

Supporting Information

Organocatalytic enantioselective cross-aldol reaction of aryl ketones to heteroaromatic trifluoromethyl ketone hydrates for the synthesis of α -trifluoromethyl tertiary alcohols

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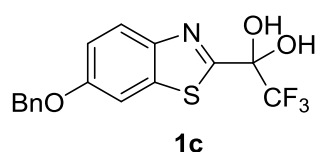
I. General Information

Flash column chromatography was performed over silica gel (200-300 mesh) purchased from Qindao Puke Co., China. All air or moisture sensitive reactions were conducted in oven-dried glassware under nitrogen atmosphere using anhydrous solvents. Anhydrous toluene was dried sodium with diphenyl ketone as an indicator, and other anhydrous solvents, such as tetrahydrofuran, methanol, and dichloromethane, were purchased from Energy Chemicals Inc. and used as received. Molecular sieves (MS) were purchased from Aldrich and treated at 120 °C in the oven for 2 h.

¹H, ¹³C, and ¹⁹F NMR spectra were collected on a Bruker 400 MHz NMR spectrometer at 20 °C using peaks of CDCl₃ as an internal standard (¹H NMR: CDCl₃ at 7.26 ppm, *d*₆-acetone at 2.05 ppm; ¹³C NMR: CDCl₃ at 77.16 ppm, *d*₆-acetone at 206.26 ppm). High-resolution mass spectra were collected on a Bruker Maxis System. Melting points were measured by a melting point instrument and were uncorrected. Optical rotations were measured on a WZZ-1S polarimeter with [α]_D values reported in degrees. The enantiomeric excesses were determined by chiral HPLC using a Shimadzu Prominence LC-20A instrument with Daicel chiral columns (Chiralcel OD-H, Chiralpak AD-H or Chiralpak IC-H). Aryl ketones **2** were all purchased from Energy Chemicals Inc. and used as received. Catalyst **A-E** were prepared by the literature procedure,¹⁻³ and other catalysts were purchased from Daicel Chiral Technologies (China) Co., Ltd. and used as received.

II. Synthesis of Ketone Hydrate Substrates

Synthesis of ketone hydrates 1c-e. To a solution of substituted benzothiazole (5.0 mmol) in toluene (20 mL) at $-20\text{ }^{\circ}\text{C}$ was added dropwise trifluoroacetic anhydride (6.0 mmol) over 10 min. The mixture was stirred for 0.5 h, and triethylamine (6.0 mmol) was slowly added. After stirring at $-20\text{ }^{\circ}\text{C}$ overnight, the resulting reaction mixture was spontaneously warmed to room temperature and stirred for 12 h. The solvent was removed in vacuo, and water (5 mL) was added to form white precipitation, which was dissolved in ethyl acetate (40 mL). The organic phase was successively washed with 1 M HCl (20 mL), water (20 mL), and brine (20 mL), dried over anhydrous Na_2SO_4 , and concentrated in vacuo to afford the crude product. The pure ketone hydrate was obtained by recrystallization from petroleum ether/ethyl acetate (5:1, v/v). Ketone hydrates **1c**, **1d**, and **1e** are unknown compounds, and others are known.⁴⁻⁵



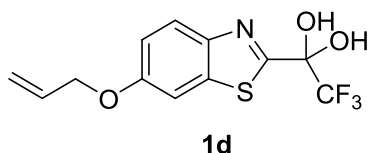
1-(6-(Benzyloxy)benzo[d]thiazol-2-yl)-2,2,2-trifluoroethane-1,1-diol (1c) was prepared from 6-(benzyloxy)benzothiazole (1.20 g, 5.0 mmol) according to the above procedure. Yellow solid, m.p. $138\text{--}139\text{ }^{\circ}\text{C}$; 0.95 g, 54% yield.

$^1\text{H NMR}$ (400 MHz, d_6 -acetone) δ 7.95 (d, $J = 9.2\text{ Hz}$, 1H), 7.72 (d, $J = 2.0\text{ Hz}$, 1H), 7.59 (s, 2H), 7.51 (d, $J = 7.6\text{ Hz}$, 2H), 7.40 (t, $J = 7.6\text{ Hz}$, 2H), 7.33 (t, $J = 7.6\text{ Hz}$, 1H), 7.25 (dd, $J_1 = 8.8\text{ Hz}$, $J_2 = 2.4\text{ Hz}$, 1H), 5.22 (s, 2H) ppm.

¹³C NMR (100 MHz, *d*₆-acetone) δ 166.0, 157.9, 147.8, 137.9, 137.4, 128.8, 128.3, 128.0, 124.6, 123.2 (q, *J* = 286.3 Hz), 117.2, 105.7, 92.8 (q, *J* = 33.0 Hz), 70.6 ppm.

¹⁹F NMR (376.5 MHz, *d*₆-acetone) δ -83.6 ppm.

HRMS (ESI) *m/z*: [M-H₂O]⁺ calcd for C₁₆H₁₀F₃NO₂S 337.0382; found 337.0382.



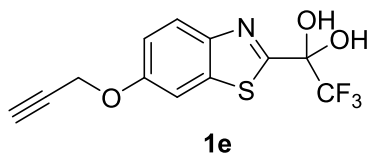
1-(6-(Allyloxy)benzo[*d*]thiazol-2-yl)-2,2,2-trifluoroethane-1,1-diol (1d) was prepared from 6-(allyloxy)benzo[*d*]thiazole (1.91 g, 10.0 mmol) according to the above procedure. Yellow solid, m.p. 115–117 °C; 1.38 g, 45% yield.

¹H NMR (400 MHz, *d*₆-acetone) δ 7.95 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 2.8 Hz, 1H), 7.18 (dd, *J*₁ = 2.8 Hz, *J*₂ = 9.2 Hz, 1H), 6.13–6.06 (m, 1H), 5.44 (d, *J* = 15.6 Hz, 1H), 5.27 (d, *J* = 12.4 Hz, 1H), 4.67 (d, *J* = 5.2 Hz, 2H) ppm.

¹³C NMR (100 MHz, *d*₆-acetone) δ 165.4, 157.3, 147.3, 137.5, 133.3, 124.2, 122.7 (q, *J* = 285.8 Hz), 117.0, 116.7, 105.1, 92.3 (q, *J* = 33.0 Hz), 69.0 ppm.

¹⁹F NMR (376.5 MHz, *d*₆-acetone) δ -83.5 ppm.

HRMS (ESI) *m/z*: [M-H₂O]⁺ calcd for C₁₂H₈F₃NO₂S 287.0228; found 287.0226.



2,2,2-Trifluoro-1-(6-(prop-2-yn-1-yloxy)benzo[*d*]thiazol-2-yl)ethane-1,1-diol (1e) was prepared from 6-(prop-2-yn-1-yloxy)benzothiazole (0.95 g, 5.0 mmol) according to the above procedure. Yellow solid, m.p. 115–117 °C; 0.66 g, 44% yield.

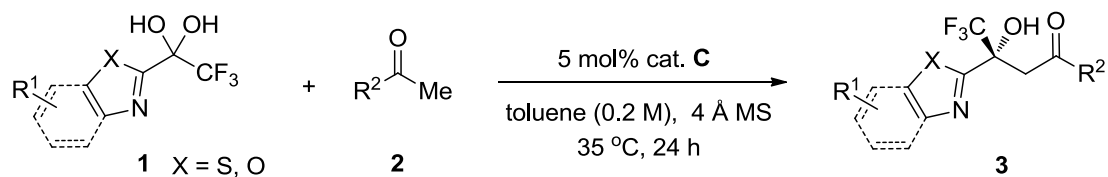
¹H NMR (400 MHz, *d*₆-acetone) δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.73 (s, 1H), 7.53 (s, 2H), 7.23 (d, *J* = 9.2 Hz, 1H), 4.91 (s, 2H), 3.12 (s, 1H) ppm.

¹³C NMR (100 MHz, *d*₆-acetone) δ 166.3, 156.7, 148.2, 137.8, 124.7, 123.2 (q, *J* = 286.2 Hz), 117.1, 106.1, 92.8 (q, *J* = 33.0 Hz), 78.9, 76.9, 56.5 ppm.

¹⁹F NMR (376.5 MHz, *d*₆-acetone) δ -83.6 ppm.

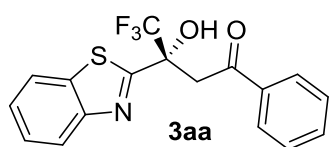
HRMS (ESI) *m/z*: [M-H₂O]⁺ calcd for C₁₂H₆F₃NO₂S 285.0071; found 285.0074.

III. Synthesis of α -Trifluoromethyl Tertiary Alcohols



General procedure for organocatalytic enantioselective cross-aldol reaction.

To a 4-mL vial equipped with a magnetic stir bar, heteroaromatic trifluoromethyl ketone hydrate **1** (0.10 mmol), catalyst **C** (5 mol%), 4 Å MS (30 mg), and toluene (0.5 mL) were sequentially added. The mixture was stirred for 30 min at room temperature (35 °C in summer), and then methyl ketone **2** (3.0 or 5.0 equiv.) was added. After stirring for 11~36 h, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired chiral α -trifluoromethyl tertiary alcohol **3**.



(S)-3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-phenylbutan-1-one

(3aa) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2a** (3.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1, v/v). White solid, m.p. 134–135 °C; 29.8 mg, 85% yield.

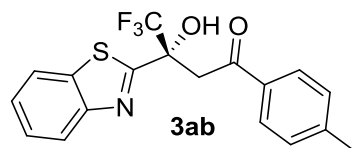
$[\alpha]_{\text{D}}^{25} = -121.5$ ($c = 0.26$, CHCl_3 , 86% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 8% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 11.4 min (minor), 12.7 min (major).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.00 (d, $J = 6.8$ Hz, 2H), 7.93 (dd, $J_1 = 8.0$ Hz, $J_2 = 16.0$ Hz, 2H), 7.61 (d, $J = 6.8$ Hz, 1H), 7.50-7.40 (m, 4H), 6.50 (s, 1H), 4.62 (d, $J = 17.2$ Hz, 1H), 3.68 (d, $J = 17.6$ Hz, 1H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 200.1, 169.9, 153.0, 136.3, 136.1, 134.6, 128.9, 128.6, 126.3, 125.8, 123.8, 123.4 (q, $J = 283.5$ Hz), 121.9, 77.7 (q, $J = 29.9$ Hz), 40.2 ppm.

$^{19}\text{F NMR}$ (376.5 MHz, CDCl_3) δ -79.7 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_{12}\text{F}_3\text{NO}_2\text{S}$ 351.0541; found 351.0543.



(S)-3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-(*p*-tolyl)butan-1-one

(3ab) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2b** (3.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1, v/v). White solid, m.p. 148–150 °C; 28.1 mg, 77% yield.

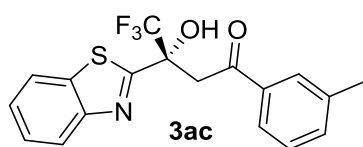
$[\alpha]_{\text{D}}^{25} = -73.1$ ($c = 0.26$, CHCl_3 , 86% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel AD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 8.5 min (major), 13.5 min (minor).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95 (d, $J = 7.6$ Hz, 1H), 7.90 (d, $J = 7.6$ Hz, 3H), 7.45-7.36 (m, 2H), 7.27 (d, $J = 7.6$ Hz, 2H), 6.62 (s, 1H), 4.56 (d, $J = 17.2$ Hz, 1H), 3.64 (d, $J = 16.8$ Hz, 1H), 2.41 (s, 3H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 199.7, 170.1, 153.1, 145.9, 136.2, 133.6, 129.6, 128.8, 126.2, 125.7, 123.7, 123.4 (q, $J = 283.5$ Hz), 121.9, 77.7 (q, $J = 29.9$ Hz), 39.9, 21.9 ppm.

$^{19}\text{F NMR}$ (376.5 MHz, CDCl_3) δ -79.7 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{18}\text{H}_{14}\text{F}_3\text{NO}_2\text{S}$ 365.0697; found 365.0698.



(S)-3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-(*m*-tolyl)butan-1-one

(3ac) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2c** (5.0 equiv.) for 36 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1, v/v). White solid, m.p. 131–133 °C; 30.3 mg, 83% yield.

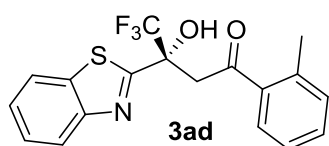
$[\alpha]_{\text{D}}^{25} = -110.0$ ($c = 0.28$, CHCl_3 , 89% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel AD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 8.0 min (major), 11.3 min (minor).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.0$ Hz, 1H), 7.91 (d, $J = 7.6$ Hz, 1H), 7.80 (s, 2H), 7.47-7.36 (m, 4H), 6.55 (s, 1H), 4.60 (d, $J = 17.6$ Hz, 1H), 3.67 (d, $J = 17.2$ Hz, 1H), 2.41 (s, 3H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 200.3, 170.0, 153.0, 138.9, 136.2, 136.0, 135.5, 129.1, 128.8, 126.6, 125.9, 125.8, 123.7, 123.4 (q, $J = 283.5$ Hz), 121.9, 77.7 (q, $J = 29.9$ Hz), 40.2, 21.3 ppm.

^{19}F NMR (376.5 MHz, CDCl_3) δ -79.6 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{18}\text{H}_{14}\text{F}_3\text{NO}_2\text{S}$ 365.0697; found 365.0695.



(S)-3-(Benzo[d]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-(o-tolyl)butan-1-one

(3ad) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2d** (5.0 equiv.) for 36 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1, v/v). White solid, m.p. 96–98 °C; 22.6 mg, 62% yield.

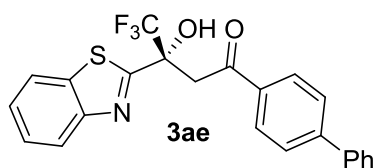
$[\alpha]_{\text{D}}^{25} = -23.3$ ($c = 0.21$, CHCl_3 , 80% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 3% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 11.4 min (major), 12.0 min (minor).

^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.0$ Hz, 1H), 7.93 (d, $J = 6.8$ Hz, 2H), 7.50–7.41 (m, 3H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.25 (d, $J = 7.2$ Hz, 1H), 6.56 (s, 1H), 4.52 (d, $J = 17.2$ Hz, 1H), 3.60 (d, $J = 16.8$ Hz, 1H), 2.38 (s, 3H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 204.0, 169.9, 152.9, 139.2, 136.6, 136.3, 132.9, 132.3, 129.6, 126.3, 126.1, 125.8, 123.7, 123.3 (q, $J = 283.4$ Hz), 122.0, 77.9 (q, $J = 29.9$ Hz), 42.5, 21.3 ppm.

^{19}F NMR (376.5 MHz, CDCl_3) δ -79.7 ppm.

HRMS (ESI) m/z: [M]⁺ calcd for C₁₈H₁₄F₃NO₂S 365.0697; found 365.0693.



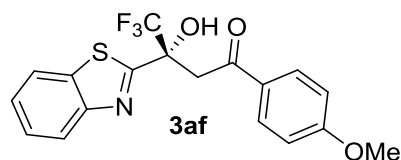
(S)-1-([1,1'-Biphenyl]-4-yl)-3-(benzo[d]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxybutan-1-one (3ae) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2e** (5.0 equiv.) for 23 h according to the above general procedure with catalyst **A** instead of catalyst **C** (eluent: petroleum ether/ethyl acetate = 20:1 to 15:1, v/v). White solid, m.p. 112–114 °C; 30.3 mg, 71% yield. $[\alpha]_{\text{D}}^{25} = -103.6$ ($c = 0.28$, CHCl₃, 78% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel AD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 6.9 min (minor), 13.2 min (major).

¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, $J = 8.4$ Hz, 2H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.93 (d, $J = 7.6$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.65 (d, $J = 7.6$ Hz, 2H), 7.53-7.39 (m, 5H), 6.60 (s, 1H), 4.66 (d, $J = 17.2$ Hz, 1H), 3.73 (d, $J = 17.2$ Hz, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 199.6, 170.0, 153.0, 147.3, 139.4, 136.2, 134.7, 129.3, 129.1, 128.7, 127.5, 127.4, 126.2, 125.8, 123.7, 123.4 (q, $J = 283.6$ Hz), 121.9, 77.7 (q, $J = 29.9$ Hz), 40.1 ppm.

¹⁹F NMR (376.5 MHz, CDCl₃) δ -79.5 ppm.

HRMS (ESI) m/z: [M]⁺ calcd for C₂₃H₁₆F₃NO₂S 427.0854; found 427.0851.



(S)-3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-(4-methoxyphenyl)butan-1-one (3af) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2f** (3.0 equiv.) for 17 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1, v/v). White solid, m.p. 105–106 °C; 30.1 mg, 79% yield.

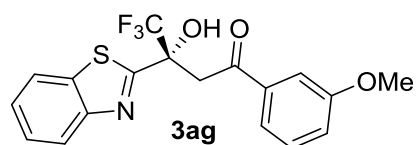
$[\alpha]_{\text{D}}^{25} = -119.3$ ($c = 0.27$, CHCl_3 , 82% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 15% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 9.0 min (minor), 13.1 min (major).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (t, $J = 7.6$ Hz, 3H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.45–7.35 (m, 2H), 6.93 (d, $J = 8.4$ Hz, 2H), 6.80 (s, 1H), 4.55 (d, $J = 16.8$ Hz, 1H), 3.84 (s, 3H), 3.62 (d, $J = 16.8$ Hz, 1H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 198.4, 170.2, 164.8, 153.1, 136.2, 131.1, 129.0, 126.2, 125.7, 123.7, 123.5 (q, $J = 283.5$ Hz), 121.9, 114.1, 77.7 (q, $J = 29.8$ Hz), 55.6, 39.4 ppm.

$^{19}\text{F NMR}$ (376.5 MHz, CDCl_3) δ -79.6 ppm.

HRMS (ESI) m/z : $[M]^+$ calcd for $\text{C}_{18}\text{H}_{14}\text{F}_3\text{NO}_3\text{S}$ 381.0646; found 381.0643.



(S)-3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-(3-methoxyphenyl)butan-1-one (3ag) was prepared from trifluoromethyl ketone hydrate **1a** and

methyl ketone **2g** (5.0 equiv.) for 17 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1, v/v). White solid, m.p. 103–105 °C; 31.6 mg, 83% yield.

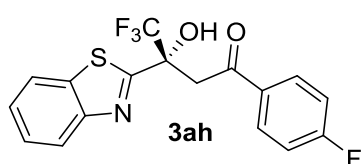
$[\alpha]_{\text{D}}^{25} = -115.0$ ($c = 0.30$, CHCl_3 , 88% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 8% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 20.6 min (minor), 21.9 min (major).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, $J = 7.6$ Hz, 1H), 7.91 (d, $J = 6.8$ Hz, 1H), 7.62 (d, $J = 6.4$ Hz, 1H), 7.47 (s, 1H), 7.45–7.38 (m, 3H), 7.17 (d, $J = 7.2$ Hz, 1H), 6.47 (s, 1H), 4.60 (d, $J = 17.6$ Hz, 1H), 3.82 (s, 3H), 3.68 (d, $J = 17.2$ Hz, 1H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 199.8, 169.9, 160.0, 153.0, 137.3, 136.2, 129.9, 126.2, 125.8, 123.7, 123.4 (q, $J = 283.5$ Hz), 121.9, 121.4, 121.2, 112.5, 77.6 (q, $J = 29.9$ Hz), 55.5, 40.4 ppm.

$^{19}\text{F NMR}$ (376.5 MHz, CDCl_3) δ -79.6 ppm.

HRMS (ESI) m/z : $[M]^+$ calcd for $\text{C}_{18}\text{H}_{14}\text{F}_3\text{NO}_3\text{S}$ 381.0646; found 381.0644.



(*S*)-3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-1-(4-fluorophenyl)-3-hydroxybutan-1-one (**3ah**) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2h** (5.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1, v/v). Yellow solid, m.p. 115–116 °C; 34.1 mg, 92% yield.

$[\alpha]_{\text{D}}^{25} = -85.6$ ($c = 0.32$, CHCl_3 , 86% ee). Enantiomeric excess was determined

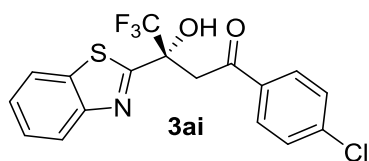
by chiral HPLC: Daicel Chiralcel OD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 6.5 min (minor), 15.8 min (major).

¹H NMR (400 MHz, CDCl₃) δ 8.03 (s, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.42 (dd, *J*₁ = 7.6 Hz, *J*₂ = 14.4 Hz, 2H), 7.14 (s, 2H), 6.48 (s, 1H), 4.61 (d, *J* = 17.2 Hz, 1H), 3.65 (d, *J* = 17.2 Hz, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 198.5, 169.8, 166.7 (d, *J* = 256.0 Hz), 153.0, 136.3, 132.6 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 9.7 Hz), 126.3, 125.9, 123.7, 123.4 (q, *J* = 283.5 Hz), 122.0, 116.2 (d, *J* = 22.0 Hz), 77.7 (q, *J* = 30.0 Hz), 40.1 ppm.

¹⁹F NMR (376.5 MHz, CDCl₃) δ -79.7, -102.1 ppm.

HRMS (ESI) *m/z*: [M]⁺ calcd for C₁₇H₁₁F₄NO₂S 369.0447; found 369.0447.



(S)-3-(Benzo[*d*]thiazol-2-yl)-1-(4-chlorophenyl)-4,4,4-trifluoro-3-hydroxybutan-1-one (3ai) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2i** (5.0 equiv.) for 18 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1, v/v). Yellow solid, m.p. 143–144 °C; 36.0 mg, 94% yield.

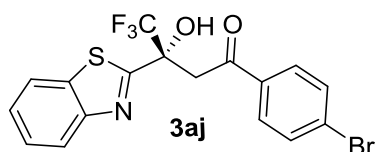
[α]_D²⁵ = -139.7 (*c* = 0.31, CHCl₃, 86% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel AD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 11.3 min (major), 15.9 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 7.92 (t, *J* = 8.4 Hz, 4H), 7.47-7.38 (m, 4H), 6.34 (s, 1H), 4.57 (d, *J* = 17.2 Hz, 1H), 3.62 (d, *J* = 17.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 199.0, 169.6, 152.9, 141.4, 136.3, 134.5, 130.1, 129.4, 126.3, 125.9, 123.8, 123.3 (q, $J = 283.5$ Hz), 122.0, 77.7 (q, $J = 30.0$ Hz), 40.2 ppm.

^{19}F NMR (376.5 MHz, CDCl_3) δ -79.7 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_{11}\text{ClF}_3\text{NO}_2\text{S}$ 385.0151; found 385.0149.



(S)-3-(Benzo[d]thiazol-2-yl)-1-(4-bromophenyl)-4,4,4-trifluoro-3-hydroxybutan-1-one (**3aj**) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2j** (3.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1). White solid, m.p. 144.5–145.8 °C; 39.5 mg, 92% yield.

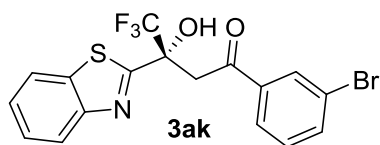
$[\alpha]_{\text{D}}^{25} = -144.4$ ($c = 0.32$, CHCl_3 , 84% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 10.8 min (major), 15.0 min (minor).

^1H NMR (400 MHz, CDCl_3) δ 7.95 (t, $J = 7.2$ Hz, 2H), 7.88 (d, $J = 8.8$ Hz, 2H), 7.65 (d, $J = 8.8$ Hz, 2H), 7.50–7.41 (m, 2H), 6.35 (s, 1H), 4.58 (d, $J = 17.2$ Hz, 1H), 3.63 (d, $J = 16.8$ Hz, 1H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 199.2, 169.6, 152.9, 136.3, 134.8, 132.3, 130.2, 130.1, 126.3, 125.9, 123.8, 123.3 (q, $J = 283.4$ Hz), 122.0, 77.7 (q, $J = 30.1$ Hz), 40.1 ppm.

^{19}F NMR (376.5 MHz, CDCl_3) δ -79.7 ppm.

HRMS (ESI) m/z : $[M]^+$ calcd for $C_{17}H_{11}BrF_3NO_2S$ 428.9646; found 428.9641.



(S)-3-(Benzo[d]thiazol-2-yl)-1-(3-bromophenyl)-4,4,4-trifluoro-3-hydroxybutan-1-one (3ak) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2k** (3.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1). Yellow solid, m.p. 121.5–123.2 °C; 39.8 mg, 93% yield.

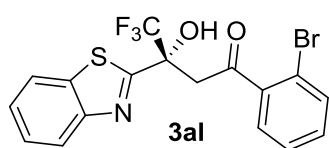
$[\alpha]_D^{25} = -69.7$ ($c = 0.33$, $CHCl_3$, 89% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel AD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 10.7 min (major), 13.8 min (minor).

1H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.96 (d, $J = 7.6$ Hz, 1H), 7.91 (d, $J = 7.2$ Hz, 2H), 7.72 (d, $J = 7.2$ Hz, 1H), 7.43 (dd, $J_1 = 8.0$ Hz, $J_2 = 12.8$ Hz, 2H), 7.34 (t, $J = 7.6$ Hz, 1H), 6.25 (s, 1H), 4.59 (d, $J = 17.2$ Hz, 1H), 3.63 (d, $J = 17.2$ Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 169.4, 152.8, 137.7, 137.4, 136.2, 131.6, 130.5, 127.2, 126.3, 125.9, 123.7, 123.3 (q, $J = 283.5$ Hz), 123.3, 121.9, 77.7 (q, $J = 30.1$ Hz), 40.4 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ -79.6 ppm.

HRMS (ESI) m/z : $[M]^+$ calcd for $C_{17}H_{11}BrF_3NO_2S$ 428.9646; found 428.9645.



(S)-3-(Benzo[d]thiazol-2-yl)-1-(2-bromophenyl)-4,4,4-trifluoro-3-hydroxybutan-1-one (3a) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2l** (3.0 equiv.) for 17 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1). White solid, m.p. 78.0–79.5 °C; 39.2 mg, 91% yield.

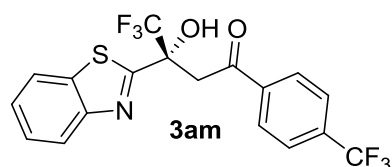
$[\alpha]_D^{25} = -26.3$ ($c = 0.35$, CHCl_3 , 79% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel AD-H column; 20% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 6.1 min (major), 16.0 min (minor).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.0$ Hz, 1H), 7.93 (d, $J = 7.6$ Hz, 1H), 7.60 (t, $J = 9.6$ Hz, 2H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.44 (d, $J = 7.6$ Hz, 1H), 7.41–7.31 (m, 2H), 6.11 (s, 1H), 4.46 (d, $J = 17.2$ Hz, 1H), 3.70 (d, $J = 17.2$ Hz, 1H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 203.4, 169.2, 152.7, 139.7, 136.3, 134.3, 133.0, 129.8, 127.6, 126.4, 126.0, 123.7, 123.2 (q, $J = 283.7$ Hz), 122.0, 119.3, 77.9 (q, $J = 30.2$ Hz), 44.2 ppm.

$^{19}\text{F NMR}$ (376.5 MHz, CDCl_3) δ -79.6 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_{11}\text{BrF}_3\text{NO}_2\text{S}$ 428.9646; found 428.9640.



(S)-3-(Benzo[d]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-(4-(trifluoromethyl)phenyl)butan-1-one (3am) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2m** (3.0 equiv.) for 23 h according to the above general

procedure (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1, v/v). White solid, m.p. 99–101 °C; 39.6 mg, 95% yield.

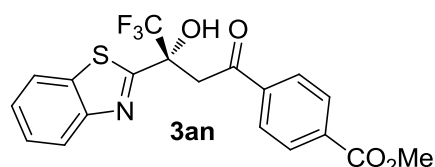
$[\alpha]_{\text{D}}^{25} = -112.9$ ($c = 0.35$, CHCl_3 , 87% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 15% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 5.7 min (minor), 12.4 min (major).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.0$ Hz, 2H), 7.93 (dd, $J_1 = 8.0$ Hz, $J_2 = 13.2$ Hz, 2H), 7.76 (d, $J = 8.0$ Hz, 2H), 7.47–7.39 (m, 2H), 6.22 (s, 1H), 4.66 (d, $J = 17.2$ Hz, 1H), 3.70 (d, $J = 17.2$ Hz, 1H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 199.2, 169.4, 152.8, 138.7, 136.3, 135.6 (q, $J = 32.7$ Hz), 129.0, 126.4, 126.0 (q, $J = 3.5$ Hz), 123.7, 123.5 (q, $J = 271.2$ Hz), 123.3 (q, $J = 283.5$ Hz), 122.1, 122.0, 77.7 (q, $J = 30.1$ Hz), 40.7 ppm.

$^{19}\text{F NMR}$ (376.5 MHz, CDCl_3) δ -63.3, -79.7 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{18}\text{H}_{11}\text{F}_6\text{NO}_2\text{S}$ 419.0415; found 419.0415.



(S)-Methyl-4-(3-(benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxybutanoyl)benzoate (3an) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2n** (3.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1, v/v). Yellow solid, m.p. 135–136 °C; 38.4 mg, 94% yield.

$[\alpha]_{\text{D}}^{25} = -129.7$ ($c = 0.35$, CHCl_3 , 89% ee). Enantiomeric excess was determined

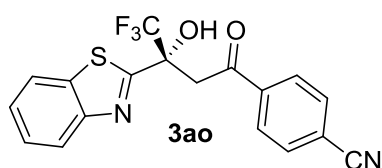
by chiral HPLC: Daicel Chiralcel AD-H column; 20% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 8.7 min (major), 11.2 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.4 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.45-7.37 (m, 2H), 6.22 (s, 1H), 4.61 (d, *J* = 17.2 Hz, 1H), 3.96 (s, 3H), 3.66 (d, *J* = 17.2 Hz, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 199.7, 169.5, 166.0, 152.8, 139.2, 136.2, 135.2, 130.1, 128.6, 126.3, 125.9, 123.7, 123.3 (q, *J* = 283.2 Hz), 122.0, 77.7 (q, *J* = 30.0 Hz), 52.7, 40.7 ppm.

¹⁹F NMR (376.5 MHz, CDCl₃) δ -79.7 ppm.

HRMS (ESI) *m/z*: [M]⁺ calcd for C₁₉H₁₄F₃NO₄S 409.0596; found 409.0594.



(*S*)-4-(3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxybutanoyl)benzonitrile (**3ao**) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2o** (3.0 equiv.) for 23 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1, v/v). White solid, m.p. 154–155 °C; 36.1 mg, 96% yield.

[α]_D²⁵ = -167.6 (*c* = 0.33, CHCl₃, 86% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel AD-H column; 20% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 10.6 min (major), 16.5 min (minor).

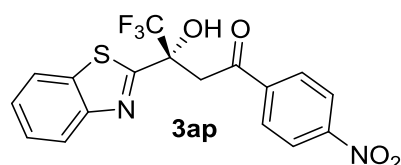
¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.91 (dd, *J*₁ = 4.8 Hz, *J*₂ =

6.4 Hz, 2H), 7.79 (d, $J = 8.0$ Hz, 2H), 7.47-7.39 (m, 2H), 6.04 (s, 1H), 4.60 (d, $J = 17.2$ Hz, 1H), 3.65 (d, $J = 17.2$ Hz, 1H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 169.0, 152.6, 138.9, 136.2, 132.7, 129.0, 126.4, 126.0, 123.7, 123.2 (q, $J = 283.6$ Hz), 122.0, 121.8, 117.7, 77.7 (q, $J = 30.2$ Hz), 40.7 ppm.

^{19}F NMR (376.5 MHz, CDCl_3) δ -79.7 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{18}\text{H}_{11}\text{F}_3\text{N}_2\text{O}_2\text{S}$ 376.0493; found 376.0496.



(S)-3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-(4-nitrophenyl)butan-1-one (3ap) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2p** (3.0 equiv.) for 11 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1, v/v). Yellow solid, m.p. 142–144 °C; 37.8 mg, 95% yield.

$[\alpha]_{\text{D}}^{25} = -130.8$ ($c = 0.36$, CHCl_3 , 85% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel AD-H column; 20% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 11.4 min (major), 15.2 min (minor).

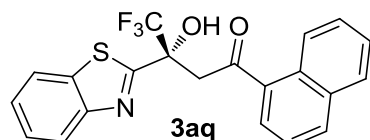
^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, $J = 8.4$ Hz, 2H), 8.16 (d, $J = 8.4$ Hz, 2H), 7.91 (t, $J = 7.2$ Hz, 2H), 7.47-7.39 (m, 2H), 6.00 (s, 1H), 4.64 (d, $J = 17.2$ Hz, 1H), 3.68 (d, $J = 17.2$ Hz, 1H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 198.7, 169.0, 152.6, 151.1, 140.4, 136.2, 129.7,

126.5, 126.1, 124.1, 123.7, 123.2 (q, $J = 283.5$ Hz), 122.0, 77.7 (q, $J = 30.2$ Hz), 41.0 ppm.

^{19}F NMR (376.5 MHz, CDCl_3) δ -79.7 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_{11}\text{F}_3\text{N}_2\text{O}_4\text{S}$ 396.0392; found 396.0389.



(S)-3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-(naphthalen-1-yl)butan-1-one (3aq) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2q** (5.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1, v/v). Yellow solid, m.p. 110–112 °C; 34.1 mg, 85% yield.

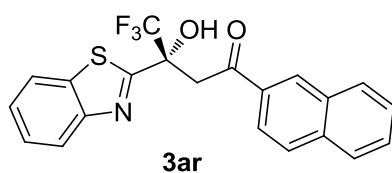
$[\alpha]_{\text{D}}^{25} = -5.0$ ($c = 0.24$, CHCl_3 , 70% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 8% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 16.1 min (major), 22.6 min (minor).

^1H NMR (400 MHz, CDCl_3) δ 8.45 (dd, $J_1 = 3.6$ Hz, $J_2 = 6.0$ Hz, 1H), 8.20 (d, $J = 7.2$ Hz, 1H), 8.05 (d, $J = 8.0$ Hz, 1H), 7.94 (d, $J = 8.0$ Hz, 2H), 7.87 (d, $J = 4.0$ Hz, 1H), 7.59–7.51 (m, 3H), 7.47–7.39 (m, 2H), 6.63 (s, 1H), 4.66 (d, $J = 17.2$ Hz, 1H), 3.75 (d, $J = 16.8$ Hz, 1H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 204.0, 169.8, 152.9, 136.3, 134.5, 134.4, 134.0, 130.0, 129.7, 128.7, 128.6, 126.9, 126.3, 125.9, 125.5, 124.4, 123.7, 123.4 (q, $J = 283.5$ Hz), 122.0, 78.1 (q, $J = 30.0$ Hz), 43.1 ppm.

^{19}F NMR (376.5 MHz, CDCl_3) δ -79.6 ppm.

HRMS (ESI) m/z: [M]⁺ calcd for C₂₁H₁₄F₃NO₂S 401.0697; found 401.0701.



(S)-3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-(naphthalen-2-yl)butan-1-one (3ar) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2r** (3.0 equiv.) for 17 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1, v/v). White solid, m.p. 142–144 °C; 37.6 mg, 94% yield.

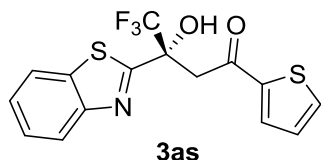
[α]_D²⁵ = -190.6 (*c* = 0.31, CHCl₃, 88% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel AD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 12.9 min (major), 20.5 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 8.58 (s, 1H), 8.00–7.86 (m, 6H), 7.64–7.57 (m, 2H), 7.44–7.37 (m, 2H), 6.62 (s, 1H), 4.76 (d, *J* = 17.2 Hz, 1H), 3.79 (d, *J* = 16.8 Hz, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 200.0, 170.0, 153.0, 136.3, 136.2, 133.3, 132.4, 131.3, 130.0, 129.4, 128.9, 127.9, 127.3, 126.3, 125.8, 123.7, 123.5 (q, *J* = 283.5 Hz), 123.4, 121.9, 77.8 (q, *J* = 29.9 Hz), 40.1 ppm.

¹⁹F NMR (376.5 MHz, CDCl₃) δ -79.6 ppm.

HRMS (ESI) m/z: [M]⁺ calcd for C₂₁H₁₄F₃NO₂S 401.0697; found 401.0696.



(S)-3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-(thiophen-2-yl)butan-1-one (3as) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2s** (3.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1, v/v). Yellow solid, m.p. 150–152 °C; 34.3 mg, 96% yield.

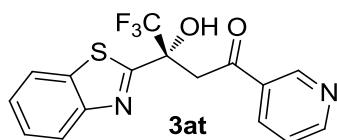
$[\alpha]_D^{25} = -74.4$ ($c = 0.25$, CHCl_3 , 79% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 8% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 11.7 min (minor), 13.3 min (major).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 (dd, $J_1 = 8.0$ Hz, $J_2 = 20.0$ Hz, 3H), 7.73 (d, $J = 3.6$ Hz, 1H), 7.48–7.38(m, 2H), 7.17 (s, 1H), 6.49 (s, 1H), 4.42 (d, $J = 16.8$ Hz, 1H), 3.66 (d, $J = 16.8$ Hz, 1H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 192.1, 169.6, 153.0, 142.8, 136.3, 136.2, 134.5, 128.7, 126.3, 125.8, 123.8, 123.3 (q, $J = 283.5$ Hz), 122.0, 77.6 (q, $J = 30.0$ Hz), 40.6 ppm.

$^{19}\text{F NMR}$ (376.5 MHz, CDCl_3) δ -79.7 ppm.

HRMS (ESI) m/z : $[M]^+$ calcd for $\text{C}_{15}\text{H}_{10}\text{F}_3\text{NO}_2\text{S}_2$ 357.0105; found 357.0108.



(S)-3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-(pyridin-3-yl)butan-

1-one (3at) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2t** (3.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1, v/v). White solid, m.p. 145–146 °C; 30.5 mg, 87% yield.

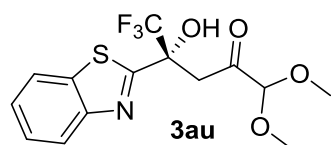
$[\alpha]_{\text{D}}^{25} = -3.1$ ($c = 0.26$, CHCl_3 , 80% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 20% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 7.1 min (minor), 11.4 min (major).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.71 (d, $J = 4.0$ Hz, 1H), 8.49 (br s, 1H), 8.02 (d, $J = 8.0$ Hz, 2H), 7.88 (d, $J = 7.2$ Hz, 2H), 7.56 (t, $J = 6.4$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 1H), 4.28 (d, $J = 15.2$ Hz, 1H), 4.04 (d, $J = 15.6$ Hz, 1H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 197.0, 170.0, 153.4, 152.1, 148.4, 138.3, 135.9, 128.2, 126.2, 125.7, 123.9, 123.9 (q, $J = 284.6$ Hz), 123.2, 121.8, 76.6 (q, $J = 29.9$ Hz), 44.9 ppm.

$^{19}\text{F NMR}$ (376.5 MHz, CDCl_3) δ -78.9 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{16}\text{H}_{11}\text{F}_3\text{N}_2\text{O}_2\text{S}$ 352.0493; found 352.0495.



(S)-4-(Benzo[*d*]thiazol-2-yl)-5,5,5-trifluoro-4-hydroxy-1,1-dimethoxypentan-2-one (3au) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2u** (3.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1, v/v). Colorless oil, 31.9 mg,

91% yield.

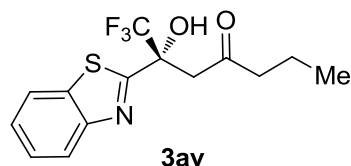
$[\alpha]_{\text{D}}^{25} = -17.8$ ($c = 0.27$, CHCl_3 , 67% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 15% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 5.4 min (minor), 6.0 min (major).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.0$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 5.62 (s, 1H), 4.52 (s, 1H), 4.11 (d, $J = 18.0$ Hz, 1H), 3.41 (s, 3H), 3.39 (s, 3H), 3.39 (d, $J = 18.0$ Hz, 1H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 205.3, 169.0, 152.7, 136.2, 126.4, 126.0, 123.7, 123.2 (q, $J = 283.5$ Hz), 121.9, 77.2 (q, $J = 30.3$ Hz), 103.7, 55.1, 54.8, 40.5 ppm.

$^{19}\text{F NMR}$ (376.5 MHz, CDCl_3) δ -79.9 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{F}_3\text{NO}_4\text{S}$ 349.0596; found 349.0595.



(S)-2-(Benzo[*d*]thiazol-2-yl)-1,1,1-trifluoro-2-hydroxyheptan-4-one (3av) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2v** (3.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1). Colorless oil, 8.9 mg, 28% yield.

$[\alpha]_{\text{D}}^{28} = -17.4$ ($c = 0.61$, CHCl_3 , 61% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 5% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 7.8 min (major), 16.7 min (minor).

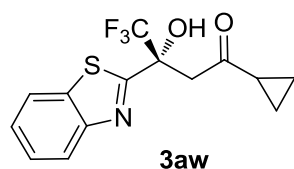
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.4$ Hz, 1H), 7.92 (d, $J = 7.6$ Hz, 1H),

7.50 (t, $J = 7.6$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 1H), 6.24 (s, 1H), 3.91 (d, $J = 16.8$ Hz, 1H), 3.15 (d, $J = 16.8$ Hz, 1H), 2.60-2.50 (m, 2H), 1.63-1.53 (m, 2H), 0.86 (t, $J = 7.6$ Hz, 3H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 212.2, 169.7, 152.9, 136.3, 126.4, 125.9, 123.7, 123.2 (q, $J = 283.4$ Hz), 122.0, 77.5 (q, $J = 30.3$ Hz), 46.5, 43.6, 16.8, 13.6 ppm.

^{19}F NMR (376.5 MHz, CDCl_3) δ -80.0 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{F}_3\text{NO}_2\text{S}$ 317.0697; found 317.0695.



(S)-3-(Benzo[*d*]thiazol-2-yl)-1-cyclopropyl-4,4,4-trifluoro-3-hydroxybutan-1-one (3aw) was prepared from trifluoromethyl ketone hydrate **1a** and methyl ketone **2w** (3.0 equiv.) for 36 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1). Colorless oil, 5.4 mg, 17% yield.

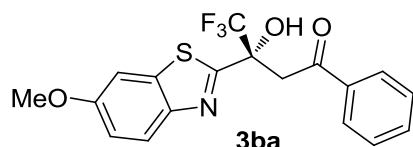
$[\alpha]_{\text{D}}^{28} = -12.3$ ($c = 0.53$, CHCl_3 , 68% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 5% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 8.0 min (major), 24.2 min (minor).

^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.4$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.49 (t, $J = 8.4$ Hz, 1H), 7.41 (t, $J = 8.4$ Hz, 1H), 6.42 (s, 1H), 4.02 (d, $J = 17.2$ Hz, 1H), 3.34 (d, $J = 17.2$ Hz, 1H), 2.07-2.01 (m, 1H), 1.19-1.13 (m, 1H), 1.02-0.96 (m, 3H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 211.4, 169.9, 153.0, 136.2, 126.3, 125.8, 123.6, 123.3 (q, $J = 283.4$ Hz), 121.9, 77.3 (q, $J = 30.3$ Hz), 43.7, 22.6, 12.3, 12.1 ppm.

^{19}F NMR (376.5 MHz, CDCl_3) δ -79.9 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{12}\text{F}_3\text{NO}_4\text{S}$ 315.0541; found 315.0545.



(S)-4,4,4-Trifluoro-3-hydroxy-3-(6-methoxybenzo[*d*]thiazol-2-yl)-1-phenylbutan-1-one (3ba) was prepared from trifluoromethyl ketone hydrate **1b** and methyl ketone **2a** (5.0 equiv.) for 16 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1, v/v). White solid, m.p. 113–115 °C; 30.1 mg, 79% yield.

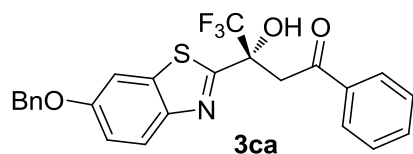
$[\alpha]_{\text{D}}^{25} = -90.0$ ($c = 0.25$, CHCl_3 , 78% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 9.7 min (major), 12.5 min (minor).

^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 7.2$ Hz, 2H), 7.80 (d, $J = 8.8$ Hz, 1H), 7.62 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.2$ Hz, 2H), 7.33 (s, 1H), 7.03 (d, $J = 8.8$ Hz, 1H), 6.44 (s, 1H), 4.56 (d, $J = 17.2$ Hz, 1H), 3.84 (s, 3H), 3.63 (d, $J = 17.2$ Hz, 1H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 200.2, 169.9, 158.1, 147.5, 137.7, 136.1, 134.6, 128.9, 128.6, 124.2, 123.4 (q, $J = 283.5$ Hz), 116.1, 103.9, 77.6 (q, $J = 29.9$ Hz), 55.9, 40.0 ppm.

^{19}F NMR (376.5 MHz, CDCl_3) δ -79.8 ppm.

HRMS (ESI) m/z : $[M]^+$ calcd for $C_{18}H_{14}F_3NO_3S$ 381.0646; found 381.0643.



(S)-3-(6-(Benzyloxy)benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-phenylbutan-1-one (3ca) was prepared from trifluoromethyl ketone hydrate **1c** and methyl ketone **2a** (3.0 equiv.) for 20 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1, v/v). Yellow solid, m.p. 111–112 °C; 36.8 mg, 80% yield.

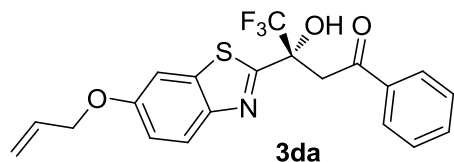
$[\alpha]_D^{25} = -130.0$ ($c = 0.33$, $CHCl_3$, 87% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 19.9 min (major), 23.0 min (minor).

1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, $J = 8.0$ Hz, 2H), 7.83 (d, $J = 8.8$ Hz, 1H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.51 (d, $J = 7.6$ Hz, 2H), 7.48–7.34 (m, 6H), 7.13 (d, $J = 9.2$ Hz, 1H), 6.46 (s, 1H), 5.12 (s, 2H), 4.58 (d, $J = 17.2$ Hz, 1H), 3.64 (d, $J = 17.2$ Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 167.1, 157.2, 147.7, 137.6, 136.5, 136.0, 134.6, 128.9, 128.8, 128.6, 128.2, 127.5, 124.3, 123.4 (q, $J = 283.4$ Hz), 116.6, 105.3, 77.6 (q, $J = 29.9$ Hz), 70.7, 40.1 ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ -79.8 ppm.

HRMS (ESI) m/z : $[M]^+$ calcd for $C_{24}H_{18}F_3NO_3S$ 457.0959; found 457.0961.



(S)-3-(6-(Allyloxy)benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-phenylbutan-1-one (3da) was prepared from trifluoromethyl ketone hydrate **1d** and methyl ketone **2a** (5.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1, v/v). Yellow solid, m.p. 105–107 °C; 37.4 mg, 92% yield.

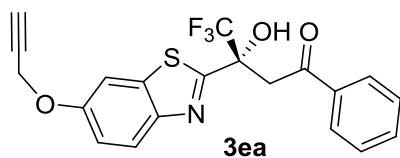
$[\alpha]_D^{25} = -210.9$ ($c = 0.32$, CHCl_3 , 86% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 8.3 min (major), 10.8 min (minor).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.99 (d, $J = 7.6$ Hz, 2H), 7.80 (d, $J = 8.8$ Hz, 1H), 7.62 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.2$ Hz, 2H), 7.35 (s, 1H), 7.07 (d, $J = 9.2$ Hz, 1H), 6.44 (s, 1H), 6.09–6.03 (m, 1H), 5.43 (d, $J = 17.2$ Hz, 1H), 5.32 (d, $J = 10.4$ Hz, 1H), 4.58 (s, 2H), 4.56 (d, $J = 17.2$ Hz, 1H), 3.63 (d, $J = 17.2$ Hz, 1H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 200.2, 167.0, 157.1, 147.6, 137.6, 136.1, 134.6, 132.9, 128.9, 128.6, 124.2, 123.4 (q, $J = 283.4$ Hz), 118.1, 116.5, 105.1, 77.4 (q, $J = 29.9$ Hz), 69.5, 40.0 ppm.

$^{19}\text{F NMR}$ (376.5 MHz, CDCl_3) δ -79.8 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{20}\text{H}_{16}\text{F}_3\text{NO}_3\text{S}$ 407.0803; found 407.0801.



(S)-4,4,4-Trifluoro-3-hydroxy-1-phenyl-3-(6-(prop-2-yn-1-yloxy)benzo[d]thiazol-2-yl)butan-1-one (**3ea**) was prepared from trifluoromethyl ketone hydrate **1e** and methyl ketone **2a** (3.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1, v/v). Yellow solid, m.p. 88–89 °C; 35.8 mg, 88% yield.

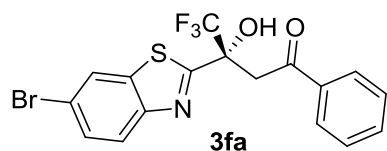
$[\alpha]_{\text{D}}^{25} = -145.1$ ($c = 0.33$, CHCl_3 , 86% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 16.5 min (major), 19.5 min (minor).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.99 (d, $J = 7.2$ Hz, 2H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.63 (t, $J = 6.8$ Hz, 1H), 7.48 (t, $J = 9.2$ Hz, 3H), 7.10 (d, $J = 8.8$ Hz, 1H), 6.43 (s, 1H), 4.75 (s, 2H), 4.56 (d, $J = 17.2$ Hz, 1H), 3.63 (d, $J = 17.2$ Hz, 1H), 2.55 (s, 1H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 200.2, 167.6, 155.9, 148.1, 137.5, 136.0, 134.7, 128.9, 128.6, 124.3, 123.4 (q, $J = 283.4$ Hz), 116.6, 105.6, 78.2, 77.6 (q, $J = 29.9$ Hz), 76.2, 56.4, 40.1 ppm.

$^{19}\text{F NMR}$ (376.5 MHz, CDCl_3) δ -79.8 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{20}\text{H}_{14}\text{F}_3\text{NO}_3\text{S}$ 405.0646; found 405.0642.



(S)-3-(6-Bromobenzo[d]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-phenylbutan-1-one (**3fa**) was prepared from trifluoromethyl ketone hydrate **1f** and methyl ketone **2a** (5.0 equiv.) for 24 h according to the above general

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procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1, v/v). White solid, m.p. 91–93 °C; 33.7 mg, 79% yield.

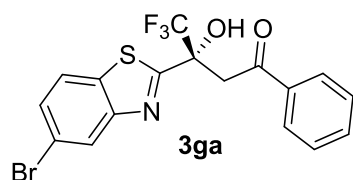
$[\alpha]_{\text{D}}^{25} = -90.6$ ($c = 0.31$, CHCl_3 , 82% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 8% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 8.3 min (major), 14.9 min (minor).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.03 (s, 1H), 7.99 (d, $J = 7.2$ Hz, 2H), 7.77 (d, $J = 4.8$ Hz, 1H), 7.63 (t, $J = 7.2$ Hz, 1H), 7.50 (q, $J = 8.0$ Hz, 3H), 6.45 (s, 1H), 4.55 (d, $J = 17.2$ Hz, 1H), 3.66 (d, $J = 17.2$ Hz, 1H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 200.0, 170.6, 151.9, 137.9, 135.9, 134.8, 129.8, 129.0, 128.7, 124.9, 124.5, 123.2 (q, $J = 283.5$ Hz), 119.6, 77.6 (q, $J = 30.0$ Hz), 40.1 ppm.

$^{19}\text{F NMR}$ (376.5 MHz, CDCl_3) δ -79.7 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_{11}\text{BrF}_3\text{NO}_2\text{S}$ 428.9646; found 428.9644.



(S)-3-(5-Bromobenzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-phenylbutan-1-one (3ga) was prepared from trifluoromethyl ketone hydrate **1g** and methyl ketone **2a** (5.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 20:1 to 10:1, v/v). White solid, m.p. 54–56 °C; 34.0 mg, 79% yield.

$[\alpha]_{\text{D}}^{25} = -30.0$ ($c = 0.30$, CHCl_3 , 86% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 8% *i*-PrOH in hexanes; 1.0

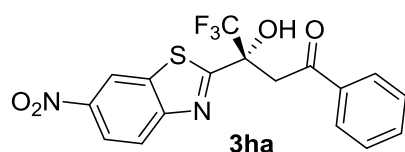
mL/min; 35 °C; retention times: 11.2 min (major), 14.1 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 8.07 (s, 1H), 7.98 (d, *J* = 5.6 Hz, 2H), 7.74 (t, *J* = 7.2 Hz, 1H), 7.62 (q, *J* = 6.0 Hz, 1H), 7.51-7.46 (m, 3H), 6.47 (s, 1H), 4.58 (d, *J* = 17.2 Hz, 1H), 3.64 (d, *J* = 17.2 Hz, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 200.1, 171.9, 154.1, 135.9, 135.0, 134.8, 129.0, 128.9, 128.6, 126.6, 123.2 (q, *J* = 283.5 Hz), 123.0, 119.9, 77.7 (q, *J* = 30.1 Hz), 40.1 ppm.

¹⁹F NMR (376.5 MHz, CDCl₃) δ -79.6 ppm.

HRMS (ESI) *m/z*: [M]⁺ calcd for C₁₇H₁₁BrF₃NO₂S 428.9646; found 428.9642.



(S)-4,4,4-Trifluoro-3-hydroxy-3-(6-nitrobenzo[*d*]thiazol-2-yl)-1-phenylbutan-1-one (3ha) was prepared from trifluoromethyl ketone hydrate **1h** and methyl ketone **2a** (5.0 equiv.) for 16 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1, v/v). Yellow solid, m.p. 168–170 °C; 24.6 mg, 62% yield.

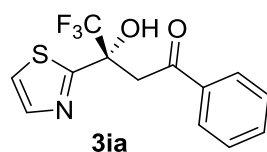
[α]_D²⁵ = -73.2 (*c* = 0.25, CHCl₃, 70% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 20% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 9.2 min (major), 18.7 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 8.85 (s, 1H), 8.31 (d, *J* = 9.2 Hz, 1H), 8.00 (t, *J*₁ = 10.0 Hz, 3H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 6.47 (s, 1H), 4.58 (d, *J* = 17.6 Hz, 1H), 3.71 (d, *J* = 17.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 199.9, 176.4, 156.5, 145.5, 136.6, 135.7, 135.0, 129.1, 128.7, 124.2, 123.0 (q, $J = 283.7$ Hz), 121.7, 118.6, 77.9 (q, $J = 30.2$ Hz), 40.2 ppm.

^{19}F NMR (376.5 MHz, CDCl_3) δ -79.5 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_{11}\text{F}_3\text{N}_2\text{O}_4\text{S}$ 396.0392; found 396.0388.



(S)-4,4,4-Trifluoro-3-hydroxy-1-phenyl-3-(thiazol-2-yl)butan-1-one (3ia) was prepared from trifluoromethyl ketone hydrate **1i** and methyl ketone **2a** (3.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1, v/v). Yellow solid, m.p. 86–88 °C; 29.4 mg, 98% yield.

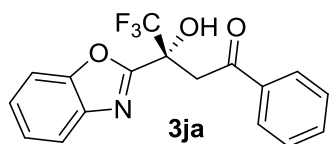
$[\alpha]_{\text{D}}^{25} = -109.6$ ($c = 0.25$, CHCl_3 , 91% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 8% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 11.0 min (minor), 16.2 min (major).

^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.0$ Hz, 2H), 7.71 (d, $J = 2.8$ Hz, 1H), 7.63 (t, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.42 (d, $J = 2.8$ Hz, 1H), 6.39 (s, 1H), 4.48 (d, $J = 17.2$ Hz, 1H), 3.56 (d, $J = 17.2$ Hz, 1H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 200.4, 168.9, 142.9, 136.1, 134.7, 129.0, 128.6, 123.3 (q, $J = 283.1$ Hz), 122.0, 77.4 (q, $J = 30.1$ Hz), 39.9 ppm.

^{19}F NMR (376.5 MHz, CDCl_3) δ -80.4 ppm.

HRMS (ESI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{13}\text{H}_{10}\text{F}_3\text{NO}_2\text{S}$ 301.0384; found 301.0387.



(R)-3-(Benzo[d]oxazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-phenylbutan-1-one

(3ja) was prepared from trifluoromethyl ketone hydrate **1j** and methyl ketone **2a** (3.0 equiv.) for 24 h according to the above general procedure (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1, v/v). Yellow solid, m.p. 101–103 °C; 27.4 mg, 82% yield.

$[\alpha]_{D}^{25} = -38.4$ ($c = 0.25$, CHCl_3 , 48% ee). Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 6.9 min (major), 9.3 min (minor).

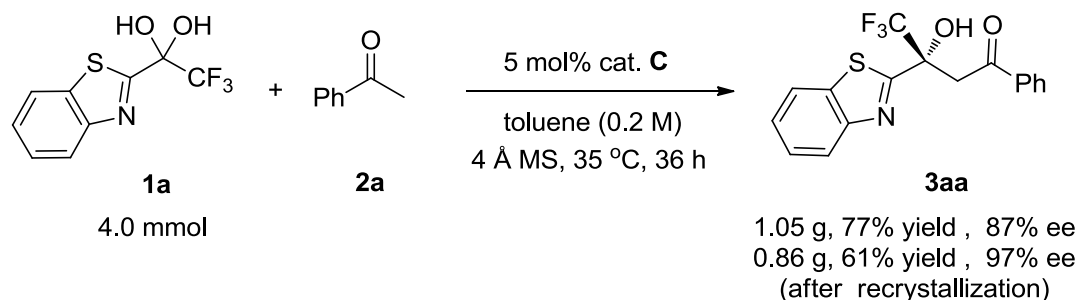
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (d, $J = 7.6$ Hz, 2H), 7.72 (d, $J = 7.2$ Hz, 1H), 7.63 (t, $J = 7.2$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 7.40–7.33 (m, 2H), 5.59 (s, 1H), 4.32 (d, $J = 17.2$ Hz, 1H), 3.79 (d, $J = 17.6$ Hz, 1H) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 197.7, 161.5, 151.5, 140.5, 136.0, 134.6, 129.0, 128.5, 126.1, 125.0, 123.4 (q, $J = 284.0$ Hz), 120.8, 111.4, 74.6 (q, $J = 30.6$ Hz), 40.3 ppm.

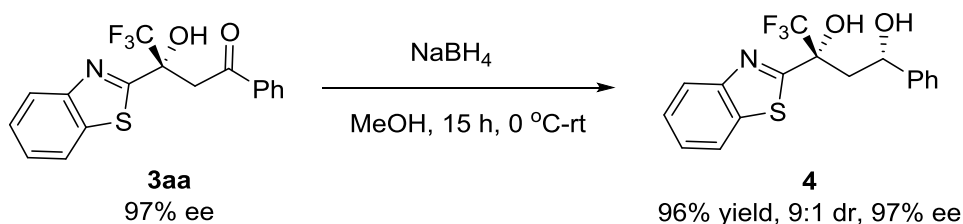
$^{19}\text{F NMR}$ (376.5 MHz, CDCl_3) δ -79.6 ppm.

HRMS (ESI) m/z : $[M]^+$ calcd for $\text{C}_{17}\text{H}_{12}\text{F}_3\text{NO}_3$ 335.0769; found 335.0767.

IV. Gram-Scale Catalytic Reaction and Product Transformations



To a 50 mL round-bottom flask equipped with a magnetic stir bar, trifluoromethyl ketone hydrate **1a** (1.00 g, 4.0 mmol), catalyst **C** (5 mol%), 4 Å MS (1.20 g), and toluene (20 mL) were sequentially added. The mixture was stirred for 30 min at 35 °C in an oil bath, and then acetophenone **2a** (1.44 g, 12.0 mmol) was added. After stirring for 36 h, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired trifluoromethyl tertiary alcohol **3aa** as a white solid (1.18 g, 84% yield, 87% ee). The product with excellent enantioselectivity (0.86 g, 61% yield, 97% ee) was obtained by a simple recrystallization from petroleum ether/CH₂Cl₂ = 5:1.



(1*S*,3*S*)-3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-1-phenylbutane-1,3-diol (**4**).

To a solution of **3aa** (70.2 mg, 0.20 mmol, 97% ee) in anhydrous MeOH (5 mL) at 0 °C in an ice bath was added NaBH₄ (15.1 mg, 0.40 mmol) in portions. Then mixture was spontaneously warmed to room temperature and stirred for 15 h. Upon completion, the reaction was quenched with water (5 mL) at 0

°C in an ice bath, and the mixture was extracted with CH₂Cl₂ (3 x 10 mL). The organic layers were combined, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1, v/v) to afford the desired diol **4** (68.0 mg, 96% yield, 97% ee, 9:1 dr). White solid, m.p. 108–110 °C.

