Supporting Information

A New Trifluoromethylated Sulfonamide Phosphine Ligand for Ag(I)-Catalyzed Enantioselective [3+2] Cycloaddition of Azomethine Ylides

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Contents

1. General Information

All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. ^{1}H NMR spectra, ^{19}F NMR spectra, ^{31}P NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 300, 400 and 500 MHz spectrometer in $CDCl_3$. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quarte, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz), and intergration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). The substrates (*R*, *Rs*)-**M1**, **M7,** (*S*, *Rs*)-**M1**, **M3**, **M4**,[1] **1b-1e**,[2] **2a-2p**,[3] **4a-4f**,[4] **6**[2] were synthesized according to published procedures. The spectral data of the substrates were consisted with that reported in the literature. The enantionmeric excesses of the products were determined by chiral stationary phase HPLC using a Chiralpak AS-H, AD-H, IE.

2. General Procedure for the Synthesis of products 3ab-3ak, 3ca-3ea, 5ab-5ap, 5ca-5fa, 7ab-7ap, 8

Typical procedure for asymmetric silver-catalyzed cycloaddition of azomethine ylides with maleimides, cyclopentene-1,3-diones, and *N*-(2-*t*-butylphenyl)maleimide.

General Procedure A

A solution of (*S,Rs*)-**M8** (5.5 mol%) and AgOAc (5 mol%) in Xylene (2 mL) was stirred at room temperature for 2 h. The reaction mixture was cooled to -30 °C and then the imino ester **2** (0.15 mmol), Cs_2CO_3 (0.045 mmol) and maleimide **1** (0.165 mmol) were added sequentially. Following complete consumption of the imino ester **2**, the solvent was removed under reduced pressure. The crude product was then purified

by flash column chromatography on silica gel to afford the desired product.

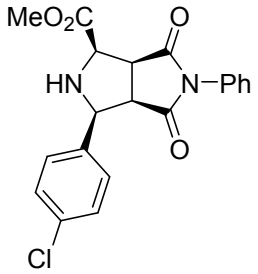
General Procedure B

A solution of (*S,Rs*)-**M8** (5.5 mol%) and AgOAc (5 mol%) in Xylene (2 mL) was stirred at room temperature for 2 h. The reaction mixture was cooled to -30 °C and then the imino ester **2** (0.15 mmol), Cs_2CO_3 (0.045 mmol) and cyclo-pentenedione **4** (0.165 mmol) were added sequentially. Following complete consumption of the imino ester **2**, the solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel to afford the desired product. Configuration of the **5** was determined by ^1H, ^{13}C NMR, HPLC Spectra, in comparison with the literature, see: [4].

General Procedure C

A solution of (*S,Rs*)-**M8** (5.5 mol%) and AgOAc (5 mol%) in Xylene (2 mL) was stirred at room temperature for 2 h. The reaction mixture was cooled to -30 °C and then the imino ester **2** (0.15 mmol), Cs_2CO_3 (0.045 mmol) and *N*-(2-*t*-butylphenyl)maleimide **6** (0.165 mmol) were added sequentially. Following complete consumption of the imino ester **2**, the solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel to afford the desired product. Configuration of the **7** was determined by ^1H, ^{13}C NMR, HPLC Spectra, in comparison with the literature, see: [5].

3.1 Synthesis of methyl (1R,3S,3aR,6aS)-3-(4-chlorophenyl)-4,6-dioxo-5-phenyloctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3ab**).

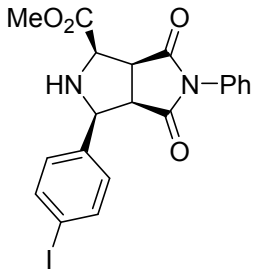


3ab

Prepared according to general procedure **A** from N-Phenylmaleimide **1a** (28.6 mg, 0.165 mmol) and imino ester **2b** (31.7 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 1:1) afforded the product **3ab** as a white solid (67.1 mg, 99% yield) and 91% *ee*. Mp: 155-156 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 4 H), 7.33 (t, *J* = 7.1 Hz, 3 H), 7.13 (d, *J* = 7.5 Hz, 2 H), 4.55 (dd, *J* = 8.5, 4.9 Hz, 1 H), 4.12-4.10 (m, 1 H), 3.86 (s, 3 H), 3.71 (t, *J* = 7.2 Hz, 1 H), 3.53 (t, *J*

= 8.2 Hz, 1 H), 2.48 (s, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.89, 173.44, 169.88, 135.24, 134.03, 131.44, 129.05, 128.62, 128.55, 128.44, 126.00, 63.38, 61.71, 52.31, 49.06, 47.94. ESI-MS calculated for $C_{20}H_{17}ClN_2NaO_4$: m/z (%): 407.0769 ($M+H^+$), found: 407.0774. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 220 nm); minor enantiomer tr = 18.5 min, major enantiomer tr = 41.4 min. $[\alpha]_D^{25}$ = -135.2 (*c* = 0.25, $CHCl_3$).

3.2 Synthesis of methyl (1R,3S,3aR,6aS)-3-(4-iodophenyl)-4,6-dioxo-5-phenyloctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3ac**).

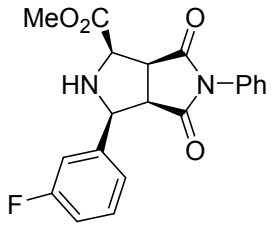


3ac

Prepared according to general procedure **A** from N-Phenylmaleimide **1a** (28.6 mg, 0.165 mmol) and imino ester **2c** (45.5 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 1:1) afforded the product **3ac** as a white solid (64.8 mg, 91% yield) and 90% *ee*. Mp: 209-210 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 4.49 (d, *J* = 8.6 Hz, 1H), 4.09 (d, *J* = 6.6 Hz, 1H), 3.85 (s, 1H), 3.68 (t, *J* = 7.2 Hz, 1H), 3.51 (t, *J* = 8.2 Hz, 1H), 2.46 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.85, 173.41, 169.86, 137.43, 136.46, 131.41, 129.03, 129.00, 128.53, 125.98, 93.95, 63.49, 61.69, 52.28, 48.97, 47.89. ESI-MS calculated for $C_{20}H_{18}IN_2O_4$: m/z (%): 477.0306 ($M+H^+$), found: 477.0316. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 220 nm); minor enantiomer tr = 20.2 min, major enantiomer tr = 47.7 min. $[\alpha]_D^{25}$ = -117.2 (*c* = 0.25, $CHCl_3$).

3.3 Synthesis of methyl (1R,3S,3aR,6aS)-3-(3-fluorophenyl)-4,6-dioxo-5-

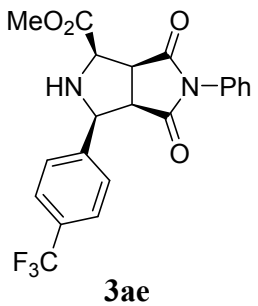
phenyloctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3ad**).



3ad

Prepared according to general procedure **A** from N-Phenylmaleimide **1a** (28.6 mg, 0.165 mmol) and imino ester **2d** (29.3 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 1:1) afforded the product **3ad** as a white solid (46.7 mg, 85% yield) and 90% *ee*. Mp: 154-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.6 Hz, 2 H), 7.34-7.30 (m, 2 H), 7.21 (dd, *J* = 14.4, 8.9 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 6.99 (t, *J* = 8.2 Hz, 1 H), 4.56 (dd, *J* = 8.5, 4.8 Hz, 1 H), 4.12-4.09 (m, 1 H), 3.86 (s, 3 H), 3.70 (t, *J* = 7.2 Hz, 1 H), 3.54 (t, *J* = 8.2 Hz, 1H) , 2.51 (s, 1 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.48 - -112.56 (m).^{13}C NMR (126 MHz, $CDCl_3$) δ 174.90, 173.41, 169.84, 162.82 (d, *J* = 246.3 Hz), 139.47 (d, *J* = 7.2 Hz), 131.46, 129.96 (d, *J* = 8.2 Hz), 129.04, 128.54, 126.05, 122.77 (d, *J* = 2.8 Hz), 115.27 (d, *J* = 21.1 Hz), 114.09 (d, *J* = 22.4 Hz), 63.37 (d, *J* = 1.7 Hz), 61.65, 52.29, 49.08, 47.93. ESI-MS calculated for $C_{20}H_{17}FN_2NaO_4$: m/z (%): 391.1065 ($M+H^+$), found: 391.1072. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 220 nm); minor enantiomer tr = 14.9 min, major enantiomer tr = 31.6 min. $[\alpha]_D^{25}$ = -84.9 (*c* = 0.25, $CHCl_3$).

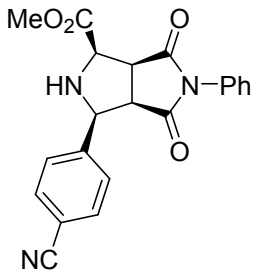
3.4 Synthesis of methyl (1R,3S,3aR,6aS)-4,6-dioxo-5-phenyl-3-(4-(trifluoromethyl)phenyl)octahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3ae**).



3ae

Prepared according to general procedure **A** from N-Phenylmaleimide **1a** (28.6 mg, 0.165 mmol) and imino ester **2e** (36.8 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 1:1) afforded the product **3ae** as a white solid (58.5 mg, 97% yield) and 91% *ee*. Mp: 122-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (q, *J* = 8.4 Hz, 4 H), 7.40 (t, *J* = 7.4 Hz, 2 H), 7.33 (t, *J* = 7.3 Hz, 1 H), 7.12 (d, *J* = 7.5 Hz, 2 H), 4.63 (dd, *J* = 8.2, 5.1 Hz, 1 H), 4.16 – 4.14 (m, 1 H), 3.87 (s, 3 H), 3.74 (t, *J* = 7.3 Hz, 1 H), 3.60 (t, *J* = 8.2 Hz, 1 H), 2.53 (s, 1 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.44.^{13}C NMR (126 MHz, $CDCl_3$) δ 174.77, 173.30, 169.82, 140.77, 131.40, 130.43 (q, *J* = 32.4 Hz), 129.10, 128.65, 127.56, 126.02, 125.38 (q, *J* = 3.7 Hz), 123.96 (q, $J_{C,\ F}$ = 272.2 Hz), 63.54, 61.82, 52.37, 49.07, 47.86. ESI-MS calculated for $C_{21}H_{18}F_3N_2O_4$: m/z (%): 419.1213 ($M+H^+$), found: 419.1220. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 220 nm); minor enantiomer tr = 12.2 min, major enantiomer tr = 20.8 min. $[\alpha]_D^{25}$ = -78.8 (*c* = 0.25, $CHCl_3$).

3.5 Synthesis of methyl (1R,3S,3aR,6aS)-3-(4-cyanophenyl)-4,6-dioxo-5-phenyloctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3af**).

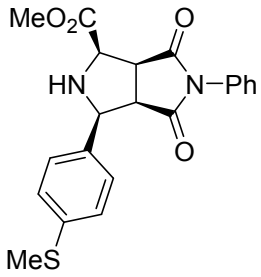


3af

Prepared according to general procedure **A** from N-Phenylmaleimide **1a** (28.6 mg, 0.165 mmol) and imino ester **2f** (30.3 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 1:1) afforded the product **3af** as a white solid (49.5 mg, 88% yield) and 98% *ee*. Mp: 109-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 20.7, 8.2 Hz, 4 H), 7.42-7.34 (m, 3 H), 7.10 (d, *J* = 7.6 Hz, 2 H), 4.63 (dd, *J* = 8.4, 4.4 Hz, 1H), 4.17-4.14 (m, 1H), 3.86 (s,3 H), 3.74 (t, *J* = 7.3 Hz, 1H), 3.60 (t, *J* = 8.2 Hz, 1H), 2.53 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.63, 173.19,

169.67, 142.27, 132.20, 131.29, 129.10, 128.69, 127.91, 125.95, 118.57, 112.14, 63.33, 61.75, 52.39, 48.99, 47.64. ESI-MS calculated for $C_{21}H_{18}N_3O_4$: m/z (%): 376.1292 ($M+H^+$), found: 376.1305. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 220 nm); minor enantiomer tr = 23.8 min, major enantiomer tr = 37.2 min. $[\alpha]_D^{25}$ = -167.6 (*c* = 0.25, $CHCl_3$).

3.6 Synthesis of methyl (1R,3S,3aR,6aS)-3-(4-(methylthio)phenyl)-4,6-dioxo-5-phenyloctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3ag**).

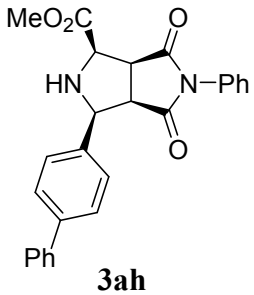


3ag

Prepared according to general procedure **A** from N-Phenylmaleimide **1a** (28.6 mg, 0.165 mmol) and imino ester **2g** (49.8 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 1:1) afforded the product **3ag** as a white solid (55.2 mg, 93% yield) and 92% *ee*. Mp: 202-203 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.32 (m, 5 H), 7.21 (d, *J* = 8.4 Hz, 2 H), 7.16-7.13 (m, 2 H), 4.51 (d, *J* = 8.7 Hz, 1 H), 4.08 (d, *J* = 6.7 Hz, 1 H), 3.86 (s, 3 H), 3.71-3.66 (m, 1 H), 3.53-3.48 (m, 1 H), 2.45 (s, 3 H), 1.26 (s, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.02, 173.57, 170.01, 138.61, 133.32, 131.53, 129.00, 128.47, 127.56, 126.23, 126.04, 63.79, 61.75, 52.27, 49.20, 48.15, 15.51. ESI-MS calculated for $C_{21}H_{20}N_2NaO_4S$: m/z (%): 419.1036 ($M+H^+$), found: 419.1042. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 254 nm); minor enantiomer tr = 26.4 min, major enantiomer tr = 59.5 min. $[\alpha]_D^{25}$ = -166.6 (*c* = 0.25, $CHCl_3$).

3.7 Synthesis of methyl (1R,3S,3aR,6aS)-3-([1,1'-biphenyl]-4-yl)-4,6-dioxo-5-

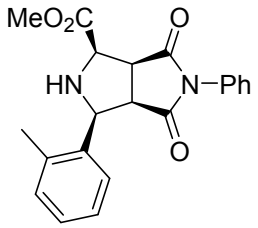
phenyloctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3ah**).



3ah

Prepared according to general procedure **A** from N-Phenylmaleimide **1a** (28.6 mg, 0.165 mmol) and imino ester **2h** (38 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 1:1) afforded the product **3ah** as a white solid (63.3 mg, 99% yield) and 98% *ee*. Mp: 244-245 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.59 (m, 4 H), 7.52 (d, *J* = 8.3 Hz, 2 H), 7.45-7.32 (m, 6 H), 7.19-7.16 (m, 2 H), 4.64 (d, *J* = 8.6 Hz, 1 H), 4.15 (d, *J* = 6.6 Hz, 1 H), 3.88 (s, 1H), 3.77-3.72 (m, 1 H), 3.63-3.57 (m, 1 H), 2.54 (s, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.04, 173.61, 170.04, 141.14, 140.56, 135.63, 131.57, 129.04, 128.69, 128.50, 127.59, 127.32, 127.13, 127.08, 126.08, 64.06, 61.89, 52.34, 49.37, 48.31. ESI-MS calculated for $C_{26}H_{22}N_2NaO_4$: m/z (%): 449.1472 ($M+H^+$), found: 449.1478. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 254 nm); minor enantiomer tr = 22.4 min, major enantiomer tr = 53.6 min. $[\alpha]_D^{25}$ = -164.8 (*c* = 0.25, $CHCl_3$).

3.8 Synthesis of methyl (1R,3S,3aR,6aS)-4,6-dioxo-5-phenyl-3-(o-tolyl)octahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3ai**).

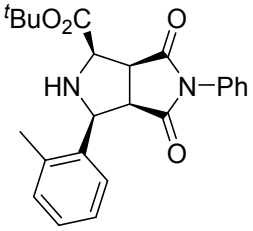


3ai

Prepared according to general procedure **A** from N-Phenylmaleimide **1a** (28.6 mg, 0.165 mmol) and imino ester **2i** (28.7 mg, 0.15 mmol) at -30 °C, after flash column

chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **3ai** as a white solid (33.9 mg, 62% yield) and 84% *ee*. Mp: 175-176 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.0, 2.5 Hz, 1 H), 7.38-7.28 (m, 3 H), 7.22-7.21 (m, 3 H), 7.07-7.03 (m, 2 H), 4.71 (dd, *J* = 8.6, 4.3 Hz, 1 H), 4.14 – 4.10 (m, 1 H), 3.88 (s, 3 H), 3.75 – 3.70 (m, 1 H), 3.66-3.60 (m, 1 H), 2.43 (d, *J* = 7.1 Hz, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.13, 173.35, 170.06, 135.76, 135.32, 131.56, 130.23, 128.89, 128.35, 127.94, 126.05, 126.05, 125.27, 61.48, 60.51, 52.24, 48.27, 46.89, 19.34. ESI-MS calculated for $C_{21}H_{20}N_2NaO_4$: m/z (%): 387.1315 ($M+H^+$), found: 387.1320. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 210 nm); minor enantiomer tr = 14.6 min, major enantiomer tr = 39.0 min. $[\alpha]_D^{25}$ = -102.6 (*c* = 0.25, $CHCl_3$).

3.9 Synthesis of tert-butyl (1R,3S,3aR,6aS)-4,6-dioxo-5-phenyl-3-(o-tolyl)octahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3aj**).

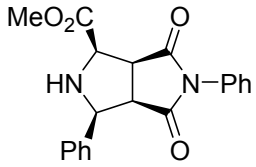


3aj

Prepared according to general procedure **A** from N-Phenylmaleimide **1a** (28.6 mg, 0.165 mmol) and imino ester **2j** (35 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **3aj** as a white solid (51.5 mg, 81% yield) and 94% *ee*. Mp: 208-209 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.58 (m, 1 H), 7.35 (t, *J* = 7.5 Hz, 2 H), 7.29 (d, *J* = 7.2 Hz, 1 H), 7.21 (d, *J* = 2.2 Hz, 3 H), 7.06 (d, *J* = 7.3 Hz, 2 H), 4.66 (d, *J* = 8.7 Hz, 1 H), 3.99 (d, *J* = 6.0 Hz, 1 H), 3.71-3.65 (m, 1 H), 3.64-3.58 (m, 1 H), 2.44 (s, 3 H), 2.28 (s, 1 H), 1.59 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.83, 173.55, 168.45, 135.73, 135.47, 131.60, 130.12, 128.85, 128.24, 127.79, 126.14, 125.95, 125.17, 82.24, 62.17, 60.23, 48.17, 47.12, 28.06, 19.35. MS (EI): m/z (%) = 406 (M+, 1.78), 305 (100)；HRMS

calculated for $[C_{24}H_{26}O_4N_2]$+: 406.1895 found: 406.1983. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 90 :10, 1.0 mL/min, 190 nm); minor enantiomer tr = 16.3 min, major enantiomer tr = 24.1 min. $[\alpha]_D^{25}$ = -93.8 (*c* = 0.4, $CHCl_3$).

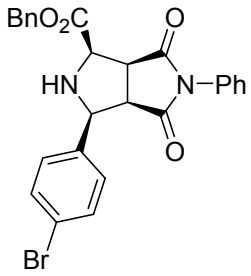
3.10 Synthesis of methyl (1R,3S,3aR,6aS)-4,6-dioxo-3,5-diphenyloctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3ak**).



3ak

Prepared according to general procedure **A** from N-Phenylmaleimide **1a** (28.6 mg, 0.165 mmol) and imino ester **2k** (26.6 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 1:1) afforded the product **3ak** as a white solid (51.5 mg, 98% yield) and 85% *ee*. Mp: 170-171 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47-7.29 (m, 8H), 7.16-7.13 (m, 2H), 4.59 (dd, *J* = 8.7, 5.3 Hz, 1H), 4.12 (dd, *J* = 6.4, 5.2 Hz, 1H), 3.87 (s, 3 H), 3.71 (t, *J* = 6.9 Hz, 1H), 3.54 (t, *J* = 8.3 Hz, 1H), 2.51 (t, *J* = 5.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.06, 173.58, 170.03, 136.64, 131.56, 128.96, 128.43, 128.43, 128.39, 127.06, 126.05, 64.16, 61.82, 52.27, 49.34, 48.26. ESI-MS calculated for $C_{20}H_{18}N_2NaO_4$: m/z (%): 373.1159 ($M+H^+$), found: 373.1167. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 210 nm); minor enantiomer tr = 15.8 min, major enantiomer tr = 28.1 min. $[\alpha]_D^{25}$ = -91.6 (*c* = 0.25, $CHCl_3$).

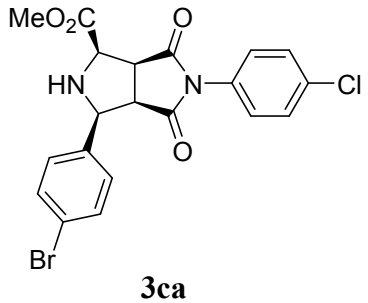
3.11 Synthesis of benzyl (1R,3S,3aR,6aS)-3-(4-bromophenyl)-4,6-dioxo-5-phenyloctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3al**).



3al

Prepared according to general procedure **A** from N-Phenylmaleimide **1a** (28.6 mg, 0.165 mmol) and imino ester **2l** (49.8 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 1:1) afforded the product **3al** as a white solid (63.2 mg, 83% yield) and 95% *ee*. Mp: 200-201 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.30 (m, 12 H), 7.16-7.13 (m, 2 H), 5.29 (dd, *J* = 28.7, 12.1 Hz, 2 H), 4.49 (dd, *J* = 8.7, 4.7 Hz, 1 H), 4.11 (dd, *J* = 6.7, 4.6 Hz, 1 H), 3.70 (t, *J* = 7.2 Hz, 1 H), 3.50 (t, *J* = 8.2 Hz, 1 H), 2.48 (t, *J* = 4.5 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.85, 173.43, 169.36, 135.77, 135.30, 131.53, 131.45, 129.06, 128.77, 128.72, 128.57, 128.53, 128.43, 126.05, 122.20, 67.39, 63.41, 61.83, 48.97, 47.88. ESI-MS calculated for $C_{26}H_{21}BrN_2NaO_4$: m/z (%): 527.0577 ($M+H^+$), found: 527.0587. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 210 nm); minor enantiomer tr = 20.5 min, major enantiomer tr = 49.5 min. $[\alpha]_D^{25}$ = -98.3 (*c* = 0.25, $CHCl_3$).

3.12 Synthesis of methyl (1R,3S,3aR,6aS)-3-(4-bromophenyl)-5-(4-chlorophenyl)-4,6-dioxooctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3ca**).

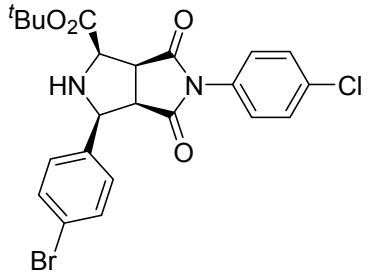


3ca

Prepared according to general procedure **A** from maleimide **1c** (34.3 mg, 0.165 mmol) and imino ester **2a**(38.4 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 1:1) afforded the product **3ca** as a white

solid (66.9 mg, 96% yield) and 84% *ee*. Mp: 245-246 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2 H), 7.38-7.35 (m, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.09 (d, *J* = 8.7 Hz, 2 H), 4.54 (d, *J* = 8.7 Hz, 1 H), 4.12 (d, *J* = 6.7 Hz, 1 H), 3.86 (s, 3 H), 3.73-3.69 (m, 1 H), 3.54 (t, *J* = 8.2 Hz, 1 H), 2.48 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.59, 173.13, 169.79, 135.65, 134.35, 131.63, 129.90, 129.26, 128.73, 127.23, 122.35, 63.47, 61.77, 52.37, 49.03, 47.90. ESI-MS calculated for $C_{20}H_{17}BrClN_2O_4$: m/z (%): 463.0055 ($M+N^+$), found: 463.0064. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 210 nm); minor enantiomer tr = 15.4 min, major enantiomer tr = 31.3 min. $[\alpha]_D^{25}$ = -73.6 (*c* = 0.25, $CHCl_3$).

3.13 Synthesis of tert-butyl (1R,3S,3aR,6aS)-3-(4-bromophenyl)-5-(4-chlorophenyl)-4,6-dioxooctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3cm**).

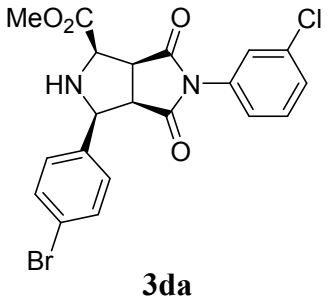


3cm

Prepared according to general procedure **A** from maleimide **1c** (34.3 mg, 0.165 mmol) and imino ester **2m** (44.7 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 1:1) afforded the product **3cm** as a white solid (66.9 mg, 80% yield) and 96% *ee*. Mp: 243-244 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2 H), 7.37 (d, *J* = 8.7 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.10 (d, *J* = 8.7 Hz, 2 H), 4.51 (d, *J* = 8.7 Hz, 1 H), 4.00 (d, *J* = 6.6 Hz, 1 H), 3.72-3.62 (m, 1 H), 3.56-3.48 (m, 1 H), 2.36 (s, 1 H), 1.56 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.37, 173.36, 168.26, 135.77, 134.27, 131.58, 129.95, 129.27, 128.69, 127.34, 122.24, 82.68, 63.24, 62.50, 49.32, 47.86, 28.06. ESI-MS calculated for $C_{23}H_{22}BrClN_2NaO_4$: m/z (%): 527.0349 ($M+Na^+$), found: 527.0342. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol

= 90:10, 0.8 mL/min, 230 nm); minor enantiomer tr = 29.7 min, major enantiomer tr = 34.0 min. $[\alpha]_D^{25}$ = -146.6 (*c* = 0.4, $CHCl_3$).

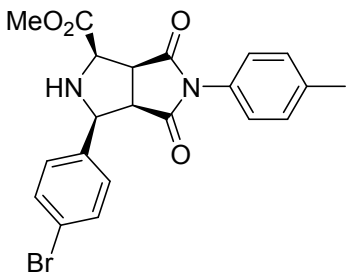
3.14 Synthesis of methyl (1R,3S,3aR,6aS)-3-(4-bromophenyl)-5-(3-chlorophenyl)-4,6-dioxooctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3da**).



3da

Prepared according to general procedure **A** from maleimide **1d** (34.3 mg, 0.165 mmol) and imino ester **2a**(38.4 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 1:1) afforded the product **3da** as a white solid (78 mg, >99% yield) and 92% *ee*. Mp: 140-141 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2 H), 7.32-7.30 (m, 4 H), 7.16 (s, 1 H), 7.05-7.02 (m, 1 H), 4.52 (d, *J* = 8.7 Hz, 1 H), 4.10 (d, *J* = 6.7 Hz, 1 H), 3.85 (s, 3 H), 3.71-3.67 (m, 1 H), 3.52 (t, *J* = 8.2 Hz, 1 H), 2.44 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.47, 173.03, 169.76, 135.67, 134.50, 132.44, 131.57, 129.98, 128.72, 128.72, 126.24, 124.20, 122.28, 63.37, 61.70, 52.31, 48.97, 47.85. ESI-MS calculated for $C_{20}H_{17}BrClN_2O_4$: m/z (%): 463.0055 ($M+H^+$), found: 463.0067. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 210 nm); minor enantiomer tr = 15.3 min, major enantiomer tr = 39.4 min. $[\alpha]_D^{25}$ = -114.2 (*c* = 0.25, $CHCl_3$).

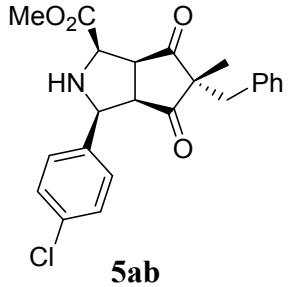
3.15 Synthesis of methyl (1R,3S,3aR,6aS)-3-(4-bromophenyl)-4,6-dioxo-5-(p-tolyl)octahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**3ea**).



3ea

Prepared according to general procedure **A** from maleimide **1e** (31 mg, 0.165 mmol) and imino ester **2a**(38.4 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 1:1) afforded the product **3ea** as a white solid (62.9 mg, 95% yield) and 91% *ee*. Mp: 193-194 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.19 (d, *J* = 8.2 Hz, 2 H), 7.00 (d, *J* = 8.3 Hz, 2 H), 4.50 (d, *J* = 8.7 Hz, 1 H), 4.08 (d, *J* = 6.7 Hz, 1 H), 3.85 (s, 3 H), 3.67 (t, *J* = 7.2 Hz, 1 H), 3.50 (t, *J* = 8.2 Hz, 1 H), 2.45 (s, 1 H), 2.33 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.96, 173.52, 169.89, 138.60, 135.86, 131.49, 129.65, 128.82, 128.79, 125.79, 122.13, 63.38, 61.69, 52.25, 49.01, 47.91, 21.09. ESI-MS calculated for $C_{21}H_{20}BrN_2O_4$: m/z (%): 443.0601 ($M+H^+$), found: 443.0613. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 210 nm); minor enantiomer tr = 17.2 min, major enantiomer tr = 34.7 min. $[\alpha]_D^{25}$ = -130.7 (*c* = 0.25, $CHCl_3$).

3.16 Synthesis of methyl (1R,3S,3aR,5R,6aS)-5-benzyl-3-(4-chlorophenyl)-5-methyl-4,6-dioxooctahydrocyclopenta[c]pyrrole-1-carboxylate (**5ab**).

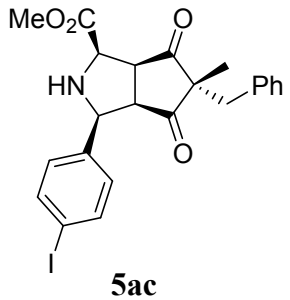


5ab

Prepared according to general procedure **B** from cyclo-pentenedione **4a** (33 mg, 0.165 mmol) and imino ester **2b**(31.7 mg, 0.15 mmol) at -30 °C, after flash column chromatography Petroleum ether : AcOEt = 2:1) afforded the product **5aa** as a white

solid (58.4mg, 95% yield) and 94% *ee*. Mp: 157-158 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.29 (m, 4 H), 7.22 (dd, *J* = 5.0, 1.8 Hz,3 H), 6.95 (dd, *J* = 6.5, 3.0 Hz, 2 H), 4.35 (d, *J* = 5.5 Hz, 1 H), 3.93 (t, *J* = 5.3 Hz, 1 H), 3.89 (s, 3 H), 2.87 (s, 2 H), 2.8-2.78 (m, 2H), 2.26 (s, 1 H), 1.15 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.32, 215.48, 170.54, 135.64, 135.64, 133.59, 129.64, 128.52, 128.36, 128.29, 127.12, 65.37, 63.44, 60.24, 55.85, 54.28, 52.11, 43.85, 18.22. ESI-MS calculated for $C_{23}H_{23}ClNO_4$: m/z (%): 412.1310 ($M+H^+$), found: 412.1318. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 210 nm); minor enantiomer tr = 8.8 min, major enantiomer tr = 12.1 min. $[\alpha]_D^{25}$ = -4.6 (*c* = 0.25, $CHCl_3$).

3.17 Synthesis of methyl (1R,3S,3aR,5R,6aS)-5-benzyl-3-(4-iodophenyl)-5-methyl-4,6-dioxooctahydrocyclopenta[c]pyrrole-1-carboxylate (**5ac**).

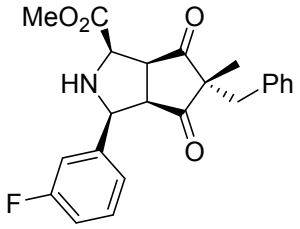


5ac

Prepared according to general procedure **B** from cyclo-pentenedione **4a** (33 mg, 0.165 mmol) and imino ester **2c**(45.5 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5ac** as a white solid (58.4mg, 85% yield) and 94% *ee*. Mp: 160-161 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2 H), 7.18 (dd, *J* = 5.0, 1.8 Hz, 3 H), 7.04 (d, *J* = 8.3 Hz, 2 H), 6.91 (dd, *J* = 6.4, 3.1 Hz, 2 H), 4.28-4.25 (m, 1 H), 3.89-3.87 (m, 1 H), 3.84 (s, 3 H), 2.82 (s, 2 H), 2.74 (dd, *J* = 4.0, 3.2 Hz, 2 H), 2.21 (s, 1 H), 1.11 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.28, 215.43, 170.51, 137.22, 136.87, 135.63, 129.63, 128.87, 128.51, 127.11, 93.42, 65.51, 63.45, 60.23, 55.78, 54.26, 52.10, 43.83, 18.22. ESI-MS calculated for $C_{23}H_{22}INNaO_4$: m/z (%): 526.0486 ($M+H^+$), found: 526.0497. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column

(hexanes: 2-propanol = 50:50, 0.8 mL/min, 210 nm); minor enantiomer tr = 9.8 min, major enantiomer tr = 14.8 min. $[\alpha]_D^{25}$ = 4.4 (*c* = 0.25, $CHCl_3$).

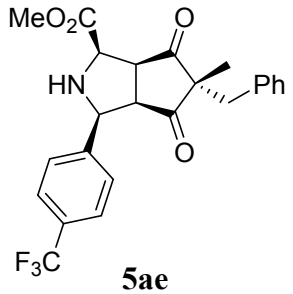
3.18 Synthesis of methyl (1R,3S,3aR,5R,6aS)-5-benzyl-3-(3-fluorophenyl)-5-methyl-4,6-dioxooctahydrocyclopenta[c]pyrrole-1-carboxylate (**5ad**).



5ad

Prepared according to general procedure **B** from cyclo-pentenedione **4a** (33 mg, 0.165 mmol) and imino ester **2d**(29.3 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5ad** as a yellow solid (36.8mg, 62% yield) and 90% *ee*. Mp: 157-158 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 10.8, 4.9 Hz, 1 H), 7.19 (dd, *J* = 5.0, 1.8 Hz, 3 H), 7.11-6.91 (m, 5 H), 4.34 (d, *J* = 7.8 Hz, 1 H), 3.91 (d, *J* = 6.9 Hz, 1 H), 3.86 (s, 3 H), 2.84 (s, 2 H), 2.78-2.75 (m, 2 H), 2.24 (s, 1 H), 1.14 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.81 (td, *J* = 8.7, 5.6 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.33, 215.34, 170.52, 162.75 (d, *J* = 245.9 Hz), 139.87 (d, *J* = 7.1 Hz), 135.70, 129.72-129.64 (m), 129.67, 128.55, 127.14, 122.72 (d, *J* = 2.8 Hz), 114.83 (d, *J* = 21.2 Hz), 113.96 (d, *J* = 22.4 Hz), 65.47, 63.45, 60.27, 55.88, 54.27, 52.14, 43.91, 18.29. ESI-MS calculated for $C_{23}H_{23}FNO_4$: m/z (%): 396.1606 ($M+H^+$), found: 396.1609. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 80:20, 0.8 mL/min, 210 nm); minor enantiomer tr = 12.9 min, major enantiomer tr =25.4 min. $[\alpha]_D^{25}$ = -5.2 (*c* = 0.25, $CHCl_3$).

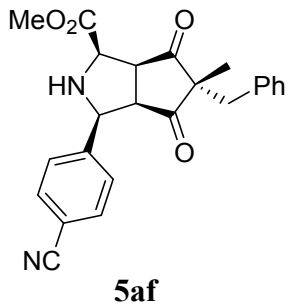
3.19 Synthesis of methyl (1R,3S,3aR,5R,6aS)-5-benzyl-5-methyl-4,6-dioxo-3-(4-(trifluoromethyl)phenyl)octahydrocyclopenta[c]pyrrole-1-carboxylate (**5ae**).



5ae

Prepared according to general procedure **B** from cyclo-pentenedione **4a** (33 mg, 0.165 mmol) and imino ester **2e**(36.8 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5ae** as a white solid (46.7mg, 70% yield) and 94% *ee*. Mp: 155-156 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.19 (d, *J* = 4.8 Hz, 3 H), 6.94-6.91 (m, 2 H), 4.39 (d, *J* = 7.0 Hz, 1 H), 3.93 (d, *J* = 6.0 Hz, 1 H), 3.86 (s, 3 H), 2.84 (s, 2 H), 2.78 (t, *J* = 7.6 Hz, 2 H), 2.27 (s, 1H), 1.13 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.47.^{13}C NMR (101 MHz, $CDCl_3$) δ 217.17, 215.40, 170.47, 141.26, 141.26, 135.61, 130.07 (q, *J* = 33.3 Hz), 129.63, 129.63, 128.56, 127.37, 127.18, 125.12 (q, *J* = 3.7 Hz), 124.04 (q, $J_{C,F}$ = 272.3 Hz), 65.48, 63.51, 60.27, 55.80, 54.23, 52.16, 43.91, 18.23. ESI-MS calculated for $C_{24}H_{23}F_3NO_4$: m/z (%): 446.1574 ($M+H^+$), found: 446.1585. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 0.8 mL/min, 220 nm); minor enantiomer tr = 6.9 min, major enantiomer tr = 8.2 min. $[\alpha]_D^{25}$ = -13.5 (*c* = 0.25, $CHCl_3$).

3.20 Synthesis of methyl (1R,3S,3aR,5R,6aS)-5-benzyl-3-(4-cyanophenyl)-5-methyl-4,6-dioxooctahydrocyclopenta[c]pyrrole-1-carboxylate (**5af**).

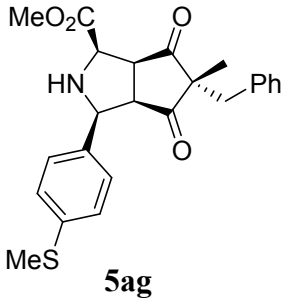


5af

Prepared according to general procedure **B** from cyclo-pentenedione **4a** (33 mg, 0.165 mmol) and imino ester **2f** (30.3 mg, 0.15 mmol) at -30 °C, after flash column

chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5af** as a white solid (50.1mg, 83% yield) and 95% *ee*. Mp: 148-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.19 (d, *J* = 4.7 Hz, 3 H), 6.91-6.90 (m, 2 H), 4.39 (d, *J* = 6.3 Hz, 1 H), 3.93 (d, *J* = 5.2 Hz, 1 H), 3.85 (s, 3 H), 2.86-2.81 (m, 2 H), 2.78 (d, *J* = 6.3 Hz, 2 H), 2.28 (s, 1 H), 1.09 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 216.92, 215.44, 170.31, 142.80, 135.45, 131.92, 129.53, 128.56, 127.74, 127.20, 118.65, 111.65, 65.25, 63.40, 60.23, 55.69, 53.99, 52.16, 43.91, 18.17. ESI-MS calculated for $C_{24}H_{23}N_2O_4$: m/z (%): 403.1652 ($M+H^+$), found: 403.1664. Enantiomeric excess was determined by HPLC with a Chiralpak IE column (hexanes: 2-propanol = 70:30, 0.8 mL/min, 210 nm); major enantiomer tr = 14.6 min, minor enantiomer tr = 17.7 min. $[\alpha]_D^{25}$ = -4.8 (*c* = 0.25, $CHCl_3$).

3.21 Synthesis of methyl (1R,3S,3aR,5R,6aS)-5-benzyl-5-methyl-3-(4-(methylthio)phenyl)-4,6-dioxooctahydrocyclopenta[c]pyrrole-1-carboxylate (**5ag**).

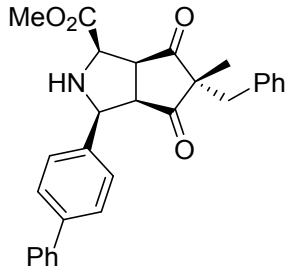


5ag

Prepared according to general procedure **B** from cyclo-pentenedione **4a** (33 mg, 0.165 mmol) and imino ester **2g** (33.5 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5ag** as a white solid (44.7mg, 70% yield) and 94% *ee*. Mp: 159-160 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.11 (m, 7 H), 6.92 (dd, *J* = 6.5, 3.0 Hz, 2 H), 4.28 (dd, *J* = 5.9, 2.6 Hz, 1 H), 3.88 (dd, *J* = 5.3, 1.8 Hz, 1 H), 3.85 (s, 3 H), 2.83 (s, 2 H), 2.75 (dd, *J* = 5.6, 2.2 Hz, 2 H), 2.46 (s, 3 H), 2.14 (s, 1H), 1.13 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.52, 215.50, 170.63, 138.06, 135.69, 133.79, 129.65, 128.45, 127.41, 127.04, 126.09, 65.77, 63.46, 60.21, 55.95, 54.40, 52.05, 43.75, 18.23, 15.60. ESI-MS calculated for

$C_{24}H_{26}NO_4S$: m/z (%): 424.1577 ($M+H^+$), found: 424.1579. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 60:40, 0.8 mL/min, 210 nm); minor enantiomer tr = 11.9 min, major enantiomer tr = 18.5 min. $[\alpha]_D^{25}$ = -14.2 (*c* = 0.25, $CHCl_3$).

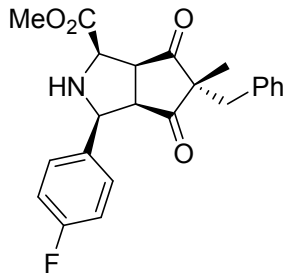
3.22 Synthesis of methyl (1R,3S,3aR,5R,6aS)-3-([1,1'-biphenyl]-4-yl)-5-benzyl-5-methyl-4,6-dioxooctahydrocyclopenta[c]pyrrole-1-carboxylate (**5ah**).



5ah

Prepared according to general procedure **B** from cyclo-pentenedione **4a** (33 mg, 0.165 mmol) and imino ester **2h** (38 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5ah** as a white solid (61.1 mg,90% yield) and 95% *ee*. Mp: 186-187 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.56 (m, 4 H), 7.40 (dt, *J* = 14.4, 6.7 Hz, 5 H), 7.19 (dd, *J* = 5.0, 1.7 Hz, 3 H), 6.95 (dd, *J* = 6.4, 2.9 Hz, 2 H), 4.38 (d, *J* = 7.9 Hz, 1 H), 3.92 (d, *J* = 6.8 Hz, 1 H), 3.87 (s, 3 H), 2.86 (s, 2 H), 2.81 (t, *J* = 6.5 Hz, 2 H), 2.21 (s, 1H) , 1.17 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.57, 215.52, 170.67, 140.66, 140.61, 136.08, 135.74, 129.69, 128.66, 128.48, 127.43, 127.24, 127.07, 127.02, 126.80, 65.97, 63.56, 60.26, 56.07, 54.50, 52.09, 43.79, 18.29. ESI-MS calculated for $C_{29}H_{28}NO_4$: m/z (%): 454.2013 ($M+H^+$), found: 454.2023. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 80:20, 0.8 mL/min, 254 nm); minor enantiomer tr = 17.4 min, major enantiomer tr =33.2 min. $[\alpha]_D^{25}$ = -6.8 (*c* = 0.25, $CHCl_3$).

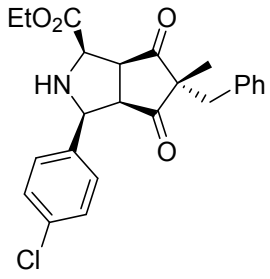
3.23 Synthesis of methyl (1R,3S,3aR,5R,6aS)-5-benzyl-3-(4-fluorophenyl)-5-methyl-4,6-dioxooctahydrocyclopenta[c]pyrrole-1-carboxylate (**5an**).



5an

Prepared according to general procedure **B** from cyclo-pentenedione **4a** (33 mg, 0.165 mmol) and imino ester **2n** (29.3mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5an** as a yellow solid (43.1 mg, 73% yield) and 92% *ee*. Mp: 135-136 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2 H), 7.18 (dd, *J* = 5.0, 1.7 Hz, 3 H), 7.02 (t, *J* = 8.7 Hz, 2 H), 6.92 (dd, *J* = 6.5, 3.0 Hz, 2 H), 4.34 (d, *J* = 8.1 Hz, 1 H), 3.92-3.90 (m, 1 H), 3.86 (s, 3 H), 2.84 (s, 2 H), 2.75 (dd, *J* = 5.0, 2.7 Hz, 2 H), 2.23 (s, 1 H), 1.12 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.06 – -114.11 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.41, 215.59, 170.61, 162.31 (d, *J* = 246.4 Hz), 135.68, 132.82 (d, *J* = 3.2 Hz), 129.67, 128.59, 128.52, 127.12, 115.11 (d, *J* = 21.5 Hz), 65.42, 63.45, 60.27, 55.96, 54.34, 52.11, 43.89, 18.22. ESI-MS calculated for $C_{23}H_{23}FNO_4$: m/z (%): 396.1606 ($M+H^+$), found: 396.1613. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 80:20, 0.8 mL/min, 220 nm); minor enantiomer tr = 15.2 min, major enantiomer tr =20.7 min. $[\alpha]_D^{25}$ = -18.9 (*c* = 0.25, $CHCl_3$).

3.24 Synthesis of ethyl (1R,3S,3aR,5R,6aS)-5-benzyl-3-(4-chlorophenyl)-5-methyl-4,6-dioxooctahydrocyclopenta[c]pyrrole-1-carboxylate (**5ao**).

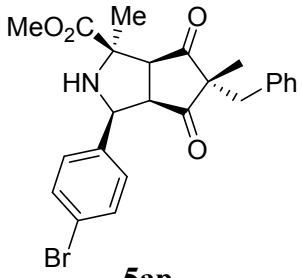


5ao

Prepared according to general procedure **B** from cyclo-pentenedione **4a** (33 mg, 0.165

mmol) and imino ester **2o** (33.8 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5ao** as a white solid (52.1 mg, 82% yield) and 94% *ee*. Mp: 170-171 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.22 (m, 4 H), 7.18 (dd, *J* = 5.0, 1.7 Hz, 3 H), 6.92 (dd, *J* = 6.7, 2.9 Hz, 2 H), 4.35-4.28 (m, 3 H), 3.89-3.86 (m, 1 H), 2.83 (s, 2 H), 2.75 (dd, *J* = 5.7, 2.1 Hz, 2 H), 2.22 (s, 1 H), 1.37 (t, *J* = 7.2 Hz, 3 H), 1.11 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.03, 215.52, 170.04, 135.72, 135.69, 133.55, 129.64, 128.48, 128.33, 128.29, 127.10, 65.33, 63.58, 61.20, 60.19, 55.93, 54.28, 43.82, 18.19, 14.11. ESI-MS calculated for $C_{24}H_{25}ClNO_4$: m/z (%):426.1467 ($M+H^+$), found: 426.1471. Enantiomeric excess was determined by HPLC with a Chiralpak ADH column (hexanes: 2-propanol = 80:20, 1.0 mL/min, 254 nm); major enantiomer tr = 11.2 min, minor enantiomer tr = 16.7 min. $[\alpha]_D^{25}$ = -7.1 (*c* = 0.25, $CHCl_3$).

3.25 Synthesis of methyl (1R,3S,3aR,5R,6aS)-5-benzyl-3-(4-bromophenyl)-1,5-dimethyl-4,6-dioxooctahydrocyclopenta[c]pyrrole-1-carboxylate (**5ap**).

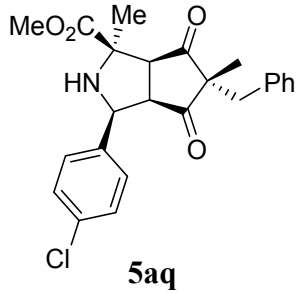


5ap

Prepared according to general procedure **B** from cyclo-pentenedione **4a** (33 mg, 0.165 mmol) and imino ester **2p** (40.5 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5ap** as a white solid (59.1 mg, 89% yield) and 92% *ee*. Mp: 187-188 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2 H), 7.18 (dd, *J* = 5.5, 3.0 Hz, 5 H), 6.90 (dd, *J* = 6.6, 2.9 Hz, 2 H), 4.62 (d, *J* = 9.3 Hz, 1 H), 3.83 (s, 3 H), 2.89 (t, *J* = 9.6 Hz, 1 H), 2.80 (s, 2 H), 2.47 (d, *J* = 9.8 Hz, 1 H), 2.10 (s, 1 H), 1.45 (s, 3 H), 1.01 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.21, 215.07, 173.10, 136.46, 135.50, 131.20, 129.61, 128.74, 128.49, 127.15, 121.61, 68.75, 63.07, 61.96, 60.16, 56.41, 52.39, 44.02, 24.12, 18.13.

ESI-MS calculated for $C_{24}H_{25}BrNO_4$: m/z (%):470.0961 ($M+H^+$), found: 470.0975. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer tr = 15.2 min, major enantiomer tr = 17.5 min. $[\alpha]_D^{25}$ = -33.2 (*c* = 0.25, $CHCl_3$).

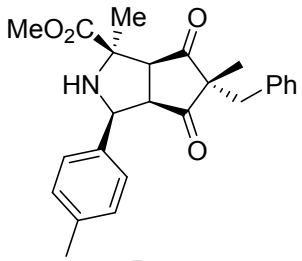
3.26 Synthesis of methyl (1R,3S,3aR,5R,6aS)-5-benzyl-3-(4-chlorophenyl)-1,5-dimethyl-4,6-dioxooctahydrocyclopenta[c]pyrrole-1-carboxylate (**5aq**).



5aq

Prepared according to general procedure **B** from cyclo-pentenedione **4a** (33 mg, 0.165 mmol) and imino ester **2q** (33.9 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5aq** as a white solid (54.2 mg, 91% yield) and 90% *ee*. Mp: 180-181 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.22 (m, 4 H), 7.20-7.17 (m, 3 H), 6.91 (dd, *J* = 6.6, 2.9 Hz, 2 H), 4.64 (d, *J* = 9.4 Hz, 1 H), 3.84 (s, 3 H), 2.90 (t, *J* = 9.6 Hz, 1 H), 2.80 (s, 2 H), 2.48 (d, *J* = 9.8 Hz, 1 H), 2.11 (s, 1 H), 1.45 (s, 3 H), 1.01 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.23, 215.09, 173.12, 135.93, 135.50, 133.44, 129.61, 128.48, 128.39, 128.27, 127.15, 68.74, 63.02, 61.97, 60.16, 56.47, 52.39, 44.02, 24.12, 18.11. ESI-MS calculated for $C_{24}H_{25}ClNO_4$: m/z (%): 426.1467 ($M+H^+$), found: 426.1476. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 210 nm); minor enantiomer tr = 23.6 min, major enantiomer tr = 29.0 min. $[\alpha]_D^{25}$ = -32.6 (*c* = 0.25, $CHCl_3$).

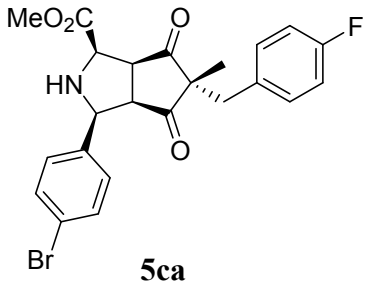
3.27 Synthesis of methyl (1R,3S,3aR,5R,6aS)-5-benzyl-1,5-dimethyl-4,6-dioxo-3-(p-tolyl)octahydrocyclopenta[c]pyrrole-1-carboxylate (**5ar**).



5ar

Prepared according to general procedure **B** from cyclo-pentenedione **4a** (33 mg, 0.165 mmol) and imino ester **2p** (30.8 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5ap** as a white solid (45.6 mg, 80% yield) and 91% *ee*. Mp: 156-157 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (dt, *J* = 12.6, 5.8 Hz, 7 H), 6.92 (dd, *J* = 6.6, 2.9 Hz, 2 H), 4.65 (d, *J* = 9.4 Hz, 1 H), 3.85 (s, 3 H), 2.92 (t, *J* = 9.6 Hz, 1 H), 2.80 (s, 2 H), 2.50 (d, *J* = 9.8 Hz, 1 H), 2.34 (s, 3 H), 2.18 (s, 1H), 1.46 (s, 3 H), 1.03 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.65, 215.22, 173.28, 137.48, 135.62, 134.02, 129.69, 128.86, 128.44, 127.08, 126.87, 68.94, 63.90, 62.48, 60.21, 57.05, 52.41, 43.98, 24.19, 21.14, 18.13. ESI-MS calculated for $C_{25}H_{28}NO_4$: m/z (%):406.2013 ($M+H^+$), found: 406.2015. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 254 nm); minor enantiomer tr = 12.5 min, major enantiomer tr = 15.9 min. $[\alpha]_D^{25}$ = -44.1 (*c* = 0.25, $CHCl_3$).

3.28 Synthesis of methyl (1R,3S,3aR,5R,6aS)-3-(4-bromophenyl)-5-(4-fluorobenzyl)-5-methyl-4,6-dioxooctahydrocyclopenta[c]pyrrole-1-carboxylate (**5ca**).

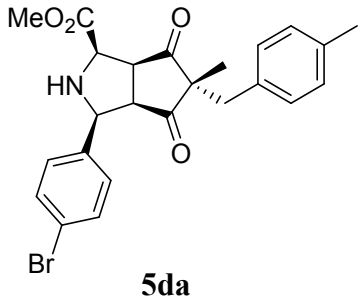


5ca

Prepared according to general procedure B from cyclo-pentenedione **4c** (36 mg, 0.165 mmol) and imino ester **2a**(38.4 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5ca** as a white

solid (58.7 mg, 83% yield) and 95% *ee*. Mp: 169-170 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2 H), 7.18 (d, *J* = 8.4 Hz, 2 H), 6.88-6.85 (m, 4 H), 4.32 (d, *J* = 7.8 Hz, 1 H), 2.94-2.92 (m, 1 H), 3.84 (s, 3 H), 2.81-2.78 (m, 4 H), 2.25 (s, 1H), 1.11 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -115.08 - -115.13 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.18, 215.35, 170.40, 161.85 (d, *J* = 246.1 Hz), 136.04, 131.47 (d, *J* = 3.3 Hz), 131.31 (d, *J* = 1.9 Hz), 131.24, 128.59, 121.77, 115.33 (d, *J* = 21.2 Hz), 65.46, 63.52, 60.17, 55.77, 54.21, 52.11, 42.44, 18.28. ESI-MS calculated for $C_{23}H_{22}BrFNO_4$: m/z (%): 474.0711 ($M+H^+$), found: 474.0722. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 80:20, 0.8 mL/min, 210 nm); minor enantiomer tr = 14.8 min, major enantiomer tr = 18.4 min. $[\alpha]_D^{25}$ = -2.2 (*c* = 0.25, $CHCl_3$).

3.29 Synthesis of methyl (1R,3S,3aR,5R,6aS)-3-(4-bromophenyl)-5-methyl-5-(4-methylbenzyl)-4,6-dioxooctahydrocyclopenta[c]pyrrole-1-carboxylate (**5da**).

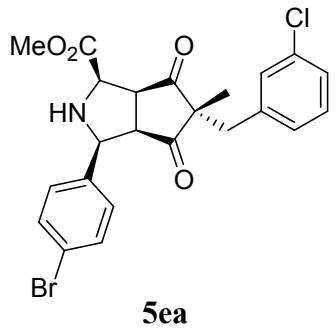


5da

Prepared according to general procedure **B** from cyclo-pentenedione **4d** (35.4 mg, 0.165 mmol) and imino ester **2a** (38.4 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5da** as a white solid (56.9 mg, 81% yield) and 95% *ee*. Mp: 131-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2 H), 7.17 (d, *J* = 8.3 Hz, 2 H), 6.98 (d, *J* = 7.8 Hz, 2 H), 6.79 (d, *J* = 7.9 Hz, 2 H), 4.28-4.27 (m, 1 H), 3.88 (d, *J* = 6.8 Hz, 1 H), 3.84 (s, 3 H), 2.77-2.73 (m, 4 H), 2.23 (d, *J* = 17.7 Hz, 4 H), 1.08 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.39, 215.55, 170.54, 136.66, 136.25, 132.42, 131.21, 129.44, 129.14, 128.62, 121.64, 65.34, 63.37, 60.25, 55.77, 54.25, 52.04, 43.56, 20.93, 18.03. ESI-MS calculated for $C_{24}H_{25}BrNO_4$: m/z (%): 470.0961 ($M+H^+$), found: 470.0967.

Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 80:20, 0.8 mL/min, 210 nm); minor enantiomer tr = 13.2 min, major enantiomer tr = 18.6 min. $[\alpha]_D^{25}$ = -14.3 (*c* = 0.25, $CHCl_3$).

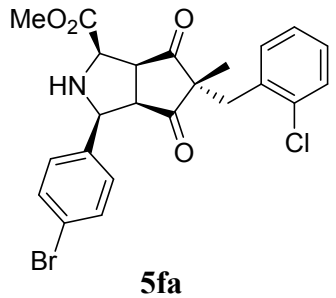
3.30 Synthesis of methyl (1R,3S,3aR,5R,6aS)-3-(4-bromophenyl)-5-(3-chlorobenzyl)-5-methyl-4,6-dioxooctahydrocyclopenta[c]pyrrole-1-carboxylate (**5ea**).



5ea

Prepared according to general procedure **B** from cyclo-pentenedione **4e** (38.7 mg, 0.165 mmol) and imino ester **2a** (38.4 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5ea** as a white solid (60.4 mg, 82% yield) and 95% *ee*. Mp: 159-160 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2 H), 7.20-7.08 (m, 4 H), 6.91 (s, 1 H), 6.80 (d, *J* = 6.9 Hz, 1 H), 4.34 (d, *J* = 7.8 Hz, 1 H), 3.95 (d, *J* = 7.0 Hz, 1 H), 3.84 (s, 3 H), 2.88-2.84 (m, 2 H), 2.79 (s, 2 H), 2.27 (s, 1 H), 1.13 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.69, 214.84, 170.38, 137.81, 135.98, 134.23, 131.31, 129.74, 129.57, 128.60, 128.00, 127.36, 121.80, 65.46, 63.52, 59.89, 55.75, 54.20, 52.13, 42.52, 18.50. ESI-MS calculated for $C_{23}H_{22}BrClNO_4$: m/z (%): 490.0415 ($M+H^+$), found: 490.0433. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 80:20, 0.8 mL/min, 210 nm); minor enantiomer tr = 16.6 min, major enantiomer tr = 21.6 min. $[\alpha]_D^{25}$ = -18.7 (*c* = 0.25, $CHCl_3$).

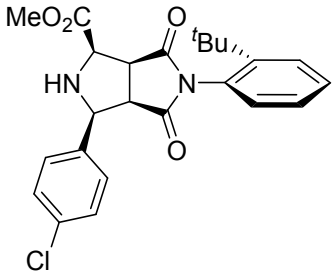
3.31 Synthesis of methyl (1R,3S,3aR,5R,6aS)-3-(4-bromophenyl)-5-(2-chlorobenzyl)-5-methyl-4,6-dioxooctahydrocyclopenta[c]pyrrole-1-carboxylate (**5fa**).



5fa

Prepared according to general procedure **B** from cyclo-pentenedione **4f** (38.7 mg, 0.165 mmol) and imino ester **2a**(38.4 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **5fa** as a white solid (63.2 mg, 86% yield) and 85% *ee*. Mp: 198-199 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2 H), 7.31-7.28 (m, 1 H), 7.19-7.12 (m, 4 H), 7.00 (dd, *J* = 6.9, 2.4 Hz, 1 H), 4.39 (d, *J* = 9.0 Hz, 1 H), 3.97 (d, *J* = 6.8 Hz, 1 H), 3.86 (s, 3 H), 3.32 (dd, *J* = 9.8, 6.9 Hz, 1 H), 3.23-3.17 (m, 1 H), 3.06 (d, *J* = 13.5 Hz, 1 H), 2.93 (d, *J* = 13.5 Hz, 1 H), 2.26 (s, 1 H), 1.06 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.06, 213.48, 170.65, 136.40, 134.53, 133.18, 131.90, 131.35, 129.91, 128.77, 128.77, 126.75, 121.81, 65.20, 62.93, 58.76, 55.52, 53.70, 52.12, 39.80, 17.15. ESI-MS calculated for $C_{23}H_{22}BrClNO_4$: m/z (%): 490.0415 ($M+H^+$), found: 490.0422. Enantiomeric excess was determined by HPLC with a Chiralpak IE column (hexanes: 2-propanol = 70:30, 0.8 mL/min, 200 nm); major enantiomer tr = 12.3 min, minor enantiomer tr = 20.1 min. $[\alpha]_D^{25}$ = -30.7 (*c* = 0.25, $CHCl_3$).

3.32 Synthesis of methyl (1R,3S,3aR,6aS)-5-(2-(tert-butyl)phenyl)-3-(4-chlorophenyl)-4,6-dioxooctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**7ab**).

