Electronic Supporting Information For

Enantioselective synthesis of spirooxindole benzoquinolizines via organo-catalyzed cascade reactions

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1. General Experimental Methods

NMR spectra were all recorded on a Bruker (400M Hz) spectrometer. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal TMS on the δ scale. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. Flash column chromatography was performed using silica gel (300–400 mesh). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 300–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Enantioselectivities were determined by high-performance liquid chromatography (HPLC) with a Jasco uv-2075 plus intelligent uv/ivs detector (λ = 254 nm) and a Phenomenex Lux 5u Cmylose-2 column, Daicel IC or Daicel OD-H column. Optical rotations were measured in CH_3CH_2OH on a Jasco P-1030 polarimeter.

2. General procedure

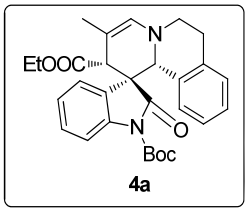
Procedure for the synthesis of spirooxindole benzoquinolizines: A solution of methyleneindolinones **2** (0.20 mmol), $PhCO_2H$ (0.020 mmol) and catalyst ***S-1*** (0.010 mmol) in toluene (1.0 mL) was added with aldehyade **1** (0.60 mmol) at rt. The resulted mixture was stirred until all the methyleneindolinones **2** was consumed (yellow disappears), then the ketimine **3** (0.30 mmol) and DABCO (0.20 mmol) were added subsequently and further stirred for 22 hours. The resulted crude product was purified by flash chromatography on a short silica gel directly to afford the desired products **4a-s.**

Procedure for gram-scale one-pot stereoselective synthesis of spirooxindole benzoquinolizines 4b: A solution of methyleneindolinones **2b** (4.0 mmol), $PhCO_2H$ (0.20 mmol) and catalyst ***S-1*** (0.040 mmol) in toluene (20.0 mL) was added with aldehyade **1a** (12.0 mmol) at rt. The resulted mixture was stirred until all the methyleneindolinones **2b** was consumed (1.5 hours), then the ketimine **3a** (6.0 mmol) and DABCO (4.0 mmol) were added subsequently and

further stirred for 22 hours. The resulted crude product was purified by flash chromatography on a short silica gel directly to afford 1.35g (65% yield, >20:1, 91% ee) of the desired product **4b**.

Procedure for the synthesis of spirooxindole benzoindolizidine 5: A solution of spirooxindole benzoquinolizines **4b** (0.10 mmol) in toluene (1.0 mL) was added with H_2O (0.10 mL), DABCO (0.10 mmol). Then NBS (0.20 mmol) was added to the mixture in three portions and further stirred for 2 hours. The resulted crude product was purified by flash chromatography on a short silica gel directly to afford the desired product **5**.

3. Characterization data



4a

(1'*R*,2'*R*,11b'*R*)-1-*tert*-butyl 2'-ethyl 3'-methyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

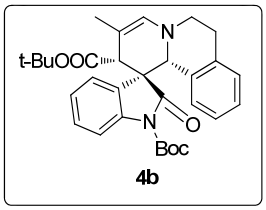
Purified by FC (PE:EtOAc = 79:1). 79% yield, white solid, 12:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 98/2); flow rate 1.0 mL/min; λ = 254 nm; τ_{minor} =15.9 min, τ_{major} = 21.5 min, 94% ee.

$[\alpha]_D^{20}$ = - 18.4 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.08 (t, *J* = 8.0 Hz, 1H), 7.01 – 6.95 (m, 3H), 6.74 (d, *J* = 6.4 Hz, 1H), 6.32 (s, 1H), 4.66 (s, 1H), 4.14 (s, 1H), 3.65 – 3.58 (m, 2H), 3.34 – 3.30 (m, 1H), 3.20 (t, *J* = 11.0 Hz, 1H), 2.62 – 2.54 (m, 1H), 2.30 (d, *J* = 15.2 Hz, 1H), 1.86 (s, 3H), 1.64 (s, 9H), 0.73 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 169.8, 148.7, 139.3, 136.8, 134.2, 131.2, 128.3, 128.2, 127.0, 126.84, 126.82, 126.0, 125.2, 123.2, 113.2, 100.6, 83.8, 63.3, 60.2, 56.8, 50.8, 47.8, 30.8, 28.1, 18.4, 13.3.

HRMS (ESI) *m/z* calcd for $C_{29}H_{32}N_2O_5$ $[M+ Na]^+$ 511.2203, found: 511.2203.



4b

(1'*R*,2'*R*,11b'*R*)-di-*tert*-butyl 3'-methyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

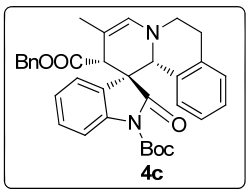
Purified by FC (PE:EtOAc = 20:1). 68% yield, white solid, >20:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 98/2); flow rate 1.0 mL/min; λ = 254 nm; τ_{minor} =7.8 min, τ_{major} = 9.3 min, 96% ee.

$[\alpha]_D^{20}$ = - 116.0 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 1H), 7.32-7.30 (m, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.00 – 6.96 (m, 3H), 6.73 (d, *J* = 6.0 Hz, 1H), 6.29 (s, 1H), 4.61 (s, 1H), 4.05 (s, 1H), 3.31 – 3.15 (m, 2H), 2.59 – 2.53 (m, 1H), 2.31 – 2.27 (m, 1H), 1.88 (s, 3H), 1.63 (s, 9H), 0.92 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 168.7, 148.8, 139.5, 136.9, 134.1, 131.2, 128.2, 128.1, 127.0, 126.9, 126.8, 126.6, 125.2, 123.2, 113.2, 101.7, 83.6, 80.8, 63.6, 57.2, 51.2, 47.4, 30.8, 28.1, 27.0, 18.5.

HRMS (ESI) *m/z* calcd for $C_{31}H_{36}N_2O_5$ $[M+ Na]^+$ 539.2516, found: 539.2516.



4c

(1'*R*,2'*R*,11b'*R*)-2'-benzyl 1-*tert*-butyl 3'-methyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

Purified by FC (PE:EtOAc = 20:1). 60% yield, white solid, >20:1 dr. The ee was

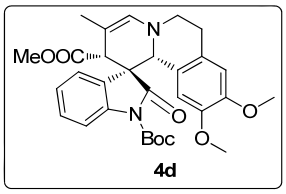
determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 95/5); flow rate 1.0 mL/min; λ = 254 nm; τ_{minor} =9.3 min, τ_{major} = 12.7 min, 91% ee.

$[\alpha]_D^{20}$ = - 77.6 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.2 Hz, 1H), 7.26-7.24 (m , 2H), 7.20-7.19 (m , 3H),7.03 (t, *J* = 7.2 Hz, 1H), 6.98 – 6.94 (m, 5H), 6.72 – 6.70 (m, 1H), 6.32 (s, 1H), 4.63 – 4.50 (m, 3H), 4.22 (s, 1H), 3.32 – 3.28 (m, 1H), 3.18 (t, *J* = 11.6 Hz, 1H), 2.57 – 2.49 (m, 1H), 2.27 (d, *J* = 15.2 Hz, 1H), 1.86 (s, 3H), 1.57 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 169.9, 148.4, 139.1, 136.8, 135.0, 134.3, 131.0, 128.3, 128.2, 128.2, 127.8, 126.9, 126.8, 126.7, 125.7, 125.2, 123.1, 113.5, 100.4, 83.5, 66.3, 63.5, 56.8, 50.5, 47.5, 30.7, 28.1, 18.4.

HRMS (ESI) *m/z* calcd for $C_{34}H_{34}N_2O_5$ $[M+Na]^+$ 573.2360, found: 573.2353



4d

(1'*R*,2'*R*,11b'*R*)-1-*tert*-butyl 2'-methyl 9',10'-dimethoxy-3'-methyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

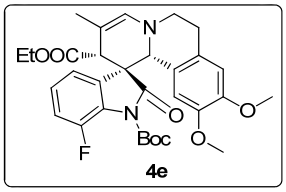
Purified by FC (PE:EtOAc = 5:1). 60% yield, white solid, 10:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 90/10); flow rate 1.0 mL/min; λ = 254 nm; τ_{major} = 20.5 min, τ_{minor} = 37.3 min, 92% ee.

$[\alpha]_D^{20}$ = - 120.8 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.12 (t, *J* = 8.6 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.84 (s, 1H), 6.31 (s, 1H), 6.25 (s, 1H), 4.65 (s, 1H), 4.13 (s, 1H), 3.85 (s, 3H), 3.71 (s, 3H), 2.34 – 2.30 (m, 1H), 3.21 (t, *J* = 11.8 Hz, 1H), 3.14 (s, 3H), 2.61 – 2.54 (m, 1H), 2.24 (d, *J* = 14.8 Hz, 1H), 1.82 (s, 3H), 1.61 (s, 9H), 0.74 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 170.3, 148.6, 147.4, 146.8, 139.1, 134.3, 129.0, 128.2, 126.8, 126.1, 123.4, 123.1, 113. 7, 111.0, 109.7, 100.0, 84.2, 62.5, 56.7, 55.7, 55.5, 52.0, 51.2, 47.9, 30.2, 28.0, 18.3.

HRMS (ESI) *m/z* calcd for $C_{30}H_{34}N_2O_7$ $[M+ Na]^+$ 557.2258, found: 557.2258



4e

(1'*R*,2'*R*,11b'*R*)-1-*tert*-butyl 2'-ethyl 7-fluoro-9',10'-dimethoxy-3'-methyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

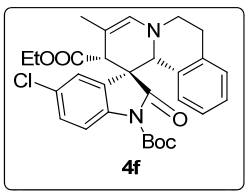
Purified by FC (PE:EtOAc = 5:1). 50% yield, white solid, 6:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 90/10); flow rate 1.0 mL/min; λ = 254 nm; τ_{minor} = 17.5 min, τ_{major} = 27.5 min, 92% ee.

$[\alpha]_D^{20}$ = - 166.8 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.2 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.91 – 6.84 (m, 2H), 6.32 (s, 1H), 6.27 (s, 1H), 4.64 (s, 1H),4.12 (s, 1H), 3.88 (s, 3H), 3.74 (s, 3H), 3.72 – 3.63 (m, 2H), 3.32 – 3.29 (m, 1H), 3.19 (t, *J* = 11.6 Hz, 1H), 2.55 – 2.47 (m, 1H), 2.23 (d, *J* = 14.8 Hz, 1H), 1.83 (s, 3H), 1.53 (s, 9H), 0.83 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 169.6, 148.9, 147.5, 147.0, 146.9, 146.4, 134.4, 129.6, 128.7, 124.2 (d, J_{C-F}= 7.0 Hz), 122.9 (d, J_{C-F} = 3.0 Hz), 122.6, 116.5 (d, J_{C-F} = 20.0 Hz), 110.9, 109.9, 100.6, 84.6, 63.0, 60.6, 57.6, 55. 7, 55.5, 51.5, 47.7, 30.1, 27.5, 18.3, 13.4.

HRMS (ESI) *m/z* calcd for $C_{31}H_{35}FN_2O_7$ $[M+ H]^+$ 567.2501, found: 567.2501.



4f

(1'*R*,2'*R*,11b'*R*)-1-*tert*-butyl 2'-ethyl 5-chloro-3'-methyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

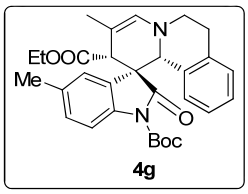
Purified by FC (PE:EtOAc = 20:1). 53% yield, white solid, 7:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 95/5); flow rate 1.0 mL/min; λ = 254 nm; τ_{major} =6.3 min, τ_{minor} = 8.5 min, 83% ee.

$[\alpha]_D^{20}$ = - 93.8 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 1H), 7.30-7.29 (d, *J* = 0.8 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 1H), 6.99 – 6.97 (m, 2H), 6.78 (s, 1H), 6.30 (s, 1H), 4.65 (s, 1H), 4.14 (s, 1H), 3.68 (t, *J* = 7.0 Hz, 2H), 3.37 – 3.33 (m, 1H), 3.21 (t, *J* = 10.8 Hz, 1H), 2.63 – 2.55 (m, 1H), 2.37 (d, *J* = 15.2 Hz, 1H), 1.84 (s, 3H), 1.63 (s, 9H), 0.78 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 169.7, 148.5, 137. 9, 136.7, 134.1, 130.8, 128.7, 128.6, 128.1, 128.0, 127.0, 126.8, 125.3, 114.4, 100.6, 84.5, 63.4, 60.4, 56. 7, 50.8, 47.6, 30.8, 28.1, 18.4, 13.4.

HRMS (ESI) *m/z* calcd for $C_{29}H_{31}ClN_2O_5$ $[M+H]^+$ 523.1994, found: 523.1998.



4g

(1'*R*,2'*R*,11b'*R*)-1-*tert*-butyl 2'-ethyl 3',5-dimethyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

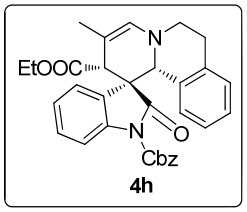
Purified by FC (PE:EtOAc = 20:1). 53% yield, white solid, 11:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 95/5); flow rate 1.0 mL/min; λ = 254 nm; τ_{major} =7.8 min, τ_{minor} = 9.9 min, 90% ee.

$[\alpha]_D^{20}$ = - 62.1 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.12 (s , 1H), 6.98 – 6.96 (m, 2H), 6.86 (d, *J* = 8.0Hz, 1H), 6.75 – 6.73 (m, 1H), 6.32 (s, 1H), 4.64 (s, 1H), 4.13 (s, 1H), 3.68 – 3.56 (m, 2H), 3.34 – 3.30 (m, 1H), 3.20 (t, *J* = 12.8 Hz, 1H), 2.60 – 2.52 (m, 1H), 2.32 (d, *J* = 14.8 Hz, 1H), 2.27 (s, 3H), 1.86 (s, 3H), 1.63 (s, 9H), 0.74 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 169.9, 148.8, 136.9, 136.7, 134.2, 132.6, 131.3, 128.6, 128.3, 127.3, 126.9, 126. 8, 126.0, 125.2, 113.0, 100.8, 83.6, 63.4, 60.2, 57.0, 50.7, 47.5, 30.8, 28.1, 21.1, 18.5, 13.3.

HRMS (ESI) *m/z* calcd for $C_{30}H_{34}N_2O_5$ $[M+H]^+$ 503.2540, found: 503.2540.



4h

(1'*R*,2'*R*,11b'*R*)-1-benzyl 2'-ethyl 3'-methyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

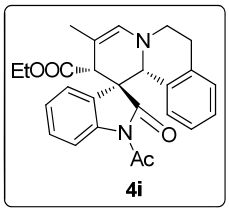
Purified by FC (PE:EtOAc = 20:1). 62% yield, white solid, 18:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 95/5); flow rate 1.0 mL/min; λ = 254 nm; τ_{major} = 15.3 min, τ_{minor} = 22.4 min, 90% ee.

$[\alpha]_D^{20}$ = - 69.8 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.32 (m, 4H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 3.8 Hz, 1H), 6.64 (t, *J* = 7.6 Hz, 1H), 6.32 (s, 1H), 5.51 – 5.38 (m, 2H), 4.67 (s, 1H), 4.16 (s, 1H), 3.64 – 3.54 (m, 2H), 3.33 – 3.29 (m, 1H), 3.18 (t, *J* = 11.8Hz, 1H), 2.59 – 2.52 (m, 1H), 2.28 (d, *J* = 14.6 Hz, 1H), 1.86 (s, 3H), 0.64 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 169.7, 150.2, 138.8, 136.7, 135.2, 134.2, 130.9, 128.6, 128.4, 128.3, 128.1, 126.92, 126.87, 126.7, 126.1, 125.3, 123.6, 113.4, 100.6, 68.2, 63.4, 60.3, 57.0, 50.8, 47.5, 30.7, 18.4, 13.2.

HRMS (ESI) *m/z* calcd for $C_{32}H_{30}N_2O_5$ [M+ Na]$^+$ 545.2047, found: 545.2047.



4i

(1'*R*,2'*R*,11b'*R*)-ethyl 1-acetyl-3'-methyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-2'-carboxylate

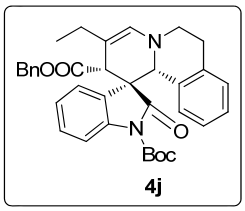
Purified by FC (PE:EtOAc = 20:1). 58% yield, white solid, 8:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 95/5); flow rate 1.0 mL/min; λ = 254 nm; τ_{minor}= 6.0 min, τ_{major} = 6.9 min, 89% ee.

$[\alpha]_D^{20}$ = - 161.1 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8 Hz, 1H), 7.36 (d, *J* = 6.4 Hz, 1H), 7.23 – 7.20 (m, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.07 – 6.98 (m, 3H), 6.76 – 6.74 (m, 1H), 6.35 (s, 1H), 4.70 (s, 1H), 4.13 (s, 1H), 3.60 (q, *J* = 6.4 Hz, 2H), 3.37 – 3.32 (m, 1H), 3.22 (t, *J* = 11.8Hz, 1H), 2.74 (s, 3H), 2.61 – 2.53 (m, 1H), 2.30 (d, *J* = 15.2 Hz, 1H), 1.87 (s, 3H), 0.70 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 170.2, 169.7, 139.6, 137.0, 134.2, 131.1, 128.6, 128.5, 127.2, 126.8, 126.4, 126.1, 125.3, 124.0, 114.9, 100.5, 63.3, 60.4, 57.1, 51.2, 47.4, 30.7, 26.7, 18.4, 13.3.

HRMS (ESI) *m/z* calcd for $C_{26}H_{26}N_2O_4$ [M+ Na]$^+$ 453.1785, found: 453.1785.



4j

(1'*R*,2'*R*,11b'*R*)-2'-benzyl 1-*tert*-butyl 3'-ethyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

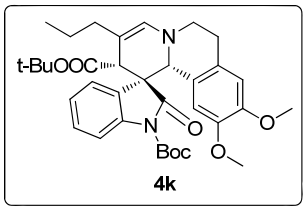
Purified by FC (PE:EtOAc = 20:1). 65% yield, white solid, 5:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 95/5); flow rate 1.0 mL/min; λ = 254 nm; τ_{major} = 6.2 min, τ_{minor} = 9.5 min, 88% ee.

$[\alpha]_D^{20}$ = - 47.2 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 3H), 7.21 – 7.19 (m, 3H), 7.04 – 6.94 (m, 6H), 6.72 – 6.70 (m, 1H), 6.33 (s, 1H), 4.62 – 4.51 (m, 3H), 4.32 (s, 1H), 3.34 – 3.30 (m, 1H), 3.21 (t, *J* = 12.8Hz, 1H), 2.58 – 2.50 (m, 1H), 2.36 – 2.17 (m, 3H), 1.57 (s, 9H), 1.10 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 170.1, 148.4, 139.1, 136.9, 135.0, 133.3, 131.0, 128.3, 128.2, 128.2, 127.8, 127.0, 126.9, 126.8, 125.7, 125.2, 123.2, 113.5, 106.8, 83.5, 66.3, 63.6, 56.6, 48.9, 47.7, 30.8, 28.1, 25.3, 13.8.

HRMS (ESI) *m/z* calcd for $C_{35}H_{36}N_2O_5$ $[M+ Na]^+$ 587.2516, found: 587.2516.



4k

(1'*R*,2'*R*,11b'*R*)-di-*tert*-butyl 9',10'-dimethoxy-2-oxo-3'-propyl-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

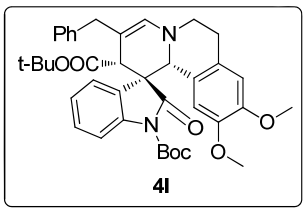
Purified by FC (PE:EtOAc = 5:1). 72% yield, white solid, 8:1 dr. The ee was determined by chiral HPLC using a Daicel OD-H column (hexane/*i*-PrOH = 90/10); flow rate 1.0 mL/min; λ = 254 nm; τ_{major} = 4.3 min, τ_{minor} = 4.9 min, 94% ee.

$[\alpha]_D^{20}$ = - 170.4 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.84 (s, 1H), 6.31 (s, 1H), 6.23 (s, 1H), 4.58 (s, 1H), 4.06 (s, 1H), 3.85 (s, 3H), 3.71 (s, 3H), 3.32 – 3.29 (m, 1H), 3.19 (t, *J* = 10.6 Hz, 1H), 2.58 – 2.50 (m, 1H), 2.42 – 2.36 (m, 1H), 2.22 (d, *J* = 14.8 Hz, 1H), 2.06 – 1.98 (m, 1H), 1.61 (s, 9H), 0.96 (s, 14H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 168.8, 148.7, 147.3, 146.7, 139.5, 134.0, 129.1, 128.0, 127.0, 126.6, 123.3, 123.2, 113.6, 110.9, 109.9, 105.6, 84.0, 80.6, 63.1, 56.8, 55.7, 55.5, 50.3, 47.8, 34.5, 30.2, 28.0, 27.1, 21.8, 13. 8.

HRMS (ESI) *m/z* calcd for $C_{35}H_{44}N_2O_7$ $[M+H]^+$ 605.3221, found: 605.3221.



4l

(1'*R*,2'*R*,11b'*R*)-di-*tert*-butyl 3'-benzyl-9',10'-dimethoxy-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

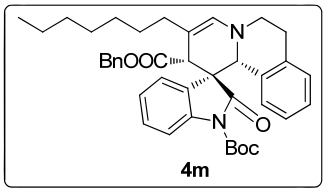
Purified by FC (PE:EtOAc = 5:1). 85% yield, white solid, 8:1 dr. The ee was determined by chiral HPLC using a Daicel OD-H column (hexane/*i*-PrOH = 90/10); flow rate 1.0 mL/min; λ = 254 nm; τ_{major} = 5.5 min, τ_{minor} = 6.2 min, 92% ee.

$[\alpha]_D^{20}$ = - 59.6 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.31-7.18 (m , 5H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.80 (s, 1H), 6.38 (s, 1H), 6.22 (s, 1H), 4.58 (s, 1H), 3.84 (s, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.48 – 3.11 (m, 4H), 2.57 – 2.49 (m, 1H), 2.21 (t, *J* = 14.8 Hz, 1H), 1.58 (s, 9H), 0.95 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 168.8, 148.7, 147.4, 146.7, 140.8, 139.5, 135.1, 129.1, 128.8, 128.3, 128.1, 126.9, 126.4, 125.9, 123.3, 122.9, 113.7, 110.9, 110.0, 105.5, 84.0, 80.7, 62.9, 56.8, 55.7, 55.4, 49.8, 47.8, 39.0, 30.2, 28.0, 27.0.

HRMS (ESI) *m/z* calcd for $C_{39}H_{44}N_2O_7$ $[M+H]^+$ 653.3221, found: 653.3221.



4m

(1'*R*,2'*R*,11b'*R*)-2'-benzyl 1-*tert*-butyl 3'-heptyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

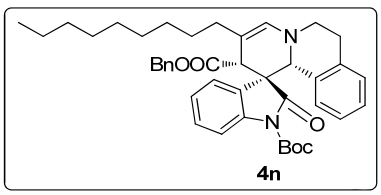
Purified by FC (PE:EtOAc = 50:1). 80% yield, yellow oil, 10:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 95/5); flow rate 1.0 mL/min; λ = 254 nm; τ_{major} = 4.3 min, τ_{minor} = 5.8 min, 88% ee.

$[\alpha]_D^{20}$ = - 35.3 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 3H), 7.21 – 7.20 (m, 3H), 7.05 – 6.94 (m, 6H), 6.73 – 6.70 (m, 1H), 6.33 (s, 1H), 4.64 – 4.48 (m, 3H), 4.29 (s, 1H), 3.33 – 3.30 (m, 1H), 3.21 (t, *J* = 12.6Hz, 1H), 2.57 – 2.49 (m, 1H), 2.36 – 2.26 (m, 2H), 2.12 – 2.04 (m, 1H), 1.57 (s, 9H), 1.28 – 1.26 (m, 10H), 0.90 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 170.1, 148.5, 139.2, 136.9, 135.1, 133.8, 131.0, 128.3, 128.2, 128.2, 127.9, 127.0, 126. 9, 126.8, 125.7, 125.2, 123.2, 113.5, 105.1, 83.4, 66.3, 63.6, 56. 6, 48. 9, 47.7, 32.5, 31.9, 30.8, 29.7, 29.4, 29.2, 29.0, 28.1, 22.7, 14.1.

HRMS (ESI) *m/z* calcd for $C_{40}H_{46}N_2O_5$ $[M+Na]^+$ 657.3299, found: 657.3299.



4n

(1'*R*,2'*R*,11b'*R*)-2'-benzyl 1-*tert*-butyl 3'-nonyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

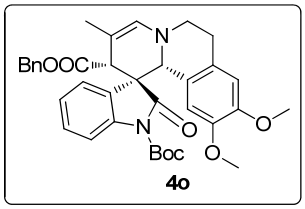
Purified by FC (PE:EtOAc = 50:1). 90% yield, yellow oil, 8:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 95/5); flow rate 1.0 mL/min; λ = 254 nm; τ_{major} = 4.1 min, τ_{minor} = 5.1 min, 87% ee.

$[\alpha]_D^{20}$ = - 20.9 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 3H), 7.21 – 7.19 (m, 3H), 7.04 – 6.94 (m, 6H), 6.72 – 6.70 (m, 1H), 6.33 (s, 1H), 4.61 – 4.51 (m, 3H), 4.29 (s, 1H), 3.33 – 3.29 (m, 1H), 3.20 (t, *J* = 12.6Hz, 1H), 2.57 – 2.49 (m, 1H), 2.37 – 2.25 (m, 2H), 2.12 – 2.04 (m, 1H), 1.57 (s, 9H), 1.33 – 1.23 (m, 14H), 0.89 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 170.1, 148.4, 139.1, 136.9, 135.1, 133.8, 131.0, 128.3, 128.2, 128.2, 127.9, 127.0, 126.9, 126.8, 125.7, 125.2, 123.2, 113.5, 105.1, 83.4, 66.3, 63.6, 56.5, 48.9, 47.6, 32.5, 31.9, 30.8, 29.6, 29.5, 29.4, 29.3, 29.0, 28.1, 22.7, 14.1.

HRMS (ESI) *m/z* calcd for $C_{42}H_{50}N_2O_5$ $[M+ Na]^+$ 663.3792, found: 663.3792.



4o

(1'*R*,2'*R*,11b'*R*)-2'-benzyl 1-*tert*-butyl 9',10'-dimethoxy-3'-methyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

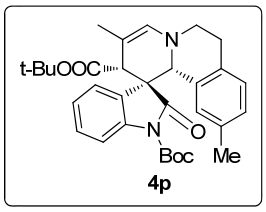
Purified by FC (PE:EtOAc = 5:1). 54% yield, white solid, 8:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 95/5); flow rate 1.0 mL/min; λ = 254 nm; τ_{major} = 34.2 min, τ_{minor} = 38.7 min, 90% ee.

$[\alpha]_D^{20}$ = - 116.6 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 6.8 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.22 – 7.20 (m, 3H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.01 – 6.97 (m, 3H), 6.80 (s, 1H), 6.32 (s, 1H), 6.22 (s, 1H), 4.66 – 4.46 (m, 3H), 4.21 (s, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.32 – 3.28 (m, 1H), 3.19 (t, *J* = 12.2Hz, 1H), 2.52 – 2.44 (m, 1H), 2.19 (d, *J* = 14.8 Hz, 1H), 1.84 (s, 3H), 1.50 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 169.9, 148.2, 147.4, 146.8, 139.2, 135.1, 134.4, 129.0, 128.3, 128.2, 127. 9, 127.8, 126. 9, 125.9, 123.3, 122. 9, 113.8, 111.0, 109.8, 100.4, 84.0, 66.1, 63.1, 56.8, 55.7, 55.5, 51.4, 47.7, 30.2, 27.9, 18.4.

HRMS (ESI) *m/z* calcd for $C_{36}H_{38}N_2O_7$ $[M+ Na]^+$ 633.2571, found: 633.2571.



4p

(1'*R*,2'*R*,11b'*R*)-di-*tert*-butyl 3',10'-dimethyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

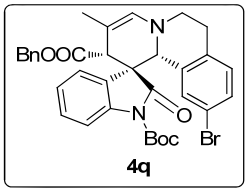
Purified by FC (PE:EtOAc = 20:1). 73% yield, white solid, > 20:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 98/2); flow rate 1.0 mL/min; λ = 254 nm; τ_{minor} =6.7 min, τ_{major} = 7.7 min, 96% ee.

$[\alpha]_D^{20}$ = - 148.1 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.15 (s , 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.0 Hz, 1H), 6.77 (d, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 7.2 Hz, 1H), 6.29 (s, 1H), 4.56 (s, 1H), 4.03 (s, 1H), 3.28 – 3.12 (m, 2H), 2.54 (t, *J* = 10.2 Hz, 1H), 2.27 – 2.23 (m, 4H), 1.86 (s, 3H), 1.64 (s, 9H), 0.93 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 168.7, 149.0, 139.5, 134.8, 134.2, 133.7, 131.2, 128.0, 127.5, 127.4, 126.8, 126.7, 123.2, 113.2, 101.6, 83.7, 80.8, 63.4, 57.2, 51.4, 47.7, 30.4, 28.1, 27.0, 21.0, 18.4.

HRMS (ESI) *m/z* calcd for $C_{32}H_{38}N_2O_5$ [M+ H]$^+$ 531.2853, found: 531.2853.



4q

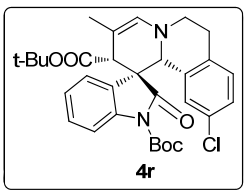
(1'*R*,2'*R*,11b'*R*)-2'-benzyl 1-*tert*-butyl 10'-bromo-3'-methyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

Purified by FC (PE:EtOAc = 20:1). 47% yield, white oil, 12:1 dr. The ee was determined by chiral HPLC using a Daicel OD-H column (hexane/*i*-PrOH = 99/1); flow rate 0.7 mL/min; λ = 254 nm; τ_{major} = 12.4 min, τ_{minor} = 13.3 min, 94% ee. $[\alpha]_D^{20}$ = - 120.7 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m , 2H), 7.24-7.13 (m , 4H), 6.89 (t, *J* = 8.0 Hz, 2H), 6.91 – 6.88 (m, 3H), 6.53 (d, *J* = 8.0 Hz, 2H), 6.23 (s, 1H), 4.56 – 4.38 (m, 3H), 4.11 (s, 1H), 3.26 – 3.22 (m, 1H), 3.06 (t, *J* = 11.4 Hz, 1H), 2.47 – 2.39 (m, 1H), 2.19 (d, *J* = 15.6 Hz, 1H), 1.77 (s, 3H), 1.53 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 169.7, 148.5, 139.3, 135.9, 134.9, 134.1, 133.5, 130.0, 129.9, 129.8, 128.5, 128.4, 128.3, 127.9, 126.7, 125.4, 123.2, 119.2, 113.6, 101.1, 84.1, 66.4, 62.8, 56.6, 51.1, 47.4, 30.4, 28.1, 18.4, 1.0.

