Organocatalytic diastereo- and atroposelective construction of eight-membered bridged (hetero)biaryls via asymmetric intramolecular [3+2] cycloaddition

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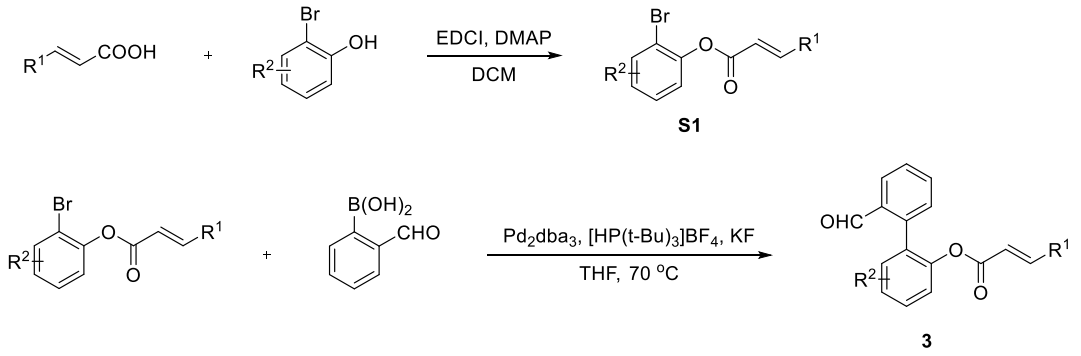
Contents

1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (200~300 mesh). Diastereoisomeric ratios (dr) were determined by ^{1}H NMR. Enantiomeric excesses (ee) were determined by HPLC using corresponding commercial chiral columns as stated at 30 °C with UV detector at 254 nm. Optical rotations were reported as follows: $[\alpha]_D^T$ (c g/100 mL, solvent). All ^{1}H NMR spectra were recorded on Bruker Avance II 400 MHz or Bruker Avance III 600 MHz. ^{19}F NMR spectra were recorded on Bruker Avance II 376 MHz and Bruker Avance III 565 MHz. ^{13}C NMR spectra were recorded on Bruker Avance II 101 MHz or Bruker Avance III 151 MHz with chemical shifts reported as ppm (in $CDCl_3$, TMS as internal standard). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad singlet, dd = double doublet, coupling constants in Hz, integration). HRMS (ESI) was obtained with a HRMS/MS instrument (LTQ Orbitrap XLTM).

3-Amino oxindole hydrochlorides **2** were prepared according to literature methods.[1]

2. General procedures for biaryl aldehydes 3 and N-Boc biaryl benzylamine 11

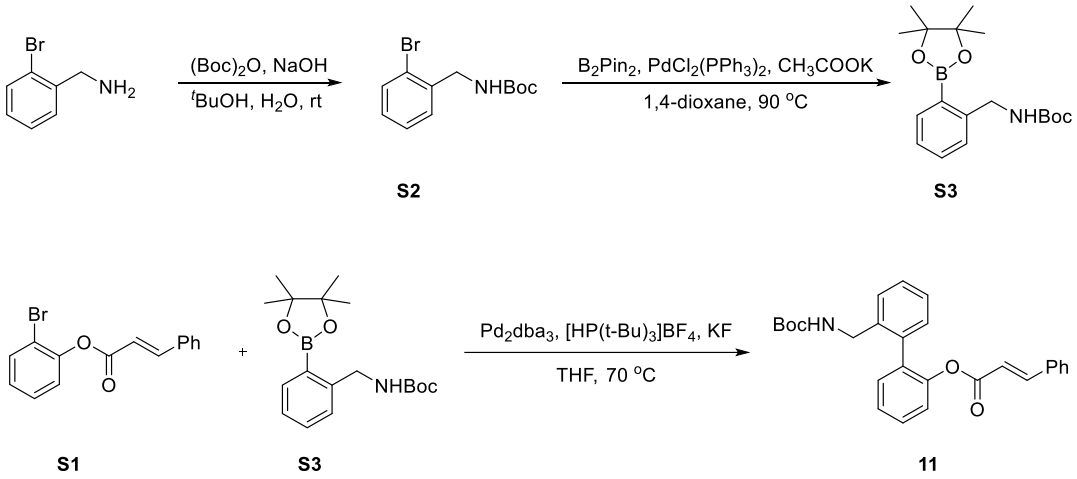


To a round-bottom flask with a magnetic stirring bar, carboxylic acid (1.1 equiv), phenol (1 equiv), DMAP (5 mol%) and EDC·HCl (1.1 equiv) were added, and the resulting mixture was stirred in DCM (0.2 M) overnight at room temperature. After the reaction reached completion, H_2O was added. The organic layer was then separated, and the aqueous layer was extracted with EtOAc three times. The organic layer was successively washed with brine. After drying over Na_2SO_4, the resulting solution was concentrated under reduced pressure. The crude mixture was purified by

flash chromatography on silica gel with eluent of hexane/ethyl acetate (100:1) affording the corresponding pure compound **S1**.

$Pd_2(dba)_3$ (0.5 mol%), $[HP(t\text{-}Bu)_3]BF_4$ (1.2 mol%), **S1** (1.0 equiv), the boronic acid (1.5 equiv) and $KF{\cdot}2H_2O$ (3.3 equiv) were added to a flask. The reaction flask was degassed three times with nitrogen and then THF (0.2 M) was added using a syringe, and the resulting solution was stirred at 70 °C for 10 h. After the reaction was completed (TLC), the mixture was diluted with Et_2O and filtered through a plug of silica gel. The crude mixture was purified by flash chromatography on silica gel with eluent of hexane/ethyl acetate (100:1) affording the corresponding pure compound **3**.

S3 were synthesized according to the literature method.[2]

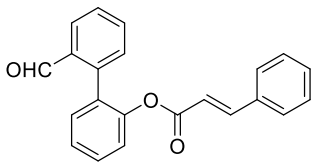


The 2-bromobenzylamine (1.0 equiv) was dissolved in $^tBuOH/H_2O$ (v/v=1, 0.5 M). NaOH (2.0 equiv) and di-*tert*-butyl dicarbonate (1.2 equiv) were successively added. The mixture was stirred for 3 h at room temperature. The reaction was quenched with H_2O (5 mL) and extracted with EtOAc (5 mL×2). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) affording the corresponding pure compound **S2**.

$PdCl_2(PPh_3)_2$ (0.5 mol%), **S2** (1.0 equiv), bis(pinacolato)diboron (1.5 equiv) and KOAc (2 equiv) were added to a flask. The reaction flask was degassed three times with nitrogen and then 1,4-dioxane (0.3 M) was added using a syringe, and the resulting solution was stirred at 90 °C for 12 h. After the reaction was completed (TLC), the mixture was diluted with DCM and filtered through a plug of silica gel. The crude mixture was purified by flash chromatography on silica gel with eluent of hexane/ethyl acetate (100:1) affording the corresponding pure compound **S3**.

$Pd_2(dba)_3$ (0.5 mol%), $[HP(t\text{-}Bu)_3]BF_4$ (1.2 mol%), **S1** (1.0 equiv), **S3** (1.5 equiv) and $KF{\cdot}2H_2O$ (3.3 equiv) were added to a flask. The reaction flask was degassed three times with nitrogen and then THF (0.2 M) was added using a syringe, and the resulting solution was stirred at 70 °C for 10 h. After the reaction was completed (TLC), the mixture was diluted with Et_2O and filtered through a plug of silica gel. The crude mixture was purified by flash chromatography on silica gel with eluent of hexane/ethyl acetate (100:1) affording the corresponding pure compound **11**.

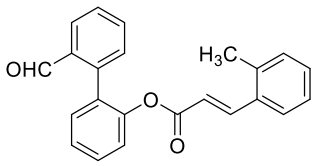
2'-Formyl-[1,1'-biphenyl]-2-yl cinnamate (3a)



3a

White solid; mp 110.1 – 110.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.02 (d, J = 7.7 Hz, 1H), 7.65 – 7.53 (m, 3H), 7.53 – 7.46 (m, 3H), 7.42 (d, J = 10.3 Hz, 6H), 7.32 (d, J = 8.1 Hz, 1H), 6.32 (d, J = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 164.7, 148.4, 146.9, 140.7, 133.9, 133.7, 133.7, 131.6, 131.3, 131.1, 130.8, 129.9, 129.0, 128.4, 127.1, 126.3, 122.8, 116.3; HRMS (ESI) *m/z* Calcd. for $C_{22}H_{17}O_3^+$ ($[M+H]^+$) 329.1172, Found 329.1170.

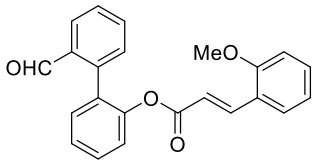
2'-Formyl-[1,1'-biphenyl]-2-yl (E)-3-(o-tolyl)acrylate (3b)



3b

White solid; mp 101.4.1 – 102.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 15.9 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.54 – 7.49 (m, 1H), 7.47 – 7.43 (m, 2H), 7.42 – 7.35 (m, 3H), 7.30 (d, J = 8.5 Hz, 1H), 7.26 (d, J = 6.6 Hz, 1H), 7.19 – 7.17 (m, 2H), 6.20 (d, J = 15.9 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 164.6, 148.5, 144.3, 140.7, 138.0, 133.8, 133.6, 132.9, 131.5, 131.3, 131.1, 130.9, 130.5, 129.8, 128.3, 127.0, 126.5, 126.4, 126.3, 122.8, 117.4, 19.7; HRMS (ESI) *m/z* Calcd. for $C_{23}H_{19}O_3^+$ ($[M+H]^+$) 343.1329, Found 343.1325.

2'-Formyl-[1,1'-biphenyl]-2-yl (E)-3-(2-methoxyphenyl)acrylate (3c)

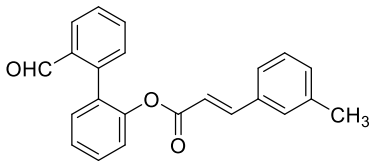


3c

White solid; mp 80.1 – 81.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.98 (d, J = 7.7 Hz, 1H), 7.85 (d, J = 16.1 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.52 – 7.46 (m, 1H), 7.45 – 7.36 (m, 5H), 7.35 – 7.30 (m, 1H), 7.26 (d, J = 11.7 Hz, 1H), 6.93 – 6.90 (m, 1H), 6.87 (d, J = 8.3 Hz, 1H), 6.40 (d, J = 16.1 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 165.2, 158.6, 148.6, 142.3, 140.9, 133.8, 133.6, 132.0, 131.6, 131.3, 131.1, 129.8, 129.4, 128.2,

127.0, 126.1, 122.9, 122.9, 120.7, 116.8, 111.2, 55.5; HRMS (ESI) *m/z* Calcd. for $C_{23}H_{18}NaO_4^+$ ([M+Na]$^+$) 381.1097, Found 381.1093.

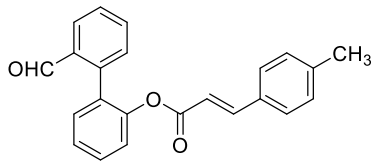
2'-Formyl-[1,1'-biphenyl]-2-yl (E)-3-(m-tolyl)acrylate (3d)



3d

White solid; mp 108.4 – 109.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.98 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.56 – 7.47 (m, 2H), 7.46 – 7.42(m, 1H), 7.41 – 7.35 (m, 3H), 7.29 – 7.24 (m, 4H), 7.19 (dd, *J* = 5.9, 2.7 Hz, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 164.7, 148.5, 147.0, 140.7, 138.6, 133.9, 133.8, 133.6, 131.6, 131.6, 131.3, 131.1, 129.8, 128.9, 128.8, 128.3, 127.0, 126.3, 125.6, 122.8, 116.1, 21.3; HRMS (ESI) *m/z* Calcd. for $C_{23}H_{18}NaO_3^+$ ([M+Na]$^+$) 365.1148, Found 365.1143.

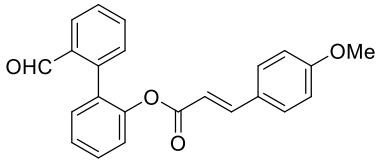
2'-Formyl-[1,1'-biphenyl]-2-yl (E)-3-(p-tolyl)acrylate (3e)



3e

White solid; mp 88.8 – 89.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.55 – 7.47 (m, 2H), 7.43 (dd, *J* = 13.0, 5.4 Hz, 1H), 7.38 – 7.33 (m, 5H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.23 (d, *J* = 16.0 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 164.9, 148.5, 146.9, 141.4, 140.8, 133.8, 133.7, 131.6, 131.3, 131.2, 131.1, 129.8, 129.7, 128.4, 128.3, 127.0, 126.3, 122.8, 115.2, 21.5; HRMS (ESI) *m/z* Calcd. for $C_{23}H_{18}NaO_3^+$ ([M+Na]$^+$) 365.1148, Found 365.1143.

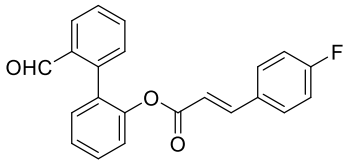
2'-Formyl-[1,1'-biphenyl]-2-yl (E)-3-(4-methoxyphenyl)acrylate (3f)



3f

White solid; mp 112.1 – 112.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.57 – 7.50 (m, 2H), 7.50 – 7.39 (m, 6H), 7.30 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.17 (d, *J* = 15.9 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 165.0, 161.8, 148.5, 146.6, 140.8, 133.7, 133.7, 131.6, 131.3, 131.1, 130.1, 129.8, 128.3, 127.0, 126.6, 126.2, 122.8, 114.4, 113.6, 55.4; HRMS (ESI) *m/z* Calcd. for $C_{23}H_{18}NaO_4^+$ ([M+H]$^+$) 381.1097, Found 381.1093.

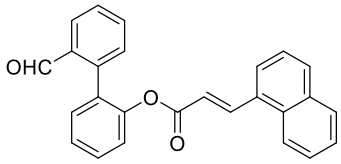
2'-Formyl-[1,1'-biphenyl]-2-yl (E)-3-(4-fluorophenyl)acrylate (3g)



3g

White solid; mp 86.6 – 87.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.99 (dd, J = 7.8, 0.9 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.55 – 7.49 (m, 2H), 7.48 – 7.38 (m, 6H), 7.28 (d, J = 7.9 Hz, 1H), 7.09 – 7.03 (m, 2H), 6.20 (d, J = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 164.5, 164.2 (d, J = 252.5 Hz), 148.4, 145.5, 140.7, 133.8, 133.6, 131.6, 131.3, 131.1, 130.3, 130.2, 130.2, 129.8, 128.3, 127.0, 126.3, 122.7, 116.1 (d, J = 21.2 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.64; HRMS (ESI) *m/z* Calcd. for $C_{22}H_{15}FNaO_3^+$ ($[M+Na]^+$) 369.0897, Found 369.0891.

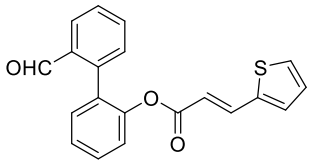
2'-Formyl-[1,1'-biphenyl]-2-yl (E)-3-(naphthalen-1-yl)acrylate (3h)



3h

White solid; mp 152.1 – 152.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.39 (d, J = 15.8 Hz, 1H), 8.10 – 8.01 (m, 2H), 7.88 (dd, J = 10.8, 8.5 Hz, 2H), 7.69 (d, J = 7.2 Hz, 1H), 7.66 – 7.59 (m, J = 9.8, 2H), 7.58 – 7.51 (m, 2H), 7.51 – 7.41 (m, 5H), 7.37 (d, J = 8.0 Hz, 1H), 6.40 (d, J = 15.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 164.5, 148.5, 143.6, 140.8, 133.9, 133.7, 131.6, 131.4, 131.3, 131.2, 131.1, 129.9, 128.7, 128.4, 127.1, 127.1, 126.3, 125.4, 125.3, 123.3, 122.8, 118.9; HRMS (ESI) *m/z* Calcd. for $C_{26}H_{18}NaO_3^+$ ($[M+Na]^+$) 401.1148, Found 401.1142.

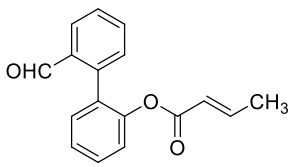
2'-Formyl-[1,1'-biphenyl]-2-yl (E)-3-(thiophen-2-yl)acrylate (3i)



3i

White solid; mp 112.0 – 112.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.99 (d, J = 7.7 Hz, 1H), 7.64 (d, J = 15.7 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.52 – 7.42 (m, 2H), 7.41 – 7.33 (m, 4H), 7.25 (s, 1H), 7.21 (d, J = 3.4 Hz, 1H), 7.02 (dd, J = 4.9, 3.7 Hz, 1H), 6.07 (d, J = 15.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 164.5, 148.4, 140.7, 139.1, 139.1, 133.8, 133.6, 131.7, 131.6, 131.3, 131.1, 129.8, 129.3, 128.3, 128.2, 127.1, 126.2, 122.8, 114.9; HRMS (ESI) *m/z* Calcd. for $C_{20}H_{14}NaO_3S^+$ ($[M+Na]^+$) 357.0556, Found 357.0547.

2'-Formyl-[1,1'-biphenyl]-2-yl (E)-but-2-enoate (3j)

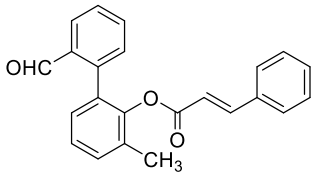


3j

White solid; mp 95.4 – 96.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.98 (dd, J = 7.8, 1.0 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.51 – 7.43 (m, 2H), 7.40 – 7.31 (m, 3H), 7.22 (d, J = 8.1 Hz, 1H), 6.93 – 6.81 (m, 1H), 5.70 (dd, J = 15.5, 1.7 Hz,

1H), 1.80 (dd, *J* = 6.9, 1.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 164.0, 148.4, 147.3, 140.8, 133.7, 133.6, 131.5, 131.3, 131.1, 129.8, 128.2, 126.9, 126.2, 122.7, 121.2, 18.1; HRMS (ESI) *m/z* Calcd. for $C_{17}H_{14}NaO_3^+$ ($[M+Na]^+$) 289.0835, Found 289.0832.

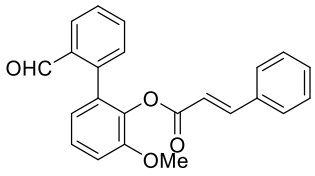
2'-Formyl-3-methyl-[1,1'-biphenyl]-2-yl cinnamate (3k)



3k

White solid; mp 113.2 – 113.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.57 (dd, *J* = 8.3, 7.6 Hz, 2H), 7.49 – 7.40 (m, 3H), 7.39 – 7.33 (m, 5H), 7.31 – 7.24 (m, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 164.2, 147.1, 146.8, 141.1, 133.9, 133.8, 133.6, 131.5, 131.5, 131.4, 131.1, 130.8, 129.1, 129.0, 128.3, 128.2, 126.9, 126.2, 116.0, 16.6; HRMS (ESI) *m/z* Calcd. for $C_{23}H_{18}NaO_3^+$ ($[M+Na]^+$) 365.1148, Found 365.1140.

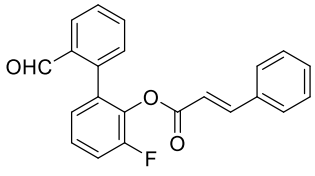
2'-Formyl-3-methoxy-[1,1'-biphenyl]-2-yl cinnamate (3l)



3l

White solid; mp 118.7 – 119.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.56 (m, 2H), 7.53 – 7.41 (m, 4H), 7.41 – 7.27 (m, 4H), 7.12 (d, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 164.3, 151.7, 146.8, 140.6, 137.6, 134.0, 133.8, 133.6, 132.6, 130.9, 130.7, 128.9, 128.3, 127.0, 126.6, 123.1, 116.2, 112.4, 56.2; HRMS (ESI) *m/z* Calcd. for $C_{23}H_{18}NaO_4^+$ ($[M+Na]^+$) 381.1097, Found 381.1091.

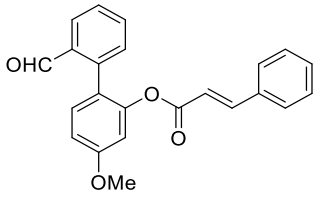
3-Fluoro-2'-formyl-[1,1'-biphenyl]-2-yl cinnamate (3m)



3m

White solid; mp 88.2 – 89.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.01 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.65 (d, *J* = 16.1 Hz, 1H), 7.60 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.51 – 7.45 (m, 3H), 7.40 – 7.27 (m, 6H), 7.20 – 7.15 (m, 1H), 6.35 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 163.7, 154.7 (d, *J* = 251.5 Hz), 147.7, 139.4 (d, *J* = 3.0 Hz), 136.4 (d, *J* = 13.1 Hz), 133.8, 133.8, 133.7, 131.0, 131.0, 129.0, 128.8, 128.4, 127.4, 126.9, 126.8, 126.7 (d, *J* = 3.0 Hz), 116.9 (d, *J* = 19.2 Hz), 115.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -127.14; HRMS (ESI) *m/z* Calcd. for $C_{22}H_{15}FNaO_3^+$ ($[M+Na]^+$) 369.0897, Found 369.0890.

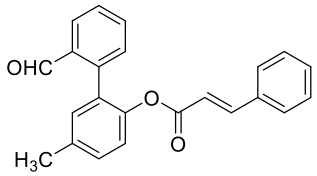
2'-Formyl-4-methoxy-[1,1'-biphenyl]-2-yl cinnamate (3n)



3n

White solid; mp 110.1 – 110.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.99 (d, J = 7.7 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.53 – 7.44 (m, 3H), 7.42 – 7.36 (m, 4H), 7.33 (d, J = 8.5 Hz, 1H), 6.97 (dd, J = 8.5, 2.4 Hz, 1H), 6.87 (d, J = 2.3 Hz, 1H), 6.31 (d, J = 16.0 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 164.6, 160.8, 149.2, 146.9, 140.7, 134.0, 133.9, 133.7, 132.1, 131.4, 130.8, 129.0, 128.4, 128.0, 127.0, 123.4, 116.2, 112.4, 108.3, 55.7; HRMS (ESI) *m/z* Calcd. for $C_{23}H_{18}NaO_4^+$ ([M+Na]$^+$) 381.1097, Found 381.1091.

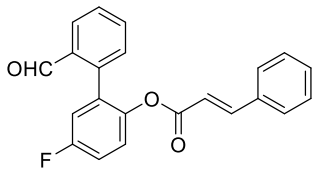
2'-Formyl-5-methyl-[1,1'-biphenyl]-2-yl cinnamate (3o)



3o

White solid; mp 116.6 – 167.8 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.00 (d, J = 7.3 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.56 (d, J = 12.7 Hz, 1H), 7.49 – 7.35 (m, 7H), 7.31 (dd, J = 8.2, 1.6 Hz, 1H), 7.21 (d, J = 1.5 Hz, 1H), 7.18 (d, J = 8.2 Hz, 1H), 6.29 (d, J = 16.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 164.9, 146.7, 146.2, 140.9, 136.0, 134.0, 133.8, 133.6, 132.1, 131.1, 130.9, 130.7, 130.4, 128.9, 128.3, 128.2, 127.0, 122.4, 116.4, 20.9; HRMS (ESI) *m/z* Calcd. for $C_{23}H_{18}NaO_3^+$ ([M+Na]$^+$) 365.1148, Found 365.1144.

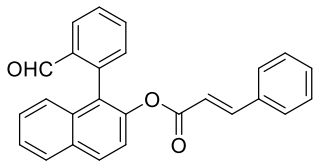
5-Fluoro-2'-formyl-[1,1'-biphenyl]-2-yl cinnamate (3p)



3p

White solid; mp 130.2 – 130.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.58 (d, J = 16.0 Hz, 1H), 7.52 – 7.46 (m, 3H), 7.43 – 7.37 (m, 4H), 7.30 – 7.27 (m, 1H) , 7.25 – 7.20 (m, 1H), 7.16 (dd, J = 8.4, 2.7 Hz, 1H), 6.29 (d, J = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 164.6, 160.2 (d, J = 247.4 Hz), 147.1, 144.3 (d, J = 3.0 Hz), 139.4, 133.8, 133.7, 133.1, 133.0, 130.9, 130.9, 129.0, 128.8, 128.4, 127.4, 124.2 (d, J = 8.1 Hz), 118.1 (d, J = 24.2 Hz), 116.5 (d, J = 23.2 Hz), 116.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.85; HRMS (ESI) *m/z* Calcd. for $C_{22}H_{15}FNaO_3^+$ ([M+Na]$^+$) 369.0897, Found 369.0890.

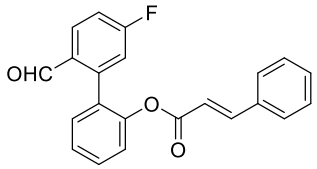
1-(2-Formylphenyl)naphthalen-2-yl cinnamate (3q)



3q

White solid; mp 150.6 – 151.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.13 (d, J = 7.8 Hz, 1H), 8.02 (d, J = 8.9 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.61 – 7.50 (m, 3H), 7.49 – 7.40 (m, 6H), 7.40 – 7.36 (m, 3H), 6.33 (d, J = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 165.1, 146.8, 146.4, 138.8, 134.9, 133.9, 133.9, 133.7, 131.9, 131.7, 130.8, 130.2, 129.0, 128.7, 128.4, 127.3, 127.2, 126.6, 126.0, 125.7, 121.5, 116.3; HRMS (ESI) *m/z* Calcd. for $C_{26}H_{18}NaO_3^+$ ($[M+Na]^+$) 401.1148, Found 401.1142.

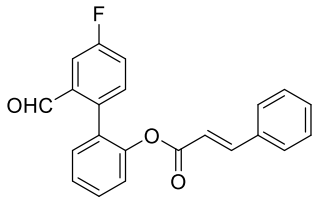
5'-Fluoro-2'-formyl-[1,1'-biphenyl]-2-yl cinnamate (3r)



3r

White solid; mp 102.3 – 102.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 8.03 (dd, J = 8.6, 5.9 Hz, 1H), 7.60 (d, J = 16.0 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.50 – 7.45 (m, 2H), 7.44 – 7.35 (m, 5H), 7.30 (d, J = 8.1 Hz, 1H), 7.17 – 7.08 (m, 2H), 6.32 (d, J = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 165.5 (d, J = 257.6 Hz), 164.6, 148.3, 147.1, 143.5 (d, J = 10.1 Hz), 133.8, 131.4, 130.9, 130.4 (d, J = 3.0 Hz), 130.3, 130.1, 130.0 (d, J = 10.1 Hz), 129.0, 128.4, 126.5, 122.9, 118.0 (d, J = 22.2 Hz), 116.1, 115.8 (d, J = 21.2 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -103.37; HRMS (ESI) *m/z* Calcd. for $C_{22}H_{15}FNaO_3^+$ ($[M+Na]^+$) 369.0897, Found 369.0890.

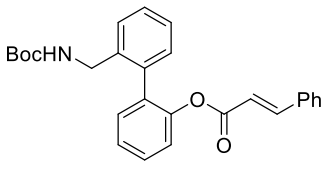
4'-Fluoro-2'-formyl-[1,1'-biphenyl]-2-yl cinnamate (3s)



3s

White solid; mp 107.8.1 – 108.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (d, J = 3.2 Hz, 1H), 7.66 (dd, J = 8.8, 2.8 Hz, 1H), 7.60 (d, J = 16.0 Hz, 1H), 7.55 – 7.45 (m, 3H), 7.44 – 7.35 (m, 6H), 7.34 – 7.27 (m, 2H), 6.31 (d, J = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 164.6, 162.5 (d, J = 251.5 Hz), 148.5, 147.1, 136.7 (d, J = 3.0 Hz), 135.5 (d, J = 6.1 Hz), 133.8, 133.1 (d, J = 8.1 Hz), 131.7, 130.9, 130.4, 130.1, 129.0, 128.4, 126.4, 122.9, 120.9 (d, J = 22.2 Hz), 116.1, 113.3 (d, J = 23.2 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.13; HRMS (ESI) *m/z* Calcd. for $C_{22}H_{15}FNaO_3^+$ ($[M+Na]^+$) 369.0897, Found 369.0890.

2'-(((tert-Butoxycarbonyl)amino)methyl)-[1,1'-biphenyl]-2-yl cinnamate (11)

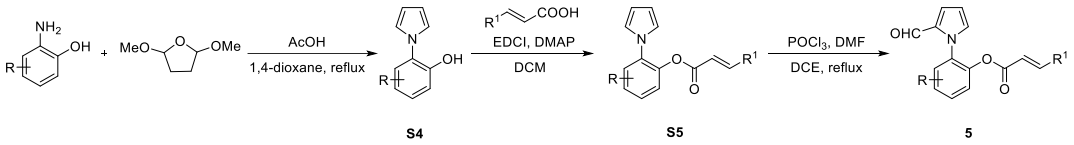


11

Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, J = 16.0 Hz, 1H), 7.49 – 7.41 (m, 4H), 7.40 – 7.34 (m, 3H), 7.34 – 7.28 (m, 3H), 7.25 – 7.22 (m, 2H), 7.19 (dd, J = 7.5,

1.1 Hz, 1H), 6.32 (d, J = 16.0 Hz, 1H), 4.90 (s, 1H), 4.28 – 4.15 (m, 2H), 1.43 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.0, 156.0, 148.2, 146.5, 137.2, 136.2, 134.1, 133.9, 131.1, 130.6, 130.2, 129.0, 128.9, 128.3, 128.2, 128.1, 126.9, 126.1, 122.7, 116.6, 79.2, 42.3, 28.5; HRMS (ESI) *m/z* Calcd. for $C_{27}H_{26}NO_4^-$ ([M–H]$^-$) 428.18673, Found 428.18711.

3. General procedure for preparation of N-aryl-2-formylpyrroles 5

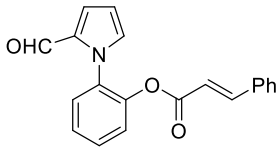


o-Aminophenols (1 equiv) was dissolved in 1,4-dioxane (0.25 M). To this solution was added 2,5-dimethoxytetrahydrofuran (1 equiv) and AcOH (0.5 M) sequentially. The mixture was heated to reflux (115 ^{o}C) in an oil bath and stirred for 5 h. After cooled to room temperature, most of the solvent was removed under reduced pressure. The residue was purified directly by flash silica gel chromatography with petroleum ether/EtOAc (50/1) to afford compound **S4**.[3]

To a round-bottom flask with a magnetic stirring bar, carboxylic acid (1.1 equiv), phenol **S4** (1 equiv), DMAP (5 mol%) and EDC·HCl (1.1 equiv) were added, and the resulting mixture was stirred in DCM (0.2 M) overnight at room temperature. After the reaction reached completion, H_2O was added. The organic layer was then separated, and the aqueous layer was extracted with EtOAc three times. The organic layer was successively washed with brine. After drying over Na_2SO_4, the resulting solution was concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel with eluent of petroleum ether /ethyl acetate (100:1) affording the corresponding pure compound **S5**.

DMF (1.2 equiv) was placed in 100 mL round-bottom flask and cooled with ice bath below 0 °C. $POCl_3$ (1.2 equiv) was added dropwise and let to stir for 30 min. The solution of **S5** (1.0 equiv.) in DCE (0.5 M) was added. Cooling bath was removed and the reaction mixture was stirred at 80 °C for 3 h. After cooling to r.t., the mixture was washed with concentrated aqueous Na_2CO_3 solution and distilled water. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The crude mixture was purified by flash chromatography on silica gel with eluent of petroleum ether /ethyl acetate (20:1) affording the corresponding pure compound **5**.[4]

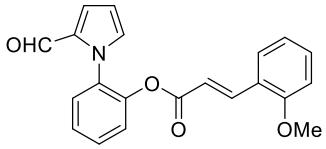
2-(2-Formyl-1H-pyrrol-1-yl)phenyl cinnamate (5a)



5a

White solid. mp 85.1 – 85.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.65 (d, J = 16.0 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.46 – 7.36 (m, 6H), 7.11 (dd, J = 4.0, 1.6 Hz, 1H), 7.03 – 6.99 (m, 1H), 6.42 – 6.36 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.9, 164.3, 147.2, 146.3, 133.9, 132.9, 132.0, 131.3, 130.9, 129.8, 129.0, 128.4, 128.3, 126.6, 123.5, 116.0, 111.0; HRMS (ESI) *m/z* Calcd. for $C_{20}H_{15}NNaO_3^+$ ([M+Na]$^+$) 340.0944, Found 340.0949.

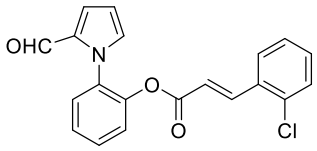
2-(2-Formyl-1H-pyrrol-1-yl)phenyl (E)-3-(2-methoxyphenyl)acrylate (5b)



5b

White solid. mp 89.9 – 90.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.93 (d, J = 16.1 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.45 (dd, J = 7.7, 1.4 Hz, 1H), 7.41 – 7.33 (m, 4H), 7.08 (dd, J = 4.0, 1.6 Hz, 1H), 7.00 – 6.89 (m, 3H), 6.47 (d, J = 16.1 Hz, 1H), 6.36 (dd, J = 3.9, 2.7 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.9, 165.0, 158.7, 146.4, 142.8, 133.0, 132.1, 132.0, 131.3, 129.8, 129.4, 128.3, 126.4, 123.6, 122.9, 120.7, 116.4, 111.2, 110.9, 55.5; HRMS (ESI) *m/z* Calcd. for $C_{21}H_{17}NNaO_4^+$ ([M+Na]$^+$) 370.1050, Found 370.1055.

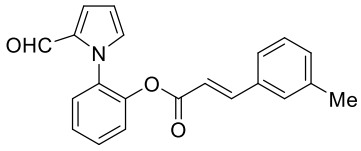
2-(2-Formyl-1H-pyrrol-1-yl)phenyl (E)-3-(2-chlorophenyl)acrylate (5c)



5c

White solid. mp 98.3 – 98.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.53 (s, 1H), 8.03 (d, J = 16.0 Hz, 1H), 7.58 (dd, J = 7.7, 1.2 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.43 – 7.36 (m, 4H), 7.35 – 7.31 (m, 1H), 7.30 – 7.26 (m, 1H), 7.09 (dd, J = 3.9, 1.5 Hz, 1H), 7.00 – 6.98 (m, 1H), 6.39 – 6.33 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 163.9, 146.2, 142.8, 135.3, 132.9, 132.2, 132.0, 131.6, 131.4, 130.3, 129.8, 128.3, 127.8, 127.2, 126.6, 123.4, 118.6, 111.0; HRMS (ESI) *m/z* Calcd. for $C_{20}H_{14}ClNNaO_3^+$ ([M+Na]$^+$) 374.0554, Found 374.0558.

2-(2-Formyl-1H-pyrrol-1-yl)phenyl (E)-3-(m-tolyl)acrylate (5d)

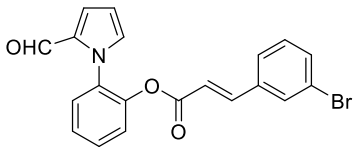


5d

White solid. mp 85.4 – 86.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.60 (d, J = 16.0 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.43 – 7.33 (m, 3H), 7.32 – 7.27 (m, 3H), 7.22 (d, J = 6.9 Hz, 1H), 7.09 – 7.07 (m, 1H), 6.99 – 6.97 (m, 1H), 6.37 – 6.33 (m, 2H), 2.37 (s, 3H); ^{13}C

NMR (101 MHz, $CDCl_3$) δ 178.9, 164.4, 147.4, 146.3, 138.7, 133.9, 133.0, 132.0, 131.7, 131.3, 129.8, 129.0, 128.9, 128.3, 126.5, 125.6, 123.5, 115.7, 110.9, 21.3; HRMS (ESI) *m/z* Calcd. for $C_{21}H_{17}NNaO_3^+$ ($[M+Na]^+$) 354.1101, Found 354.1102.

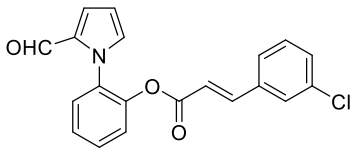
2-(2-Formyl-1H-pyrrol-1-yl)phenyl (E)-3-(3-bromophenyl)acrylate (5e)



5e

White solid. mp 102.4 – 103.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.61 – 7.58 (m, 1H), 7.54 – 7.46 (m, 3H), 7.42 – 7.32 (m, 4H), 7.25 – 7.20 (m, 1H), 7.08 (d, *J* = 2.5 Hz, 1H), 7.00 – 6.95 (m, 1H), 6.38 – 6.29 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 163.9, 146.1, 145.4, 135.9, 133.6, 132.9, 131.9, 131.3, 131.0, 130.5, 129.9, 128.3, 127.0, 126.7, 123.4, 123.1, 117.5, 111.0; HRMS (ESI) *m/z* Calcd. for $C_{20}H_{14}BrNNaO_3^+$ ($[M+Na]^+$) 418.0049, Found 418.0045.

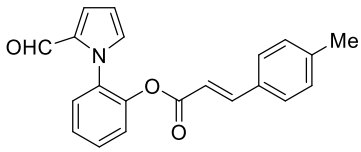
2-(2-Formyl-1H-pyrrol-1-yl)phenyl (E)-3-(3-chlorophenyl)acrylate (5f)



5f

White solid. mp 94.2 – 94.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.58 – 7.49 (m, 2H), 7.48 – 7.45 (m, 1H), 7.44 – 7.38 (m, 2H), 7.37 – 7.29 (m, 4H), 7.09 (dd, *J* = 3.9, 1.3 Hz, 1H), 6.99 – 6.97 (m, 1H), 6.40 – 6.32 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 163.9, 146.2, 145.5, 135.7, 135.1, 132.9, 131.9, 131.3, 130.7, 130.2, 129.9, 128.3, 128.1, 126.7, 126.5, 123.4, 117.5, 111.0; HRMS (ESI) *m/z* Calcd. for $C_{20}H_{14}ClNNaO_3^+$ ($[M+Na]^+$) 374.0554, Found 374.0557.

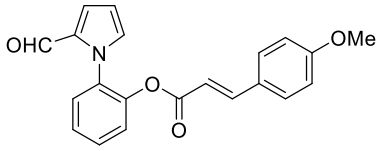
2-(2-Formyl-1H-pyrrol-1-yl)phenyl (E)-3-(p-tolyl)acrylate (5g)



5g

White solid. mp 93.7 – 94.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.59 (d, *J* = 16.0 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.40 – 7.32 (m, 5H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.07 (dd, *J* = 3.9, 1.5 Hz, 1H), 6.98 – 6.96 (m, 1H), 6.34 (dd, *J* = 3.8, 2.7 Hz, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.9, 164.5, 147.3, 146.3, 141.5, 133.0, 132.0, 131.3, 131.2, 129.8, 129.7, 128.4, 128.3, 126.5, 123.5, 114.8, 111.0, 21.6; HRMS (ESI) *m/z* Calcd. for $C_{21}H_{17}NNaO_3^+$ ($[M+Na]^+$) 354.1101, Found 354.1104.

2-(2-Formyl-1H-pyrrol-1-yl)phenyl (E)-3-(4-methoxyphenyl)acrylate (5h)

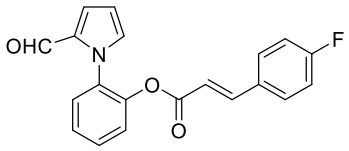


5h

White solid. mp 107.2 – 107.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.58 (d, *J* = 15.9 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.46 – 7.32 (m, 5H), 7.08 (dd, *J* = 3.9,

1.5 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.36 (dd, *J* = 3.8, 2.7 Hz, 1H), 6.22 (d, *J* = 15.9 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 164.7, 161.9, 147.0, 146.4, 132.9, 132.0, 131.3, 130.2, 129.8, 128.3, 126.6, 126.5, 123.6, 114.4, 113.3, 110.9, 55.4; HRMS (ESI) *m/z* Calcd. for $C_{21}H_{17}NNaO_4^+$ ($[M+Na]^+$) 370.1050, Found 370.1054.

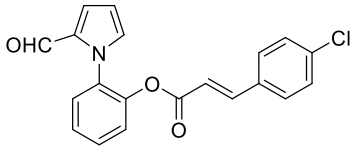
2-(2-Formyl-1H-pyrrol-1-yl)phenyl (E)-3-(4-fluorophenyl)acrylate (5i)



5i

White solid. mp 94.2 – 94.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.58 (d, *J* = 16.0 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.44 – 7.37 (m, 2H), 7.37 – 7.32 (m, 1H), 7.12 – 7.04 (m, 3H), 7.01 – 6.96 (m, 1H), 6.37 (dd, *J* = 3.9, 2.7 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.9, 164.3 (d, *J* = 252.2 Hz), 164.2, 146.2, 145.9, 132.9, 132.0, 131.3, 130.4 (d, *J* = 9.1 Hz), 130.2 (d, *J* = 3.1 Hz), 129.9, 128.3, 126.6, 123.4, 116.2 (d, *J* = 22.7 Hz), 115.7, 111.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.39; HRMS (ESI) *m/z* Calcd. for $C_{20}H_{14}FNNaO_3^+$ ($[M+Na]^+$) 358.0850, Found 358.0855.

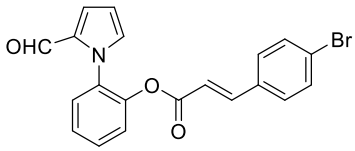
2-(2-Formyl-1H-pyrrol-1-yl)phenyl (E)-3-(4-chlorophenyl)acrylate (5j)



5j

White solid. mp 97.8 – 98.7 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.56 (d, *J* = 16.0 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.44 – 7.38 (m, 4H), 7.37 – 7.32 (m, 3H), 7.08 (dd, *J* = 4.0, 1.6 Hz, 1H), 6.99 – 6.97 (m, 1H), 6.37 (dd, *J* = 4.0, 2.6 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 164.1, 146.2, 145.7, 136.9, 132.9, 132.4, 131.9, 131.3, 129.9, 129.5, 129.3, 128.3, 126.6, 123.4, 116.5, 111.0; HRMS (ESI) *m/z* Calcd. for $C_{20}H_{14}ClNNaO_3^+$ ($[M+Na]^+$) 374.0554, Found 374.0558.

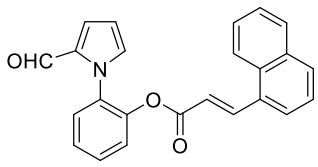
2-(2-Formyl-1H-pyrrol-1-yl)phenyl (E)-3-(4-bromophenyl)acrylate (5k)



5k

White solid. mp 109.8 – 110.3 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.58 – 7.48 (m, 4H), 7.44 – 7.37 (m, 2H), 7.37 – 7.32 (m, 3H), 7.08 (dd, *J* = 4.0, 1.5 Hz, 1H), 7.00 – 6.96 (m, 1H), 6.39 – 6.31 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.8, 164.1, 146.2, 145.8, 132.9, 132.8, 132.3, 131.9, 131.3, 129.9, 129.7, 128.3, 126.7, 125.3, 123.4, 116.6, 111.0; HRMS (ESI) *m/z* Calcd. for $C_{20}H_{14}BrNNaO_3^+$ ($[M+Na]^+$) 418.0049, Found 418.0049.

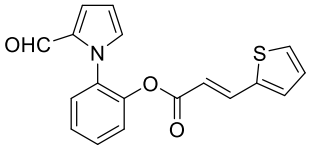
2-(2-Formyl-1H-pyrrol-1-yl)phenyl (E)-3-(naphthalen-1-yl)acrylate (5l)



5l

Yellow solid. mp 136.3 – 136.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.46 (d, J = 15.8 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.89 (dd, J = 14.5, 8.0 Hz, 2H), 7.73 (d, J = 7.2 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.56 – 7.51 (m, 2H), 7.50 – 7.47 (m, 1H), 7.46 – 7.37 (m, 3H), 7.10 (dd, J = 4.0, 1.5 Hz, 1H), 7.04 – 7.01 (m, 1H), 6.46 (d, J = 15.7 Hz, 1H), 6.39 (dd, J = 3.9, 2.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.9, 164.2, 146.3, 144.1, 133.7, 133.0, 132.0, 131.4, 131.2, 131.1, 129.9, 128.8, 128.3, 127.1, 126.6, 126.4, 125.4, 125.4, 123.5, 123.3, 118.5, 111.0; HRMS (ESI) *m/z* Calcd. for $C_{24}H_{17}NNaO_3^+$ ([M+Na]$^+$) 390.1101, Found 390.1104.

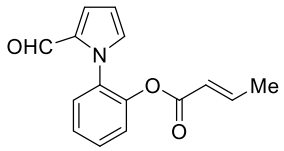
2-(2-Formyl-1H-pyrrol-1-yl)phenyl (E)-3-(thiophen-2-yl)acrylate (5m)



5m

White solid. mp 95.5 – 96.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.72 (d, J = 15.7 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.44 – 7.35 (m, 3H), 7.33 (d, J = 8.1 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.09 (d, J = 3.8 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.98 (s, 1H), 6.39 – 6.34 (m, 1H), 6.14 (d, J = 15.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 164.2, 146.3, 139.5, 139.0, 132.9, 132.0, 131.9, 131.3, 129.8, 129.5, 128.3, 128.3, 126.5, 123.5, 114.5, 110.9; HRMS (ESI) *m/z* Calcd. for $C_{18}H_{13}NNaO_3S^+$ ([M+Na]$^+$) 346.0508, Found 346.0504.

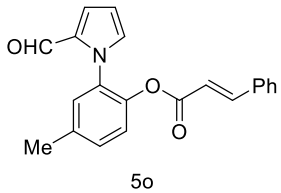
2-(2-Formyl-1H-pyrrol-1-yl)phenyl (E)-but-2-enoate (5n)



5n

White solid. mp 61.8 – 62.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.42 – 7.37 (m, 1H), 7.32 – 7.25 (m, 2H), 7.21 – 7.18 (m, 1H), 7.01 (dd, J = 4.0, 1.5 Hz, 1H), 6.91 – 6.83 (m, 2H), 6.28 (dd, J = 3.9, 2.7 Hz, 1H), 5.70 (dd, J = 15.5, 1.7 Hz, 1H), 1.78 (dd, J = 6.9, 1.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.9, 163.7, 147.9, 146.2, 132.9, 131.9, 131.2, 129.8, 128.3, 126.5, 123.5, 120.9, 110.9, 18.2; HRMS (ESI) *m/z* Calcd. for $C_{15}H_{13}NNaO_3^+$ ([M+Na]$^+$) 278.0788, Found 278.0792.

2-(2-Formyl-1H-pyrrol-1-yl)-4-methylphenyl cinnamate (5o)

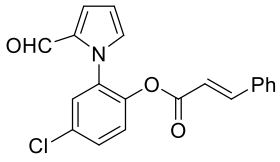


5o

White solid. mp 91.6 – 92.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.62 (d, J = 16.0 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.41 – 7.35 (m, 3H), 7.30 (dd, J = 8.4, 1.3 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.07 (dd, J = 4.0, 1.6 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.38 – 6.31 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 164.6, 147.1, 143.9, 136.7, 133.9, 132.9, 131.5, 131.3, 130.9, 130.4,

129.0, 128.7, 128.4, 123.0, 116.0, 110.9, 20.9; HRMS (ESI) *m/z* Calcd. for $C_{21}H_{17}NNaO_3^+$ ([M+Na]$^+$) 354.1101, Found 354.1099.

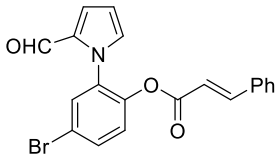
4-Chloro-2-(2-formyl-1H-pyrrol-1-yl)phenyl cinnamate (5p)



5p

White solid. mp 93.4 – 94.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.61 (d, *J* = 16.0 Hz, 1H), 7.49 – 7.45 (m, 3H), 7.42 – 7.37 (m, 4H), 7.29 (d, *J* = 8.7 Hz, 1H), 7.06 (dd, *J* = 3.9, 1.5 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.37 (dd, *J* = 3.8, 2.7 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 164.1, 147.6, 145.0, 133.8, 133.1, 132.8, 131.5, 131.4, 131.1, 129.8, 129.0, 128.4, 128.3, 124.4, 115.6, 111.3; HRMS (ESI) *m/z* Calcd. for $C_{20}H_{14}ClNNaO_3^+$ ([M+Na]$^+$) 374.0554, Found 374.0551.

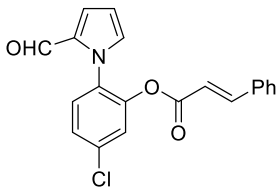
4-Bromo-2-(2-formyl-1H-pyrrol-1-yl)phenyl cinnamate (5q)



5q

White solid. mp 128.7 – 129.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.62 – 7.57 (m, 2H), 7.55 – 7.52 (m, 1H), 7.49 – 7.44 (m, 2H), 7.41 – 7.34 (m, 3H), 7.22 (d, *J* = 8.7 Hz, 1H), 7.07 – 7.03 (m, 1H), 6.97 – 6.93 (m, 1H), 6.38 – 6.34 (m, 1H), 6.31 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 163.9, 147.6, 145.5, 133.8, 133.4, 132.8, 132.7, 131.4, 131.1, 131.0, 129.0, 128.4, 124.7, 118.9, 115.6, 111.3; HRMS (ESI) *m/z* Calcd. for $C_{20}H_{14}BrNNaO_3^+$ ([M+Na]$^+$) 418.0049, Found 418.0044.

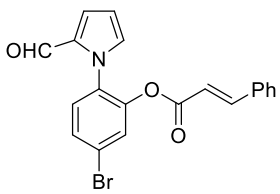
5-Chloro-2-(2-formyl-1H-pyrrol-1-yl)phenyl cinnamate (5r)



5r

White solid. mp 93.8 – 94.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.62 (d, *J* = 16.0 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.43 – 7.37 (m, 4H), 7.37 – 7.32 (m, 2H), 7.07 (dd, *J* = 4.0, 1.6 Hz, 1H), 6.97 – 6.94 (m, 1H), 6.37 (dd, *J* = 4.0, 2.6 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.6, 163.9, 147.7, 146.7, 135.0, 133.7, 132.8, 131.5, 131.1, 130.9, 129.0, 128.9, 128.4, 126.7, 124.0, 115.5, 111.2; HRMS (ESI) *m/z* Calcd. for $C_{20}H_{14}ClNNaO_3^+$ ([M+Na]$^+$) 374.0554, Found 374.0549.

5-Bromo-2-(2-formyl-1H-pyrrol-1-yl)phenyl cinnamate (5s)



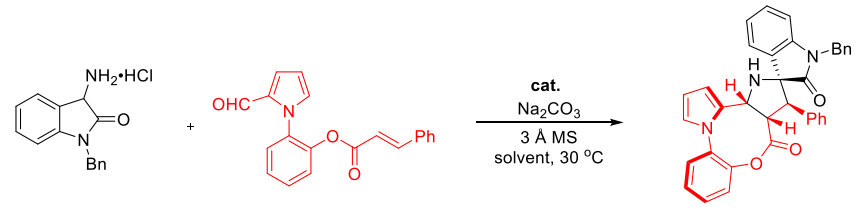
5s

White solid. mp 125.6 – 126.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.62 (d, *J* = 16.0 Hz, 1H), 7.55 – 7.44 (m, 4H), 7.39 (d, *J* = 6.6 Hz, 3H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.06 (d, *J* = 2.5 Hz, 1H), 6.97 – 6.93 (m, 1H), 6.41 – 6.29 (m, 2H); ^{13}C

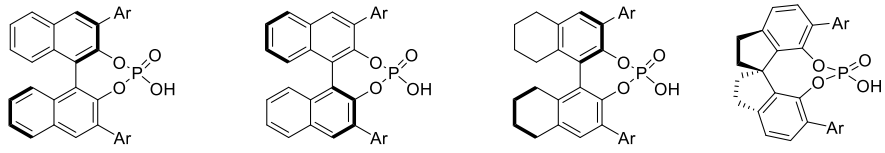
NMR (101 MHz, $CDCl_3$) δ 178.6, 163.9, 147.7, 146.8, 133.8, 132.8, 131.5, 131.4, 131.1, 129.7, 129.2, 129.0, 128.5, 126.8, 122.6, 115.5, 111.2; HRMS (ESI) *m/z* Calcd. for $C_{20}H_{14}BrNNaO_3^+$ ([M+Na]$^+$) 418.0049, Found 418.0045.

4. Optimization of reaction conditions

Table 1 Optimization of reaction conditions



2a **5a** **6aa**



1b, Ar = 2-naphthyl
1c, Ar = 3,5-$(CF_3)_2$-C_6H_3
1e, Ar = 9-phenanthryl
1f, Ar = 9-anthryl

1g, Ar = 2,4,6-(*i*-Pr)$_3$-C_6H_2

1h, Ar = 9-anthryl
1i, Ar = 9-phenanthryl
1j, Ar = 9-pyrenyl

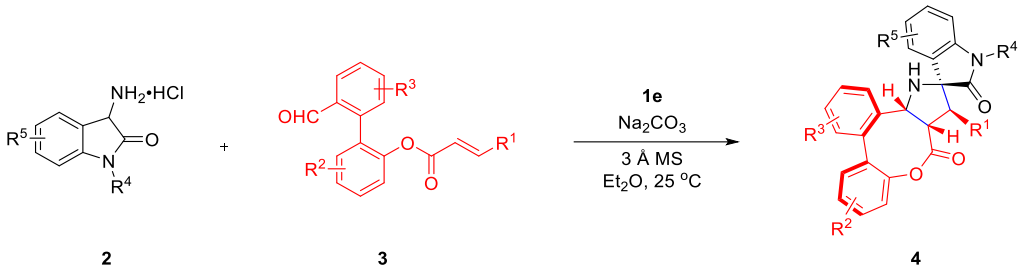
1k, Ar = 9-anthryl

Entry[a]	**Cat.**	Solvent	t [h]	Yield [%][b]	dr[c]	ee [%][d]
1	DPP	DCM	24	66	> 20:1	-
2	**1b**	DCM	48	56	> 20:1	33
3	**1c**	DCM	48	67	> 20:1	49
4	**1e**	DCM	48	70	> 20:1	61
5	**1f**	DCM	48	64	> 20:1	40
6	**1g**	DCM	48	77	> 20:1	-60
7	**1h**	DCM	48	78	> 20:1	77
8	**1i**	DCM	48	45	> 20:1	73
9	**1j**	DCM	48	70	> 20:1	40
10	**1k**	DCM	48	76	> 20:1	-31
11	**1h**	DCE	48	80	> 20:1	67
12	**1h**	toluene	60	88	> 20:1	87
13	**1h**	THF	48	Trace	-	-
14	**1h**	Et_2O	72	50	> 20:1	87
15	**1h**	xylene	72	81	> 20:1	85
16	**1h**	mesitylene	72	74	> 20:1	80
17	**1h**	bromobenzene	72	80	> 20:1	81

18	**1h**	Tol.:DCM=1:1	60	76	> 20:1	87
19[e]	**1h**	toluene	48	81	> 20:1	90
20[f]	**1h**	**toluene**	**60**	**84**	**> 20:1**	**93**
21[f, g]	**1h**	toluene	96	80	> 20:1	88

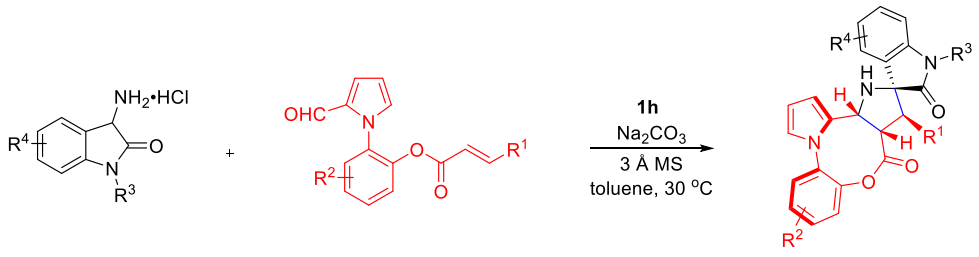
[a]The reaction was carried out on a 0.1 mmol scale with Na_2CO_3 (1.5 equiv), 3 Å MS (100 mg), **cat.** (10 mol%) in 1.0 mL solvent at 30 °C under nitrogen, and the ratio of **2a/5a** was 1.5/1. [b]Isolated yield. [c]The dr was determined by ^{1}H NMR of the crude reaction mixture. [d]The ee was determined by chiral HPLC. [e]In 0.5 mL toluene. [f]In 2.0 mL toluene. [g]Without base.

5. General procedure for the synthesis of products 4/6



2 **3** **4**

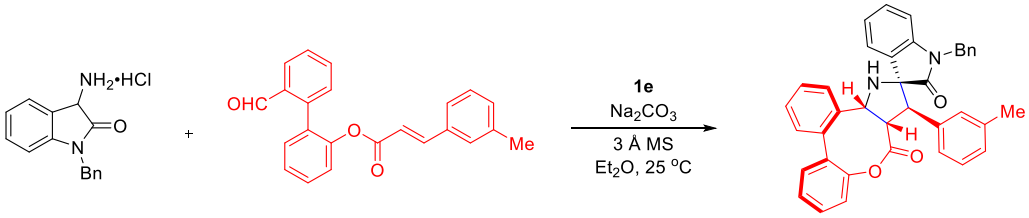
In a Schlenk tube, 3-amino oxindole hydrochlorides **2** (0.24 mmol), Na_2CO_3 (0.3 mmol), 3 Å MS (200 mg), biaryl aldehydes **3** (0.2 mmol) and catalyst **1e** (0.02 mmol) were added into Et_2O (2 mL) under nitrogen atmosphere. The reaction solution was stirred at room temperature. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10 to 1/5) on silica gel to give the product **4**.



2 **5** **6**

In a Schlenk tube, 3-amino oxindole hydrochlorides **2** (0.24 mmol), Na_2CO_3 (0.3 mmol), 3 Å MS (200 mg), N-aryl-2-formylpyrroles **5** (0.2 mmol) and catalyst **1h** (0.02 mmol) were added into toluene (4 mL) under nitrogen atmosphere. The reaction solution was stirred at 30 °C. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10 to 1/5) on silica gel to give the product **6**.

Gram-scale reaction



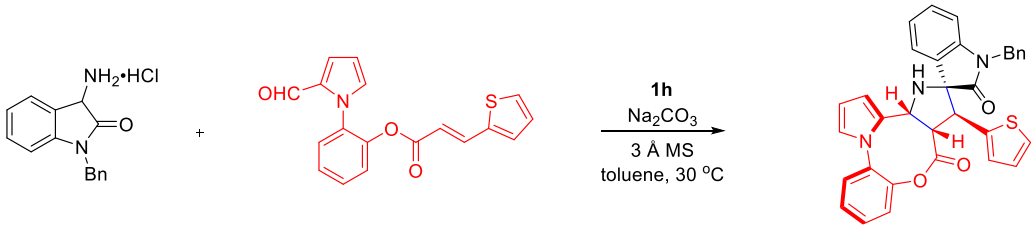
2a 3.0 mmol, 0.82 g

3d 2.0 mmol, 0.68 g

4ad 0.84 g, 75% yield, > 20:1 dr, 98% ee

In a Schlenk tube, 3-amino oxindole hydrochloride **2a** (2.4 mmol), Na_2CO_3 (3.0 mmol), 3 Å MS (2000 mg), biaryl aldehyde **3d** (2.0 mmol) and catalyst **1e** (0.2 mmol) were added into Et_2O (20 mL) under nitrogen atmosphere. The reaction solution was stirred at room temperature. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10 to 1/5) on silica gel to give the product **4ad** with 75% yield, > 20:1 dr and 98% ee.

The scale-up reaction

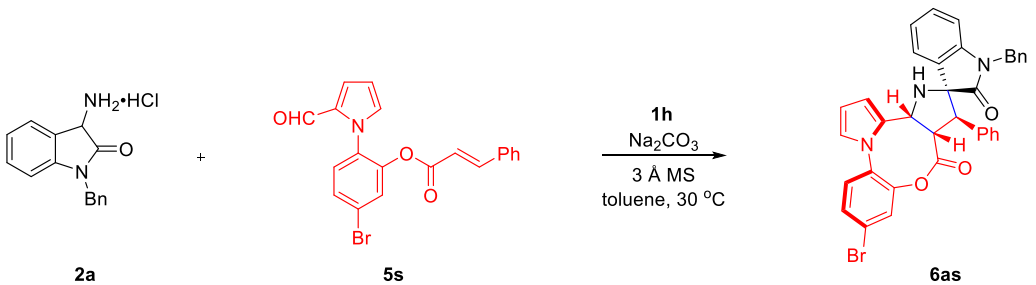


2a 1.5 mmol, 0.41 g

5m 1.0 mmol, 0.32 g

6am 0.49 g, 90% yield, > 20:1 dr , 96% ee

In a Schlenk tube, 3-amino oxindole hydrochloride **2a** (1.5 mmol), Na_2CO_3 (1.5 mmol), 3 Å MS (1000 mg), N-aryl-2-formylpyrrole **5m** (1.0 mmol) and catalyst **1h** (0.1 mmol) were added into toluene (20 mL) under nitrogen atmosphere. The reaction solution was stirred at 30 °C. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10 to 1/5) on silica gel to give the product **6am** with 90% yield, > 20:1 dr and 96% ee.



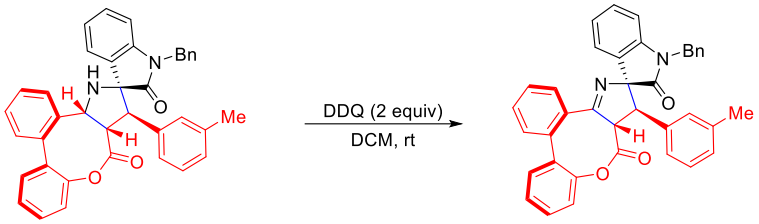
2a 1.5 mmol, 0.41 g

5s 1.0 mmol, 0.40 g

6as 0.48 g, 78% yield, > 20:1 dr , 87% ee

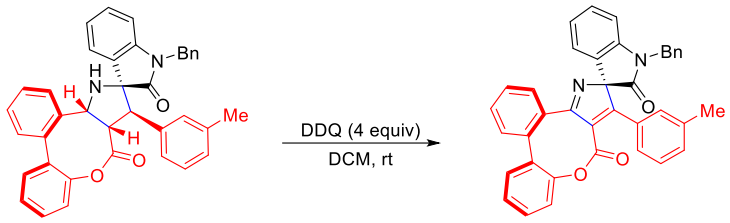
In a Schlenk tube, 3-amino oxindole hydrochloride **2a** (1.5 mmol), Na_2CO_3 (1.5 mmol), 3 Å MS (1000 mg), N-aryl-2-formylpyrrole **5s** (1.0 mmol) and catalyst **1h** (0.1 mmol) were added into toluene (20 mL) under nitrogen atmosphere. The reaction solution was stirred at 30 °C. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10 to 1/5) on silica gel to give the product **6as** with 78% yield, > 20:1 dr and 87% ee.

Synthetic transformations



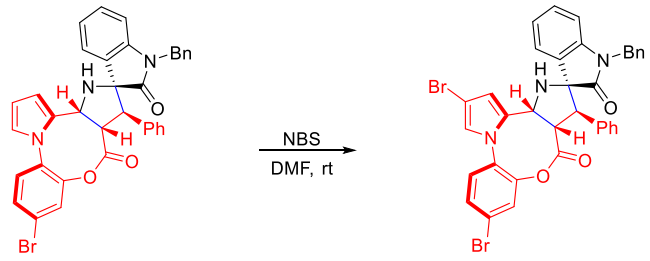
4ad → **7** (90% yield, > 20:1 dr, 98% ee)

A reaction tube was charged with **4ad** (1.0 equiv, 0.2 mmol) and DCM (2 mL), and then DDQ (2.0 equiv, 0.4 mmol) was added. The reaction was stirred at room temperature until it was complete (monitored by TLC). Then the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10) on silica gel to give the product **7** as a white solid.



4ad → **8** (95% yield, 1.6:1 dr, 99% ee, 99% ee)

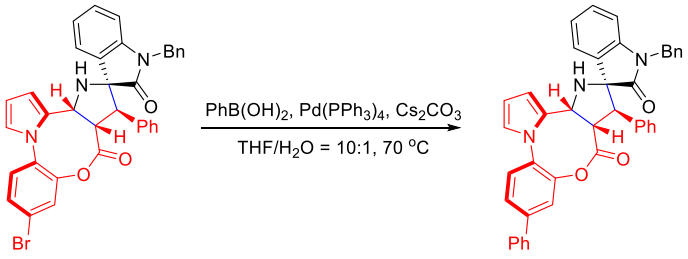
A reaction tube was charged with **4ad** (1.0 equiv, 0.2 mmol) and DCM (2 mL), and then DDQ (4.0 equiv, 0.8 mmol) was added. The reaction was stirred at room temperature until it was complete (monitored by TLC). Then the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10) on silica gel to give the product **8** as a white solid.



6as **9**

(90% yield, > 20:1 dr, 87% *ee*)

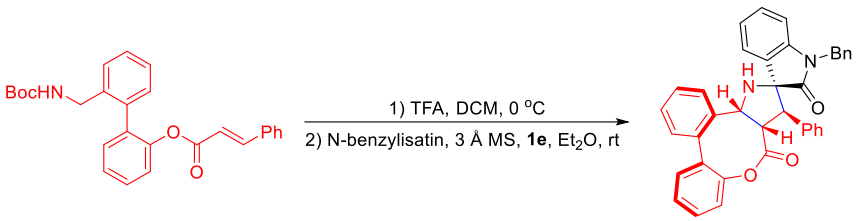
A reaction tube was charged with **6as** (1.0 equiv, 0.1 mmol) and DMF (1 mL), and then NBS (1.1 equiv, 0.11 mmol) was added. The reaction was stirred at room temperature until it was complete (monitored by TLC). After the reaction reached completion, H_2O was added. The organic layer was then separated, and the aqueous layer was extracted with EtOAc three times. The organic layer was successively washed with brine. After drying over Na_2SO_4, the resulting solution was concentrated under reduced pressure. The crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10) on silica gel to give the product **9** as a white solid.



6as **10**

(90% yield, > 20:1 dr, 87% ee)

To a solution of **6as** (1.0 equiv, 0.1 mmol) in 2.0 mL THF/H_2O (10:1) was added phenylboronic acid (1.5 equiv, 0.15 mmol), $Pd(PPh_3)_4$ (0.15 equiv, 0.015 mmol) and Cs_2CO_3 (1.5 equiv, 0.15 mmol). After that, the reaction system was degassed and filled with nitrogen for three times. The reaction mixture was then stirred under N_2 at 70 °C for 6 h. After that, the reaction mixture was washed with H_2O and extracted with EtOAc. The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4. Then the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography to afford pure product **10** as a yellow solid in 90% yield.



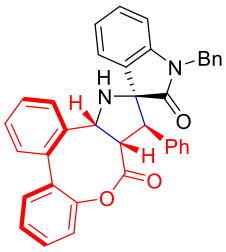
11 **4aa**

(40% yield, > 20:1 dr, 75% ee)

To a solution of N-Boc biaryl benzylamine **11** (1.0 equiv, 0.2 mmol) in DCM was added TFA (10.0 equiv, 2.0 mmol) at 0 °C. The mixture was stirred for 1 h at this temperature until TLC showed complete N-Boc deprotection. Evaporation of the reaction mixture was followed by coevaporation using DCM for the removal of excess TFA. Dry Et_2O was added to the mixture followed by N-benzylisatin (1.1 equiv, 0.22 mmol), freshly activated 3 Å MS and catalyst **1e** (10 mol%). Then, the reaction mixture was stirred for 48 h until TLC showed complete conversion. The reaction mixture was concentrated in vacuo and purified using silica gel chromatography to give the pure product **4aa**.

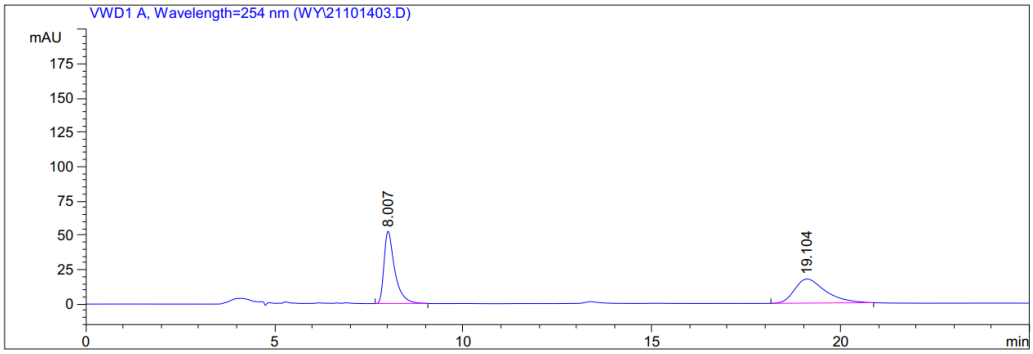
Characterization Data

(4bR,6S,7R,7aS)-1'-Benzyl-7-phenyl-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4aa)

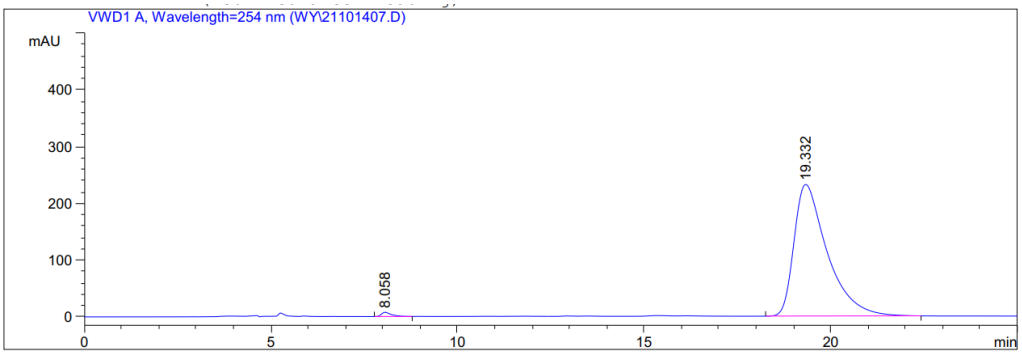


4aa

Prepared according to the procedure within 2 days as white solid (100.8 mg, 92% yield, dr > 20:1); mp 208.3 – 208.9 °C; $[\alpha]_D^{18}$= 37.98 (*c* 0.13, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 7.1 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.45 – 7.35 (m, 3H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.24 – 7.02 (m, 8H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.43 (d, *J* = 7.5 Hz, 2H), 6.36 (d, *J* = 7.5 Hz, 1H), 5.23 (d, *J* = 11.2 Hz, 1H), 4.89 (d, *J* = 16.0 Hz, 1H), 4.51 (t, *J* = 11.3 Hz, 1H), 4.38 (d, *J* = 11.4 Hz, 1H), 4.19 (d, *J* = 16.0 Hz, 1H), 2.25 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 170.8, 149.7, 143.1, 141.0, 135.3, 134.9, 134.8, 134.0, 130.2, 130.1, 129.5, 128.9, 128.8, 128.8, 128.6, 128.5, 128.0, 128.0, 127.7, 127.2, 127.0, 126.4, 125.4, 124.1, 123.2, 121.1, 109.3, 72.0, 57.4, 54.9, 50.8, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{37}H_{29}N_2O_3^+$ ($[M+H]^+$) 549.2173, Found 549.2170; Enantiomeric excess was determined to be 98% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 80/20, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 19.3 min, t_{minor} = 8.0 min).

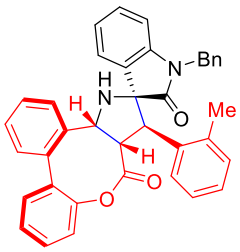


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.007	BB	0.2923	1043.10059	52.64264	50.8070
2	19.104	BB	0.8400	1009.96289	17.63408	49.1930



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.058	PB	0.2755	141.21617	7.48354	0.9728
2	19.332	BB	0.9150	1.43751e4	232.01321	99.0272

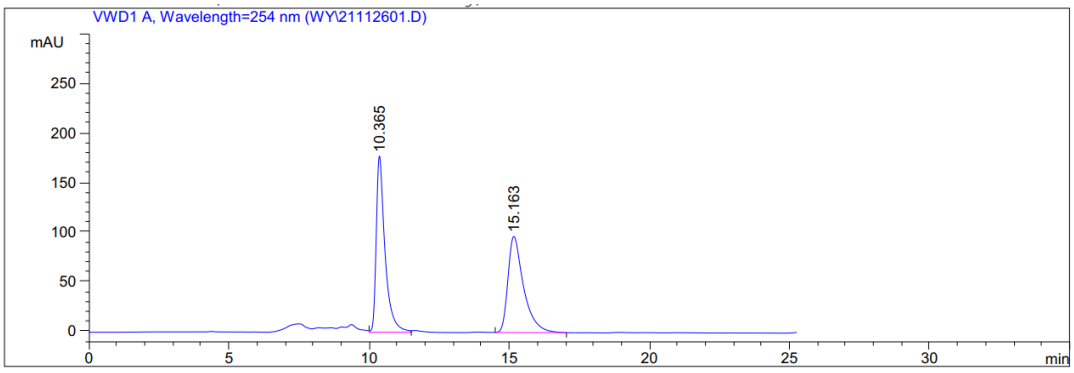
(4bR,6S,7R,7aS)-1'-Benzyl-7-(o-tolyl)-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4ab)



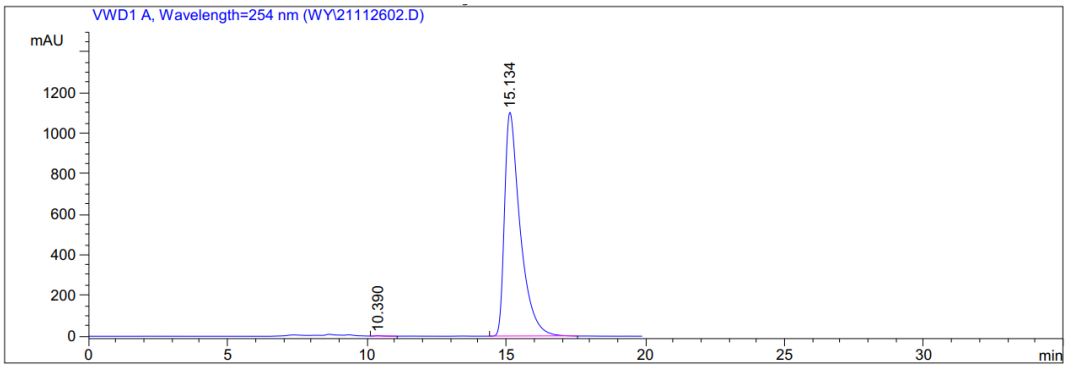
4ab

Prepared according to the procedure within 3 days as white solid (78.7 mg, 70% yield, dr > 20:1); mp 244.1 – 244.8 °C; $[\alpha]_D^{18}$= 16.47 (*c* 0.17, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.7 Hz, 1H), 7.83 (dd, *J* = 5.4, 2.9 Hz, 1H), 7.59 – 7.48 (m, 2H), 7.46 – 7.38 (m, 4H), 7.29 (d, *J* = 3.3 Hz, 1H), 7.22 – 7.08 (m, 7H), 7.07 – 6.97 (m, 2H), 6.62 (d, *J* = 7.3 Hz, 2H), 6.37 (dd, *J* = 5.7, 2.7 Hz, 1H), 5.32 (d, *J* = 11.4 Hz, 1H), 4.99 (d, *J* = 16.0 Hz, 1H), 4.87 (d, *J* = 11.1 Hz, 1H), 4.34 (t, *J* = 10.8 Hz, 1H), 4.29 (d, *J* = 16.3 Hz, 1H), 2.30 (s, 1H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.8, 171.1, 149.7, 143.1, 141.1, 138.7, 135.3, 135.0, 134.8, 132.9, 130.7, 130.2, 130.0, 129.5, 128.9, 128.8, 128.7, 128.6, 127.9, 127.3, 126.9, 126.6, 126.3, 125.4, 124.6, 122.7, 121.1, 109.3, 72.2, 57.8, 54.1, 49.9, 43.4, 20.0; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{31}N_2O_3^+$ ([M+H]$^+$) 563.2329, Found

563.2320; Enantiomeric excess was determined to be >99% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 ºC, 0.8 mL/min, t_{major} = 15.1 min, t_{minor} = 10.3 min).

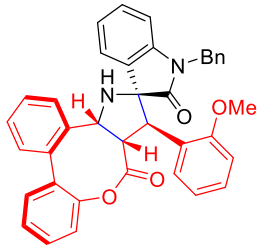


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.365	VB	0.3184	3874.53735	177.71999	50.6842
2	15.163	BB	0.5744	3769.93750	96.98093	49.3158



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.390	VP	0.3091	53.95297	2.48065	0.1249
2	15.134	BB	0.5768	4.31365e4	1103.83032	99.8751

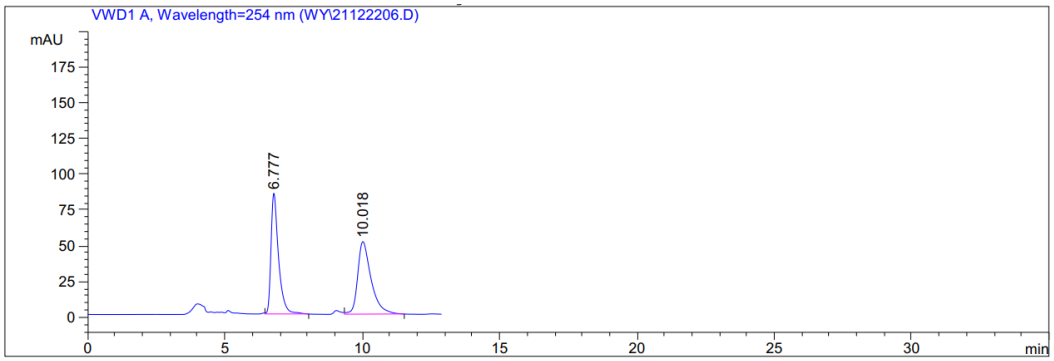
(4bR,6S,7R,7aS)-1'-Benzyl-7-(2-methoxyphenyl)-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4ac)



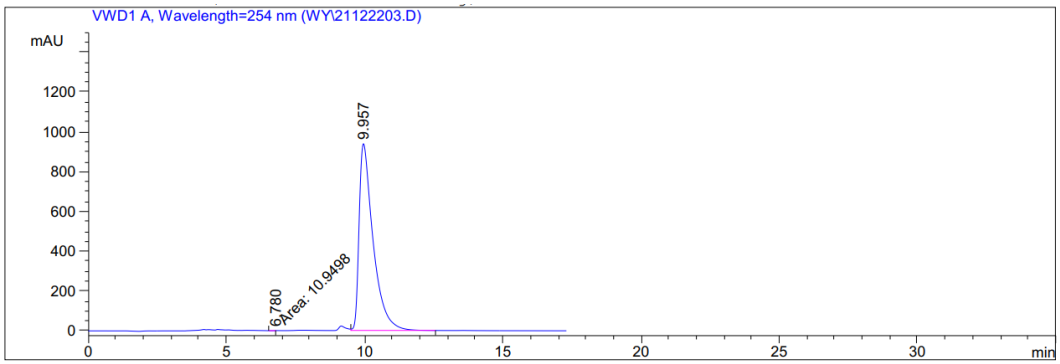
4ac

Prepared according to the procedure within 7 days as white solid (76.4 mg, 66% yield, dr > 20:1); mp 240.8 – 245.8 ºC; $[\alpha]_D^{18}$= 11.74 (*c* 0.41, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 7.1 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.42 – 7.33 (m, 3H), 7.24 – 7.20 (m, 3H), 7.19 – 7.01 (m, 6H), 6.83 – 6.75 (m, 1H), 6.61 (d, *J* = 8.1 Hz, 1H), 6.49 (d, *J* = 7.3 Hz, 2H), 6.31 (d, *J* = 7.6 Hz, 1H), 5.21 (d, *J* = 11.3 Hz, 1H), 5.13 (d, *J* = 11.6

Hz, 1H), 4.92 (d, J = 16.0 Hz, 1H), 4.47 (t, J = 11.4 Hz, 1H), 4.18 (d, J = 16.0 Hz, 1H), 3.28 (s, 3H), 2.21 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 170.8, 158.4, 149.8, 142.8, 141.2, 135.4, 135.1, 134.8, 130.2, 130.0, 129.0, 128.9, 128.8, 128.8, 128.6, 128.5, 127.9, 127.3, 127.1, 126.9, 126.4, 125.5, 125.5, 123.0, 122.4, 121.2, 120.6, 111.0, 108.7, 71.9, 57.5, 55.1, 51.6, 46.1, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{31}N_2O_4^+$ ([M+H]$^+$) 579.2278, Found 579.2276; Enantiomeric excess was determined to be >99% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 9.9 min, t_{minor} = 6.7 min).

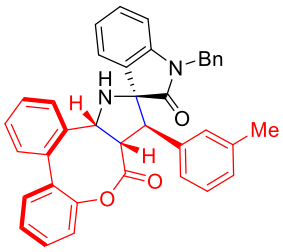


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.777	VB	0.2812	1613.74048	84.44579	48.2173
2	10.018	VB	0.5089	1733.06641	50.76937	51.7827



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.780	MM	0.1764	10.94982	1.03435	0.0331
2	9.957	VB	0.5143	3.30632e4	938.68280	99.9669

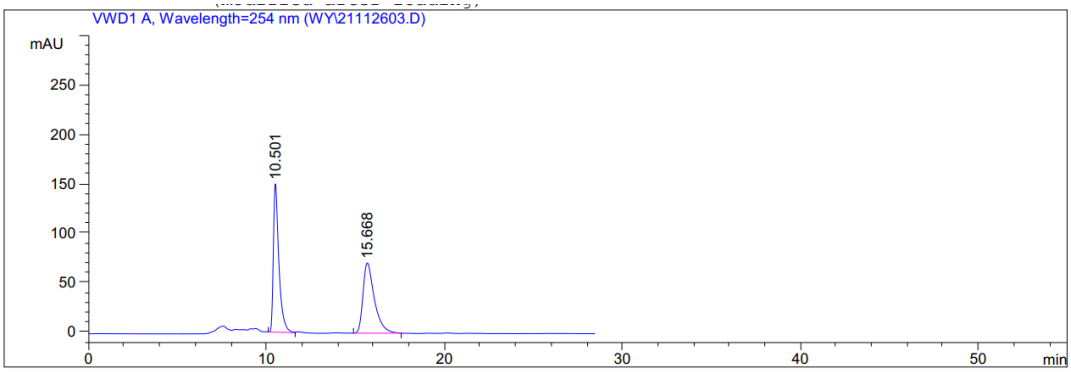
(4bR,6S,7R,7aS)-1'-Benzyl-7-(m-tolyl)-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4ad)



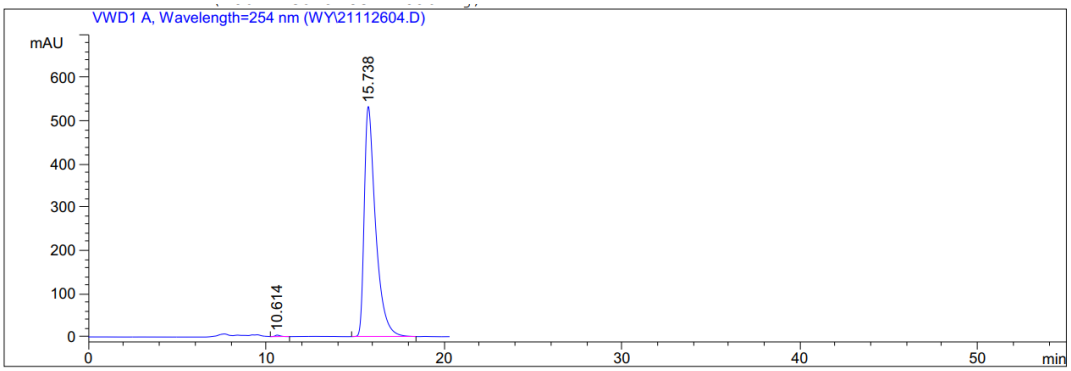
4ad

Prepared according to the procedure within 2 days as white solid (90.0 mg, 80% yield, dr > 20:1); mp 212.2 – 212.8 °C; $[\alpha]_D^{18}$= 40.10 (*c* 0.21, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.7 Hz, 1H), 7.79 (d, J = 7.0 Hz, 1H), 7.53 – 7.46

(m, 2H), 7.45 – 7.35 (m, 3H), 7.26 (d, J = 8.9 Hz, 2H), 7.21 – 7.11 (m, 3H), 7.08 – 6.98 (m, 4H), 6.76 (d, J = 6.5 Hz, 1H), 6.71 (s, 1H), 6.43 (d, J = 7.5 Hz, 2H), 6.36 (d, J = 7.5 Hz, 1H), 5.22 (d, J = 10.1 Hz, 1H), 4.93 (d, J = 16.0 Hz, 1H), 4.49 (t, J = 11.3 Hz, 1H), 4.34 (d, J = 11.4 Hz, 1H), 4.17 (d, J = 16.0 Hz, 1H), 2.24 (s, 1H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 170.8, 149.7, 143.2, 141.1, 137.9, 135.3, 134.9, 134.8, 133.9, 130.2, 130.1, 129.5, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.0, 127.2, 127.0, 126.3, 125.4, 125.0, 124.1, 123.1, 121.1, 109.2, 72.0, 57.4, 54.8, 50.8, 43.3, 21.4; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{31}N_2O_3^+$ ($[M+H]^+$) 563.2329, Found 563.2322; Enantiomeric excess was determined to be >99% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 15.7 min, t_{minor} = 10.6 min).

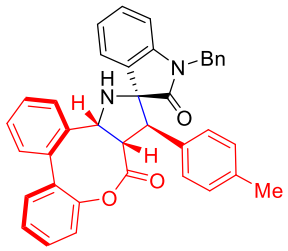


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.501	VB	0.3169	3229.41284	149.87688	50.4627
2	15.668	BB	0.6613	3170.18579	71.12328	49.5373



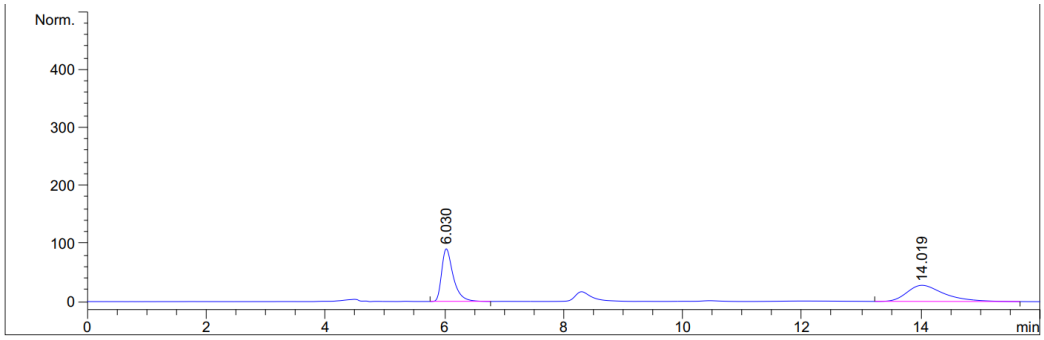
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.614	VB	0.3093	75.28782	3.56114	0.3185
2	15.738	BB	0.6531	2.35628e4	532.49054	99.6815

(4bR,6S,7R,7aS)-1'-Benzyl-7-(p-tolyl)-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4ae)

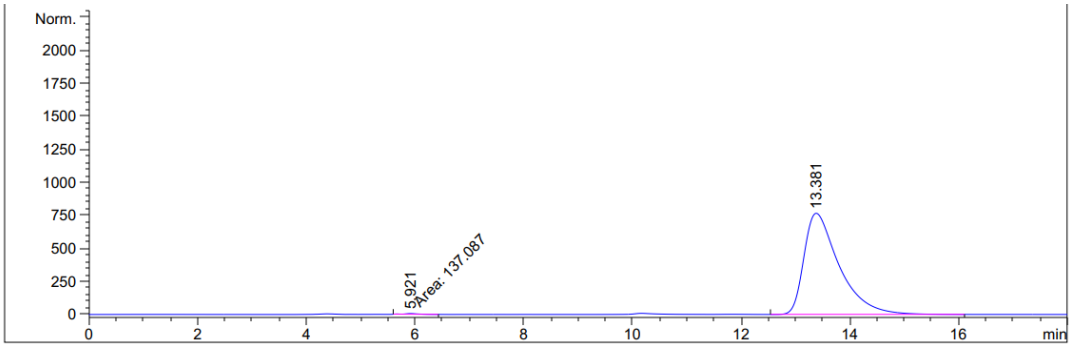


4ae

Prepared according to the procedure within 3 days as white solid (78.8 mg, 70% yield, dr > 20:1); mp 212.6 – 213.5 °C; $[\alpha]_D^{18}$= 58.97 (*c* 0.15, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 6.4 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.44 – 7.32 (m, 3H), 7.25 – 7.22 (m, 2H), 7.20 – 7.11 (m, 3H), 7.08 – 7.02 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.1 Hz, 2H), 6.48 (d, *J* = 7.4 Hz, 2H), 6.36 (d, *J* = 7.3 Hz, 1H), 5.22 (d, *J* = 11.2 Hz, 1H), 4.93 (d, *J* = 16.0 Hz, 1H), 4.47 (t, *J* = 11.3 Hz, 1H), 4.34 (d, *J* = 11.4 Hz, 1H), 4.18 (d, *J* = 16.0 Hz, 1H), 2.28 (s, 3H), 2.24 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 170.8, 149.7, 143.1, 141.0, 137.2, 135.3, 134.9, 134.8, 131.0, 130.2, 130.1, 129.4, 129.2, 128.9, 128.9, 128.8, 128.5, 127.9, 127.2, 126.9, 126.5, 125.4, 124.1, 123.1, 121.1, 109.2, 72.0, 57.4, 54.6, 51.0, 43.3, 21.2; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{31}N_2O_3^+$ ($[M+H]^+$) 563.2329, Found 563.2320; Enantiomeric excess was determined to be 99% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 13.4 min, t_{minor} = 5.9 min).

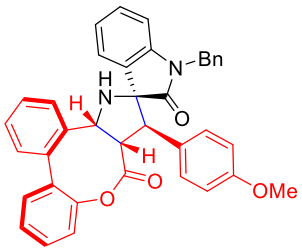


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.030	BP	0.2032	1227.62463	90.63689	50.0682
2	14.019	VB	0.6566	1224.27844	27.95267	49.9318



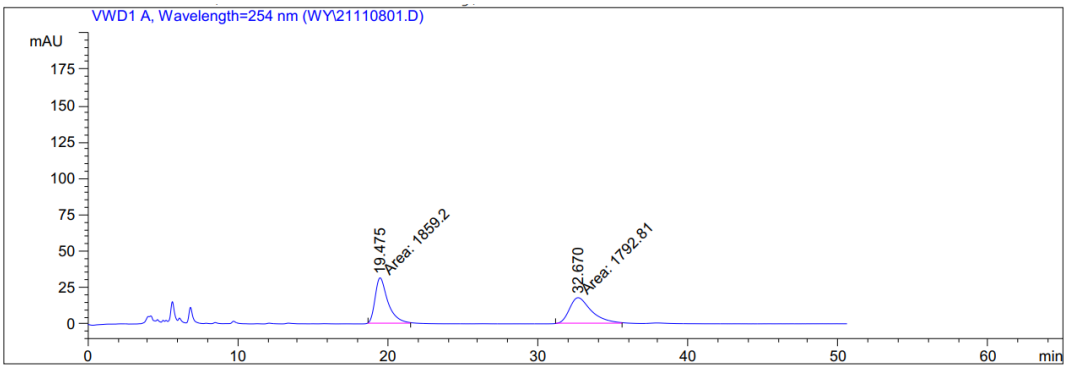
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.921	MM	0.3552	137.08684	6.43182	0.3962
2	13.381	VB	0.6690	3.44610e4	766.07513	99.6038

(4bR,6S,7R,7aS)-1'-Benzyl-7-(4-methoxyphenyl)-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4af)

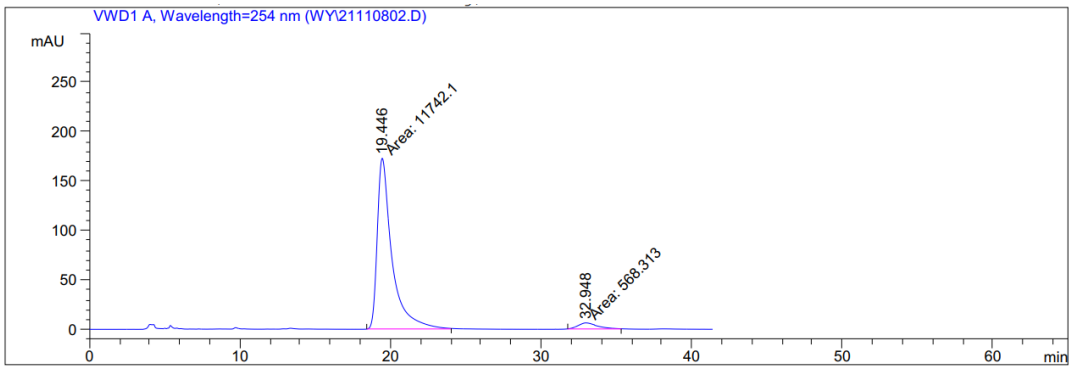


4af

Prepared according to the procedure within 4 days as white solid (106.47 mg, 92% yield, dr > 20:1); mp 238.7 – 239.5 °C; $[\alpha]_D^{18}$ = 75.42 (*c* 0.18, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 7.1 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.44 – 7.35 (m, 3H), 7.25 – 7.23 (m, 2H), 7.21 – 7.11 (m, 3H), 7.09 – 7.04 (m, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 6.45 (d, *J* = 7.5 Hz, 2H), 6.38 (d, *J* = 7.3 Hz, 1H), 5.21 (d, *J* = 11.2 Hz, 1H), 4.93 (d, *J* = 16.0 Hz, 1H), 4.45 (t, *J* = 11.3 Hz, 1H), 4.33 (d, *J* = 11.4 Hz, 1H), 4.19 (d, *J* = 16.0 Hz, 1H), 3.72 (s, 3H), 2.24 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 170.8, 159.2, 149.7, 143.1, 141.0, 135.3, 134.9, 134.8, 130.2, 130.1, 129.5, 129.0, 128.9, 128.9, 128.8, 128.5, 127.9, 127.3, 126.9, 126.4, 126.0, 125.4, 124.1, 123.2, 121.1, 113.9, 109.2, 72.0, 57.4, 55.1, 54.3, 51.0, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{31}N_2O_4^+$ ($[M+H]^+$) 579.2278, Found 579.2271; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 19.4 min, t_{minor} = 32.9 min).

