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Supporting Information

Organocatalytic Asymmetric Friedel-Crafts Alkylation/ Hemiketalization/Lactonization Cascade Reactions: Highly Enantioselective Synthesis of Furo[2,3-*b*]benzofuranones

Kunhua Xu,[a] Wenming Chen,[b] Xu Chen,[a] Biao Wang,[a] Jun Huang*[c] and Xu Tian*[a]

[a]*Key Laboratory of Molecular Target & Clinical Pharmacologyand the State Key Laboratory of Respiratory Disease, School of Pharmaceutical Sciences & the Fifth Affiliated Hospital, Guangzhou Medical University, Guangzhou, Guangdong 511436, P. R. China. Email: xtian@gzhmu.edu.cn*

[b]*Department of Pharmaceutical Production Center,The First Affiliated Hospital of Hunan University of Chinese Medicine, Changsha, Hunan 410007, P. R. China.*

[c]*Sino-French Hoffmann Institute, Guangdong Provincial Key Laboratory of Allergy & Clinical Immunology, The second Affiliated Hospital, Guangzhou Medical University, Guangzhou 511436, China*
E-mail: 2007990004@gzhmu.edu.cn.

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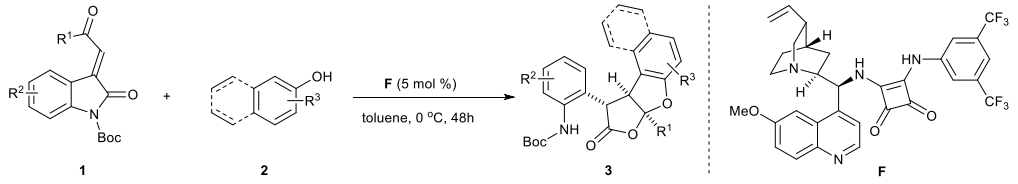
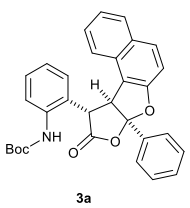
1. General information

Catalytic reactions were carried out in Sealing tubes under an air atmosphere with dry toluene. All the 3-ylidene oxindole (**1**) [1] and 2-naphthol (**2**) [2] have been synthesized following procedures reported in the literature. Other chemical reagent was obtained from commercial sources and was used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded on JEOL at 400 MHz for ^{1}H or at 100 MHz for ^{13}C, respectively. The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvent ($CDCl_3$ 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR). Mass spectra and high-resolution mass spectra were measured on a Thermo-DFS mass spectrometer. Optical rotation data were examined in $CHCl_3$ solution at 25 °C and λ = 589 nm. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used, Silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) were used for general chromatography, using UV light as the visualizing agent. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

2. General Procedure for the Asymmetric Synthesis of 3.



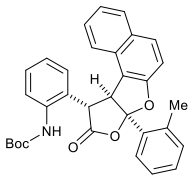
The reaction was carried out with 3-ylideneoxidole **1** (0.1 mmol), 2-naphthol **2** (0.15 mmol) and catalyst **F** (3.2 mg, 5 mol %) in toluene (0.4 mL) at 0 °C for 48 h. The reaction mixture was direct purified by flash column chromatography on a silica gel (Petroleum Ether/EtOAc) to afford the desired product **3**.


3a

***tert*-butyl (2-((7a*R*,10*S*,10a*S*)-9-oxo-7a-phenyl-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3a)**

The reaction was carried out following the general procedure to furnish the crude product. The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 40:1) in

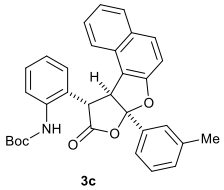
85% yield as white solid. The enantiomeric excess was determined to be 90% ee by HPLC analysis on a Daicel Chiralpak IA column: 95/5 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 215nm, t_{minor} = 12.5 min, t_{major} = 15.0 min; $[\alpha]_D^{25}$ = -155.0 (*c* = 0.55, $CHCl_3$), m.p. 90 – 92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.54 (br s, 1H), 7.52 – 7.48 (m, 3H), 7.46 – 7.39 (m, 2H), 7.37 – 7.32 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.0 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.90 (d, *J* = 2.4 Hz, 1H), 4.69 (d, *J* = 2.4 Hz, 1H), 1.43 (s, 9H) ppm. ^{13}C NMR (100 MHz,$CDCl_3$) δ 175.8, 154.9, 153.8, 137.8, 137.3, 131.8, 130.7, 130.2, 129.6, 129.5, 129.2, 129.1, 128.4, 126.3, 125.5, 125.2, 124.5, 121.9, 118.4, 117.7, 112.3, 80.8, 55.5, 48.5, 28.4 ppm. HR-MS (ESI) *m/z* calcd for $C_{31}H_{27}NO_5$ $[M+Na]^+$ 516.17814, found 516.17844.



3b

tert-butyl (2-((7a*R*,10*S*,10a*S*)-9-oxo-7a-(*o*-tolyl)-7a,9,10,10a-tetrahydrofuro[2,3-*b*] naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3b)

The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 40:1) in 63% yield as white solid. The enantiomeric excess was determined to be 90% ee by HPLC analysis on a Daicel Chiralpak AD column: 80/20 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 215 nm, t_{major} = 6.2 min, t_{minor} = 7.4 min; $[\alpha]_D^{25}$ = -76.0 (*c* = 0.37, $CHCl_3$), m.p. 88 – 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.65 (br s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.46 – 7.40 (m, 2H), 7.36 – 7.30 (m, 4H), 7.28 – 7.24 (m, 2H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 4.93 (s, 1H), 4.76 (d, *J* = 1.2 Hz, 1H), 2.29 (s, 3H), 1.44 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 154.4, 153.9, 137.3, 136.3, 134.9, 132.6, 132.2, 130.8, 130.4, 129.6, 129.4, 129.0, 128.4, 127.0, 126.6, 126.3, 126.1, 125.8, 125.0, 124.5, 121.8, 118.4, 112.5, 80.8, 54.1, 47.5, 28.4, 20.5 ppm. HR-MS (ESI) *m/z* calcd for $C_{32}H_{29}NO_5$ $[M+Na]^+$ 530.19379, found 530.19358.

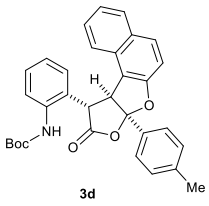


3c

tert-butyl (2-((7a*R*,10*S*,10a*S*)-9-oxo-7a-(*m*-tolyl)-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3c)

The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 40:1) in 61% yield as white solid. The enantiomeric excess was determined to be

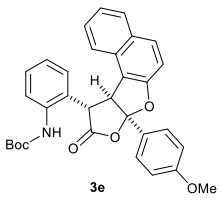
88% ee by HPLC analysis on a Daicel Chiralpak AD column: 80/20 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 254 nm, t_{minor} = 4.9 min, t_{major} = 6.1 min, $[\alpha]_D^{25}$ = -118.0 (*c* = 0.55, $CHCl_3$), m.p. 85 – 87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.91 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.54 (br s, 1H), 7.47 – 7.42 (m, 2H), 7.40 – 7.36 (m, 4H), 7.35 – 7.30 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 4.88 (d, *J* = 2.4 Hz, 1H), 4.67 (d, *J* = 2.8 Hz, 1H), 2.40 (s, 3H), 1.42 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 154.9, 153.8, 139.0, 137.7, 137.3, 131.7, 130.9, 130.7, 129.6, 129.5, 129.1, 129.0, 128.4, 126.4, 126.1, 125.2, 124.5, 122.6, 121.9, 118.4, 117.8, 112.3, 80.8, 55.4, 48.4, 28.4, 21.6 ppm. HR-MS (ESI) *m/z* calcd for $C_{32}H_{29}NO_5$ $[M+Na]^+$ 530.19379, found 530.19365.



3d

tert-butyl (2-((7a*R*,10*S*,10a*S*)-9-oxo-7a-(*p*-tolyl)-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3d)

The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 40:1) in 63% yield as white solid. The enantiomeric excess was determined to be 86% ee by HPLC analysis on a Daicel Chiralpak AD column: 80/20 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 215 nm, t_{minor} = 8.5 min, t_{major} = 9.7 min, $[\alpha]_D^{25}$ = -96.0 (*c* = 0.53, $CHCl_3$), m.p. 126 – 128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.55 (br s, 1H), 7.50 – 7.47 (m, 2H), 7.45 – 7.38 (m, 2H), 7.37 – 7.33 (m, 1H), 7.30 (t, *J* = 9.2 Hz, 3H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.01 (td, *J* = 8.0, 0.8 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 4.87 (d, *J* = 2.8 Hz, 1H), 4.67 (d, *J* = 2.8 Hz, 1H), 2.44 (s, 3H), 1.42 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 154.9, 153.8, 140.2, 137.2, 134.9, 131.7, 130.6, 129.72, 129.65, 129.5, 129.1, 128.4, 126.4, 125.4, 125.2, 124.4, 121.9, 118.5, 118.0, 112.3, 80.7, 55.4, 48.5, 28.3, 21.4 ppm. HR-MS (ESI) *m/z* calcd for $C_{32}H_{29}NO_5$ $[M+Na]^+$ 530.19379, found 530.19358.

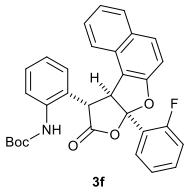


3e

tert-butyl (2-((7a*R*,10*S*,10a*S*)-7a-(4-methoxyphenyl)-9-oxo-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3e)

The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 20:1) in 73% yield as white solid. The enantiomeric excess was determined to be

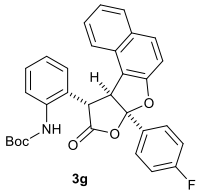
93% ee by HPLC analysis on a Daicel Chiralpak AD column: 80/20 hexane/i-PrOH, flow rate 1.00 mL/min, λ = 215 nm, t_{minor} = 11.0 min, t_{major} = 14.7 min; $[\alpha]_D^{25}$ = -85.0 (*c* = 0.5, $CHCl_3$), m.p. 130 – 132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.57 (br s, 1H), 7.53 (dd, *J* = 6.4, 2.4 Hz, 2H), 7.47 – 7.39 (m, 2H), 7.37 – 7.33 (m, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.03 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.99 (dd, *J* = 6.8, 2.0 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 4.87 (d, *J* = 2.8 Hz, 1H), 4.68 (d, *J* = 2.4Hz, 1H), 3.87 (s, 3H), 1.43 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 160.9, 154.8, 153.9, 137.2, 131.7, 130.6, 129.8, 129.6, 129.5, 129.1, 128.3, 127.0, 126.4, 125.3, 124.4, 121.9, 118.4, 118.0, 114.3, 112.3, 80.8, 55.6, 55.3, 48.5, 28.3 ppm. HR-MS (ESI) *m/z* calcd for $C_{32}H_{29}NO_6$ $[M+Na]^+$ 546.18871, found 546.18845.



3f

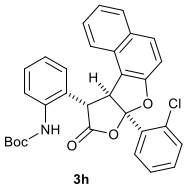
tert-butyl (2-((7a*R*,10*S*,10a*S*)-7a-(2-fluorophenyl)-9-oxo-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3f)

The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 40:1) in 80% yield as white solid. The enantiomeric excess was determined to be 90% ee by HPLC analysis on a Daicel Chiralpak IA column: 90/10 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 254 nm, t_{minor} = 7.7 min, t_{major} = 9.1 min; $[\alpha]_D^{25}$ = -74.0 (*c* = 0.52, $CHCl_3$), m.p. 93 – 95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.74 (td, *J* = 7.6, 1.6 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.46 – 7.39 (m, 2H), 7.36 – 7.32 (m, 1H), 7.31 – 7.28 (m, 2H), 7.24 – 7.21 (m, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.09 (s, 1H), 4.71 (d, *J* = 2.8 Hz, 1H), 1.43 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz,) δ 175.3, 160.3 (d, J_{CF} = 250.7 Hz), 154.4, 153.8, 137.3, 132.4 (d, J_{CF} = 8.5 Hz), 131.7, 130.7, 129.6, 129.5, 129.1, 128.3, 127.6 (d, J_{CF} = 2.5 Hz), 125.8, 125.3, 125.1, 125.0, 124.6 (d, J_{CF} = 3.9 Hz), 124.4, 121.9, 118.5, 116.9 (d, J_{CF} = 20.7 Hz), 115.5 (d, J_{CF} = 1.7 Hz), 112.2, 80.8, 54.2, 47.7, 28.4 ppm.^{19}F NMR (376 MHz, $CDCl_3$) δ -112.431 ppm. HR-MS (ESI) *m/z* calcd for $C_{31}H_{26}FNO_5$ $[M+Na]^+$ 534.16872, found 534.16898.



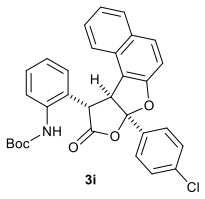
tert-butyl (2-((7a*R*,10*S*,10a*S*)-7a-(4-fluorophenyl)-9-oxo-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3g)

The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 40:1) in 84% yield as white solid. The enantiomeric excess was determined to be 91% ee by HPLC analysis on a Daicel Chiralpak IA column: 80/20 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 215 nm, t_{minor} = 12.8 min, t_{major} = 15.6 min; $[\alpha]_D^{25}$ = -129.0 (*c* = 0.5, $CHCl_3$), m.p. 88 – 89 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.49 (br s, 1H), 7.48 – 7.41 (m, 2H), 7.39 – 7.35 (m, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.01 (td, *J* = 7.6, 0.8 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 4.84 (d, *J* = 2.8 Hz, 1H), 4.66 (d, *J* = 2.8 Hz, 1H), 1.40 (s, 9H) ppm. ^{13}C NMR (100 MHz,$CDCl_3$) δ 175.7, 163.8 (d, J_{CF} = 250.0 Hz), 154.7, 153.9, 137.3, 133.9 (d, J_{CF} = 3.3 Hz), 131.7, 130.7, 129.6, 129.4 (d, J_{CF} = 23.4 Hz), 128.2, 127.7 (d, J_{CF} = 8.6 Hz), 126.2, 125.3, 124.6, 121.9, 118.3, 117.3, 116.3, 116.1, 112.2, 80.8, 55.5, 48.4, 28.4 ppm. ^{19}F NMR (376 MHz,$CDCl_3$) δ -110.712 ppm. HR-MS (ESI) *m/z* calcd for $C_{31}H_{26}FNO_5$ $[M+Na]^+$ 534.16872, found 534.16845.



tert-butyl (2-((7a*R*,10*S*,10a*S*)-7a-(2-chlorophenyl)-9-oxo-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3h)

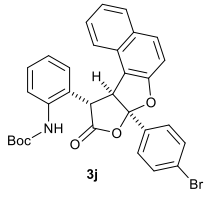
The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 40:1) in 64% yield as white solid. The enantiomeric excess was determined to be 91% ee by HPLC analysis on a Daicel Chiralpak IC column: 95/5 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 254 nm, t_{major} = 8.5 min, t_{minor} = 9.3 min; $[\alpha]_D^{25}$ = -59.0 (*c* = 0.53, $CHCl_3$), m.p. 97 – 98 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 2H), 7.83 – 7.79 (m, 2H), 7.63 (br s, 1H), 7.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.45 – 7.41 (m, 1H), 7.40 – 7.29 (m, 4H), 6.90 (t, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 5.26 (d, *J* = 1.6 Hz, 1H), 4.77 (d, *J* = 2.0 Hz, 1H), 1.45 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 154.8, 153.8, 137.3, 134.2, 132.9, 131.8, 131.71, 131.68, 130.8, 129.6, 129.5, 129.1, 128.4, 128.3, 127.3, 125.7, 125.0, 124.4, 121.9, 118.5, 116.9, 112.4, 80.8, 53.4, 47.2, 28.4 ppm. HR-MS (ESI) *m/z* calcd for $C_{31}H_{26}ClNO_5$ $[M+Na]^+$ 550.13917, found 550.13946



3i

***tert*-butyl (2-((7a*R*,10*S*,10a*S*)-7a-(4-chlorophenyl)-9-oxo-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3i)**

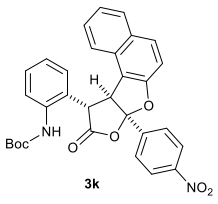
The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 40:1) in 76% yield as white solid. The enantiomeric excess was determined to be 93% ee by HPLC analysis on a Daicel Chiralpak AD column: 80/20 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 215 nm, t_{minor} = 8.6 min, t_{major} = 9.9 min; $[\alpha]_D^{25}$ = -57.0 (*c* = 0.5, $CHCl_3$), m.p. 92 – 94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.47 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.41 – 7.35 (m, 4H), 7.34 – 7.26 (m, 2H), 7.23 (d, *J* = 9.2 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 4.78 (d, *J* = 2.0 Hz, 1H), 4.59 (d, *J* = 2.8 Hz, 1H), 1.34 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 153.5, 152.6, 136.0, 135.23, 135.16, 130.7, 129.5, 128.3, 128.2, 127.3, 125.9, 125.0, 124.2, 123.4, 120.7, 117.0, 116.0, 111.0, 79.7, 54.2, 47.2, 27.2 ppm. HR-MS (ESI) *m/z* calcd for $C_{31}H_{26}ClNO_5$ $[M+Na]^+$ 550.13917, found 550.13931.



3j

***tert*-butyl (2-((7a*R*,10*S*,10a*S*)-7a-(4-bromophenyl)-9-oxo-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3j)**

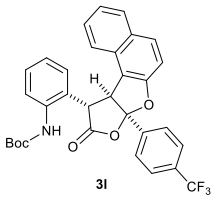
The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 40:1) in 88% yield as white solid. The enantiomeric excess was determined to be 92% ee by HPLC analysis on a Daicel Chiralpak IA column: 95/5 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 215 nm, t_{minor} = 20.7 min, t_{major} = 22.1 min; $[\alpha]_D^{25}$ = -33.0 (*c* = 0.5, $CHCl_3$), m.p. 90 – 92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.62 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.49 – 7.45 (m, 3H), 7.44 – 7.35 (m, 3H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.05 (td, *J* = 7.6, 0.8 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 4.84 (d, *J* = 2.8 Hz, 1H), 4.66 (d, *J* = 2.8 Hz, 1H), 1.41 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 154.7, 153.8, 137.2, 137.0, 132.3, 131.9, 130.7, 129.6, 129.5, 129.3, 128.5, 127.3, 126.2, 125.5, 124.6, 121.9, 118.3, 117.2, 112.2, 80.9, 55.4, 48.5, 28.3 ppm. HR-MS (ESI) *m/z* calcd for $C_{31}H_{26}BrNO_5$ $[M+Na]^+$ 594.08866, found 594.08910.



3k

***tert*-butyl (2-((7a*R*,10*S*,10a*S*)-7a-(4-nitrophenyl)-9-oxo-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3k)**

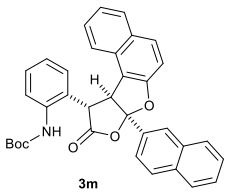
The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 30:1) in 91% yield as white solid. The enantiomeric excess was determined to be 94% ee by HPLC analysis on a Daicel Chiralpak IA column: 90/10 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 215 nm, t_{minor} = 20.1 min, t_{major} = 23.9 min; $[\alpha]_D^{25}$ = -44.0 (*c* = 0.5, $CHCl_3$), m.p. 105 – 106 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.33 (dd, *J* = 10.8, 2.4 Hz, 2H), 7.96 – 7.93 (m, 2H), 7.82 – 7.79 (m, 3H), 7.48 – 7.43 (m, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 9.2 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 4.88 (d, *J* = 2.8 Hz, 1H), 4.67 (d, *J* = 3.2 Hz, 1H), 1.41 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 154.6, 153.8, 149.1, 144.5, 137.2, 132.2, 130.8, 129.6, 129.53, 129.49, 128.7, 126.9, 125.6, 124.8, 124.3, 121.9, 118.0, 116.3, 112.1, 81.0, 55.6, 48.6, 28.3 ppm. HR-MS (ESI) *m/z* calcd for $C_{31}H_{26}N_2O_7$ $[M+Na]^+$ 561.16322, found 561.15395.



3l

***tert*-butyl (2-((7a*R*,10*S*,10a*S*)-9-oxo-7a-(4-(trifluoromethyl)phenyl)-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3l)**

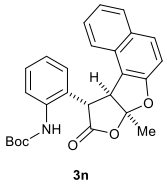
The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 30:1) in 71% yield as white solid. The enantiomeric excess was determined to be 92% ee by HPLC analysis on a Daicel Chiralpak AD column: 80/20 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 254 nm, t_{minor} = 6.9 min, t_{major} = 12.7 min; $[\alpha]_D^{25}$ = -125.0 (*c* = 0.5, $CHCl_3$), m.p. 140 – 141 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.2 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.67 (dd, *J* = 11.2, 8.8 Hz, 4H), 7.40 – 7.28 (m, 4H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 4.80 (d, *J* = 2.4 Hz, 1H), 4.59 (d, *J* = 2.8 Hz, 1H), 1.33 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 154.7, 153.8, 141.7, 137.2, 132.4 (q, *J* = 32.7 Hz), 132.0, 130.7, 129.5, 129.4, 128.6, 126.1, 125.5, 124.7, 123.8 (q, *J* = 272.5 Hz), 121.9, 118.1, 116.8, 112.1, 80.9, 55.5, 48.5, 28.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.669 ppm. HR-MS (ESI) *m/z* calcd for $C_{32}H_{26}F_3NO_5$ $[M+Na]^+$ 584.16553, found 584.16492.



3m

tert-butyl (2-((7a*R*,10*S*,10a*S*)-7a-(naphthalen-2-yl)-9-oxo-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3m)

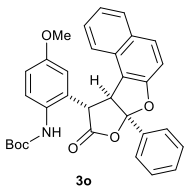
The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 30:1) in 92% yield as white solid. The enantiomeric excess was determined to be 90% ee by HPLC analysis on a Daicel Chiralpak AD column: 80/20 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 215 nm, t_{major}= 8.7 min, t_{minor} = 14.4 min; $[\alpha]_D^{25}$ = -89.0 (*c* = 0.56, $CHCl_3$), m.p. 100 – 102 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.99 – 7.89 (m, 5H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.52 (m, 4H), 7.49 – 7.41 (m, 2H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.26 – 7.25 (m, 2H), 6.89 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 5.00 (d, *J* = 2.4 Hz, 1H), 4.73 (d, *J* = 2.4 Hz, 1H), 1.42 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 154.9, 153.9, 137.2, 134.9, 134.0, 132.9, 131.8, 130.7, 129.7, 129.5, 129.4, 129.1, 128.9, 128.4, 127.9, 127.5, 127.1, 126.3, 125.4, 125.1, 124.5, 122.6, 122.0, 118.5, 117.9, 112.3, 80.8, 55.4, 48.5, 28.3 ppm. HR-MS (ESI) *m/z* calcd for $C_{35}H_{29}NO_5$ $[M+Na]^+$ 566.19379, found 566.19430.



3n

tert-butyl (2-((7a*S*,10*S*,10a*S*)-7a-methyl-9-oxo-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3n)

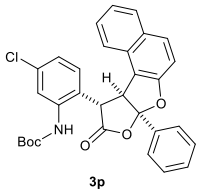
The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 30:1) in 60% yield as white solid. The enantiomeric excess was determined to be 83% ee by HPLC analysis on a Daicel Chiralpak AD column: 95/5 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 254 nm, t_{minor} = 11.1 min, t_{major} = 21.3 min; $[\alpha]_D^{25}$ = -118.0 (*c* = 0.5, $CHCl_3$), m.p. 150 – 152 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 3H), 7.47 – 7.35 (m, 5H), 7.29 (d, *J* =7.6 Hz, 1H), 7.20 (d, *J* = 8.8 Hz, 2H), 4.64 (d, *J* = 3.6 Hz, 1H), 4.46 (d, *J* = 3.6 Hz, 1H), 2.12 (s, 3H), 1.43 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 154.4, 154.0, 137.2, 131.4, 130.4, 129.7, 129.38, 129.36, 128.2, 126.6, 125.6, 124.3, 122.1, 119.0, 117.9, 112.2, 80.9, 52.2, 49.6, 28.4, 24.8 ppm. HR-MS (ESI) *m/z* calcd for $C_{26}H_{25}NO_5$ $[M+Na]^+$ 454.16249, found 454.16281.



3o

tert-butyl (4-methoxy-2-((7a*R*,10*S*,10a*S*)-9-oxo-7a-phenyl-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3o)

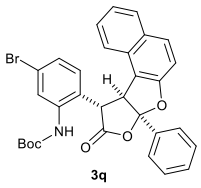
The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 20:1) in 90% yield as white solid. The enantiomeric excess was determined to be 90% ee by HPLC analysis on a Daicel Chiralpak AD column: 80/20 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 215 nm, t_{major} = 9.1 min, t_{minor} = 11.7 min; $[\alpha]_D^{25}$ = -172.0 (*c* = 0.5, $CHCl_3$), m.p. 103 – 105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.67 – 7.65 (m, 2H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.52 – 7.49 (m, 3H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.32 – 7.30 (m, 2H), 7.09 (br s, 1H), 6.87 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.25 (d, *J* = 2.4 Hz, 1H), 4.85 (d, *J* = 1.6 Hz, 1H), 4.69 (d, *J* = 2.4 Hz, 1H), 3.33 (s, 3H), 1.39 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 157.5, 154.8, 154.4, 138.1, 131.8, 130.7, 130.2, 129.7, 129.6, 129.5, 129.2, 128.7, 128.4, 125.7, 124.5, 122.0, 118.3, 117.5, 115.6, 112.2, 110.9, 80.5, 56.0, 55.1, 48.5, 28.4 ppm. HR-MS (ESI) *m/z*calcd for $C_{32}H_{29}NO_6$ $[M+Na]^+$ 546.18871, found 546.18895.



3p

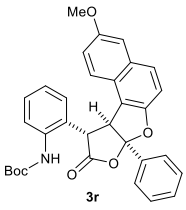
tert-butyl (5-chloro-2-((7a*R*,10*S*,10a*S*)-9-oxo-7a-phenyl-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3p)

The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 40:1) in 84% yield as white solid. The enantiomeric excess was determined to be 93% ee by HPLC analysis on a Daicel Chiralpak AD column: 80/20 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 254 nm, t_{minor} = 5.1 min, t_{major} = 5.5 min; $[\alpha]_D^{25}$ = -86.0 (*c* = 0.5, $CHCl_3$), m.p. 113 – 114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.92 (m, 3H), 7.73 (br s, 1H), 7.60 – 7.58 (m, 2H), 7.53 – 7.49 (m, 3H), 7.48 – 7.41 (m, 2H), 7.33 (d, *J* = 9.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.95 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.67 (d, *J* = 8.8 Hz, 1H), 4.86 (d, *J* = 2.4 Hz, 1H), 4.61 (d, *J* = 2.8 Hz, 1H), 1.44 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 154.9, 153.4, 138.6, 137.6, 134.9, 131.9, 130.7, 130.3, 129.6, 129.5, 129.2, 128.5, 127.2, 125.5, 125.3, 124.9, 124.6, 121.7, 118.0, 117.8, 112.3, 81.3, 55.4, 48.0, 28.3 ppm. HR-MS (ESI) *m/z* calcd for $C_{31}H_{26}ClNO_5$ $[M+Na]^+$ 550.13917, found 550.13945.



tert-butyl (5-bromo-2-((7a*R*,10*S*,10a*S*)-9-oxo-7a-phenyl-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3q)

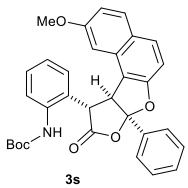
1 mmol scale reaction: The reaction was carried out with 3-ylideneoxidole **1q** (1 mmol, 427mg), 2-naphthol **2q** (1.5 mmol, 216mg) and catalyst **F** (32 mg, 5 mol %) in toluene (4 mL) at 0 ºC for 48 h following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 40:1) in 89% yield as white solid. The enantiomeric excess was determined to be 94% ee by HPLC analysis on a Daicel Chiralpak AD column: 80/20 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 254 nm, t_{minor} = 5.3 min, t_{major} = 5.8 min; $[\alpha]_D^{25}$ = -67.0 (*c* = 0.5, $CHCl_3$), m.p. 120 – 122 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.94 – 7.92 (m, 2H), 7.72 (br s, 1H), 7.60 – 7.58 (m, 2H), 7.52 – 7.46 (m, 4H), 7.45 – 7.41 (m, 1H), 7.33 (d, *J* = 9.2 Hz, 1H), 7.20 (d, *J*= 8.0 Hz, 1H), 7.10 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.61 (d, *J* = 8.8 Hz, 1H), 4.85 (d, *J* = 2.0 Hz, 1H), 4.60 (d, *J* = 2.4 Hz, 1H), 1.44 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 154.8, 153.3, 138.7, 137.4, 131.9, 130.7, 130.3, 129.6, 129.5, 129.2, 128.5, 128.0, 127.8, 127.4, 125.4, 124.6, 122.8, 121.7, 117.9, 117.8, 112.3, 81.3, 55.2, 48.0, 28.3 ppm. HR-MS (ESI) *m/z* calcd for $C_{31}H_{26}BrNO_5$ $[M+Na]^+$ 594.08866, found 594.08910.



tert-butyl (2-((7a*R*,10*S*,10a*S*)-3-methoxy-9-oxo-7a-phenyl-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3r)

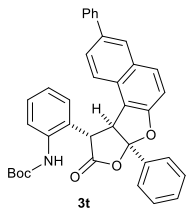
The reaction was carried out following the general procedure, but running the reaction over 72 hours, to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 20:1) in 62% yield as white solid. The enantiomeric excess was determined to be 90% ee by HPLC analysis on a Daicel Chiralpak AD column: 95/5 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 215 nm, t_{minor} = 31.3 min, t_{major} = 35.0 min; $[\alpha]_D^{25}$ = -156.0 (c = 0.5, $CHCl_3$), m.p. 95 – 96 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 9.2 Hz, 2H), 7.61 – 7.59 (m, 2H), 7.53 (br s, 1H), 7.51 – 7.48 (m, 3H), 7.36 – 7.32 (m, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.24 (t, *J* = 1.2 Hz, 1H), 7.14 (d, *J* = 1.2 Hz, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 4.85 (d, *J* = 2.8 Hz, 1H), 4.64 (d, *J* = 2.8 Hz, 1H), 3.91 (s, 3H), 1.43 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 156.7, 153.9, 153.3, 137.9, 137.3, 131.8, 130.2, 130.1, 129.2, 129.1, 126.4, 125.6, 125.2, 124.9, 123.3, 112.6,

107.9, 80.8, 55.6, 55.5, 48.6, 28.4 ppm. HR-MS (ESI) *m/z* calcd for $C_{32}H_{29}NO_6$ $[M+Na]^+$ 546.18871, found 546.18859.



***tert*-butyl (2-((7a*R*,10*S*,10a*S*)-2-methoxy-9-oxo-7a-phenyl-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3s)**

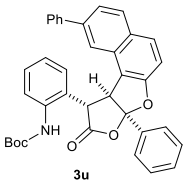
The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 20:1) in 67% yield as white solid. The enantiomeric excess was determined to be 95% eeby HPLC analysis on a Daicel Chiralpak IA column: 95/5 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 215 nm, t_{minor} = 12.0 min, t_{major} = 15.8 min; $[\alpha]_D^{25}$ = -237.0 (*c* = 0.5, $CHCl_3$), m.p. 85 – 87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 9.2 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.51 – 7.48 (m, 3H), 7.34 (td, *J* = 8.0, 1.2 Hz, 1H), 7.24 (br s, 1H), 7.16 (d, *J* = 8.8 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.01 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.33 (d, *J* = 2.4 Hz, 1H), 4.80 (d, *J* = 3.2 Hz, 1H), 4.64 (d, *J* = 3.6 Hz, 1H), 3.54 (s, 3H), 1.39 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 159.6, 155.6, 153.8, 138.1, 137.1, 131.2, 131.0, 130.2, 129.11, 129.10, 126.9, 126.6, 125.9, 125.5, 125.4, 117.9, 117.6, 117.5, 109.4, 99.8, 80.9, 55.5, 55.2, 48.4, 28.3 ppm. HR-MS (ESI) *m/z* calcd for $C_{32}H_{29}NO_6$ $[M+Na]^+$ 546.18871, found 546.18866.



***tert*-butyl (2-((7a*R*,10*S*,10a*S*)-9-oxo-3,7a-diphenyl-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3t)**

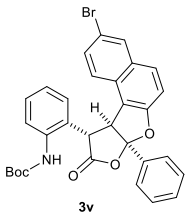
The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 40:1) in 67% yield as white solid. The enantiomeric excess was determined to be 91% ee by HPLC analysis on a Daicel Chiralpak AD column: 80/20 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 254 nm, t_{minor} = 8.5 min, t_{major} = 9.4 min; $[\alpha]_D^{25}$ = -198.0 (*c* = 0.5, $CHCl_3$), m.p. 120 – 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 1.6 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.73 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.68 – 7.66 (m, 2H), 7.64 – 7.61 (m, 2H), 7.57 (br s, 1H), 7.52 – 7.50 (m, 3H), 7.49 – 7.46 (m, 2H), 7.40 – 7.34 (m, 3H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 4.92 (d, *J* = 2.4 Hz, 1H), 4.71 (d, *J* = 2.8 Hz, 1H), 1.42 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 155.0, 153.9, 140.7, 137.7, 137.3, 137.2, 132.1, 131.0, 130.2, 129.2, 129.1, 128.7, 128.1, 127.6,

127.3, 126.3, 125.5, 125.3, 122.5, 118.4, 117.8, 112.7, 80.8, 55.4, 48.5, 28.3 ppm. HR-MS (ESI) *m/z* calcd for $C_{37}H_{31}NO_5$ $[M+Na]^+$ 592.20944, found 592.20903.



tert-butyl (2-((7aR,10S,10aS)-9-oxo-2,7a-diphenyl-7a,9,10,10a-tetrahydrofuro[2,3-b]naphtho[1,2-d]furan-10-yl)phenyl)carbamate (3u)

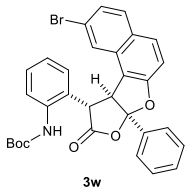
The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 40:1) in 76% yield as white solid. The enantiomeric excess was determined to be 95% ee by HPLC analysis on a Daicel Chiralpak AD column: 80/20 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 254 nm, t_{major} = 12.0 min, t_{minor} = 23.7 min; $[\alpha]_D^{25}$ = -368.0 (*c* = 0.57, $CHCl_3$), m.p. 112 – 114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 5.2 Hz, 1H), 7.68 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.64 – 7.62 (m, 2H), 7.52 – 7.49 (m, 3H), 7.45 – 7.31 (m, 9H), 7.32 – 7.30 (m, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 4.90 (d, *J* = 2.8 Hz, 1H), 4.80 (s, 1H), 1.37 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 155.3, 153.6, 141.2, 140.4, 137.8, 137.2, 131.4, 130.2, 130.0, 129.7, 129.2, 129.1, 127.9, 127.6, 126.5, 125.5, 125.2, 124.3, 119.8, 118.8, 117.8, 112.2, 80.8, 55.4, 48.7, 28.3 ppm. HR-MS (ESI) *m/z* calcd for $C_{37}H_{31}NO_5$ $[M+Na]^+$ 592.20944, found 592.20890.



tert-butyl (2-((7a*R*,10*S*,10a*S*)-3-bromo-9-oxo-7a-phenyl-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3v)

The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 30:1) in 61% yield as white solid. The enantiomeric excess was determined to be 92% ee by HPLC analysis on a Daicel Chiralpak AD column: 80/20 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 254 nm, t_{minor} = 6.5 min, t_{major} = 10.4 min; $[\alpha]_D^{25}$ = -149.0 (*c* = 0.5, $CHCl_3$), m.p. 88 – 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.0 Hz, 1H), 7.75 (d, *J* = 9.2 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.46 – 7.41 (m, 4H), 7.31 – 7.28 (m, 1H), 7.28 – 7.25 (m, 1H), 7.02 (d, *J* = 9.2 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 4.77 (d, *J* = 2.8 Hz, 1H), 4.53 (d, *J* = 2.8 Hz, 1H), 1.35 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 154.0, 152.7, 136.4, 135.9, 130.6, 130.5, 130.3,

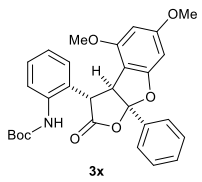
129.7, 129.1, 128.1, 128.0, 126.9, 125.2, 124.4, 124.3, 122.5, 117.7, 117.0, 116.5, 112.2, 79.8, 54.3, 47.3, 27.2 ppm. HR-MS (ESI) *m/z* calcd for $C_{31}H_{26}BrNO_5$ $[M+Na]^+$ 594.08866, found 594.07169.



3w

***tert*-butyl (2-((7a*R*,10*S*,10a*S*)-2-bromo-9-oxo-7a-phenyl-7a,9,10,10a-tetrahydrofuro[2,3-*b*]naphtho[1,2-*d*]furan-10-yl)phenyl)carbamate (3w)**

The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 30:1) in 60% yield as white solid. The enantiomeric excess was determined to be 96% ee by HPLC analysis on a Daicel Chiralpak AD column: 85/15 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 215 nm, t_{minor} = 13.3 min, t_{major} = 19.6 min; $[\alpha]_D^{25}$ = -186.0 (*c* = 0.5, $CHCl_3$), m.p. 82 – 83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.2 Hz, 1H), 7.78 – 7.75 (m, 2H), 7.60 – 7.58 (m, 2H), 7.51 – 7.47 (m, 2H), 7.38 – 7.34 (m, 2H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 4.80 (d, *J* = 3.2 Hz, 1H), 4.57 (d, *J* = 3.2 Hz, 1H), 1.42 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 155.8, 153.7, 137.6, 137.1, 131.8, 131.1, 130.9, 130.3, 129.4, 129.1, 129.0, 128.0, 126.9, 125.5, 125.4, 124.3, 122.8, 118.0, 117.7, 112.7, 80.9, 55.4, 48.9, 28.3 ppm. HR-MS (ESI) *m/z* calcd for $C_{31}H_{26}BrNO_5$ $[M+Na]^+$ 594.08866, found 594.08910.



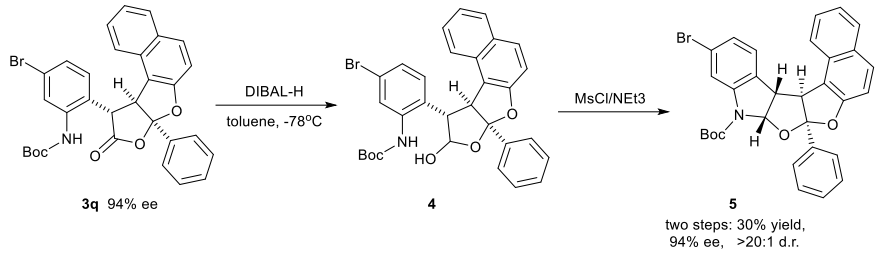
3x

***tert*-butyl (2-((3*S*,3a*S*,8a*R*)-4,6-dimethoxy-2-oxo-8a-phenyl-2,3,3a,8a-tetrahydrofuro[2,3-*b*]benzofuran-3-yl)phenyl)carbamate (3x)**

The reaction was carried out following the general procedure to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/Ethyl Acetate = 20:1) in 85% yield as white solid. The enantiomeric excess was determined to be 96% ee by HPLC analysis on a Daicel Chiralpak IC column: 90/10 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 215 nm, t_{minor} = 14.8 min, t_{major} = 16.6 min; $[\alpha]_D^{25}$ = +39.0 (*c* = 0.5, $CHCl_3$), m.p. 92 – 94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.71 (s, 1H), 7.53 – 7.50 (m, 2H), 7.42 – 7.38 (m, 3H), 7.25 – 7.21 (m, 1H), 6.87 – 6.83 (m, 1H), 6.71 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.23 (dd, *J* = 5.6, 2.0 Hz, 2H), 4.50 (d, *J* = 2.0 Hz, 1H), 4.30 (d, *J* = 1.6 Hz, 1H), 3.92 (s, 3H), 3.82 (s, 3H), 1.54 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 163.4, 159.0, 156.5, 153.5, 137.4, 136.7, 130.0, 128.8, 128.6, 127.0,

126.8, 125.6, 124.2, 124.0, 118.0, 105.5, 93.4, 89.3, 80.9, 56.2, 55.9, 54.3, 48.2, 28.5 ppm. HR-MS (ESI) *m/z* calcd for $C_{29}H_{29}NO_7$ $[M+Na]^+$ 526.18362, found 526.18307.

