Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

N-Heterocyclic Carbene-Catalyzed [4+2] Annulation of α,β-Unsaturated Carboxylic Acids: Enantioselective Synthesis of Dihydropyridinones and Spirocyclic Oxindolodihydropyridinones

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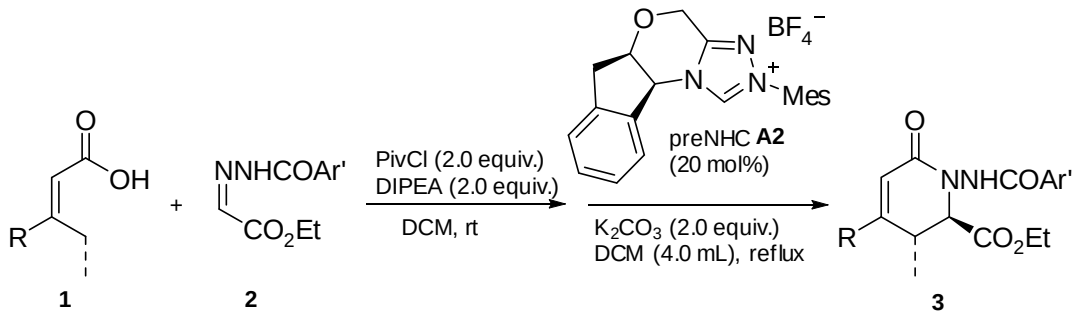
Part I Experimental part

1. General Information

Unless otherwise indicated, all reactions were carried out under N_2 atmosphere in oven-dried glassware with magnetic stirring. Cat A,[1] Cat. B[2] and isatin-derived *N*-Boc ketimines[3] were prepared according to literatures. Anhydrous THF and toluene were distilled from sodium and benzophenone. Anhydrous CH_2Cl_2 was distilled from CaH_2. Column chromatograph was performed on silica gel 200~300 mesh.

^1H NMR (300 MHz), ^{13}C NMR (75 MHz) spectra were recorded on a Bruker-DMX 300 spectrometer in $CDCl_3$, with tetramethylsilane as an internal standard and reported in ppm (δ). Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and reported as wavenumber (cm^{-1}). Optical rotations were measured on AA-10R/Optical activity LTD operating at the sodium D line with a 100 mm path length cell, and reported as follows: $[\alpha]_D^T$ (concentration (g/100ml), solvent).

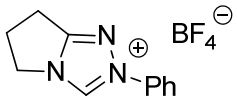
2. Synthesis of dihydropyridinones 3 (Table 2)



Typical Procedure. To an oven-dried 25 mL Schlenk tube equipped with a stir bar was charged with the unsaturated carboxylic acid **1a** (48.6 mg, 0.3 mmol) and

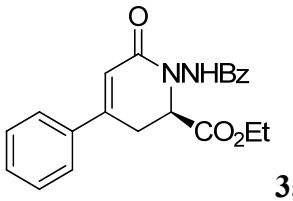
pivaloylchloride (37.0 μL, 0.3 mmol) in dry DCM under N_2. DIPEA (51.8 μL, 0.3 mmol.) was then added at room temperature. After stirring at room temperature for 20 min, the NHC precursors **A2** (12.5 mg, 20 mol%), K_2CO_3 (41.4 mg, 0.3 ml) and hydrazone **2a** (33.0 mg, 0.15 mmol) was added. The reaction mixture was heated to reflux until the full consumption of the hydrazone (monitored by TLC). The mixture was diluted with ethyl acetate and passed through a short pad of silica gel. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to give the desired annulation product **3a**.

The racemic samples for standard for HPLC analysis were prepared as the typical procedure but using the achiral NHC **S1** as the catalyst.



S1

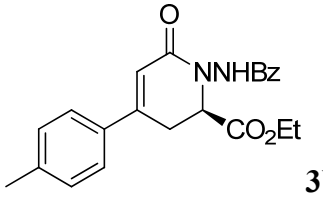
The absolute stereochemistry of known compounds **3** was established by the comparison of its optical rotation and HPLC spectra with literature.[4]



3a

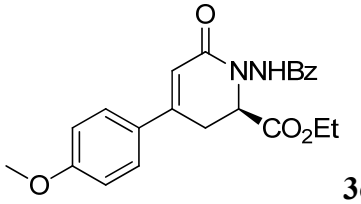
(*R*)-ethyl 1-benzamido-6-oxo-4-phenyl-1,2,3,6-tetrahydropyridine-2-carboxylate (**3a**).[4] Yield: 45.2 mg (83%), white waxy solid. R_f = 0.3 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{15}$ -7.3 (*c* 2.2, $CHCl_3$), HPLC analysis: 97% ee [Daicel CHIRALPAK IA-H column, 20 ^oC, 254 nm DCM, 0.8 mL /min, 7.7 min (minor), 18.7 min (major)]. ^1H

NMR (300 MHz, $CDCl_3$) δ 9.16 (brs, 1H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.55 – 7.49 (m, 3H), 7.44 – 7.40 (m, 5H), 6.35 (d, *J* = 2.4 Hz, 1H), 4.79 (dd, *J* = 6.6, 2.1 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.61 (ddd, *J* = 17.4, 6.9, 2.1 Hz, 1H), 3.38 (dd, *J* = 17.6, 2.2 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 166.3, 164.4, 149.7, 136.8, 132.5, 132.0, 130.3, 129.1, 128.7, 127.6, 126.2, 118.7, 62.3, 61.2, 30.2, 14.3. IR (KBr) ν 3232, 2981, 1737, 1614, 1488, 1368, 1235, 1021, 756, 689. HRMS (ESI) *m/z*: $[M+Na]^+$ Calc. for: $C_{21}H_{20}O_4N_2Na$, 387.1315, Found 387.1314.



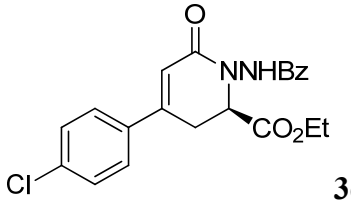
3b

(*R*)-ethyl 1-benzamido-6-oxo-4-p-tolyl-1,2,3,6-tetrahydropyridine-2-carboxylate (**3b**). Yield: 51.4 mg (91%), yellow solid, mp: 97-99 ^{o}C. R_f = 0.3 (petroleum ether/ethyl acetate, 10:1); $[\alpha]_D^{15}$ -17.6 (*c* 2.5, $CHCl_3$), HPLC analysis: 96% ee [Daicel CHIRALPAK IA-H column, 20 ^{o}C, 254 nm DCM, 0.8 mL /min, 7.4 min (minor), 26.1 min (major)]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.02 (brs, 1H), 7.85 (d, *J* = 7.5 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.45 – 7.40 (m, 4H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.32 (d, *J* = 2.2 Hz, 1H), 4.78 (d, *J* = 5.2 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.57 (dd, *J* = 17.5, 5.0 Hz, 1H), 3.37 (dd, *J* = 17.5, 2.0 Hz, 1H), 2.39 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 166.3, 164.6, 149.6, 140.7, 133.9, 132.4, 132.1, 129.7, 128.7, 127.6, 126.1, 117.7, 62.3, 61.2, 30.1, 21.4, 14.3. IR (KBr) ν 3235, 2978, 1737, 1609, 1418, 1236, 1019, 713. HRMS (ESI) *m/z*: $[M+Na]^+$ Calc. for: $C_{22}H_{22}O_4N_2Na$, 401.1472, Found 401.1474.



3c

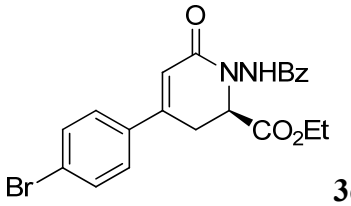
(*R*)-ethyl 1-benzamido-4-(4-methoxyphenyl)-6-oxo-1,2,3,6-tetrahydropyridine-2-carboxylate (**3c**).[4] Yield: 35.6 mg (60%), yellow wax, mp: 53-55 ^{o} C. R_f = 0.3 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{15}$ -36.5 (*c* 1.7, $CHCl_3$), HPLC analysis: 96% ee [Daicel CHIRALPAK IA-H column, 20 ^{o}C, 254 nm DCM, 0.8 mL /min, 7.7 min (minor), 25.7 min (major)]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.40 – 9.36 (brs, 1H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.45 (m, 3H), 7.38 (t, *J* = 7.5 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.28 (s, 1H), 4.76 (d, *J* = 5.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.54 (dd, *J* = 18.1, 6.4 Hz, 1H), 3.36 (d, *J* = 17.2 Hz, 1H), 1.22 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 166.2, 164.6, 161.4, 149.1, 132.3, 128.9, 128.6, 127.7, 127.6, 116.6, 114.4, 62.2, 61.1, 55.5, 30.1, 14.3. IR (KBr) ν 3222, 2962, 1735, 1603, 1423, 1235, 1027, 831, 713. HRMS (ESI) *m/z*: $[M+Na]^+$ Calc. for: $C_{22}H_{22}O_5N_2Na$, 417.1421, Found 417.1427.



3d

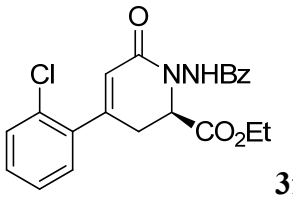
(*R*)-ethyl 1-benzamido-4-(4-chlorophenyl)-6-oxo-1,2,3,6-tetrahydropyridine-2-carboxylate (**3d**). Yield: 49.0 mg (82%), white solid, mp: 120-122 ^{o}C. R_f = 0.3 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{15}$ -27.9 (*c* 2.4, $CHCl_3$), HPLC analysis: 96% ee [Daicel CHIRALPAK IA-H column, 20 ^{o} C, 254 nm DCM, 0.8 mL /min, 7.4 min (minor), 18.7 min (major)]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.49 (brs, 1H), 7.82 (d, *J* =

7.6 Hz, 2H), 7.48 – 7.29 (m, 7H), 6.31 (s, 1H), 4.76 (d, *J* = 6.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.57 (dd, *J* = 17.7, 6.4 Hz, 1H), 3.31 (d, *J* = 17.4 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 166.2, 164.0, 148.4, 136.3, 135.2, 132.4, 131.7, 129.3, 128.6, 127.6, 127.4, 119.0, 62.3, 61.1, 30.1, 14.3. IR (KBr) ν 3228, 2980, 1737, 1489, 1289, 1197, 827, 712. HRMS (ESI) *m/z*: $[M+Na]^+$ Calc. for: $C_{21}H_{19}O_4N_2ClNa$, 421.0926, Found 421.0927.



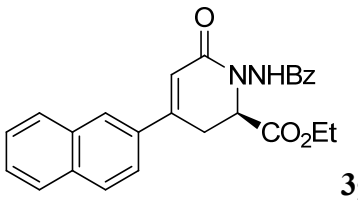
3e

(*R*)-ethyl 1-benzamido-4-(4-bromophenyl)-6-oxo-1,2,3,6-tetrahydropyridine-2-carboxylate (**3e**).[4] Yield: 54.6 mg (82%), white solid, mp: 120-122 ^{o} C. R_f = 0.3 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{15}$ -23.7 (*c* 2.7, $CHCl_3$), HPLC analysis: 96% ee [Daicel CHIRALPAK IA-H column, 20 ^{o} C, 254 nm DCM, 0.8 mL /min, 7.4 min (minor), 21.0 min (major)]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.58 (brs, 1H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.55 – 7.45 (m, 3H), 7.38 – 7.34 (m, 4H), 6.31 (d, *J* = 2.0 Hz, 1H), 4.75 (d, *J* = 5.2 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.57 (dd, *J* = 17.5, 6.8 Hz, 1H), 3.30 (d, *J* = 17.5 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 166.2, 164.0, 148.4, 135.7, 132.3, 132.2, 131.7, 128.6, 127.64, 127.62, 124.6, 119.0, 62.2, 61.1, 30.1, 14.3. IR (KBr) ν 3233, 2980, 1737, 1526, 1291, 1074, 823, 712. HRMS (ESI) *m/z*: $[M+Na]^+$ Calc. for: $C_{21}H_{19}O_4N_2BrNa$, 465.0420, Found 465.0422.



3f

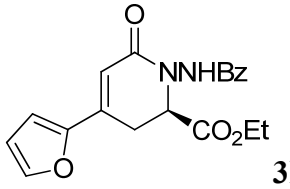
(*R*)-ethyl 1-benzamido-4-(2-chlorophenyl)-6-oxo-1,2,3,6-tetrahydropyridine-2-carboxylate (**3f**). Yield: 37.3 mg (62%), yellow oil. R_f = 0.3 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{15}$ 5.0 (*c* 1.8, $CHCl_3$), HPLC analysis: 90% ee [Daicel CHIRALPAK IA-H column, 20 ^oC, 254 nm DCM, 0.8 mL /min, 8.8 min (minor), 10.7 min (major)]. ^1H NMR (300 MHz, $CDCl_3$) δ 9.38 (brs, 1H), 7.84 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.32 – 7.26 (m, 2H), 7.22 – 7.19 (m, 1H), 6.07 (d, *J* = 2.6 Hz, 1H), 4.74 (d, *J* = 6.0 Hz, 1H), 4.32 – 4.18 (m, 2H), 3.61 (ddd, *J* = 17.8, 7.3, 2.5 Hz, 1H), 3.25 (dd, *J* = 17.8, 1.6 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 166.4, 163.8, 150.0, 137.5, 132.5, 131.9, 131.8, 130.4, 130.3, 129.6, 128.7, 127.7, 127.3, 123.4, 62.3, 61.4, 32.1, 14.3. IR (KBr) ν 2917, 1735, 1471, 1187, 757, 711. HRMS (ESI) *m/z*: $[M+Na]^+$ Calc. for: $C_{21}H_{19}O_4N_2ClNa$, 421.0926, Found 421.0933.



3g

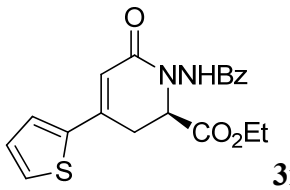
(*R*)-ethyl 1-benzamido-4-(naphthalen-2-yl)-6-oxo-1,2,3,6-tetrahydropyridine -2-carboxylate (**3g**).[4] Yield: 47.9 mg (77%), yellow oil. R_f = 0.3 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{15}$ -32.6 (*c* 2.3, $CHCl_3$), HPLC analysis: 96% ee [Daicel CHIRALPAK IA-H column, 20 ^{o} C, 254 nm DCM, 0.8 mL /min, 6.8 min (minor), 23.9 min (major)]. ^1H NMR (300 MHz, $CDCl_3$) δ 9.43 (brs, 1H), 7.97 – 7.86 (m, 6H), 7.64 – 7.38 (m, 6H), 6.51 (s, 1H), 4.85 (d, *J* = 6.4 Hz, 1H), 4.33 – 4.20 (m, 2H), 3.71 (dd, *J* = 17.1, 6.6 Hz, 1H), 3.54 (d, *J* = 17.4 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 166.3, 164.4, 149.3, 134.0, 133.9, 133.1, 132.4, 131.9, 128.8, 128.8,

128.7, 127.8, 127.7, 127.5, 127.0, 126.2, 123.2, 118.9, 62.3, 61.2, 30.2, 14.3. IR (KBr) ν 2978, 1737, 1414, 1237, 1131, 856, 711. HRMS (ESI) *m/z*: $[M+Na]^+$ Calc. for: $C_{25}H_{22}O_4N_2Na$, 437.1472, Found 437.1482.



3h

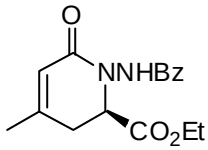
(*R*)-ethyl 1-benzamido-4-(furan-2-yl)-6-oxo-1,2,3,6-tetrahydropyridine-2-carboxylate (**3h**).[4] Yield: 34.4 mg (65%), yellow oil. R_f = 0.3 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{15}$ -18.8 (*c* 1.7, $CHCl_3$), HPLC analysis: 93% ee [Daicel CHIRALPAK IA-H column, 20 ^{o} C, 254 nm DCM, 0.8 mL /min, 7.2 min (minor), 22.9 min (major)]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.18 (brd, *J* = 17.6 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 1.2 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 6.63 (d, *J* = 3.4 Hz, 1H), 6.43 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.30 (d, *J* = 2.2 Hz, 1H), 4.68 – 4.66 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.40 (ddd, *J* = 17.2, 7.0, 2.2 Hz, 1H), 3.17 (dd, *J* = 17.2, 2.1 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 166.2, 164.5, 150.6, 145.3, 137.5, 132.4, 131.9, 128.7, 127.6, 114.3, 112.5, 62.3, 61.0, 28.0, 14.3. IR (KBr) ν 3250, 2980, 1738, 1526, 1299, 1197, 751, 713. HRMS (ESI) *m/z*: $[M+Na]^+$ Calc. for: $C_{19}H_{18}O_5N_2Na$, 377.1108, Found 377.1115.



3i

(*R*)-ethyl 1-benzamido-6-oxo-4-(thiophen-2-yl)-1,2,3,6-tetrahydropyridine-2-carboxylate (**3i**).[4] Yield: 34.1 mg (61%), yellow oil. R_f = 0.3 (petroleum ether/ethyl

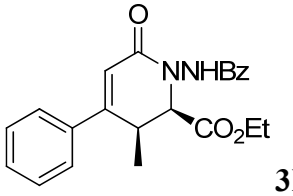
acetate, 3:1); $[\alpha]_D^{15}$ -47.1 (*c* 1.7, $CHCl_3$), HPLC analysis: 94% ee [Daicel CHIRALPAK IA-H column, 20 °C, 254 nm DCM, 0.8 mL /min, 7.6 min (minor), 19.0 min (major)]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.22 (brd, *J* = 13.2 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.37 – 7.32 (m, 3H), 7.29 – 7.24 (m, 1H), 7.04 – 7.01 (m, 1H), 6.24 (d, *J* = 1.8 Hz, 1H), 4.69 (d, *J* = 5.3 Hz, 1H), 4.14 (qd, *J* = 7.2, 2.1 Hz, 2H), 3.55 – 3.47 (m, 1H), 3.30 (dd, *J* = 17.3, 1.8 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 166.2, 164.3, 142.8, 140.7, 132.4, 131.9, 129.0, 128.7, 128.4, 127.6, 127.6, 115.9, 62.3, 61.0, 30.4, 14.3. IR (KBr) ν 3241, 2980, 1738, 1603, 1296, 1196, 853, 710. HRMS (ESI) *m/z*: $[M+Na]^+$ Calc. for: $C_{19}H_{18}O_4N_2NaS$, 393.0880, Found 393.0888.



3j

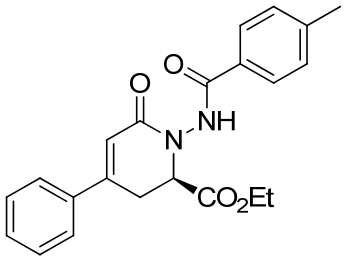
(*R*)-ethyl 1-benzamido-4-methyl-6-oxo-1,2,3,6-tetrahydropyridine-2-carboxylate (**3j**).[4] Yield: 10.6 mg (23%), (Method B 39%, 48% ee) yellow wax. R_f = 0.3 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{15}$ 31.8 (*c* 0.88, $CHCl_3$), HPLC analysis: 53% ee [Daicel CHIRALPAK IA-H column, 20 °C, 254 nm DCM, 0.8 mL /min, 8.4 min (minor), 15.4 min (major)]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (brd, *J* = 15.5 Hz, 1H), 7.85 – 7.80 (m, 2H), 7.56 – 7.51 (m, 1H), 7.47 – 7.41 (m, 2H), 5.83 (s, 1H), 4.63 (d, *J* = 6.1 Hz, 1H), 4.28 – 4.18 (m, 2H), 3.24 (dd, *J* = 17.8, 7.0 Hz, 1H), 2.75 (dd, *J* = 17.9, 1.8 Hz, 1H), 1.95 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 166.3, 164.2, 151.2, 132.4, 132.2, 128.8, 127.6, 127.5, 119.7, 62.2, 61.1, 32.8, 23.1, 14.3. IR (KBr) ν 3237, 2928, 1813, 1733.1633, 1288, 849, 713, 692. HRMS (ESI) *m/z*: $[M+Na]^+$ Calc.

for: $C_{16}H_{18}O_4N_2Na$, 325.1159, Found 325.1167.



3k

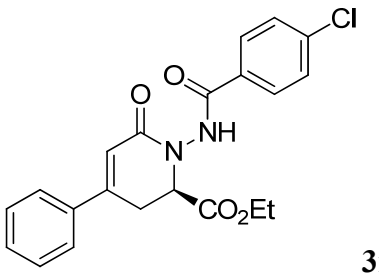
(2*R*,3*S*)-ethyl 1-benzamido-3-methyl-6-oxo-4-phenyl-1,2,3,6-tetrahydropyridine-2-carboxylate (**3k**).[4] Yield: 25.9 mg (46%), yellow oil. R_f = 0.3 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{15}$ 117.5 (*c* 1.2, $CHCl_3$), HPLC analysis: 95% ee [Daicel CHIRALPAK IA-H column, 20 ^oC, 254 nm DCM, 0.8 mL /min, 8.4 min (minor), 12.0 min (major)]. ^1H NMR (300 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.49 – 7.44 (m, 3H), 7.39 – 7.34 (m, 5H), 6.26 (s, 1H), 5.06 (d, *J* = 4.8 Hz, 1H), 4.25 – 4.14 (m, 2H), 3.53 – 3.44 (m, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.13 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 165.8, 165.4, 155.4, 136.0, 132.5, 132.0, 130.1, 129.1, 128.8, 127.6, 126.7, 118.1, 65.4, 61.9, 34.9, 15.2, 14.4. IR (KBr) ν 3258, 2978, 1732, 1518, 1379, 1190, 764, 692. HRMS (ESI) *m/z*: $[M+Na]^+$ Calc. for: $C_{22}H_{22}O_4N_2Na$, 401.1472, Found 401.1466.



3l

(*R*)-ethyl 1-(4-methylbenzamido)-6-oxo-4-phenyl-1,2,3,6-tetrahydropyridine-2-carboxylate (**3l**). Yield: 44.5 mg (79%), yellow solid, mp: 116-118 ^oC. R_f = 0.3 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{15}$ -5.1 (*c* 2.2, $CHCl_3$), HPLC analysis: 98% ee

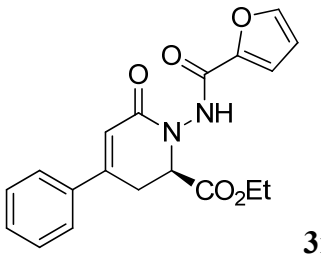
[Daicel CHIRALPAK IA-H column, 20 ^{o} C, 254 nm DCM, 0.8 mL /min, 7.9 min (minor), 20.8 min (major)]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.26 (brd, *J* = 20.5 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.48 (m, 2H), 7.43 – 7.41 (m, 3H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.33 (d, *J* = 2.3 Hz, 1H), 4.77 (d, *J* = 5.1 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.63 – 3.55 (m, 1H), 3.36 (dd, *J* = 17.5, 2.2 Hz, 1H), 2.37 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 166.3, 164.3, 149.6, 142.9, 136.9, 130.2, 129.3, 129.0, 127.6, 126.2, 118.7, 62.2, 61.2, 30.2, 21.6, 14.3. IR (KBr) ν 3239, 2963, 1737, 1612, 1191, 1019, 798, 690. HRMS (ESI) *m/z*: $[M+Na]^+$ Calc. for: $C_{22}H_{22}O_4N_2Na$, 401.1472, Found 401.1468.



3m

(*R*)-ethyl 1-(4-chlorobenzamido)-6-oxo-4-phenyl-1,2,3,6-tetrahydropyridine-2-carboxylate (**3m**). Yield: 49.4 mg (83%), yellow wax. R_f = 0.3 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{15}$ -6.3 (*c* 2.4, $CHCl_3$), HPLC analysis: 95% ee [Daicel CHIRALPAK IA-H column, 20 ^{o}C, 254 nm DCM, 0.8 mL /min, 8.9 min (minor), 33.2 min (major)]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.49 (m, 2H), 7.44 – 7.42 (m, 3H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.33 (d, *J* = 2.3 Hz, 1H), 4.87 – 4.64 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.59 (ddd, J = 17.6, 7.2, 2.2 Hz, 1H), 3.38 (dd, *J* = 17.6, 2.2 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 165.3, 164.4, 149.9, 138.7, 136.8, 130.3, 130.2, 129.1, 129.1, 129.0, 126.2, 118.6, 62.3, 61.2, 30.3, 14.3. IR (KBr) ν 3227, 2982, 1738, 1531, 1447, 1234, 1094, 846, 691. HRMS

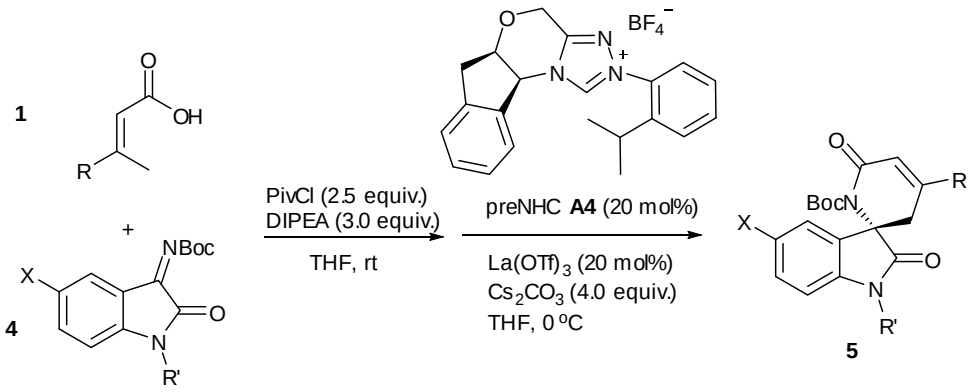
(ESI) *m/z*: $[M+Na]^+$ Calc. for: $C_{21}H_{19}O_4N_2ClNa$, 421.0926, Found 421.0922.



3n

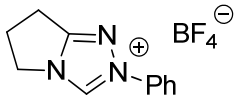
(*R*)-ethyl 1-(furan-2-carboxamido)-6-oxo-4-phenyl-1,2,3,6-tetrahydropyridine-2-carboxylate (**3n**).[4] Yield: 35.8 mg (67%), yellow oil. R_f = 0.3 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{15}$ -19.4 (*c* 1.7, $CHCl_3$), HPLC analysis: 95% ee [Daicel CHIRALPAK IA-H column, 20 ^oC, 254 nm DCM, 0.8 mL /min, 7.3 min (minor), 19.8 min (major)]. ^1H NMR (300 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.44 – 7.41 (m, 3H), 7.36 – 7.34 (m, 3H), 7.13 (d, *J* = 3.5 Hz, 1H), 6.43 (dd, *J* = 3.4, 1.6 Hz, 1H), 6.27 (d, *J* = 2.5 Hz, 1H), 4.65 (dd, *J* = 7.0, 2.1 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.51 (ddd, *J* = 17.6, 7.0, 2.5 Hz, 1H), 3.30 (dd, *J* = 17.6, 2.2 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 164.3, 157.1, 149.7, 146.1, 145.0, 136.8, 130.3, 129.0, 126.1, 118.6, 116.2, 112.2, 62.3, 61.5, 30.2, 14.9. IR (KBr) ν 3200, 2980, 1737, 1588, 1447, 1198, 870, 690. HRMS (ESI) *m/z*: $[M+Na]^+$ Calc. for: $C_{19}H_{18}O_5N_2Na$, 377.1108, Found 377.1104.

3. Synthesis Spirocyclic oxindolodihydropyridinones **5** (Table 4)



Typical procedure. To an oven-dried 25 mL Schlenk tube equipped with a stir bar was charged with **1a** (24.3 mg, 0.15 mmol). This tube was closed with a septum, evacuated, and back-filled with nitrogen. To this mixture was added freshly distilled THF (2 mL), DIPEA (53.6 μL, 0.3 mmol) and PivCl (30.2 mg, 0.25 mmol) at room temperature. After stirring at room temperature for 30 minutes, the reaction mixtrue was cooled to 0 ^{o}C, and then was added the NHC precursor **A4** (8.38 mg, 0.02 mmol), $La(OTf)_3$ (11.72 mg, 0.02mmol), isatin-derived ketimine **4a** (33.6 mg, 0.1 mmol) and Cs_2CO_3 (130.4 mg, 0.4 mmol). The reaction mixture was stirred at 0 ^{o}C, typically for 16-30 h, until the full consumption of the ketimine. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (ethyl acetate /petroleum ether, typically 1/7) to give the desired product **5a**.

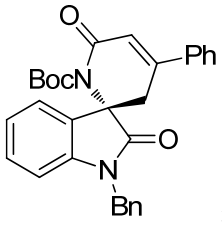
Racemic samples for the standard of chiral HPLC spectra were prepared using the triazolium salts **S1** as the catalyst.



S1

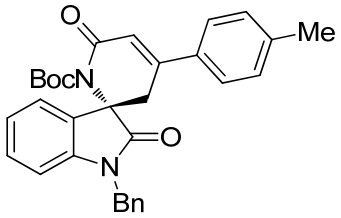
The absolute stereochemistry of products **5** was established by comparison of its

optical rotation and HPLC spectra with the literauture.[5]



5a

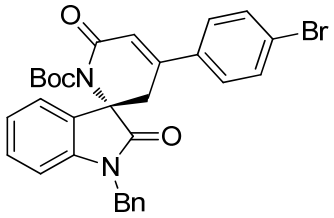
(*S*)-tert-butyl 1-benzyl-2,6'-dioxo-4'-phenyl-3',6'-dihydro-1'H-spiro[indoline-3,2'-pyridine]-1'-carboxylate (**5a**) (zhm-1306-B).[5] Yield: 33.6 mg (70%), white solid. mp 197-200 °C; R_f = 0.28 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{25}$ -118.5 (c 1.30, CH_2Cl_2); HPLC analysis: 92% ee [Daicel CHIRALPAK IA column, 20 ^oC, 254 nm hexane/i-PrOH = 70:30, 1.0 mL /min, 254 nm, 18.6 min (minor), 39.2 min (major)]; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43-7.25 (m, 11H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.53 (d, *J* = 1.5 Hz, 1H), 5.07 (d, *J* = 15.6 Hz, 1H), 4.87 (d, *J* = 15.6 Hz, 1H), 3.51 (dd, *J* = 17.1, 2.1 Hz, 1H), 2.80 (d, *J* = 16.8 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$); δ 175.3, 163.6, 151.8, 148.7, 141.5, 136.5, 135.6, 130.5, 130.3, 128.9, 127.8, 127.5, 126.0, 123.0, 122.5, 119.7, 109.8, 84.3, 64.8, 44.4, 37.7, 27.9; IR (KBr) ν 2926, 1725, 1278, 1152, 752; HRMS (ESI) calcd for $C_{30}H_{28}N_2O_2Na$ $[M+Na]^+$ 503.1941, Found 503.1943.



5b

(*S*)-(tert-butyl 1-benzyl-2,6'-dioxo-4'-p-tolyl-3',6'-dihydro-1'H-spiro[indoline-3,2'-pyridine]-1'-carboxylate (**5b**) (zhm-1368). Yield: 36.1 mg (73%), white solid. mp 205-207 °C; R_f = 0.27 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{25}$ -65.3 (c 0.70,

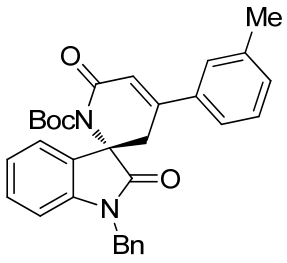
CH_2Cl_2); HPLC analysis: 75% ee [Daicel CHIRALPAK IA column, 20 ^oC, 254 nm hexane/i-PrOH = 60:40, 1.0 mL /min, 254 nm, 14.6 min (minor), 19.8 min (major)]; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41-7.28 (m, 8H), 7.20-7.17 (m, 3H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.51 (d, *J* = 1.8 Hz, 1H), 5.06 (d, *J* = 15.6 Hz, 1H), 4.88 (d, *J* = 15.6 Hz, 1H), 3.49 (dd, *J* = 17.1, 2.1 Hz, 1H), 2.78 (d, *J* = 17.1 Hz, 1H), 2.36 (s, 3H) 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$); δ 175.4, 163.8, 151.9, 148.6, 141.5, 141.0, 135.7, 133.7, 130.5, 129.8, 129.6, 129.0, 127.9, 127.6, 126.1, 123.0, 122.7, 118.9, 109.9, 84.3, 64.9, 44.4, 37.7, 28.0, 21.5; IR (KBr) ν 2924, 1724, 1362, 1258, 751; HRMS (ESI) calcd for $C_{31}H_{30}N_2O_4Na$ $[M+Na]^+$ 517.2098, Found 517.2103.



5c

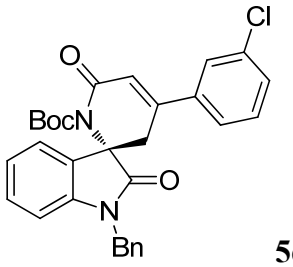
(*S*)-*tert*-butyl 1-benzyl-4'-(4-bromophenyl)-2,6'-dioxo-3',6'-dihydro-1'H-spiro[indoline -3,2'-pyridine]-1'-carboxylate (**5c**) (zhm-1314). Yield: 20.7 mg (37%), white solid. mp 218-220 °C; R_f = 0.42 (petroleum ether/ethyl acetate, 4:1); $[\alpha]_D^{25}$ -66.4 (c 1.4, CH_2Cl_2); HPLC analysis: 68% ee [Daicel CHIRALPAK IA column, 20 ^oC, 254 nm hexane/i-PrOH = 60:40, 1.0 mL /min, 254 nm, 18.6 min (minor), 32.3 min (major)]; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 9.3, 2H), 7.41-7.27 (m, 8H), 7.20 (d, *J* = 7.8, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.52 (s, 1H), 5.05 (d, *J* = 15.6 Hz, 1H), 4.87 (d, *J* = 15.6 Hz, 1H), 3.45 (d, *J* = 17.4 Hz, 1H), 2.76 (d, *J* = 17.1 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$); δ 175.2, 163.4, 151.7, 147.4, 141.6, 135.6, 135.5, 132.3, 130.2, 129.7, 129.0, 128.7, 127.9, 127.6, 125.9, 123.1, 122.5, 120.2,

109.9, 84.5, 64.7, 44.5, 37.5, 27.9; IR (KBr) ν 2925, 1724, 1277, 1151, 751; HRMS (ESI) calcd for $C_{30}H_{27}N_2O_4BrNa$ $[M+Na]^+$ 581.1064, Found 581.1050.



