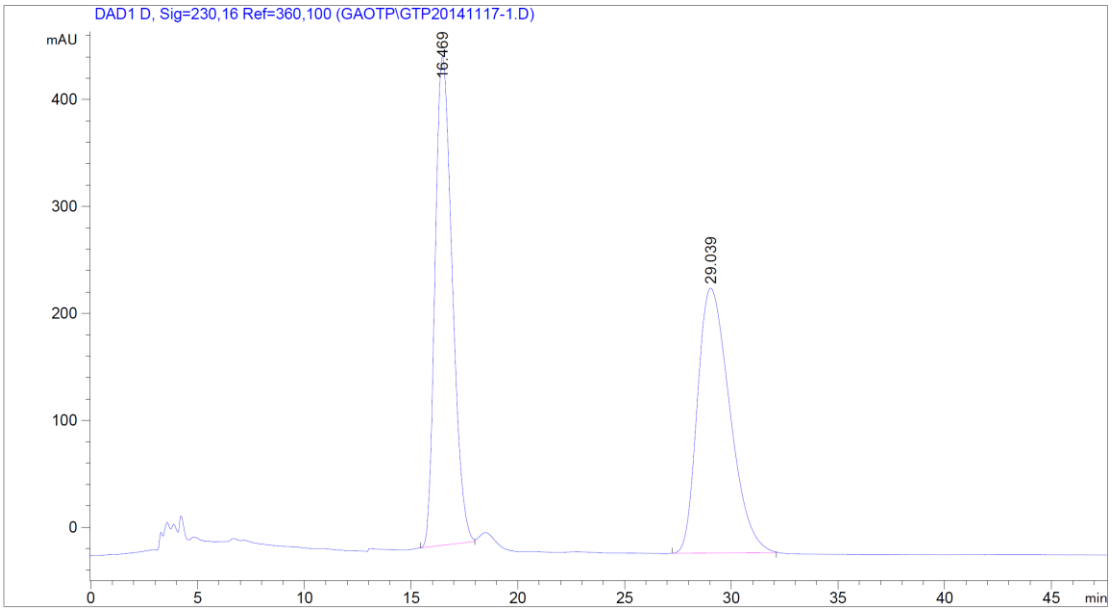


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	15.599	1.07801e4	160.41425	49.0136
2	PDA 280.16 nm	20.952	1.12140e4	124.56598	50.9864

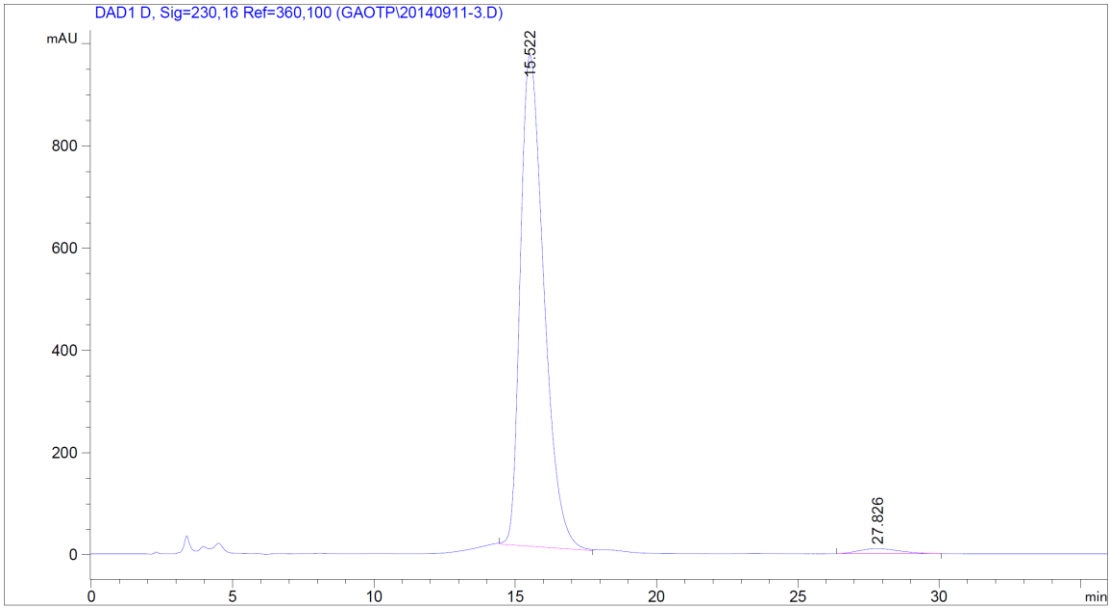


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	14.987	3.79199e4	525.66583	98.5521
2	PDA 280.16 nm	21.030	557.10852	6.94353	1.4479

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

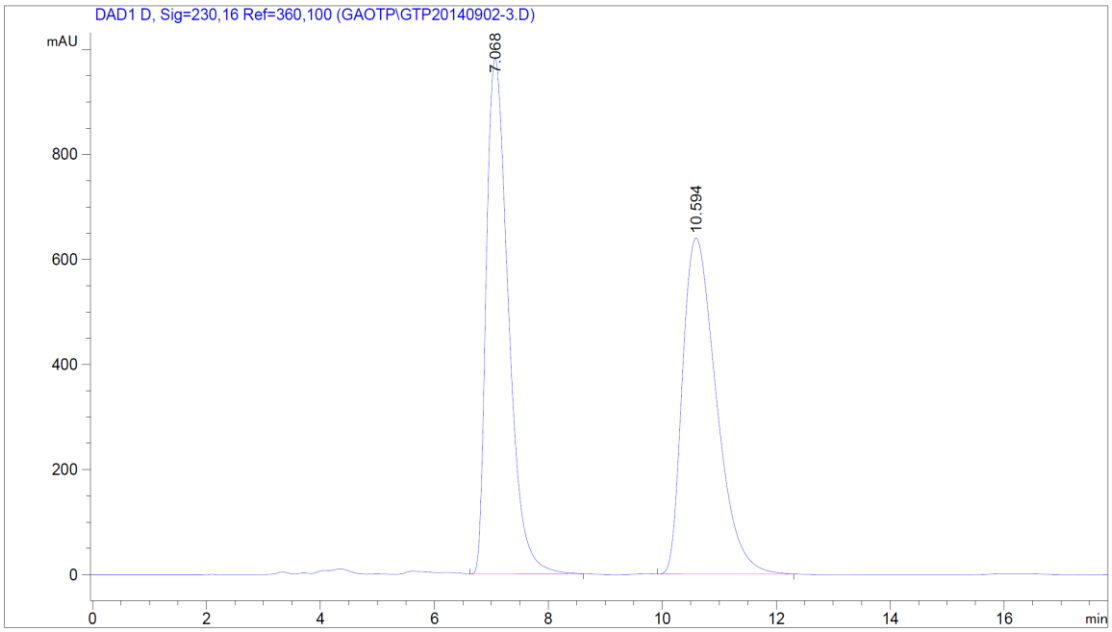


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	16.469	2.55653e4	457.23441	49.4744
2	PDA 230.16 nm	29.039	2.61085e4	247.77898	50.5256

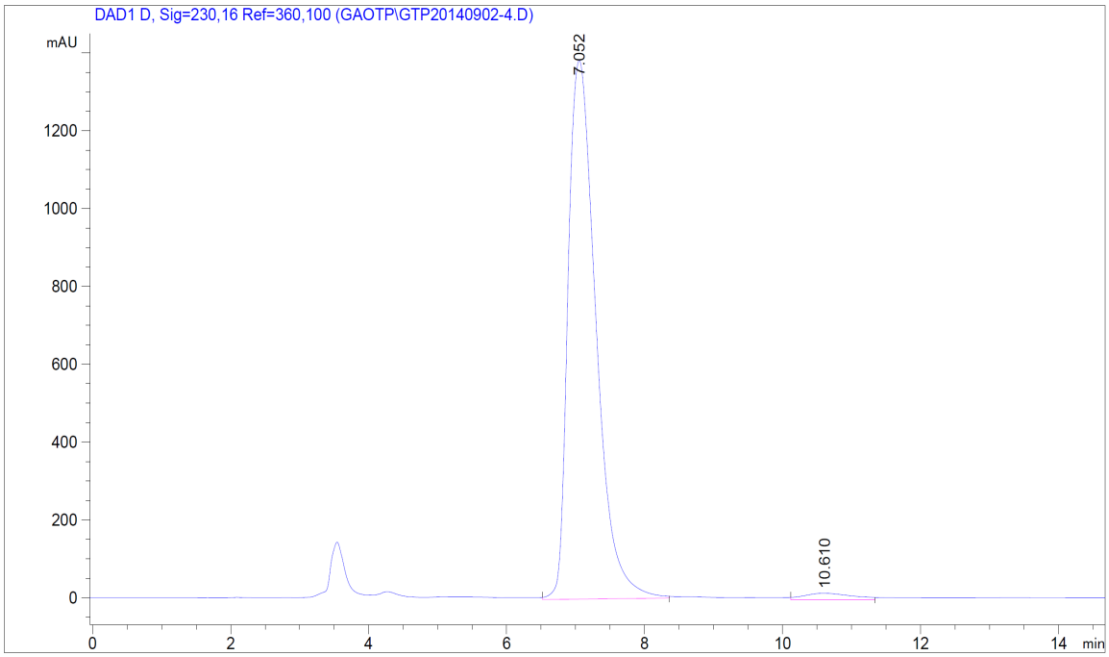


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	15.522	5.57031e4	960.58618	98.2575
2	PDA 230.16 nm	27.826	987.83948	9.91690	1.7425

4g HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)

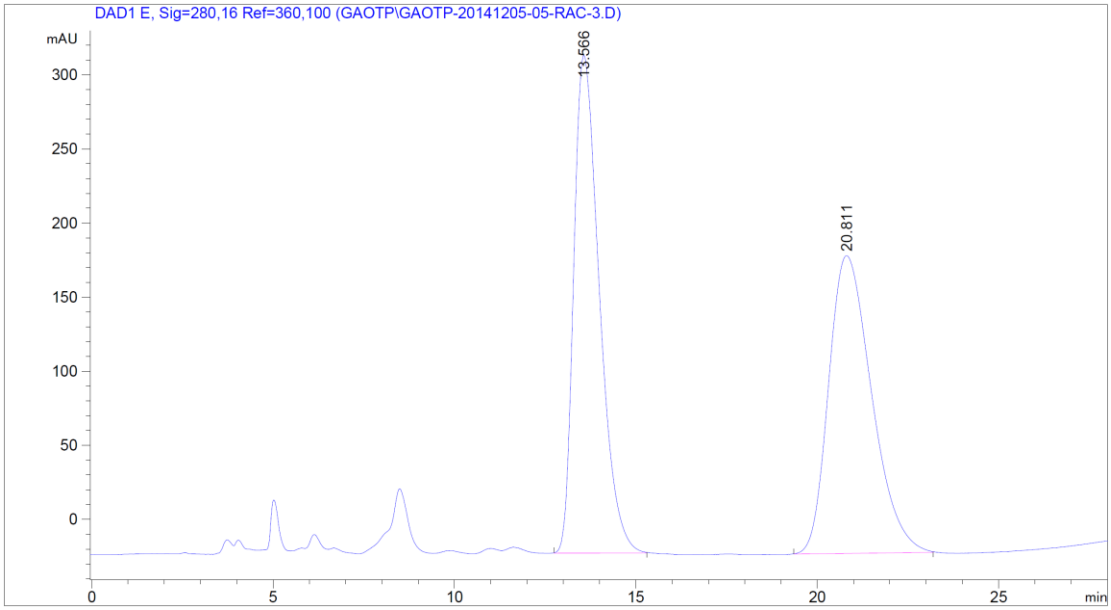


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	7.068	2.64403e4	981.43048	50.0956
2	PDA 230.16 nm	10.594	2.63393e4	639.64905	49.9044