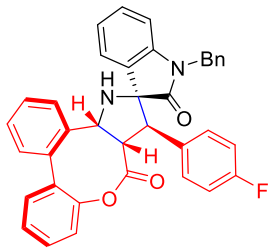


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.475	MM	0.9918	1859.19836	31.24228	50.9089
2	32.670	MM	1.6953	1792.81445	17.62515	49.0911



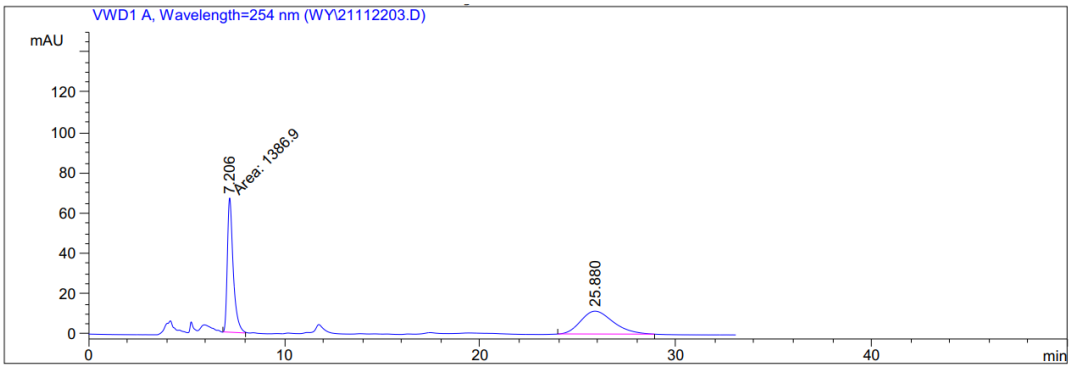
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.446	MM	1.1334	1.17421e4	172.66150	95.3835
2	32.948	MM	1.5245	568.31262	6.21327	4.6165

(4bR,6S,7R,7aS)-1'-Benzyl-7-(4-fluorophenyl)-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4ag)

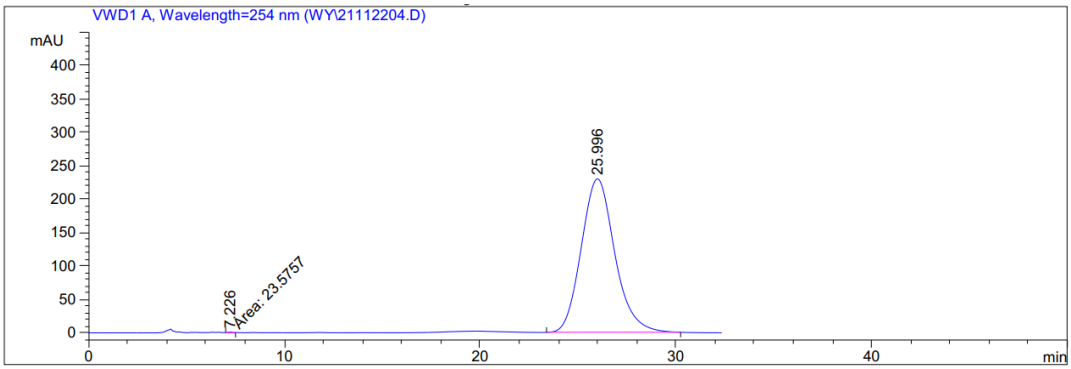


4ag

Prepared according to the procedure within 6 days as white solid (70.26 mg, 62% yield, dr > 20:1); mp 188.1 – 189.0 °C; $[\alpha]_D^{18}$= 22.96 (*c* 0.10, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.81 – 7.76 (m, 1H), 7.55 – 7.47 (m, 2H), 7.46 – 7.37 (m, 3H), 7.29 – 7.27 (m, 2H), 7.23 – 7.09 (m, 5H), 6.95 – 6.90 (m, 2H), 6.81 – 6.75 (m, 2H), 6.51 (d, *J* = 7.1 Hz, 2H), 6.43 (dd, *J* = 6.5, 2.0 Hz, 1H), 5.22 (d, *J* = 11.0 Hz, 1H), 4.89 (d, *J* = 15.9 Hz, 1H), 4.44 (t, *J* = 11.2 Hz, 1H), 4.35 (d, *J* = 11.4 Hz, 1H), 4.23 (d, *J* = 16.0 Hz, 1H), 2.27 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 170.7, 162.5 (d, *J* = 198.0 Hz), 149.6, 143.1, 140.8, 135.3, 134.8, 134.7, 130.2, 130.1, 129.9 (d, *J* = 3.0 Hz), 129.7, 129.6, 128.9, 128.8, 128.6, 128.6, 128.0, 127.4, 127.0, 126.4, 125.4, 124.1, 123.3, 121.1, 115.4 (d, *J* = 17.2 Hz), 109.3, 71.9, 57.3, 54.2, 51.1, 43.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.55; HRMS (ESI) *m/z* Calcd. for $C_{37}H_{28}FN_2O_3^+$ ($[M+H]^+$) 567.2078, Found 567.2069; Enantiomeric excess was determined to be >99% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 25.9 min, t_{minor} = 7.2 min).

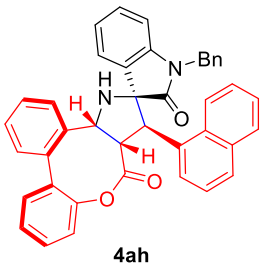


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.206	MM	0.3470	1386.90039	66.60762	51.1050
2	25.880	BB	1.3685	1326.92517	11.39727	48.8950



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.226	MM	0.3781	23.57570	1.03921	0.0862
2	25.996	BB	1.8046	2.73352e4	229.73177	99.9138

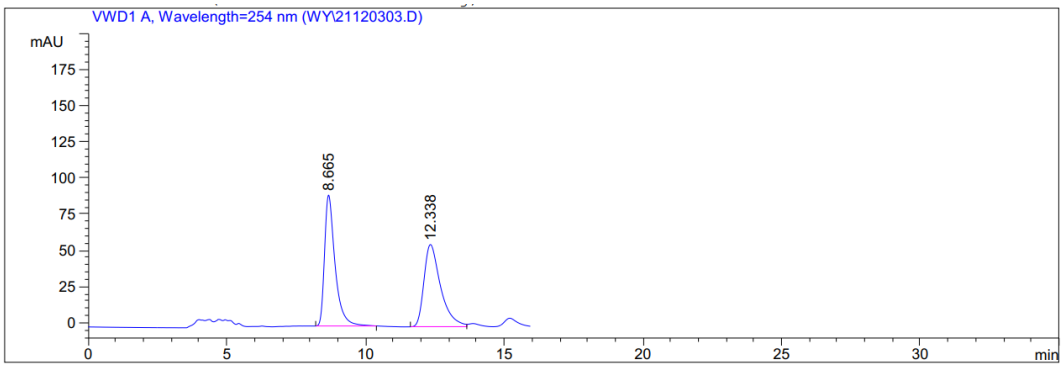
(4bR,6S,7R,7aS)-1'-Benzyl-7-(naphthalen-1-yl)-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4ah)



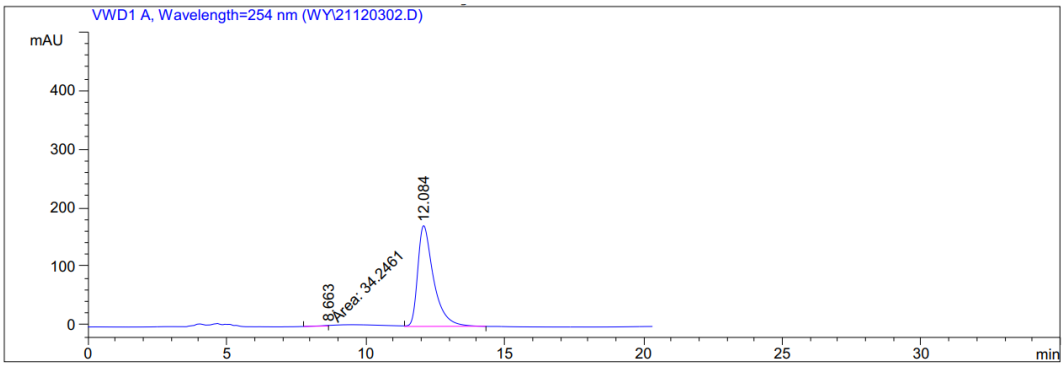
4ah

Prepared according to the procedure within 4 days as white solid (101.78 mg, 85% yield, dr > 20:1); mp 258.4 – 259.0 °C; $[\alpha]_D^{18}$= -109.70 (*c* 0.69, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.7 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 7.3 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.44 – 7.34 (m, 3H), 7.30 – 7.21 (m, 4H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.11 – 7.05 (m, 2H), 7.01 – 6.96 (m, 2H), 6.94 – 6.88 (m, 1H), 6.37 (d, *J* = 7.5 Hz, 2H), 6.10 (d, *J* = 7.8 Hz, 1H), 5.45 (d, *J* = 11.0 Hz, 1H), 5.36 (d, *J* = 11.3 Hz, 1H), 4.82 (d, *J* = 16.0 Hz, 1H), 4.56 (t, *J* = 11.2 Hz, 1H), 4.14 (d, *J* = 16.0 Hz, 1H), 2.33 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 171.0, 149.8, 142.9, 141.1, 135.4, 134.9, 134.8, 133.8, 132.7, 131.0, 130.3, 130.1, 129.5, 129.0, 128.9, 128.6, 128.3, 128.2, 128.0, 127.2, 127.0, 126.4, 125.6, 125.5, 125.5, 125.2, 124.5,

124.5, 123.8, 122.8, 121.2, 109.2, 72.5, 57.8, 53.8, 48.4, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{41}H_{31}N_2O_3^+$ ($[M+H]^+$) 599.2329, Found 599.2321; Enantiomeric excess was determined to be >99% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 12.0 min, t_{minor} = 8.6 min).

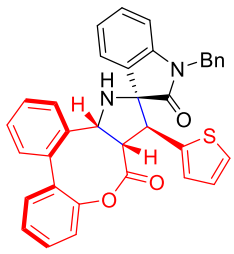


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	8.665	BB	0.3940	2388.73706		90.44166	50.0669
2	12.338	BV	0.6271	2382.35693		56.85996	49.9331



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	8.663	MM	0.4935	34.24607		1.15658	0.4985
2	12.084	VB	0.5891	6835.82324		171.91708	99.5015

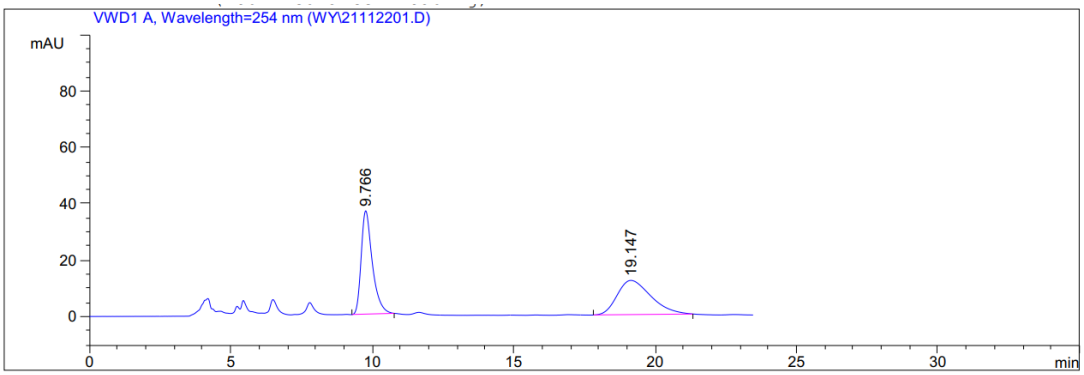
(4bR,6S,7S,7aS)-1'-Benzyl-7-(thiophen-2-yl)-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4ai)



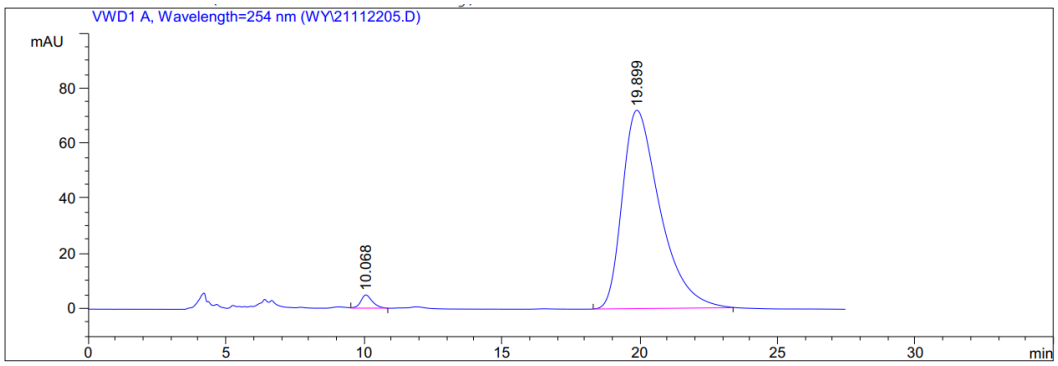
4ai

Prepared according to the procedure within 4 days as white solid (66.56 mg, 60% yield, dr > 20:1); mp 222.3 – 222.1 °C; $[\alpha]_D^{18}$= 55.77 (*c* 0.52, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 1H), 7.77 – 7.68 (m, 1H), 7.53 – 7.43 (m, 2H), 7.42 – 7.33 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.17 – 7.08 (m, 3H), 7.02 (d, *J* = 5.0 Hz, 1H), 6.84 – 6.76 (m, 1H), 6.62 – 6.57 (m, 3H), 6.51 – 6.44 (m, 1H), 5.19 (dd, *J* = 11.1, 3.5 Hz, 1H), 4.92 (d, *J* = 15.9 Hz, 1H), 4.58 (d, *J* = 11.1 Hz, 1H), 4.41 (t, *J* = 11.2 Hz,

1H), 4.25 (d, J = 15.9 Hz, 1H), 2.18 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 170.6, 149.6, 143.6, 140.7, 137.4, 135.3, 135.0, 134.7, 130.2, 129.9, 128.9, 128.9, 128.7, 128.3, 128.1, 127.3, 127.1, 126.9, 126.6, 125.4, 125.3, 124.5, 124.2, 123.3, 121.2, 109.3, 71.5, 57.3, 52.9, 50.5, 43.4; HRMS (ESI) *m/z* Calcd. for $C_{35}H_{27}N_2O_3S^+$ ($[M+H]^+$) 555.1737, Found 555.1728; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 19.8 min, t_{minor} = 10.0 min).

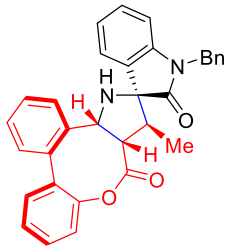


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.766	PB	0.4095	1008.69080	36.70193	49.8833
2	19.147	BB	1.1072	1013.41003	12.16640	50.1167



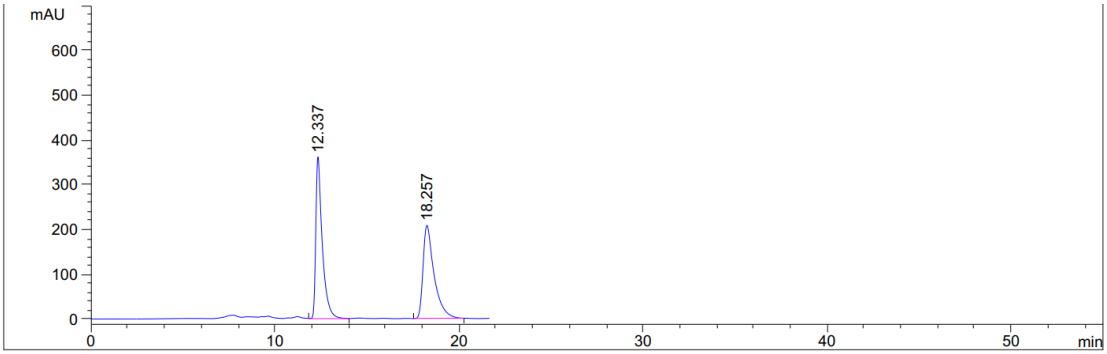
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.068	VB	0.4409	142.56955	4.82462	2.0373
2	19.899	BB	1.3962	6855.50879	72.09888	97.9627

(4bR,6S,7S,7aS)-1'-Benzyl-7-methyl-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4aj)

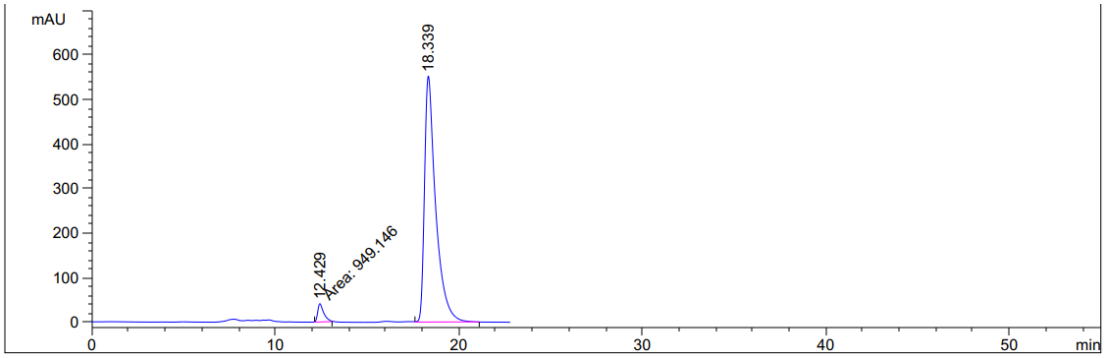


4aj

Prepared according to the procedure within 3 days as white solid (89.53 mg, 92% yield, dr > 20:1); mp 140.5 – 141.3 °C; $[\alpha]_D^{18}$= -127.07 (*c* 0.53, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.37 – 7.30 (m, 3H), 7.25 – 7.18 (m, 8H), 7.15 – 7.09 (m, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 4.97 (d, *J* = 3.0 Hz, 1H), 4.93 (d, *J* = 7.5 Hz, 1H), 4.62 (d, *J* = 15.6 Hz, 1H), 3.64 (t, *J* = 11.1 Hz, 1H), 3.19 – 3.08 (m, 1H), 2.02 (s, 1H), 0.82 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 171.4, 149.6, 143.4, 141.2, 135.8, 135.3, 134.7, 130.0, 129.9, 129.4, 129.1, 128.9, 128.8, 128.7, 127.9, 127.8, 127.3, 126.9, 125.5, 124.1, 123.3, 121.3, 109.1, 70.8, 57.5, 53.7, 44.9, 43.7, 12.4; HRMS (ESI) *m/z* Calcd. for $C_{32}H_{27}N_2O_3^+$ ($[M+H]^+$) 487.2016, Found 487.2013; Enantiomeric excess was determined to be 92% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 18.3 min, t_{minor} =12.4 min).

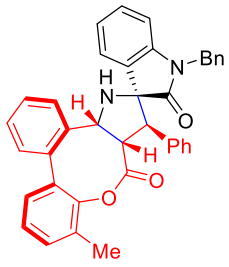


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.337	VB	0.3512	8847.62988	361.34042	50.5158
2	18.257	VB	0.6100	8666.93359	207.94753	49.4842



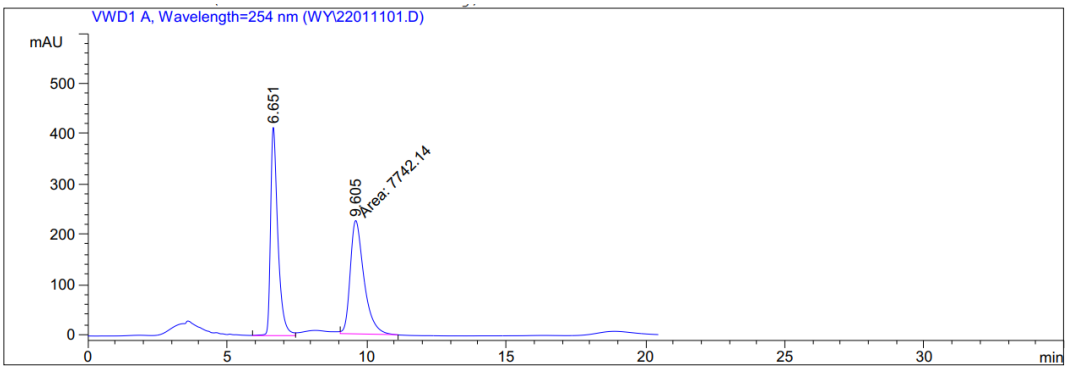
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.429	MM	0.3845	949.14594	41.13959	3.9019
2	18.339	VB	0.6148	2.33760e4	552.14771	96.0981

(4bR,6S,7R,7aS)-1'-Benzyl-10-methyl-7-phenyl-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4ak)

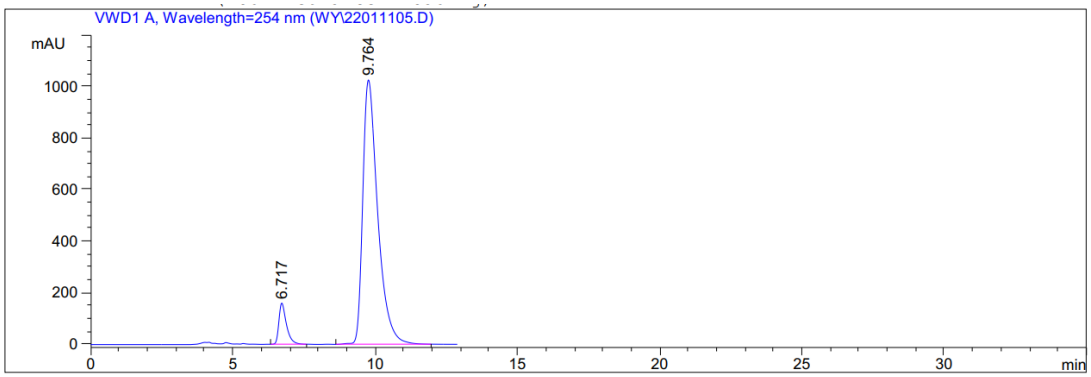


4ak

Prepared according to the procedure within 4 days as white solid (105.78 mg, 94% yield, dr > 20:1); mp 262.3 – 263.3 °C; $[\alpha]_D^{18}$= -7.12 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 6.9 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.38 – 7.28 (m, 3H), 7.24 – 7.17 (m, 4H), 7.14 – 7.01 (m, 6H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.41 (d, *J* = 7.3 Hz, 2H), 6.35 (d, *J* = 7.5 Hz, 1H), 5.25 – 5.10 (m, 1H), 4.88 (d, *J* = 16.0 Hz, 1H), 4.37 (d, *J* = 4.6 Hz, 2H), 4.17 (d, *J* = 16.0 Hz, 1H), 2.26 (s, 3H), 2.18 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 171.1, 148.0, 143.1, 141.0, 135.8, 134.9, 134.7, 134.1, 131.4, 130.1, 129.6, 128.8, 128.7, 128.7, 128.6, 127.9, 127.9, 127.8, 127.6, 127.2, 126.7, 126.3, 125.4, 124.2, 123.2, 109.3, 72.1, 57.3, 54.7, 51.1, 43.3, 16.8; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{31}N_2O_3^+$ ([M+H]$^+$) 563.2329, Found 563.2319; Enantiomeric excess was determined to be 85% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 14.6 min, t_{minor} = 5.7 min).

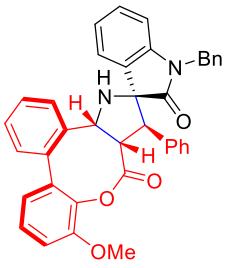


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.651	BV	0.2702	7590.18896	414.99014	49.5045
2	9.605	MM	0.5712	7742.13867	225.89011	50.4955



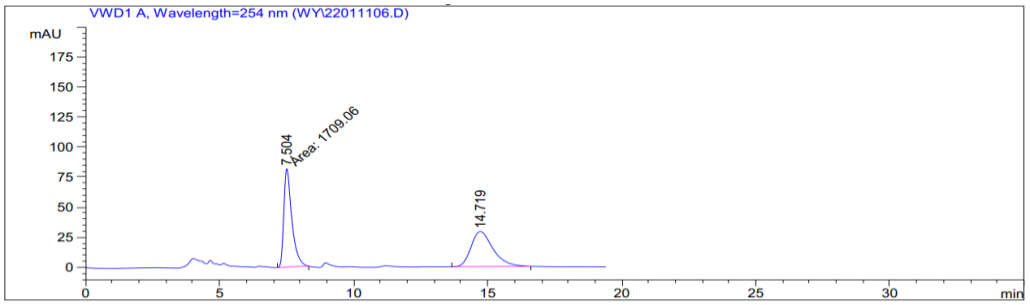
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.717	VB	0.2738	2958.68994	160.12941	7.3262
2	9.764	VB	0.5494	3.74266e4	1025.96362	92.6738

(4bR,6S,7R,7aS)-1'-Benzyl-10-methoxy-7-phenyl-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4al)

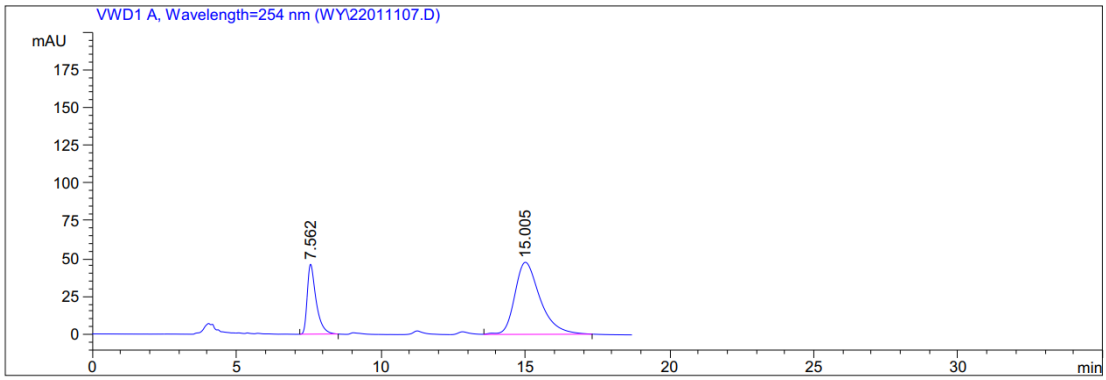


4al

Prepared according to the procedure within 4 days as white solid (63.65 mg, 55% yield, dr > 20:1); mp 286.5 – 287.3 °C; $[\alpha]_D^{18}$= -2.68 (*c* 0.11, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 6.7 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.42 – 7.32 (m, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.23 – 7.14 (m, 3H), 7.14 – 7.02 (m, 6H), 7.00 – 6.93 (m, 3H), 6.42 (d, *J* = 7.0 Hz, 2H), 6.37 (d, *J* = 7.2 Hz, 1H), 5.19 (d, *J* = 10.1 Hz, 1H), 4.89 (d, *J* = 16.0 Hz, 1H), 4.49 – 4.34 (m, 2H), 4.18 (d, *J* = 15.9 Hz, 1H), 3.91 (s, 3H), 2.23 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 171.1, 151.2, 143.1, 140.9, 138.4, 136.2, 135.4, 134.8, 134.1, 129.5, 128.9, 128.7, 128.6, 128.4, 127.9, 127.6, 127.3, 127.2, 126.3, 125.6, 124.2, 123.2, 121.1, 112.4, 109.3, 71.9, 57.1, 56.1, 54.4, 50.4, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{31}N_2O_4^+$ ($[M+H]^+$) 579.2278, Found 579.2276; Enantiomeric excess was determined to be 49% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 15.0 min, t_{minor} = 7.5 min).

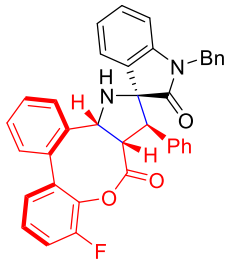


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.504	MM	0.3476	1709.06018	81.94855	50.4844
2	14.719	BB	0.8555	1676.26624	29.35551	49.5156



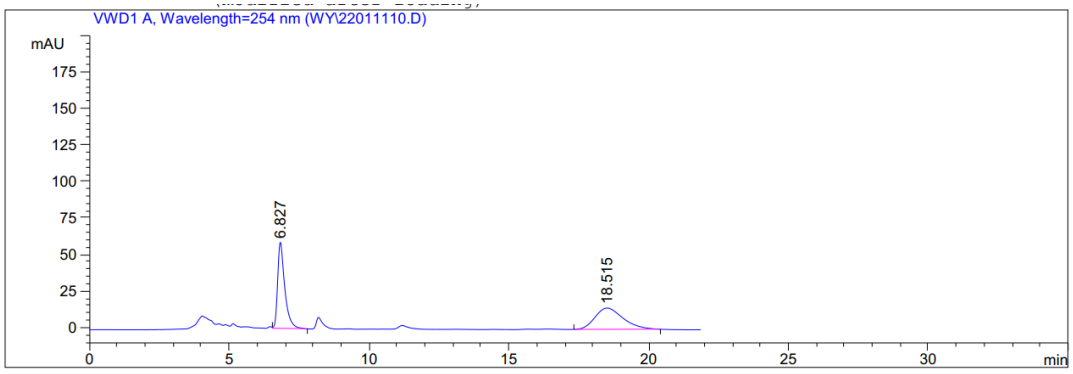
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.562	BB	0.3178	995.78351	46.32310	25.4284
2	15.005	BB	0.9132	2920.24194	47.73516	74.5716

(4bR,6S,7R,7aS)-1'-Benzyl-10-fluoro-7-phenyl-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4am)

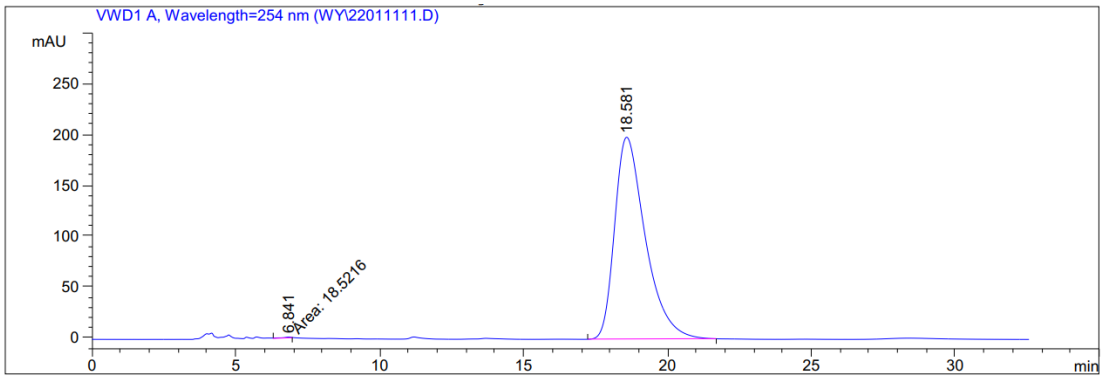


4am

Prepared according to the procedure within 3 days as white solid (99.73 mg, 88% yield, dr > 20:1); mp 282.0 – 282.8 °C; $[\alpha]_D^{18}$= 53.61 (*c* 0.66, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 6.8 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.43 – 7.28 (m, 4H), 7.25 – 7.06 (m, 9H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.47 (d, *J* = 7.3 Hz, 2H), 6.40 (d, *J* = 7.4 Hz, 1H), 5.22 (d, *J* = 11.2 Hz, 1H), 4.93 (d, *J* = 16.0 Hz, 1H), 4.55 (t, *J* = 11.4 Hz, 1H), 4.39 (d, *J* = 11.4 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H), 2.20 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 170.0, 153.8 (d, *J* = 252.5 Hz), 143.2, 141.0, 137.3, 137.3 (d, *J* = 12.1 Hz), 134.8, 134.3, 134.3, 133.7, 129.7, 129.3, 128.7, 128.6, 128.6, 128.2, 127.9, 127.6, 127.5, 127.3, 126.4, 125.8, 125.0 (d, *J* = 3.0 Hz), 124.1, 123.3, 116.9 (d, *J* = 21.2 Hz), 109.4, 71.9, 57.1, 54.6, 50.7, 43.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -128.72; HRMS (ESI) *m/z* Calcd. for $C_{37}H_{28}FN_2O_3^+$ ($[M+H]^+$) 567.2078, Found 567.2071; Enantiomeric excess was determined to be >99% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 18.5 min, t_{minor} = 6.8 min).

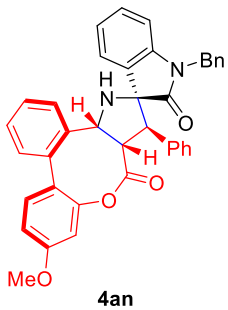


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.827	VB	0.2611	1047.31812	58.95049	50.4810
2	18.515	BB	0.9317	1027.35779	14.59801	49.5190



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.841	MM	0.4077	18.52155	7.57161e-1	0.1254
2	18.581	BB	1.1214	1.47470e4	198.53874	99.8746

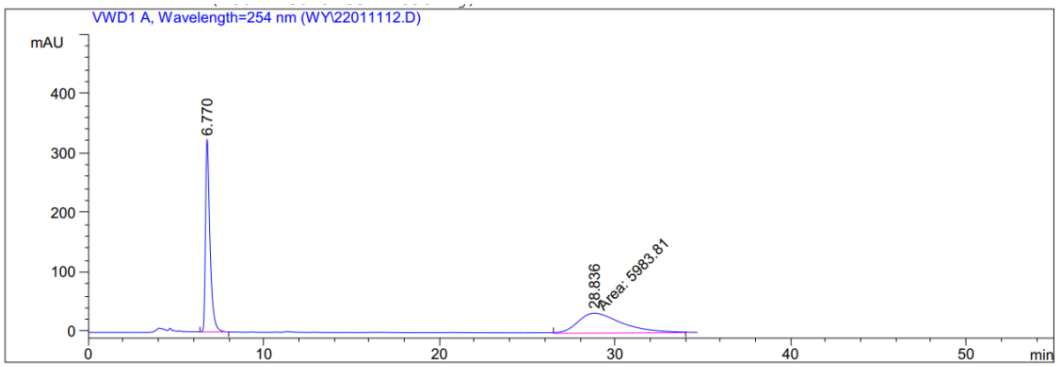
(4bR,6S,7R,7aS)-1'-Benzyl-11-methoxy-7-phenyl-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4an)



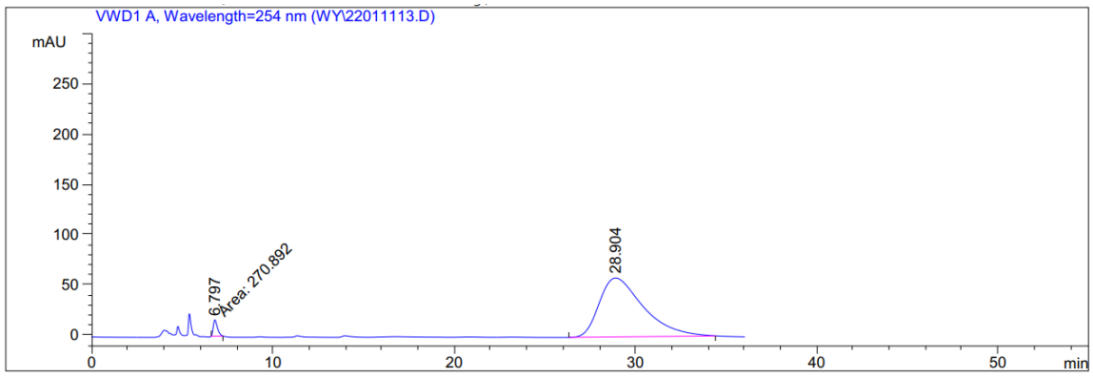
4an

Prepared according to the procedure within 4 days as white solid (81.01 mg, 70% yield, dr > 20:1); mp 172.6 – 173.8 °C; $[\alpha]_D^{18}$= 19.21 (*c* 0.33, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.38 – 7.33 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.23 – 7.16 (m, 3H), 7.16 – 7.03 (m, 6H), 6.99 – 6.93 (m, 3H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.45 (d, *J* = 7.3 Hz, 2H), 6.36 (d, *J* = 7.4 Hz, 1H), 5.26 (d, *J* = 11.2 Hz, 1H), 4.89 (d, *J* = 16.0 Hz, 1H), 4.54 (t, *J* = 11.3 Hz, 1H), 4.37 (d, *J* = 11.3 Hz, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 3.89 (s, 3H), 2.23 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 170.7, 160.9, 150.4, 143.1, 141.2, 135.2, 134.9, 134.1, 130.7, 129.5, 129.3,

128.8, 128.6, 128.6, 128.5, 128.1, 127.9, 127.8, 127.2, 126.8, 126.4, 125.4, 124.1, 123.2, 112.5, 109.3, 106.9, 72.0, 57.5, 55.7, 55.0, 50.7, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{31}N_2O_4^+$ ($[M+H]^+$) 579.2278, Found 579.2270; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 28.9 min, t_{minor} = 6.7 min).

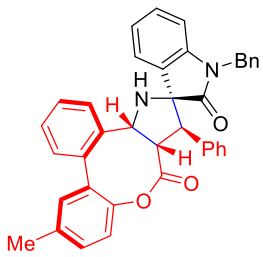


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.770	VB	0.2625	5785.02686	323.46078	49.1555
2	28.836	MM	2.9578	5983.81055	33.71758	50.8445



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.797	MM	0.2756	270.89197	16.38338	2.6576
2	28.904	BB	2.2921	9922.18848	58.57800	97.3424

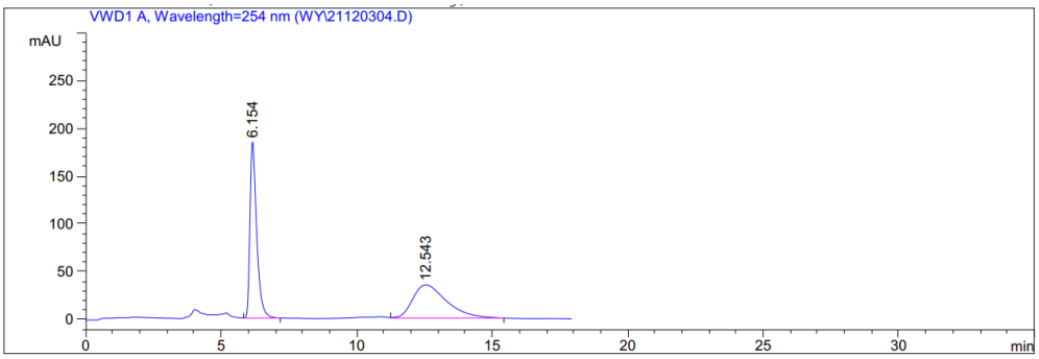
(4bR,6S,7R,7aS)-1'-Benzyl-12-methyl-7-phenyl-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4ao)



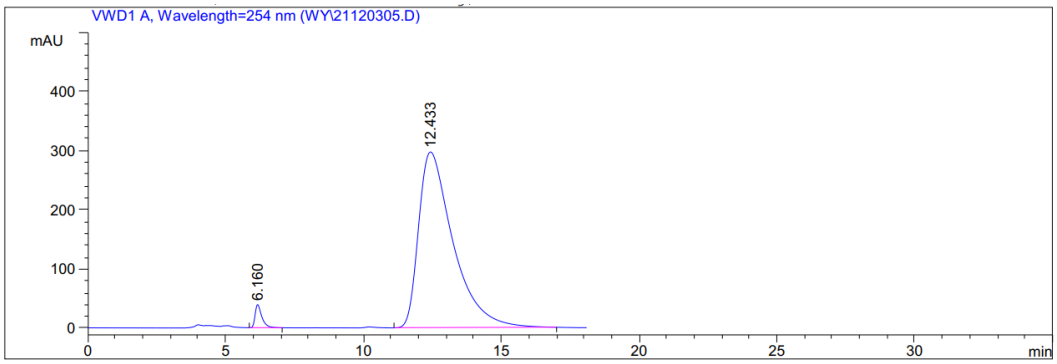
4ao

Prepared according to the procedure within 3 days as white solid (110.28 mg, 98% yield, dr > 20:1); mp 205.8 – 106.7 °C; $[\alpha]_D^{18}$= 51.86 (*c* 0.80, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.42 – 7.37 (m, 1H), 7.33 – 7.27 (m, 2H), 7.25 – 7.18

(m, 3H), 7.18 – 7.05 (m, 7H), 6.98 (d, *J* = 7.6 Hz, 2H), 6.47 (d, *J* = 7.4 Hz, 2H), 6.38 (d, *J* = 7.4 Hz, 1H), 5.28 (d, *J* = 11.2 Hz, 1H), 4.90 (d, *J* = 16.0 Hz, 1H), 4.53 (t, *J* = 11.3 Hz, 1H), 4.40 (d, *J* = 11.4 Hz, 1H), 4.22 (d, *J* = 16.0 Hz, 1H), 2.47 (s, 3H), 2.28 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 171.1, 147.5, 143.1, 140.9, 136.7, 135.5, 134.9, 134.4, 134.1, 130.6, 129.5, 128.9, 128.8, 128.7, 128.6, 128.5, 128.1, 127.9, 127.7, 127.2, 126.4, 125.4, 124.1, 123.2, 120.8, 109.3, 72.1, 57.5, 55.0, 50.7, 43.3, 21.0; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{31}N_2O_3^+$ ($[M+H]^+$) 563.2329, Found 563.2322; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 12.4 min, t_{minor} = 6.1 min).

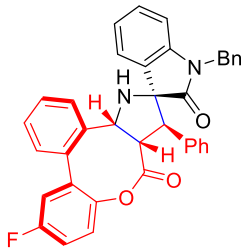


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.154	VB	0.2577	3170.27612	184.09076	50.8701
2	12.543	VB	1.2538	3061.82642	34.94222	49.1299



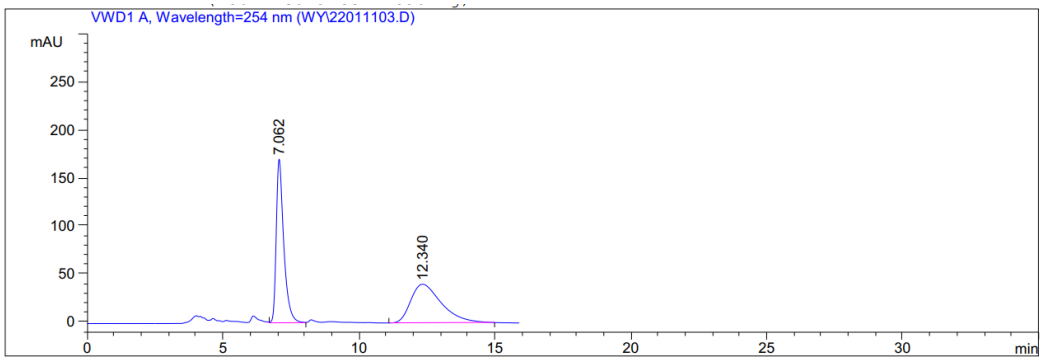
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.160	VB	0.2544	672.30438	39.12313	2.5381
2	12.433	BB	1.2836	2.58167e4	296.95450	97.4619

(4bR,6S,7R,7aS)-1'-Benzyl-12-fluoro-7-phenyl-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4ap)

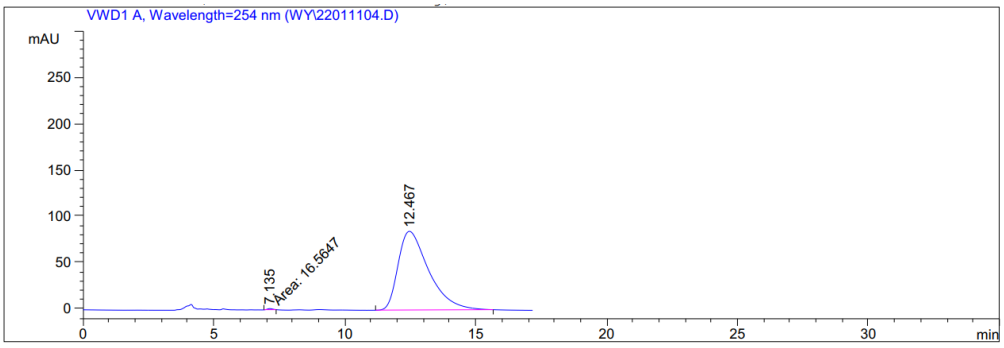


4ap

Prepared according to the procedure within 3 days as white solid (104.26 mg, 92% yield, dr > 20:1); mp 252.9 – 254.0 °C; $[\alpha]_D^{18}$= 41.91 (*c* 0.42, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.5 Hz, 1H), 7.77 (d, *J* = 6.7 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.40 – 7.34 (m, 1H), 7.24 – 7.03 (m, 12H), 6.96 (d, *J* = 7.1 Hz, 2H), 6.45 (d, *J* = 7.0 Hz, 2H), 6.36 (d, *J* = 7.2 Hz, 1H), 5.23 (d, *J* = 10.9 Hz, 1H), 4.89 (d, *J* = 16.0 Hz, 1H), 4.49 (t, *J* = 11.2 Hz, 1H), 4.35 (d, *J* = 11.2 Hz, 1H), 4.19 (d, *J* = 15.9 Hz, 1H), 2.22 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 170.7, 160.5 (d, *J* = 248.5 Hz), 145.8, 145.7, 143.1, 140.8, 136.5 (d, *J* = 8.1 Hz), 134.8, 134.3, 133.9, 129.6, 129.3, 128.7, 128.6, 128.6, 128.1, 128.0, 127.8, 127.2, 126.4, 125.7, 124.1, 123.2, 122.7 (d, *J* = 9.1 Hz), 116.9 (d, *J* = 12.1Hz), 116.7 (d, *J* = 11.1 Hz), 109.4, 72.0, 57.3, 54.9, 50.8, 43.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.68; HRMS (ESI) *m/z* Calcd. for $C_{37}H_{28}FN_2O_3^+$ ($[M+H]^+$) 567.2078, Found 567.2073; Enantiomeric excess was determined to be 99% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 12.4 min, t_{minor} = 7.1 min).

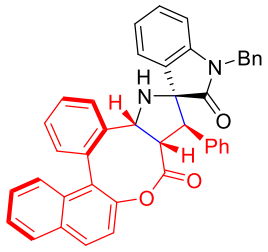


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.062	BV	0.2855	3273.36768	170.19456	50.9036
2	12.340	PB	1.1817	3157.15796	40.18075	49.0964



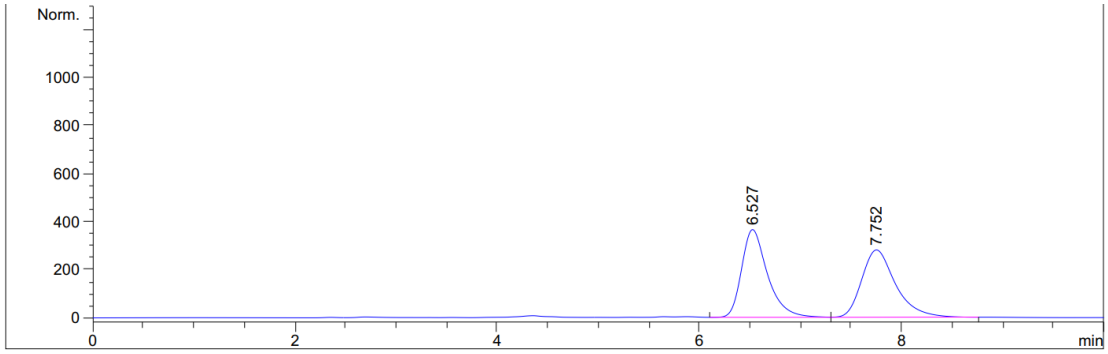
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.135	MM	0.2311	16.56470	1.19450	0.2380
2	12.467	BB	1.2099	6942.31006	85.06021	99.7620

(8aS,9R,10S,11aR)-1'-Benzyl-9-phenyl-8a,9,11,11a-tetrahydro-8H-spiro[benzo[5,6]naphtho[1',2':7,8]oxocino[4,3-b]pyrrole-10,3'-indoline]-2',8-dione (4aq)

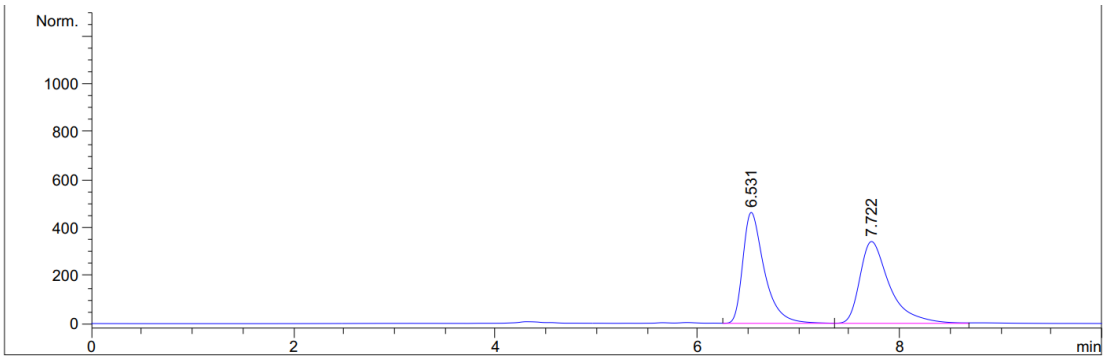


4aq

Prepared according to the procedure within 3 days as white solid (86.21 mg, 72% yield, dr > 20:1); mp 214.3 – 214.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 7.4 Hz, 1H), 8.02 (dd, J = 16.2, 8.4 Hz, 2H), 7.83 (d, J = 6.9 Hz, 1H), 7.67 (d, J = 8.1 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.53 – 7.47 (m, 2H), 7.43 (d, J = 8.7 Hz, 1H), 7.37 (d, J = 7.0 Hz, 1H), 7.25 – 7.05 (m, 8H), 6.97 (d, J = 7.1 Hz, 2H), 6.45 (d, J = 6.8 Hz, 2H), 6.37 (d, J = 7.2 Hz, 1H), 5.13 (d, J = 9.6 Hz, 1H), 4.81 (d, J = 15.9 Hz, 1H), 4.51 – 4.34 (m, 2H), 4.18 (d, J = 16.1 Hz, 1H), 2.28 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 170.7, 146.9, 143.1, 142.2, 134.9, 134.0, 132.5, 132.5, 132.3, 130.7, 130.2, 129.7, 129.5, 129.0, 128.8, 128.6, 128.5, 128.1, 127.8, 127.7, 127.3, 127.2, 126.4, 126.2, 125.8, 124.1, 123.2, 119.9, 109.2, 72.1, 57.7, 54.9, 51.7, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{41}H_{31}N_2O_3^+$ ([M+H]$^+$) 599.2329, Found 599.2323; Enantiomeric excess was determined to be 0% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/35, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 7.7 min, t_{minor} = 6.5 min).

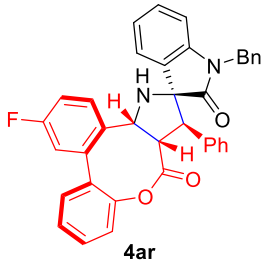


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.527	VV	0.2693	6514.49902	365.12204	49.9903
2	7.752	VB	0.3515	6517.02637	280.08643	50.0097



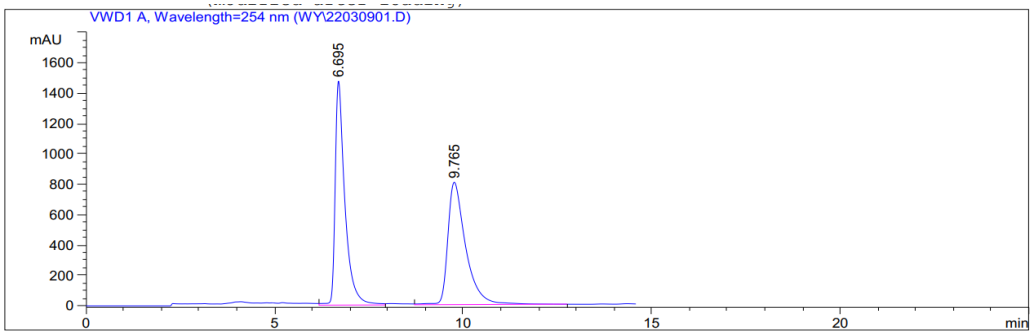
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.531	VV	0.2227	6864.87549	462.34409	49.4976
2	7.722	VB	0.3065	7004.23438	341.20056	50.5024

(4bR,6S,7R,7aS)-1'-Benzyl-2-fluoro-7-phenyl-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4ar)

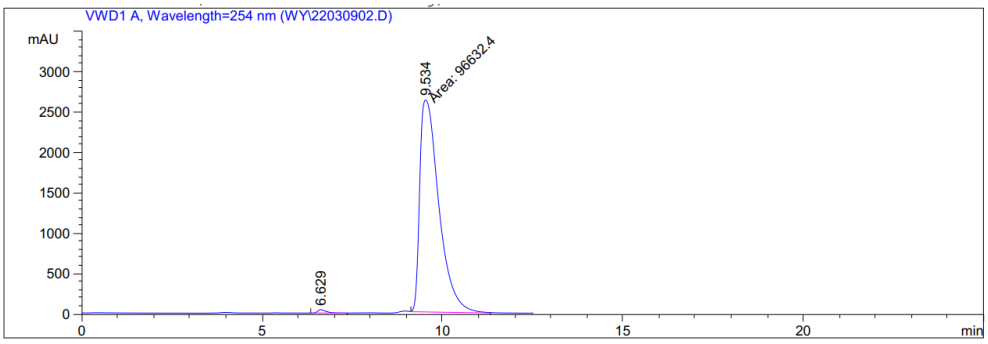


4ar

Prepared according to the procedure within 3 days as white solid (104.25 mg, 92% yield, dr > 20:1); mp 175.6 – 176.4 °C; $[\alpha]_D^{18}$= 42.87 (*c* 0.49, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.4, 5.8 Hz, 1H), 7.83 – 7.74 (m, 1H), 7.58 – 7.52 (m, 1H), 7.48 – 7.38 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.05 (m, 9H), 7.03 – 6.95 (m, 3H), 6.47 (d, *J* = 7.4 Hz, 2H), 6.39 (d, *J* = 7.3 Hz, 1H), 5.20 (d, *J* = 11.1 Hz, 1H), 4.90 (d, *J* = 16.0 Hz, 1H), 4.51 (t, *J* = 11.3 Hz, 1H), 4.38 (d, *J* = 11.4 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H), 2.25 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 170.7, 162.3 (d, *J* = 248.5 Hz), 149.5, 143.1, 137.0 (d, *J* = 9.1 Hz), 136.8 (d, *J* = 3.0 Hz), 134.8, 133.9, 133.6, 130.6, 130.0, 129.6, 128.7, 128.6, 128.6, 128.0, 127.8, 127.5 (d, *J* = 9.1 Hz), 127.2, 127.2, 126.4, 124.1, 123.2, 121.4, 116.1 (d, *J* = 22.2 Hz), 115.1 (d, *J* = 21.2 Hz), 109.1, 72.0, 56.9, 54.8, 50.7, 43.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.66; HRMS (ESI) *m/z* Calcd. for $C_{37}H_{28}FN_2O_3^+$ ($[M+H]^+$) 567.2078, Found 567.2072; Enantiomeric excess was determined to be 99% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 9.5 min, t_{minor} = 6.6 min).

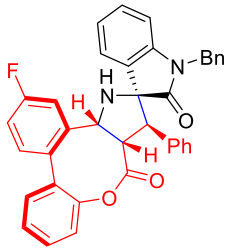


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.695	VV	0.2610	2.65370e4	1474.09424	49.8801
2	9.765	VB	0.4895	2.66646e4	805.60828	50.1199



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.629	VB	0.2599	755.15686	42.16830	0.7754
2	9.534	MM	0.6125	9.66324e4	2629.52246	99.2246

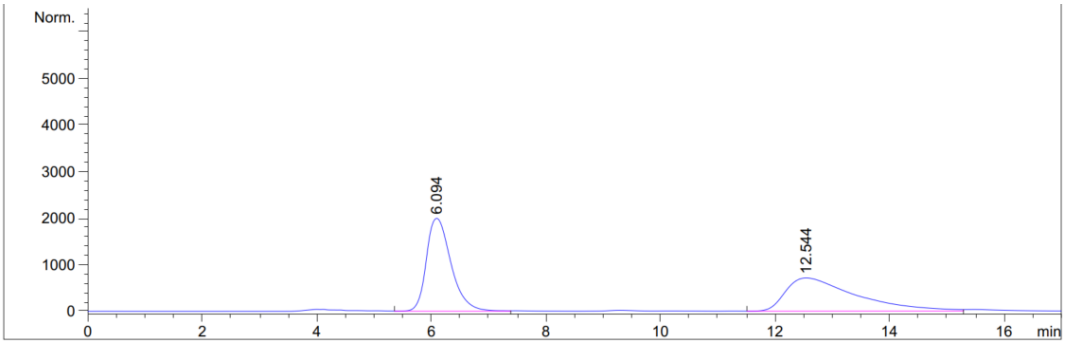
(4bR,6S,7R,7aS)-1'-Benzyl-3-fluoro-7-phenyl-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4as)



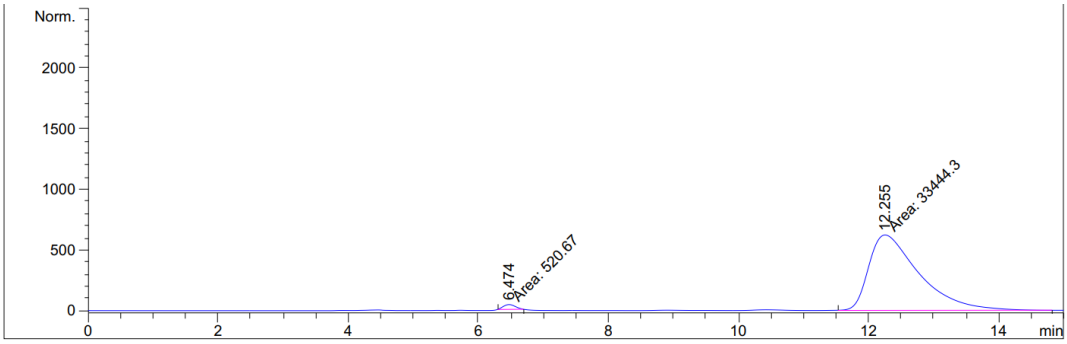
4as

Prepared according to the procedure within 4 days as white solid (56.67 mg, 50% yield, dr > 20:1); mp 200.4 – 201.4 °C; $[\alpha]_D^{18}$= 29.38 (*c* 0.20, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 6.5 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.45 – 7.35 (m, 2H), 7.25 – 7.19 (m, 4H), 7.18 – 7.03 (m, 7H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.45 (d, *J* = 7.3 Hz, 2H), 6.37 (d, *J* = 7.5 Hz, 1H), 5.19 (d, *J* = 10.4 Hz, 1H), 4.87 (d, *J* = 16.0 Hz, 1H), 4.50 (t, *J* = 11.3 Hz, 1H), 4.36 (d, *J* = 11.4 Hz, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 2.29 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 170.5, 163.5 (d, *J* = 247.4 Hz), 149.8, 143.9 (d, *J* = 8.1 Hz), 143.1, 134.8, 133.8, 133.7, 131.0 (d, *J* = 3.0 Hz), 130.7, 130.6, 130.4, 129.6, 128.6, 128.5, 128.5, 128.0, 127.8, 127.2, 127.1, 126.4, 124.2, 123.3, 121.2, 114.8 (d, *J* = 22.2 Hz), 113.1 (d, *J* = 24.2 Hz), 109.3, 72.0, 57.1, 54.8, 50.7, 43.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -

112.19; HRMS (ESI) *m/z* Calcd. for $C_{37}H_{28}FN_2O_3^+$ ($[M+H]^+$) 567.2078, Found 567.2073; Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 12.3 min, t_{minor} = 6.5 min).

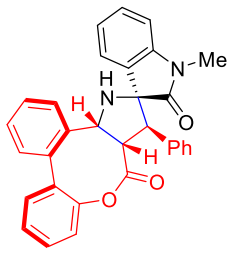


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.094	VV	0.4629	5.99906e4	1995.23303	49.5595
2	12.544	VV	1.2532	6.10570e4	714.55048	50.4405



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.474	MM	0.2164	520.66980	40.09602	1.5330
2	12.255	MM	0.8946	3.34443e4	623.06061	98.4670

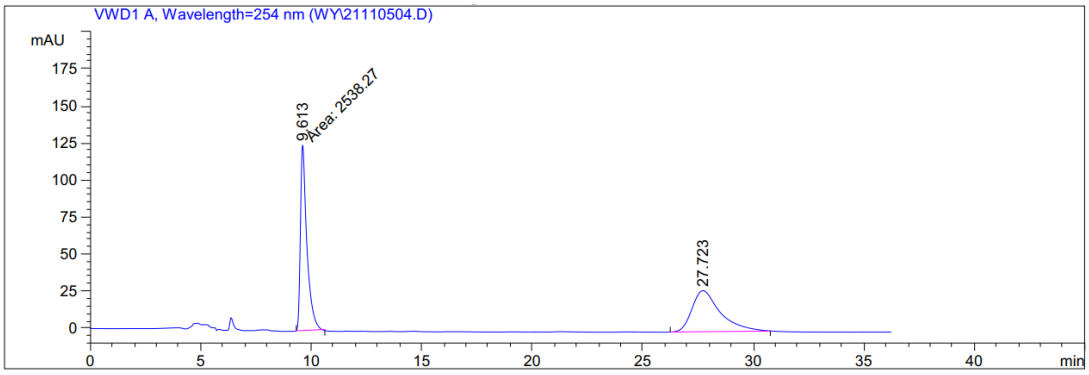
(4bR,6S,7R,7aS)-1'-Methyl-7-phenyl-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4ba)



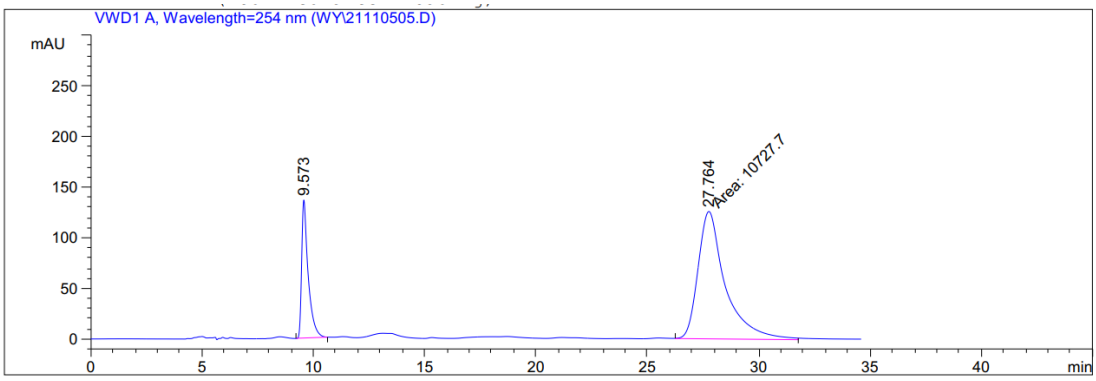
4ba

Prepared according to the procedure within 4 days as white solid (83.17 mg, 88% yield, dr > 20:1); mp 278.2 – 279.0 °C; $[\alpha]_D^{18}$= -25.58 (*c* 0.09, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.45 – 7.36 (m, 3H), 7.29 – 7.26 (m, 1H), 7.25 – 7.17 (m, 3H), 7.13 – 7.02 (m, 3H), 6.90 (d, *J* = 7.3 Hz, 2H), 6.54 (d, *J* = 7.6 Hz, 1H),

5.21 (d, J = 11.2 Hz, 1H), 4.38 (t, J = 11.3 Hz, 1H), 4.25 (d, J = 11.4 Hz, 1H), 2.75 (s, 3H), 2.19 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 170.8, 149.7, 143.7, 141.1, 135.3, 134.7, 134.0, 130.1, 130.1, 129.4, 128.8, 128.8, 128.8, 128.0, 127.9, 127.8, 127.6, 126.9, 125.4, 123.8, 123.1, 121.1, 108.0, 72.2, 57.6, 55.5, 51.0, 25.4; HRMS (ESI) *m/z* Calcd. for $C_{31}H_{25}N_2O_3^+$ ($[M+H]^+$) 473.1860, Found 473.1858; Enantiomeric excess was determined to be 59% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 27.7 min, t_{minor} = 9.5 min).

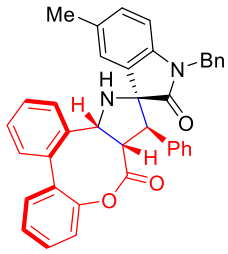


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.613	MM	0.3384	2538.26514	125.02699	50.6194
2	27.723	BB	1.2559	2476.14844	27.72734	49.3806



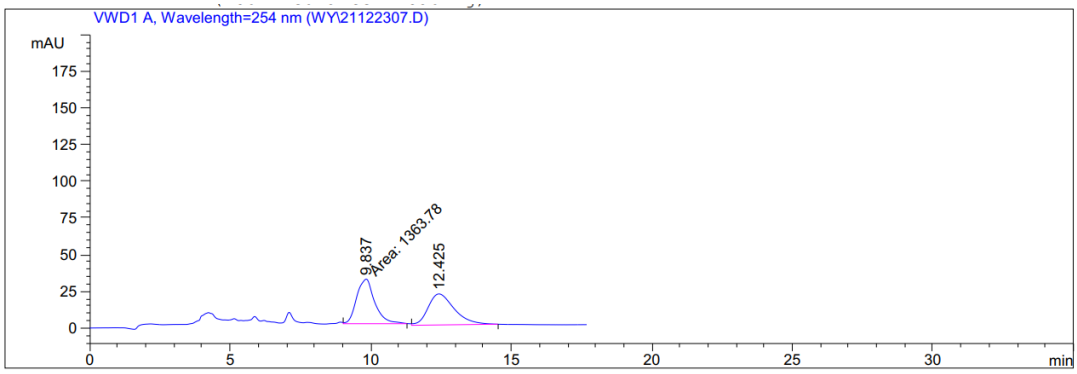
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.573	VB	0.2913	2777.50171	136.50038	20.5662
2	27.764	MM	1.4196	1.07277e4	125.94410	79.4338

(4bR,6S,7R,7aS)-1'-Benzyl-5'-methyl-7-phenyl-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4ca)

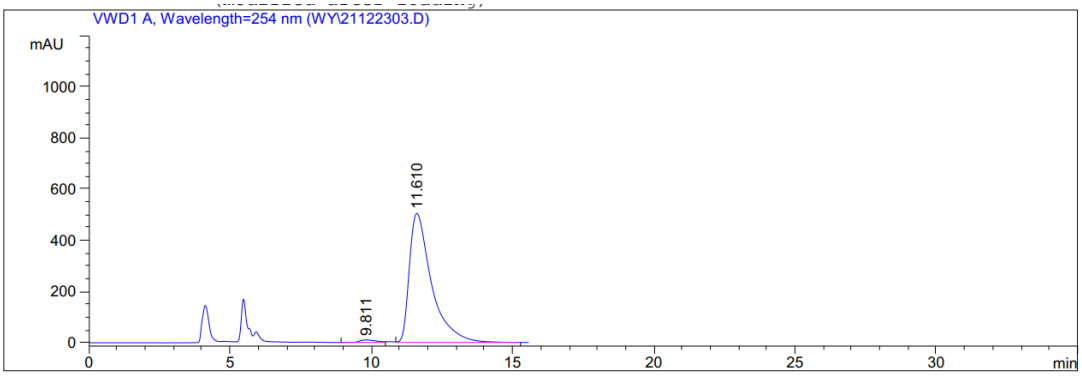


4ca

Prepared according to the procedure within 7 days as white solid (78.77 mg, 70% yield, dr > 20:1); mp 187.8 – 188.5 °C; $[\alpha]_D^{18}$= 52.47 (*c* 0.32, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 1H), 7.60 (s, 1H), 7.54 – 7.47 (m, 2H), 7.44 – 7.35 (m, 3H), 7.25 – 7.18 (m, 3H), 7.14 – 7.02 (m, 5H), 7.00 – 6.91 (m, 3H), 6.43 (d, *J* = 7.3 Hz, 2H), 6.24 (d, *J* = 7.9 Hz, 1H), 5.23 (d, *J* = 11.2 Hz, 1H), 4.86 (d, *J* = 16.0 Hz, 1H), 4.49 (t, *J* = 11.3 Hz, 1H), 4.36 (d, *J* = 11.3 Hz, 1H), 4.16 (d, *J* = 16.0 Hz, 1H), 2.43 (s, 3H), 2.22 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 171.0, 149.7, 141.0, 140.7, 135.3, 135.0, 134.8, 134.2, 132.9, 130.2, 130.1, 129.8, 128.9, 128.8, 128.8, 128.6, 128.5, 128.1, 128.0, 127.7, 127.1, 127.0, 126.4, 125.5, 124.8, 121.1, 109.0, 72.1, 57.5, 54.9, 50.9, 43.3, 21.2; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{31}N_2O_3^+$ ($[M+H]^+$) 563.2329, Found 563.2323; Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 11.6 min, t_{minor} = 9.8 min).

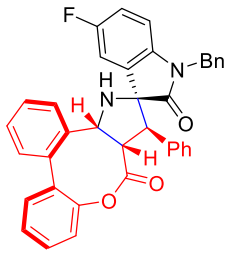


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.837	MM	0.7477	1363.77551	30.39775	49.4184
2	12.425	BB	0.9580	1395.87390	21.26602	50.5816



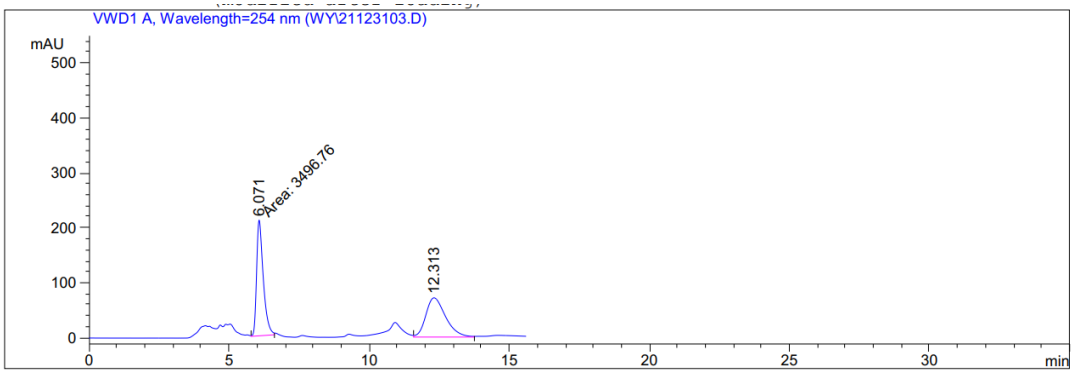
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.811	VV	0.6477	421.23514	9.93094	1.5083
2	11.610	VB	0.8112	2.75066e4	504.15973	98.4917

(4bR,6S,7R,7aS)-1'-Benzyl-5'-fluoro-7-phenyl-4b,5,7,7a-tetrahydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (4da)

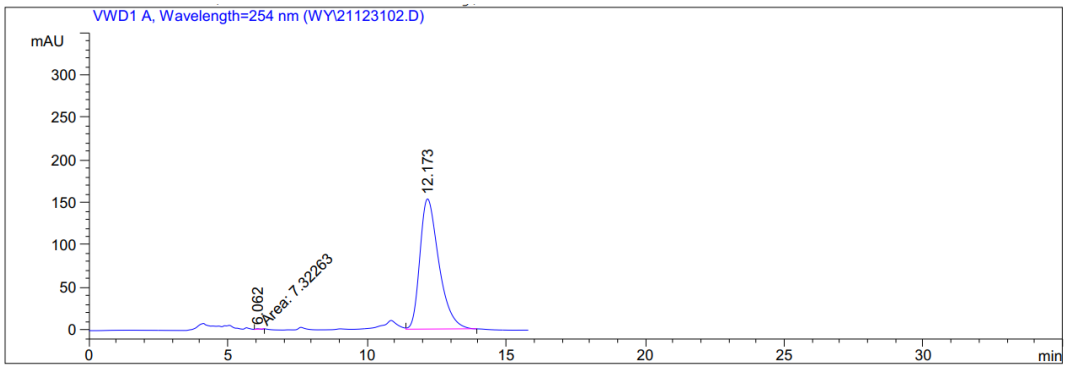


4da

Prepared according to the procedure within 7 days as white solid (58.93 mg, 52% yield, dr > 20:1); mp 196.4 – 197.5 °C; $[\alpha]_D^{18}$= 30.06 (*c* 0.17, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.49 (m, 3H), 7.44 – 7.31 (m, 3H), 7.26 – 7.20 (m, 3H), 7.16 – 7.04 (m, 5H), 6.98 (d, *J* = 7.5 Hz, 2H), 6.87 – 6.80 (m, 1H), 6.43 (d, *J* = 7.4 Hz, 2H), 6.26 (dd, *J* = 8.4, 3.9 Hz, 1H), 5.22 (d, *J* = 11.2 Hz, 1H), 4.87 (d, *J* = 16.0 Hz, 1H), 4.48 (t, *J* = 11.3 Hz, 1H), 4.33 (d, *J* = 11.4 Hz, 1H), 4.17 (d, *J* = 16.0 Hz, 1H), 2.27 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 170.6, 159.7 (d, *J* = 243.4 Hz), 149.7, 140.7, 138.9, 135.3, 134.7, 134.5, 133.7, 130.8, 130.7, 130.2, 130.1, 128.9, 128.9, 128.7, 128.6, 128.1, 127.9, 127.3, 127.0, 126.4, 125.4, 121.2, 115.9 (d, *J* = 24.2 Hz), 112.1 (d, *J* = 25.3 Hz), 110.0 (d, *J* = 7.1 Hz), 72.3, 57.5, 55.2, 50.8, 43.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -119.20; HRMS (ESI) *m/z* Calcd. for $C_{37}H_{28}FN_2O_3^+$ ($[M+H]^+$) 567.2078, Found 567.2074; Enantiomeric excess was determined to be >99% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 12.1 min, t_{minor} = 6.0 min).

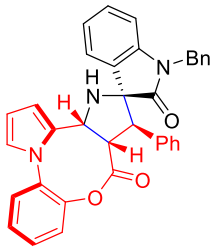


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.071	MM	0.2765	3496.76050	210.76863	49.5076
2	12.313	VB	0.7572	3566.31616	71.78394	50.4924



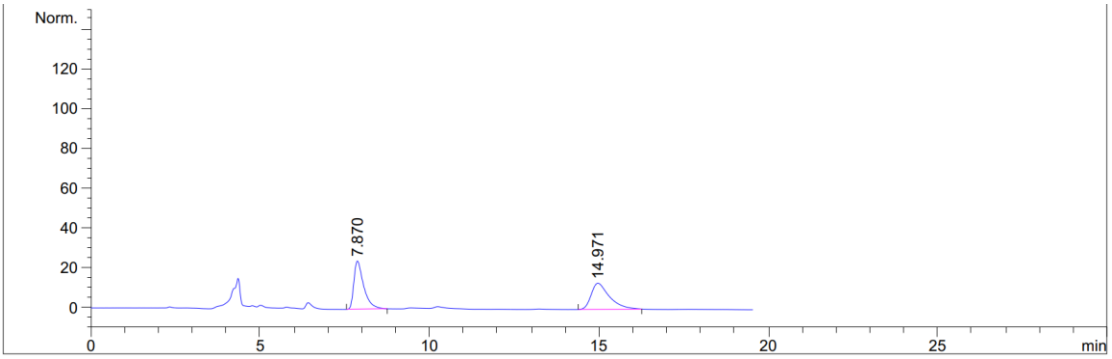
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.062	MM	0.1633	7.32263	7.47340e-1	0.1003
2	12.173	VB	0.7250	7293.05566	153.41624	99.8997

(3bR,5S,6R,6aS)-1'-Benzyl-6-phenyl-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6aa)

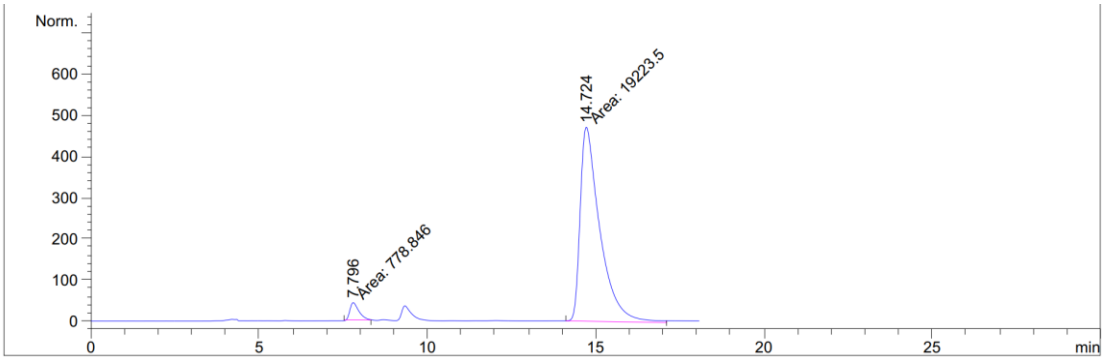


6aa

Prepared according to the procedure within 2.5 days as white solid (90.3 mg, 84% yield, dr > 20:1). mp 173.2 – 174.0 °C; $[\alpha]_D^{18}$ = 67.67 (*c* 0.23, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 1H), 7.55 – 7.48 (m, 2H), 7.46 – 7.39 (m, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.03 (m, 8H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.79 – 6.75 (m, 1H), 6.45 (d, *J* = 7.4 Hz, 3H), 6.36 (d, *J* = 7.0 Hz, 1H), 6.34 – 6.29 (m, 1H), 5.35 (d, *J* = 10.6 Hz, 1H), 4.88 (d, *J* = 16.0 Hz, 1H), 4.47 (d, *J* = 10.4 Hz, 1H), 4.28 (t, *J* = 10.5 Hz, 1H), 4.19 (d, *J* = 16.0 Hz, 1H), 2.53 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 169.8, 147.5, 143.1, 134.9, 134.6, 134.2, 133.0, 130.3, 129.6, 128.6, 128.5, 128.2, 128.2, 128.1, 127.7, 127.4, 127.2, 126.4, 123.9, 123.2, 122.5, 122.0, 109.8, 109.3, 107.0, 72.1, 55.8, 54.6, 50.0, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{35}H_{28}N_3O_3^+$ ($[M+H]^+$) 538.2125, Found 538.2125; Enantiomeric excess was determined to be 93% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 14.7 min, t_{minor} = 7.8 min).

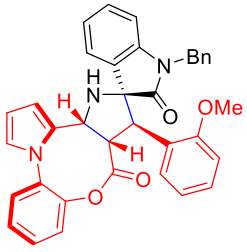


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.870	PB	0.3002	488.51675	24.14030	49.8185
2	14.971	BB	0.5544	492.07629	13.10981	50.1815



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.796	MM	0.3083	778.84552	42.10896	3.8938
2	14.724	MM	0.6801	1.92235e4	471.09012	96.1062

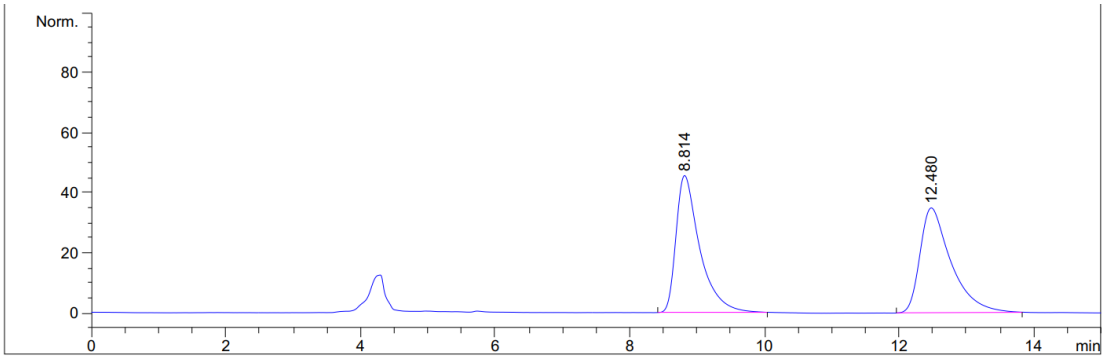
(3bR,5S,6R,6aS)-1'-Benzyl-6-(2-methoxyphenyl)-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6ab)



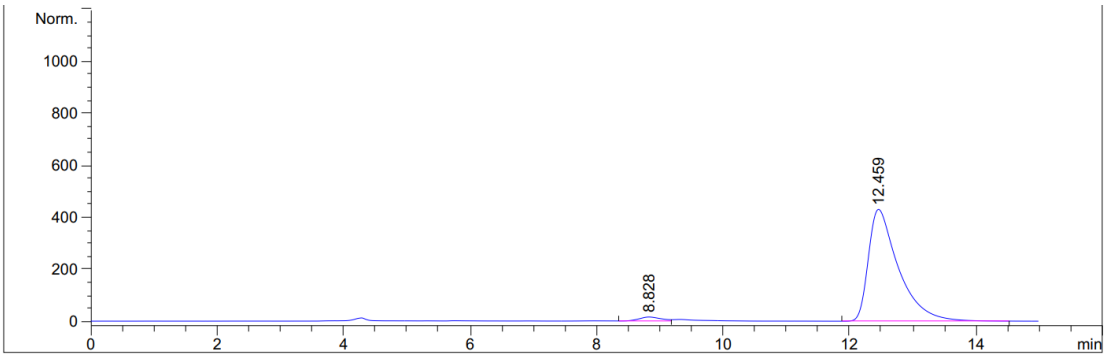
6ab

Prepared according to the procedure within 3 days as white solid (96.5 mg, 85% yield, dr > 20:1). mp 173.9 – 174.8 °C; $[\alpha]_D^{18}$= 50.59 (*c* 0.34, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 6.9 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.45 – 7.38 (m, 1H), 7.29 – 7.21 (m, 2H), 7.19 – 7.03 (m, 6H), 6.82 – 6.74 (m, 2H), 6.62 (d, *J* = 8.1 Hz, 1H), 6.50 (d, *J* = 7.3 Hz, 2H), 6.45 (d, *J* = 1.3 Hz, 1H), 6.35 – 6.28 (m, 2H), 5.35 (d, *J* = 10.5 Hz, 1H), 5.23 (d, *J* = 10.3 Hz, 1H), 4.93 (d, *J* = 16.0 Hz, 1H), 4.27 – 4.13 (m, 2H), 3.28 (s, 3H), 2.43 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 170.0, 158.3, 147.6, 142.8, 135.1, 134.7, 133.0, 130.2, 129.0, 128.6, 128.5, 128.4, 128.1, 127.8, 127.3, 127.1, 126.5, 125.1,

123.3, 122.5, 122.4, 121.9, 120.6, 111.0, 109.7, 108.8, 106.9, 72.0, 55.1, 55.0, 50.9, 47.1, 43.2; HRMS (ESI) *m/z* Calcd. for $C_{36}H_{30}N_3O_4^+$ ($[M+H]^+$) 568.2231, Found 568.2224; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 12.4 min, t_{minor} = 8.8 min).

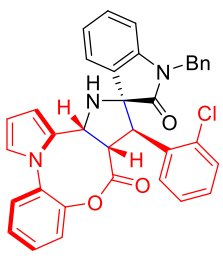


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.814	BB	0.3617	1116.49170	45.54860	49.9016
2	12.480	BB	0.4708	1120.89551	34.89931	50.0984



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.828	VV	0.3646	385.85458	15.58014	2.6401
2	12.459	PB	0.4819	1.42291e4	430.24365	97.3599

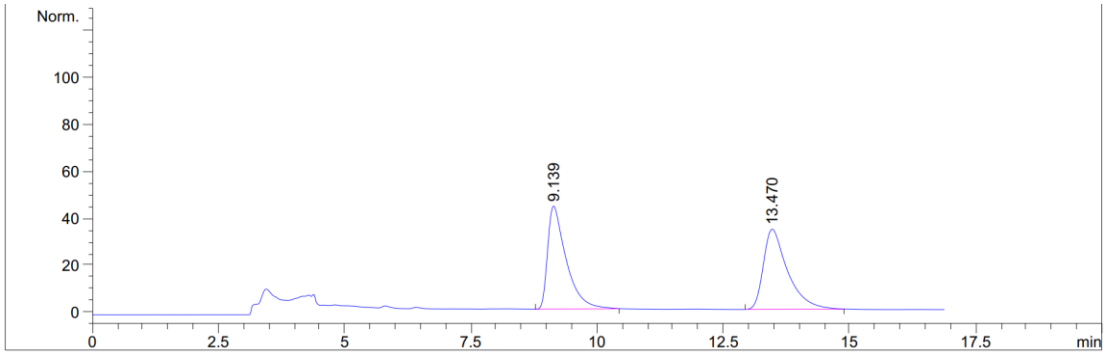
(3bR,5S,6R,6aS)-1'-Benzyl-6-(2-chlorophenyl)-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6ac)



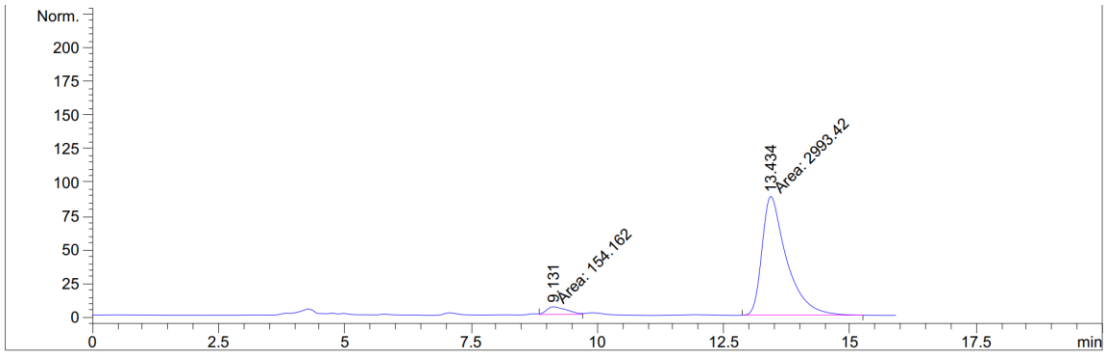
6ac

Prepared according to the procedure within 4 days as white solid (91.5 mg, 80% yield, dr > 20:1). mp 181.8 – 182.4 °C; $[\alpha]_D^{18}$ = 23.76 (*c* 0.36, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 1H), 7.52 – 7.46 (m, 2H), 7.45 – 7.38 (m, 2H), 7.24 – 7.22 (m, 1H), 7.18 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.16 – 7.02 (m, 7H), 6.79 –

6.74 (m, 1H), 6.62 (d, J = 7.5 Hz, 2H), 6.49 – 6.44 (m, 1H), 6.39 (dd, J = 6.1, 2.4 Hz, 1H), 6.34 – 6.30 (m, 1H), 5.38 (d, J = 10.6 Hz, 1H), 5.31 (d, J = 10.2 Hz, 1H), 4.92 (d, J = 15.9 Hz, 1H), 4.28 (d, J = 15.9 Hz, 1H), 4.11 (t, J = 10.4 Hz, 1H), 2.45 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 169.6, 147.4, 142.8, 136.0, 135.0, 134.3, 133.0, 132.6, 130.3, 130.0, 129.7, 129.0, 128.6, 128.6, 128.1, 127.4, 127.3, 127.0, 126.9, 126.6, 125.7, 122.9, 122.4, 122.1, 109.8, 109.0, 107.1, 72.2, 55.0, 52.7, 50.1, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{35}H_{27}ClN_3O_3^+$ ([M+H]$^+$) 572.1735, Found 572.1739; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 13.4 min, t_{minor} = 9.1 min).

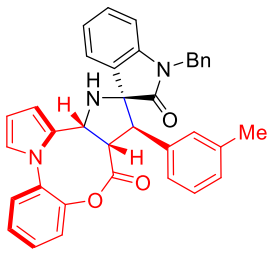


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.139	PB	0.3704	1126.14136	43.93664	49.6355
2	13.470	BB	0.4900	1142.68286	34.22232	50.3645



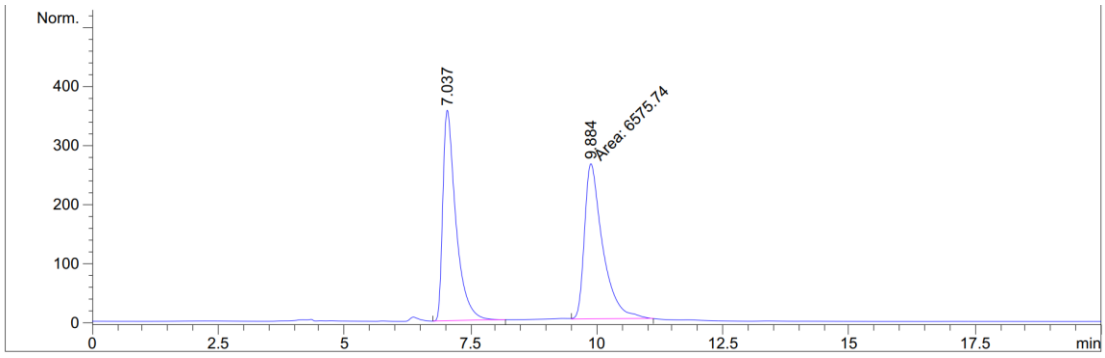
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.131	MM	0.4553	154.16229	5.64379	4.8978
2	13.434	MM	0.5664	2993.42261	88.07903	95.1022

(3bR,5S,6R,6aS)-1'-Benzyl-6-(m-tolyl)-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6ad)

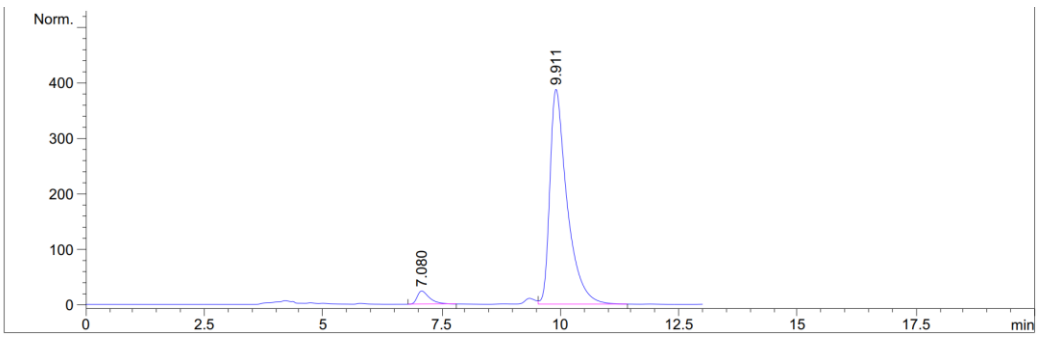


6ad

Prepared according to the procedure within 3 days as white solid (93.8 mg, 85% yield, dr > 20:1). mp 169.5 – 170.0 °C; $[\alpha]_D^{18}$= 84.79 (*c* 0.26, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.45 – 7.40 (m, 1H), 7.30 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.18 – 7.11 (m, 3H), 7.08 – 7.03 (m, 2H), 7.03 – 6.97 (m, 2H), 6.79 – 6.72 (m, 3H), 6.47 – 6.43 (m, 3H), 6.36 (d, *J* = 7.3 Hz, 1H), 6.32 – 6.29 (m, 1H), 5.33 (d, *J* = 10.7 Hz, 1H), 4.93 (d, *J* = 16.0 Hz, 1H), 4.43 (d, *J* = 10.4 Hz, 1H), 4.26 (t, *J* = 10.5 Hz, 1H), 4.18 (d, *J* = 16.0 Hz, 1H), 2.43 (s, 1H), 2.09 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 169.9, 147.5, 143.1, 138.0, 135.0, 134.7, 134.1, 133.0, 130.3, 129.6, 128.9, 128.6, 128.5, 128.4, 128.3, 128.0, 127.4, 127.2, 126.3, 125.2, 123.9, 123.2, 122.5, 121.9, 109.7, 109.2, 106.9, 72.1, 55.7, 54.6, 49.9, 43.3, 21.4; HRMS (ESI) *m/z* Calcd. for $C_{36}H_{30}N_3O_3^+$ ($[M+H]^+$) 552.2282, Found 552.2284; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 9.9 min, t_{minor} = 7.1 min).

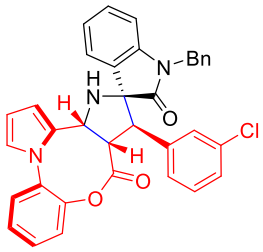


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.037	VB	0.2662	6434.84619	356.01816	49.4585
2	9.884	MM	0.4175	6575.73926	262.52737	50.5415



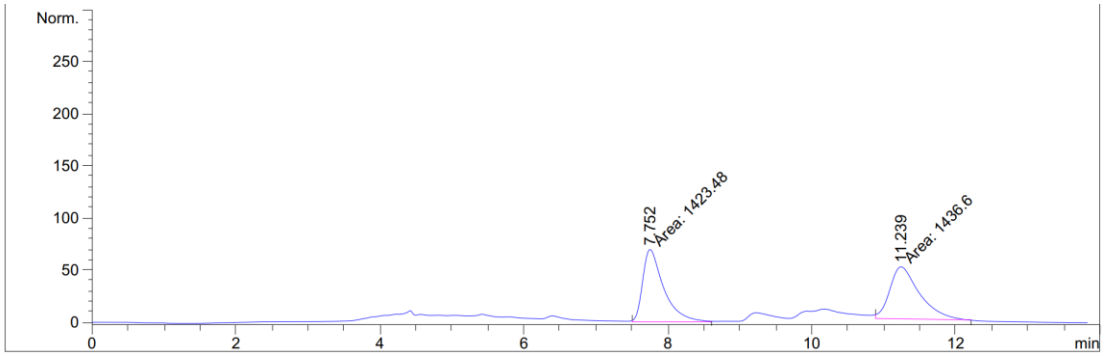
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.080	PB	0.2682	427.45135	23.74780	4.1983
2	9.911	VB	0.3687	9753.98047	386.48398	95.8017

(3bR,5S,6R,6aS)-1'-Benzyl-6-(3-chlorophenyl)-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6ae)

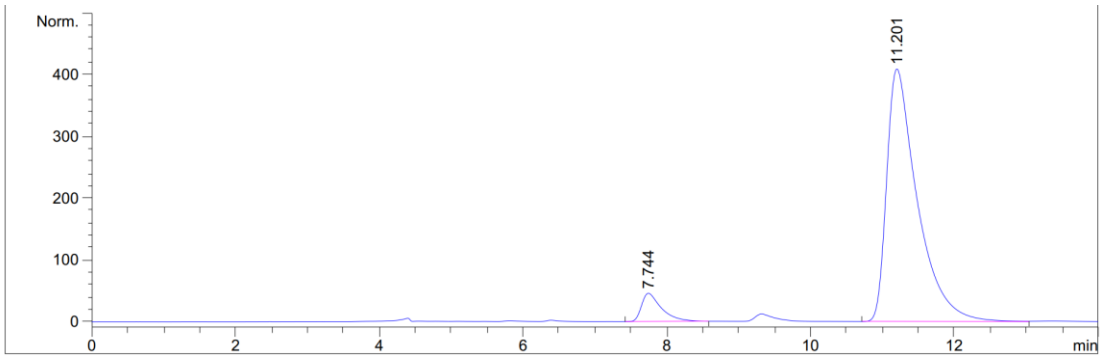


6ae

Prepared according to the procedure within 4 days as white solid (91.5 mg, 80% yield, dr > 20:1). mp 178.1 – 179.0 °C; $[\alpha]_D^{18}$= 78.16 (*c* 0.59, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 1H), 7.58 – 7.49 (m, 2H), 7.48 – 7.42 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.09 (m, 6H), 7.03 – 6.98 (m, 2H), 6.86 (d, *J* = 7.7 Hz, 1H), 6.81 – 6.76 (m, 1H), 6.61 (d, *J* = 7.4 Hz, 2H), 6.48 – 6.42 (m, 2H), 6.36 – 6.30 (m, 1H), 5.32 (d, *J* = 10.6 Hz, 1H), 4.91 (d, *J* = 15.9 Hz, 1H), 4.42 (d, *J* = 10.5 Hz, 1H), 4.30 – 4.20 (m, 2H), 2.48 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.1, 169.6, 147.3, 143.1, 136.4, 134.9, 134.5, 134.3, 132.9, 130.4, 129.9, 129.7, 128.7, 128.2, 128.0, 127.7, 127.5, 127.4, 126.6, 126.5, 123.9, 123.4, 122.5, 122.0, 109.8, 109.4, 107.1, 71.8, 55.2, 54.4, 50.0, 43.4; HRMS (ESI) *m/z* Calcd. for $C_{35}H_{27}ClN_3O_3^+$ ($[M+H]^+$) 572.1735, Found 572.1736; Enantiomeric excess was determined to be 87% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 11.2 min, t_{minor} = 7.7 min).

