

Organocatalytic Domino Annulation of In Situ Generated *tert*-Butyl 2-Hydroxybenzylidenecarbamates and 2-Isothiocyanato-1-indanones for Synthesis of Bridged and Fused Ring Heterocycles

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Supporting Information

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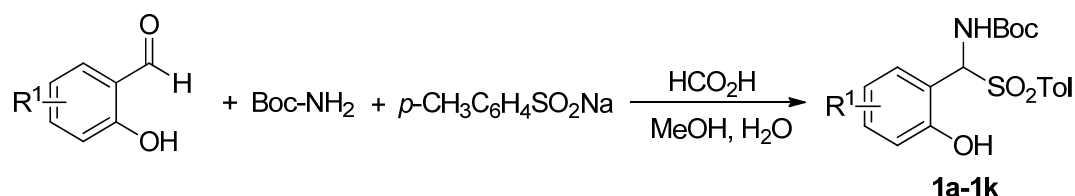
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1. General information and starting materials

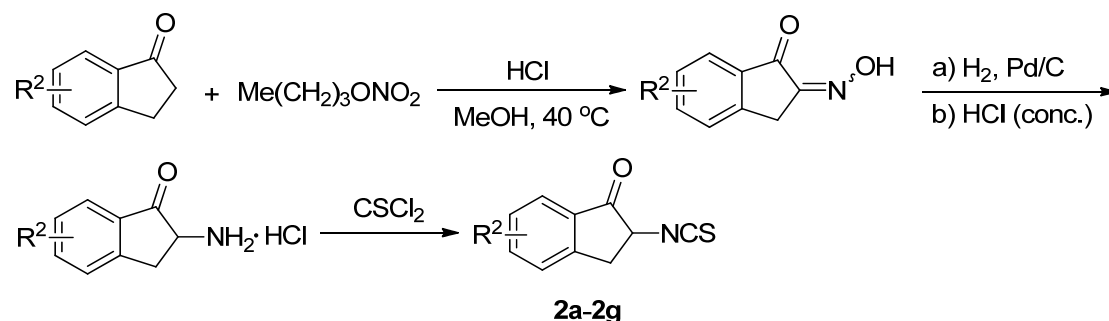
Commercially available compounds were used without further purification. Solvents were dried according to standard procedures. Column chromatography was performed with silica gel (200-300 mesh). Melting points were determined with an XT-4 melting-point apparatus and are uncorrected. ^1H NMR spectra were measured with Bruker Ascend 400 MHz spectrometer in acetone- d_6 , CDCl_3 or $\text{DMSO-}d_6$, chemical shifts were reported in δ (ppm) units relative to tetramethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were measured at 100 MHz (Bruker Ascend 400 MHz spectrometer), chemical shifts were reported in ppm relative to TMS with the solvent resonance as internal standard (acetone- d_6 at 2.05 ppm). ^{19}F NMR spectra were measured at 377 MHz (Bruker Ascend 400 MHz spectrometer). Proton coupling patterns are described as broad (br) singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). High resolution mass spectra were measured with an Agilent 6520 Accurate-Mass-Q-TOF MS system equipped with an electrospray ionization (ESI) source. Enantiomeric excesses were determined by chiral HPLC analysis using an Agilent 1200 LC instrument with a Daicel Chiralpak IA, IC or AD-H column.

2. General procedures for the preparation of substrates.

The 2-hydroxyaryl-substituted α -amido sulfones **1a–1k** were prepared according to the reported literature procedures.¹



The 2-isothiocyanato-1-indanones **2a–2g** were prepared according to the reported literature procedures.²

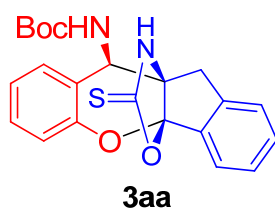


References

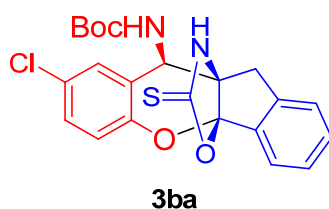
1. Zheng, B.; Hou, W.-D.; Peng, Y.-G. *ChemCatChem* **2014**, *6*, 2527.
2. Zhao, B.-L.; Du, D.-M. *Org. Lett.* **2018**, *20*, 3797.

3. General procedure for the enantioselective synthesis and characterization of compounds 3

2-Hydroxyaryl-substituted α -amido aulfones **1** (0.15 mmol), 2-isothiocyanato-1-indanones **2** (0.1 mmol), **C7** (6.0 mg, 10% mol) and $K_3PO_4 \cdot 3H_2O$ (26.6 mg, 0.1 mmol) were dissolved in xylene (1.0 mL), and the mixture was stirred at room temperature for 15 h. After completion of the reaction, the reaction mixture was concentrated and directly purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1 to 3:1) to afford the pure products **3** as solid.

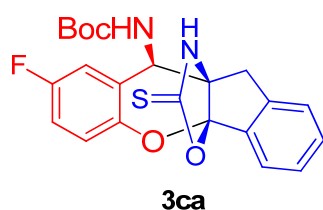


tert-Butyl ((4*bR*,10*R*,10*aR*)-13-thioxo-10*H*,11*H*-4*b*,10*a*-(epoxymethanoimino)indeno[1,2-*b*]chromen-10-yl)carbamate (**3aa**). From 56.6 mg (0.15 mmol) **1a** and 18.9 mg (0.15 mmol) **2a**, purified by silica gel (200-300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3aa** as a white solid (34.8 mg, 85% yield), mp 224–226 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: $t_R = 7.7$ min (minor), $t_R = 6.4$ min (major); 97% *ee*. $[\alpha]_D^{20} = +72.2$ ($c = 0.50$, CH_2Cl_2). 1H NMR (400 MHz, $DMSO-d_6$): δ 10.09 (s, 1H, NH), 7.73 (d, $J = 7.6$ Hz, 1H, ArH), 7.60–7.56 (m, 1H, ArH), 7.52–7.47 (m, 2H, ArH), 7.40–7.37 (m, 2H, ArH), 7.29–7.23 (m, 3H, ArH + NH), 4.83 (d, $J = 9.6$ Hz, 1H, CH), 3.57 (d, $J = 17.6$ Hz, 1H, CH_2), 3.45 (d, $J = 17.6$ Hz, 1H, CH_2), 1.50 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $DMSO-d_6$): δ 185.9, 155.8, 150.8, 140.1, 135.7, 131.8, 129.1, 128.3, 126.3, 126.1, 125.1, 124.6, 123.9, 120.1, 118.5, 79.3, 74.1, 52.2, 42.4, 28.0 ppm. HRMS (ESI): m/z calcd. for $C_{22}H_{23}N_2O_4S$ [$M + H$] $^+$ 411.1373, found 411.1374.

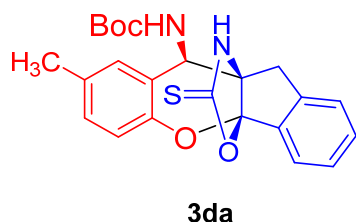


tert-Butyl ((4*bR*,10*R*,10*aR*)-8-chloro-13-thioxo-10*H*,11*H*-4*b*,10*a*-(epoxymethanoimino)indeno[1,2-*b*]chromen-10-yl)carbamate (**3ba**). From 61.6 mg (0.15 mmol) **1b** and 18.9 mg (0.10 mmol) **2a**, purified by silica gel (200-300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3ba** as a light white solid (36.0 mg, 81% yield), mp 185–188 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 85:15, flow rate

1.0 mL/min, detection at 254 nm): for major diastereomer: $t_R = 6.2$ min (minor), $t_R = 6.9$ min (major); 95% *ee*. $[\alpha]_D^{20} = +85.6$ ($c = 0.70$, CH_2Cl_2). ^1H NMR (400 MHz, acetone- d_6): δ 9.16 (s, 1H, NH), 7.76 (d, $J = 7.2$ Hz, 1H, ArH), 7.60–7.56 (m, 1H, ArH), 7.53–7.46 (m, 2H, ArH), 7.44–7.41 (m, 1H, ArH), 7.34 (s, 1H, ArH), 7.26 (d, $J = 8.4$ Hz, 1H, ArH), 6.93 (d, $J = 9.6$ Hz, 1H, NH), 5.10 (d, $J = 10.4$ Hz, 1H, CH), 3.82 (d, $J = 17.6$ Hz, 1H, CH_2), 3.55 (d, $J = 17.2$ Hz, 1H, CH_2), 1.53 (s, 9H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, acetone- d_6): δ 189.1, 157.9, 152.3, 142.3, 138.2, 133.9, 131.2, 131.0, 130.7, 130.3, 128.1, 127.4, 126.1, 122.7, 122.5, 81.7, 76.4, 54.6, 44.7, 29.5 ppm. HRMS (ESI): m/z calcd. for $\text{C}_{22}\text{H}_{22}\text{ClN}_2\text{O}_4\text{S}$ $[\text{M} + \text{H}]^+$ 445.0983, found 445.0964.

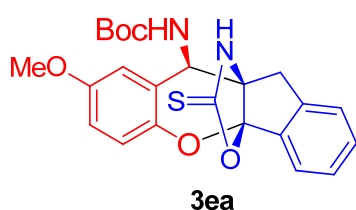


tert-Butyl ((4bR,10R,10aR)-8-fluoro-13-thioxo-10H,11H-4b,10a-(epoxymethanoimino)-indeno[1,2-b]chromen-10-yl)carbamate (3ca). From 59.2 mg (0.15 mmol) **1c** and 18.9 mg (0.10 mmol) **2a**, purified by silica gel (200–300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3ca** as a light white solid (36.4 mg, 85% yield), mp 198–200 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 80:20, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: $t_R = 5.4$ min (minor), $t_R = 6.2$ min (major); 95% *ee*. $[\alpha]_D^{20} = +102.0$ ($c = 0.75$, CH_2Cl_2). ^1H NMR (400 MHz, acetone- d_6) δ 9.15 (s, 1H, NH), 7.75 (d, $J = 7.2$ Hz, 1H, ArH), 7.59–7.46 (m, 3H, ArH), 7.27 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.8$ Hz, 1H, ArH), 7.18–7.10 (m, 2H, ArH), 6.91 (d, $J = 10.0$ Hz, 1H, NH), 5.09 (d, $J = 10.4$ Hz, 1H, CH), 3.80 (d, $J = 17.2$ Hz, 1H, CH_2), 3.54 (d, $J = 17.2$ Hz, 1H, CH_2), 1.53 (s, 9H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, acetone- d_6): δ 189.2, 161.4 ($^1J_{\text{C-F}} = 239.9$ Hz), 157.9, 149.5, 142.3, 138.3, 133.8, 130.8 (d, $^3J_{\text{C-F}} = 7.7$), 130.3, 128.1, 126.1, 122.9, 122.3 (d, $^3J_{\text{C-F}} = 8.5$ Hz), 117.3 (d, $^2J_{\text{C-F}} = 23.6$ Hz), 114.3 (d, $^2J_{\text{C-F}} = 25.5$ Hz), 81.6, 76.4, 54.8, 44.6, 29.5 ppm. HRMS (ESI): m/z calcd. for $\text{C}_{22}\text{H}_{22}\text{FN}_2\text{O}_4\text{S}$ $[\text{M} + \text{H}]^+$ 429.1279, found 429.1276.

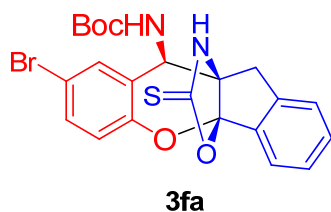


tert-Butyl ((4bR,10R,10aR)-8-methyl-13-thioxo-10H,11H-4b,10a-(epoxymethanoimino)-indeno[1,2-b]chromen-10-yl)carbamate (3da). From 58.65 mg (0.15 mmol) **1d** and 18.9 mg (0.10 mmol) **2a**, purified by silica gel (200–300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3da** as a white solid (38.6 mg, 91% yield),

mp 225–228 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: t_R = 8.2 min (minor), t_R = 6.5 min (major); 96% *ee*. $[\alpha]_D^{20}$ = +26.2 (c = 1.75, CH₂Cl₂). ¹H NMR (400 MHz, acetone-*d*₆): δ 9.07 (s, 1H, NH), 7.75 (d, J = 7.6 Hz, 1H, ArH), 7.58–7.54 (m, 1H, ArH), 7.52–7.45 (m, 2H, ArH), 7.18–7.15 (m, 2H, ArH), 7.09 (d, J = 8.0 Hz, 1H, ArH), 6.77 (d, J = 10.0 Hz, 1H, NH), 5.06 (d, J = 10.4 Hz, 1H, CH), 3.80 (d, J = 17.6 Hz, 1H, CH₂), 3.52 (d, J = 18.0 Hz, 1H, CH₂), 2.33 (s, 3H, CH₃), 1.53 (s, 9H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz, acetone-*d*₆): δ 189.3, 158.1, 151.4, 142.3, 138.7, 135.9, 133.7, 131.4, 130.2, 128.1, 127.9, 127.6, 126.1, 122.7, 120.4, 81.4, 76.5, 54.7, 44.8, 29.6, 22.1 ppm. HRMS (ESI): m/z calcd. for C₂₃H₂₅N₂O₄S [M + H]⁺ 425.1530, found 425.1526.

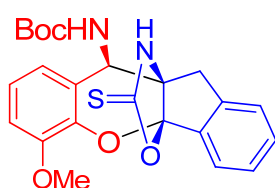


tert-Butyl ((4bR,10R,10aR)-8-methoxy-13-thioxo-10H,11H-4b,10a-(epoxymethanoimino)-indeno[1,2-b]chromen-10-yl)carbamate (3ea). From 61.1 mg (0.15 mmol) **1e** and 18.9 mg (0.10 mmol) **2a**, purified by silica gel (200–300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3ea** as a white solid (33.0 mg, 75% yield), mp 230–232 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: t_R = 6.2 min (minor), t_R = 7.9 min (major); 98% *ee*. $[\alpha]_D^{20}$ = +94.8 (c = 0.55, CH₂Cl₂). ¹H NMR (400 MHz, acetone-*d*₆): δ 9.07 (s, 1H, NH), 7.74 (d, J = 7.2 Hz, 1H, NH), 7.58–7.44 (m, 3H, ArH), 7.15 (d, J = 8.4 Hz, 1H, ArH), 6.93–6.87 (m, 2H, ArH), 6.82 (d, J = 10.4 Hz, 1H, NH), 5.05 (d, J = 10.4 Hz, 1H, CH), 3.78 (d, J = 17.2 Hz, 1H, CH₂), 3.79 (s, 3H, OCH₃), 3.52 (d, J = 17.6 Hz, 1H, CH₂), 1.53 (s, 9H, CH₃) ppm. ¹³C{¹H} (100 MHz, acetone-*d*₆) δ 189.3, 158.6, 158.0, 146.8, 142.2, 138.6, 133.7, 130.2, 129.5, 128.1, 126.1, 123.0, 121.4, 114.9, 113.4, 81.5, 76.3, 56.9, 54.9, 44.7, 29.5 ppm. HRMS (ESI): m/z calcd. for C₂₃H₂₅N₂O₅S [M + H]⁺ 441.1479, found 441.1470.



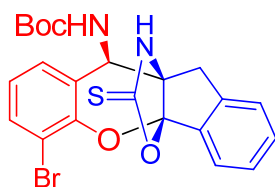
tert-Butyl ((4bR,10R,10aR)-8-bromo-13-thioxo-10H,11H-4b,10a-(epoxymethanoimino)-indeno[1,2-b]chromen-10-yl)carbamate (3fa). From 68.40 mg (0.15 mmol) **1f** and 18.90 mg (0.10 mmol) **2a**, purified by silica gel (200–300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3fa** as a light white solid (39.0 mg, 80%

yield), mp 265–267 °C. HPLC (Daicel Chiralpak IA, *n*-hexane/2-propanol = 95:5, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: $t_R = 7.8$ min (minor), $t_R = 8.9$ min (major); 95% *ee*. $[\alpha]_D^{20} = +57.5$ ($c = 0.67$, CH_2Cl_2). ^1H NMR (400 MHz, acetone- d_6): δ 9.17 (s, 1H, NH), 7.75 (d, $J = 7.6$ Hz, 1H, NH), 7.60–7.56 (m, 2H, ArH), 7.53–7.46 (m, 3H, ArH), 7.21 (d, $J = 8.4$ Hz, 1H, ArH), 6.93 (d, $J = 10.0$ Hz, 1H, NH), 5.11 (d, $J = 10.0$ Hz, 1H, CH), 3.82 (d, $J = 17.2$ Hz, 1H, CH₂), 3.55 (d, $J = 17.6$ Hz, 1H, CH₂), 1.53 (s, 9H, CH₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, acetone- d_6): δ 189.1, 157.9, 152.9, 142.3, 138.2, 134.0, 133.9, 131.6, 131.0, 130.3, 128.1, 126.1, 122.8, 122.6, 118.7, 81.7, 76.5, 54.5, 44.7, 29.5 ppm. HRMS (ESI): m/z calcd. for $\text{C}_{22}\text{H}_{22}\text{BrN}_2\text{O}_4\text{S}$ $[\text{M} + \text{H}]^+$ 489.0478, found 489.0446; calcd. for $\text{C}_{22}\text{H}_{22}^{81}\text{BrN}_2\text{O}_4\text{S}$ $[\text{M} + \text{H}]^+$ 491.0458, found 491.0446.



3ga

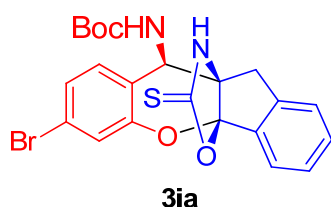
***tert*-Butyl ((4*bR*,10*R*,10*aR*)-6-methoxy-13-thioxo-10*H*,11*H*-4*b*,10*a*-(epoxymethanoimino)-indeno[1,2-*b*]chromen-10-yl)carbamate (3ga).** From 61.1 mg (0.15 mmol) **1g** and 18.9 mg (0.10 mmol) **2a**, purified by silica gel (200–300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3ga** as a white solid (38.3 mg, 87% yield), mp 213–215 °C. HPLC (Daicel Chiralpak IA, *n*-hexane/2-propanol = 80:20, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: $t_R = 6.2$ min (minor), $t_R = 10.2$ min (major); 96% *ee*. $[\alpha]_D^{20} = +51.0$ ($c = 0.65$, CH_2Cl_2). ^1H NMR (400 MHz, acetone- d_6): δ 9.10 (s, 1H, NH), 7.77 (d, $J = 7.2$ Hz, 1H, ArH), 7.59–7.45 (m, 3H, ArH), 7.17–7.06 (m, 2H, ArH), 6.92 (d, $J = 7.6$ Hz, 1H, ArH), 6.78 (d, $J = 10.0$ Hz, 1H, NH), 5.05 (d, $J = 10.4$ Hz, 1H, CH), 3.93 (s, 3H, OCH₃), 3.78 (d, $J = 17.2$ Hz, 1H, CH₂), 3.53 (d, $J = 17.6$ Hz, 1H, CH₂), 1.52 (s, 9H, CH₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, acetone- d_6): δ 189.3, 158.0, 152.1, 142.4, 142.3, 138.6, 133.7, 131.6, 130.2, 129.7, 128.1, 126.4, 126.2, 122.8, 118.6, 115.3, 81.4, 76.6, 58.0, 54.7, 44.8, 29.5 ppm. HRMS (ESI): m/z calcd. for $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}_5\text{S}$ $[\text{M} + \text{H}]^+$ 441.1479, found 441.1470.



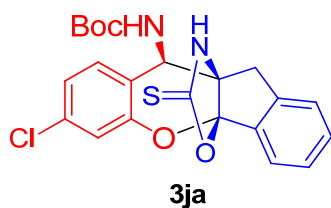
3ha

***tert*-Butyl ((4*bR*,10*R*,10*aR*)-6-bromo-13-thioxo-10*H*,11*H*-4*b*,10*a*-(epoxymethanoimino)-indeno[1,2-*b*]chromen-10-yl)carbamate (3ha).** From 68.4 mg (0.15 mmol) **1h** and 18.9 mg (0.10 mmol) **2a**, purified by silica gel (200–300 mesh) column chromatography using petroleum

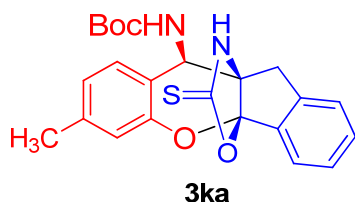
ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3ha** as a white solid (40.0 mg, 82% yield), mp 256–258 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: $t_R = 10.8$ min (minor), $t_R = 8.7$ min (major); 93% *ee*. $[\alpha]_D^{20} = +30.9$ ($c = 0.85$, CH_2Cl_2). ^1H NMR (400 MHz, acetone- d_6): δ 9.14 (s, 1H, NH), 7.80 (d, $J = 7.2$ Hz, 1H, ArH), 7.63 (d, $J = 8.0$ Hz, 1H, ArH), 7.61–7.52 (m, 2H, ArH), 7.48 (d, $J = 7.2$ Hz, 1H, ArH), 7.37 (d, $J = 7.6$ Hz, 1H, ArH), 7.18 (t, $J = 7.8$ Hz, 1H, ArH), 6.90 (d, $J = 10.0$ Hz, 1H, NH), 5.11 (d, $J = 10.0$ Hz, 1H, CH), 3.81 (d, $J = 17.6$ Hz, 1H, CH_2), 3.57 (d, $J = 17.6$ Hz, 1H, CH_2), 1.52 (s, 9H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, acetone- d_6) δ 189.0, 157.9, 150.4, 142.4, 138.1, 134.5, 134.0, 130.6, 130.3, 128.2, 127.5, 126.7, 126.2, 122.8, 114.7, 81.6, 76.6, 55.1, 44.7, 29.5 ppm. HRMS (ESI): m/z calcd. for $\text{C}_{22}\text{H}_{22}^{79}\text{BrN}_2\text{O}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 489.0478, found 489.0483; calcd. for $\text{C}_{22}\text{H}_{22}^{81}\text{BrN}_2\text{O}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 491.0458, found 491.0456.



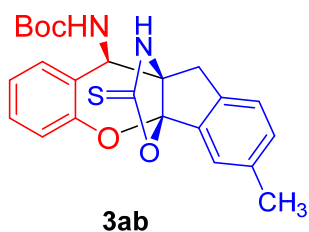
tert-Butyl ((4bR,10R,10aR)-7-bromo-13-thioxo-10H,11H-4b,10a-(epoxymethanoimino)-indeno[1,2-b]chromen-10-yl)carbamate (3ia). From 68.4 mg (0.15 mmol) **1i** and 18.9 mg (0.10 mmol) **2a**, purified by silica gel (200–300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3ia** as a white solid (38.6 mg, 79% yield), mp 179–182 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: $t_R = 7.9$ min (minor), $t_R = 6.7$ min (major); 95% *ee*. $[\alpha]_D^{20} = +28.1$ ($c = 0.50$, CH_2Cl_2). ^1H NMR (400 MHz, acetone- d_6): δ 9.15 (s, 1H, NH), 7.76 (d, $J = 7.6$ Hz, 1H, ArH), 7.59–7.50 (m, 2H, ArH), 7.47–7.41 (m, 3H, ArH), 7.12 (d, $J = 8.0$ Hz, 1H, ArH), 6.90 (d, $J = 10.0$ Hz, 1H, NH), 5.06 (d, $J = 10.0$ Hz, 1H, CH), 3.80 (d, $J = 17.6$ Hz, 1H, CH_2), 3.55 (d, $J = 17.6$ Hz, 1H, CH_2), 1.52 (s, 9H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 187.5, 157.6, 155.8, 151.9, 139.7, 135.6, 132.1, 128.5, 127.9, 126.3, 125.9, 124.6, 124.4, 122.7, 122.5, 121.3, 81.3, 74.8, 52.4, 42.9, 28.3 ppm. HRMS (ESI): m/z calcd. for $\text{C}_{22}\text{H}_{22}^{79}\text{BrN}_2\text{O}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 489.0478, found 489.0478; calcd. for $\text{C}_{22}\text{H}_{22}^{81}\text{BrN}_2\text{O}_4\text{S}$ [$\text{M} + \text{H}$] $^+$ 491.0458, found 491.0460.



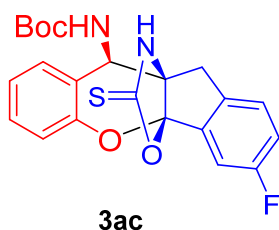
***tert*-Butyl ((4*bR*,10*R*,10*aR*)-7-chloro-13-thioxo-10*H*,11*H*-4*b*,10*a*-(epoxymethanoimino)-indeno[1,2-*b*]chromen-10-yl)carbamate (3*ja*)**. From 61.7 mg (0.15 mmol) **1j** and 18.9 mg (0.10 mmol) **2a**, purified by silica gel (200-300 mesh) column chromatography using petroleum ether/ethyl acetate (5/1 to 3/1 v/v) as eluent to obtain **3ja** as a white solid (35.5 mg, 80% yield), mp 187–190 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: $t_R = 7.4$ min (minor), $t_R = 6.4$ min (major); 92% *ee*. $[\alpha]_D^{20} = +68.8$ ($c = 0.60$, CH₂Cl₂). ¹H NMR (400 MHz, Acetone-*d*₆): δ 9.15 (s, 1H, NH), 7.76 (d, $J = 7.6$ Hz, 1H, ArH), 7.60–7.46 (m, 3H, ArH), 7.38 (d, $J = 8.0$ Hz, 1H, ArH), 7.31–7.26 (m, 2H, ArH), 6.89 (d, $J = 10.0$ Hz, 1H, NH), 5.07 (d, $J = 10.0$ Hz, 1H, CH), 3.81 (d, $J = 17.6$ Hz, 1H, CH₂), 3.55 (d, $J = 17.6$ Hz, 1H, CH₂), 1.52 (s, 9H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz, acetone-*d*₆): δ 189.1, 157.9, 154.3, 142.3, 138.2, 135.7, 133.9, 131.6, 130.3, 128.7, 128.2, 127.5, 126.6, 126.1, 122.7, 121.0, 81.6, 76.6, 54.5, 44.7, 29.5 ppm. HRMS (ESI): m/z calcd. for C₂₂H₂₂ClN₂O₄S [M + H]⁺ 445.0983, found 445.0972.



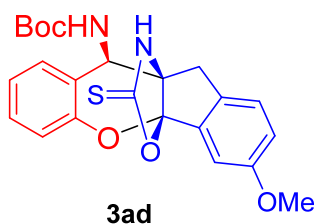
***tert*-Butyl ((4*bR*,10*R*,10*aR*)-7-methyl-13-thioxo-10*H*,11*H*-4*b*,10*a*-(epoxymethanoimino)-indeno[1,2-*b*]chromen-10-yl)carbamate (3*ka*)**. From 58.7 mg (0.15 mmol) **1k** and 18.9 mg (0.10 mmol) **2a**, purified by silica gel (200-300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3ka** as a white solid (34.8 mg, 82% yield), mp 205–208 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 90:10, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: $t_R = 13.6$ min (minor), $t_R = 11.4$ min (major); 99% *ee*. $[\alpha]_D^{20} = +66.5$ ($c = 0.90$, CH₂Cl₂). ¹H NMR (400 MHz, acetone-*d*₆): δ 9.07 (s, 1H, NH), 7.75 (d, $J = 7.6$ Hz, 1H, ArH), 7.58–7.44 (m, 3H, ArH), 7.21 (d, $J = 7.2$ Hz, 1H, ArH), 7.04 (s, 1H, ArH), 7.03 (d, $J = 8.4$ Hz, 1H, ArH), 6.76 (d, $J = 10.0$ Hz, 1H, NH), 5.04 (d, $J = 10.0$ Hz, 1H, CH), 3.79 (d, $J = 17.6$ Hz, 1H, CH₂), 3.52 (d, $J = 17.6$ Hz, 1H, CH₂), 2.35 (s, 1H, CH₃), 1.52 (s, 9H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz, acetone-*d*₆): δ 189.3, 158.0, 153.4, 142.2, 141.3, 138.7, 133.7, 130.2, 128.1, 127.0, 126.8, 126.0, 125.1, 122.6, 121.1, 81.4, 76.5, 54.5, 44.8, 29.5, 22.1 ppm. HRMS (ESI): m/z calcd. for C₂₃H₂₅N₂O₄S [M + H]⁺ 425.1530, found 425.1514.



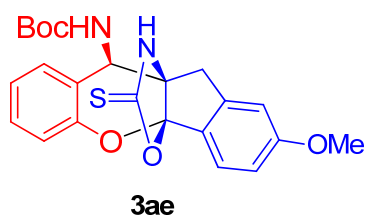
tert-Butyl ((4*bR*,10*R*,10*aR*)-3-methyl-13-thioxo-10*H*,11*H*-4*b*,10*a*-(epoxymethanoimino)-indeno[1,2-*b*]chromen-10-yl)carbamate (3*ab*). From 56.6 mg (0.15 mmol) **1a** and 20.3 mg (0.10 mmol) **2b**, purified by silica gel (200-300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3ab** as a white solid (36.1 mg, 85% yield), mp 224–226 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: $t_R = 4.9$ min (minor), $t_R = 4.1$ min (major); 97% *ee*. $[\alpha]_D^{20} = +72.2$ ($c = 0.5$, CH₂Cl₂). ¹H NMR (400 MHz, DMSO-*d*₆): δ 10.06 (s, 1H, NH), 7.53 (s, 1H, ArH), 7.39–7.34 (m, 4H, ArH), 7.28–7.21 (m, 3H, ArH + NH), 4.81 (d, $J = 9.6$ Hz, 1H, CH), 3.51 (d, $J = 17.2$ Hz, 1H, CH₂), 3.38 (d, $J = 17.2$ Hz, 1H, CH₂), 2.41 (s, 3H, CH₃), 1.50 (s, 9H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 185.9, 155.8, 150.8, 137.9, 137.0, 135.8, 132.8, 129.1, 126.1, 126.0, 125.1, 124.6, 124.0, 120.1, 118.5, 79.3, 74.4, 52.2, 42.1, 28.0, 20.6 ppm. HRMS (ESI): m/z calcd. for C₂₃H₂₅N₂O₄S [M + H]⁺ 425.1530, found 425.1515.