5d

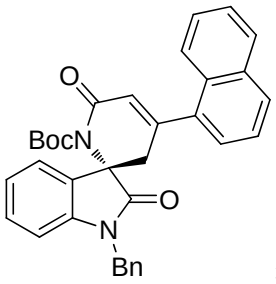
(*S*)-*tert*-butyl 1-benzyl-2,6'-dioxo-4'-m-tolyl-3',6'-dihydro-1'H-spiro[indoline-3,2'-pyridine]-1'-carboxylate (**5d**) (zhm-1414-A). Yield: 32.1 mg (65%), white solid. mp 201-202 °C; R_f = 0.41 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{25}$ -84.3 (c 1.10, CH_2Cl_2); HPLC analysis: 71% ee [Daicel CHIRALPAK IA column, 20 °C, 254 nm hexane/i-PrOH = 75/25, 1.0 mL /min, 254 nm, 14.1 min (minor), 21.0 min (major)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.18 (m, 11H), 6.95 (t, *J* = 8.7 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.52 (d, *J* = 1.8 Hz, 1H), 5.06 (d, *J* = 15.6 Hz, 1H), 4.89 (d, *J* = 15.6 Hz, 1H), 3.50 (dd, *J* = 17.1, 2.1 Hz, 1H), 2.80 (d, *J* = 17.1 Hz, 1H), 2.36 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$); δ 175.4, 163.9, 161.6, 151.9, 148.1, 141.5, 135.7, 130.5, 129.5, 128.9, 128.6, 127.9, 127.7, 127.6, 123.0, 122.7, 117.7, 114.5, 109.8, 84.2, 64.8, 55.6, 44.4, 37.5, 28.0; IR (KBr) ν 2919, 1724, 1276, 1151, 751; HRMS (ESI) calcd for $C_{31}H_{30}N_2O_4Na$ $[M+Na]^+$ 517.2098, Found 517.2103.



5e

(*S*)-*tert*-butyl 1-benzyl-4'-(3-chlorophenyl)-2,6'-dioxo-3',6'-dihydro-1'H-spiro

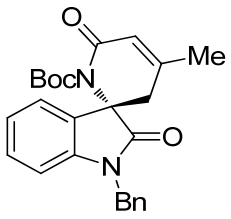
[indoline-3,2'-pyridine]-1'-carboxylate (**5e**) (zhm-1410-B). Yield: 22.1 mg (43%), white solid. mp 206-208 °C; R_f = 0.41 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{25}$ -108.3 (c 1.5, CH_2Cl_2); HPLC analysis: 73% ee [Daicel CHIRALPAK IA column, 20 ^oC, 254 nm hexane/i-PrOH = 60:40, 1.0 mL /min, 254 nm, 9.5 min (minor), 20.1 min (major)]; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41-7.19 (m, 11H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.52 (d, *J* = 1.8 Hz, 1H), 5.10 (d, *J* = 15.9 Hz, 1H), 4.89 (d, *J* = 15.6 Hz, 1H), 3.44 (dd, *J* = 17.1, 1.8 Hz, 1H), 2.77 (d, *J* = 17.4 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$); δ 175.2, 163.3, 151.7,141.6, 138.4, 135.6, 135.2, 130.4, 130.2, 129.7, 129.0, 127.9, 127.6, 124.2, 123.1, 122.5, 120.8, 110.0, 84.5, 64.7, 55.6, 44.5, 37.6, 27.9; IR (KBr) ν 2928, 1725, 1750, 1488, 1278, 751; HRMS (ESI) calcd for $C_{30}H_{27}N_2O_4ClNa$ $[M+Na]^+$ 537.1552, Found 537.1557.



5f

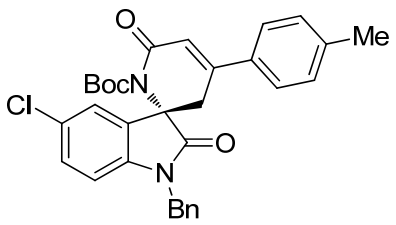
(*S*)-tert-butyl 1-benzyl-4'-(naphthalen-1-yl)-2,6'-dioxo-3',6'-dihydro-1'H-spiro [indoline-3,2'-pyridine]-1'-carboxylate (**5f**) (zhm-1427-B). Yield: 30.8 mg (58%), white solid. mp 198-196 °C; R_f = 0.32 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{25}$ -54.3 (c 0.80, CH_2Cl_2); HPLC analysis: 83% ee [Daicel CHIRALPAK IA column, 20 ^oC, 254 nm hexane/i-PrOH = 65:35, 1.0 mL /min, 254 nm, 15.0 min (minor), 31.2 min (major)]; ^1H NMR (300 MHz, $CDCl_3$) δ 7.87-7.62 (m, 4H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.51 (t, *J* = 3.6 Hz, 2H), 7.44 - 7.29 (m, 6H), 7.21 (t, J = 7.7 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 1.5 Hz, 1H), 5.07 (d, *J* = 15.9 Hz, 1H), 4.91 (d, *J* = 15.6

Hz, 1H), 3.61 (dd, J = 16.8, 1.8 Hz, 1H), 2.97 (d, J = 16.8 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$); δ 175.4, 163.7, 151.9, 148.3, 141.7, 135.7, 134.2, 133.7, 130.4, 129.6, 129.0, 128.8, 127.9, 127.8, 127.6, 127.1, 126.3, 123.1, 123.0, 122.7, 120.0, 109.9, 84.4, 64.9, 44.5, 37.6, 28.0; IR (KBr) ν 2925, 1724, 1368, 1278; 1150, 750; HRMS (ESI) calcd for $C_{34}H_{30}N_2O_4Na$ $[M+Na]^+$ 553.2098, Found 553.2097.



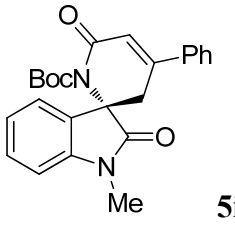
5g

(*S*)-tert-butyl 1-benzyl-4'-methyl-2,6'-dioxo-3',6'-dihydro-1'H-spiro[indoline-3,2'-pyridine]-1'-carboxylate (**5g**) (zhm-1383-B). Yield: 7.5 mg (18%), white solid. mp 178-180 °C; R_f = 0.28 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{25}$ +14.3 (c 1.00, CH_2Cl_2); HPLC analysis: 19% ee [Daicel CHIRALPAK AD column, 20 ^{o}C, 254 nm hexane/i-PrOH = 70:30, 1.0 mL /min, 254 nm, 8.6 min (minor), 10.4 min (major)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.18 (m, 7H), 6.96 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 8.1 Hz, 1H), 6.00 (d, 1H), 5.07 (d, J = 15.6 Hz, 1H), 4.79 (d, J = 15.6 Hz, 1H), 3.08 (d, J = 17.4 Hz, 1H), 2.26 (d, J = 17.4 Hz, 1H), 1.91 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$); δ 175.4, 163.3, 151.8, 150.4, 141.5, 135.7, 130.7, 129.5,128.9, 127.8, 127.5, 122.9, 122.4, 121.0, 109.8, 84.1, 64.8, 44.3, 40.2, 27.9, 23.1; IR (KBr) ν 2978, 1724, 1277, 1149, 752; HRMS (ESI) calcd for $C_{25}H_{26}N_2O_4Na$ $[M+Na]^+$ 441.1785, Found 441.1783.



5h

(*S*)-*tert*-butyl 1-benzyl-5-chloro-2,6'-dioxo-4'-p-tolyl-3',6'-dihydro-1'H-spiro[indoline-3,2'-pyridine]-1'-carboxylate (**5h**) (zhm-1394). Yield: 34.3 mg (65%), white solid. mp 232-235 °C; R_f = 0.38 (petroleum ether/ethyl acetate, 3:1); $[\alpha]_D^{25}$ -42.3 (c 1.80, CH_2Cl_2); HPLC analysis: 74% ee [Daicel CHIRALPAK IA column, 20 ^oC, 254 nm, hexane/i-PrOH = 65:35, 1.0 mL /min, 254 nm, 12.3 min (minor), 18.2 min (major)]; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.14 (m, 11H), 6.67 (t, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 1.8 Hz, 1H), 4.97 (dd, *J* = 23.4, 15.9 Hz, 2H), 3.52 (dd, *J* = 17.1, 1.8 Hz, 1H), 2.77 (d, *J* = 16.8 Hz, 1H), 2.37 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$); δ 175.0, 163.3, 152.1, 148.6, 141.3, 140.1, 135.2, 133.3, 132.0, 129.9, 129.5, 129.0, 128.3, 128.0, 127.5, 126.1, 123.1, 118.7, 110.9, 84.7, 64.8, 44.6, 37.4, 28.0, 21.5; IR (KBr) ν 2928, 1727, 1480, 1277, 814; HRMS (ESI) calcd for $C_{31}H_{29}N_2O_4ClNa$ $[M+Na]^+$ 551.1708, Found 551.1714.



5i

(*S*)-tert-butyl 1-methyl-2,6'-dioxo-4'-phenyl-3',6'-dihydro-1'H-spiro[indoline-3,2'-pyridine]-1'-carboxylate (**5i**) (zhm-1311). Yield: 25.1 mg (62%), white solid. mp 179-180 °C; R_f = 0.19 (petroleum ether/ethyl acetate, 4:1); $[\alpha]_D^{25}$ -66.5 (c 1.5, CH_2Cl_2); HPLC analysis: 89% ee [Daicel CHIRALPAK IA column, 20 ^oC, 254 nm

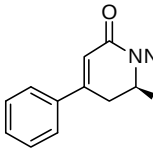
hexane/i-PrOH = 85:15, 1.0 mL /min, 254 nm, 24.0 min (major), 28.1 min (minor)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ744-7.31 (m, 7H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 2.1 Hz, 1H), 3.42 (dd, *J* = 17.1, 2.1 Hz, 1H), 3.28 (s, 3H), 2.80 (d, *J* = 17.1 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$); δ 175.3, 163.7, 151.1, 148.5, 142.4, 136.5,130..5, 130.4, 129.7, 129.1, 126.1, 123.1, 122.6, 119.6, 108.8, 84.2, 64.7, 37.4, 27.8, 26.8; IR (KBr) ν 2927, 1724, 1276, 1151, 752; HRMS (ESI) calcd for $C_{30}H_{30}N_2O_4Na$ $[M+Na]^+$ 427.1614, Found 427.1613.

4. Reference

1. (a) M. S. Kerr, J. Alaniz, J. R. de Alaniz and T. Rovis, *J. Org. Chem.,* 2005, **70**, 5725; (b) M. S. Kerr, J. R. de Alaniz and T. Rovis, *J. Am. Chem. Soc.,* 2002, **124**, 10298.
2. (a) Y.-R. Zhang, L. He, X. Wu, P.-L. Shao and S. Ye, *Org. Lett.,* 2008, **10**, 277; (b) D. Enders, O. Niemeier and T. Balensiefer, *Angew. Chem. Int. Ed.,* 2006, **45**, 1463; (c) D. Enders and J. Han, *Tetrahedron: Asymmetry,* 2008, **19**, 1367.
3. W.-J. Yan, D. Wang, J.-C. Feng, P. Li, D.-P. Zhao and R. Wang *Org. Lett.,* 2012, **14**, 2512.
4. J. Xu, Z. Jin and Y. R. Chi, *Org. Lett.*, 2013, **15**, 5028.
5. B. S. Li, Y. Wang, Z. Jin, P. Zheng, R. Ganguly and Y. R. Chi, *Nat. Commun.*, 2015, **6**, 6207.

# #

Part II NMR Spectra



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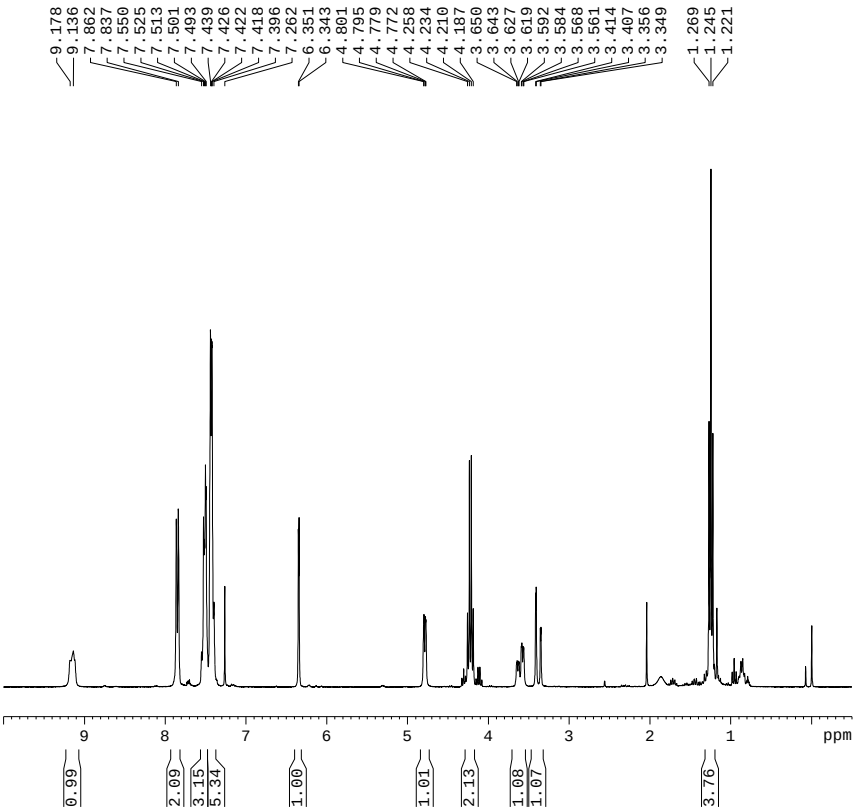


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TD                 32768
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DS                     0
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FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                   181
DW                55.600 usec
DE                 6.50 usec
TE                296.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1        300.1318534 MHz
SI                 32768
SF          300.1300062 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
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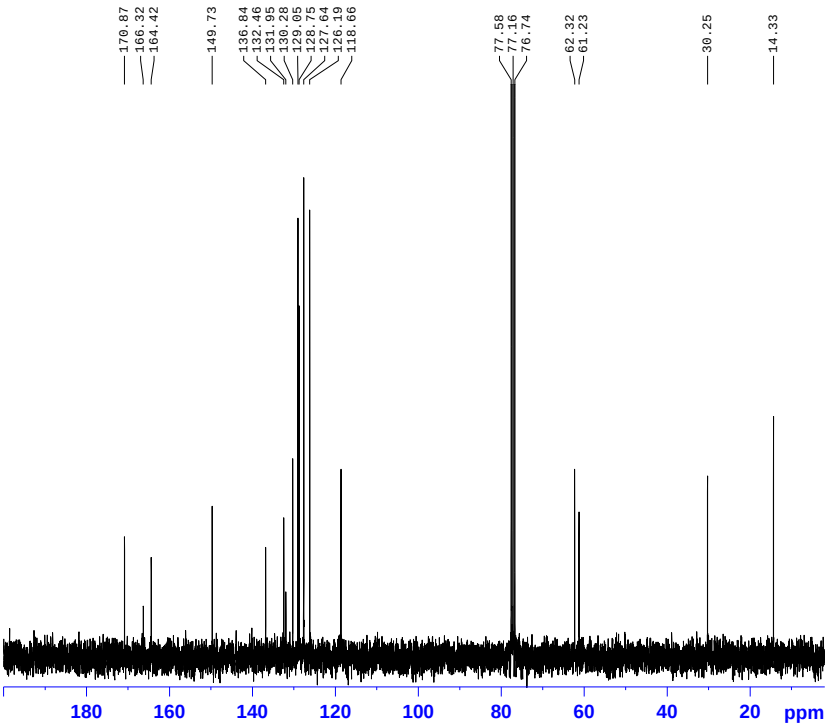


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PROCNO                 1
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PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   101
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 574.7
DW                27.800 usec
DE                 6.50 usec
TE                296.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
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P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
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NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2        300.1312005 MHz
SI                 32768
SF          75.4677410 MHz
WDW                   EM
SSB                    0
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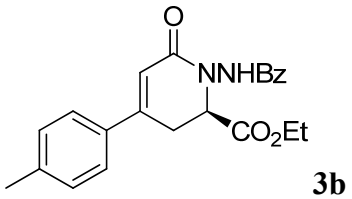
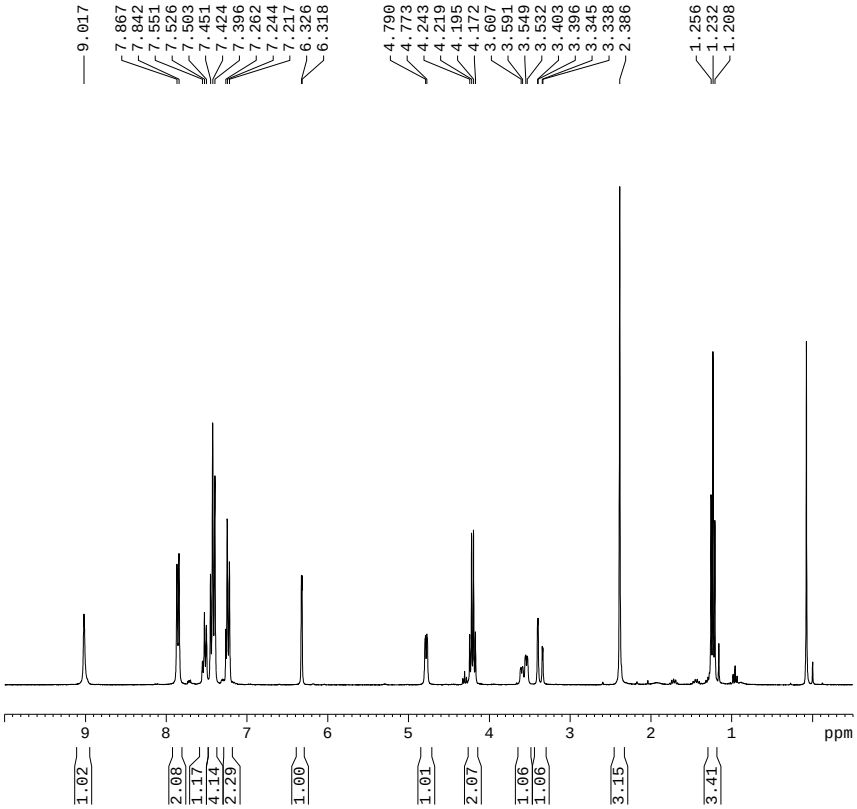


3b

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PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     6
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                   181
DW                55.600 usec
DE                 6.50 usec
TE                297.8 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1         300.1318534 MHz
SI                 32768
SF           300.1300062 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
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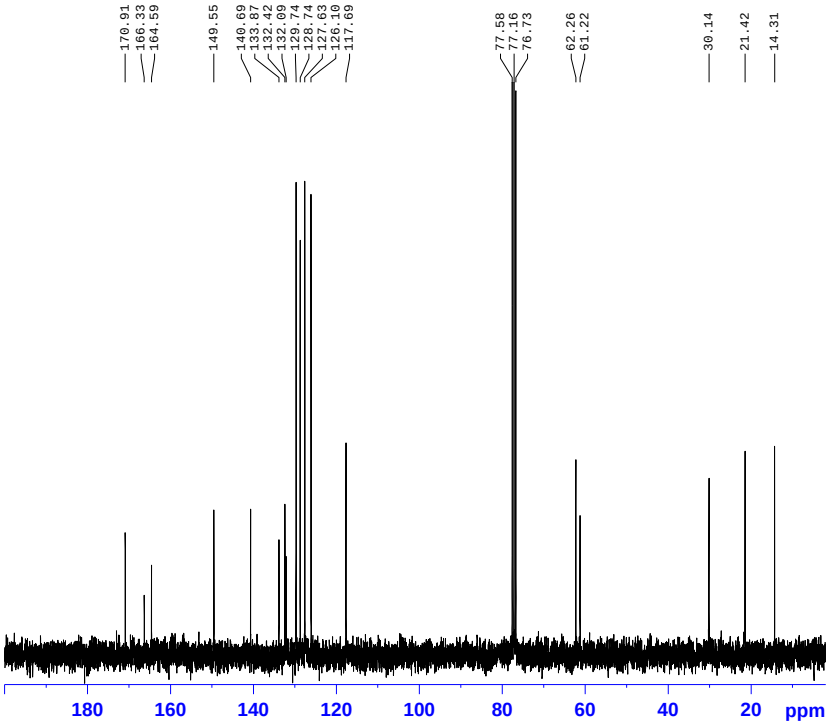


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TD                 65536
SOLVENT            CDCl3
NS                    80
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 574.7
DW                27.800 usec
DE                 6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2         300.1312005 MHz
SI                 32768
SF           75.4677419 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
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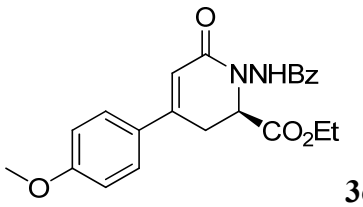

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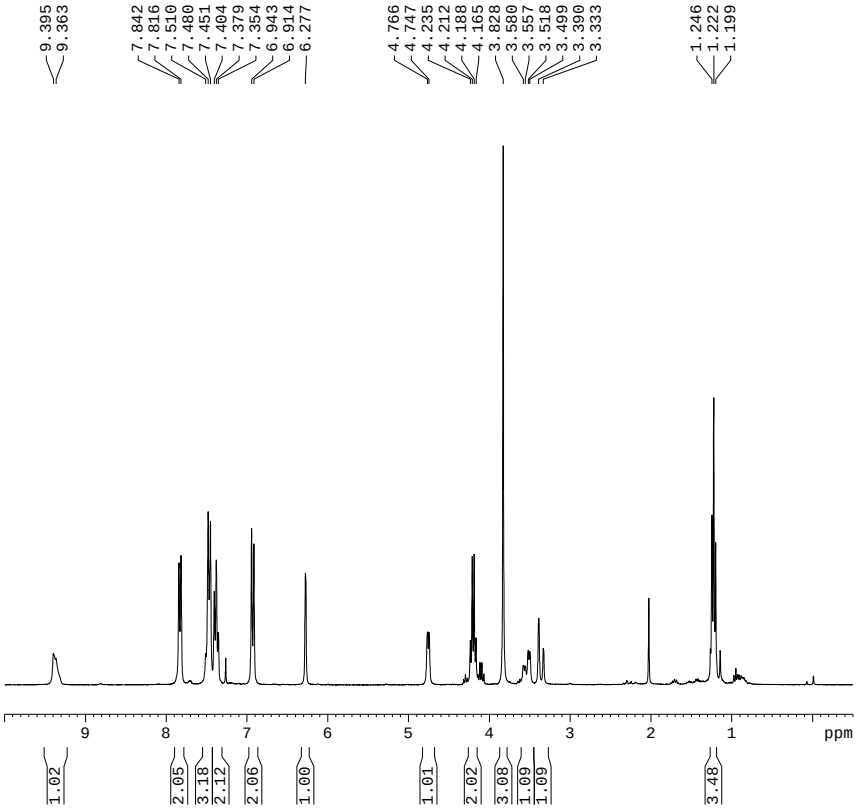


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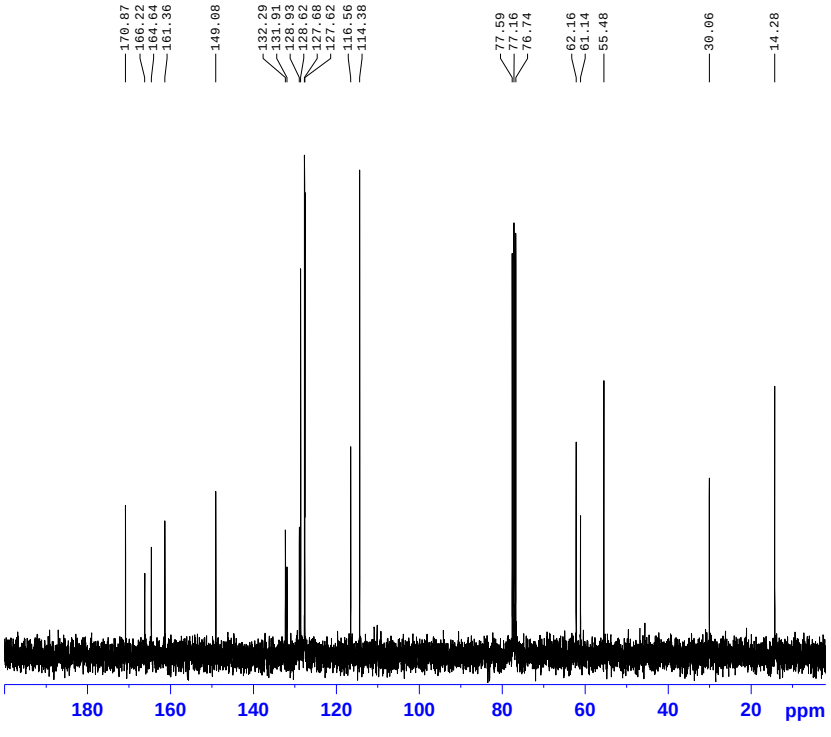
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     5
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                  90.5
DW                55.600 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1         300.1318534 MHz
SI                 32768
SF           300.1300062 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

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PROCNO                 1
Date_           20140101
Time               19.49
INSTRUM            spect
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PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    50
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                   362
DW                27.800 usec
DE                 6.50 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2         300.1312005 MHz
SI                 32768
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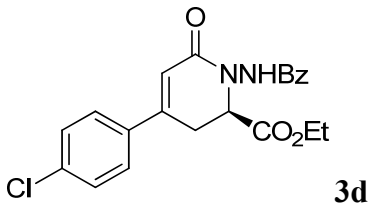

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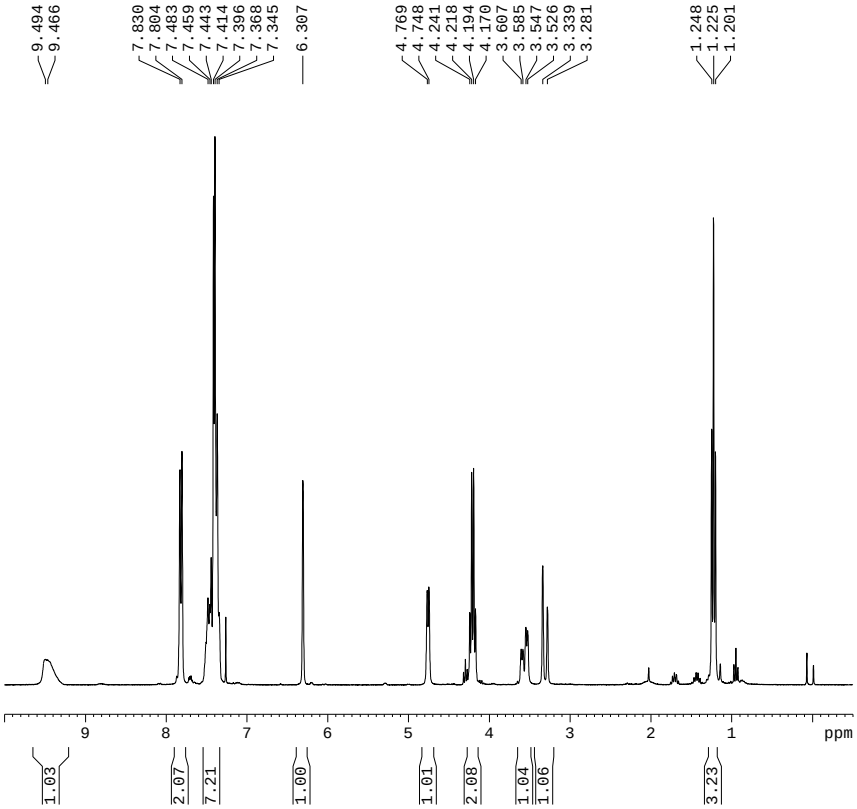


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PROCNO                 1
Date_           20140101
Time               20.10
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PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     5
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                   128
DW                55.600 usec
DE                 6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.30 usec
PL1                 3.00 dB
SFO1         300.1318534 MHz
SI                 32768
SF           300.1300062 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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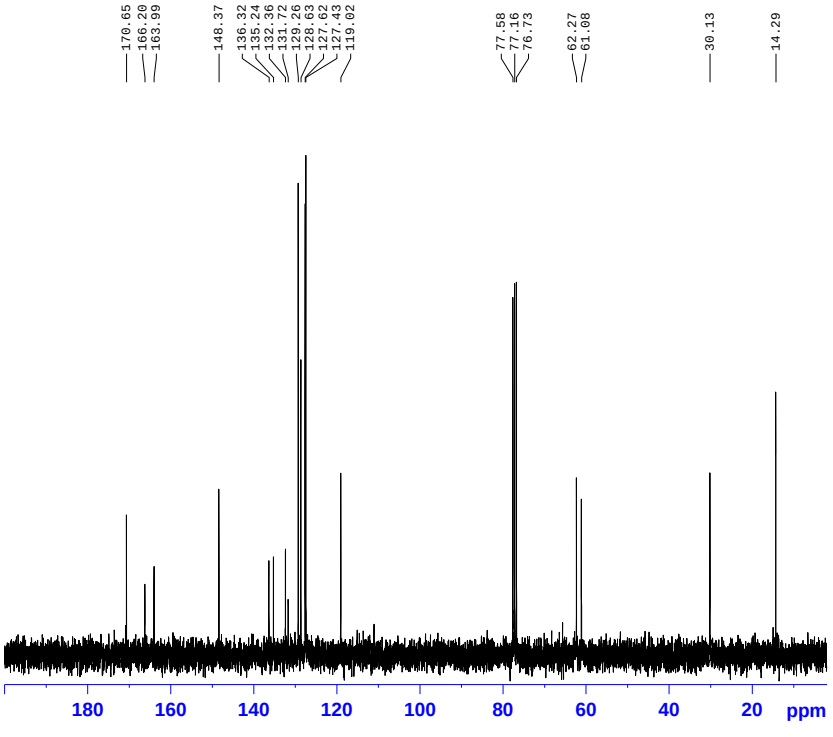


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PROCNO                 1
Date_           20140101
Time               20.11
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TD                 65536
SOLVENT            CDCl3
NS                    37
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                 812.7
DW                27.800 usec
DE                 6.50 usec
TE                298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 3.00 dB
PL12               22.74 dB
PL13               23.00 dB
SFO2         300.1312005 MHz
SI                 32768
SF           75.4677436 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
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PC                  1.40
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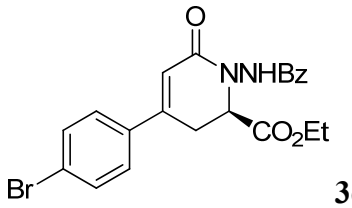

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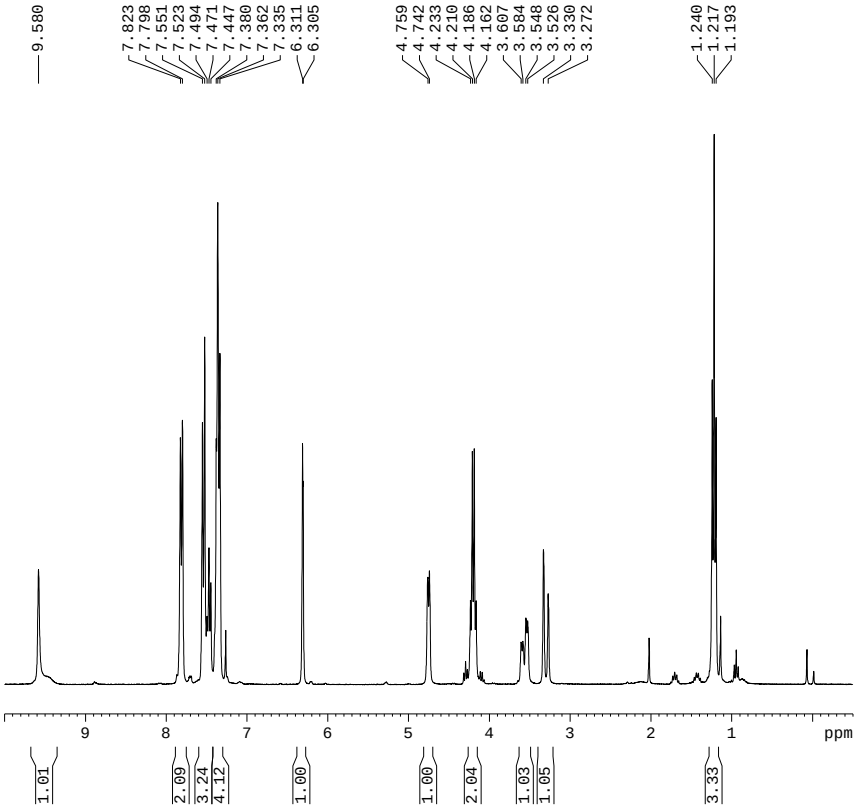


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PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    5
DS                    0
SWH            8992.806 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                 90.5
DW                55.600 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.30 usec
PL1                3.00 dB
SFO1         300.1318534 MHz
SI                32768
SF           300.1300062 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
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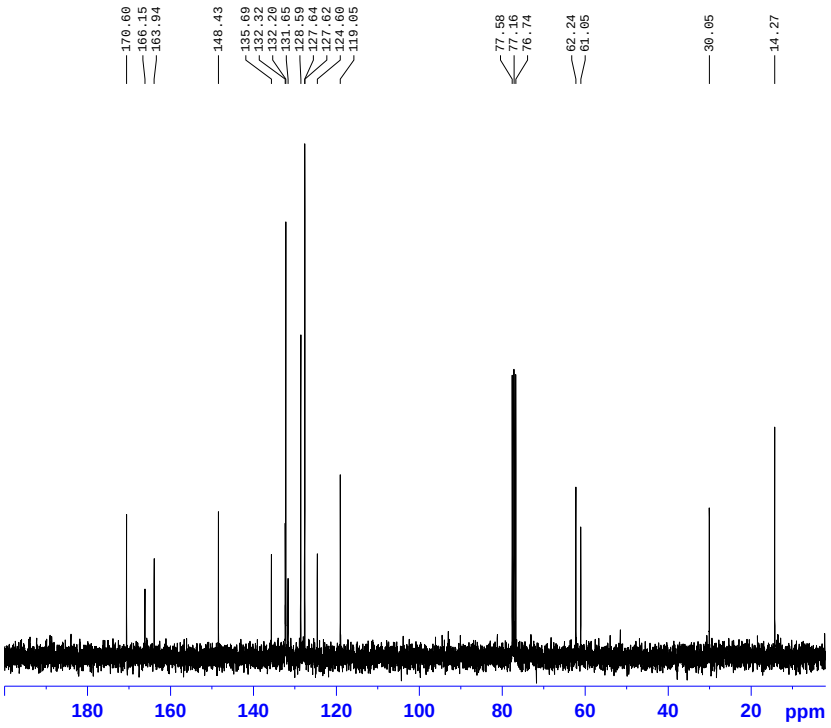


