

Supplementary Information

Chiral cyclopropenimine-catalyzed enantioselective Michael additions between benzophenone-imine of glycine esters and α,β -unsaturated pyrazolamides

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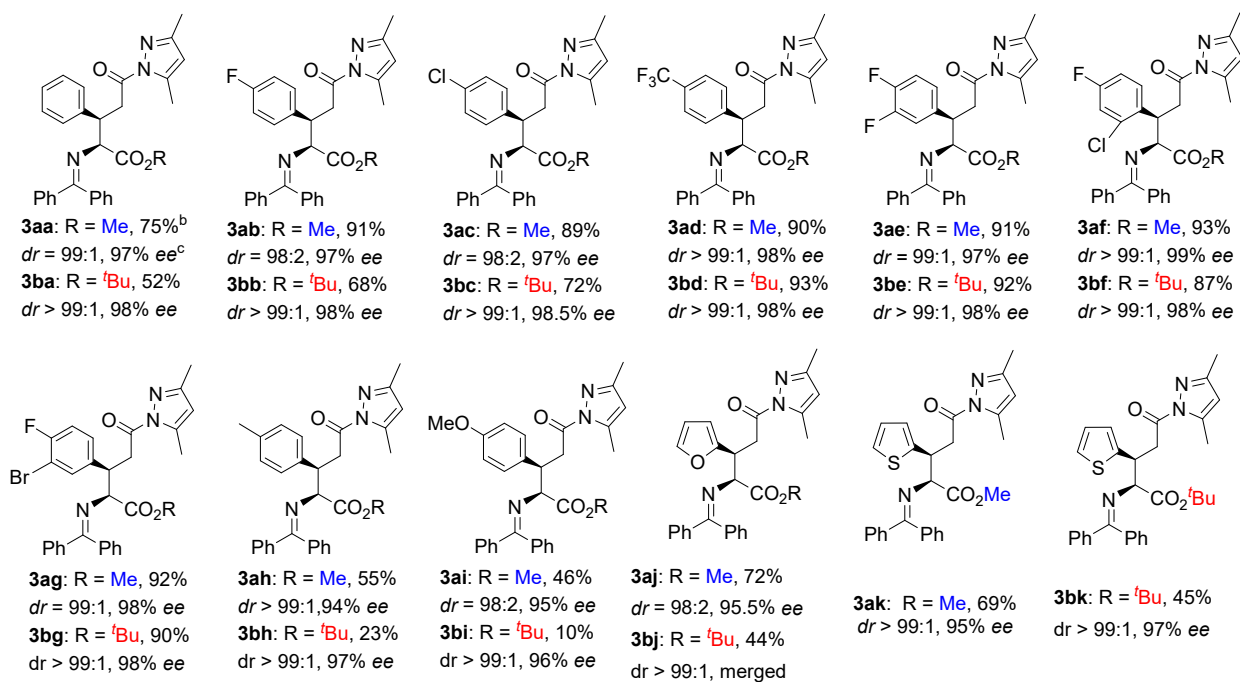
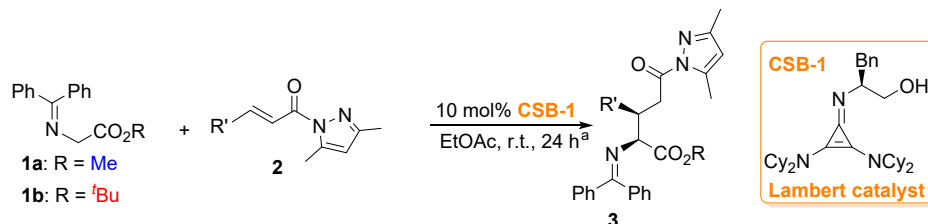
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1. General

The ^1H NMR, ^{13}C NMR, ^{19}F NMR spectra were measured in CDCl_3 , Acetone- d_6 or DMSO- d_6 solution on a Bruker AV-400 spectrometer using TMS as an internal reference. Coupling constant (J) values are given in Hz. Multiplicities are designated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; br, broad; m, multiplet. High-resolution mass spectra (HRMS) were performed on a Bruker microTOF-Q II Mass Spectrometer with ES ionization (ESI). All commercially available reagents were used as received. Thin-layer chromatography on silica (with GF_{254}) was used to monitor all reactions. Products were purified by flash column chromatography on silica gel purchased from Qingdao Haiyang Chemical Co., Ltd. Chiral High Performance Liquid Chromatography (HPLC) analyses were performed using an Agilent 1260 Series apparatus and Chiralpak AD-H, OD-H and AS-H columns purchased from Daicel Chemical Industries. The configurations of the products have been assigned by single crystal X-ray diffraction analysis. All solvents, organic and inorganic reagents were from commercial sources and used without purification unless otherwise noted. Glycine esters **1a** and **1b**, β -substituted α,β -unsaturated pyrazolamides **2** were prepared according to literatures reported methods.^[1,2] Chiral cyclopropenimine organosuperbsaes (CSBs) **CSB-1**, *ent*-**CSB-1**, **CSB-2**, **CSB-3**, **CSB-5**, *ent*-**CSB-5** were prepared following literature reported procedure, and their characterization data are consistent with reference report.^[3] The synthesis of **CSB-4**, **CSB-6** and **CSB-8** were described in our previous report^[4]. The characterization data of all new compounds were listed in the Supplementary Information.

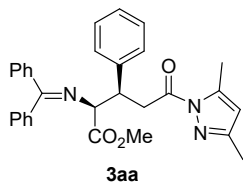
2. Experimental sections

2.1 General procedure for CSB-1 catalyzed asymmetric Michael additions

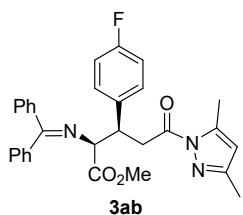


a. All reactions were performed in 1.0 mmol scale; b. Isolated yield based on **2**; c. The *dr* and *ee* of products were determined by chiral HPLC column (Daicel ChiralPak AD-H).

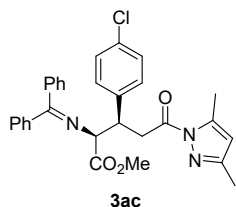
Glycine imine **1** (1.0 mmol), β -substituted α,β -unsaturated pyrazolamides **2** (1.1 mmol, 1.1 equiv.), and **CSB-1** (56.0 mg, 10 mol%) in 10.0 mL of anhydrous EtOAc were stirred at r.t. for 24 h. The reaction was checked by a thin layer chromatography (TLC). The solvent was removed by a rotary evaporator and the residue was purified by a flash column chromatography (*n*-hexane: EtOAc: Et₃N = 10:1:0.01 to 1:1:0.01, V/V. Note: The silica gel which used in purification was buffered by *n*-hexane and Et₃N (V/V = 100/1). The *dr* and *ee* values of adducts **3** were determined by chiral HPLC analysis.



White solid; 75% yield; $[\alpha]_{\text{D}}^{25} = -75.4^\circ$ ($c = 0.1$, CH₂Cl₂), m.p. 37.2-38.4 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm) 7.59 (d, $J = 7.2$ Hz, 2H), 7.45-7.35 (m, 6H), 7.23-7.16 (m, 5H), 6.85 (d, $J = 5.2$ Hz, 2H), 5.95 (s, 1H), 4.29 (d, $J = 6.0$ Hz, 1H), 4.23 (q, $J = 6.8$ Hz, 1H), 3.80-3.75 (m, 2H), 3.56 (s, 3H), 2.36 (s, 3H), 2.18 (s, 3H); ¹³C NMR (101 MHz, Acetone-*d*₆) δ (ppm) 172.83, 172.06, 171.51, 152.16, 144.34, 142.55, 140.13, 136.97, 131.39, 129.45, 129.28, 129.10, 128.89, 128.39, 127.60, 111.65, 71.49, 52.14, 45.69, 37.31, 14.46, 13.81; HRMS (ESI): Exact mass calcd. for C₃₀H₃₀N₃O₃⁺ [M+H]⁺, 480.2282, Found 480.2285; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 98:2, 0.8 mL/min, 254 nm, t_{R} (major) = 26.818 min, t_{R} (minor) = 43.017 min, major: 97% *ee*.

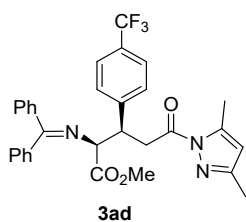


White solid; 91% yield; $[\alpha]_{\text{D}}^{25} = -150.1^\circ$ ($c = 0.1$, CH₂Cl₂), m.p. 51.9-52.7 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm) 7.60 (d, $J = 7.2$ Hz, 2H), 7.45-7.42 (m, 5H), 6.93-6.92 (m, 2H), 5.96 (s, 1H), 4.27 (d, $J = 6.4$ Hz, 1H), 4.22 (q, $J = 6.8$ Hz, 1H), 3.74 (d, $J = 6.8$ Hz, 2H), 3.56 (s, 3H), 2.36 (s, 3H), 2.18 (s, 3H); ¹³C NMR (101 MHz, Acetone-*d*₆) δ (ppm) 172.71, 172.24, 171.42, 163.79, 161.37, 152.24, 144.37, 140.09, 138.54, 138.51, 136.92, 131.46, 131.10, 131.02, 129.54, 129.47, 129.35, 128.92, 128.37, 115.78, 115.57, 111.70, 71.39, 52.18, 45.04, 37.54, 14.44, 13.80; ¹⁹F NMR (376 MHz, Acetone-*d*₆) δ (ppm) 59.88; HRMS (ESI): Exact mass calcd. for C₃₀H₂₉FN₃O₃⁺ [M+H]⁺, 498.2187, Found 498.2192; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_{R} (major) = 7.707 min, t_{R} (minor) = 12.670 min, major: 97% *ee*.

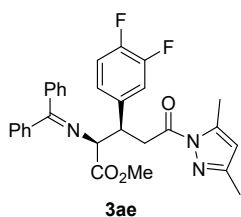


White solid; 89% yield; $[\alpha]_{\text{D}}^{25} = -53.2^\circ$ ($c = 0.1$, CH₂Cl₂), m.p. 44.5-45.6 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm) 7.60 (d, $J = 7.6$ Hz, 2H), 7.45-7.42 (m, 4H), 7.36 (d, $J = 7.6$ Hz, 2H), 7.22 (dd, $J = 8.4$ Hz, $J = 20.0$ Hz, 4H), 6.93 (d, $J = 7.6$ Hz, 2H), 5.96 (s, 1H), 4.28 (d, $J = 6.0$ Hz, 1H), 4.20 (q, $J = 6.8$ Hz, 1H), 3.75 (d, $J = 7.2$ Hz, 1H), 3.57 (s, 3H), 2.37 (s, 3H), 2.18 (s, 3H); ¹³C NMR (101 MHz, Acetone-*d*₆) δ (ppm) 172.65, 172.34, 171.35, 152.28, 144.39, 141.45, 140.08, 136.88, 132.92, 131.47, 131.02, 129.55, 129.48, 129.35, 129.07, 128.92, 128.38, 111.72,

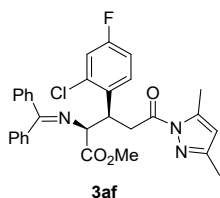
71.18, 52.21, 45.18, 37.34, 14.41, 13.78; HRMS (ESI): Exact mass calcd. for $C_{30}H_{29}ClN_3O_3^+$ $[M+H]^+$, 514.1892. Found 514.1895; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R (major) = 8.049 min, t_R (minor) = 13.203 min, major: 97% *ee*.



White solid; 90% yield; $[\alpha]_D^{25} = -40.3^\circ$ ($c = 0.1$, CH_2Cl_2), m.p. 42.7-43.8 °C. 1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.59 (dd, $J_1 = 10.1$ Hz, $J_2 = 8.5$ Hz, 4H), 7.47-7.36 (m, 8H), 6.86 (d, $J = 6.6$ Hz, 2H), 5.98 (s, 1H), 4.30 (dt, $J_1 = 13.8$ Hz, $J_2 = 5.7$ Hz, 2H), 3.85 (ddd, $J_1 = 17.5$ Hz, $J_2 = 6.7$ Hz, 2H), 3.59 (s, 3H), 2.37 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 172.60, 172.49, 171.28, 152.39, 147.31, 144.43, 140.02, 136.75, 131.54, 130.07, 129.58, 129.51, 129.33, 128.95, 128.29, 125.97, 125.93, 111.77, 70.93, 52.33, 45.51, 36.97, 14.42, 13.81; ^{19}F NMR (376 MHz, Acetone d_6) δ (ppm) 114.62; HRMS (ESI): Exact mass calcd. for $C_{31}H_{29}F_3N_3O_3^+$ $[M+H]^+$, 548.2156. Found 548.2158; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R (major) = 7.108 min, t_R (minor) = 13.529 min, 97% *ee*.

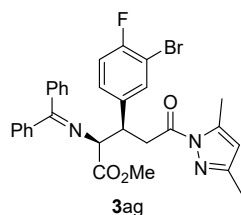


White solid; 91% yield; $[\alpha]_D^{25} = -53.0^\circ$ ($c = 0.1$, CH_2Cl_2), m.p. 106.7-107.8 °C. 1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.64 (s, 1H), 7.62 (s, 1H), 7.49-7.45 (m, 4H), 7.39 (t, $J = 7.4$ Hz, 2H), 7.23-7.16 (m, 2H), 7.07-7.04 (m, 1H), 6.98-6.96 (m, 2H), 6.00 (s, 1H), 4.31 (d, $J = 5.9$ Hz, 1H), 4.23-4.18 (m, 1H), 3.80 (ddd, $J_1 = 17.3$ Hz, $J_2 = 7.2$ Hz, 2H), 3.61 (s, 3H), 2.39 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 172.57, 172.51, 171.28, 152.36, 144.42, 140.01, 136.83, 131.55, 129.63, 129.50, 129.40, 128.96, 128.34, 125.81, 125.77, 125.74, 118.36, 118.19, 117.88, 117.71, 111.77, 70.98, 52.30, 45.02, 37.31, 14.43, 13.80; ^{19}F NMR (376 MHz, Acetone- d_6) δ (ppm) 37.23, 37.18, 34.74, 34.68; HRMS (ESI): Exact mass calcd. for $C_{30}H_{28}F_2N_3O_3^+$ $[M+H]^+$, 516.2093. Found 514.2098; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 95:5, 1.0 mL/min, 254 nm, t_R (major) = 7.005 min, t_R (minor) = 12.474 min, 97% *ee*.

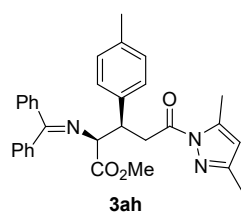


White solid; 93% yield; $[\alpha]_D^{25} = -109.4^\circ$ ($c = 0.1$, CH_2Cl_2), m.p. 41.8-43.2 °C. 1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.65 (s, 2H), 7.63 (s, 1H), 7.49-7.35 (m, 7H), 7.21 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.7$ Hz, 1H), 7.02 (td, $J = 8.5, 2.7$ Hz, 1H), 6.69 (d, $J = 14.9$ Hz, 2H), 6.05 (s, 1H), 4.69 (dt, $J_1 = 9.4$ Hz, $J_2 = 4.6$ Hz, 1H), 4.40 (d, $J = 4.2$ Hz, 1H), 4.15 (dd, $J_1 = 17.8$ Hz, $J_2 = 9.8$ Hz, 1H), 3.81 (dd, $J_1 = 17.8$ Hz, $J_2 = 4.88$ Hz, 1H), 3.69 (s, 3H), 2.39 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 172.60, 171.40, 163.29, 160.83, 152.45, 144.43, 139.97, 136.76, 135.91, 135.62, 135.51, 131.51, 129.56, 129.51, 129.33, 128.98, 128.03, 117.56, 117.31, 114.67, 114.47, 111.80,

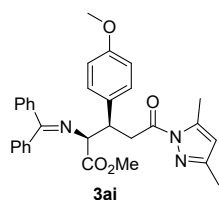
68.04, 52.49, 40.98, 36.09, 14.38, 13.84; ^{19}F NMR (376 MHz, Acetone- d_6) δ 61.9; HRMS (ESI): Exact mass calcd. for $\text{C}_{30}\text{H}_{28}\text{ClFN}_3\text{O}_3^+$ $[\text{M}+\text{H}]^+$, 532.1798. Found 532.1805; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 98:2, 0.4 mL/min, 254 nm, $t_{\text{R}}(\text{major}) = 66.839$ min, $t_{\text{R}}(\text{minor}) = 71.248$ min, 99% *ee*.



White solid; 92% yield; $[\alpha]_{\text{D}}^{25} = -54.8^\circ$ ($c = 0.1$, CH_2Cl_2), m.p. 45.6-46.2 $^\circ\text{C}$. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.66-7.58 (m, 2H), 7.50 (dd, $J = 6.7, 2.1$ Hz, 1H), 7.45 (dt, $J = 8.3, 3.6$ Hz, 4H), 7.38 (t, $J = 7.4$ Hz, 2H), 7.26-7.20 (m, 1H), 7.13 (t, $J = 8.6$ Hz, 1H), 6.96-6.87 (m, 2H), 5.99 (s, 1H), 4.28 (d, $J = 5.6$ Hz, 1H), 4.18 (dt, $J = 9.1, 5.5$ Hz, 1H), 3.86 (dd, $J_1 = 17.3$ Hz, $J_2 = 9.1$ Hz, 1H), 3.79-3.69 (m, 1H), 3.60 (s, 3H), 2.37 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 172.61, 172.54, 171.28, 159.90, 157.47, 152.40, 144.42, 140.54, 140.51, 140.01, 136.82, 134.52, 131.55, 130.36, 130.28, 129.63, 129.51, 129.39, 128.97, 128.30, 117.11, 116.89, 111.80, 108.81, 108.60, 70.91, 52.33, 44.83, 37.13, 14.43, 13.82; ^{19}F NMR (376 MHz, Acetone- d_6) δ (ppm) 65.33; HRMS (ESI): Exact mass calcd. for $\text{C}_{30}\text{H}_{28}\text{FBrN}_3\text{O}_3^+$ $[\text{M}+\text{H}]^+$, 576.1293. Found 576.1299; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_{\text{R}}(\text{major}) = 7.834$ min, $t_{\text{R}}(\text{minor}) = 10.536$ min, 98% *ee*.

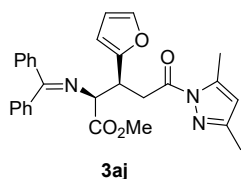


White solid; 55% yield; $[\alpha]_{\text{D}}^{25} = -62.3^\circ$ ($c = 0.1$, CH_2Cl_2), m.p. 42.6-43.8 $^\circ\text{C}$. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.45-7.44 (m, 2H), 7.36-7.28 (m, 4H), 7.25-7.21 (m, 2H), 6.93-6.87 (m, 4H), 6.77-6.74 (m, 2H), 5.81 (s, 1H), 4.14 (d, $J = 6.1$ Hz, 1H), 4.06 (dd, $J_1 = 13.4$ Hz, $J_2 = 6.9$ Hz, 1H), 3.59 (d, $J = 7.1$ Hz, 2H), 3.43 (s, 3H), 2.24 (s, 3H), 2.11 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 172.85, 171.96, 171.54, 152.10, 144.32, 140.17, 139.47, 137.01, 136.98, 131.36, 129.69, 129.44, 129.27, 129.12, 128.87, 128.45, 111.63, 71.65, 52.10, 45.29, 37.39, 20.97, 14.48, 13.80; HRMS (ESI): Exact mass calcd. for $\text{C}_{31}\text{H}_{32}\text{N}_3\text{O}_3^+$ $[\text{M}+\text{H}]^+$, 492.2438. Found 492.2445; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_{\text{R}}(\text{major}) = 7.856$ min, $t_{\text{R}}(\text{minor}) = 10.332$ min, 94% *ee*.

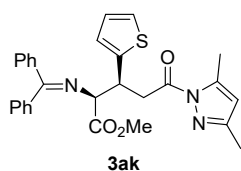


White solid; 46% yield; $[\alpha]_{\text{D}}^{25} = -47.6^\circ$ ($c = 0.1$, CH_2Cl_2), m.p. 107.5-108.2 $^\circ\text{C}$. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.60-7.57 (m, 2H), 7.45-7.42 (m, 4H), 7.36 (t, $J = 7.4$ Hz, 2H), 7.08 (d, $J = 8.7$ Hz, 2H), 6.93 (dd, $J_1 = 6.3$ Hz, $J_2 = 2.7$ Hz, 2H), 6.77 (d, $J = 8.7$ Hz, 2H), 5.94 (s, 1H), 4.26 (d, $J = 6.2$ Hz, 1H), 4.18 (q, $J = 6.88$ Hz, 1H), 3.74-3.69 (m, 2H), 3.72 (s, 3H), 3.56 (s, 3H), 2.37 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 172.87, 171.94, 171.57, 159.57, 152.10, 144.32, 140.17, 137.02, 134.30, 131.37, 130.21, 129.45, 129.30, 128.88, 128.46, 114.44, 111.63, 71.75, 55.44, 52.09, 44.96, 37.64, 14.48, 13.81; HRMS (ESI): Exact mass calcd. for

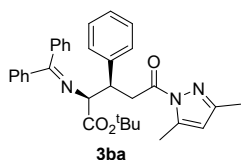
$C_{31}H_{32}N_3O_4^+ [M+H]^+$, 510.2387. Found 510.2396; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R (major) = 11.882 and 19.703 min, t_R (minor) = 14.327 and 18.148 min, dr = 98:2, major: 95 % *ee*.



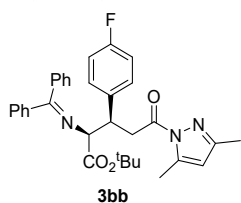
Yellow oil; 72% yield; $[\alpha]_D^{25} = -65.7^\circ$ ($c = 0.12$, CH_2Cl_2). 1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.56 (d, $J = 7.2$ Hz, 2H), 7.49-7.40 (m, 4H), 7.42 (d, $J = 7.3$ Hz, 1H), 7.39-7.33 (m, 3H), 6.98 (d, $J = 3.6$ Hz, 2H), 6.26 (dd, $J_1 = 2.0$ Hz, $J_2 = 3.2$ Hz, 1H), 6.09 (d, $J = 3.2$ Hz, 1H), 6.00 (s, 1H), 4.41 (d, $J = 5.6$ Hz, 1H), 4.32-4.29 (m, 1H), 3.79-3.67 (m, 2H), 3.64 (s, 3H), 2.43 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 172.59, 172.36, 171.41, 155.72, 152.35, 144.48, 142.50, 140.20, 136.92, 131.41, 129.58, 129.50, 129.35, 128.85, 128.51, 111.78, 111.07, 107.21, 69.00, 52.36, 39.57, 35.73, 14.49, 13.81; HRMS (ESI): Exact mass calcd. for $C_{28}H_{28}N_3O_4^+ [M+H]^+$, 470.2074. Found 470.2084; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R (major) = 9.163 and 16.063 min, 95.5 % *ee*.



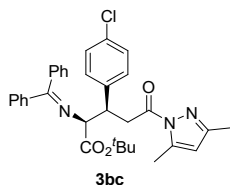
Yellow oil; 69% yield; $[\alpha]_D^{25} = -103.3^\circ$ ($c = 0.11$, CH_2Cl_2). 1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.64-7.62 (m, 2H), 7.47-7.36 (m, 6H), 7.24-7.23 (m, 1H), 6.95-6.93 (m, 2H), 6.90-6.85 (m, 2H), 5.99 (s, 1H), 4.55-4.51 (m, 1H), 4.31 (d, $J = 5.2$ Hz, 1H), 3.87-3.75 (m, 2H), 3.63 (s, 3H), 2.40 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 172.57, 172.40, 171.28, 152.33, 145.59, 144.42, 140.15, 136.93, 131.49, 130.58, 129.59, 129.52, 129.34, 129.29, 128.91, 128.35, 127.37, 125.98, 124.98, 111.75, 71.52, 52.35, 41.02, 38.94, 14.46, 13.81; HRMS (ESI): Exact mass calcd. for $C_{28}H_{28}N_3O_3S^+ [M+H]^+$, 486.1846. Found 486.1852; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R (major) = 7.937 min, t_R (minor) = 11.742 min, 95 % *ee*.



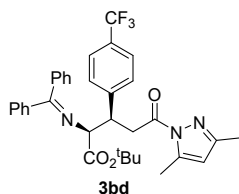
Yellow oil; 52% yield; $[\alpha]_D^{25} = -54.4^\circ$ ($c = 0.12$, CH_2Cl_2). 1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.60-7.57 (m, 2H), 7.47-7.34 (m, 6H), 7.24-7.15 (m, 5H), 6.99-6.96 (m, 2H), 5.92 (s, 1H), 4.25-4.18 (m, 2H), 3.74-3.62 (m, 2H), 2.35 (s, 3H), 2.17 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 171.95, 170.83, 169.21, 151.18, 143.41, 141.75, 139.39, 136.33, 130.37, 128.60, 128.50, 128.36, 128.15, 128.08, 127.94, 127.68, 126.62, 110.71, 80.48, 71.36, 45.08, 37.04, 27.09, 13.58, 12.90; HRMS (ESI): Exact mass calcd. for $C_{33}H_{35}N_3O_3 [M+H]^+$, 522.2757. Found 522.2745; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 97:3, 0.7 mL/min, 254nm, t_R (major) = 28.096 min, t_R (minor) = 38.664 min, 98% *ee*.



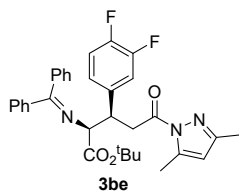
Yellow oil; 68% yield; $[\alpha]_D^{25} = -31.1^\circ$ ($c = 0.14$, CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, Acetone- d_6) δ (ppm) 7.62-7.60 (m, 2H), 7.50-7.36 (m, 6H), 7.27-7.23 (m, 2H), 7.06-6.99 (m, 4H), 5.95 (s, 1H), 4.26-4.19 (m, 2H), 3.74-3.61 (m, 2H), 2.37 (s, 3H), 2.18 (s, 3H), 1.30 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, Acetone- d_6) δ (ppm) 171.84, 171.02, 169.11, 162.88, 160.46, 151.27, 143.43, 139.34, 137.74, 137.71, 136.28, 130.42, 130.34, 128.61, 128.53, 128.43, 127.98, 127.66, 114.77, 114.56, 110.77, 80.62, 71.27, 44.42, 37.23, 27.10, 13.57, 12.91; $^{19}\text{F NMR}$ (376 MHz, Acetone- d_6) δ (ppm) 59.75; HRMS (ESI): Exact mass calcd for $\text{C}_{33}\text{H}_{34}\text{FN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$, 540.2622. Found 540.2656; HPLC: ChiralPak AD-H, n -hex/ i -PrOH = 95:5, 0.5 mL/min, 254 nm, $t_{\text{R}}(\text{major}) = 15.452$ min, $t_{\text{R}}(\text{minor}) = 26.122$ min, 98 % *ee*.



Yellow oil; 72% yield; $[\alpha]_D^{25} = -38.5^\circ$ ($c = 0.21$, CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, Acetone- d_6) δ (ppm) 7.60 (s, 1H), 7.58 (s, 1H), 7.49-7.47 (m, 3H), 7.45-7.41 (m, 1H), 7.38-7.34 (m, 2H), 7.24 (q, $J = 8.36$ Hz, 4H), 7.03-7.01 (m, 2H), 5.94 (s, 1H), 4.23-4.17 (m, 2H), 3.74-3.62 (m, 2H), 2.35 (s, 3H), 2.16 (s, 3H), 1.28 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, Acetone- d_6) δ (ppm) 171.77, 171.12, 169.05, 151.32, 143.46, 140.65, 139.31, 136.23, 131.94, 130.47, 130.35, 128.64, 128.54, 128.44, 128.08, 127.99, 127.65, 110.80, 80.73, 71.04, 44.52, 36.98, 27.11, 13.58, 12.91; HRMS (ESI): Exact mass calcd for $\text{C}_{33}\text{H}_{34}\text{ClN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$, 556.2367. Found 556.2360. HPLC: ChiralPak AD-H, n -hex/ i -PrOH = 90:10, 1.0 mL/min, 254 nm, $t_{\text{R}}(\text{major}) = 5.513$ min, $t_{\text{R}}(\text{minor}) = 9.225$ min, 98.5 % *ee*.

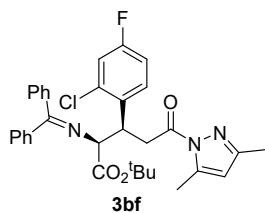


Yellow oil; 93% yield; $[\alpha]_D^{25} = -41.5^\circ$ ($c = 0.21$, CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, Acetone- d_6) δ (ppm) 7.61-7.58 (m, 4H), 7.48-7.42 (m, 6H), 7.39-7.35 (m, 2H), 6.99-6.96 (m, 2H), 5.95 (s, 1H), 4.28 (q, $J = 7.60$ Hz, 1H), 4.22 (d, $J = 6.60$ Hz, 1H), 3.81-3.70 (m, 2H), 2.35 (s, 3H), 2.17 (s, 3H), 1.28 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, Acetone- d_6) δ (ppm) 171.71, 171.27, 168.96, 151.42, 146.52, 143.50, 139.27, 136.14, 130.52, 129.39, 128.66, 128.56, 128.42, 128.22, 128.01, 127.58, 124.97, 124.93, 110.85, 80.87, 70.82, 44.96, 36.72, 27.08, 13.55, 12.90; $^{19}\text{F NMR}$ (376 MHz, Acetone- d_6) δ (ppm) -62.85; HRMS (ESI): Exact mass calcd for $\text{C}_{33}\text{H}_{34}\text{F}_3\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$, 590.2631. Found 590.2624; HPLC: ChiralPak AD-H, n -hex/ i -PrOH = 90:10, 1.0 mL/min, 254 nm, $t_{\text{R}}(\text{major}) = 4.984$ min, $t_{\text{R}}(\text{minor}) = 8.483$ min, 98% *ee*.

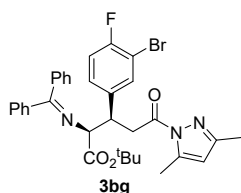


Yellow oil; 92% yield; $[\alpha]_D^{25} = -41.3^\circ$ ($c = 0.18$, CH_2Cl_2). $^1\text{H NMR}$ (400 MHz, Acetone- d_6) δ (ppm) 7.63-7.61 (m, 2H), 7.51-7.44 (m, 4H), 7.38-7.37 (m, 2H), 7.24-7.17 (m, 2H), 7.08-7.05 (m, 3H), 5.97 (s, 1H), 4.23-4.18 (m, 2H), 3.72-3.70 (m, 2H), 2.38 (s, 3H), 2.19 (s, 3H), 1.32 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, Acetone- d_6) δ (ppm) 171.70, 171.28, 168.97, 151.41, 143.49, 139.26, 136.17, 130.53, 128.69, 128.54, 128.47, 128.02, 127.61, 125.09, 125.06, 125.02, 117.65, 117.48, 116.89, 116.72, 110.85, 80.86, 70.87, 44.42, 36.94, 27.10, 13.56, 12.90; $^{19}\text{F NMR}$ (376 MHz, Acetone- d_6) δ (ppm) -140.46, -140.52, -142.84, -142.90; HRMS (ESI): Exact mass calcd for $\text{C}_{33}\text{H}_{33}\text{F}_2\text{N}_3\text{O}_3$

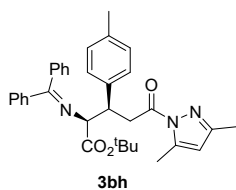
[M+H]⁺, 558.2568. Found 558.2565. HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 95:5, 1.0 mL/min, 254 nm, *t*_R(major) = 6.929 min, *t*_R(minor) = 11.534 min, 98% *ee*.



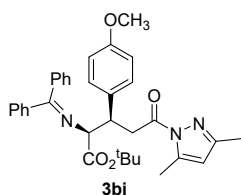
Yellow oil; 87% yield; $[\alpha]_{\text{D}}^{25} = -57.6^\circ$ ($c = 0.13$, CH₂Cl₂). ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm) 7.63-7.60 (m, 2H), 7.46-7.33 (m, 6H), 7.20 (dd, $J_1 = 2.64$ Hz, $J_2 = 6.12$ Hz, 1H), 7.03-6.98 (m, 1H), 6.78 (d, $J = 5.40$ Hz, 2H), 6.00 (s, 1H), 4.71-4.69 (m, 1H), 4.29 (d, $J = 5.04$ Hz, 1H), 3.97 (dd, $J_1 = 9.62$ Hz, $J_2 = 7.64$ Hz, 1H), 3.77 (dd, $J_1 = 12.28$ Hz, $J_2 = 5.0$ Hz, 1H), 2.36 (s, 3H), 2.21 (s, 3H), 1.36 (s, 9H); ¹³C NMR (101 MHz, Acetone-*d*₆) δ (ppm) 177.77, 171.72, 171.34, 169.10, 162.34, 159.89, 151.45, 143.50, 139.24, 136.17, 135.29, 135.26, 134.73, 134.63, 130.77, 130.68, 130.48, 128.62, 128.56, 128.40, 128.03, 127.30, 121.90, 116.59, 116.34, 113.72, 113.51, 110.88, 102.71, 96.59, 95.52, 80.91, 68.29, 40.47, 35.68, 27.17, 13.52, 12.93.; ¹⁹F NMR (376 MHz, Acetone-*d*₆) -115.62; HRMS (ESI): Exact mass calcd for C₃₃H₃₃ClFN₃O₃ [M+H]⁺, 574.2273. Found 574.2265; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 95:5, 0.5 mL/min, 254 nm, *t*_R(major) = 14.634 min, *t*_R(minor) = 16.468 min, 98% *ee*.



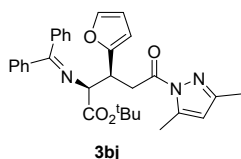
Yellow oil; 90% yield; $[\alpha]_{\text{D}}^{25} = -47.8^\circ$ ($c = 0.21$, CH₂Cl₂). ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm) 7.62-7.60 (m, 2H), 7.53-7.35 (m, 8H), 7.27-7.23 (m, 1H), 7.15 (t, $J = 8.64$ Hz, 1H), 7.03-7.01 (m, 1H), 5.96 (s, 1H), 4.19-4.16 (m, 2H), 3.73-3.66 (m, 2H), 2.36 (s, 3H), 2.19 (s, 3H), 1.30 (s, 9H); ¹³C NMR (101 MHz, Acetone-*d*₆) δ (ppm) 171.72, 171.30, 168.96, 151.44, 143.49, 139.67, 139.27, 136.18, 133.85, 130.53, 129.63, 129.56, 128.70, 128.56, 128.47, 128.02, 127.60, 117.56, 116.14, 115.92, 110.88, 109.65, 107.78, 107.57, 96.40, 80.89, 70.85, 44.31, 36.86, 27.11, 13.55, 12.91; ¹⁹F NMR (376 MHz, Acetone-*d*₆) δ (ppm) -112.26; HRMS (ESI): Exact mass calcd for C₃₃H₃₃BrFN₃O₃ [M+H]⁺, 618.1768. Found 618.1750; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 95:5, 0.5 mL/min, 254 nm, *t*_R(major) = 13.978 min, *t*_R(minor) = 22.215 min, 98.4% *ee*.



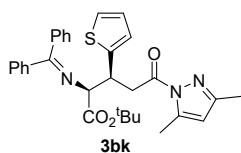
Yellow oil; 23% yield; $[\alpha]_{\text{D}}^{25} = -24.2^\circ$ ($c = 0.14$, CH₂Cl₂). ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm) 7.59-7.57 (m, 2H), 7.47-7.40 (m, 4H), 7.37-7.34 (m, 2H), 7.04 (q, $J = 8.0$ Hz, 4H), 6.99-6.96 (m, 2H), 5.92 (s, 3H), 4.21-4.15 (m, 2H), 3.70-3.59 (m, 2H), 2.35 (s, 3H), 2.24 (s, 3H), 2.16 (s, 3H), 1.28 (s, 9H); ¹³C NMR (101 MHz, Acetone-*d*₆) δ (ppm) 172.00, 170.72, 169.27, 151.13, 143.39, 139.43, 138.70, 136.35, 136.00, 130.35, 128.66, 128.50, 128.45, 128.34, 127.93, 127.71, 110.70, 80.43, 71.47, 44.62, 37.05, 27.13, 20.10, 13.61, 12.91; HRMS (ESI): Exact mass calcd for C₃₄H₃₇N₃O₃ [M+H]⁺, 536.2913. Found 536.2910; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, *t*_R(major) = 5.147 min, *t*_R(minor) = 7.191 min, 97% *ee*.



Yellow oil; 10% yield; $[\alpha]_{\text{D}}^{25} = -25.4^{\circ}$ ($c = 0.05$, CH_2Cl_2). ^1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.60 (s, 1H), 7.58 (s, 1H), 7.48-7.34 (m, 6H), 7.11 (s, 1H), 7.09 (s, 1H), 7.03-7.01 (m, 2H), 6.79 (s, 1H), 6.77 (s, 1H), 5.92 (s, 1H), 4.20-4.15 (m, 2H), 3.72 (s, 3H), 3.64-3.61 (m, 2H), 2.35 (s, 3H), 2.16 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 172.01, 170.70, 169.30, 158.65, 151.12, 143.38, 139.43, 136.37, 133.53, 130.35, 129.52, 128.50, 128.36, 127.94, 127.72, 113.42, 110.69, 80.39, 71.59, 54.55, 44.29, 37.28, 27.13, 13.60, 12.90; HRMS (ESI): Exact mass calcd for $\text{C}_{34}\text{H}_{37}\text{N}_3\text{O}_4$ $[\text{M}+\text{H}]^+$, 552.2862. Found 552.2855; HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_{\text{R}}(\text{major}) = 6.600$ min, $t_{\text{R}}(\text{minor}) = 12.092$ min, 96% *ee*.

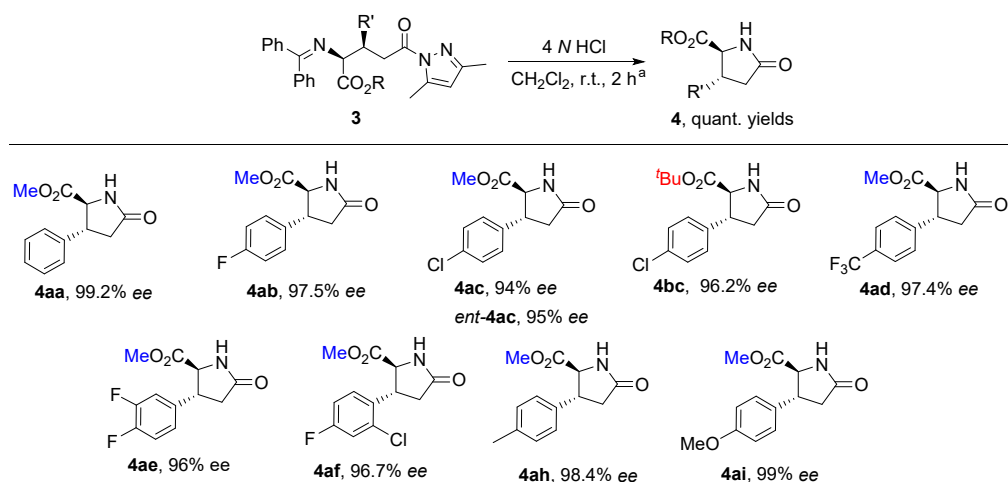


Yellow oil; 44% yield; $[\alpha]_{\text{D}}^{25} = -94.2^{\circ}$ ($c = 0.11$, CH_2Cl_2). ^1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.57-7.55 (m, 2H), 7.52-7.49 (m, 3H), 7.41 (d, $J = 7.24$ Hz, 1H), 7.37-7.32 (m, 3H), 7.05-7.03 (m, 2H), 6.27 (dd, $J_1 = 1.88$ Hz, $J_2 = 1.2$ Hz, 1H), 6.09 (d, $J = 2.84$ Hz, 1H), 5.97 (s, 1H), 4.34-4.27 (m, 2H), 3.75-3.63 (m, 2H), 2.42 (s, 3H), 2.17 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 171.75, 171.12, 169.10, 155.04, 151.39, 143.55, 141.46, 139.42, 136.27, 130.40, 128.64, 128.54, 128.41, 127.92, 127.73, 110.86, 110.13, 106.34, 80.82, 68.92, 38.71, 35.12, 27.19, 13.63, 12.91; HRMS (ESI): Exact mass calcd for $\text{C}_{31}\text{H}_{33}\text{N}_3\text{O}_4$ $[\text{M}+\text{H}]^+$, 512.2549. Found 512.2546. HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 98:2, 0.5 mL/min, 254 nm, merged; ChiralPak OD-H, *n*-hex/*i*-PrOH = 98:2, 0.5 mL/min, 254 nm, merged.



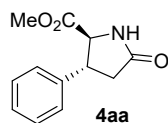
Yellow oil; 45% yield; $[\alpha]_{\text{D}}^{25} = -105.0^{\circ}$ ($c = 0.12$, CH_2Cl_2). ^1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.62 (d, $J = 7.2$ Hz, 2H), 7.48-7.42 (m, 4H), 7.37 (t, $J = 7.64$ Hz, 2H), 7.23 (d, $J = 4.96$ Hz, 1H), 7.03-7.00 (m, 2H), 6.89-6.85 (m, 2H), 5.96 (s, 1H), 4.53 (q, $J = 5.96$ Hz, 1H), 4.20 (d, $J = 5.64$ Hz, 1H), 3.75 (dd, $J_1 = 4.48$ Hz, $J_2 = 3.44$ Hz, 2H), 2.39 (s, 3H), 2.17 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 171.54, 171.29, 168.98, 151.38, 144.76, 143.50, 139.38, 136.27, 130.47, 128.63, 128.60, 128.39, 127.98, 127.61, 126.32, 125.14, 124.02, 110.83, 80.88, 71.33, 40.23, 38.37, 27.17, 13.60, 12.92; HRMS (ESI): Exact mass calcd for $\text{C}_{31}\text{H}_{33}\text{N}_3\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$, 528.2321. Found 528.2319. HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_{\text{R}}(\text{major}) = 5.484$ min, $t_{\text{R}}(\text{minor}) = 6.355$ min, 97.2% *ee*.

2.2 General procedure for acidic hydrolysis and *in-situ* lactamation

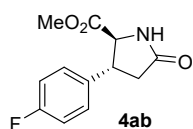


a. All reactions were performed in 0.5 mmol scale; b. The ee of products was determined by chiral HPLC column (Diacel ChiralPak AD-H).

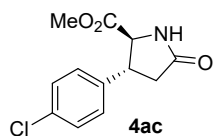
The Michael adduct **3aa** (0.5 mmol, 0.24 g) was treated by 4.0 M HCl aq. (0.5 mL) in CH₂Cl₂ (2.0 mL) at room temperature. When **3aa** was completely consumed (checked by a TLC), the reaction mixture was diluted by 10.0 mL of CH₂Cl₂, the organic layer was washed by 5.0 mL of water and 5.0 mL of brine, then it was dried over anhydrous Na₂SO₄. The solvent was removed by an evaporator and the residue was purified by a flash column chromatography to provide pure **4aa** in quant. yield as white solid.



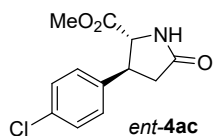
White solid; quant. yield; $[\alpha]_{\text{D}}^{25} = 52.4^\circ$ ($c = 0.05$, CH₂Cl₂), m.p. 108.5-109.6 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm) 7.38-7.36(m, 4H), 7.34-7.26 (m, 1H), 7.21 (br, 1H), 4.26 (d, $J = 4.92$ Hz, 1H), 3.73-3.68 (m, 1H, merged), 3.70 (s, 3H, OCH₃), 2.73 (dd, $J_1 = 9.32$ Hz, $J_2 = 7.52$ Hz, 1H), 2.33 (dd, $J_1 = 10.6$ Hz, $J_2 = 6.28$ Hz, 1H); ¹³C NMR (101 MHz, Acetone-*d*₆) δ (ppm) 176.15, 173.17, 143.83, 129.70, 128.01, 127.79, 63.43, 52.54, 44.91, 38.37; HRMS (ESI): Exact mass calcd for C₁₂H₁₄NO₃ [M+H]⁺, 220.0974. Found 220.0978. HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, t_{R} (major) = 17.442 min, t_{R} (minor) = 23.850 min, 99.2% ee.



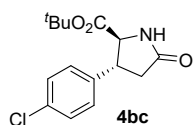
White solid; quant. yield; $[\alpha]_{\text{D}}^{25} = 57.1^\circ$ ($c = 0.05$, CH₂Cl₂), m.p. 75.2-76.5 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm) 7.43 (dd, $J_1 = 5.56$ Hz, $J_2 = 2.52$ Hz, 2H), 7.36 (br, 1H), 7.13 (t, $J = 8.72$ Hz, 2H), 4.26 (d, $J = 5.2$ Hz, 1H), 3.76-3.72 (m, 1H), 3.73 (s, 3H, OCH₃), 2.74 (dd, $J_1 = 9.28$ Hz, $J_2 = 7.6$ Hz, 1H), 2.35 (dd, $J_1 = 10.24$ Hz, $J_2 = 6.6$ Hz, 1H); ¹³C NMR (101 MHz, Acetone-*d*₆) δ (ppm) 176.24, 173.01, 164.00, 161.58, 139.72 (d, $J_{\text{C-F}} = 3.06$ Hz), 129.82, 116.39, 116.18, 63.53, 52.60, 44.26, 38.54; ¹⁹F NMR (376 MHz, Acetone-*d*₆) δ (ppm) 60.27; HRMS (ESI): Exact mass calcd for C₁₂H₁₃FNO₃ [M+H]⁺, 238.0879. Found 238.0884. HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, t_{R} (major) = 16.263 min, t_{R} (minor) = 22.227 min, 97.5% ee.



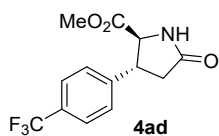
White solid; quant. yield; $[\alpha]_D^{25} = 61.9^\circ$ ($c = 0.05$, CH_2Cl_2), 104.1-104.9 °C. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.43-7.38 (m, 4H), 7.24 (m, 1H), 4.26 (d, $J = 5.16$ Hz, 1H), 3.74-3.72 (m, 1H), 3.70 (s, 3H, OCH_3), 2.73 (dd, $J_1 = 9.28$ Hz, $J_2 = 7.56$ Hz, 1H), 2.34 (dd, $J_1 = 10.32$ Hz, $J_2 = 6.56$ Hz, 1H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 175.90, 172.92, 142.59, 133.29, 129.72, 129.67, 63.25, 52.58, 44.34, 38.34; HRMS (ESI): Exact mass calcd for $\text{C}_{12}\text{H}_{13}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$, 254.0578. Found 254.0588. HPLC: ChiralPak AD-H, n -hex/ i -PrOH = 80:20, 1.0 mL/min, 230 nm, $t_{\text{R}}(\text{major}) = 8.933$ min, $t_{\text{R}}(\text{minor}) = 12.187$ min, 94% *ee*.



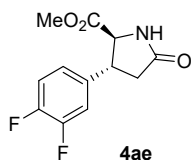
White solid; quant. yield; $[\alpha]_D^{25} = -63.3^\circ$ ($c = 0.05$, CH_2Cl_2), m.p. 103.4-104.2 °C. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.43-7.40 (m, 4H), 7.24 (br, 1H), 4.26 (d, $J = 5.16$ Hz, 1H), 3.74-3.72 (m, 1H), 3.70 (s, 3H, OCH_3), 2.73 (dd, $J_1 = 9.28$ Hz, $J_2 = 7.56$ Hz, 1H), 2.34 (dd, $J_1 = 10.32$ Hz, $J_2 = 6.56$ Hz, 1H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 175.85, 172.93, 142.60, 133.28, 129.74, 129.67, 63.23, 52.58, 44.34, 38.34; HPLC: ChiralPak AD-H, n -hex/ i -PrOH = 80:20, 1.0 mL/min, 230 nm, $t_{\text{R}}(\text{major}) = 12.578$ min, $t_{\text{R}}(\text{minor}) = 9.064$ min, 95% *ee*.



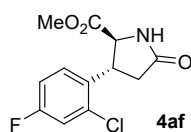
Yellow oil; quant. yield; $[\alpha]_D^{25} = 107.2^\circ$ ($c = 0.052$, CH_2Cl_2). ^1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.45-7.38 (m, 4H), 7.28 (m, 1H), 4.14 (d, $J = 5.96$ Hz, 1H), 3.70-3.64 (m, 1H), 2.70 (dd, $J_1 = 9.2$ Hz, $J_2 = 7.56$ Hz, 1H), 2.36 (dd, $J_1 = 9.4$ Hz, $J_2 = 7.4$ Hz, 1H), 1.41 (s, 9H, $t\text{Bu}$); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 175.84, 171.53, 142.56, 133.18, 129.96, 129.56, 82.21, 63.99, 44.77, 38.73, 28.08; HRMS (ESI): Exact mass calcd for $\text{C}_{15}\text{H}_{19}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$, 296.1048. Found 296.1057. HPLC: ChiralPak AD-H, n -hex/ i -PrOH = 90:10, 1.0 mL/min, 230 nm, $t_{\text{R}}(\text{major}) = 13.567$ min, $t_{\text{R}}(\text{minor}) = 21.331$ min, 96.2% *ee*.



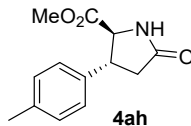
White solid; quant. yield; $[\alpha]_D^{25} = 73.4^\circ$ ($c = 0.05$, CH_2Cl_2), m.p. 106.5-108.2 °C. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.73 (d, $J = 8.16$ Hz, 2H), 7.64 (d, $J = 8.12$ Hz, 2H), 7.25 (br, 1H), 4.33 (d, $J = 5.2$ Hz, 1H), 3.88-3.83 (m, 1H), 3.1 (s, 3H, OCH_3), 2.78 (dd, $J_1 = 9.24$ Hz, $J_2 = 7.64$ Hz, 1H), 2.40 (dd, $J_1 = 10.32$ Hz, $J_2 = 6.56$ Hz, 1H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 175.64, 172.82, 148.28, 128.83, 126.56 (q, $J_{\text{C-F}} = 3.90$ Hz), 62.95, 52.62, 44.64, 38.24; ^{19}F NMR (376 MHz, Acetone- d_6) δ (ppm) 114.51; HRMS (ESI): Exact mass calcd for $\text{C}_{13}\text{H}_{12}\text{F}_3\text{NO}_3$ $[\text{M}+\text{H}]^+$, 288.0848. Found 288.0853. HPLC: ChiralPak AD-H, n -hex/ i -PrOH = 90:10, 1.0 mL/min, 230 nm, $t_{\text{R}}(\text{major}) = 12.691$ min, $t_{\text{R}}(\text{minor}) = 21.193$ min, 97.4% *ee*.



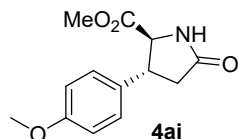
White solid; quant. yield; $[\alpha]_D^{25} = 21.7^\circ$ ($c = 0.05$, CH_2Cl_2), m.p. 87.7-88.6 °C. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.45-7.40 (m, 2H), 7.35-7.29 (m, 1H), 7.26 (br, 1H), 4.31 (d, $J = 5.68$ Hz, 1H), 3.78-3.73 (m, 1H), 3.70 (s, 3H, OCH₃), 2.74 (dd, $J_1 = 9.28$ Hz, $J_2 = 7.6$ Hz, 1H), 2.39 (dd, $J_1 = 9.8$ Hz, $J_2 = 7.08$ Hz, 1H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 175.89, 172.78, 151.75 (dd, $J_{\text{C-F}} = 74.62$, 12.76 Hz), 149.31 (dd, $J_{\text{C-F}} = 74.18$, 12.70 Hz), 141.09 (dd, $J_{\text{C-F}} = 3.90$, 1.12 Hz), 124.79 (dd, $J_{\text{C-F}} = 3.54$, 1.24 Hz), 118.40 (d, $J_{\text{C-F}} = 17.10$ Hz), 117.11 (d, $J_{\text{C-F}} = 17.80$ Hz), 63.19, 52.65, 44.23, 38.50; ^{19}F NMR (376 MHz, Acetone- d_6) δ (ppm) 38.05, 37.99, 35.16, 35.10; HRMS (ESI): Exact mass calcd for $\text{C}_{12}\text{H}_{11}\text{F}_2\text{NO}_3$ $[\text{M}+\text{H}]^+$, 256.0785. Found 256.0787. HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_{\text{R}}(\text{major}) = 17.222$, $t_{\text{R}}(\text{minor}) = 21.366$ min, 96% *ee*.



White solid; quant. yield; $[\alpha]_D^{25} = 65.3^\circ$ ($c = 0.05$, CH_2Cl_2), m.p. 67.8-69.4 °C. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.61 (dd, $J_1 = 2.68$ Hz, $J_2 = 6.0$ Hz, 1H), 7.37 (brs, 1H), 7.31 (dd, $J_1 = 2.6$ Hz, $J_2 = 6.08$ Hz, 1H), 7.20 (td, $J_1 = 2.52$ Hz, $J_2 = 5.84$ Hz, 1H), 4.32 (d, $J = 4.88$ Hz, 1H), 4.16-4.11 (m, 1H), 3.71 (s, 3H), 2.79 (dd, $J_1 = 7.6$ Hz, $J_2 = 9.32$ Hz, 1H), 2.35 (dd, $J_1 = 6.08$ Hz, $J_2 = 10.84$ Hz, 1H); ^{19}F NMR (376 MHz, Acetone- d_6) δ (ppm) 62.78; HRMS (ESI): Exact mass calcd for $\text{C}_{12}\text{H}_{11}\text{ClFNO}_3$ $[\text{M}+\text{H}]^+$, 272.0490. Found 272.0494. HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_{\text{R}}(\text{major}) = 17.278$ min, $t_{\text{R}}(\text{minor}) = 23.051$ min, 96.7% *ee*.

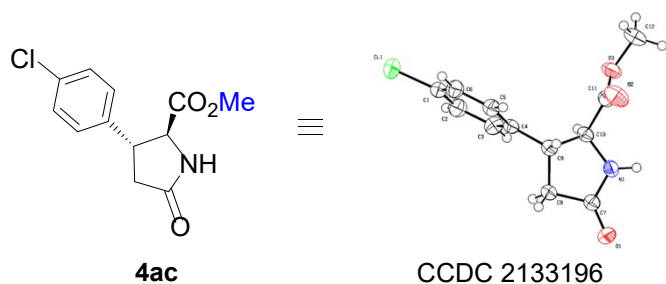


White solid; quant. yield; $[\alpha]_D^{25} = 41.7^\circ$ ($c = 0.05$, CH_2Cl_2), m.p. 83.5-84.4 °C. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.34 (brs, 1H), 7.24 (d, $J = 8.0$ Hz, 4H), 7.17 ((d, $J = 7.88$ Hz, 2H), 4.22 ((d, $J = 5.0$ Hz, 1H), 3.69 (s, 3H, OCH₃), 3.68-3.62 (m, 1H), 2.71 (dd, $J_1 = 7.56$ Hz, $J_2 = 9.28$ Hz, 1H), 2.32 (dd, $J_1 = 6.36$ Hz, $J_2 = 10.6$ Hz, 1H), 2.30 (s, 3H, CH₃); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 176.48, 173.22, 140.76, 137.48, 130.29, 127.70, 63.62, 52.56, 44.61, 38.48, 21.04; HRMS (ESI): Exact mass calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{H}]^+$, 234.1130. Found 234.1113. HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_{\text{R}}(\text{major}) = 15.964$ min, $t_{\text{R}}(\text{minor}) = 20.338$ min, 98.4% *ee*.



Yellow oil; quant. yield; $[\alpha]_D^{25} = 43.8^\circ$ ($c = 0.05$, CH_2Cl_2). ^1H NMR (400 MHz, Acetone- d_6) δ (ppm) 7.30 (d, $J = 8.68$ Hz, 2H), 7.16 (br, 1H), 6.93 (d, $J = 8.72$ Hz, 2H), 4.22 (d, $J = 5.12$ Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.68-3.63 (m, 1H), 2.70 (dd, $J_1 = 7.6$ Hz, $J_2 = 9.24$ Hz, 1H), 2.32 (dd, $J_1 = 6.48$ Hz, $J_2 = 10.32$ Hz, 1H); ^{13}C NMR (101 MHz, Acetone- d_6) δ (ppm) 176.20, 173.22, 159.85, 135.61, 128.84, 115.00, 63.70, 55.53, 52.48, 44.33, 38.48; HRMS (ESI): Exact mass calcd for $\text{C}_{13}\text{H}_{16}\text{NO}_4$ $[\text{M}+\text{H}]^+$, 250.1079. Found 250.1081. HPLC: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_{\text{R}}(\text{major}) = 22.536$, $t_{\text{R}}(\text{minor}) = 30.339$ min, 99% *ee*.

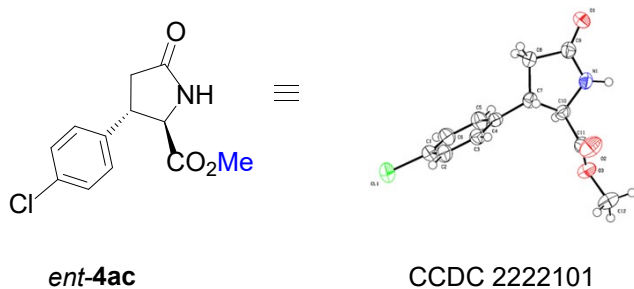
3. X-ray single crystal diffraction analysis of **4ac** and *ent-4ac*



Crystals of **4ac** was obtained by recrystallization from the mixed solvent of *n*-hexane and dichloromethane. CCDC 2133196 contains its detail crystal structure data.

Table S1 Crystal data and structure refinement for C₁₂H₁₂ClNO₃ of **4ac**

Empirical formula	C ₁₂ H ₁₂ ClNO ₃
Formula weight	253.68
Temperature/K	230.00(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	5.78020(10)
<i>b</i> /Å	7.48790(10)
<i>c</i> /Å	27.7844(5)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	1202.55(3)
<i>Z</i>	4
ρ_{calc} /cm ³	1.401
μ /mm ⁻¹	2.798
<i>F</i> (000)	528.0
Crystal size/mm ³	0.11 × 0.1 × 0.09
Radiation	CuK α (λ = 1.54184)
2 θ range for data collection/°	12.242 to 131.862
Index ranges	-6 ≤ <i>h</i> ≤ 6, -8 ≤ <i>k</i> ≤ 8, -29 ≤ <i>l</i> ≤ 32
Reflections collected	4506
Independent reflections	2082 [<i>R</i> _{int} = 0.0181, <i>R</i> _{sigma} = 0.0221]
Data/restraints/parameters	2082/0/156
Goodness-of-fit on <i>F</i> ²	1.084
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0251, <i>wR</i> ₂ = 0.0661
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0261, <i>wR</i> ₂ = 0.0669
Largest diff. peak/hole / e Å ⁻³	0.14/-0.19
Flack parameter	0.004(6)

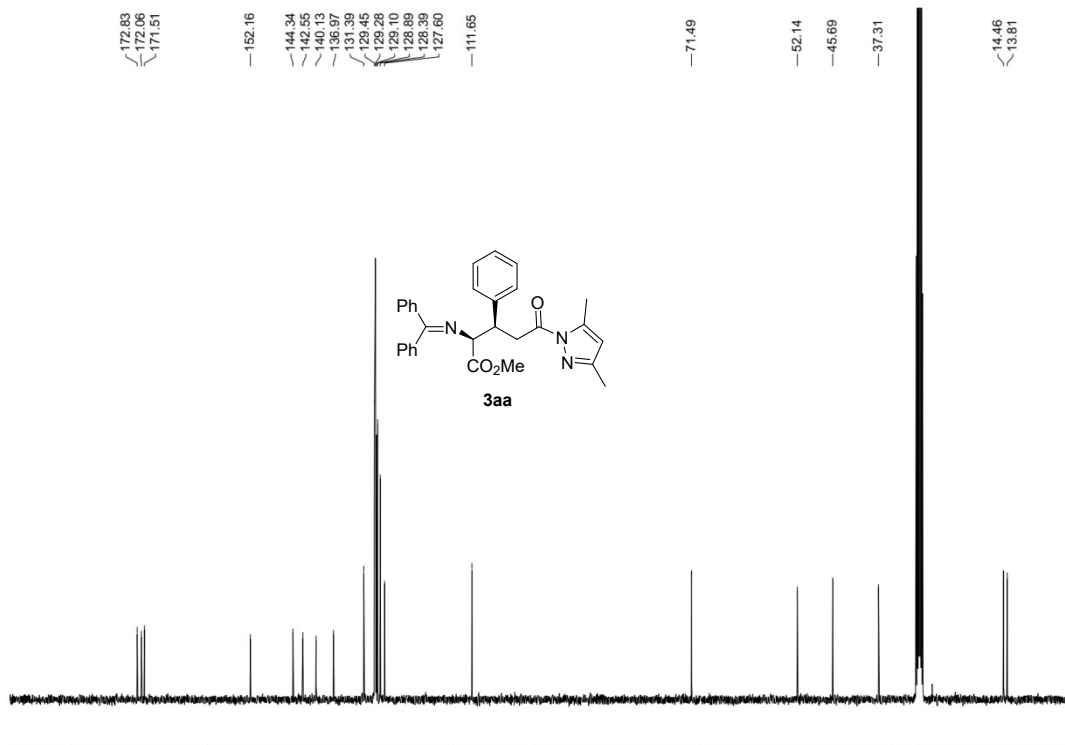
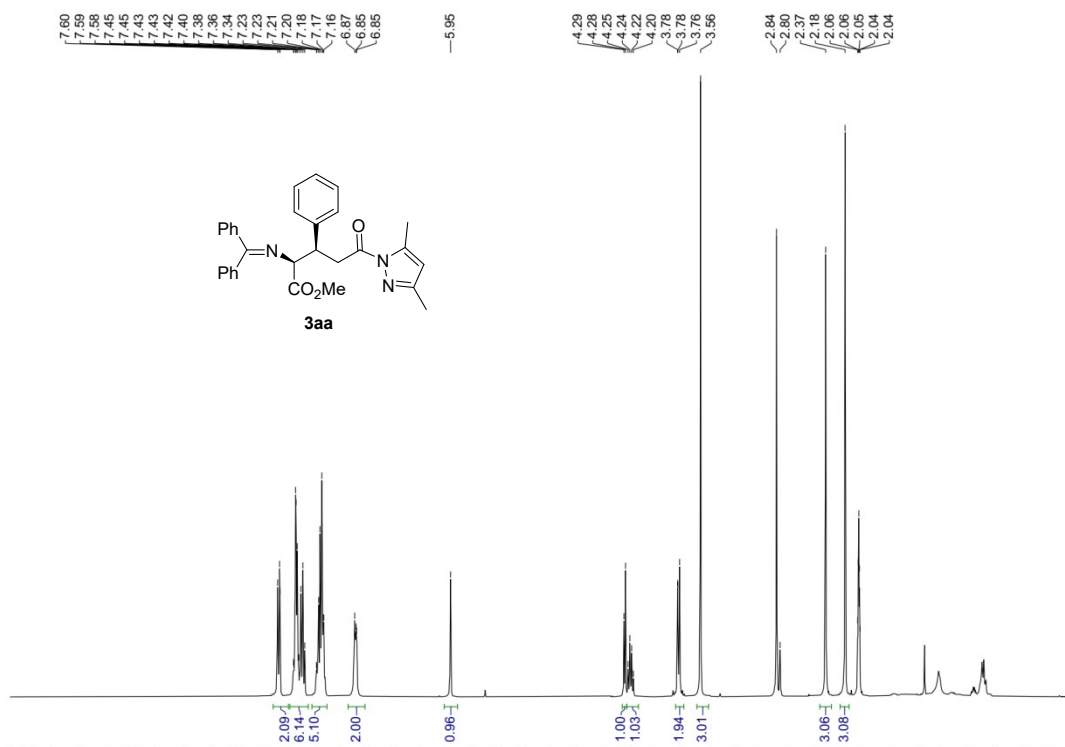


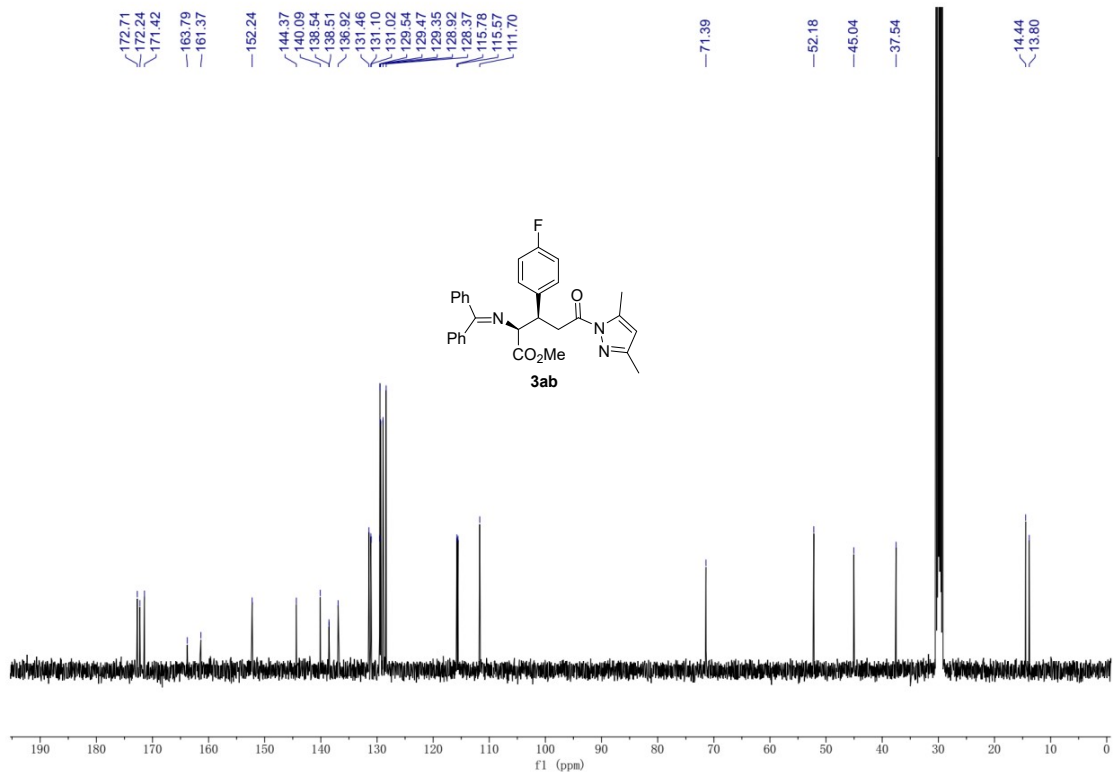
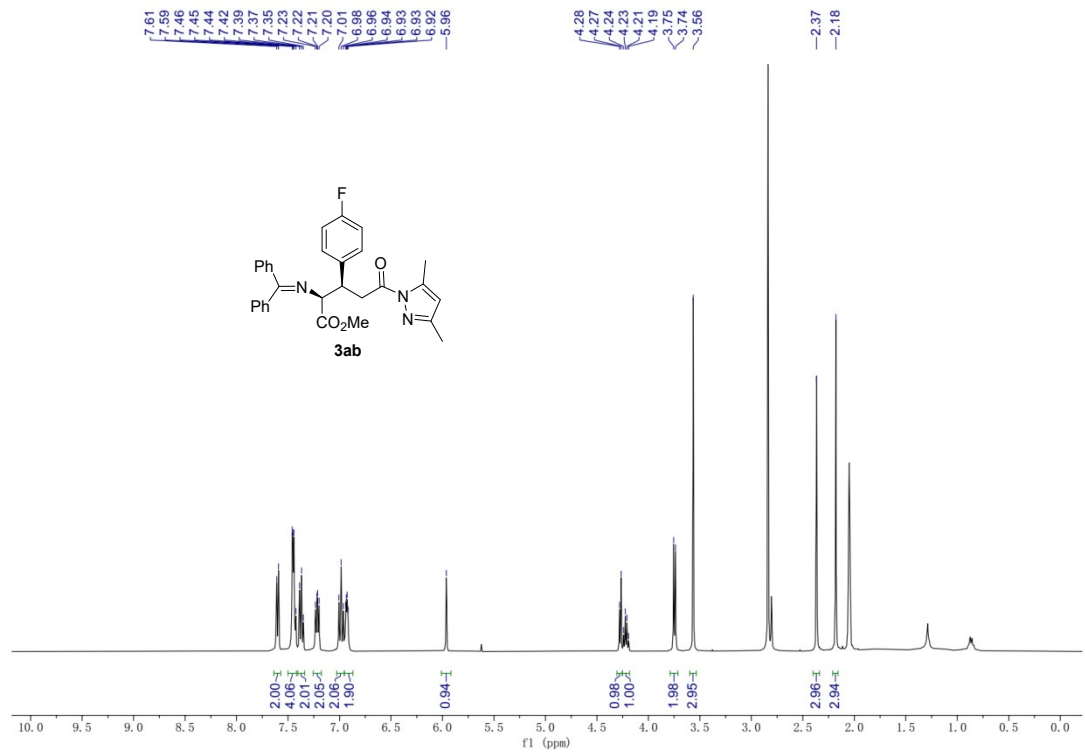
Crystals of *ent*-4ac was obtained by recrystallization from the mixed solvent of *n*-hexane and dichloromethane. CCDC 2222101 contains its detail crystal structure data.