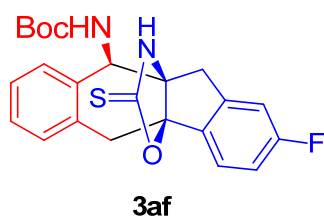
tert-Butyl ((4*bR*,10*R*,10*aR*)-3-fluoro-13-thioxo-10*H*,11*H*-4*b*,10*a*-(epoxymethanoimino)-indeno[1,2-*b*]chromen-10-yl)carbamate (3*ac*). From 56.6 mg (0.15 mmol) **1a** and 20.7 mg (0.10 mmol) **2c**, purified by silica gel (200-300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3ac** as a white solid (38.1 mg, 89% yield), mp 204–207 °C. HPLC (Daicel Chiralpak IA, *n*-hexane/2-propanol = 75:25, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: $t_R = 5.0$ min (minor), $t_R = 4.3$ min (major); 95% *ee*. $[\alpha]_D^{20} = +78.8$ ($c = 0.89$, CH₂Cl₂). ¹H NMR (400 MHz, acetone-*d*₆): δ 9.15 (s, 1H, NH), 7.54–7.48 (m, 2H, ArH), 7.41–7.33 (m, 3H, ArH), 7.25–7.22 (m, 2H, ArH), 6.83 (d, $J = 10.0$ Hz, 1H, NH), 5.10 (d, $J = 10.0$ Hz, CH), 3.78 (d, $J = 17.6$ Hz, 1H, CH₂), 3.52 (d, $J = 17.2$ Hz, 1H, CH₂), 1.53 (s, 9H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz, acetone-*d*₆): δ 189.1, 164.6 (d, $^1J_{C-F} = 243.6$ Hz), 158.0, 153.3, 140.4 (d, $^3J_{C-F} = 8.2$ Hz), 138.1, 131.1, 130.1 (d, $^3J_{C-F} = 8.6$ Hz), 128.1, 127.1, 126.6, 121.8 (d, $^4J_{C-F} = 1.6$ Hz), 121.2 (d, $^2J_{C-F} = 22.9$ Hz), 120.6, 112.4 (d, $^2J_{C-F} = 23.4$ Hz), 81.5, 77.2, 54.6, 44.2, 29.5 ppm. HRMS (ESI): m/z calcd. for C₂₂H₂₂FN₂O₄S [M + H]⁺ 429.1279, found 429.1276.



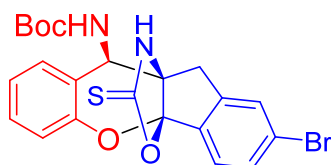
***tert*-Butyl ((4*bR*,10*R*,10*aR*)-3-methoxy-13-thioxo-10*H*,11*H*-4*b*,10*a*-(epoxymethanoimino)-indeno[1,2-*b*]chromen-10-yl)carbamate (3*ad*)**. From 56.6 mg (0.15 mmol) **1a** and 21.9 mg (0.10 mmol) **2d**, purified by silica gel (200-300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3ad** as a white solid (34.3 mg, 78% yield), mp 210–214 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: t_R = 5.9 min (minor), t_R = 4.7 min (major); 90% *ee*. $[\alpha]_D^{20}$ = +88.7 (c = 0.55, CH₂Cl₂). ¹H NMR (400 MHz, acetone-*d*₆): δ 9.09 (s, 1H, NH), 7.40–7.33 (m, 3H, ArH), 7.26–7.21 (m, 3H, ArH), 7.12 (dd, J_1 = 8.6 Hz, J_2 = 2.6 Hz, 1H, ArH), 6.80 (d, J = 10.4 Hz, 1H, NH), 5.07 (d, J = 10.0 Hz, 1H, CH), 3.91 (s, 3H, OCH₃), 3.70 (d, J = 17.2 Hz, 1H, CH₂), 3.42 (d, J = 17.2 Hz, 1H, CH₂), 1.52 (s, 9H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz, acetone-*d*₆): δ 189.2, 162.1, 158.0, 153.5, 139.6, 133.7, 131.0, 128.9, 128.3, 127.1, 126.4, 122.5, 121.6, 120.6, 109.2, 81.4, 77.2, 57.0, 54.7, 44.1, 29.5 ppm. HRMS (ESI): m/z calcd. for C₂₃H₂₅N₂O₅S [M + H]⁺ 441.1479, found 441.1465.



***tert*-Butyl ((4*bR*,10*R*,10*aR*)-2-methoxy-13-thioxo-10*H*,11*H*-4*b*,10*a*-(epoxymethanoimino)-indeno[1,2-*b*]chromen-10-yl)carbamate (3*ae*)**. From 56.6 mg (0.15 mmol) **1a** and 21.9 mg (0.10 mmol) **2e**, purified by silica gel (200-300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3ae** as a white solid (39.6 mg, 90% yield), mp 238–241 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: t_R = 6.3 min (minor), t_R = 4.8 min (major); 96% *ee*. $[\alpha]_D^{20}$ = +73.8 (c = 0.68, CH₂Cl₂). ¹H NMR (400 MHz, acetone-*d*₆): δ 9.08 (s, 1H, NH), 7.40–7.33 (m, 3H, ArH), 7.26–7.21 (m, 3H, ArH), 7.12 (dd, J_1 = 8.6 Hz, J_2 = 2.6 Hz, 1H, ArH), 6.80 (d, J = 10.0 Hz, 1H, NH), 5.07 (d, J = 10.4 Hz, 1H, CH), 3.91 (s, 3H, OCH₃), 3.70 (d, J = 17.2 Hz, 1H, CH₂), 3.42 (d, J = 17.2 Hz, 1H, CH₂), 1.52 (s, 9H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz, acetone-*d*₆): δ 189.2, 162.1, 158.0, 153.5, 139.6, 133.7, 131.0, 128.9, 128.3, 127.1, 126.4, 122.5, 121.6, 120.6, 109.2, 81.4, 77.1, 57.0, 54.7, 44.1, 29.5 ppm. HRMS (ESI): m/z calcd. for C₂₃H₂₅N₂O₅S [M + H]⁺ 441.1479, found 441.1471.

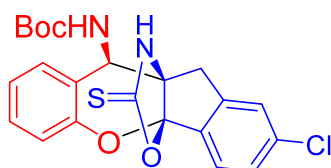


***tert*-Butyl ((4*bR*,10*R*,10*aR*)-2-fluoro-13-thioxo-5,10-dihydro-11*H*-4*b*,10*a*-(epoxymethanoimino)benzo[*b*]fluoren-10-yl)carbamate (3af).** From 56.6 mg (0.15 mmol) **1a** and 20.7 mg (0.10 mmol) **2f**, purified by silica gel (200-300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3ad** as a white solid (34.2 mg, 80% yield), mp 228–230 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: t_R = 8.2 min (minor), t_R = 5.4 min (major); 96% *ee*. $[\alpha]_D^{20}$ = +50.0 (c = 0.25, CH₂Cl₂). ¹H NMR (400 MHz, acetone-*d*₆): δ 9.11 (s, 1H, NH), 7.83–7.79 (m, 1H, ArH), 7.41–7.35 (m, 2H, ArH), 7.32–7.21 (m, 4H, ArH), 6.84 (d, J = 10.0 Hz, 1H, NH), 5.10 (d, J = 10.4 Hz, 1H, CH), 3.82 (d, J = 17.6 Hz, 1H, CH₂), 3.57 (d, 1H, CH₂), 1.53 (m, 9H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 197.8, 175.5 (d, ¹ J_{C-F} = 246.9 Hz), 166.6, 162.0, 153.9 (d, ³ J_{C-F} = 9.3 Hz), 143.5, 139.7, 136.8, 136.77 (d, ³ J_{C-F} = 9.9 Hz), 135.7, 135.1, 130.3, 129.2, 126.5 (d, ² J_{C-F} = 23.7 Hz), 123.4 (d, ² J_{C-F} = 22.8 Hz), 90.1, 85.5, 63.3, 53.3, 38.2 ppm. HRMS (ESI): m/z calcd. for C₂₂H₂₂FN₂O₄S [M + H]⁺ 429.1279, found 429.1266.



3ag

***tert*-Butyl ((4*bR*,10*R*,10*aR*)-2-bromo-13-thioxo-10*H*,11*H*-4*b*,10*a*-(epoxymethanoimino)indeno[1,2-*b*]chromen-10-yl)carbamate (3ag).** From 36.6 mg (0.15 mmol) **1a** and 26.8 mg (0.10 mmol) **2g**, purified by silica gel (200-300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3ag** as a light yellow brown solid (38.6 mg, 79% yield), mp 212–214 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 80:20, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: t_R = 5.8 min (minor), t_R = 4.9 min (major); 95% *ee*. $[\alpha]_D^{20}$ = +85 (c = 0.6, CH₂Cl₂). ¹H NMR (400 MHz, acetone-*d*₆): δ 9.12 (s, 1H, NH), 7.73–7.70 (m, 3H, ArH), 7.40–7.35 (m, 2H, ArH), 7.23 (t, J = 8.4 Hz, 2H, ArH), 6.83 (d, J = 10.0 Hz, 1H, NH), 5.10 (d, J = 10.0 Hz, 1H, CH), 3.82 (d, J = 18.0 Hz, 1H, CH₂), 3.57 (d, J = 18.0 Hz, 1H, CH₂), 1.53 (s, 9H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz, acetone-*d*₆): δ 189.1, 158.0, 153.3, 144.9, 137.8, 133.5, 131.3, 131.1, 128.1, 127.8, 127.4, 127.1, 126.5, 121.9, 120.6, 81.5, 76.7, 54.6, 44.5, 29.5 ppm. HRMS (ESI): m/z calcd. for C₂₂H₂₂BrN₂O₄S [M + H]⁺ 489.0478, found 489.0471; calcd. for C₂₂H₂₂⁸¹BrN₂O₄S [M + H]⁺ 491.0458, found 491.0456.



3ah

tert-Butyl ((4*R*,10*R*,10*aR*)-2-chloro-13-thioxo-10*H*,11*H*-4*b*,10*a*-(epoxymethanoimino)-indeno[1,2-*b*]chromen-10-yl)carbamate (**3ah**). From 56.6 mg (0.15 mmol) **1a** and 22.3 mg (0.10 mmol) **2h**, purified by silica gel (200-300 mesh) column chromatography using petroleum ether/ethyl acetate (5:1 to 3:1 v/v) as eluent to obtain **3ah** as a light yellow brown solid (42.2 mg, 95% yield), mp 213–215 °C. HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 85:15, flow rate 1.0 mL/min, detection at 254 nm): for major diastereomer: $t_R = 7.2$ min (minor), $t_R = 5.5$ min (major); 95% *ee*. $[\alpha]_D^{20} = +82.0$ ($c = 1.00$, CH₂Cl₂). ¹H NMR (400 MHz, acetone-*d*₆): δ 9.13 (s, 1H, NH), 7.77 (d, $J = 8.4$ Hz, 1H, ArH), 7.55–7.53 (m, 2H, ArH), 7.40–7.34 (m, 2H, ArH), 7.25–7.20 (m, 2H, ArH), 6.82 (d, $J = 10.0$ Hz, 1H, NH), 5.10 (d, $J = 10.0$ Hz, 1H, CH), 3.81 (d, $J = 18.0$ Hz, 1H, CH₂), 3.56 (d, $J = 17.6$ Hz, 1H, CH₂), 1.53 (s, 9H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz, acetone-*d*₆): δ 189.1, 158.0, 153.4, 144.7, 139.1, 137.4, 131.1, 130.7, 128.3, 128.1, 127.6, 127.1, 126.6, 121.8, 120.6, 81.5, 76.8, 54.6, 44.6, 29.5 ppm. HRMS (ESI): m/z calcd. for C₂₂H₂₂ClN₂O₄S [M + H]⁺ 445.0983, found 445.0967.

7. X-ray crystallographic analysis

Single crystals suitable for X-ray diffraction experiment were obtained by diffusion method of *n*-hexane/CH₂Cl₂ containing the corresponding compound **3ka**.

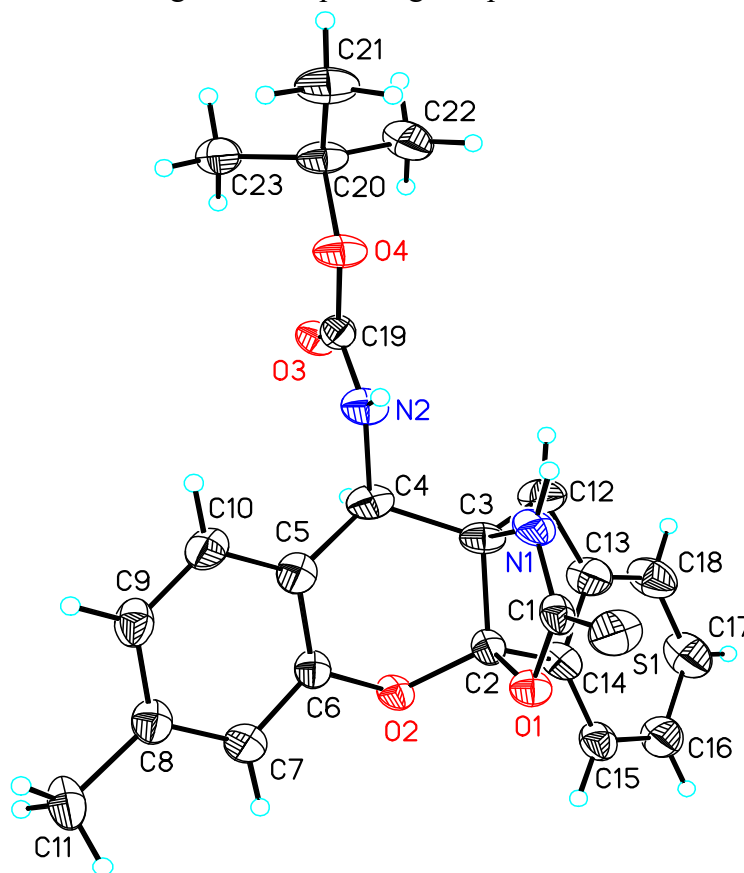
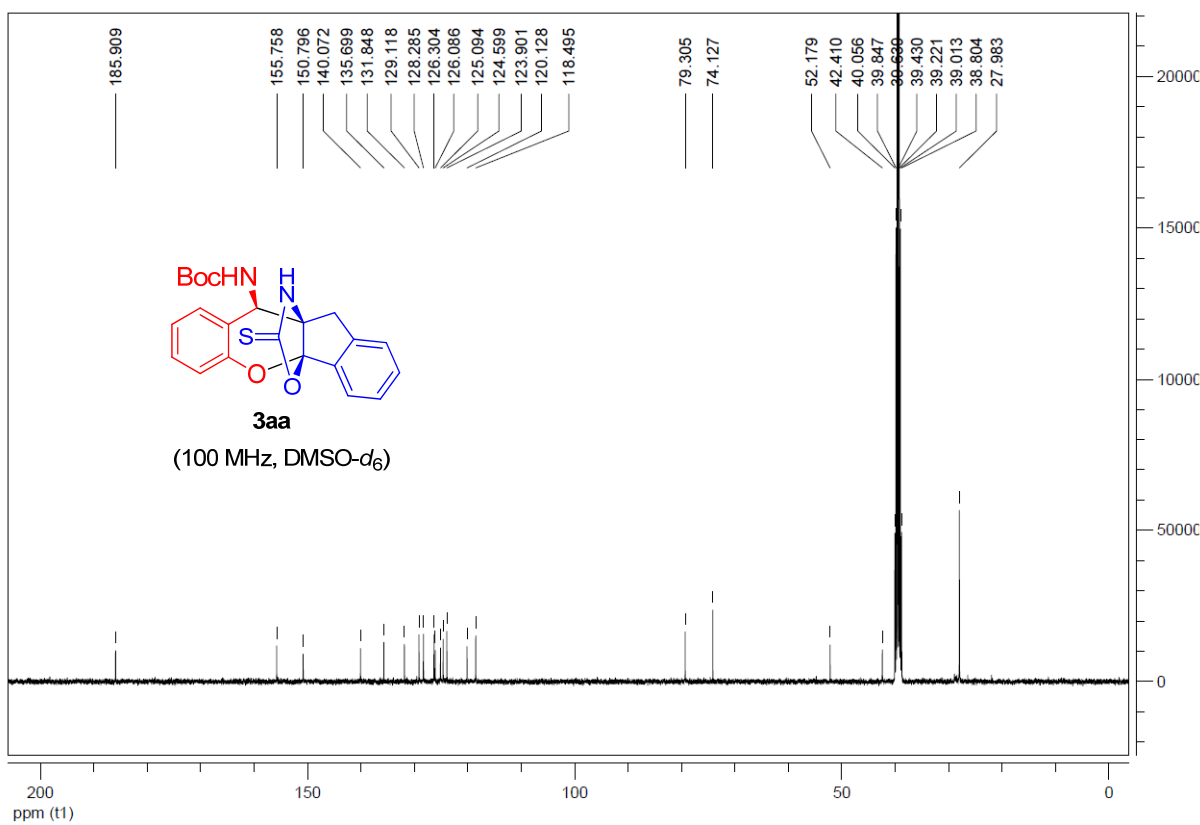
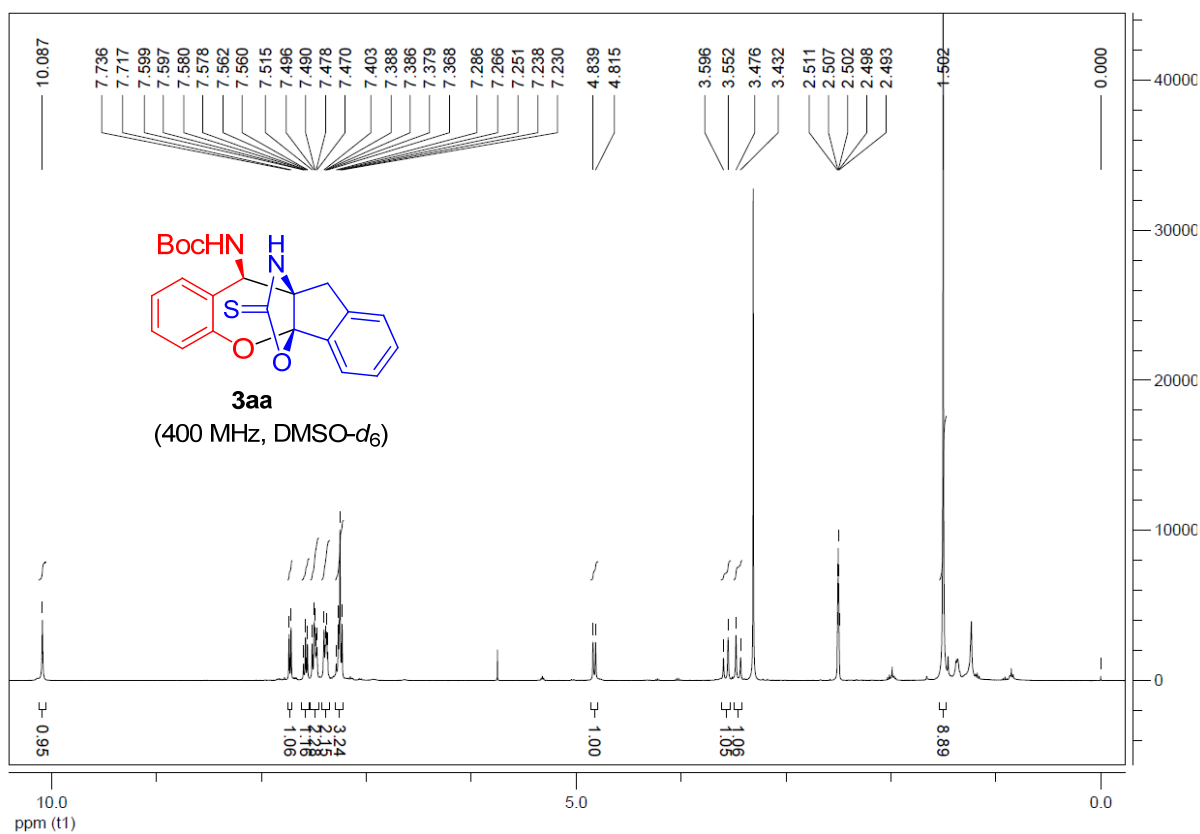


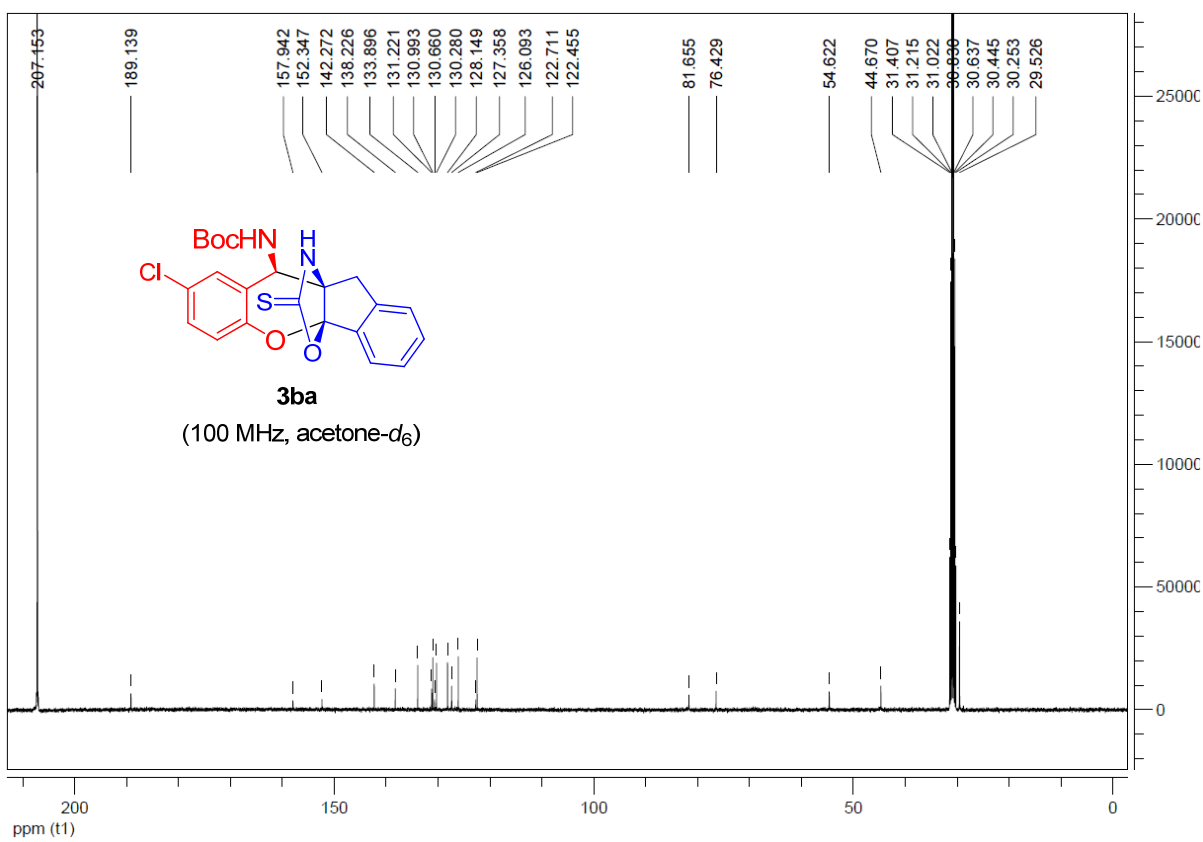
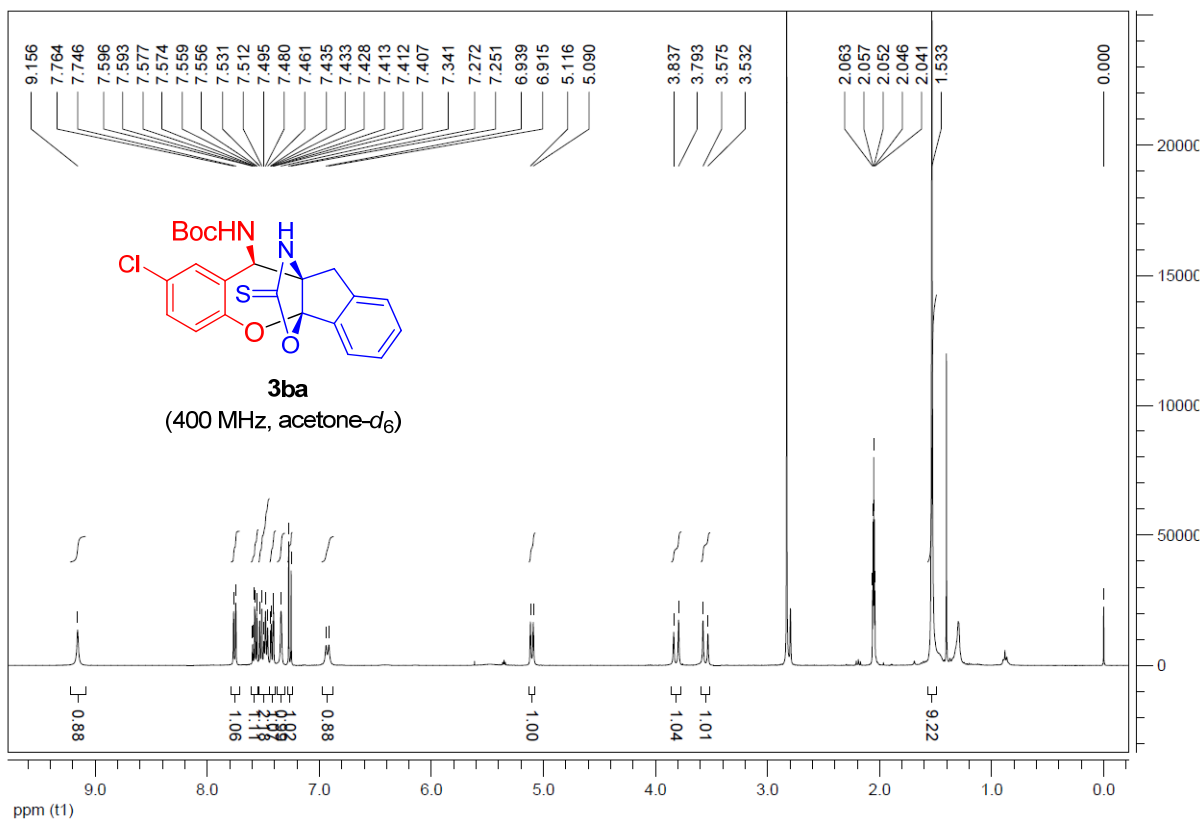
Figure S1. X-ray structure of **3ka**

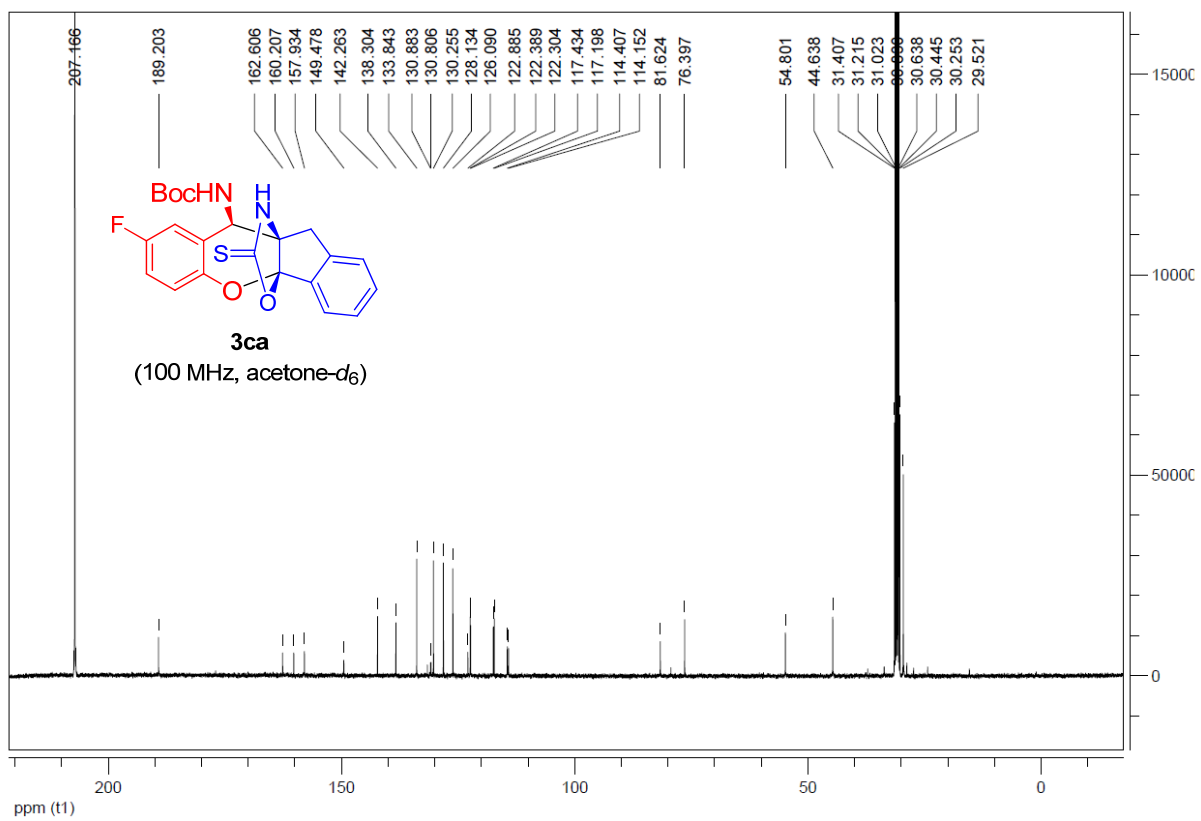
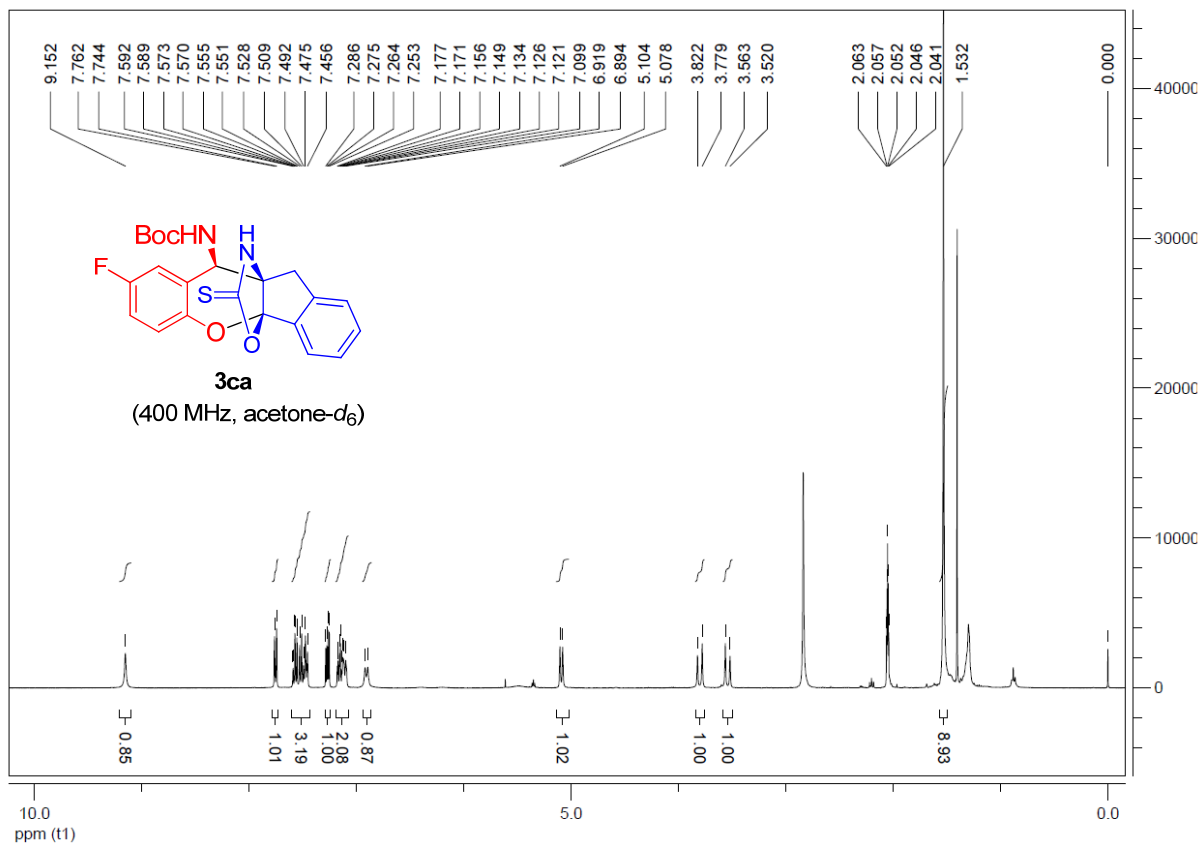
Table S1. Crystal data and structure refinement for **3ka**.