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TD                65536
SOLVENT           CDCl3
NS                   33
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                645.1
DW               27.800 usec
DE                 6.50 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1               12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2           100.00 usec
PL2                3.00 dB
PL12               22.74 dB
PL13               23.00 dB
SFO2         300.1312005 MHz
SI                32768
SF           75.4677447 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
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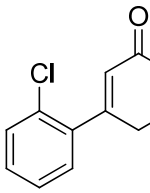

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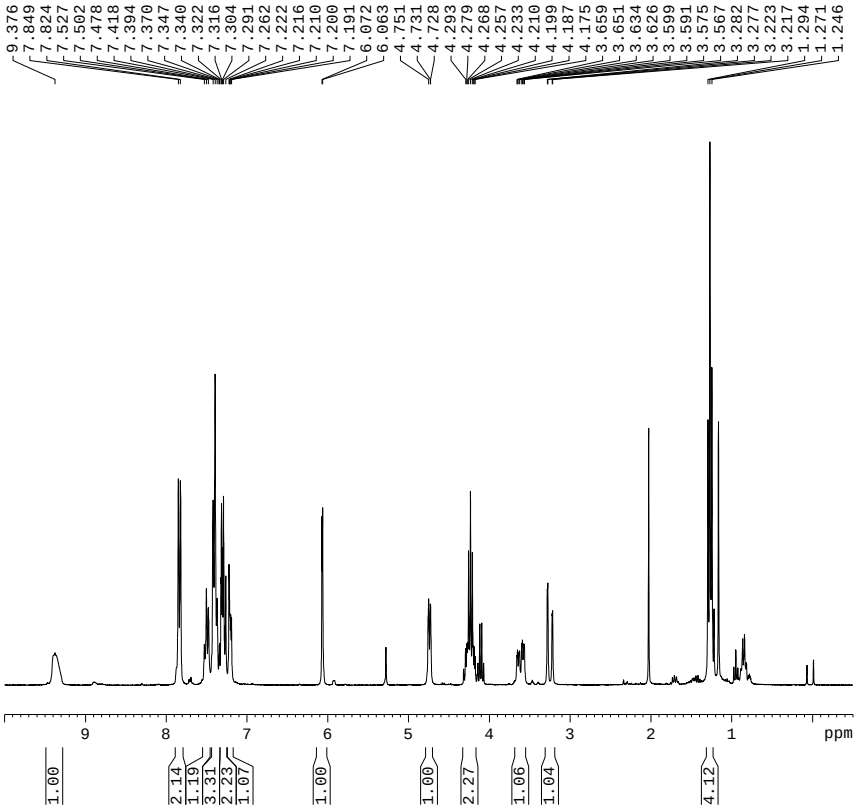


```
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TD                 32768
SOLVENT            CDCl3
NS                     4
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                   128
DW                55.600 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1         300.1318534 MHz
SI                 32768
SF           300.1300062 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
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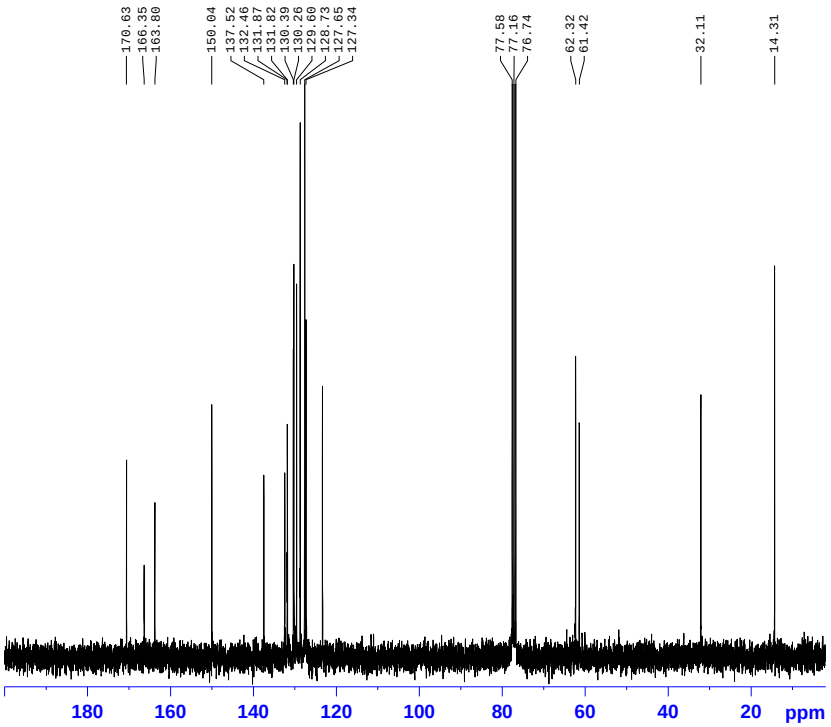


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NS                   281
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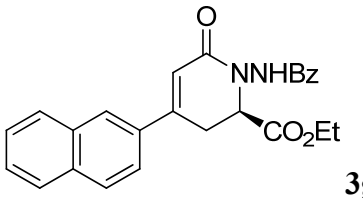
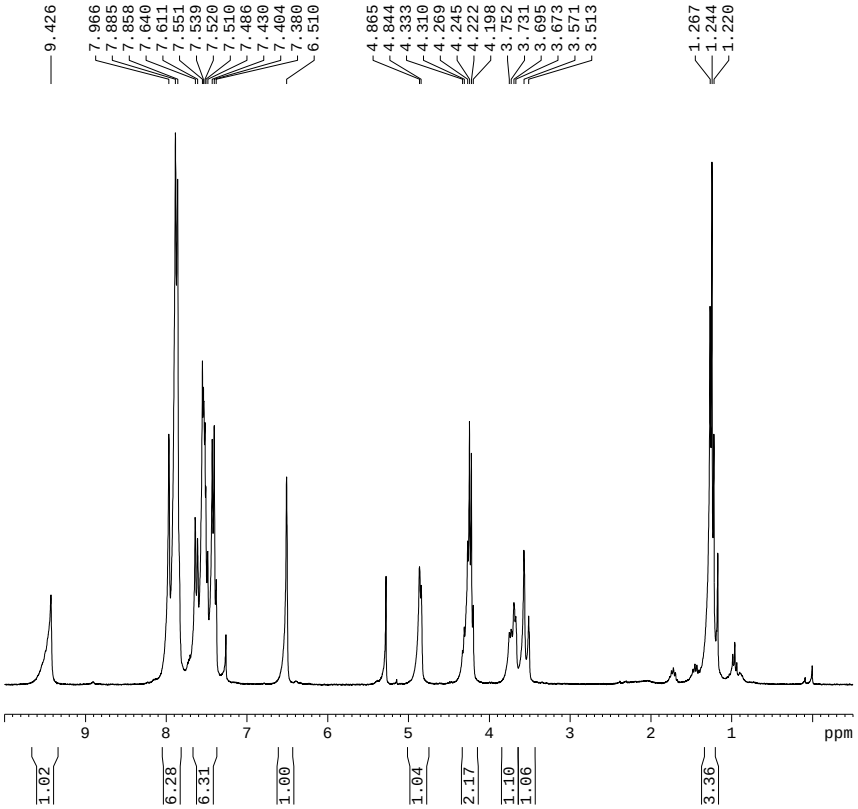
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                  2048
DW                27.800 usec
DE                 6.50 usec
TE                296.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2         300.1312005 MHz
SI                 32768
SF           75.4677413 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

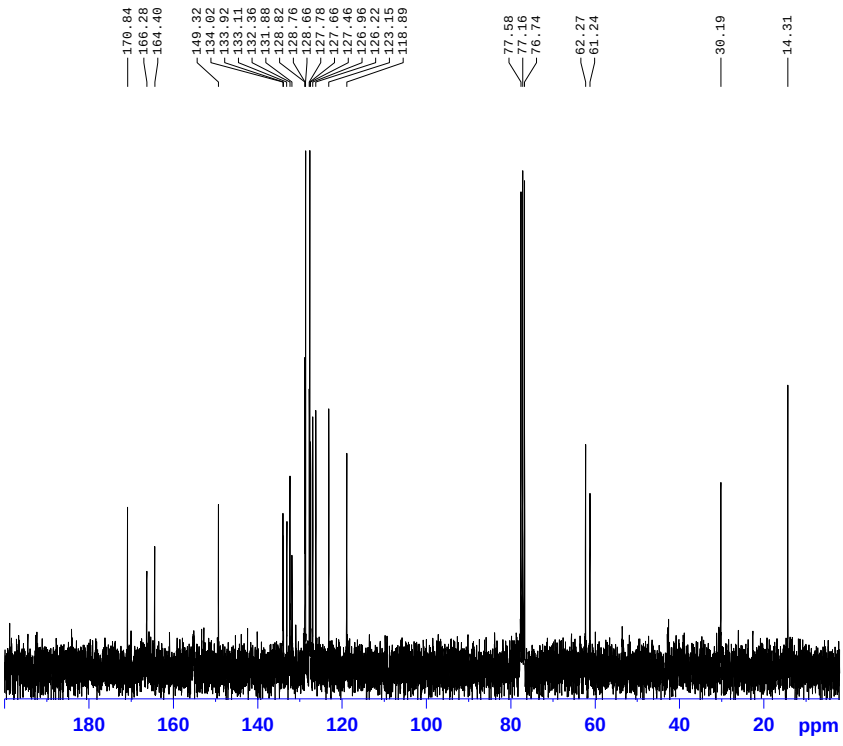


3g




```
NAME      jwq-625c-059g1
EXPNO                 10
PROCNO                 1
Date_           20140101
Time               20.17
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     4
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                   128
DW                55.600 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

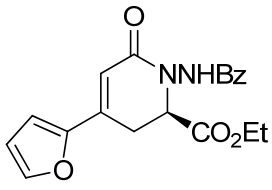
======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1         300.1318534 MHz
SI                 32768
SF           300.1300062 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



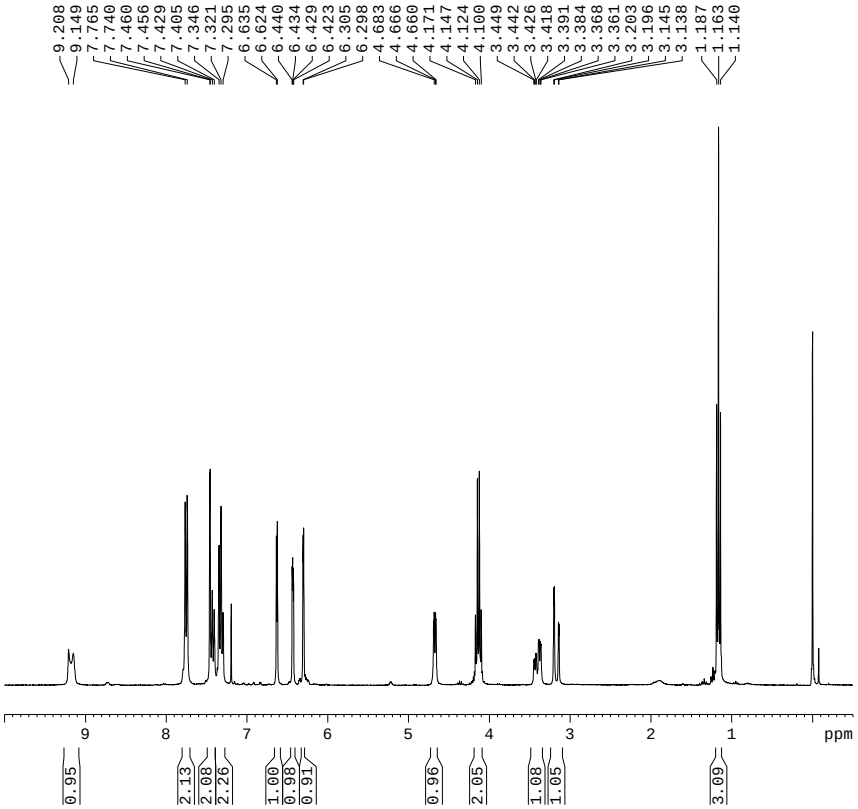

```
NAME      jwq-625c-059g1
EXPNO                 11
PROCNO                 1
Date_           20140101
Time               20.20
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    57
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                   512
DW                27.800 usec
DE                 6.50 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12               22.74 dB
PL13               23.00 dB
SFO2         300.1312005 MHz
SI                 32768
SF           75.4677443 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

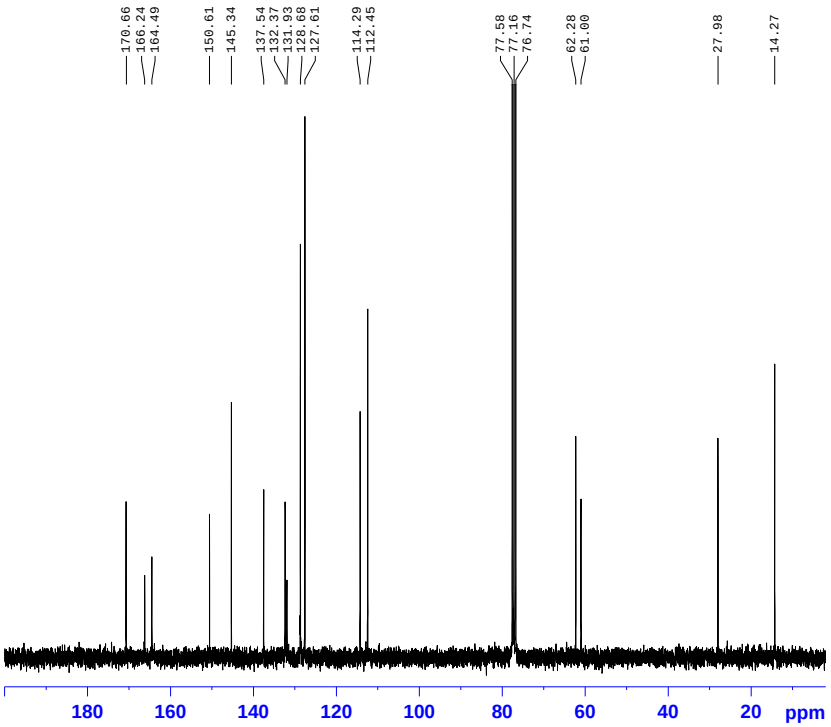


3h




```
NAME      jwq-626c-060c1
EXPNO                 10
PROCNO                 1
Date_           20140122
Time               18.38
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     7
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 161.3
DW                55.600 usec
DE                 6.50 usec
TE                296.1 K
D1           1.00000000 sec
TD0                    1

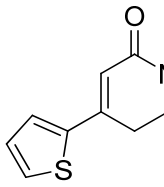
======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1         300.1318534 MHz
SI                 32768
SF           300.1300262 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



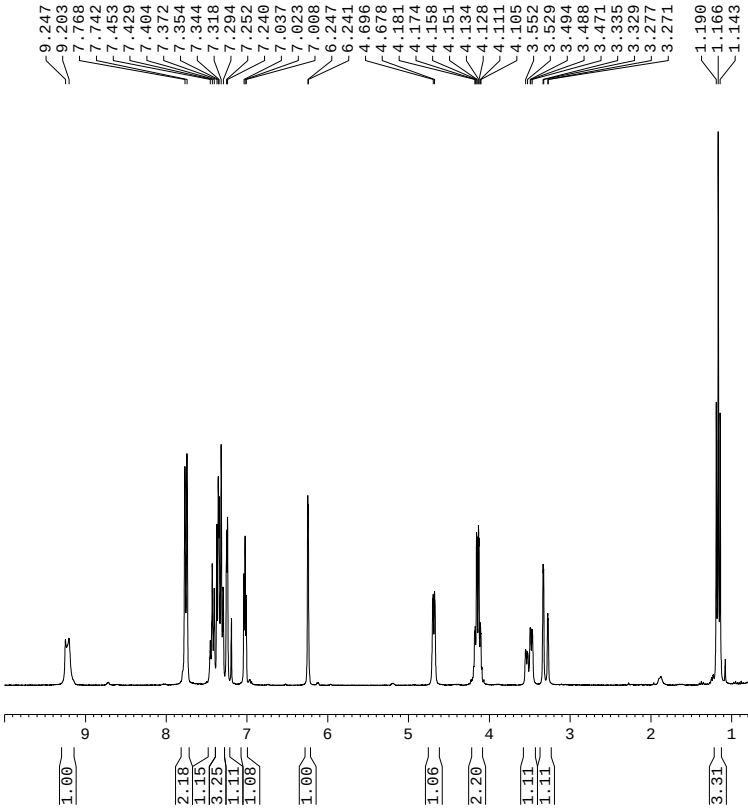

```
NAME      jwq-626c-060c1
EXPNO                 11
PROCNO                 1
Date_           20140122
Time               18.44
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   202
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 645.1
DW                27.800 usec
DE                 6.50 usec
TE                296.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2         300.1312005 MHz
SI                 32768
SF           75.4677417 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

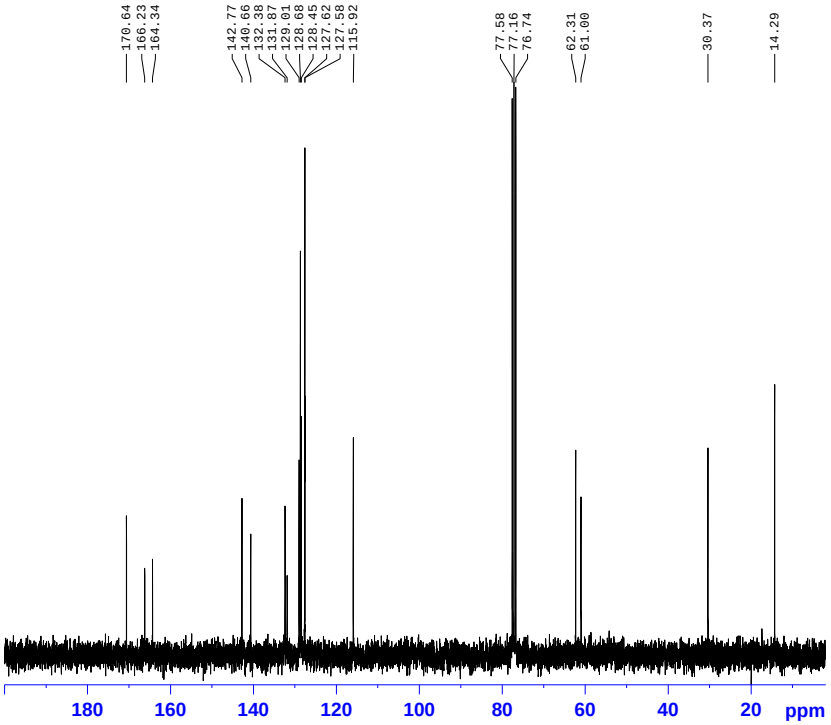


3i




```
NAME      jwq-632c-067c1
EXPNO                 20
PROCNO                 1
Date_           20140122
Time               18.16
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                   181
DW                55.600 usec
DE                 6.50 usec
TE                295.9 K
D1           1.00000000 sec
TD0                    1

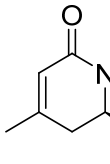
======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1         300.1318534 MHz
SI                 32768
SF           300.1300271 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



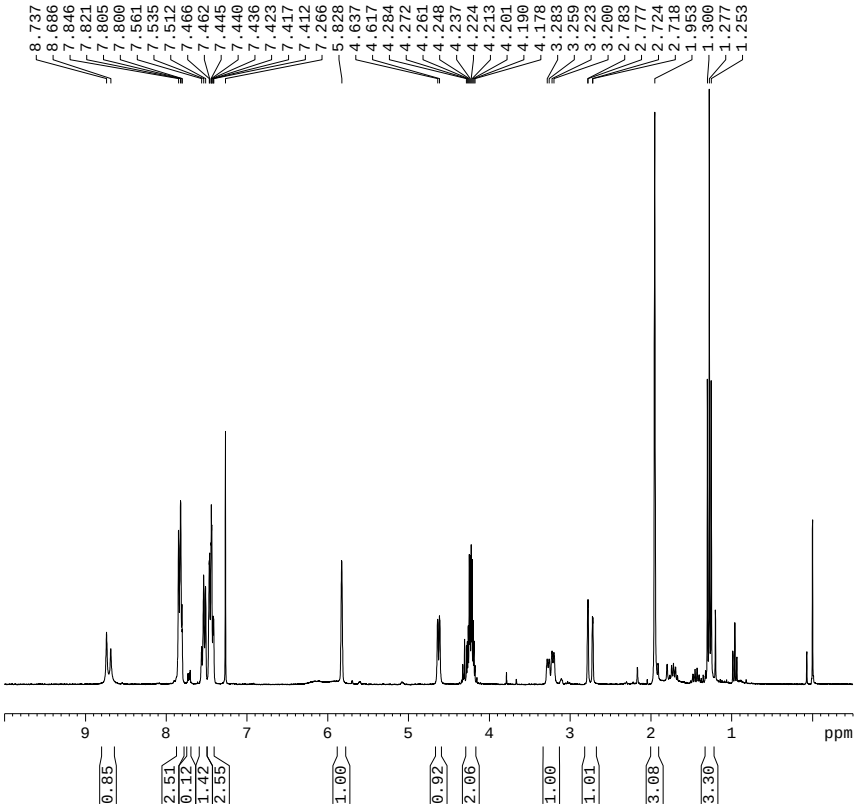

```
NAME      jwq-632c-067c1
EXPNO                 21
PROCNO                 1
Date_           20140122
Time               18.18
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    77
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                 574.7
DW                27.800 usec
DE                 6.50 usec
TE                296.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2         300.1312005 MHz
SI                 32768
SF           75.4677426 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

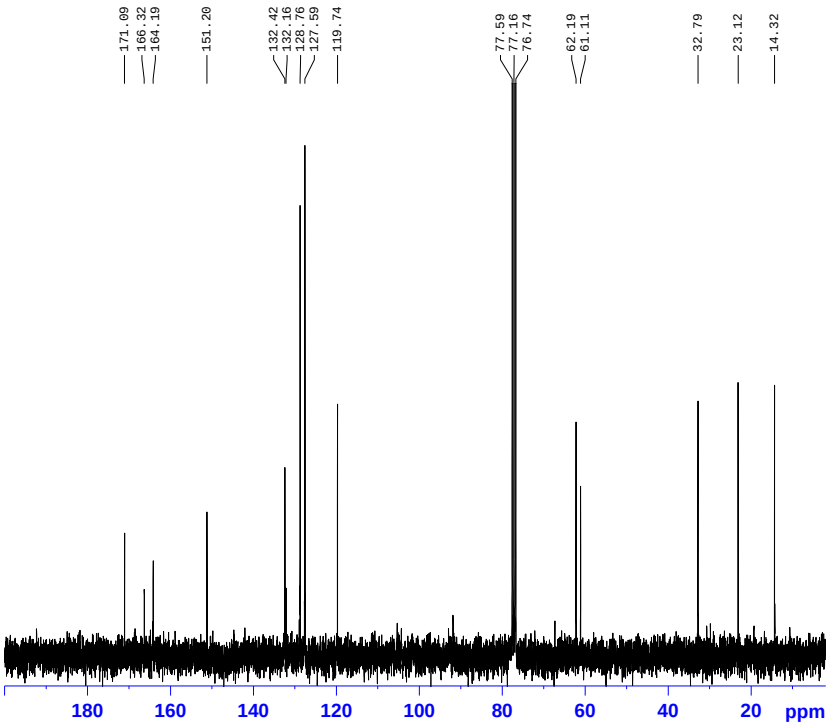


3j




```
NAME      jwq-633b-068g1
EXPNO                 10
PROCNO                 1
Date_           20140116
Time                20.59
INSTRUM             spect
PROBHD   5 mm DUL 13C-1
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8992.806 Hz
FIDRES           0.274439 Hz
AQ               1.8219508 sec
RG                  456.1
DW                 55.600 usec
DE                  6.50 usec
TE                 296.2 K
D1            1.00000000 sec
TD0                     1

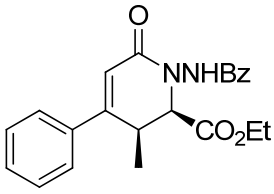
======== CHANNEL f1 ========
NUC1                   1H
P1                 10.30 usec
PL1                 3.00 dB
SFO1         300.1318534 MHz
SI                  32768
SF           300.1300049 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



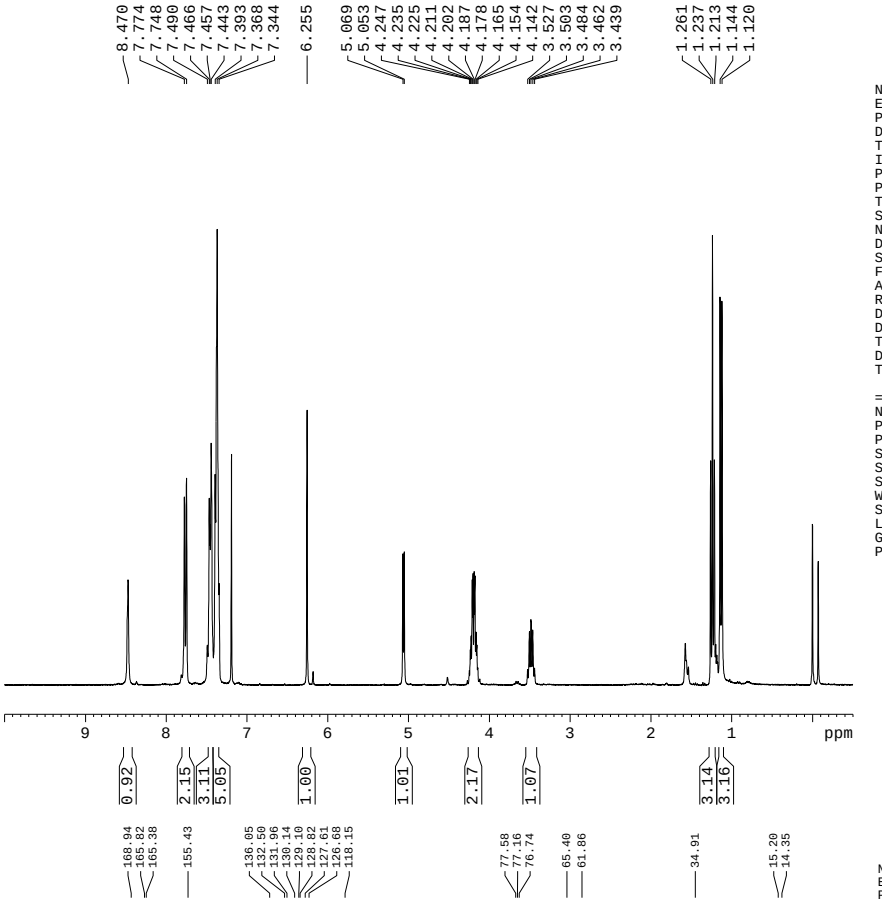

```
NAME      jwq-633c-068g1
EXPNO                 11
PROCNO                 1
Date_           20140119
Time                13.10
INSTRUM             spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    150
DS                      4
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ               1.8219508 sec
RG                  1290.2
DW                 27.800 usec
DE                  6.50 usec
TE                 296.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 3.00 dB
PL12               22.74 dB
PL13               23.00 dB
SFO2         300.1312005 MHz
SI                  32768
SF           75.4677404 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

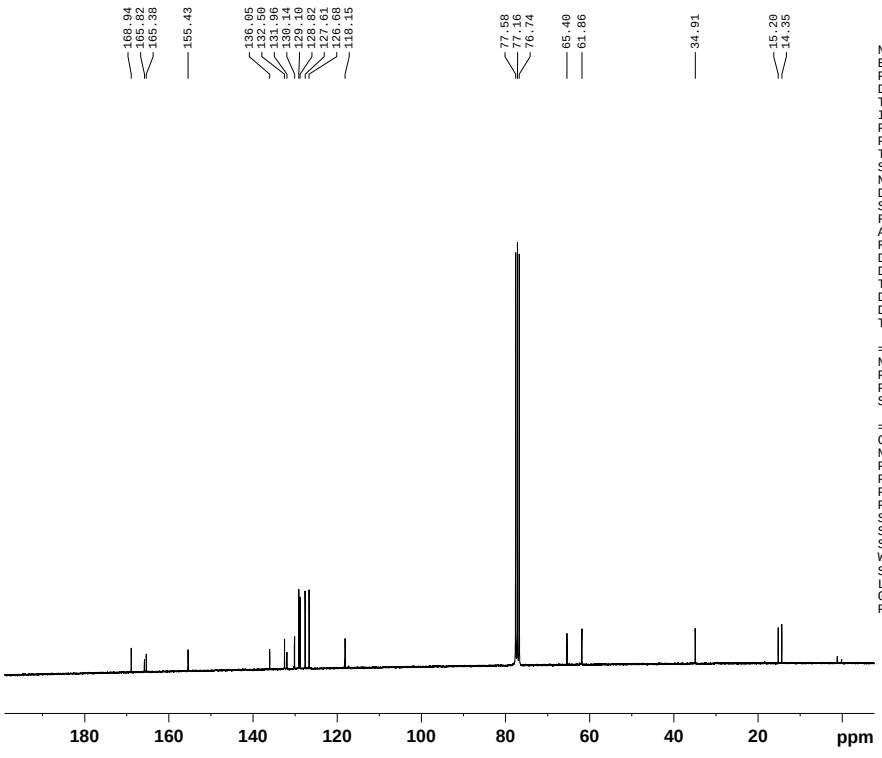


3k




```
NAME      jwq-637a-074c1
EXPNO                 10
PROCNO                 1
Date_           20140125
Time               21.49
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                 456.1
DW                55.600 usec
DE                 6.50 usec
TE                295.8 K
D1           1.00000000 sec
TD0                    1

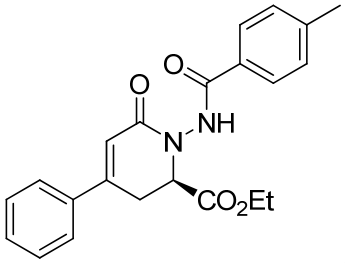
======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1         300.1318534 MHz
SI                 32768
SF           300.1300275 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```



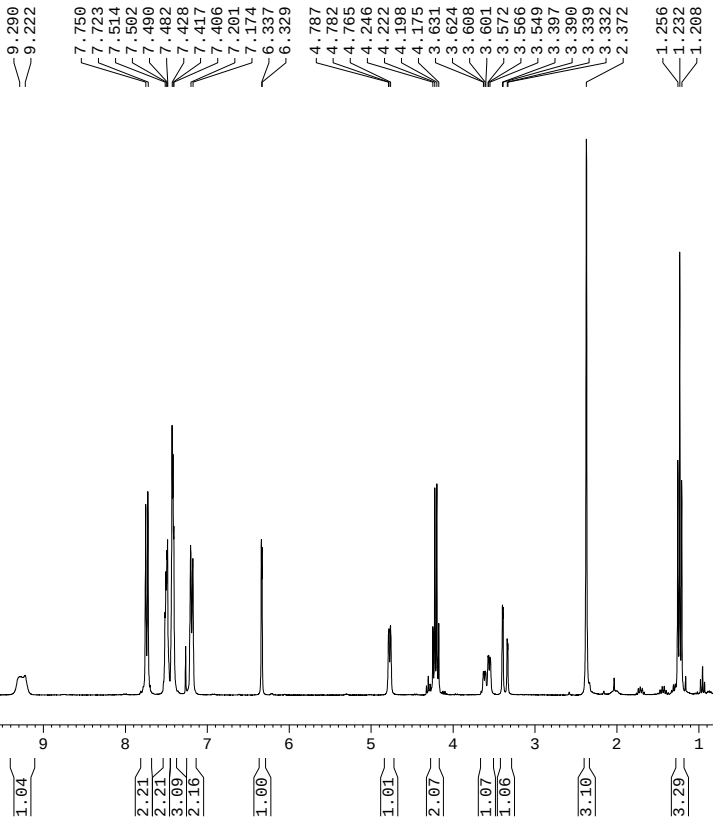

```
NAME      jwq-637a-074c1
EXPNO                 11
PROCNO                 1
Date_           20140125
Time               21.53
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                 10240
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                   512
DW                27.800 usec
DE                 6.50 usec
TE                296.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2         300.1312005 MHz
SI                 32768
SF           75.4677391 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```

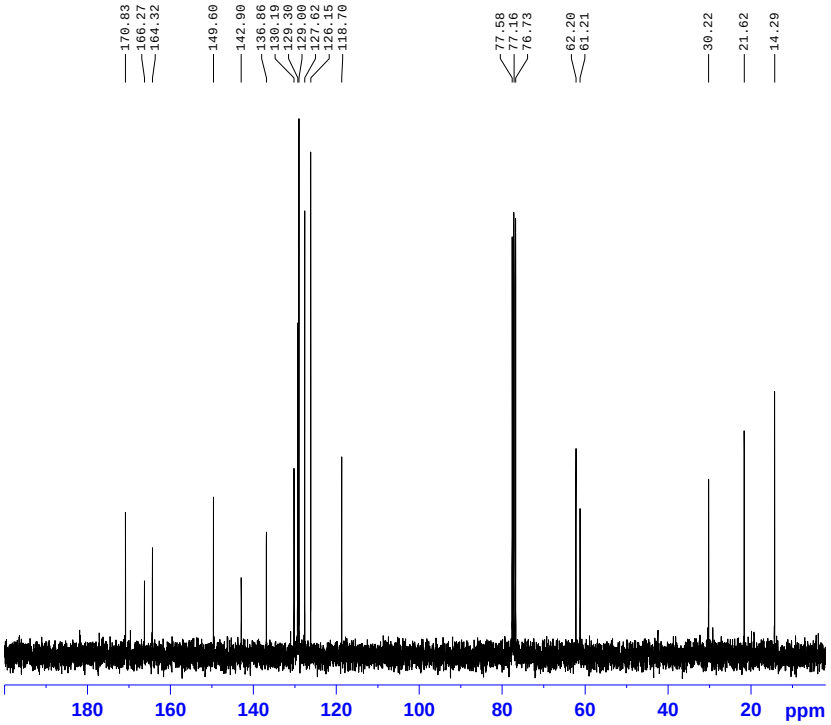


3l