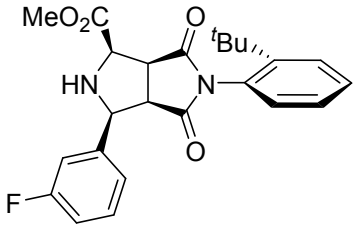


7ab

Prepared according to general procedure **C** from *N*-(2-*t*-butylphenyl)maleimide **6** (37.8 mg, 0.165 mmol) and imino ester **2b** (31.7 mg, 0.15 mmol) at -30 °C, after flash

column chromatography (Petroleum ether : AcOEt = 1:1) afforded the product **7ab** as a white solid (48.1 mg, 73% yield) and 90% *ee*. Mp: 191-192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.3 Hz, 1 H), 7.41 (d, *J* = 8.4 Hz, 2 H), 7.33 (dd, *J* = 12.3, 8.0 Hz, 3 H), 7.28-7.24 (m, 1 H), 6.86 (dd, *J* = 7.6, 0.9 Hz, 1 H), 4.53 (dd, *J* = 7.8, 3.0 Hz, 1 H), 4.12 (dd, *J* = 6.7, 3.2 Hz, 1 H), 3.84 (s, 3 H), 3.68 (t, *J* = 7.5 Hz, 1 H), 3.54 (t, *J* = 8.1 Hz, 1 H), 2.48 (s, 1 H), 1.22 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.05, 174.64, 169.87, 147.67, 135.09, 133.89, 130.81, 129.90, 129.79, 128.77, 128.54, 128.37, 127.55, 63.51, 61.81, 52.30, 49.05, 47.72, 35.59, 31.57. ESI-MS calculated for $C_{24}H_{25}ClN_2NaO_4$: m/z (%):463.1395 ($M+H^+$), found: 463.1402. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 1.0 mL/min, 220 nm); minor enantiomer tr = 5.6 min, major enantiomer tr = 8.8 min. $[\alpha]_D^{25}$ = -88.6 (*c* = 0.25, $CHCl_3$).

3.33 Synthesis of methyl (1R,3S,3aR,6aS)-5-(2-(tert-butyl)phenyl)-3-(3-fluorophenyl)-4,6-dioxooctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**7ad**).

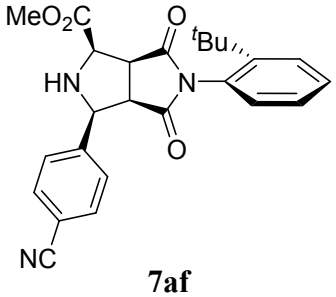


7ad

Prepared according to general procedure **C** from *N*-(2-*t*-butylphenyl)maleimide **6** (37.8 mg, 0.165 mmol) and imino ester **2d** (29.3 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **7ad** as a white solid (45.7 mg, 72% yield) and 90% *ee*. Mp: 203-204 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.1, 1.3 Hz, 1 H), 7.35-7.30 (m, 2 H), 7.28-7.21 (m, 3 H), 6.98-6.93 (m, 1 H), 6.88 (dd, *J* = 7.7, 1.4 Hz, 1 H), 4.54 (dd, *J* = 8.2, 3.3 Hz, 1 H), 4.11 (dd, *J* = 6.8, 3.4 Hz, 1 H), 3.84 (s, 3 H), 3.68 (t, *J* = 7.5 Hz, 1 H), 3.54 (t, *J* = 8.1 Hz, 1 H), 2.49 (s, 1 H), 1.22 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.65 (td, *J* = 8.8, 5.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.05, 174.53, 169.84, 162.78 (d, *J* = 246.1 Hz), 147.63, 139.32 (d, *J* = 7.2 Hz), 130.86, 129.90 (d, *J* = 3.9 Hz), 129.80,

129.75, 128.72, 127.54, 122.72 (d, J = 2.8 Hz), 115.08 (d, J = 21.1 Hz), 114.03 (d, J = 22.5 Hz), 63.47, 61.71, 52.28, 49.05, 47.71, 35.58, 31.56. ESI-MS calculated for $C_{24}H_{25}FN_2NaO_4$: m/z (%): 447.1691 ($M+H^+$), found: 447.1704. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 80:20, 1.0 mL/min, 210 nm); minor enantiomer tr = 11.3 min, major enantiomer tr = 24.4 min. $[\alpha]_D^{25}$ = -75.5 (c = 0.25, $CHCl_3$).

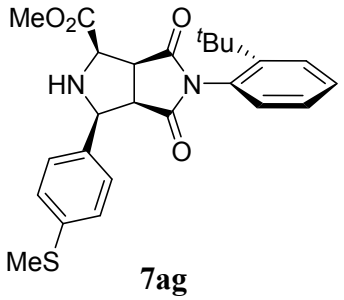
3.34 Synthesis of methyl (1R,3S,3aR,6aS)-5-(2-(tert-butyl)phenyl)-3-(4-cyanophenyl)-4,6-dioxooctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**7af**).



7af

Prepared according to general procedure **C** from *N*-(2-*t*-butylphenyl)maleimide **6** (37.8 mg, 0.165 mmol) and imino ester **2f** (30.3 mg, 0.15 mmol) at -30 °C, after flash column chromatography (hexanes : AcOEt = 1:1) afforded the product **7af** as a white solid (63.2 mg, 98% yield) and 95% *ee*. Mp: 123-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.58 (m, 4 H), 7.49 (dd, J = 8.1, 1.2 Hz, 1 H), 7.33 (t, J = 7.7 Hz, 1 H), 7.25 (t, J = 7.5 Hz, 1 H), 6.82 (dd, J = 7.7, 1.4 Hz, 1 H), 4.61 (dd, J = 8.2, 4.3 Hz, 1 H), 4.16 (dd, J = 7.2, 4.1 Hz, 1 H), 3.83 (s, 3 H), 3.72 (t, J = 7.5 Hz, 1 H), 3.60 (t, J = 8.1 Hz, 1 H), 2.55 (s, 1 H), 1.21 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.78, 174.46, 169.65, 147.64, 142.22, 132.06, 130.68, 129.85, 129.76, 128.78, 127.84, 127.53, 118.57, 111.90, 63.42, 61.79, 52.33, 48.97, 47.45, 35.54, 31.52. ESI-MS calculated for $C_{25}H_{25}N_3NaO_4$: m/z (%): 454.1737 ($M+H^+$), found: 454.1749. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 1.0 mL/min, 220 nm); minor enantiomer tr = 8.3 min, major enantiomer tr = 10.0 min. $[\alpha]_D^{25}$ = -140.6 (c = 0.25, $CHCl_3$).

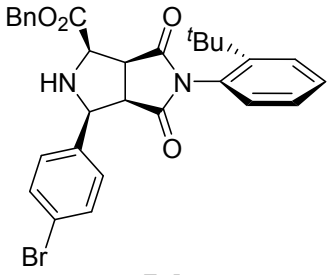
3.35 Synthesis of methyl (1R,3S,3aR,6aS)-5-(2-(tert-butyl)phenyl)-3-(4-(methylthio)phenyl)-4,6-dioxooctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**7ag**).



7ag

Prepared according to general procedure **C** from *N*-(2-*t*-butylphenyl)maleimide **6** (37.8 mg, 0.165 mmol) and imino ester **2g** (33.5 mg, 0.15 mmol) at -30 °C, after flash column chromatography (hexanes : AcOEt = 1:1) afforded the product **7ag** as a white solid (66.7 mg, 98% yield) and 98% *ee*. Mp: 219-220 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.1 Hz, 1 H), 7.38 (d, *J* = 8.2 Hz, 2 H), 7.35-7.31 (m, 1 H), 7.28-7.24 (m, 1 H), 7.21 (d, *J* = 8.3 Hz, 2 H), 6.88 (dd, *J* = 7.6, 1.1 Hz, 1 H), 4.51 (d, *J* = 8.1 Hz, 1 H), 4.10 (d, *J* = 6.9 Hz, 1 H), 3.84 (s, 3 H), 3.67 (t, *J* = 7.5 Hz, 1 H), 3.52 (t, *J* = 8.1 Hz, 1 H), 2.46 (s, 1 H), 2.43 (s, 3 H), 1.22 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.19, 174.76, 170.00, 147.69, 138.46, 133.14, 130.90, 129.99, 129.75, 128.75, 127.56, 127.51, 126.22, 63.97, 61.88, 52.29, 49.16, 47.87, 35.61, 31.58, 15.49. ESI-MS calculated for $C_{25}H_{28}N_2NaO_4S$: m/z (%): 475.1662 ($M+H^+$), found: 475.1675. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 50:50, 1.0 mL/min, 210 nm); minor enantiomer tr = 7.0 min, major enantiomer tr = 12.2 min. $[\alpha]_D^{25}$ = -106.4 (*c* = 0.25, $CHCl_3$).

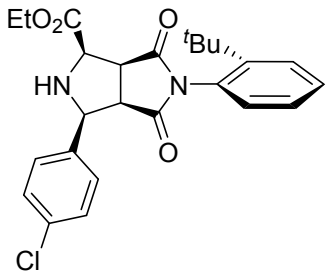
3.36 Synthesis of benzyl (1R,3S,3aR,6aS)-3-(4-bromophenyl)-5-(2-(tert-butyl)phenyl)-4,6-dioxooctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**7al**).



7al

Prepared according to general procedure **C** from *N*-(2-*t*-butylphenyl)maleimide **6** (37.8 mg, 0.165 mmol) and imino ester **2l** (49.8 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **7al** as a white solid (74.6 mg, 89% yield) and 96% *ee*. Mp: 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.44 (m, 5 H), 7.41-7.33 (m, 6 H), 7.25 (td, *J* = 7.6, 1.3 Hz, 1 H), 6.86 (dd, *J* = 7.7, 1.3 Hz, 1 H), 5.33 (d, *J* = 12.1 Hz, 1 H), 5.21 (d, *J* = 12.1 Hz, 1 H), 4.47 (d, *J* = 8.3 Hz, 1 H), 4.11 (d, *J* = 7.1 Hz, 1 H), 3.68 (t, *J* = 7.5 Hz, 1 H), 3.51 (t, *J* = 8.1 Hz, 1 H), 2.48 (s, 1 H), 1.25 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.03, 174.59, 169.35, 147.63, 135.67, 135.37, 131.41, 131.41, 130.83, 129.93, 129.77, 128.69, 128.69, 128.47, 128.35, 127.54, 122.00, 67.33, 63.48, 61.85, 48.93, 47.71, 35.55, 31.54. ESI-MS calculated for $C_{30}H_{29}BrN_2NaO_4$: m/z (%): 583.1203 ($M+H^+$), found: 583.1205. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 80:20, 1.0 mL/min, 220 nm); minor enantiomer tr = 15.1 min, major enantiomer tr = 43.6 min. $[\alpha]_D^{25}$ = -94.1 (*c* = 0.25, $CHCl_3$).

3.37 Synthesis of ethyl (1R,3S,3aR,6aS)-5-(2-(tert-butyl)phenyl)-3-(4-chlorophenyl)-4,6-dioxooctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**7ao**).

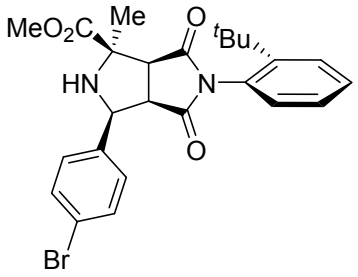


7ao

Prepared according to general procedure **C** from *N*-(2-*t*-butylphenyl)maleimide **6** (37.8 mg, 0.165 mmol) and imino ester **2o** (33.9 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **7ao** as a white solid (49.4 mg, 72% yield) and 91% *ee*. Mp: 202-203 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.1, 1.2 Hz, 1 H), 7.41 (d, *J* = 8.4 Hz, 2 H), 7.35-7.30 (m, 3 H), 7.25 (td, *J* = 7.5, 1.3 Hz, 1 H), 6.86 (dd, *J* = 7.7, 1.3 Hz, 1 H), 4.53 (d, *J* = 8.1 Hz, 1 H), 4.31 (q, *J* = 6.8 Hz, 2 H), 4.11 (d, *J* = 7.0 Hz, 1 H), 3.69 (t, *J* = 7.5 Hz,

1 H), 3.54 (t, *J* = 8.1 Hz, 1 H), 2.48 (s, 1 H), 1.34 (t, *J* = 7.2 Hz, 3 H), 1.22 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.89, 174.70, 169.43, 147.67, 135.10, 133.89, 130.87, 129.94, 129.77, 128.79, 128.55, 128.38, 127.53, 63.57, 62.04, 61.54, 49.18, 47.78, 35.62, 31.58, 14.09. ESI-MS calculated for $C_{25}H_{27}ClN_2NaO_4$: m/z (%): 477.1552 ($M+H^+$), found: 477.1565. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 80:20, 1.0 mL/min, 220 nm); minor enantiomer tr = 9.6 min, major enantiomer tr = 21.2 min. $[\alpha]_D^{25}$ = -96.6 (*c* = 0.25, $CHCl_3$).

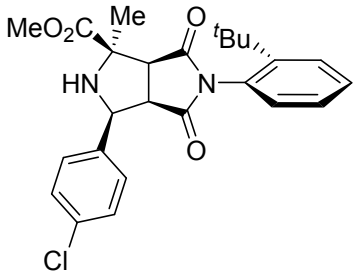
3.38 Synthesis of methyl (1R,3S,3aR,6aS)-3-(4-bromophenyl)-5-(2-(tert-butyl)phenyl)-1-methyl-4,6-dioxooctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**7ap**).



7ap

Prepared according to general procedure **C** from *N*-(2-*t*-butylphenyl)maleimide **6** (37.8 mg, 0.165 mmol) and imino ester **2p** (40.5 mg, 0.15 mmol) at -30 °C, after flash column chromatography (hexanes : AcOEt = 2:1) afforded the product **7ap** as a white solid (52.3 mg, 70% yield) and 88% *ee*. Mp: 109-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 11.5, 4.8 Hz, 3 H), 7.37-7.31 (m, 3 H), 7.25-7.22 (m, 1 H), 6.78 (dd, *J* = 7.7, 1.3 Hz, 1 H), 4.83-4.79 (m, 1 H), 3.84 (s, 3 H), 3.66 (t, *J* = 8.3 Hz, 1 H), 3.42 (d, *J* = 7.9 Hz, 1 H), 2.51 (d, *J* = 6.6 Hz, 1 H), 1.66 (s, 3 H), 1.21 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.83, 174.52, 172.60, 147.63, 135.80, 131.44, 130.66, 129.77, 129.65, 128.88, 128.76, 127.46, 122.05, 67.38, 61.44, 55.32, 52.71, 49.79, 35.63, 31.57, 23.86. ESI-MS calculated for $C_{25}H_{27}BrN_2NaO_4$: m/z (%): 521.1046 ($M+H^+$), found: 521.1056. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 80:20, 1.0 mL/min, 220 nm); minor enantiomer tr = 9.6 min, major enantiomer tr = 21.2 min. $[\alpha]_D^{25}$ = -88.2 (*c* = 0.25, $CHCl_3$).

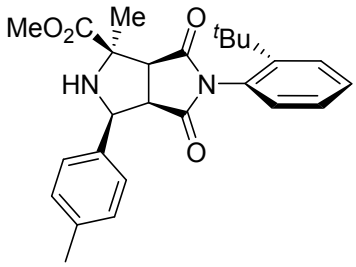
3.39 Synthesis of methyl (1R,3S,3aR,6aS)-5-(2-(tert-butyl)phenyl)-3-(4-chlorophenyl)-1-methyl-4,6-dioxooctahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**7aq**).



7aq

Prepared according to general procedure **C** from *N*-(2-*t*-butylphenyl)maleimide **6** (37.8 mg, 0.165 mmol) and imino ester **2q** (33.9 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **7aq** as a white solid (56.7 mg, 83% yield) and 94% *ee*. Mp: 99-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.1, 1.4 Hz, 1 H), 7.42 (d, *J* = 8.5 Hz, 2 H), 7.33 (dd, *J* = 11.4, 5.1 Hz, 3 H), 7.26-7.22 (m, 1 H), 6.78 (dd, *J* = 7.7, 1.5 Hz, 1 H), 4.83 (d, *J* = 8.6 Hz, 1 H), 3.84 (s, 3 H), 3.69-3.64 (m, 1 H), 3.42 (d, *J* = 7.9 Hz, 1 H), 2.52 (s, 1 H), 1.67 (s, 3 H), 1.21 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.86, 174.56, 172.64, 147.66, 135.26, 133.90, 130.67, 129.79, 129.66, 128.91, 128.55, 128.43, 127.47, 67.40, 61.42, 55.36, 52.73, 49.88, 35.65, 31.58, 23.89. ESI-MS calculated for $C_{25}H_{27}ClN_2NaO_4$: m/z (%): 477.1552 ($M+H^+$), found: 477.1563. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 80:20, 1.0 mL/min, 220 nm); minor enantiomer tr = 7.3 min, major enantiomer tr = 10.8 min. $[\alpha]_D^{25}$ = -87.7 (*c* = 0.25, $CHCl_3$).

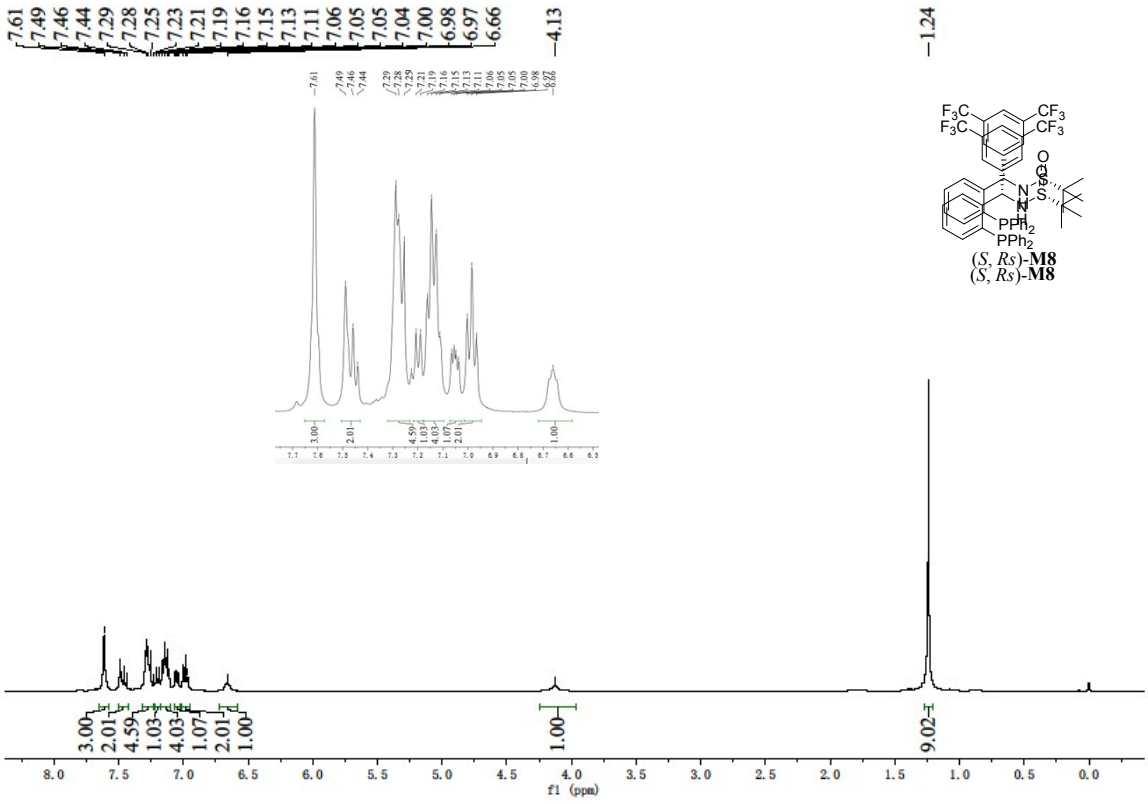
3.40 Synthesis of methyl (1R,3S,3aR,6aS)-5-(2-(tert-butyl)phenyl)-1-methyl-4,6-dioxo-3-(p-tolyl)octahydropyrrolo[3,4-c]pyrrole-1-carboxylate (**7ar**).



7ar

Prepared according to general procedure **C** from *N*-(2-*t*-butylphenyl)maleimide **6** (37.8 mg, 0.165 mmol) and imino ester **2r** (30.8 mg, 0.15 mmol) at -30 °C, after flash column chromatography (Petroleum ether : AcOEt = 2:1) afforded the product **7ar** as a white solid (46.0 mg, 71% yield) and 88% *ee*. Mp: 86-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.1, 1.2 Hz, 1 H), 7.36-7.32 (m, 3 H), 7.26-7.22 (m, 1 H), 7.17 (d, *J* = 7.9 Hz, 2 H), 6.84 (dd, *J* = 7.7, 1.3 Hz, 1 H), 4.84 (d, *J* = 7.1 Hz, 1 H), 3.85 (s, 3 H), 3.68 (dd, *J* = 19.3, 11.1 Hz, 1 H), 3.43 (d, *J* = 7.9 Hz, 1 H), 2.67 (s, 1 H), 2.31 (s, 3 H), 1.68 (s, 3 H), 1.21 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.12, 174.76, 172.81, 147.70, 137.91, 133.40, 130.79, 129.80, 129.68, 129.13, 128.89, 127.43, 126.89, 67.55, 62.25, 55.86, 52.73, 50.40, 35.68, 31.61, 23.95, 21.17. ESI-MS calculated for $C_{26}H_{30}N_2NaO_4$: m/z (%): 457.2098 ($M+H^+$), found: 457.2108. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 80:20, 1.0 mL/min, 210 nm); minor enantiomer tr = 6.8 min, major enantiomer tr = 10.7 min. $[\alpha]_D^{25}$ = -90.8 (*c* = 0.25, $CHCl_3$)

3. ^{1}H , ^{19}F, ^{13}C NMR and HPLC Spectra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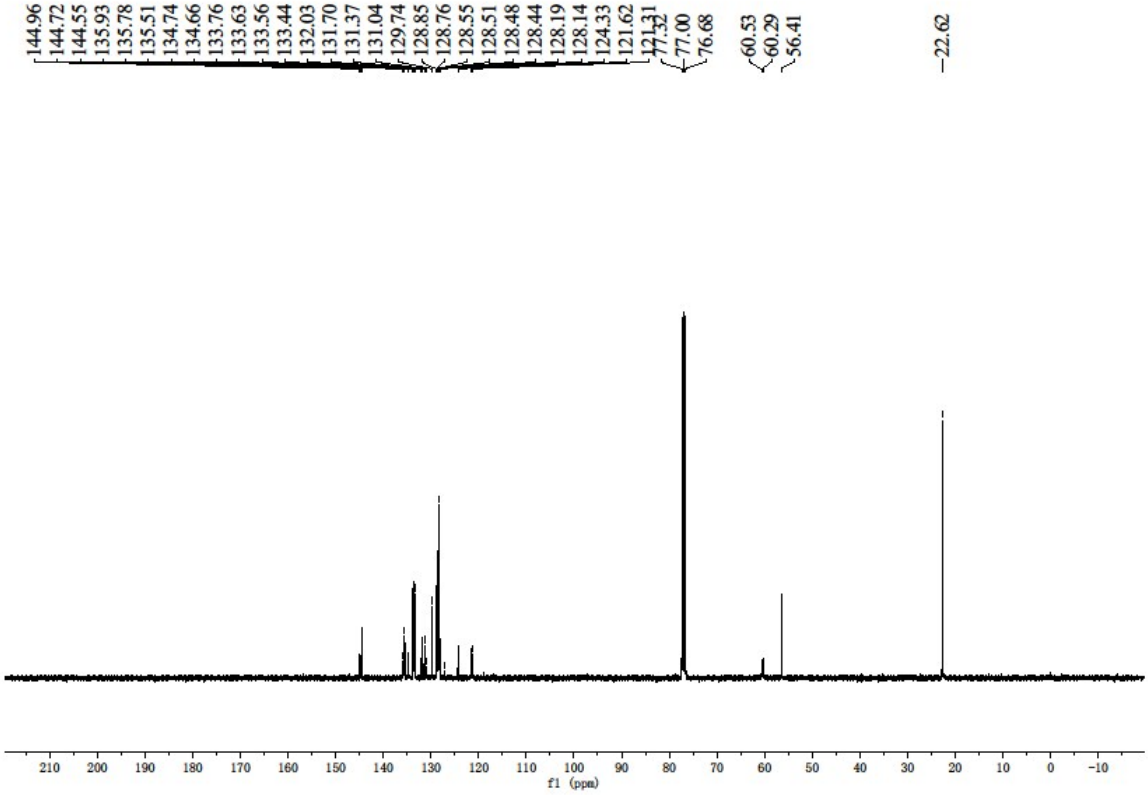
2.01
1.00
1.00
9.02
f1 (ppm)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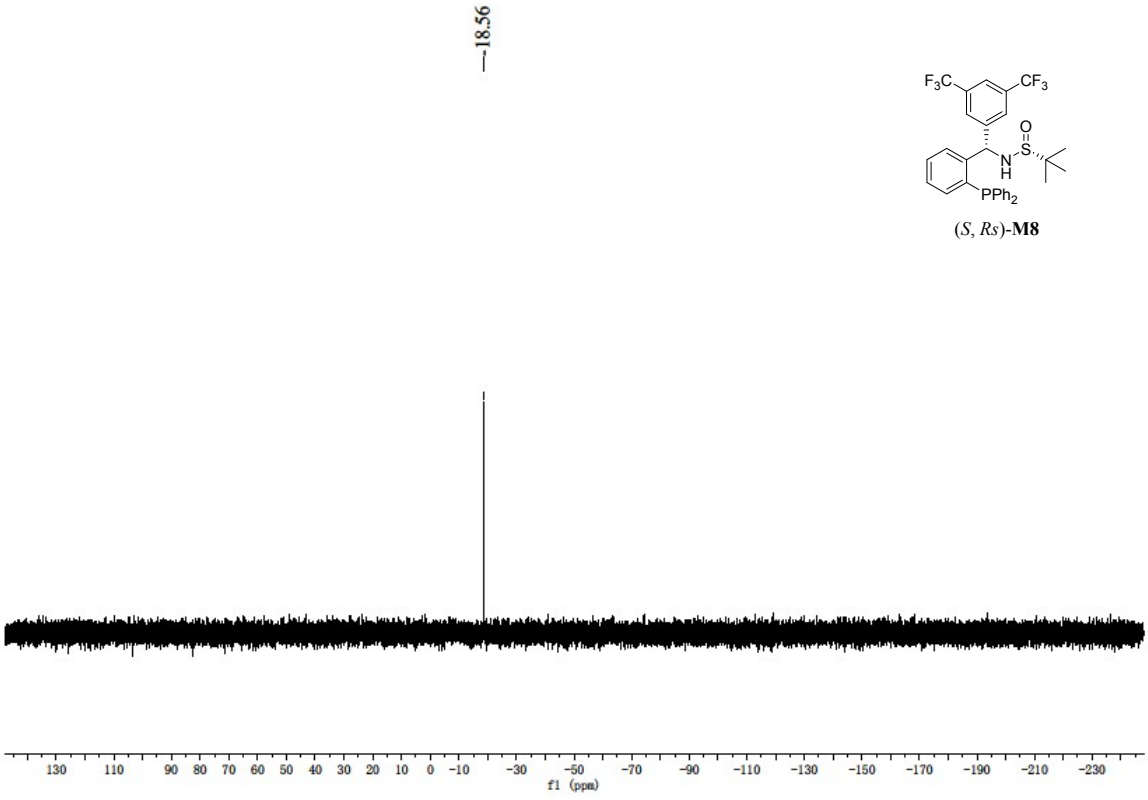
22.62
f1 (ppm)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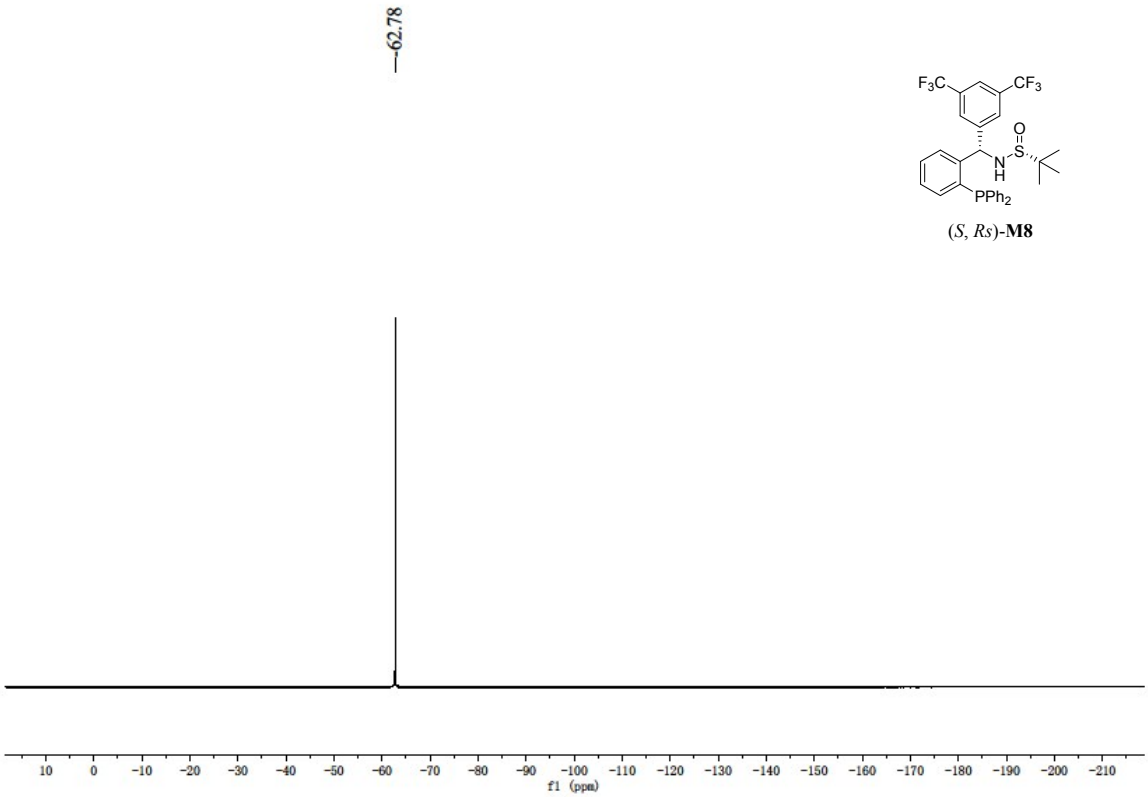
f1 (ppm)

(*S*, *Rs*)-**M8**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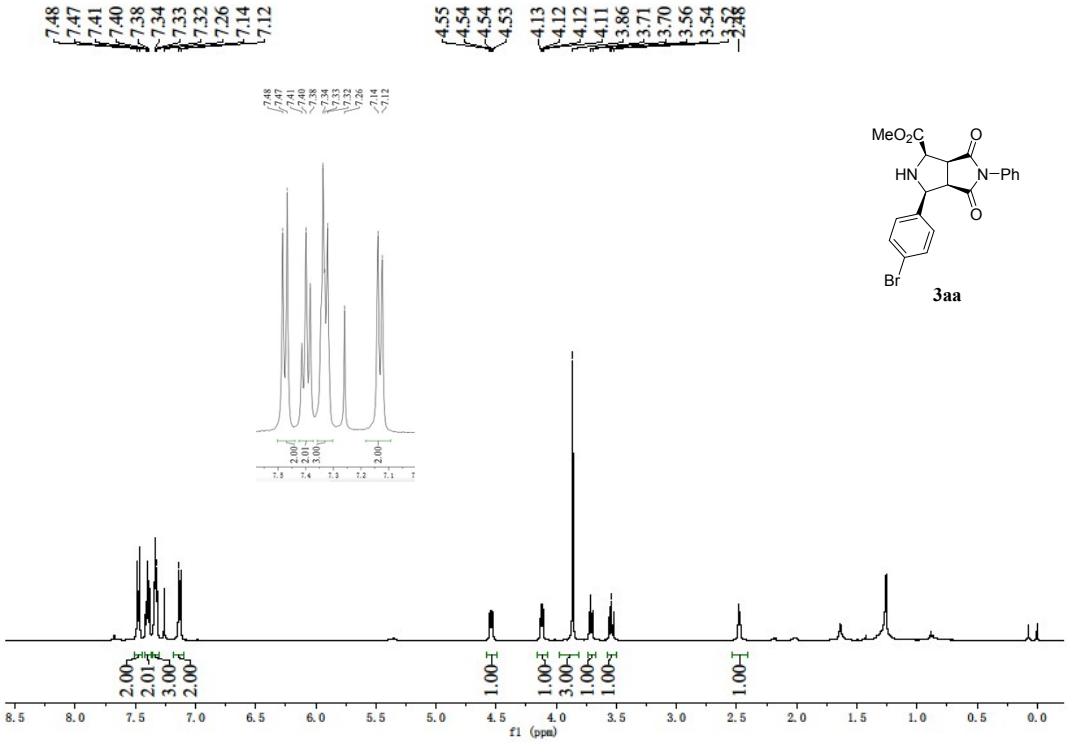
f1 (ppm)

(*S*, *Rs*)-**M8**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4.54
4.54
4.53
4.13
4.12
4.12
4.11
3.86
3.71
3.70
3.56
3.54
3.52
2.48
MeO2C
HN
O
N–Ph
O
Br
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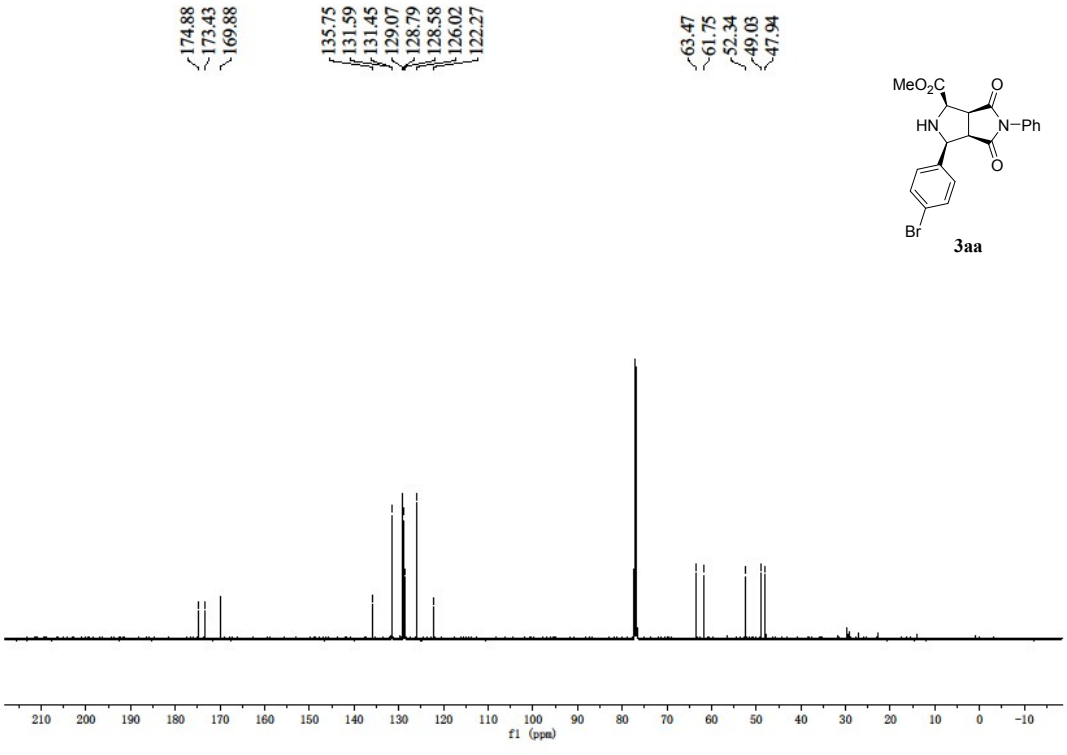
2.00
1.00
1.00
3.00
1.00
1.00
1.00
f1 (ppm)

3aa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126.02
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47.94
MeO2C
HN
O
N–Ph
O
Br
f1 (ppm)

3aa

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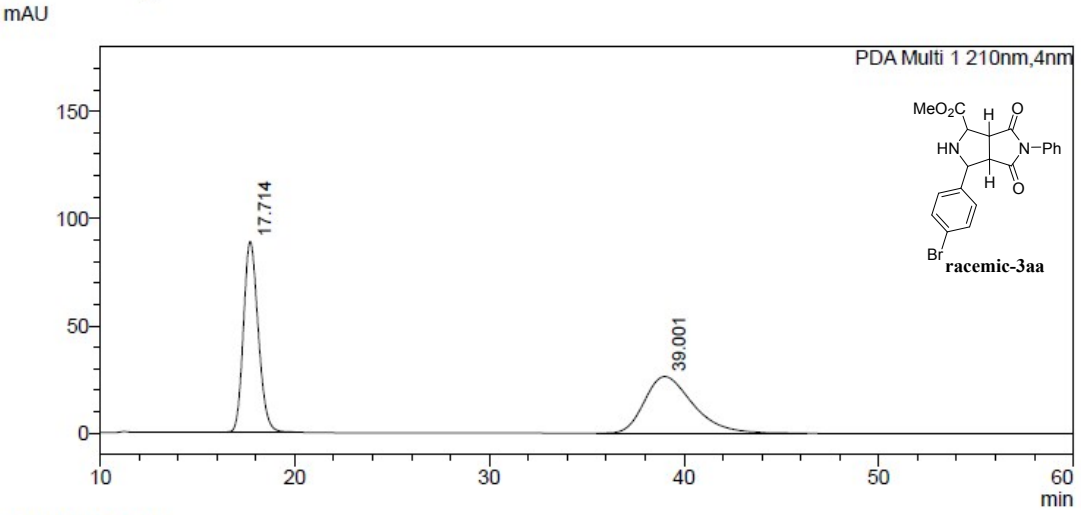
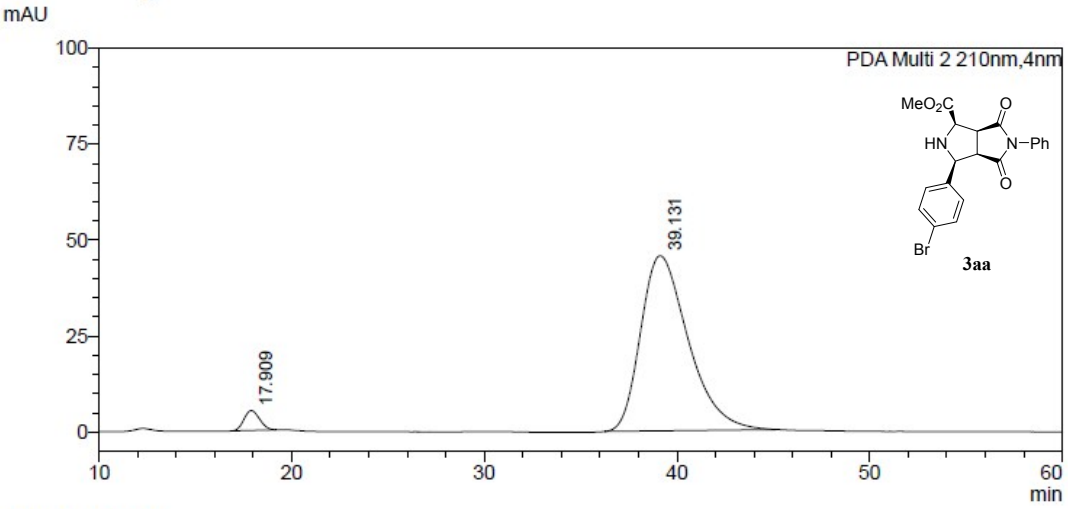


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	17.714	4680020	50.421	88801	77.059
2	39.001	4601802	49.579	26436	22.941
Total		9281822	100.000	115237	100.000

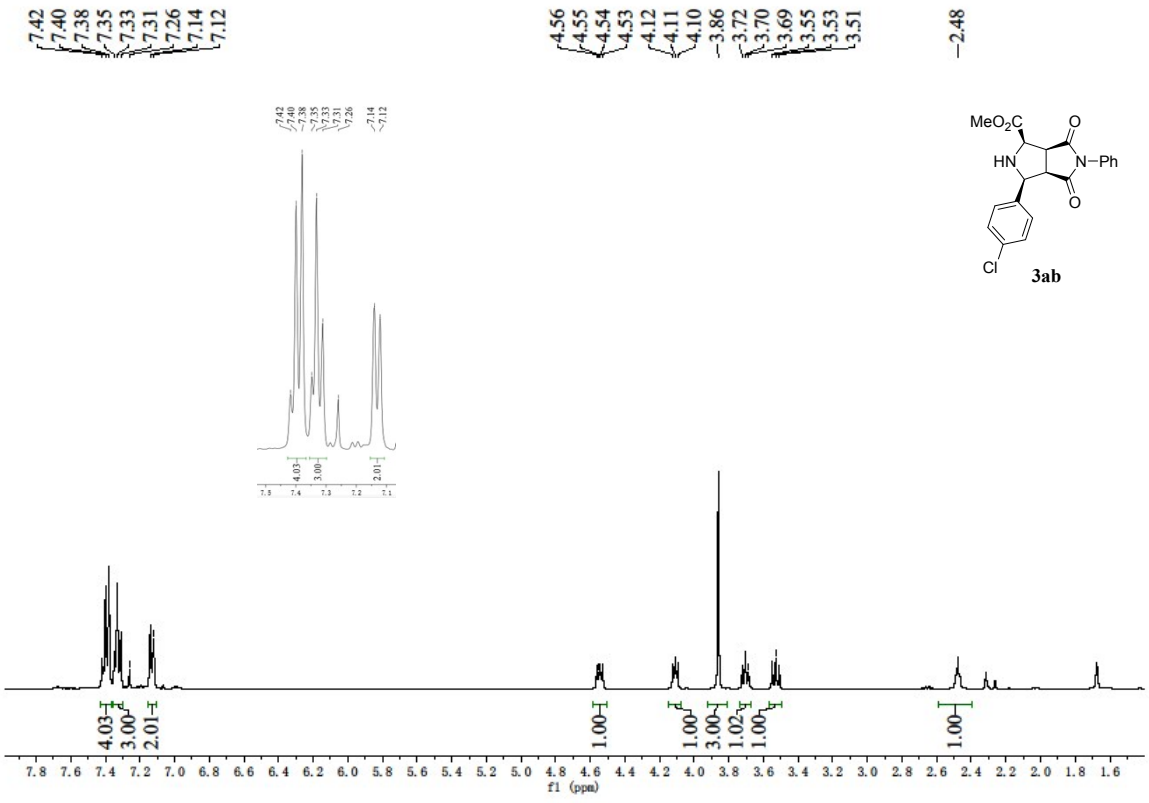
<Chromatogram>



<Peak Table>

PDA Ch2 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	17.909	291637	3.577	5175	10.182
2	39.131	7861029	96.423	45651	89.818
Total		8152666	100.000	50826	100.000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7.31
7.26
7.14
7.12
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4.55
4.54
4.53
4.12
4.11
4.10
3.86
3.72
3.70
3.69
3.55
3.53
3.51
2.48
MeO2C
O
HN
N–Ph
O
Cl
3ab
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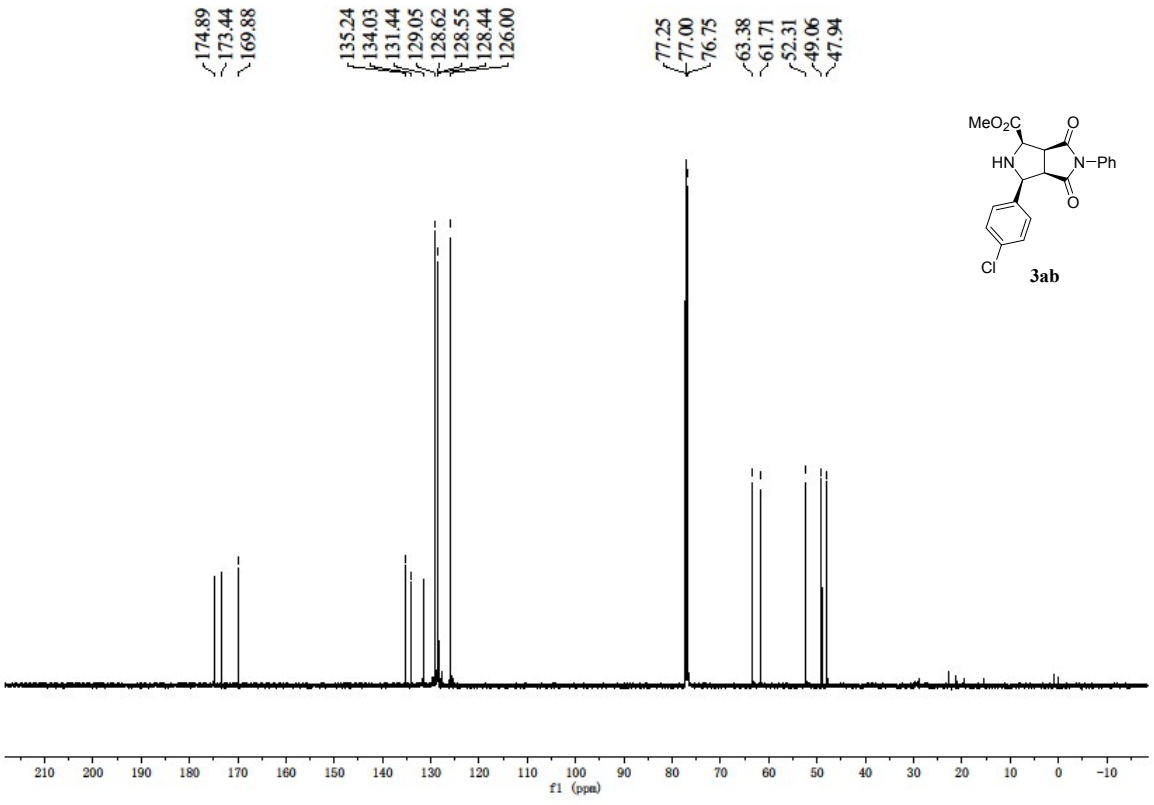
3.00
2.01
1.00
1.00
3.00
1.02
1.00
1.00
f1 (ppm)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169.88
135.24
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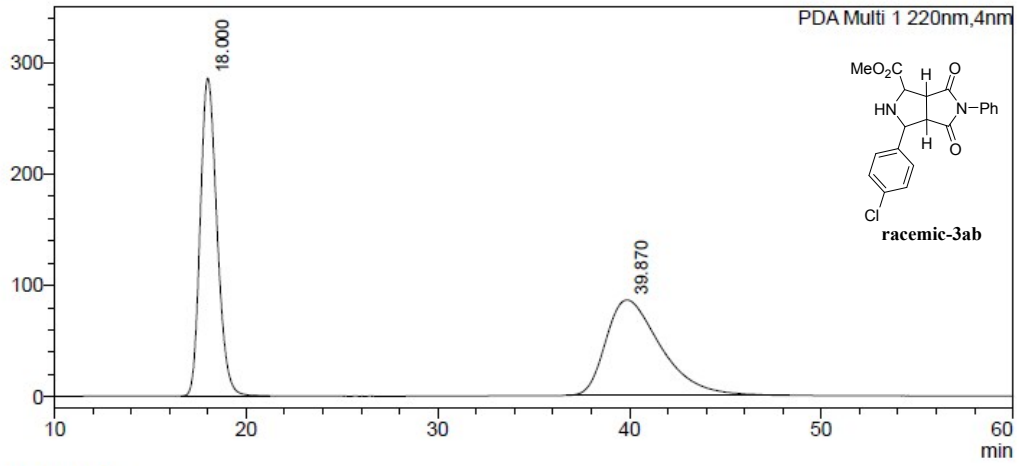
131.44
129.05
128.62
128.55
128.44
126.00
77.25
77.00
76.75
63.38
61.71
52.31
49.06
47.94
MeO2C
O
HN
N–Ph
O
Cl
3ab
f1 (ppm)

<Chromatogram>

mAU



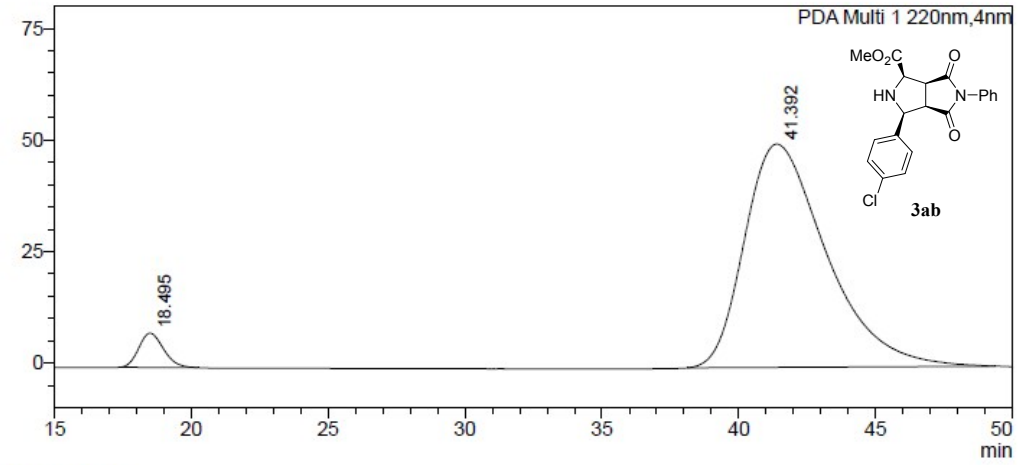
<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	18.000	17300629	50.337	285480	76.922
2	39.870	17068829	49.663	85648	23.078
Total		34369458	100.000	371127	100.000

<Chromatogram>

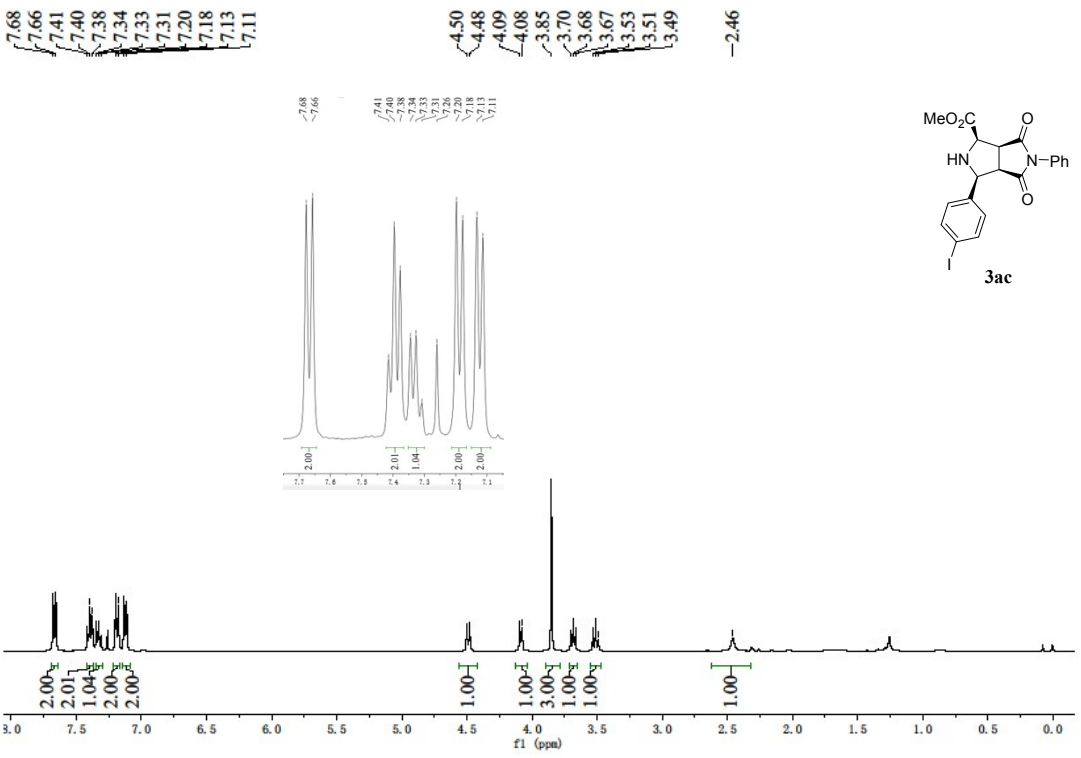
mAU



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	18.495	483198	4.433	7681	13.306
2	41.392	10416890	95.567	50042	86.694
Total		10900087	100.000	57723	100.000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7.34
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7.18
7.13
7.11
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4.09
4.08
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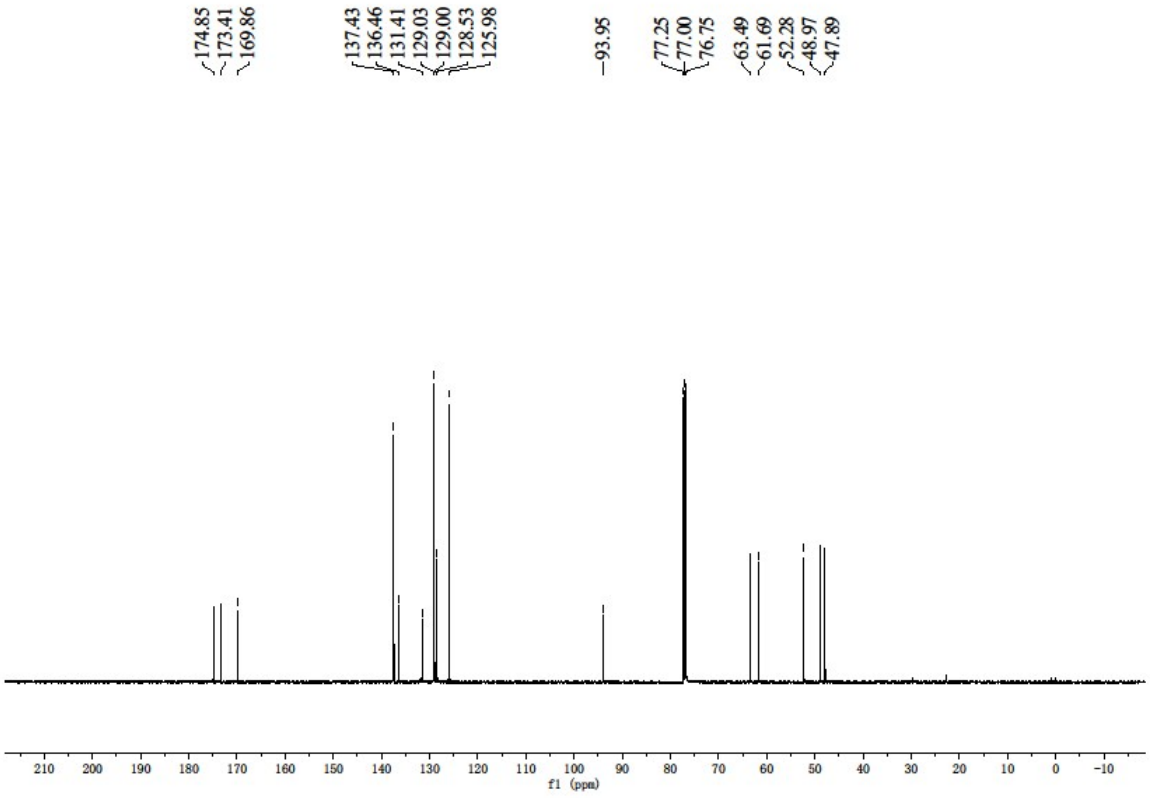
HN
N–Ph
O
I
3ac
f1 (ppm)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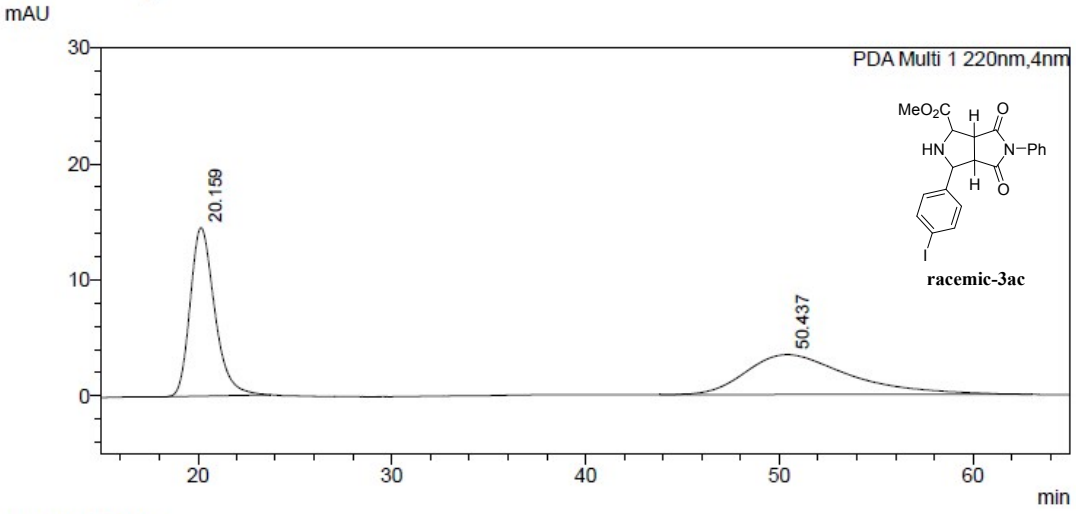
47.89
f1 (ppm)

<Chromatogram>

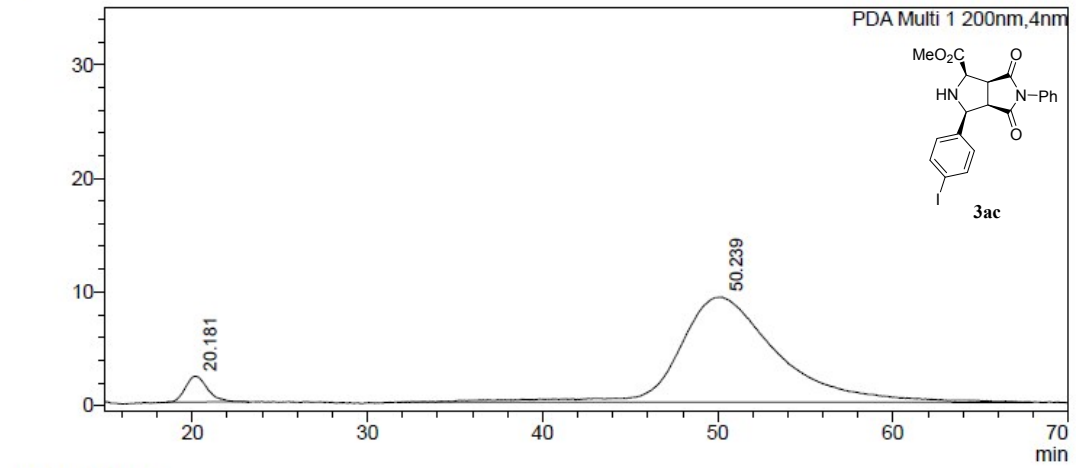


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.159	1276953	49.982	14510	80.865
2	50.437	1277865	50.018	3433	19.135
Total		2554818	100.000	17943	100.000

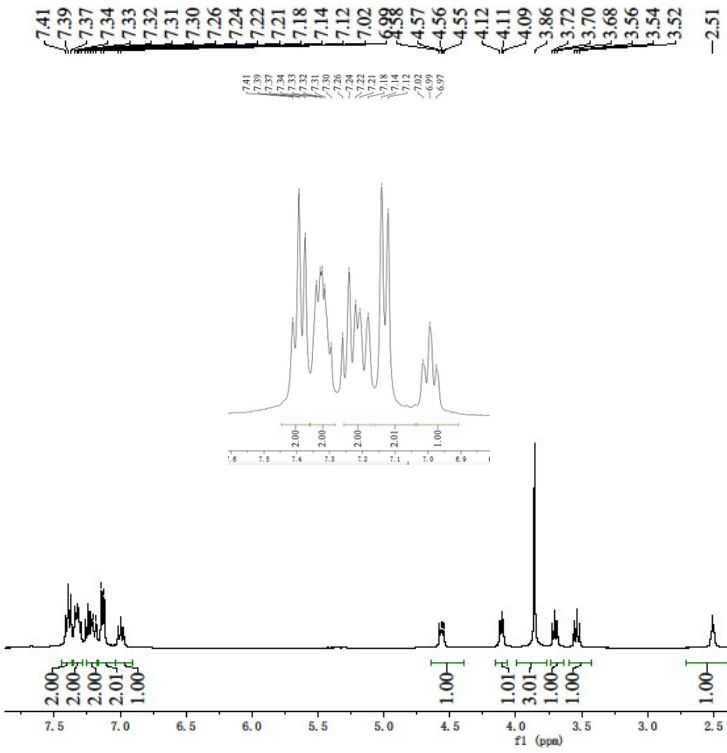
<Chromatogram>



<Peak Table>

PDA Ch1 200nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.181	199045	5.178	2269	19.694
2	50.239	3645339	94.822	9254	80.306
Total		3844384	100.000	11523	100.000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7.32
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7.26
7.24
7.22
7.21
7.18
7.14
7.12
7.02
6.99
4.58
4.57
4.56
4.55
4.12
4.11
4.09
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3.70
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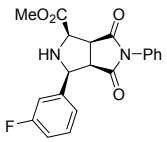
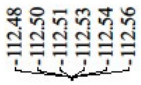
3.01
1.00
1.00
1.00
f1 (ppm)