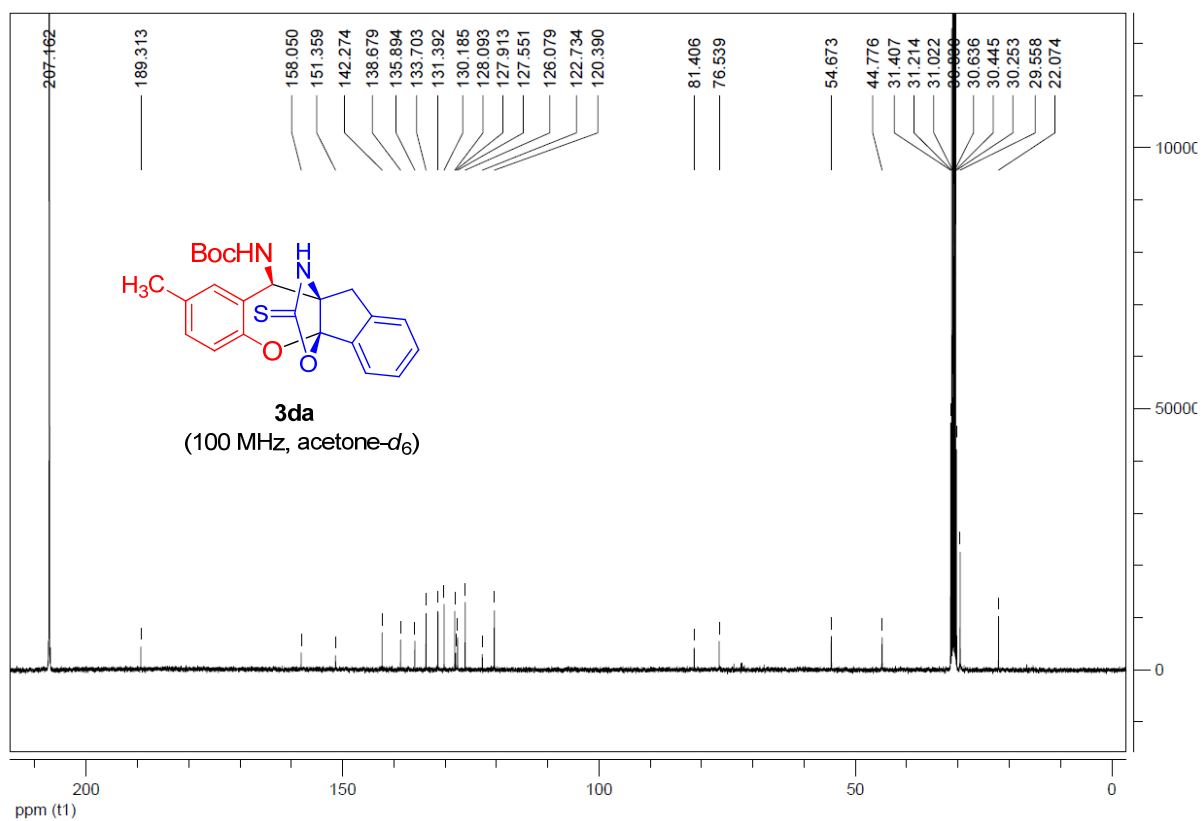
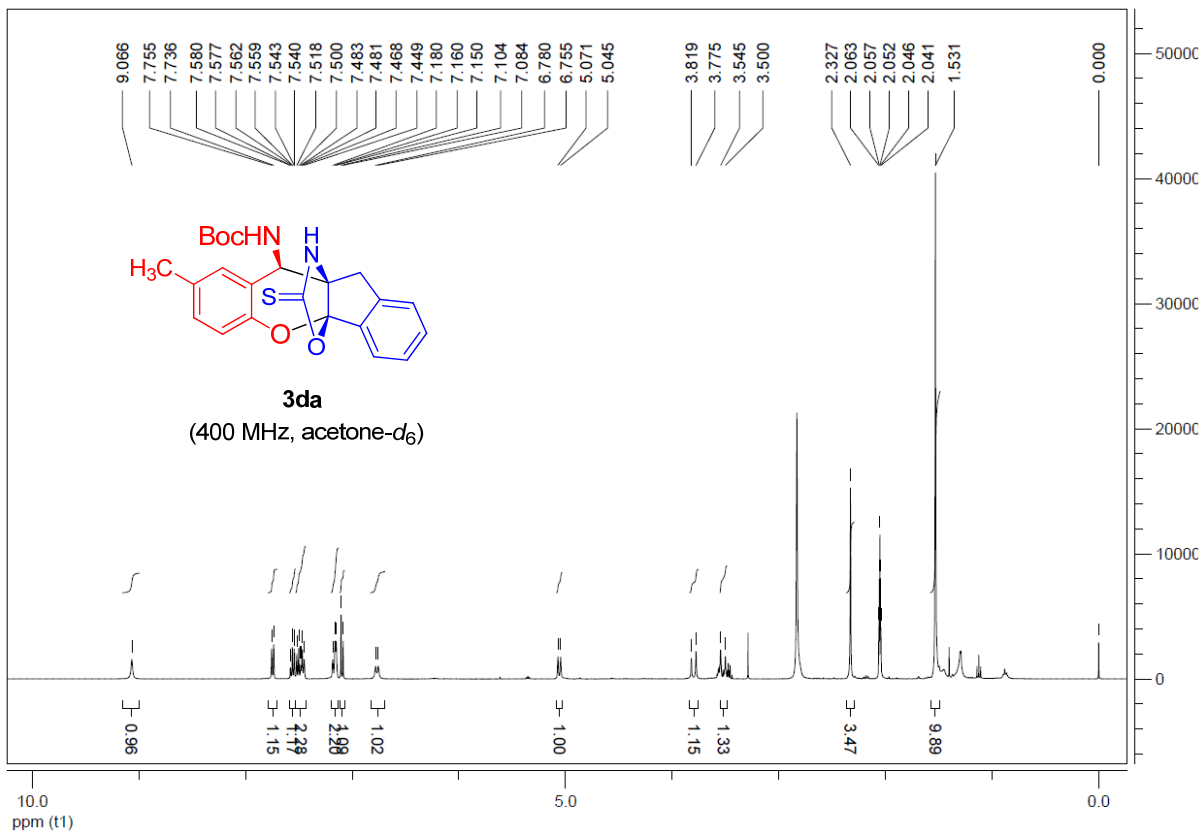
Identification code	1	
Empirical formula	C _{23.50} H ₂₄ Cl N ₂ O ₄ S	
Formula weight	465.96	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 11.9485(5) Å	α = 90°.
	b = 15.6227(6) Å	β = 90°.
	c = 25.4354(11) Å	γ = 90°.
Volume	4748.0(3) Å ³	
Z	8	
Density (calculated)	1.304 Mg/m ³	
Absorption coefficient	2.511 mm ⁻¹	
F(000)	1952	
Crystal size	0.14 x 0.11 x 0.09 mm ³	
Theta range for data collection	3.475 to 66.991°.	
Index ranges	-14 ≤ h ≤ 13, -18 ≤ k ≤ 18, -30 ≤ l ≤ 30	
Reflections collected	35839	
Independent reflections	8428 [R(int) = 0.0863]	
Completeness to theta = 66.991°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.84567	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8428 / 2 / 576	
Goodness-of-fit on F ²	1.051	
Final R indices [I > 2σ(I)]	R1 = 0.0721, wR2 = 0.1955	
R indices (all data)	R1 = 0.0752, wR2 = 0.1986	
Absolute structure parameter	0.030(15)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.014 and -1.135 e.Å ⁻³	

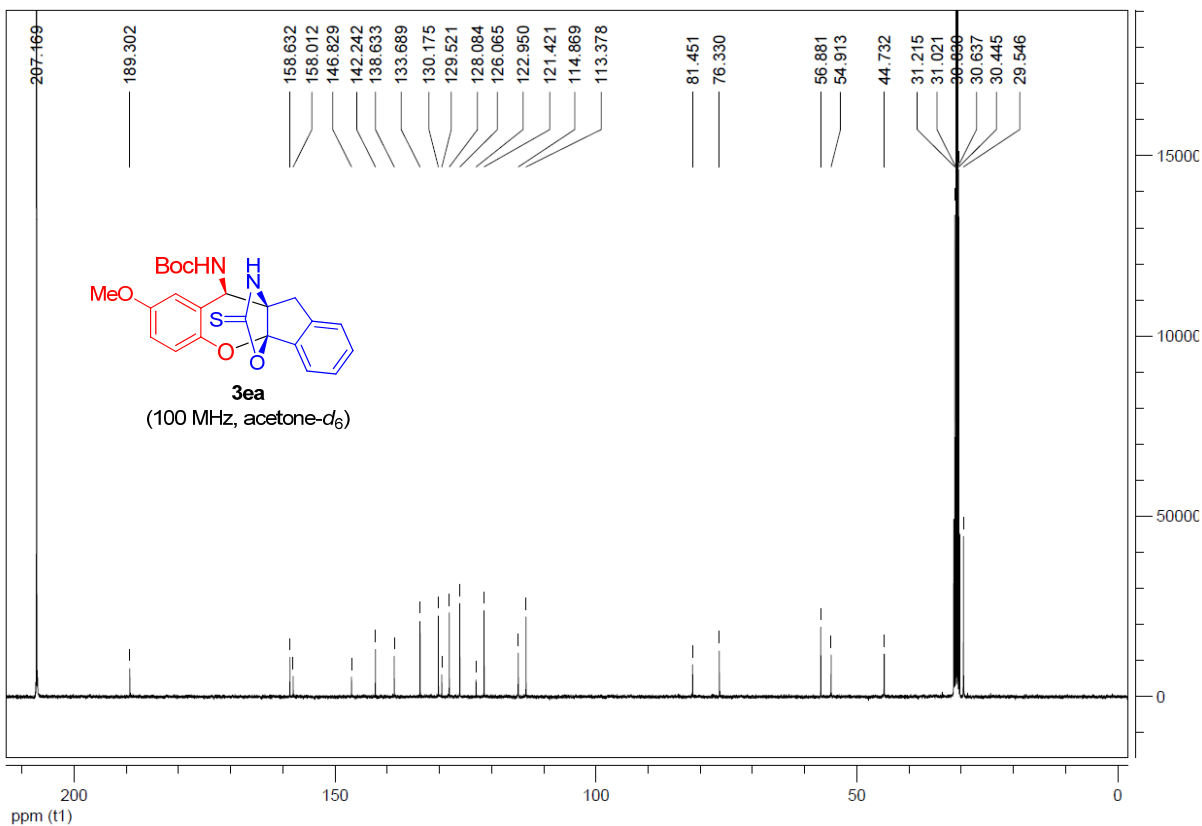
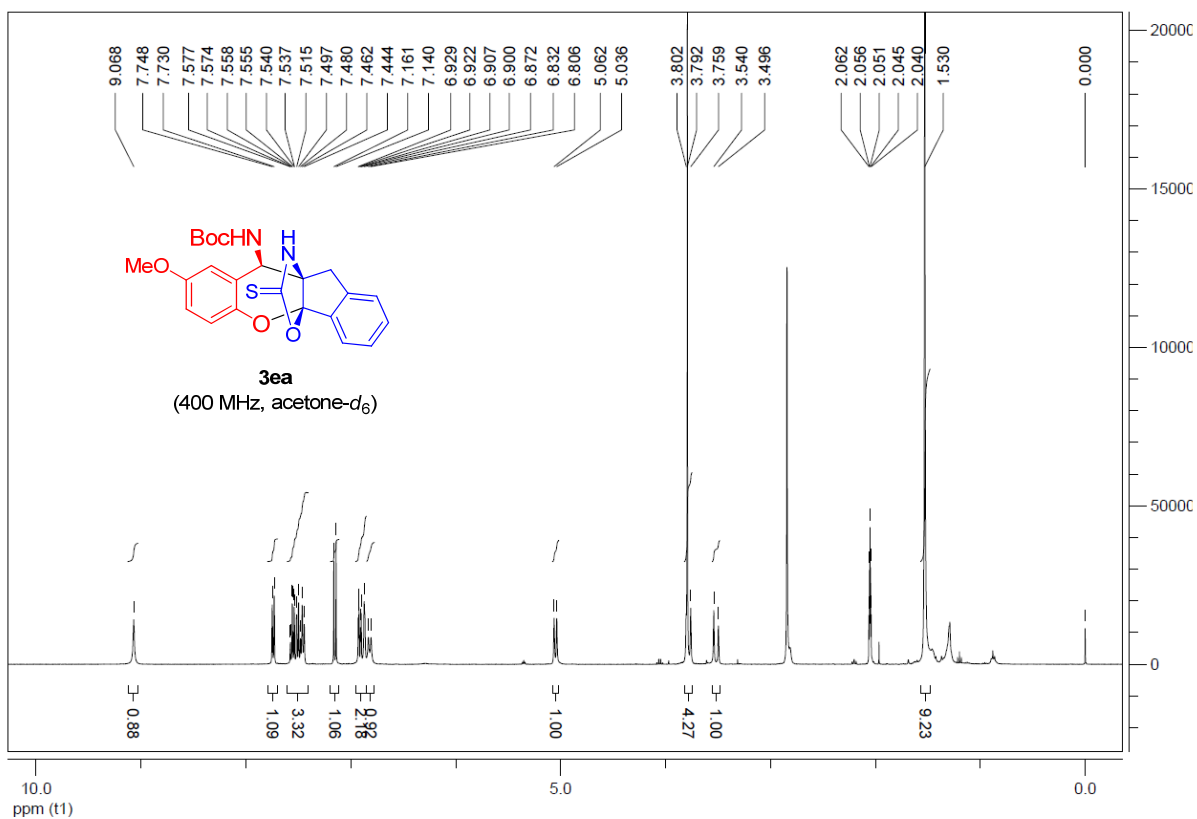
5. Copies of ¹H and ¹³C NMR spectra of new products

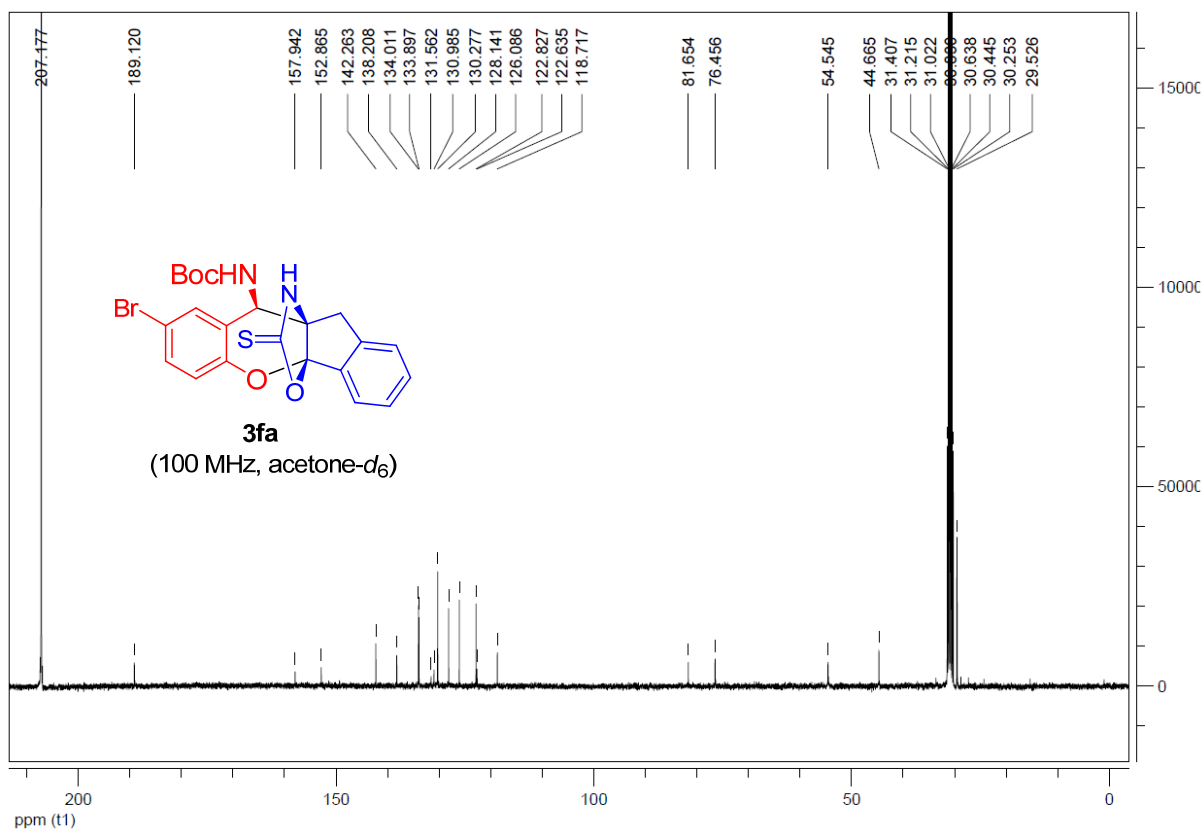
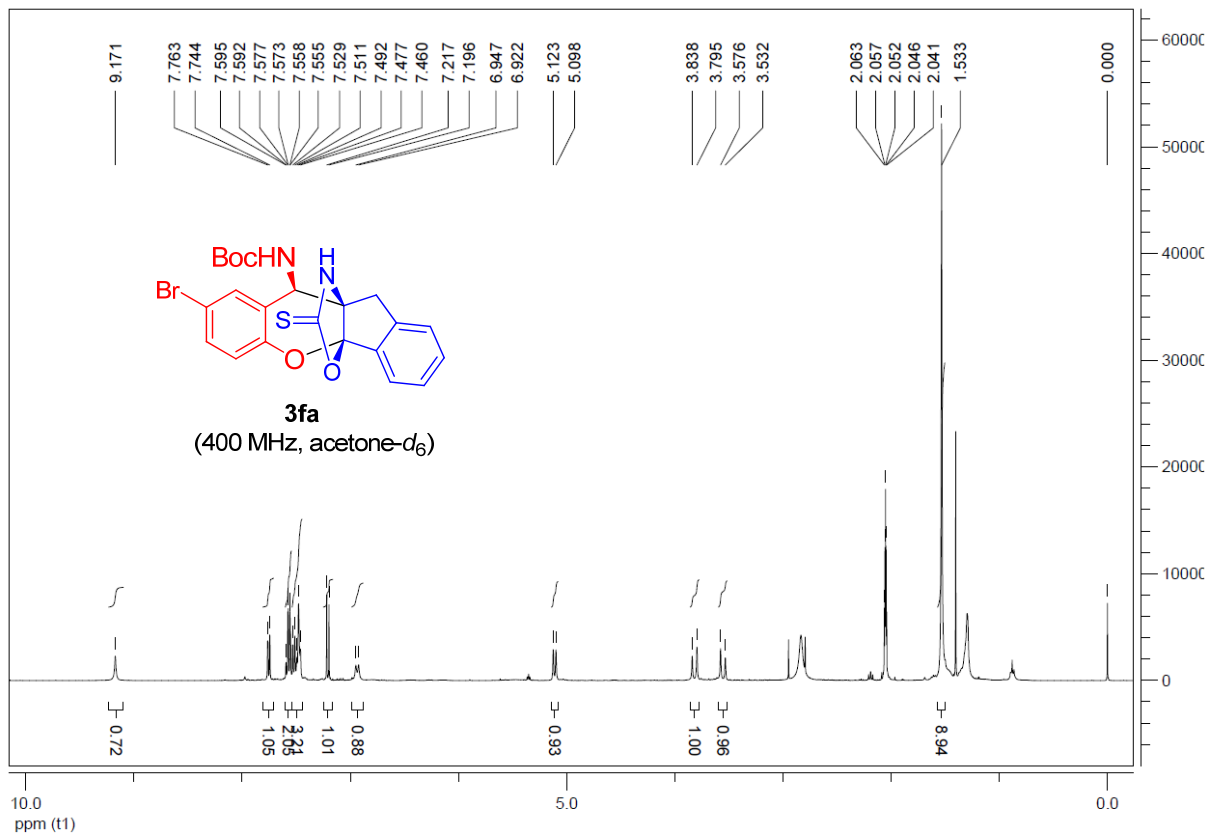


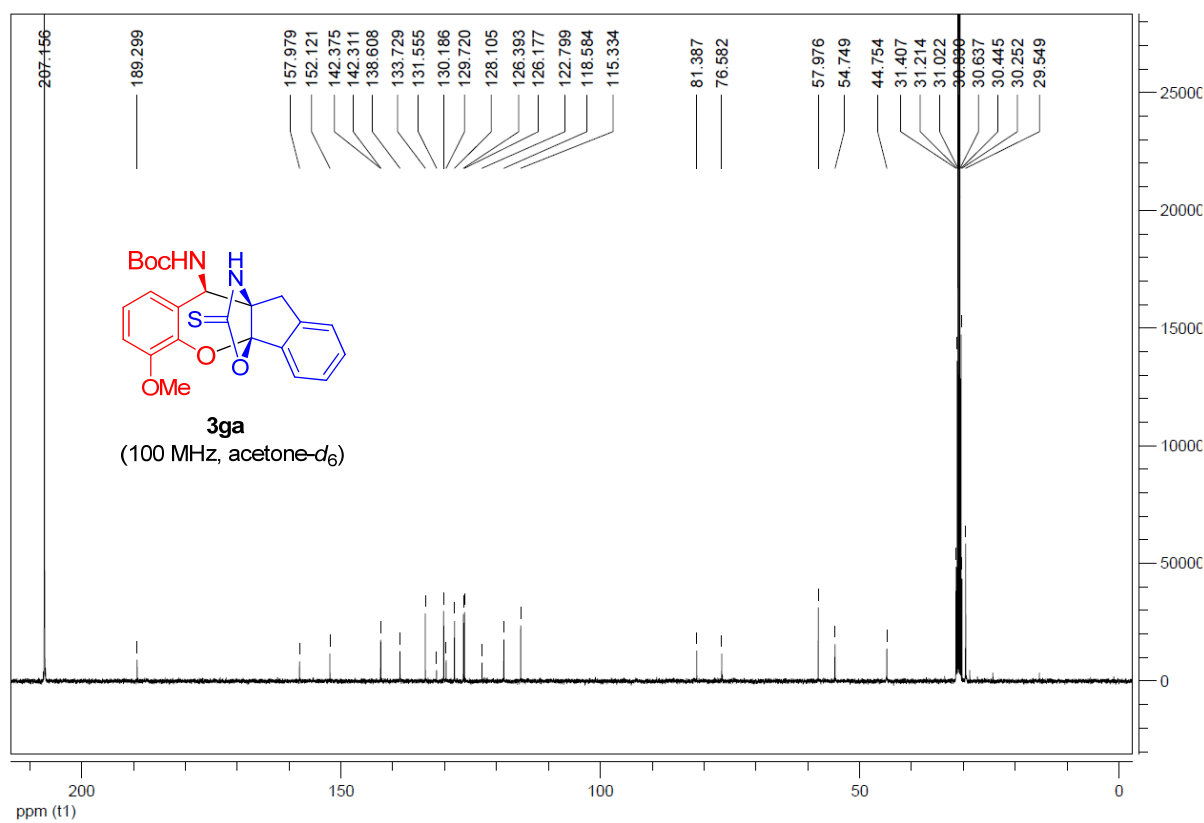
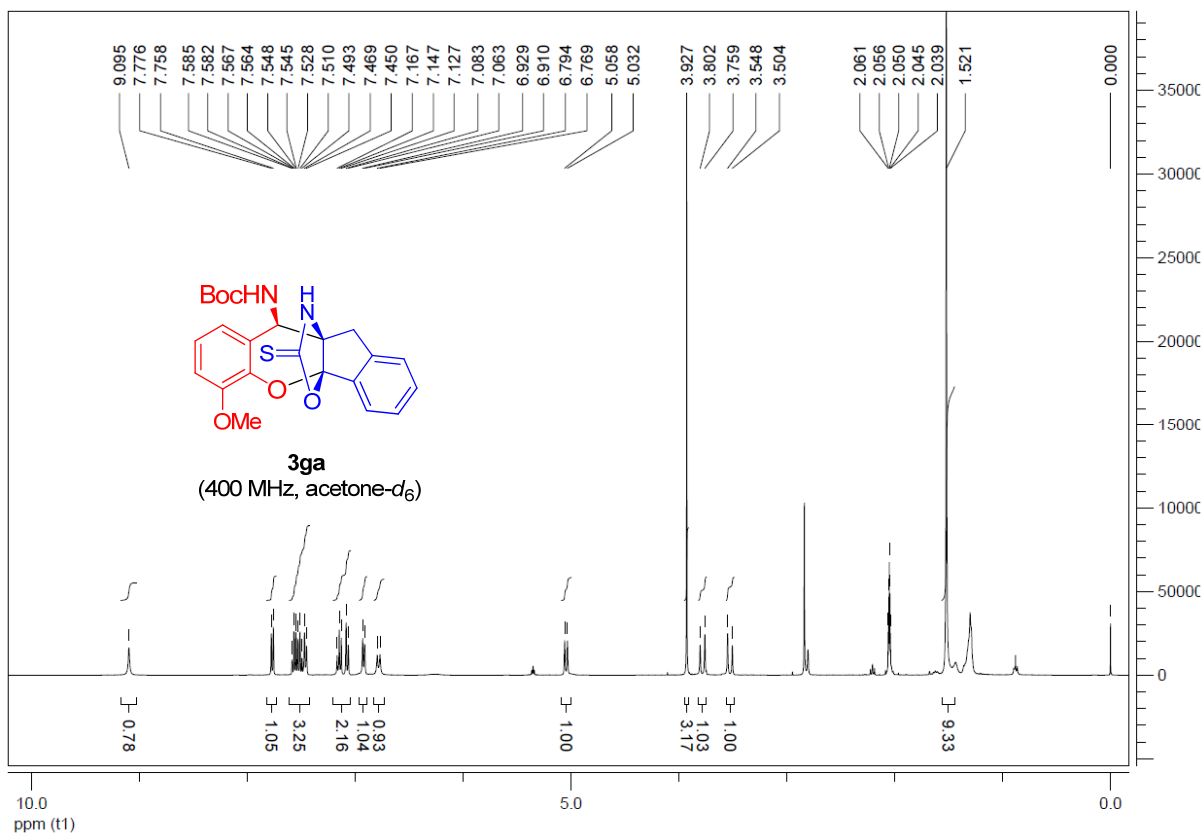


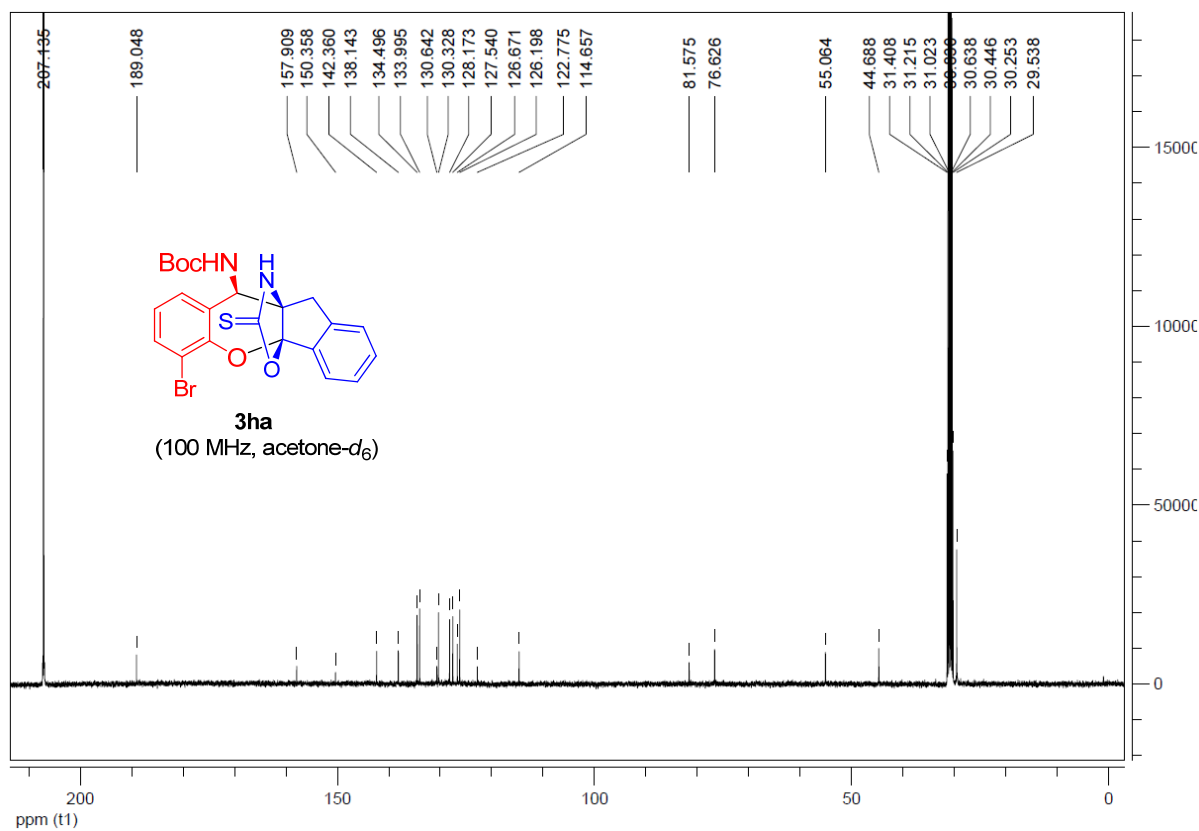
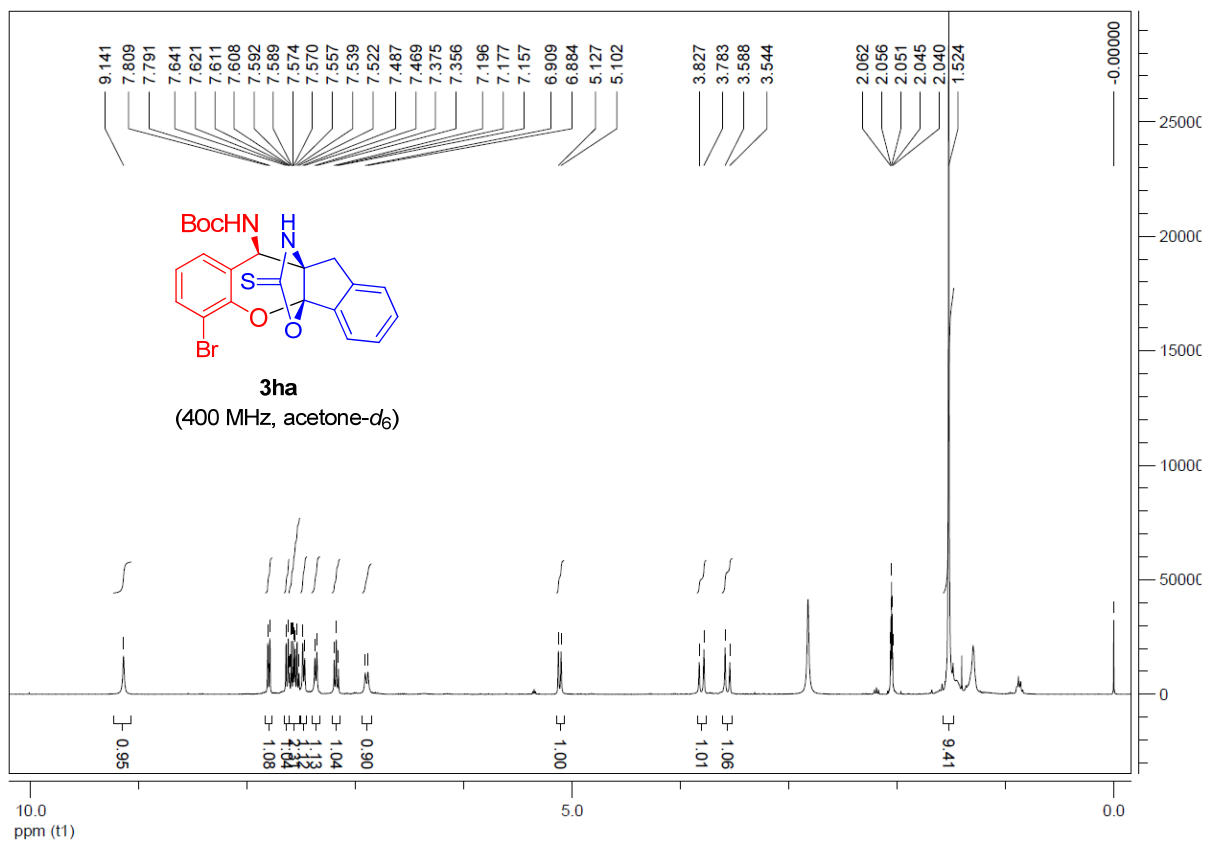