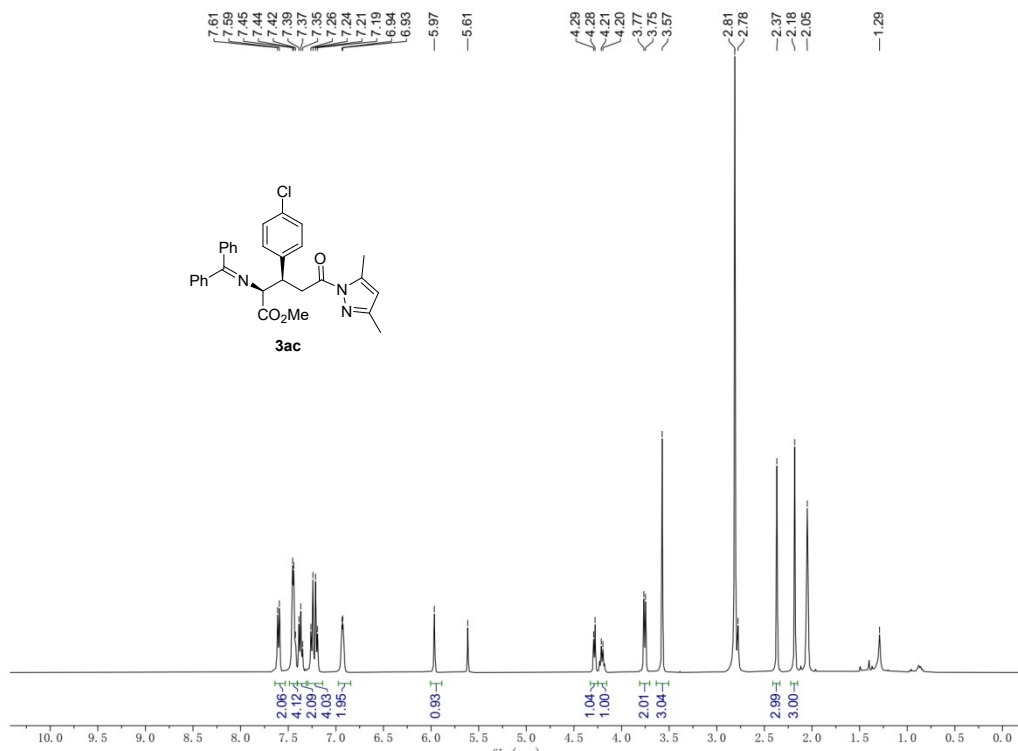
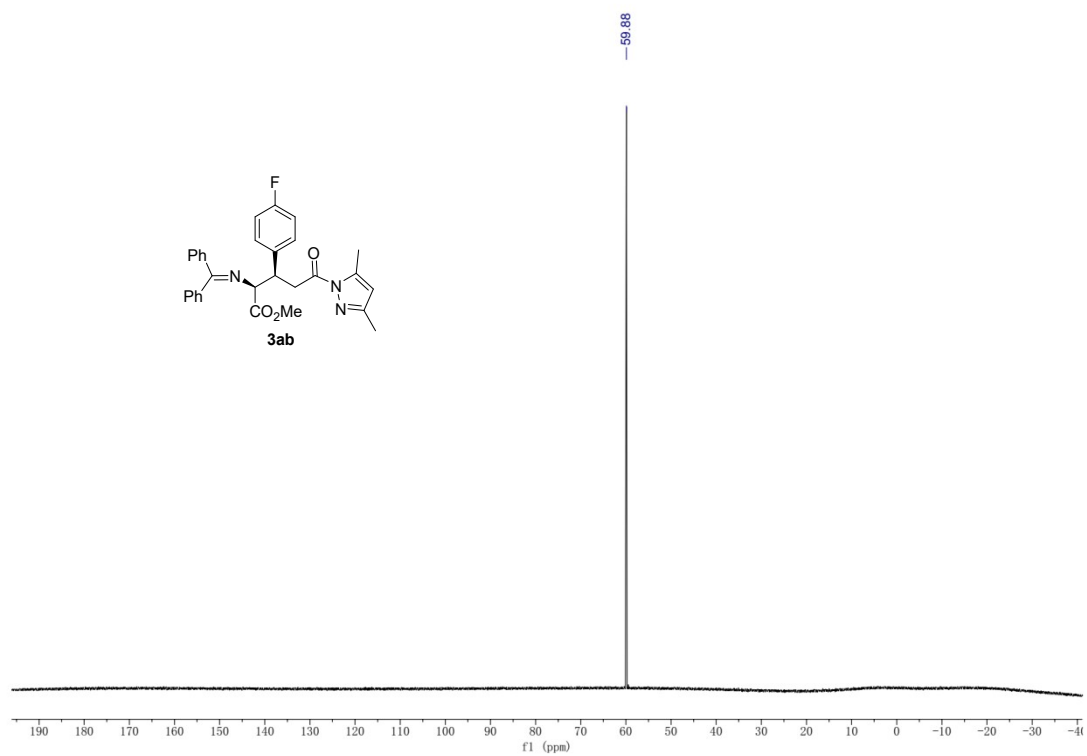
Table S2 Crystal data and structure refinement for C₁₂H₁₂ClNO₃ of *ent*-4ac

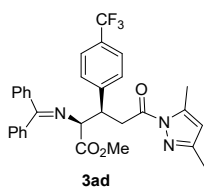
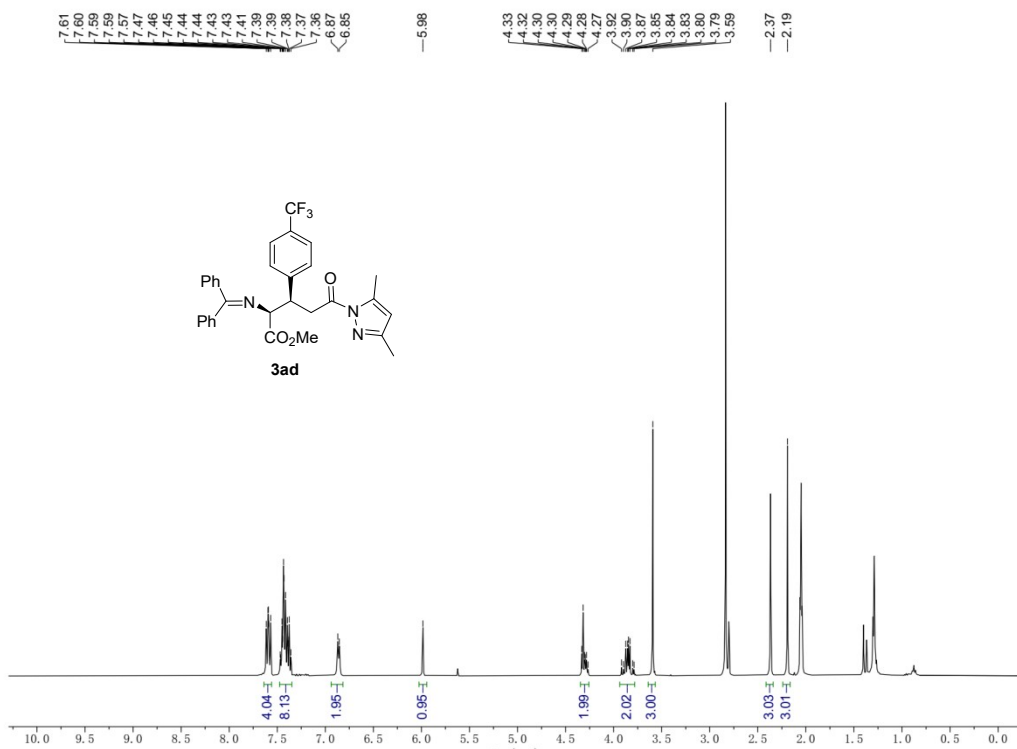
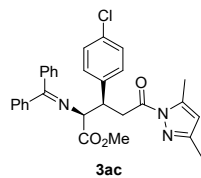
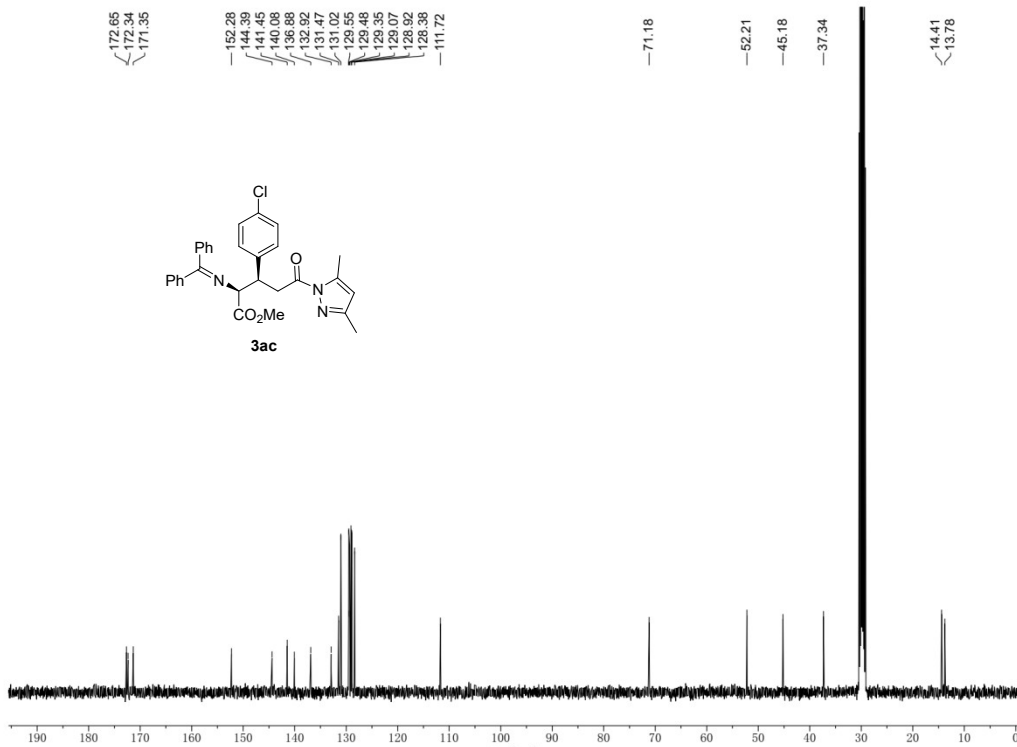
Empirical formula	C ₁₂ H ₁₂ ClNO ₃
Formula weight	253.68
Temperature/K	240.00(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	5.7785(3)
b/Å	7.4826(3)
c/Å	27.8645(11)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1204.81(9)
Z	4
ρ _{calc} /cm ³	1.399
μ/mm ⁻¹	2.793
F(000)	528.0
Crystal size/mm ³	0.13 × 0.12 × 0.11
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	12.248 to 133.028
Index ranges	-6 ≤ h ≤ 4, -6 ≤ k ≤ 8, -22 ≤ l ≤ 33
Reflections collected	3366
Independent reflections	2090 [R _{int} = 0.0225, R _{sigma} = 0.0339]
Data/restraints/parameters	2090/0/155
Goodness-of-fit on F ²	1.045
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0348, wR ₂ = 0.0792
Final R indexes [all data]	R ₁ = 0.0405, wR ₂ = 0.0840
Largest diff. peak/hole / e Å ⁻³	0.13/-0.17
Flack parameter	0.029(13)

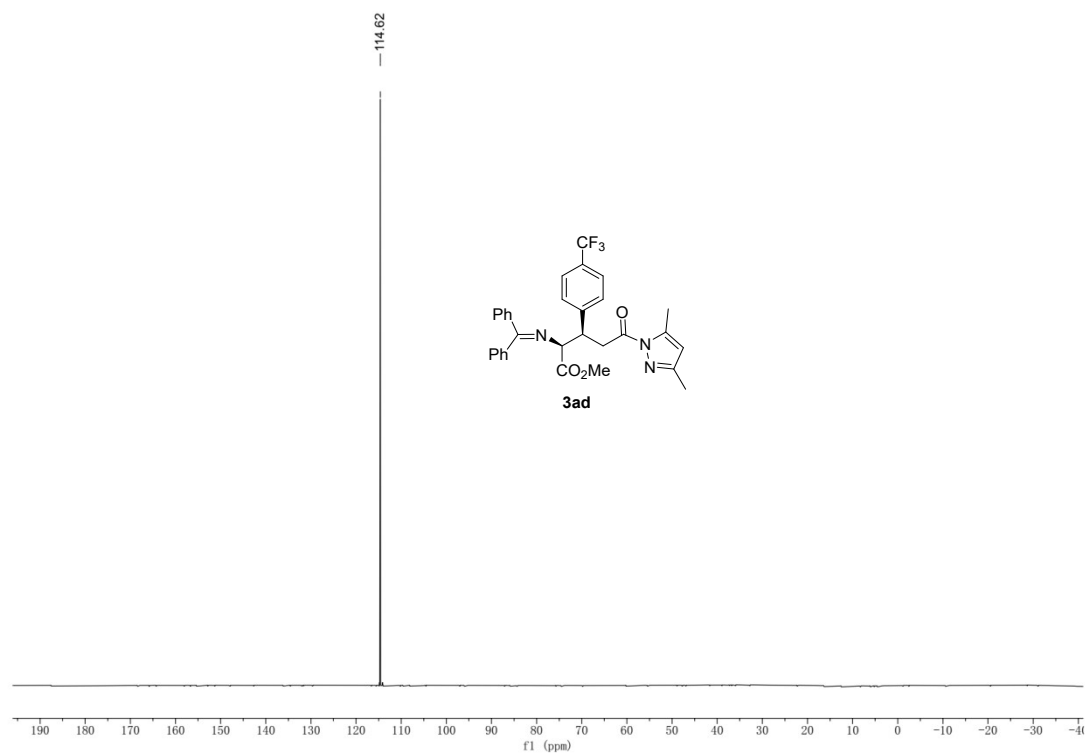
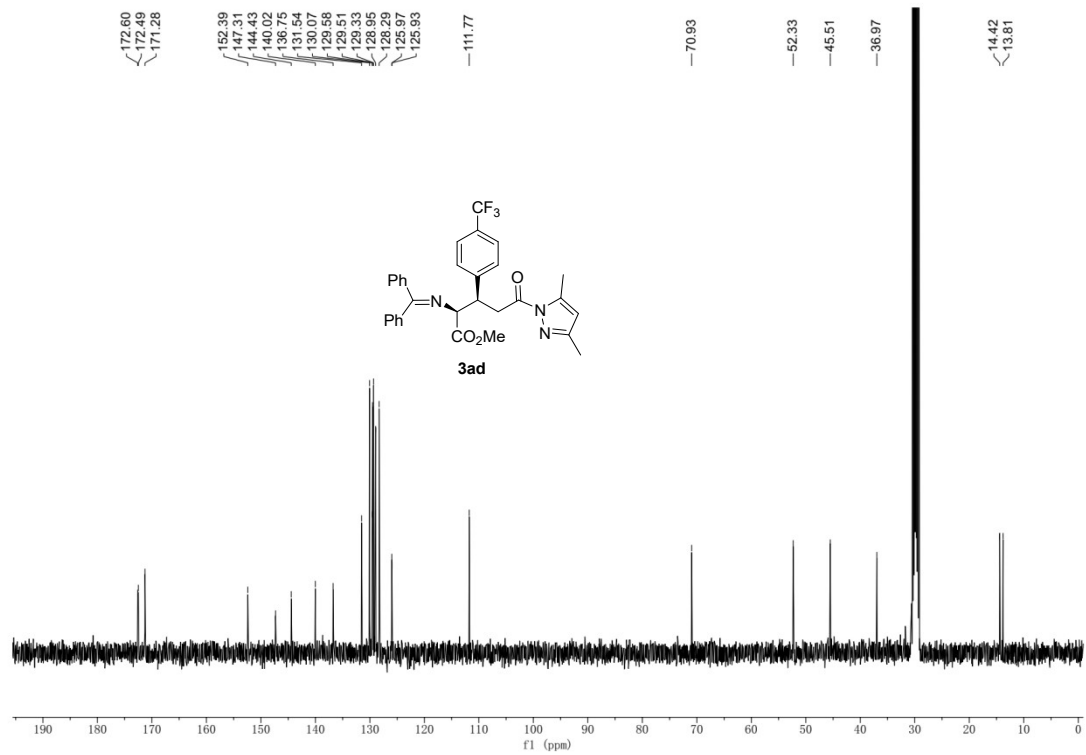
4. NMR Copies

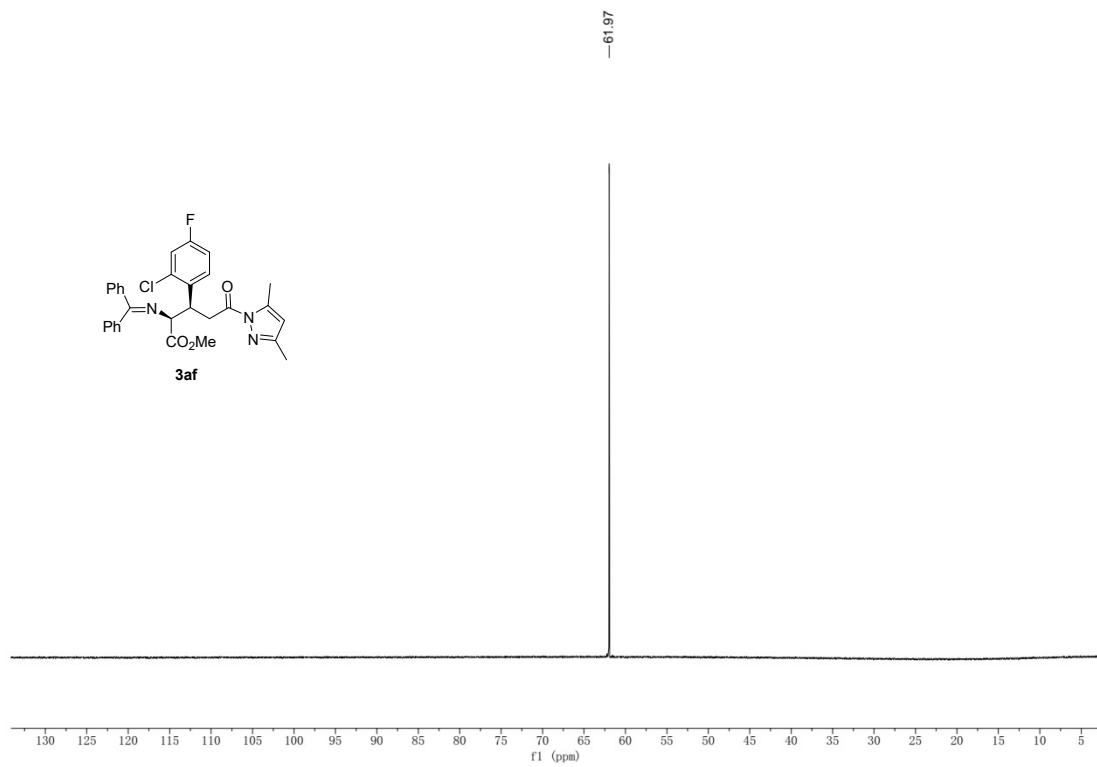
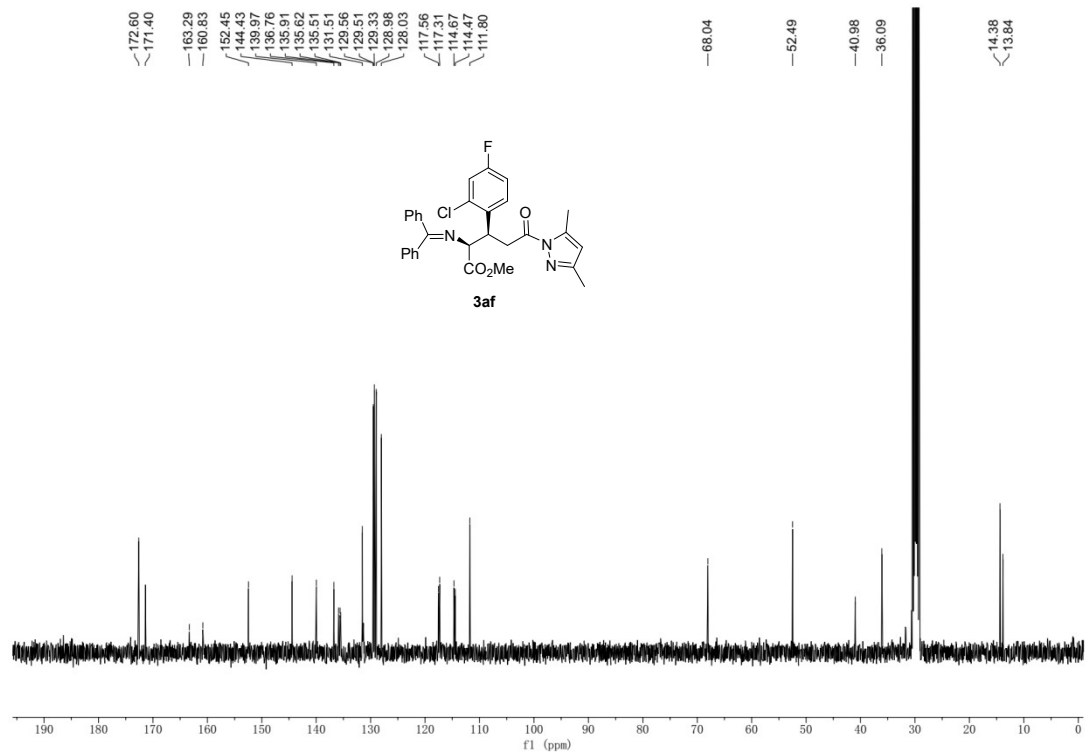


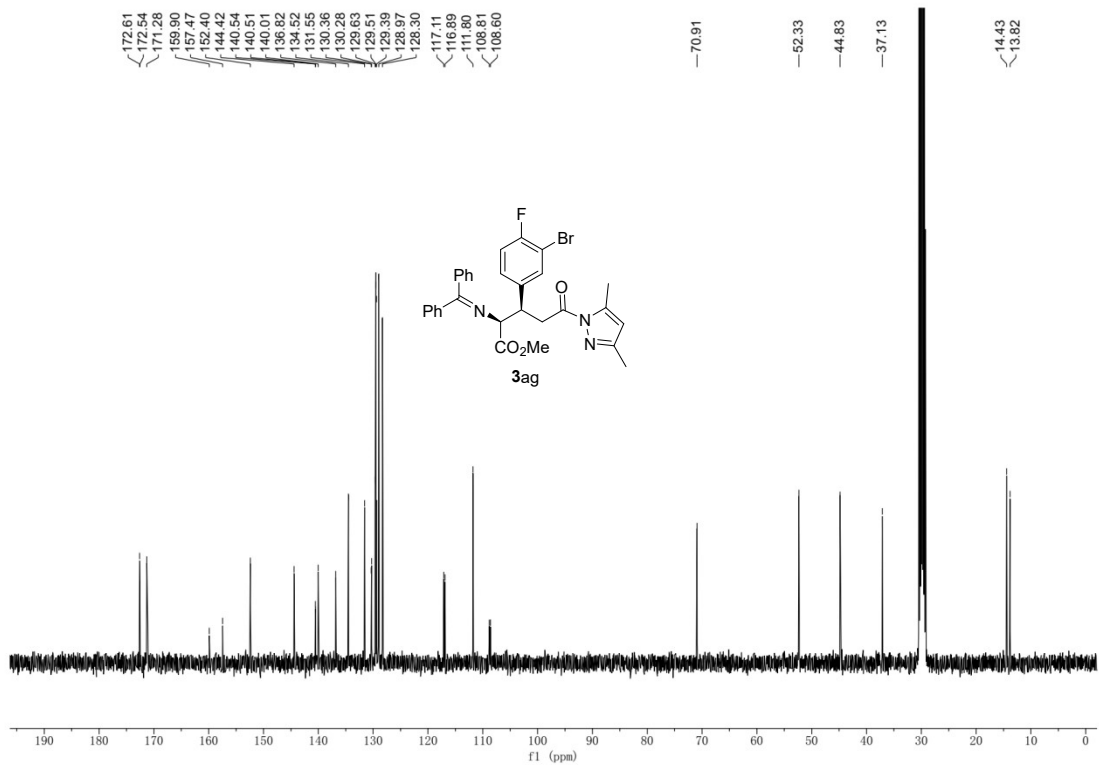
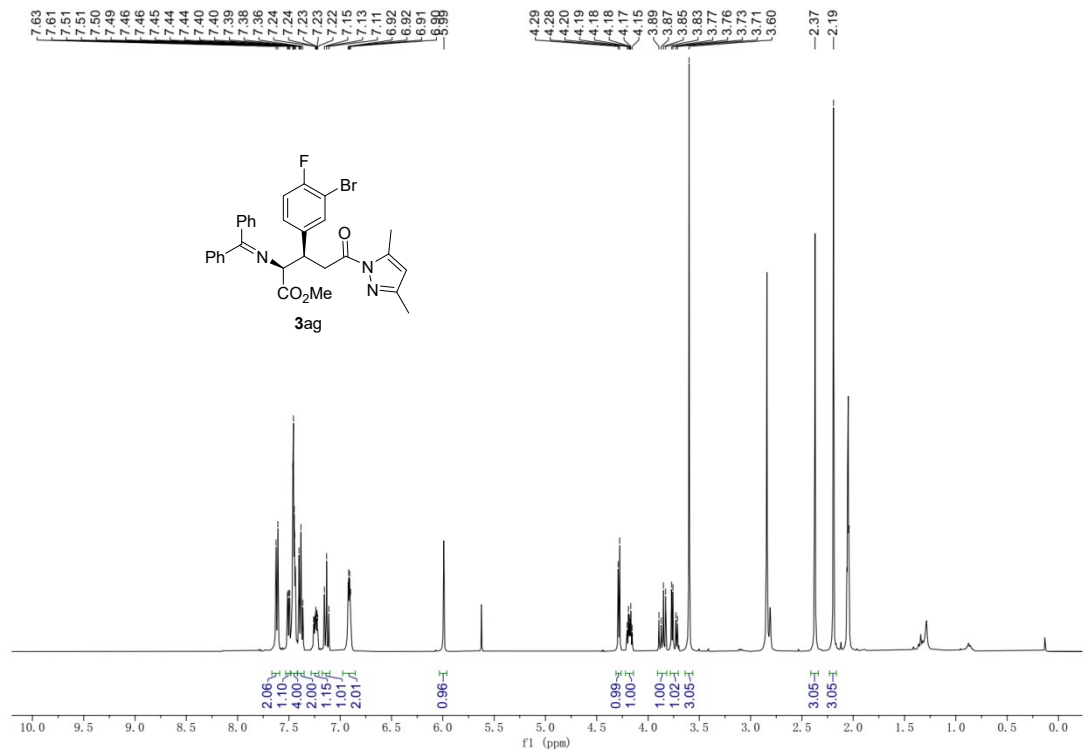


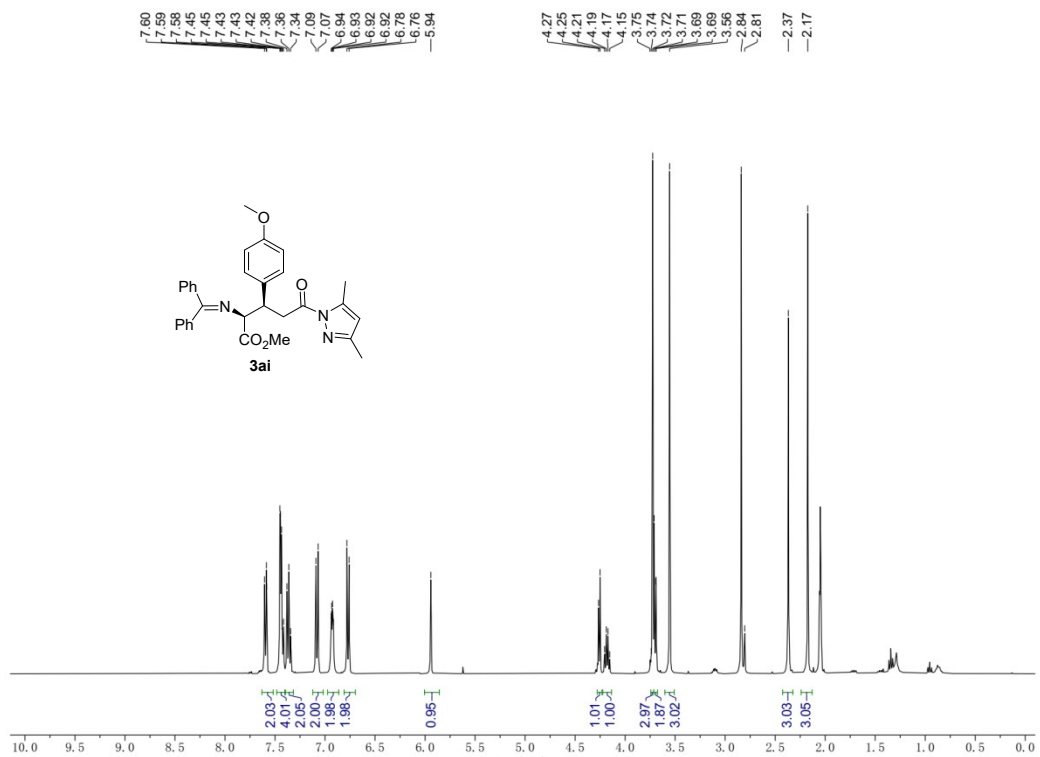
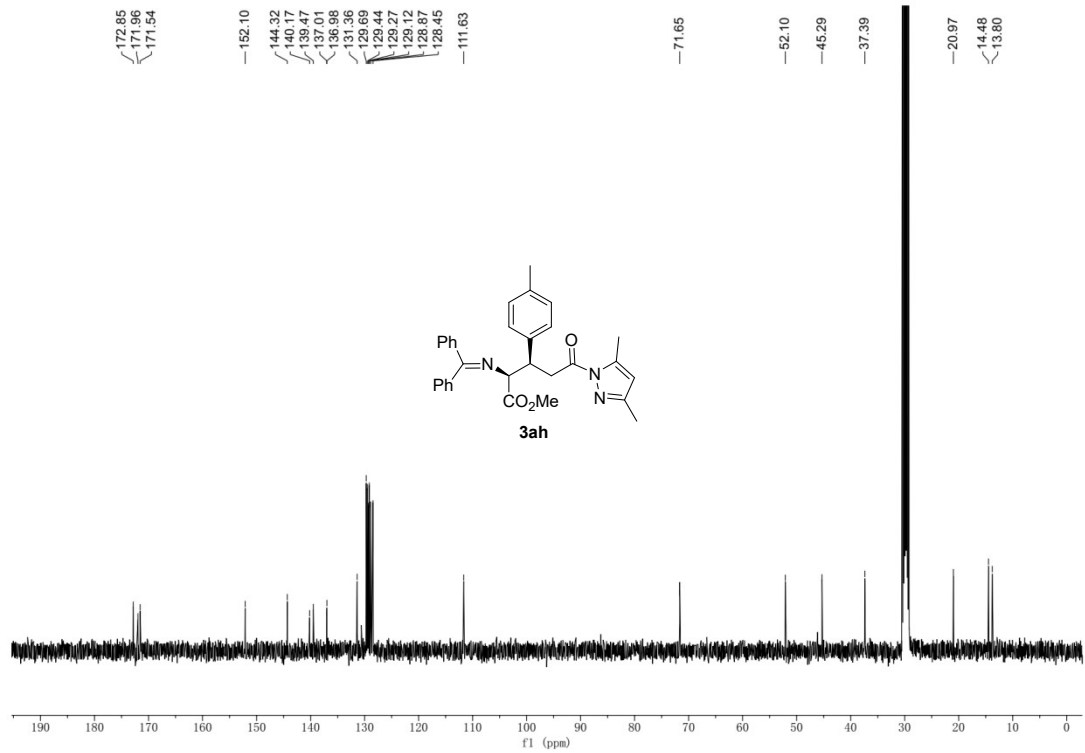


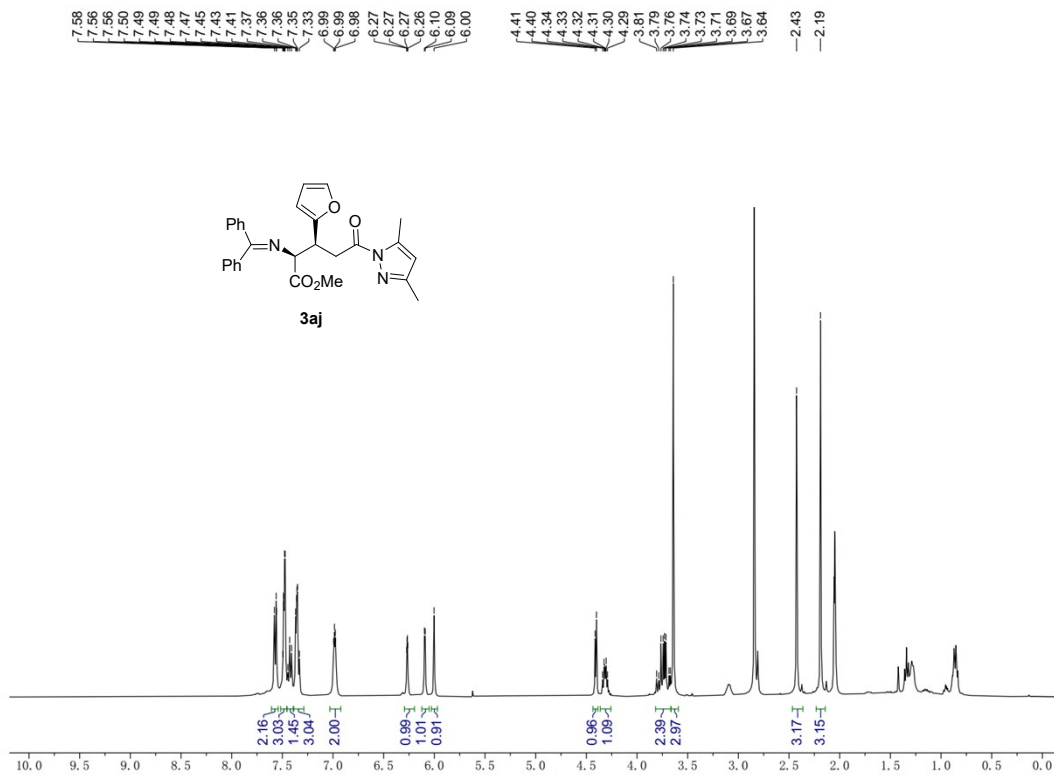
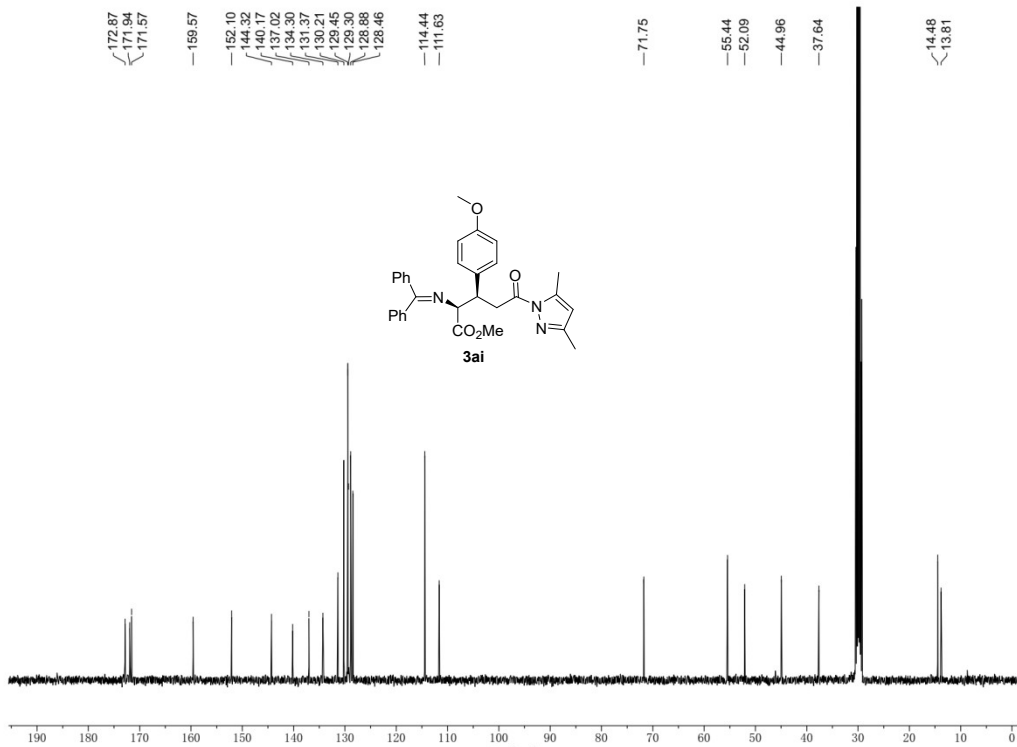


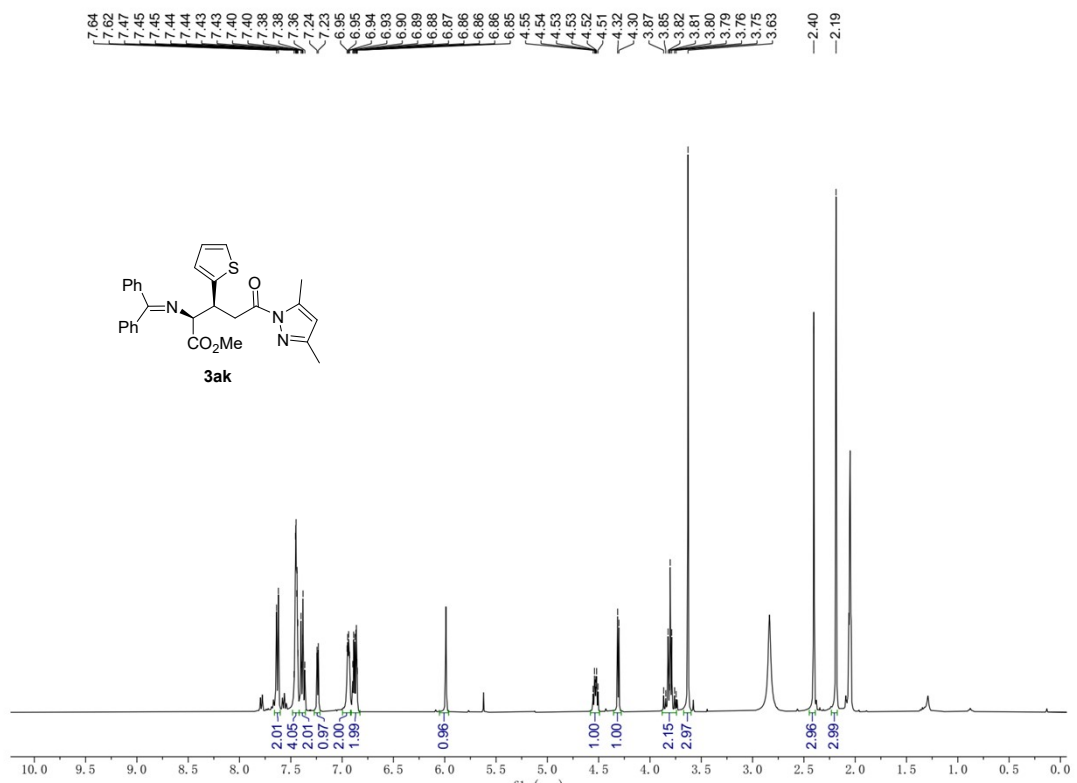
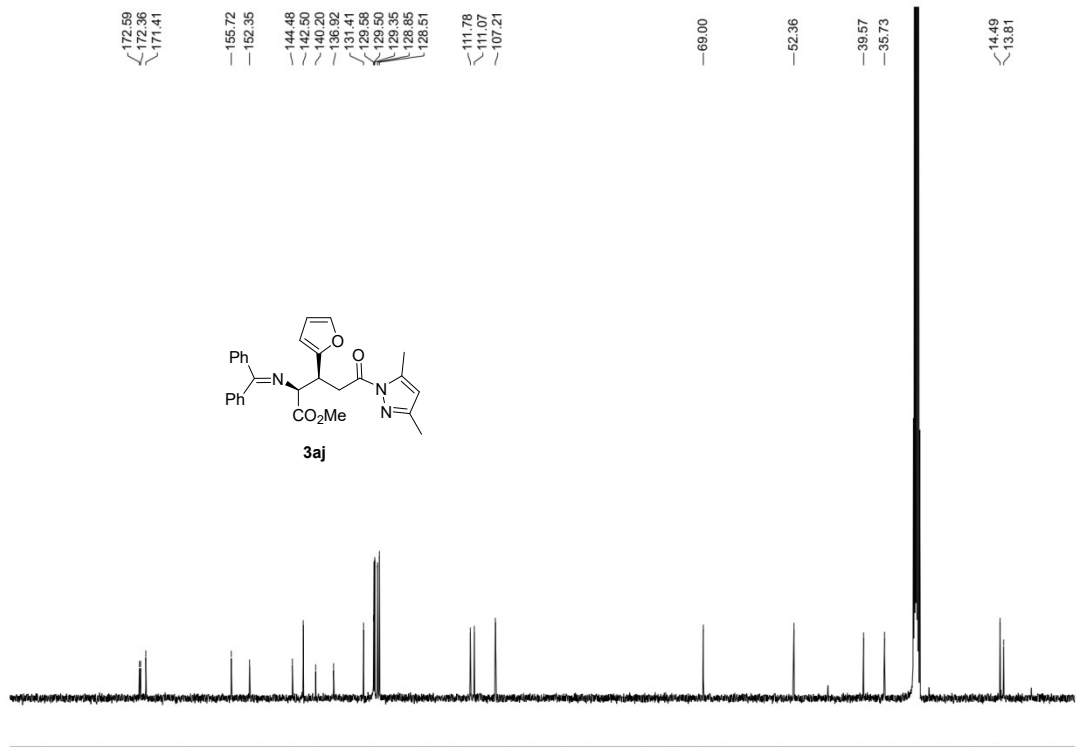


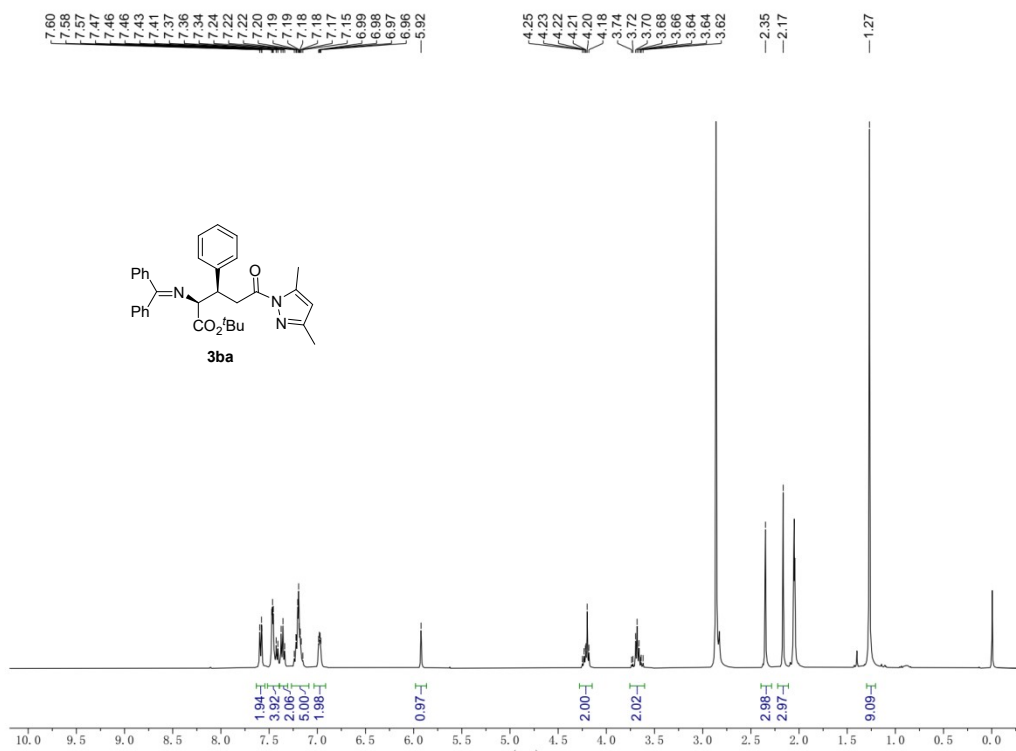
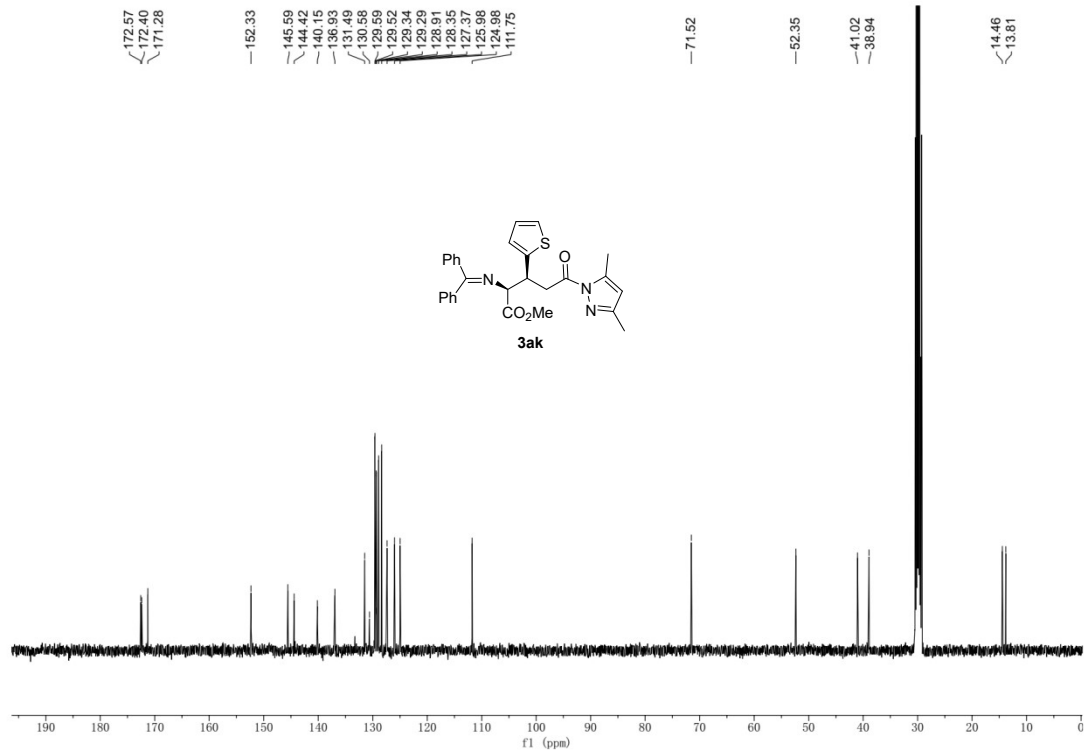


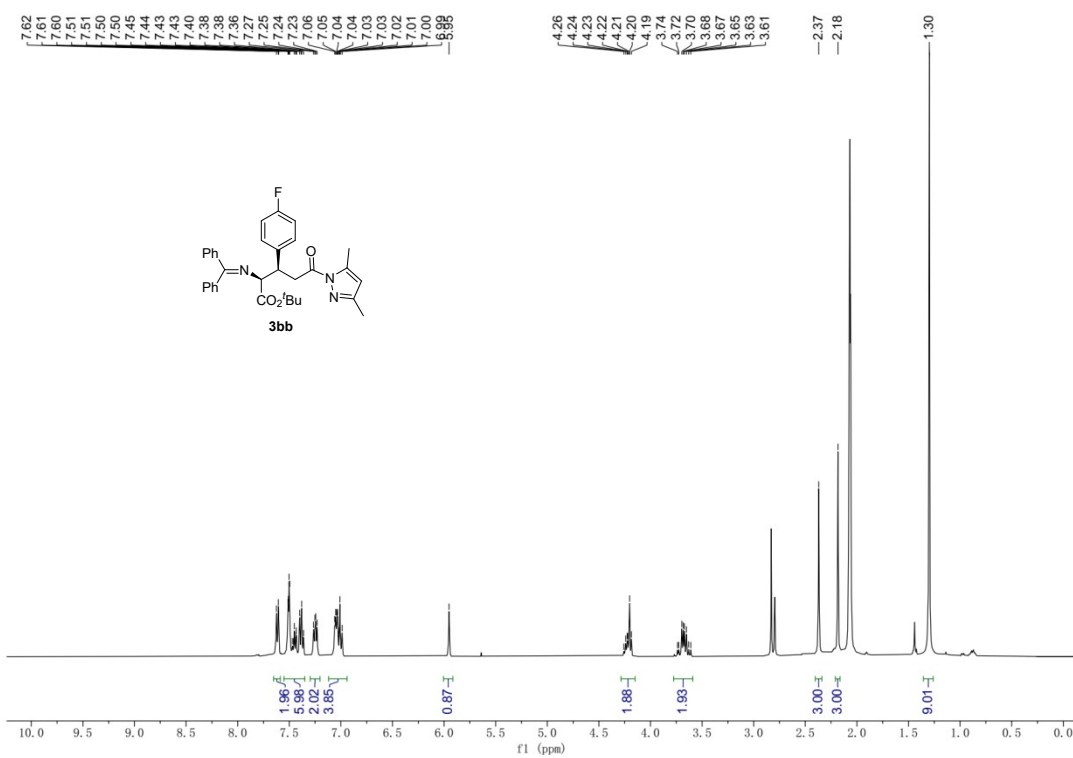
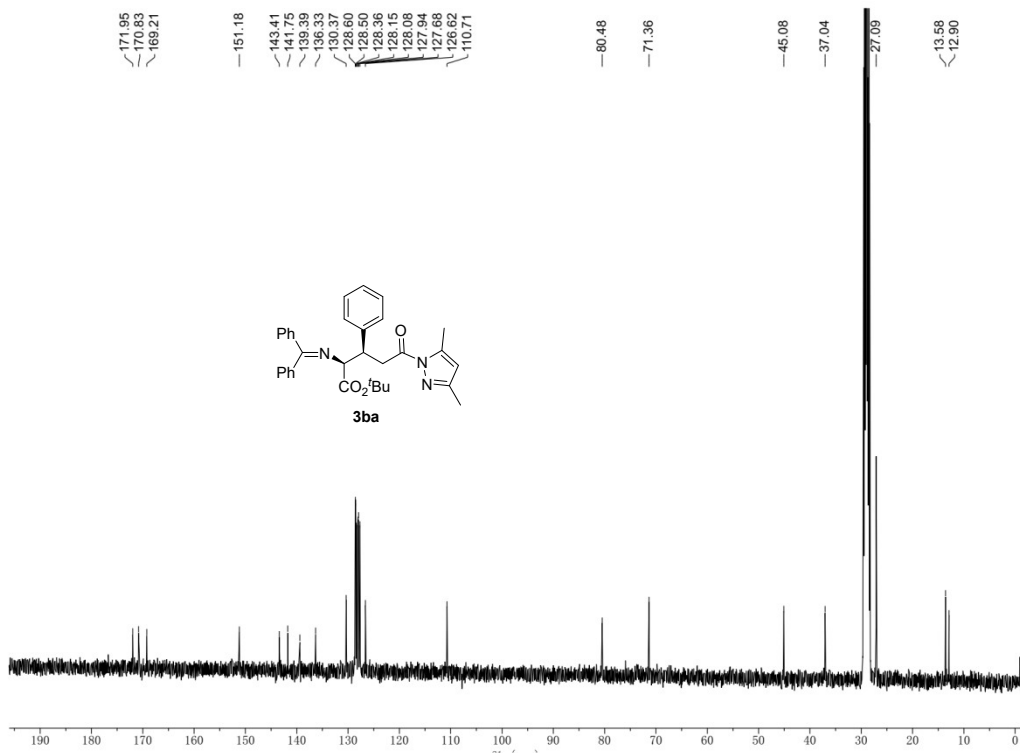


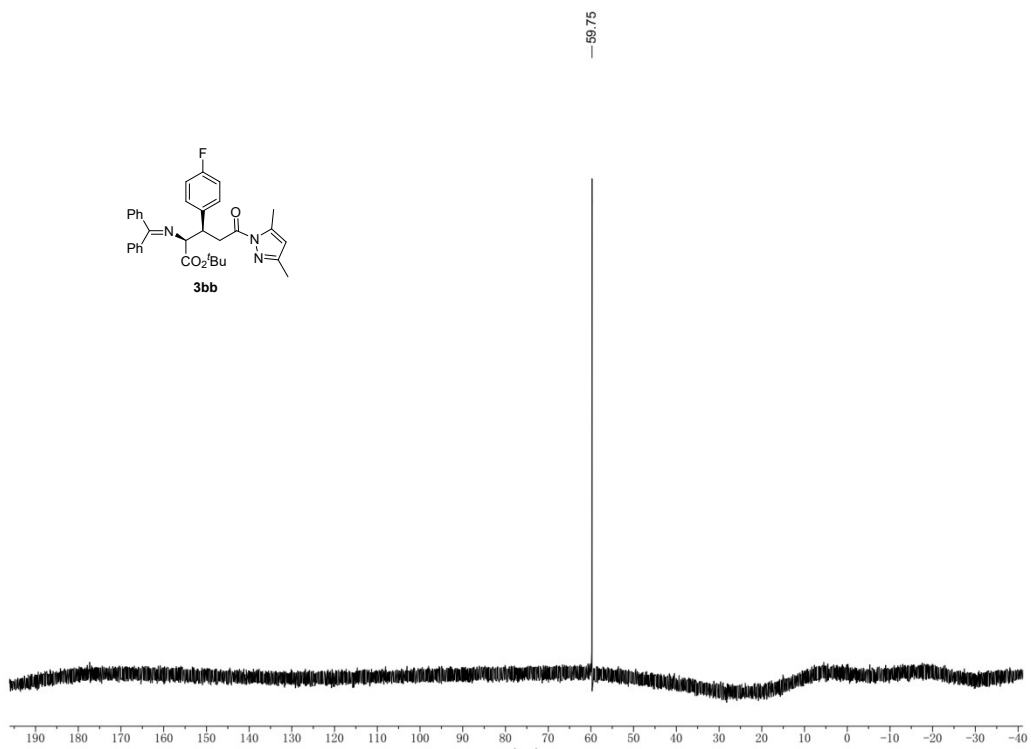
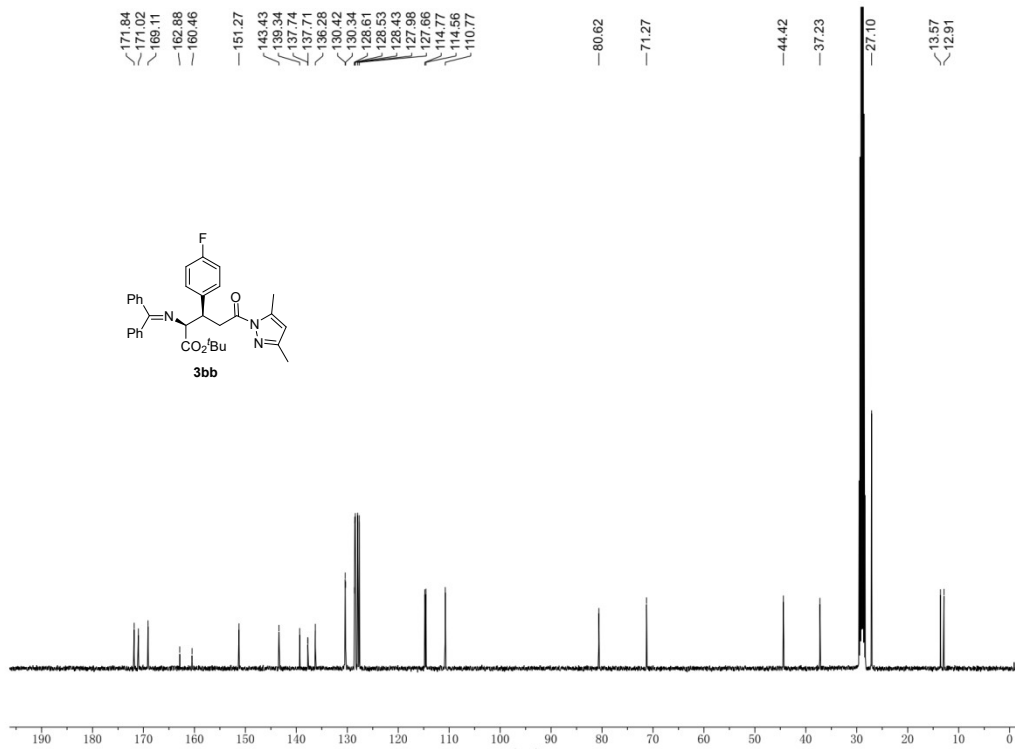


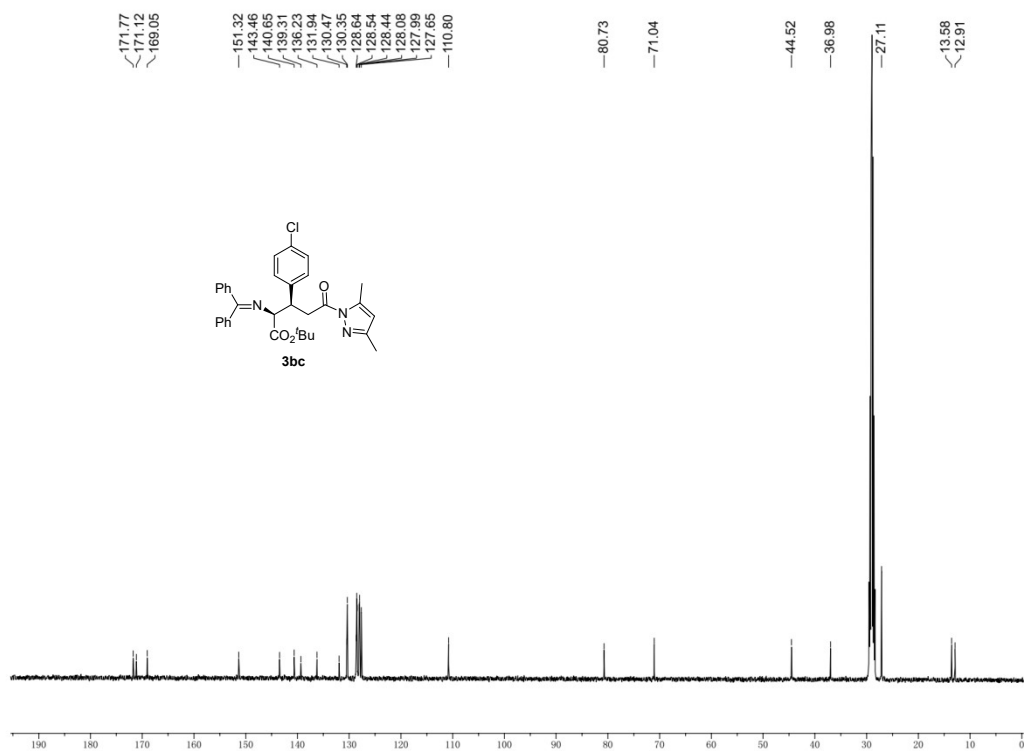
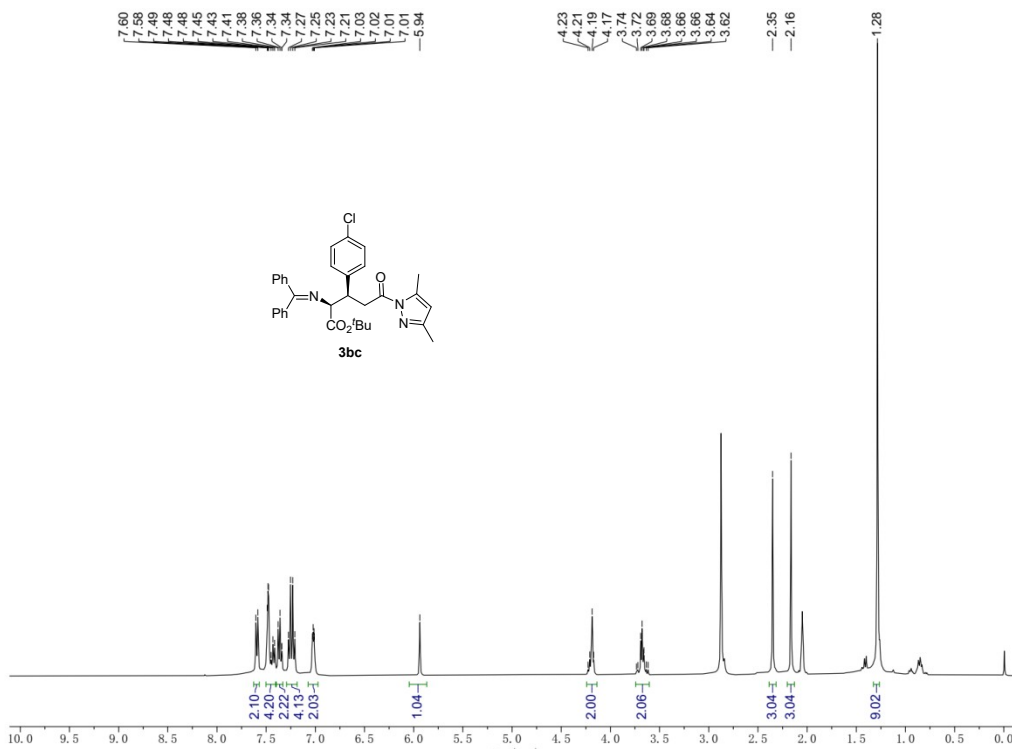