MeO2C
O
HN
N–Ph
O
F

3ad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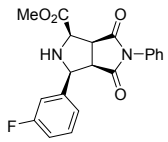
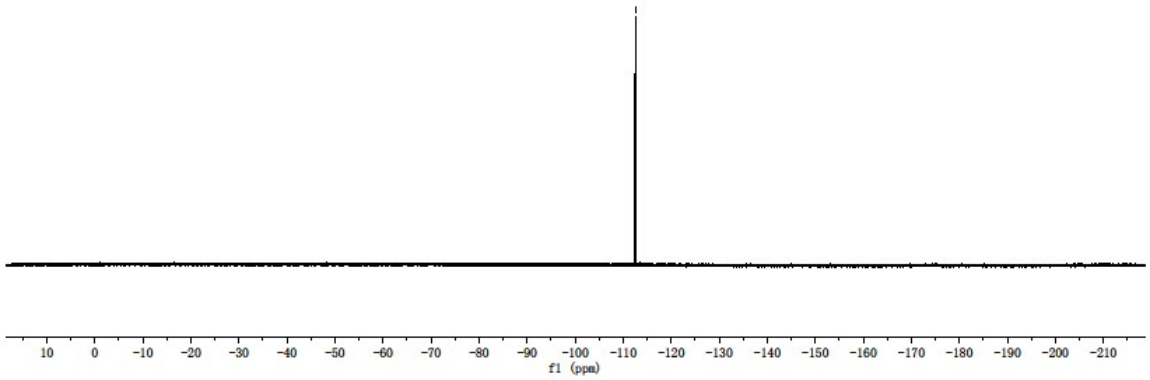
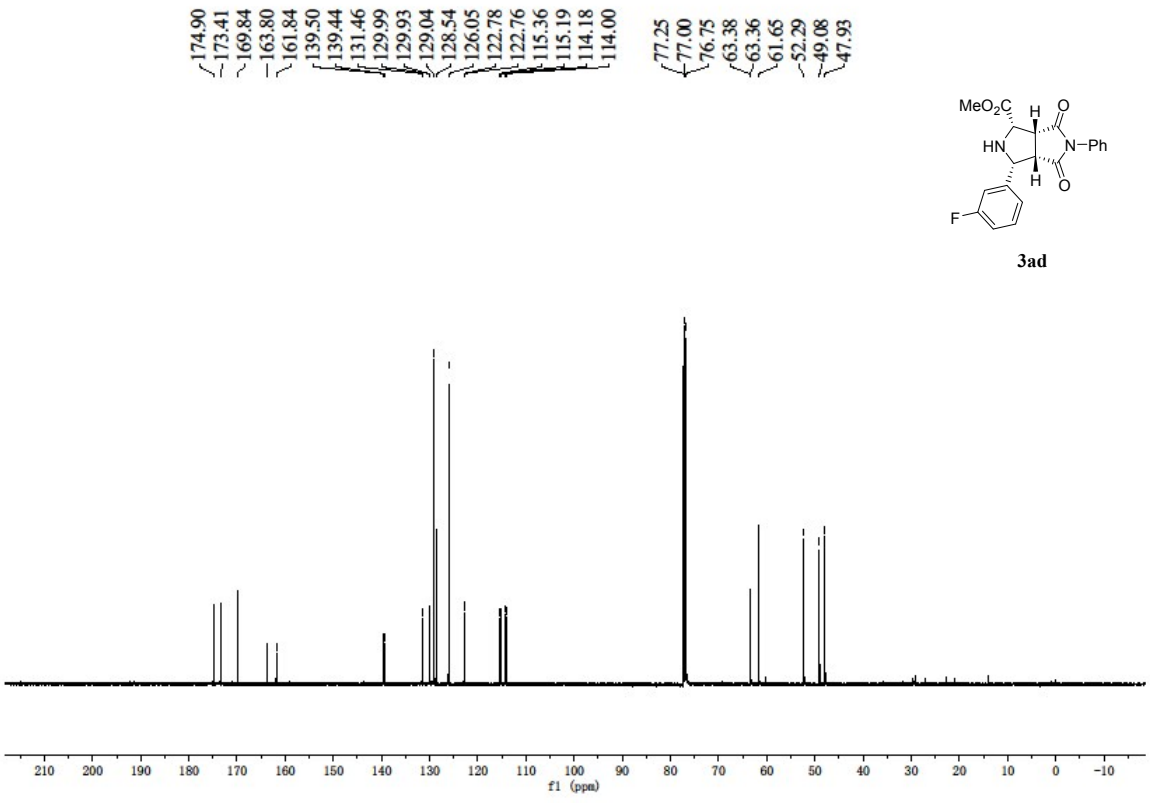
112.56


MeO2C
O
HN
N–Ph
O
F

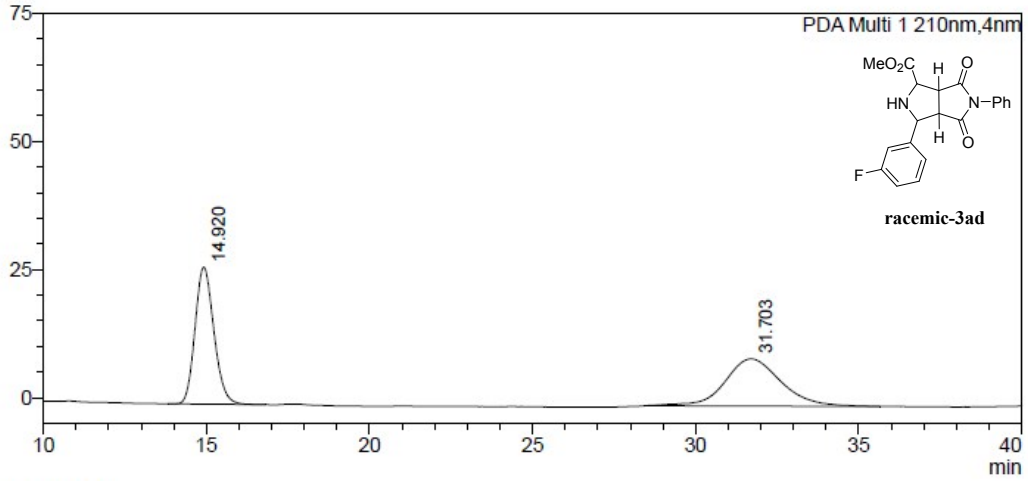
3ad


f1 (ppm)



<Chromatogram>

mAU

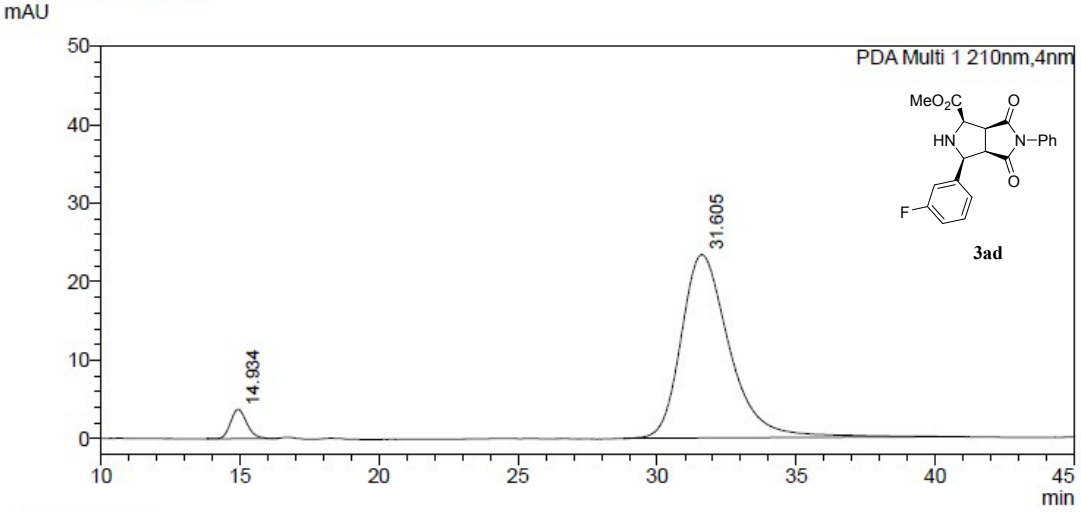


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	14.920	1078958	49.454	26752	74.385
2	31.703	1102761	50.546	9213	25.615
Total		2181719	100.000	35965	100.000

<Chromatogram>

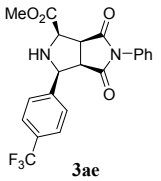


3ad

<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	14.934	148857	4.998	3707	13.704
2	31.605	2829346	95.002	23343	86.296
Total		2978203	100.000	27050	100.000



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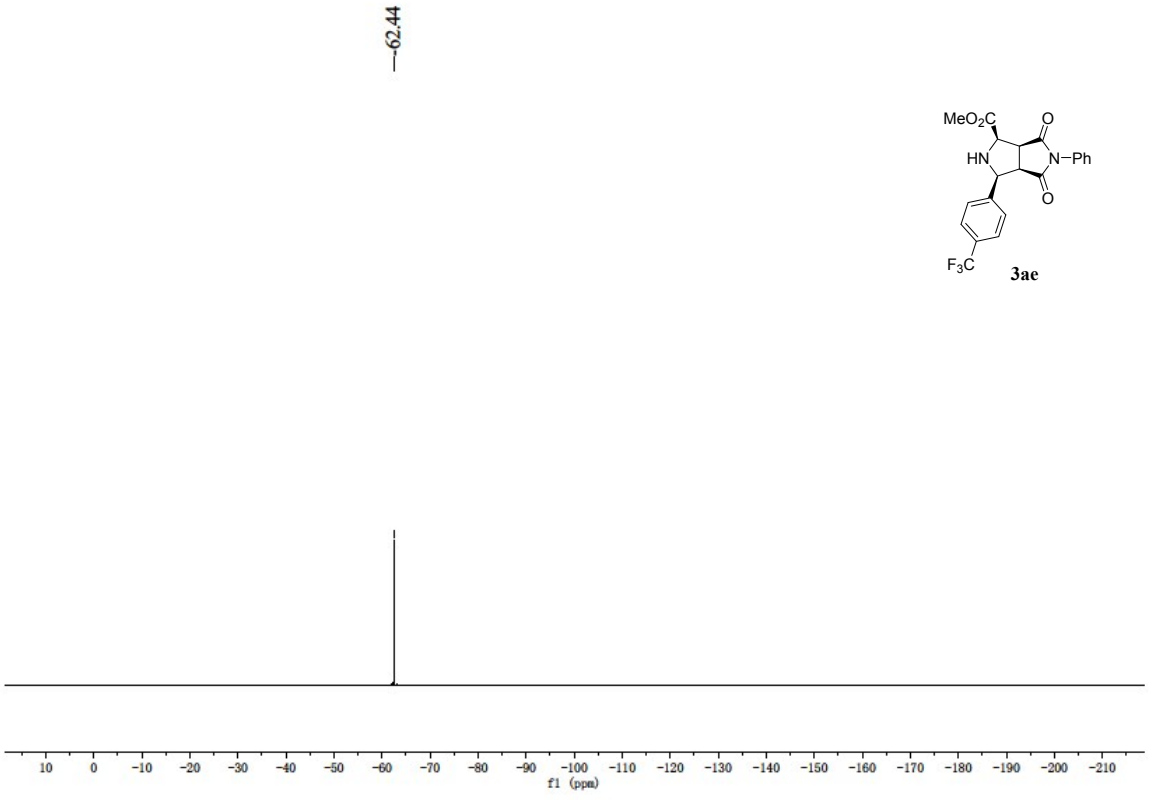
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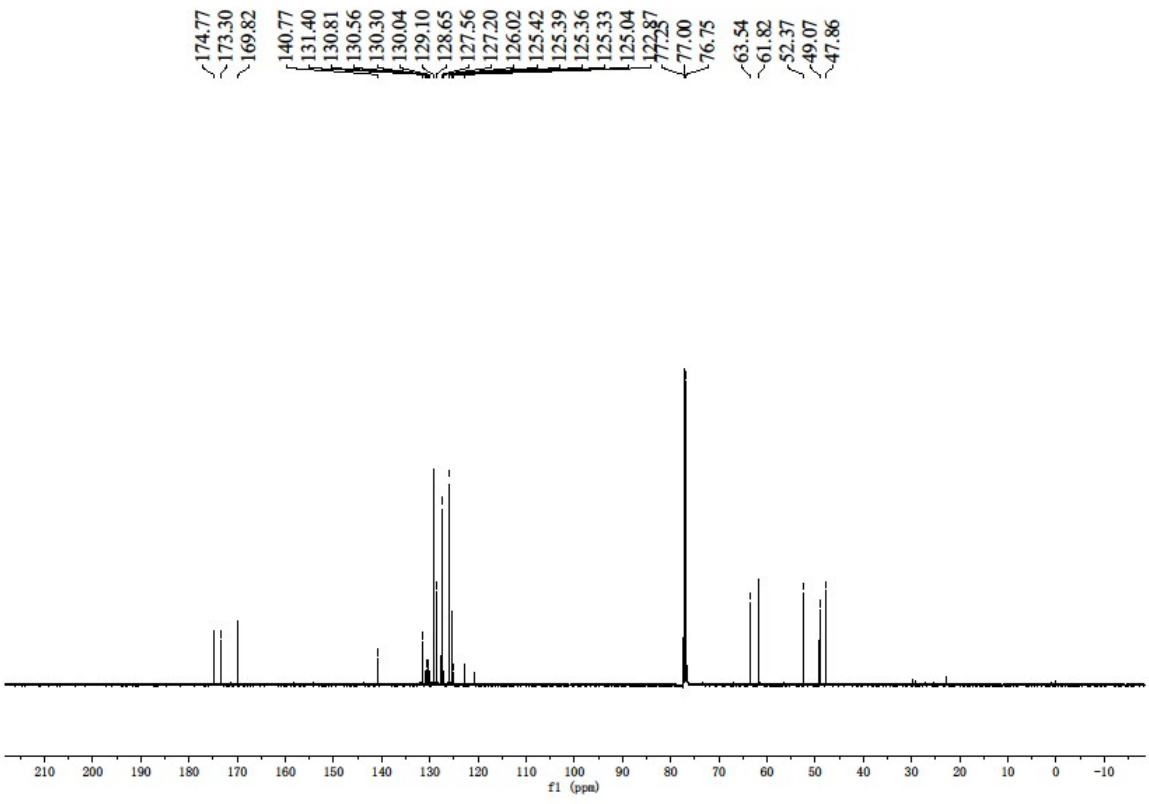
MeO2C
HN
O
N–Ph
O
F3C
3ae
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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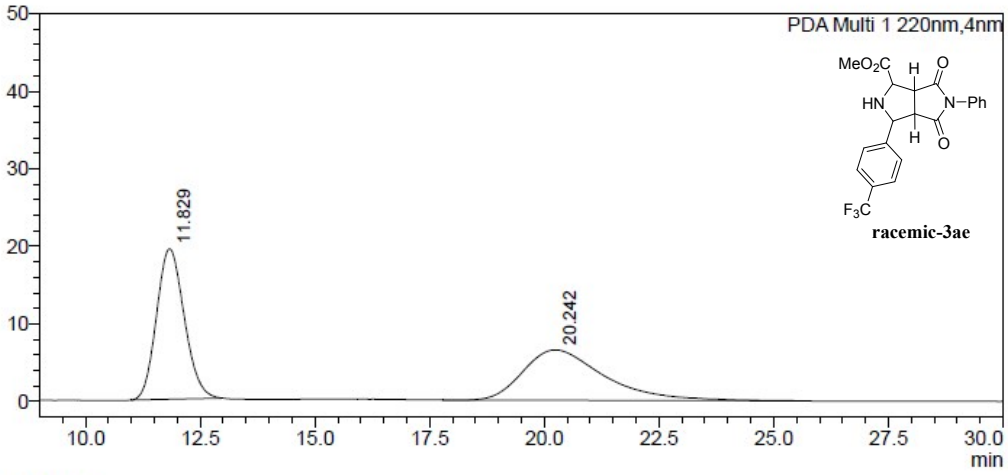
130.30
130.04
129.10
128.65
127.56
127.20
126.02
125.42
125.39
125.36
125.33
125.04
122.87
77.25
77.00
76.75
63.54
61.82
52.37
49.07
47.86
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

<Chromatogram>

mAU



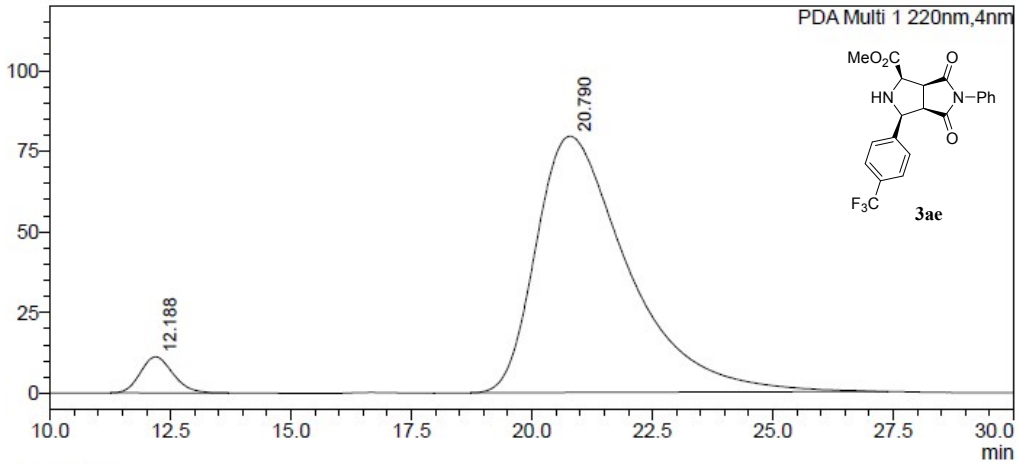
<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	11.829	817401	50.757	19413	74.970
2	20.242	793021	49.243	6481	25.030
Total		1610422	100.000	25894	100.000

<Chromatogram>

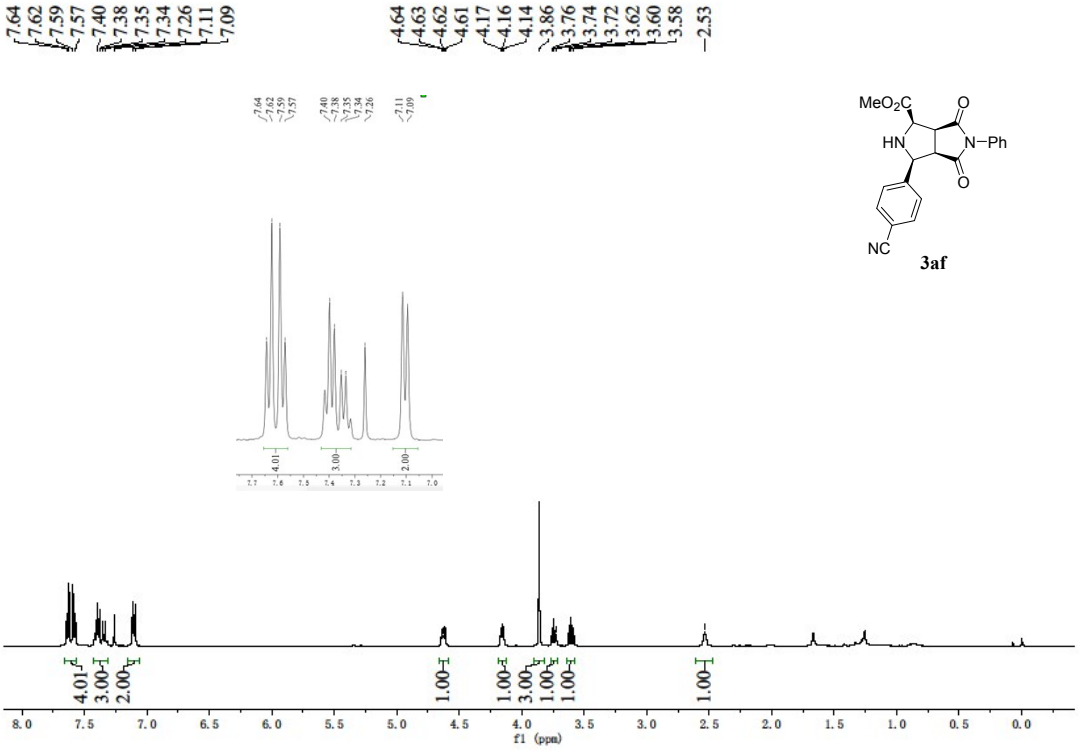
mAU



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	12.188	527184	4.740	11170	12.325
2	20.790	10594941	95.260	79463	87.675
Total		11122125	100.000	90633	100.000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7.26
7.11
7.09
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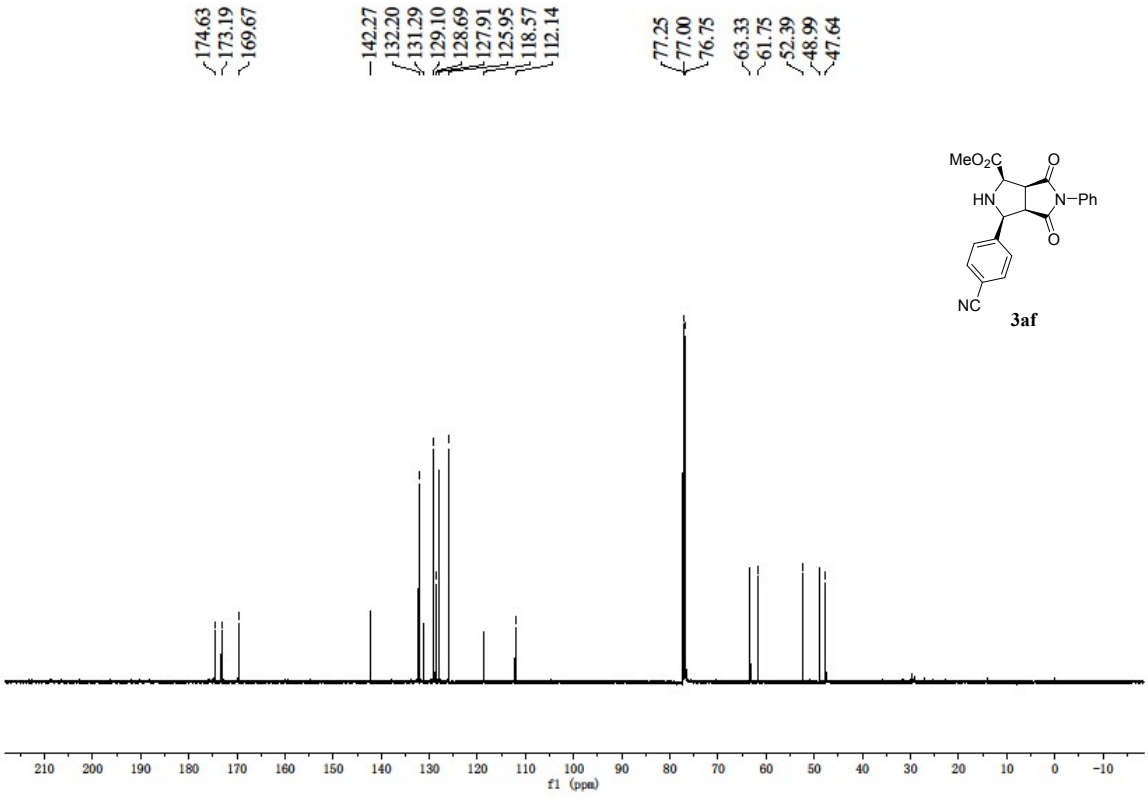
4.63
4.62
4.61
4.17
4.16
4.14
3.86
3.76
3.74
3.72
3.62
3.60
3.58
2.53
MeO2C
O
HN
N−Ph
O
NC
4.01
3.00
2.00
1.00
1.00
3.00
1.00
1.00
1.00
f1 (ppm)

3af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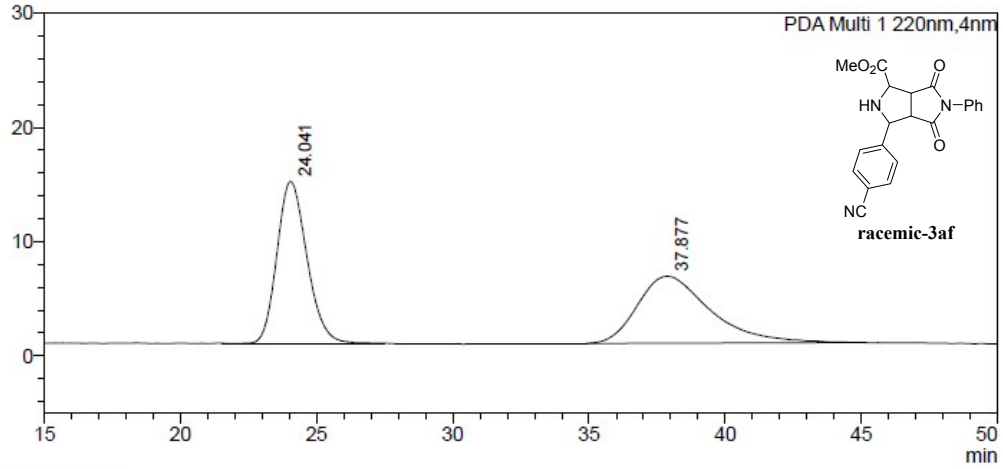
77.25
77.00
76.75
63.33
61.75
52.39
48.99
47.64
MeO2C
O
HN
N−Ph
O
NC
f1 (ppm)

3af

<Chromatogram>

mAU



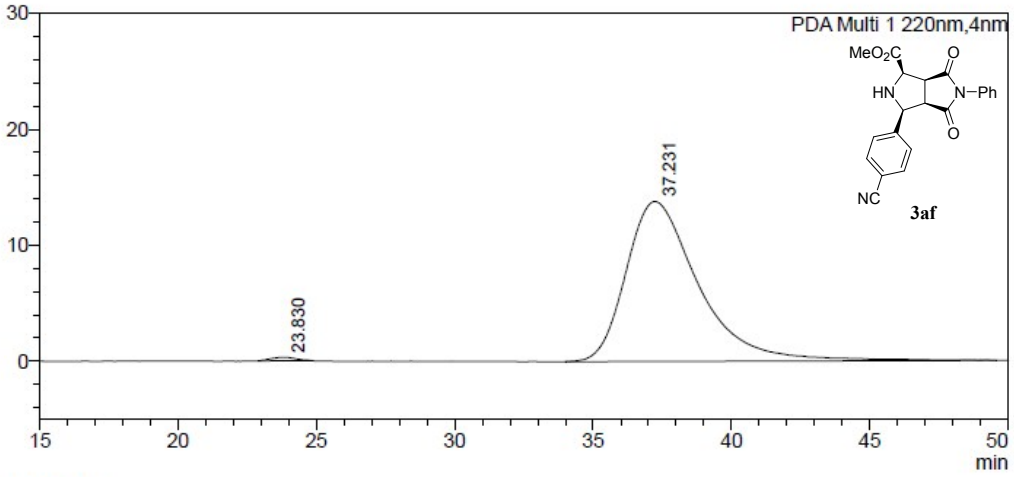
<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	24.041	1082525	49.812	14170	70.722
2	37.877	1090699	50.188	5866	29.278
Total		2173224	100.000	20036	100.000

<Chromatogram>

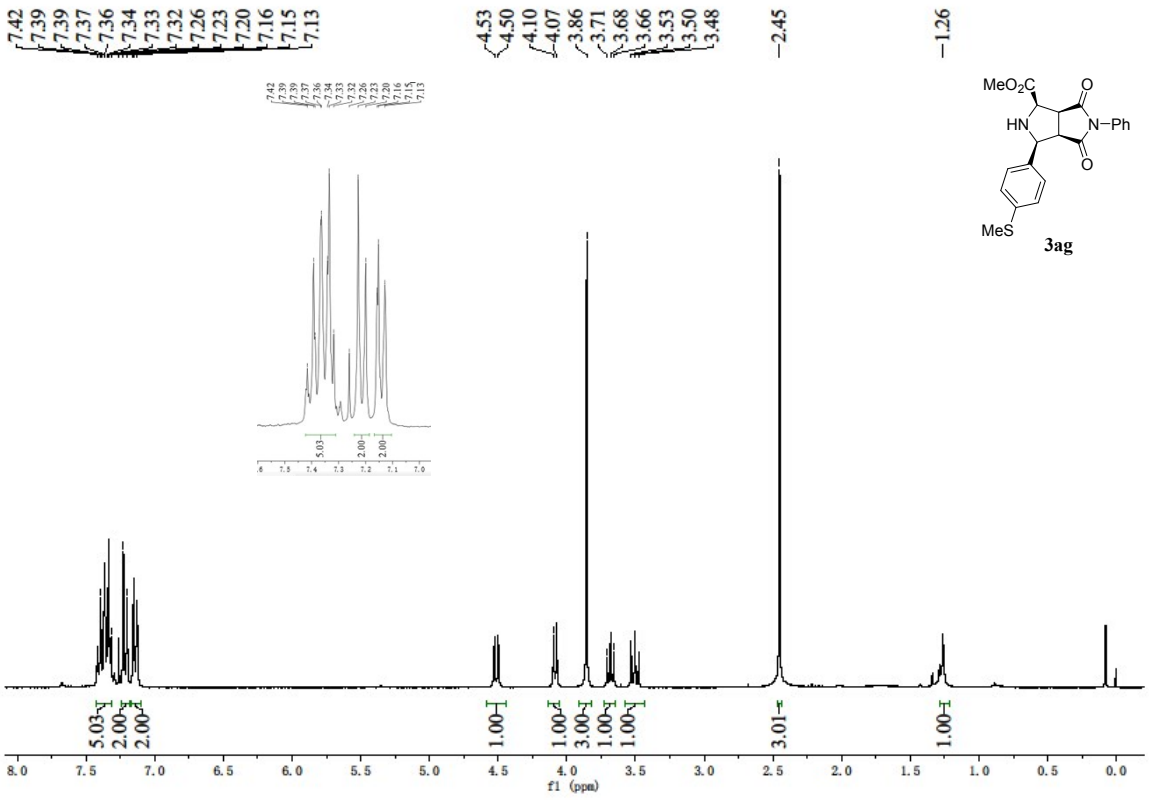
mAU



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	23.830	18645	0.734	296	2.101
2	37.231	2522556	99.266	13796	97.899
Total		2541202	100.000	14092	100.000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7.37
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7.34
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7.32
7.26
7.23
7.20
7.16
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7.13
4.53
4.50
4.10
4.07
3.86
3.71
3.68
3.66
3.53
3.50
3.48
2.45
1.26
MeO2C
HN
O
N–Ph
O
MeS
3ag
5.03
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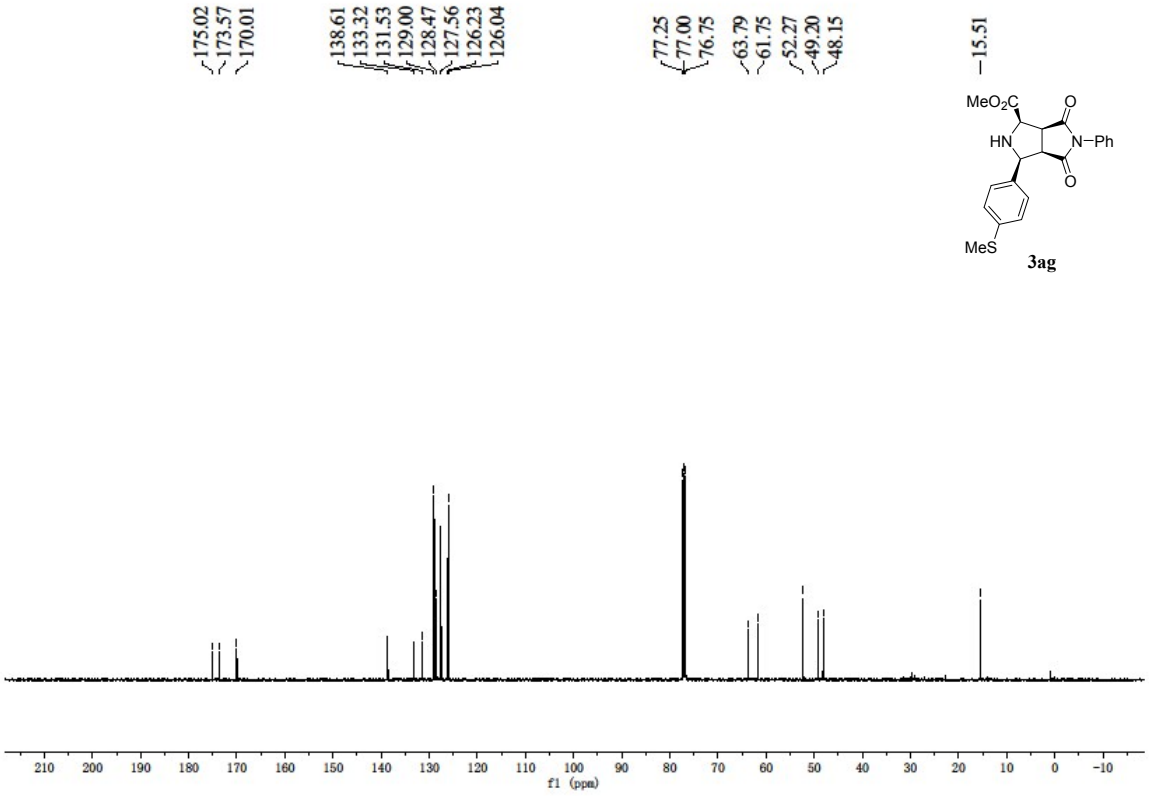
2.00
1.00
1.00
3.00
1.00
1.00
3.01
1.00
f1 (ppm)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131.53
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128.47
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77.00
76.75
63.79
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MeO2C
HN
O
N–Ph
O
MeS
3ag
f1 (ppm)

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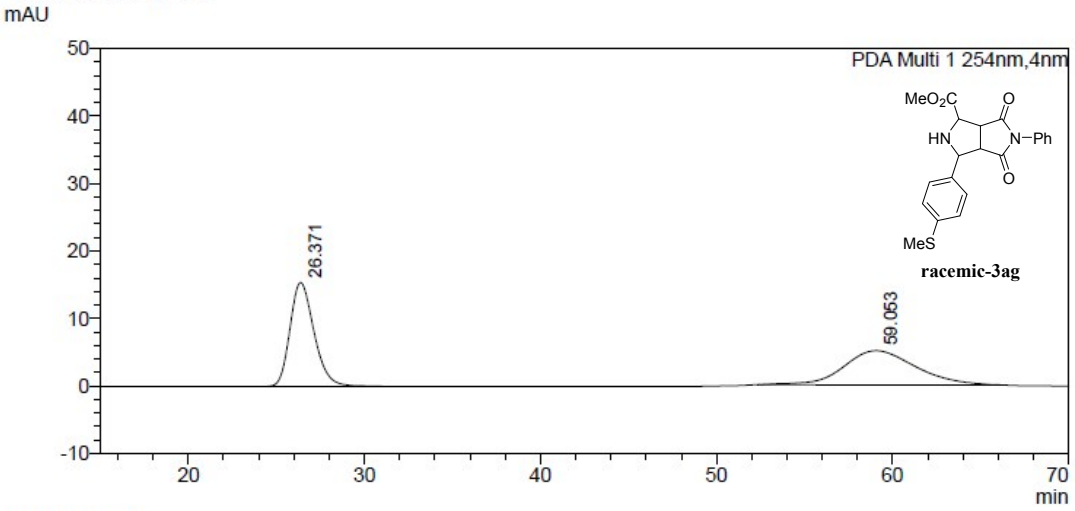
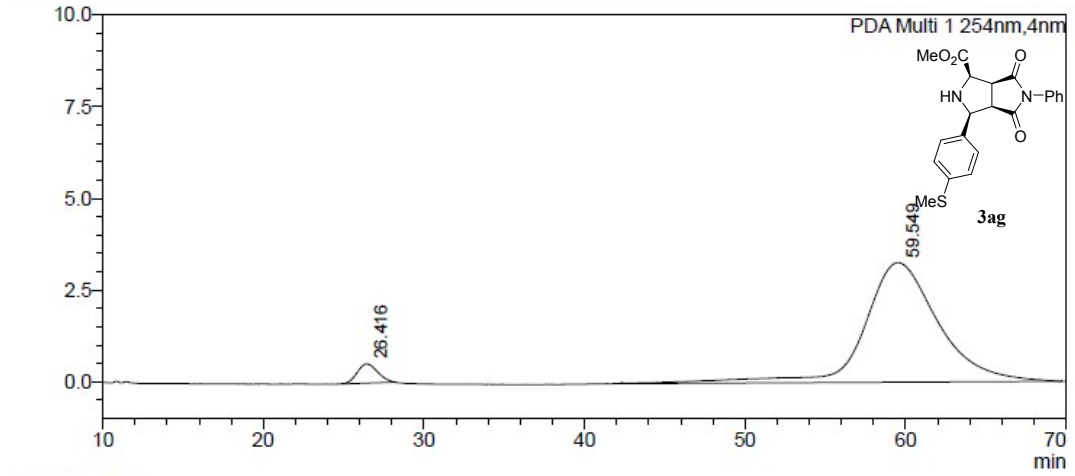


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	26.371	1466516	50.389	15384	75.231
2	59.053	1443864	49.611	5065	24.769
Total		2910380	100.000	20449	100.000

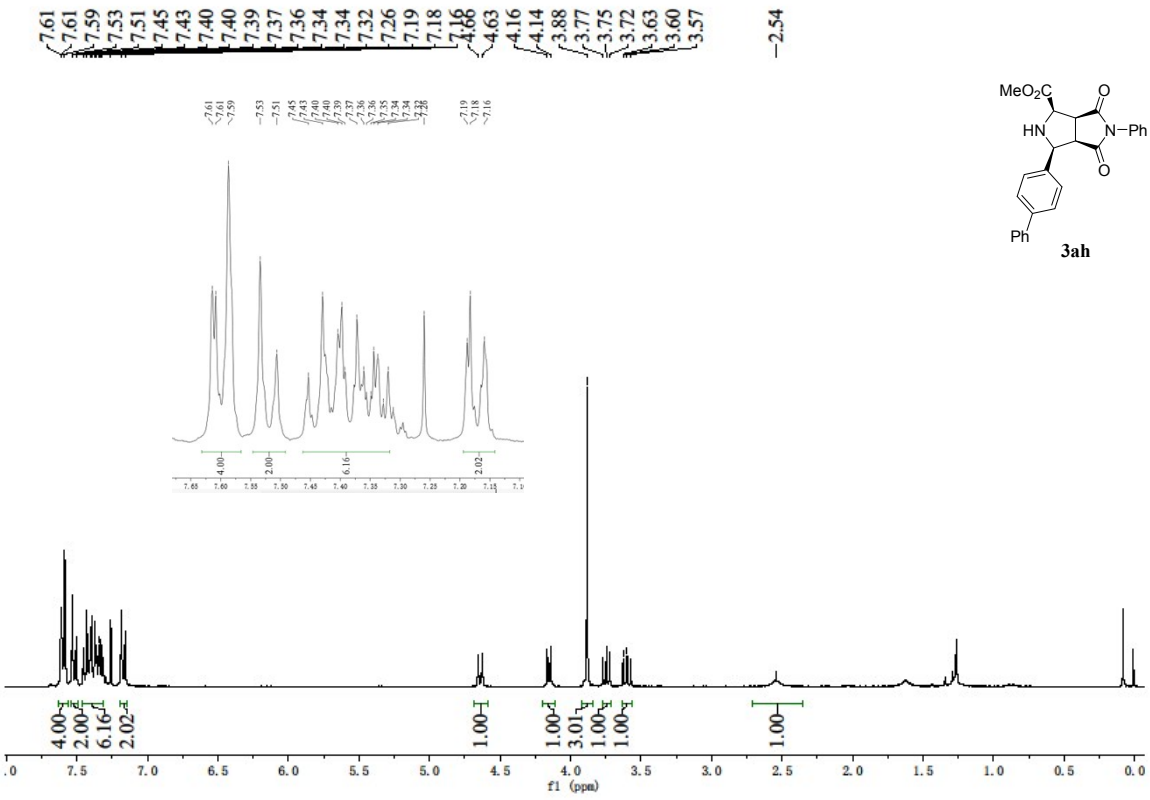
<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	26.416	46331	4.238	525	13.865
2	59.549	1046923	95.762	3263	86.135
Total		1093253	100.000	3788	100.000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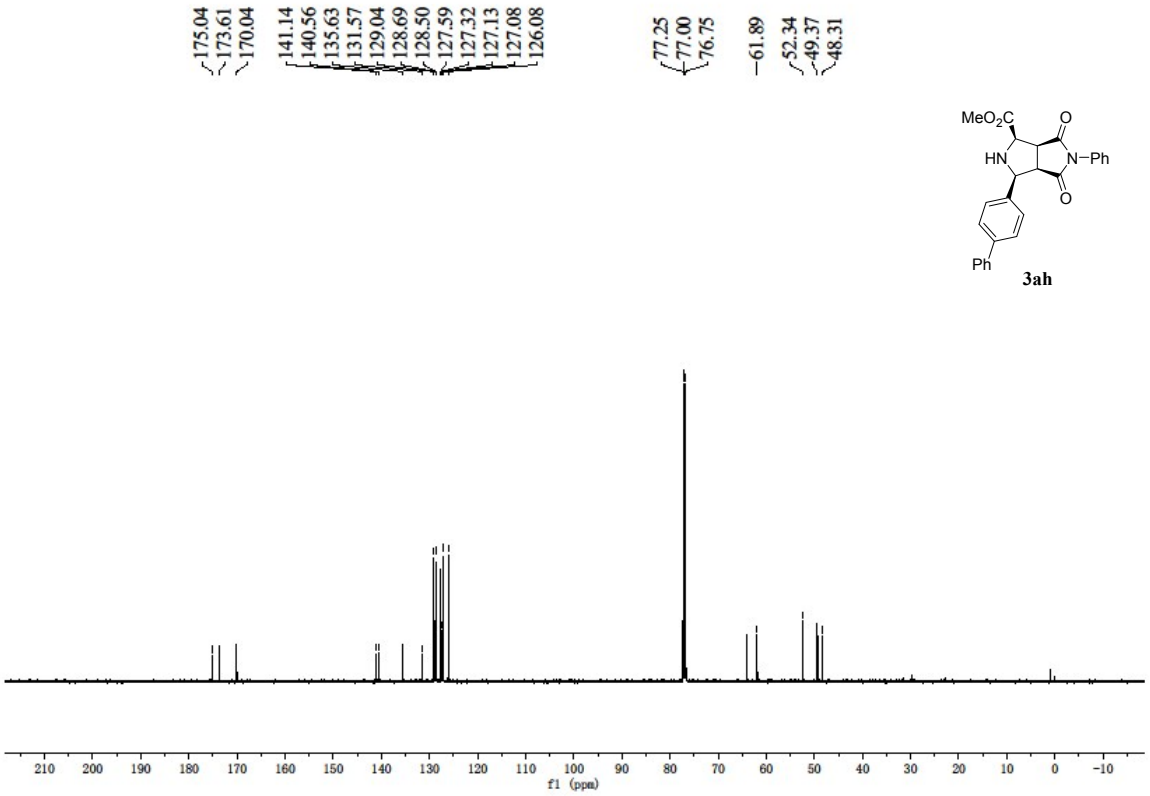
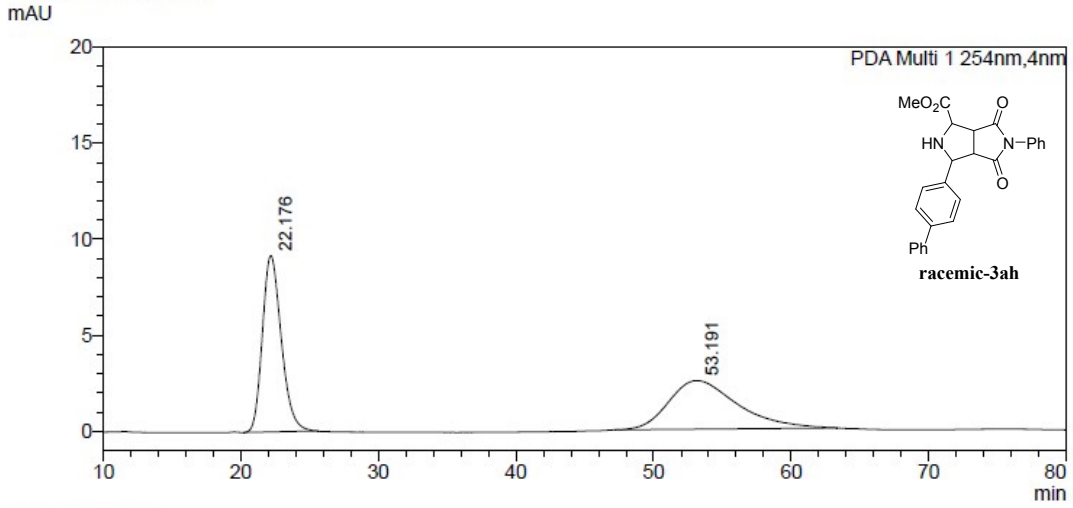
7.61
7.59
7.53
7.51
7.45
7.43
7.40
7.40
7.39
7.37
7.36
7.34
7.34
7.32
7.26
7.19
7.18
7.16
4.66
4.63
4.16
4.14
3.88
3.77
3.75
3.72
3.63
3.60
3.57
2.54
MeO2C
HN
N–Ph
O
O
Ph
3ah
4.00
2.00
6.16
2.02
1.00
1.00
3.01
1.00
1.00
1.00
f1 (ppm)


175.04
173.61
170.04
141.14
140.56
135.63
131.57
129.04
128.69
128.50
127.59
127.32
127.13
127.08
126.08
77.25
77.00
76.75
61.89
52.34
49.37
48.31
MeO2C
HN
N–Ph
O
O
Ph
3ah
f1 (ppm)

<Chromatogram>

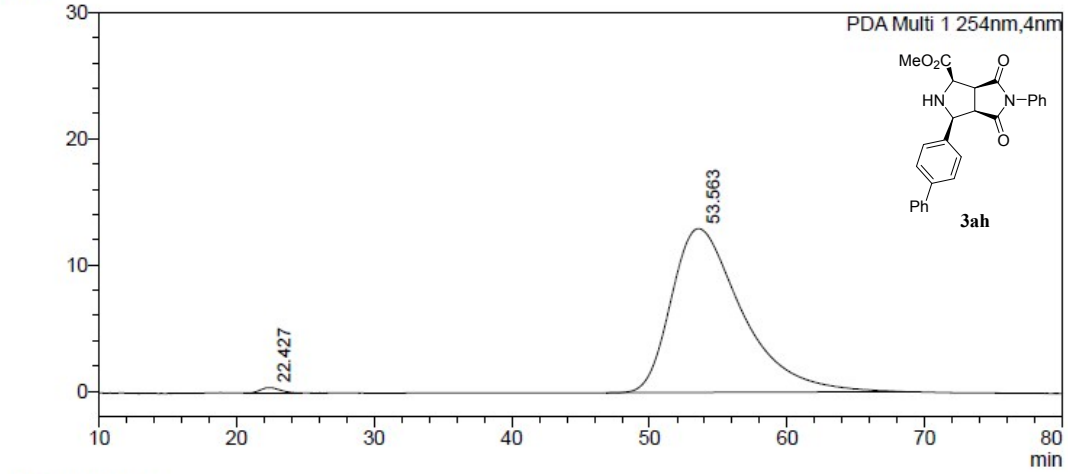


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	22.176	878195	49.874	9183	78.393
2	53.191	882630	50.126	2531	21.607
Total		1760825	100.000	11714	100.000

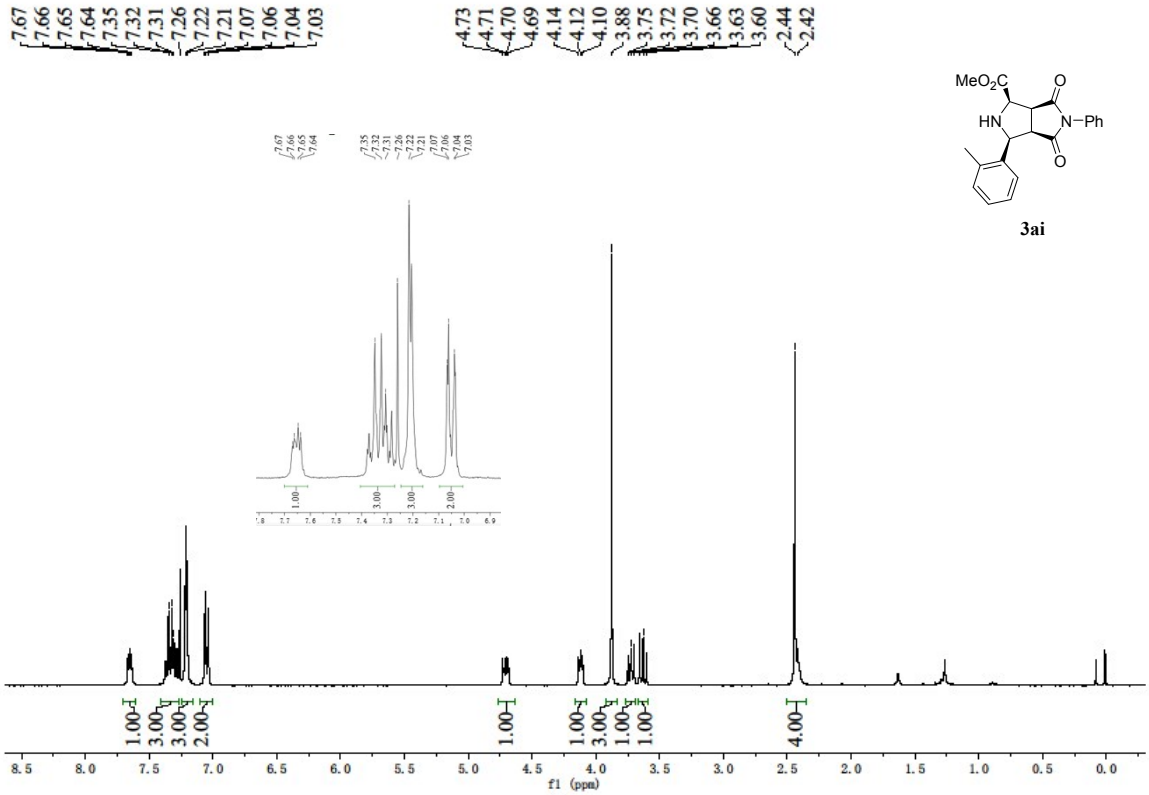
<Chromatogram>



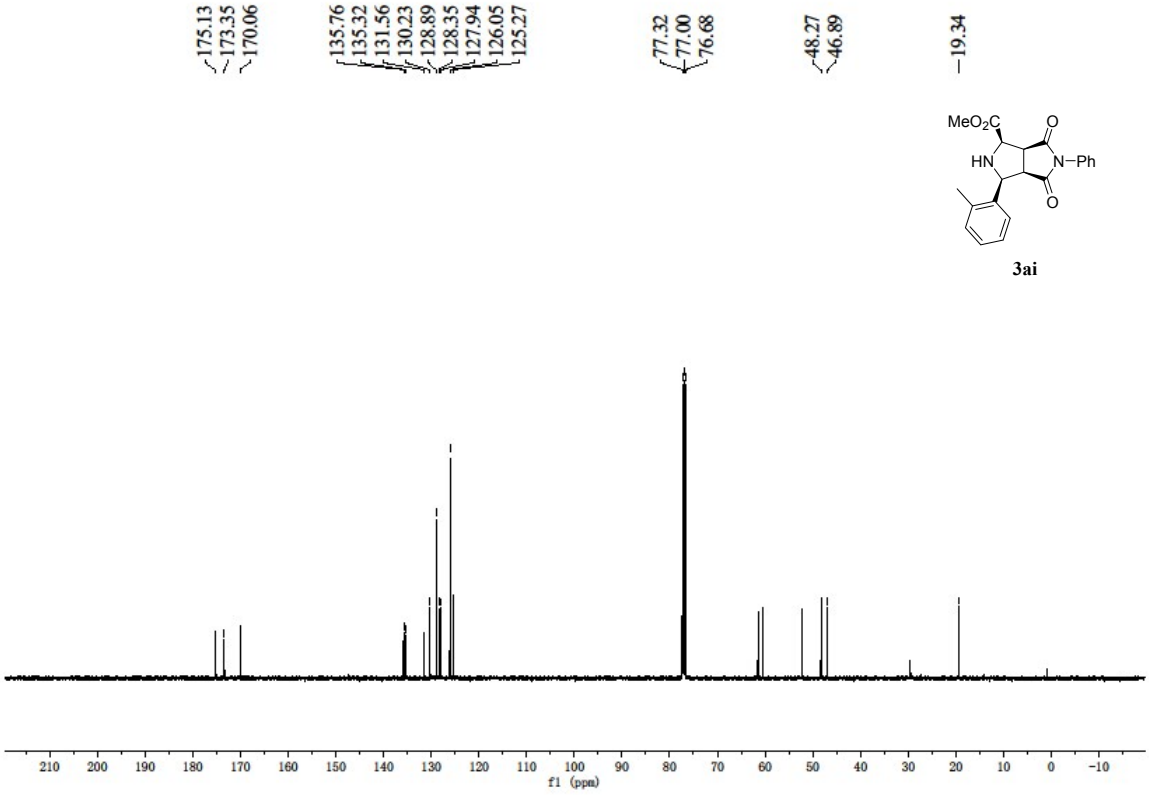
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	22.427	42356	0.901	434	3.235
2	53.563	4661007	99.099	12995	96.765
Total		4703363	100.000	13429	100.000

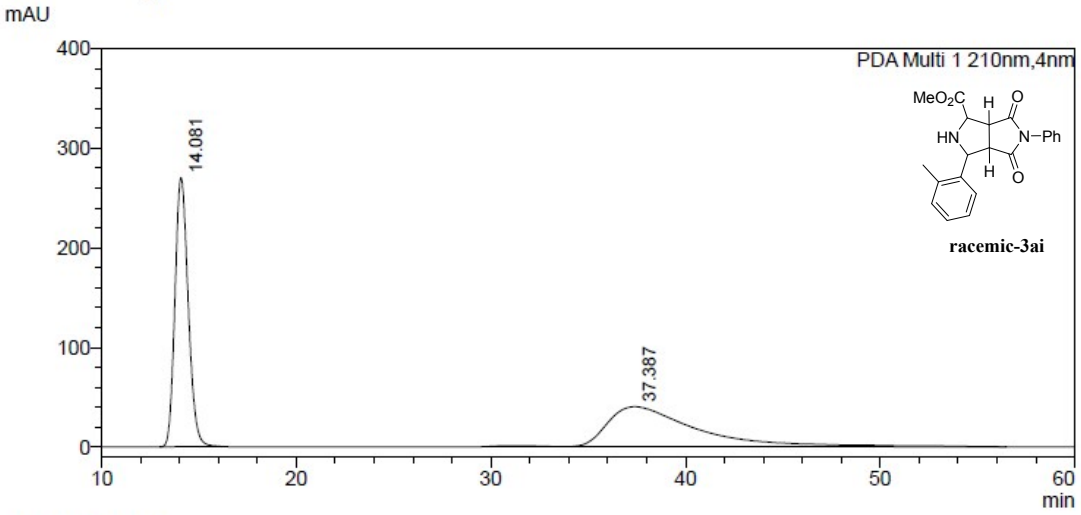

7.67
7.66
7.65
7.64
7.35
7.32
7.31
7.26
7.22
7.21
7.07
7.06
7.04
7.03
4.73
4.71
4.70
4.69
4.14
4.12
4.10
3.88
3.75
3.72
3.70
3.66
3.63
3.60
2.44
2.42
MeO2C
O
HN
N−Ph
O
1.00
3.00
3.00
2.00
1.00
1.00
3.00
1.00
1.00
4.00
f1 (ppm)

3ai


175.13
173.35
170.06
135.76
135.32
131.56
130.23
128.89
128.35
127.94
126.05
125.27
77.32
77.00
76.68
48.27
46.89
19.34
MeO2C
O
HN
N−Ph
O
f1 (ppm)

3ai

<Chromatogram>

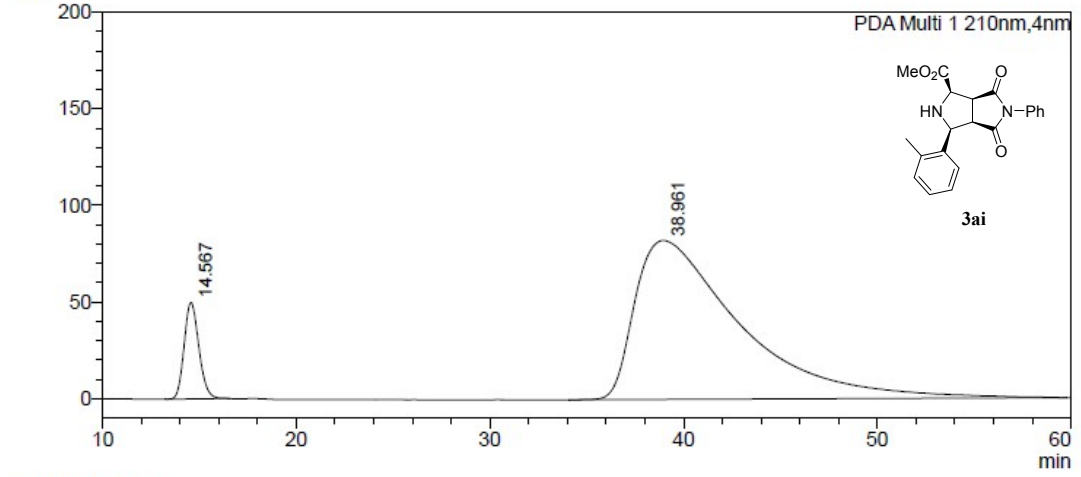


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	14.081	12821883	50.183	270312	87.111
2	37.387	12728119	49.817	39996	12.889
Total		25550002	100.000	310309	100.000