HRMS (ESI) *m/z* calcd for $C_{34}H_{33}BrN_2O_5$ [M+ H]$^+$ 629.1646, found: 629.1646.



4r

(1'*R*,2'*R*,11b'*R*)-di-*tert*-butyl 10'-chloro-3'-methyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

Purified by FC (PE:EtOAc = 20:1). 58% yield, white solid, >20:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column

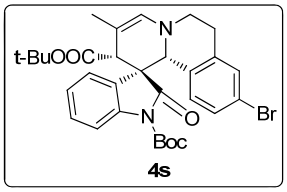
(hexane/*i*-PrOH = 98/2); flow rate 1.0 mL/min; λ = 254 nm; τ_{minor} = 6.0 min, τ_{major} = 6.8 min, 98% ee.

$[\alpha]_D^{20}$ = - 234.6 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 7.00 – 6.93 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.27 (s, 1H), 4.53 (s, 1H), 4.02 (s, 1H), 3.32 – 3.28 (m, 1H), 3.13 (t, *J* = 10.8 Hz, 1H), 2.58 – 2.50 (m, 1H), 2.29 (d, *J* = 15.2 Hz, 1H), 1.86 (s, 3H), 1.67 (s, 9H), 0.93 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 168.5, 149.0, 139.6, 135.4, 133.9, 133.2, 131.2, 129.5, 128.3, 127.0, 126.9, 126.8, 126.3, 123.3, 113.4, 102.2, 84.1, 81.0, 63.1, 57.0, 51.4, 47.4, 30.4, 28.0, 27.0, 18.4.

HRMS (ESI) *m/z* calcd for $C_{31}H_{35}ClN_2O_5$ $[M+H]^+$ 551.2307, found: 551.2307.



4s

(1'*R*,2'*R*,11b'*R*)-di-*tert*-butyl 9'-bromo-3'-methyl-2-oxo-2',6',7',11b'-tetrahydrospiro[indoline-3,1'-pyrido[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

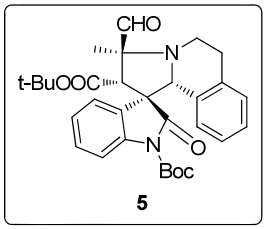
Purified by FC (PE:EtOAc = 20:1). 62% yield, white solid, >20:1 dr. The ee was determined by chiral HPLC using a Phenomenex Lux 5u Cmylose -2 column (hexane/*i*-PrOH = 95/5); flow rate 1.0 mL/min; λ = 254 nm; τ_{minor} = 4.8 min, τ_{major} = 5.9 min, 97% ee.

$[\alpha]_D^{20}$ = -113.2 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.14 – 7.08 (m, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.90 (s, 1H), 6.27 (s, 1H), 4.54 (s, 1H), 4.03 (s, 1H), 3.31 – 3.27 (m, 1H), 3.14 (t, *J* = 10.8 Hz, 1H), 2.57 – 2.50 (m, 1H), 2.26 (d, *J* = 15.2 Hz, 1H), 1.86 (s, 3H), 1.64 (s, 9H), 0.93 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 168.5, 148.6, 139.4, 139.2, 133.9, 131.1, 130.4, 128.8, 128.4, 128.3, 126.9, 126.2, 123.4, 120.8, 113.4, 102.2, 83. 9, 81.0, 63.2, 57.0, 51.2, 47.1, 30.6, 28.1, 27.0, 18.4.

HRMS (ESI) *m/z* calcd for $C_{31}H_{35}BrN_2O_5$ $[M+H]^+$ 595.1802, found: 595.1764.



5

(1'*R*,2'*S*,3'*S*,10b'*R*)-di-*tert*-butyl 3'-formyl-3'-methyl-2-oxo-3',5',6',10b'-tetrahydro-2'*H*-spiro[indoline-3,1'-pyrrolo[2,1-*a*]isoquinoline]-1,2'-dicarboxylate

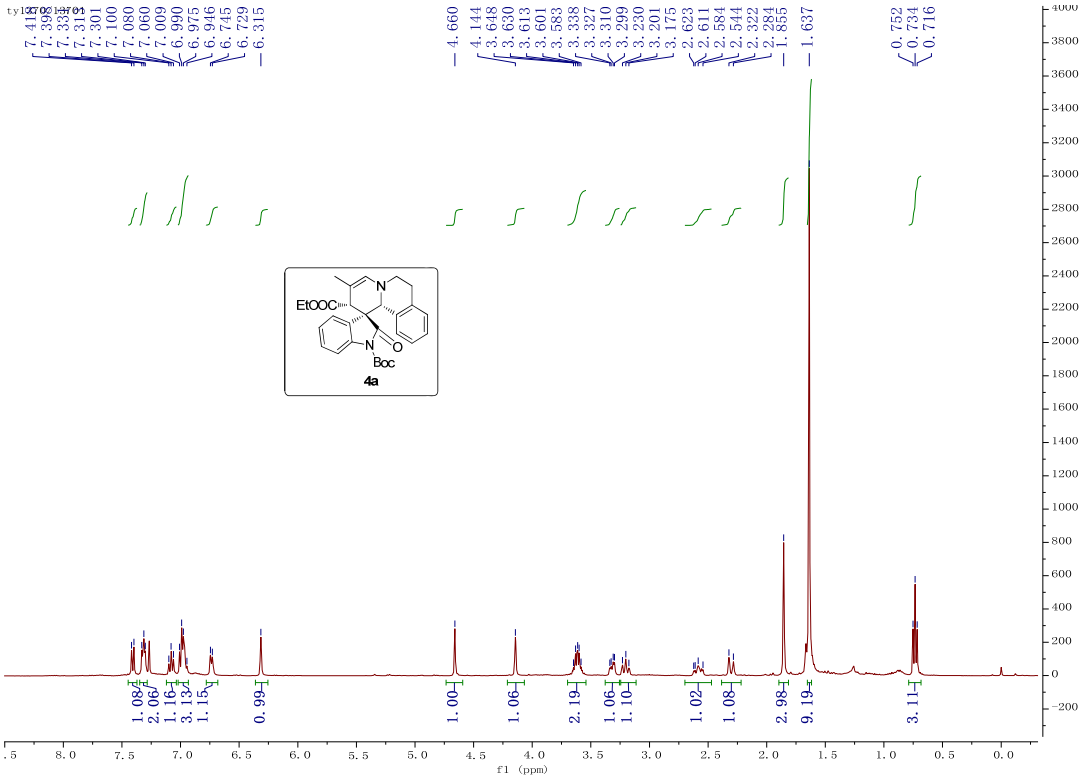
Purified by FC (PE:EtOAc = 5:1). 63% yield, white solid, 15:1 dr. The ee was determined by chiral HPLC using a Daicel IC column (hexane/*i*-PrOH = 95/5); flow rate 0.7 mL/min; λ = 214 nm; τ_{minor} = 17.2 min, τ_{major} = 20.1 min, 95% ee. $[\alpha]_D^{20}$ = +6.0 (c = 1.0, CH_3CH_2OH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H)，7.76 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.12 (t, *J* = 8.6 Hz, 1H), 6.95 – 6.80 (m, 4H), 6.58 (d, *J* = 8.0 Hz, 1H), 4.74 (s, 1H), 4.26 (s, 1H), 3.52 – 3.44 (m, 1H), 3.06 – 3.97 (m, 2H), 2.74 – 2.67 (m, 1H), 1.70 (s, 9H), 1.67 (s, 3H), 1.04 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 176.2, 166.6, 149.2, 140.5, 135.2, 132.8, 129.0, 128.2, 127.2, 126.6, 125.8, 124.7, 124.0, 123.9, 114.2, 84.5, 82.1, 68.5, 67.6, 59.0, 56. 6, 41.3, 31.2, 28.1, 27.3, 15.8.

HRMS (ESI) *m/z* calcd for $C_{31}H_{36}N_2O_6$ $[M+H]^+$ 533.2646, found: 533.2653.