```
NAME      jwq-630a-064g1
EXPNO                 10
PROCNO                 1
Date_           20140107
Time               18.39
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     6
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                  71.8
DW                55.600 usec
DE                 6.50 usec
TE                296.2 K
D1           1.00000000 sec
TD0                    1

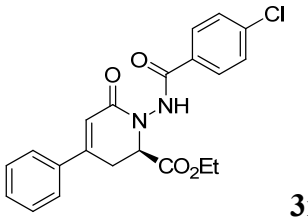
======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1         300.1318534 MHz
SI                 32768
SF           300.1300062 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



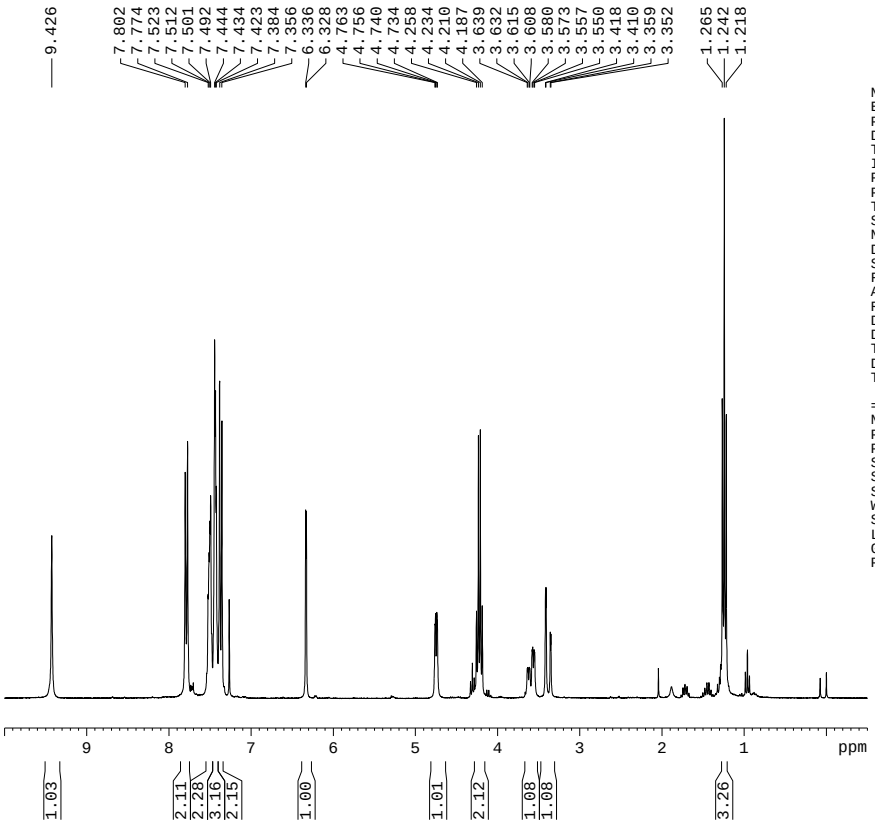

```
NAME      jwq-630a-064g1
EXPNO                 11
PROCNO                 1
Date_           20140107
Time               18.41
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    51
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                1625.5
DW                27.800 usec
DE                 6.50 usec
TE                296.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2         300.1312005 MHz
SI                 32768
SF           75.4677437 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                  1.40
```

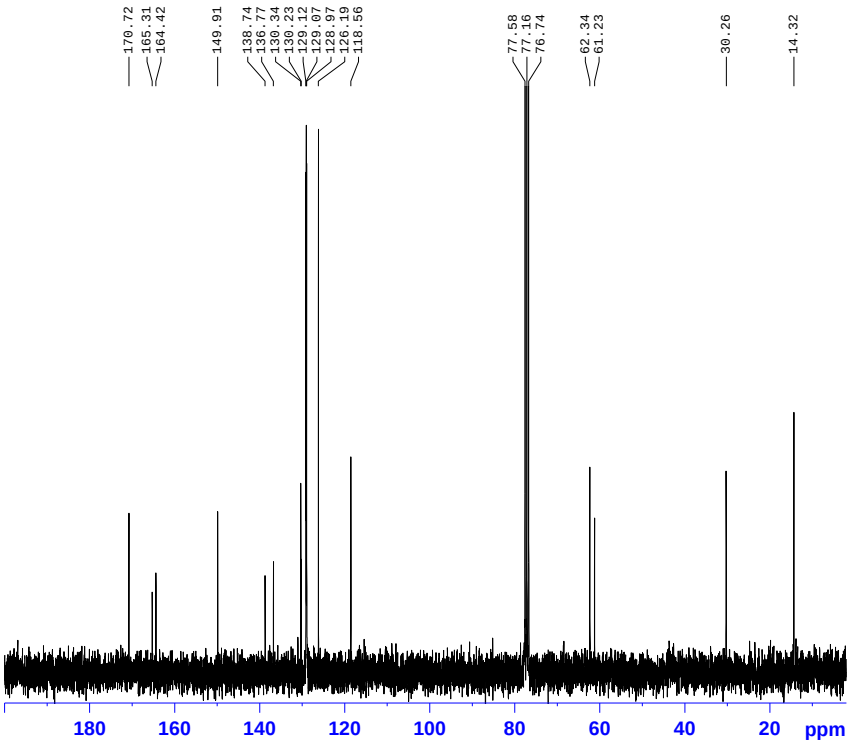


3m




```
NAME      jwq-630d-064g1
EXPNO                 10
PROCNO                 1
Date_           20140107
Time               18.28
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     6
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                   181
DW                55.600 usec
DE                 6.50 usec
TE                296.0 K
D1           1.00000000 sec
TD0                    1

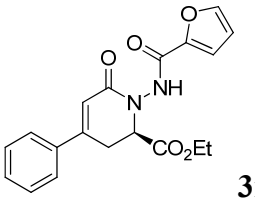
======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1         300.1318534 MHz
SI                 32768
SF           300.1300050 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



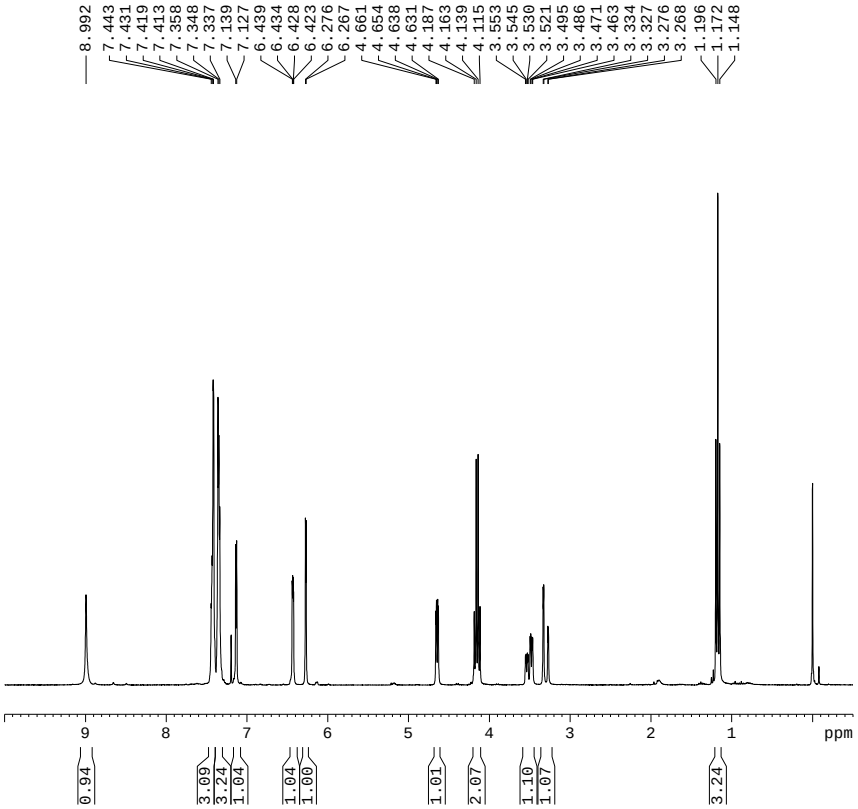

```
NAME      jwq-630d-064g1
EXPNO                 11
PROCNO                 1
Date_           20140107
Time               18.30
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    82
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                2580.3
DW                27.800 usec
DE                 6.50 usec
TE                296.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2         300.1312005 MHz
SI                 32768
SF           75.4677412 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

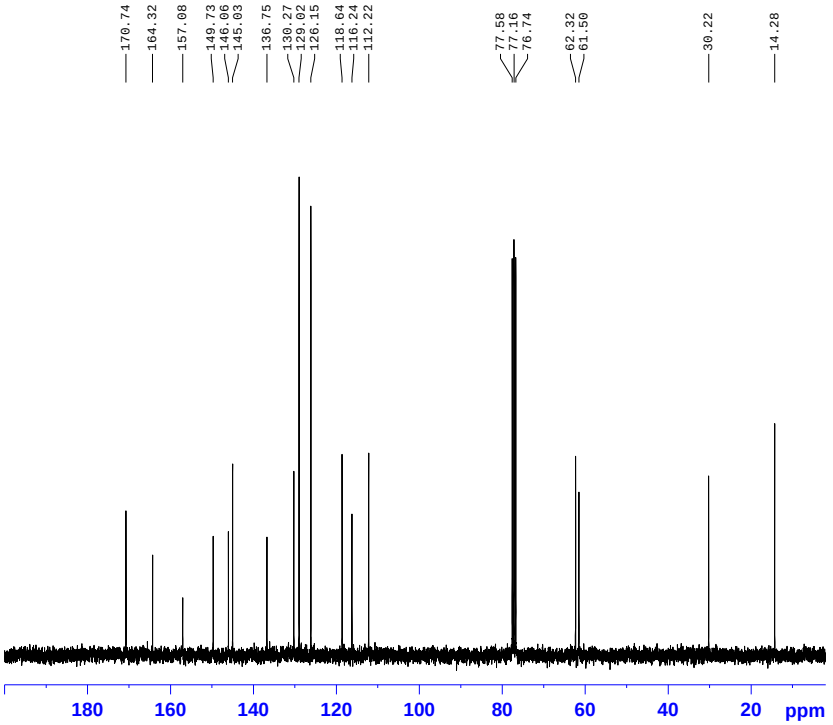


3n




```
NAME      jwq-632a-067c1
EXPNO                 10
PROCNO                 1
Date_           20140122
Time               18.26
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     6
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                   128
DW                55.600 usec
DE                 6.50 usec
TE                296.0 K
D1           1.00000000 sec
TD0                    1

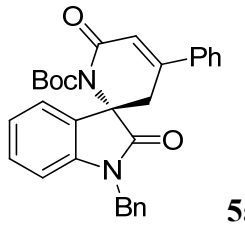
======== CHANNEL f1 ========
NUC1                  1H
P1                10.30 usec
PL1                3.00 dB
SFO1         300.1318534 MHz
SI                 32768
SF           300.1300260 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



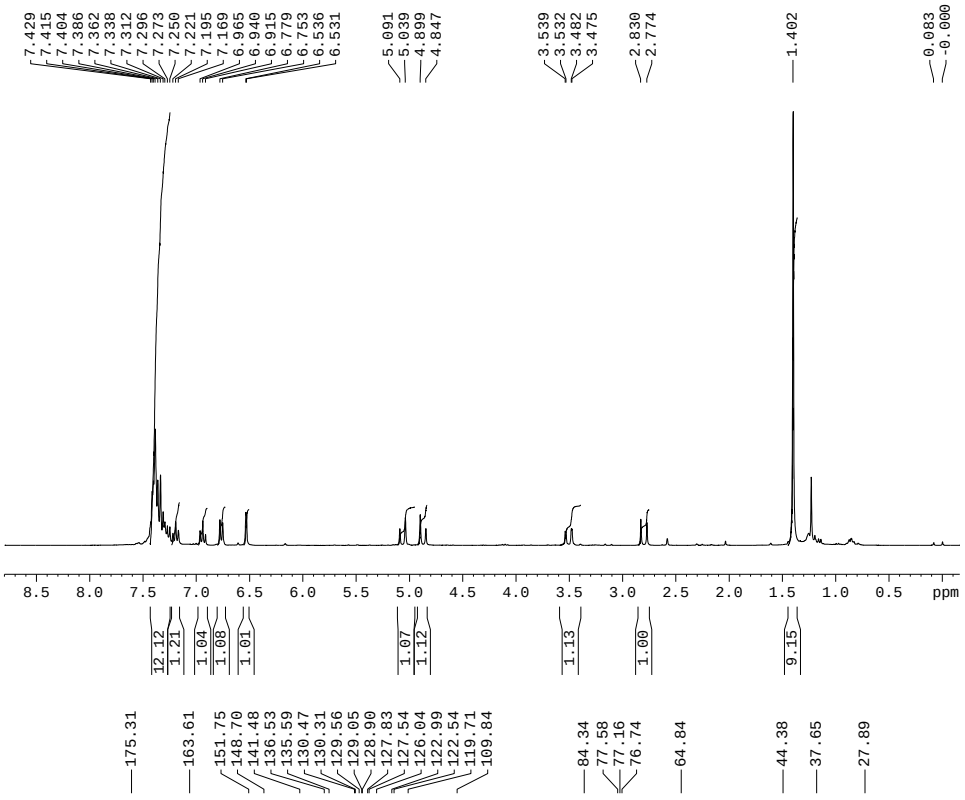

```
NAME      jwq-632a-067c1
EXPNO                 11
PROCNO                 1
Date_           20140122
Time               18.28
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   110
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                  1024
DW                27.800 usec
DE                 6.50 usec
TE                296.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.74 dB
PL13              23.00 dB
SFO2         300.1312005 MHz
SI                 32768
SF           75.4677435 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```


O
Ph
BocN
O
N
Bn

5a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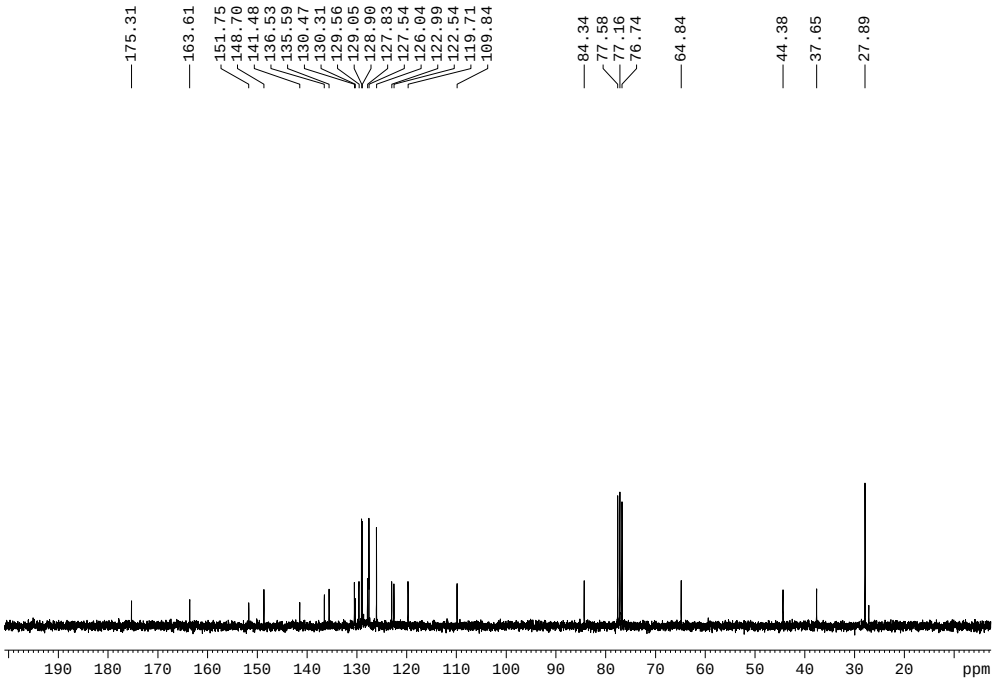
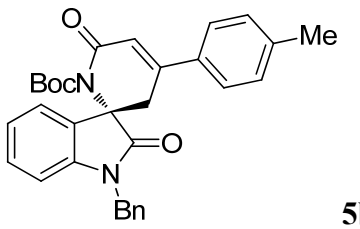
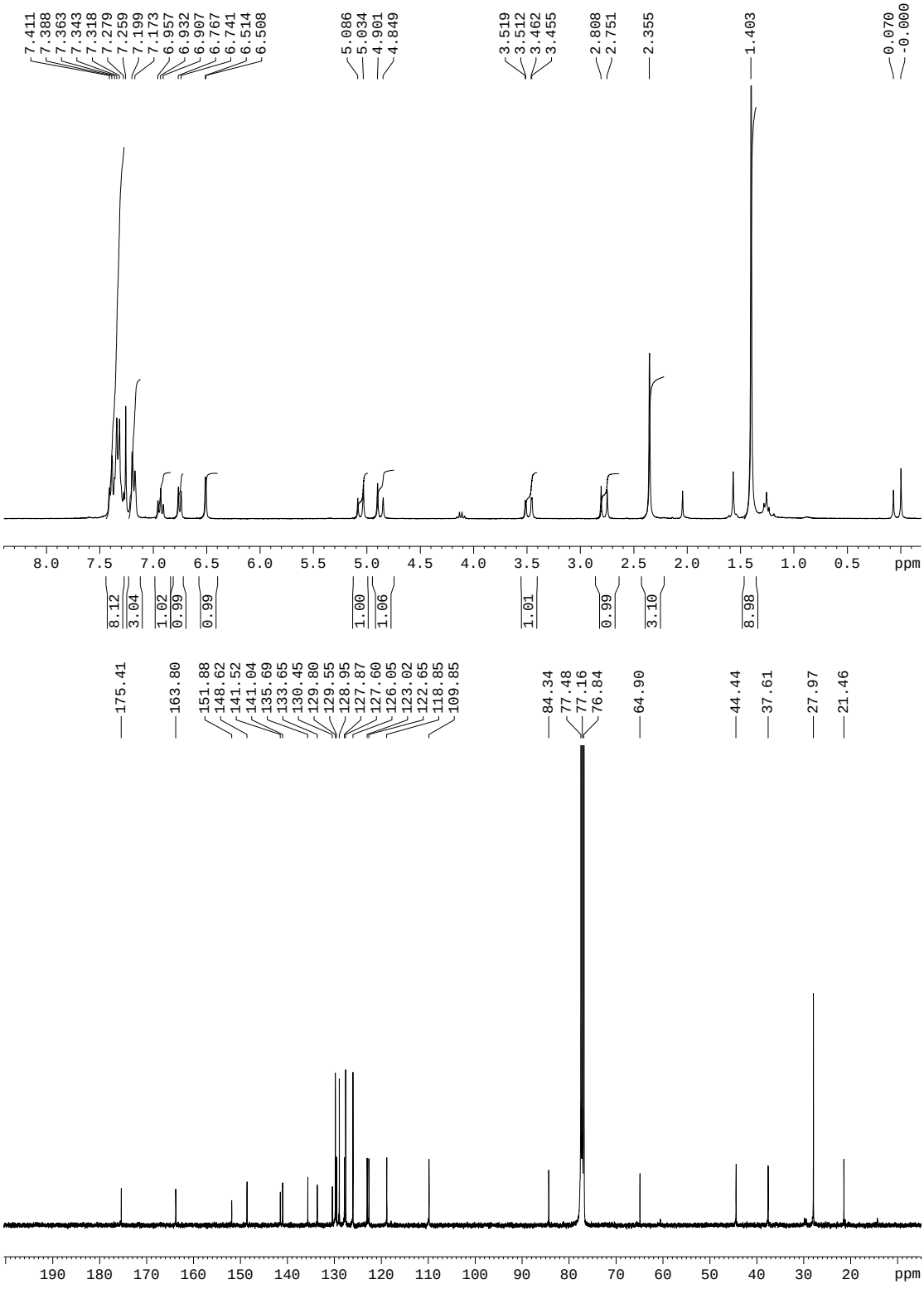
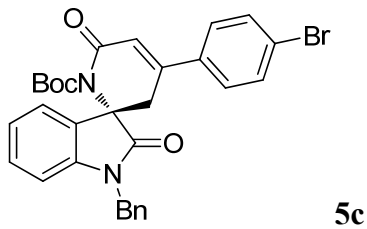
7.415
7.404
7.386
7.362
7.338
7.312
7.296
7.273
7.250
7.221
7.195
7.169
6.965
6.940
6.915
6.779
6.753
6.536
6.531
5.091
5.039
4.899
4.847
3.539
3.532
3.482
3.475
2.830
2.774
1.402
0.083
-0.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
12.12
1.21
1.04
1.08
1.01
1.07
1.12
1.13
1.00
9.15


175.31
163.61
151.75
148.70
141.48
136.53
135.59
130.47
130.31
129.56
129.05
128.90
127.83
127.54
126.04
122.99
122.54
119.71
109.84
84.34
77.58
77.16
76.74
64.84
44.38
37.65
27.89
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

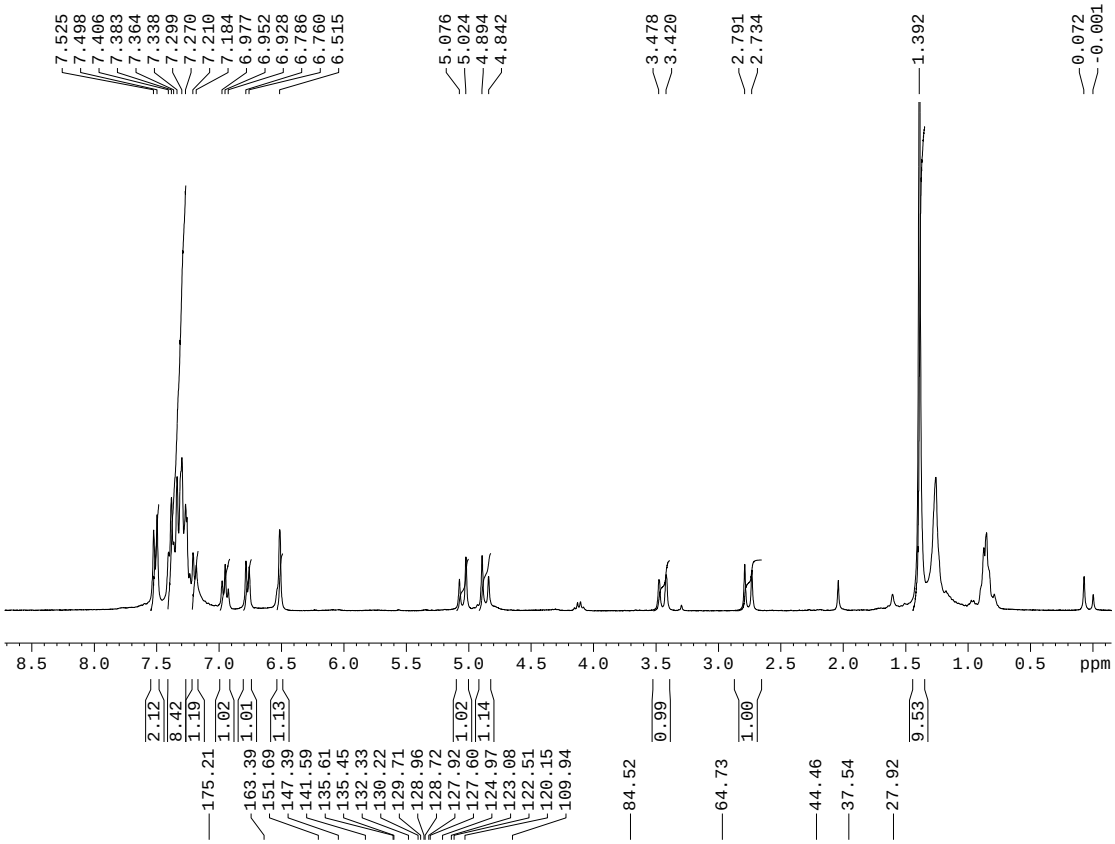

O
Me
BocN
O
N
Bn

5b


7.411
7.388
7.363
7.343
7.318
7.279
7.259
7.199
7.173
6.957
6.932
6.907
6.767
6.741
6.514
6.508
5.086
5.034
4.901
4.849
3.519
3.512
3.462
3.455
2.808
2.751
2.355
1.403
0.070
-0.000
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
ppm
8.12
3.04
1.02
0.99
0.99
1.00
1.06
1.01
0.99
3.10
8.98
175.41
163.80
151.88
148.62
141.52
141.04
135.69
133.65
130.45
129.80
129.55
128.95
127.87
127.60
126.05
123.02
122.65
118.85
109.85
84.34
77.48
77.16
76.84
64.90
44.44
37.61
27.97
21.46
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


O
Br
BocN
O
N
Bn

5c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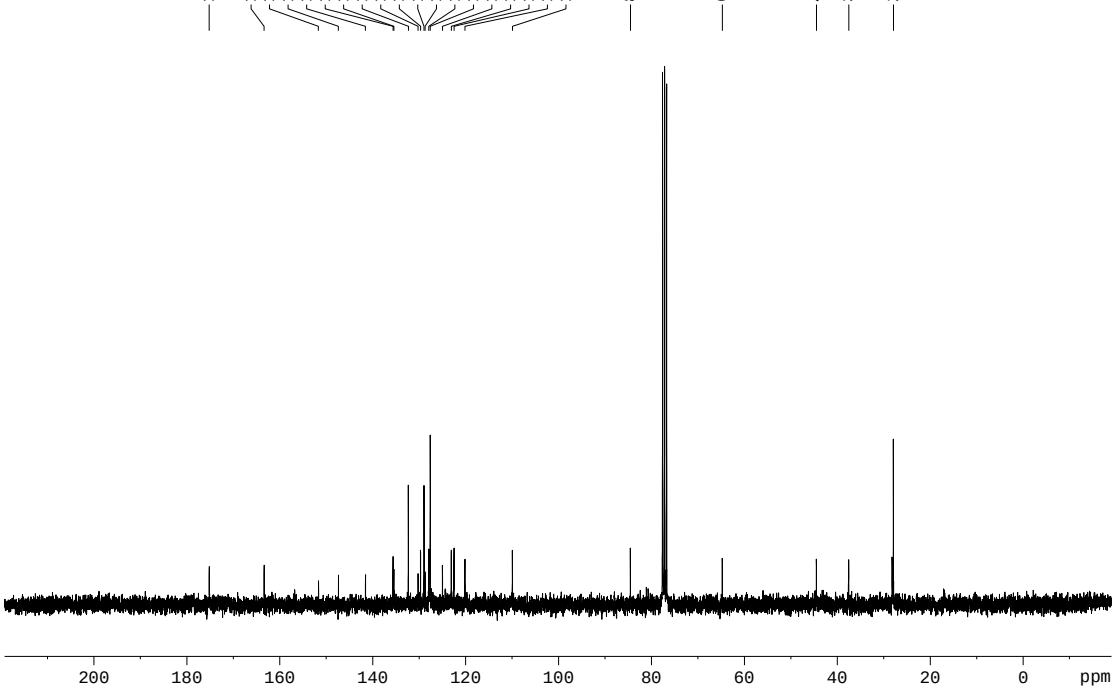
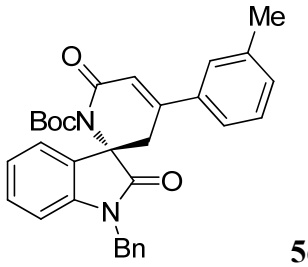
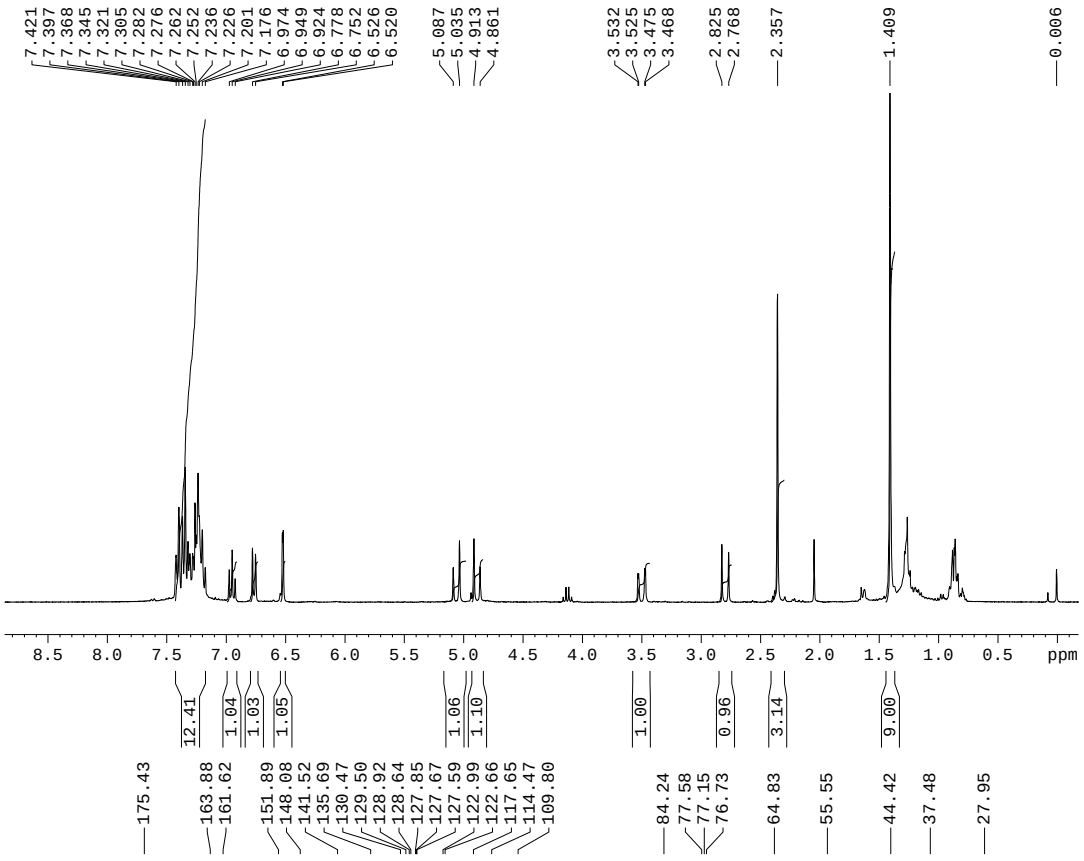
7.498
7.406
7.383
7.364
7.338
7.299
7.270
7.210
7.184
6.977
6.952
6.928
6.786
6.760
6.515
5.076
5.024
4.894
4.842
3.478
3.420
2.791
2.734
1.392
0.072
-0.001
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.12
8.42
1.19
1.02
1.01
1.13
1.02
1.14
0.99
1.00
9.53


175.21
163.39
151.69
147.39
141.59
135.61
135.45
132.33
130.22
129.71
128.96
128.72
127.92
127.60
124.97
123.08
122.51
120.15
109.94
84.52
64.73
44.46
37.54
27.92
200 180 160 140 120 100 80 60 40 20 0 ppm


Me
O
BocN
O
N
Bn

5d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7.368
7.345
7.321
7.305
7.282
7.276
7.262
7.252
7.236
7.226
7.201
7.176
6.974
6.949
6.924
6.778
6.752
6.526
6.520
5.087
5.035
4.913
4.861
3.532
3.525
3.475
3.468
2.825
2.768
2.357
1.409
0.006
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 ppm
12.41
1.04
1.03
1.05
1.06
1.10
1.00
0.96
3.14
9.00

175.43
163.88
161.62
151.89
148.08
141.52
135.69
130.47
129.50
128.92
128.64
127.85
127.67
127.59
122.99
122.66
117.65
114.47
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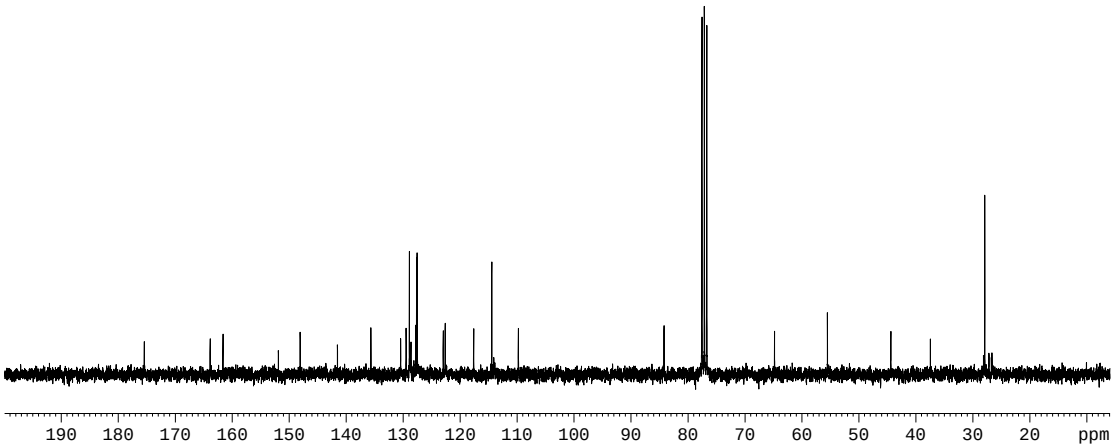
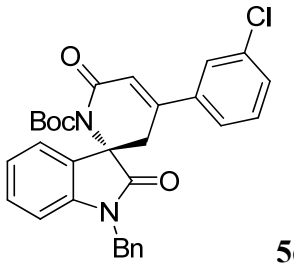
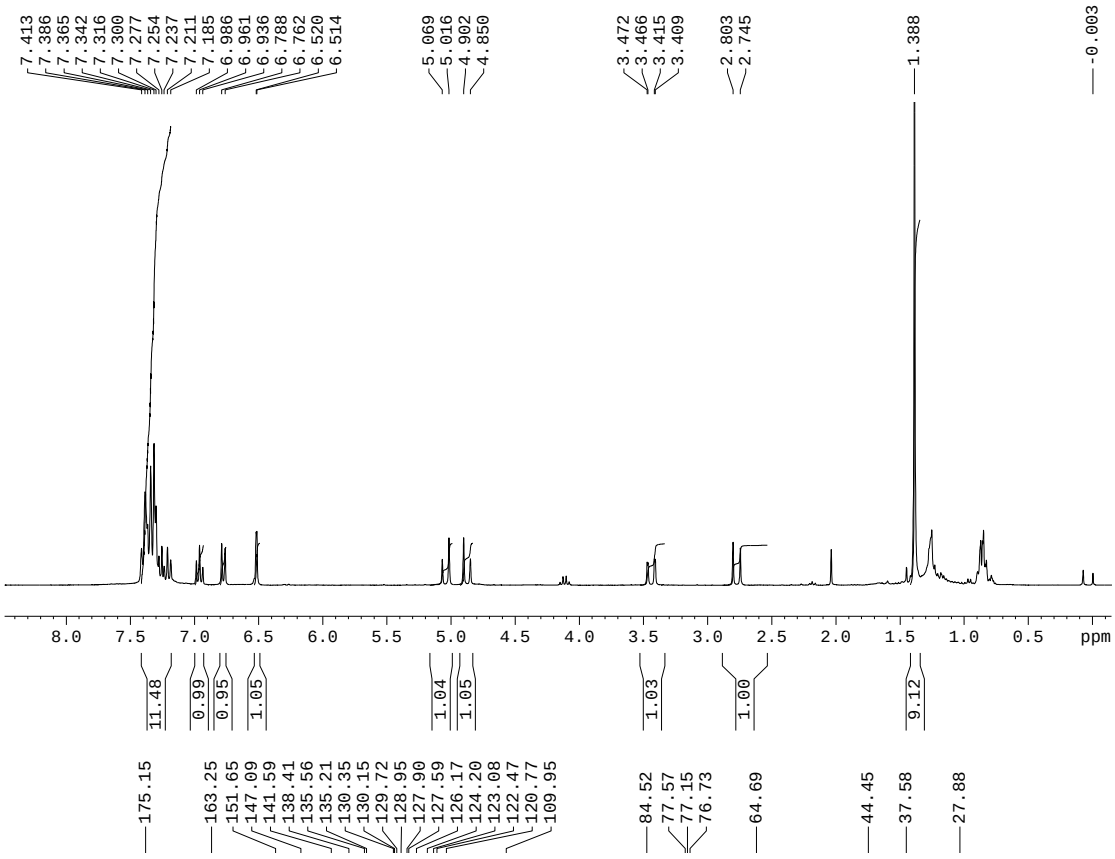
77.58
77.15
76.73
64.83
55.55
44.42
37.48
27.95