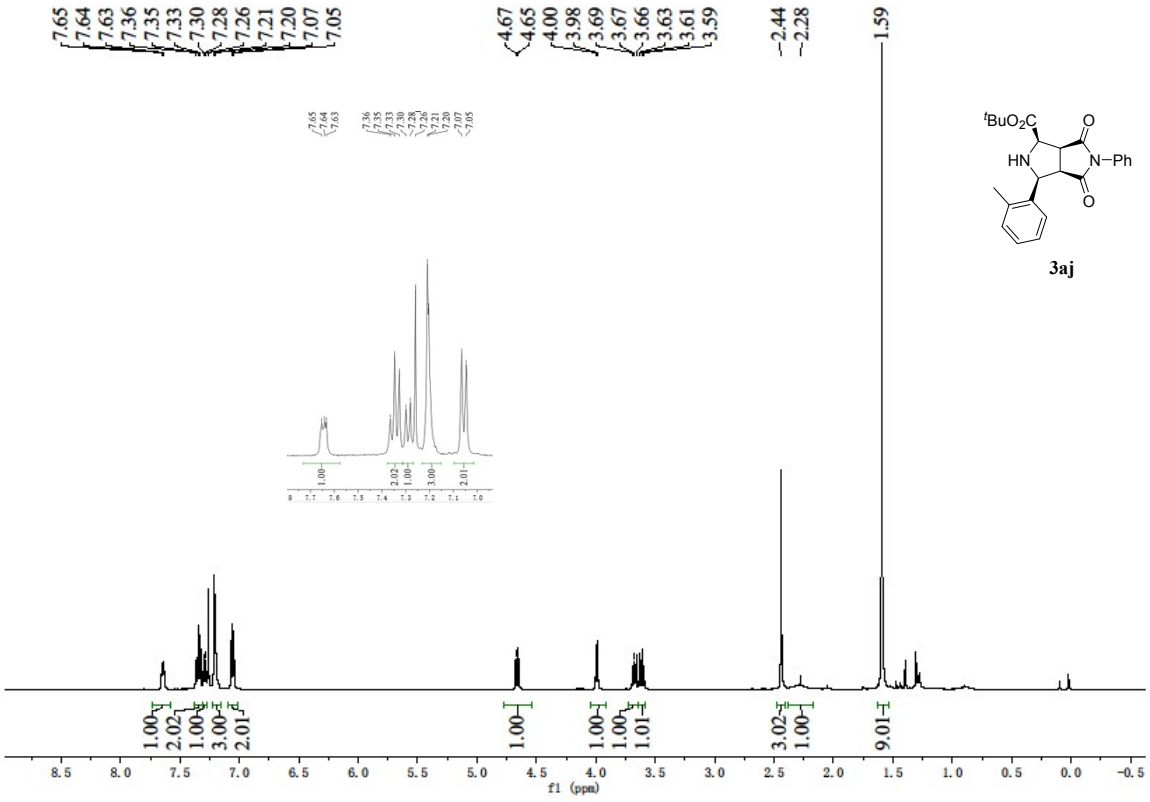
<Chromatogram>



<Peak Table>

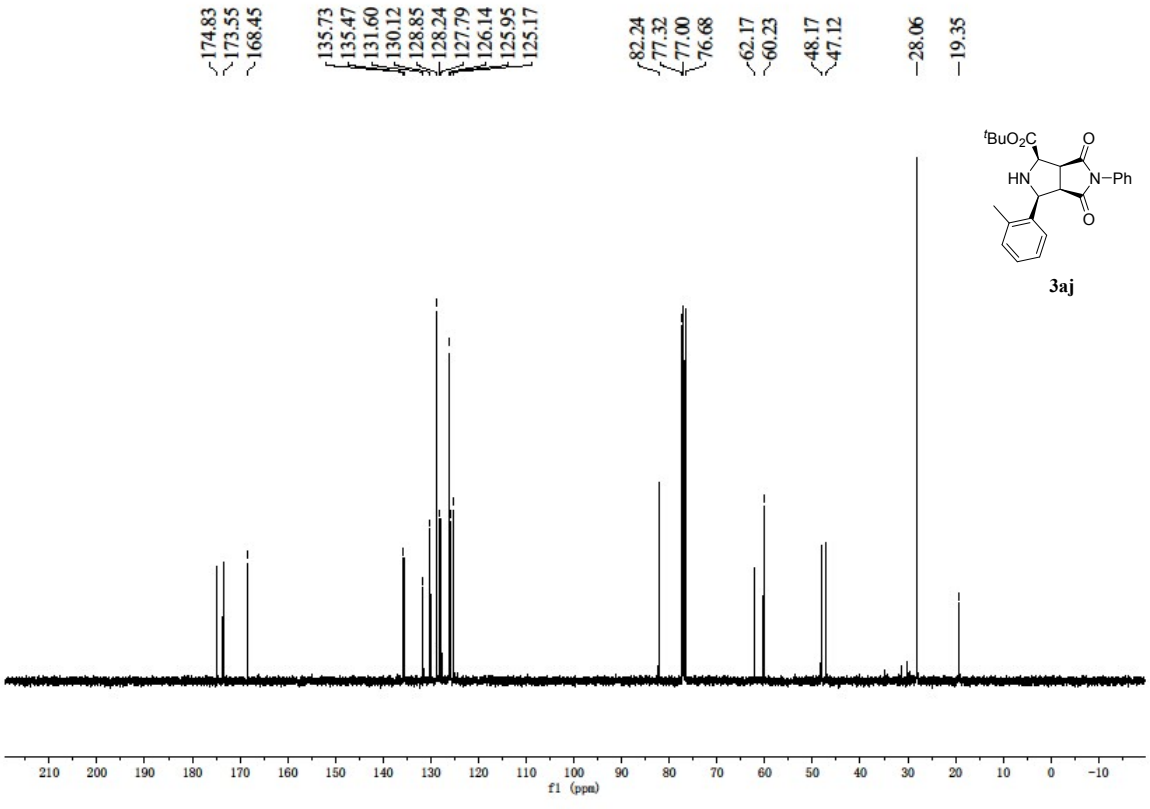
PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	14.567	2649010	7.872	49923	37.790
2	38.961	31001955	92.128	82183	62.210
Total		33650964	100.000	132106	100.000


7.65
7.64
7.63
7.36
7.35
7.33
7.30
7.28
7.26
7.21
7.20
7.07
7.05
4.67
4.65
4.00
3.98
3.69
3.67
3.66
3.63
3.61
3.59
2.44
2.28
1.59
1.00
2.02
1.00
3.00
2.01
1.00
1.00
1.00
1.01
3.02
1.00
9.01
f1 (ppm)

tBuO2C
HN
N–Ph
O
O
O

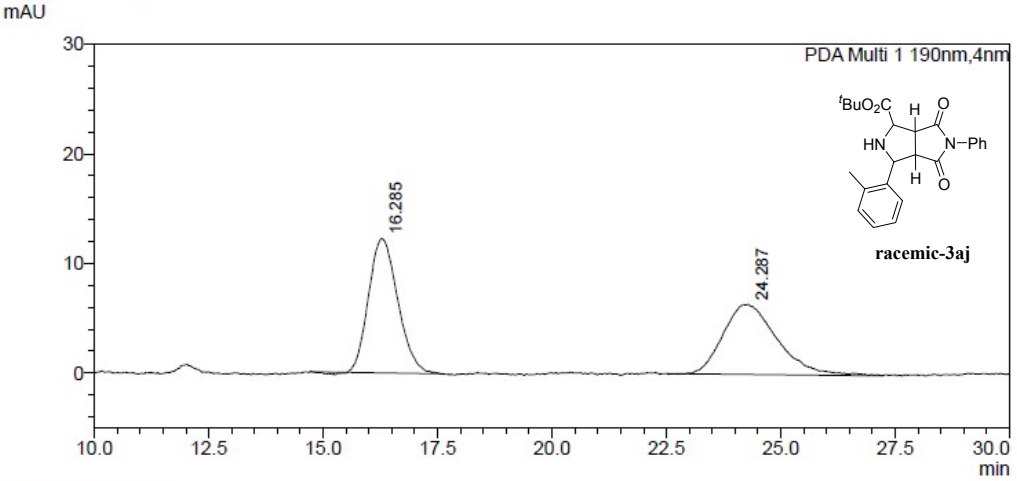
3aj


174.83
173.55
168.45
135.73
135.47
131.60
130.12
128.85
128.24
127.79
126.14
125.95
125.17
82.24
77.32
77.00
76.68
62.17
60.23
48.17
47.12
28.06
19.35
f1 (ppm)

tBuO2C
HN
N–Ph
O
O
O

3aj

<Chromatogram>

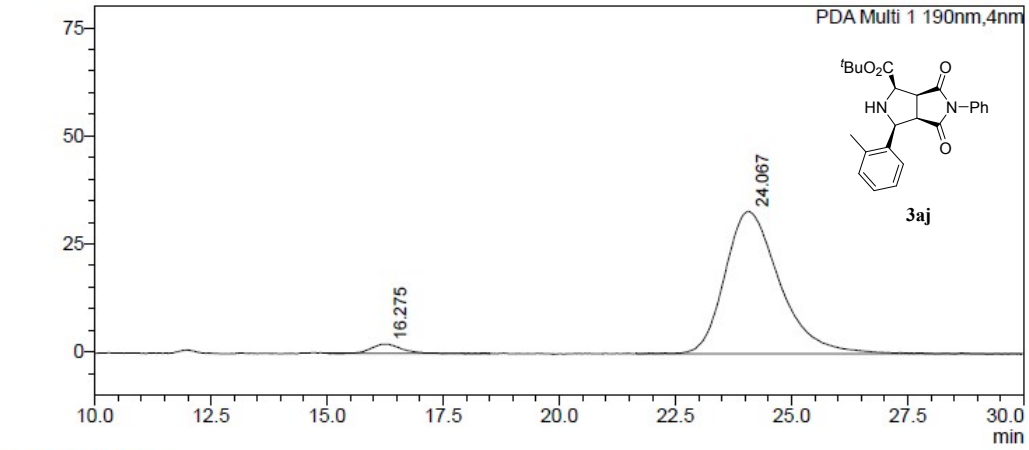


<Peak Table>

PDA Ch1 190nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.285	541806	12274	50.878	65.745
2	24.287	523114	6395	49.122	34.255
Total		1064920	18669	100.000	100.000

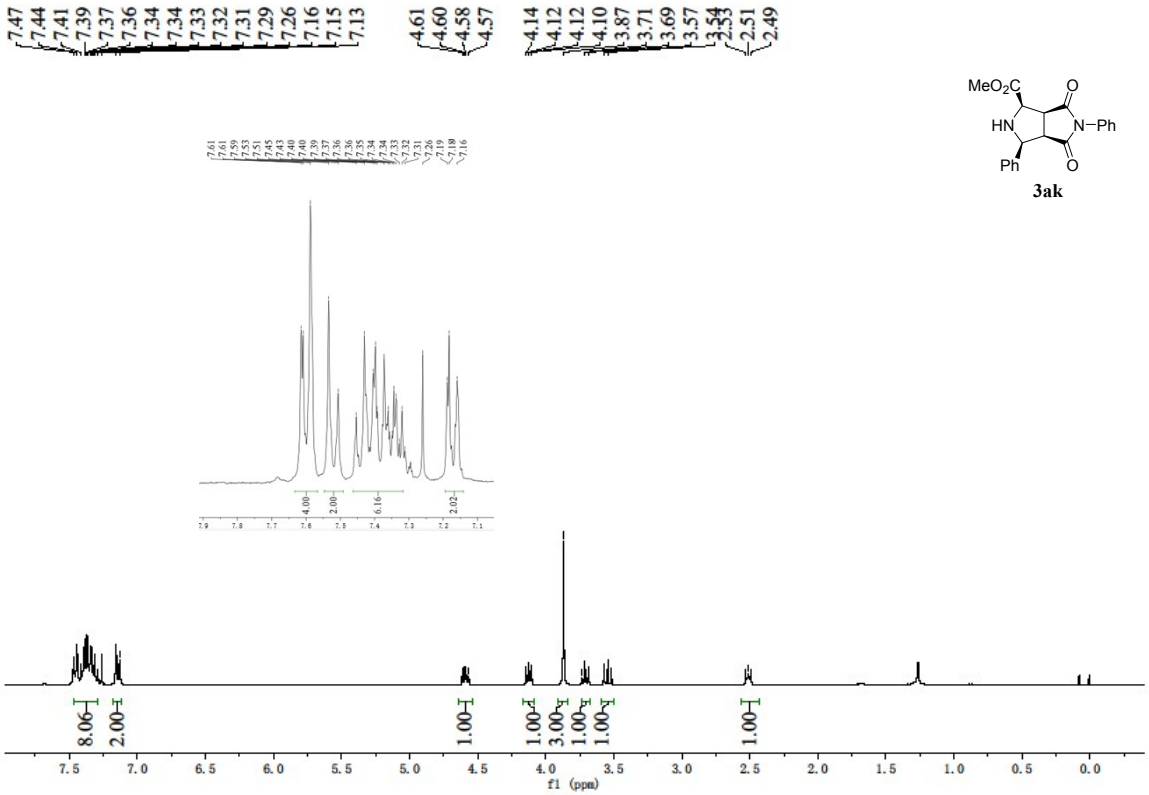
<Chromatogram>

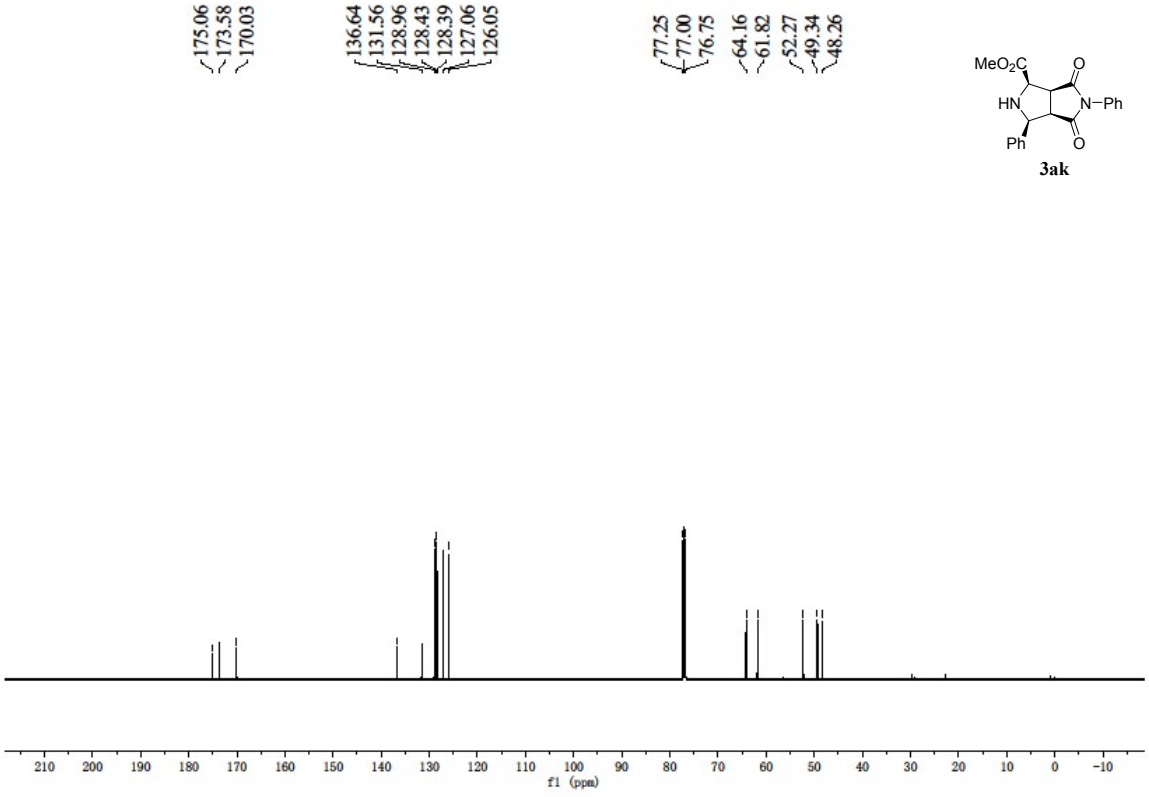


<Peak Table>

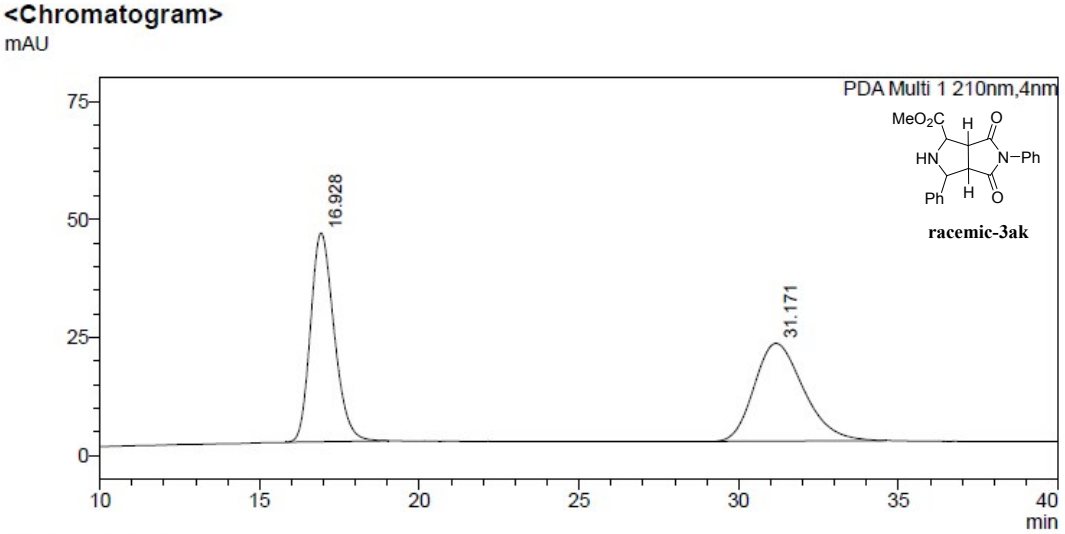
PDA Ch1 190nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	16.275	91895	2103	6.001	3.272
2	24.067	2716695	32950	93.999	96.728
Total		2808590	35054	100.000	100.000


7.47
7.44
7.41
7.39
7.37
7.36
7.34
7.34
7.33
7.32
7.31
7.29
7.26
7.16
7.15
7.13
4.61
4.60
4.58
4.57
4.14
4.12
4.12
4.10
3.87
3.71
3.69
3.57
3.54
2.53
2.51
2.49
MeO2C
O
HN
N–Ph
Ph
O
3ak
8.06
2.00
1.00
1.00
3.00
1.00
1.00
1.00
f1 (ppm)


175.06
173.58
170.03
136.64
131.56
128.96
128.43
128.39
127.06
126.05
77.25
77.00
76.75
64.16
61.82
52.27
49.34
48.26
MeO2C
O
HN
N–Ph
Ph
O
3ak
f1 (ppm)

<Chromatogram>

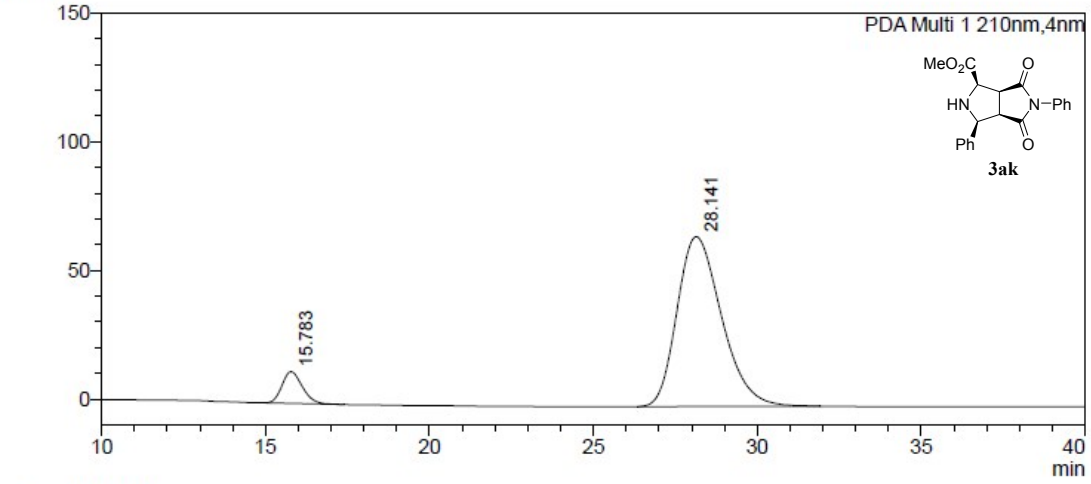


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	16.928	2271922	50.542	44209	68.136
2	31.171	2223238	49.458	20674	31.864
Total		4495160	100.000	64883	100.000

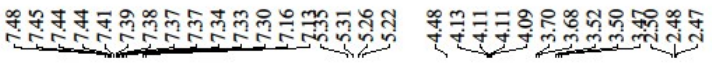
<Chromatogram>



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.783	533375	7.880	12336	15.748
2	28.141	6235203	92.120	65996	84.252
Total		6768578	100.000	78331	100.000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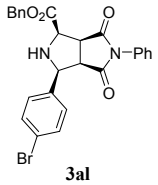
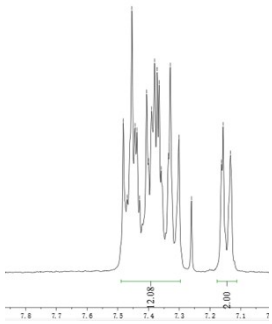
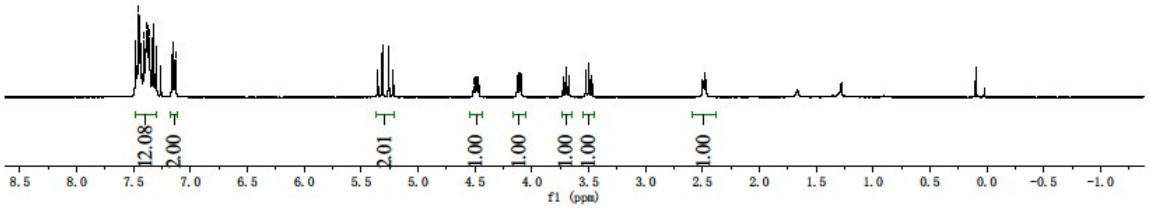
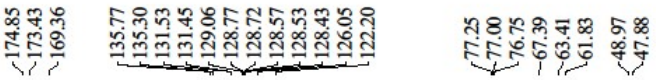
7.44
7.44
7.41
7.39
7.38
7.37
7.37
7.34
7.33
7.30
7.16
7.13
5.35
5.31
5.26
5.22
4.48
4.13
4.11
4.11
4.09
3.70
3.68
3.52
3.50
3.47
3.30
2.48
2.47

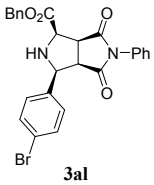

BnO2C
O
HN
N–Ph
O
Br

3al

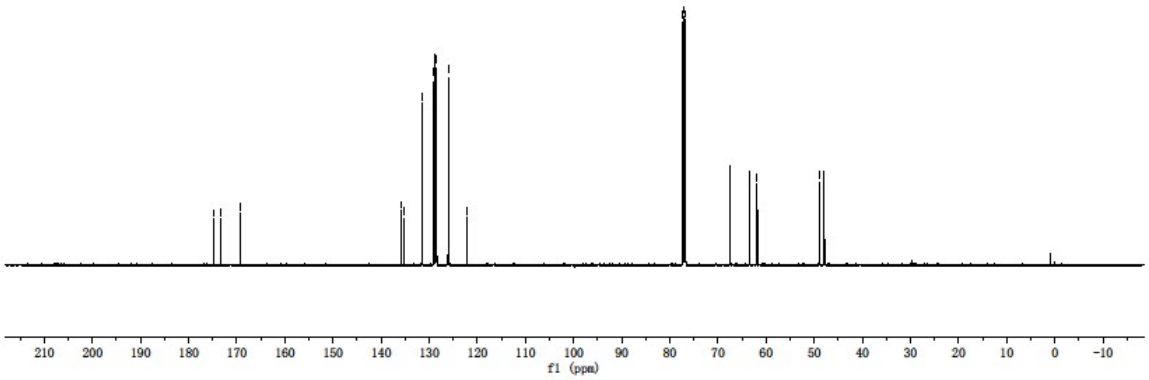



12.08
2.00
2.01
1.00
1.00
1.00
1.00
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

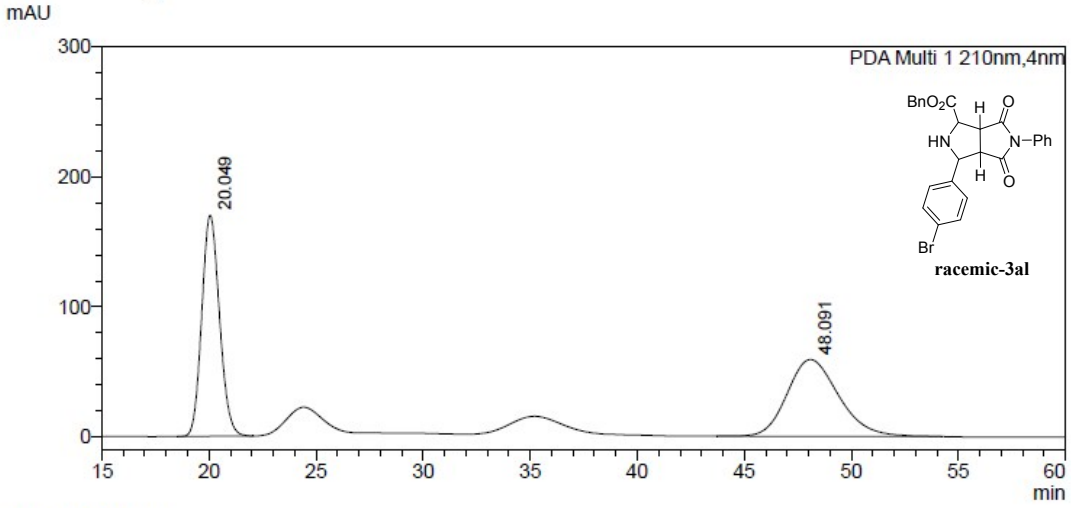

174.85
173.43
169.36
135.77
135.30
131.53
131.45
129.06
128.77
128.72
128.57
128.53
128.43
126.05
122.20
77.25
77.00
76.75
67.39
63.41
61.83
48.97
47.88


BnO2C
O
HN
N–Ph
O
Br

3al


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

<Chromatogram>

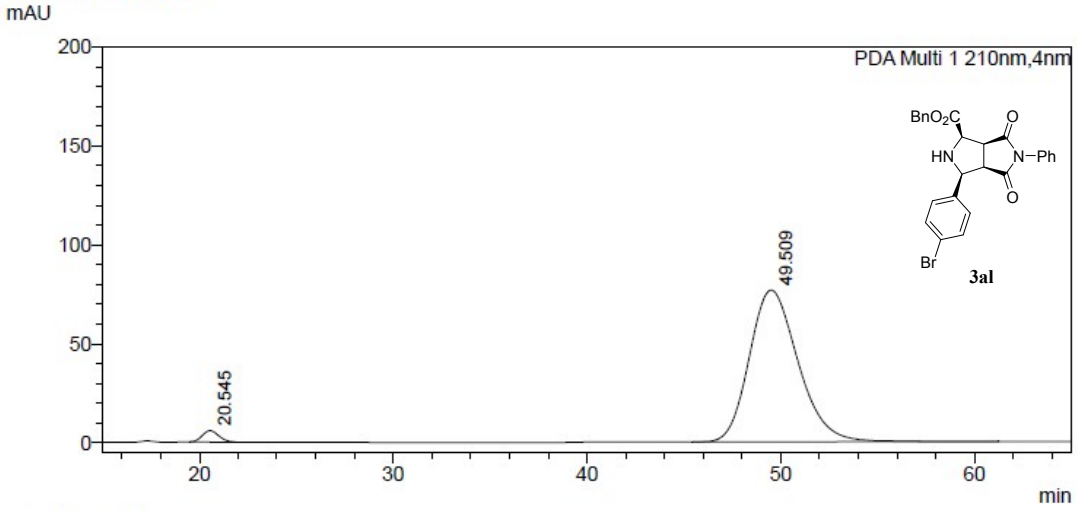


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.049	9797632	49.726	170046	74.236
2	48.091	9905597	50.274	59015	25.764
Total		19703229	100.000	229061	100.000

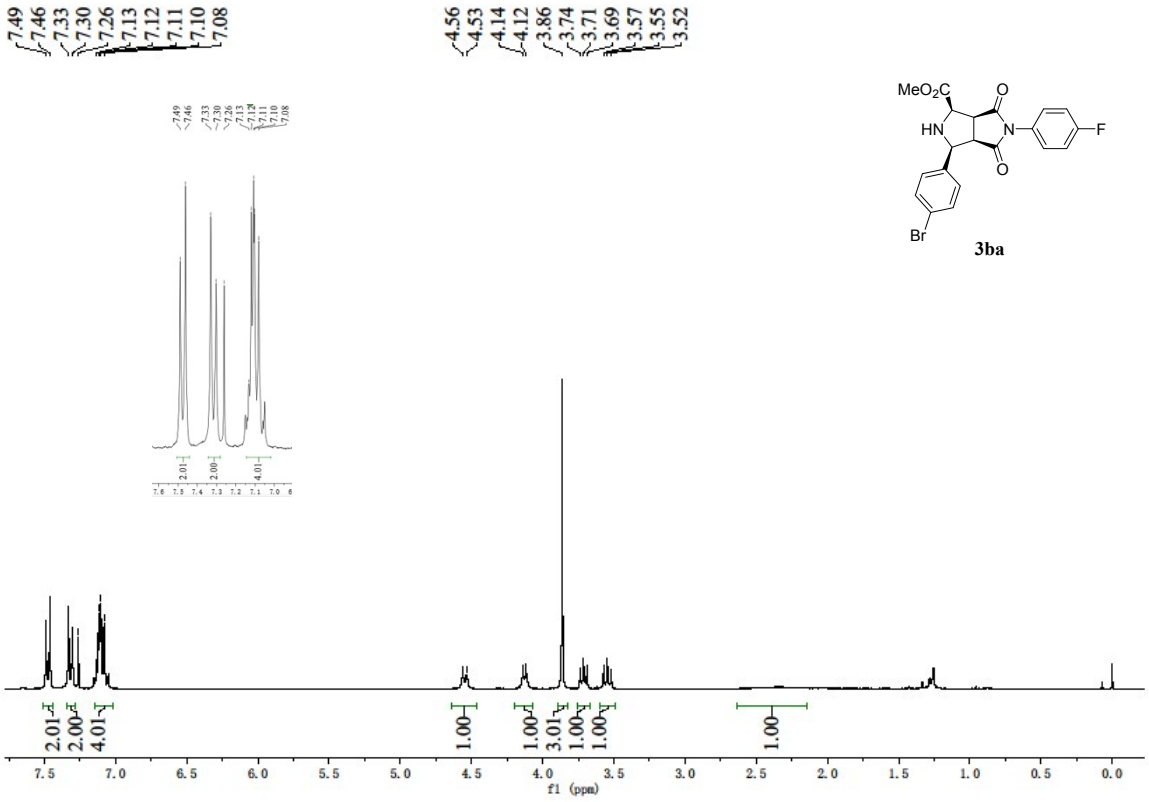
<Chromatogram>



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	20.545	341867	2.478	5729	6.947
2	49.509	13453821	97.522	76743	93.053
Total		13795688	100.000	82473	100.000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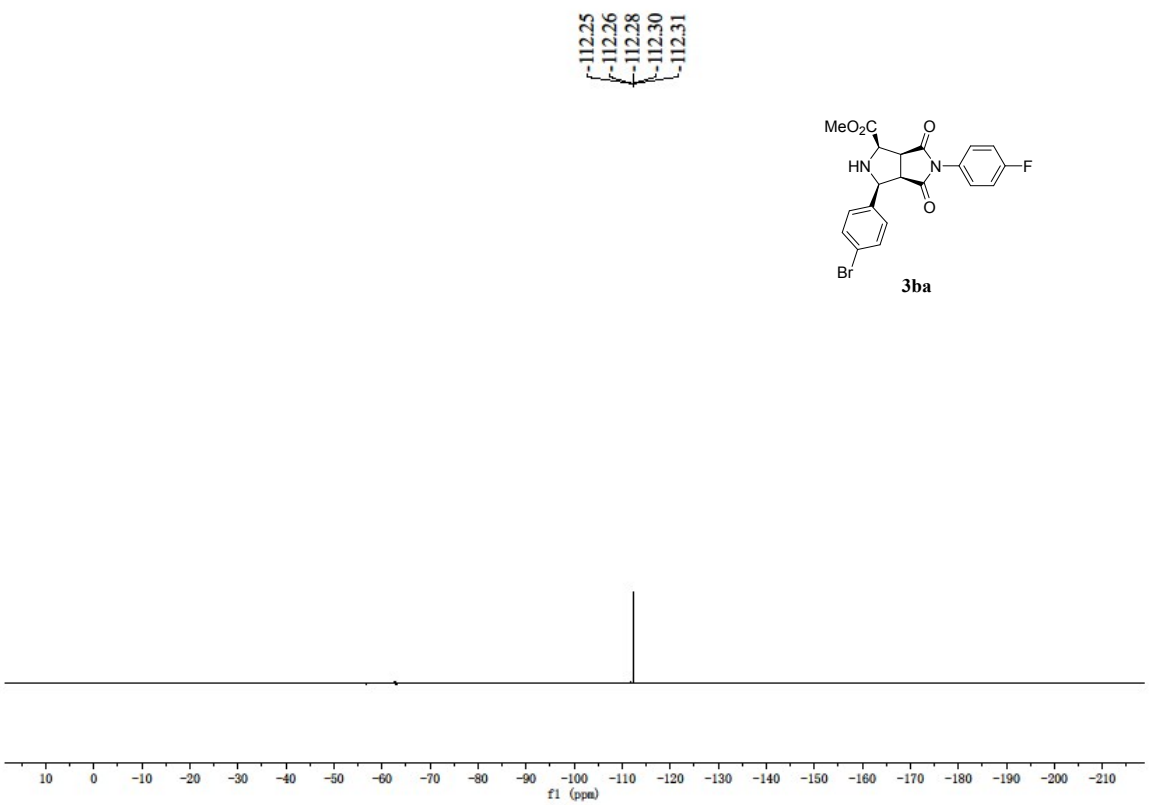
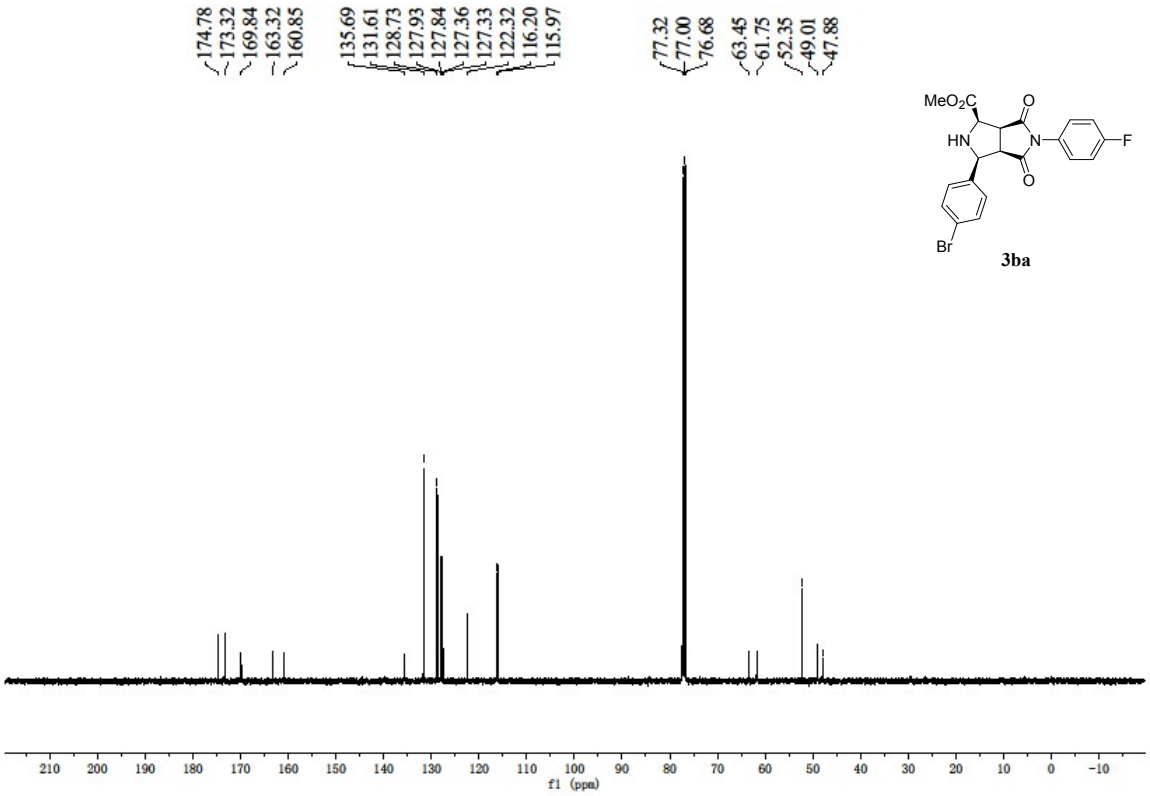
7.46
7.33
7.30
7.26
7.13
7.12
7.11
7.10
7.08
4.56
4.53
4.14
4.12
3.86
3.74
3.71
3.69
3.57
3.55
3.52
MeO2C
HN
O
N
F
O
Br
2.01
2.00
4.01
1.00
1.00
3.01
1.00
1.00
1.00
f1 (ppm)

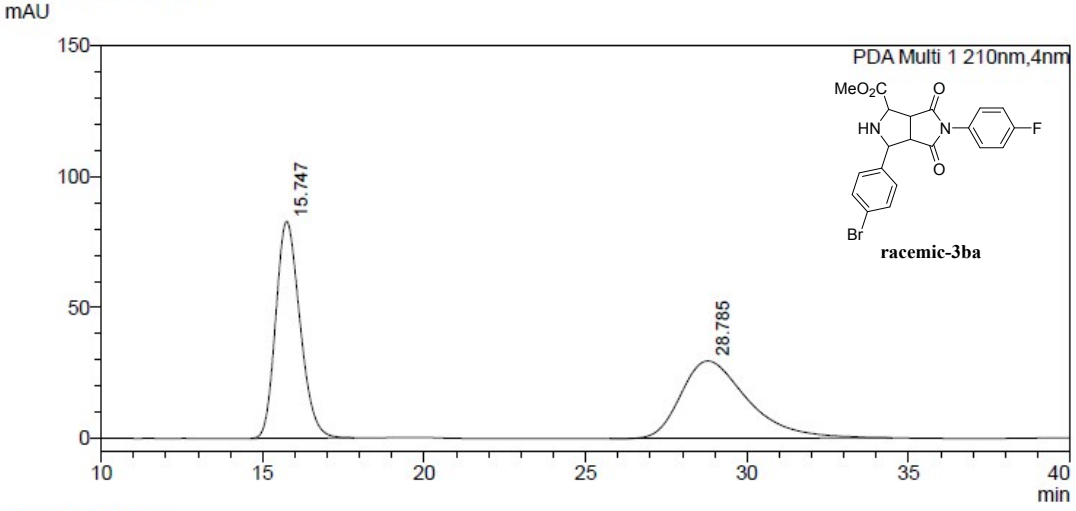
3ba


-112.25
-112.26
-112.28
-112.30
-112.31
MeO2C
HN
O
N
F
O
Br
f1 (ppm)

3ba



<Chromatogram>

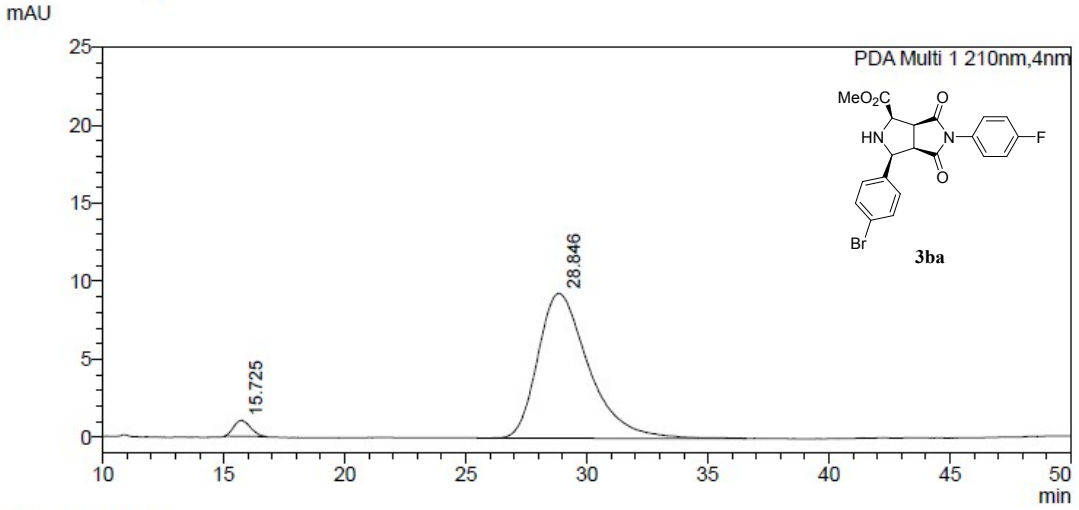


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.747	4321491	50.442	82833	73.708
2	28.785	4245834	49.558	29547	26.292
Total		8567325	100.000	112380	100.000

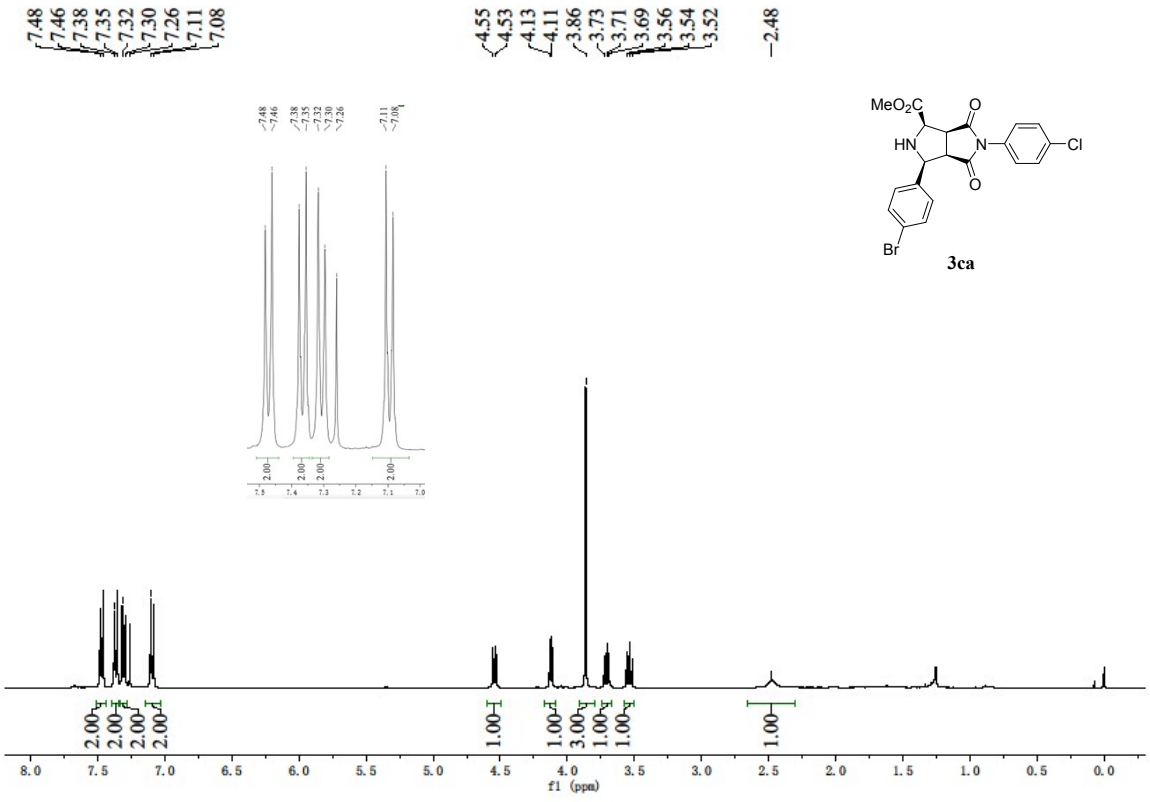
<Chromatogram>

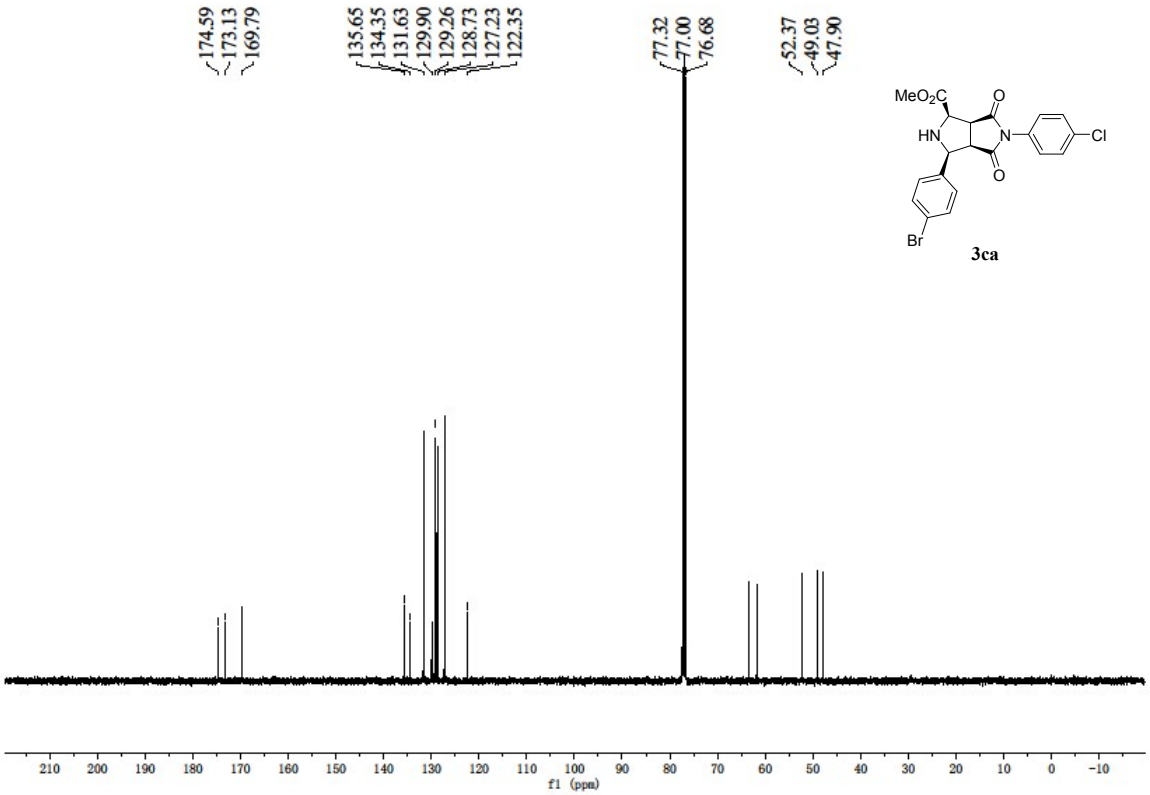


<Peak Table>

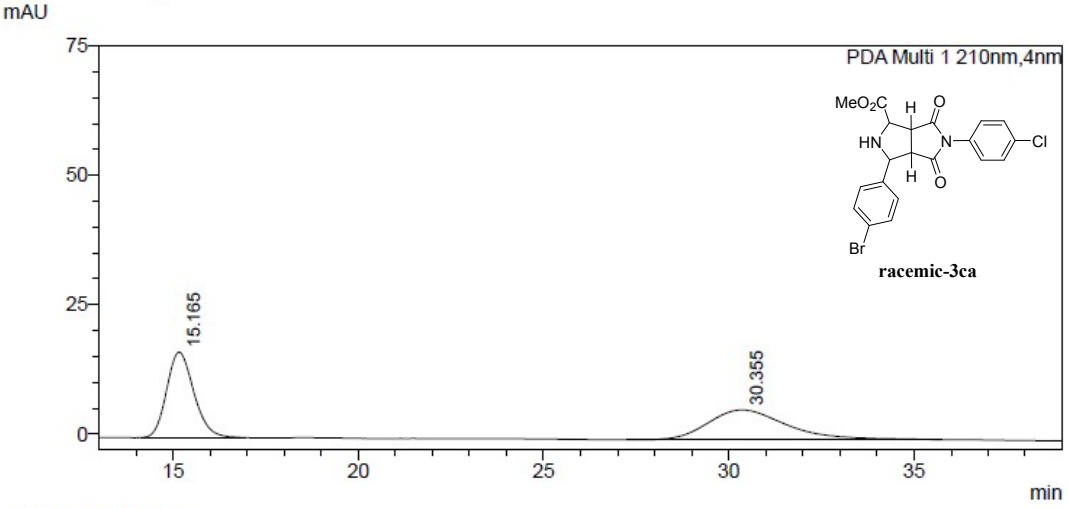
PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.725	49057	3.487	1022	9.921
2	28.846	1357720	96.513	9282	90.079
Total		1406777	100.000	10304	100.000





<Chromatogram>



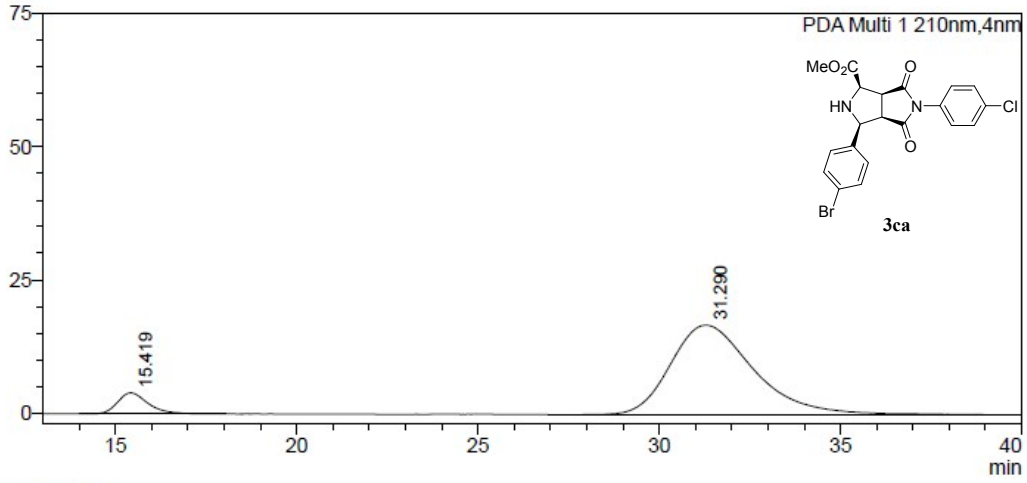
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.165	841677	49.847	16494	74.213
2	30.355	846845	50.153	5731	25.787
Total		1688523	100.000	22225	100.000

<Chromatogram>

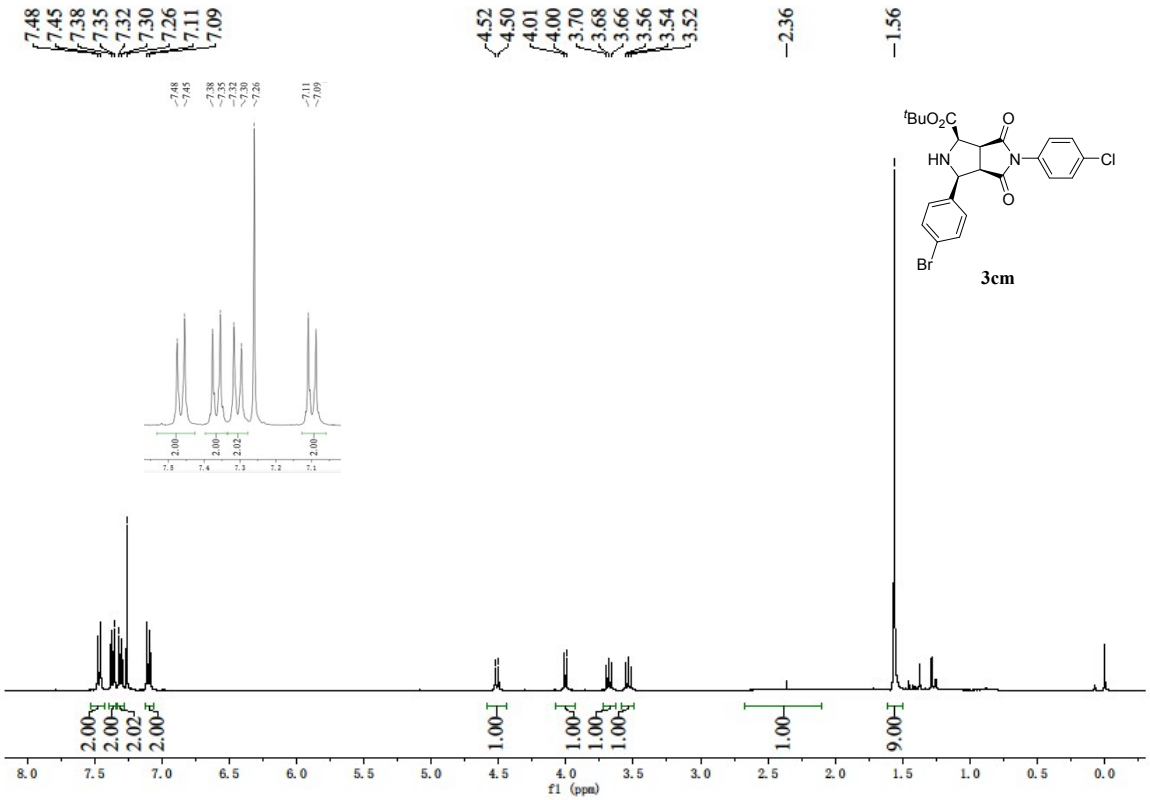
mAU

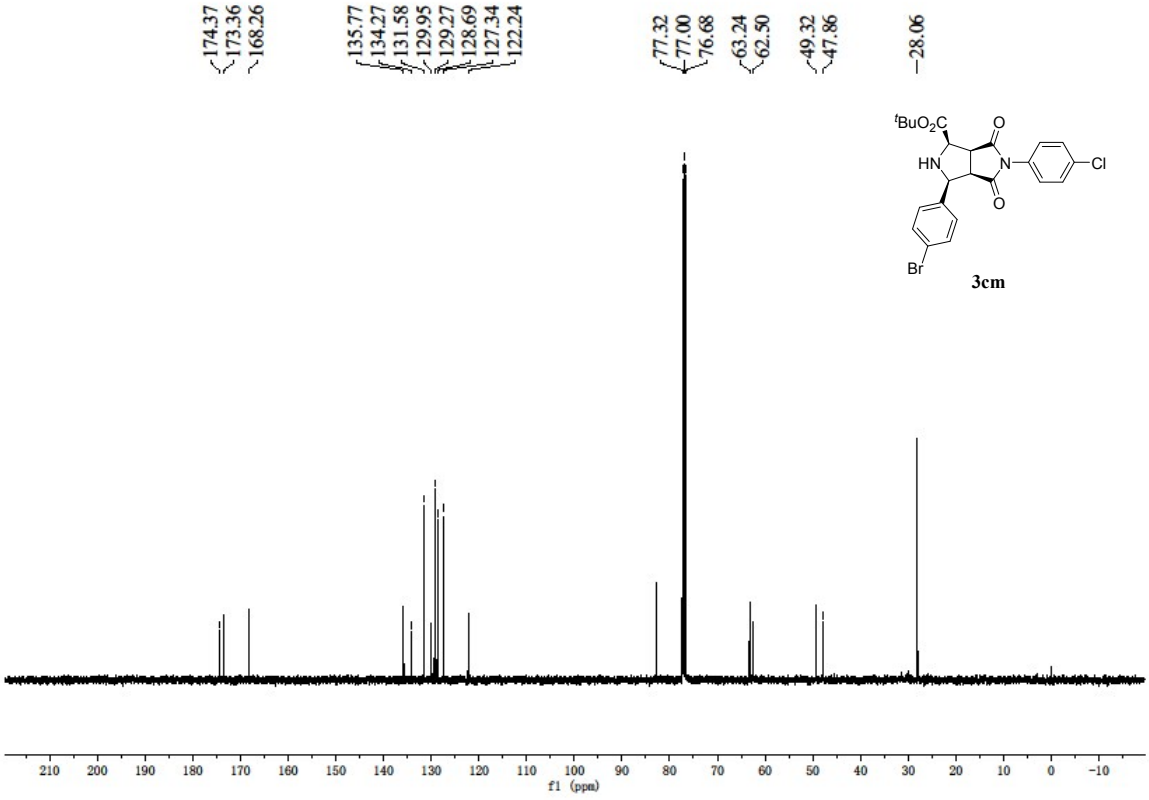


<Peak Table>

PDA Ch1 210nm

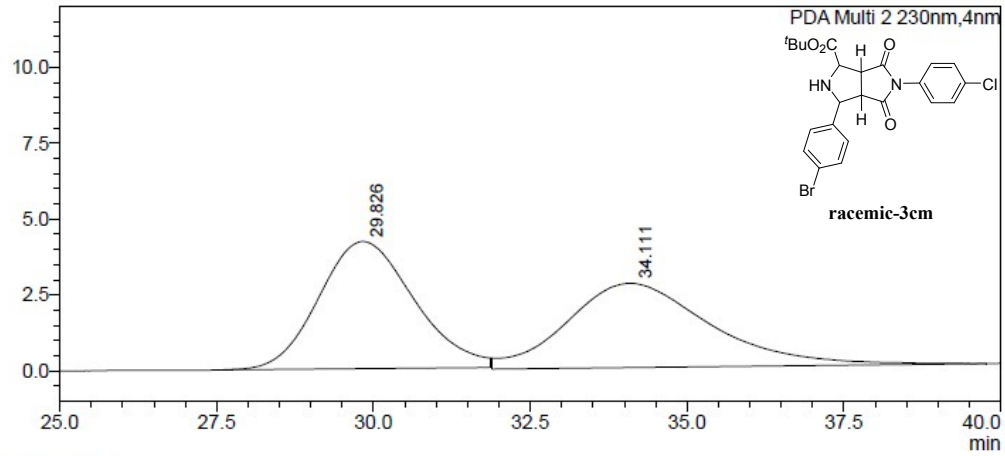
Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.419	228319	7.843	3925	18.935
2	31.290	2682828	92.157	16802	81.065
Total		2911147	100.000	20727	100.000





<Chromatogram>

mAU

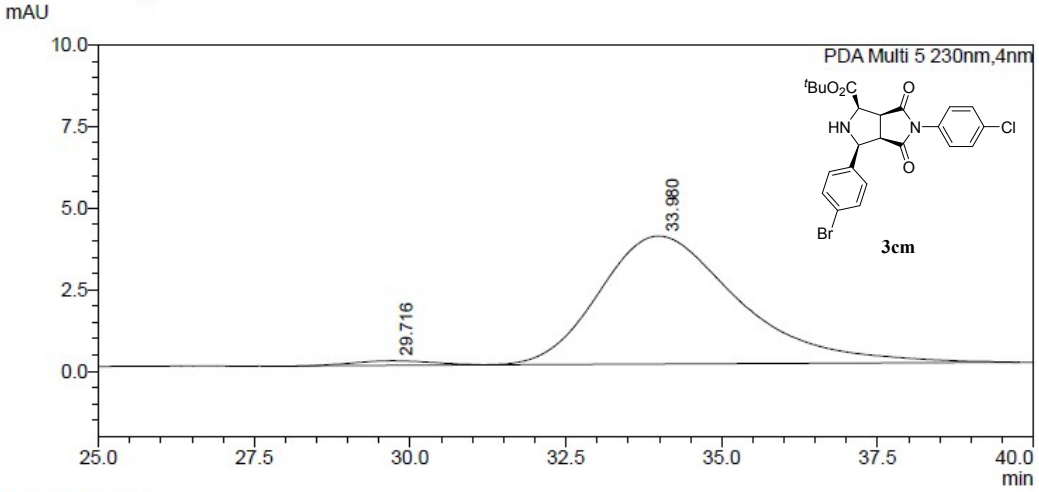


<Peak Table>

PDA Ch2 230nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	29.826	442682	4187	60.140	50.034
2	34.111	442089	2775	39.860	49.966
Total		884770	6963	100.000	100.000