4. ^{1}H and ^{13}C NMR Spectra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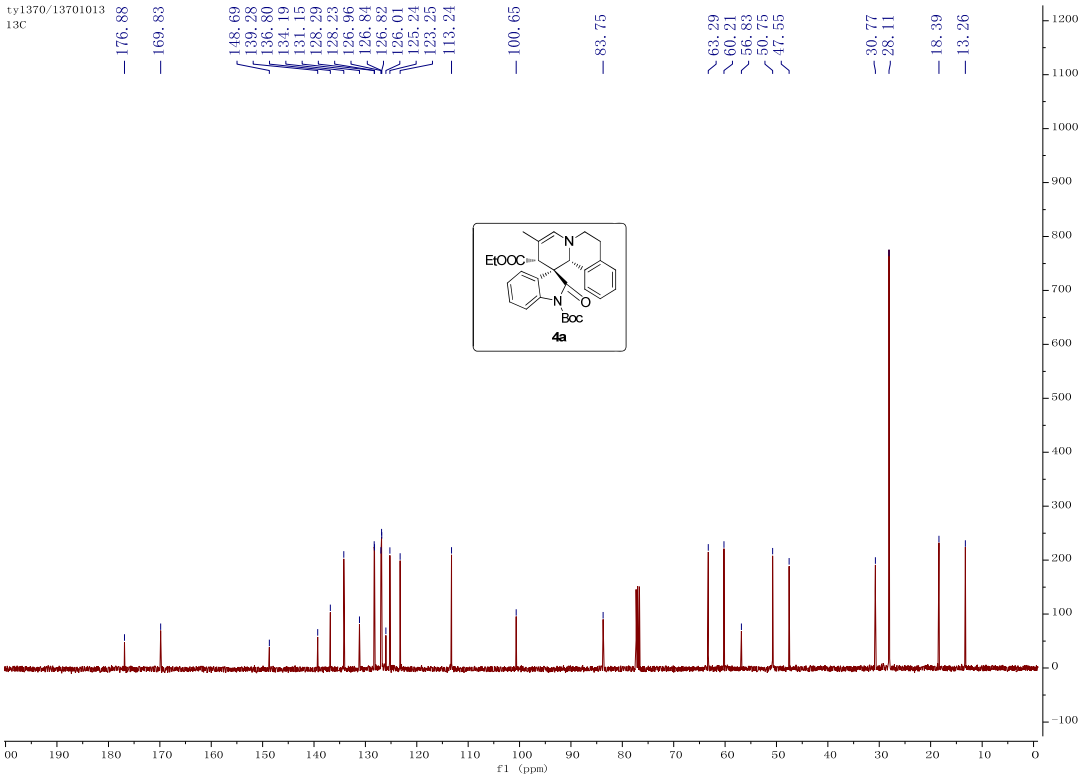
7.080
7.060
7.009
6.990
6.975
6.946
6.745
6.729
6.315
4.660
4.144
3.648
3.630
3.613
3.601
3.583
3.338
3.327
3.310
3.299
3.230
3.201
3.175
2.623
2.611
2.584
2.544
2.322
2.284
1.855
1.637
0.752
0.734
0.716
EtOOC
N
O
Boc
4a
1.08
2.06
1.16
3.13
1.15
0.99
1.00
1.06
2.19
1.06
1.10
1.02
1.08
2.98
9.19
3.11
f1 (ppm)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136.80
134.19
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128.23
126.96
126.84
126.82
126.01
125.24
123.25
113.24
100.65
83.75
63.29
60.21
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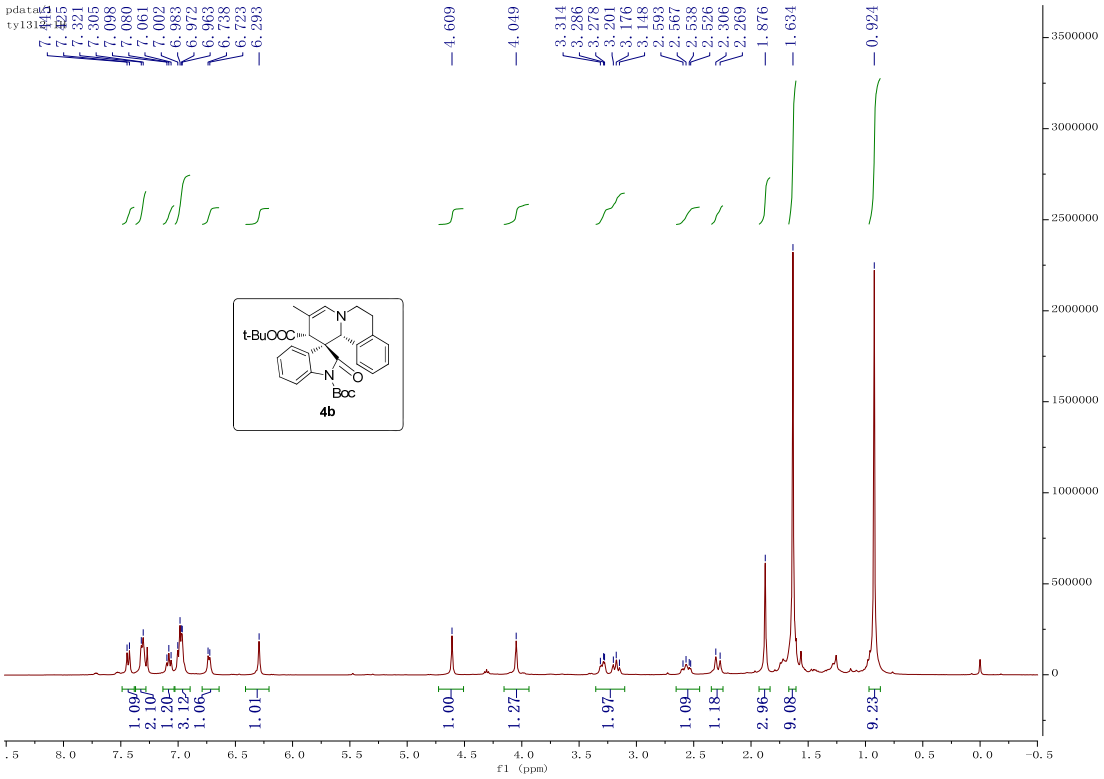
18.39
13.26
EtOOC
N
O
Boc
4a
f1 (ppm)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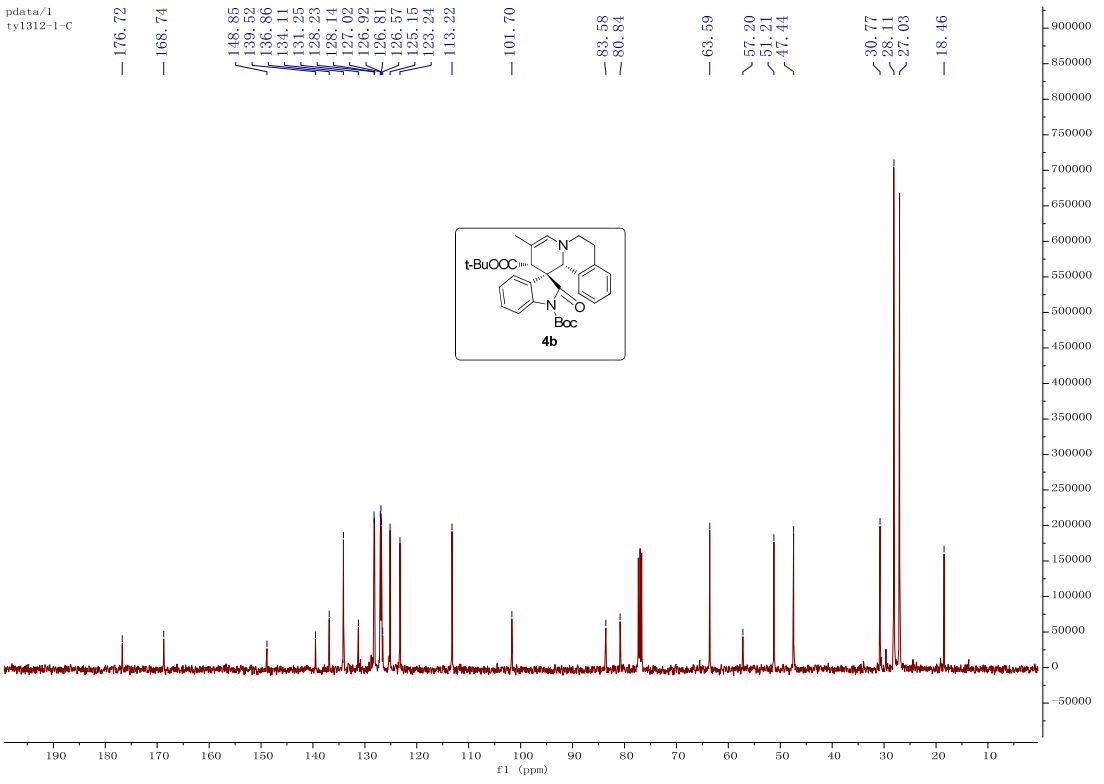
6.963
6.738
6.723
6.293
4.609
4.049
3.314
3.286
3.278
3.201
3.176
3.148
2.593
2.567
2.538
2.526
2.306
2.269
1.876
1.634
0.924
t-BuOOC
N
O
Boc
4b
1.09
2.10
1.20
3.12
1.06
1.01
1.00
1.27
1.97
1.09
1.18
2.96
9.08
9.23
f1 (ppm)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127.02
126.92
126.81
126.57
125.15
123.24
113.22
101.70
83.58
80.84
63.59
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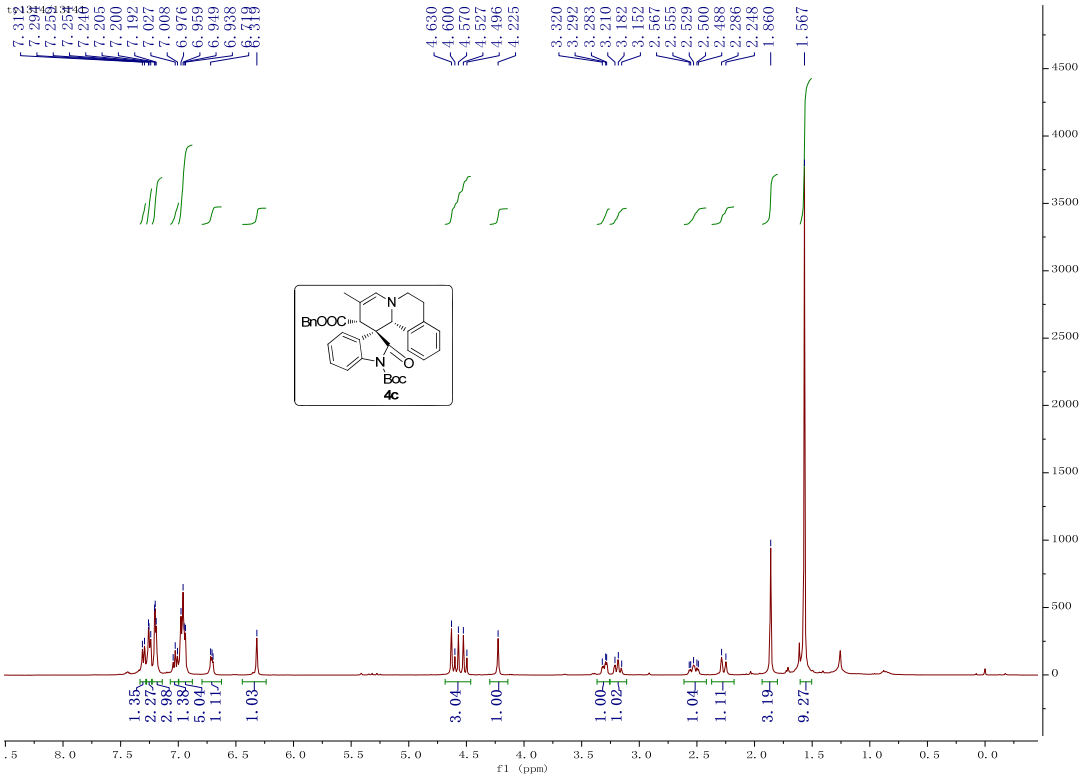
O
Boc
4b
f1 (ppm)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7.192
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6.949
6.938
6.319
4.630
4.600
4.570
4.527
4.496
4.225
3.320
3.292
3.283
3.210
3.182
3.152
2.567
2.555
2.529
2.500
2.488
2.286
2.248
1.860
1.567
BnOOC
N
O
Boc
4c
1.35
2.27
2.98
1.38
5.04
1.11
1.03
3.04
1.00
1.00
1.02
1.04
1.11
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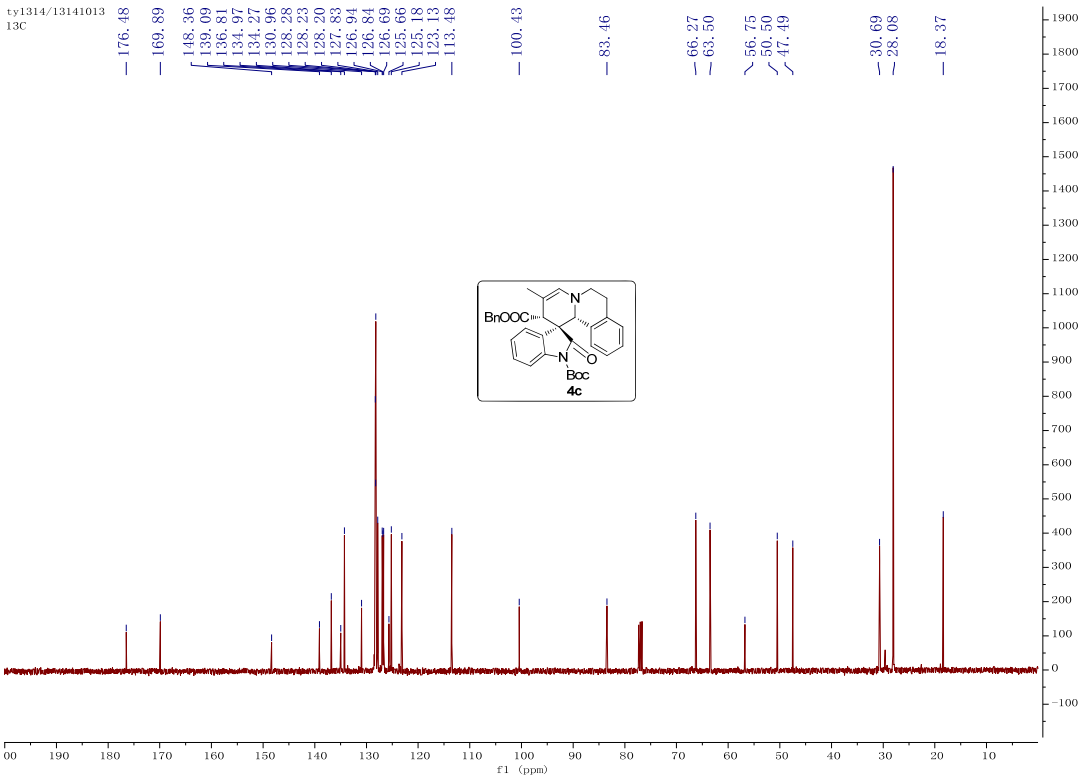
9.27
f1 (ppm)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128.20
127.83
126.94
126.84
126.69
125.66
125.18
123.13
113.48
100.43
83.46
66.27
63.50
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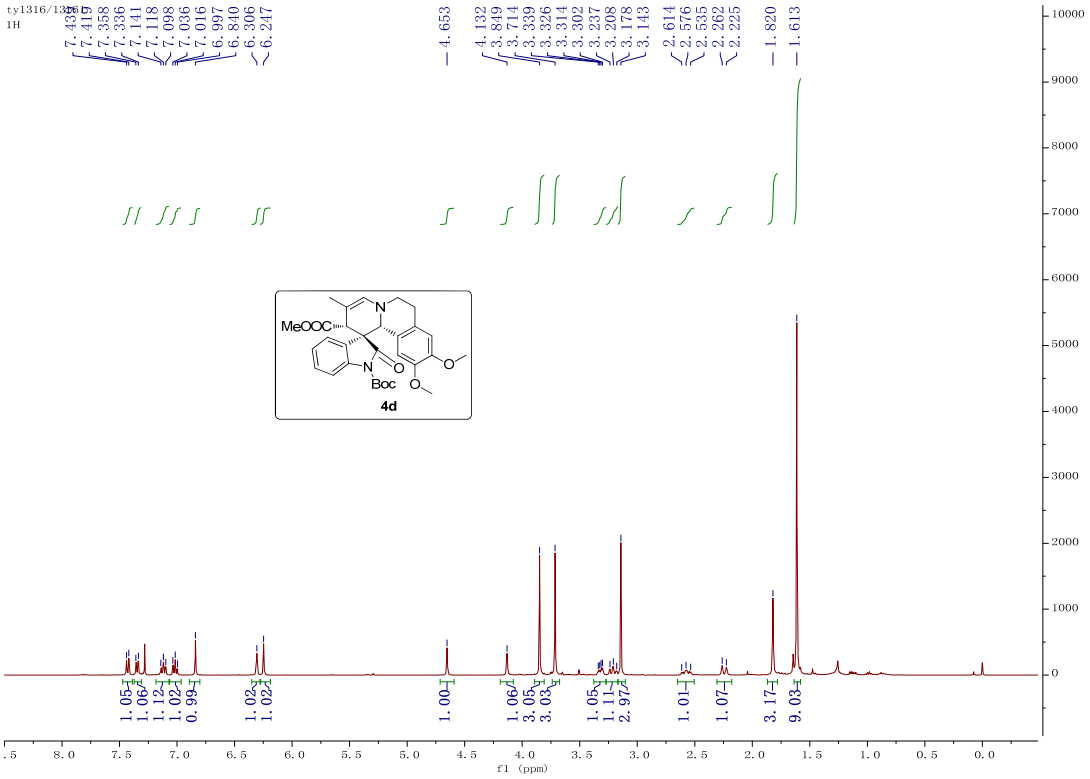
28.08
18.37
BnOOC
N
O
Boc
4c
f1 (ppm)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7.118
7.098
7.036
7.016
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6.840
6.306
6.247
4.653
4.132
3.849
3.714
3.339
3.326
3.314
3.302
3.237
3.208
3.178
3.143
2.614
2.576
2.535
2.262
2.225
1.820
1.613
MeOOC
N
O
Boc
O
4d
1.05
1.06
1.12
1.02
0.99
1.02
1.02
1.00
1.06
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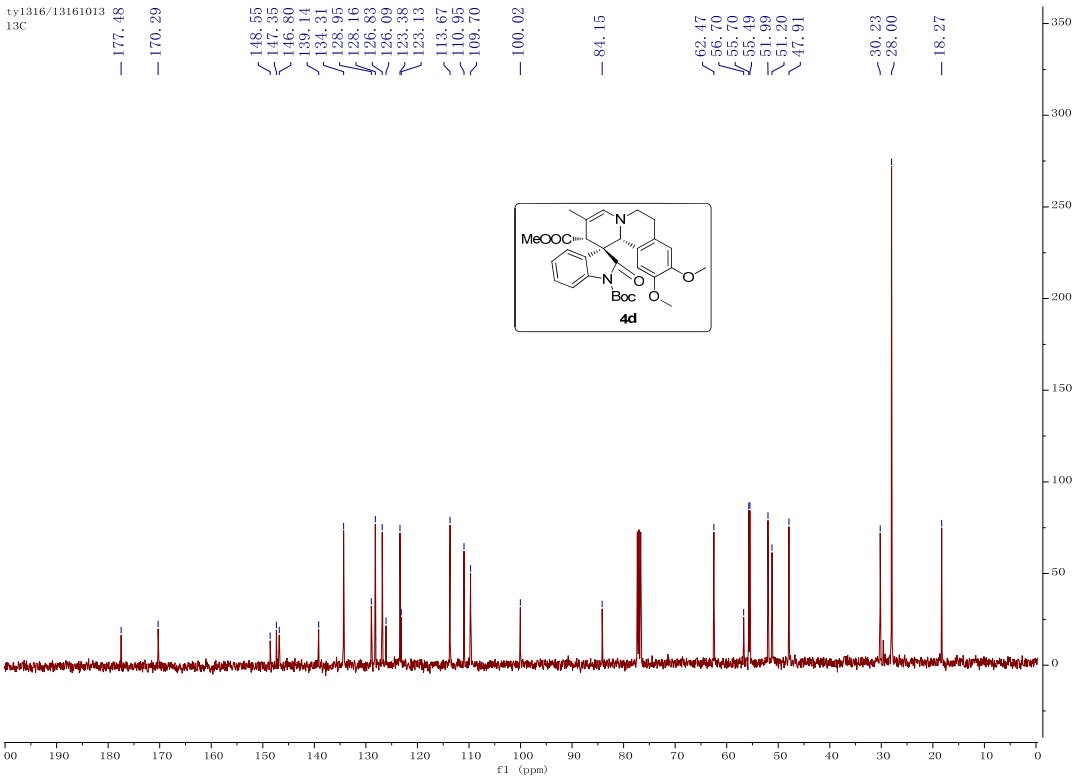
3.03
1.05
1.11
2.97
1.01
1.07
3.17
9.03
f1 (ppm)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134.31
128.95
128.16
126.83
126.09
123.38
123.13
113.67
110.95
109.70
100.02
84.15
62.47
56.70
55.70
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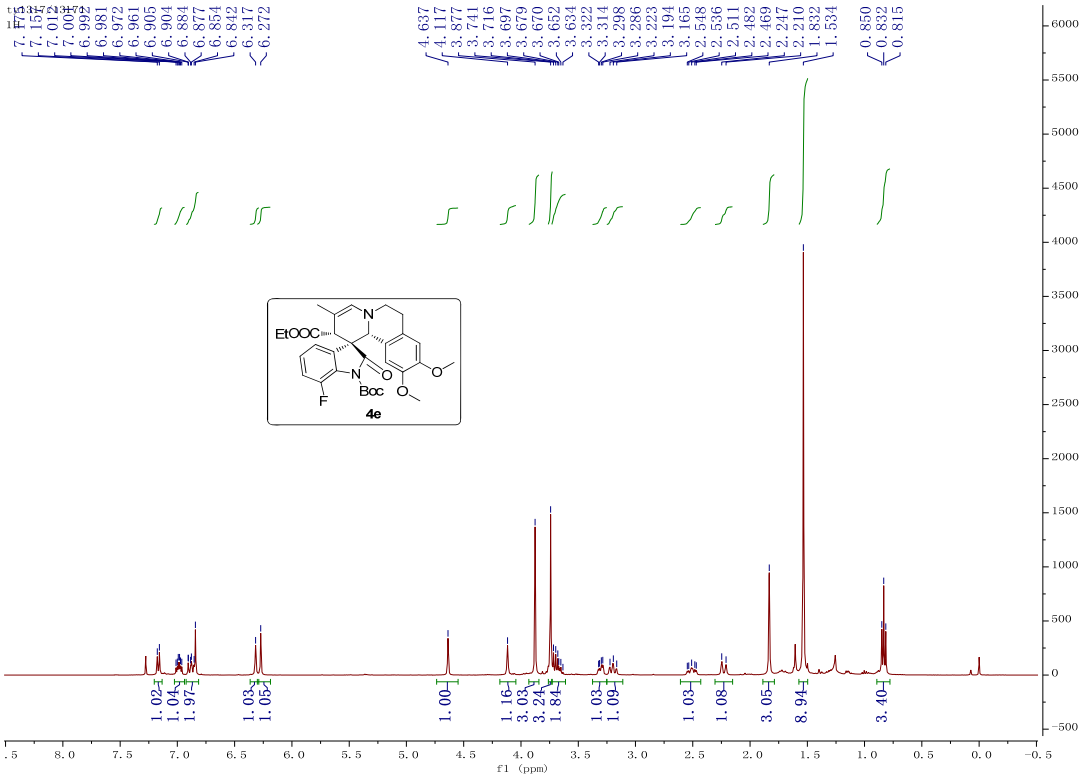
N
O
Boc
O
4d
f1 (ppm)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6.884
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6.854
6.842
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6.272
4.637
4.117
3.877
3.741
3.716
3.697
3.679
3.670
3.652
3.634
3.322
3.314
3.298
3.286
3.223
3.194
3.165
2.548
2.536
2.511
2.482
2.469
2.247
2.210
1.832
1.534
0.850
0.832
0.815
EtOOC
N
O
N
Boc
O
O
F
4e
1.02
1.04
1.97
1.03
1.05
1.00
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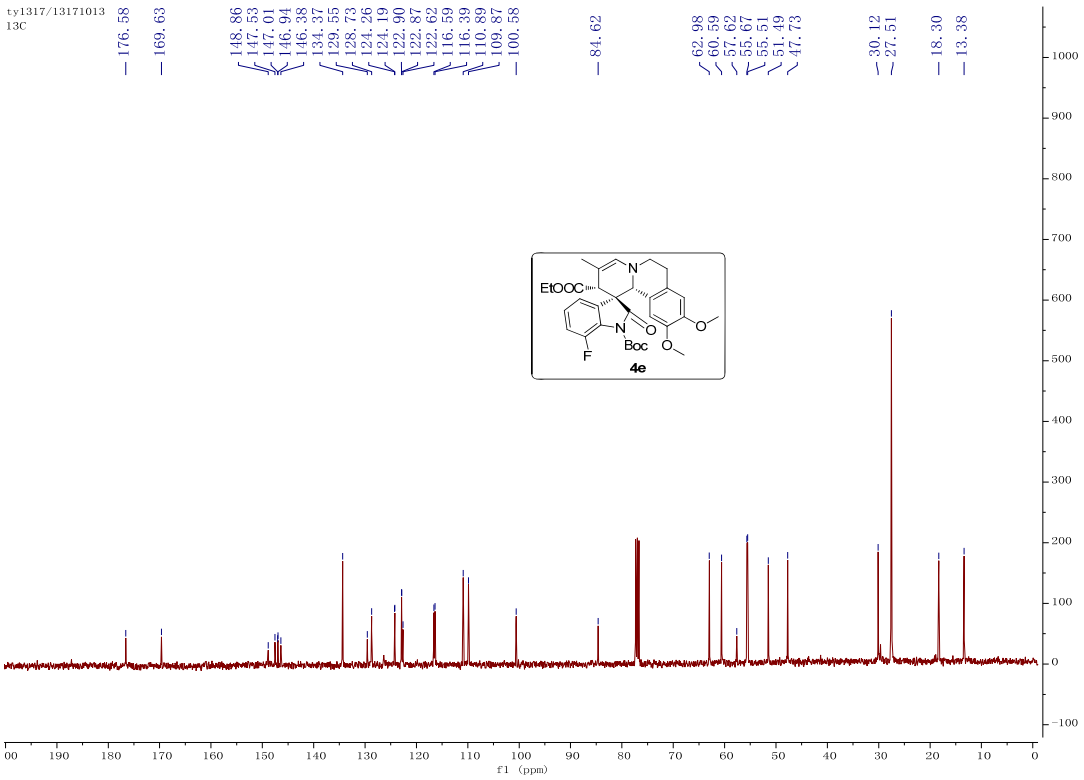
3.40
f1 (ppm)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146.38
134.37
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124.26
124.19
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122.87
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116.59
116.39
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62.98
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55.51
51.49
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18.30
13.38
EtOOC
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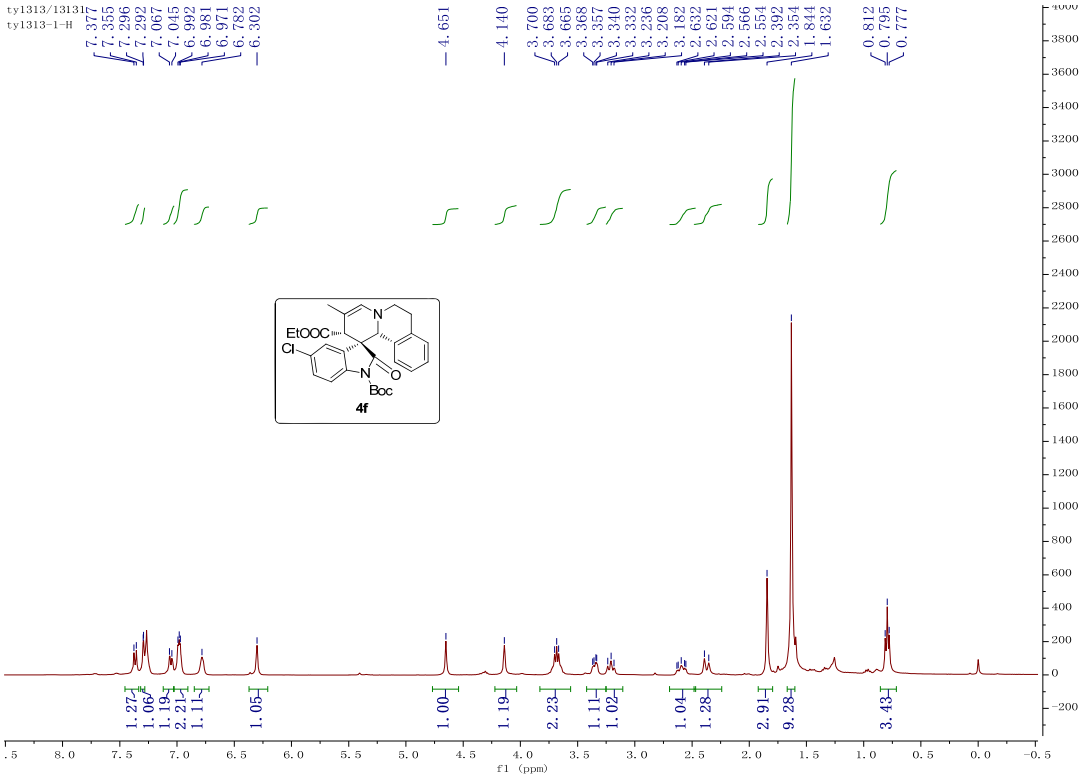
N
Boc
O
O
F
4e
f1 (ppm)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6.782
6.302
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4.140
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3.340
3.332
3.236
3.208
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2.594
2.566
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2.392
2.354
1.844
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0.795
0.777
EtOOC
Cl
N
O
Boc
4f
1.27
1.06
1.19
2.21
1.11
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1.02
1.04
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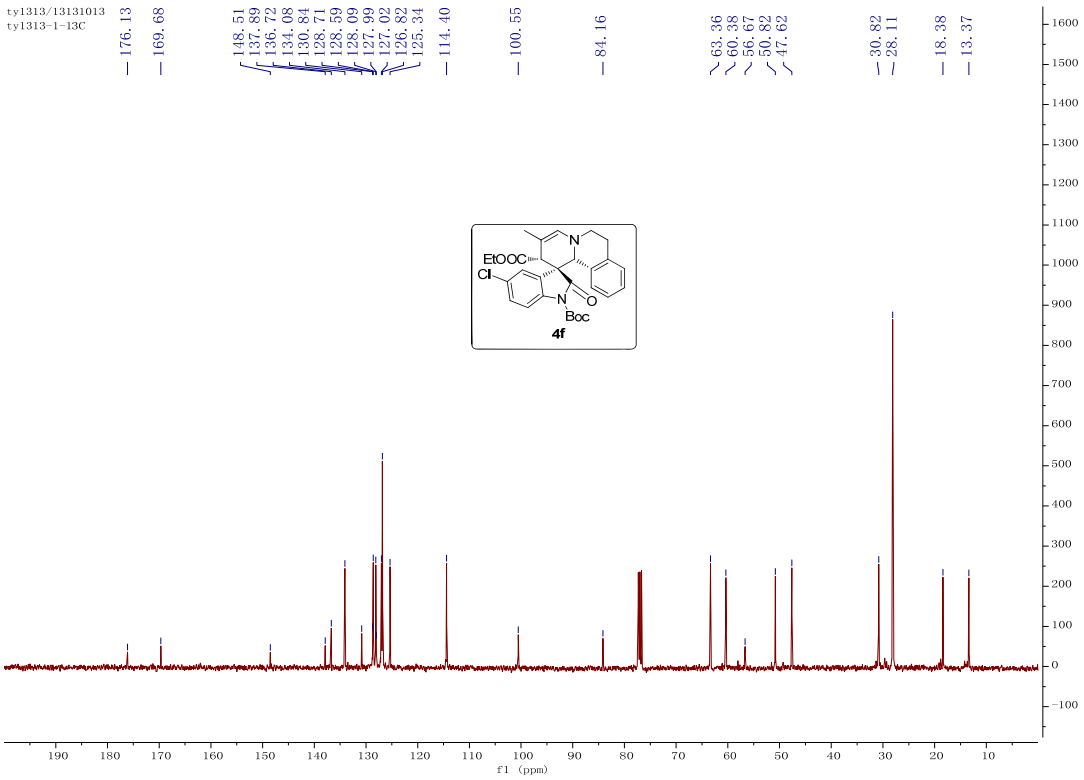
f1 (ppm)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125.34
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84.16
63.36
60.38
56.67
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28.11
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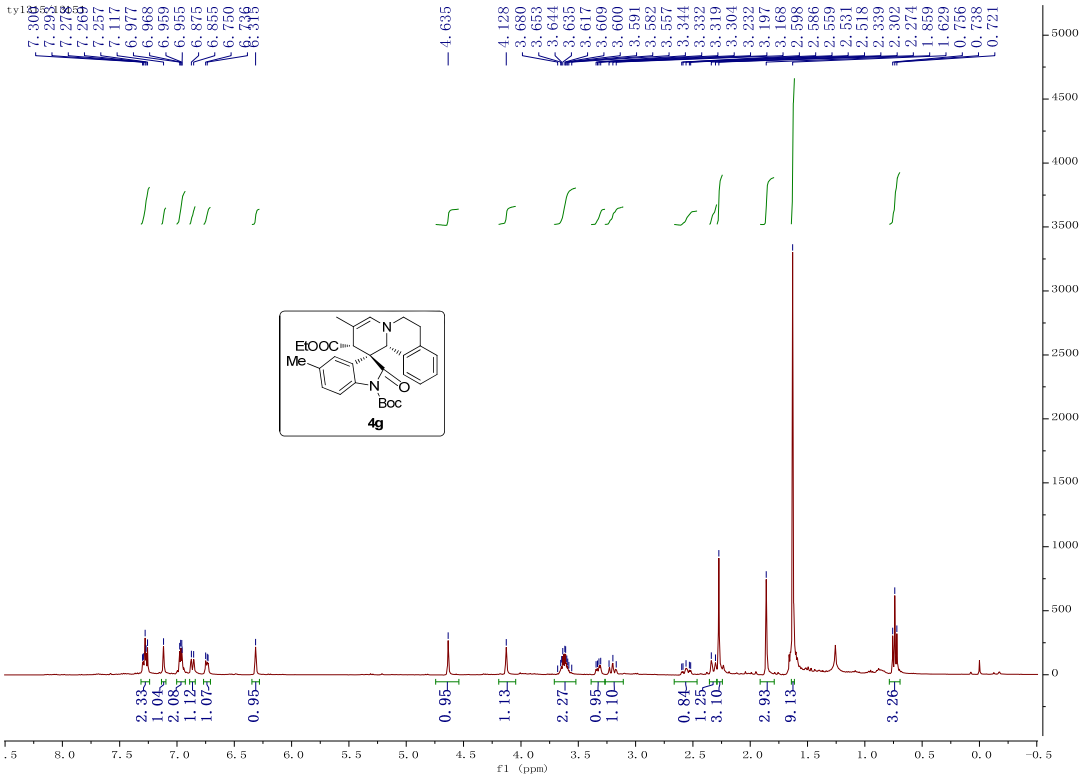
Cl
N
O
Boc
4f
f1 (ppm)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6.736
6.315
4.635
4.128
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3.653
3.644
3.635
3.617
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3.600
3.591
3.582
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2.586
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1.629
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0.721
EtOOC
Me
N
O
Boc
4g
2.33
1.04
2.08
1.12
1.07
0.95
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2.93
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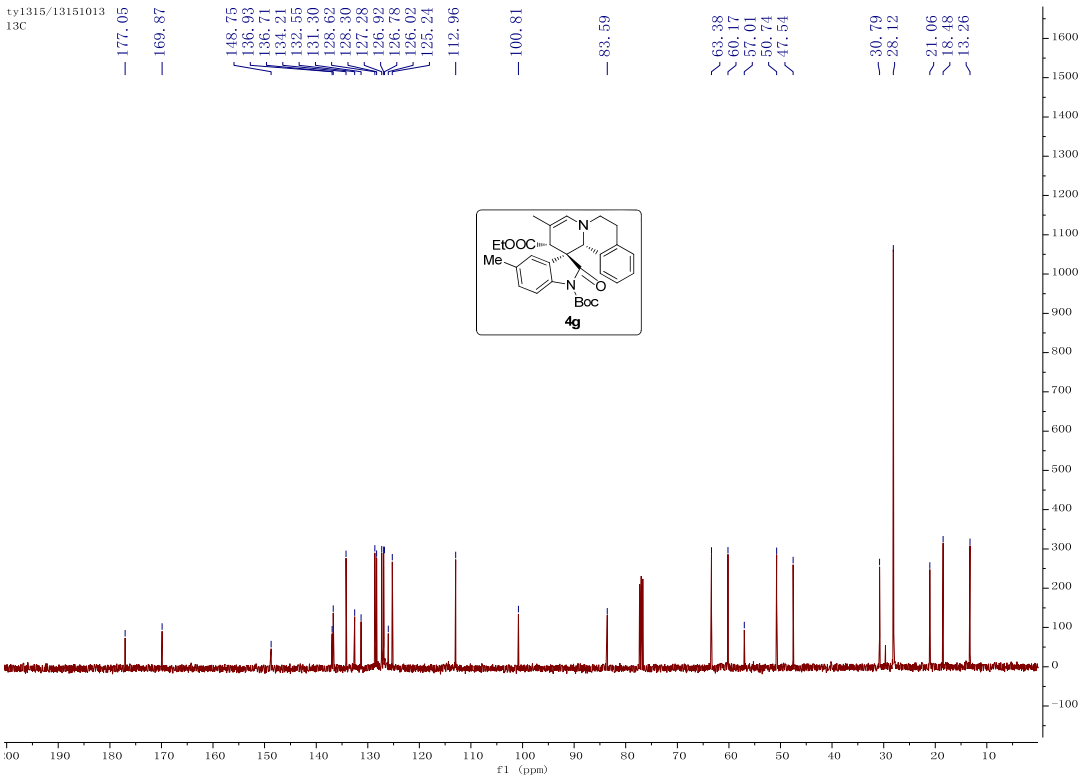
3.26
f1 (ppm)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126.78
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112.96
100.81
83.59
63.38
60.17
57.01
50.74
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21.06
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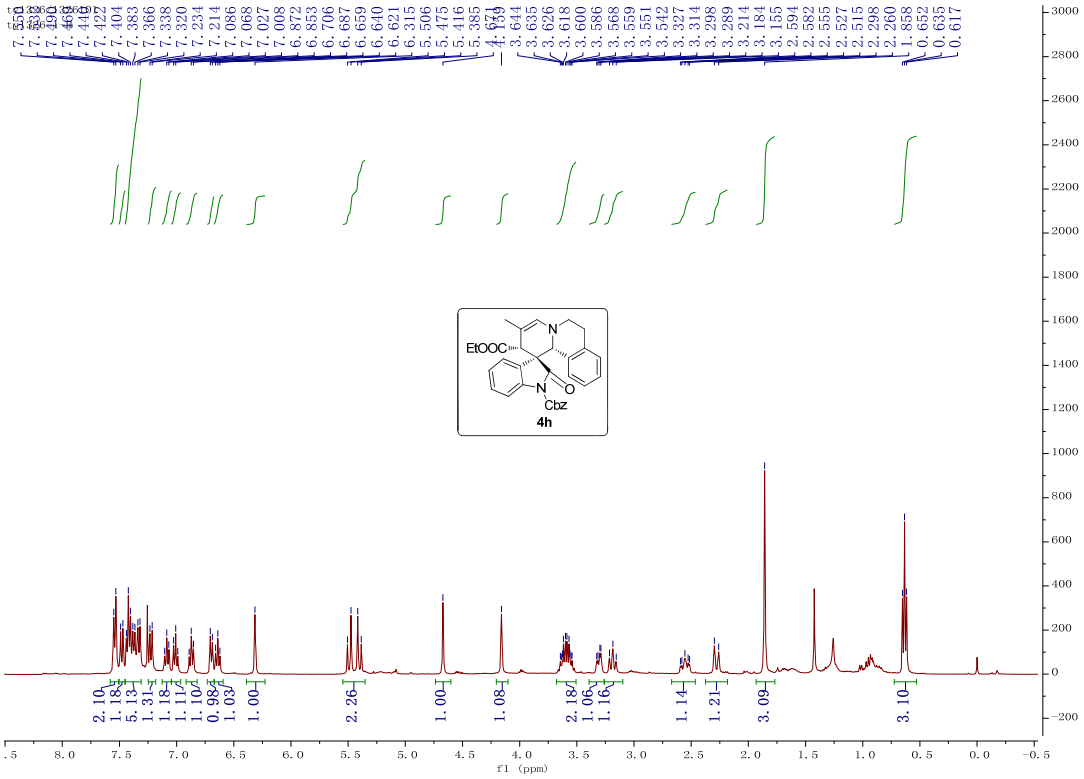
13.26
EtOOC
Me
N
O
Boc
4g
f1 (ppm)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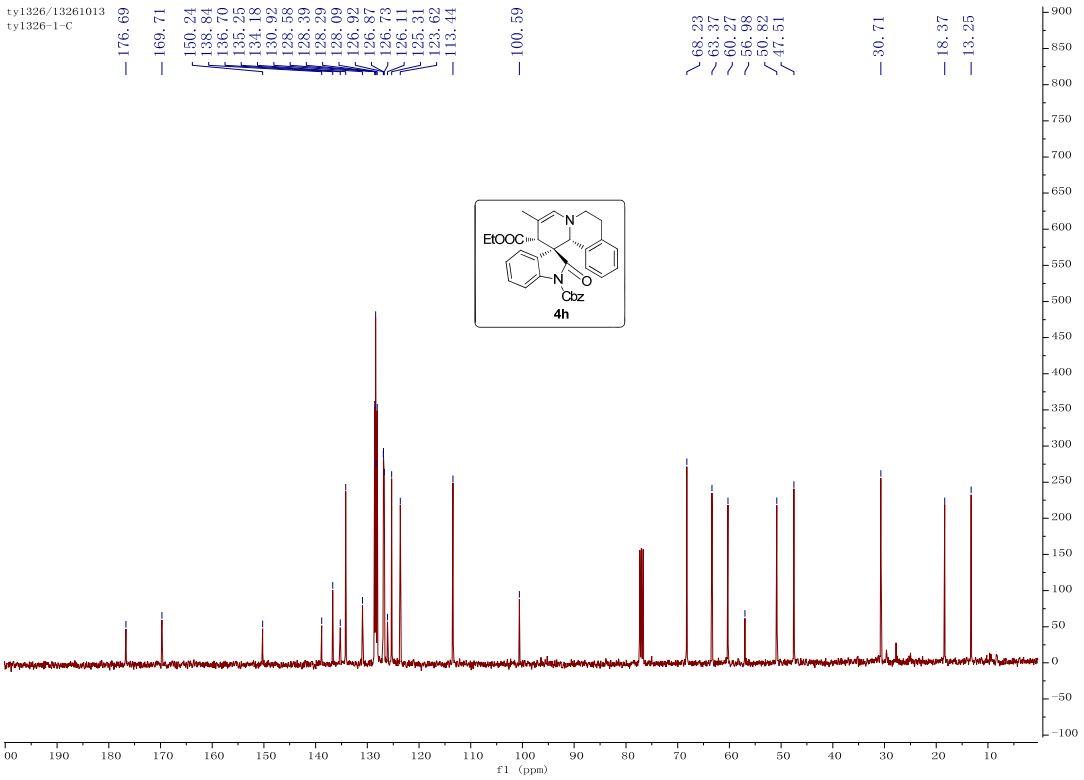
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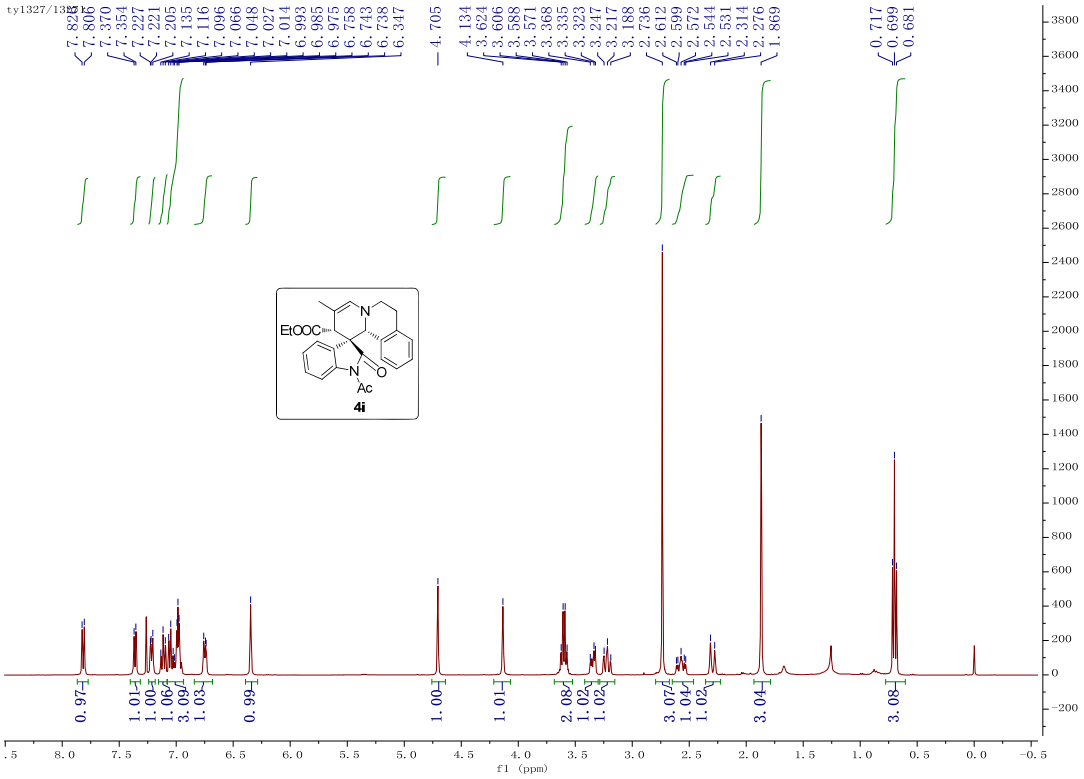
N
O
Cbz
4h
f1 (ppm)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N
O
Ac
4i
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1.00
1.06
3.09
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1.02
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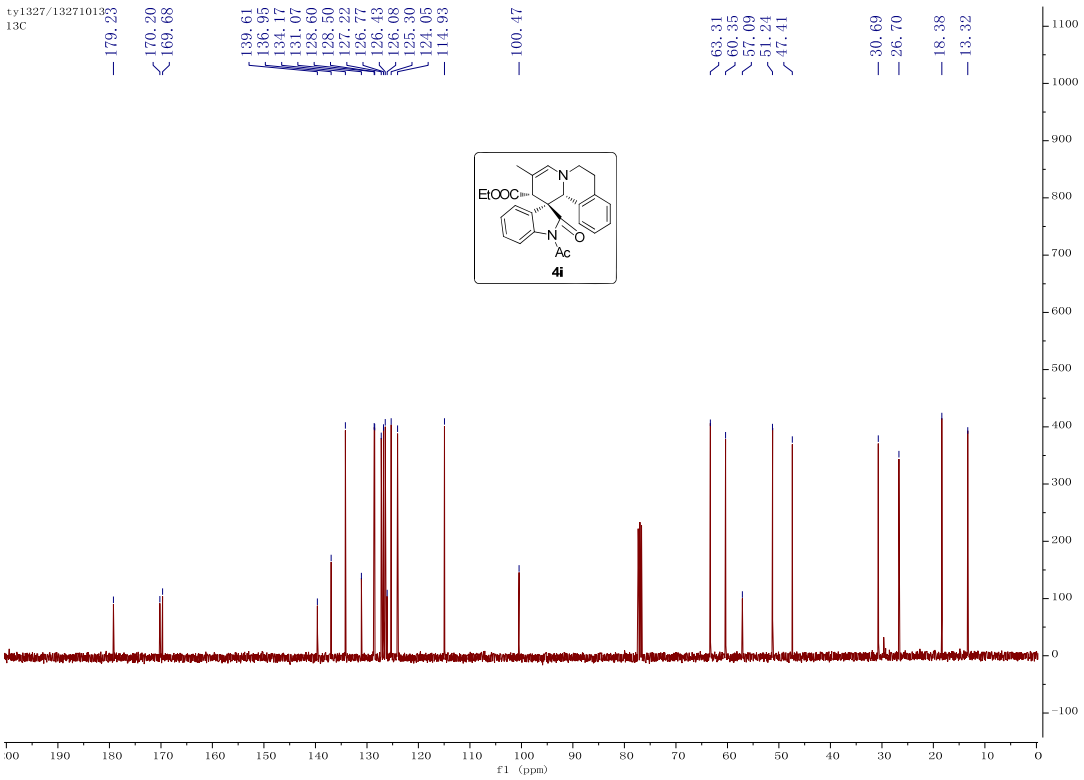
3.08
f1 (ppm)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125.30
124.05
114.93
100.47
63.31
60.35
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26.70
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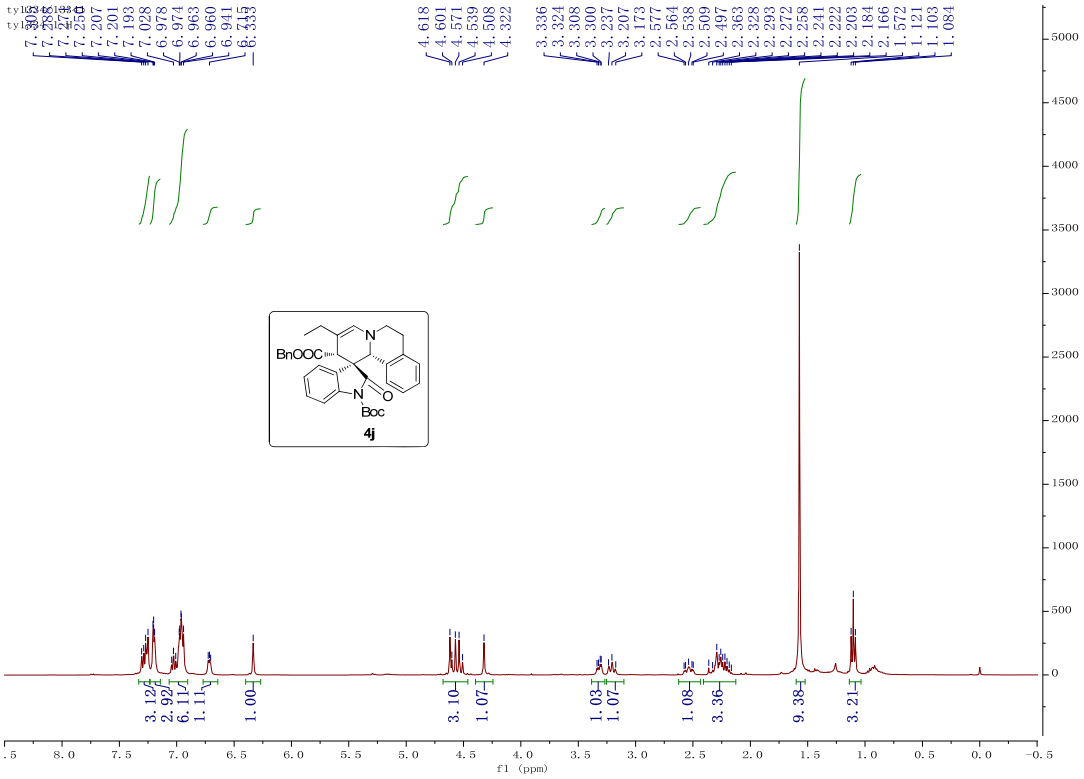
O
Ac
4i
f1 (ppm)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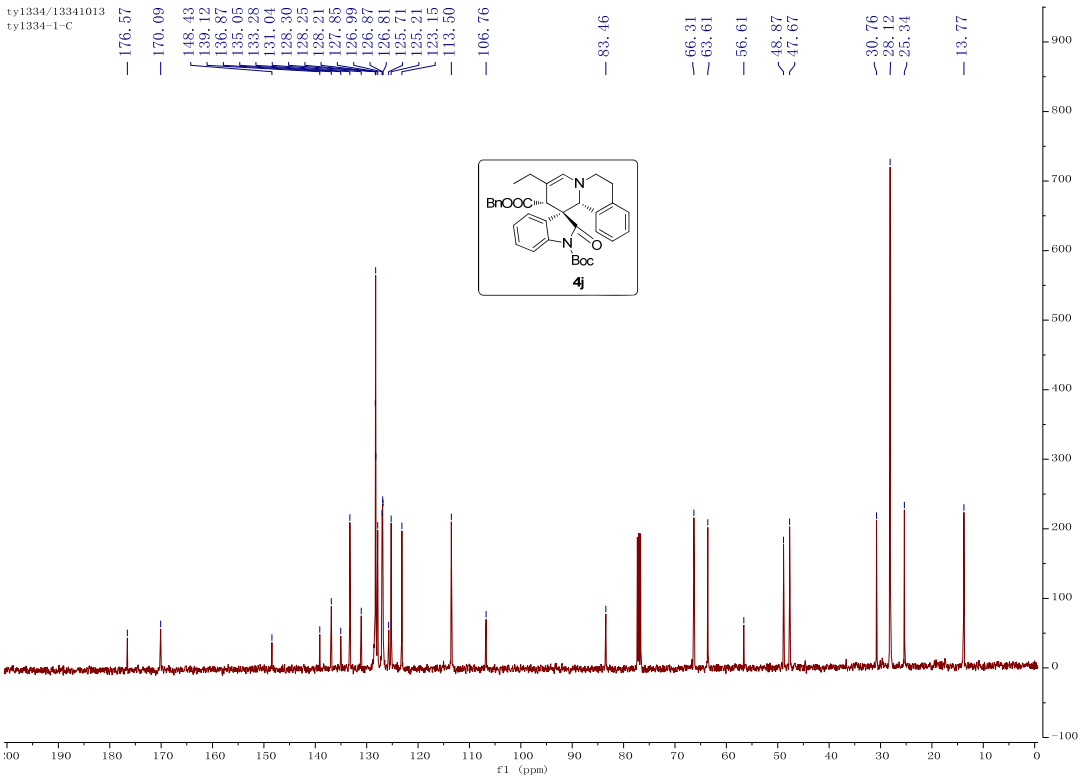
Boc
4j
f1 (ppm)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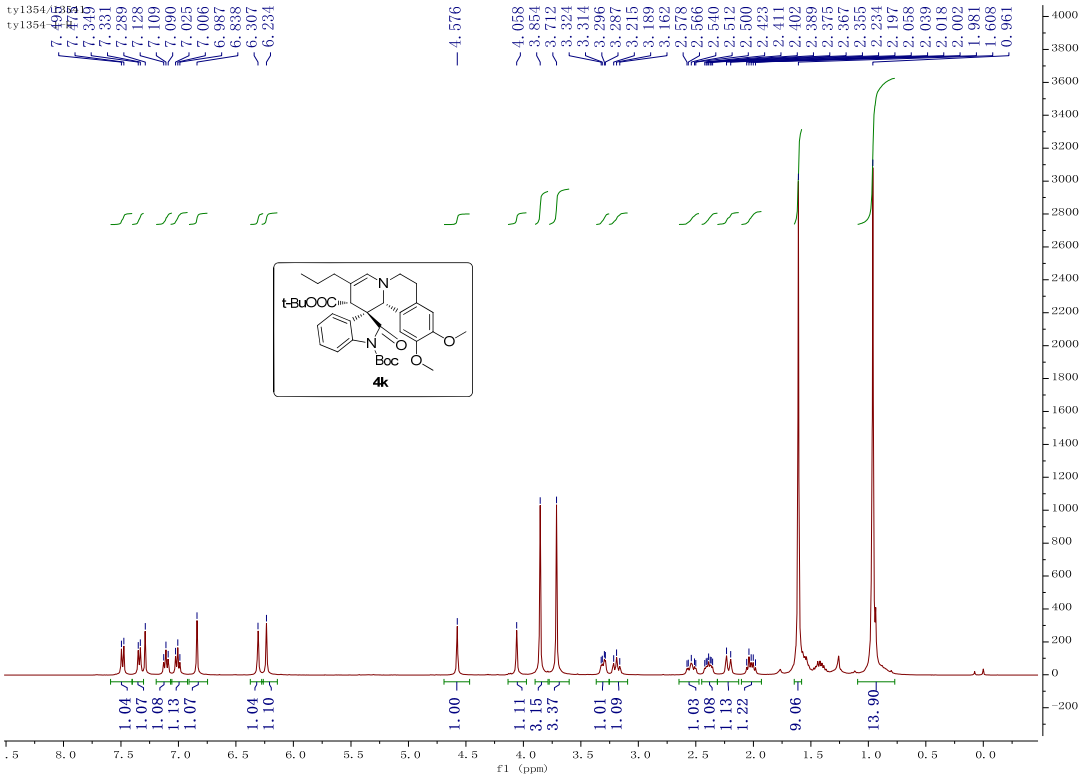
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6.234
4.576
4.058
3.854
3.712
3.324
3.314
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3.215
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2.578
2.566
2.540
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1.07
1.08
1.13
1.07
1.04
1.10
1.00
1.11
3.15
3.37
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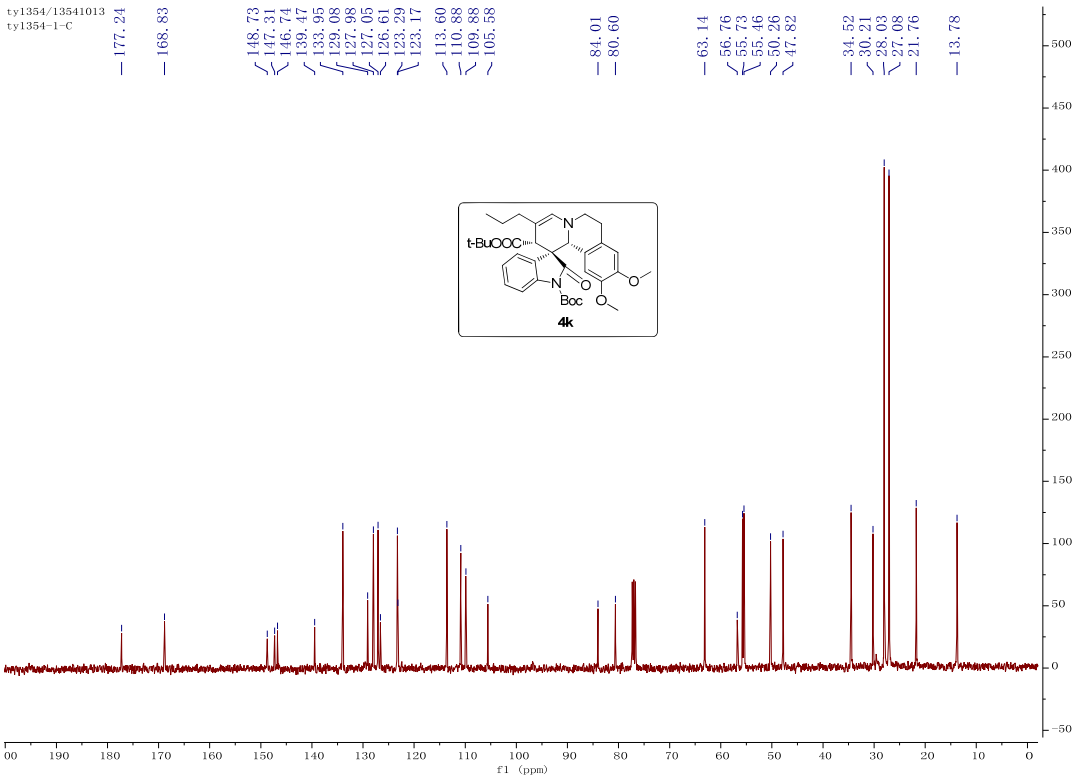
t-BuOOC
Boc
4k
f1 (ppm)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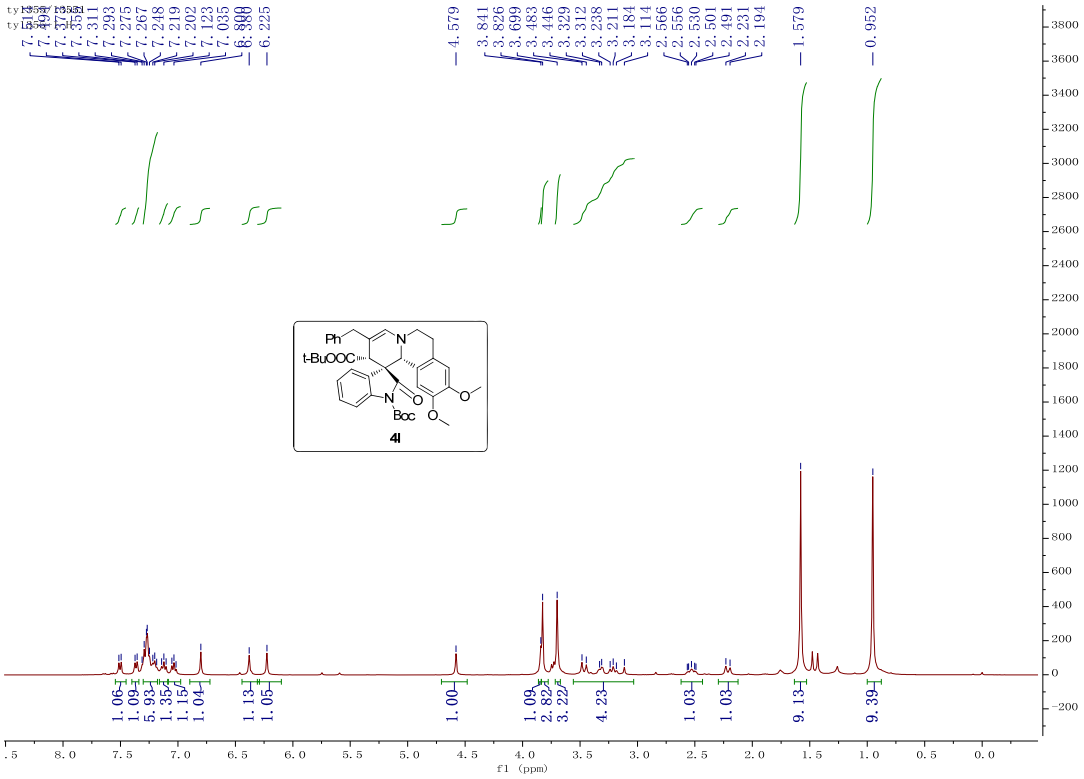
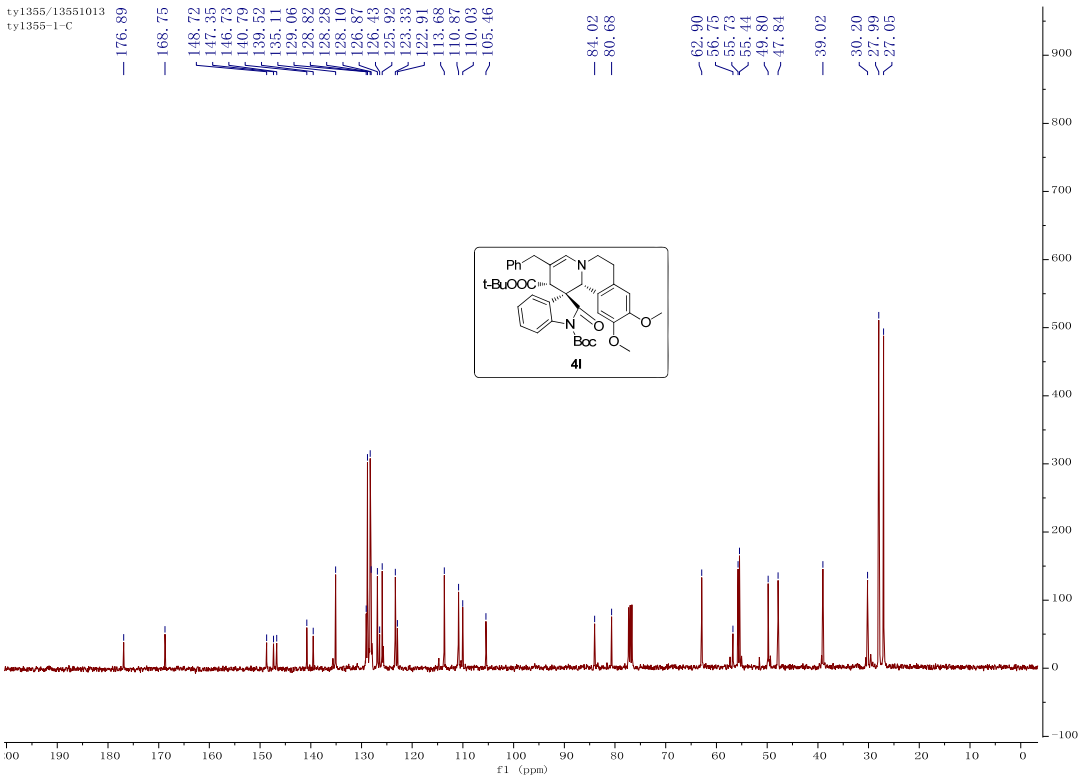
123.17
113.60
110.88
109.88
105.58
84.01
80.60
63.14
56.76
55.73
55.46
50.26
47.82
34.52
30.21
28.03
27.08
21.76
13.78
t-BuOOC
Boc
4k
f1 (ppm)