3. Synthesis of 5



To solution of **3q** (114.2 mg, 0.2 mmol) in toluene (4 mL) was added DIBAL-H (1.0 mol/L in hexanes) at -78 °C and stirred until completed disappearance of the starting material (monitored by TLC, 8 h).Then the reaction was quenched by saturated ammonium chloride. The mixture was extracted with ethyl acetate and the organic phase was washed with saturated ammonium chloride, dried over Na_2SO_4, filtered and evaporated. The crude product was dissolved in a CH_2Cl_2 (2 ml) solution of Et_3N (30.3 mg, 0.3 mmol) and DMAP (2.5 mg, 0.02 mmol). Then methanesulfonyl chloride (23 mg, 0.2 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at rt until complete disappearance of the starting materials (monitored by TLC, 14 h). Then saturated ammonium chloride was added to quench the reaction. The mixture was extracted with EA and washed with saturated sodium chloride, the organic phase was dried over Na_2SO_4. After evaporation of the volatile, the residue was purified by silica gel column chromatography (Petroleum Ether/EtOAc =20:1) to obtained the product **5** in 30% yield as a white solid. The enantiomeric excess was determined to be 94% *ee* by HPLC analysis on a Daicel Chiralpak AD column: 80/20 *n*-hexane/*i*-PrOH, flow rate 1.00 mL/min, λ = 254 nm, t_{major}= 4.1 min, t_{minor} = 5.4 min; $[\alpha]_D^{25}$ = +304.0 (*c* = 0.5, $CHCl_3$), m.p. 148 – 150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (br s, 1H),7.91 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.33 (dd, *J* = 12.4, 8.4 Hz, 2H), 7.26 – 7.25 (m, 1H), 7.24 – 7.22 (m, 5H), 6.35 (s, 1H), 4.51 (s, 1H), 4.21 (d, *J* = 5.2 Hz, 1H), 1.59 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 151.6, 139.8, 131.0, 130.0, 129.6, 128.9, 128.5, 127.7, 126.6, 125.5, 125.2, 123.7, 122.7, 121.3, 120.4, 119.1, 117.9, 112.4,

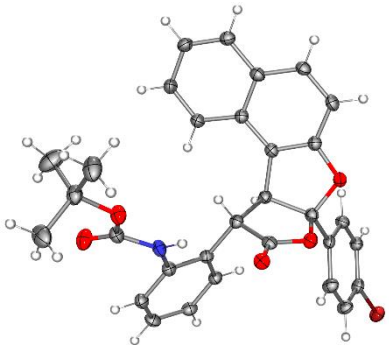
95.3, 58.9, 51.7, 28.4 ppm. HR-MS (ESI) *m/z* calcd for $C_{31}H_{26}BrNO_4$ $[M+Na]^+$ 578.09374, found 578.09340.

4. References

[1] L.-L. Zhang, J.-W. Zhang, S.-H. Xiang, Z. Guo and B. Tan, *Org. Lett.*, 2018, **20**, 6022.

[2] Y.-H. Chen, D.-J. Cheng, J. Zhang, Y. Wang, X.-Y. Liu and B. Tan, *J. Am. Chem. Soc.*, 2015, **137**, 15062.

5. Crystal Data of 3j



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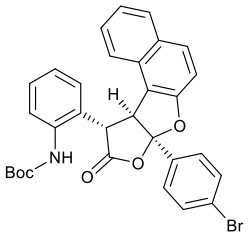
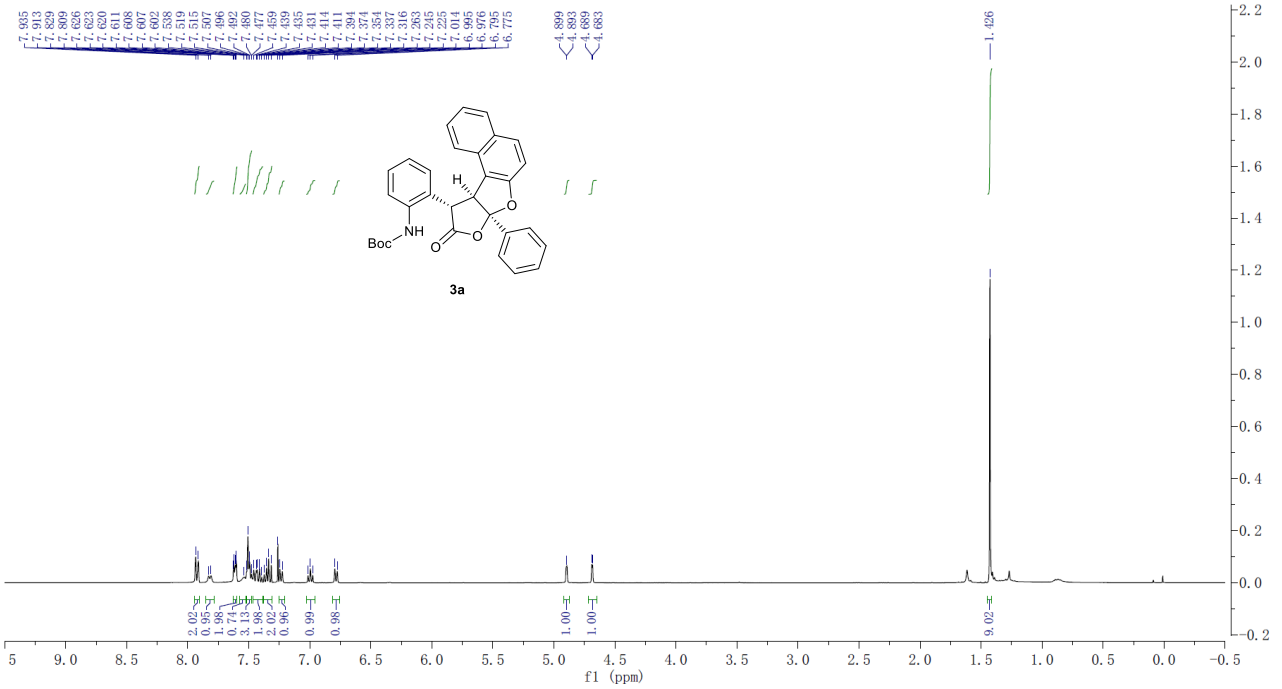


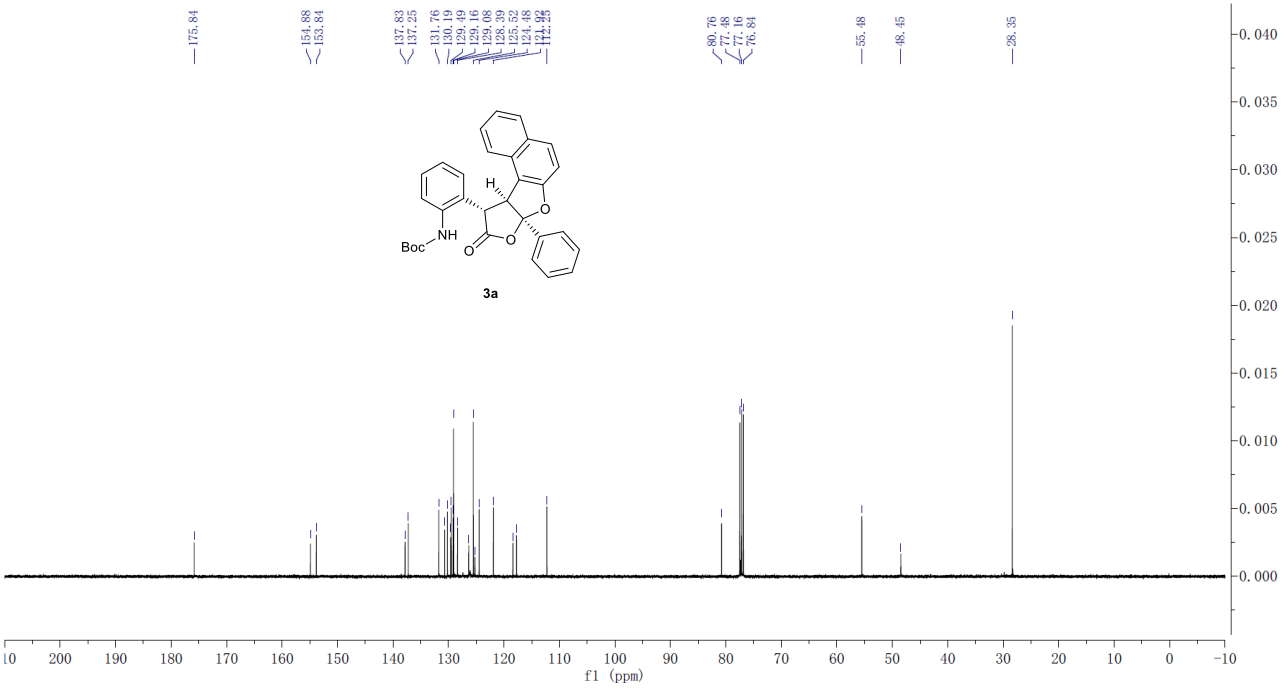
3j, CCDC: 1974974

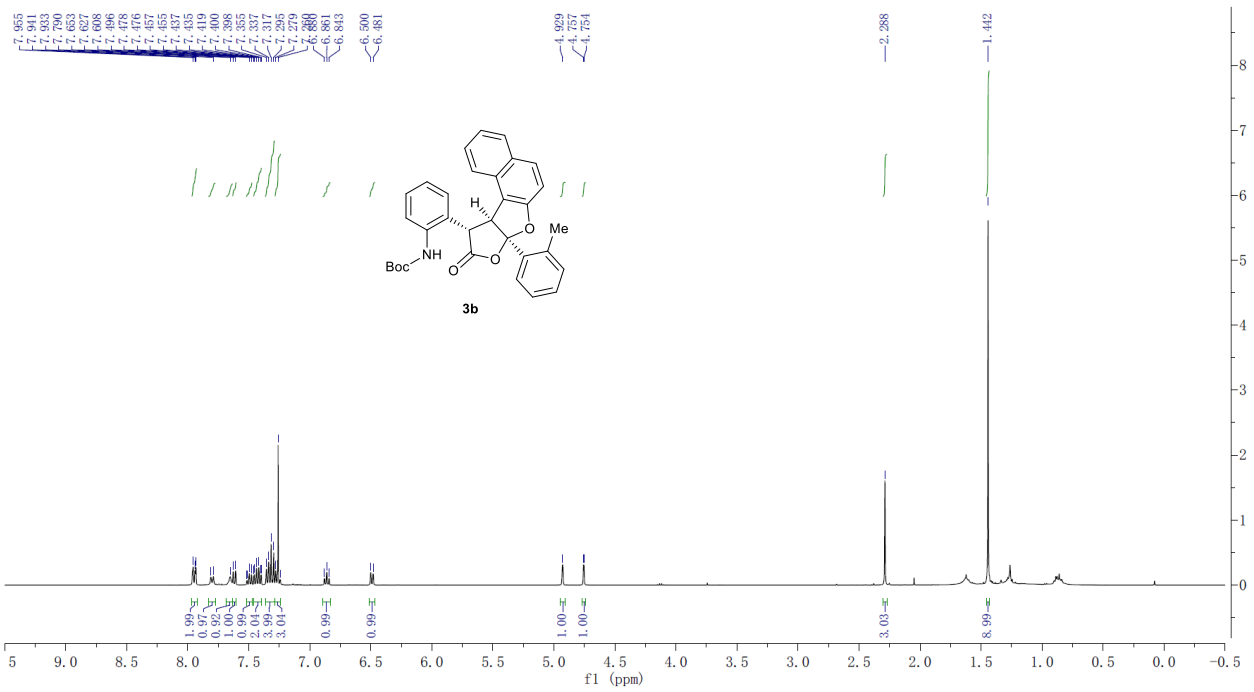
Identification code	**3j**	
Empirical formula	$C_{31}H_{26}BrNO_5$	
Formula weight	1231.04	
Temperature	150.0 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 10.1246(4) Å	α = 92.396(2) °.
	b = 10.7766(4) Å	β = 96.373(2) °.
	c = 14.6208(5) Å	γ = 104.996(2) °.
Volume	1527.27(10) $Å^3$	
Z	1	
Density (calculated)	1.338 Mg/m^3	
Absorption coefficient	2.170 mm^{-1}	
F(000)	638	
Crystal size	0.12 × 0.11 × 0.11 mm^3	
Theta range for data collection	4.259 to 72.115 °.	
Index ranges	-12<=h<=12, -13<=k<=13, -17<=l<=9	
Reflections collected	19940	
Independent reflections	7654 [R(int) = 0.0327]	
Completeness to theta = 67.679 °	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0872 and 0.0108	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7654 / 3 / 747	

Goodness-of-fit on F^2	1.125
Final R indices [I>2sigma(I)]	R1 = 0.0565, wR2 = 0.1440
R indices (all data)	R1 = 0.0584, wR2 = 0.1474
Absolute structure parameter	0.040(13)
Extinction coefficient	n/a
Largest diff. peak and hole	0.707 and -0.336 e.$Å^{-3}$

6. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra



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4.754
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Boc
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H
O
Me
3b
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0.97
0.92
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3.04
0.99
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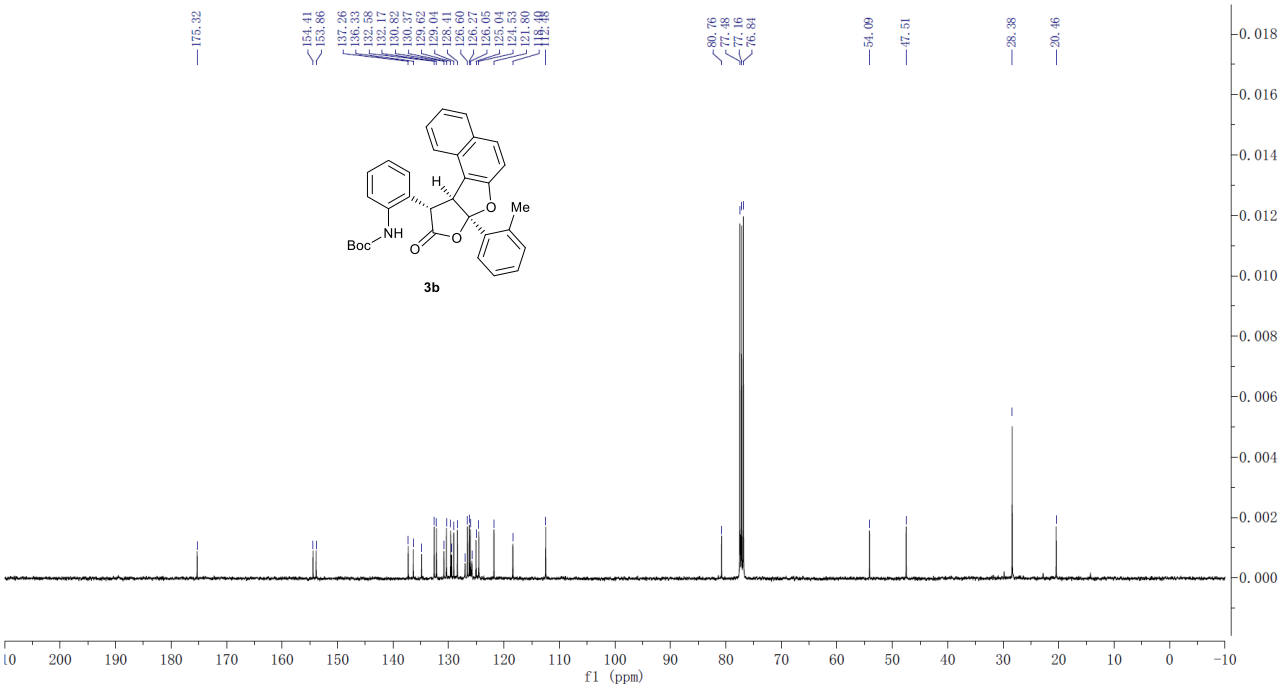
8.99
f1 (ppm)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Boc
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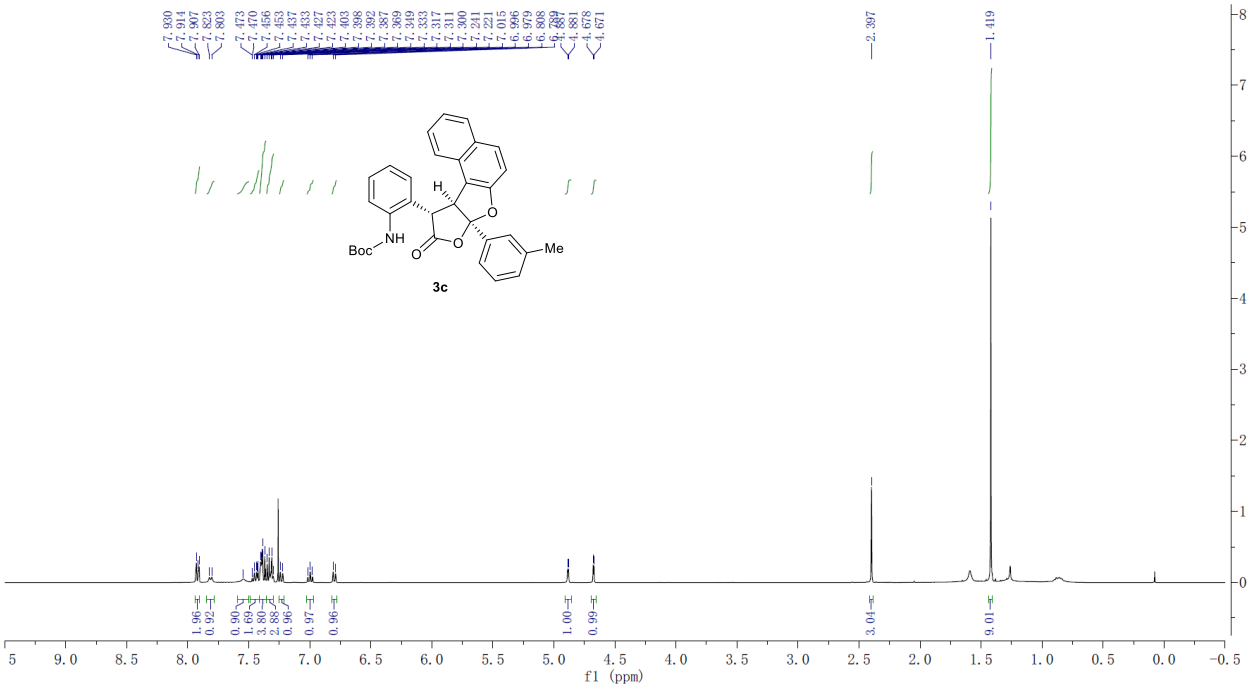
3b
f1 (ppm)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O
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Me
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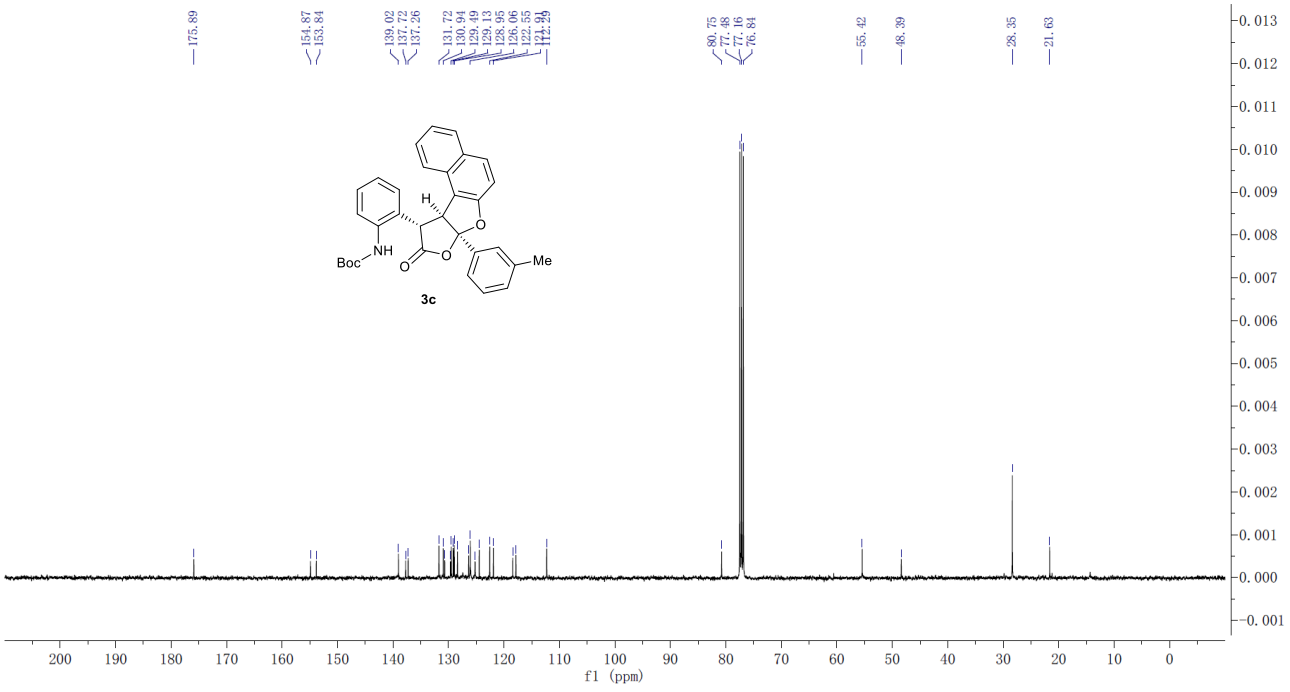
f1 (ppm)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NH
Boc
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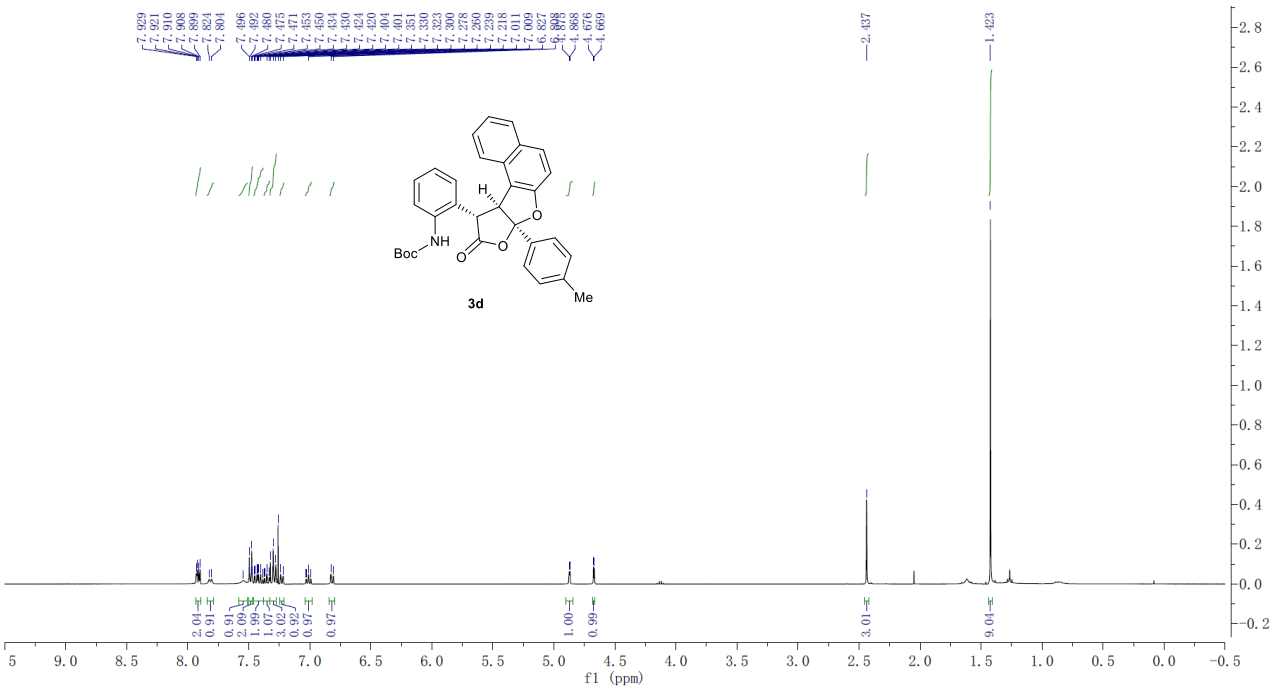
O
Me
3c
f1 (ppm)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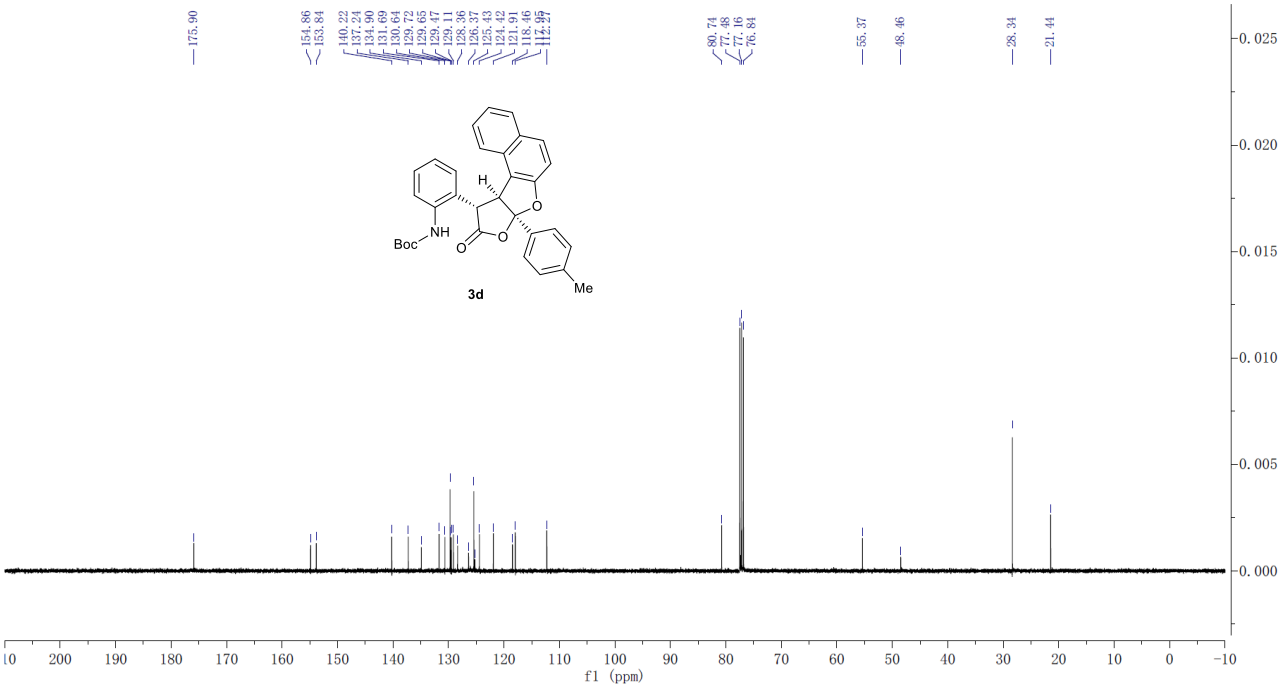
7.910
7.908
7.899
7.824
7.804
7.496
7.492
7.480
7.475
7.471
7.453
7.450
7.434
7.430
7.424
7.420
7.404
7.401
7.351
7.330
7.323
7.300
7.278
7.260
7.239
7.218
7.011
7.009
6.827
4.888
4.676
4.669
2.437
1.423
NH
Boc
O
H
Me
3d
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
−0.2
2.04
0.91
0.91
2.09
1.99
1.07
3.02
0.92
0.97
0.97
1.00
0.99
3.01
9.04
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)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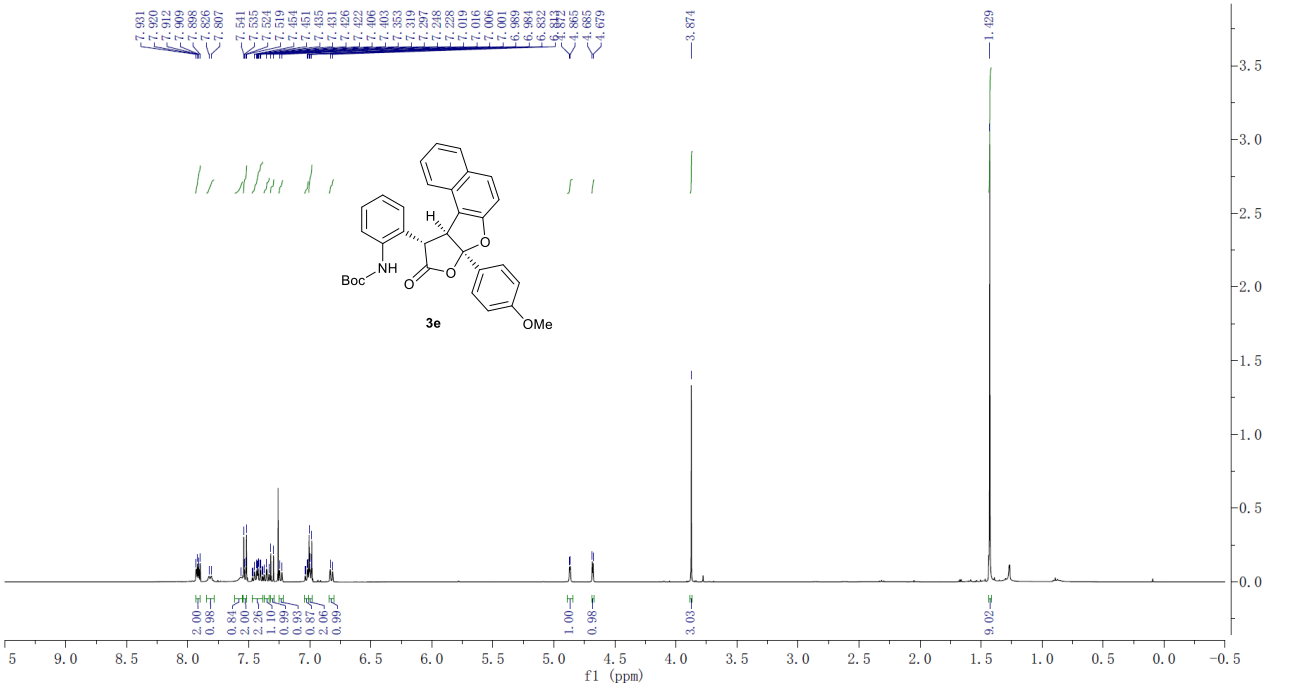
154.86
153.84
140.22
137.24
134.90
131.89
130.64
129.72
129.65
129.47
129.11
128.36
126.37
125.43
124.42
121.91
118.46
80.74
77.48
77.16
76.84
55.37
48.46
28.34
21.44
NH
Boc
O
H
Me
3d
0.025
0.020
0.015
0.010
0.005
0.000
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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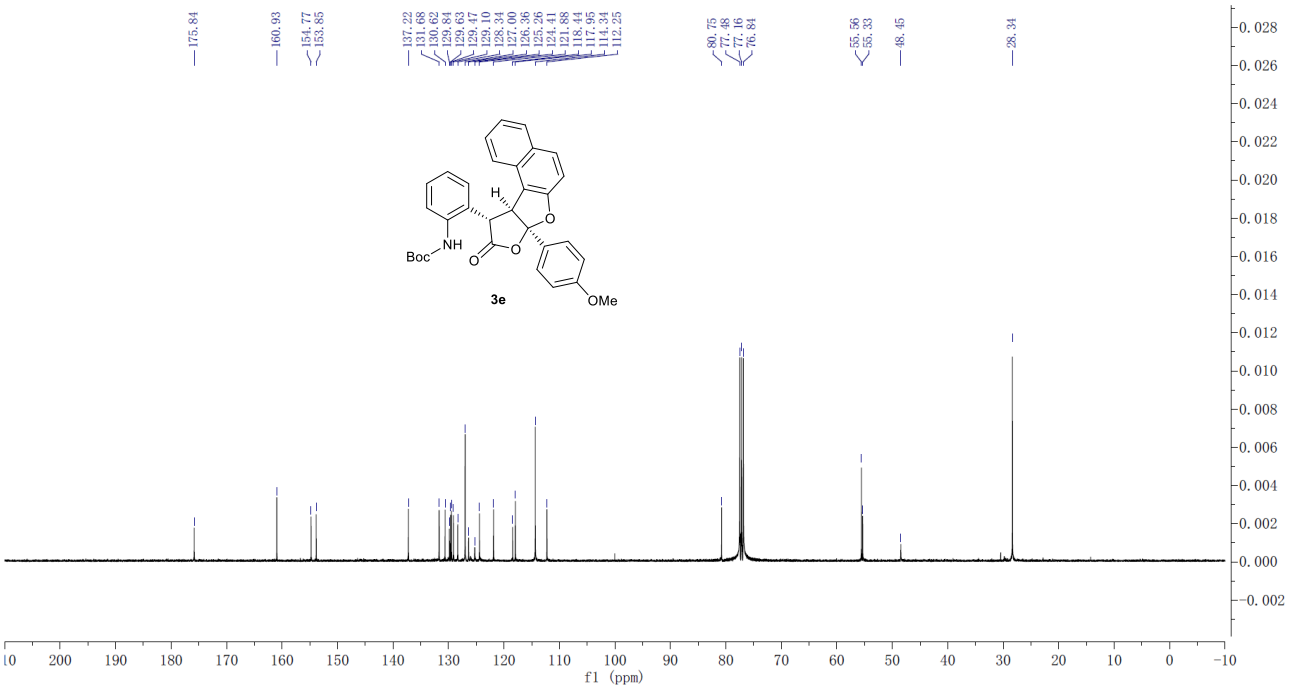
7.912
7.909
7.898
7.826
7.807
7.541
7.535
7.524
7.519
7.454
7.451
7.435
7.431
7.426
7.422
7.406
7.403
7.353
7.319
7.297
7.248
7.228
7.019
7.016
7.006
7.001
6.989
6.984
6.832
6.829
4.865
4.685
4.679
3.874
1.429
H
O
NH
Boc
O
O
3e
OMe
2.00
0.98
0.84
2.00
2.26
1.10
0.93
0.93
0.87
2.06
0.99
1.00
0.98
3.03
9.02
f1 (ppm)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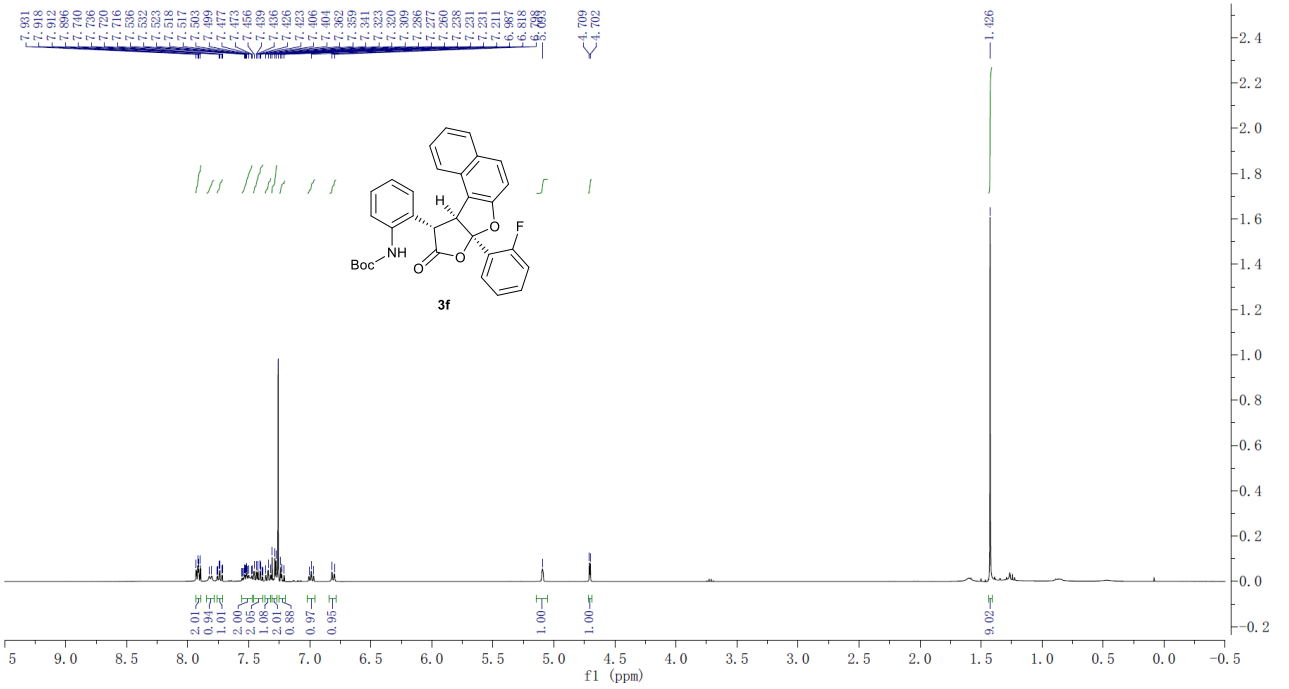
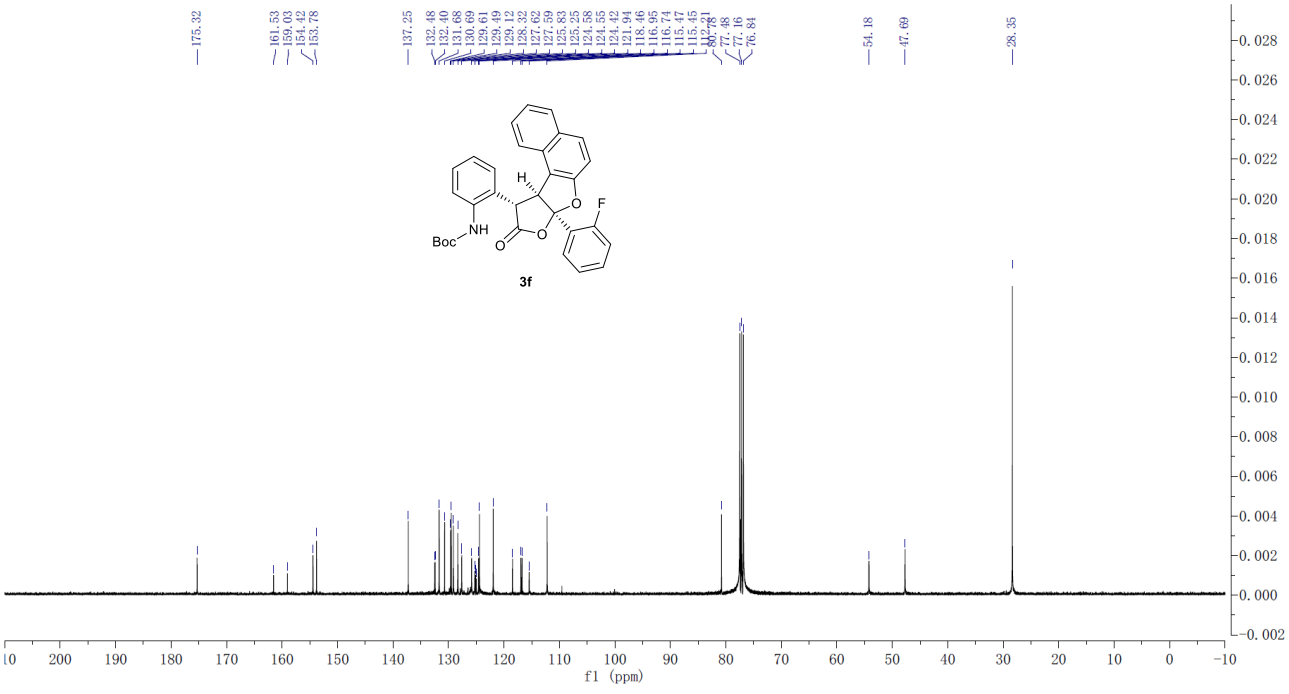
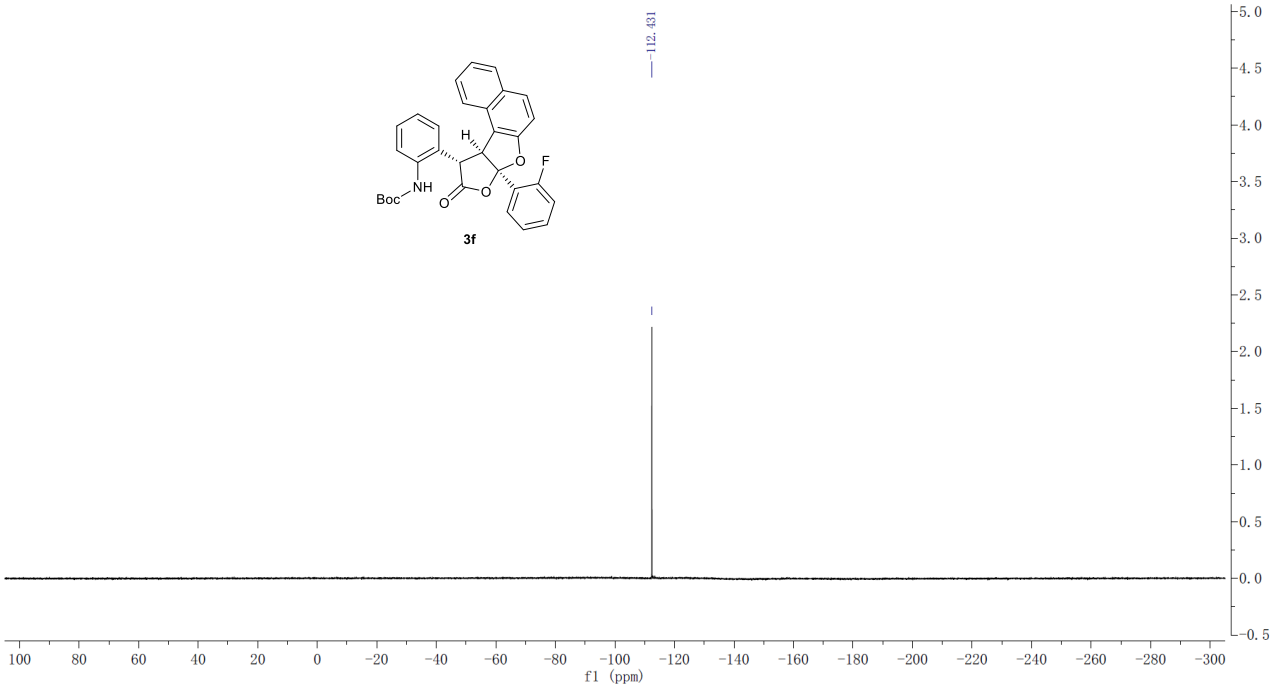
160.93
154.77
153.85
137.22
131.68
130.62
129.84
129.63
129.47
129.10
128.34
127.00
126.36
125.26
124.41
121.88
118.44
117.95
114.34
112.25
80.75
77.48
77.16
76.84
55.56
55.33
48.45
28.34
H
O
NH
Boc
O
O
3e
OMe
f1 (ppm)