<Chromatogram>

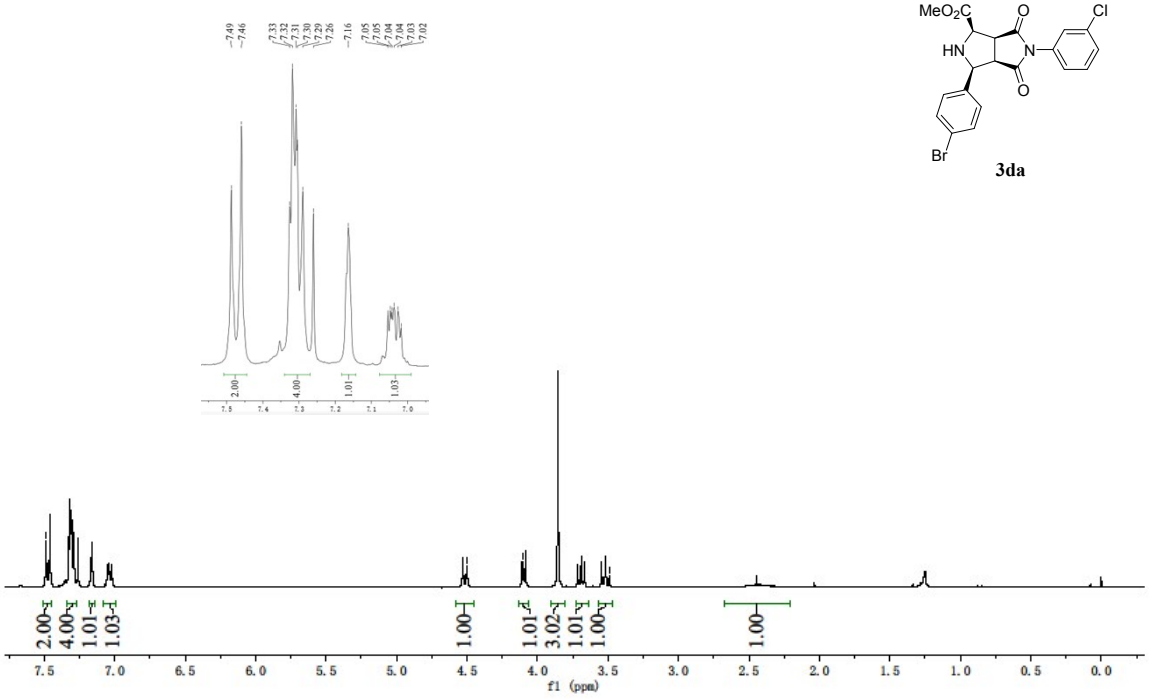


3cm

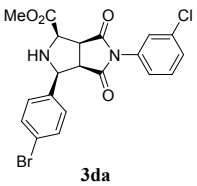
<Peak Table>

PDA Ch5 230nm

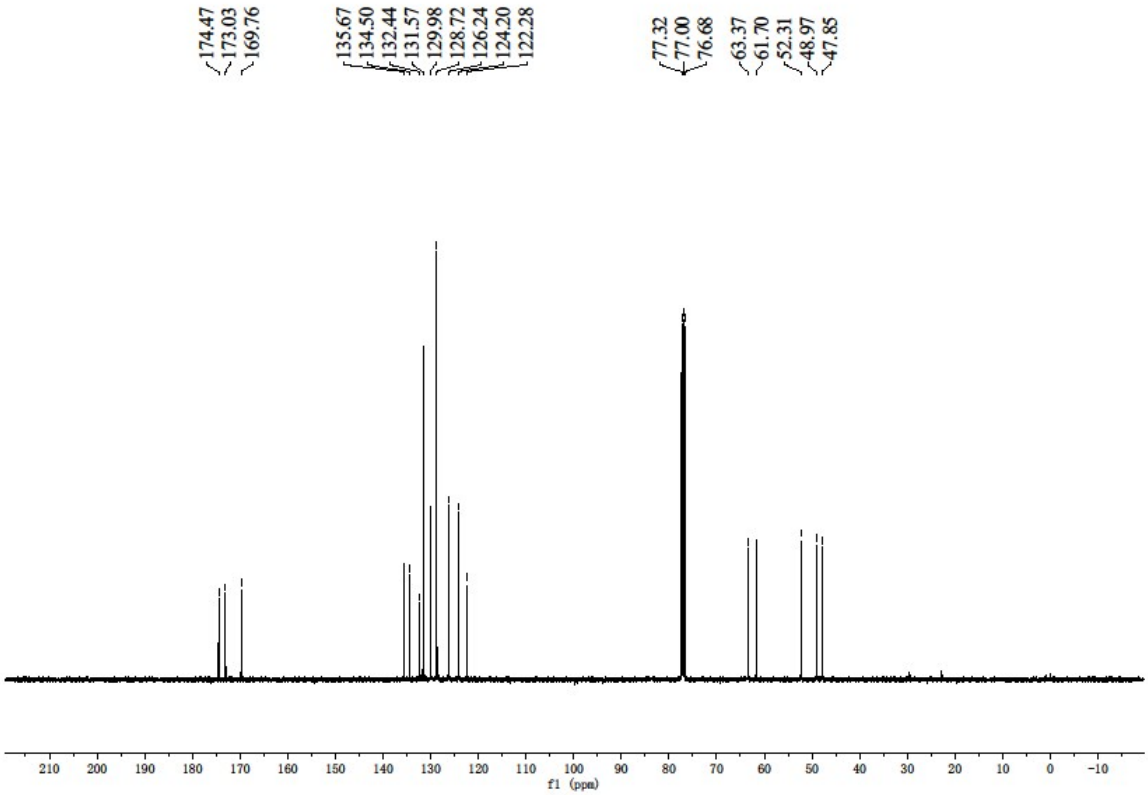
Peak#	Ret. Time	Area	Height	Height%	Area%
1	29.716	12366	140	3.457	1.989
2	33.980	609347	3918	96.543	98.011
Total		621713	4058	100.000	100.000



3da



3da



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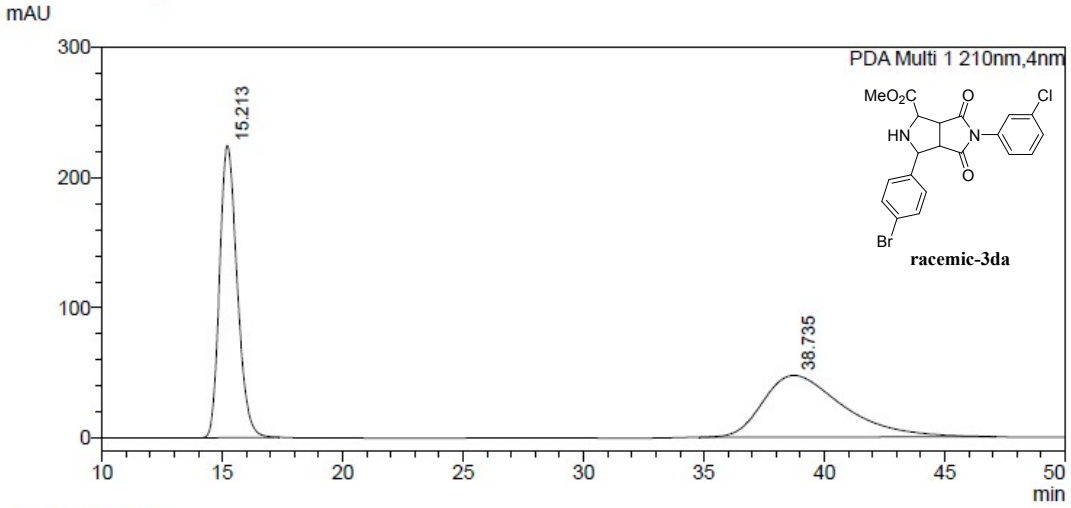
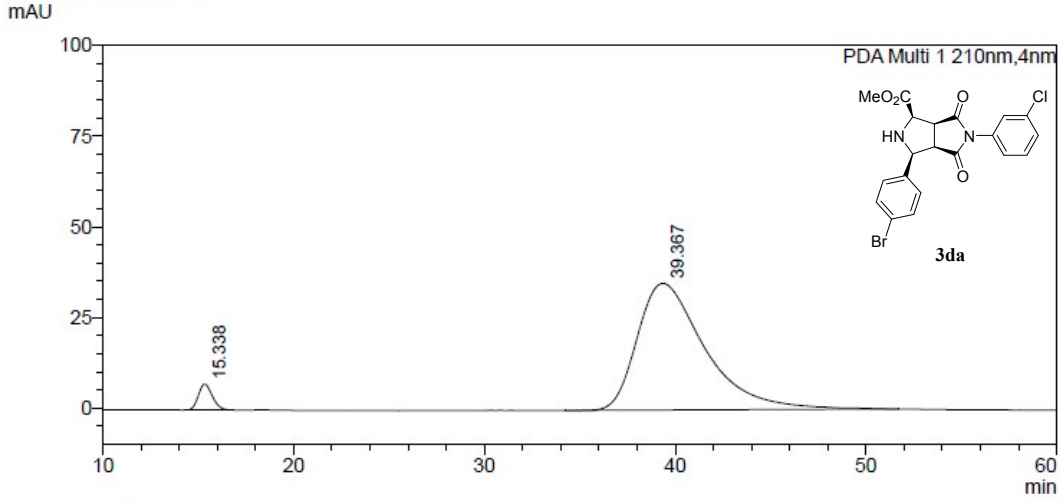


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.213	11369665	50.914	224411	82.573
2	38.735	10961670	49.086	47361	17.427
Total		22331335	100.000	271771	100.000

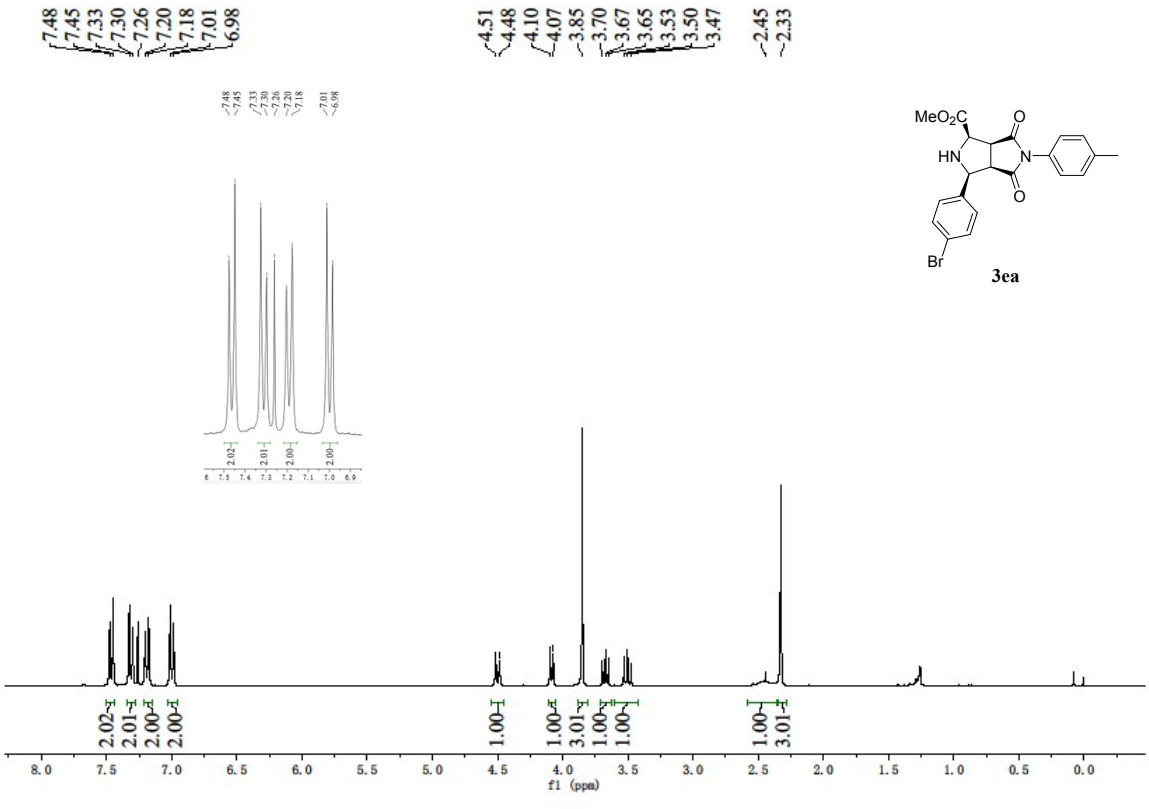
<Chromatogram>

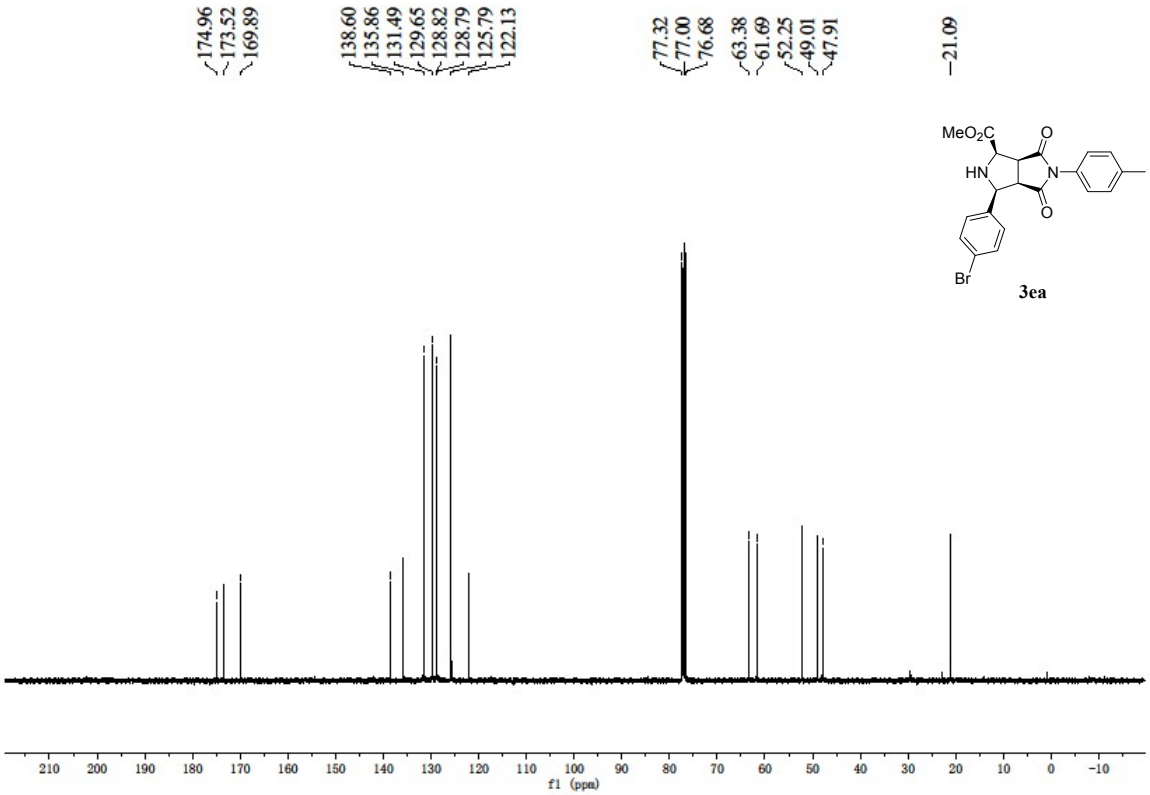


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.338	362227	4.032	7137	16.974
2	39.367	8622556	95.968	34910	83.026
Total		8984783	100.000	42047	100.000





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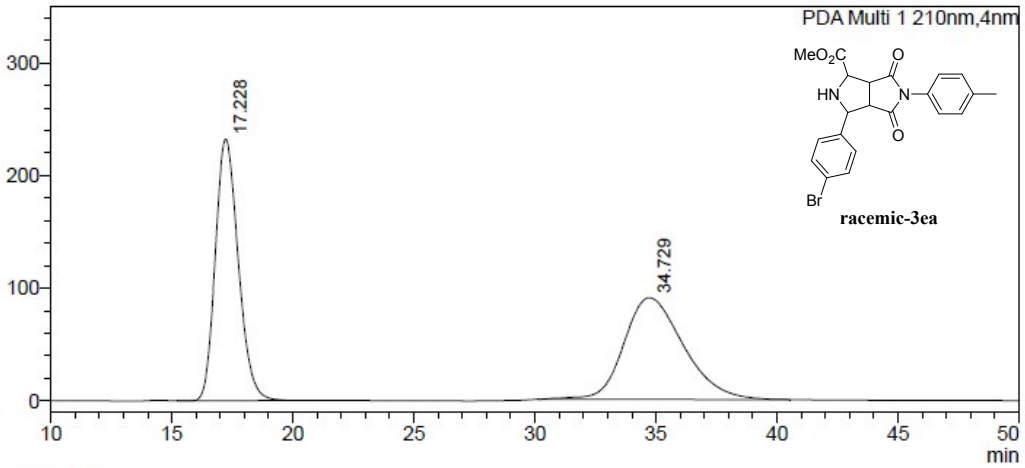
mAU

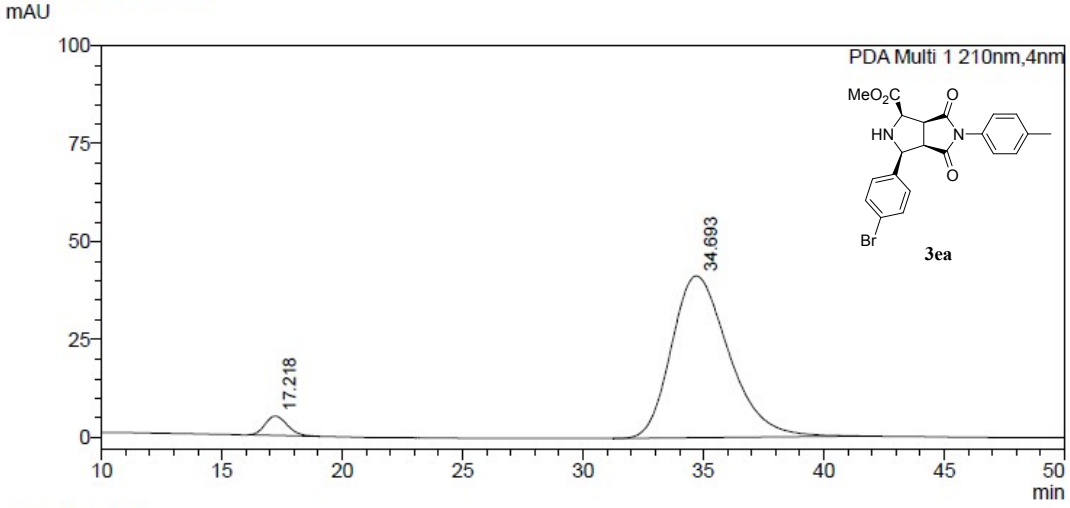


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	17.228	15304608	49.711	232174	71.993
2	34.729	15482338	50.289	90322	28.007
Total		30786947	100.000	322496	100.000

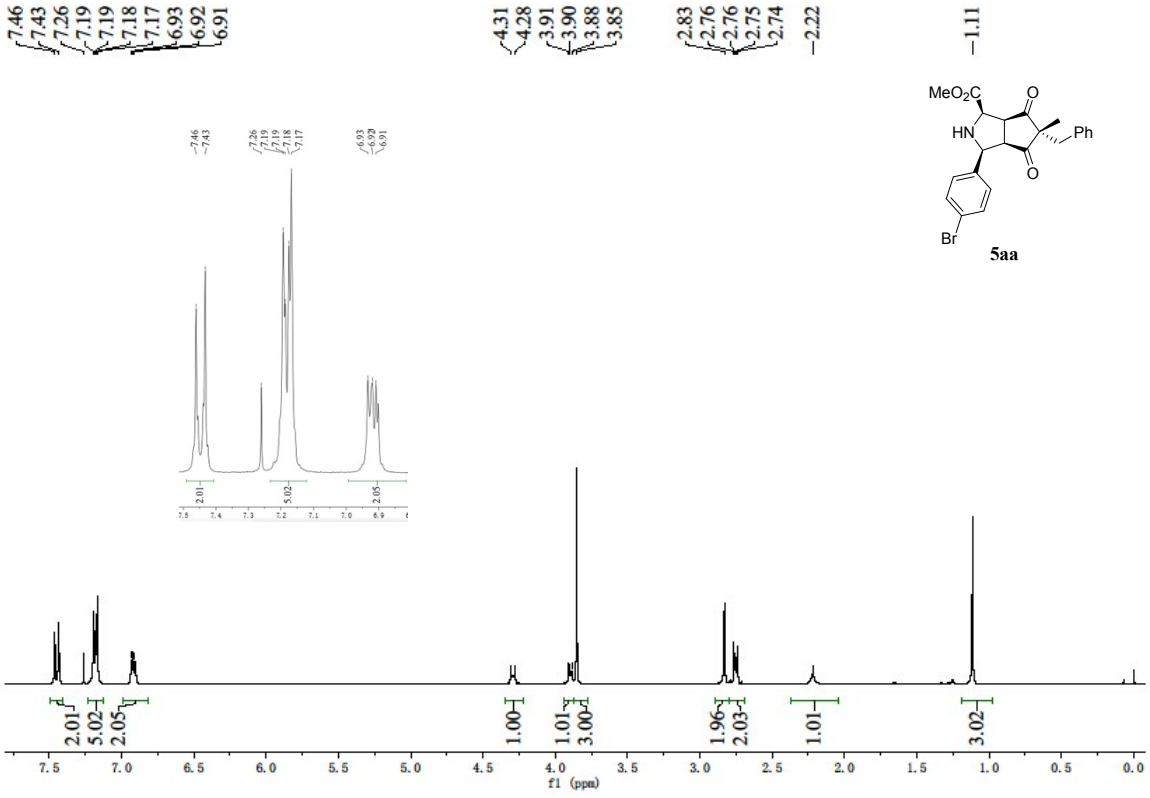
<Chromatogram>

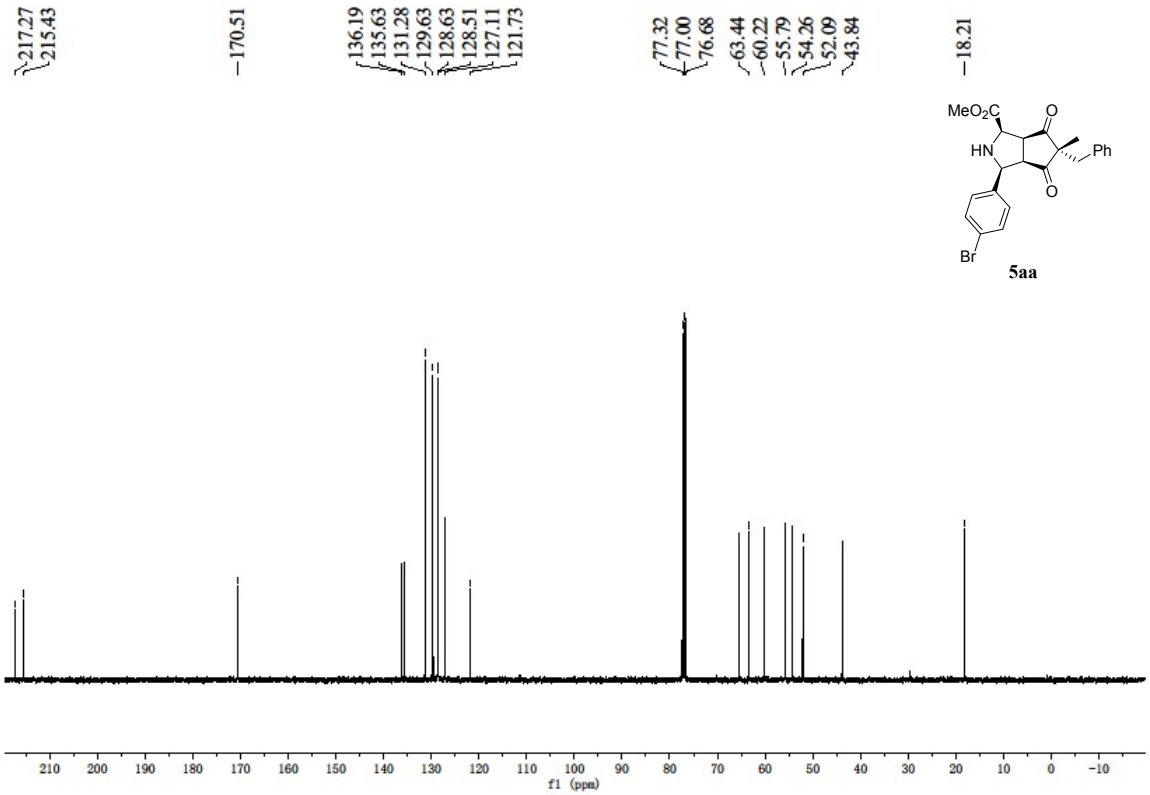


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	17.218	313786	4.376	4922	10.655
2	34.693	6856128	95.624	41268	89.345
Total		7169914	100.000	46190	100.000





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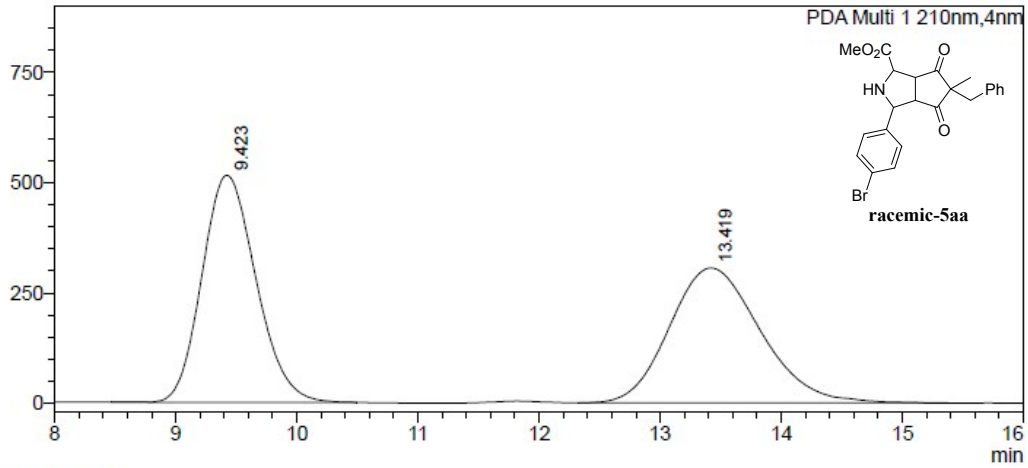

<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	9.423	15982387	50.020	514927	62.735
2	13.419	15969831	49.980	305874	37.265
Total		31952218	100.000	820801	100.000

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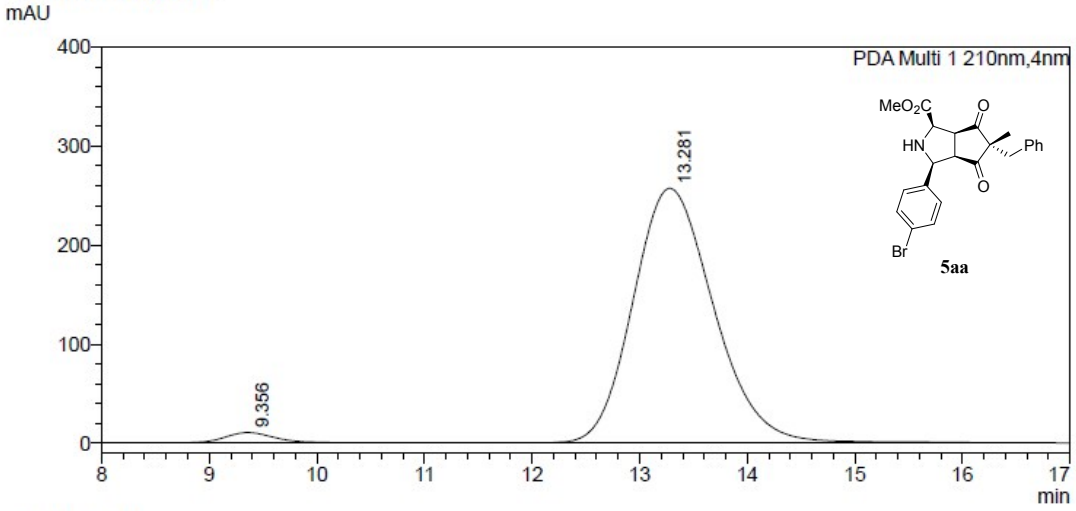
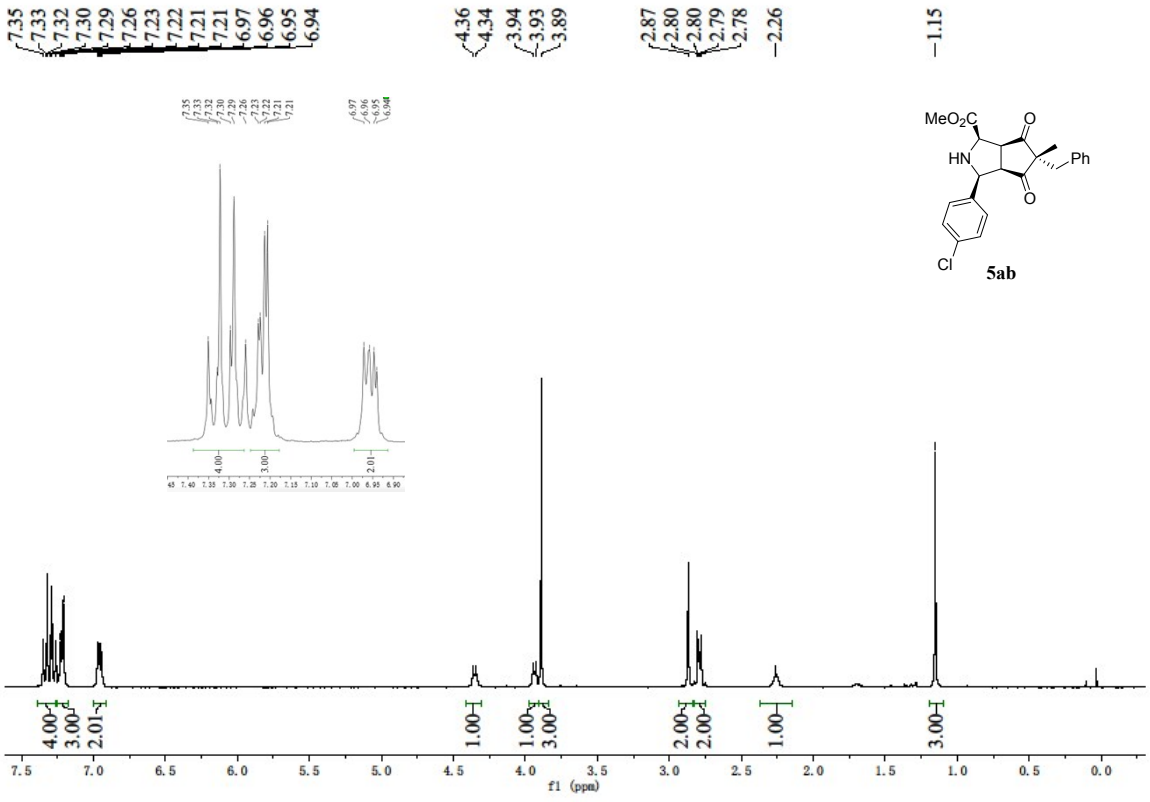
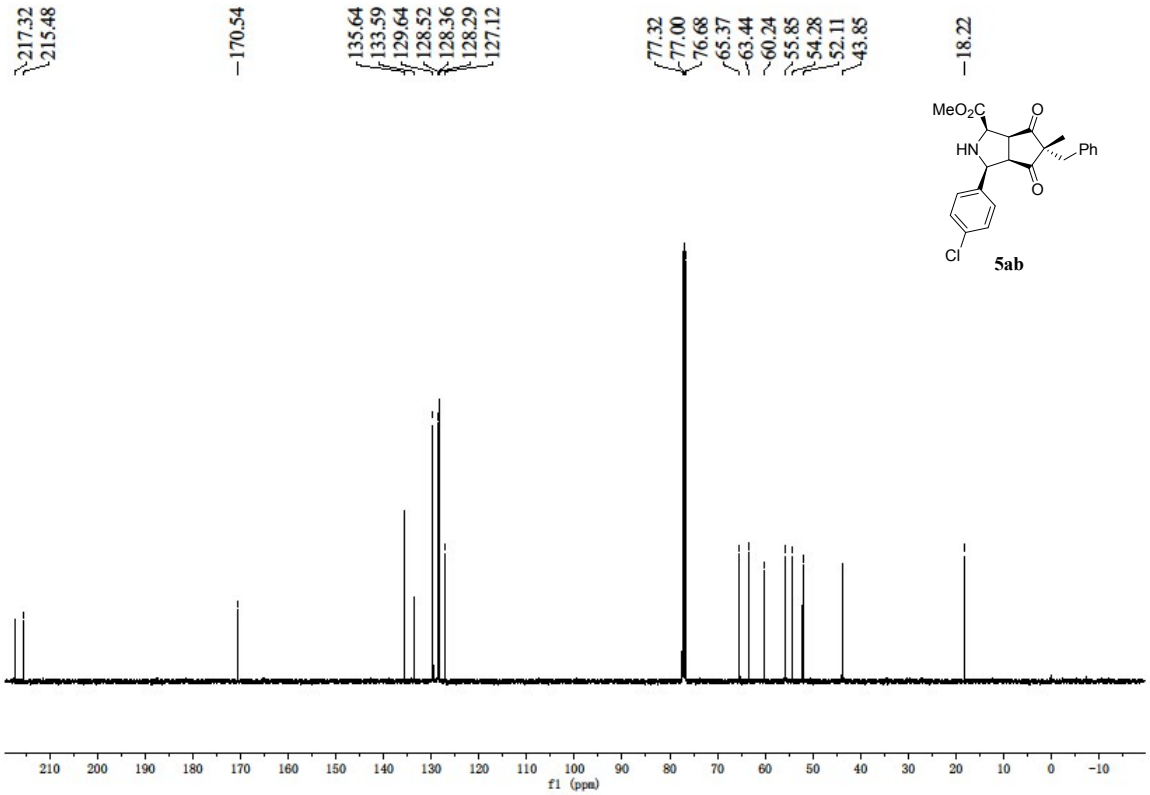


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	9.356	312532	2.284	10178	3.810
2	13.281	13372971	97.716	256974	96.190
Total		13685504	100.000	267152	100.000





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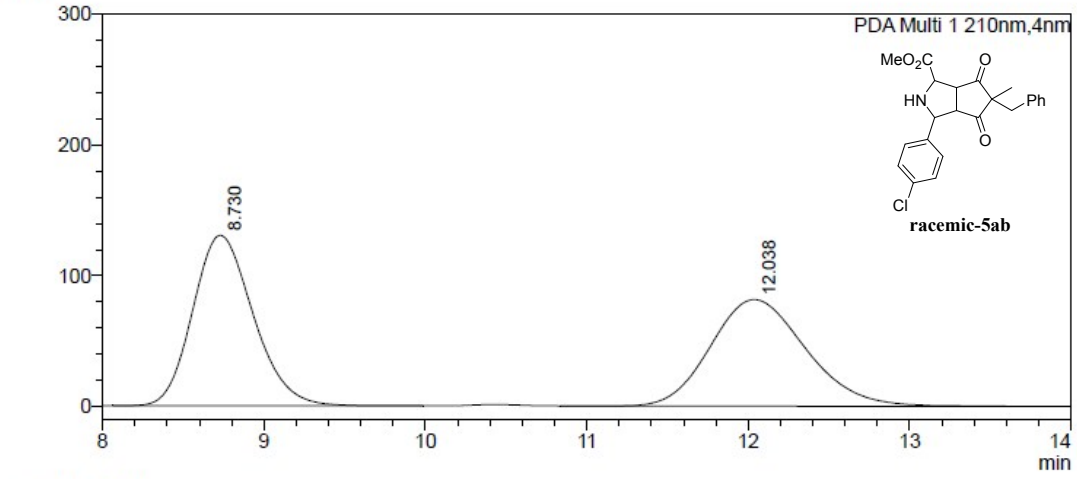
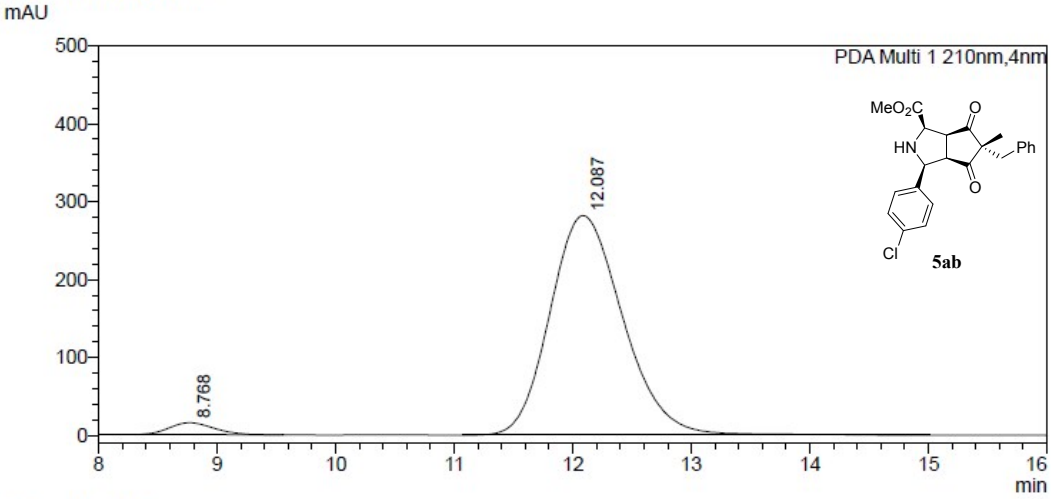


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	8.730	3396526	50.377	130172	61.508
2	12.038	3345741	49.623	81461	38.492
Total		6742268	100.000	211633	100.000

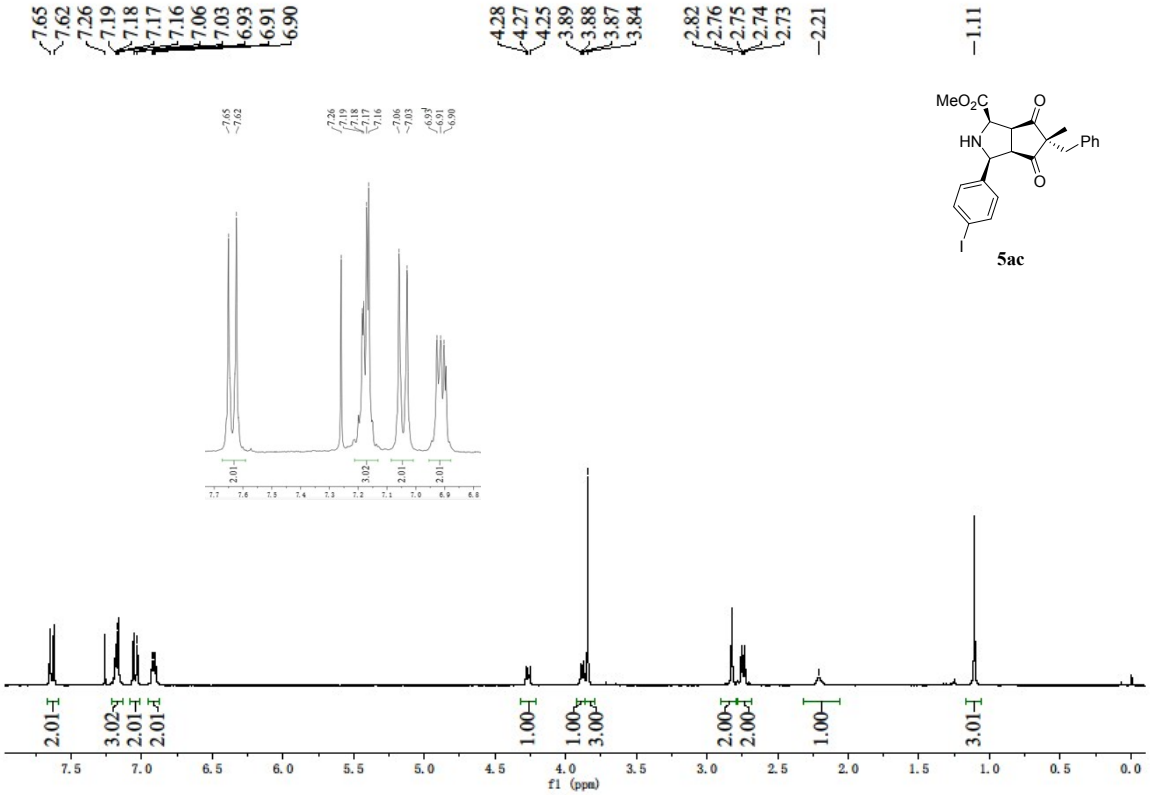
<Chromatogram>

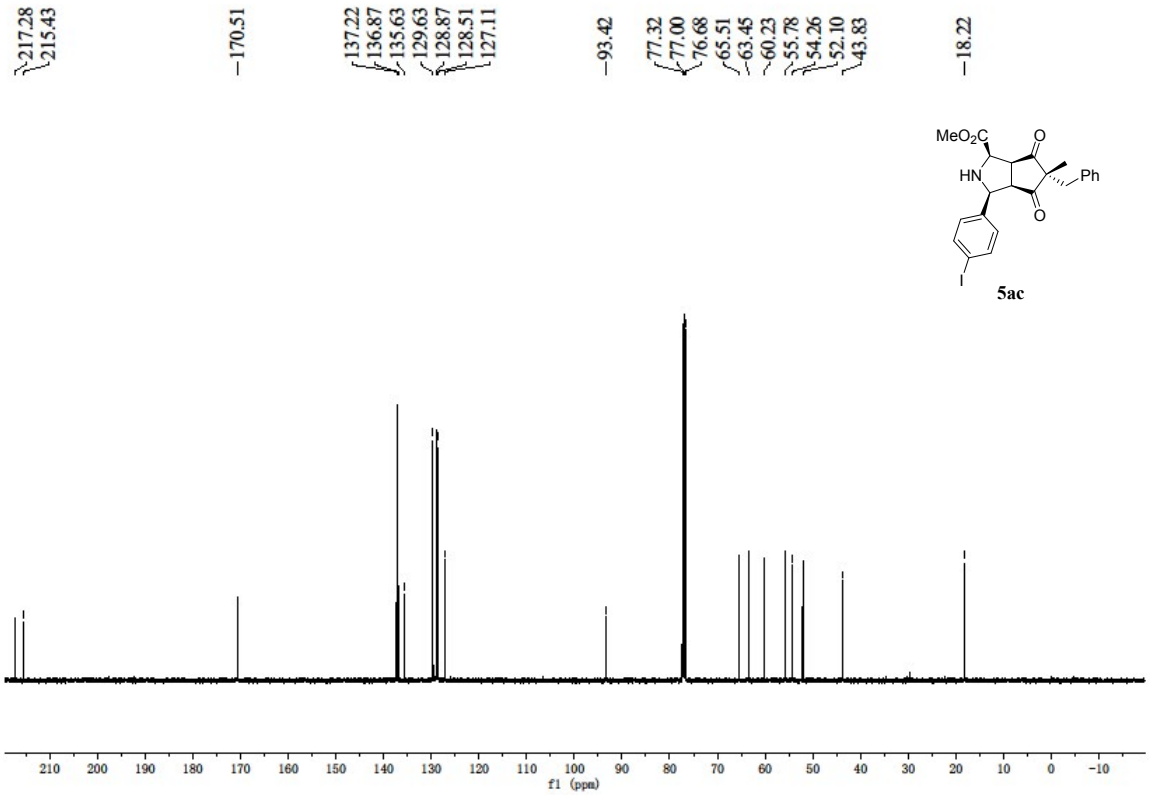


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	8.768	395157	3.166	15166	5.106
2	12.087	12086409	96.834	281864	94.894
Total		12481566	100.000	297030	100.000





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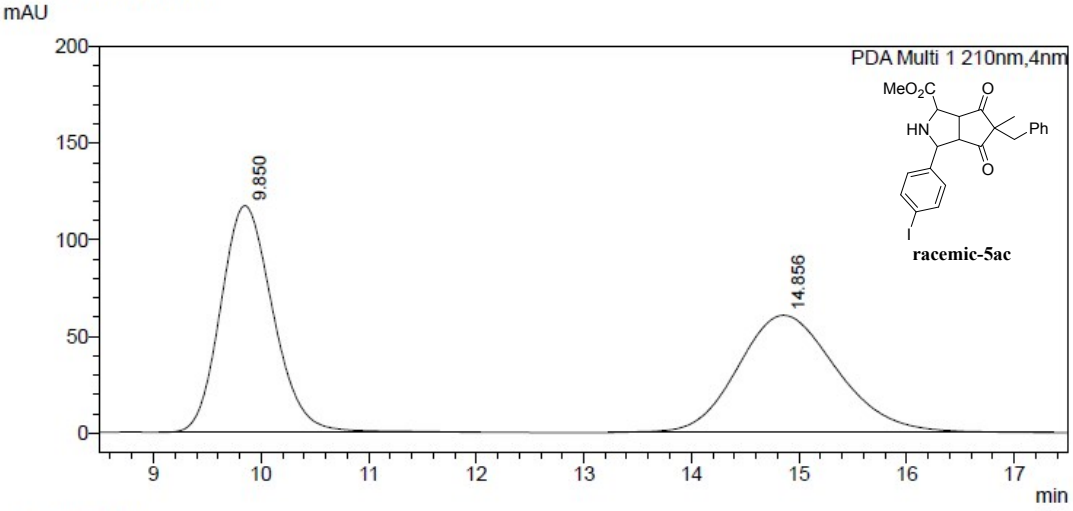
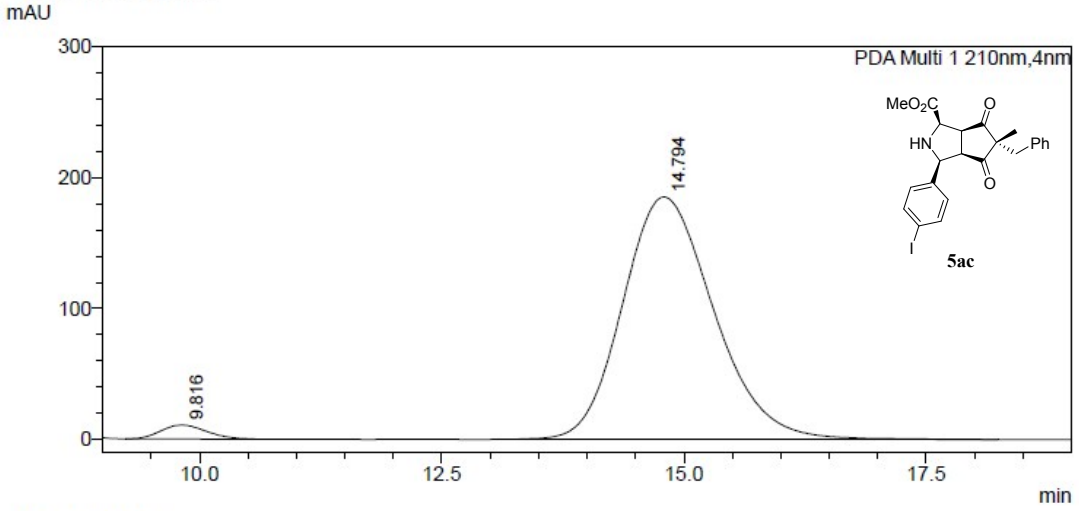


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	9.850	3969097	50.468	117226	65.921
2	14.856	3895447	49.532	60603	34.079
Total		7864544	100.000	177829	100.000

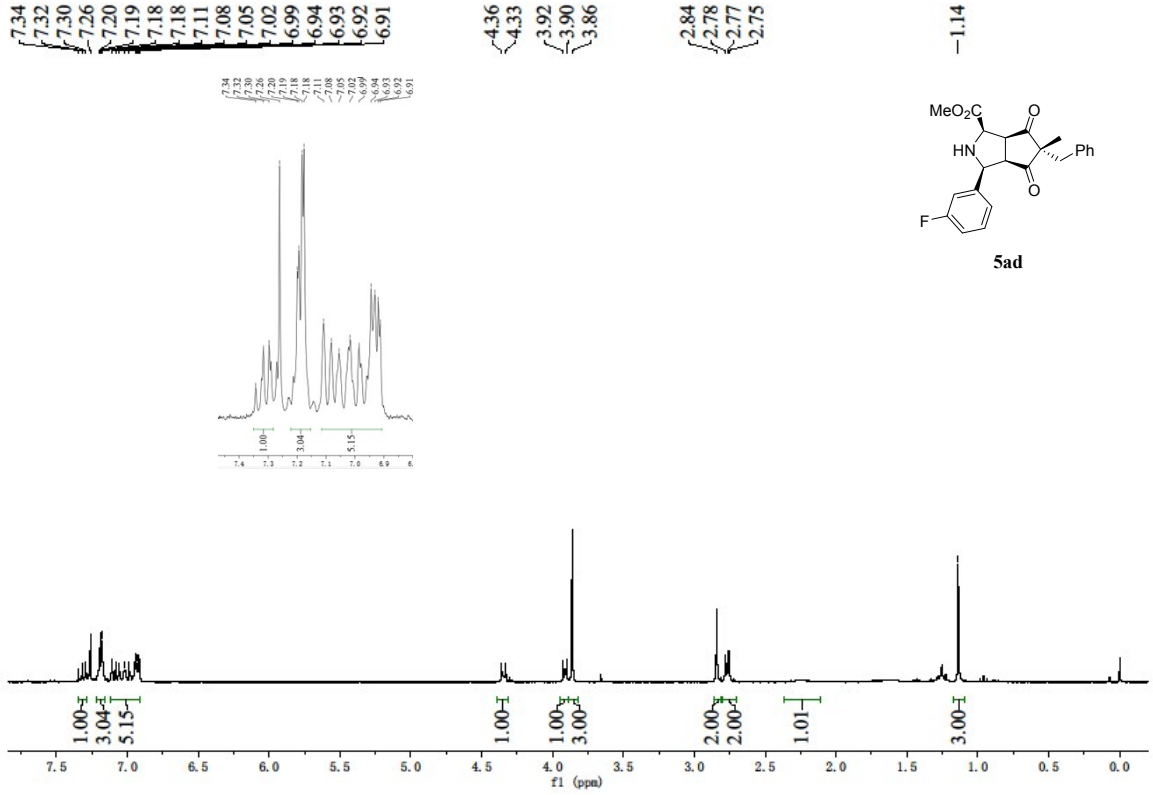
<Chromatogram>

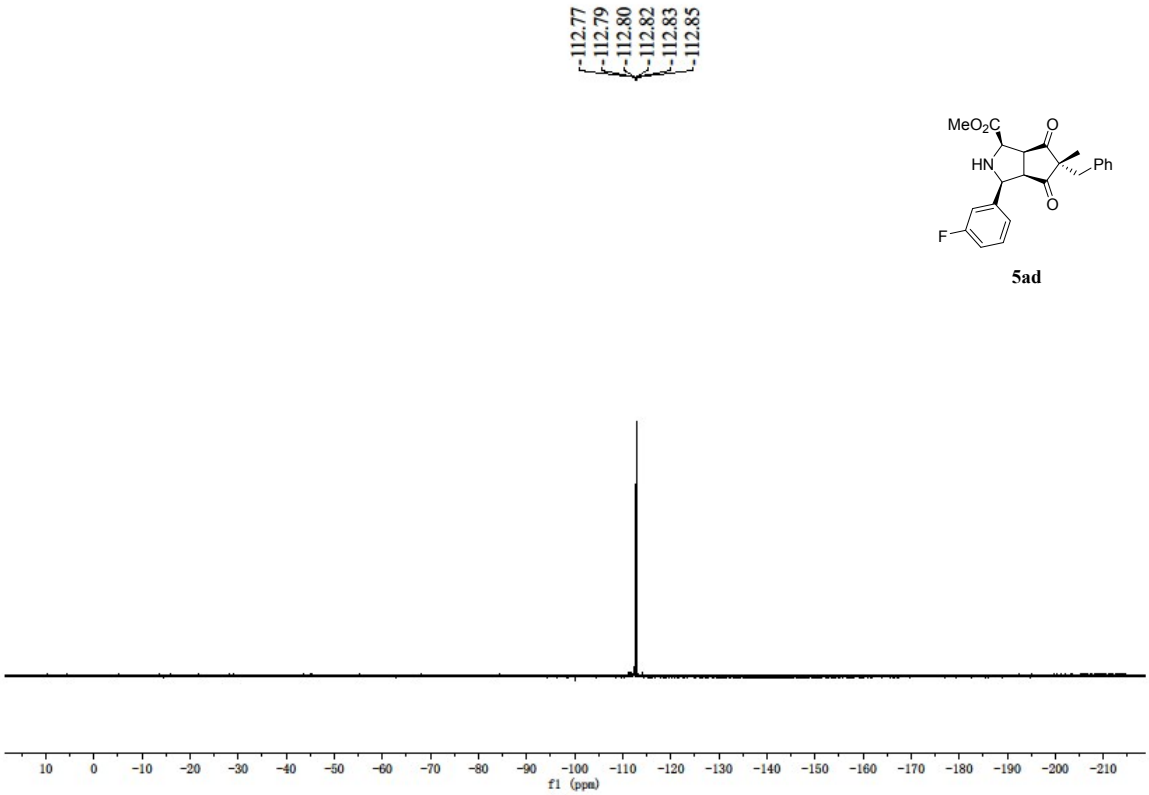


<Peak Table>

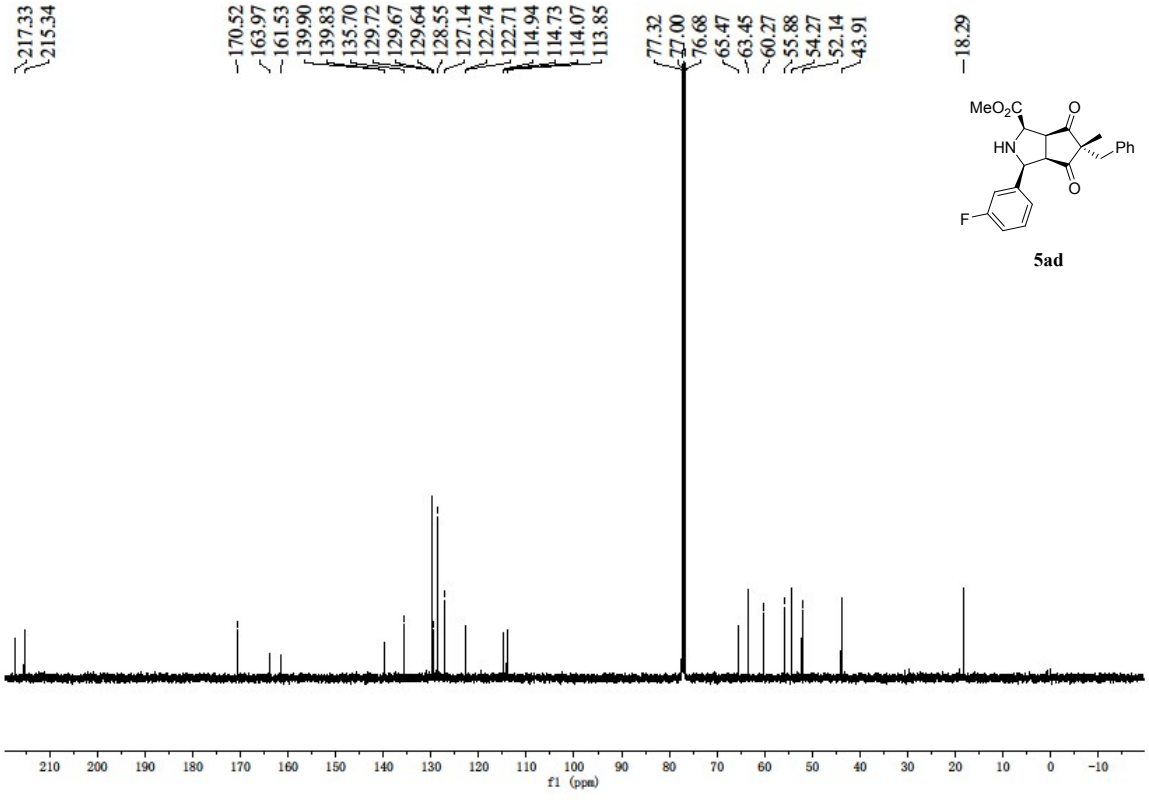
PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	9.816	351577	2.818	10662	5.445
2	14.794	12123282	97.182	185136	94.555
Total		12474858	100.000	195797	100.000




-112.77
-112.79
-112.80
-112.82
-112.83
-112.85
MeO2C
HN
O
Ph
O
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

5ad


217.33
215.34
170.52
163.97
161.53
139.90
139.83
135.70
129.72
129.67
129.64
128.55
127.14
122.74
122.71
114.94
114.73
114.07
113.85
77.32
77.00
76.68
65.47
63.45
60.27
55.88
54.27
52.14
43.91
18.29
MeO2C
HN
O
Ph
O
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

5ad

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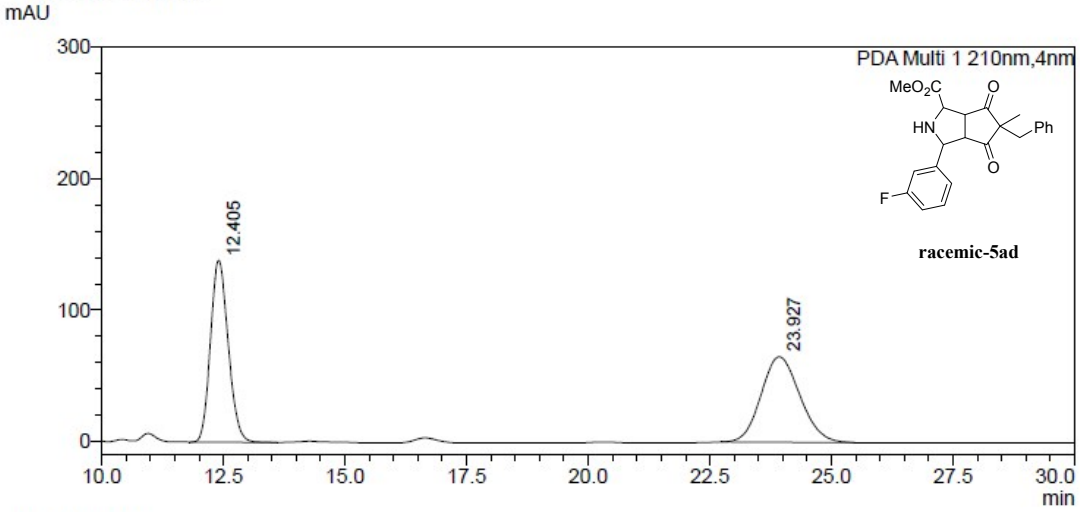
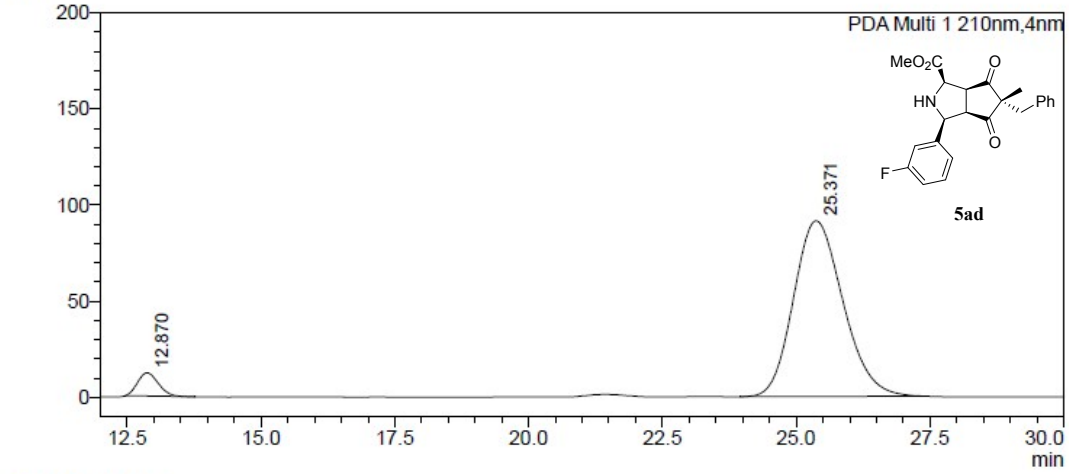


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	12.405	3508487	49.300	138307	68.023
2	23.927	3608088	50.700	65015	31.977
Total		7116576	100.000	203322	100.000