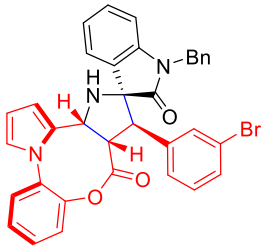


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.752	MM	0.3410	1423.47876	69.57114	49.7706
2	11.239	MM	0.4790	1436.60303	49.98846	50.2294



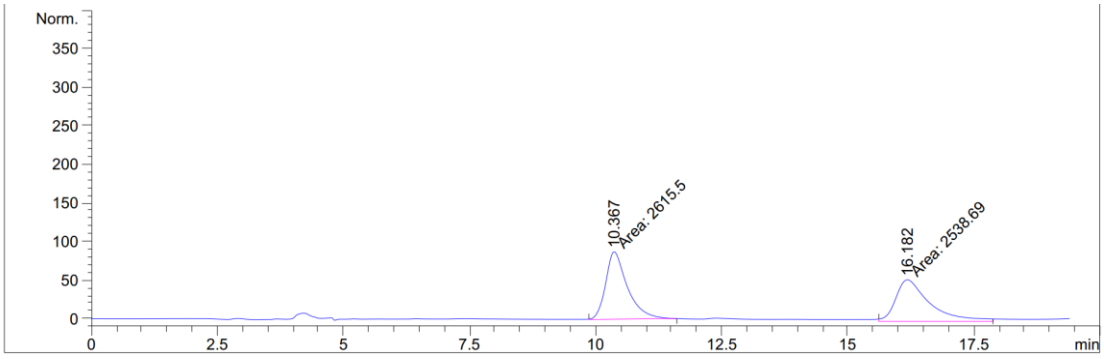
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.744	PB	0.2811	879.54340	45.73726	6.7648
2	11.201	PB	0.4304	1.21223e4	408.82529	93.2352

(3bR,5S,6R,6aS)-1'-Benzyl-6-(3-bromophenyl)-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6af)

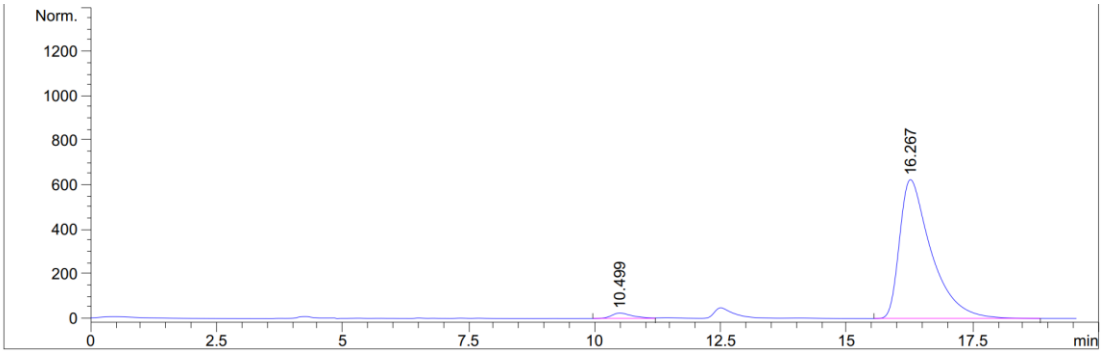


6af

Prepared according to the procedure within 3 days as white solid (106.0 mg, 86% yield, dr > 20:1). mp 177.7 – 178.5 °C; $[\alpha]_D^{18}$= 77.03 (*c* 0.21, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 1H), 7.59 – 7.40 (m, 3H), 7.38 – 7.28 (m, 2H), 7.23 – 7.07 (m, 6H), 7.00 – 6.85 (m, 2H), 6.82 – 6.75 (m, 1H), 6.65 – 6.49 (m, 2H), 6.48 – 6.28 (m, 3H), 5.32 (d, *J* = 10.5 Hz, 1H), 4.89 (d, *J* = 15.8 Hz, 1H), 4.40 (d, *J* = 10.2 Hz, 1H), 4.32 – 4.14 (m, 2H), 2.11 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.1, 169.6, 147.3, 143.1, 136.7, 134.9, 134.4, 132.9, 131.1, 131.0, 130.4, 130.0, 129.9, 128.7, 128.0, 127.5, 127.4, 127.0, 126.5, 123.9, 123.4, 122.6, 122.5, 122.0, 109.8, 109.4, 107.1, 71.9, 55.2, 54.4, 50.0, 43.4; HRMS (ESI) *m/z* Calcd. for $C_{35}H_{27}BrN_3O_3^+$ ([M+H]$^+$) 616.1230, Found 616.1232; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 80/20, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 16.2 min, t_{minor} = 10.5 min).

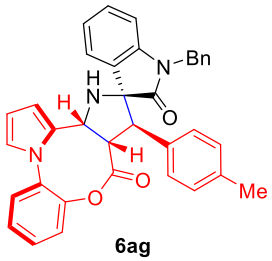


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.367	MM	0.4990	2615.49902	87.35246	50.7451
2	16.182	MM	0.7842	2538.69385	53.95298	49.2549



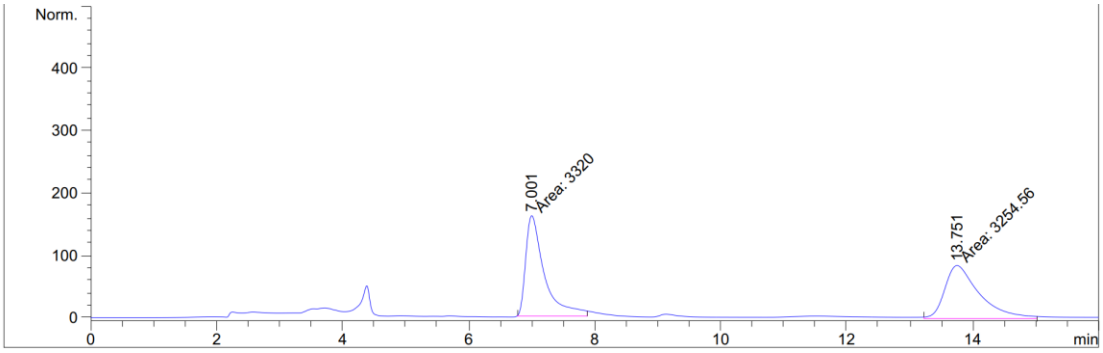
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.499	PV	0.4297	739.98486	24.90297	2.6361
2	16.267	PB	0.6419	2.73307e4	624.12042	97.3639

(3bR,5S,6R,6aS)-1'-Benzyl-6-(p-tolyl)-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6ag)

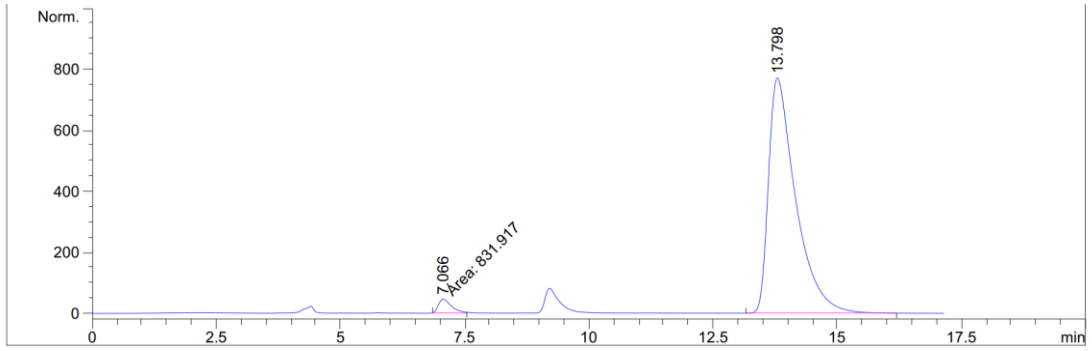


6ag

Prepared according to the procedure within 3 days as white solid (104.8 mg, 95% yield, dr > 20:1). mp 181.3 – 184.0 °C; $[\alpha]_D^{18}$= 90.06 (*c* 0.32, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 1H), 7.53 – 7.47 (m, 2H), 7.45 – 7.38 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.18 – 7.10 (m, 3H), 7.08 – 7.01 (m, 2H), 6.93 – 6.82 (m, 4H), 6.78 – 6.74 (m, 1H), 6.49 (d, *J* = 7.5 Hz, 2H), 6.43 (d, *J* = 1.2 Hz, 1H), 6.36 (d, *J* = 6.8 Hz, 1H), 6.33 – 6.28 (m, 1H), 5.33 (d, *J* = 10.6 Hz, 1H), 4.92 (d, *J* = 16.0 Hz, 1H), 4.43 (d, *J* = 10.4 Hz, 1H), 4.30 – 4.10 (m, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 169.8, 147.5, 143.1, 137.3, 135.0, 134.7, 133.0, 131.2, 130.3, 129.5, 129.2, 128.5, 128.3, 128.1, 128.0, 127.4, 127.2, 126.6, 123.9, 123.2, 122.5, 121.9, 109.7, 109.3, 106.9, 72.1, 55.5, 54.6, 50.2, 43.3, 21.1; HRMS (ESI) *m/z* Calcd. for $C_{36}H_{30}N_3O_3^+$ ($[M+H]^+$) 552.2282, Found 552.2270; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 13.8 min, t_{minor} = 7.0 min).

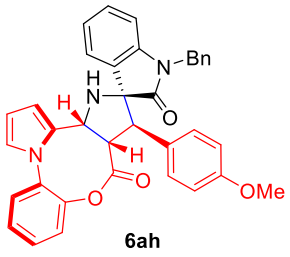


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.001	MM	0.3439	3319.99731	160.91309	50.4977
2	13.751	MM	0.6387	3254.56030	84.93006	49.5023



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.066	MM	0.3030	831.91742	45.75506	2.7683
2	13.798	BB	0.5551	2.92199e4	769.59216	97.2317

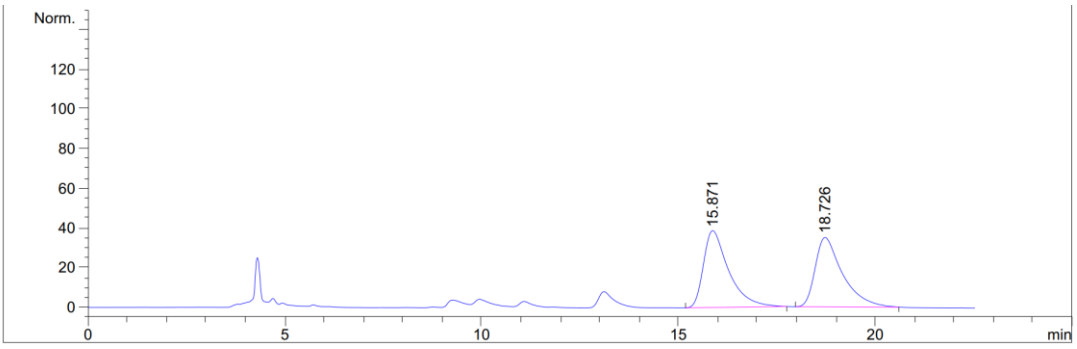
(3bR,5S,6R,6aS)-1'-Benzyl-6-(4-methoxyphenyl)-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6ah)



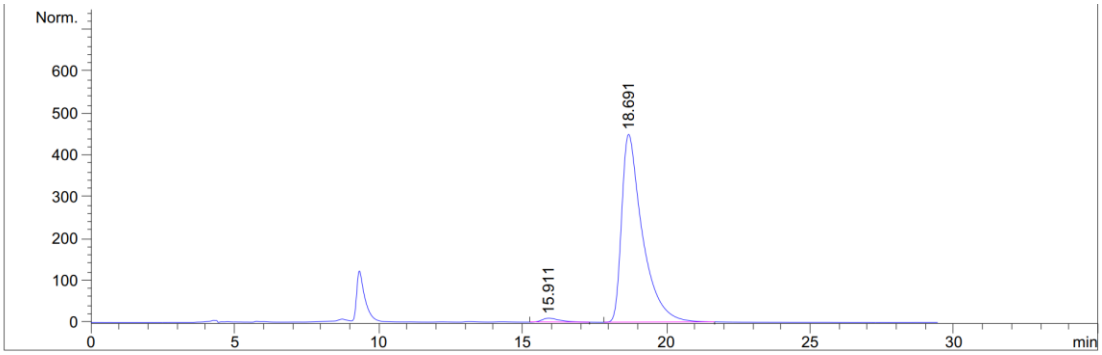
6ah

Prepared according to the procedure within 3 days as white solid (90.8 mg, 80% yield, dr > 20:1). mp 182.4 – 183.1 °C; $[\alpha]_D^{18}$= 102.81 (*c* 0.39, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.46 – 7.41 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.12 (m, 3H), 7.10 – 7.04 (m, 2H), 6.89 (d, *J* = 7.5 Hz, 2H), 6.80 – 6.75 (m, 1H), 6.64 (d, *J* = 8.4 Hz, 2H), 6.48 (d, *J* = 7.6 Hz, 2H), 6.45 (d, *J* = 1.5 Hz, 1H), 6.39 (d, *J* = 7.3 Hz, 1H), 6.34 – 6.29 (m, 1H), 5.33 (d, *J* = 10.7 Hz, 1H), 4.94 (d, *J* = 16.0 Hz, 1H), 4.43 (d, *J* = 10.4 Hz, 1H), 4.27 – 4.15 (m, 2H), 3.72 (s, 3H), 2.43 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.5, 169.9, 159.2, 147.5, 143.1, 134.9, 134.7, 133.0,

130.3, 129.6, 129.3, 128.5, 128.3, 128.1, 127.4, 127.3, 126.5, 126.2, 123.9, 123.2, 122.4, 121.9, 113.9, 109.7, 109.3, 106.9, 72.1, 55.1, 55.1, 54.5, 50.2, 43.2; HRMS (ESI) *m/z* Calcd. for $C_{36}H_{30}N_3O_4^+$ ([M+H]$^+$) 568.2231, Found 568.2232; Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 18.7 min, t_{minor} = 15.9 min).

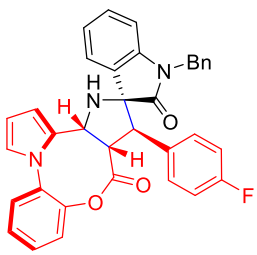


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.871	BB	0.6570	1731.45947	38.72827	50.6131
2	18.726	PB	0.7041	1689.51038	34.92804	49.3869



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.911	BB	0.6375	417.08780	9.52604	1.8212
2	18.691	PB	0.7282	2.24844e4	449.16461	98.1788

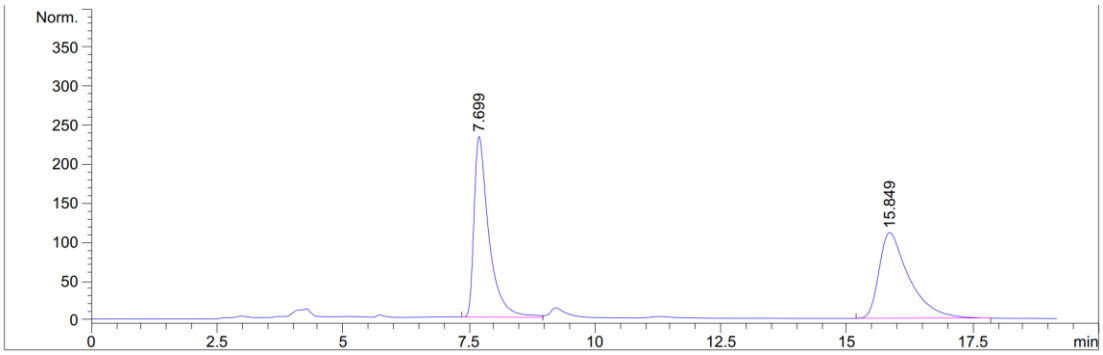
(3bR,5S,6R,6aS)-1'-Benzyl-6-(4-fluorophenyl)-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6ai)



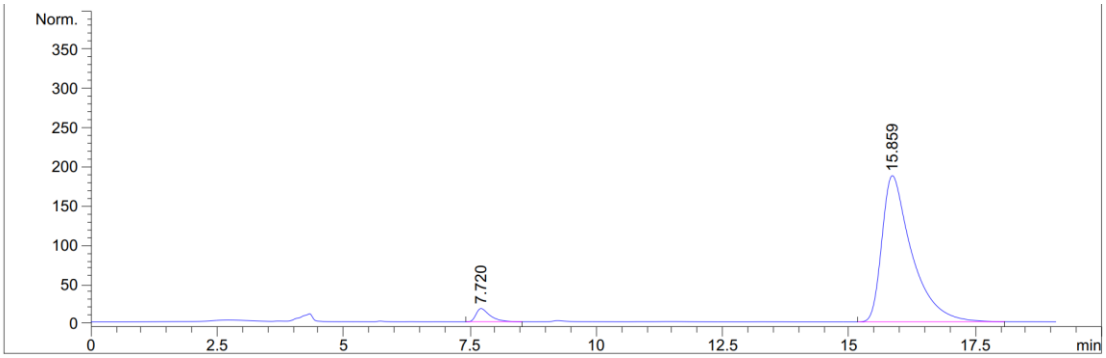
6ai

Prepared according to the procedure within 4 days as white solid (91.1 mg, 82% yield, dr > 20:1). mp 179.1 – 180.5 °C; $[\alpha]_D^{18}$= 60.75 (*c* 0.56, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 1H), 7.57 – 7.49 (m, 2H), 7.48 – 7.41 (m, 1H),

7.31 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.08 (m, 5H), 6.99 – 6.89 (m, 2H), 6.84 – 6.73 (m, 3H), 6.54 (d, *J* = 7.2 Hz, 2H), 6.50 – 6.41 (m, 2H), 6.36 – 6.29 (m, 1H), 5.33 (d, *J* = 10.6 Hz, 1H), 4.89 (d, *J* = 15.9 Hz, 1H), 4.44 (d, *J* = 10.5 Hz, 1H), 4.30 – 4.08 (m, 2H), 2.37 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 169.7, 162.5 (d, *J* = 247.5 Hz), 147.4, 143.1, 134.9, 134.6, 133.0, 130.3, 130.0 (d, *J* = 4.0 Hz), 129.9 (d, *J* = 8.1 Hz), 129.7, 128.6, 128.1, 128.0, 127.5, 127.4, 126.5, 123.9, 123.3, 122.4, 122.0, 115.4 (d, *J* = 21.2 Hz), 109.8, 109.3, 107.0, 72.0, 55.0, 54.5, 50.2, 43.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.50; HRMS (ESI) *m/z* Calcd. for $C_{35}H_{27}FN_3O_3^+$ ($[M+H]^+$) 556.2031, Found 556.2030; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 15.8 min, t_{minor} = 7.7 min).

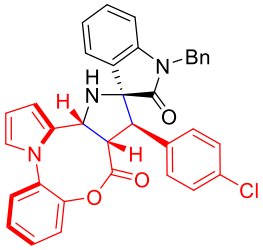


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.699	BV	0.2993	4763.06006	231.94888	51.0540
2	15.849	BB	0.5998	4566.39258	110.23215	48.9460



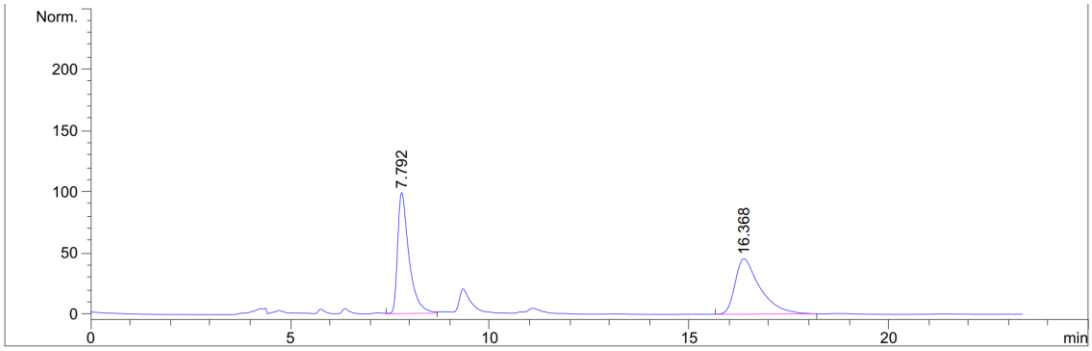
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.720	BB	0.2872	329.41296	17.00260	4.1184
2	15.859	BB	0.5966	7669.18359	186.91556	95.8816

(3bR,5S,6R,6aS)-1'-Benzyl-6-(4-chlorophenyl)-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6aj)

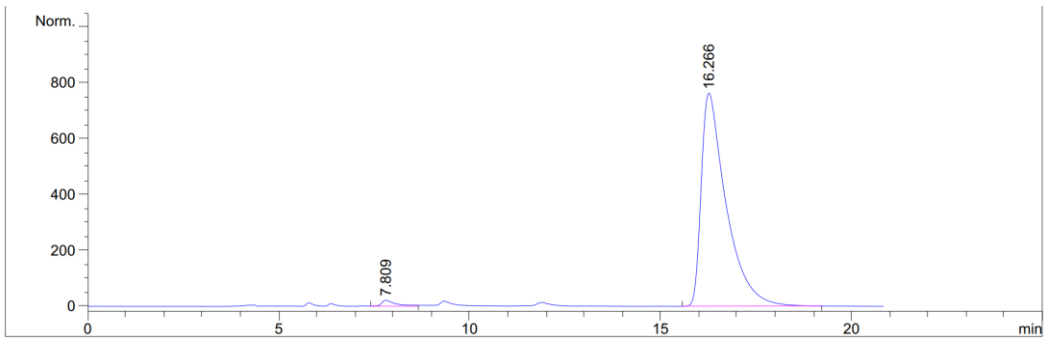


6aj

Prepared according to the procedure within 3 days as white solid (85.8 mg, 75% yield, dr > 20:1). mp 183.8 – 184.3 °C; $[\alpha]_D^{18}$= 106.31 (*c* 0.71, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 1H), 7.57 – 7.49 (m, 2H), 7.47 – 7.42 (m, 1H), 7.33 – 7.29 (m, 1H), 7.22 – 7.13 (m, 5H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.80 – 6.76 (m, 1H), 6.52 (d, *J* = 7.0 Hz, 2H), 6.47 – 6.41 (m, 2H), 6.35 – 6.30 (m, 1H), 5.33 (d, *J* = 10.6 Hz, 1H), 4.93 (d, *J* = 15.9 Hz, 1H), 4.43 (d, *J* = 10.4 Hz, 1H), 4.33 – 4.10 (m, 2H), 2.48 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.1, 169.6, 147.4, 143.1, 134.8, 134.5, 133.8, 132.9, 132.8, 130.4, 129.8, 129.6, 128.7, 128.7, 128.1, 127.9, 127.5, 127.5, 126.4, 123.9, 123.4, 122.4, 122.0, 109.8, 109.4, 107.0, 71.9, 55.1, 54.5, 50.1, 43.4; HRMS (ESI) *m/z* Calcd. for $C_{35}H_{27}ClN_3O_3^+$ ($[M+H]^+$) 572.1735, Found 572.1741; Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 16.3 min, t_{minor} = 7.8 min).

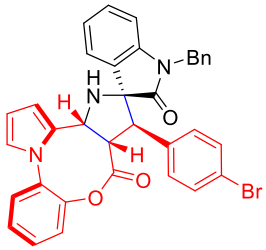


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.792	VV	0.2907	1957.60144	98.85339	50.0192
2	16.368	BB	0.6287	1956.09497	45.19791	49.9808



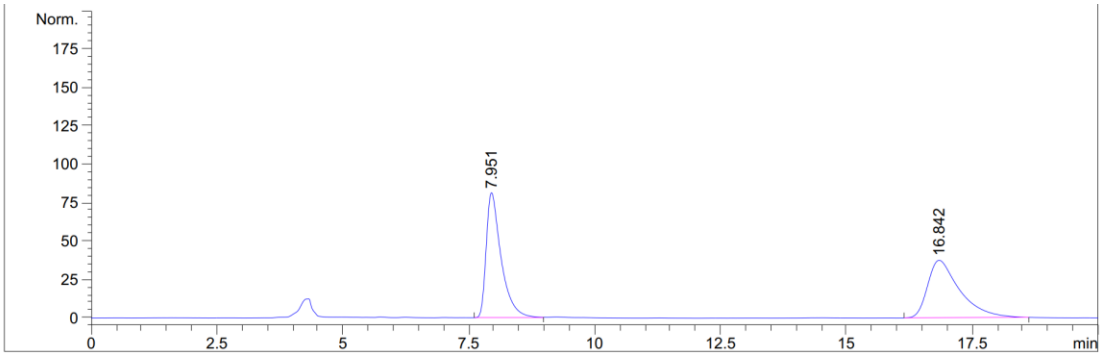
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.809	VB	0.3748	571.24188	21.25062	1.6287
2	16.266	PB	0.6551	3.45030e4	761.81549	98.3713

(3bR,5S,6R,6aS)-1'-Benzyl-6-(4-bromophenyl)-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6ak)

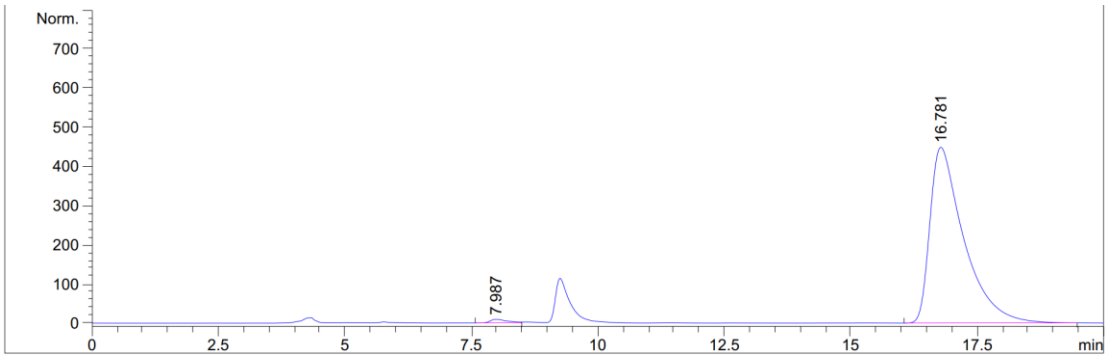


6ak

Prepared according to the procedure within 3 days as white solid (101.1 mg, 82% yield, dr > 20:1). mp 185.1 – 186.0 °C; $[\alpha]_D^{18}$= 89.80 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 1H), 7.56 – 7.50 (m, 2H), 7.47 – 7.42 (m, 1H), 7.30 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.20 – 7.15 (m, 5H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.80 – 6.76 (m, 1H), 6.55 – 6.51 (m, 2H), 6.47 – 6.41 (m, 2H), 6.35 – 6.30 (m, 1H), 5.32 (d, *J* = 10.6 Hz, 1H), 4.93 (d, *J* = 15.9 Hz, 1H), 4.41 (d, *J* = 10.4 Hz, 1H), 4.32 – 4.11 (m, 2H), 2.49 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 169.6, 147.4, 143.1, 134.8, 134.5, 133.4, 132.9, 131.7, 130.4, 130.0, 129.8, 128.7, 128.1, 127.8, 127.5, 127.5, 126.5, 123.9, 123.4, 122.4, 122.0, 122.0, 109.8, 109.4, 107.1, 71.9, 55.2, 54.5, 50.1, 43.4; HRMS (ESI) *m/z* Calcd. for $C_{35}H_{27}BrN_3O_3^+$ ($[M+H]^+$) 616.1230, Found 616.1231; Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 16.8 min, t_{minor} = 8.0 min).

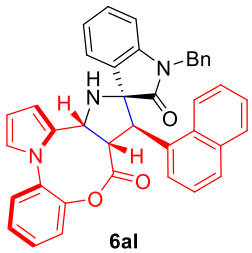


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.951	BB	0.3030	1674.73987	81.28655	50.2690
2	16.842	BB	0.6387	1656.81799	37.43505	49.7310



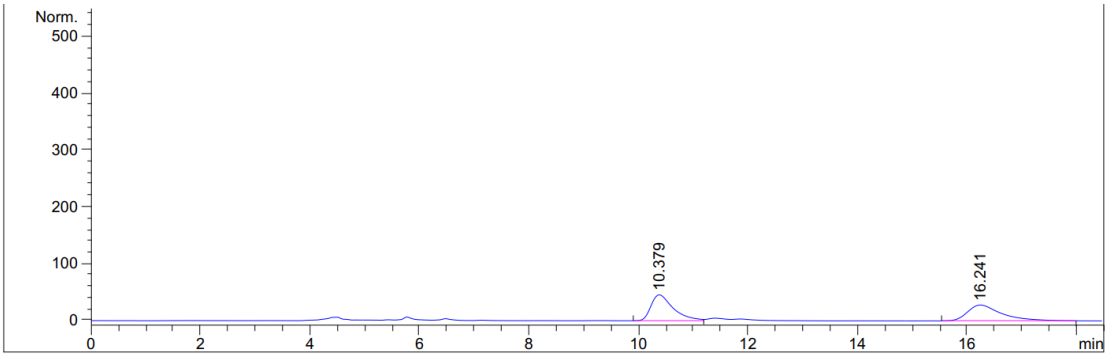
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.987	BV	0.3530	234.20956	9.40867	1.1079
2	16.781	BB	0.6733	2.09058e4	448.54404	98.8921

(3bR,5S,6R,6aS)-1'-Benzyl-6-(naphthalen-1-yl)-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6al)

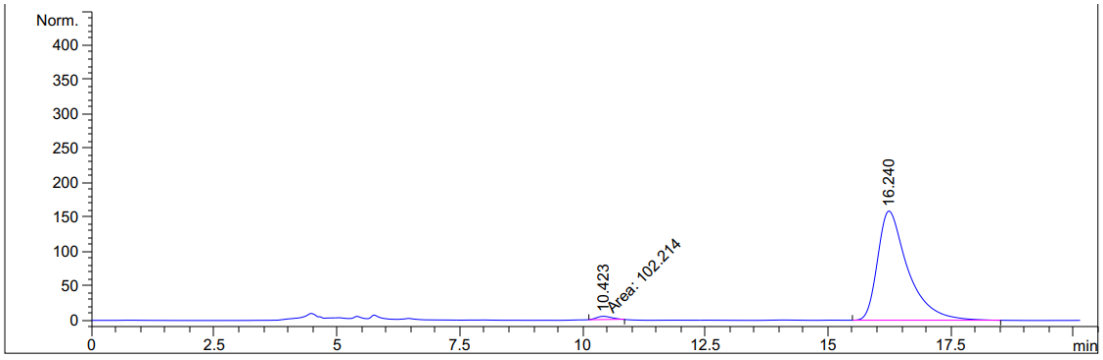


6al

Prepared according to the procedure within 3 days as white solid (105.8 mg, 90% yield, dr > 20:1). mp 228.2 – 229.1 °C; $[\alpha]_D^{18}$= 65.17 (*c* 0.71, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.7 Hz, 1H), 7.87 (d, *J* = 7.3 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.52 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.44 – 7.39 (m, 1H), 7.30 – 7.24 (m, 2H), 7.24 – 7.17 (m, 2H), 7.11 – 7.04 (m, 2H), 6.99 – 6.91 (m, 3H), 6.76 (s, 1H), 6.51 (d, *J* = 1.6 Hz, 1H), 6.37 – 6.29 (m, 3H), 6.11 (d, *J* = 7.8 Hz, 1H), 5.56 (d, *J* = 9.6 Hz, 1H), 5.51 (d, *J* = 10.5 Hz, 1H), 4.83 (d, *J* = 16.0 Hz, 1H), 4.31 (t, *J* = 10.1 Hz, 1H), 4.12 (d, *J* = 16.0 Hz, 1H), 2.67 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.8, 170.3, 147.5, 142.9, 134.8, 134.6, 133.7, 133.1, 132.5, 131.3, 130.3, 129.6, 128.5, 128.3, 128.3, 128.1, 127.5, 127.2, 126.3, 125.8, 125.6, 125.2, 125.1, 124.3, 123.7, 122.9, 122.5, 122.2, 109.8, 109.2, 107.2, 72.7, 55.4, 53.1, 49.5, 43.2; HRMS (ESI) *m/z* Calcd. for $C_{39}H_{30}N_3O_3^+$ ($[M+H]^+$) 588.2282, Found 588.2286; Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 80/20, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 16.2 min, t_{minor} = 10.4 min).

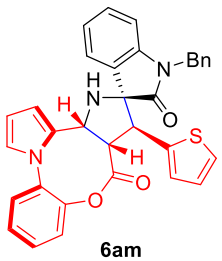


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.379	BV	0.4213	1290.09753	45.46581	51.7704
2	16.241	BB	0.6310	1201.86389	27.88065	48.2296



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.423	MM	0.3598	102.21376	4.73505	1.4784
2	16.240	BB	0.6301	6811.66406	158.77936	98.5216

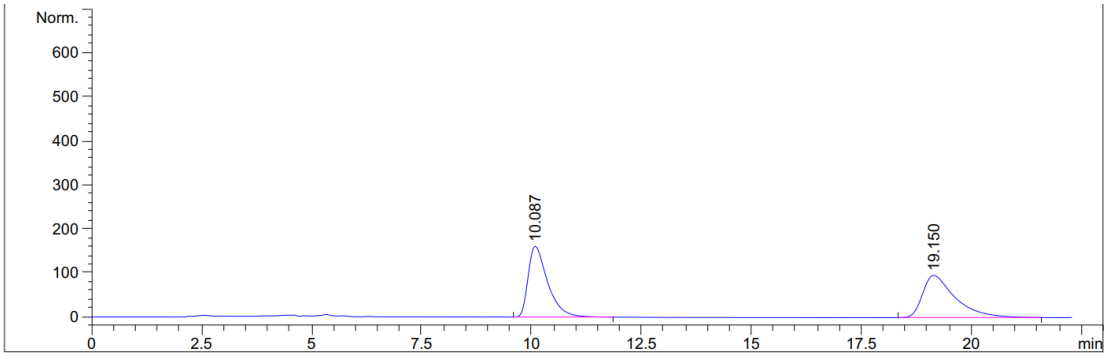
(3bR,5S,6S,6aS)-1'-Benzyl-6-(thiophen-2-yl)-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6am)



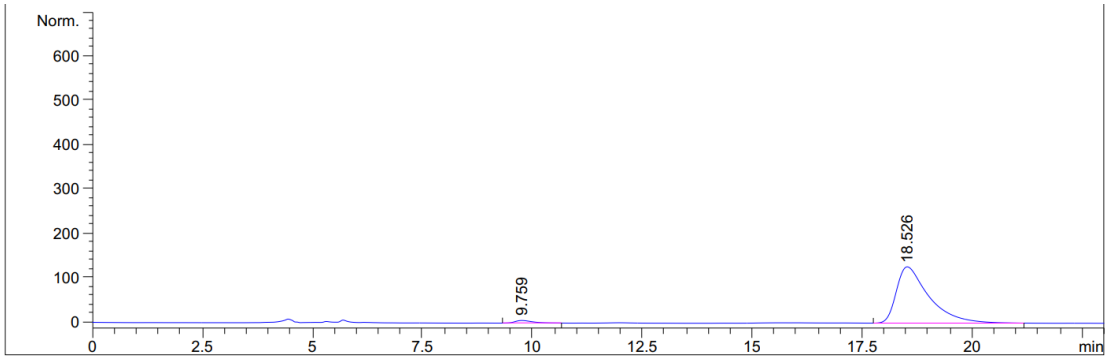
6am

Prepared according to the procedure within 3 days as white solid (103.3 mg, 95% yield, dr > 20:1). mp 176.8 – 177.4 °C; $[\alpha]_D^{18}$= 54.40 (*c* 0.77, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.46 – 7.42 (m, 1H), 7.35 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.24 – 7.12 (m, 5H), 7.04 (dd, *J* = 5.1, 1.0 Hz, 1H), 6.82 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.79 – 6.77 (m, 1H), 6.64 (dd, *J* = 10.9, 5.2 Hz, 3H), 6.54 – 6.48 (m, 1H), 6.45 – 6.42 (m, 1H), 6.34 – 6.28 (m, 1H), 5.32 (d, *J* = 10.7 Hz, 1H), 4.93 (d, *J* = 15.9 Hz, 1H), 4.69 (d, *J* = 10.3 Hz, 1H), 4.30 (d, *J* = 15.9 Hz, 1H), 4.24 (t, *J* = 10.5 Hz, 1H), 2.44 (s, 1H); ^{13}C NMR (151

MHz, $CDCl_3$) δ 178.0, 169.5, 147.4, 143.6, 137.4, 135.0, 134.3, 132.9, 130.4, 129.9, 128.7, 128.1, 127.7, 127.5, 127.3, 126.9, 126.7, 125.4, 124.5, 124.0, 123.3, 122.5, 122.0, 109.8, 109.3, 107.0, 71.5, 54.3, 51.9, 51.0, 43.4; HRMS (ESI) *m/z* Calcd. For $C_{33}H_{26}N_3O_3S^+$ ($[M+H]^+$) 544.1689, Found 544.1694; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 80/20, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 18.5 min, t_{minor} = 9.8 min).

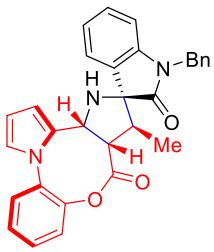


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.087	BB	0.4660	4963.15283	160.32707	50.1010
2	19.150	BB	0.7519	4943.14014	95.80633	49.8990



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.759	BB	0.4208	164.60437	5.88726	2.4549
2	18.526	PB	0.7510	6540.66602	126.95496	97.5451

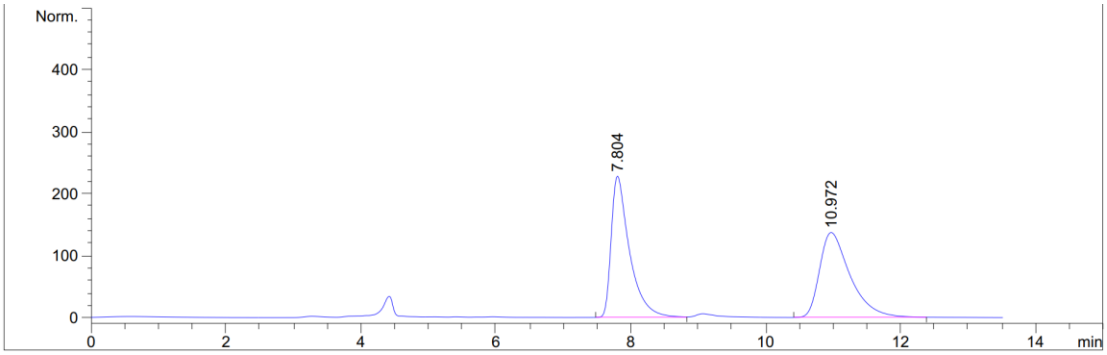
(3bR,5S,6S,6aS)-1'-Benzyl-6-methyl-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6an)



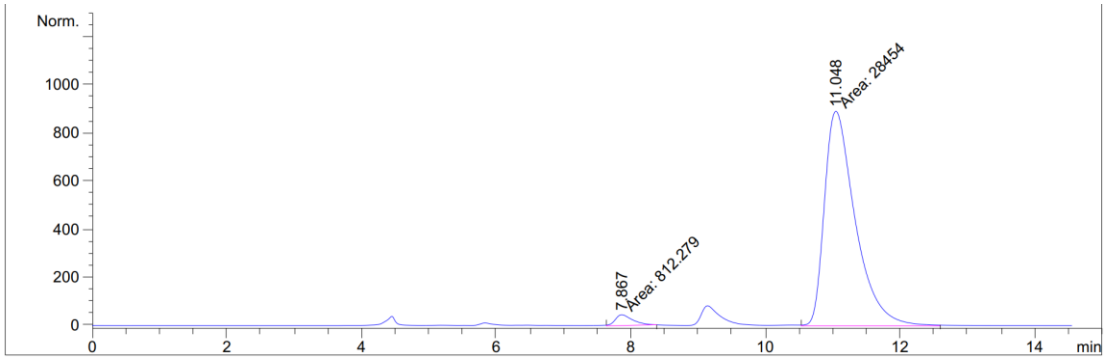
6an

Prepared according to the procedure within 3 days as white solid (66.6 mg, 70% yield, dr > 20:1). mp 136.8 – 137.4 °C; $[\alpha]_D^{18}$ = 87.11 (*c* 0.57, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.43 (m, 3H), 7.40 – 7.35 (m, 1H), 7.34 – 7.27 (m, 3H) , 7.27 – 7.19 (m,

4H), 7.15 – 7.09 (m, 1H), 6.78 – 6.67 (m, 2H), 6.33 (d, J = 59.8 Hz, 2H), 5.07 (d, J = 10.7 Hz, 1H), 4.93 (d, J = 15.5 Hz, 1H), 4.64 (d, J = 15.6 Hz, 1H), 3.48 (t, J = 10.1 Hz, 1H), 3.32 – 3.07 (m, 1H), 2.16 (s, 1H), 0.83 (d, J = 6.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.0, 170.4, 147.4, 143.3, 135.8, 135.0, 132.9, 130.1, 129.5, 128.9, 128.5, 127.9, 127.8, 127.3, 124.0, 123.3, 122.6, 121.6, 109.7, 109.1, 106.8, 70.7, 54.3, 52.4, 45.3, 43.6, 12.7; HRMS (ESI) *m/z* Calcd. for $C_{30}H_{26}N_3O_3^+$ ($[M+H]^+$) 476.1969, Found 476.1975; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 11.0 min, t_{minor} = 7.9 min).

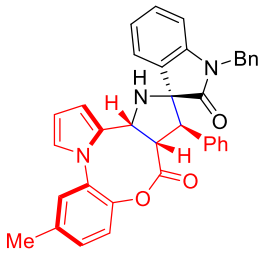


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.804	BV	0.2745	4298.10107	227.32347	50.0183
2	10.972	PB	0.4670	4294.95459	136.71100	49.9817



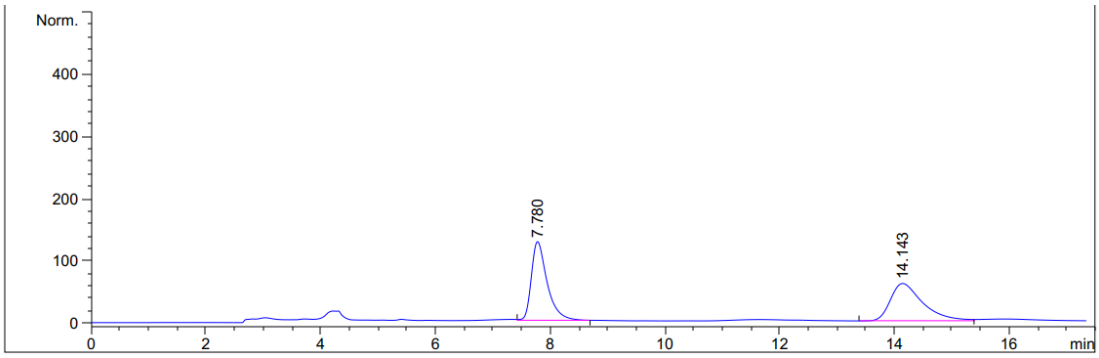
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.867	MM	0.2980	812.27948	45.43024	2.7755
2	11.048	MM	0.5323	2.84540e4	890.86481	97.2245

(3bR,5S,6R,6aS)-1'-Benzyl-11-methyl-6-phenyl-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6ao)

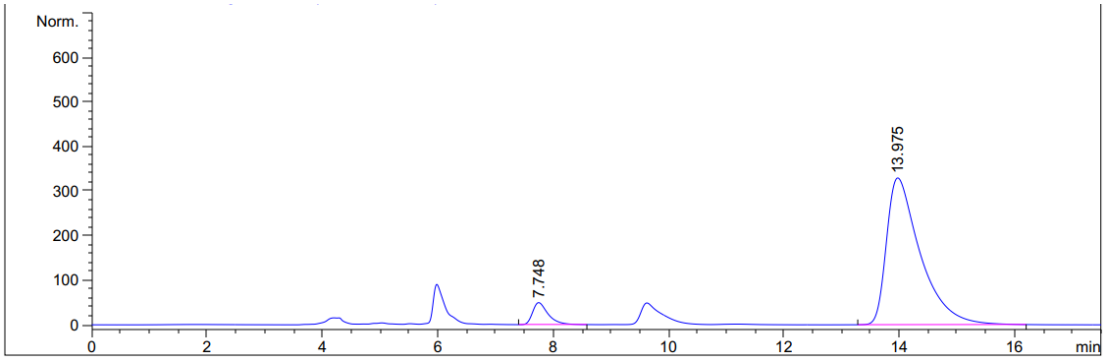


6ao

Prepared according to the procedure within 3 days as white solid (88.3 mg, 80% yield, dr > 20:1). mp 173.8 – 174.4 °C; $[\alpha]_D^{18}$= 81.25 (*c* 0.32, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.22 – 7.05 (m, 9H), 6.98 (d, *J* = 7.5 Hz, 2H), 6.78 – 6.75 (m, 1H), 6.47 (d, *J* = 7.5 Hz, 2H), 6.45 – 6.42 (m, 1H), 6.37 (d, *J* = 7.3 Hz, 1H), 6.32 – 6.30 (m, 1H), 5.37 (d, *J* = 10.7 Hz, 1H), 4.90 (d, *J* = 16.0 Hz, 1H), 4.47 (d, *J* = 10.3 Hz, 1H), 4.29 (t, *J* = 10.5 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 170.2, 145.1, 143.1, 137.6, 134.9, 134.5, 134.3, 132.6, 130.8, 129.6, 128.6, 128.5, 128.4, 128.2, 128.2, 127.7, 127.2, 126.4, 123.9, 123.2, 122.0, 121.9, 109.6, 109.3, 106.8, 72.2, 55.9, 54.7, 49.9, 43.3, 20.9; HRMS (ESI) *m/z* Calcd. for $C_{36}H_{30}N_3O_3^+$ ($[M+H]^+$) 552.2282, Found 552.2280; Enantiomeric excess was determined to be 87% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 14.0 min, t_{minor} = 7.7 min).

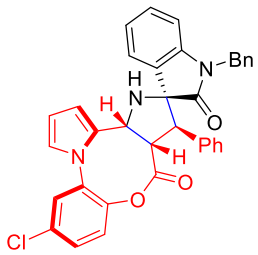


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.780	VB	0.2862	2424.52075	126.50131	50.6784
2	14.143	VB	0.5834	2359.61255	60.08018	49.3216



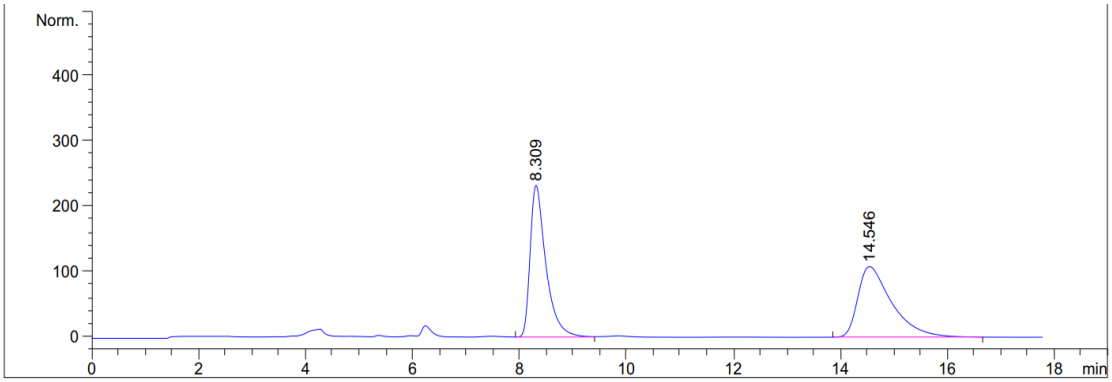
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.748	VB	0.2805	921.54401	49.34382	6.4358
2	13.975	BB	0.6013	1.33975e4	329.34894	93.5642

(3bR,5S,6R,6aS)-1'-Benzyl-11-chloro-6-phenyl-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6ap)

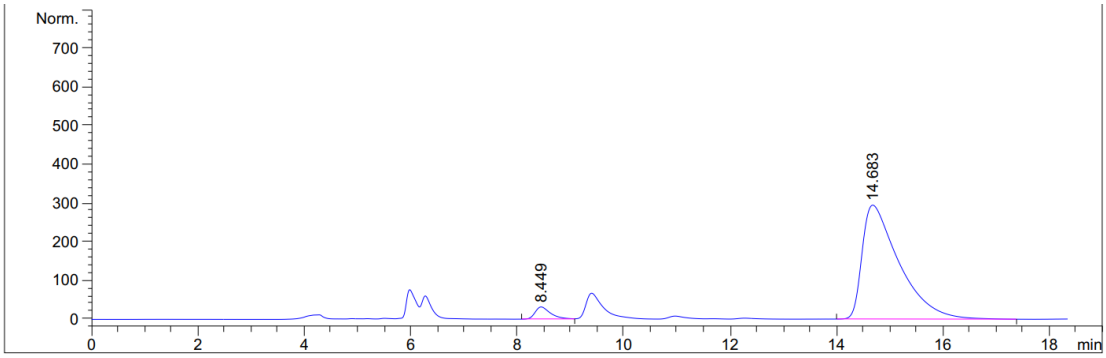


6ap

Prepared according to the procedure within 3 days as white solid (93.8 mg, 82% yield, dr > 20:1). mp 178.4 – 179.3 °C; $[\alpha]_D^{18}$= 87.71 (*c* 0.48, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 1H), 7.53 – 7.45 (m, 2H), 7.25 – 7.03 (m, 9H), 6.97 (d, *J* = 7.5 Hz, 2H), 6.78 – 6.73 (m, 1H), 6.52 – 6.43 (m, 3H), 6.40 – 6.35 (m, 1H), 6.34 – 6.30 (m, 1H), 5.37 (d, *J* = 10.6 Hz, 1H), 4.88 (d, *J* = 15.9 Hz, 1H), 4.44 (d, *J* = 10.4 Hz, 1H), 4.32 – 4.14 (m, 2H), 2.10 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 169.3, 146.1, 143.1, 134.9, 134.5, 134.0, 133.9, 132.5, 130.3, 129.7, 128.6, 128.5, 128.2, 128.2, 128.0, 127.8, 127.2, 126.5, 123.9, 123.5, 123.2, 121.9, 110.3, 109.3, 107.5, 72.1, 55.7, 54.4, 50.0, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{35}H_{27}ClN_3O_3^+$ ([M+H]$^+$) 572.1735, Found 572.1740; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 14.7 min, t_{minor} = 8.4 min).

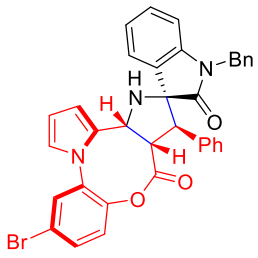


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.309	VB	0.3039	4783.12402	232.62761	50.0508
2	14.546	BB	0.6510	4773.40869	108.31654	49.9492



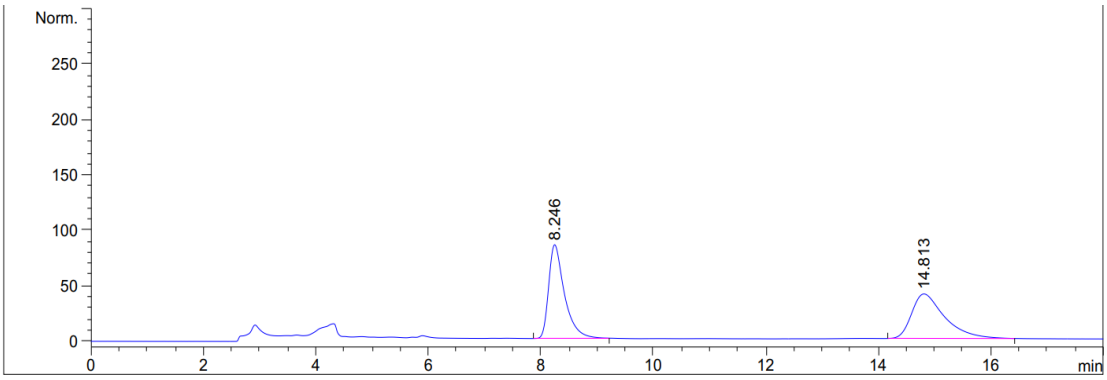
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.449	BV	0.3037	643.83746	31.53329	4.3234
2	14.683	BB	0.7059	1.42480e4	294.37244	95.6766

(3bR,5S,6R,6aS)-1'-Benzyl-11-bromo-6-phenyl-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6aq)

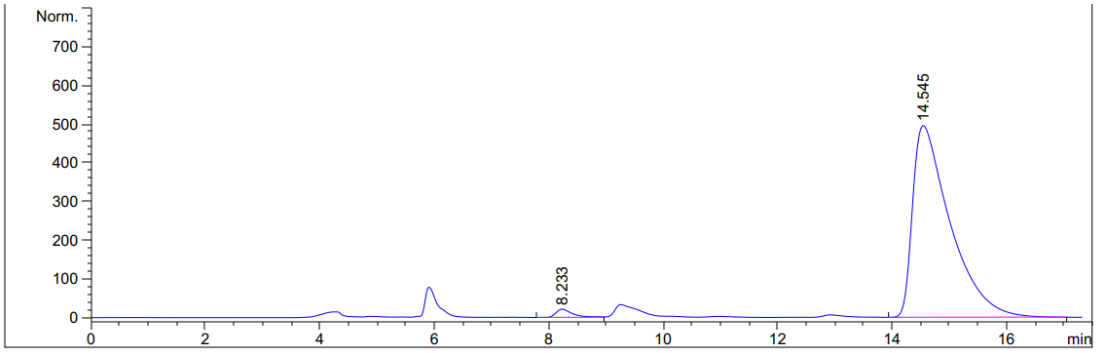


6aq

Prepared according to the procedure within 3 days as white solid (91.5 mg, 80% yield, dr > 20:1). mp 186.4 – 187.4 °C; $[\alpha]_D^{18}$= 122.67 (*c* 0.32, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 6.8 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.22 – 7.05 (m, 9H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.76 (s, 1H), 6.51 – 6.43 (m, 3H), 6.39 – 6.30 (m, 2H), 5.36 (d, *J* = 10.7 Hz, 1H), 4.89 (d, *J* = 16.0 Hz, 1H), 4.44 (d, *J* = 10.4 Hz, 1H), 4.32 – 4.13 (m, 2H), 2.31 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 169.3, 146.6, 143.1, 134.8, 134.6, 134.2, 134.0, 133.3, 131.1, 129.7, 128.6, 128.5, 128.2, 128.0, 127.8, 127.2, 126.5, 123.9, 123.9, 123.2, 121.9, 119.8, 110.3, 109.3, 107.5, 72.1, 55.7, 54.4, 50.0, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{35}H_{27}BrN_3O_3^+$ ($[M+H]^+$) 616.1230, Found 616.1221; Enantiomeric excess was determined to be 96% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 14.5 min, t_{minor} = 8.2 min).

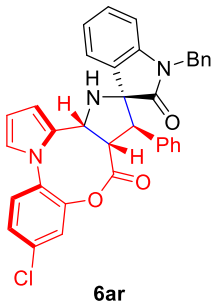


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.246	PB	0.2905	1652.02979	84.59119	50.1329
2	14.813	BB	0.6078	1643.26770	40.21438	49.8671



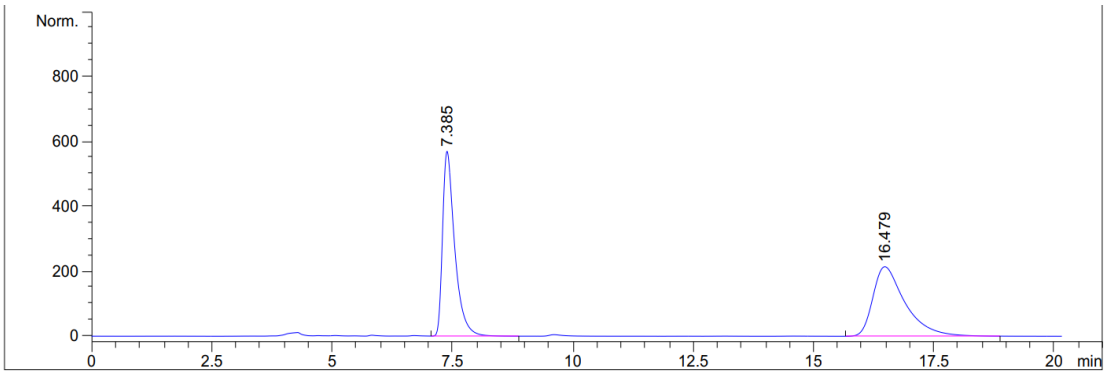
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.233	VV	0.3023	446.51083	21.46840	1.9406
2	14.545	VB	0.6611	2.25628e4	495.24957	98.0594

(3bR,5S,6R,6aS)-1'-Benzyl-10-chloro-6-phenyl-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6ar)

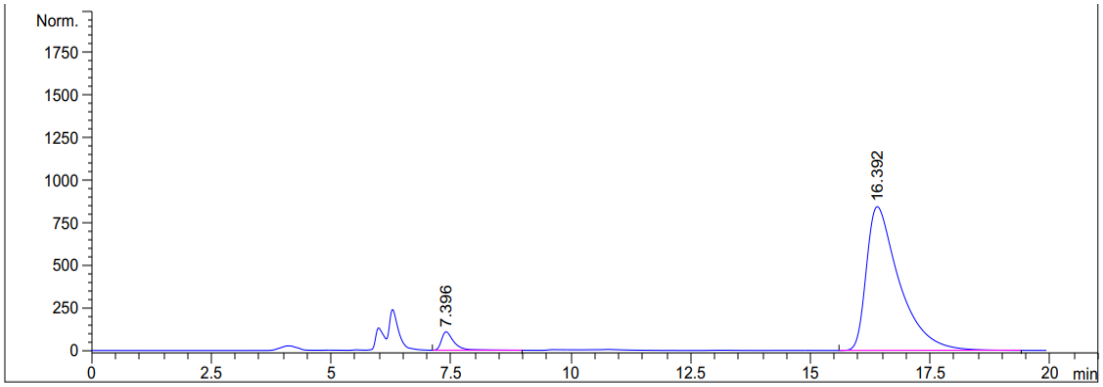


6ar

Prepared according to the procedure within 3 days as white solid (91.5 mg, 80% yield, dr > 20:1). mp 186.3 – 187.2 °C; $[\alpha]_D^{18}$ = 53.63 (*c* 0.29, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 6.4 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.32 (s, 1H), 7.22 – 7.03 (m, 8H), 6.98 (d, *J* = 7.6 Hz, 2H), 6.73 (s, 1H), 6.53 – 6.43 (m, 3H), 6.37 (d, *J* = 7.0 Hz, 1H), 6.33 – 6.29 (m, 1H), 5.34 (d, *J* = 10.6 Hz, 1H), 4.89 (d, *J* = 15.9 Hz, 1H), 4.44 (d, *J* = 10.4 Hz, 1H), 4.34 – 4.15 (m, 2H), 2.48 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 169.0, 147.8, 143.1, 135.5, 134.8, 134.6, 133.9, 131.6, 129.7, 128.8, 128.6, 128.6, 128.2, 128.0, 127.8, 127.7, 127.3, 126.5, 123.9, 123.2, 122.9, 122.0, 110.1, 109.3, 107.3, 72.1, 55.7, 54.4, 50.1, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{35}H_{27}ClN_3O_3^+$ ($[M+H]^+$) 572.1735, Found 572.1737; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 16.4 min, t_{minor} = 7.4 min).

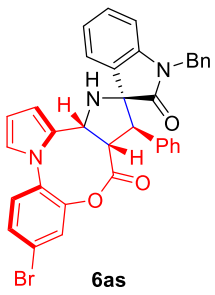


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.385	VB	0.2621	1.00165e4	569.28601	50.1122
2	16.479	BB	0.6888	9971.70020	214.18037	49.8878



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.396	VB	0.2726	2023.16418	109.36850	4.7778
2	16.392	PB	0.7029	4.03217e4	846.32373	95.2222

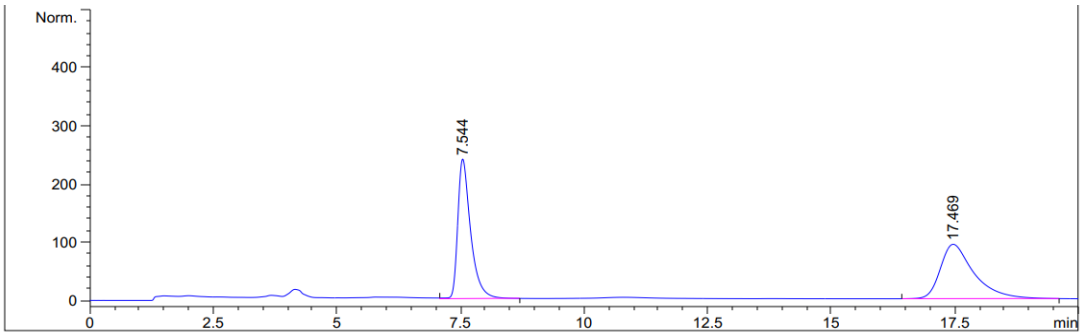
(3bR,5S,6R,6aS)-1'-Benzyl-10-bromo-6-phenyl-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6as)



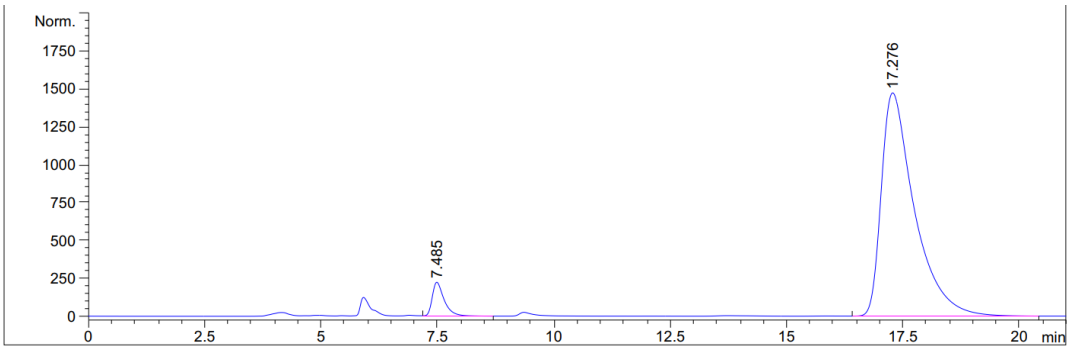
6as

Prepared according to the procedure within 3 days as white solid (91.0 mg, 74% yield, dr > 20:1). mp 176.2 – 177.0 °C; $[\alpha]_D^{18}$ = 54.32 (*c* 0.67, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.57 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.48 (d, *J* = 2.1 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.19 – 7.12 (m, 5H), 7.10 – 7.06 (m, 2H), 7.00 (d, *J* = 7.7 Hz, 2H), 6.76 – 6.72 (m, 1H), 6.52 – 6.45 (m, 3H), 6.39 (d, *J* = 7.2 Hz, 1H), 6.34 – 6.30 (m, 1H), 5.35 (d, *J* = 10.6 Hz, 1H), 4.91 (d, *J* = 16.0 Hz, 1H), 4.45 (d, *J* = 10.5 Hz, 1H), 4.30 (t, *J* = 10.5 Hz, 1H), 4.23 (d, *J* = 16.0 Hz, 1H), 2.40 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3,

169.0, 147.9, 143.1, 134.8, 134.6, 133.9, 132.1, 130.6, 129.7, 129.1, 128.7, 128.6, 128.2, 128.0, 127.8, 127.3, 126.5, 125.8, 123.9, 123.2, 123.1, 121.9, 110.1, 109.4, 107.4, 72.1, 55.7, 54.4, 50.0, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{35}H_{27}BrN_3O_3^+$ ($[M+H]^+$) 616.1230, Found 616.1234; Enantiomeric excess was determined to be 89% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 17.3 min, t_{minor} = 7.5 min).

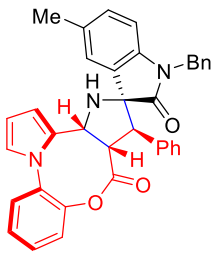


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.544	VB	0.2698	4355.20166	240.16383	49.5865
2	17.469	BB	0.7034	4427.83203	93.59225	50.4135



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.485	VB	0.2660	4002.57935	223.18607	5.2214
2	17.276	VB	0.7281	7.26543e4	1469.78540	94.7786

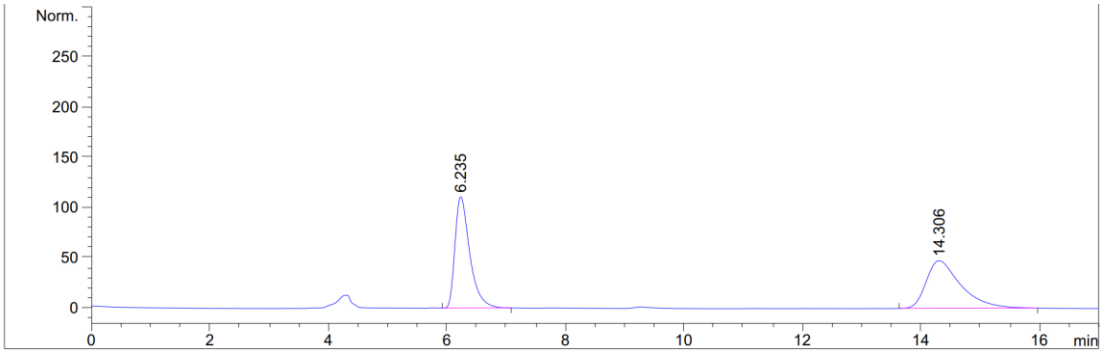
(3bR,5S,6R,6aS)-1'-Benzyl-5'-methyl-6-phenyl-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6ba)



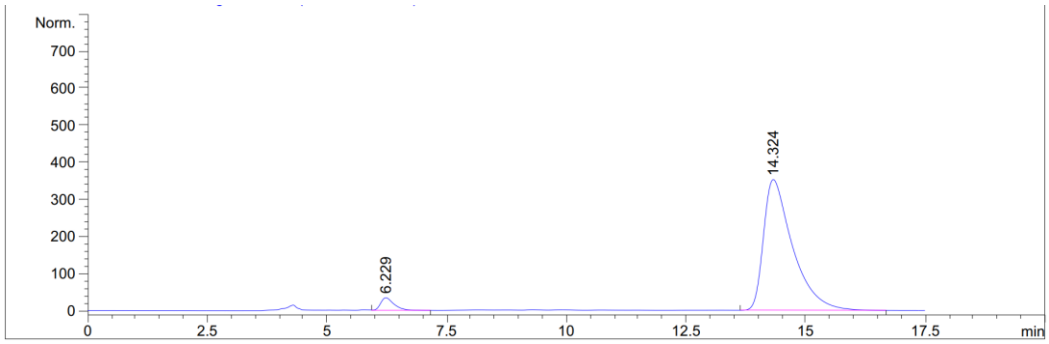
6ba

Prepared according to the procedure within 3 days as white solid (77.2 mg, 70% yield, dr > 20:1). mp 175.2 – 176.0 °C; $[\alpha]_D^{18}$ = 71.15 (*c* 0.26, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 3H), 7.45 – 7.41 (m, 1H), 7.32 – 7.28 (m, 1H), 7.23 – 7.18 (m, 1H), 7.14 – 7.09 (m, 3H), 7.08 – 7.03 (m, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.80 – 6.76 (m, 1H), 6.48 – 6.43 (m,

3H), 6.34 – 6.30 (m, 1H), 6.25 (d, *J* = 7.9 Hz, 1H), 5.35 (d, *J* = 10.6 Hz, 1H), 4.86 (d, *J* = 16.0 Hz, 1H), 4.45 (d, *J* = 10.3 Hz, 1H), 4.27 (t, *J* = 10.5 Hz, 1H), 4.18 (d, *J* = 16.0 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.2, 170.0, 147.5, 140.7, 135.0, 134.6, 134.3, 133.0, 132.9, 130.3, 129.9, 128.6, 128.5, 128.2, 128.2, 128.1, 127.7, 127.4, 127.1, 126.4, 124.6, 122.4, 122.0, 109.7, 109.0, 106.9, 72.2, 55.8, 54.7, 50.1, 43.3, 21.2; HRMS (ESI) *m/z* Calcd. for $C_{36}H_{30}N_3O_3^+$ ($[M+H]^+$) 552.2282, Found 552.2282; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 14.3 min, t_{minor} = 6.2 min).

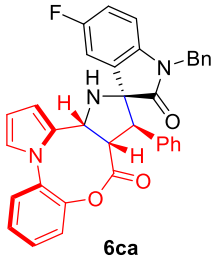


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.235	VB	0.2642	1931.32776	110.97221	49.8959
2	14.306	BB	0.5976	1939.38428	47.60297	50.1041



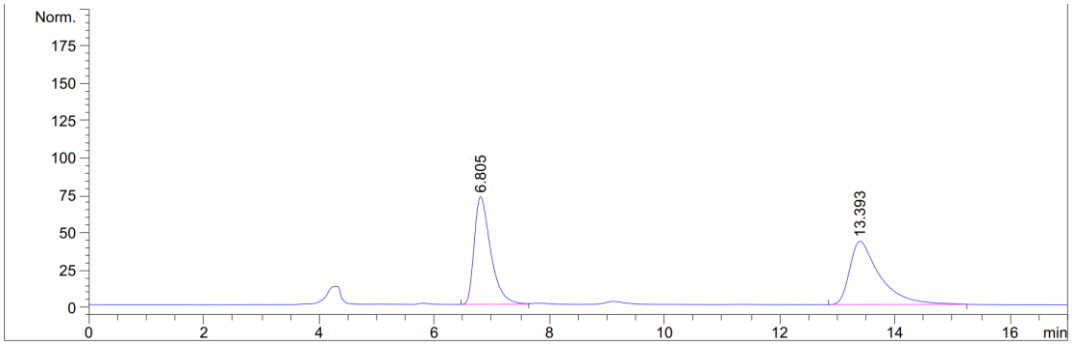
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.229	VB	0.2915	665.45862	34.13357	4.2568
2	14.324	BB	0.6229	1.49673e4	352.94476	95.7432

(3bR,5S,6R,6aS)-1'-Benzyl-5'-fluoro-6-phenyl-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6ca)

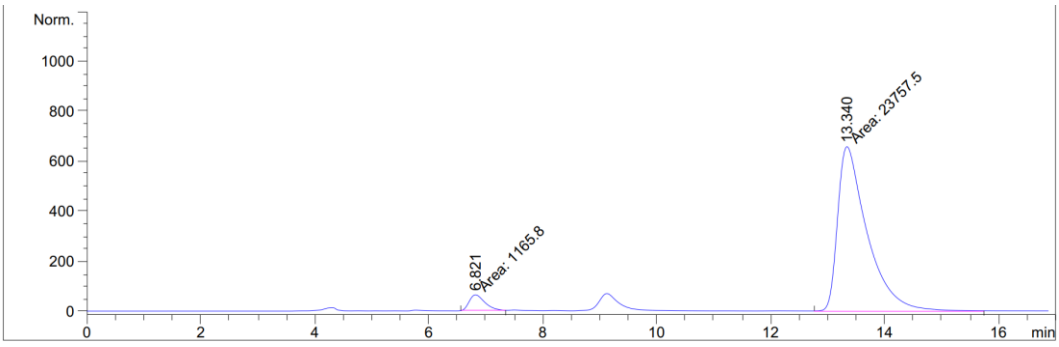


6ca

Prepared according to the procedure within 3 days as white solid (97.8 mg, 88% yield, dr > 20:1). mp 180.4 – 181.3 °C; $[\alpha]_D^{18}$ = 60.07 (*c* 0.62, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.48 (dd, *J* = 7.6, 2.6 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.31 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.16 – 7.11 (m, 3H), 7.10 – 7.06 (m, 2H), 7.01 (d, *J* = 7.6 Hz, 2H), 6.85 – 6.80 (m, 1H), 6.79 – 6.75 (m, 1H), 6.49 – 6.41 (m, 3H), 6.36 – 6.30 (m, 1H), 6.27 (dd, *J* = 8.5, 4.0 Hz, 1H), 5.34 (d, *J* = 10.7 Hz, 1H), 4.89 (d, *J* = 16.0 Hz, 1H), 4.43 (d, *J* = 10.4 Hz, 1H), 4.28 (t, *J* = 10.6 Hz, 1H), 4.18 (d, *J* = 16.0 Hz, 1H), 2.48 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.2, 169.6, 159.7 (d, *J* = 243.1 Hz), 158.1, 147.4, 138.9, 134.5 (d, *J* = 3.0 Hz), 133.9, 132.9, 130.3, 130.2 (d, *J* = 7.6 Hz), 128.7, 128.6, 128.3, 128.0, 127.9, 127.5, 127.4, 126.4, 122.5, 122.0, 115.9 (d, *J* = 22.7 Hz), 112.0 (d, *J* = 25.7 Hz), 110.0 (d, *J* = 7.6 Hz), 109.8, 107.1, 72.2, 55.9, 54.5, 49.8, 43.4; ^{19}F NMR (565 MHz, $CDCl_3$) δ -119.09; HRMS (ESI) *m/z* Calcd. for $C_{35}H_{27}FN_3O_3^+$ ($[M+H]^+$) 556.2031, Found 556.2032; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 13.3 min, t_{minor} = 6.8 min).

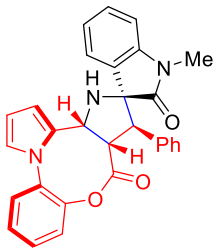


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.805	BB	0.3020	1430.32190	71.90580	48.1349
2	13.393	PB	0.5283	1541.16736	42.31447	51.8651



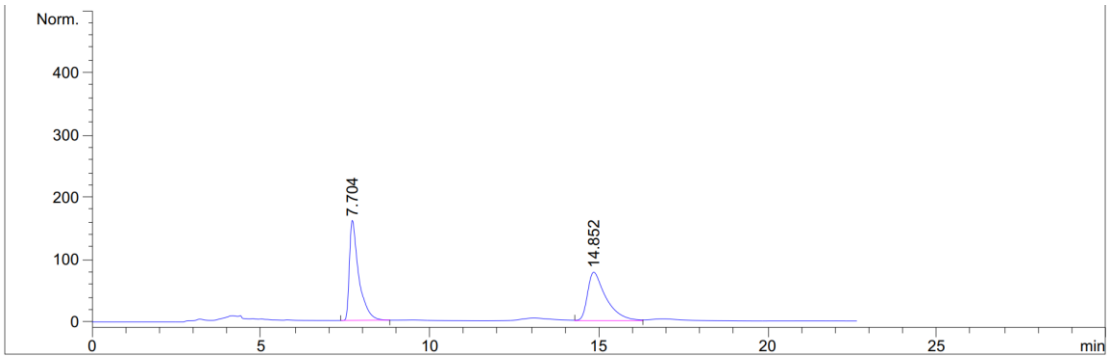
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.821	MM	0.3121	1165.80261	62.24791	4.6776
2	13.340	MM	0.6024	2.37575e4	657.32379	95.3224

(3bR,5S,6R,6aS)-1'-Methyl-6-phenyl-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (6da)

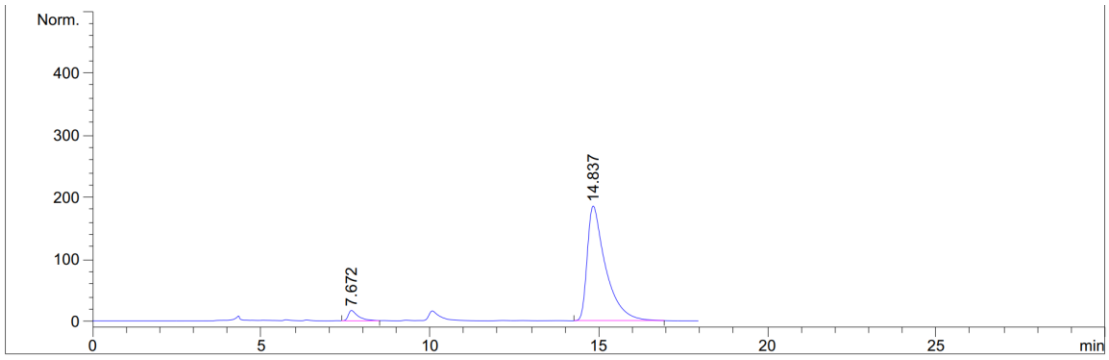


6da

Prepared according to the procedure within 2.5 days as white solid (81.2 mg, 88% yield, dr > 20:1). mp 166.3 – 167.2 °C; $[\alpha]_D^{18}$ = 16.32 (*c* 0.24, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.1 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.45 – 7.40 (m, 1H), 7.30 – 7.24 (m, 2H), 7.20 – 7.15 (m, 1H), 7.12 – 7.03 (m, 3H), 6.92 (d, *J* = 7.3 Hz, 2H), 6.78 – 6.73 (m, 1H), 6.55 (d, *J* = 7.7 Hz, 1H), 6.46 – 6.40 (m, 1H), 6.34 – 6.29 (m, 1H), 5.31 (d, *J* = 10.7 Hz, 1H), 4.34 (d, *J* = 10.5 Hz, 1H), 4.17 (t, *J* = 10.6 Hz, 1H), 2.75 (s, 3H), 2.16 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 169.8, 147.5, 143.7, 134.8, 134.1, 132.9, 130.3, 129.6, 128.2, 128.1, 128.0, 128.0, 127.6, 127.4, 123.7, 123.1, 122.5, 121.9, 109.7, 108.0, 106.9, 72.2, 56.2, 54.7, 50.1, 25.4; HRMS (ESI) *m/z* Calcd. for $C_{29}H_{24}N_3O_3^+$ ($[M+H]^+$) 462.1812, Found 462.1812; Enantiomeric excess was determined to be 91% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 14.8 min, t_{minor} = 7.7 min).



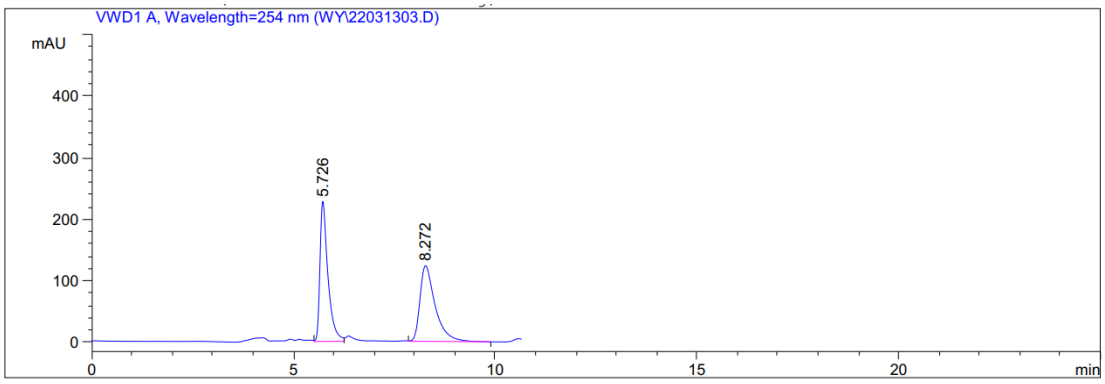
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.704	BB	0.2744	3072.86816	160.43619	50.7891
2	14.852	VB	0.5488	2977.38892	77.98033	49.2109



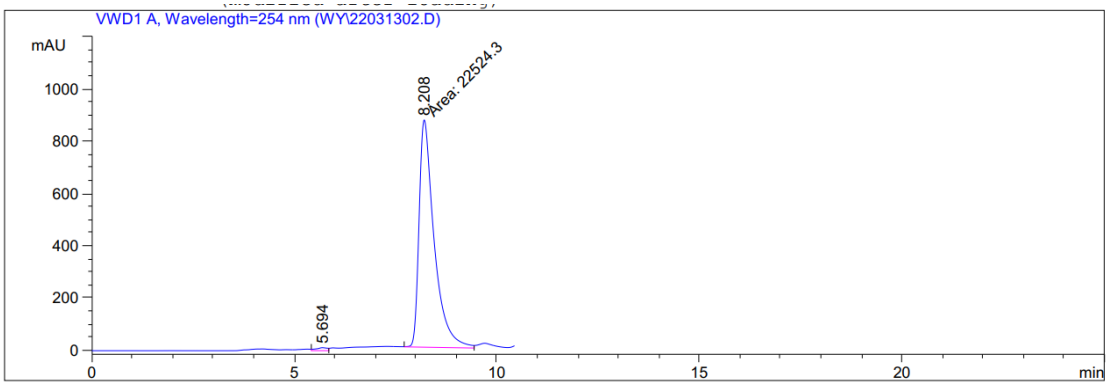
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.672	VB	0.2905	339.37653	16.63311	4.6322
2	14.837	PB	0.5453	6987.04102	184.44702	95.3678

Gram scale synthesis of compound 4ad

Enantiomeric excess was determined to be 98% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 8.2 min, t_{minor} = 5.6 min)



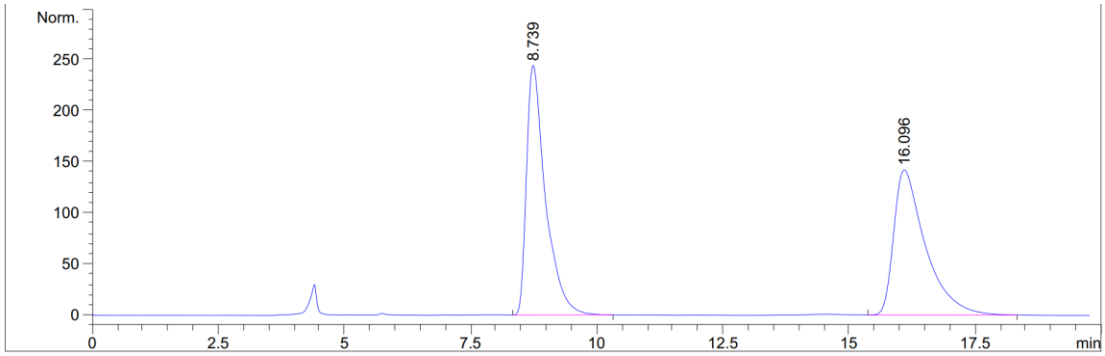
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.726	VV	0.1994	3124.04541	227.68483	49.1177
2	8.272	VB	0.3911	3236.28101	123.11414	50.8823



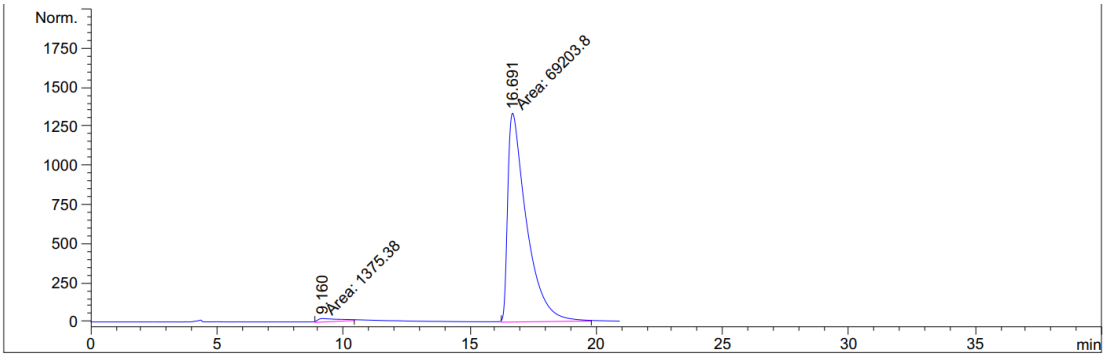
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.694	VV	0.2682	225.44318	11.42075	0.9910
2	8.208	MM	0.4317	2.25243e4	869.60437	99.0090

The scale-up synthesis of compound 6am

Enantiomeric excess was determined to be 96% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 16.7 min, t_{minor} = 9.2 min).



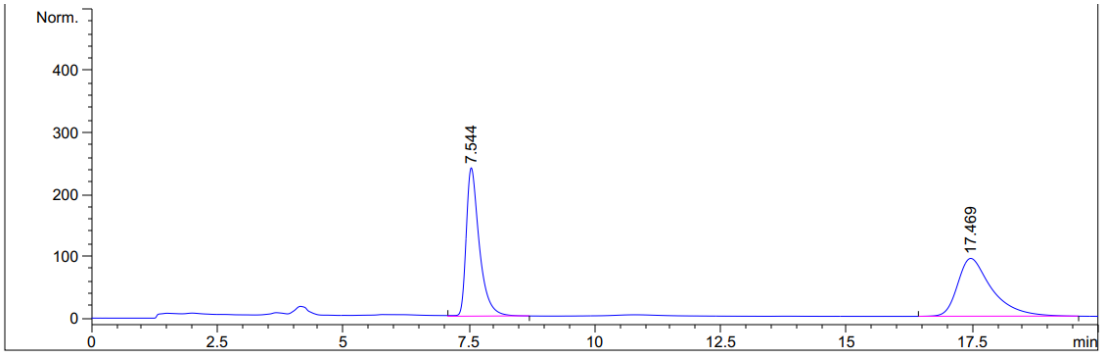
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.739	PB	0.3870	6400.20459	244.46620	50.6994
2	16.096	VB	0.6384	6223.61572	142.29416	49.3006



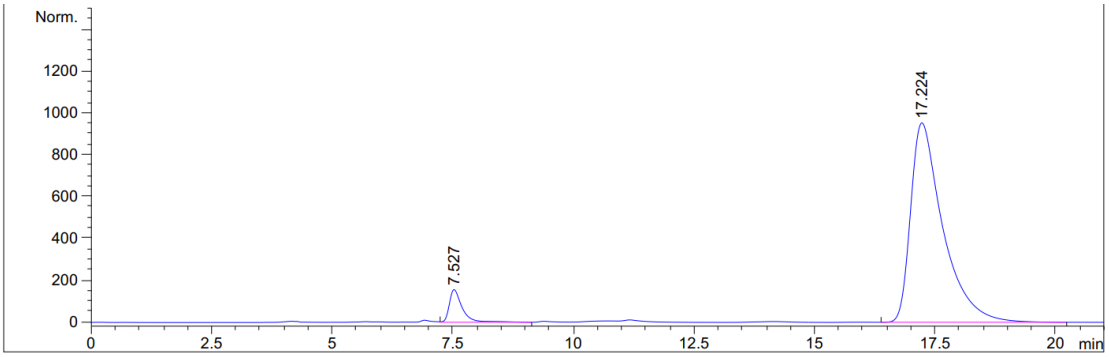
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.160	MM	0.9763	1375.37964	23.47963	1.9487
2	16.691	MM	0.8631	6.92038e4	1336.29236	98.0513

The scale-up synthesis of compound 6as

Enantiomeric excess was determined to be 87% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 17.2 min, t_{minor} = 7.5 min).

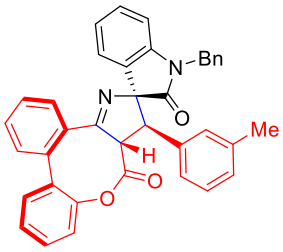


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.544	VB	0.2698	4355.20166	240.16383	49.5865
2	17.469	BB	0.7034	4427.83203	93.59225	50.4135



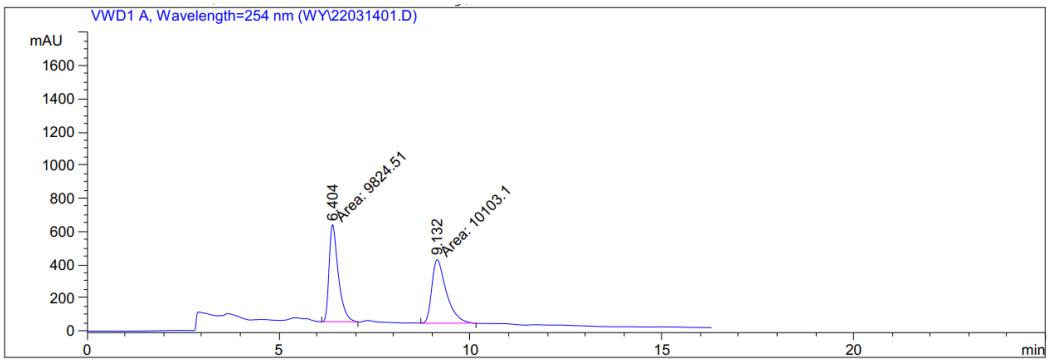
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.527	VV	0.2819	3009.85864	157.01492	6.3517
2	17.224	VB	0.6822	4.43767e4	954.44525	93.6483

(6S,7R,7aS)-1'-Benzyl-7-(m-tolyl)-7,7a-dihydro-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (7)

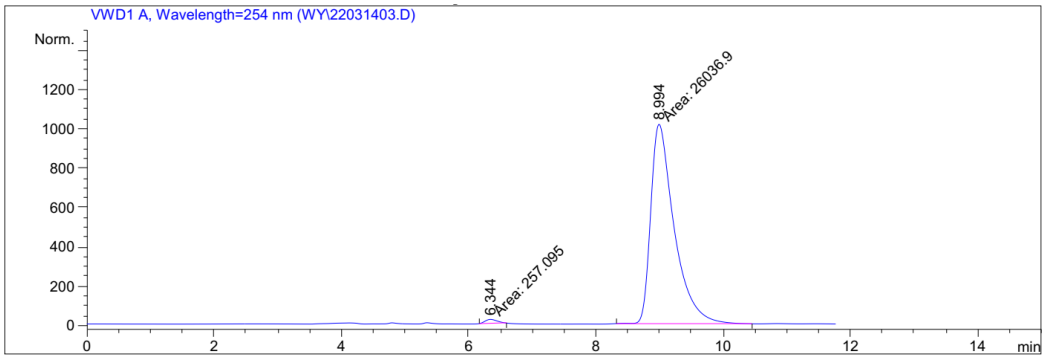


7

Prepared according to the procedure within 10 h as white solid (100.92 mg, 90% yield, dr > 20:1); mp 220.2 – 220 9 °C; $[\alpha]_D^{18}$= 148.74 (*c* 0.28, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.62 – 7.54 (m, 2H), 7.51 – 7.48 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.22 (dd, *J* = 5.5, 3.2 Hz, 2H), 7.15 – 7.01 (m, 6H), 6.67 (d, *J* = 7.2 Hz, 1H), 6.61 (s, 1H), 6.52 – 6.45 (m, 1H), 6.41 (d, *J* = 7.5 Hz, 2H), 5.38 (d, *J* = 11.2 Hz, 1H), 4.97 (d, *J* = 16.0 Hz, 1H), 4.78 (d, *J* = 11.2 Hz, 1H), 4.17 (d, *J* = 16.0 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 173.3, 168.6, 148.9, 143.5, 138.2, 136.3, 134.8, 134.0, 133.6, 133.0, 132.6, 131.9, 131.6, 130.6, 129.9, 129.6, 129.3, 128.9, 128.7, 128.6, 128.5, 127.8, 127.2, 126.3, 124.5, 124.4, 123.5, 120.5, 109.4, 83.6, 57.7, 56.3, 43.7, 21.4; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{29}N_2O_3^+$ ($[M+H]^+$) 561.2173, Found 561.2173; Enantiomeric excess was determined to be 98% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 m L/min, t_{major} = 8.9 min, t_{minor} = 6.3 min).

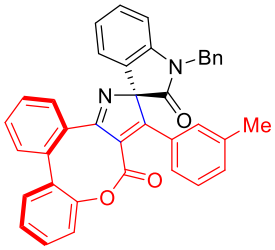


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.404	MM	0.2795	9824.50781	585.83295	49.3010
2	9.132	MM	0.4390	1.01031e4	383.54129	50.6990



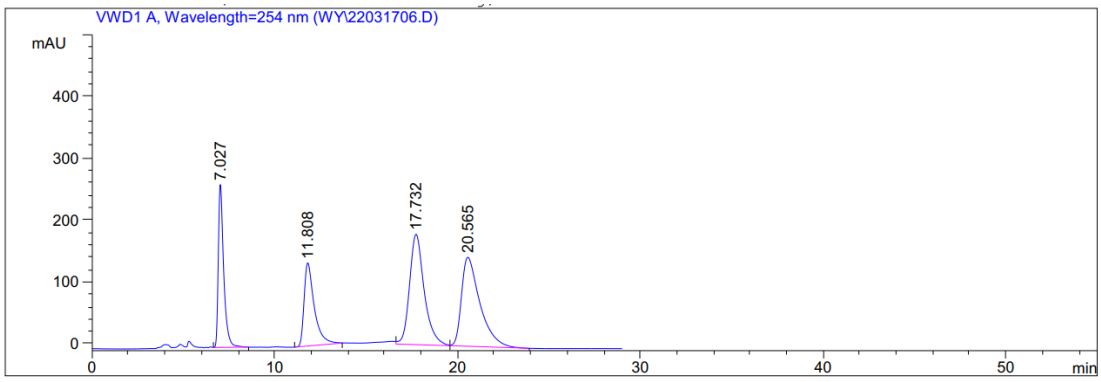
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.344	MM	0.2131	257.09460	20.10881	0.9778
2	8.994	MM	0.4277	2.60369e4	1014.50995	99.0222

(S)-1'-Benzyl-7-(m-tolyl)-8H-spiro[dibenzo[5,6:7,8]oxocino[4,3-b]pyrrole-6,3'-indoline]-2',8-dione (8)

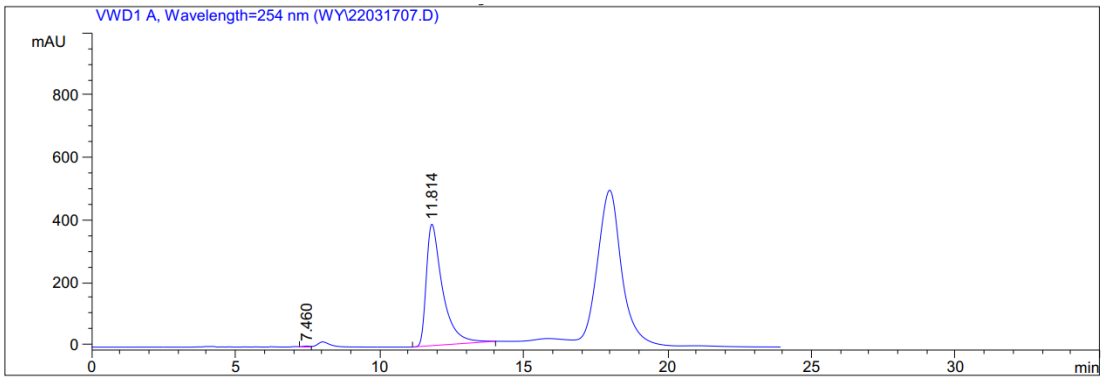


8

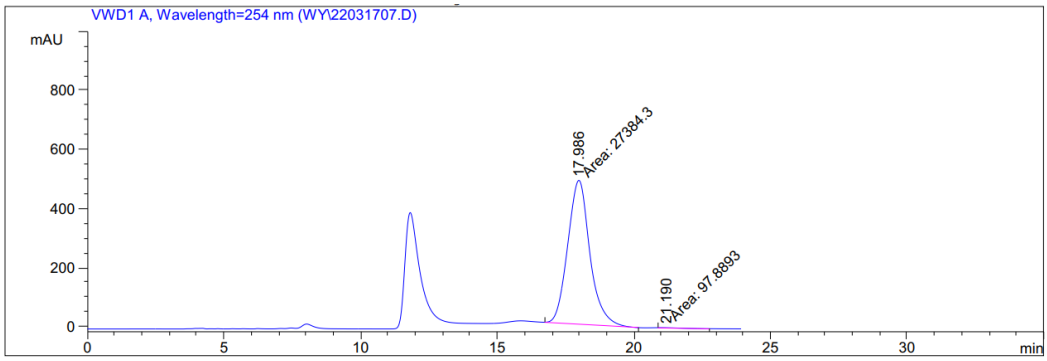
Prepared according to the procedure within 10 h as white solid (106.14 mg, 95% yield, dr = 1.6:1); mp 224.6 – 225.7 °C; $[\alpha]_D^{18}$= 14.56 (*c* 0.47, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 1H), 7.64 – 7.60 (m, 1H), 7.55 – 7.33 (m, 5H), 7.32 – 7.26 (m, 1H), 7.24 – 7.21 (m, 2H), 7.19 – 7.03 (m, 6H), 6.96 (s, 1H), 6.89 – 6.81 (m, 1H), 6.80 – 6.64 (m, 2H), 5.59 (d, *J* = 7.3 Hz, 1H), 5.17 (d, *J* = 15.7 Hz, 1H), 4.70 (d, *J* = 15.7 Hz, 1H), 2.16 (s, 3H); ^{113}C NMR (101 MHz, $CDCl_3$) δ 175.1, 169.3, 165.3, 163.2, 148.7, 144.0, 138.6, 136.0, 135.0, 133.7, 133.4, 133.1, 132.5, 131.3, 131.2, 131.2, 130.0, 129.9, 129.1, 128.9, 128.7, 128.5, 128.2, 127.8, 127.4, 127.3, 124.7, 123.3, 123.0, 122.8, 122.0, 110.1, 89.3, 44.6, 21.5; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{27}N_2O_3^+$ ($[M+H]^+$) 559.2016, Found 559.2009; Enantiomeric excess was determined to be 99%, 99% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 m L/min, t_{major} = 11.8 min, t_{minor} = 7.6 min, t_{major} = 17.9 min, t_{minor} = 21.1 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.027	VB	0.3047	5398.82080	263.36807	17.5747
2	11.808	PB	0.5709	5217.59375	134.38542	16.9848
3	17.732	VV	0.8393	9996.55664	178.61017	32.5417
4	20.565	VP	1.0402	1.01063e4	143.99014	32.8988

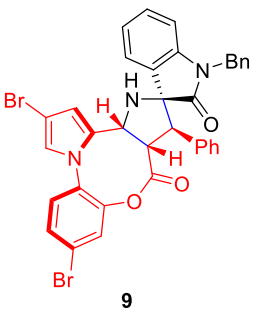


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.460	VV	0.2743	53.13895	2.92853	0.3454
2	11.814	PB	0.5784	1.53310e4	389.68433	99.6546



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.986	MM	0.9371	2.73843e4	487.04340	99.6438
2	21.190	MM	1.2339	97.88932	1.32217	0.3562

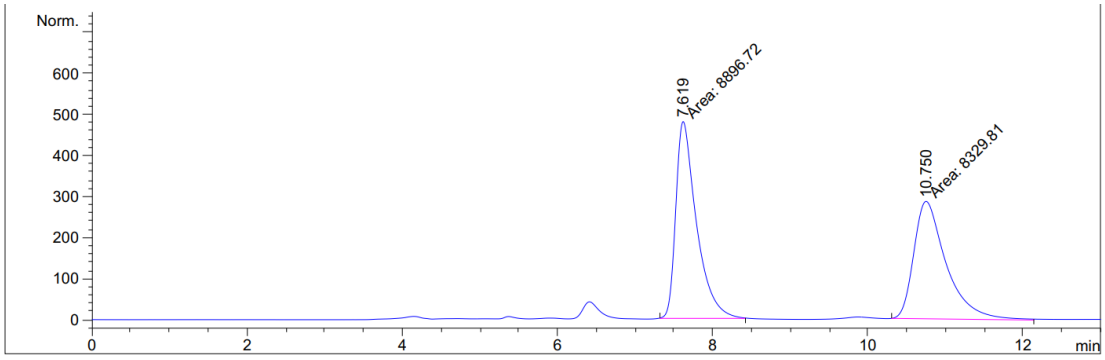
(3bR,5S,6R,6aS)-1'-Benzyl-2,10-dibromo-6-phenyl-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (9)



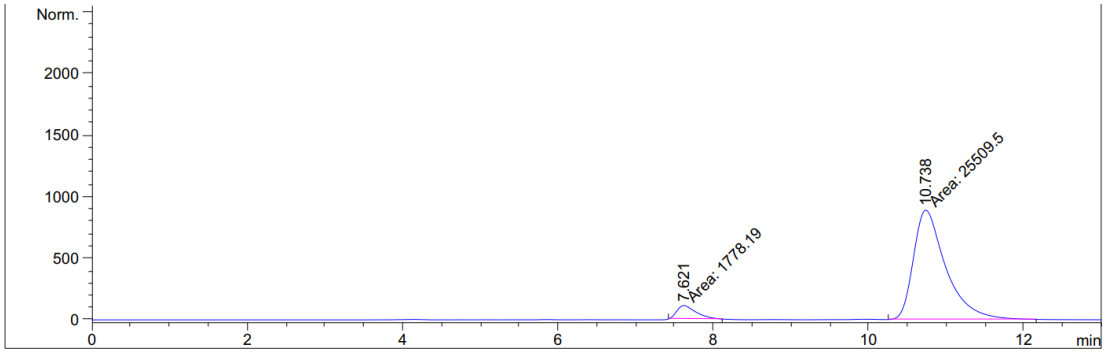
9

Prepared according to the procedure within 12 h as white solid (62.6 mg, 90% yield, dr > 20:1). mp 228.2 – 229.3 °C; $[\alpha]_D^{18}$= 42.80 (*c* 0.26, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.61 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.51 (d, *J* = 2.1 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.18 – 7.10 (m, 5H), 7.09 – 7.05 (m, 2H), 6.97 (d, *J* = 7.4 Hz, 2H), 6.50 – 6.44 (m, 3H), 6.38 – 6.36 (m, 1H), 6.34 (d, *J* = 3.7 Hz, 1H), 5.26 (d, *J* = 10.3 Hz, 1H), 4.88 (d, *J* = 16.0 Hz, 1H), 4.40 (d, *J* = 10.6 Hz, 1H), 4.28 – 4.18 (m, 2H), 2.43 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 168.7, 148.3, 143.1, 136.2, 134.7, 133.6, 131.2, 130.5, 129.7, 128.7, 128.6, 128.2, 127.9, 127.8,

127.3, 126.4, 126.0, 124.0, 124.0, 123.3, 112.4, 109.4, 108.0, 102.2, 71.9, 55.3, 54.7, 50.2, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{35}H_{26}Br_2N_3O_3^+$ ($[M+H]^+$) 694.0335, Found 694.0339; Enantiomeric excess was determined to be 87% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 10.7 min, t_{minor} = 7.6 min).