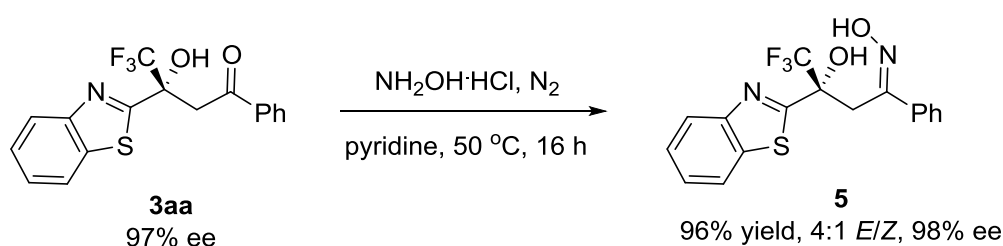
[α]_D²⁵ = -36.3 (*c* = 0.32, CHCl₃, 97% ee); Enantiomeric excess was determined by chiral HPLC: Daicel Chiralcel OD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 13.1 min (major), 22.1 min (minor).

¹H NMR (400 MHz, *d*₆-acetone) δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J*₁ = 8.0 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 3H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 2H), 5.57 (t, *J* = 1.6 Hz, 1H), 5.42 (d, *J* = 10.8 Hz, 1H), 2.79 (d, *J* = 14.8 Hz, 1H), 2.65–2.58 (m, 1H) ppm.

¹³C NMR (100 MHz, *d*₆-acetone) δ 172.2, 154.2, 144.9, 136.2, 129.1, 128.3, 126.8, 126.3, 126.1, 124.0, 125.8 (q, *J* = 285.5 Hz), 122.7, 78.8 (q, *J* = 28.7 Hz), 71.6, 43.9 ppm.

¹⁹F NMR (376.5 MHz, *d*₆-acetone) δ -77.1 ppm.

HRMS (ESI) *m/z*: [M]⁺ calcd for C₁₇H₁₄F₃NO₂S 354.0776; found 354.0772.



(*S,E*)-3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-1-phenylbutan-1-one oxime (5). To a solution of **3aa** (0.53 g, 1.50 mmol, 97% ee) in pyridine (5.0 mL) at room temperature was added hydroxylamine hydrochloride (260 mg, 3.75 mmol). Under N₂, the reaction mixture was heated to 50 °C in an oil bath and stirred for 16 h. Upon completion, the mixture was concentrated in vacuo for

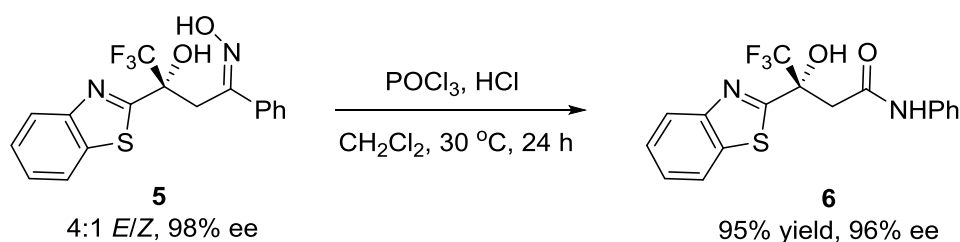
the removal of pyridine. The resulting residue was dissolved in CH₂Cl₂ (50 mL), and washed with water (2 x 30 mL) and brine (30 mL), sequentially. The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1, v/v) to afford the desired oxime **5** (0.53 g, 97% yield). White solid, m.p. 142–144 °C.

¹H NMR (400 MHz, CDCl₃) δ 11.08 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.48-7.31 (m, 4H), 7.07 (s, 3H), 6.26 (s, 1H), 4.19 (d, *J* = 13.6 Hz, 1H), 3.90 (d, *J* = 13.2 Hz, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 170.0, 156.1, 152.9, 135.1, 134.3, 129.8, 128.2, 126.8, 126.3, 125.7, 123.2, 124.7 (q, *J* = 233.8 Hz), 121.6, 78.2 (q, *J* = 29.8 Hz), 33.2 ppm.

¹⁹F NMR (376.5 MHz, CDCl₃) δ -79.3 ppm.

HRMS (ESI) *m/z*: [M]⁺ calcd for C₁₇H₁₃F₃N₂O₂S 366.0650; found 366.0651.



(S)-3-(Benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-3-hydroxy-*N*-phenylbutanamide

(6). Under N₂, to a solution of oxime **5** (73.2 mg, 0.20 mmol, 98% ee) in CH₂Cl₂ (5.0 mL) at room temperature was added POCl₃ (0.5 mL) and *conc.* HCl (0.5 mL). The reaction mixture was stirred for 24 h. Upon completion, the reaction was quenched with water (5 mL) at 0 °C in an ice bath. The organic layer was

separated, and the aqueous layer was extracted with CH₂Cl₂ (2 x 15 mL). The organic layers were combined, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 15:1 to 10:1, v/v) to afford the desired amide **6** (69.7 mg, 95% yield, 96% ee). White solid, m.p. 153–155 °C.

$[\alpha]_{D^{25}} = +18.7$ ($c = 0.30$, CHCl₃, 96% ee); Enantiomeric excess was determined by chiral HPLC: Daicel CHIRALCEL OD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min; 35 °C; retention times: 9.3 min (major), 14.8 min (minor).

¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.49-7.40 (m, 2H), 7.37 (s, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.22 (t, $J = 8.0$ Hz, 2H), 7.09 (t, $J = 7.2$ Hz, 1H), 3.64 (d, $J = 14.8$ Hz, 1H), 3.31 (d, $J = 15.2$ Hz, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 170.2, 168.7, 152.9, 136.4, 136.1, 129.1, 126.5, 126.0, 125.5, 123.4, 123.2 (q, $J = 283.8$ Hz), 121.1, 120.7, 77.1 (q, $J = 30.1$ Hz), 38.9 ppm.

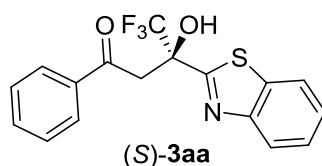
¹⁹F NMR (376.5 MHz, CDCl₃) δ -79.7 ppm.

HRMS (ESI) m/z : $[M]^+$ calcd for C₁₇H₁₃F₃N₂O₂S 366.0650; found 366.0656.

V. X-ray Crystallographic Analysis of Product 3aa

In a 4 mL vial, 30 mg of **3aa** (97% ee, from the gram-scale preparation) was completely dissolved in DCM (1.0 mL), then 5.0 mL of petroleum ether was added slowly. The vial was placed on a stable experimental table. After several days, the crystal was obtained by slow evaporation of the solvents at room temperature. A suitable single crystal was selected for X-ray diffraction on a Bruker D8 Advance X-Ray diffractometer, Eos fitted with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection and unit cell refinement were executed by using CrysAlisPro software. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. The absolute configuration was established by anomalous dispersion effects in diffraction measurements on the crystal. The thermal ellipsoids are shown at 50% probability level.

The absolute stereochemistry of product **3aa** was determined by X-ray diffraction. The X-ray data of **3aa** have been deposited at the Cambridge Crystallographic Data Center (CCDC 2235492). The stereochemistry of other products was assumed by analogy.



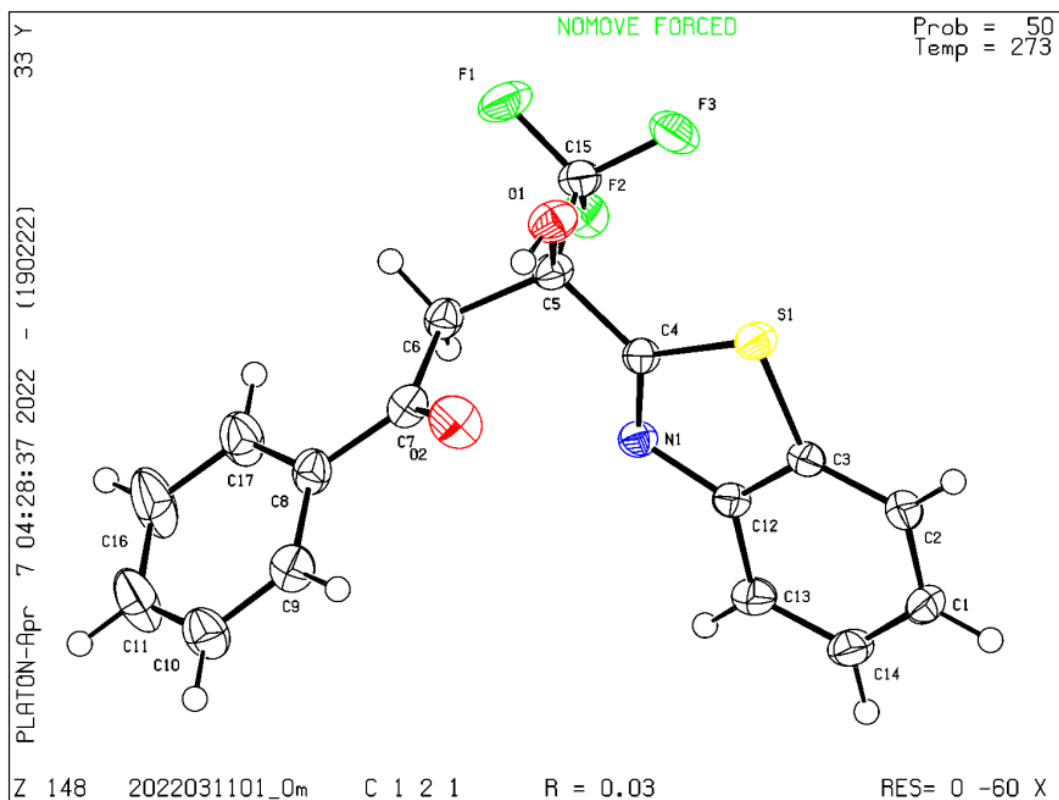


Figure S1. ORTEP representation of (*S*)-**3aa** (The thermal ellipsoids are shown at 50% probability level.)

Table 1. Crystal data and structure refinement for **3aa**.

Identification code	3aa
Empirical formula	$C_{17}H_{12}F_3NO_2S$
Formula weight	351.34
Temperature	273.15 K
Wavelength/ \AA	0.71073
Crystal system	Monoclinic
Space group	C 121
$a/\text{\AA}$	25.755(3)

b/Å	6.9641(8)
c/Å	8.7584(10)
α /°	90
β /°	94.153
γ /°	90°
Volume/Å ³	1566.8(3)
Z	4
Density (calculated)	1.489 g/cm ³
Absorption coefficient	0.249 mm ⁻¹
F(000)	720
Crystal size	0.35 x 0.26 x 0.23 mm ³
Theta range for data collection/°	2.331 to 28.338
Index ranges	-33<=h<=34, -9<=k<=9, -11<=l<=11
Reflections collected	10899
Independent reflections	3882 [R(int) = 0.0345]
Completeness to theta = 25.242	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3882/1/221
Goodness-of-fit on F ²	1.077
Final R indices [I>2sigma(I)]	R ₁ = 0.0275, wR ₂ = 0.0699
R indices (all data)	R ₁ = 0.0279, wR ₂ = 0.0702

Absolute structure parameter	0.04(2)
Extinction coefficient	n/a
Largest diff. peak and hole/ e Å ⁻³	0.233 and -0.223

Table 2. Atomic coordinates (x10⁴) and equivalent isotropic displacement parameters (Å²x10³) for 2022031101_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
S(1)	3319(1)	8471(1)	8182(1)	28(1)
F(1)	3340(1)	2821(2)	11073(1)	43(1)
F(2)	2979(1)	2781(2)	8780(1)	32(1)
F(3)	2858(1)	5179(2)	10258(1)	39(1)
O(1)	3886(1)	6058(2)	10499(1)	31(1)
O(2)	4674(1)	5882(2)	8485(2)	39(1)
N(1)	3516(1)	5538(2)	6482(2)	23(1)
C(1)	2959(1)	10134(3)	3801(2)	32(1)
C(2)	3012(1)	10298(3)	5378(2)	30(1)
C(3)	3204(1)	8721(3)	6212(2)	23(1)
C(4)	3524(1)	6121(2)	7881(2)	22(1)
C(5)	3694(1)	4894(3)	9262(2)	24(1)
C(6)	4077(1)	3343(3)	8840(2)	26(1)

C(7)	4579(1)	4181(3)	8333(2)	27(1)
C(8)	4950(1)	2854(3)	7645(2)	28(1)
C(9)	5348(1)	3627(3)	6834(2)	32(1)
C(10)	5691(1)	2441(3)	6132(3)	38(1)
C(11)	5645(1)	480(4)	6280(4)	52(1)
C(12)	3336(1)	6999(2)	5494(2)	22(1)
C(13)	3285(1)	6871(3)	3898(2)	28(1)
C(14)	3098(1)	8443(4)	3070(2)	32(1)
C(15)	3211(1)	3909(3)	9851(2)	28(1)
C(16)	5262(1)	-309(3)	7123(4)	60(1)
C(17)	4909(1)	875(3)	7789(3)	42(1)

Table 3. Bond lengths and angles for 3aa.

Atom-Atom	Length/ Å
S(1)-C(3)	1.7387(17)
S(1)-C(4)	1.7452(17)
F(1)-C(15)	1.334(2)
F(2)-C(15)	1.332(2)
F(3)-C(15)	1.336(2)
O(1)-C(5)	1.414(2)
O(1)-H(1)	0.80(3)

O(2)-C(7)	1.215(2)
N(1)-C(4)	1.290(2)
N(1)-C(12)	1.393(2)
C(1)-H(1A)	0.9300
C(1)-C(2)	1.382(3)
C(1)-C(14)	1.400(3)
C(2)-H(2)	0.9300
C(2)-C(3)	1.390(2)
C(3)-C(12)	1.407(2)
C(4)-C(5)	1.519(2)
C(5)-C(6)	1.527(2)
C(5)-C(15)	1.540(2)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(6)-C(7)	1.515(2)
C(7)-C(8)	1.488(3)
C(8)-C(9)	1.396(3)
C(8)-C(17)	1.389(3)
C(9)-H(9)	0.9300
C(9)-C(10)	1.385(3)
C(10)-H(10)	0.9300
C(10)-C(11)	1.377(4)

C(11)-H(11)	0.9300
C(11)-C(16)	1.389(4)
C(12)-C(13)	1.398(2)
C(13)-H(13)	0.9300
C(13)-C(14)	1.380(3)
C(14)-H(14)	0.9300
C(16)-H(16)	0.9300
C(16)-C(17)	1.387(3)
C(17)-H(17)	0.9300

Atom-Atom-Atom	Length/Å
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C(3)-S(1)-C(4)	88.59(8)
C(5)-O(1)-H(1)	107(2)
C(4)-N(1)-C(12)	109.98(14)
C(2)-C(1)-H(1A)	119.4
C(2)-C(1)-C(14)	121.11(17)
C(14)-C(1)-H(1A)	119.4
C(1)-C(2)-H(2)	121.1
C(1)-C(2)-C(3)	117.72(17)
C(3)-C(2)-H(2)	121.1
C(2)-C(3)-S(1)	128.98(14)
C(2)-C(3)-C(12)	121.80(15)
C(12)-C(3)-S(1)	109.22(12)

N(1)-C(4)-S(1)	117.05(13)
N(1)-C(4)-C(5)	124.25(15)
C(5)-C(4)-S(1)	118.69(12)
O(1)-C(5)-C(4)	110.63(14)
O(1)-C(5)-C(6)	113.20(14)
O(1)-C(5)-C(15)	104.20(14)
C(4)-C(5)-C(6)	111.09(14)
C(4)-C(5)-C(15)	108.90(14)
C(6)-C(5)-C(15)	108.50(14)
C(5)-C(6)-H(6A)	109.1
C(5)-C(6)-H(6B)	109.1
H(6A)-C(6)-H(6B)	107.9
C(7)-C(6)-C(5)	112.29(15)
C(7)-C(6)-H(6A)	109.1
C(7)-C(6)-H(6B)	109.1
O(2)-C(7)-C(6)	120.79(17)
O(2)-C(7)-C(8)	121.41(17)
C(8)-C(7)-C(6)	117.80(16)
C(9)-C(8)-C(7)	118.85(18)
C(17)-C(8)-C(7)	121.62(18)
C(17)-C(8)-C(9)	119.52(19)
C(8)-C(9)-H(9)	119.7

C(10)-C(9)-C(8)	120.7(2)
C(10)-C(9)-H(9)	119.7
C(9)-C(10)-H(10)	120.4
C(11)-C(10)-C(9)	119.2(2)
C(11)-C(10)-H(10)	120.4
C(10)-C(11)-H(11)	119.6
C(10)-C(11)-C(16)	120.7(2)
C(16)-C(11)-H(11)	119.6
N(1)-C(12)-C(3)	115.16(14)
N(1)-C(12)-C(13)	125.29(16)
C(13)-C(12)-C(3)	119.55(16)
C(12)-C(13)-H(13)	120.7
C(14)-C(13)-C(12)	118.60(17)
C(14)-C(13)-H(13)	120.7
C(1)-C(14)-H(14)	119.4
C(13)-C(14)-C(1)	121.20(16)
C(13)-C(14)-H(14)	119.4
F(1)-C(15)-F(3)	107.21(15)
F(1)-C(15)-C(5)	111.26(15)
F(2)-C(15)-F(1)	107.64(15)
F(2)-C(15)-F(3)	107.39(15)
F(2)-C(15)-C(5)	111.02(14)

F(3)-C(15)-C(5)	112.09(14)
C(11)-C(16)-H(16)	120.0
C(17)-C(16)-C(11)	120.1(2)
C(17)-C(16)-H(16)	120.0
C(8)-C(17)-H(17)	120.2
C(16)-C(17)-C(8)	119.7(2)
C(16)-C(17)-H(17)	120.2

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 2022031101_0m.

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2$

$a^*2U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Atom	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
S(1)	44(1)	20(1)	21(1)	-2(1)	7(1)	6(1)
F(1)	48(1)	49(1)	33(1)	19(1)	7(1)	-2(1)
F(2)	32(1)	28(1)	38(1)	-1(1)	5(1)	-4(1)
F(3)	42(1)	35(1)	43(1)	-1(1)	21(1)	4(1)
O(1)	41(1)	31(1)	21(1)	-3(1)	-1(1)	-3(1)
O(2)	39(1)	28(1)	51(1)	-6(1)	9(1)	-8(1)
N(1)	27(1)	20(1)	21(1)	-1(1)	4(1)	0(1)
C(1)	28(1)	37(1)	31(1)	14(1)	5(1)	5(1)

C(2)	32(1)	28(1)	32(1)	5(1)	10(1)	9(1)
C(3)	24(1)	24(1)	22(1)	0(1)	6(1)	2(1)
C(4)	26(1)	18(1)	22(1)	0(1)	4(1)	1(1)
C(5)	30(1)	22(1)	20(1)	0(1)	2(1)	-1(1)
C(6)	27(1)	21(1)	28(1)	3(1)	2(1)	0(1)
C(7)	27(1)	26(1)	28(1)	3(1)	-2(1)	-2(1)
C(8)	22(1)	29(1)	33(1)	3(1)	-2(1)	0(1)
C(9)	27(1)	31(1)	37(1)	1(1)	-1(1)	-5(1)
C(10)	24(1)	44(1)	49(1)	-1(1)	5(1)	-2(1)
C(11)	33(1)	41(1)	84(2)	-4(1)	18(1)	7(1)
C(12)	22(1)	22(1)	21(1)	0(1)	4(1)	-1(1)
C(13)	31(1)	32(1)	22(1)	-1(1)	4(1)	-1(1)
C(14)	30(1)	44(1)	22(1)	6(1)	2(1)	0(1)
C(15)	34(1)	27(1)	25(1)	3(1)	7(1)	2(1)
C(16)	42(1)	29(1)	110(2)	4(1)	25(1)	8(1)
C(17)	34(1)	30(1)	65(1)	8(1)	14(1)	3(1)

Table 5. Hydrogen coordinates ($\text{\AA}\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2\times 10^3$) for 2022031101_0m.

Atom	x	y	z	U(eq)
H(1A)	2828	11164	3217	38

H(2)	2922	11425	5864	36
H(6A)	4155	2518	9719	31
H(6B)	3916	2559	8021	31
H(9)	5383	4953	6765	38
H(10)	5948	2962	5567	46
H(11)	5874	-324	5811	62
H(13)	3375	5750	3404	34
H(14)	3064	8377	2007	38
H(16)	5242	-1634	7240	71
H(17)	4646	346	8330	51
H(1)	4175(11)	6350(40)	10330(30)	44(8)

Table 6. Torsion angles for 3aa.

A	B	C	D	Angle/°
S(1)	C(3)	C(12)	N(1)	0.50(18)
S(1)	C(3)	C(12)	C(13)	-178.79(13)
S(1)	C(4)	C(5)	O(1)	-27.31(19)
S(1)	C(4)	C(5)	C(6)	-153.91(12)
S(1)	C(4)	C(5)	C(15)	86.64(16)
O(1)	C(5)	C(6)	C(7)	-61.54(18)
O(1)	C(5)	C(15)	F(1)	-61.48(18)

O(1)-C(5)-C(15)-F(2)	178.66(14)
O(1)-C(5)-C(15)-F(3)	58.56(18)
O(2)-C(7)-C(8)-C(9)	-15.5(3)
O(2)-C(7)-C(8)-C(17)	164.6(2)
N(1)-C(4)-C(5)-O(1)	153.23(16)
N(1)-C(4)-C(5)-C(6)	26.6(2)
N(1)-C(4)-C(5)-C(15)	-92.82(19)
N(1)-C(12)-C(13)-C(14)	179.78(16)
C(1)-C(2)-C(3)-S(1)	179.67(15)
C(1)-C(2)-C(3)-C(12)	-0.8(3)
C(2)-C(1)-C(14)-C(13)	1.1(3)
C(2)-C(3)-C(12)-N(1)	-179.13(16)
C(2)-C(3)-C(12)-C(13)	1.6(2)
C(3)-S(1)-C(4)-N(1)	0.35(14)
C(3)-S(1)-C(4)-C(5)	-179.15(14)
C(3)-C(12)-C(13)-C(14)	-1.0(2)
C(4)-S(1)-C(3)-C(2)	179.15(17)
C(4)-S(1)-C(3)-C(12)	-0.44(12)
C(4)-N(1)-C(12)-C(3)	-0.3(2)
C(4)-N(1)-C(12)-C(13)	178.99(16)
C(4)-C(5)-C(6)-C(7)	63.63(18)
C(4)-C(5)-C(15)-F(1)	-179.57(15)

C(4)-C(5)-C(15)-F(2)	60.58(18)
C(4)-C(5)-C(15)-F(3)	-59.52(18)
C(5)-C(6)-C(7)-O(2)	9.9(2)
C(5)-C(6)-C(7)-C(8)	-170.03(15)
C(6)-C(5)-C(15)-F(1)	59.39(18)
C(6)-C(5)-C(15)-F(2)	-60.46(17)
C(6)-C(5)-C(15)-F(3)	179.44(14)
C(6)-C(7)-C(8)-C(9)	164.44(16)
C(6)-C(7)-C(8)-C(17)	-15.4(3)
C(7)-C(8)-C(9)-C(10)	-177.79(18)
C(7)-C(8)-C(17)-C(16)	179.7(2)
C(8)-C(9)-C(10)-C(11)	-2.0(3)
C(9)-C(8)-C(17)-C(16)	-0.2(4)
C(9)-C(10)-C(11)-C(16)	0.0(4)
C(10)-C(11)-C(16)-C(17)	1.9(5)
C(11)-C(16)-C(17)-C(8)	-1.8(5)
C(12)-N(1)-C(4)-S(1)	-0.12(18)
C(12)-N(1)-C(4)-C(5)	179.35(15)
C(12)-C(13)-C(14)-C(1)	-0.3(3)
C(14)-C(1)-C(2)-C(3)	-0.5(3)
C(15)-C(5)-C(6)-C(7)	-176.69(14)
C(17)-C(8)-C(9)-C(10)	2.1(3)

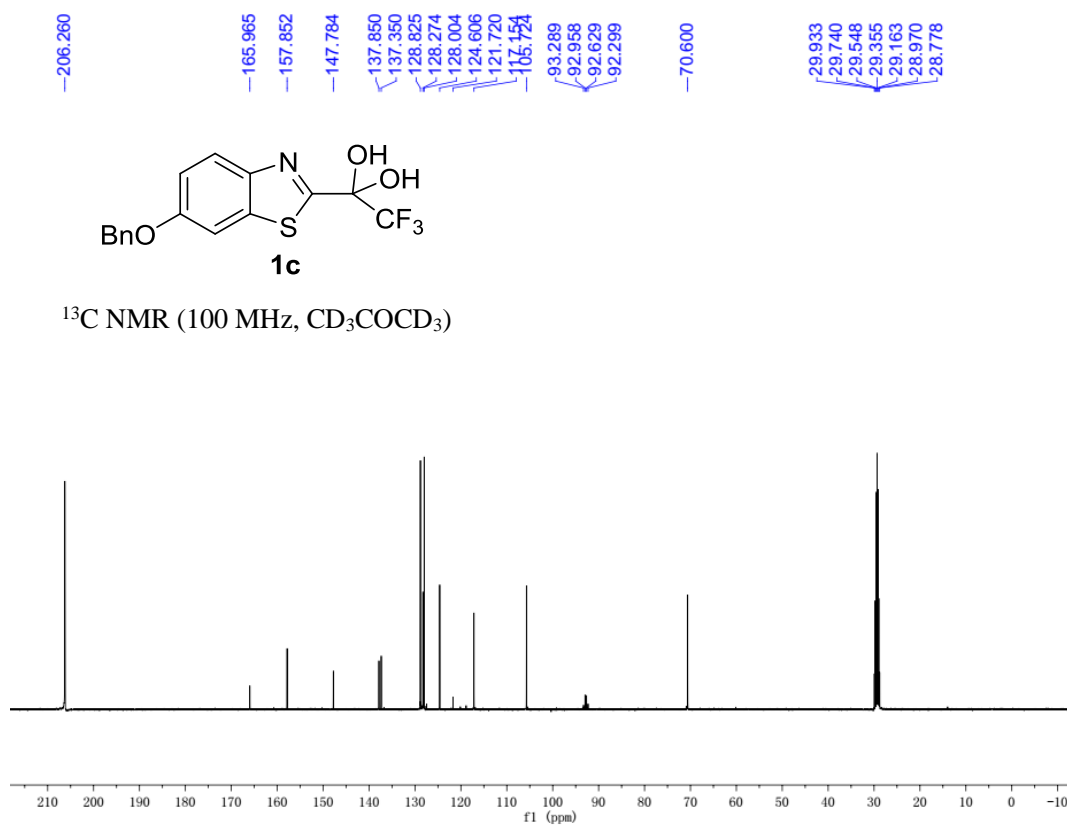
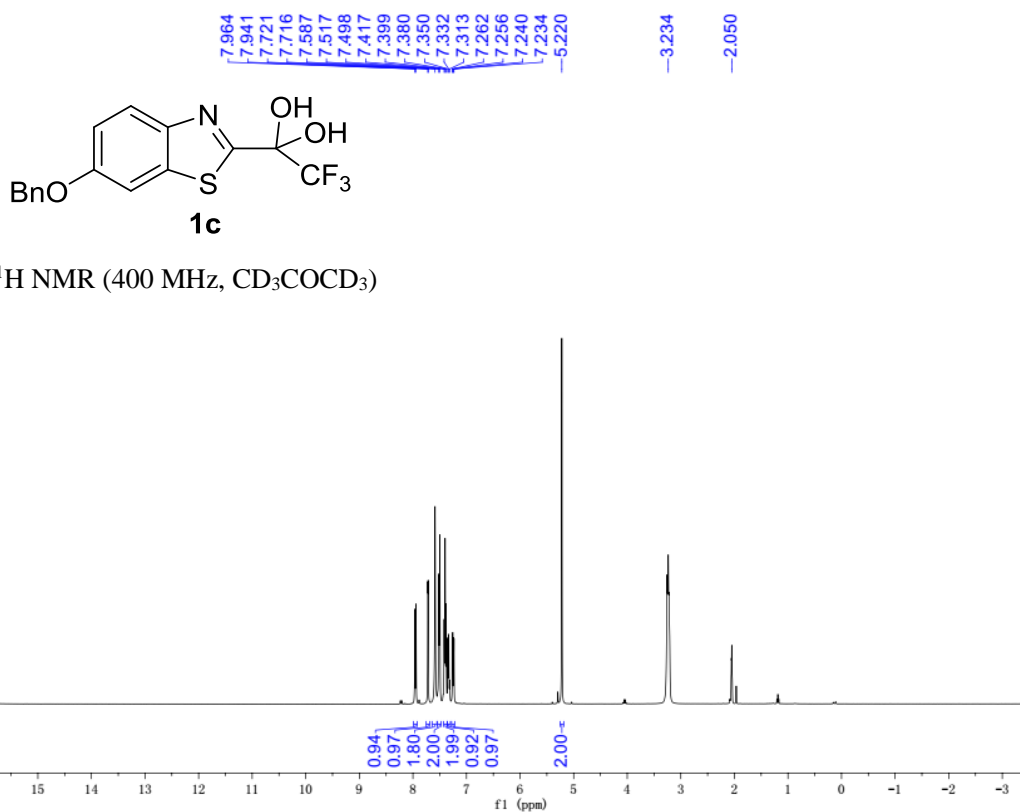
Crystal structure determination of 3aa

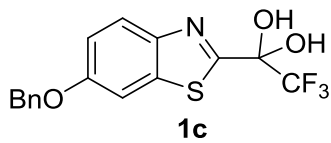
Crystal Data for $C_{17}H_{12}F_3NO_2S$ ($M = 351.34$ g/mol): orthorhombic, space group $C 121$, $a = 25.755(3)$ Å, $b = 6.9641(8)$ Å, $c = 8.7584(10)$ Å, $V = 1566.8(3)$ Å³, $Z = 4$, $T = 273.15$ K, $\mu(\text{MoK}\alpha) = 0.249$ mm⁻¹, $D_{\text{calc}} = 1.489$ g/cm³, 10899 reflections measured ($2.331^\circ \leq 2\Theta \leq 28.338^\circ$), 3882 unique ($R_{\text{int}} = 0.0345$) which were used in all calculations. The final R_1 was 0.0275 ($I > 2\sigma(I)$) and wR_2 was 0.0699 (all data).

VI. References

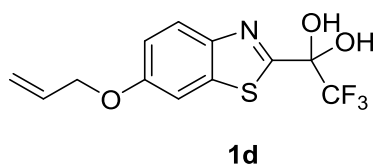
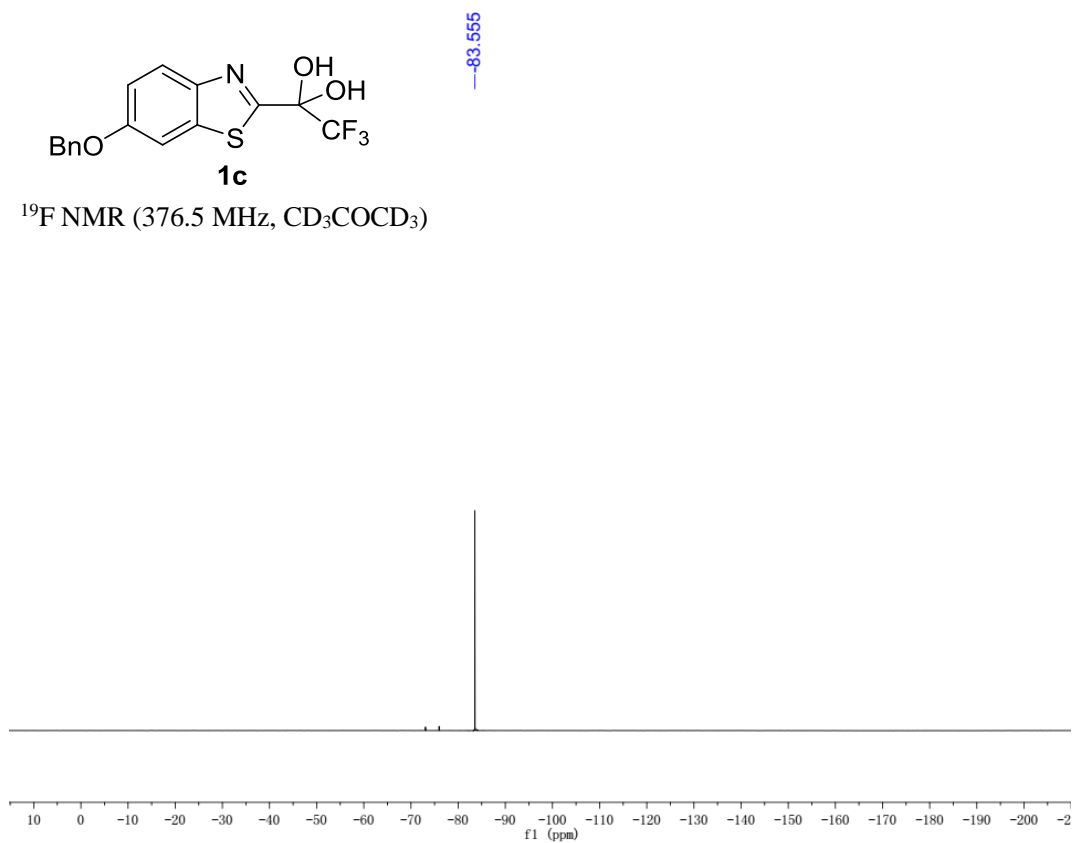
- 1 Y. Fukata, T. Okamura, K. Asano and S. Matsubara, *Org. Lett.*, 2014, **16**, 2184–2187.
- 2 N. R. Amarasinghe, P. Turner and M. H. Todd, *Adv. Synth. Catal.*, 2012, **354**, 2954–2958.
- 3 L.-N. Jia, J. Huang, L. Peng, L.-L. Wang, J.-F. Bai, F. Tian, G.-Y. He, X.-Y. Xu and L.-X. Wang, *Org. Biomol. Chem.*, 2012, **10**, 236–239.
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- 5 W. Wang, W. Xiong, J. Wang, Q.-A. Wang and W. Yang, *J. Org. Chem.*, 2020, **85**, 4398–4407.

VII. Copies of NMR Spectra

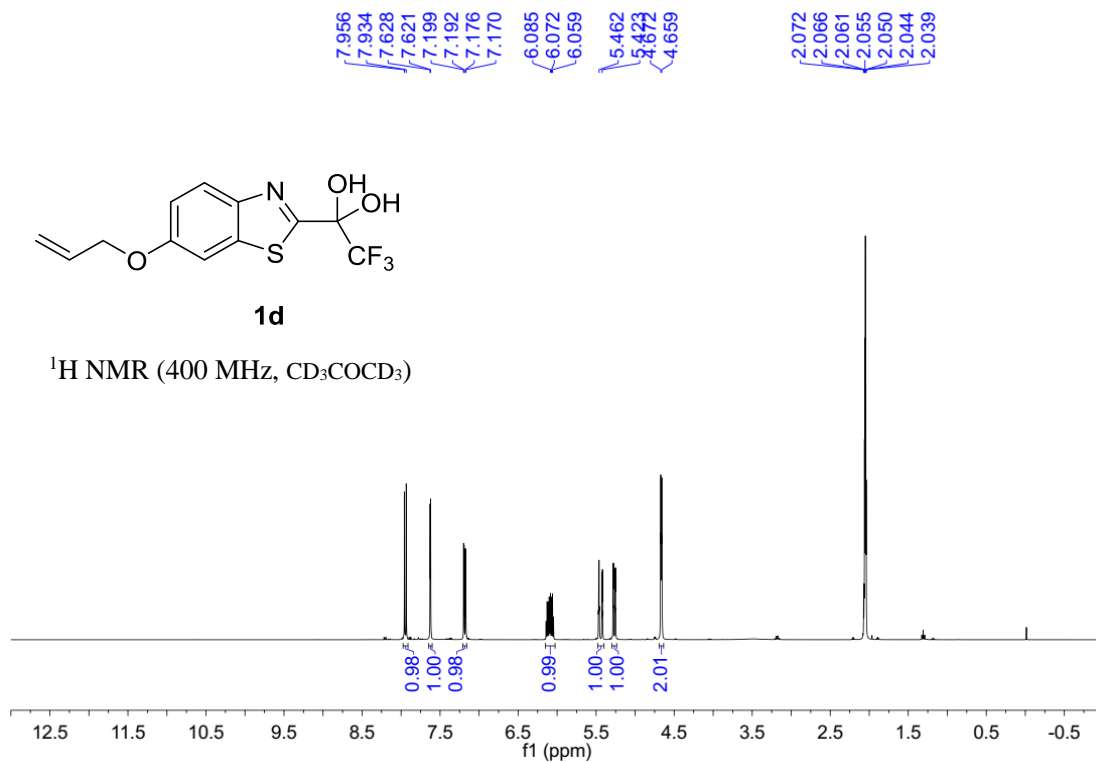




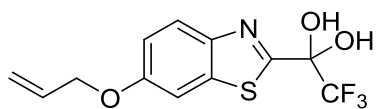
¹⁹F NMR (376.5 MHz, CD₃COCD₃)



¹H NMR (400 MHz, CD₃COCD₃)

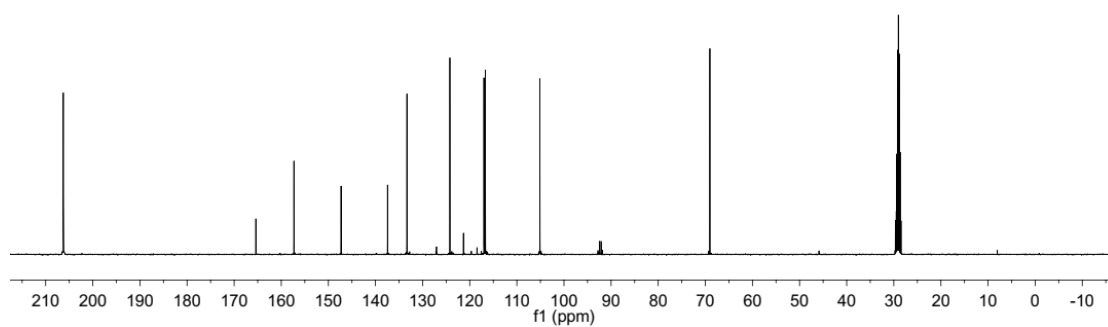


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 -157.333
 -147.323
 137.463
 133.331
 127.057
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 124.207
 121.346
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 105.977
 92.789
 92.469
 92.140
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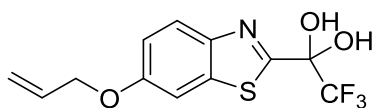


1d

^{13}C NMR (100 MHz, CD_3COCD_3)

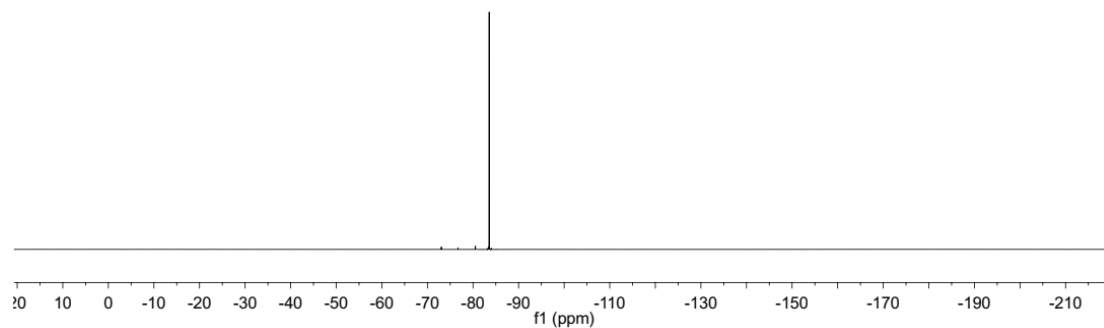


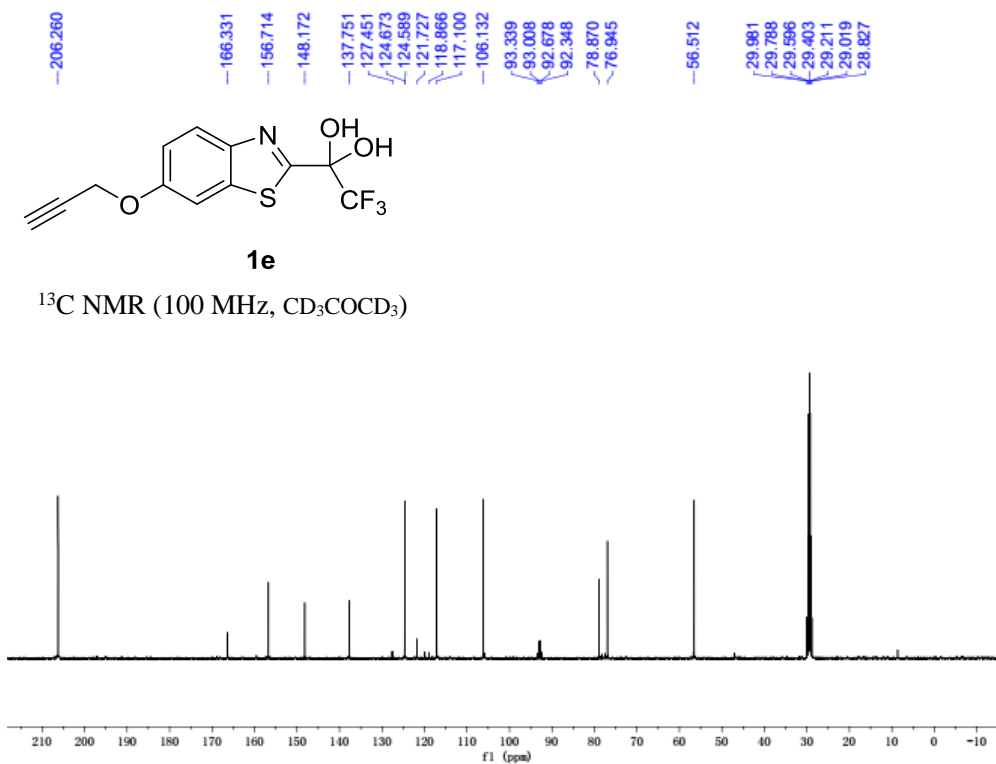
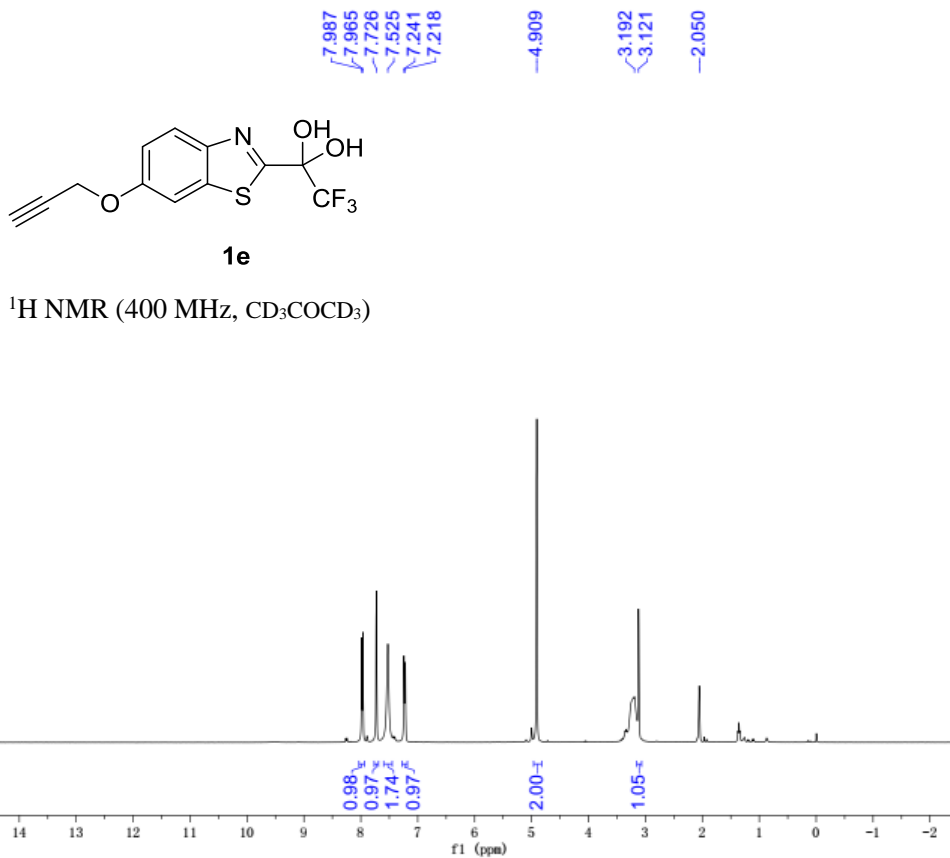
-83.534

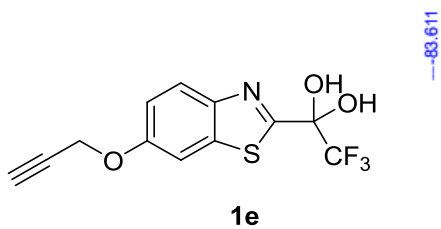


1d

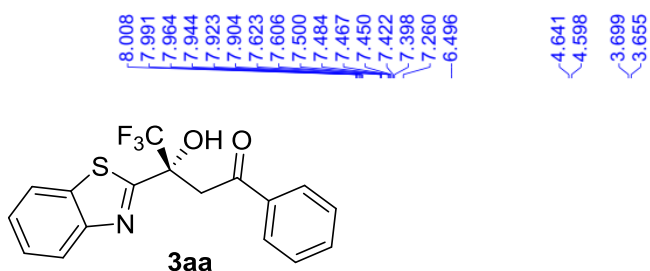
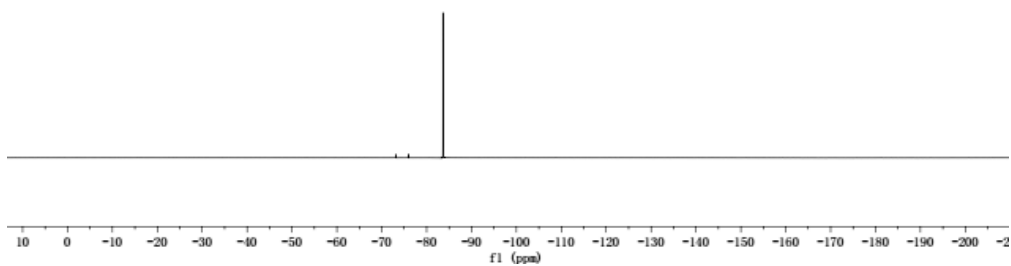
^{19}F NMR (376.5 MHz, CD_3COCD_3)



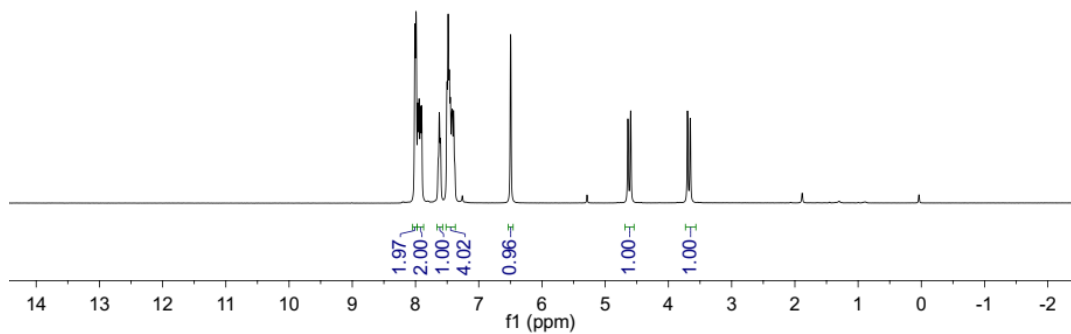


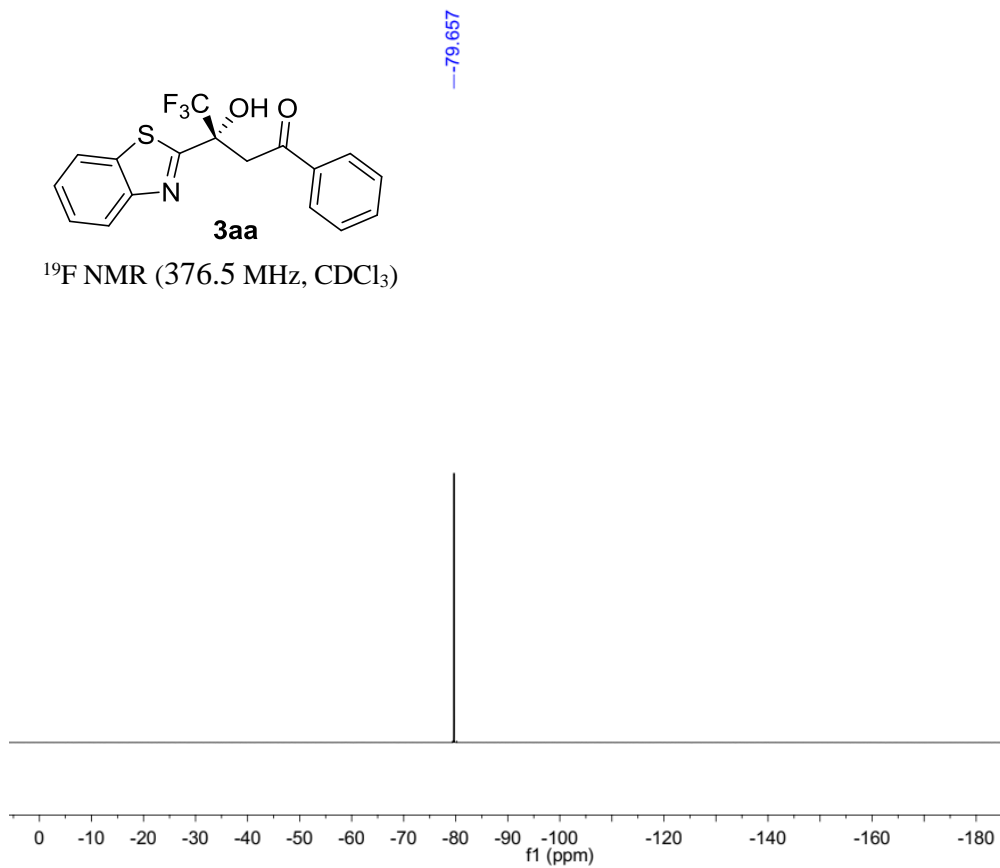
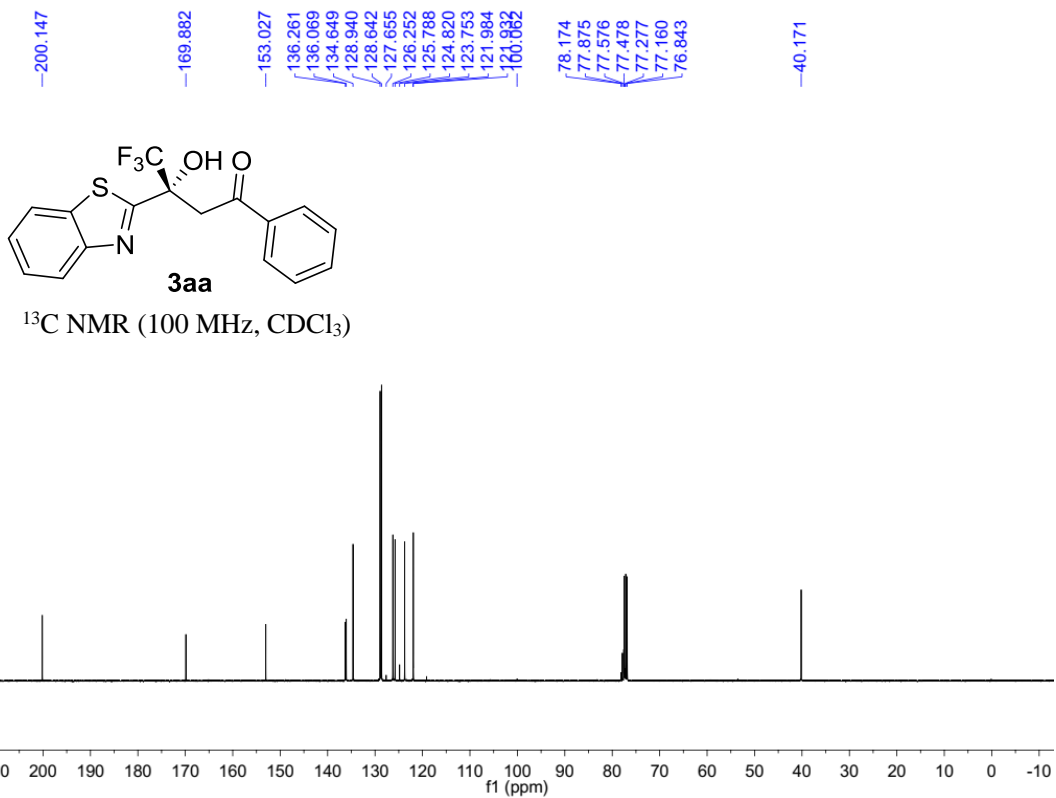


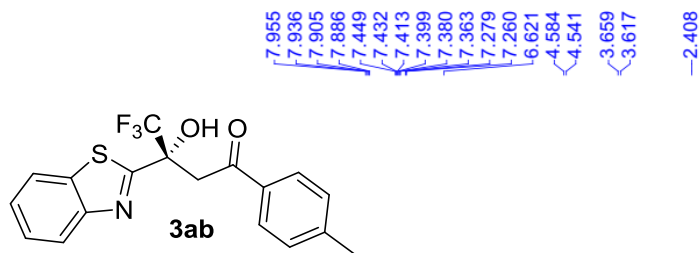
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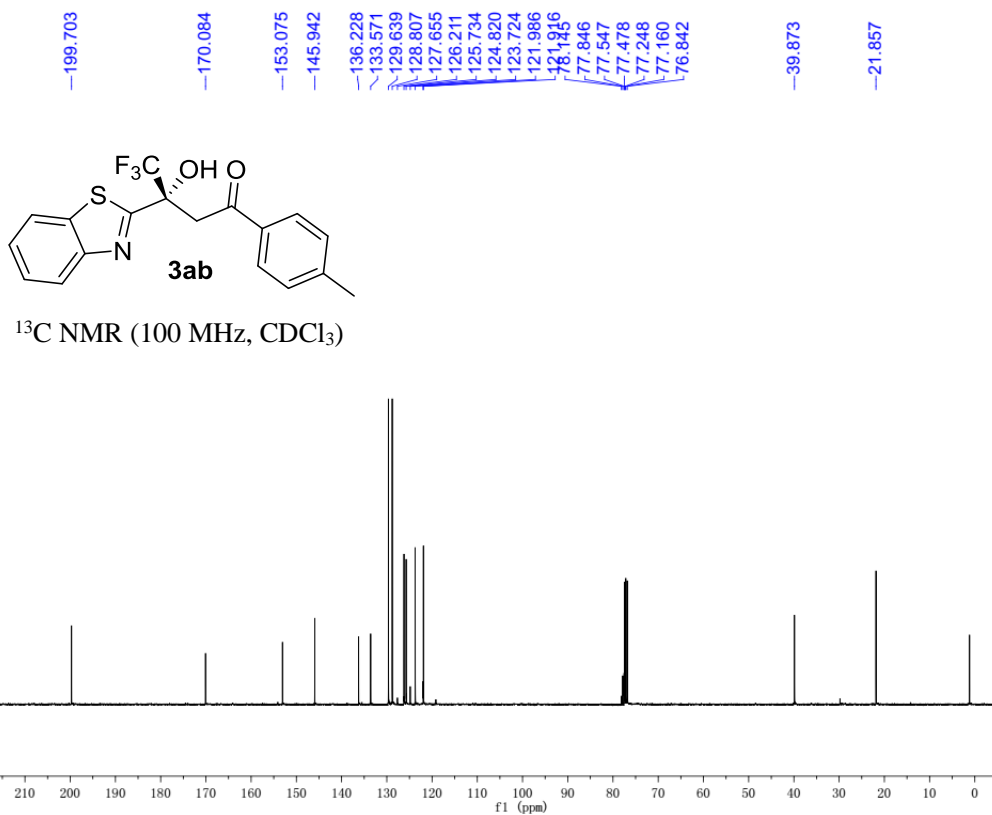
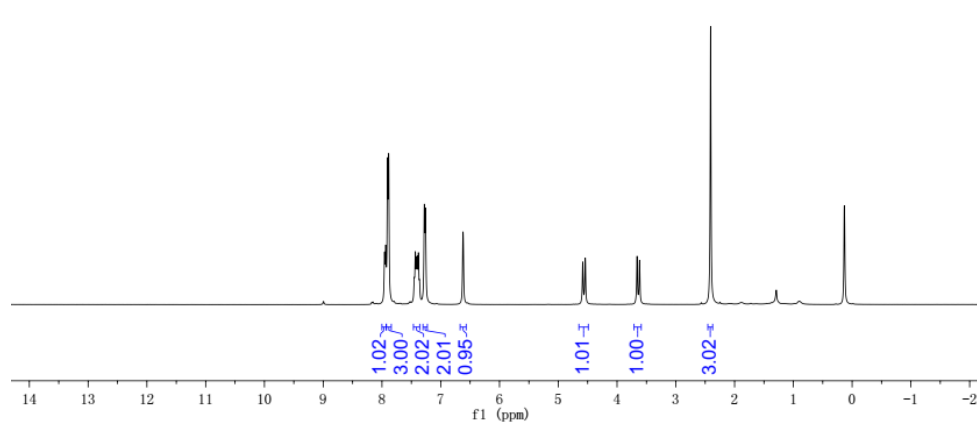
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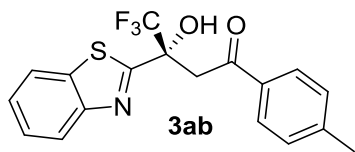




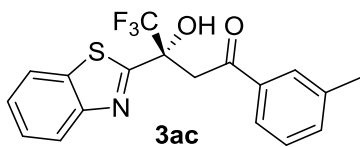
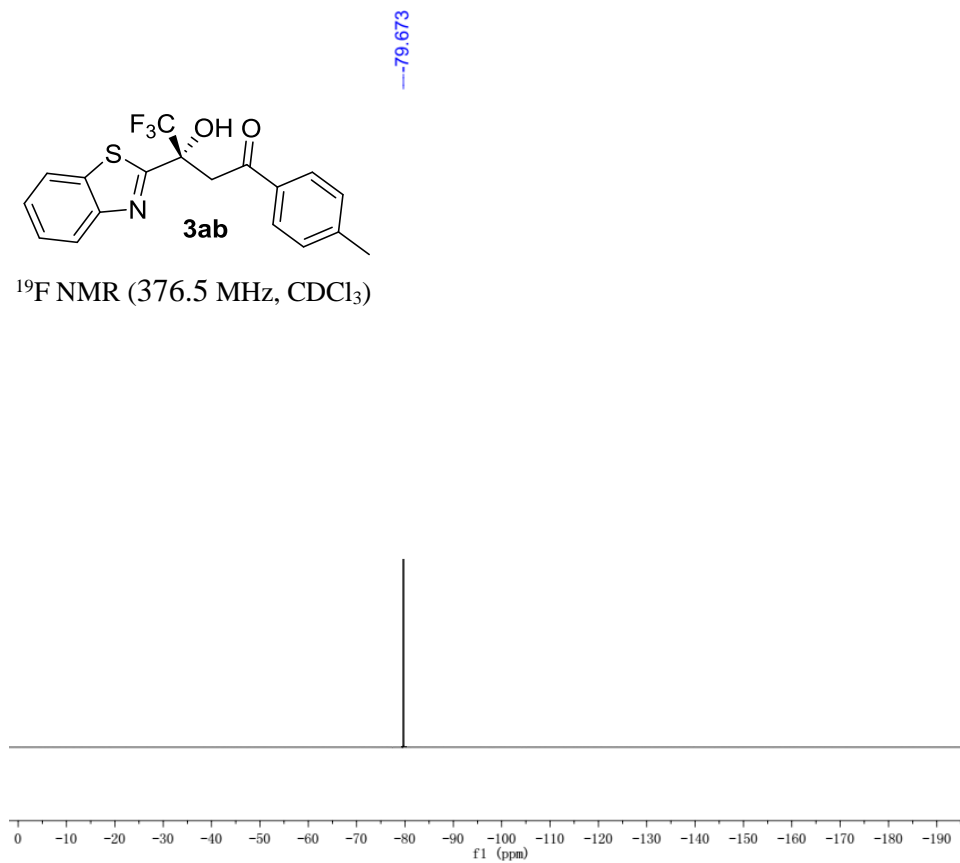


$^1\text{H NMR}$ (400 MHz, CDCl_3)