Ph
t-BuOOC
N
O
Boc
O
4l
f1 (ppm)


Ph
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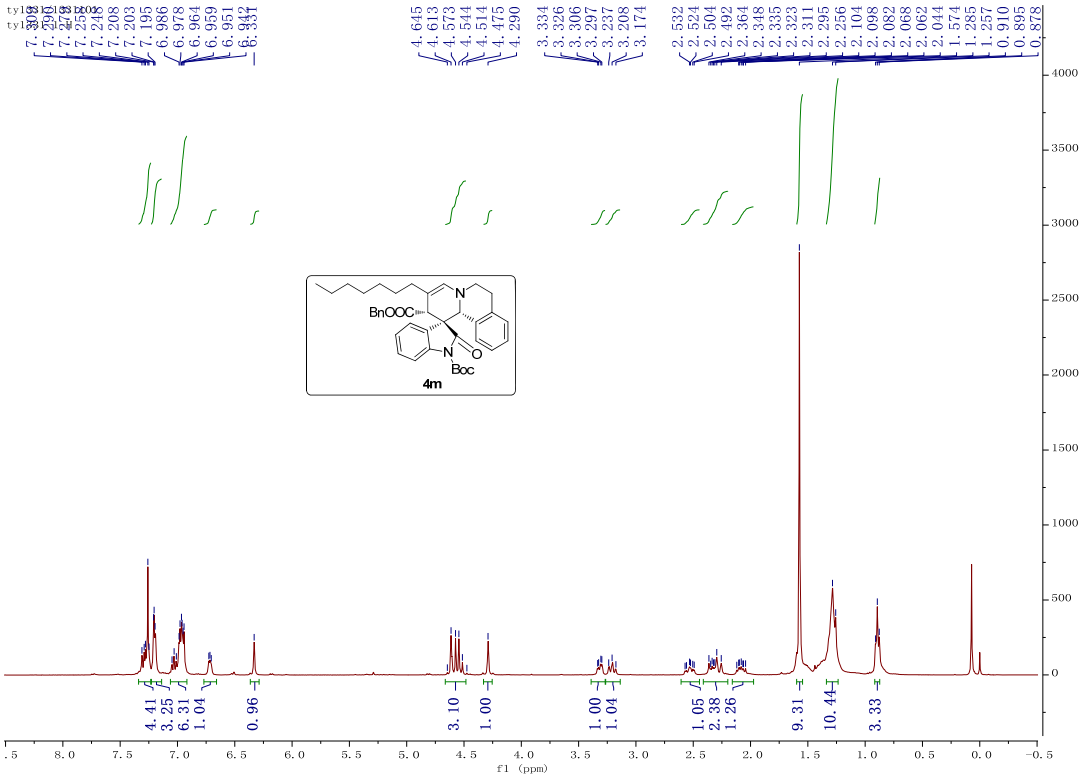
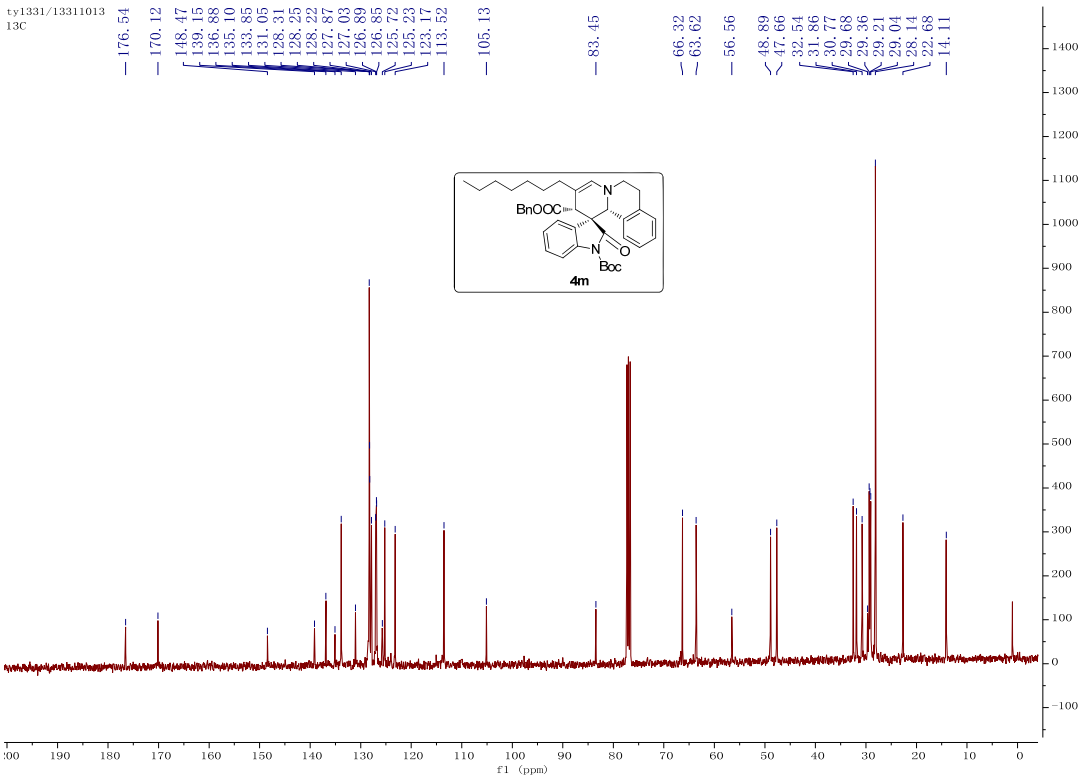
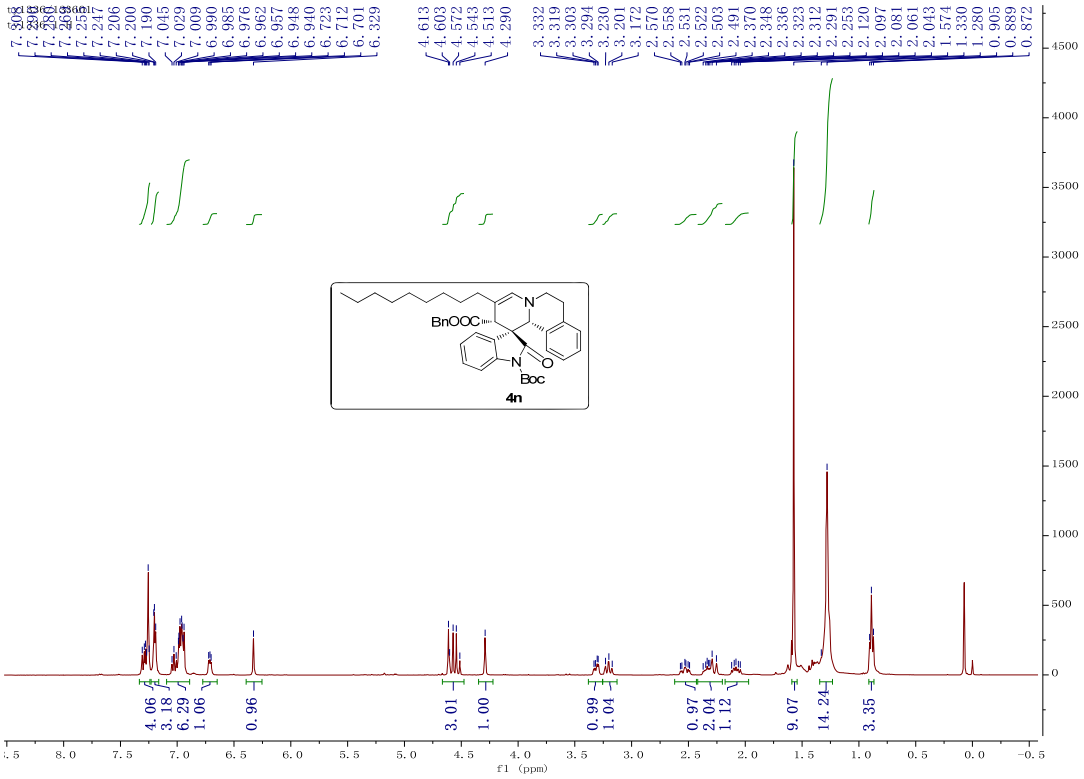
N
O
Boc
O
4l
f1 (ppm)


BnOOC
N
N
O
Boc
4m
f1 (ppm)


ty1331/13311013
13C
BnOOC
N
N
O
Boc
4m
f1 (ppm)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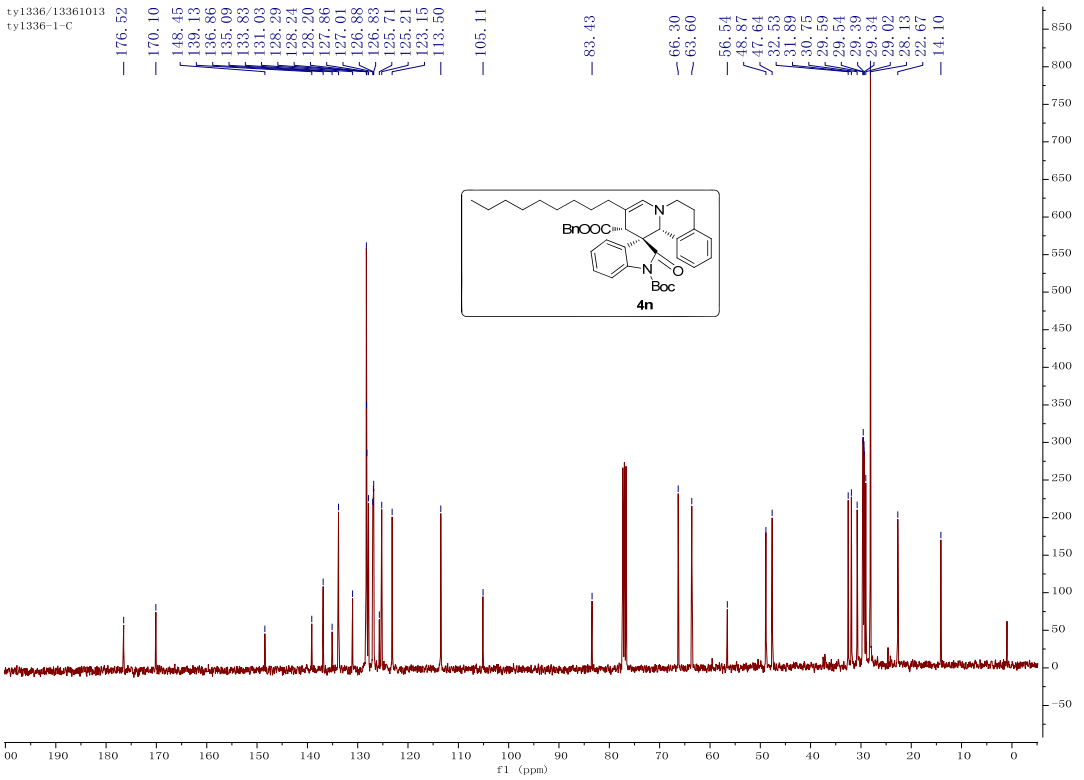
N
O
Boc
4n
f1 (ppm)