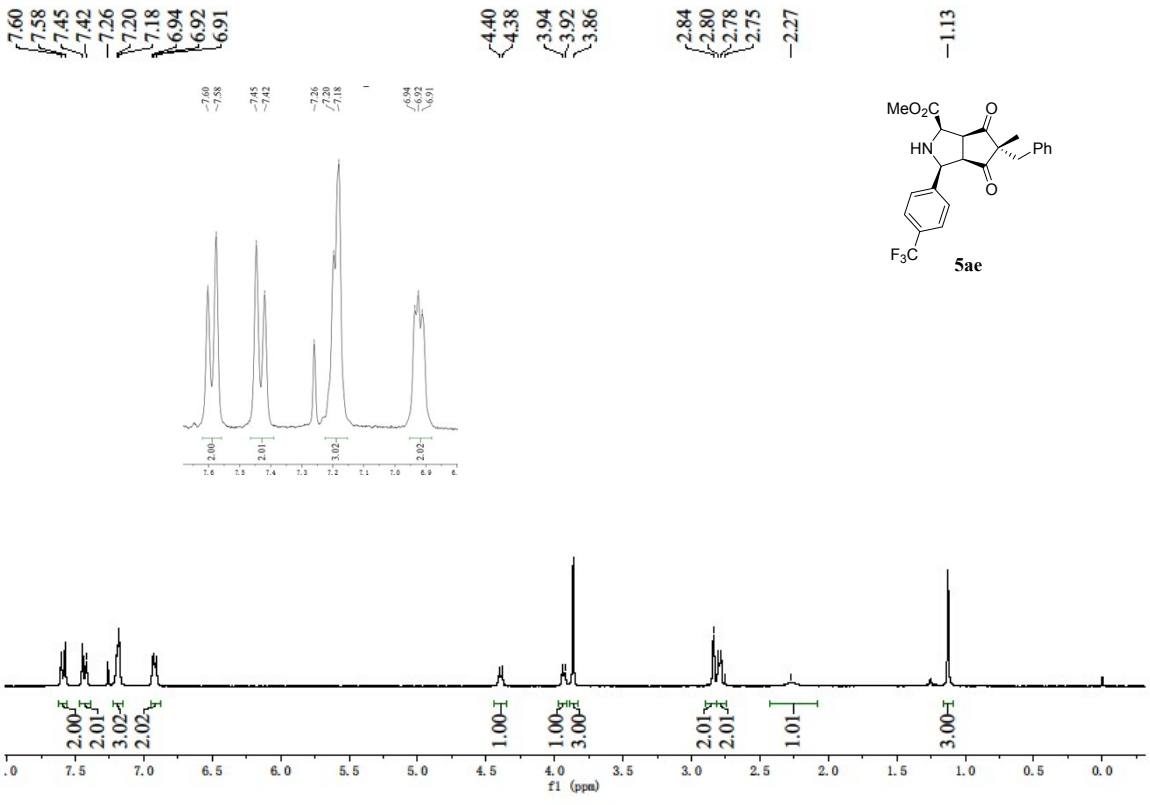
<Chromatogram>



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	12.870	322629	5.207	12005	11.618
2	25.371	5873308	94.793	91328	88.382
Total		6195937	100.000	103332	100.000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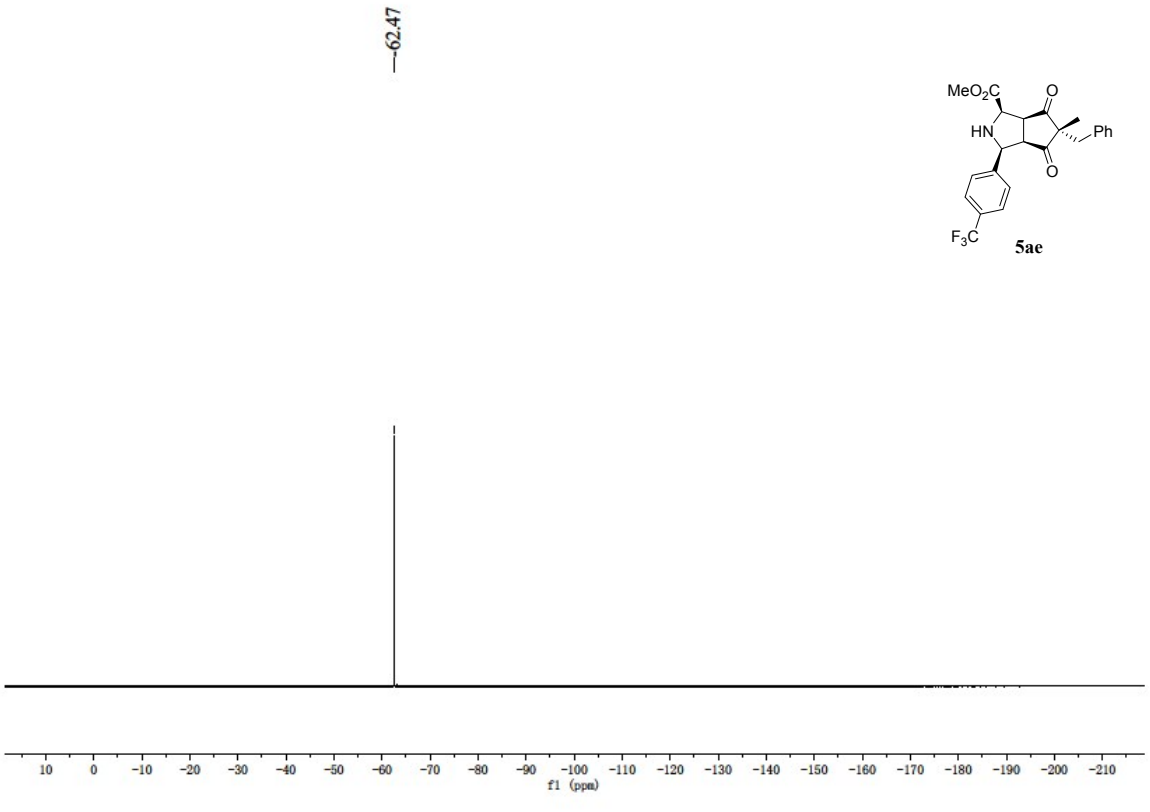
7.42
7.26
7.20
7.18
6.94
6.92
6.91
4.40
4.38
3.94
3.92
3.86
2.84
2.80
2.78
2.75
2.27
1.13
MeO2C
HN
O
Ph
F3C
5ae
2.00
2.01
3.02
2.02
1.00
1.00
3.00
2.01
2.01
1.01
3.00
f1 (ppm)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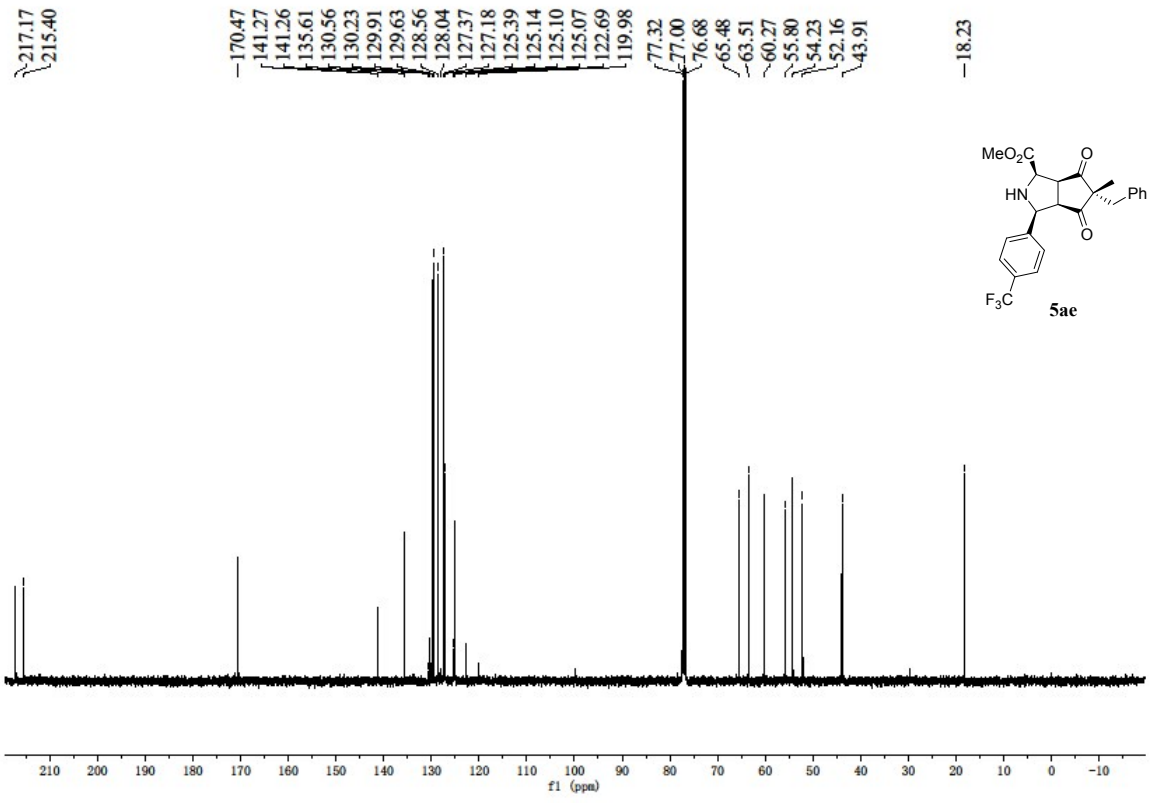
MeO2C
HN
O
Ph
F3C
5ae
f1 (ppm)



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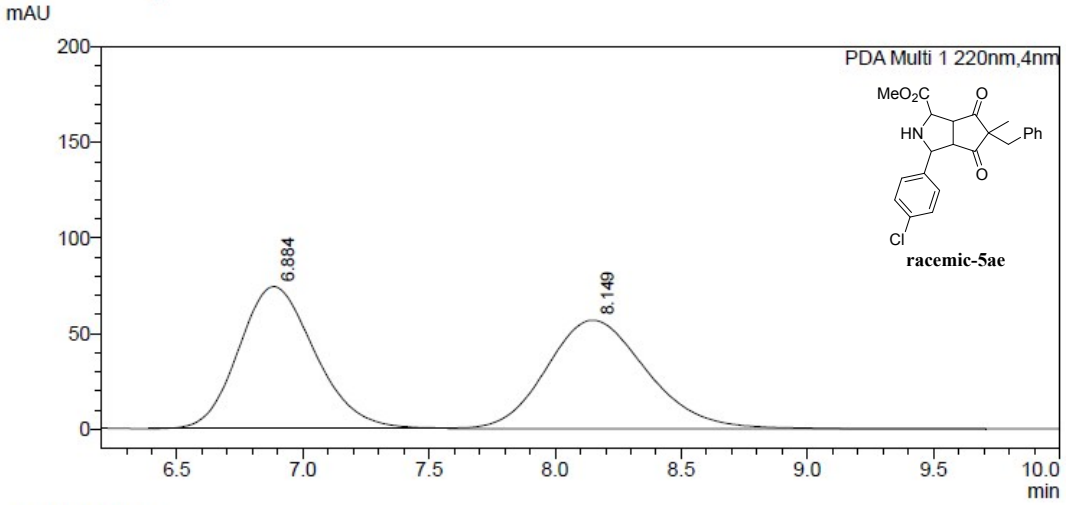
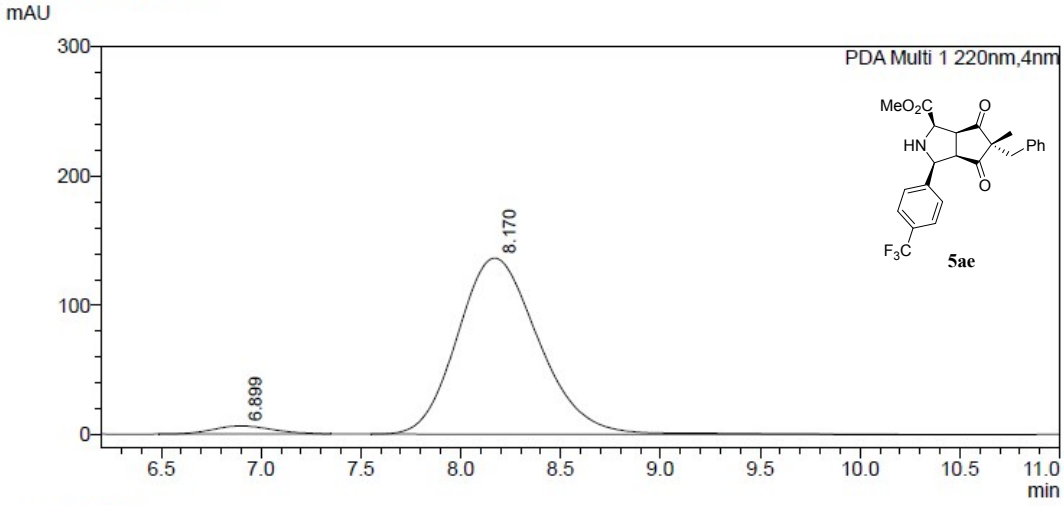


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	6.884	1568728	49.847	74264	56.668
2	8.149	1578340	50.153	56787	43.332
Total		3147068	100.000	131051	100.000

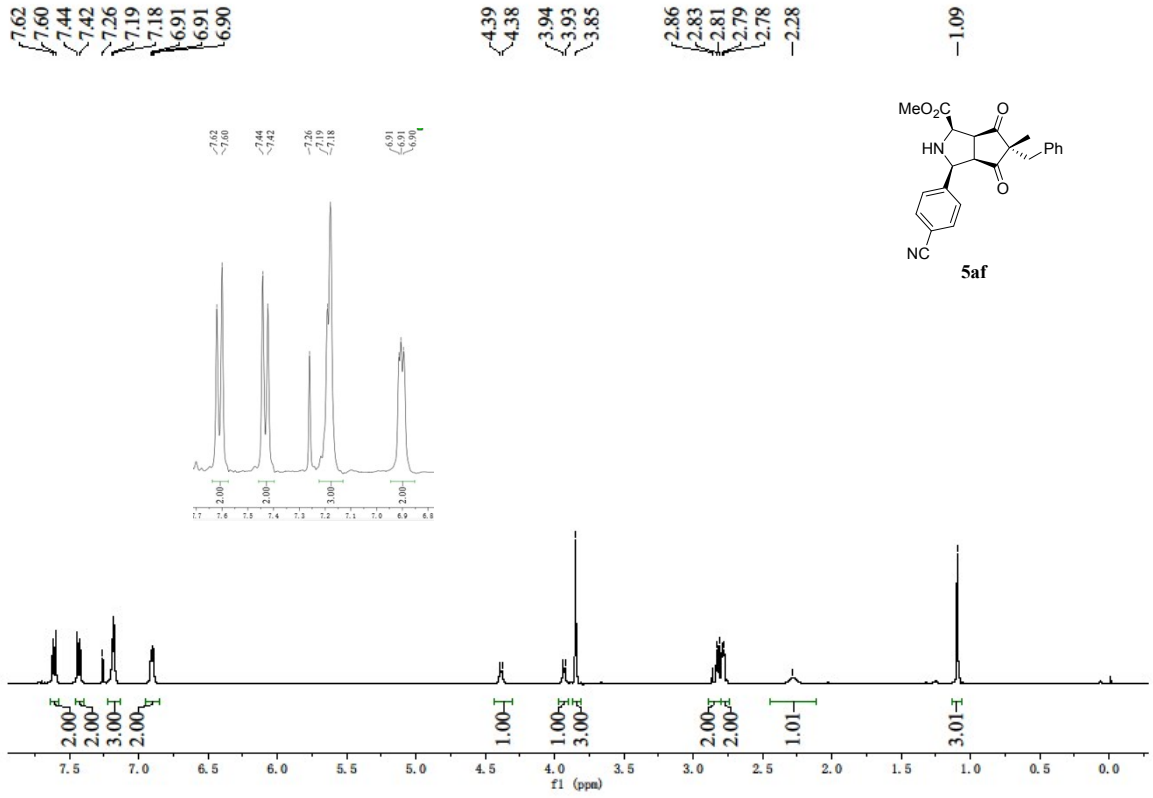
<Chromatogram>

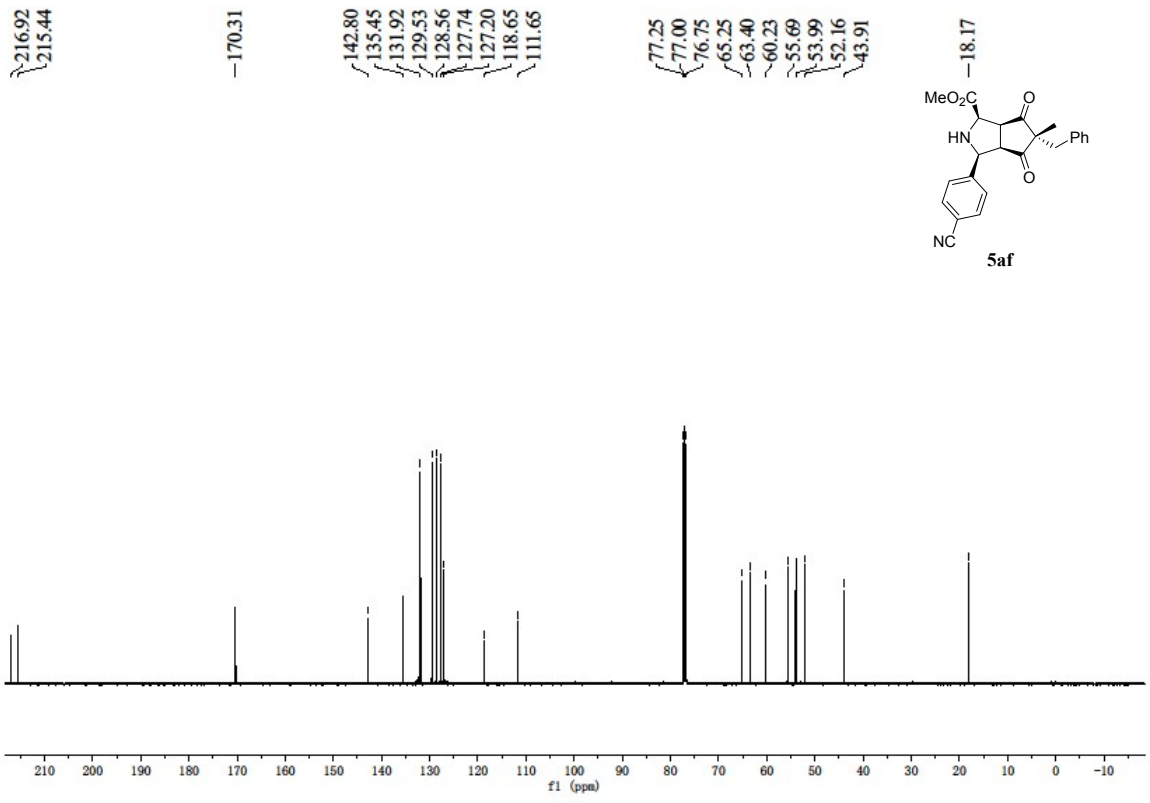


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	6.899	130061	3.254	6273	4.405
2	8.170	3866675	96.746	136140	95.595
Total		3996737	100.000	142413	100.000

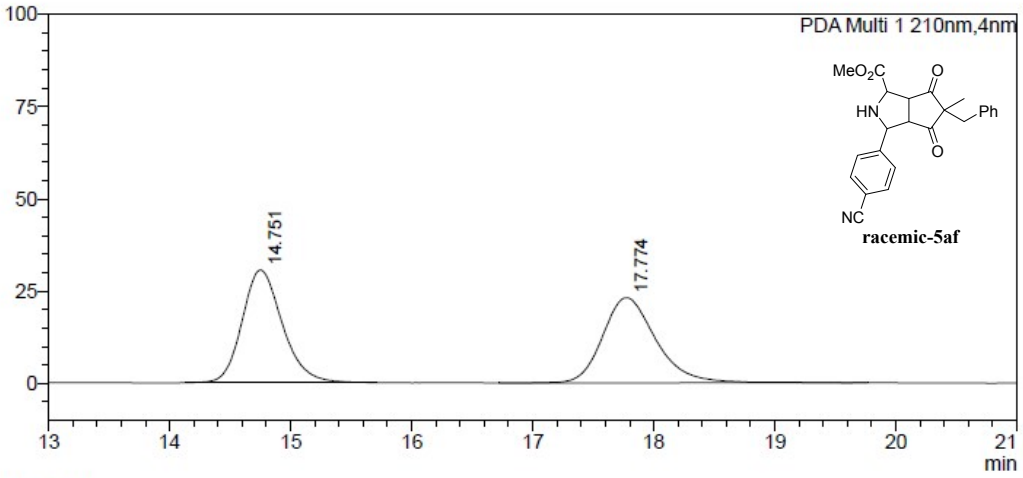




5af

<Chromatogram>

mAU



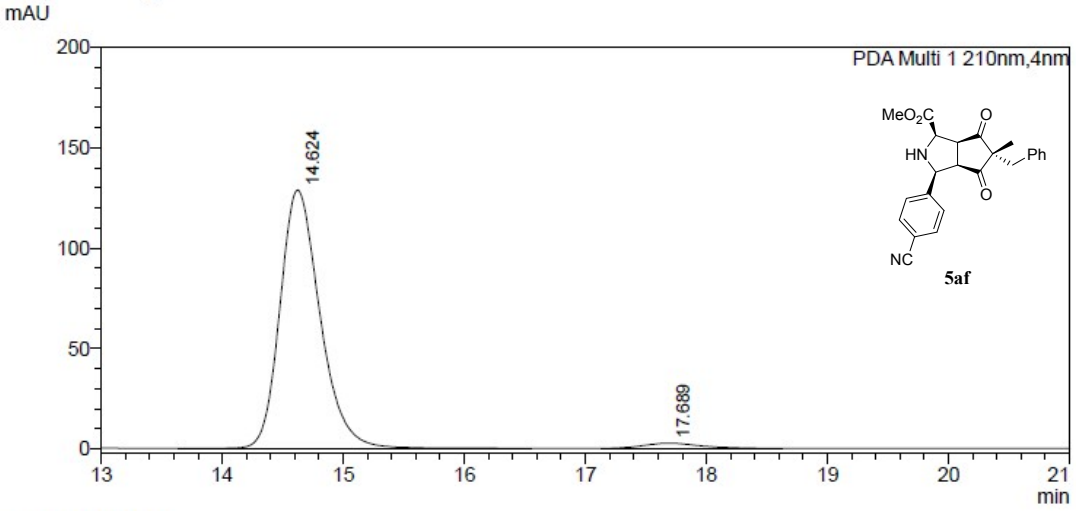
racemic-5af

<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	14.751	708110	50.165	30536	56.986
2	17.774	703459	49.835	23049	43.014
Total		1411569	100.000	53584	100.000

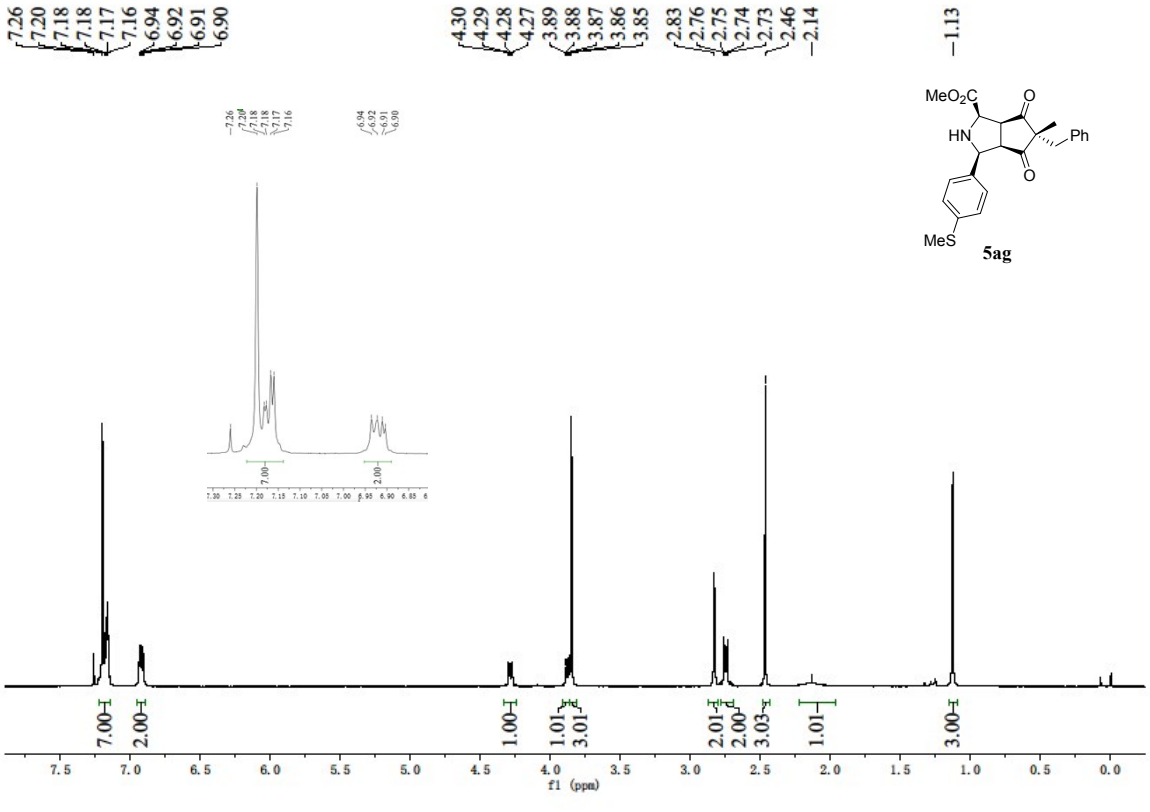
<Chromatogram>

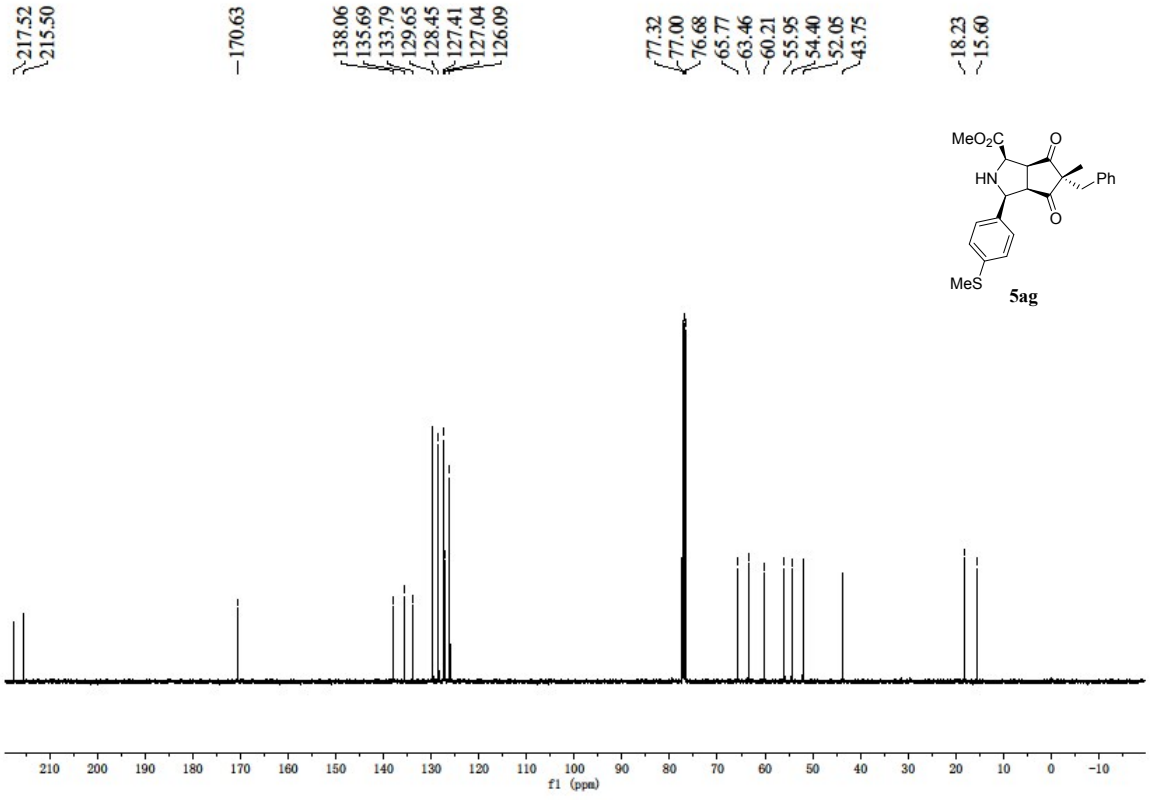


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	14.624	2957085	97.354	128587	98.072
2	17.689	80380	2.646	2528	1.928
Total		3037465	100.000	131116	100.000





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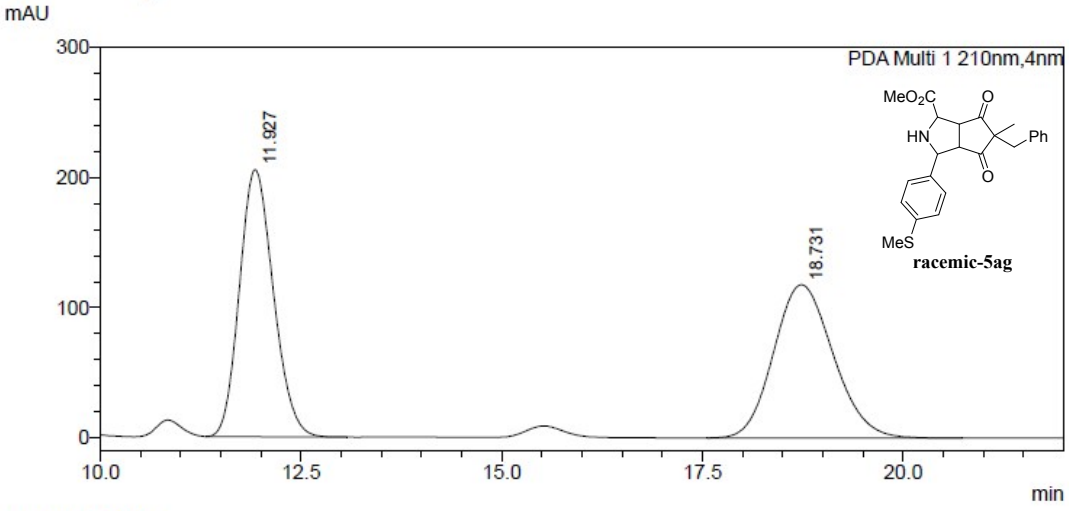
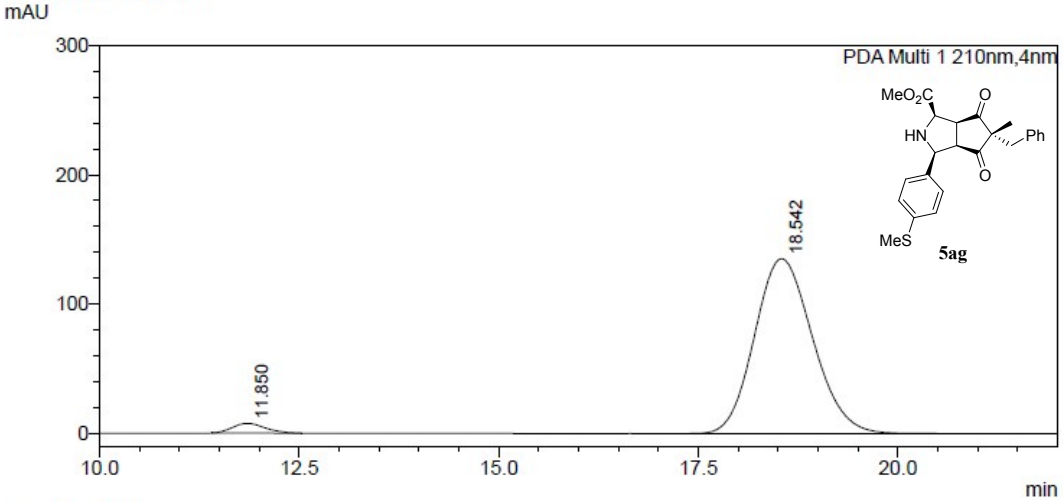


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	11.927	6044705	49.859	205262	63.554
2	18.731	6078772	50.141	117709	36.446
Total		12123476	100.000	322971	100.000

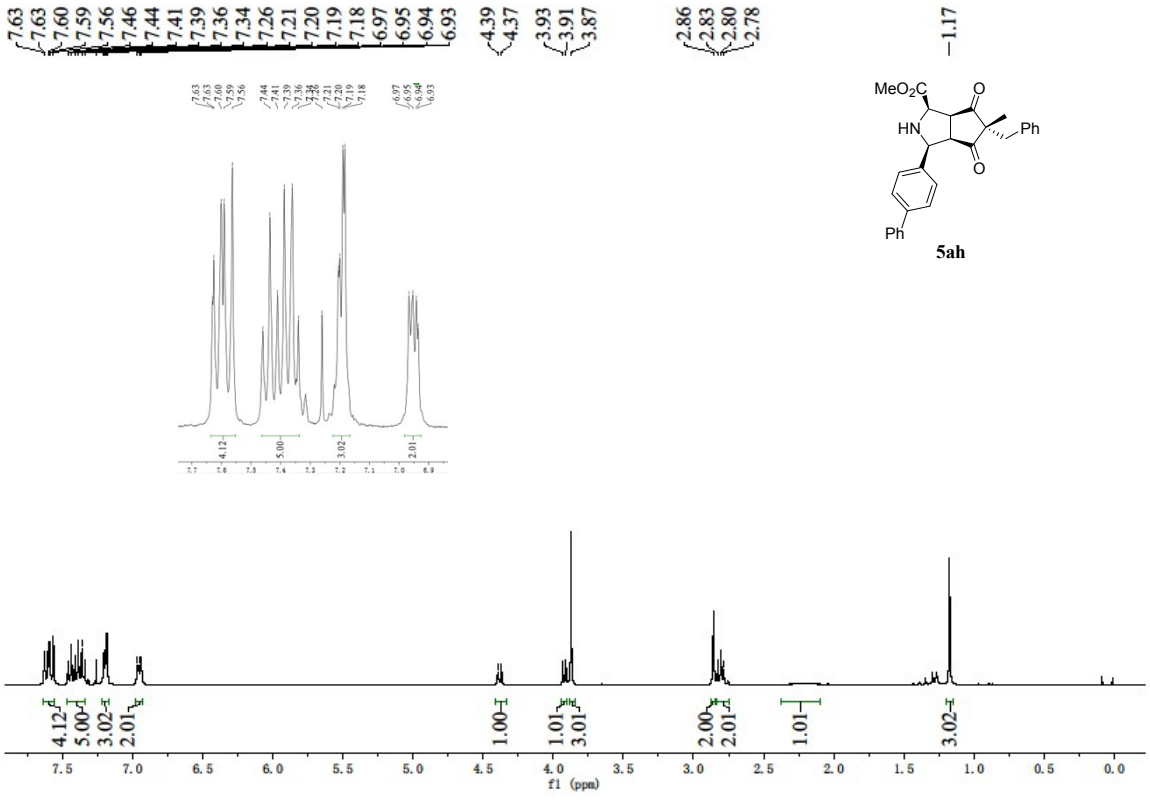
<Chromatogram>

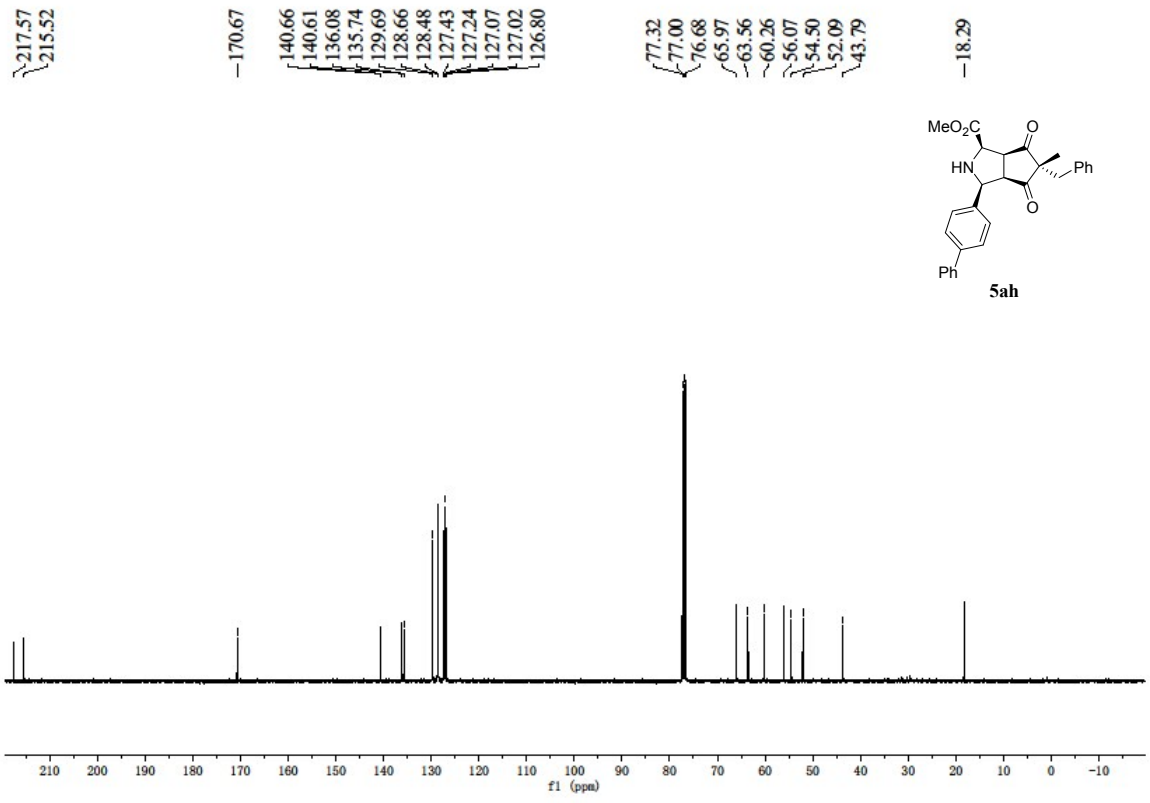


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	11.850	212657	3.004	7481	5.240
2	18.542	6866853	96.996	135289	94.760
Total		7079510	100.000	142770	100.000





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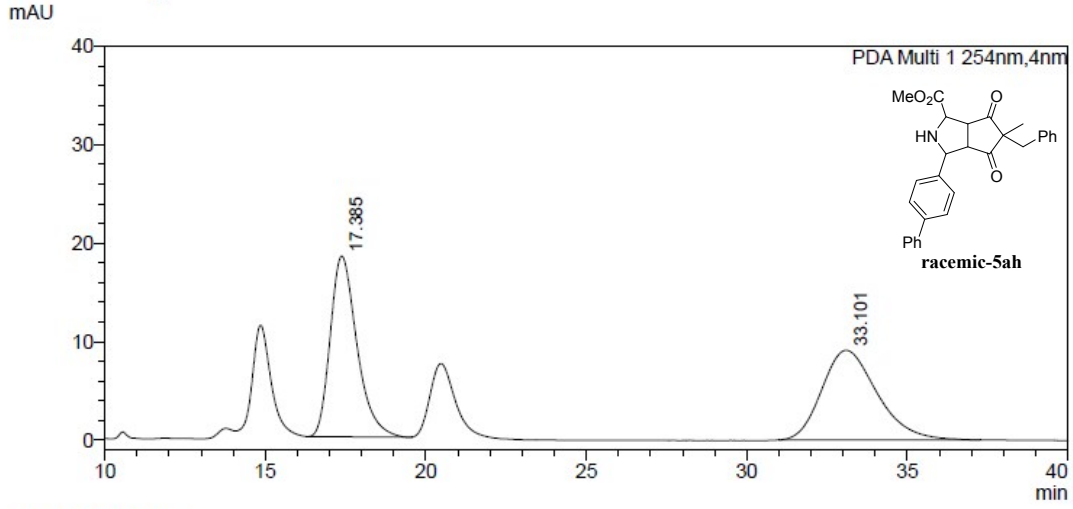
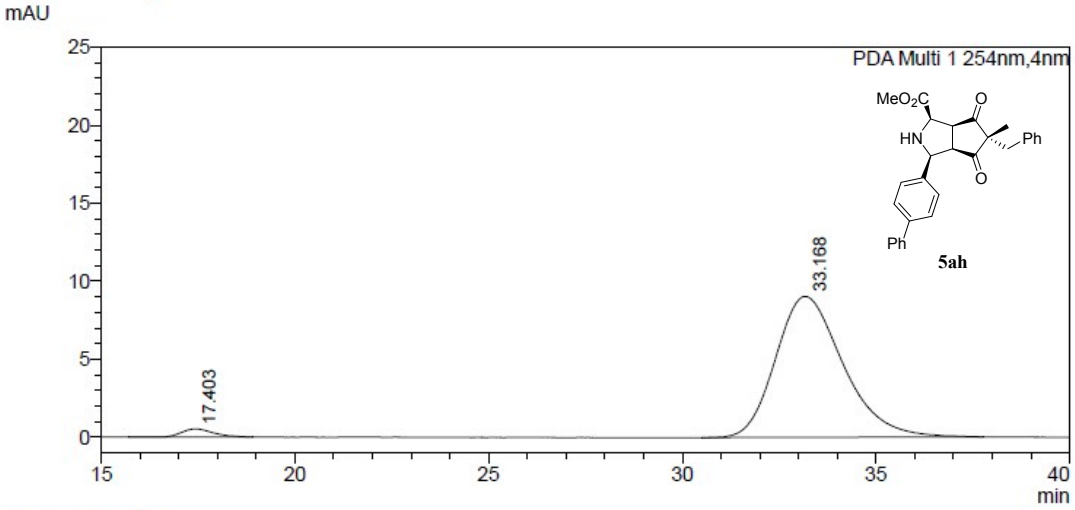


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	17.385	1062462	49.290	18368	66.829
2	33.101	1093068	50.710	9117	33.171
Total		2155529	100.000	27485	100.000

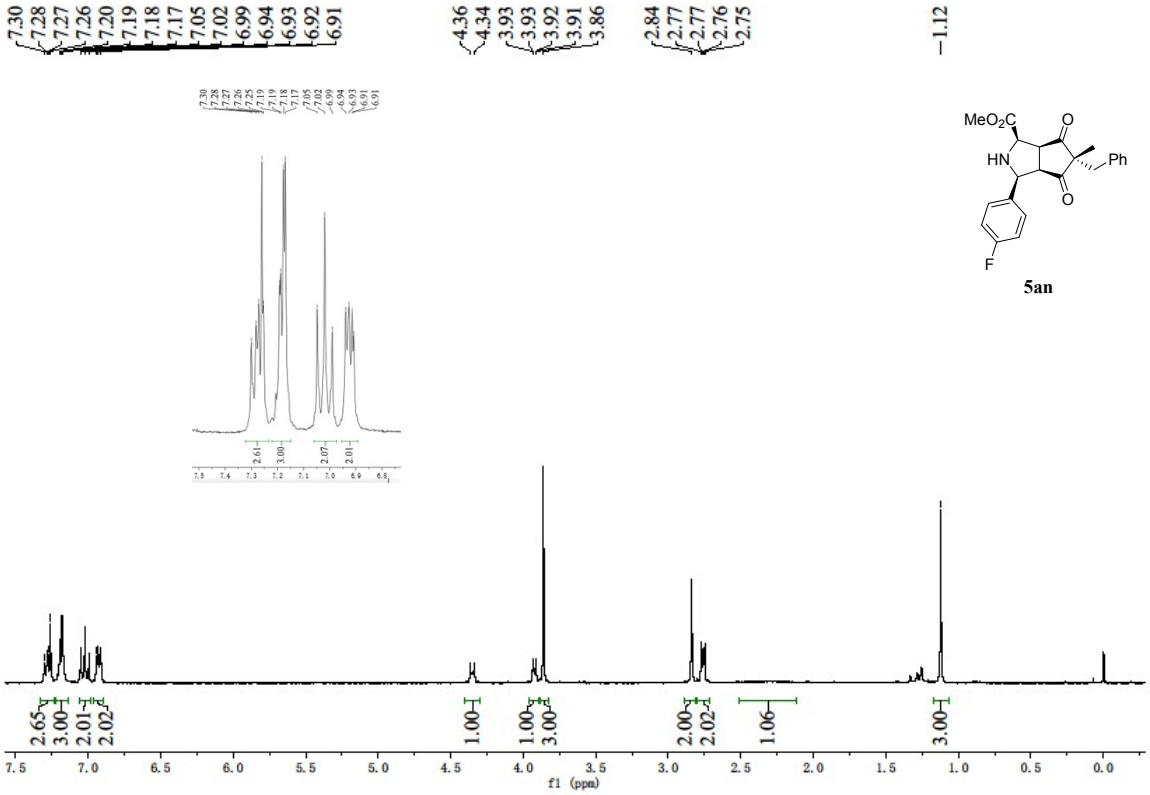
<Chromatogram>

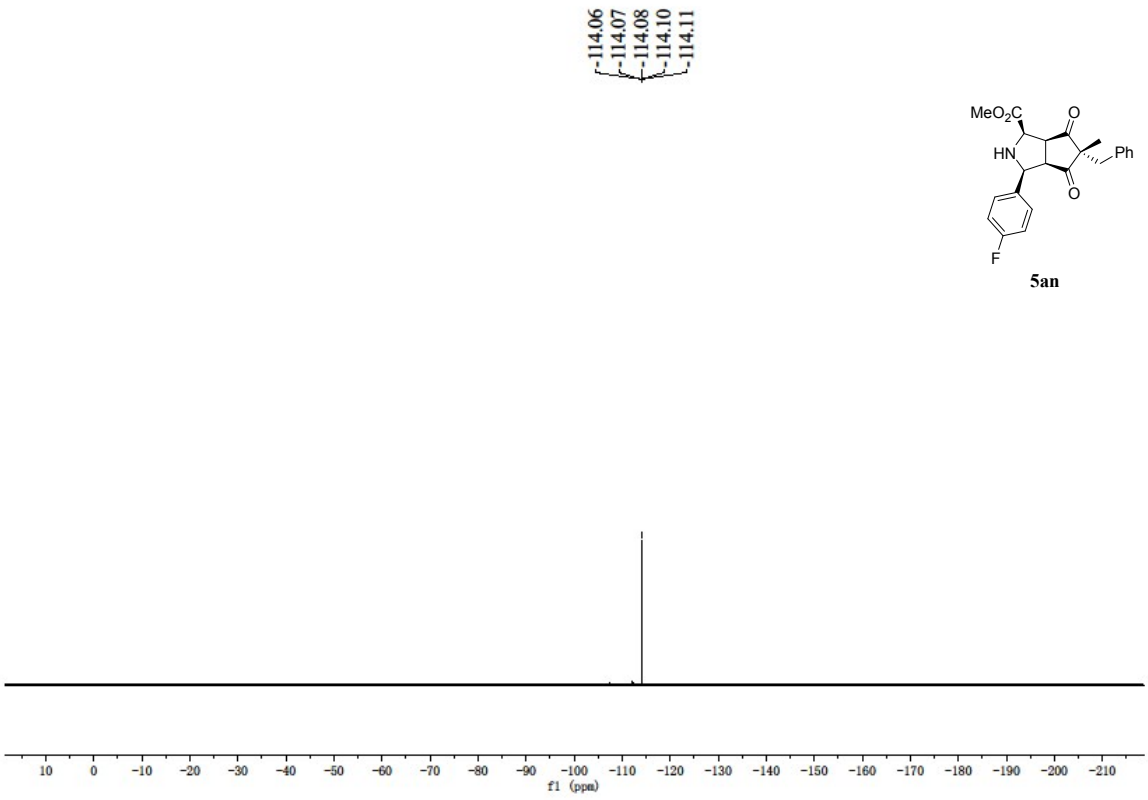


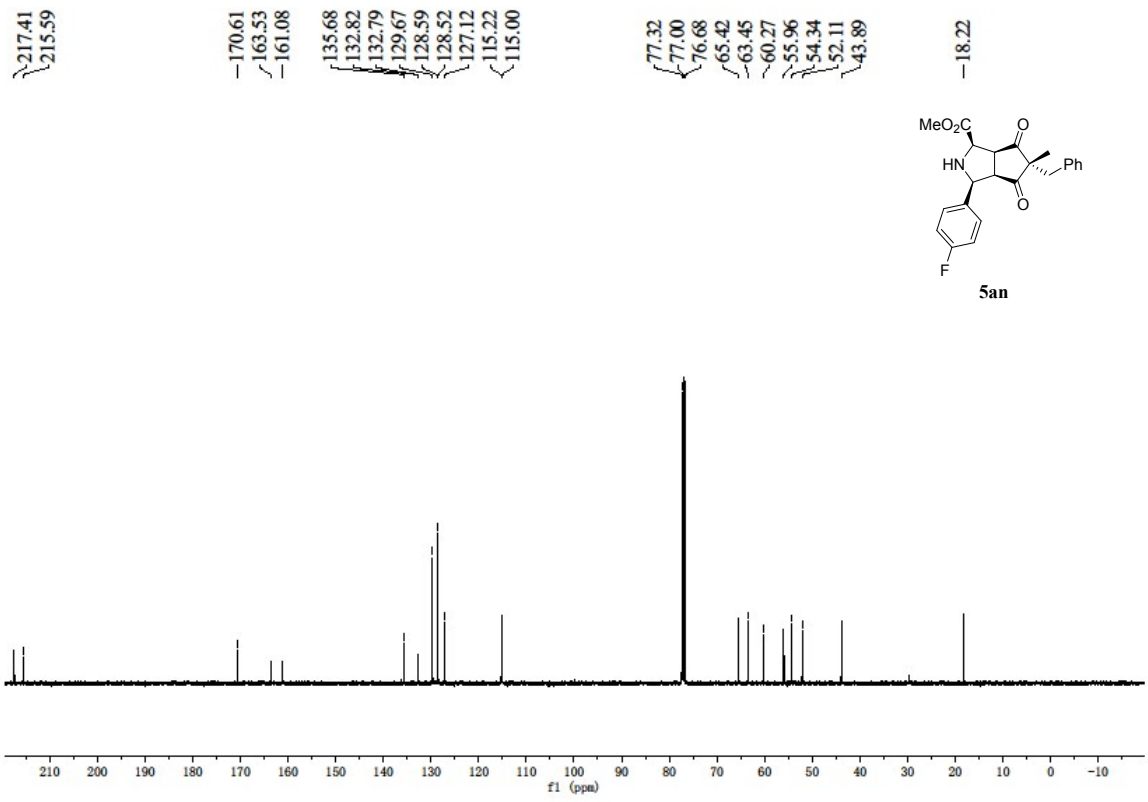
<Peak Table>

PDA Ch1 254nm

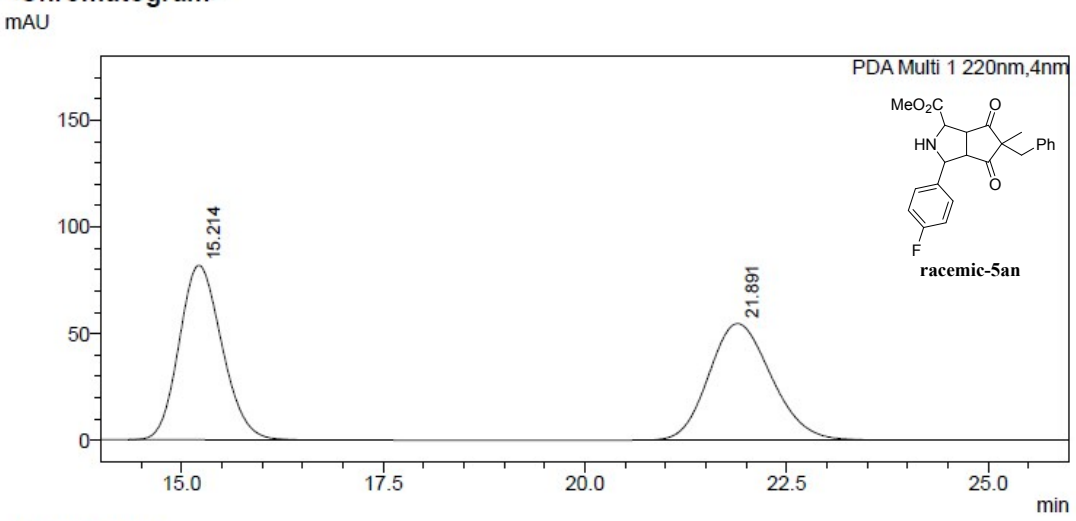
Peak#	Ret. Time	Area	Area%	Height	Height%
1	17.403	29134	2.596	520	5.437
2	33.168	1093053	97.404	9036	94.563
Total		1122187	100.000	9555	100.000




-114.06
-114.07
-114.08
-114.10
-114.11
MeO2C
O
HN
Ph
O
F
5an
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


217.41
215.59
170.61
163.53
161.08
135.68
132.82
132.79
129.67
128.59
128.52
127.12
115.22
115.00
77.32
77.00
76.68
65.42
63.45
60.27
55.96
54.34
52.11
43.89
18.22
MeO2C
O
HN
Ph
O
F
5an
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

<Chromatogram>

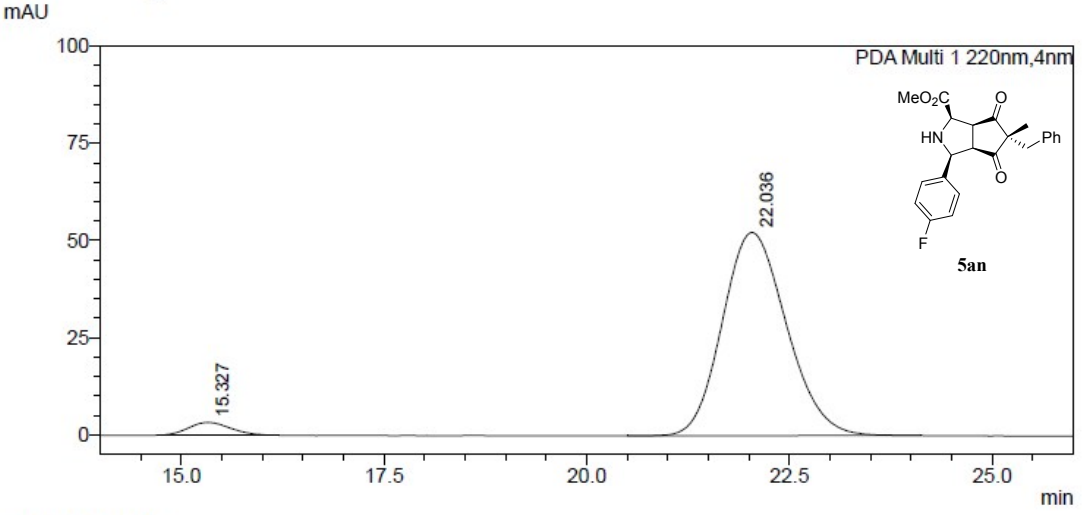


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.214	3017117	50.654	81728	59.969
2	21.891	2939204	49.346	54555	40.031
Total		5956321	100.000	136284	100.000

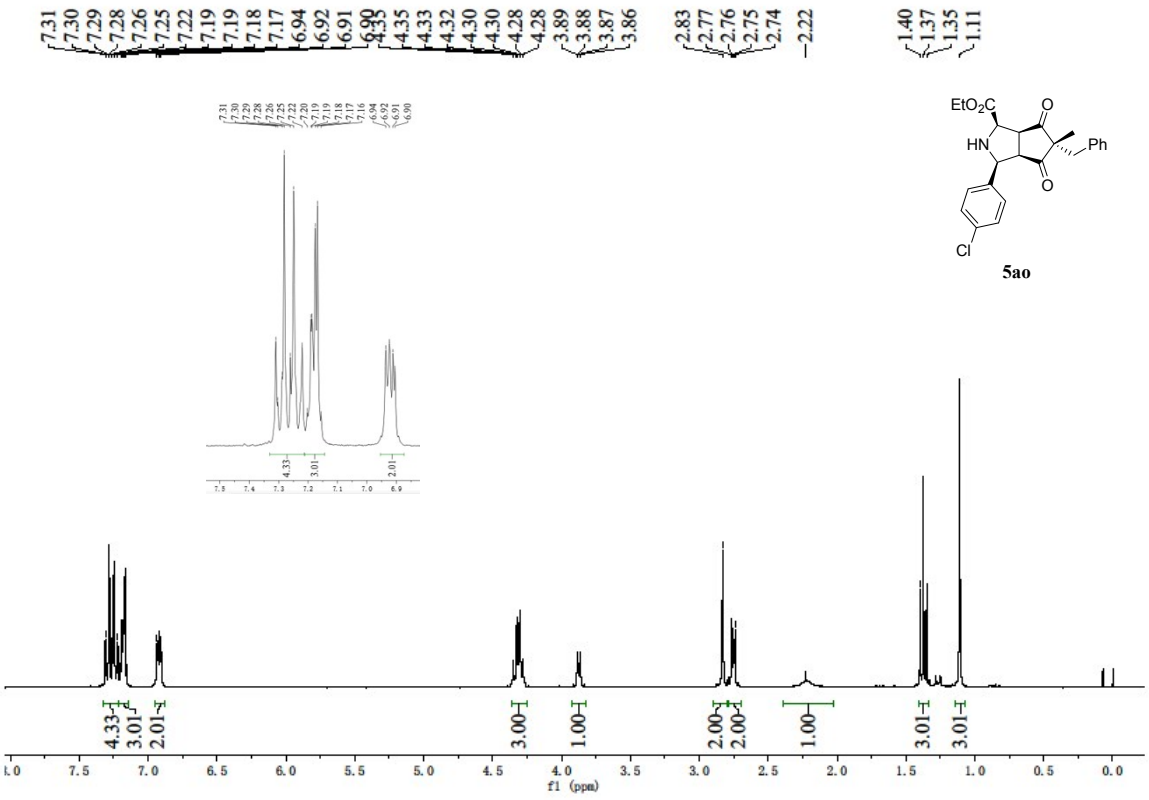
<Chromatogram>

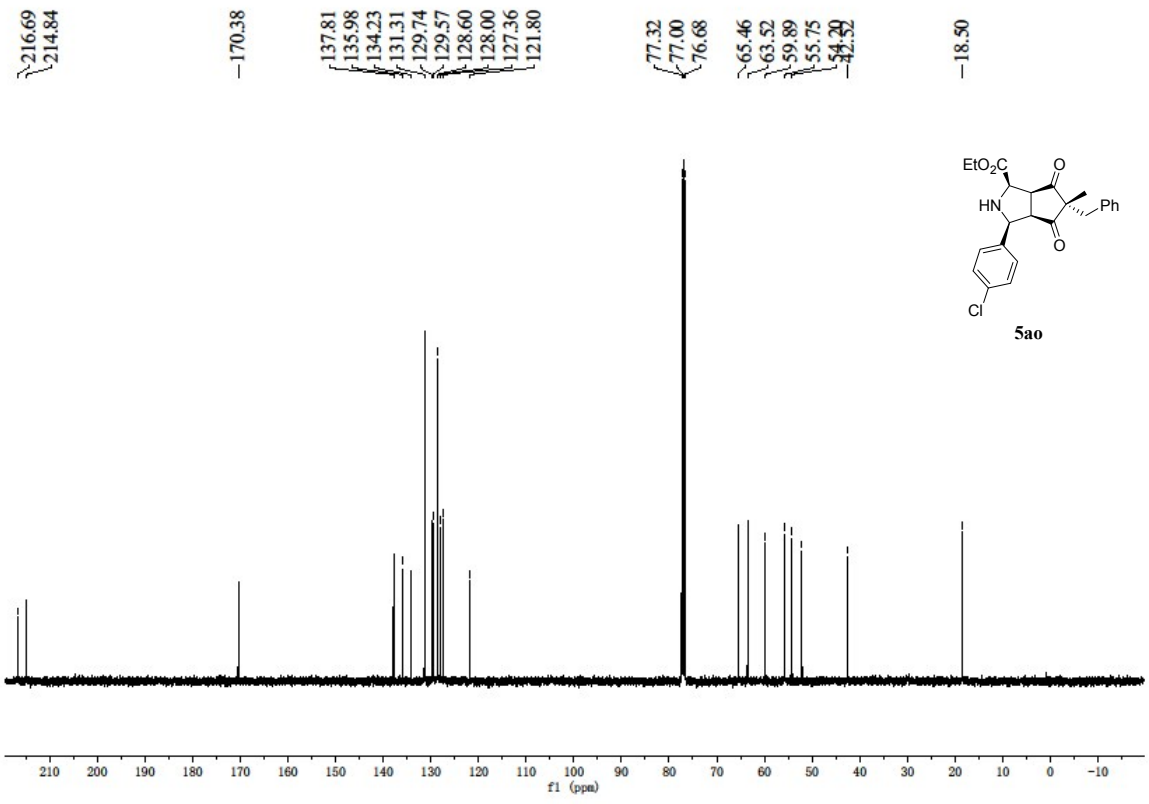


<Peak Table>

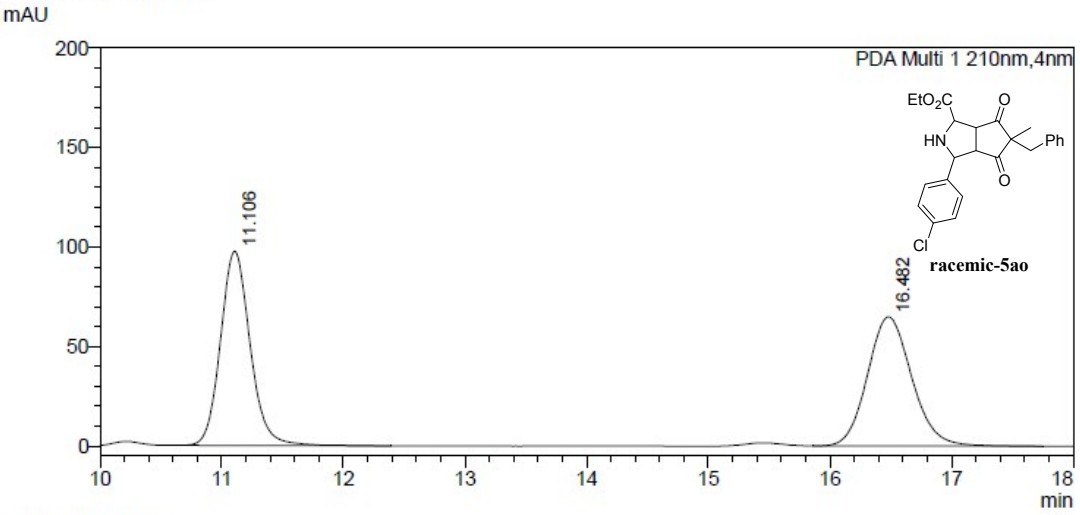
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.327	120032	4.000	3316	5.964
2	22.036	2881134	96.000	52289	94.036
Total		3001166	100.000	55606	100.000