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


Cl
O
BocN
O
N
Bn

5e


7.413
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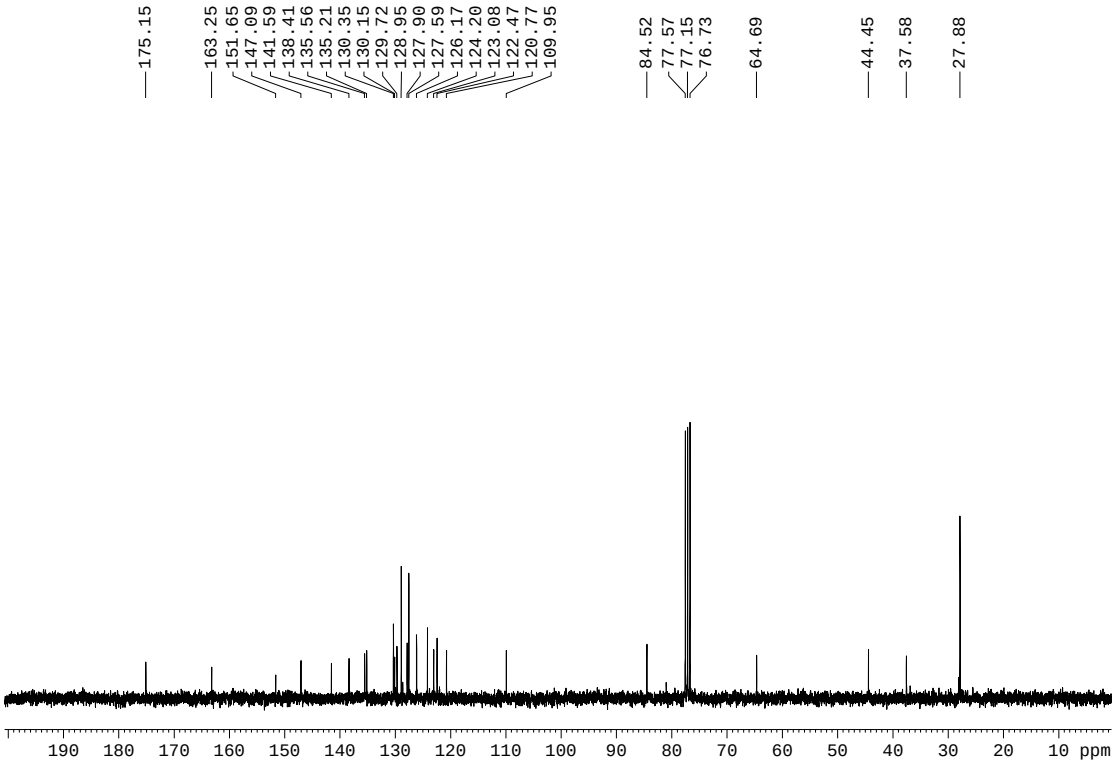
7.365
7.342
7.316
7.300
7.277
7.254
7.237
7.211
7.185
6.986
6.961
6.936
6.788
6.762
6.520
6.514
5.069
5.016
4.902
4.850
3.472
3.466
3.415
3.409
2.803
2.745
1.388
-0.003
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
11.48
0.99
0.95
1.05
1.04
1.05
1.03
1.00
9.12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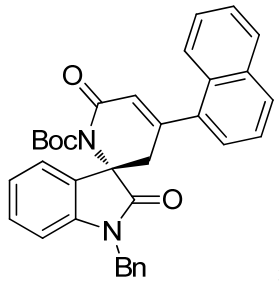
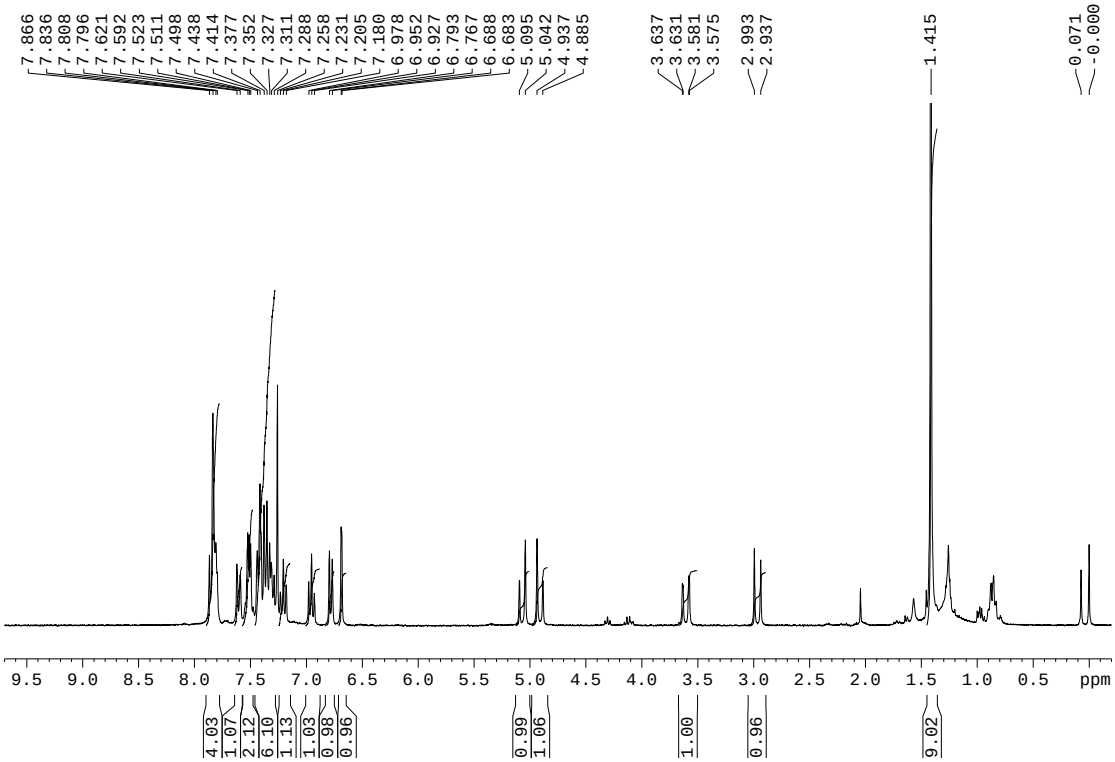
163.25
151.65
147.09
141.59
138.41
135.56
135.21
130.35
130.15
129.72
128.95
127.90
127.59
126.17
124.20
123.08
122.47
120.77
109.95
84.52
77.57
77.15
76.73
64.69
44.45
37.58
27.88
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
BocN
O
N
Bn

5f


7.866
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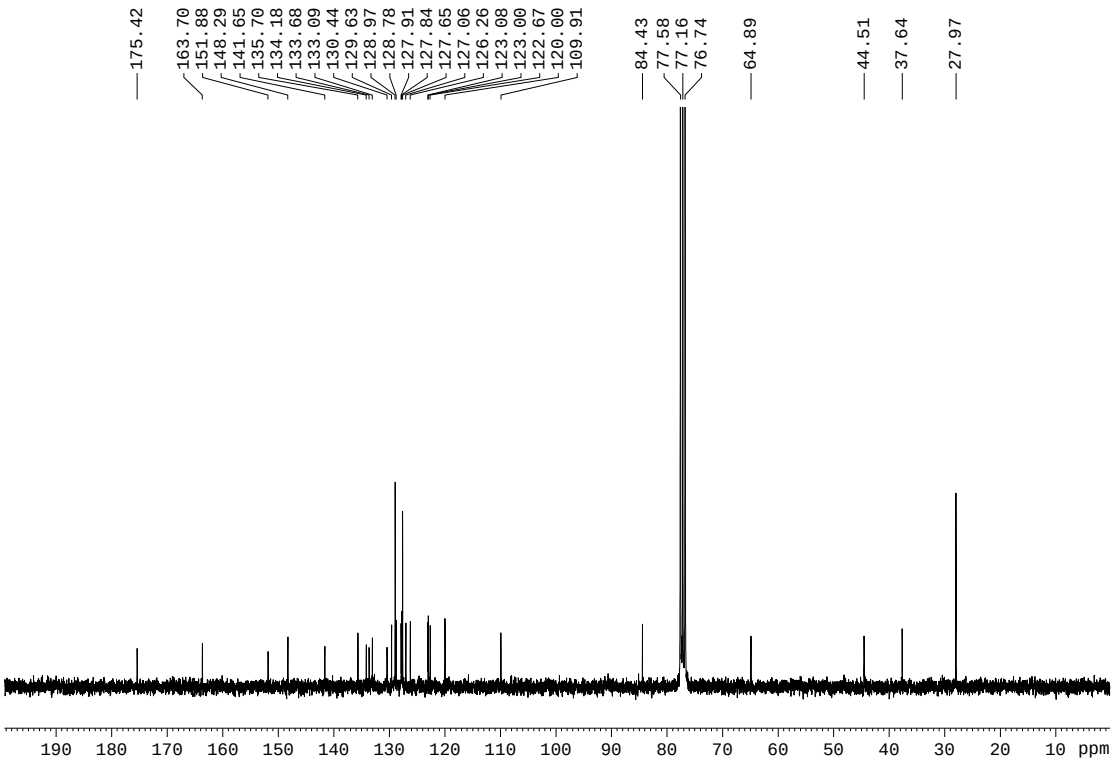
7.808
7.796
7.621
7.592
7.523
7.511
7.498
7.438
7.414
7.377
7.352
7.327
7.311
7.288
7.258
7.231
7.205
7.180
6.978
6.952
6.927
6.793
6.767
6.688
6.683
5.095
5.042
4.937
4.885
3.637
3.631
3.581
3.575
2.993
2.937
1.415
0.071
-0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.03
1.07
2.12
6.10
1.13
1.03
0.98
0.96
0.99
1.06
1.00
0.96
9.02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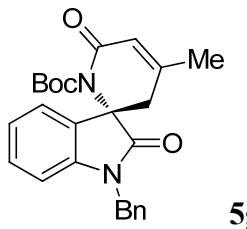
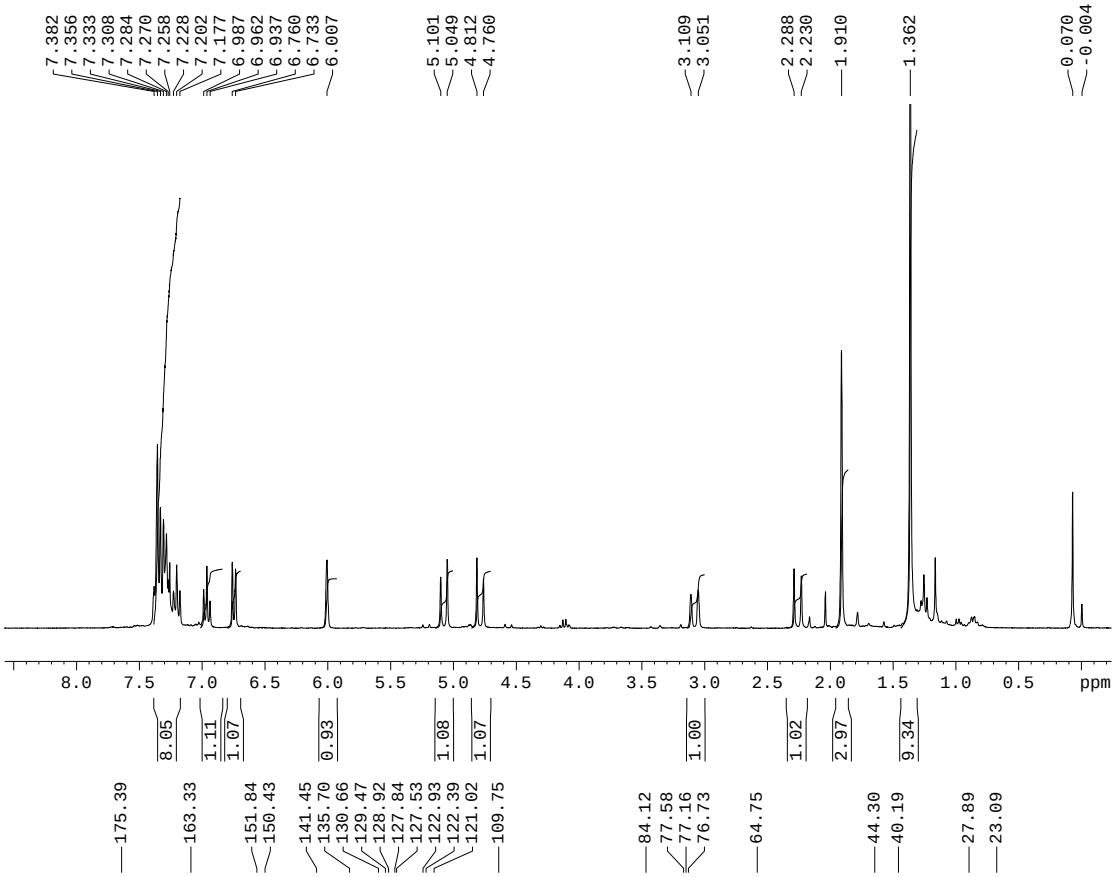
163.70
151.88
148.29
141.65
135.70
134.18
133.68
133.09
130.44
129.63
128.97
128.78
127.91
127.84
127.65
127.06
126.26
123.08
123.00
122.67
120.00
109.91
84.43
77.58
77.16
76.74
64.89
44.51
37.64
27.97
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
Me
BocN
O
N
Bn

5g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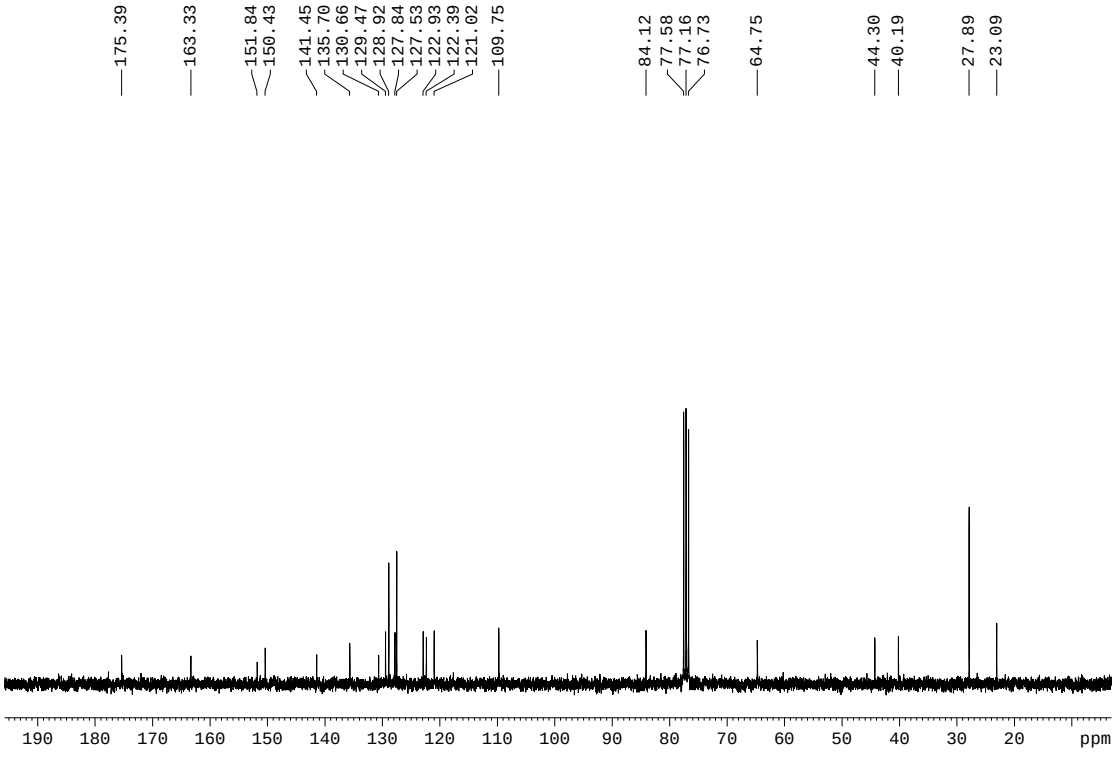
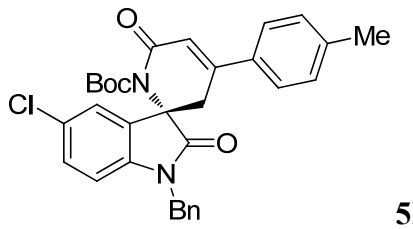
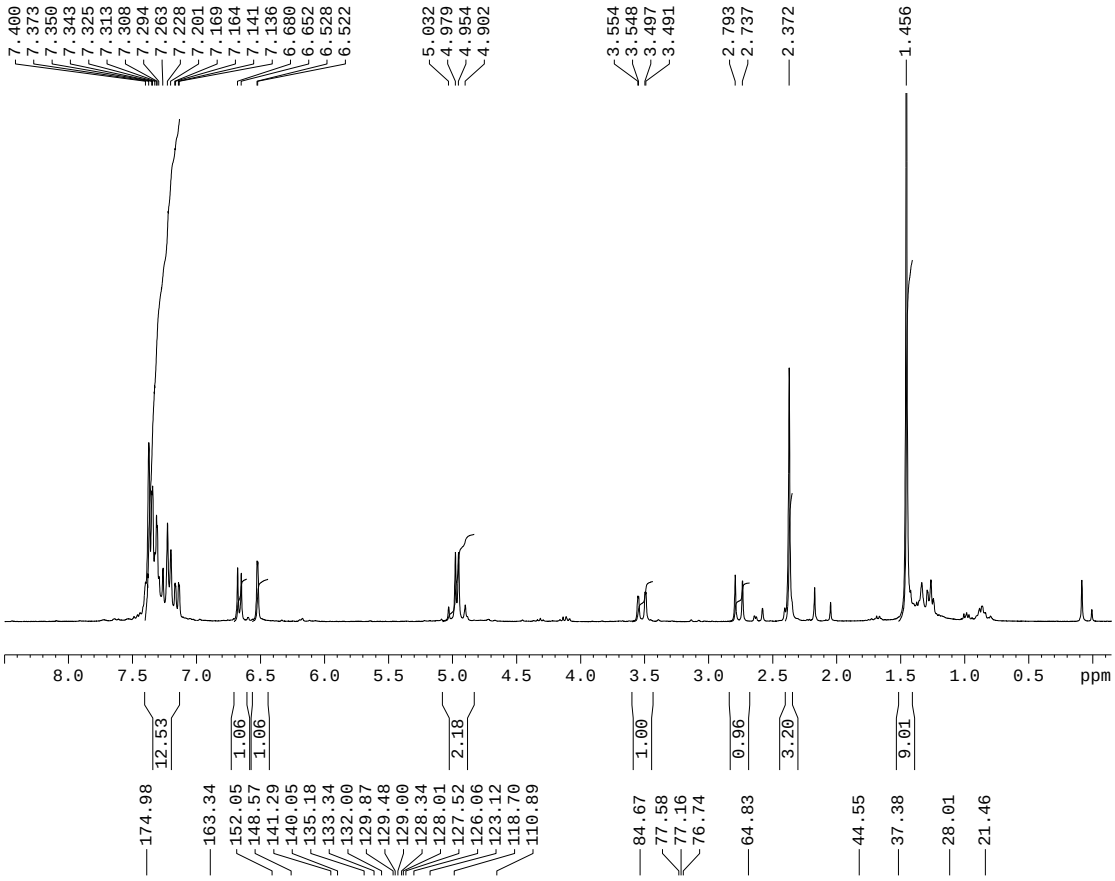
7.308
7.284
7.270
7.258
7.228
7.202
7.177
6.987
6.962
6.937
6.760
6.733
6.007
5.101
5.049
4.812
4.760
3.109
3.051
2.288
2.230
1.910
1.362
0.070
-0.004
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
8.05
1.11
1.07
0.93
1.08
1.07
1.00
1.02
2.97
9.34


175.39
163.33
151.84
150.43
141.45
135.70
130.66
129.47
128.92
127.84
127.53
122.93
122.39
121.02
109.75
84.12
77.58
77.16
76.73
64.75
44.30
40.19
27.89
23.09
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


O
Me
BocN
Cl
O
N
Bn

5h


7.400
7.373
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7.325
7.313
7.308
7.294
7.263
7.228
7.201
7.169
7.164
7.141
7.136
6.680
6.652
6.528
6.522
5.032
4.979
4.954
4.902
3.554
3.548
3.497
3.491
2.793
2.737
2.372
1.456
ppm
12.53
1.06
1.06
2.18
1.00
0.96
3.20
9.01
174.98
163.34
152.05
148.57
141.29
140.05
135.18
133.34
132.00
129.87
129.48
129.00
128.34
128.01
127.52
126.06
123.12
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110.89
84.67
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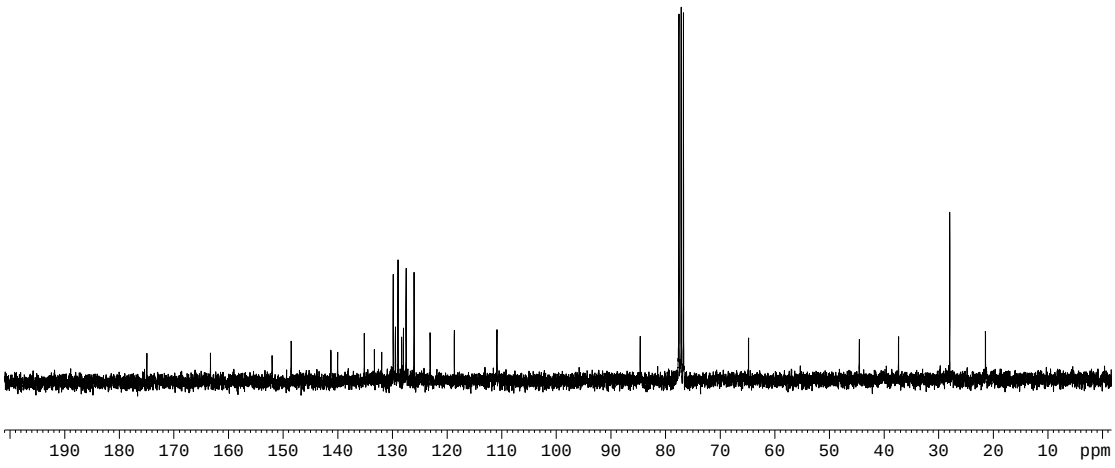
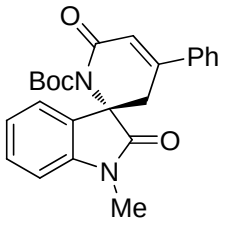
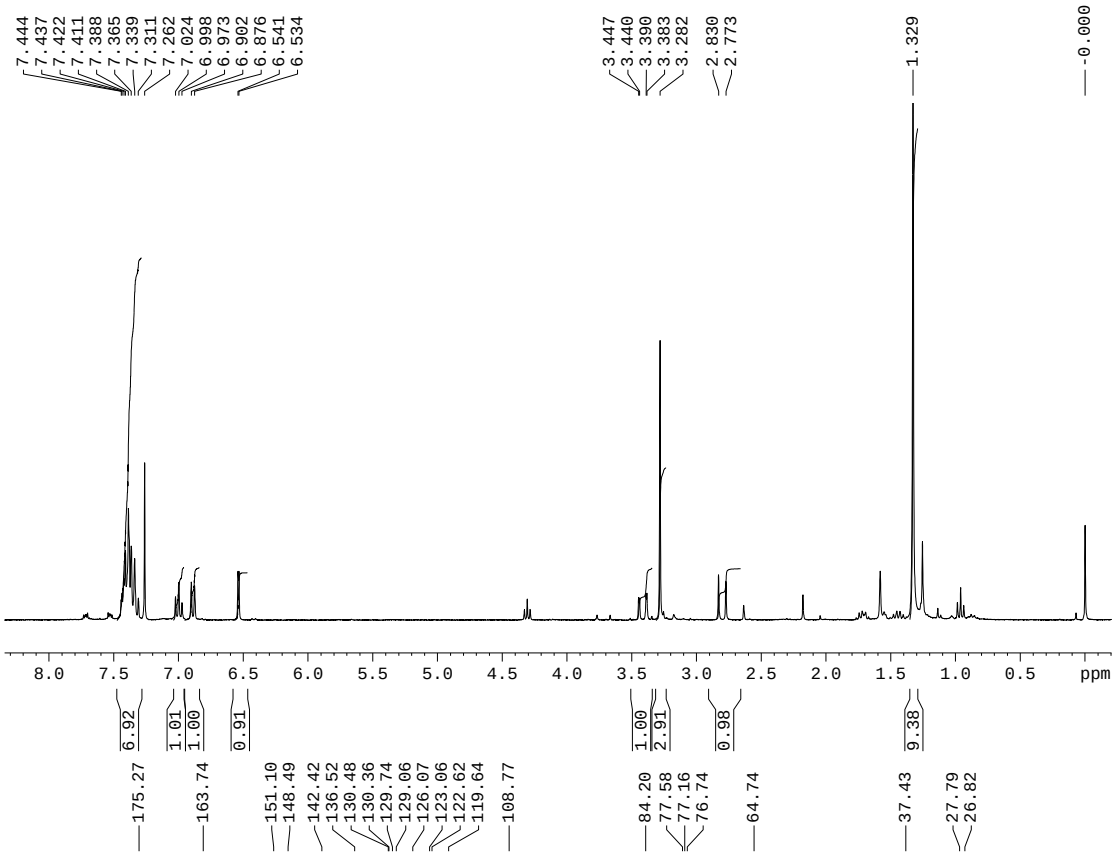
77.16
76.74
64.83
44.55
37.38
28.01
21.46


ppm


O
Ph
BocN
O
N
Me

5i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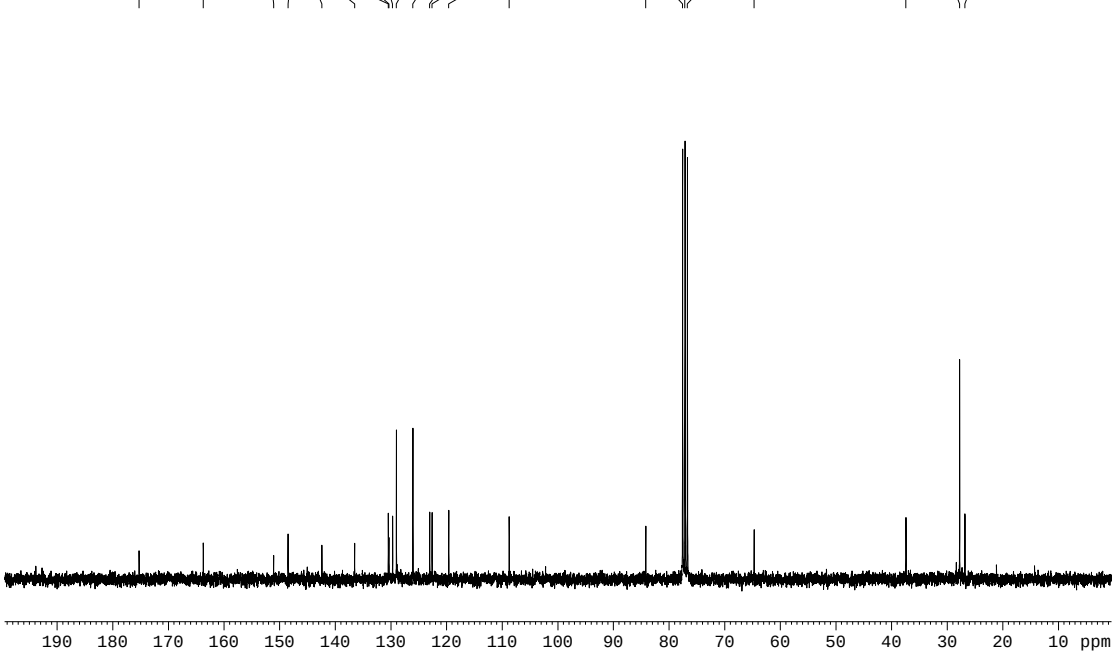
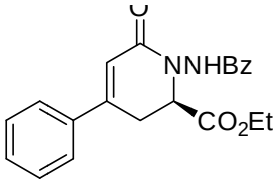
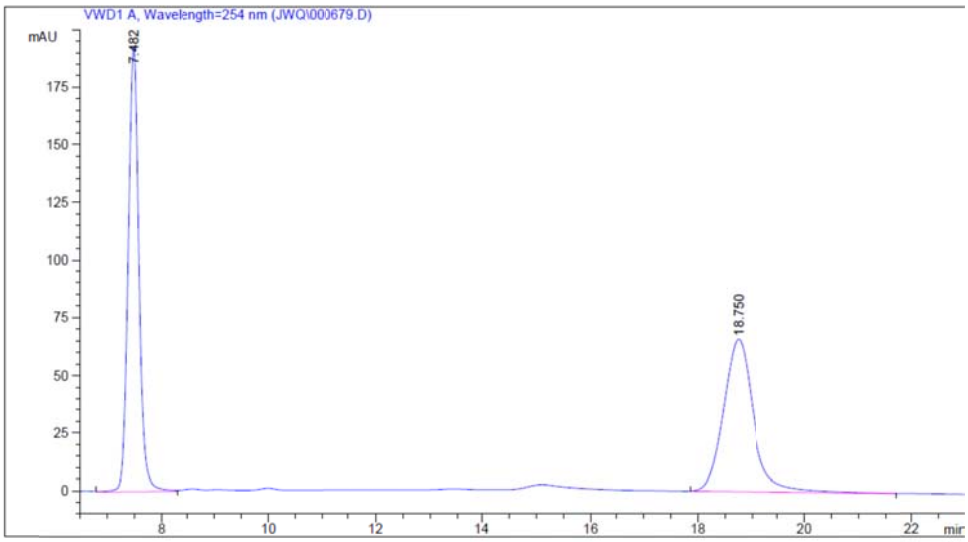
7.388
7.365
7.339
7.311
7.262
7.024
6.998
6.973
6.902
6.876
6.541
6.534
3.447
3.440
3.390
3.383
3.282
2.830
2.773
1.329
-0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
6.92
1.01
1.00
0.91
1.00
2.91
0.98
9.38

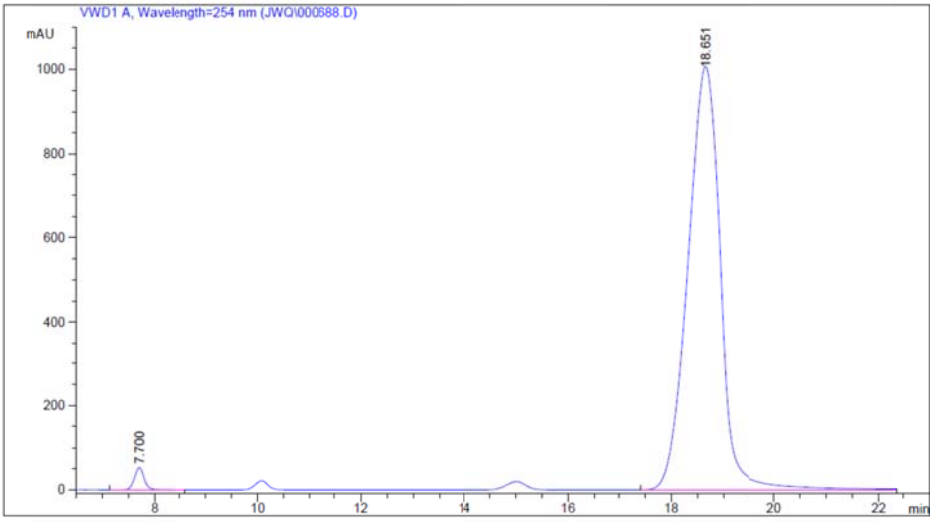

175.27
163.74
151.10
148.49
142.42
136.52
130.48
130.36
129.74
129.06
126.07
123.06
122.62
119.64
108.77
84.20
77.58
77.16
76.74
64.74
37.43
27.79
26.82
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Part III HPLC Spectra