ty1336/13361013
ty1336-1-C
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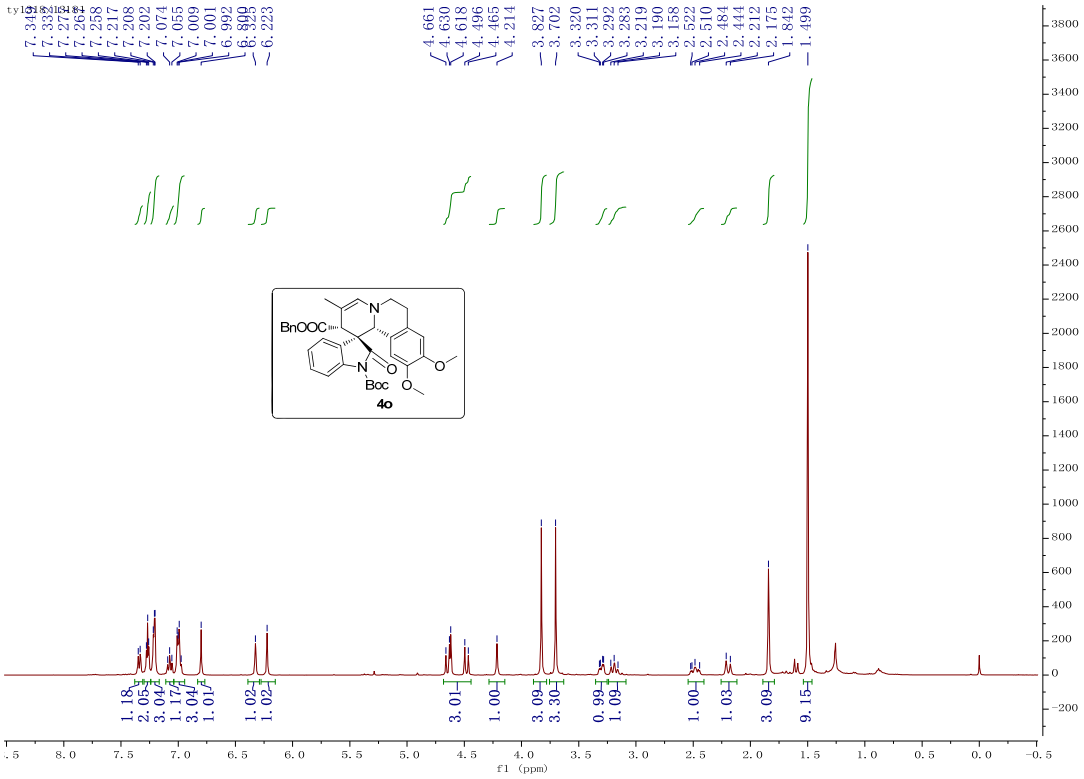
O
Boc
4n
f1 (ppm)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7.208
7.202
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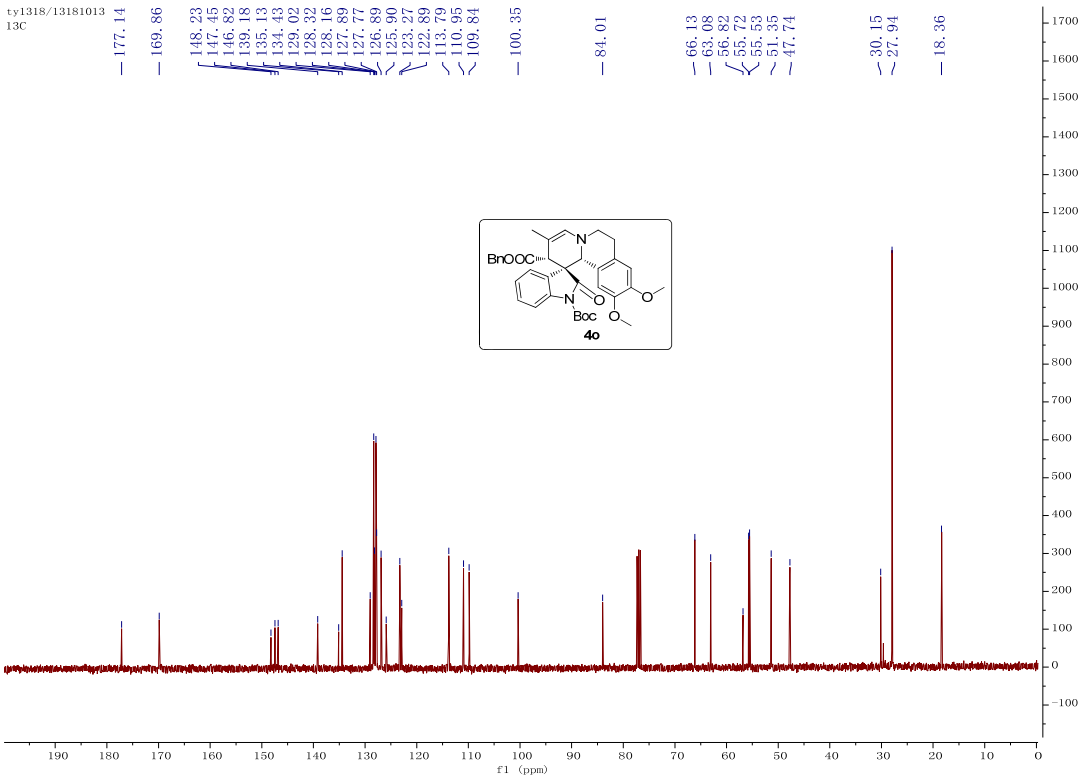
7.055
7.009
7.001
6.992
6.940
6.935
6.223
4.661
4.630
4.618
4.496
4.465
4.214
3.827
3.702
3.320
3.311
3.292
3.283
3.219
3.190
3.158
2.522
2.510
2.484
2.444
2.212
2.175
1.842
1.499
BnOOC
N
O
Boc
O
4o
1.18
2.05
3.04
1.17
3.04
1.01
1.02
1.02
3.01
1.00
3.09
3.30
0.99
1.09
1.00
1.03
3.09
9.15
f1 (ppm)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13C
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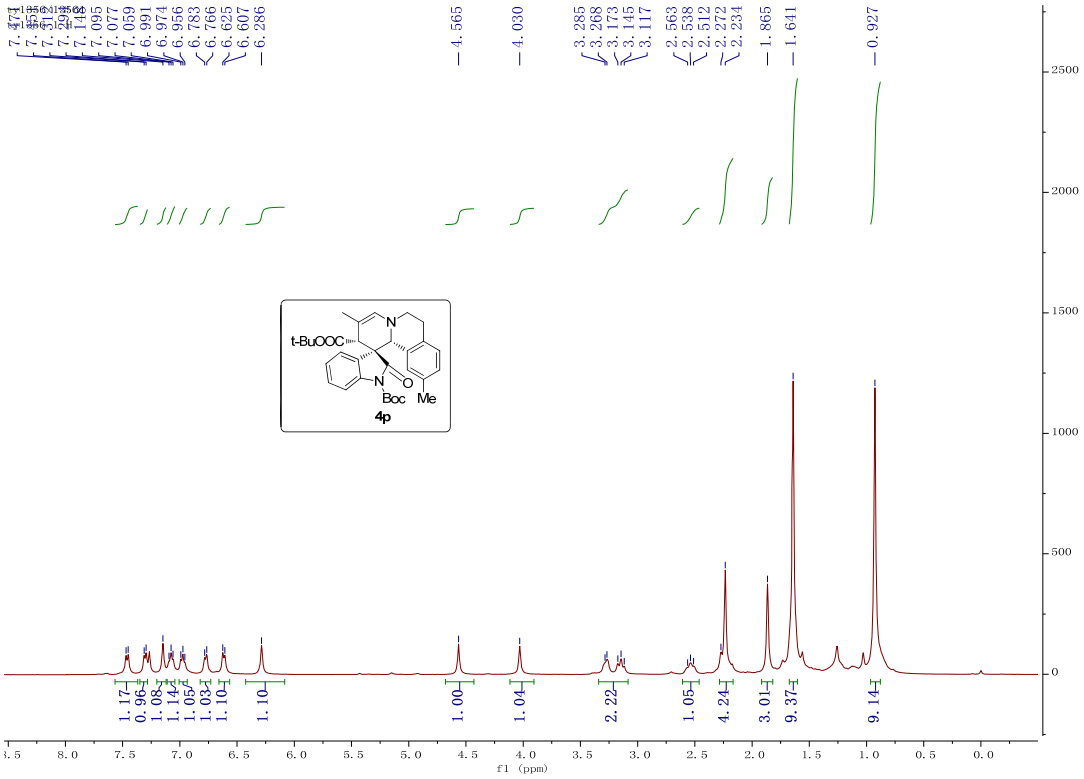
148.23
147.45
146.82
139.18
135.13
134.43
129.02
128.32
128.16
127.89
127.77
126.89
125.90
123.27
122.89
113.79
110.95
109.84
100.35
84.01
66.13
63.08
56.82
55.72
55.53
51.35
47.74
30.15
27.94
18.36
BnOOC
N
O
Boc
O
4o
f1 (ppm)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7.077
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6.956
6.783
6.766
6.625
6.607
6.286
4.565
4.030
3.285
3.268
3.173
3.145
3.117
2.563
2.538
2.512
2.272
2.234
1.865
1.641
0.927
t-BuOOC
N
O
Boc
Me
4p
1.17
0.96
1.08
1.14
1.05
1.03
1.10
1.10
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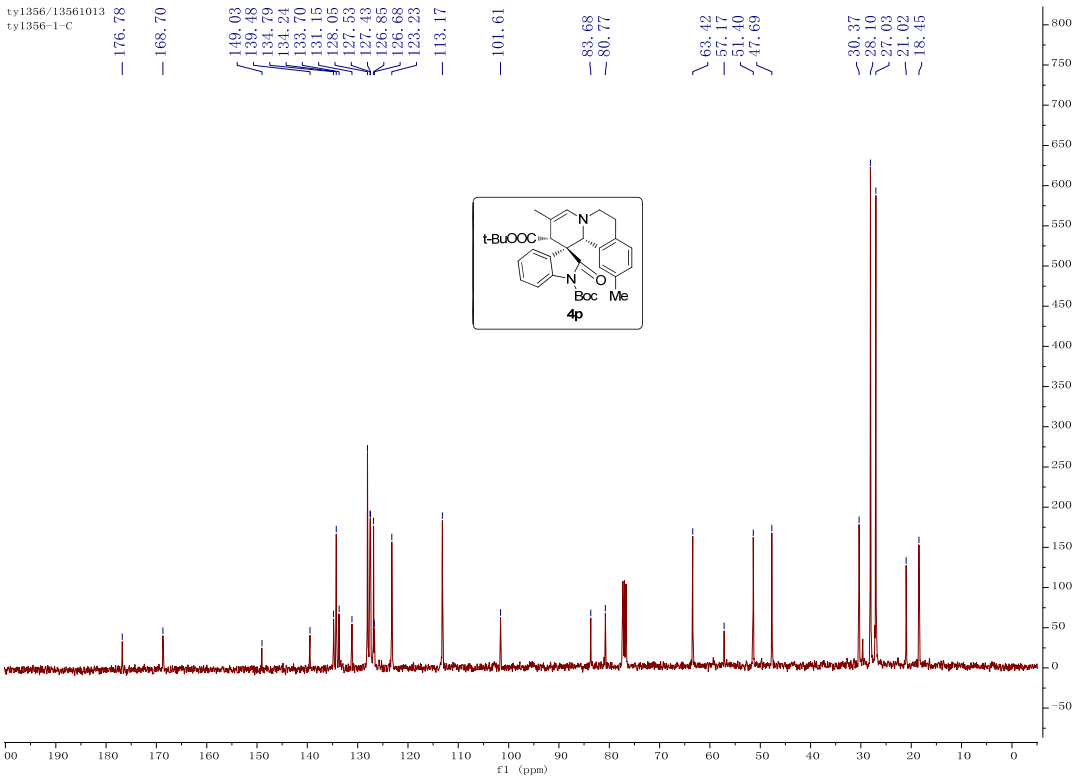
4.24
3.01
9.37
9.14
f1 (ppm)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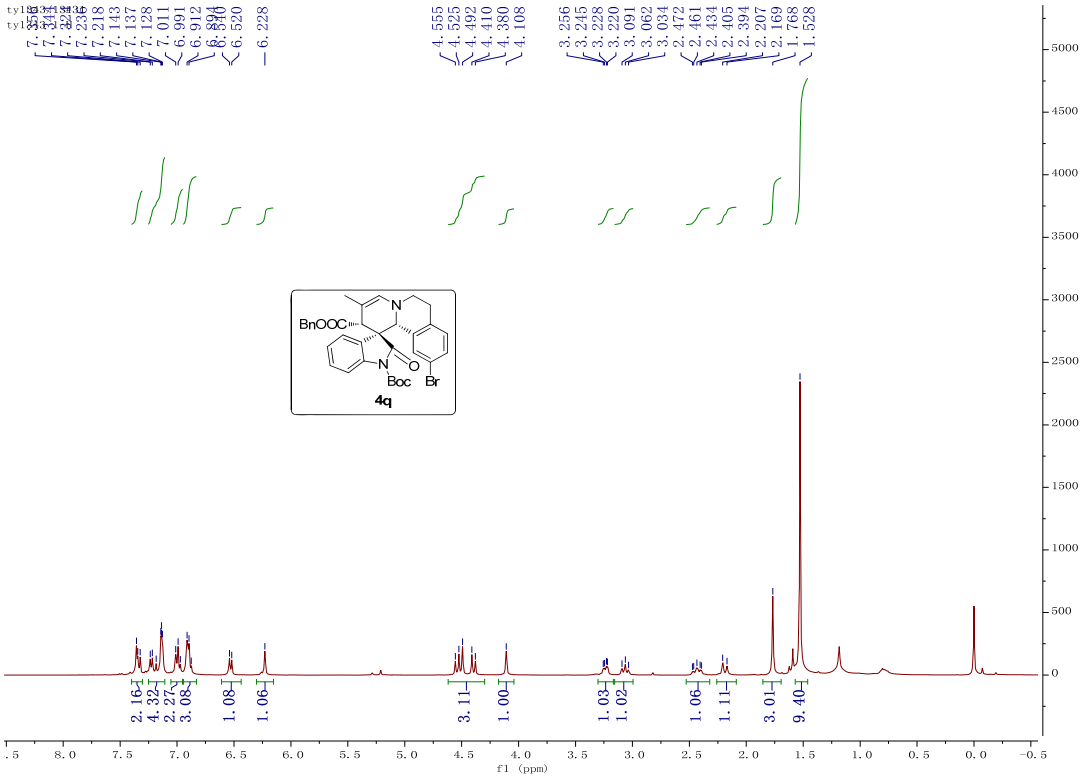
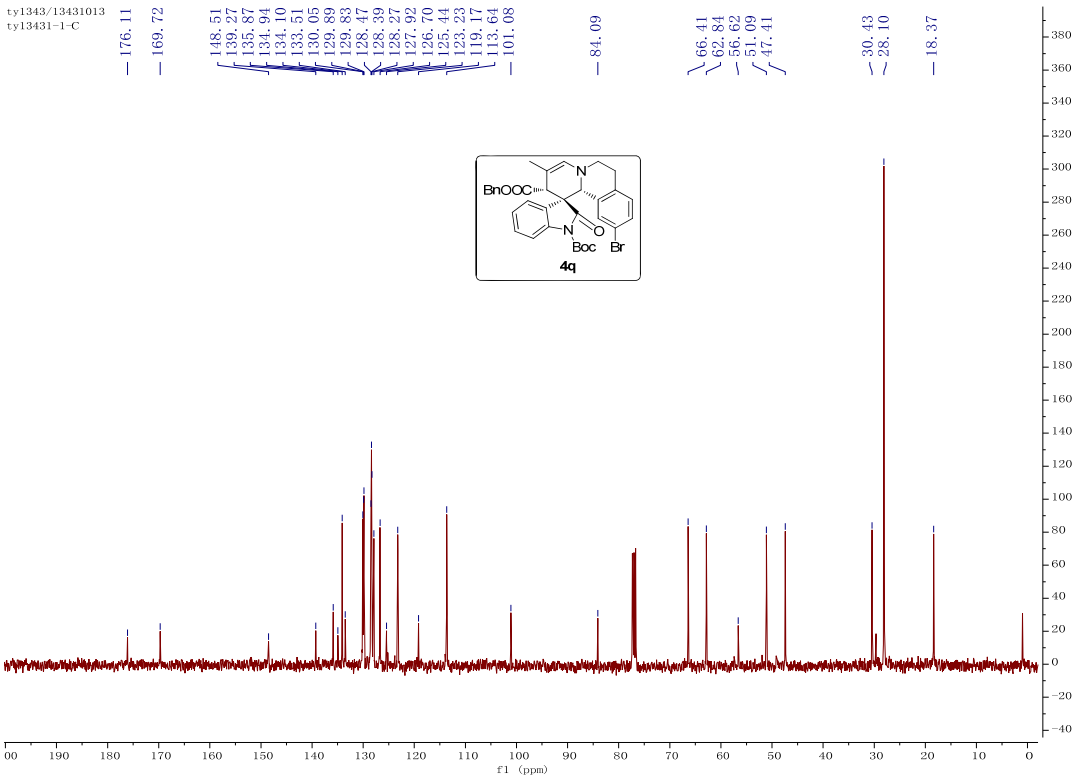
ty1356-1-C
176.78
168.70
149.03
139.48
134.79
134.24
133.70
131.15
128.05
127.53
127.43
126.85
126.68
123.23
113.17
101.61
83.68
80.77
63.42
57.17
51.40
47.69
30.37
28.10
27.03
21.02
18.45
t-BuOOC
N
O
Boc
Me
4p
f1 (ppm)


BnOOC
N
O
Boc
Br
4q
f1 (ppm)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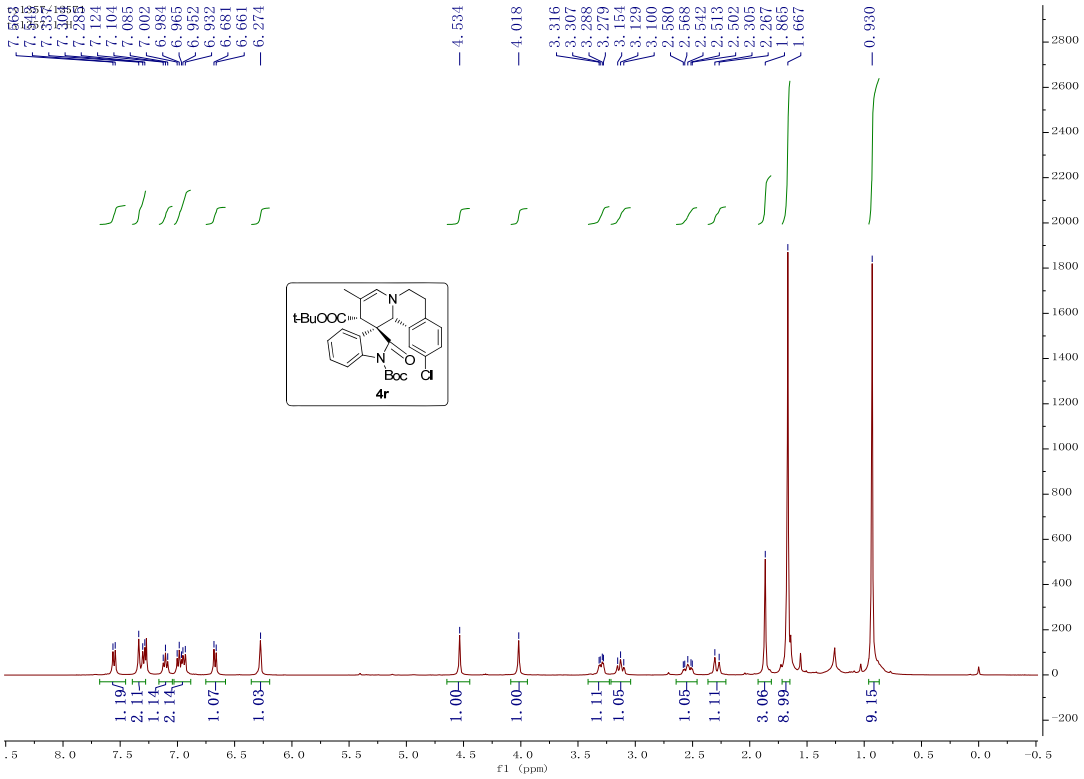
ty13431-1-C
BnOOC
N
O
Boc
Br
4q
f1 (ppm)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6.932
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6.661
6.274
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4.018
3.316
3.307
3.288
3.279
3.154
3.129
3.100
2.580
2.568
2.542
2.513
2.502
2.305
2.267
1.865
1.667
0.930
t-BuOOC
N
O
Boc
Cl
4r
1.19
2.11
1.14
2.14
1.07
1.03
1.00
1.00
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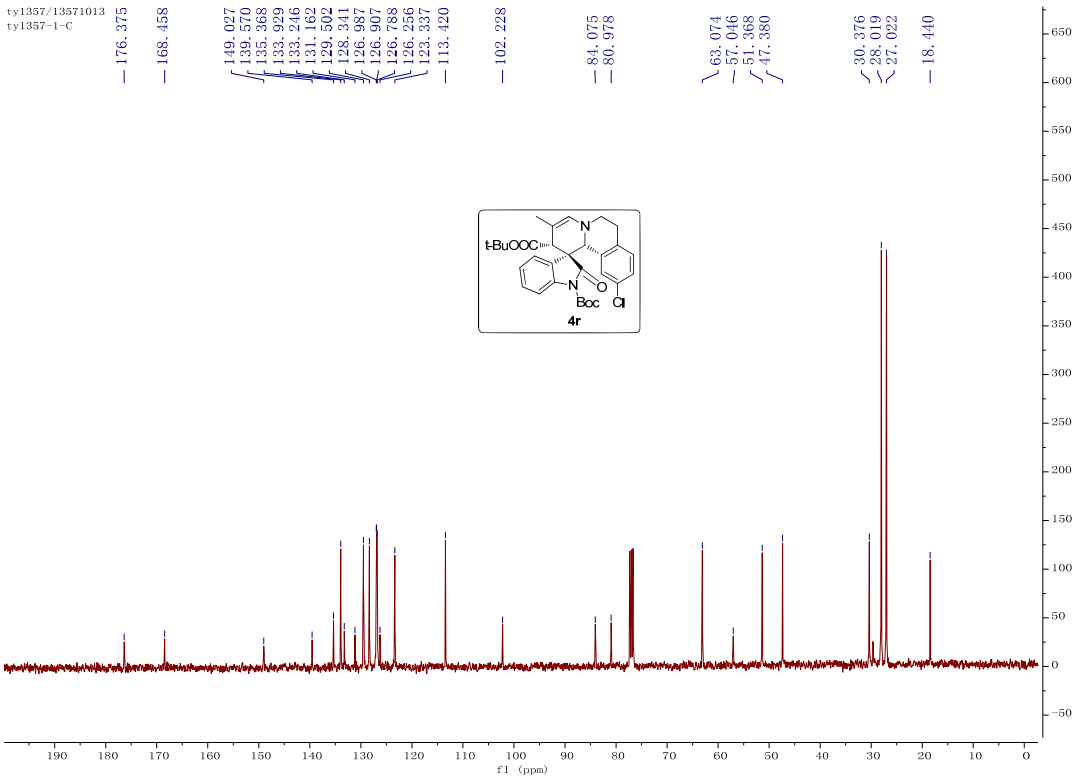
1.11
3.06
8.99
9.15
f1 (ppm)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ty1357-1-C
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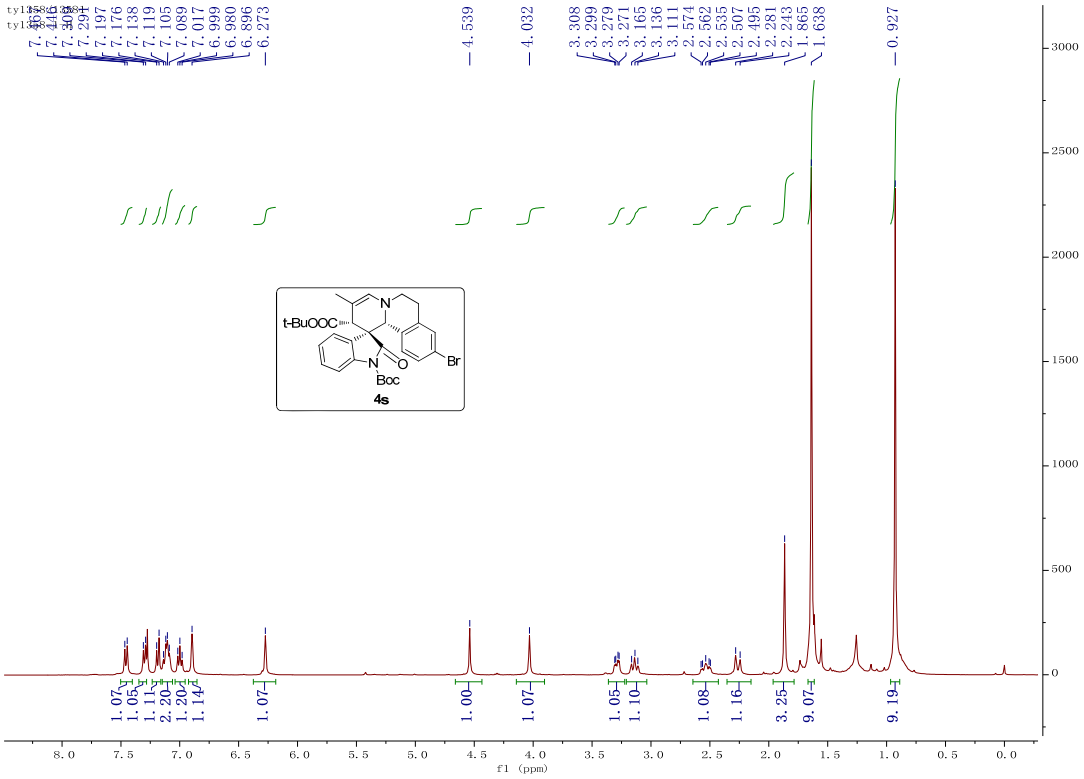
168.458
149.027
139.570
135.368
133.929
133.246
131.162
129.502
128.341
126.987
126.907
126.788
126.256
123.337
113.420
102.228
84.075
80.978
63.074
57.046
51.368
47.380
30.376
28.019
27.022
18.440
t-BuOOC
N
O
Boc
Cl
4r
f1 (ppm)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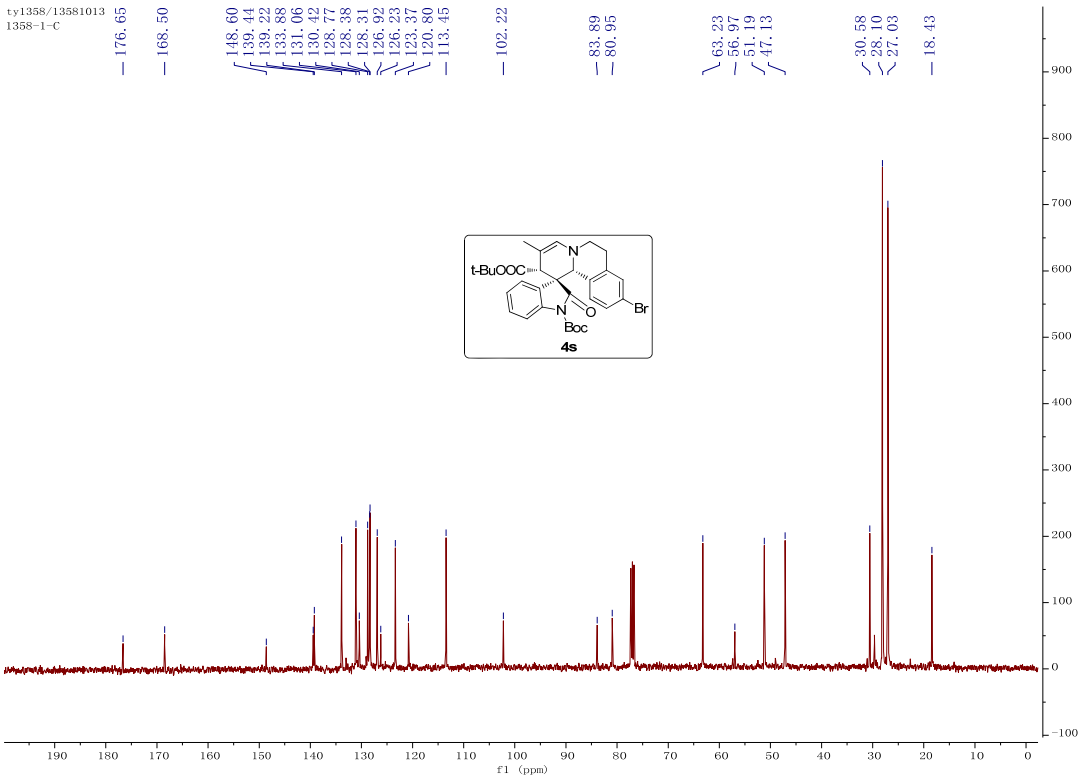
7.197
7.176
7.138
7.119
7.105
7.089
7.017
6.999
6.980
6.896
6.273
4.539
4.032
3.308
3.299
3.279
3.271
3.165
3.136
3.111
2.574
2.562
2.535
2.507
2.495
2.281
2.243
1.865
1.638
0.927
t-BuOOC
N
O
Br
Boc
4s
1.07
1.05
1.11
2.20
1.20
1.14
1.07
1.00
1.07
1.05
1.10
1.08
1.16
3.25
9.07
9.19
f1 (ppm)


ty1358/13581013
1358-1-C
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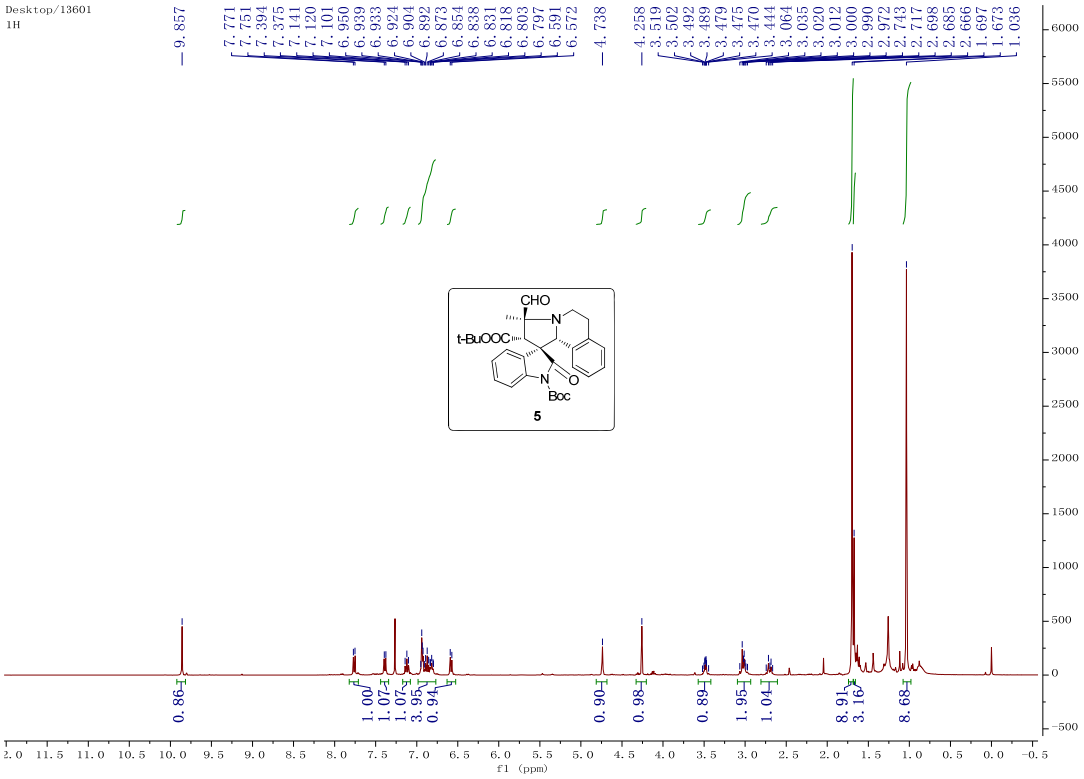
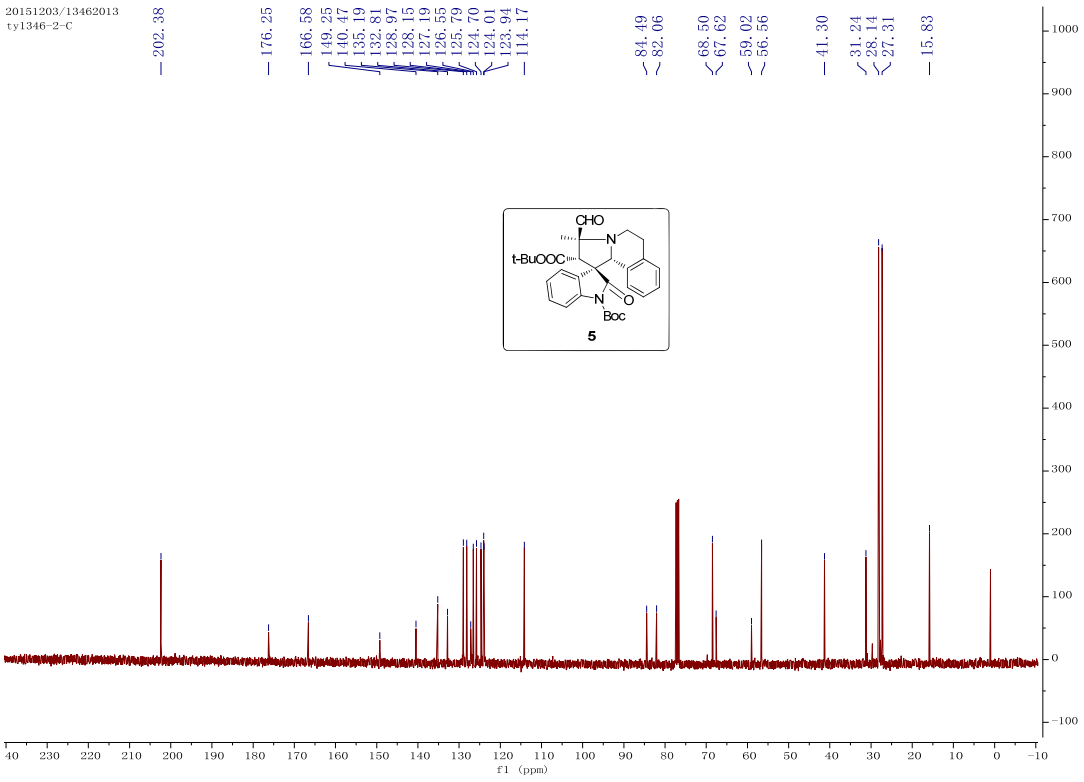
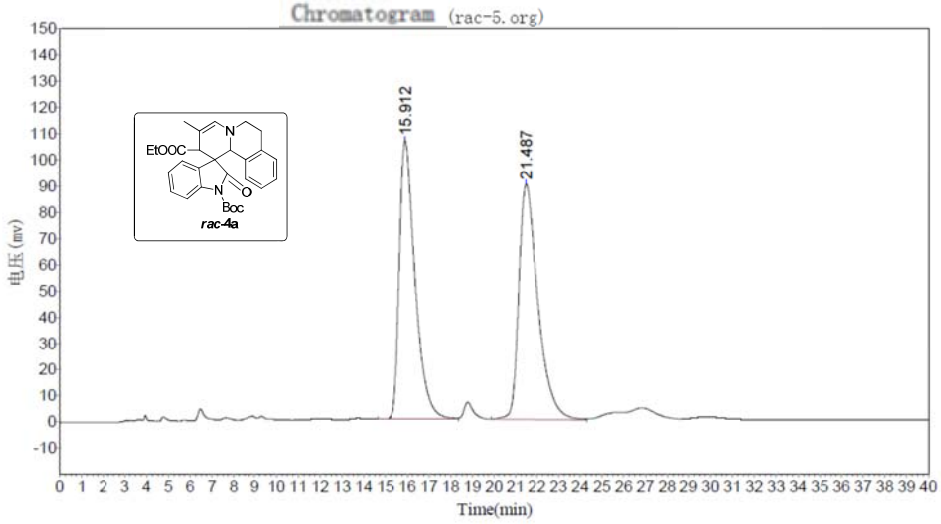
148.60
139.44
139.22
133.88
131.06
130.42
128.77
128.38
128.31
126.92
126.23
123.37
120.80
113.45
102.22
83.89
80.95
63.23
56.97
51.19
47.13
30.58
28.10
27.03
18.43
t-BuOOC
N
O
Br
Boc
4s
f1 (ppm)