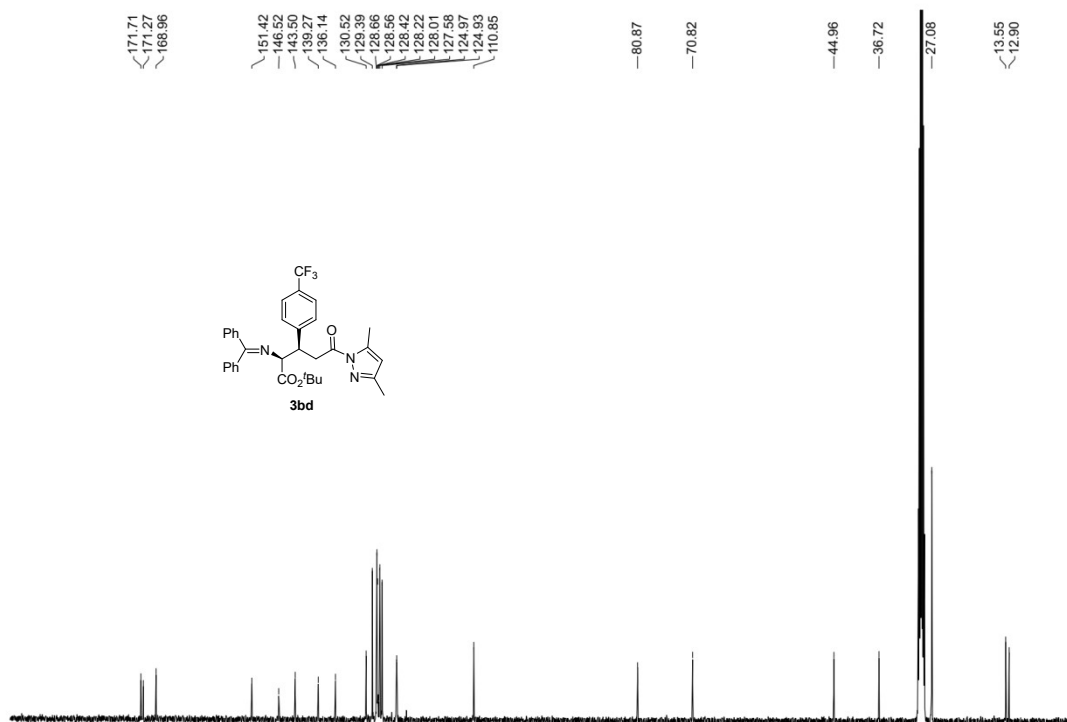
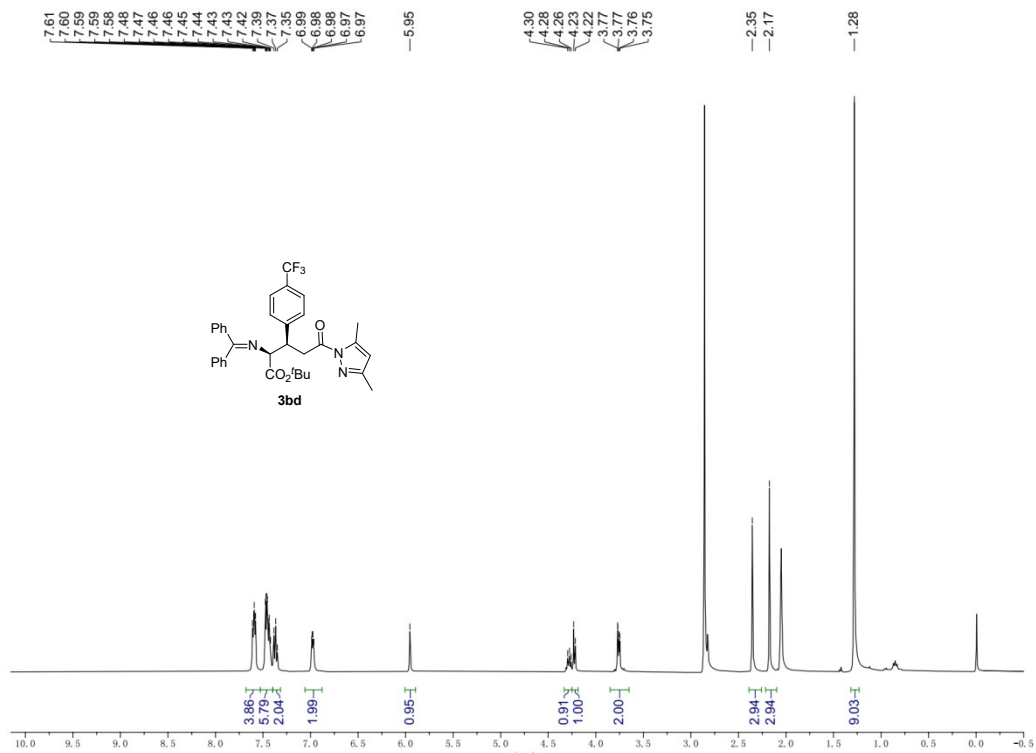


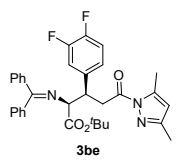
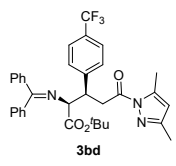
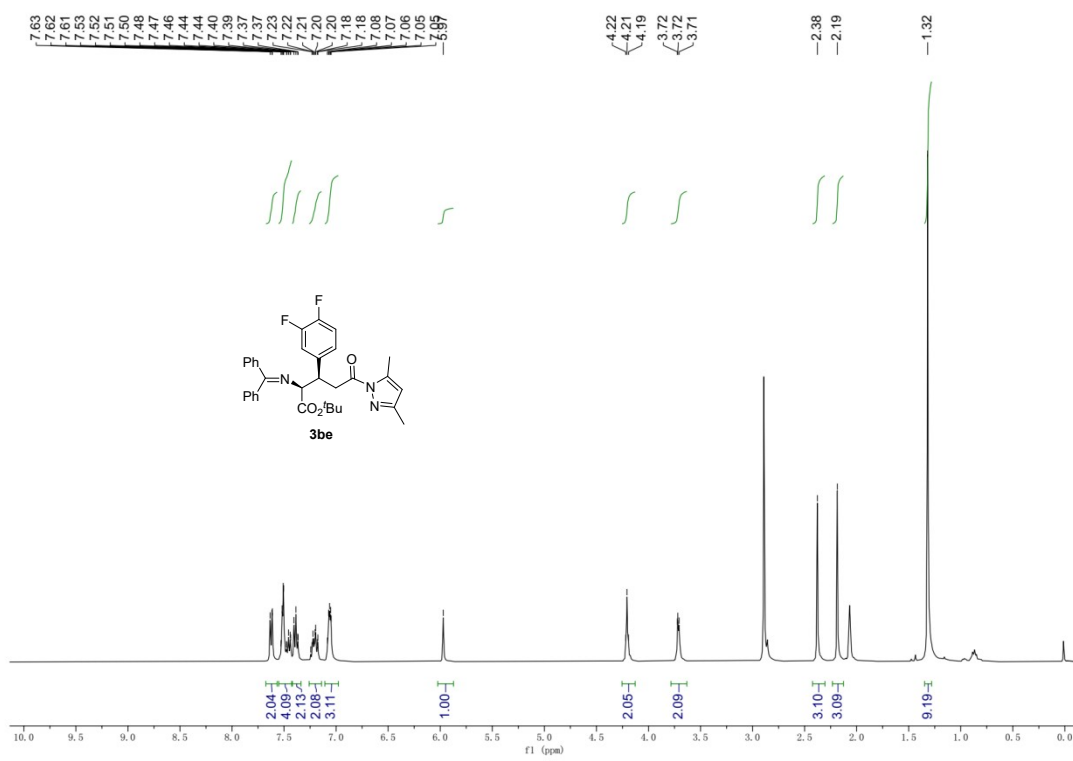
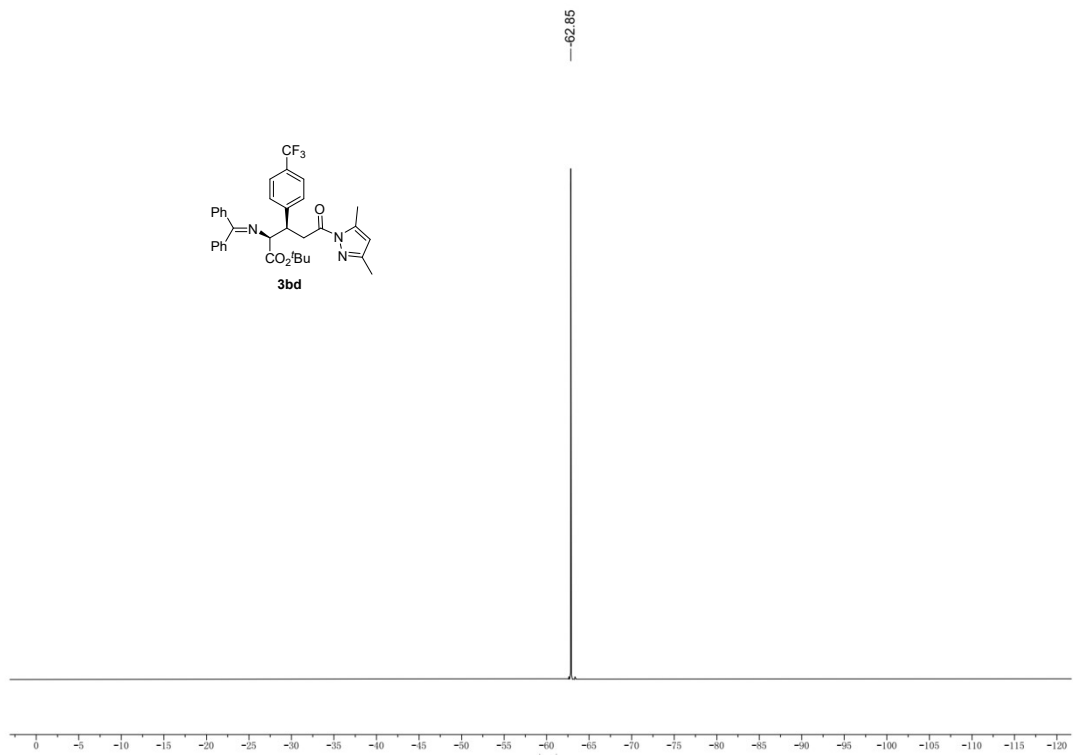


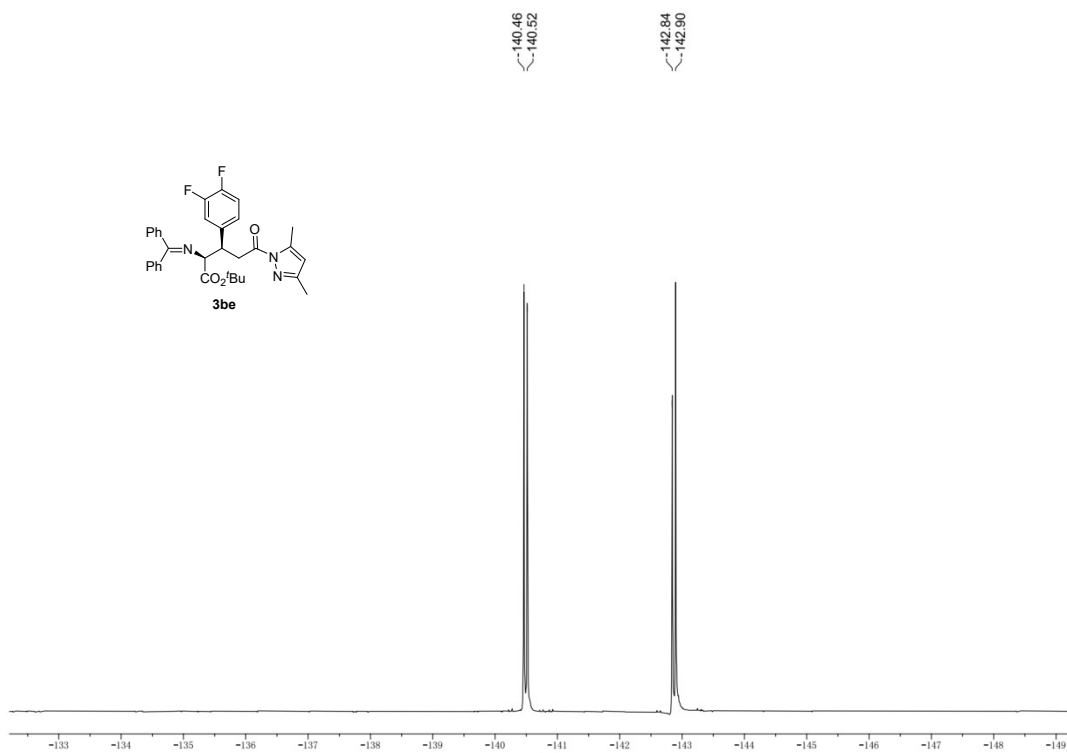
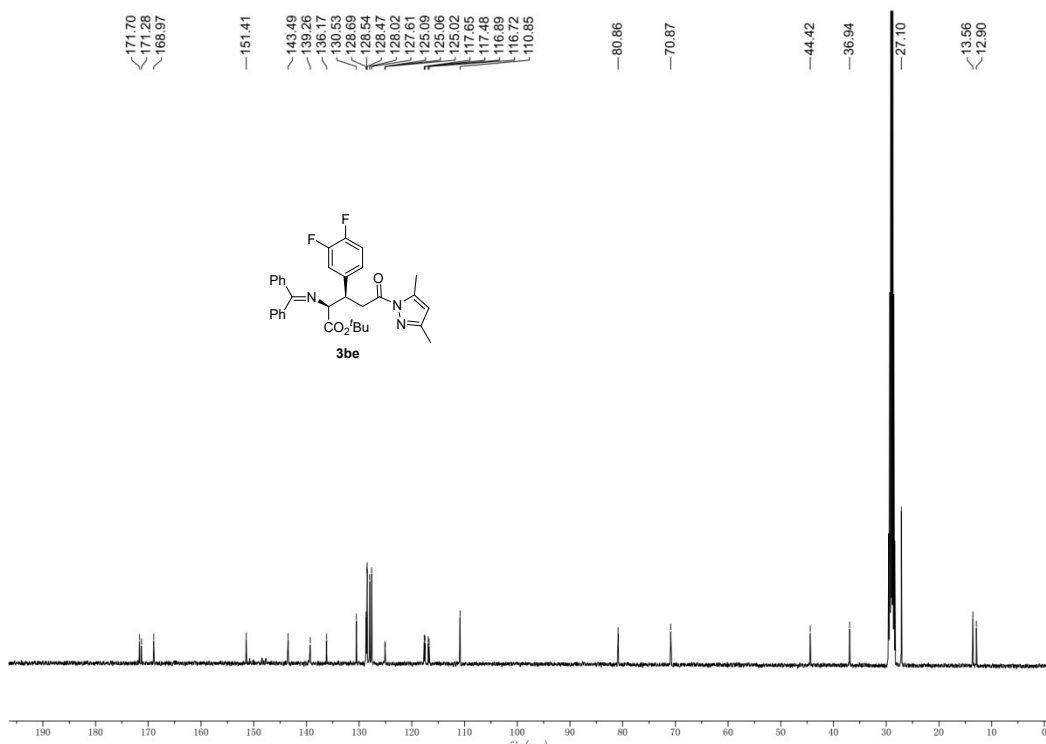


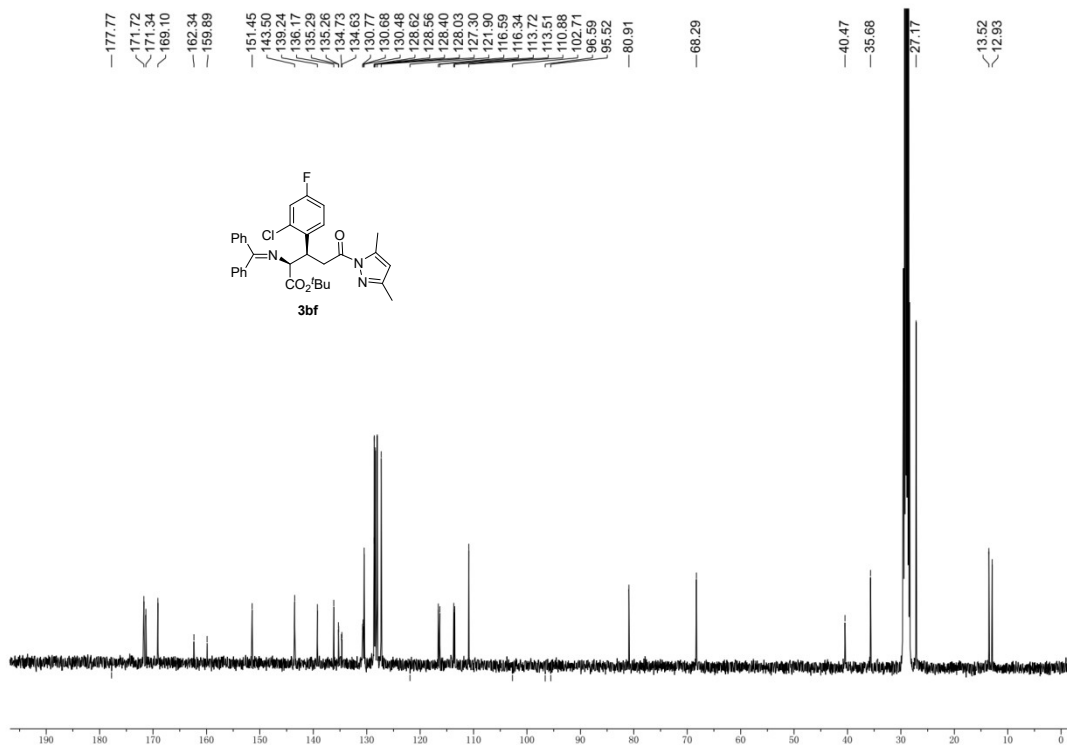
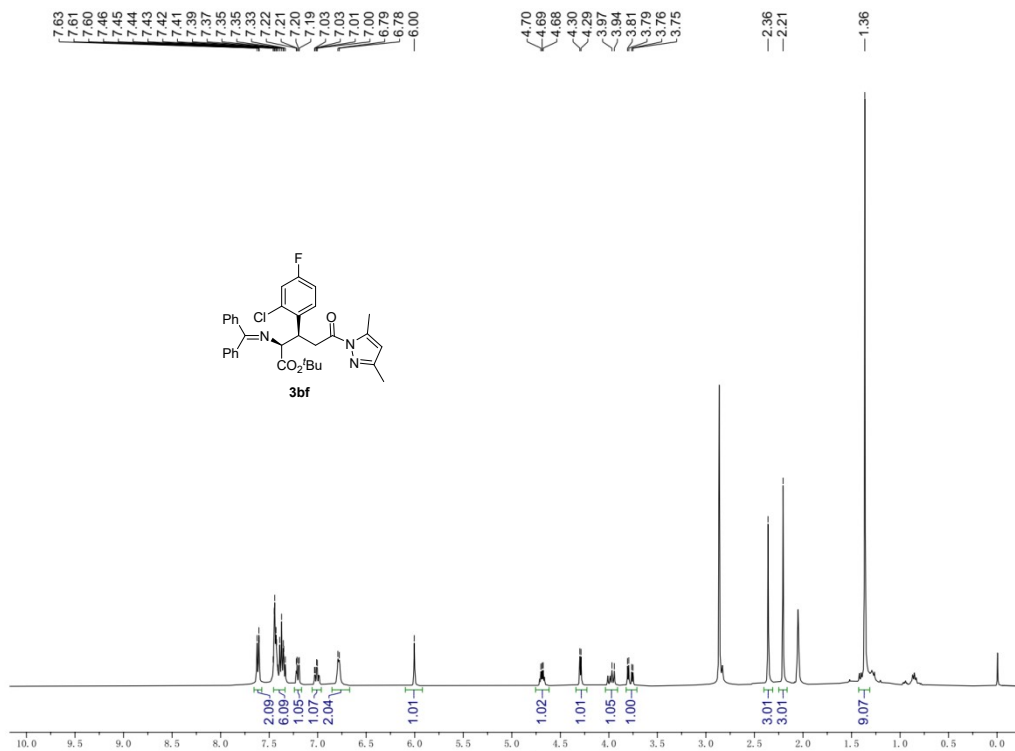


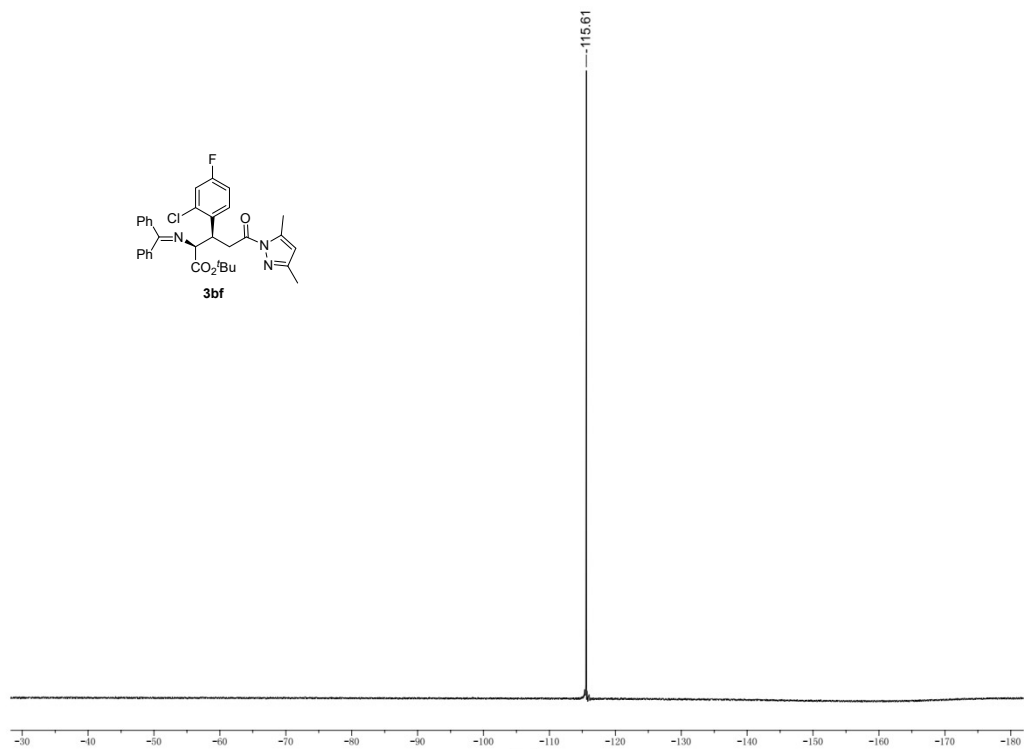
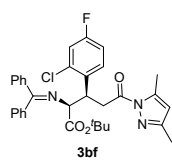






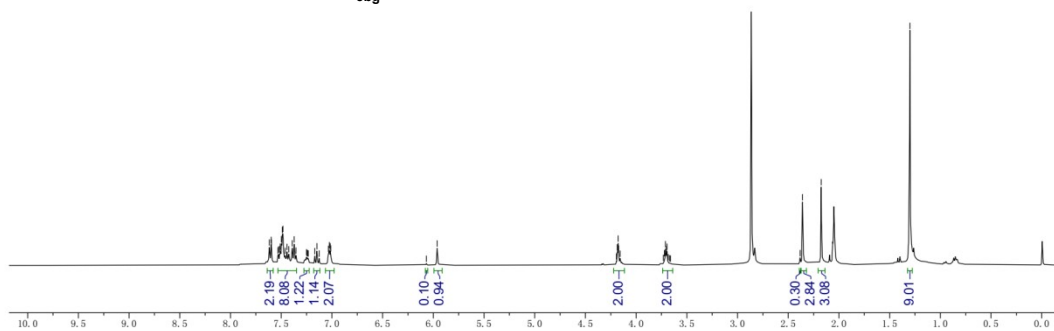
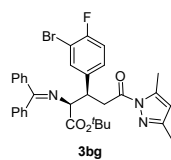


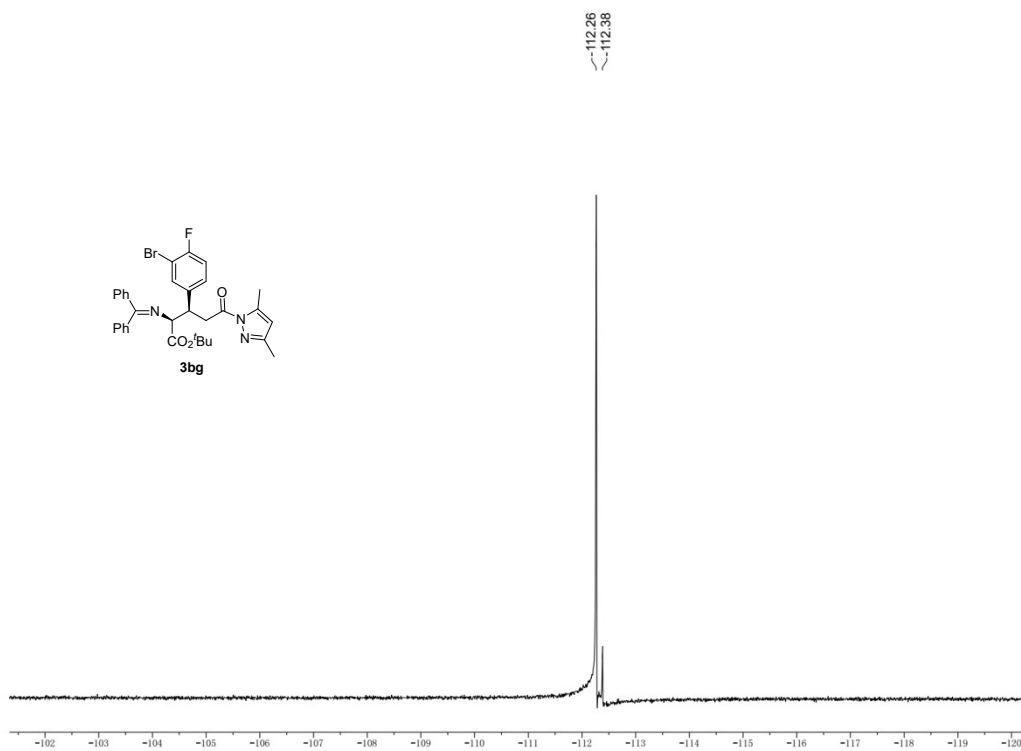
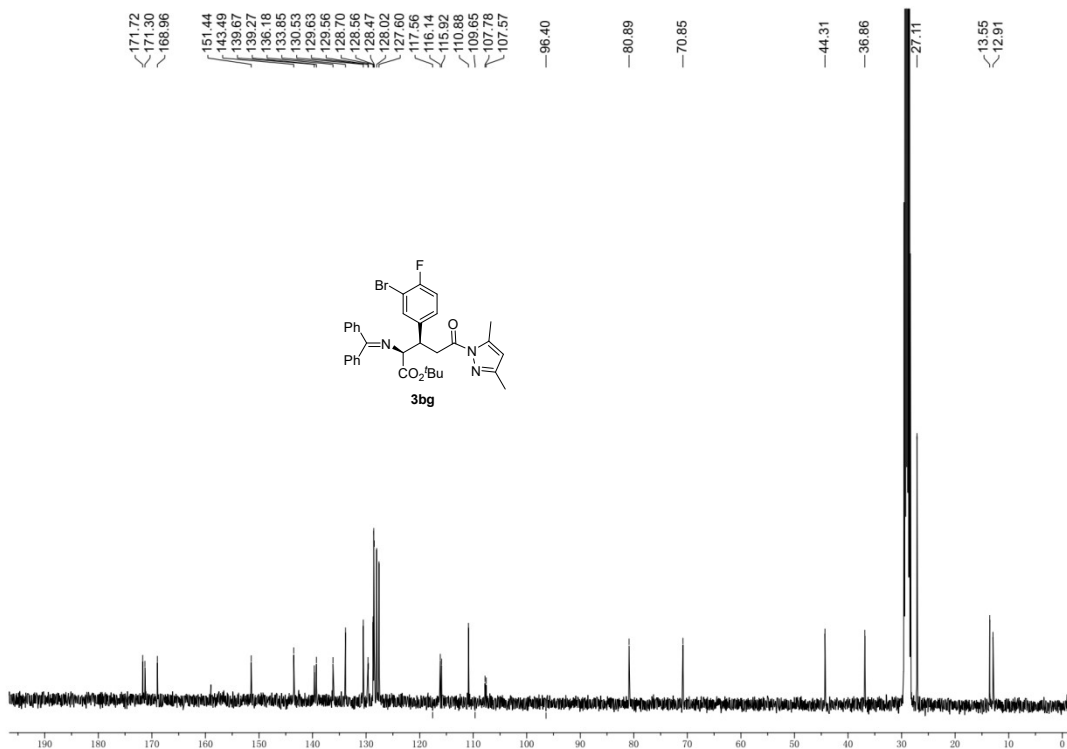


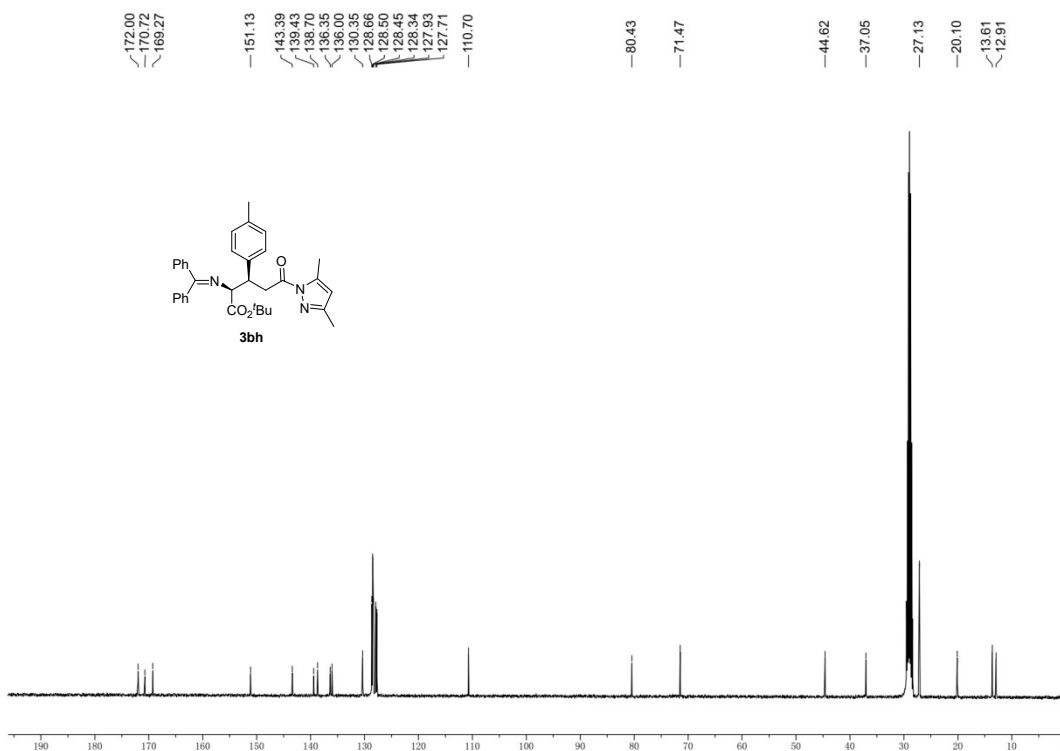
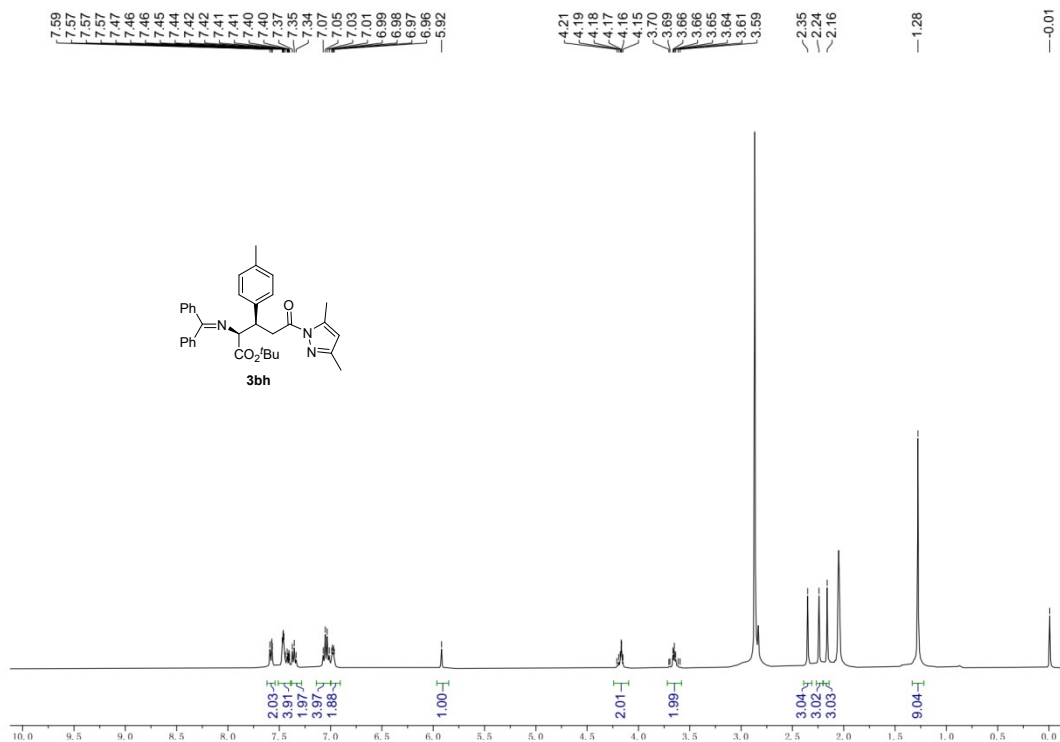


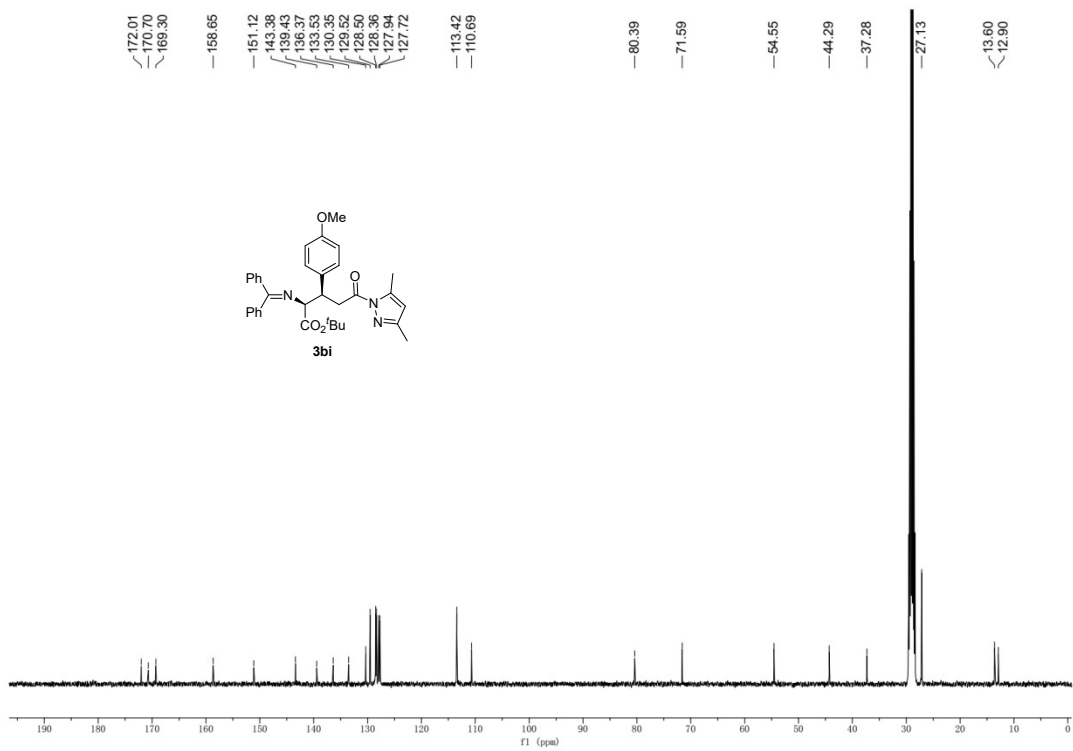
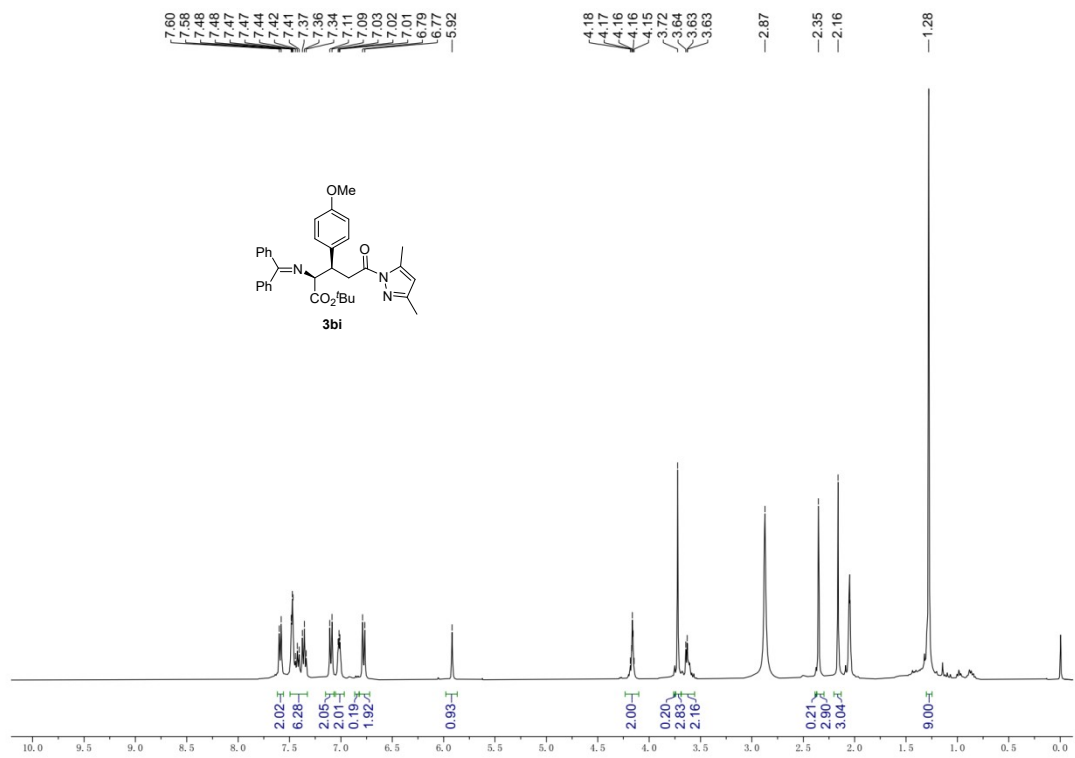
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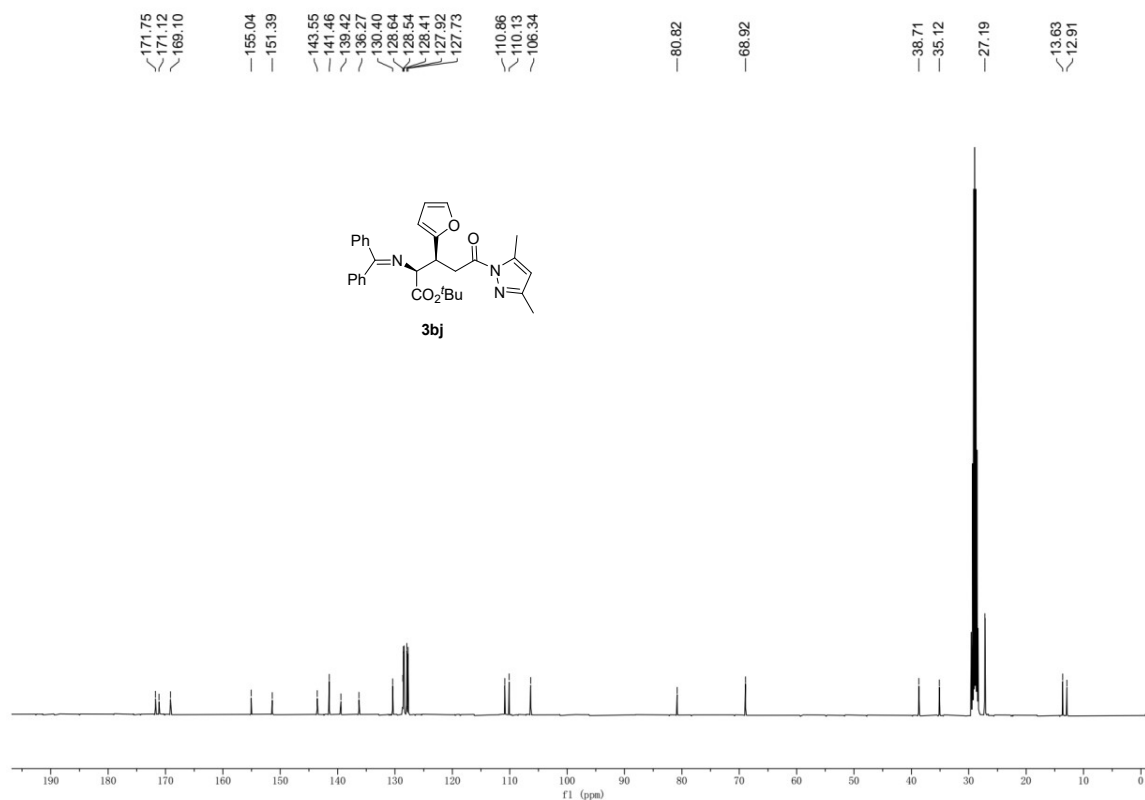
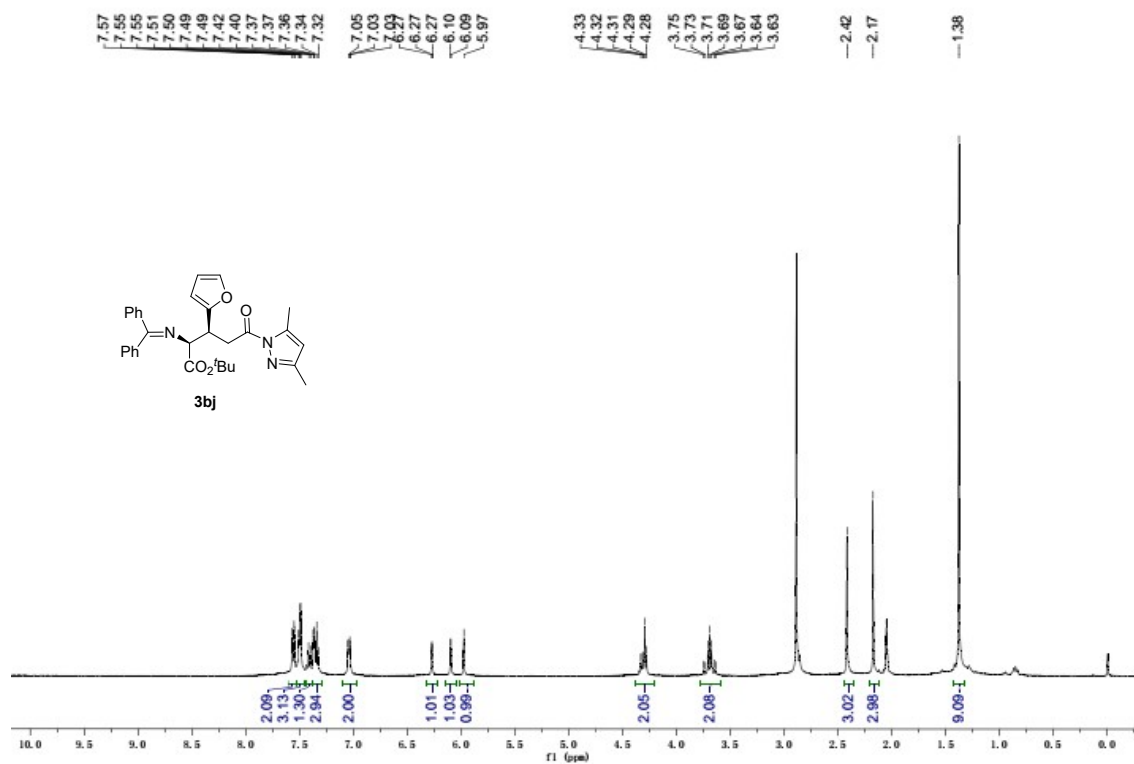
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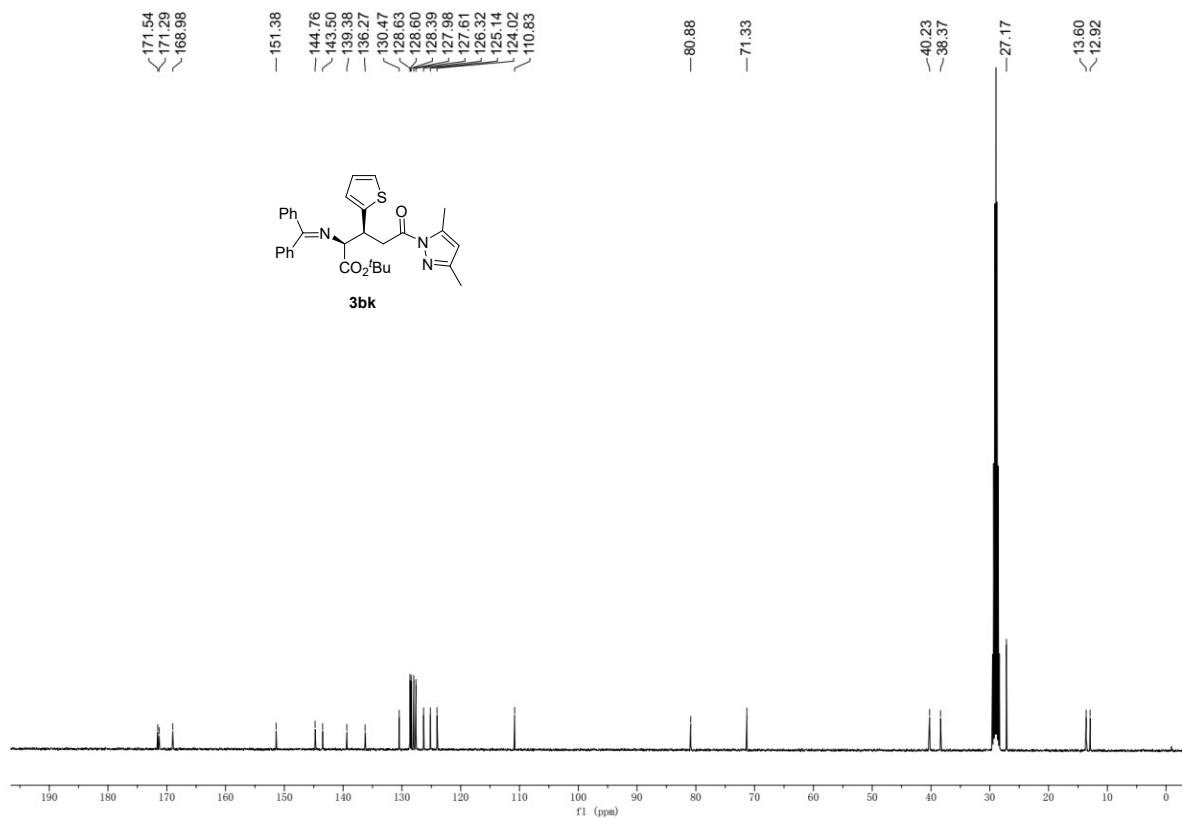
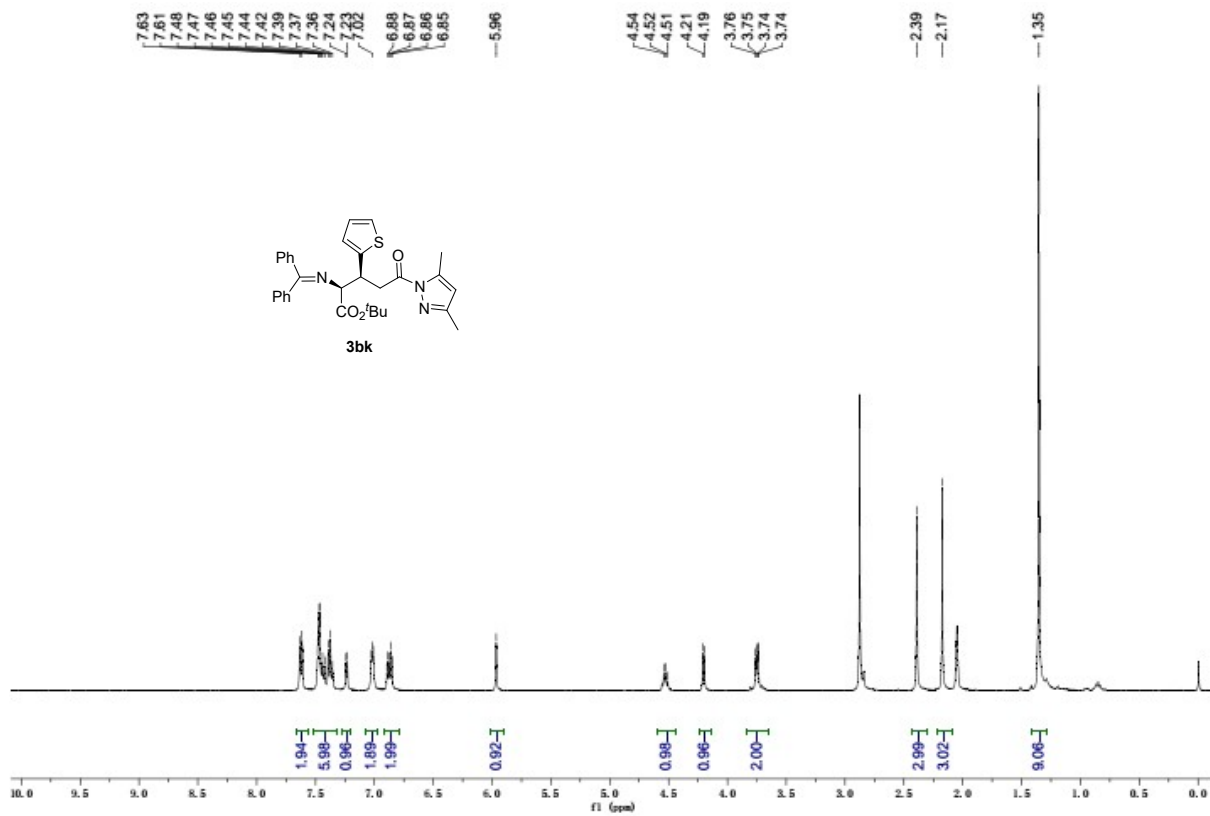


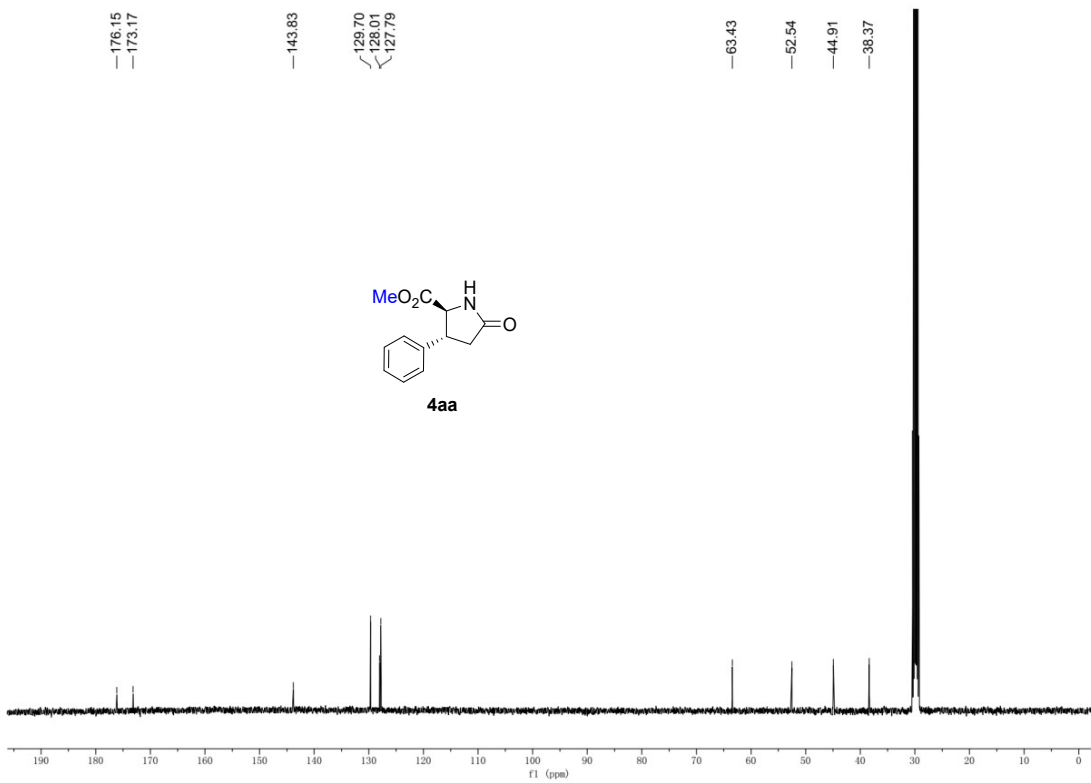
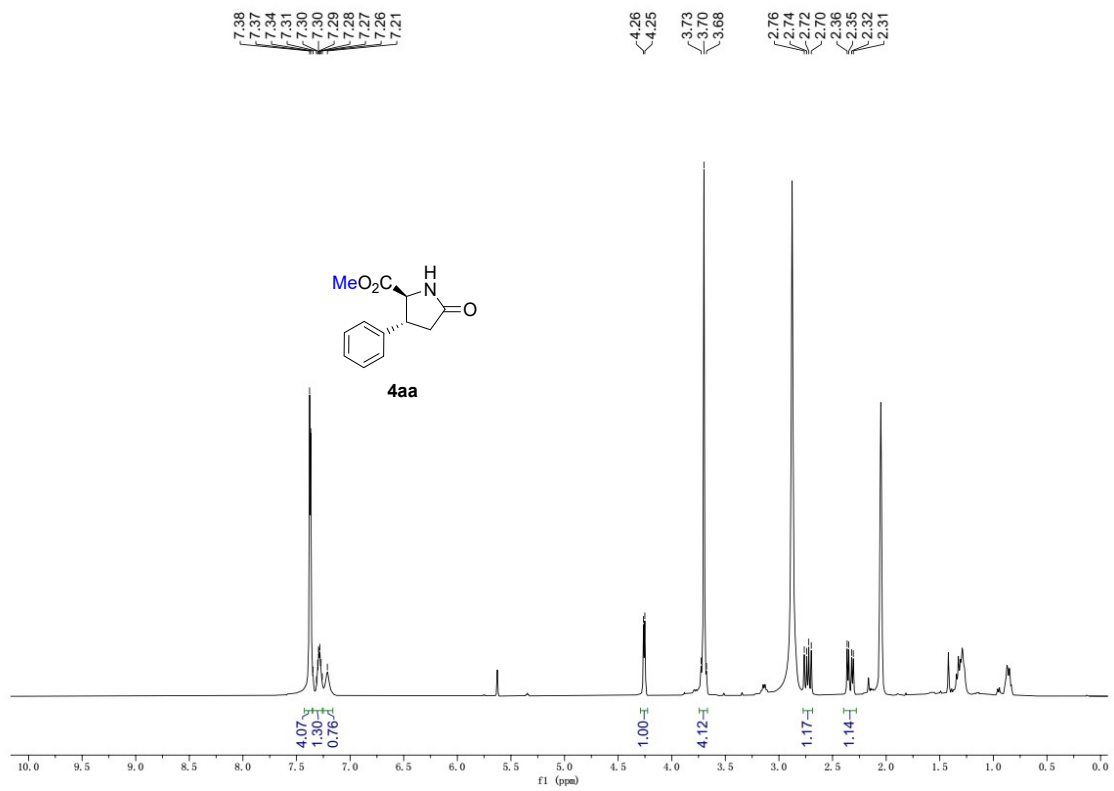


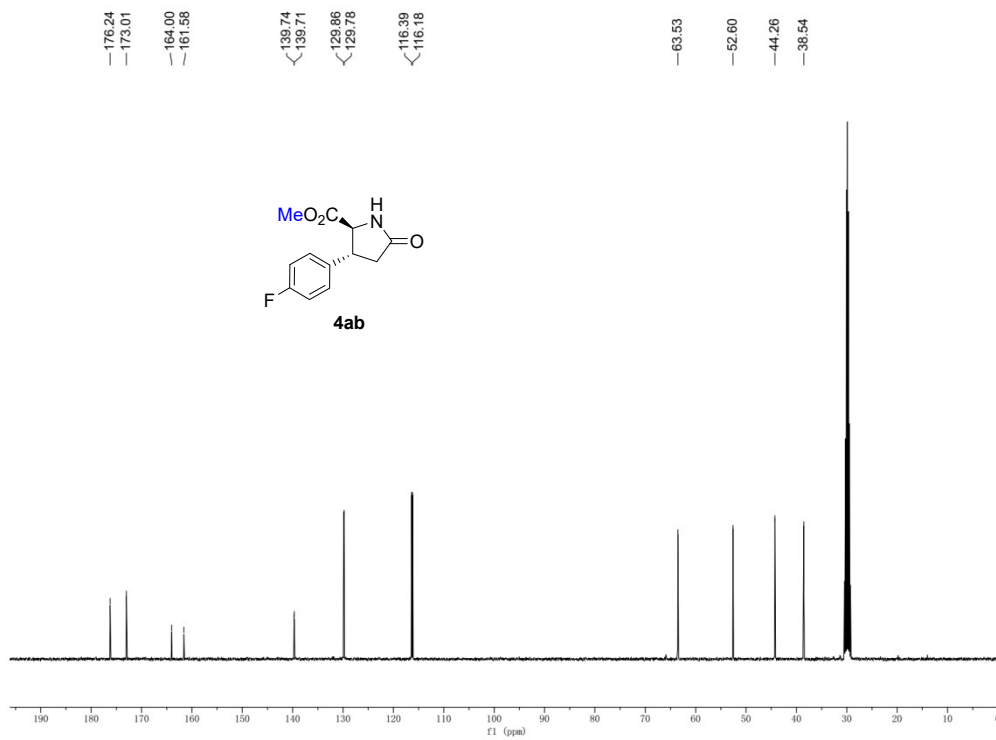
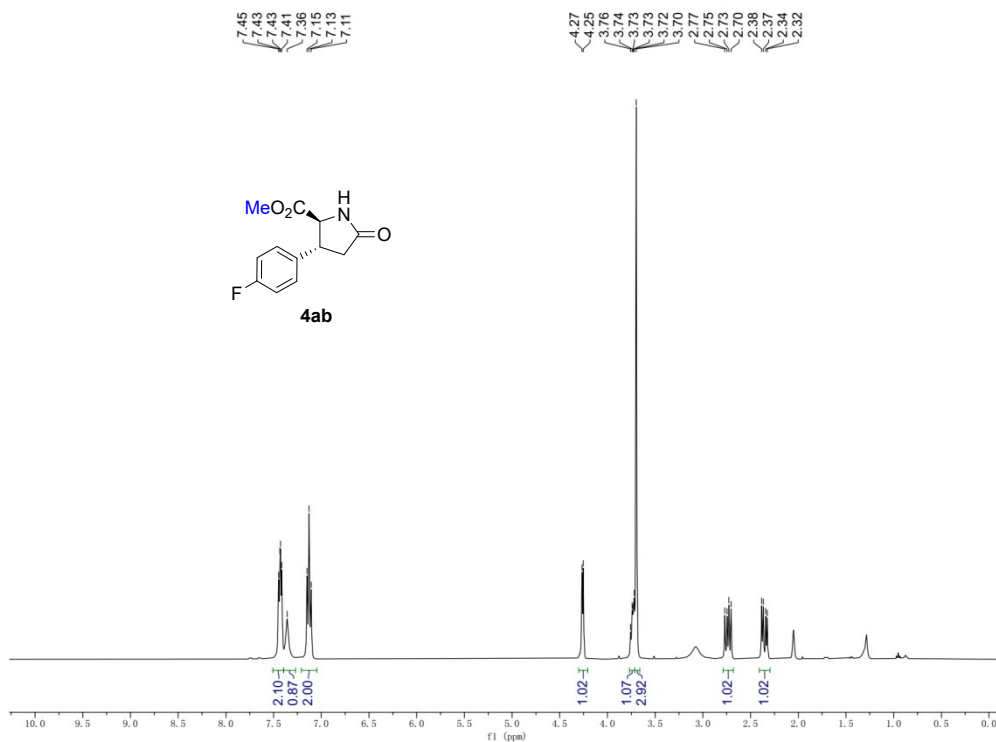


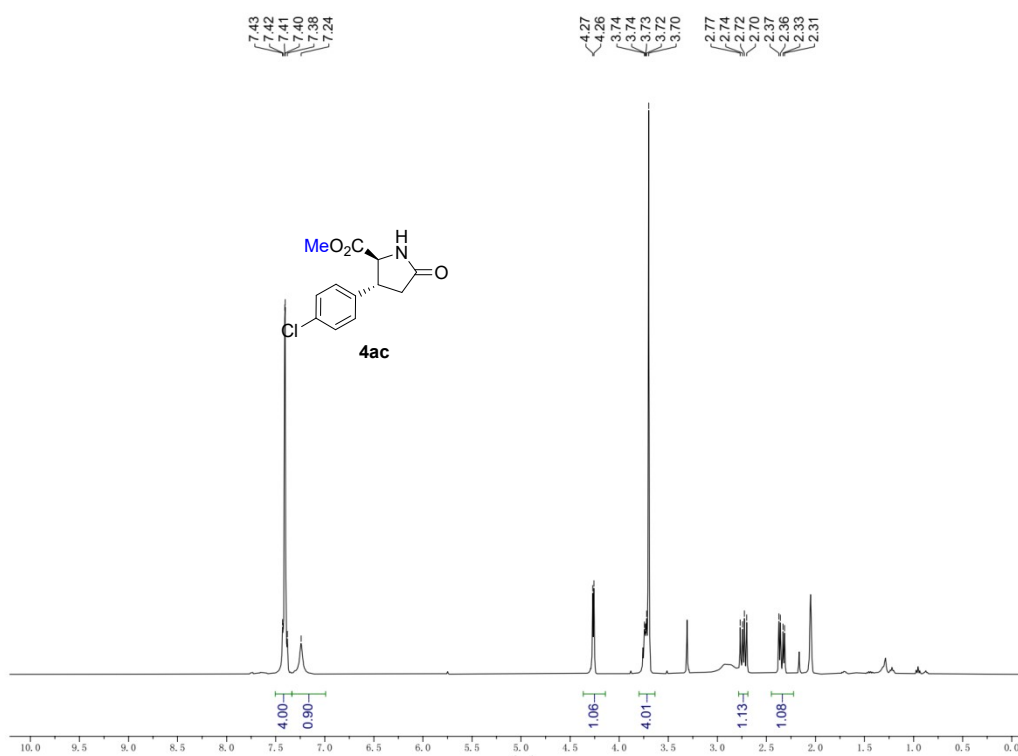
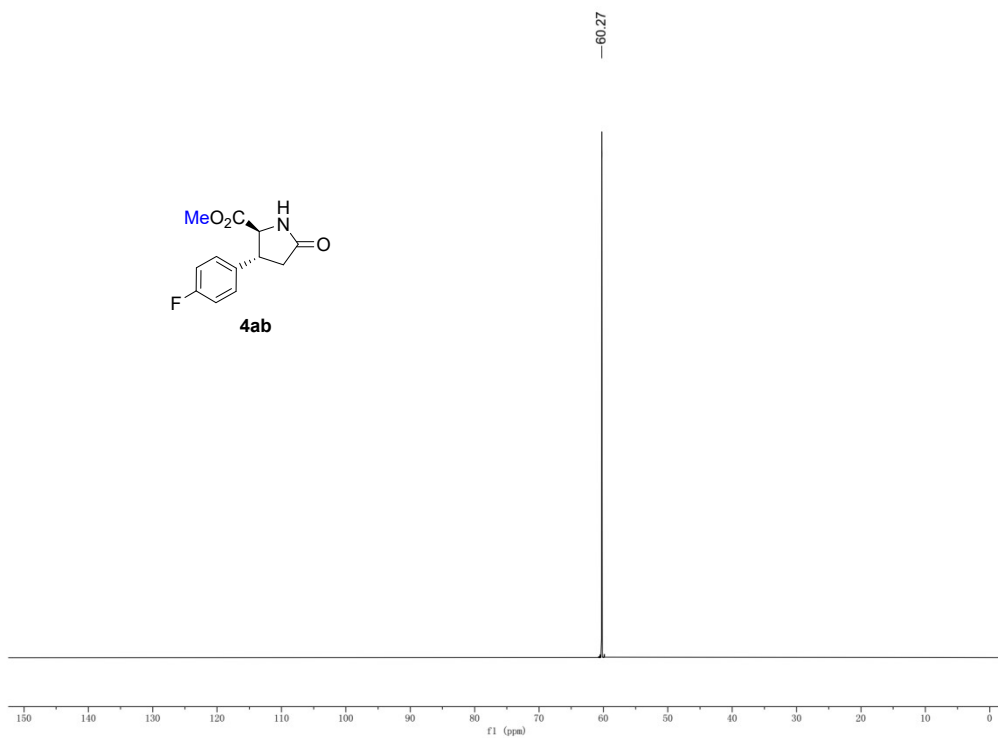