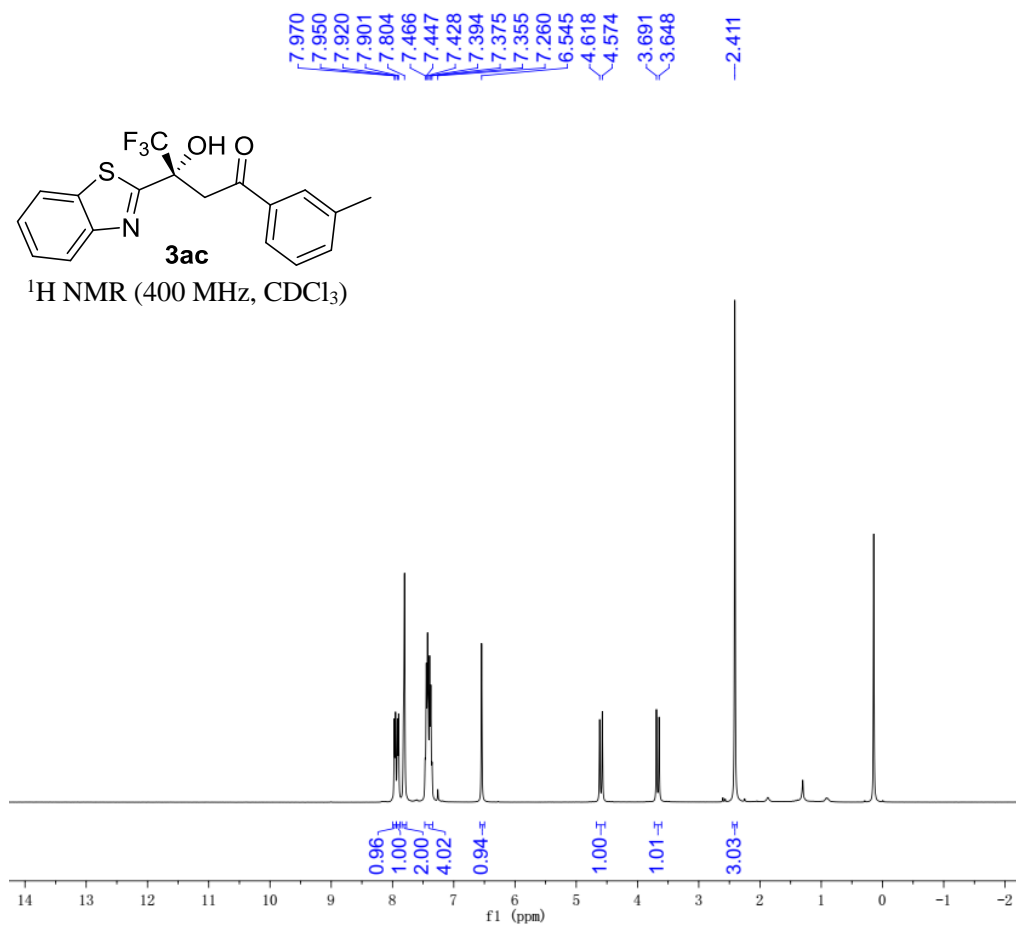


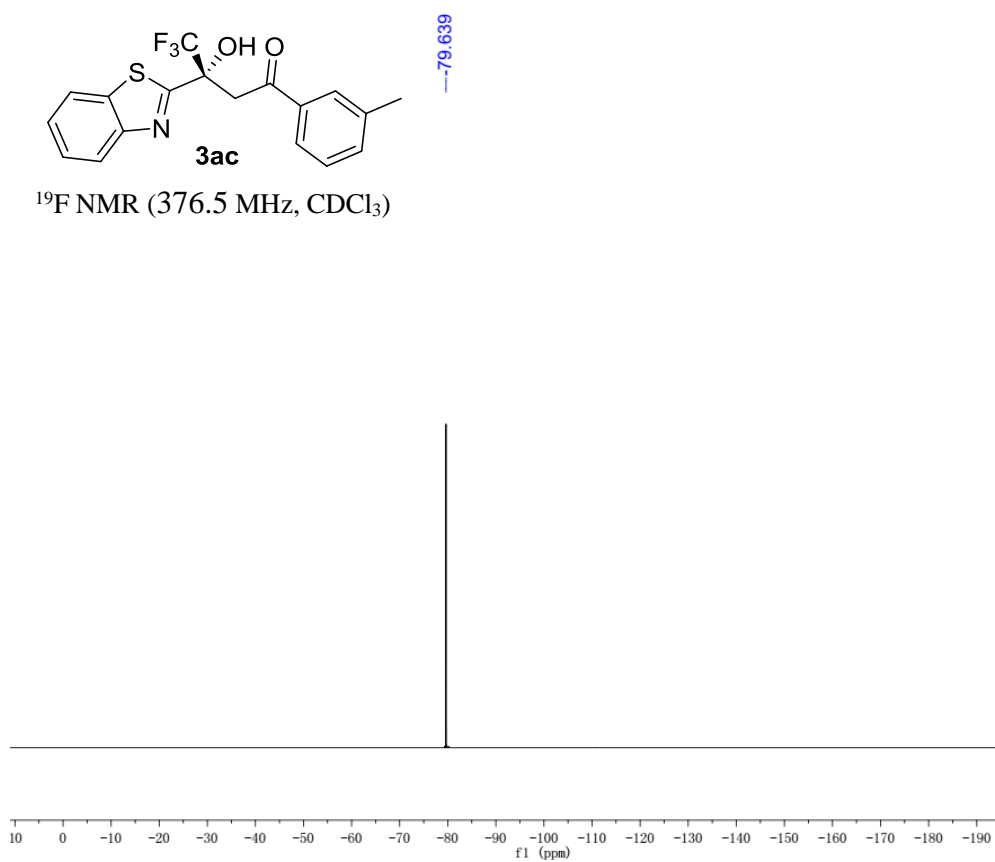
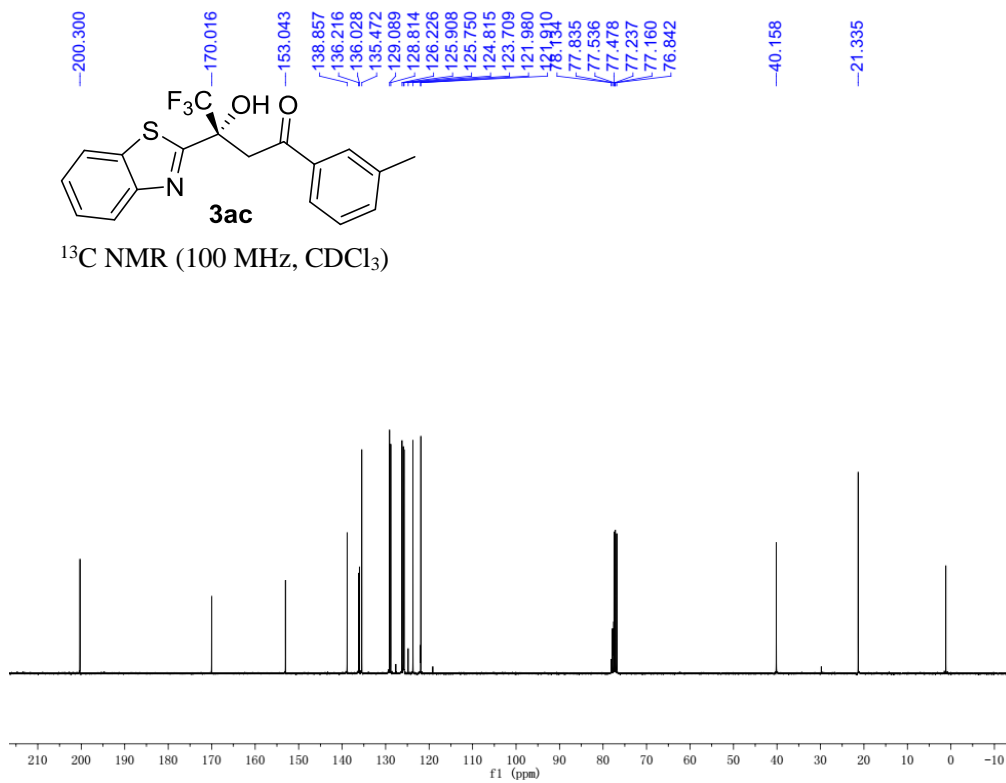


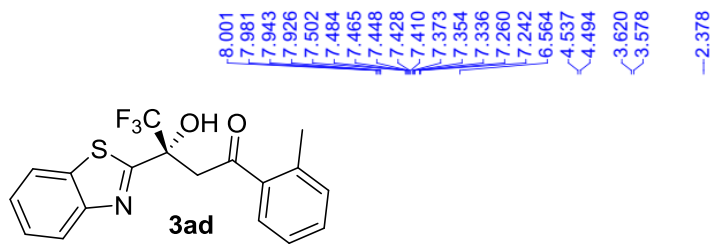
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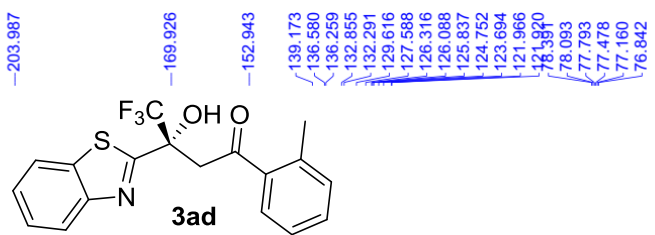
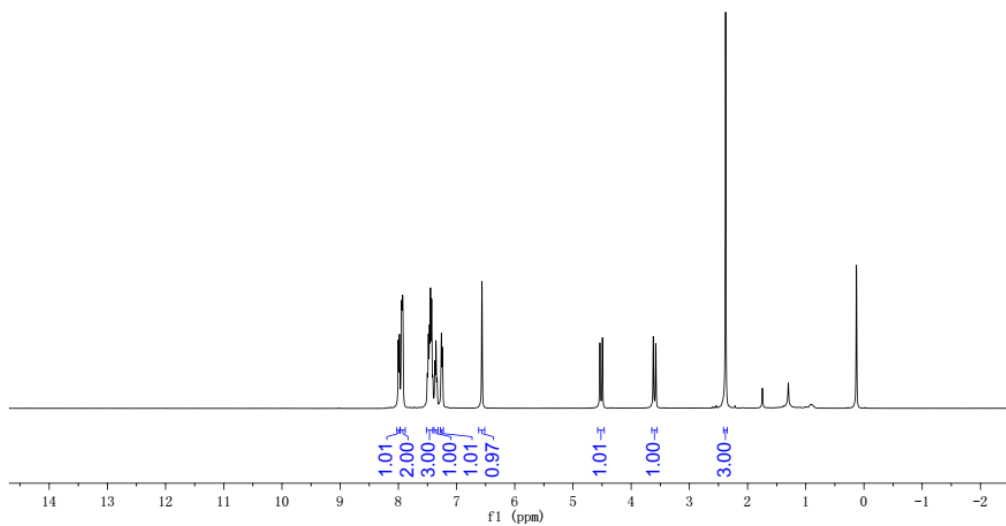
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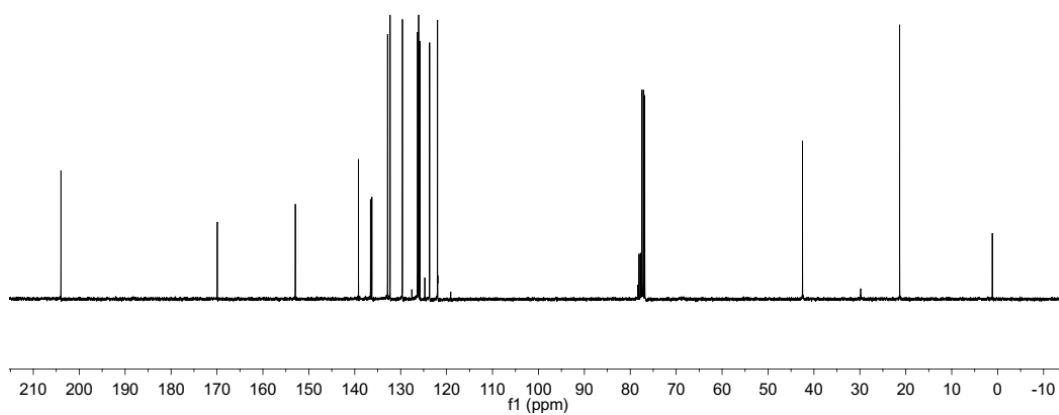


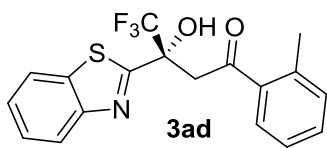


¹H NMR (400 MHz, CDCl₃)

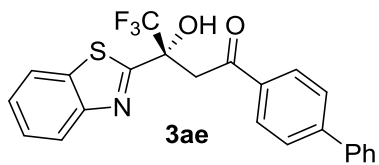
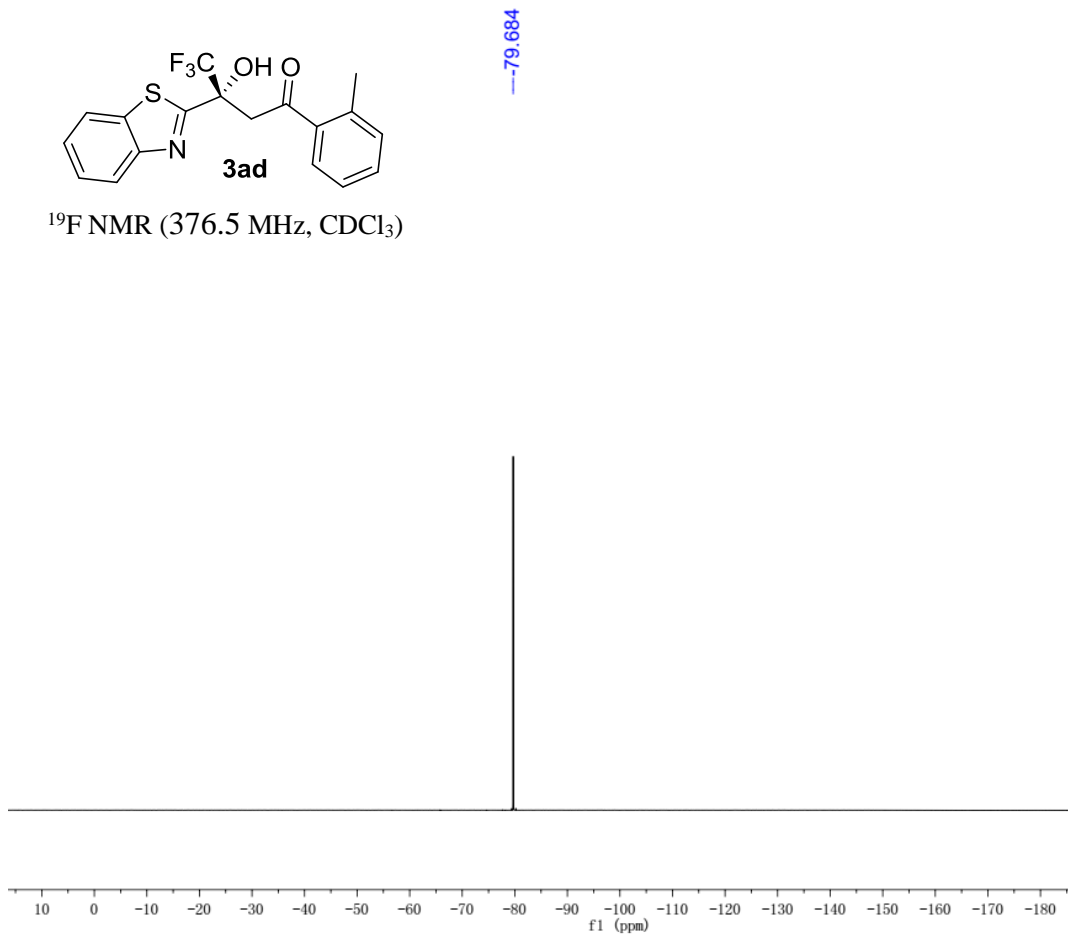


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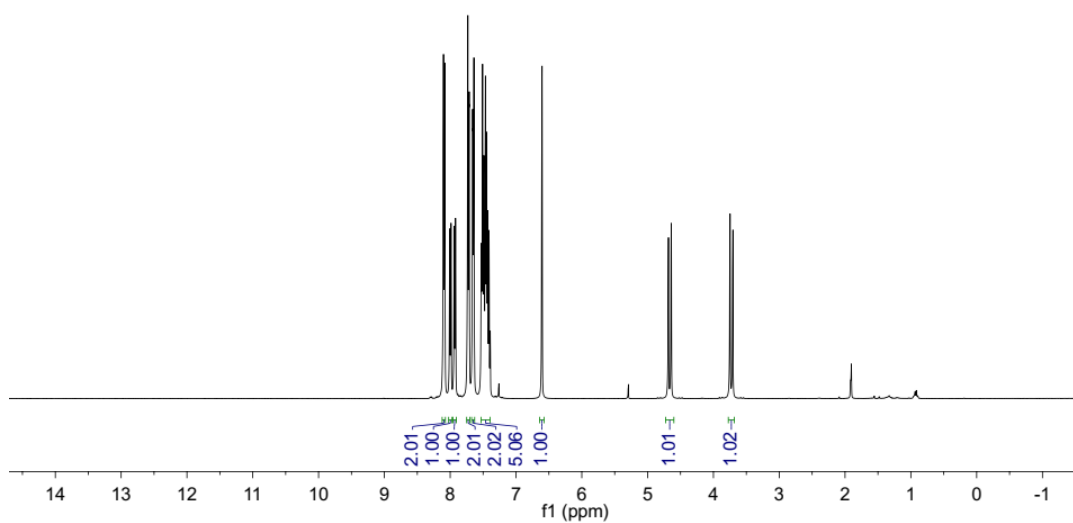


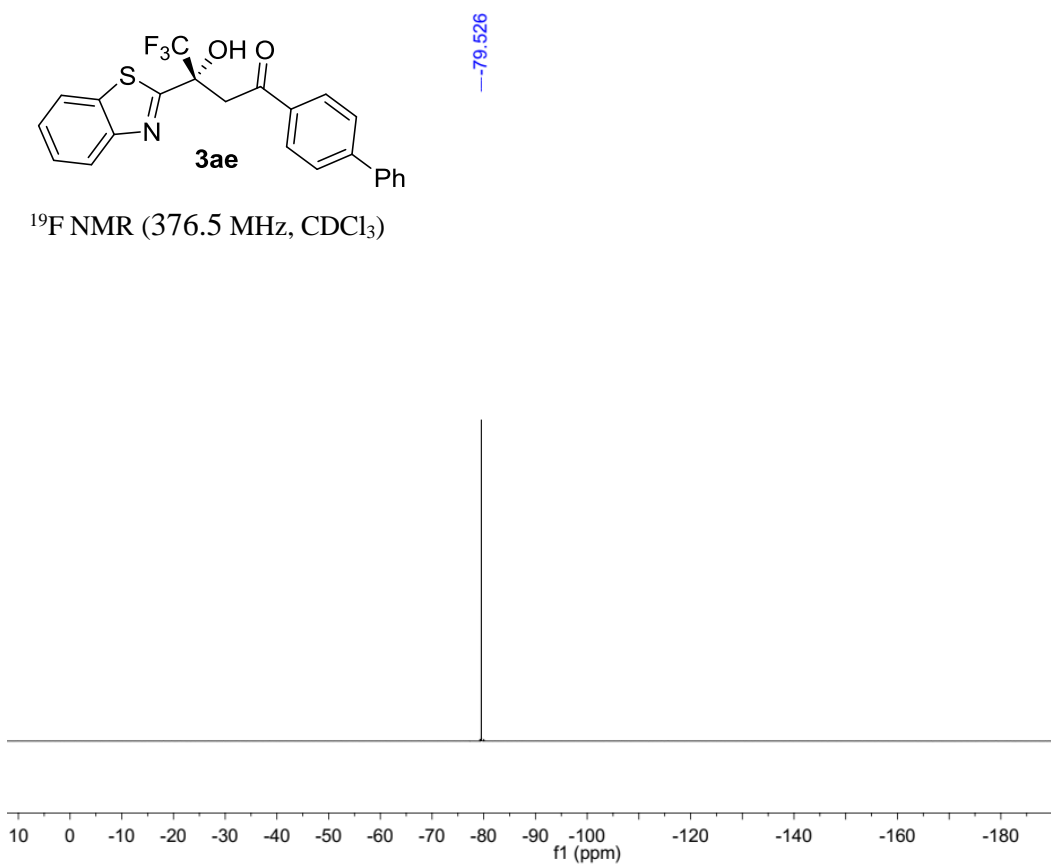
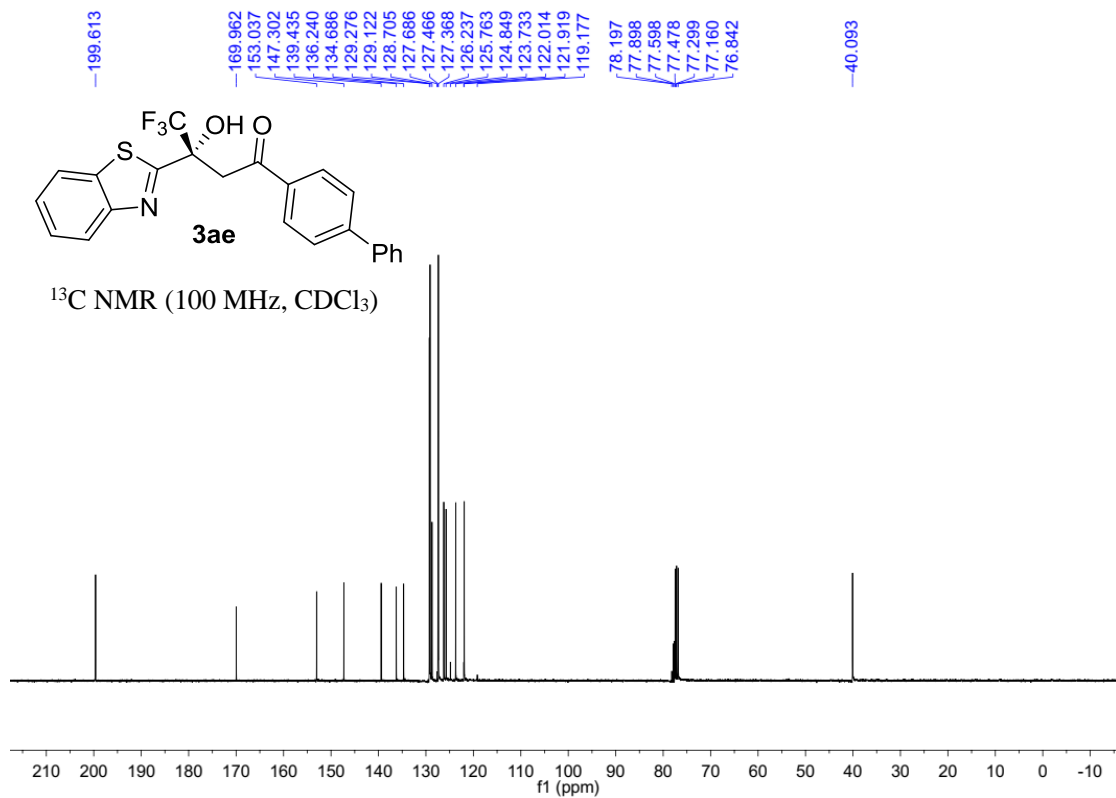


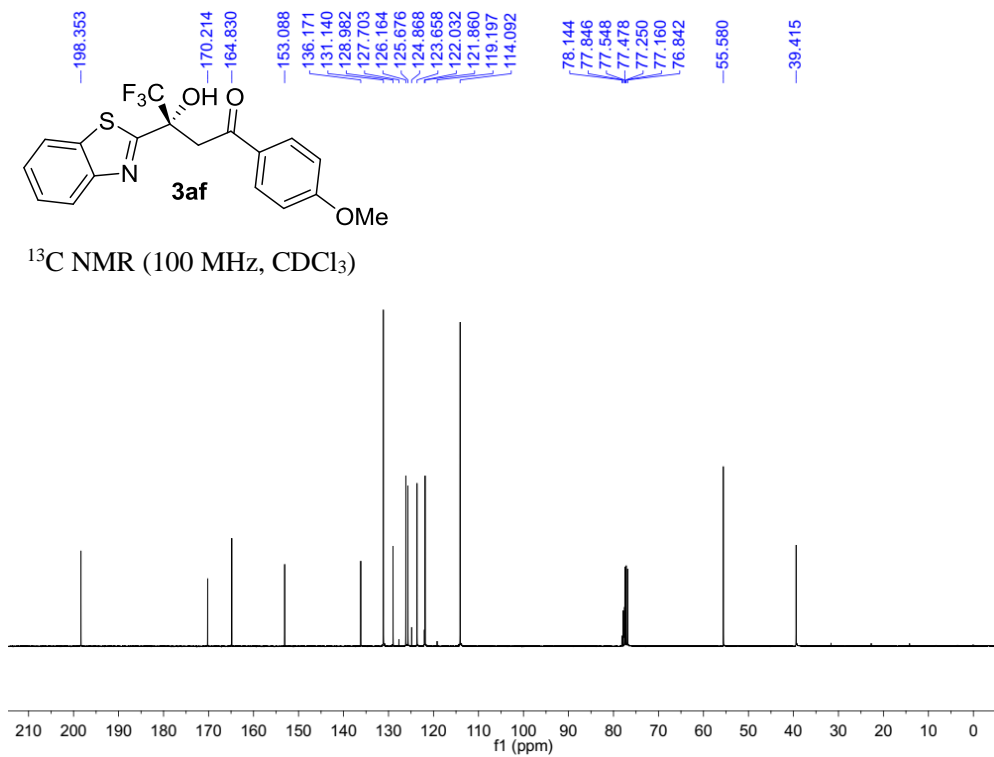
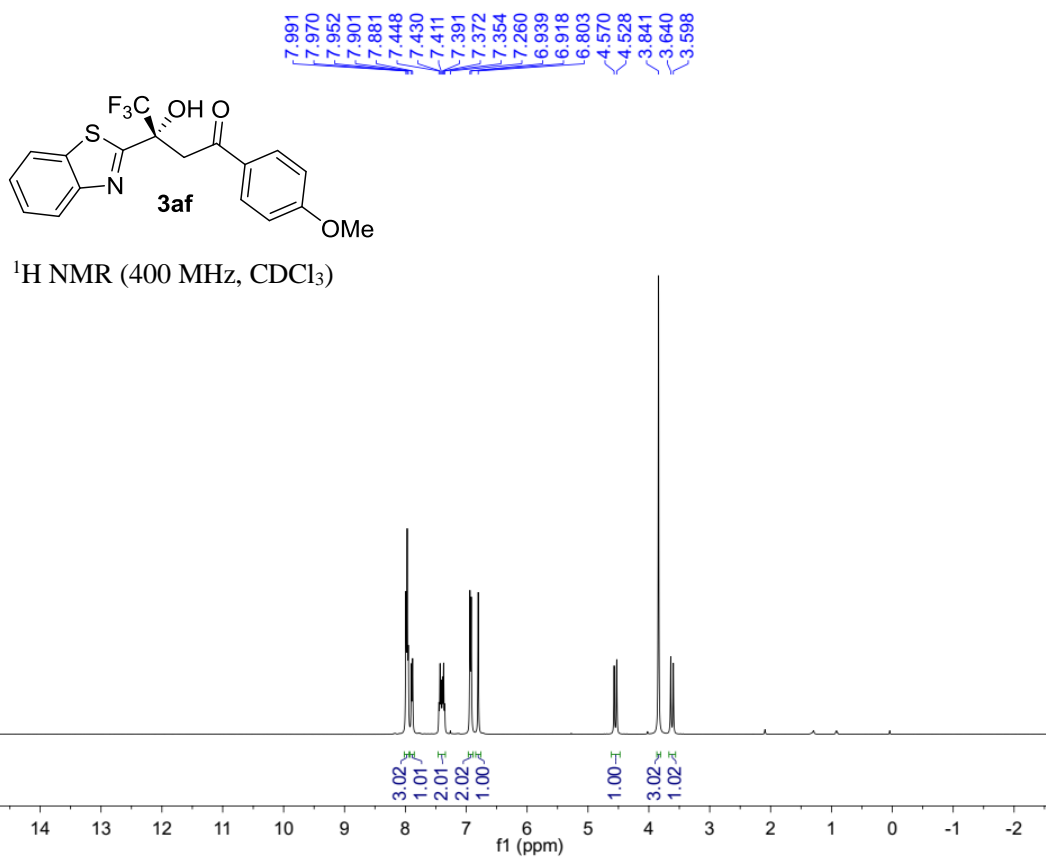
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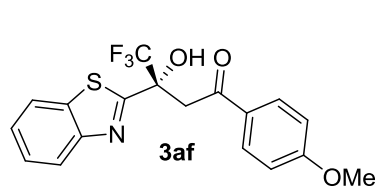


^1H NMR (400 MHz, CDCl_3)



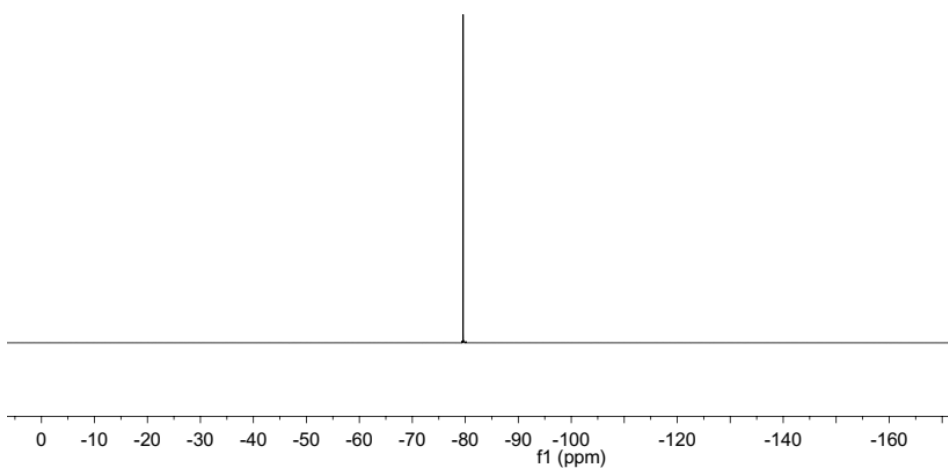




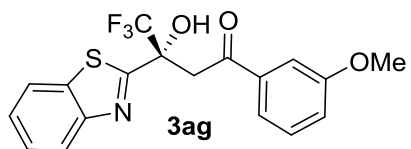


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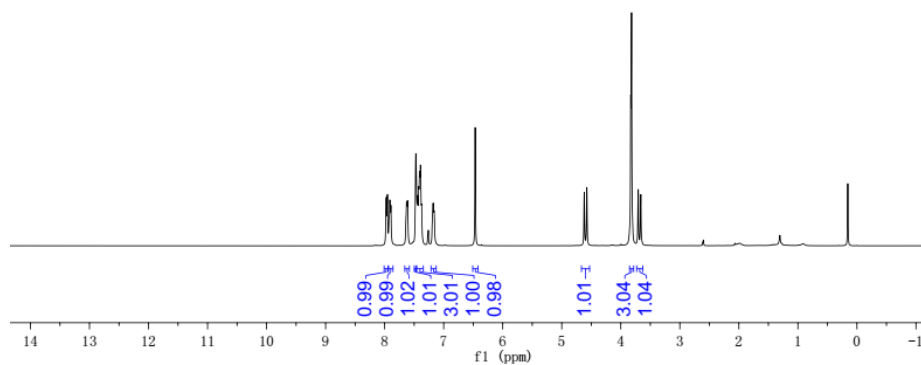
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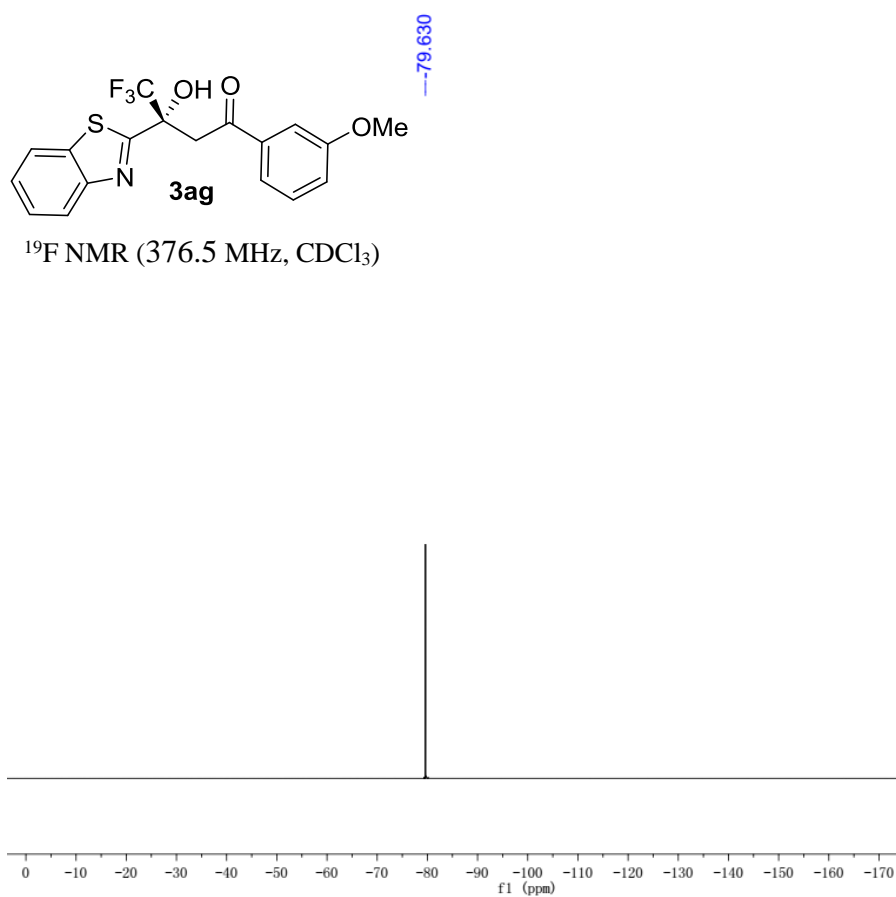
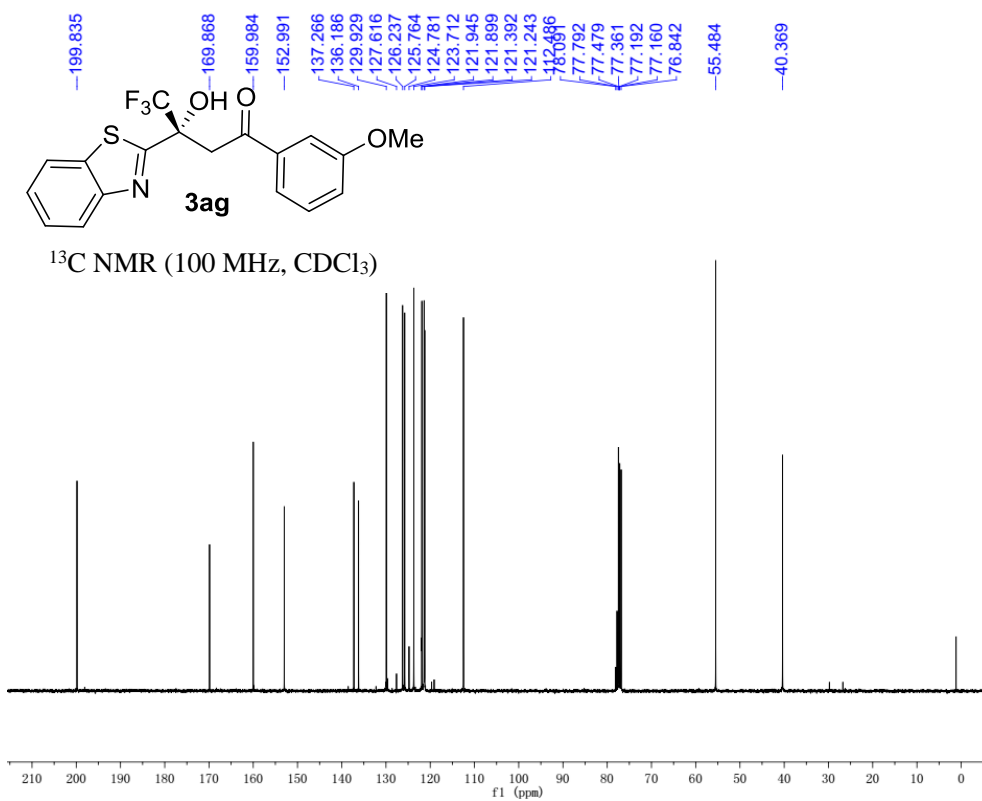


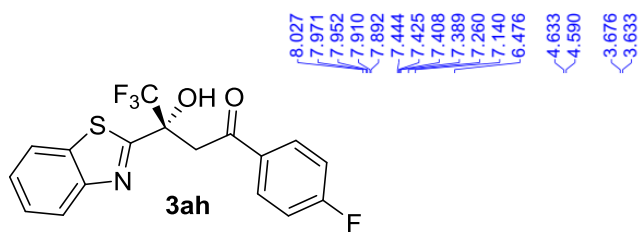
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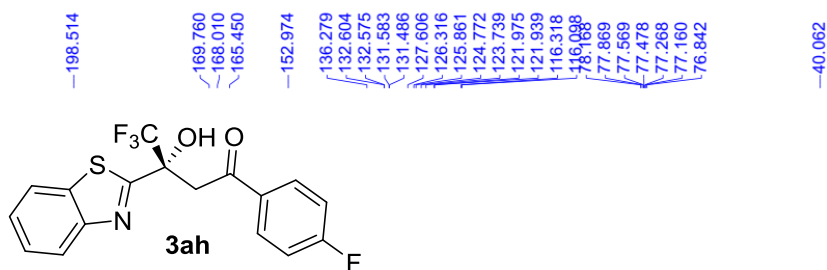
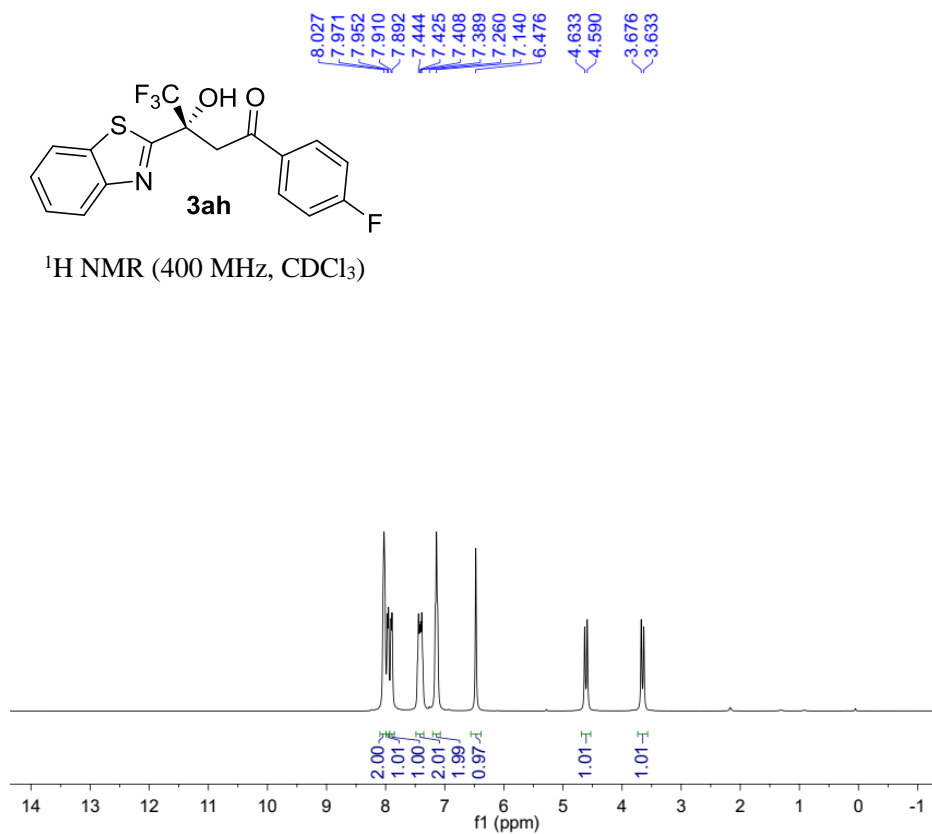
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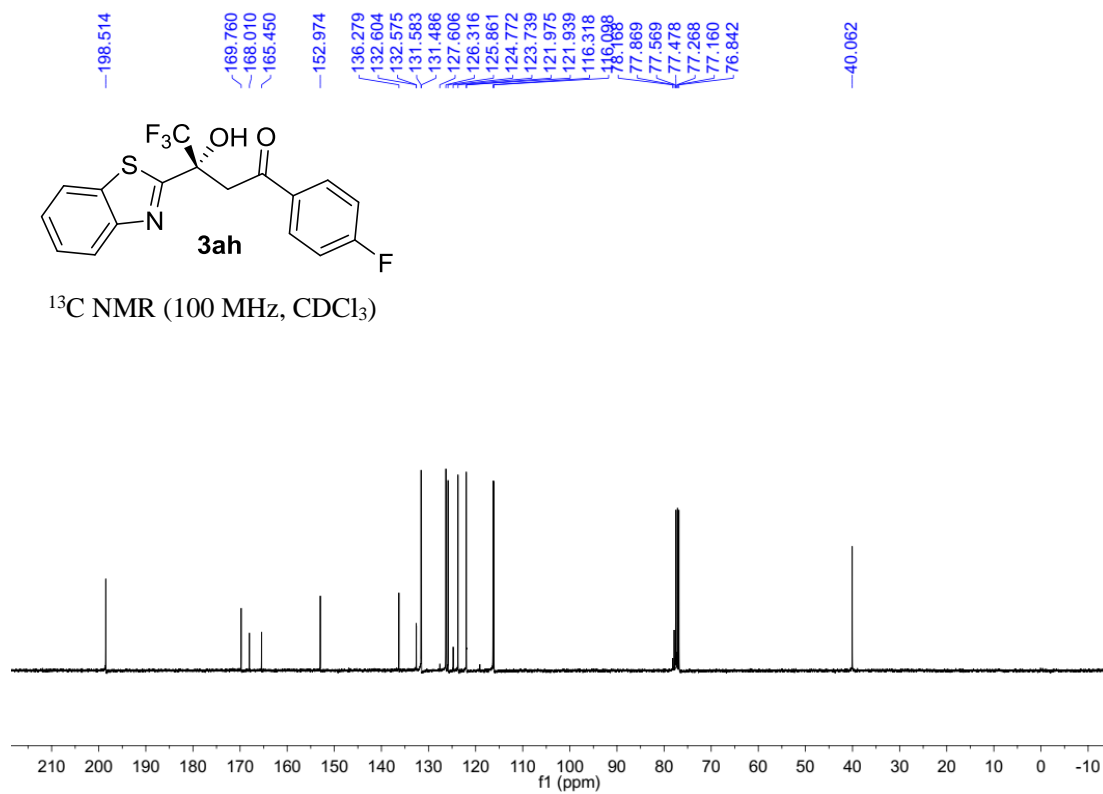


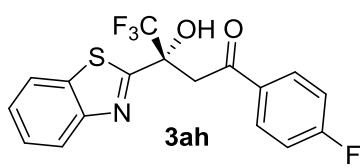


$^1\text{H NMR}$ (400 MHz, CDCl_3)

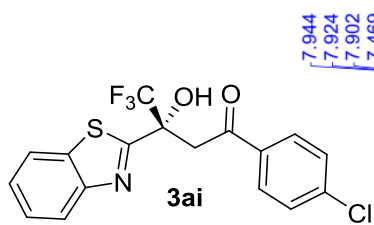
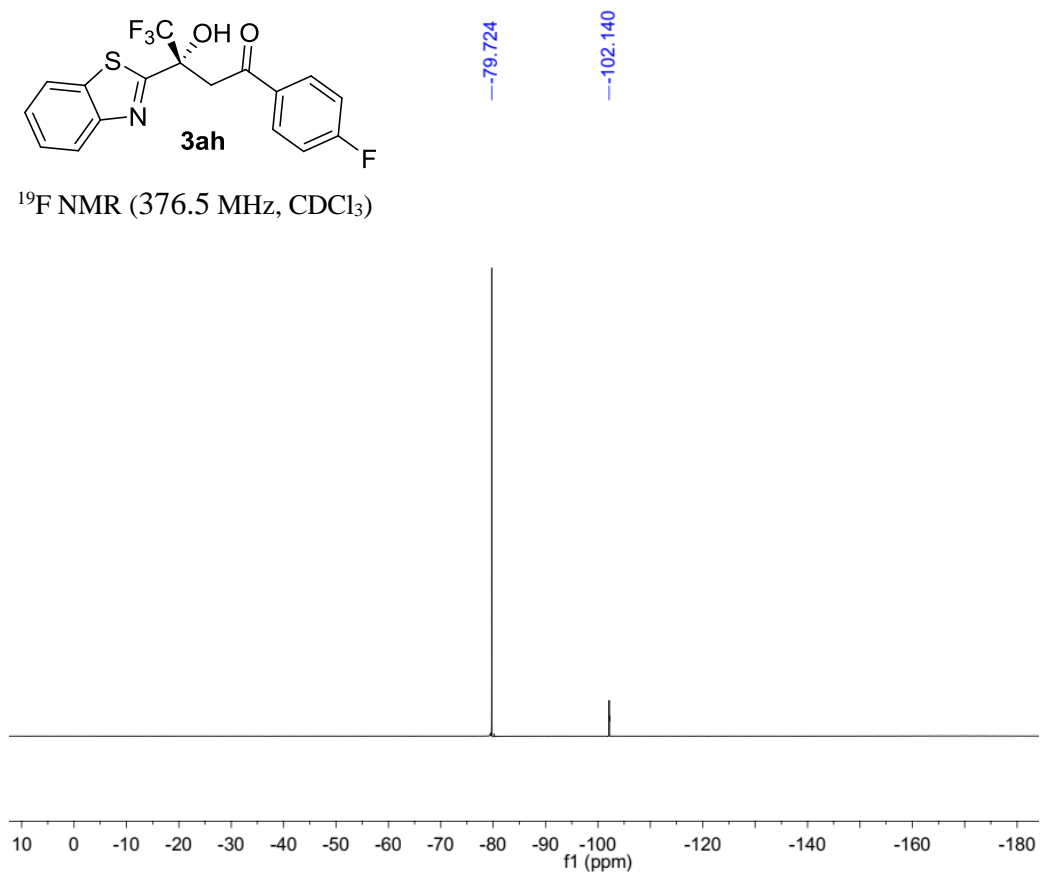


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

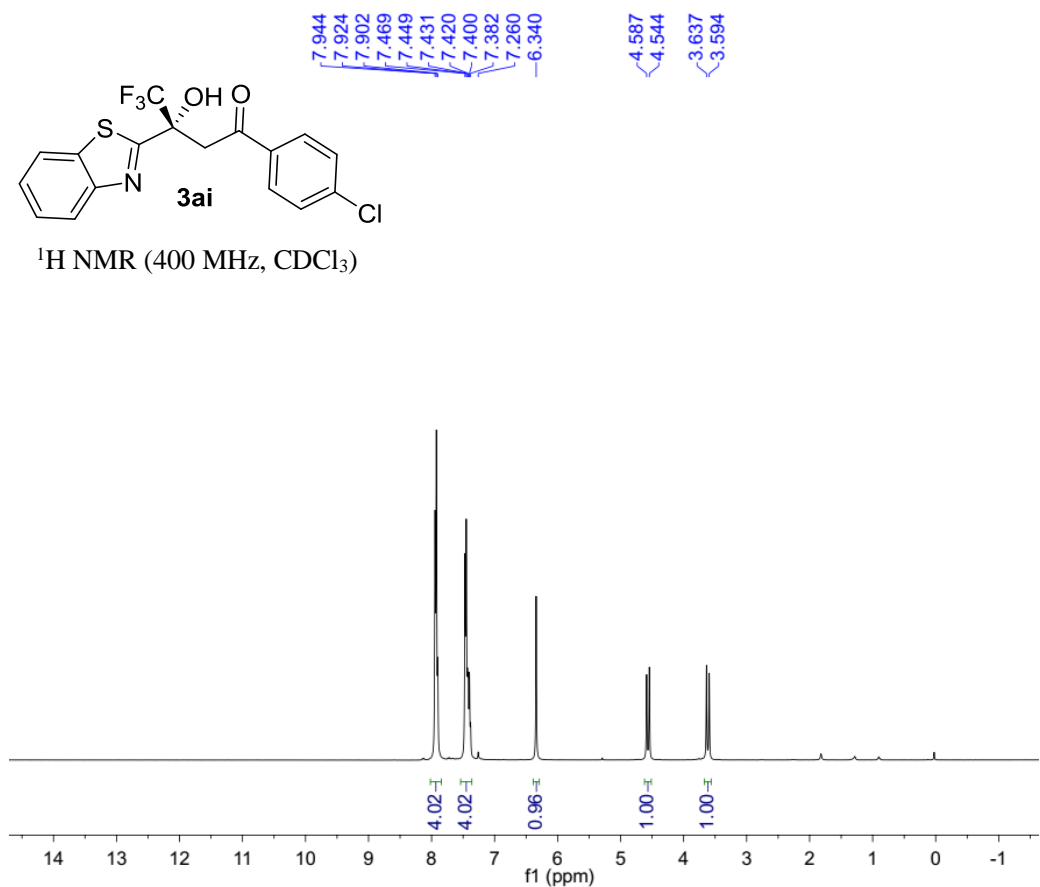


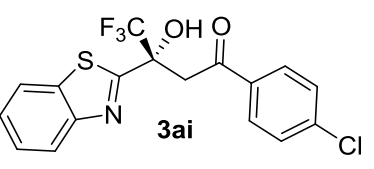
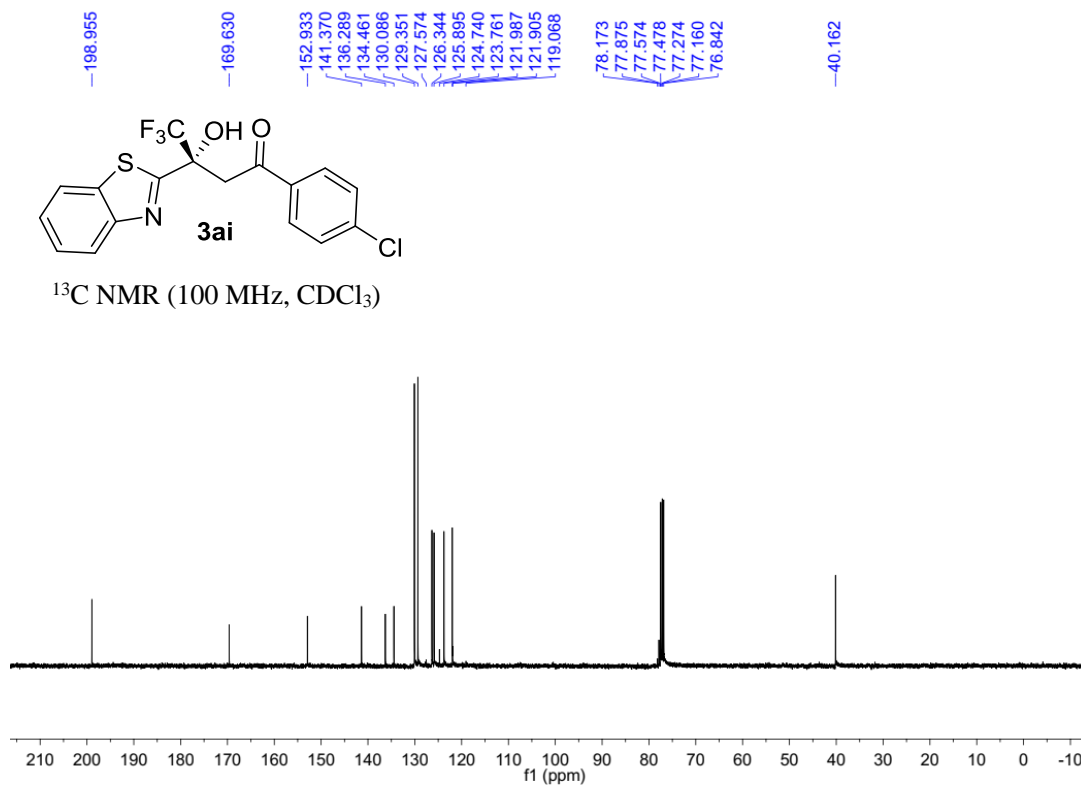


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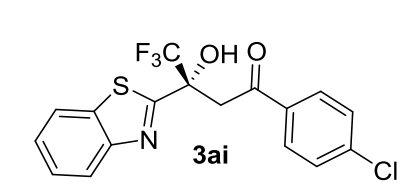


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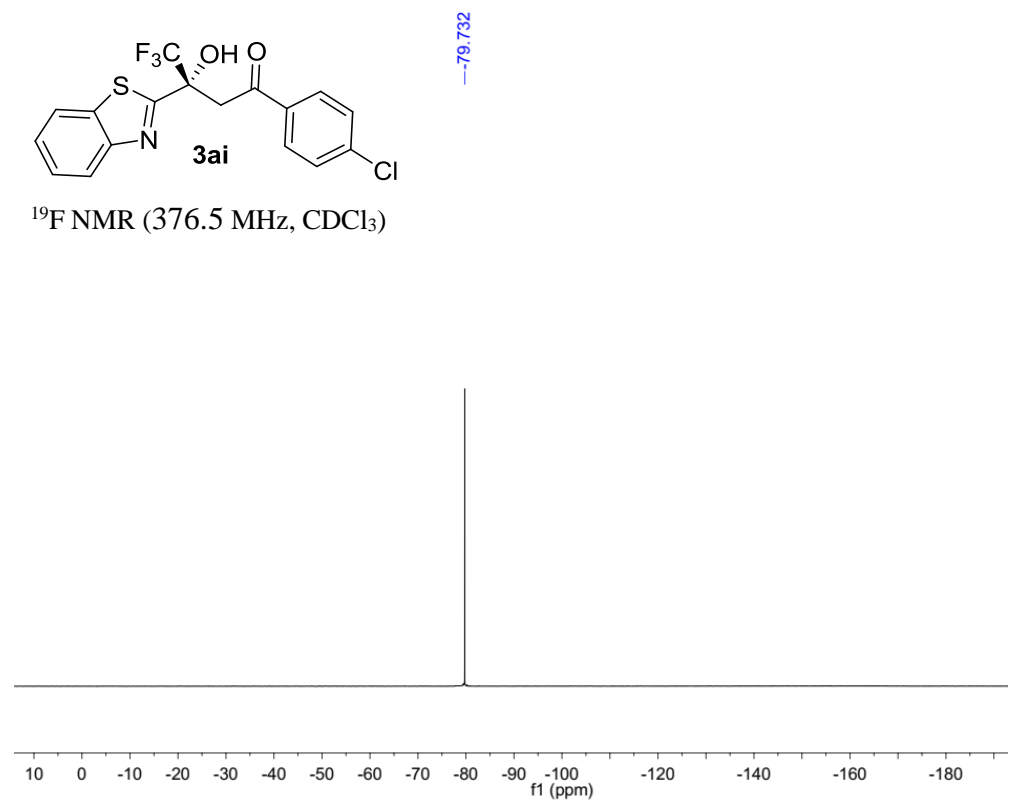


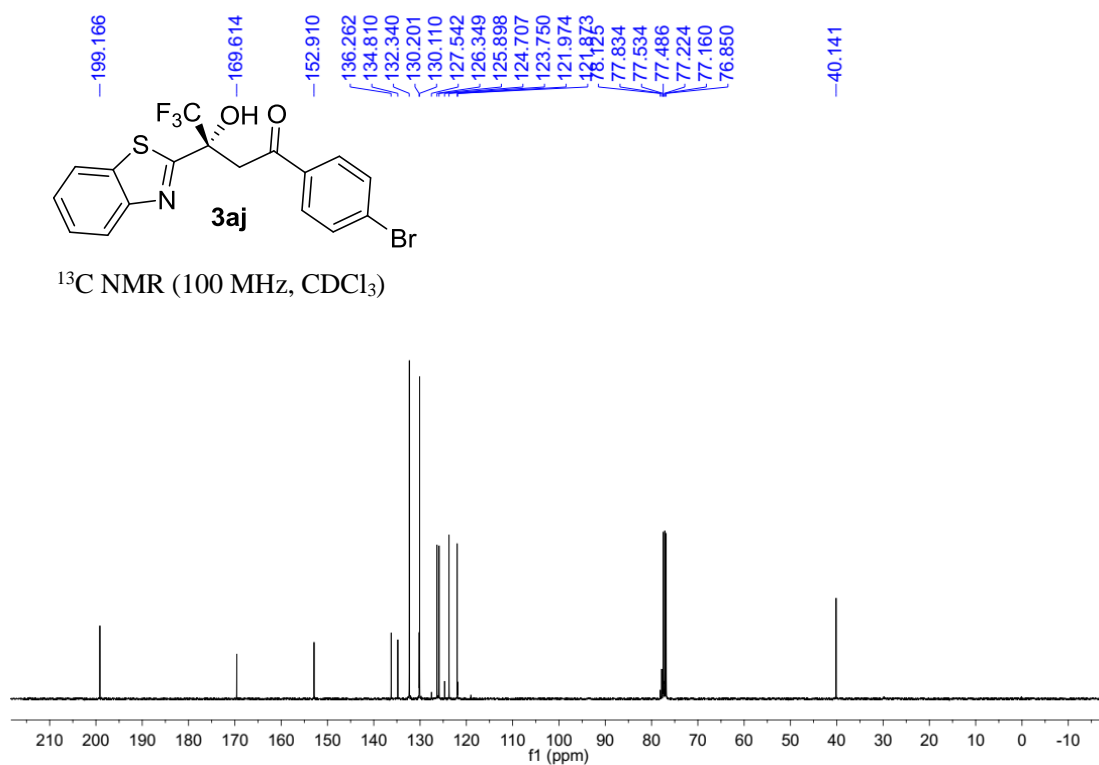
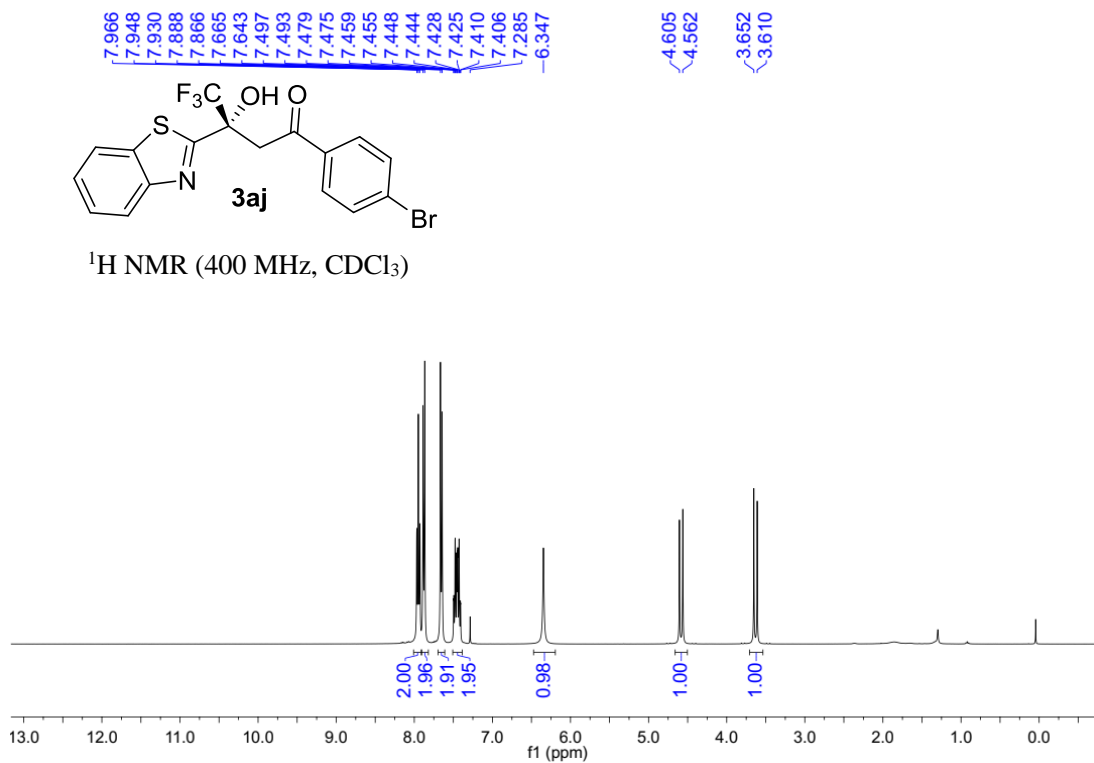