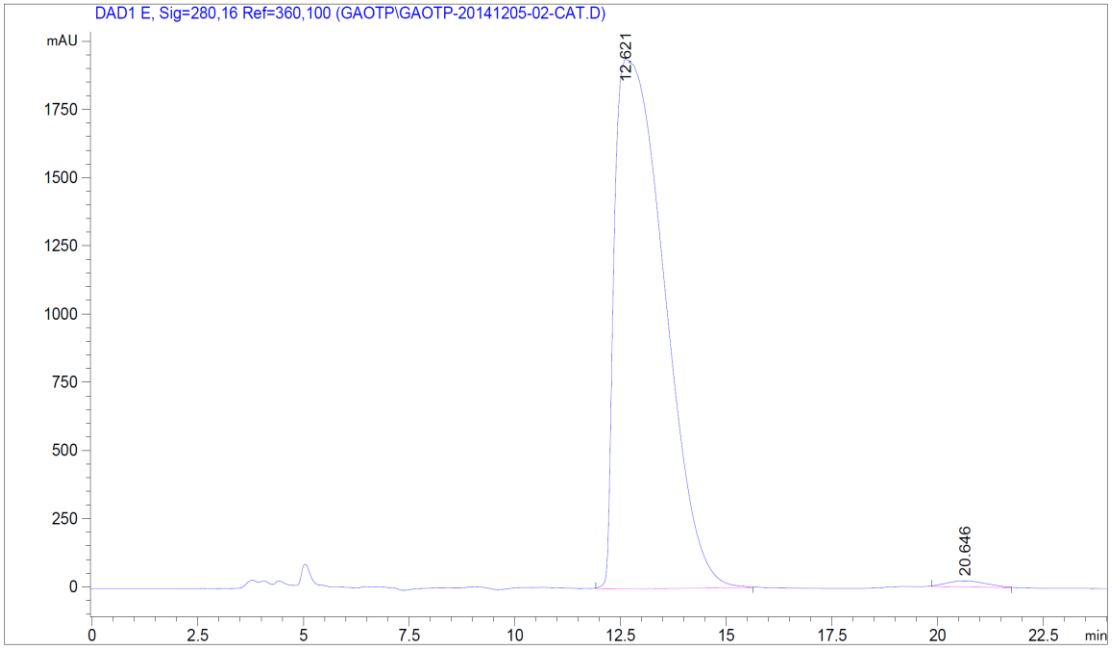


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	7.052	3.87657e4	1384.62134	98.0215
2	PDA 230.16 nm	10.610	782.44354	16.05111	1.9785

4h HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)

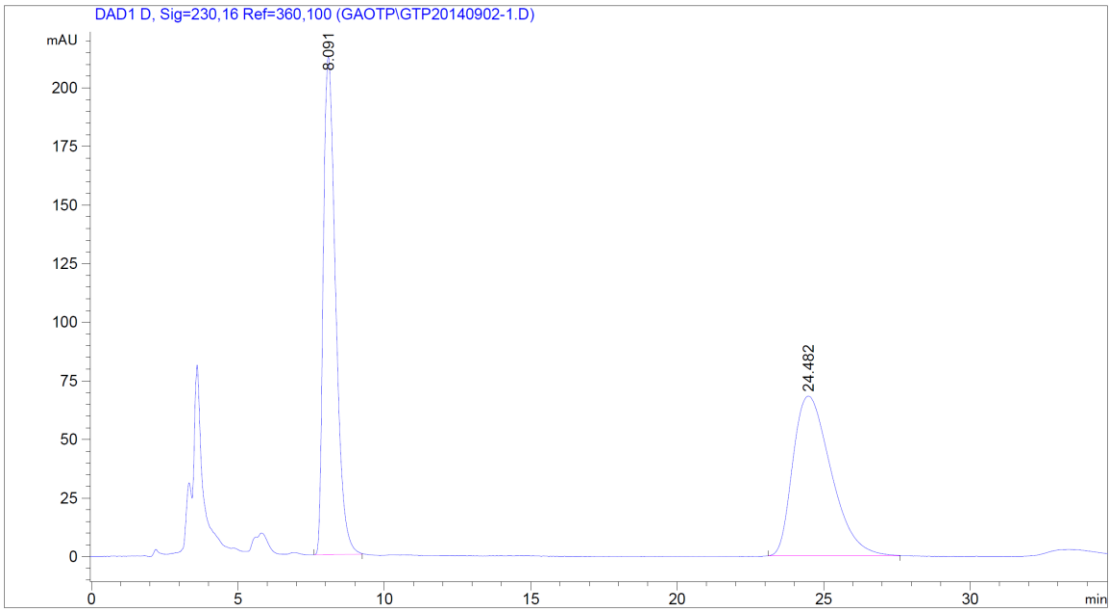


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	13.566	1.64277e4	335.72144	49.8683
2	PDA 280.16 nm	20.811	1.65145e4	200.89761	50.1317

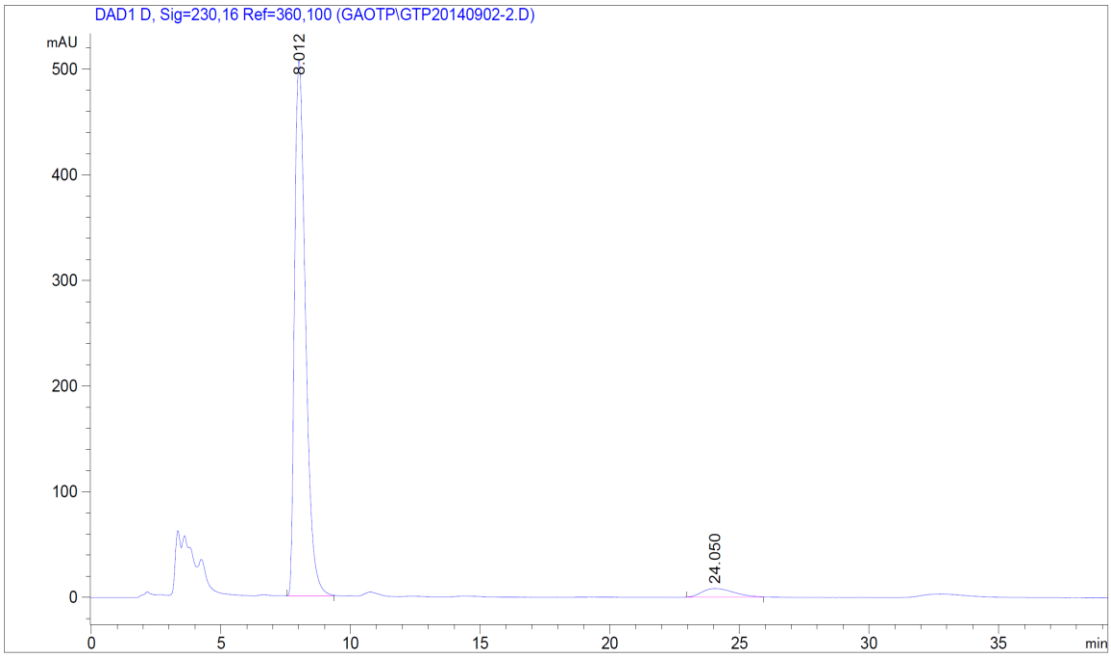


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	12.621	1.58389e5	1945.46082	99.0719
2	PDA 280.16 nm	20.646	1483.82394	22.72461	0.9281

4i HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)

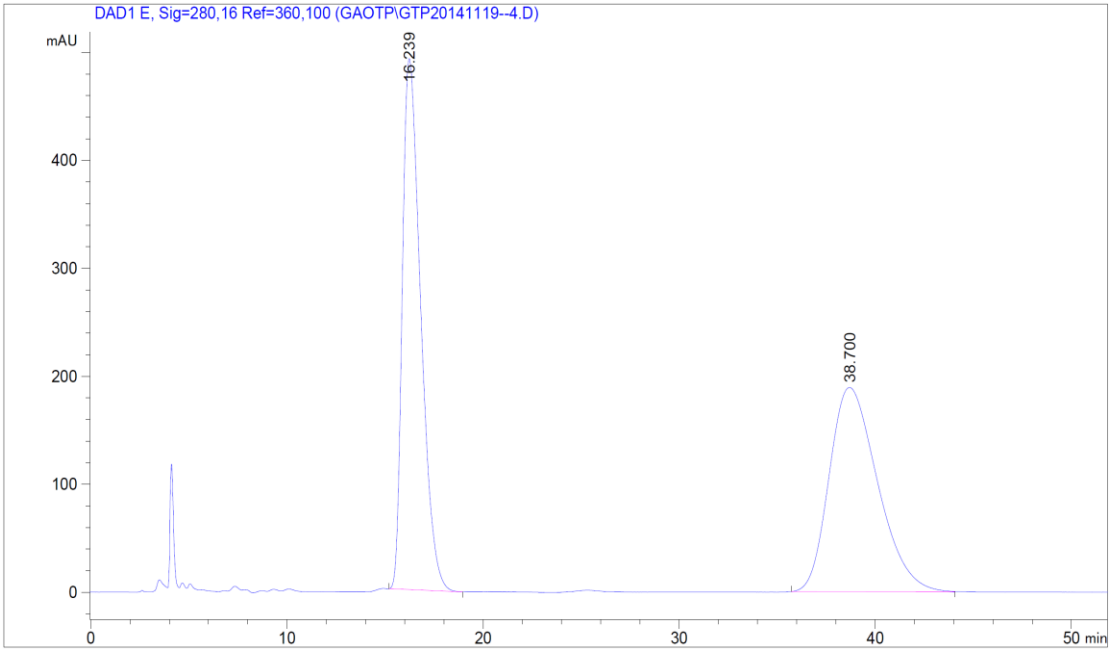


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	8.091	6206.48145	212.42874	50.0651
2	PDA 230.16 nm	24.482	6190.35205	68.21718	49.9349