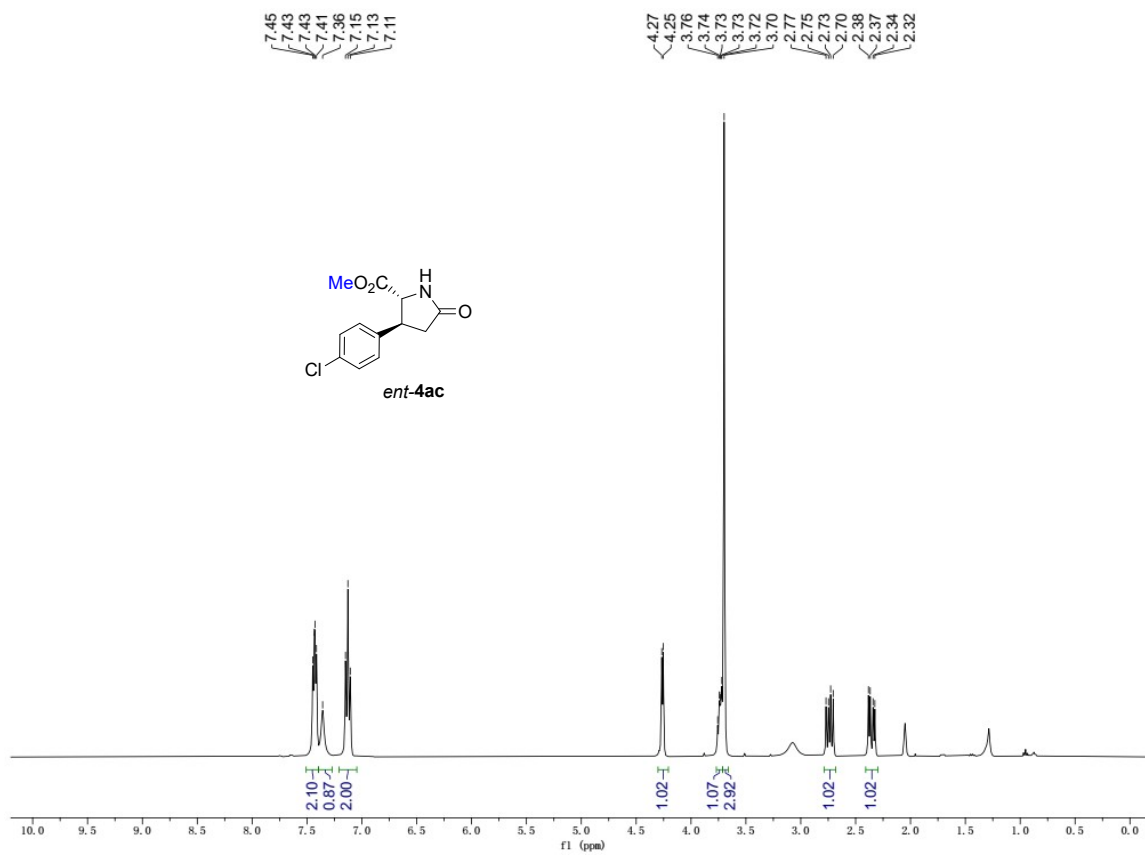
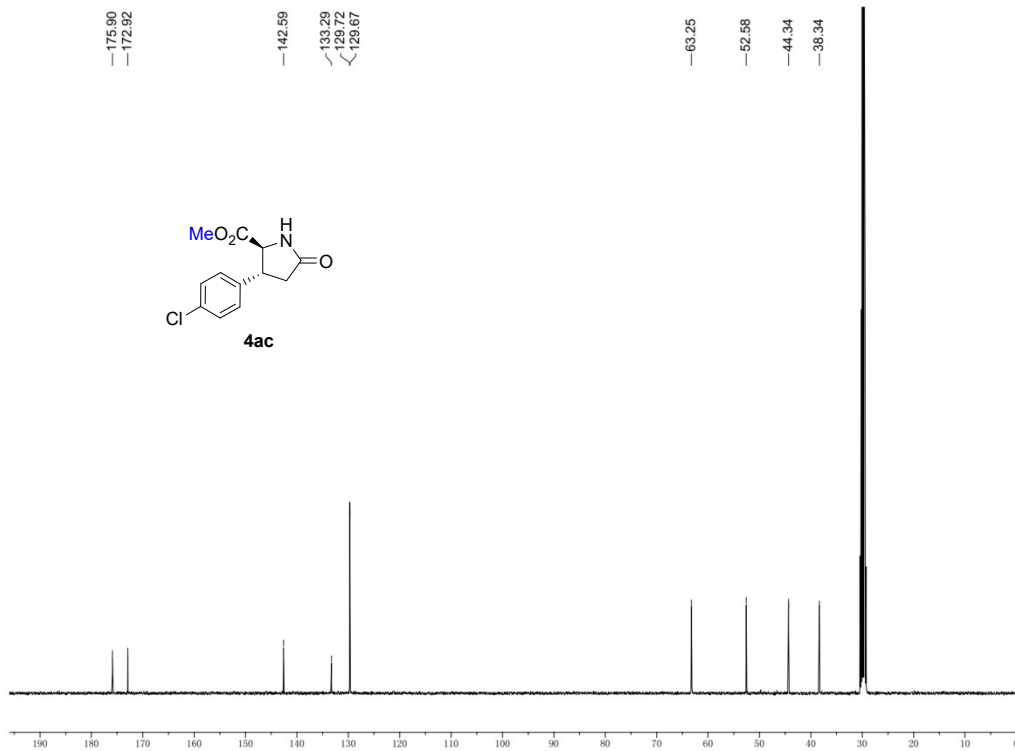


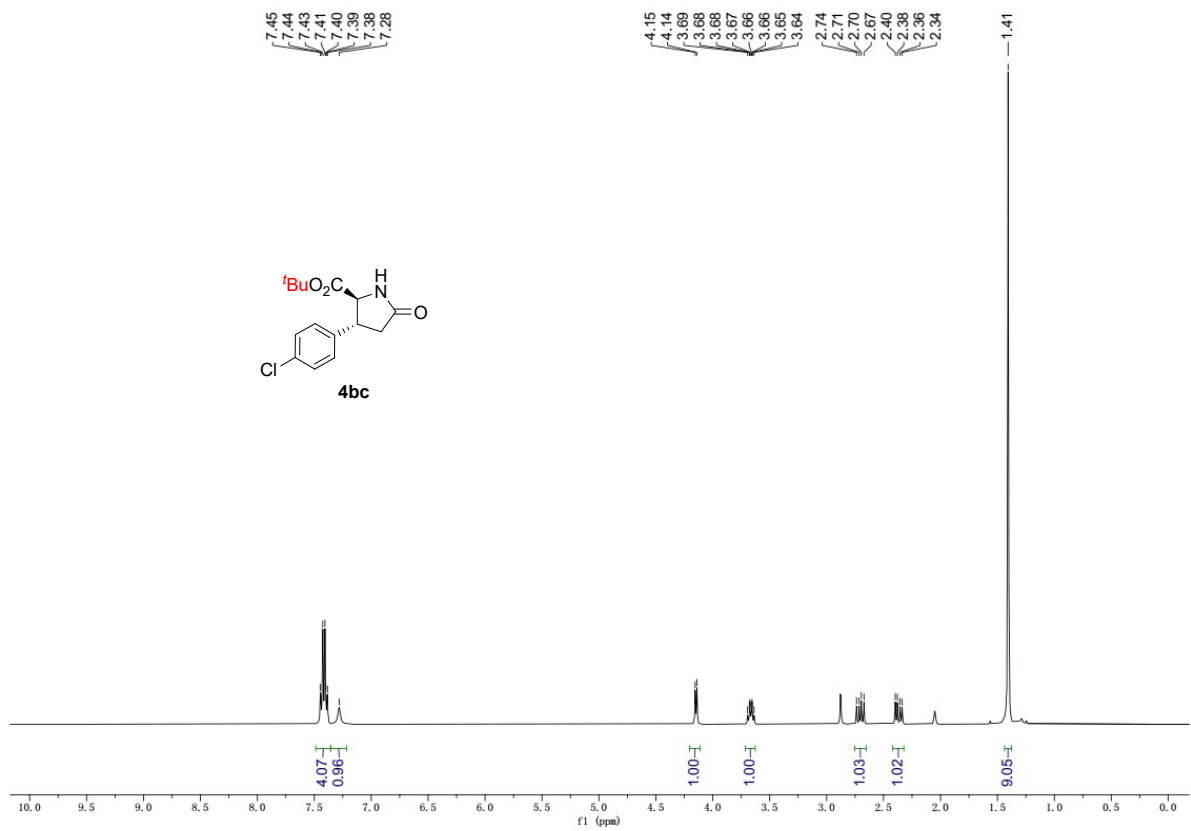
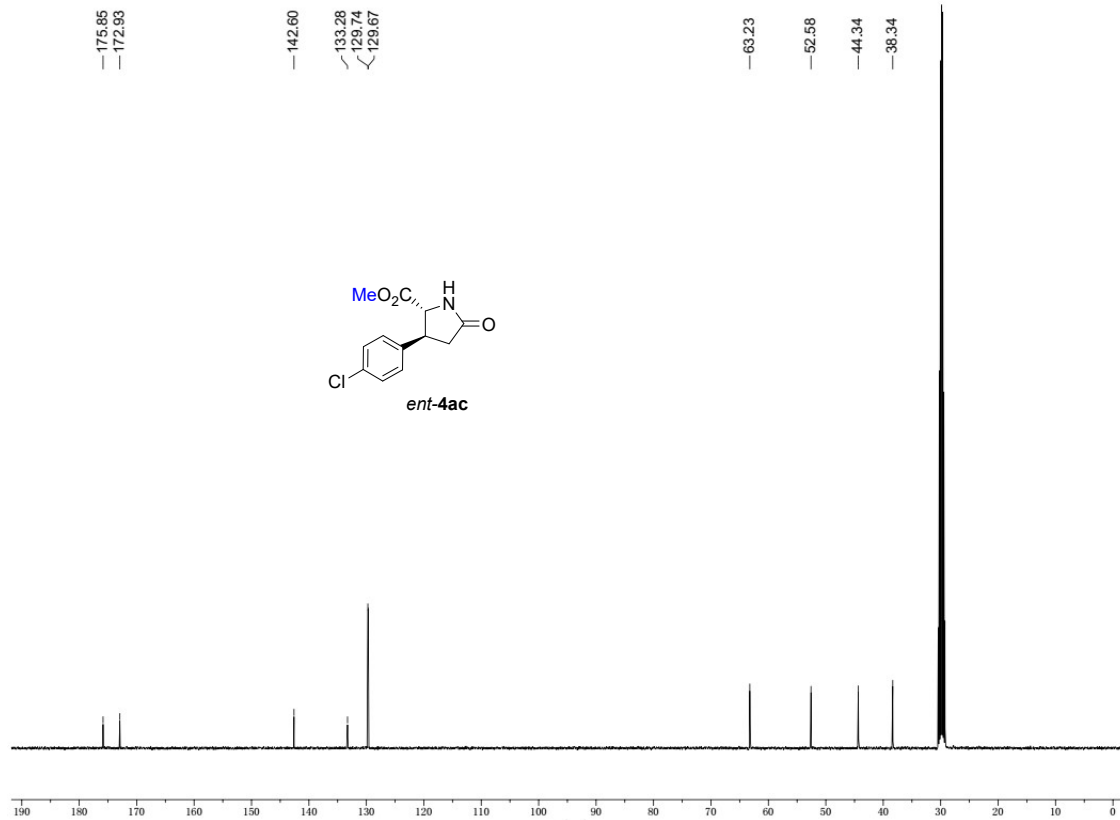












—175.84
—171.53

—142.56
—133.18
—129.96
—126.56

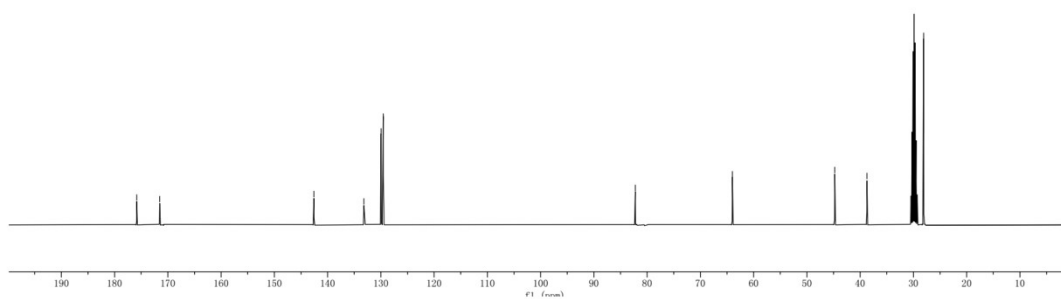
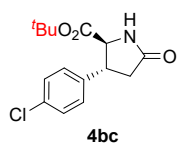
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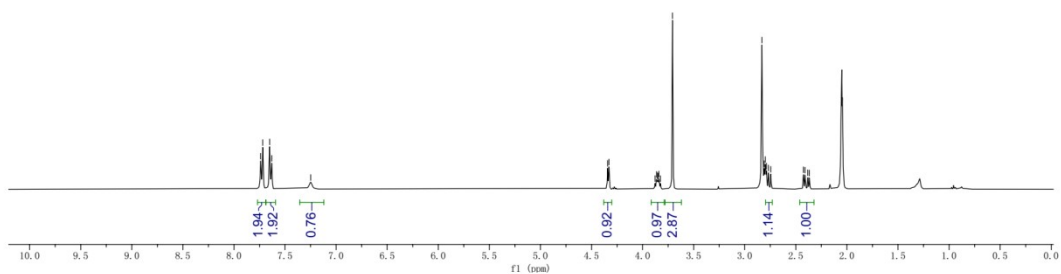
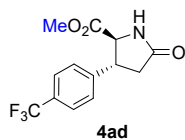
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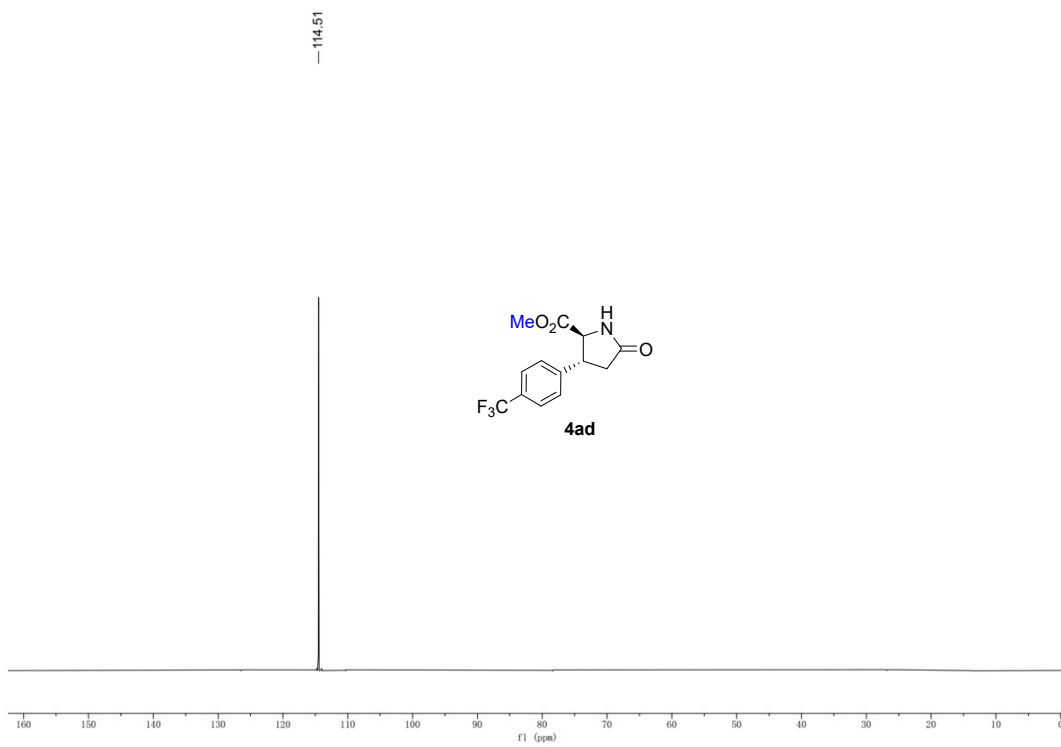
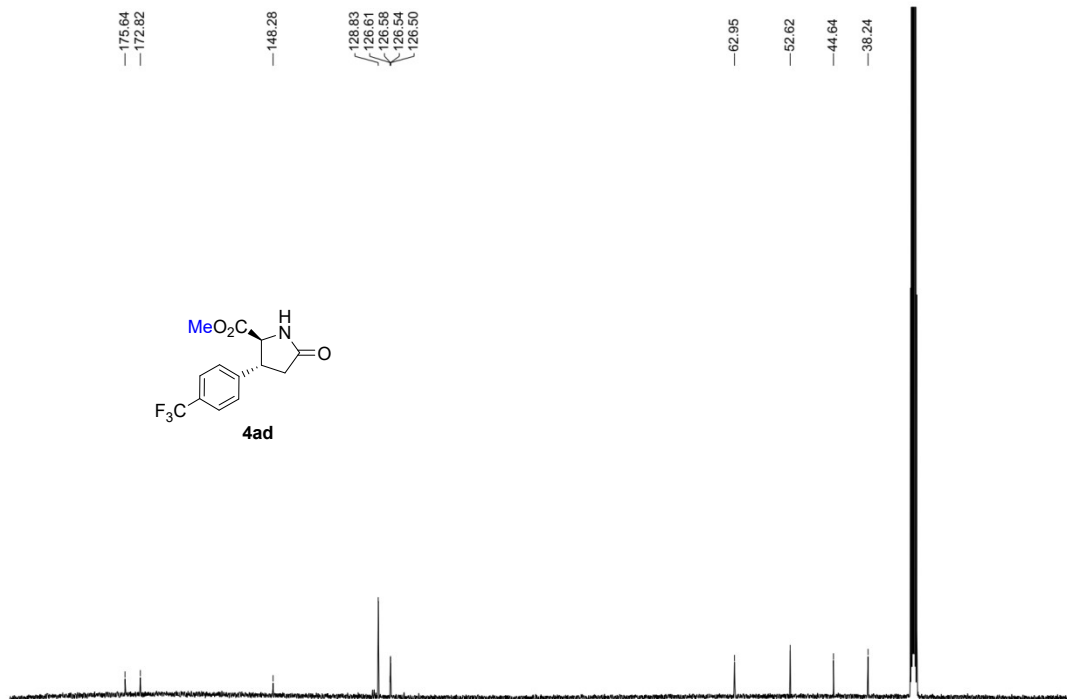
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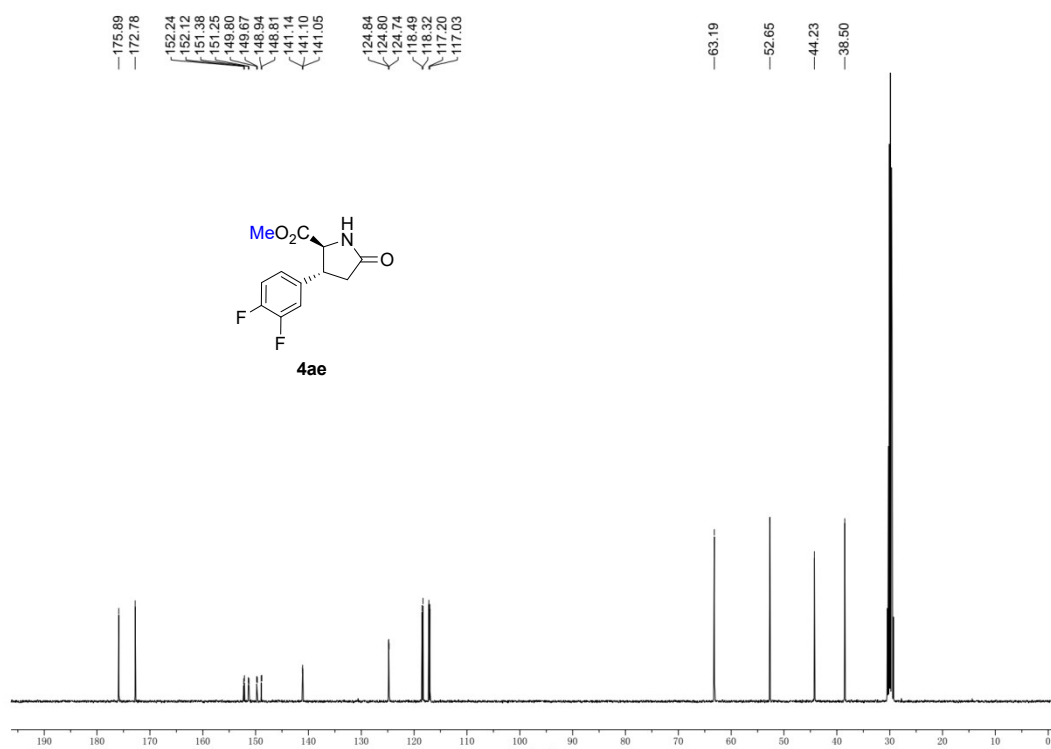
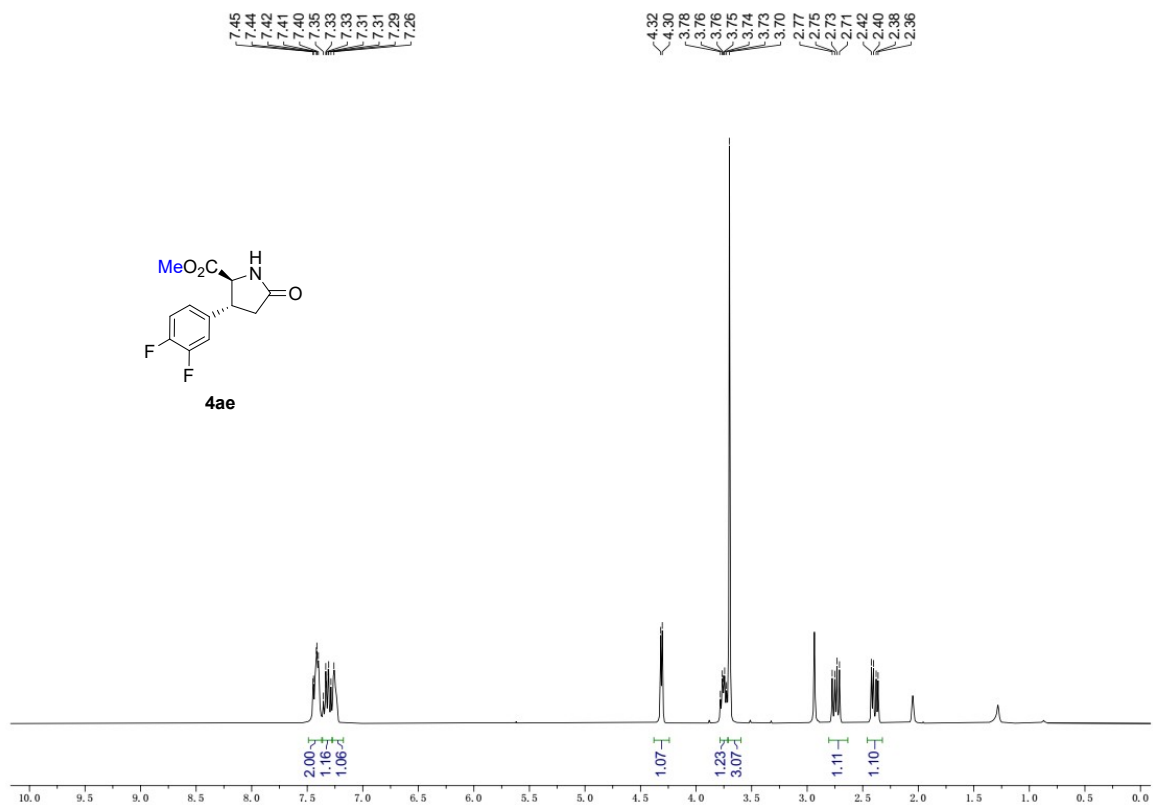


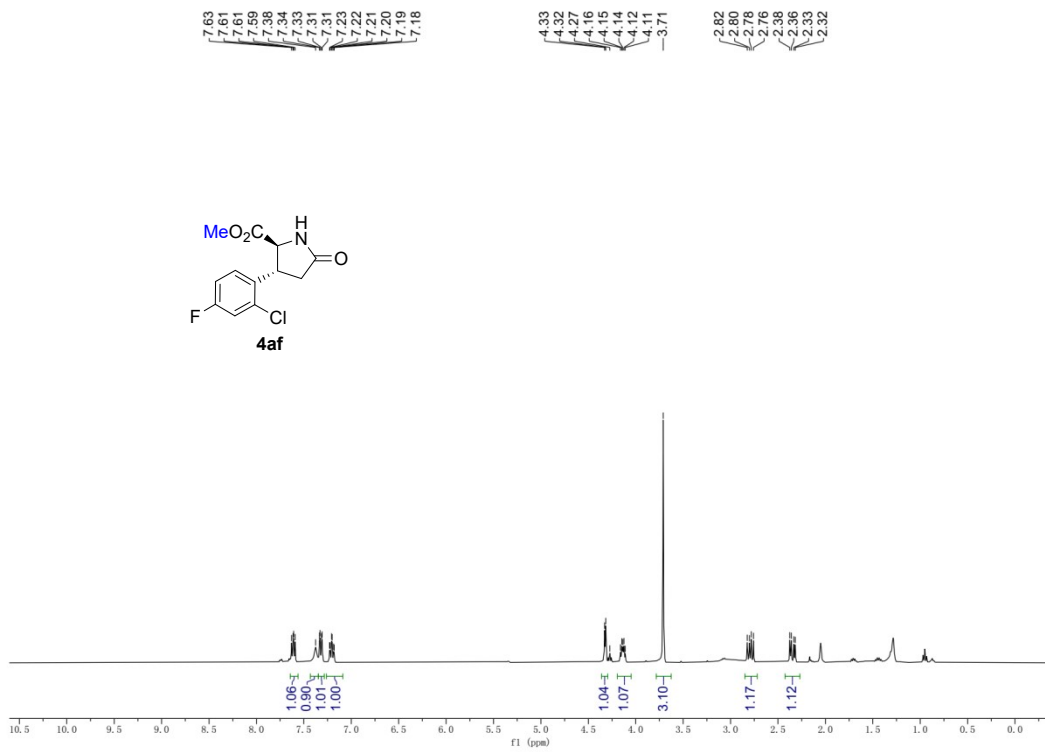
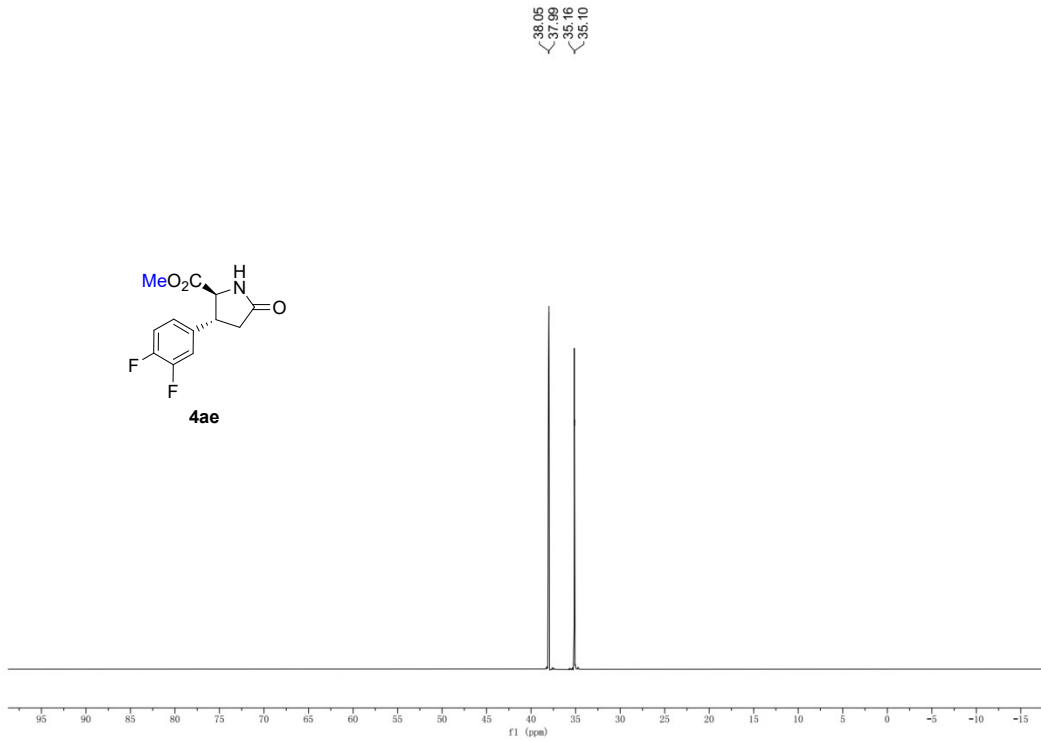
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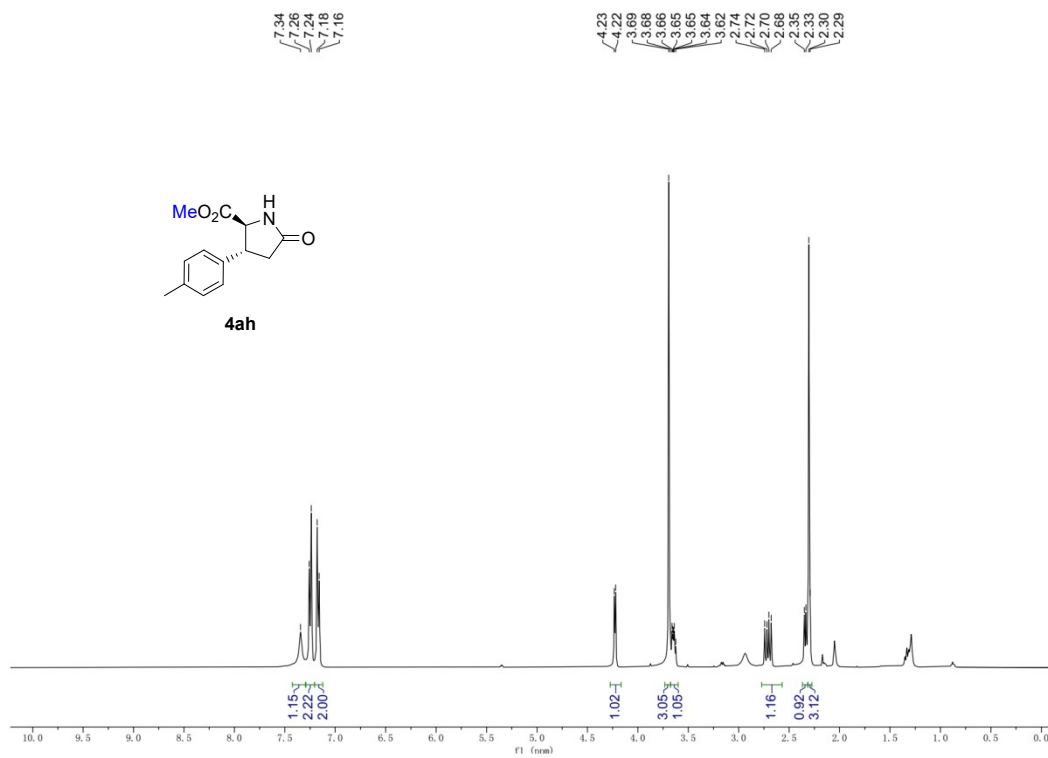
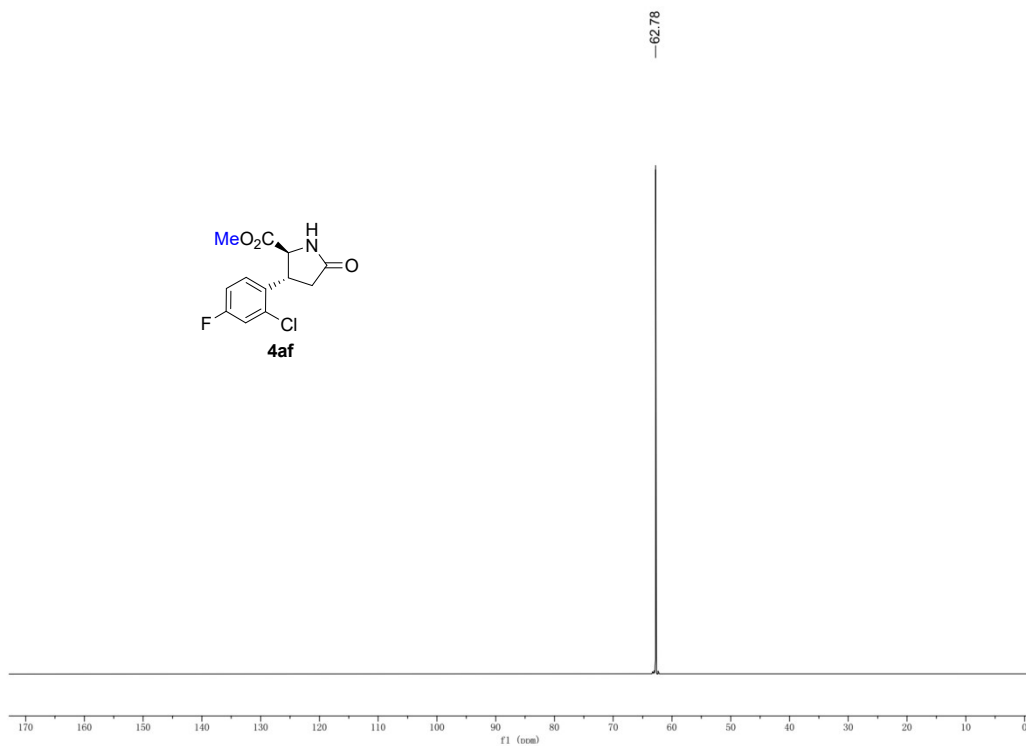
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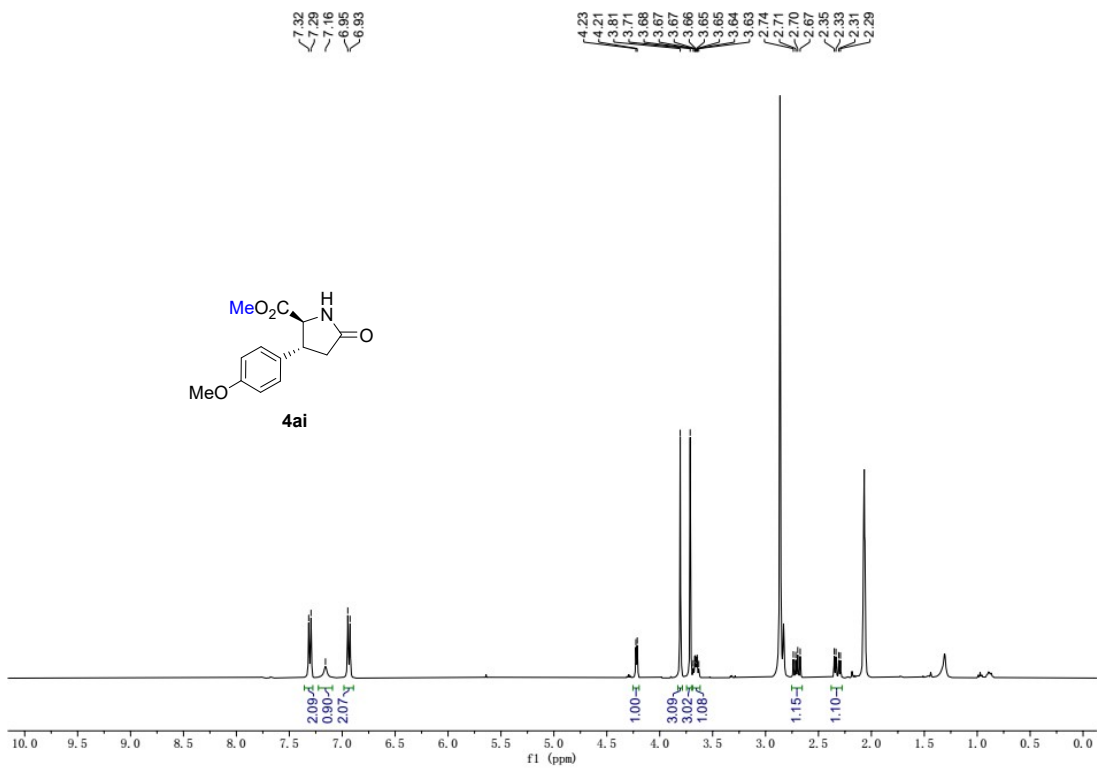
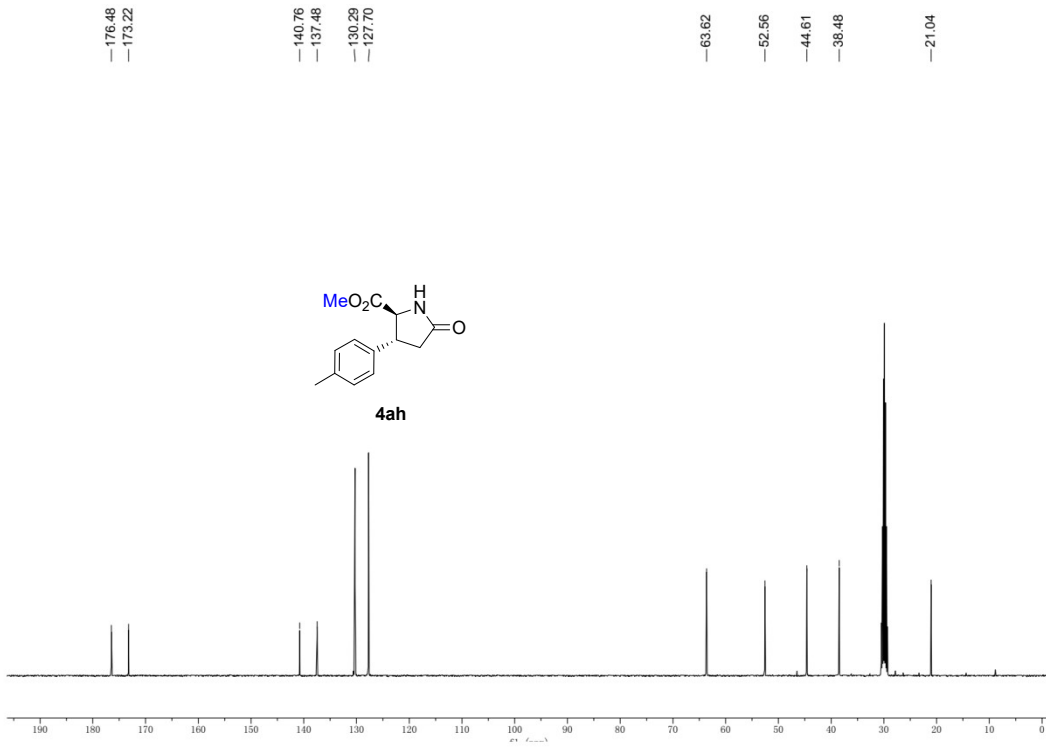


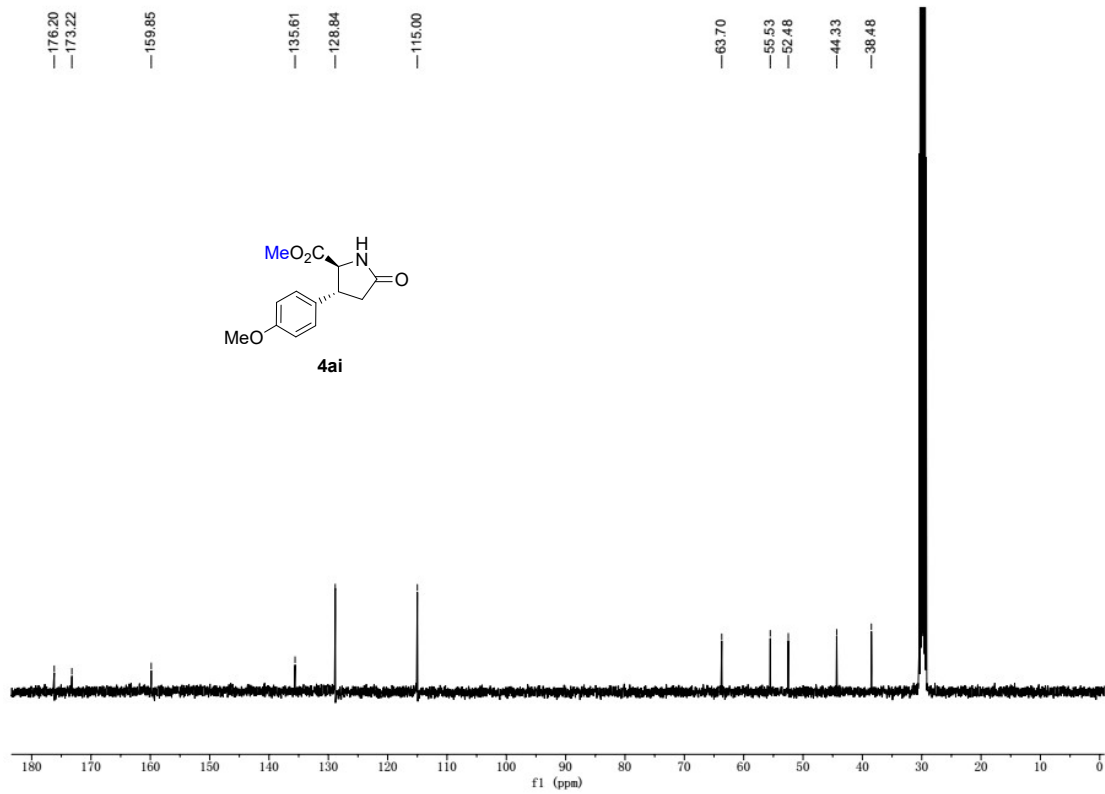




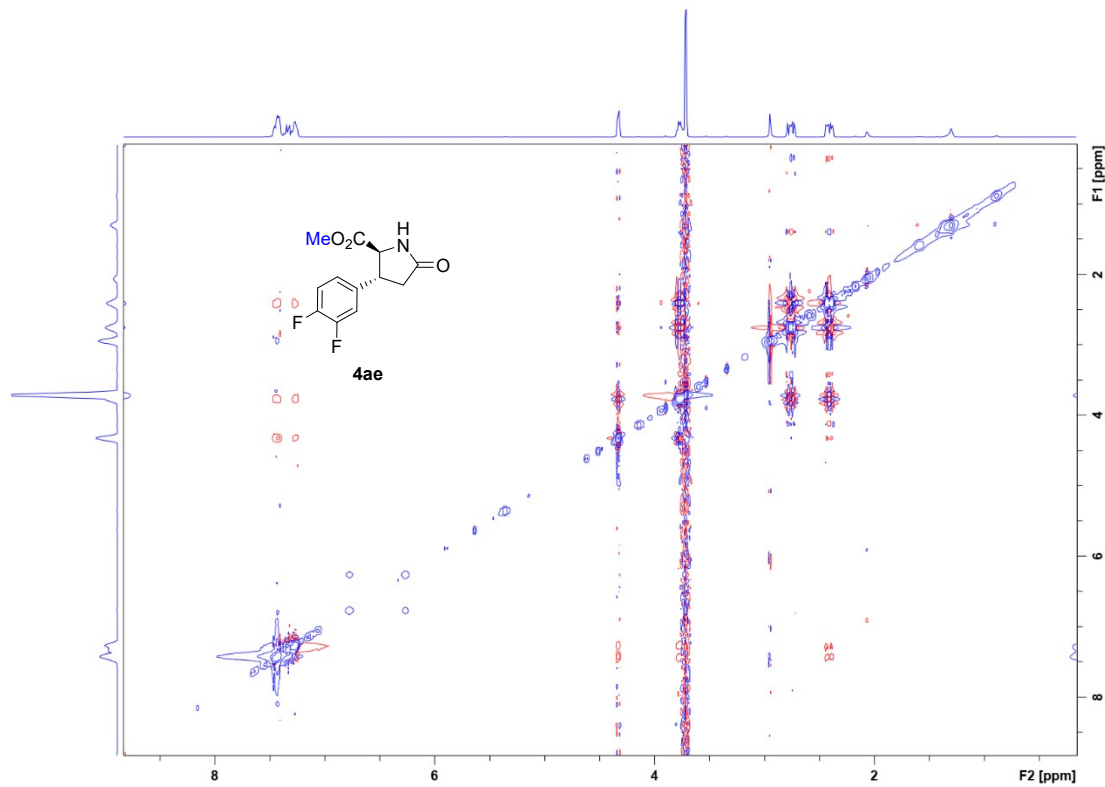
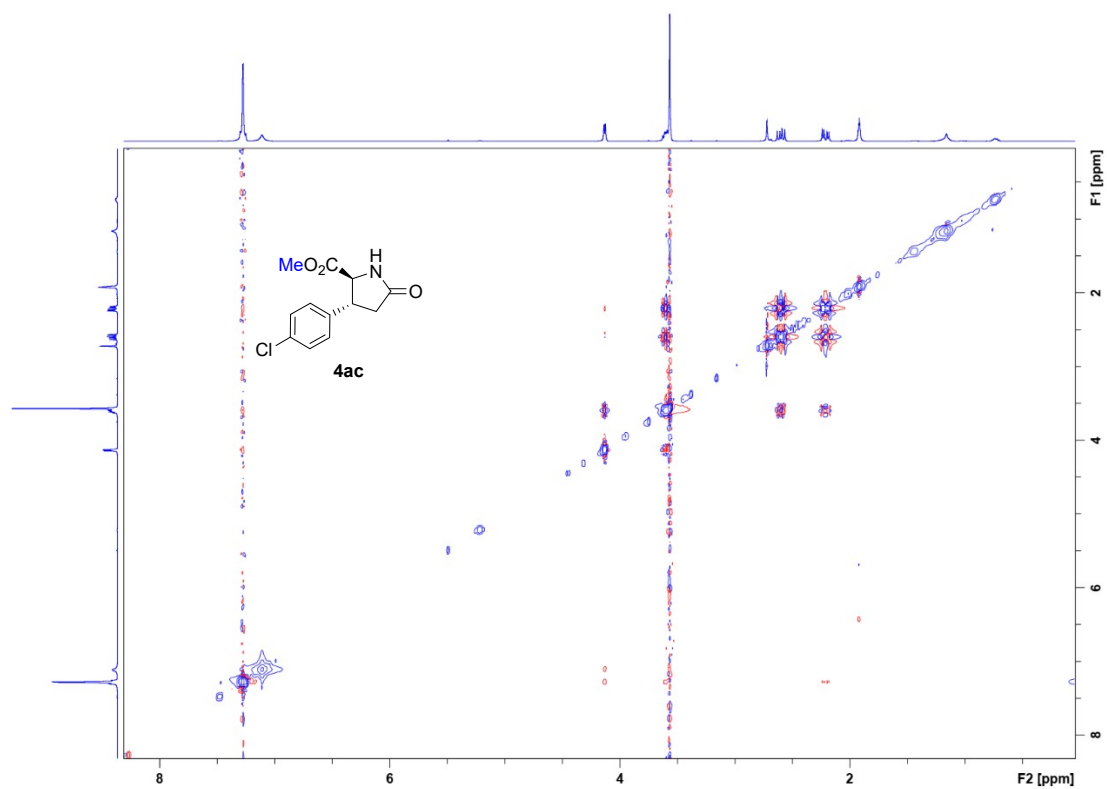


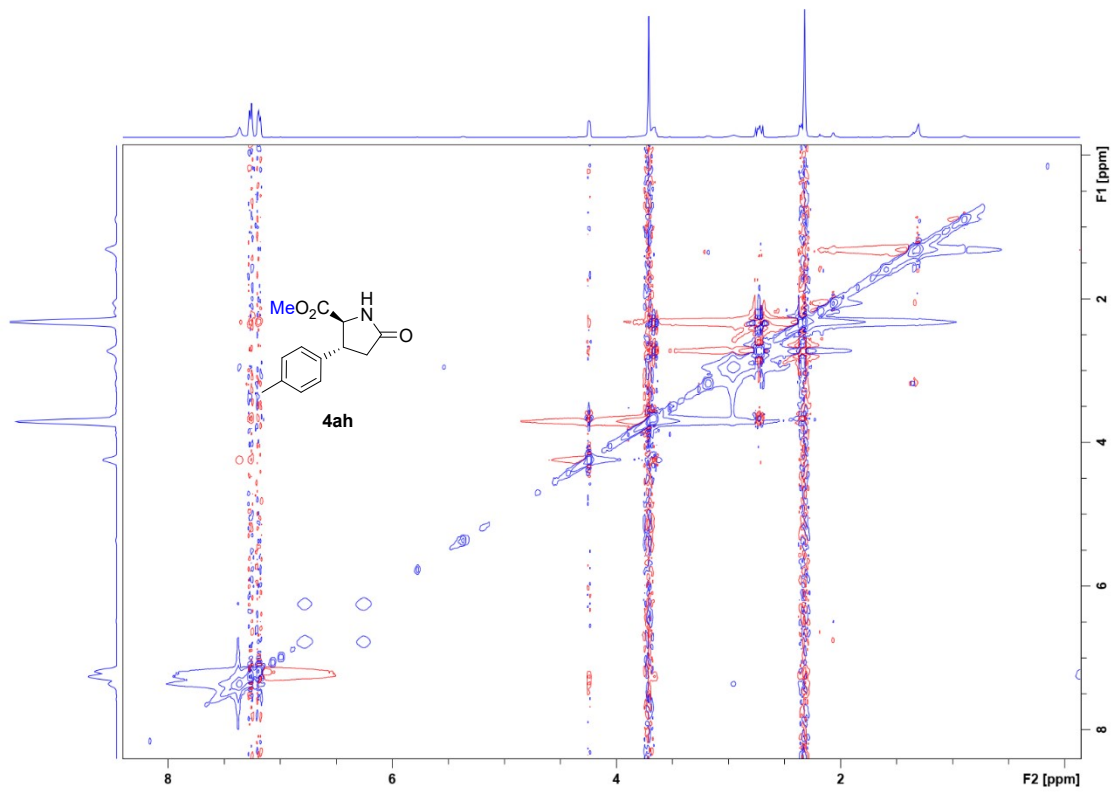
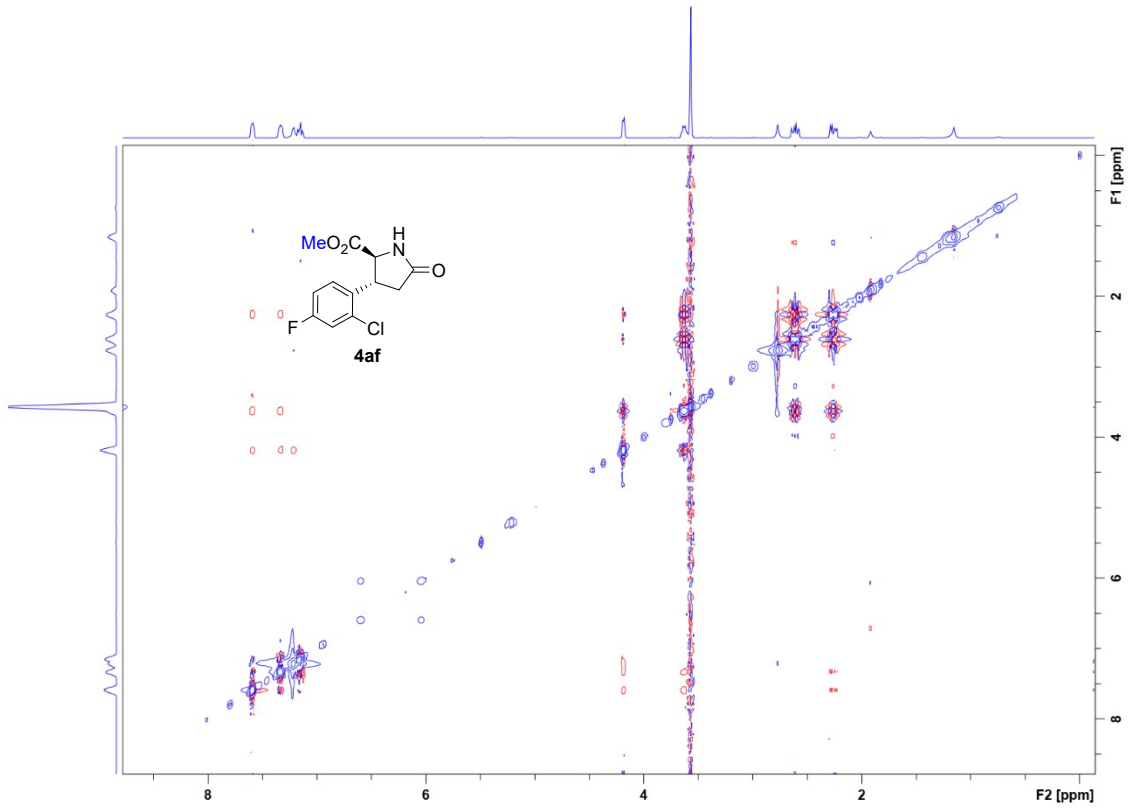




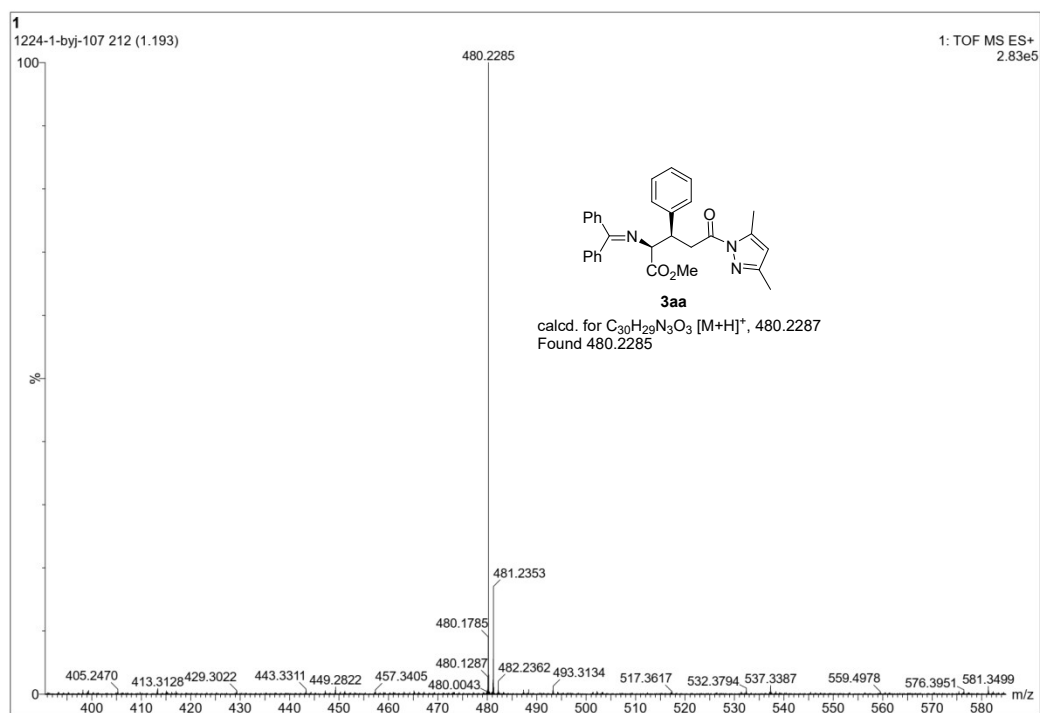


5. NOESY Copies





6. HRMS scanning copies



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

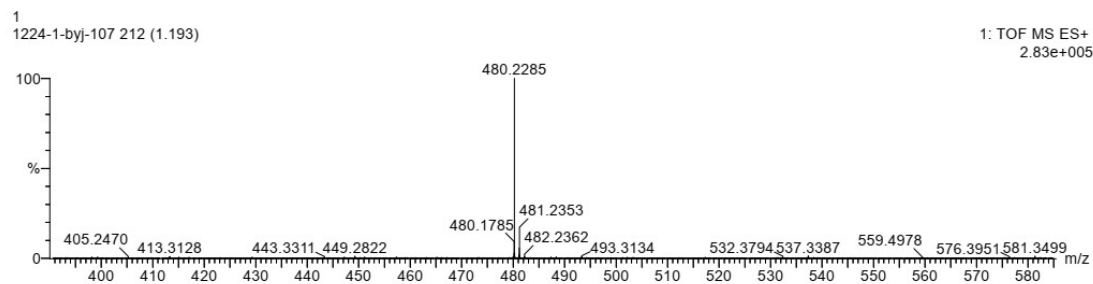
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

997 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

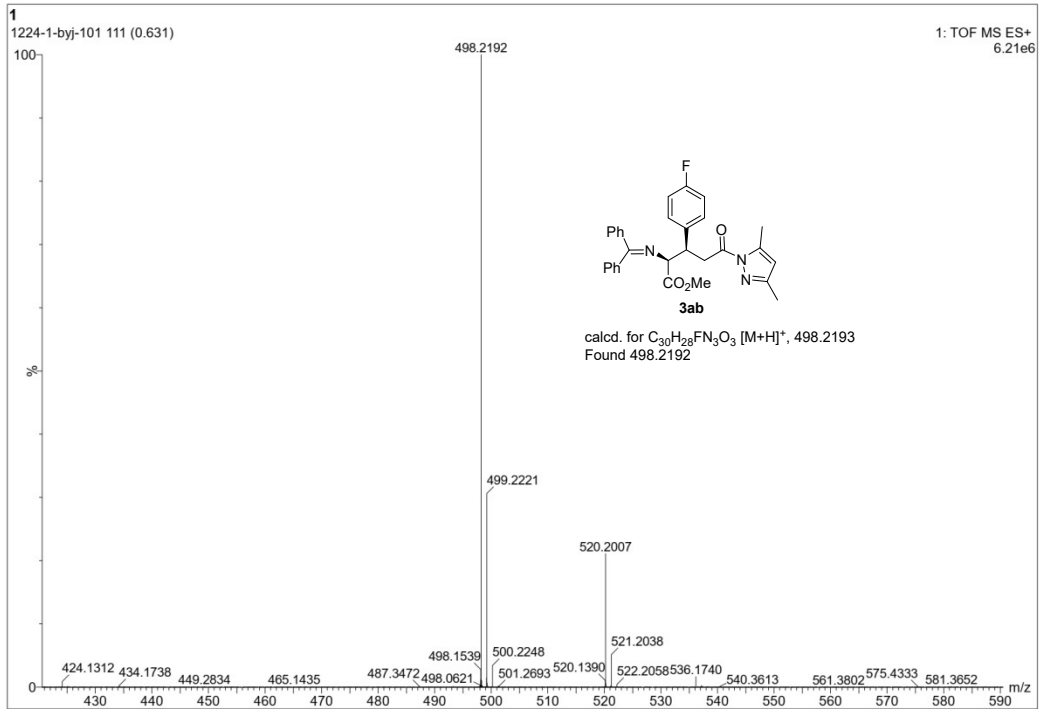
C: 30-31 H: 0-32 N: 0-6 O: 0-20 Br: 0-8 Mo: 0-1



Minimum: -1.5

Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
480.2285	480.2287	-0.2	-0.4	17.5	896.5	n/a	n/a	C ₃₀ H ₃₀ N ₃ O ₃



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

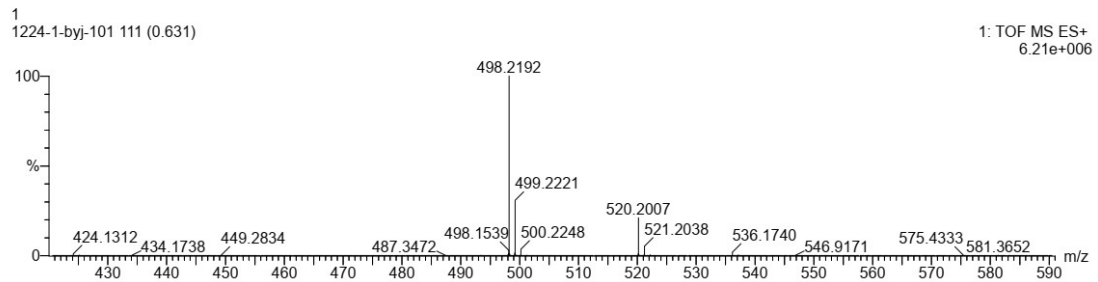
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

2501 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

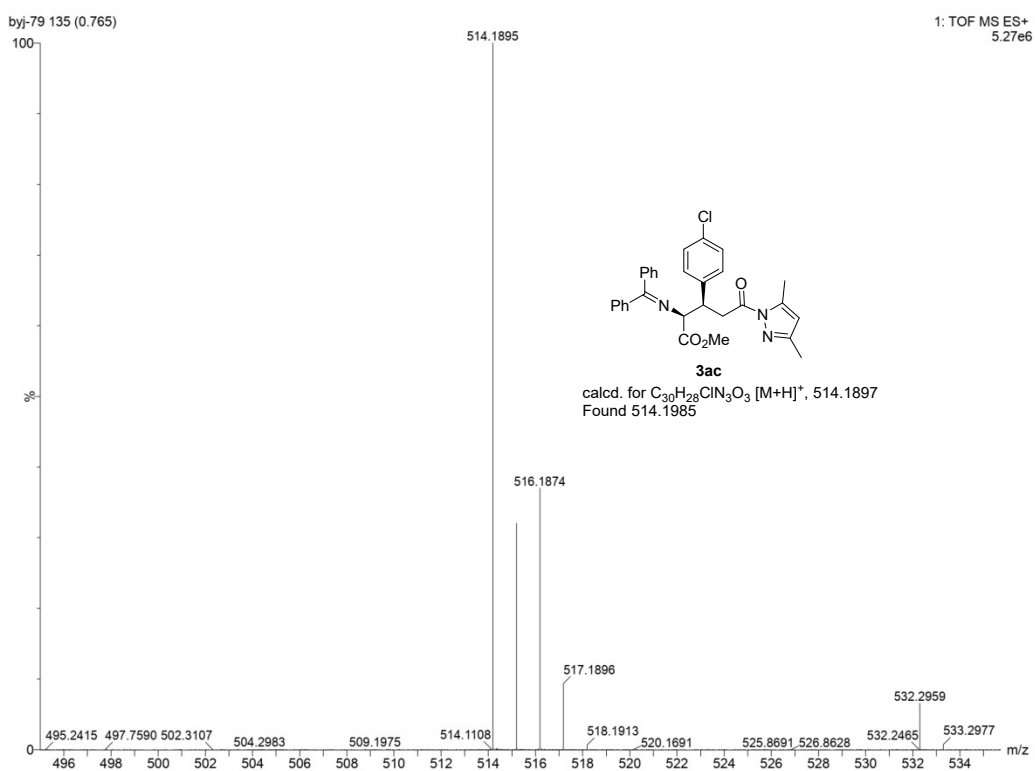
Elements Used:

C: 30-30 H: 29-29 N: 0-6 O: 0-20 S: 0-4 Mo: 0-1 F: 0-1



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
498.2192	498.2193	-0.1	-0.2	17.5	973.0	n/a	n/a	C30 H29 N3 O3 F



Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

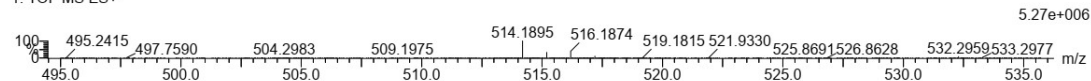
15 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 20-30 H: 0-50 N: 3-6 O: 3-3 Cl: 1-1

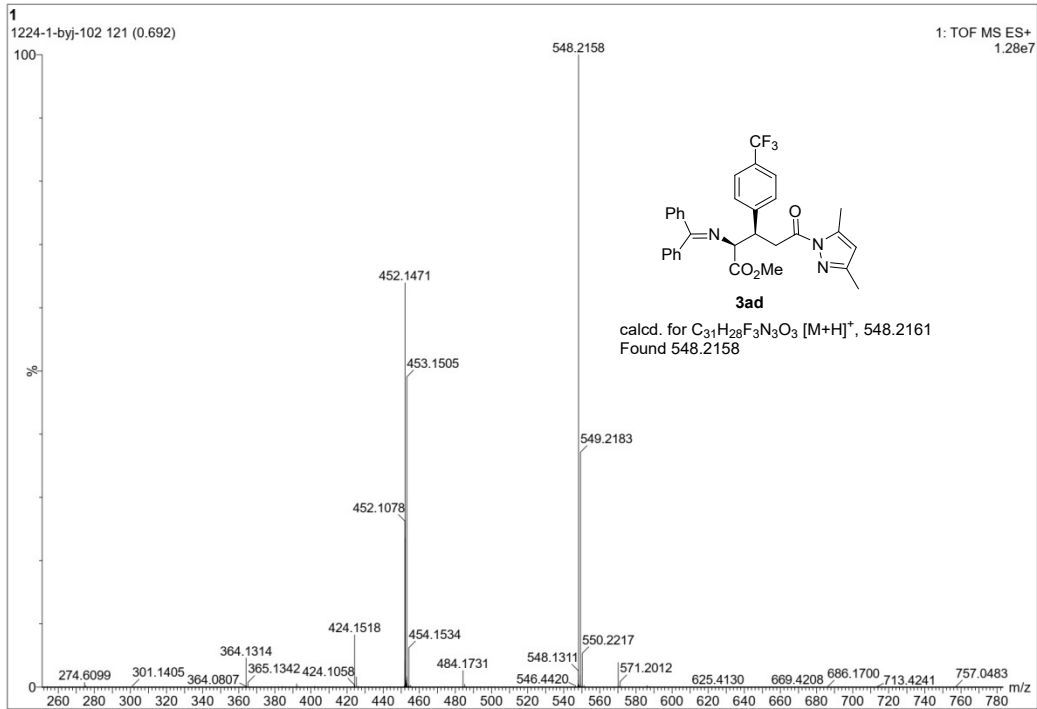
byj-79 135 (0.765)

1: TOF MS ES+



Minimum: -1.5
 Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
514.1895	514.1897	-0.2	-0.4	17.5	887.8	n/a	n/a	C ₃₀ H ₂₉ N ₃ O ₃ Cl



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

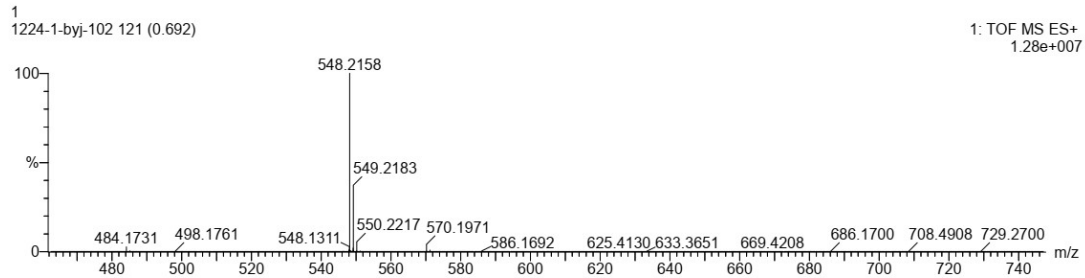
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

6323 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

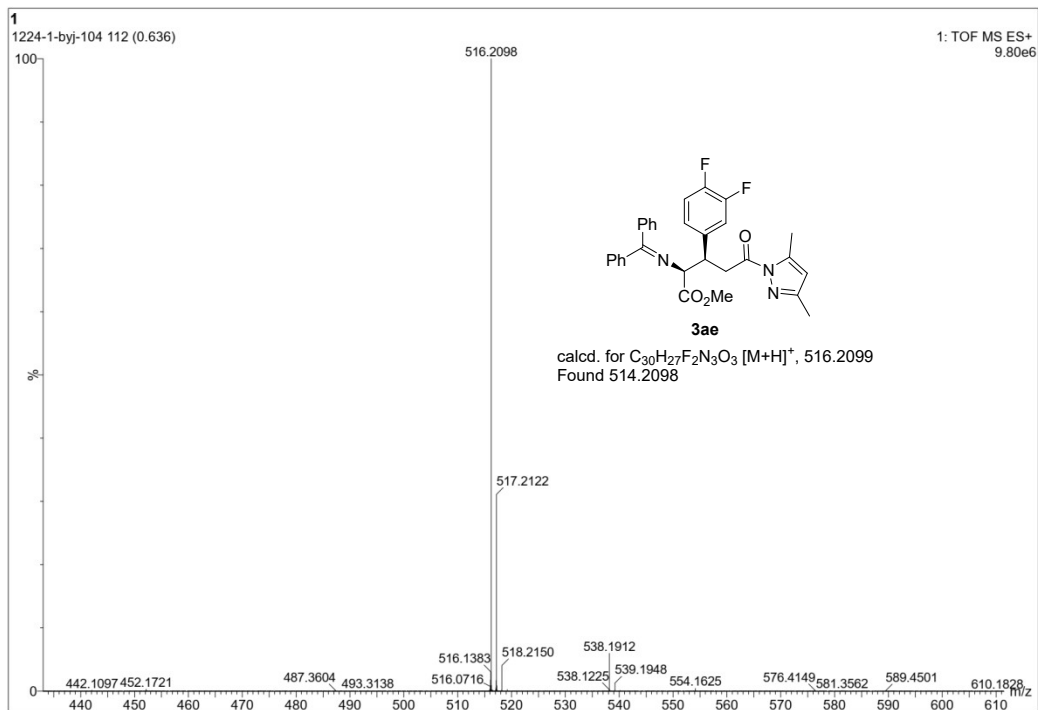
C: 31-31 H: 29-29 N: 0-6 O: 0-20 F: 0-4 S: 0-4 Mo: 0-1