3f
f1 (ppm)


3f
f1 (ppm)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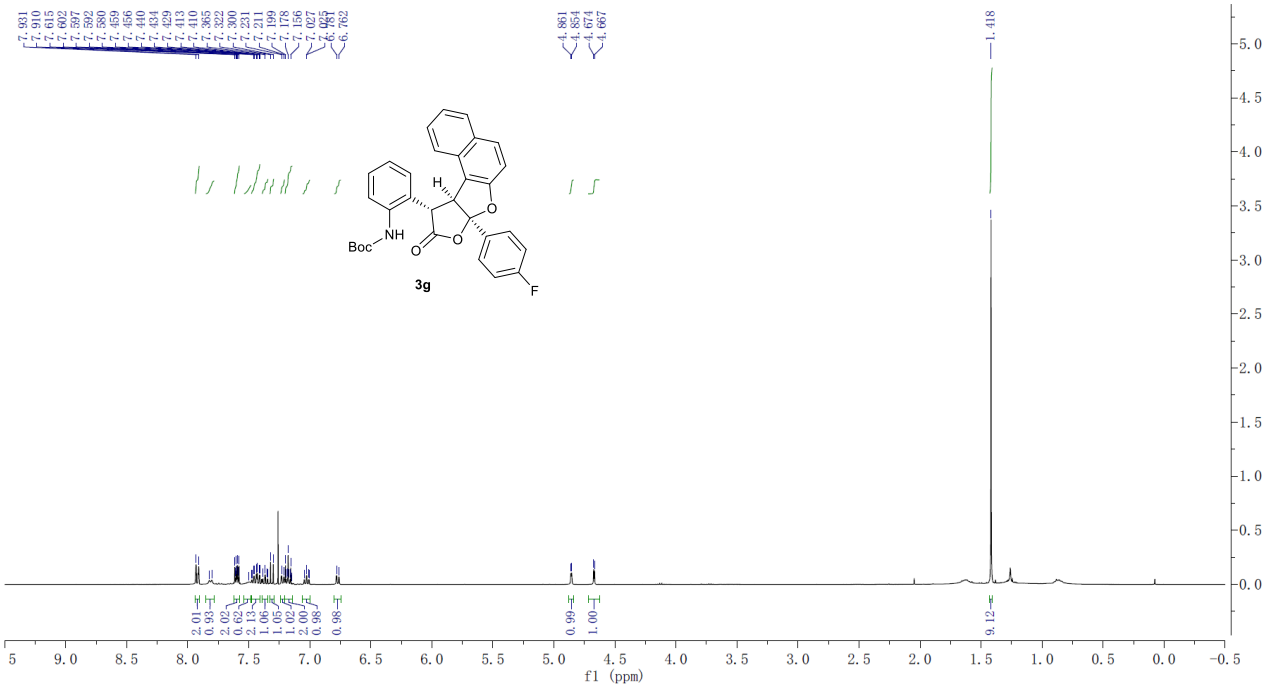
H
O
F
NH
Boc
O
O
3f
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)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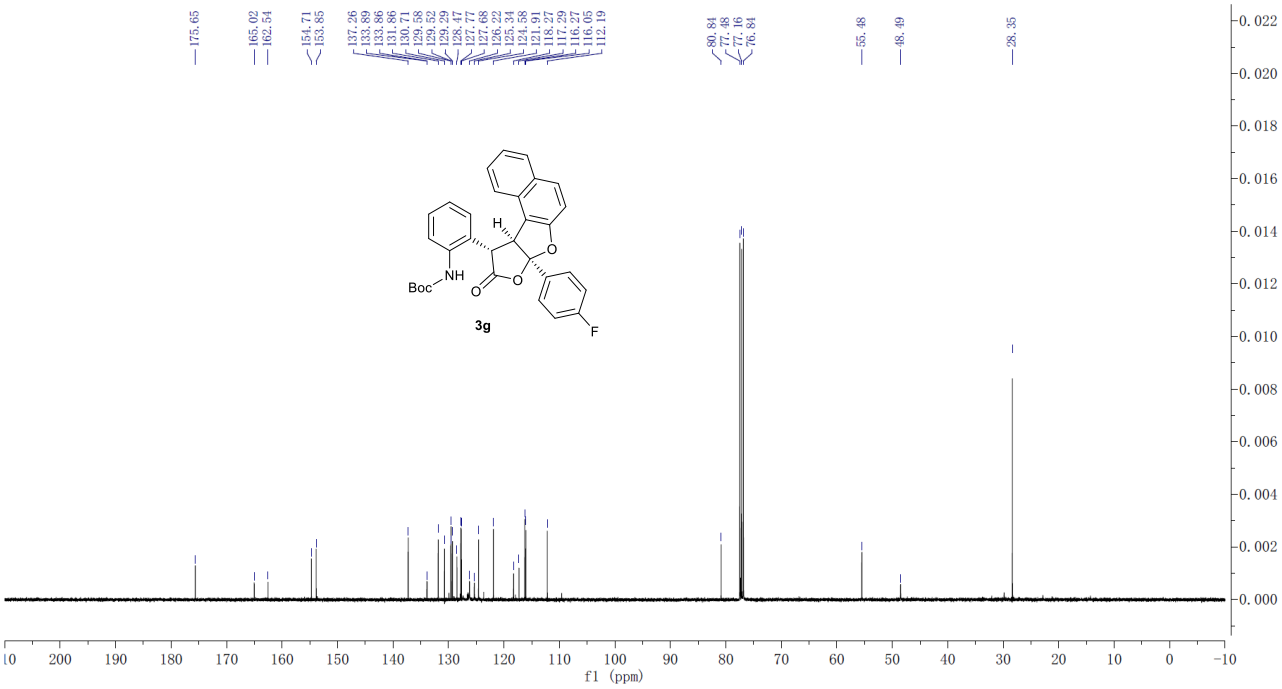
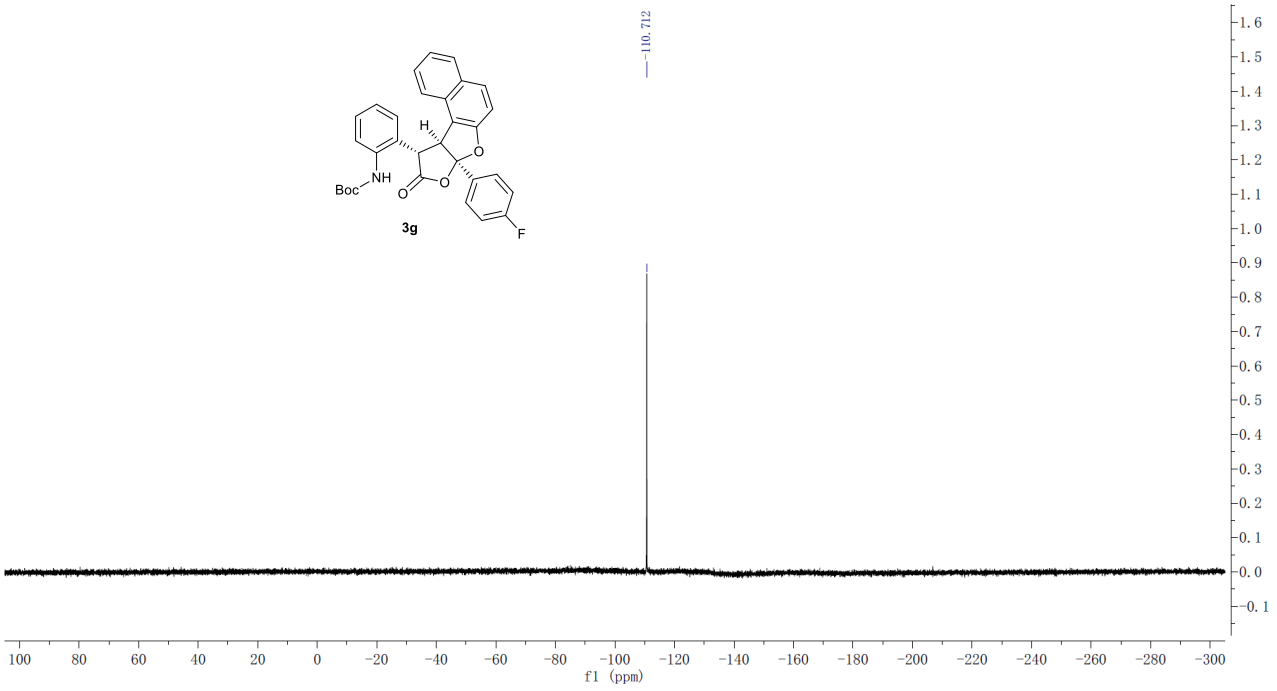
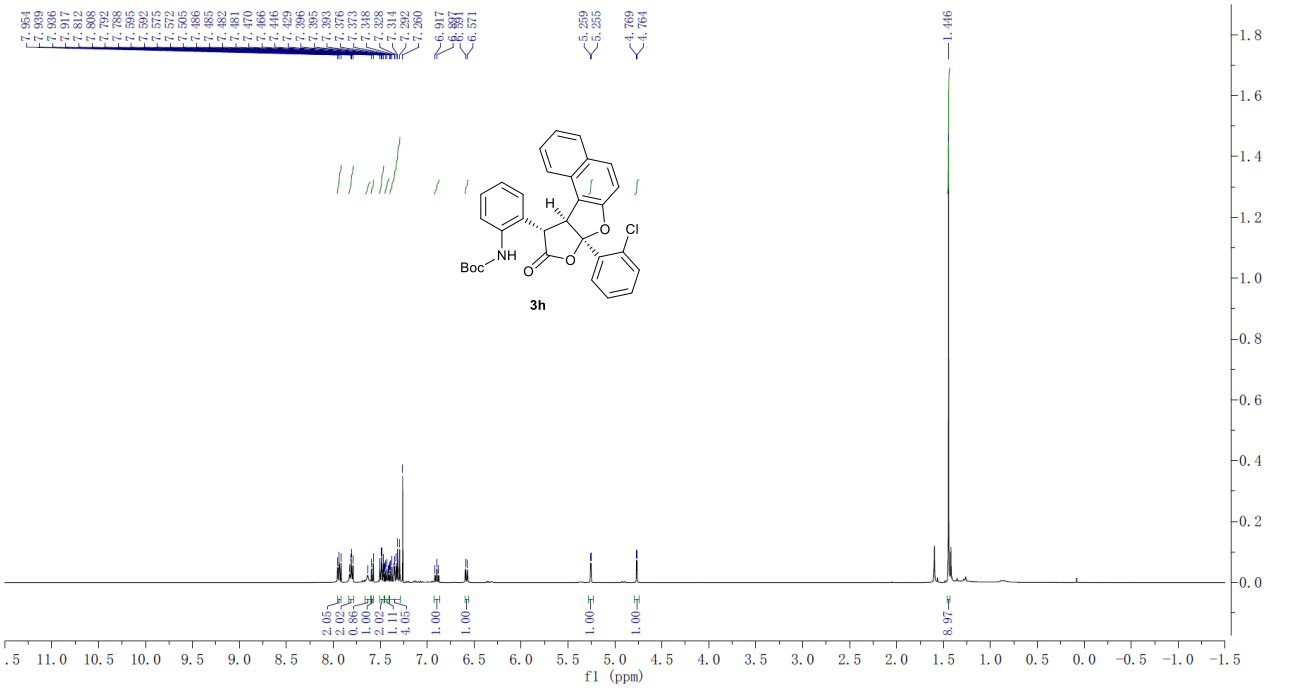
7.910
7.615
7.602
7.597
7.592
7.586
7.459
7.456
7.440
7.434
7.429
7.413
7.410
7.365
7.322
7.300
7.231
7.211
7.199
7.178
7.156
7.027
7.025
6.781
6.762
4.861
4.854
4.674
4.667
1.418
NH
Boc
O
H
F
3g
2.01
0.93
2.02
0.62
2.13
1.06
1.05
1.02
2.00
0.98
0.98
0.99
1.00
9.12
f1 (ppm)


175.65
165.02
162.54
154.71
153.85
137.26
133.89
133.86
131.86
130.71
129.58
129.52
129.29
128.47
127.77
127.68
126.22
125.34
124.38
121.91
118.27
117.29
116.27
116.05
112.19
80.84
77.48
77.16
76.84
55.48
48.49
28.35
NH
Boc
O
H
F
3g
f1 (ppm)


-110.712
Boc
NH
H
O
O
O
F
3g
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)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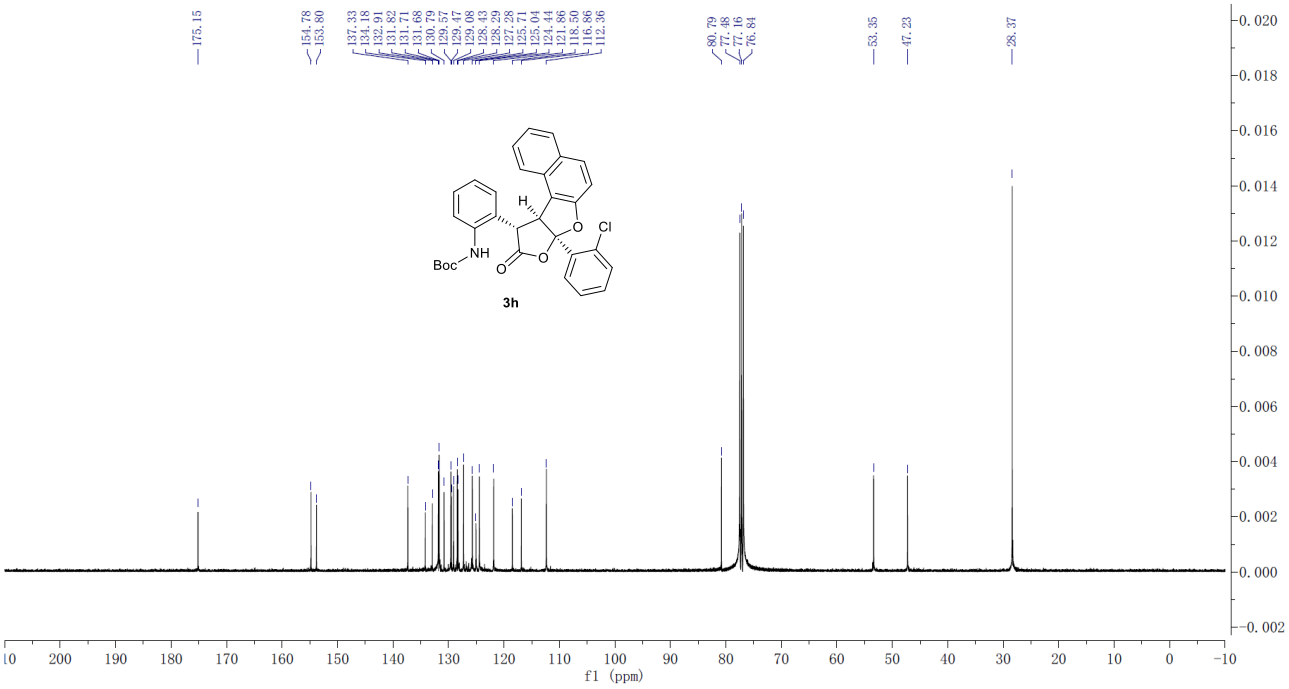
7.936
7.917
7.812
7.808
7.792
7.788
7.695
7.592
7.575
7.572
7.505
7.486
7.485
7.482
7.481
7.470
7.466
7.446
7.429
7.396
7.395
7.393
7.375
7.373
7.348
7.328
7.314
7.292
7.260
6.917
6.897
6.891
6.571
5.259
5.255
4.769
4.764
1.446
H
O
Cl
NH
Boc
O
O
3h
2.05
2.02
0.86
1.00
2.02
1.11
4.05
1.00
1.00
1.00
1.00
8.97
f1 (ppm)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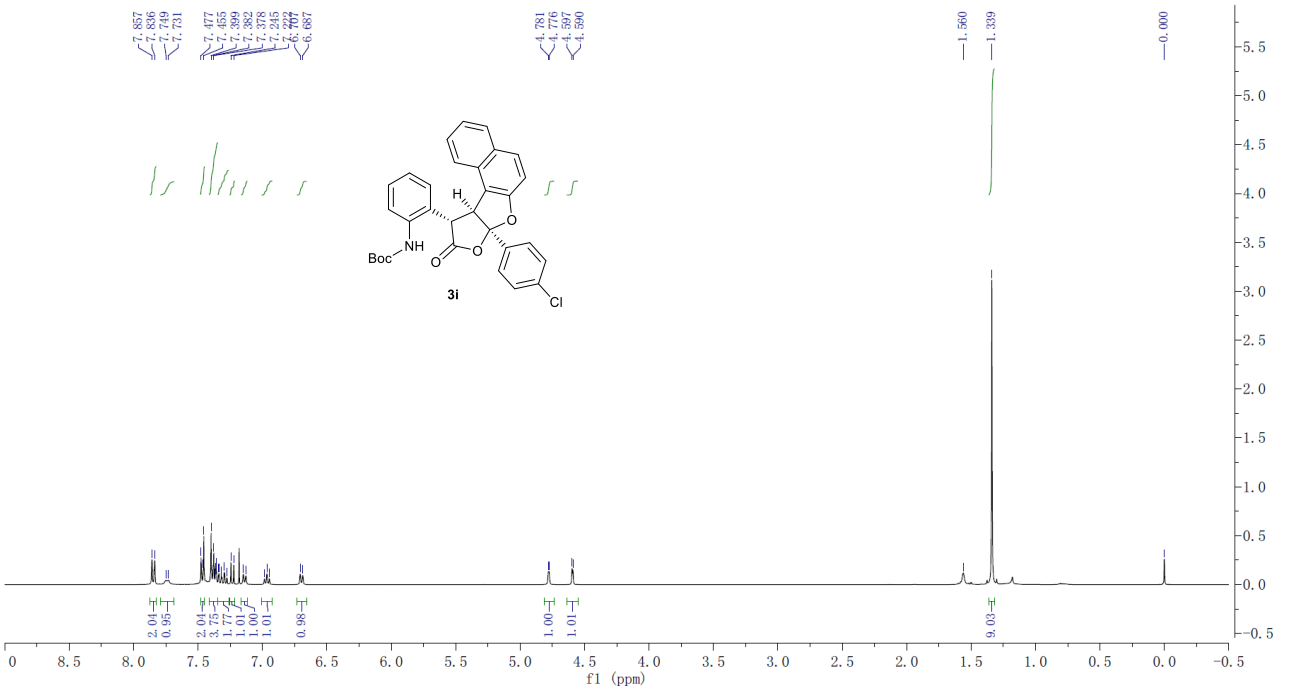
154.78
153.80
137.33
134.18
132.91
131.82
131.71
131.68
130.79
129.57
129.47
129.08
128.43
128.29
127.28
127.21
125.04
124.44
121.86
118.50
116.86
112.36
80.79
77.48
77.16
76.84
53.35
47.23
28.37
H
O
Cl
NH
Boc
O
O
3h
f1 (ppm)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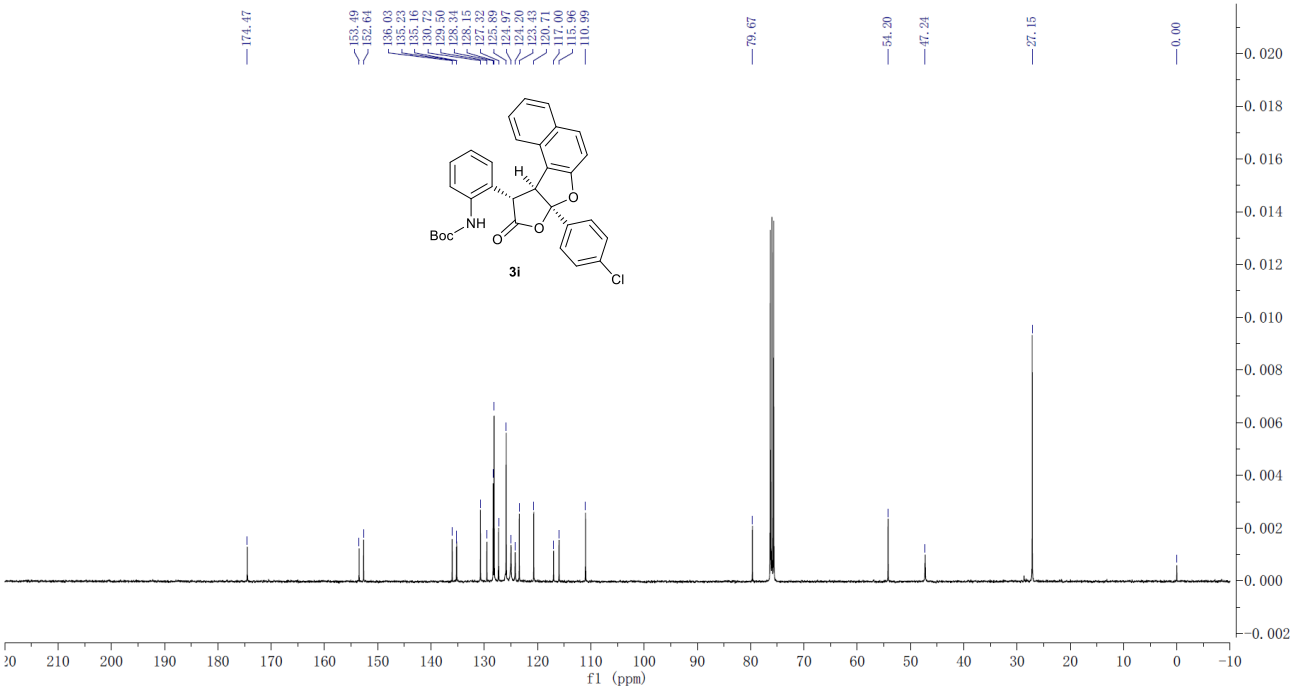
7.749
7.731
7.477
7.455
7.399
7.382
7.378
7.245
6.687
4.781
4.776
4.597
4.590
1.560
1.339
0.000
NH
Boc
O
H
Cl
3i
f1 (ppm)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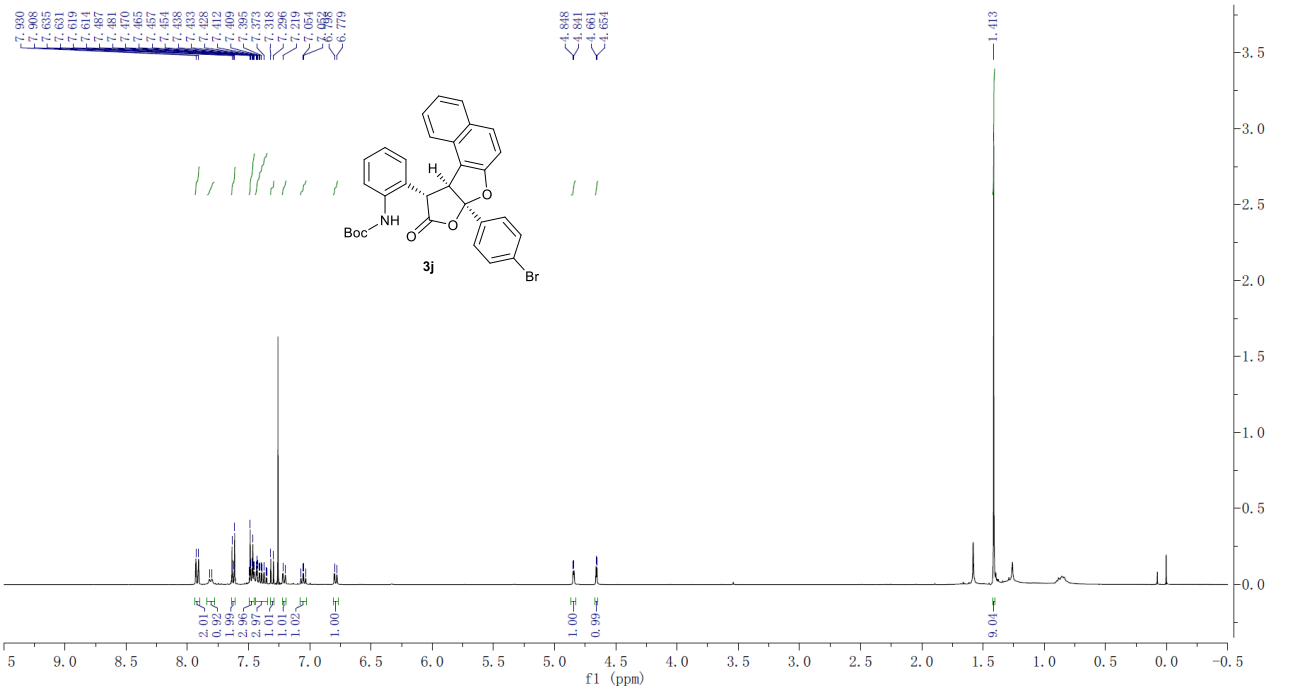
152.64
136.03
135.23
135.16
130.72
129.50
128.34
128.15
127.32
125.89
124.97
124.20
123.43
120.71
117.00
115.96
110.99
79.67
54.20
47.24
27.15
0.00
NH
Boc
O
H
Cl
3i
f1 (ppm)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7.908
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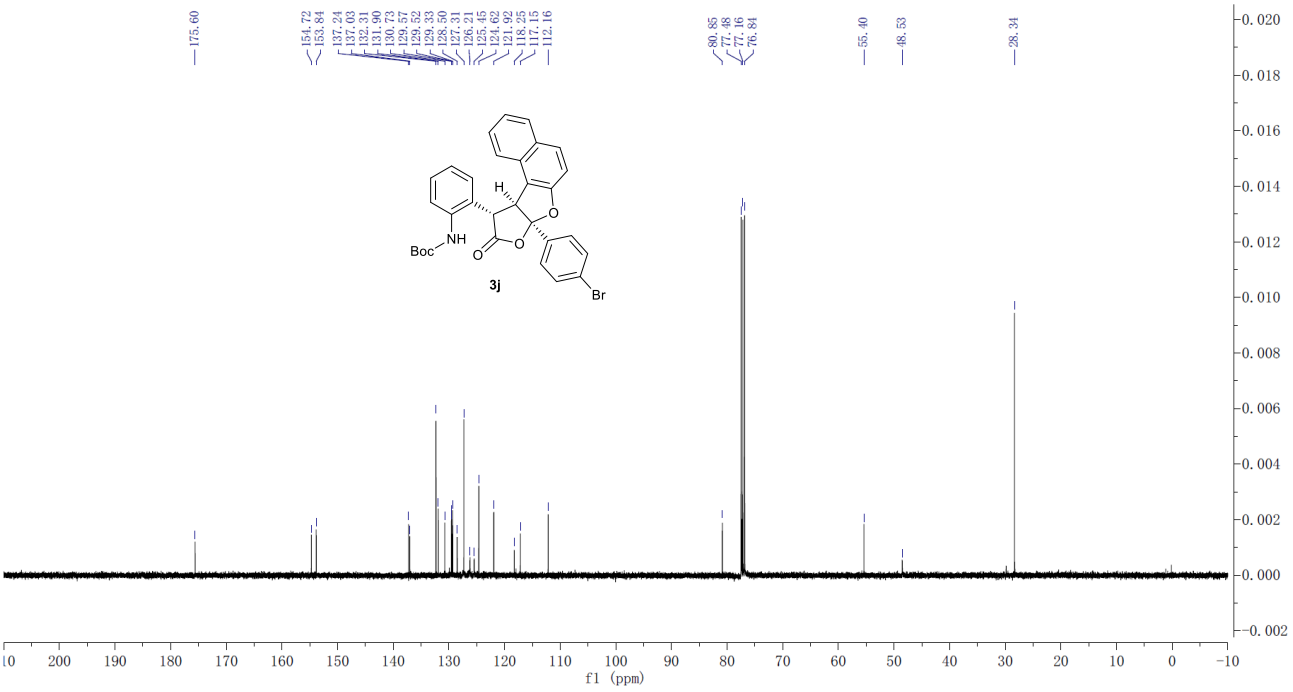
7.633
7.619
7.614
7.487
7.481
7.470
7.465
7.457
7.454
7.438
7.433
7.428
7.412
7.409
7.395
7.373
7.318
7.296
7.219
7.054
6.798
6.779
4.848
4.841
4.661
4.654
1.413
H
NH
Boc
O
O
O
Br
3j
2.01
0.92
1.99
1.96
2.97
1.01
1.02
1.00
1.00
0.99
9.04
f1 (ppm)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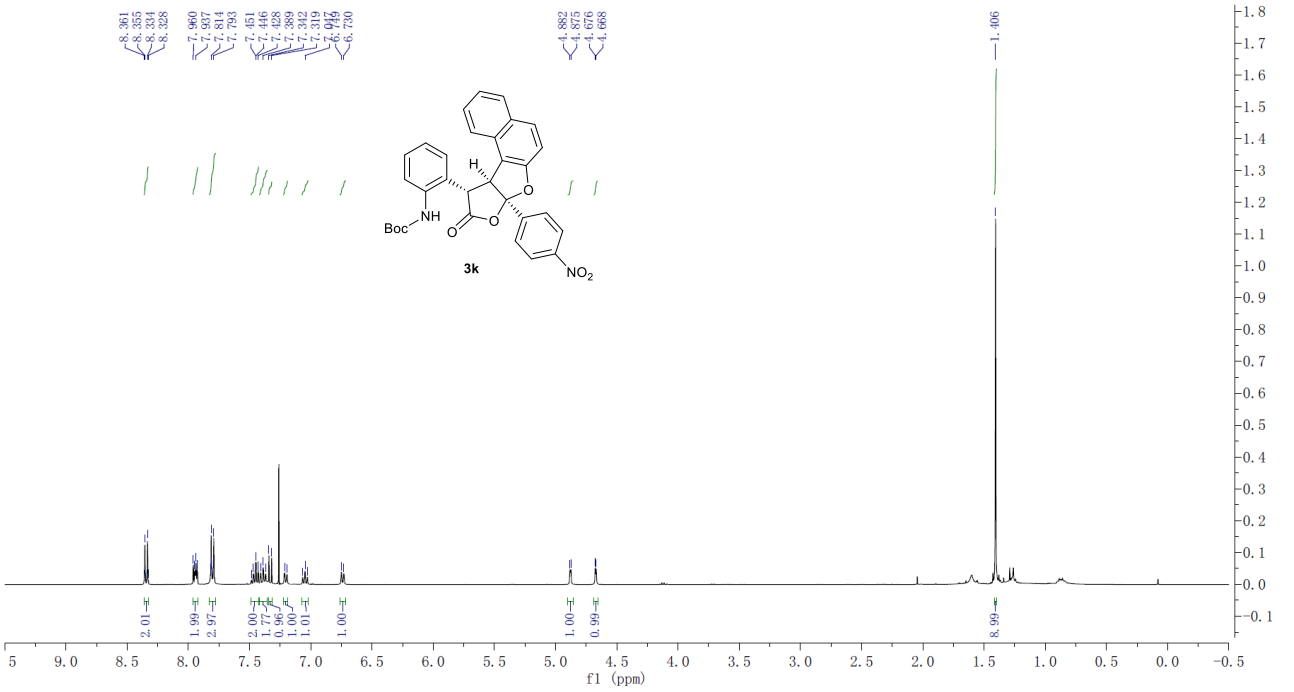
154.72
153.84
137.24
137.03
132.31
131.90
130.73
129.57
129.52
129.33
128.50
127.31
126.21
125.45
124.62
121.92
121.35
117.15
112.16
80.85
77.48
77.16
76.84
55.40
48.53
28.34
H
NH
Boc
O
O
O
Br
3j
f1 (ppm)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8.334
8.328
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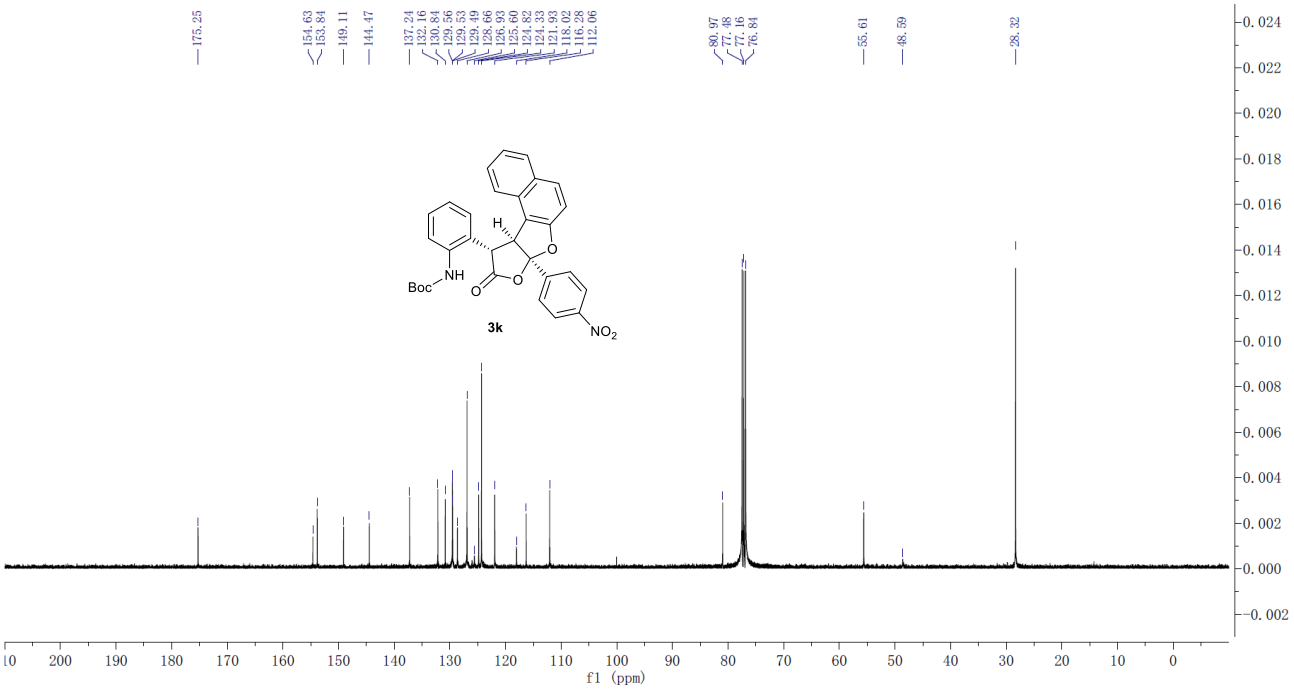
7.937
7.814
7.793
7.451
7.446
7.428
7.389
7.342
7.319
6.745
6.730
4.882
4.875
4.676
4.668
1.406
H
O
NH
Boc
O
O
NO2
3k
2.01
1.99
2.97
2.00
1.77
0.96
1.00
1.01
1.00
1.00
0.99
8.99
f1 (ppm)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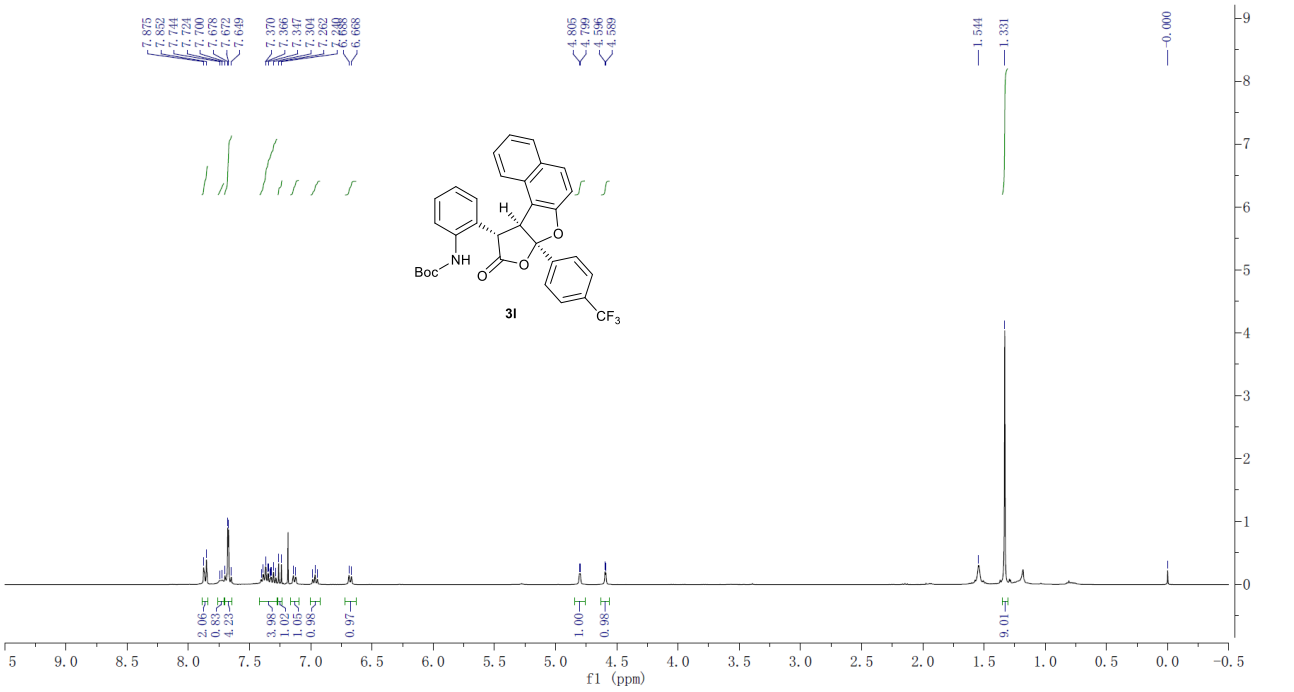
154.63
153.84
149.11
144.47
137.24
132.16
130.84
129.56
129.53
129.49
128.66
126.93
125.60
124.82
124.33
121.93
118.02
116.28
112.06
80.97
77.48
77.16
76.84
55.61
48.59
28.32
H
O
NH
Boc
O
O
NO2
3k
f1 (ppm)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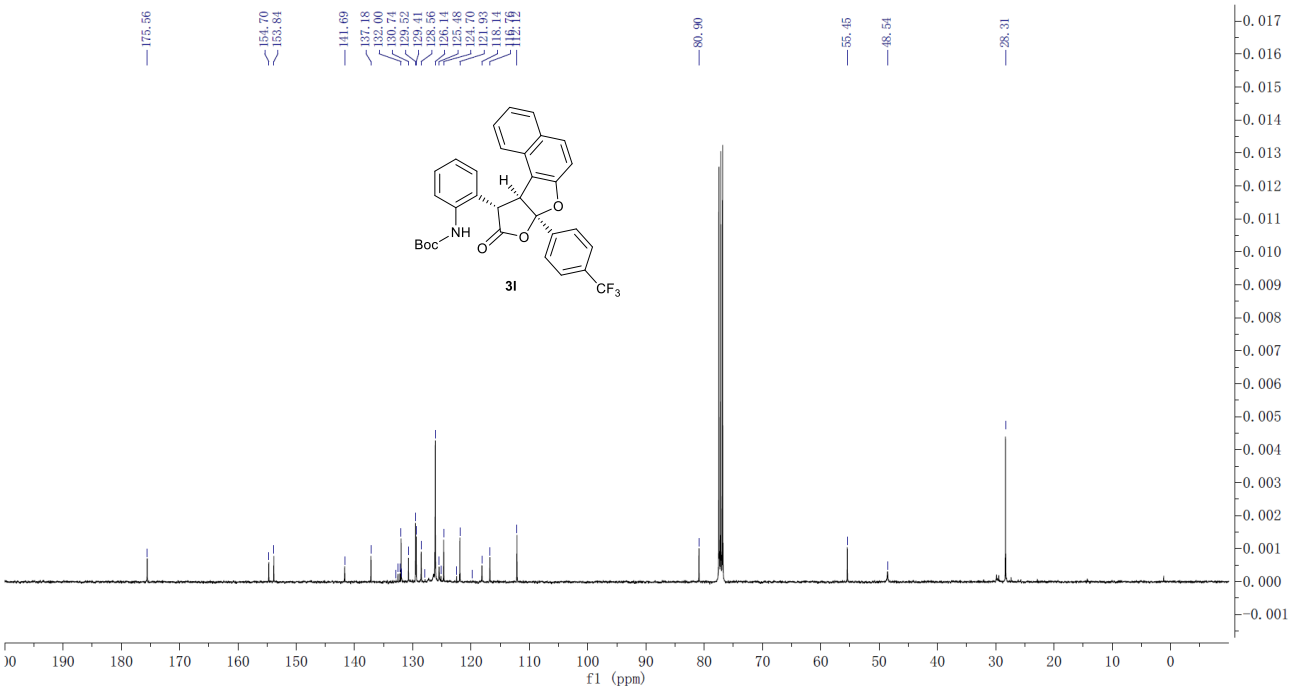
7.734
7.724
7.700
7.678
7.672
7.649
7.370
7.366
7.347
7.304
7.262
6.688
6.668
4.805
4.799
4.596
4.589
1.544
1.331
0.000
Boc
NH
H
O
O
O
CF3
3l
2.06
0.83
4.23
3.98
1.02
1.05
0.98
0.97
1.00
0.98
9.01
f1 (ppm)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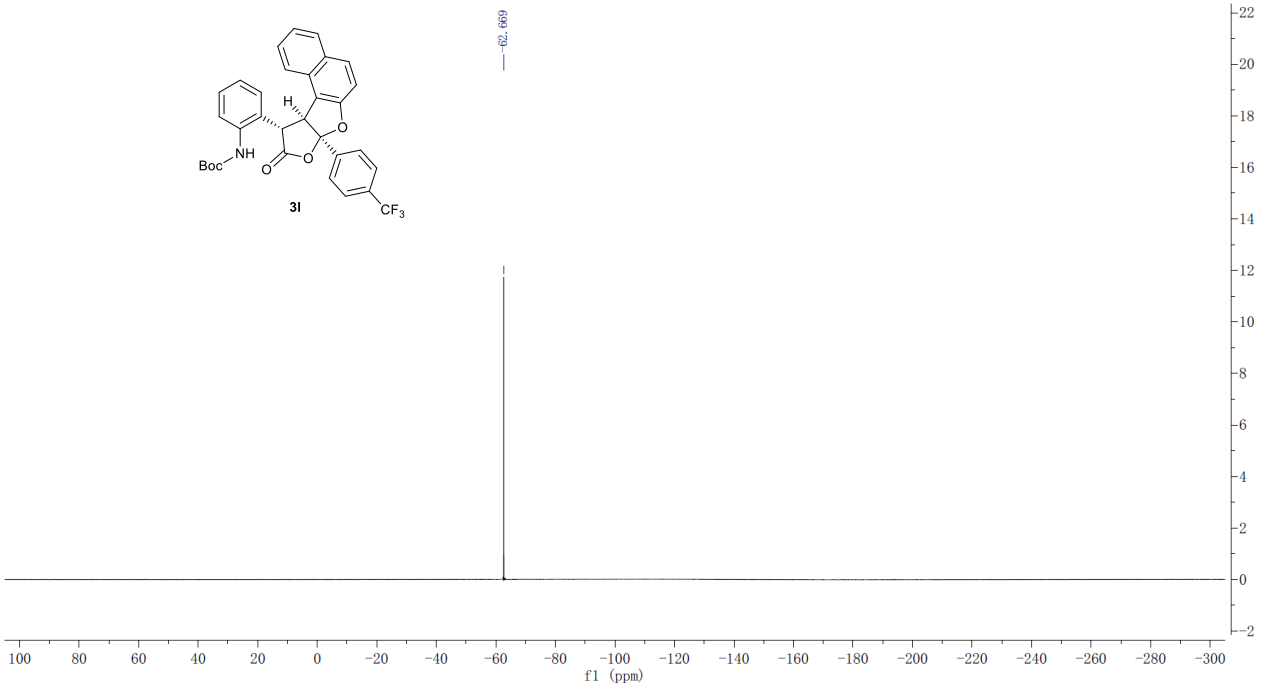
141.69
137.18
132.00
130.74
129.52
129.41
128.56
126.14
125.48
124.70
121.93
118.14
80.90
55.45
48.54
28.31
Boc
NH
H
O
O
O
CF3
3l
f1 (ppm)