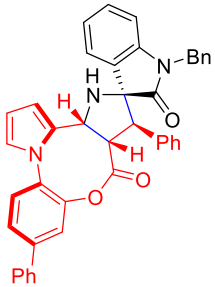


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.619	MM	0.3088	8896.72266	480.18582	51.6455
2	10.750	MM	0.4846	8329.80664	286.48193	48.3545



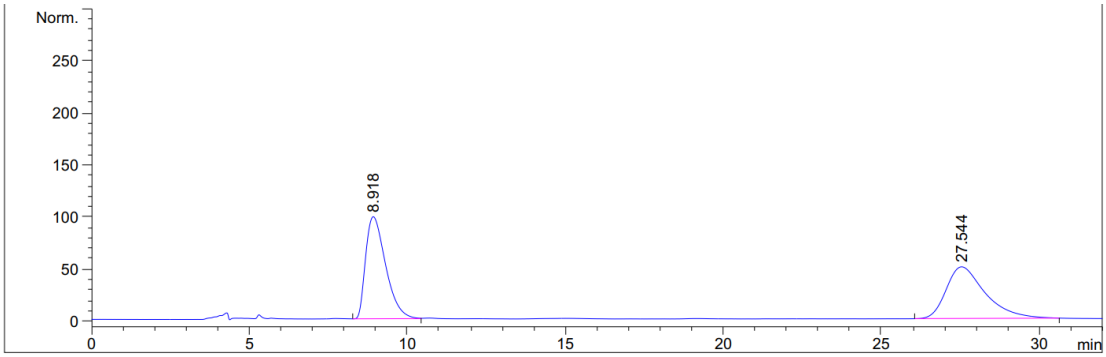
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.621	MM	0.2792	1778.18542	106.15471	6.5164
2	10.738	MM	0.4805	2.55095e4	884.77563	93.4836

(3bR,5S,6R,6aS)-1'-Benzyl-6,10-diphenyl-3b,4,6,6a-tetrahydro-7H-spiro[benzo[b]dipyrrolo[1,2-d:2',3'-f][1,4]oxazocine-5,3'-indoline]-2',7-dione (10)



Prepared according to the procedure within 8 h as white solid (55.2 mg, 90% yield, dr > 20:1). mp 245.4 – 246.2 °C; $[\alpha]_D^{18}$= 50.88 (*c* 0.23, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.71 – 7.65 (m, 3H), 7.62 – 7.51 (m, 4H), 7.50 – 7.44 (m, 1H), 7.26 – 7.06 (m, 8H), 7.02 (d, *J* = 7.4 Hz, 2H), 6.86 – 6.80 (m,

1H), 6.53 – 6.46 (m, 3H), 6.42 – 6.34 (m, 2H), 5.46 (d, J = 10.5 Hz, 1H), 4.92 (d, J = 16.0 Hz, 1H), 4.53 (d, J = 10.4 Hz, 1H), 4.39 (t, J = 10.5 Hz, 1H), 4.23 (d, J = 16.0 Hz, 1H), 2.52 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 169.8, 147.6, 143.7, 143.1, 138.9, 134.9, 134.7, 134.2, 131.7, 129.6, 129.1, 128.6, 128.5, 128.4, 128.2, 128.2, 127.7, 127.3, 127.2, 126.5, 125.9, 123.9, 123.2, 122.1, 120.8, 109.8, 109.3, 107.1, 72.1, 55.9, 54.7, 50.0, 43.3; HRMS (ESI) *m/z* Calcd. for $C_{41}H_{32}N_3O_3^+$ ($[M+H]^+$) 614.2438, Found 614.2437; Enantiomeric excess was determined to be 87% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 8.9 min, t_{minor} = 27.4 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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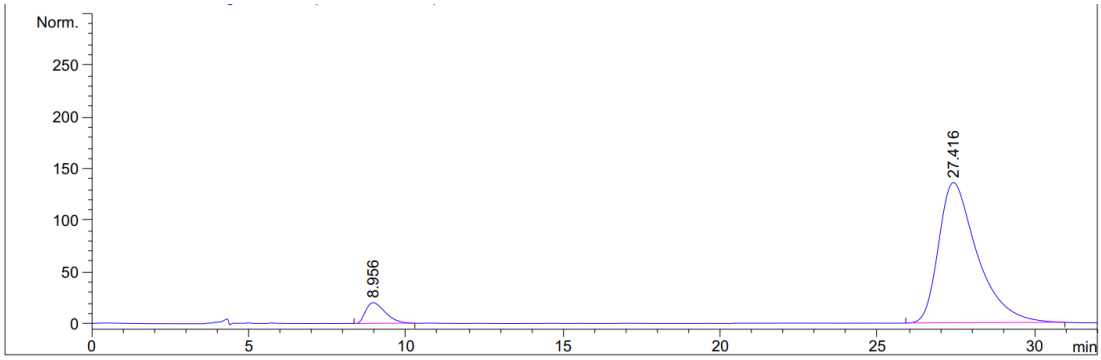
2	27.544	BB	1.2577	4279.32617	49.70784	49.6759

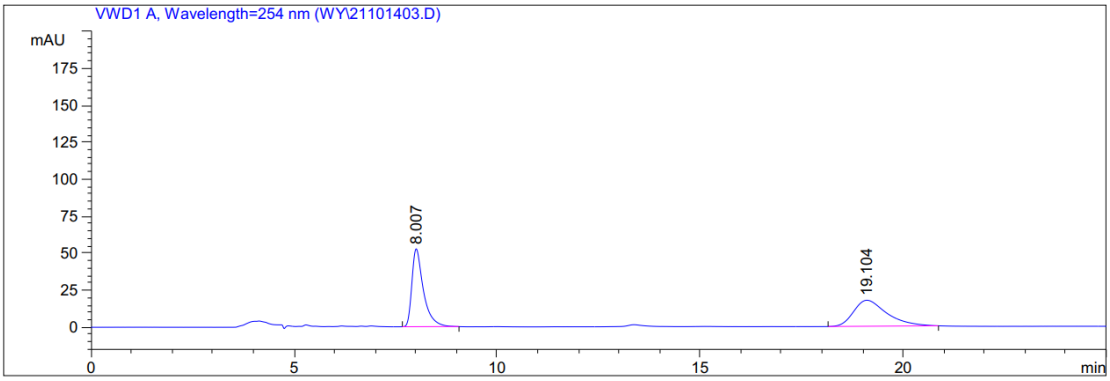


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.956	PB	0.6384	875.26666	20.06952	7.0056
2	27.416	BB	1.2575	1.16185e4	135.77116	92.9944

Compound 11 to 4aa

Enantiomeric excess was determined to be 75% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 80/20, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} =

19.3 min, t_{minor} = 8.0 min).



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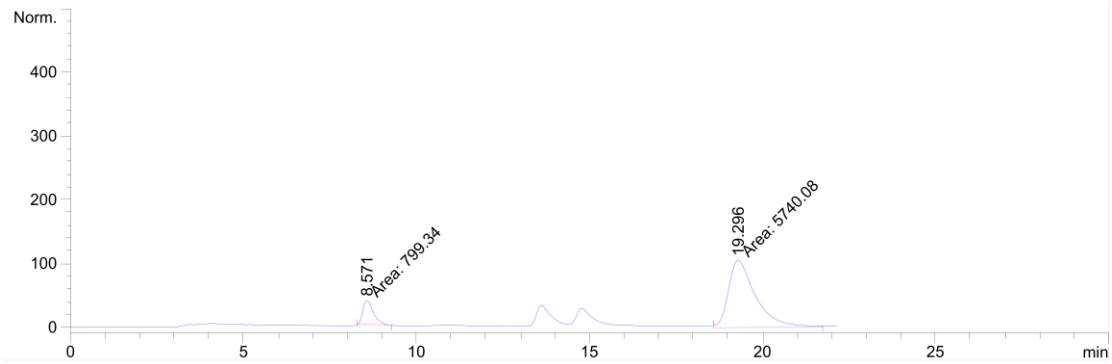
2	19.104	BB	0.8400	1009.96289	17.63408	49.1930



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1	8.571	MM	0.3574	799.34033	37.27414	12.2234
2	19.296	MM	0.9075	5740.08350	105.41896	87.7766

6. References

[1] The synthesis of 3-amino oxindole hydrochloride, see: W.-B. Chen, Z.-J. Wu, J. Hu, L.-F. Cun, X.-M. Zhang, W.-C. Yuan, *Org. Lett.* **2011**, *13*, 2472.

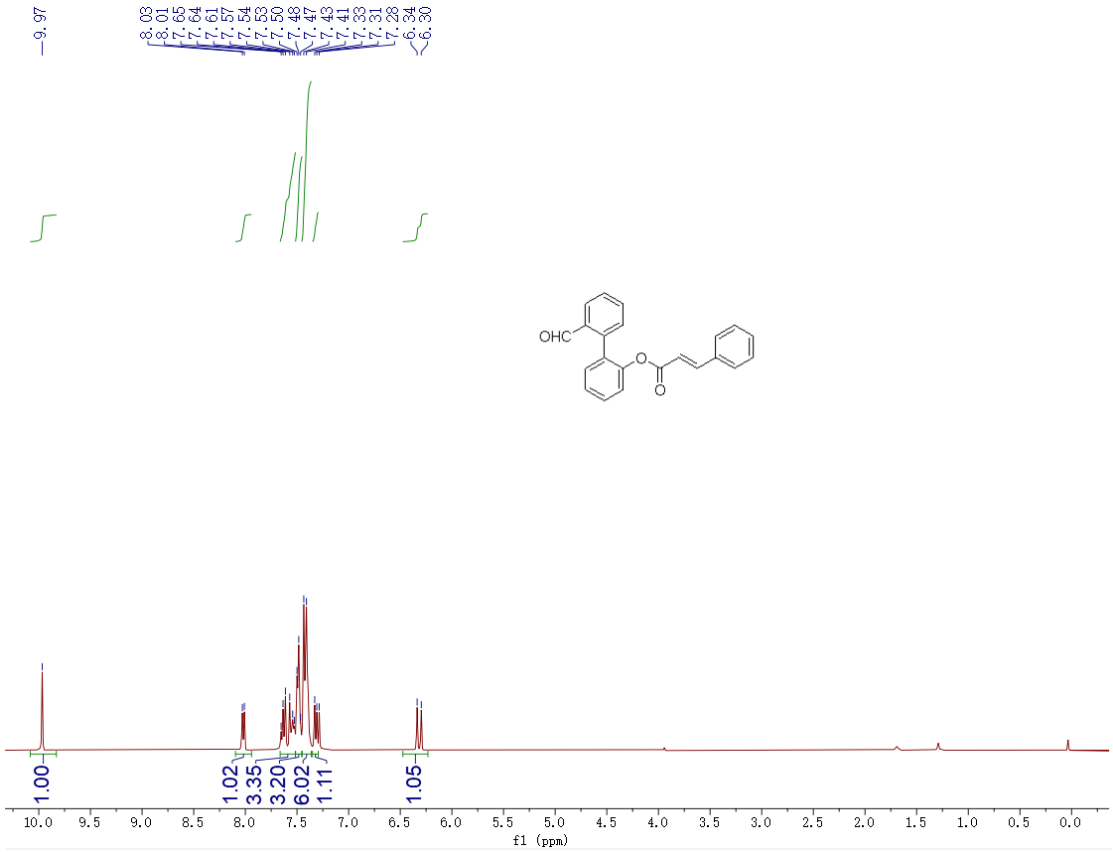
[2] T. Yang, X.-C. Guo, Q. Yin, X.-M. Zhang. *Chem. Sci.* **2019**, *10*, 2473-2477.

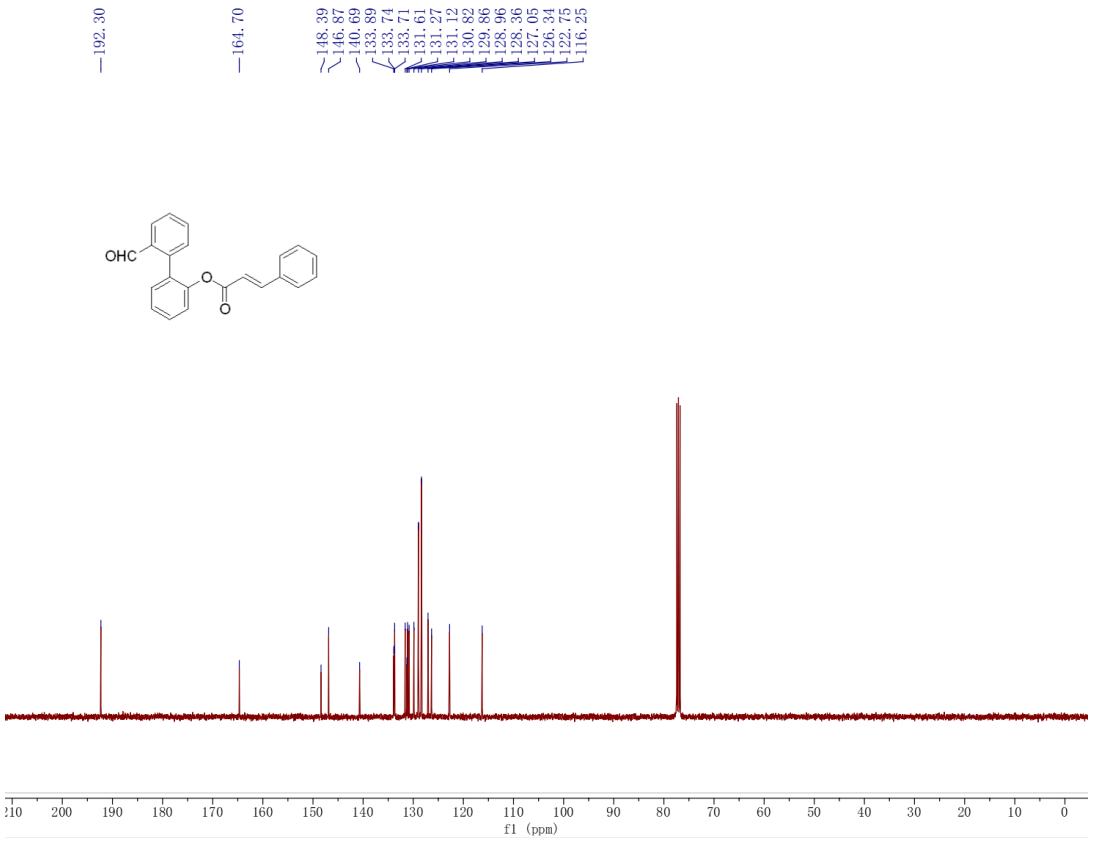
[3] L. Fu, S. Li, Z. Cai, Y. Ding, X.-Q. Guo, L.-P. Zhou, D. Yuan, Q.-F. Sun, G. Li, *Nat. Catal.* **2018**, *1*, 469-478.

[4] K. Grudzień, B. Trzaskowski, M. Smoleń, R. Gajda, K. Woźniak, K. Grela, *Dalton Trans.* **2017**, *46*, 11790-11799.

7. ^{1}H NMR and ^{13}C NMR spectra

3a





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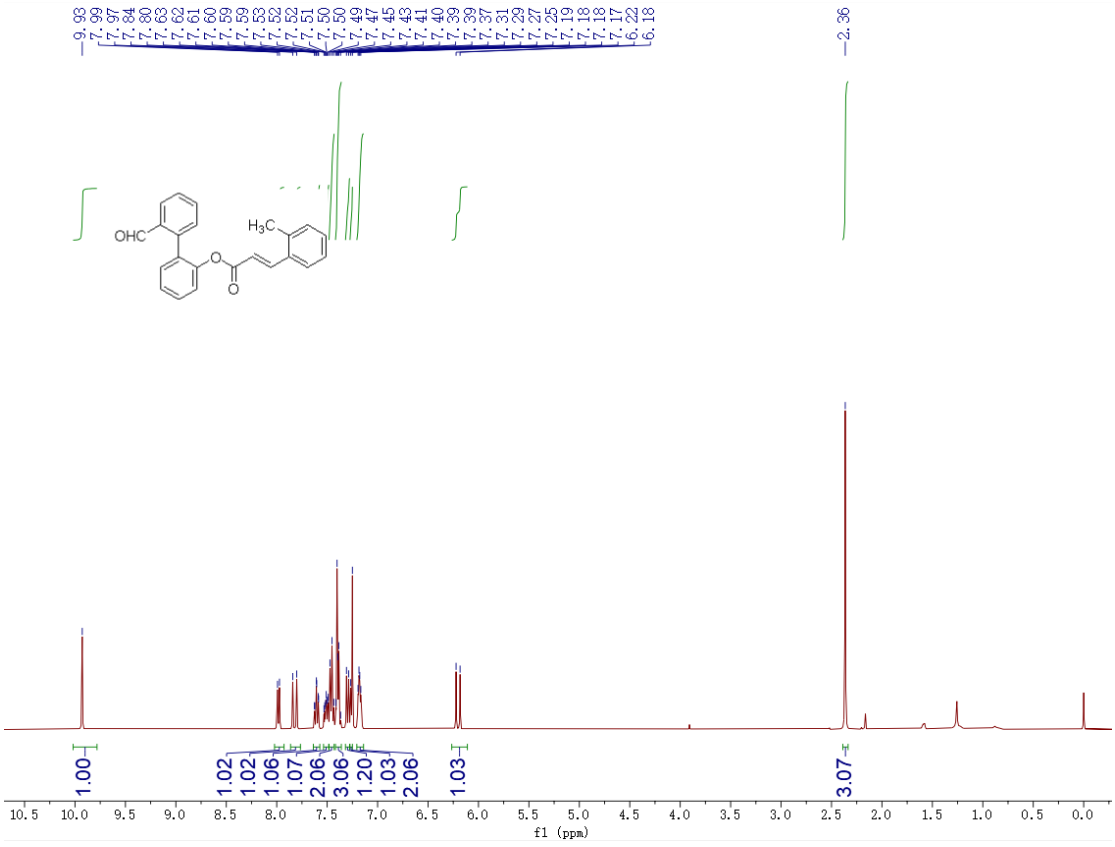
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6.18
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H3C
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O
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2.06
3.06
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2.06
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3.07
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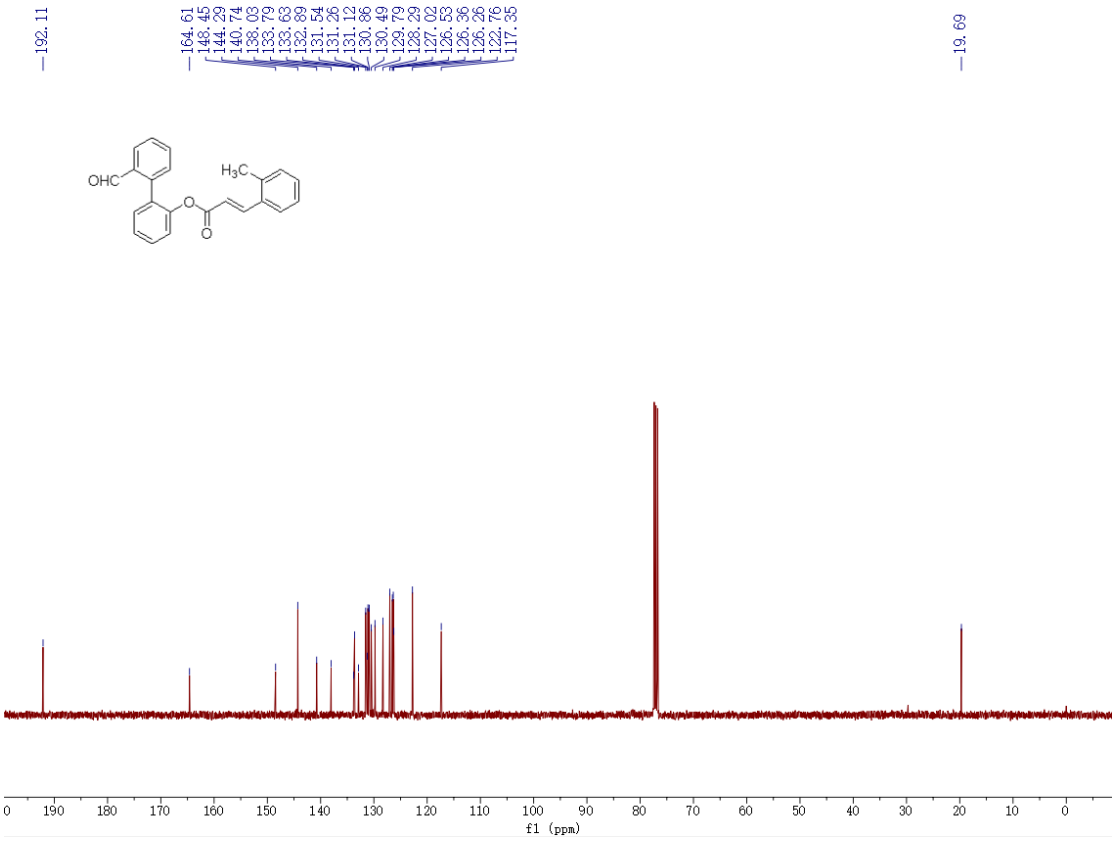
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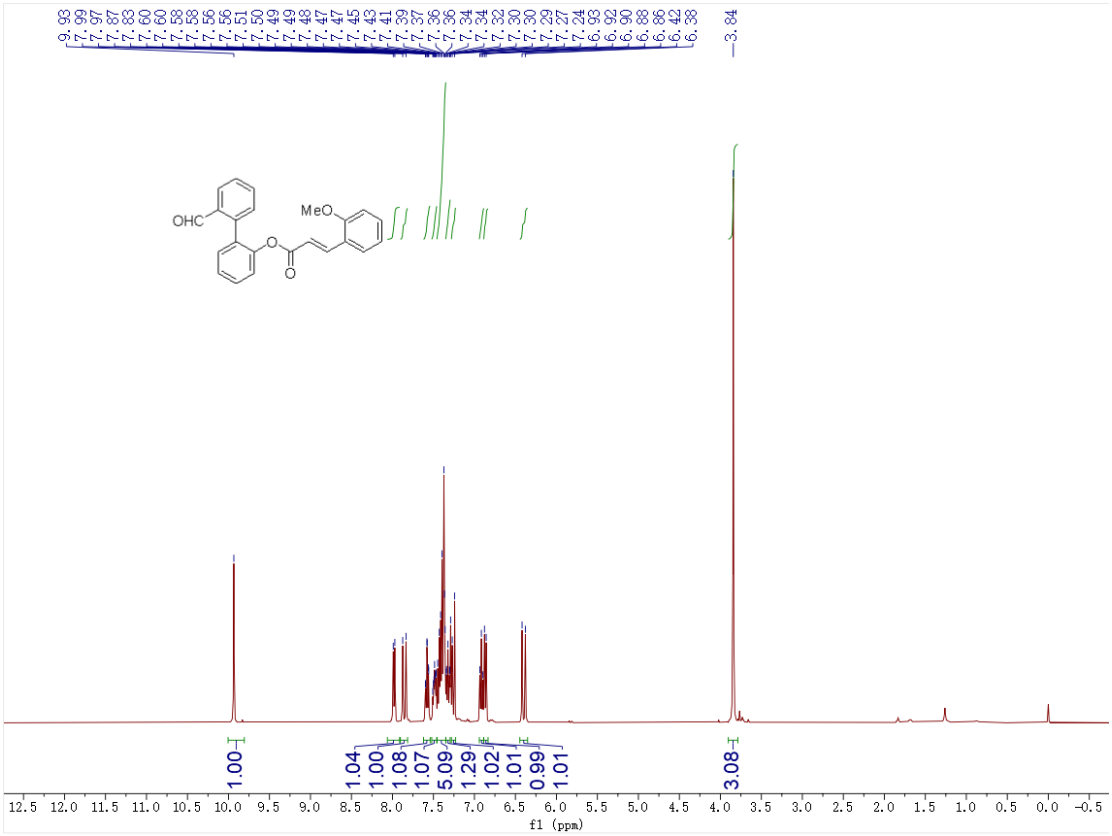
O
f1 (ppm)

3c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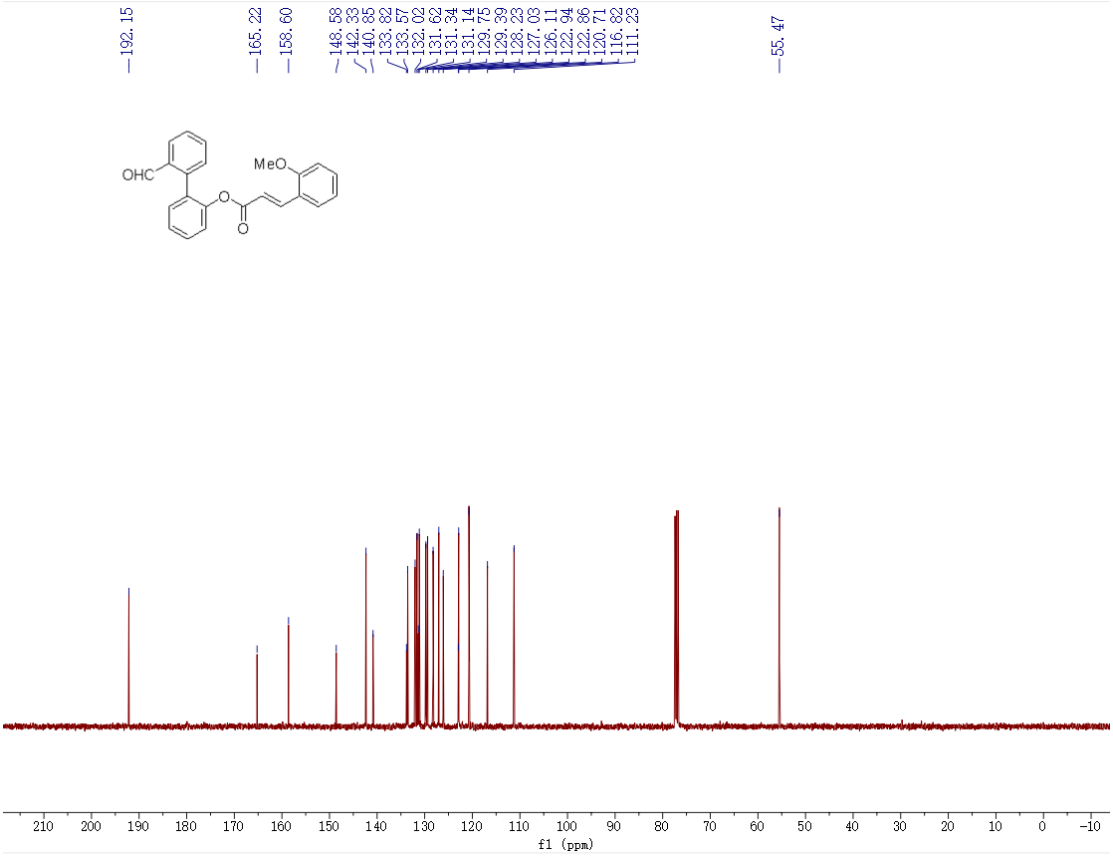
f1 (ppm)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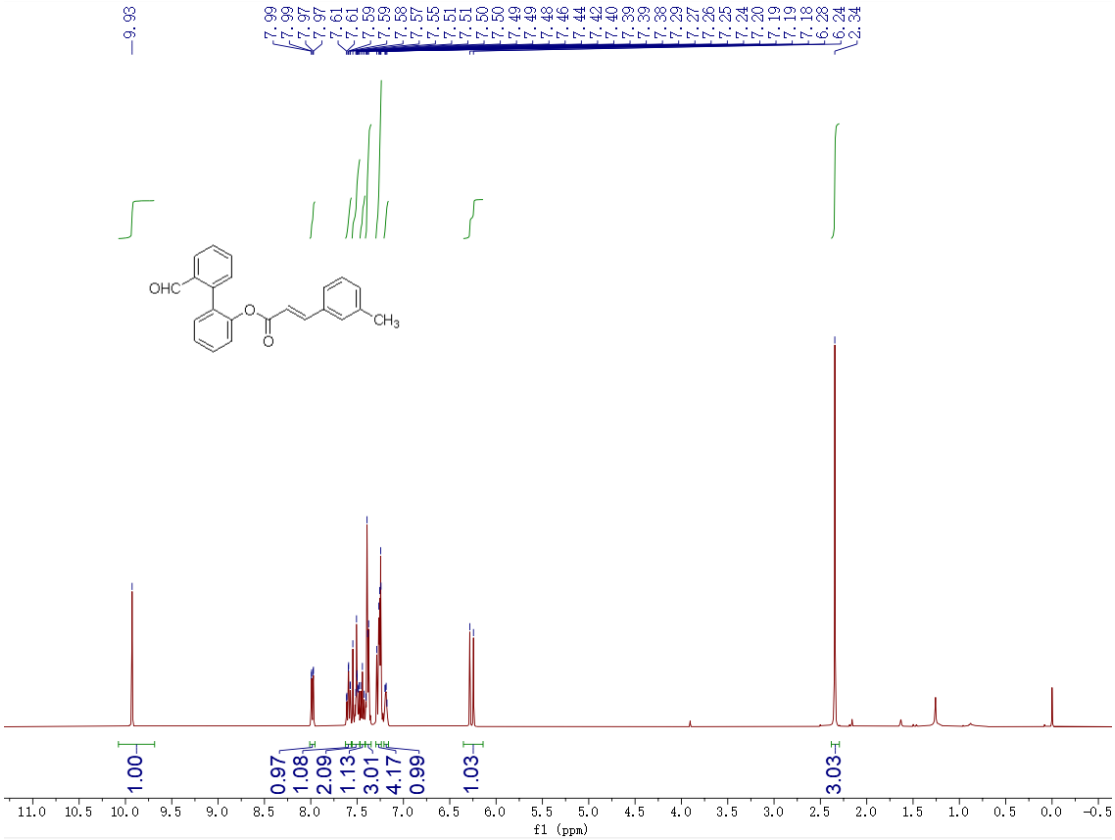
O
f1 (ppm)

3d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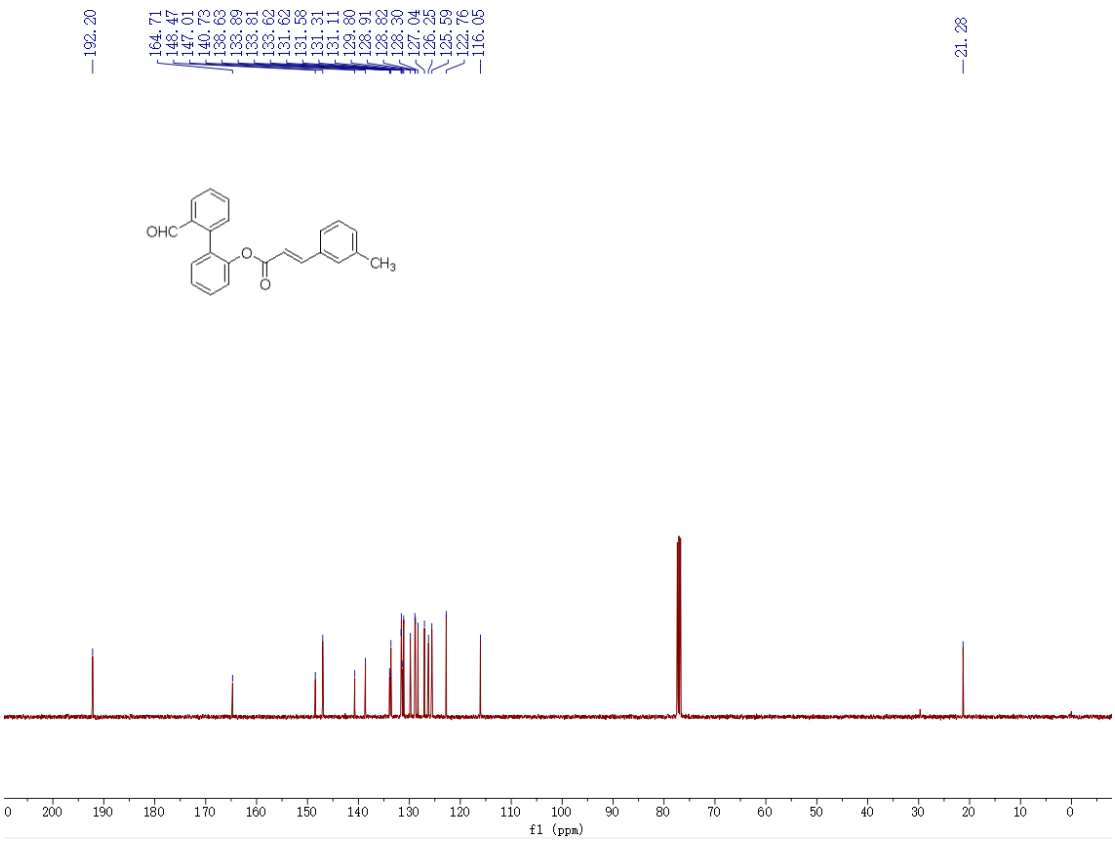
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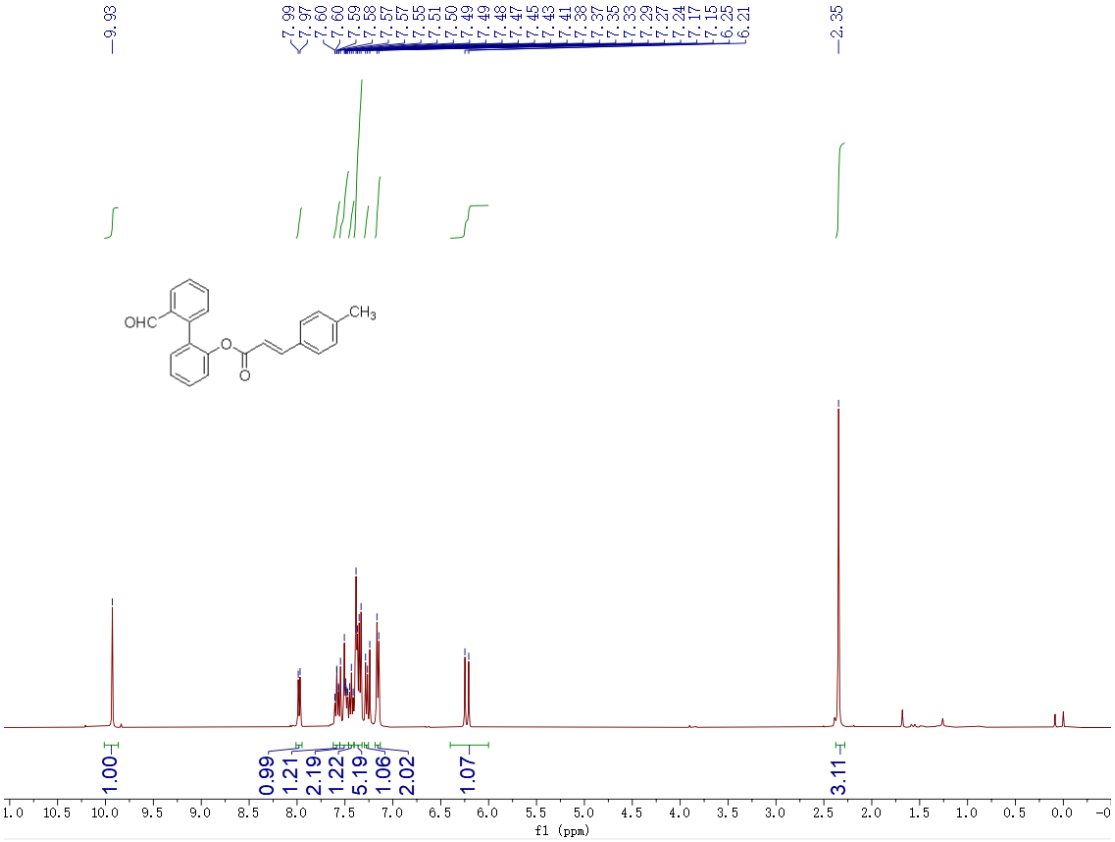
3e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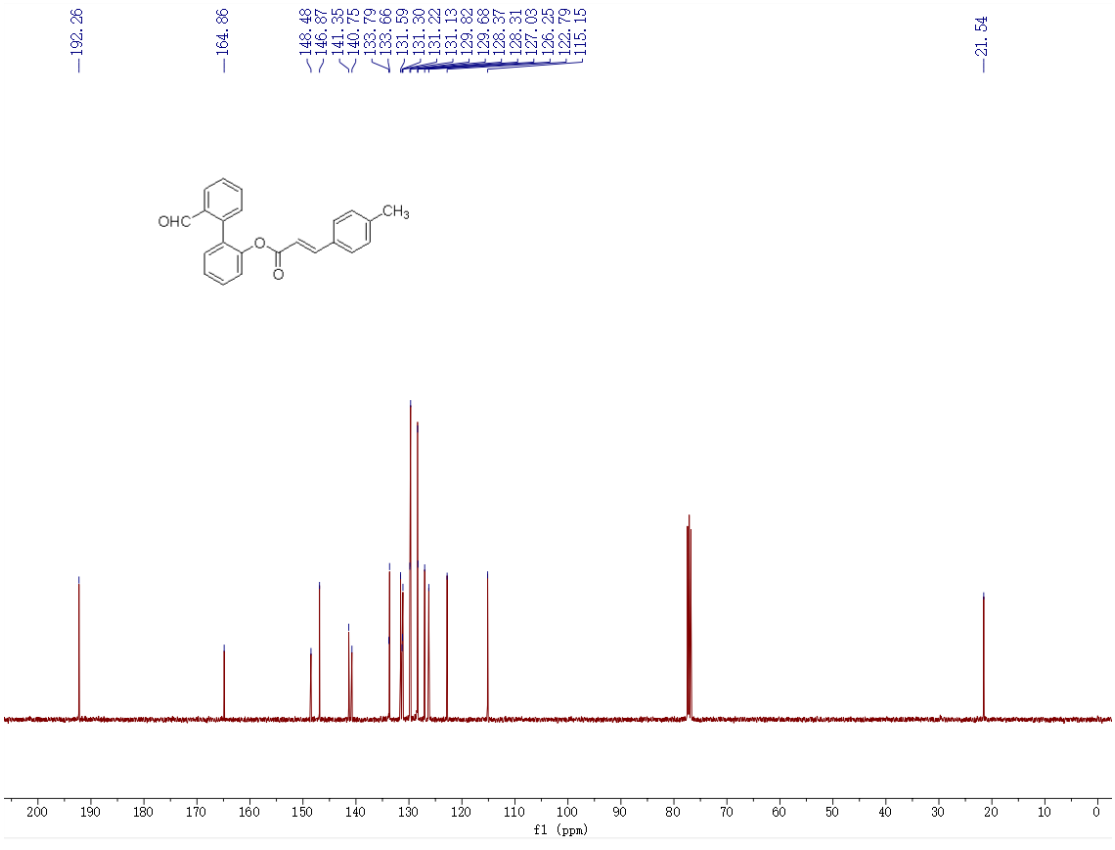
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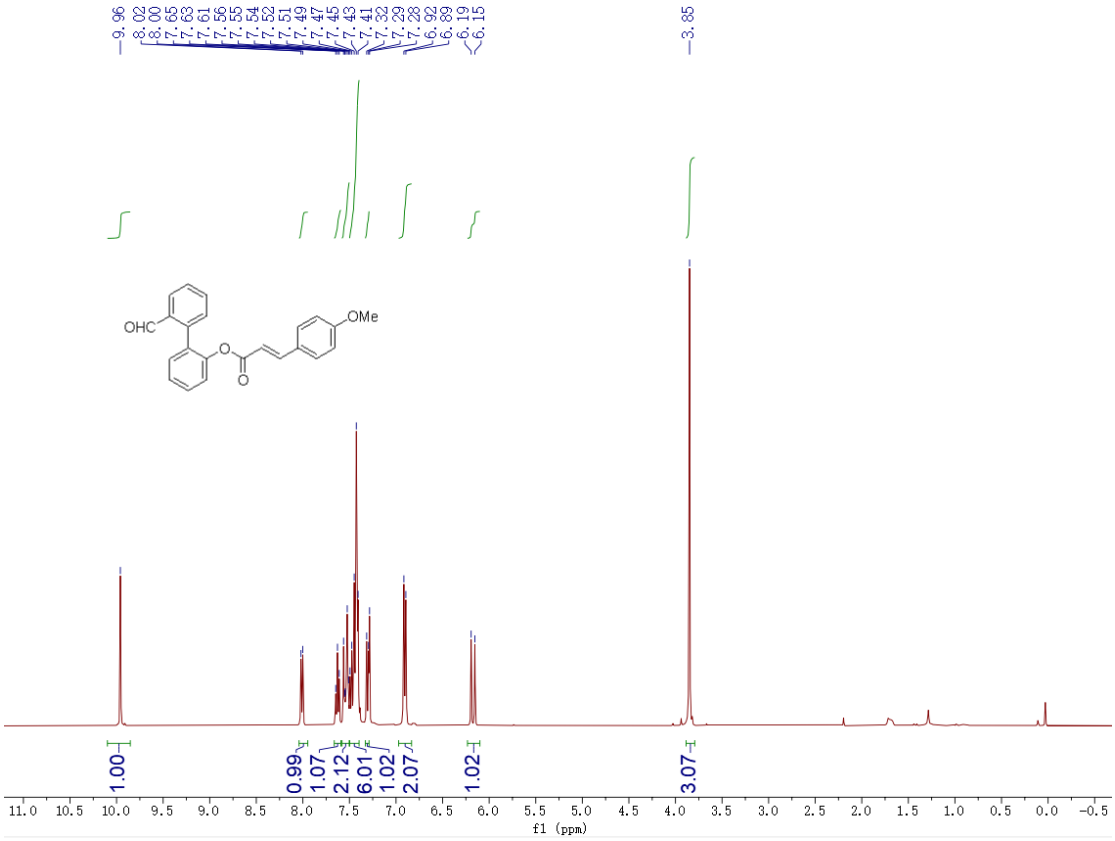
3f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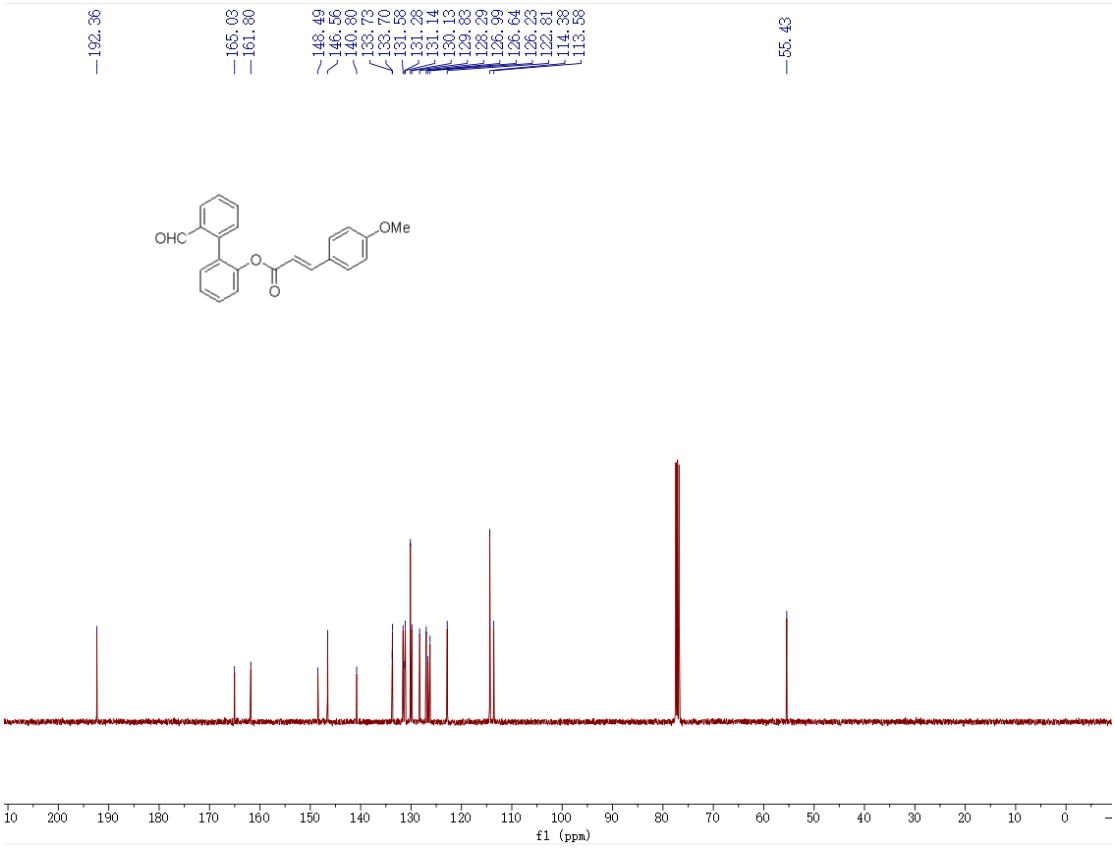
2.07
1.02
3.07
f1 (ppm)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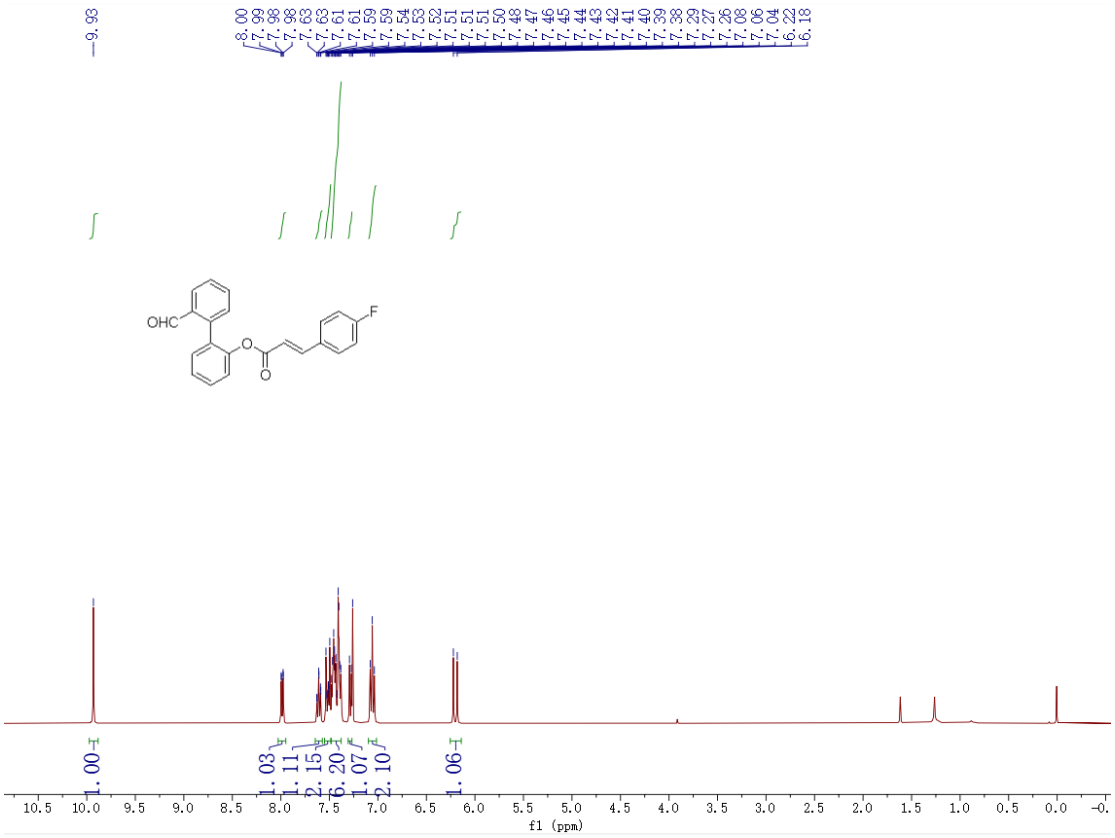
O
f1 (ppm)

3g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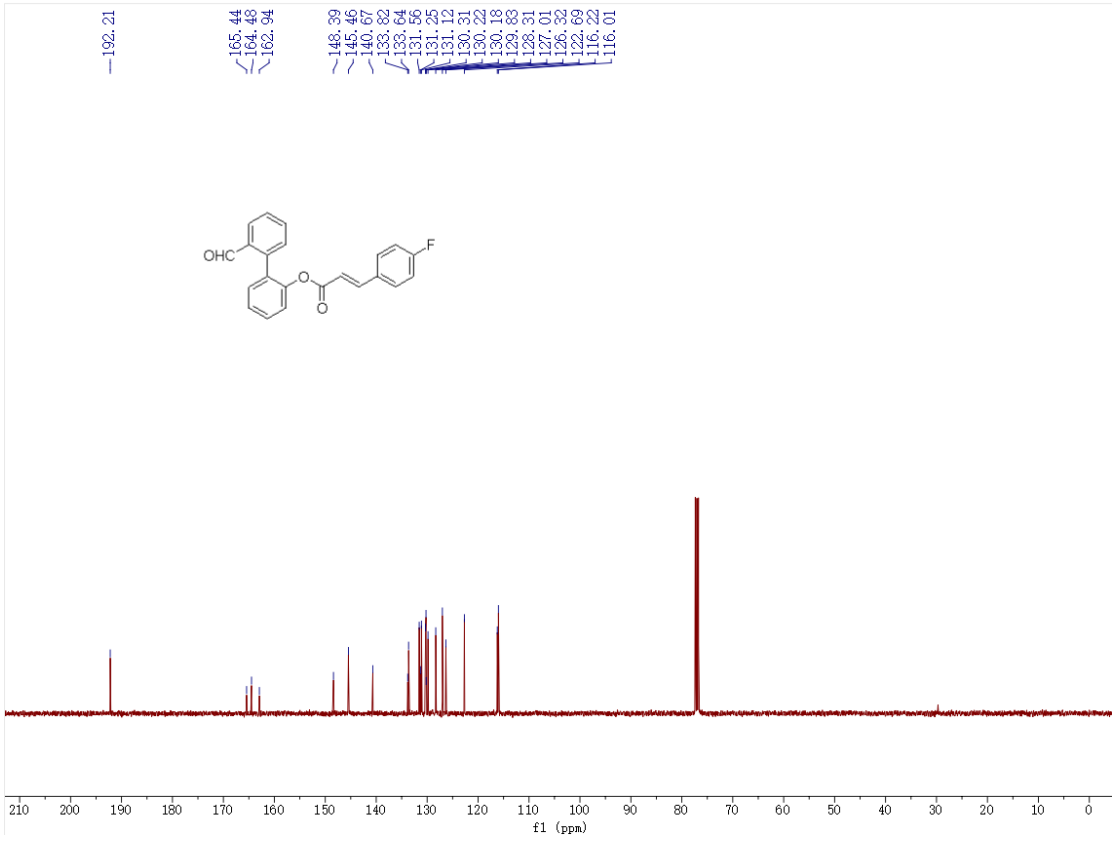
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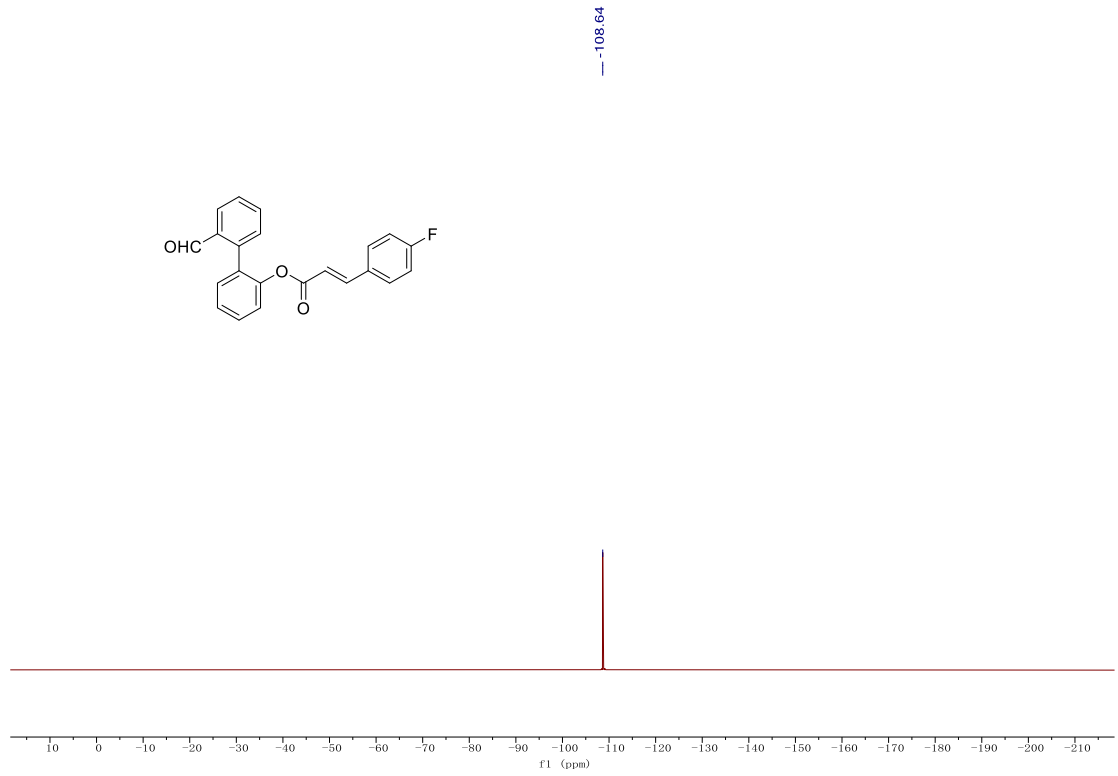
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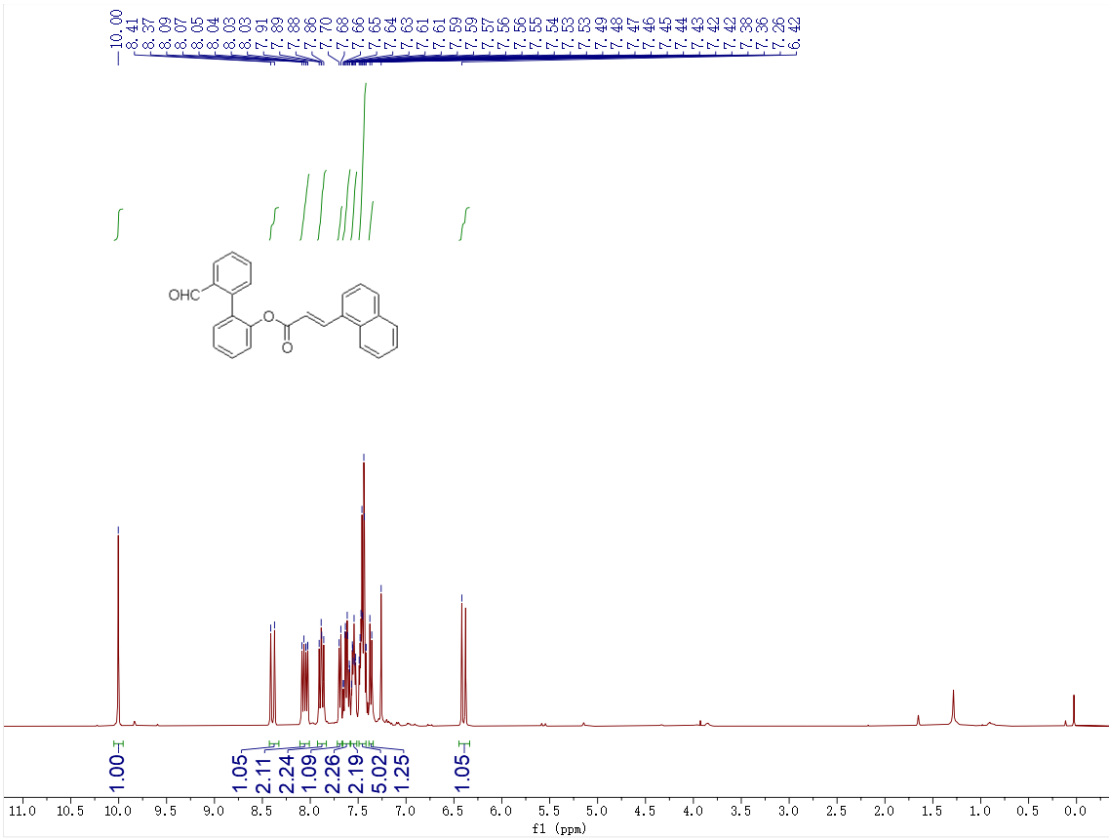
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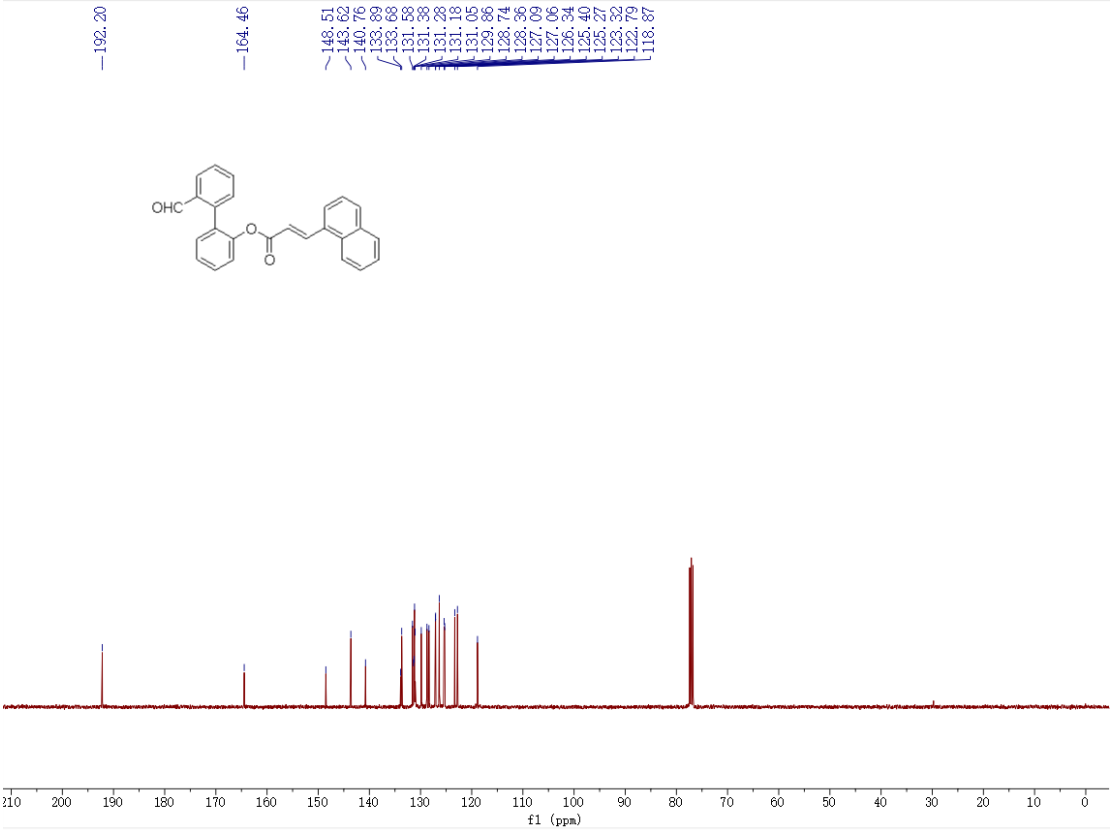
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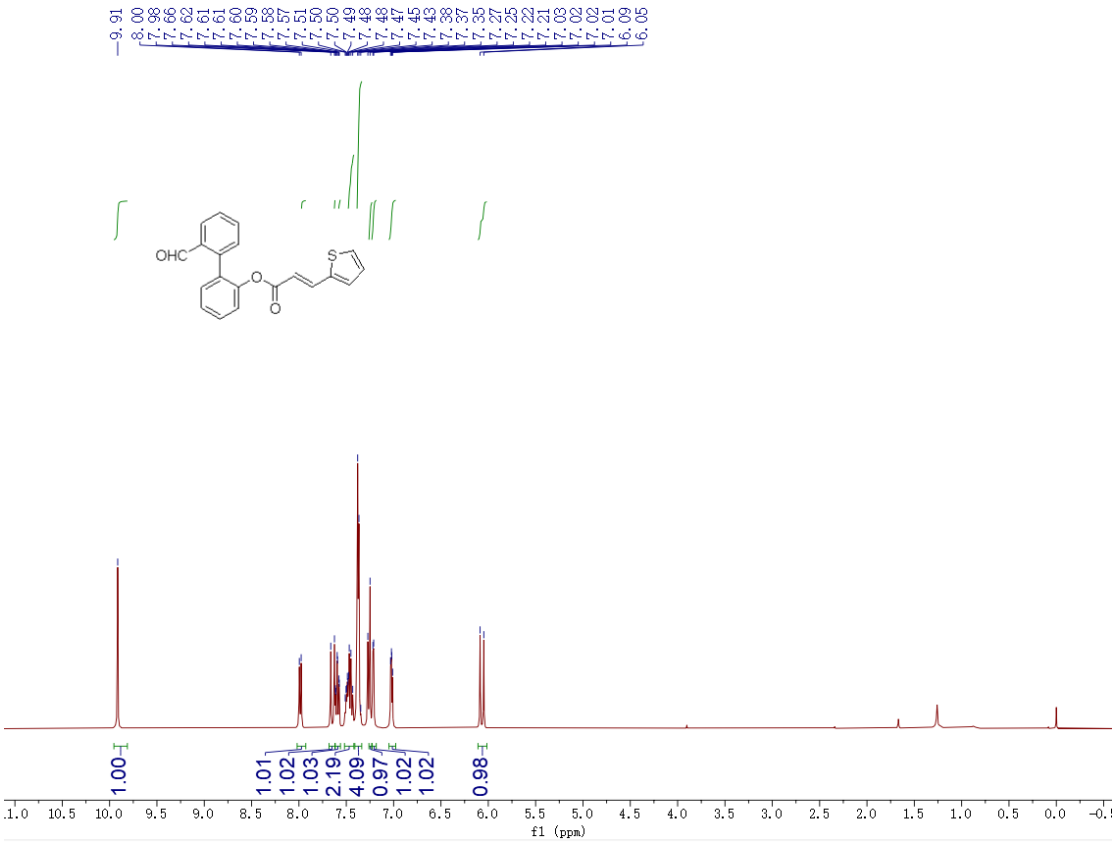
131.88
131.38
131.28
131.18
131.05
129.86
128.74
128.36
127.09
127.06
126.34
125.40
125.27
123.32
122.79
118.87
OHC
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3i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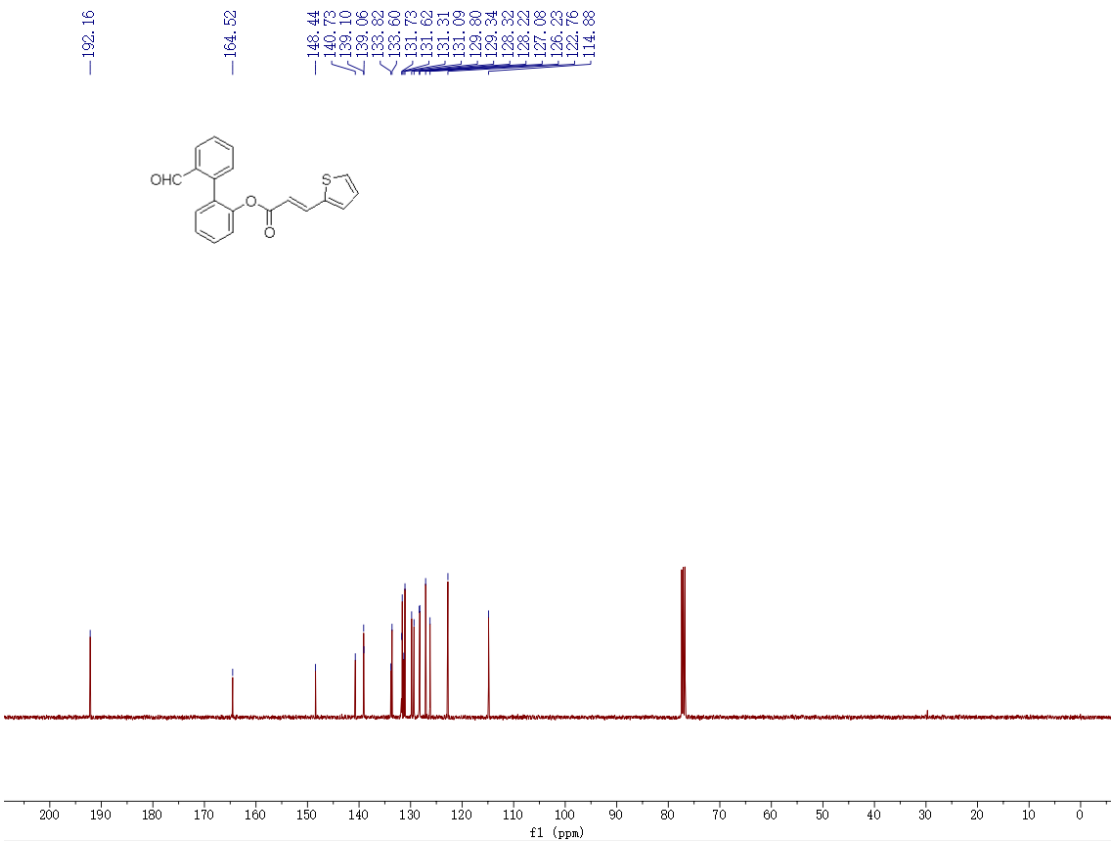
7.61
7.61
7.60
7.59
7.58
7.57
7.51
7.50
7.50
7.49
7.48
7.48
7.47
7.45
7.43
7.38
7.37
7.35
7.27
7.25
7.22
7.21
7.03
7.02
7.02
7.01
6.09
6.05
OHC
O
O
S
1.00
1.01
1.02
1.03
2.19
4.09
0.97
1.02
1.02
0.98
f1 (ppm)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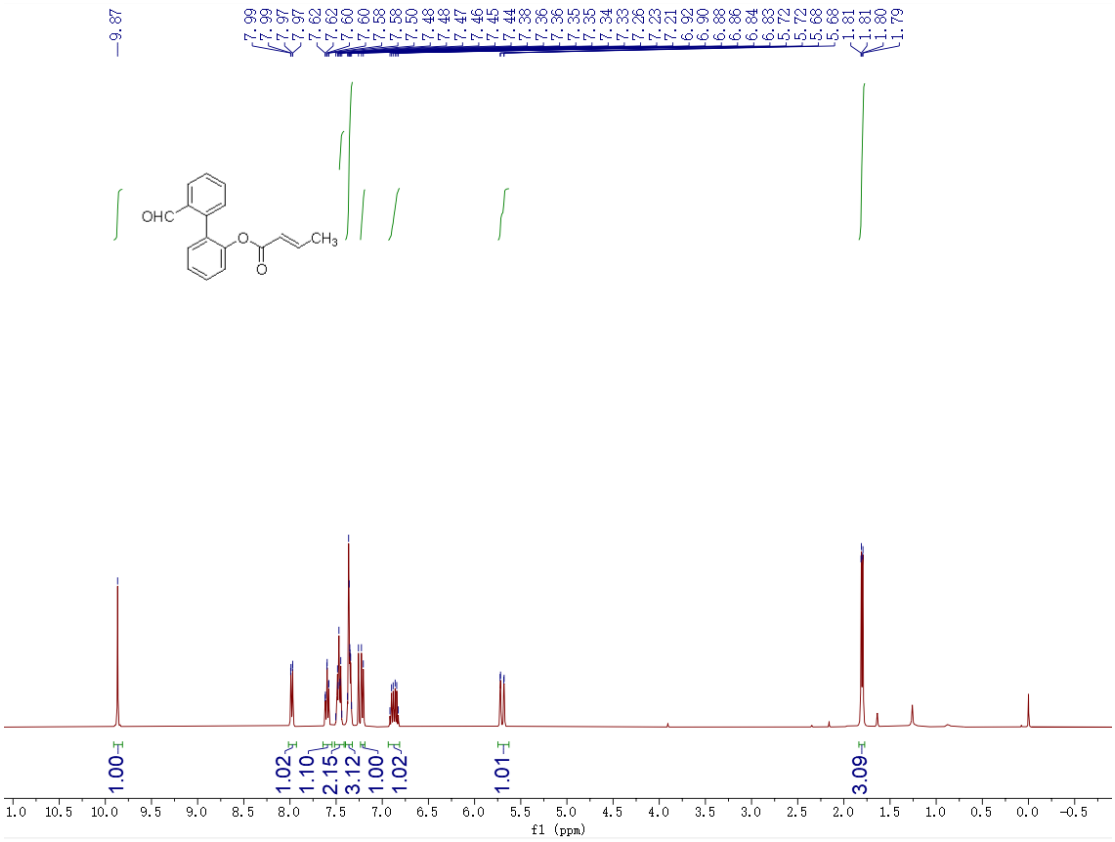
164.52
148.44
140.73
139.10
139.06
133.82
133.60
131.73
131.62
131.31
131.09
129.80
129.34
128.32
128.22
127.08
126.23
122.76
114.88
OHC
O
O
S
f1 (ppm)

3j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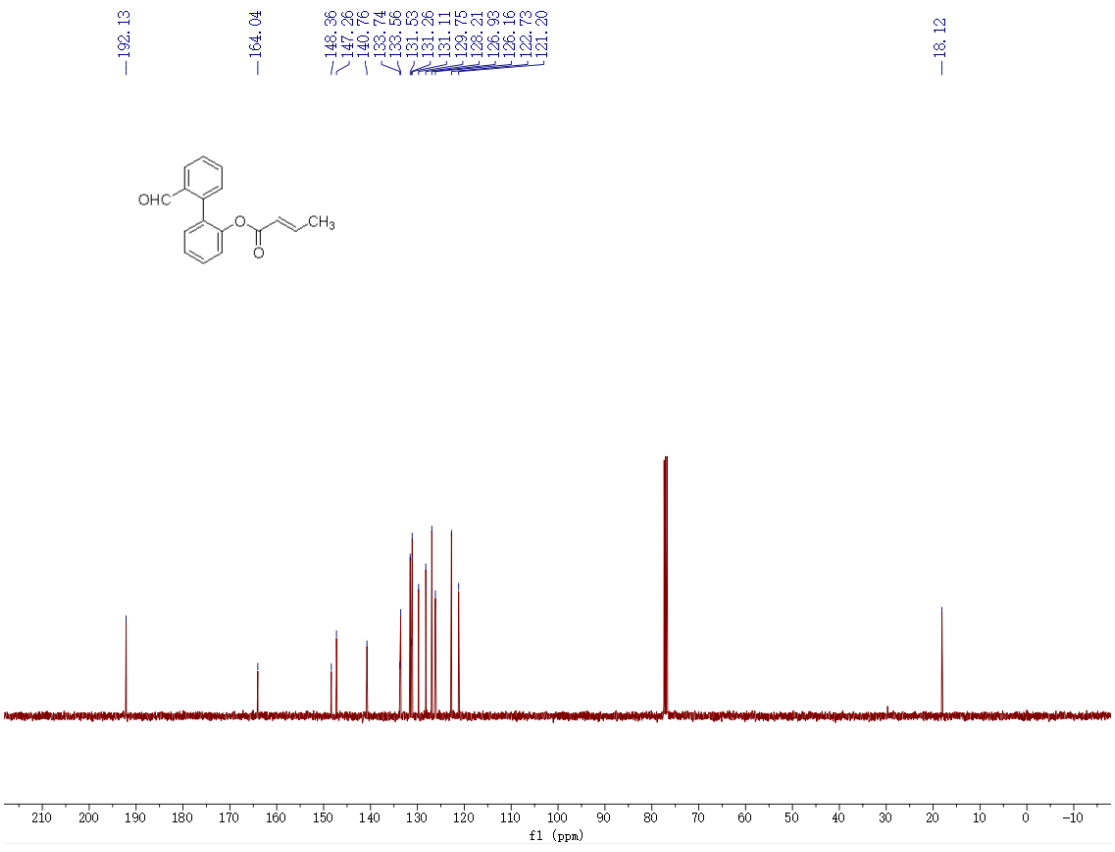
7.99
7.97
7.62
7.60
7.58
7.50
7.48
7.47
7.46
7.45
7.44
7.38
7.36
7.35
7.34
7.33
7.26
7.23
7.21
6.92
6.90
6.88
6.86
6.84
6.83
5.72
5.68
1.81
1.80
1.79
OHC
O
CH3
O
1.00
1.02
1.10
2.15
3.12
1.00
1.02
1.01
3.09
f1 (ppm)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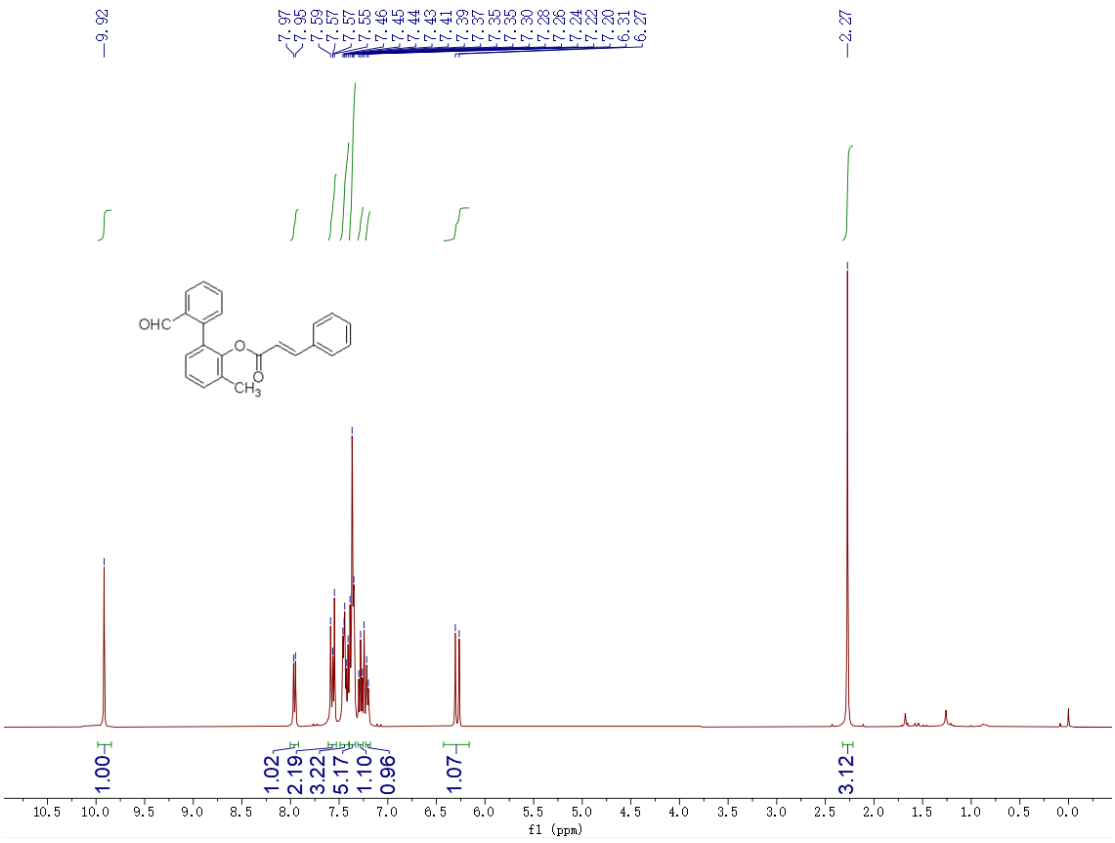
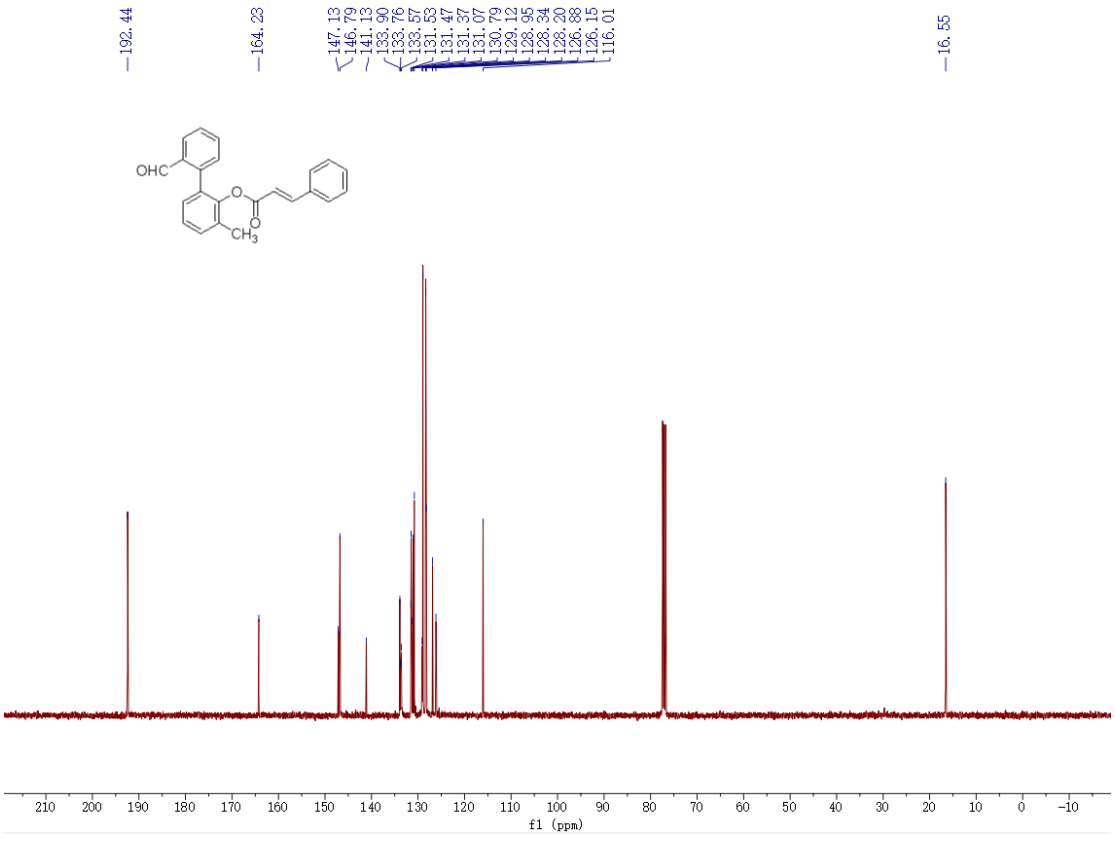
148.36
147.26
140.76
133.74
133.56
131.53
131.26
131.11
129.75
128.21
126.93
126.16
122.73
121.20
18.12
OHC
O
CH3
O
f1 (ppm)

3k


9.92
7.97
7.95
7.59
7.57
7.57
7.55
7.46
7.45
7.44
7.43
7.41
7.39
7.37
7.35
7.35
7.30
7.28
7.26
7.24
7.22
7.20
6.31
6.27
2.27
OHC
O
O
CH3
1.00
1.02
2.19
3.22
5.17
1.10
0.96
1.07
3.12
f1 (ppm)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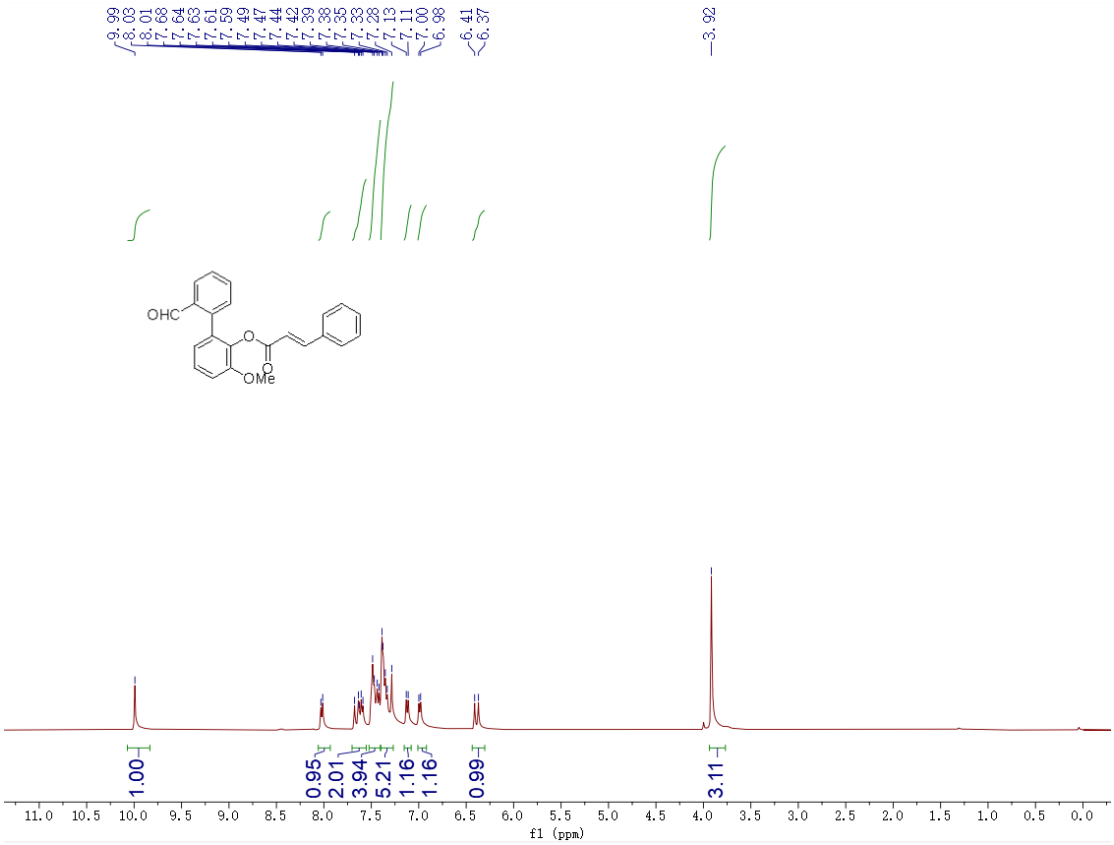
164.23
147.13
146.79
141.13
133.90
133.76
133.57
131.53
131.47
131.37
131.07
130.79
129.12
128.95
128.34
128.20
126.88
126.15
116.01
16.55
OHC
O
O
CH3
f1 (ppm)

3l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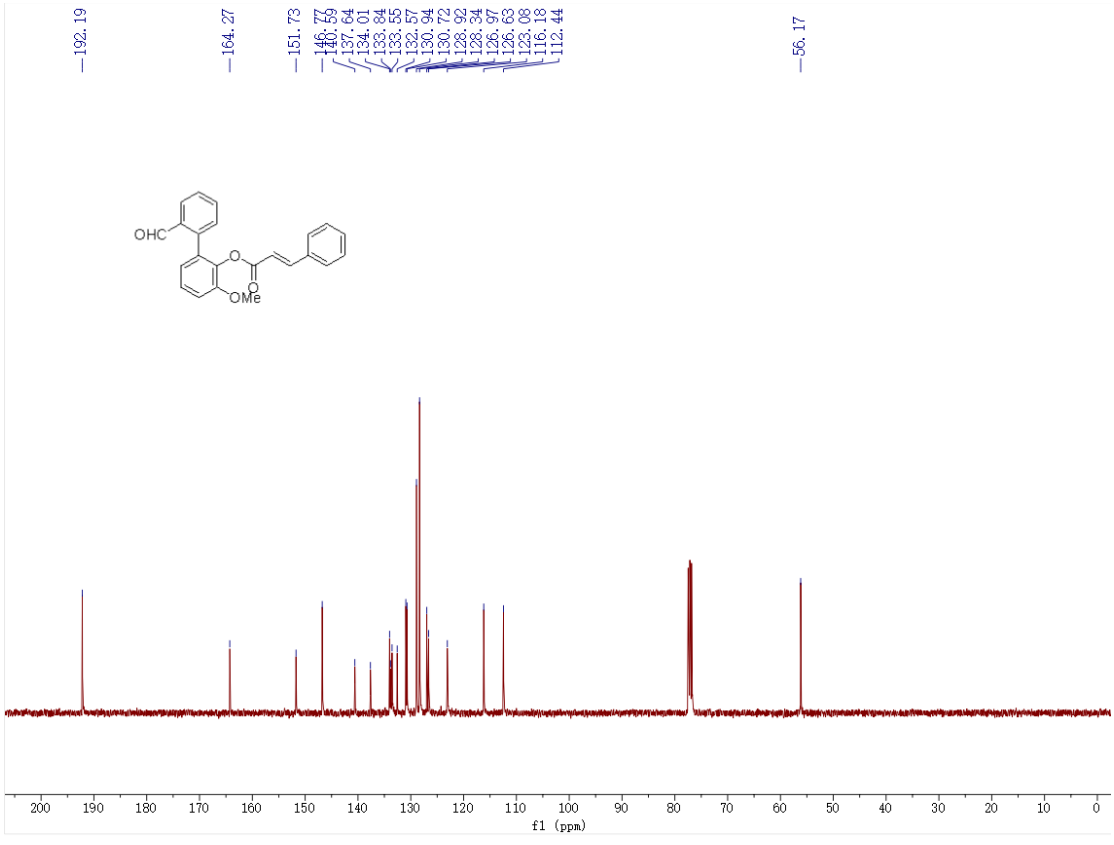
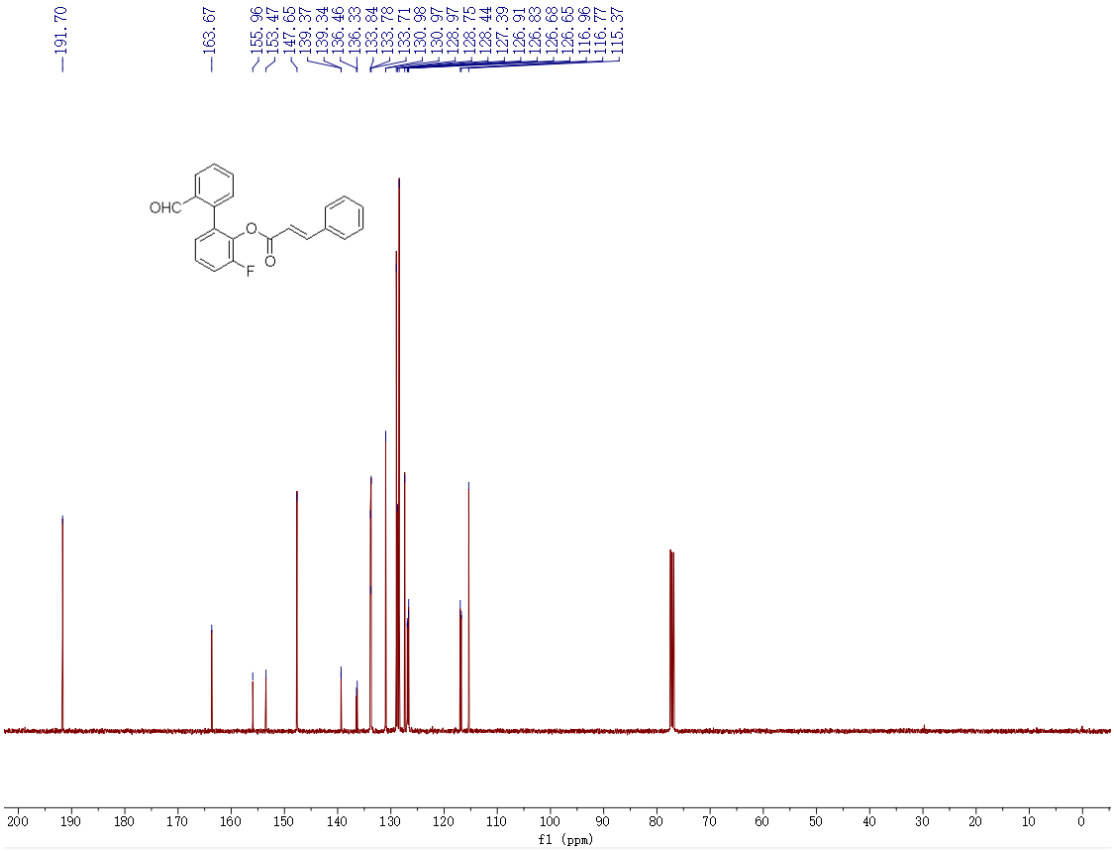
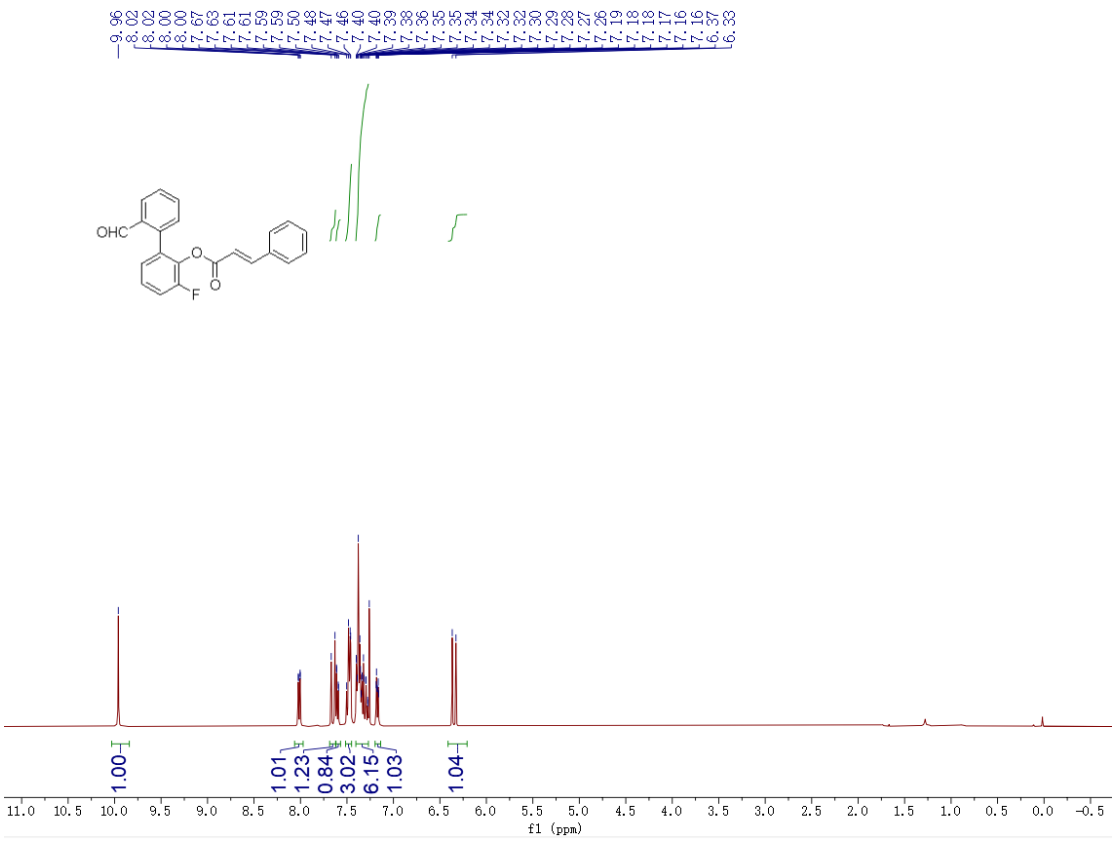
7.63
7.61
7.59
7.49
7.47
7.44
7.42
7.39
7.38
7.35
7.33
7.28
7.13
7.11
7.00
6.98
6.41
6.37
3.92
OHC
O
O
OMe
1.00
0.95
2.01
3.94
5.21
1.16
1.16
0.99
3.11
f1 (ppm)


192.19
164.27
151.73
146.77
140.59
137.64
134.01
133.84
133.55
132.57
130.94
130.72
128.92
128.34
126.97
126.63
123.08
116.18
112.44
56.17
OHC
O
O
OMe
f1 (ppm)