7.31
7.30
7.29
7.28
7.26
7.25
7.22
7.19
7.19
7.18
7.17
6.94
6.92
6.91
6.90
4.35
4.33
4.32
4.30
4.30
4.28
4.28
3.89
3.88
3.87
3.86
2.83
2.77
2.76
2.75
2.74
2.22
1.40
1.37
1.35
1.11
EtO2C
HN
Ph
Cl
5ao
4.33
3.01
2.01
3.00
1.00
2.00
2.00
1.00
3.01
3.01
f1 (ppm)


216.69
214.84
170.38
137.81
135.98
134.23
131.31
129.74
129.57
128.60
128.00
127.36
121.80
77.32
77.00
76.68
65.46
63.52
59.89
55.75
18.50
EtO2C
HN
Ph
Cl
5ao
f1 (ppm)

<Chromatogram>

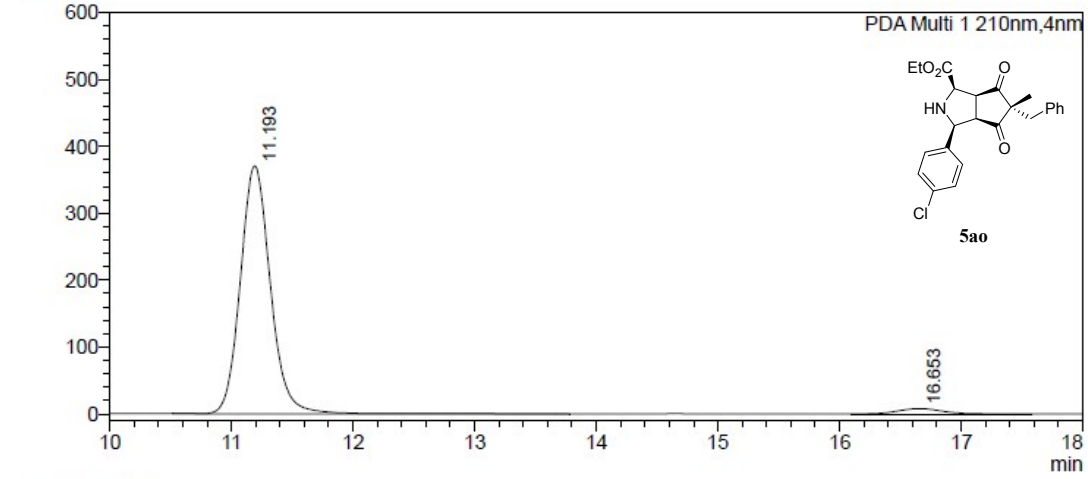


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	11.106	1658508	50.229	97690	60.079
2	16.482	1643397	49.771	64914	39.921
Total		3301904	100.000	162604	100.000

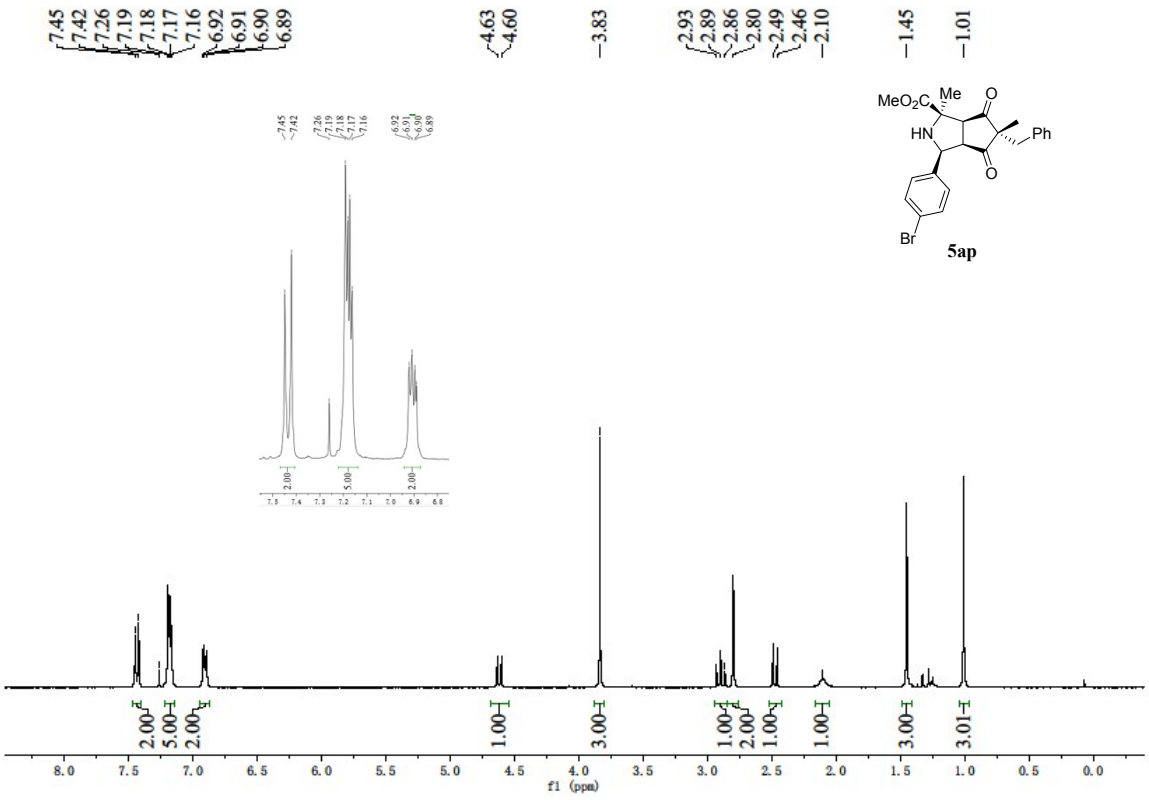
<Chromatogram>



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	11.193	6350962	96.861	370567	97.865
2	16.653	205833	3.139	8086	2.135
Total		6556795	100.000	378653	100.000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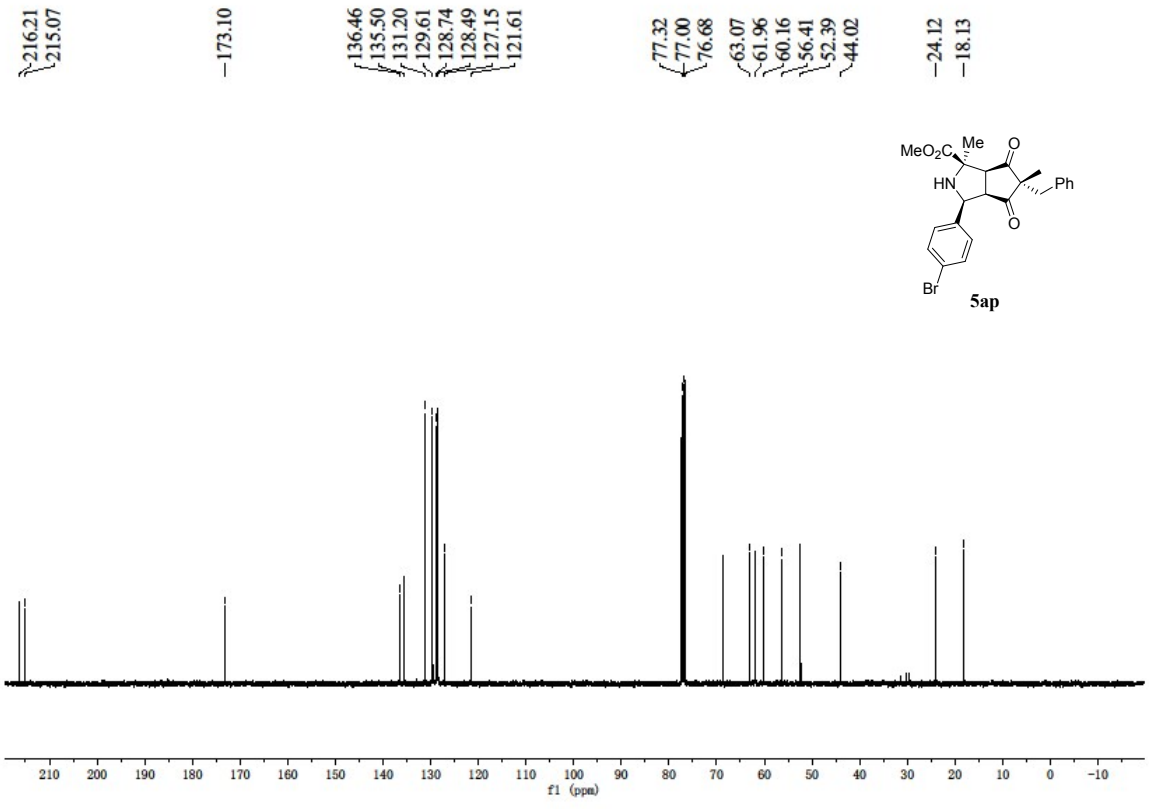
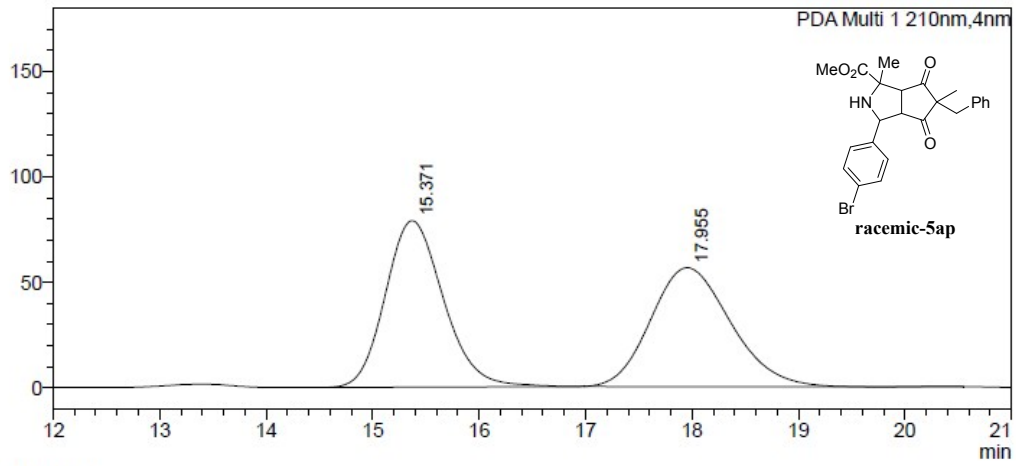
7.26
7.19
7.18
7.17
7.16
6.92
6.91
6.90
6.89
4.63
4.60
3.83
2.93
2.89
2.86
2.80
2.49
2.46
2.10
1.45
1.01
MeO2C
Me
HN
Ph
O
O
Br
5ap
2.00
5.00
2.00
1.00
3.00
1.00
2.00
1.00
1.00
3.00
3.01
f1 (ppm)


216.21
215.07
173.10
136.46
135.50
131.20
129.61
128.74
128.49
127.15
121.61
77.32
77.00
76.68
63.07
61.96
60.16
56.41
52.39
44.02
24.12
18.13
MeO2C
Me
HN
Ph
O
O
Br
5ap
f1 (ppm)

<Chromatogram>

mAU



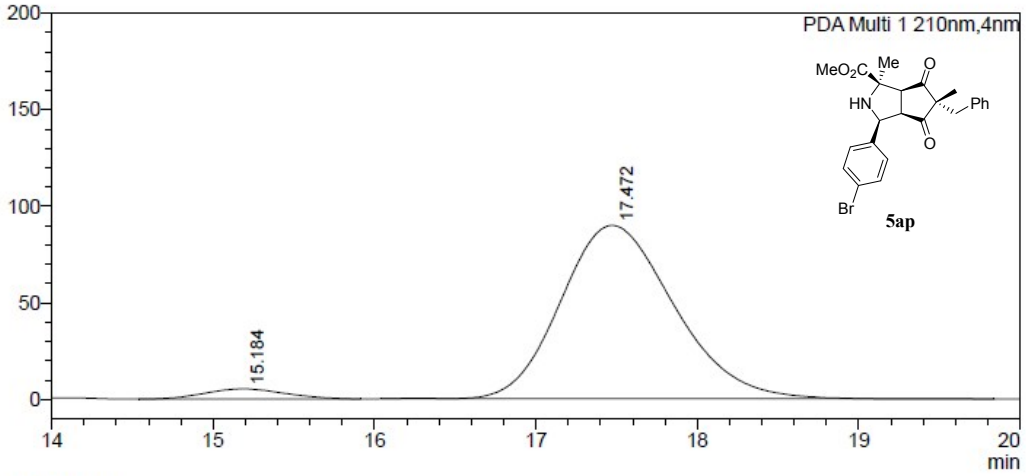
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.371	2994336	50.579	78871	58.357
2	17.955	2925838	49.421	56282	41.643
Total		5920174	100.000	135153	100.000

<Chromatogram>

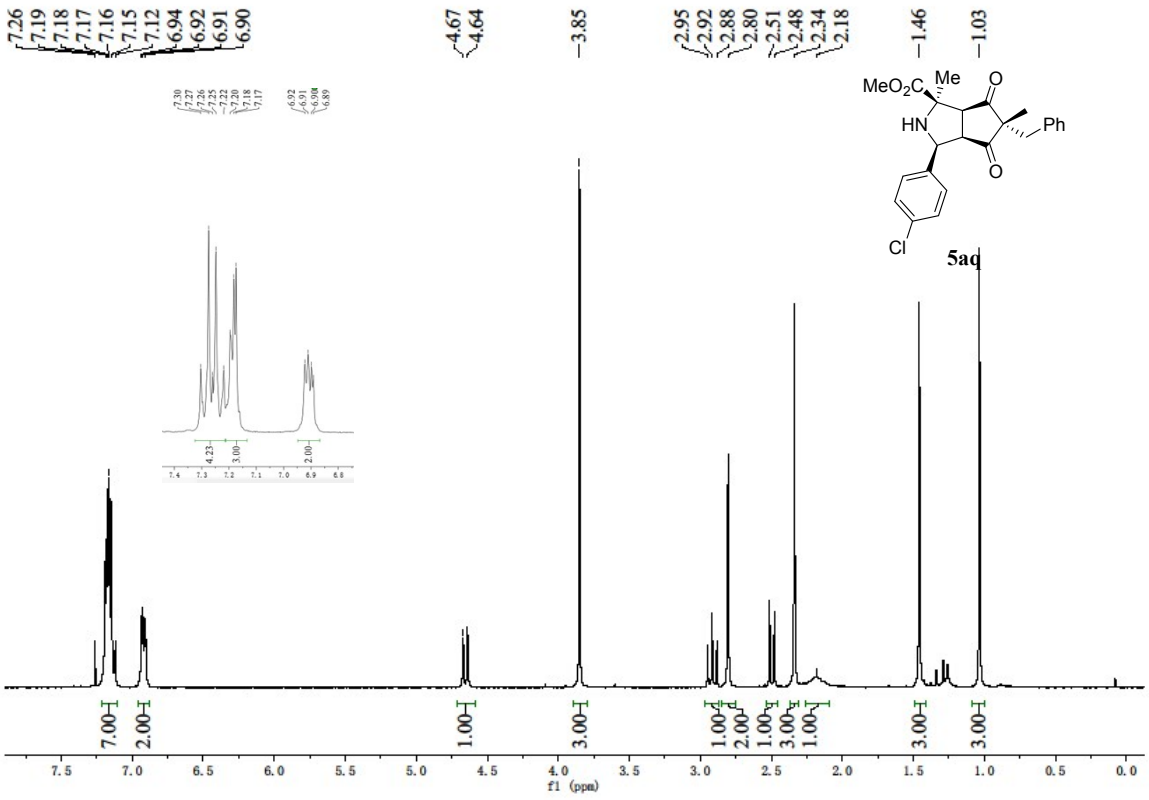
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.184	177221	3.883	5171	5.447
2	17.472	4387027	96.117	89767	94.553
Total		4564248	100.000	94939	100.000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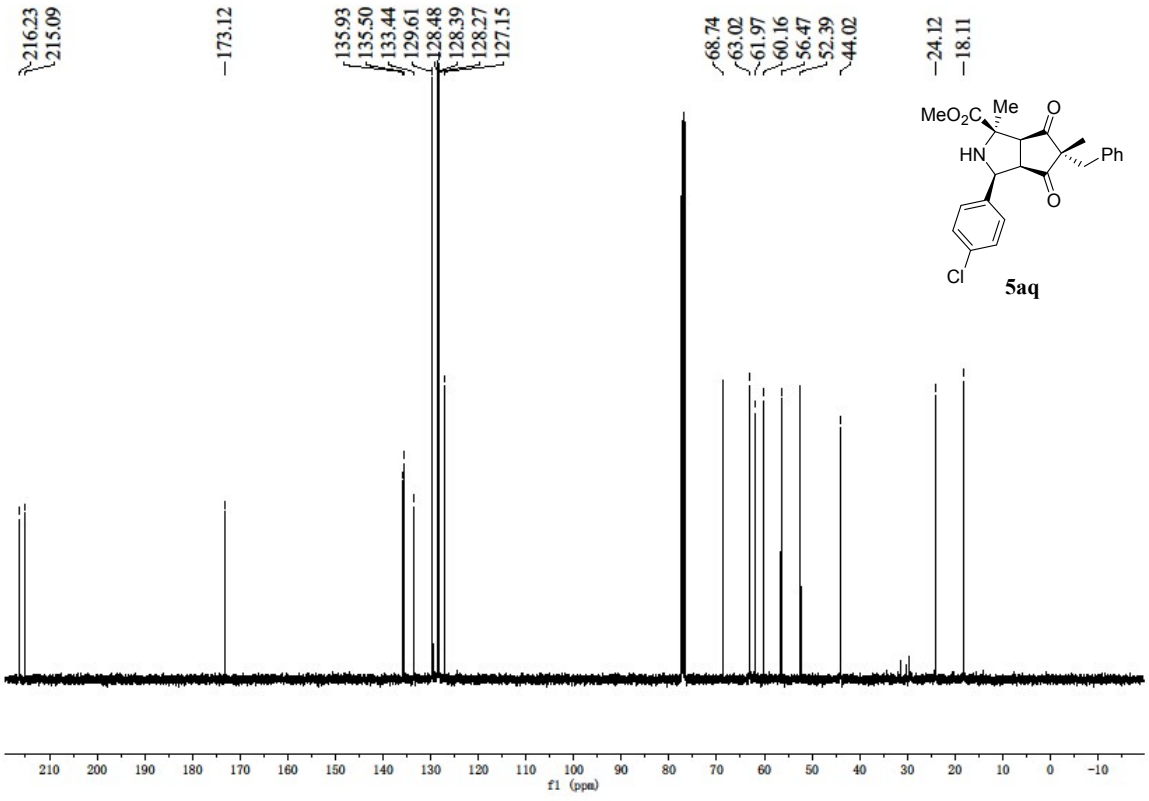
7.19
7.18
7.17
7.16
7.15
7.12
6.94
6.92
6.91
6.90
4.67
4.64
3.85
2.95
2.92
2.88
2.80
2.51
2.48
2.34
2.18
1.46
1.03
MeO2C
Me
HN
Ph
Cl
5aq
7.00
2.00
1.00
3.00
1.00
2.00
1.00
3.00
1.00
3.00
3.00
f1 (ppm)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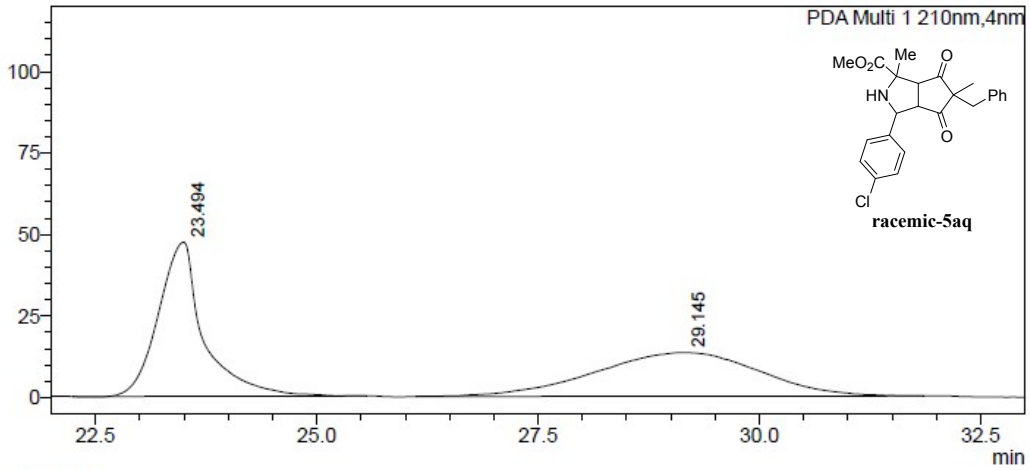
215.09
173.12
135.93
135.50
133.44
129.61
128.48
128.39
128.27
127.15
68.74
63.02
61.97
60.16
56.47
52.39
44.02
24.12
18.11
MeO2C
Me
HN
Ph
Cl
5aq
f1 (ppm)

<Chromatogram>

mAU



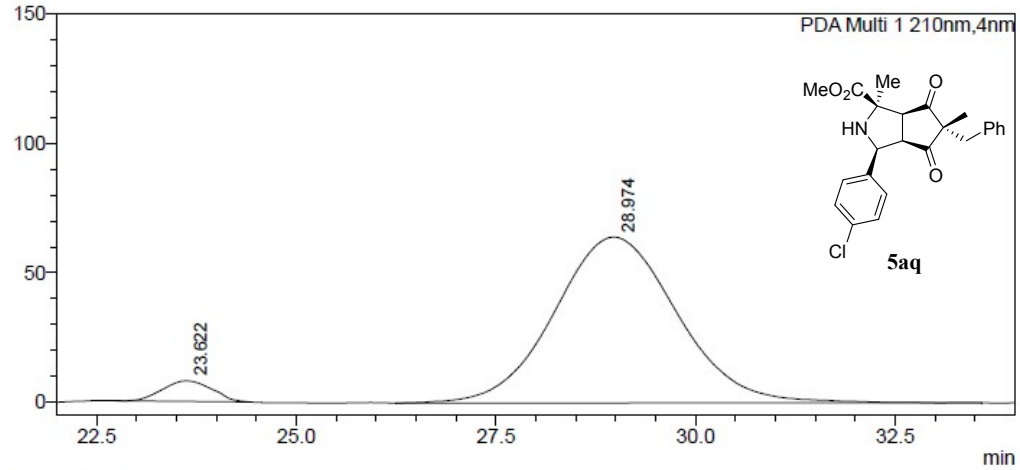
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	23.494	1676028	49.329	47289	77.953
2	29.145	1721653	50.671	13374	22.047
Total		3397680	100.000	60663	100.000

<Chromatogram>

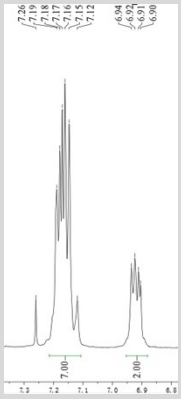
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	23.622	339546	4.712	7905	10.985
2	28.974	6866253	95.288	64063	89.015
Total		7205799	100.000	71968	100.000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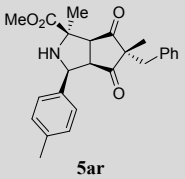
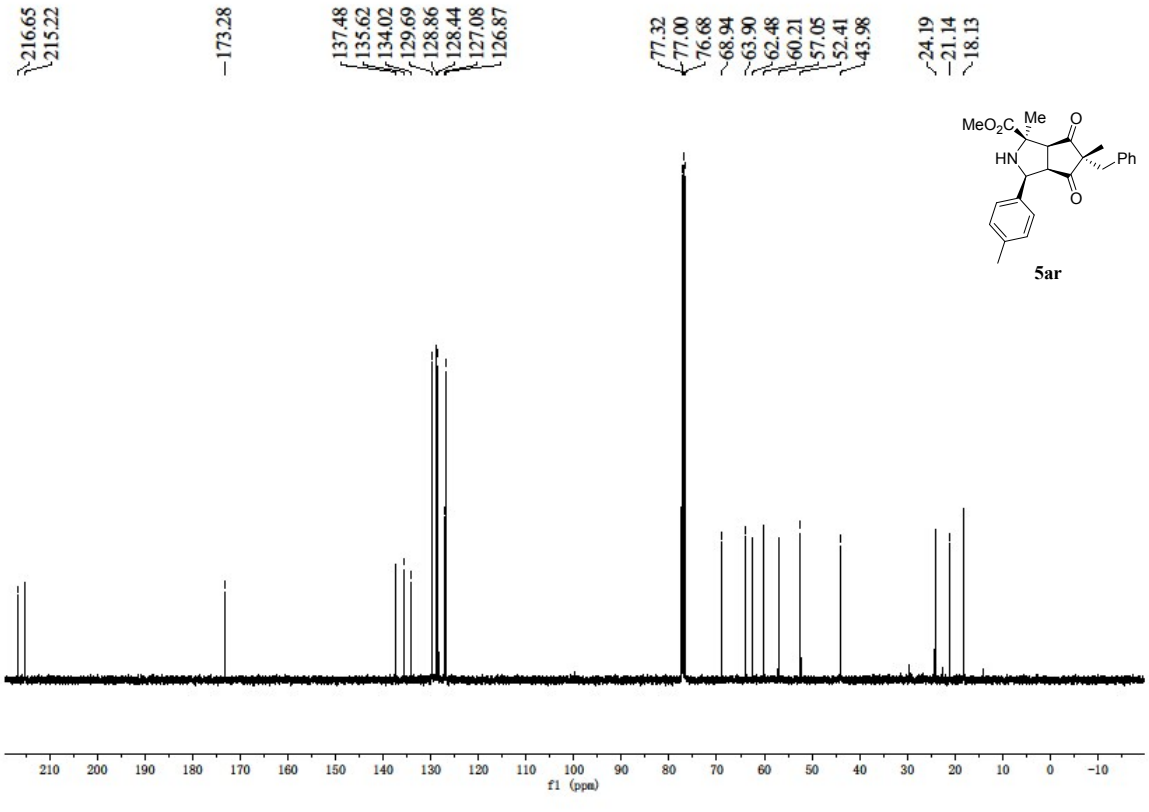
7.19
7.18
7.17
7.16
7.15
7.13
7.12
6.94
6.92
6.91
6.90
7.00
2.00
7.3
7.2
7.1
7.0
6.9
6.8


MeO2C
Me
O
HN
Ph
O

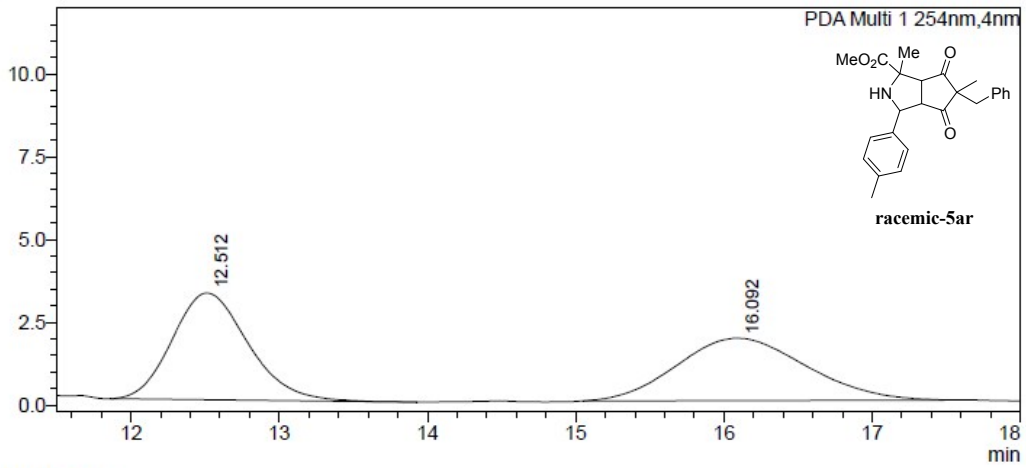
5ar


216.65
215.22
173.28
137.48
135.62
134.02
129.69
128.86
128.44
127.08
126.87
77.32
77.00
76.68
68.94
63.90
62.48
60.21
57.05
52.41
43.98
24.19
21.14
18.13
MeO2C
Me
O
HN
Ph
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

5ar

<Chromatogram>

mAU



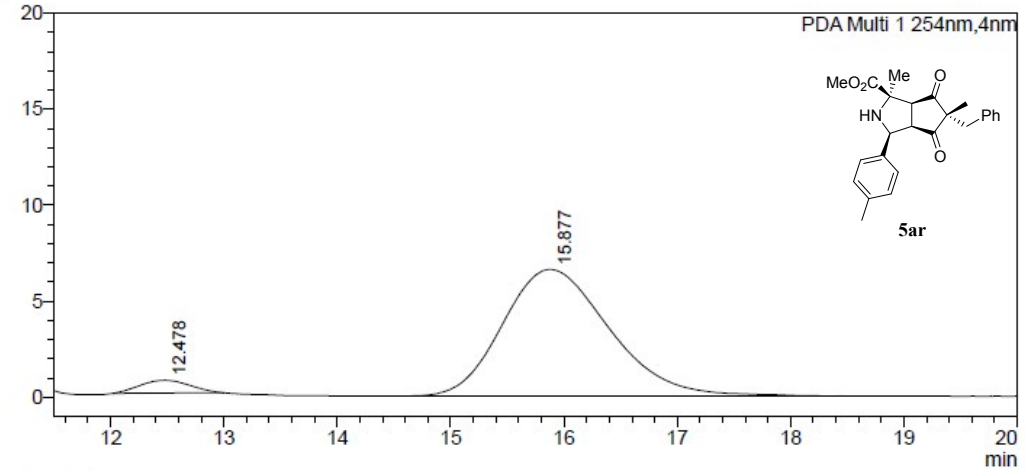
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	12.512	114732	50.058	3228	63.107
2	16.092	114465	49.942	1887	36.893
Total		229197	100.000	5114	100.000

<Chromatogram>

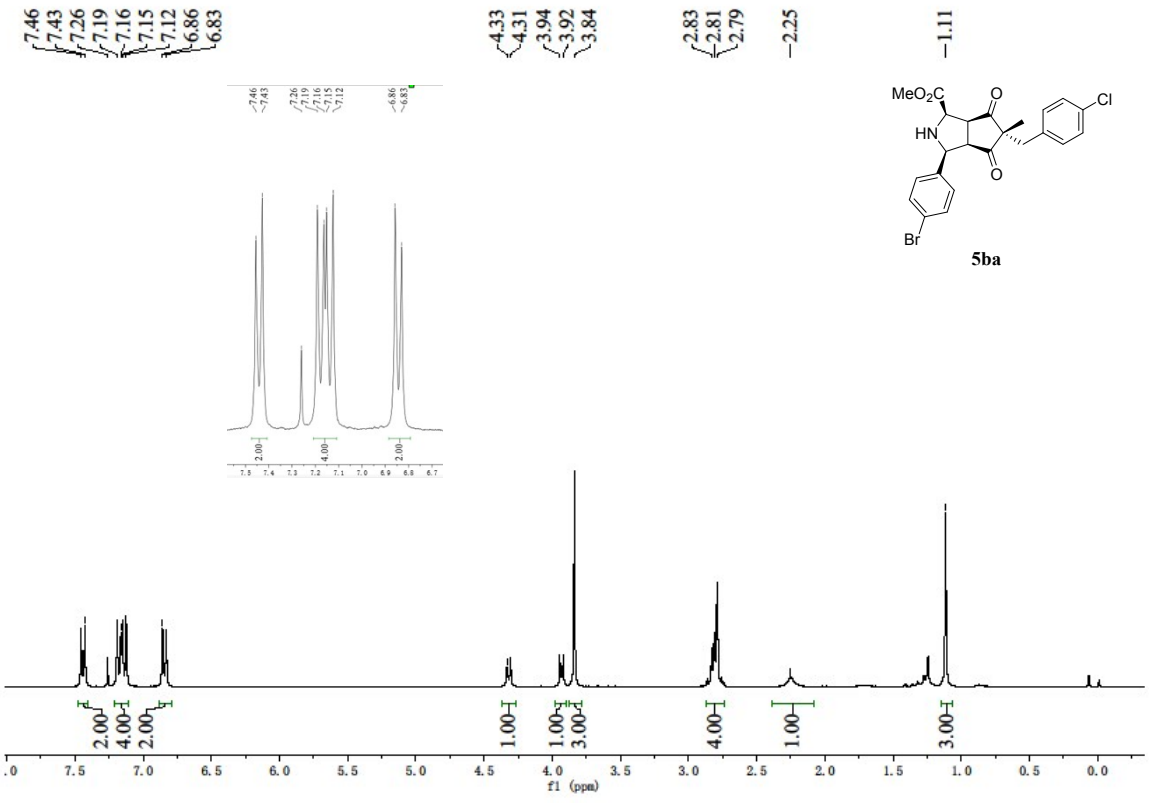
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	12.478	20416	4.516	667	9.189
2	15.877	431710	95.484	6595	90.811
Total		452126	100.000	7263	100.000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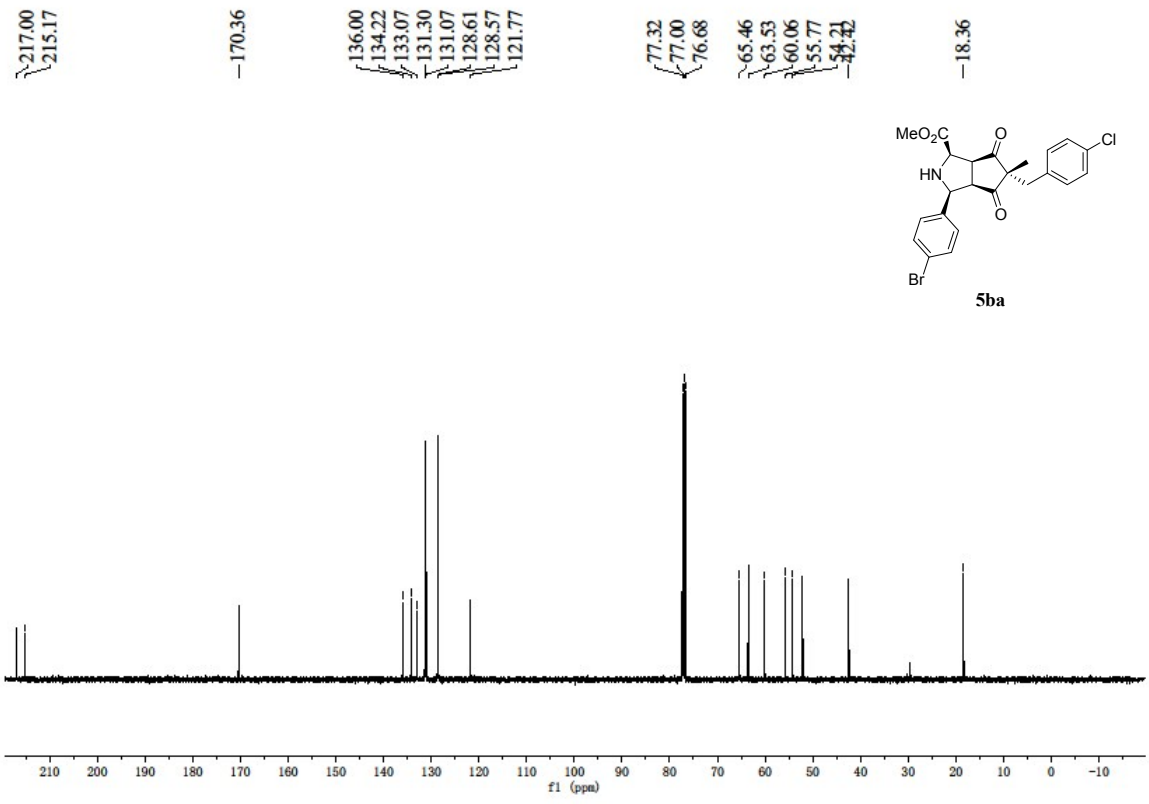
7.43
7.26
7.19
7.16
7.15
7.12
6.86
6.83
4.33
4.31
3.94
3.92
3.84
2.83
2.81
2.79
2.25
1.11
MeO2C
HN
O
O
Cl
Br
2.00
4.00
2.00
1.00
1.00
3.00
4.00
1.00
3.00
f1 (ppm)

5ba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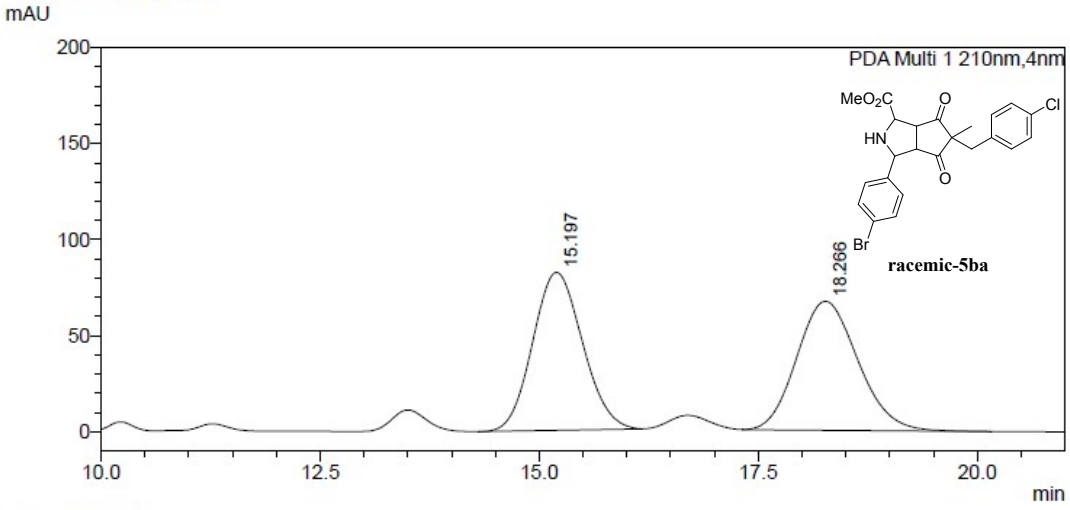
215.17
170.36
136.00
134.22
133.07
131.30
131.07
128.61
128.57
121.77
77.32
77.00
76.68
65.46
63.53
60.06
55.77
18.36
MeO2C
HN
O
O
Cl
Br
f1 (ppm)

5ba

<Chromatogram>

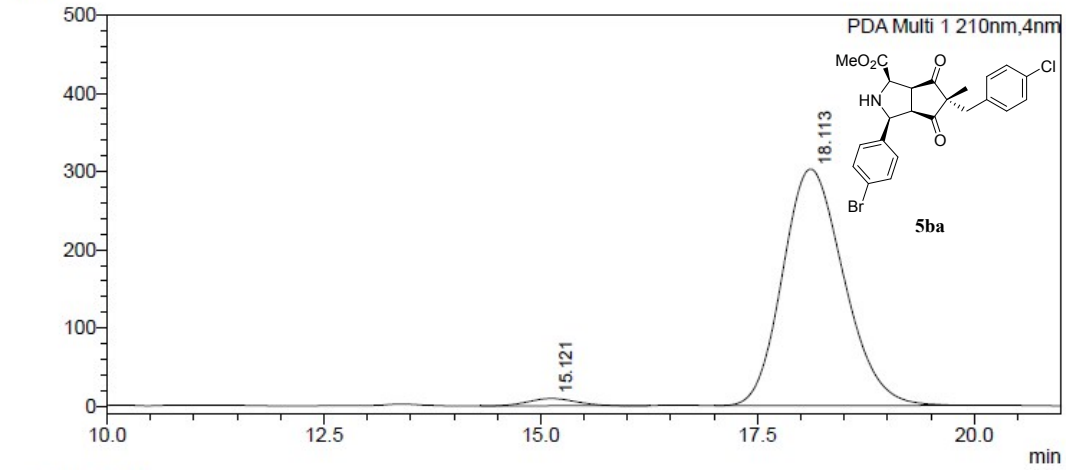


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.197	3255268	49.939	82246	55.043
2	18.266	3263172	50.061	67175	44.957
Total		6518440	100.000	149420	100.000

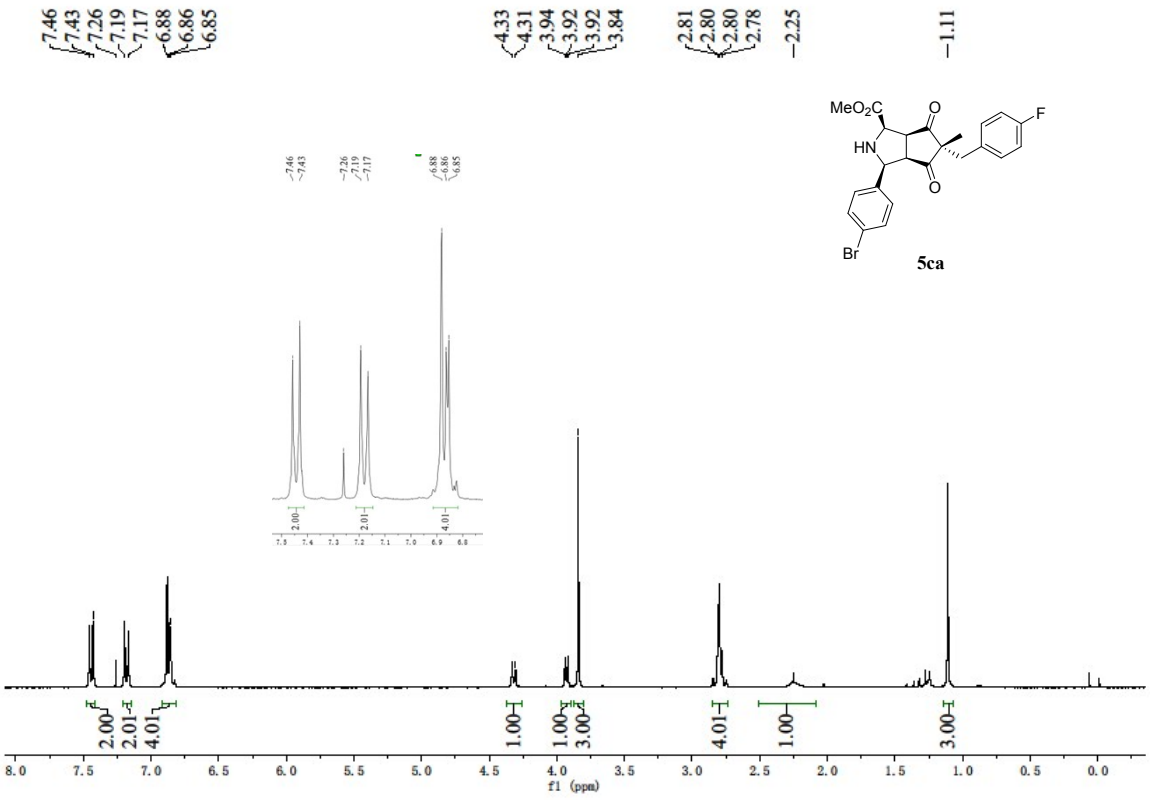
<Chromatogram>



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.121	358253	2.347	9367	3.003
2	18.113	14904197	97.653	302538	96.997
Total		15262450	100.000	311905	100.000


7.46
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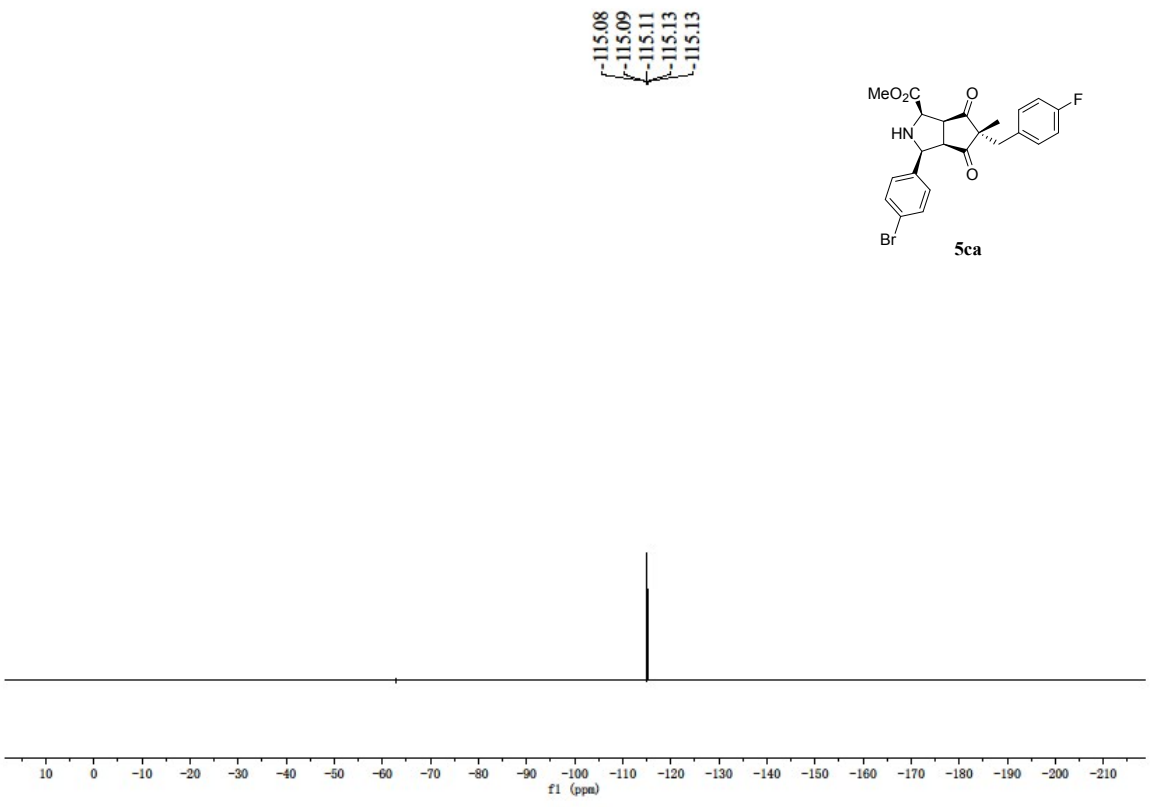
7.19
7.17
6.88
6.86
6.85
4.33
4.31
3.94
3.92
3.92
3.84
2.81
2.80
2.80
2.78
2.25
1.11
MeO2C
HN
O
O
F
Br
5ca
2.00
2.01
4.01
1.00
1.00
3.00
4.01
1.00
3.00
f1 (ppm)


115.08
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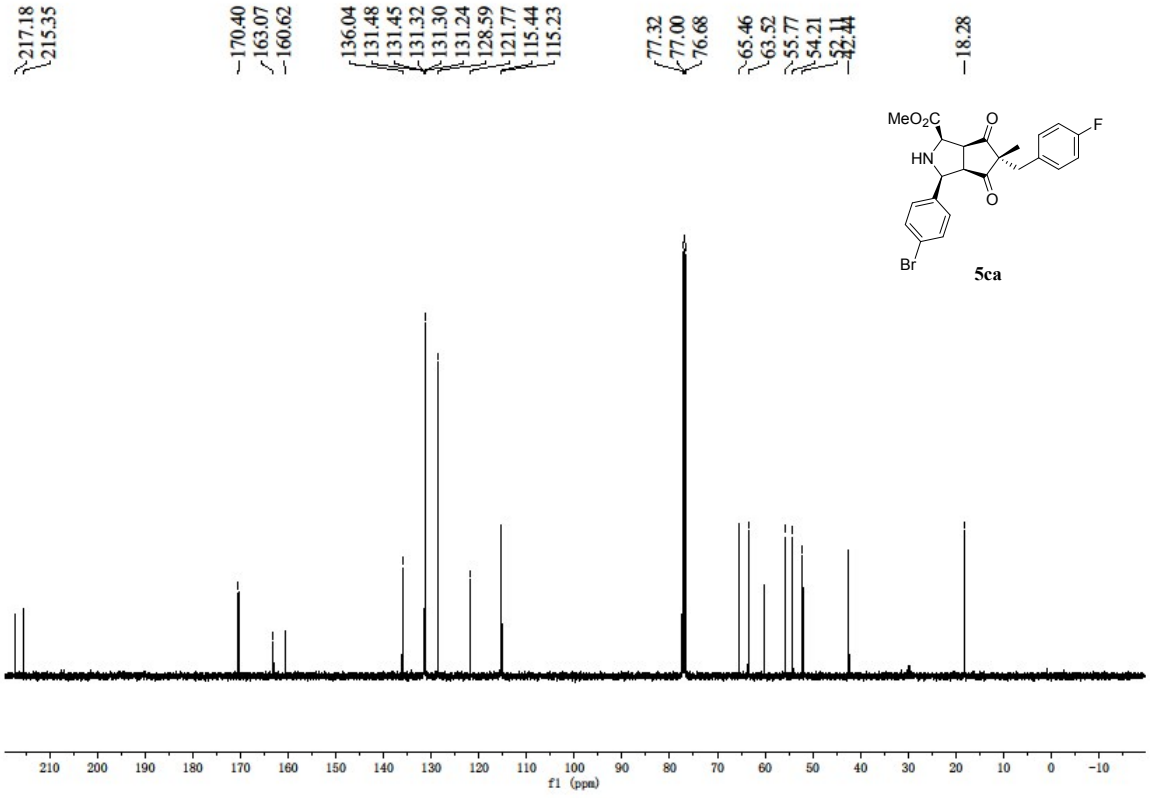
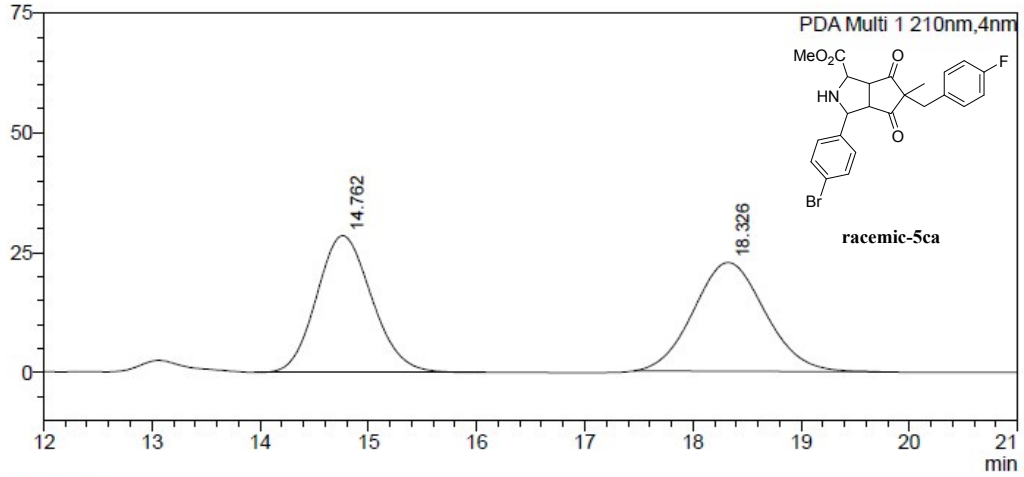
115.11
115.13
115.13
MeO2C
HN
O
O
F
Br
5ca
f1 (ppm)



<Chromatogram>

mAU

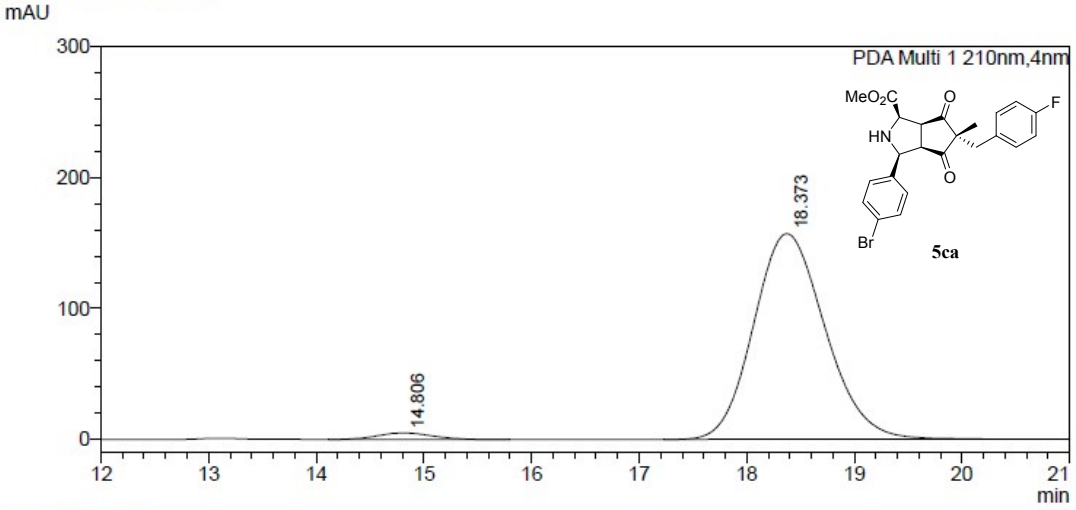


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	14.762	1014559	49.205	28539	55.701
2	18.326	1047358	50.795	22697	44.299
Total		2061917	100.000	51236	100.000

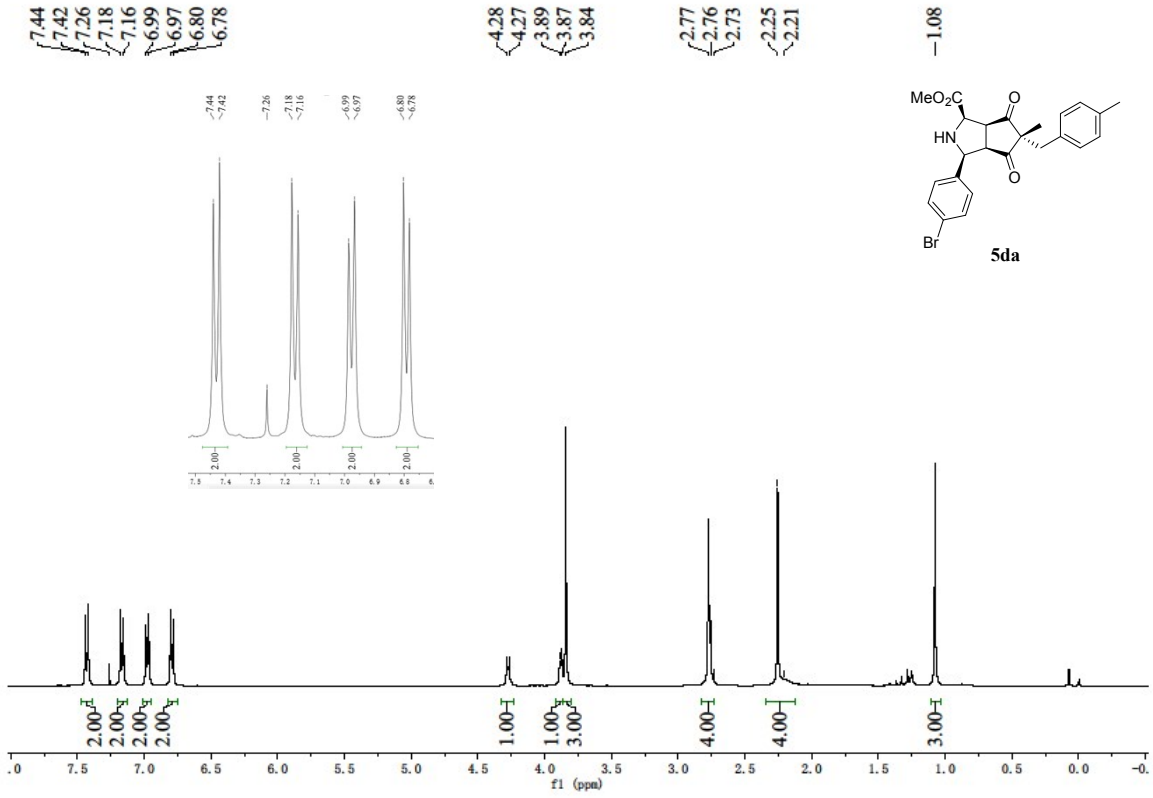
<Chromatogram>

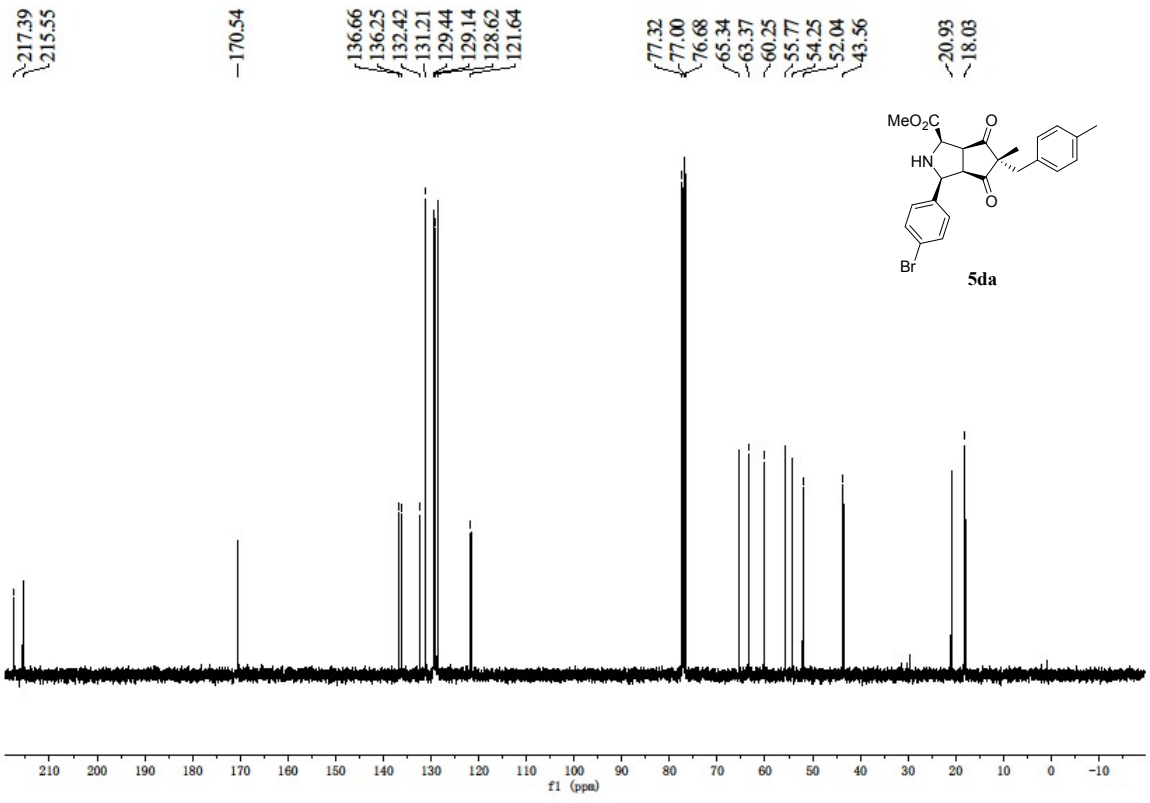


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	14.806	176898	2.375	4997	3.083
2	18.373	7272236	97.625	157101	96.917
Total		7449134	100.000	162098	100.000





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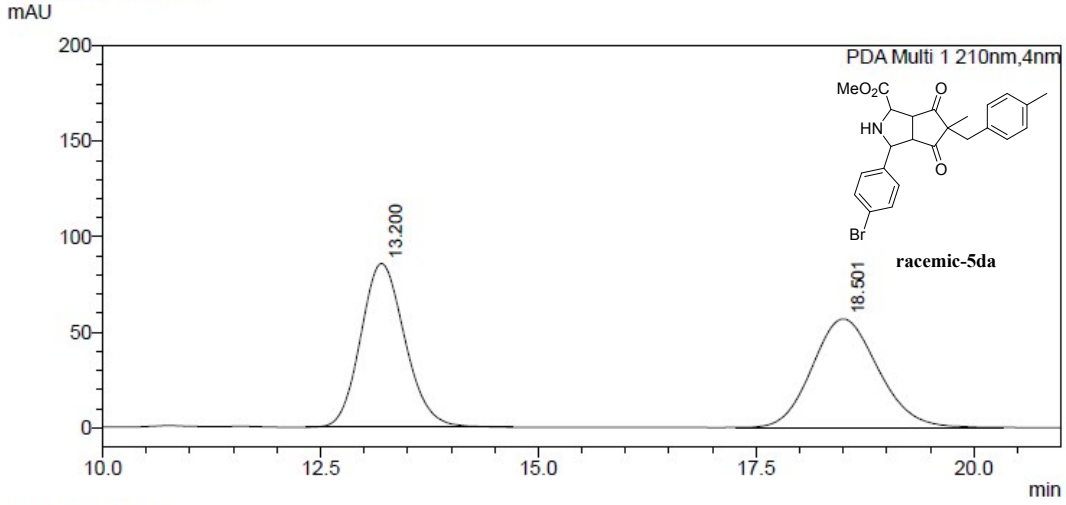