-62.669
Boc
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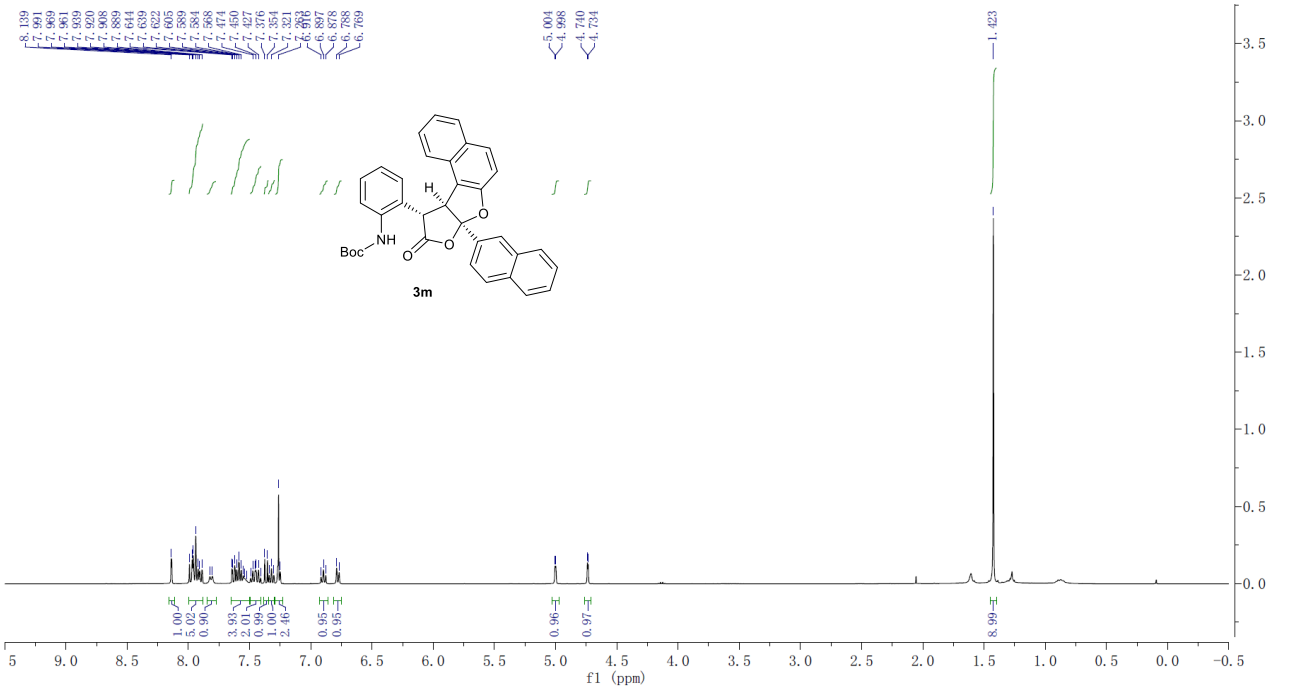
O
O
H
O
O
CF3
3l
22
20
18
16
14
12
10
8
6
4
2
0
-2
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)


8.139
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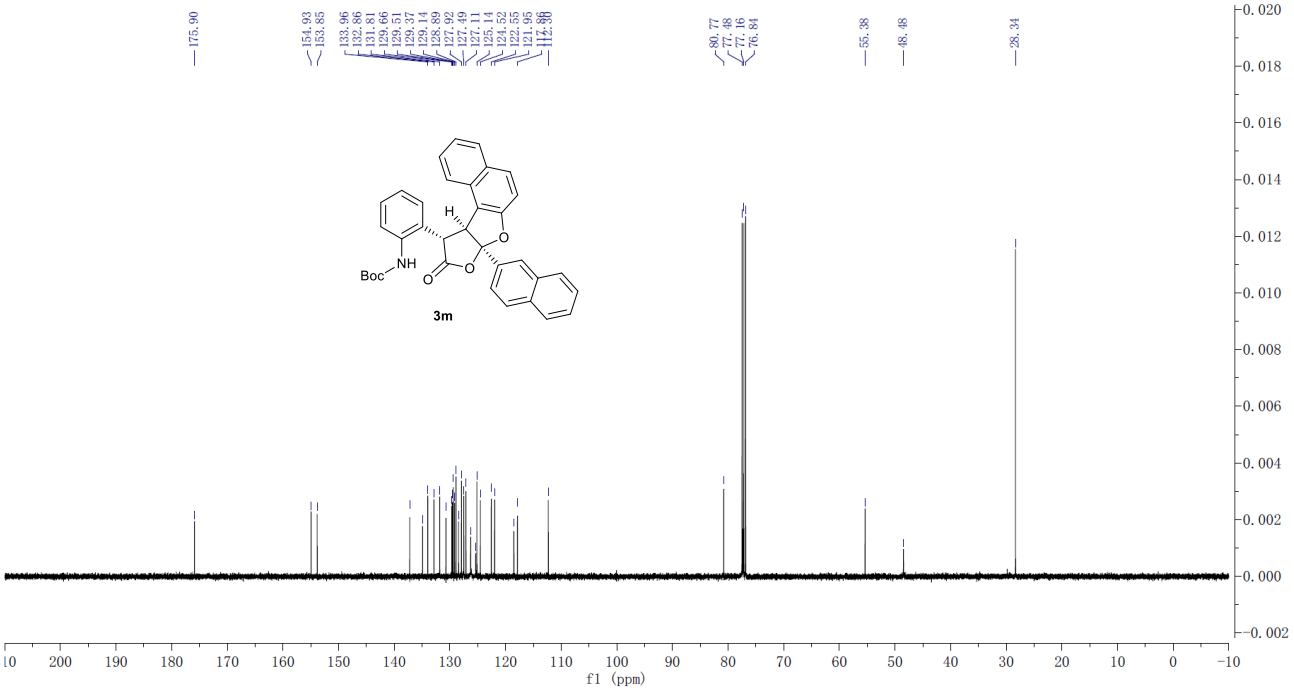
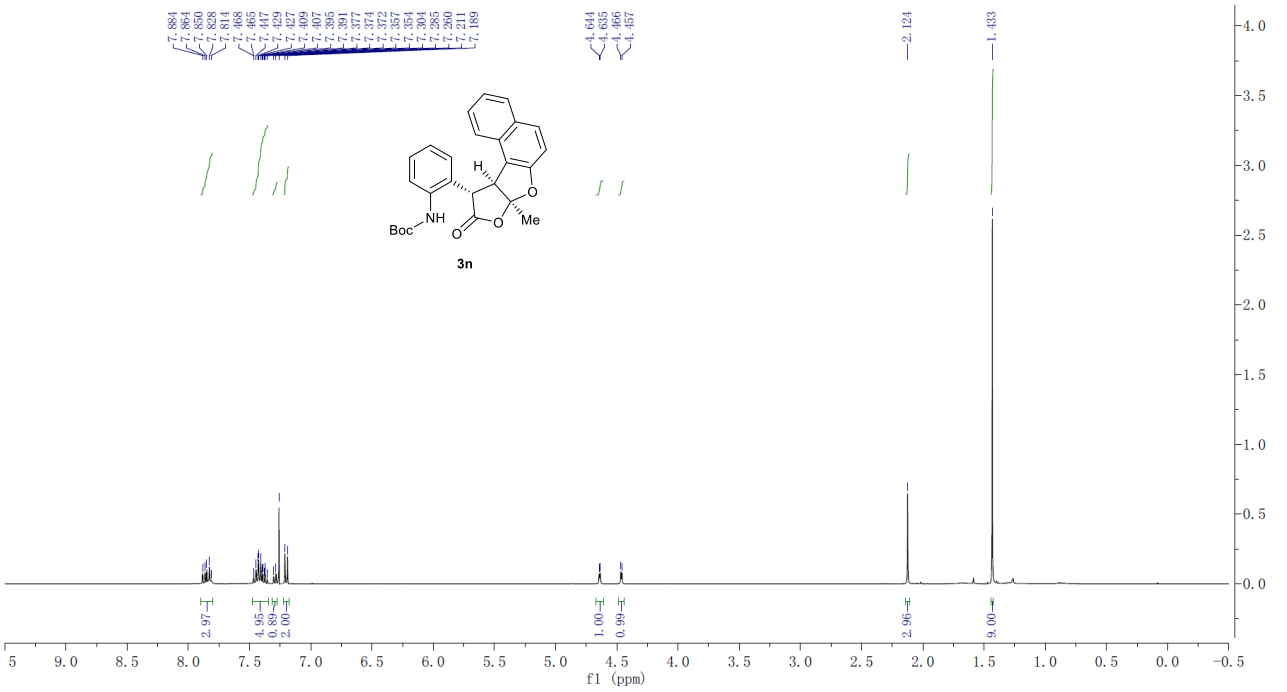
7.969
7.961
7.939
7.920
7.908
7.899
7.644
7.639
7.622
7.605
7.589
7.584
7.568
7.474
7.450
7.427
7.376
7.354
7.321
6.897
6.878
6.788
6.769
5.004
4.998
4.740
4.734
1.423
H
NH
Boc
O
3m
1.00
5.02
0.90
3.93
2.01
0.99
1.00
2.46
0.95
0.95
0.96
0.97
8.99
f1 (ppm)


175.90
154.93
153.85
133.96
132.86
131.61
129.66
129.51
129.37
129.14
128.89
127.92
127.49
127.11
125.14
124.52
122.55
121.95
80.77
77.48
77.16
76.84
55.38
48.48
28.34
H
NH
Boc
O
3m
f1 (ppm)


7.884
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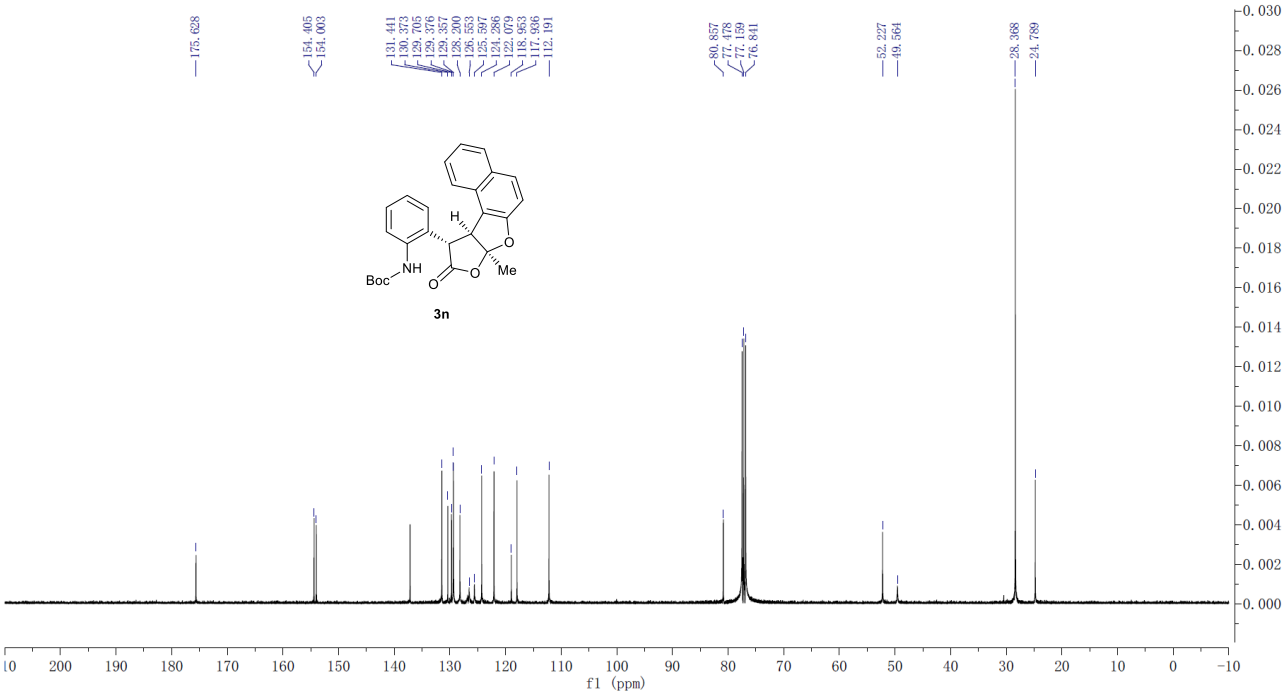
7.850
7.828
7.814
7.468
7.465
7.447
7.429
7.427
7.409
7.407
7.395
7.391
7.377
7.374
7.372
7.357
7.354
7.304
7.285
7.260
7.211
7.189
4.644
4.635
4.466
4.457
2.124
1.433
Boc
NH
H
O
O
O
Me
3n
2.97
4.95
0.89
2.00
1.00
0.99
2.96
9.00
f1 (ppm)


175.628
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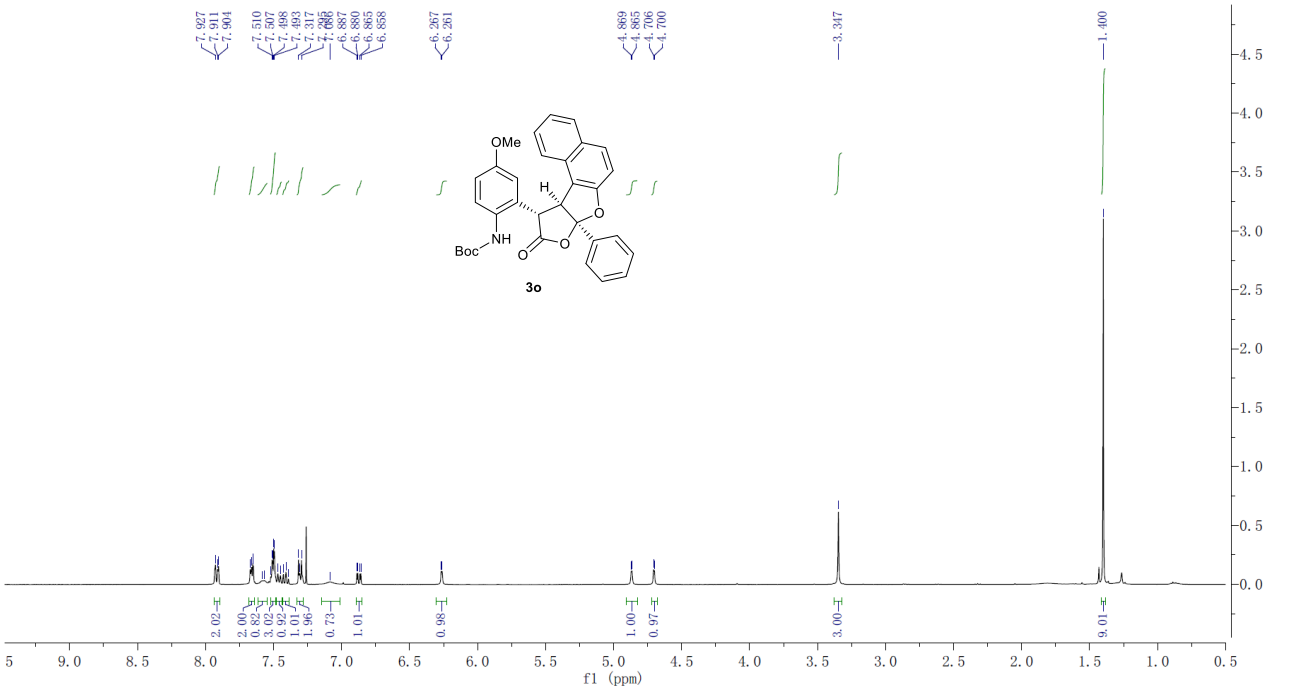
154.003
131.441
130.373
129.705
129.376
129.357
128.200
126.553
125.597
124.286
123.079
118.953
117.936
112.191
80.857
77.478
77.139
76.841
52.227
49.564
28.368
24.789
Boc
NH
H
O
O
O
Me
3n
f1 (ppm)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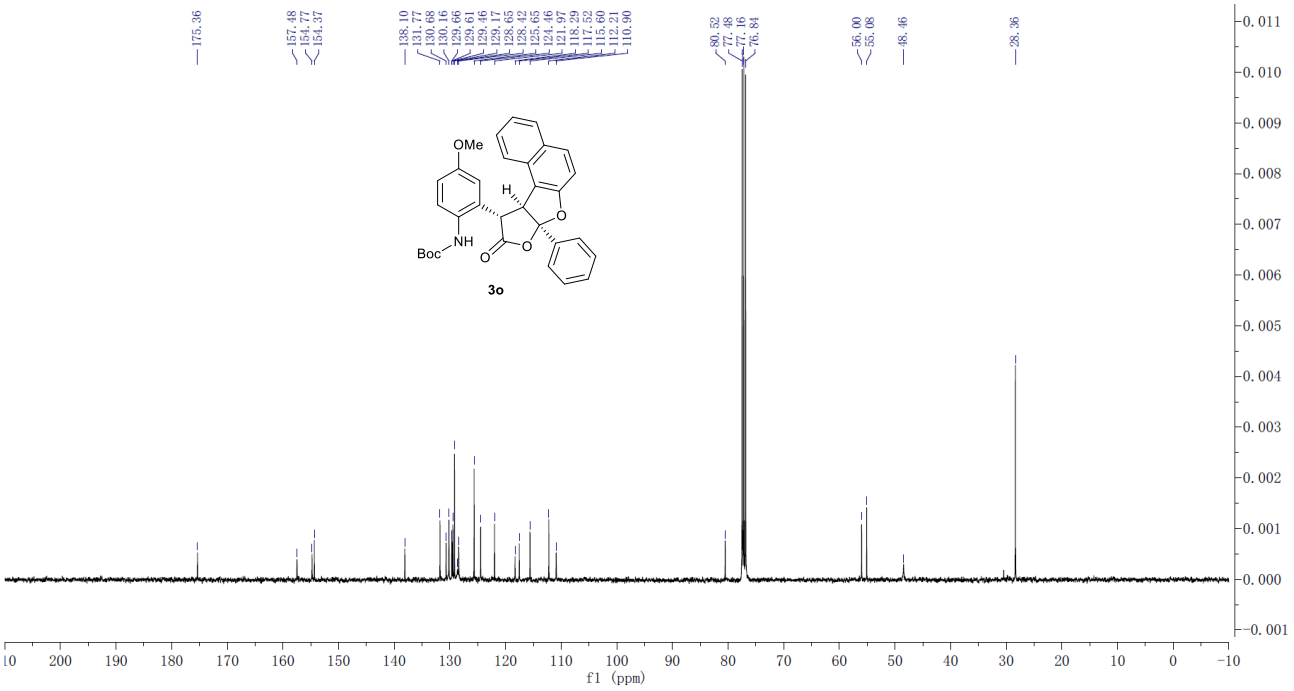
7.911
7.904
7.510
7.507
7.498
7.493
7.317
6.887
6.880
6.865
6.858
6.267
6.261
4.869
4.865
4.706
4.700
3.347
1.400
OMe
H
NH
Boc
O
3o
2.02
2.00
0.82
3.02
0.92
1.01
1.96
0.73
1.01
0.98
1.00
0.97
3.00
9.01
f1 (ppm)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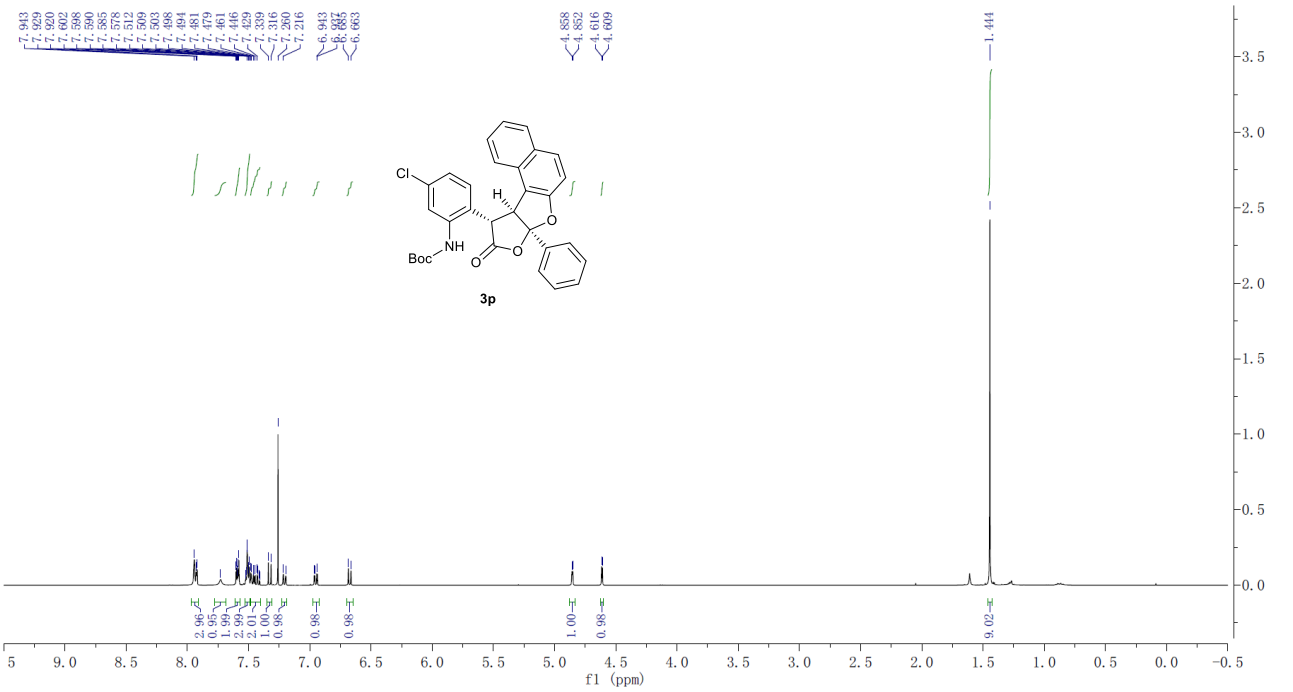
157.48
154.77
154.37
138.10
131.77
130.68
130.16
129.66
129.61
129.46
129.17
128.65
128.32
125.65
124.46
121.97
118.29
117.52
115.60
112.21
110.90
80.52
77.48
77.16
76.84
56.00
55.08
48.46
28.36
OMe
H
NH
Boc
O
3o
f1 (ppm)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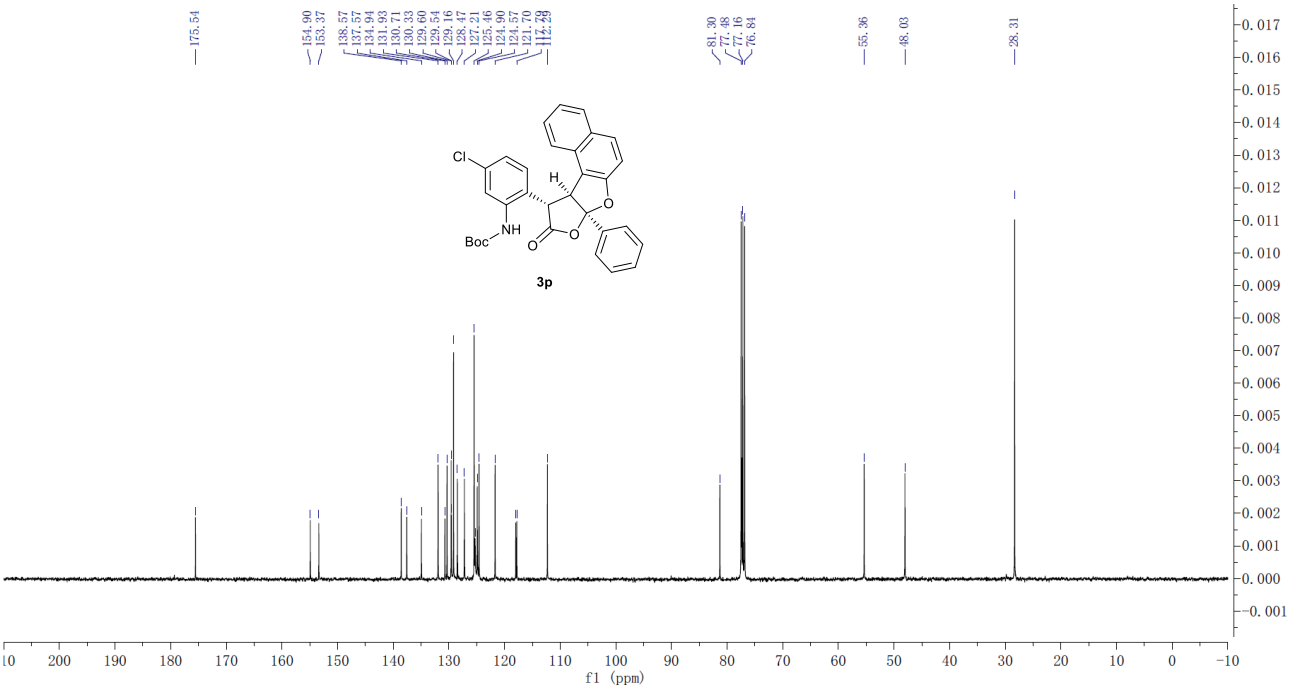
7.929
7.920
7.602
7.598
7.590
7.585
7.578
7.512
7.509
7.503
7.498
7.494
7.481
7.479
7.461
7.446
7.429
7.339
7.316
7.290
7.216
6.943
6.937
6.885
6.663
4.858
4.852
4.616
4.609
1.444
Cl
H
O
NH
Boc
O
O
3p
2.96
0.95
1.99
2.99
2.01
1.00
0.98
0.98
0.98
1.00
0.98
9.02
f1 (ppm)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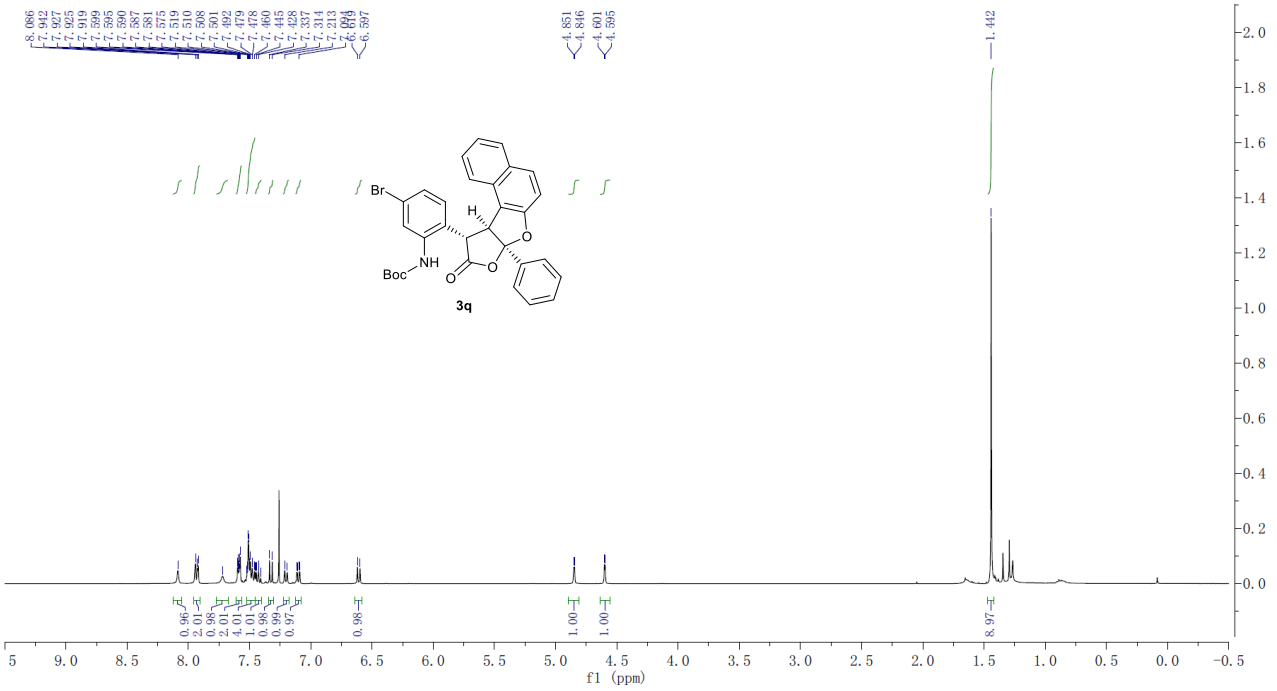
138.57
137.57
134.94
131.93
130.71
130.33
129.60
129.54
129.16
128.47
127.21
125.46
124.90
124.57
121.70
81.30
77.48
77.16
76.84
55.36
48.03
28.31
Cl
H
O
NH
Boc
O
O
3p
f1 (ppm)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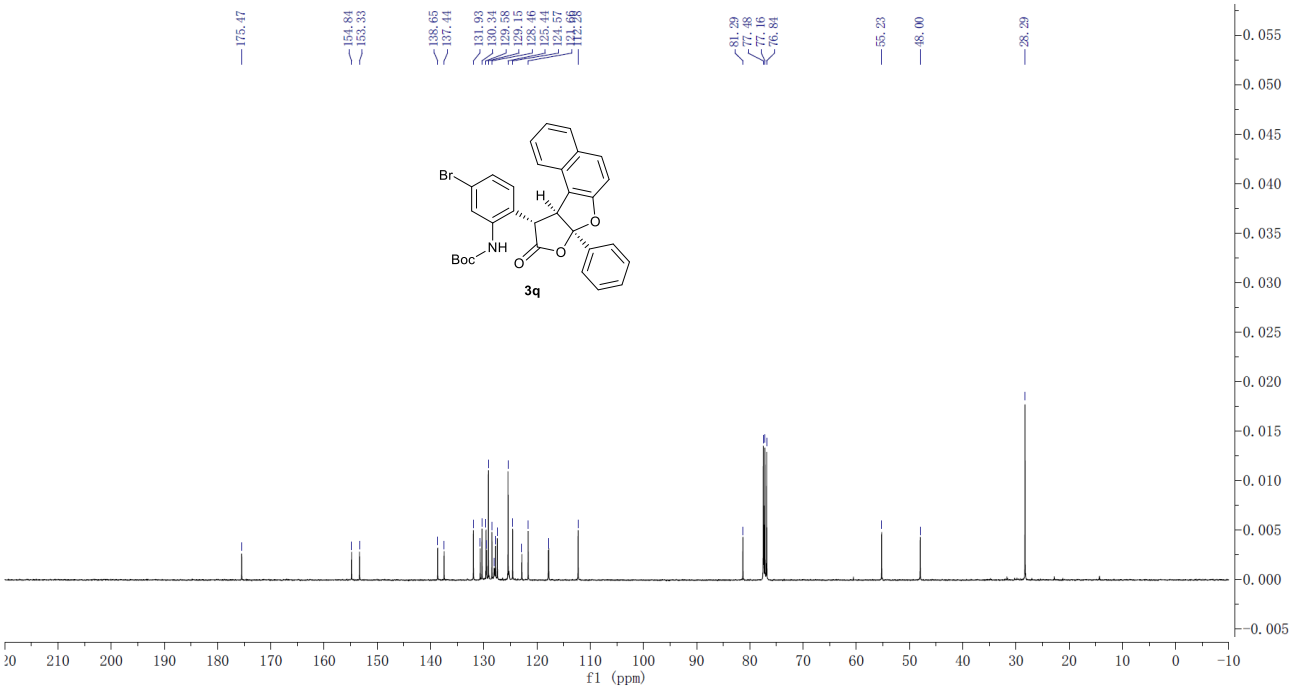
7.927
7.925
7.919
7.599
7.595
7.590
7.587
7.581
7.575
7.519
7.510
7.508
7.501
7.492
7.479
7.478
7.460
7.445
7.428
7.337
7.314
7.213
6.604
6.597
4.651
4.646
4.601
4.595
1.442
Br
NH
Boc
O
H
3q
0.96
2.01
0.98
2.01
4.01
1.01
0.98
0.99
0.97
0.98
1.00
1.00
8.97
f1 (ppm)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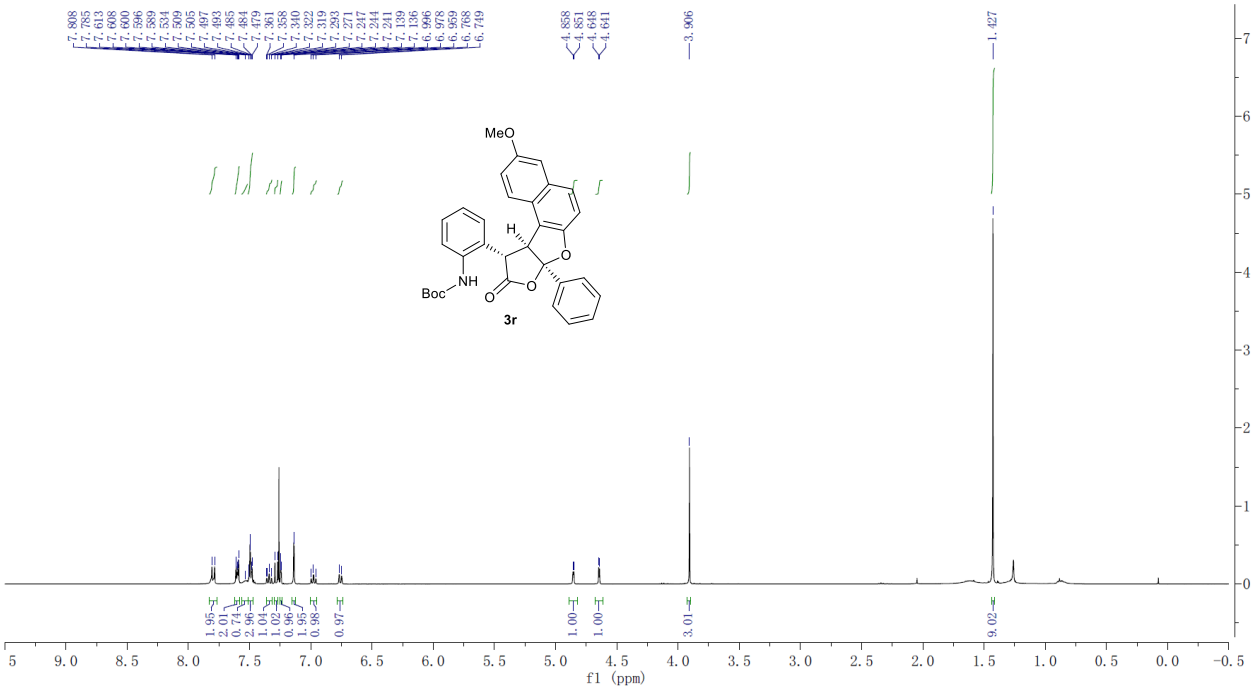
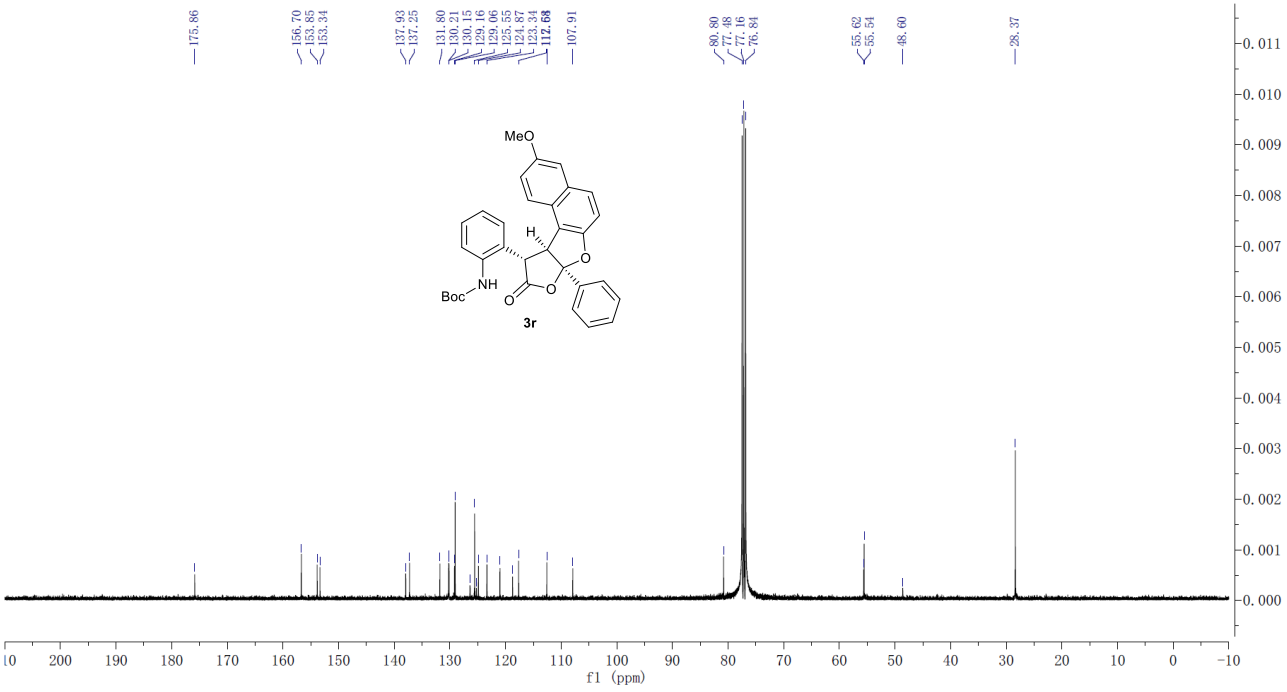
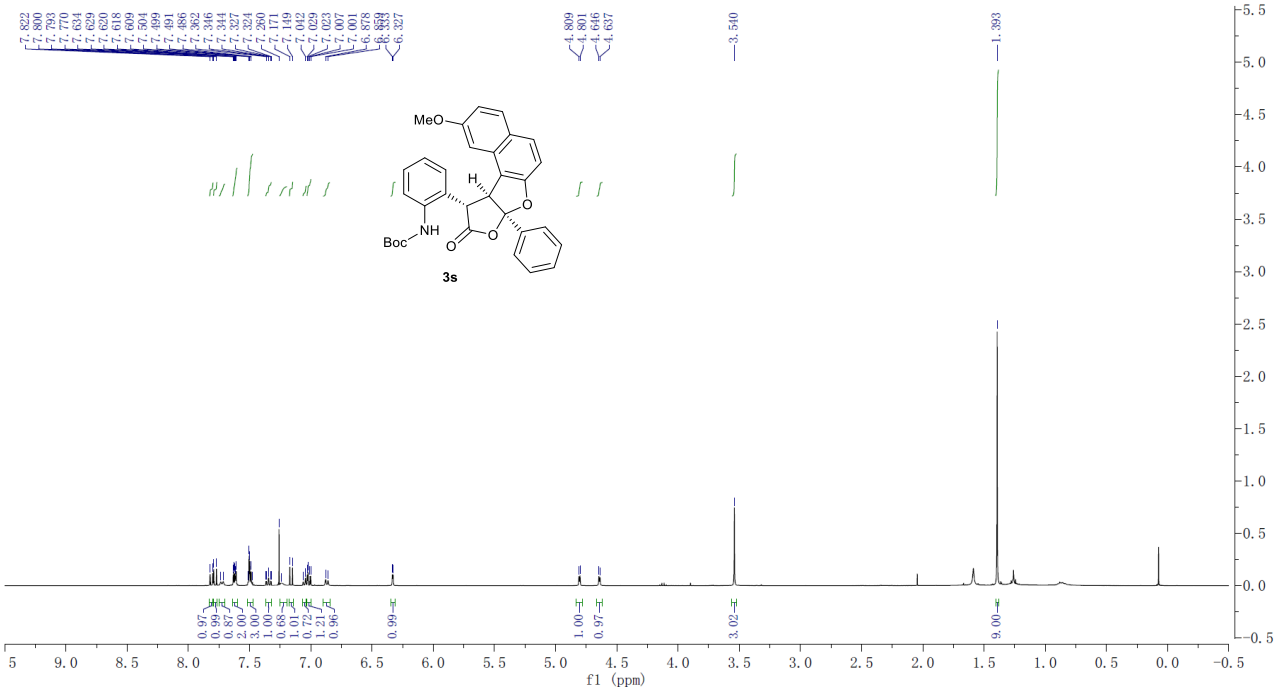
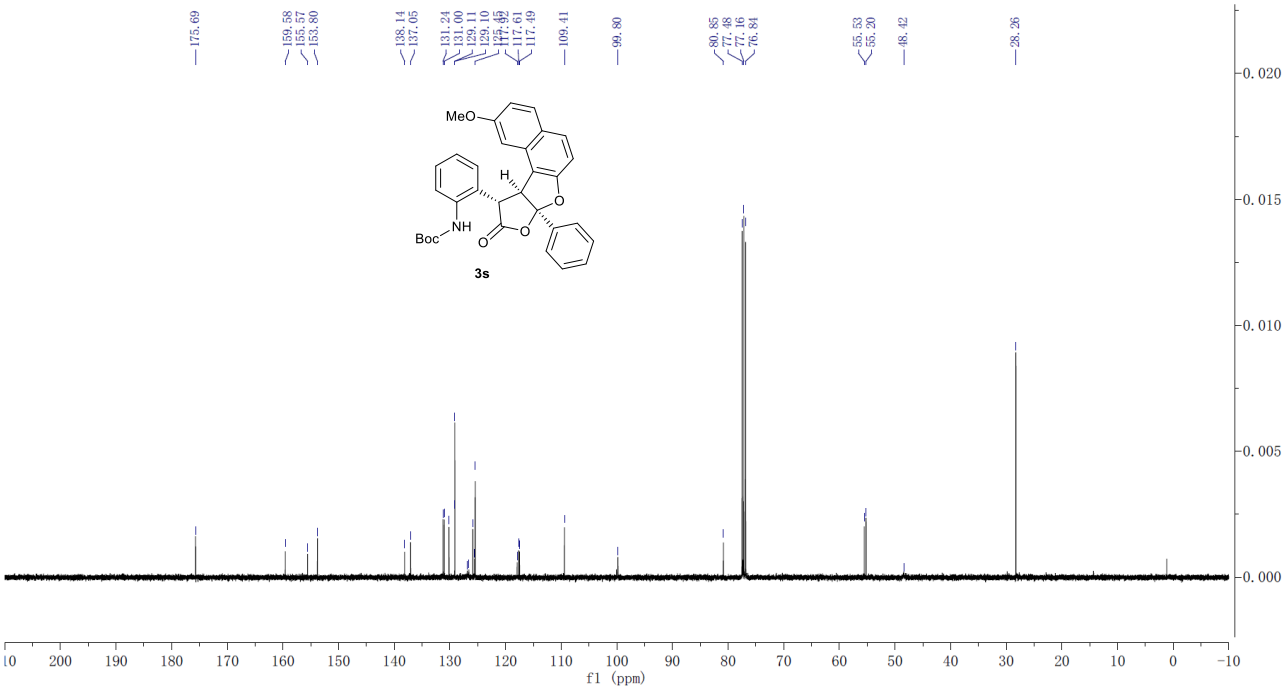
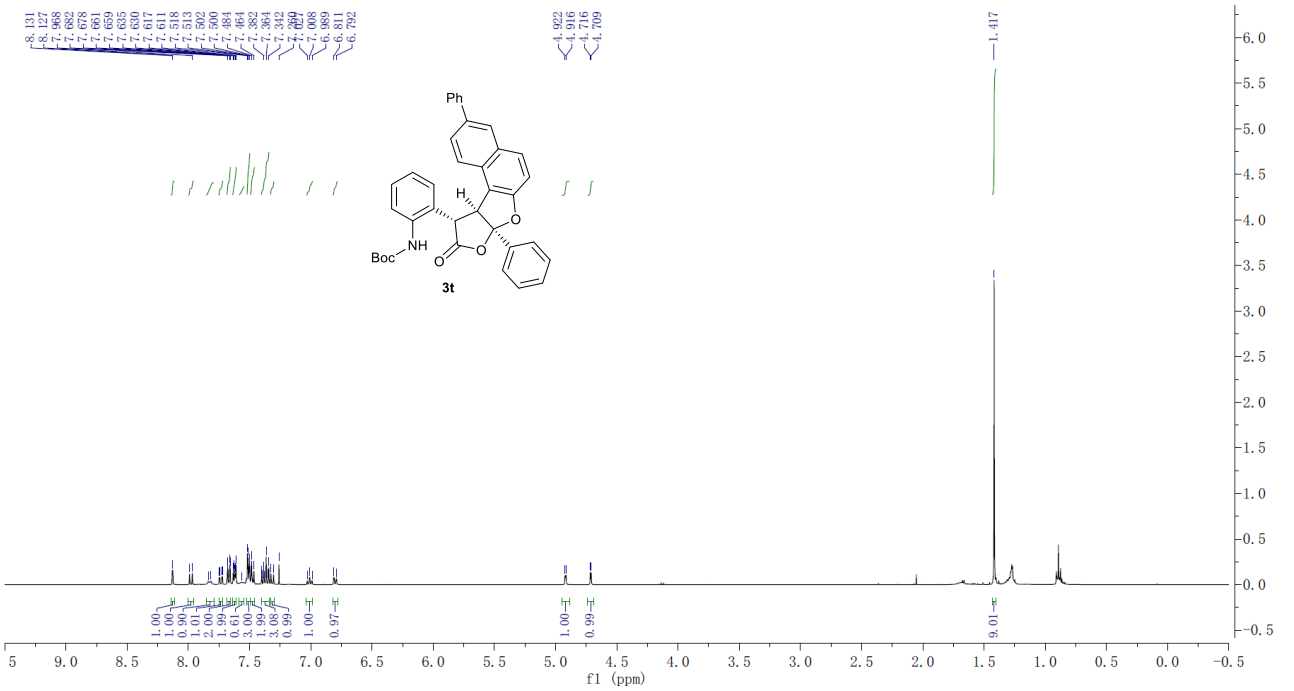
153.33
138.65
137.44
131.93
130.34
129.58
129.15
128.46
125.44
124.57
122.66
112.28
81.29
77.48
77.16
76.84
55.23
48.00
28.29
Br
NH
Boc
O
H
3q
f1 (ppm)