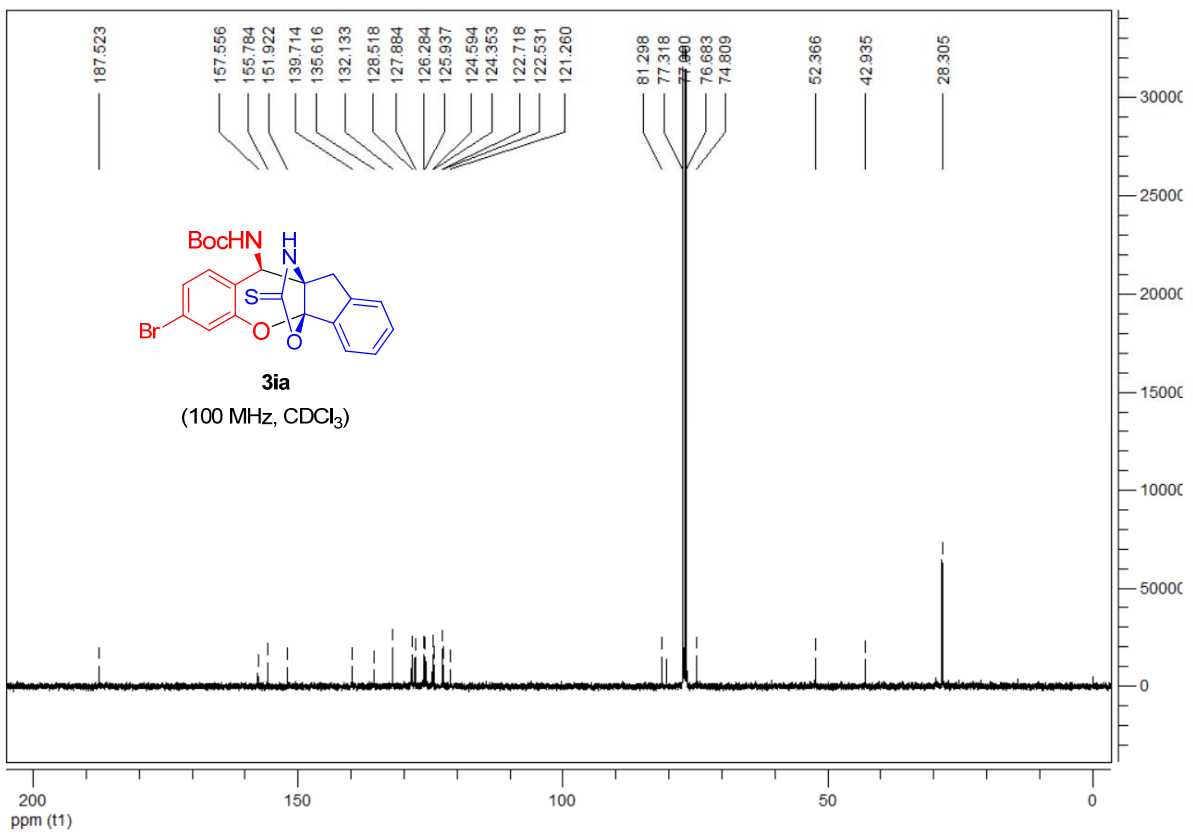
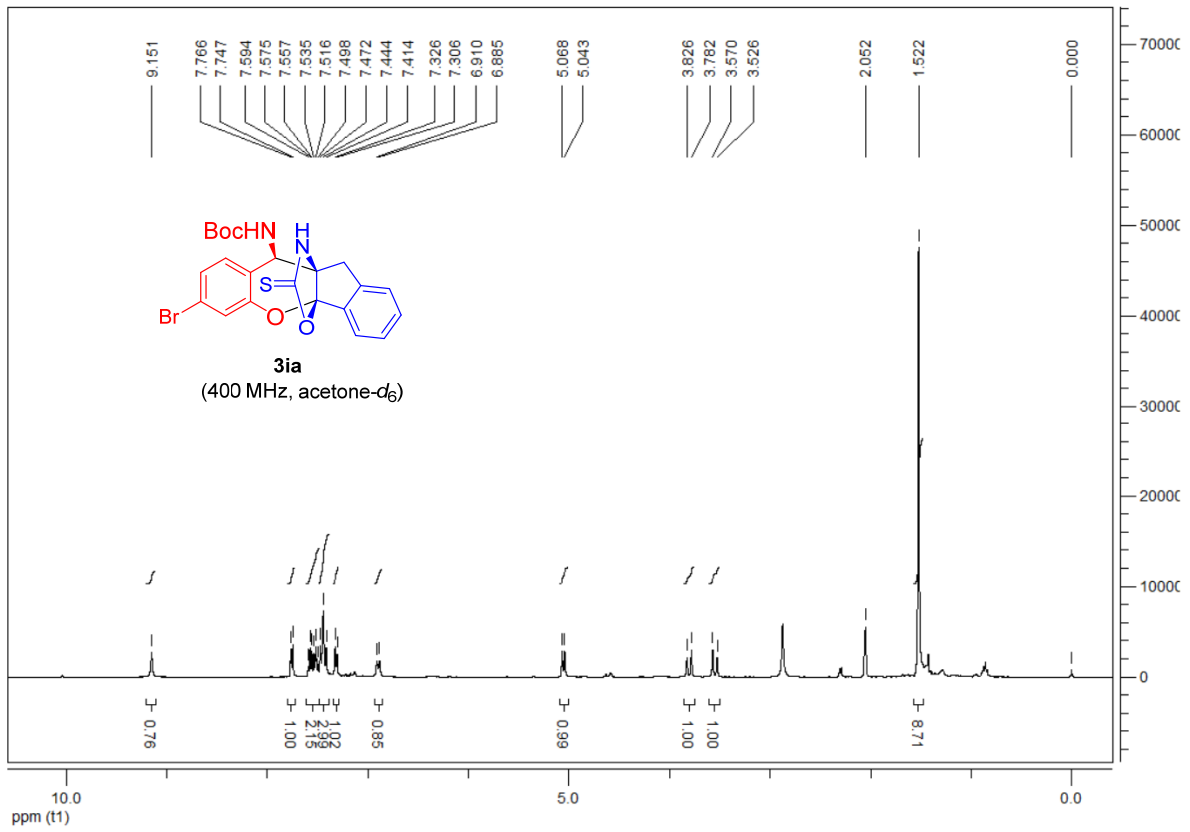


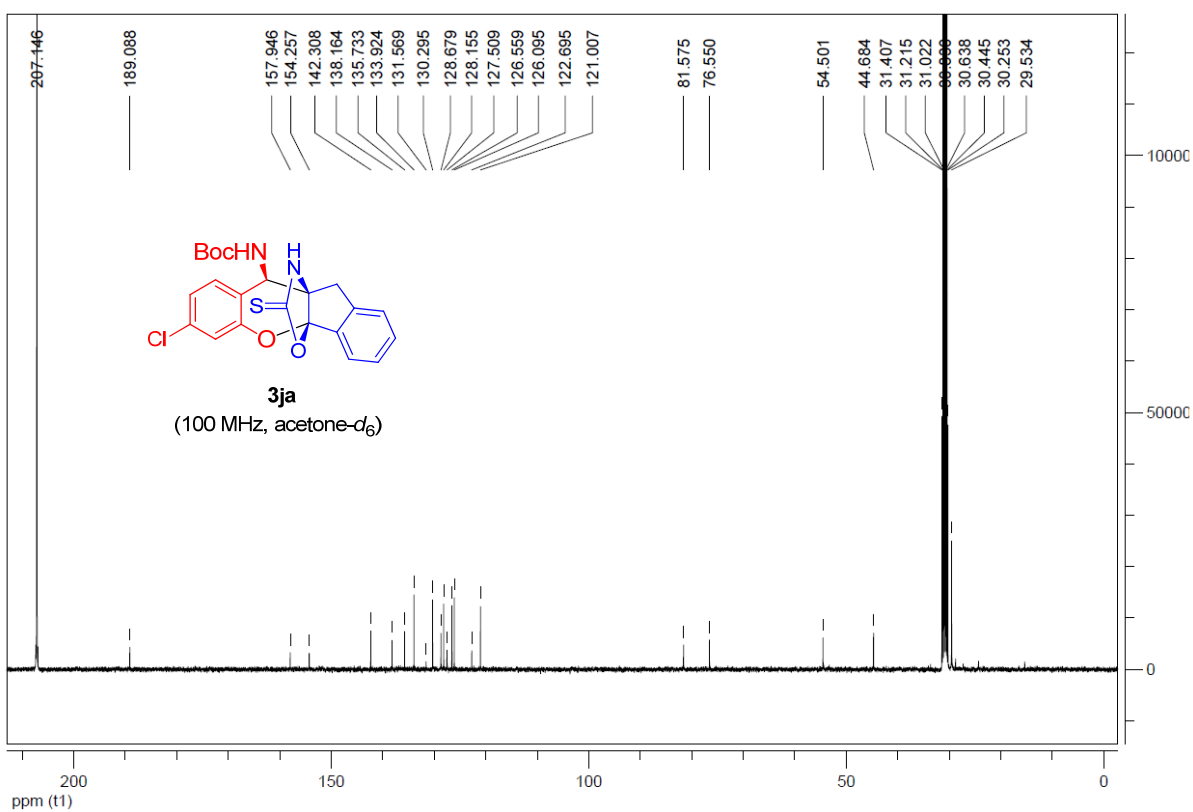
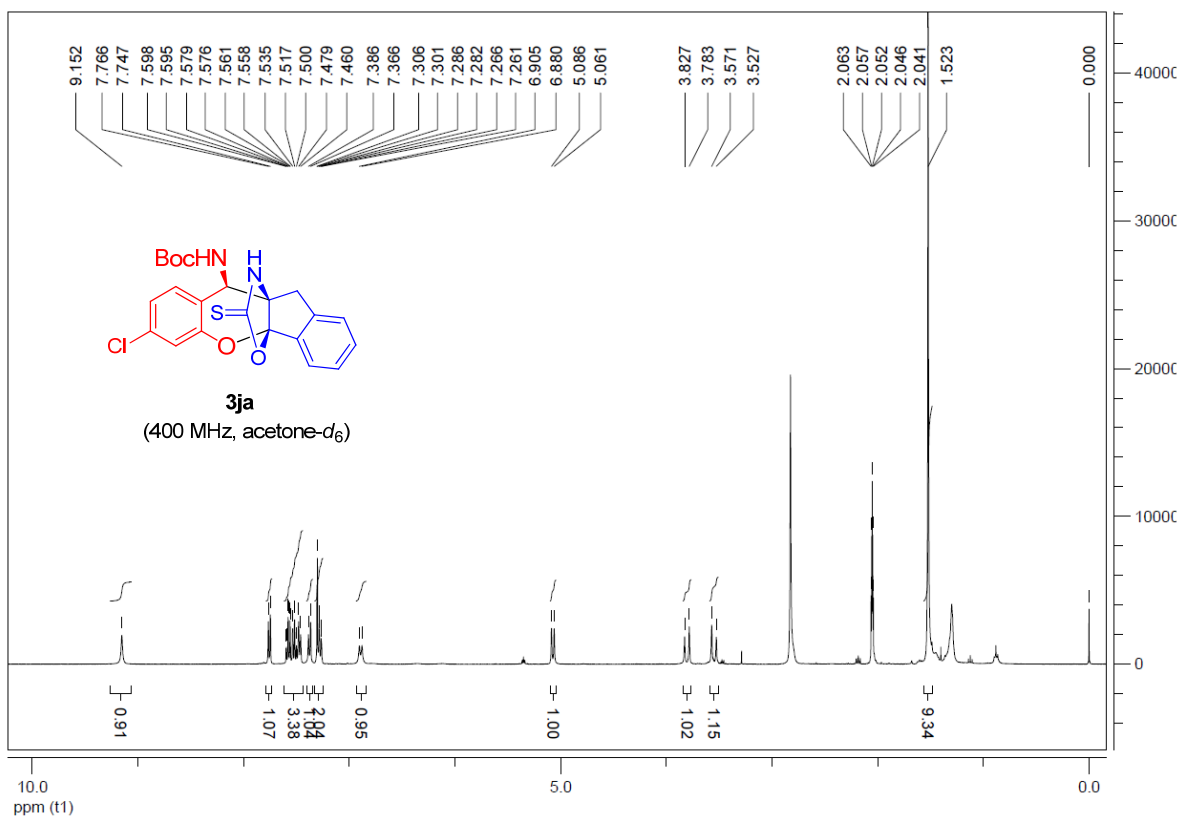


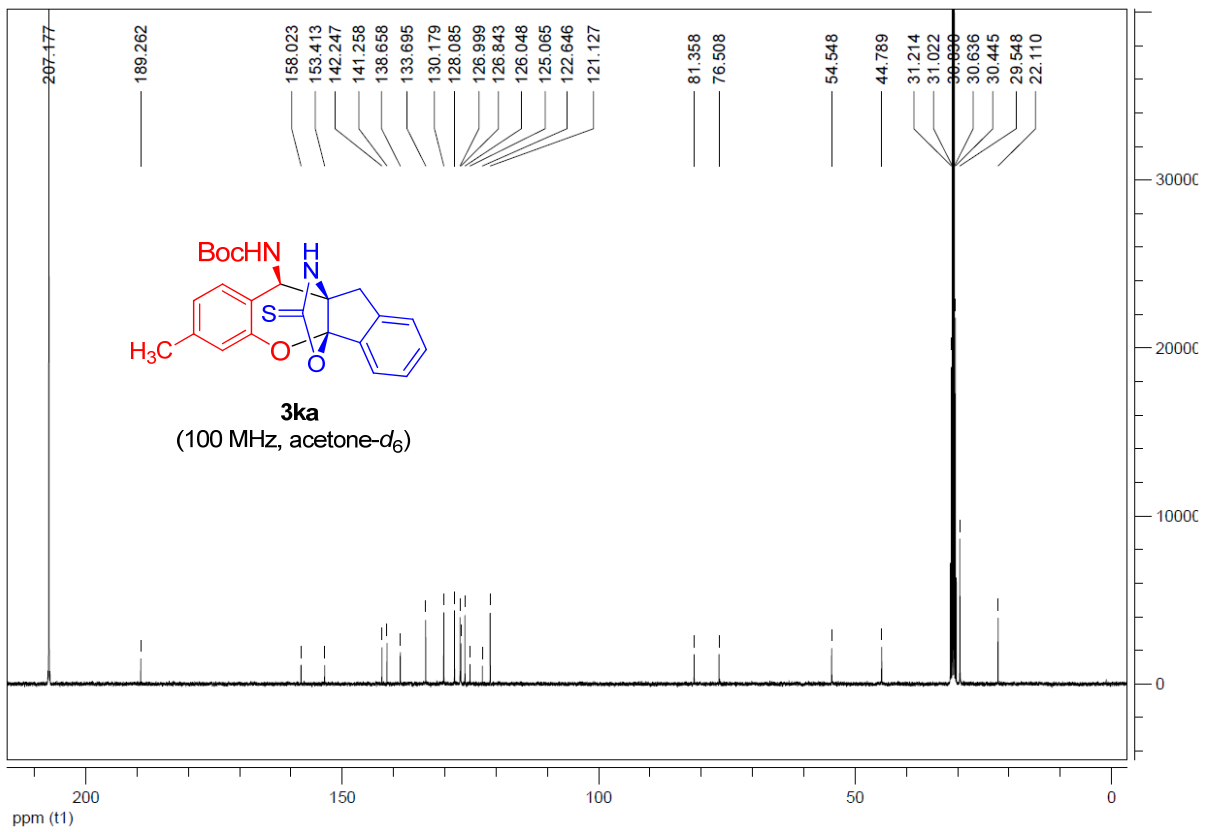
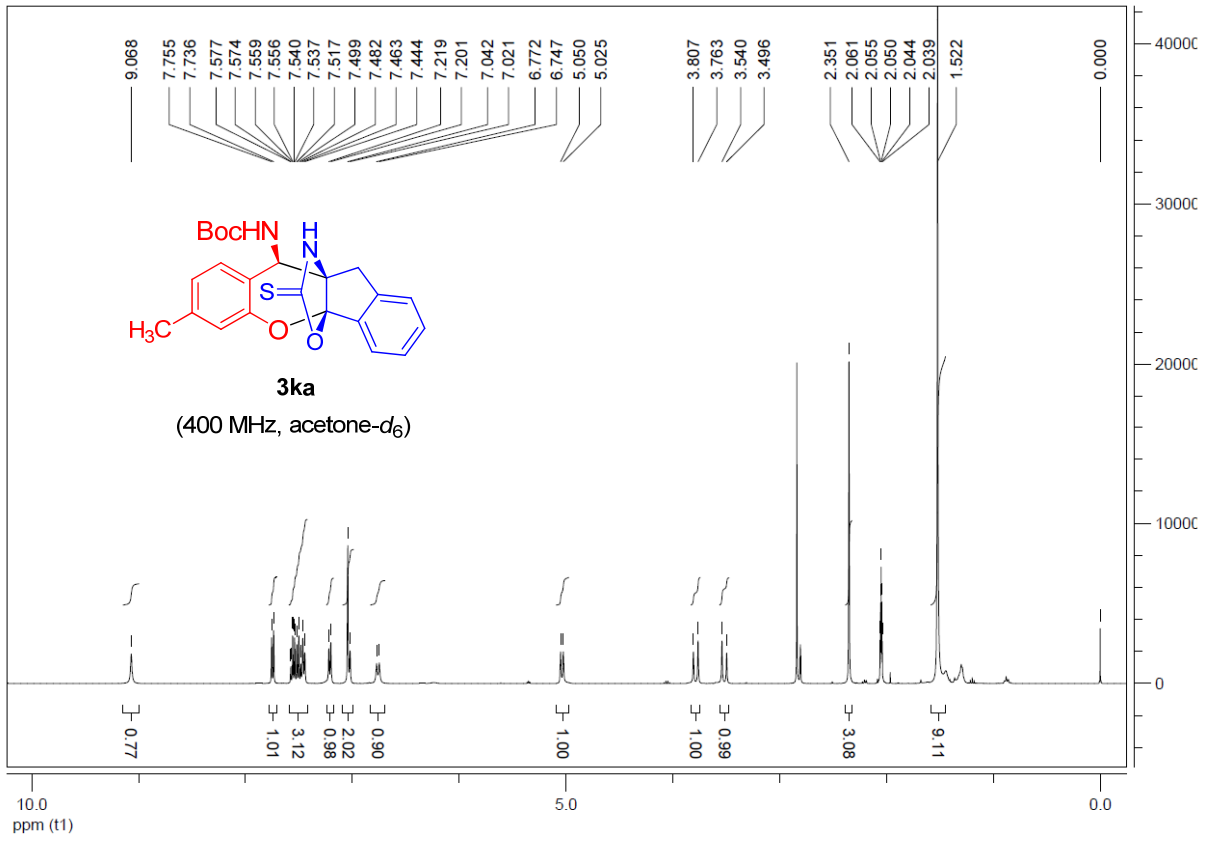


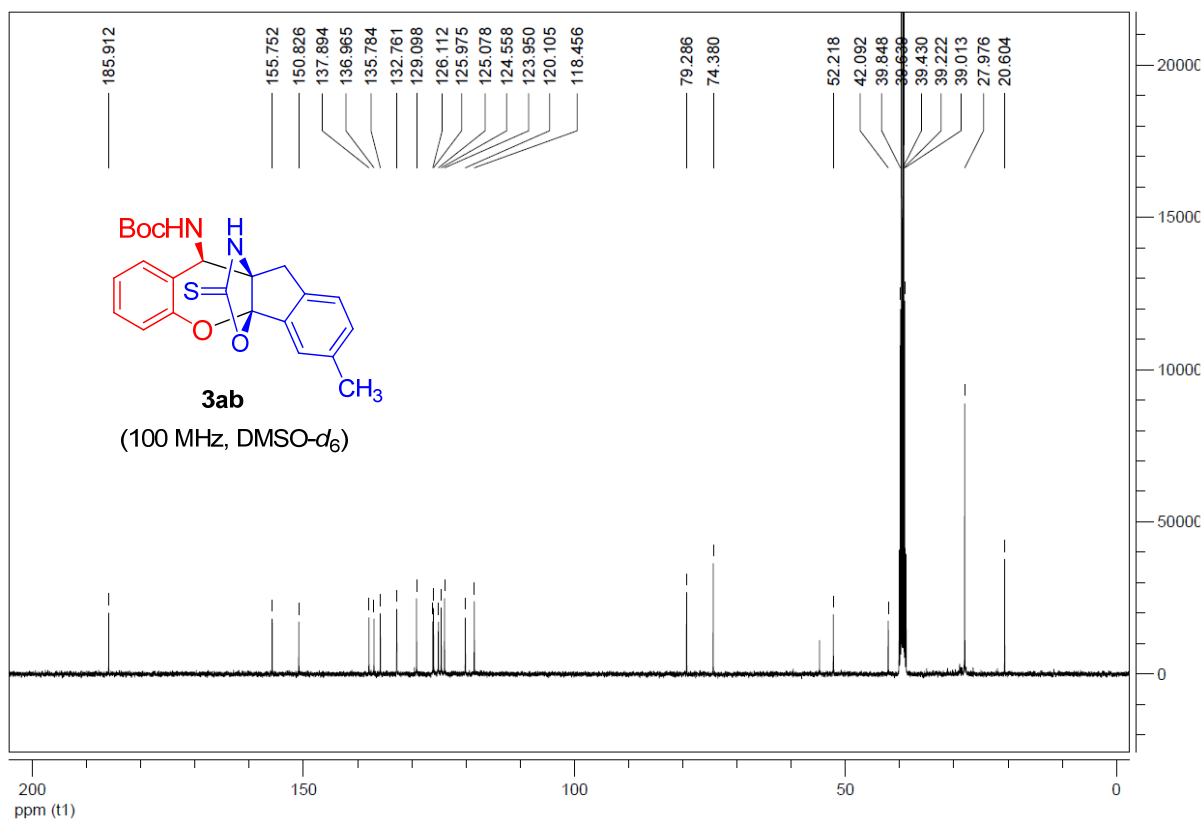
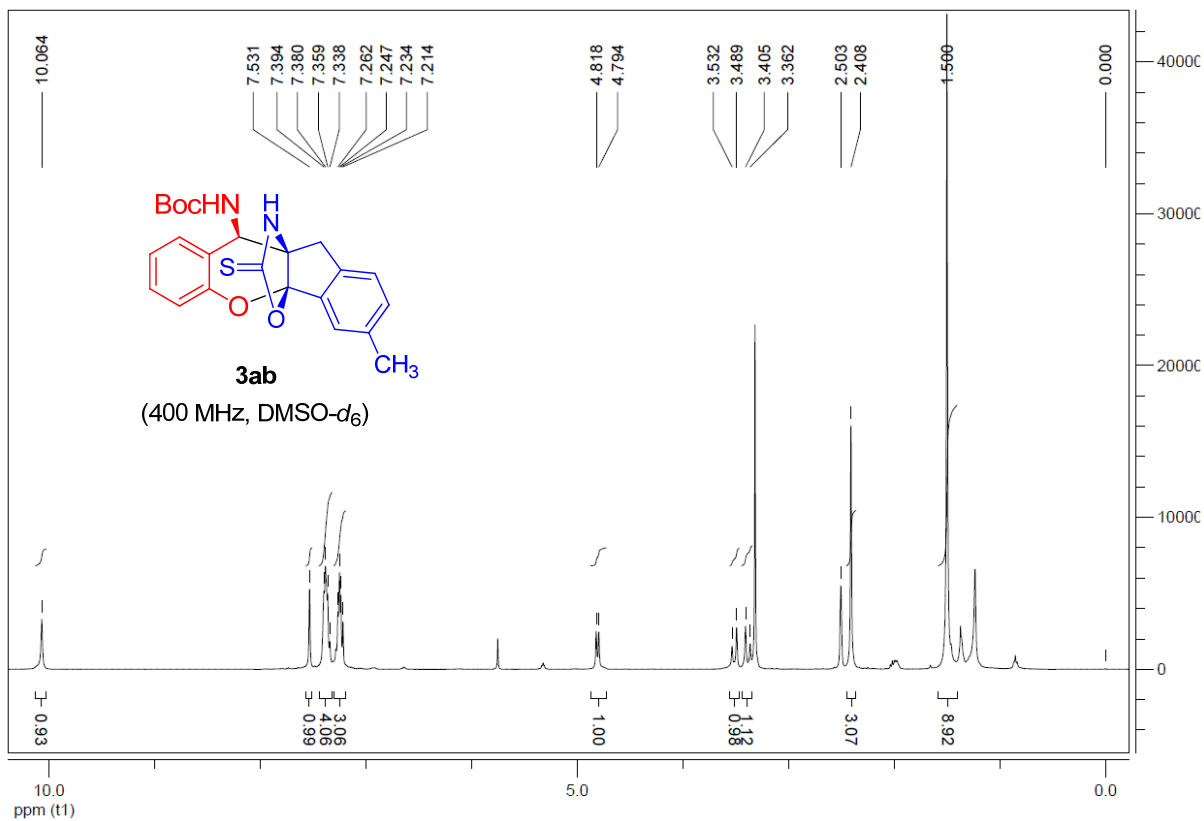


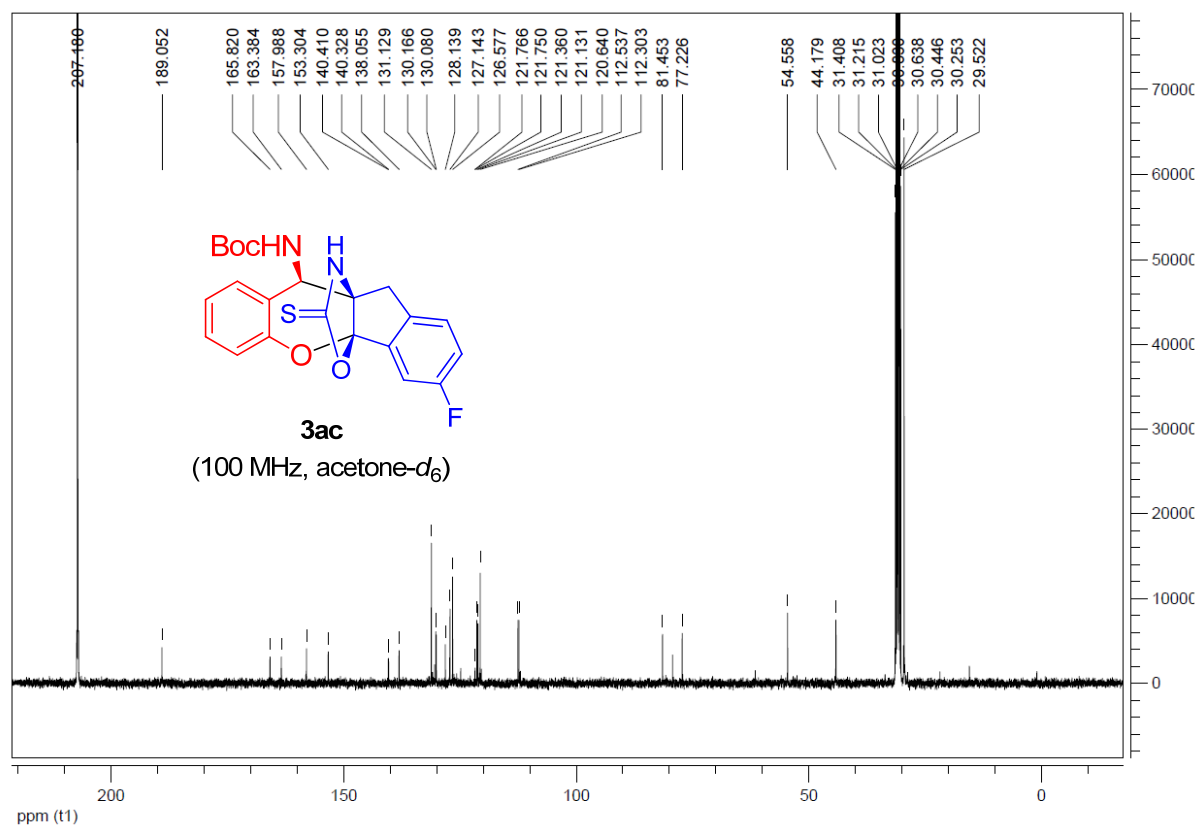
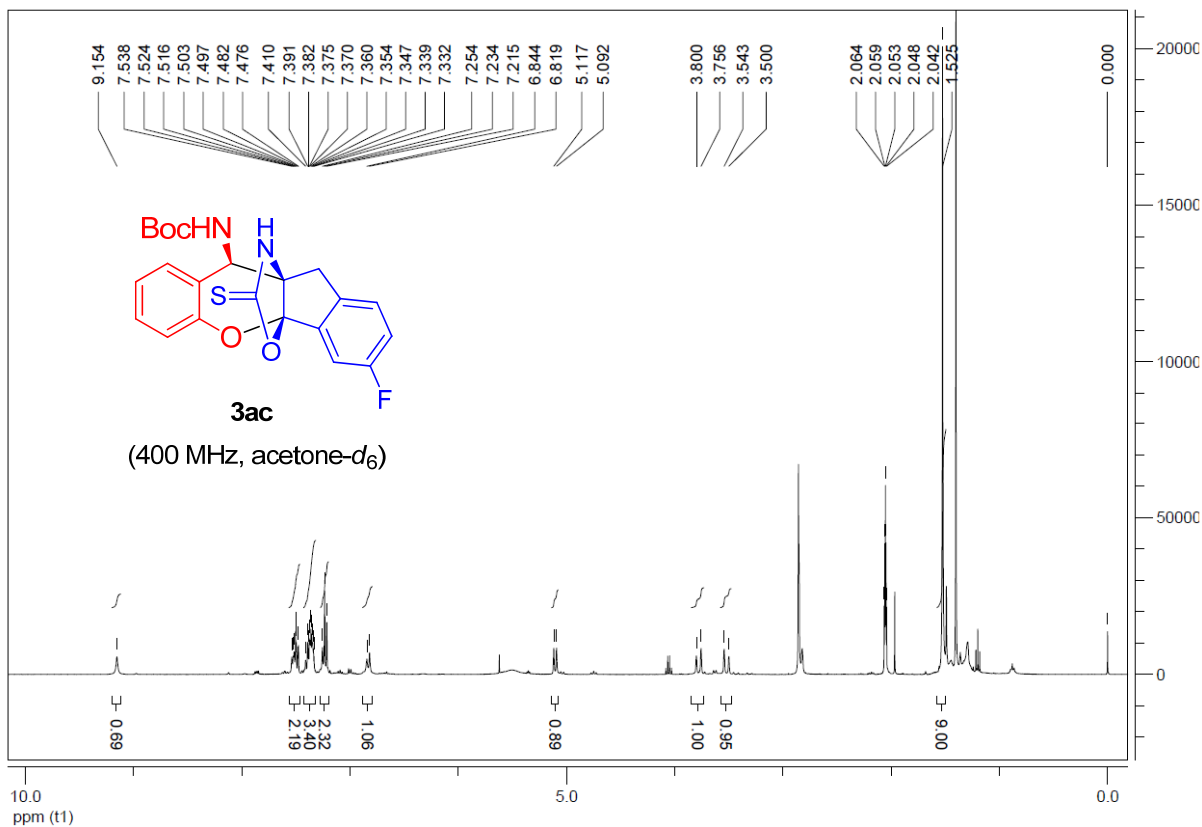