3m


191.70
163.67
155.96
153.47
147.65
139.37
139.34
136.46
136.33
133.84
133.78
133.71
130.98
130.97
128.97
128.75
128.44
127.39
126.91
126.83
126.68
126.65
116.96
116.77
115.37
OHC
O
O
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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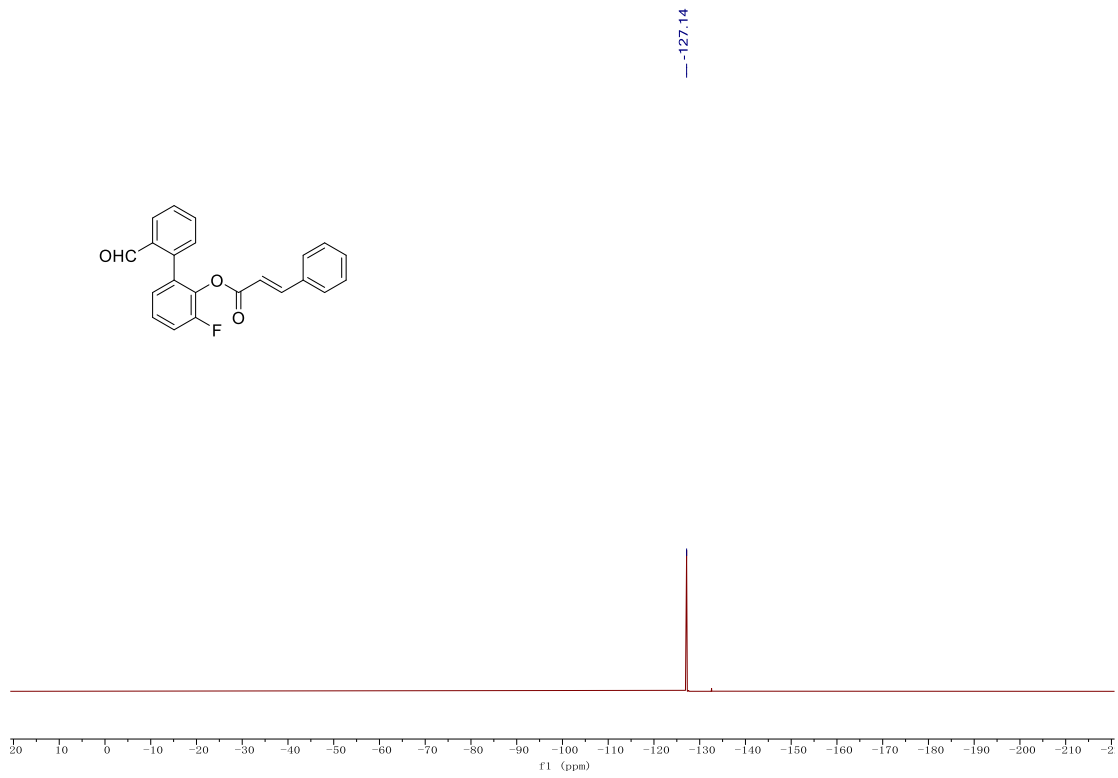
8.02
8.00
8.00
7.67
7.63
7.61
7.61
7.59
7.59
7.50
7.48
7.47
7.46
7.40
7.40
7.39
7.38
7.36
7.35
7.35
7.34
7.34
7.32
7.32
7.30
7.29
7.28
7.27
7.26
7.19
7.18
7.17
7.16
7.16
6.37
6.33
OHC
O
O
F
1.00
1.01
1.23
0.84
3.02
6.15
1.03
1.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


-127.14
OHC
O
O
F
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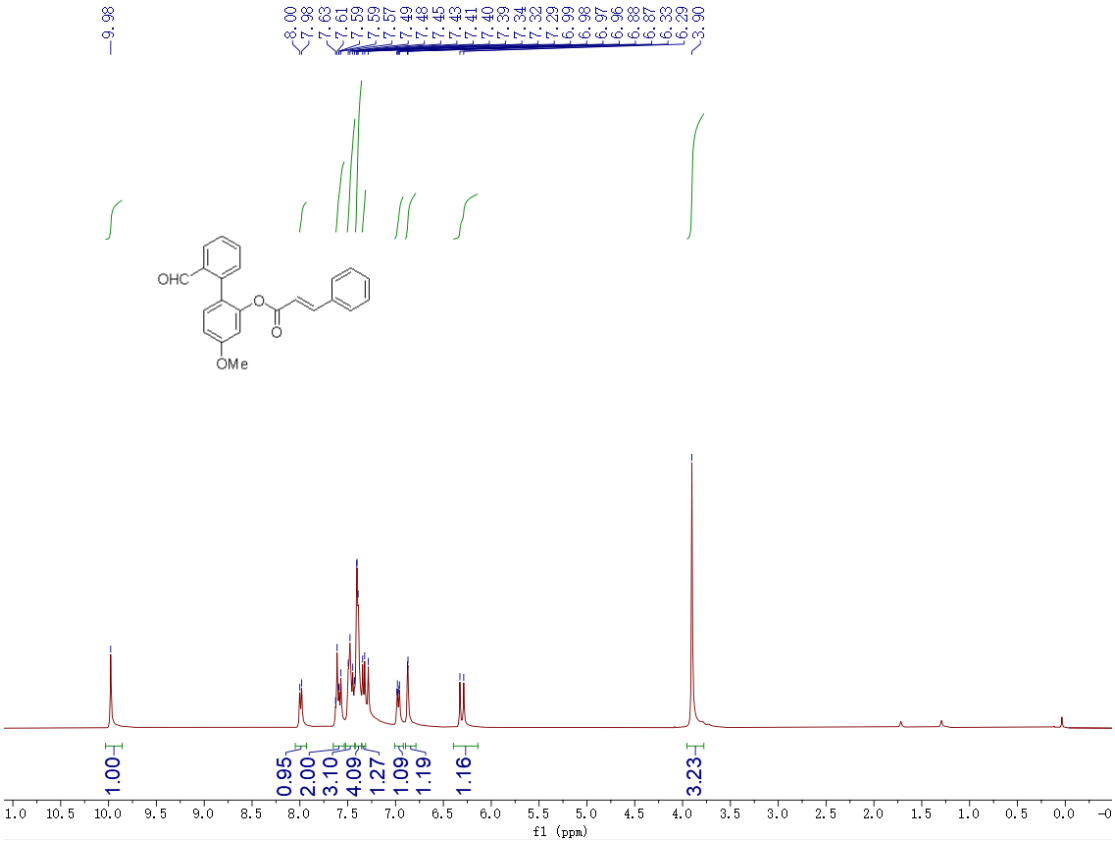
f1 (ppm)

3n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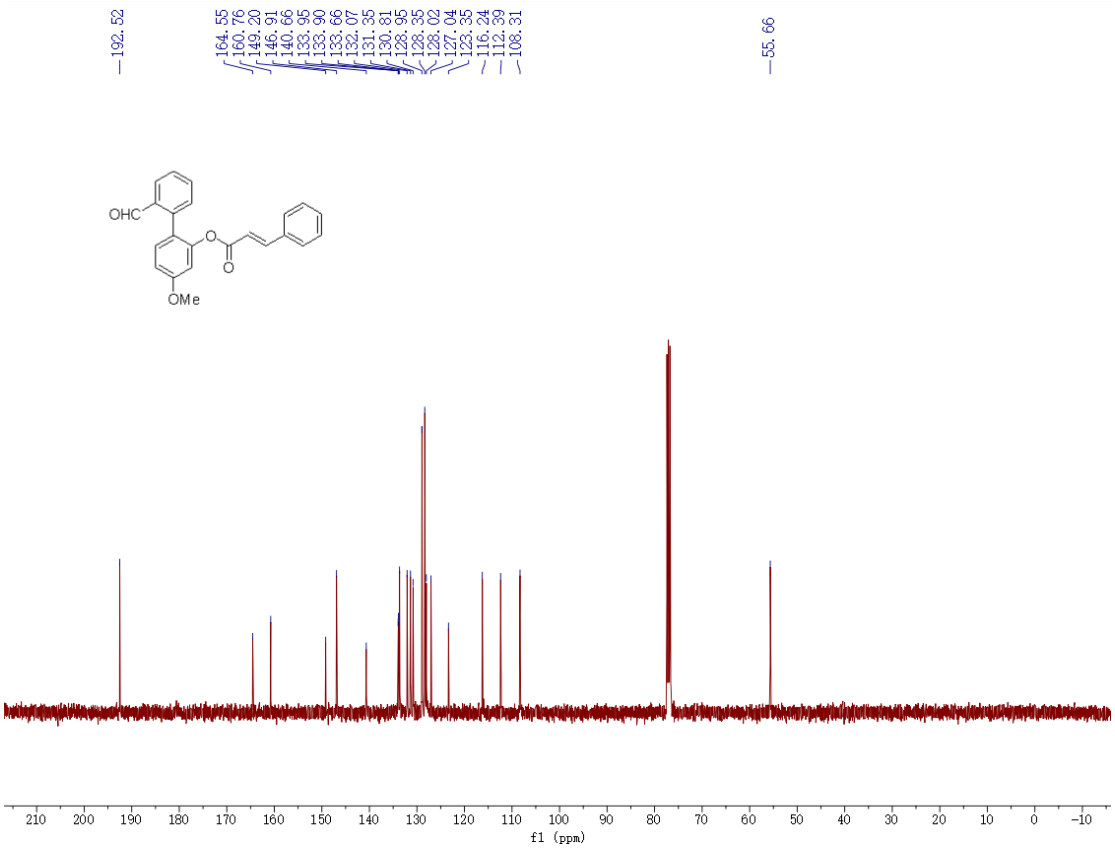
8.00
7.98
7.63
7.61
7.59
7.59
7.57
7.49
7.48
7.45
7.43
7.41
7.40
7.39
7.34
7.32
7.29
6.99
6.98
6.97
6.96
6.88
6.87
6.33
6.29
3.90
OHC
O
O
OMe
1.00
0.95
2.00
3.10
4.09
1.27
1.09
1.19
1.16
3.23
f1 (ppm)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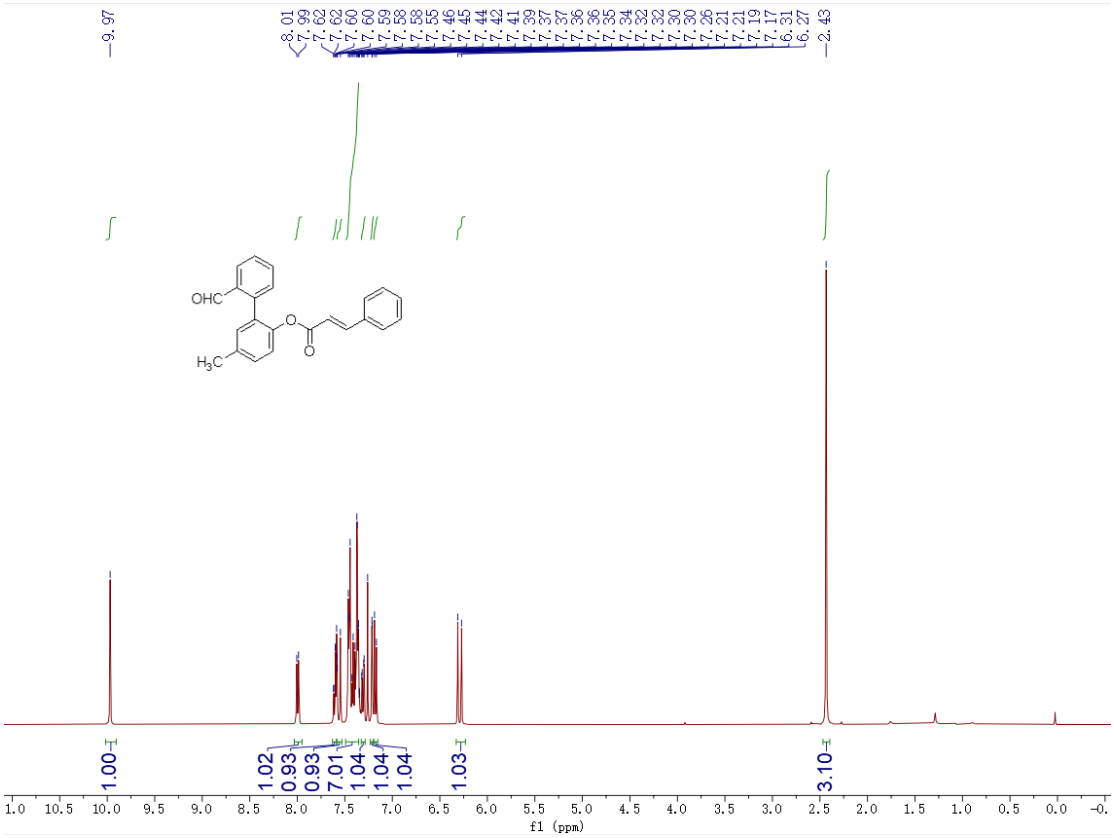
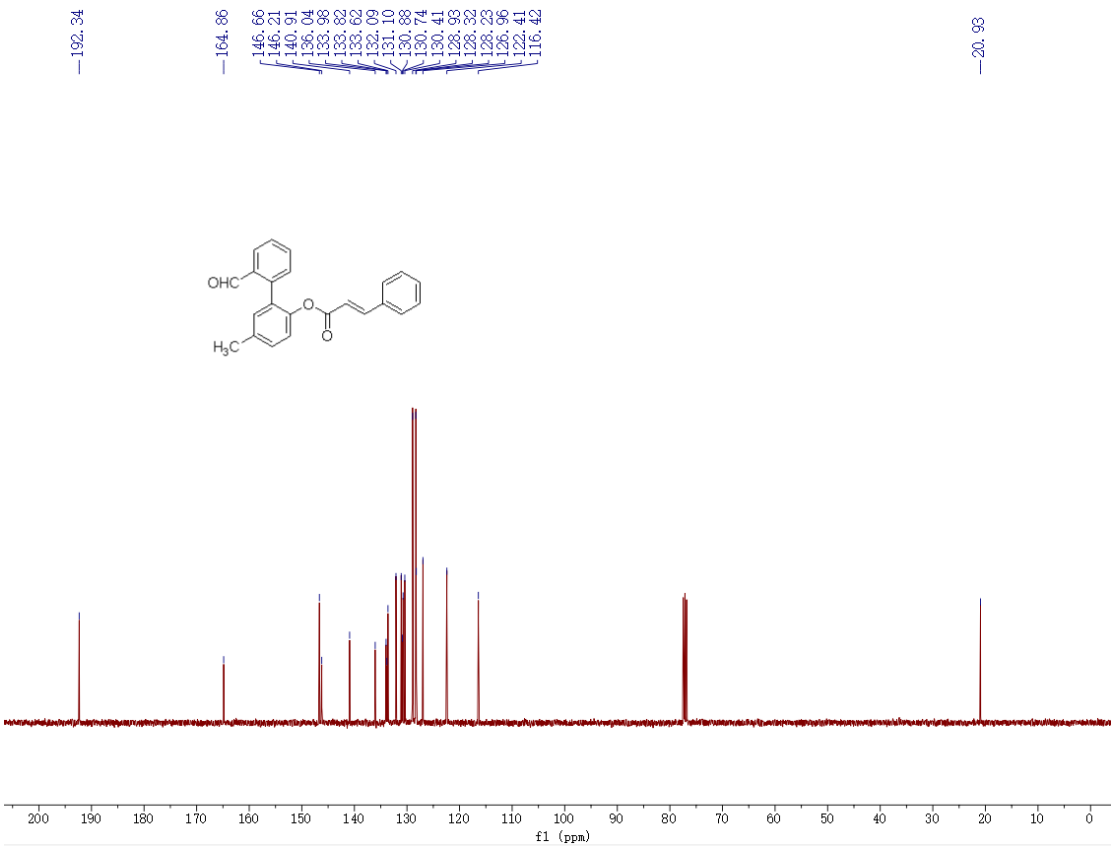
164.55
160.76
149.20
146.91
140.66
133.95
133.90
133.66
132.07
131.35
130.81
128.95
128.35
128.02
127.04
123.35
116.24
112.39
108.31
55.66
OHC
O
O
OMe
f1 (ppm)

3o


9.97
8.01
7.99
7.62
7.60
7.59
7.58
7.55
7.46
7.45
7.44
7.42
7.41
7.39
7.37
7.37
7.36
7.36
7.35
7.34
7.32
7.30
7.30
7.26
7.21
7.21
7.19
7.17
6.31
6.27
2.43
OHC
O
O
H3C
1.00
1.02
0.93
0.93
7.01
1.04
1.04
1.04
1.03
3.10
f1 (ppm)


192.34
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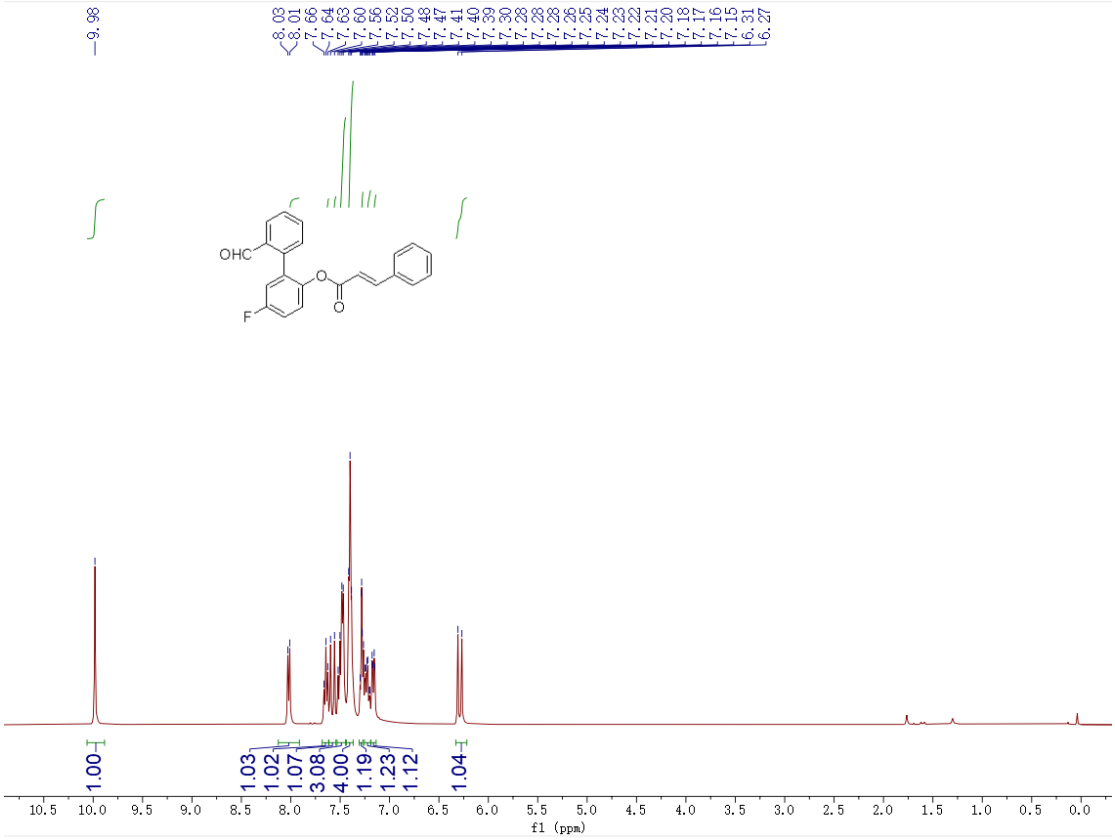
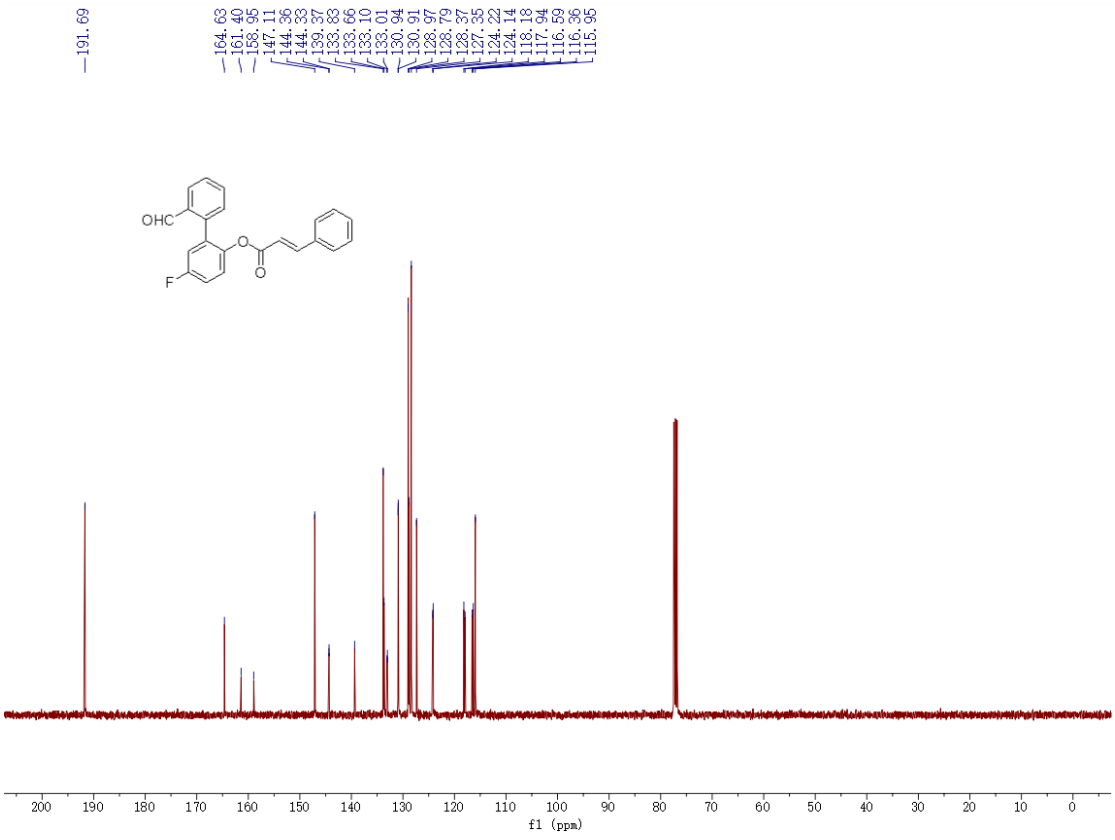
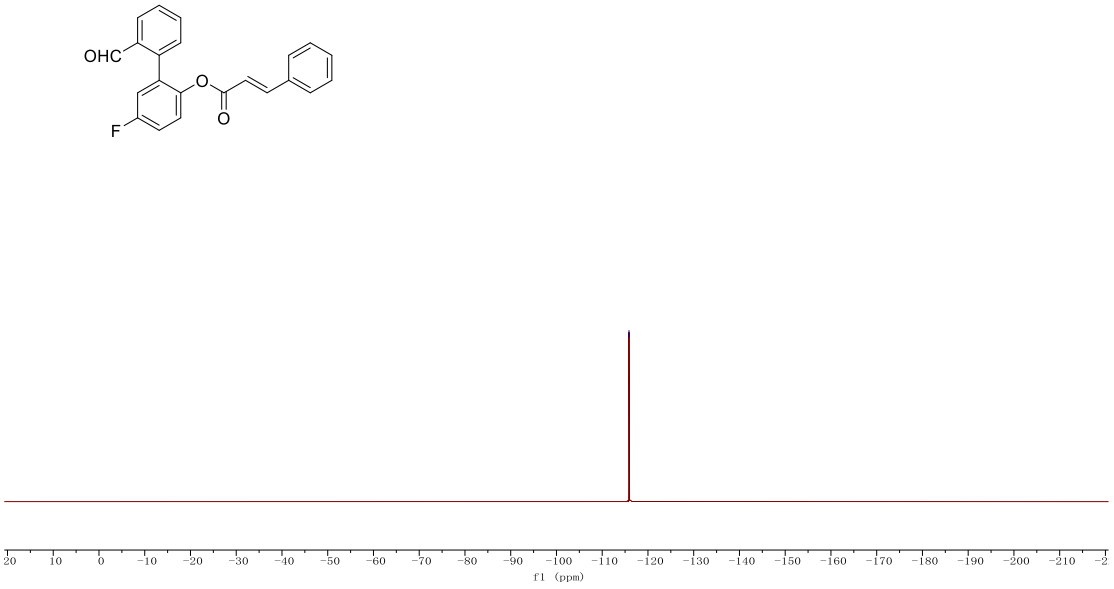
146.66
146.21
140.91
136.04
133.98
133.82
133.62
132.09
131.10
130.88
130.74
130.41
128.93
128.32
128.23
126.96
122.41
116.42
20.93
OHC
O
O
H3C
f1 (ppm)

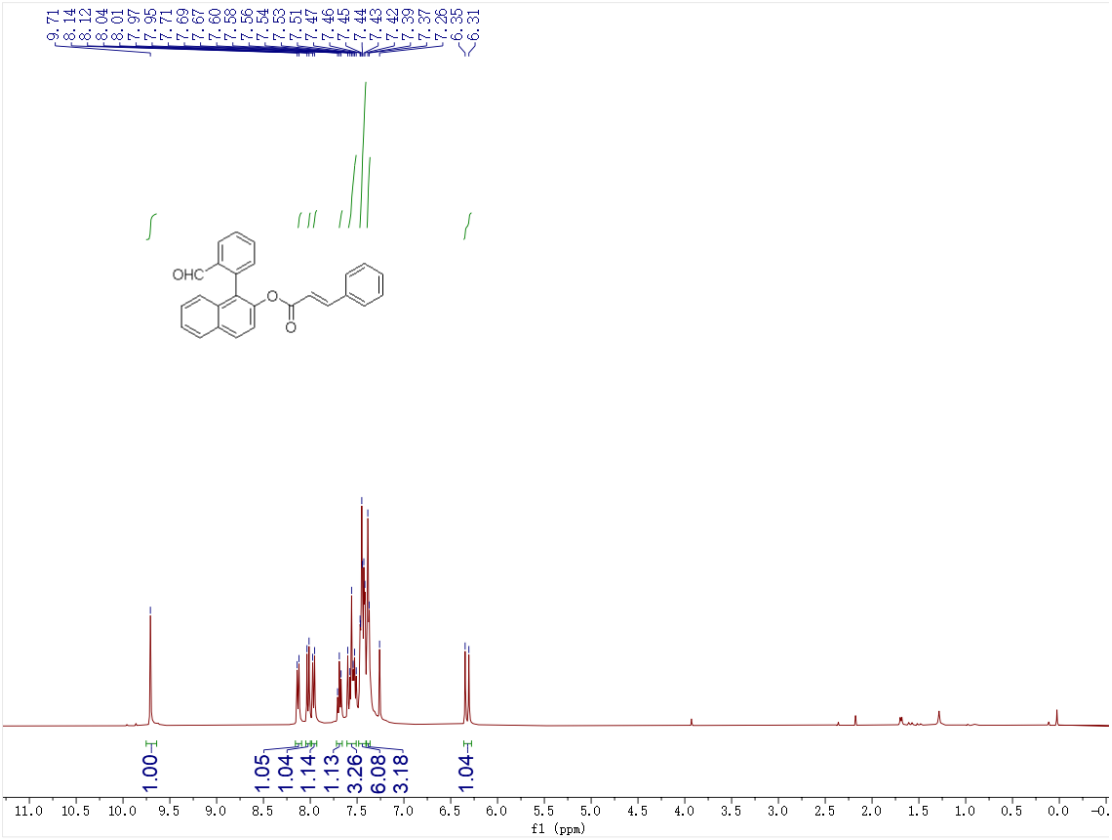
3p


9.98
8.03
8.01
7.66
7.64
7.63
7.60
7.56
7.52
7.50
7.48
7.47
7.41
7.40
7.39
7.30
7.28
7.28
7.28
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.18
7.17
7.16
7.15
6.31
6.27
OHC
O
O
F
1.00
1.03
1.02
1.07
3.08
4.00
1.19
1.23
1.12
1.04
f1 (ppm)


191.69
164.63
161.40
158.95
147.11
144.36
144.33
139.37
133.83
133.66
133.10
133.01
130.94
130.91
128.97
128.79
128.37
127.35
124.22
124.14
118.18
117.94
116.59
116.36
115.95
OHC
O
O
F
f1 (ppm)


-115.85
OHC
O
O
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

3q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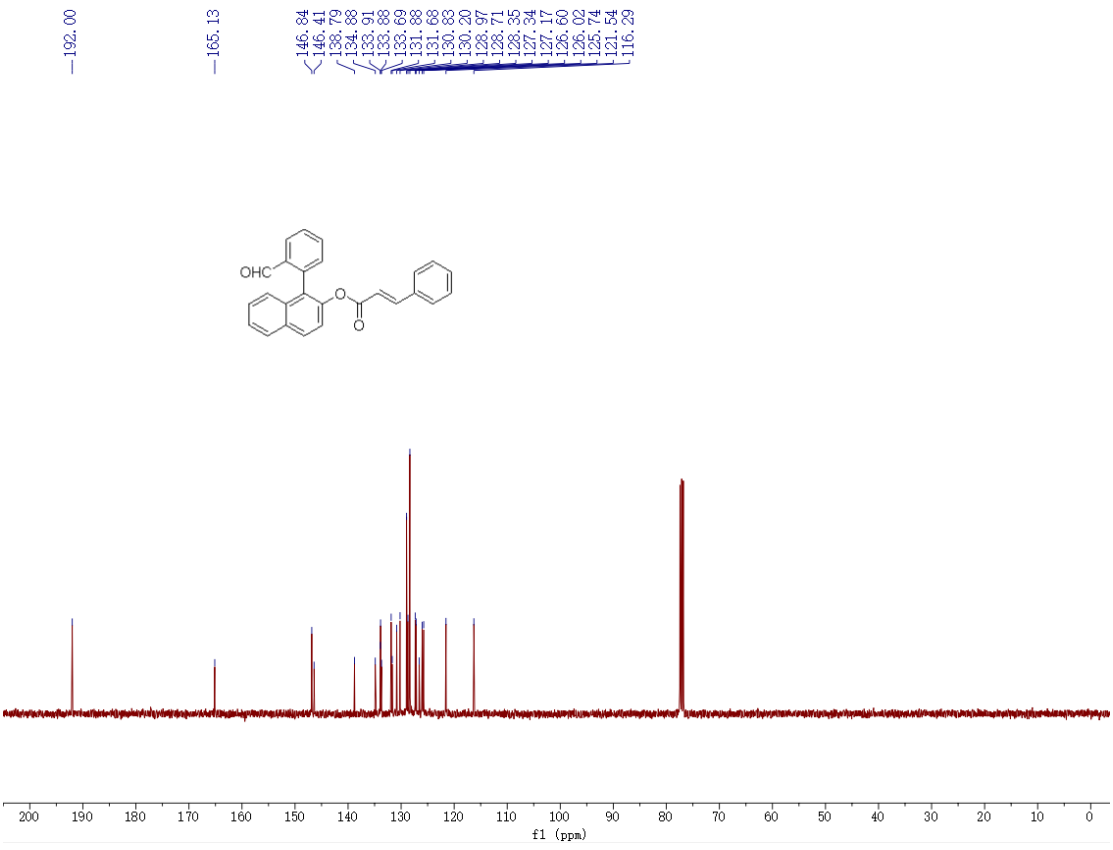
8.14
8.12
8.04
8.01
7.97
7.95
7.71
7.69
7.67
7.60
7.58
7.56
7.54
7.53
7.51
7.47
7.46
7.45
7.44
7.43
7.42
7.39
7.37
7.26
6.35
6.31
OHC
O
O
1.00
1.05
1.04
1.14
1.13
3.26
6.08
3.18
1.04
f1 (ppm)


192.00
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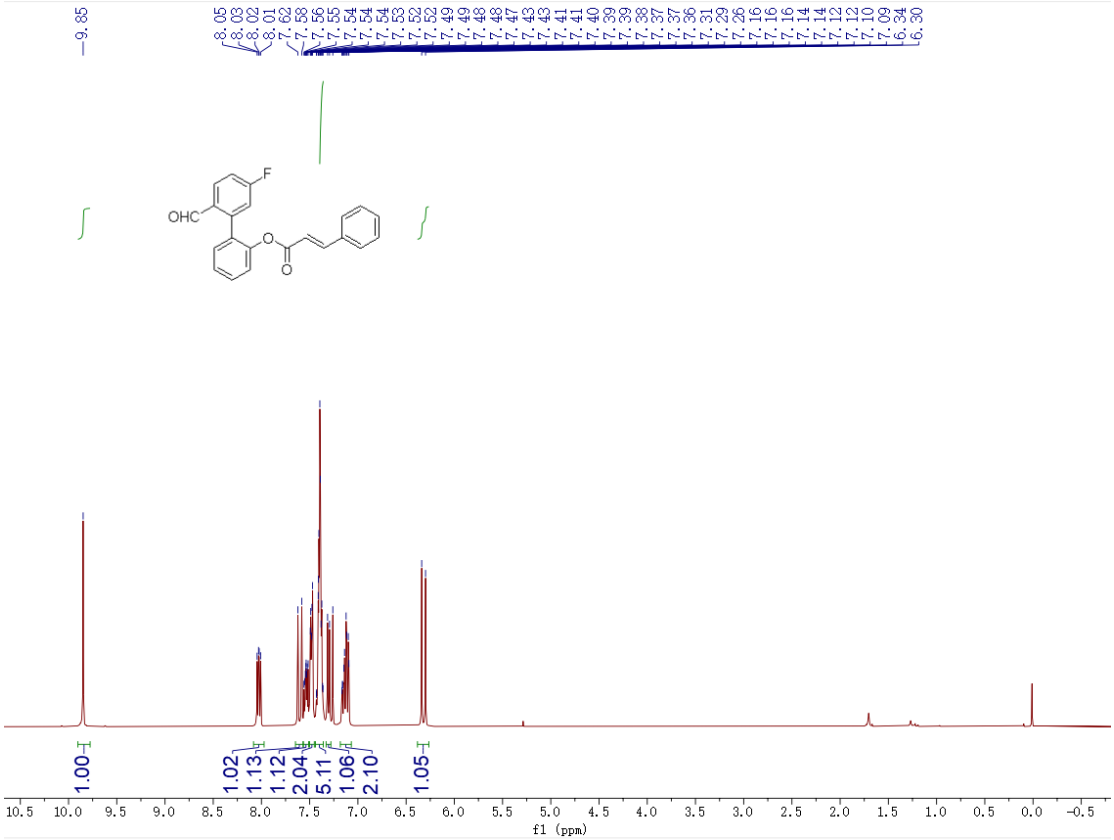
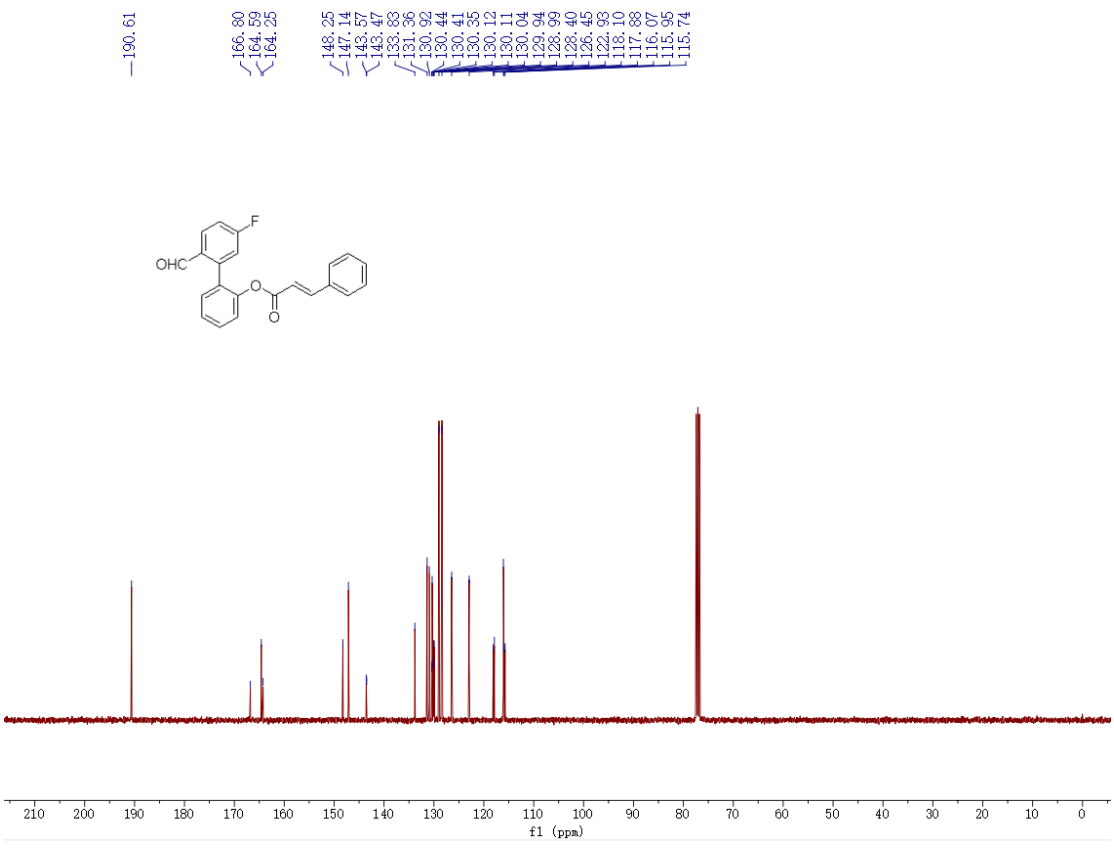
146.84
146.41
138.79
134.88
133.91
133.88
133.69
131.88
131.68
130.83
130.20
128.97
128.71
128.35
127.34
127.17
126.60
126.02
125.74
121.54
116.29
OHC
O
O
f1 (ppm)

3r


9.85
8.05
8.03
8.02
8.01
7.62
7.58
7.56
7.55
7.54
7.54
7.54
7.53
7.52
7.52
7.49
7.49
7.48
7.48
7.47
7.43
7.43
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.31
7.29
7.26
7.16
7.16
7.16
7.14
7.12
7.12
7.10
7.09
6.34
6.30
F
OHC
O
O
1.00
1.02
1.13
1.12
2.04
5.11
1.06
2.10
1.05
f1 (ppm)


190.61
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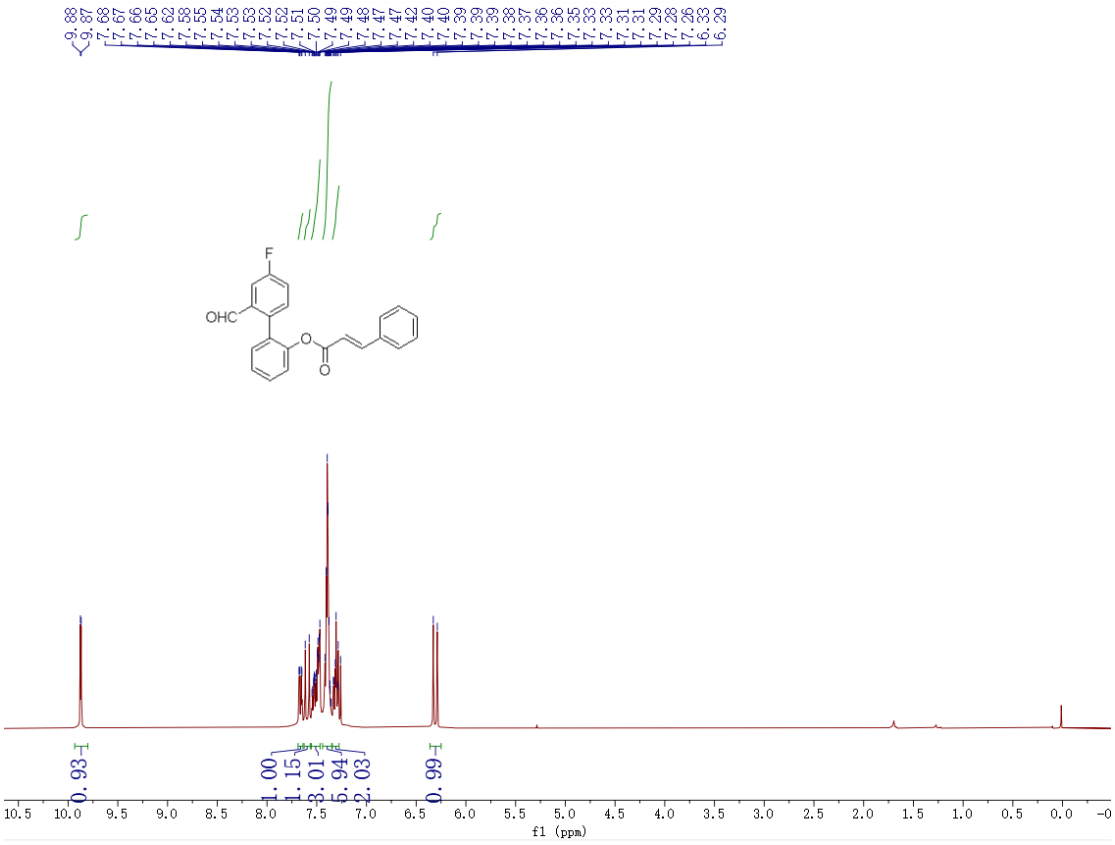
164.25
148.25
147.14
143.57
143.47
133.83
131.36
130.92
130.44
130.41
130.35
130.12
130.11
130.04
129.94
128.99
128.40
126.45
122.93
118.10
117.88
116.07
115.95
115.74
F
OHC
O
O
f1 (ppm)


-103.37
F
OHC
O
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

3s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7.58
7.55
7.54
7.53
7.52
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7.50
7.49
7.49
7.48
7.47
7.47
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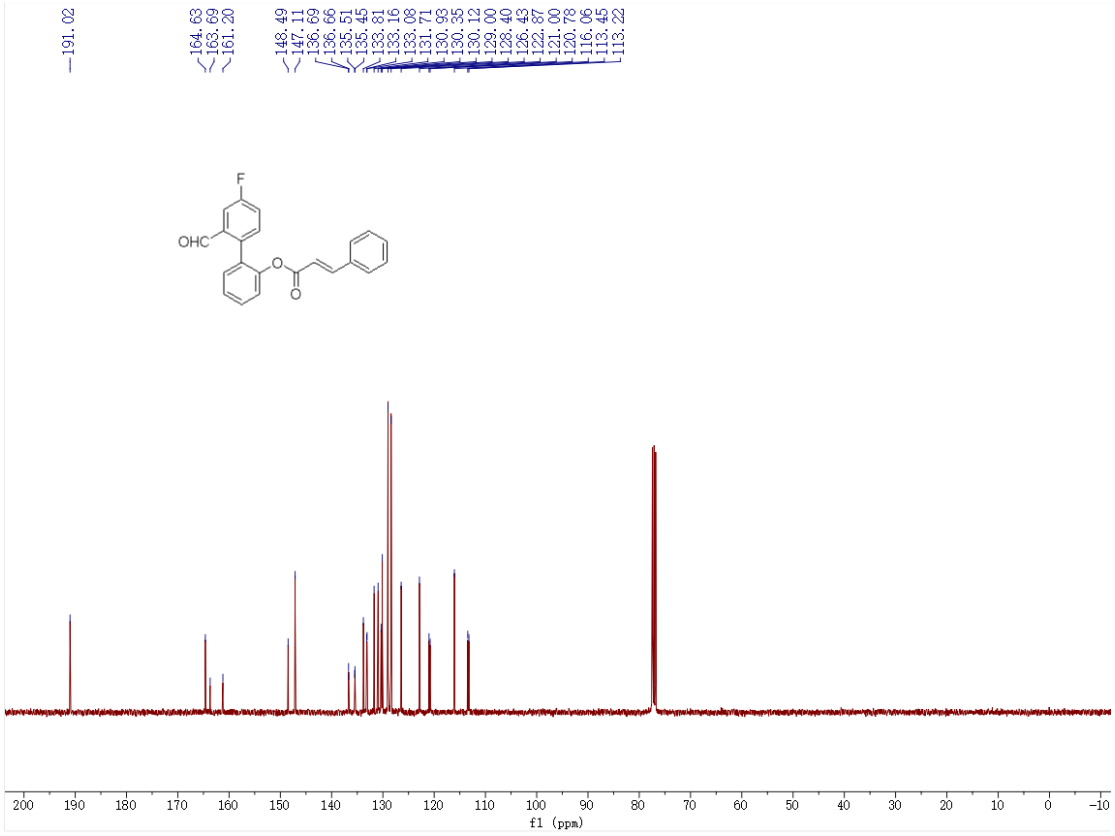
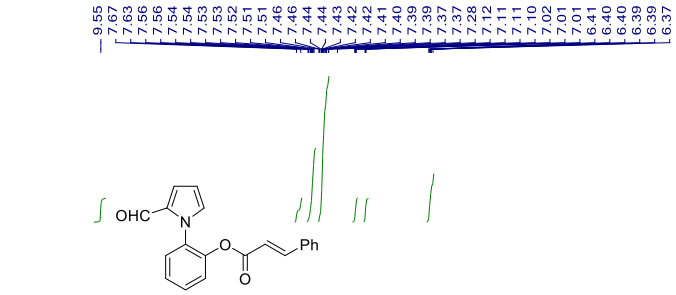
7.40
7.40
7.39
7.39
7.39
7.38
7.37
7.36
7.36
7.35
7.33
7.33
7.31
7.31
7.29
7.28
7.26
6.33
6.29
F
OHC
O
O
0.93
1.00
1.15
3.01
6.94
2.03
0.99
f1 (ppm)


191.02
164.63
163.69
161.20
148.49
147.11
136.69
136.66
135.51
135.45
133.81
133.16
133.08
131.71
130.93
130.35
130.12
129.00
128.40
126.43
122.87
121.00
120.78
116.06
113.45
113.22
F
OHC
O
O
f1 (ppm)


-112.13
F
OHC
O
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

5a


9.55
7.67
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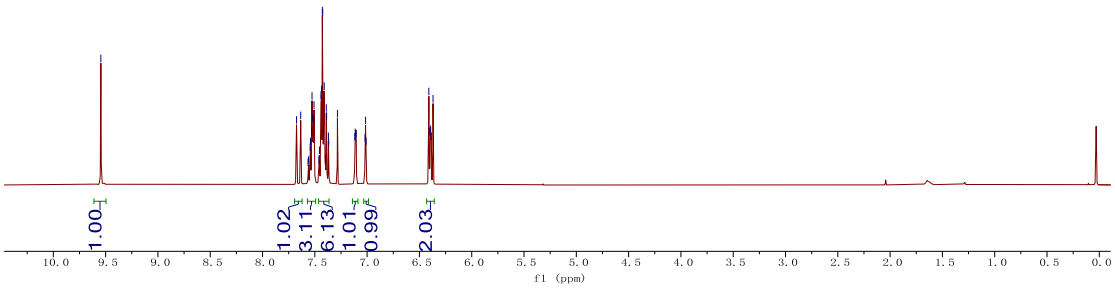
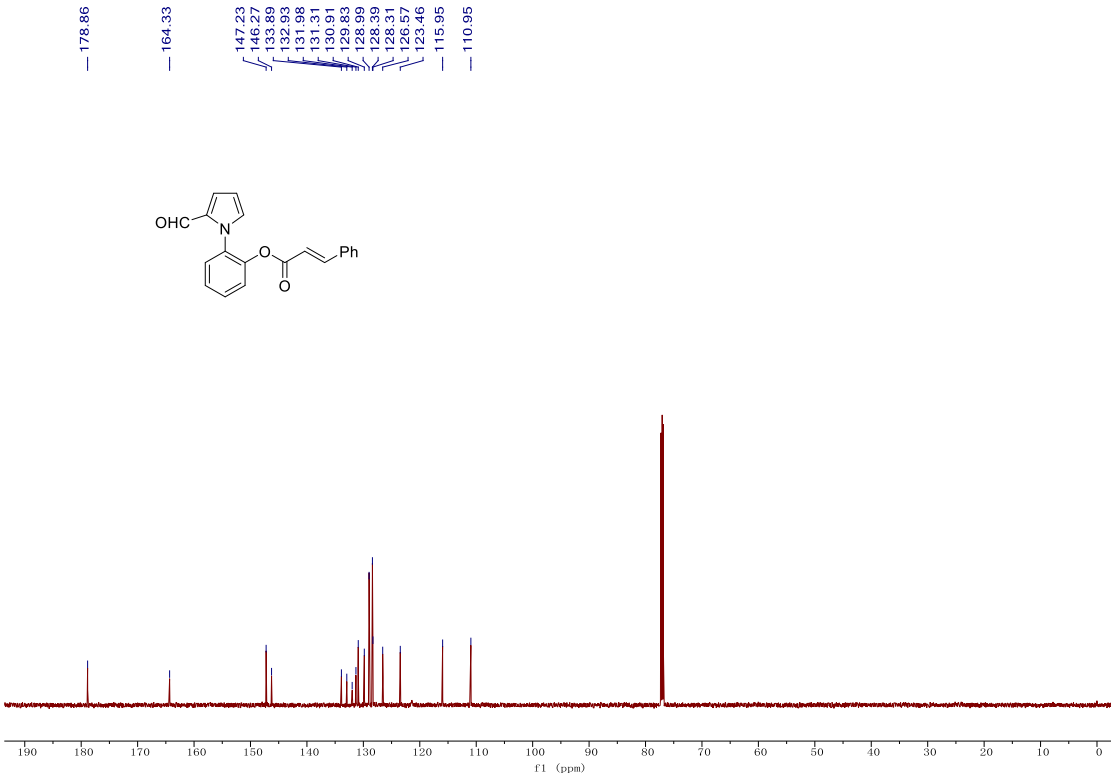
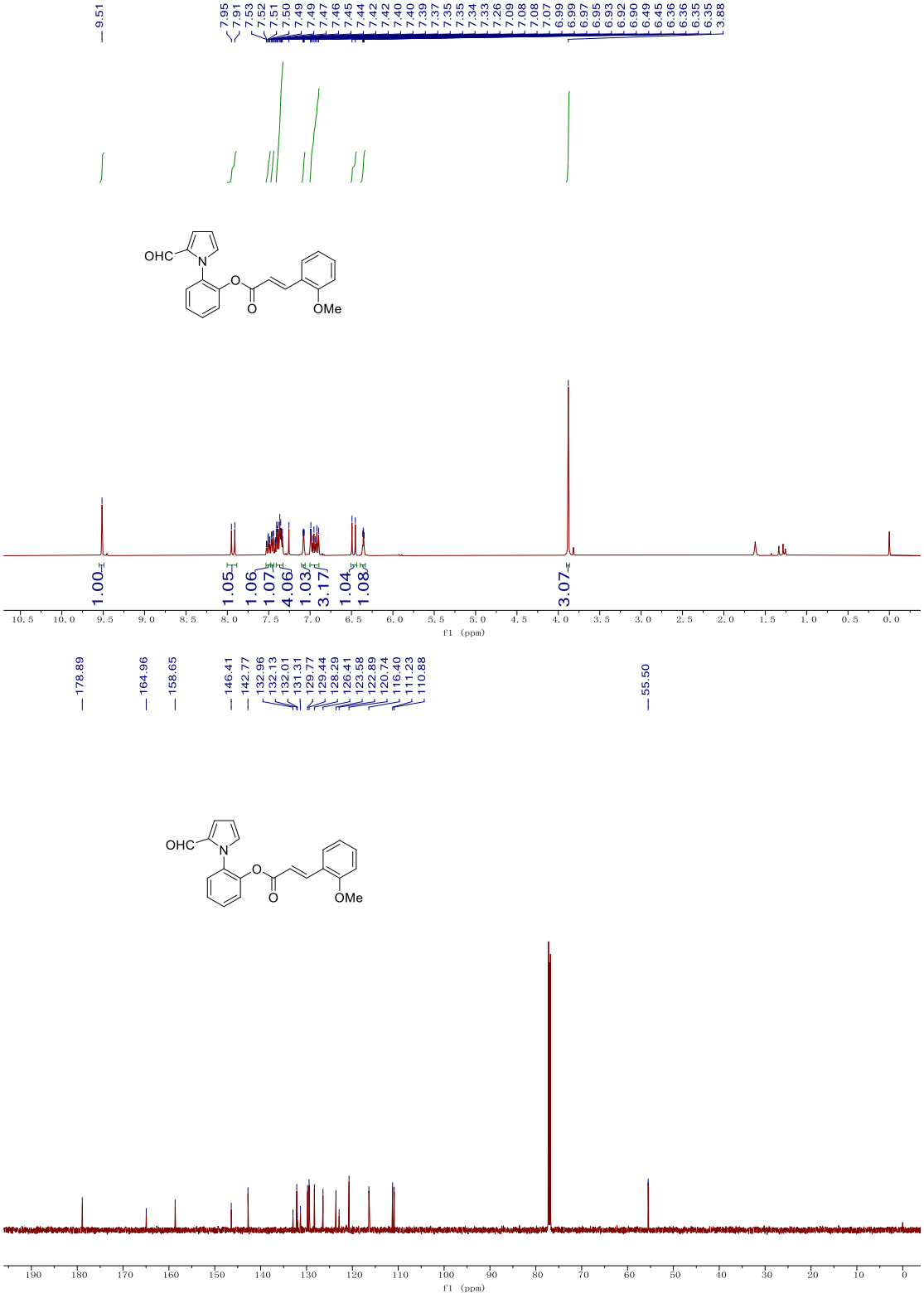
7.56
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.46
7.46
7.44
7.44
7.43
7.42
7.42
7.41
7.40
7.39
7.39
7.37
7.37
7.28
7.12
7.11
7.11
7.10
7.02
7.01
7.01
6.41
6.40
6.40
6.39
6.39
6.37
OHC
N
O
O
Ph


1.00
1.02
3.11
6.13
1.01
0.99
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


178.86
164.33
147.23
146.27
133.89
132.93
131.98
131.31
130.91
129.83
128.99
128.39
128.31
126.57
123.46
115.95
110.95
OHC
N
O
O
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5b


9.51
7.95
7.91
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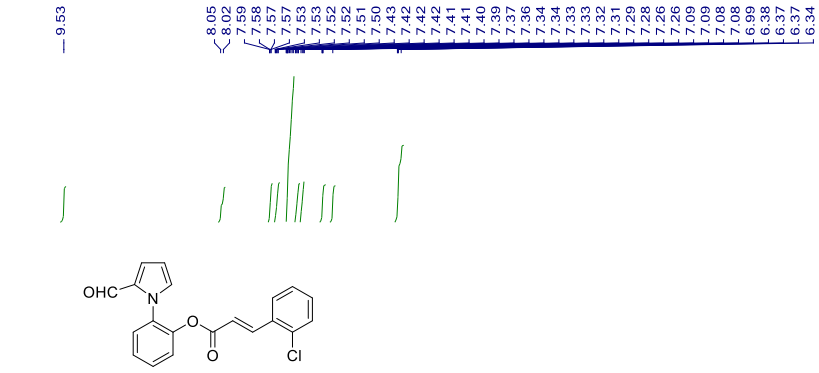
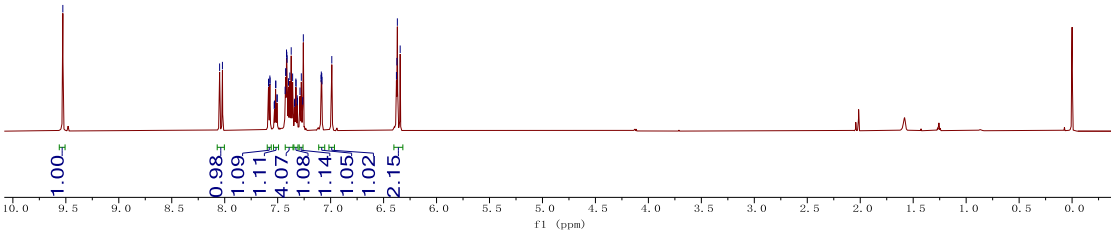
7.52
7.51
7.50
7.49
7.49
7.47
7.46
7.45
7.44
7.42
7.42
7.40
7.40
7.39
7.37
7.35
7.35
7.34
7.33
7.26
7.09
7.08
7.08
7.07
6.99
6.99
6.97
6.95
6.93
6.92
6.90
6.49
6.45
6.36
6.36
6.35
6.35
3.88
OHC
N
O
O
OMe
1.00
1.05
1.06
1.07
4.06
1.03
3.17
1.04
1.08
3.07
f1 (ppm)
178.89
164.96
158.65
146.41
142.77
132.96
132.13
132.01
131.31
129.77
129.44
128.29
126.41
123.58
122.89
120.74
116.40
111.23
110.88
55.50
OHC
N
O
O
OMe
f1 (ppm)

5c


9.53
8.05
8.02
7.59
7.58
7.57
7.57
7.53
7.53
7.52
7.52
7.51
7.50
7.43
7.42
7.42
7.41
7.40
7.39
7.37
7.36
7.34
7.33
7.33
7.32
7.31
7.29
7.28
7.26
7.26
7.09
7.09
7.08
7.08
6.99
6.38
6.37
6.37
6.34

OHC
N
O
O
Cl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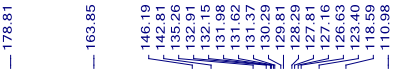
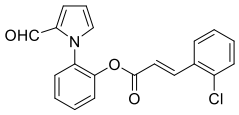
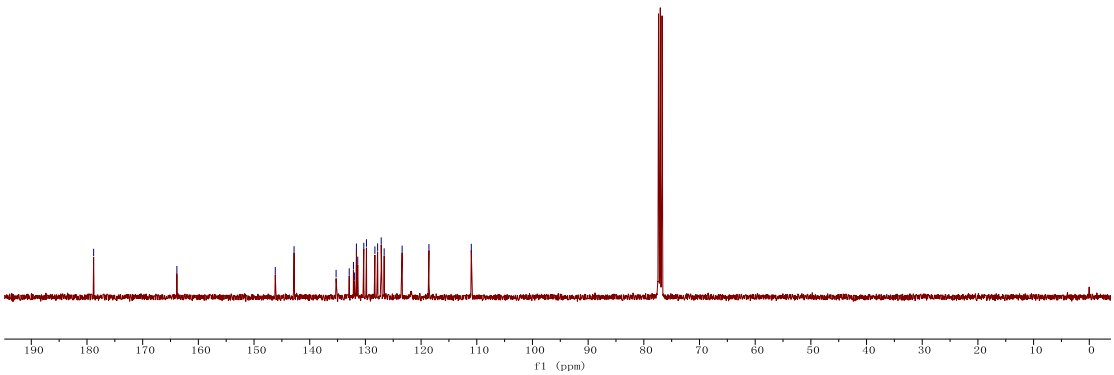
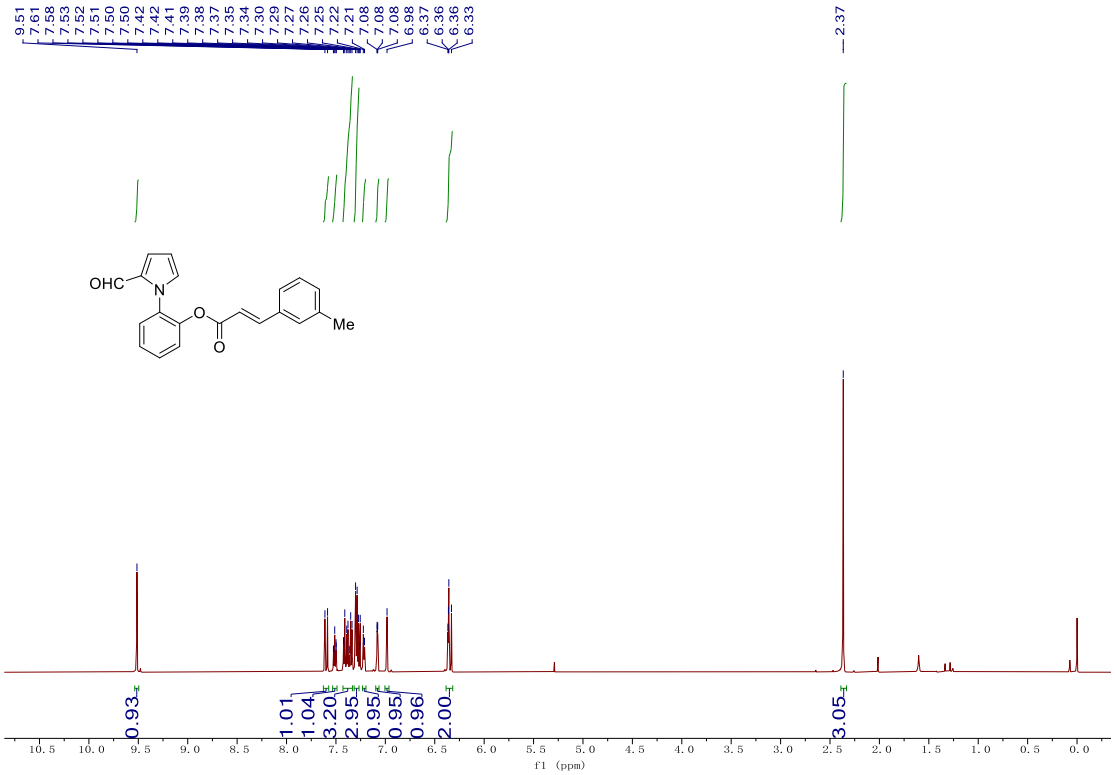
0.98
1.09
1.11
4.07
1.08
1.14
1.05
1.02
2.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


178.81
163.85
146.19
142.81
135.26
132.91
132.15
131.98
131.62
131.37
130.29
129.81
128.29
127.81
127.16
126.63
123.40
118.59
110.98


OHC
N
O
O
Cl


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5d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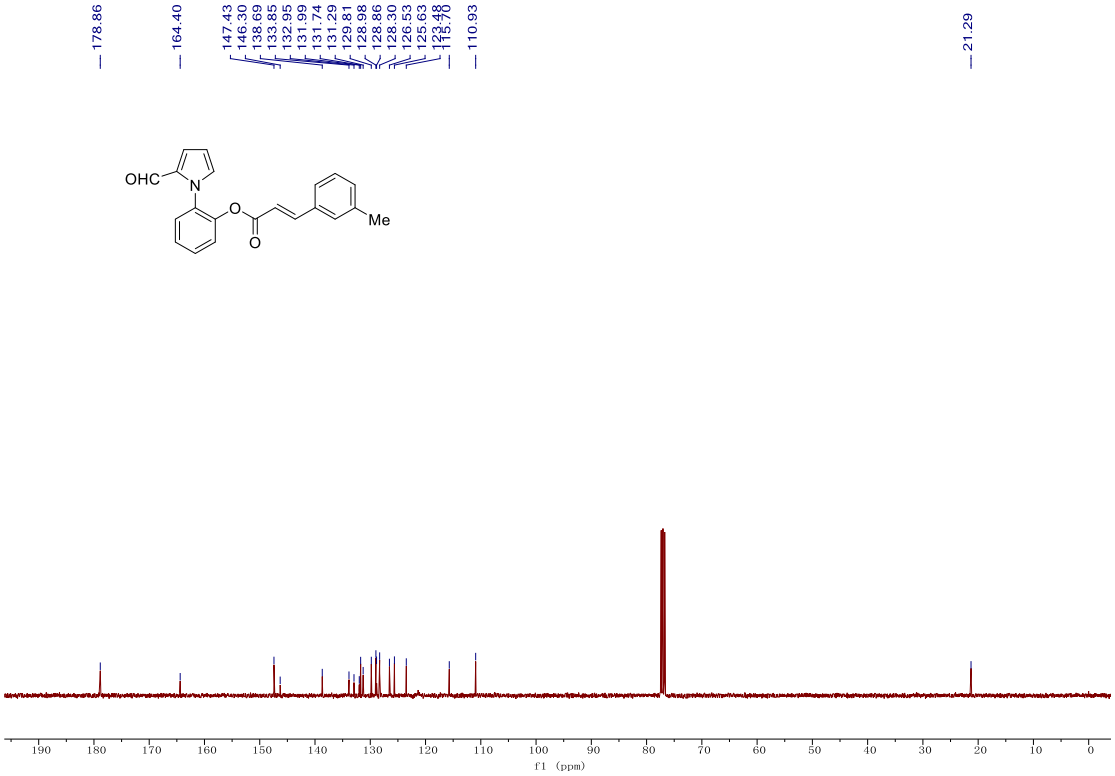
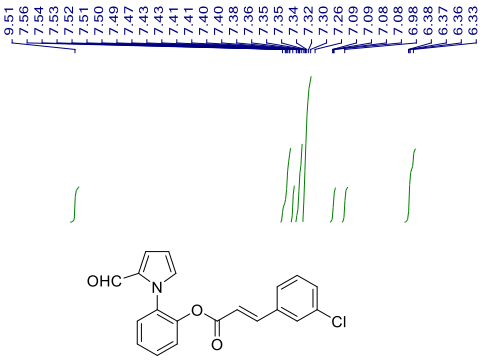
7.61
7.58
7.53
7.52
7.51
7.50
7.50
7.42
7.42
7.41
7.39
7.38
7.37
7.35
7.34
7.30
7.29
7.27
7.26
7.25
7.22
7.21
7.08
7.08
7.08
6.98
6.37
6.36
6.36
6.33
2.37
OHC
N
O
O
Me
0.93
1.01
1.04
3.20
2.95
0.95
0.95
0.96
2.00
3.05
f1 (ppm)


178.86
164.40
147.43
146.30
138.69
133.85
132.95
131.99
131.74
131.29
129.81
128.98
128.86
128.30
126.53
125.63
123.48
113.70
110.93
21.29
OHC
N
O
O
Me
f1 (ppm)

5e


9.51
7.56
7.54
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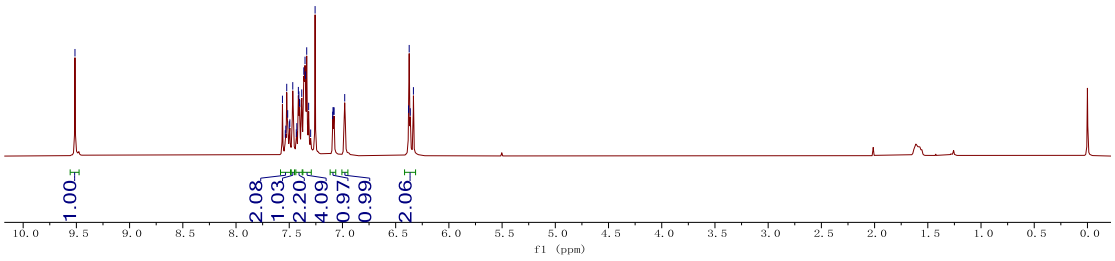
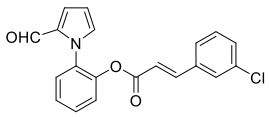
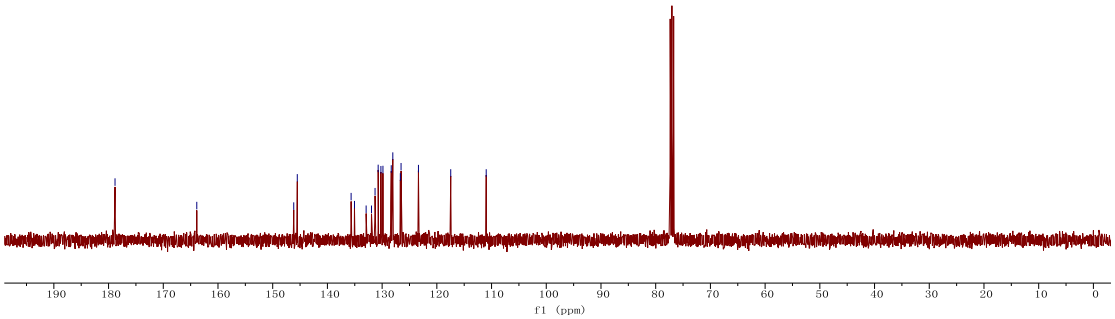
7.52
7.51
7.50
7.49
7.47
7.43
7.43
7.41
7.41
7.40
7.40
7.38
7.36
7.35
7.35
7.34
7.32
7.30
7.26
7.09
7.09
7.08
7.08
6.98
6.38
6.37
6.36
6.33
OHC
N
O
O
Cl

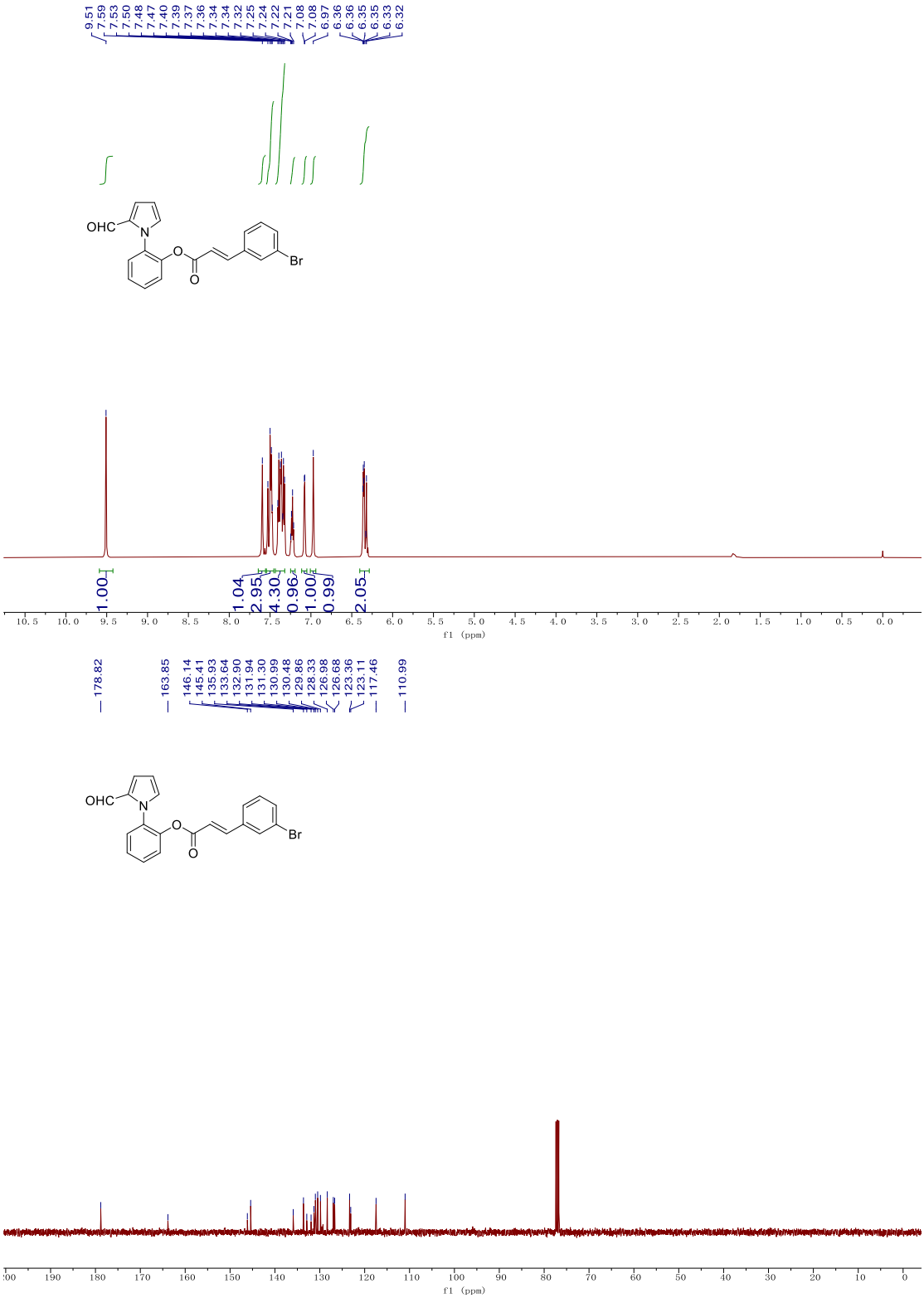

1.00
2.08
1.03
2.20
4.09
0.97
0.99
2.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


178.82
163.88
146.16
145.51
135.67
135.05
132.92
131.94
131.29
130.72
130.22
129.85
128.33
128.05
126.67
126.54
123.36
117.46
110.98


OHC
N
O
O
Cl


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5f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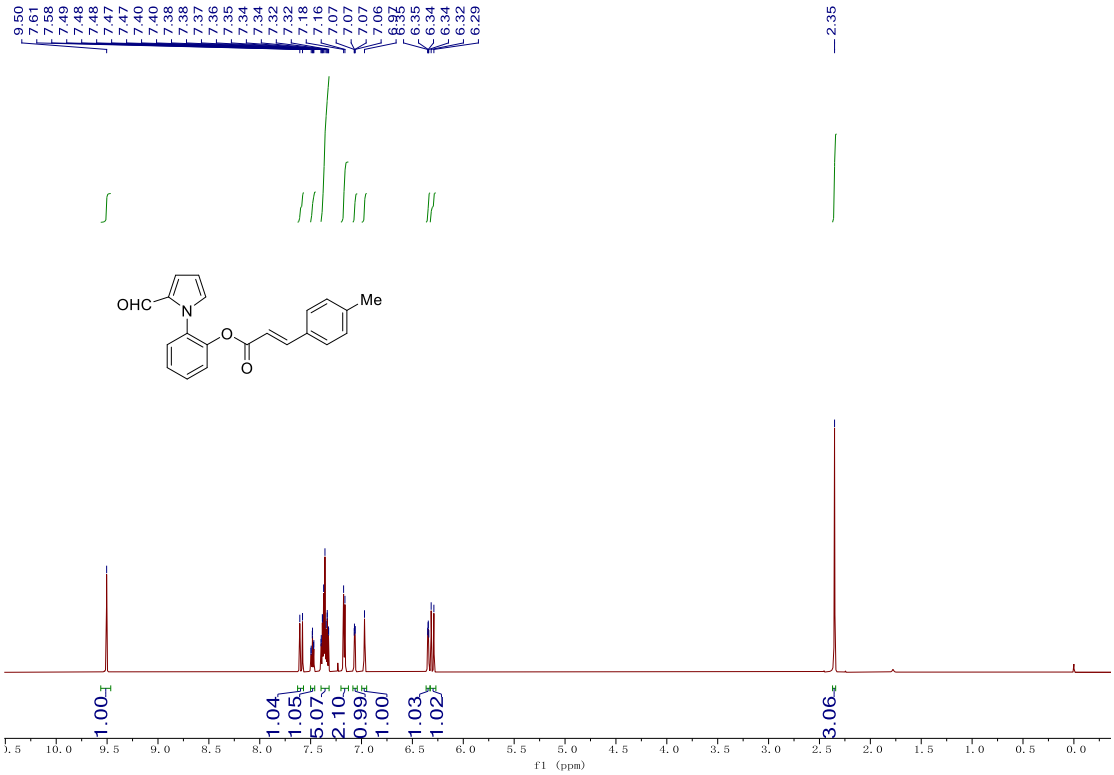
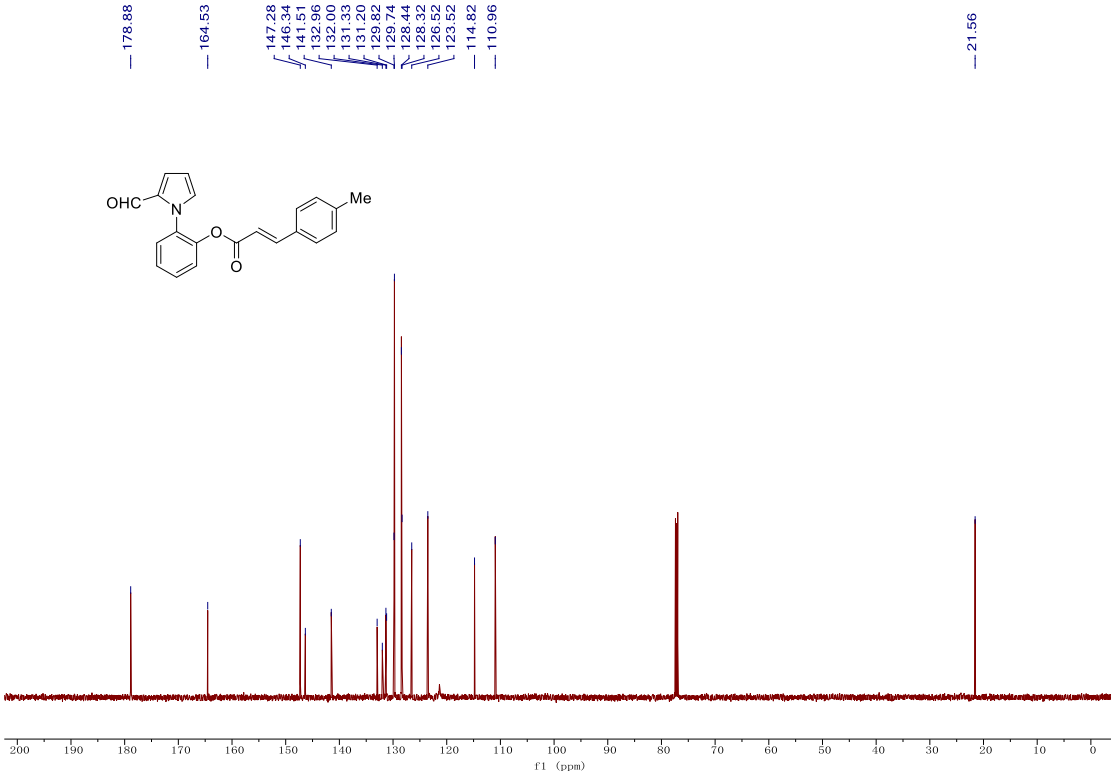
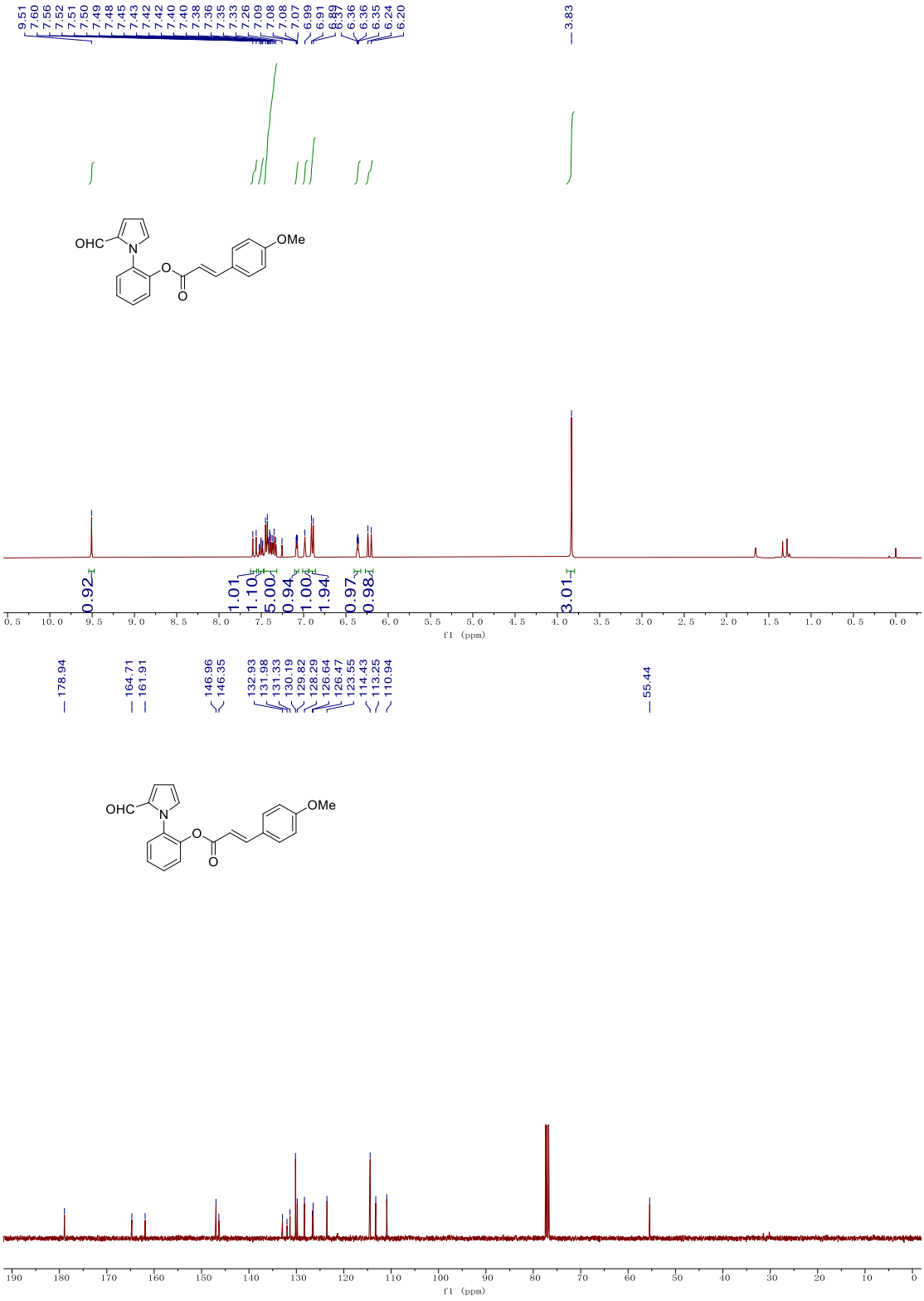
7.59
7.53
7.50
7.48
7.47
7.40
7.39
7.37
7.36
7.34
7.34
7.32
7.25
7.24
7.22
7.21
7.08
7.08
6.97
6.36
6.36
6.35
6.35
6.33
6.32
OHC
N
O
O
Br
1.00
1.04
2.95
4.30
0.96
1.00
0.99
2.05
f1 (ppm)
178.82
163.85
146.14
145.41
135.93
133.64
132.90
131.94
131.30
130.99
130.48
129.86
128.33
126.98
126.68
123.36
123.11
117.46
110.99
OHC
N
O
O
Br
f1 (ppm)

5g

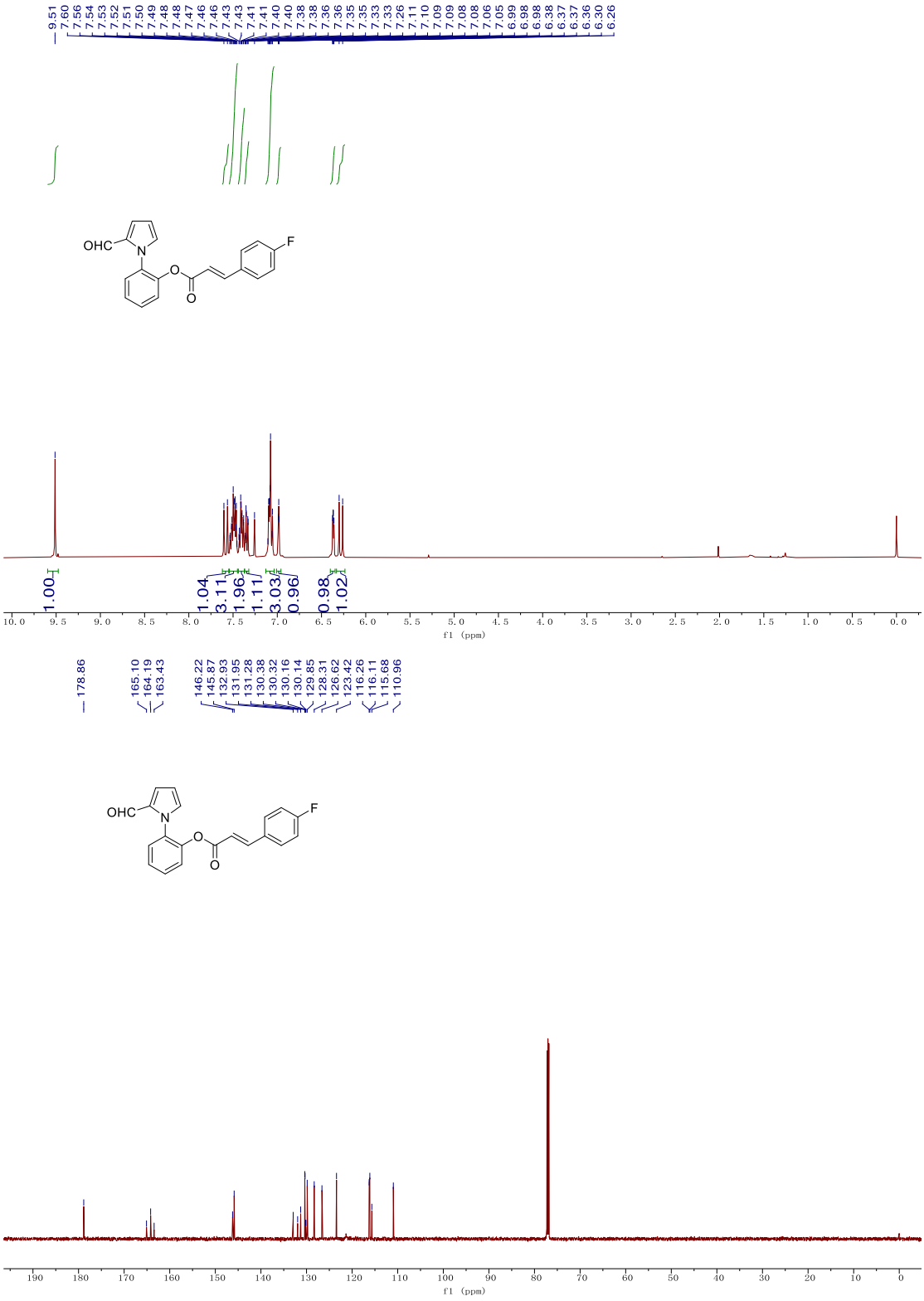

9.50
7.61
7.58
7.49
7.48
7.48
7.47
7.47
7.40
7.40
7.38
7.38
7.37
7.36
7.35
7.34
7.34
7.32
7.32
7.18
7.16
7.07
7.07
7.07
7.06
6.35
6.35
6.34
6.34
6.32
6.29
2.35
OHC
N
O
O
Me
1.00
1.04
1.05
5.07
2.10
0.99
1.00
1.03
1.02
3.06
f1 (ppm)

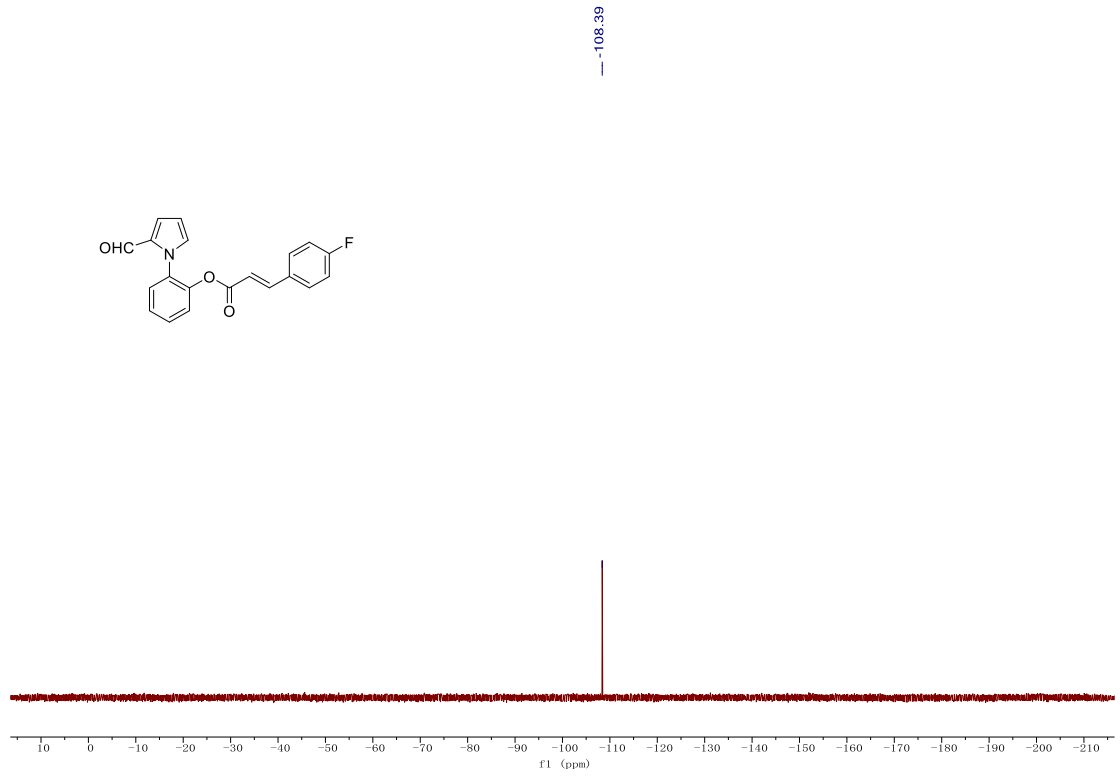

178.88
164.53
147.28
146.34
141.51
132.96
132.00
131.33
131.20
129.82
129.74
128.44
128.32
126.52
123.52
114.82
110.96
21.56
OHC
N
O
O
Me
f1 (ppm)

5h

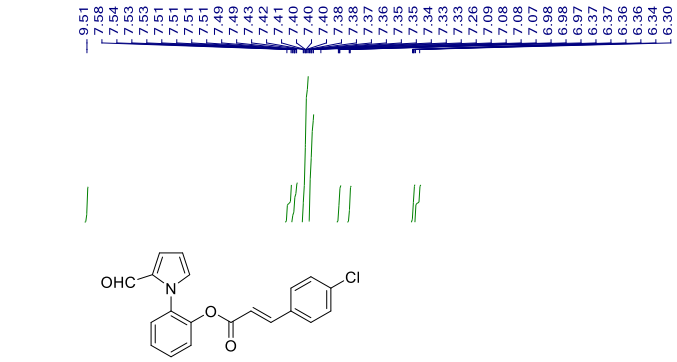

9.51
7.60
7.56
7.52
7.51
7.50
7.49
7.48
7.45
7.43
7.42
7.42
7.40
7.40
7.38
7.36
7.35
7.33
7.26
7.09
7.08
7.08
7.07
6.99
6.91
6.89
6.37
6.36
6.36
6.35
6.24
6.20
3.83
OHC
N
O
O
OMe
0.92
1.01
1.10
5.00
0.94
1.00
1.94
0.97
0.98
3.01
f1 (ppm)
178.94
164.71
161.91
146.96
146.35
132.93
131.98
131.33
130.19
129.82
128.29
126.64
126.47
123.55
114.43
113.25
110.94
55.44
OHC
N
O
O
OMe
f1 (ppm)

5i

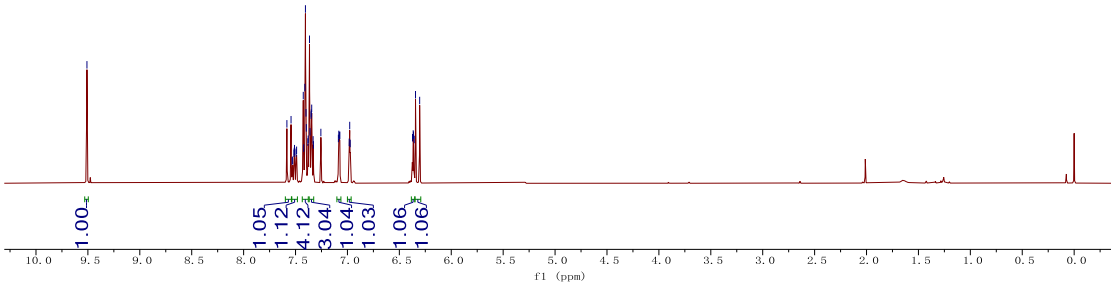

9.51
7.60
7.56
7.54
7.53
7.52
7.51
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.43
7.43
7.41
7.41
7.40
7.40
7.38
7.38
7.36
7.36
7.35
7.35
7.33
7.33
7.26
7.11
7.10
7.09
7.09
7.08
7.08
7.06
7.05
6.99
6.98
6.98
6.38
6.37
6.37
6.36
6.30
6.26
OHC
N
O
O
F
1.00
1.04
3.11
1.96
1.11
3.03
0.96
0.98
1.02
f1 (ppm)
178.86
165.10
164.19
163.43
146.22
145.87
132.93
131.95
131.28
130.38
130.32
130.16
130.14
129.85
128.31
126.62
123.42
116.26
116.11
115.68
110.96
OHC
N
O
O
F
f1 (ppm)

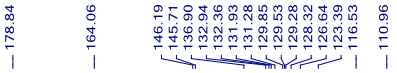

-108.39
OHC
N
O
O
F
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

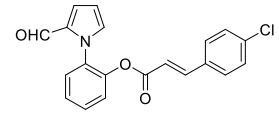
5j

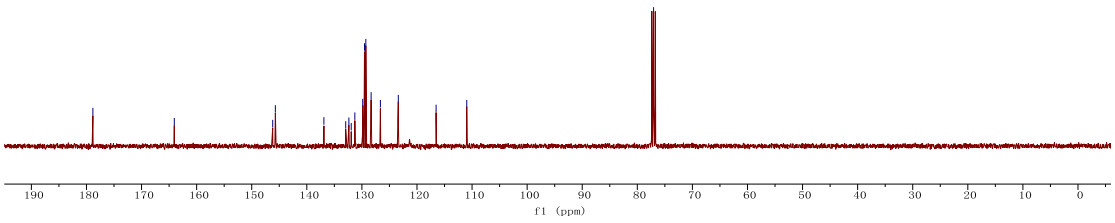

9.51
7.58
7.54
7.53
7.53
7.51
7.51
7.51
7.49
7.49
7.43
7.42
7.41
7.40
7.40
7.40
7.38
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.26
7.09
7.08
7.08
7.07
6.98
6.98
6.97
6.37
6.37
6.36
6.36
6.34
6.30

OHC
N
O
O
Cl

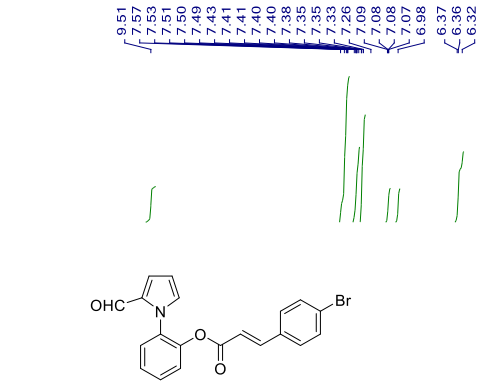

1.00
1.05
1.12
4.12
3.04
1.04
1.03
1.06
1.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


178.84
164.06
146.19
145.71
136.90
132.94
132.36
131.93
131.28
129.85
129.53
129.28
128.32
126.64
123.39
116.53
110.96

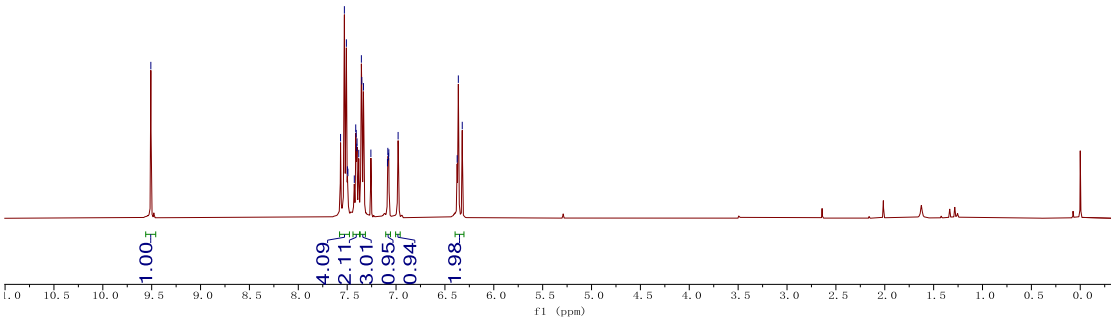

OHC
N
O
O
Cl


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

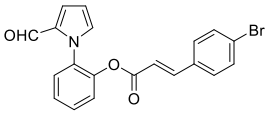
5k

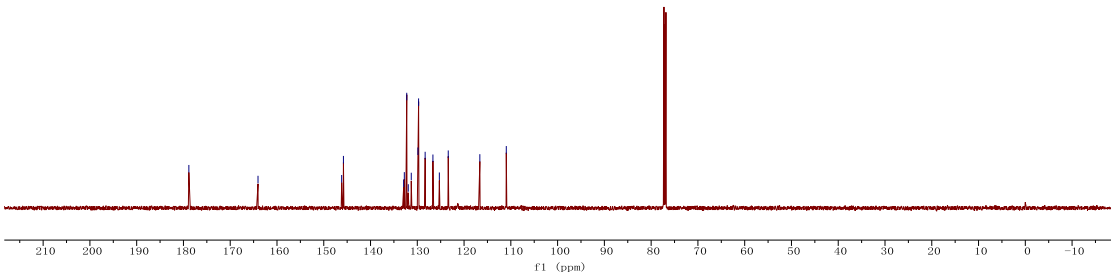

9.51
7.57
7.53
7.51
7.50
7.49
7.43
7.41
7.41
7.40
7.40
7.38
7.35
7.35
7.33
7.26
7.09
7.08
7.08
7.07
6.98
6.37
6.36
6.32