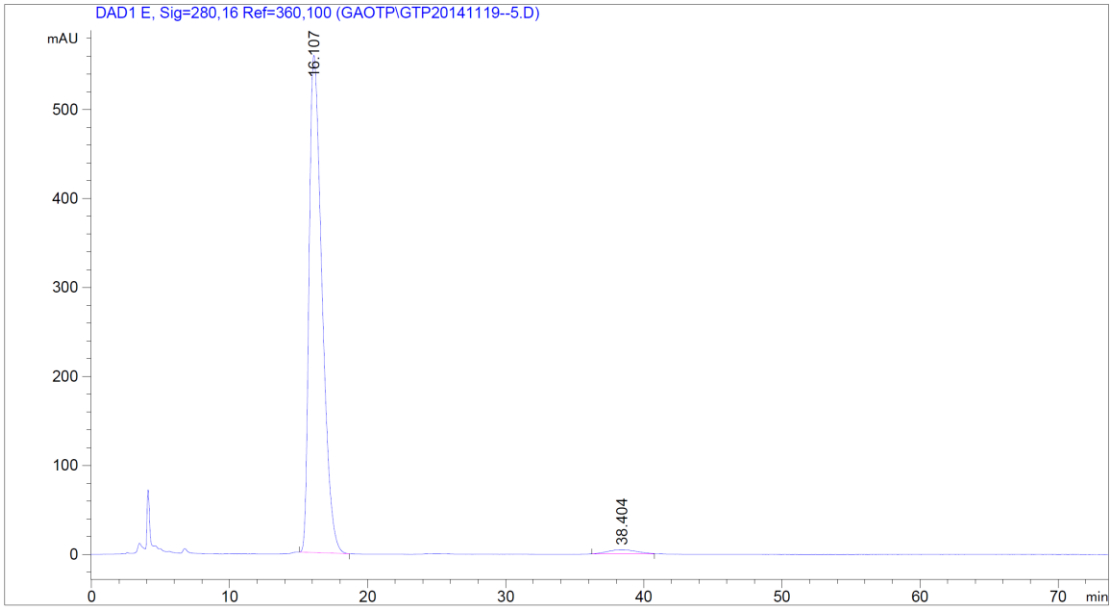


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	8.012	1.48405e4	506.72058	95.5997
2	PDA 230.16 nm	24.050	683.07977	8.12337	4.4003

4j HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)

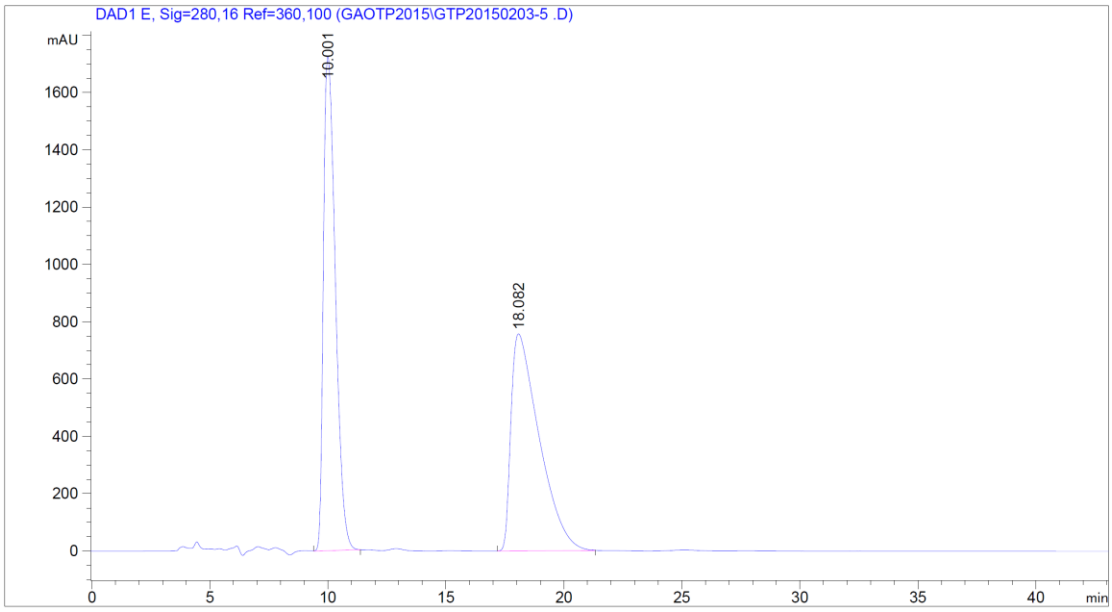


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	16.239	3.19464e4	491.58728	49.6392
2	PDA 280.16 nm	38.700	3.24108e4	189.12885	50.3608

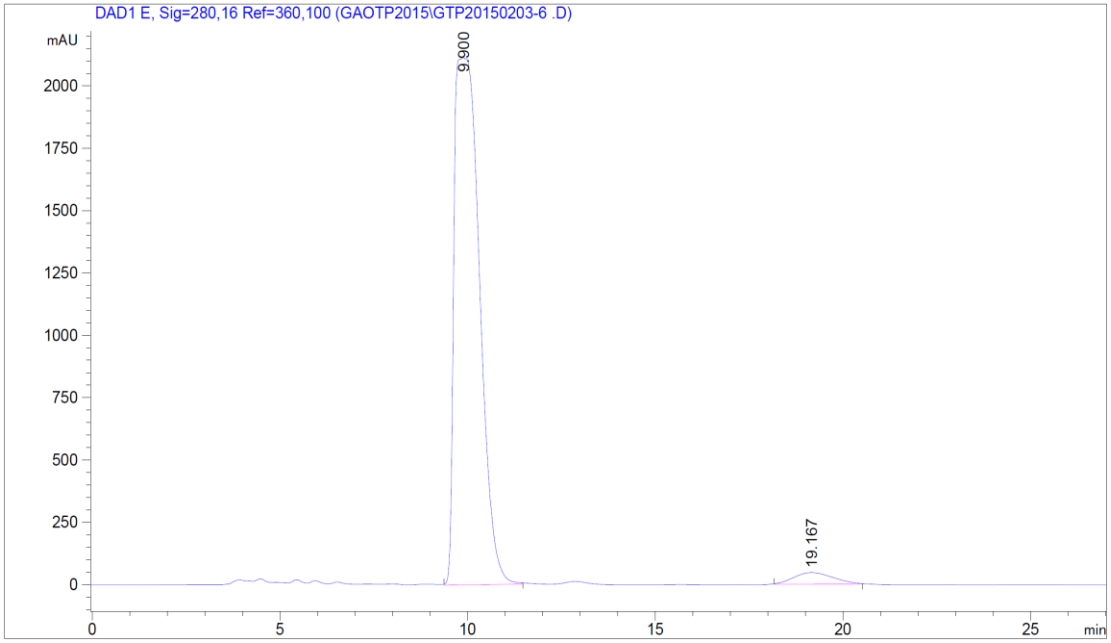


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	16.107	3.62413e4	558.87482	98.0730
2	PDA 280.16 nm	38.404	712.08362	4.85604	1.9270

4k HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)

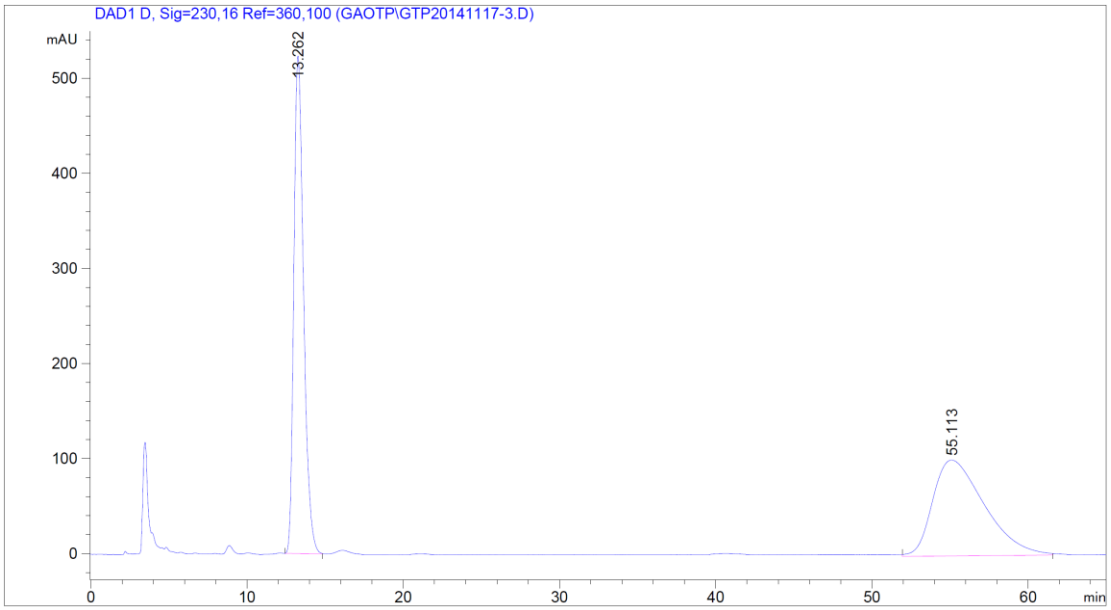


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	10.001	6.07063e4	1724.97791	49.1599
2	PDA 280.16 nm	18.082	6.27811e4	757.72504	50.8401

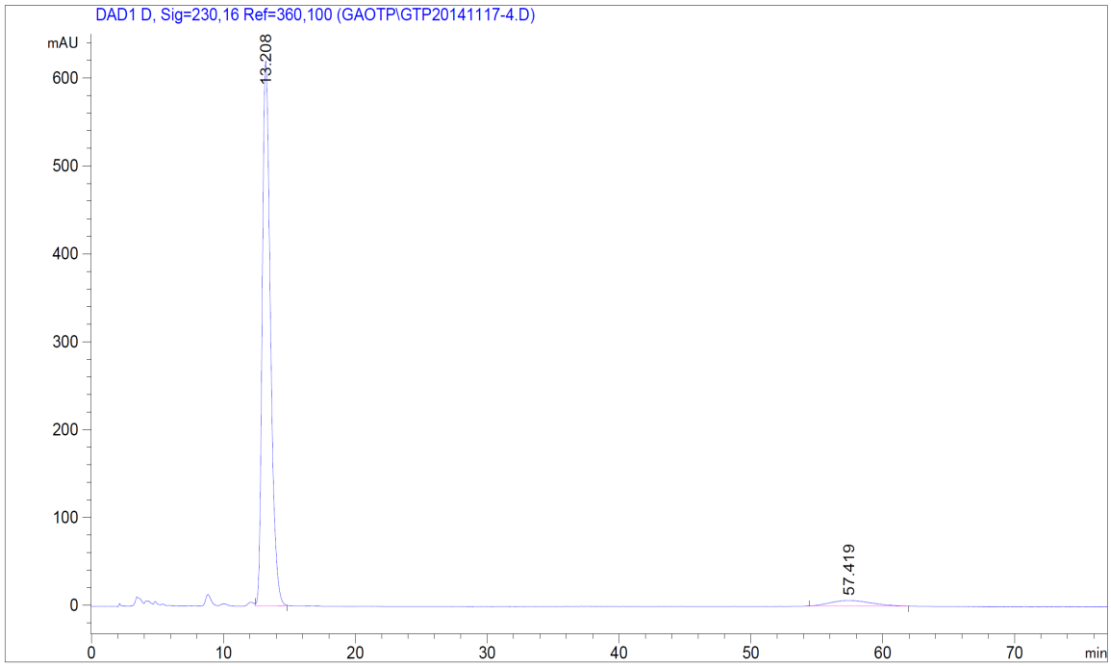


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	9.900	9.92224e4	2114.36694	96.6731
2	PDA 280.16 nm	19.167	3414.64209	46.77760	3.3269