Minimum: 5.0 10.0 -1.5

Maximum: 50.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
548.2158	548.2161	-0.3	-0.5	17.5	1023.3	n/a	n/a	C31 H29 N3 O3 F3



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

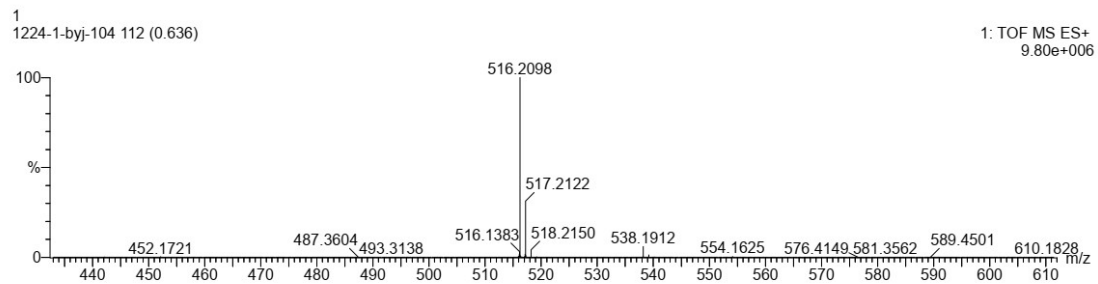
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

26636 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

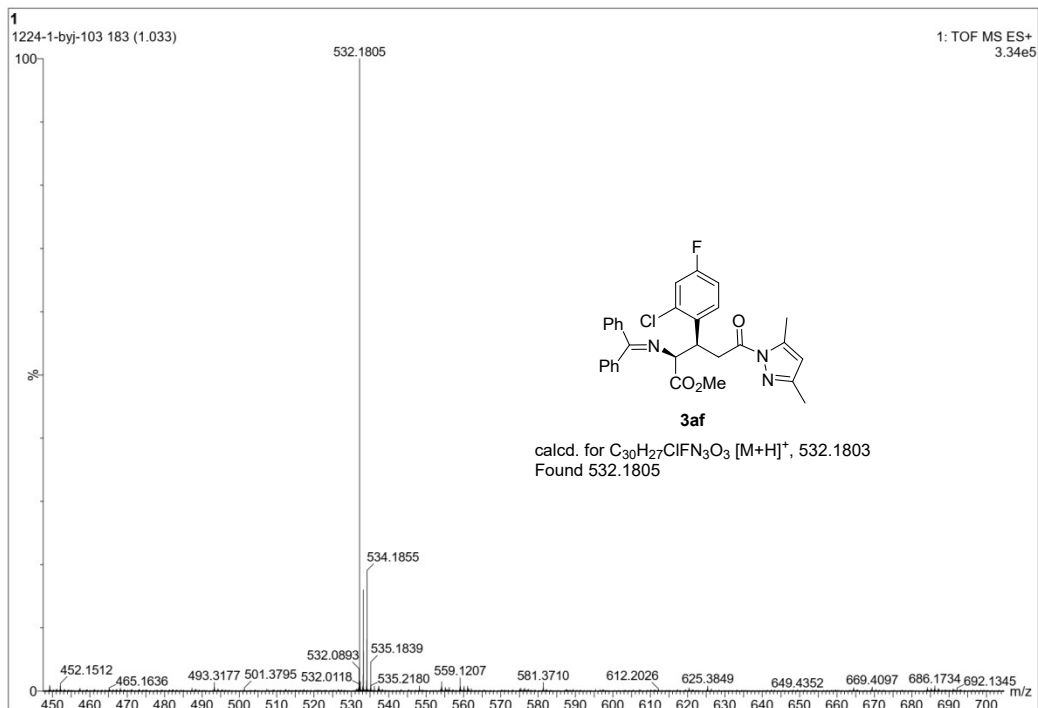
C: 30-30 H: 28-28 N: 0-6 O: 0-20 F: 0-4 S: 0-4 Cl: 0-4 Mo: 0-1



Minimum: -1.5

Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
516.2098	516.2099	-0.1	-0.2	17.5	1115.3	n/a	n/a	C ₃₀ H ₂₈ N ₃ O ₃ F ₂



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

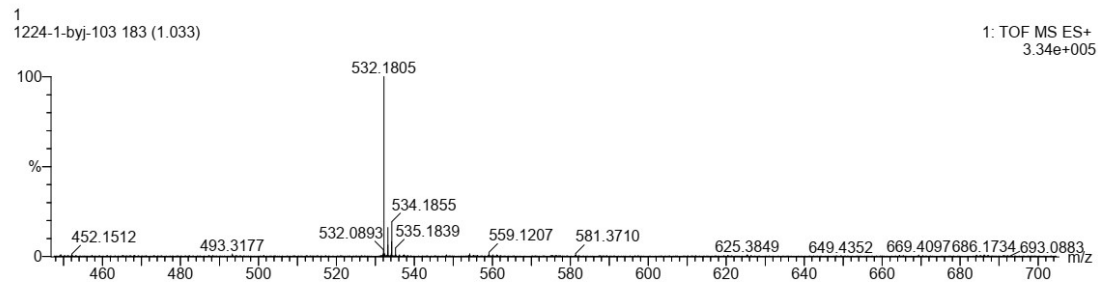
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

27669 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

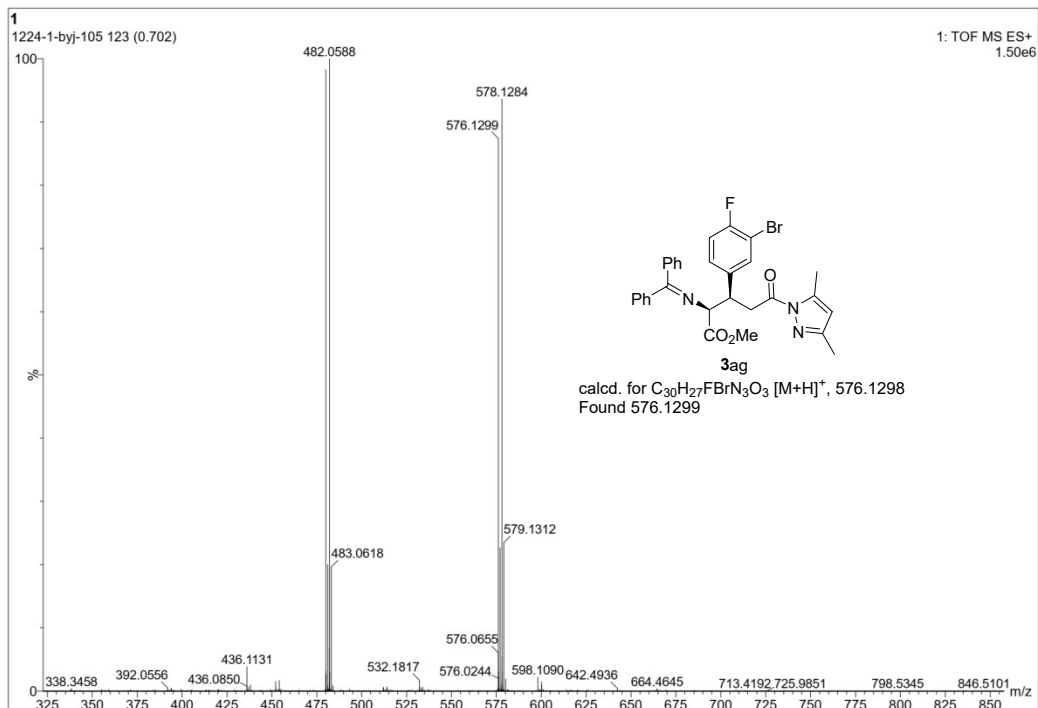
Elements Used:

C: 30-30 H: 28-28 N: 0-6 O: 0-20 F: 0-4 S: 0-4 Cl: 0-4 Mo: 0-1



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
532.1805	532.1803	0.2	0.4	17.5	846.7	n/a	n/a	C ₃₀ H ₂₈ N ₃ O ₃ FCl



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

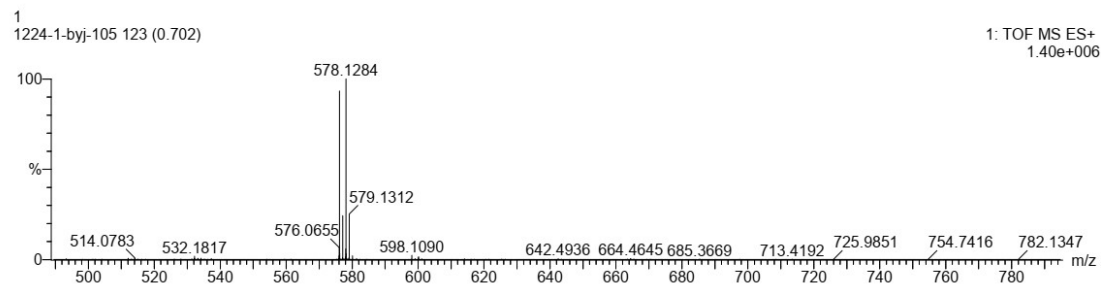
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

23180 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

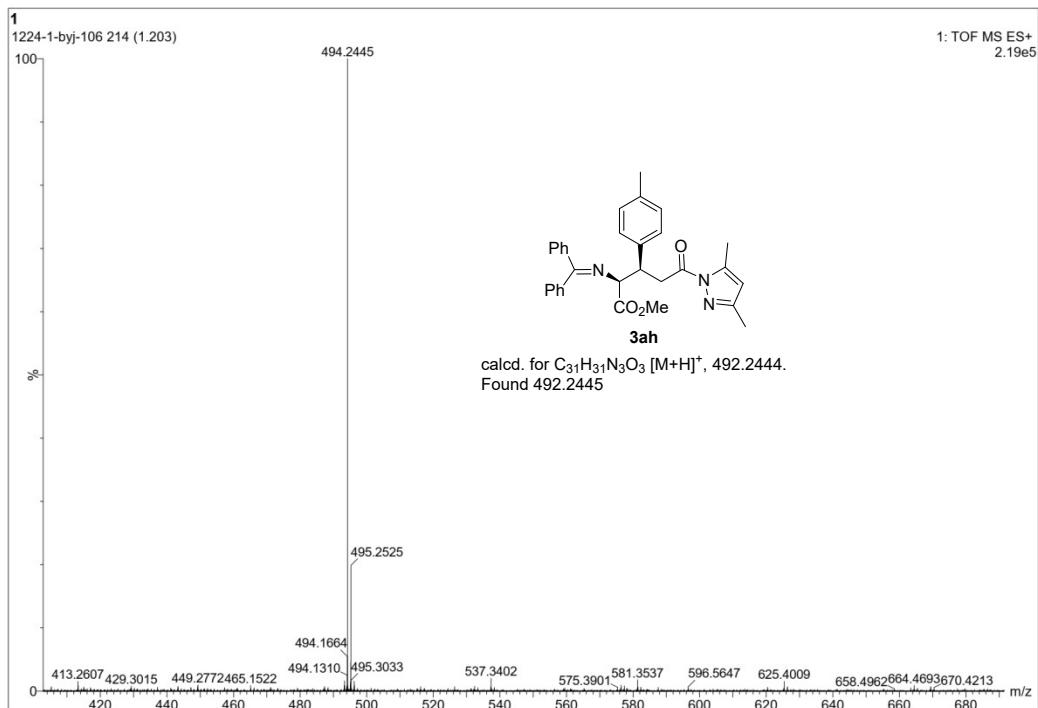
Elements Used:

C: 30-30 H: 28-28 N: 0-6 O: 0-20 F: 0-4 S: 0-4 Br: 0-8 Mo: 0-1



Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
576.1299	576.1298	0.1	0.2	17.5	961.7	n/a	n/a	C ₃₀ H ₂₈ N ₃ O ₃ F Br



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

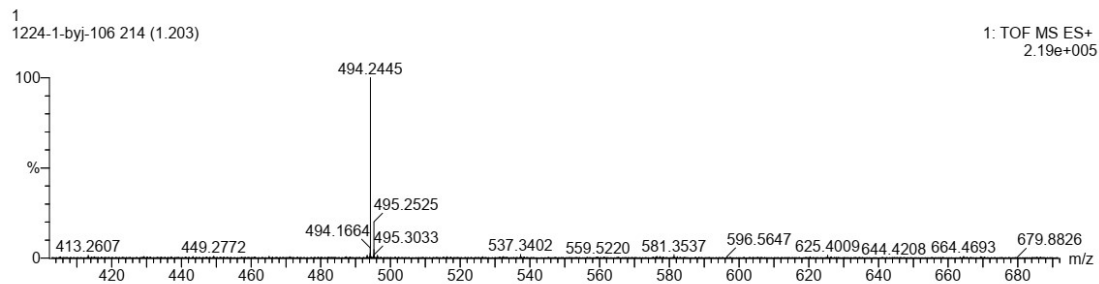
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1032 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

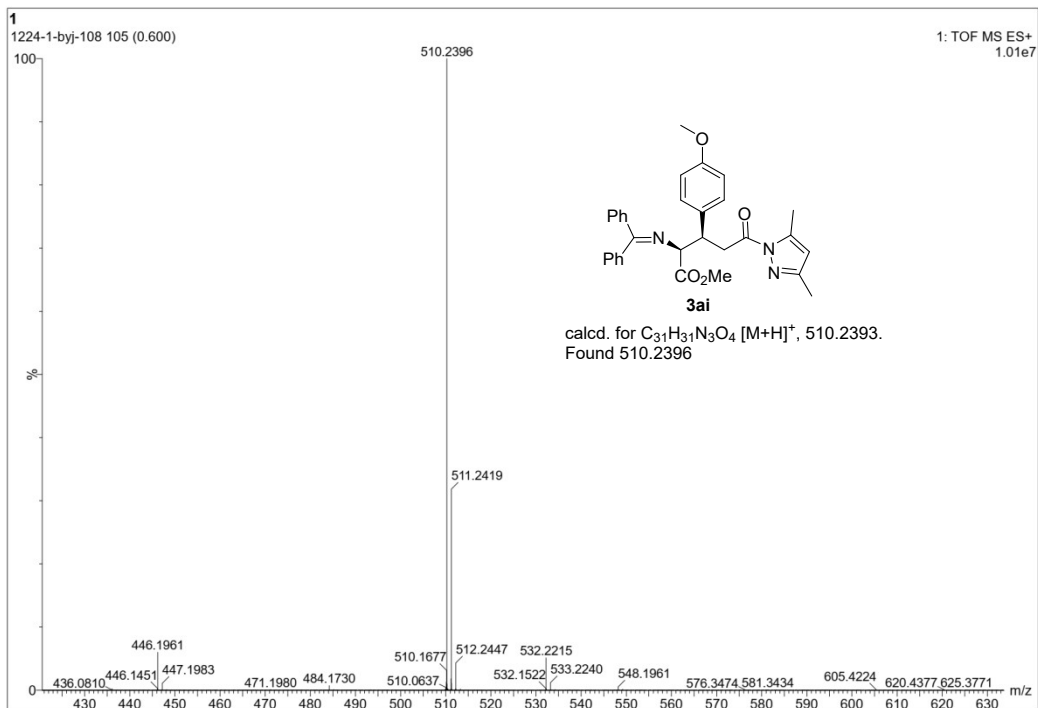
C: 31-31 H: 0-32 N: 0-6 O: 0-20 Br: 0-8 Mo: 0-1



Minimum: -1.5

Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
494.2445	494.2444	0.1	0.2	17.5	880.5	n/a	n/a	C ₃₁ H ₃₂ N ₃ O ₃



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

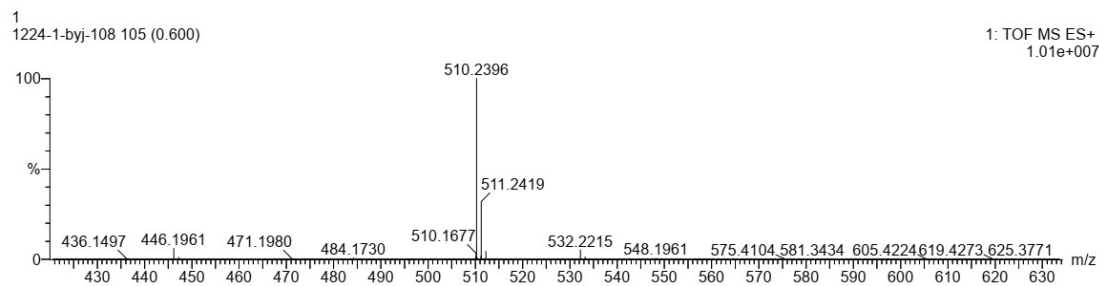
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1107 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

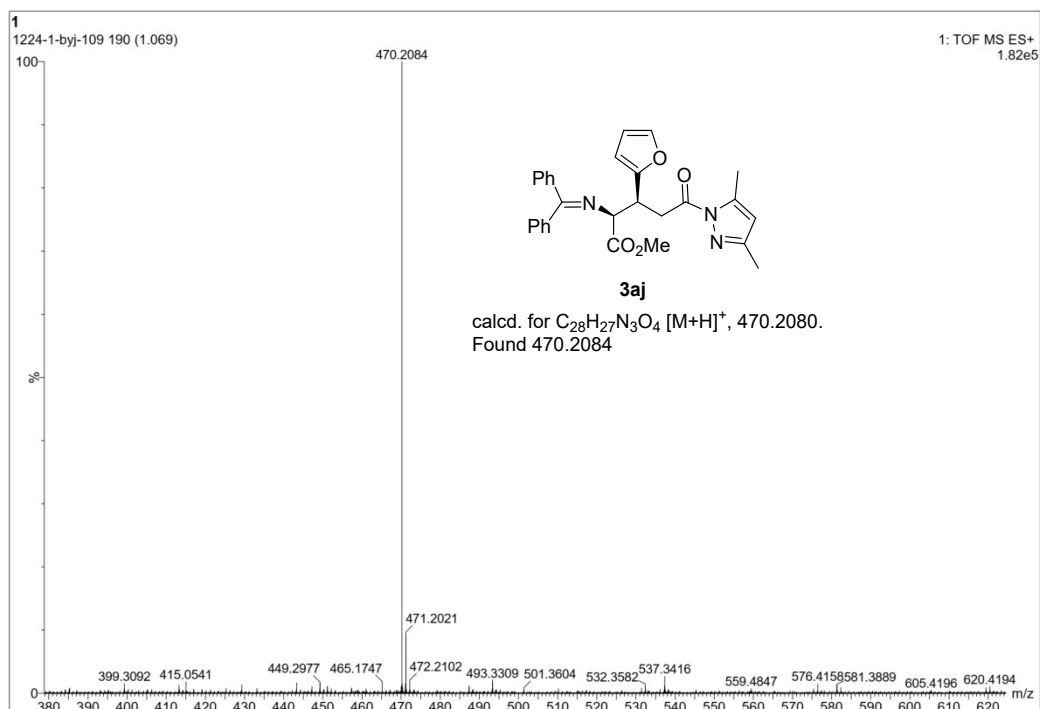
Elements Used:

C: 30-31 H: 0-32 N: 0-6 O: 0-20 Br: 0-8 Mo: 0-1



Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
510.2396	510.2393	0.3	0.6	17.5	1092.0	n/a	n/a	C ₃₁ H ₃₂ N ₃ O ₄



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

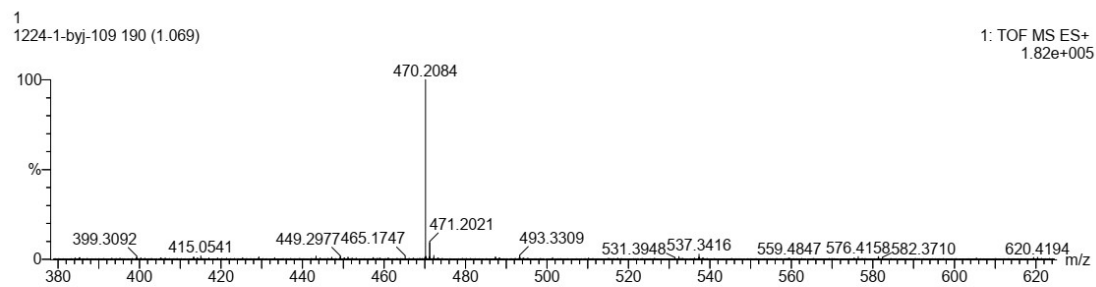
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

938 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

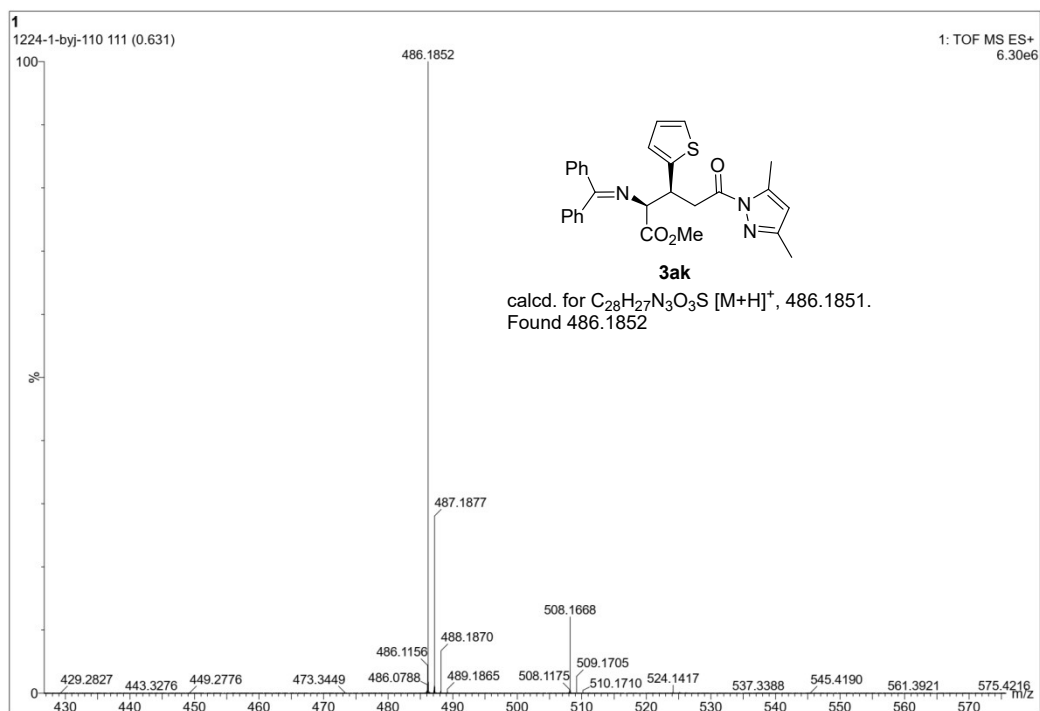
C: 28-28 H: 0-32 N: 0-6 O: 0-20 Br: 0-8 Mo: 0-1



Minimum: -1.5

Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
470.2084	470.2080	0.4	0.9	16.5	809.0	n/a	n/a	C ₂₈ H ₂₈ N ₃ O ₄



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

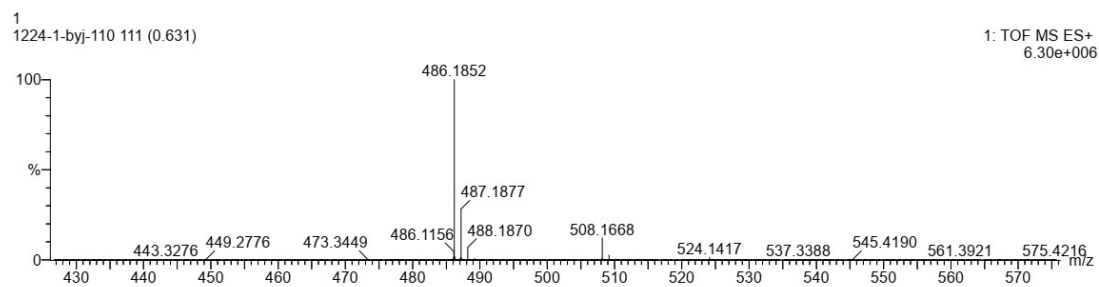
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

3872 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

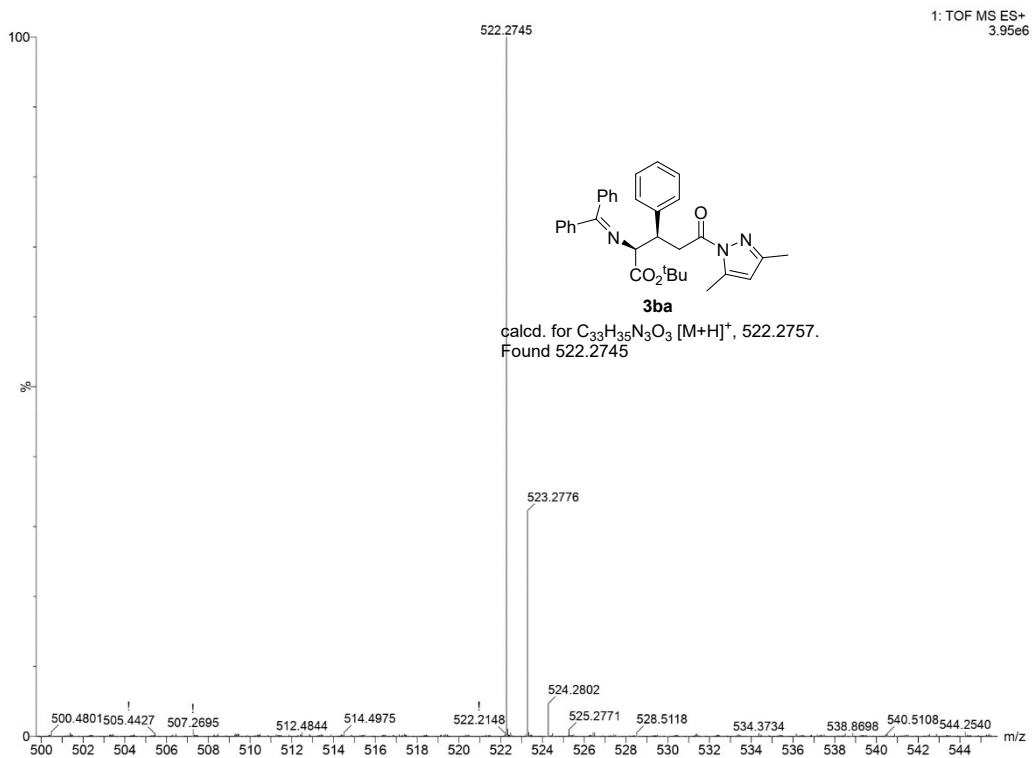
Elements Used:

C: 28-28 H: 0-32 N: 0-6 O: 0-20 S: 0-4 Br: 0-8 Mo: 0-1



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
486.1852	486.1851	0.1	0.2	16.5	1115.6	n/a	n/a	C ₂₈ H ₂₈ N ₃ O ₃ S



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

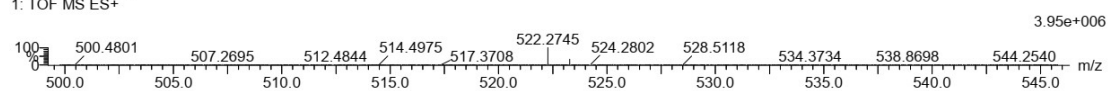
140 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 33-33 H: 0-50 N: 0-8 O: 0-8 Na: 0-1

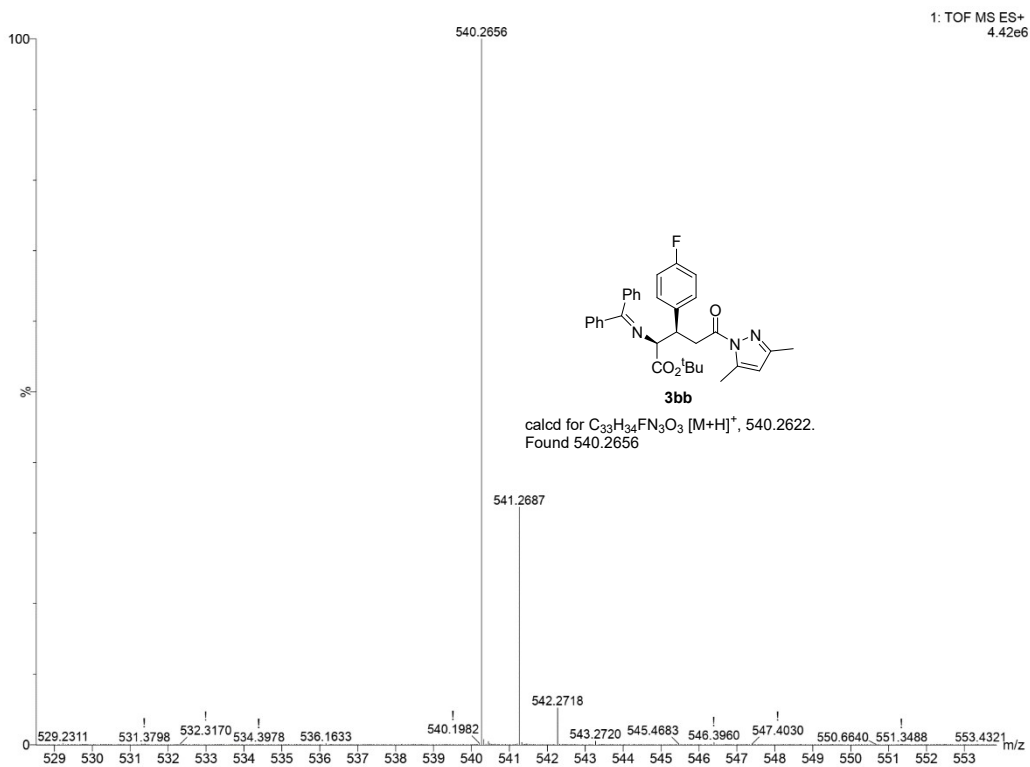
BYJ-1 362 (3.291)

1: TOF MS ES+



Minimum: -1.5
Maximum: 20.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
522.2745	522.2757	-1.2	-2.3	17.5	1012.7	n/a	n/a	C33 H36 N3 O3



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

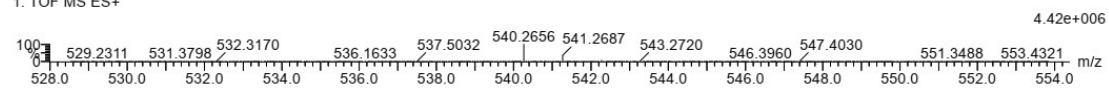
54 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 31-31 H: 0-50 N: 0-5 O: 0-5 Na: 0-1

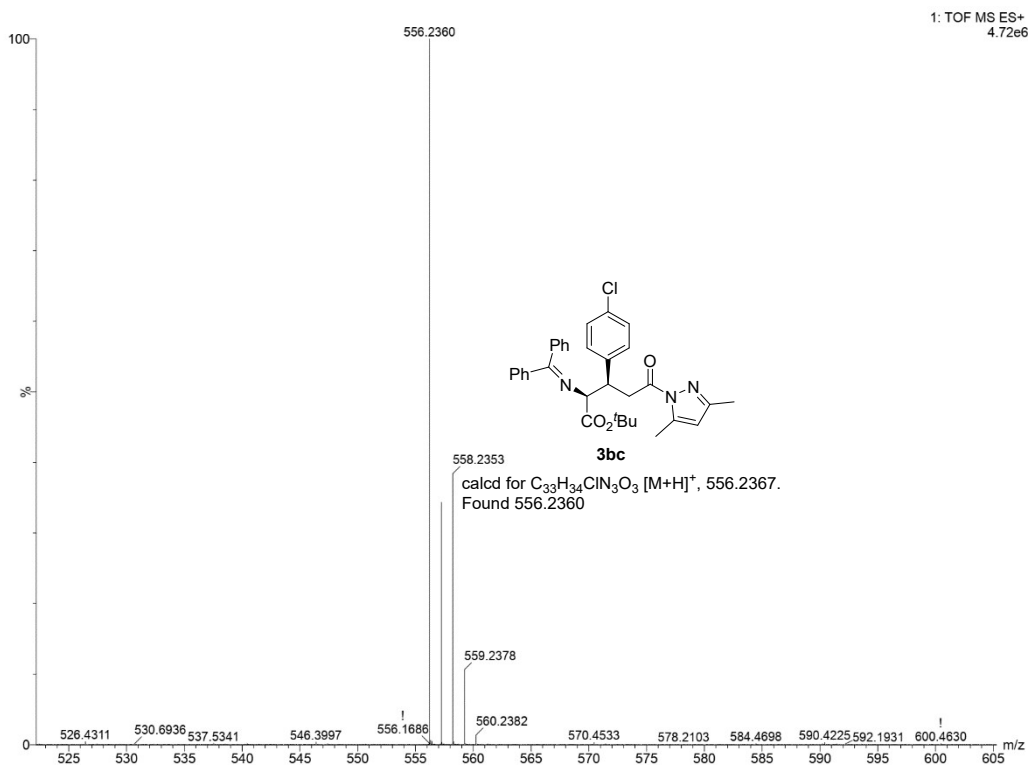
BYJ-7 210 (1.174)

1: TOF MS ES+



Minimum: -1.5
Maximum: 20.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
540.2656	540.2611	4.5	8.3	17.5	886.4	n/a	n/a	C31 H34 N5 O4



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

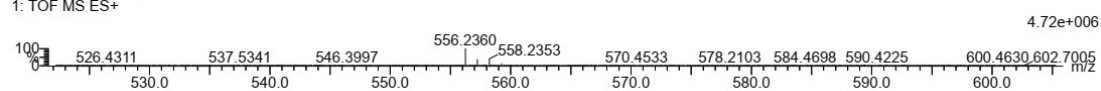
113 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 33-33 H: 0-50 N: 0-5 O: 0-5 Na: 0-1 Cl: 1-2

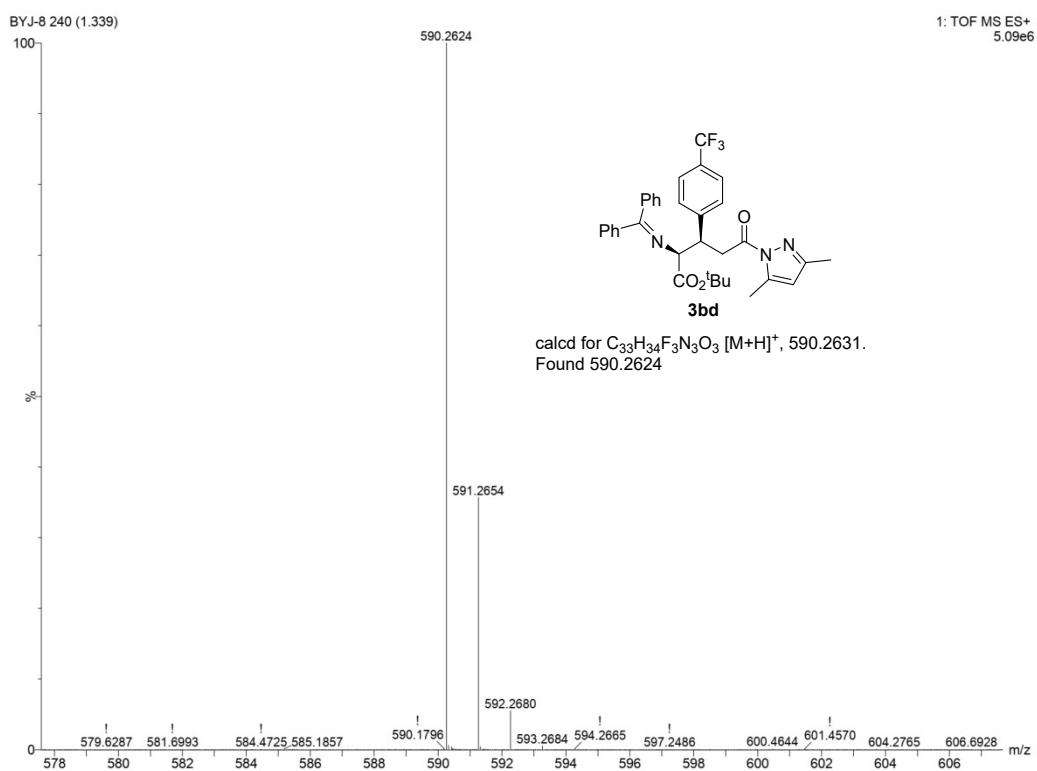
BYJ-10 236 (1.318)

1: TOF MS ES+



Minimum: -1.5
Maximum: 20.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
556.2360	556.2367	-0.7	-1.3	17.5	882.5	n/a	n/a	C33 H35 N3 O3 Cl



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

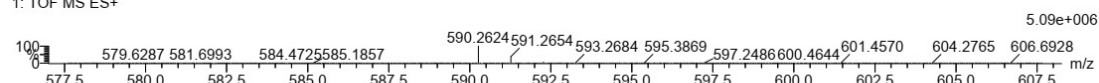
156 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 34-34 H: 0-50 N: 0-5 O: 0-5 Na: 0-1 F: 1-3

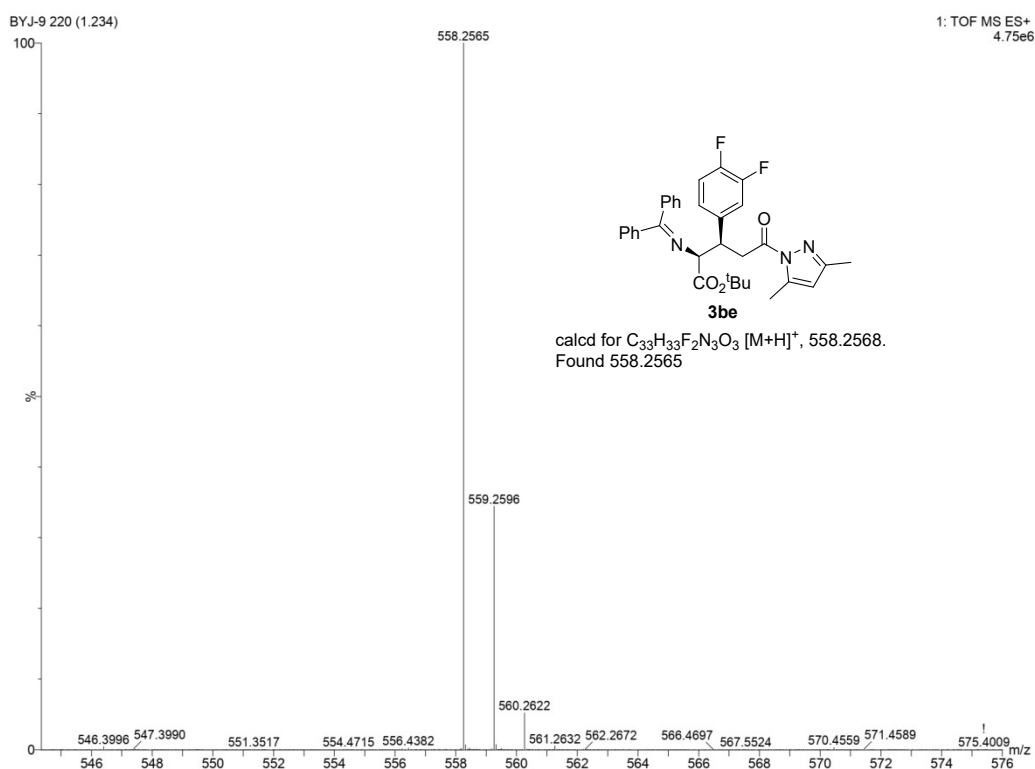
BYJ-8 240 (1.339)

1: TOF MS ES+



Minimum: -1.5
Maximum: 20.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
590.2624	590.2631	-0.7	-1.2	17.5	859.2	n/a	n/a	C ₃₄ H ₃₅ N ₃ O ₃ F ₃



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

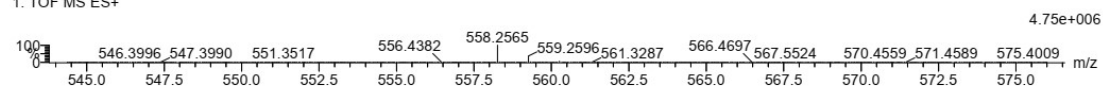
107 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 33-33 H: 0-50 N: 0-5 O: 0-5 F: 1-2 Na: 0-1

BYJ-9 220 (1.234)

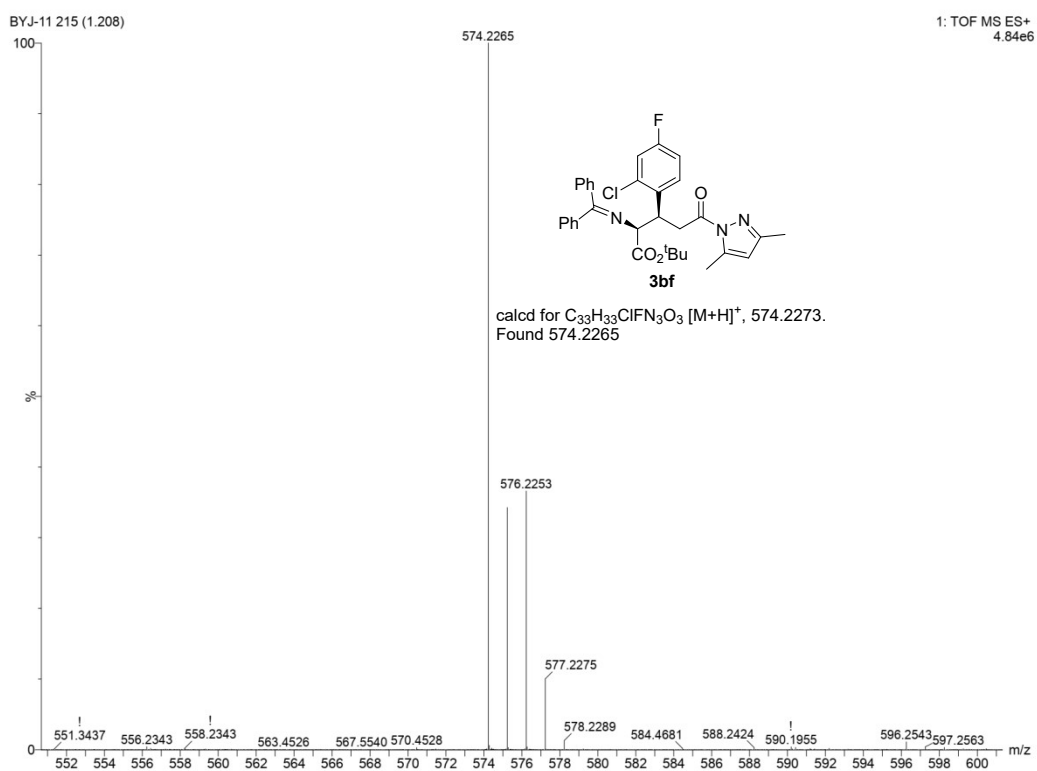
1: TOF MS ES+



Minimum: -1.5

Maximum: 20.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
558.2565	558.2568	-0.3	-0.5	17.5	879.2	n/a	n/a	C33 H34 N3 O3 F2



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

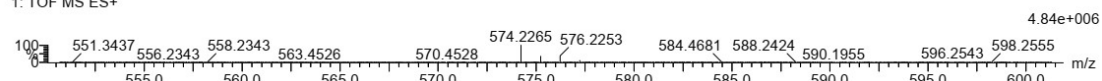
116 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 33-33 H: 0-50 N: 0-5 O: 0-5 Na: 0-1 Cl: 1-2 F: 1-1

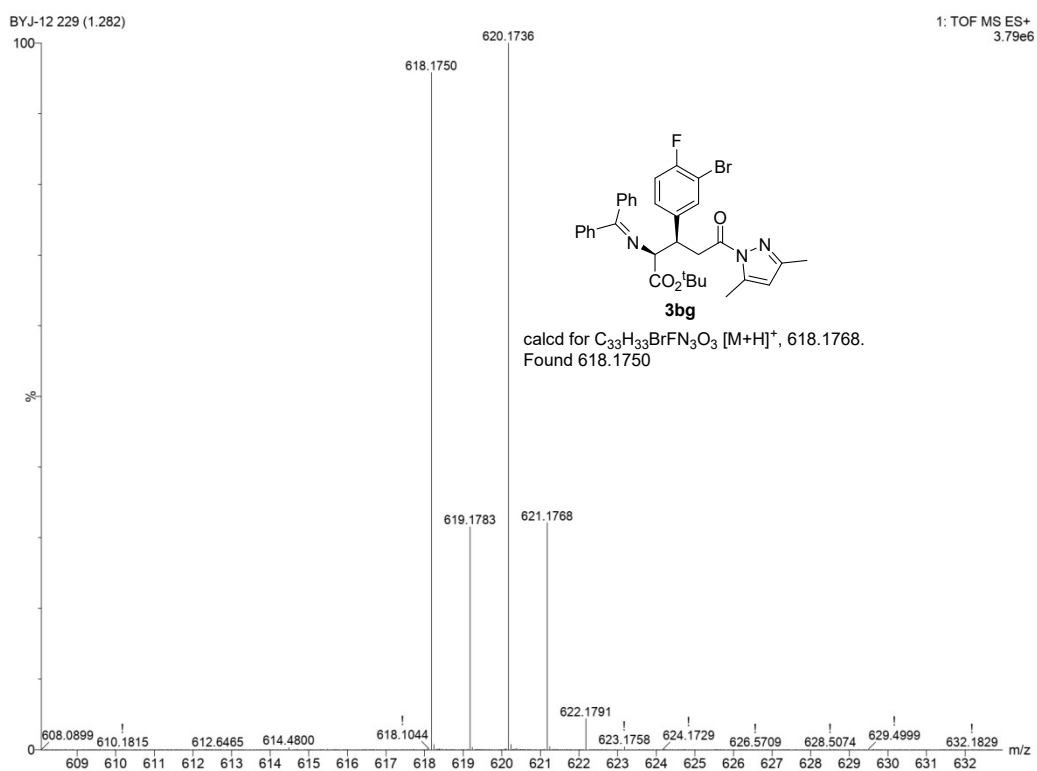
BYJ-11 215 (1.208)

1: TOF MS ES+



Minimum: -1.5
Maximum: 20.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
574.2265	574.2273	-0.8	-1.4	17.5	926.4	n/a	n/a	C ₃₃ H ₃₄ N ₃ O ₃ Cl F



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

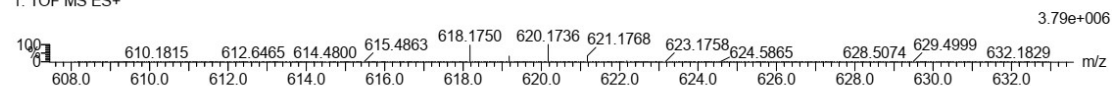
125 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 33-33 H: 0-50 N: 0-5 O: 0-5 F: 1-1 Na: 0-1 Br: 1-2

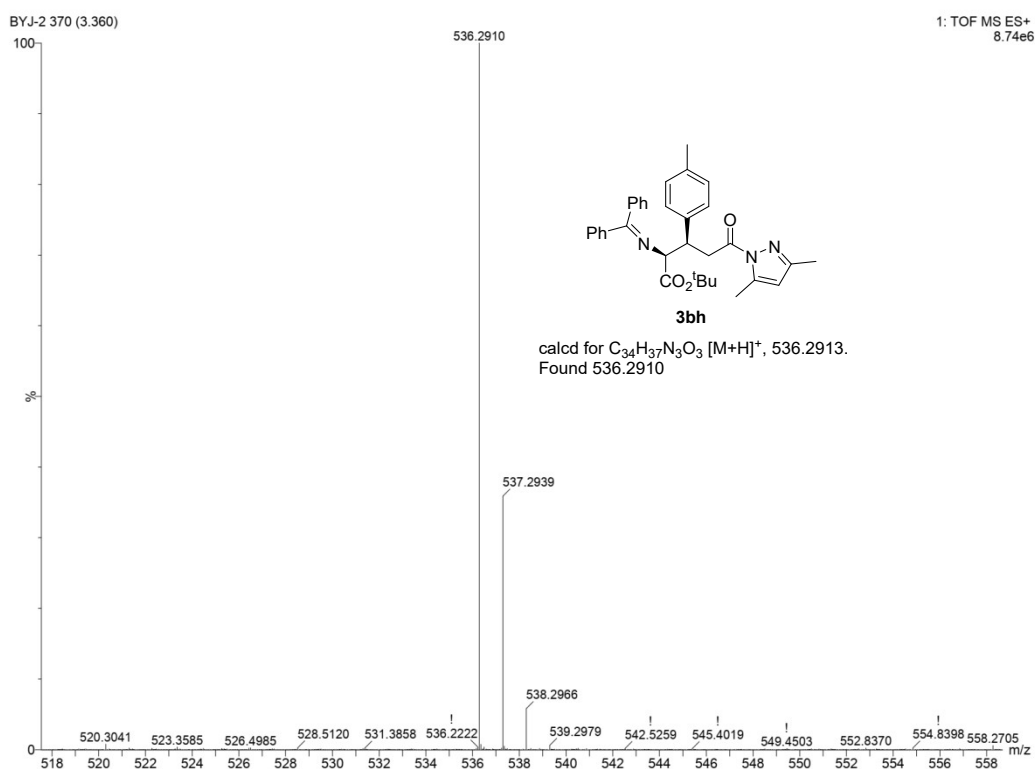
BYJ-12 229 (1.282)

1: TOF MS ES+



Minimum: -1.5
Maximum: 20.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
618.1750	618.1768	-1.8	-2.9	17.5	914.3	n/a	n/a	C ₃₃ H ₃₄ N ₃ O ₃ F Br



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

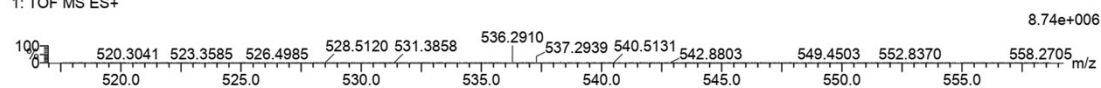
180 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 33-34 H: 0-50 N: 0-8 O: 0-8 Na: 0-1

BYJ-2 370 (3.360)

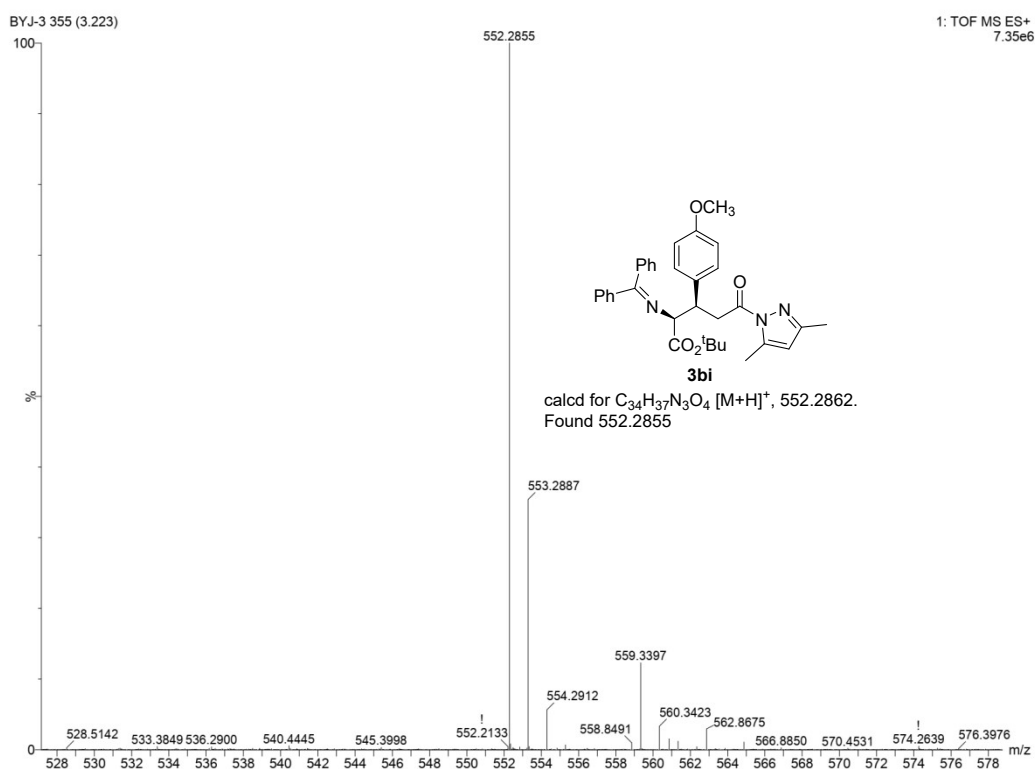
1: TOF MS ES+



Minimum: -1.5

Maximum: 20.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
536.2910	536.2913	-0.3	-0.6	17.5	967.8	n/a	n/a	C ₃₄ H ₃₈ N ₃ O ₃



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

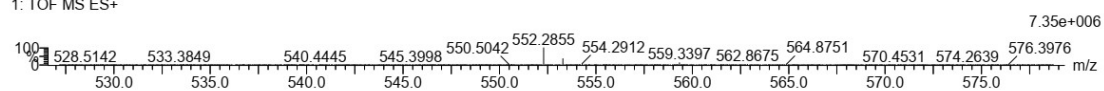
69 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 33-34 H: 0-50 N: 0-5 O: 0-5 Na: 0-1

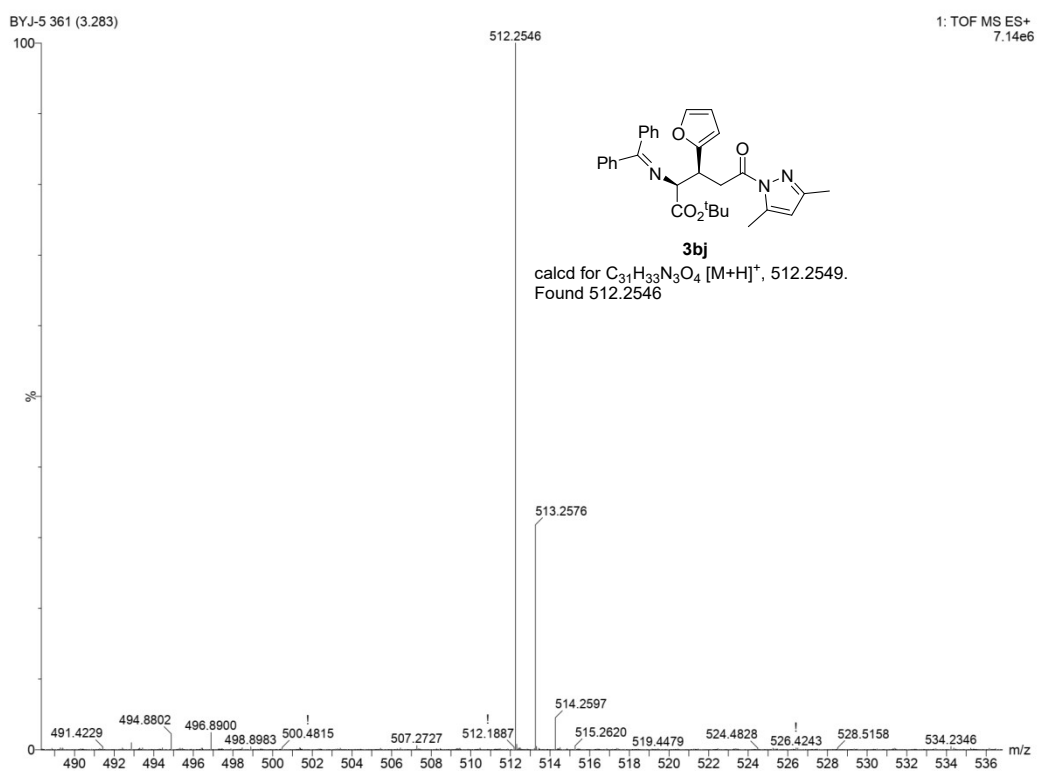
BYJ-3 355 (3.223)

1: TOF MS ES+



Minimum: -1.5
Maximum: 20.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
552.2855	552.2862	-0.7	-1.3	17.5	939.4	n/a	n/a	C ₃₄ H ₃₈ N ₃ O ₄



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

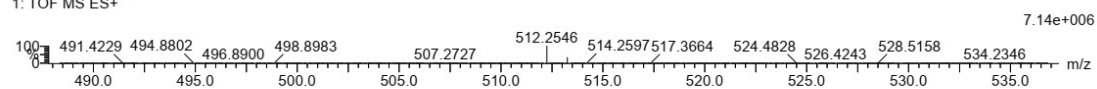
53 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 31-31 H: 0-50 N: 0-5 O: 0-5 Na: 0-1

BYJ-5 361 (3.283)

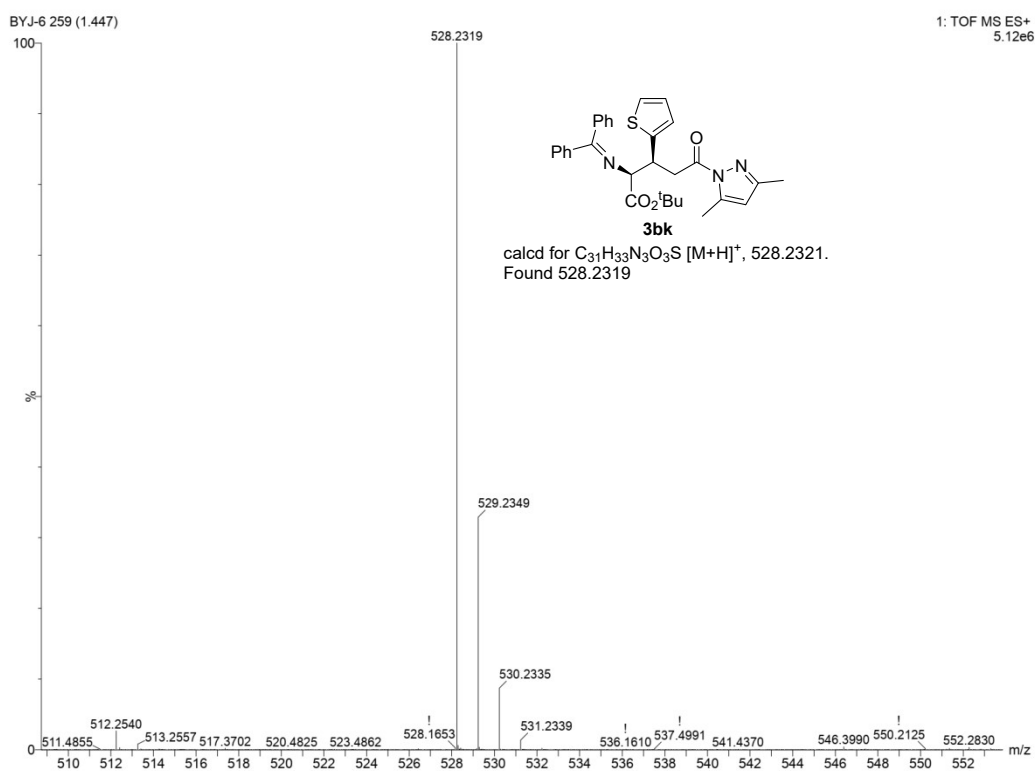
1: TOF MS ES+



Minimum: -1.5

Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
512.2546	512.2549	-0.3	-0.6	16.5	1007.8	n/a	n/a	C ₃₁ H ₃₄ N ₃ O ₄



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

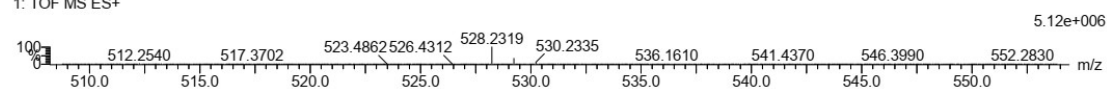
109 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 31-31 H: 0-50 N: 0-5 O: 0-5 Na: 0-1 S: 0-1

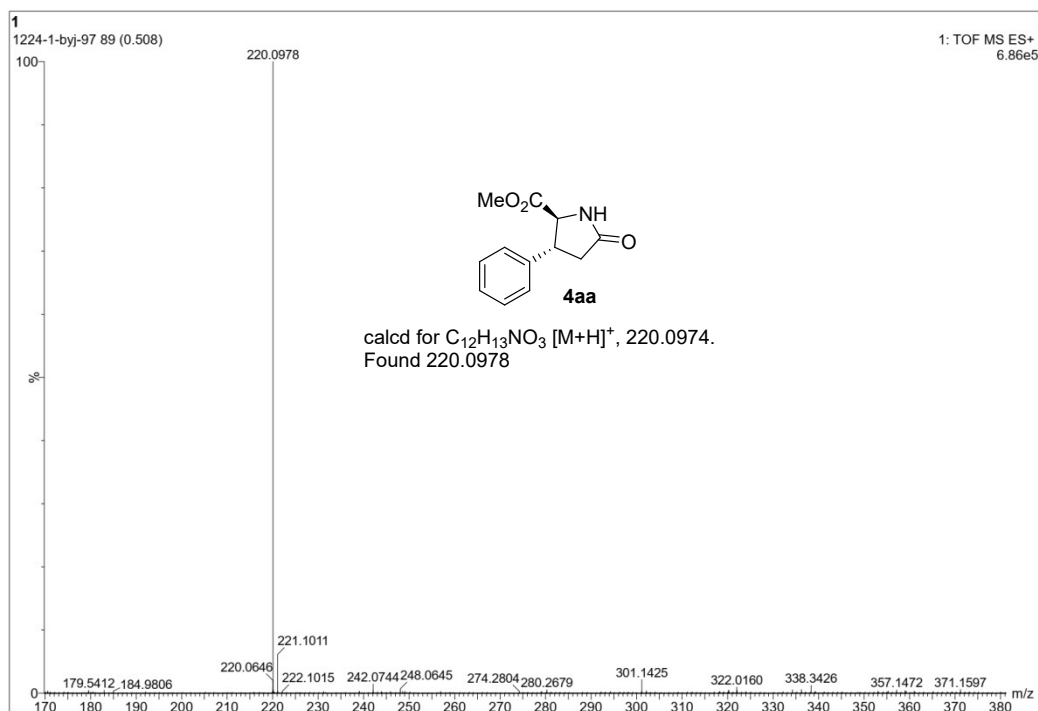
BYJ-6 259 (1.447)

1: TOF MS ES+



Minimum: -1.5
Maximum: 20.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
528, 2319	528, 2321	-0.2	-0.4	16.5	897.8	n/a	n/a	C31 H34 N3 O3 S



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

80 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

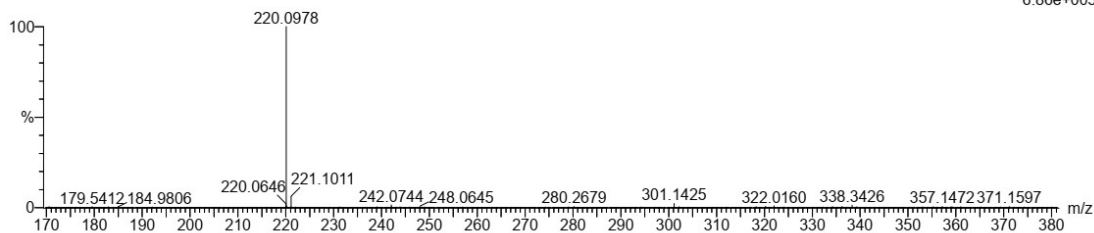
Elements Used:

C: 12-12 H: 0-35 N: 0-6 O: 0-20

1

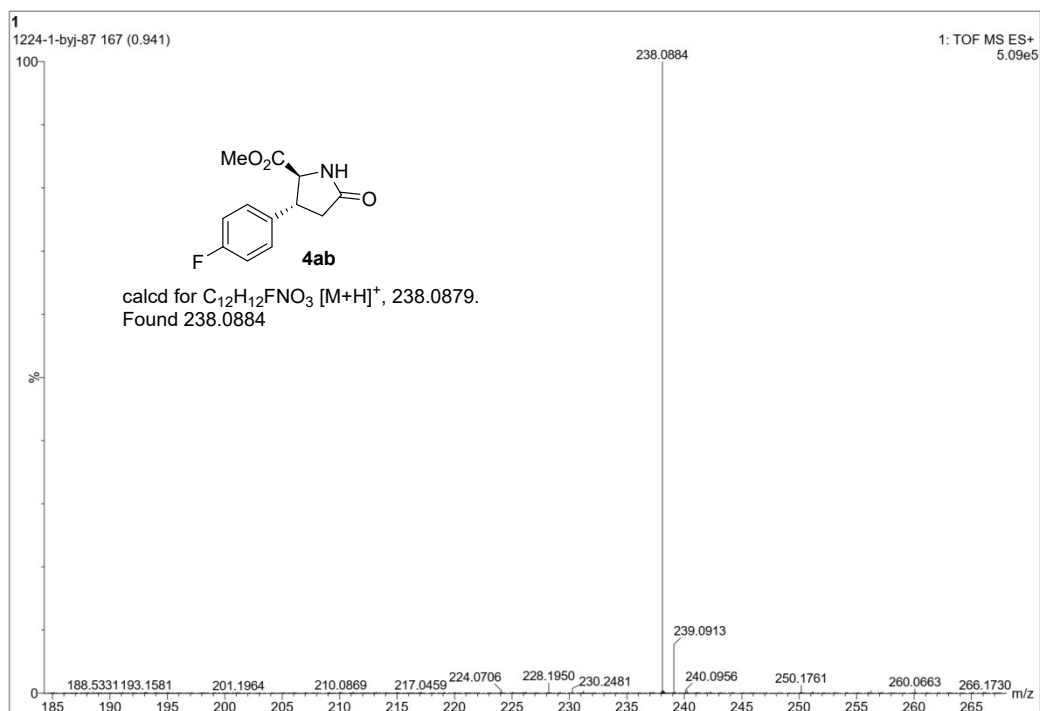
1224-1-byj-97 89 (0.508)