MeO
H
O
NH
Boc
O
O
3r
f1 (ppm)


MeO
H
O
NH
Boc
O
O
3r
f1 (ppm)


MeO
H
NH
Boc
O
3s
f1 (ppm)


MeO
H
NH
Boc
O
3s
f1 (ppm)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8.127
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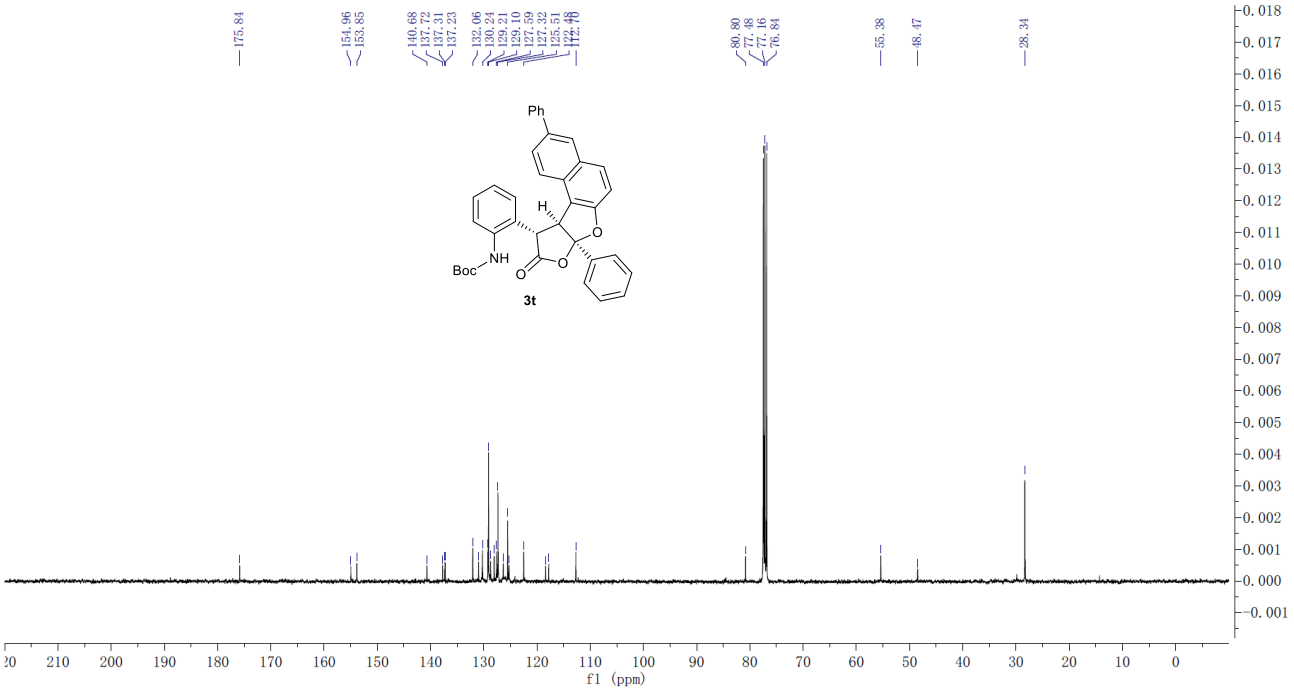
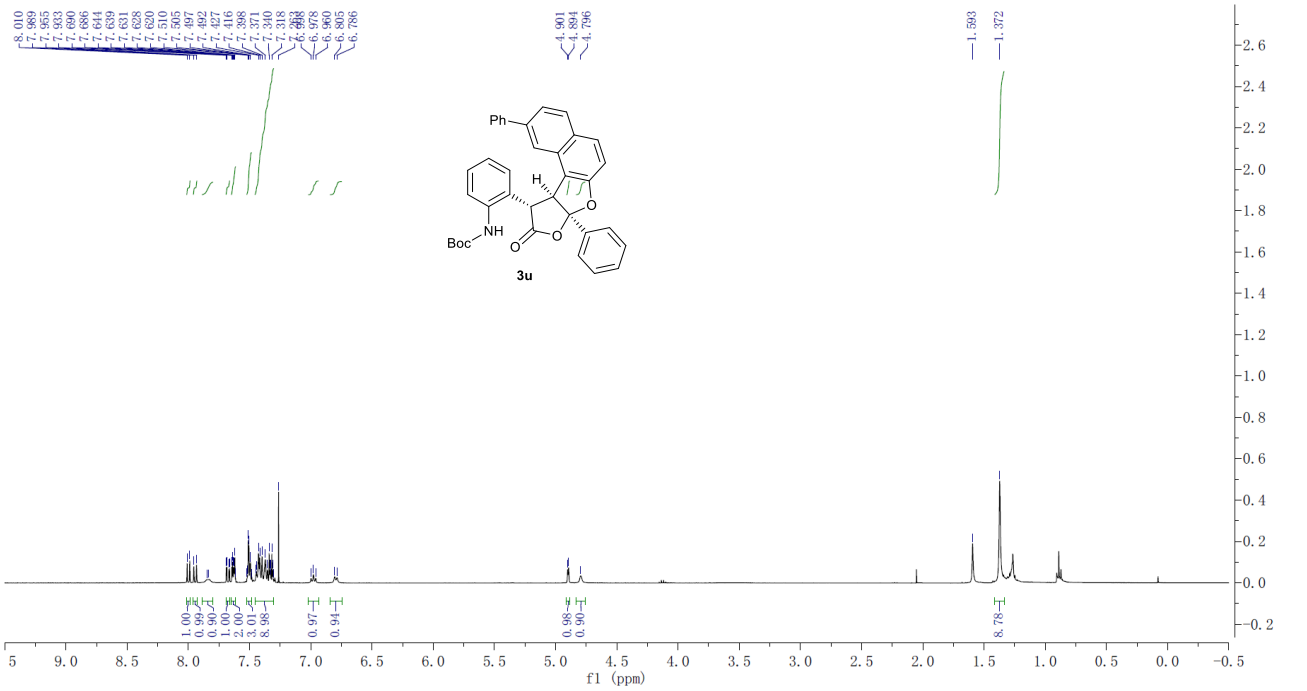
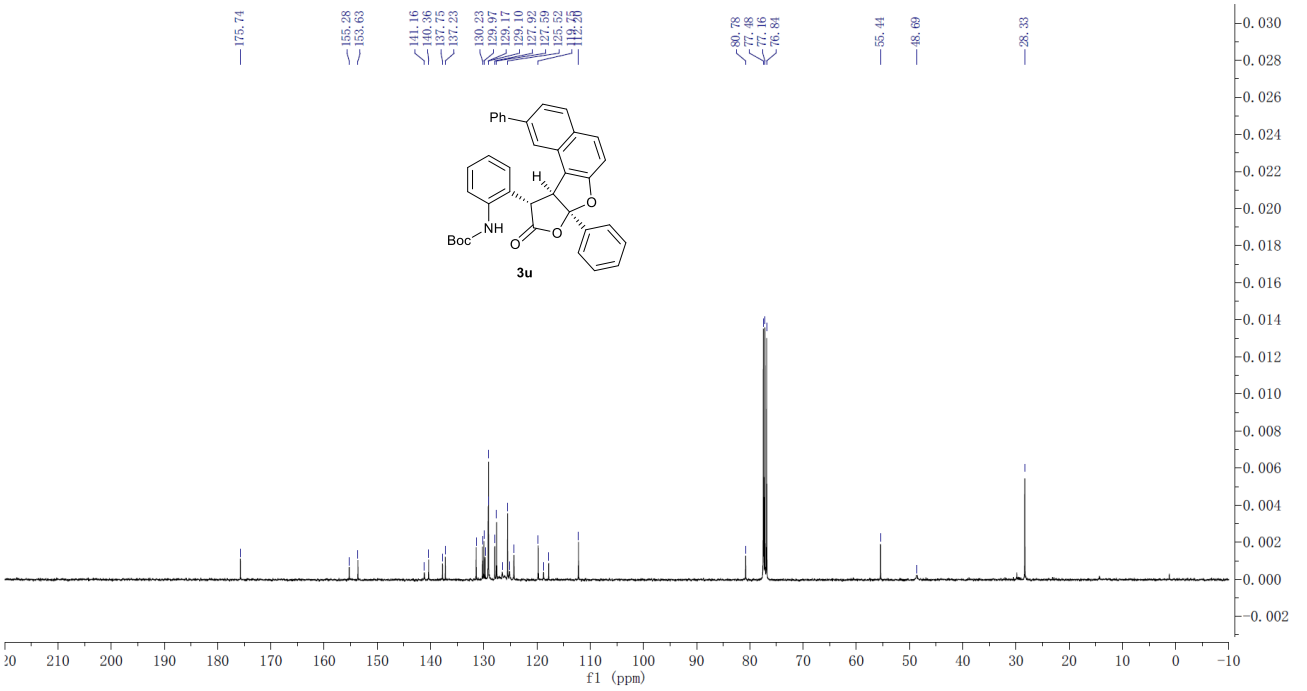
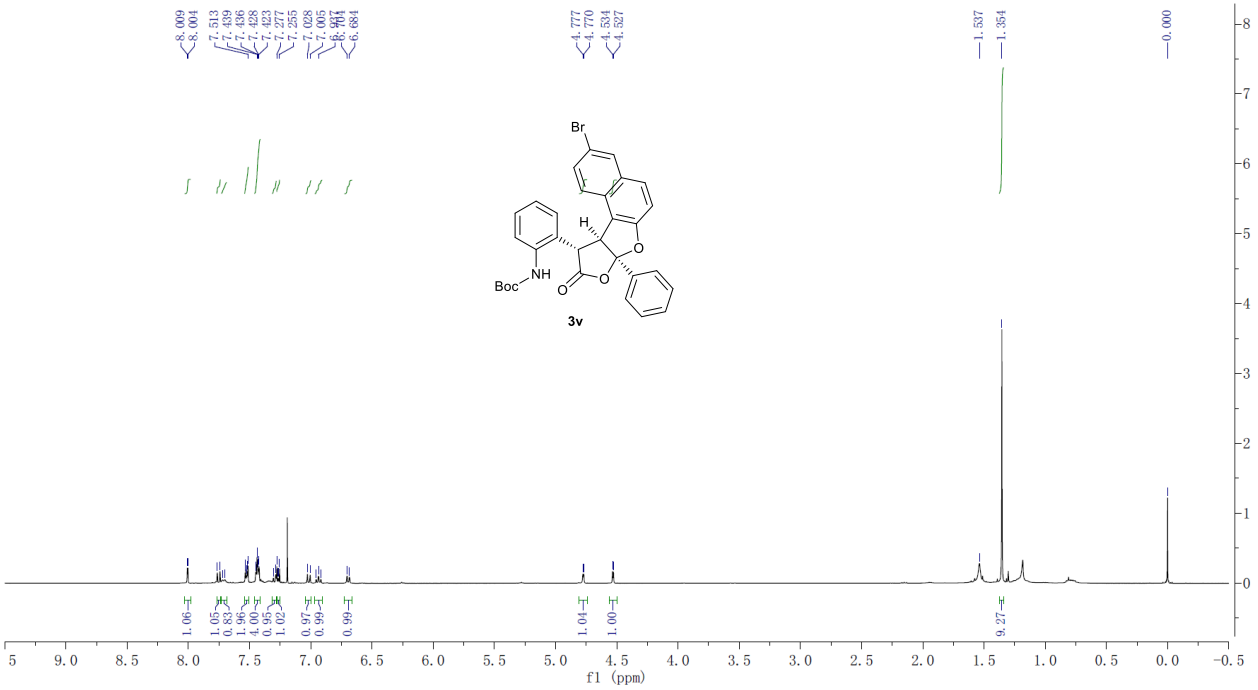
7.682
7.678
7.661
7.659
7.635
7.630
7.617
7.611
7.518
7.513
7.502
7.500
7.484
7.464
7.382
7.364
7.342
7.289
7.008
6.989
6.811
6.792
4.922
4.916
4.716
4.709
1.417
Ph
H
O
O
O
NH
Boc
3t
f1 (ppm)


175.84
154.96
153.85
140.68
137.72
137.31
137.23
132.06
130.24
129.21
129.10
127.59
127.32
125.51
122.48
122.40
80.80
77.48
77.16
76.84
55.38
48.47
28.34
Ph
H
O
O
O
NH
Boc
3t
f1 (ppm)


Ph
H
O
NH
Boc
O
O
3u
f1 (ppm)


Ph
H
O
NH
Boc
O
O
3u
f1 (ppm)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8.004
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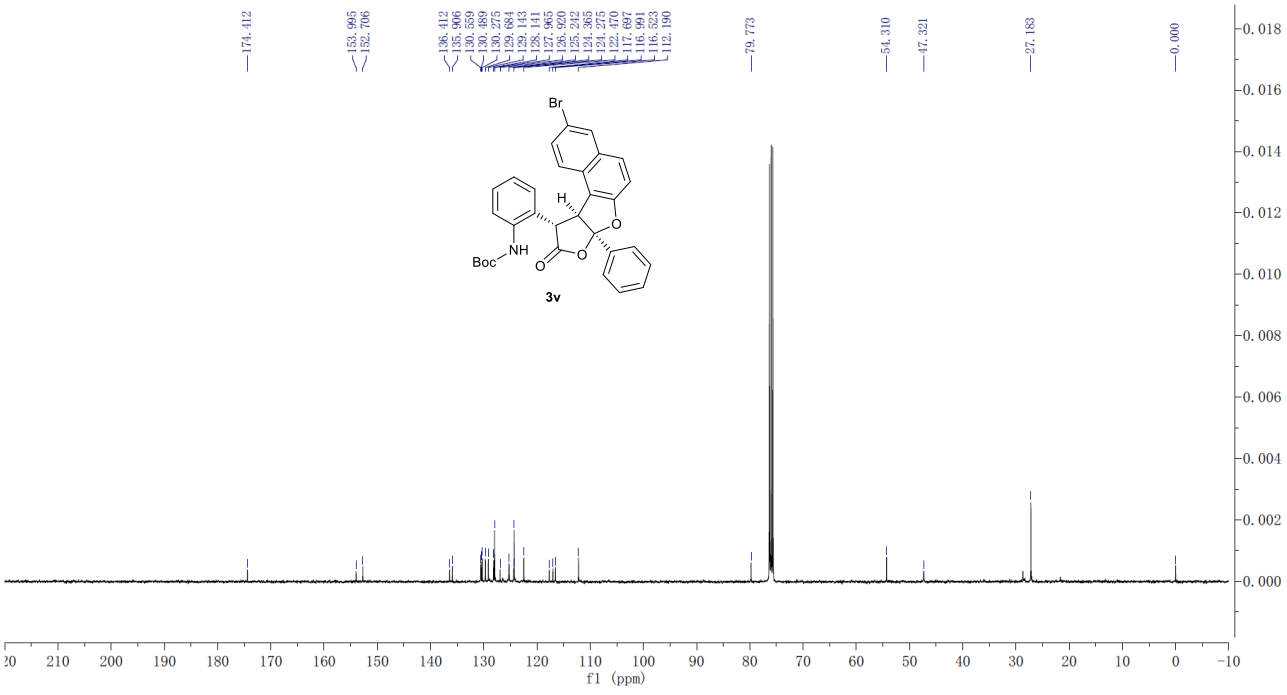
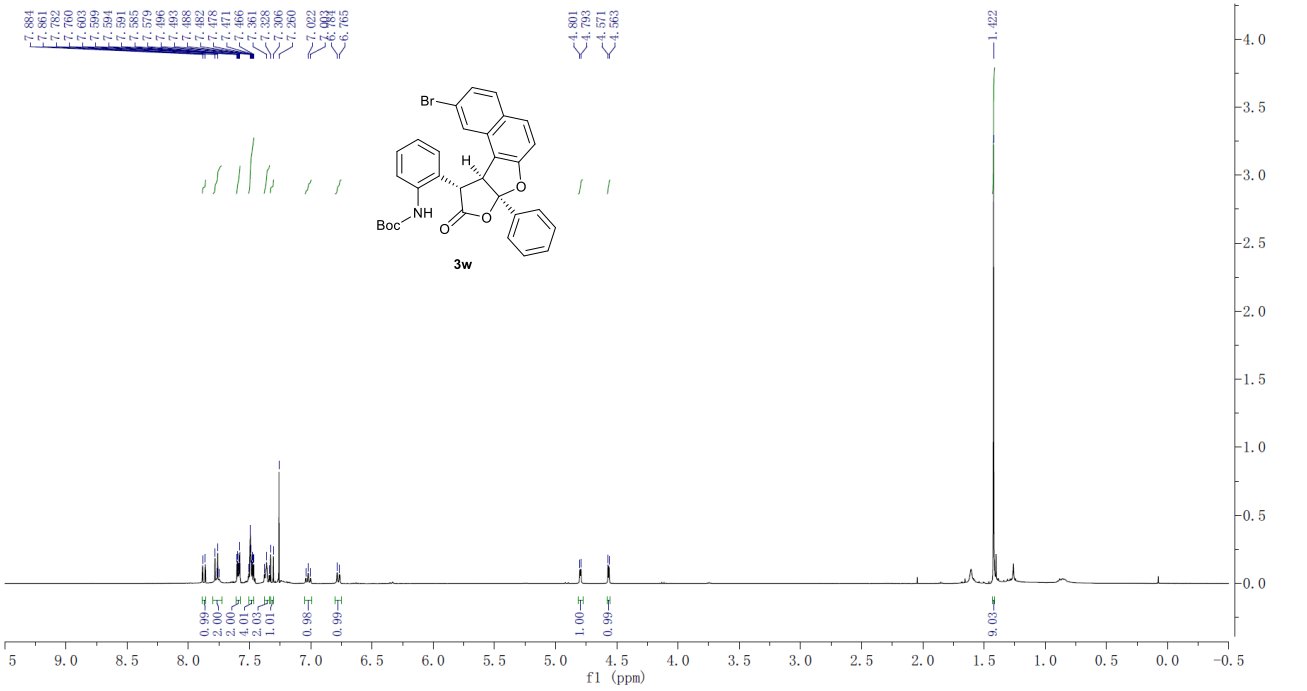
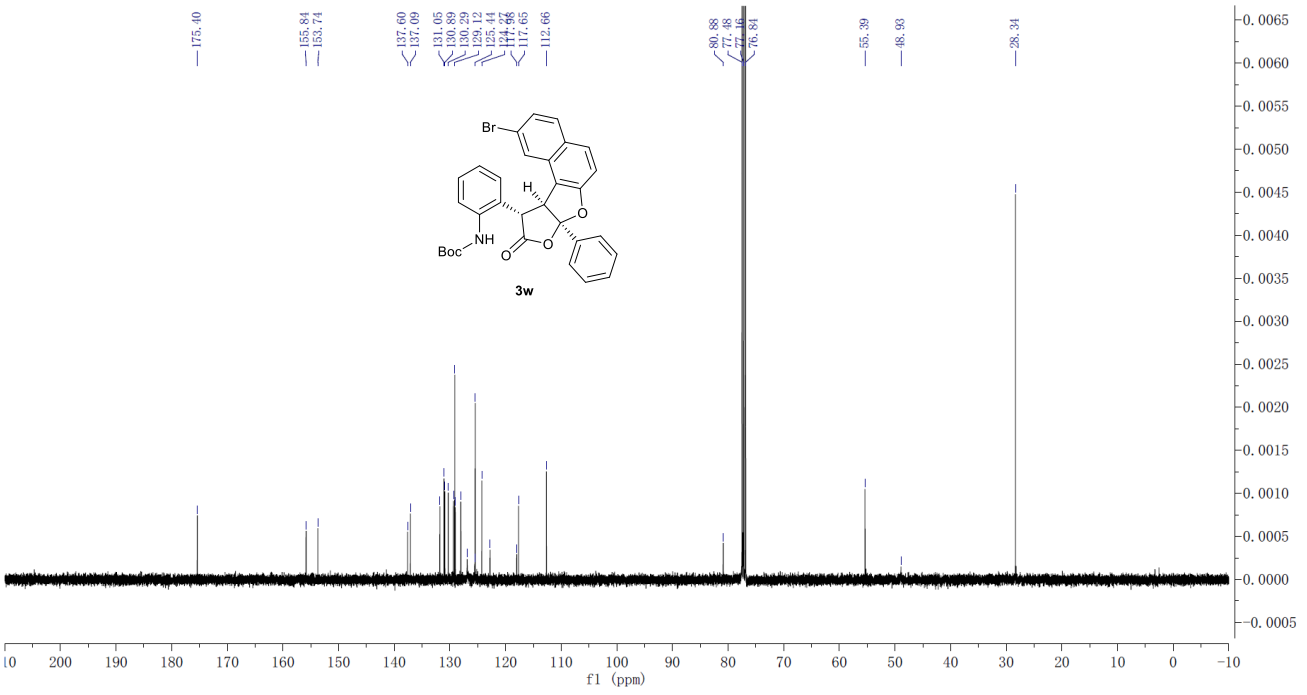
7.439
7.436
7.428
7.423
7.277
7.255
7.028
7.005
6.947
6.944
6.684
4.777
4.770
4.534
4.527
1.537
1.354
0.000
Br
H
O
NH
Boc
O
O
3v
1.06
1.05
0.83
1.96
4.00
0.95
1.02
0.97
0.99
0.99
1.04
1.00
9.27
f1 (ppm)


174.412
153.995
152.706
136.412
135.906
130.559
130.489
130.275
129.884
129.143
128.141
127.965
126.920
125.242
124.365
124.275
122.470
117.697
116.991
116.523
112.190
79.773
54.310
47.321
27.183
0.000
Br
H
O
NH
Boc
O
O
3v
f1 (ppm)


7.884
7.861
7.782
7.760
7.603
7.599
7.594
7.591
7.585
7.579
7.496
7.493
7.488
7.482
7.478
7.471
7.466
7.361
7.328
7.306
7.260
7.022
7.003
6.784
6.765
4.801
4.793
4.571
4.563
1.422
Br
H
O
NH
Boc
O
O
3w
0.99
2.00
2.00
4.03
2.01
1.01
0.98
0.99
1.00
0.99
9.03
f1 (ppm)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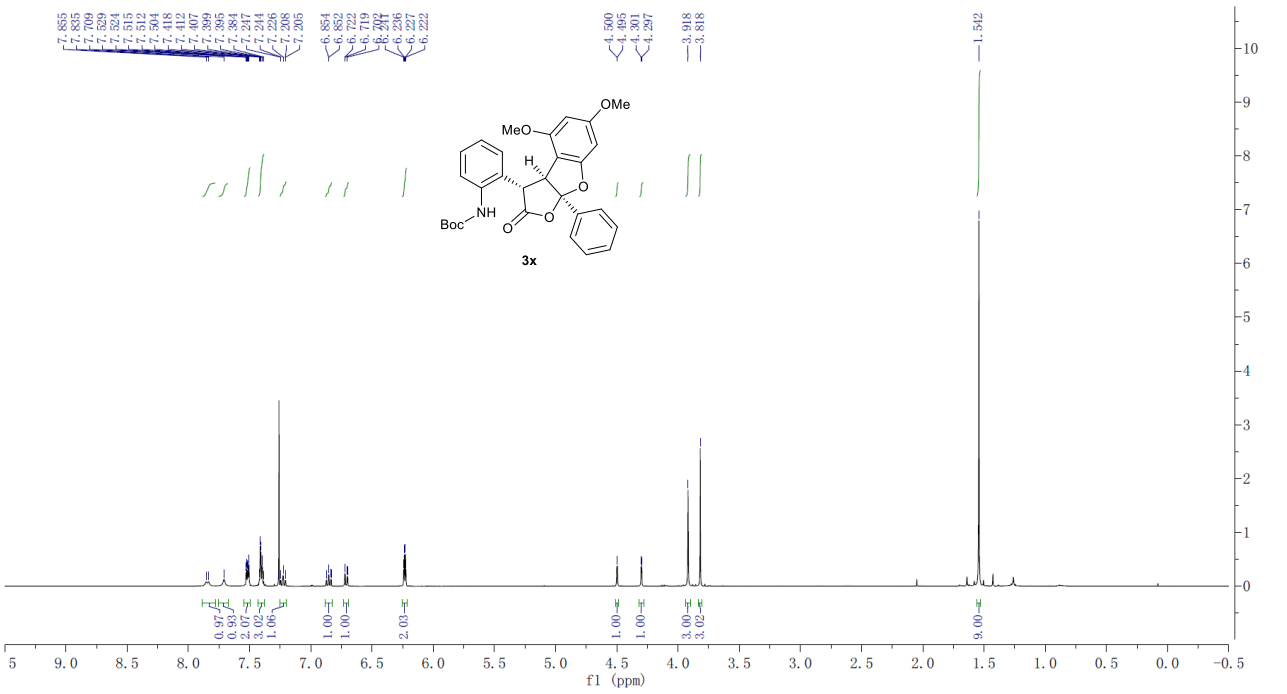
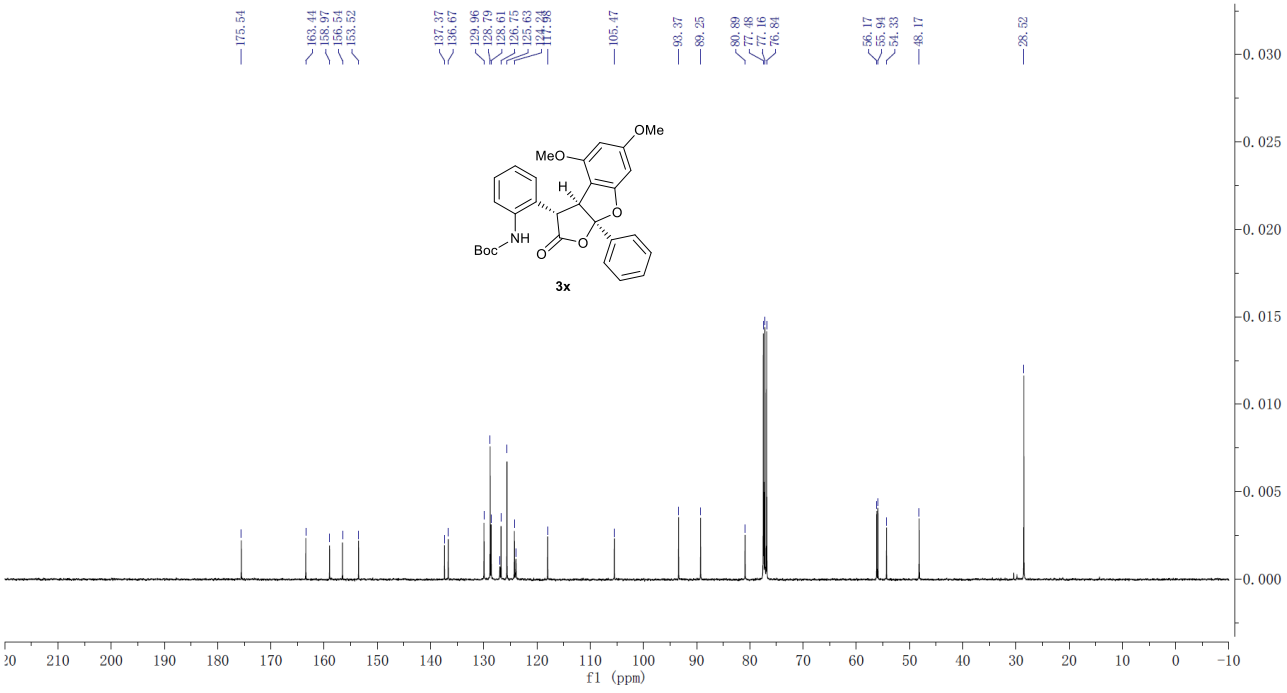
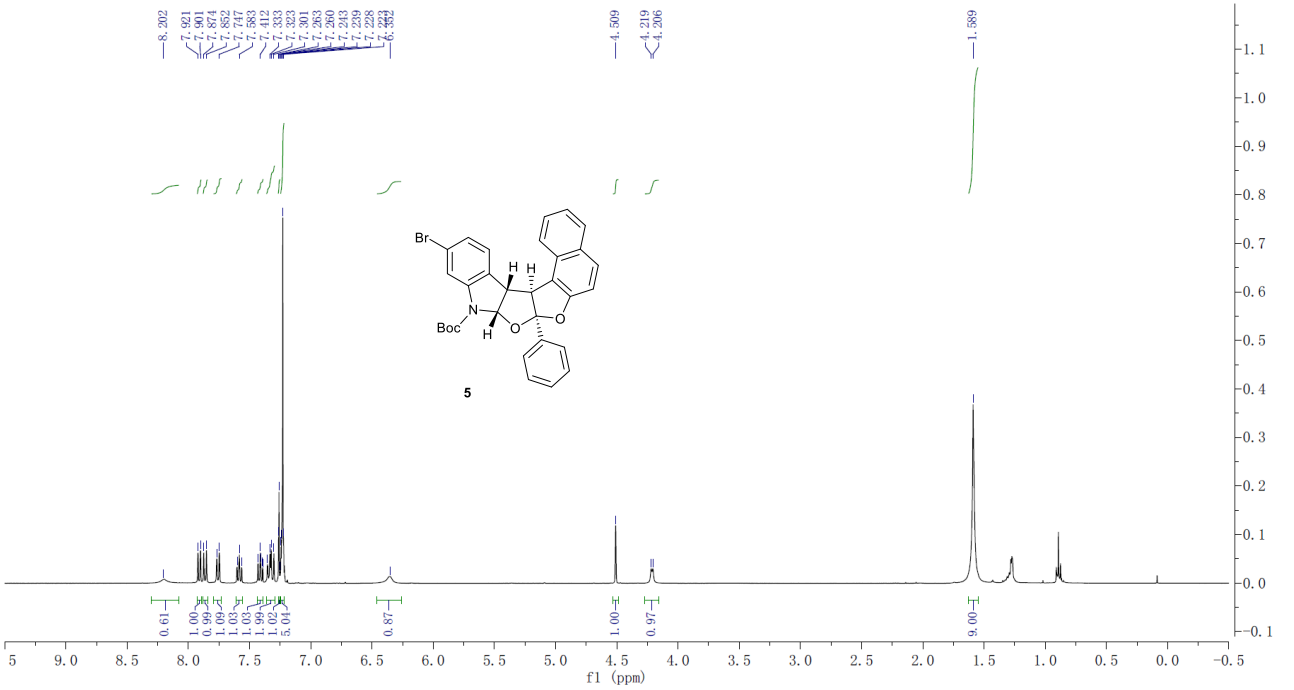
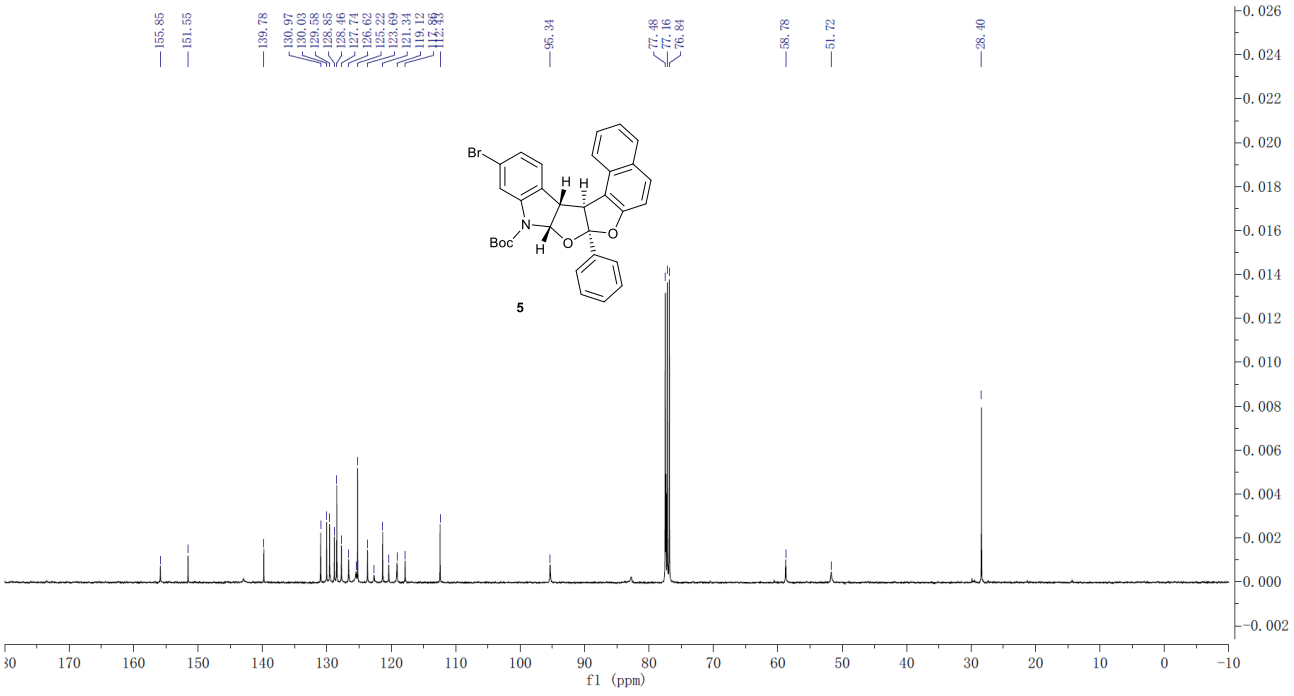
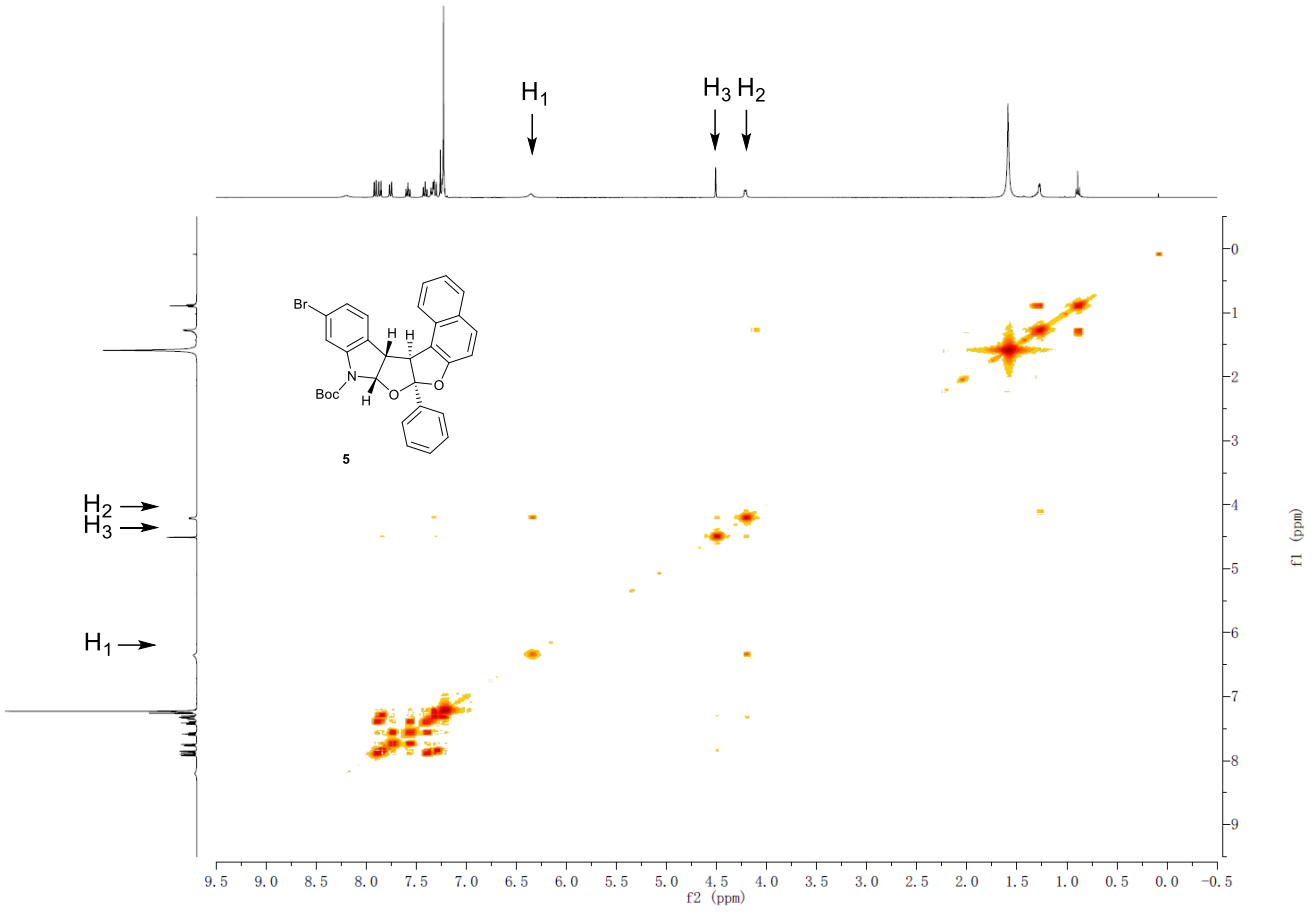
153.74
137.60
137.09
131.05
130.89
130.29
129.12
125.44
124.27
124.08
117.65
112.66
80.88
77.48
77.16
76.84
55.39
48.93
28.34
Br
H
O
NH
Boc
O
O
3w
f1 (ppm)