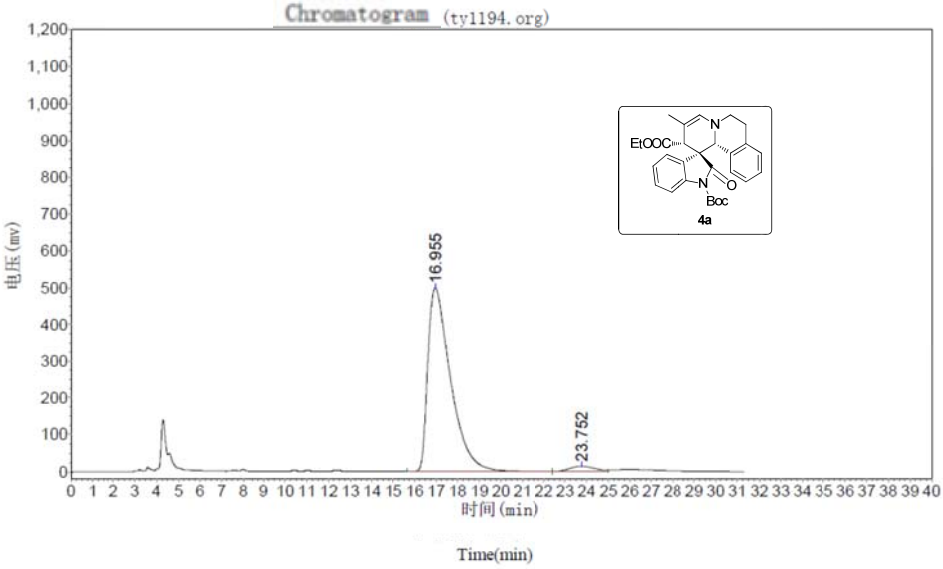


5. Chiral HPLC Traces



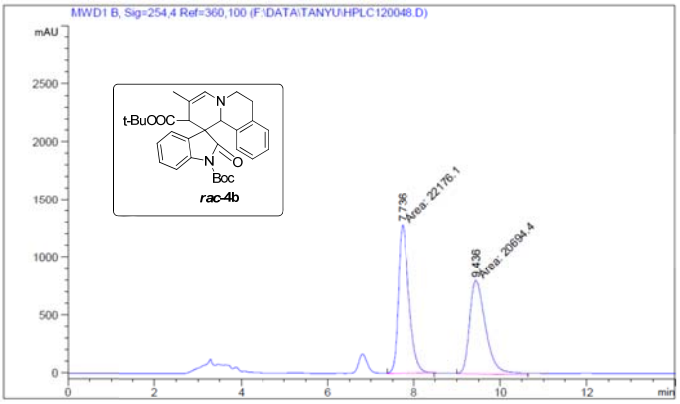
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.912	106397.578	5421580.000	49.4371
2		21.487	89847.313	5545048.500	50.5629
Total			196244.891	10966628.500	100.0000

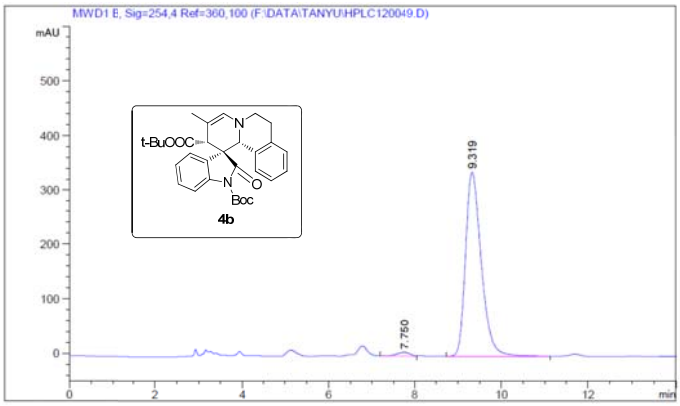


Results

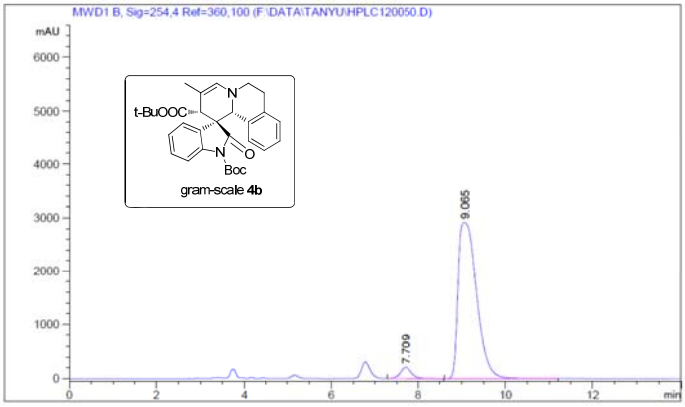
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
2		23.752	14849.878	1217029.000	3.2223
Total			514755.128	37768733.000	100.0000



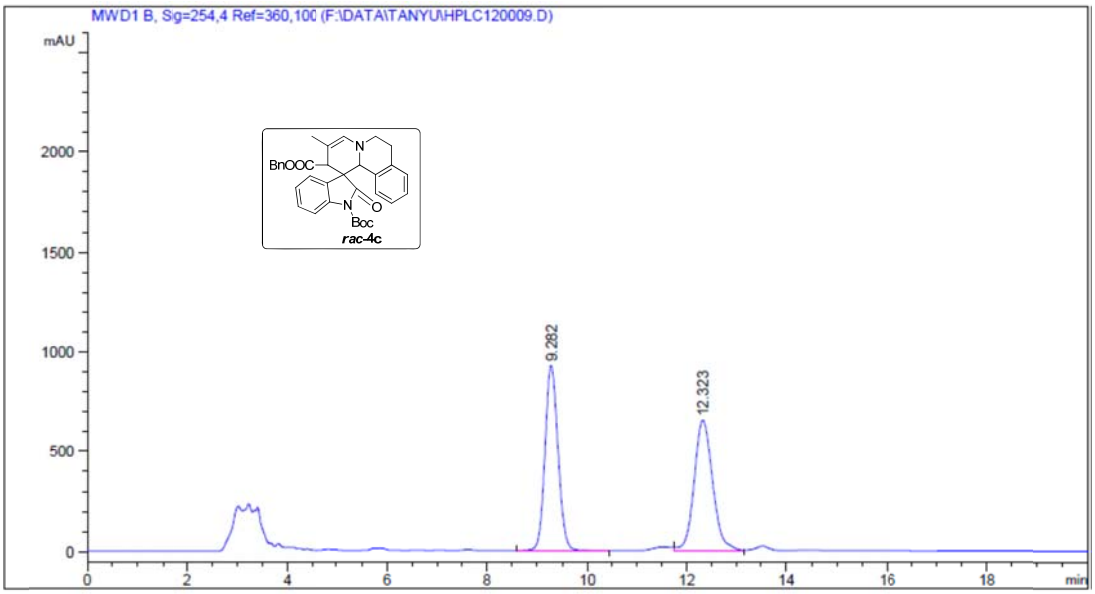
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.736	MM	0.2885	2.21761e4	1281.16589	51.7281
2	9.436	MM	0.4287	2.06944e4	804.49139	48.2719
Totals :				4.28704e4	2085.65729	



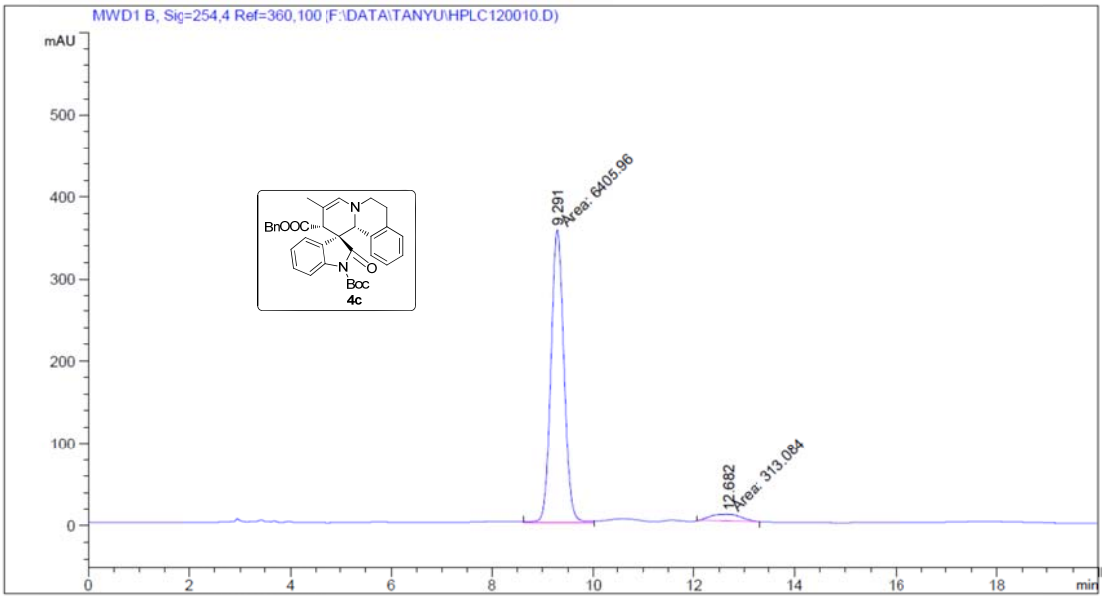
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.750	BV	0.3250	154.36952	7.17553	1.7961
2	9.319	VB	0.3827	8440.41211	336.42966	98.2039
Totals :				8594.78163	343.60519	



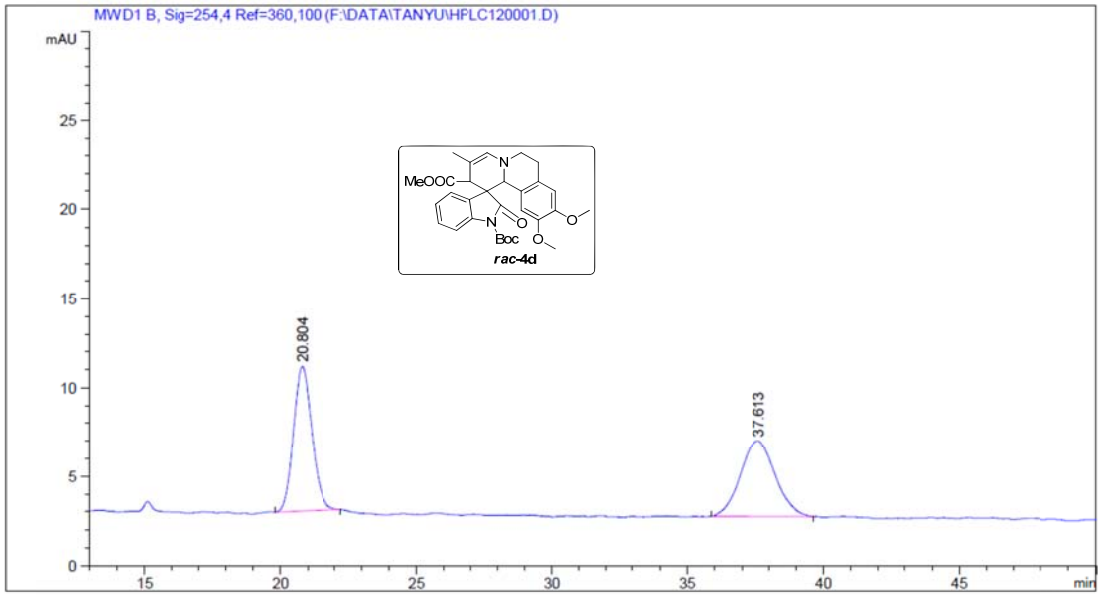
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.709	BB	0.2674	3816.88208	214.66258	4.2768
2	9.065	BV	0.4548	8.54303e4	2924.23584	95.7232
Totals :				8.92472e4	3138.89842	



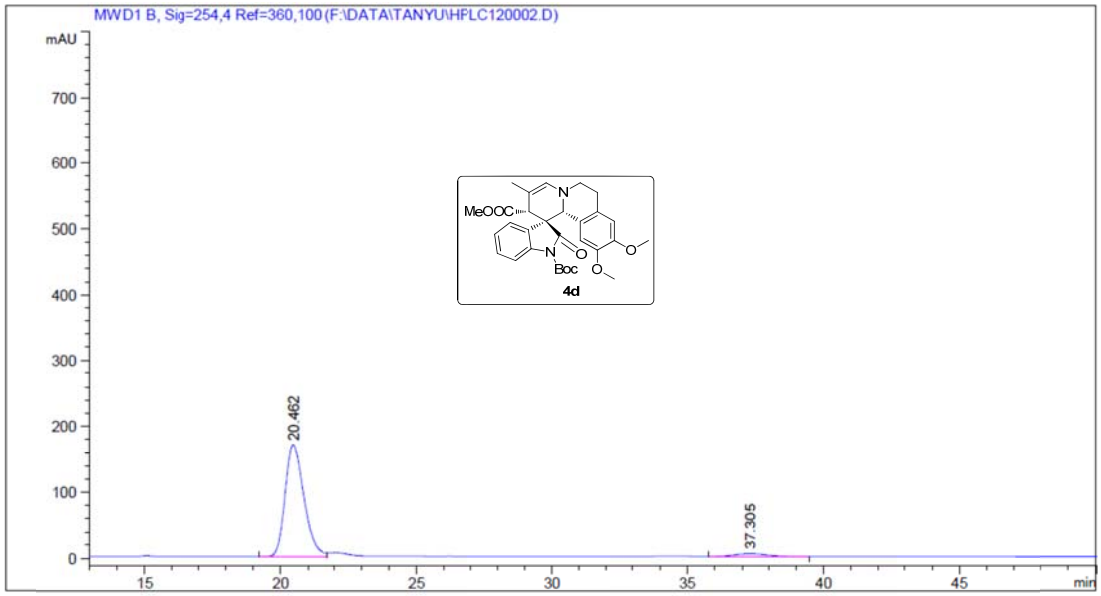
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.282	VB	0.2776	1.66567e4	927.00977	50.0025
2	12.323	VV	0.3938	1.66551e4	652.48743	49.9975
Totals :				3.33118e4	1579.49719	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.291	MM	0.2993	6405.96484	356.76532	95.3403
2	12.682	MM	0.6795	313.08435	7.67948	4.6597
Totals :				6719.04919	364.44480	

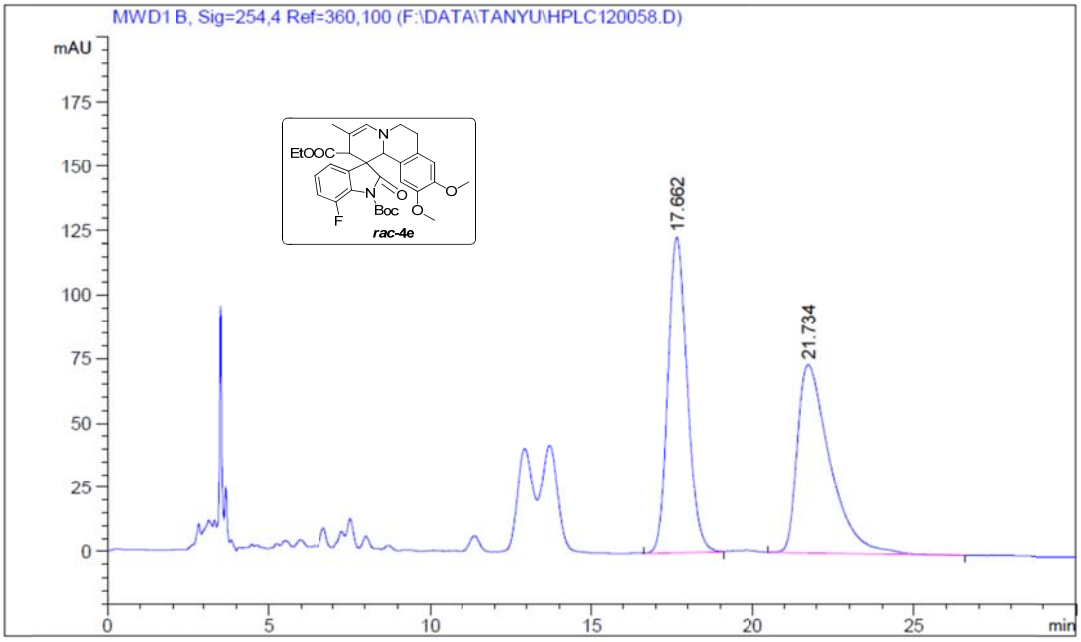


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.804	BB	0.7039	387.92657	8.14139	50.2405
2	37.613	BB	1.0758	384.21231	4.28604	49.7595
Totals :				772.13889	12.42743	

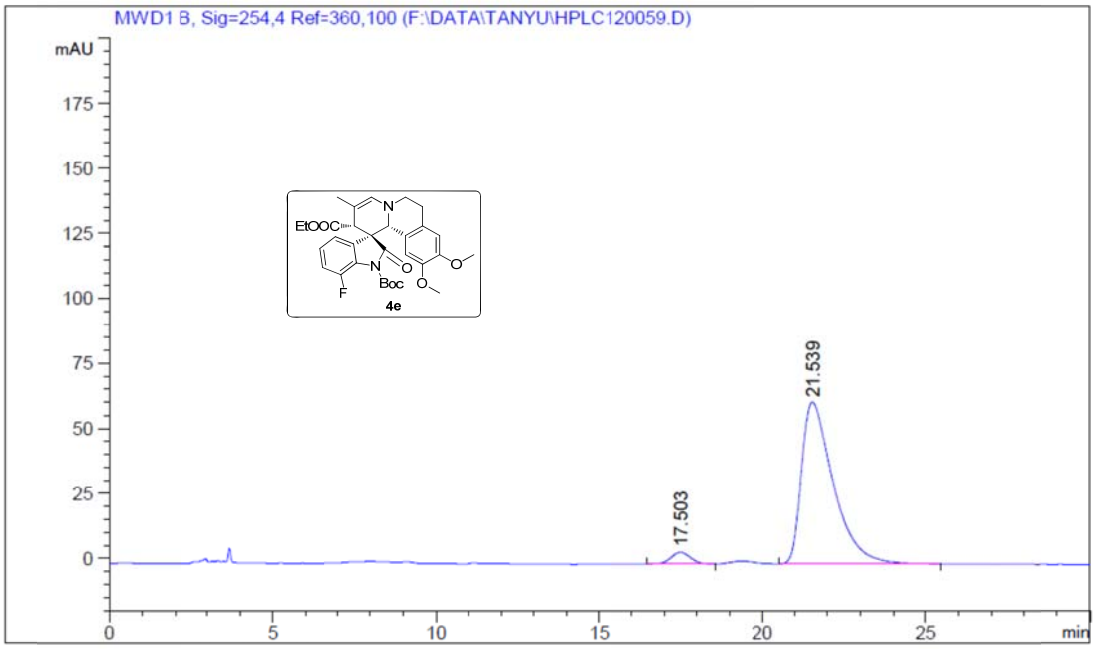


Signal 1: MWD1 B, Sig=254,4 Ref=360,100

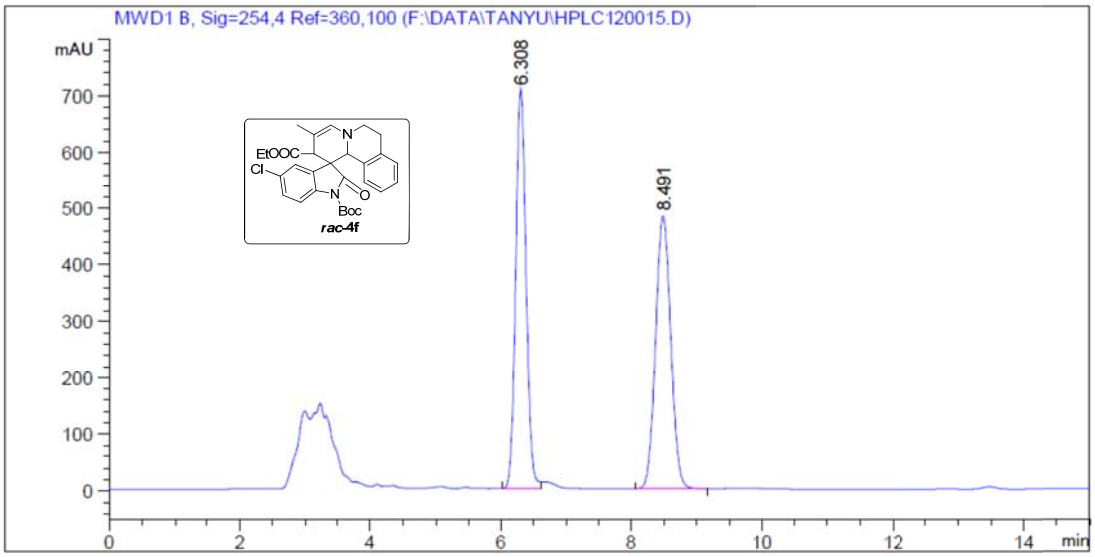
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.462	BV	0.7344	8064.72266	169.10286	95.7740
2	37.305	BB	1.0198	355.85403	4.13599	4.2260
Totals :				8420.57669	173.23885	



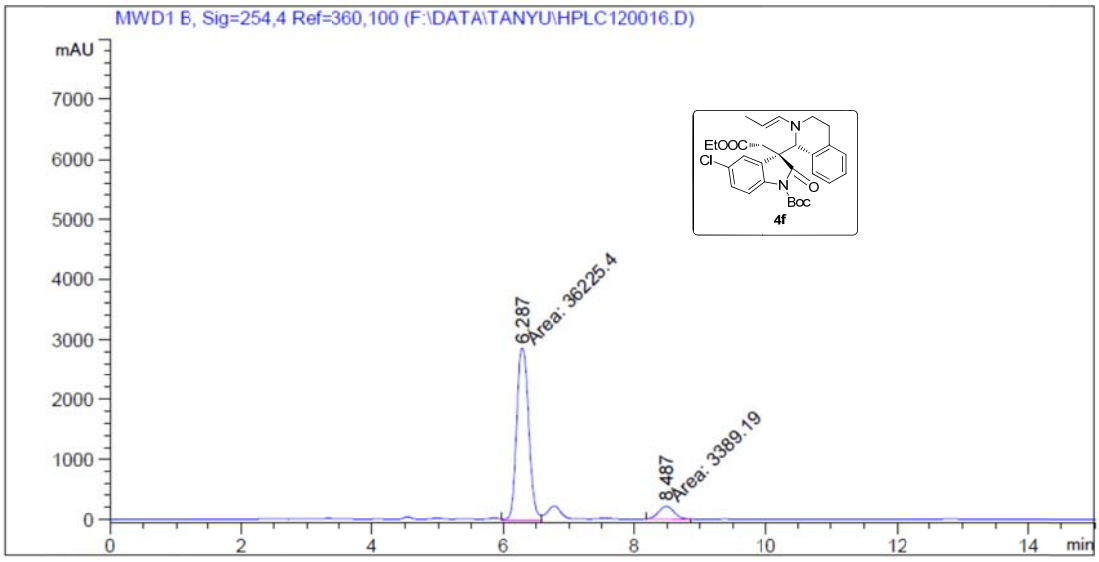
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.662	BB	0.6419	5088.83691	122.67832	49.9566
2	21.734	BB	1.0298	5097.68262	73.25954	50.0434
Totals :				1.01865e4	195.93786	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.503	BB	0.5805	185.38742	4.53879	4.2401
2	21.539	BB	0.9873	4186.84766	62.04665	95.7599
Totals :				4372.23508	66.58544	

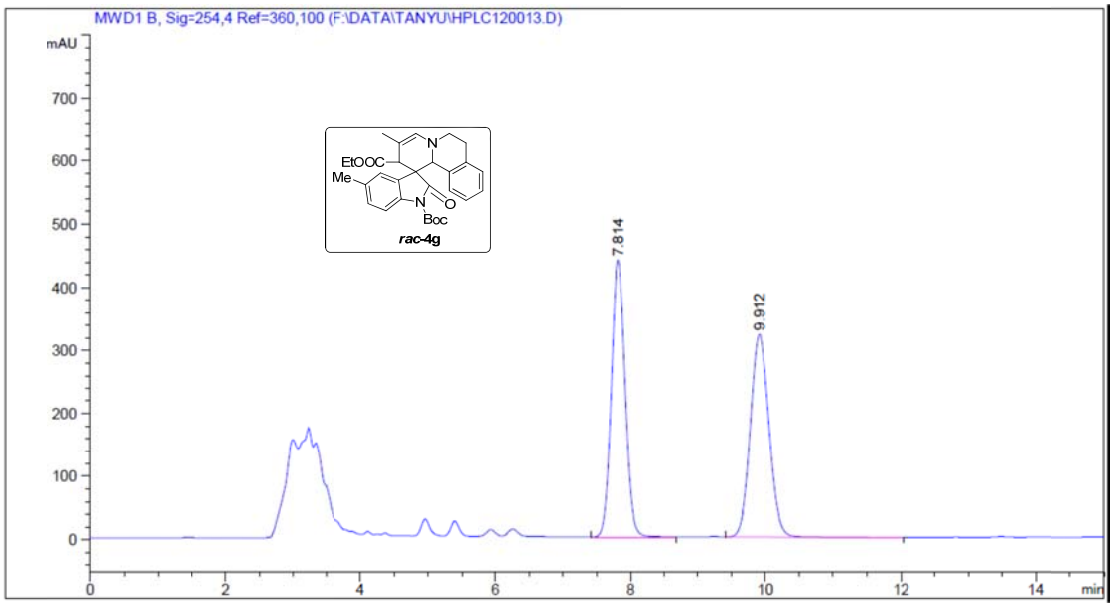


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.308	BV	0.1700	7761.79834	707.21570	49.9767
2	8.491	VV	0.2518	7769.04492	482.51242	50.0233
Totals :				1.55308e4	1189.72812	

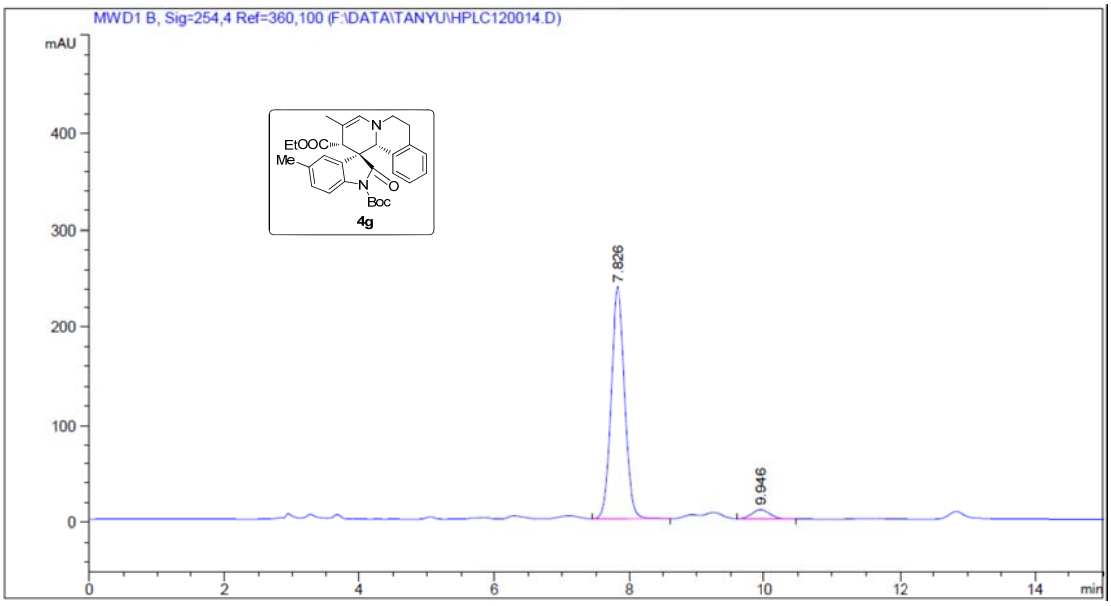


Signal 1: MWD1 B, Sig=254,4 Ref=360,100

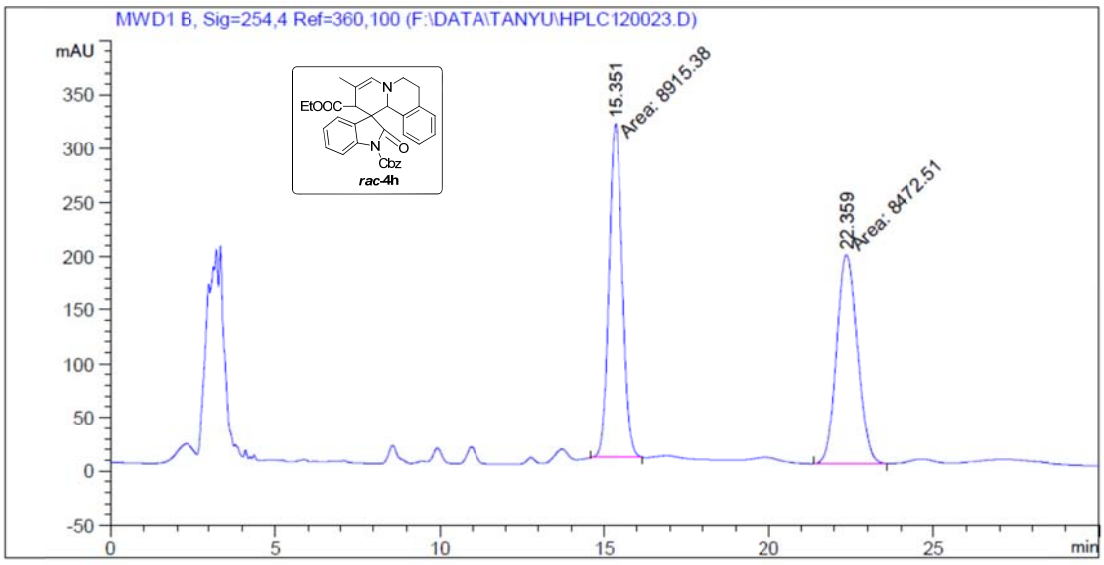
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.287	MM	0.2106	3.62254e4	2866.23779	91.4446
2	8.487	MM	0.2699	3389.19458	209.28830	8.5554
Totals :				3.96146e4	3075.52609	