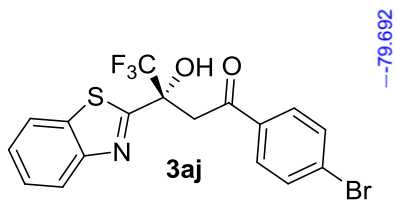
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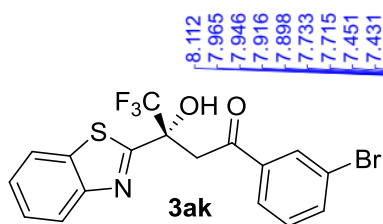
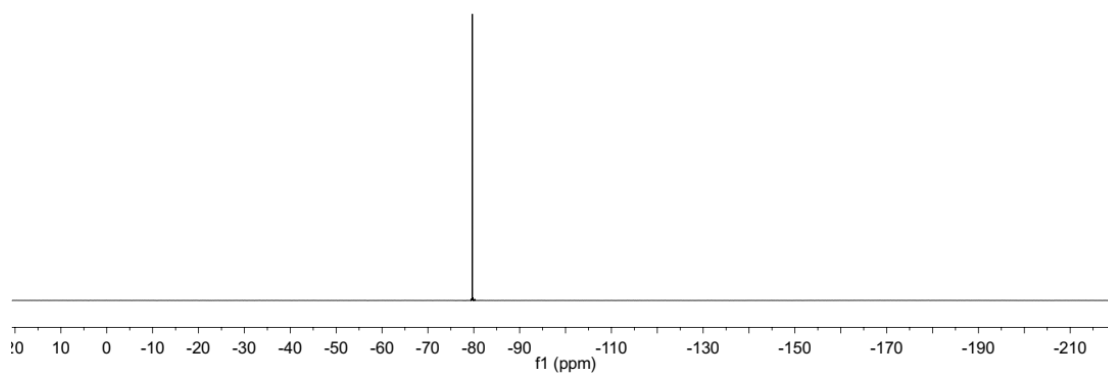
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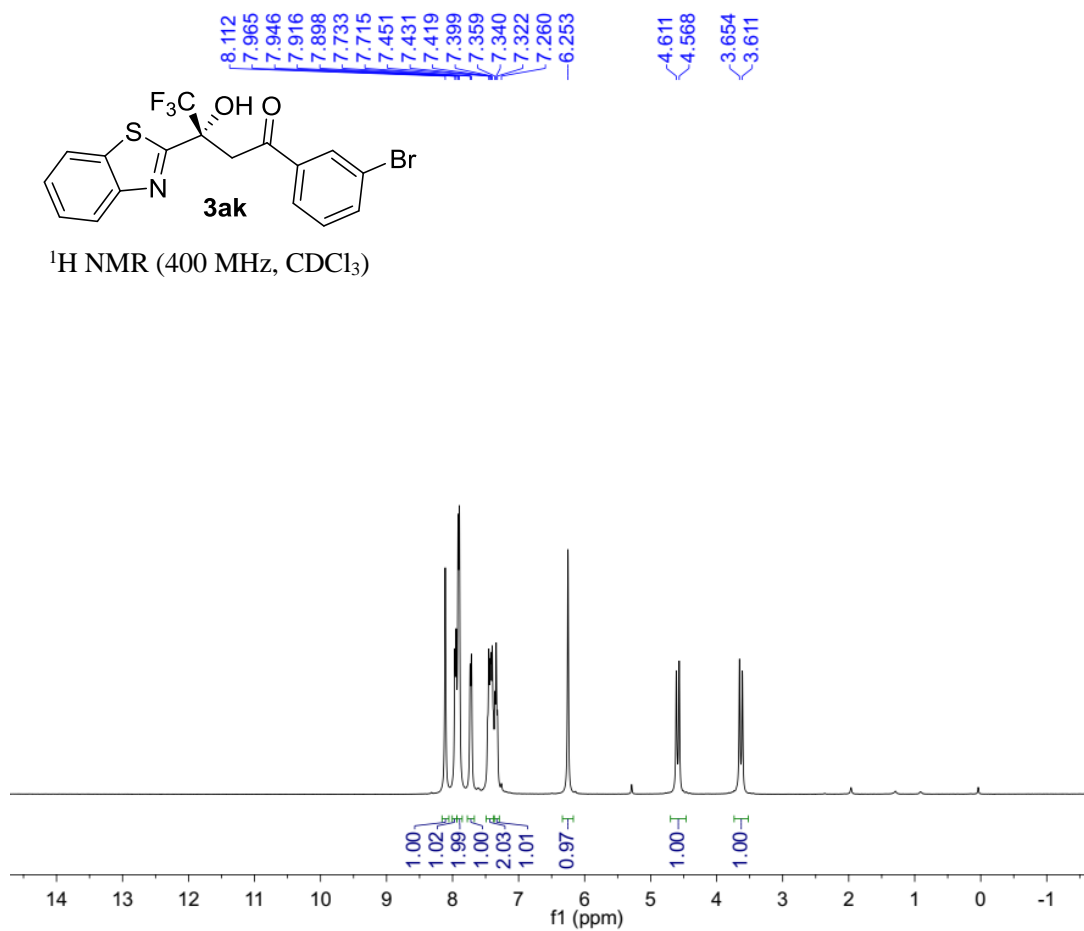


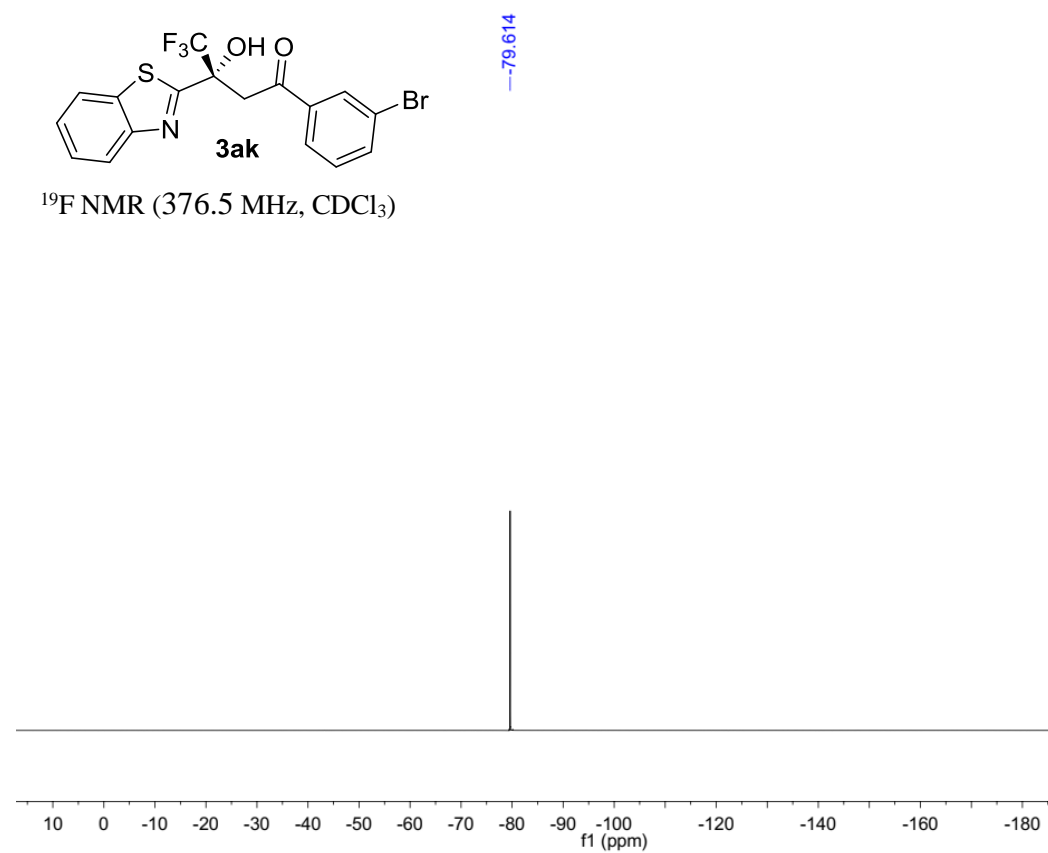
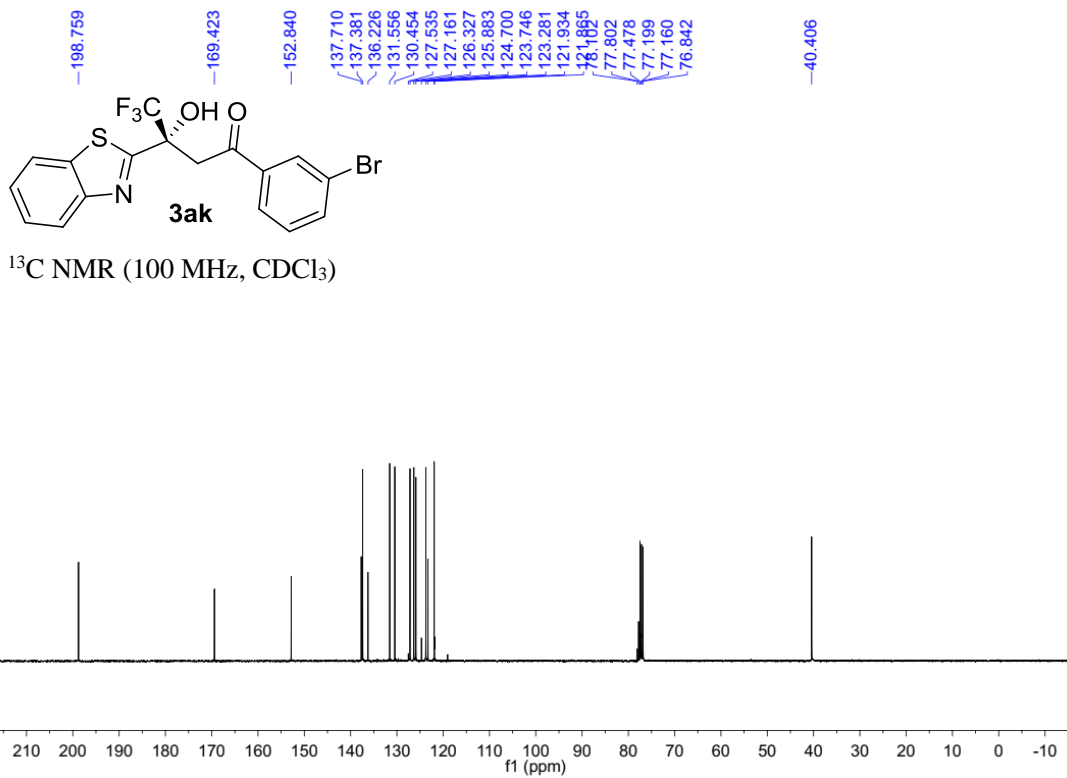


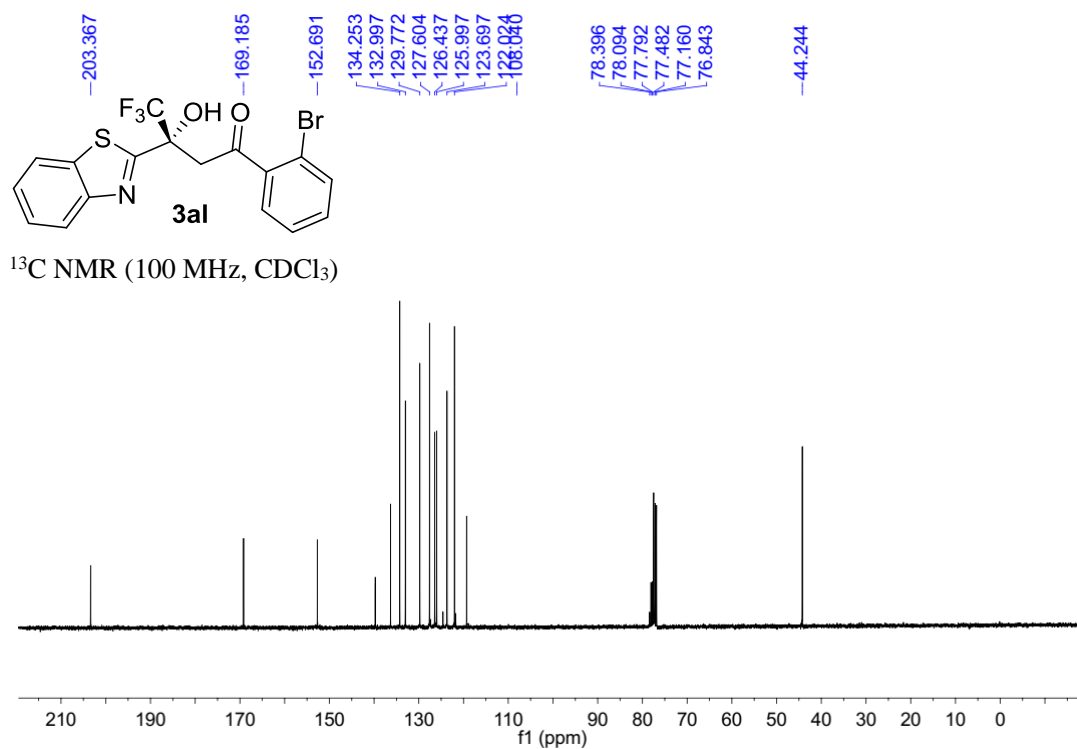
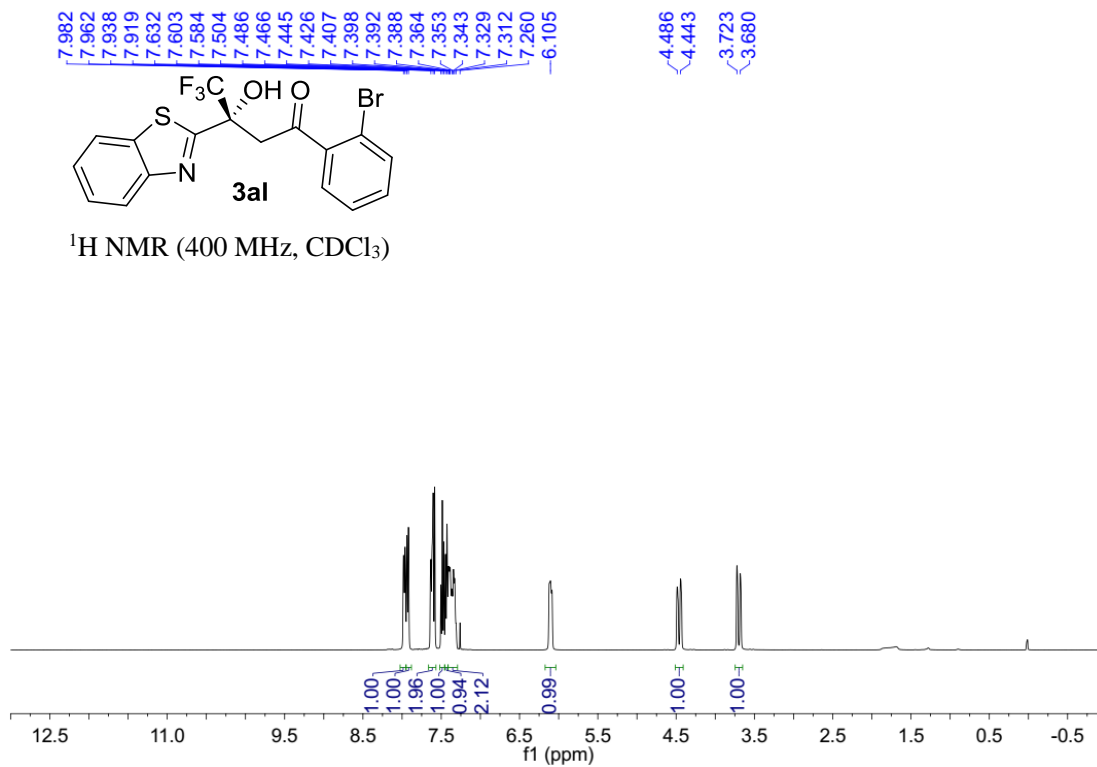
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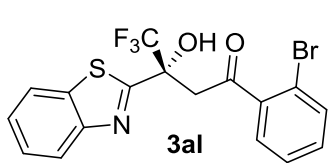


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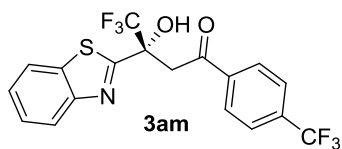
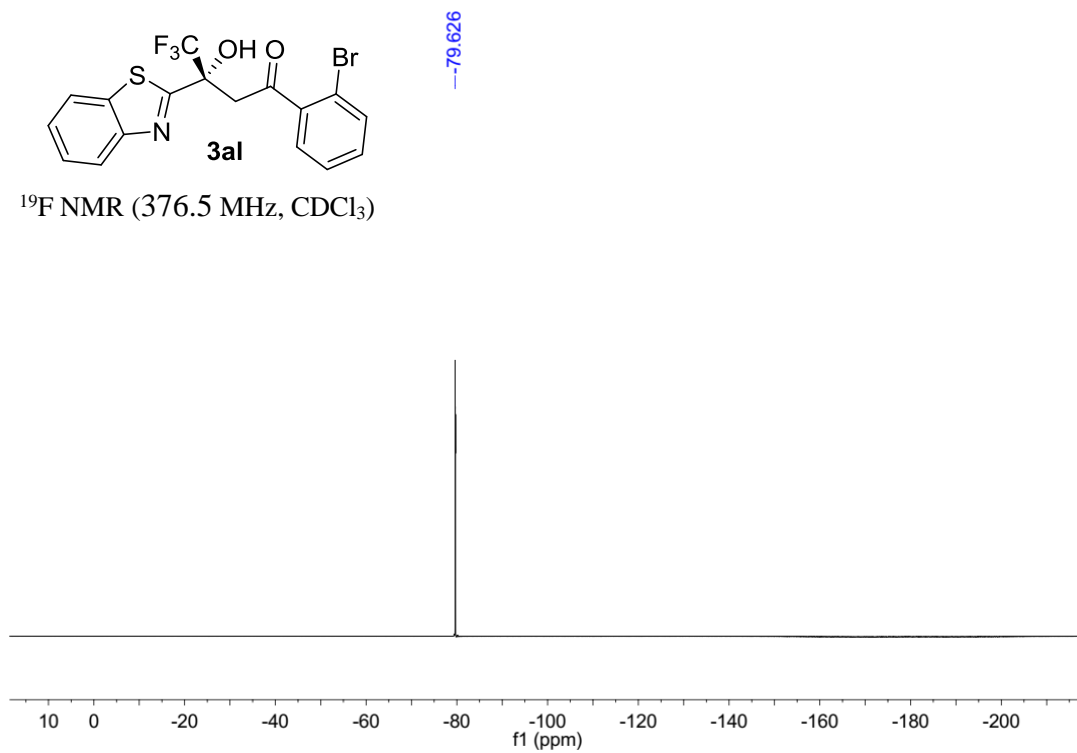




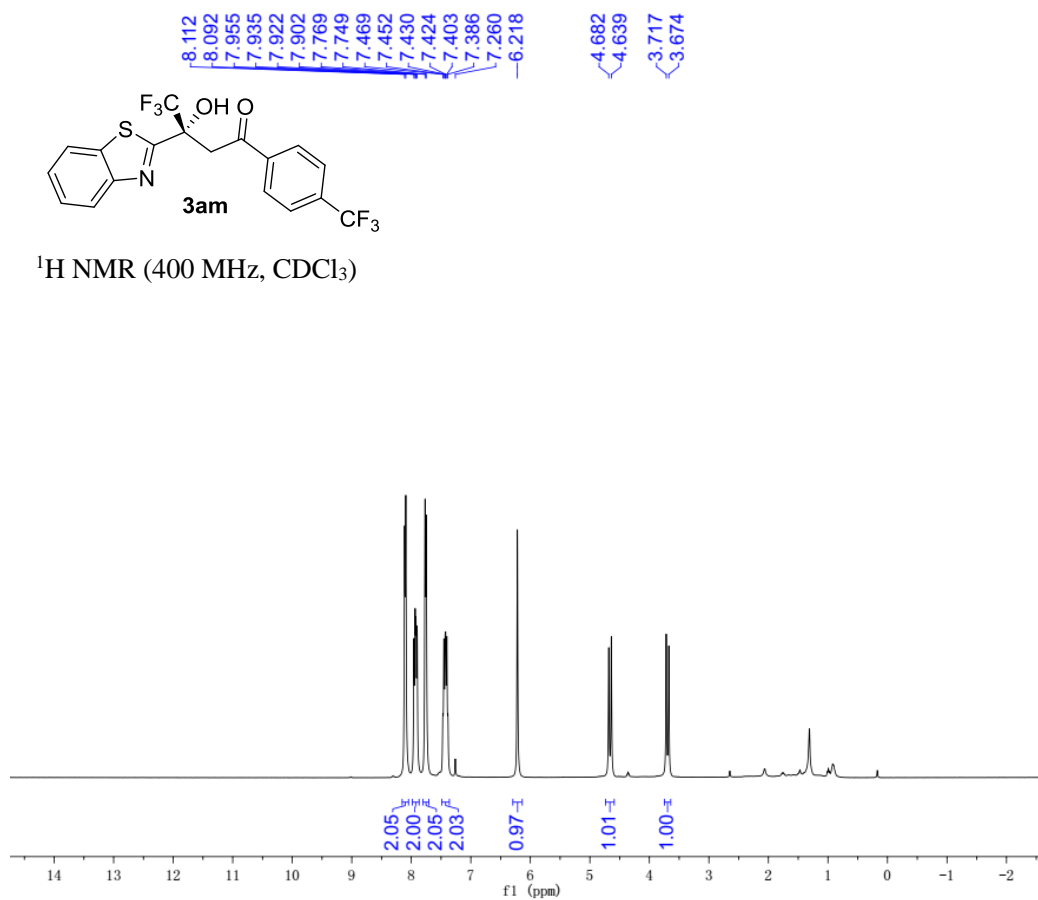


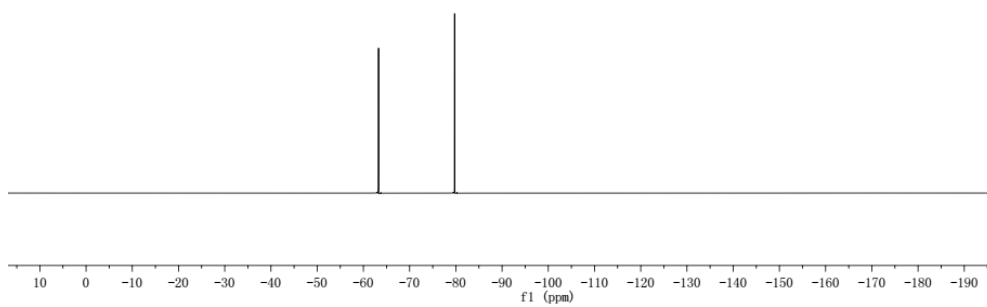
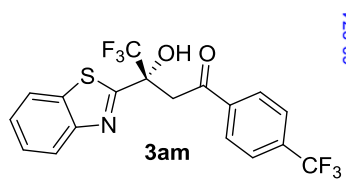
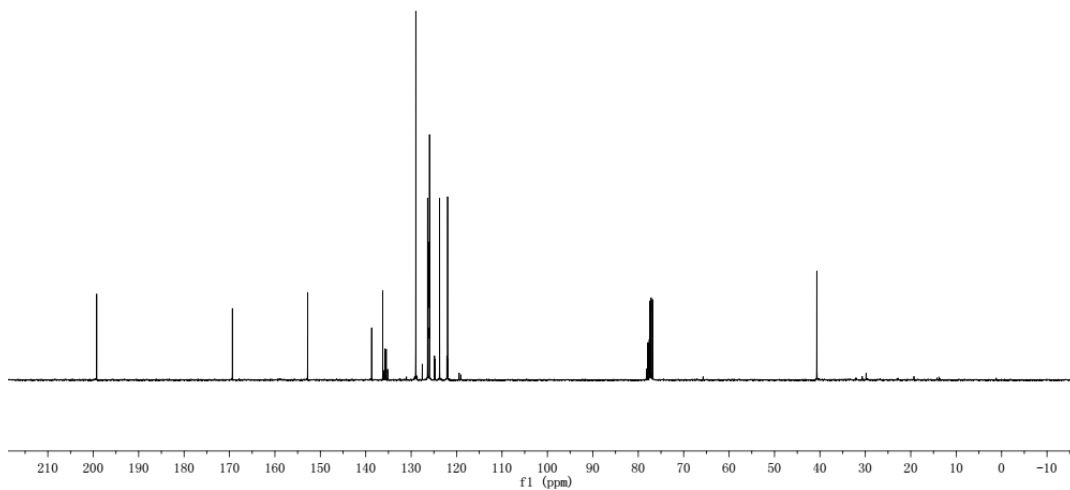
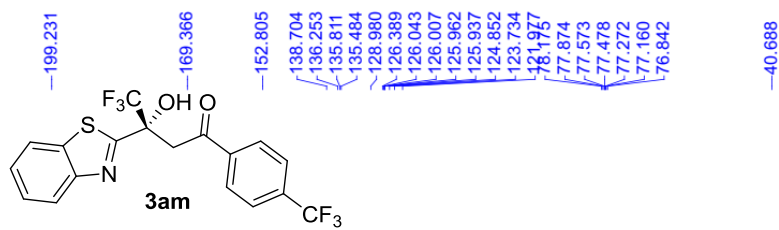


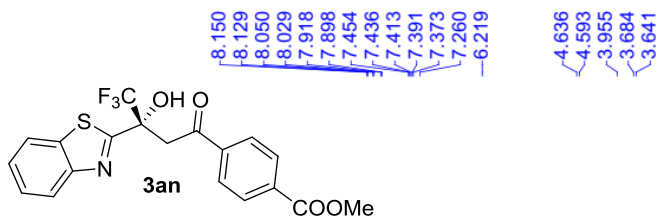
^{19}F NMR (376.5 MHz, CDCl_3)



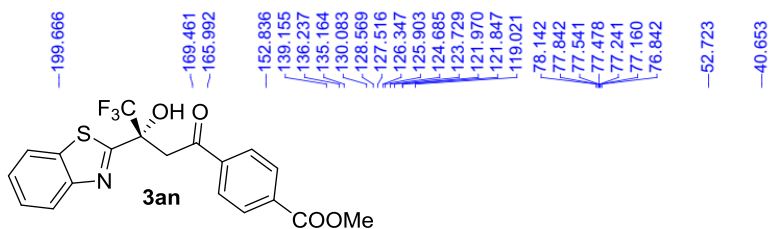
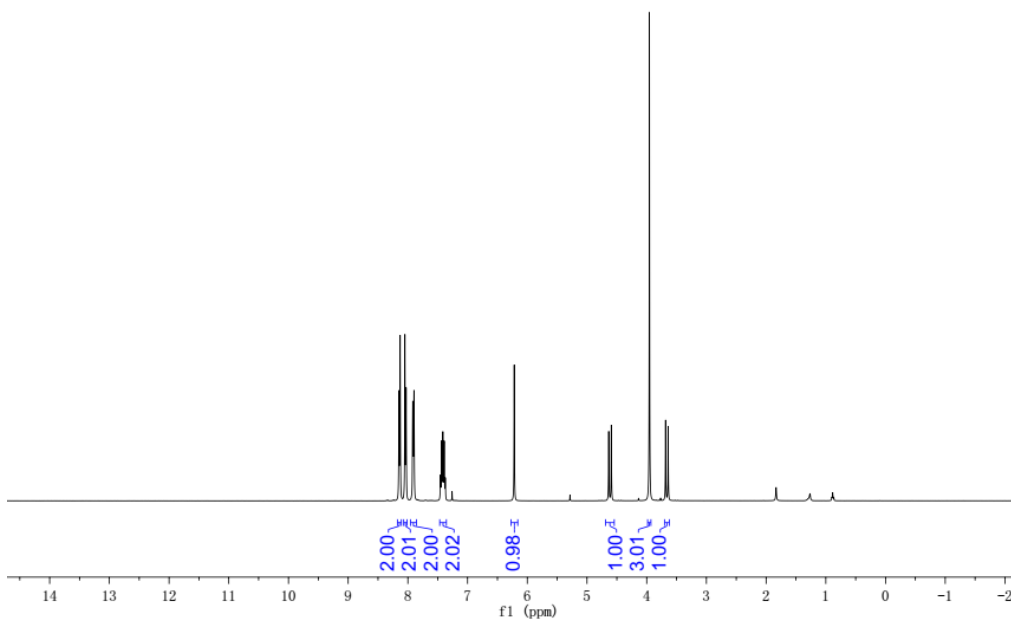
^1H NMR (400 MHz, CDCl_3)



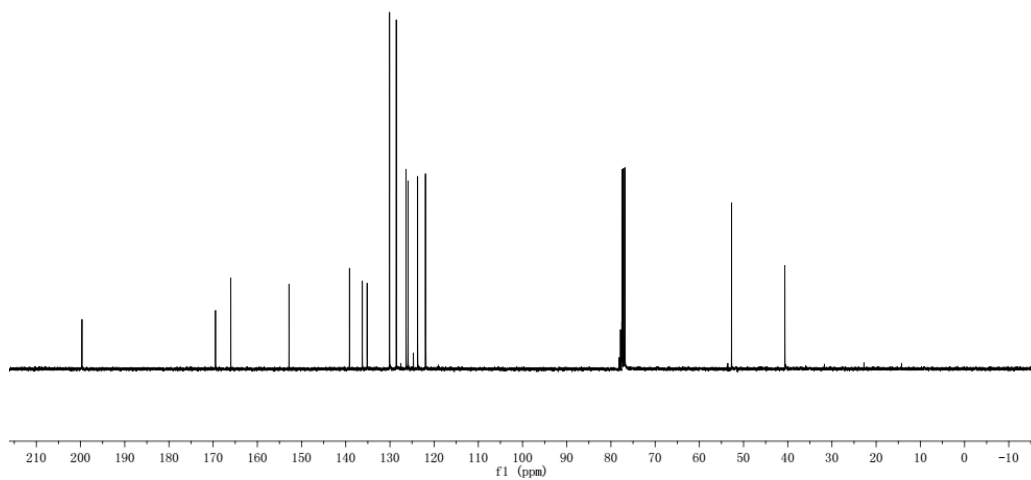


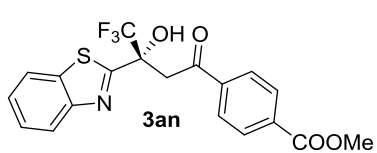


^1H NMR (400 MHz, CDCl_3)



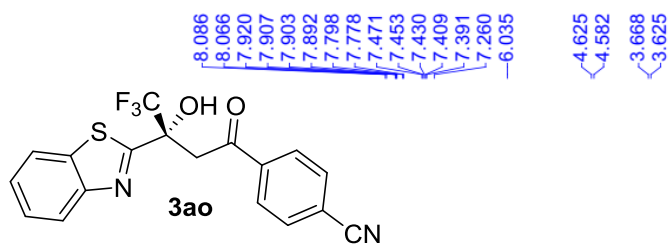
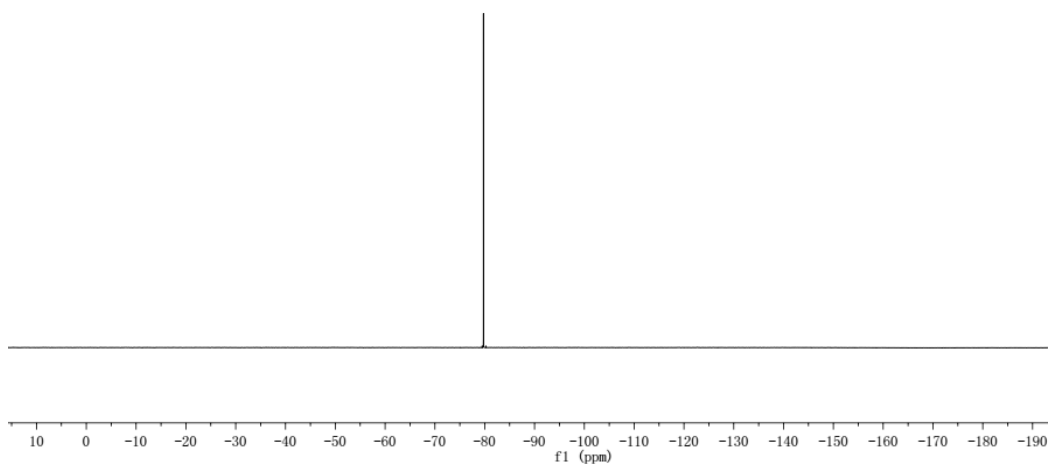
^{13}C NMR (100 MHz, CDCl_3)



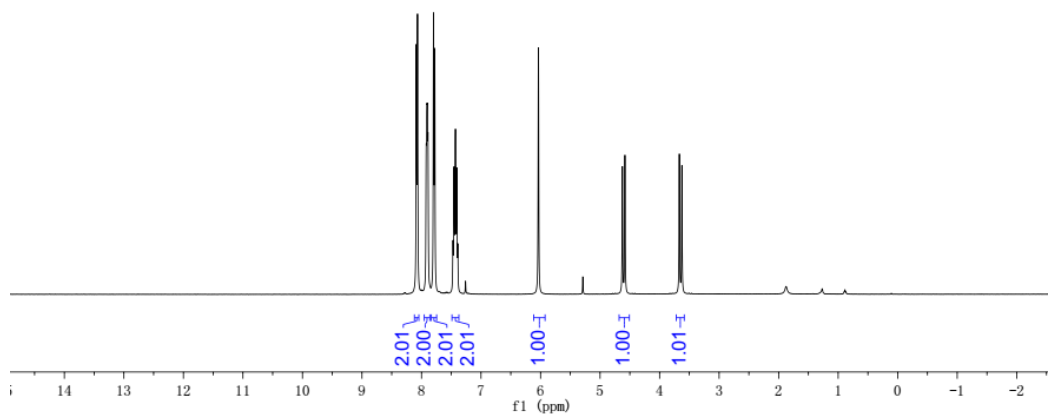


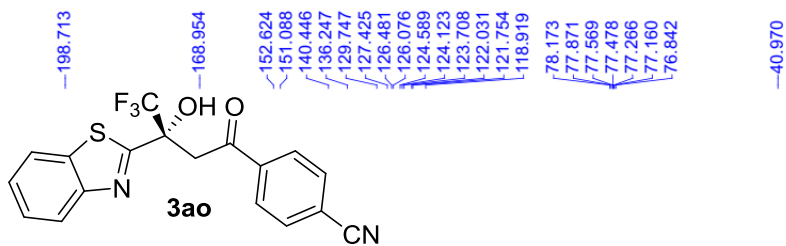
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¹⁹F NMR (376.5 MHz, CDCl₃)

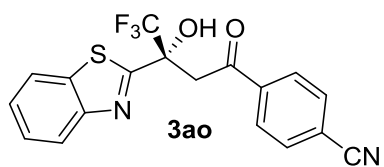
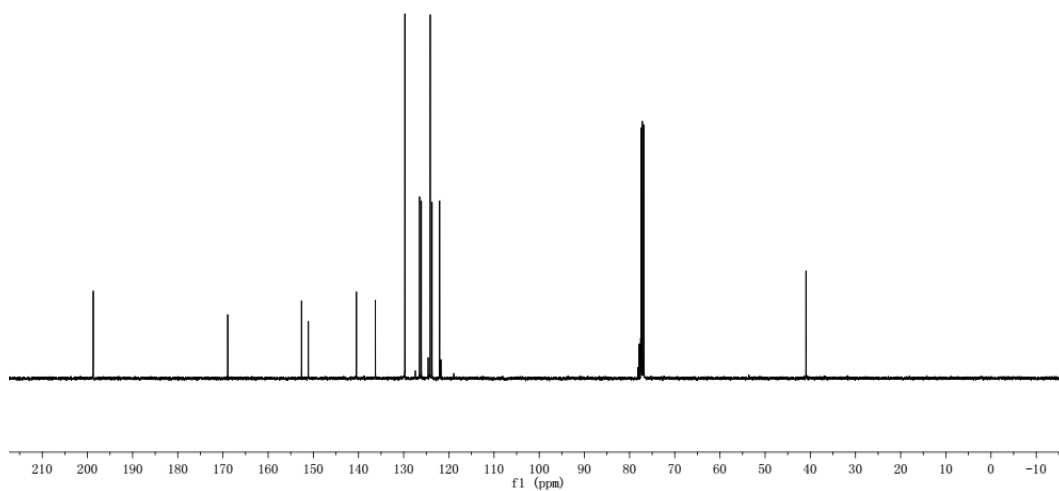


¹H NMR (400 MHz, CDCl₃)

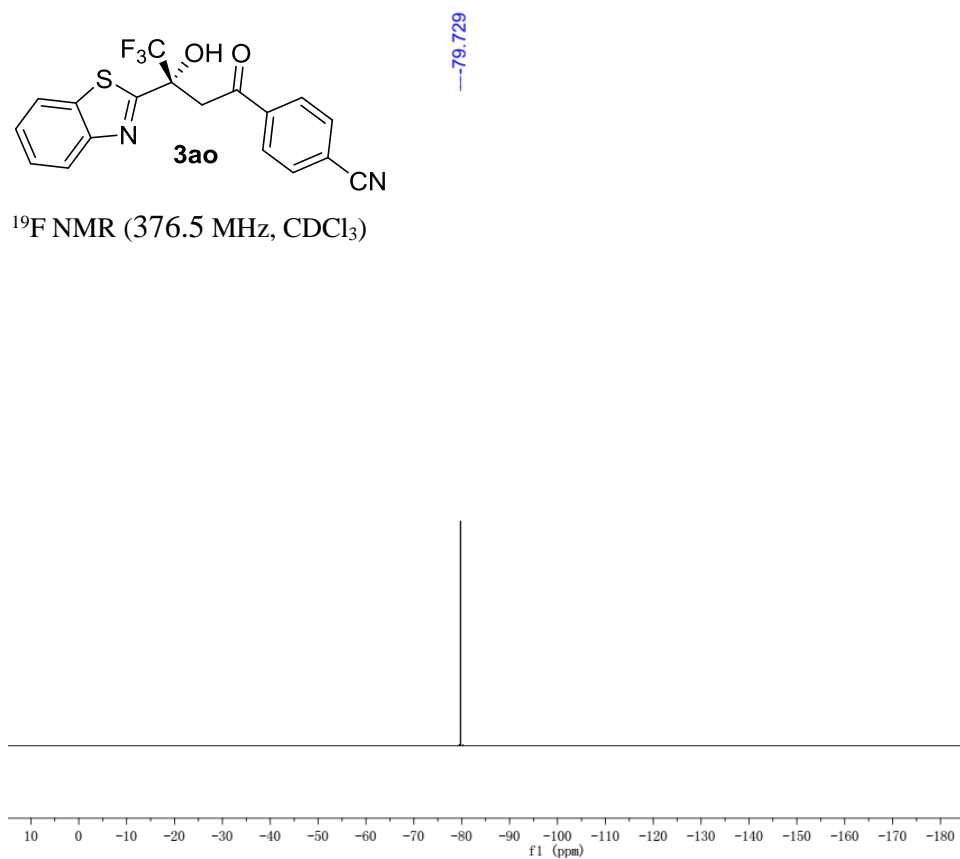


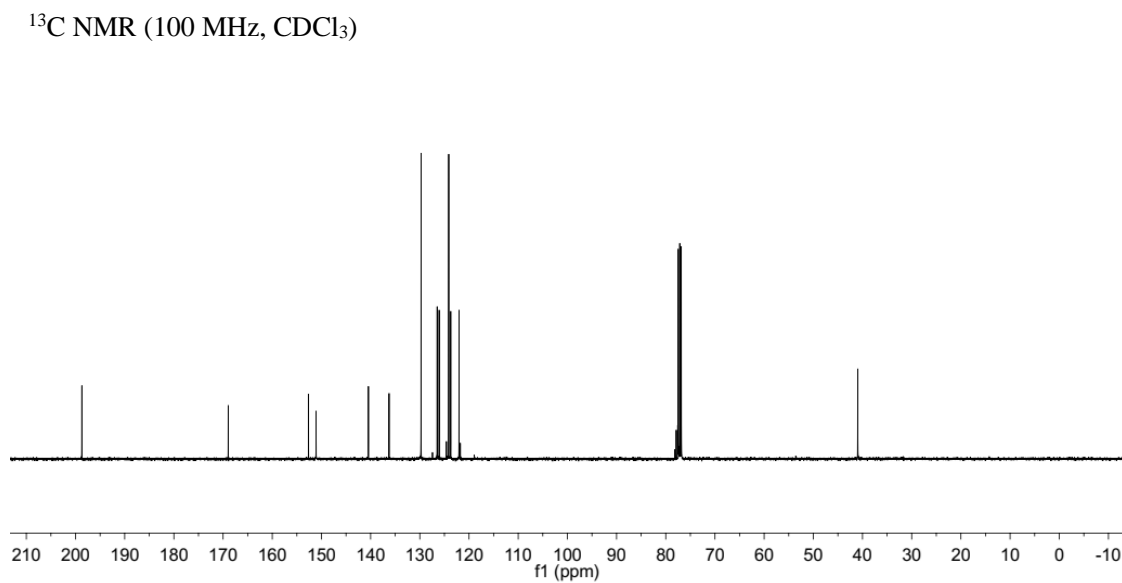
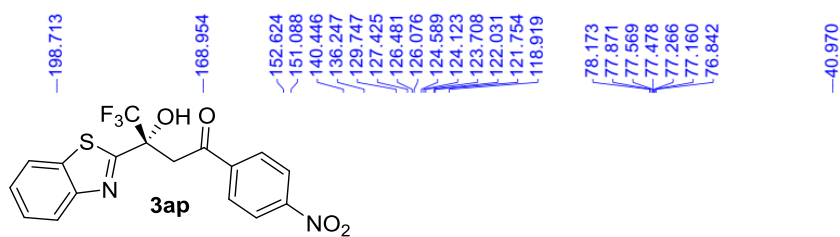
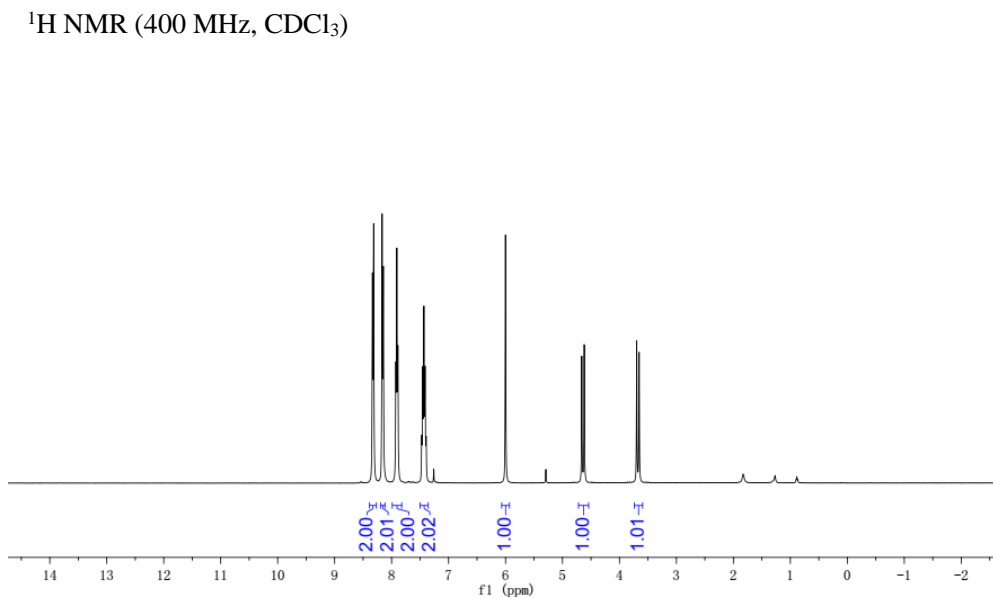
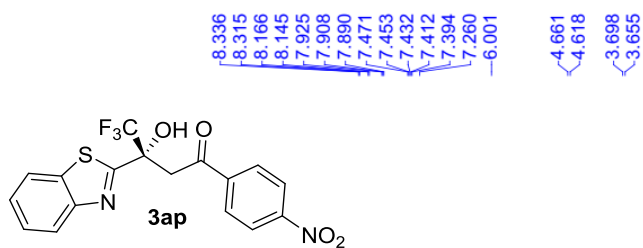


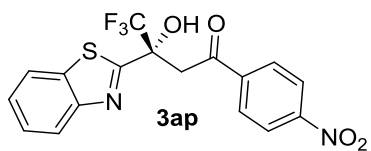
^{13}C NMR (100 MHz, CDCl_3)



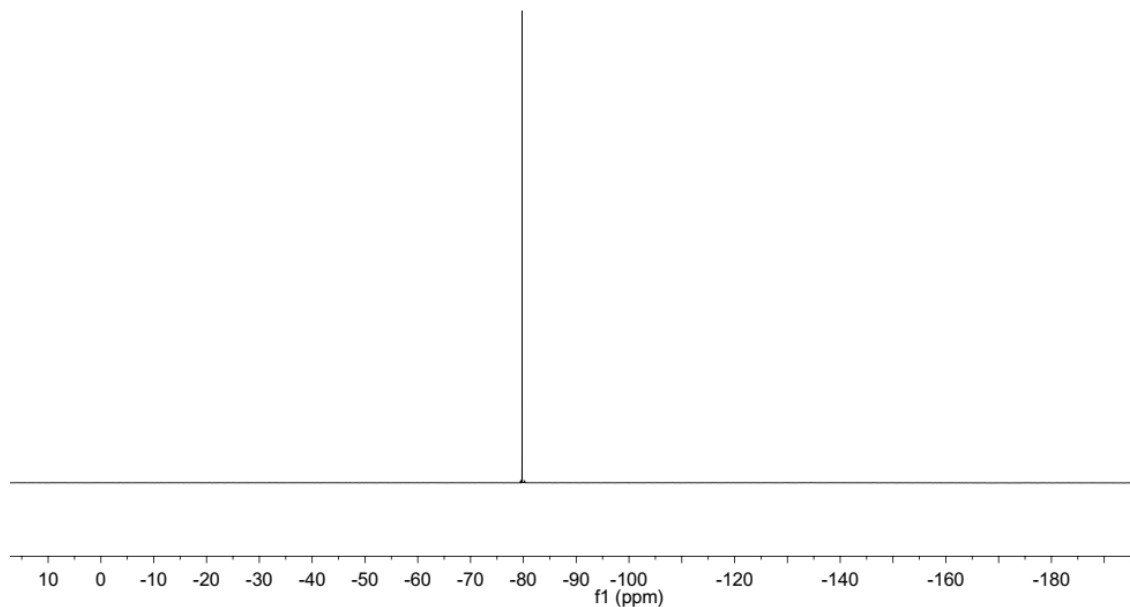
^{19}F NMR (376.5 MHz, CDCl_3)



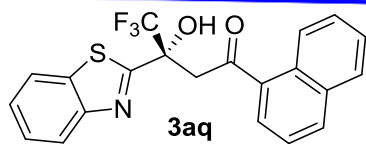




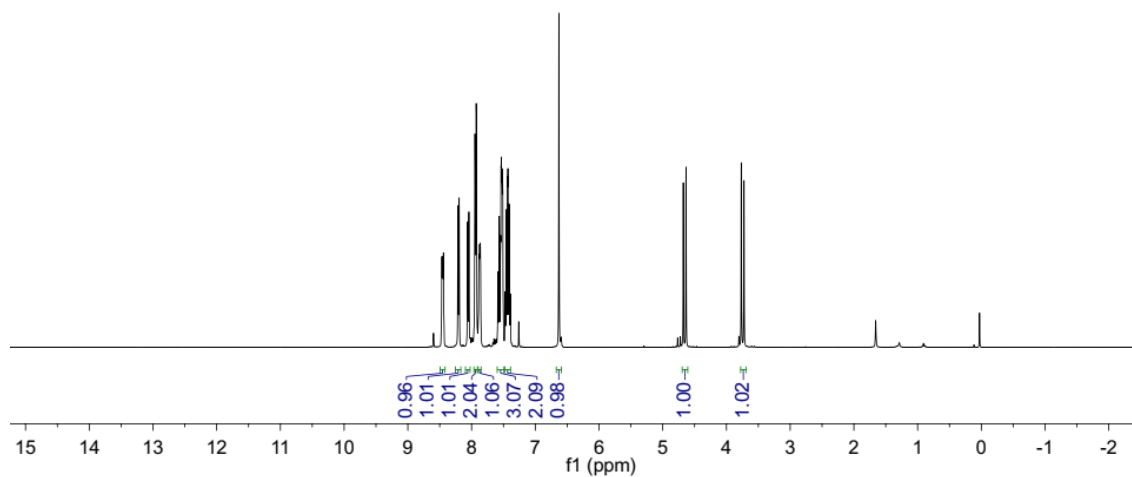
^{19}F NMR (376.5 MHz, CDCl_3)

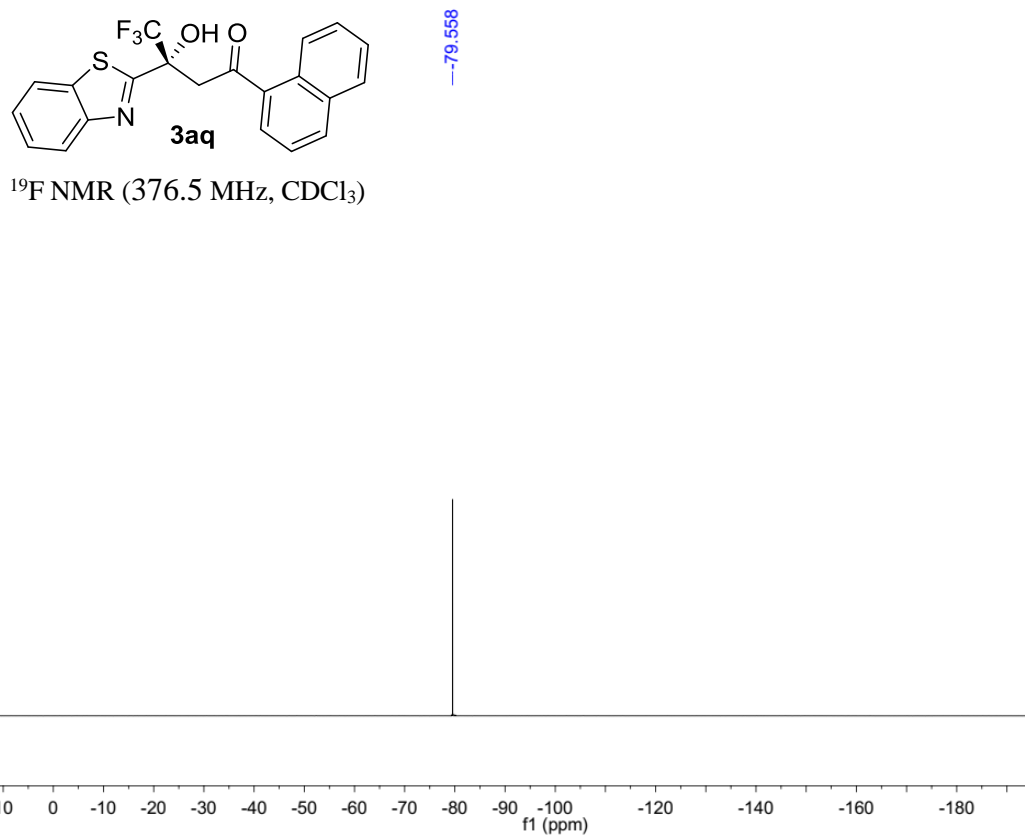
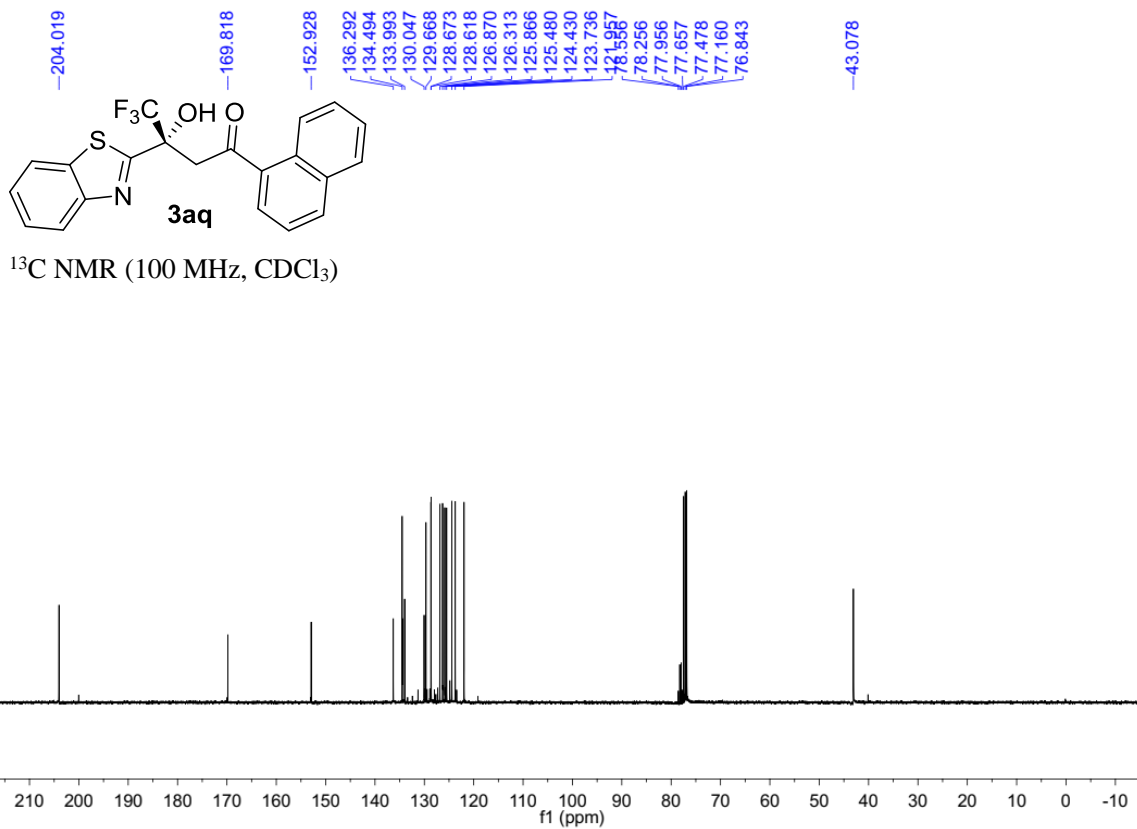


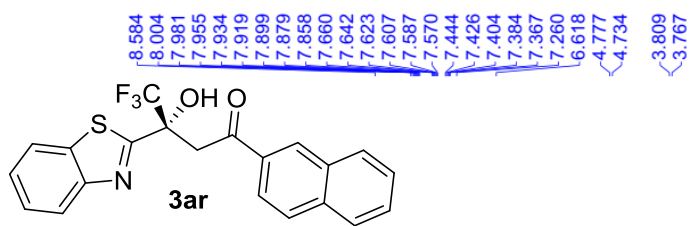
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 7.583
 7.565
 7.543
 7.538
 7.534
 7.530
 7.525
 7.522
 7.514
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 3.767
 3.725



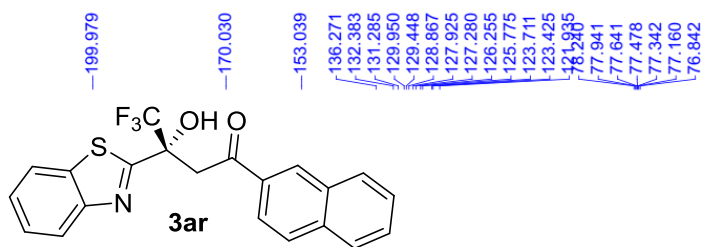
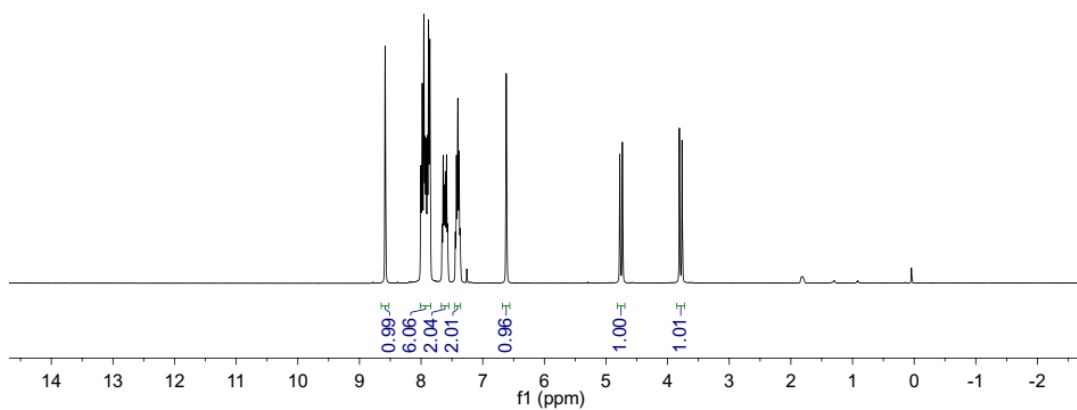
^1H NMR (400 MHz, CDCl_3)



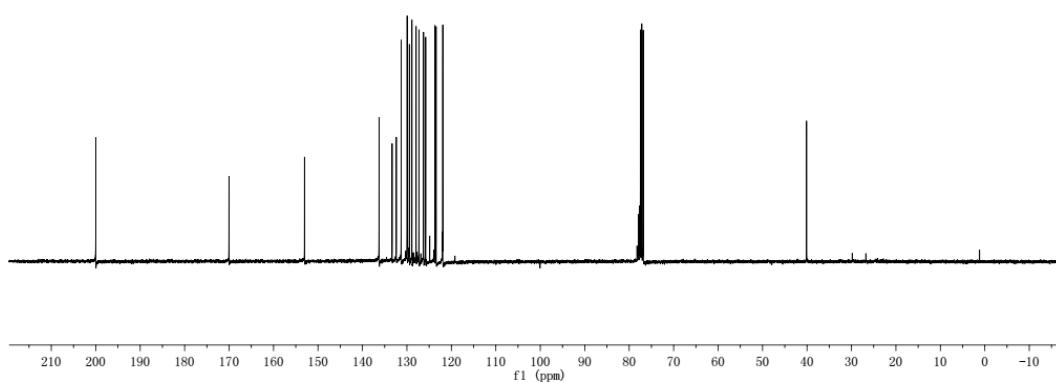


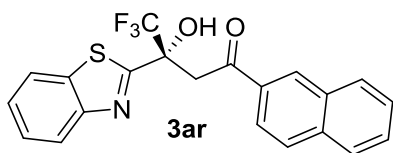


^1H NMR (400 MHz, CDCl_3)

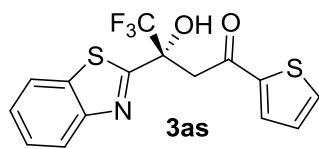
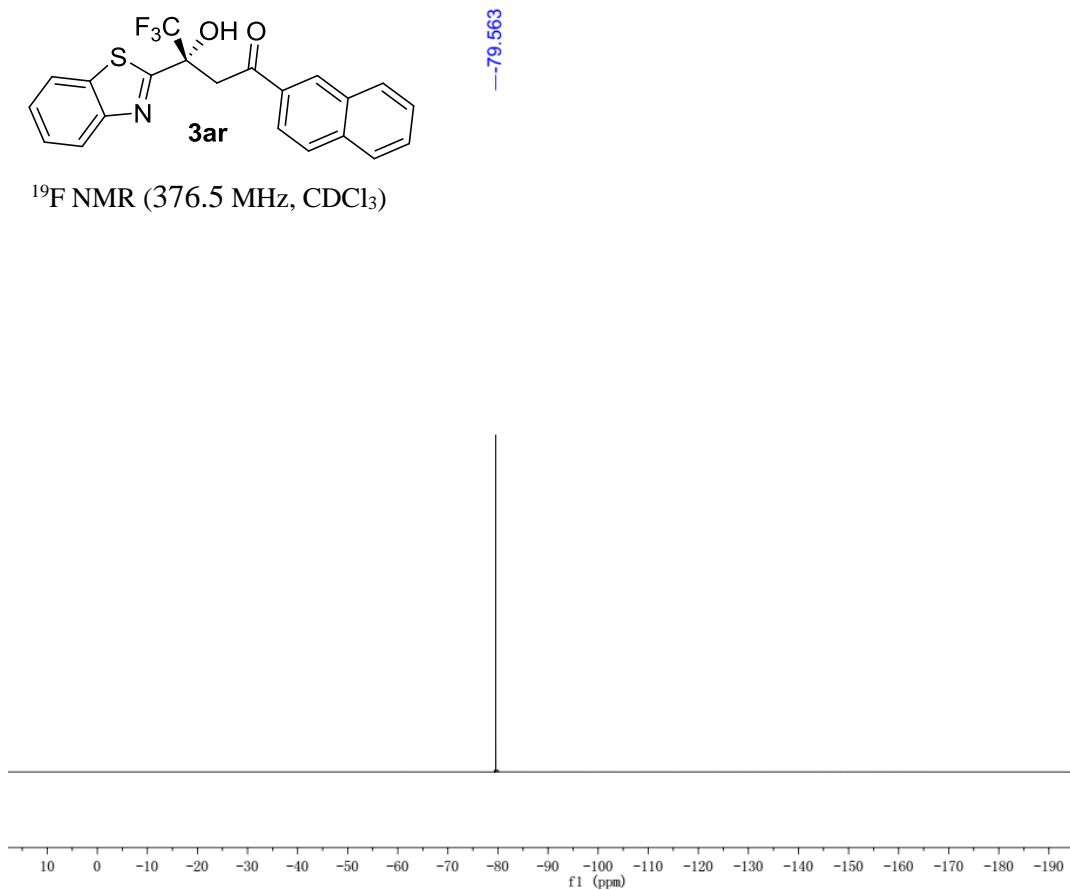