4l HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)

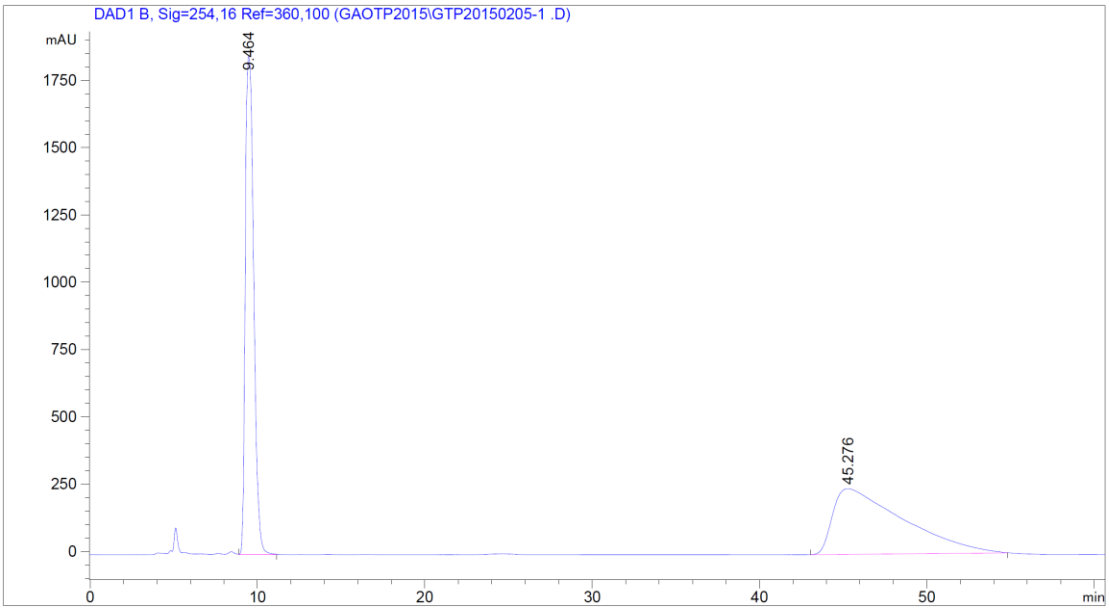


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	13.262	2.26318e4	523.30908	49.3955
2	PDA 230.16 nm	55.113	2.31858e4	100.86430	50.6045

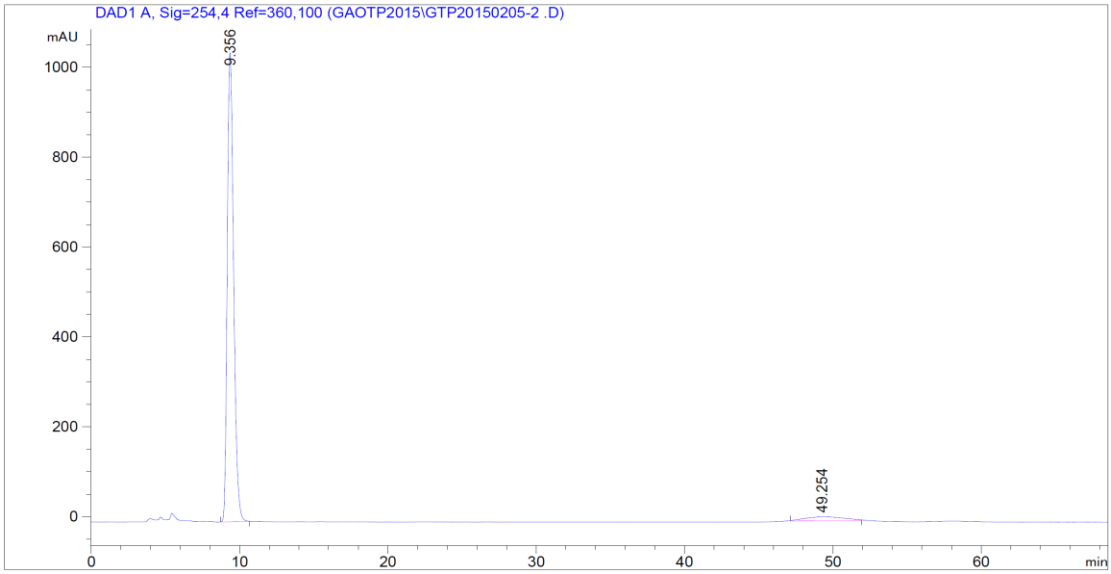


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	13.208	2.68202e4	620.07025	95.2641
2	PDA 230.16 nm	57.419	1333.33191	6.29375	4.7359

4m HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)



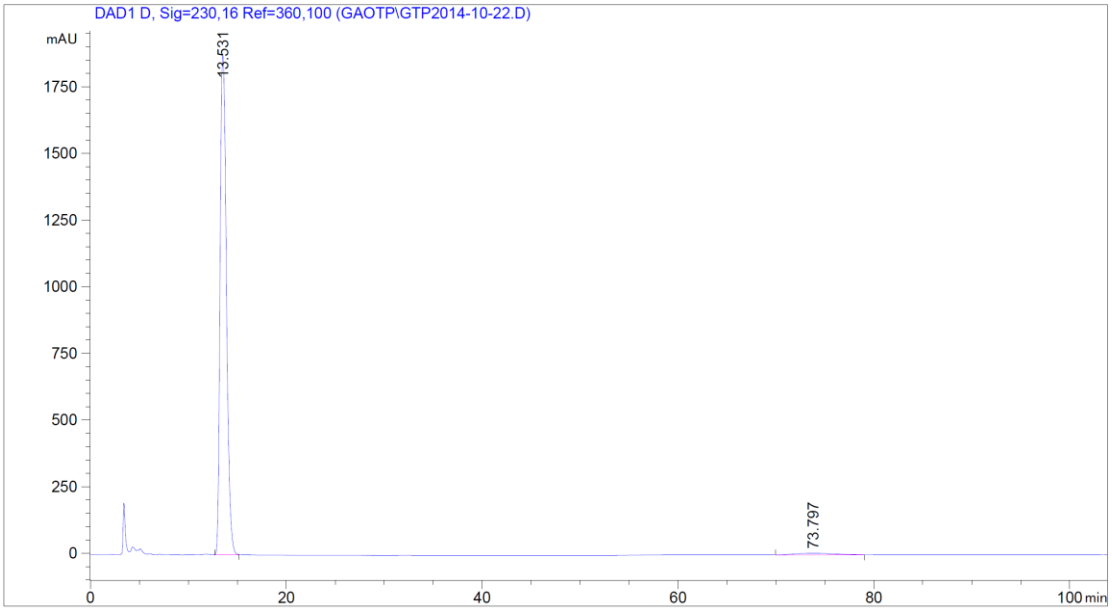
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.16 nm	9.464	6.44850e4	1849.70911	47.5420
2	PDA 254.16 nm	45.276	7.11529e4	243.80779	52.4580



Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.4 nm	9.356	3.10980e4	1044.12183	94.9796
2	PDA 254.4 nm	49.254	1643.75293	9.03994	5.0204

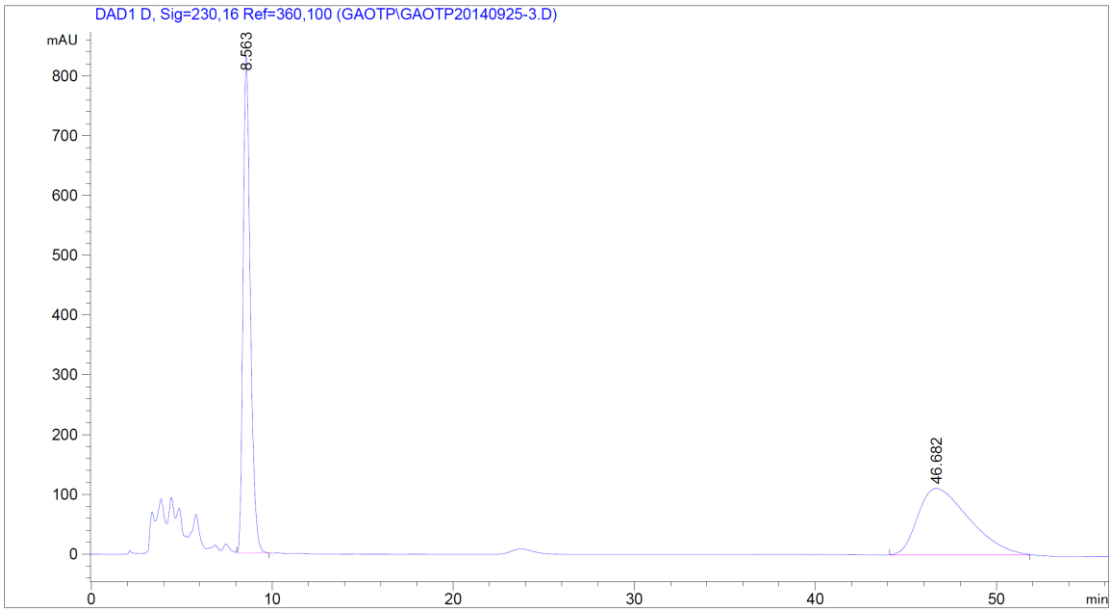
4n HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)

Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	13.382	1.62787e4	399.65228	49.5205
2	PDA 230.16 nm	75.229	1.65940e4	53.77774	50.4795



Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	13.531	8.42408e4	1872.19104	97.5967
2	PDA 230.16 nm	73.797	2074.41528	6.90655	2.4033

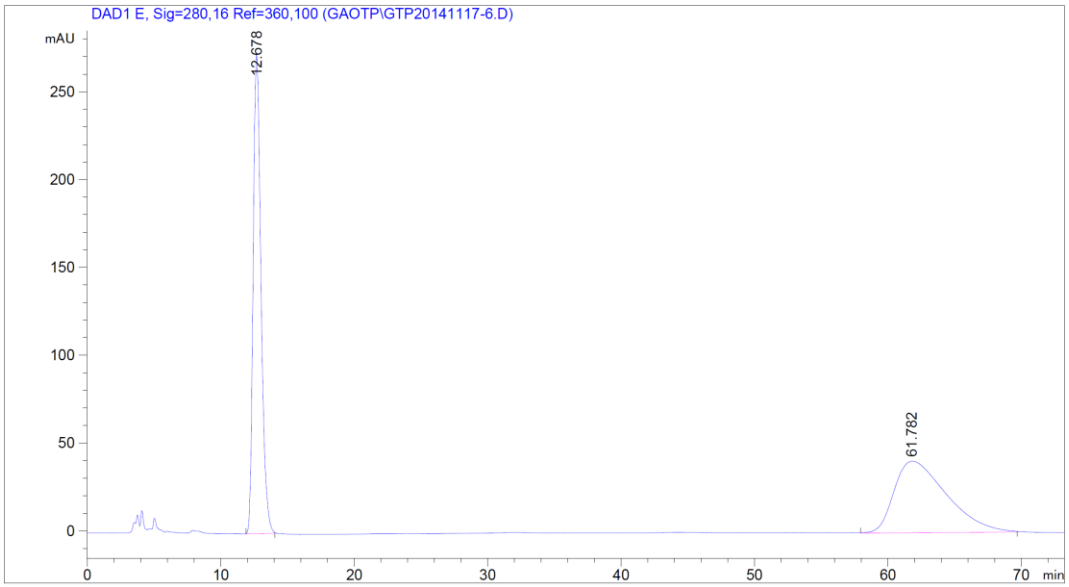
4o HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)