OHC
N
O
O
Br

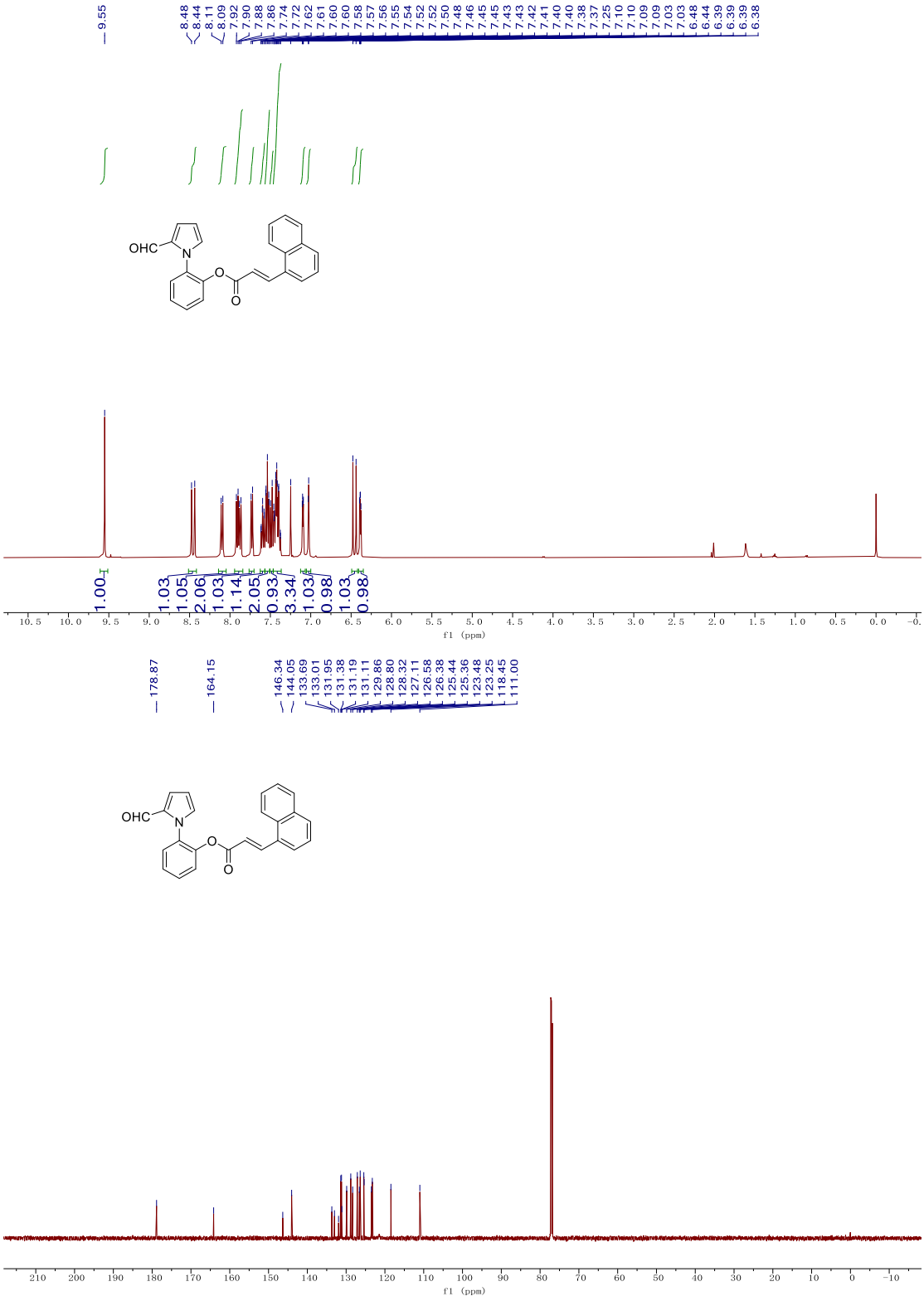

1.00
4.09
2.11
3.01
0.95
0.94
1.98
f1 (ppm)


178.84
164.06
146.17
145.79
132.92
132.78
132.26
131.93
131.29
129.86
129.72
128.32
126.66
125.29
110.97

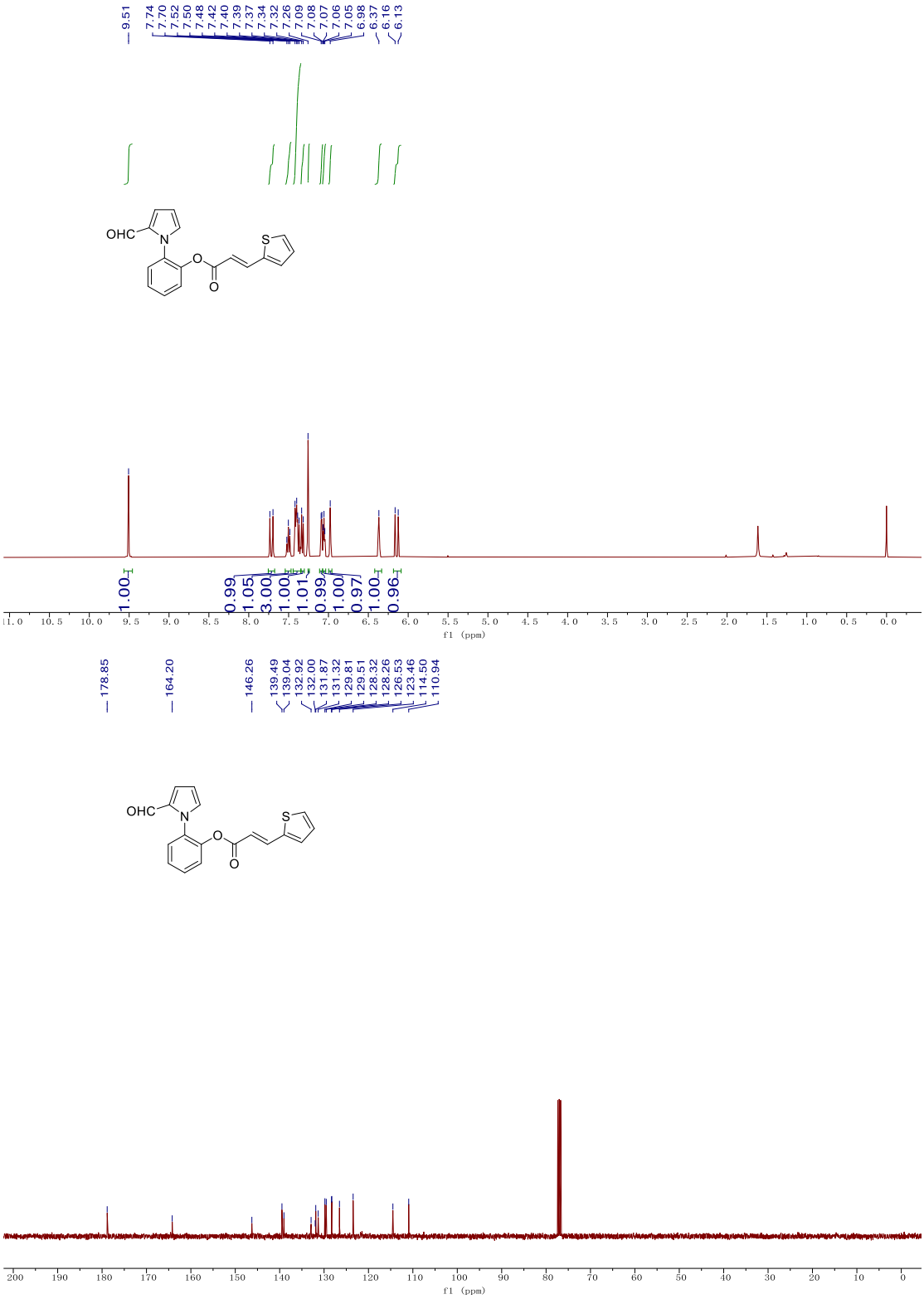

OHC
N
O
O
Br


f1 (ppm)

5l


9.55
8.48
8.44
8.11
8.09
7.92
7.90
7.88
7.86
7.74
7.72
7.62
7.61
7.60
7.60
7.58
7.57
7.56
7.55
7.54
7.52
7.52
7.50
7.48
7.46
7.45
7.45
7.43
7.43
7.42
7.41
7.40
7.40
7.38
7.37
7.25
7.10
7.10
7.09
7.09
7.03
6.48
6.44
6.39
6.39
6.39
6.38
OHC
N
O
O
1.00
1.03
1.05
2.06
1.03
1.14
2.05
0.93
3.34
1.03
0.98
1.03
0.98
f1 (ppm)
178.87
164.15
146.34
144.05
133.69
133.01
131.95
131.38
131.19
131.11
129.86
128.80
128.32
127.11
126.58
126.38
125.44
125.36
123.48
123.25
118.45
111.00
OHC
N
O
O
f1 (ppm)

5m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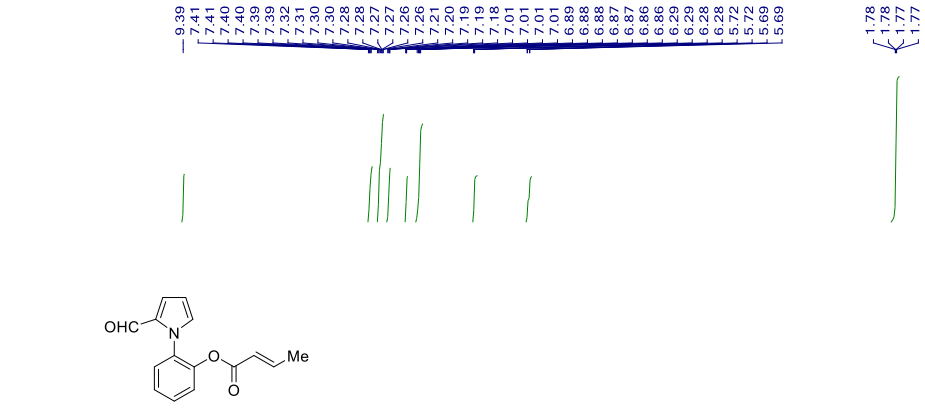
7.48
7.42
7.40
7.39
7.37
7.34
7.32
7.26
7.09
7.08
7.07
7.06
7.05
6.98
6.37
6.16
6.13
OHC
N
O
O
S
1.00
0.99
1.05
3.00
1.00
1.01
0.99
1.00
0.97
1.00
0.96
f1 (ppm)
178.85
164.20
146.26
139.49
139.04
132.92
132.00
131.87
131.32
129.81
129.51
128.32
128.26
126.53
123.46
114.50
110.94
OHC
N
O
O
S
f1 (ppm)

5n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7.39
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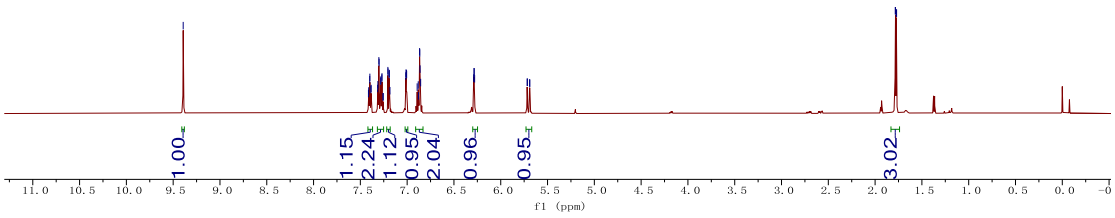
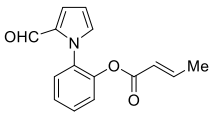
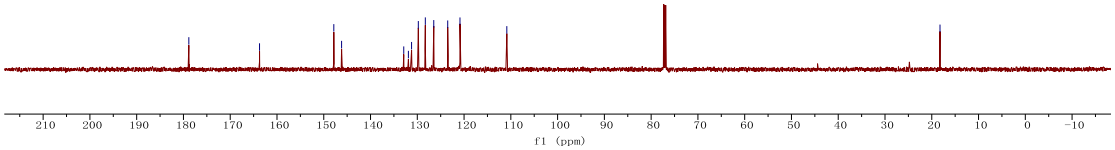
7.30
7.30
7.28
7.28
7.27
7.27
7.26
7.26
7.21
7.20
7.19
7.19
7.18
7.01
7.01
7.01
6.89
6.88
6.88
6.87
6.87
6.86
6.86
6.29
6.28
6.28
5.72
5.72
5.69
5.69
1.78
1.78
1.77
1.77

OHC
N
O
O
Me

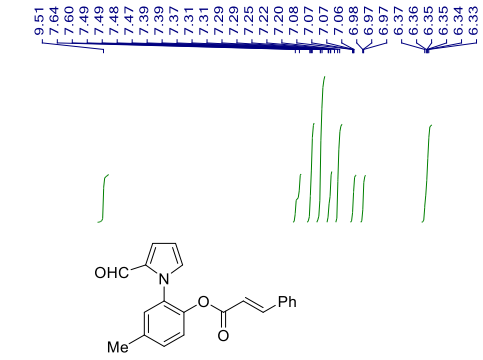

1.00
1.15
2.24
1.12
0.95
2.04
0.96
0.95
3.02
f1 (ppm)


178.85
163.73
147.85
146.19
132.90
131.90
131.22
129.78
128.28
126.48
123.49
120.87
110.86
18.24


OHC
N
O
O
Me


f1 (ppm)

5o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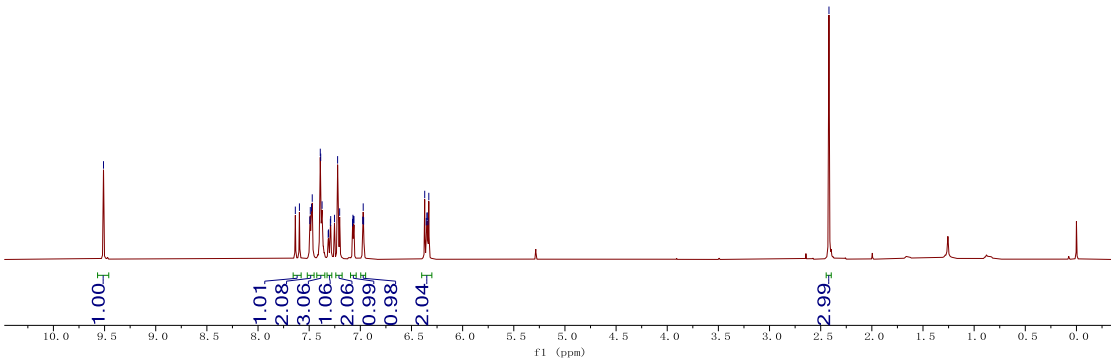
7.49
7.48
7.47
7.39
7.39
7.37
7.31
7.31
7.29
7.29
7.25
7.22
7.20
7.08
7.07
7.07
7.06
6.98
6.97
6.97
6.37
6.36
6.35
6.35
6.34
6.33
2.42
OHC
N
O
Ph
O
Me


1.00
1.01
2.08
3.06
1.06
2.06
0.99
0.98
2.04
2.99
f1 (ppm)


178.97
164.56
147.07
143.86
136.71
133.92
132.91
131.48
131.25
130.86
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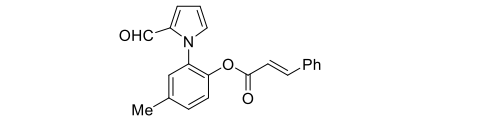
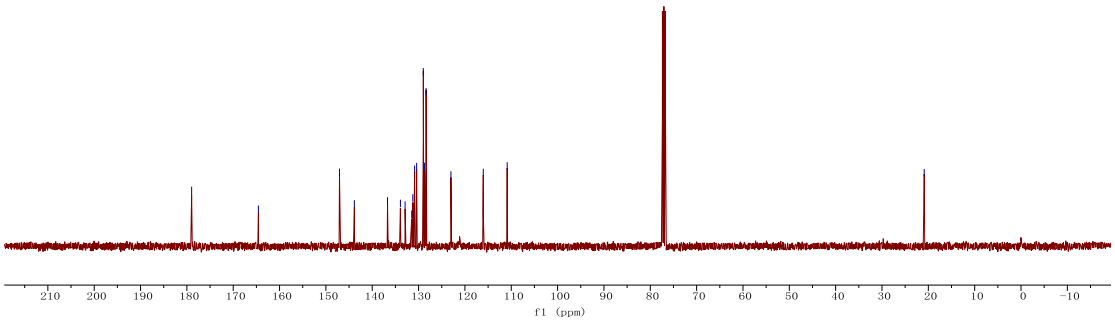
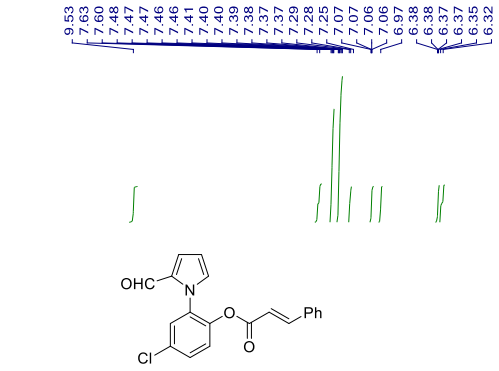
128.71
128.38
123.02
116.04
110.88
20.89


OHC
N
O
Ph
O
Me


f1 (ppm)

5p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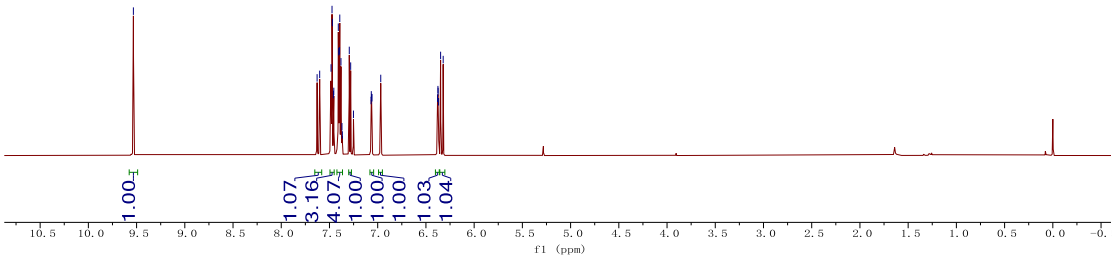
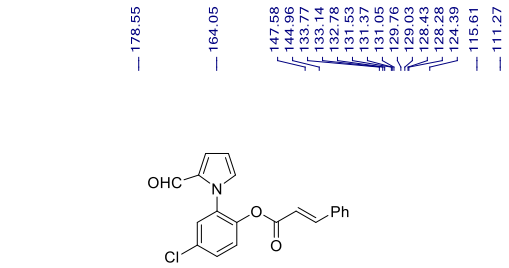
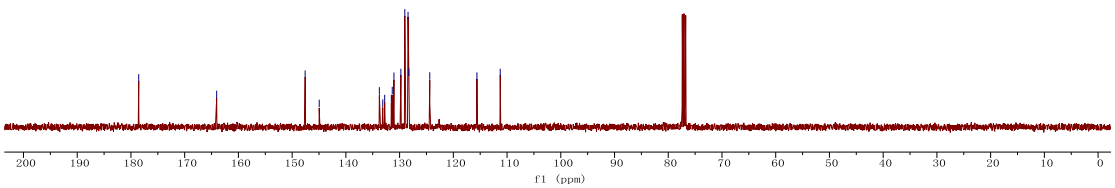
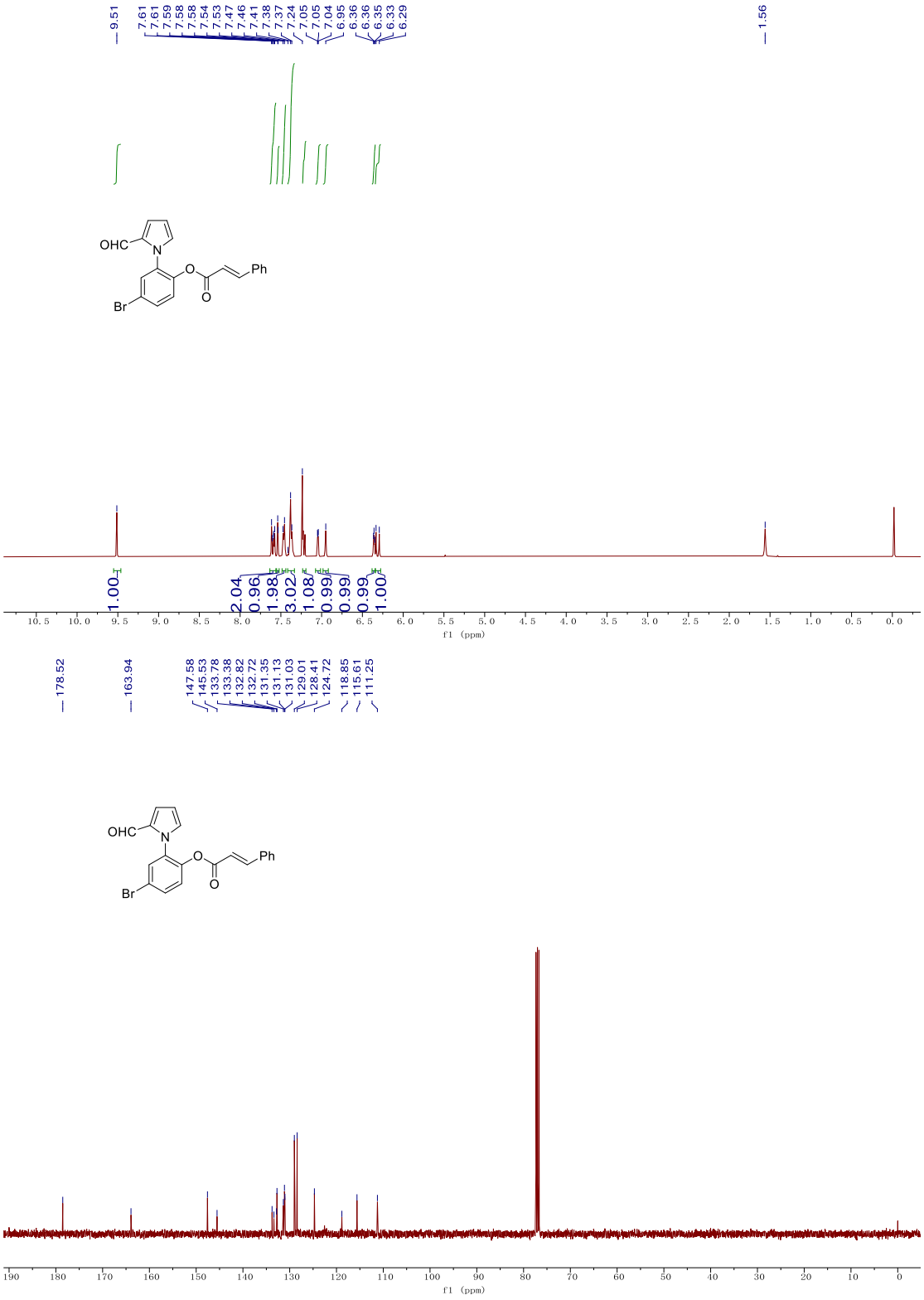
7.63
7.60
7.48
7.47
7.47
7.46
7.46
7.41
7.40
7.40
7.39
7.38
7.37
7.37
7.29
7.28
7.25
7.07
7.07
7.06
7.06
6.97
6.38
6.38
6.37
6.37
6.35
6.32
OHC
N
O
O
Ph
Cl


1.00
1.07
3.16
4.07
1.00
1.00
1.00
1.03
1.04
f1 (ppm)


178.55
164.05
147.58
144.96
133.77
133.14
132.78
131.53
131.37
131.05
129.76
129.03
128.43
128.28
124.39
115.61
111.27
OHC
N
O
O
Ph
Cl


f1 (ppm)

5q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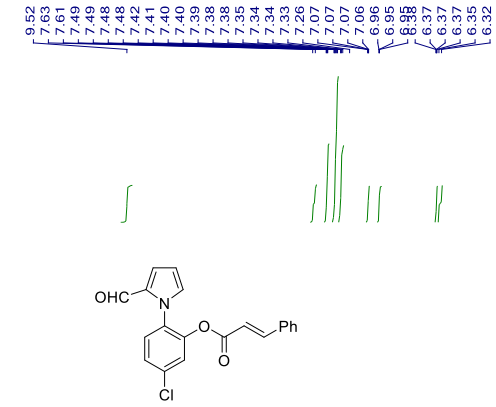
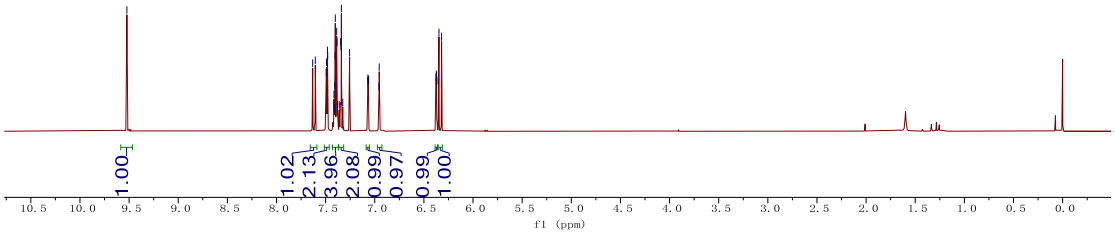
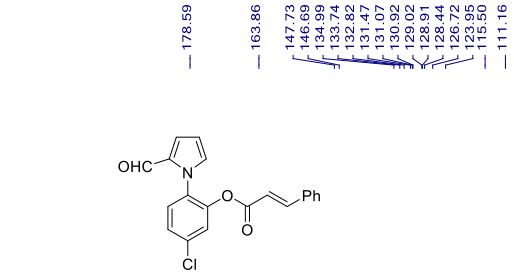
7.61
7.61
7.59
7.58
7.58
7.54
7.53
7.47
7.46
7.41
7.38
7.37
7.24
7.05
7.05
7.04
6.95
6.36
6.36
6.35
6.33
6.29
1.56
OHC
N
O
Ph
O
Br
1.00
2.04
0.96
1.98
3.02
1.08
0.99
0.99
0.99
1.00
f1 (ppm)
178.52
163.94
147.58
145.53
133.78
133.38
132.82
132.72
131.35
131.13
131.03
129.01
128.41
124.72
118.85
115.61
111.25
OHC
N
O
Ph
O
Br
f1 (ppm)

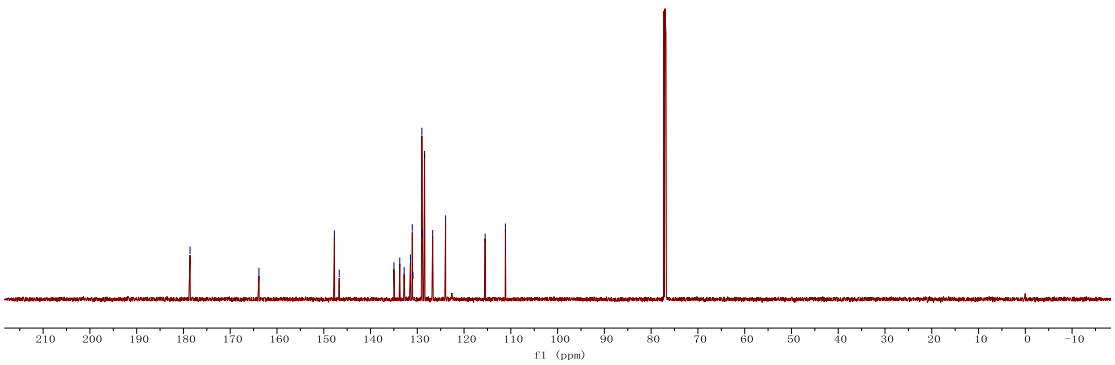
5r


9.52
7.63
7.61
7.49
7.49
7.48
7.48
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.35
7.34
7.34
7.33
7.26
7.07
7.07
7.07
7.06
6.96
6.95
6.95
6.38
6.37
6.37
6.37
6.35
6.32
OHC
N
O
O
Ph
Cl

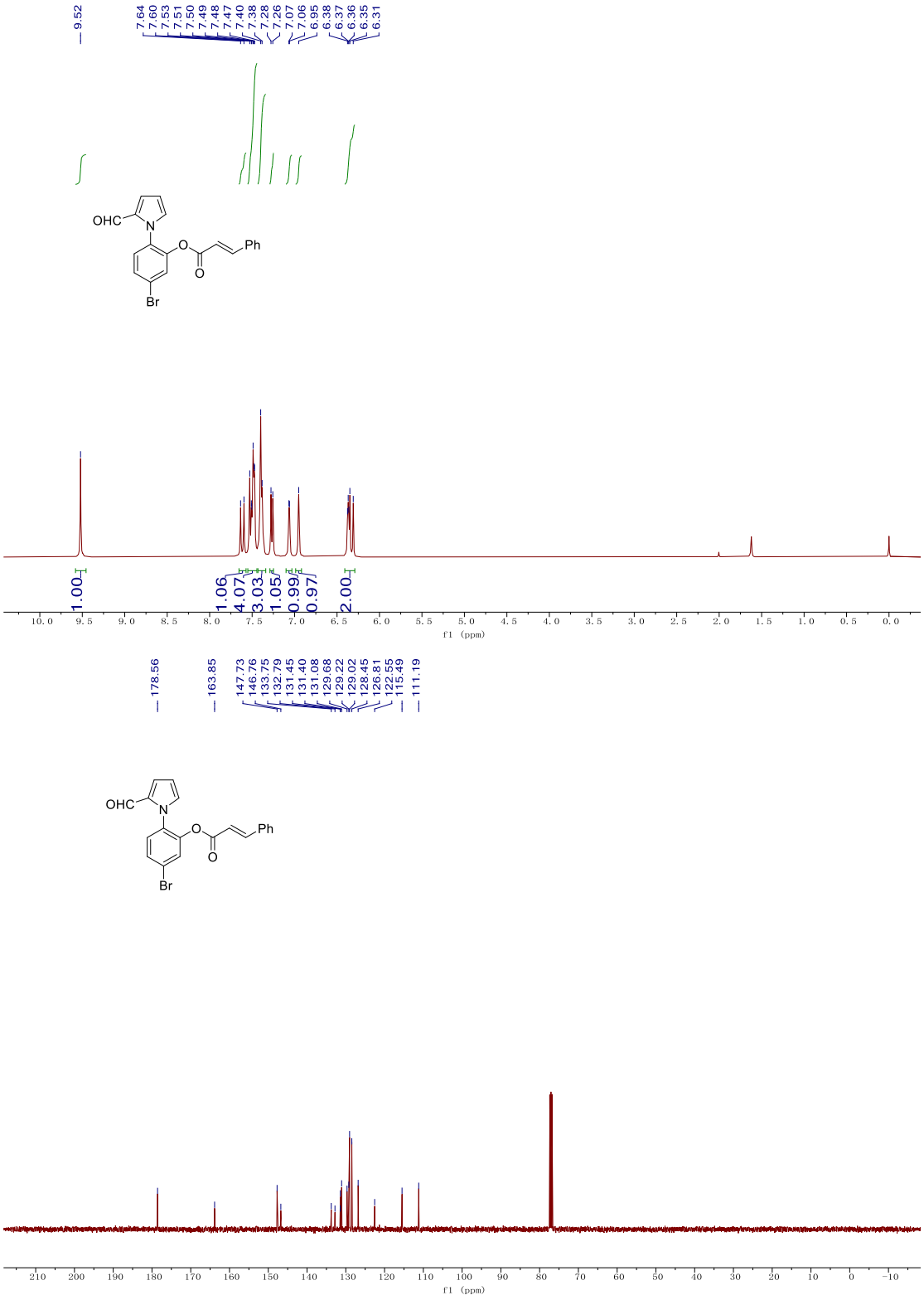

1.00
1.02
2.13
3.96
2.08
0.99
0.97
0.99
1.00
f1 (ppm)


178.59
163.86
147.73
146.69
134.99
133.74
132.82
131.47
131.07
130.92
129.02
128.91
128.44
126.72
123.95
115.50
111.16

OHC
N
O
O
Ph
Cl


f1 (ppm)

5s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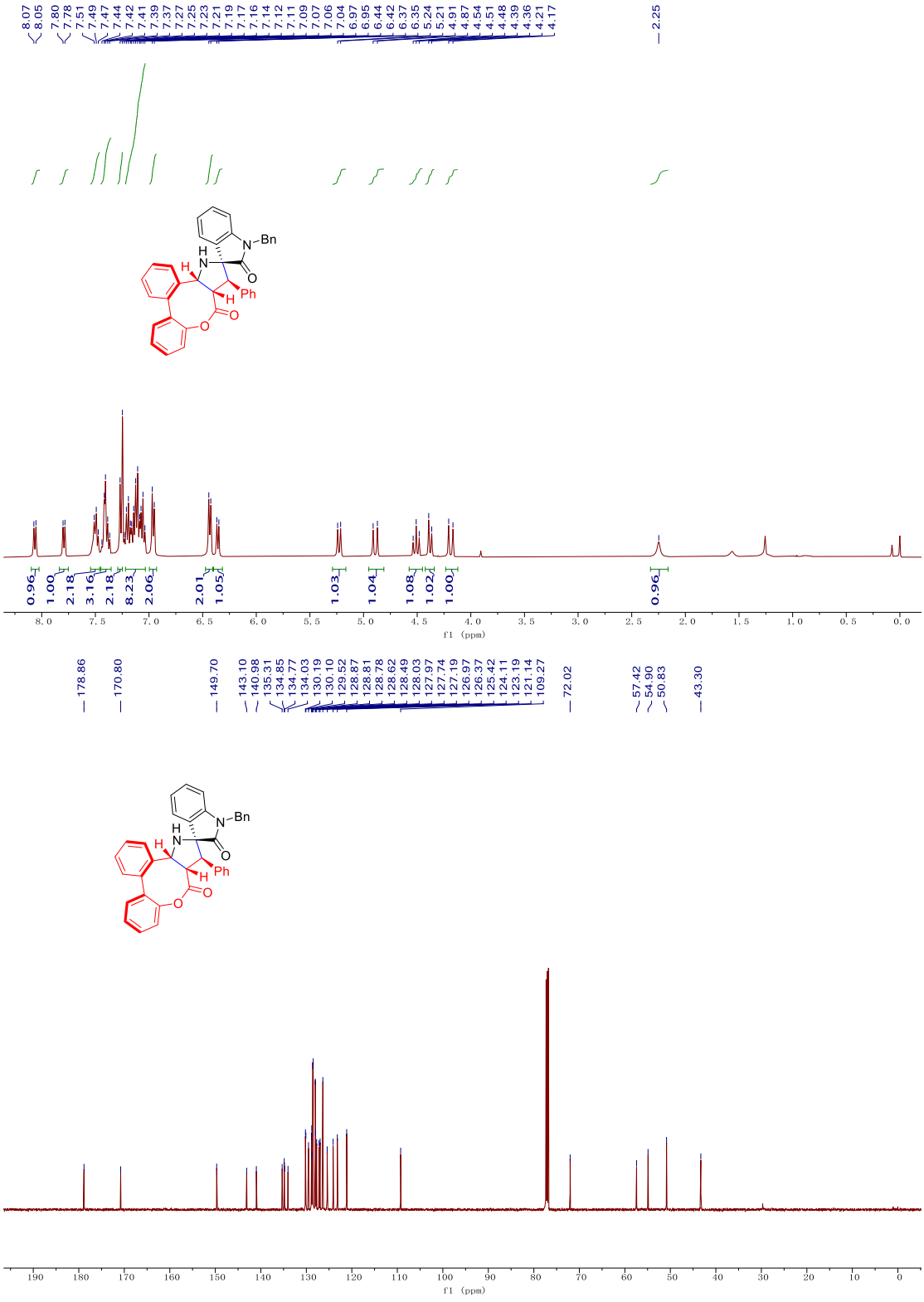
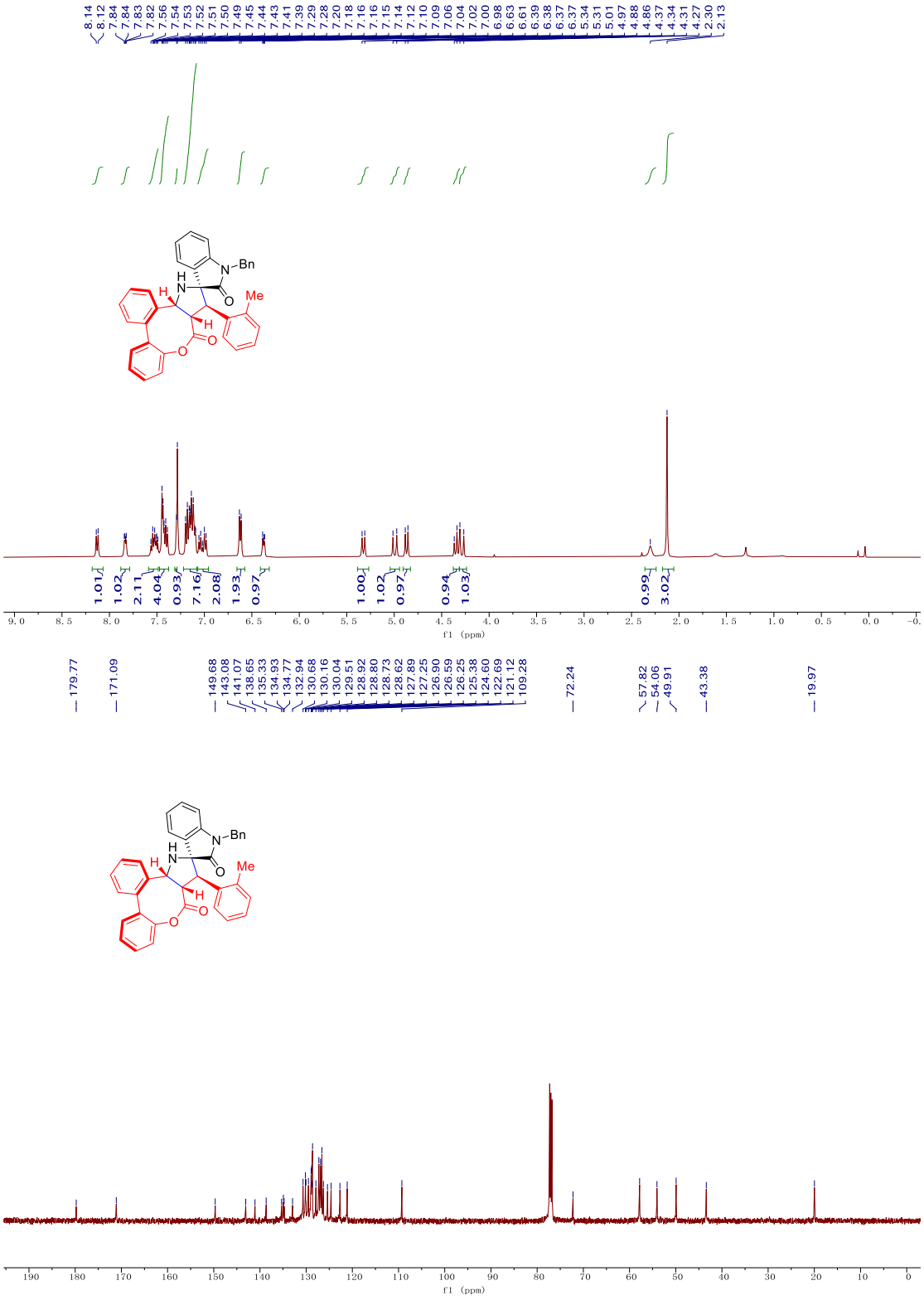
7.50
7.49
7.48
7.47
7.40
7.38
7.28
7.26
7.07
7.06
6.95
6.38
6.37
6.36
6.35
6.31
OHC
N
O
O
Ph
Br
1.00
1.06
4.07
3.03
1.05
0.99
0.97
2.00
f1 (ppm)
178.56
163.85
147.73
146.76
133.75
132.79
131.45
131.40
131.08
129.88
129.22
129.02
128.45
126.81
122.55
115.49
111.19
f1 (ppm)

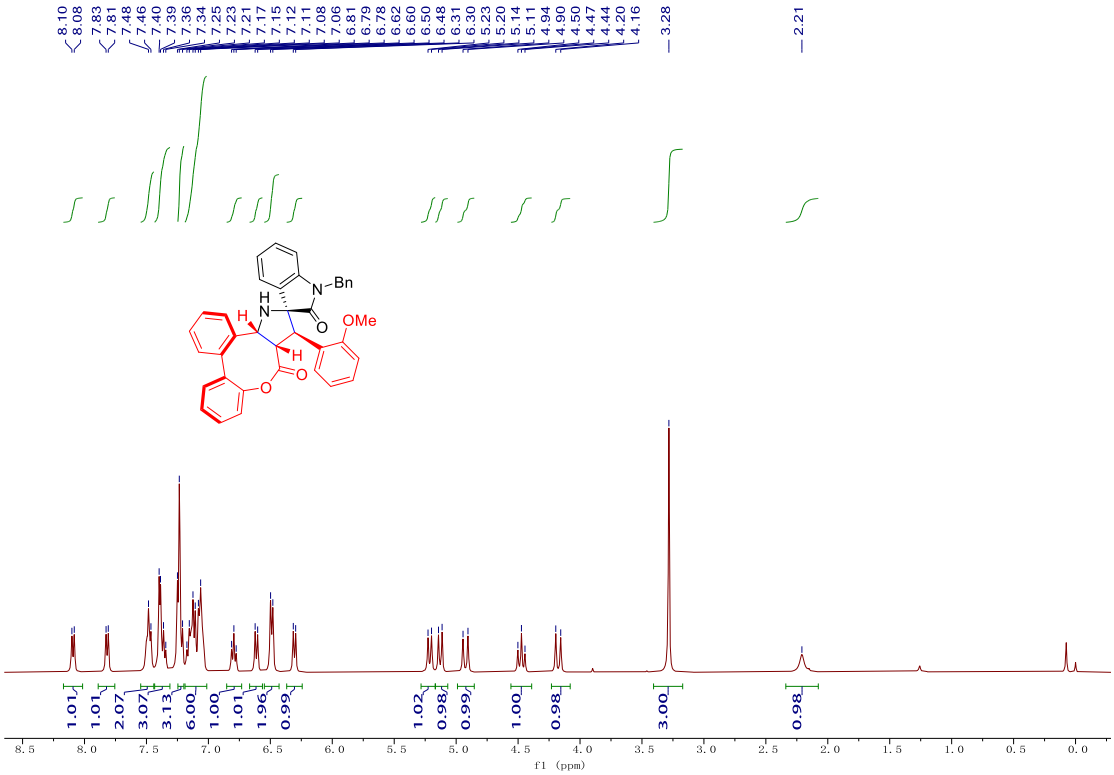
4aa

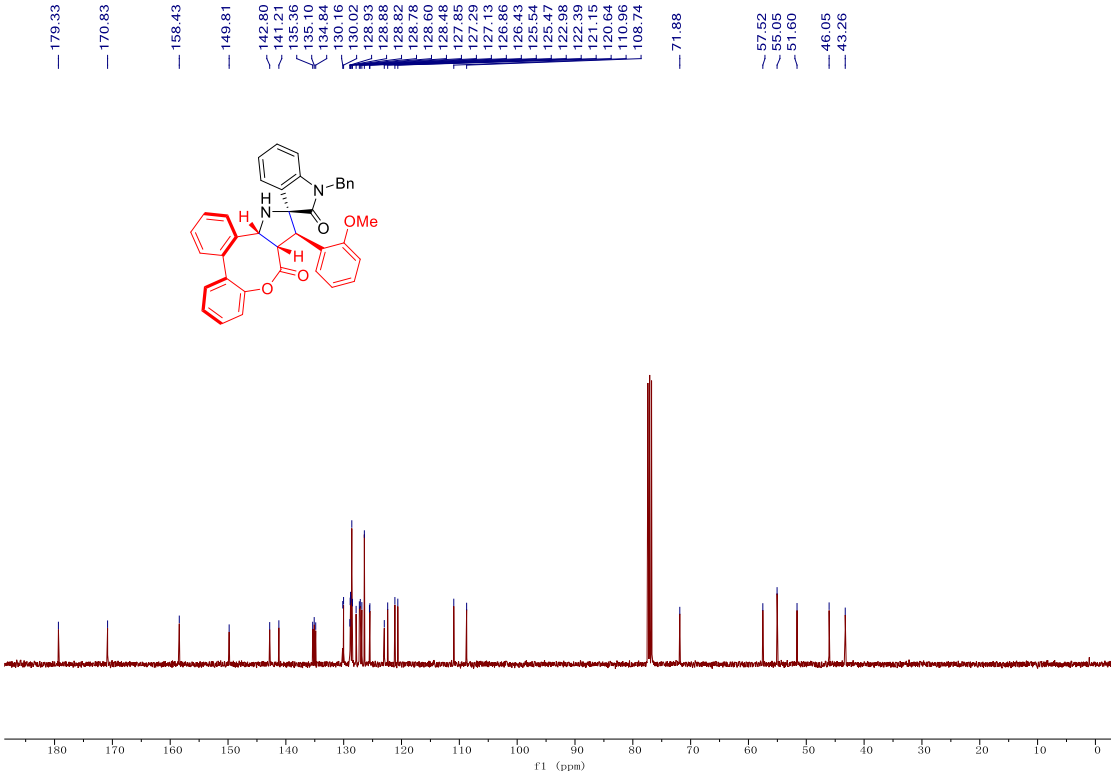

8.07
8.05
7.80
7.78
7.51
7.49
7.47
7.44
7.42
7.41
7.39
7.37
7.27
7.25
7.23
7.21
7.19
7.17
7.16
7.14
7.12
7.11
7.09
7.07
7.06
7.04
6.97
6.95
6.44
6.42
6.37
6.35
5.24
5.21
4.91
4.87
4.54
4.51
4.48
4.39
4.36
4.21
4.17
2.25
N-Bn
H
N
O
H
Ph
O
O
0.96
1.00
2.18
3.16
2.18
8.23
2.06
2.01
1.05
1.03
1.04
1.08
1.02
1.00
0.96
f1 (ppm)
178.86
170.80
149.70
143.10
140.98
135.31
134.85
134.77
134.03
130.19
130.10
129.52
128.87
128.81
128.78
128.62
128.49
128.03
127.97
127.74
127.19
126.97
126.37
125.42
124.11
123.19
121.14
109.27
72.02
57.42
54.90
50.83
43.30
N-Bn
H
N
O
H
Ph
O
O
f1 (ppm)

4ab

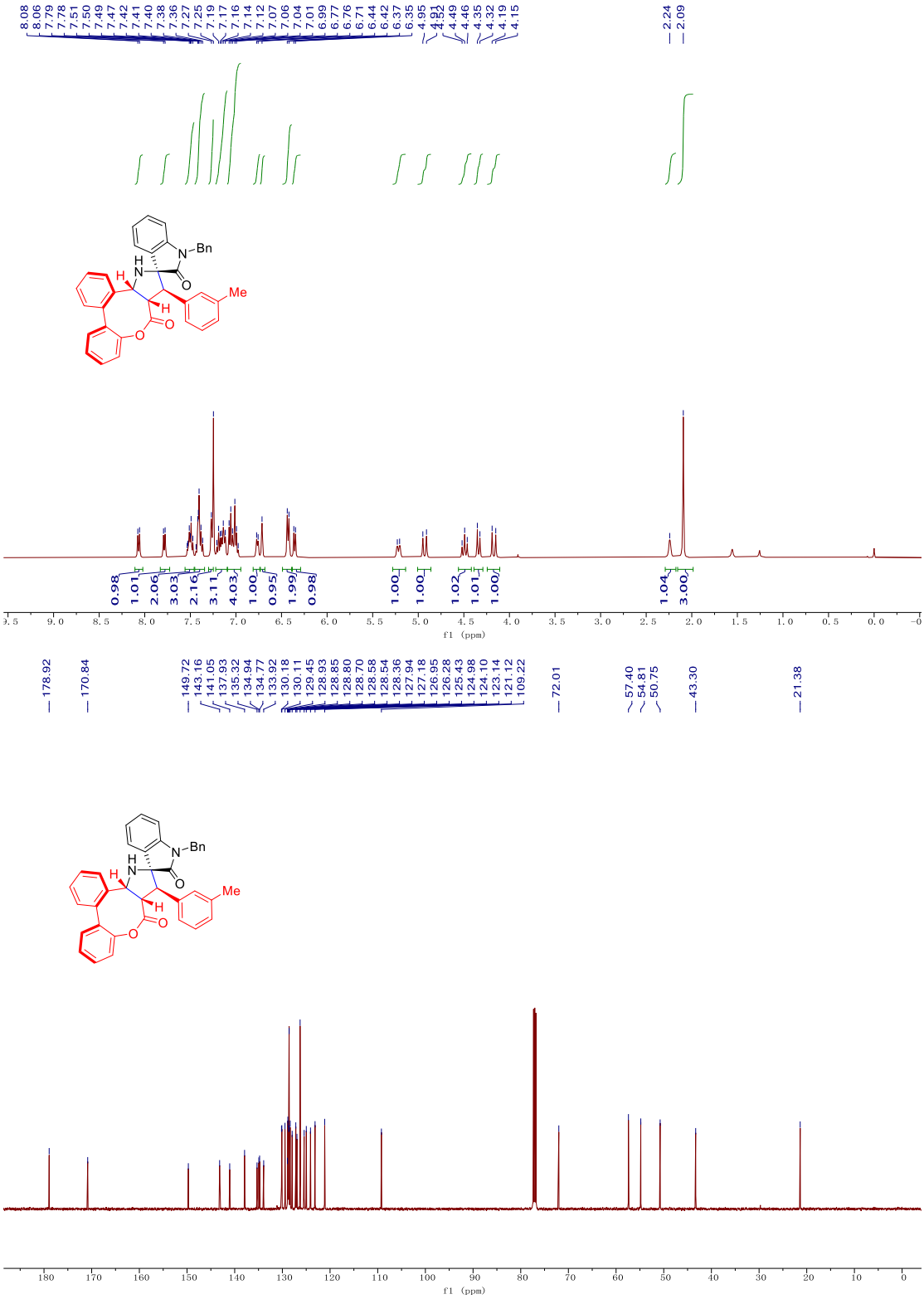

8.14 8.12 7.84 7.84 7.83 7.82 7.56 7.54 7.53 7.52 7.51 7.50 7.49 7.45 7.44 7.43 7.41 7.39 7.29 7.28 7.20 7.18 7.16 7.16 7.15 7.14 7.12 7.10 7.09 7.06 7.04 7.02 7.00 6.98 6.63 6.61 6.39 6.38 6.37 6.37 5.34 5.31 5.01 4.97 4.88 4.86 4.37 4.34 4.31 4.27 2.30 2.13
N-Bn
H
N
O
Me
H
O
O
1.01 1.02 2.11 4.04 0.93 7.16 2.08 1.93 0.97 1.00 1.02 0.97 0.94 1.03 0.99 3.02
f1 (ppm)
179.77 171.09 149.68 143.08 141.07 138.65 135.33 134.93 134.77 132.94 130.68 130.16 130.04 129.51 128.92 128.80 128.73 128.62 127.89 127.25 126.90 126.59 126.25 125.38 124.60 122.69 121.12 109.28 72.24 57.82 54.06 49.91 43.38 19.97
f1 (ppm)

4ac


8.10
8.08
7.83
7.81
7.48
7.46
7.40
7.39
7.36
7.34
7.25
7.23
7.21
7.17
7.15
7.12
7.11
7.08
7.06
6.81
6.79
6.78
6.62
6.60
6.50
6.48
6.31
6.30
5.23
5.20
5.14
5.11
4.94
4.90
4.50
4.47
4.44
4.20
4.16
3.28
2.21
N-Bn
H
N
O
OMe
H
O
O
1.01
1.01
2.07
3.07
3.13
6.00
1.00
1.01
1.96
0.99
1.02
0.98
0.99
1.00
0.98
3.00
0.98
f1 (ppm)


179.33
170.83
158.43
149.81
142.80
141.21
135.36
135.10
134.84
130.16
130.02
128.93
128.88
128.82
128.78
128.60
128.48
127.85
127.29
127.13
126.86
126.43
125.54
125.47
122.98
122.39
121.15
120.64
110.96
108.74
71.88
57.52
55.05
51.60
46.05
43.26
N-Bn
H
N
O
OMe
H
O
O
f1 (ppm)

4ad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8.06
7.79
7.78
7.51
7.50
7.49
7.47
7.42
7.41
7.40
7.38
7.36
7.27
7.25
7.19
7.17
7.16
7.14
7.12
7.07
7.06
7.04
7.01
6.99
6.77
6.76
6.71
6.44
6.42
6.37
6.35
4.95
4.91
4.49
4.46
4.35
4.32
4.19
4.15
2.24
2.09
N-Bn
H
N
O
H
O
Me
0.98
1.01
2.06
3.03
2.16
3.11
4.03
1.00
0.95
1.99
0.98
1.00
1.00
1.02
1.01
1.00
1.04
3.00
f1 (ppm)
178.92
170.84
149.72
143.16
141.05
137.93
135.32
134.94
134.77
133.92
130.18
130.11
129.45
128.93
128.85
128.80
128.70
128.58
128.54
128.36
127.94
127.18
126.95
126.28
125.43
124.98
124.10
123.14
121.12
109.22
72.01
57.40
54.81
50.75
43.30
21.38
N-Bn
H
N
O
H
O
Me
f1 (ppm)

4ae


8.07
8.05
7.79
7.77
7.52
7.52
7.50
7.50
7.49
7.47
7.43
7.41
7.41
7.40
7.38
7.36
7.34
7.26
7.25
7.23
7.20
7.18
7.17
7.16
7.16
7.15
7.14
7.12
7.07
7.05
7.03
6.92
6.90
6.85
6.83
6.49
6.47
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6.35
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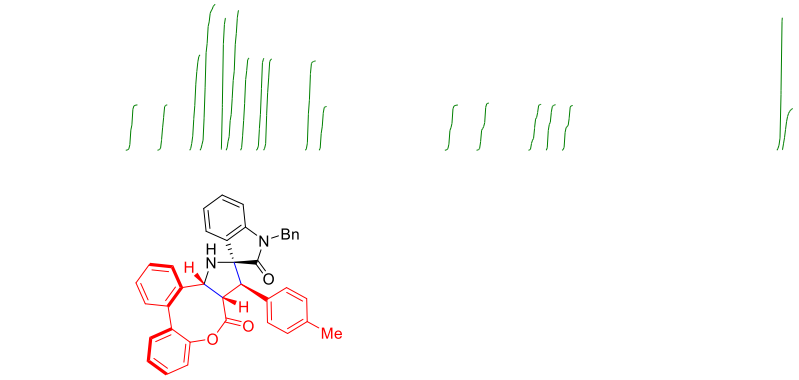
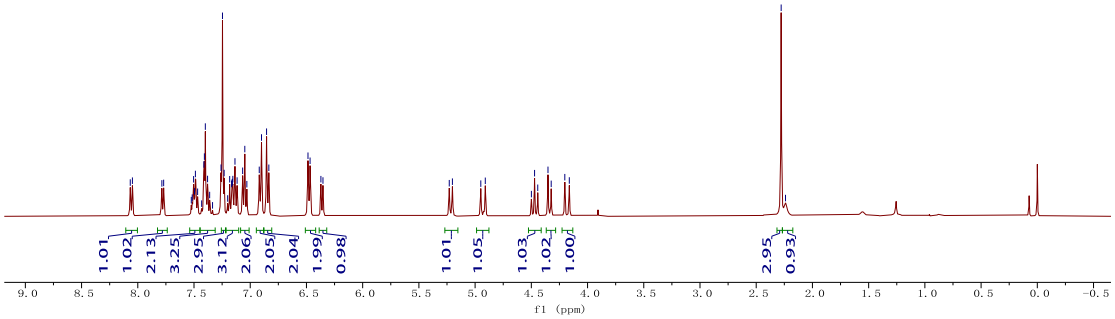
5.20
4.95
4.91
4.50
4.47
4.44
4.35
4.32
4.20
4.16
2.28
2.24



N-Bn
H
N
O
H
H
O
O
Me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1.02
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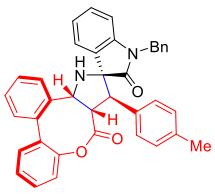
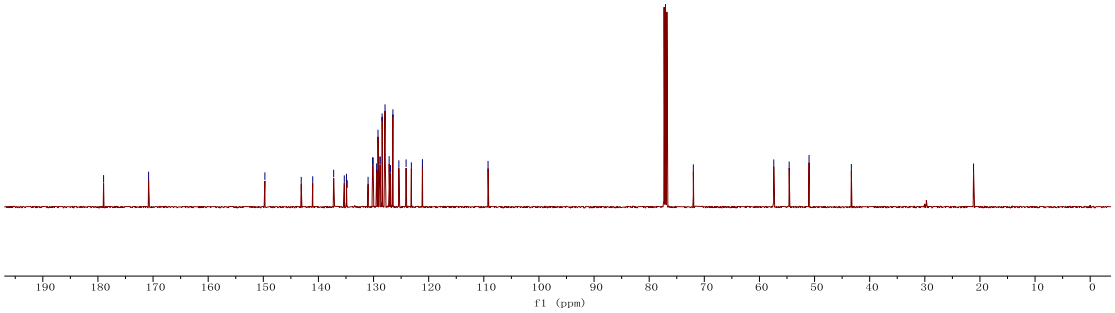
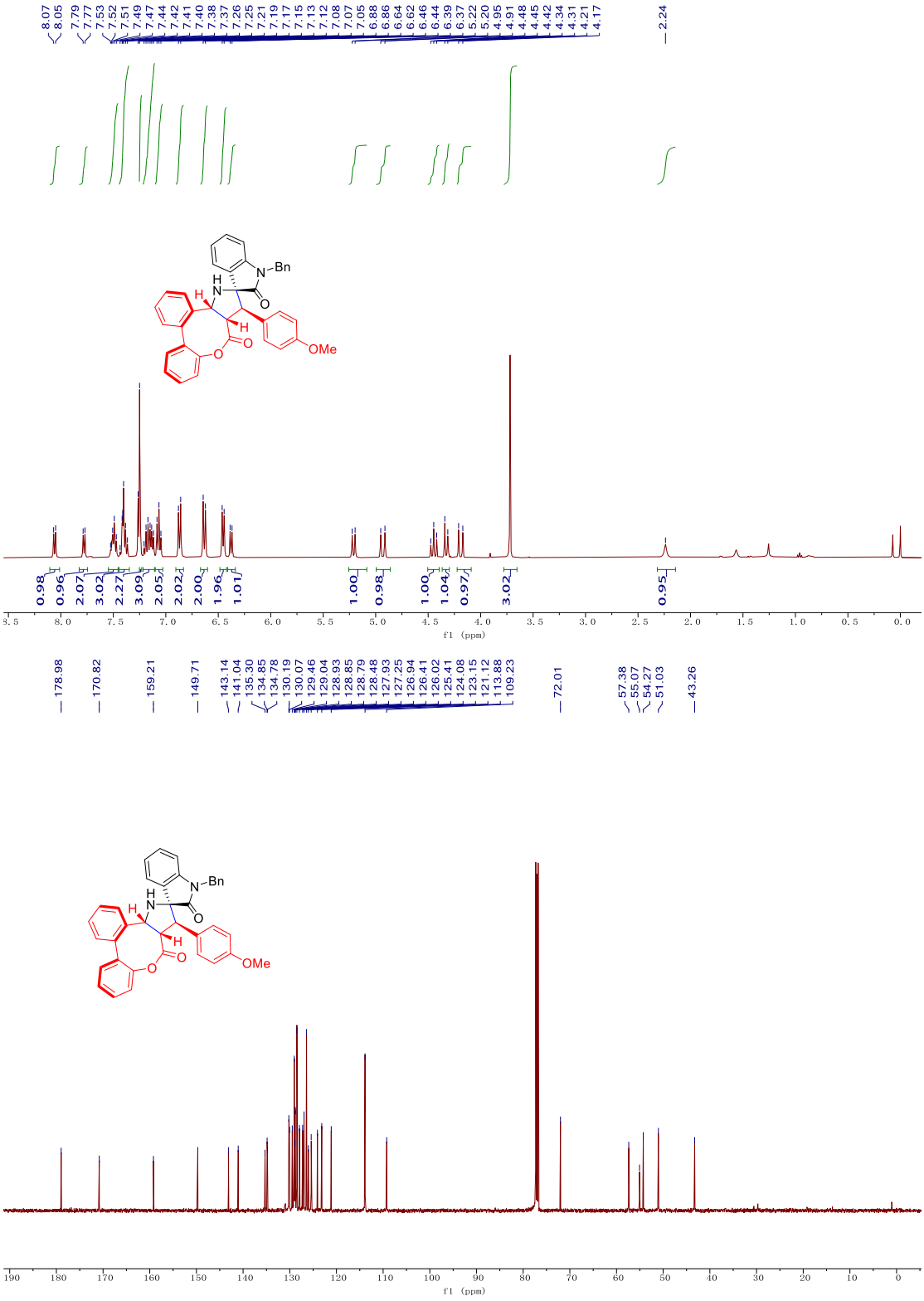
3.12
2.06
2.05
2.04
1.99
0.98
1.01
1.05
1.03
1.02
1.00
2.95
0.93
f1 (ppm)


178.98
170.81
149.71
143.12
141.04
137.24
135.31
134.92
134.78
130.99
130.17
130.07
129.44
129.19
128.91
128.85
128.79
128.45
127.92
127.17
126.92
126.49
125.41
124.10
123.14
121.13
109.23
71.99
57.40
54.61
51.00
43.33
21.16


N-Bn
H
N
O
H
H
O
O
Me


f1 (ppm)

4af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8.05
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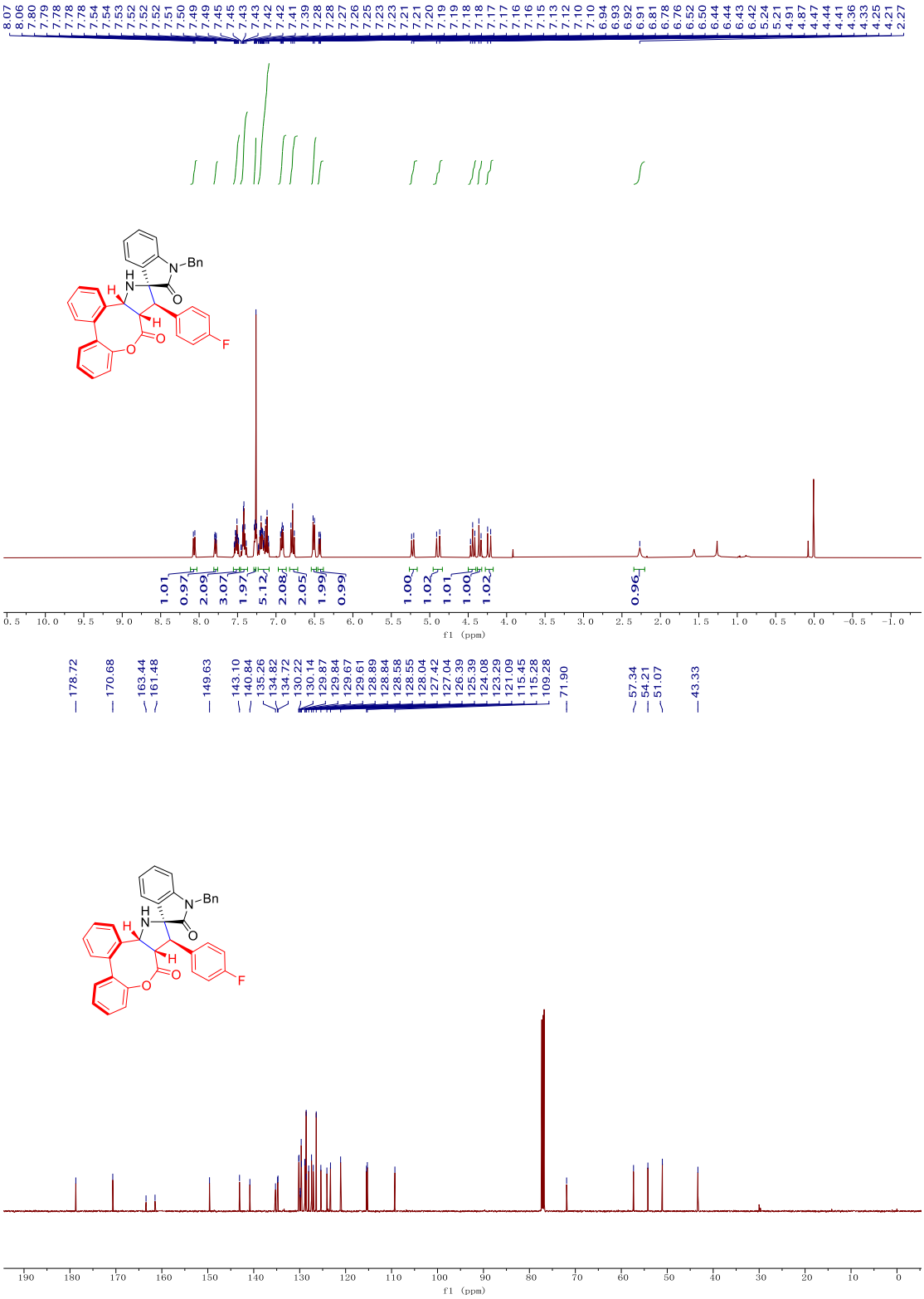
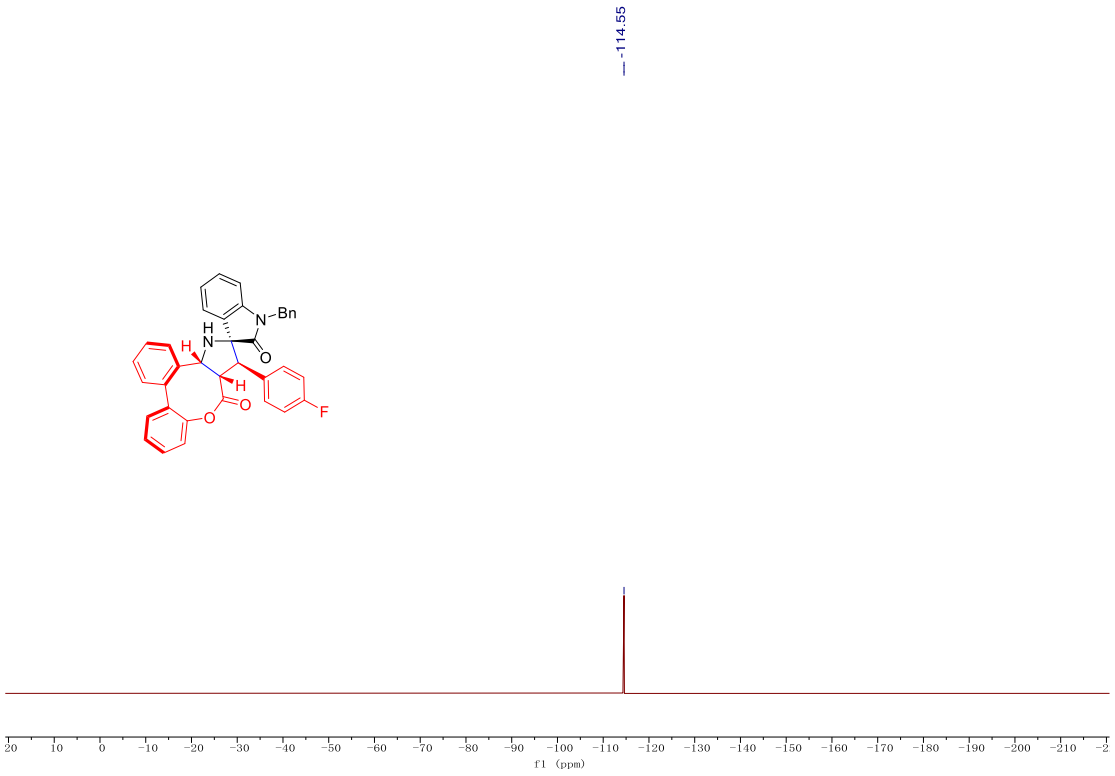
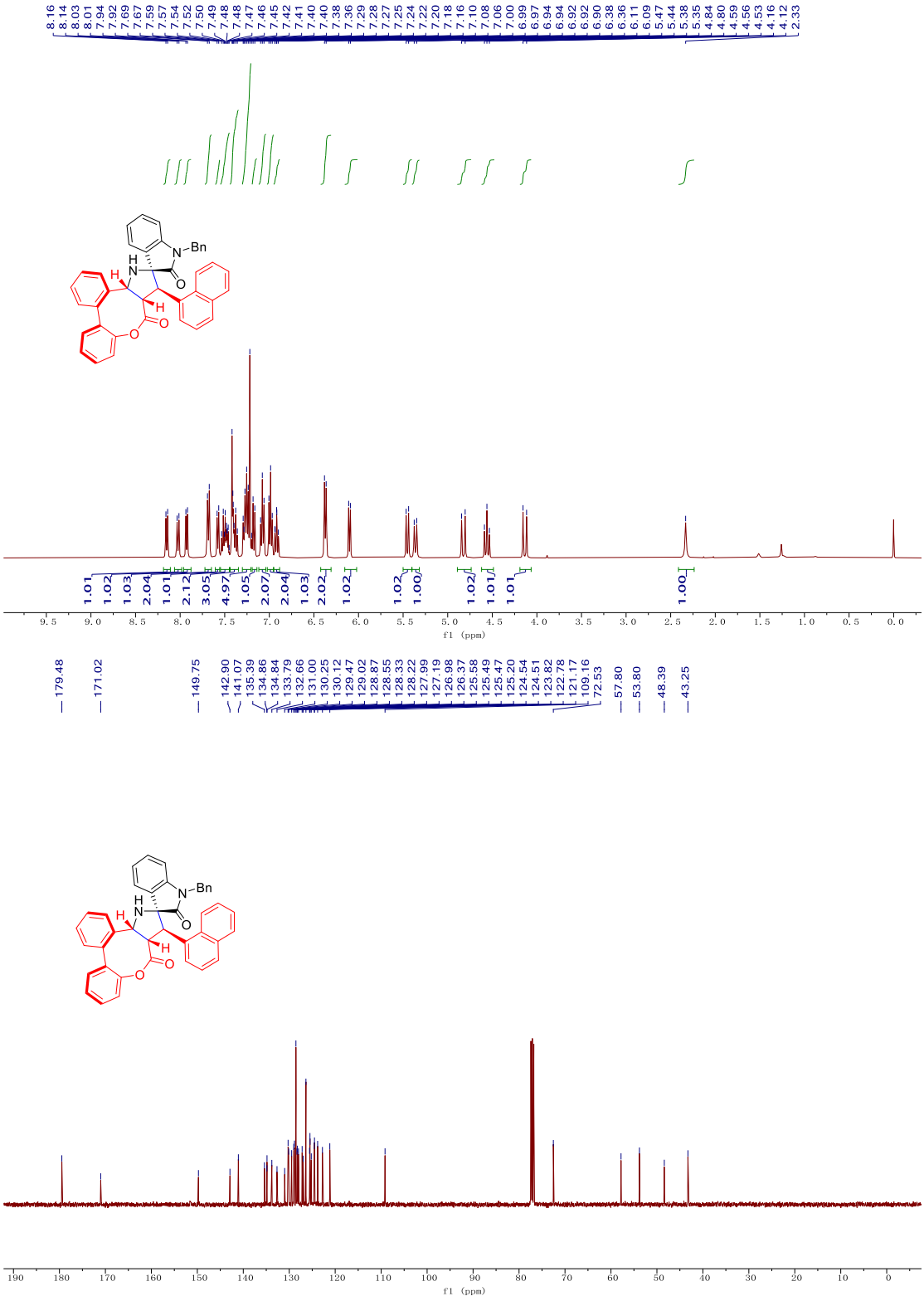
7.52
7.51
7.49
7.47
7.44
7.42
7.41
7.40
7.38
7.37
7.26
7.25
7.21
7.19
7.17
7.15
7.13
7.12
7.08
7.07
7.05
6.88
6.86
6.64
6.62
6.46
6.44
6.39
6.37
5.22
5.20
4.95
4.91
4.48
4.45
4.42
4.34
4.31
4.21
4.17
2.24
N-Bn
H
N
O
H
O
O
OMe
0.98
0.96
2.07
3.02
2.27
3.09
2.05
2.02
2.00
1.96
1.01
1.00
0.98
1.00
1.04
0.97
3.02
0.95
f1 (ppm)
178.98
170.82
159.21
149.71
143.14
141.04
135.30
134.85
134.78
130.19
130.07
129.46
129.04
128.93
128.85
128.79
128.48
127.93
127.25
126.94
126.41
126.02
125.41
124.08
123.15
121.12
113.88
109.23
72.01
57.38
55.07
54.27
51.03
43.26
f1 (ppm)

4ag

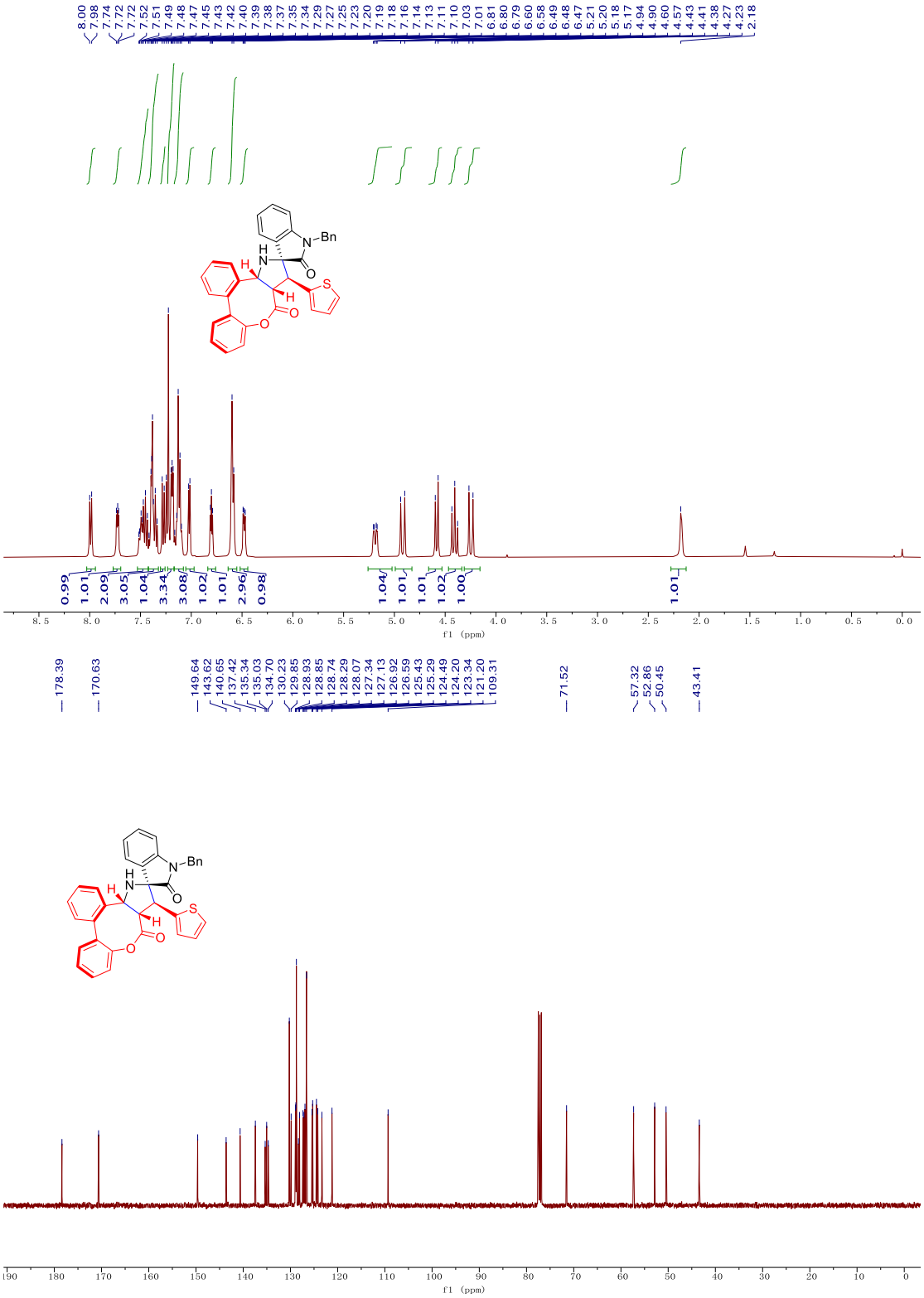

8.07 8.06 7.80 7.79 7.78 7.78 7.78 7.54 7.53 7.52 7.52 7.52 7.51 7.50 7.49 7.49 7.45 7.45 7.43 7.43 7.42 7.42 7.41 7.39 7.28 7.28 7.27 7.26 7.25 7.23 7.23 7.21 7.21 7.20 7.19 7.19 7.18 7.18 7.17 7.17 7.16 7.16 7.15 7.13 7.12 7.10 7.10 6.94 6.93 6.92 6.91 6.81 6.78 6.76 6.52 6.50 6.44 6.44 6.43 6.42 5.24 5.21 4.91 4.87 4.47 4.44 4.41 4.36 4.33 4.25 4.21 2.27
N-Bn
H
N
O
H
O
O
F
1.01 0.97 2.09 3.07 1.97 5.12 2.08 2.05 1.99 0.99 1.00 1.02 1.01 1.00 1.02 0.96
f1 (ppm)
178.72 170.68 163.44 161.48 149.63 143.10 140.84 135.26 134.82 134.72 130.22 130.14 129.87 129.84 129.67 129.61 128.89 128.84 128.58 128.55 128.04 127.42 127.04 126.39 125.39 124.08 123.29 121.09 115.45 115.28 109.28 71.90 57.34 54.21 51.07 43.33
N-Bn
H
N
O
H
O
O
F
f1 (ppm)


-114.55
Bn
N
H
N
O
H
H
O
O
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

4ah


8.16 8.14 8.03 8.01 7.94 7.92 7.69 7.67 7.59 7.57 7.54 7.52 7.50 7.49 7.48 7.48 7.47 7.46 7.45 7.42 7.41 7.40 7.40 7.38 7.36 7.29 7.28 7.27 7.25 7.24 7.22 7.20 7.18 7.16 7.10 7.08 7.06 7.00 6.99 6.97 6.94 6.94 6.92 6.92 6.90 6.38 6.36 6.11 6.09 5.47 5.44 5.38 5.35 4.84 4.80 4.59 4.56 4.53 4.16 4.12 2.33
N-Bn
H
N
O
H
O
O
1.01 1.02 1.03 2.04 1.01 2.12 3.05 4.97 1.05 2.07 2.04 1.03 2.02 1.02 1.02 1.00 1.02 1.01 1.01 1.00
f1 (ppm)
179.48 171.02 149.75 142.90 141.07 135.39 134.86 134.84 133.79 132.66 131.00 130.25 130.12 129.47 129.02 128.87 128.55 128.33 128.22 127.99 127.19 126.98 126.37 125.58 125.49 125.47 125.20 124.54 124.51 123.82 122.78 121.17 109.16 72.53 57.80 53.80 48.39 43.25
N-Bn
H
N
O
H
O
O
f1 (ppm)

4ai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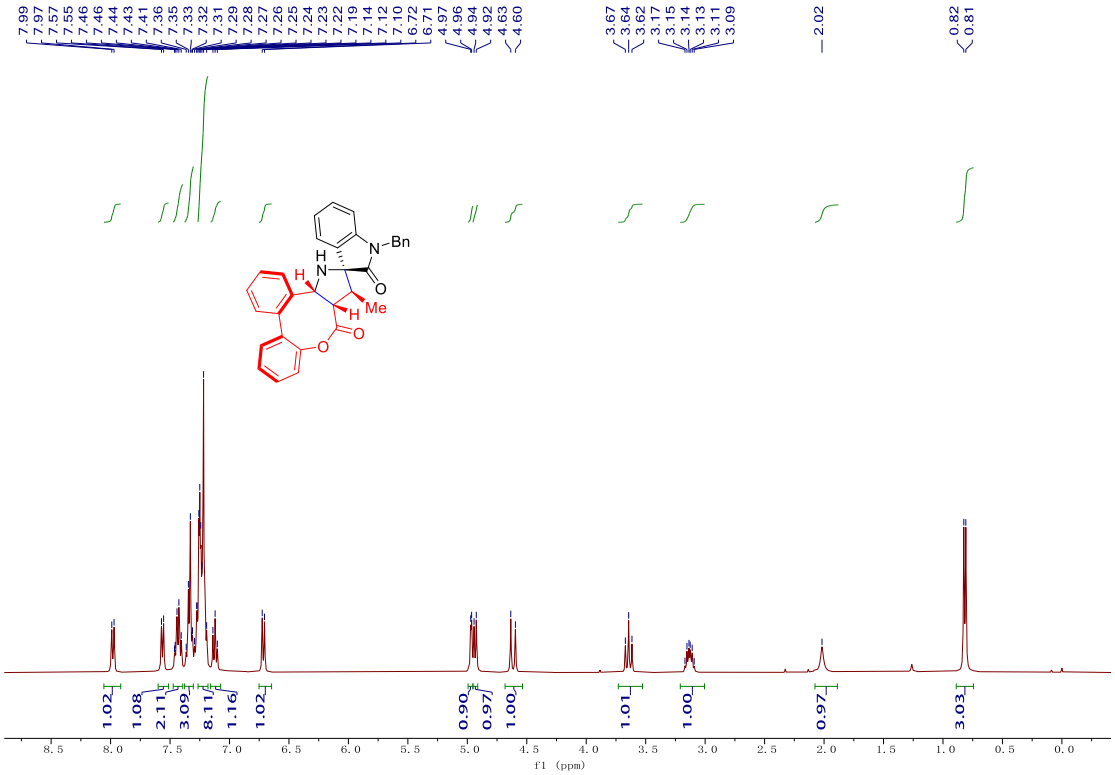
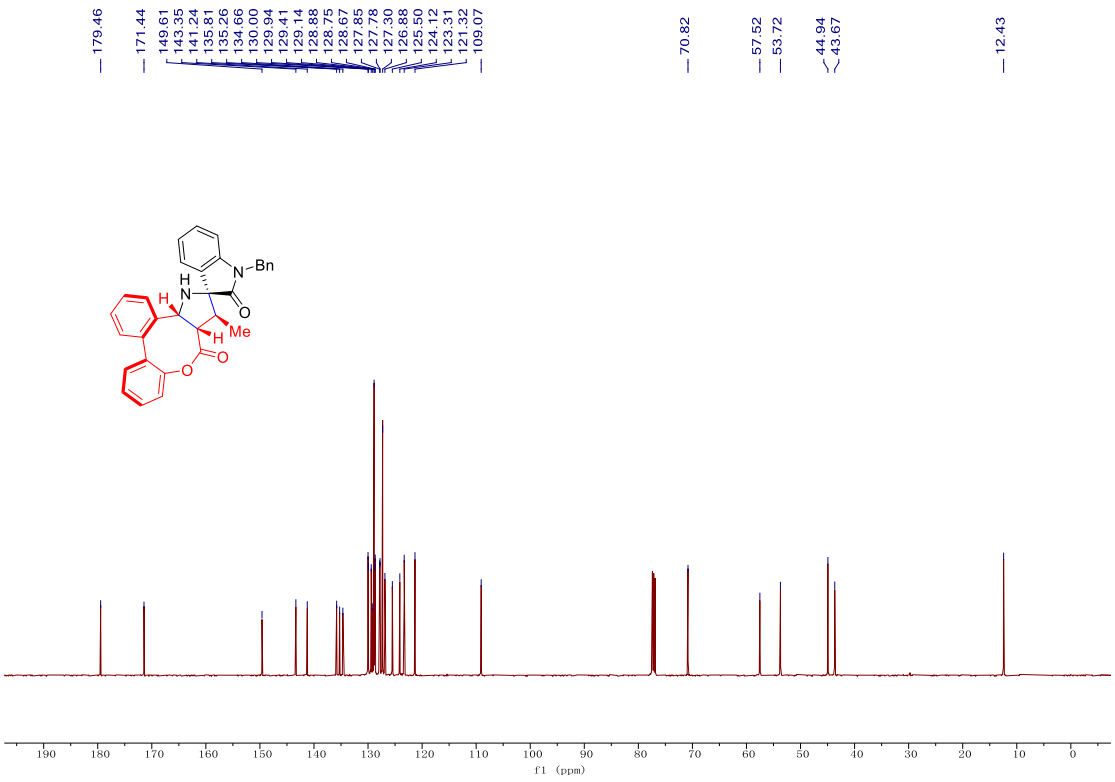
7.98
7.74
7.72
7.72
7.52
7.51
7.49
7.48
7.47
7.45
7.43
7.42
7.40
7.39
7.38
7.37
7.35
7.34
7.29
7.27
7.25
7.23
7.20
7.19
7.18
7.16
7.14
7.13
7.11
7.10
7.03
7.01
6.81
6.80
6.79
6.60
6.58
6.49
6.48
6.47
5.21
5.20
5.18
5.17
4.94
4.90
4.60
4.57
4.43
4.41
4.38
4.27
4.23
2.18
N-Bn
H
N
O
H
S
O
O
0.99
1.01
2.09
3.05
1.04
3.34
3.08
1.02
1.01
2.96
0.98
1.04
1.01
1.01
1.02
1.00
1.01
f1 (ppm)
178.39
170.63
149.64
143.62
140.65
137.42
135.34
135.03
134.70
130.23
129.85
128.93
128.85
128.74
128.29
128.07
127.34
127.13
126.92
126.59
125.43
125.29
124.49
124.20
123.34
121.20
109.31
71.52
57.32
52.86
50.45
43.41
f1 (ppm)

4aj


7.99
7.97
7.57
7.55
7.46
7.46
7.44
7.43
7.41
7.36
7.35
7.33
7.32
7.31
7.29
7.28
7.27
7.26
7.25
7.24
7.23
7.22
7.19
7.14
7.12
7.10
6.72
6.71
4.97
4.96
4.94
4.92
4.63
4.60
3.67
3.64
3.62
3.17
3.15
3.14
3.13
3.11
3.09
2.02
0.82
0.81
N-Bn
H
N
O
H
Me
H
O
O
1.02
1.08
2.11
3.09
8.11
1.16
1.02
0.90
0.97
1.00
1.01
1.00
0.97
3.03
f1 (ppm)


179.46
171.44
149.61
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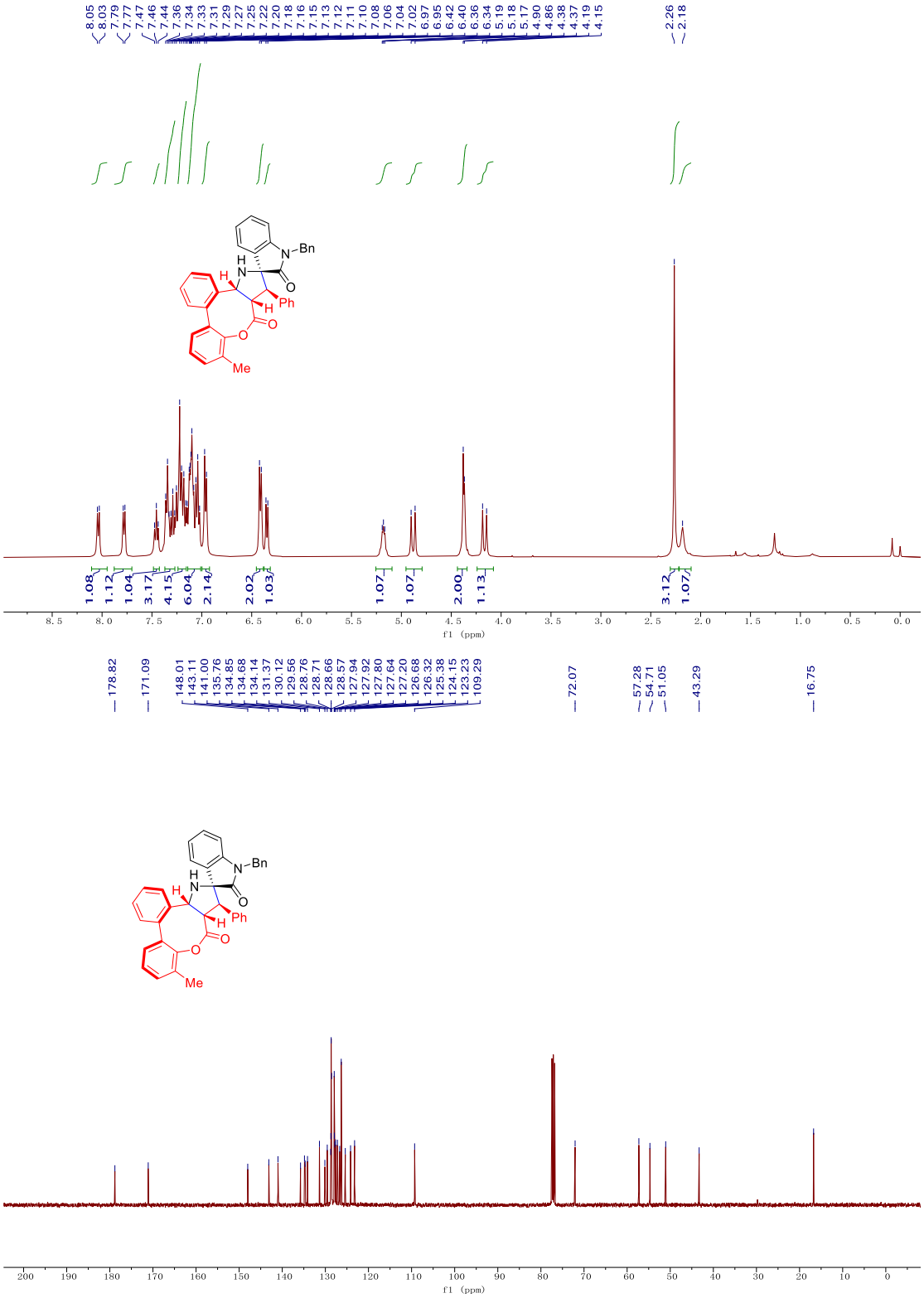
141.24
135.81
135.26
134.66
130.00
129.94
129.41
129.14
128.88
128.75
128.67
127.85
127.78
127.30
126.88
125.50
124.12
123.31
121.32
109.07
70.82
57.52
53.72
44.94
43.67
12.43
N-Bn
H
N
O
H
Me
H
O
O
f1 (ppm)

4ak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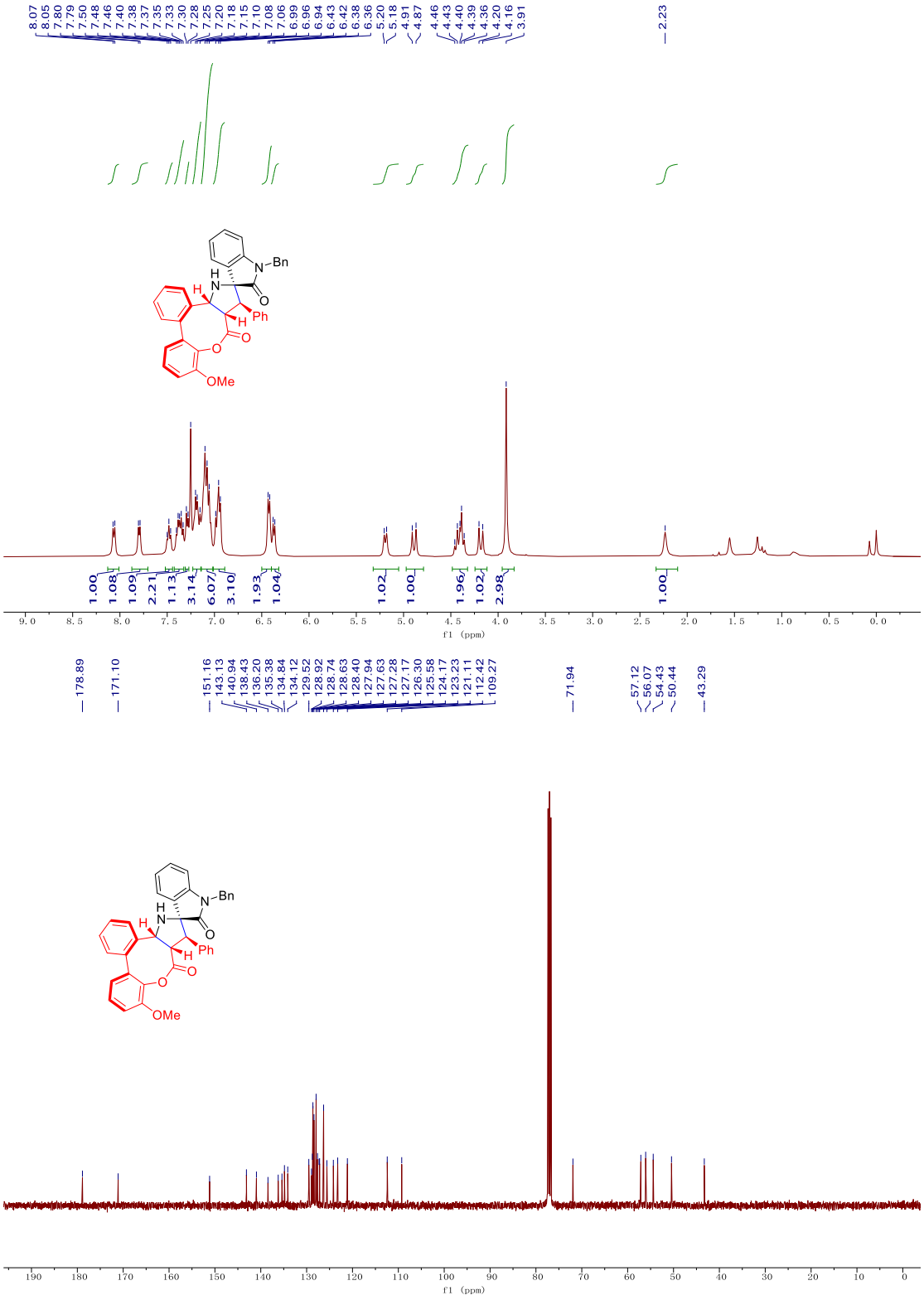
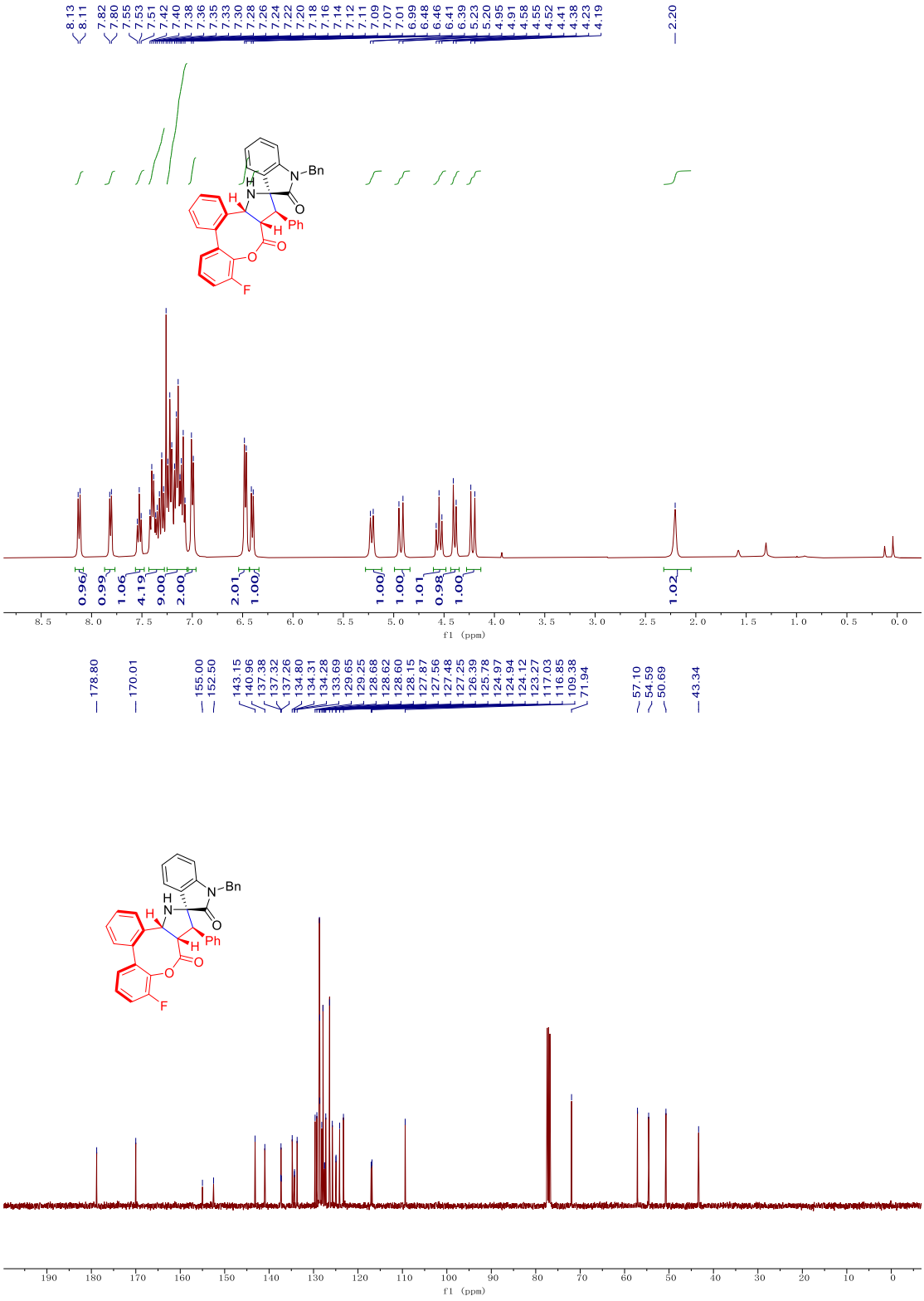
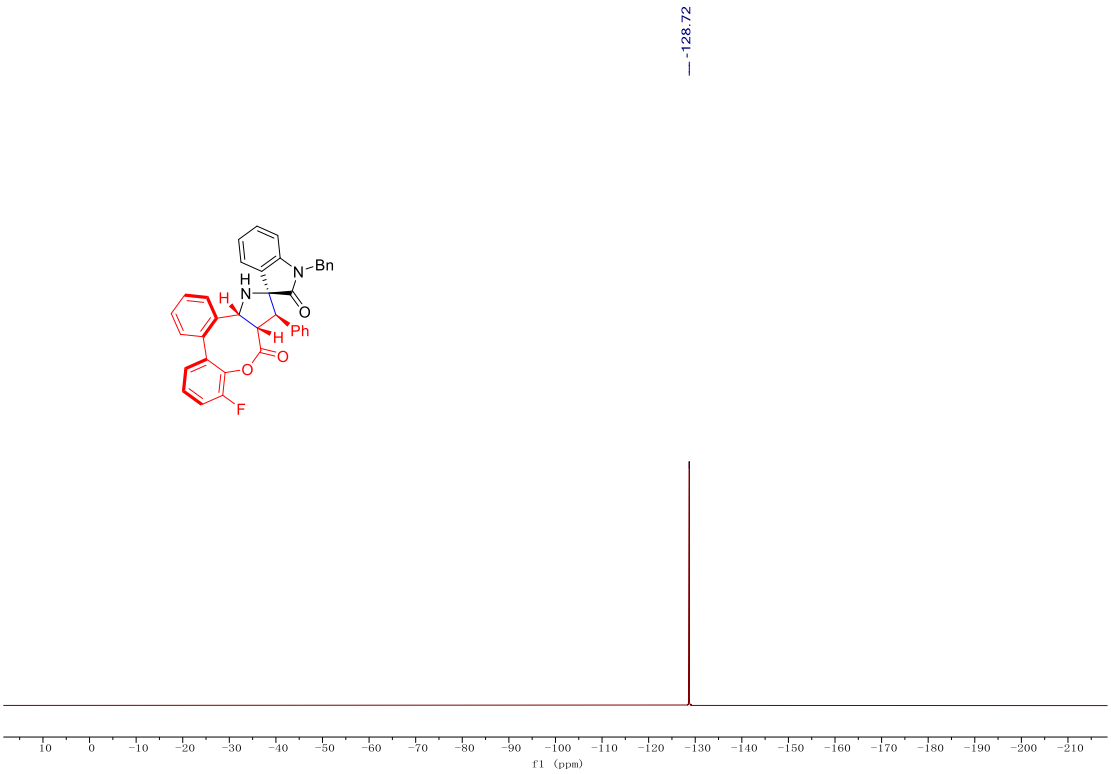
8.03
7.79
7.77
7.47
7.46
7.44
7.36
7.34
7.33
7.31
7.29
7.27
7.25
7.22
7.20
7.18
7.16
7.15
7.13
7.12
7.11
7.10
7.08
7.06
7.04
7.02
6.97
6.95
6.42
6.40
6.36
6.34
5.19
5.18
5.17
4.90
4.86
4.38
4.37
4.19
4.15
2.26
2.18
Bn
N
H
N
O
H
Ph
O
O
Me
1.08
1.12
1.04
3.17
4.15
6.04
2.14
2.02
1.03
1.07
1.07
2.00
1.13
3.12
1.07
f1 (ppm)
178.82
171.09
148.01
143.11
141.00
135.76
134.85
134.68
134.14
131.37
130.12
129.56
128.76
128.71
128.66
128.57
127.94
127.92
127.80
127.64
127.20
126.68
126.32
125.38
124.15
123.23
109.29
72.07
57.28
54.71
51.05
43.29
16.75
f1 (ppm)