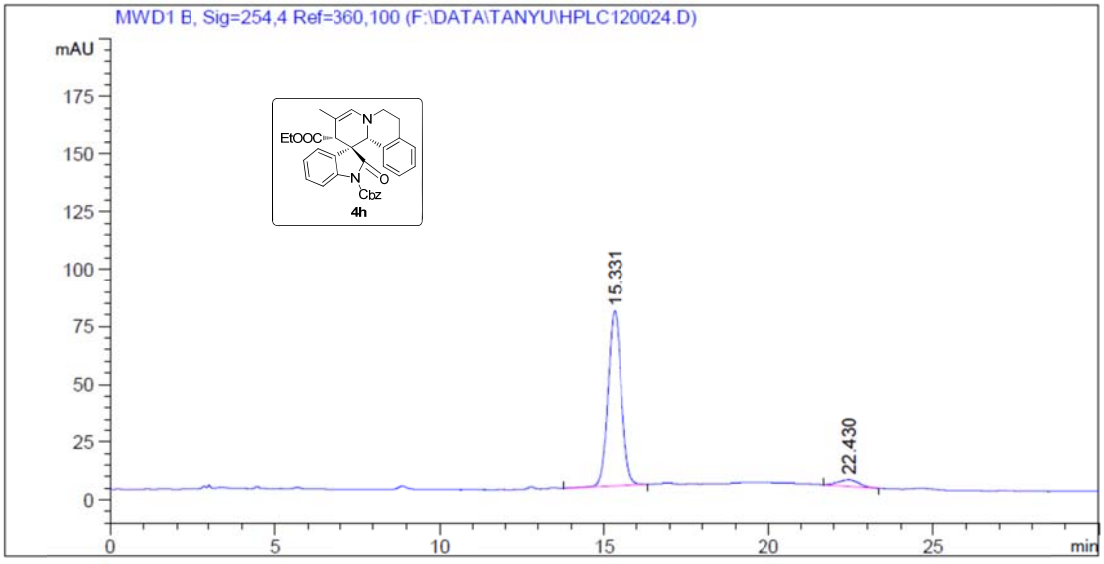
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.814	BB	0.2234	6305.00195	439.29425	50.3312
2	9.912	VB	0.2996	6222.03271	321.77618	49.6688
Totals :				1.25270e4	761.07043	



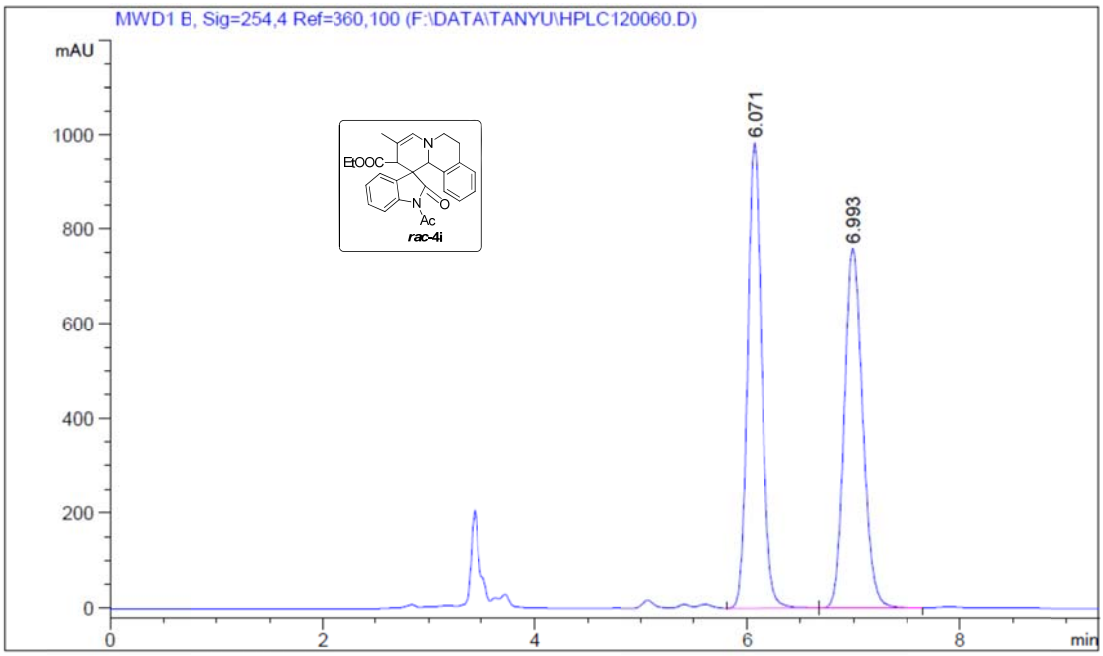
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.826	VB	0.2252	3468.24902	239.17160	94.9059
2	9.946	VB	0.3010	186.15739	9.65302	5.0941
Totals :				3654.40642	248.82462	



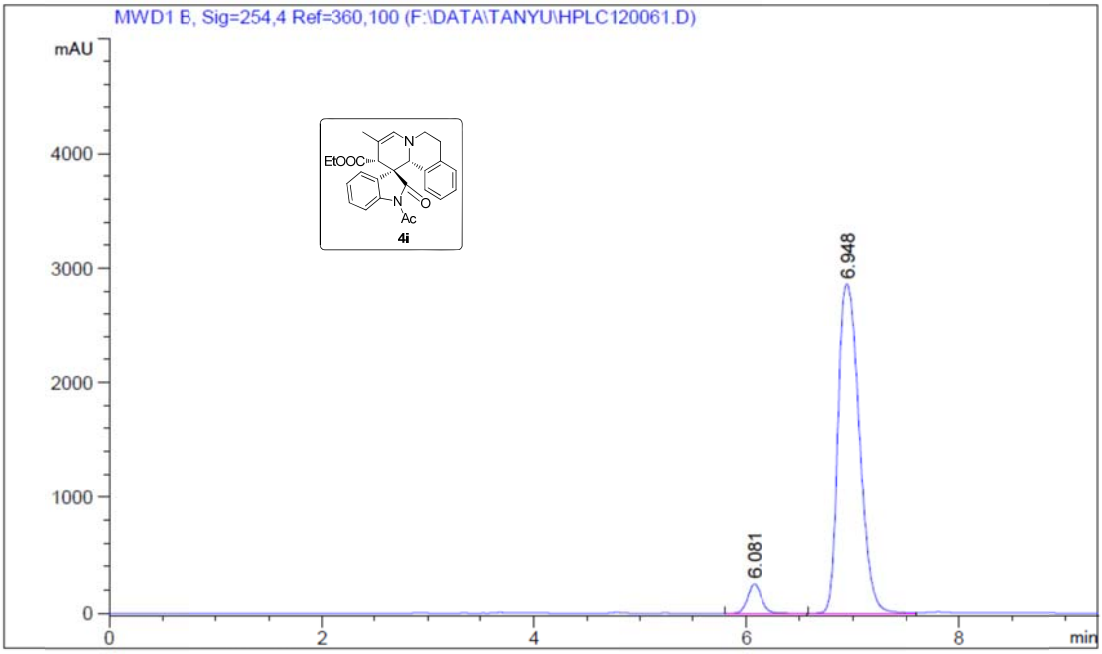
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.351	MM	0.4781	8915.37500	310.76102	51.2735
2	22.359	MM	0.7244	8472.51074	194.92230	48.7265
Totals :				1.73879e4	505.68332	



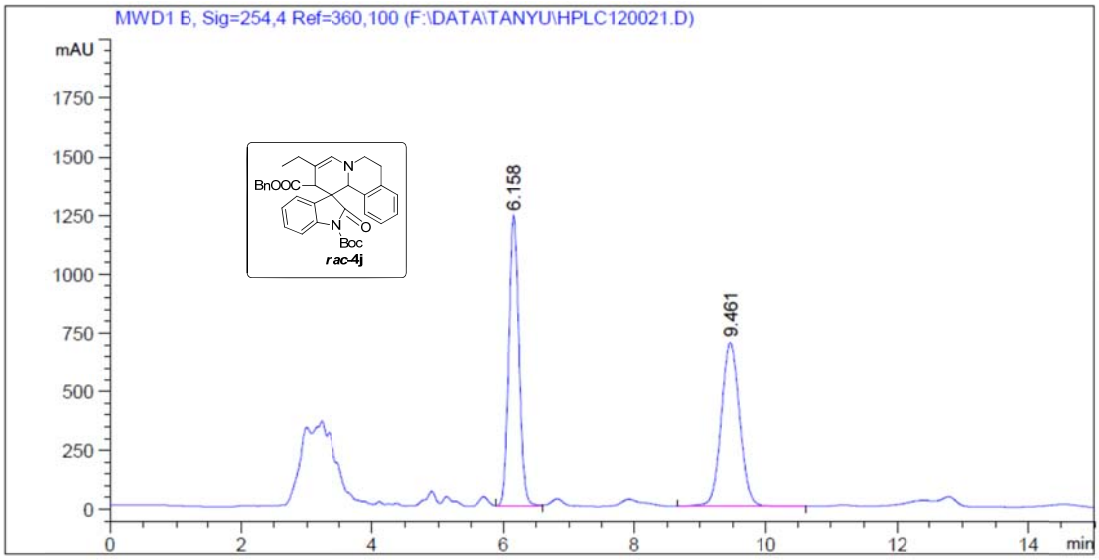
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.331	BB	0.4461	2166.01074	75.63376	94.7532
2	22.430	BB	0.5953	119.93933	2.76940	5.2468
Totals :				2285.95007	78.40315	



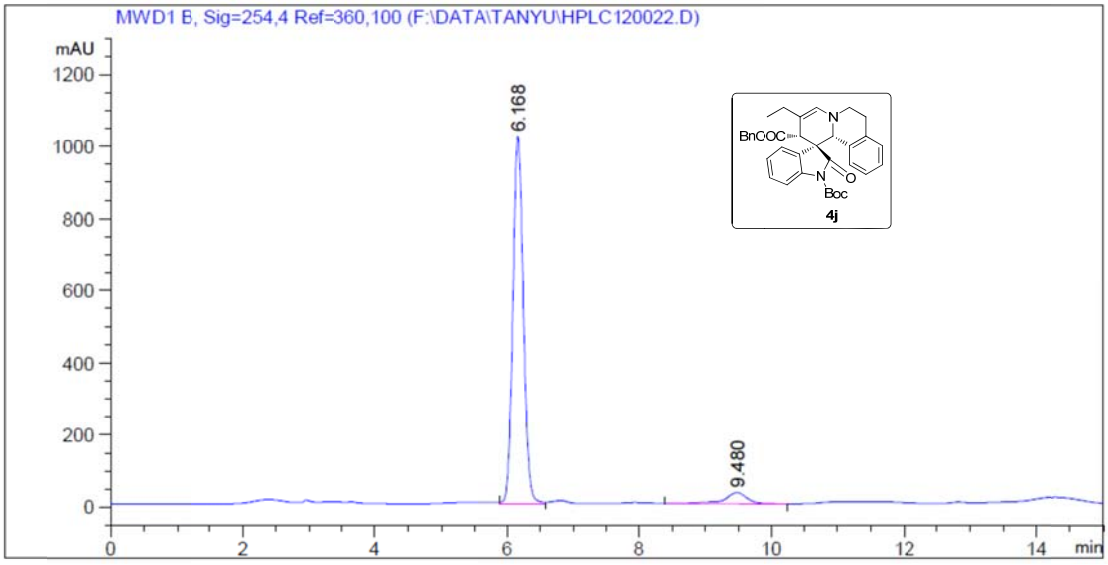
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.071	BB	0.1453	9220.62305	984.16754	50.3834
2	6.993	BB	0.1855	9080.28613	759.63306	49.6166
Totals :				1.83009e4	1743.80060	



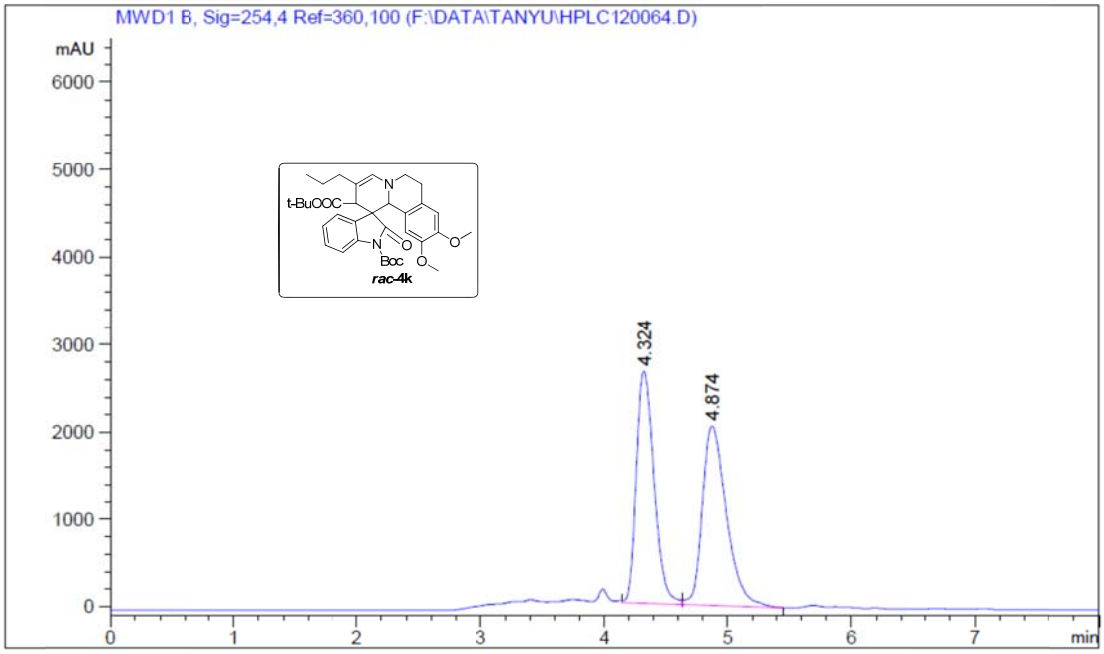
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.081	BB	0.1438	2339.77661	253.26733	5.6365
2	6.948	BV	0.2157	3.91716e4	2861.42603	94.3635
Totals :				4.15114e4	3114.69336	



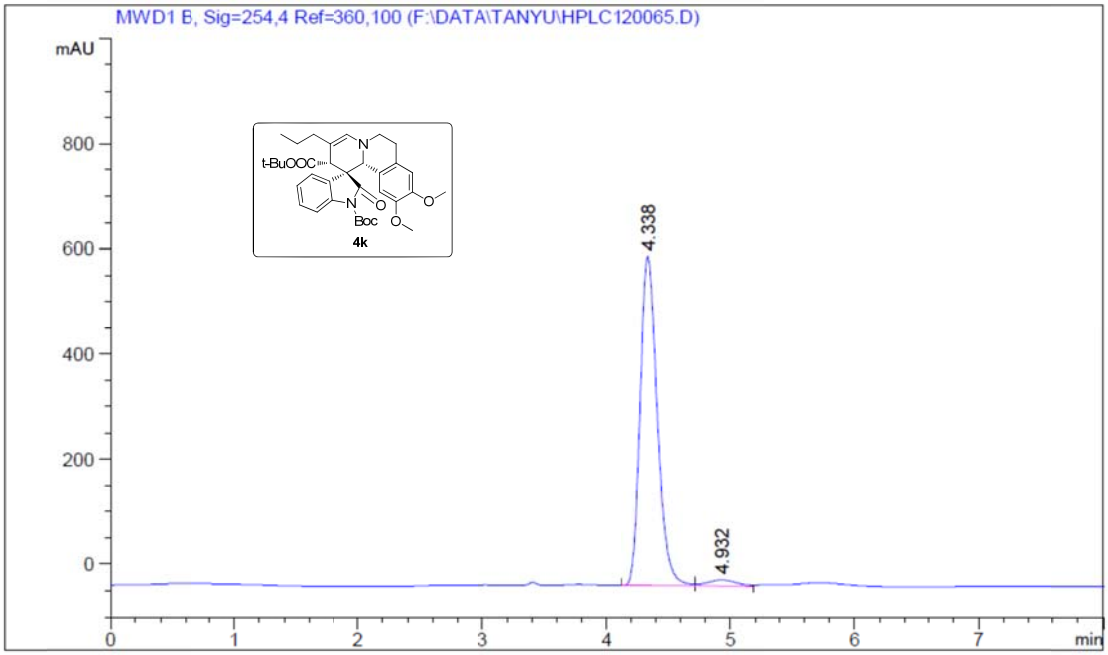
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.158	VV	0.1683	1.33745e4	1235.64551	49.5678
2	9.461	VB	0.3038	1.36077e4	696.87408	50.4322
Totals :				2.69822e4	1932.51959	



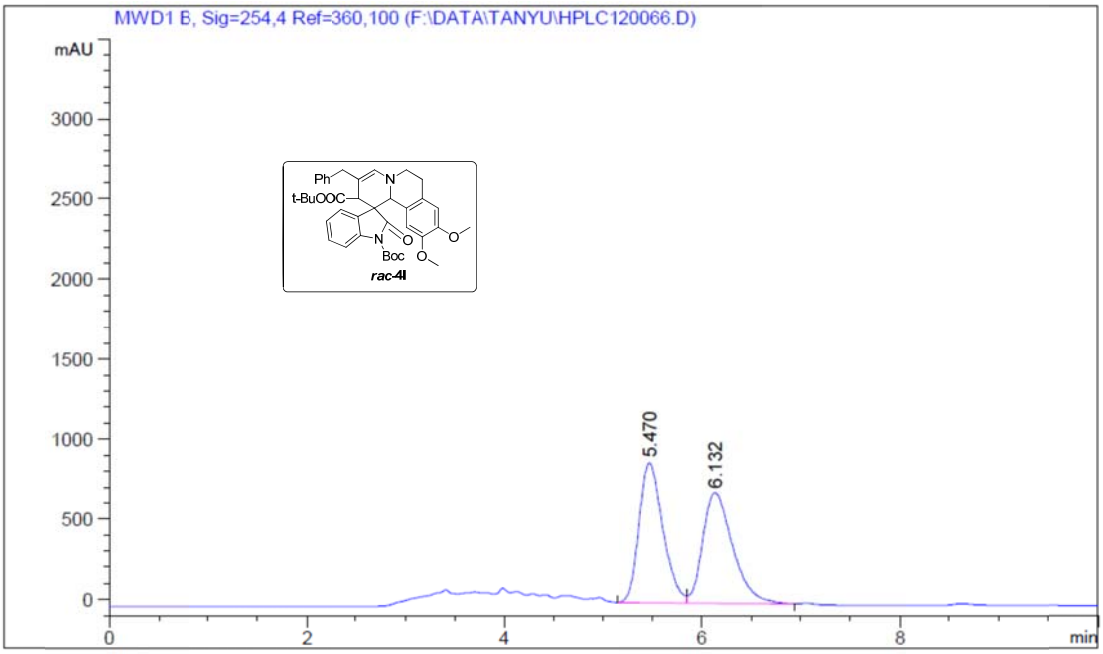
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.168	VV	0.1701	1.11949e4	1019.44836	93.7051
2	9.480	VB	0.3557	752.04352	31.15056	6.2949
Totals :				1.19469e4	1050.59893	



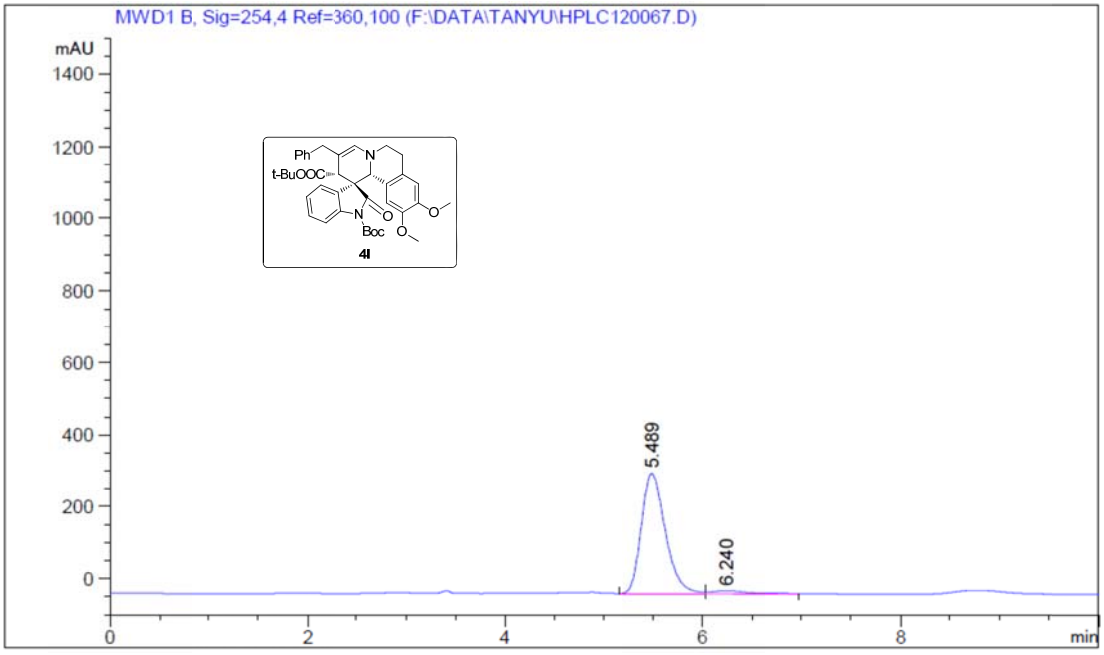
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.324	VV	0.1561	2.64884e4	2661.91162	48.7297
2	4.874	VB	0.2077	2.78695e4	2061.41431	51.2703
Totals :				5.43579e4	4723.32593	



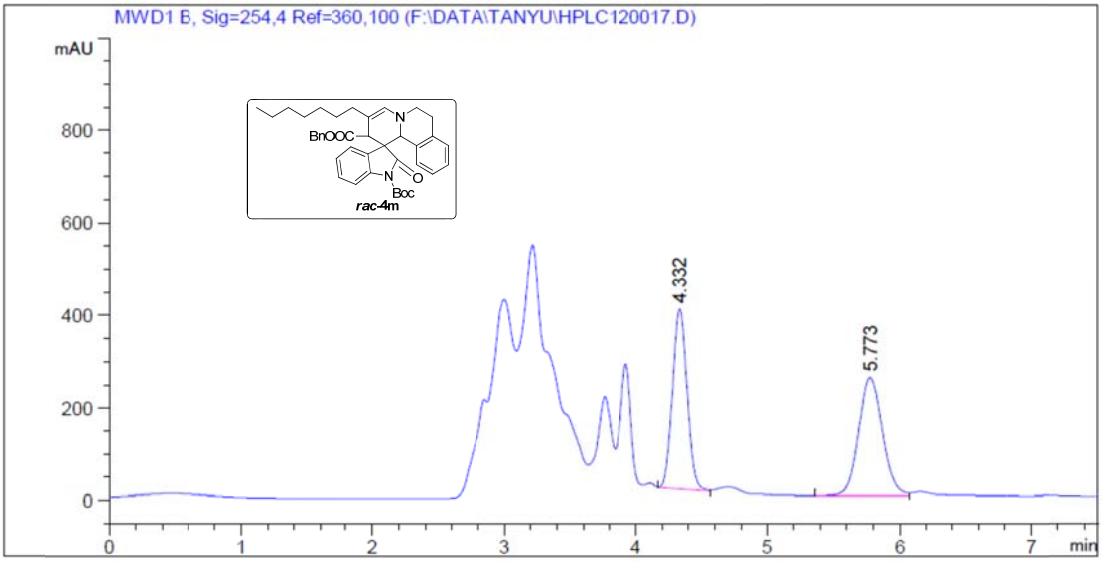
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.338	BV	0.1469	5952.39600	626.35358	97.0056
2	4.932	VV	0.2475	183.73865	11.31114	2.9944
Totals :				6136.13464	637.66472	



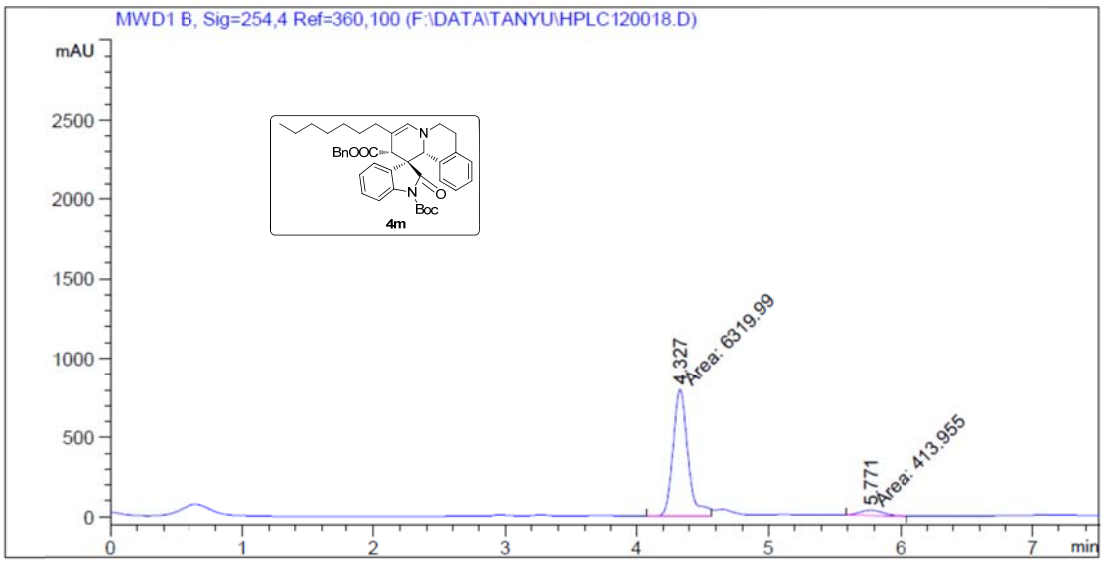
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.470	BV	0.2548	1.45455e4	871.15039	50.1643
2	6.132	VB	0.3198	1.44502e4	685.79095	49.8357
Totals :				2.89958e4	1556.94135	



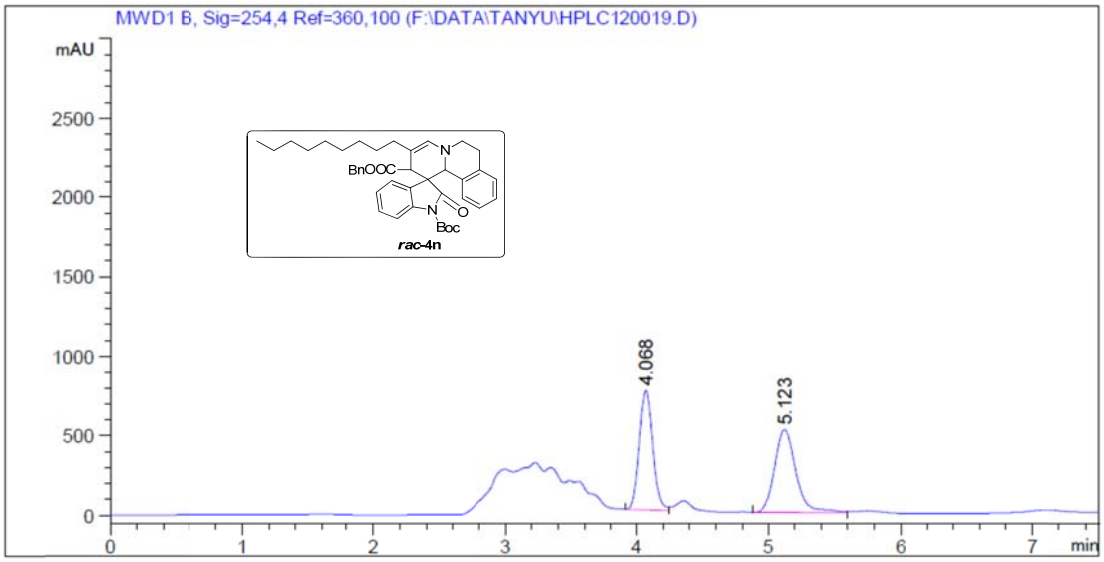
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.489	BV	0.2597	5615.74561	334.75345	95.8584
2	6.240	VV	0.3867	242.62761	8.93916	4.1416
Totals :				5858.37321	343.69261	



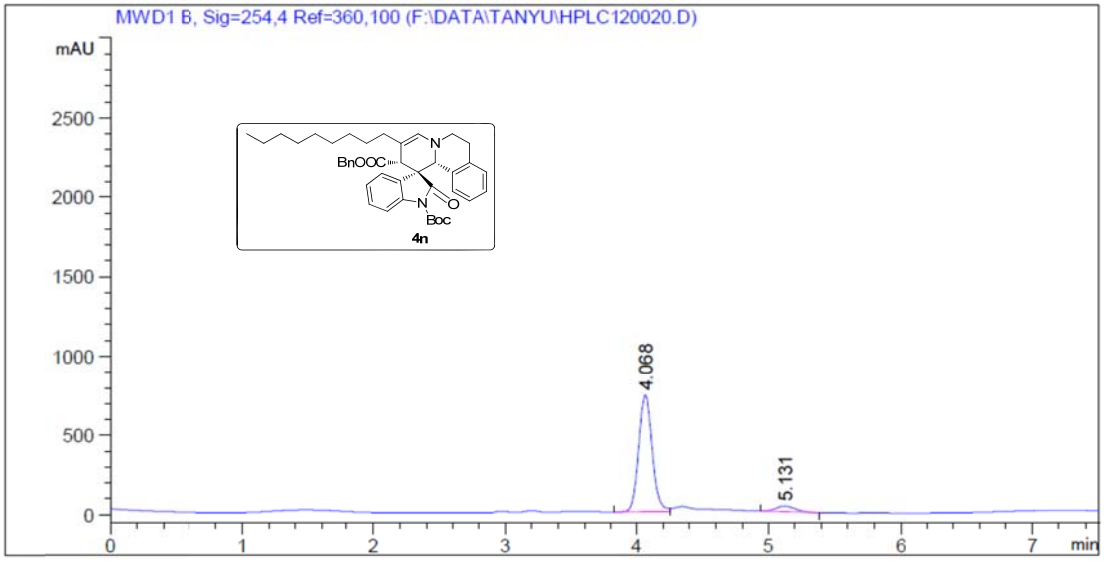
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.332	BV	0.1194	2983.47681	389.40619	48.3371
2	5.773	BV	0.1933	3188.75903	256.00009	51.6629
Totals :				6172.23584	645.40628	