1: TOF MS ES+
6.86e+005



Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
220.0978	220.0974	0.4	1.8	6.5	1190.7	n/a	n/a	C12 H14 N O3



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

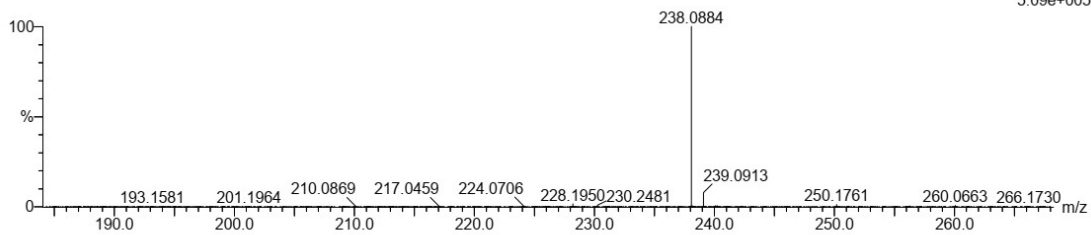
3087 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 12-12 H: 13-13 N: 0-6 O: 0-20 S: 0-4 Cl: 0-4 Mo: 0-1 F: 0-4

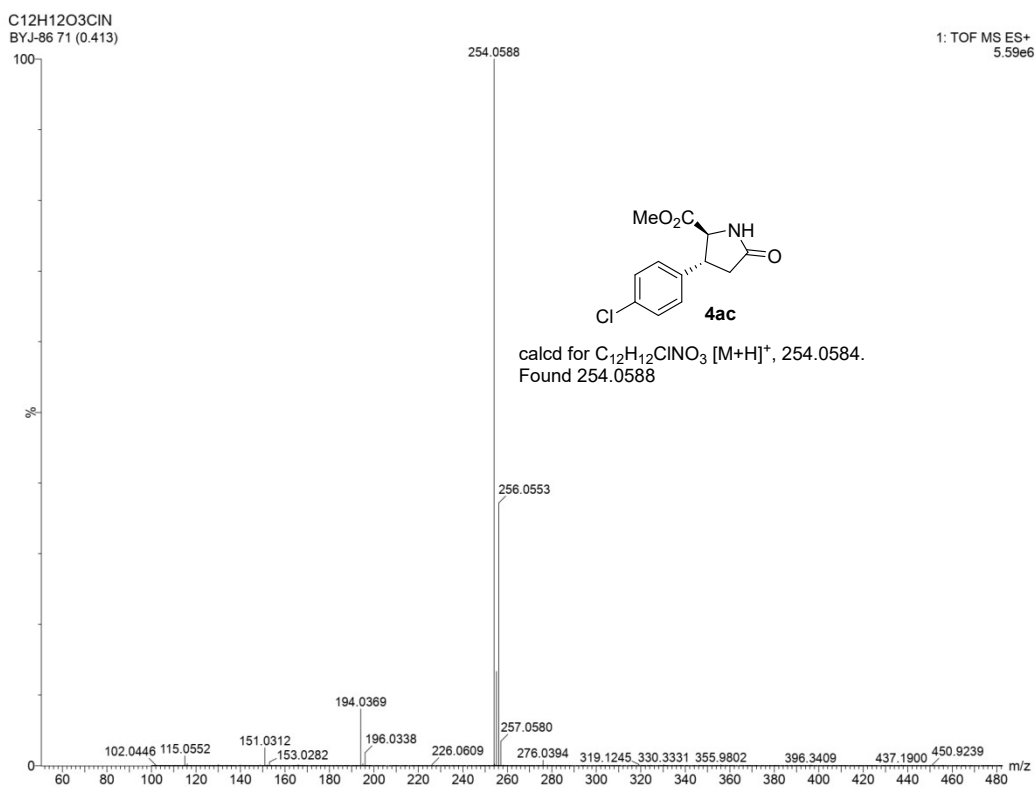
1
1224-1-byj-87 167 (0.941)

1: TOF MS ES+
5.09e+005



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
238.0884	238.0879	0.5	2.1	6.5	844.2	n/a	n/a	C12 H13 N O3 F



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

147 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

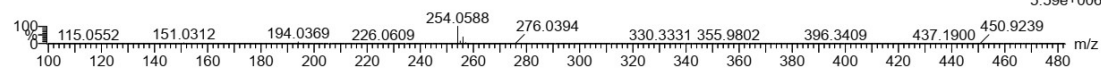
Elements Used:

C: 12-12 H: 0-75 N: 0-6 O: 0-12 Si: 0-1 Cl: 1-1

C₁₂H₁₂O₃ClN

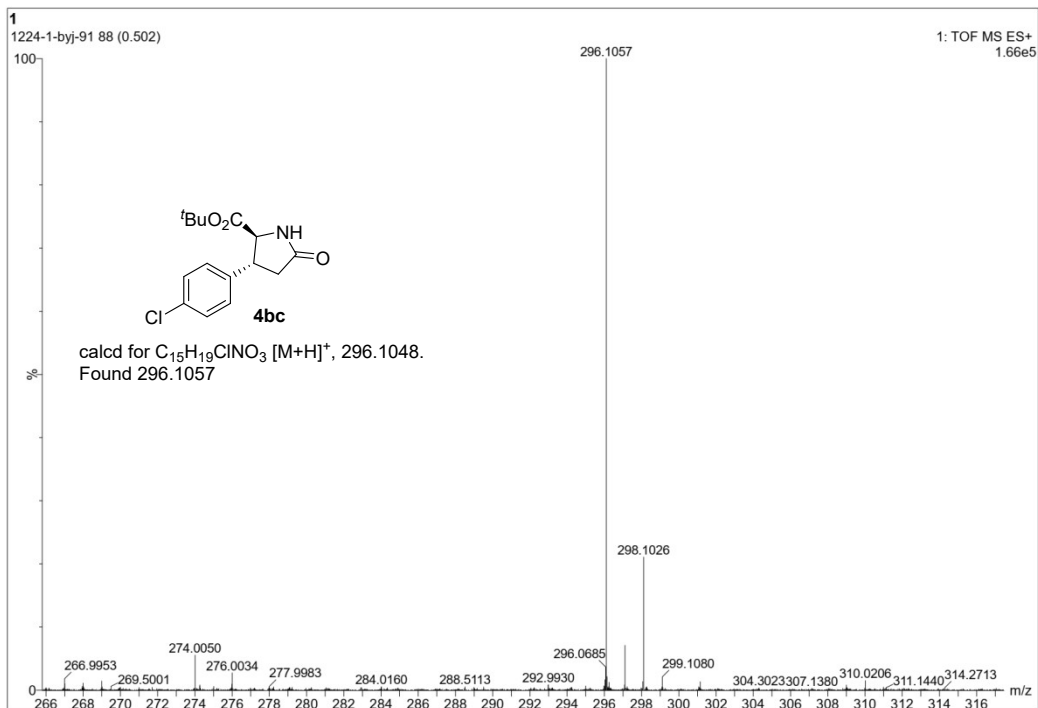
BYJ-86 71 (0.413)

1: TOF MS ES+
5.59e+006



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
254.0588	254.0584	0.4	1.6	6.5	1187.6	n/a	n/a	C12 H13 N O3 Cl



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

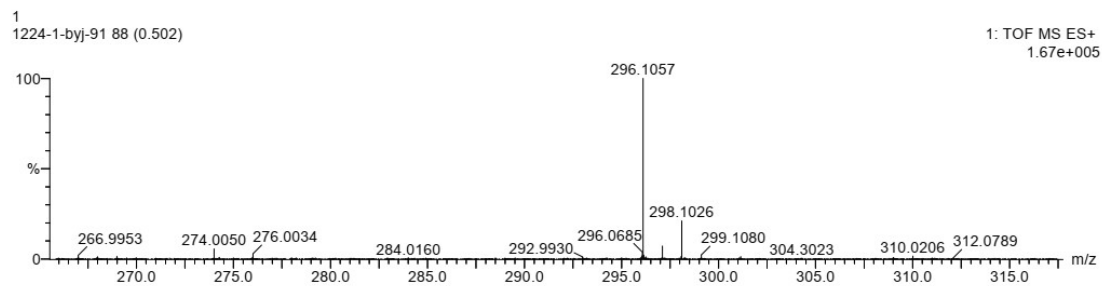
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

6597 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

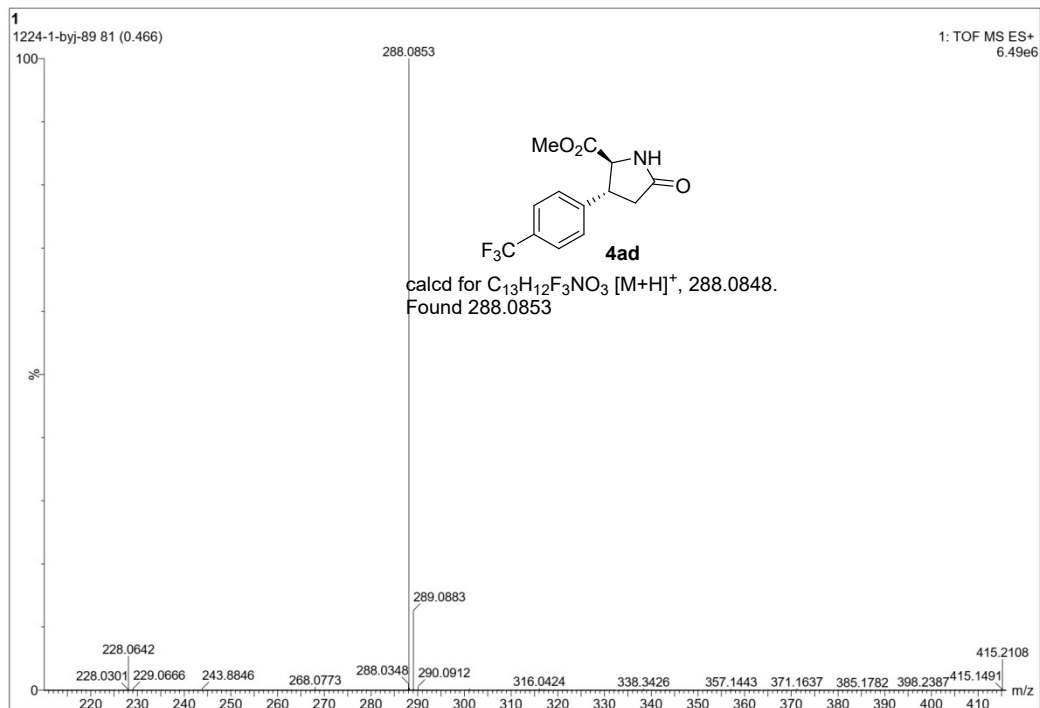
Elements Used:

C: 15-15 H: 0-20 N: 0-6 O: 0-20 F: 0-4 S: 0-4 Cl: 0-4 Mo: 0-1



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
296.1057	296.1053	0.4	1.4	6.5	949.3	n/a	n/a	C ₁₅ H ₁₉ N O ₃ Cl



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

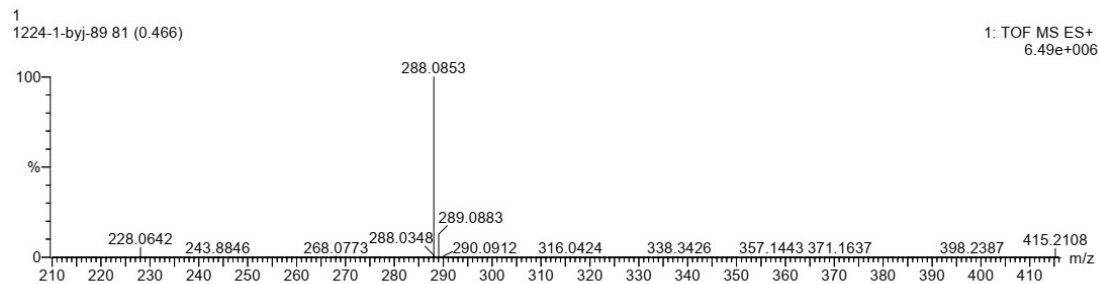
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

5786 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

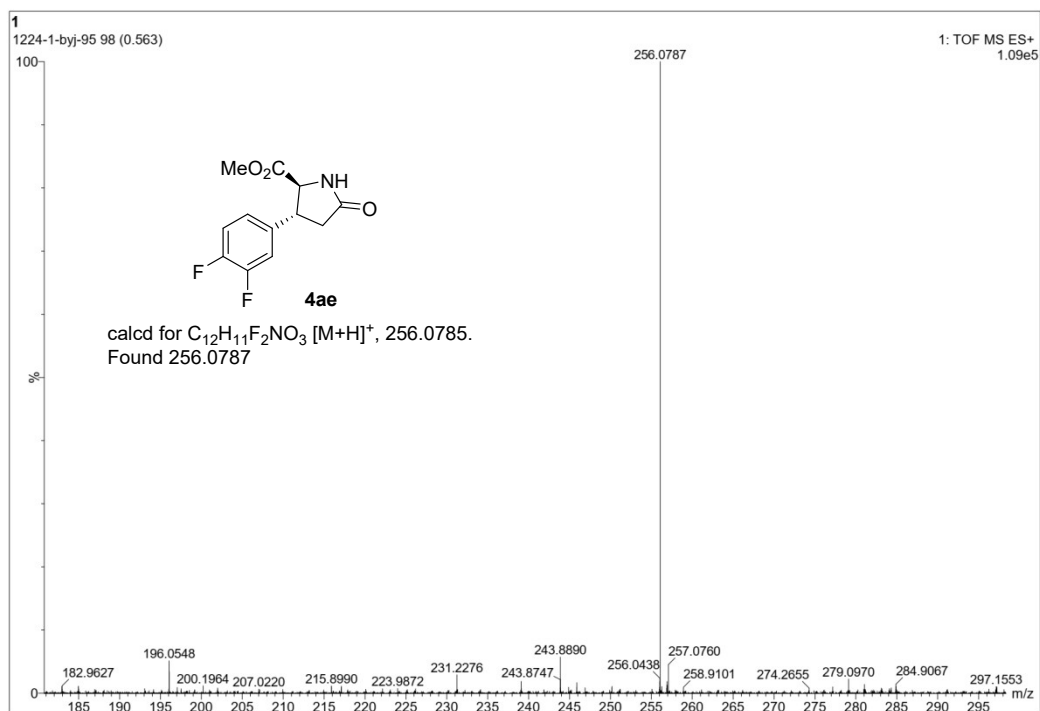
Elements Used:

C: 13-13 H: 13-13 N: 0-6 O: 0-20 F: 0-4 S: 0-4 Cl: 0-4 Mo: 0-1



Minimum: -1.5
 Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
288.0853	288.0848	0.5	1.7	6.5	1329.7	n/a	n/a	C13 H13 N 03 F3



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

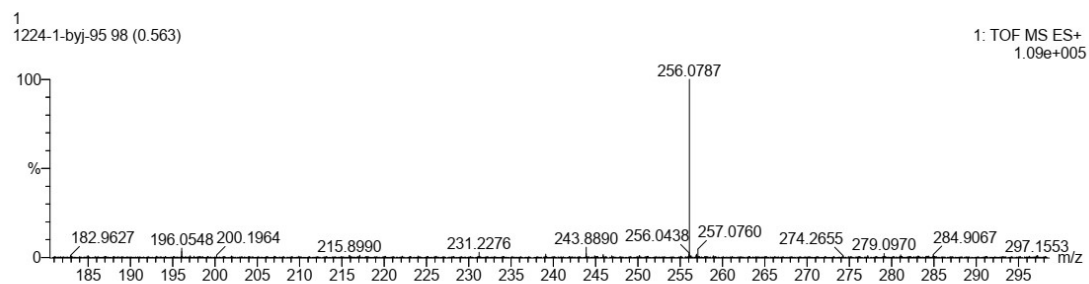
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

3932 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

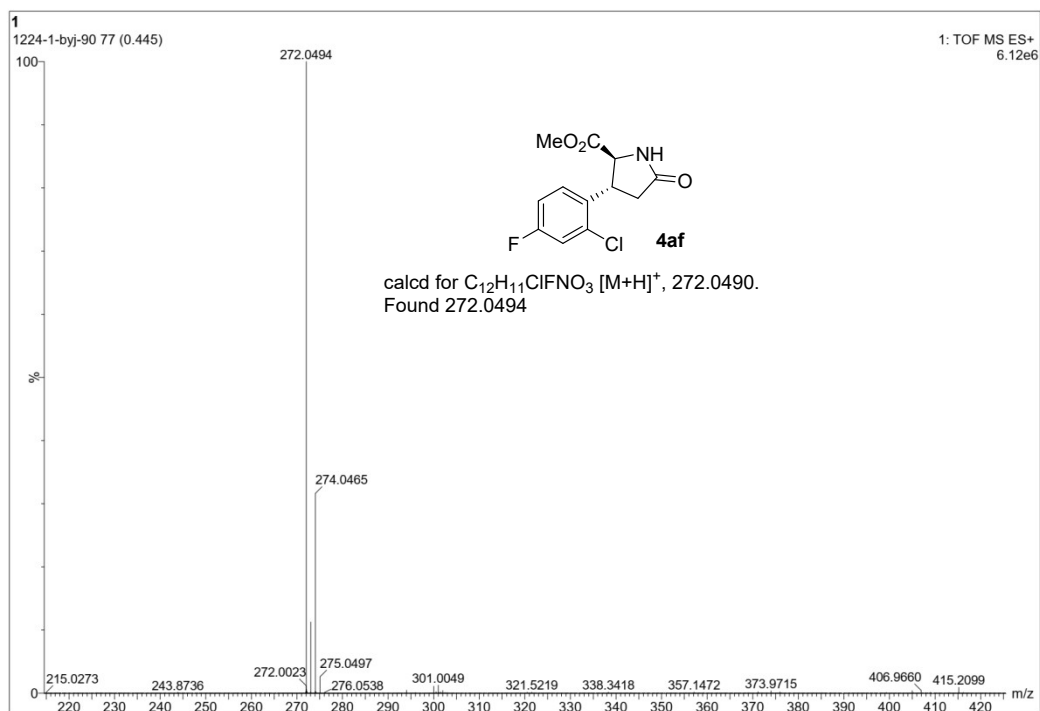
Elements Used:

C: 12-12 H: 12-12 N: 0-6 O: 0-20 S: 0-4 Cl: 0-4 Mo: 0-1 F: 0-4



Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
256.0787	256.0785	0.2	0.8	6.5	794.9	n/a	n/a	C ₁₂ H ₁₂ N ₀₃ F ₂



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

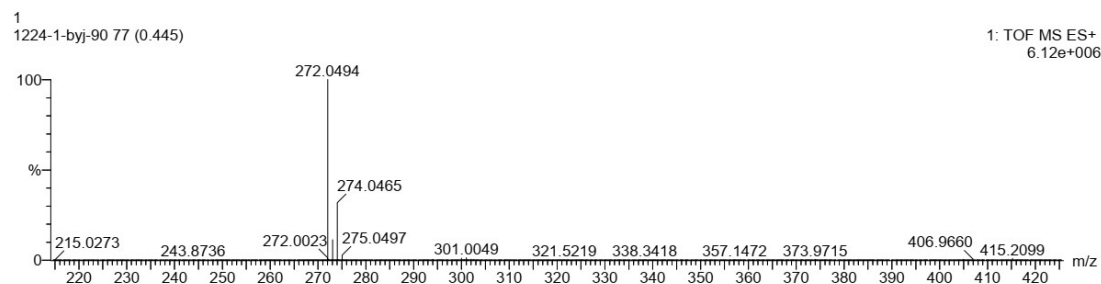
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

4906 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

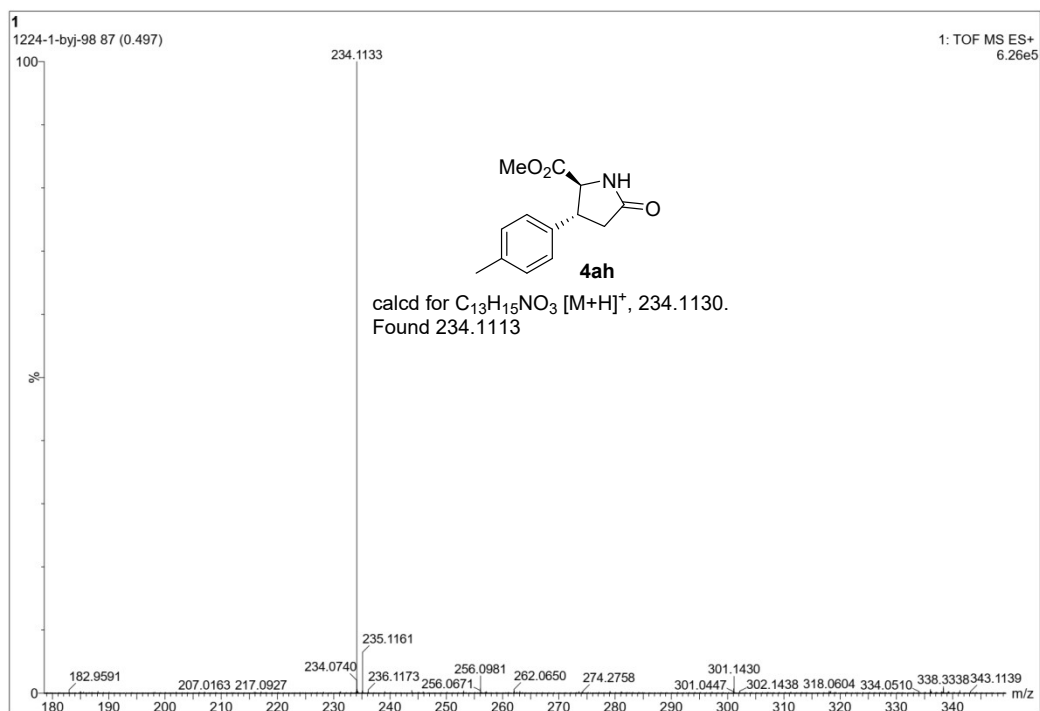
Elements Used:

C: 12-12 H: 0-13 N: 0-6 O: 0-20 F: 0-4 S: 0-4 Cl: 0-4 Mo: 0-1



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
272.0494	272.0490	0.4	1.5	6.5	1514.3	n/a	n/a	C12 H12 N O3 F Cl



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
 Element prediction: Off
 Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

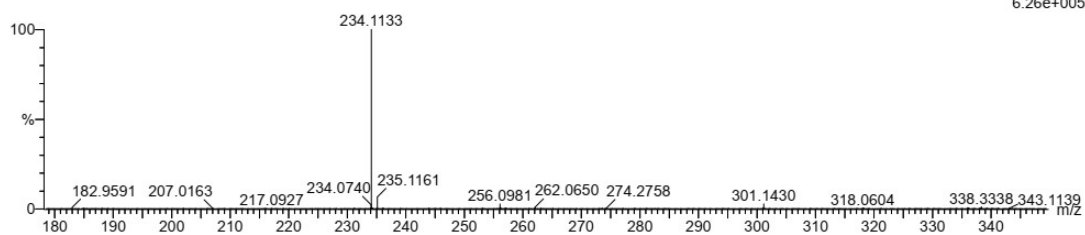
85 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 13-13 H: 0-35 N: 0-6 O: 0-20

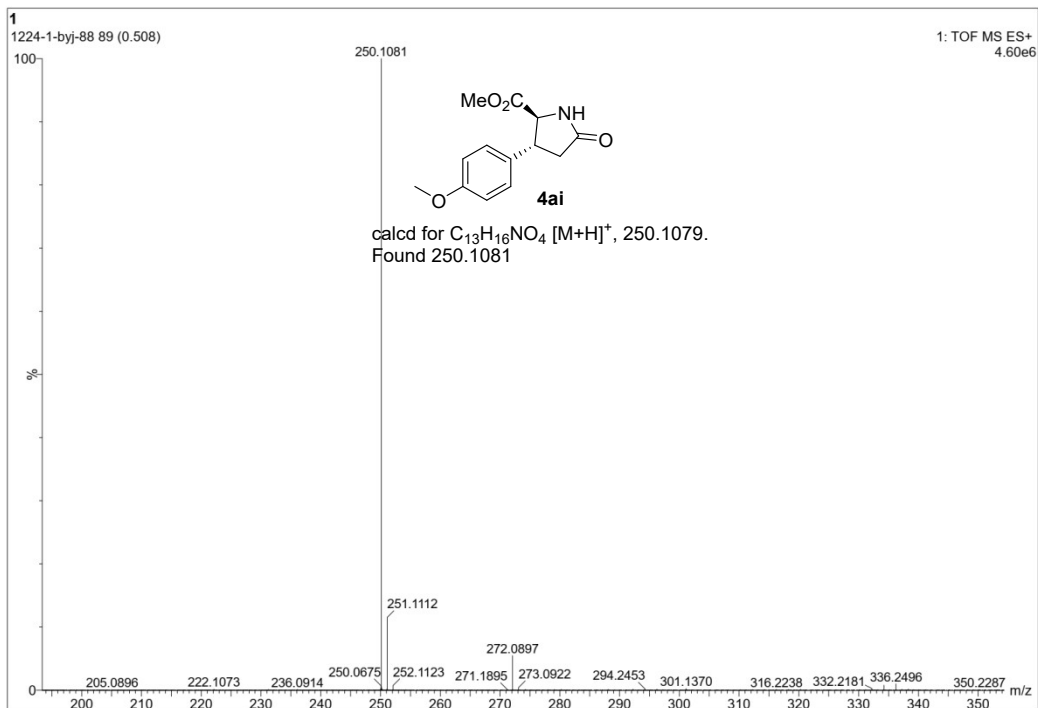
1224-1-byj-98 87 (0.497)

1: TOF MS ES+
6.26e+005



Minimum: -1.5
 Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
234.1133	234.1130	0.3	1.3	6.5	995.1	n/a	n/a	C13 H16 N O3



Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

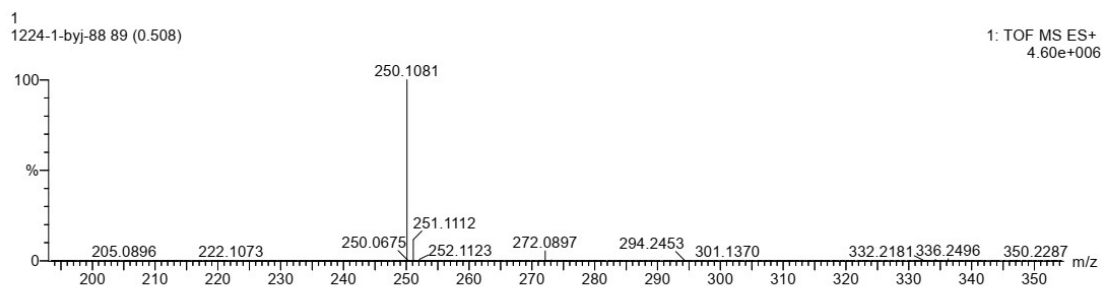
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

3787 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 13-13 H: 0-30 N: 0-6 O: 0-20 F: 0-4 S: 0-4 Cl: 0-4 Mo: 0-1



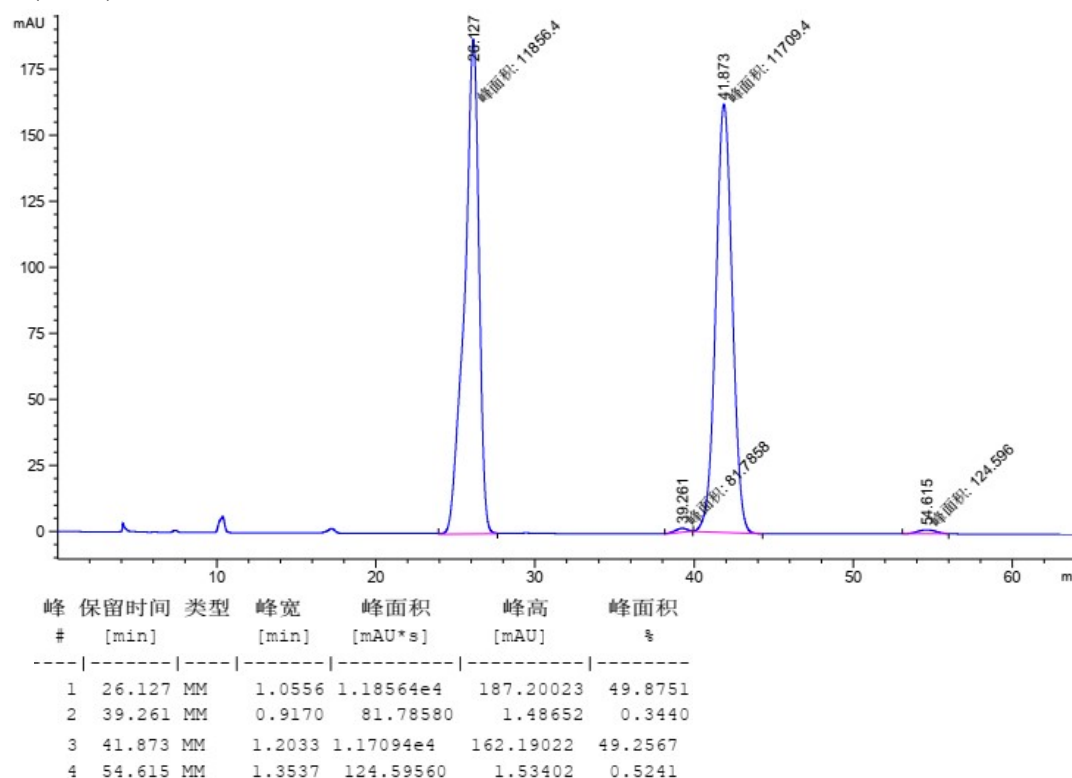
Minimum: -1.5

Maximum: 5.0 10.0 50.0

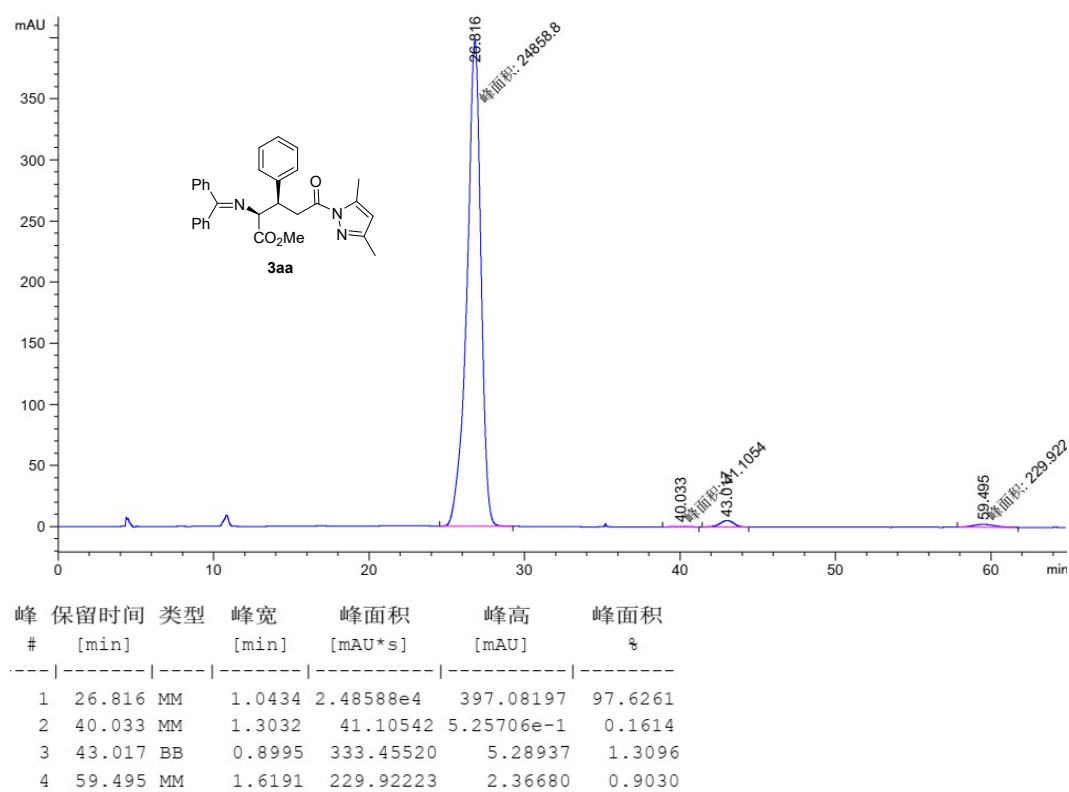
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
250.1081	250.1079	0.2	0.8	6.5	1360.9	n/a	n/a	C13 H16 N O4

7. HPLC copies

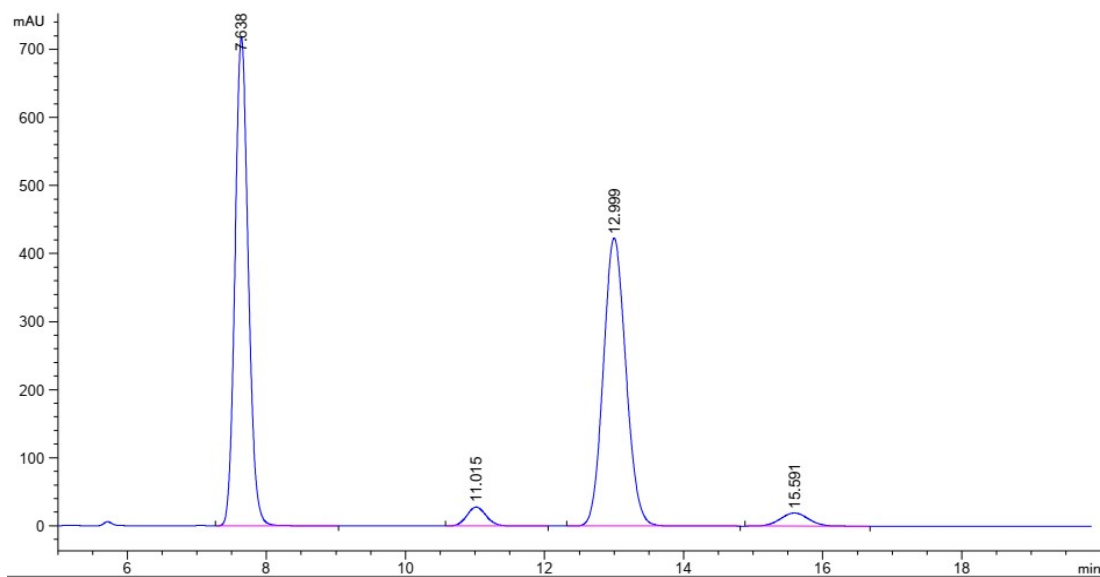
rac-3aa: ChiralPak AD-H, *n*-hex/*i*-PrOH = 98:2, 0.8 mL/min, 254 nm, $t_R(\text{major}) = 26.127$ min and 41.873 min, $t_R(\text{minor}) = 39.261$ and 54.615 min, $dr = 99:1$.



enan-3aa: ChiralPak AD-H, *n*-hex/*i*-PrOH = 98:2, 0.8 mL/min, 254 nm, $t_R(\text{major}) = 26.818$ min, $t_R(\text{minor}) = 43.017$ min, major: 97% *ee*.

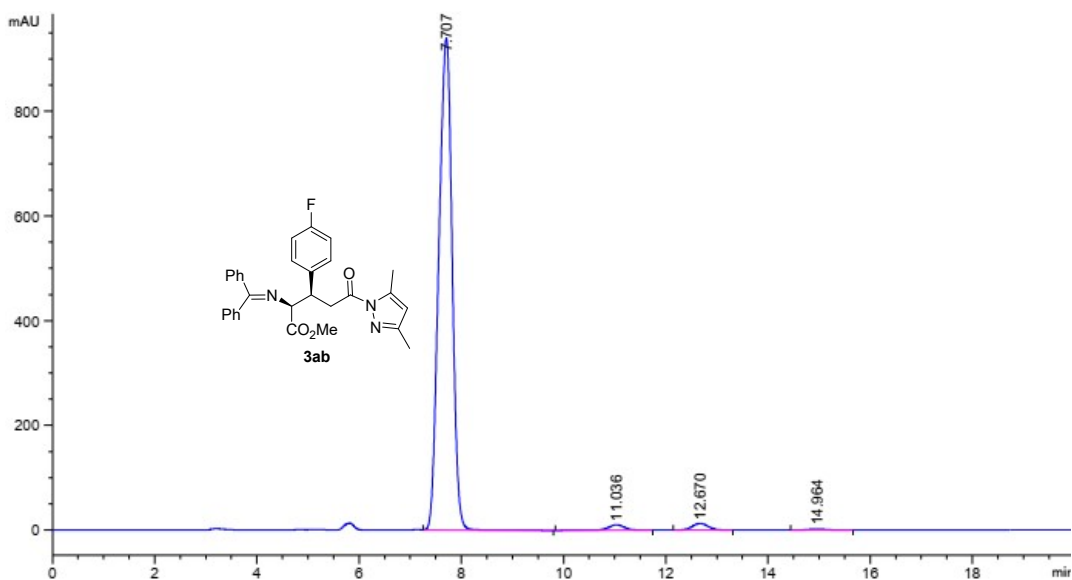


rac-3ab: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 7.638$ min and 12.999 min, $t_R(\text{minor}) = 11.015$ and 15.591 min, $dr = 95:5$.



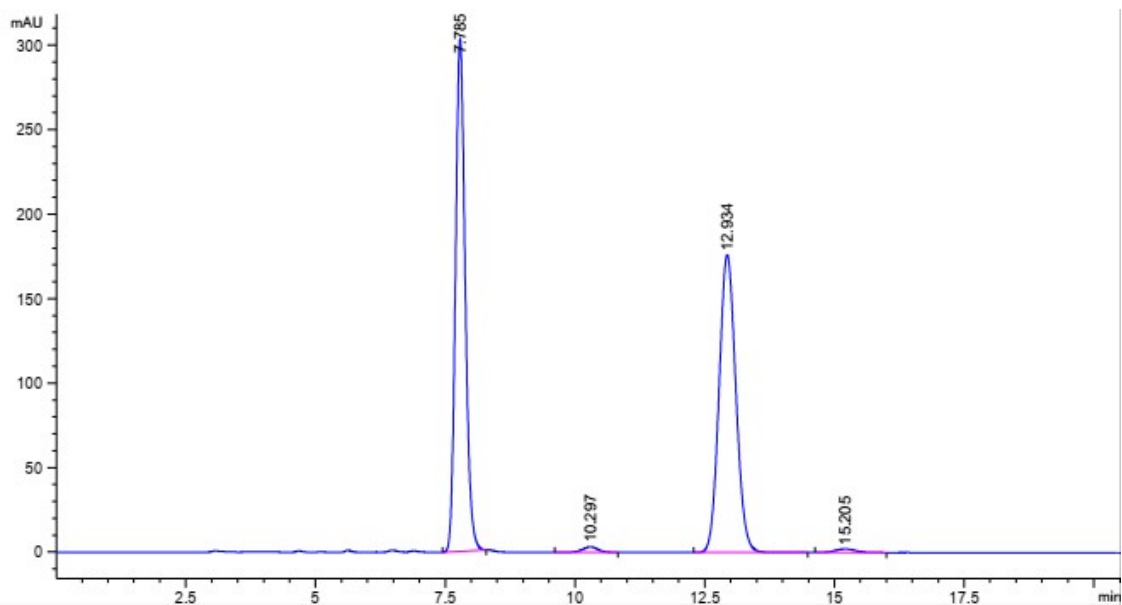
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.638	VB	0.2059	9527.01563	717.72510	47.2712
2	11.015	BB	0.3006	536.83368	27.75618	2.6637
3	12.999	BB	0.3512	9549.80469	423.23633	47.3843
4	15.591	BB	0.4373	540.29559	19.25997	2.6808

enan-3ab: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 7.707$ min, $t_R(\text{minor}) = 12.670$ min, major: 97% *ee*.



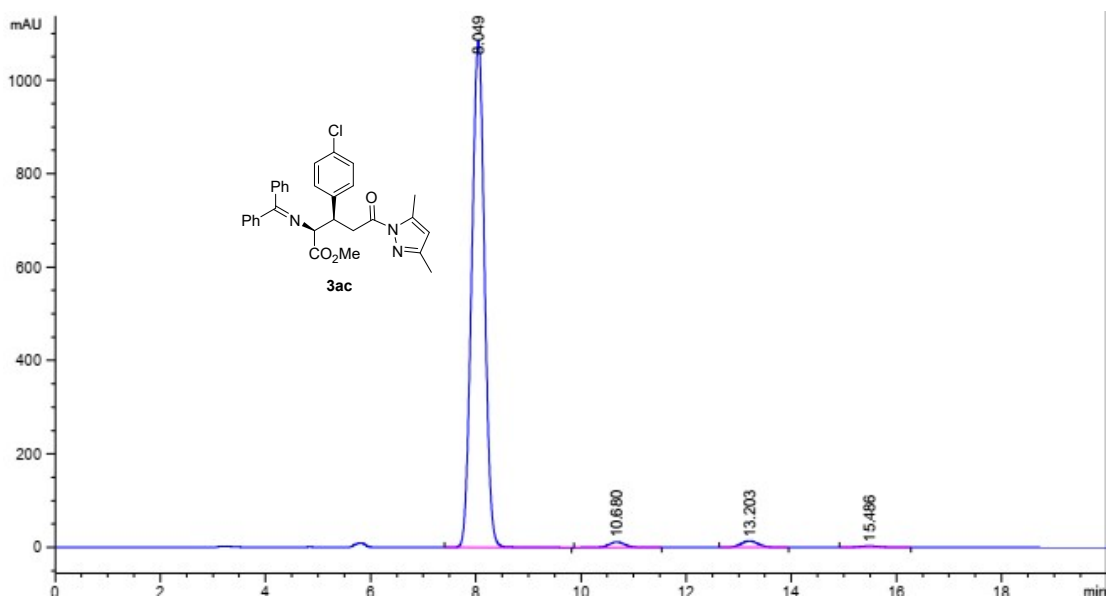
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.707	VB	0.2944	1.69529e4	939.89227	96.8160
2	11.036	BB	0.3382	231.98331	10.36213	1.3248
3	12.670	BB	0.3345	270.63654	12.60508	1.5456
4	14.964	BB	0.3883	54.91762	2.15510	0.3136

rac-3ac: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 7.785$ min and 12.934 min, $t_R(\text{minor}) = 10.297$ and 15.205 min, $dr = 98.5:1.5$.



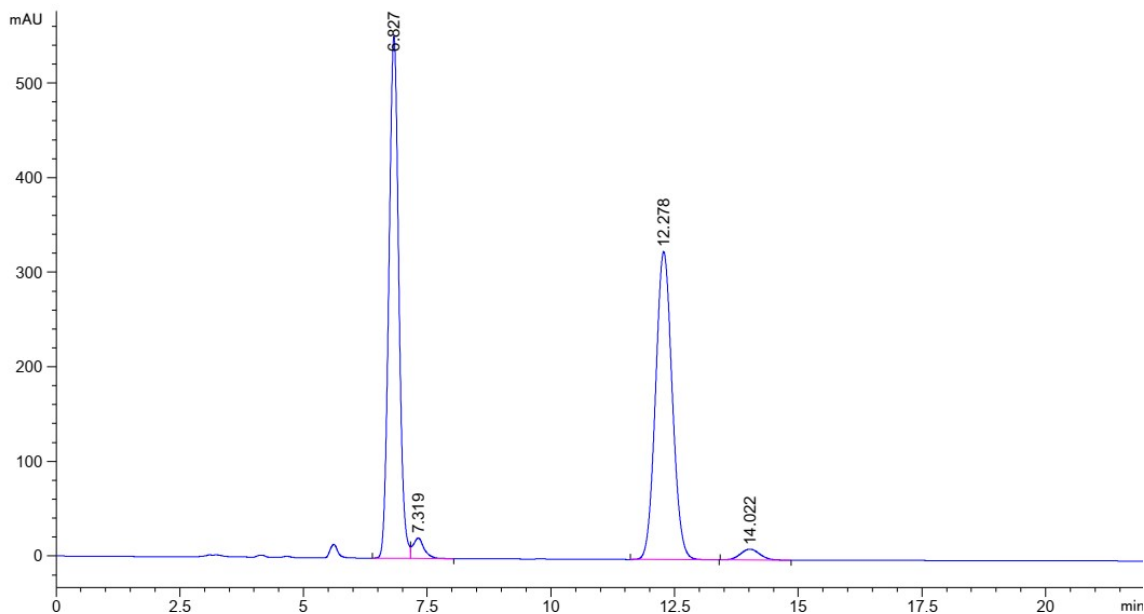
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.785	BB	0.2005	3935.17065	303.01117	49.0455
2	10.297	BB	0.3020	65.66937	3.28776	0.8185
3	12.934	BB	0.3496	3965.27393	176.18336	49.4207
4	15.205	BB	0.4087	57.39943	2.12798	0.7154

enan-3ac: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 8.049$ min, $t_R(\text{minor}) = 13.203$ min, major: 97% *ee*.



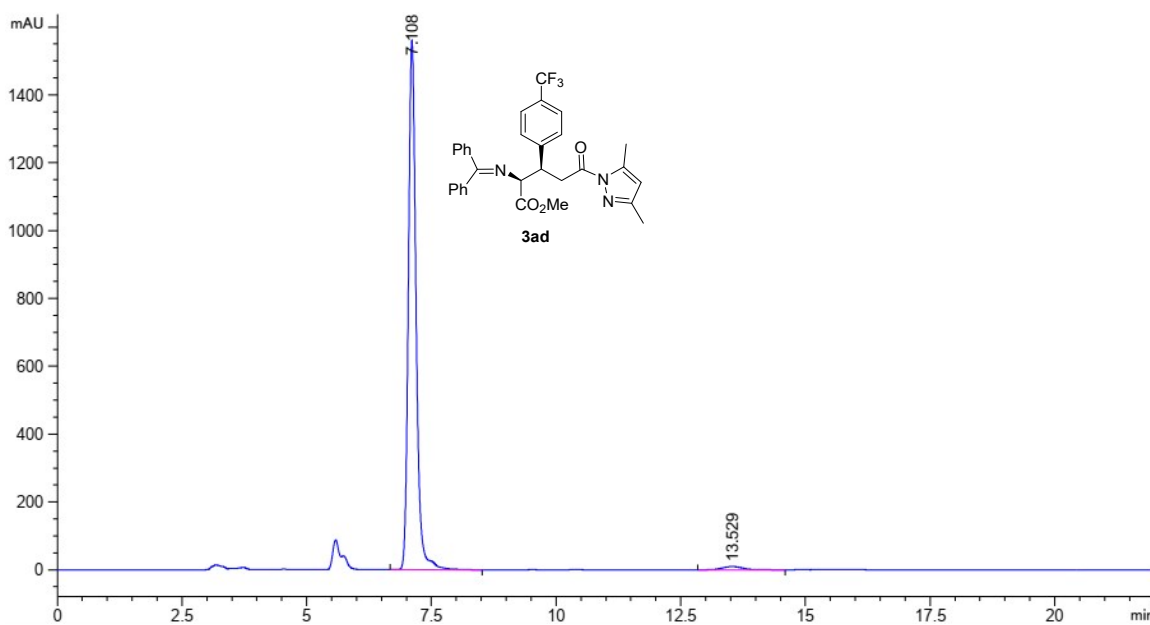
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.049	BB	0.2656	1.83679e4	1084.32898	96.5541
2	10.680	BB	0.3250	259.30829	12.09974	1.3631
3	13.203	BB	0.3511	313.48825	13.90347	1.6479
4	15.486	BB	0.4096	82.73270	3.11795	0.4349

rac-3ad: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 6.827$ and 12.278 min, $t_R(\text{minor}) = 7.319$ and 14.022 min, *dr* > 96:4.



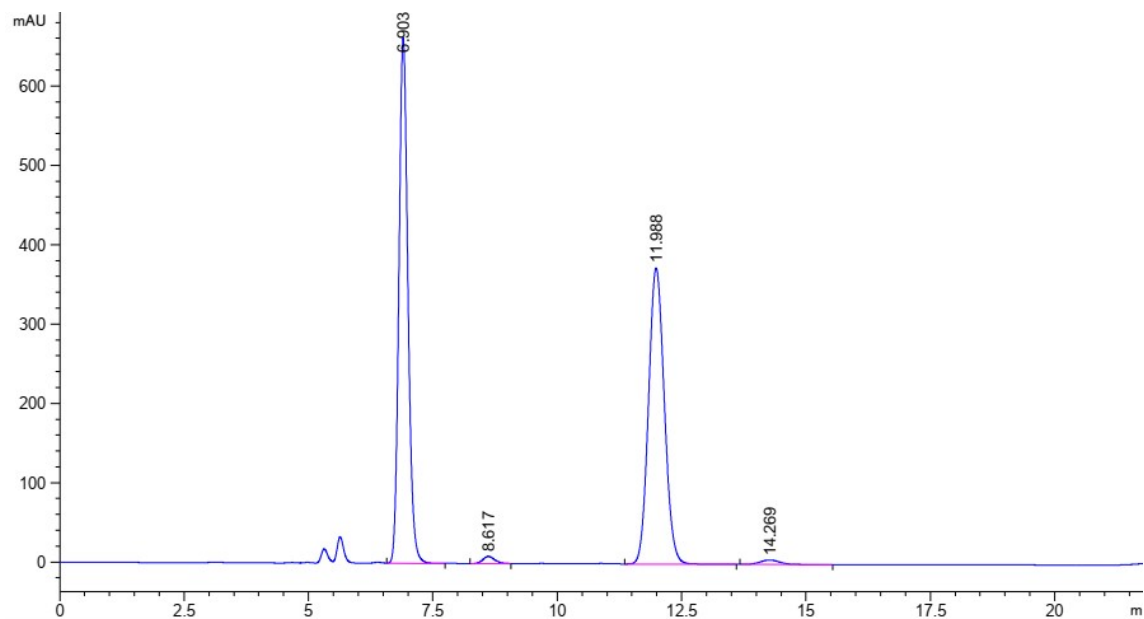
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.827	BV	0.2151	7656.04248	551.07117	48.0594
2	7.319	VB	0.2246	332.68820	21.49391	2.0884
3	12.278	BB	0.3657	7634.63428	325.41895	47.9250
4	14.022	BB	0.4148	307.02325	11.45067	1.9273

enan-3ad: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 7.108$ min, $t_R(\text{minor}) = 13.529$ min, 97% *ee*.



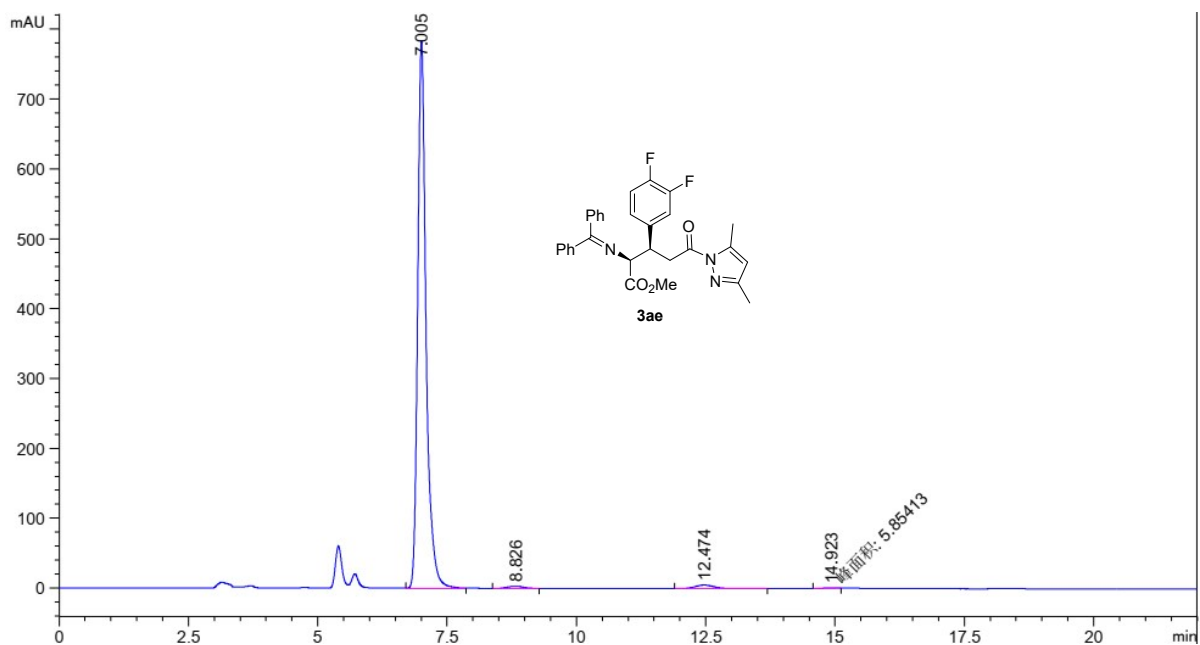
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.108	BB	0.1633	1.67545e4	1560.49609	98.3840
2	13.529	BB	0.4381	275.20343	9.69721	1.6160

rac-3ae: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 6.903$ and 11.988min, $t_R(\text{minor}) = 8.617$ and 14.269 min, $dr = 98:2$.



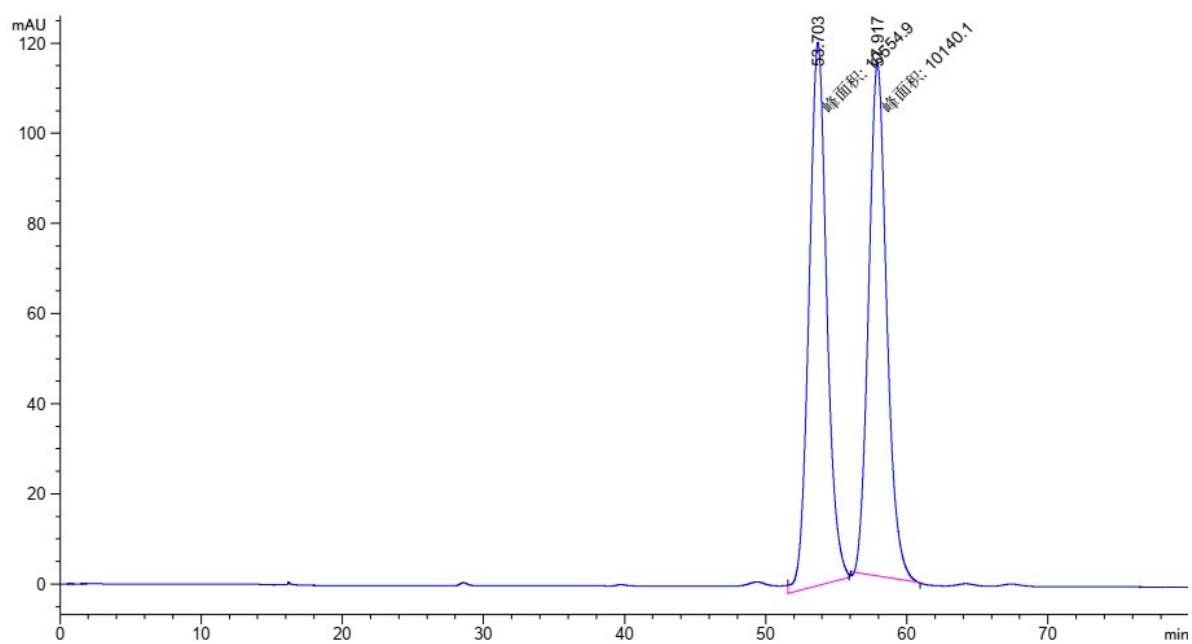
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.903	VV	0.1931	8350.28223	662.37164	49.4786
2	8.617	BB	0.2558	150.94916	9.03841	0.8944
3	11.988	BB	0.3422	8225.60645	373.16745	48.7398
4	14.269	BB	0.4179	149.71959	5.54634	0.8871

enan-3ae: ChiralPak AD-H, *n*-hex/*i*-PrOH = 95:5, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 7.005$ min, $t_R(\text{minor}) = 12.474$ min, 97% *ee*.



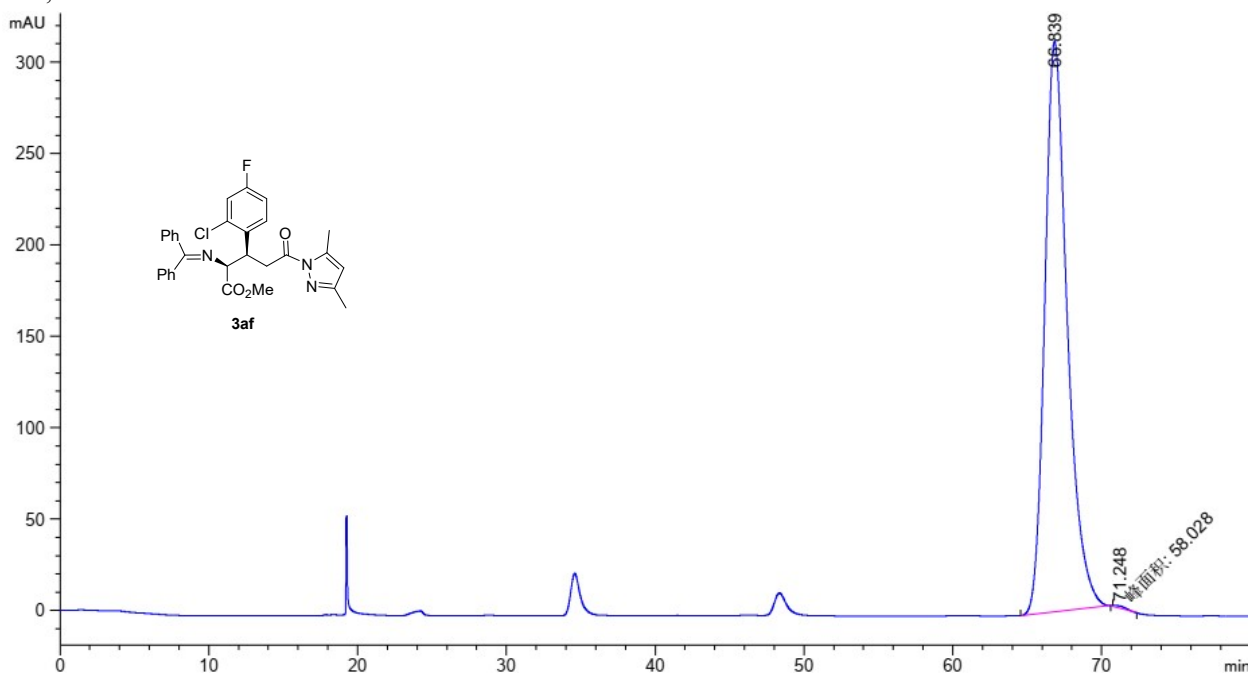
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.005	VV	0.1693	8817.55859	783.45496	97.7886
2	8.826	BB	0.3276	66.03829	3.18937	0.7324
3	12.474	BB	0.3860	127.50979	5.13047	1.4141
4	14.923	MM	0.3086	5.85413	3.16154e-1	0.0649

rac-**3af**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 98:2, 0.4 mL/min, 254 nm, t_R = 53.703 and 57.917 min, *dr* > 99:1.



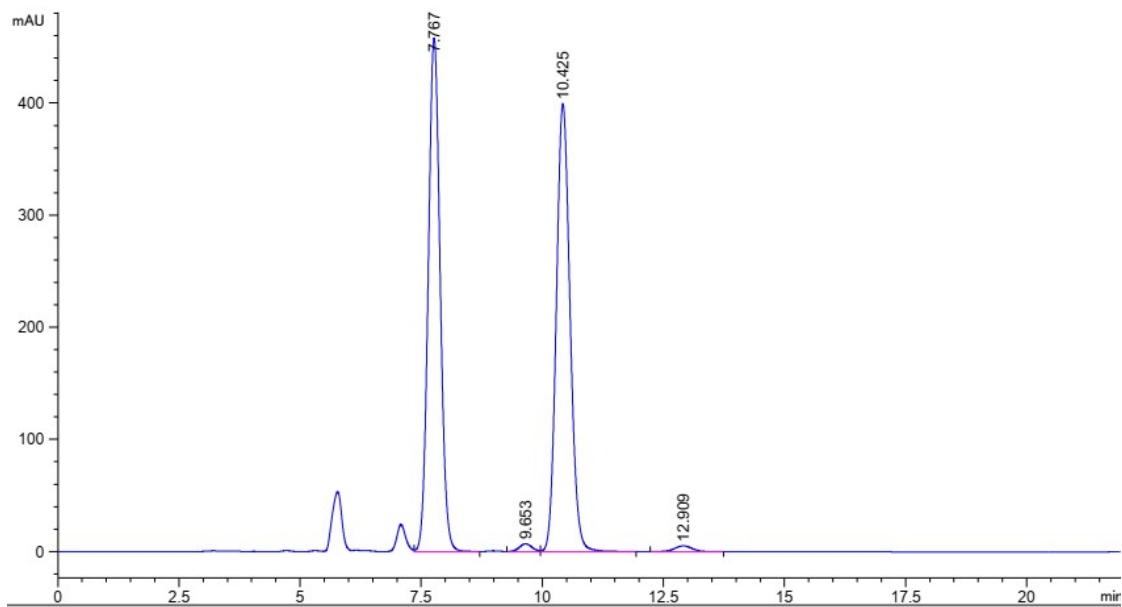
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	53.703	MM	1.4605	1.05549e4	120.45188	51.0023
2	57.917	MM	1.4863	1.01401e4	113.70750	48.9977

enan-**3af**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 98:2, 0.4 mL/min, 254 nm, t_R (major) = 66.839 min, t_R (minor) = 71.248 min, 99% *ee*.



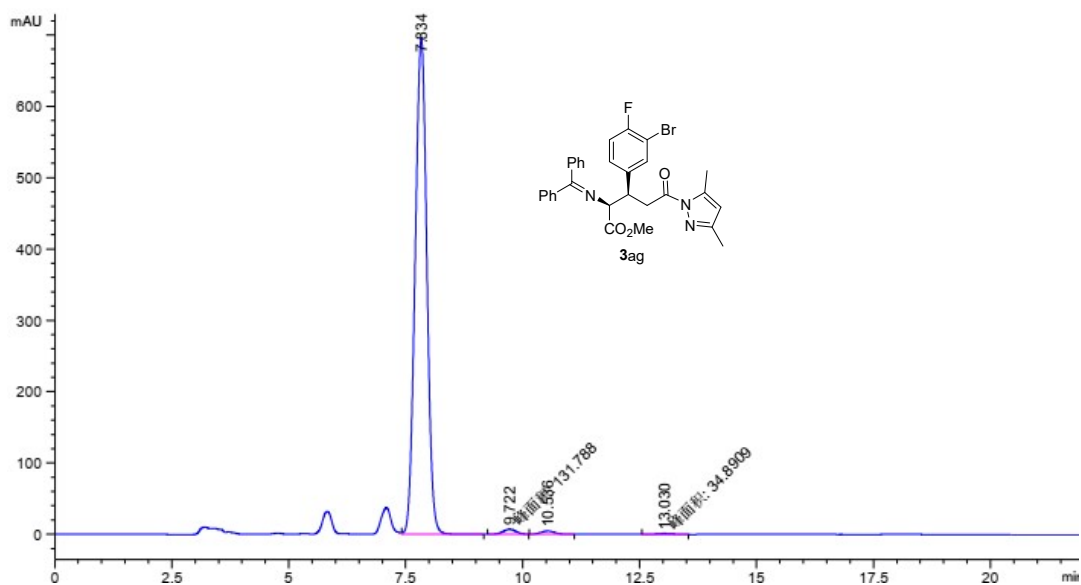
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	66.839	BB	1.5511	3.28929e4	311.96848	99.8239
2	71.248	MM	0.8275	58.02803	1.16868	0.1761

rac-3ag: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 13.846$ and 10.425 , $t_R(\text{minor}) = 9.653$ and 12.909 min, $dr = 98:2$.



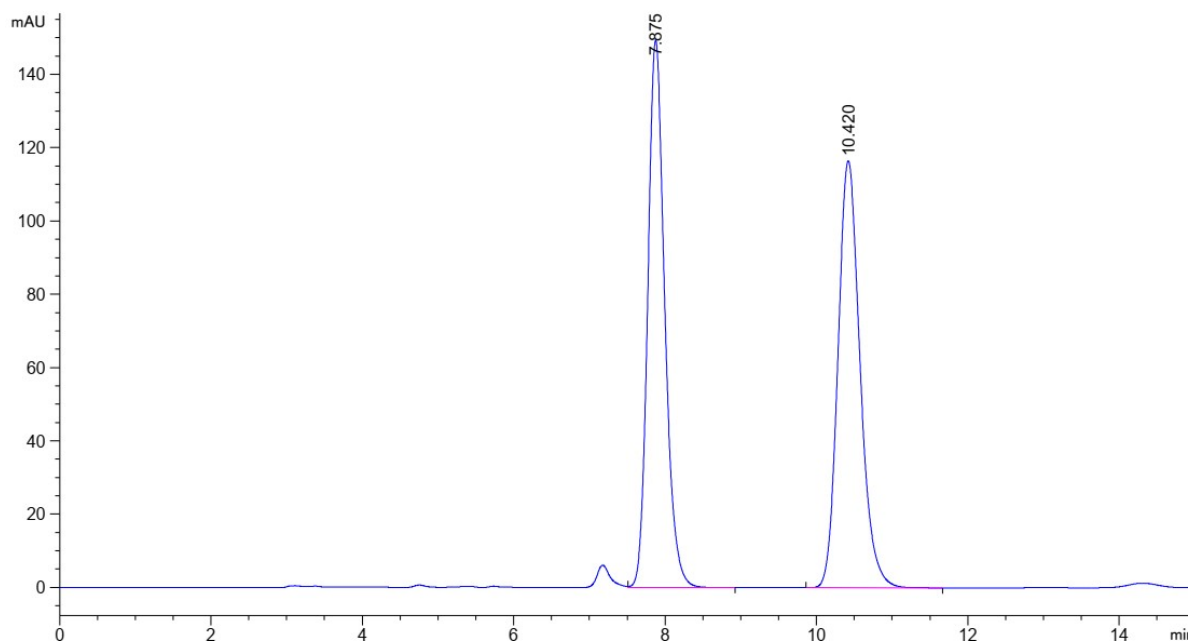
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.767	VB	0.2629	7772.61768	458.28308	49.0636
2	9.653	BV	0.2812	121.83543	6.79345	0.7691
3	10.425	VB	0.3046	7822.30908	399.17081	49.3773
4	12.909	BB	0.3841	125.15193	5.06734	0.7900

enan-3ag: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 7.834$ min, $t_R(\text{minor}) = 10.536$ min, 98% *ee*.