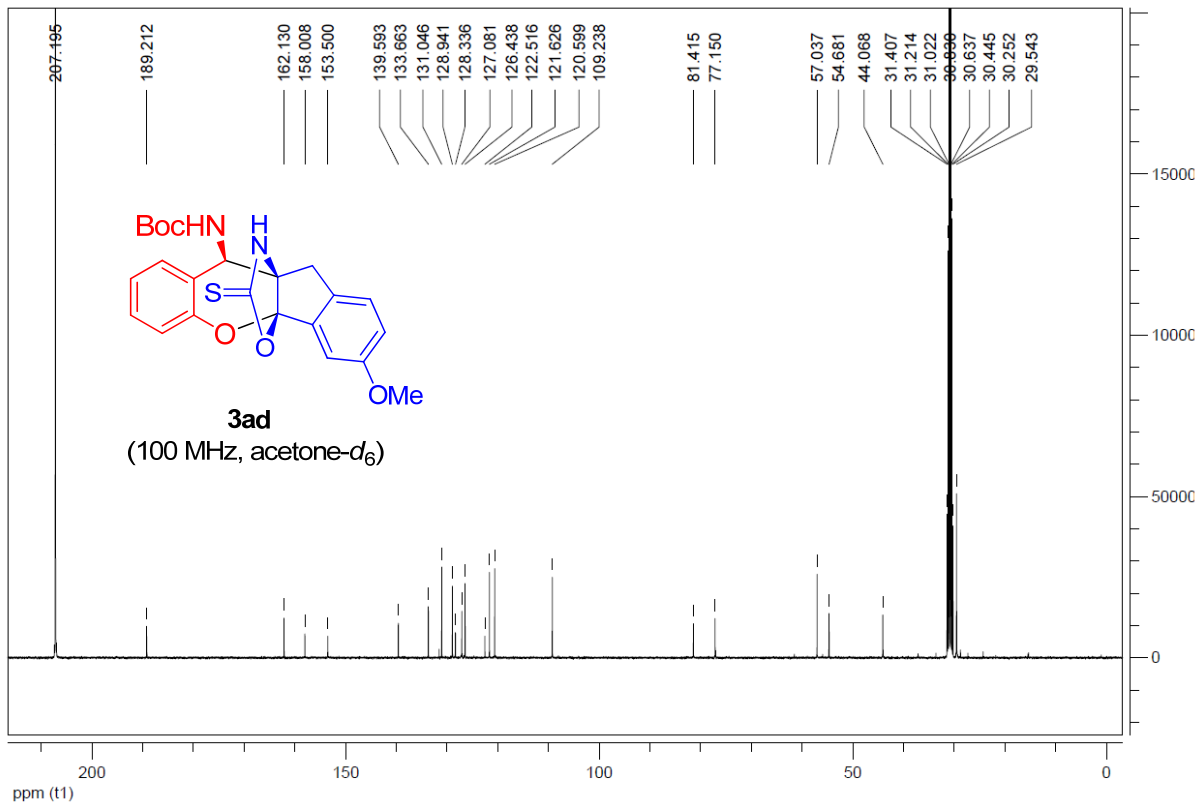
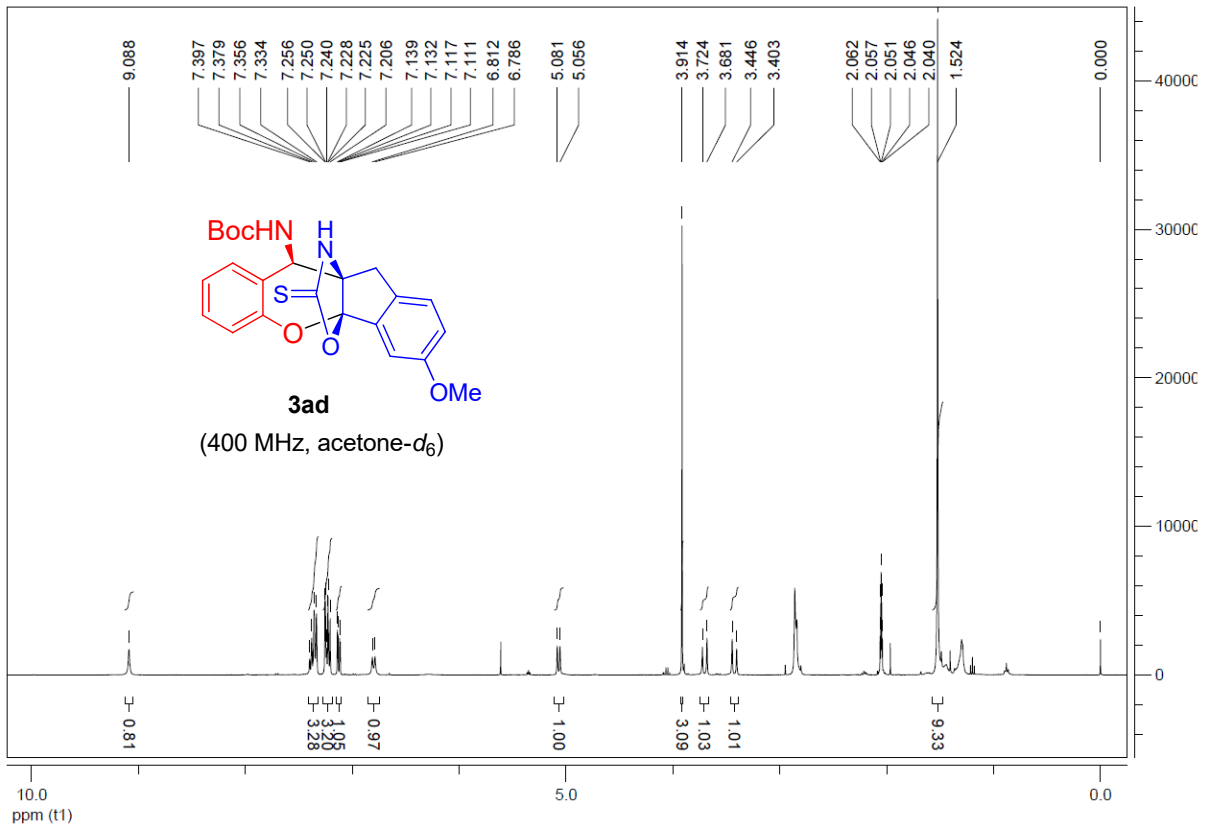


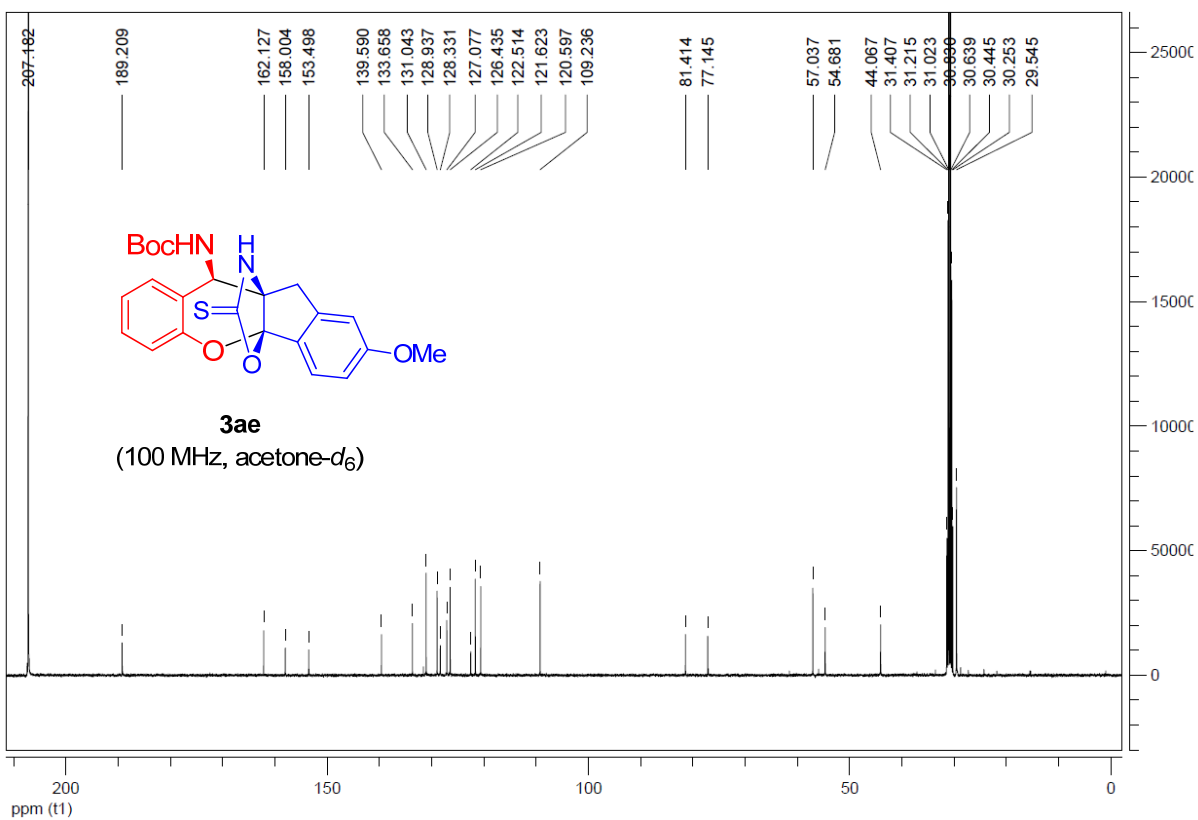
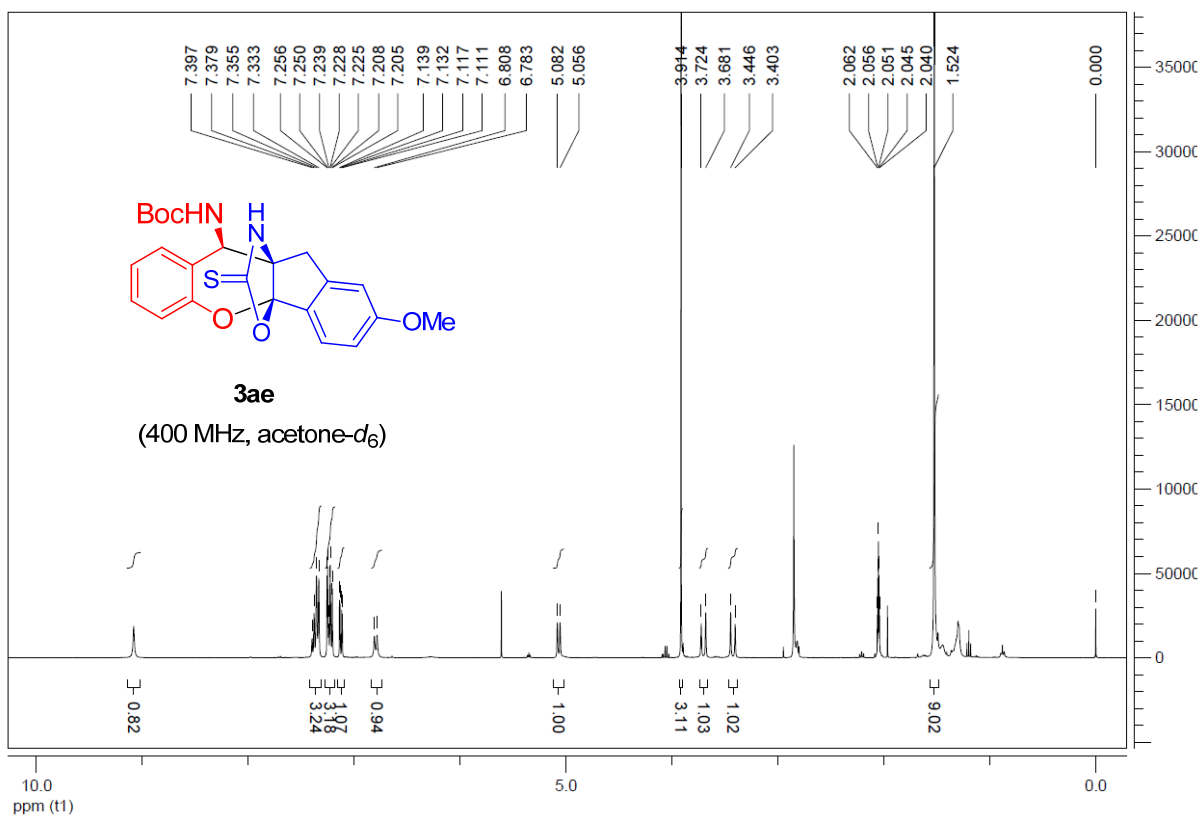


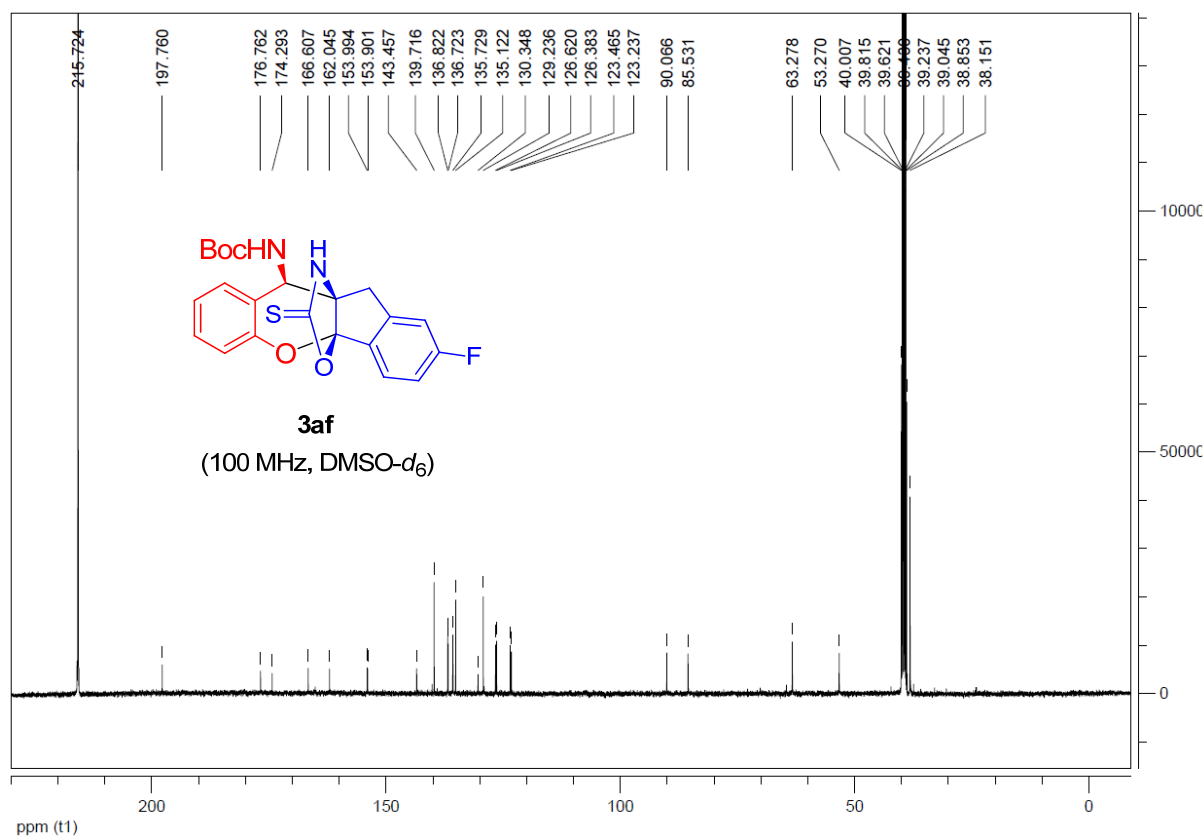
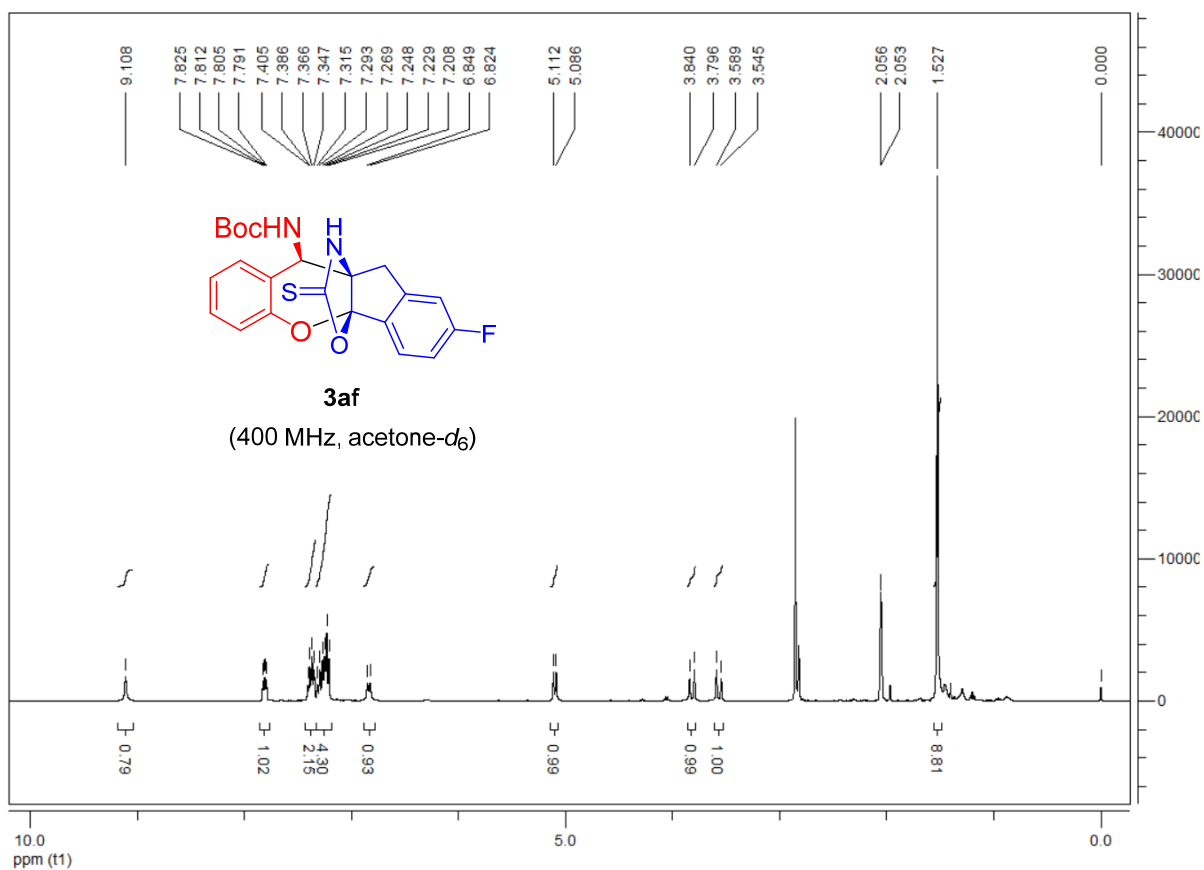


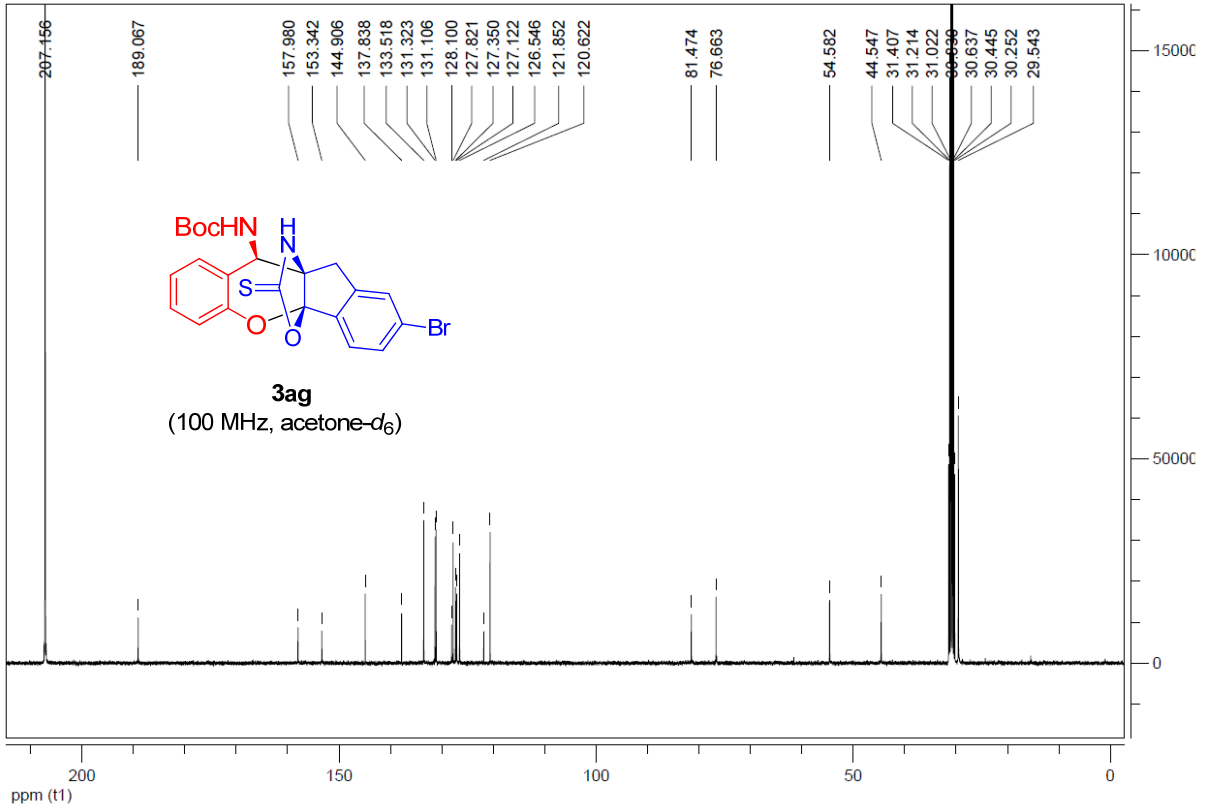
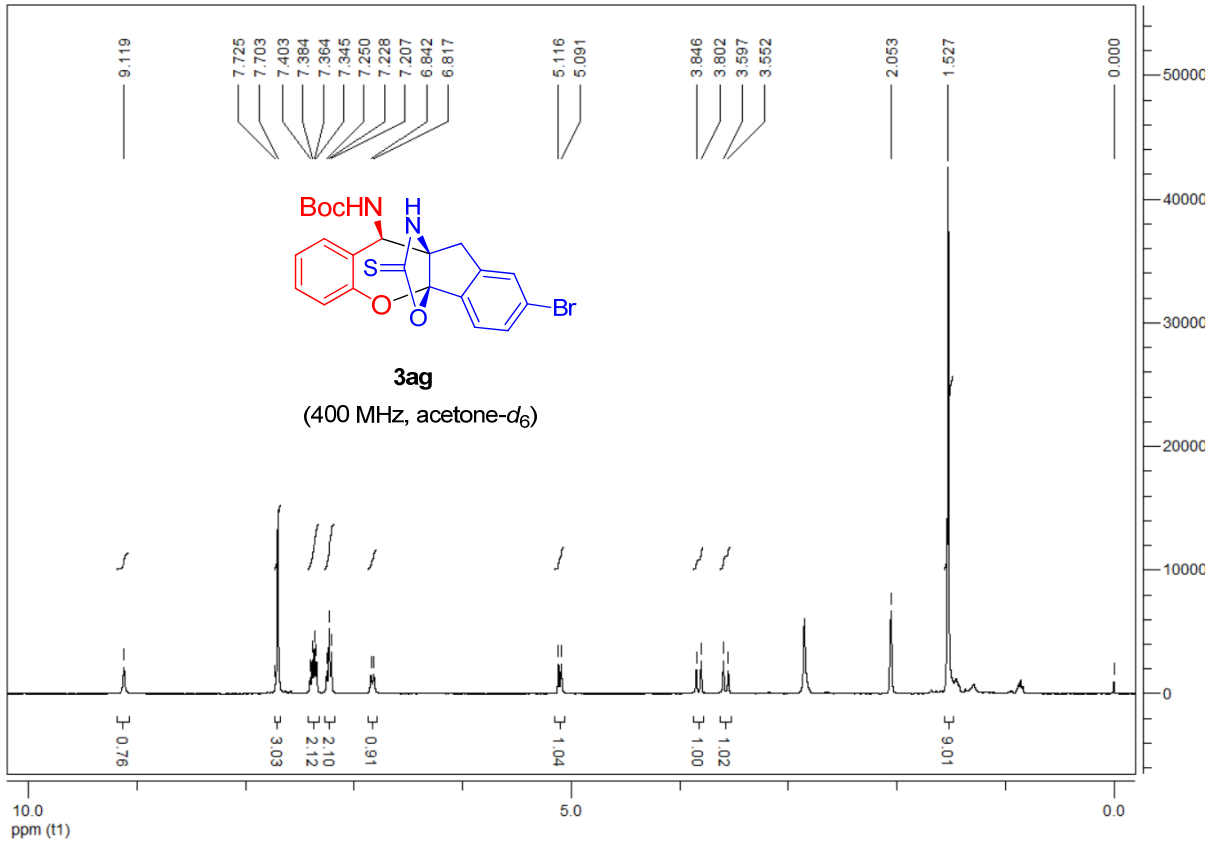