^{13}C NMR (100 MHz, CDCl_3)

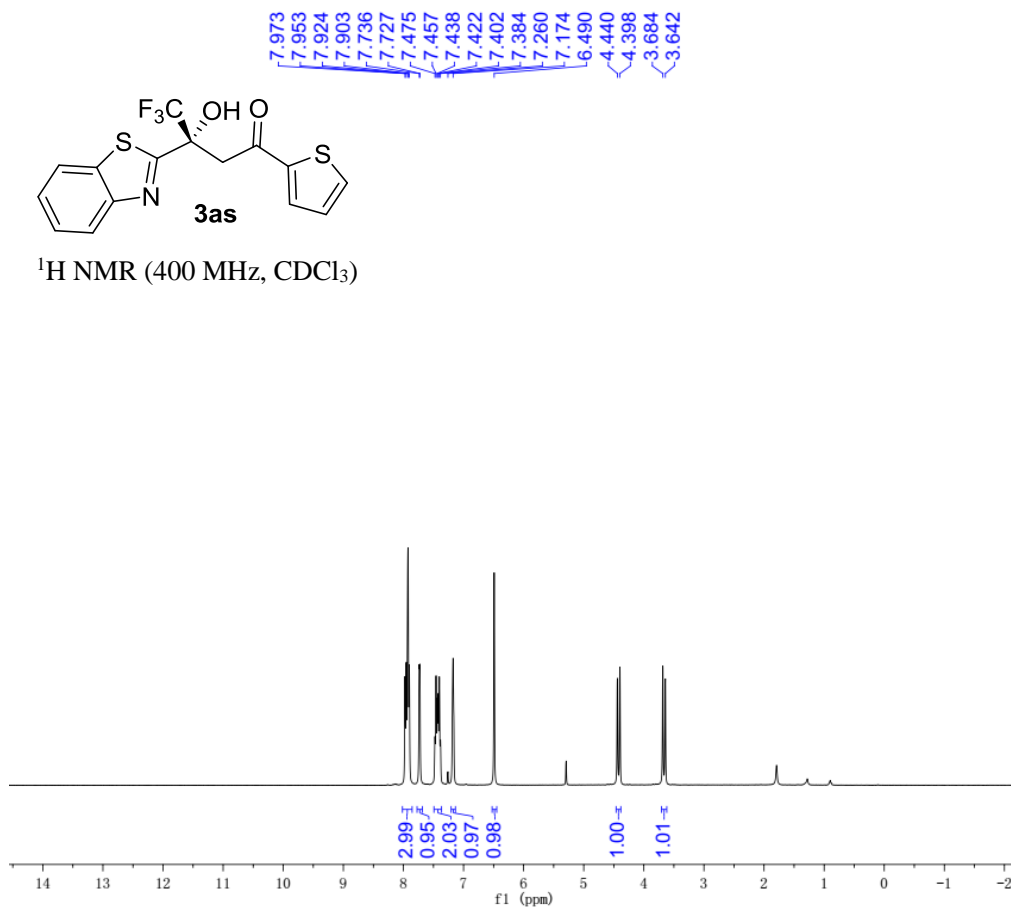


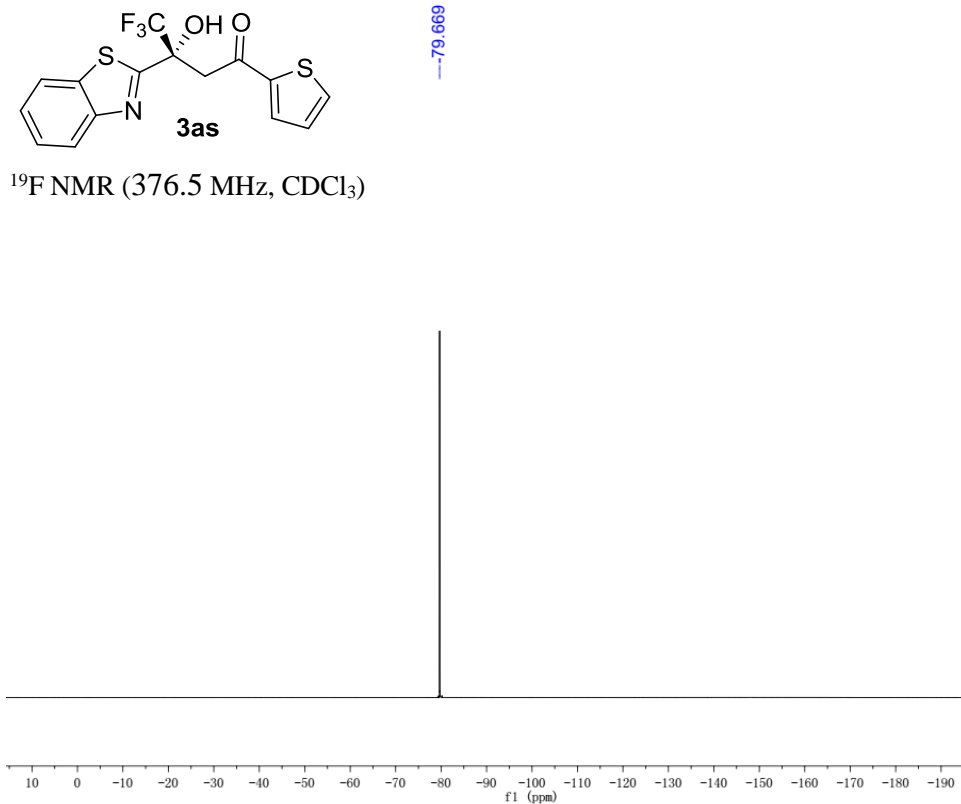
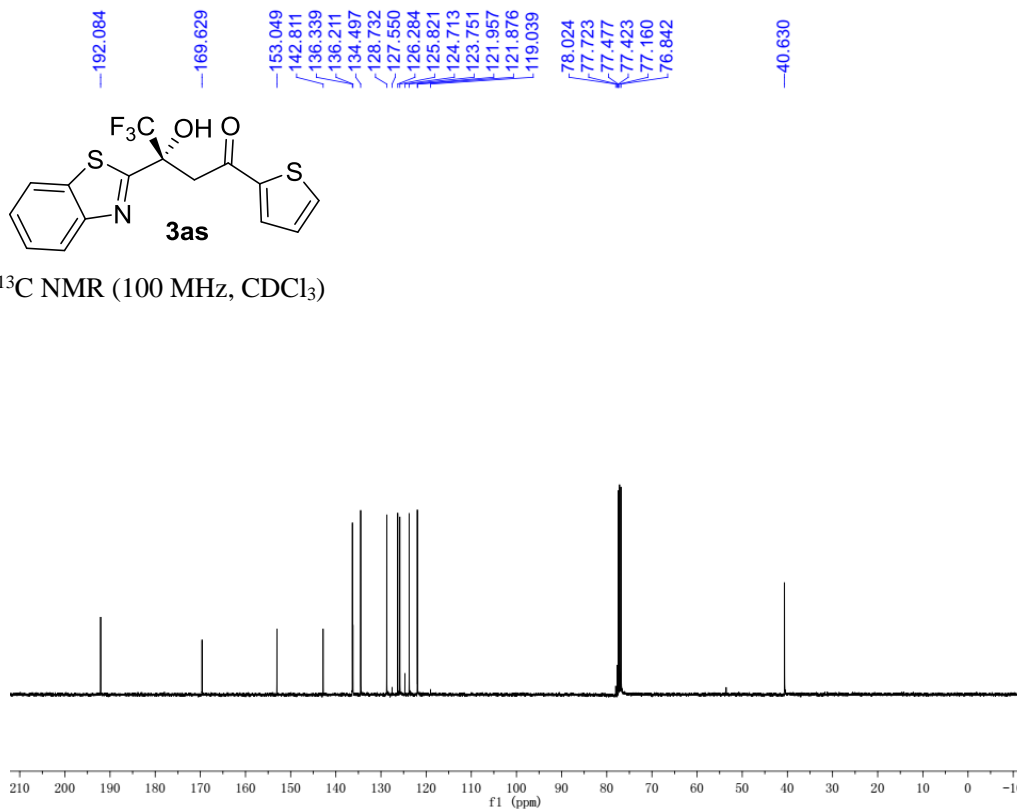


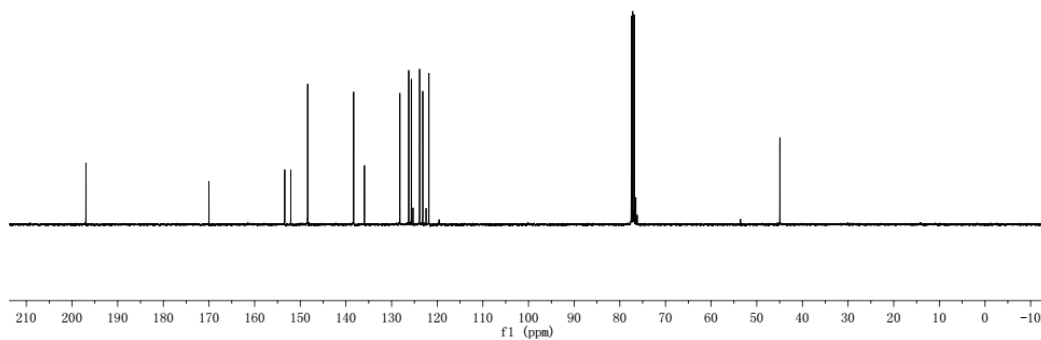
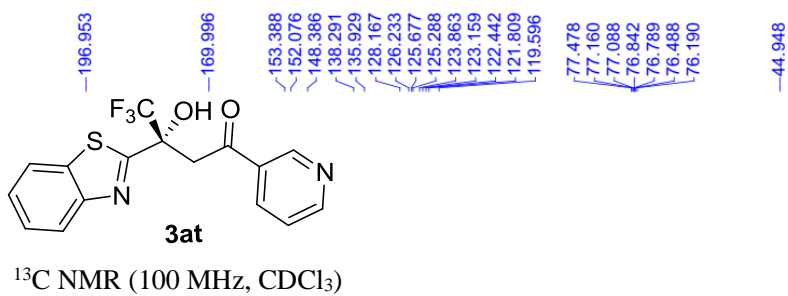
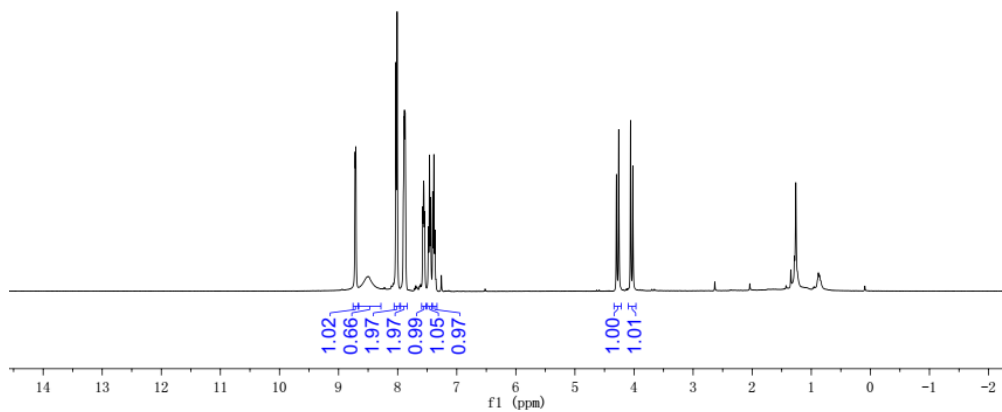
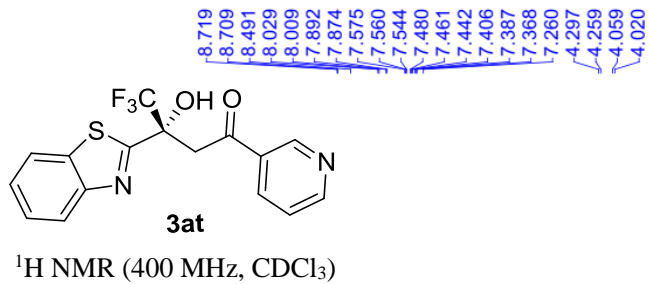
^{19}F NMR (376.5 MHz, CDCl_3)

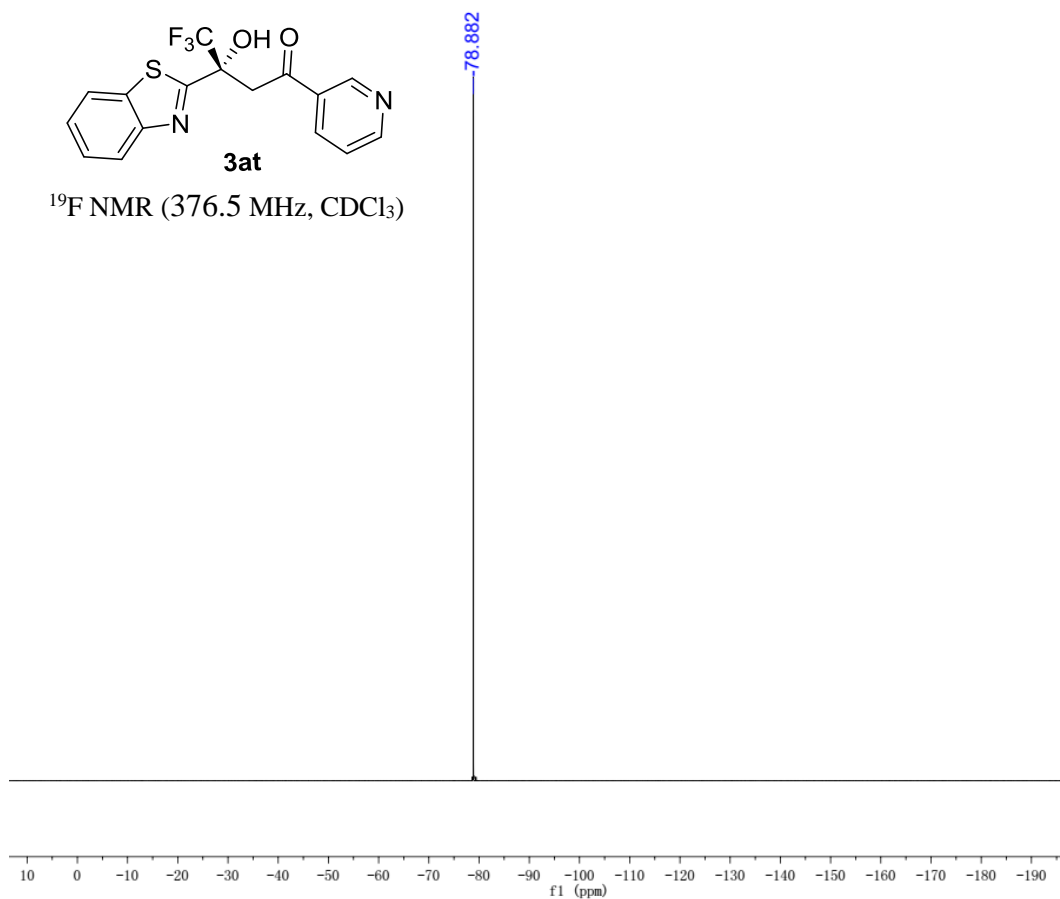
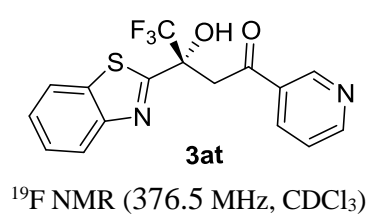


^1H NMR (400 MHz, CDCl_3)

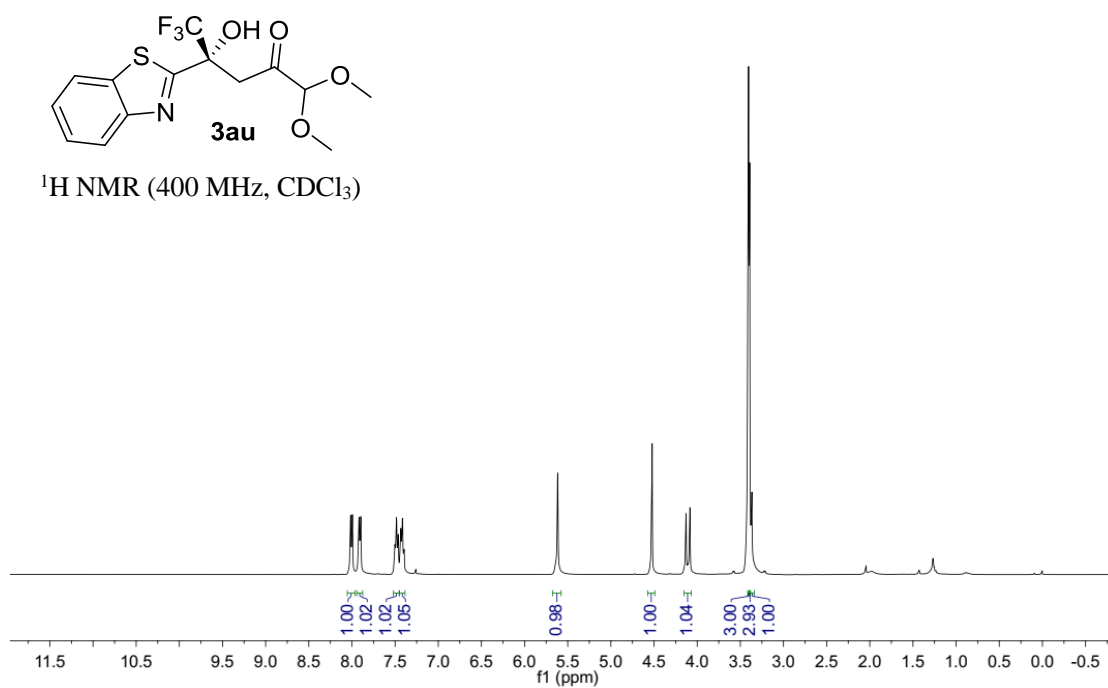
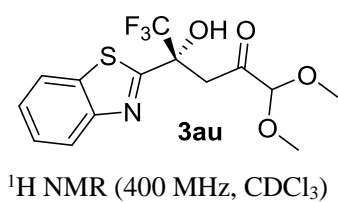




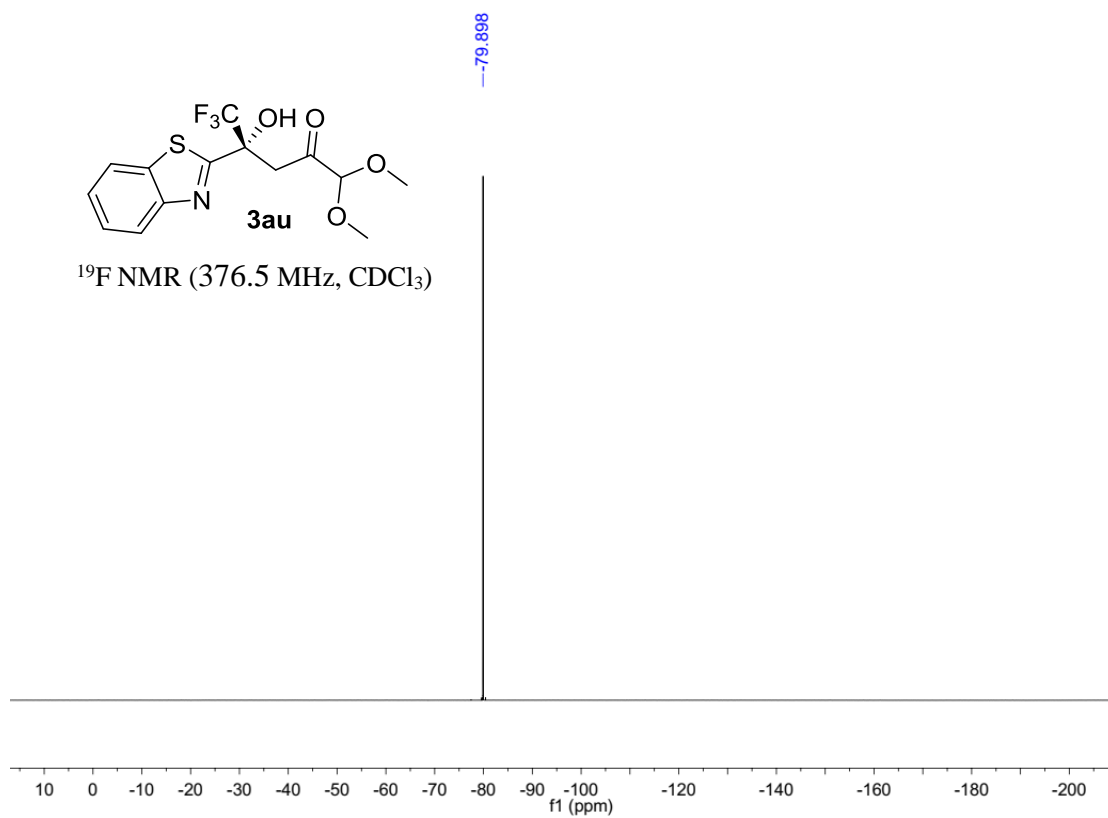
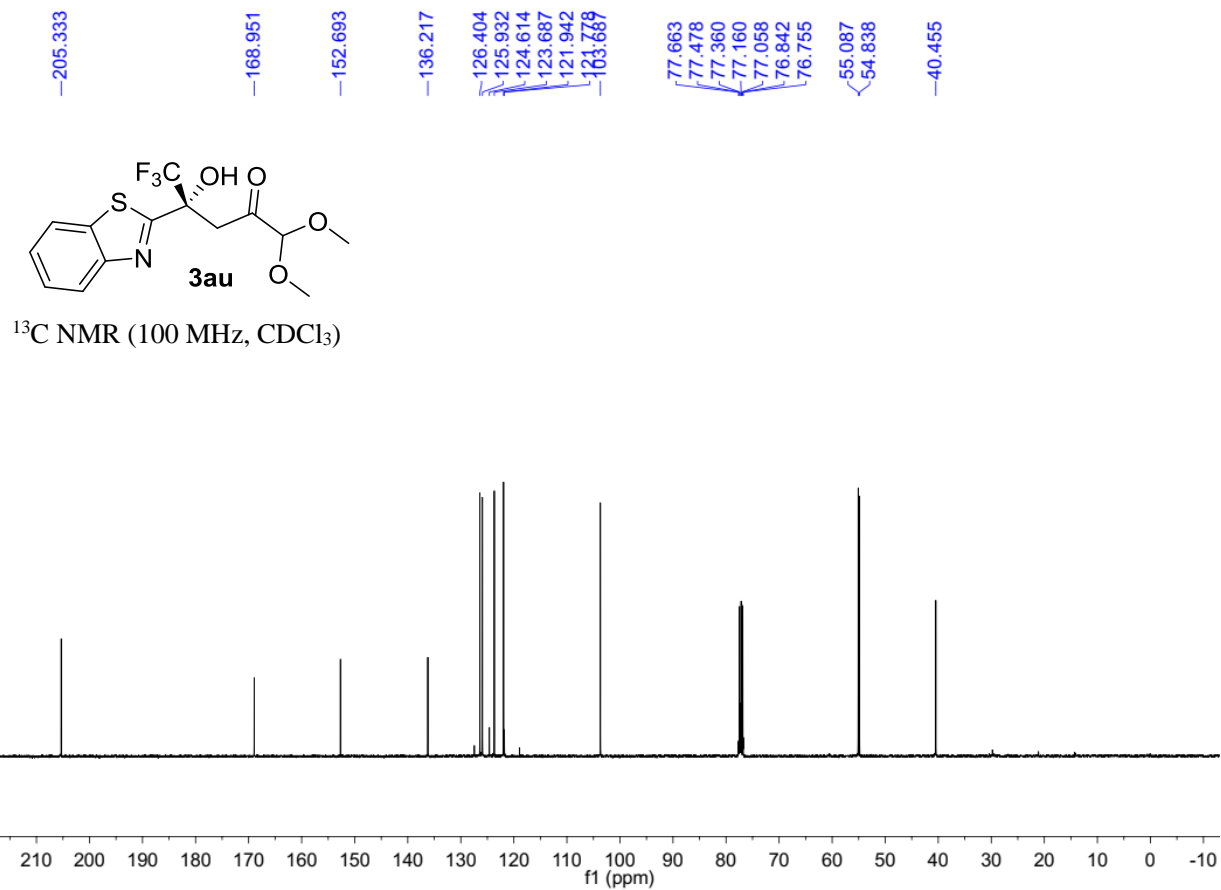


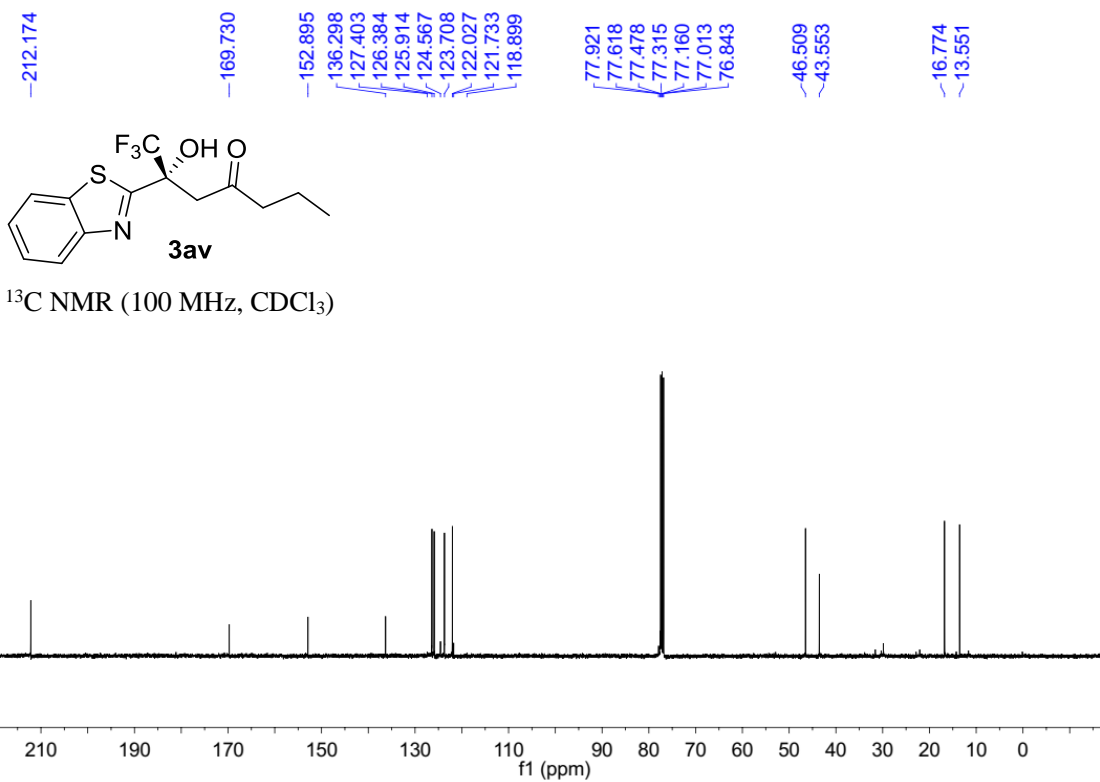
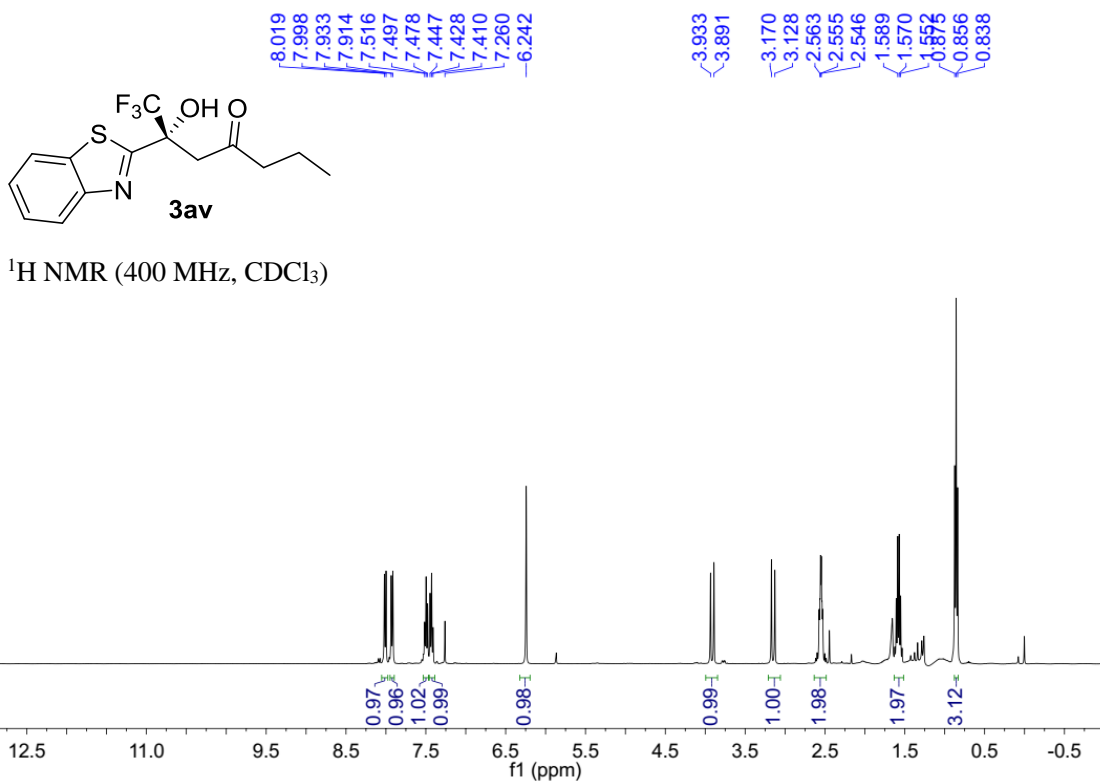


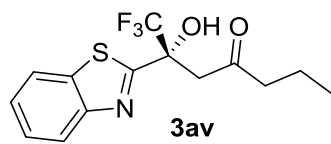
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 -4.521
 -4.129
 -4.084
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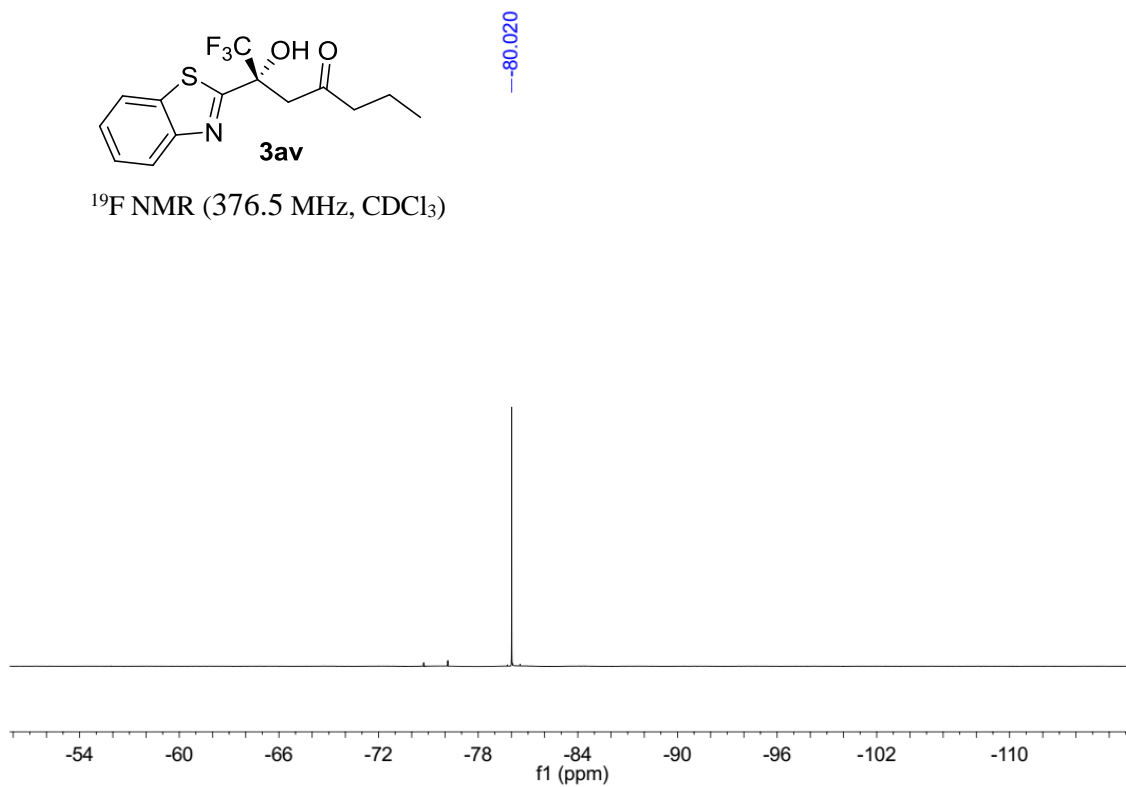
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 3.00
 2.93
 1.00







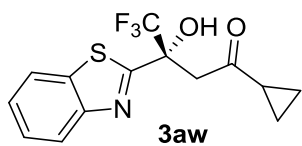
^{19}F NMR (376.5 MHz, CDCl_3)



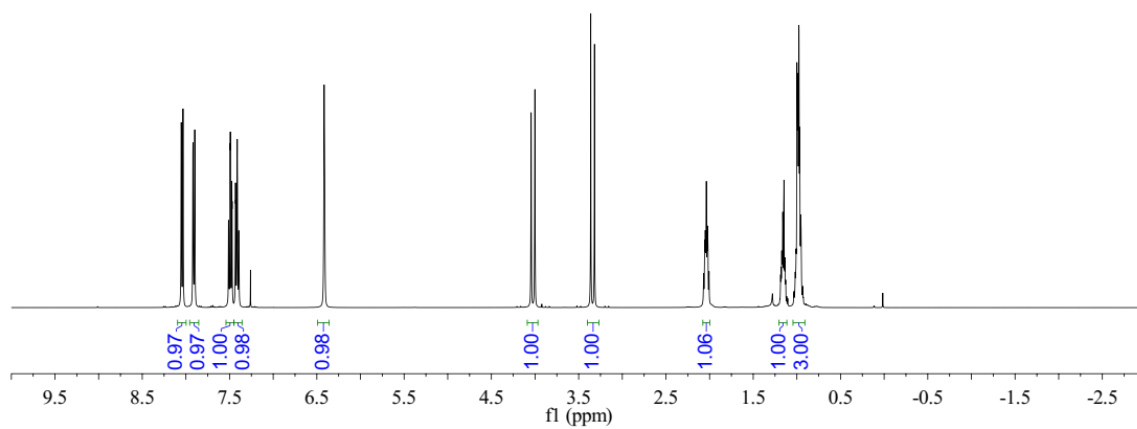
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7.391
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6.416

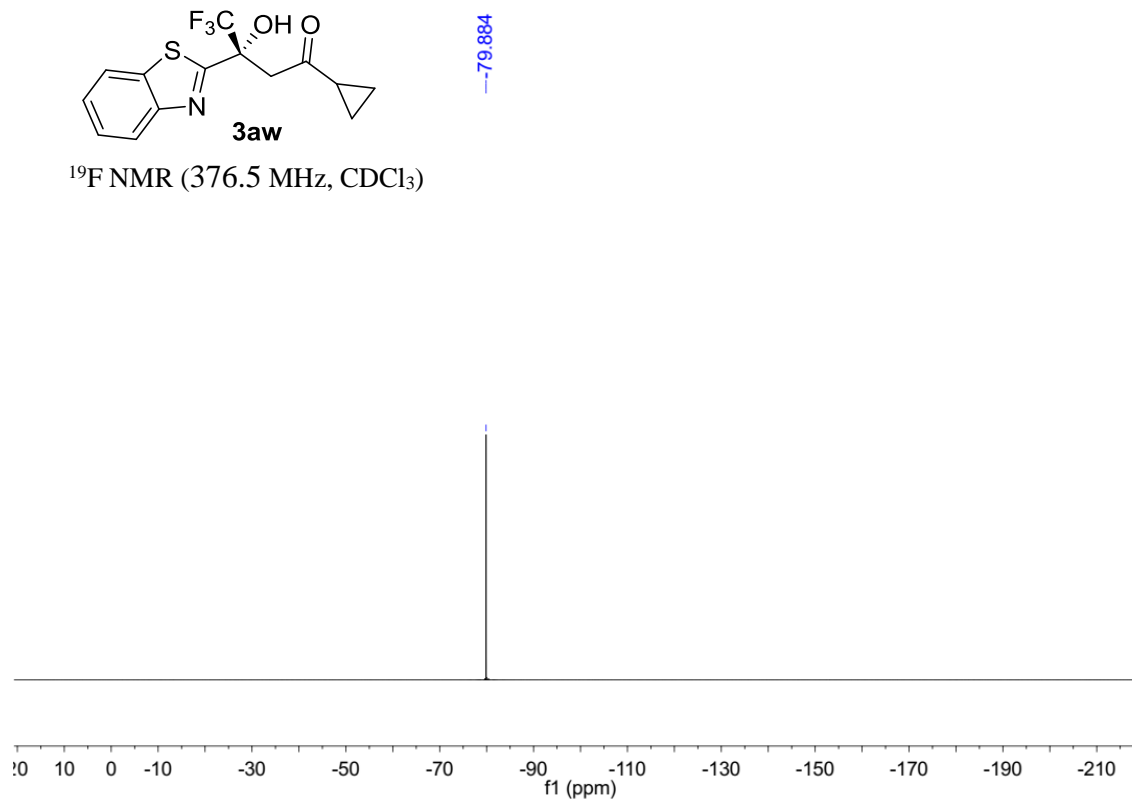
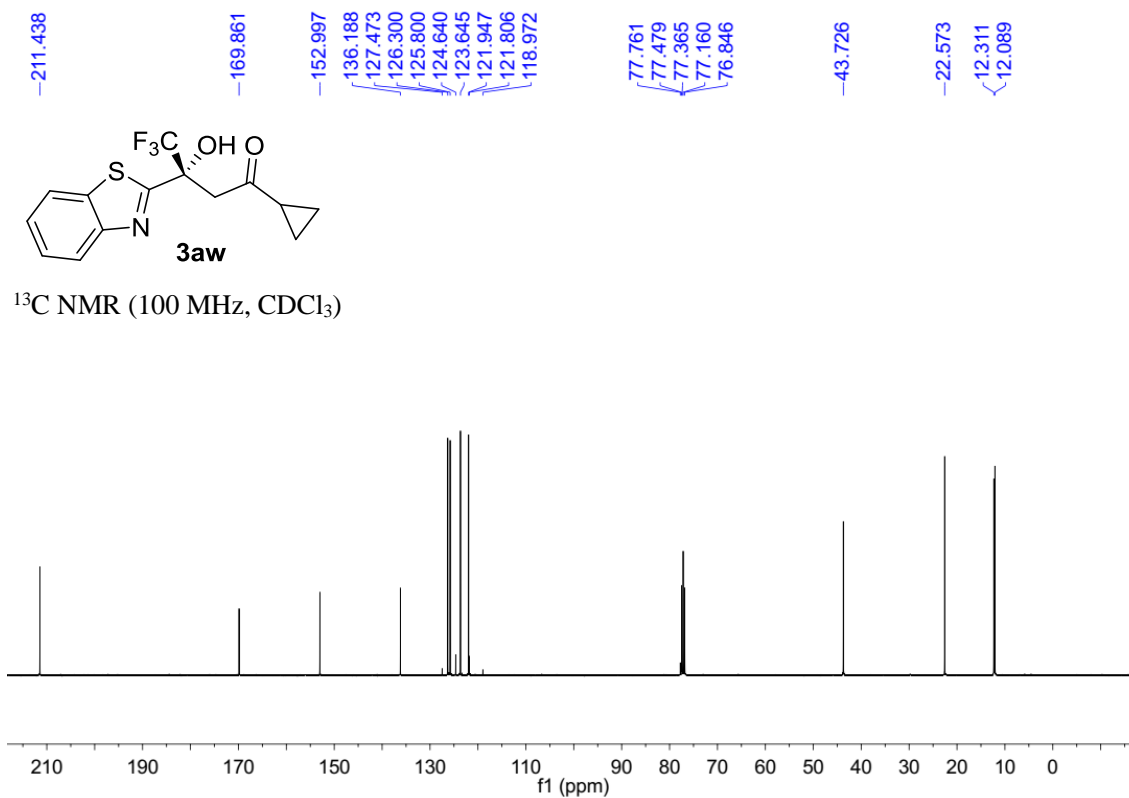
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4.002
3.362
3.319

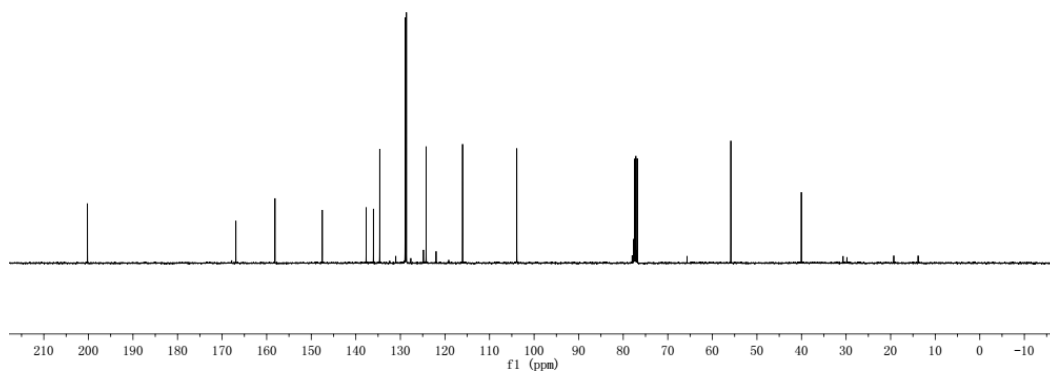
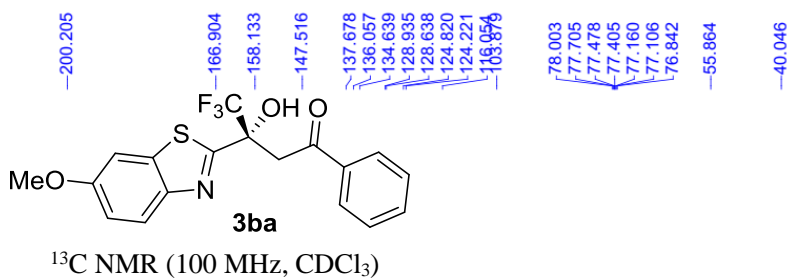
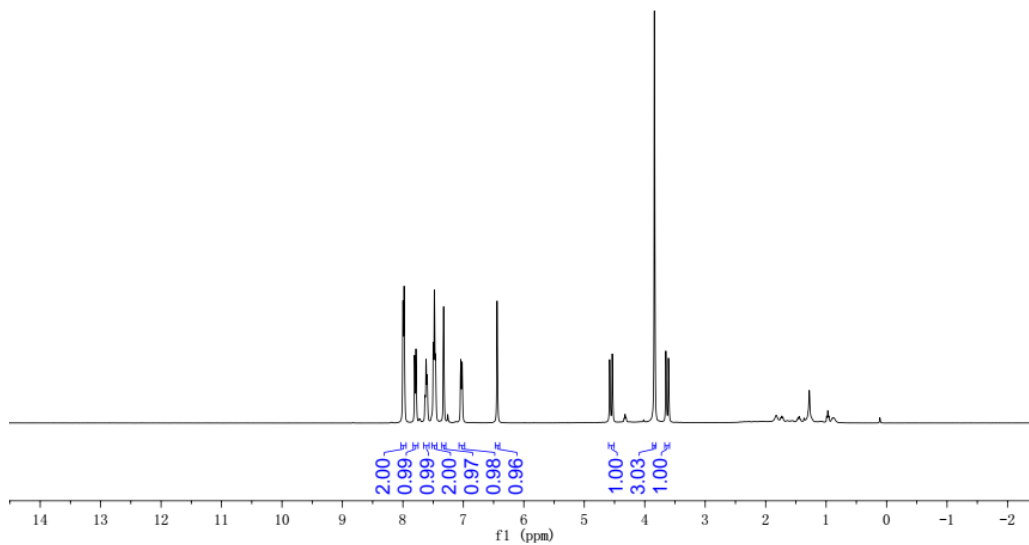
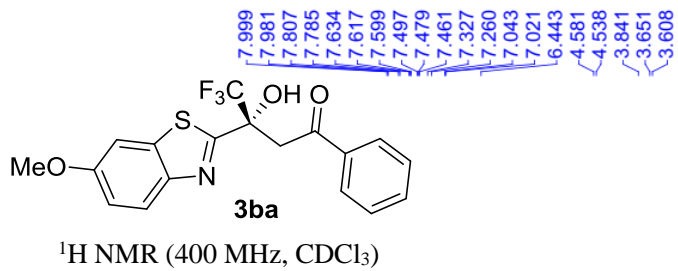
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1.173
1.169
1.162
1.148
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1.128
1.019
1.008
0.999
0.996
0.987
0.977
0.967
0.955

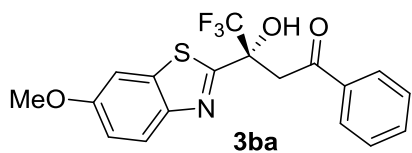


^1H NMR (400 MHz, CDCl_3)

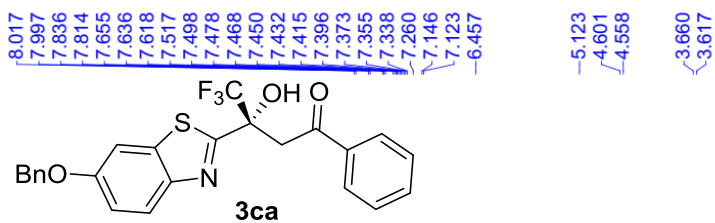
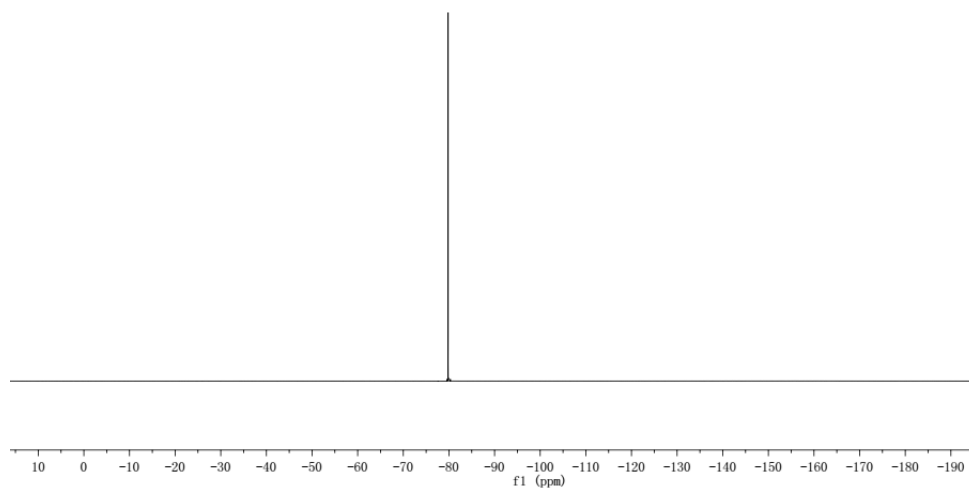




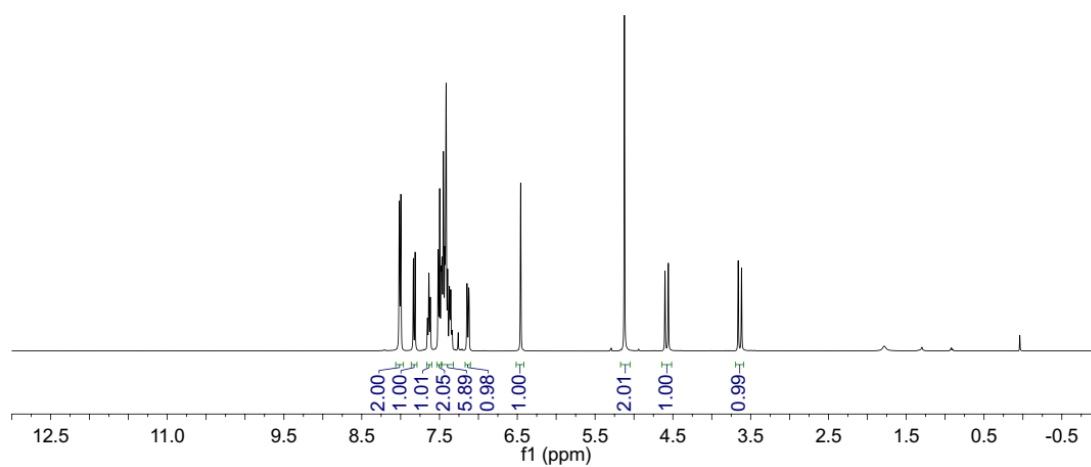


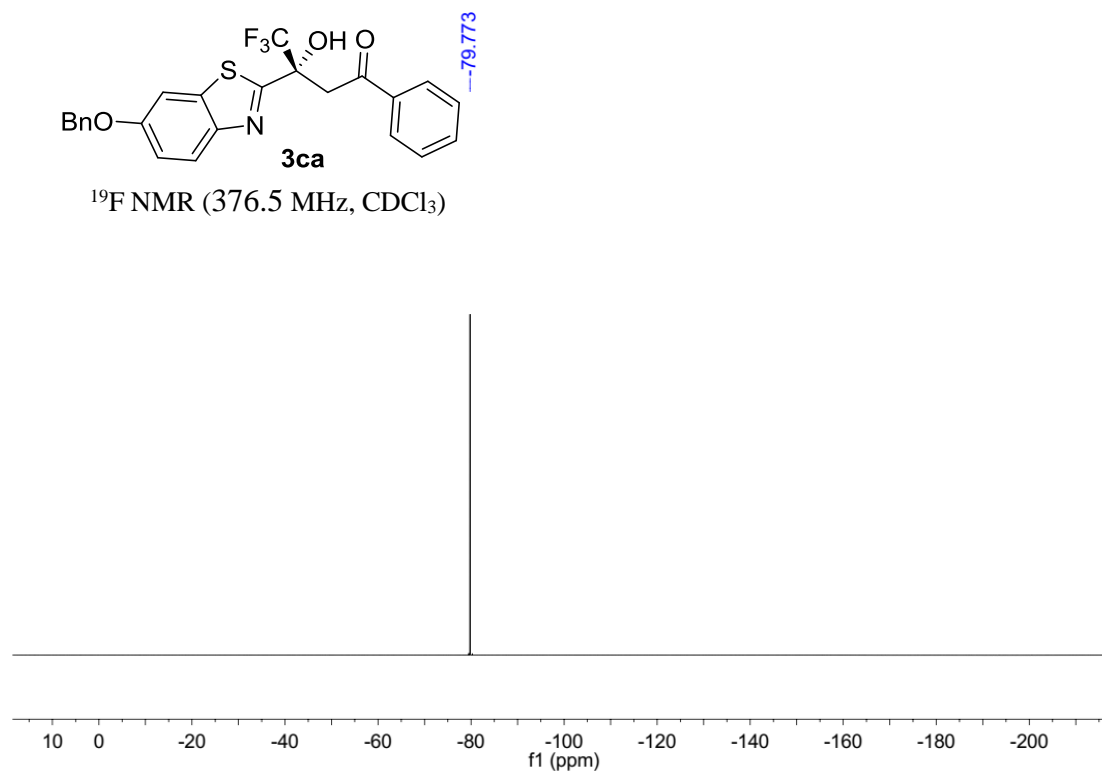
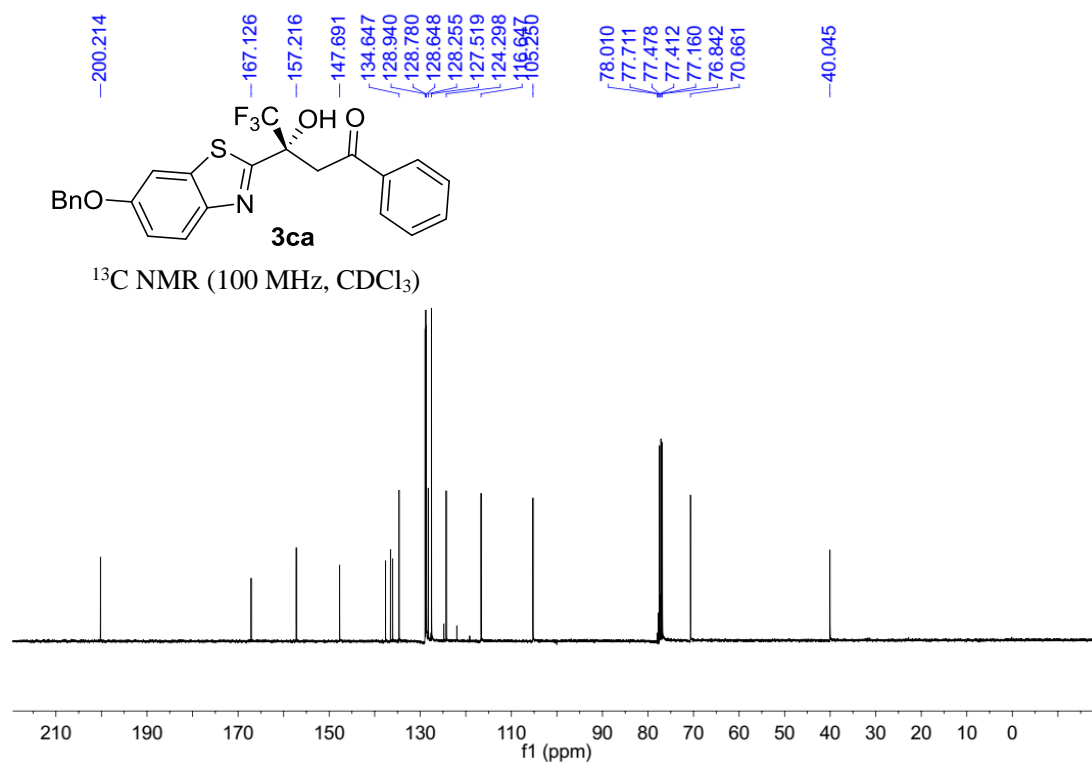


^{19}F NMR (376.5 MHz, CDCl_3)

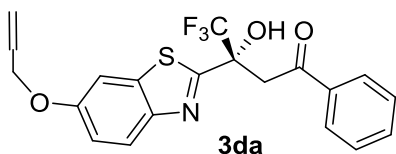


^1H NMR (400 MHz, CDCl_3)

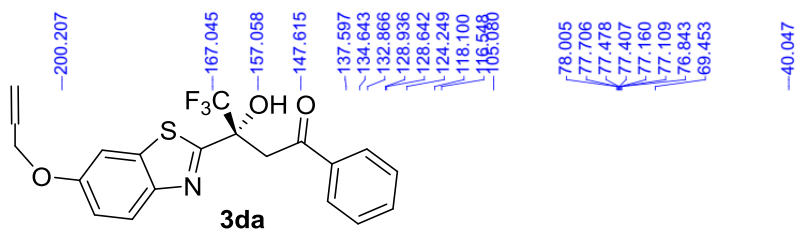
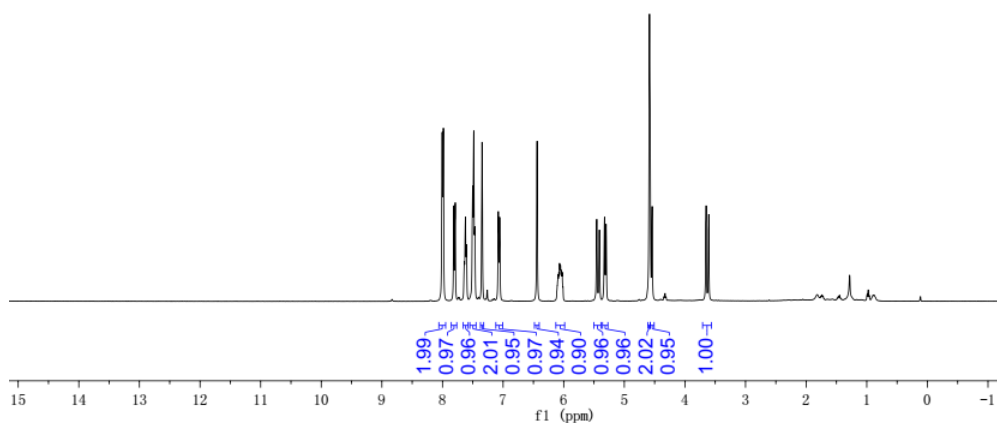




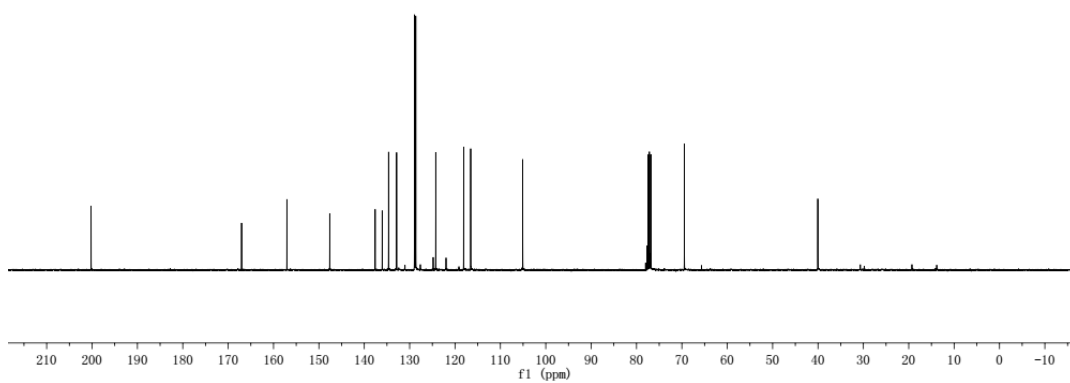
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7.079
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6.440
6.094
6.081
6.067
6.054
6.051
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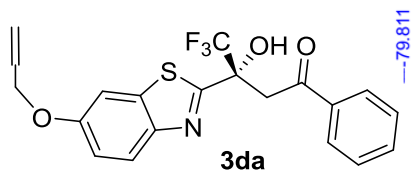


$^1\text{H NMR}$ (400 MHz, CDCl_3)

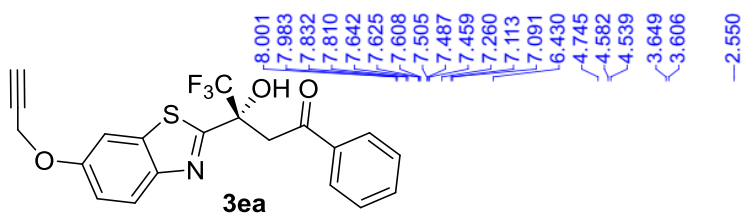
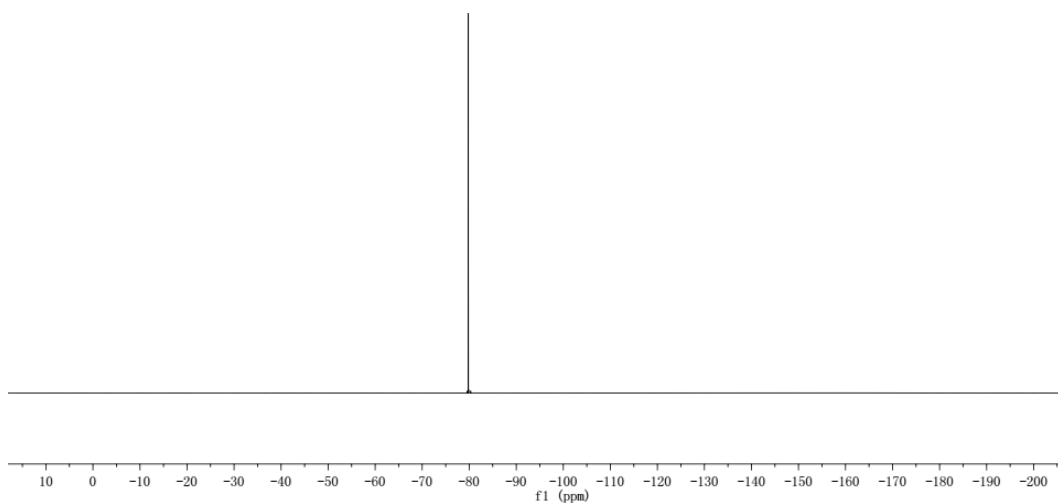