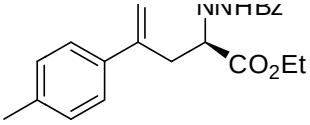
3a



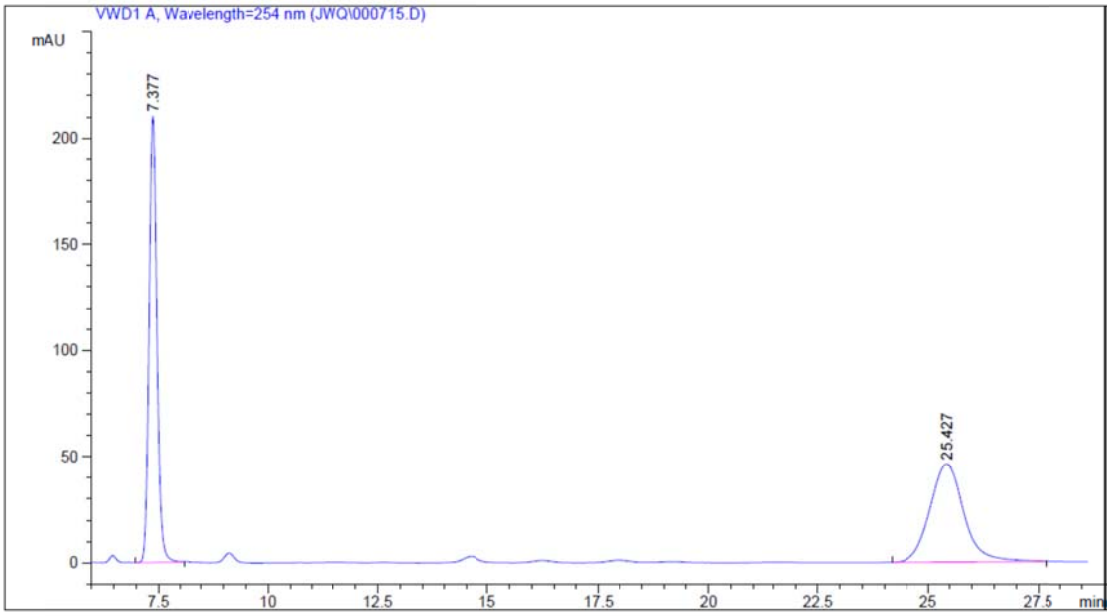


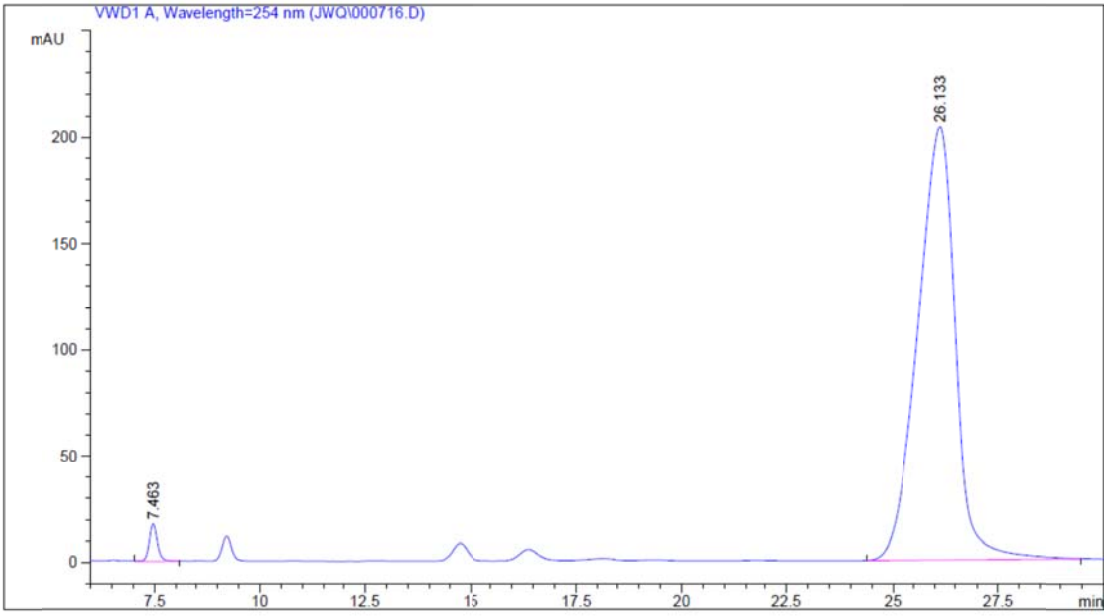
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.700	VB	0.1979	690.24554	53.22517	1.5660
2	18.651	BBA	0.6774	4.33869e4	1006.87292	98.4340



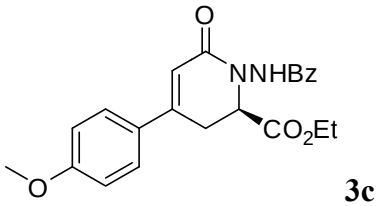
3b



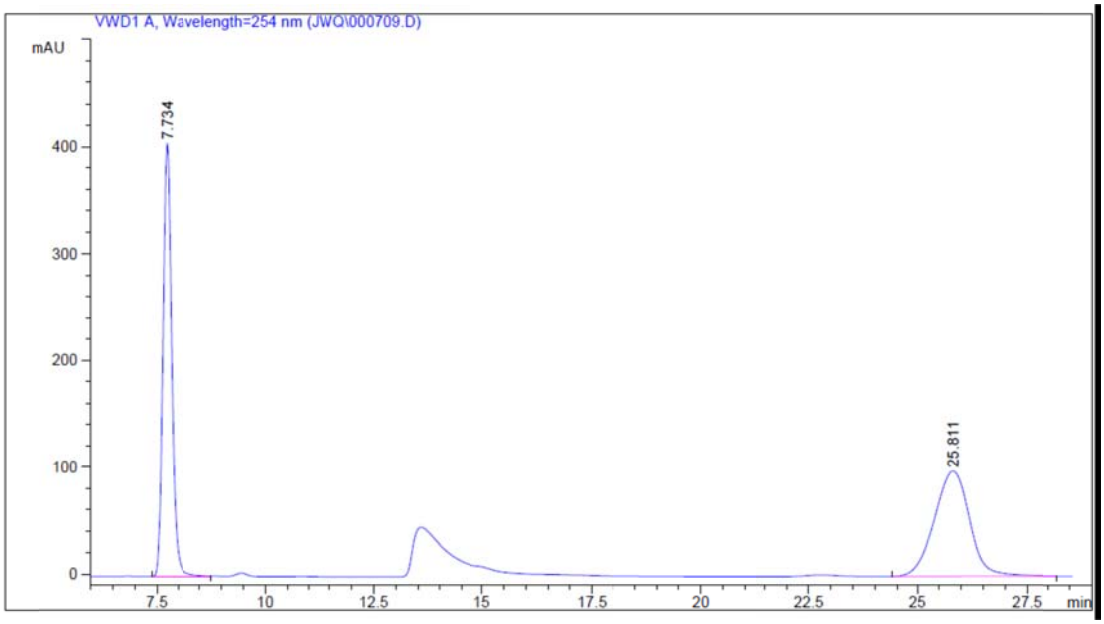


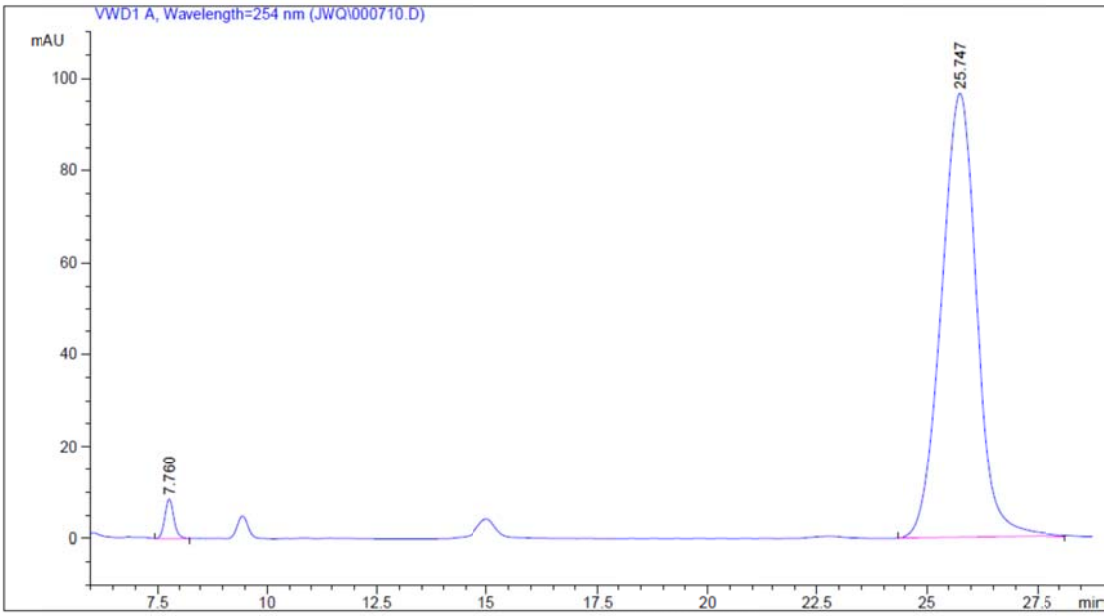
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.463	VB	0.2020	233.06381	17.49189	1.8161
2	26.133	BB	0.9543	1.26004e4	203.80099	98.1839



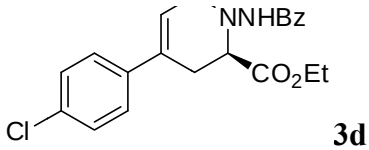
3c



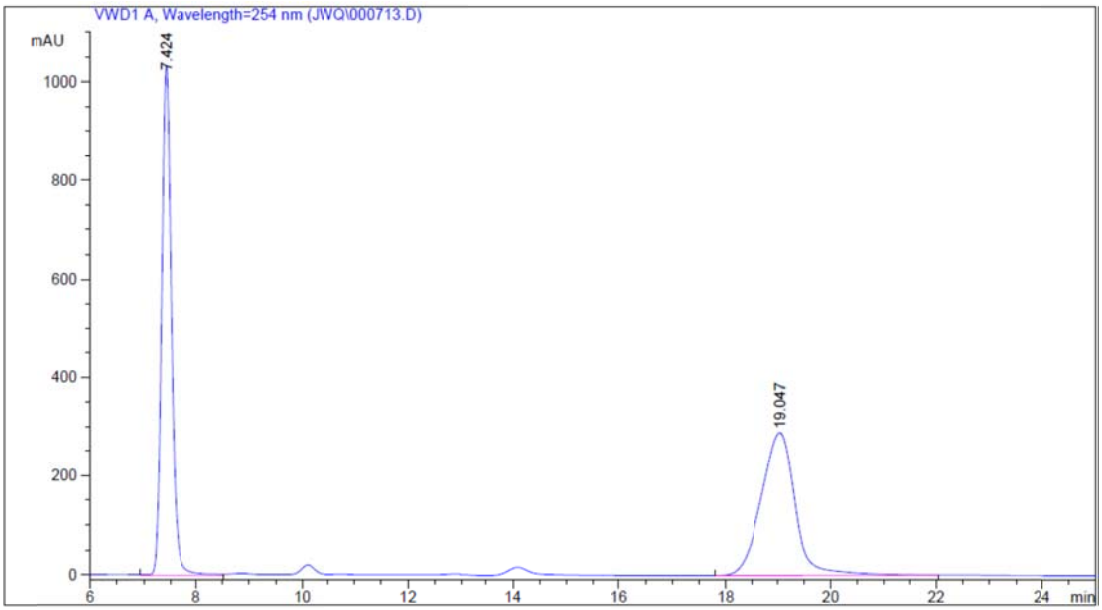


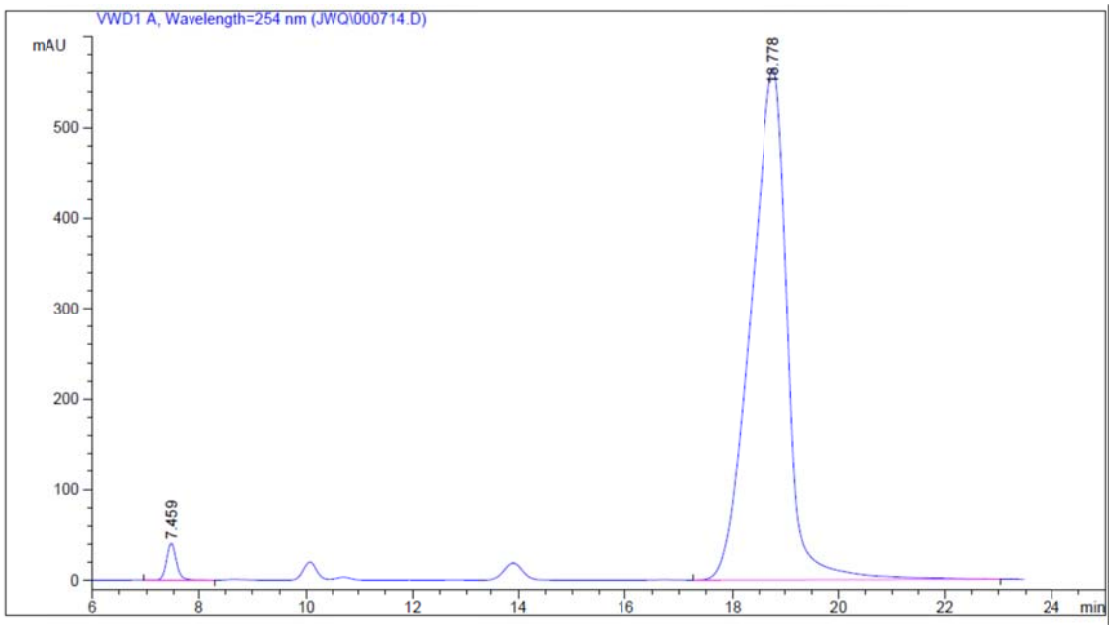
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.760	VB	0.2164	120.75956	8.59378	2.2154
2	25.747	BB	0.8592	5330.24170	96.59957	97.7846



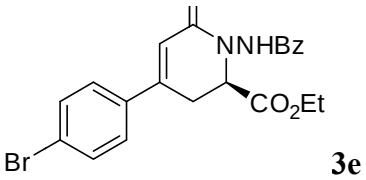
3d



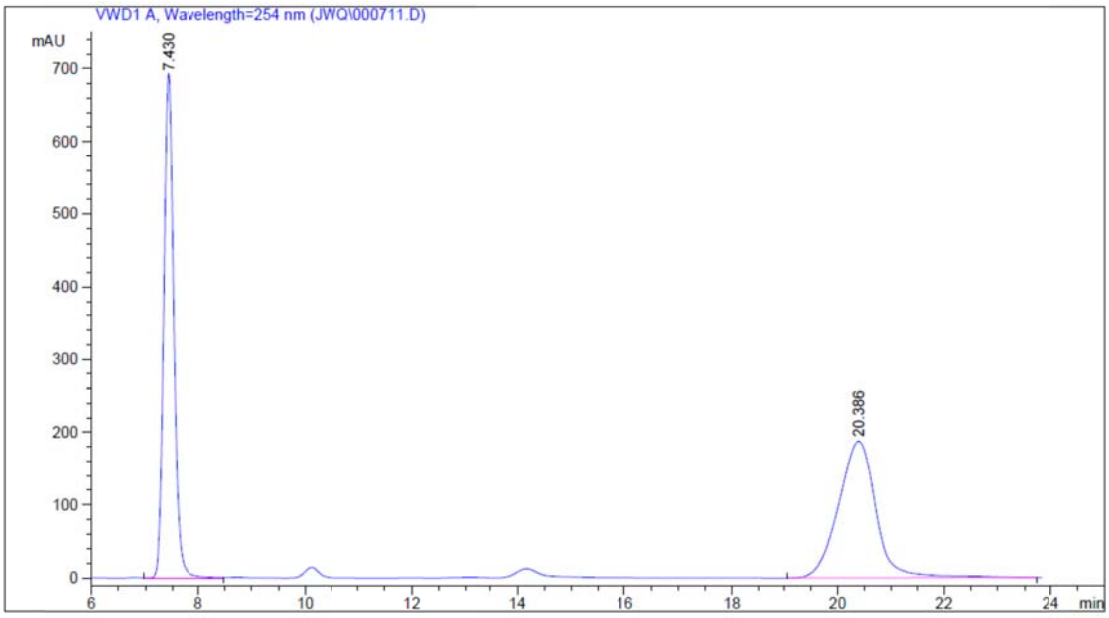


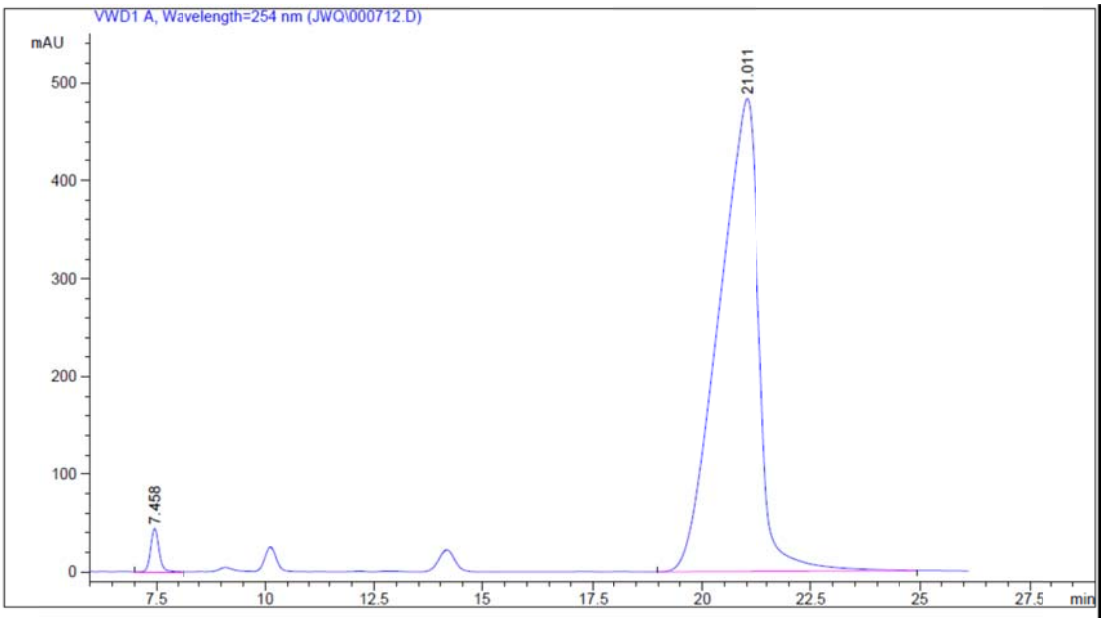
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.459	VB	0.1999	521.71521	40.47533	1.8626
2	18.778	VB	0.7516	2.74882e4	564.49622	98.1374



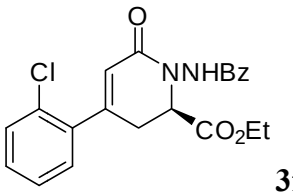
3e





Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.458	VB	0.2024	580.11591	44.26323	1.8028
2	21.011	BB	1.0737	3.15993e4	483.71671	98.1972



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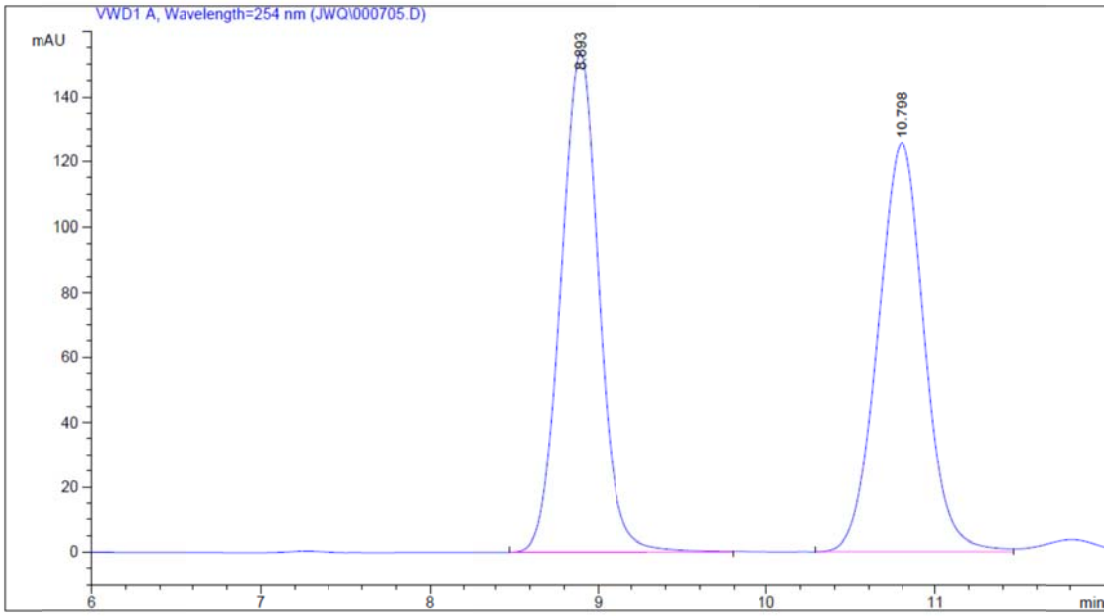
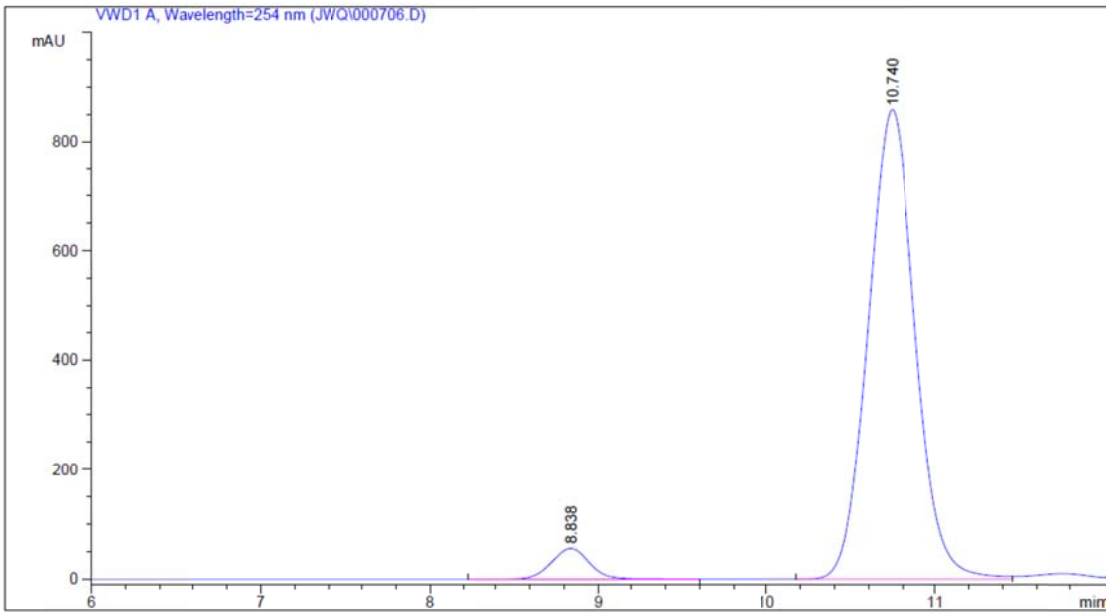
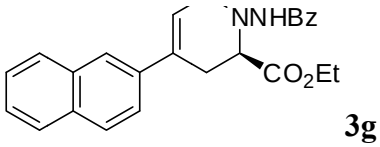


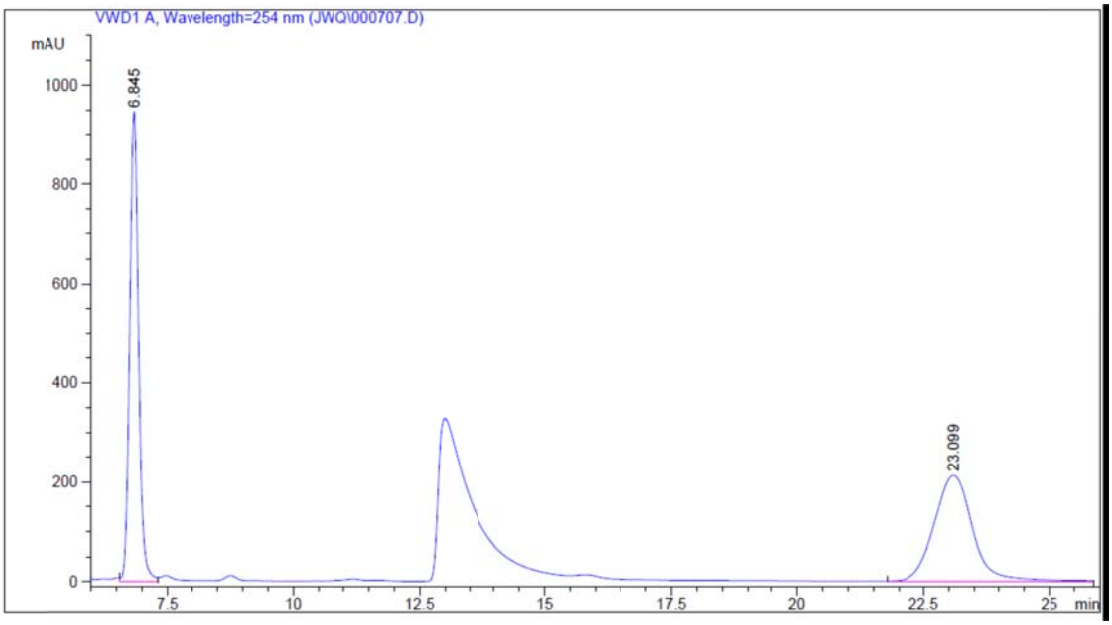


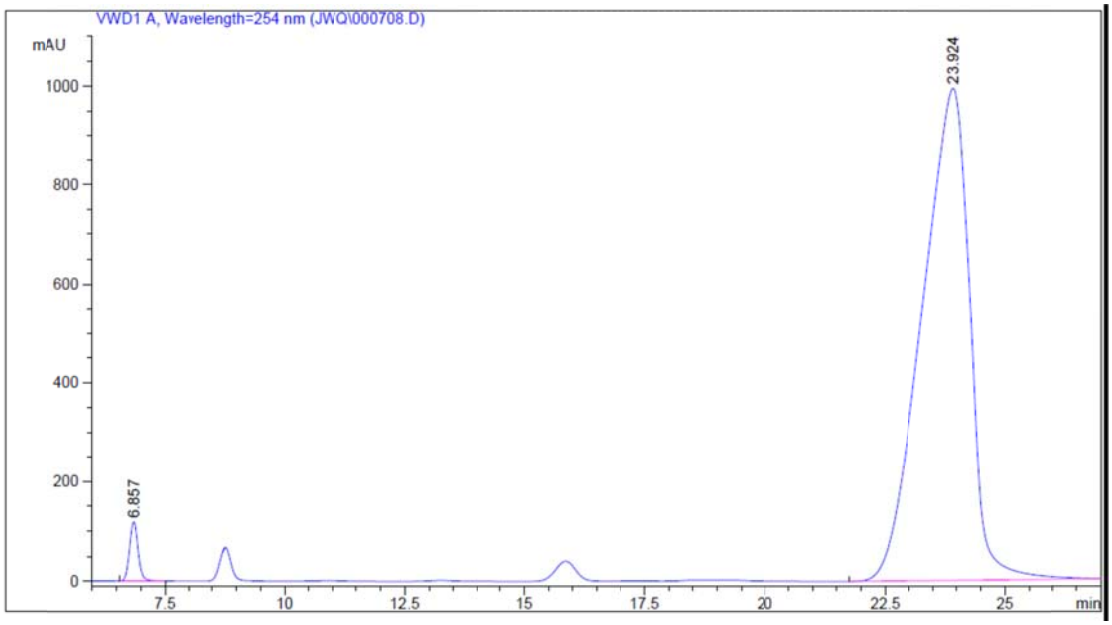
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.838	BB	0.2375	856.37323	55.72307	4.8953
2	10.740	BV	0.2989	1.66374e4	858.61255	95.1047



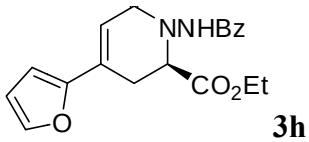
3g



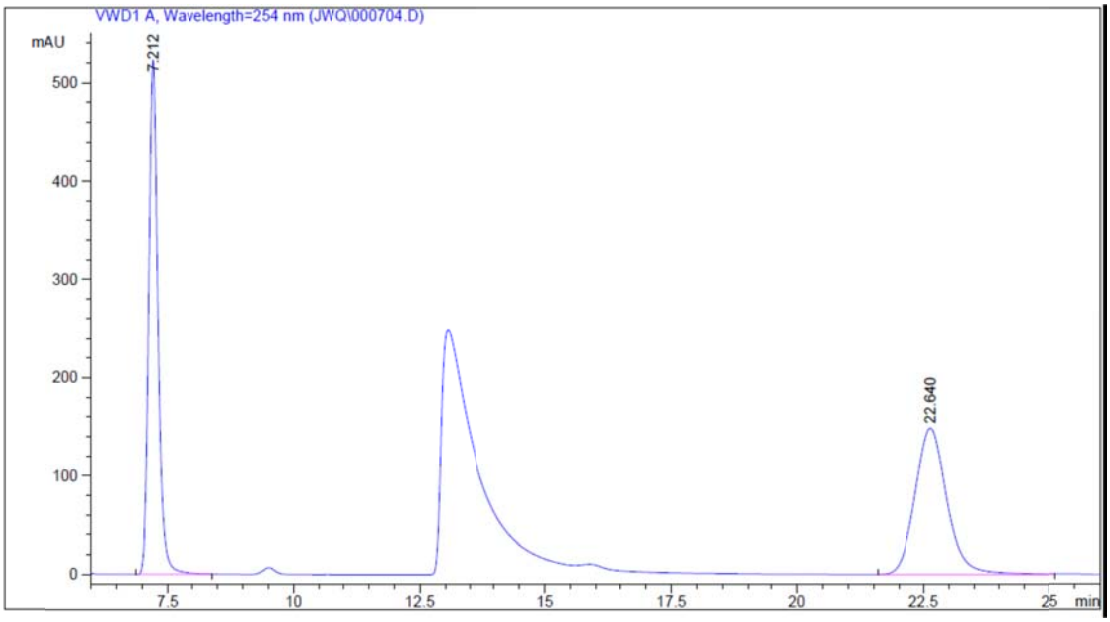


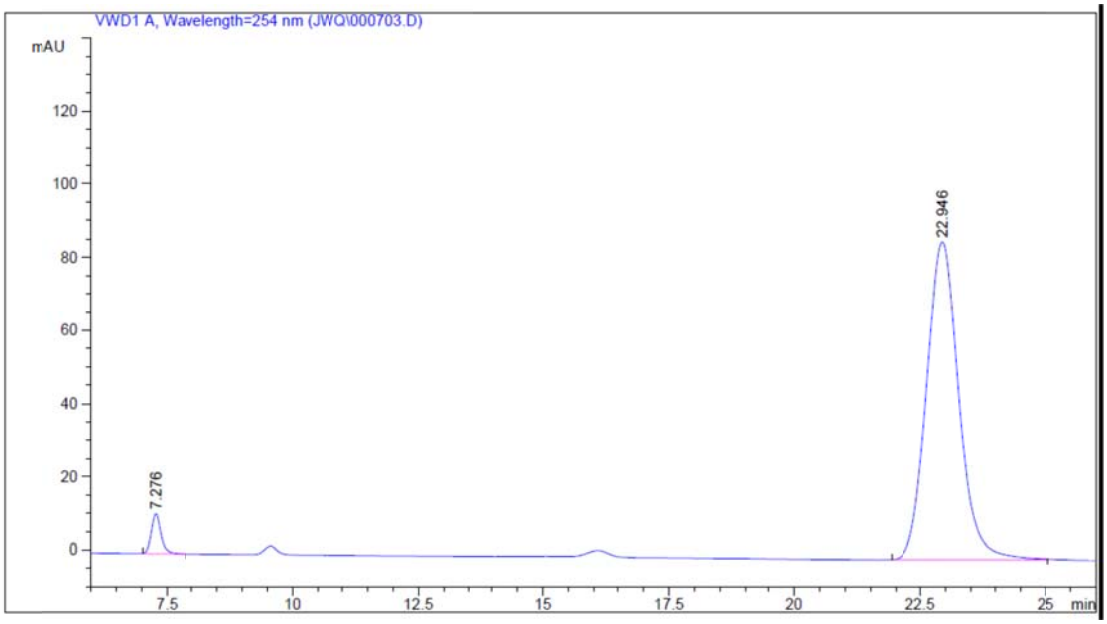
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.857	VB	0.1911	1470.46973	118.69445	2.1046
2	23.924	BB	1.1200	6.83978e4	994.28461	97.8954