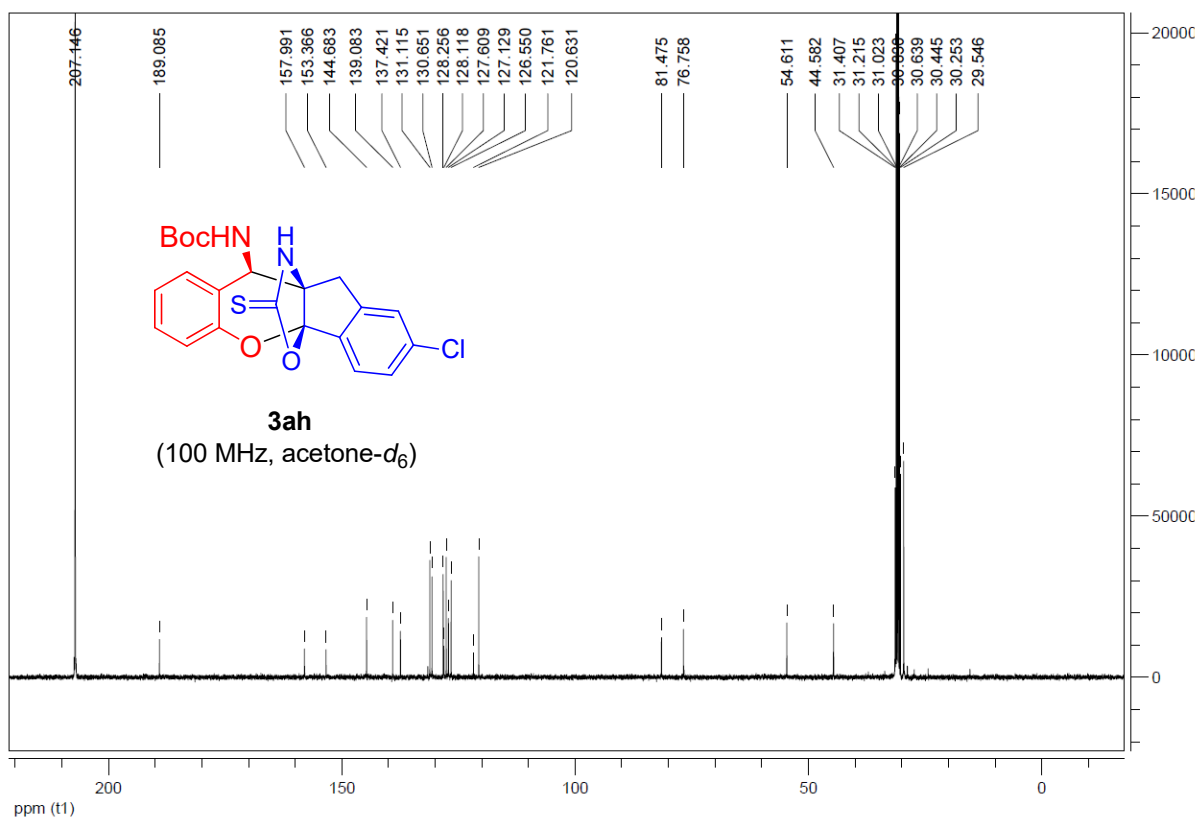
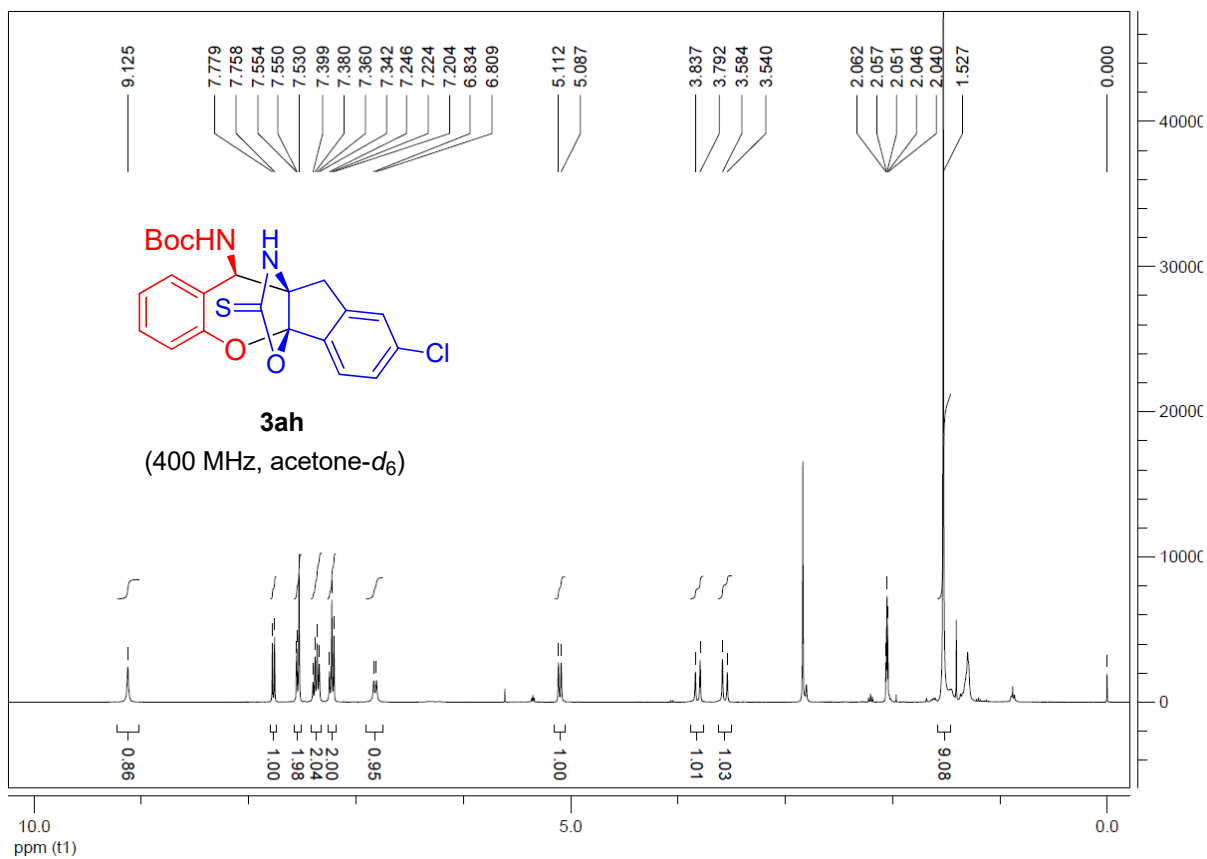




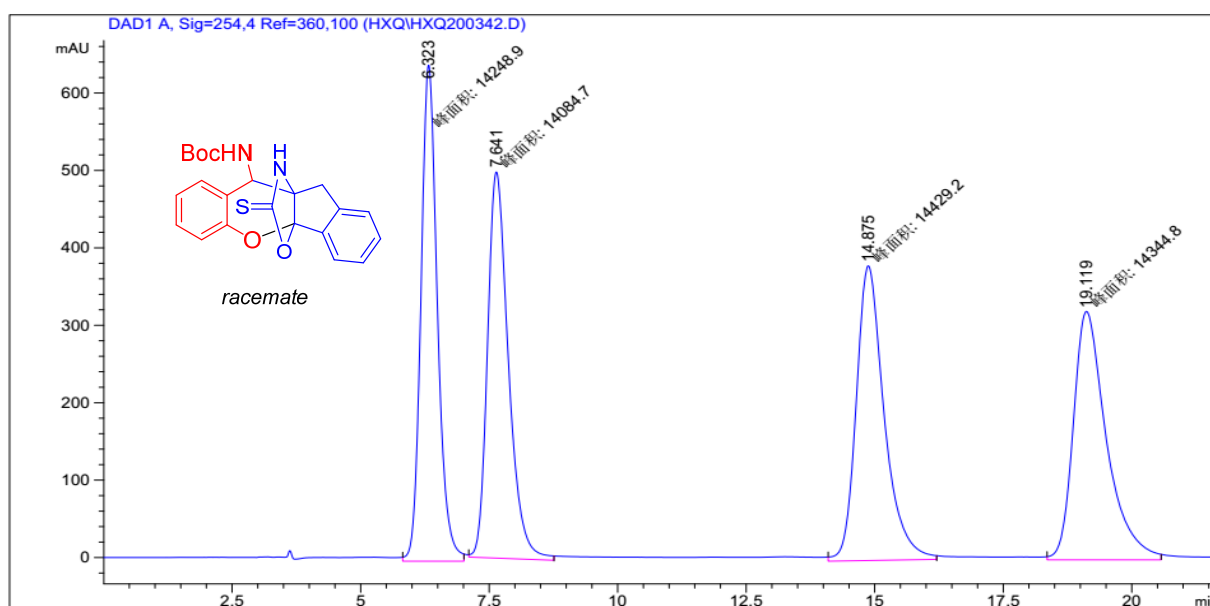




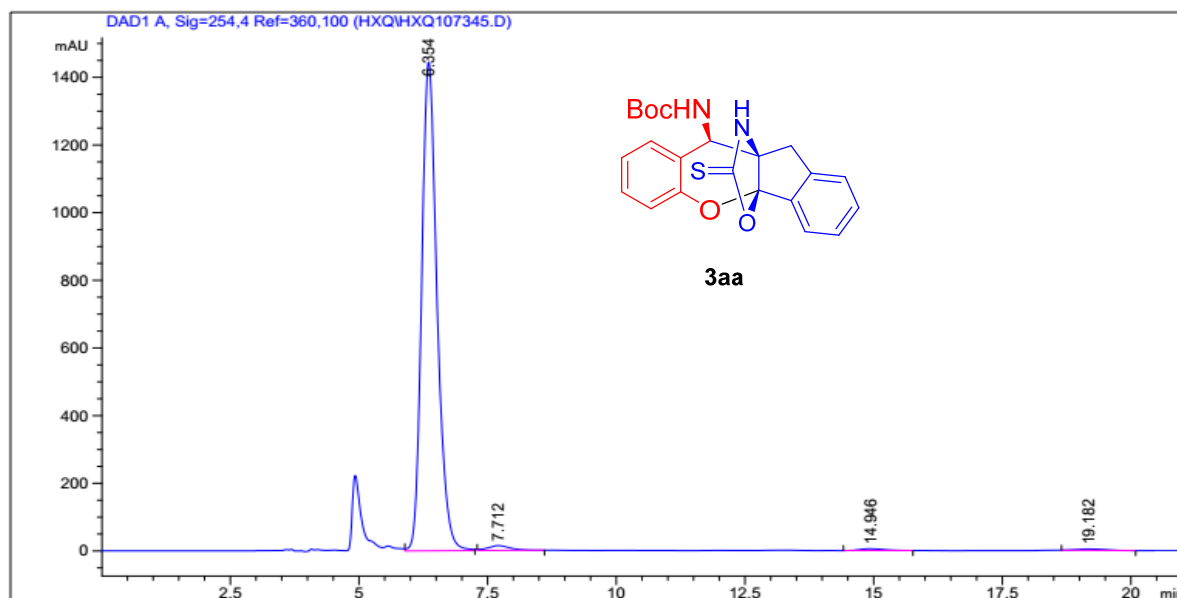




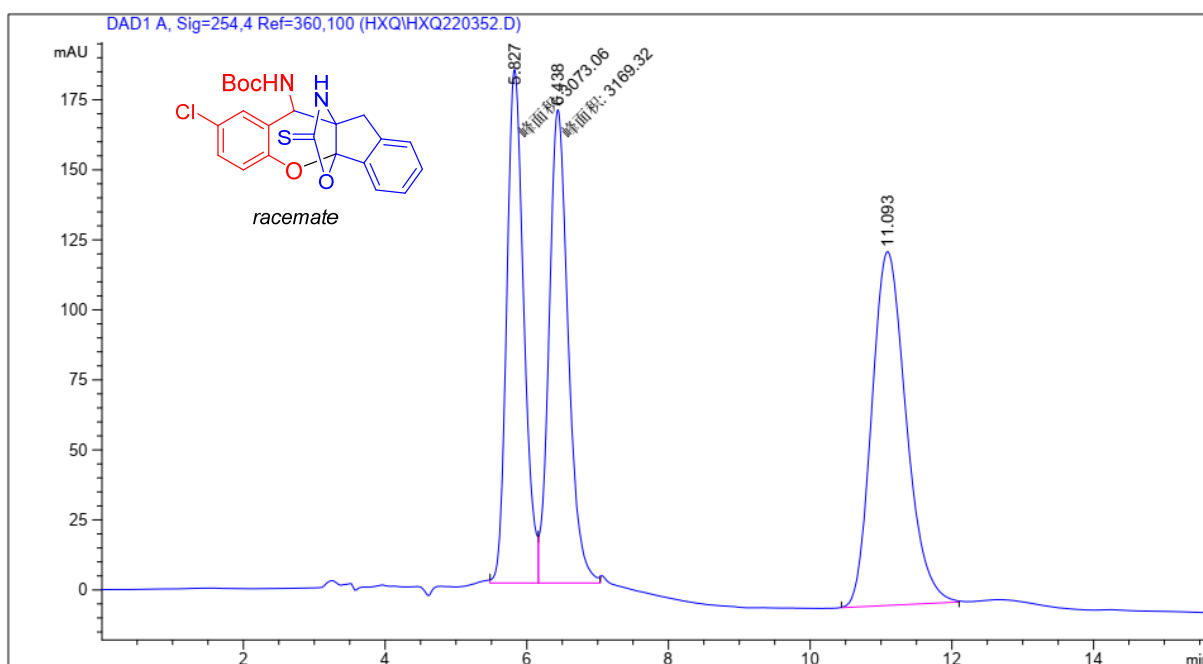
6. Copies of HPLC chromatograms of new products



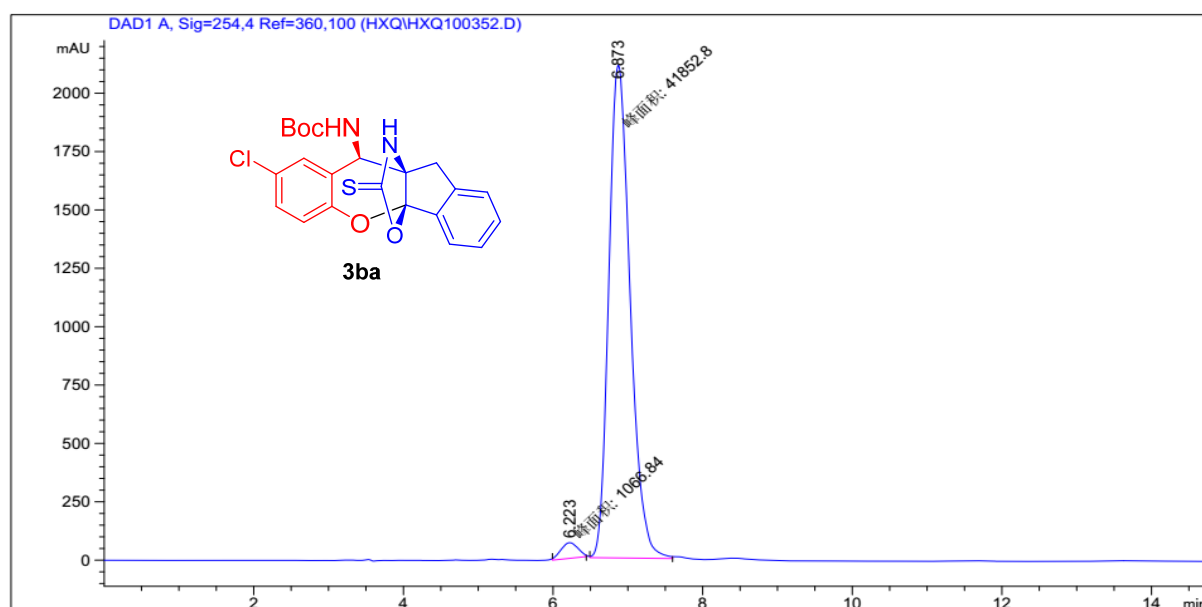
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.323	MM	0.3706	1.42489e4	640.72955	24.9510
2	7.641	MM	0.4706	1.40847e4	498.79898	24.6634
3	14.875	MM	0.6319	1.44292e4	380.58676	25.2666
4	19.119	MM	0.7454	1.43448e4	320.73920	25.1189



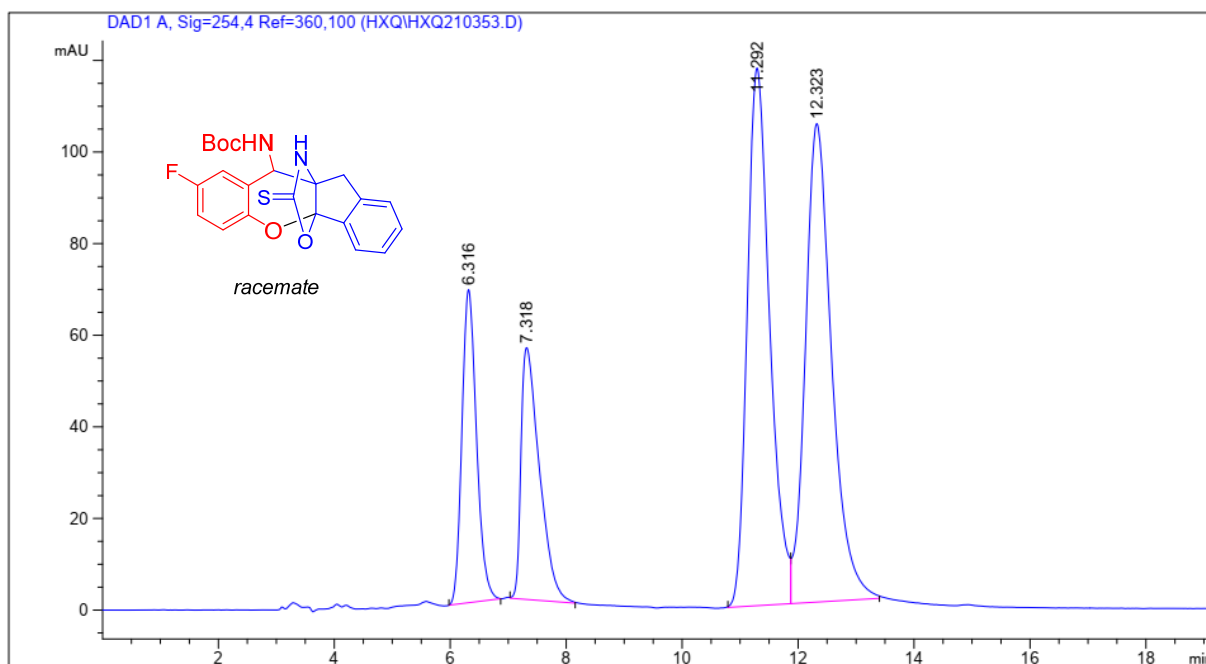
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.354	VB	0.3185	3.00247e4	1444.62939	97.4977
2	7.712	BB	0.4326	434.78241	14.46852	1.4118
3	14.946	BB	0.4436	178.64456	5.54883	0.5801
4	19.182	BB	0.4568	157.16670	4.21682	0.5104



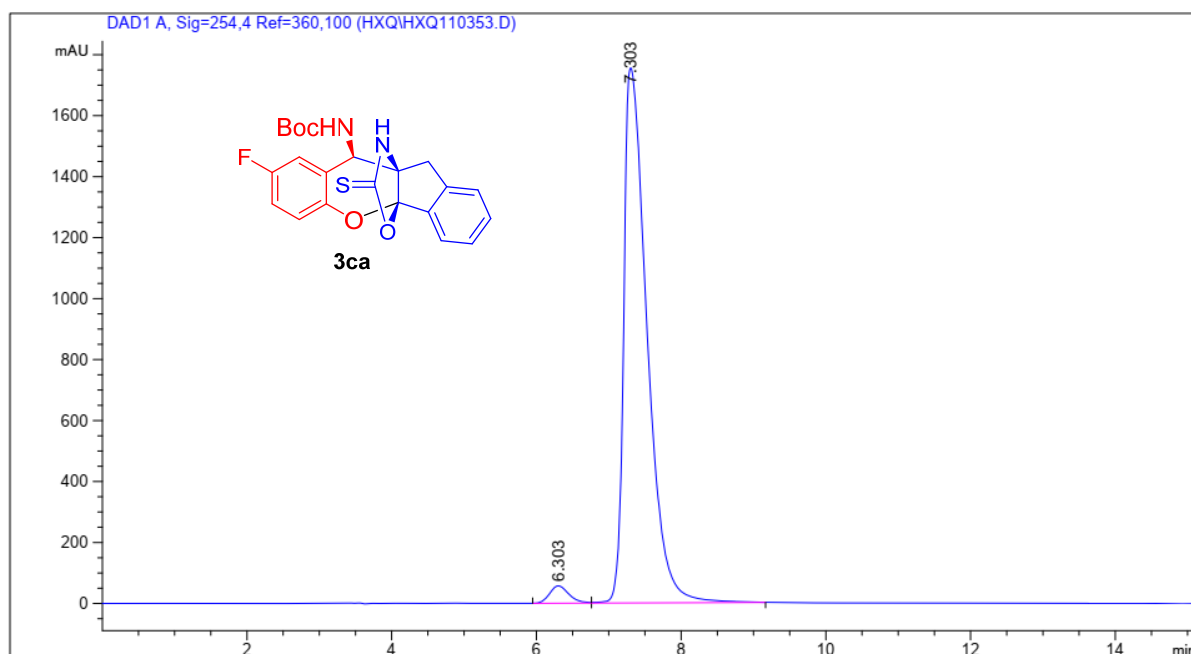
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.827	MF	0.2793	3073.05884	183.37549	29.3016
2	6.438	FM	0.3125	3169.31738	169.00400	30.2195
3	11.093	BB	0.5221	4245.29150	126.32825	40.4789



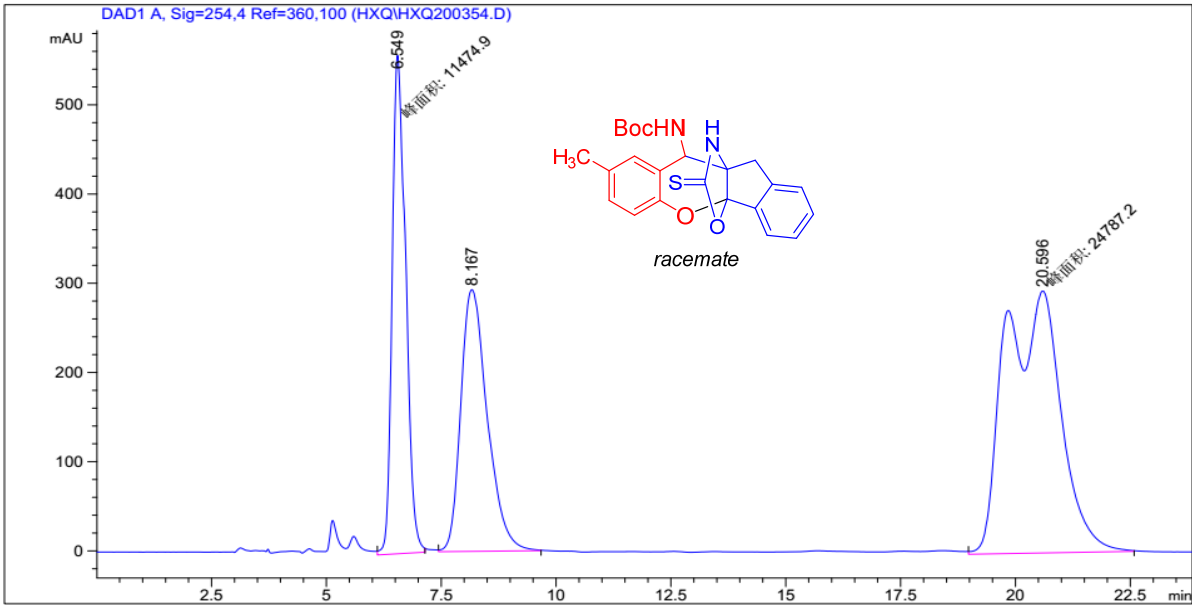
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.223	MM	0.2631	1066.84448	67.58096	2.4857
2	6.873	MM	0.3306	4.18528e4	2109.82446	97.5143



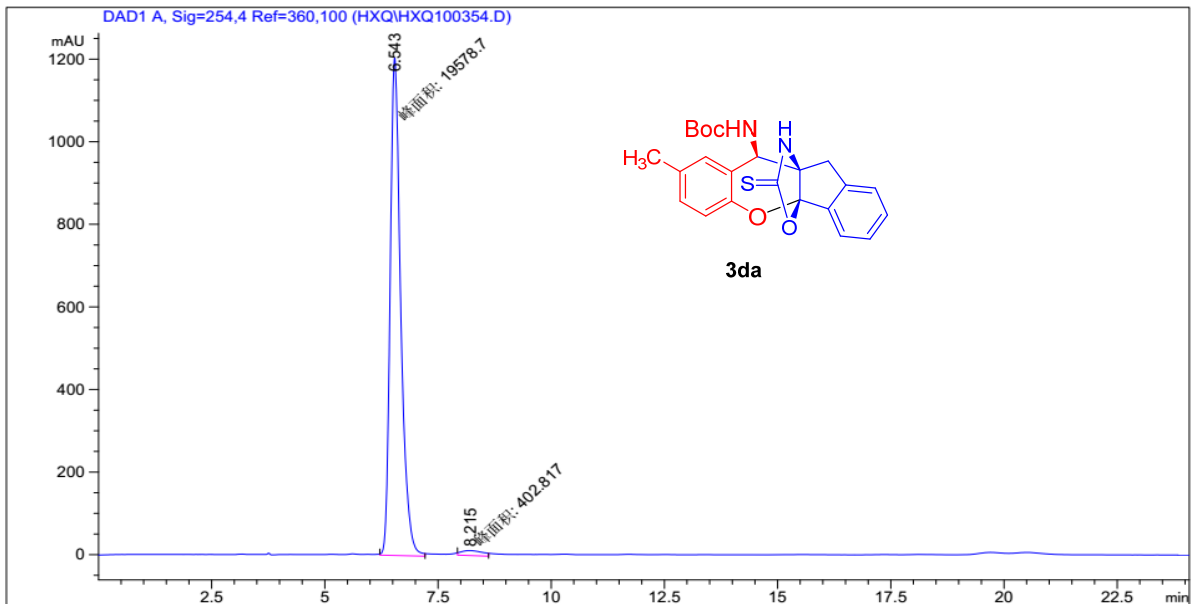
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.316	BB	0.2678	1194.14136	68.36604	13.4823
2	7.318	BB	0.3307	1210.09973	55.00116	13.6625
3	11.292	BV	0.4121	3160.52173	117.40256	35.6836
4	12.323	VB	0.4777	3292.30884	104.46291	37.1715



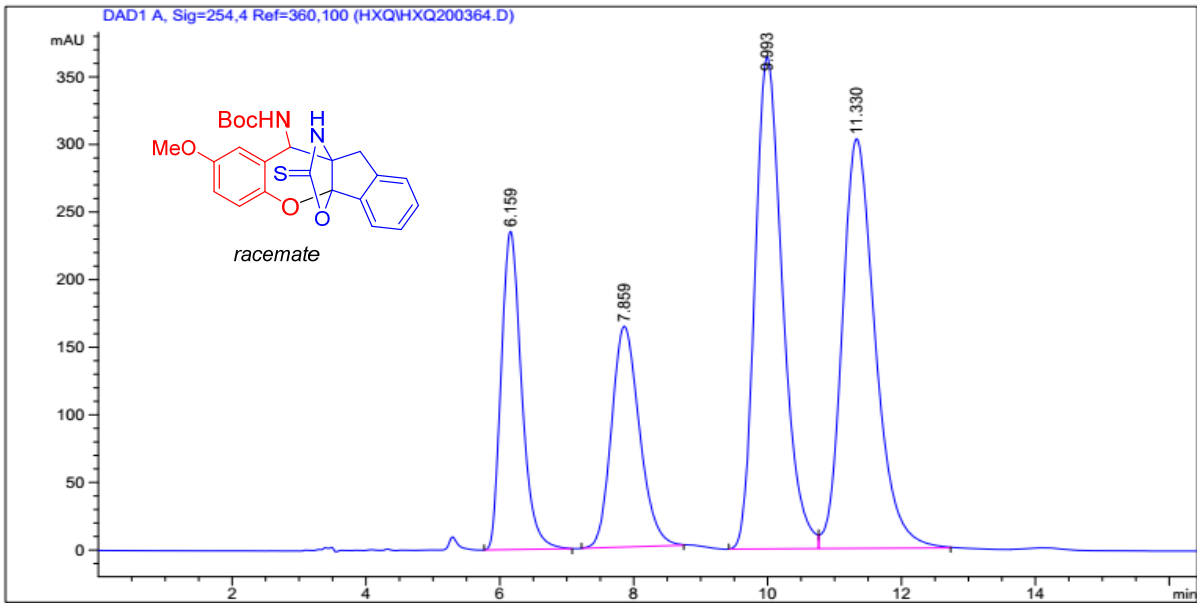
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.303	BV	0.2860	1052.67822	56.85926	2.6249
2	7.303	VB	0.3356	3.90504e4	1754.91028	97.3751



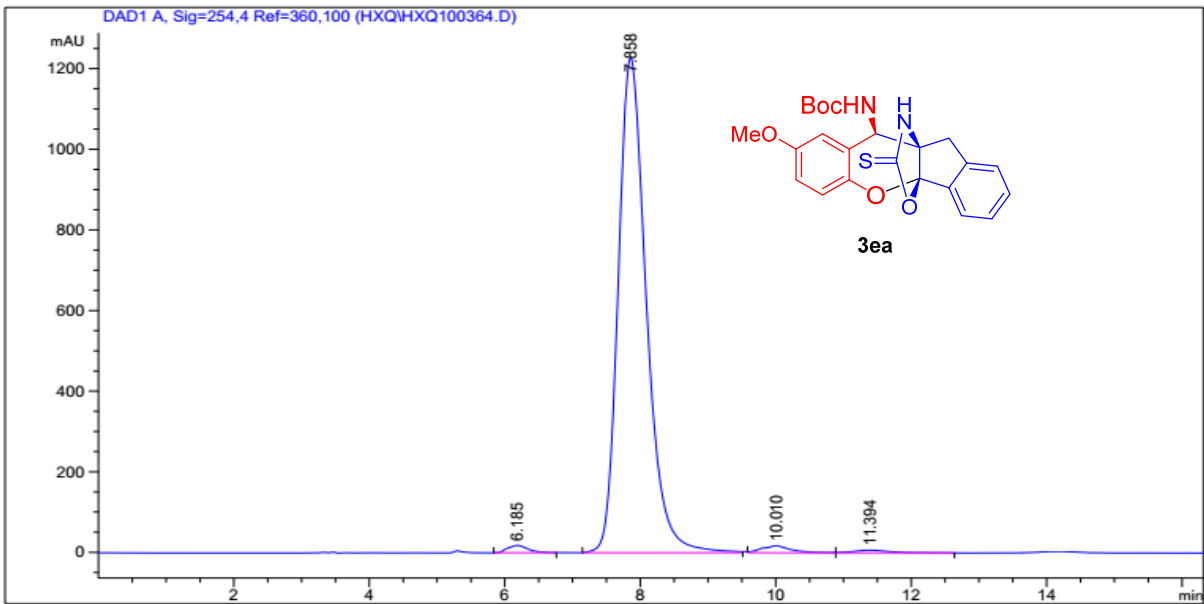
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.549	MM	0.3423	1.14749e4	558.78845	23.8844
2	8.167	BB	0.6085	1.17815e4	293.41626	24.5226
3	20.596	MM	1.4062	2.47872e4	293.78629	51.5930



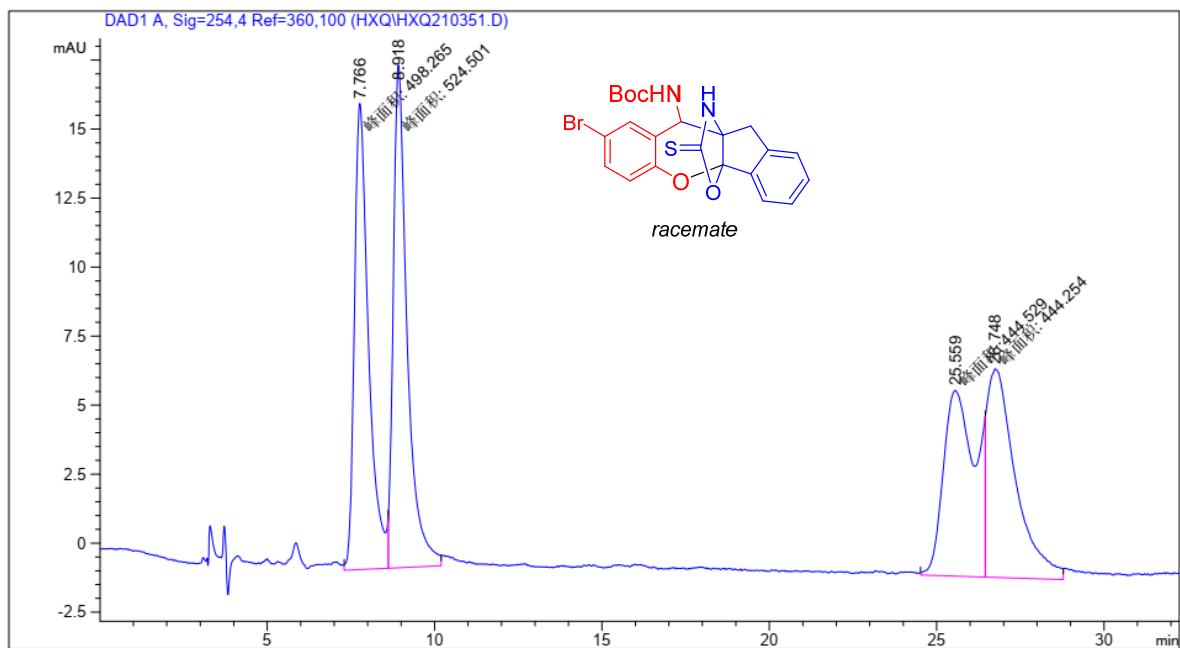
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.543	MM	0.2708	1.95787e4	1204.94250	97.9841
2	8.215	MM	0.5523	402.81689	12.15635	2.0159