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

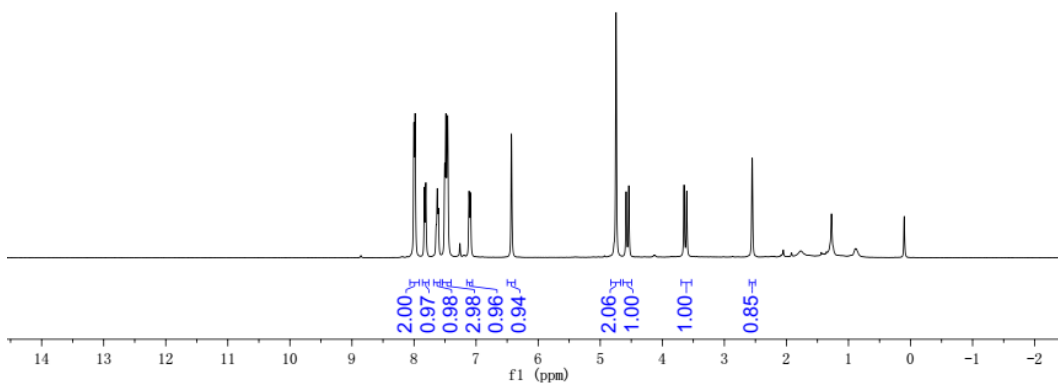


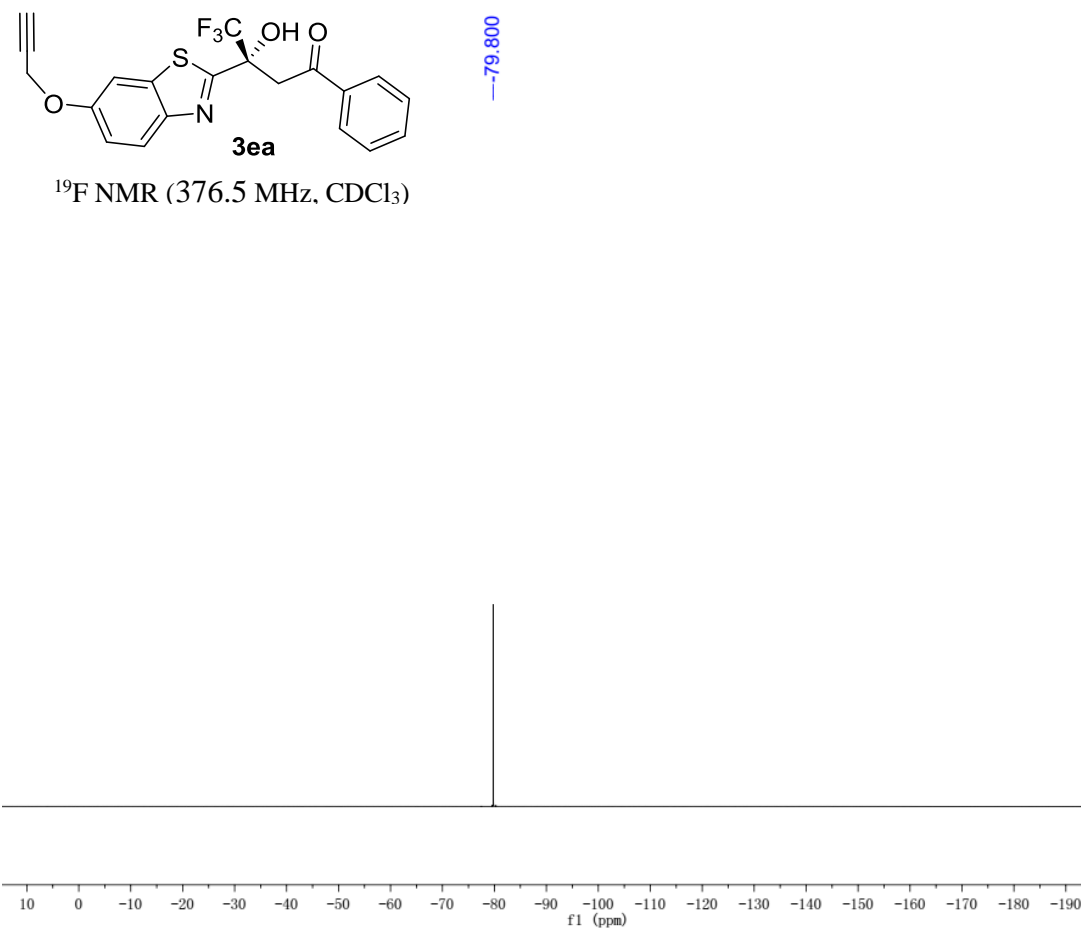
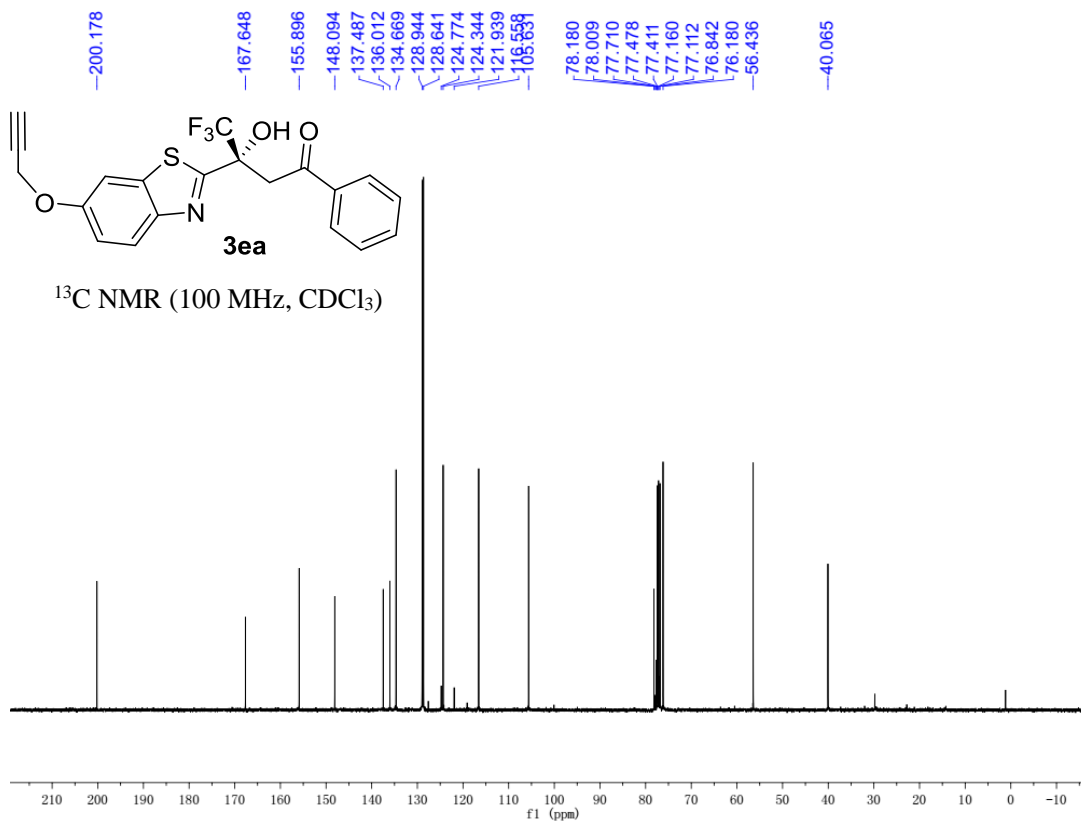


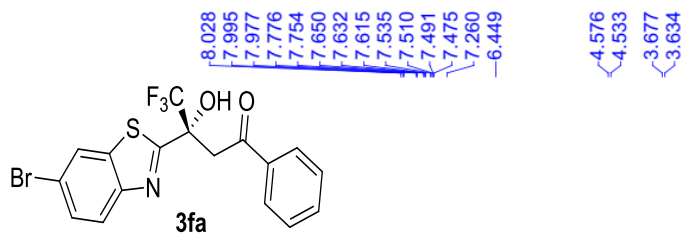
^{19}F NMR (376.5 MHz, CDCl_3)



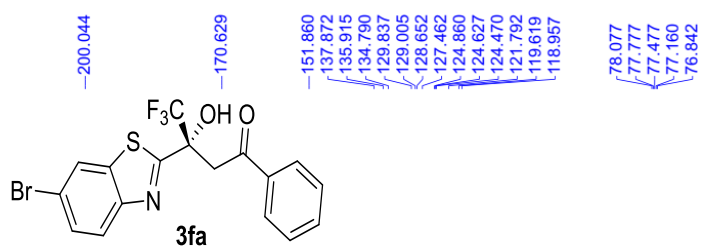
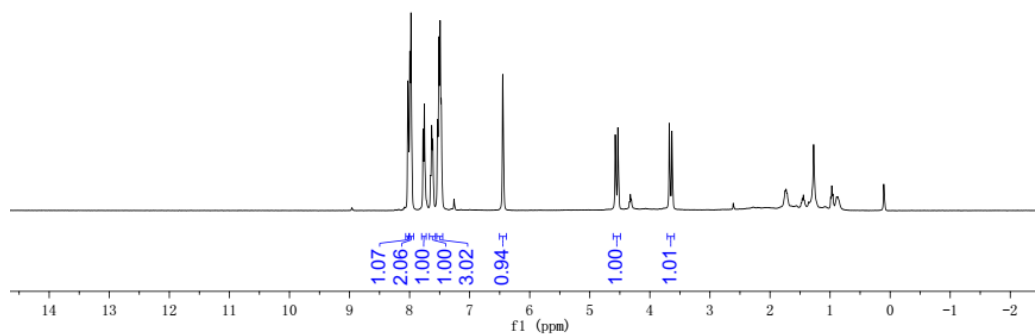
^1H NMR (400 MHz, CDCl_3)



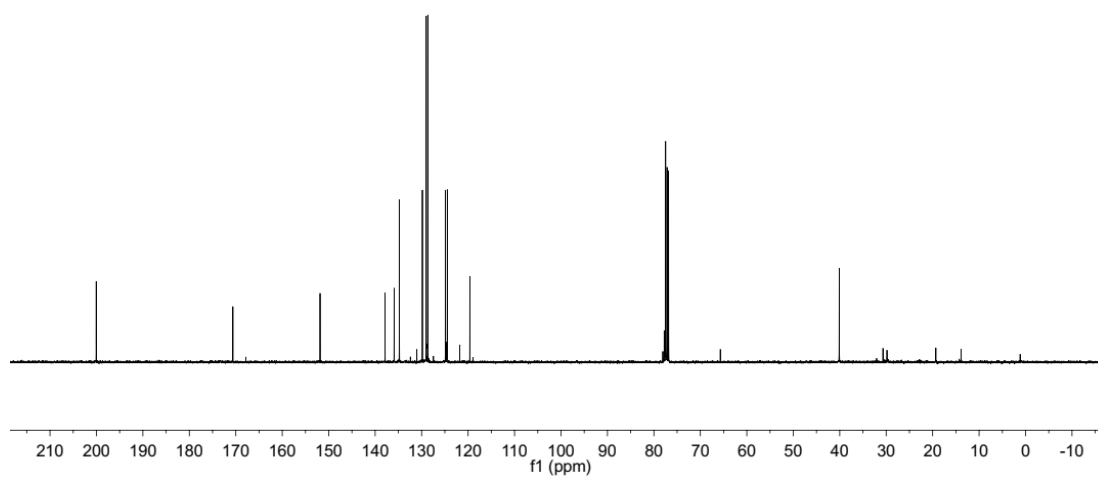


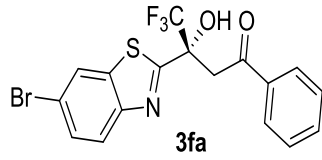


$^1\text{H NMR}$ (400 MHz, CDCl_3)

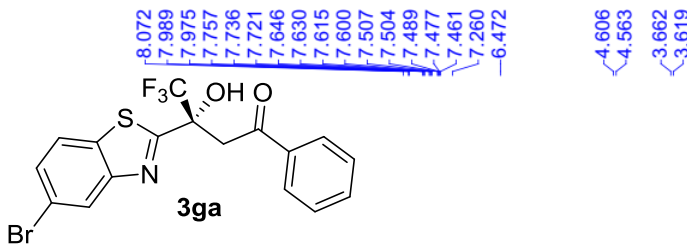
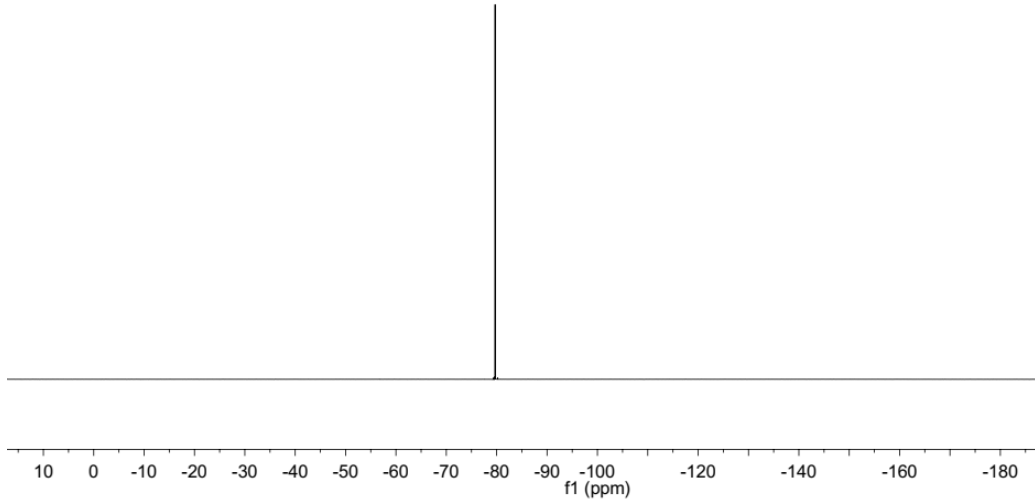


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

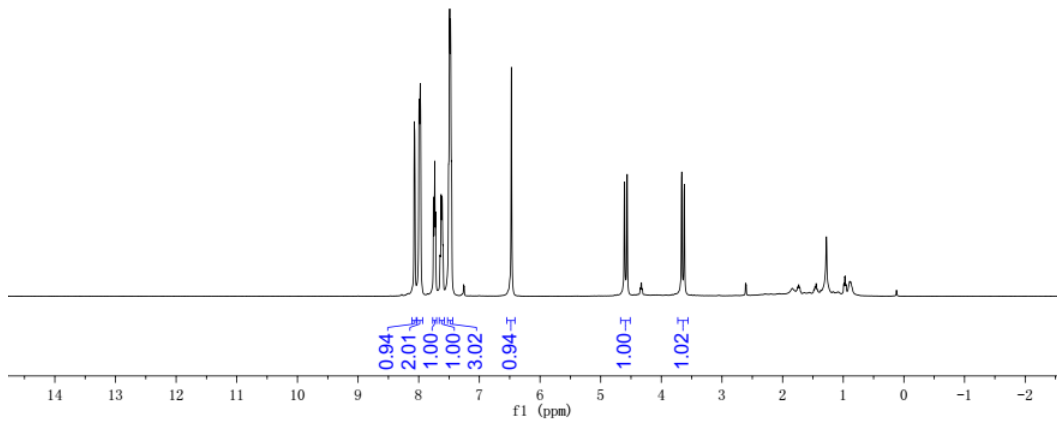




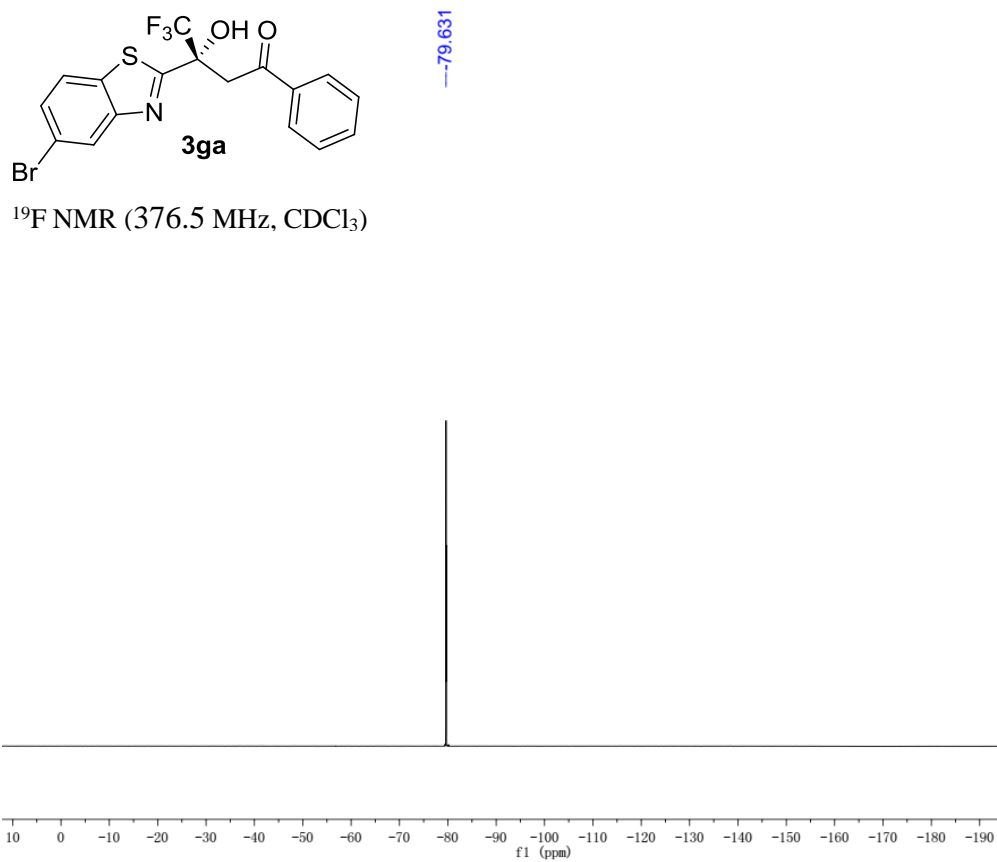
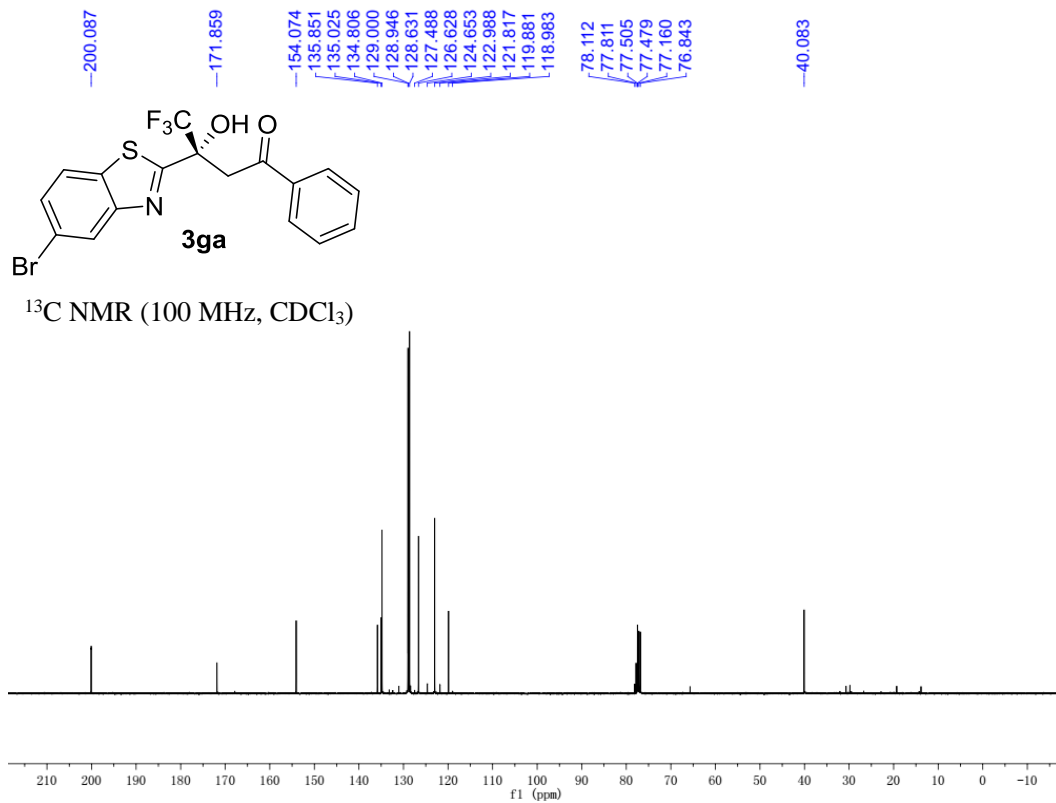
^{19}F NMR (376.5 MHz, CDCl_3)

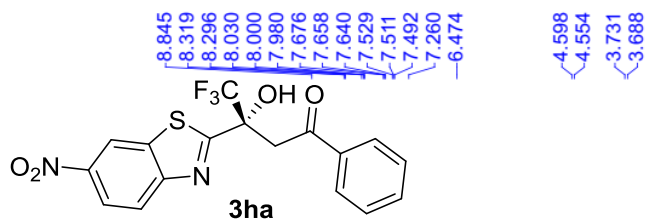


^1H NMR (400 MHz, CDCl_3)

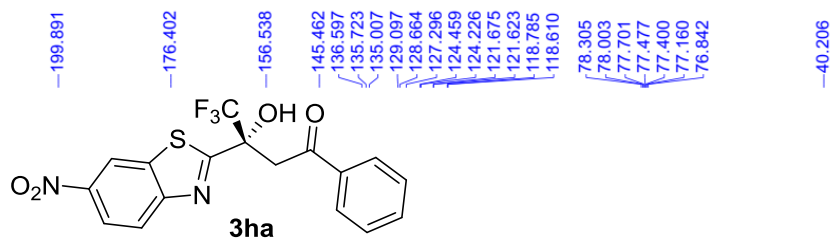
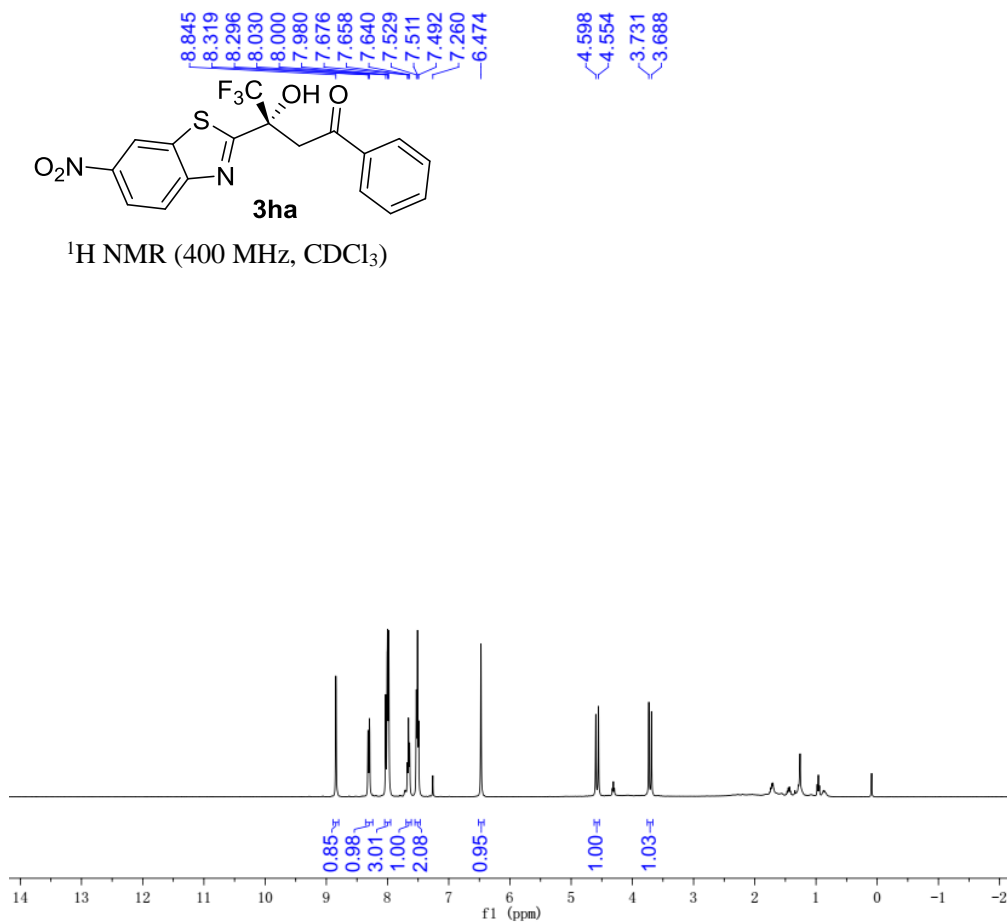


S99

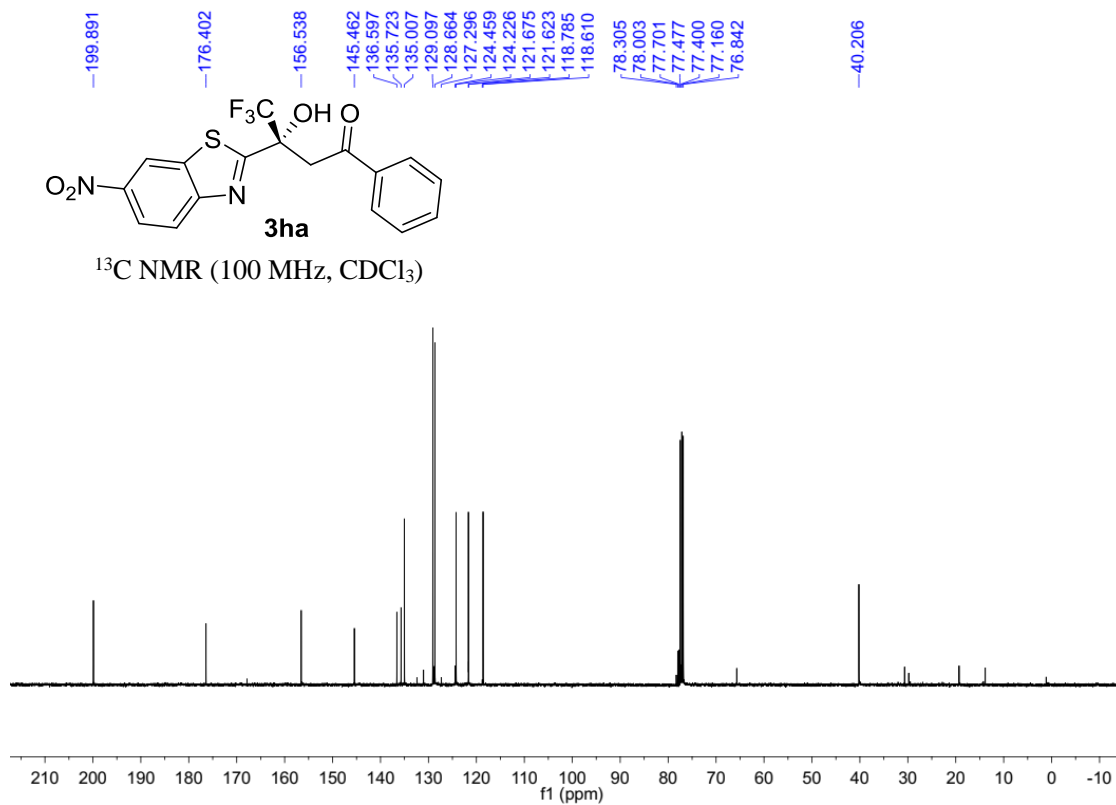


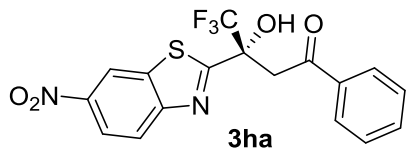


^1H NMR (400 MHz, CDCl_3)

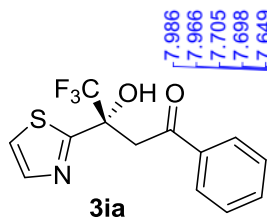
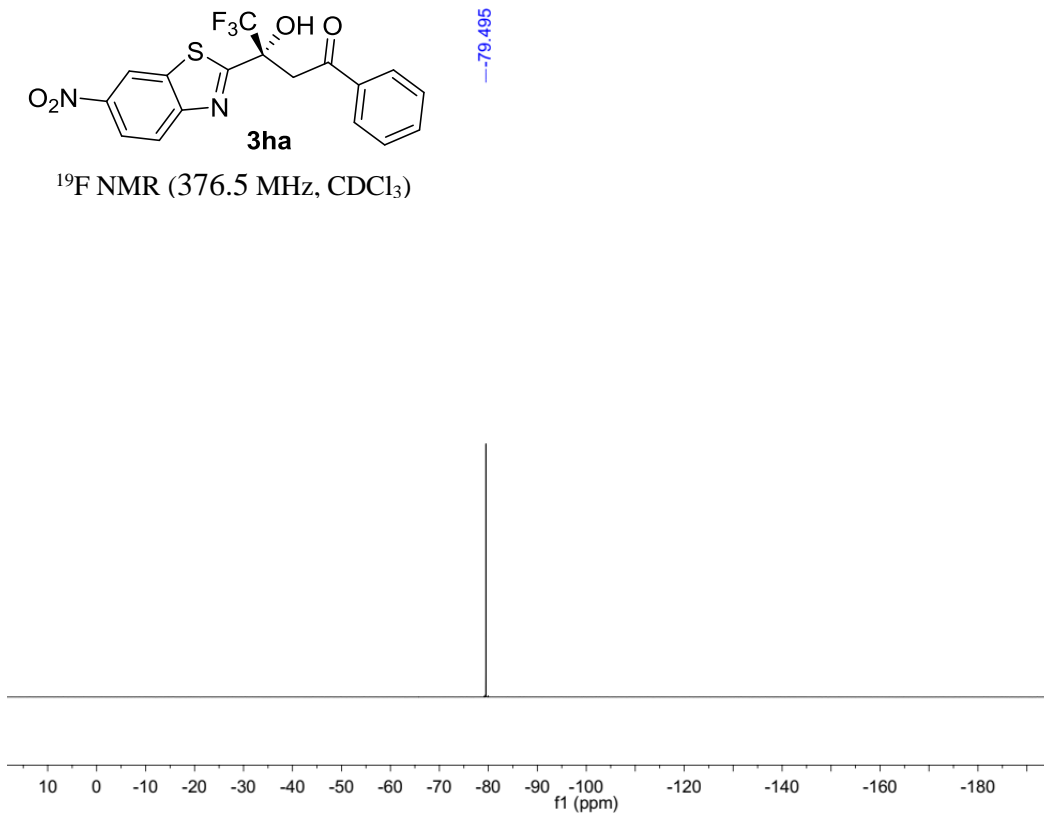


^{13}C NMR (100 MHz, CDCl_3)

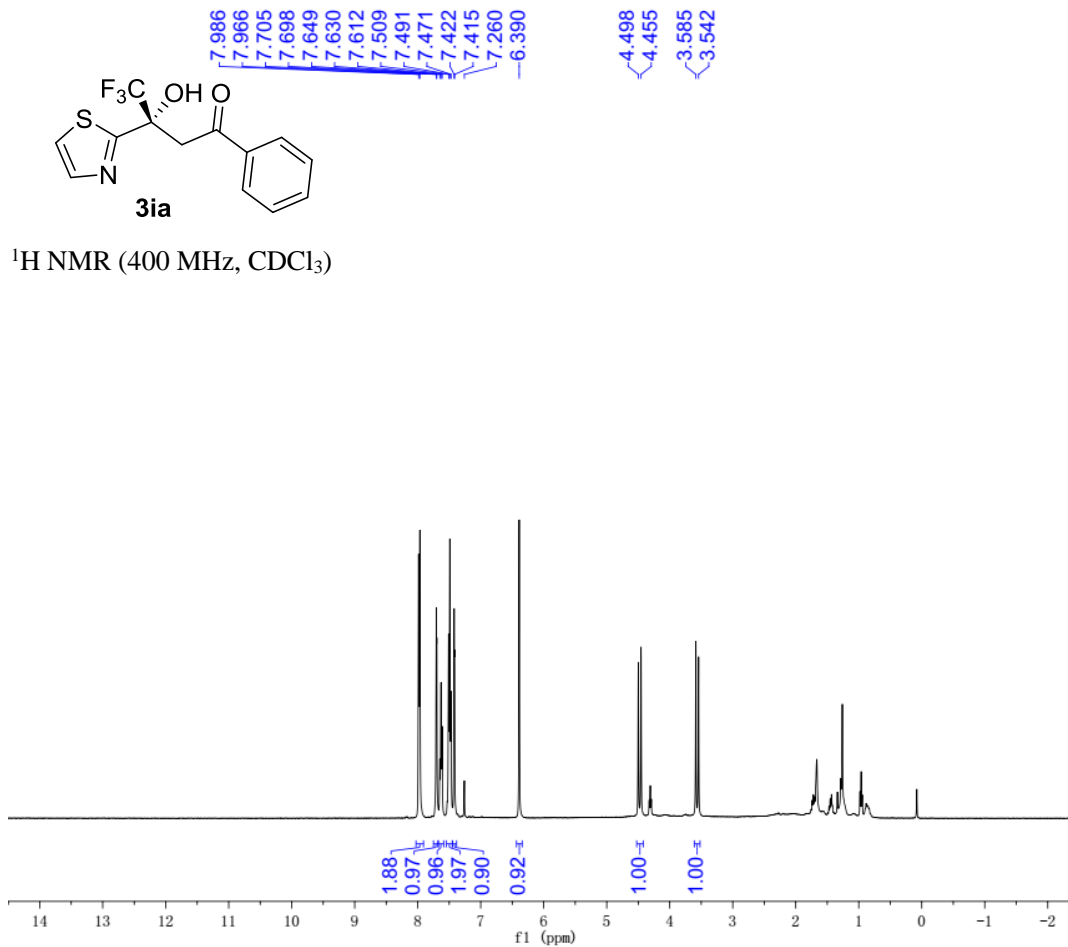


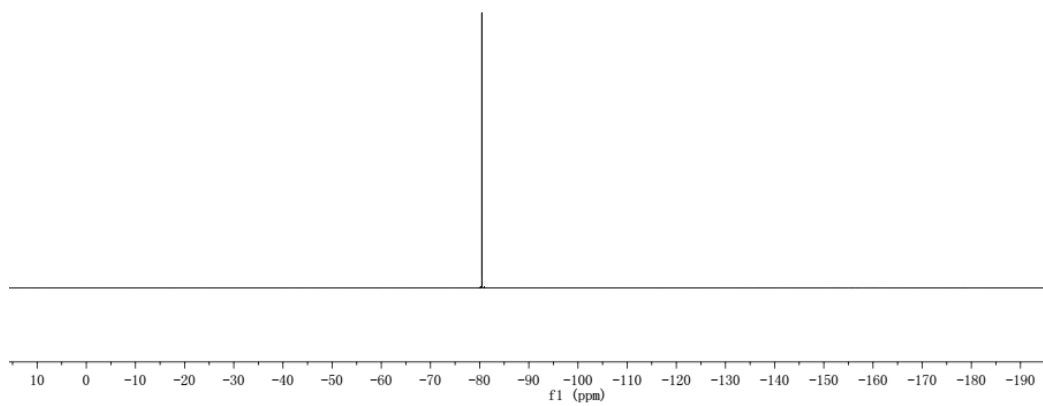
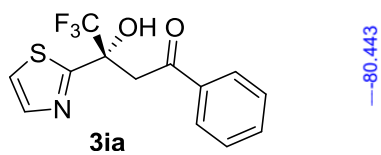
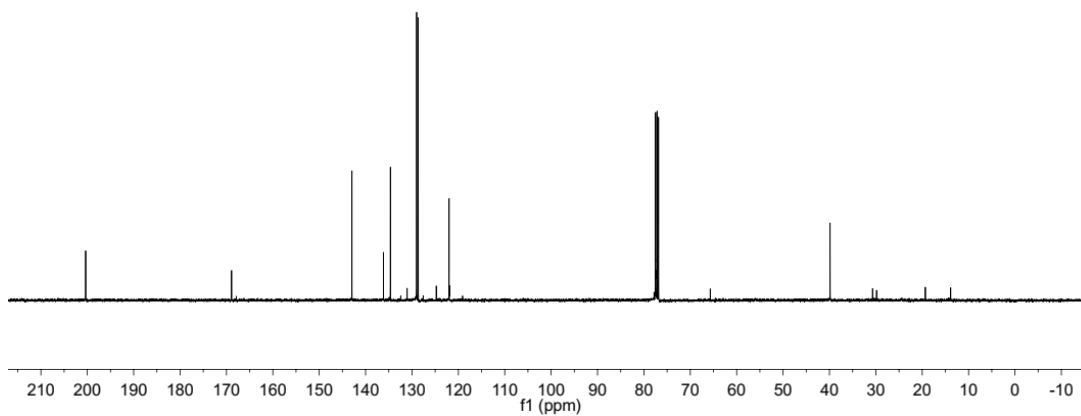
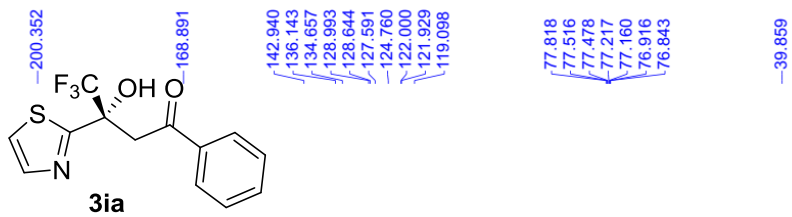


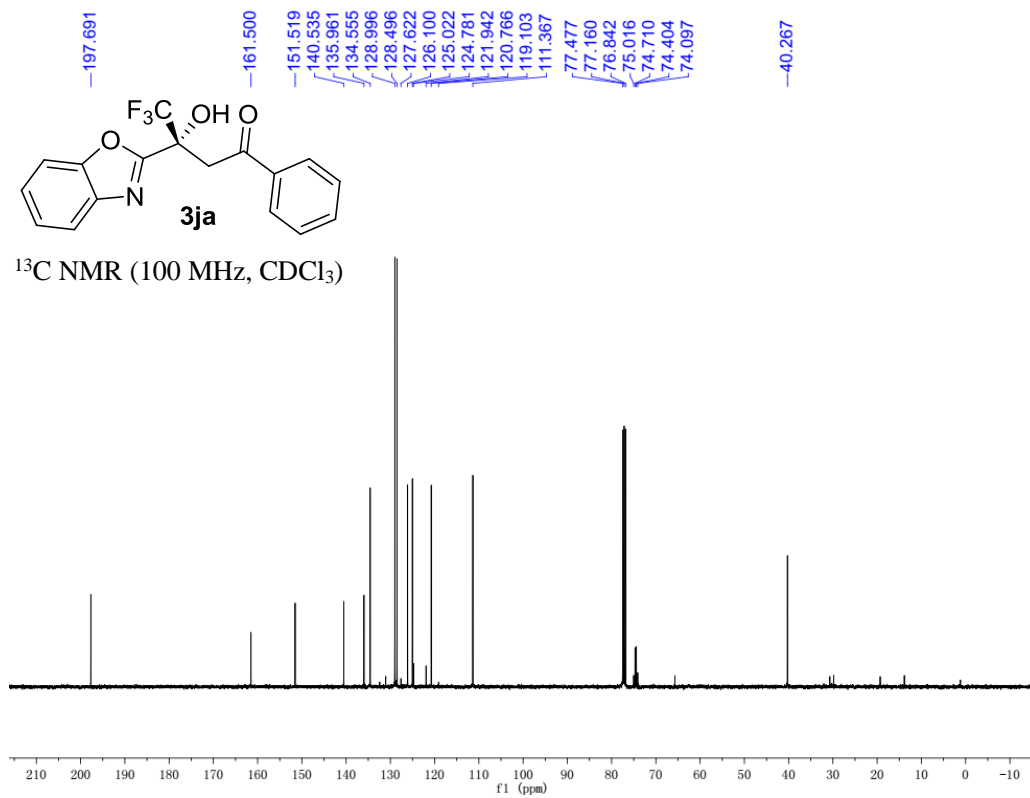
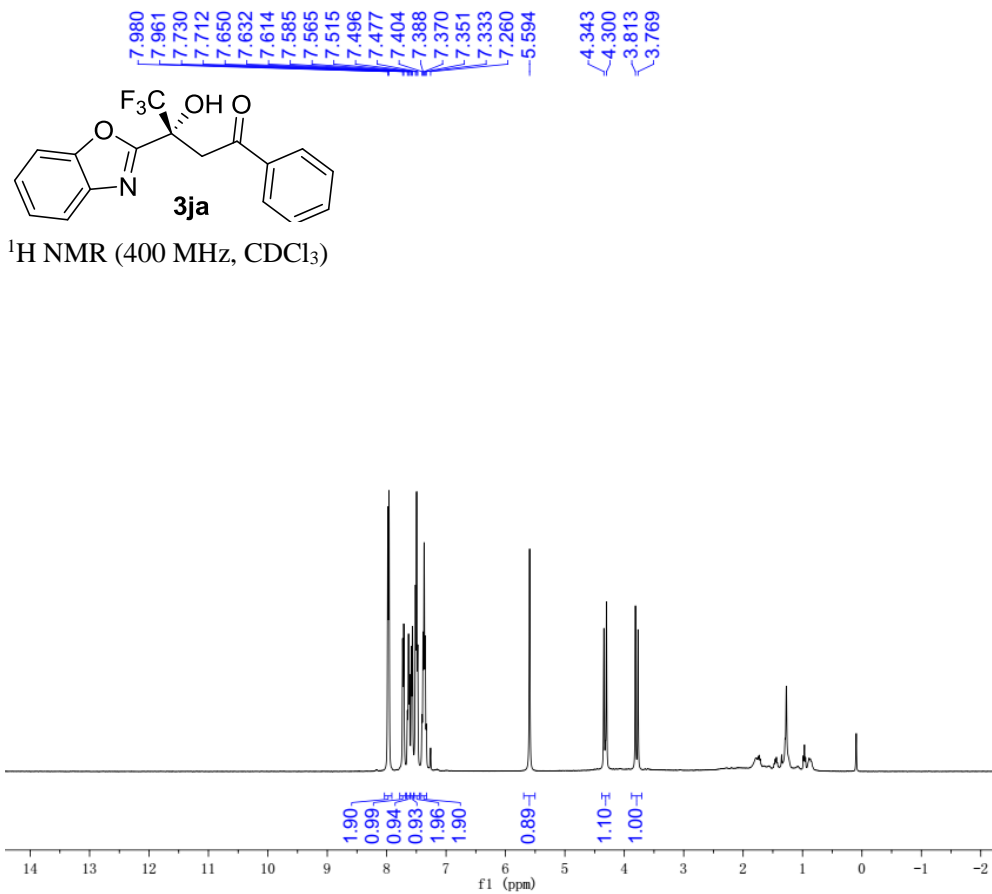
^{19}F NMR (376.5 MHz, CDCl_3)

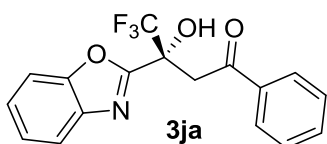


^1H NMR (400 MHz, CDCl_3)

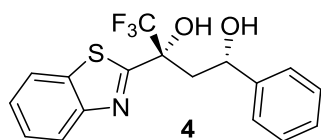
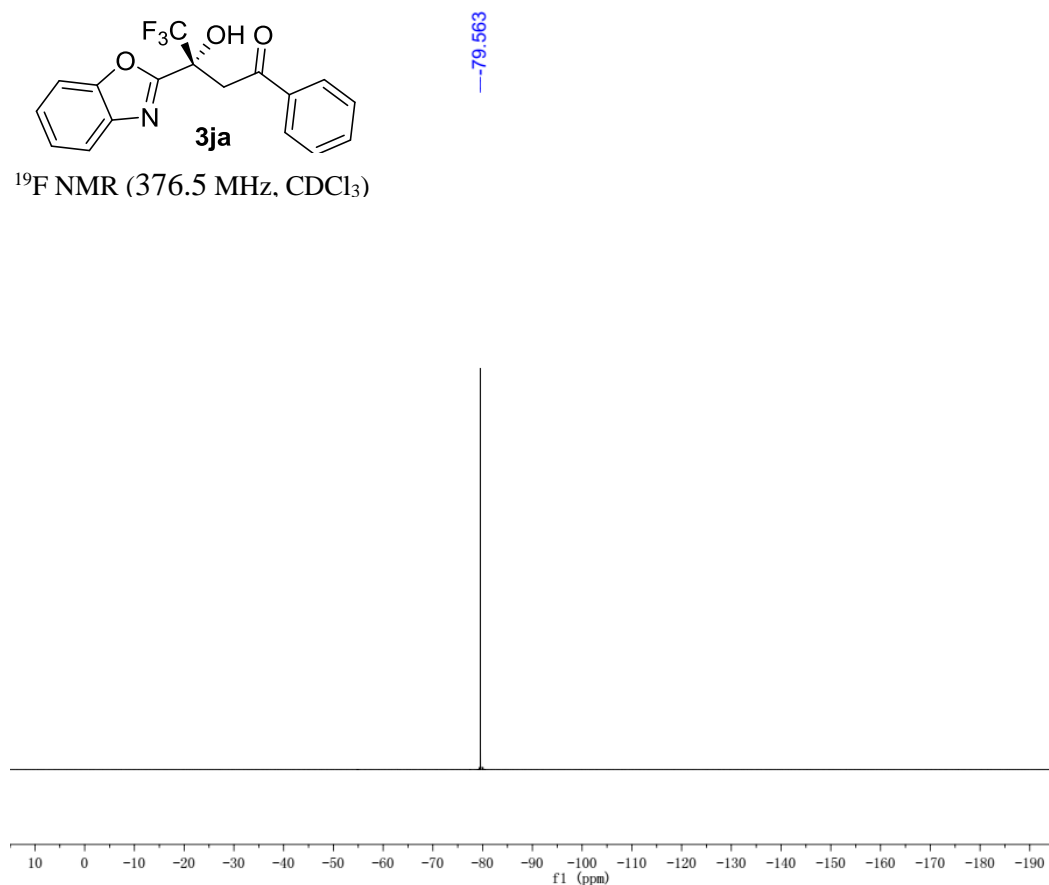




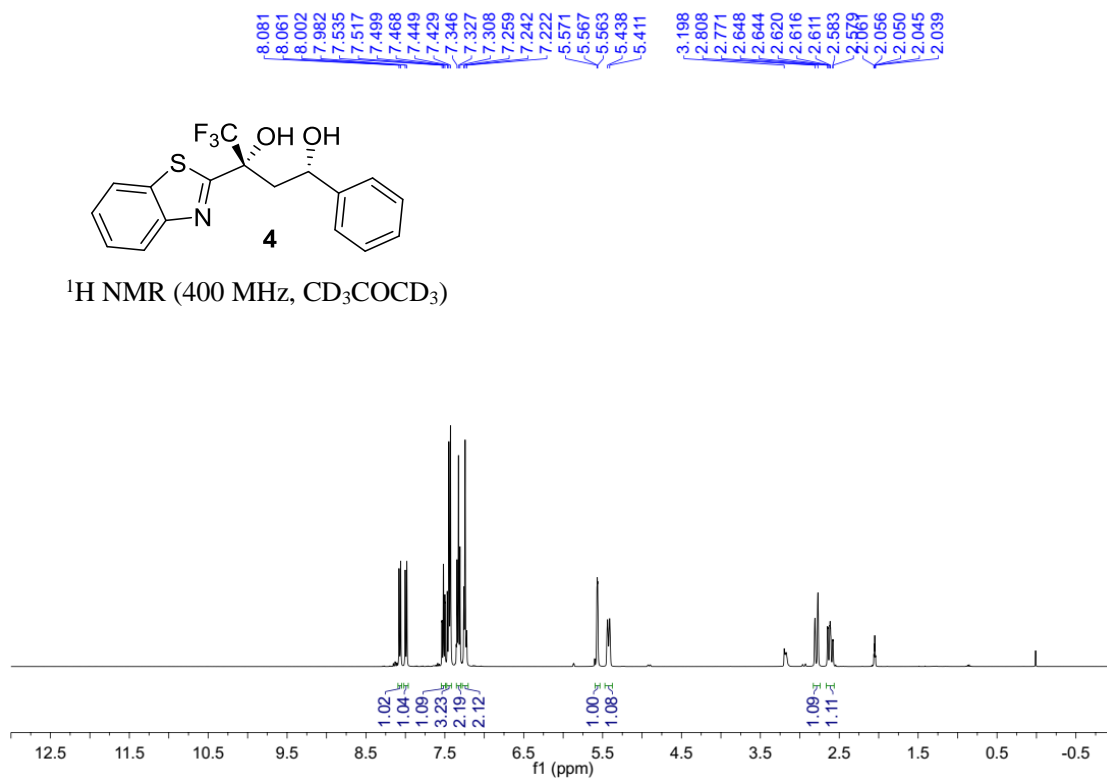


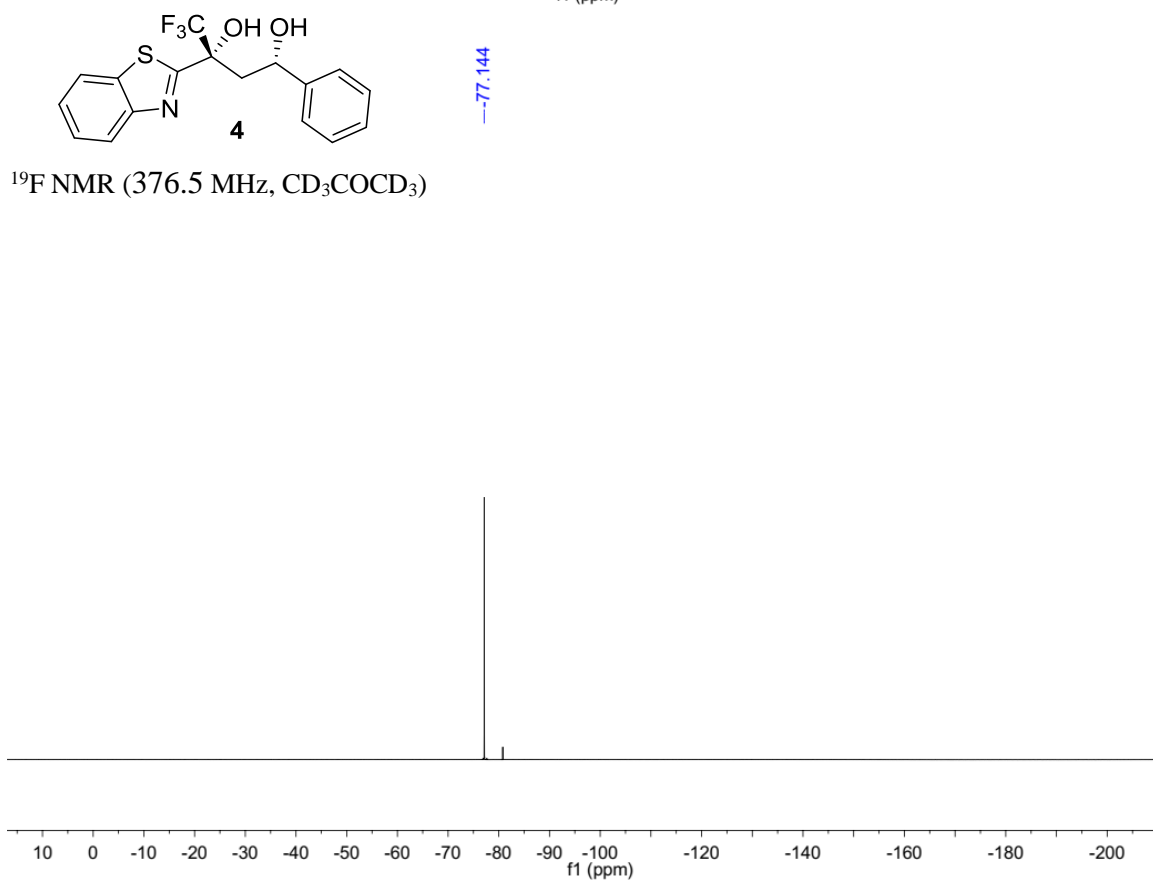
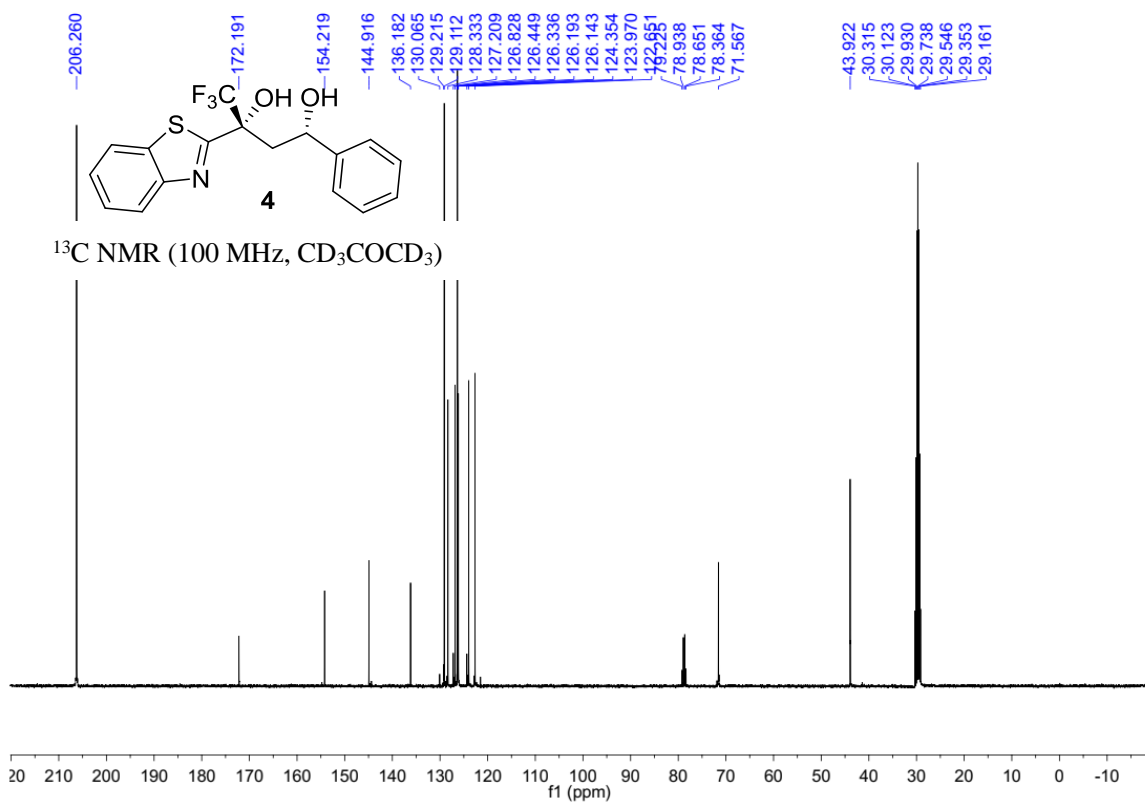


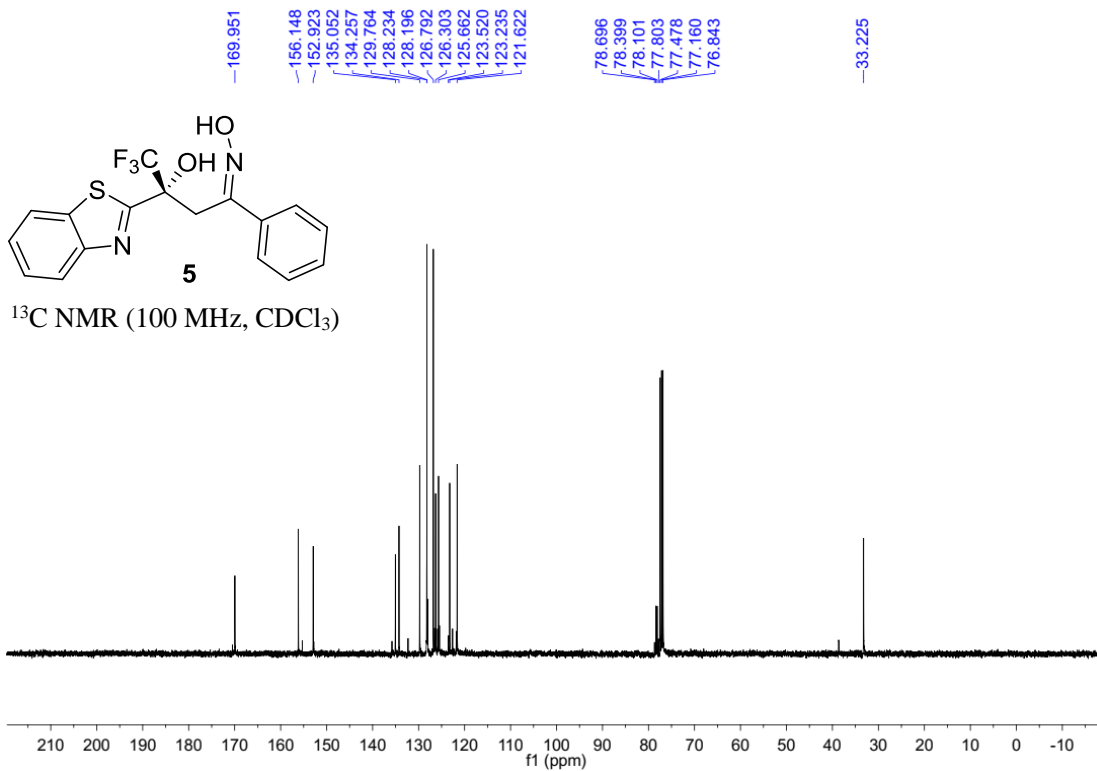
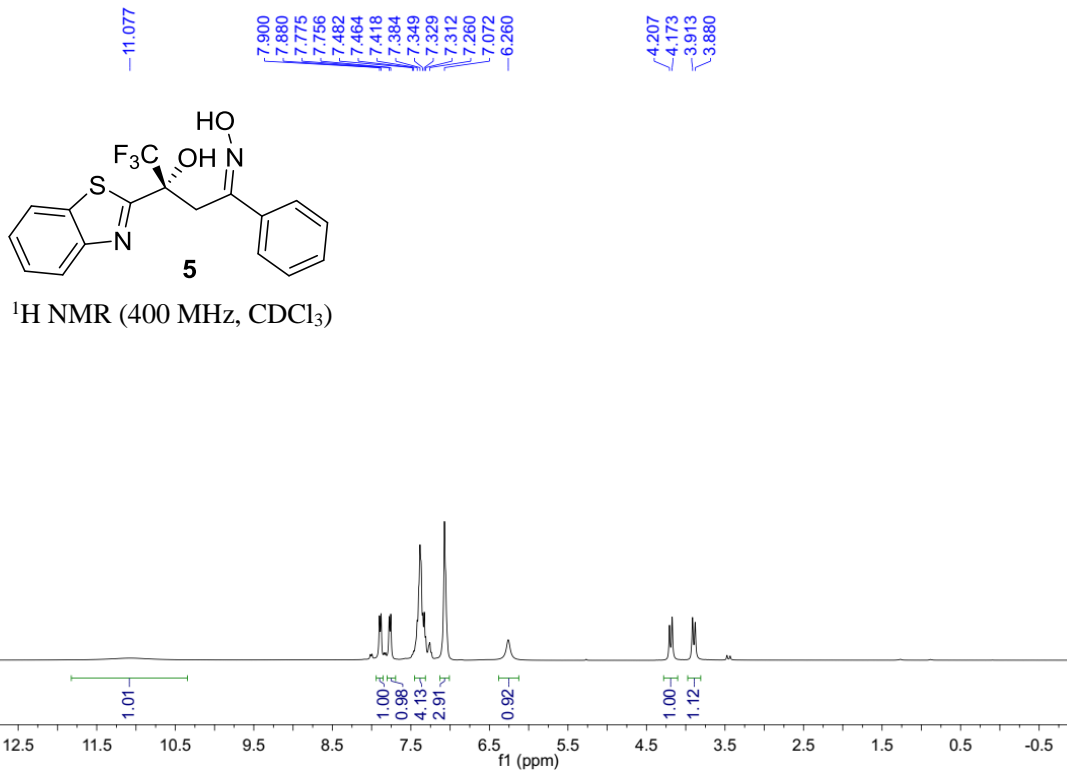
^{19}F NMR (376.5 MHz, CDCl_3)