OMe
MeO
H
O
NH
Boc
O
O
3x
f1 (ppm)


OMe
MeO
H
O
NH
Boc
O
O
3x
f1 (ppm)

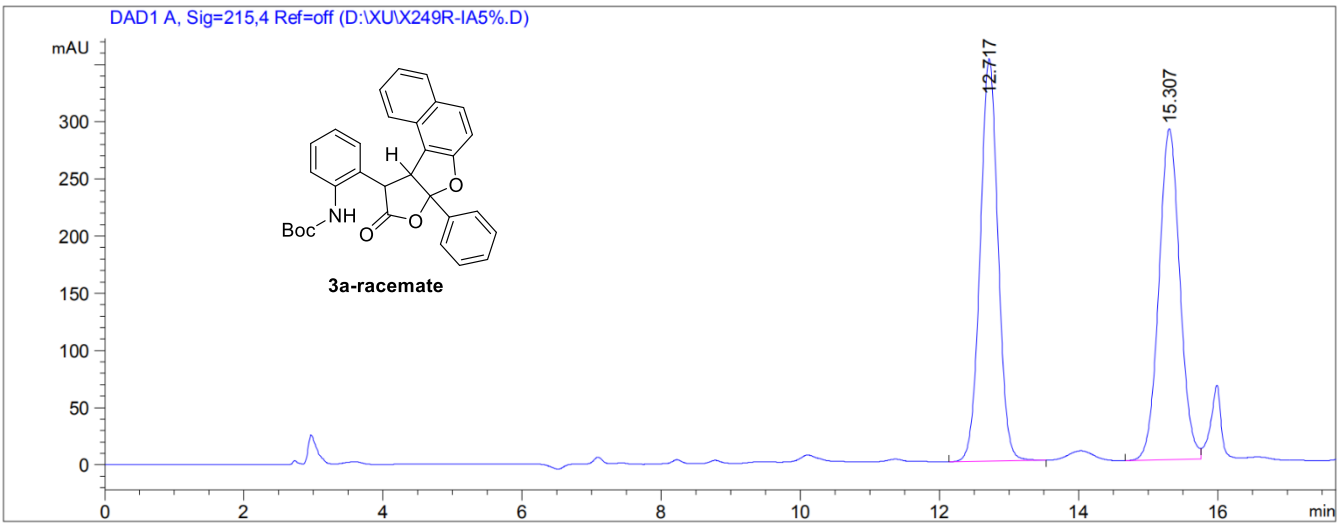

8.202
7.921
7.901
7.874
7.852
7.747
7.583
7.412
7.333
7.323
7.301
7.263
7.260
7.243
7.239
7.228
4.509
4.219
4.206
1.589
Br
H
H
N
Boc
H
O
O
5
0.61
1.00
0.99
1.09
1.03
1.03
1.99
1.02
5.04
0.87
1.00
0.97
9.00
f1 (ppm)


155.85
151.55
139.78
130.97
130.03
129.58
128.85
128.46
127.74
126.62
125.22
123.69
121.34
119.12
95.34
77.48
77.16
76.84
58.78
51.72
28.40
Br
H
H
N
Boc
H
O
O
5
f1 (ppm)



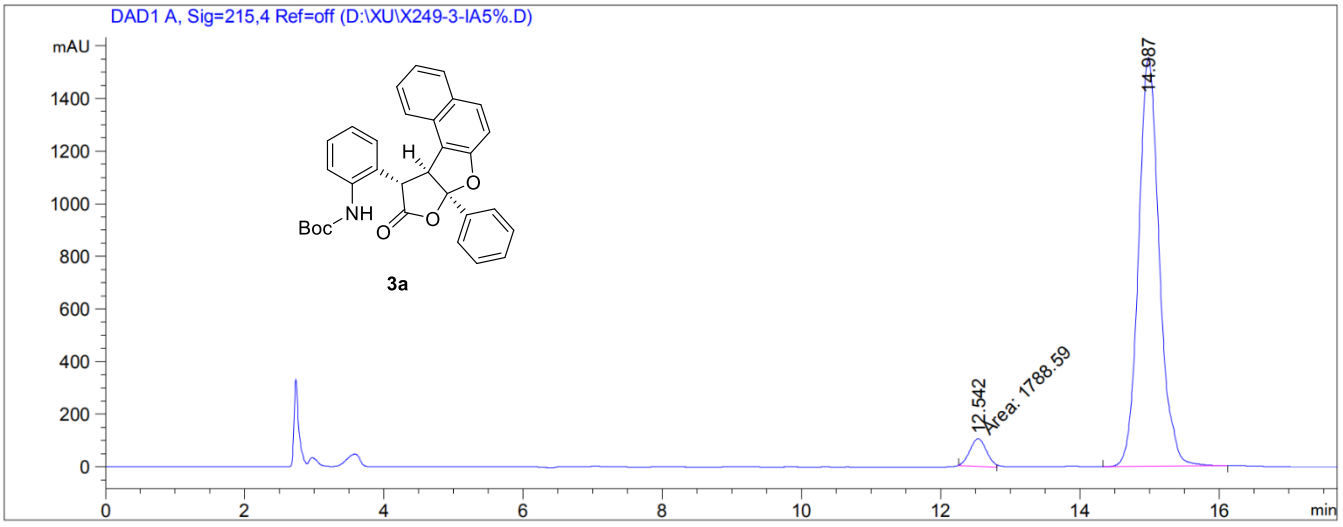
FigureS1. 2D-COSY Spectrum and Structure Assignment of Compound **6**.

7. HPLC Chromatography



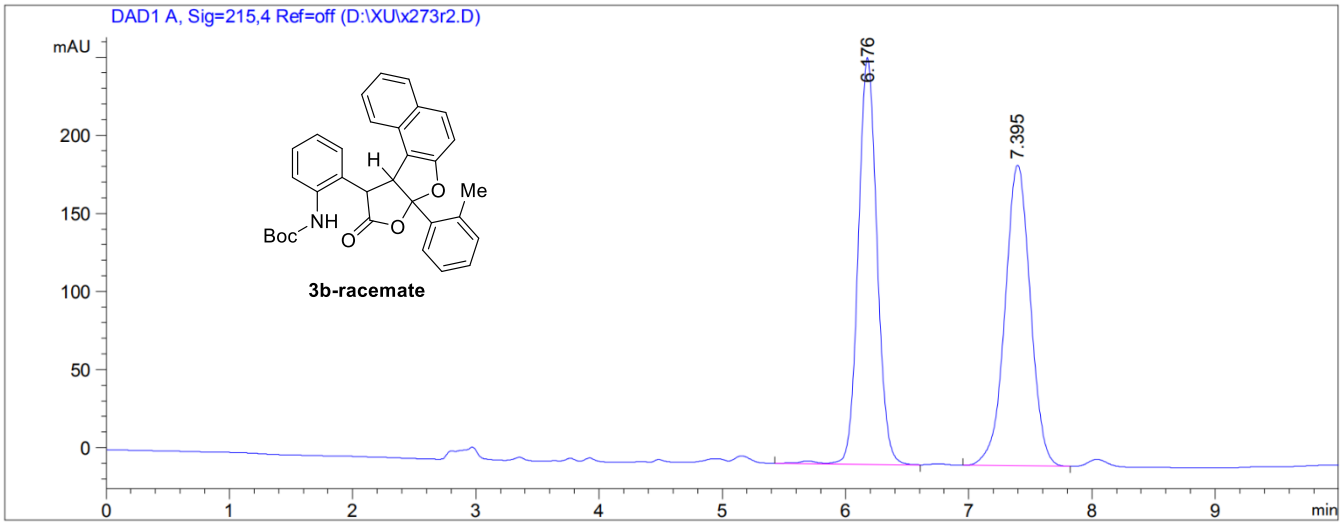
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.717	BB	0.2760	6274.39502	351.89288	50.8810
2	15.307	BV	0.3222	6057.12207	289.36621	49.1190



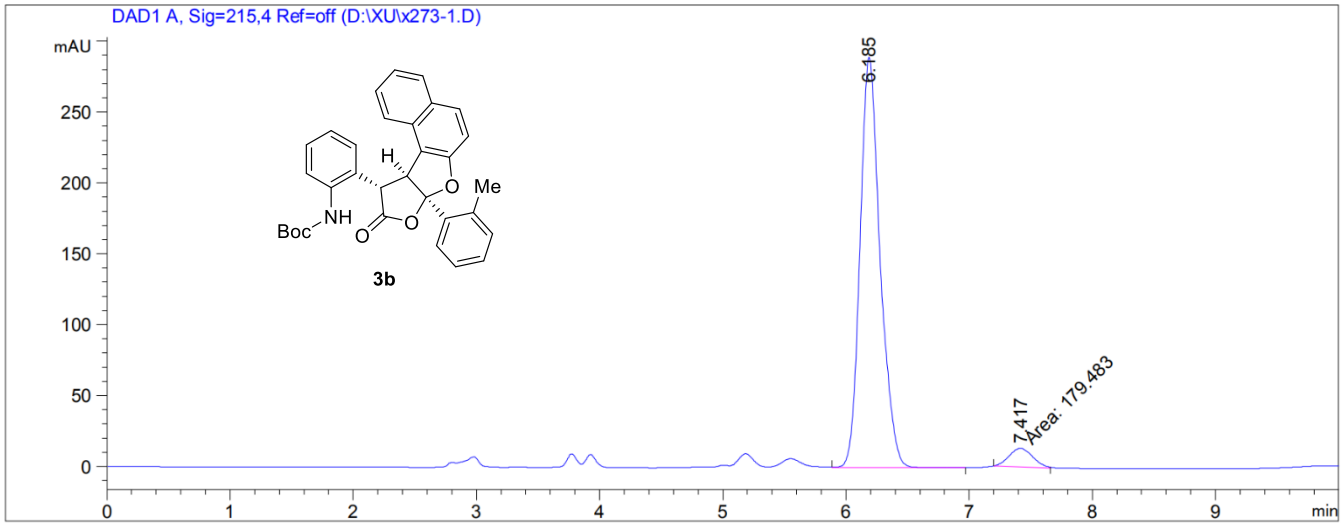
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.542	MM	0.2799	1788.59106	106.49339	5.2539
2	14.987	BB	0.3181	3.22548e4	1554.18201	94.7461



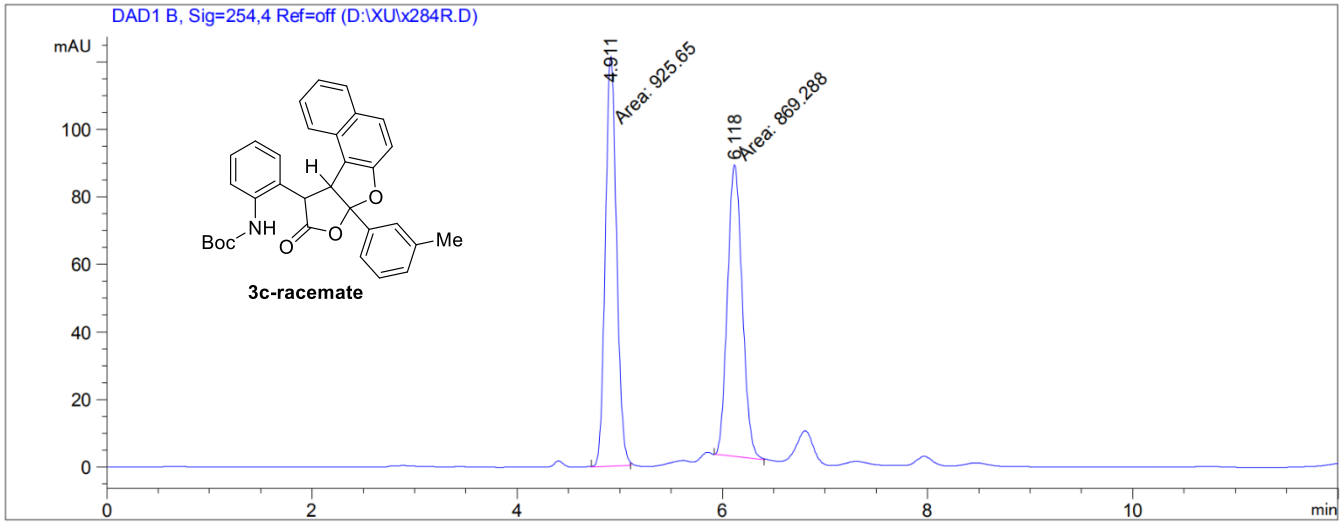
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.176	VB R	0.1624	2751.32153	260.57388	49.9351
2	7.395	BB	0.2230	2758.47485	192.67719	50.0649



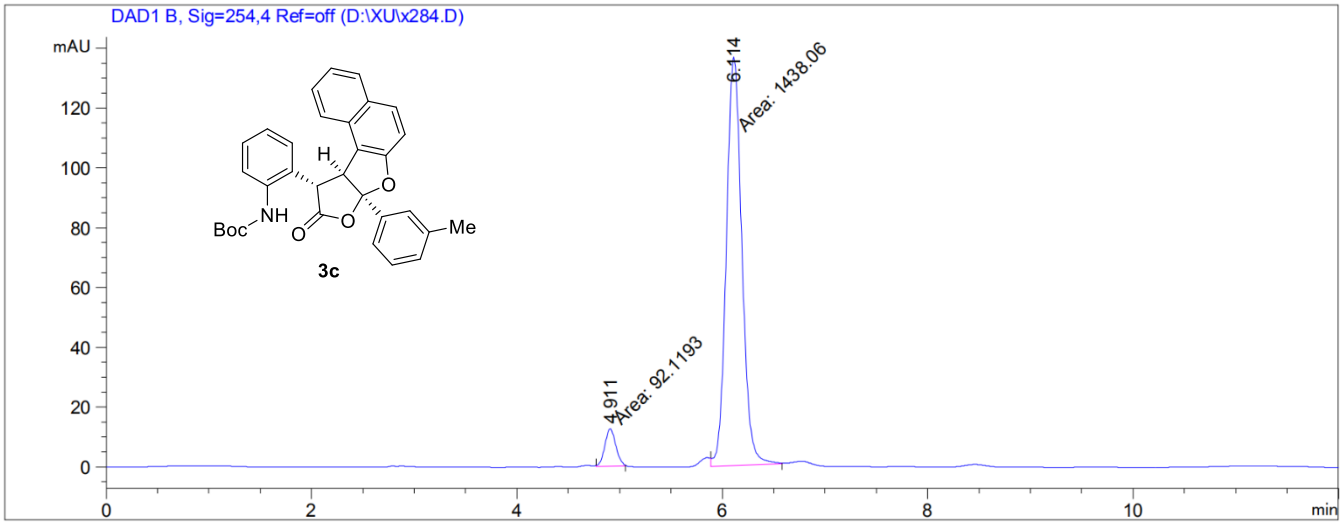
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.185	VB	0.1722	3280.83032	289.44366	94.8131
2	7.417	MM	0.2258	179.48282	13.24993	5.1869



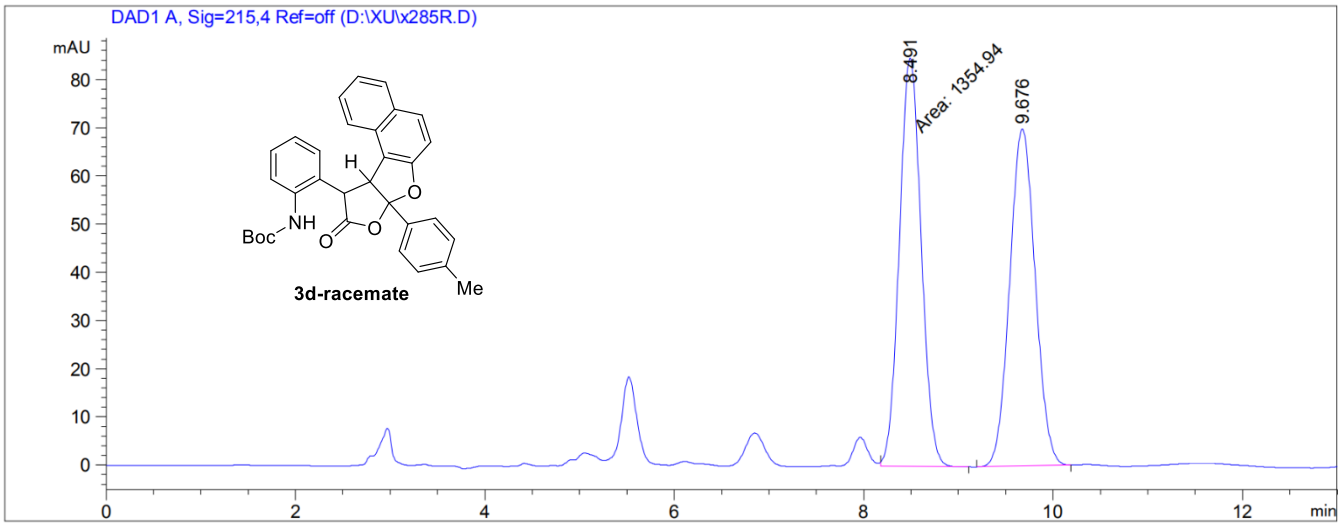
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.911	MM	0.1269	925.64954	121.53663	51.5700
2	6.118	MM	0.1676	869.28821	86.46539	48.4300



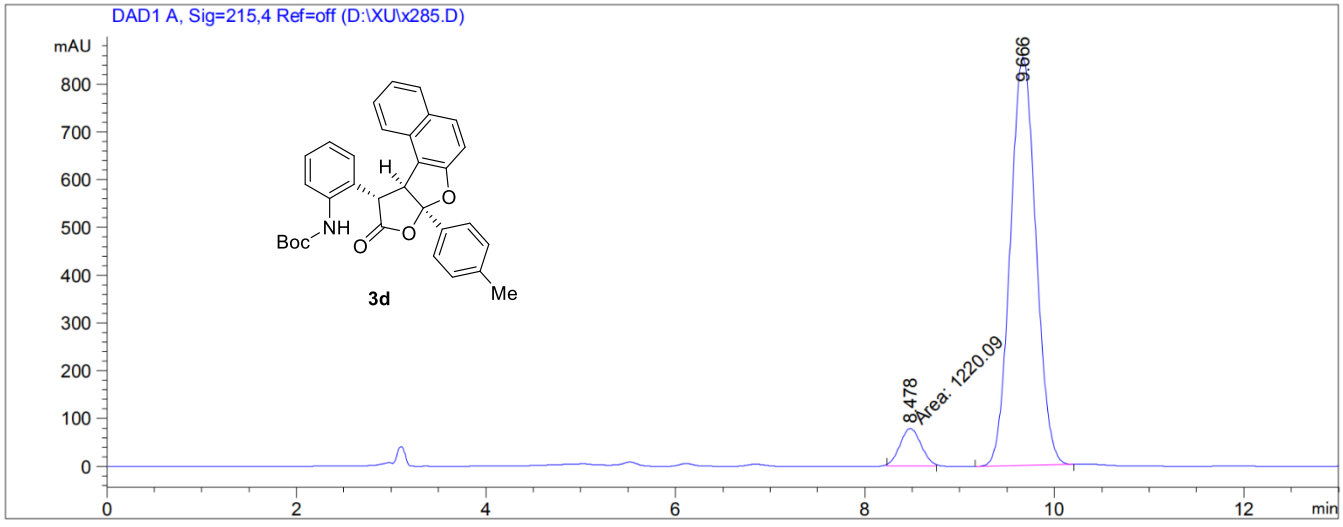
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.911	MM	0.1233	92.11935	12.45011	6.0202
2	6.114	FM	0.1753	1438.05725	136.70586	93.9798



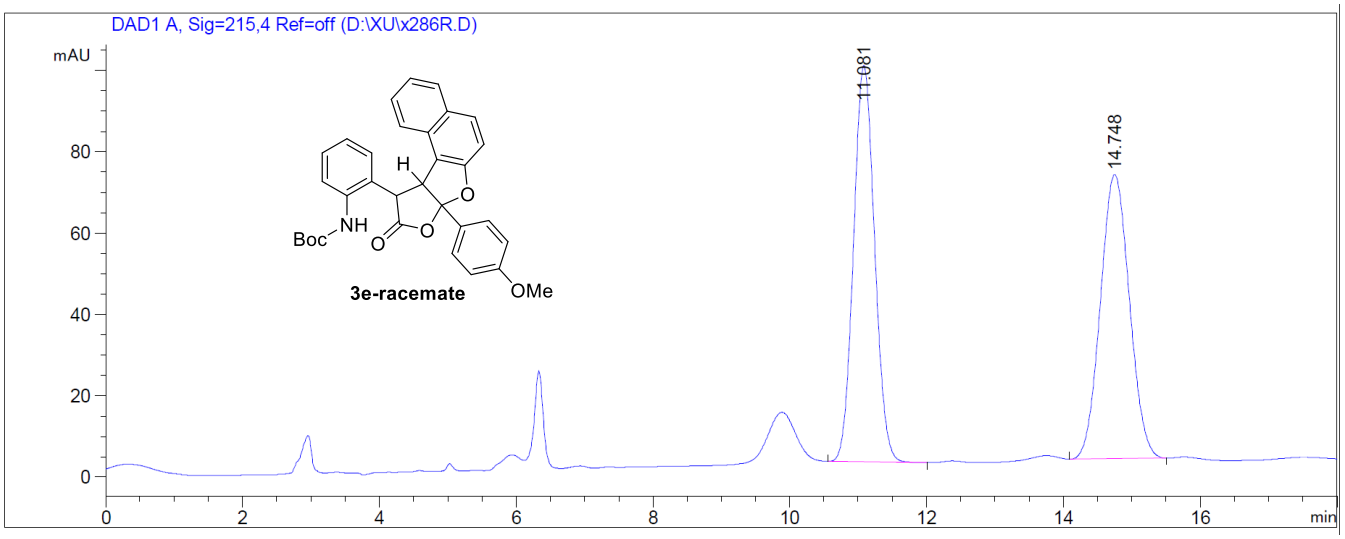
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.491	FM	0.2665	1354.94287	84.73129	50.8384
2	9.676	BB	0.2924	1310.25220	69.97993	49.1616



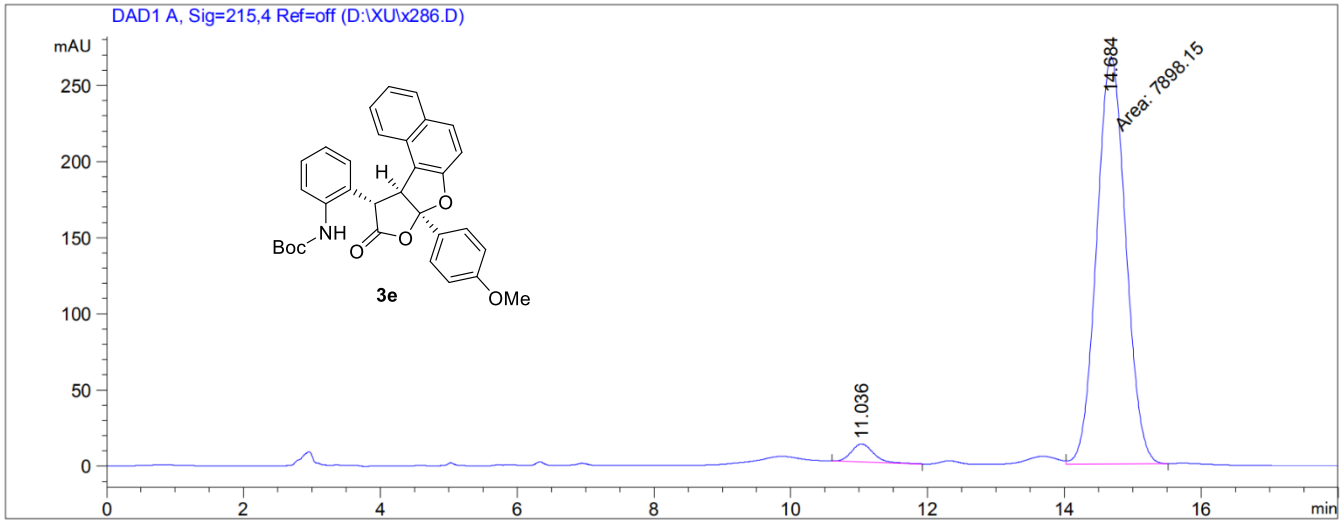
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.478	MM	0.2581	1220.09192	78.78511	7.0683
2	9.666	BB	0.2928	1.60414e4	855.25653	92.9317



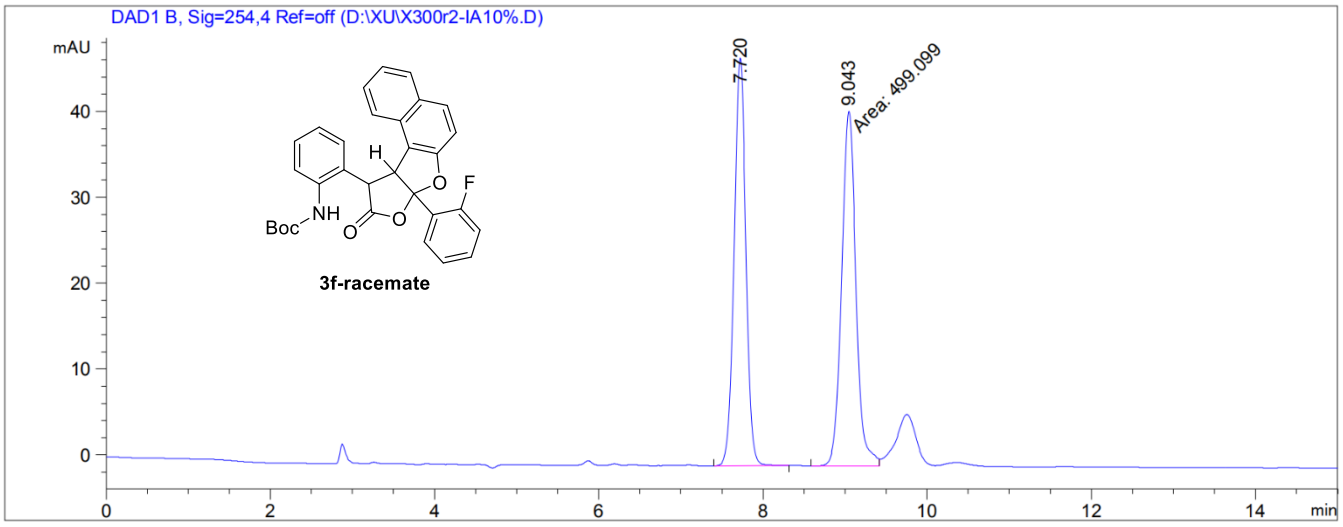
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.081	BB	0.3335	2083.72070	97.43663	50.3213
2	14.748	BB	0.4616	2057.11011	69.83942	49.6787



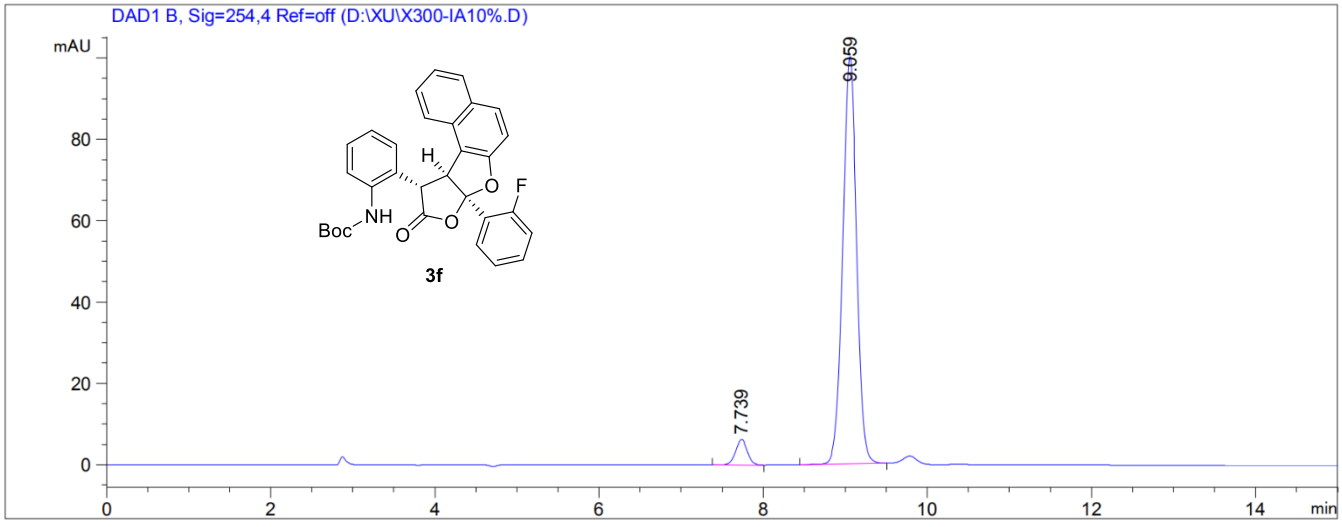
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.036	BB	0.3409	263.31558	11.86439	3.2263
2	14.684	FM	0.4925	7898.15088	267.29187	96.7737



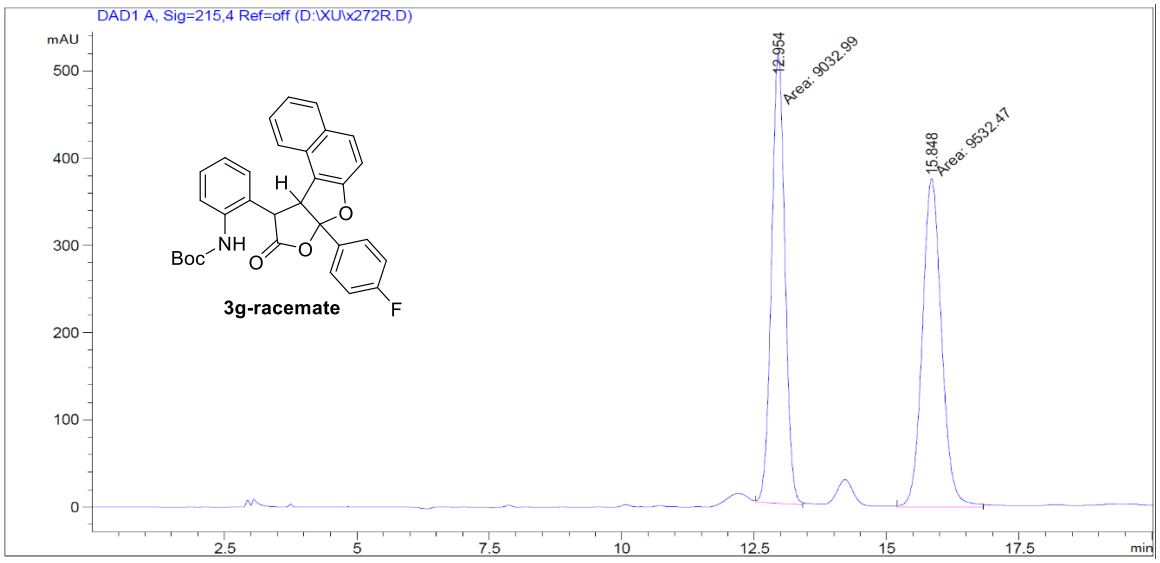
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.720	BB	0.1542	472.86539	47.48503	48.6505
2	9.043	MF	0.2014	499.09872	41.30740	51.3495



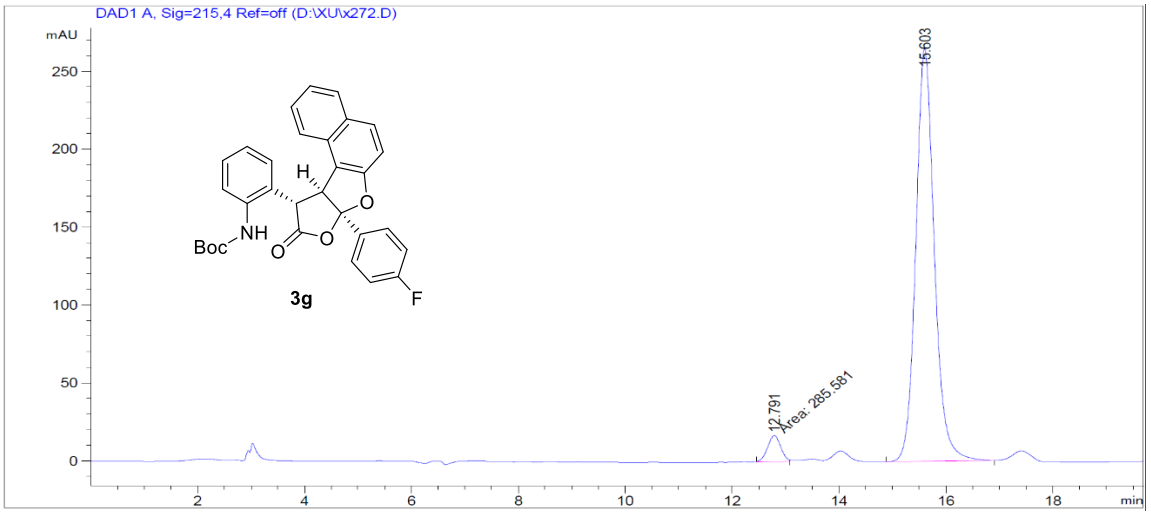
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.739	BB	0.1523	62.84294	6.30304	5.0704
2	9.059	BB	0.1810	1176.55383	100.18233	94.9296



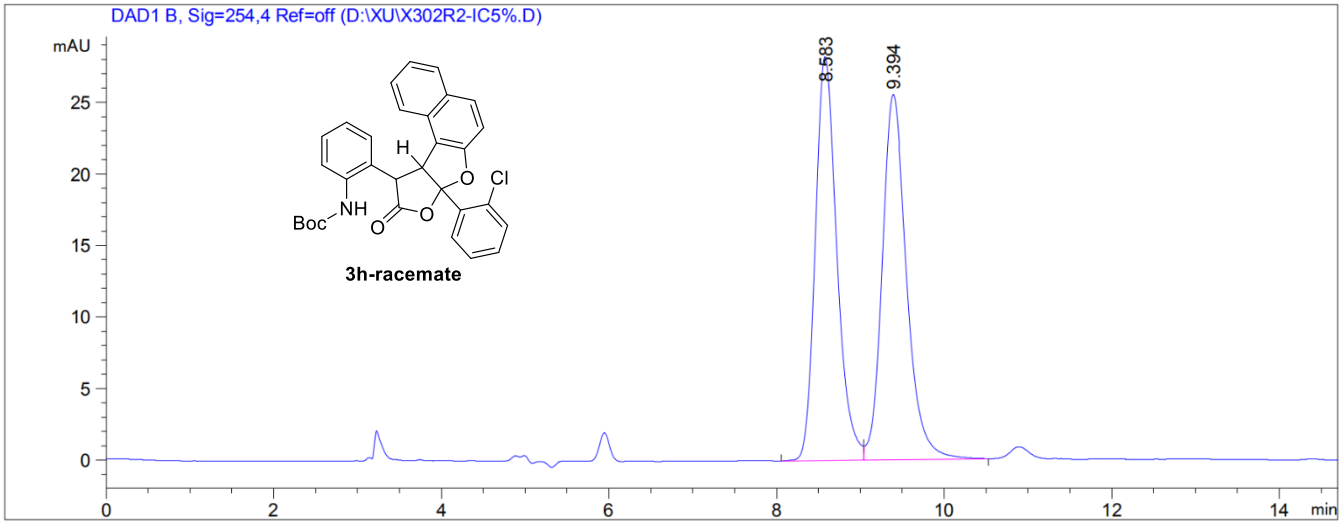
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.954	MM	0.2925	9032.99219	514.65948	48.6548
2	15.848	MM	0.4220	9532.47070	376.46310	51.3452