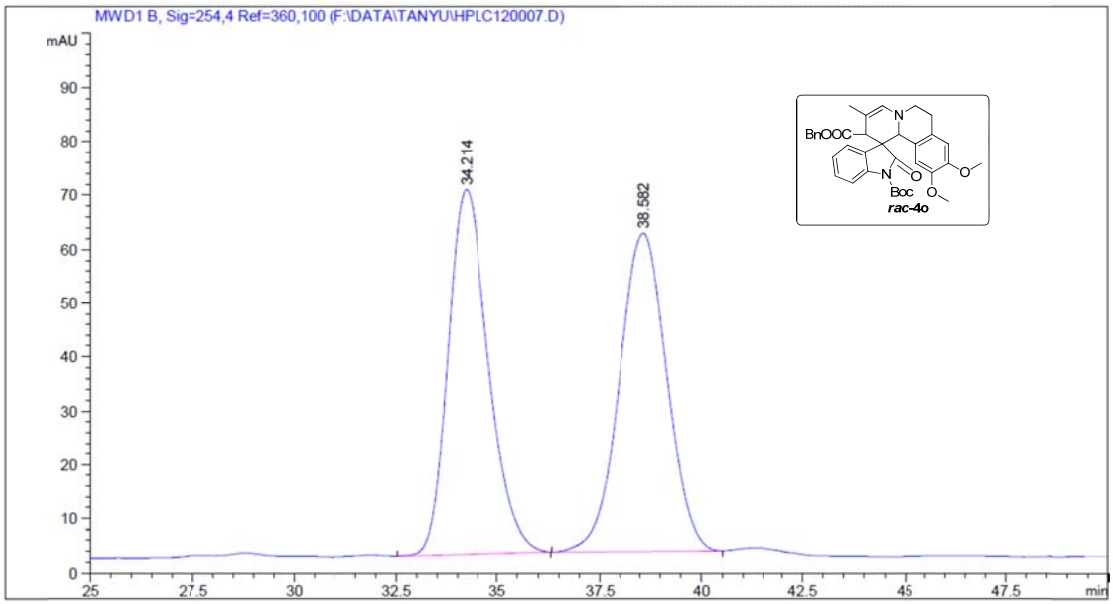
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.327	MF	0.1314	6319.99023	801.84888	93.8527
2	5.771	MM	0.2127	413.95502	32.43170	6.1473
Totals :				6733.94525	834.28058	



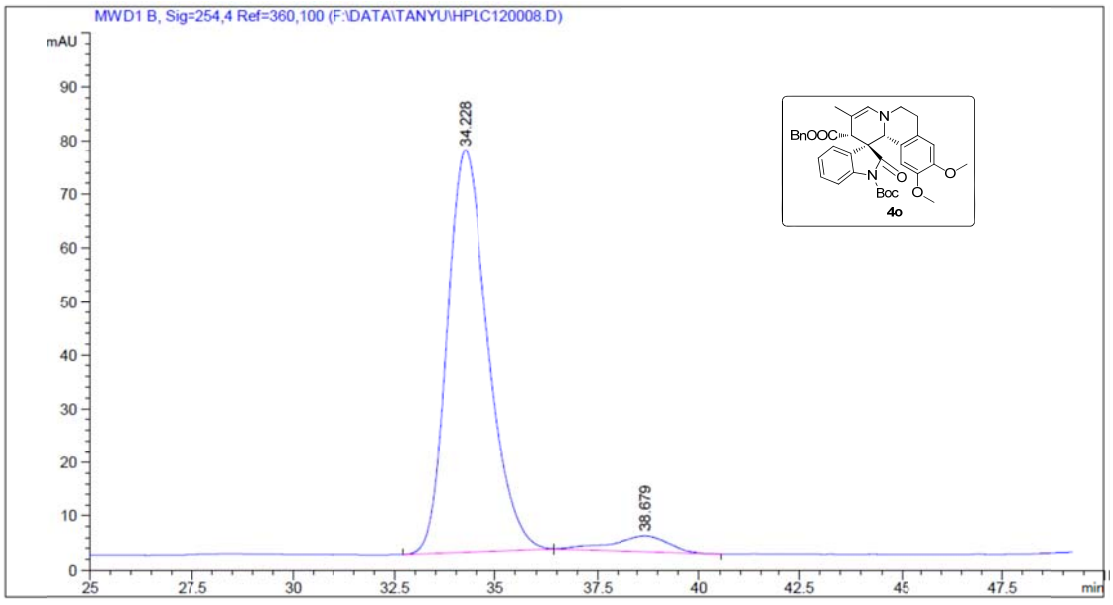
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.068	BV	0.1107	5310.37598	749.39984	47.6356
2	5.123	BV	0.1732	5837.53027	518.96124	52.3644
Totals :				1.11479e4	1268.36108	



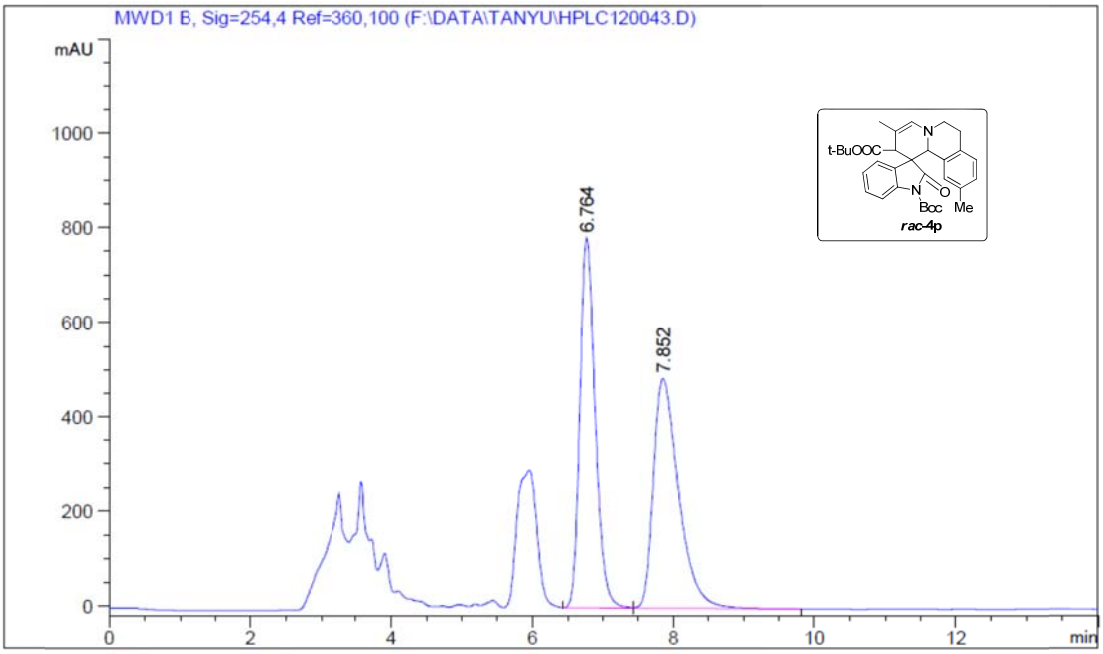
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.068	BV	0.1090	5251.10205	738.34369	93.5930
2	5.131	BB	0.1580	359.46982	35.53224	6.4070
Totals :				5610.57187	773.87593	



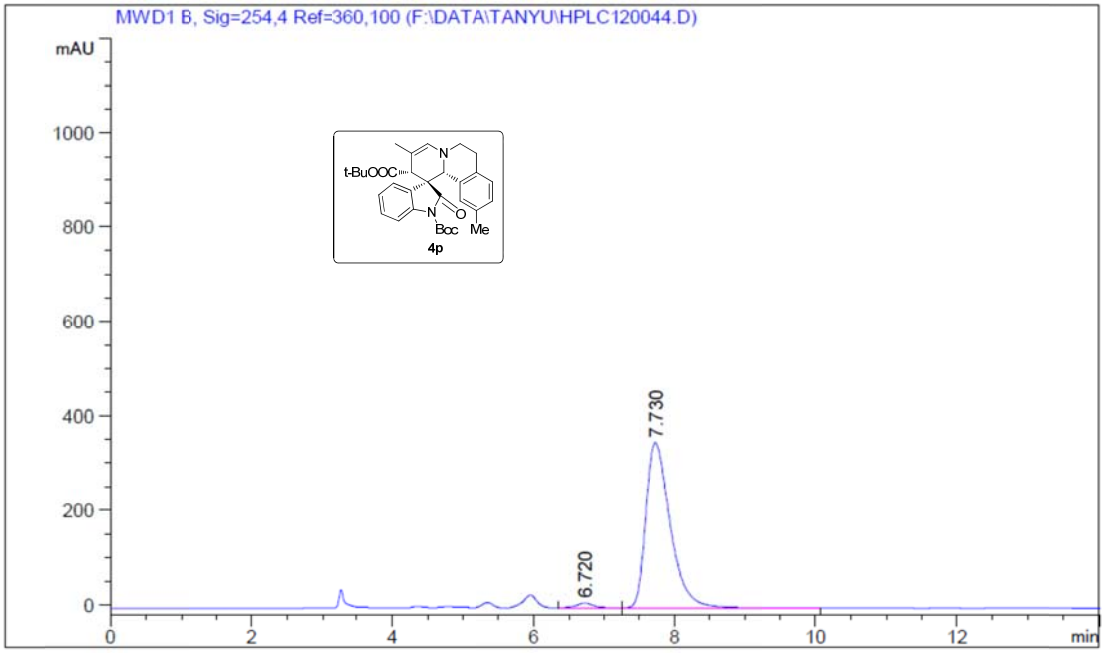
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.214	BB	1.0574	4738.63330	67.63196	49.7615
2	38.582	BB	1.2541	4784.05859	59.11623	50.2385
Totals :				9522.69189	126.74819	



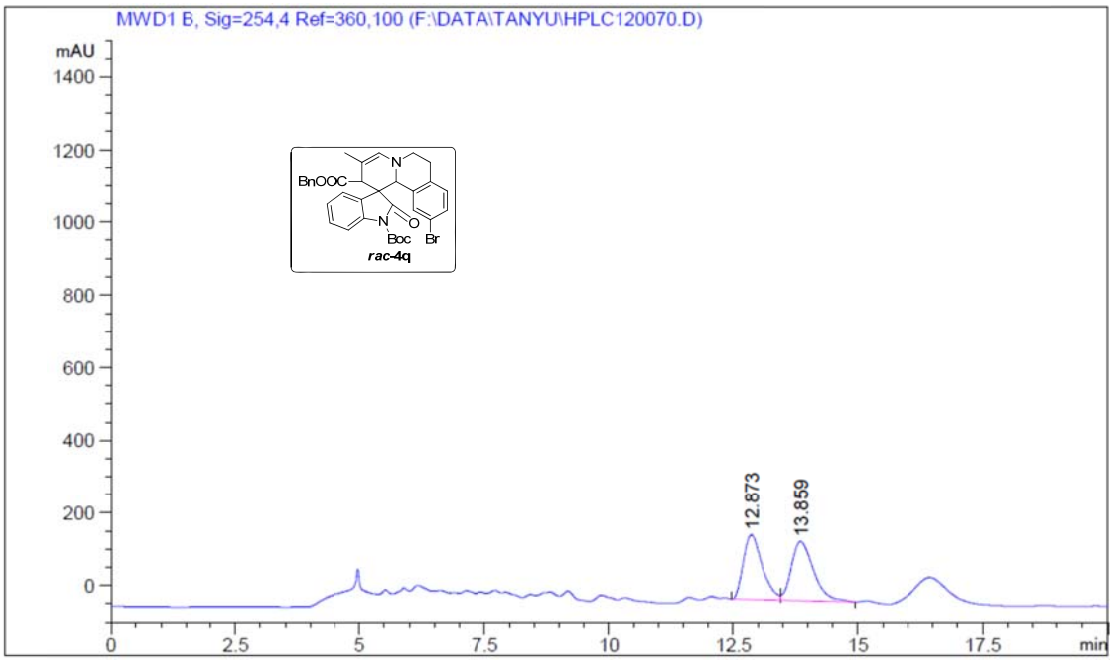
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.228	BB	1.0733	5323.93555	74.89566	95.0004
2	38.679	BB	1.1158	280.18570	2.96131	4.9996
Totals :				5604.12125	77.85697	



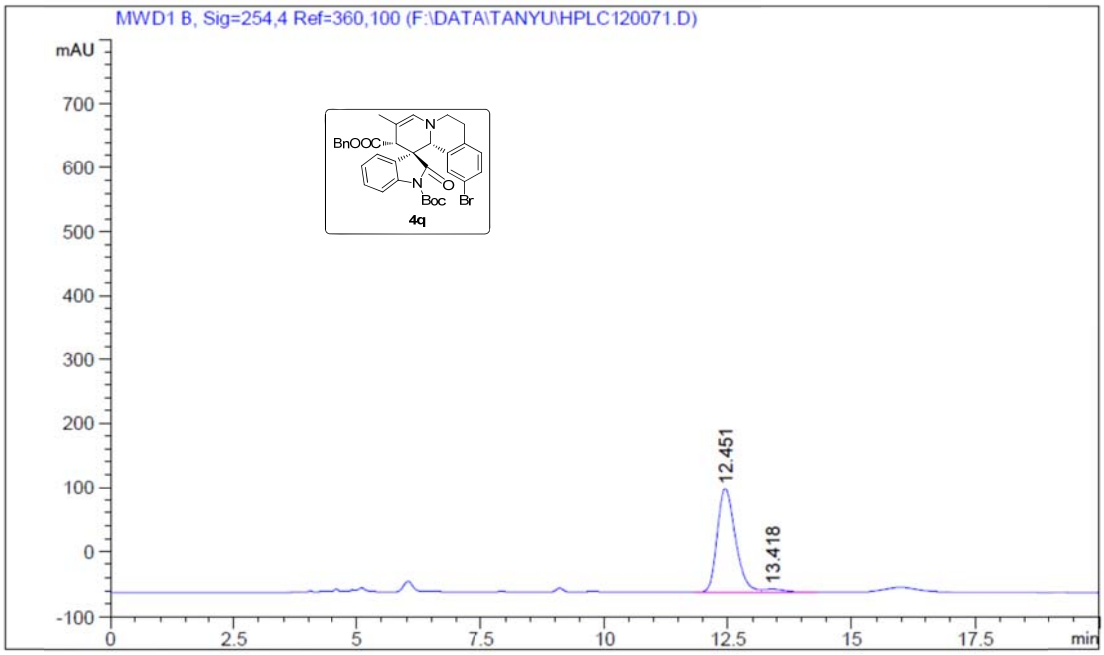
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.764	BV	0.2322	1.18203e4	782.48029	49.5382
2	7.852	VB	0.3770	1.20407e4	486.05148	50.4618
Totals :				2.38609e4	1268.53177	



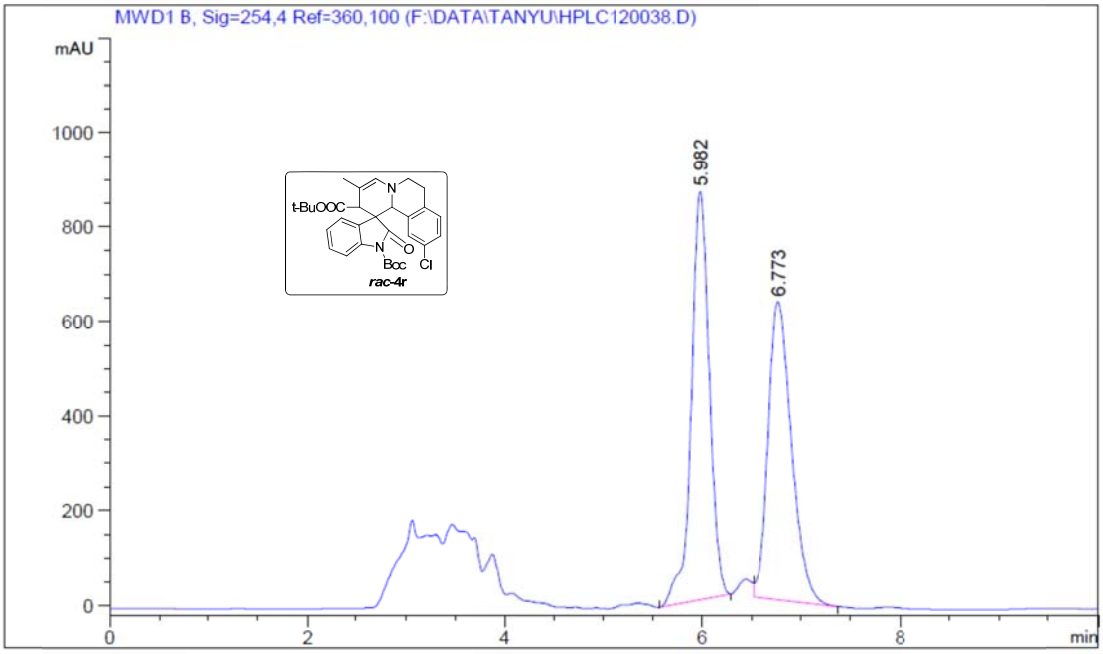
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.720	BV	0.2481	176.87326	10.52344	2.0760
2	7.730	VB	0.3617	8343.09473	350.52072	97.9240
Totals :				8519.96799	361.04416	



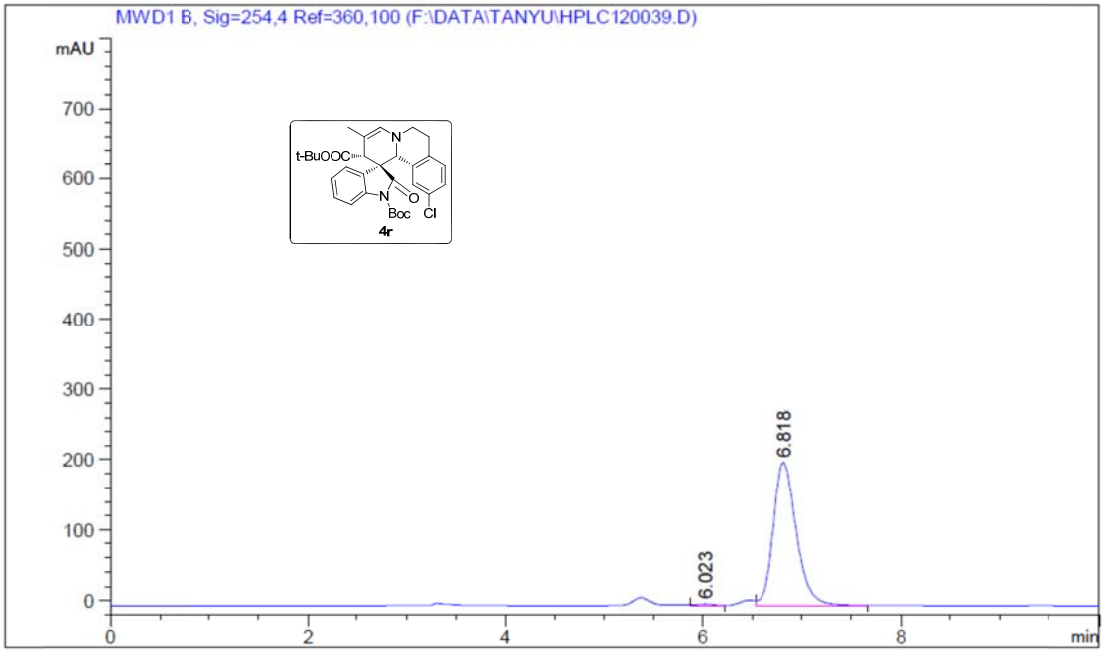
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.873	BV	0.4081	4733.23730	178.07530	48.4276
2	13.859	VB	0.4803	5040.60254	162.32549	51.5724
Totals :				9773.83984	340.40079	



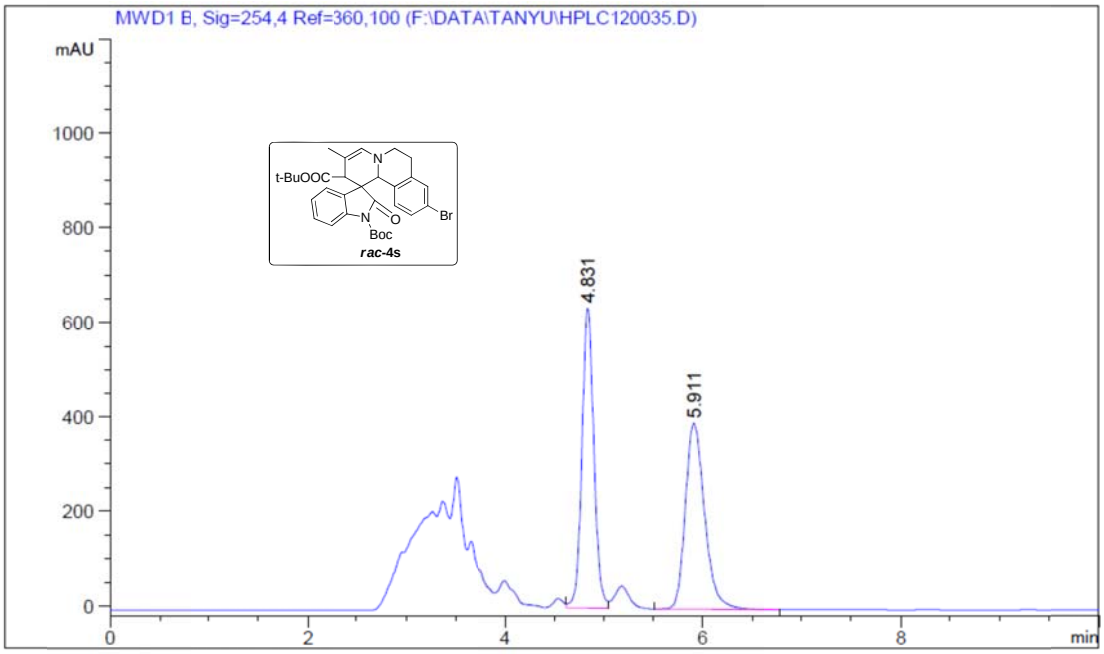
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.451	BV	0.3897	4056.83984	160.05438	96.7459
2	13.418	VB	0.4266	136.45395	4.64695	3.2541
Totals :				4193.29379	164.70134	



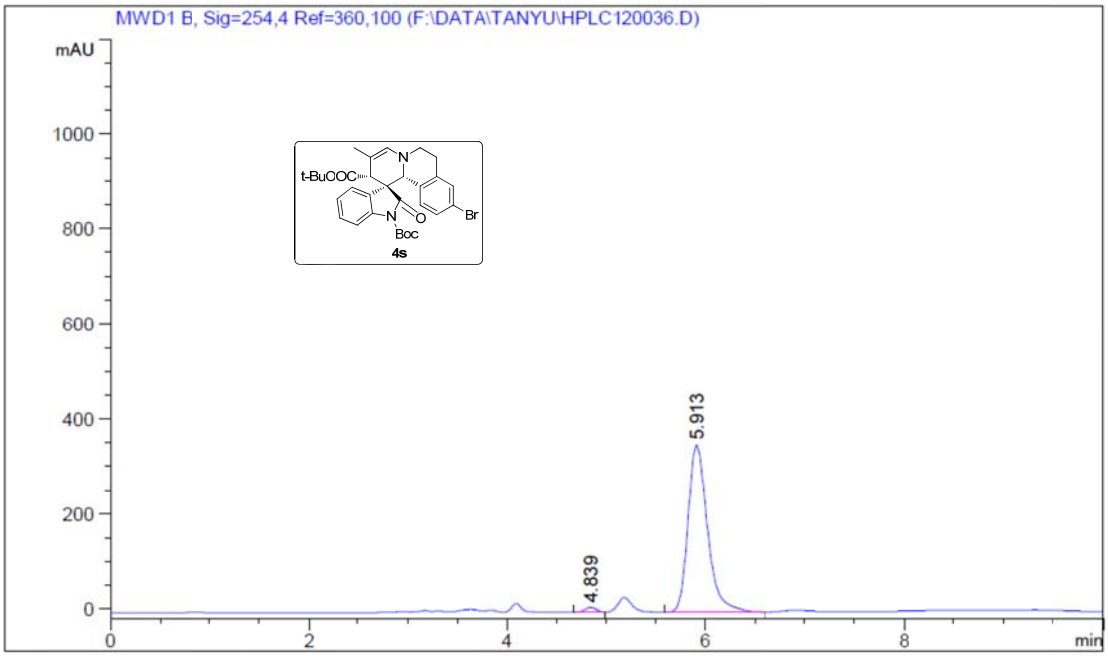
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.982	BB	0.1949	1.08633e4	862.95648	51.3300
2	6.773	VB	0.2507	1.03003e4	630.29230	48.6700
Totals :				2.11636e4	1493.24878	



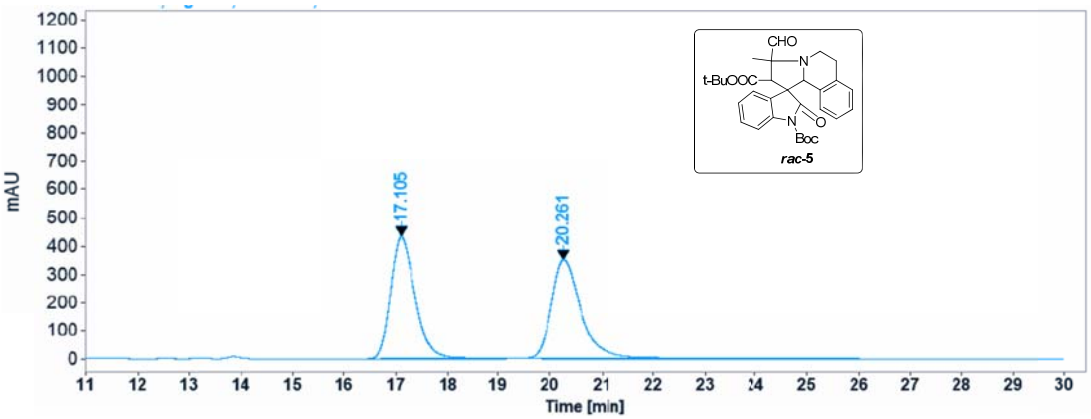
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.023	VB	0.1702	26.55394	2.38012	0.8015
2	6.818	VB	0.2462	3286.54175	203.70131	99.1985
Totals :				3313.09569	206.08143	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.831	VV	0.1275	5298.54004	634.15271	50.1059
2	5.911	BB	0.2066	5276.14209	393.11136	49.8941
Totals :				1.05747e4	1027.26407	

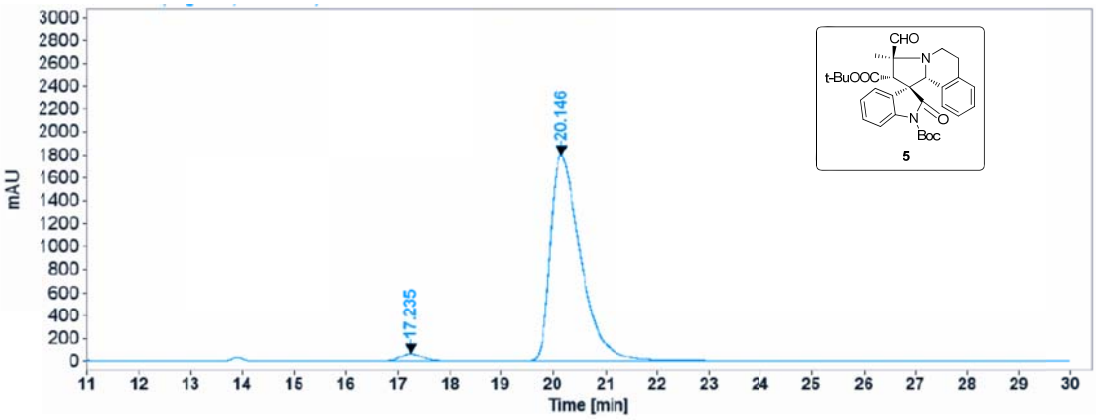


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.839	BV	0.1211	79.97144	10.24253	1.6472
2	5.913	BB	0.2083	4774.91846	351.85852	98.3528
Totals :				4854.88989	362.10105	



Signal: DAD1 B, Sig=214,8 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
17.105	0.495	13854.473	431.573	49.6742
20.261	0.607	14036.236	349.499	50.3258
	Sum	27890.7090		



Signal: DAD1 B, Sig=214,8 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
17.235	0.475	1983.970	64.516	2.6605
20.146	0.616	72588.344	1794.098	97.3395
	Sum	74572.3137		

6. X-ray Crystallography Data of 4l.

Crystals of **4l** were grown from PE:EA =10:1 to give colourless crystals that were submitted to X-Ray crystallography.

Table 1. Crystal data and structure refinement for cu_60113b.

Identification code	cu_60113b	
Empirical formula	C_{39} H_{44} N_2 O_7	
Formula weight	652.76	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 22.0361(10) Å	a= 90°.
	b = 8.9726(4) Å	b= 98.967(3)°.
	c = 18.4215(8) Å	g = 90°.
Volume	3597.8(3) $Å^3$	
Z	4	
Density (calculated)	1.205 Mg/m^3	
Absorption coefficient	0.668 mm^{-1}	
F(000)	1392	
Crystal size	0.640 x 0.500 x 0.020 mm^3	
Theta range for data collection	2.428 to 69.495°.	
Index ranges	-25<=h<=26, -10<=k<=10, -22<=l<=22	
Reflections collected	9159	
Independent reflections	4929 [R(int) = 0.0440]	
Completeness to theta = 67.679°	93.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.753 and 0.561	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	4929 / 67 / 442
Goodness-of-fit on F^2	1.334
Final R indices [I>2sigma(I)]	R1 = 0.0977, wR2 = 0.2925
R indices (all data)	R1 = 0.1055, wR2 = 0.3097
Absolute structure parameter	0.1(2)
Extinction coefficient	0.0013(5)
Largest diff. peak and hole	1.028 and -0.479 e.$Å^{-3}$

X-ray Crystallography Data of 5.

Crystals of **5** were grown from PE:EA =10:1 to give colourless crystals that were submitted to X-Ray crystallography.

Table 1. Crystal data and structure refinement for cu_60121a.

Identification code	cu_60121a	
Empirical formula	C_{31} H_{36} N_2 O_6	
Formula weight	532.62	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.9835(14) Å	a= 90°.
	b = 12.2707(16) Å	b= 90°.
	c = 23.460(3) Å	g = 90°.
Volume	2873.9(6) $Å^3$	
Z	4	
Density (calculated)	1.231 Mg/m^3	
Absorption coefficient	0.693 mm^{-1}	
F(000)	1136	

Crystal size	0.250 x 0.220 x 0.180 mm^3
Theta range for data collection	3.768 to 67.416°.
Index ranges	-11<=h<=10, -14<=k<=14, -24<=l<=28
Reflections collected	14287
Independent reflections	4523 [R(int) = 0.0593]
Completeness to theta = 67.679°	91.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.753 and 0.589
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4523 / 42 / 360
Goodness-of-fit on F^2	1.778
Final R indices [I>2sigma(I)]	R1 = 0.1890, wR2 = 0.3905
R indices (all data)	R1 = 0.1975, wR2 = 0.4010
Absolute structure parameter	-0.11(17)
Extinction coefficient	0.109(16)
Largest diff. peak and hole	1.483 and -0.831 $e.Å^{-3}$