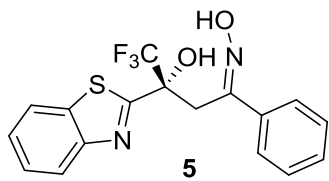


^1H NMR (400 MHz, CD_3COCD_3)

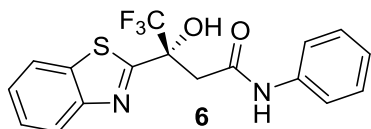
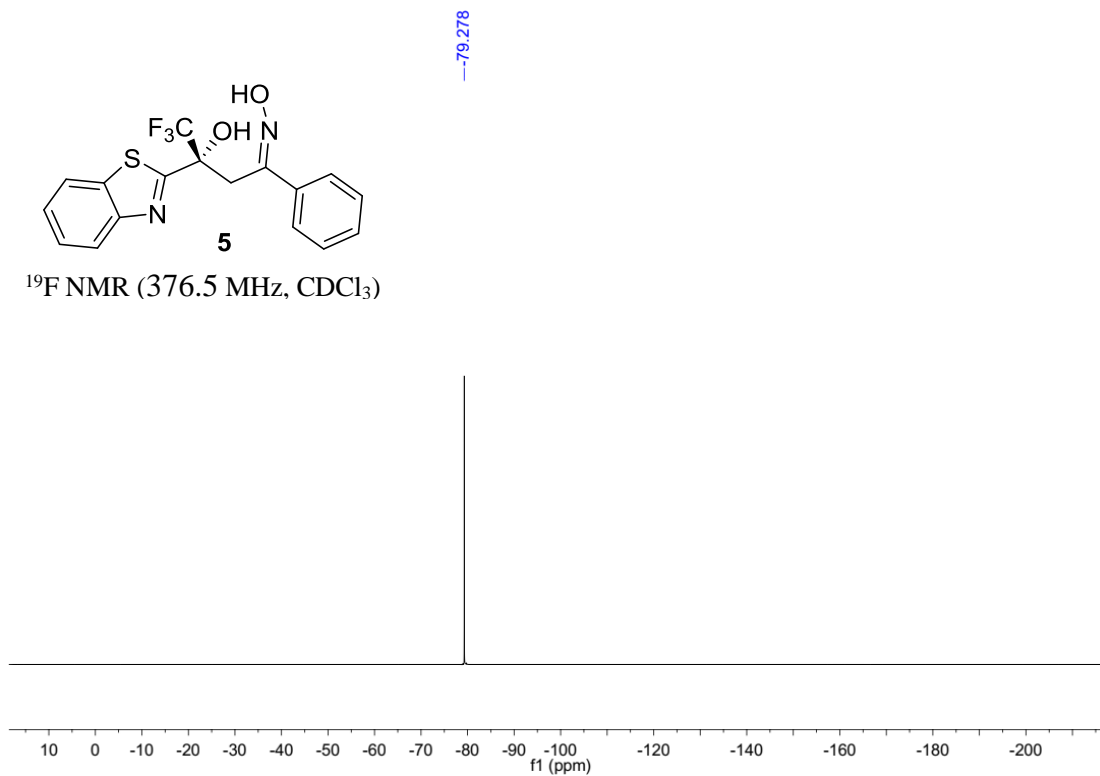




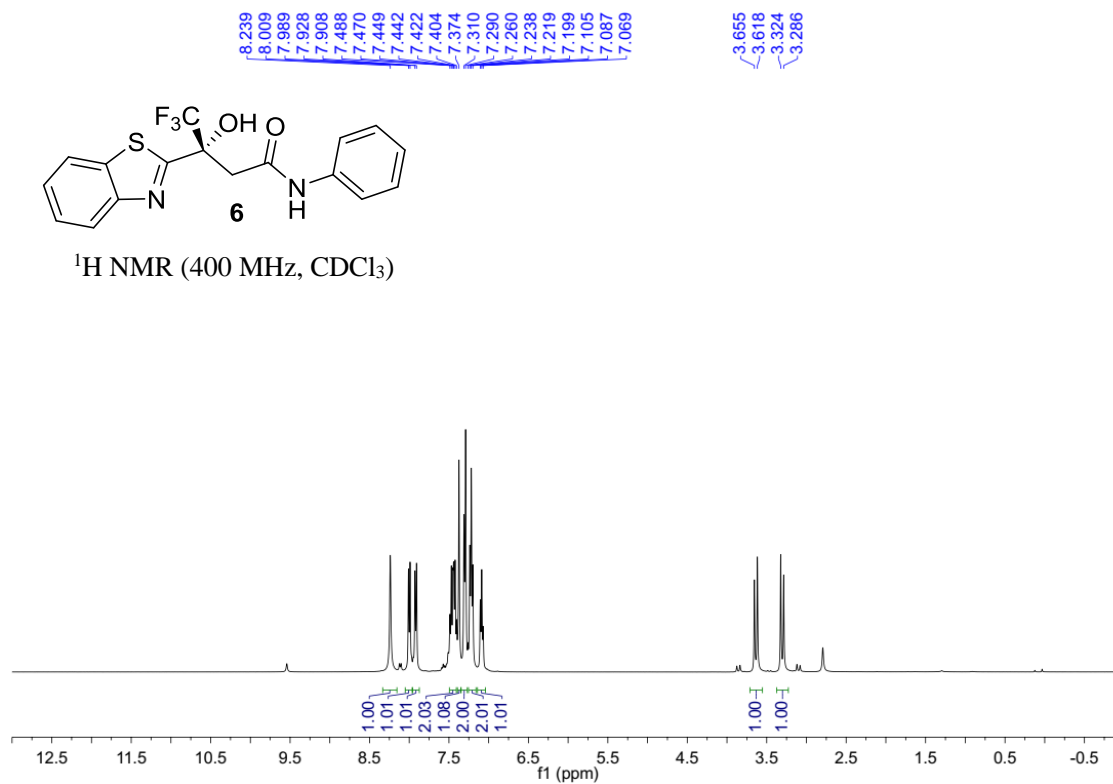


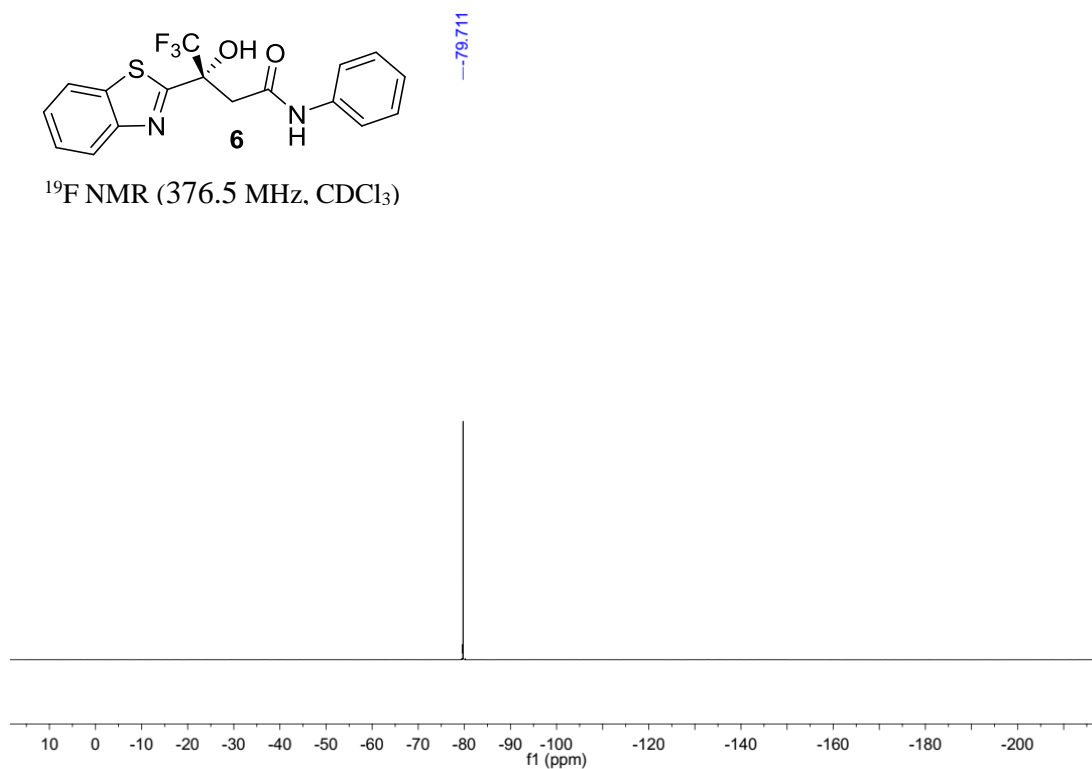
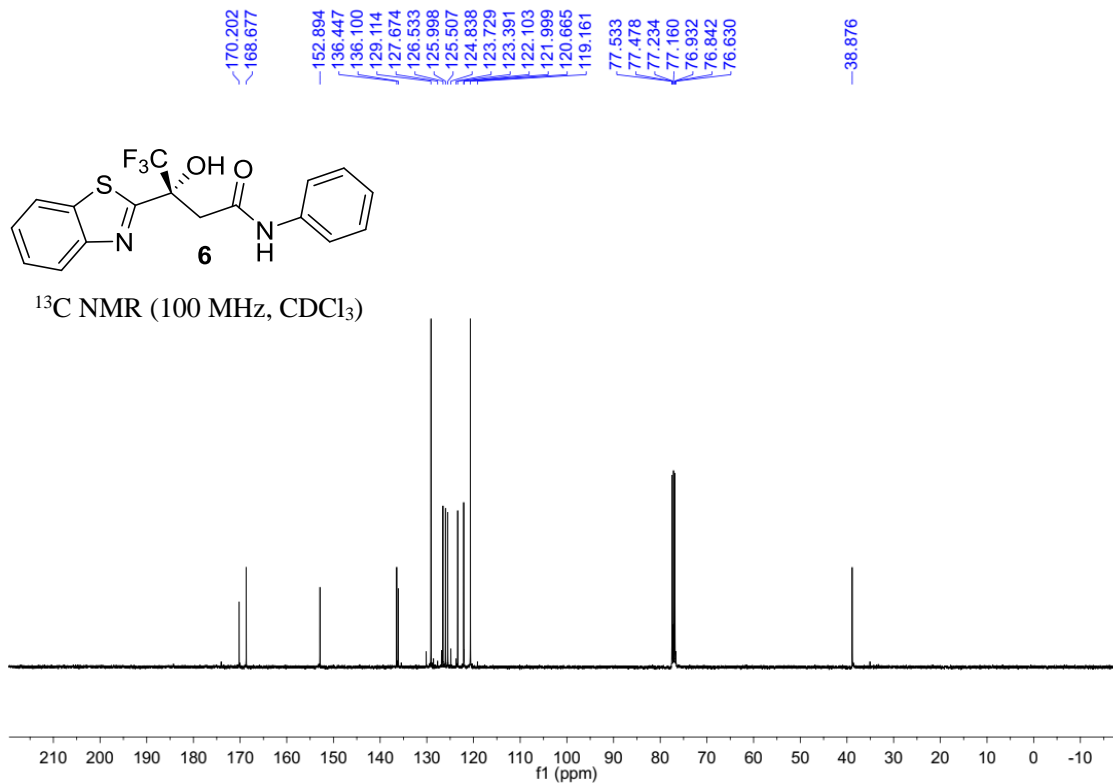


^{19}F NMR (376.5 MHz, CDCl_3)

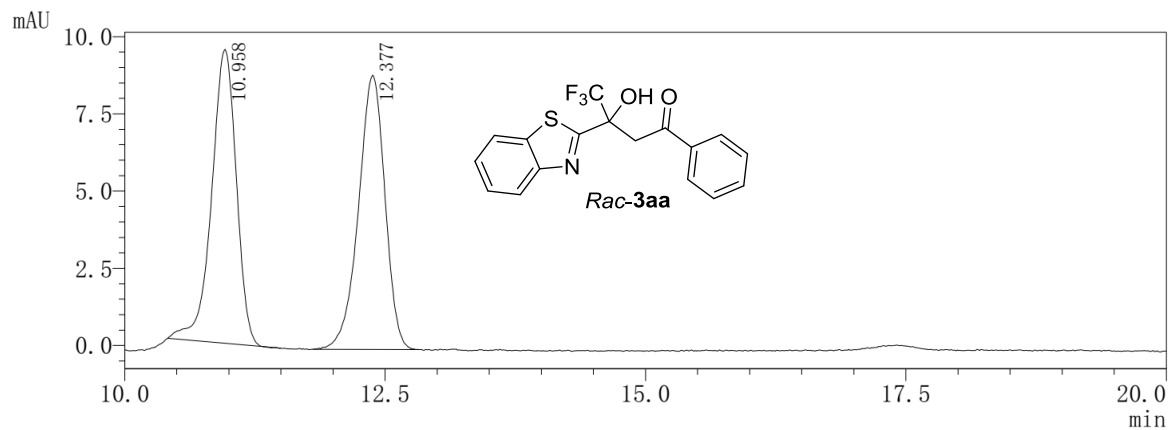


^1H NMR (400 MHz, CDCl_3)



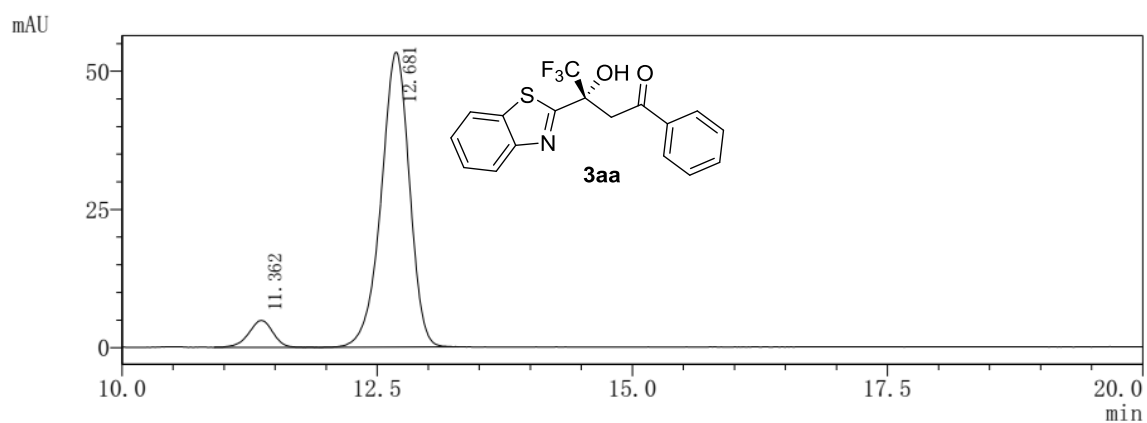


VIII. HPLC Profiles



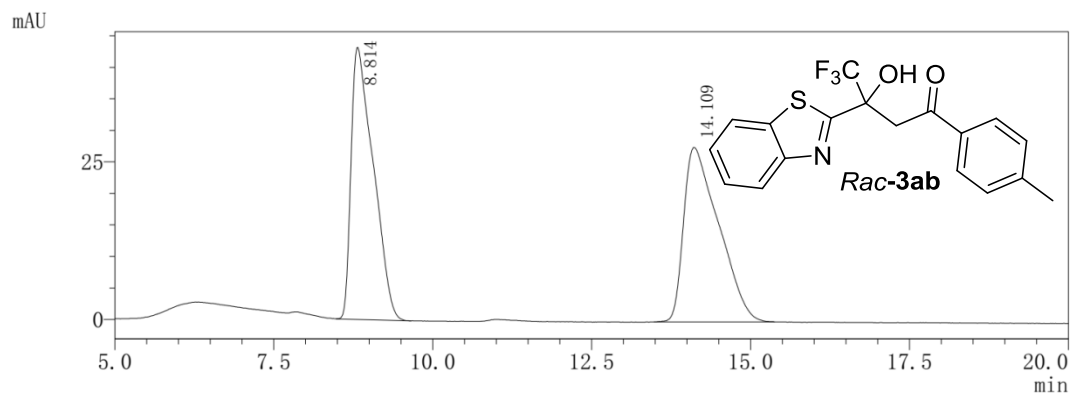
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	10.958	0.433	156902	9520	49.921
2	12.377	0.472	157401	8883	50.079



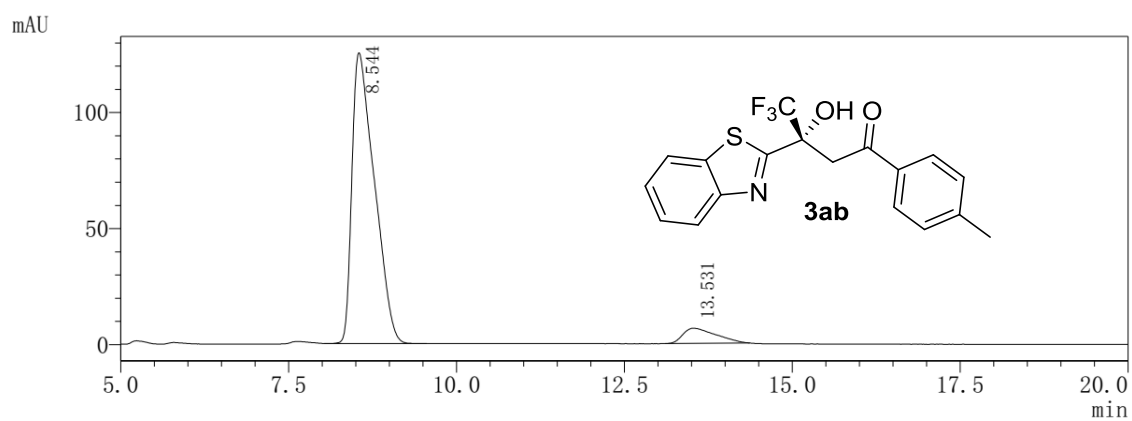
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	11.362	0.436	80386	4869	7.253
2	12.681	0.509	1027981	53326	92.747



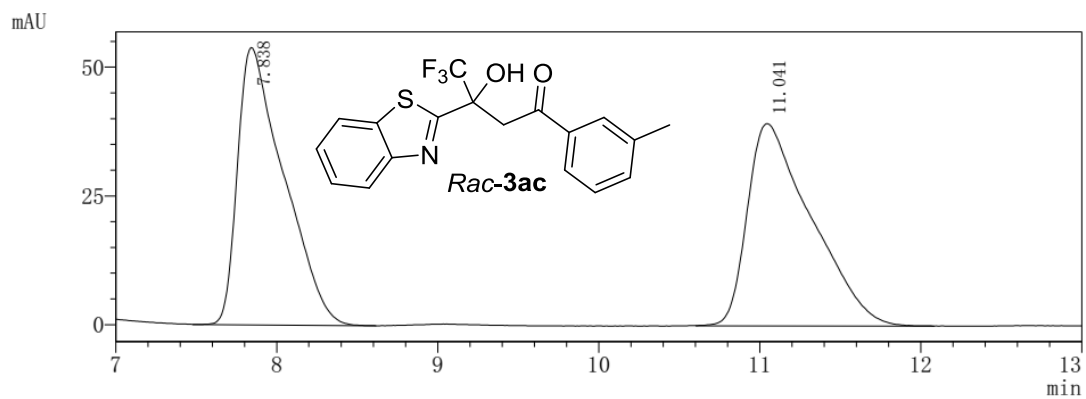
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	8.814	0.694	1049078	43182	49.706
2	14.109	1.076	1061469	27693	50.294



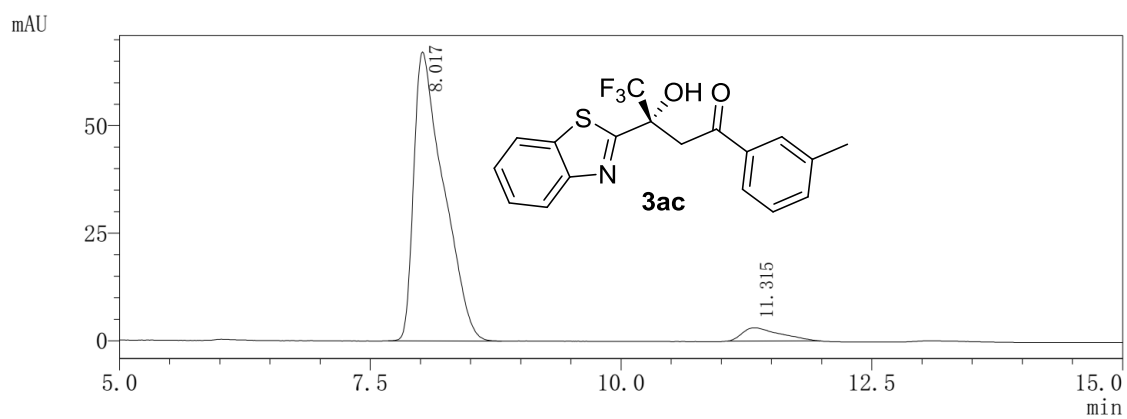
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	8.544	0.655	2907221	125287	92.856
2	13.531	1.022	223661	6551	7.144



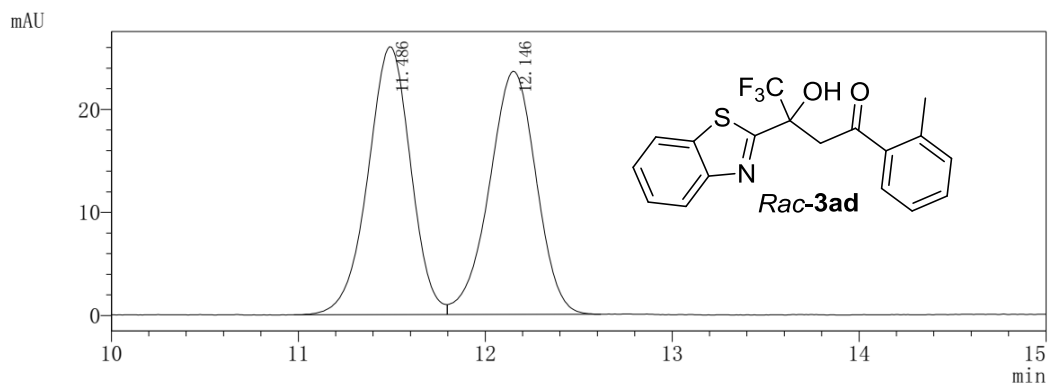
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	7.838	0.529	1076466	53851	49.850
2	11.041	0.721	1082948	39279	50.150



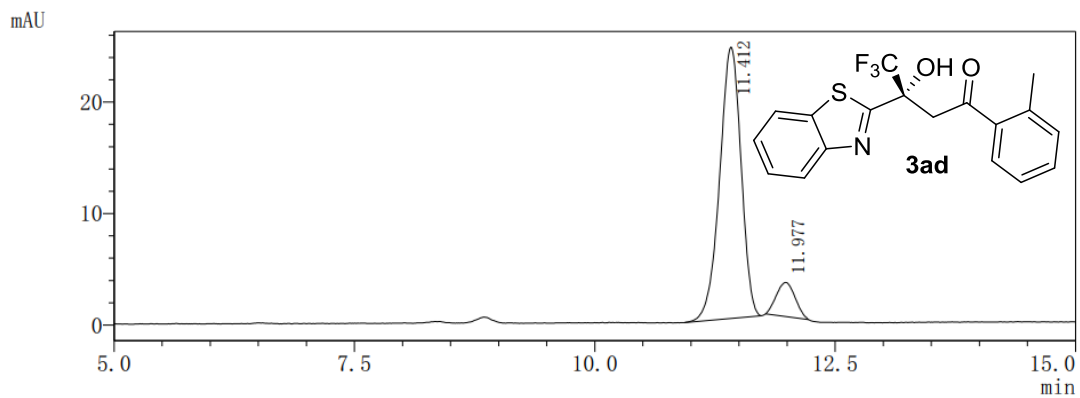
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	8.017	0.540	1387194	67246	94.498
2	11.315	0.694	80764	3082	5.502



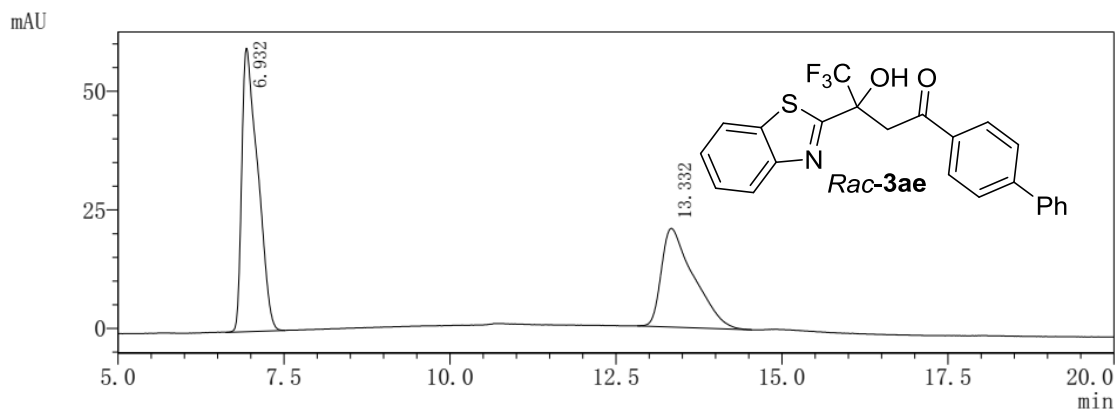
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	11.486	0.426	414517	26011	50.232
2	12.146	0.467	410694	23617	49.768



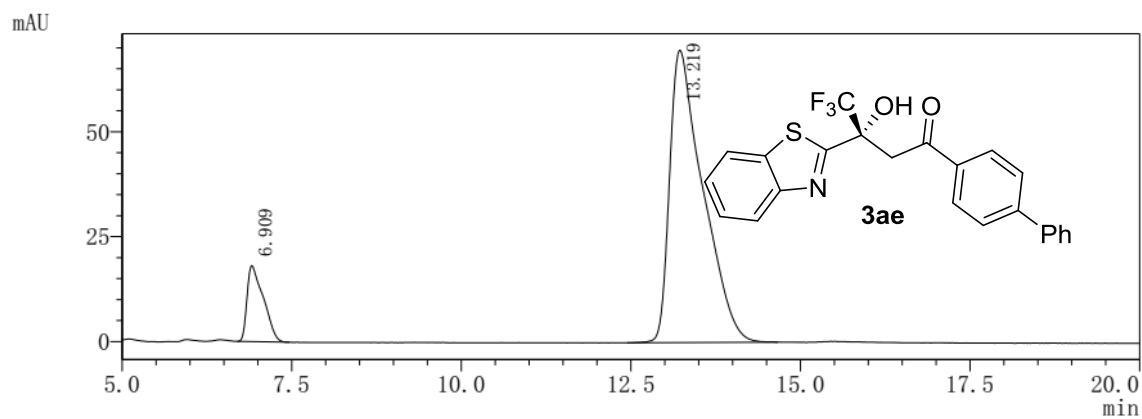
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	11.412	0.417	375845	24348	90.059
2	11.977	0.382	41486	3042	9.941



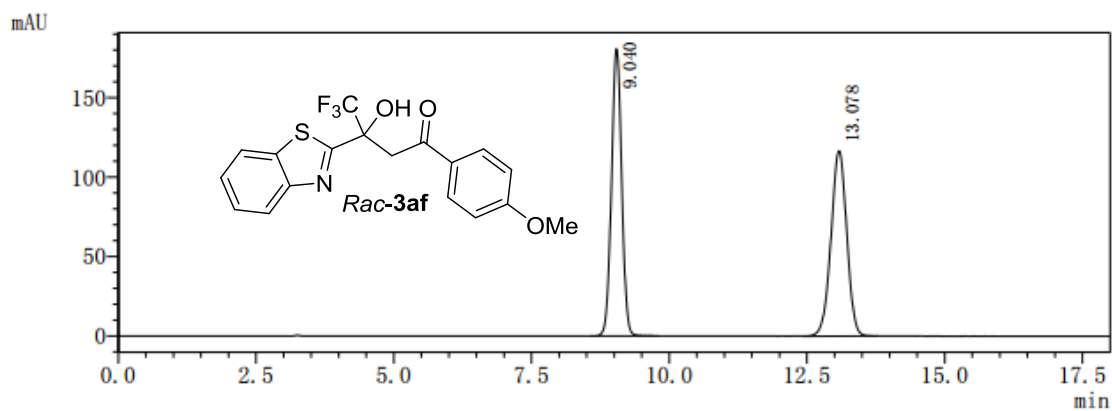
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	6.932	0.494	998458	59785	58.668
2	13.332	0.852	703419	20813	41.332



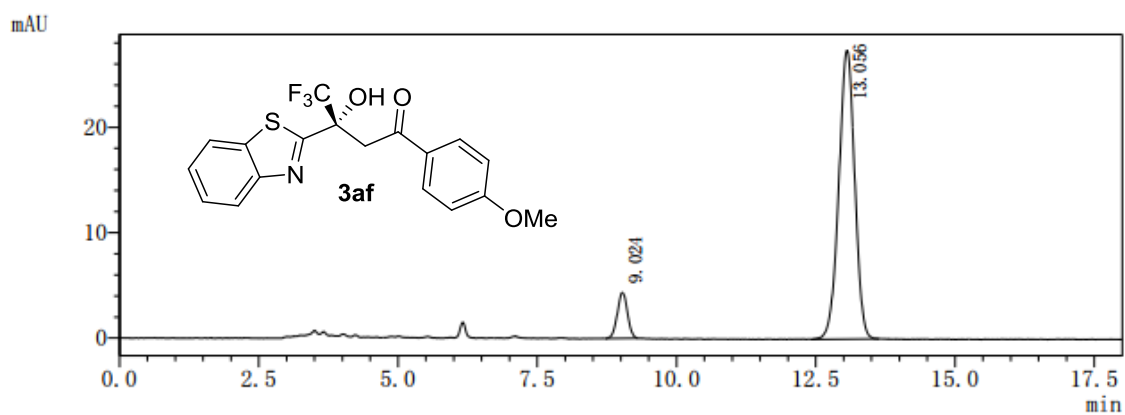
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	6.909	0.493	302790	18121	11.265
2	13.219	0.868	2385070	69688	88.735



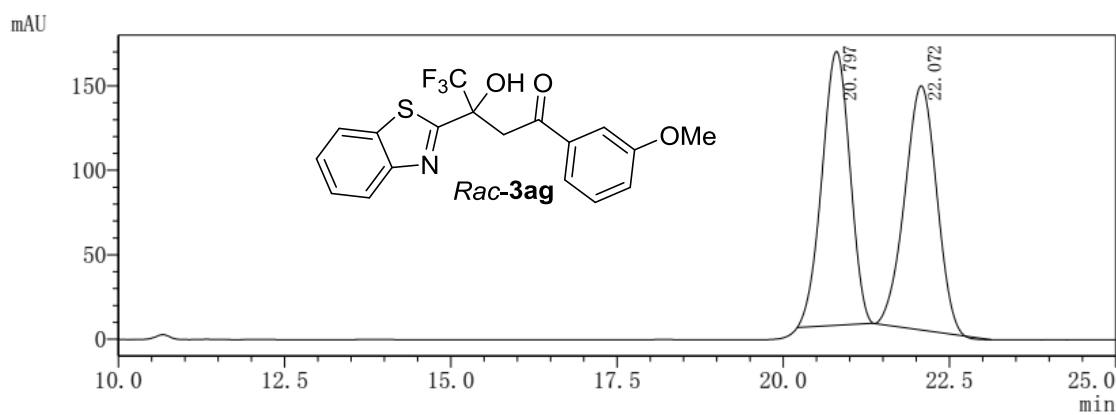
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	9.040	0.349	2327578	180821	50.059
2	13.078	0.531	2322081	116518	49.941



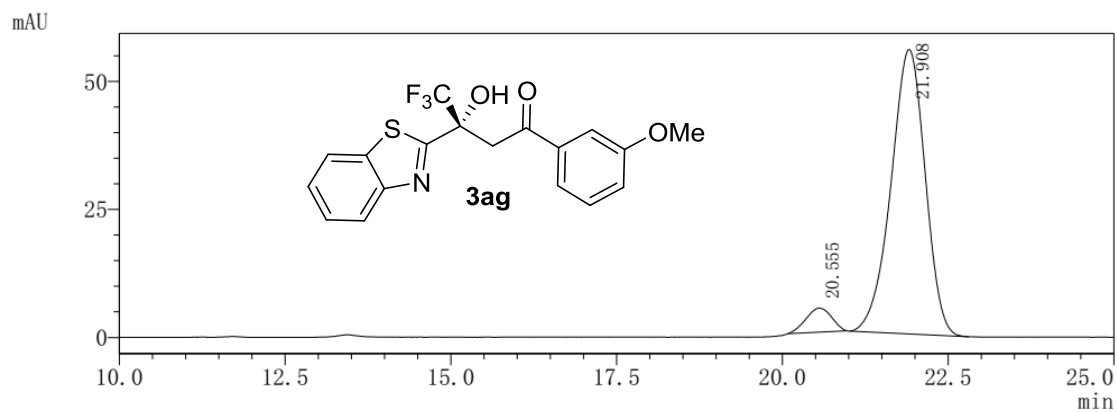
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	9.024	0.348	55506	4363	9.233
2	13.056	0.532	545666	27369	90.767



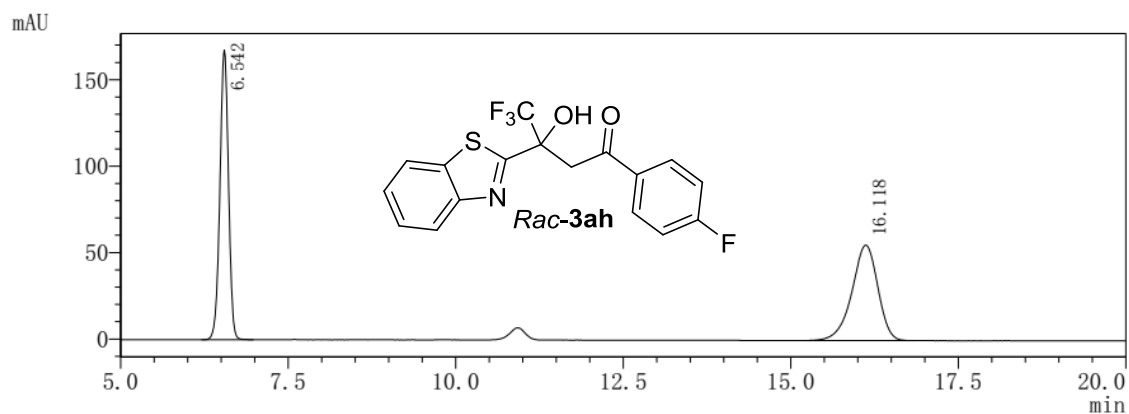
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	20.797	0.790	4737246	162171	49.658
2	22.072	0.900	4802425	144527	50.342



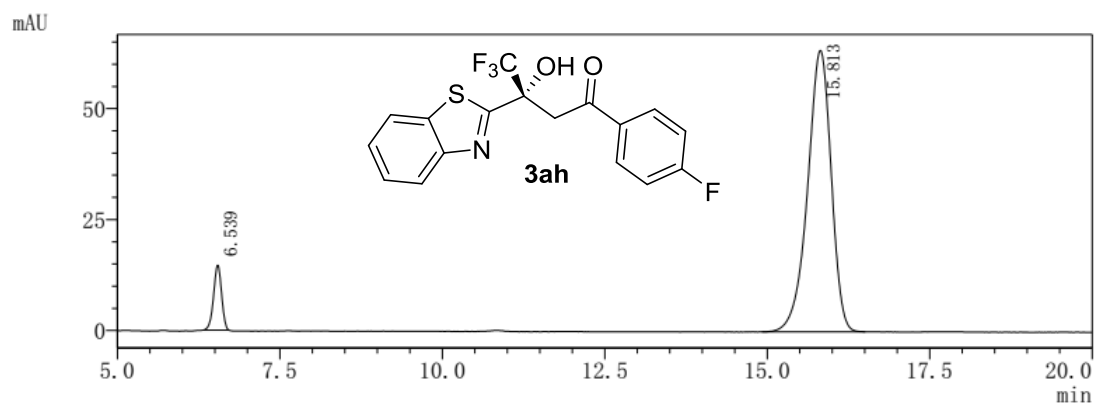
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	20.555	0.737	126139	4707	5.965
2	21.908	0.949	1988638	55528	94.035



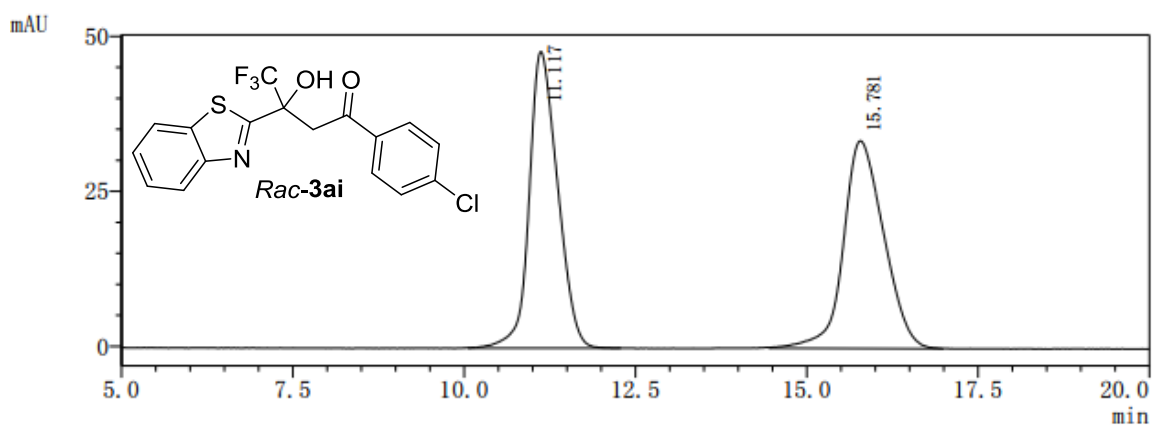
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	6.542	0.248	1492994	167707	50.086
2	16.118	0.707	1487854	55173	49.914



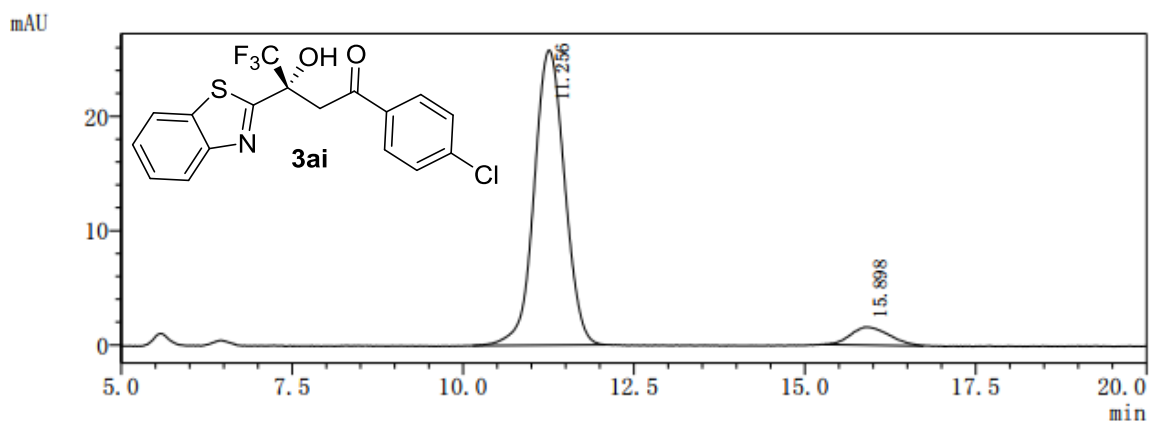
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	6.539	0.241	125308	14607	7.246
2	15.813	0.665	1604004	63436	92.754



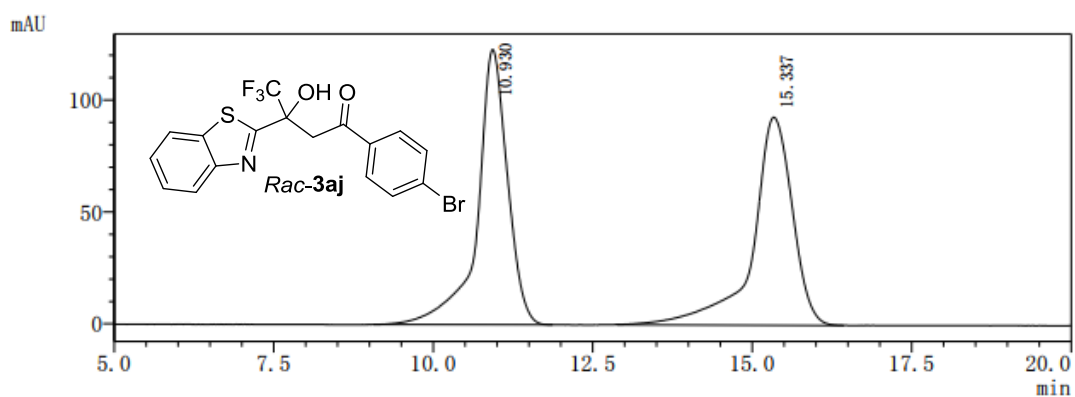
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	11.117	0.772	1383258	47855	50.155
2	15.781	1.083	1374713	33490	49.845



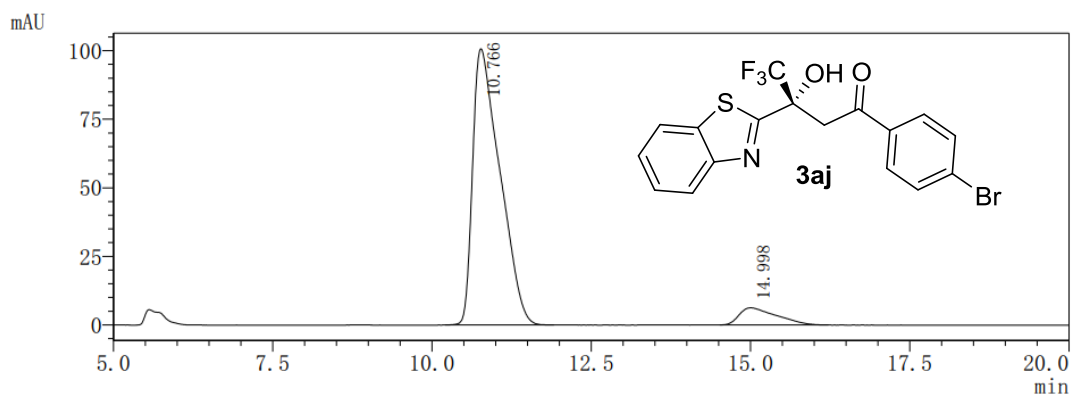
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	11.256	0.806	800755	25786	92.833
2	15.898	1.058	61825	1586	7.167



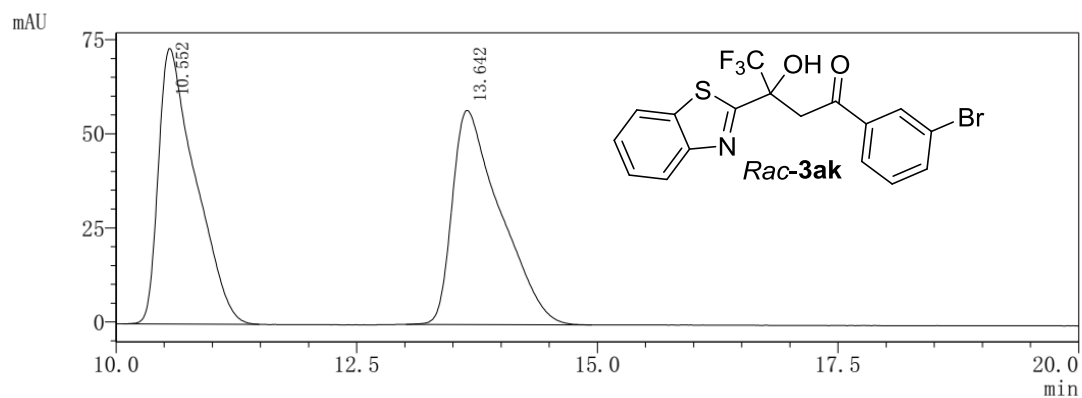
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	10.930	0.773	4066488	123037	50.121
2	15.337	0.976	4046865	92928	49.879



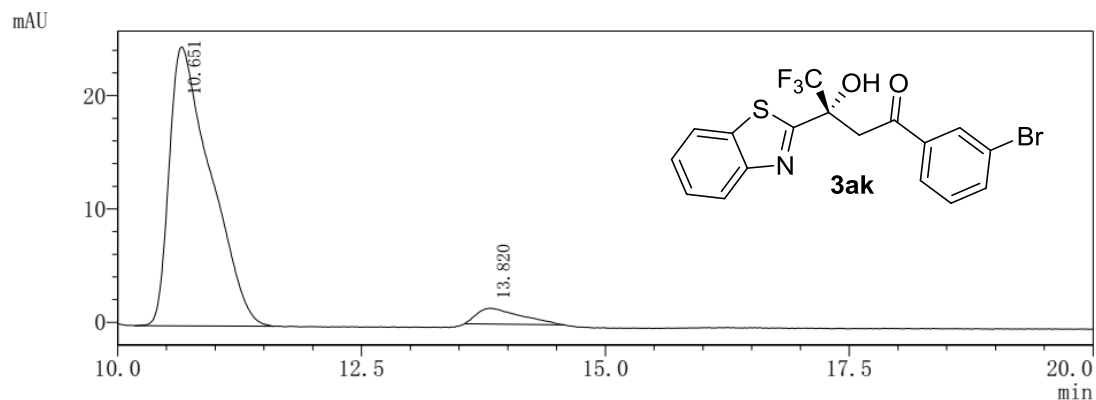
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	10.766	0.830	3006900	100792	92.212
2	14.998	1.206	253960	6242	7.788



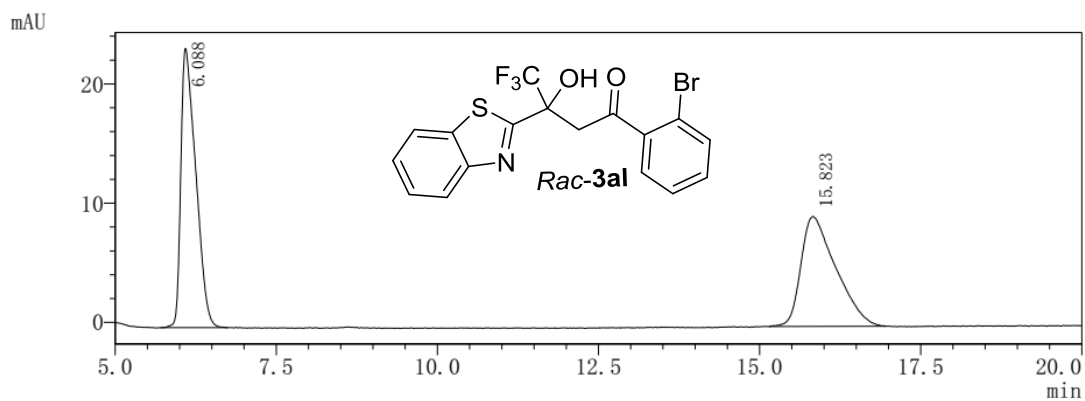
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	10.552	0.688	1956424	73210	49.741
2	13.642	0.890	1976808	56895	50.259



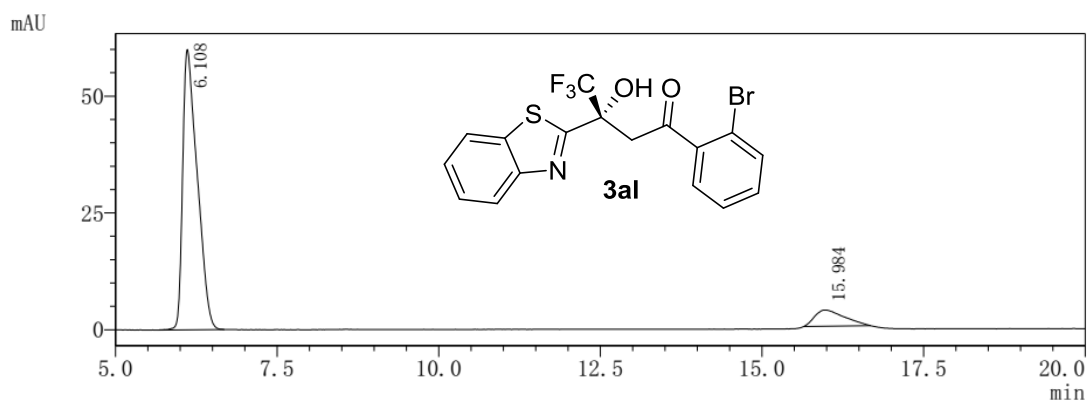
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	10.651	0.769	729617	24622	94.338
2	13.820	0.942	43791	1396	5.662



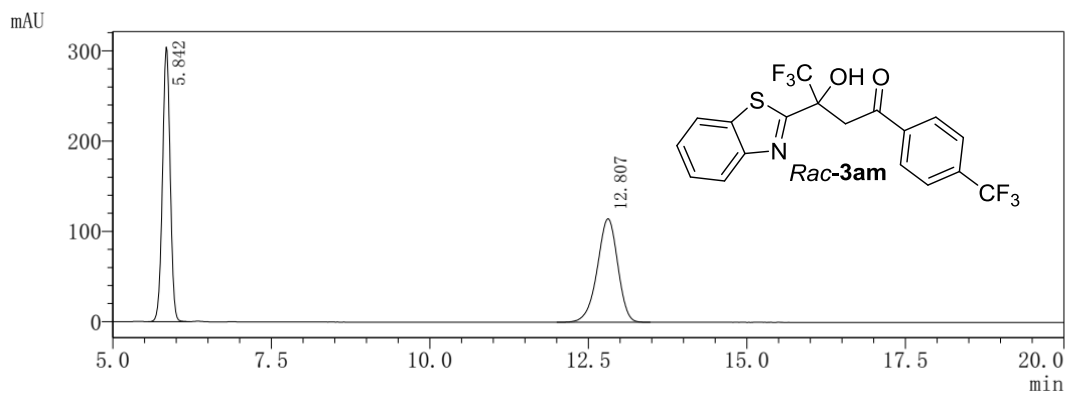
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	6.088	0.465	376957	23434	52.024
2	15.823	1.043	347621	9208	47.976



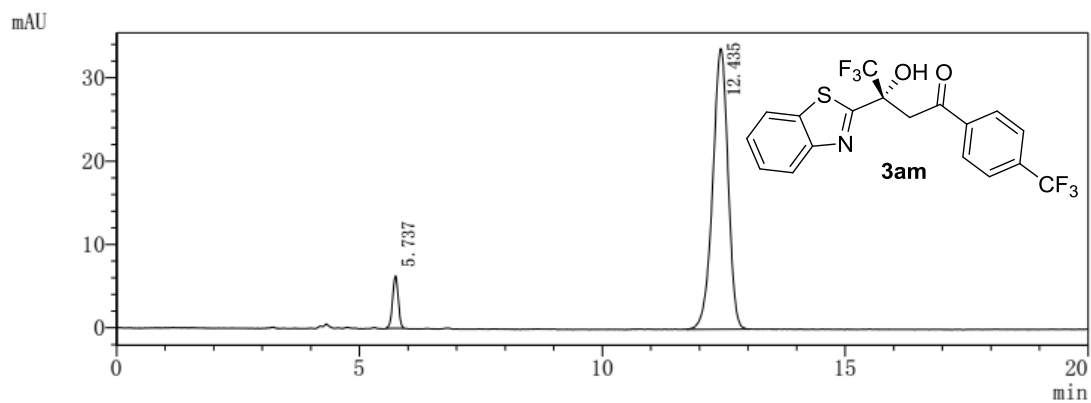
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	6.108	0.447	938434	60033	89.368
2	15.984	0.939	111642	3482	10.632



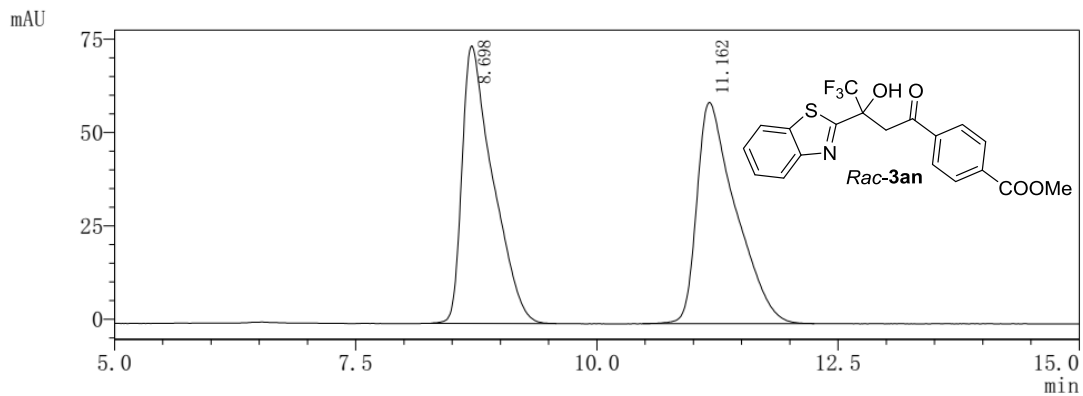
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	5.842	0.236	2557638	304291	49.849
2	12.807	0.593	2573152	114692	50.151



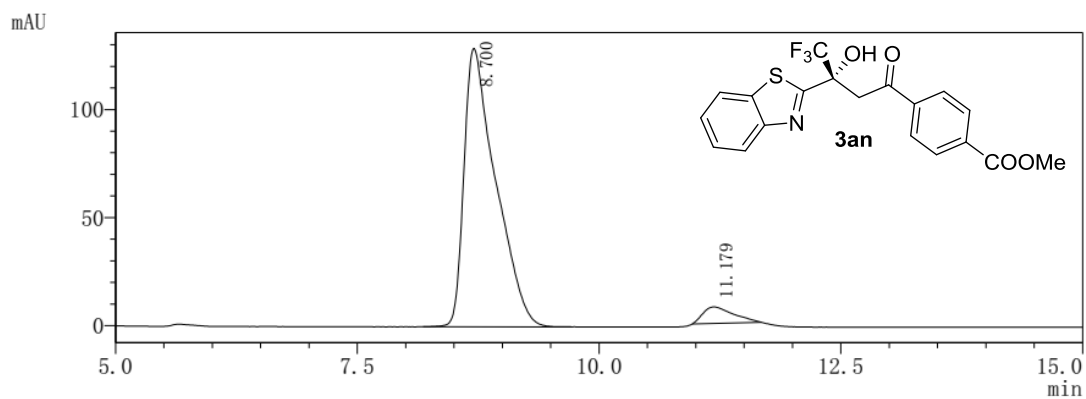
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	5.737	0.233	51728	6300	6.560
2	12.435	0.579	736753	33666	93.440



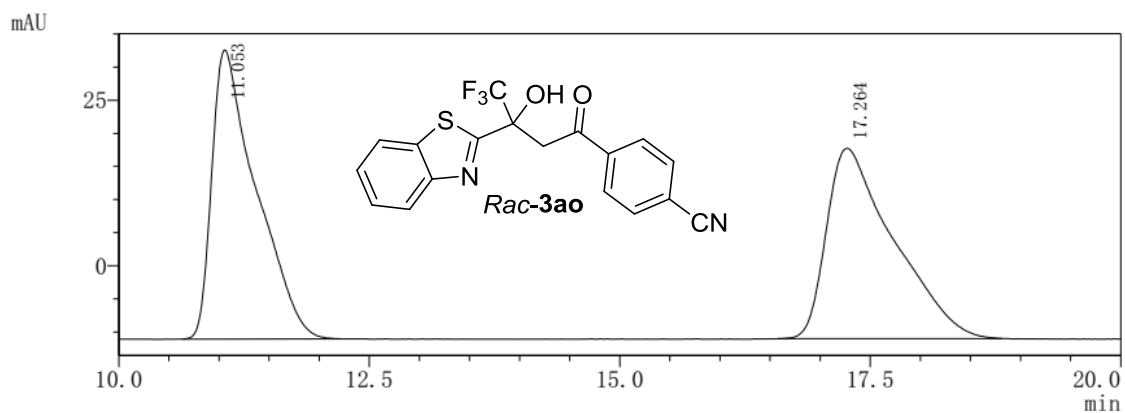
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	8.698	0.571	1653223	74356	49.953
2	11.162	0.719	1656343	59248	50.047



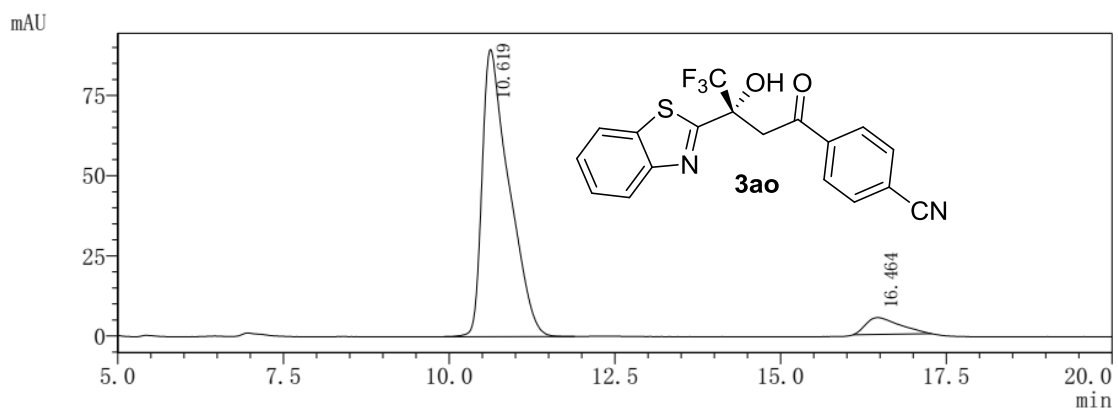
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	8.700	0.581	2939408	128947	94.609
2	11.179	0.596	167508	7668	5.391



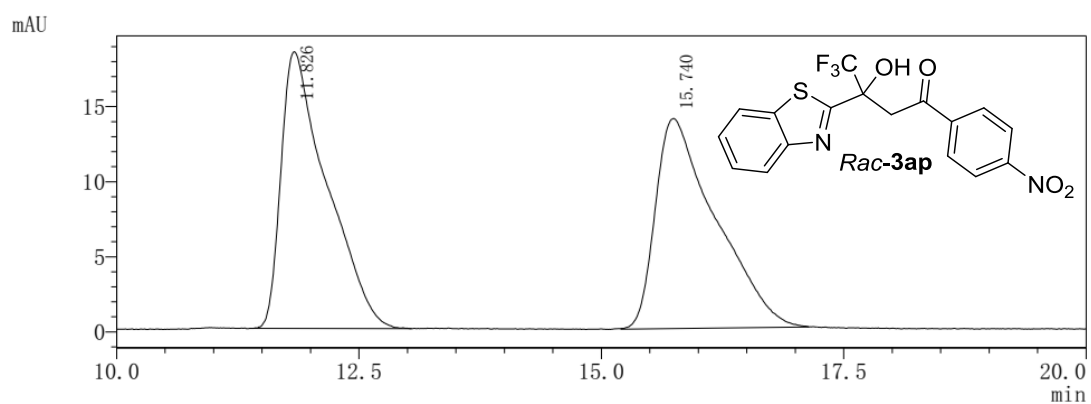
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	11.053	0.753	1346788	43678	50.179
2	17.264	1.166	1337173	28738	49.821



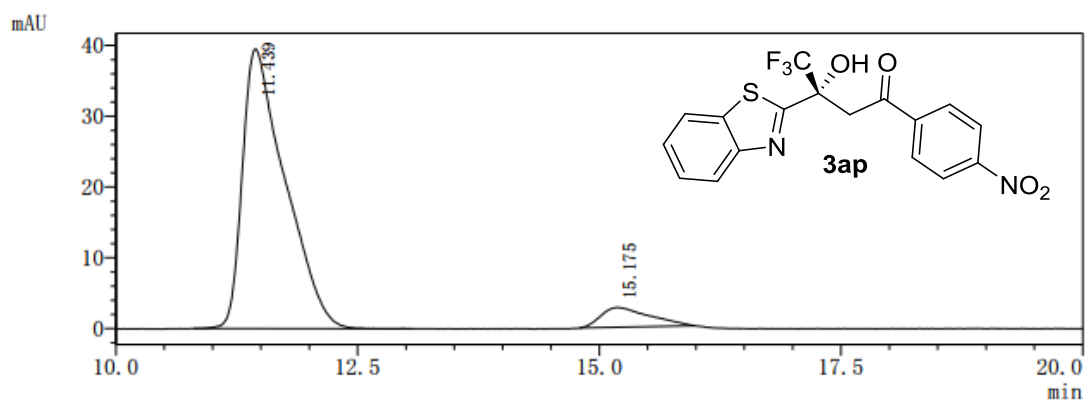
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	10.619	0.731	2535233	89544	93.118
2	16.464	1.054	187362	5277	6.882