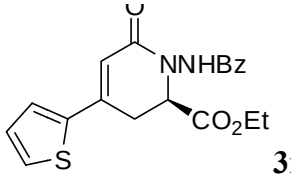
3h



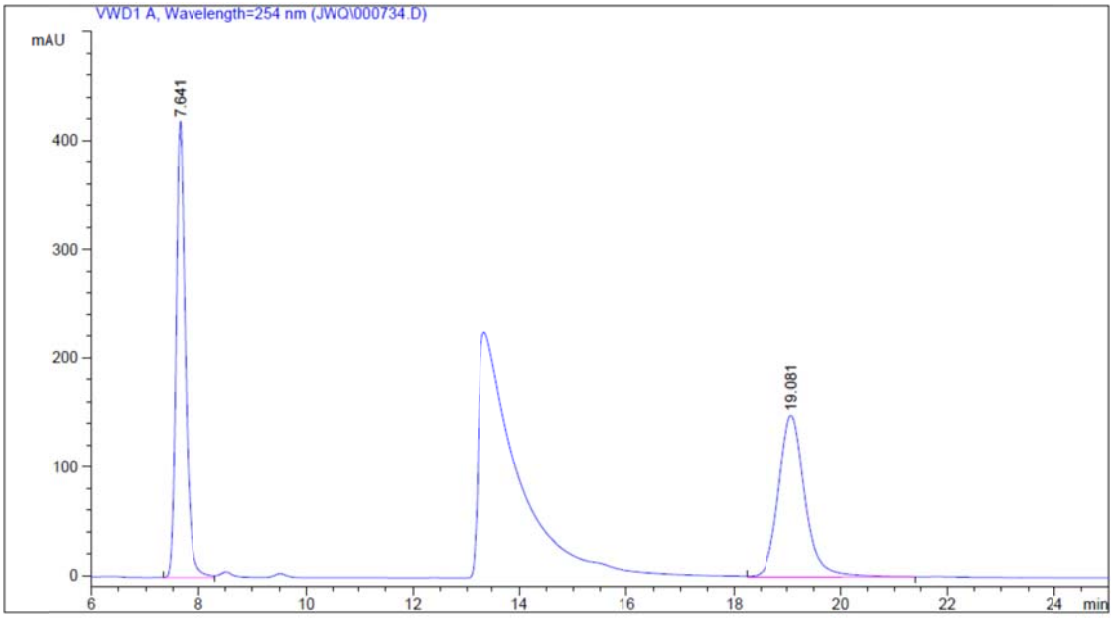


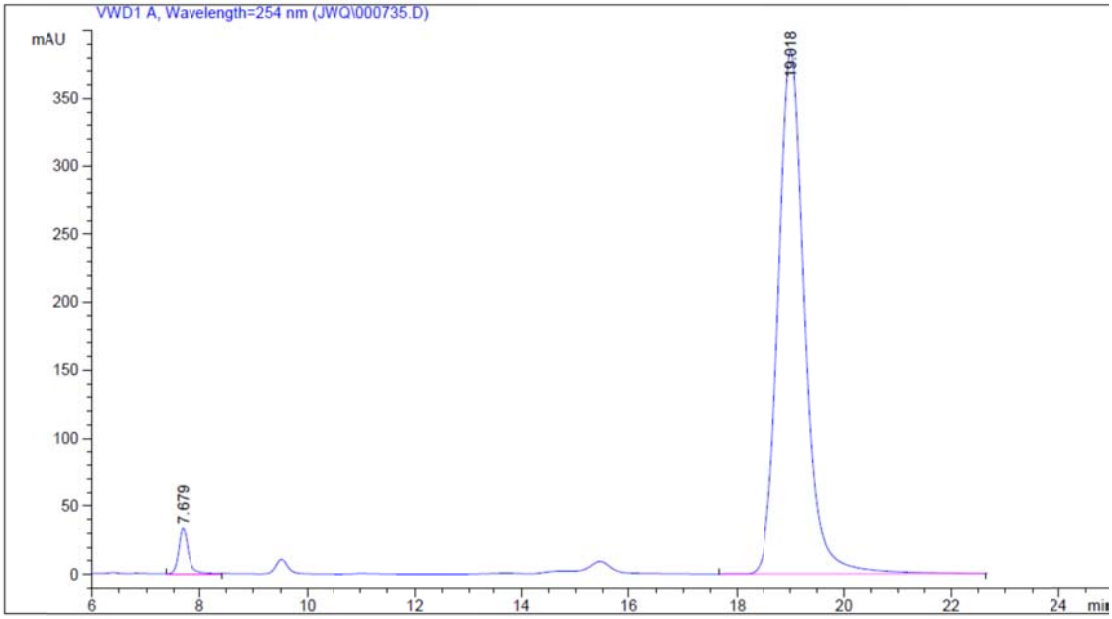
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.276	BB	0.2010	143.23706	10.82545	3.5729
2	22.946	BB	0.6820	3865.74634	86.90881	96.4271



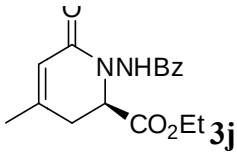
3i



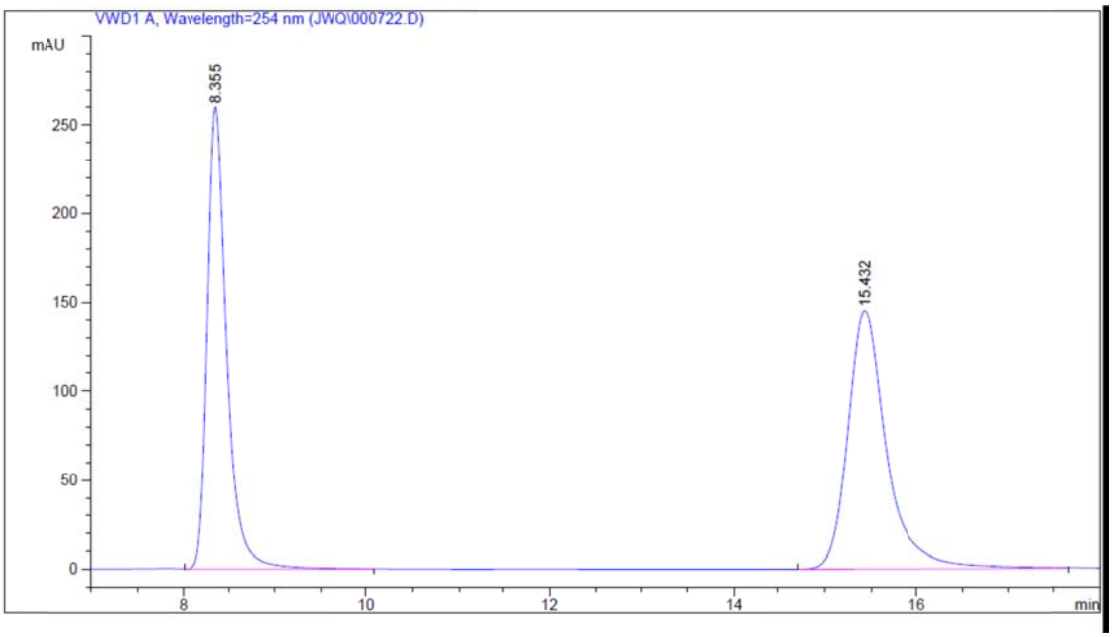


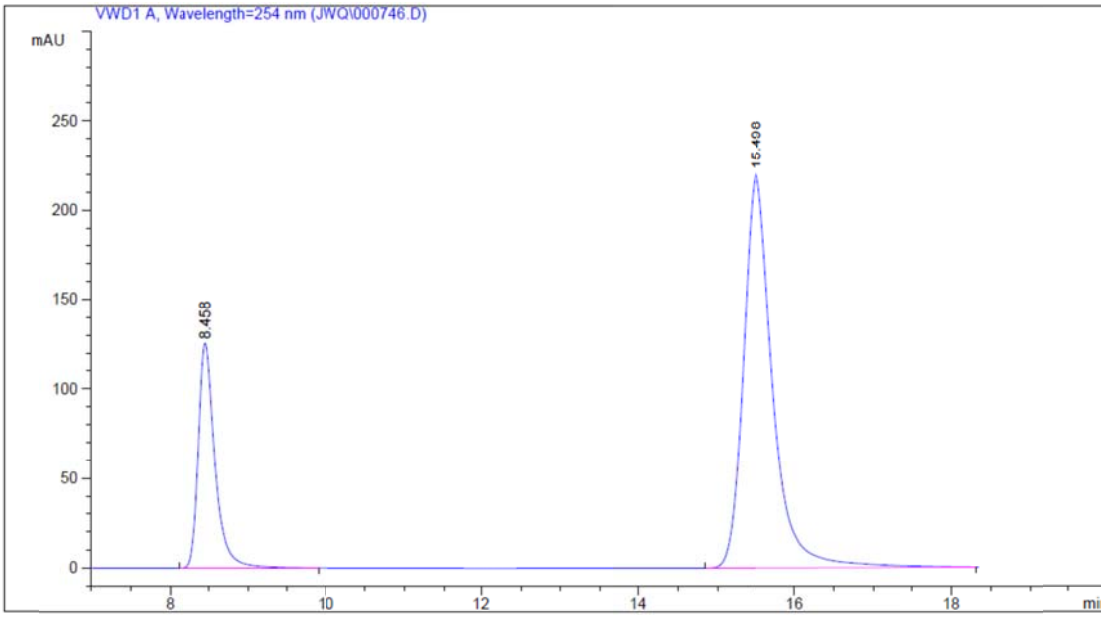
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.679	BB	0.1945	430.56934	33.30230	3.1760
2	19.018	BB	0.5206	1.31262e4	384.50650	96.8240



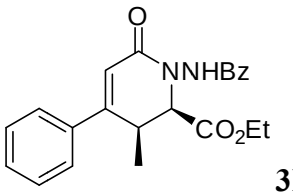
3j



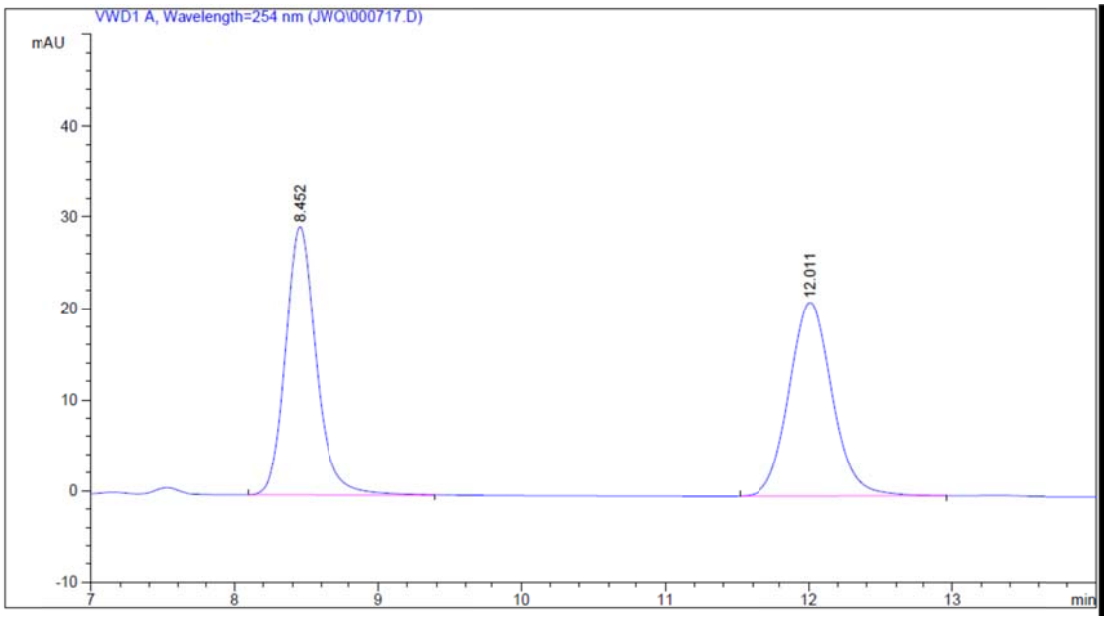


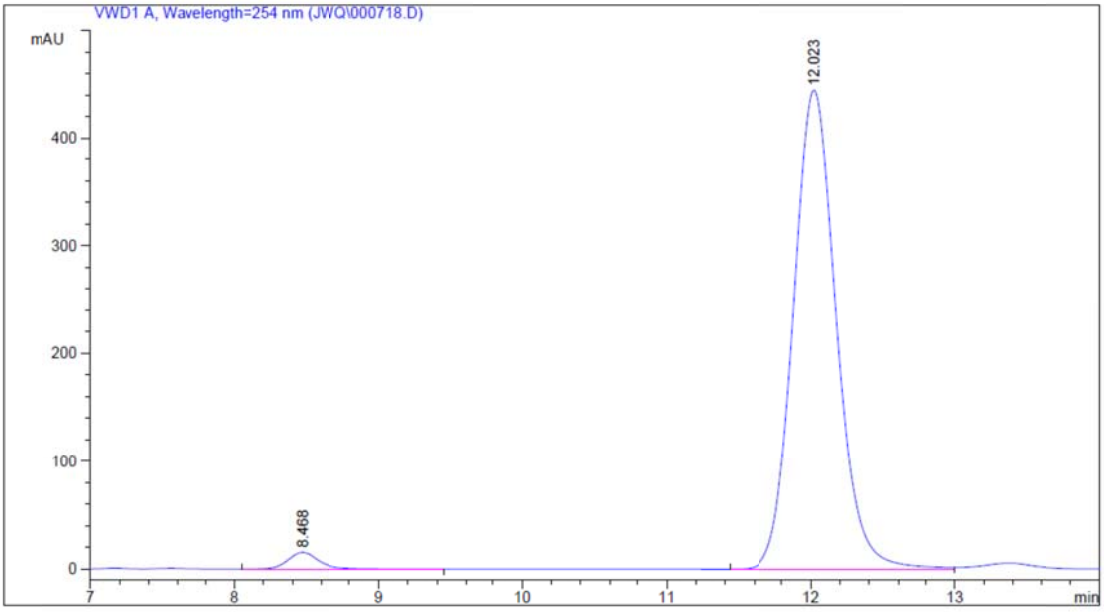
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.458	VB	0.2209	1842.63770	125.46210	23.5494
2	15.498	BB	0.4035	5981.93262	220.78899	76.4506



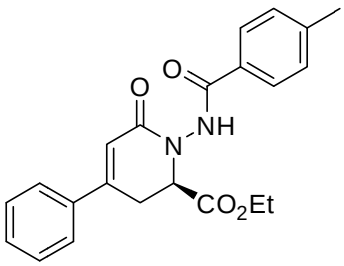
3k



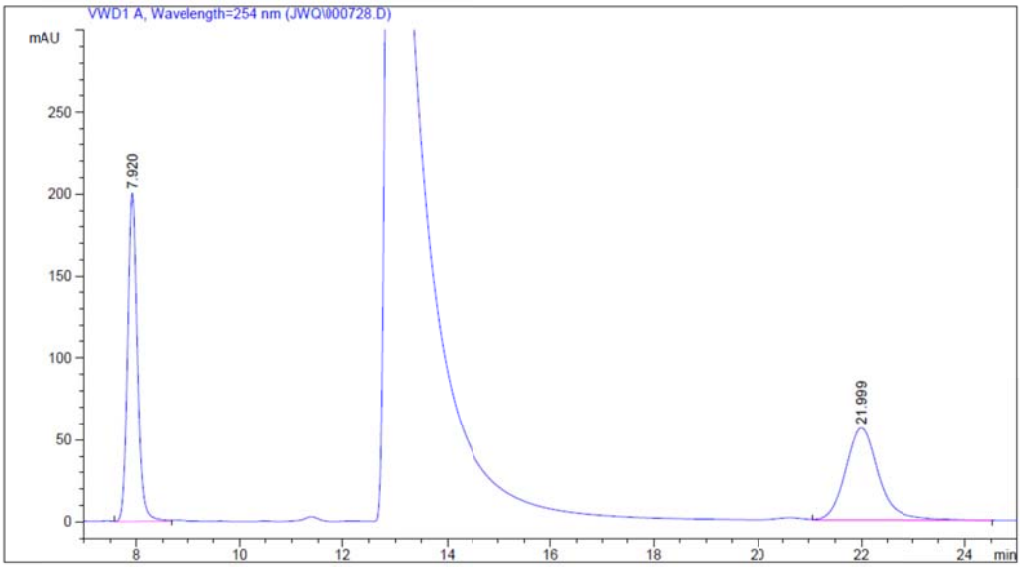


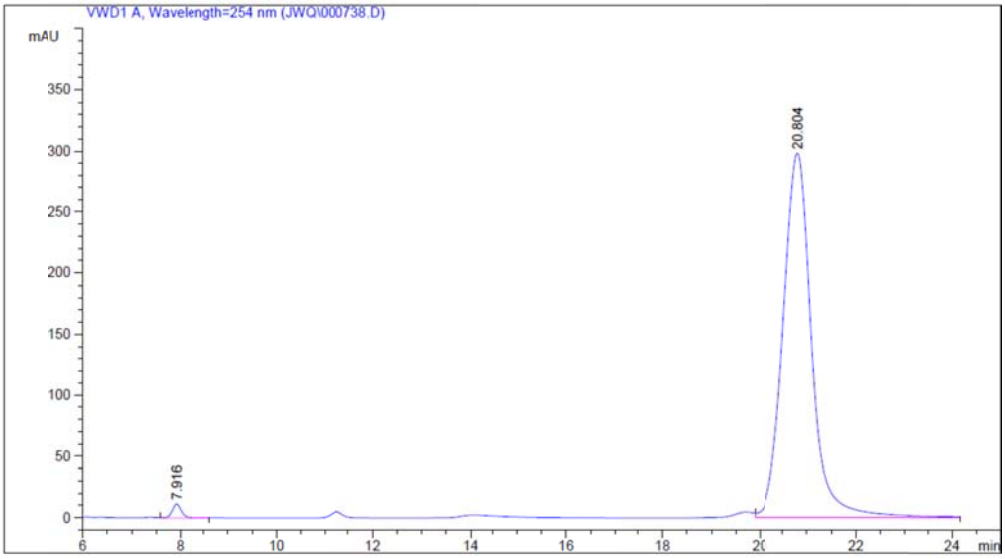
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.468	BB	0.2323	234.42555	15.45820	2.5157
2	12.023	BV	0.3140	9084.18457	444.68723	97.4843



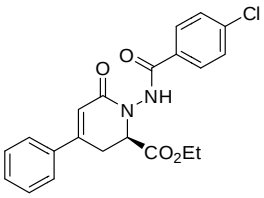
3l



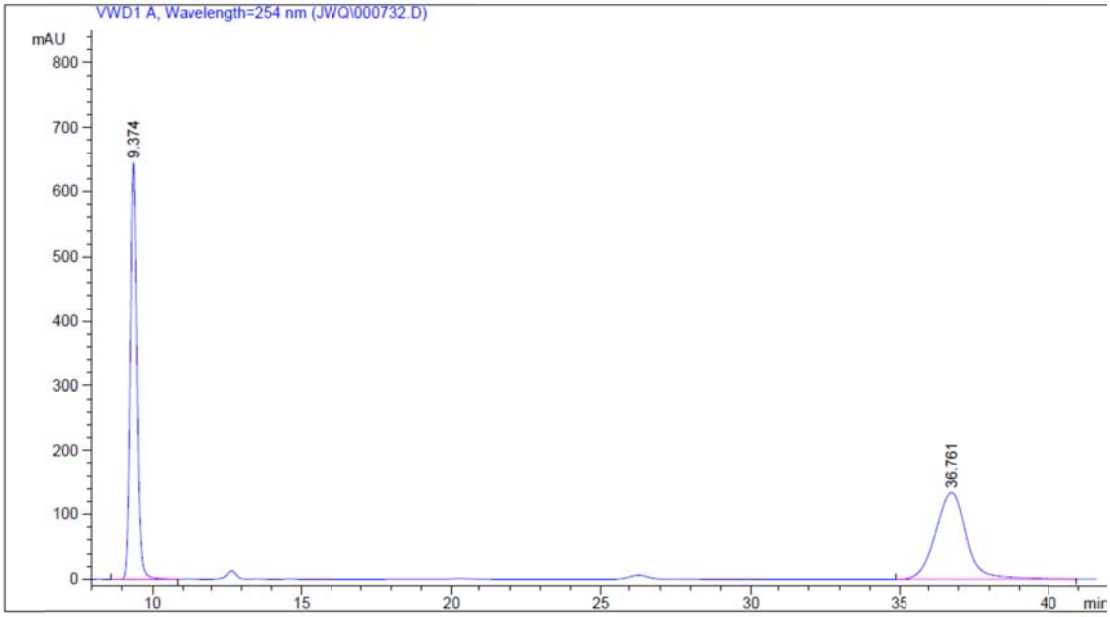


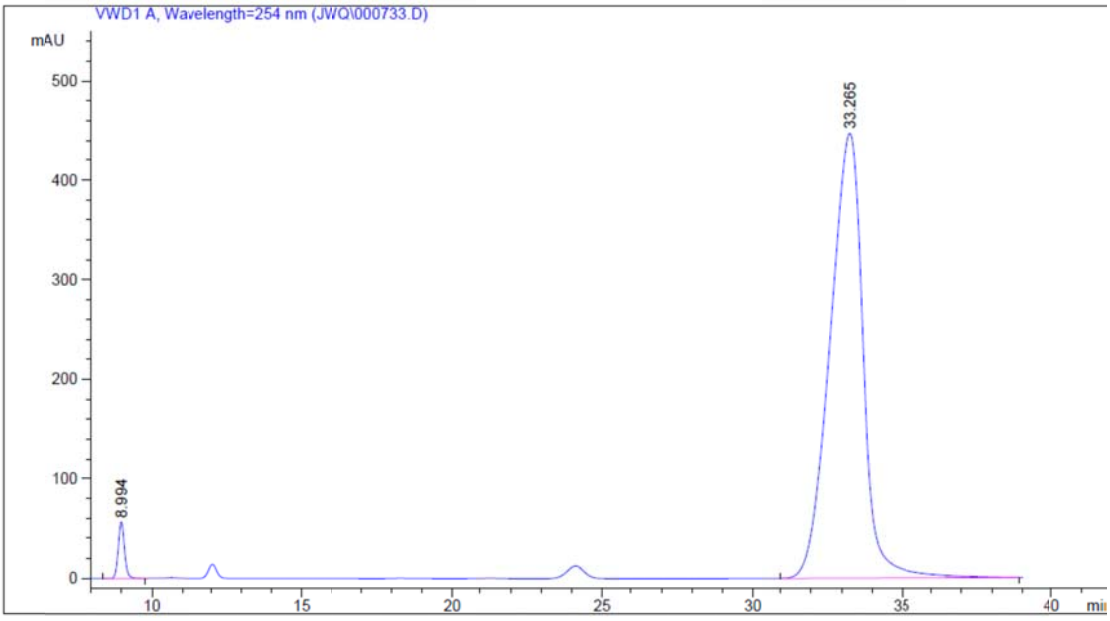
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.916	VB	0.1944	146.96880	11.37367	1.1843
2	20.804	VBA	0.6246	1.22628e4	298.64899	98.8157



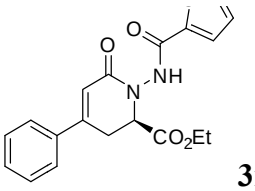
3m



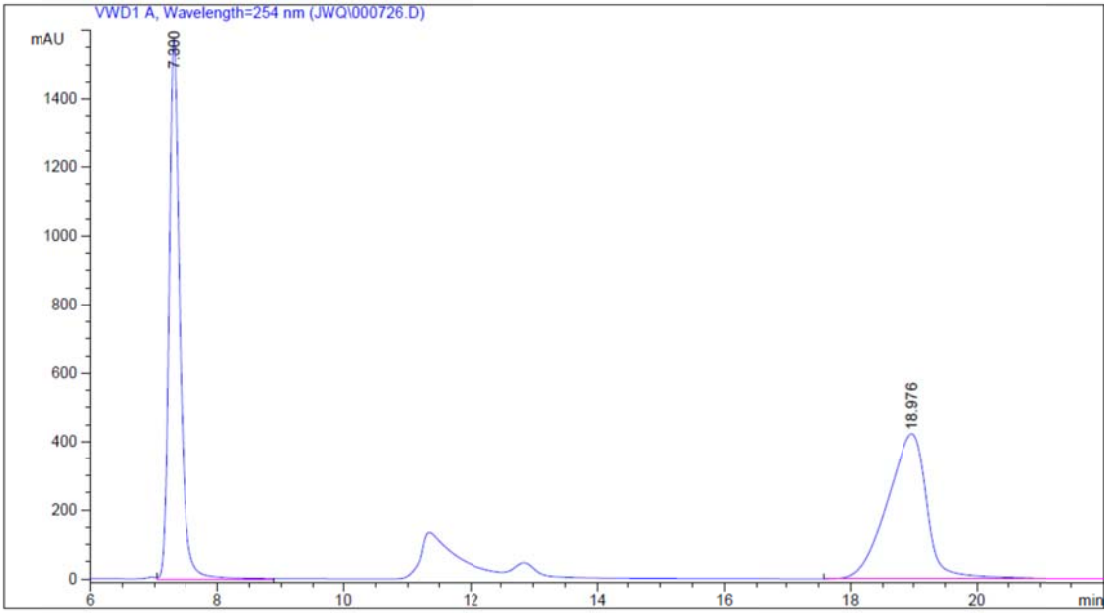


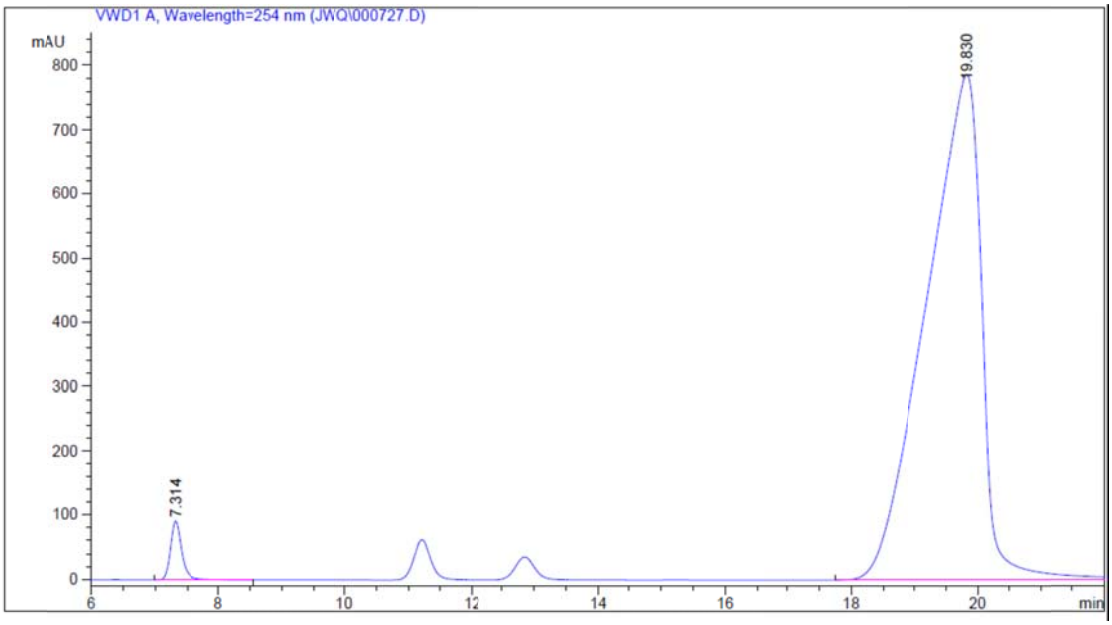
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.994	BB	0.2202	810.22089	56.33526	2.3463
2	33.265	BB	1.1560	3.37221e4	447.40094	97.6537



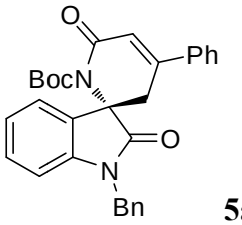
3n



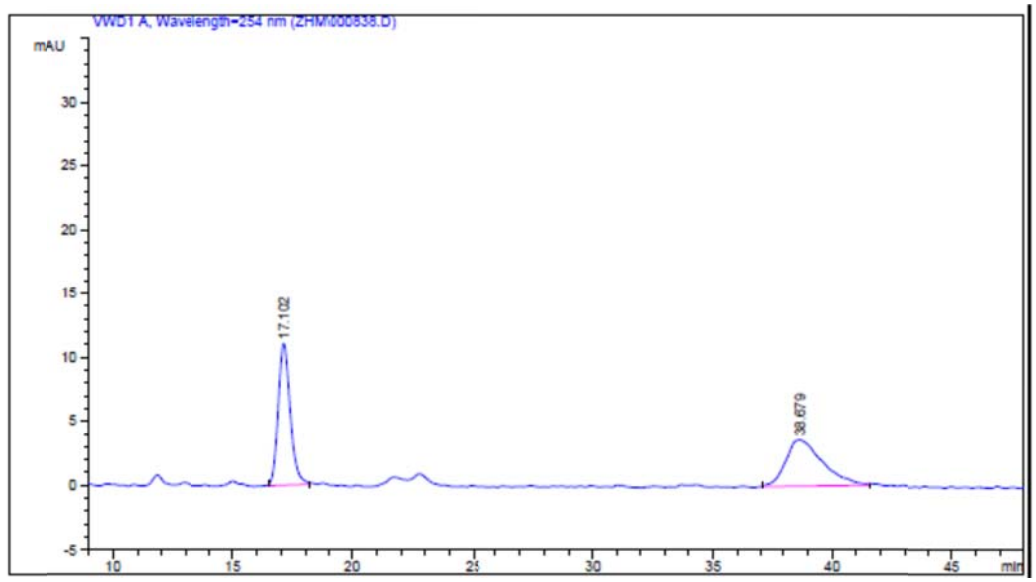


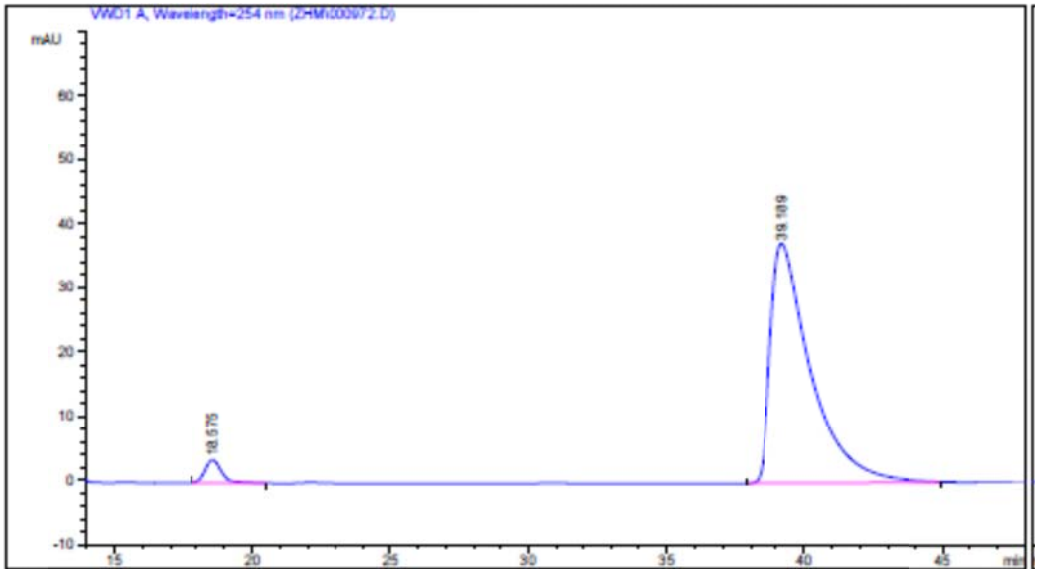
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.314	VB	0.1890	1127.90808	90.53302	2.2860
2	19.830	BBA	0.9133	4.82124e4	786.41113	97.7140



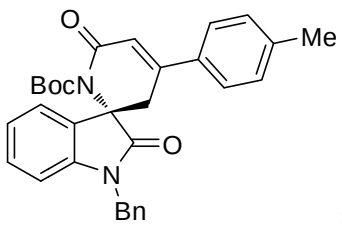
5a



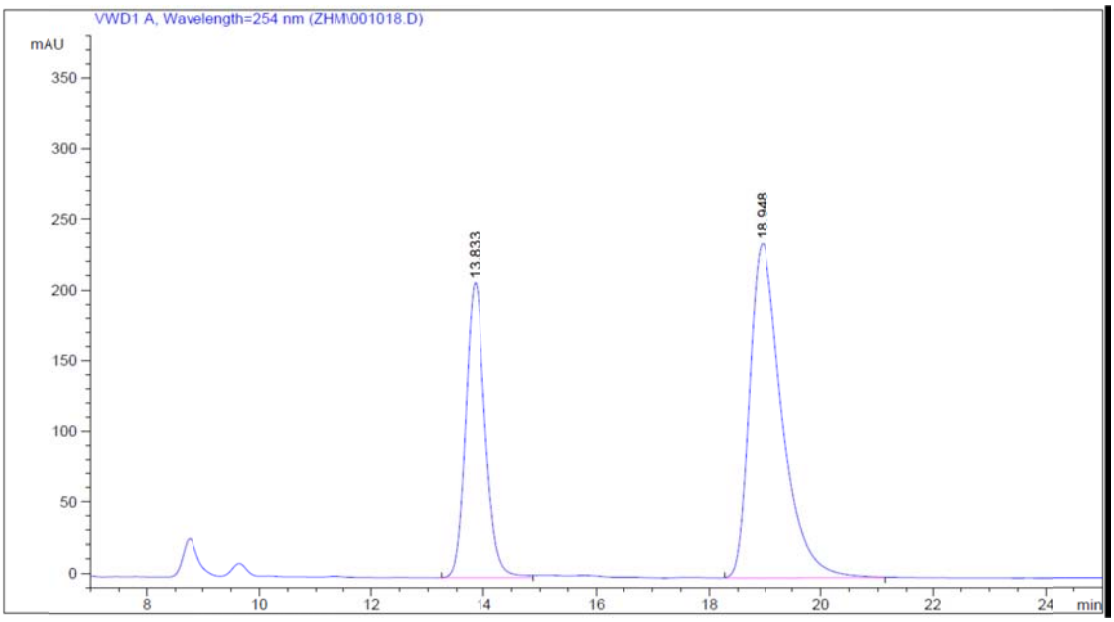


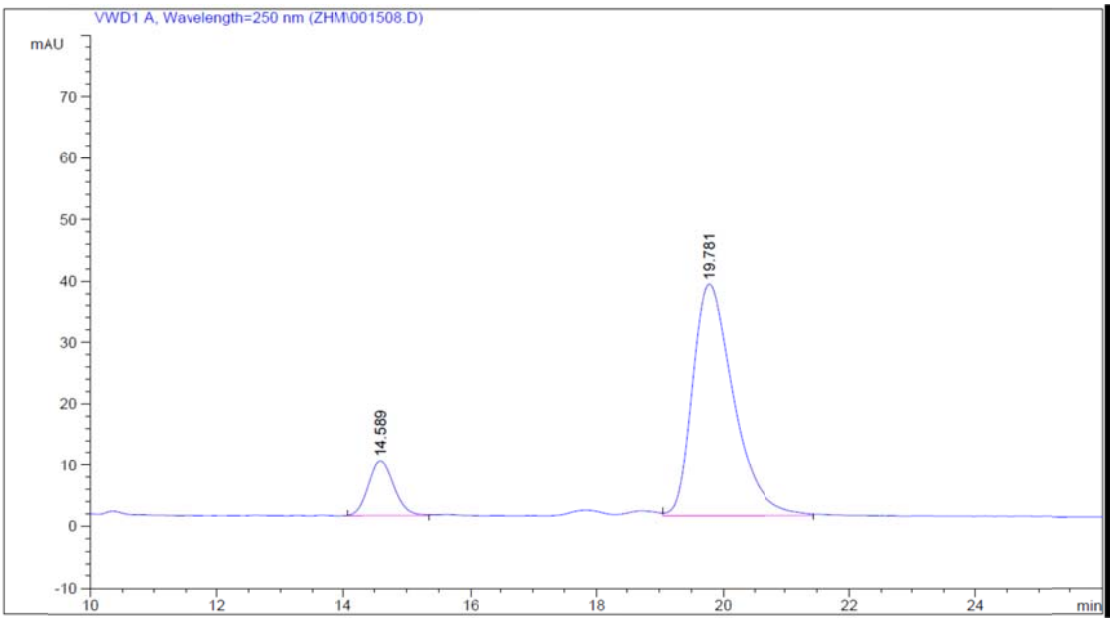
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.575	BB	0.6398	151.79791	3.62657	3.8408
2	39.189	BB	1.4654	3800.42139	37.39086	96.1592