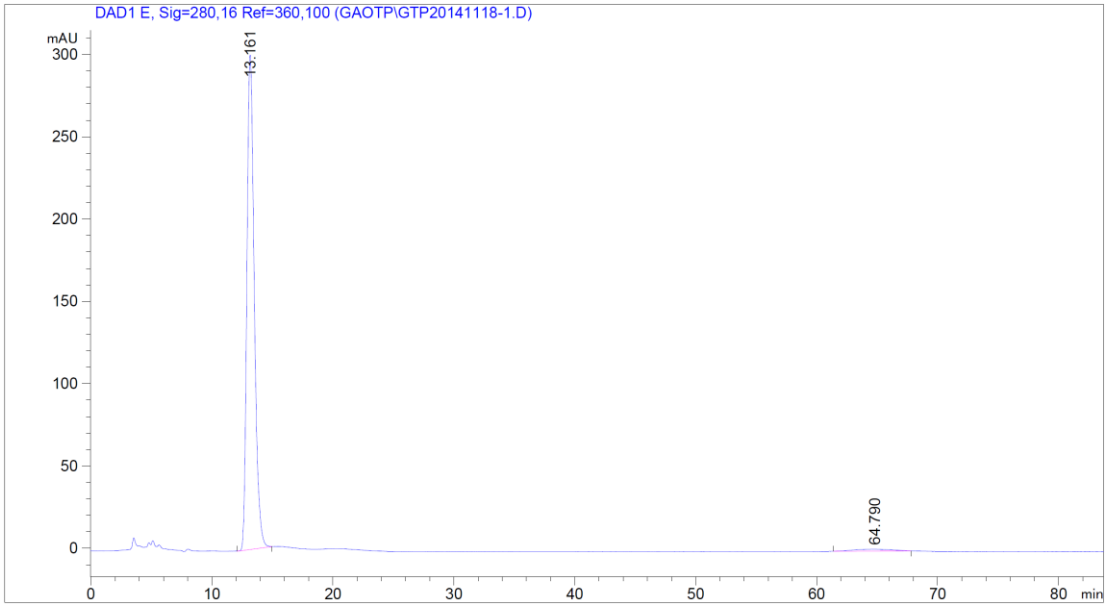
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	8.563	2.31538e4	830.47711	51.4830
2	PDA 230.16 nm	46.682	2.18199e4	110.94320	48.5170

Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	8.501	2.36574e4	858.63104	98.5709
2	PDA 230.16 nm	47.513	342.97812	2.45105	1.4291

4p HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)

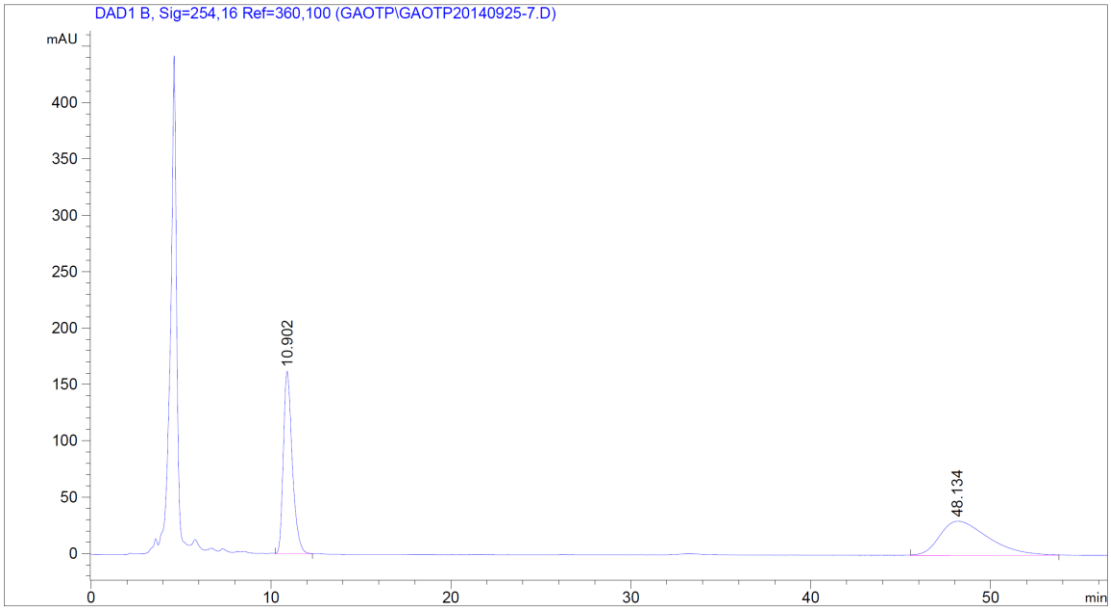


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	12.678	1.11332e4	272.55786	50.0134
2	PDA 280.16 nm	61.782	1.11272e4	40.80041	49.9866

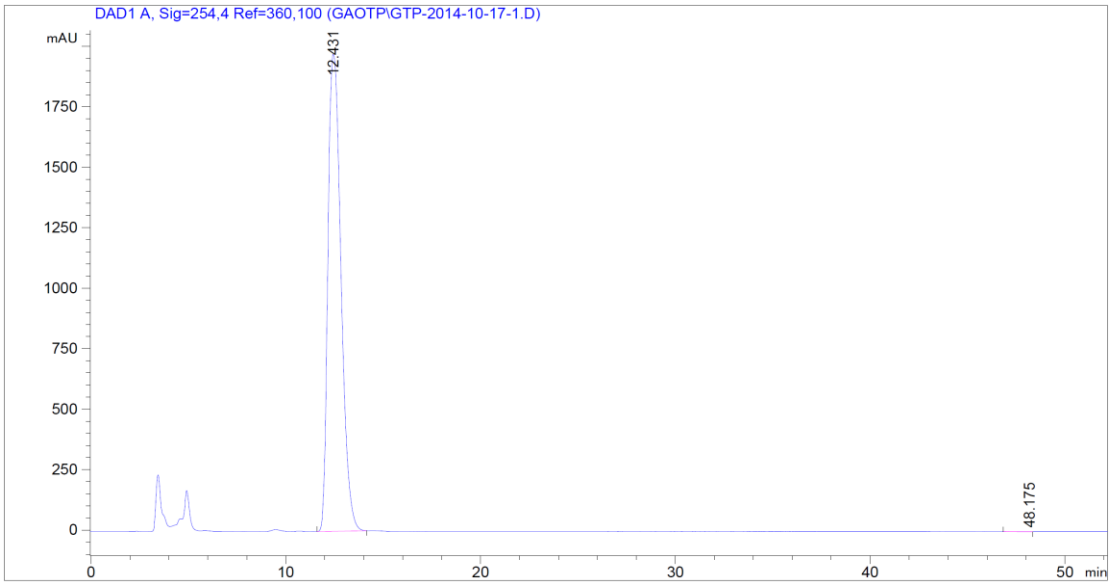


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	13.161	1.27049e4	300.39340	97.9392
2	PDA 280.16 nm	64.790	267.33527	1.22478	2.0608

4q HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)

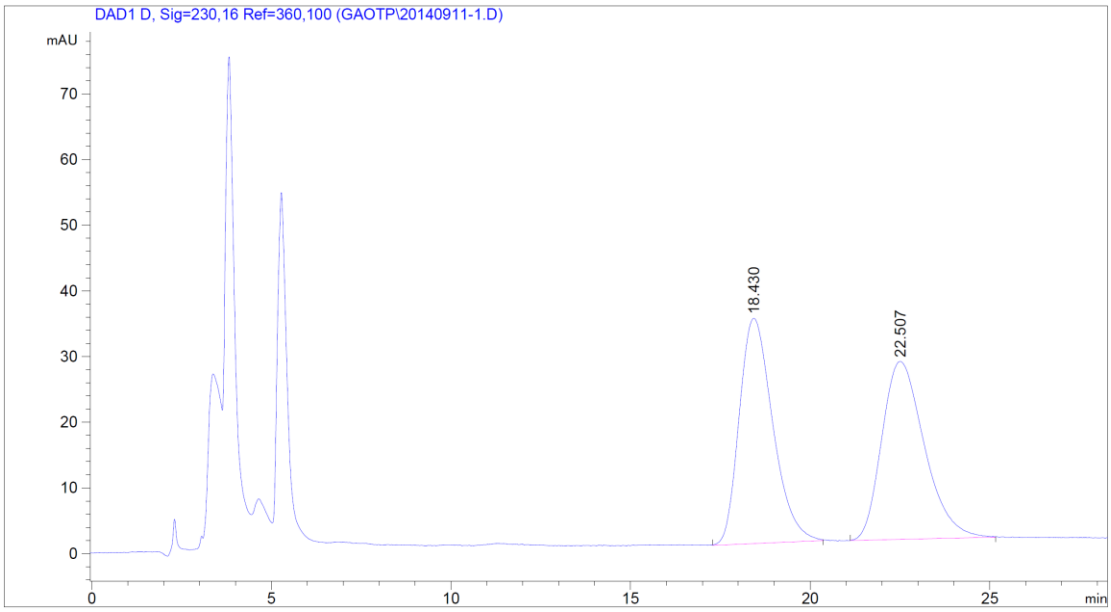


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.4 nm	10.902	5577.58643	161.88264	49.1647
2	PDA 254.4 nm	48.134	5767.11230	30.51305	50.8353

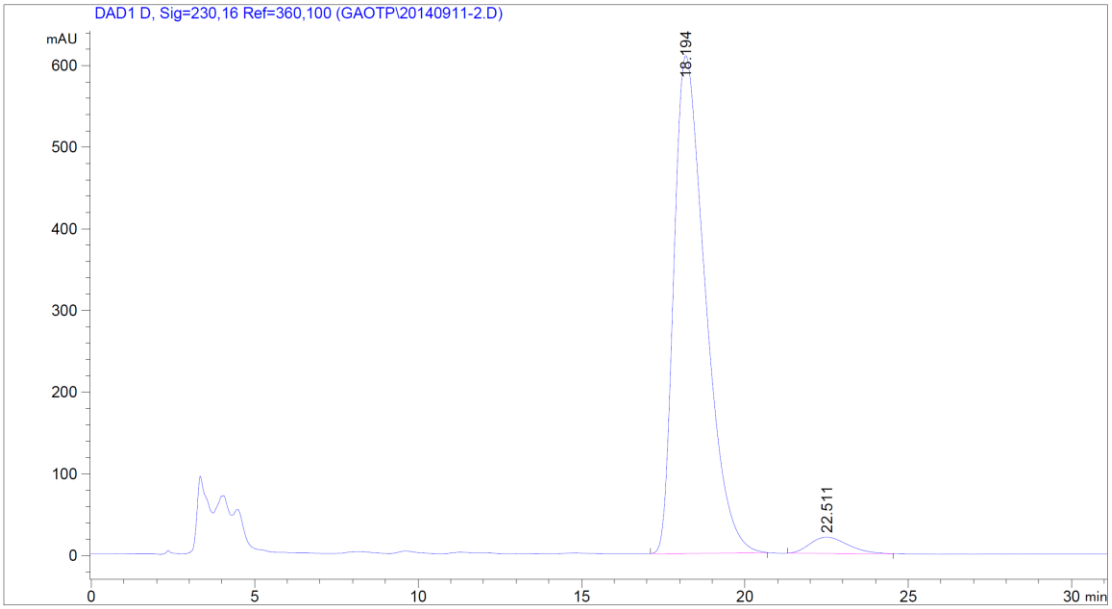


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 254.4 nm	12.431	9.17808e4	1972.66406	99.9451
2	PDA 254.4 nm	48.175	50.41419	8.03084e-4	0.0549