4al

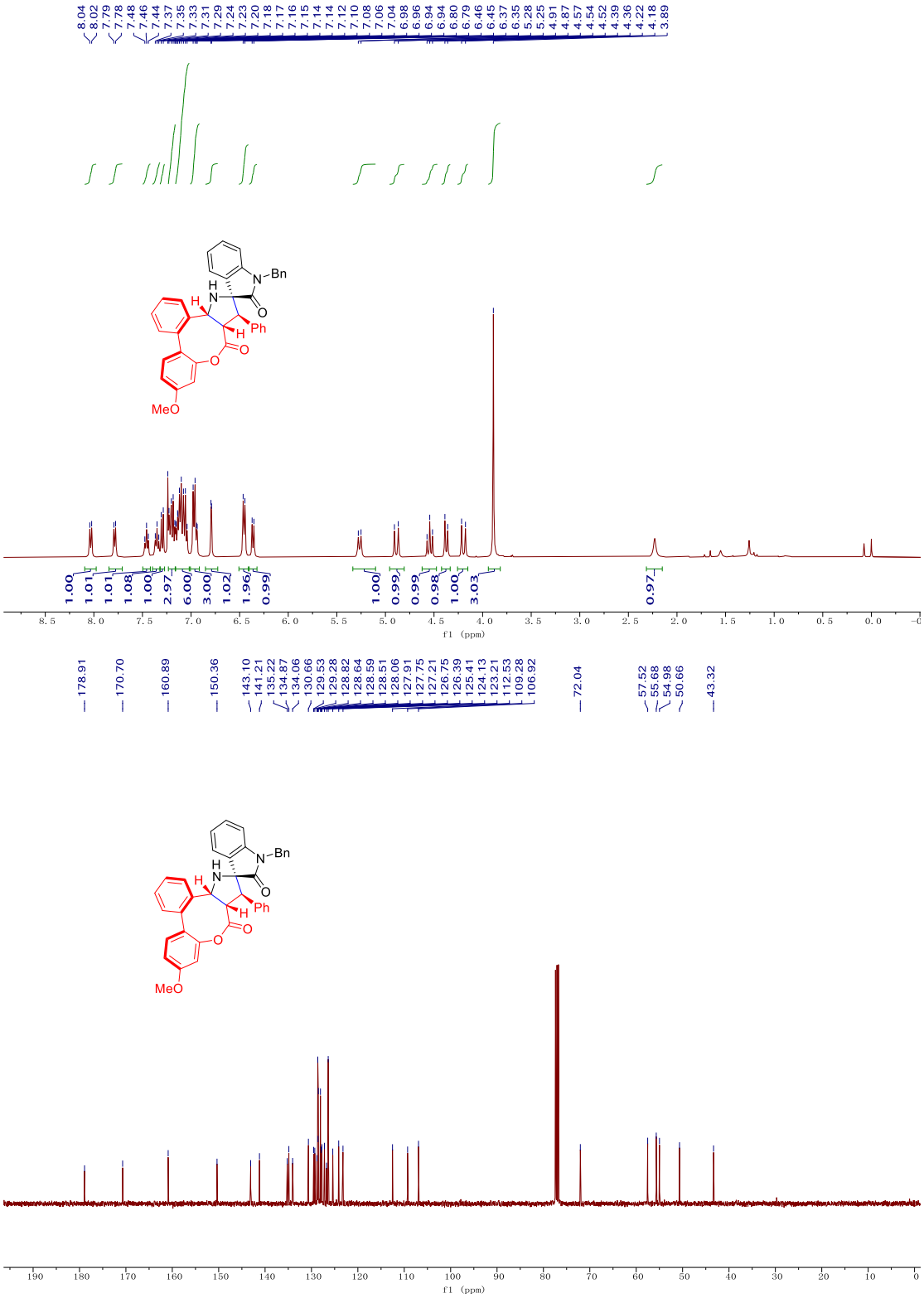

8.07
8.05
7.80
7.79
7.50
7.48
7.46
7.40
7.38
7.37
7.35
7.33
7.30
7.28
7.25
7.20
7.18
7.15
7.10
7.08
7.06
6.99
6.96
6.94
6.43
6.42
6.38
6.36
5.20
5.18
4.91
4.87
4.46
4.43
4.40
4.39
4.36
4.20
4.16
3.91
2.23
N-Bn
H
N
O
H
Ph
O
O
OMe
1.00
1.08
1.09
2.21
1.13
3.14
6.07
3.10
1.93
1.04
1.02
1.00
1.96
1.02
2.98
1.00
f1 (ppm)
178.89
171.10
151.16
143.13
140.94
138.43
136.20
135.38
134.84
134.12
129.52
128.92
128.74
128.63
128.40
127.94
127.63
127.28
127.17
126.30
125.58
124.17
123.23
121.11
112.42
109.27
71.94
57.12
56.07
54.43
50.44
43.29
f1 (ppm)

4am

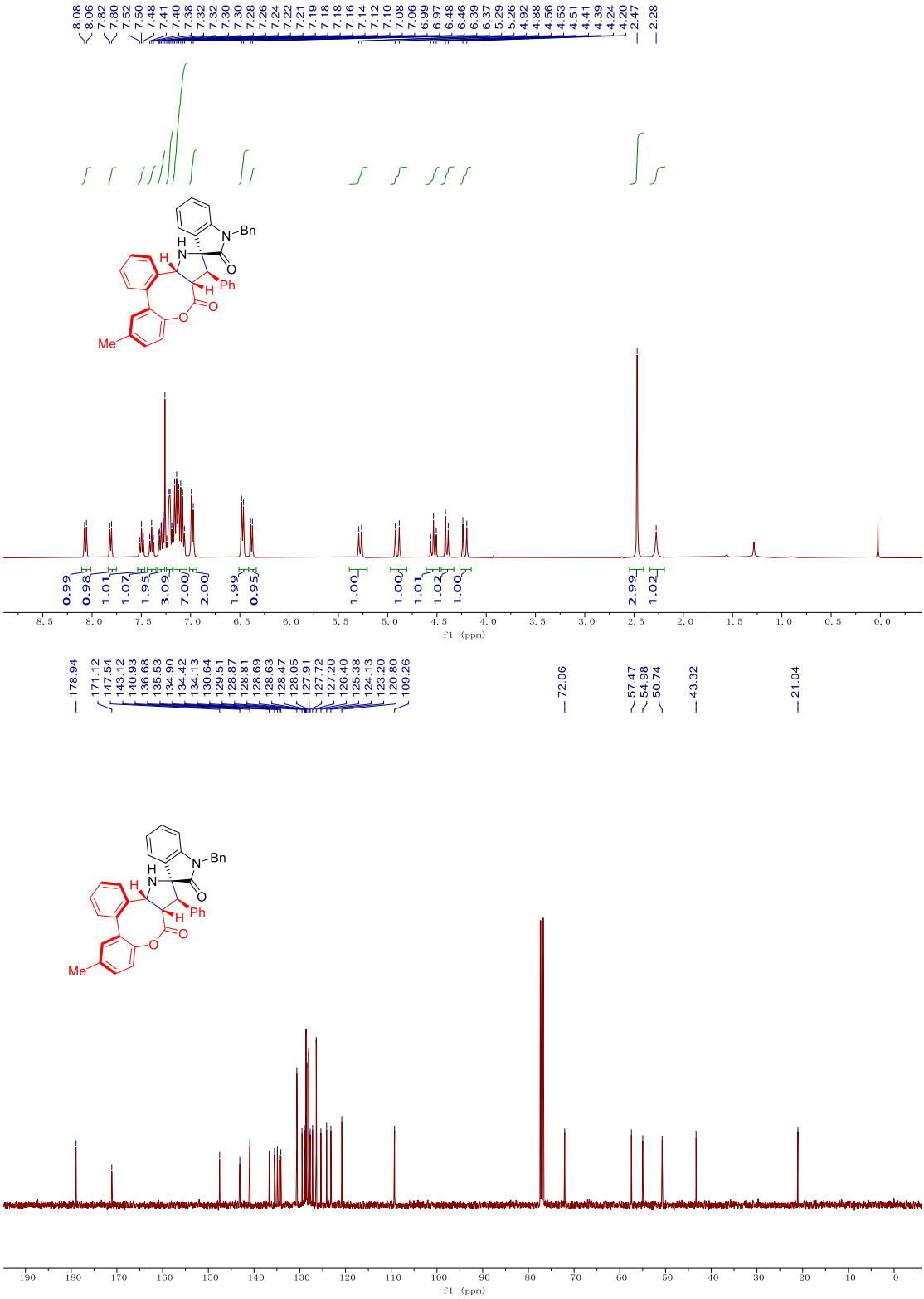

8.13
8.11
7.82
7.80
7.55
7.53
7.51
7.42
7.40
7.38
7.36
7.35
7.33
7.30
7.28
7.26
7.24
7.22
7.20
7.18
7.16
7.14
7.12
7.11
7.09
7.07
7.01
6.99
6.48
6.46
6.41
6.39
5.23
5.20
4.95
4.91
4.58
4.55
4.52
4.41
4.38
4.23
4.19
2.20
N-Bn
H
N
O
H
Ph
H
O
O
F
0.96
0.93
1.06
4.19
9.00
2.00
2.01
1.00
1.00
1.00
1.01
0.98
1.00
1.02
f1 (ppm)
178.80
170.01
155.00
152.50
143.15
140.96
137.38
137.32
137.26
134.80
134.31
134.28
133.69
129.65
129.25
128.68
128.62
128.60
128.15
127.87
127.56
127.48
127.25
126.39
125.78
124.97
124.94
124.12
123.27
117.03
116.85
109.38
71.94
57.10
54.59
50.69
43.34
f1 (ppm)


-128.72
N
Bn
H
N
O
H
Ph
H
O
O
F
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

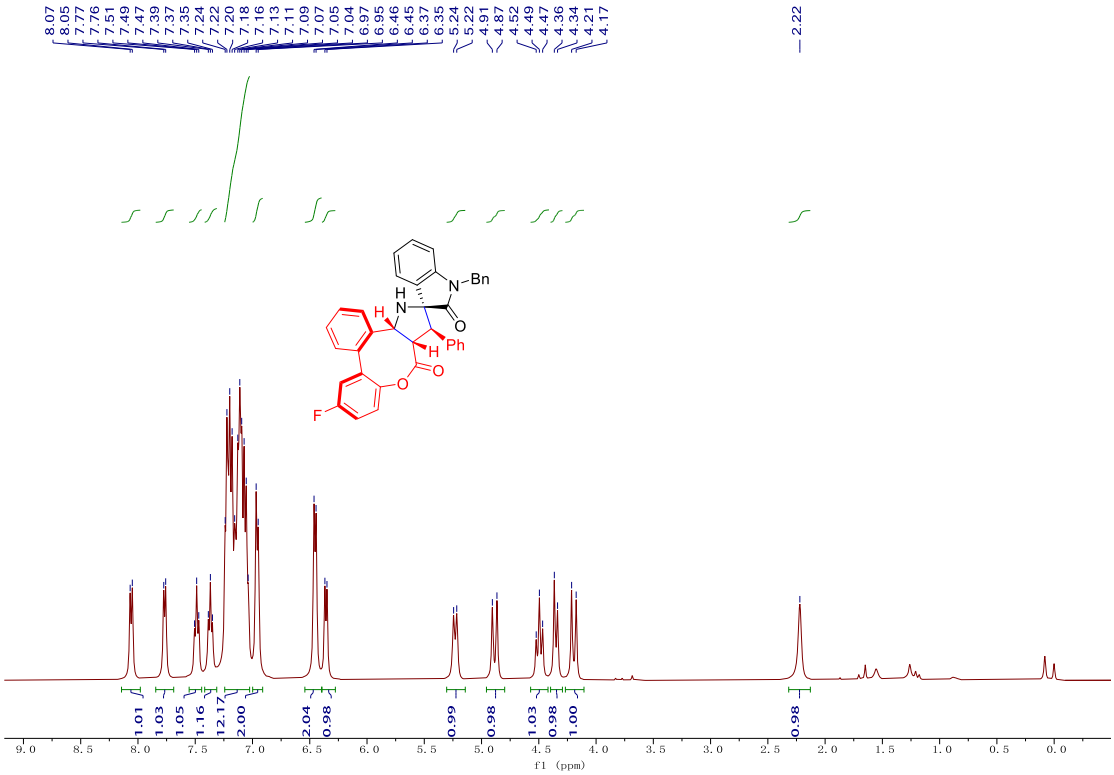
4an

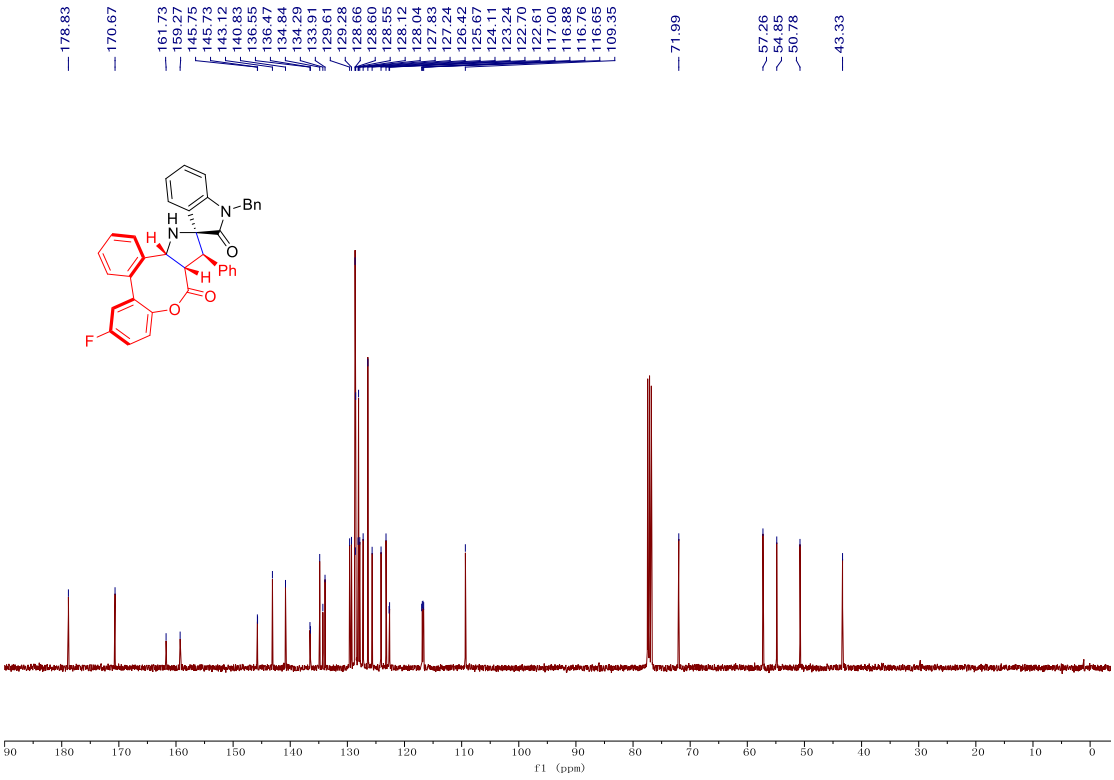

8.04 8.02 7.79 7.78 7.48 7.46 7.44 7.37 7.35 7.33 7.31 7.29 7.24 7.23 7.20 7.18 7.17 7.16 7.15 7.14 7.14 7.12 7.10 7.08 7.06 7.04 6.98 6.96 6.94 6.94 6.80 6.79 6.46 6.45 6.37 6.35 5.28 5.25 4.91 4.87 4.57 4.54 4.52 4.39 4.36 4.22 4.18 3.89
N-Bn
H
N
O
H
Ph
H
O
O
MeO
1.00 1.01 1.01 1.08 1.00 2.97 6.00 3.00 1.02 1.96 0.99 1.00 0.99 0.99 0.98 1.00 3.03 0.97
f1 (ppm)
178.91 170.70 160.89 150.36 143.10 141.21 135.22 134.87 134.06 130.66 129.53 129.28 128.82 128.64 128.59 128.51 128.06 127.91 127.75 127.21 126.75 126.39 125.41 124.13 123.21 112.53 109.28 106.92 72.04 57.52 55.68 54.98 50.66 43.32
N-Bn
H
N
O
H
Ph
H
O
O
MeO
f1 (ppm)

4ao


8.08 8.06 7.82 7.80 7.52 7.50 7.48 7.41 7.40 7.38 7.32 7.32 7.30 7.30 7.28 7.26 7.24 7.22 7.21 7.19 7.18 7.18 7.16 7.14 7.12 7.10 7.08 7.06 6.99 6.97 6.48 6.46 6.39 6.37 5.29 5.26 4.92 4.88 4.56 4.53 4.51 4.41 4.39 4.24 4.20 2.47 2.28
N-Bn
H
N
O
H
Ph
H
O
O
Me
0.99 0.98 1.01 1.07 1.95 3.09 7.00 2.00 1.99 0.95 1.00 1.00 1.01 1.02 1.00 2.99 1.02
f1 (ppm)
178.94 171.12 147.54 143.12 140.93 136.68 135.53 134.90 134.42 134.13 130.64 129.51 128.87 128.81 128.69 128.63 128.47 128.05 127.91 127.72 127.20 126.40 125.38 124.13 123.20 120.80 109.26 72.06 57.47 54.98 50.74 43.32 21.04
f1 (ppm)

4ap


8.07
8.05
7.77
7.76
7.51
7.49
7.47
7.39
7.37
7.35
7.24
7.22
7.20
7.18
7.16
7.13
7.11
7.09
7.07
7.05
7.04
6.97
6.95
6.46
6.45
6.37
6.35
5.24
5.22
4.91
4.87
4.52
4.49
4.47
4.36
4.34
4.21
4.17
2.22
Bn
N
H
O
Ph
F
1.01
1.03
1.05
1.16
12.17
2.00
2.04
0.98
0.99
0.98
1.03
0.98
1.00
0.98
f1 (ppm)


178.83
170.67
161.73
159.27
145.75
145.73
143.12
140.83
136.55
136.47
134.84
134.29
133.91
129.61
129.28
128.66
128.60
128.55
128.12
128.04
127.83
127.24
126.42
125.67
124.11
123.24
122.70
122.61
117.00
116.88
116.76
116.65
109.35
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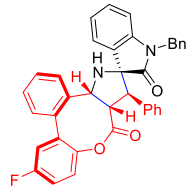
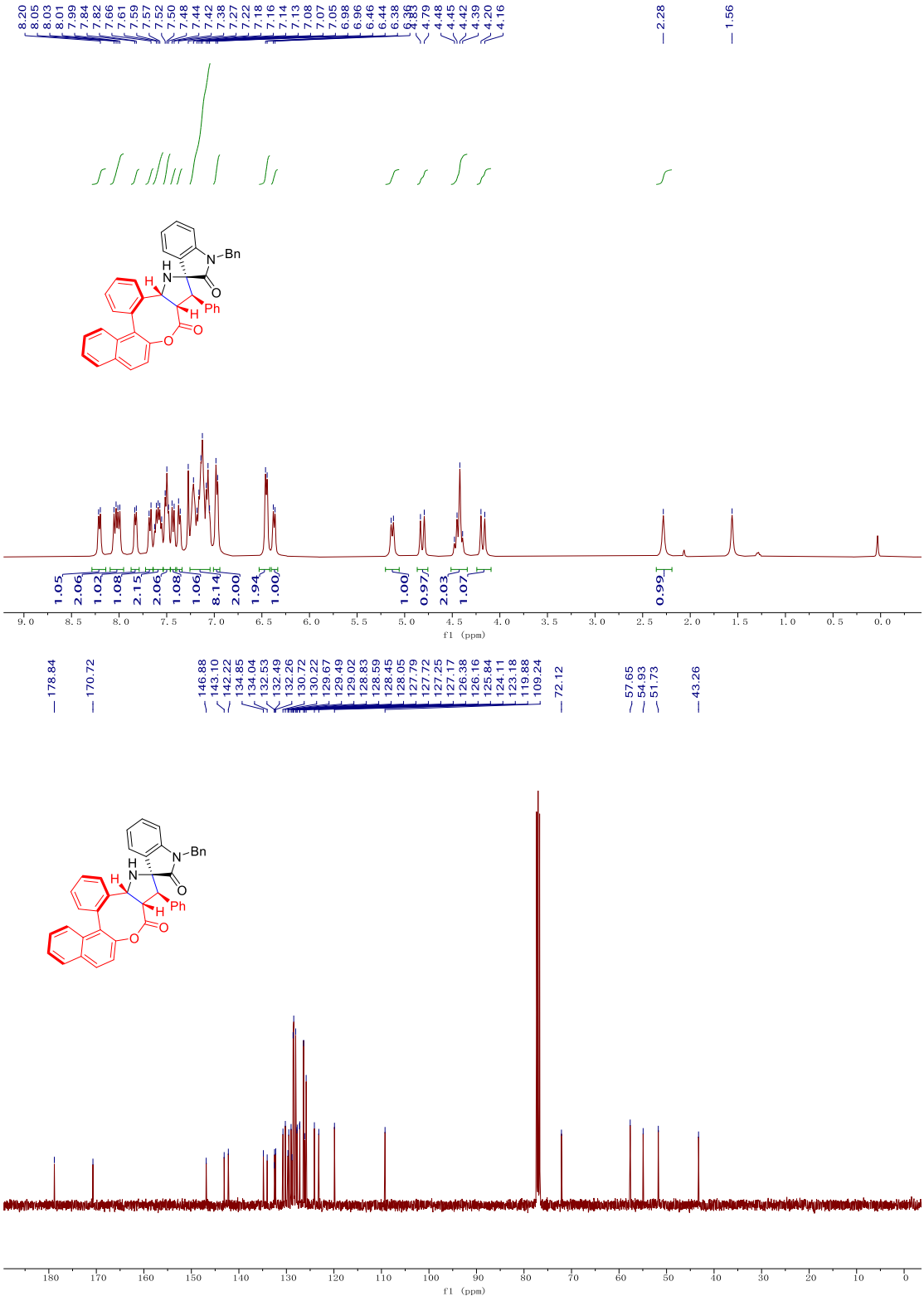
57.26
54.85
50.78
43.33
Bn
N
H
O
Ph
F
f1 (ppm)


N
Bn
H
N
O
H
Ph
H
O
O
F

-114.68
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

4aq


8.20
8.05
8.03
8.01
7.99
7.84
7.82
7.66
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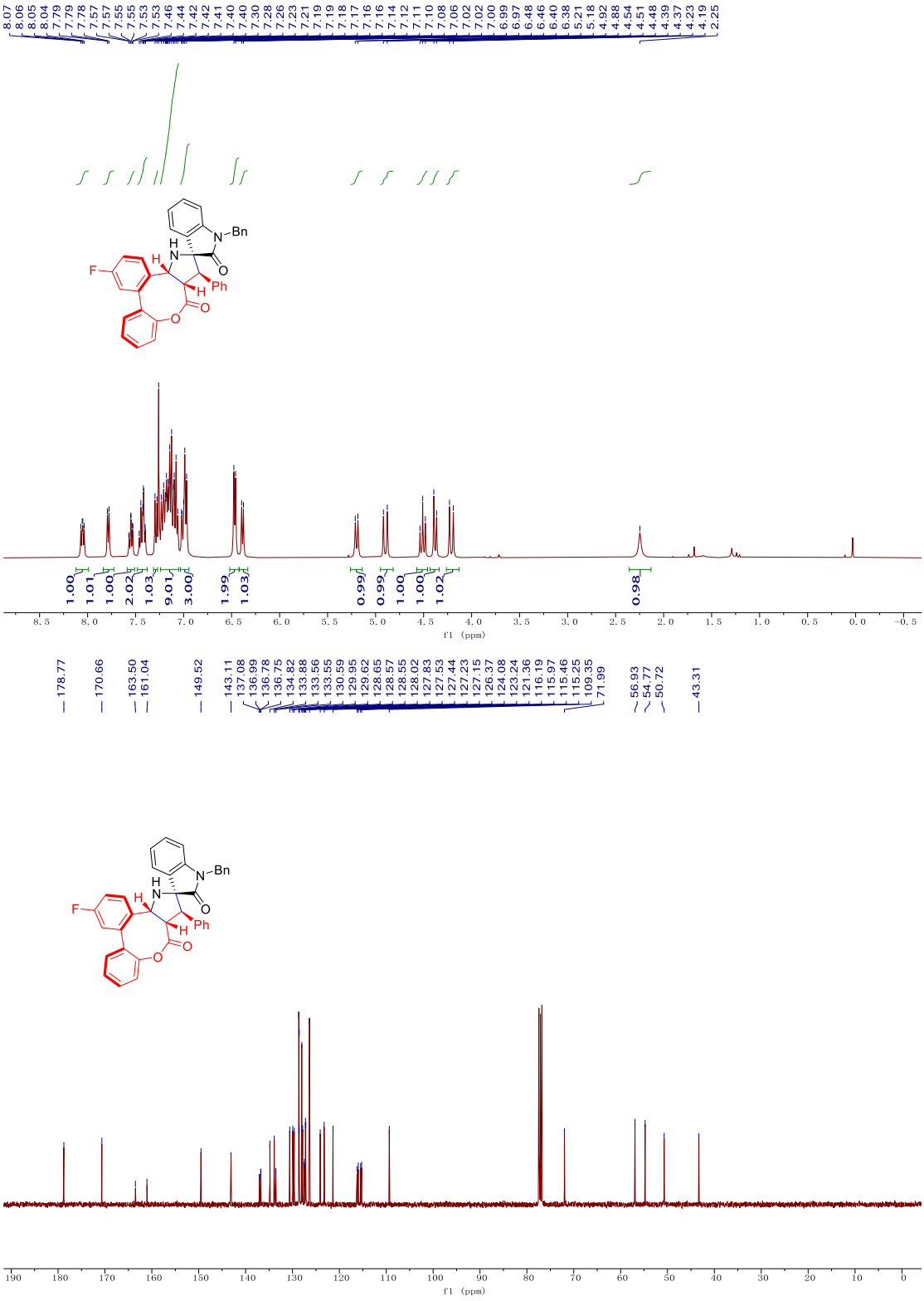
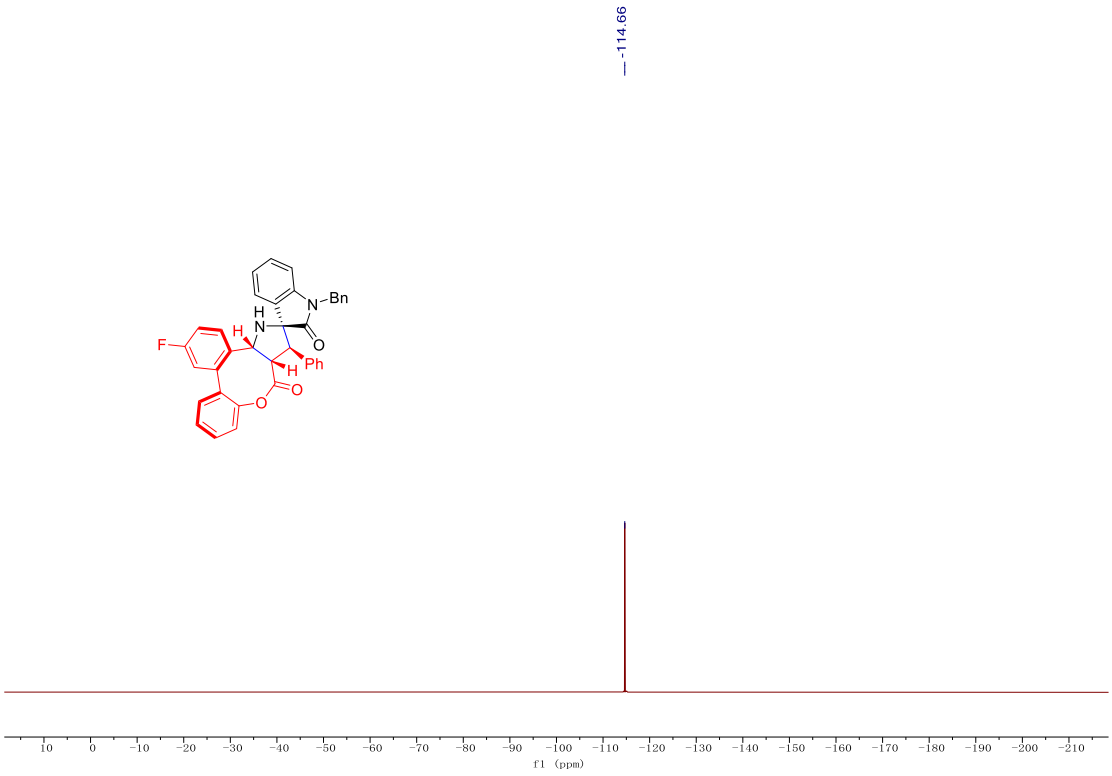
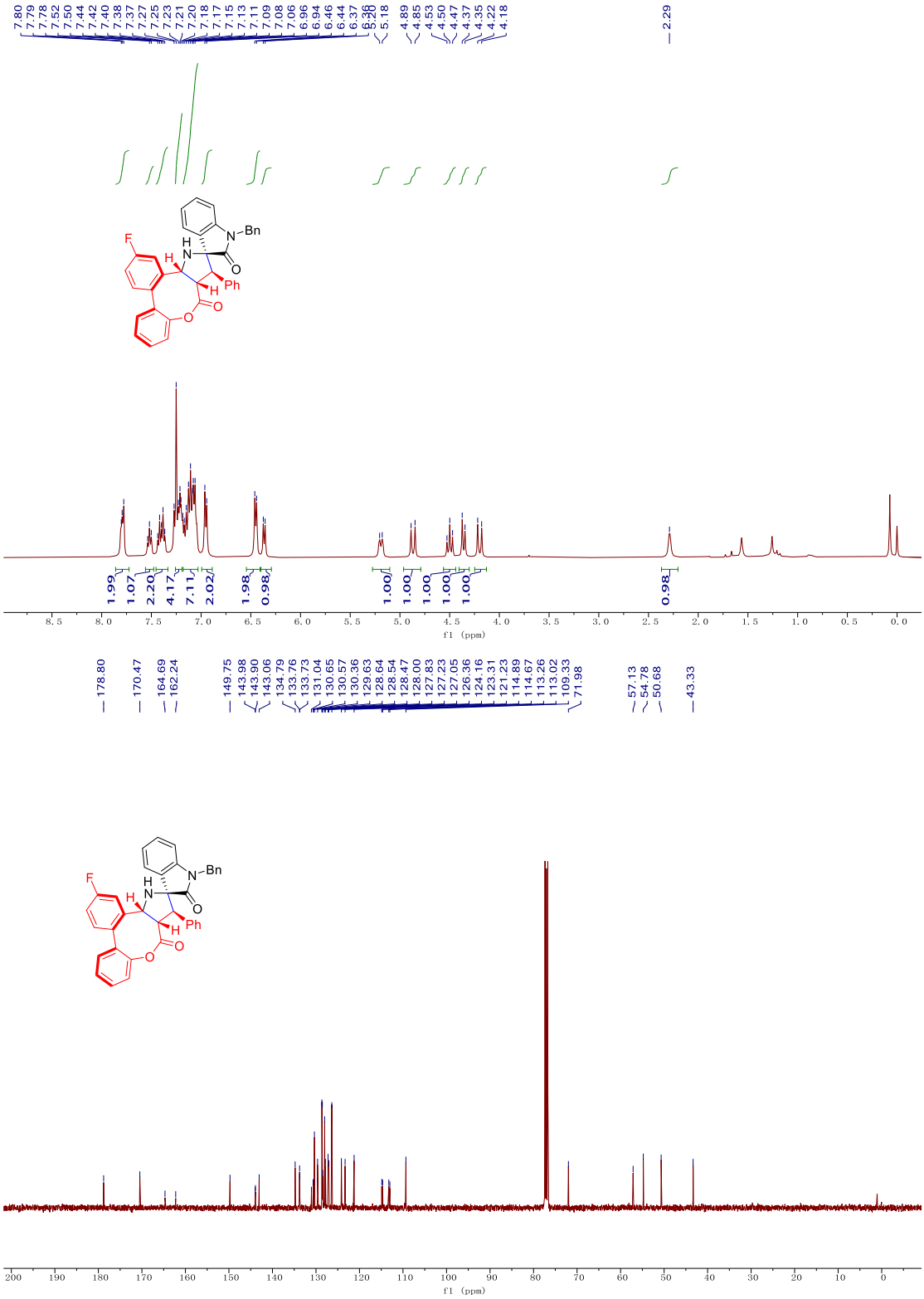
7.52
7.50
7.48
7.44
7.42
7.38
7.27
7.22
7.18
7.16
7.14
7.13
7.08
7.07
7.05
6.98
6.96
6.46
6.44
6.38
6.36
4.83
4.79
4.48
4.45
4.42
4.39
4.20
4.16
2.28
1.56
N-Bn
H
N
O
H
Ph
H
O
O
1.05
2.06
1.02
1.08
2.15
2.06
1.08
1.06
8.14
2.00
1.94
1.00
1.00
0.97
2.03
1.07
0.99
f1 (ppm)
178.84
170.72
146.88
143.10
142.22
134.85
134.04
132.53
132.49
132.26
130.72
130.22
129.67
129.49
129.02
128.83
128.59
128.45
128.05
127.79
127.72
127.25
127.17
126.38
126.16
125.84
124.11
123.18
119.88
109.24
72.12
57.65
54.93
51.73
43.26
N-Bn
H
N
O
H
Ph
H
O
O
f1 (ppm)

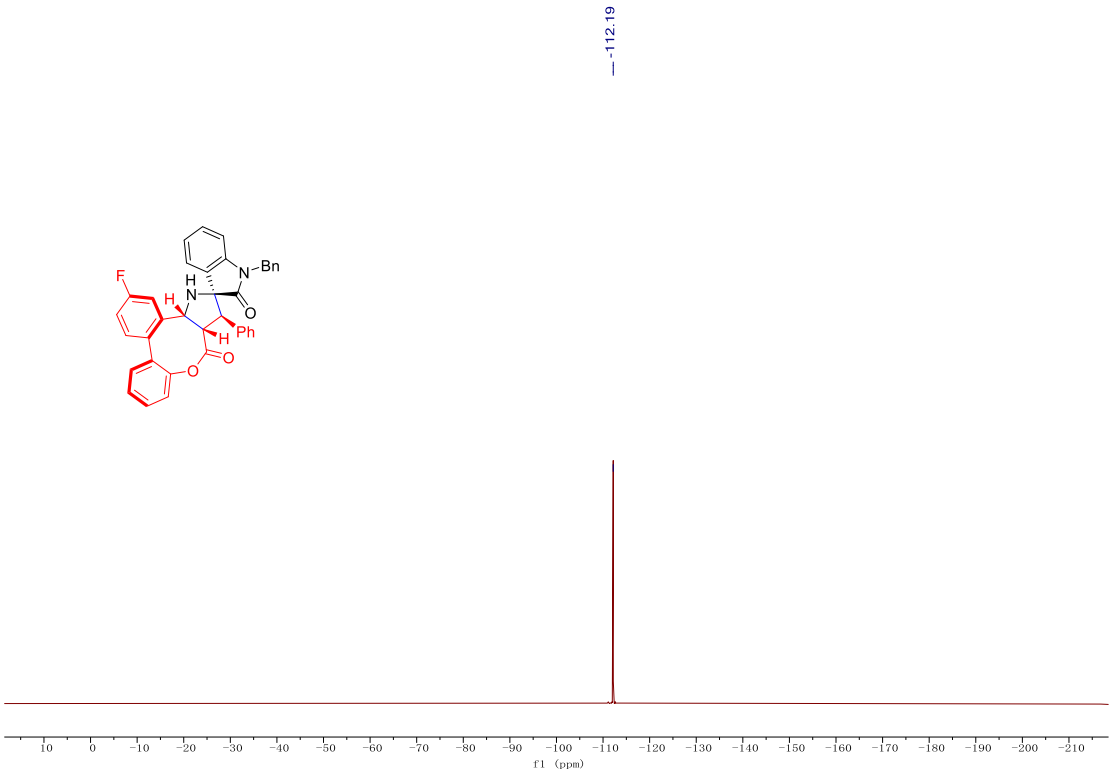
4ar


8.07 8.06 8.05 8.04 7.79 7.78 7.57 7.55 7.53 7.46 7.44 7.42 7.41 7.40 7.40 7.30 7.28 7.26 7.23 7.21 7.19 7.18 7.17 7.16 7.16 7.14 7.12 7.11 7.10 7.08 7.06 7.02 7.02 7.00 6.99 6.97 6.48 6.46 6.40 6.38 5.21 5.18 4.92 4.88 4.54 4.51 4.48 4.39 4.37 4.23 4.19 2.25
N-Bn
H
N
O
F
H
Ph
H
O
O
1.00 1.01 1.00 2.02 1.03 9.01 3.00 1.99 1.03 0.99 0.99 1.00 1.00 1.02 0.98
f1 (ppm)
178.77 170.66 163.50 161.04 149.52 143.11 137.08 136.99 136.78 136.75 134.82 133.88 133.66 133.55 130.59 129.95 129.62 128.65 128.57 128.55 128.02 127.83 127.53 127.44 127.23 127.15 126.37 124.08 123.24 121.36 116.19 115.97 115.46 115.25 109.35 71.99 56.93 54.77 50.72 43.31
f1 (ppm)

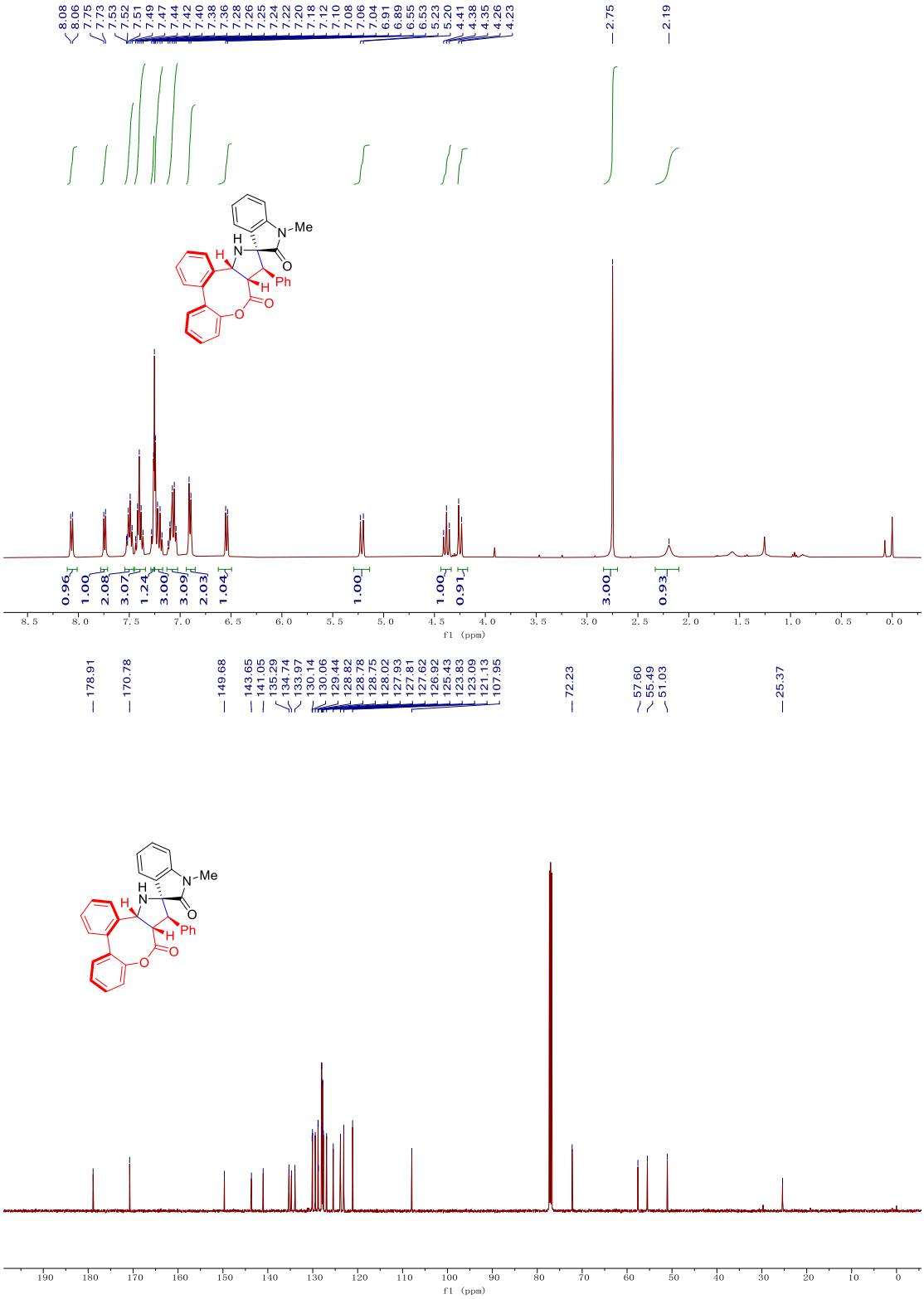

-114.66
N
Bn
H
N
O
F
H
Ph
H
O
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

4as

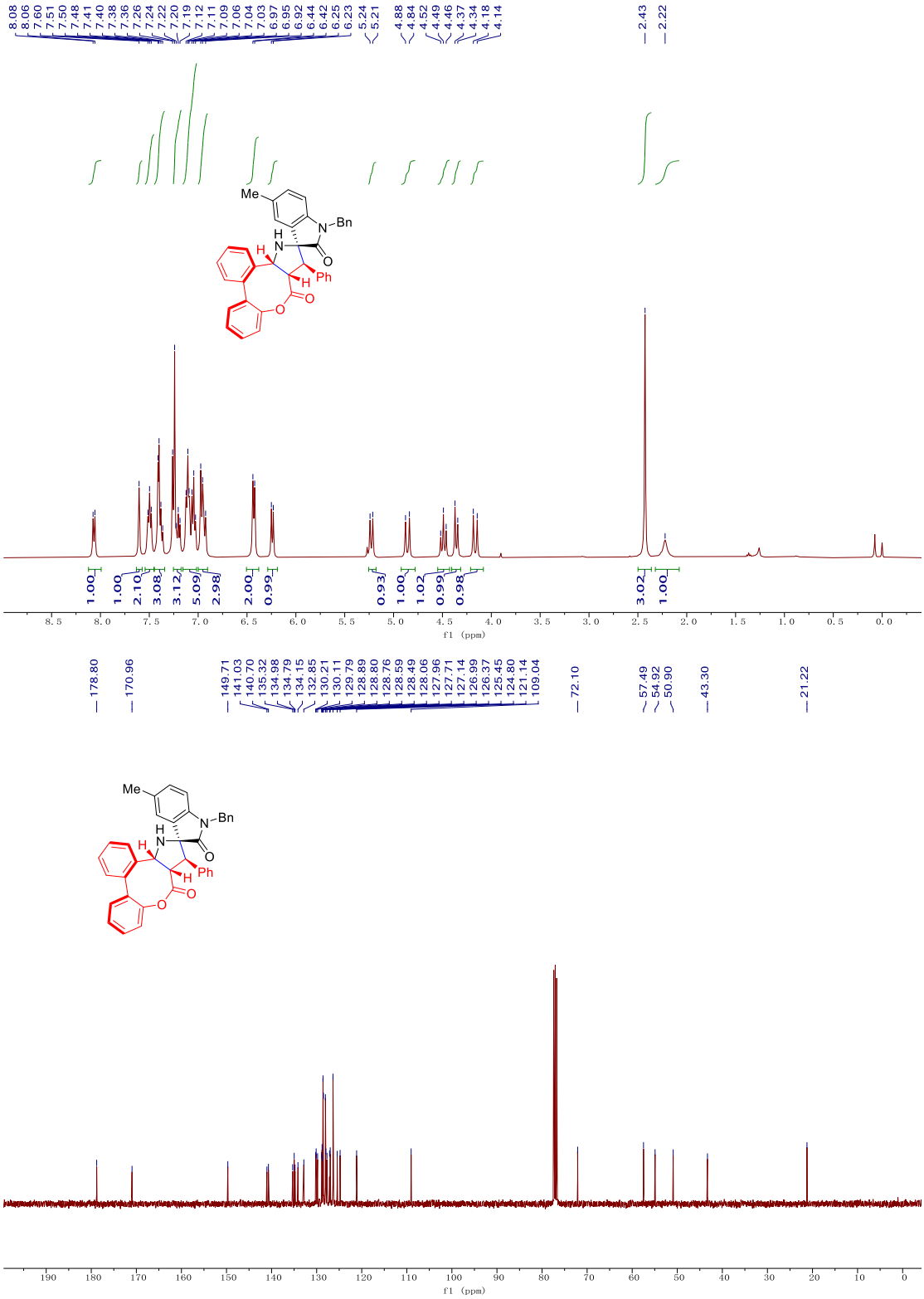

7.80 7.79 7.78 7.52 7.50 7.44 7.42 7.40 7.38 7.37 7.27 7.25 7.23 7.21 7.20 7.18 7.17 7.15 7.13 7.11 7.09 7.08 7.06 6.96 6.94 6.46 6.44 6.37 6.36 5.18 4.89 4.85 4.53 4.50 4.47 4.37 4.35 4.22 4.18 2.29
F
H
N
Bn
O
H
Ph
O
O
1.99 1.07 2.20 4.17 7.11 2.02 1.98 0.98 1.00 1.00 1.00 1.00 1.00 0.98
f1 (ppm)
178.80 170.47 164.69 162.24 149.75 143.98 143.90 143.06 134.79 133.76 133.73 131.04 130.65 130.57 130.36 129.63 128.64 128.54 128.47 128.00 127.83 127.23 127.05 126.36 124.16 123.31 121.23 114.89 114.67 113.26 113.02 109.33 71.98 57.13 54.78 50.68 43.33
f1 (ppm)


-112.19
F
H
N
N
Bn
O
Ph
H
O
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

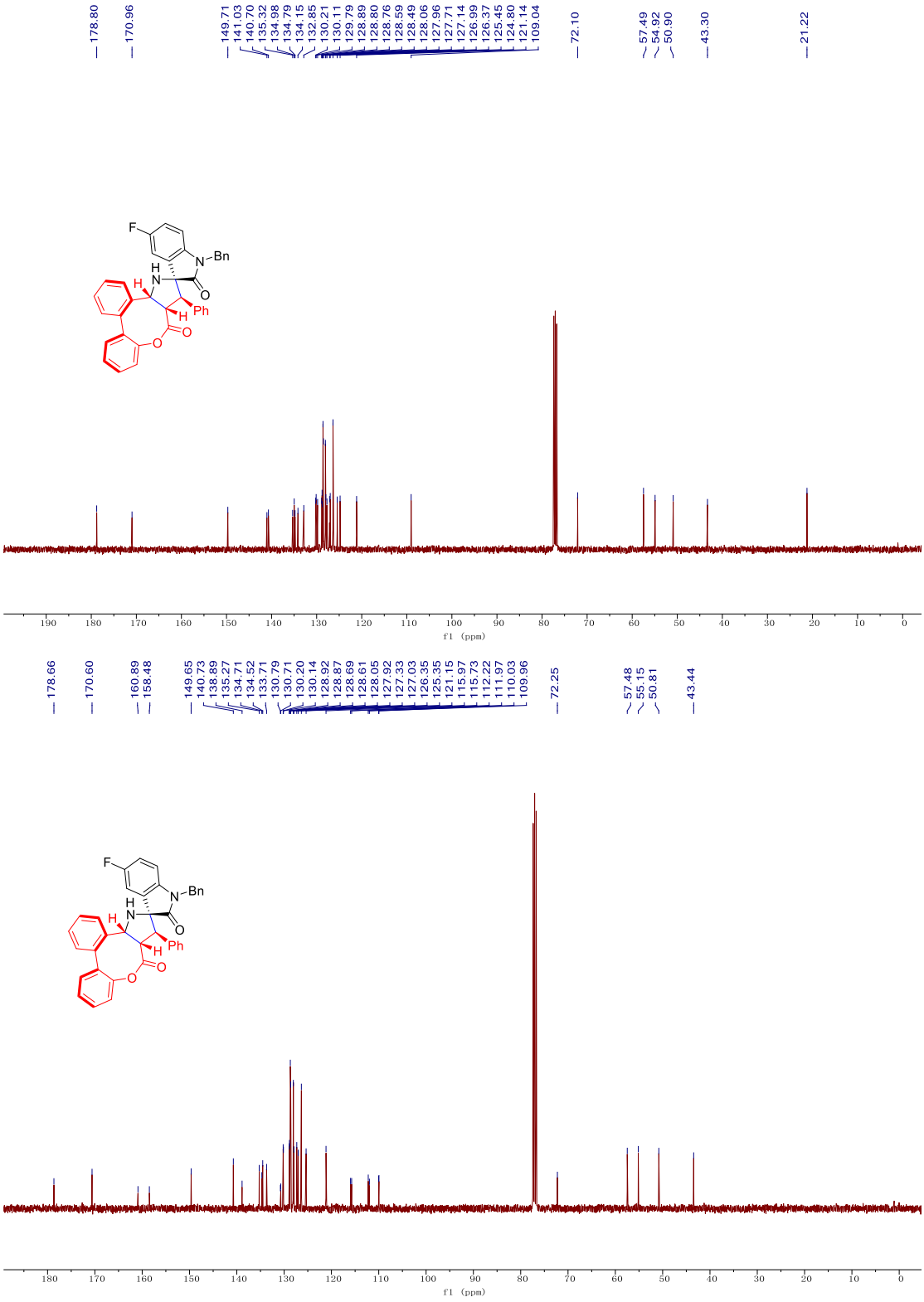
4ba

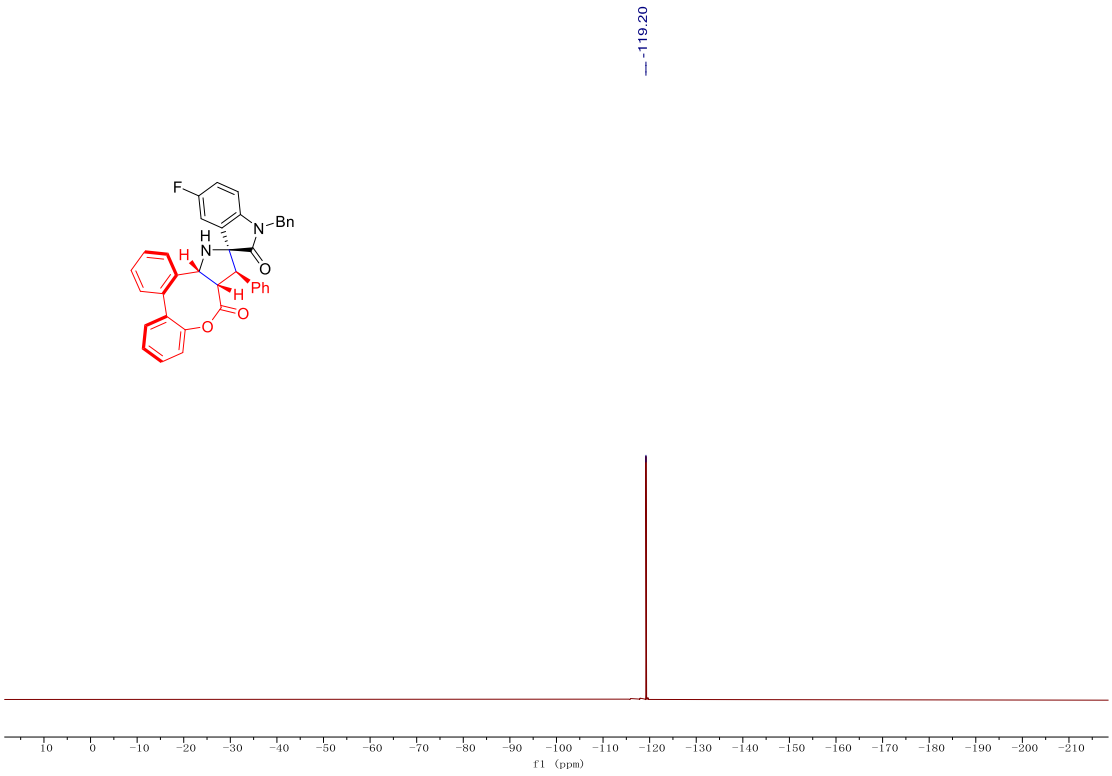

8.08
8.06
7.75
7.73
7.53
7.52
7.51
7.49
7.47
7.44
7.42
7.40
7.38
7.36
7.28
7.26
7.25
7.24
7.22
7.20
7.18
7.12
7.10
7.08
7.06
7.04
6.91
6.89
6.55
6.53
5.23
5.20
4.41
4.38
4.35
4.26
4.23
2.75
2.19
N-Me
H
N
O
H
Ph
H
O
O
0.96
1.00
2.08
3.07
1.24
3.00
3.09
2.03
1.04
1.00
1.00
0.91
3.00
0.93
f1 (ppm)
178.91
170.78
149.68
143.65
141.05
135.29
134.74
133.97
130.14
130.06
129.44
128.82
128.78
128.75
128.02
127.93
127.81
127.62
126.92
125.43
123.83
123.09
121.13
107.95
72.23
57.60
55.49
51.03
25.37
f1 (ppm)

4ca

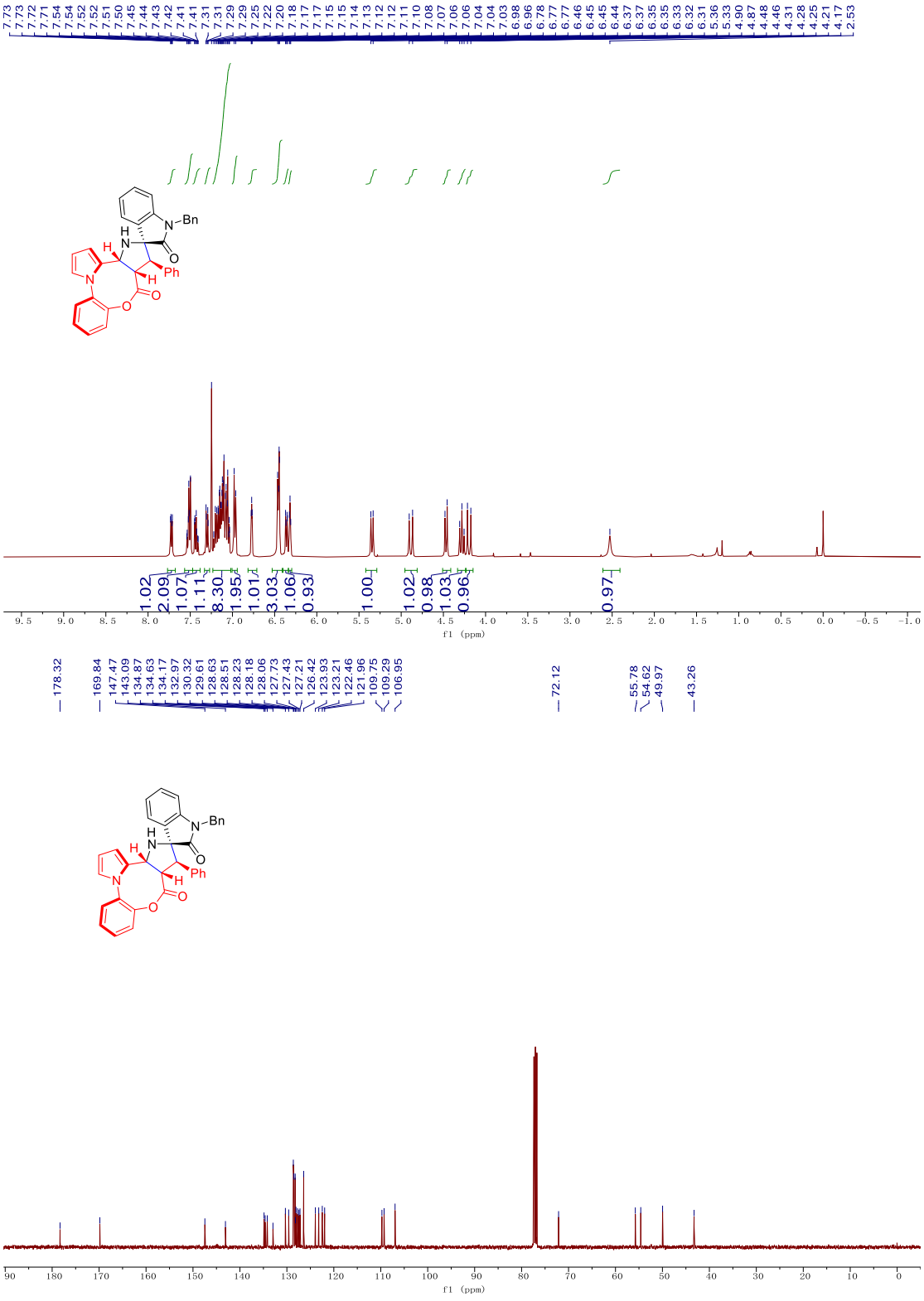

8.08
8.06
7.60
7.51
7.50
7.48
7.41
7.40
7.38
7.36
7.26
7.24
7.22
7.20
7.19
7.12
7.11
7.09
7.06
7.04
7.03
6.97
6.95
6.92
6.44
6.42
6.25
6.23
5.24
5.21
4.88
4.84
4.52
4.49
4.46
4.37
4.34
4.18
4.14
2.43
2.22
Me
N
Bn
H
N
O
H
Ph
H
O
O
1.00
1.00
2.10
3.08
3.12
5.09
2.98
2.00
0.99
0.93
1.00
1.02
0.99
0.98
3.02
1.00
f1 (ppm)
178.80
170.96
149.71
141.03
140.70
135.32
134.98
134.79
134.15
132.85
130.21
130.11
129.79
128.89
128.80
128.76
128.59
128.49
128.06
127.96
127.71
127.14
126.99
126.37
125.45
124.80
121.14
109.04
72.10
57.49
54.92
50.90
43.30
21.22
f1 (ppm)

4da

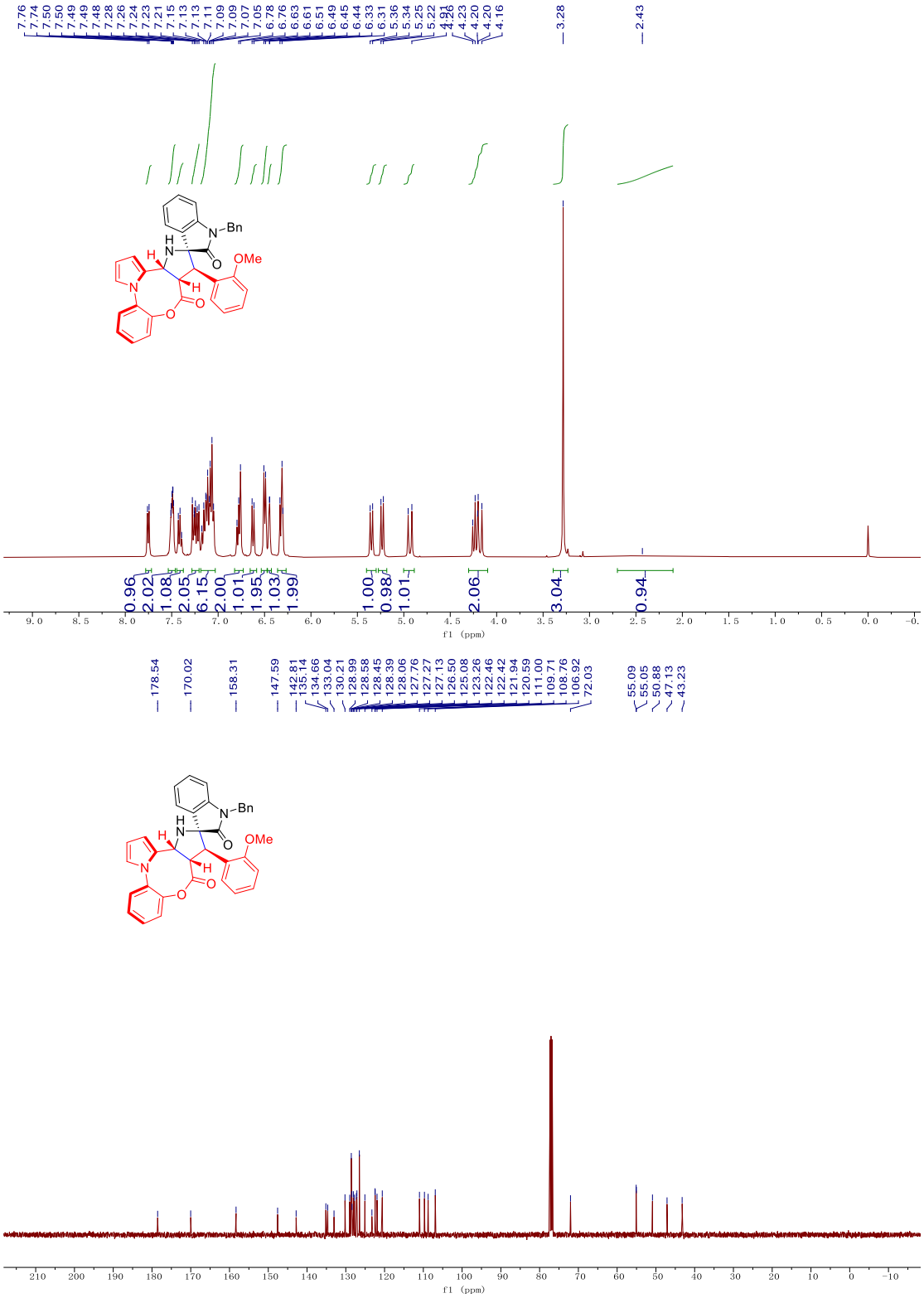

178.80
170.96
149.71
141.03
140.70
135.32
134.98
134.79
134.15
132.85
130.21
130.11
129.79
128.89
128.80
128.76
128.59
128.49
128.06
127.96
127.71
127.14
126.99
126.37
125.45
124.80
121.14
109.04
72.10
57.49
54.92
50.90
43.30
21.22
F
N-Bn
H
N
O
H
Ph
O
O
f1 (ppm)
178.66
170.60
160.89
158.48
149.65
140.73
138.89
135.27
134.71
134.52
133.71
130.79
130.71
130.20
130.14
128.92
128.87
128.69
128.61
128.05
127.92
127.33
127.03
126.35
125.35
121.15
115.97
115.73
112.22
111.97
110.03
109.96
72.25
57.48
55.15
50.81
43.44
F
N-Bn
H
N
O
H
Ph
O
O
f1 (ppm)


-119.20
F
N
Bn
H
N
O
H
Ph
H
O
O
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

6aa


7.73 7.73 7.72 7.71 7.54 7.54 7.52 7.52 7.51 7.50 7.45 7.44 7.43 7.42 7.41 7.41 7.31 7.31 7.29 7.29 7.25 7.22 7.20 7.18 7.17 7.17 7.15 7.15 7.14 7.13 7.12 7.12 7.11 7.10 7.08 7.07 7.06 7.06 7.04 7.04 7.03 6.98 6.96 6.78 6.77 6.77 6.46 6.45 6.45 6.44 6.37 6.35 6.33 6.32 6.31 5.36 5.33 4.90 4.87 4.48 4.46 4.31 4.28 4.25 4.21 4.17 2.53
N-Bn
H
N
O
H
Ph
N
H
O
O
1.02 2.09 1.07 1.11 8.30 1.95 1.01 3.03 1.06 0.93 1.00 1.02 0.98 1.03 0.96 0.97
f1 (ppm)
178.32 169.84 147.47 143.09 134.87 134.63 134.17 132.97 130.32 129.61 128.63 128.51 128.23 128.18 128.06 127.73 127.43 127.21 126.42 123.93 123.21 122.46 121.96 109.75 109.29 106.95 72.12 55.78 54.62 49.97 43.26
N-Bn
H
N
O
H
Ph
N
H
O
O
f1 (ppm)

6ab


7.76
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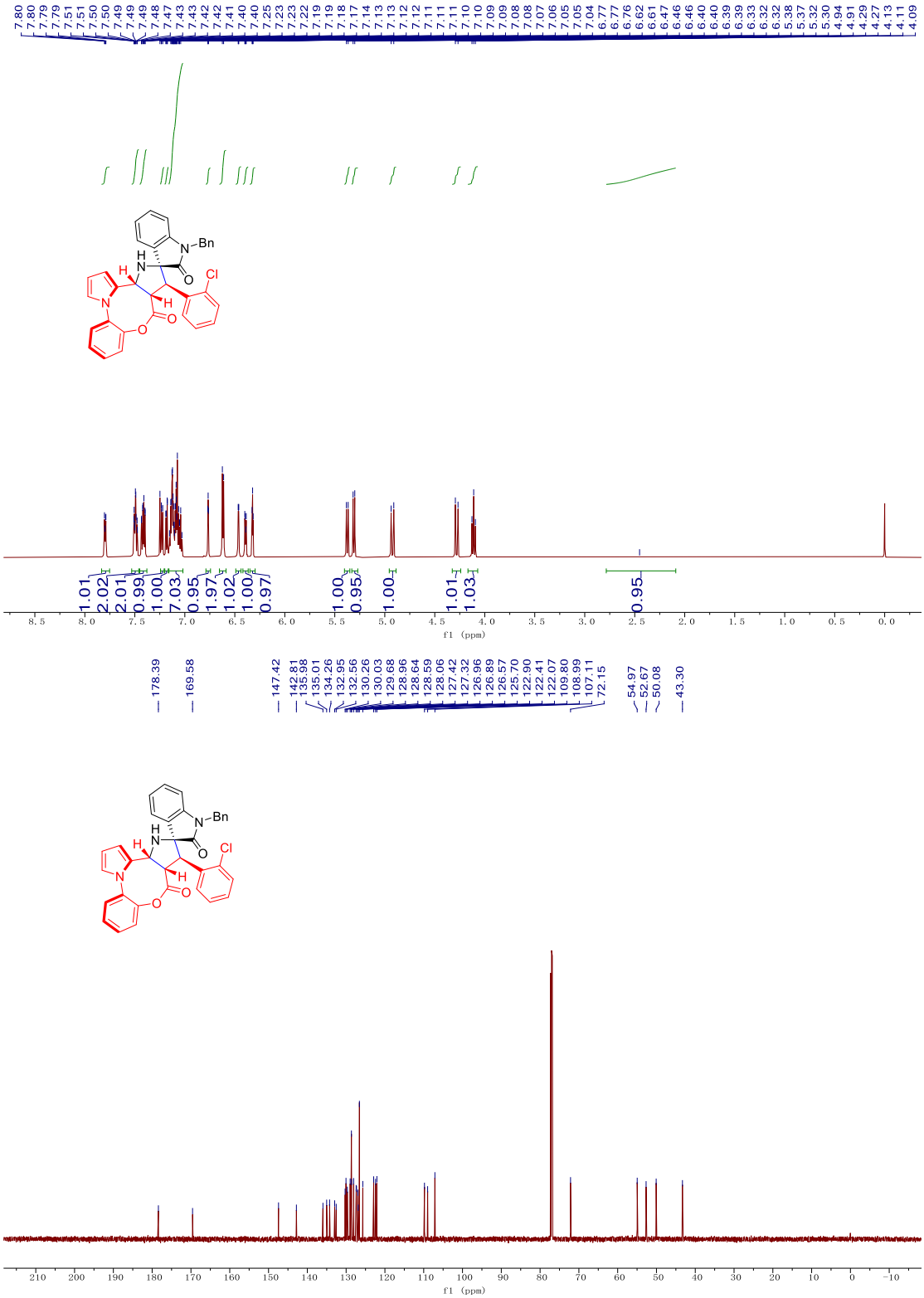
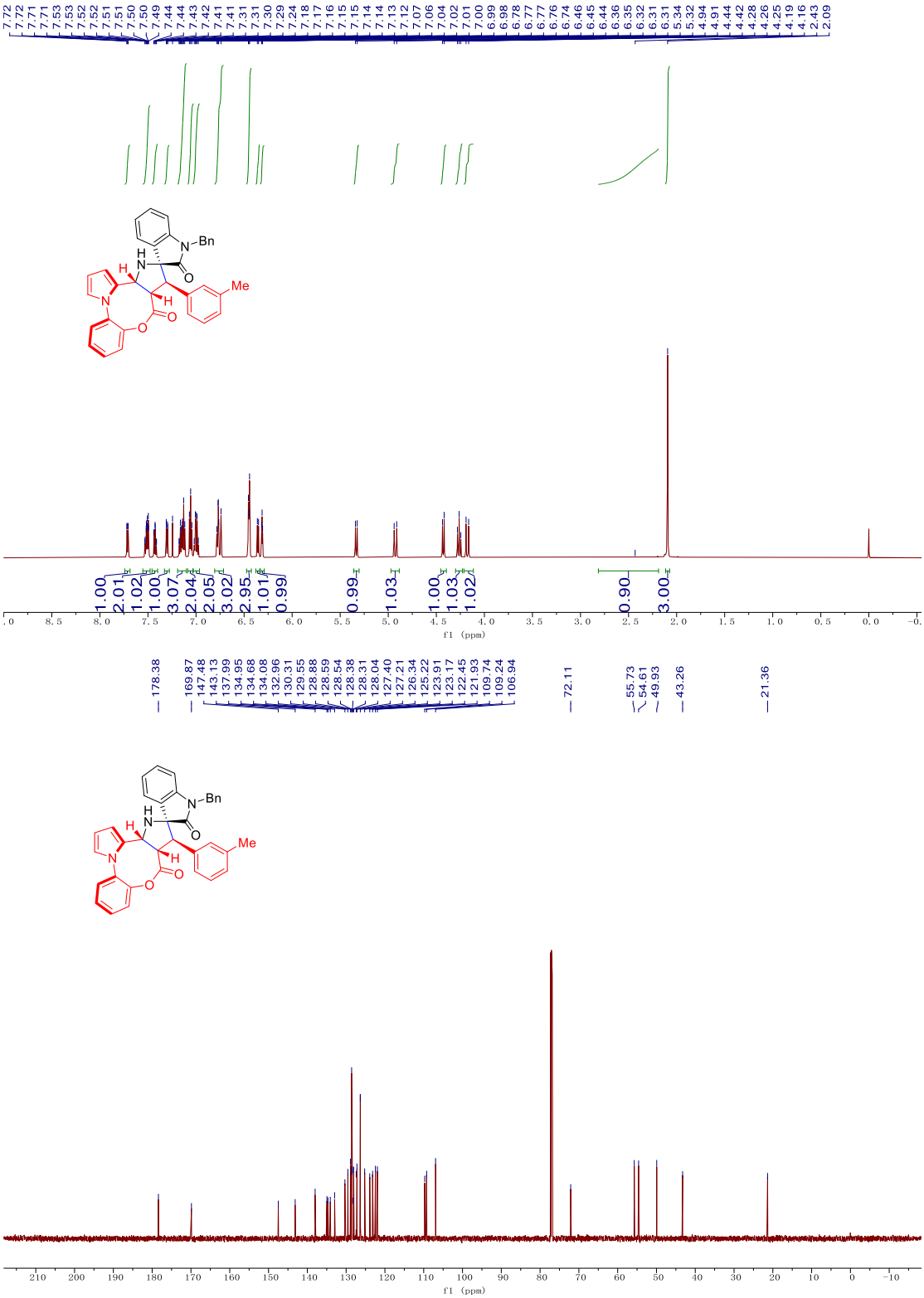
7.50
7.50
7.49
7.49
7.48
7.28
7.26
7.24
7.23
7.21
7.15
7.13
7.13
7.11
7.09
7.09
7.07
7.05
6.78
6.76
6.63
6.61
6.51
6.49
6.45
6.44
6.33
6.31
5.36
5.34
5.25
5.22
4.23
4.20
4.20
4.16
3.28
2.43
N-Bn
H
N
O
OMe
H
N
H
O
O
0.96
2.02
1.08
2.05
6.15
2.00
1.01
1.95
1.03
1.99
1.00
0.98
1.01
2.06
3.04
0.94
f1 (ppm)
178.54
170.02
158.31
147.59
142.81
135.14
134.66
133.04
130.21
128.99
128.58
128.45
128.39
128.06
127.76
127.27
127.13
126.50
125.08
123.26
122.46
122.42
121.94
120.59
111.00
109.71
108.76
106.92
72.03
55.09
55.05
50.88
47.13
43.23
f1 (ppm)

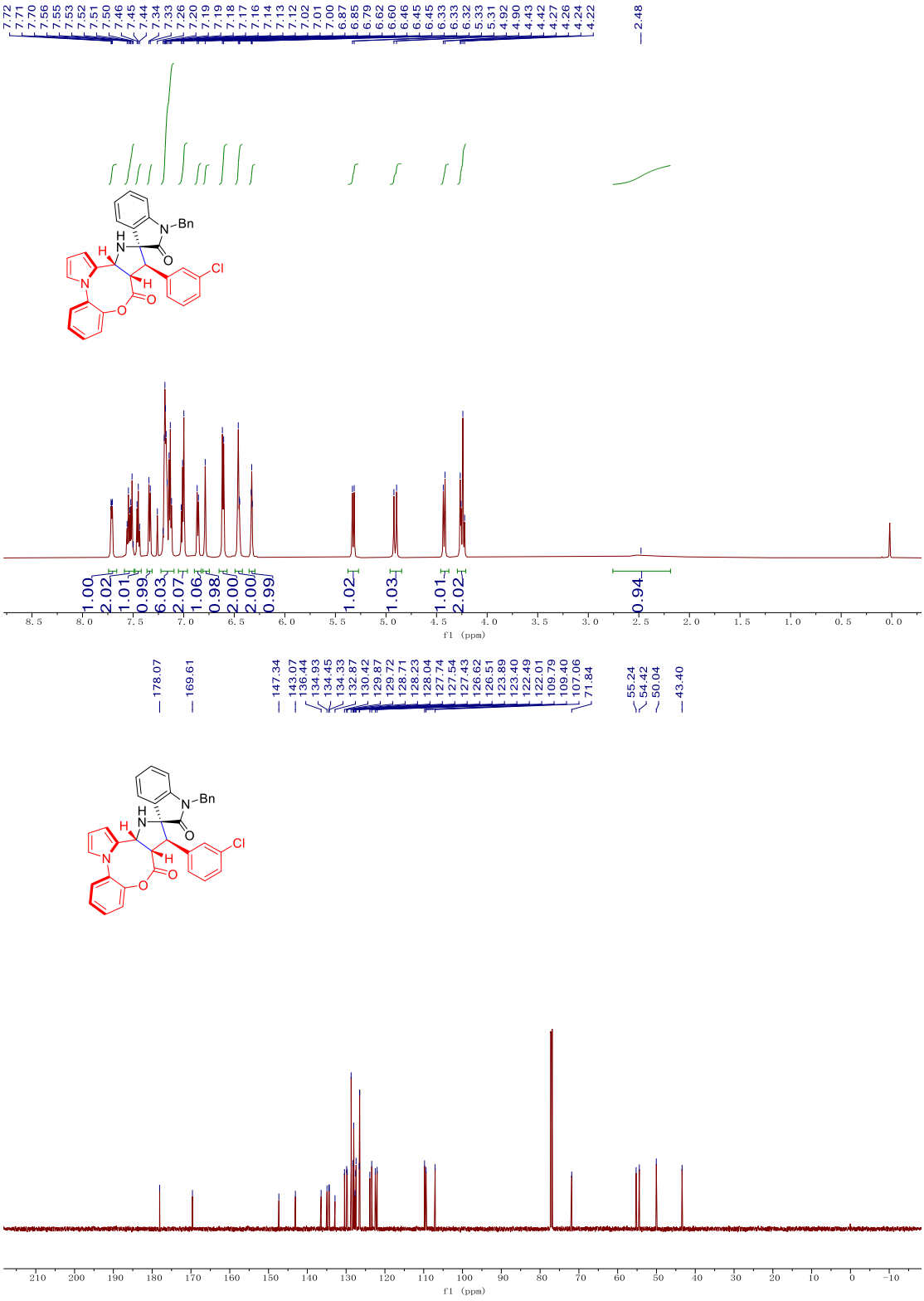
6ac


7.80 7.80 7.79 7.79 7.51 7.51 7.50 7.50 7.49 7.49 7.49 7.48 7.47 7.43 7.43 7.42 7.42 7.41 7.40 7.40 7.25 7.23 7.22 7.19 7.19 7.18 7.17 7.14 7.13 7.12 7.12 7.11 7.11 7.11 7.10 7.10 7.09 7.09 7.08 7.08 7.07 7.06 7.05 7.05 7.04 6.77 6.77 6.76 6.62 6.61 6.47 6.46 6.46 6.40 6.40 6.39 6.39 6.33 6.32 6.32 5.38 5.37 5.32 5.30 4.94 4.91 4.29 4.27 4.13 4.11 4.09
N-Bn
H
N
O
Cl
H
N
H
O
O
1.01 2.02 2.01 0.99 1.00 7.03 0.95 1.97 1.02 1.00 0.97 1.00 0.95 1.00 1.01 1.03 0.95
f1 (ppm)
178.39 169.58 147.42 142.81 135.98 135.01 134.26 132.95 132.56 130.26 130.03 129.68 128.96 128.64 128.59 128.06 127.42 127.32 126.96 126.89 126.57 125.70 122.90 122.41 122.07 109.80 108.99 107.11 72.15 54.97 52.67 50.08 43.30
N-Bn
H
N
O
Cl
H
N
H
O
O
f1 (ppm)

6ad


7.72 7.72 7.71 7.71 7.53 7.53 7.52 7.52 7.51 7.51 7.50 7.50 7.49 7.44 7.44 7.43 7.42 7.41 7.41 7.31 7.31 7.30 7.29 7.24 7.18 7.17 7.16 7.15 7.15 7.14 7.14 7.13 7.12 7.07 7.06 7.04 7.02 7.01 7.00 6.99 6.98 6.78 6.77 6.77 6.76 6.74 6.46 6.45 6.44 6.36 6.35 6.32 6.31 6.31 5.34 5.32 4.94 4.91 4.44 4.42 4.28 4.26 4.25 4.19 4.16 2.43 2.09
N-Bn
H
N
O
H
N
H
O
O
Me
1.00 2.01 1.02 1.00 3.07 2.04 2.05 3.02 2.95 1.01 0.99 0.99 1.03 1.00 1.03 1.02 0.90 3.00
f1 (ppm)
178.38 169.87 147.48 143.13 137.99 134.95 134.68 134.08 132.96 130.31 129.55 128.88 128.59 128.54 128.38 128.31 128.04 127.40 127.21 126.34 125.22 123.91 123.17 122.45 121.93 109.74 109.24 106.94 72.11 55.73 54.61 49.93 43.26 21.36
N-Bn
H
N
O
H
N
H
O
O
Me
f1 (ppm)

6ae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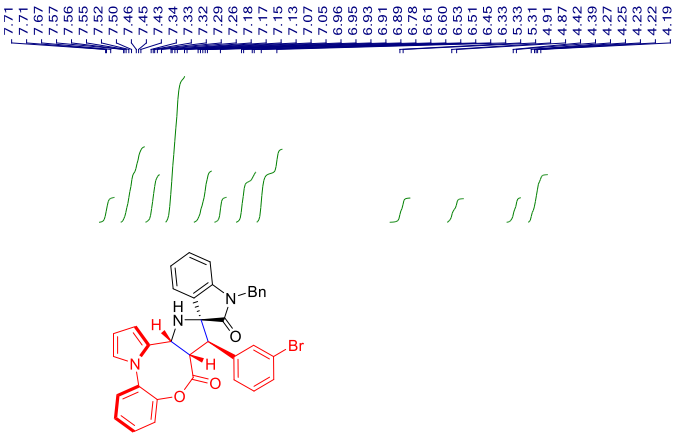
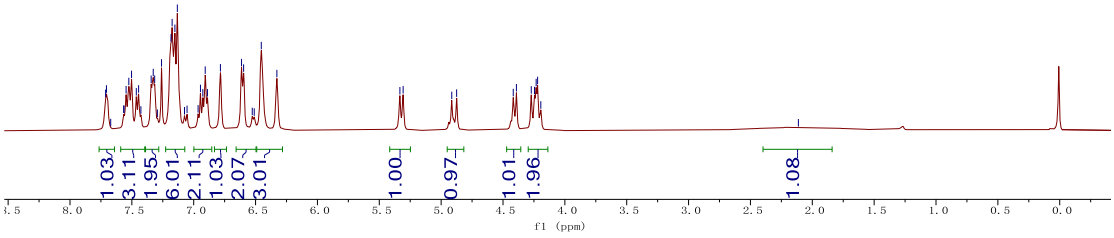
7.53
7.52
7.51
7.50
7.46
7.45
7.44
7.34
7.33
7.26
7.20
7.19
7.19
7.18
7.17
7.16
7.14
7.13
7.12
7.02
7.01
7.00
6.87
6.85
6.79
6.62
6.60
6.46
6.45
6.45
6.33
6.32
5.33
5.31
4.92
4.90
4.43
4.42
4.27
4.26
4.24
4.22
2.48
N-Bn
H
N
O
H
N
H
O
O
Cl
1.00
2.02
1.01
0.99
6.03
2.07
1.06
0.98
2.00
2.00
0.99
1.02
1.03
1.01
2.02
0.94
f1 (ppm)
178.07
169.61
147.34
143.07
136.44
134.93
134.45
134.33
132.87
130.42
129.87
129.72
128.71
128.23
128.04
127.74
127.54
127.43
126.62
126.51
123.89
123.40
122.49
122.01
109.79
109.40
107.06
71.84
55.24
54.42
50.04
43.40
N-Bn
H
N
O
H
N
H
O
O
Cl
f1 (ppm)

6af


7.71
7.71
7.67
7.57
7.56
7.55
7.52
7.50
7.46
7.45
7.43
7.34
7.33
7.32
7.29
7.26
7.18
7.17
7.15
7.13
7.07
7.05
6.96
6.95
6.93
6.91
6.89
6.78
6.61
6.60
6.53
6.51
6.45
6.33
5.33
5.31
4.91
4.87
4.42
4.39
4.27
4.25
4.23
4.22
4.19
2.11
N-Bn
H
N
O
H
N
H
O
O
Br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1.03
2.07
3.01
1.00
0.97
1.01
1.96
1.08
f1 (ppm)


178.05
169.57
147.34
143.07
136.71
134.91
134.42
132.86
131.14
130.96
130.42
129.99
129.86
128.73
128.02
127.52
127.42
127.01
126.50
123.87
123.40
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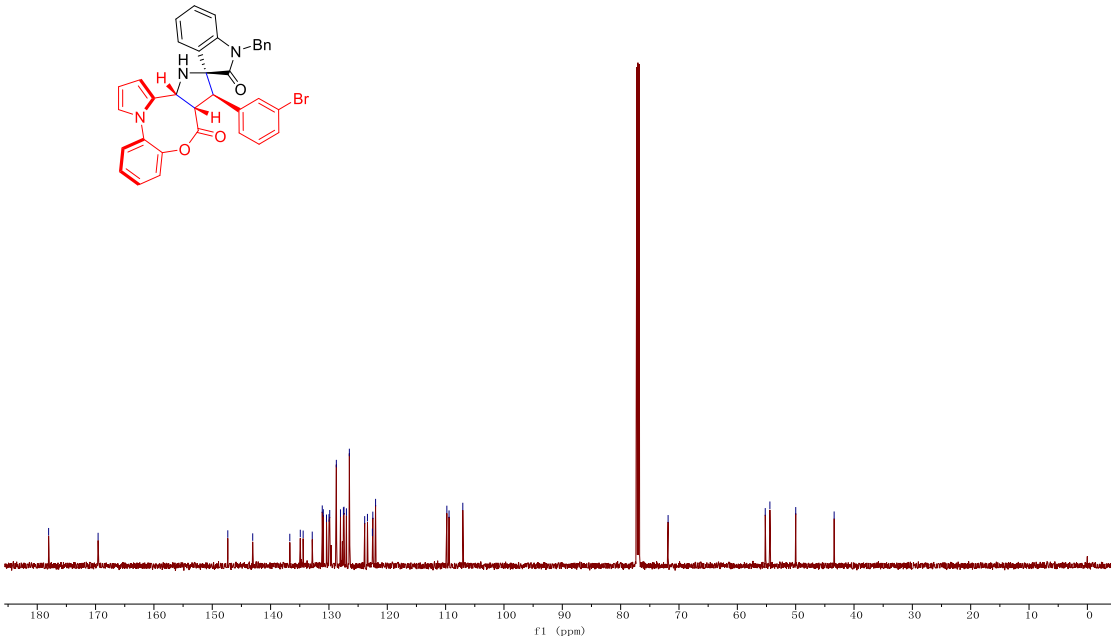
122.01
109.79
109.41
107.06
71.87
55.21
54.42
49.99
43.41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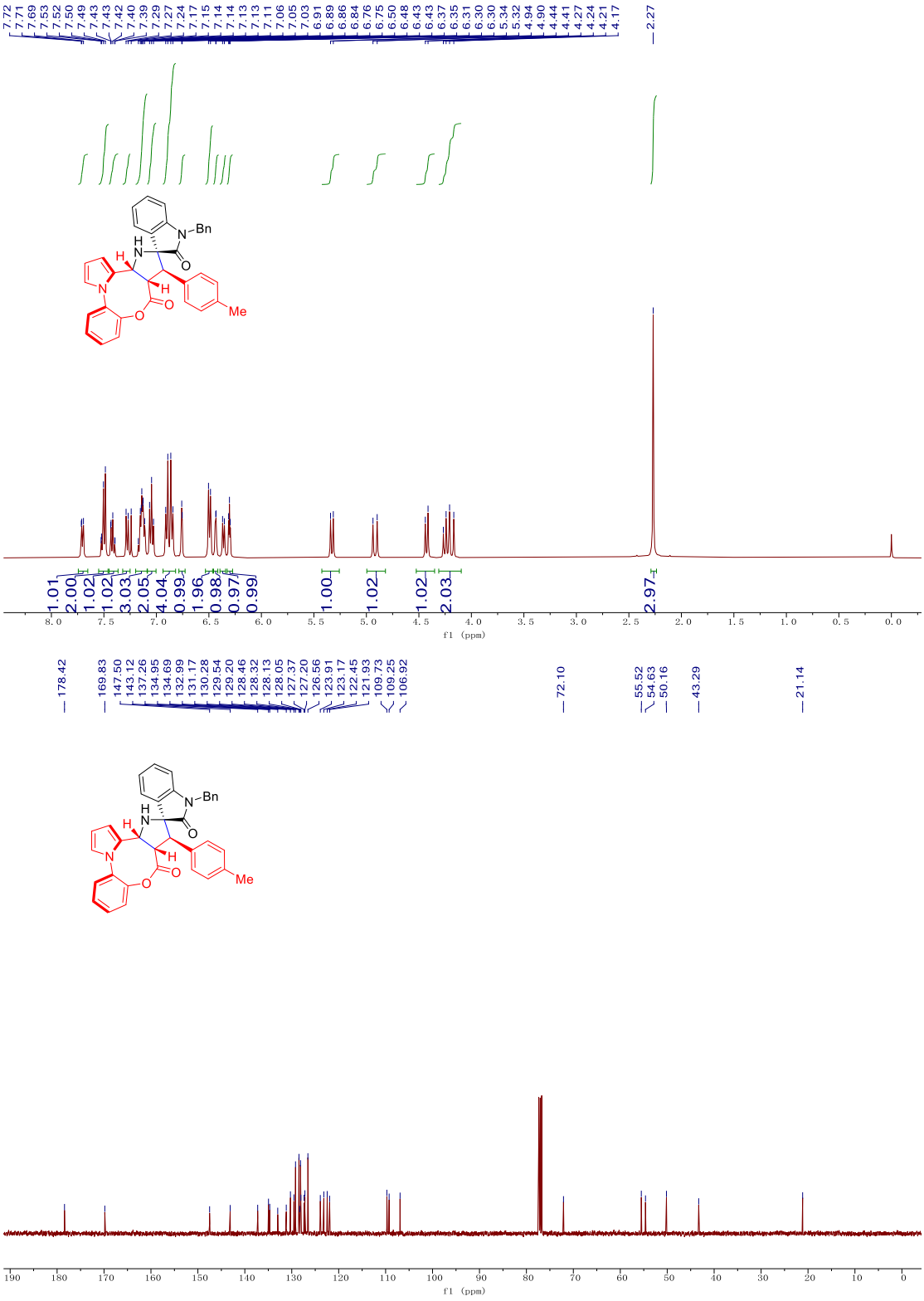
N
O
H
N
H
O
O
Br
f1 (ppm)

6ag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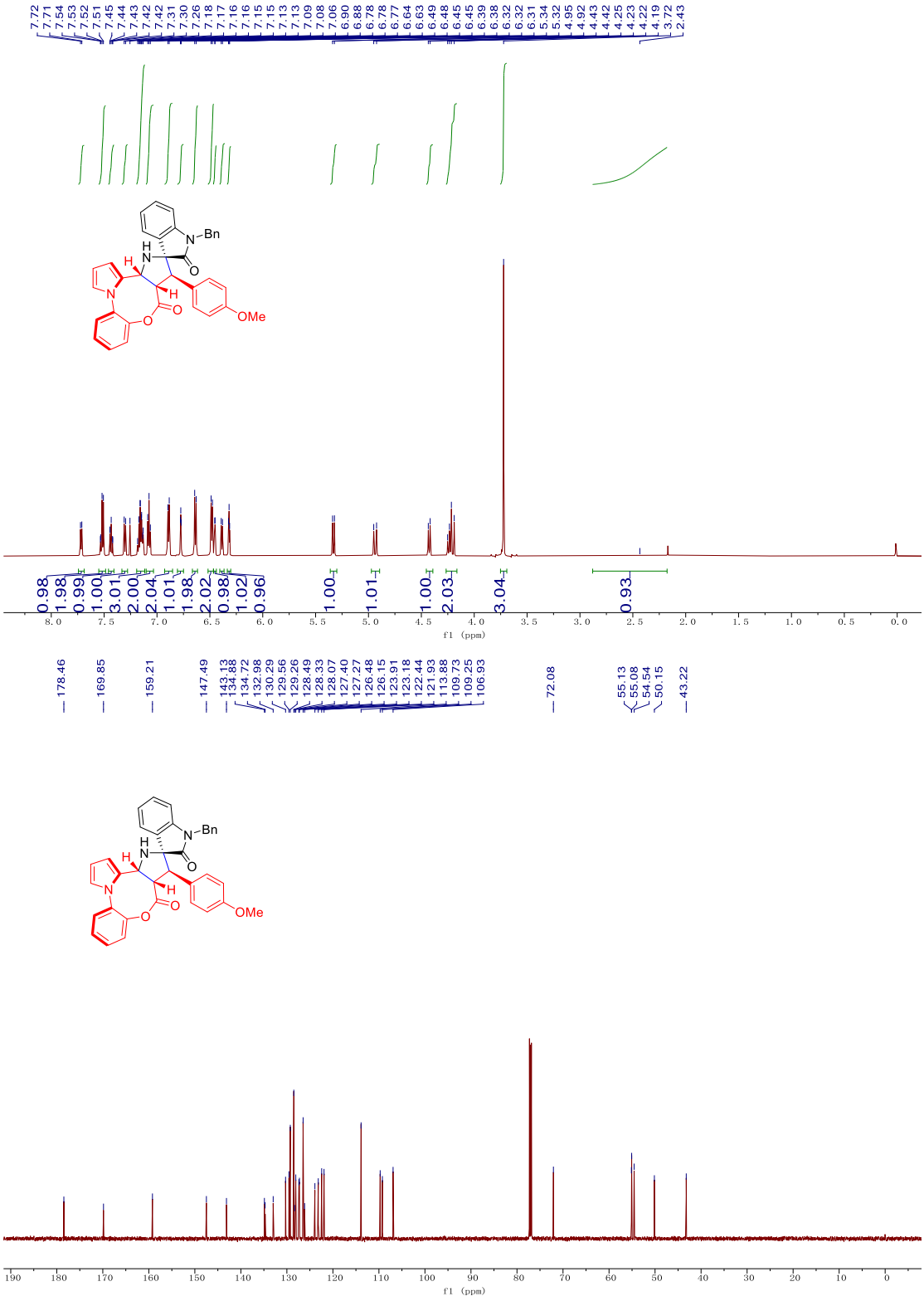
N-Bn
H
N
O
H
N
H
O
O
Me
1.01 2.00 1.02 1.02 3.03 2.05 4.04 0.99 1.96 0.98 0.97 0.99 1.00 1.02 1.02 2.03 2.97
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
178.42 169.83 147.50 143.12 137.26 134.95 134.69 132.99 131.17 130.28 129.54 129.20 128.46 128.32 128.13 128.05 127.37 127.20 126.56 123.91 123.17 122.45 121.93 109.73 109.25 106.92 72.10 55.52 54.63 50.16 43.29 21.14
N-Bn
H
N
O
H
N
H
O
O
Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