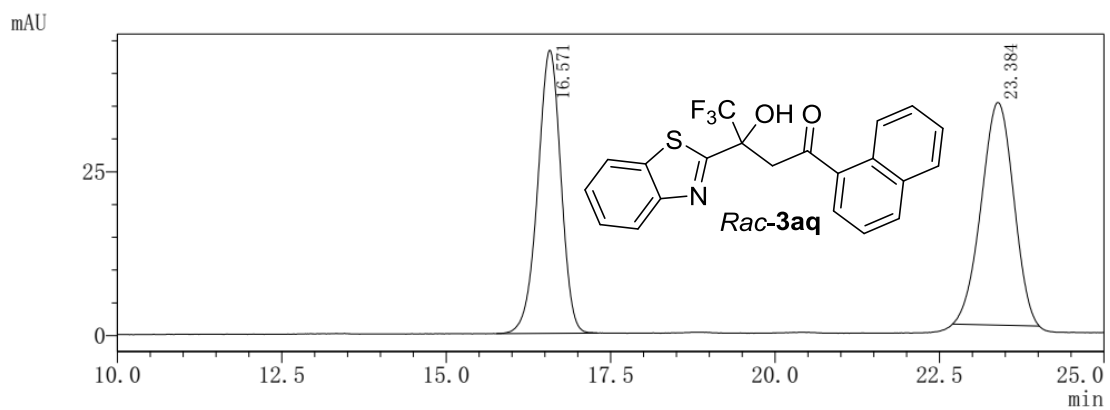
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	11.826	0.797	606886	18440	50.086
2	15.740	1.064	604813	14001	49.914



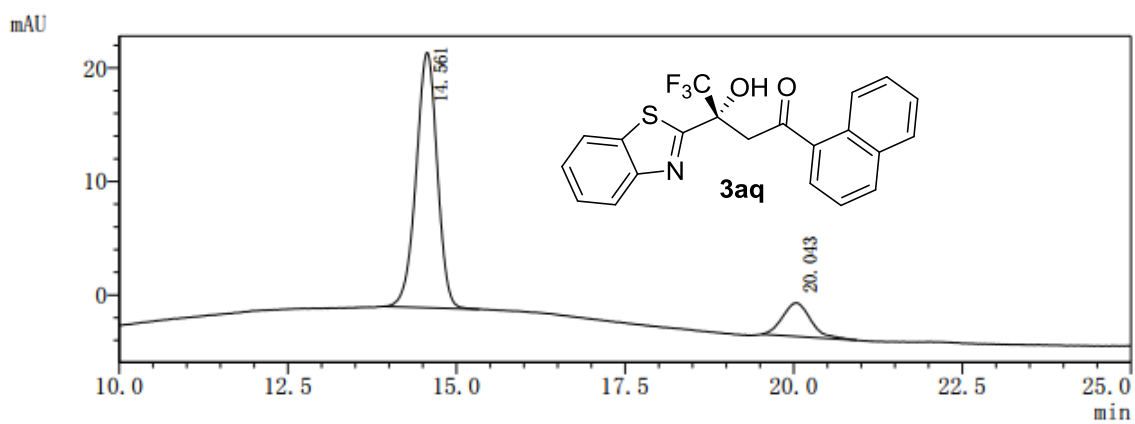
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	11.439	0.790	1213465	39524	92.527
2	15.175	1.038	98002	2797	7.473



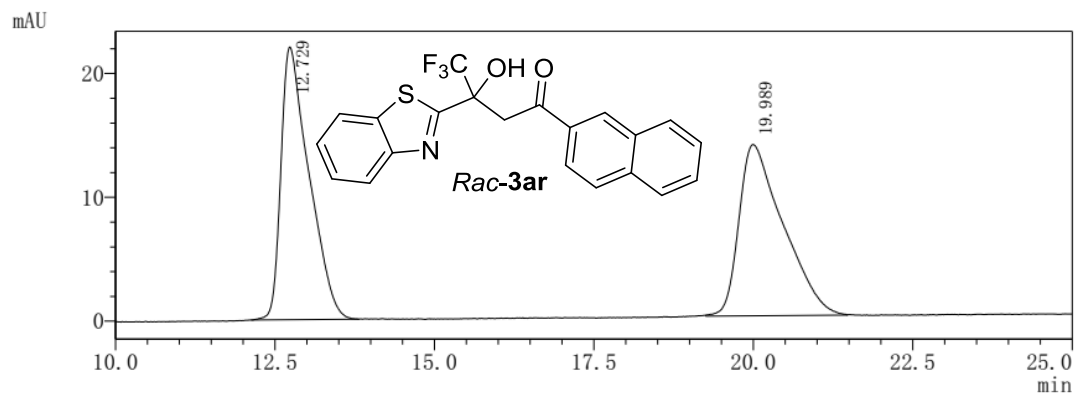
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	16.571	0.646	1056536	43223	47.568
2	23.384	0.926	1164589	33991	52.432



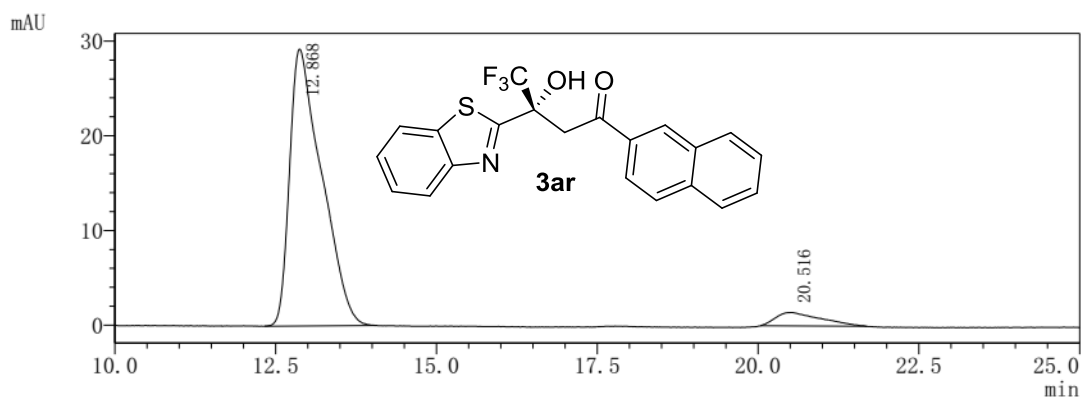
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	14.561	0.580	493124	22493	85.120
2	20.043	0.771	86201	2952	14.880



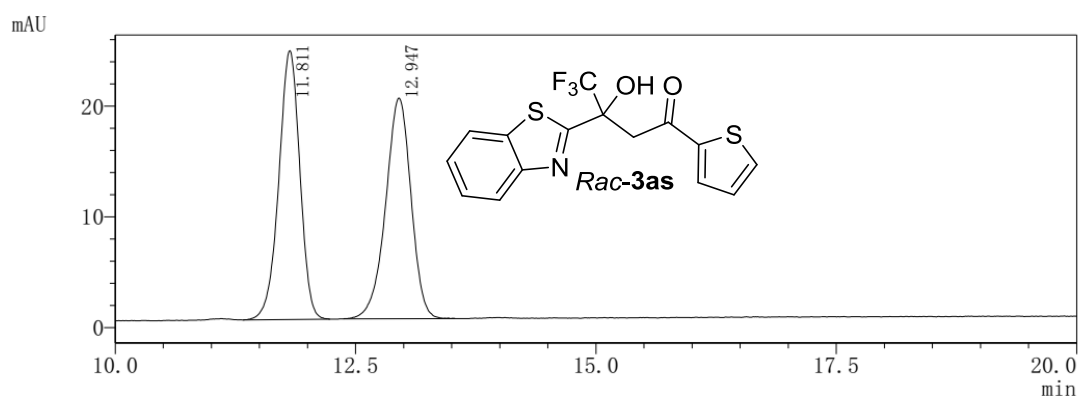
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	12.729	0.801	674407	22035	50.278
2	19.989	1.384	666936	13842	49.722



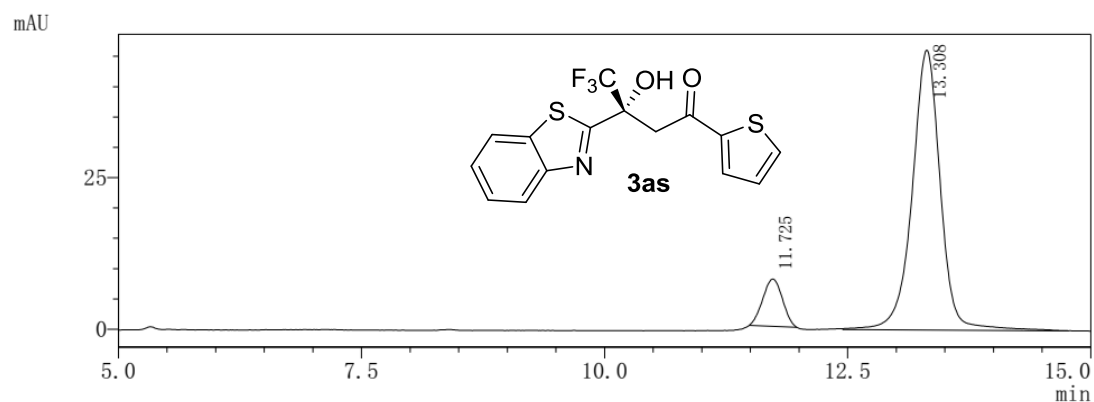
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	12.868	0.903	1014748	29243	93.720
2	20.516	1.444	67998	1403	6.280



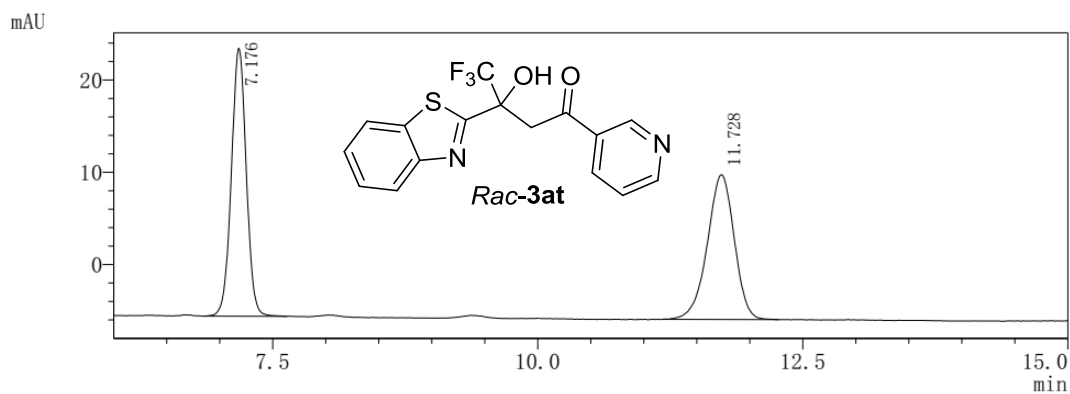
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	11.811	0.407	369527	24300	50.189
2	12.947	0.486	366749	19940	49.811



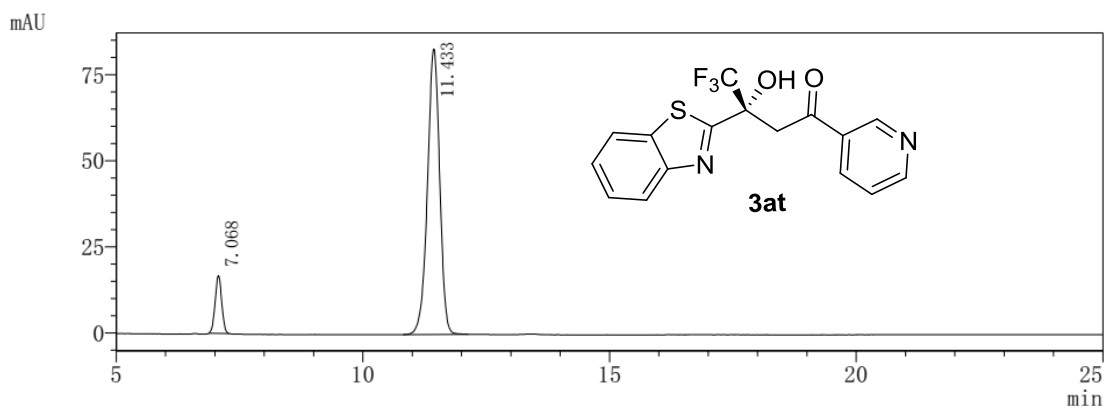
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	11.725	0.392	109779	7791	10.528
2	13.308	0.509	932911	46151	89.472



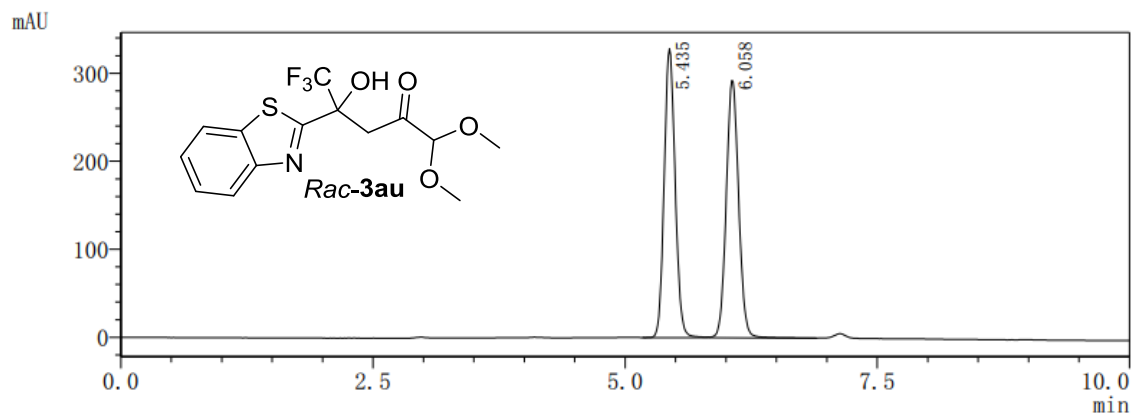
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	7.176	0.269	284473	29027	50.581
2	11.728	0.471	277941	15675	49.419



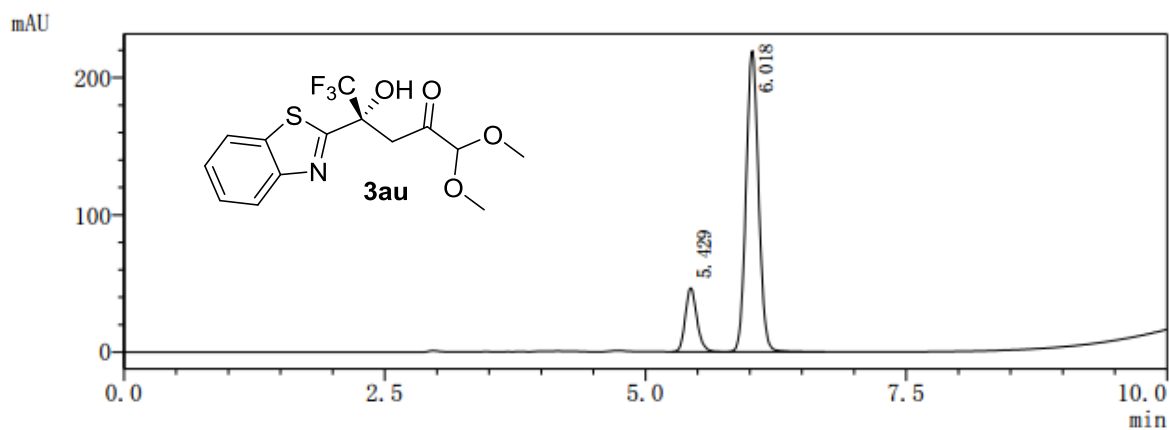
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	7.068	0.261	155757	16761	9.823
2	11.433	0.457	1429879	82956	90.177



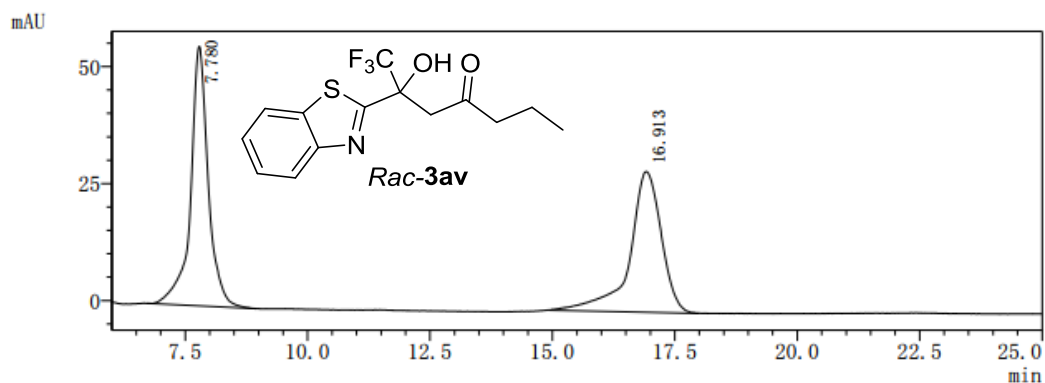
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	5.435	0.216	2484001	328150	49.844
2	6.058	0.239	2499568	292316	50.156



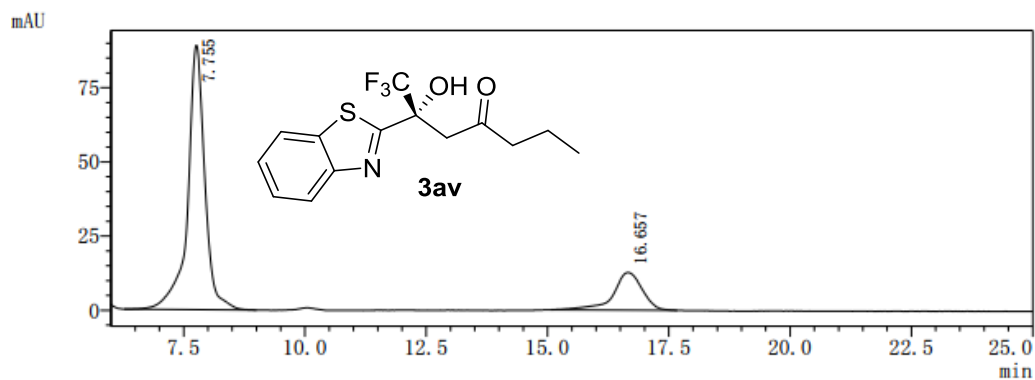
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	5.429	0.218	362473	46466	16.538
2	6.018	0.234	1829291	219507	83.462



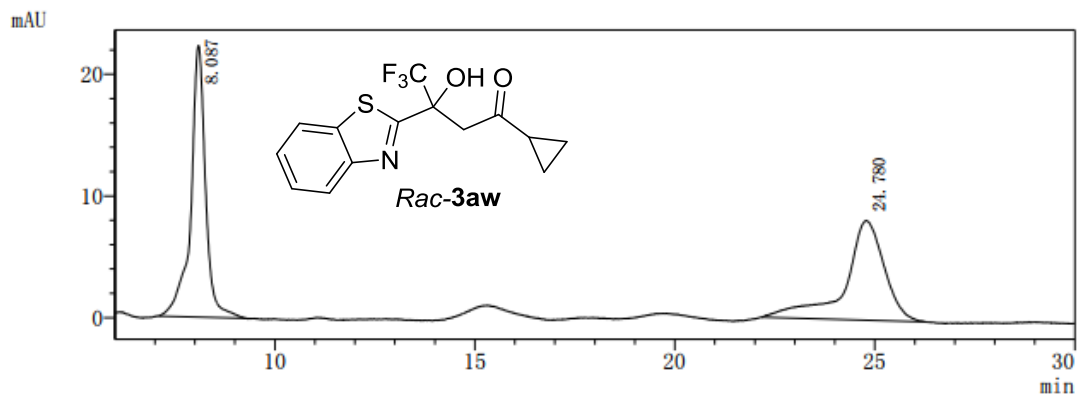
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	7.780	0.576	1395477	55472	50.805
2	16.913	1.039	1351272	30048	49.195



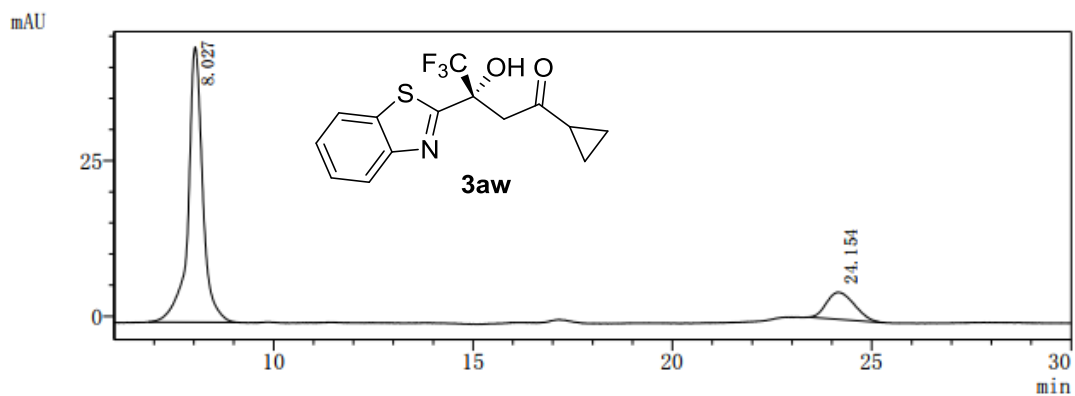
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	7.755	0.565	2196386	89049	80.670
2	16.657	0.994	526302	12675	19.330



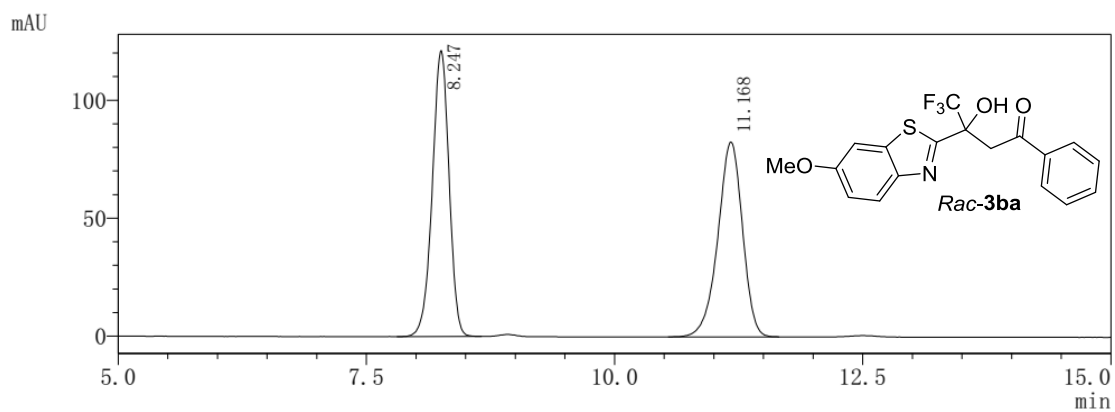
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	8.087	0.569	573022	22318	50.705
2	24.780	1.473	557096	8175	49.295



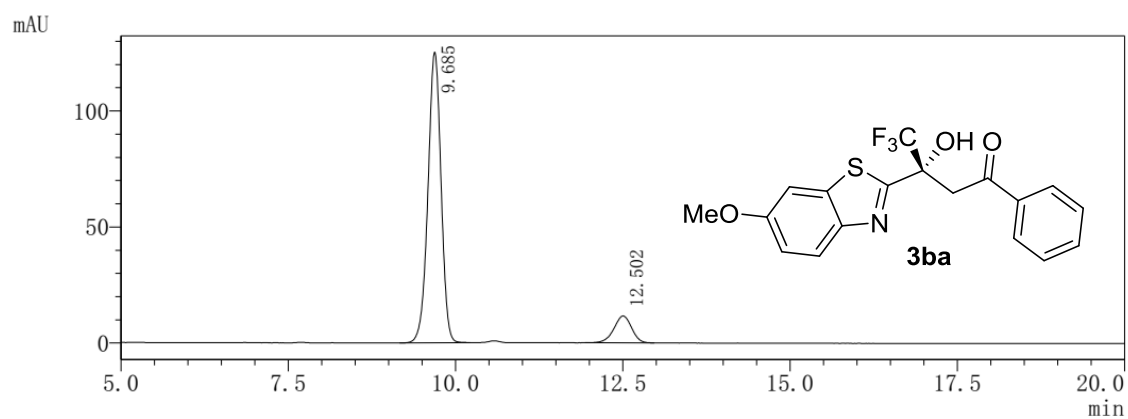
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	8.027	0.572	1125660	44214	84.195
2	24.154	1.329	211304	4339	15.805



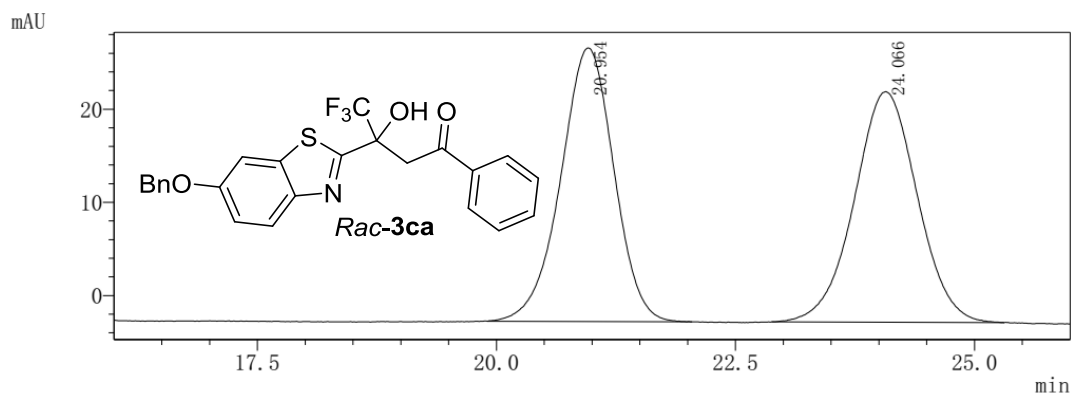
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	8.247	0.319	1424734	121291	49.950
2	11.168	0.459	1427588	82581	50.050



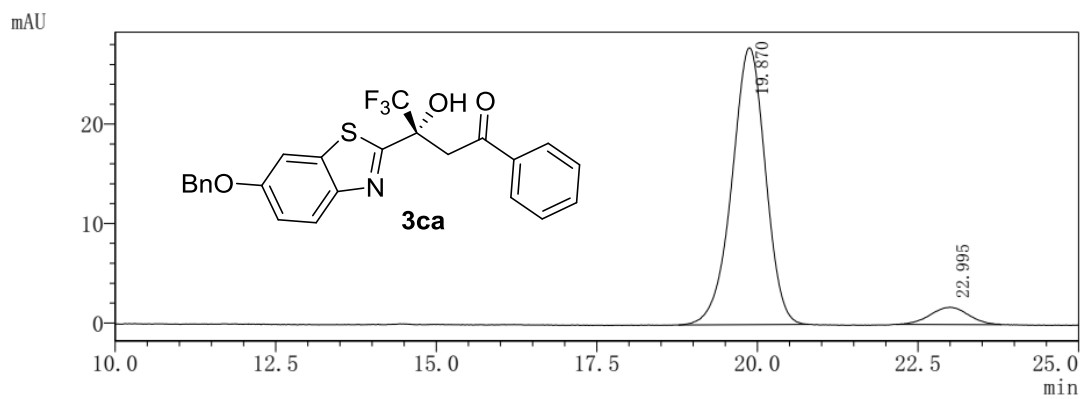
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	9.685	0.365	1702035	125159	88.815
2	12.502	0.491	214342	11573	11.185



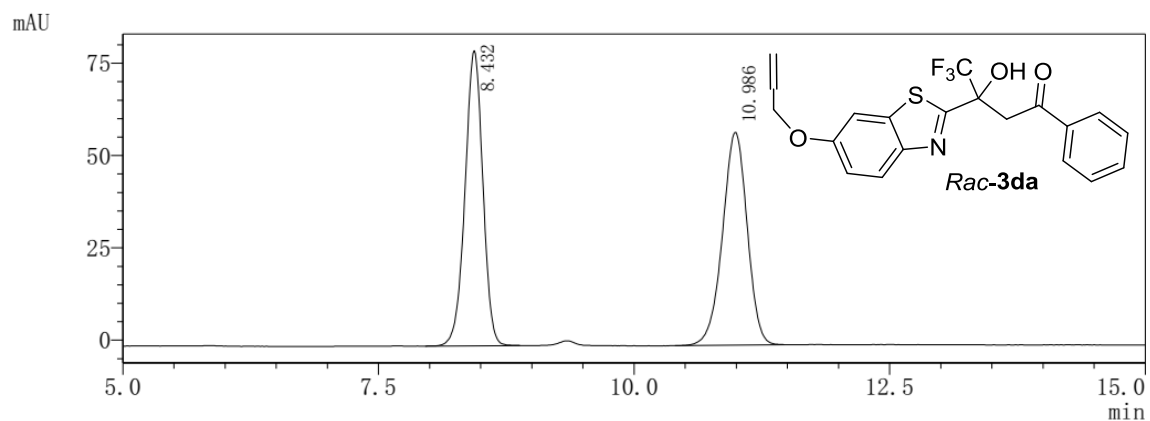
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	20.954	1.018	1138711	29378	50.074
2	24.066	1.206	1135339	24750	49.926



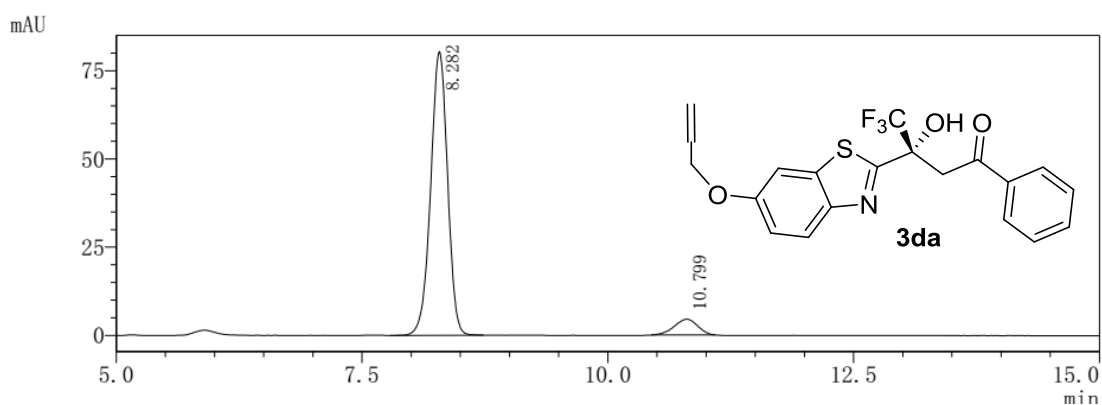
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	19.870	0.958	1014408	27859	93.318
2	22.995	1.098	72636	1748	6.682



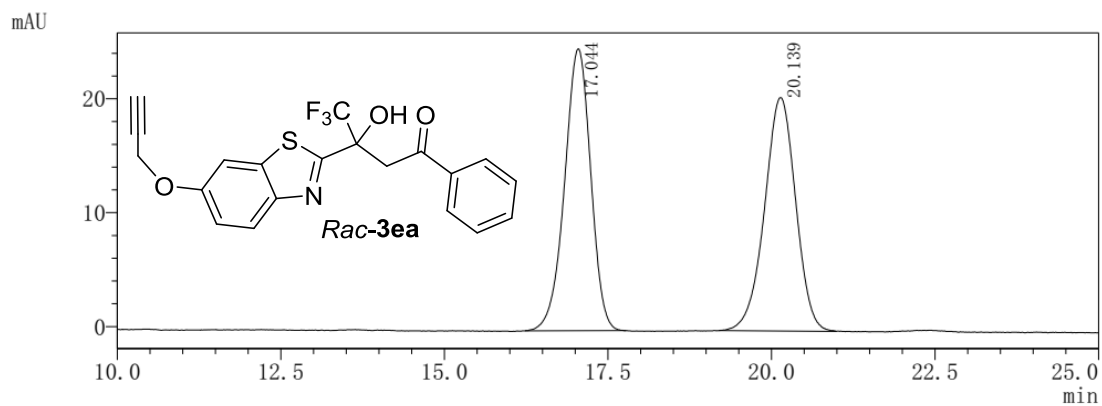
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	8.432	0.330	972549	79956	50.097
2	10.986	0.449	968796	57649	49.903



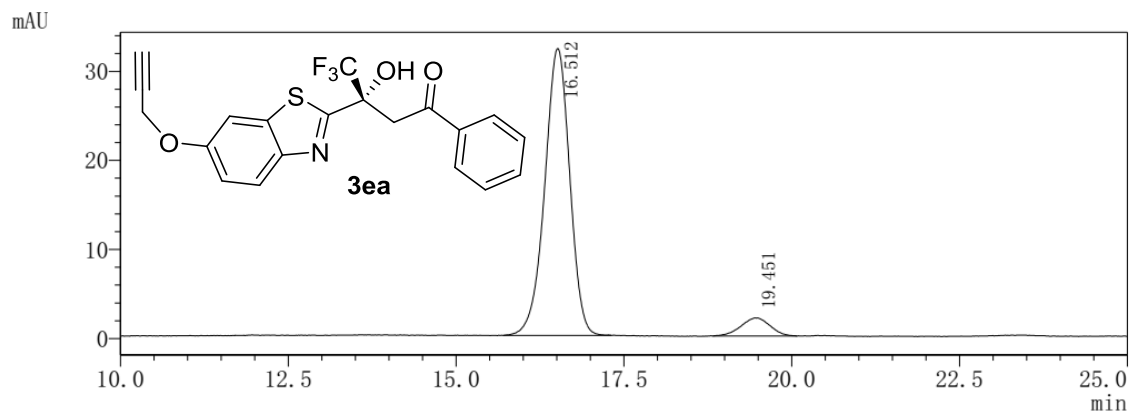
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	8.282	0.324	961940	80461	92.904
2	10.799	0.453	73478	4472	7.096



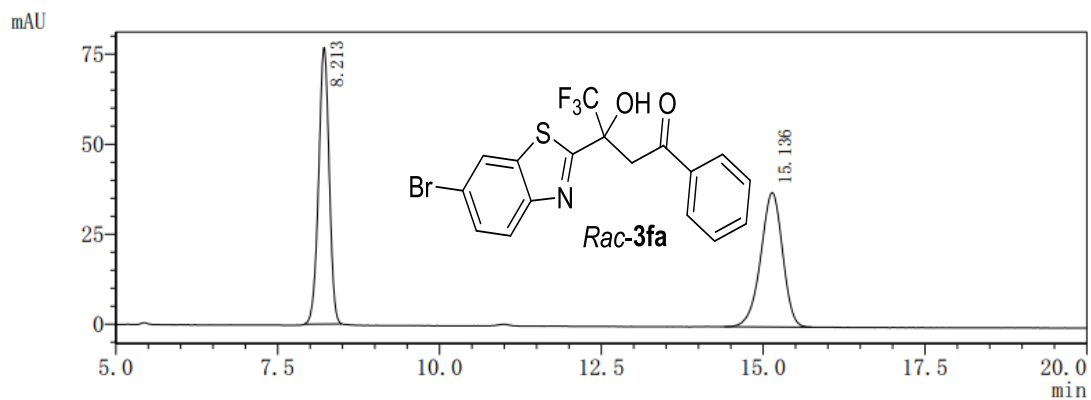
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	17.044	0.733	688871	24759	50.297
2	20.139	0.874	680731	20494	49.703



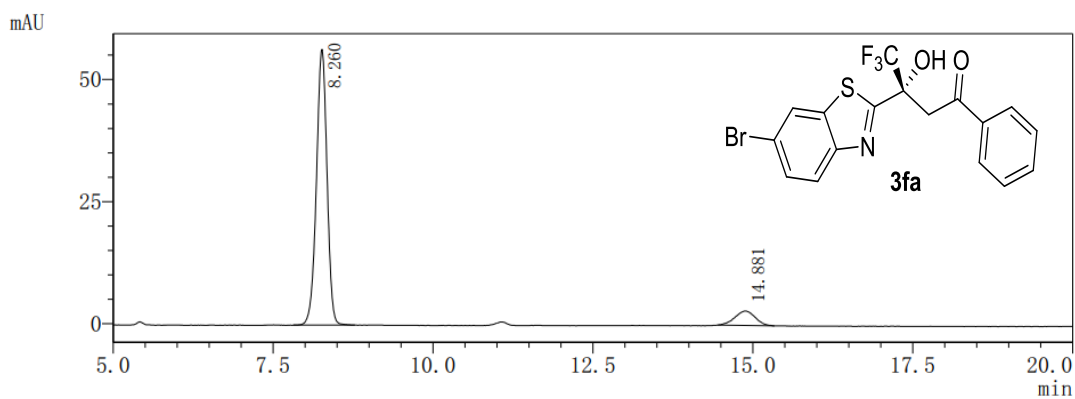
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	16.512	0.681	834418	32211	93.141
2	19.451	0.812	61448	2030	6.859



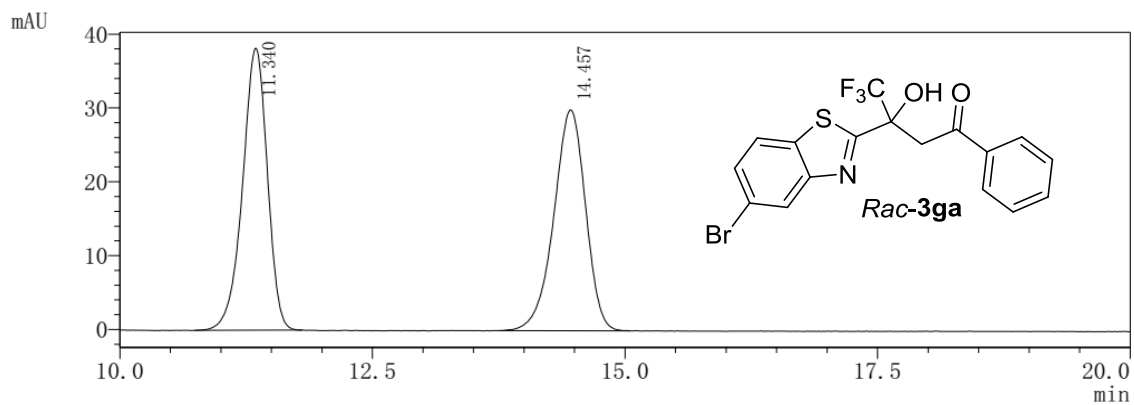
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	8.213	0.310	869994	76716	49.778
2	15.136	0.621	877768	37316	50.222



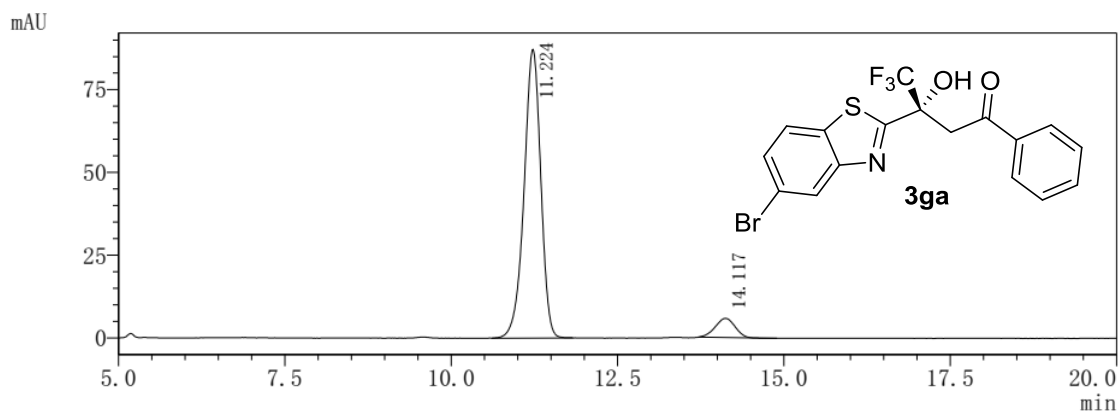
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	8.260	0.313	650545	56507	91.038
2	14.881	0.600	64040	2941	8.962



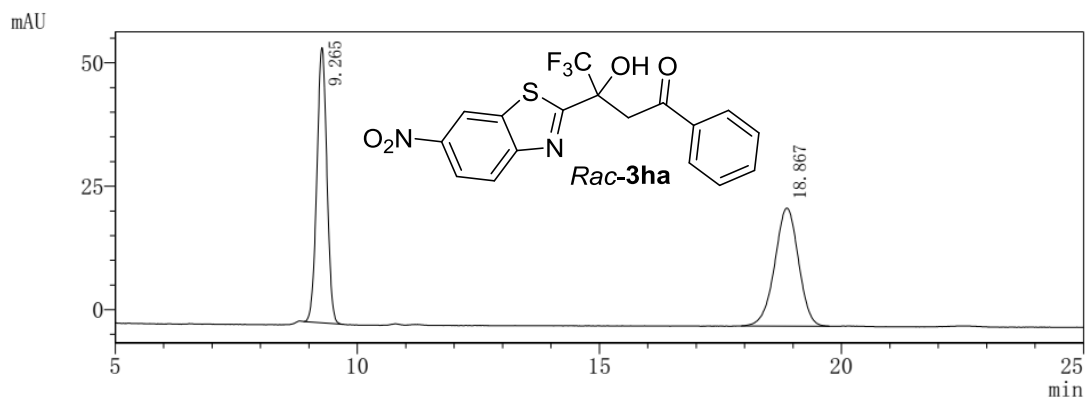
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	11.340	0.453	652620	38207	49.946
2	14.457	0.578	654037	29924	50.054



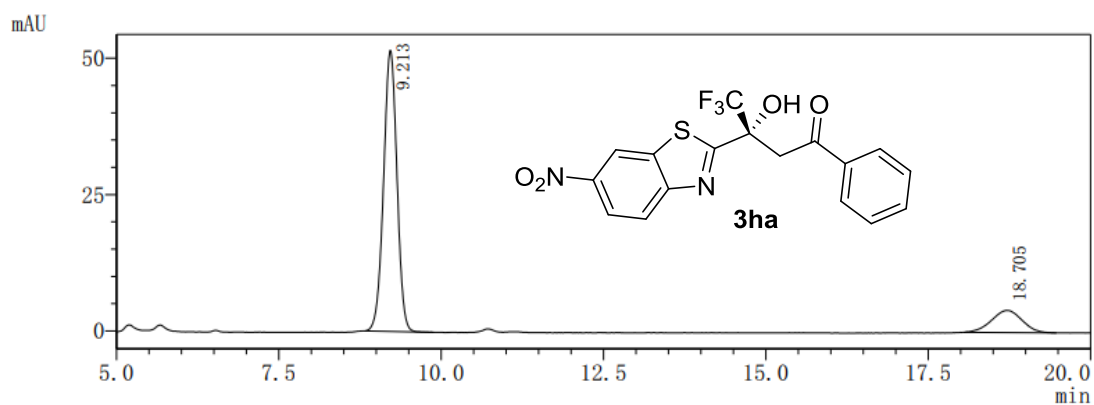
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	11.224	0.463	1522239	87243	92.758
2	14.117	0.563	118843	5788	7.242



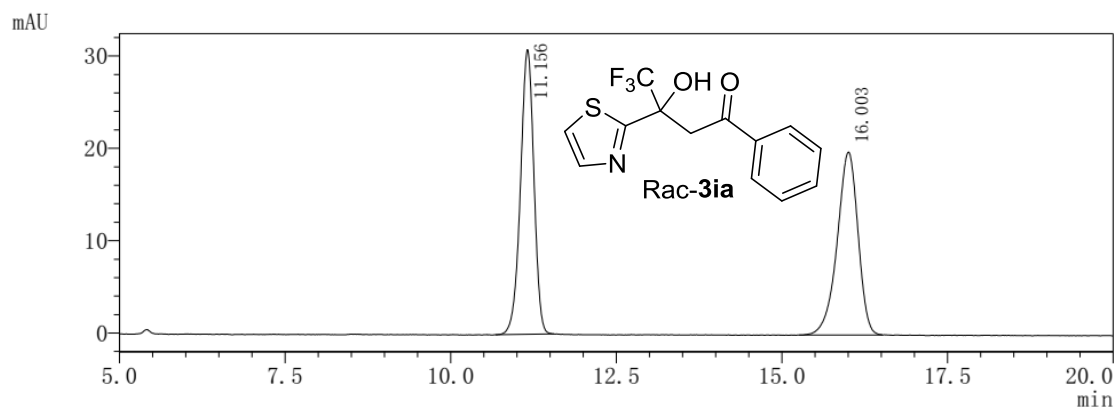
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	9.265	0.389	801631	55760	49.594
2	18.867	0.901	814768	23915	50.406



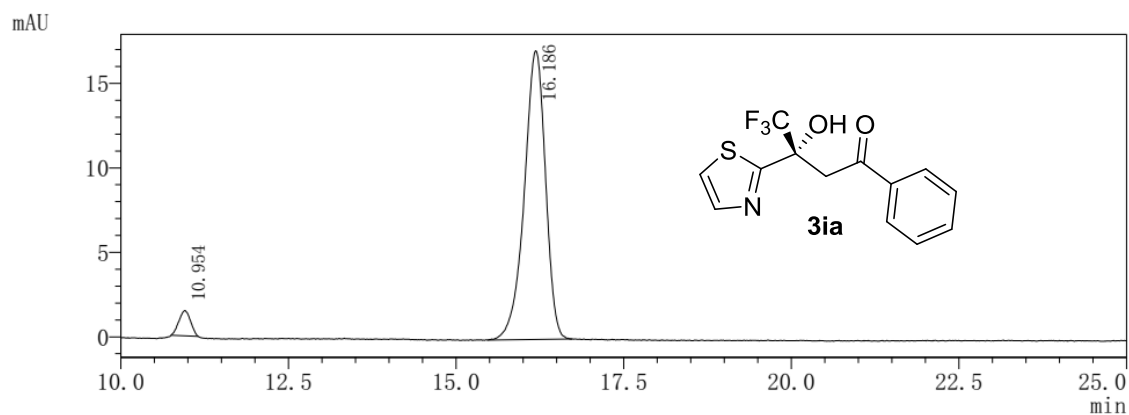
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	9.213	0.388	740581	51545	84.814
2	18.705	0.882	132598	4062	15.186



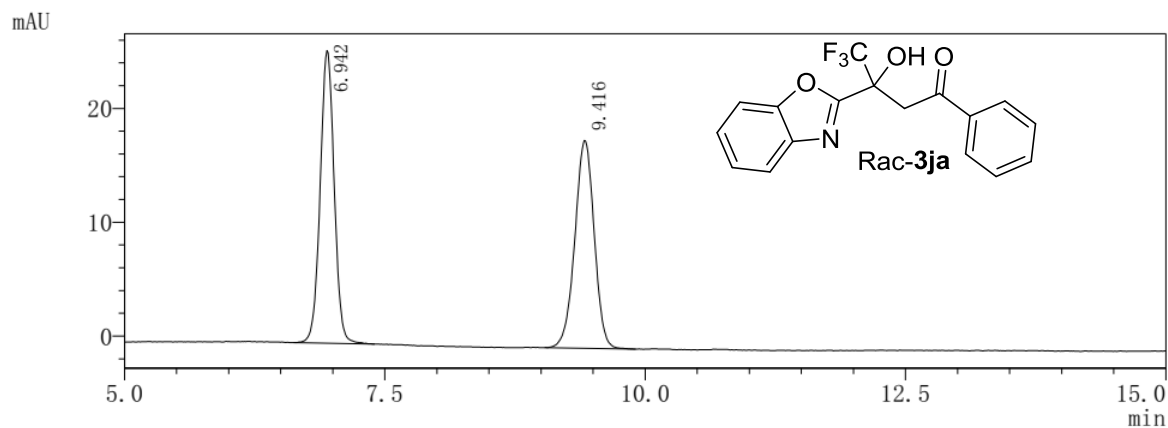
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	11.156	0.379	434678	30823	50.005
2	16.003	0.577	434596	19827	49.995



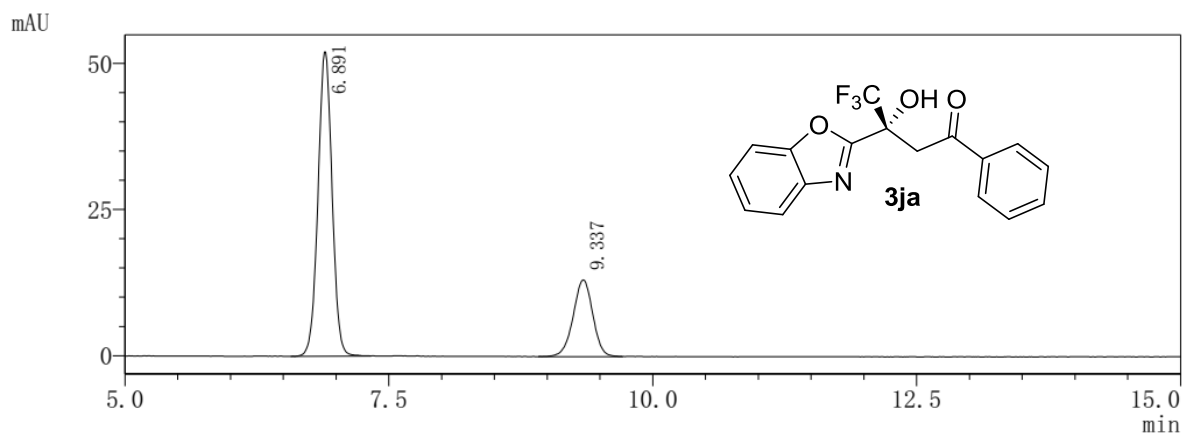
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	10.954	0.345	17973	1494	4.556
2	16.186	0.577	376527	17096	95.444



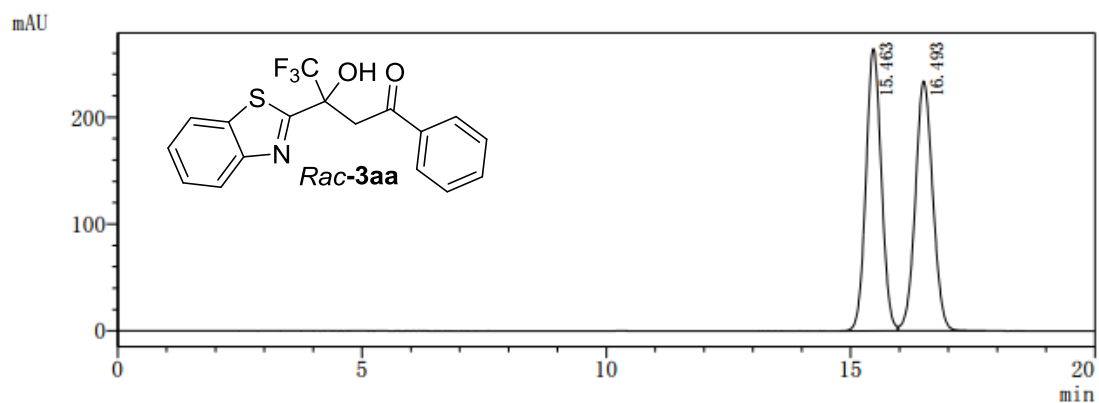
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	6.942	0.258	240867	25708	50.411
2	9.416	0.350	236941	18270	49.589



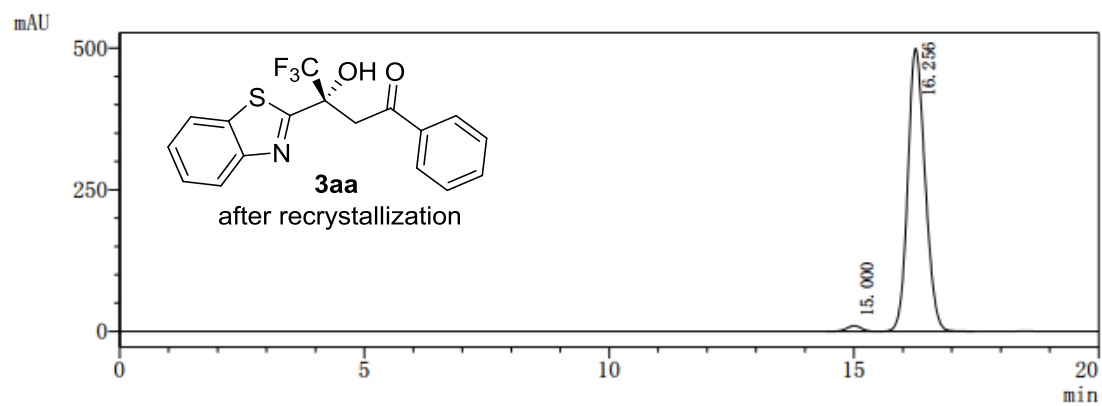
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	6.891	0.256	482946	52051	73.989
2	9.337	0.348	169785	13127	26.011



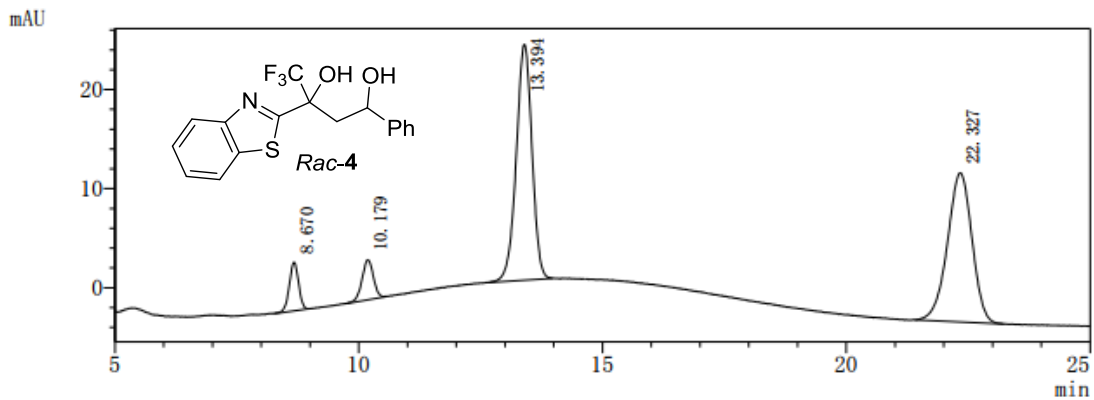
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	15.463	0.586	5798162	264155	49.897
2	16.493	0.661	5822183	233885	50.103



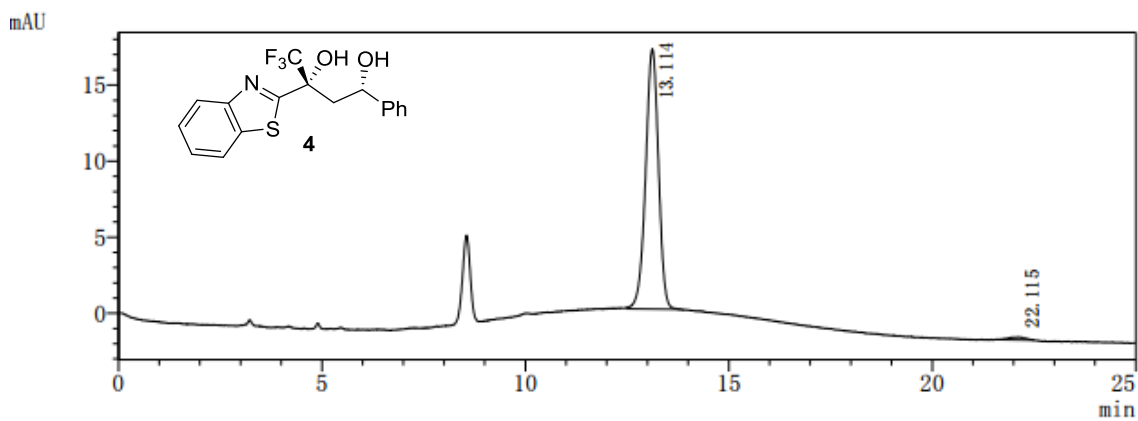
PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	15.000	0.562	207010	9919	1.657
2	16.256	0.655	12284441	499340	98.343



PDA Ch1 254nm 4nm

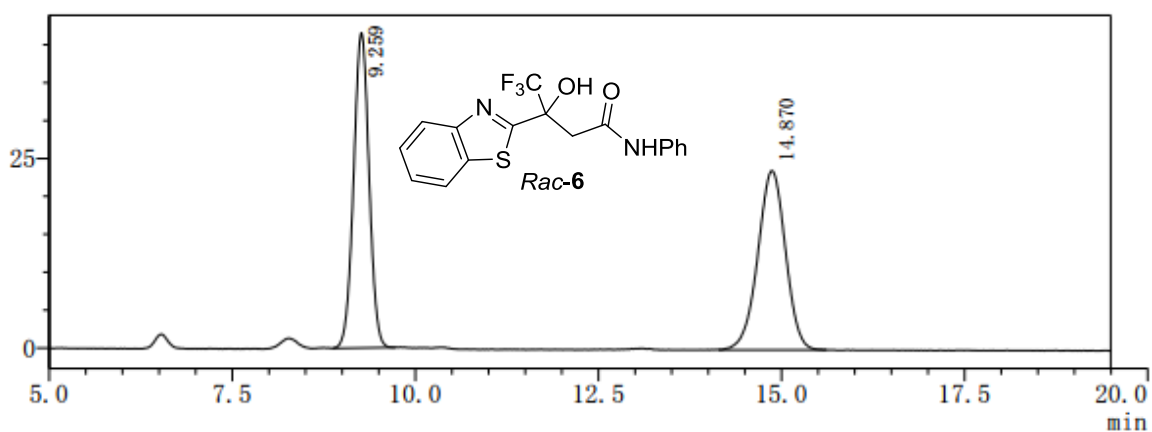
Peak	Ret Time	Width	Area	Height	Area %
1	8.670	0.361	65541	4909	5.496
2	10.179	0.436	65196	4033	5.467
3	13.394	0.595	534918	23792	44.855
4	22.327	0.927	526882	15024	44.182



PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	13.114	0.582	376244	17102	98.665
2	22.115	0.759	5092	197	1.335

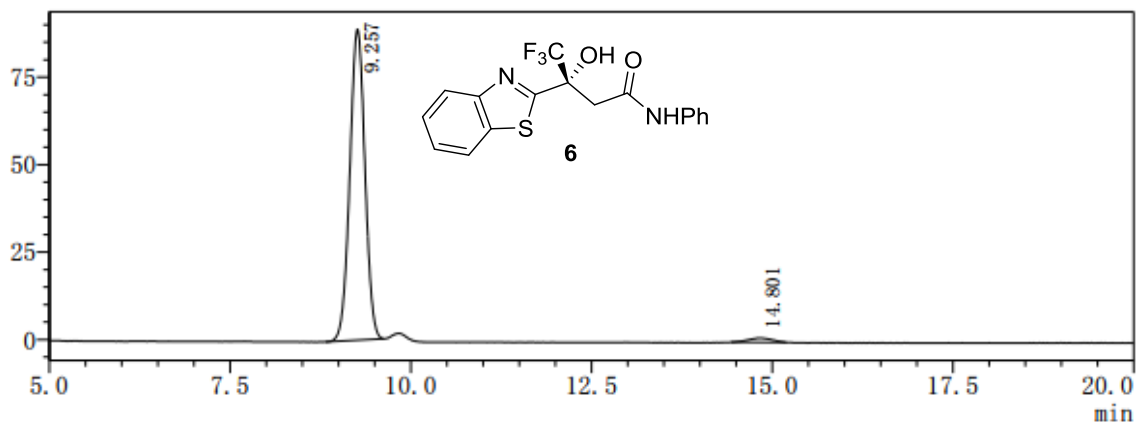
mAU



PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	9.259	0.399	613794	41535	49.606
2	14.870	0.696	623550	23647	50.394

mAU



PDA Ch1 254nm 4nm

Peak	Ret Time	Width	Area	Height	Area %
1	9.257	0.396	1301473	88872	97.938
2	14.801	0.650	27401	1180	2.062