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

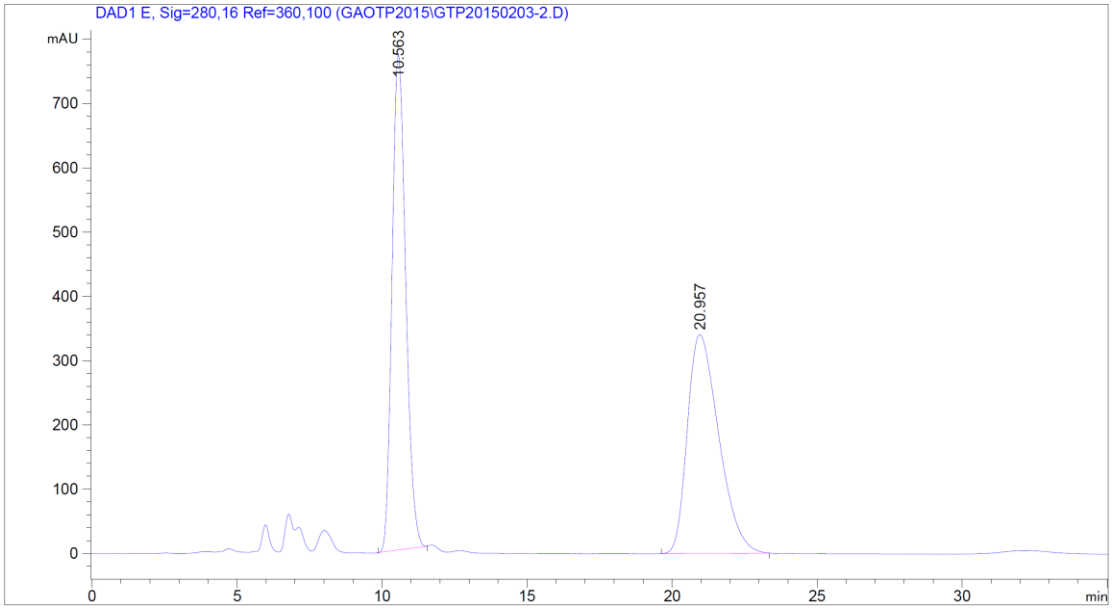


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	18.430	2225.48486	34.29328	49.9772
2	PDA 230.16 nm	22.507	2227.51147	27.10798	50.0228

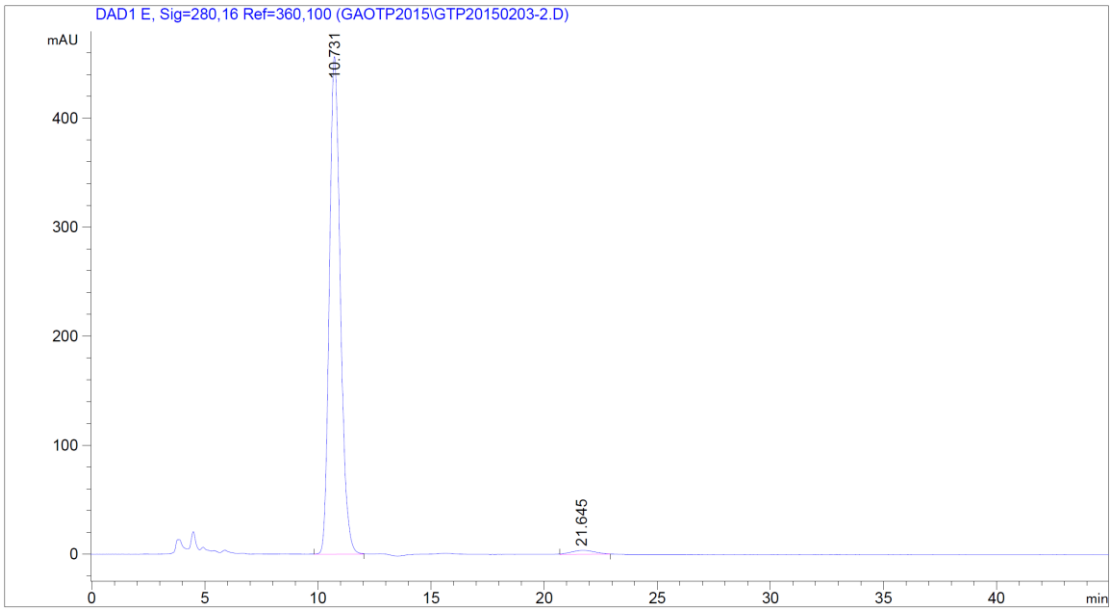


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 230.16 nm	18.194	4.06911e4	609.39734	96.2154
2	PDA 230.16 nm	22.511	1600.67212	19.90050	3.7848

4s HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 50:50, 1.0 mL/min)



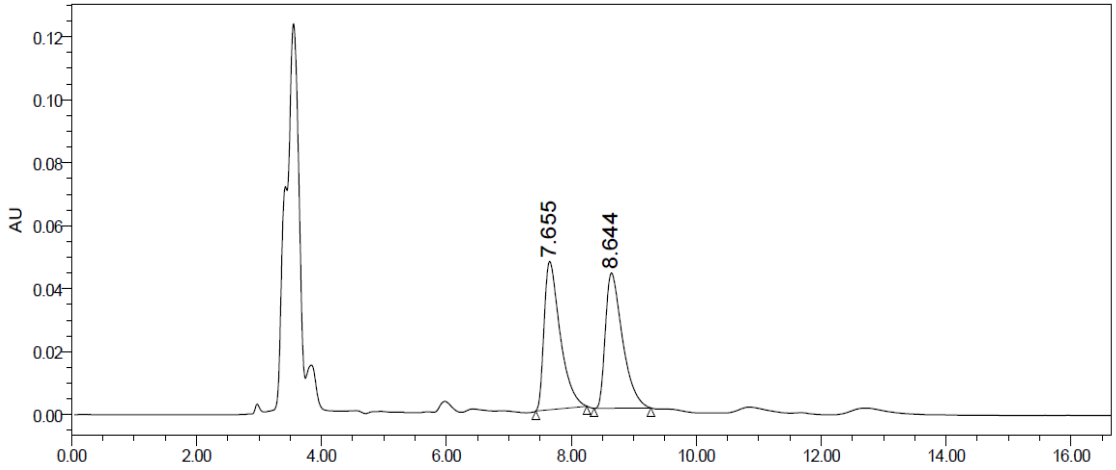
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	10.563	2.51831e4	769.90417	49.5167
2	PDA 280.16 nm	20.957	2.56748e4	340.99194	50.4833



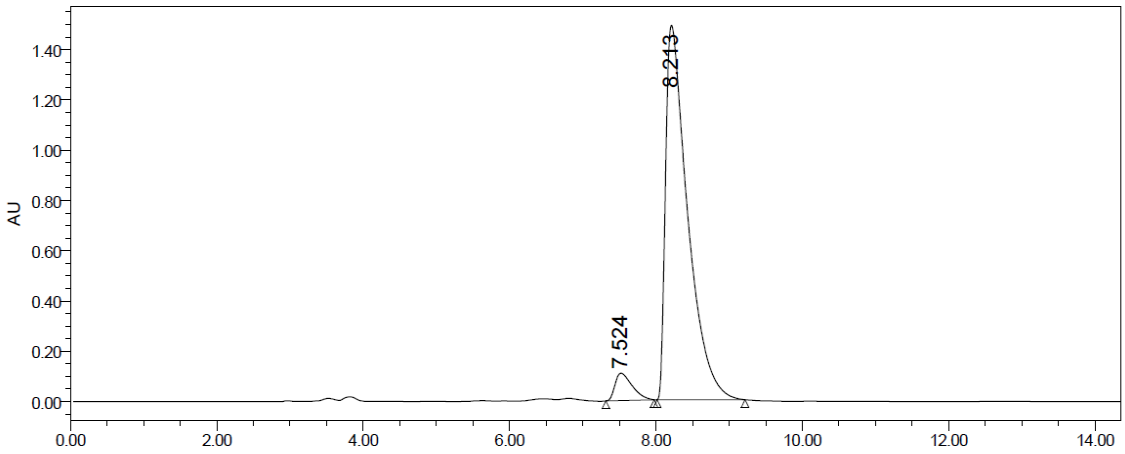
Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	PDA 280.16 nm	10.731	1.54091e4	456.45029	98.3100
2	PDA 280.16 nm	21.645	264.89679	3.62046	1.6900

10. HPLC spectra of compounds **5**

5a HPLC analysis using chiral IA-H Column (*n*-hexane: DCM = 50:50, 1.0 mL/min)

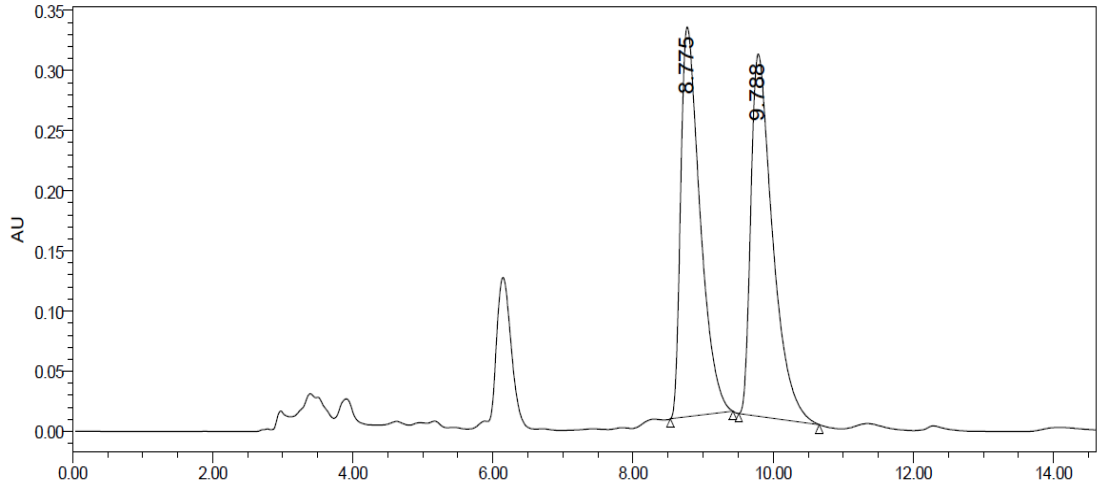


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	280.0 nm	7.655	839578	47093	50.57
2	280.0 nm	8.644	820629	42972	49.43