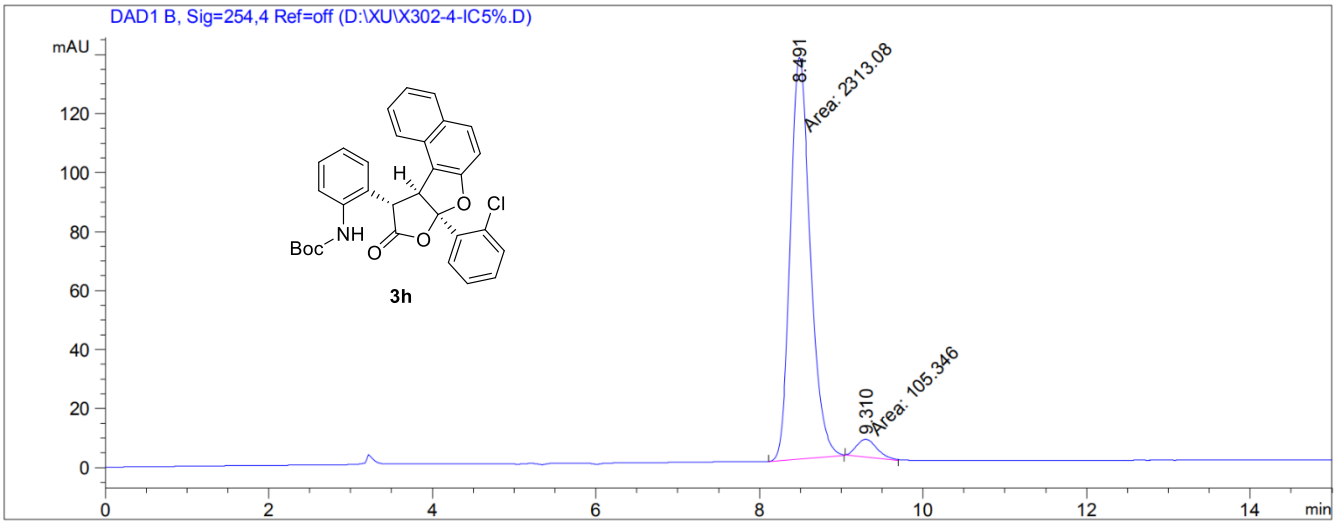
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.791	MM	0.2846	285.58087	16.72608	4.2898
2	15.603	BB	0.3667	6371.60938	264.79294	95.7102



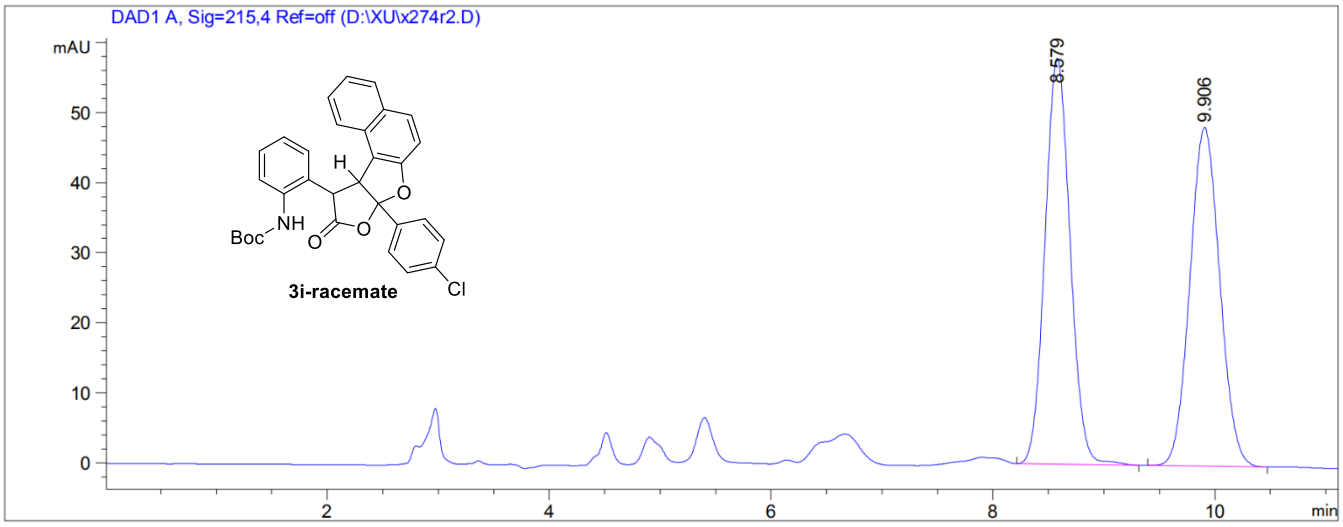
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.583	BV	0.2735	501.85040	28.21617	49.1208
2	9.394	VB	0.3095	519.81628	25.53336	50.8792



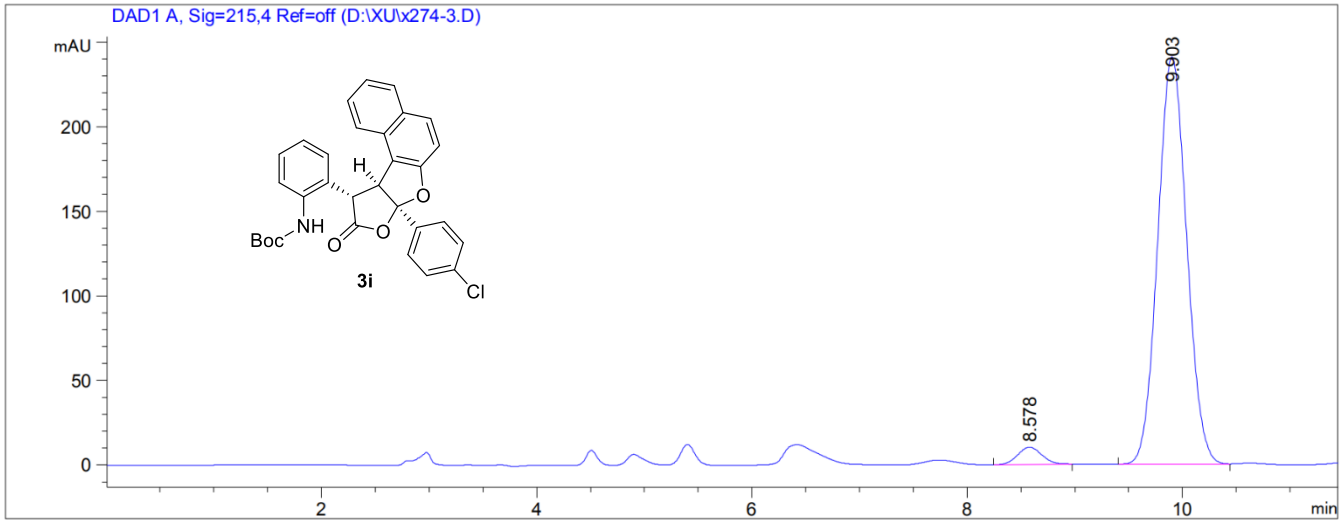
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.491	MM	0.2831	2313.07520	136.15459	95.6440
2	9.310	MM	0.2932	105.34649	5.98878	4.3560



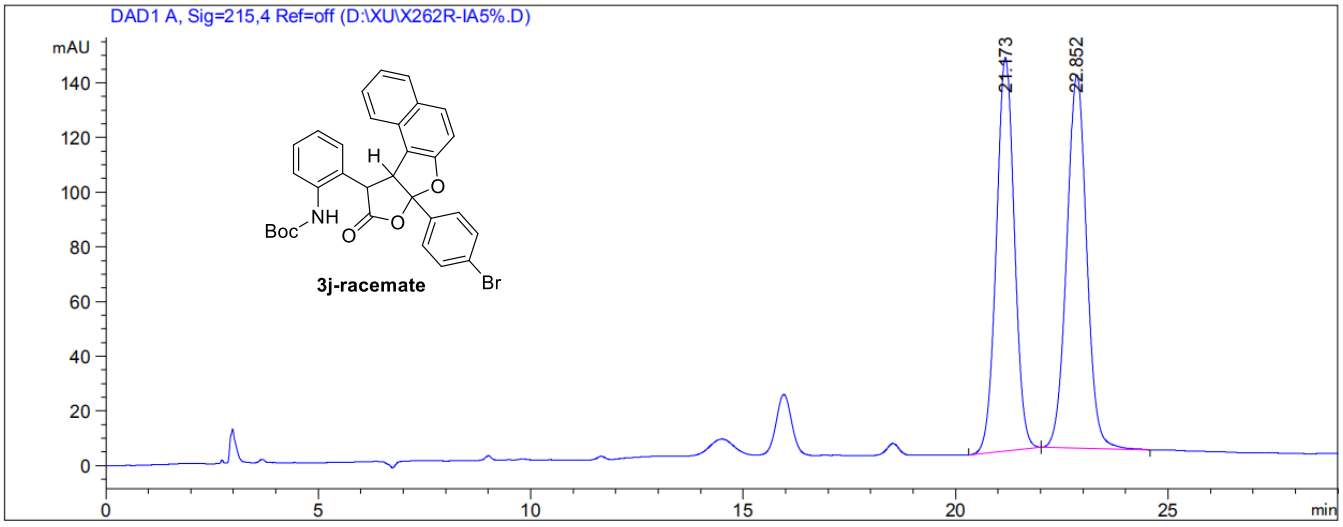
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.579	BB	0.2453	909.79633	57.89734	50.1795
2	9.906	BB	0.2923	903.28693	48.28510	49.8205



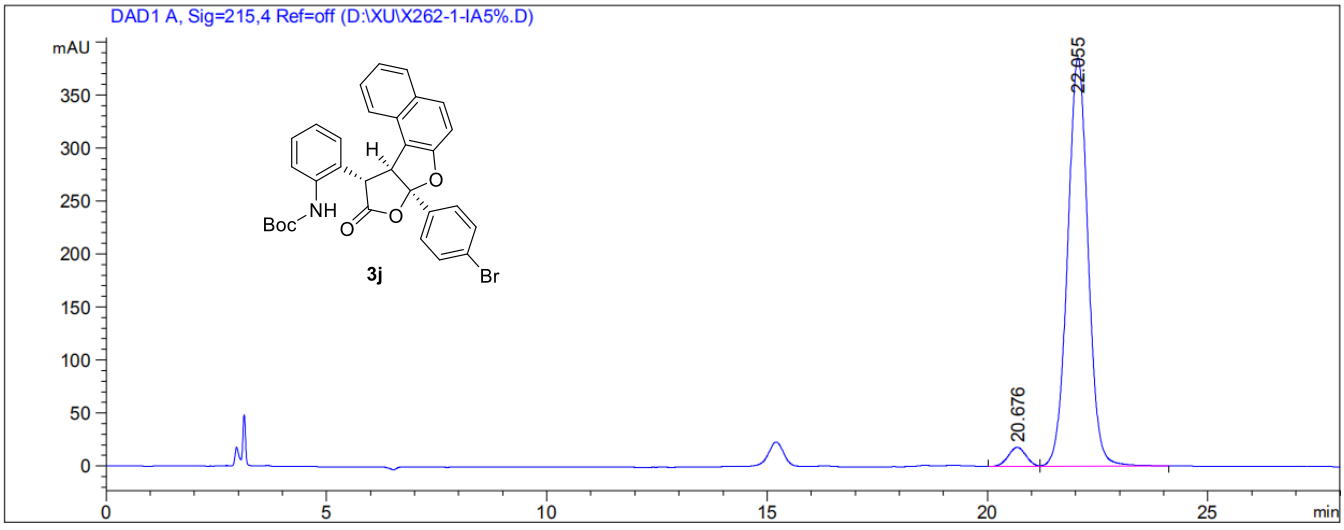
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.578	BB	0.2415	156.89336	10.19465	3.3726
2	9.903	BB	0.2919	4495.16113	240.64717	96.6274



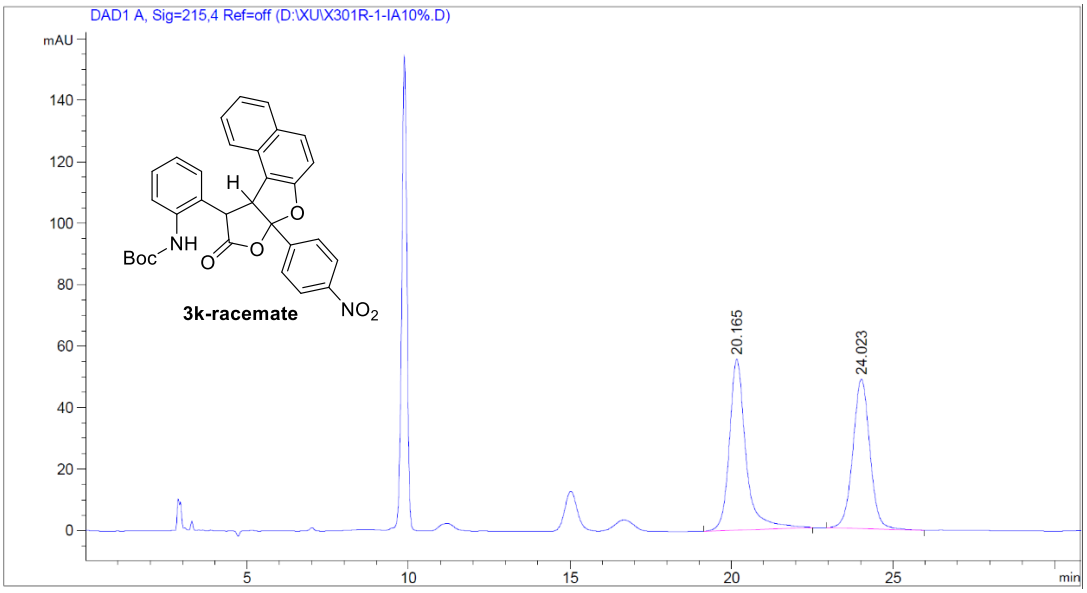
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.173	BB	0.4562	4246.44043	143.95065	48.8052
2	22.852	BB	0.5027	4454.34717	136.52254	51.1948



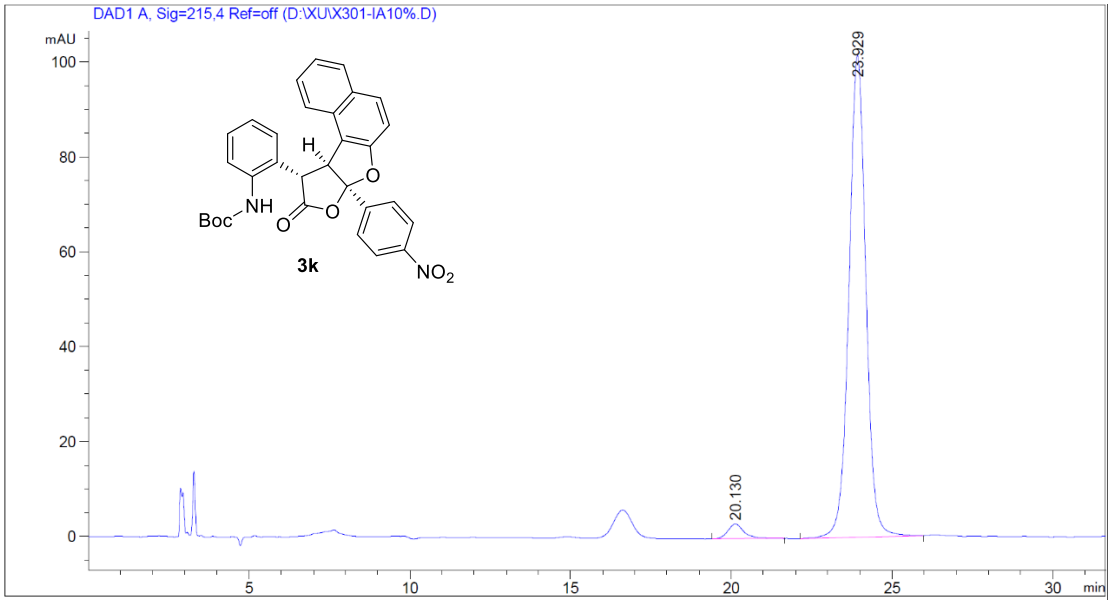
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.676	BV	0.4346	505.26483	18.05069	3.9048
2	22.055	VB	0.4966	1.24343e4	385.18887	96.0952



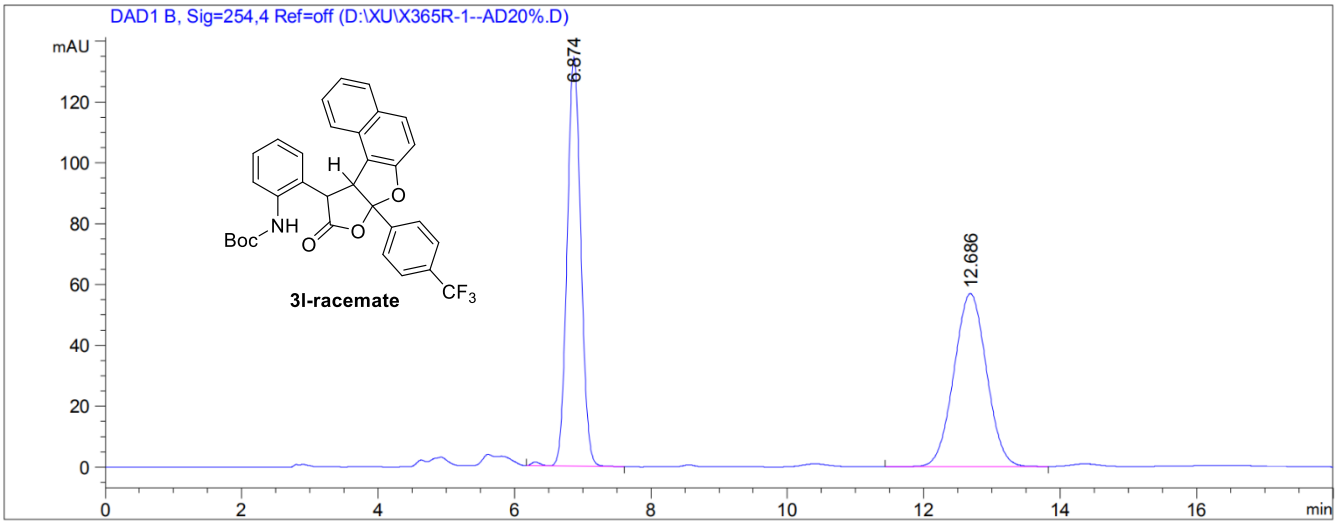
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.165	BB	0.5291	1977.18372	55.57030	52.5678
2	24.023	BB	0.5614	1784.02515	48.69760	47.4322



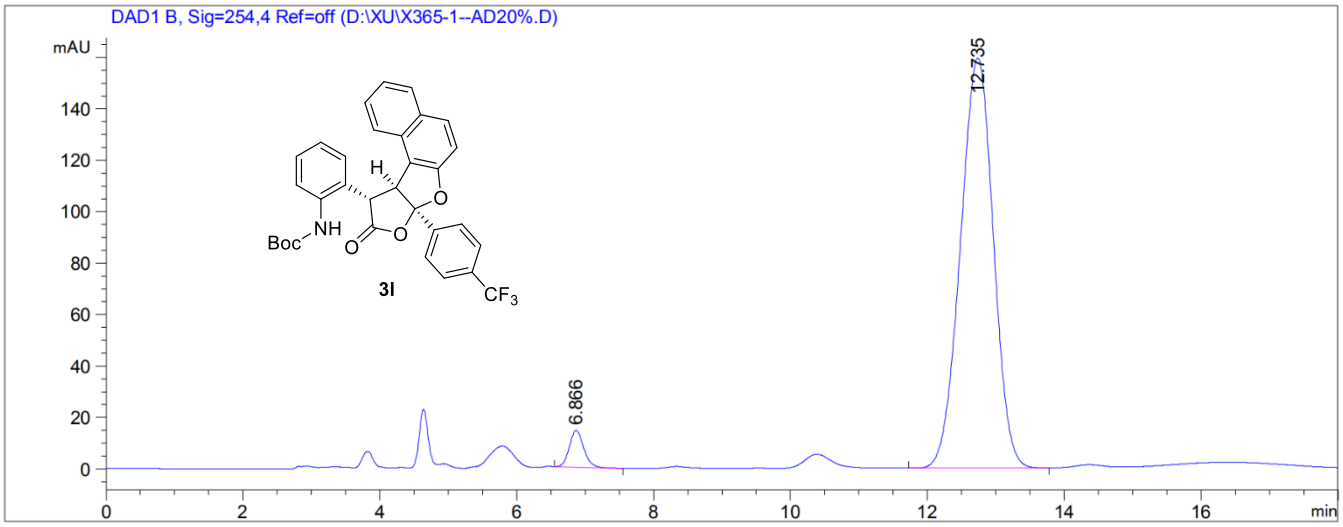
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.130	BB	0.5169	107.70631	3.07326	2.8198
2	23.929	BB	0.5606	3711.88062	101.50512	97.1802



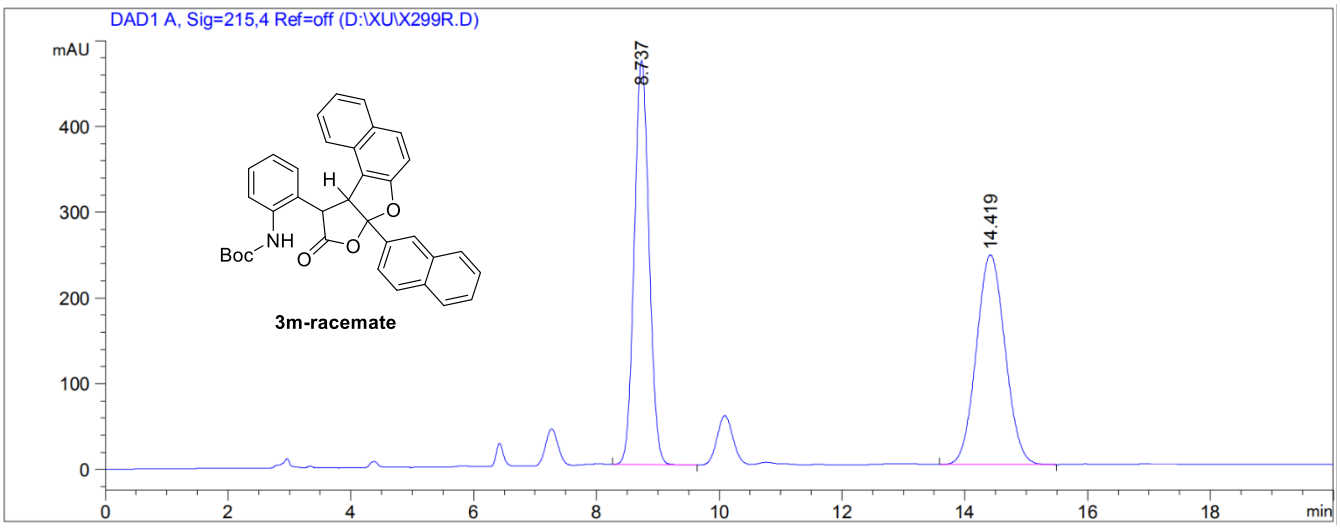
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.874	VB R	0.2190	1889.25354	134.41695	50.0400
2	12.686	BB	0.5192	1886.23059	56.84082	49.9600



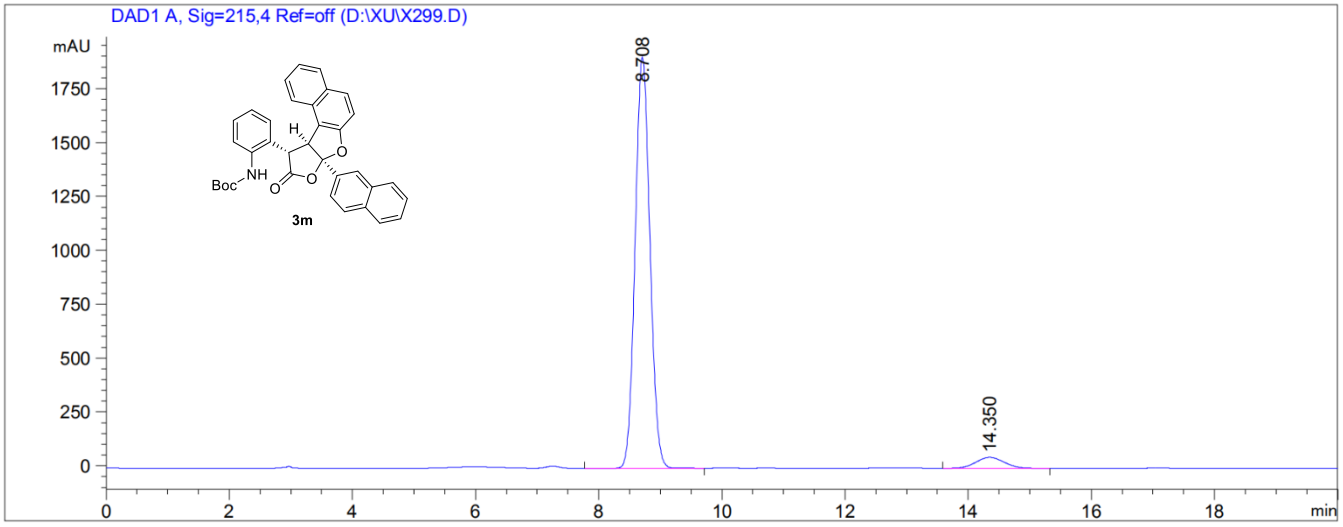
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.866	BB	0.2242	208.71344	14.31035	3.7717
2	12.735	BB	0.5216	5324.96777	159.45212	96.2283



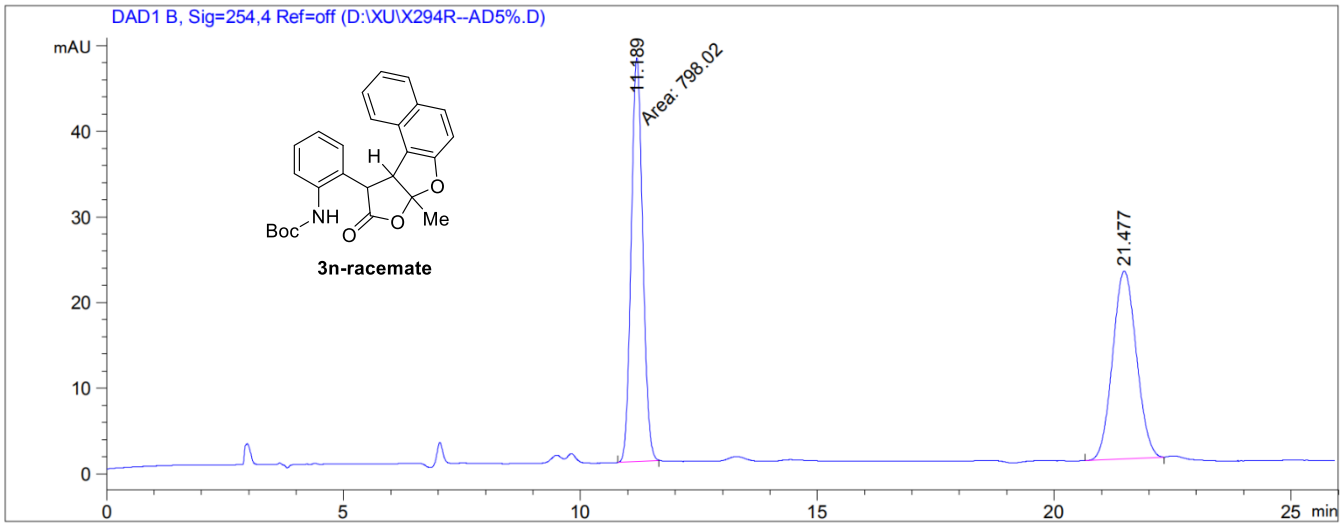
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.737	BB	0.2611	7878.32666	471.07153	49.7567
2	14.419	BB	0.5073	7955.36572	244.67725	50.2433



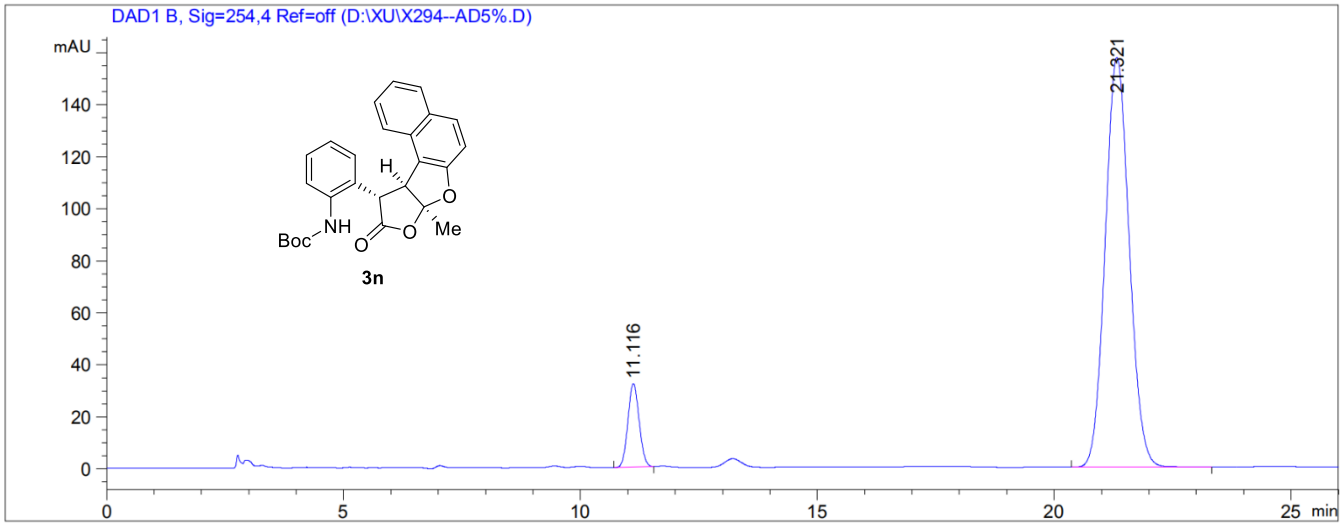
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.708	BB	0.2603	3.17702e4	1907.70044	95.1626
2	14.350	BB	0.5020	1614.97119	50.37462	4.8374



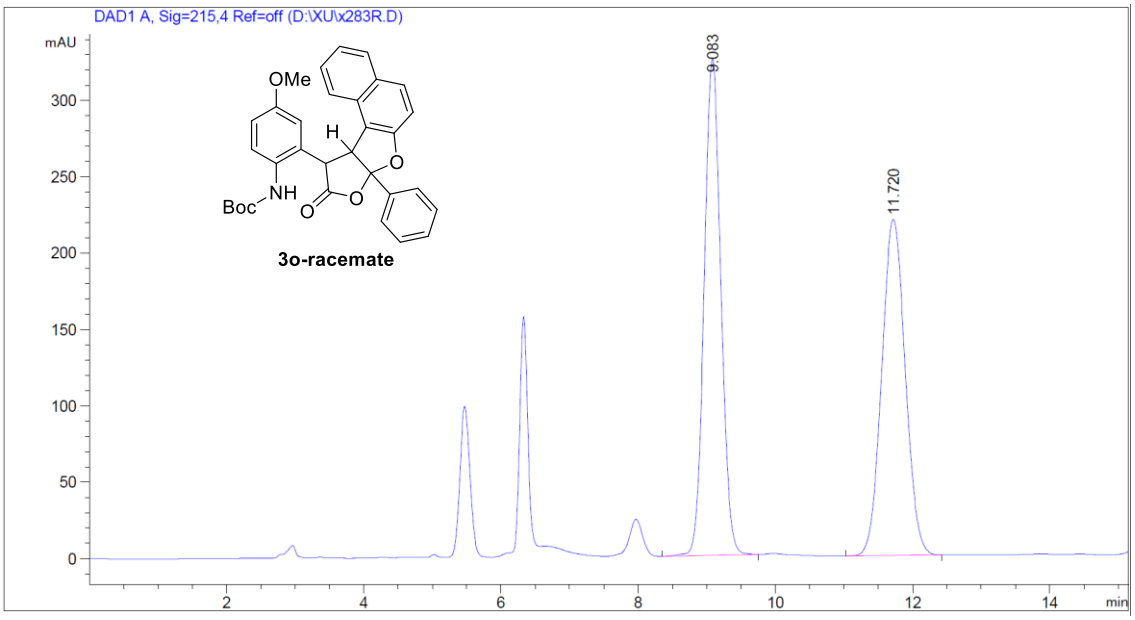
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.189	MM	0.2821	798.01953	47.13942	51.0675
2	21.477	BB	0.5425	764.65503	21.94746	48.9325



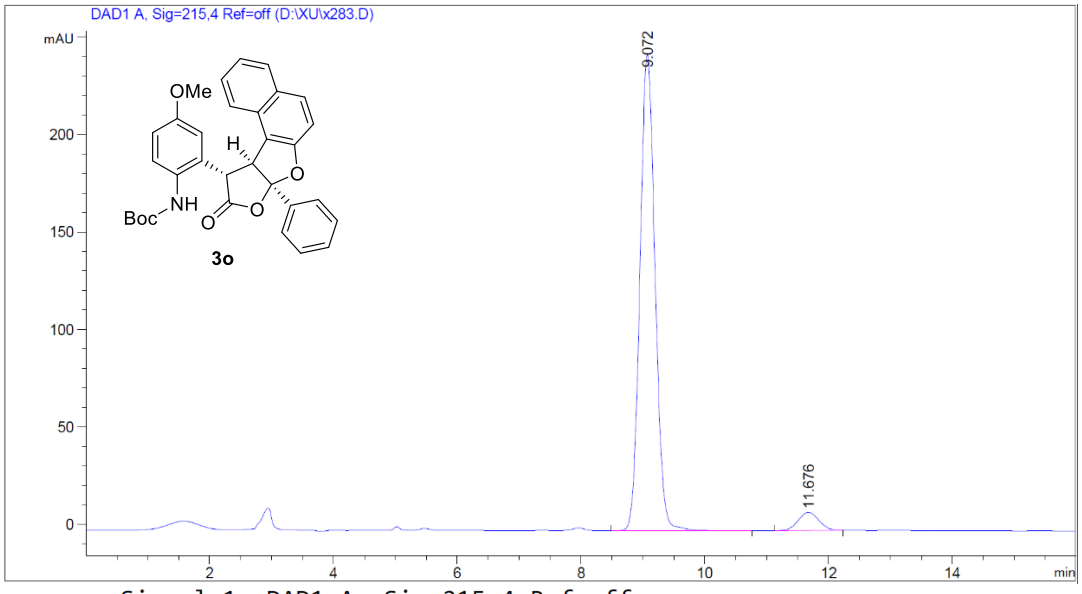
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.116	BB	0.2563	529.87958	32.15114	8.7032
2	21.321	BB	0.5474	5558.47461	157.63200	91.2968



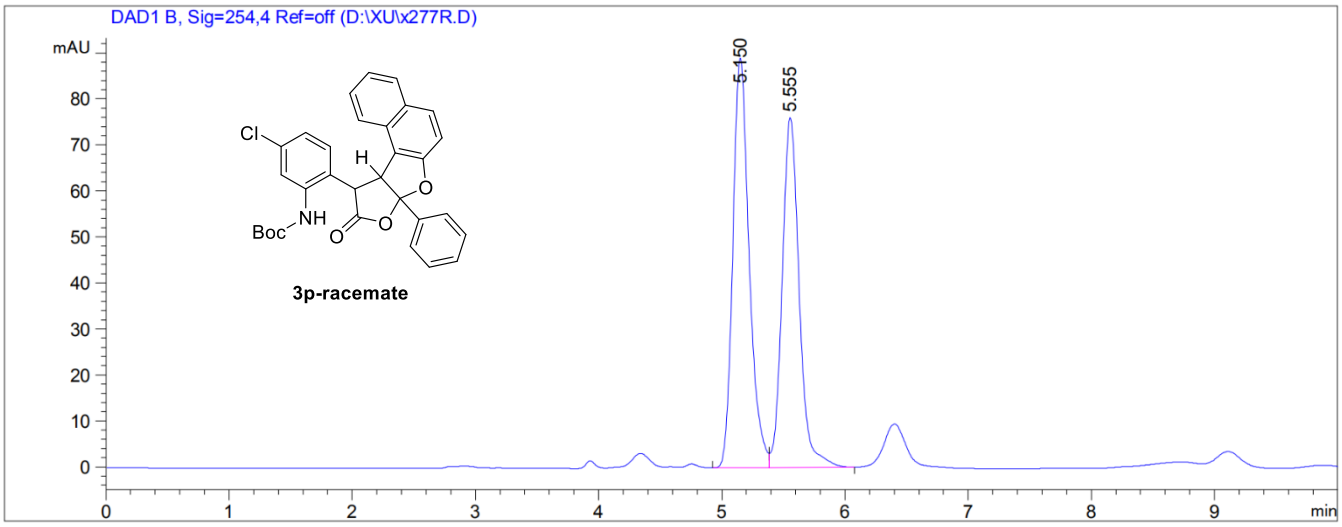
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.083	BB	0.2631	5492.79834	325.18536	51.1945
2	11.720	BB	0.3715	5236.48193	220.11279	48.8055



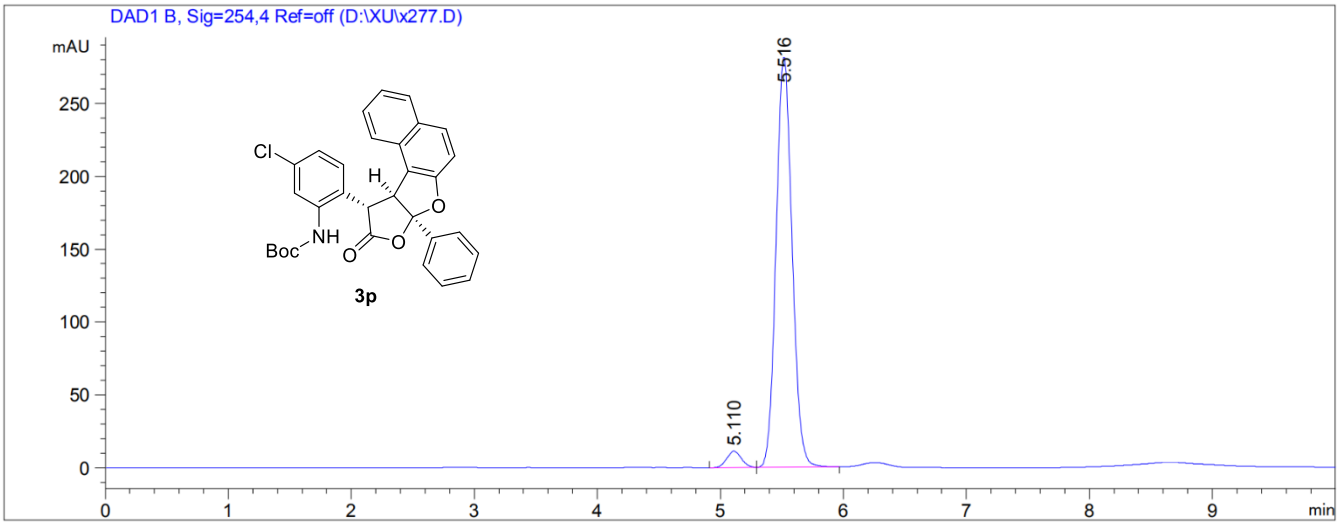
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.072	BB	0.2636	4131.11865	243.94597	95.0116
2	11.676	BB	0.3625	216.89424	9.28732	4.9884



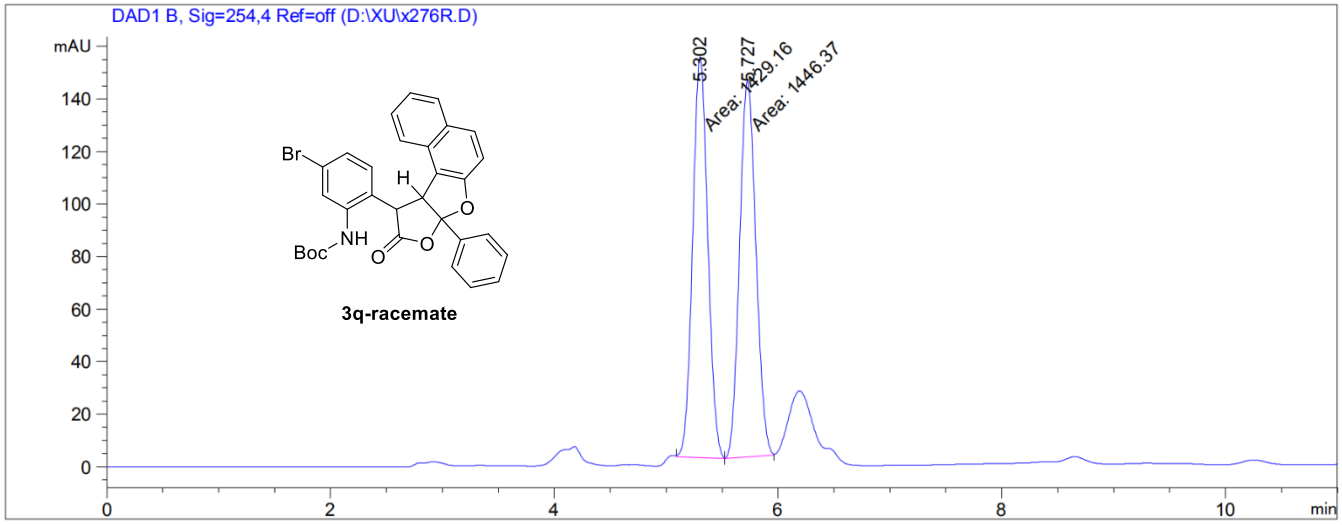
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.150	BV	0.1395	821.45093	89.16396	52.9517
2	5.555	VB	0.1479	729.87097	76.11176	47.0483