6ah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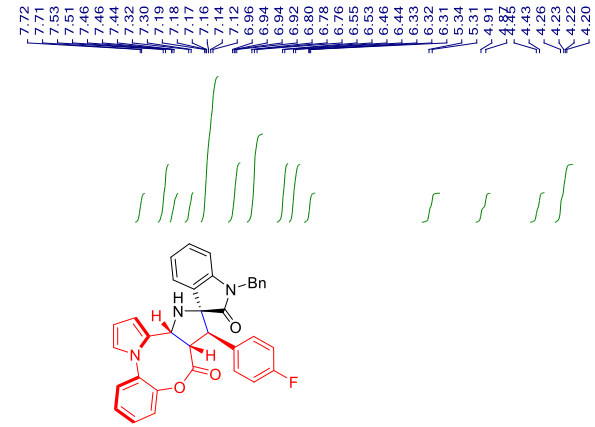
N-Bn
H
N
O
H
N
O
O
OMe
0.98 1.98 0.99 1.00 3.01 2.00 2.04 1.01 1.98 2.02 0.98 1.02 0.96 1.00 1.01 1.00 2.03 3.04 0.93
f1 (ppm)
178.46 169.85 159.21 147.49 143.13 134.88 134.72 132.98 130.29 129.56 129.26 128.49 128.33 128.07 127.40 127.27 126.48 126.15 123.91 123.18 122.44 121.93 113.88 109.73 109.25 106.93 72.08 55.13 55.08 54.54 50.15 43.22
f1 (ppm)

6ai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7.19
7.18
7.17
7.16
7.14
7.12
6.96
6.94
6.94
6.92
6.80
6.78
6.76
6.55
6.53
6.46
6.44
6.33
6.32
6.31
5.34
5.31
4.91
4.87
4.85
4.43
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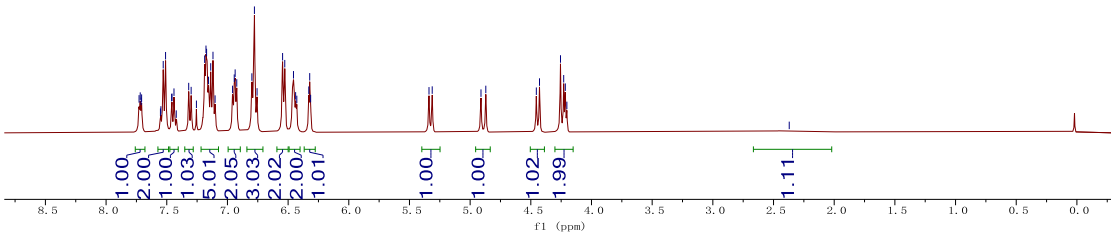
4.23
4.22
4.20
2.37
N-Bn
H
N
O
H
N
O
O
F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1.00
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2.05
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2.02
2.00
1.01
1.00
1.00
1.02
1.99
1.11
f1 (ppm)


178.24
169.65
163.68
161.23
147.43
143.11
134.87
134.56
132.95
130.33
130.03
129.99
129.89
129.81
129.74
128.59
128.08
127.99
127.48
127.44
126.48
123.92
123.31
122.42
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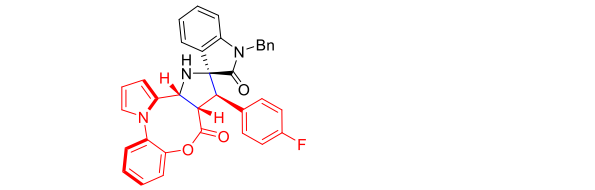
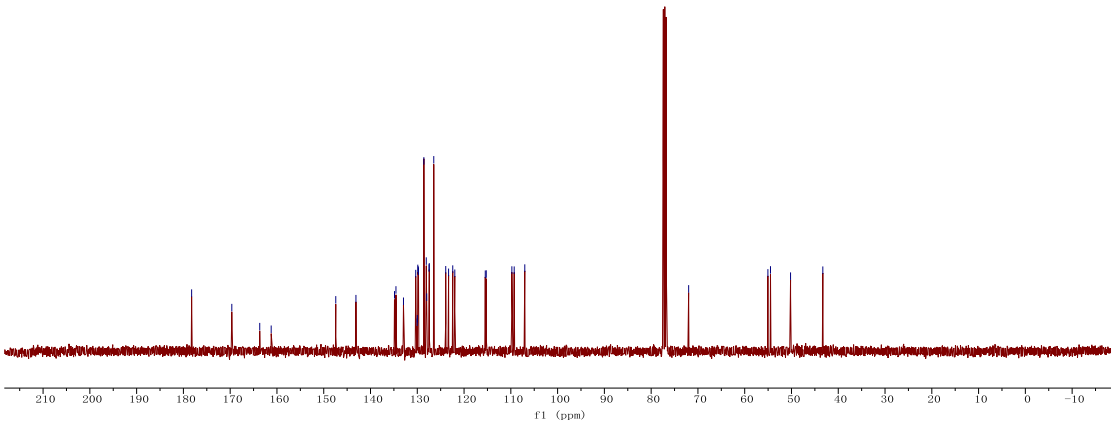
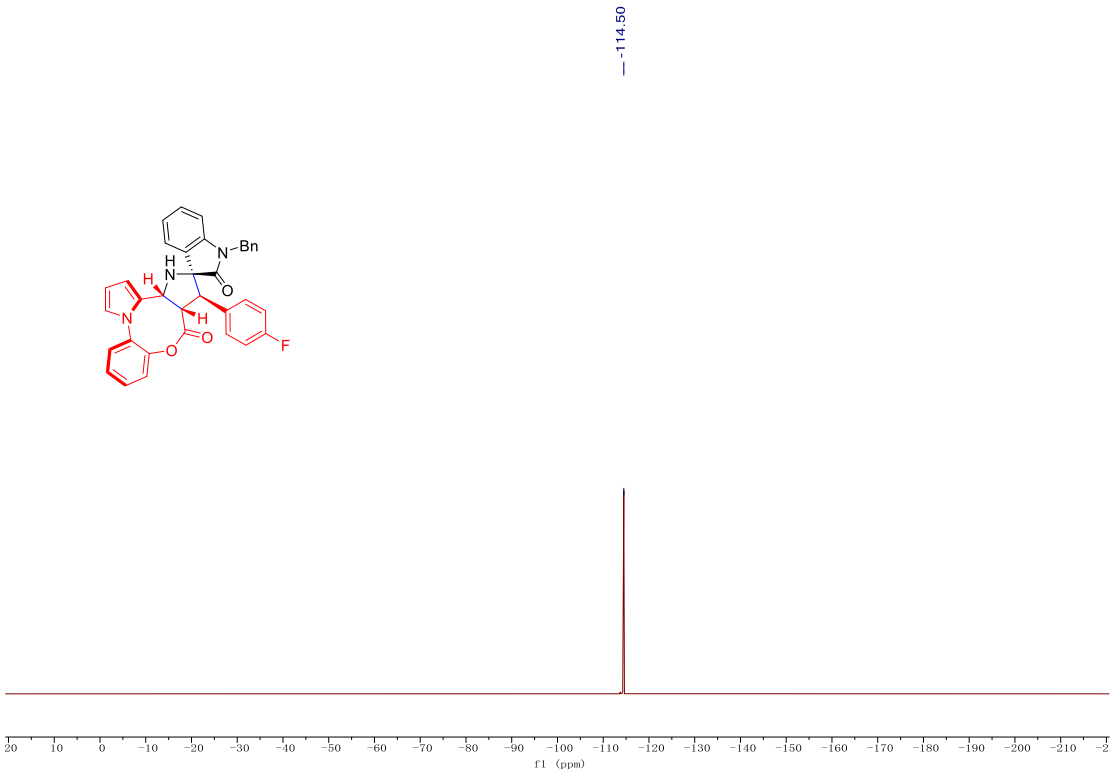
115.26
109.78
109.28
107.02
71.98
55.04
54.49
50.20
43.30


N-Bn
H
N
O
H
N
O
O
F


f1 (ppm)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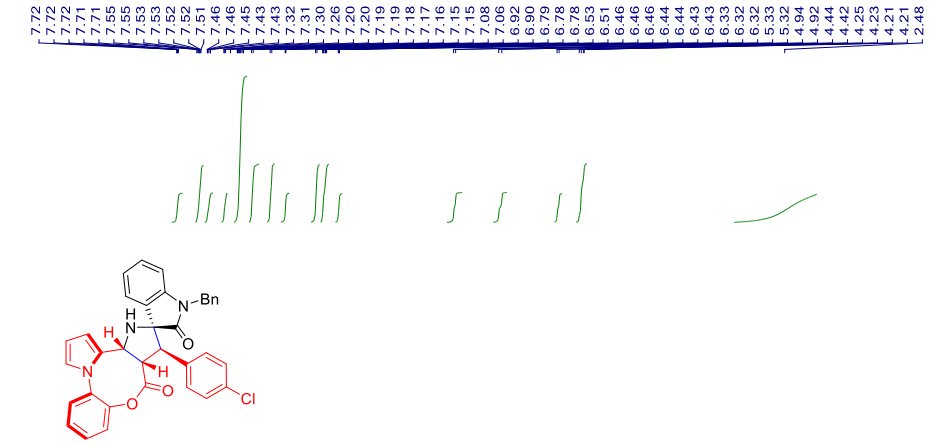
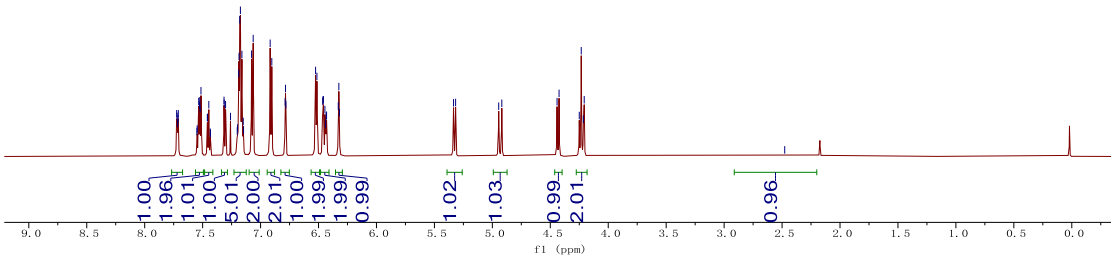
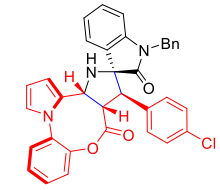
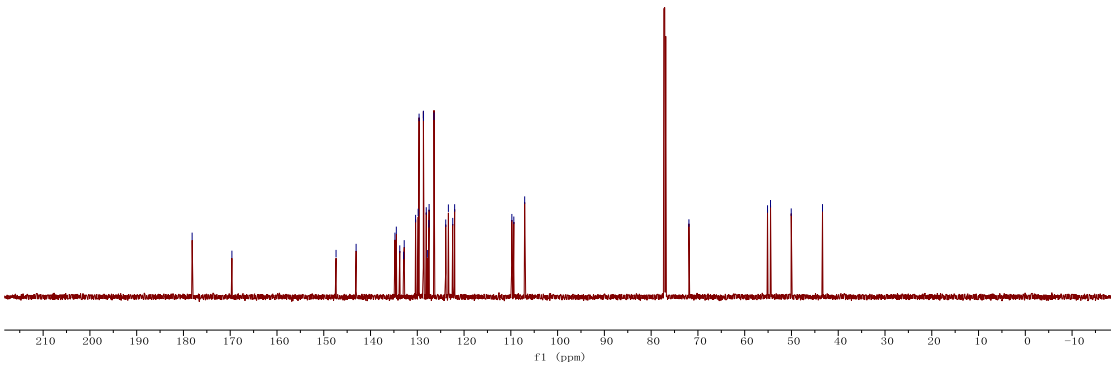
N-Bn
H
N
O
H
N
H
O
O
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

6aj









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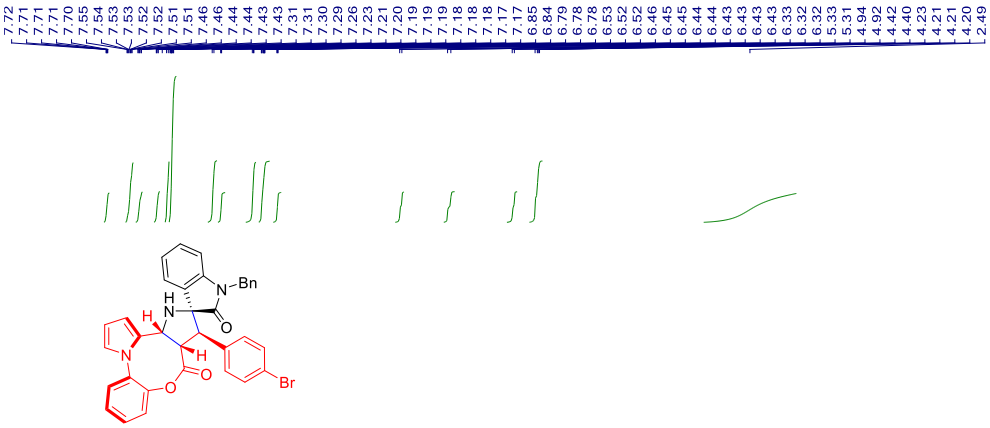
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7.46
7.44
7.44
7.43
7.43
7.31
7.31
7.30
7.29
7.26
7.23
7.21
7.20
7.19
7.19
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7.18
7.18
7.17
7.17
6.85
6.84
6.79
6.78
6.78
6.53
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6.44
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6.43
6.43
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6.32
6.32
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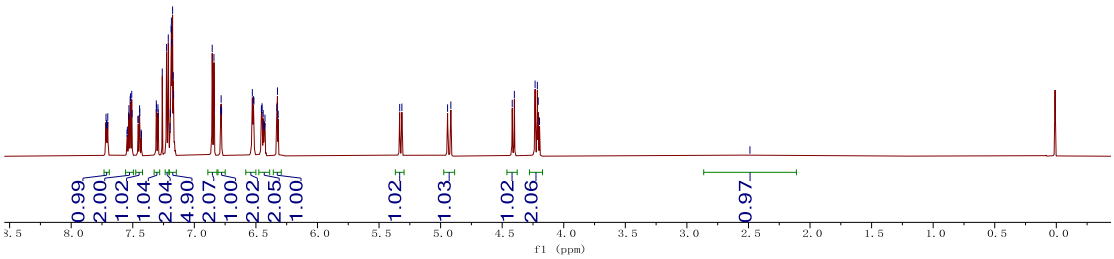
5.31
4.94
4.92
4.42
4.40
4.23
4.21
4.21
4.20
2.49
N-Bn
H
N
O
H
N
H
O
O
Br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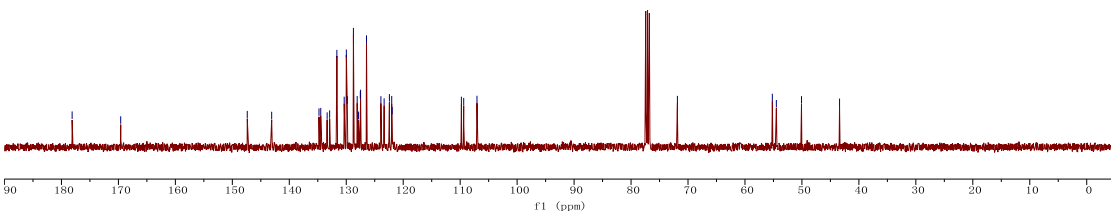
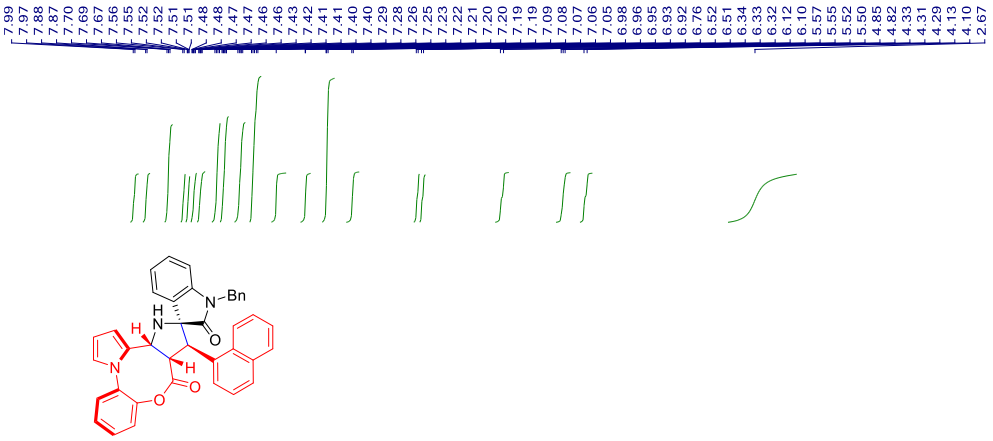
1.02
1.04
2.04
4.90
2.07
1.00
2.02
2.05
1.00
1.02
1.03
1.02
2.06
0.97
f1 (ppm)

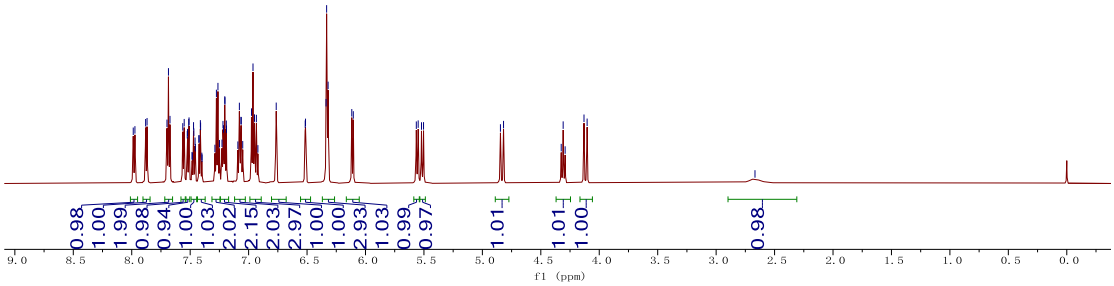

178.13
169.60
147.38
143.09
134.79
134.48
133.36
132.92
131.65
130.36
129.98
129.82
128.74
128.08
127.84
127.53
127.49
126.45
123.92
123.35
122.42
122.02
121.95
109.79
109.38
107.05
71.86
55.20
54.49
50.07
43.39

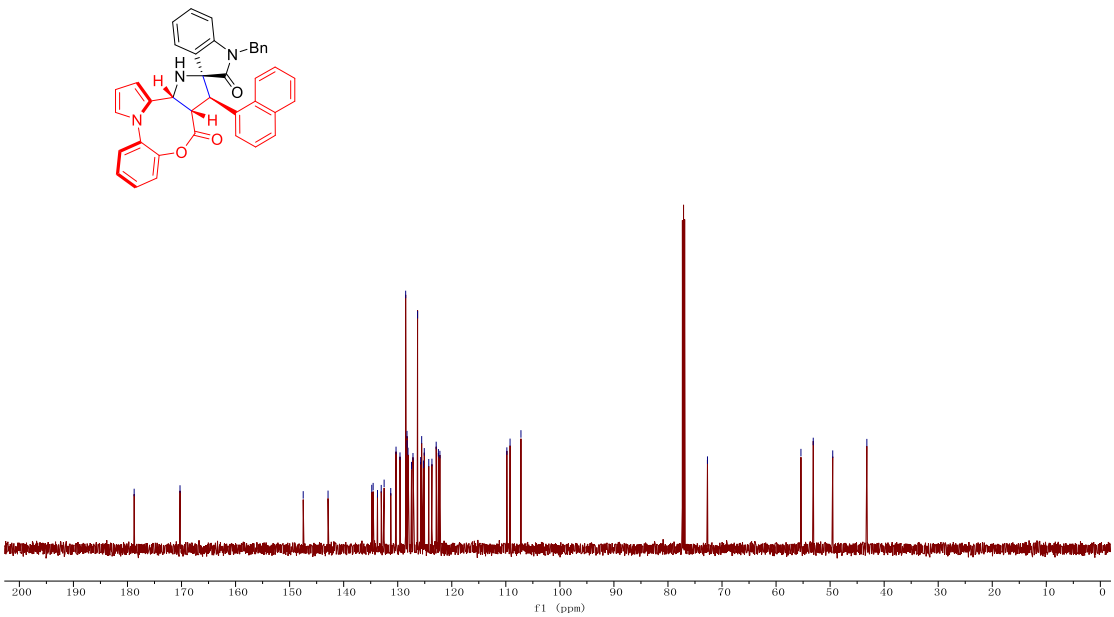

N-Bn
H
N
O
H
N
H
O
O
Br


f1 (ppm)

6al







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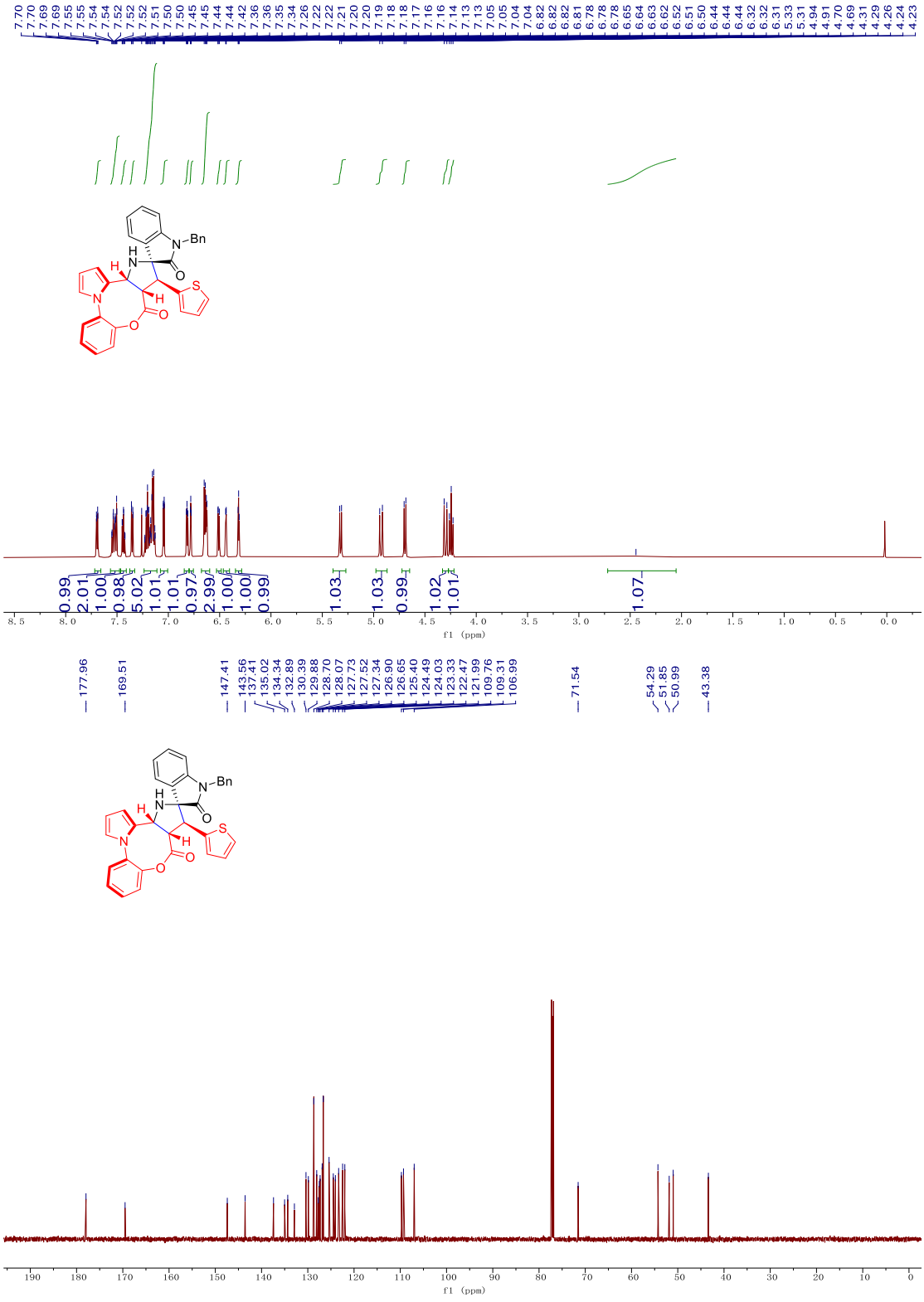

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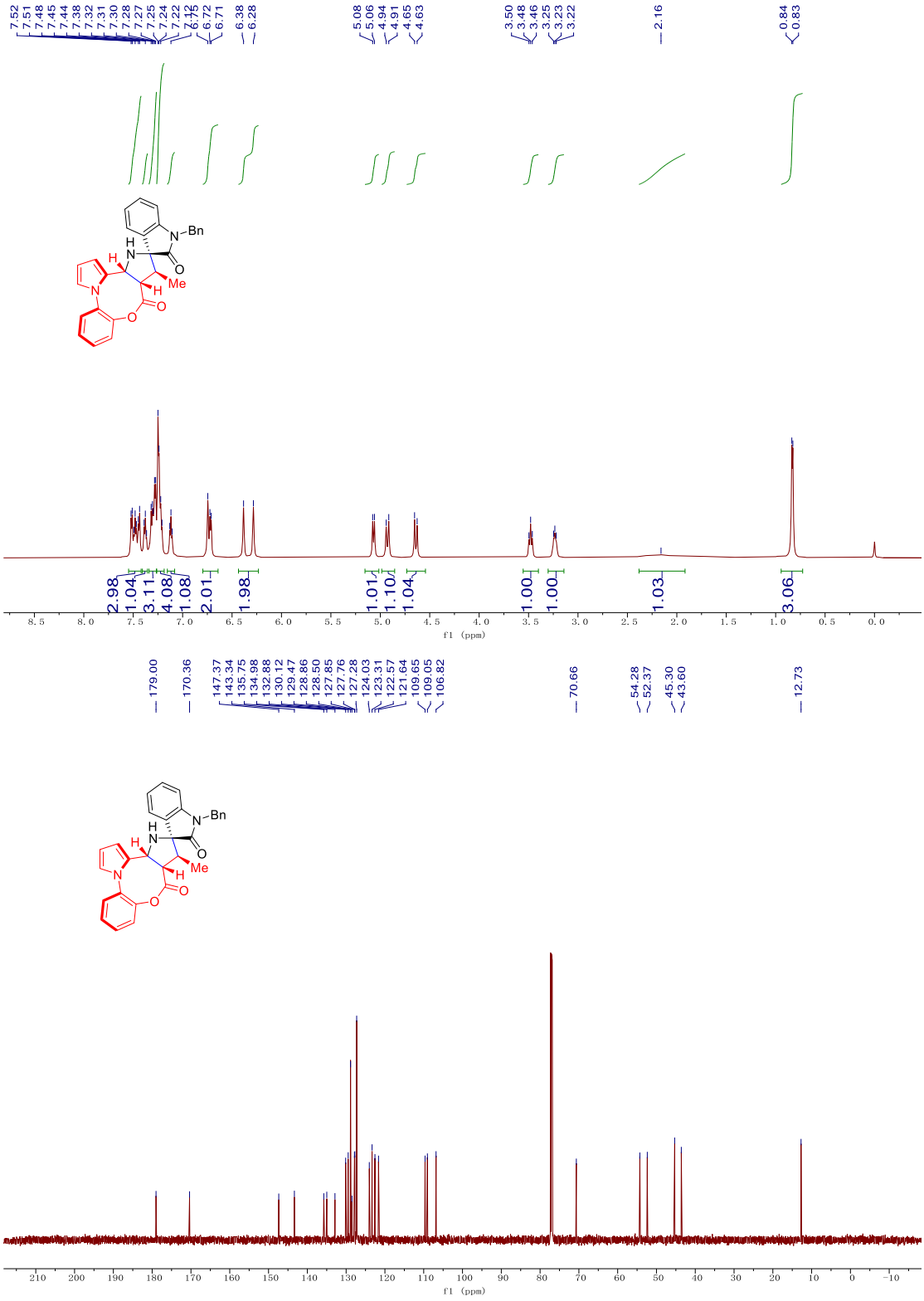
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7.25
7.24
7.22
7.12
6.72
6.71
6.38
6.28
5.08
5.06
4.94
4.91
4.65
4.63
3.50
3.48
3.46
3.25
3.23
3.22
2.16
0.84
0.83
N-Bn
H
N
O
H
Me
N
H
O
O
2.98
1.04
3.11
4.08
1.08
2.01
1.98
1.01
1.10
1.04
1.00
1.00
1.03
3.06
f1 (ppm)
179.00
170.36
147.37
143.34
135.75
134.98
132.88
130.12
129.47
128.86
128.50
127.85
127.76
127.28
124.03
123.31
122.57
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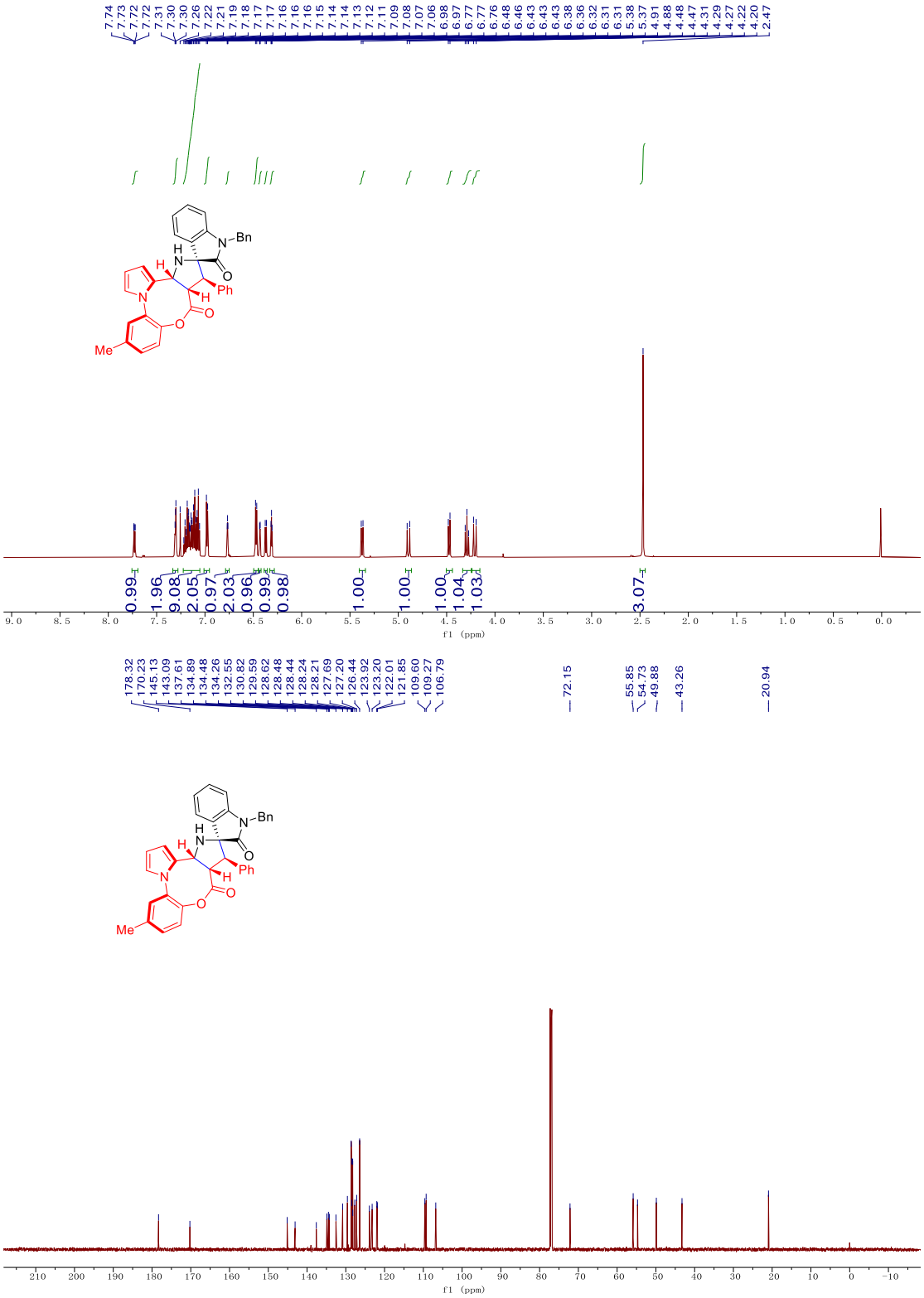
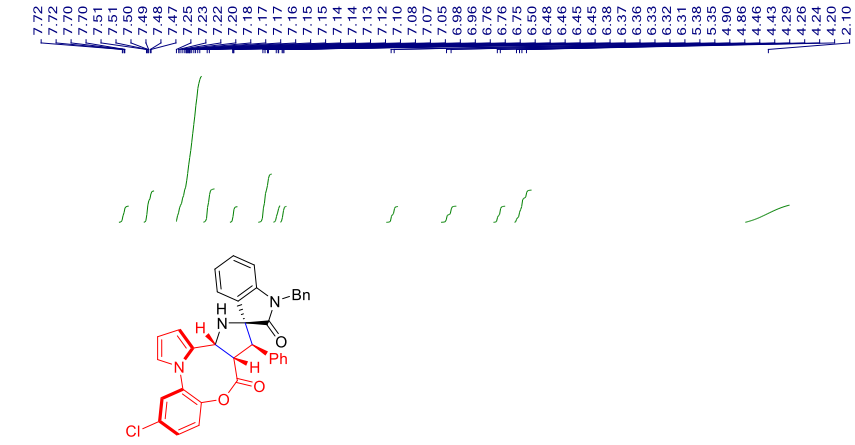
106.82
70.66
54.28
52.37
45.30
43.60
12.73
f1 (ppm)

6ao


7.74 7.73 7.72 7.72 7.31 7.30 7.30 7.26 7.22 7.21 7.19 7.18 7.17 7.17 7.16 7.16 7.16 7.15 7.14 7.13 7.12 7.11 7.09 7.08 7.07 7.06 6.98 6.97 6.77 6.77 6.76 6.48 6.46 6.43 6.43 6.43 6.38 6.36 6.32 6.31 6.31 5.38 5.37 4.91 4.88 4.48 4.47 4.31 4.29 4.27 4.22 4.20 2.47
N-Bn
H
N
O
H
Ph
N
H
O
O
Me
0.99 1.96 9.08 2.05 0.97 2.03 0.96 0.99 0.98 1.00 1.00 1.00 1.04 1.03 3.07
f1 (ppm)
178.32 170.23 145.13 143.09 137.61 134.89 134.48 134.26 132.55 130.82 129.59 128.62 128.48 128.44 128.24 128.21 127.69 127.20 126.44 123.92 123.20 122.01 121.85 109.60 109.27 106.79 72.15 55.85 54.73 49.88 43.26 20.94
f1 (ppm)

6ap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7.47
7.25
7.23
7.22
7.20
7.18
7.17
7.17
7.16
7.15
7.15
7.14
7.14
7.13
7.12
7.10
7.08
7.07
7.05
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6.76
6.75
6.50
6.48
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6.37
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6.33
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6.31
5.38
5.35
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4.46
4.43
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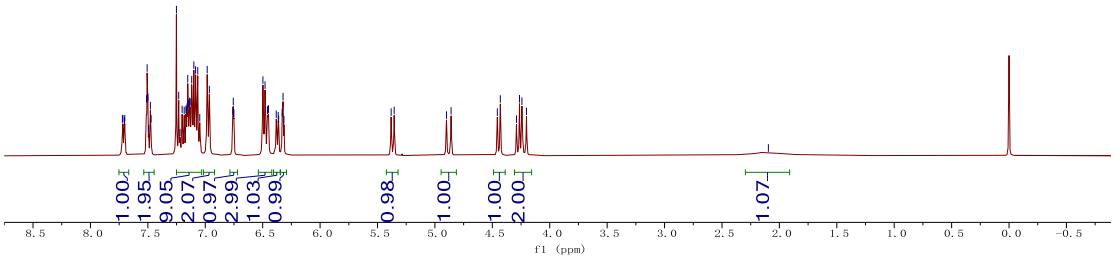
4.20
2.10
Bn
N
H
N
O
H
Ph
N
H
O
O
Cl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9.05
2.07
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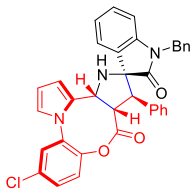
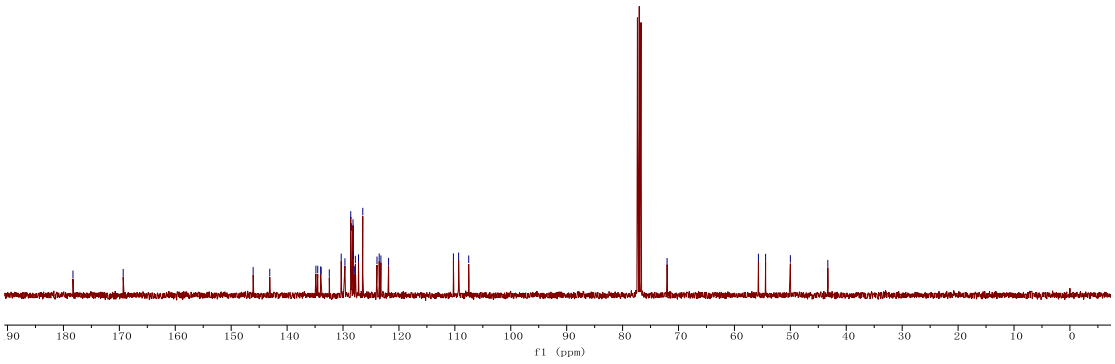
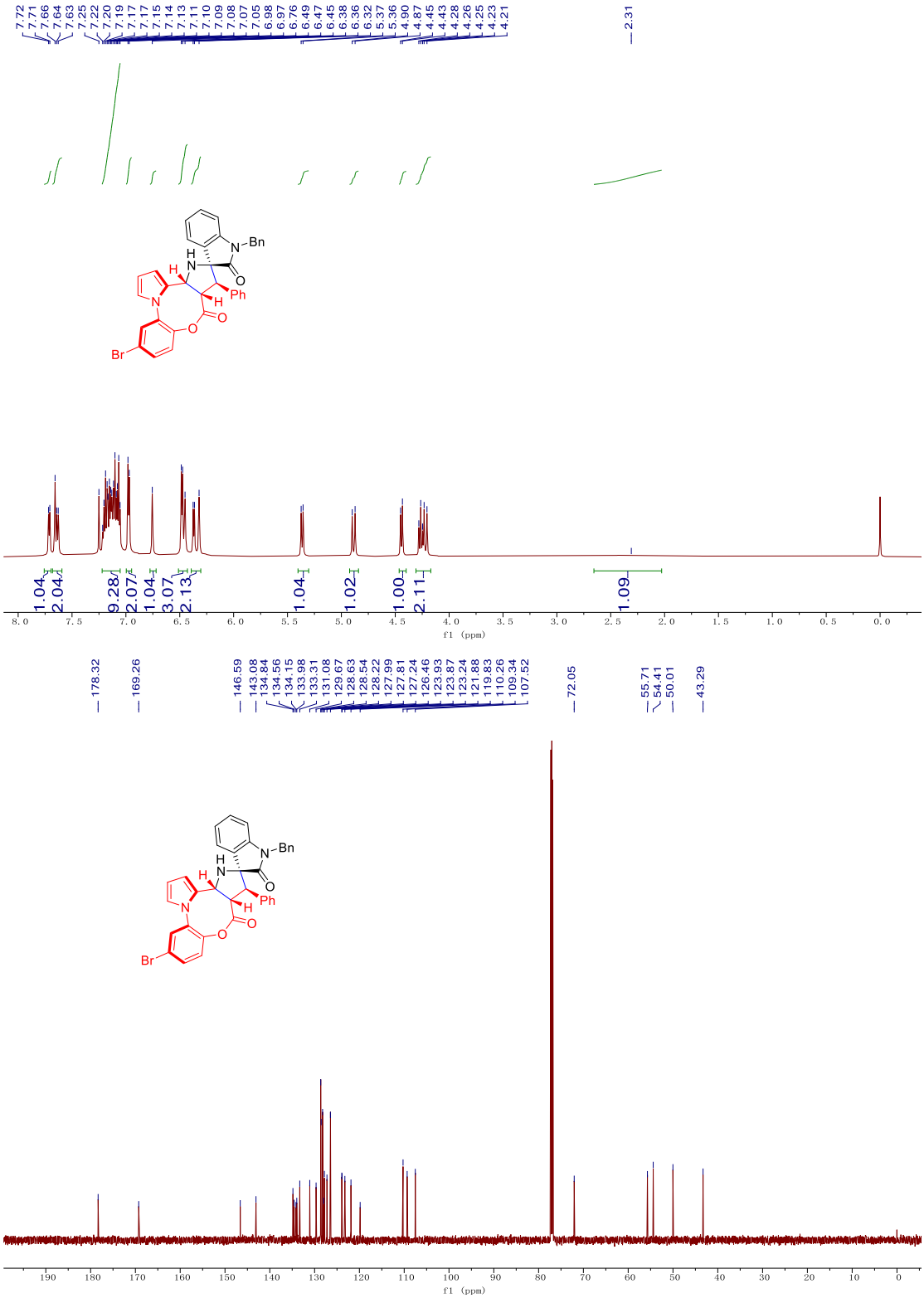
2.99
1.03
0.99
0.98
1.00
1.00
2.00
1.07
f1 (ppm)


178.30
169.31
146.07
143.10
134.85
134.52
133.99
133.92
132.45
130.32
129.66
128.62
128.52
128.21
128.17
127.98
127.79
127.23
126.47
123.92
123.53
123.23
121.85
110.26
109.32
107.52
72.05
55.71
54.43
50.00
43.30


Bn
N
H
N
O
H
Ph
N
H
O
O
Cl


f1 (ppm)

6aq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7.63
7.25
7.22
7.20
7.19
7.17
7.17
7.15
7.14
7.13
7.11
7.10
7.09
7.08
7.07
7.05
6.98
6.97
6.76
6.49
6.47
6.45
6.38
6.36
6.32
5.37
5.36
4.90
4.87
4.45
4.43
4.28
4.26
4.25
4.23
4.21
2.31
N-Bn
H
N
O
H
Ph
N
O
Br
1.04
2.04
9.28
2.07
1.04
3.07
2.13
1.04
1.02
1.00
2.11
1.09
f1 (ppm)
178.32
169.26
146.59
143.08
134.84
134.56
134.15
133.98
133.31
131.08
129.67
128.63
128.54
128.22
127.99
127.81
127.24
126.46
123.93
123.87
123.24
121.88
119.83
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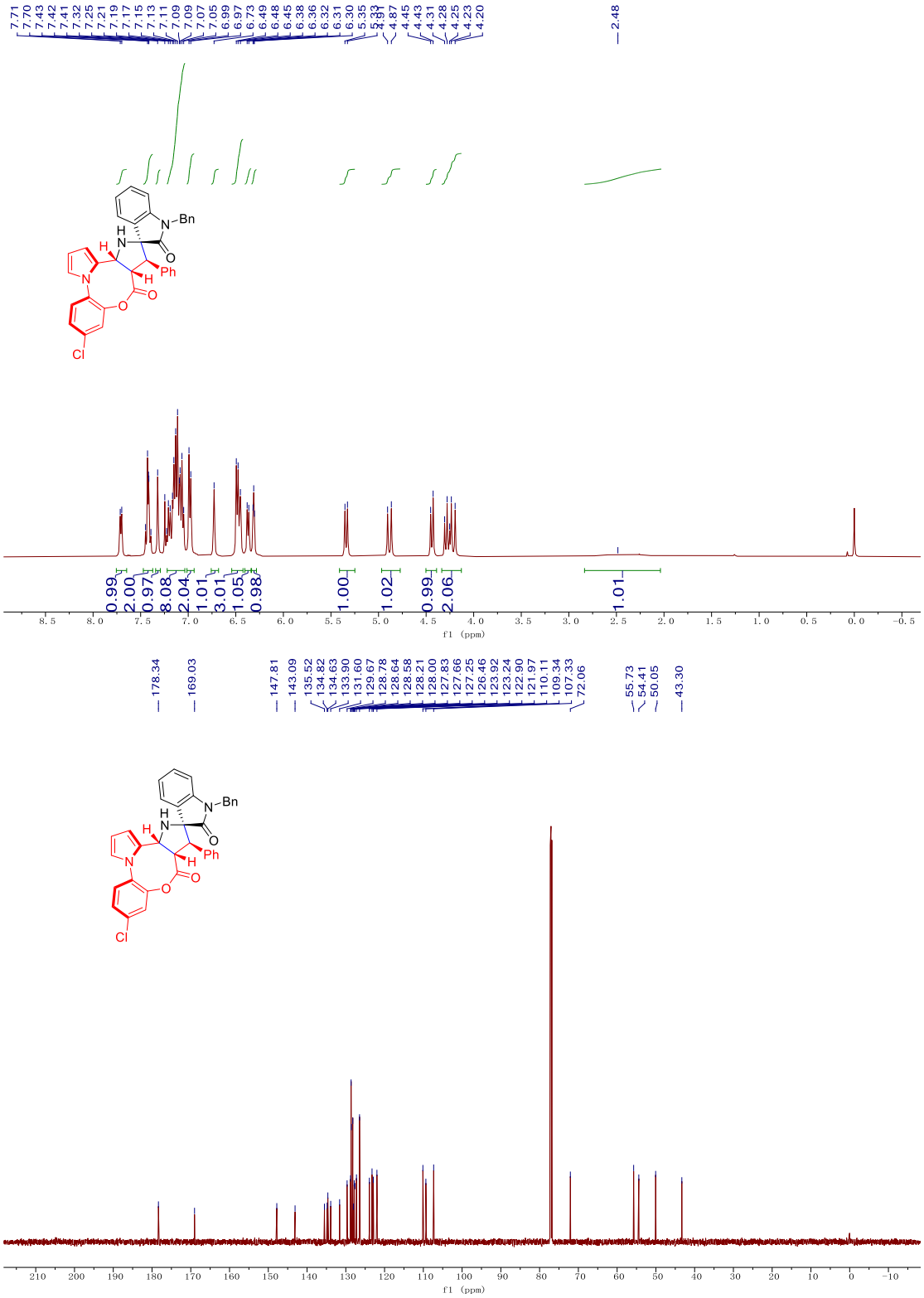
109.34
107.52
72.05
55.71
54.41
50.01
43.29
f1 (ppm)

6ar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7.32
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7.19
7.17
7.15
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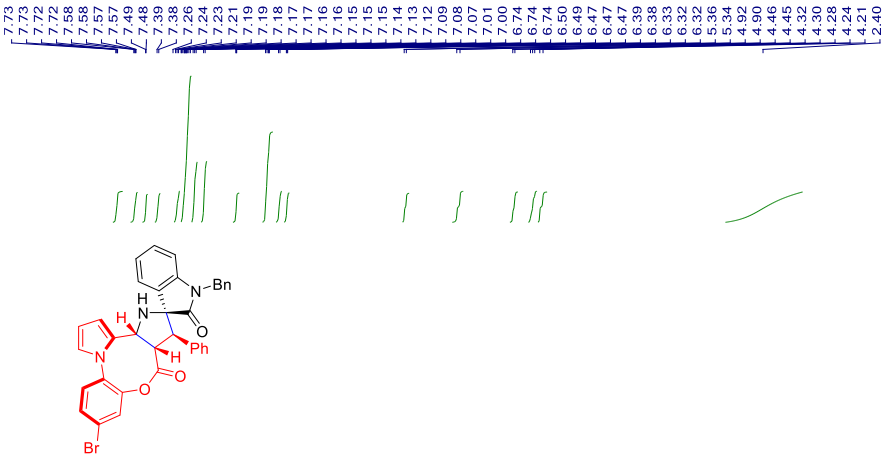
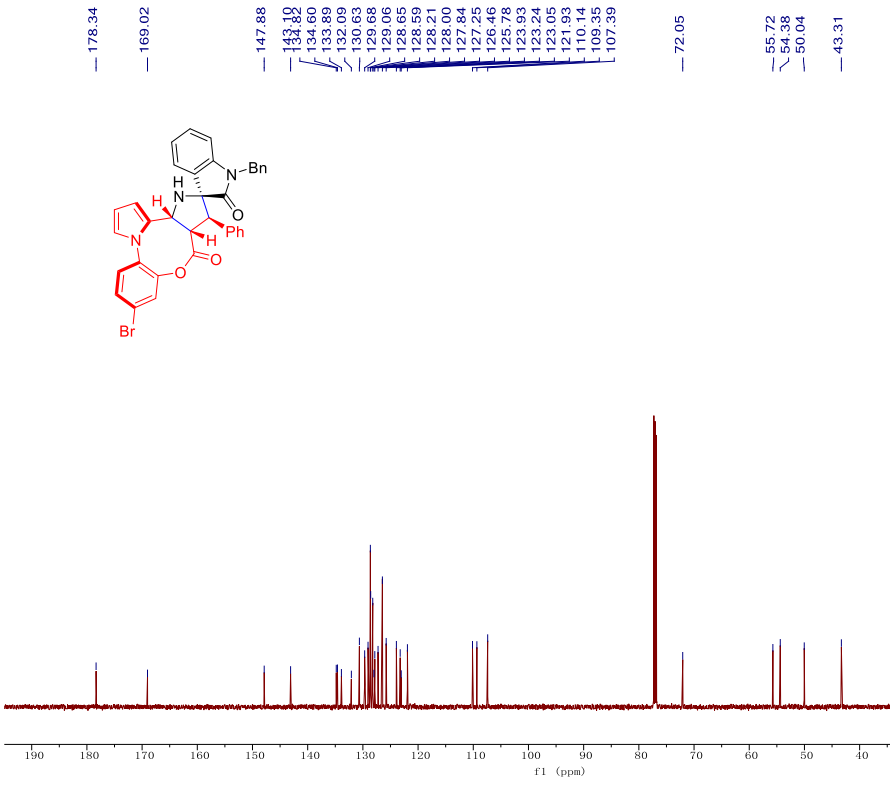
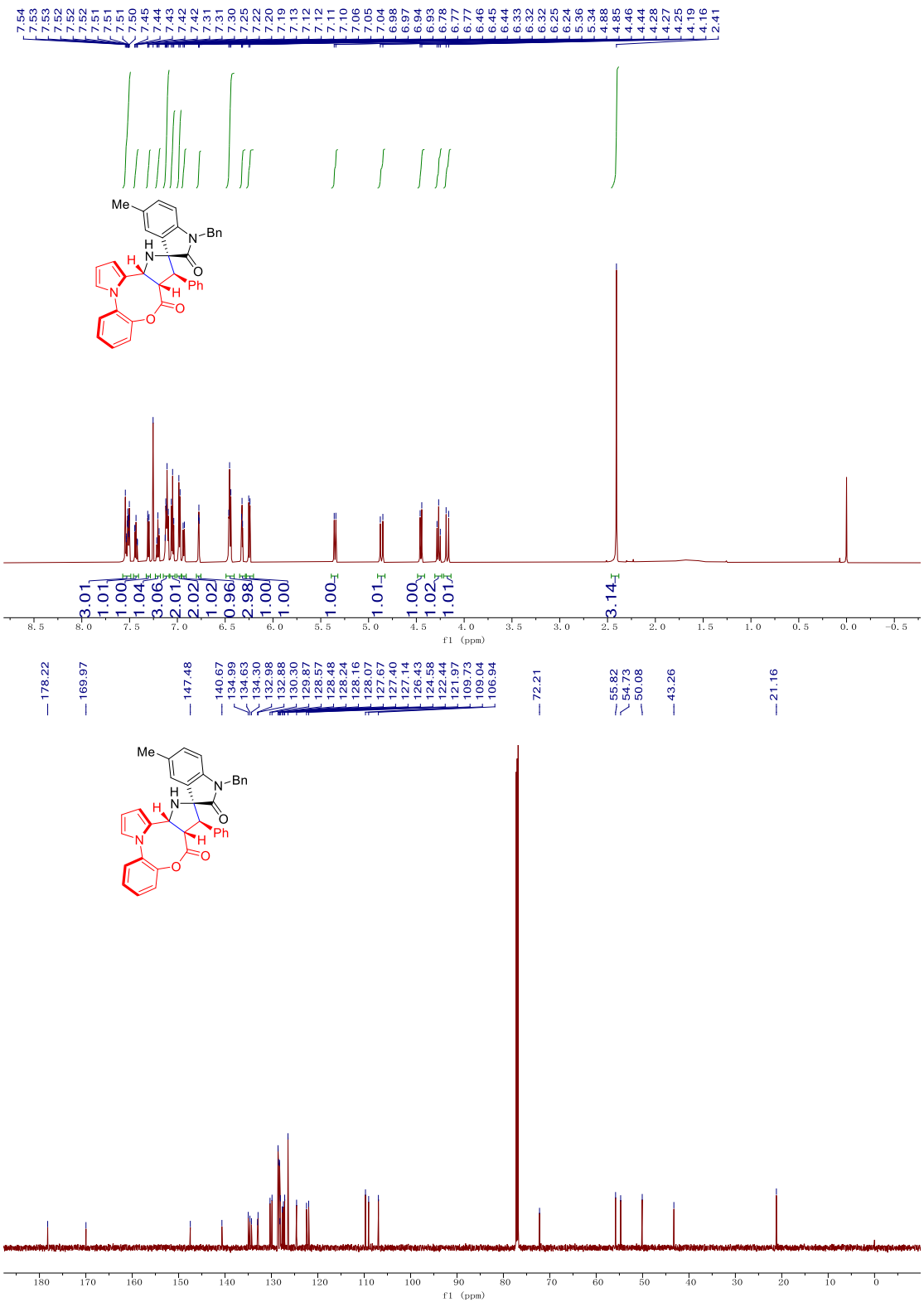
4.31
4.28
4.25
4.23
4.20
2.48
N-Bn
H
N
O
Ph
H
N
O
H
O
Cl
0.99
2.00
0.97
8.08
2.04
1.01
3.01
1.05
0.98
1.00
1.02
0.99
2.06
1.01
f1 (ppm)
178.34
169.03
147.81
143.09
135.52
134.82
134.63
133.90
131.60
129.67
128.78
128.64
128.58
128.21
128.00
127.83
127.66
127.25
126.46
123.92
123.24
122.90
121.97
110.11
109.34
107.33
72.06
55.73
54.41
50.05
43.30
f1 (ppm)

6as

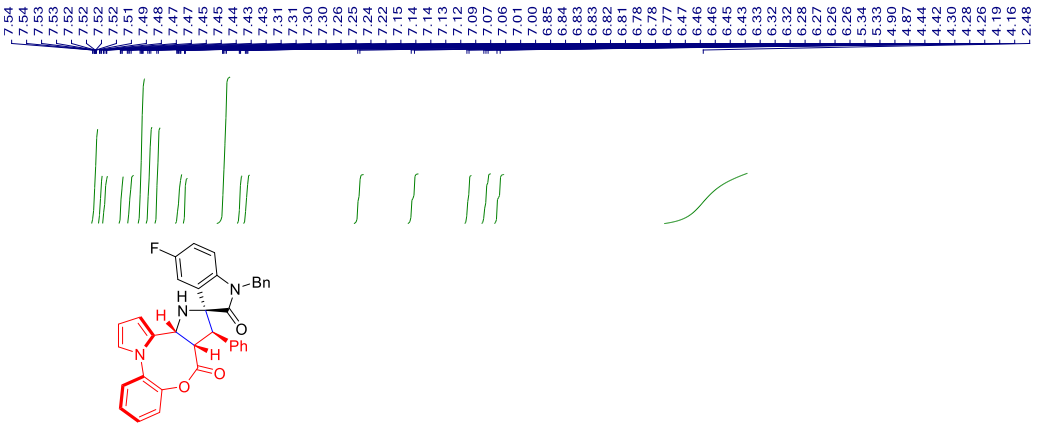

7.73 7.73 7.72 7.72 7.58 7.58 7.57 7.57 7.49 7.48 7.39 7.38 7.26 7.24 7.23 7.21 7.19 7.19 7.18 7.17 7.17 7.16 7.16 7.15 7.15 7.14 7.13 7.12 7.09 7.08 7.07 7.01 7.00 6.74 6.74 6.74 6.50 6.49 6.47 6.47 6.47 6.39 6.38 6.33 6.32 6.32 5.36 5.34 4.92 4.90 4.46 4.45 4.32 4.30 4.28 4.24 4.21 2.40
N-Bn
H
N
O
H
Ph
N
H
O
O
Br
1.06 1.02 0.96 0.99 1.07 5.00 2.06 2.09 1.00 3.09 1.07 1.01 0.99 1.06 1.04 1.06 1.04 1.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

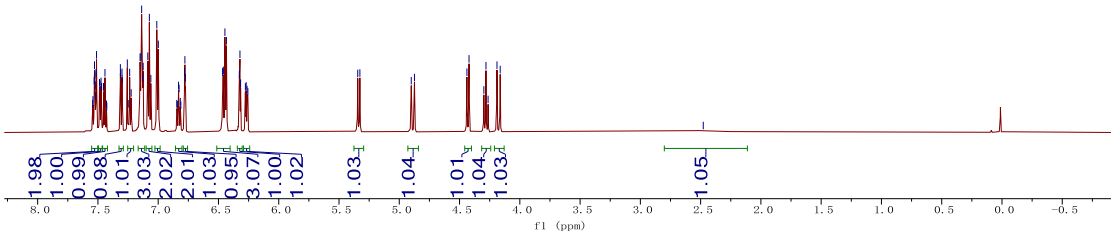

178.34 169.02 147.88 143.10 134.82 134.60 133.89 132.09 130.63 129.68 129.06 128.65 128.59 128.21 128.00 127.84 127.25 126.46 125.78 123.93 123.24 123.05 121.93 110.14 109.35 107.39 72.05 55.72 54.38 50.04 43.31
N-Bn
H
N
O
H
Ph
N
H
O
O
Br
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

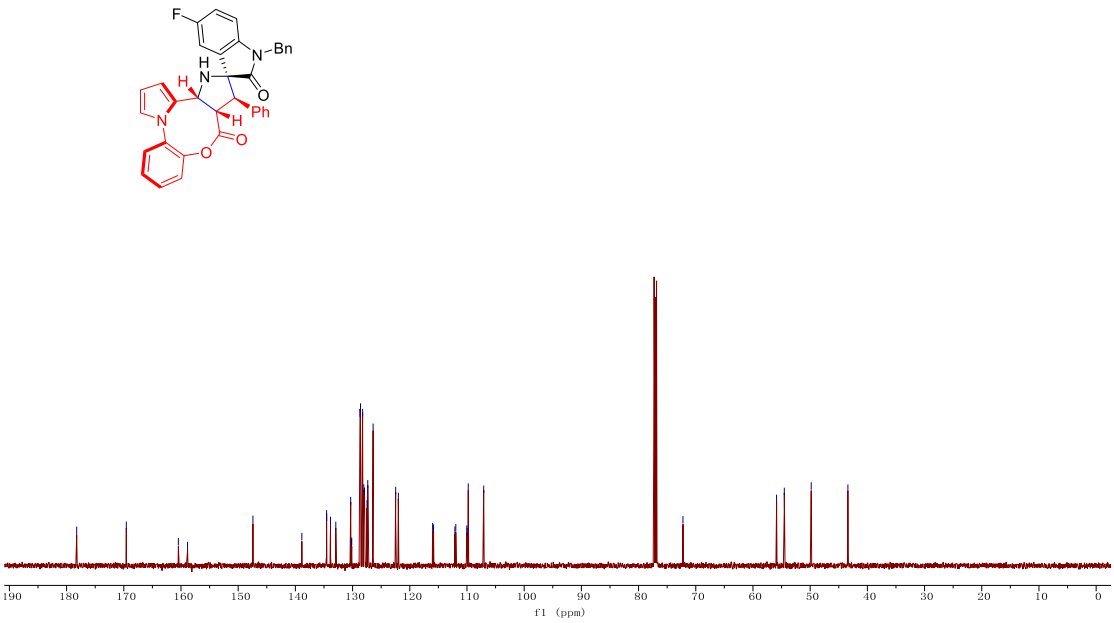
6ba

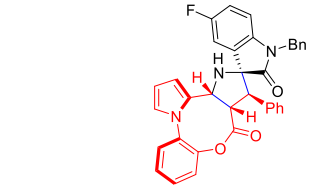

7.54 7.53 7.53 7.52 7.52 7.51 7.51 7.51 7.50 7.45 7.44 7.43 7.42 7.42 7.31 7.31 7.30 7.25 7.22 7.20 7.19 7.13 7.12 7.12 7.11 7.10 7.06 7.05 7.04 6.98 6.97 6.94 6.93 6.78 6.77 6.77 6.46 6.45 6.44 6.33 6.32 6.32 6.25 6.24 5.36 5.34 4.88 4.85 4.46 4.44 4.28 4.27 4.25 4.19 4.16 2.41
Me
N-Bn
H
N
O
H
Ph
N
H
O
3.01 1.01 1.00 1.04 3.06 2.01 2.02 1.02 0.96 2.98 1.00 1.00 1.00 1.01 1.00 1.02 1.01 3.14
f1 (ppm)
178.22 169.97 147.48 140.67 134.99 134.63 134.30 132.98 132.88 130.30 129.87 128.57 128.48 128.24 128.16 128.07 127.67 127.40 127.14 126.43 124.58 122.44 121.97 109.73 109.04 106.94 72.21 55.82 54.73 50.08 43.26 21.16
Me
N-Bn
H
N
O
H
Ph
N
H
O
f1 (ppm)

6ca



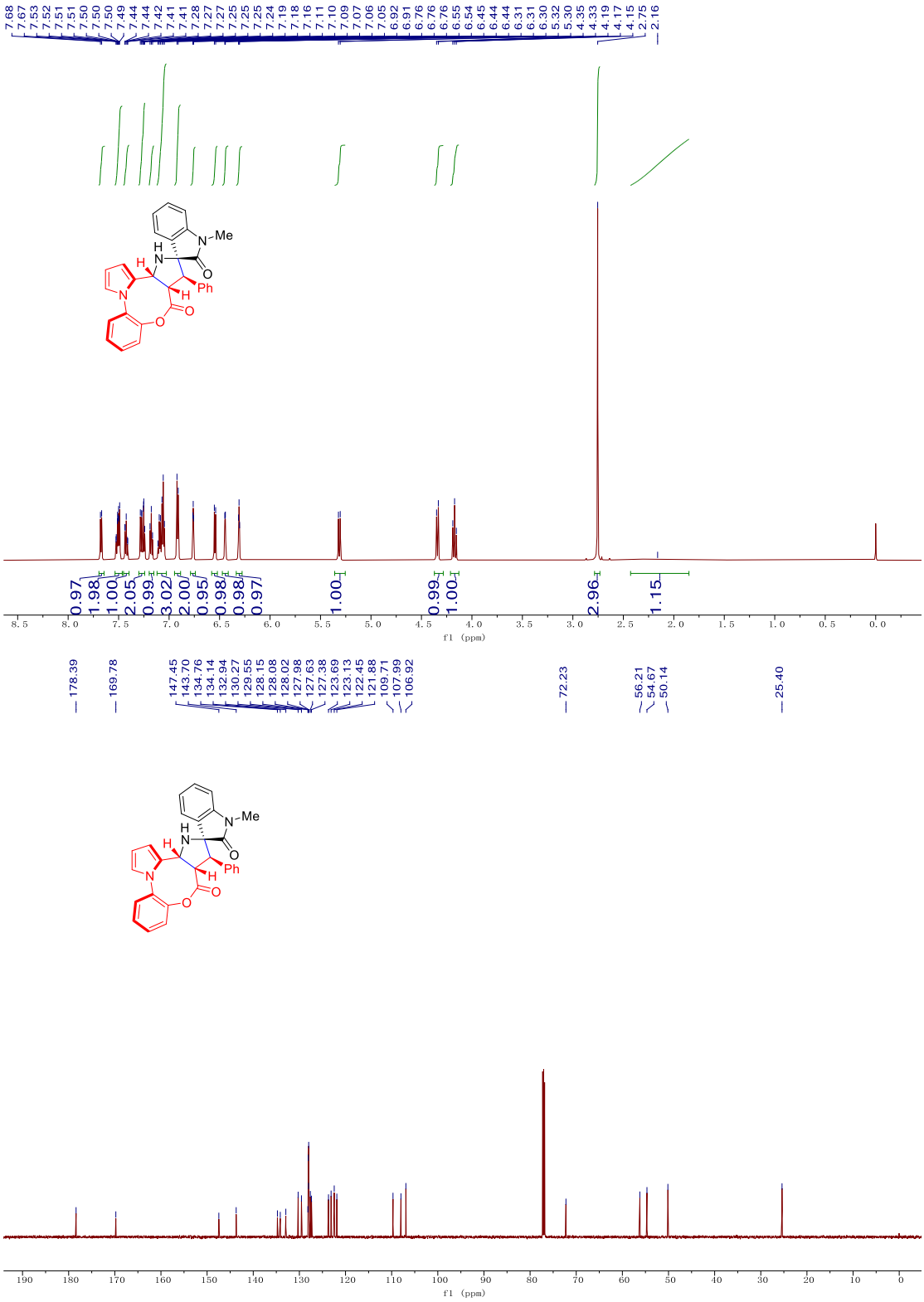




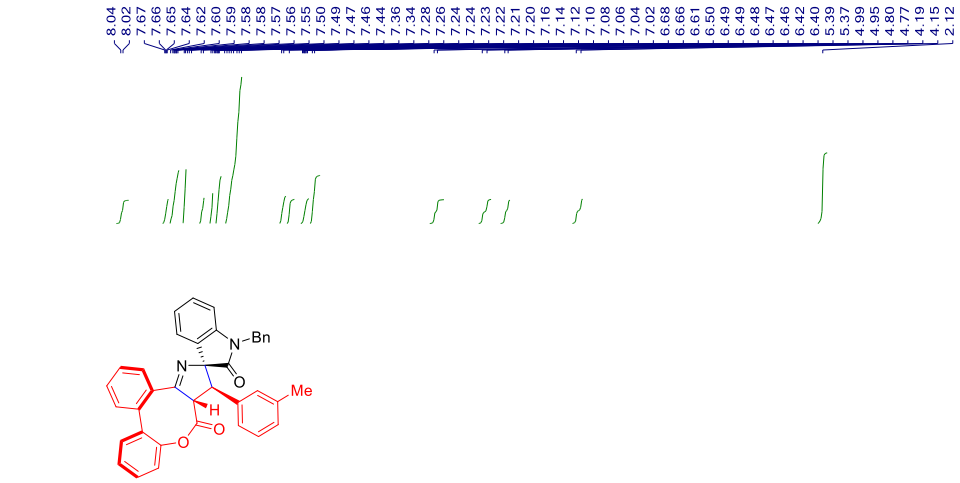

F
N
Bn
H
N
O
H
Ph
N
H
O
O

-119.09
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

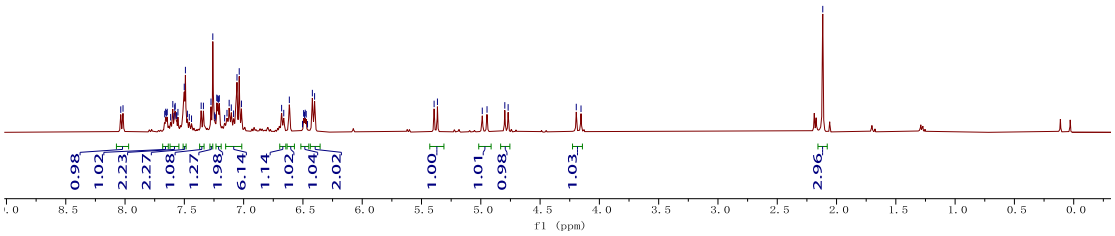
6da


7.68 7.67 7.53 7.52 7.51 7.51 7.50 7.50 7.50 7.49 7.44 7.44 7.42 7.41 7.41 7.28 7.27 7.27 7.25 7.25 7.24 7.19 7.18 7.16 7.11 7.10 7.09 7.07 7.06 7.05 6.92 6.91 6.76 6.76 6.76 6.55 6.54 6.45 6.44 6.44 6.31 6.31 6.30 5.32 5.30 4.35 4.33 4.19 4.17 4.15 2.75 2.16
N-Me
H
N
O
Ph
H
N
O
O
0.97 1.98 1.00 2.05 0.99 3.02 2.00 0.95 0.98 0.98 0.97 1.00 0.99 1.00 2.96 1.15
f1 (ppm)
178.39 169.78 147.45 143.70 134.76 134.14 132.94 130.27 129.55 128.15 128.08 128.02 127.98 127.63 127.38 123.69 123.13 122.45 121.88 109.71 107.99 106.92 72.23 56.21 54.67 50.14 25.40
f1 (ppm)

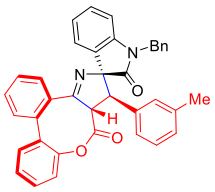
7

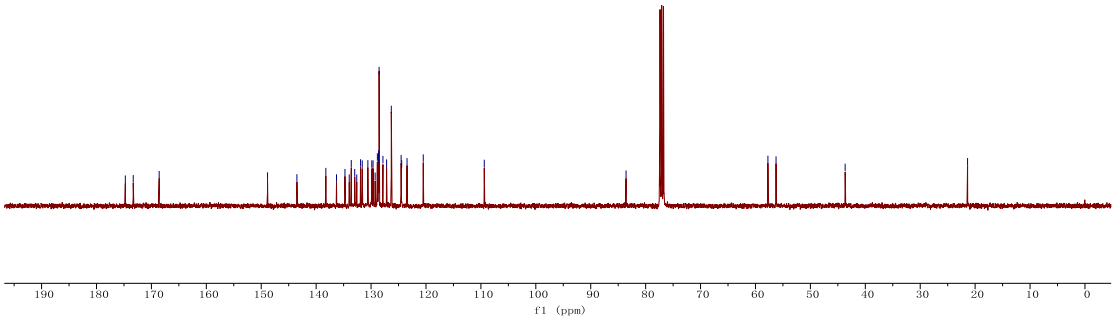

8.04
8.02
7.67
7.66
7.65
7.64
7.62
7.60
7.59
7.58
7.58
7.57
7.56
7.55
7.50
7.49
7.47
7.46
7.44
7.36
7.34
7.28
7.26
7.24
7.24
7.23
7.22
7.21
7.20
7.16
7.14
7.12
7.10
7.08
7.06
7.04
7.02
6.68
6.66
6.61
6.50
6.49
6.49
6.48
6.47
6.46
6.42
6.40
5.39
5.37
4.99
4.95
4.80
4.77
4.19
4.15
2.12

N-Bn
N
O
Me
H
O
O

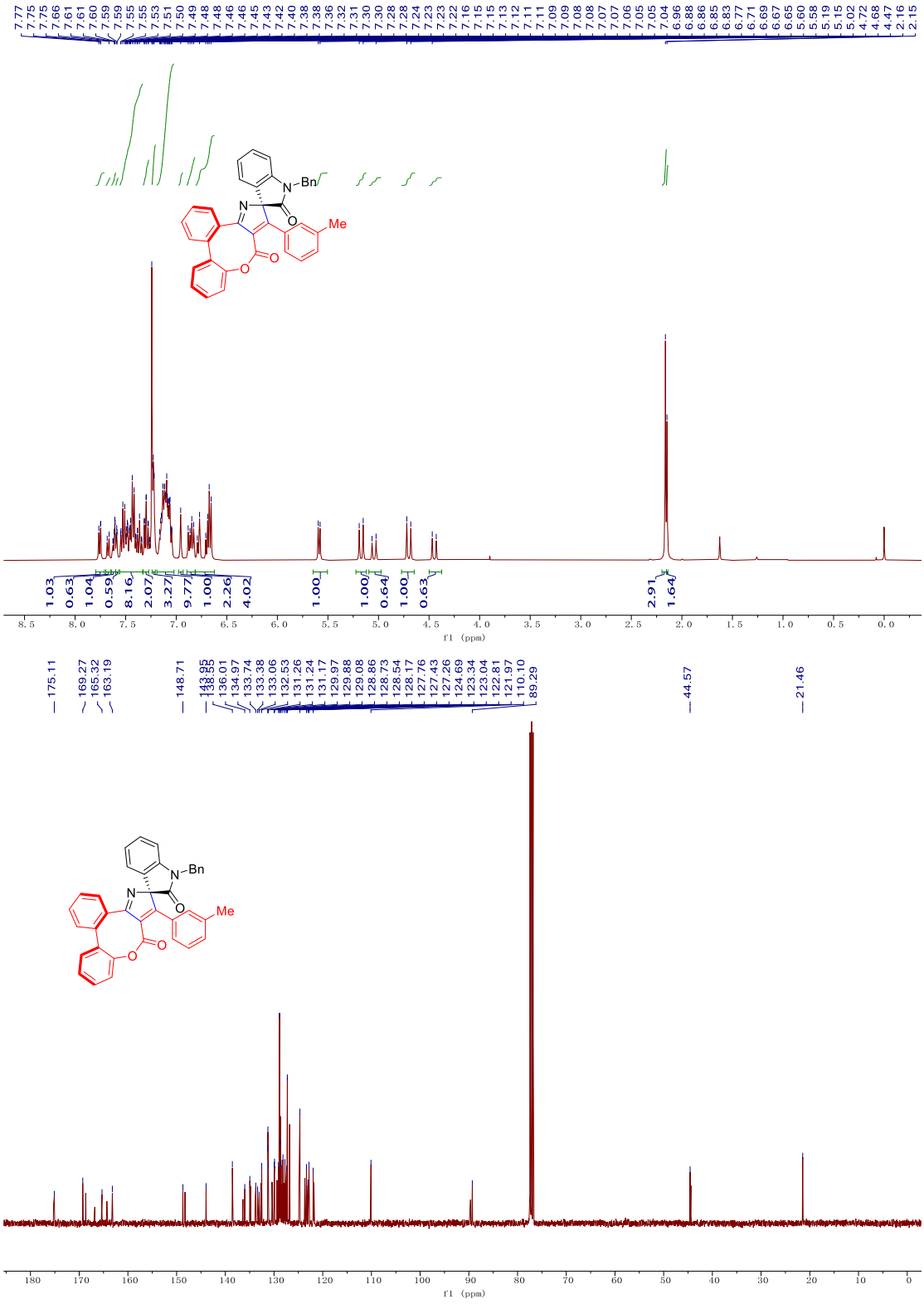

0.98
1.02
2.23
2.27
1.08
1.27
1.98
6.14
1.14
1.02
1.04
2.02
1.00
1.01
0.98
1.03
2.96
f1 (ppm)


174.75
173.31
168.59
148.85
143.51
138.23
136.29
134.75
133.98
133.61
132.98
132.61
131.91
131.60
130.58
129.87
129.64
129.26
128.85
128.69
128.62
128.54
127.84
127.18
126.31
124.53
124.42
123.45
120.50
109.39
83.57
57.73
56.25
43.67
21.38

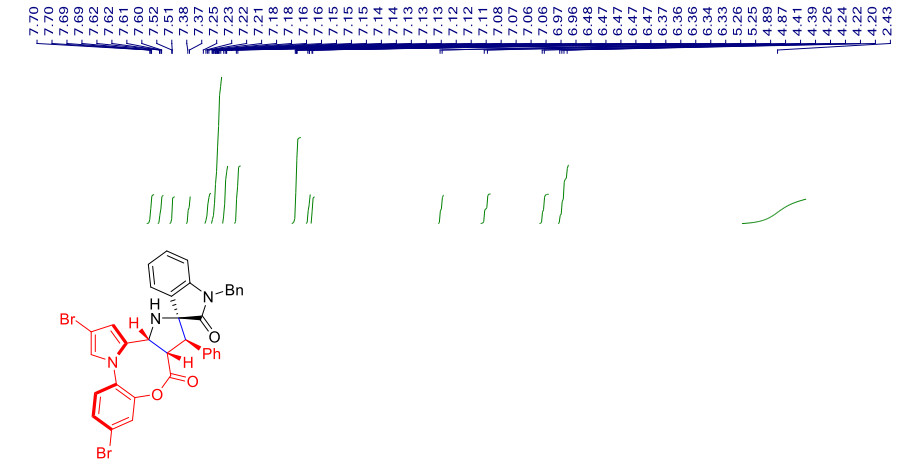

N-Bn
N
O
Me
H
O
O


f1 (ppm)

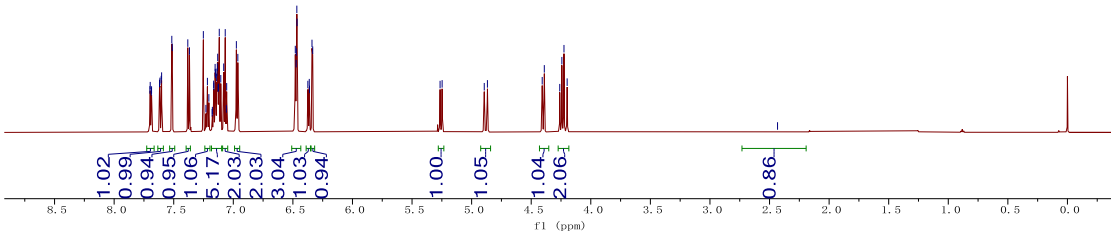
8


7.77 7.75 7.75 7.66 7.61 7.61 7.60 7.59 7.59 7.55 7.55 7.53 7.51 7.50 7.49 7.48 7.48 7.46 7.46 7.45 7.43 7.42 7.40 7.38 7.36 7.32 7.31 7.30 7.30 7.28 7.28 7.24 7.23 7.22 7.16 7.15 7.15 7.13 7.12 7.11 7.11 7.09 7.09 7.08 7.08 7.07 7.07 7.06 7.05 7.05 7.04 6.96 6.88 6.86 6.85 6.83 6.77 6.71 6.69 6.67 6.65 5.60 5.58 5.19 5.15 5.02 4.72 4.68 4.47 2.16 2.15
N-Bn
N
O
Me
O
O
1.03 0.63 1.04 0.59 8.16 2.07 3.27 9.77 1.00 2.26 4.02 1.00 1.00 0.64 1.00 0.63 2.91 1.64
f1 (ppm)
175.11 169.27 165.32 163.19 148.71 136.01 134.97 133.74 133.38 133.06 132.53 131.26 131.24 131.17 129.97 129.88 129.08 128.86 128.73 128.54 128.17 127.76 127.43 127.26 124.69 123.34 123.04 122.81 121.97 110.10 89.29 44.57 21.46
N-Bn
N
O
Me
O
O
f1 (ppm)

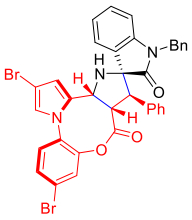
9

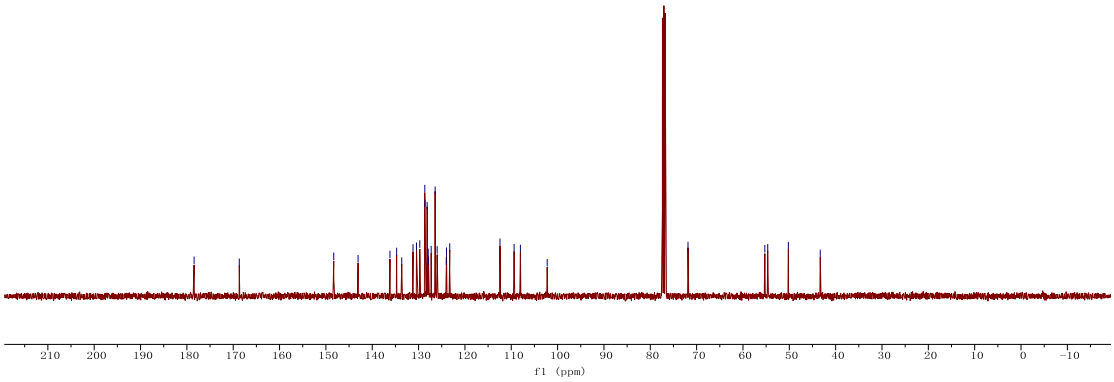

7.70
7.70
7.69
7.69
7.62
7.62
7.61
7.60
7.52
7.51
7.38
7.37
7.25
7.23
7.22
7.21
7.18
7.18
7.16
7.16
7.15
7.15
7.15
7.14
7.14
7.13
7.13
7.13
7.12
7.12
7.11
7.08
7.07
7.06
7.06
6.97
6.96
6.48
6.47
6.47
6.47
6.47
6.37
6.36
6.36
6.34
6.33
5.26
5.25
4.89
4.87
4.41
4.39
4.26
4.24
4.22
4.20
2.43

Br
N
H
N
Bn
O
H
Ph
N
H
O
O
Br

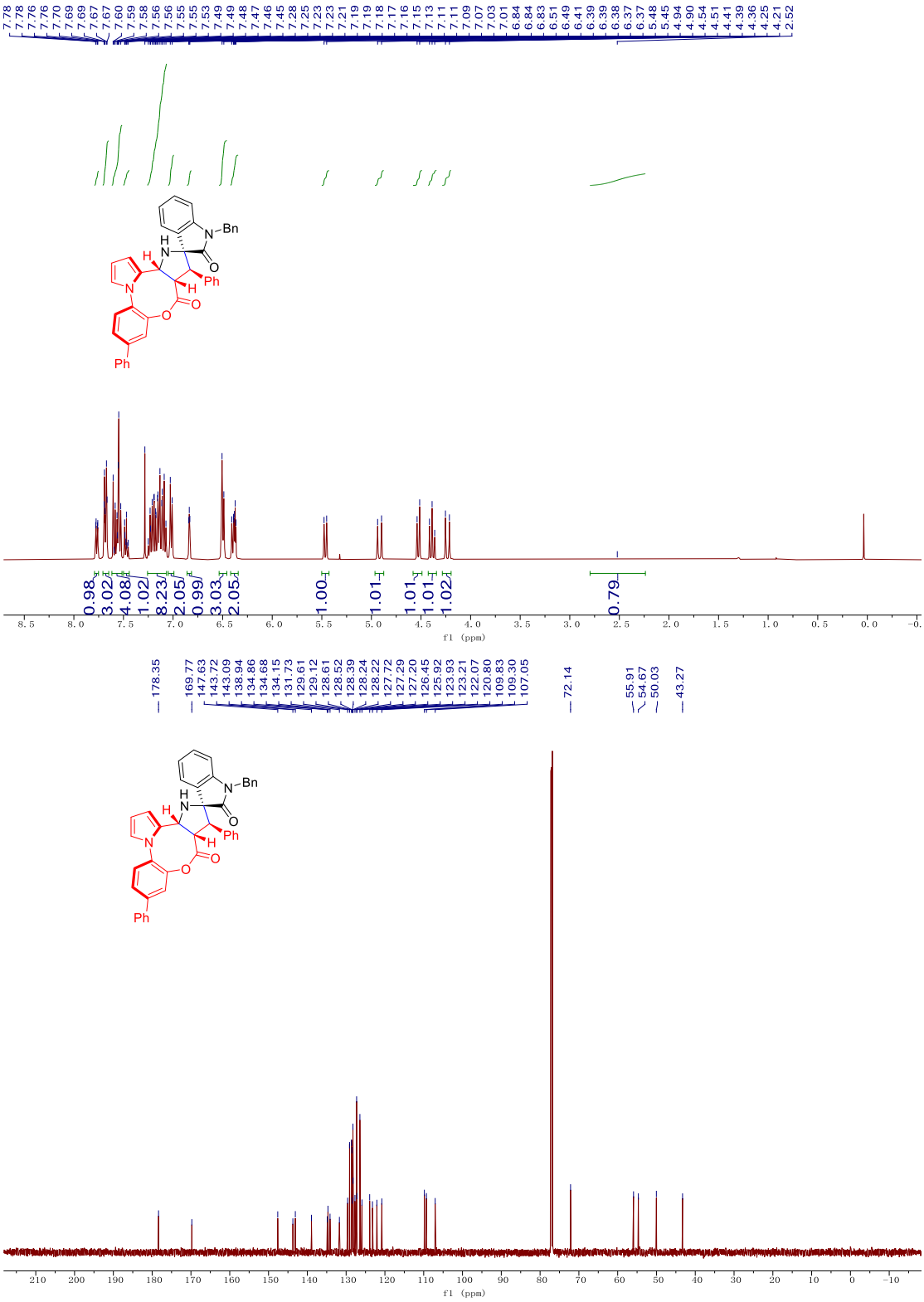

1.02
0.99
0.94
0.95
1.06
5.17
2.03
2.03
3.04
1.03
0.94
1.00
1.05
1.04
2.06
0.86
f1 (ppm)


178.44
168.69
148.31
143.06
136.18
134.73
133.63
131.20
130.45
129.74
128.66
128.62
128.15
127.92
127.84
127.28
126.43
125.99
124.02
123.98
123.28
112.44
109.39
108.03
102.24
71.86
55.28
54.66
50.21
43.32

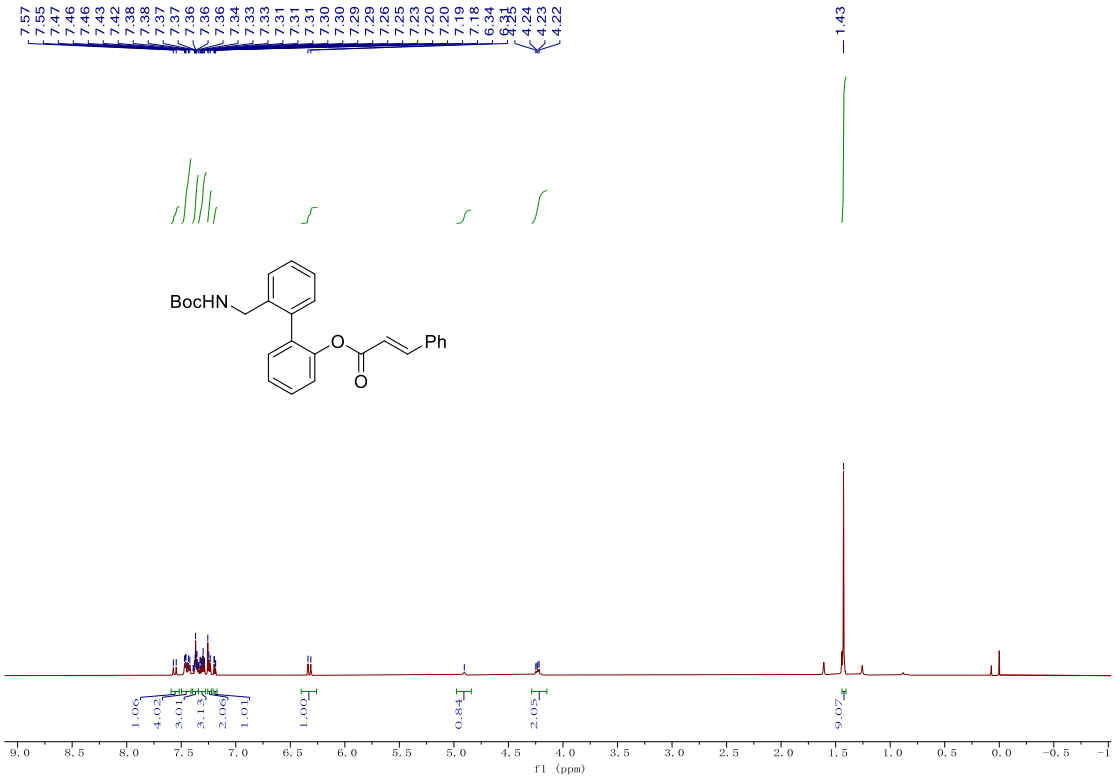

Br
N
H
N
Bn
O
H
Ph
N
H
O
O
Br

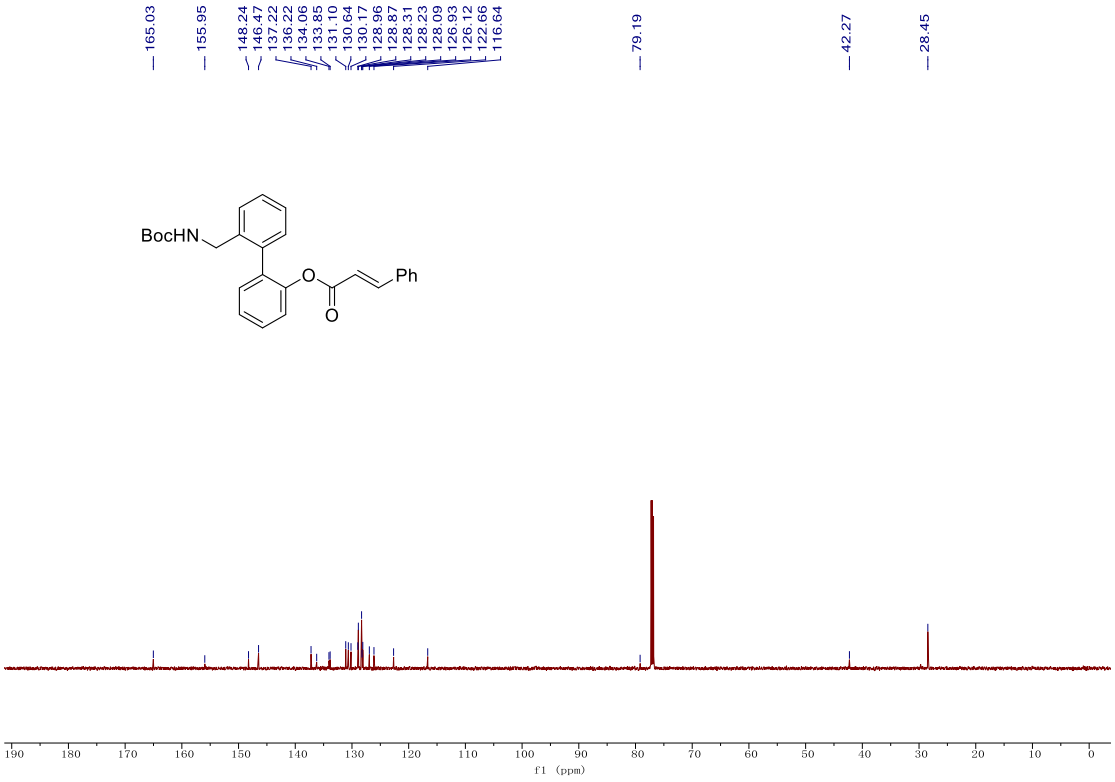

f1 (ppm)

10

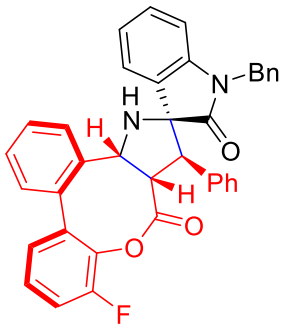

7.78 7.78 7.76 7.76 7.70 7.69 7.69 7.67 7.67 7.60 7.59 7.58 7.56 7.56 7.55 7.55 7.53 7.49 7.49 7.48 7.47 7.46 7.45 7.28 7.25 7.23 7.23 7.21 7.19 7.19 7.18 7.17 7.16 7.15 7.13 7.11 7.11 7.09 7.07 7.03 7.01 6.84 6.84 6.83 6.51 6.49 6.41 6.39 6.39 6.38 6.37 6.37 5.48 5.45 4.94 4.90 4.54 4.51 4.41 4.39 4.36 4.25 4.21 2.52
N-Bn
H
N
O
H
Ph
N
H
O
O
Ph
0.98 3.02 4.08 1.02 8.23 2.05 0.99 3.03 2.05 1.00 1.01 1.01 1.01 1.02 0.79
f1 (ppm)
178.35 169.77 147.63 143.72 143.09 138.94 134.86 134.68 134.15 131.73 129.61 129.12 128.61 128.52 128.39 128.24 128.22 127.72 127.29 127.20 126.45 125.92 123.93 123.21 122.07 120.80 109.83 109.30 107.05 72.14 55.91 54.67 50.03 43.27
f1 (ppm)

11

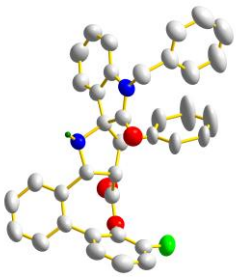

7.57
7.55
7.47
7.46
7.46
7.43
7.42
7.38
7.38
7.37
7.37
7.36
7.36
7.36
7.34
7.33
7.33
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.26
7.25
7.23
7.20
7.20
7.19
7.18
6.34
6.31
4.24
4.23
4.22
1.43
BocHN
O
O
Ph
1.06
4.02
3.01
3.13
2.06
1.01
1.00
0.84
2.05
9.07
f1 (ppm)


165.03
155.95
148.24
146.47
137.22
136.22
134.06
133.85
131.10
130.64
130.17
128.96
128.87
128.31
128.23
128.09
126.93
126.12
122.66
116.64
79.19
42.27
28.45
BocHN
O
O
Ph
f1 (ppm)

8. X-ray crystal structure



4am

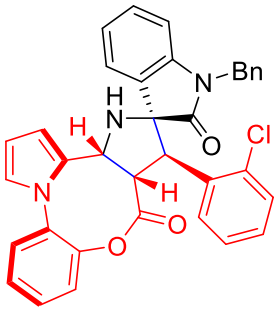


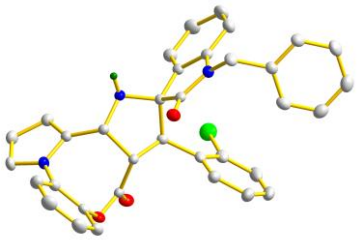
X-ray crystal structure of **4am**

CCDC: 2234268

Table 1 Crystal data and structure refinement for 1.

Identification code	1
Empirical formula	$C_{41}H_{35}FN_2O_5$
Formula weight	654.71
Temperature/K	302.0
Crystal system	triclinic
Space group	P1
a/Å	9.0844(3)
b/Å	10.3859(4)
c/Å	18.7463(6)
α/°	75.426(2)
β/°	89.765(2)
γ/°	88.695(2)
Volume/Å^3	1711.35(10)
Z	2
ρ_{calc}g/cm^3	1.271
μ/mm^{-1}	0.710
F(000)	688.0
Crystal size/mm^3	0.27 × 0.24 × 0.22
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.87 to 125.132
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -21 ≤ l ≤ 21
Reflections collected	15849
Independent reflections	9711 [R_{int} = 0.0423, R_{sigma} = 0.0589]
Data/restraints/parameters	9711/90/898
Goodness-of-fit on F^2	1.094
Final R indexes [I>=2σ (I)]	R_1 = 0.0635, wR_2 = 0.1510
Final R indexes [all data]	R_1 = 0.0800, wR_2 = 0.1708
Largest diff. peak/hole / e Å^{-3}	0.18/-0.20
Flack parameter	0.02(10)





6ac (4 d, 80% yield
> 20:1 dr, 91% ee)

X-ray crystal structure of **6ac**
CCDC: 2321325

Table 1 Crystal data and structure refinement for 123.

Identification code	123
Empirical formula	$C_{36}H_{28}Cl_3N_3O_3$
Formula weight	656.96
Temperature/K	120.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.2162(3)
b/Å	16.7001(4)
c/Å	19.1032(5)
α/°	90
β/°	105.0240(10)
γ/°	90
Volume/Å^3	3147.82(15)
Z	4
ρ_{calc}g/cm^3	1.386
μ/mm^{-1}	0.333
F(000)	1360.0
Crystal size/mm^3	0.33 × 0.3 × 0.23
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.796 to 54.942
Index ranges	-13 ≤ h ≤ 13, -21 ≤ k ≤ 21, -24 ≤ l ≤ 23
Reflections collected	25485
Independent reflections	13422 [R_{int} = 0.0218, R_{sigma} = 0.0365]
Data/restraints/parameters	13422/1/819
Goodness-of-fit on F^2	1.001
Final R indexes [I>=2σ (I)]	R_1 = 0.0359, wR_2 = 0.0850
Final R indexes [all data]	R_1 = 0.0399, wR_2 = 0.0876
Largest diff. peak/hole / e Å^{-3}	0.32/-0.38
Flack parameter	0.011(13)