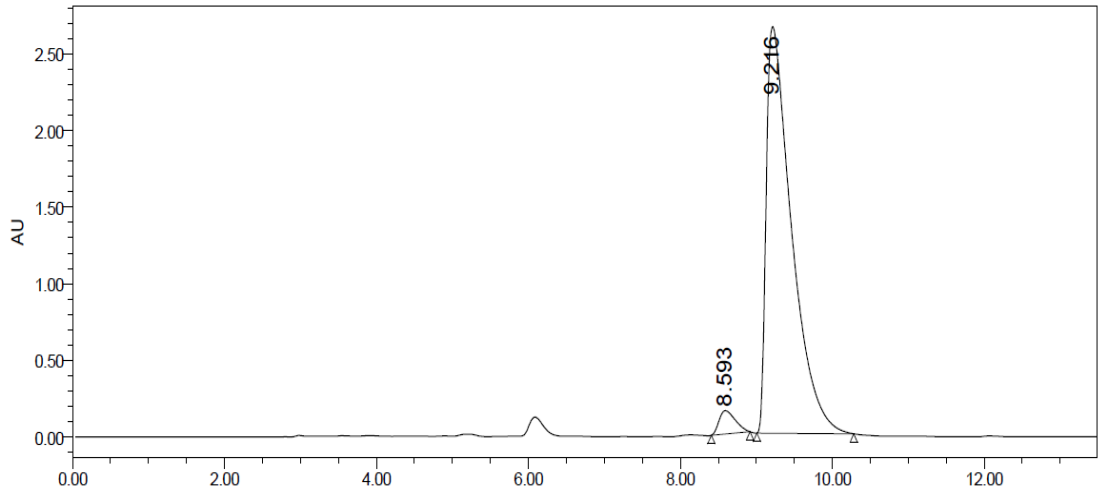


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	280.0 nm	7.524	1776799	109040	5.40
2	280.0 nm	8.213	31122867	1490003	94.60

5b HPLC analysis using chiral ID-H Column (*n*-hexane: DCM = 50:50, 1.0 mL/min)

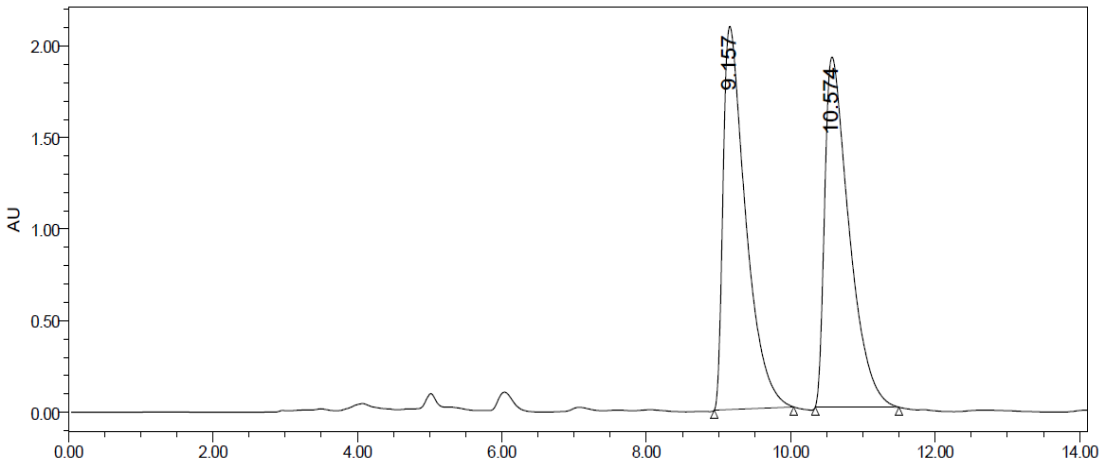


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	280.0 nm	8.775	6222902	324122	48.86
2	280.0 nm	9.788	6512554	301181	51.14

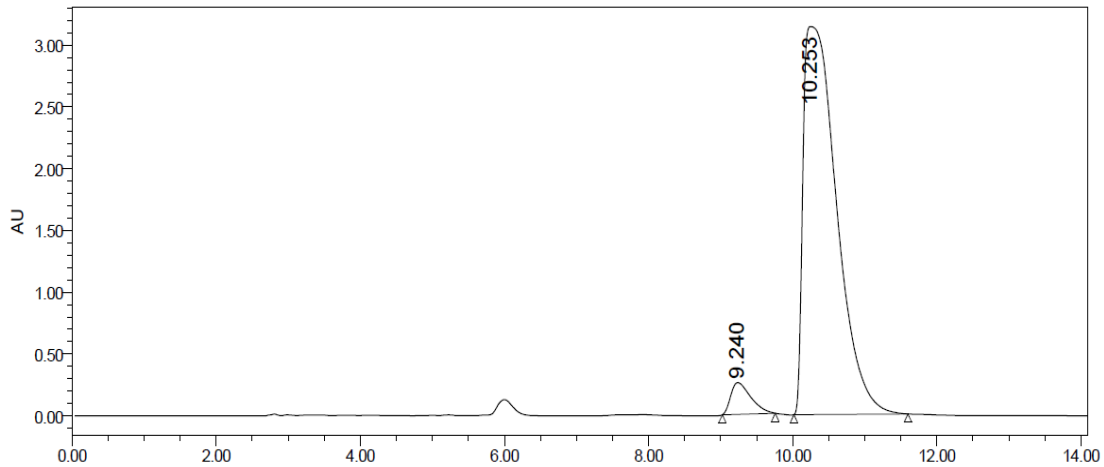


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	280.0 nm	8.593	2247248	152100	3.54
2	280.0 nm	9.216	61245800	2652840	96.46

5c HPLC analysis using chiral IA-H Column (*n*-hexane: DCM = 50:50, 1.0 mL/min)

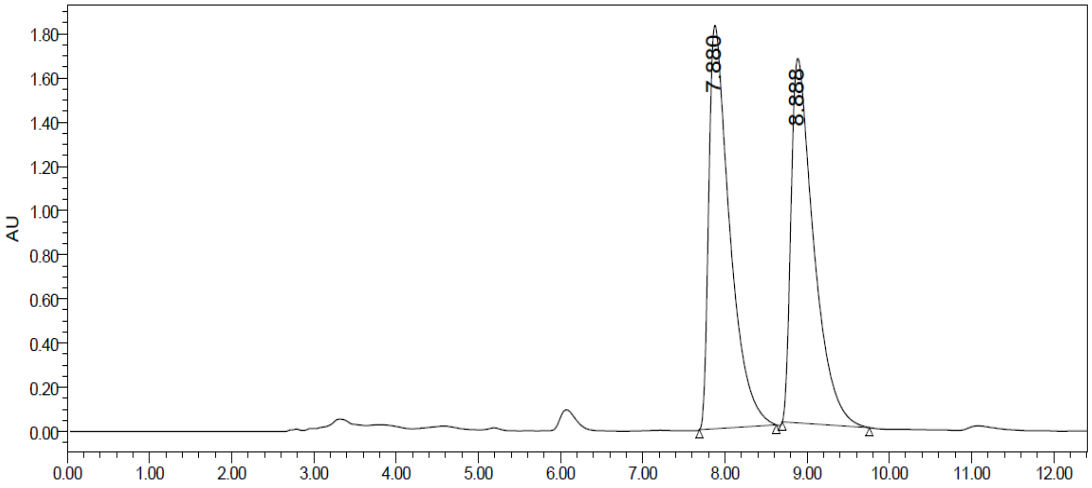


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	280.0 nm	9.157	45318776	2092629	50.24
2	280.0 nm	10.574	44883108	1911529	49.76

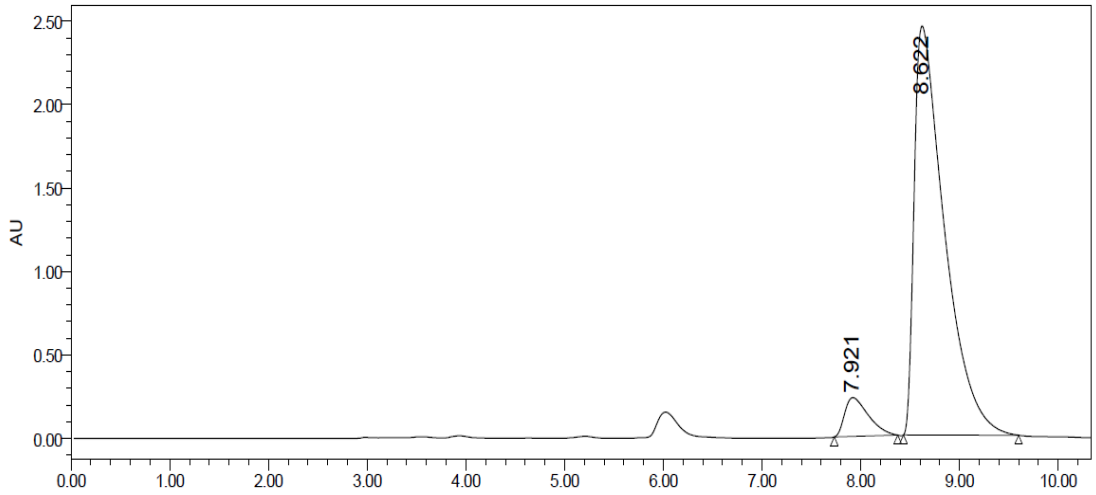


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	280.0 nm	9.240	4937644	256246	4.65
2	280.0 nm	10.253	101157285	3138656	95.35

5d HPLC analysis using chiral IA-H Column (*n*-hexane: DCM = 50:50, 1.0 mL/min)

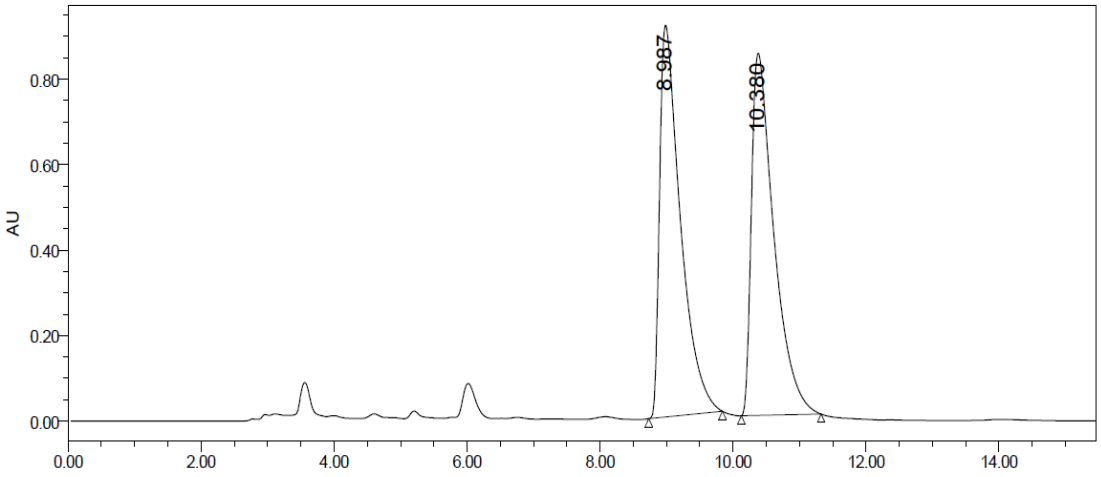


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	280.0 nm	7.880	32288370	1826702	50.61
2	280.0 nm	8.888	31505239	1649463	49.39