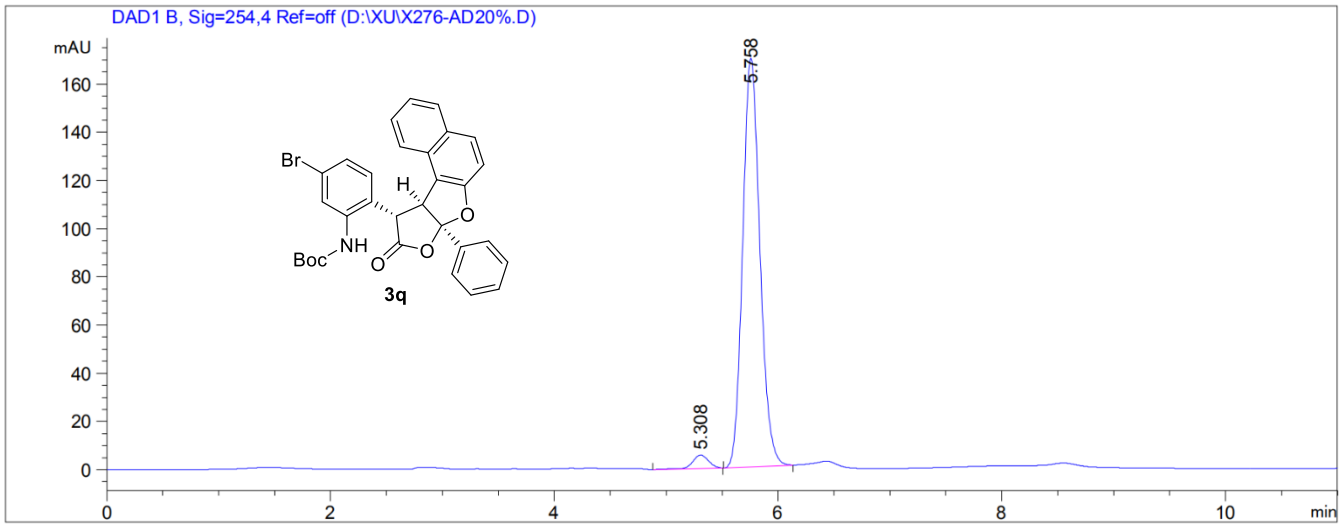
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.110	BV	0.1284	92.30889	11.16994	3.5089
2	5.516	VB	0.1412	2538.41528	281.45657	96.4911



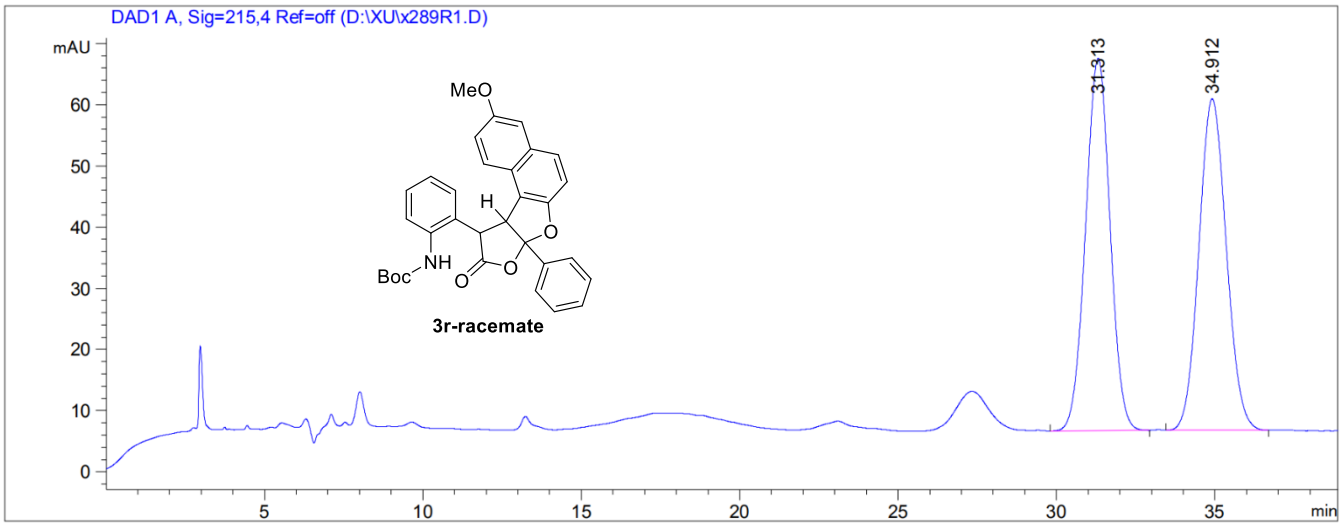
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.302	MM	0.1559	1429.16223	152.74222	49.7007
2	5.727	MM	0.1683	1446.37231	143.19722	50.2993



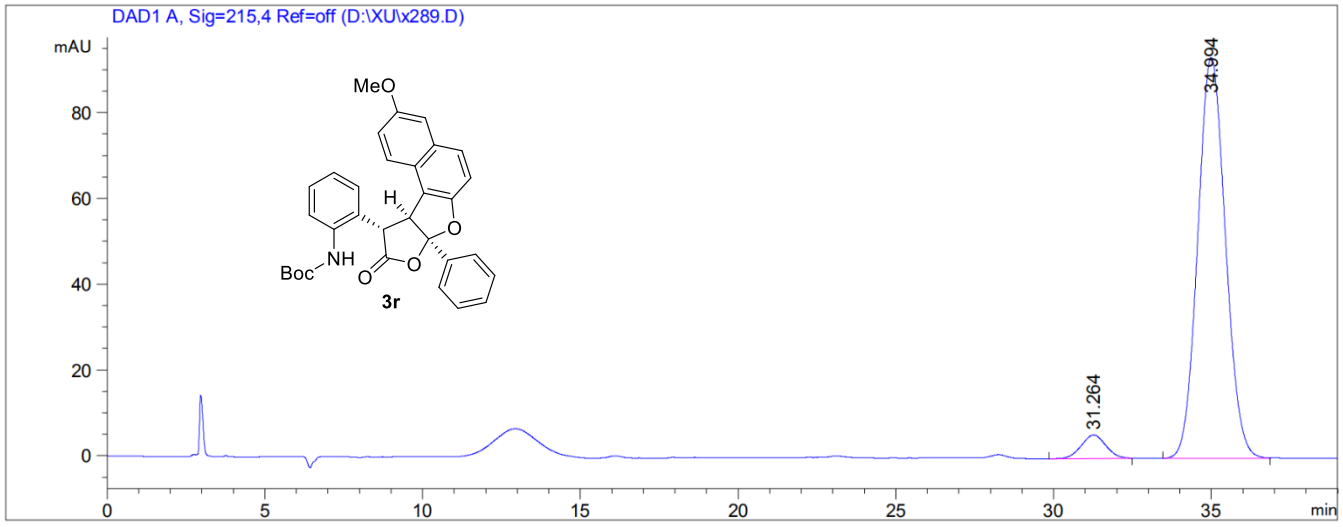
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.308	BB	0.1544	55.99766	5.61096	3.0068
2	5.758	BB	0.1643	1806.34473	169.58110	96.9932



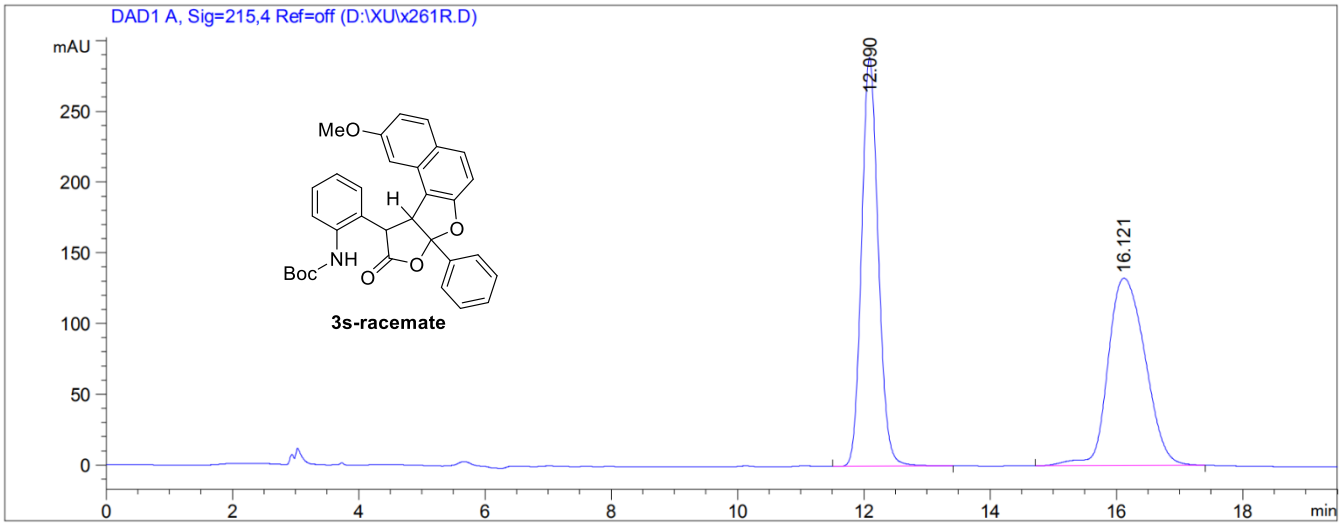
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.313	BB	0.8376	3275.46558	60.88692	50.1149
2	34.912	BB	0.9380	3260.45117	54.18291	49.8851



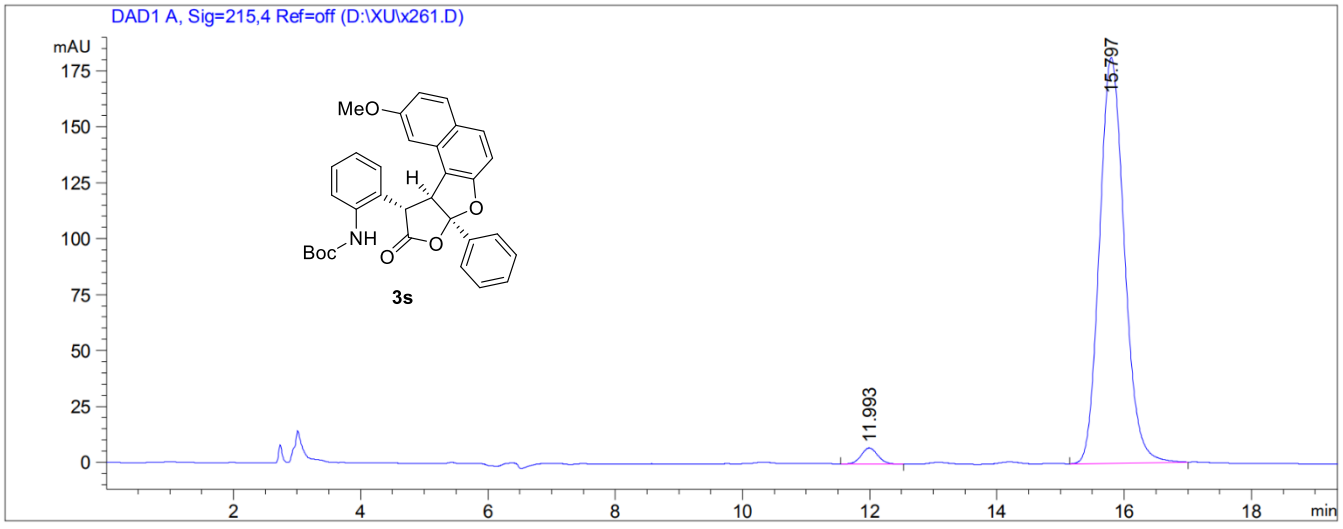
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.264	BB	0.7772	296.21054	5.47500	4.9449
2	34.994	BB	0.9430	5694.05469	93.43017	95.0551



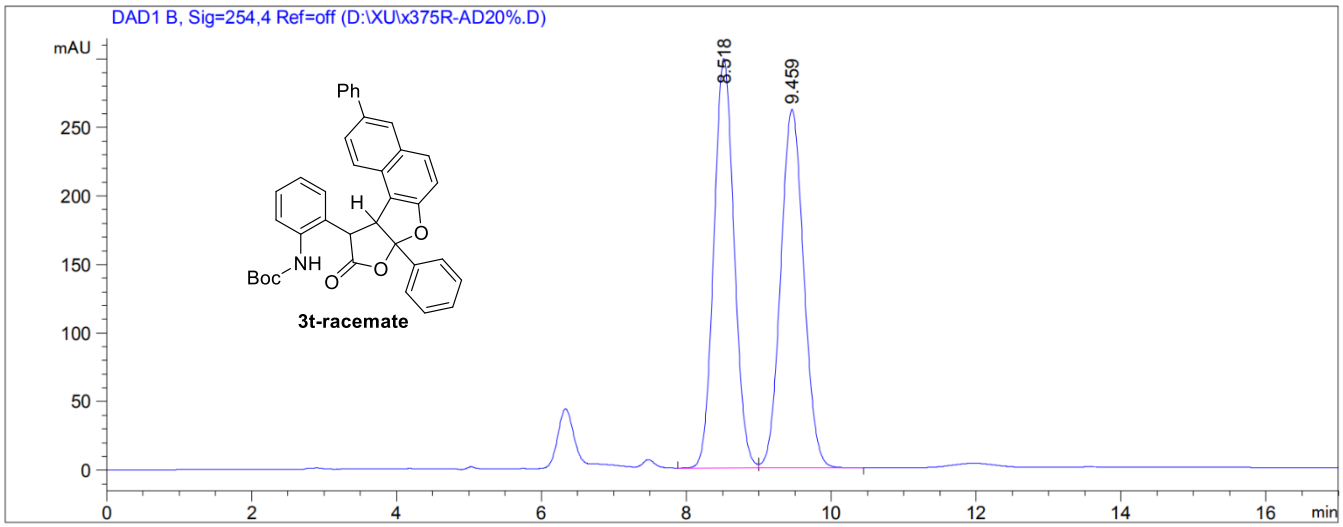
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.090	BB	0.2845	5313.74951	289.04984	49.5049
2	16.121	BB	0.6613	5420.03223	132.47444	50.4951



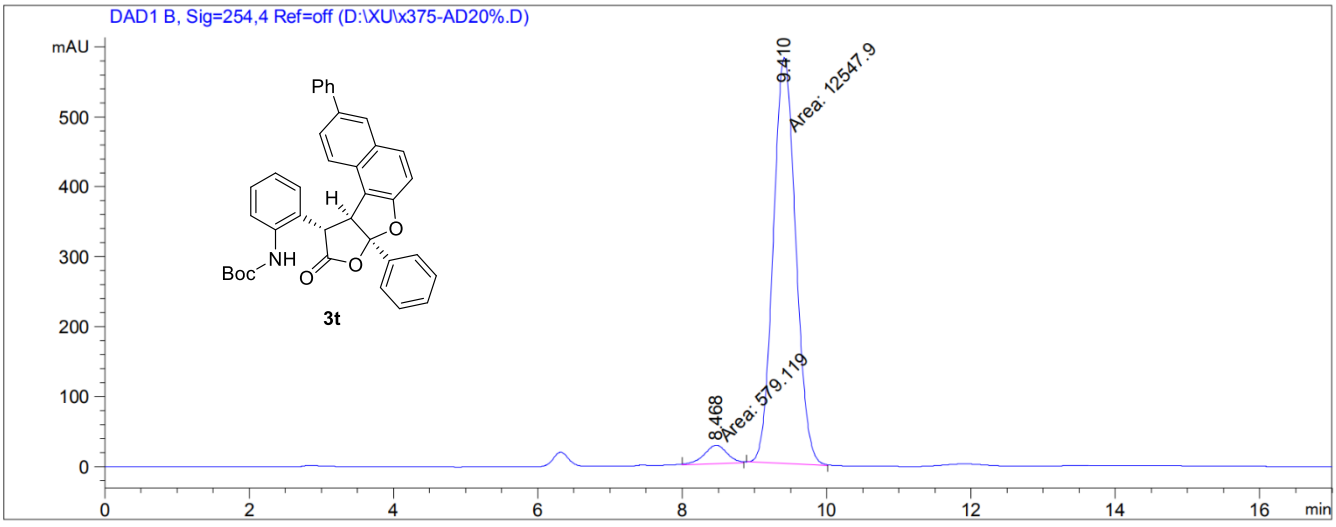
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.993	BB	0.2819	130.53026	7.18786	2.5850
2	15.797	BB	0.4223	4918.98730	181.42331	97.4150



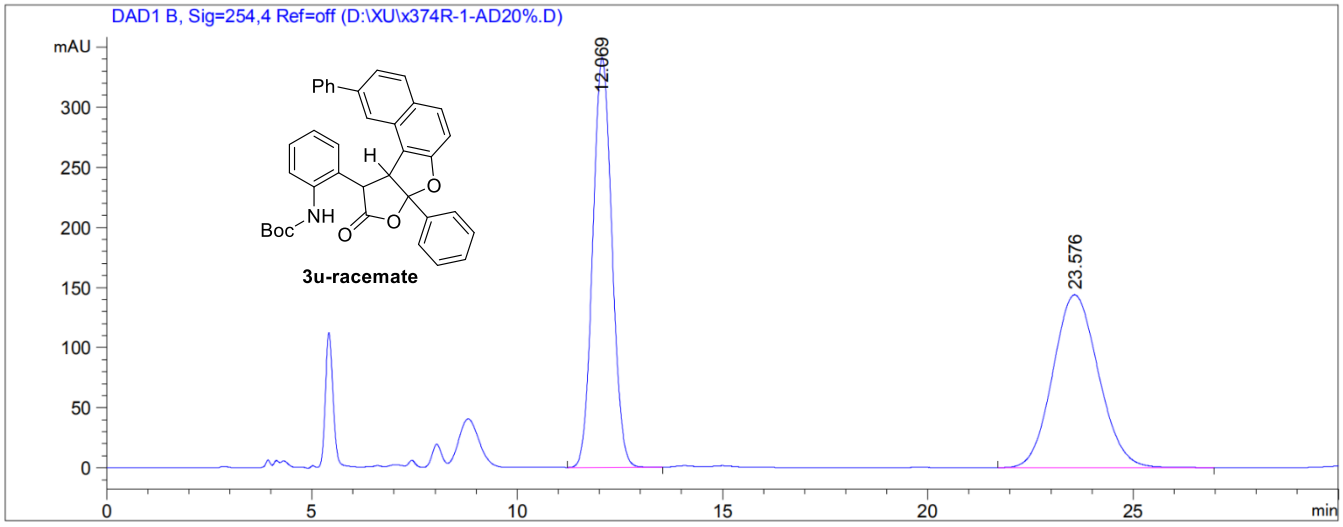
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.518	BV	0.3029	5808.07422	298.67532	50.1462
2	9.459	VB	0.3436	5774.21289	261.48273	49.8538



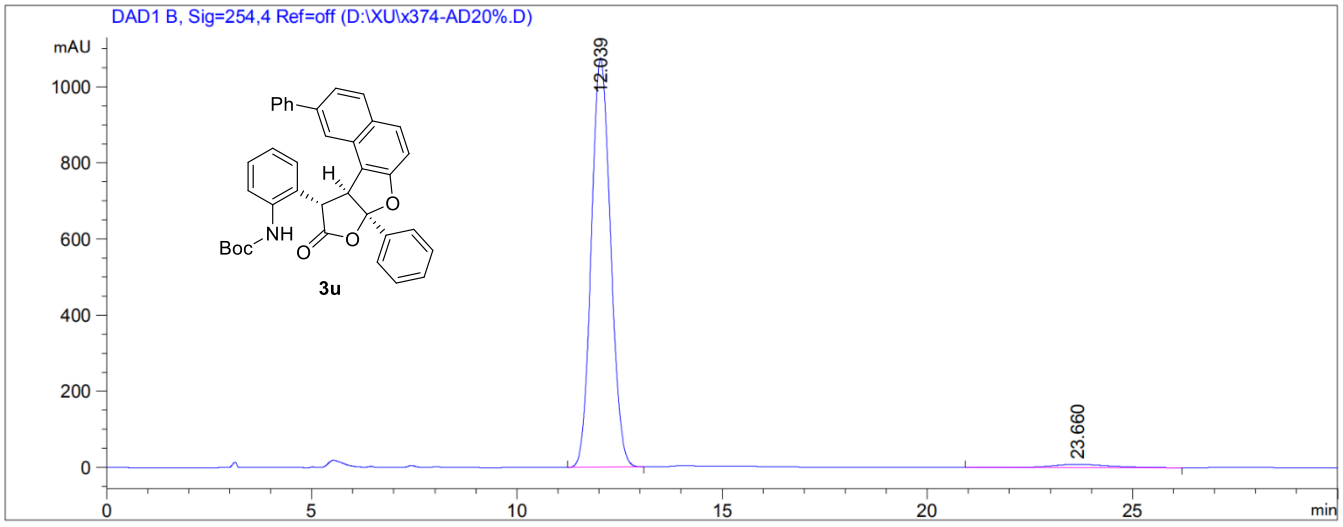
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.468	MM	0.3670	579.11859	26.30059	4.4117
2	9.410	MM	0.3604	1.25479e4	580.34650	95.5883



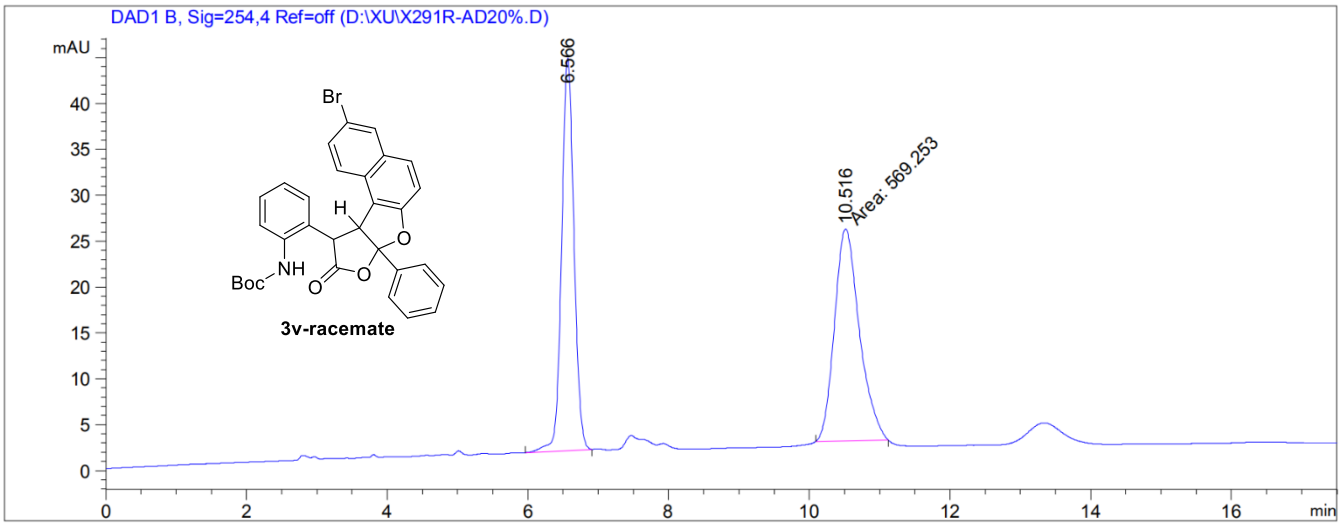
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.069	BB	0.5056	1.10430e4	341.15945	49.8818
2	23.576	BB	1.1966	1.10953e4	143.73357	50.1182



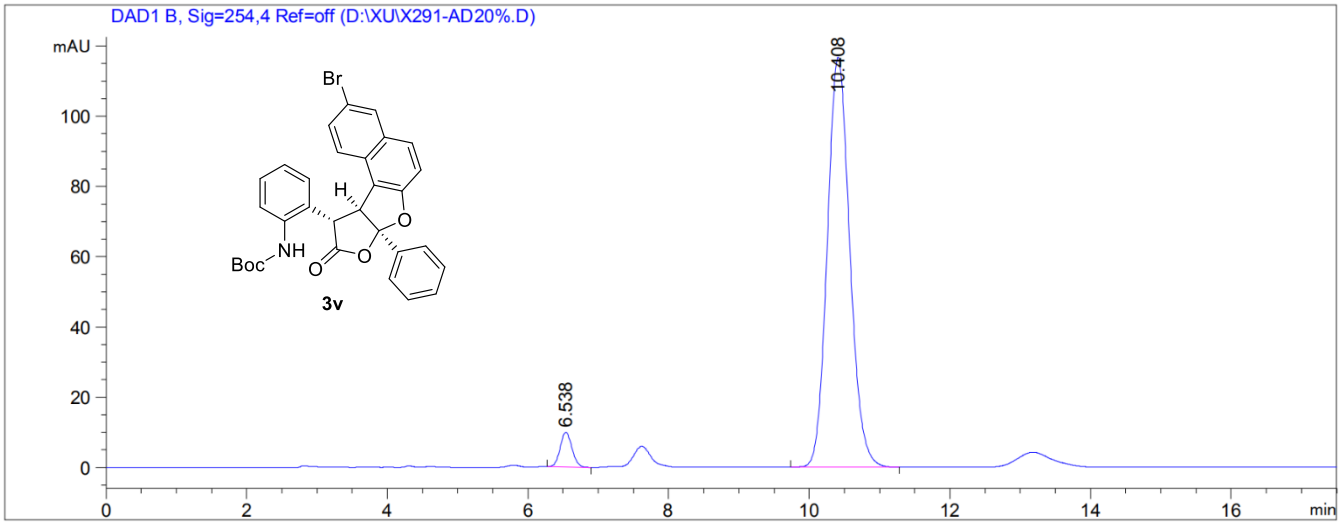
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.039	BB	0.5092	3.49628e4	1075.69470	97.6250
2	23.660	BB	1.1464	850.58002	8.77862	2.3750



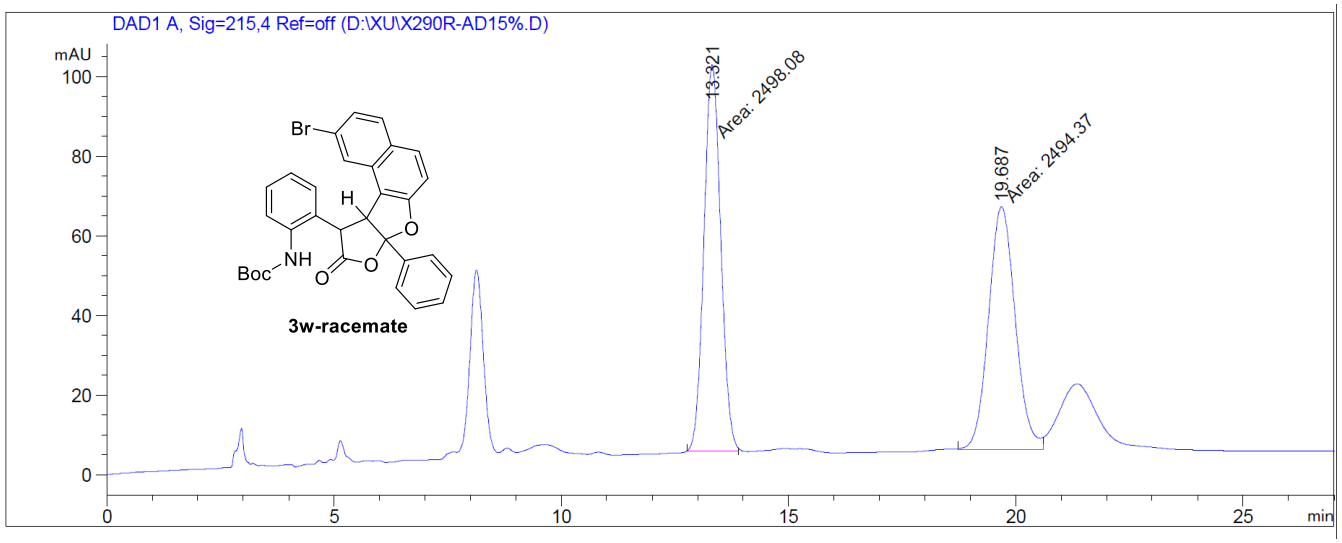
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.566	BB	0.1885	522.11163	42.74889	47.8403
2	10.516	MM	0.4104	569.25281	23.11877	52.1597



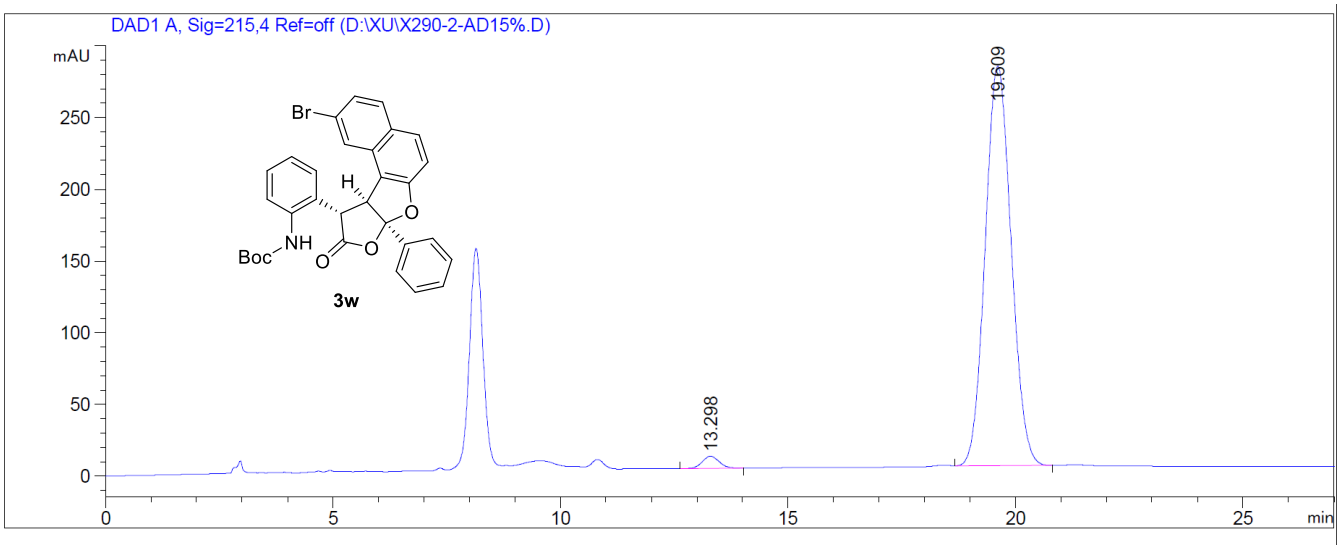
Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.538	BB	0.1811	114.34937	9.87792	4.2349
2	10.408	BB	0.3425	2585.78979	116.71417	95.7651



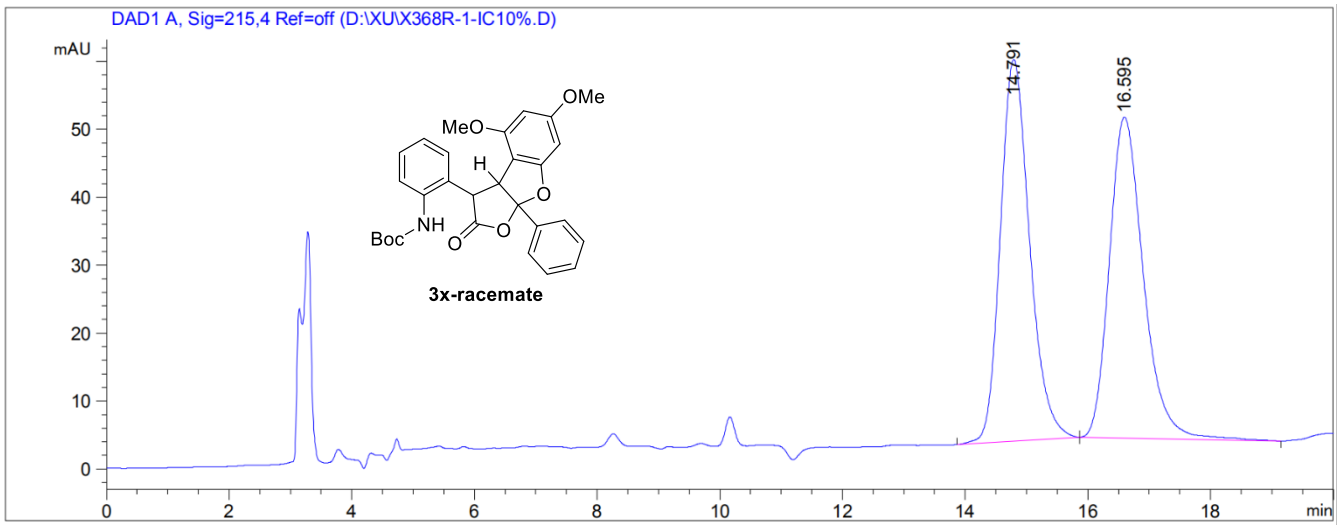
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.321	MM	0.4285	2498.08228	97.15487	50.0372
2	19.687	MF	0.6814	2494.37134	61.00734	49.9628



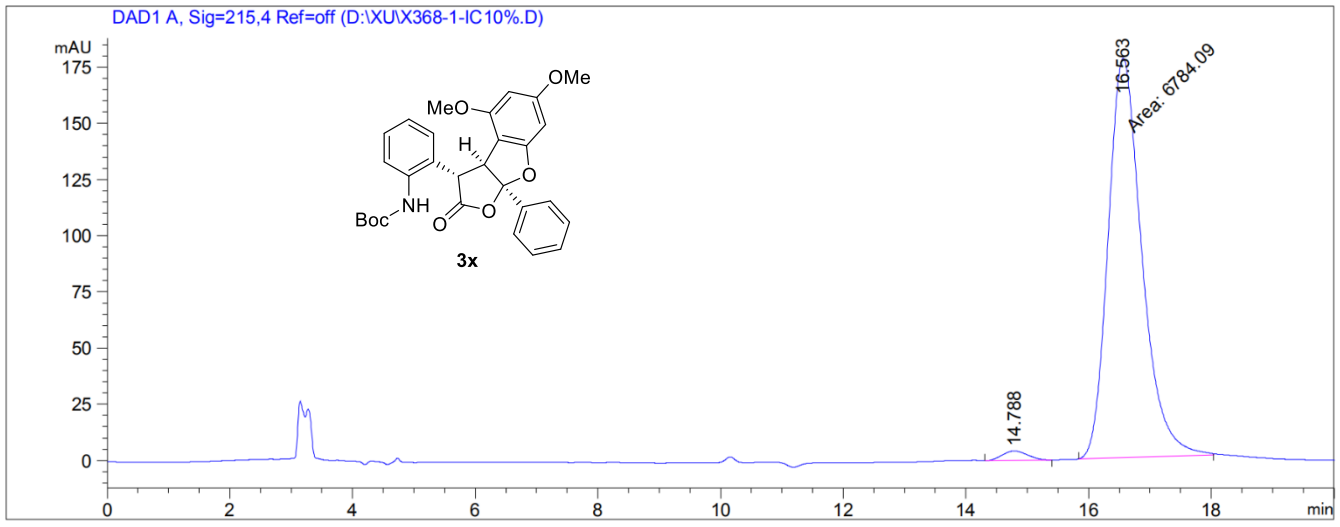
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.298	BB	0.3965	215.83185	8.43613	1.9162
2	19.609	BB	0.6207	1.10476e4	278.56210	98.0838



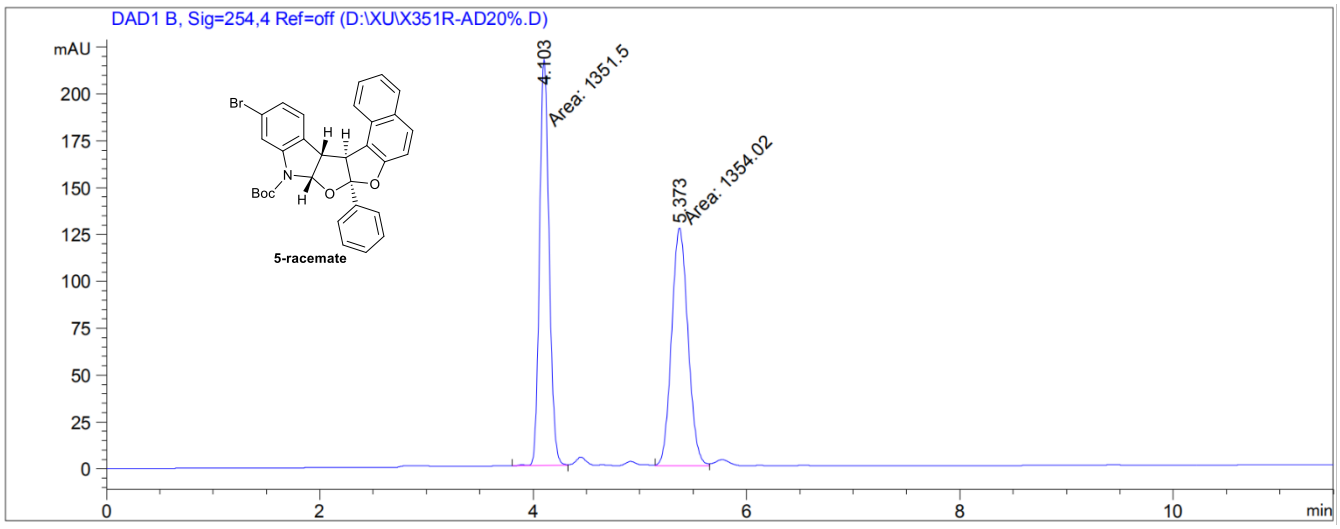
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.791	BB	0.5086	1860.69177	56.15201	50.5118
2	16.595	BB	0.5924	1822.98694	47.22077	49.4882



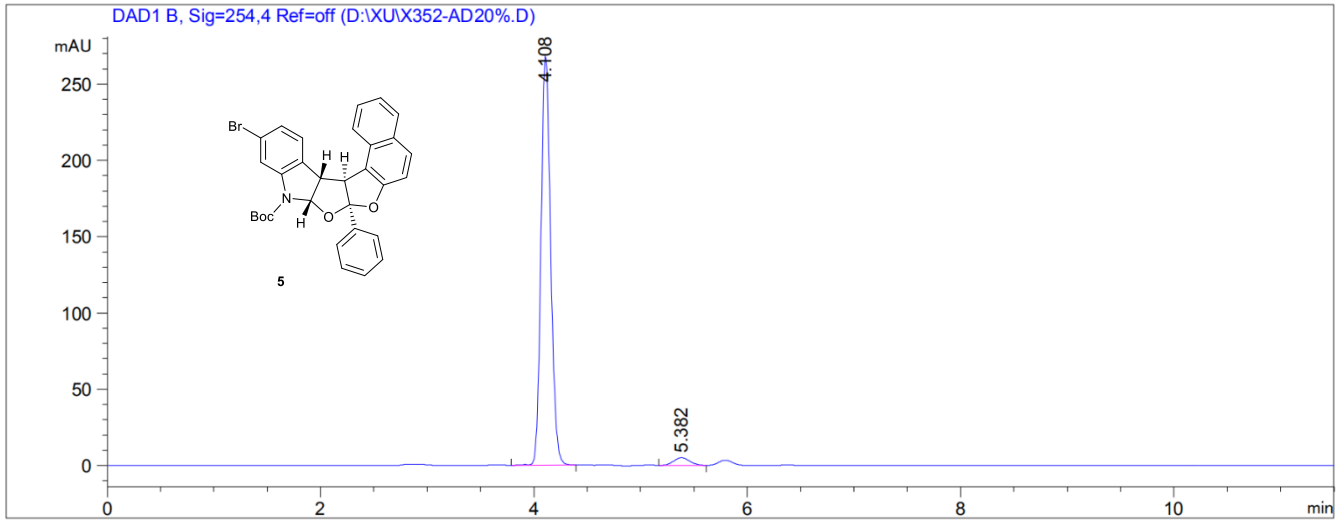
Signal 1: DAD1 A, Sig=215,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.788	BB	0.4402	117.89622	4.16496	1.7082
2	16.563	MM	0.6362	6784.08643	177.73055	98.2918



Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.103	MF	0.1037	1351.50342	217.17780	49.9534
2	5.373	MF	0.1779	1354.02271	126.83463	50.0466



Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.108	BB	0.0975	1690.20386	268.19348	96.9612
2	5.382	BV	0.1648	52.97248	5.03389	3.0388