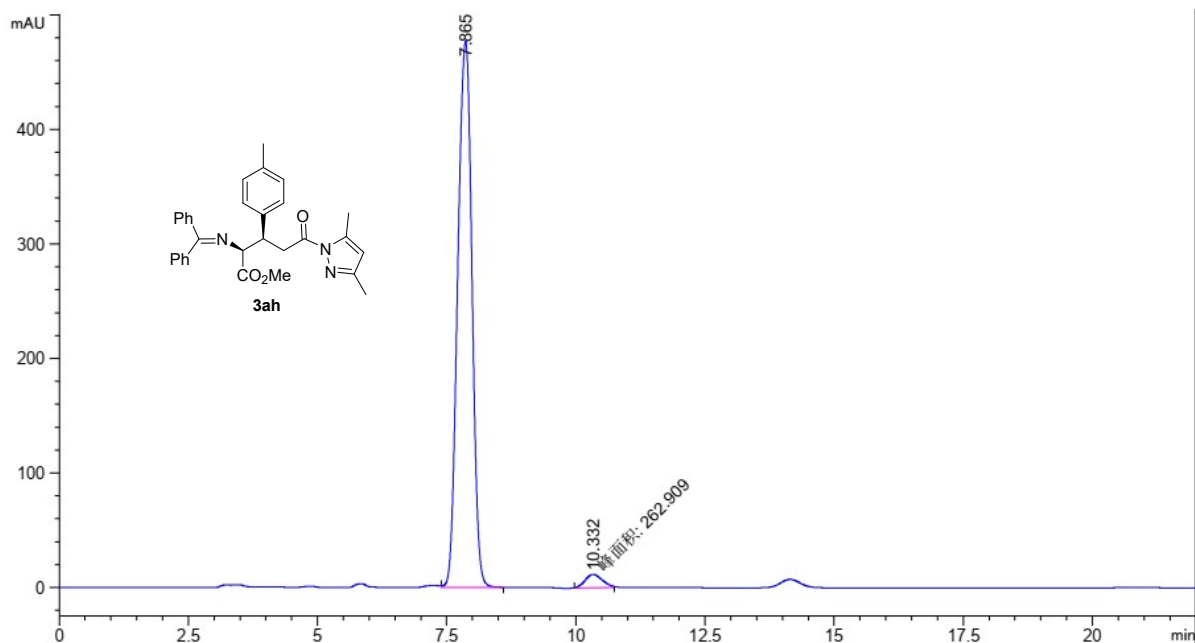
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.834	VB	0.2730	1.20362e4	695.09381	97.9154
2	9.722	MM	0.3147	131.78838	6.97891	1.0721
3	10.536	BB	0.3077	89.57288	4.53022	0.7287
4	13.030	MM	0.4214	34.89092	1.38004	0.2838

rac-3ah: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R = 7.875$ and 10.420 min, *dr* > 99:1.



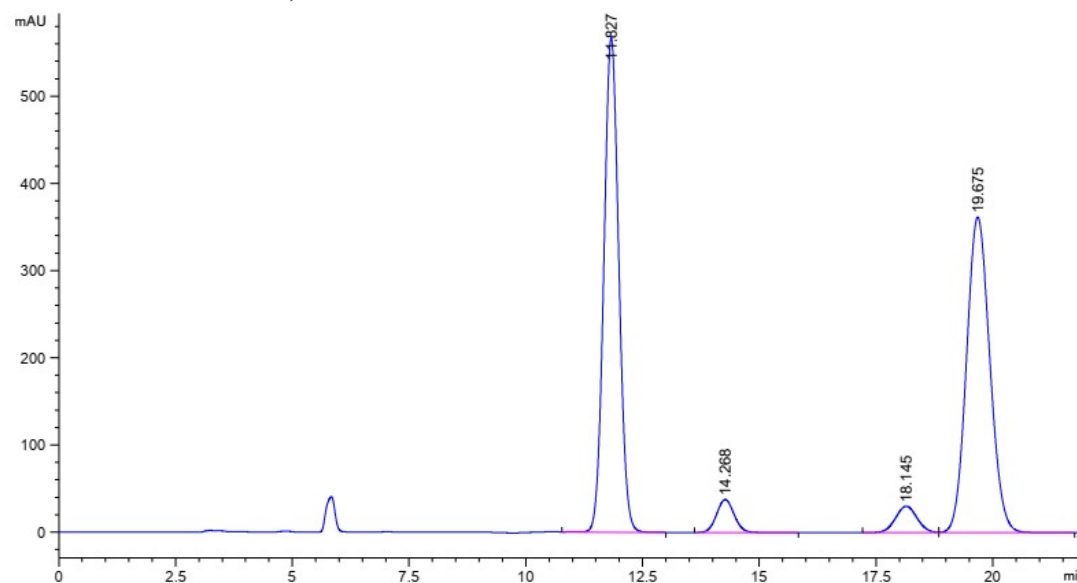
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.875	VB	0.2376	2325.64990	149.38385	49.6346
2	10.420	BB	0.3114	2359.89624	116.47906	50.3654

enan-3ah: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 7.856$ min, $t_R(\text{minor}) = 10.332$ min, 94% *ee*.



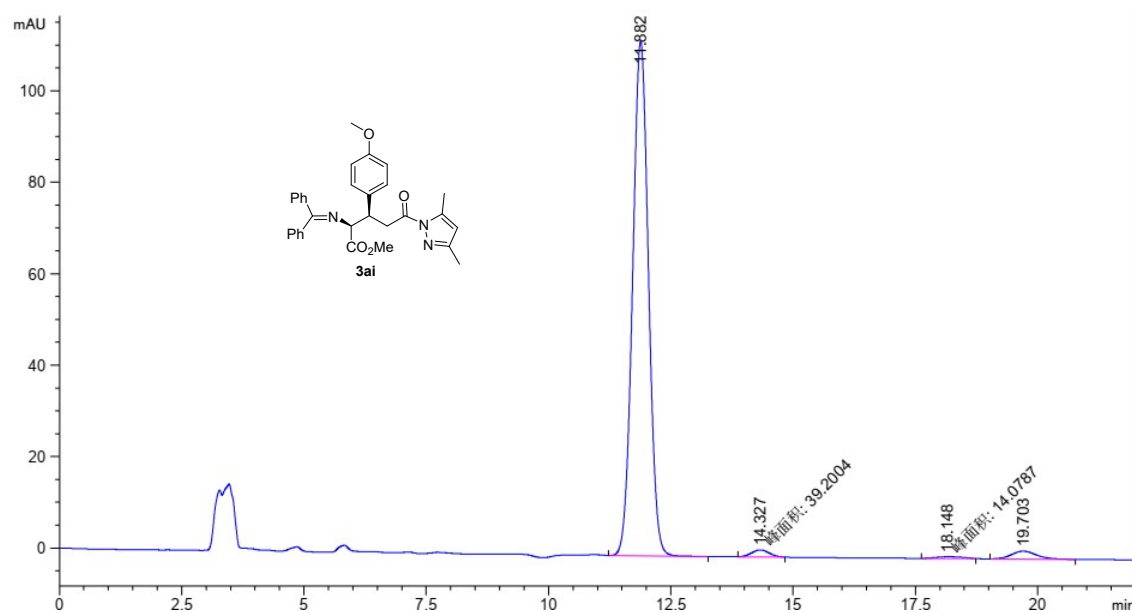
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.865	VB	0.3092	9083.50684	476.97144	97.1871
2	10.332	MM	0.3797	262.90906	11.53943	2.8129

rac-3ai: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 11.827$ and 19.675 min, $t_R(\text{minor}) = 14.268$ and 18.145 min, $dr = 93:7$.



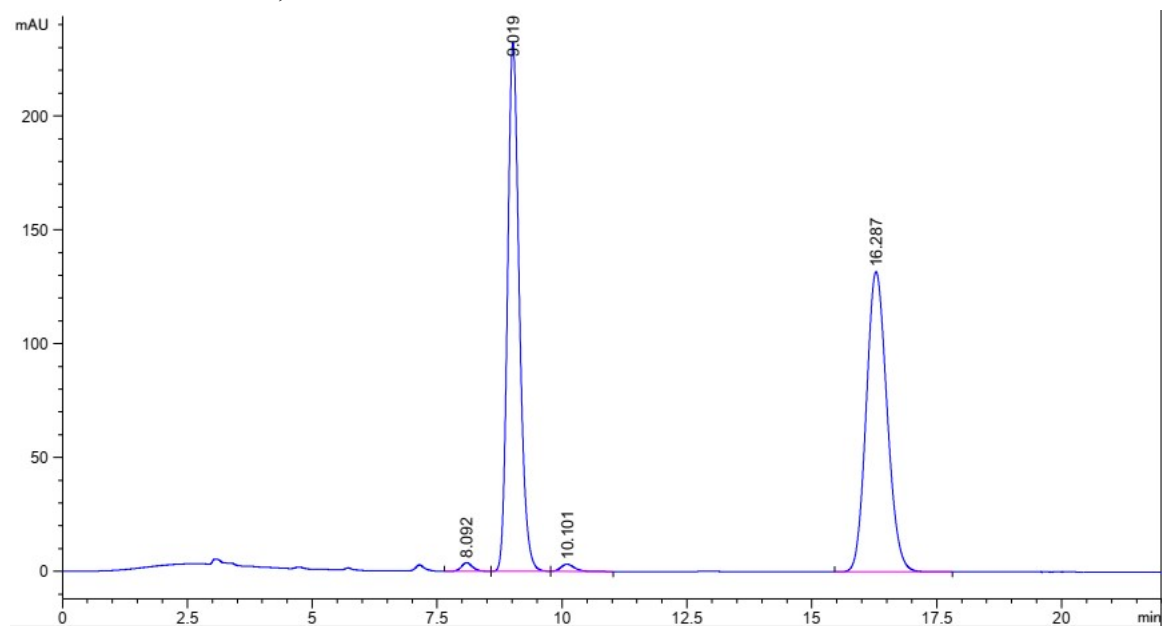
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.827	BB	0.3442	1.25440e4	566.82074	46.3462
2	14.268	BB	0.4035	978.35217	37.73576	3.6147
3	18.145	BV	0.4990	966.85895	30.23919	3.5723
4	19.675	VB	0.5425	1.25766e4	361.85284	46.4668

enan-3ai: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 11.882$ and 19.703 min, $t_R(\text{minor}) = 14.327$ and 18.148 min, $dr = 98:2$, 95 % *ee*.



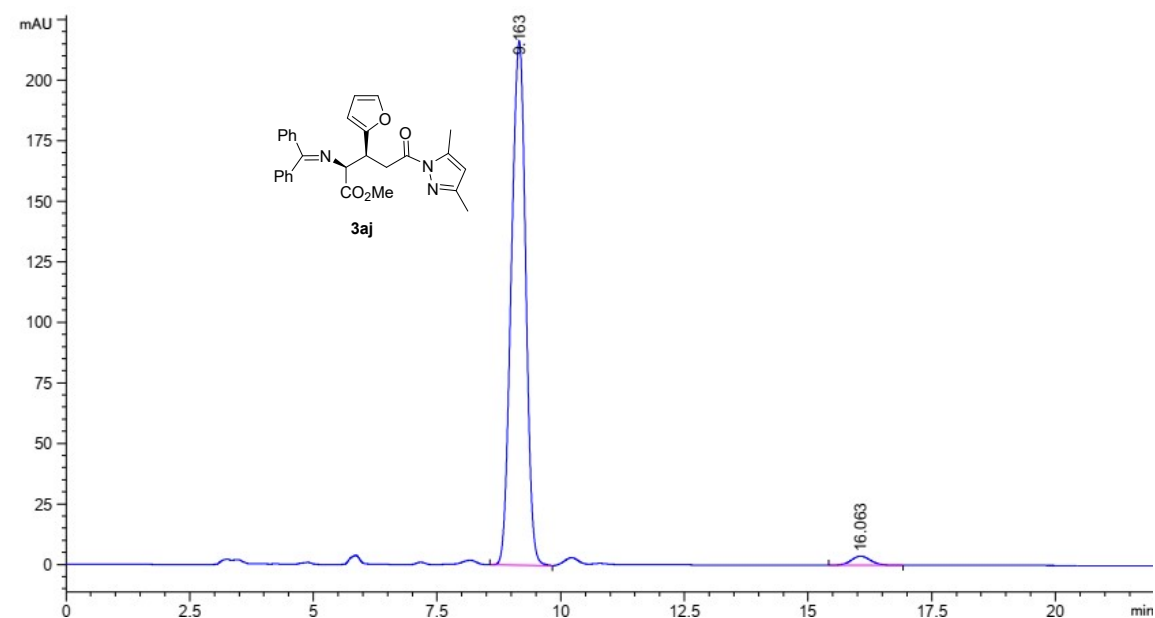
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.882	BB	0.3477	2523.27271	112.49429	95.6486
2	14.327	MM	0.4224	39.20037	1.54669	1.4860
3	18.148	MM	0.6175	14.07875	3.79983e-1	0.5337
4	19.703	BB	0.5311	61.51308	1.72900	2.3317

rac-3aj: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 9.019$ and 16.287 min, $t_R(\text{minor}) = 8.092$ and 10.101 min, $dr = 98.5:1.5$.



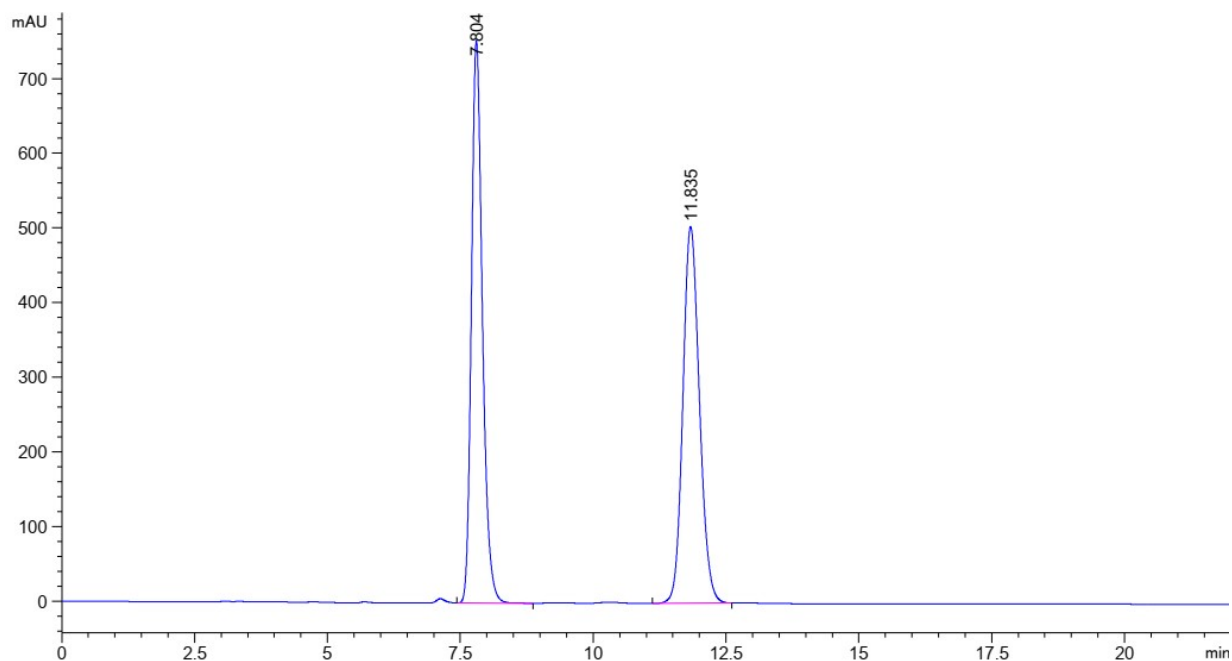
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.092	BB	0.2348	57.07224	3.72327	0.7408
2	9.019	BB	0.2492	3787.35156	232.29094	49.1604
3	10.101	BB	0.2906	59.76531	3.13235	0.7758
4	16.287	BB	0.4482	3799.88354	131.87317	49.3230

enan-3aj: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 9.163$ and 16.063 min, 95.5 % *ee*.



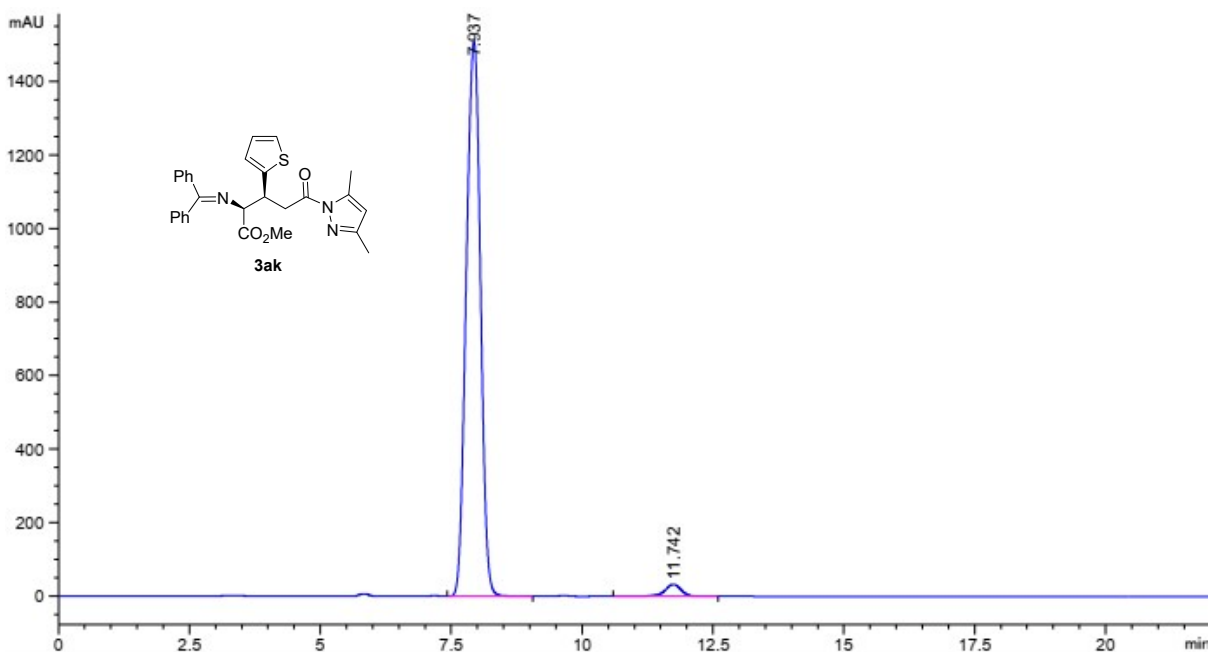
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.163	BB	0.3238	4354.79150	216.39275	97.7529
2	16.063	BB	0.4147	100.10626	3.73461	2.2471

rac-3ak: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 7.804$ and 11.835 min, $dr > 99:1$.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.804	VB	0.2190	1.07834e4	753.34802	49.7393
2	11.835	BB	0.3340	1.08965e4	504.50000	50.2607

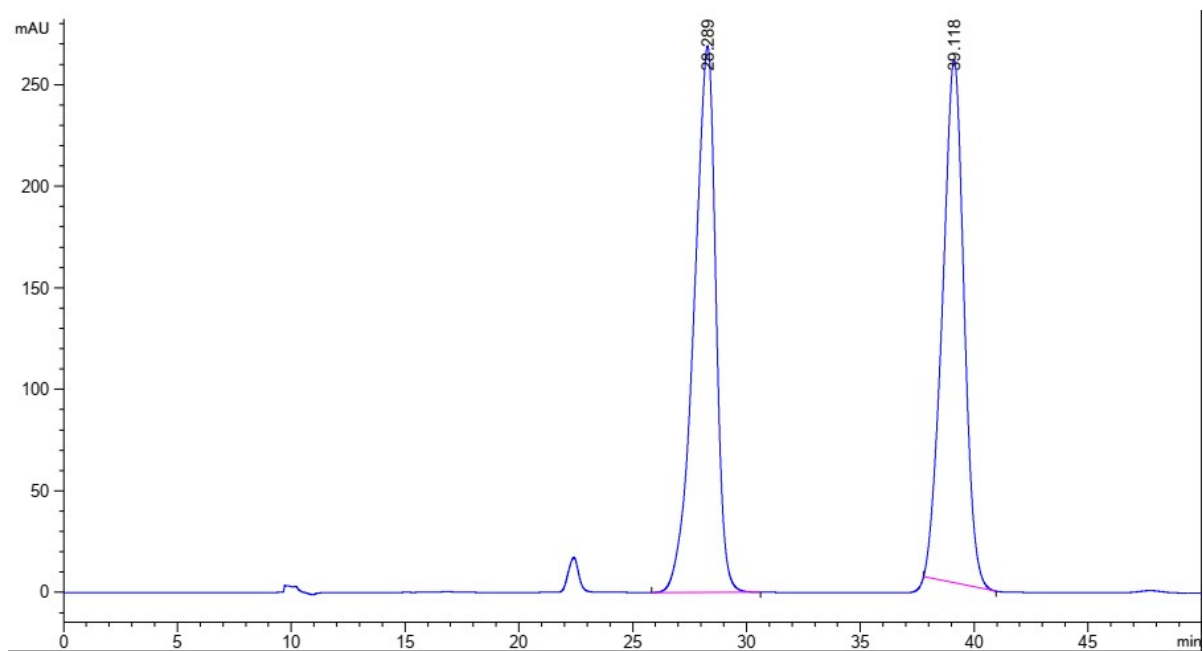
enan-3ak: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 7.937$ min, $t_R(\text{minor}) = 11.742$ min, 95 % *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.937	VB	0.3042	2.83547e4	1509.06909	97.5321
2	11.742	BB	0.3309	717.47205	32.83446	2.4679

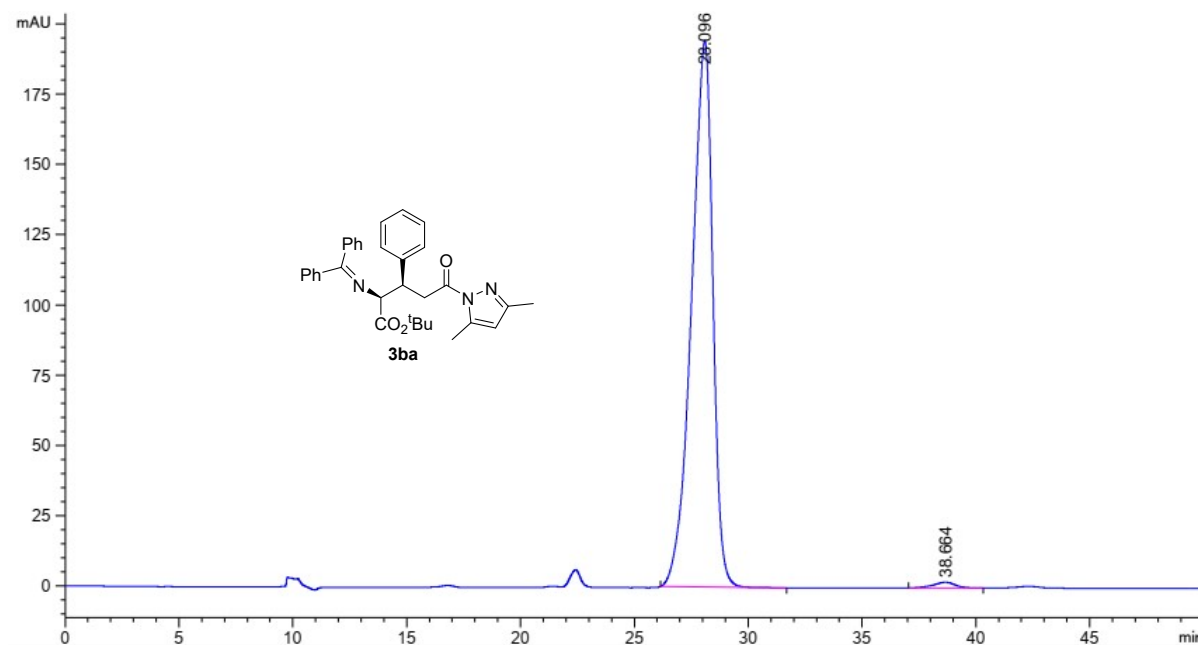
S98

rac-**3ba**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 97:3, 0.7 mL/min, 254 nm, t_R = 28.289 and 39.118 min, dr > 99:1.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.289	BB	1.0338	1.78887e4	269.01865	51.4181
2	39.118	BB	0.9619	1.69020e4	257.46701	48.5819

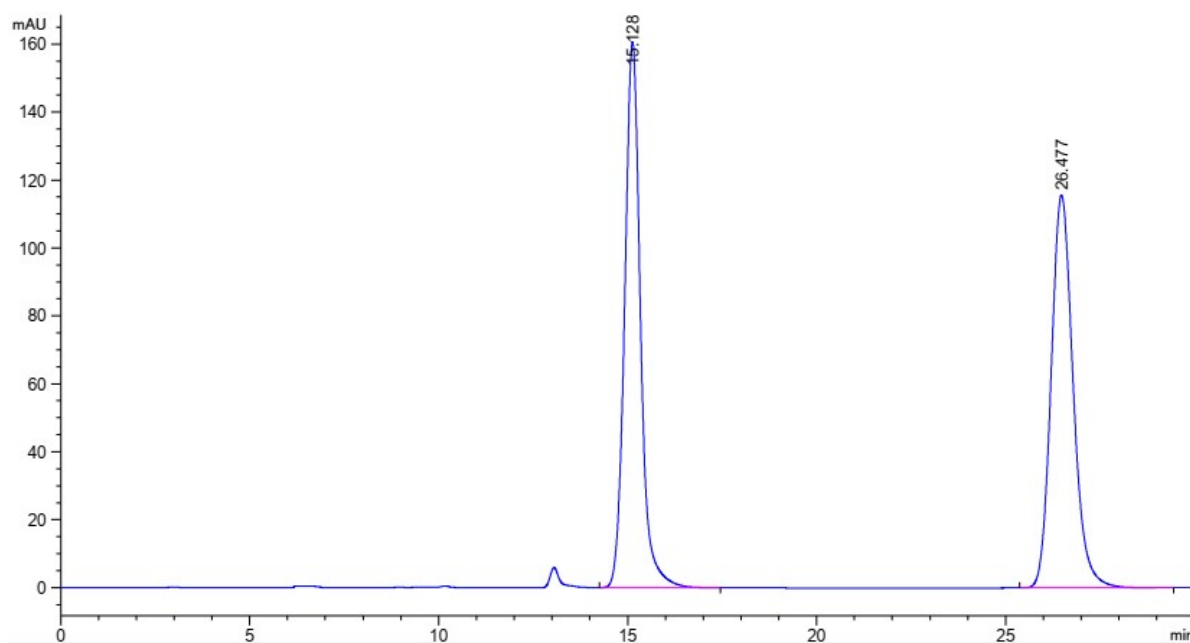
enan-**3ba**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 97:3, 0.7 mL/min, 254 nm, t_R (major) = 28.096 min, t_R (minor) = 38.664 min, 98 % *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.096	BB	0.9693	1.26072e4	194.48280	98.9298
2	38.664	BB	0.8501	136.38406	2.02415	1.0702

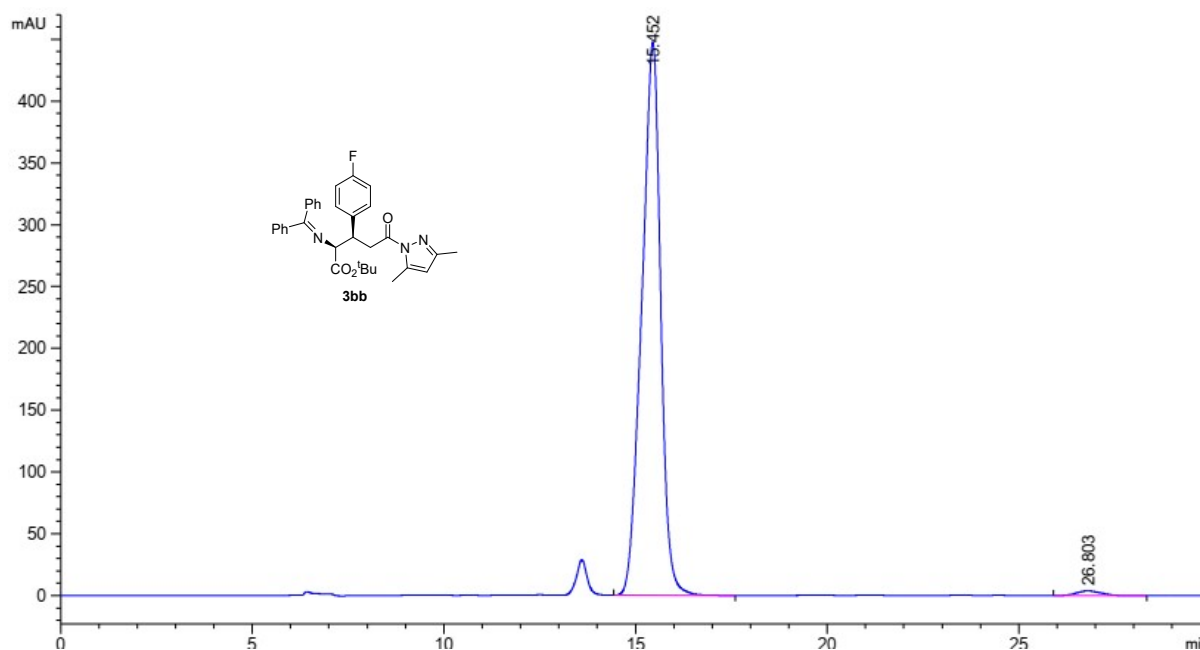
S99

rac-**3bb**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 95:5, 0.5 mL/min, 254 nm, $t_R = 15.128$ and 26.477 min, *dr* > 99:1.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.128	BB	0.4410	4656.90479	160.73123	49.9209
2	26.477	BB	0.6233	4671.66992	115.65311	50.0791

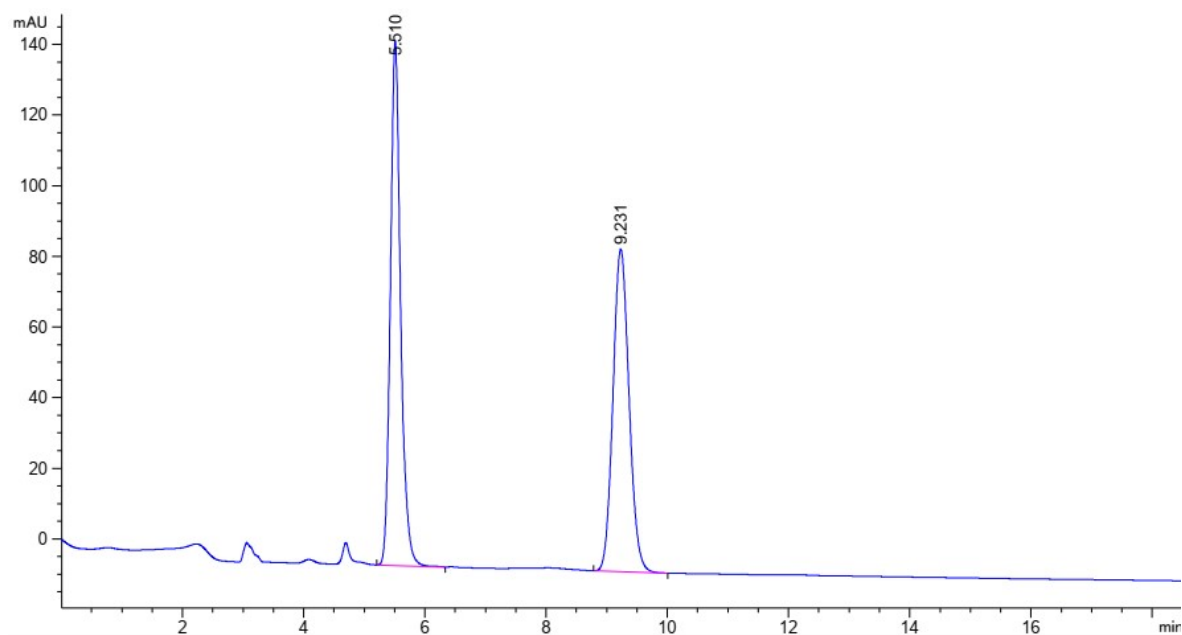
enan-**3bb**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 95:5, 0.5 mL/min, 254 nm, $t_R(\text{major}) = 15.452$ min, $t_R(\text{minor}) = 26.122$ min, 98 % *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.452	BB	0.4996	1.52856e4	447.41663	98.9137
2	26.803	BB	0.6534	167.87830	3.77070	1.0863

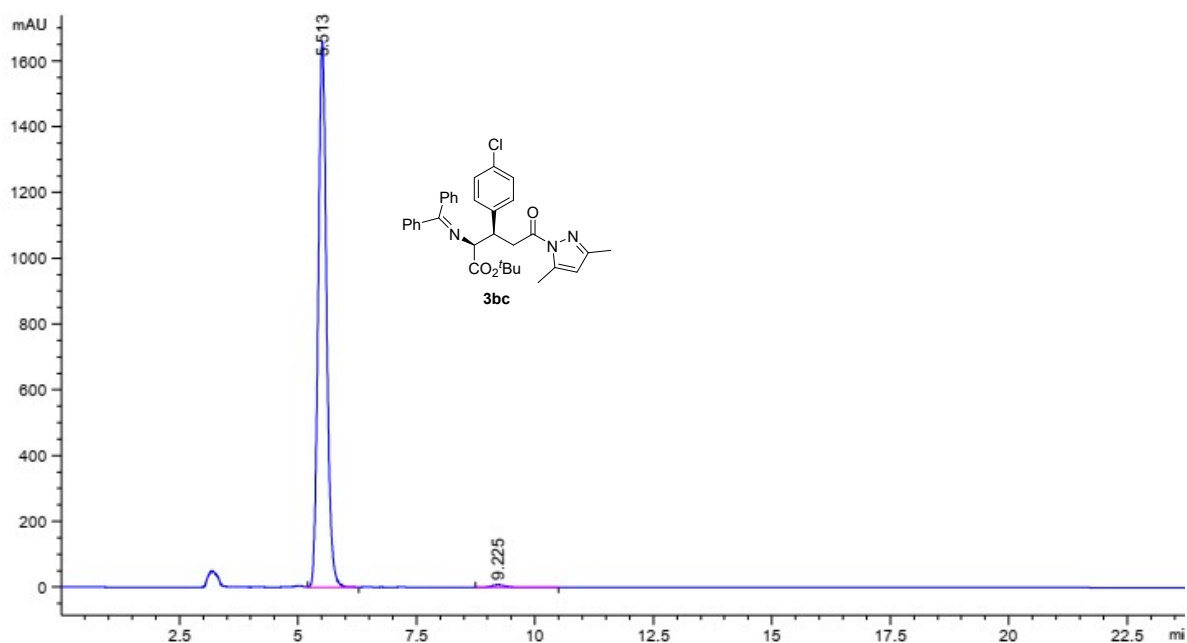
S100

rac-**3bc**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R = 5.510 and 9.231 min, dr > 99:1.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.510	VB	0.1769	1743.13196	148.56671	50.9063
2	9.231	BB	0.2859	1681.06775	91.28247	49.0937

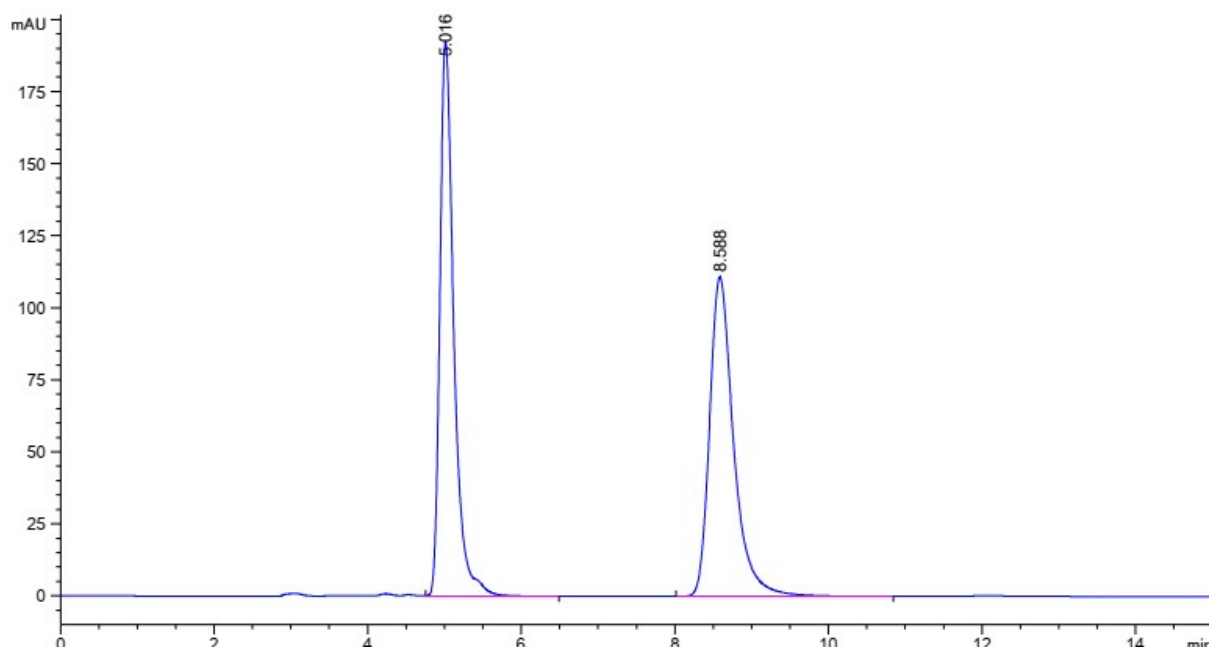
enan-**3bc**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R (major) = 5.513 min, t_R (minor) = 9.225 min, 98.5 % ee.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.513	VB	0.1894	2.03783e4	1657.51709	99.2687
2	9.225	BB	0.3212	150.13121	7.35409	0.7313

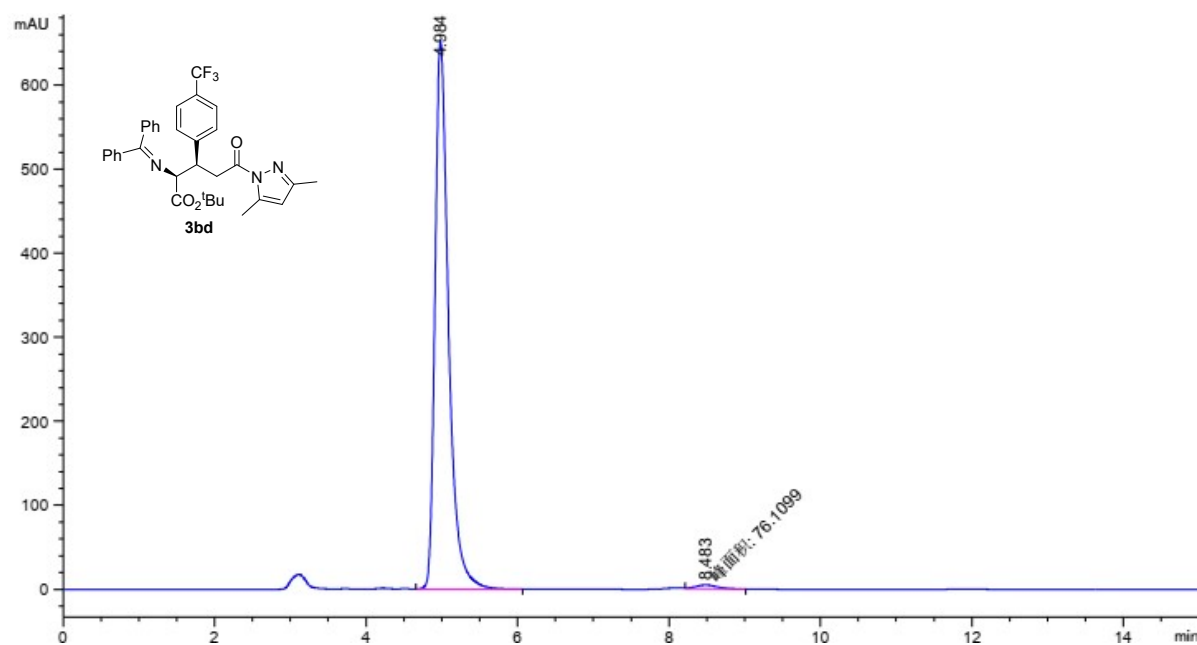
S101

rac-**3bd**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R = 5.016$ and 8.588 min, dr > 99:1.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.016	VB	0.1904	2429.68726	192.31837	50.2274
2	8.588	BB	0.3273	2407.68359	110.91646	49.7726

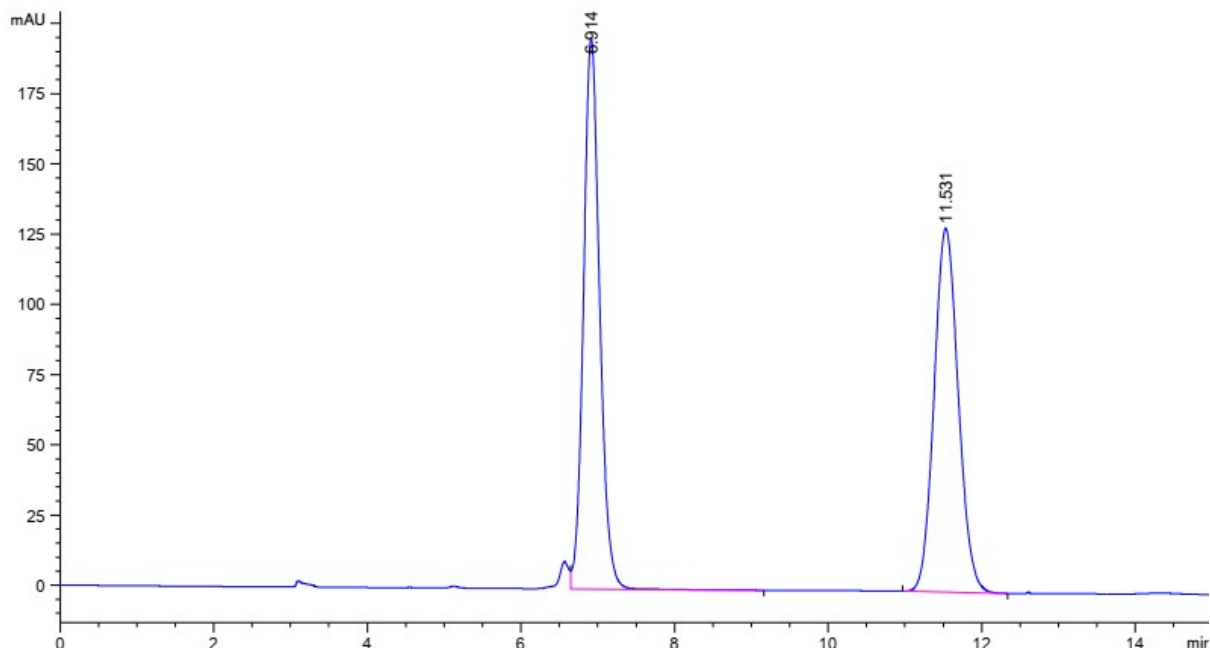
enan-**3bd**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 4.984$ min, $t_R(\text{minor}) = 8.483$ min, 98.1% *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	4.984	VB	0.1884	8118.44141	651.39435	99.0712
2	8.483	MM	0.2955	76.10994	4.29308	0.9288

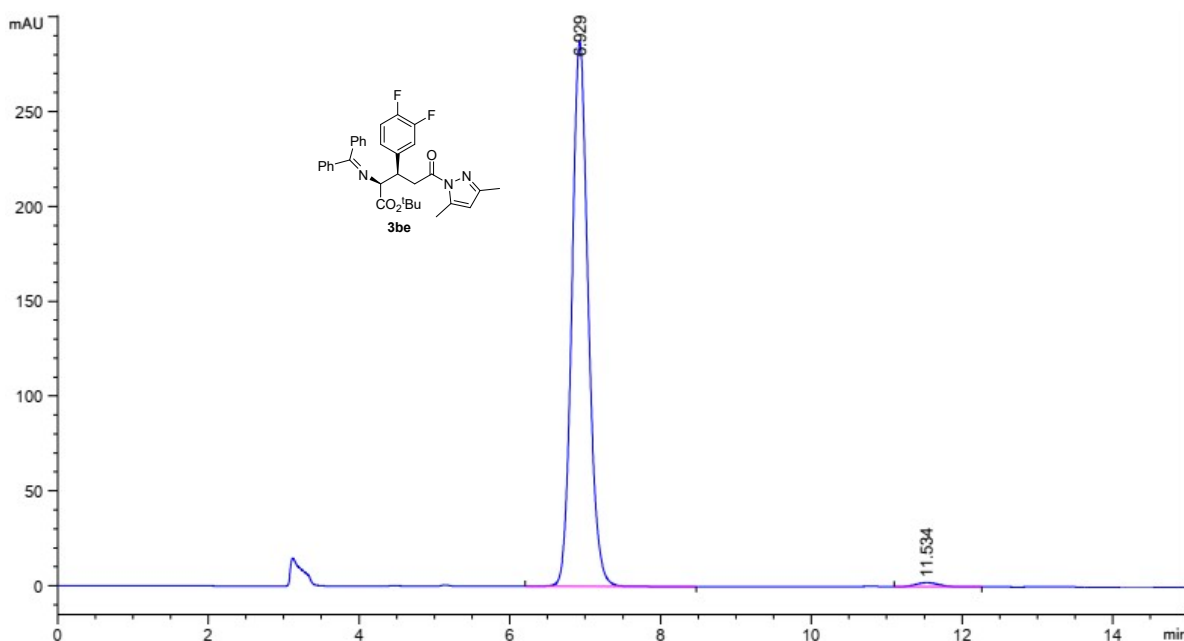
S102

rac-**3be**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 95:5, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 6.914$ and 11.531 min, *dr* > 99:1.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.914	VB	0.2234	2863.43530	196.01173	50.3267
2	11.531	BB	0.3385	2826.25464	129.55185	49.6733

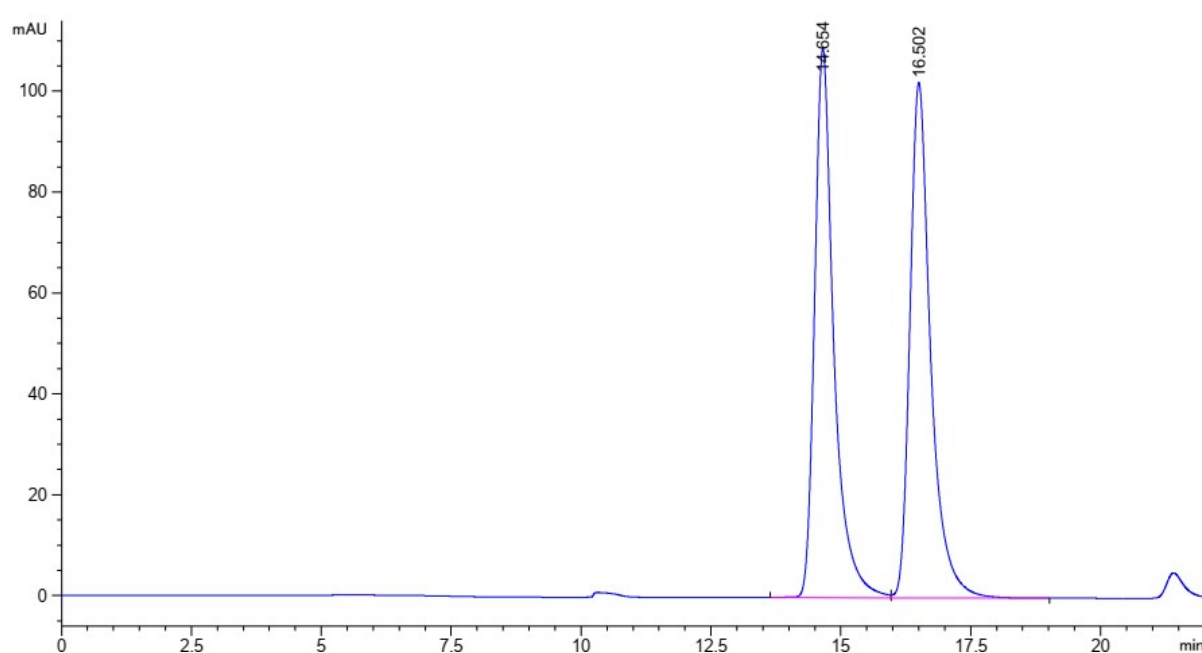
enan-**3be**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 95:5, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 6.929$ min, $t_R(\text{minor}) = 11.534$ min, 97.8% *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.929	BB	0.2307	4321.90771	287.02921	98.9134
2	11.534	BB	0.3329	47.47823	2.19855	1.0866

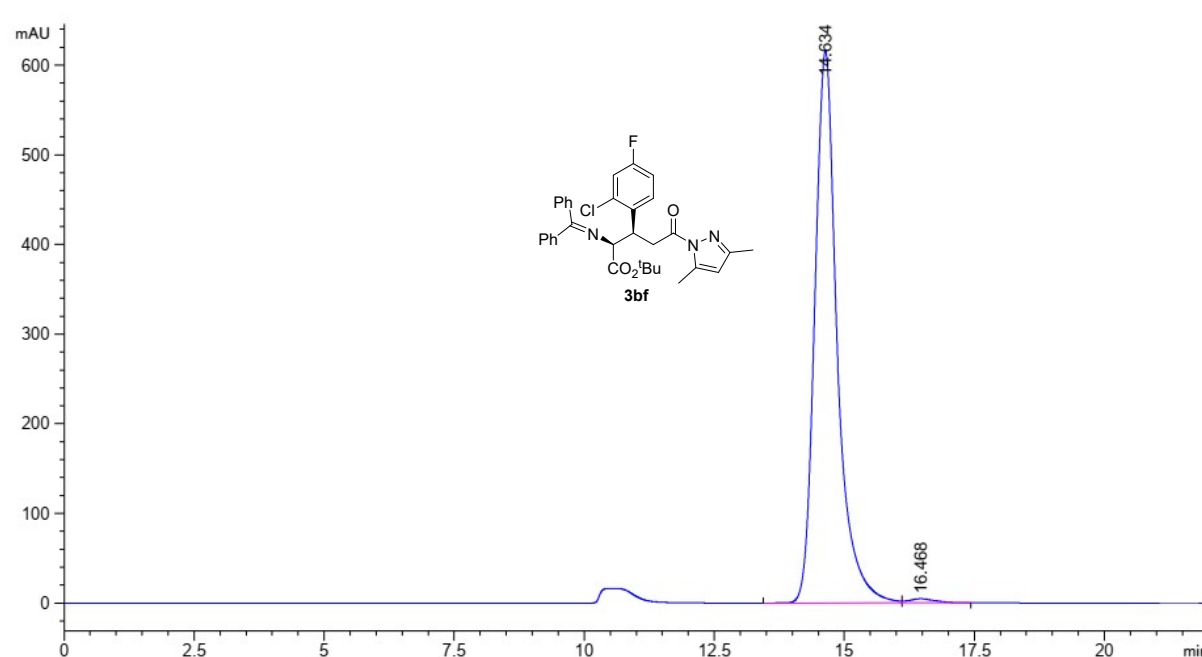
S103

rac-**3bf**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 95:5, 0.5 mL/min, 254 nm, $t_R(\text{major}) = 14.654$ and 16.502 min, $dr > 99:1$.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.654	BV	0.3844	2815.62500	108.96989	49.8703
2	16.502	VB	0.4133	2830.27441	102.14868	50.1297

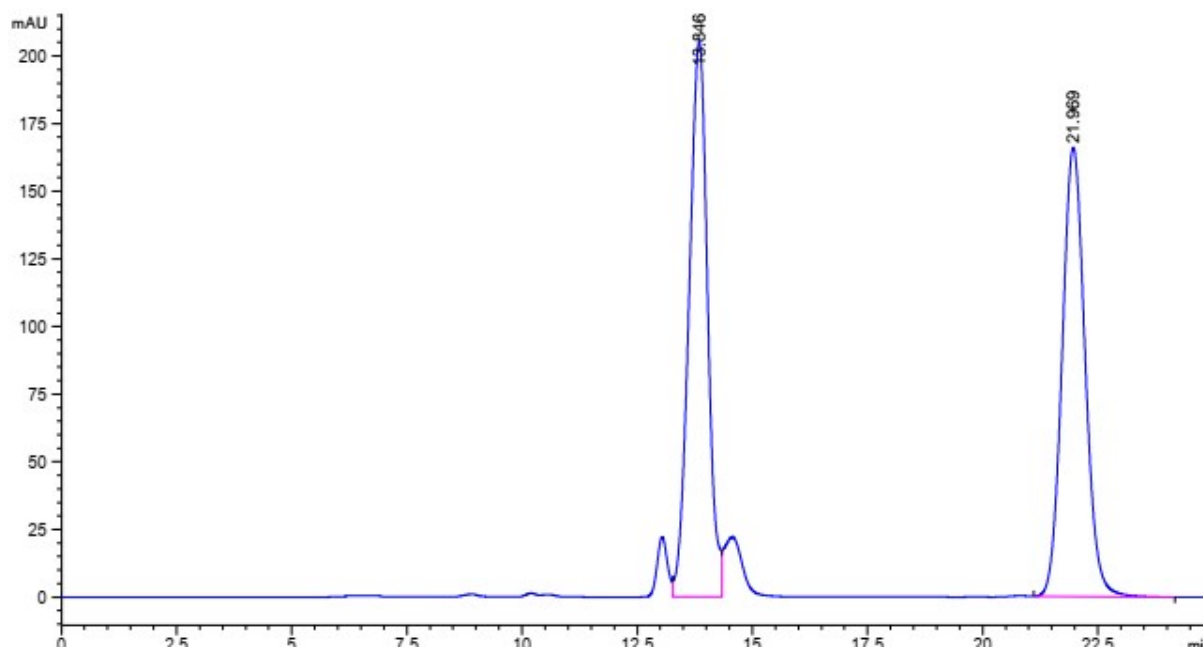
enan-**3bf**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 95:5, 0.5 mL/min, 254 nm, $t_R(\text{major}) = 14.634$ min, $t_R(\text{minor}) = 16.468$ min, 98.3% *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.634	BV	0.4548	1.84563e4	615.48553	99.1277
2	16.468	VB	0.4883	162.41096	4.67544	0.8723

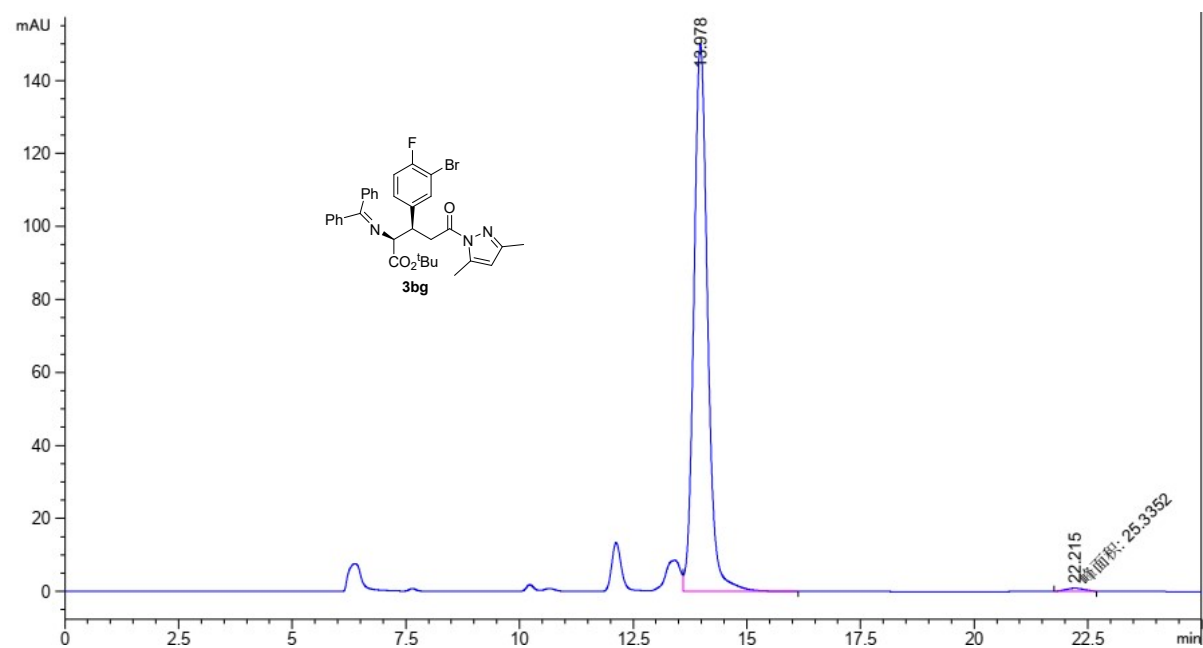
S104

rac-**3bg**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 95:5, 0.5 mL/min, 254 nm, t_R (major) = 13.846 and 21.969 min, *dr* > 99:1.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.846	VV	0.4283	5727.67773	205.40201	50.0203
2	21.969	BB	0.5351	5723.01807	166.03745	49.9797

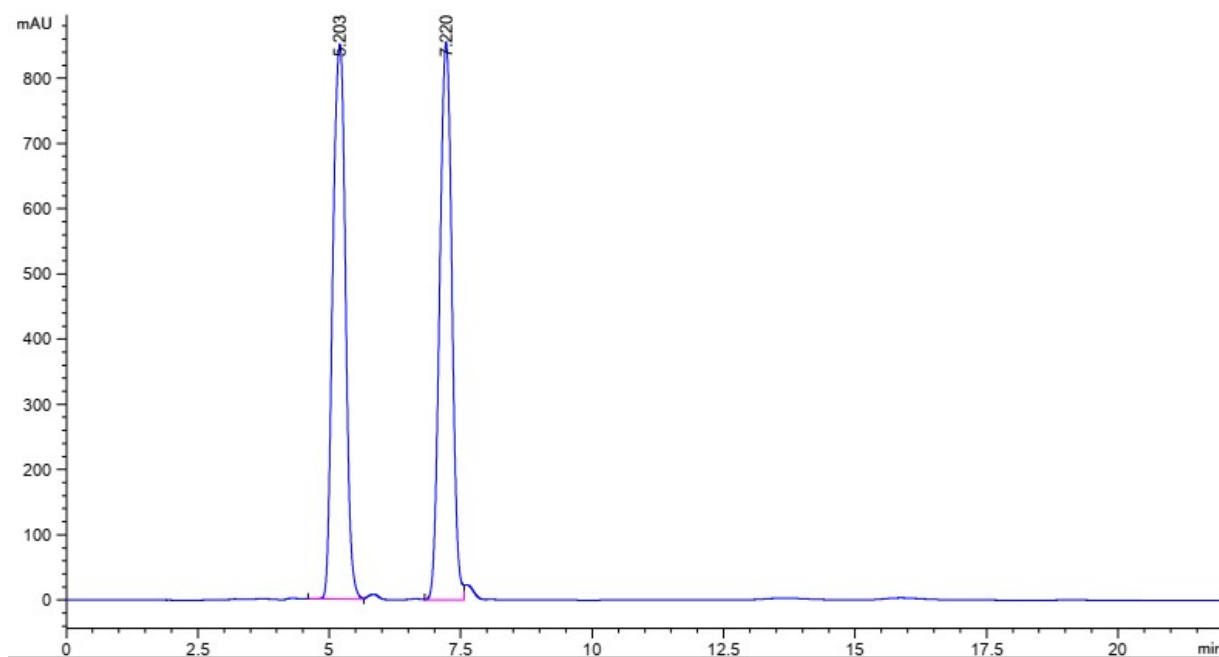
enan-**3bg**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 95:5, 0.5 mL/min, 254 nm, t_R (major) = 13.978 min, t_R (minor) = 22.215 min, 98.4% *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.978	VB	0.3226	3142.62695	149.90631	99.2003
2	22.215	MM	0.4925	25.33522	8.57378e-1	0.7997

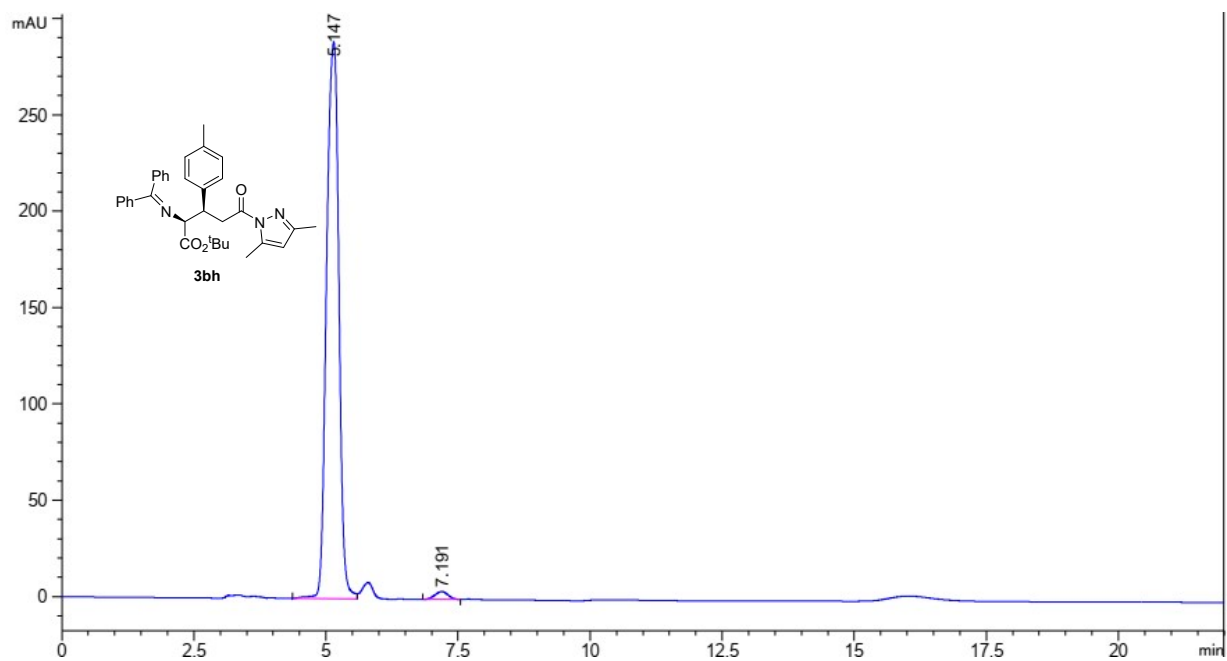
S105

rac-**3bh**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 5.203$ and 7.220 min, $dr > 99:1$.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.203	BV	0.2741	1.42282e4	850.63849	50.5148
2	7.220	VV	0.2612	1.39382e4	854.89087	49.4852

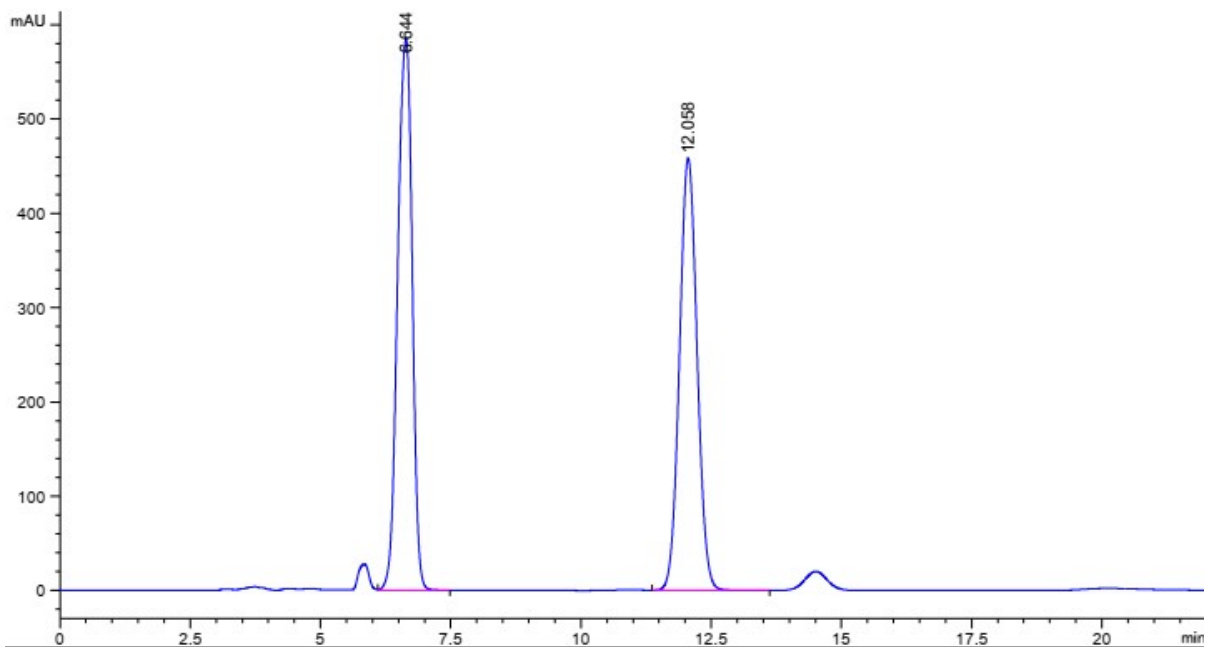
enan-**3bh**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 5.147$ min, $t_R(\text{minor}) = 7.191$ min, 97% *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.147	BV	0.2628	4676.67383	288.93625	98.5326
2	7.191	BB	0.2683	69.64677	4.07631	1.4674