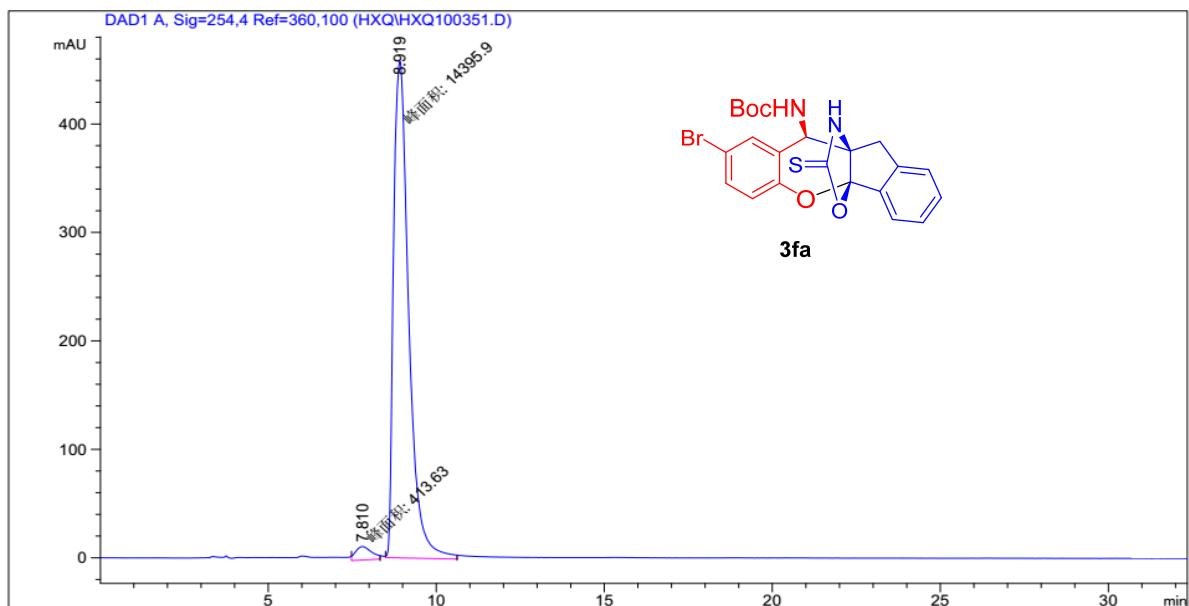
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.159	BB	0.3279	4963.22070	235.49333	16.2907
2	7.859	BB	0.4473	4722.49658	163.32339	15.5006
3	9.993	BV	0.4385	1.04344e4	363.87500	34.2486
4	11.330	VB	0.5225	1.03465e4	302.93085	33.9601



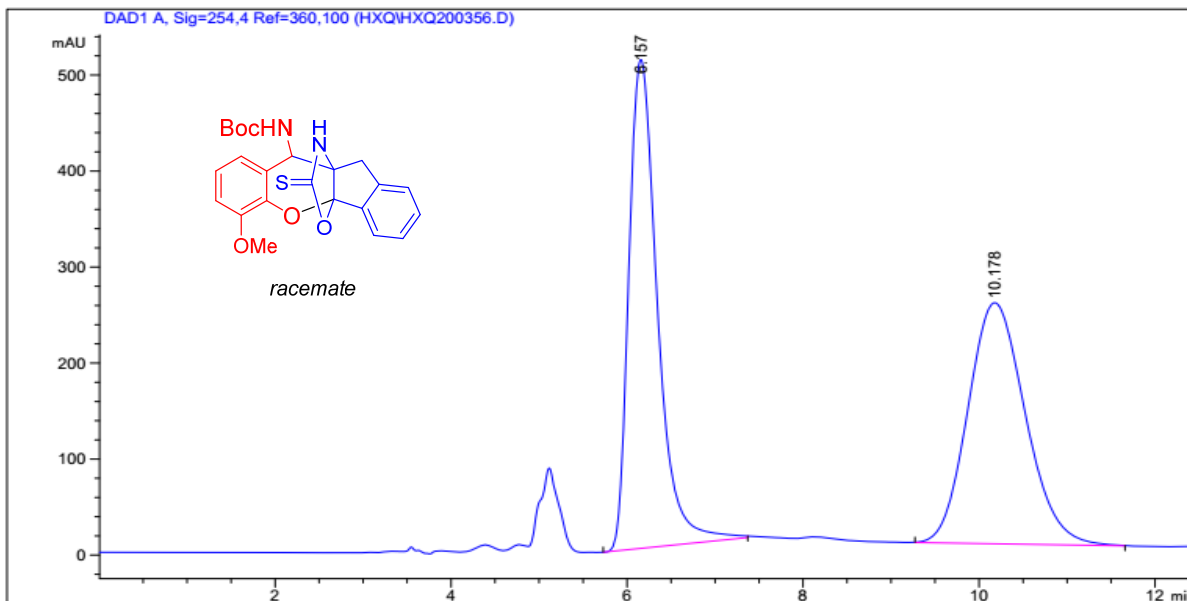
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.185	BB	0.3079	380.56161	18.05624	1.0422
2	7.858	BB	0.4402	3.53818e4	1227.86304	96.8919
3	10.010	BB	0.3921	522.27399	17.70538	1.4302
4	11.394	BB	0.4485	232.12878	6.56505	0.6357



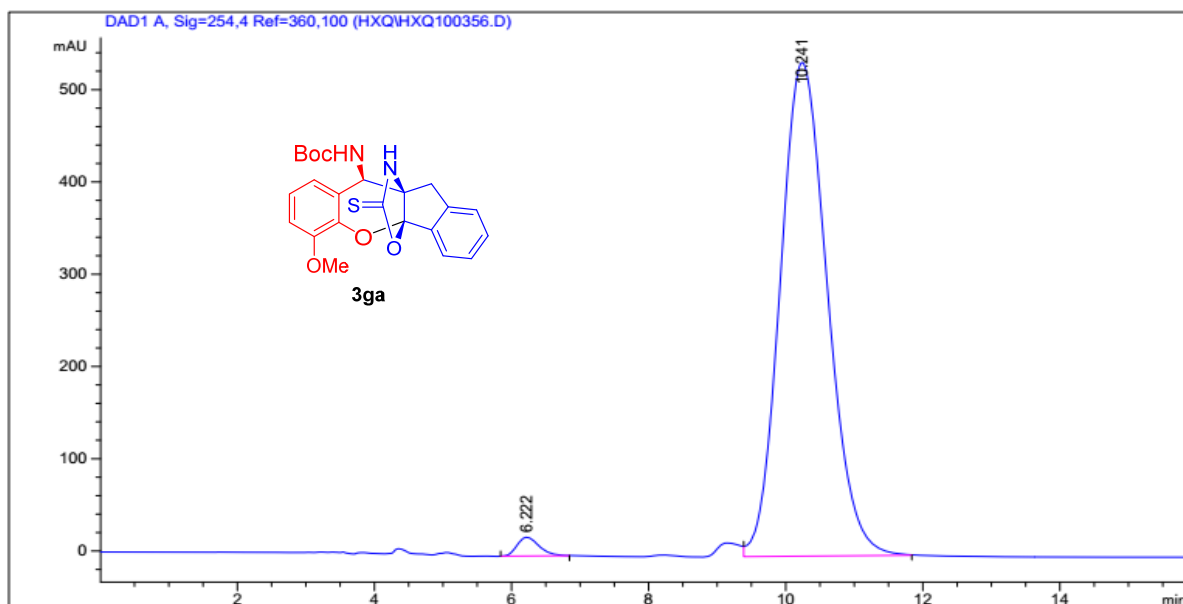
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.647	MF	0.5475	1.37955e4	419.97220	33.6795
2	8.866	FM	0.5787	1.44885e4	417.30038	35.3715
3	25.434	MF	1.2529	5921.99561	78.77982	14.4576
4	26.962	FM	1.3433	6755.04980	83.81290	16.4914



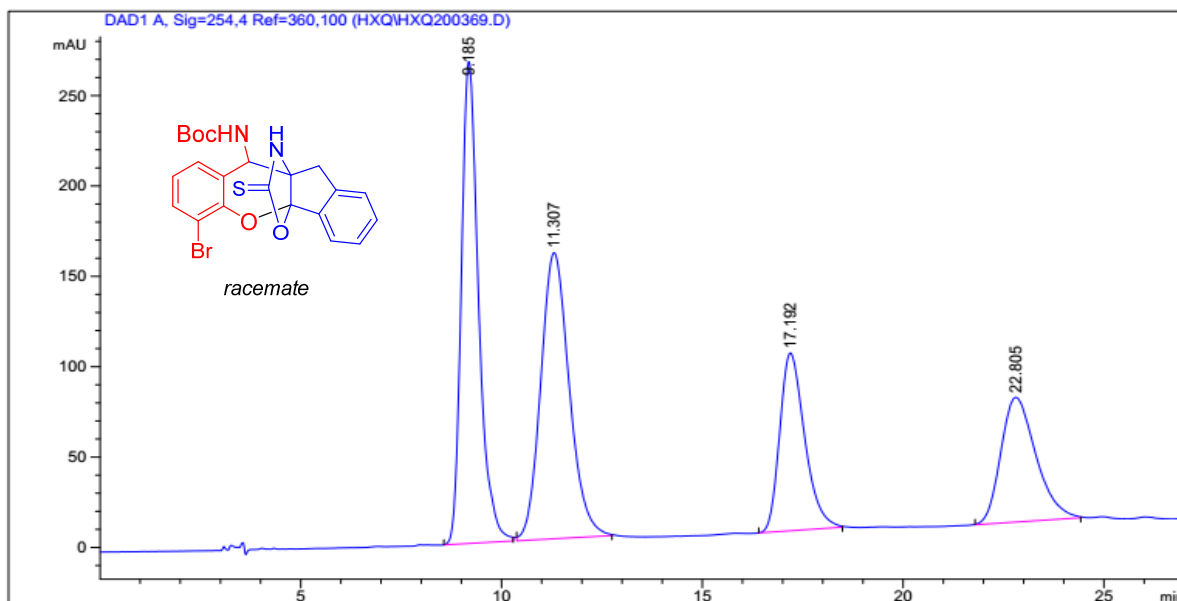
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.810	MM	0.5560	413.62994	12.39866	2.7930
2	8.919	MM	0.5242	1.43959e4	457.68817	97.2070



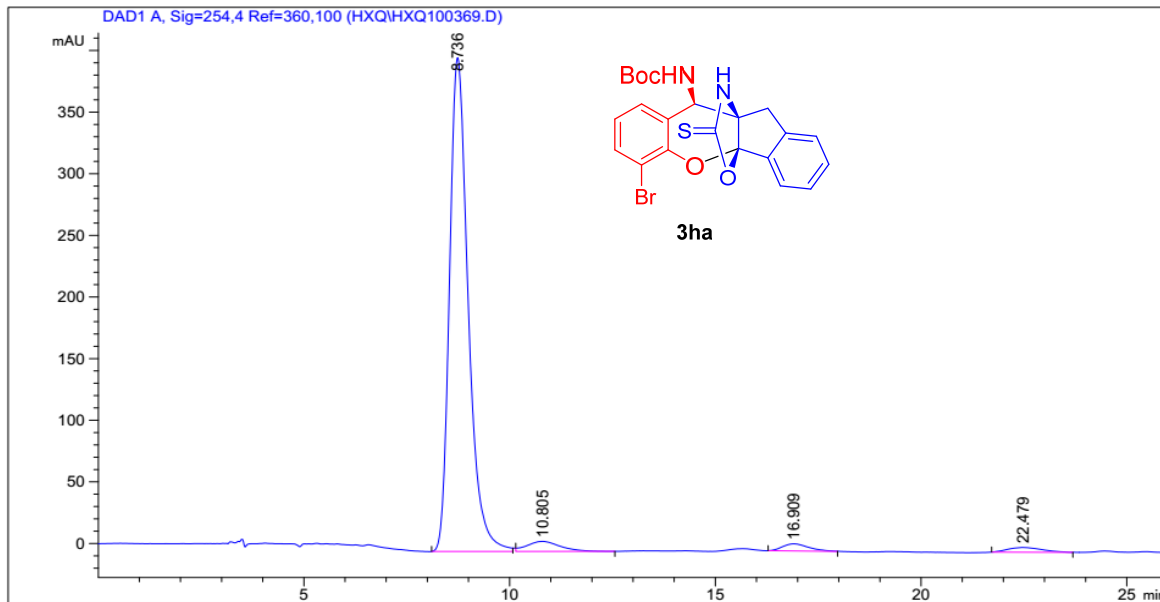
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.157	BB	0.3494	1.14986e4	509.21933	50.2970
2	10.178	BB	0.7000	1.13628e4	251.05444	49.7030



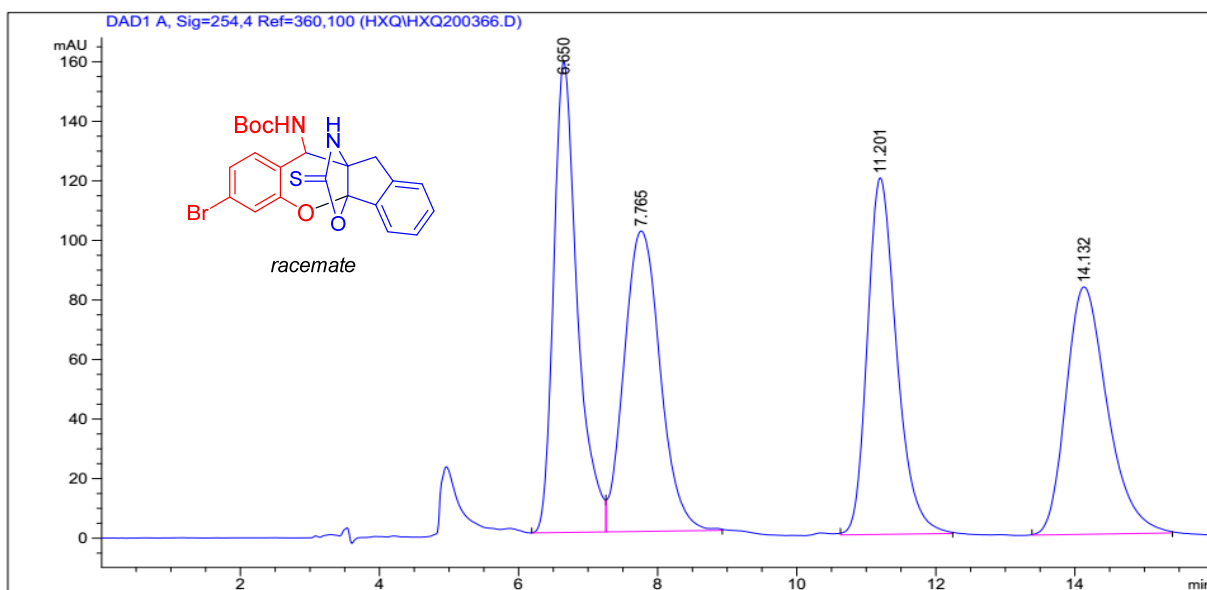
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1	6.222	BB	0.3475	455.32629	20.31703	1.7515
2	10.241	VB	0.7409	2.55408e4	535.04486	98.2485



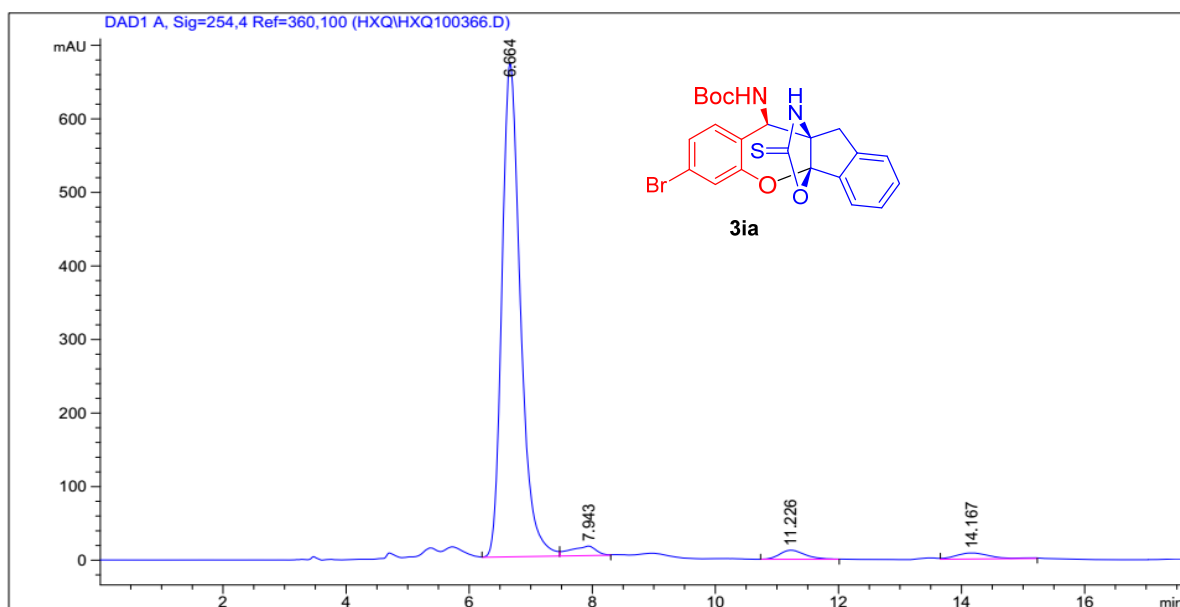
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.185	BB	0.4568	7973.33154	266.65991	32.9348
2	11.307	BB	0.7554	7805.36719	158.25801	32.2410
3	17.192	BB	0.6657	4247.08936	98.37597	17.5431
4	22.805	BB	0.8717	4183.63379	68.96882	17.2810



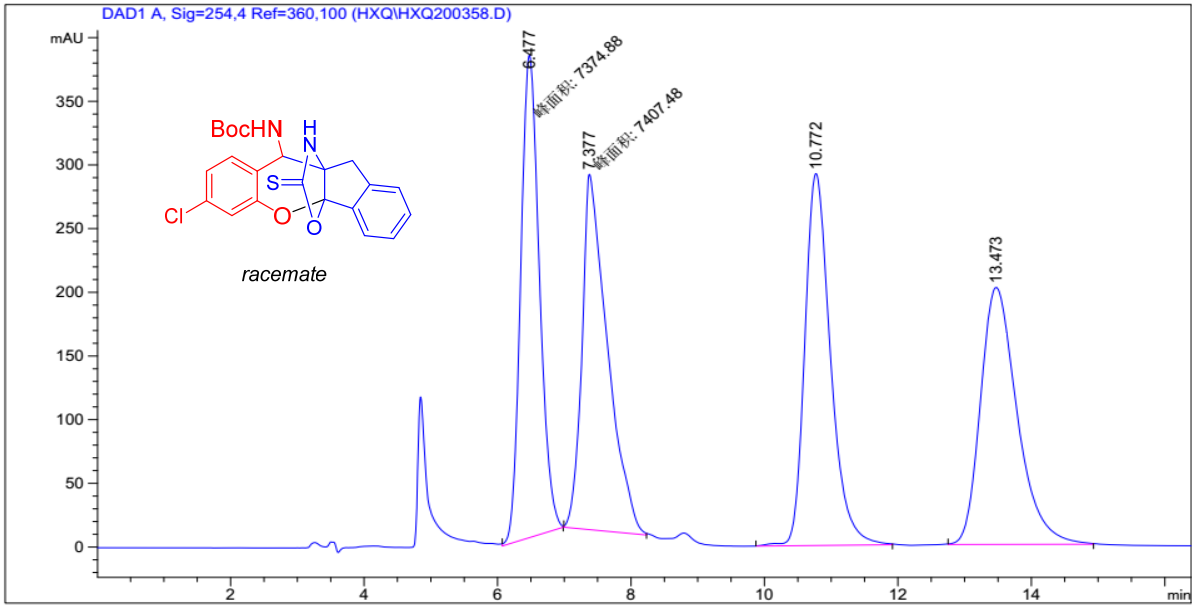
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.736	BB	0.4792	1.26084e4	400.59616	93.0668
2	10.805	BB	0.6626	456.92188	8.11877	3.3727
3	16.909	BB	0.5289	256.19095	5.80491	1.8910
4	22.479	BB	0.6943	226.18362	3.87879	1.6695



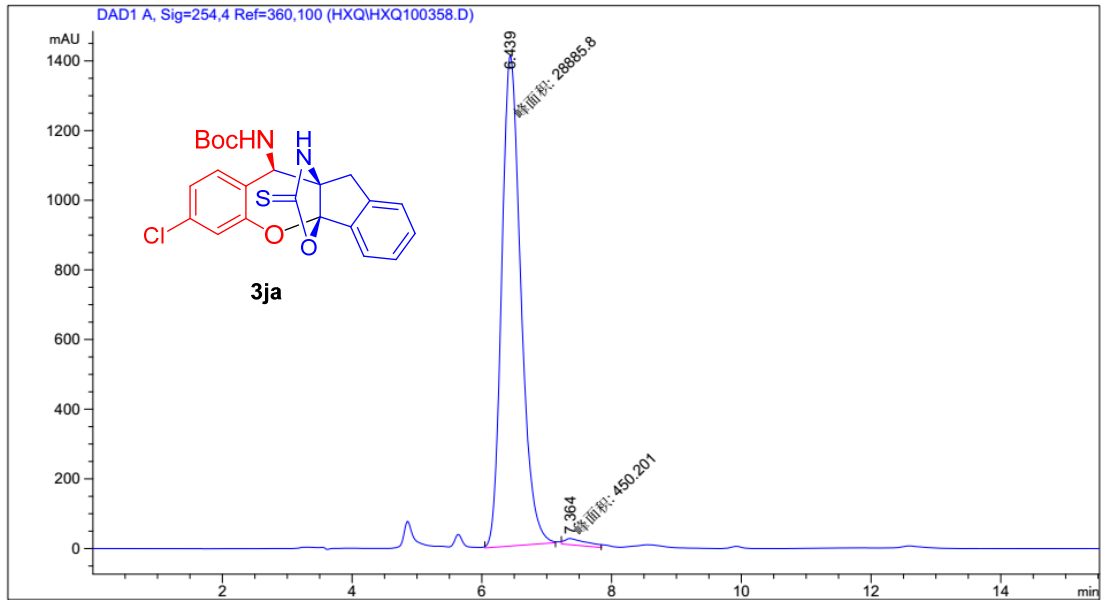
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.650	BV	0.3577	3763.12842	158.11107	26.2074
2	7.765	VB	0.5685	3653.68481	100.89804	25.4452
3	11.201	BB	0.4496	3507.00806	119.76006	24.4237
4	14.132	BB	0.6223	3435.19604	83.10249	23.9236



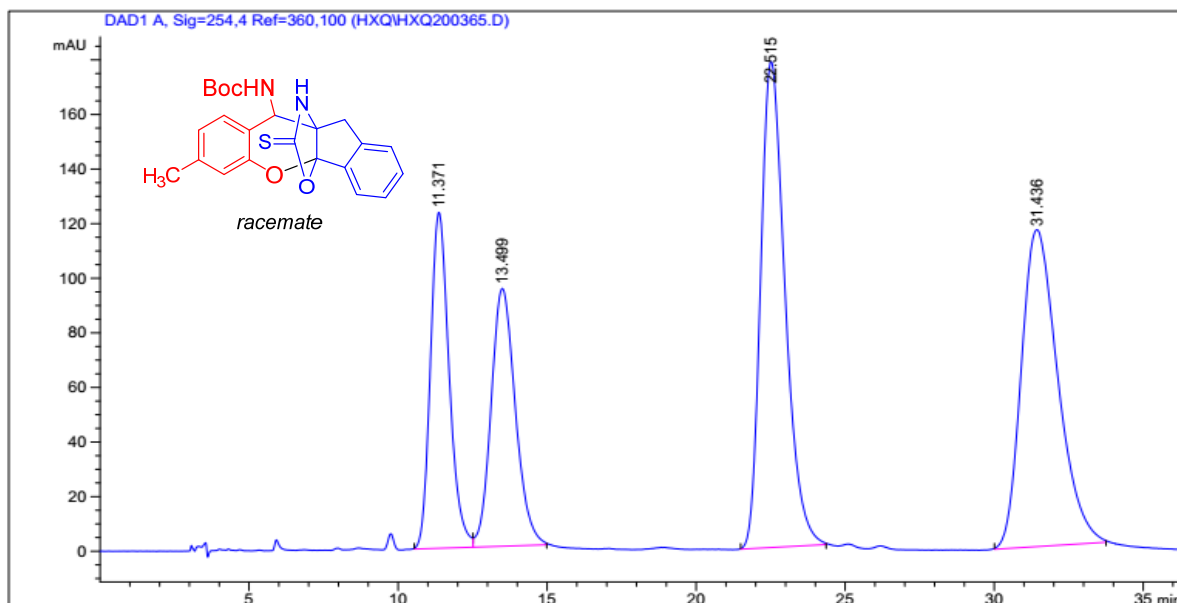
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.664	VV	0.3199	1.40226e4	670.63910	93.0484
2	7.943	VV	0.3802	372.75439	12.93565	2.4734
3	11.226	BB	0.4255	348.96463	12.28004	2.3156
4	14.167	VB	0.4712	325.89850	8.31691	2.1625



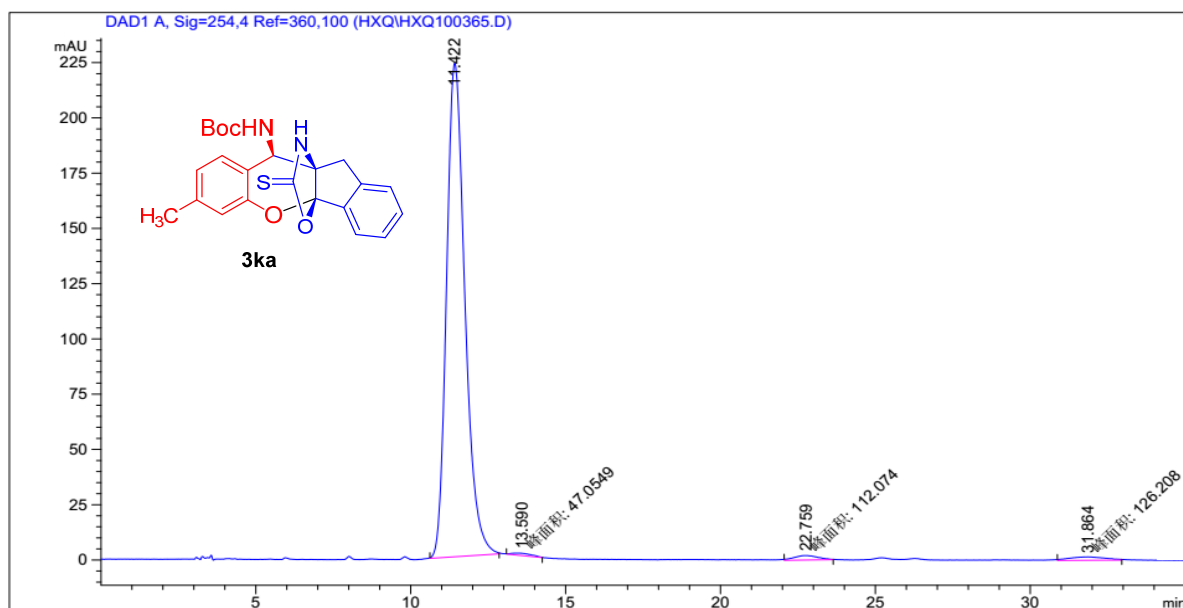
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.477	MM	0.3244	7374.87988	378.94574	24.3450
2	7.377	MM	0.4424	7407.47510	279.05606	24.4526
3	10.772	BB	0.4096	7800.10156	292.06445	25.7487
4	13.473	BB	0.5857	7710.72656	201.85234	25.4537



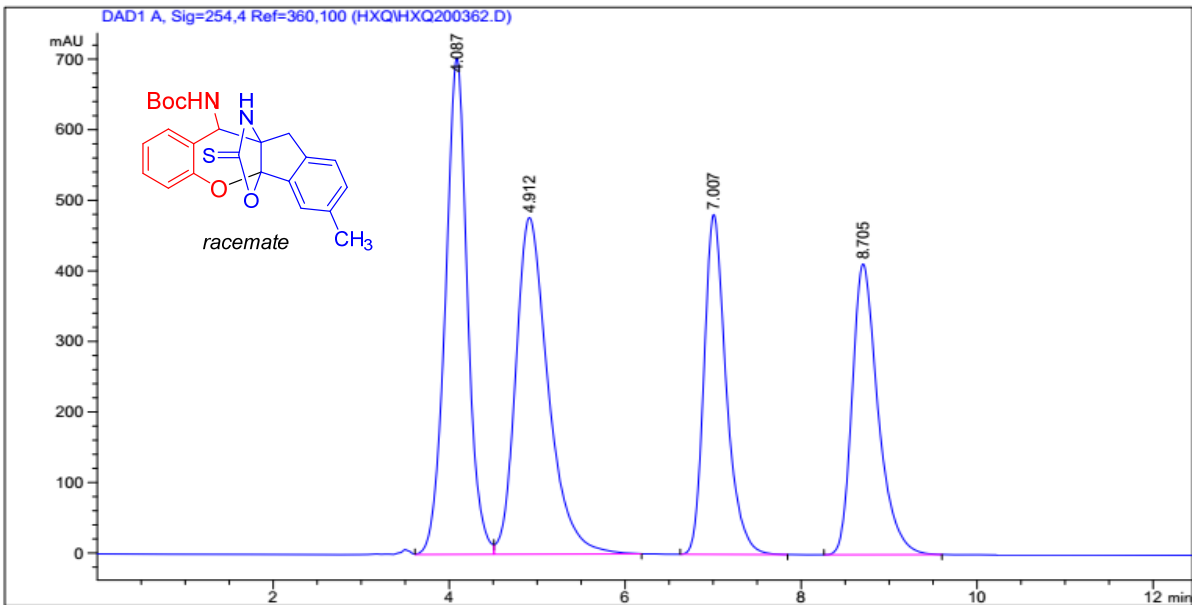
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.439	MM	0.3420	2.88858e4	1407.54797	98.4654
2	7.364	MM	0.4215	450.20114	17.79947	1.5346