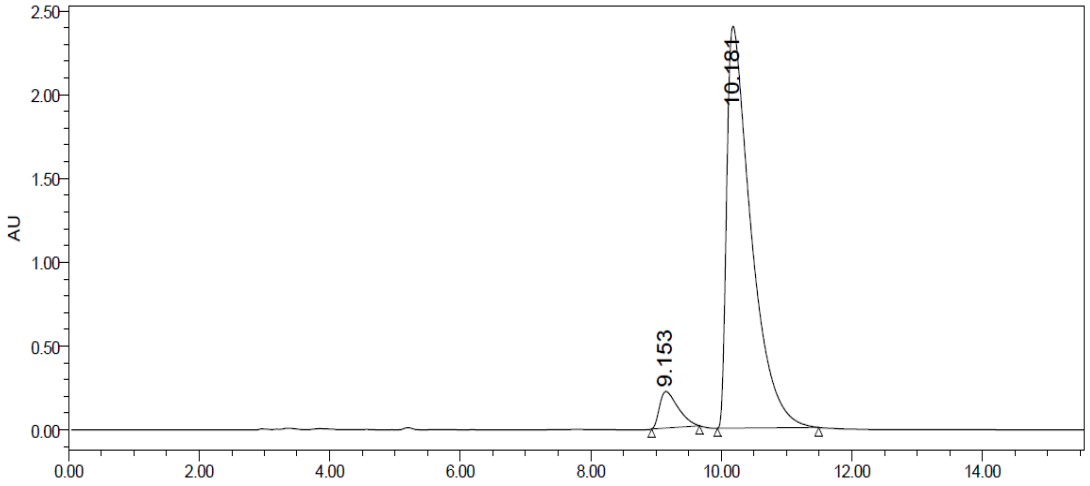


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	280.0 nm	7.921	3883906	232884	6.91
2	280.0 nm	8.622	52296843	2450006	93.09

5e HPLC analysis using chiral IA-H Column (*n*-hexane: DCM = 50:50, 1.0 mL/min)

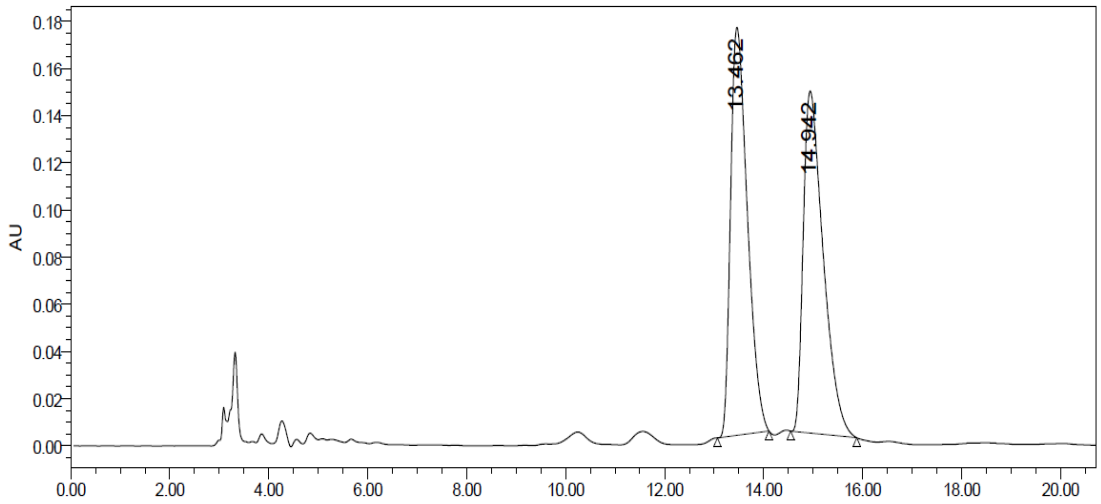


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	280.0 nm	8.987	19916511	916837	50.07
2	280.0 nm	10.380	19861576	847363	49.93

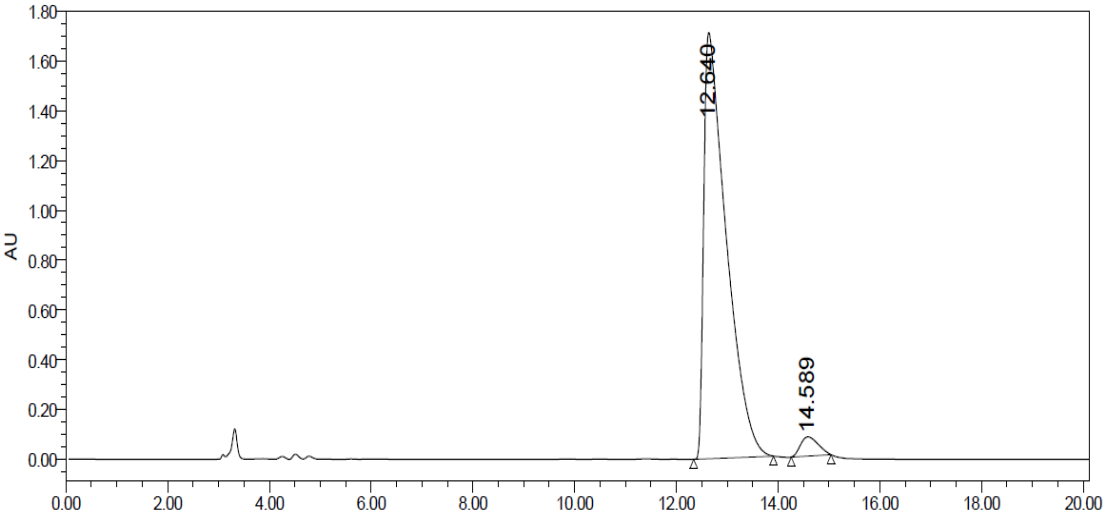


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	280.0 nm	9.153	4293328	217386	6.47
2	280.0 nm	10.181	62074883	2398289	93.53

5f HPLC analysis using chiral IA-H Column (*n*-hexane: DCM = 50:50, 1.0 mL/min)

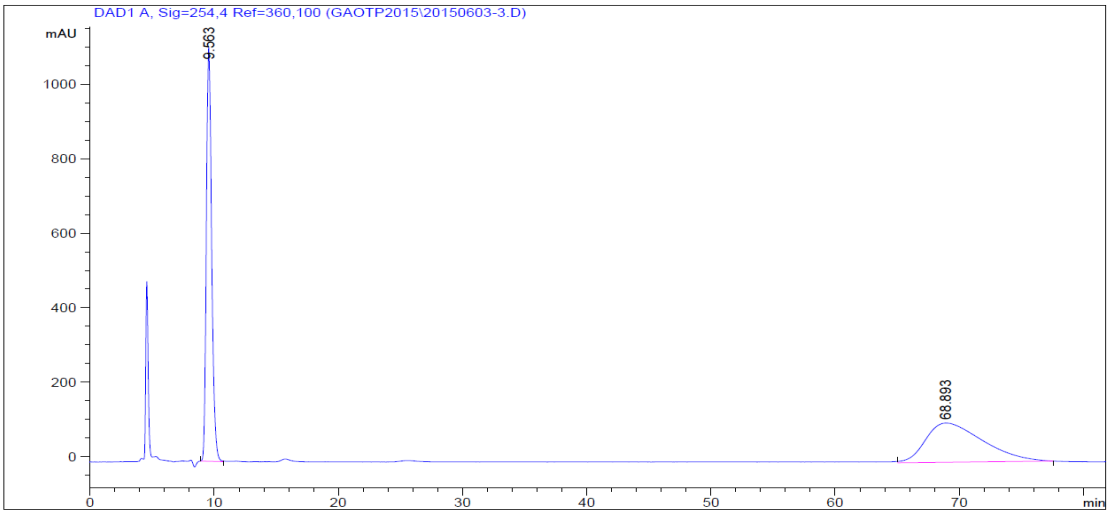


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	280.0 nm	13.462	4072243	172965	50.04
2	280.0 nm	14.942	4066487	145018	49.96

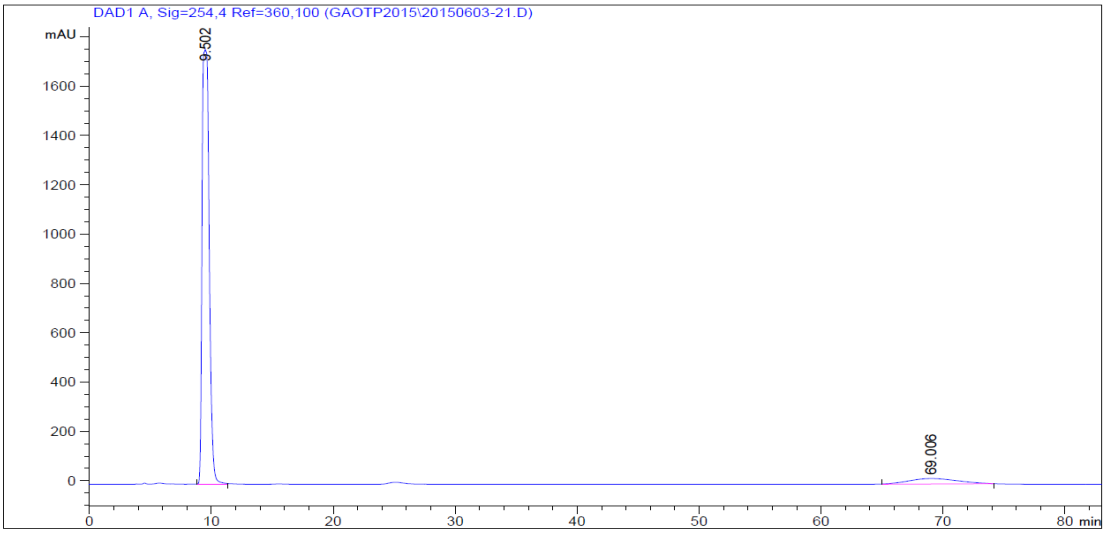


Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	280.0 nm	12.640	52591885	1712711	96.59
2	280.0 nm	14.589	1857775	77003	3.41

5g HPLC analysis using chiral AD-H Column (*n*-hexane: EtOH = 30:70, 1.0 mL/min)



Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	254.4 nm	9.563	3.31569e4	1109.92297	49.67
2	254.4 nm	68.893	3.35970e4	105.25744	50.32



Peak	Processed channel	Retention time (min)	Peak area (mAU*s)	Peak height (mAU)	Peak area (%)
1	254.4 nm	9.502	7.11790e4	1762.96118	92.00
2	254.4 nm	69.006	6181.79883	22.16992	7.99