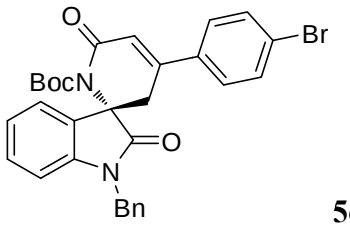


5b

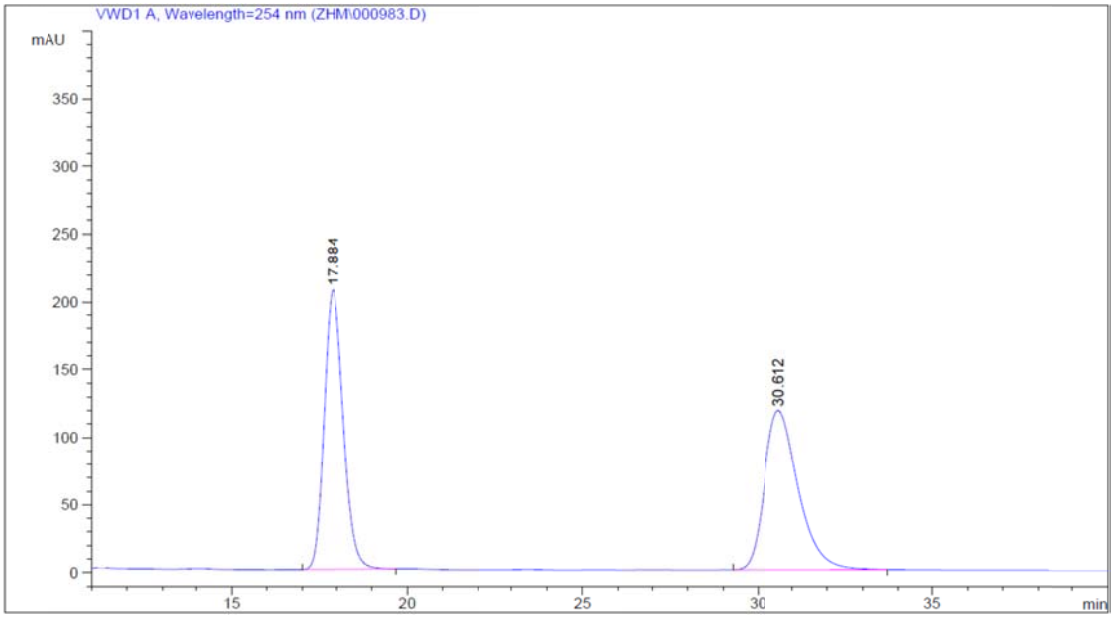


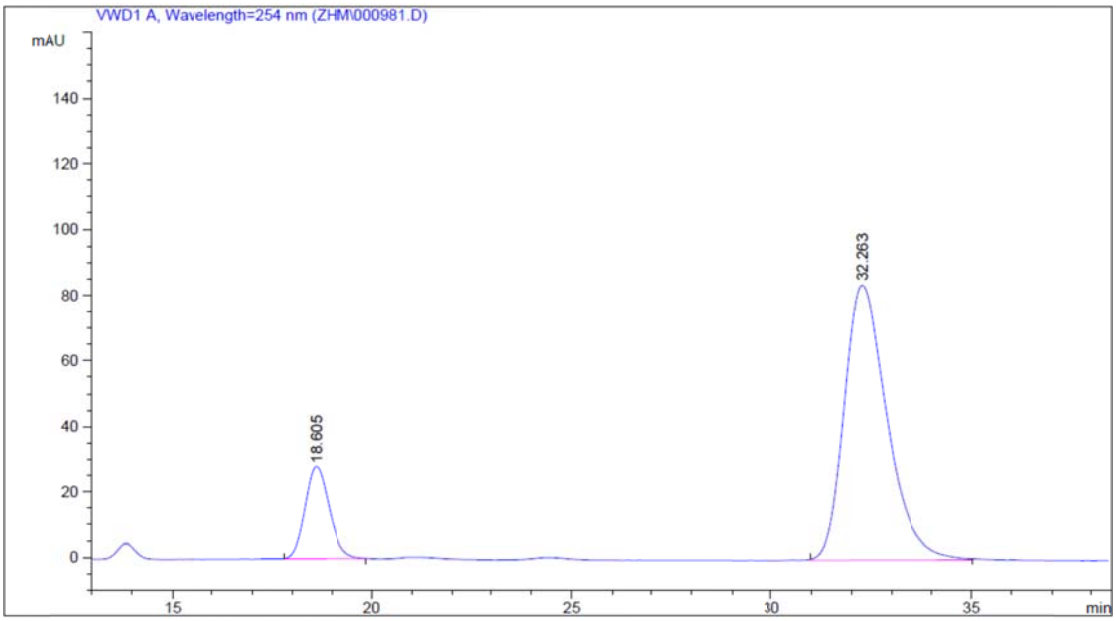


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.589	BB	0.4252	245.85345	8.95279	12.7110
2	19.781	VB	0.6783	1688.32703	37.79994	87.2890



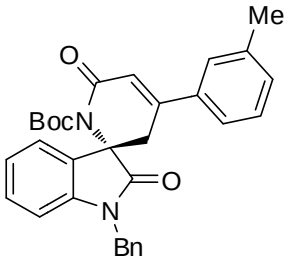
5c



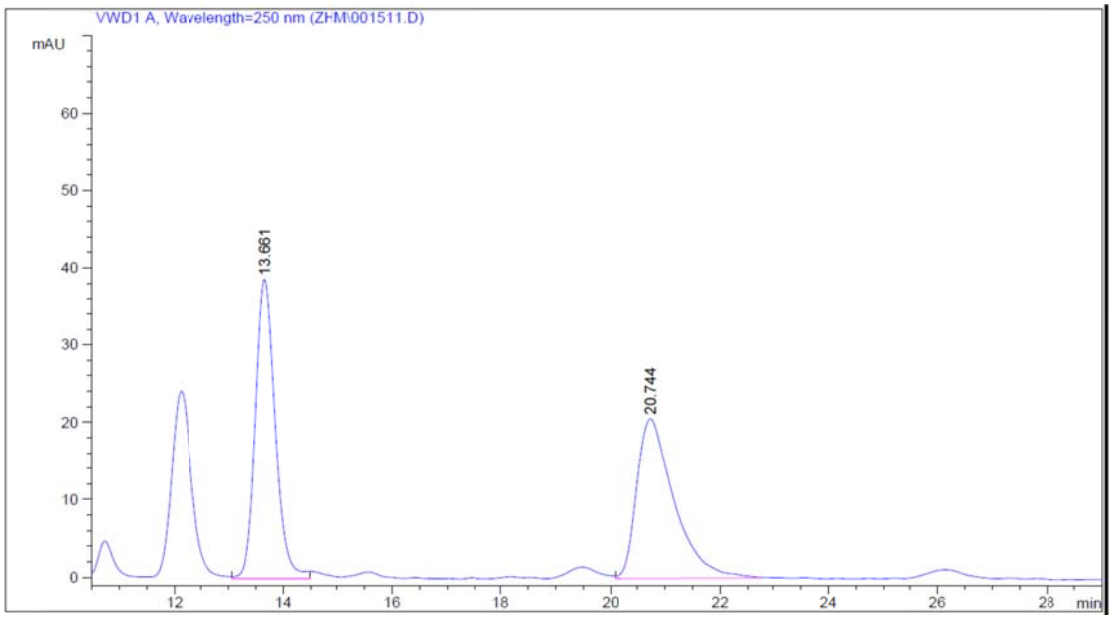


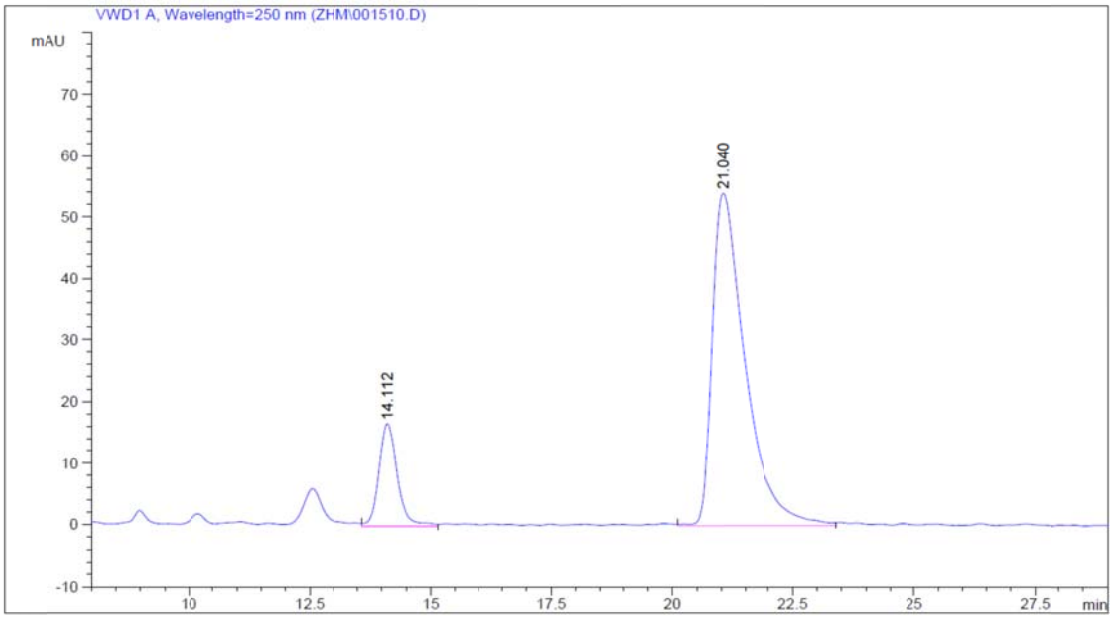
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.605	BB	0.6574	1193.34314	28.16276	16.1579
2	32.263	BB	1.0998	6192.16357	83.90727	83.8421

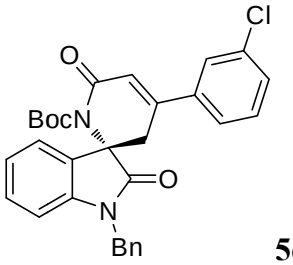


5d

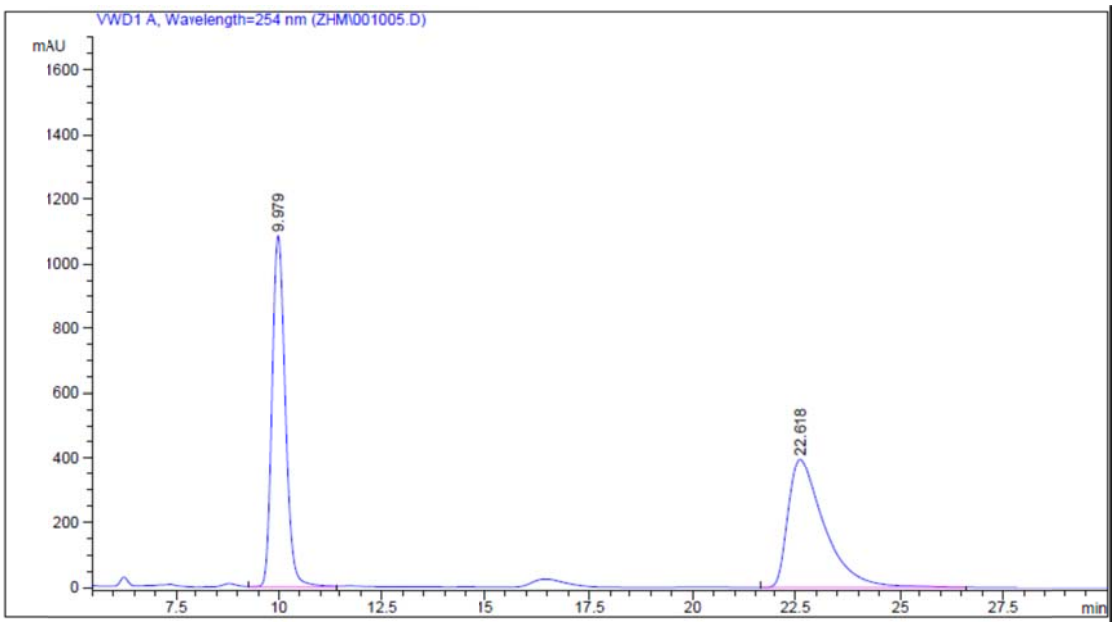


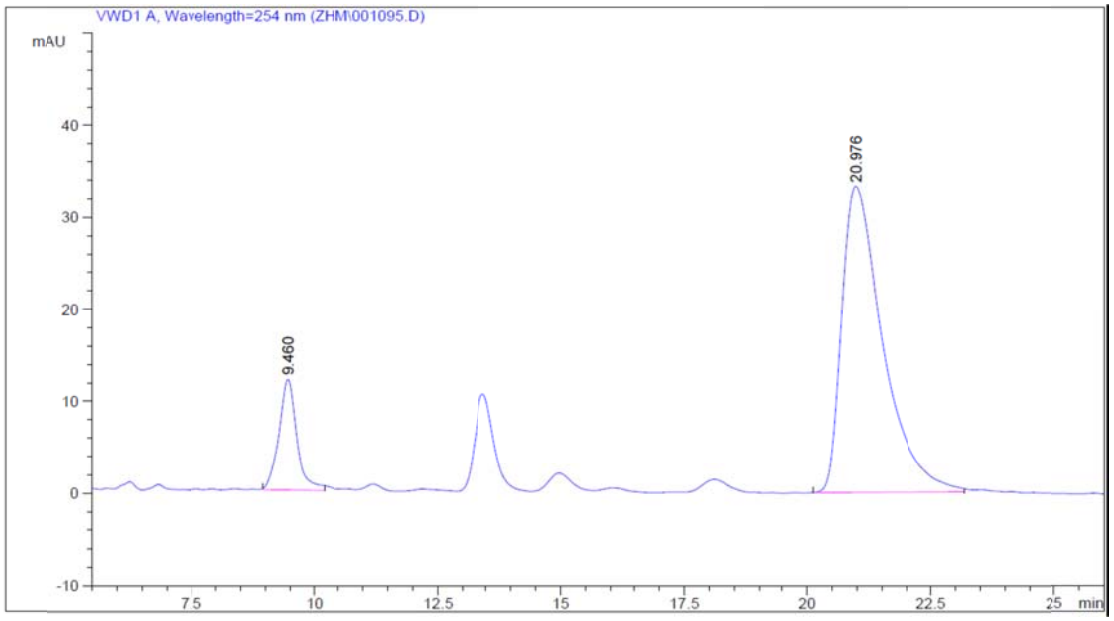


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.112	VV	0.4008	434.13733	16.62298	14.5186
2	21.040	VB	0.7033	2556.07617	54.04023	85.4814

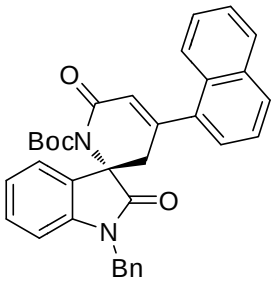


5e

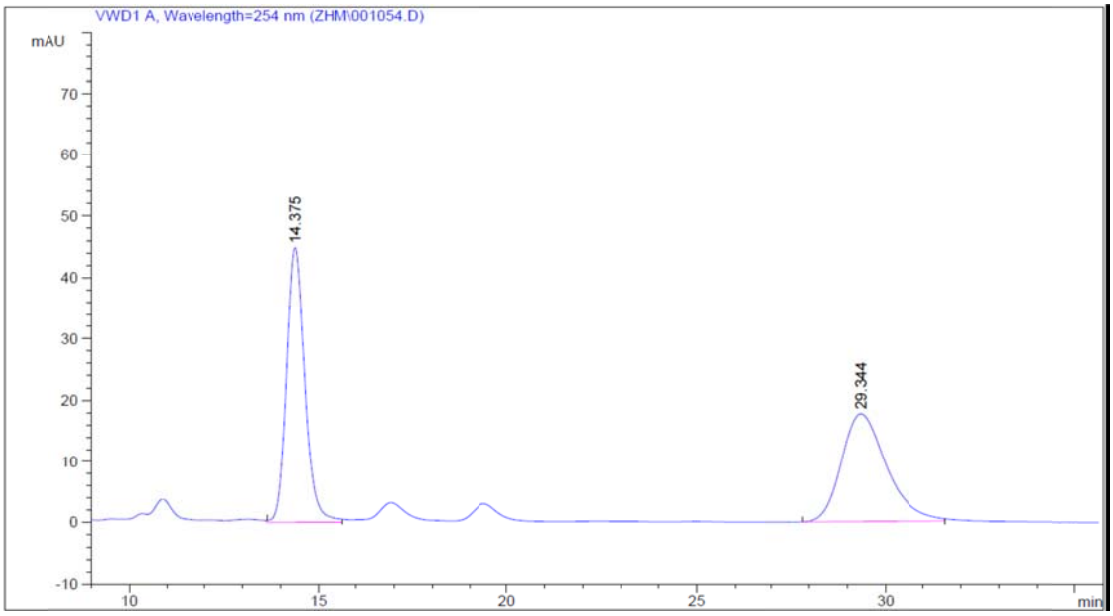


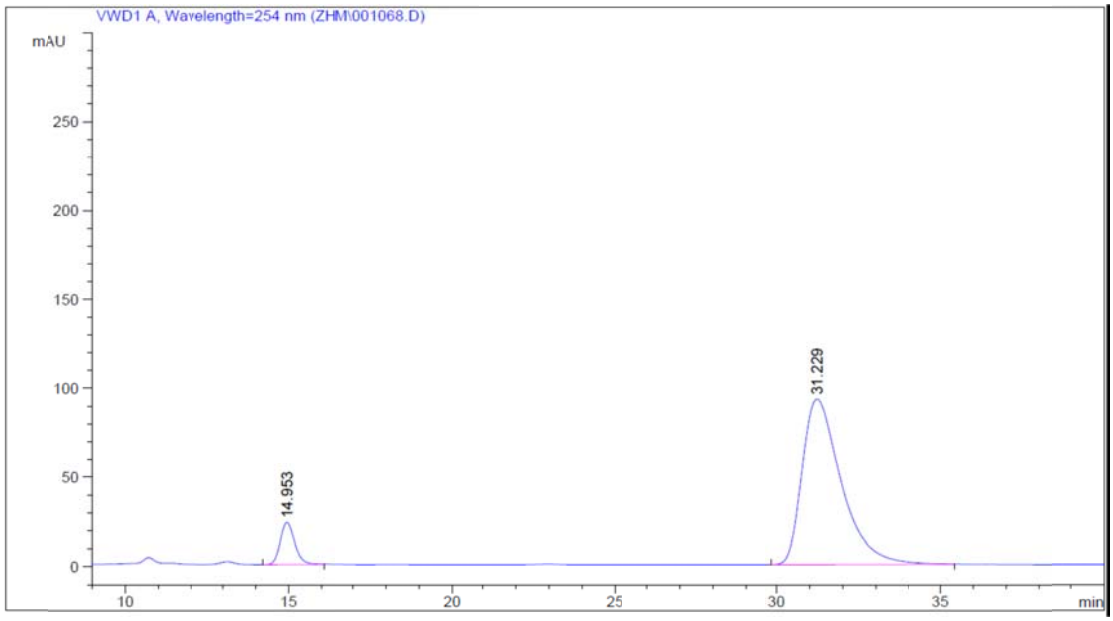


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.460	BB	0.3687	301.65298	12.01358	13.6903
2	20.976	BB	0.8595	1901.74585	33.24639	86.3097



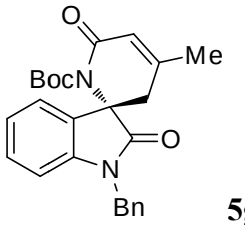
5f



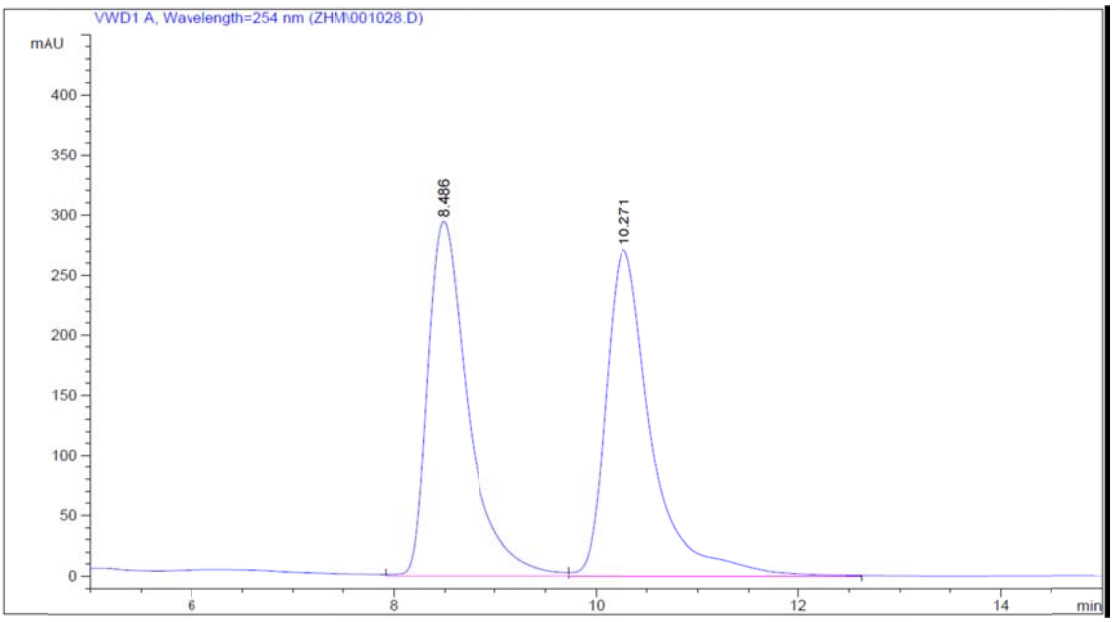


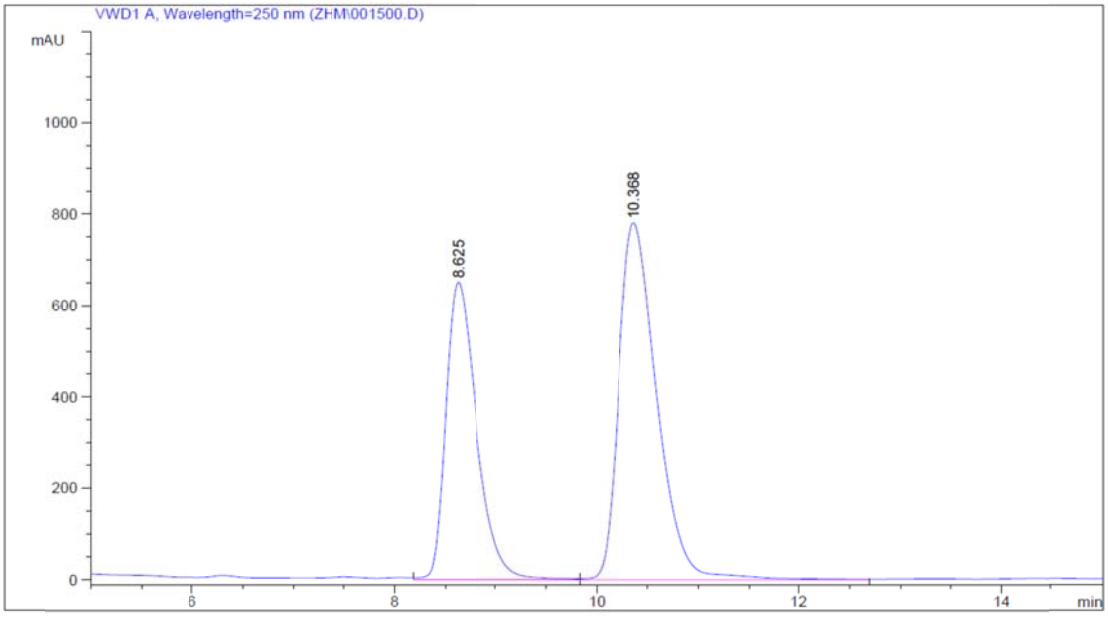
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.953	VB	0.4713	714.28961	23.29566	8.5836
2	31.229	BB	1.2450	7607.24512	92.76277	91.4164

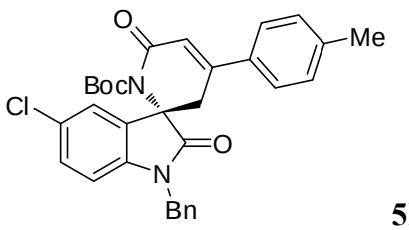


5g

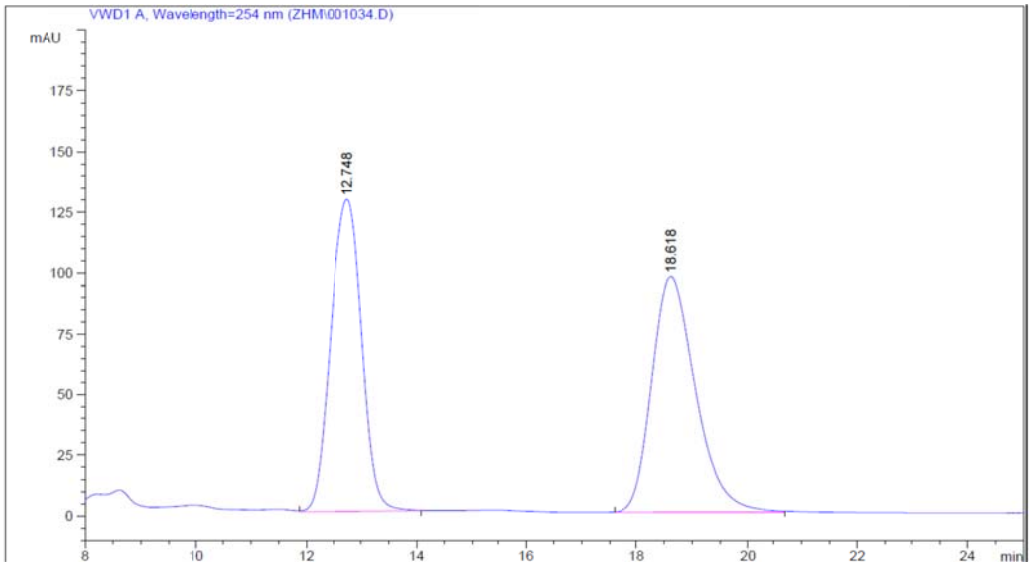


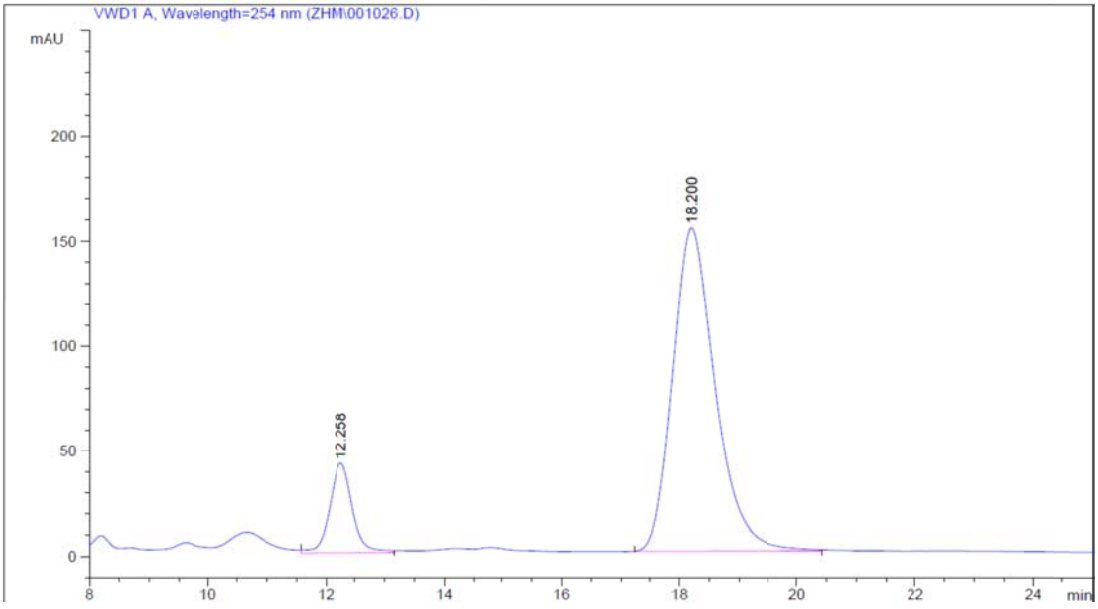


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.625	VV	0.3345	1.41127e4	650.80212	40.7804
2	10.368	VV	0.4054	2.04938e4	780.26263	59.2196



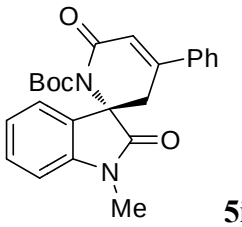
5h



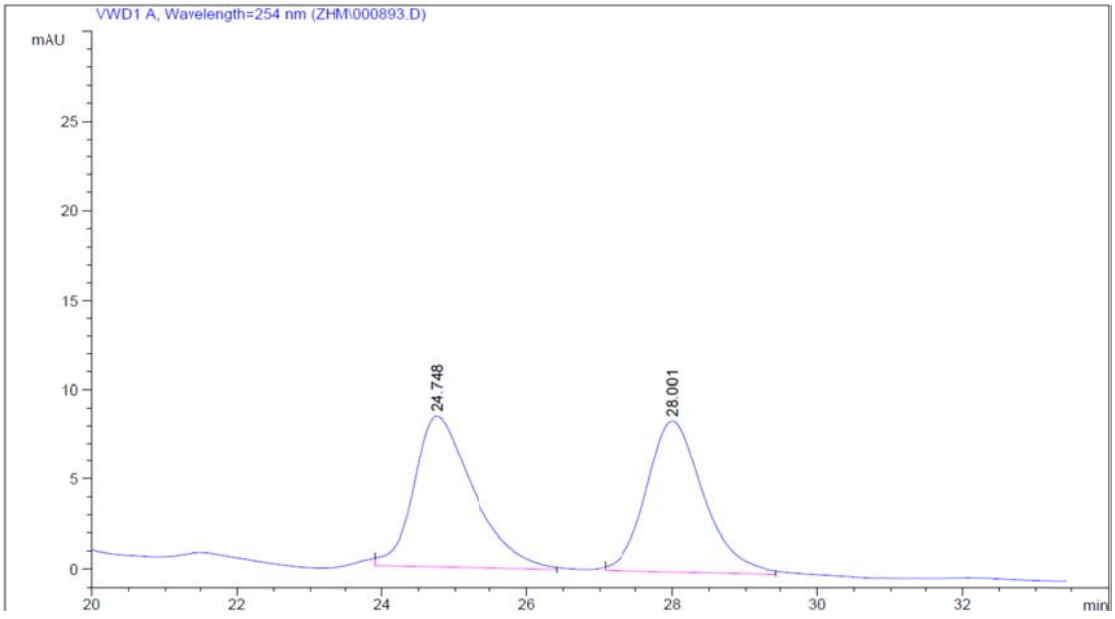


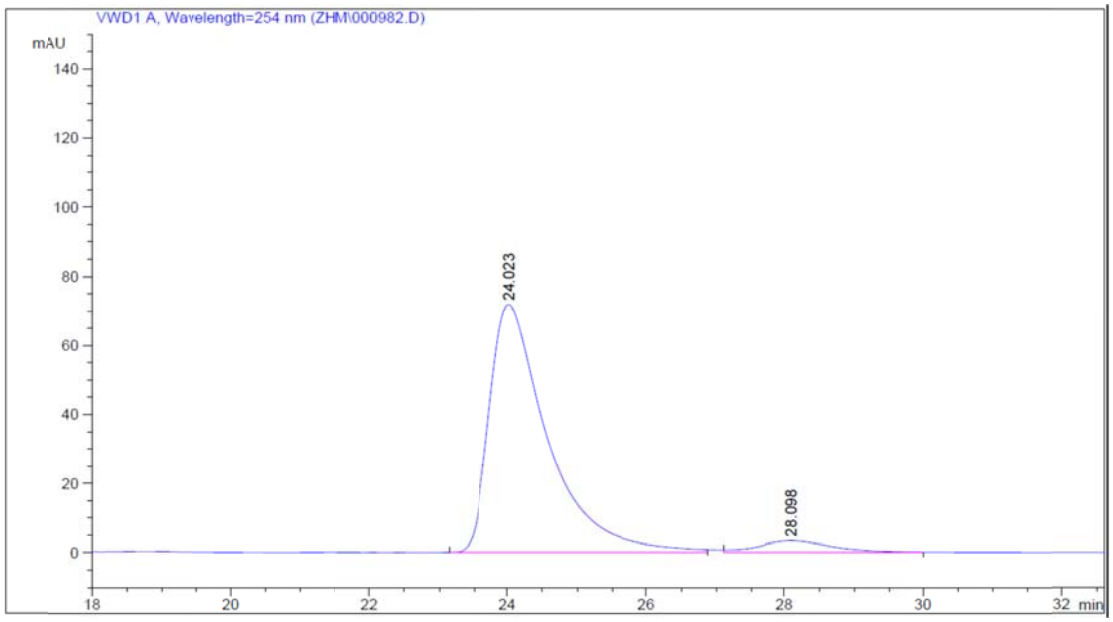
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.258	VB	0.4171	1161.48047	42.60037	13.2562
2	18.200	BB	0.7395	7600.27881	153.81854	86.7438



5i





Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.023	BB	0.8590	4175.91406	71.80349	94.4808
2	28.098	BB	1.1266	243.93996	3.33679	5.5192