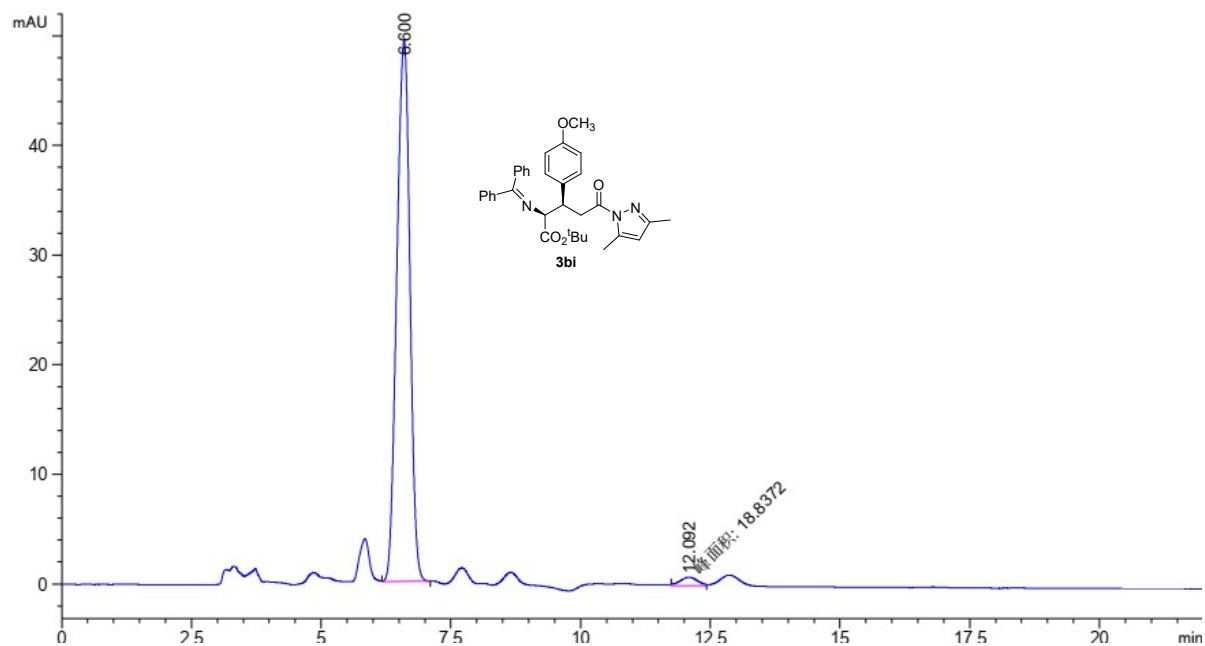
S106

rac-**3bi**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, t_R (major) = 6.644 and 12.058 min, dr > 99:1.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.644	VB	0.3143	1.13511e4	585.17999	51.2293
2	12.058	BB	0.3681	1.08063e4	458.23309	48.7707

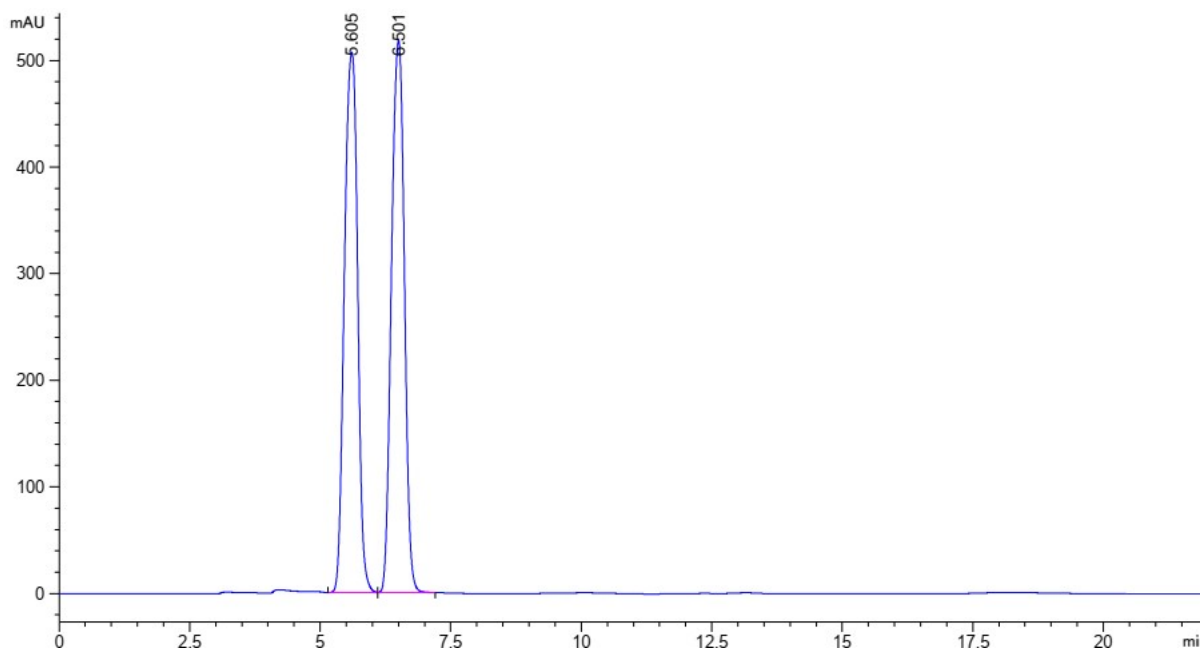
enan-3bi: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 6.600$ min, $t_R(\text{minor}) = 12.092$ min, 96% *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.600	VB	0.2824	863.90839	49.31248	97.8661
2	12.092	MM	0.4006	18.83720	7.83677e-1	2.1339

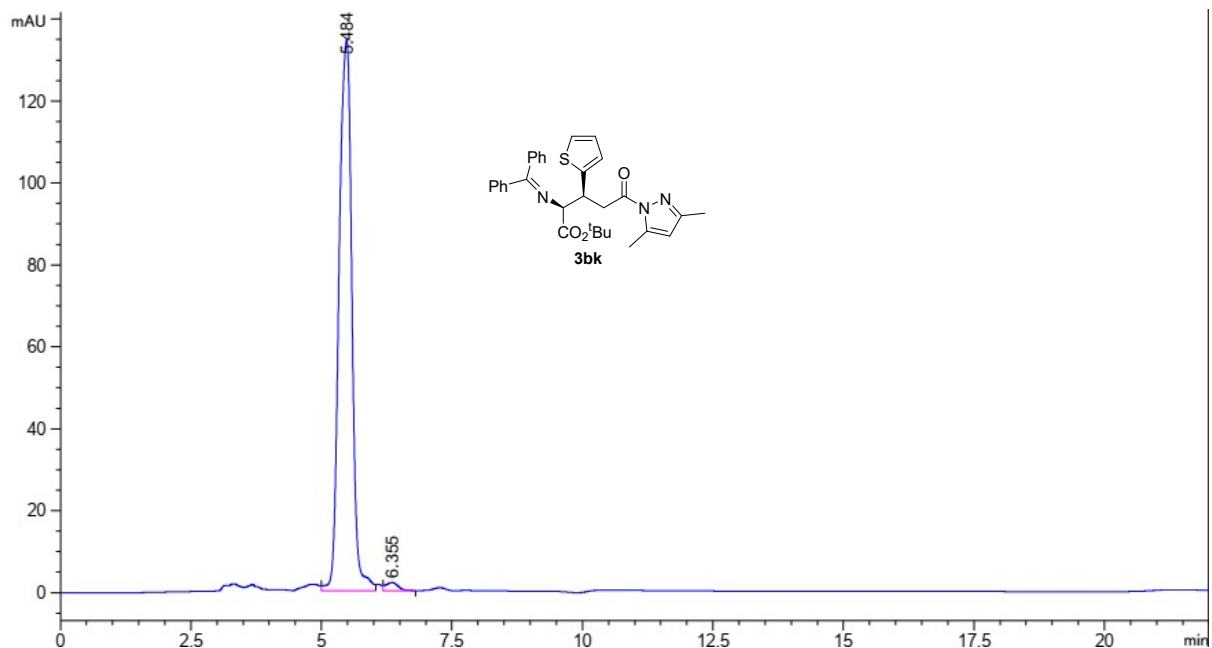
S107

rac-3bk: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 5.605$ and 6.501 min, *dr* > 99:1.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.605	BB	0.2854	8878.02051	506.74911	50.0265
2	6.501	BB	0.2777	8868.62500	517.99438	49.9735

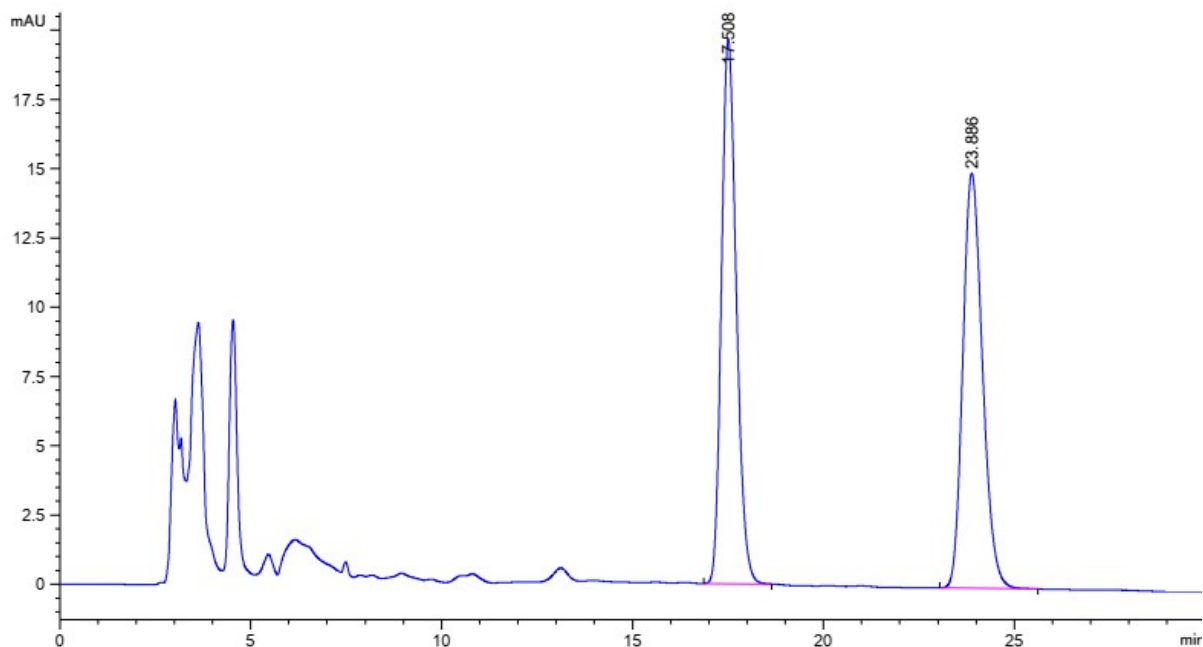
enan-3bk: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm, $t_R(\text{major}) = 5.484$ min, $t_R(\text{minor}) = 6.355$ min, 97.2% *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.484	VV	0.2738	2280.42822	134.51379	98.6218
2	6.355	VB	0.2503	31.86747	1.95354	1.3782

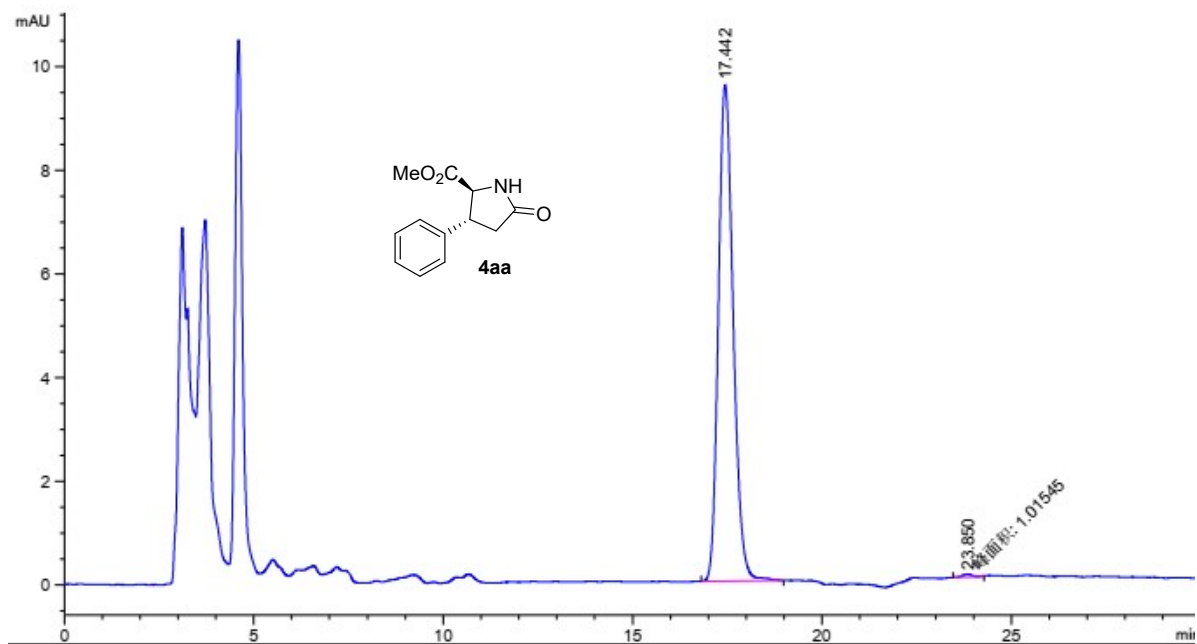
S108

rac-4aa: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_R = 17.508$ and 23.886 min.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.508	BB	0.4194	530.75739	19.62968	49.7764
2	23.886	BB	0.5542	535.52612	14.97653	50.2236

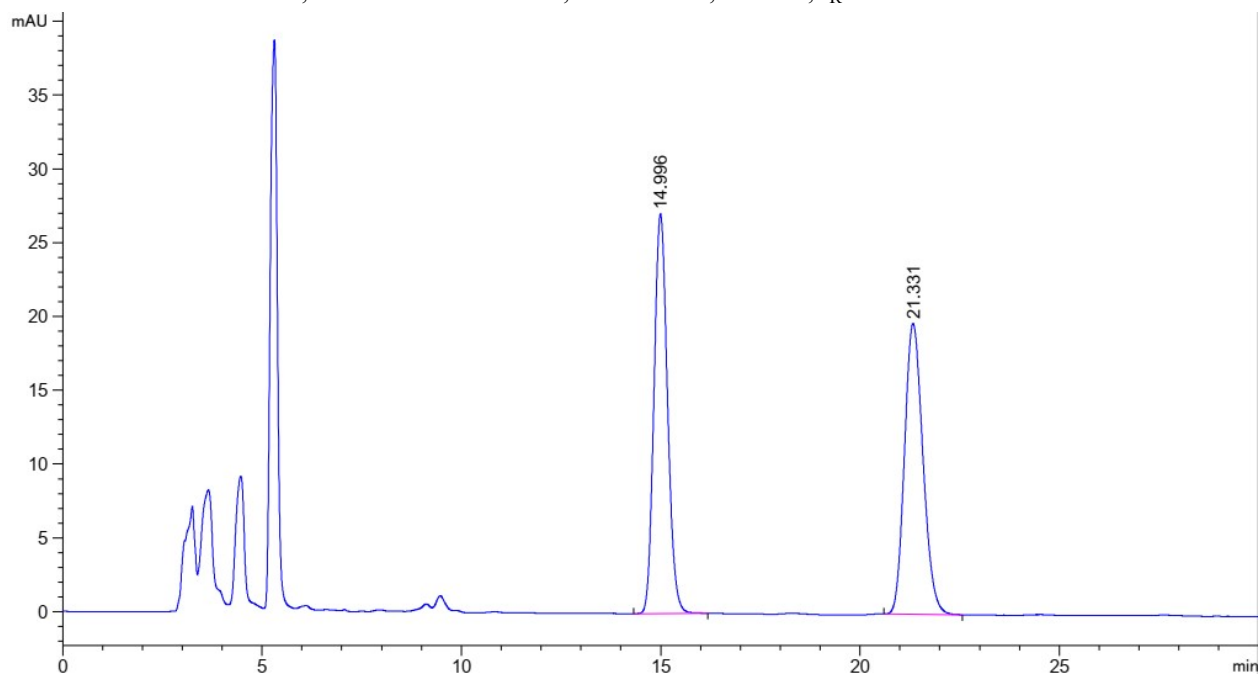
enan-4aa: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_R(\text{major}) = 17.442$ min, $t_R(\text{minor}) = 23.850$ min, 99.2% *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.442	BB	0.4181	259.46307	9.57684	99.6102
2	23.850	MM	0.3192	1.01545	5.30211e-2	0.3898

S109

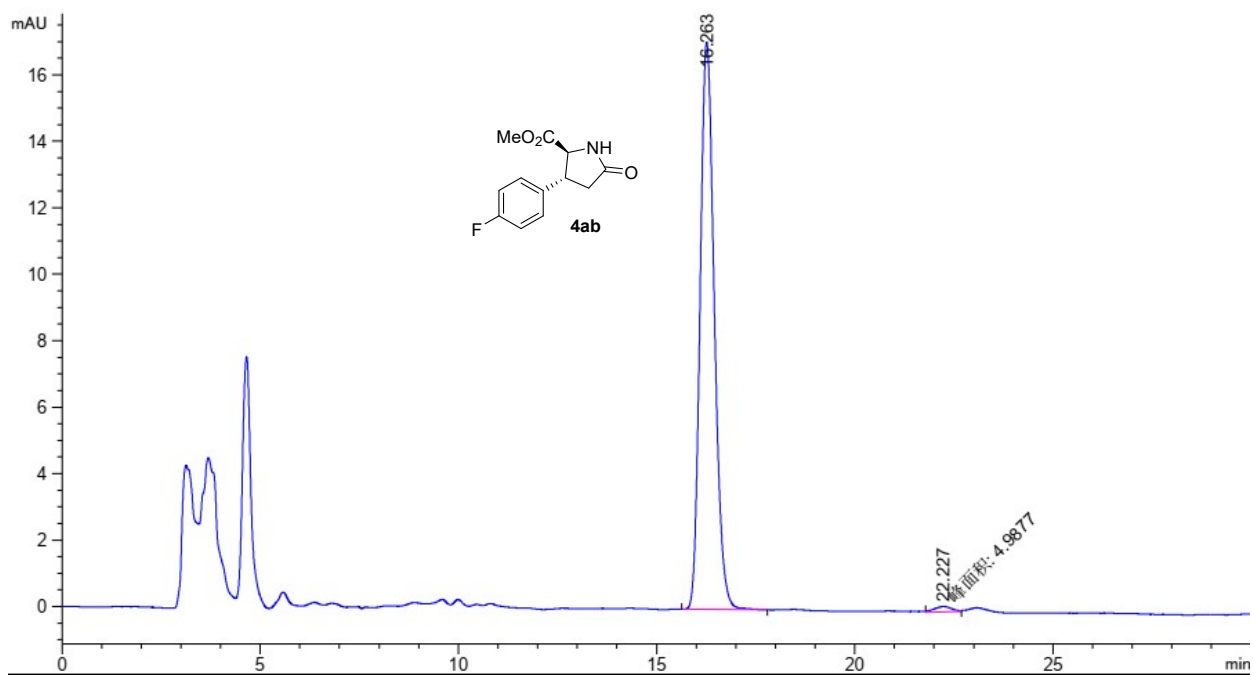
rac-4ab: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_R = 14.996$ and 21.331 min.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.996	BB	0.3652	636.78210	27.09485	50.1329
2	21.331	BB	0.5000	633.40680	19.70706	49.8671

enan-4ab: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_R(\text{major}) = 16.263$ min, $t_R(\text{minor}) = 22.227$ min.

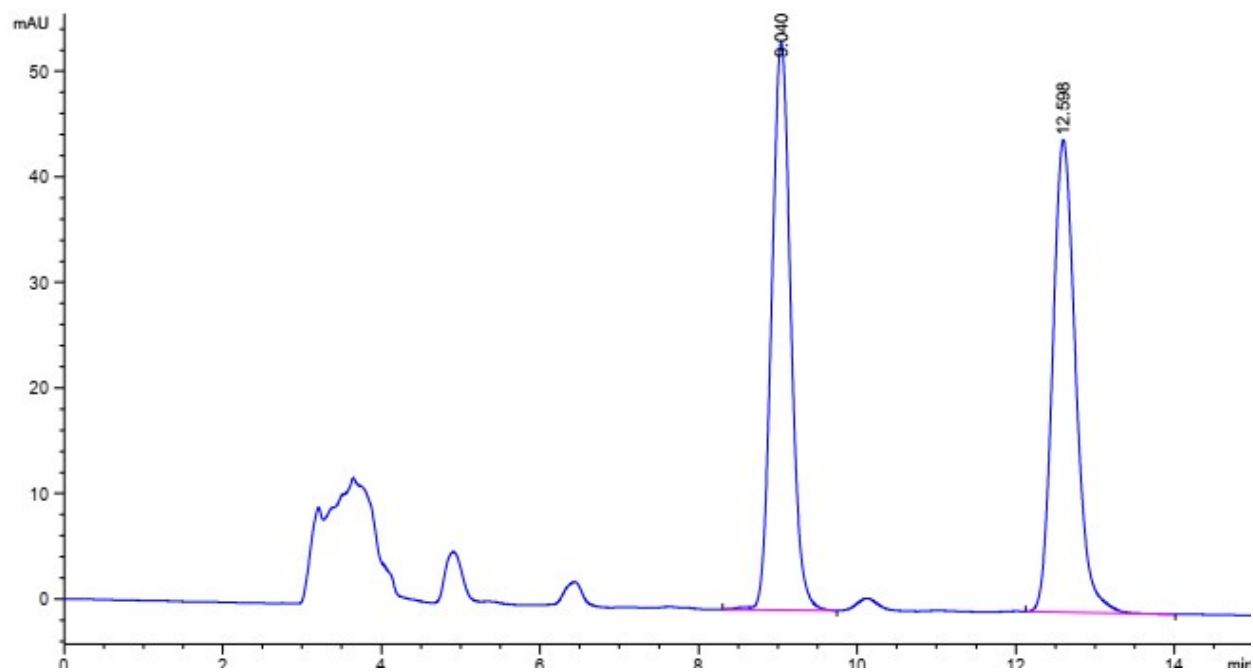
min, 97.5% ee.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.263	BB	0.3860	424.59796	17.08199	98.8390
2	22.227	MM	0.5164	4.98770	1.60961e-1	1.1610

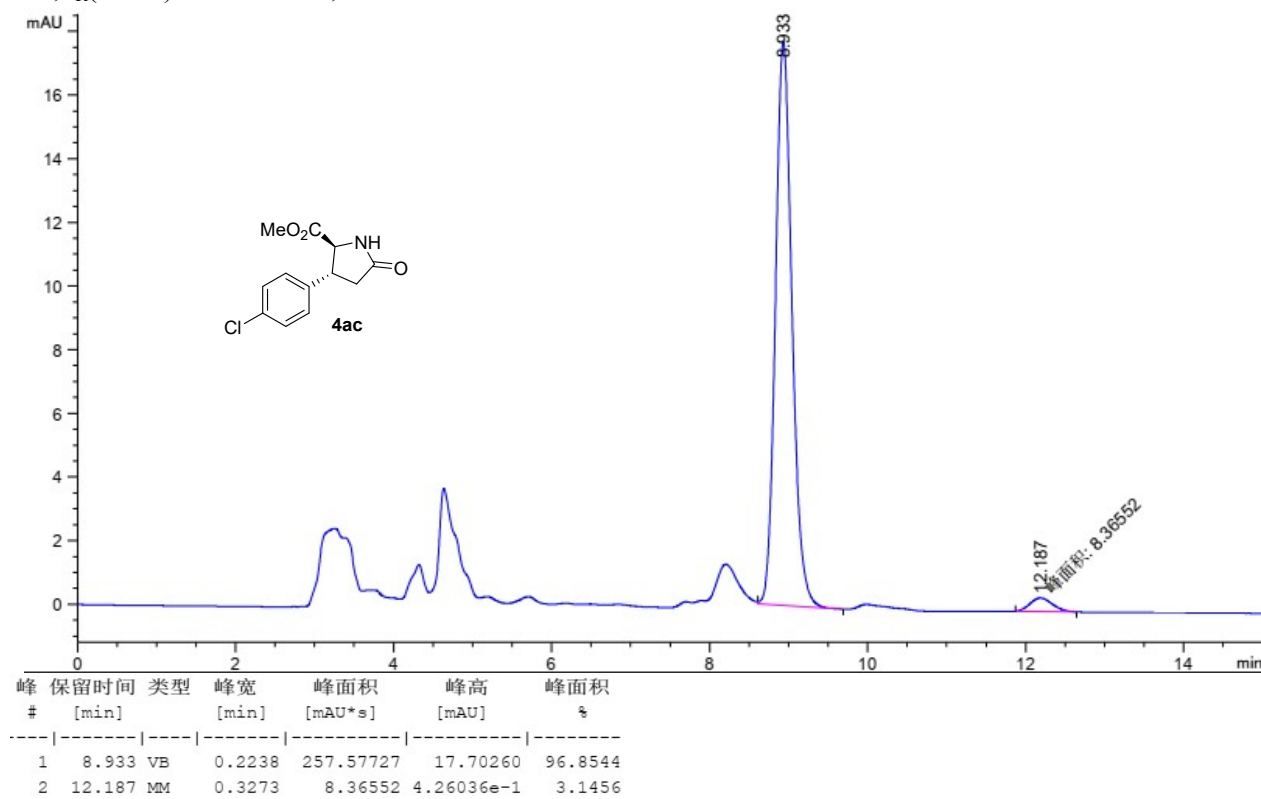
S110

rac-4ac: ChiralPak AD-H, *n*-hex/*i*-PrOH = 80:20, 1.0 mL/min, 230 nm, t_R = 8.528 and 11.827 min.



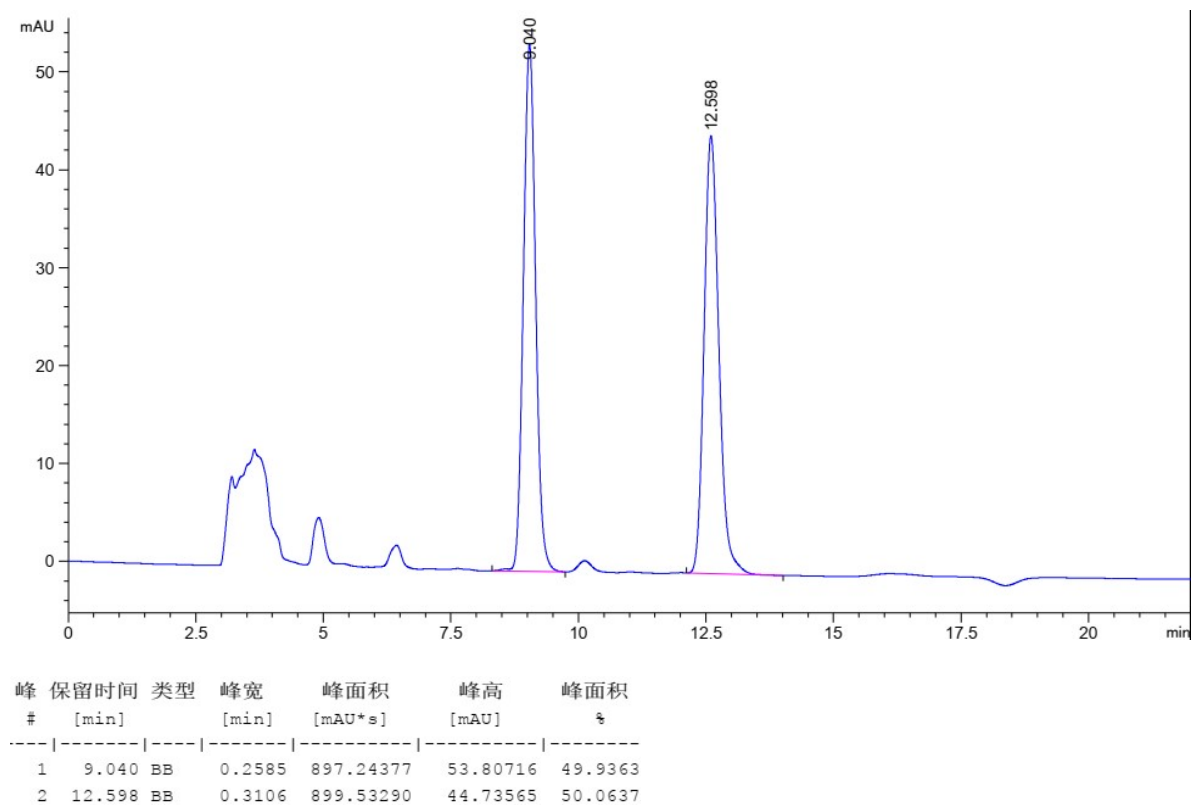
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.528	BB	0.2077	2322.38770	171.78299	49.2872
2	11.827	BB	0.2913	2389.55859	126.55750	50.7128

enan-**4ac** (by using *S*-CSB cat.): ChiralPak AD-H, *n*-hex/*i*-PrOH = 80:20, 1.0 mL/min, 230 nm, $t_R(\text{major}) = 8.933$ min, $t_R(\text{minor}) = 12.187$ min, 94% *ee*.

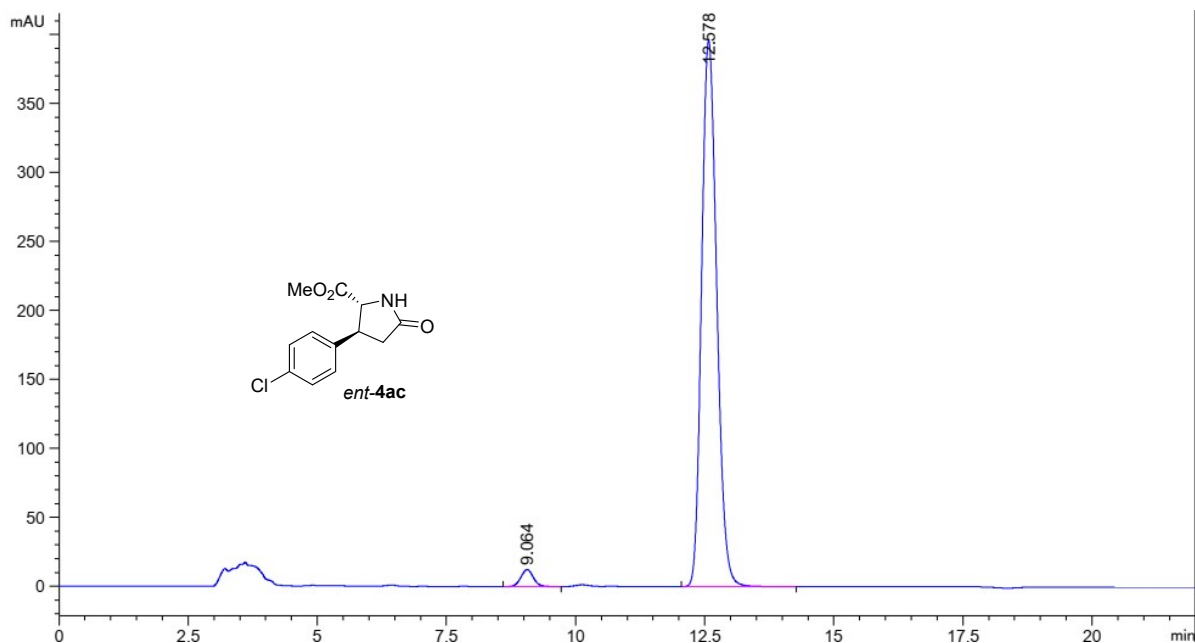


S111

rac-**4ac**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 80:20, 1.0 mL/min, 230 nm, $t_R = 9.040$ and 12.598 min.



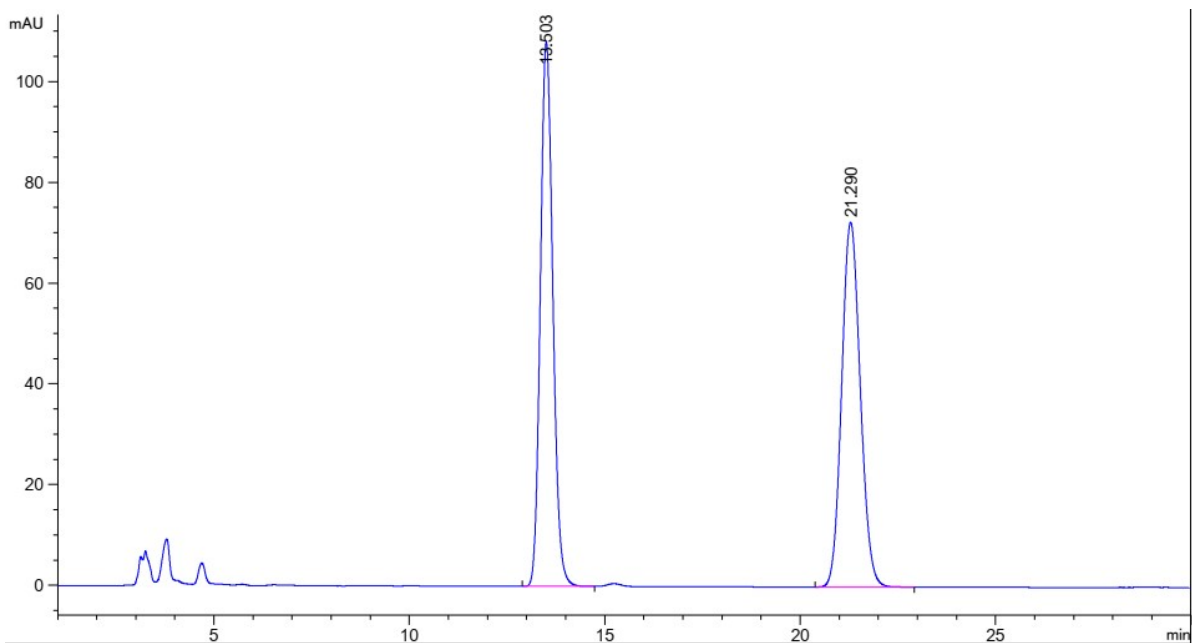
ent-**4ac** (by using *R*-CSB cat.): ChiralPak AD-H, *n*-hex/*i*-PrOH = 80:20, 1.0 mL/min, 230 nm, $t_R(\text{major}) = 12.578$ min, $t_R(\text{minor}) = 9.064$ min, 95.1% *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.064	BB	0.2577	204.56171	12.31980	2.4666
2	12.578	BB	0.3202	8088.60303	396.22943	97.5334

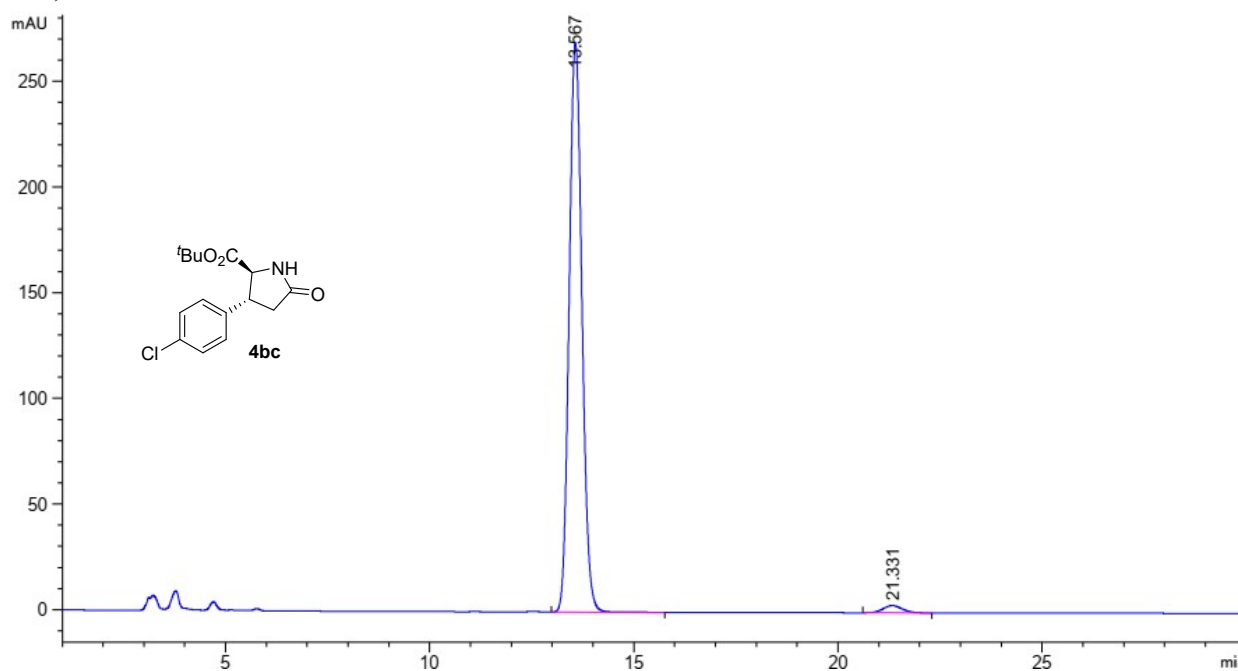
S112

rac-**4bc**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_R = 13.503$ and 21.290 min.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.503	BB	0.3438	2398.82495	108.12263	50.0126
2	21.290	BB	0.5153	2397.61426	72.41576	49.9874

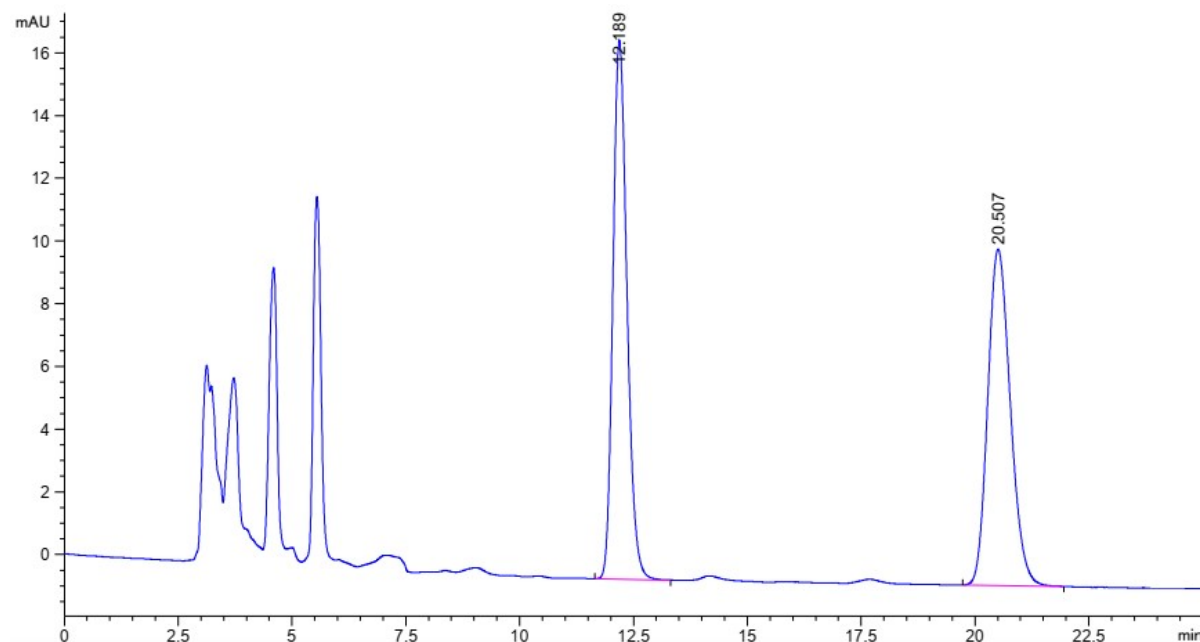
enan-4bc: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_R(\text{major}) = 13.567$ min, $t_R(\text{minor}) = 21.331$ min, 96.2% *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.567	BB	0.33399	5859.35010	269.26233	98.1228
2	21.331	BB	0.4975	112.09694	3.43681	1.8772

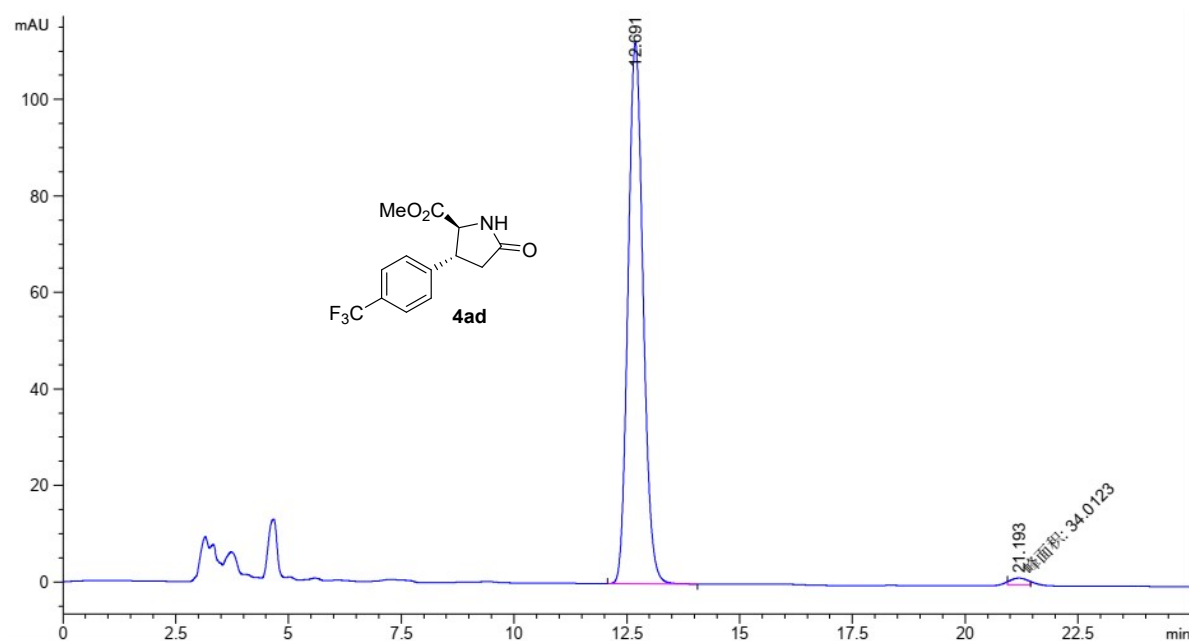
S113

rac-4ad: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_R = 12.189$ and 20.507 min.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.189	BB	0.3323	368.69989	17.18773	49.9789
2	20.507	BB	0.5294	369.01190	10.72428	50.0211

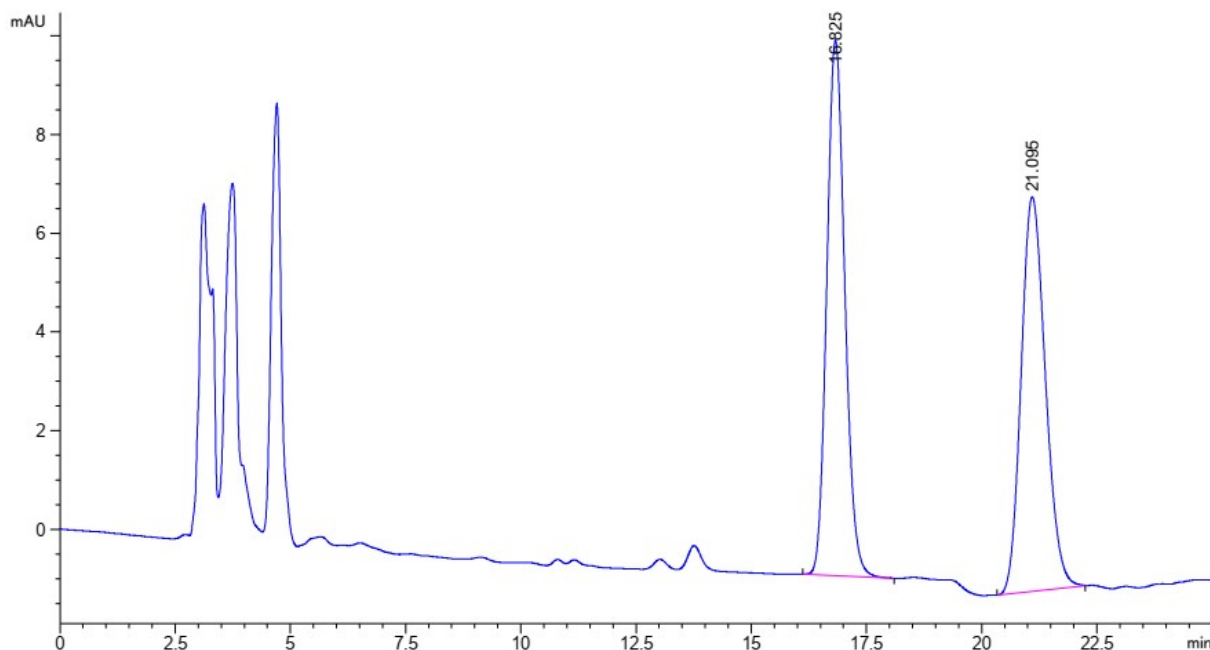
enan-4ad: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_R(\text{major}) = 12.691$ min, $t_R(\text{minor}) = 21.193$ min, 97.4% *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.691	BB	0.3623	2607.47803	112.11224	98.7124
2	21.193	MM	0.4095	34.01228	1.38419	1.2876

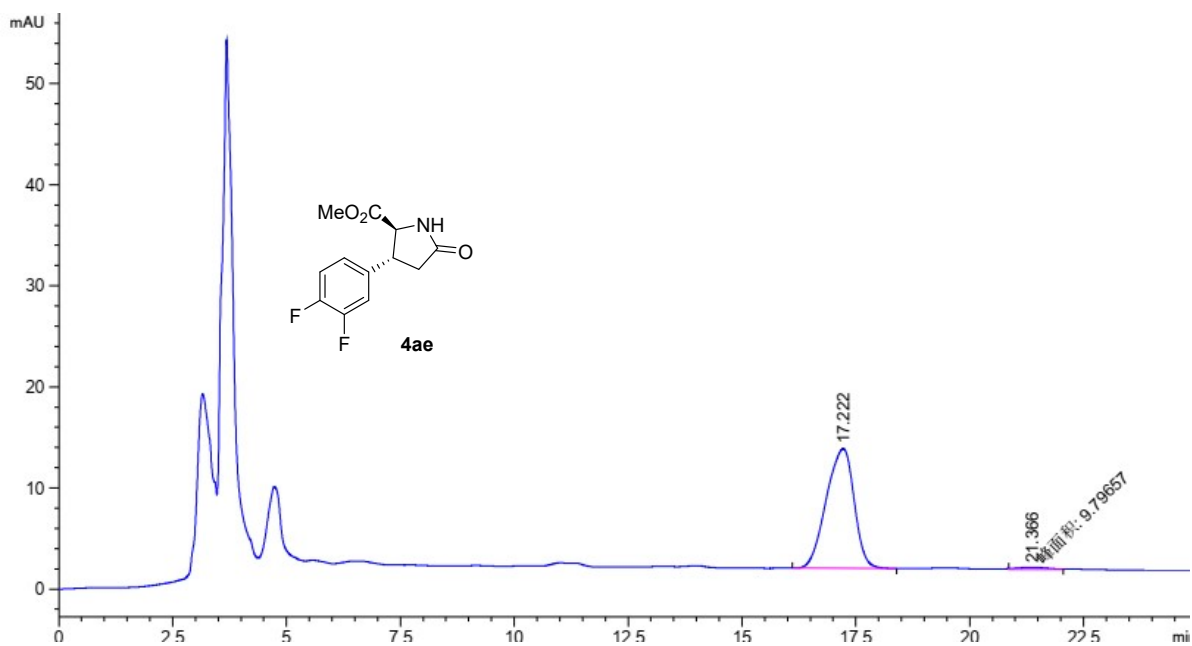
S114

rac-4ae: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_R = 16.825$ and 21.095 min.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.825	BB	0.4228	294.54974	10.84710	50.2610
2	21.095	BB	0.5607	291.49072	7.98931	49.7390

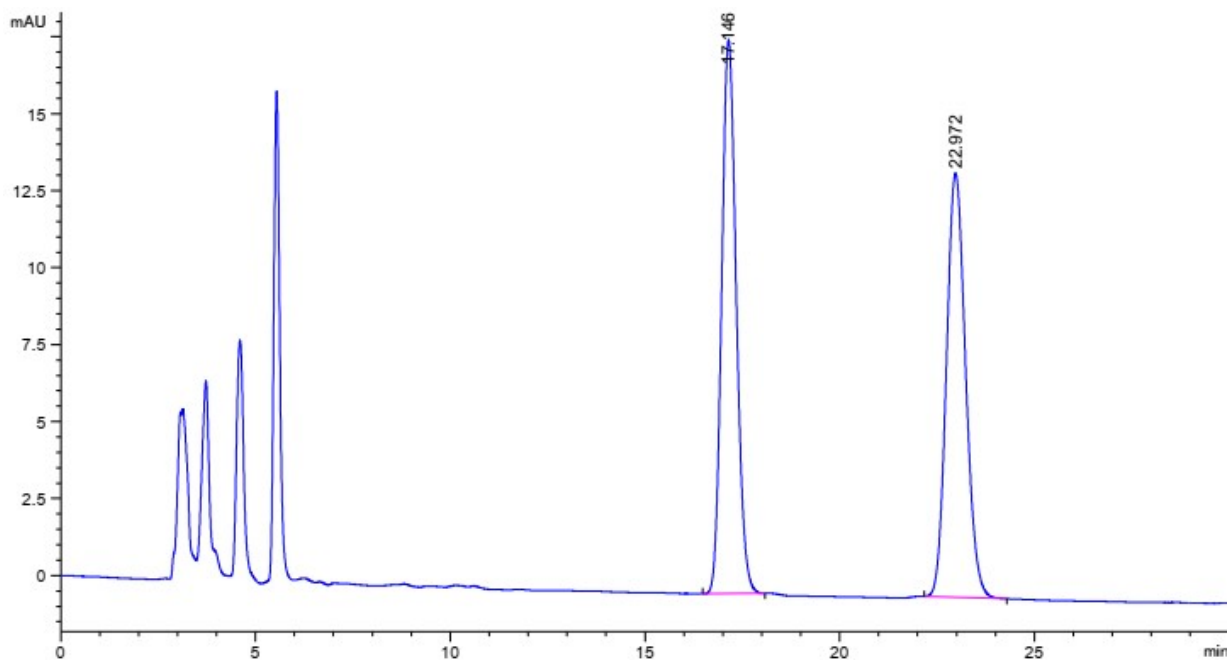
enan-4ae: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_R = 17.222$ and 21.366 min, 96.2% *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.222	BB	0.6840	503.33582	11.83975	98.0908
2	21.366	MM	0.7621	9.79657	2.14259e-1	1.9092

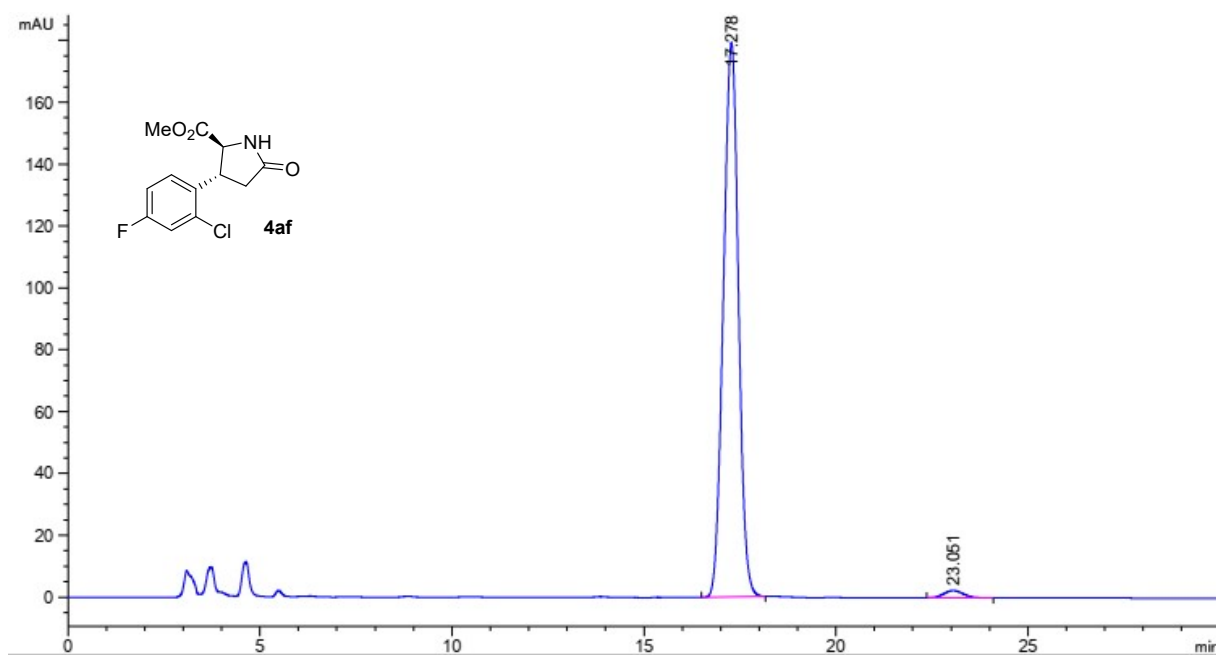
S115

rac-**4af**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_R = 17.146$ and 22.972 min.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.146	BB	0.4031	467.28745	17.98620	49.9150
2	22.972	BB	0.5302	468.87970	13.77116	50.0850

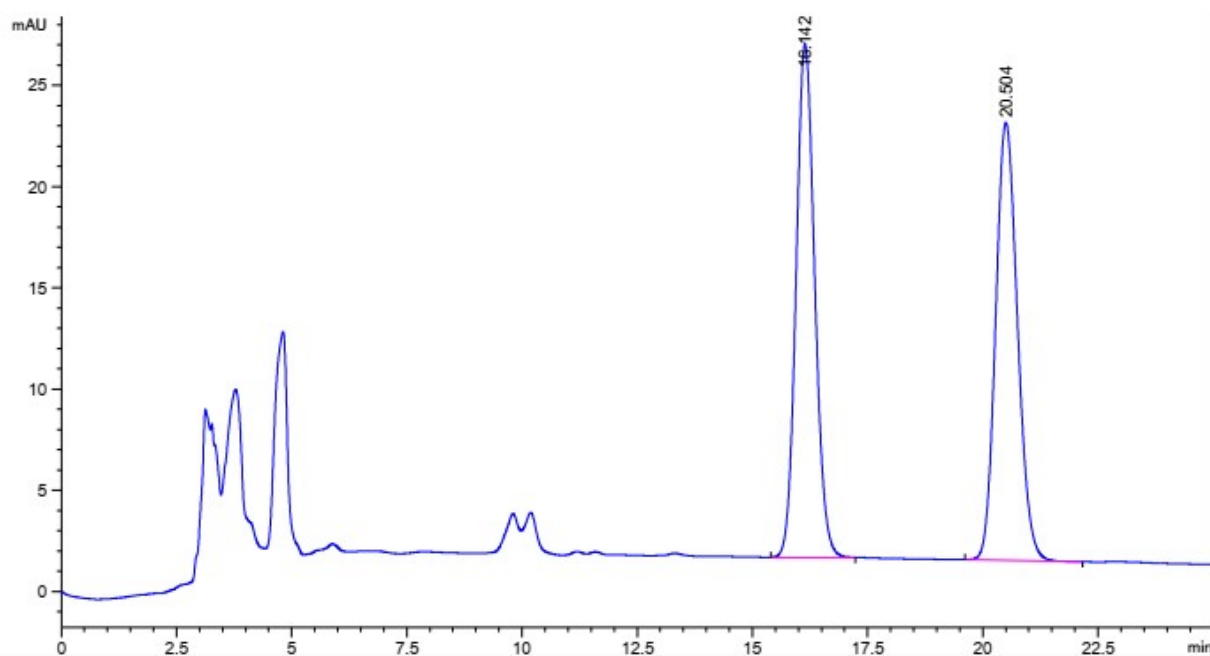
enan-4af: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_R = 17.278$ and 23.051 min, 96.7% *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.278	BB	0.4245	4864.03809	179.28975	98.3405
2	23.051	BB	0.5243	82.08263	2.35685	1.6595

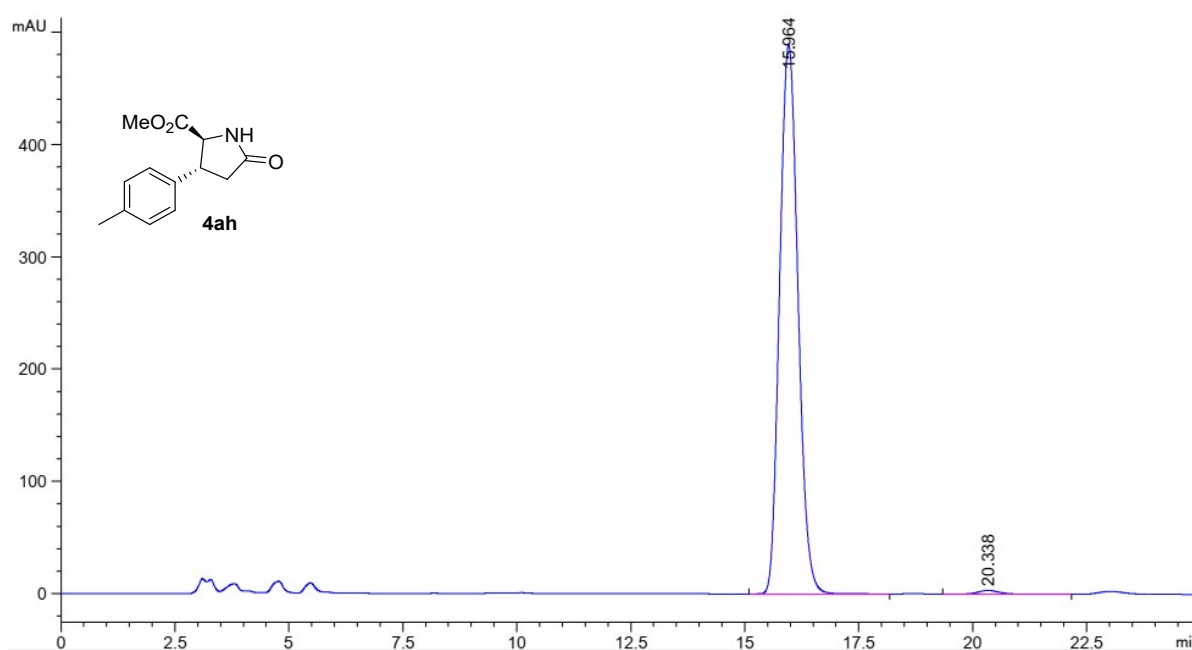
S116

rac-4ah: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, $t_R = 16.142$ and 20.504 min.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.142	BB	0.4345	711.88556	25.36188	50.0059
2	20.504	BB	0.5110	711.71667	21.62458	49.9941

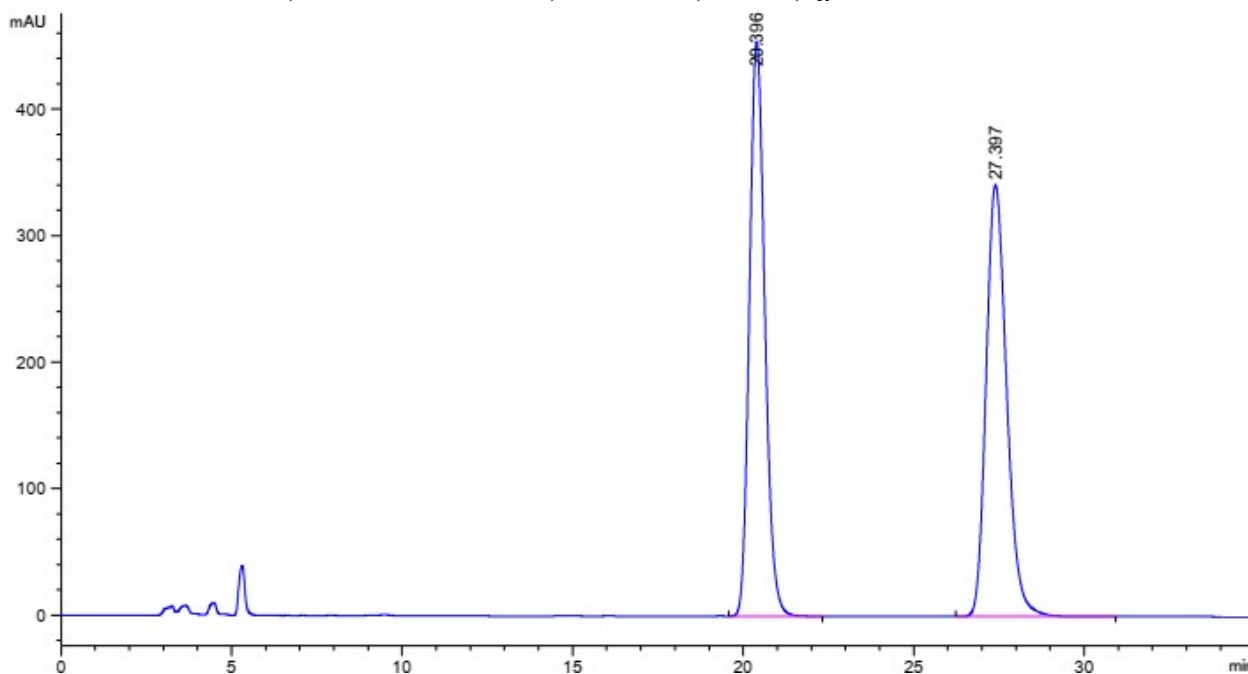
enan-4ah: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, t_R = 15.964 and 20.338 min, 98.4% *ee*.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.964	BB	0.4432	1.36714e4	489.01108	99.2089
2	20.338	BB	0.5016	109.01885	3.29001	0.7911

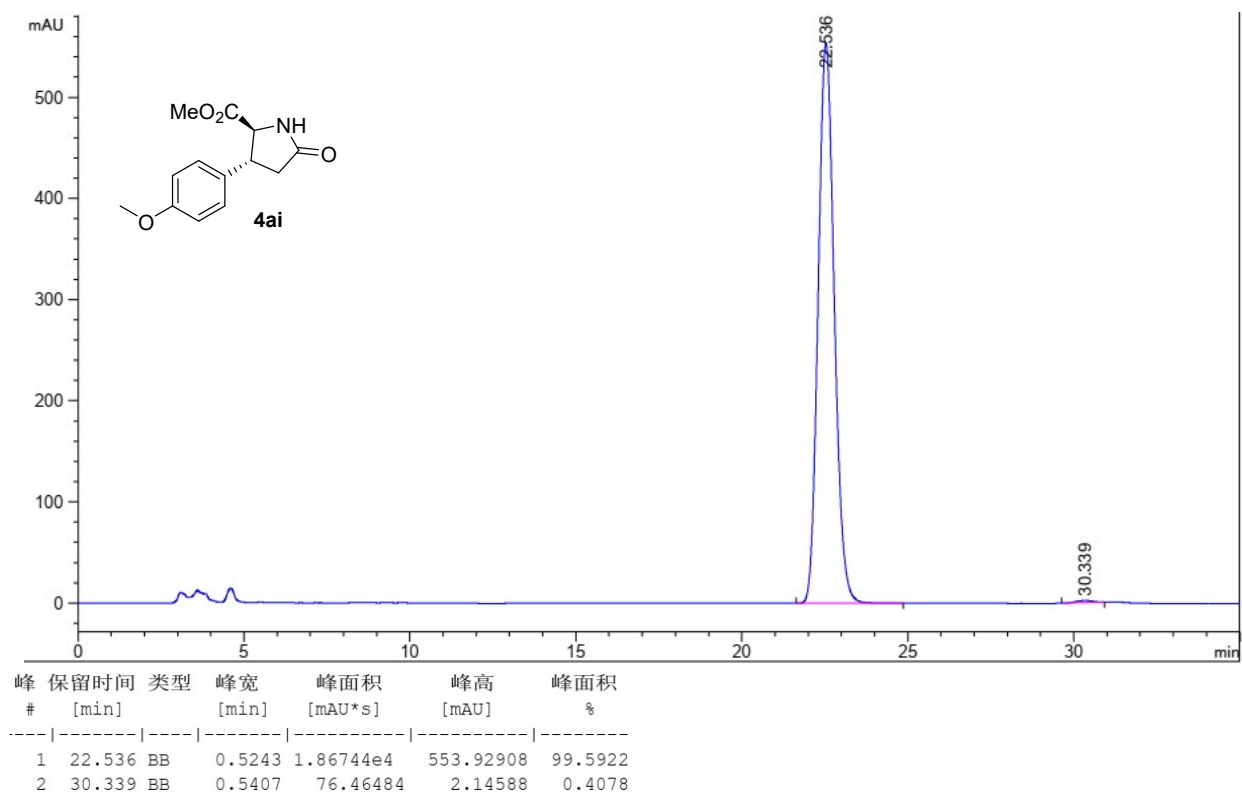
S117

rac-4ai: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, t_R = 20.396 and 27.397 min.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.396	BB	0.4865	1.42298e4	454.20392	49.9528
2	27.397	BB	0.6484	1.42566e4	341.28345	50.0472

enan-**4ai**: ChiralPak AD-H, *n*-hex/*i*-PrOH = 90:10, 1.0 mL/min, 230 nm, t_R = 22.536 and 30.339 min, 99.2% *ee*.



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8. References

- [1] T. Ooi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.* 1999, **121**, 6519-6520.
- [2] K. Itoh, S. Kanemasa, *J. Am. Chem. Soc.* 2002, **124**, 13394-13395.
- [3] J. S. Bandar, A. Barthelme, A.Y. Mazori, T. H. Lambert, *Chem. Sci.* 2015, **6**, 1537-1547.
- [4] Y-J. Bai, M-L. Cheng, X-H. Zheng, S-Y. Zhang, P-A. Wang, *Chem Asian J.* 2022, **17**, e202200131.