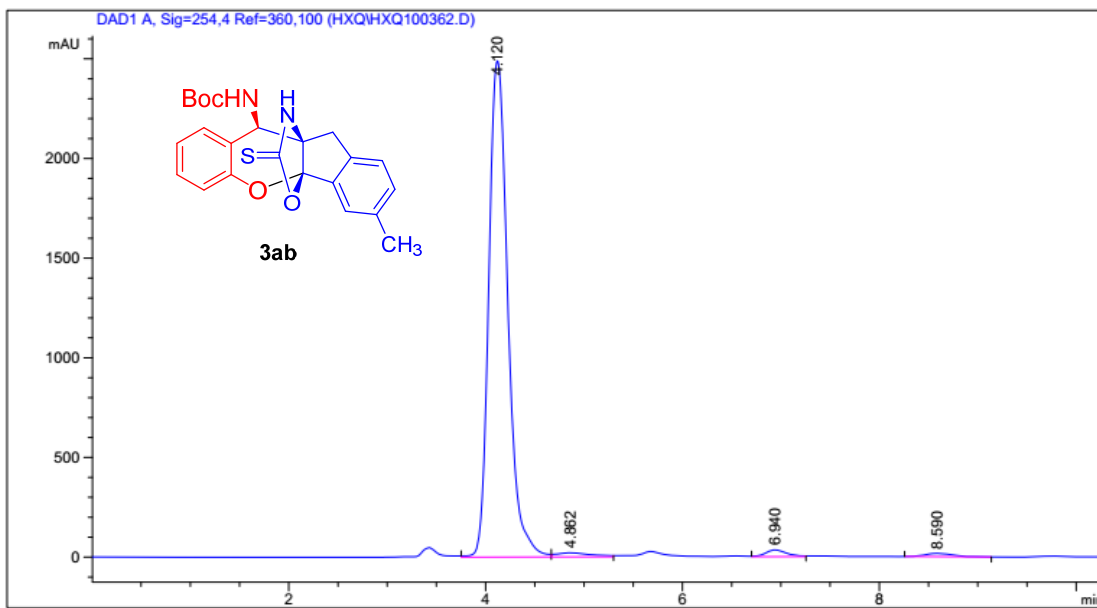
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.371	BB	0.6702	5360.91260	123.06074	17.4757
2	13.499	BB	0.7980	5339.58301	94.39321	17.4061
3	22.515	BB	0.8604	1.01075e4	178.02406	32.9487
4	31.436	BB	1.1920	9868.46289	116.05772	32.1695



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.422	BB	0.6346	9197.67090	223.28380	96.9911
2	13.590	MM	0.7394	47.05494	1.06061	0.4962
3	22.759	MM	0.9085	112.07368	2.05603	1.1818
4	31.864	MM	1.3576	126.20786	1.54938	1.3309



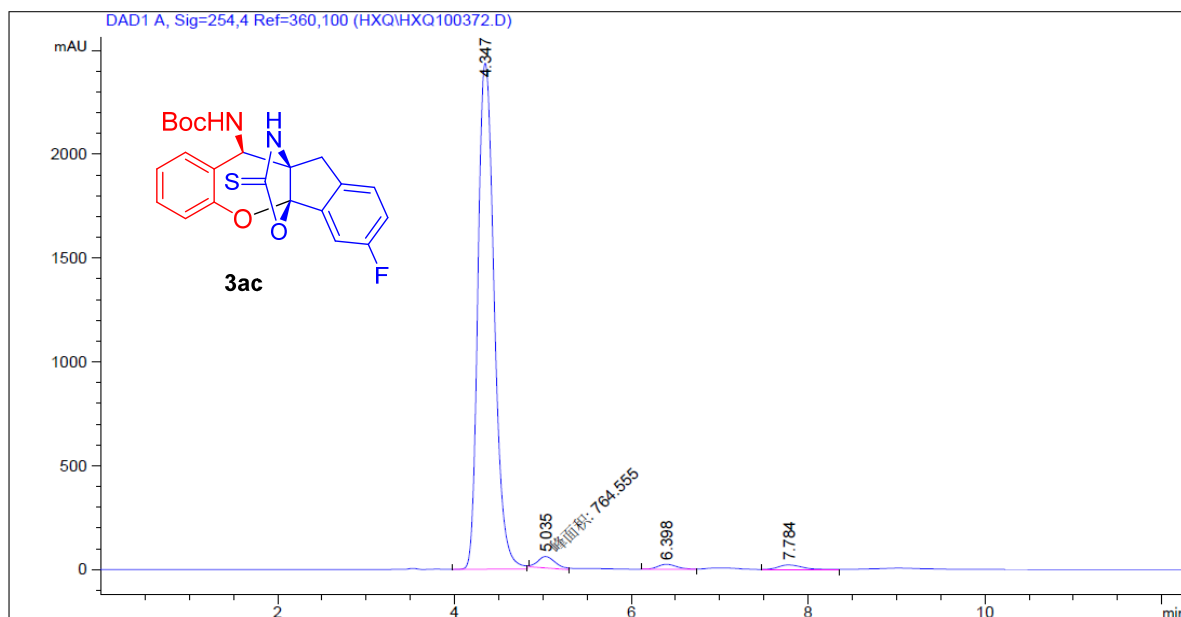
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.087	VV	0.2606	1.22166e4	703.56036	29.6148
2	4.912	VB	0.3864	1.22047e4	477.11353	29.5858
3	7.007	BB	0.2636	8407.46191	481.77304	20.3808
4	8.705	BB	0.3105	8423.03809	412.09412	20.4186



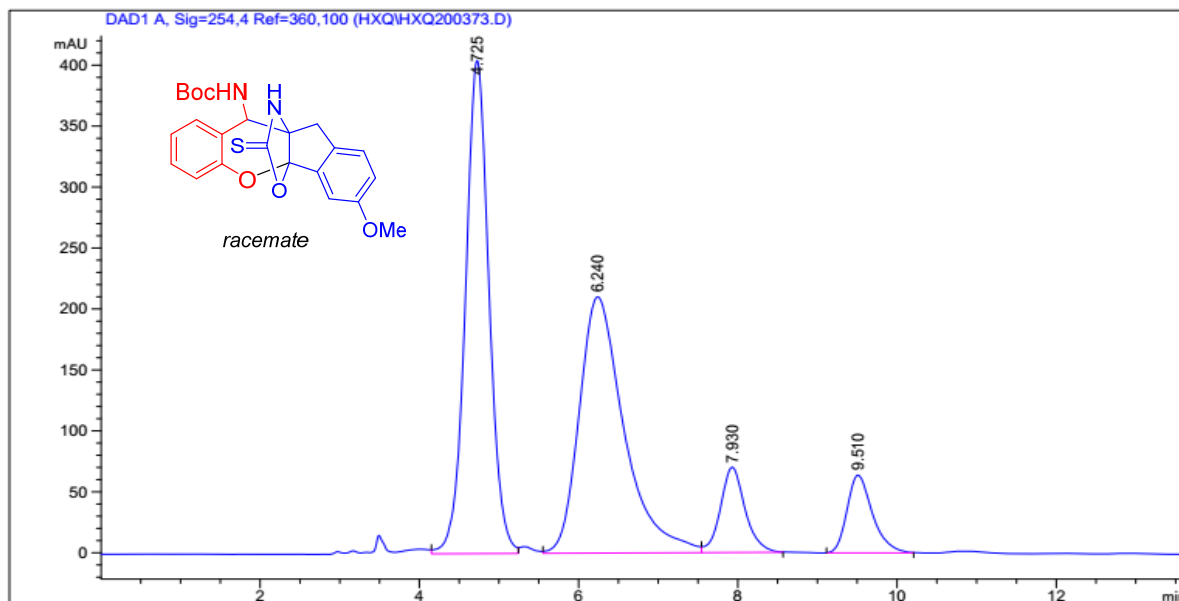
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.120	BV	0.2088	3.34553e4	2489.69312	96.1113
2	4.862	VV	0.3569	521.63208	20.91739	1.4986
3	6.940	VV	0.2227	501.58975	33.88525	1.4410
4	8.590	BB	0.3002	330.40500	16.89294	0.9492



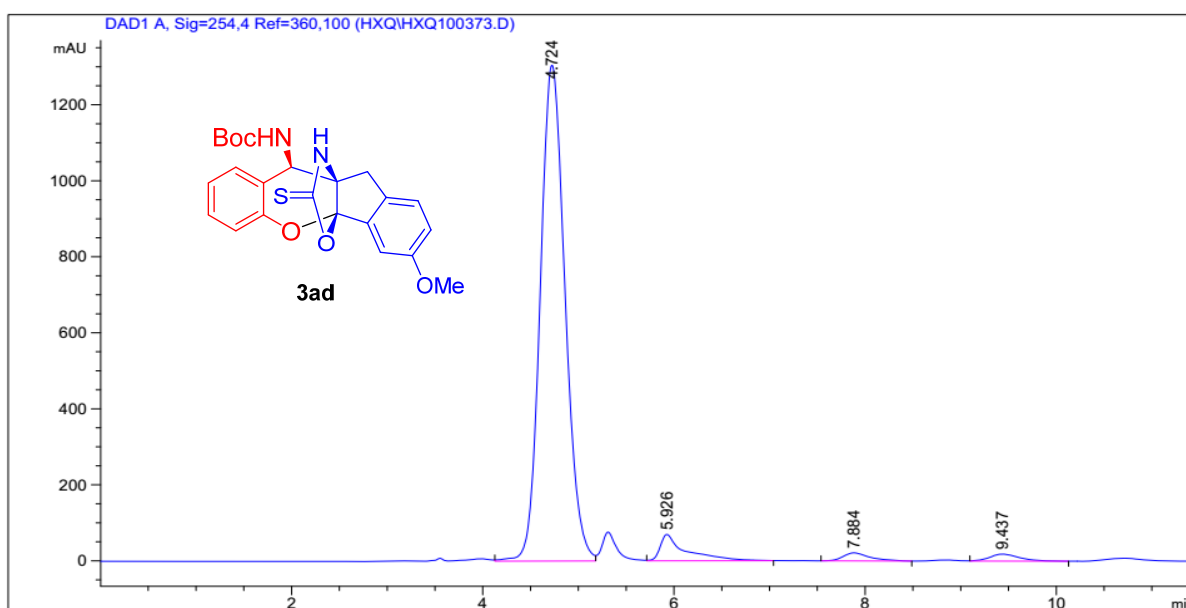
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.343	VV	0.2000	1.05981e4	813.50702	26.4316
2	5.024	VV	0.2181	1.06919e4	759.96777	26.6654
3	6.390	VB	0.2443	9503.25781	601.52625	23.7010
4	7.798	BB	0.2822	9303.15820	516.29169	23.2020



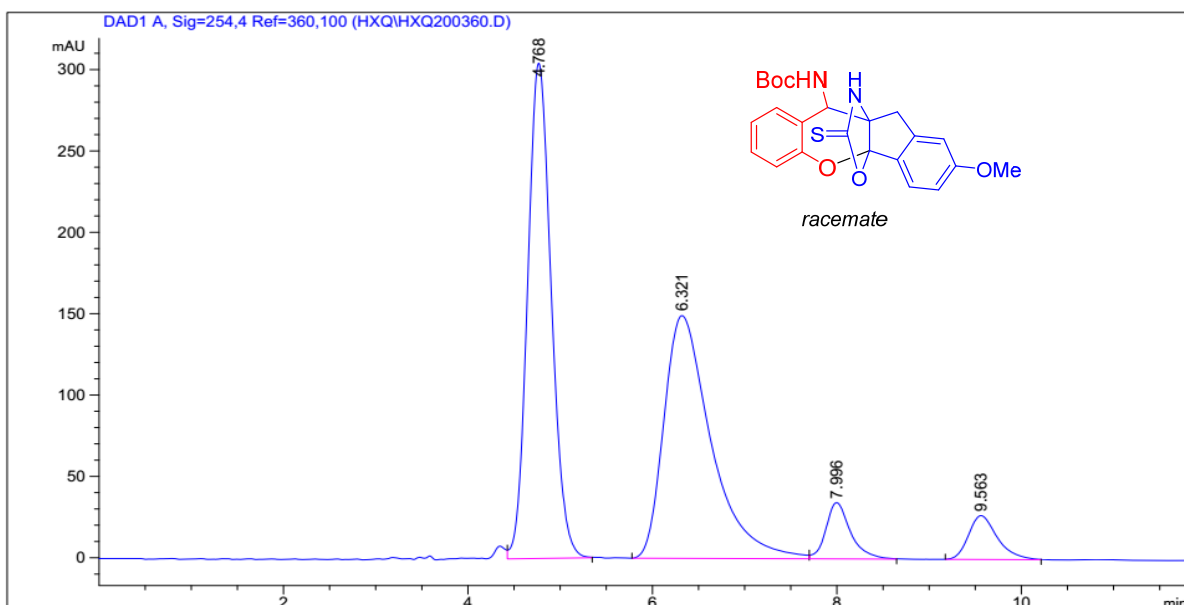
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.347	VV	0.2014	3.12157e4	2437.51343	95.4029
2	5.035	MM	0.2309	764.55469	55.18095	2.3367
3	6.398	BV	0.2308	350.53452	23.66393	1.0713
4	7.784	VB	0.2855	389.06775	21.46355	1.1891



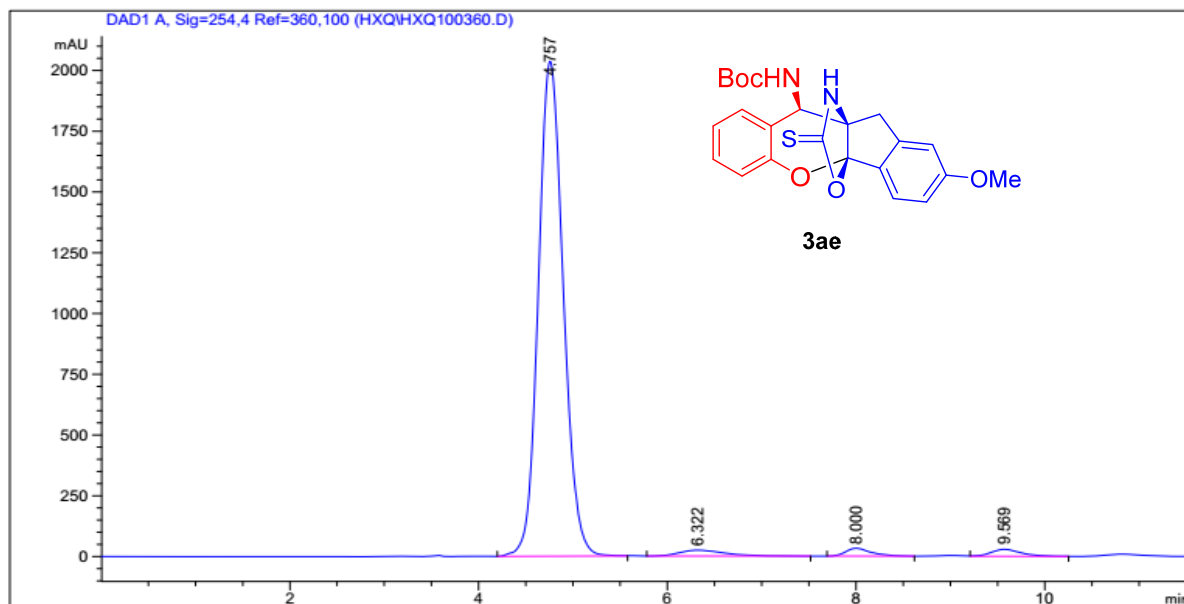
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.725	VV	0.3164	8333.89258	404.51917	42.7984
2	6.240	VV	0.5864	8222.51270	210.20456	42.2264
3	7.930	VB	0.3230	1505.11707	69.95995	7.7295
4	9.510	BB	0.3383	1410.90503	63.72546	7.2457



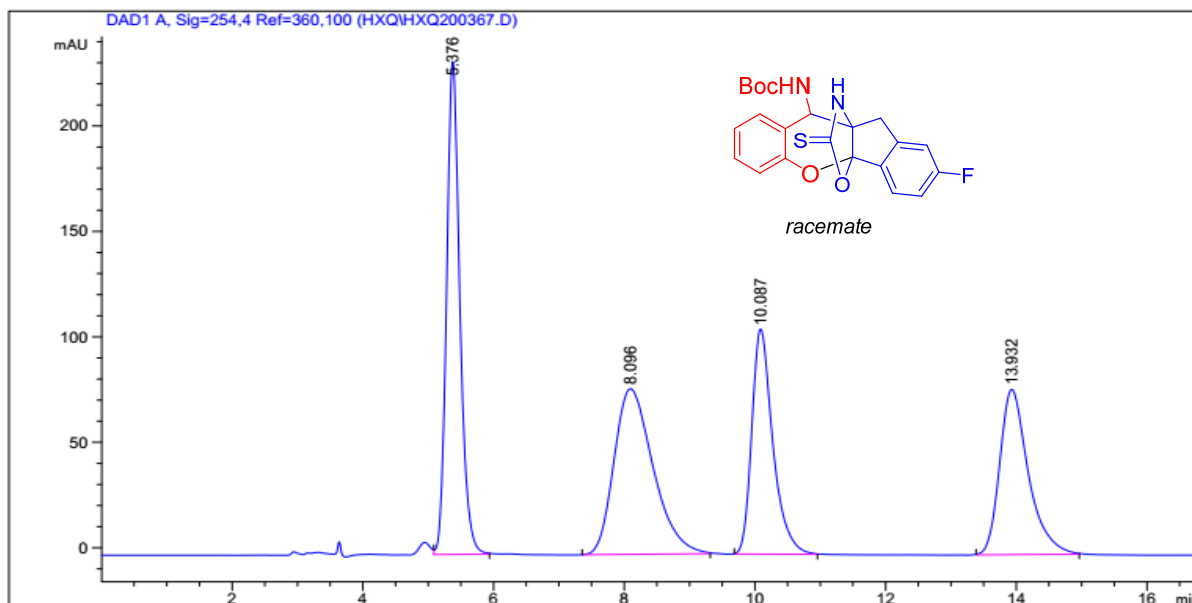
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.724	VV	0.2799	2.34752e4	1304.98547	91.7166
2	5.926	VB	0.2557	1307.23633	69.40694	5.1073
3	7.884	BB	0.2879	408.81808	21.10962	1.5972
4	9.437	VB	0.3248	404.11371	18.50172	1.5789



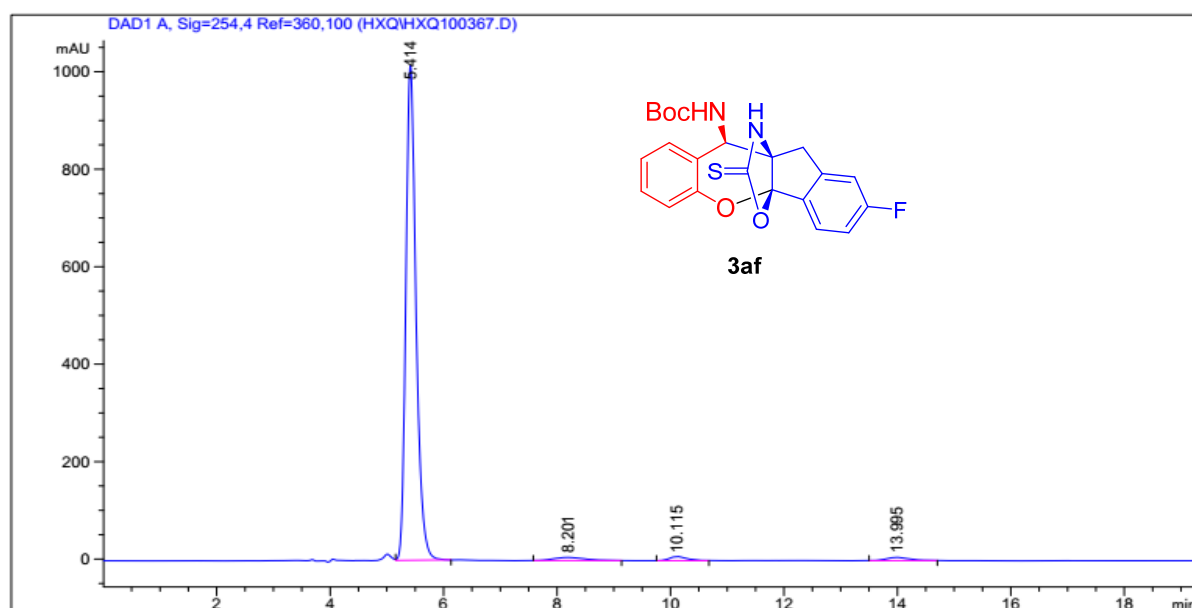
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.768	VB	0.2772	5407.81250	304.42902	45.3075
2	6.321	VB	0.5346	5301.39063	149.18591	44.4159
3	7.996	BB	0.2756	640.09570	34.64110	5.3628
4	9.563	BB	0.3317	586.50690	26.96690	4.9138



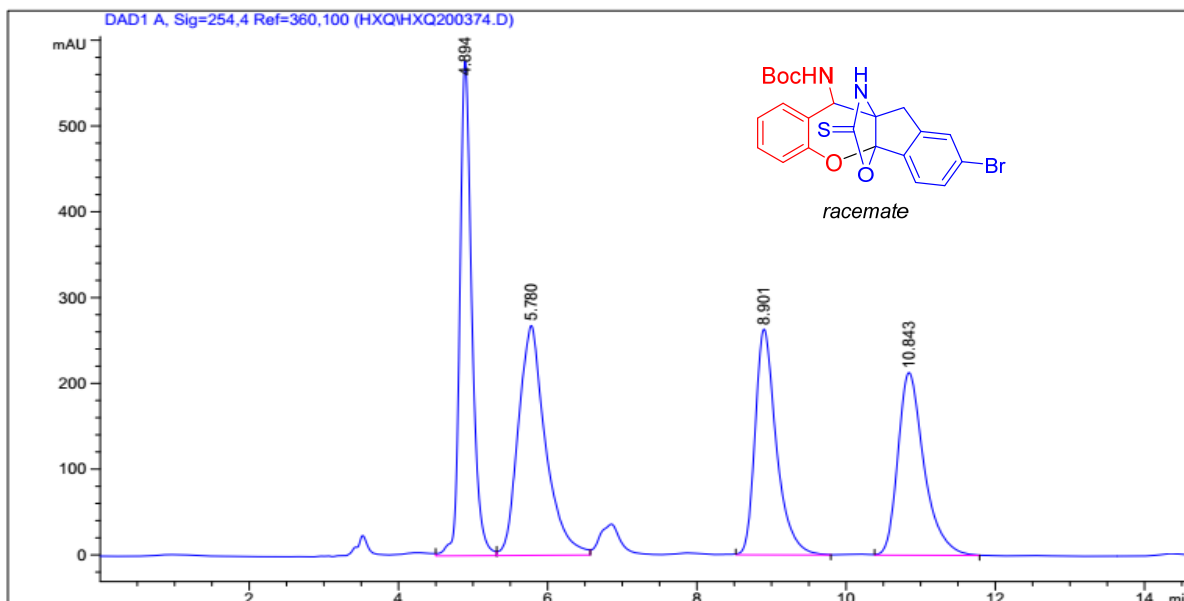
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.757	BB	0.2842	3.73963e4	2036.97644	94.7826
2	6.322	BB	0.5046	808.01190	24.13292	2.0479
3	8.000	BB	0.2796	612.95935	32.56181	1.5536
4	9.569	VB	0.3357	637.53381	28.86248	1.6159



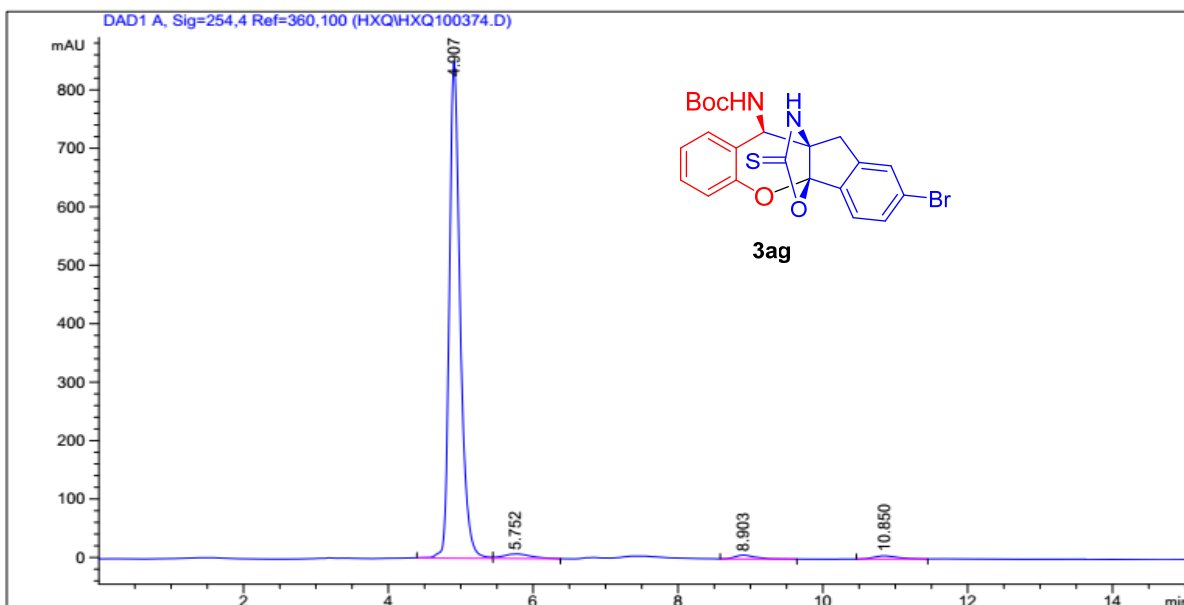
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.376	VB	0.2123	3292.27588	233.73698	29.0684
2	8.096	BB	0.6342	3258.55029	78.51941	28.7706
3	10.087	BB	0.3349	2387.09863	106.73078	21.0763
4	13.932	BB	0.4594	2388.04395	78.39133	21.0847



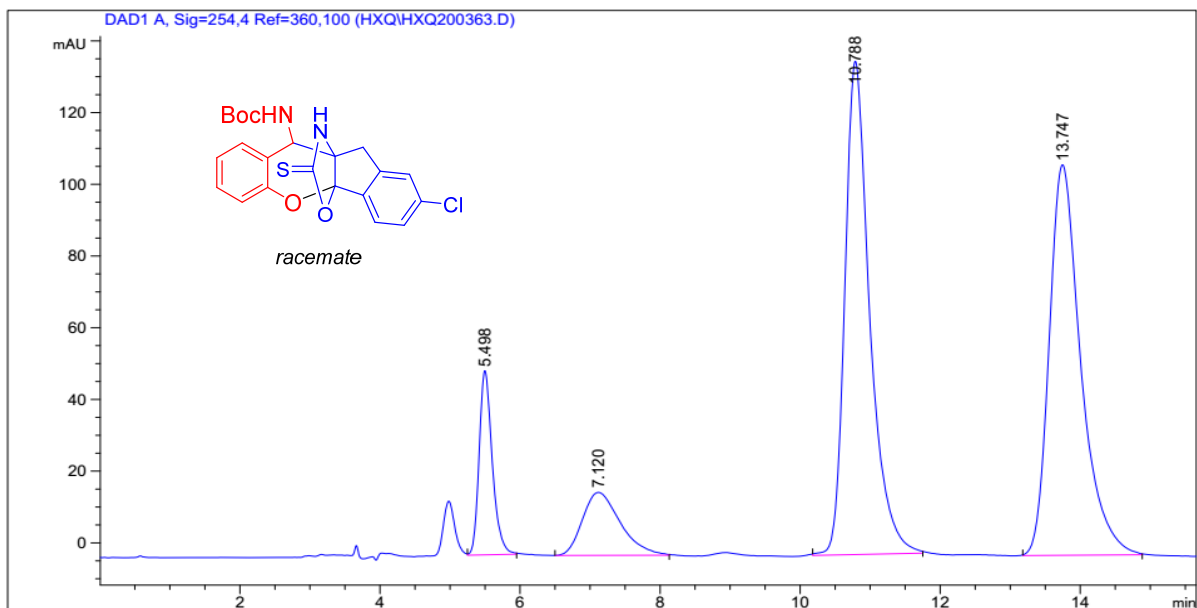
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.414	VB	0.1887	1.25974e4	1015.83667	95.2226
2	8.201	BB	0.4900	257.45020	6.50098	1.9460
3	10.115	BB	0.3097	182.00073	8.43496	1.3757
4	13.995	BB	0.3904	192.56865	6.63992	1.4556



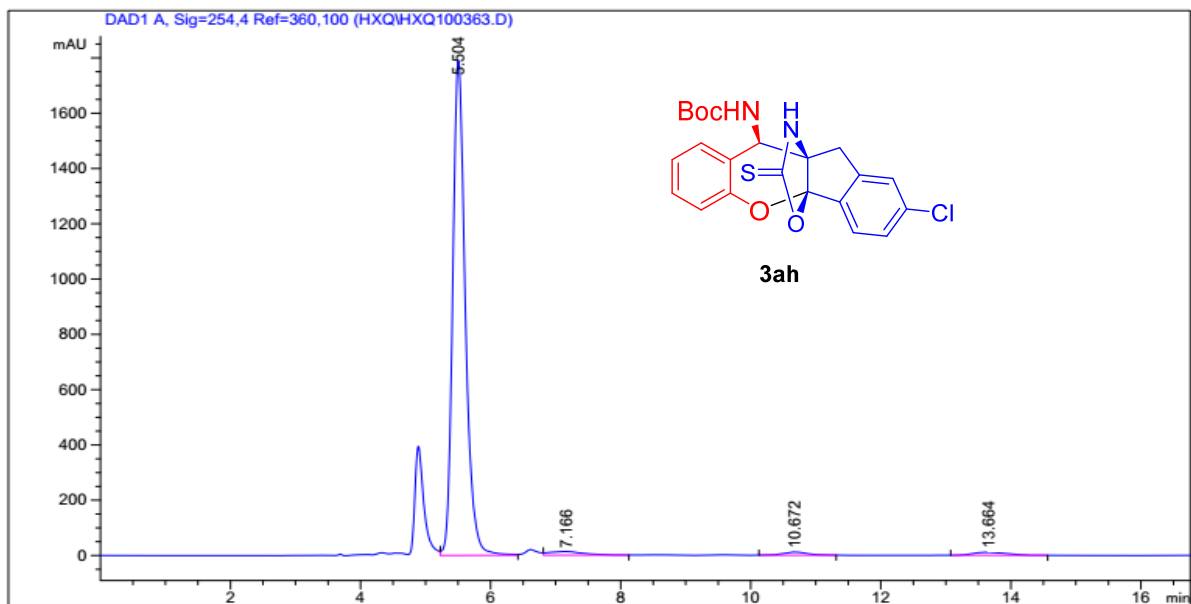
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.894	VV	0.1685	6447.94580	576.60516	27.2911
2	5.780	VV	0.3794	6784.72412	267.94006	28.7166
3	8.901	BB	0.2967	5202.52441	263.08109	22.0198
4	10.843	BB	0.3685	5191.33105	212.91194	21.9725



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.907	BV	0.1574	8829.25391	848.61237	94.9322
2	5.752	VB	0.3556	212.43828	7.90389	2.2841
3	8.903	BB	0.2975	133.46523	6.66734	1.4350
4	10.850	BB	0.3165	125.42873	5.45079	1.3486



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.498	VB	0.1977	667.75104	51.36112	8.2313
2	7.120	BB	0.5171	657.67004	17.55529	8.1070
3	10.788	BB	0.3668	3382.89160	137.59703	41.7004
4	13.747	BB	0.4725	3404.06714	108.94039	41.9614



Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.504	VB	0.2050	2.40885e4	1789.62451	95.2676
2	7.166	VB	0.4850	490.89789	13.28653	1.9415
3	10.672	BB	0.3875	307.83972	11.60560	1.2175
4	13.664	BB	0.4458	397.86145	11.16380	1.5735