<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	13.200	3029915	50.267	85662	60.110
2	18.501	2997676	49.733	56846	39.890
Total		6027592	100.000	142508	100.000

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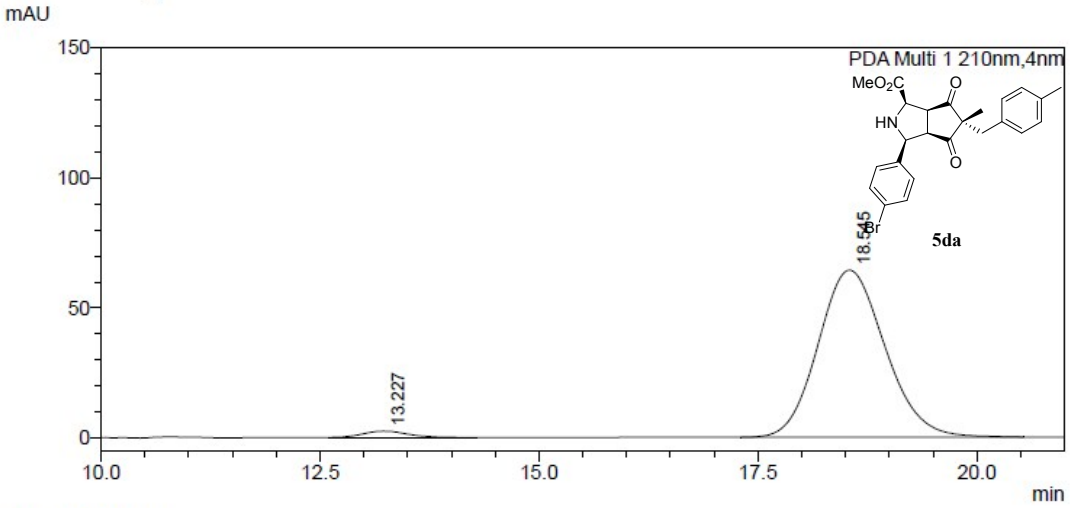
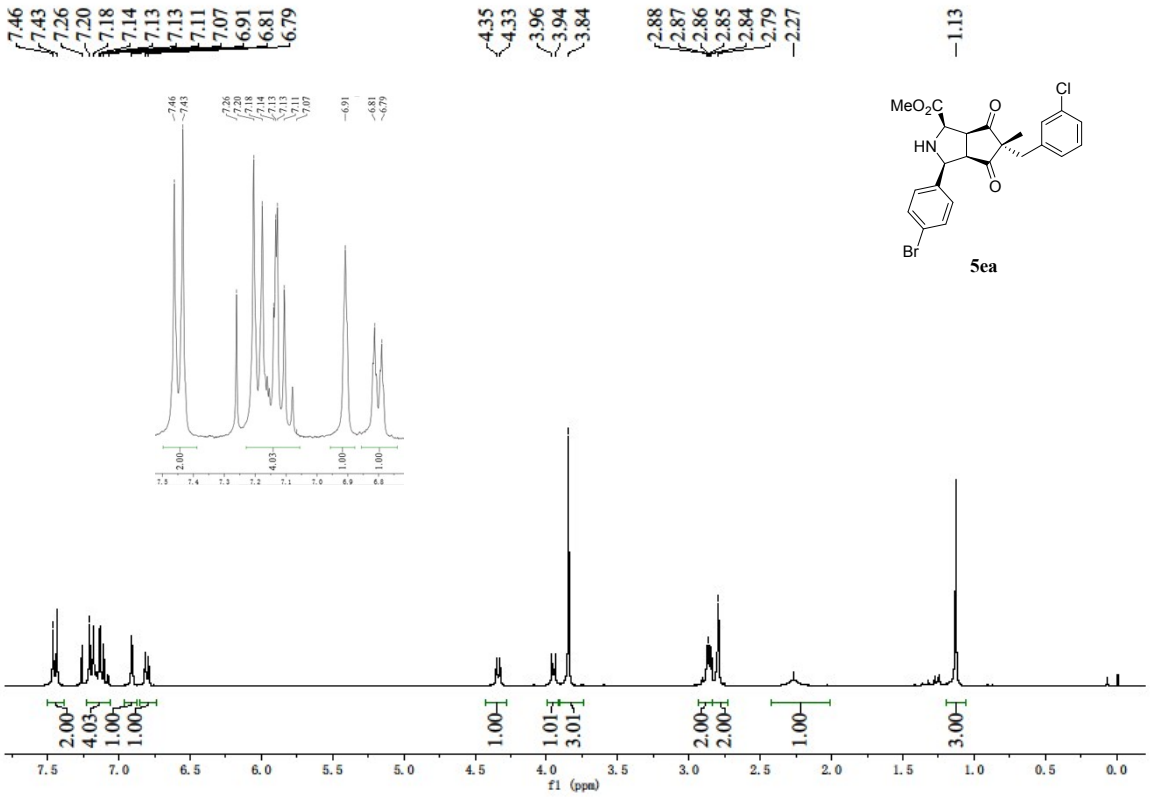
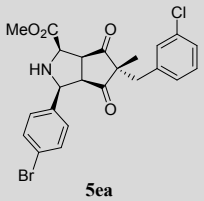


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	13.227	89570	2.556	2497	3.744
2	18.545	3415076	97.444	64193	96.256
Total		3504646	100.000	66689	100.000





5ea

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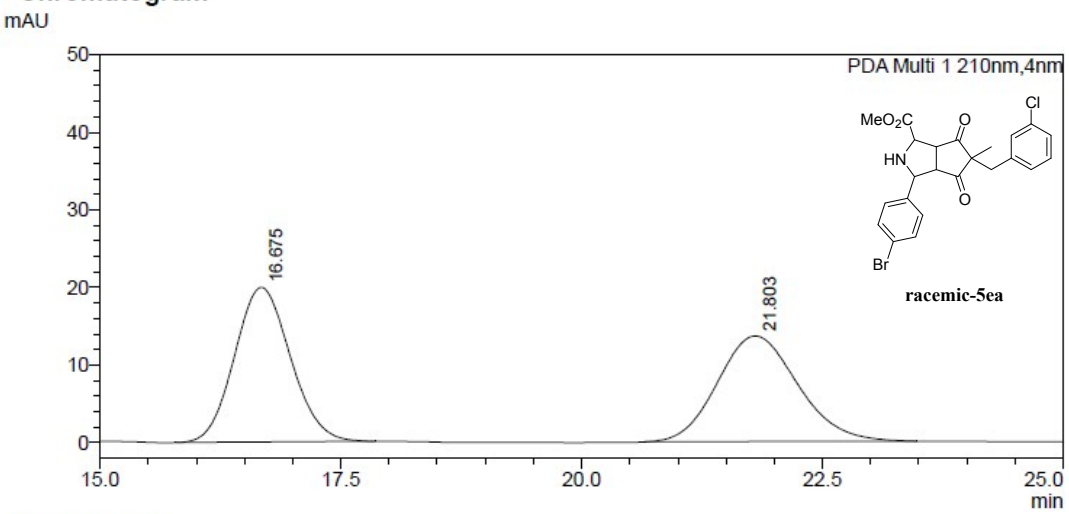
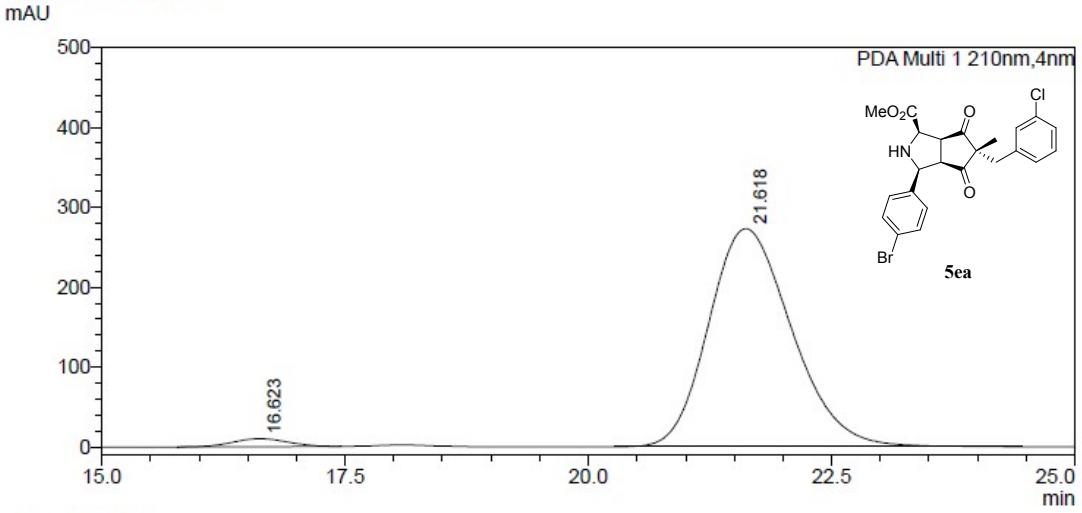


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	16.675	806378	50.526	19936	59.428
2	21.803	789591	49.474	13610	40.572
Total		1595969	100.000	33546	100.000

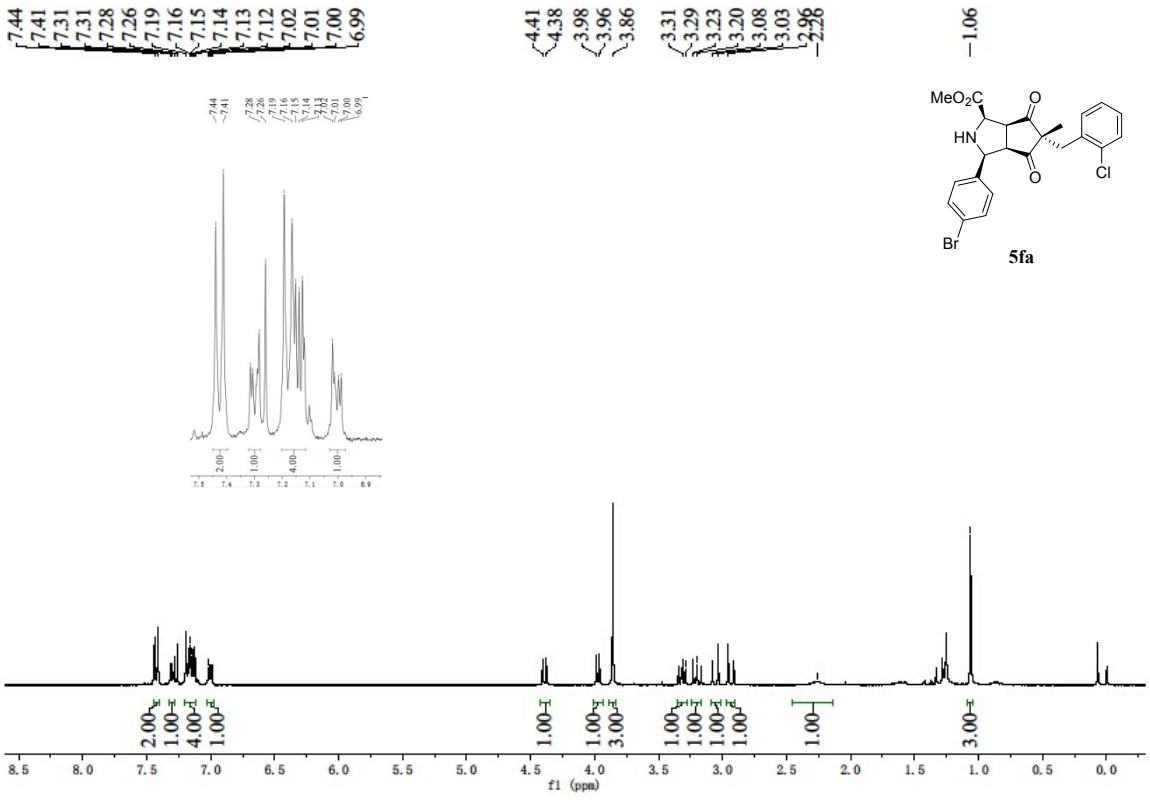
<Chromatogram>

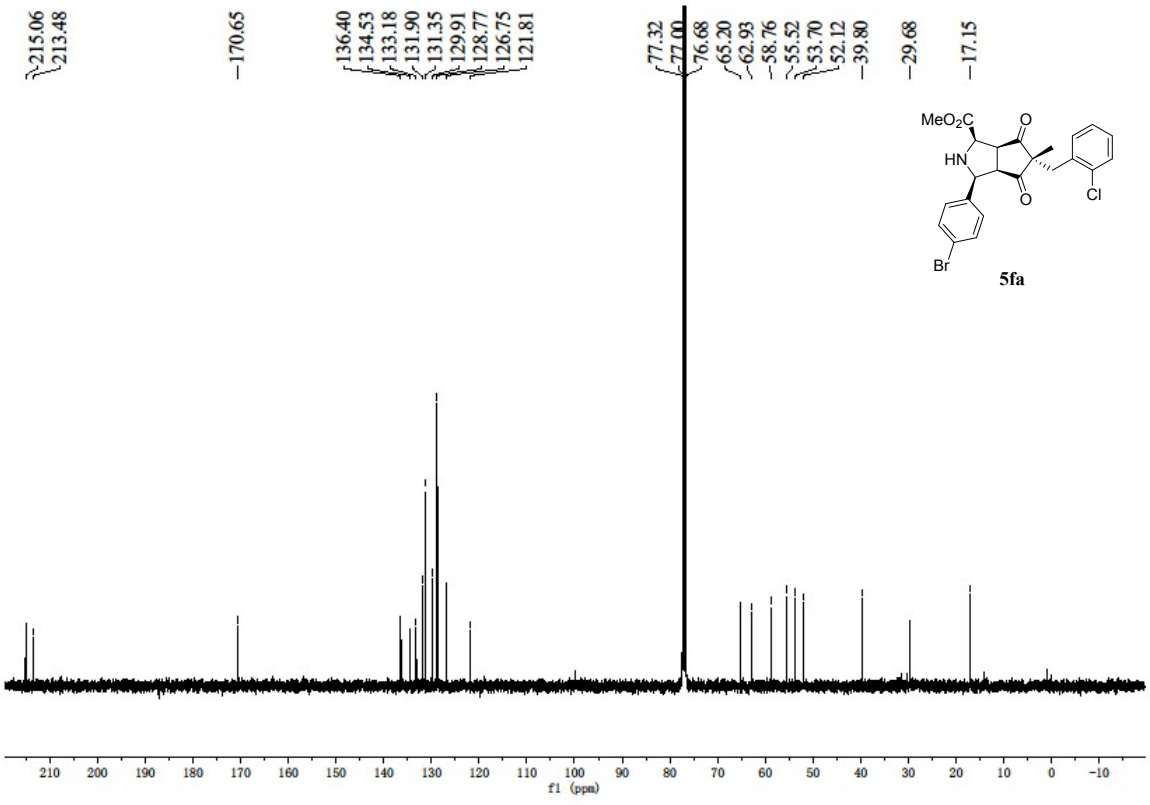


<Peak Table>

PDA Ch1 210nm

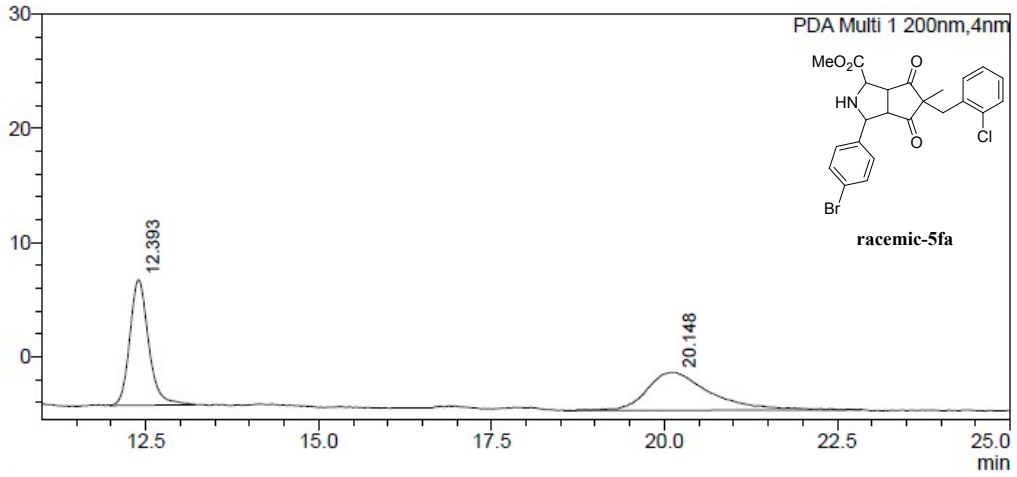
Peak#	Ret. Time	Area	Area%	Height	Height%
1	16.623	394302	2.370	10074	3.560
2	21.618	16240112	97.630	272903	96.440
Total		16634413	100.000	282976	100.000





<Chromatogram>

mAU

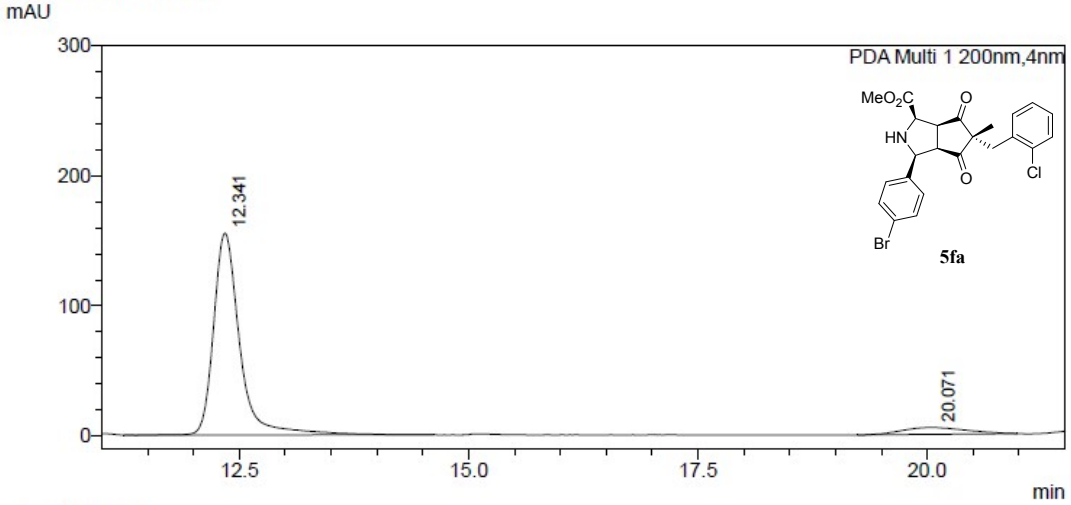


<Peak Table>

PDA Ch1 200nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	12.393	208288	49.519	10995	76.793
2	20.148	212334	50.481	3323	23.207
Total		420622	100.000	14317	100.000

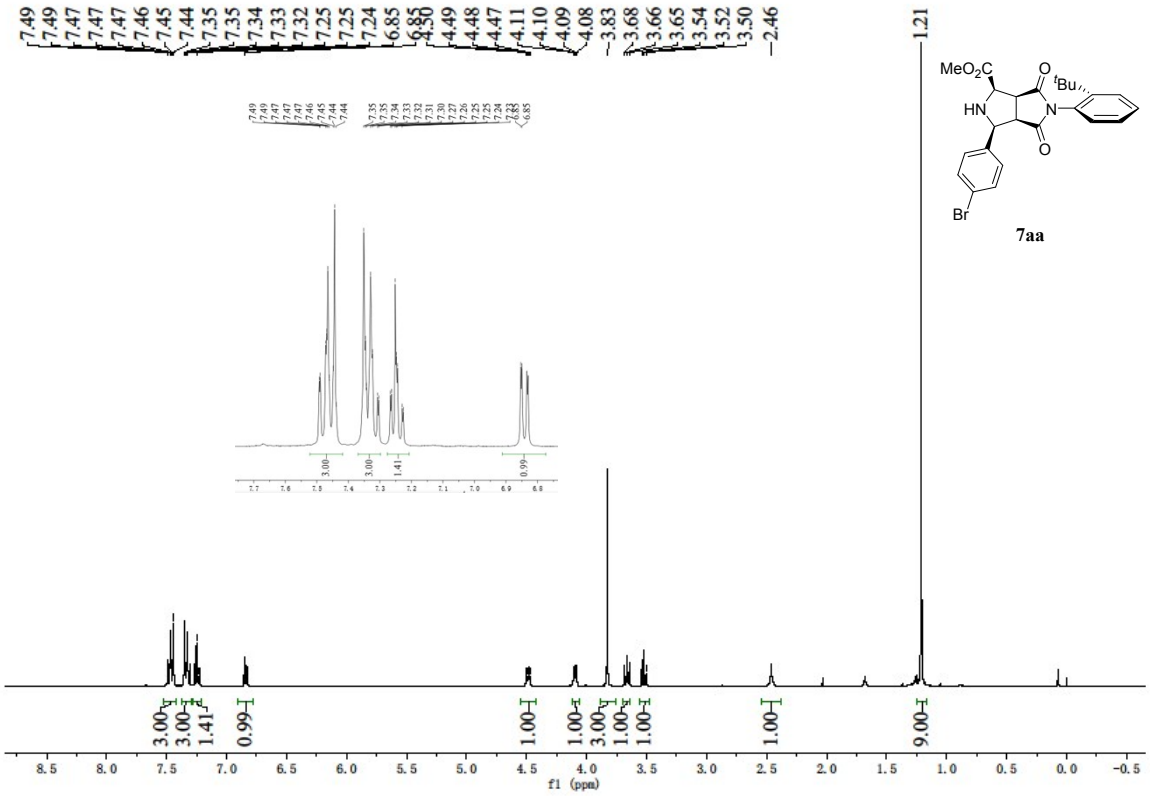
<Chromatogram>

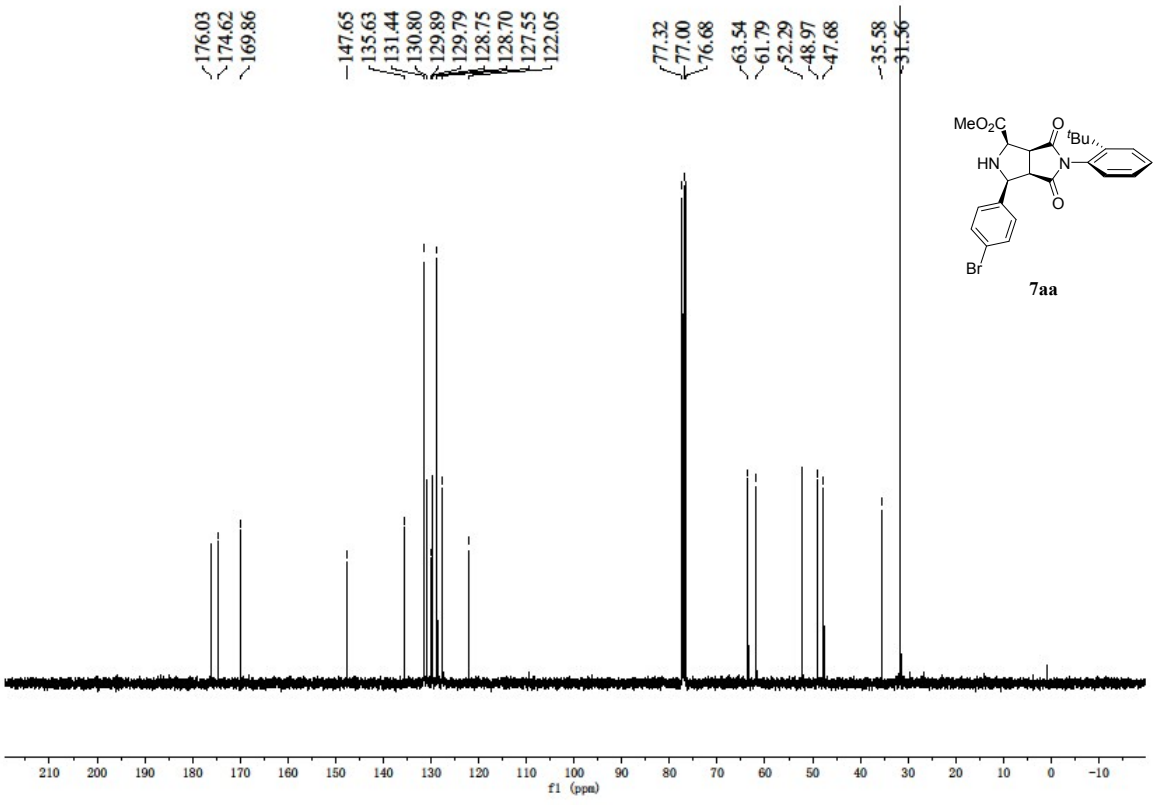


<Peak Table>

PDA Ch1 200nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	12.341	3086819	92.270	155287	96.723
2	20.071	258607	7.730	5261	3.277
Total		3345426	100.000	160549	100.000





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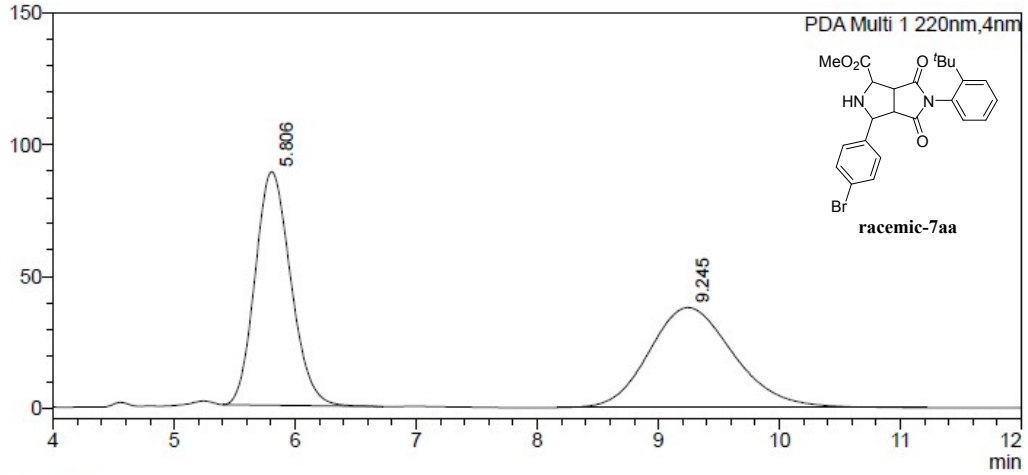
mAU

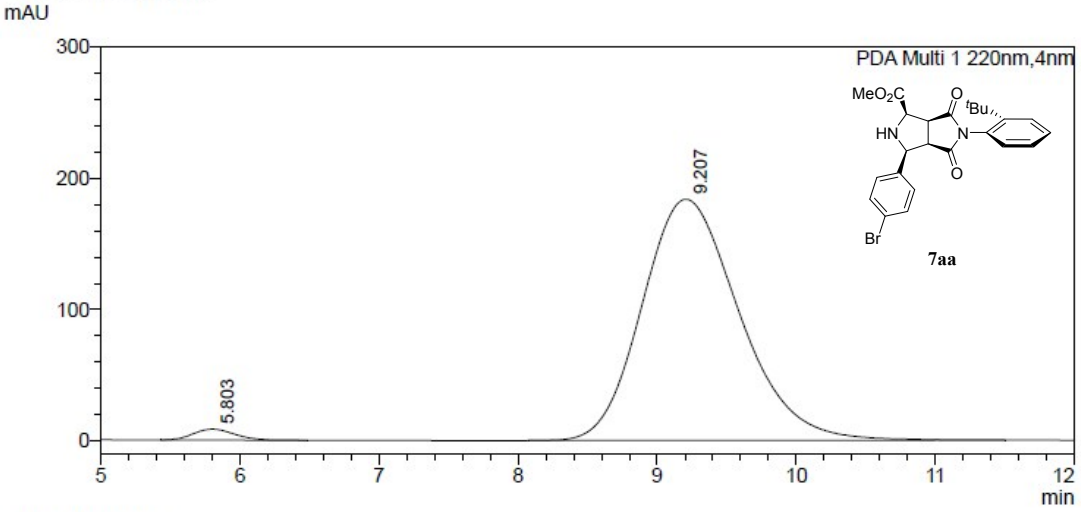


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	5.806	1817999	49.578	88680	70.034
2	9.245	1848976	50.422	37944	29.966
Total		3666975	100.000	126623	100.000

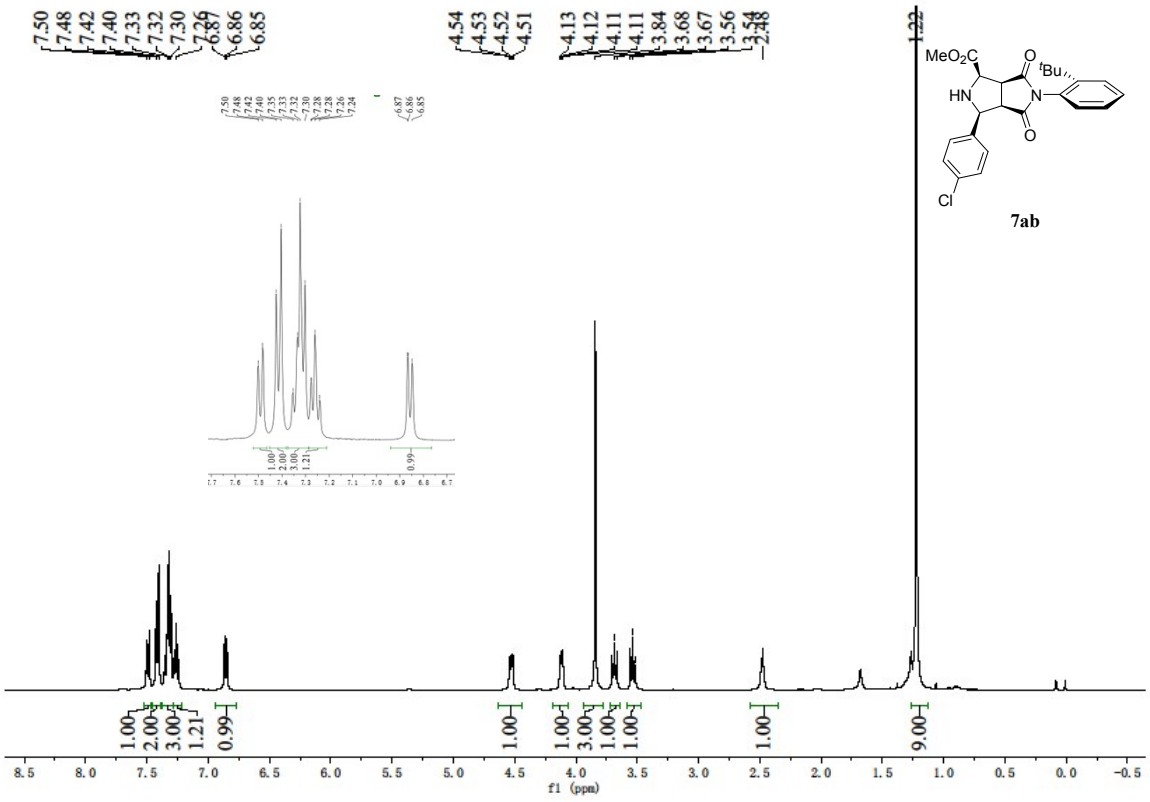
<Chromatogram>

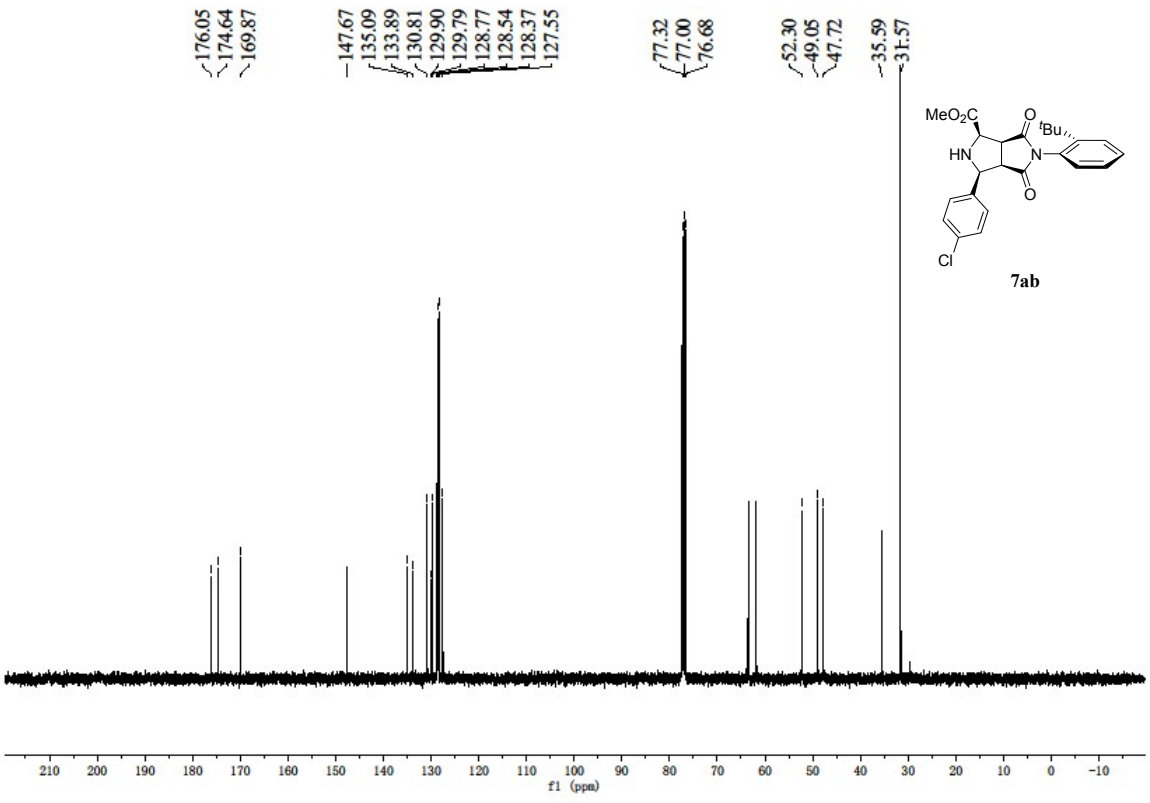


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	5.803	170429	1.874	8280	4.313
2	9.207	8923006	98.126	183709	95.687
Total		9093435	100.000	191988	100.000





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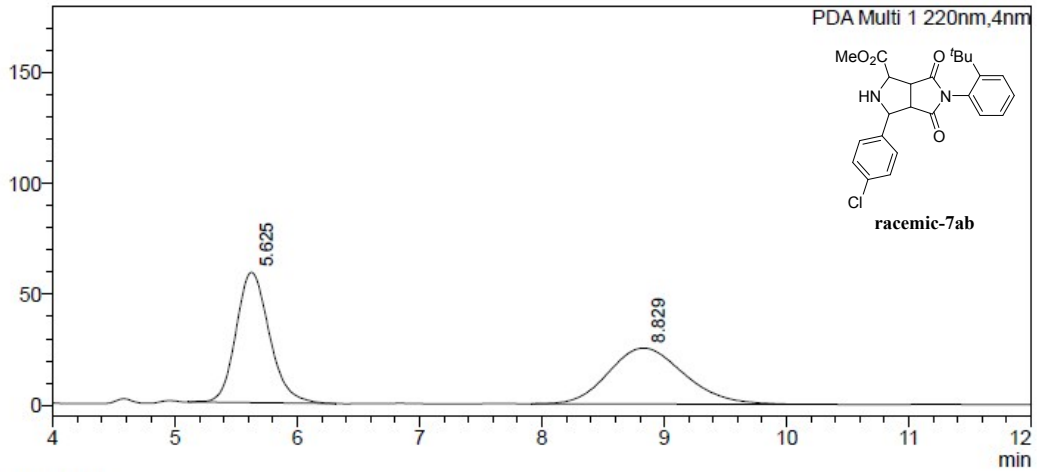
mAU

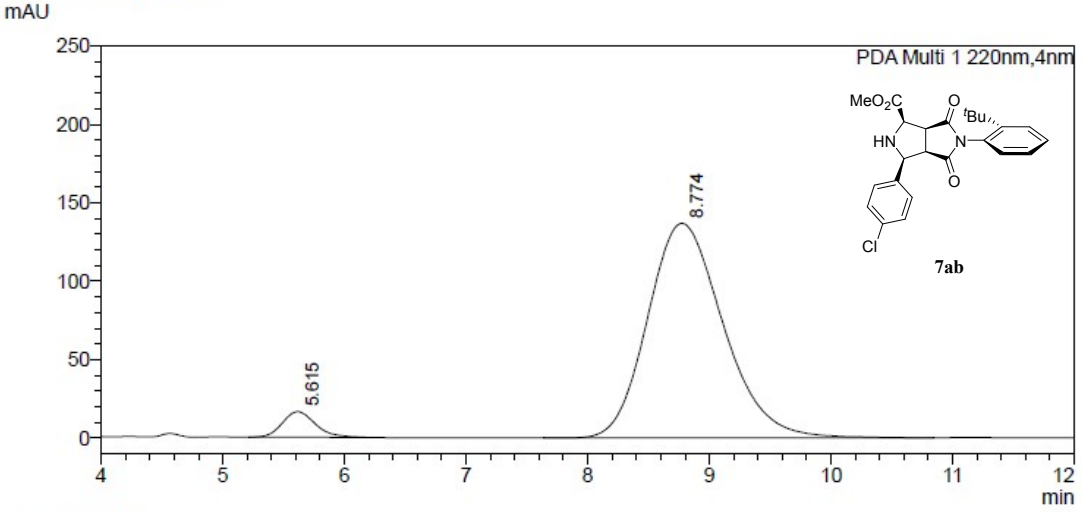


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	5.625	1119910	50.675	58892	69.974
2	8.829	1090056	49.325	25270	30.026
Total		2209967	100.000	84162	100.000

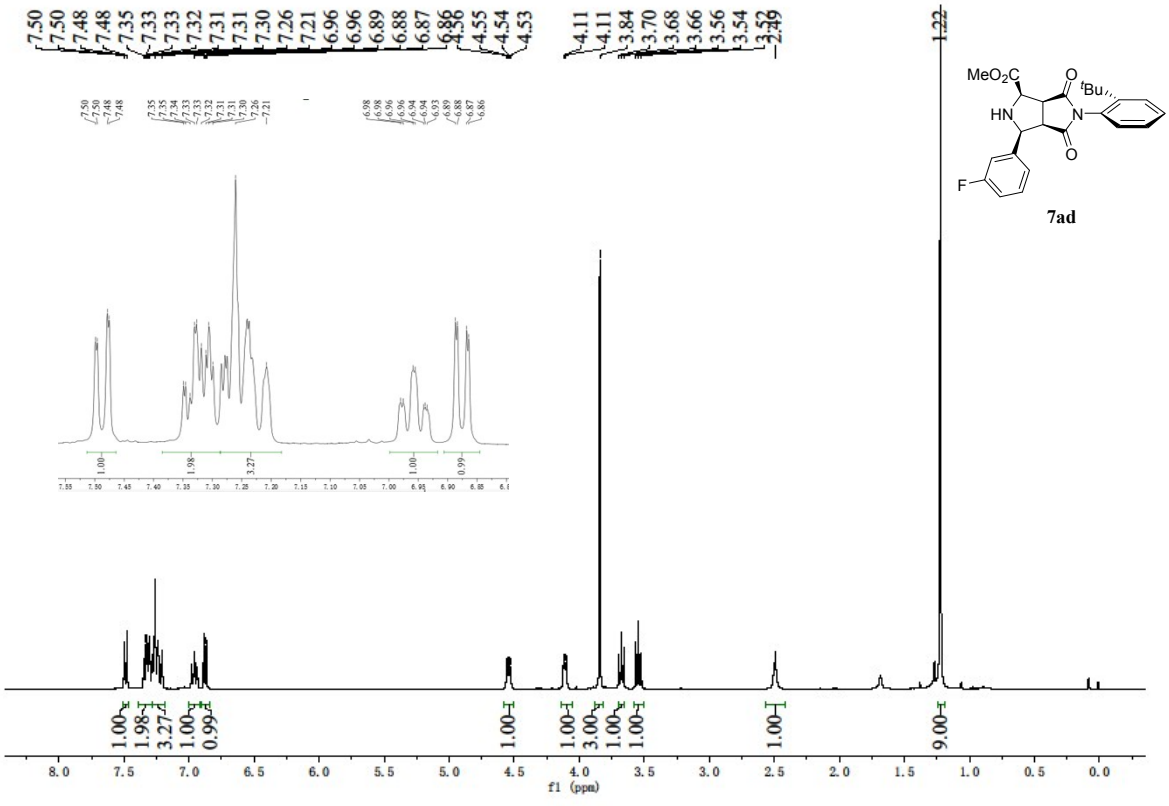
<Chromatogram>

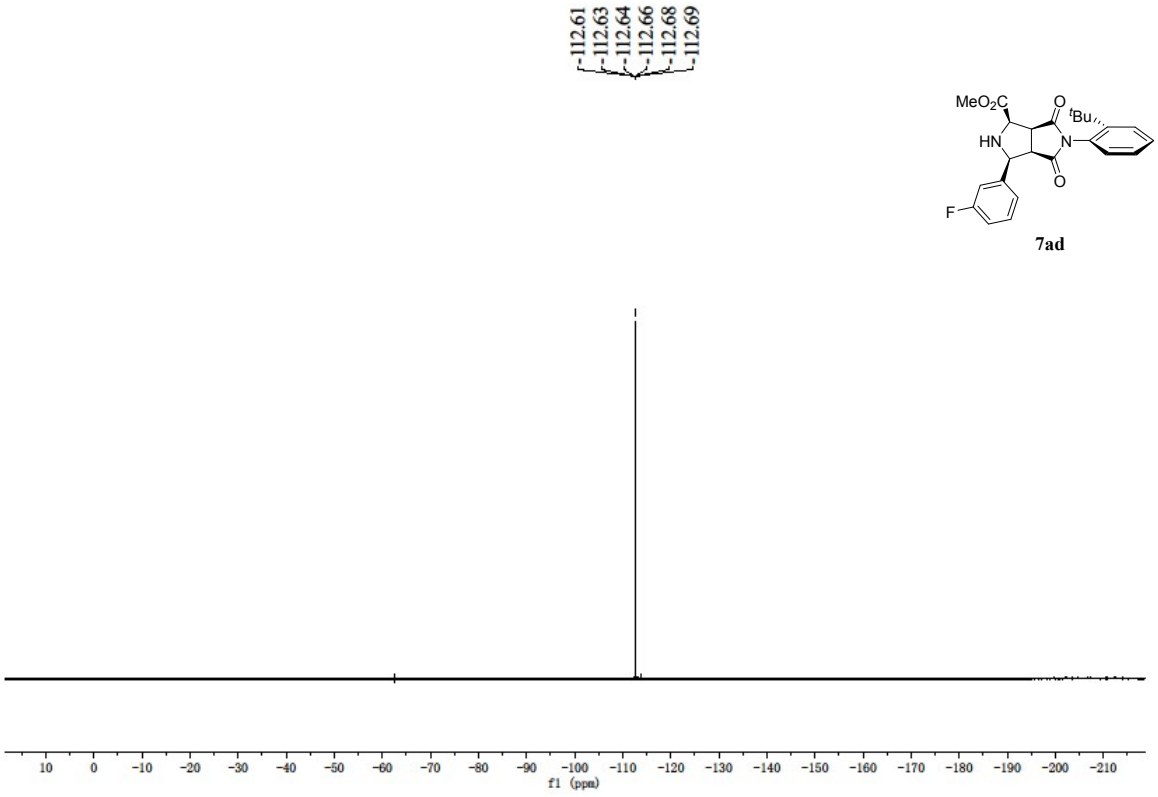


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	5.615	310571	4.997	16330	10.663
2	8.774	5904293	95.003	136815	89.337
Total		6214863	100.000	153145	100.000

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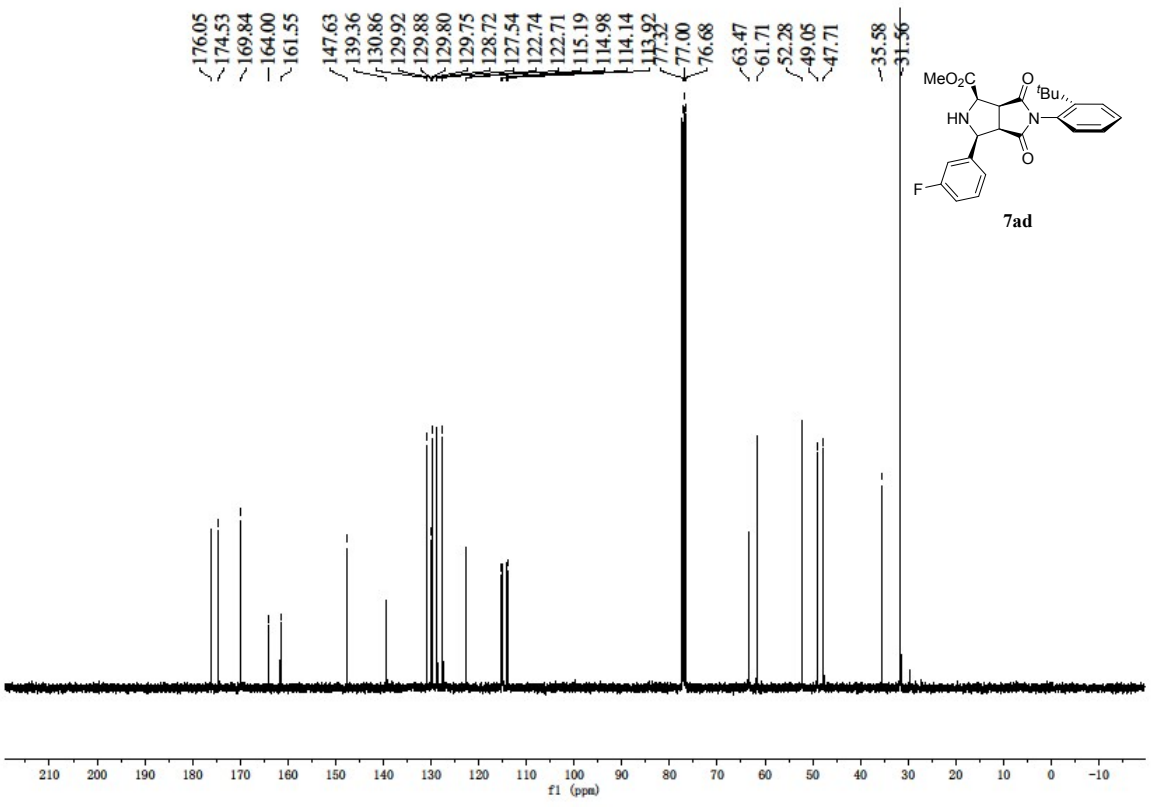
-112.63
-112.64
-112.66
-112.68
-112.69
MeO2C
O
tBu
HN
N
O
F
7ad
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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129.80
129.75
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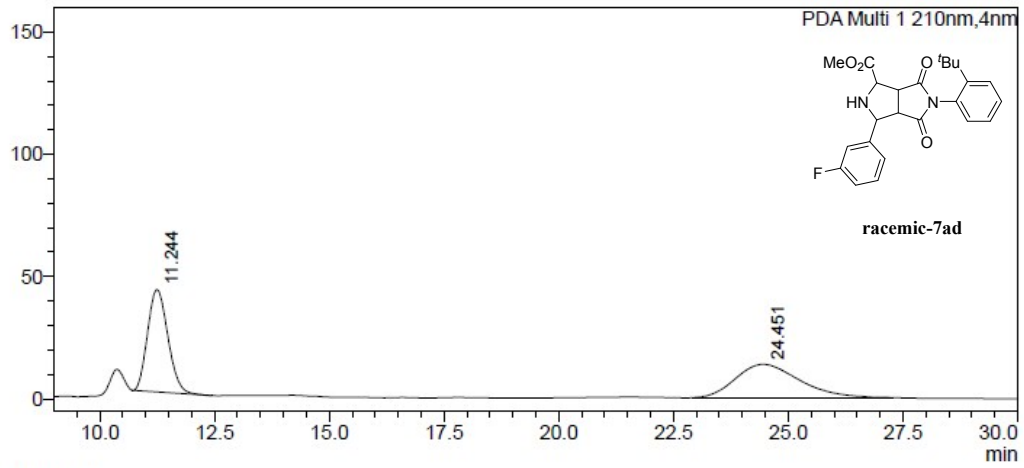
127.54
122.74
122.71
115.19
114.98
114.14
113.92
77.32
77.00
76.68
63.47
61.71
52.28
49.05
47.71
35.58
31.56
MeO2C
O
tBu
HN
N
O
F
7ad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

<Chromatogram>

mAU



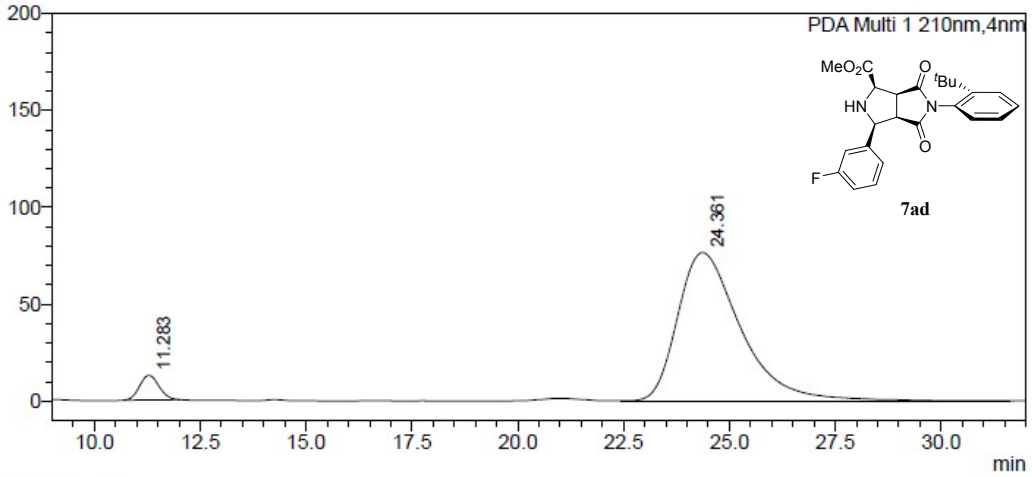
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	11.244	1288029	49.249	41818	75.399
2	24.451	1327299	50.751	13645	24.601
Total		2615329	100.000	55463	100.000

<Chromatogram>

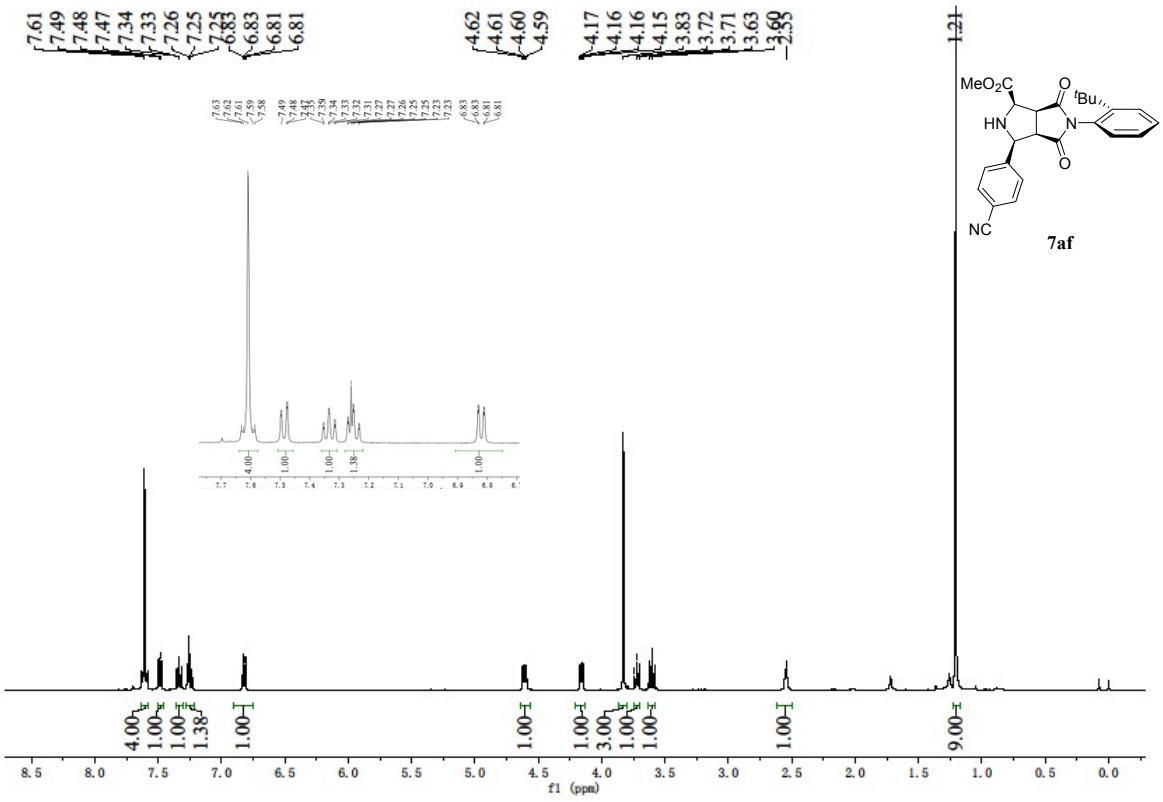
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	11.283	402740	4.826	12711	14.249
2	24.361	7941743	95.174	76496	85.751
Total		8344483	100.000	89207	100.000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6.81
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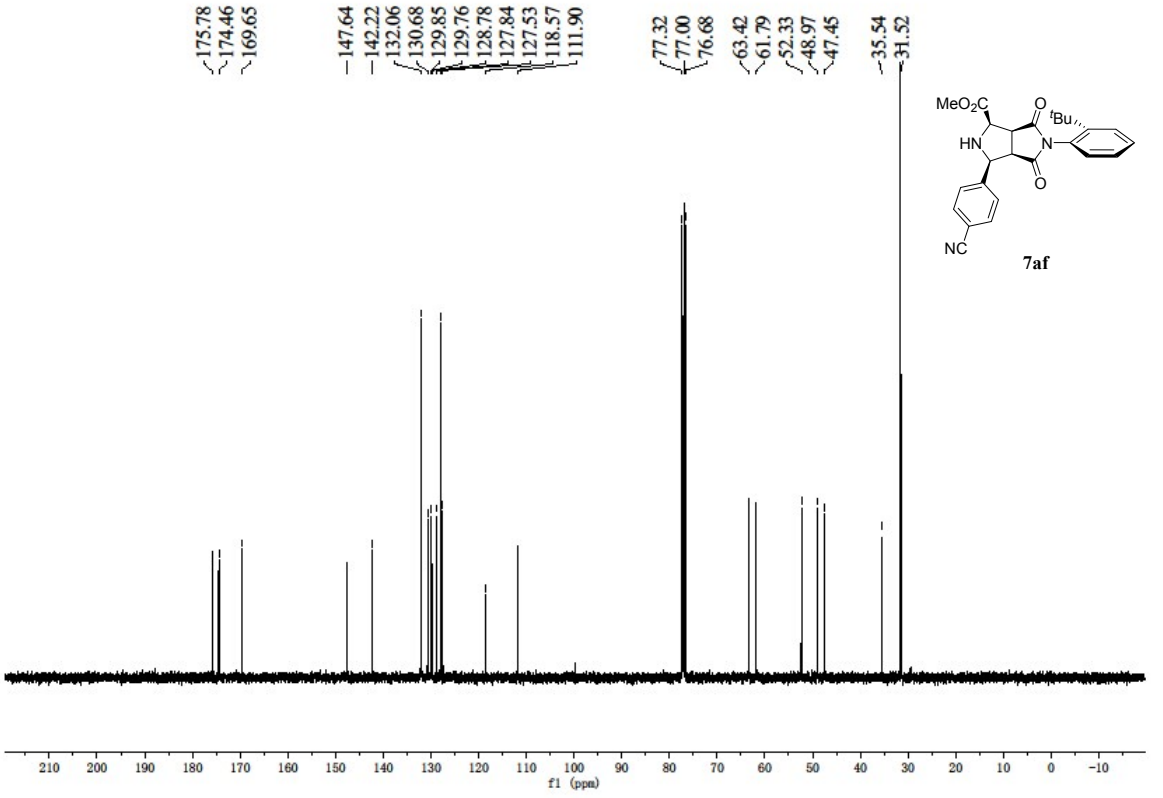
4.61
4.60
4.59
4.17
4.16
4.15
3.83
3.72
3.71
3.63
3.60
2.55
1.21
MeO2C
HN
O
tBu
N
NC
7af
4.00
1.00
1.00
1.38
1.00
1.00
3.00
1.00
1.00
1.00
9.00
f1 (ppm)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127.53
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111.90
77.32
77.00
76.68
63.42
61.79
52.33
48.97
47.45
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31.52
MeO2C
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N
NC
7af
f1 (ppm)

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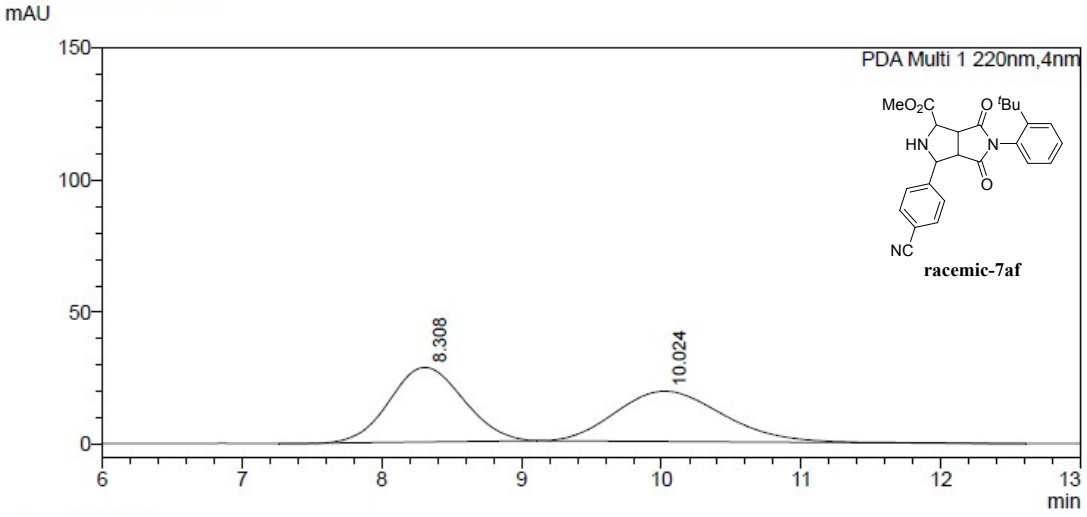
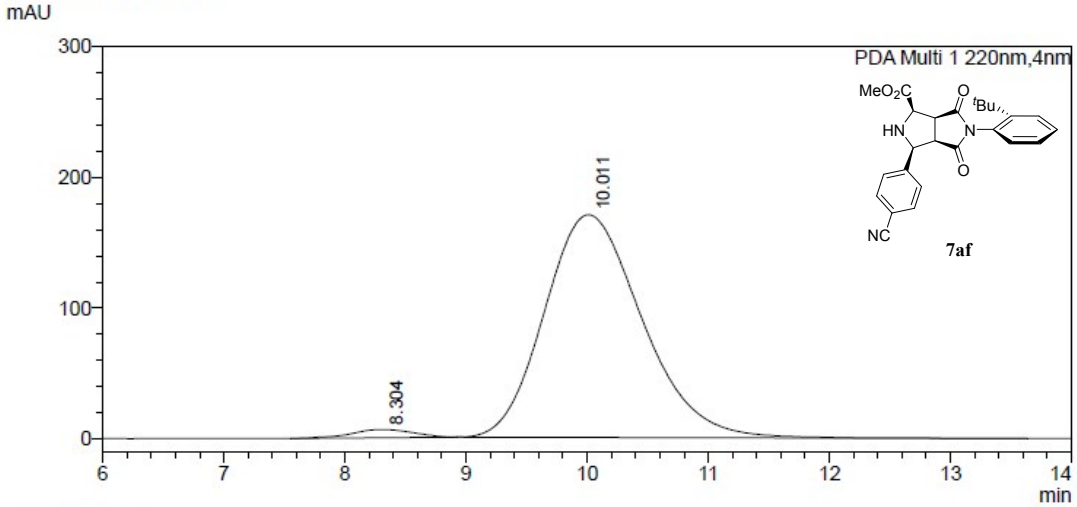


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	8.308	1039231	50.605	28199	59.742
2	10.024	1014381	49.395	19002	40.258
Total		2053611	100.000	47201	100.000

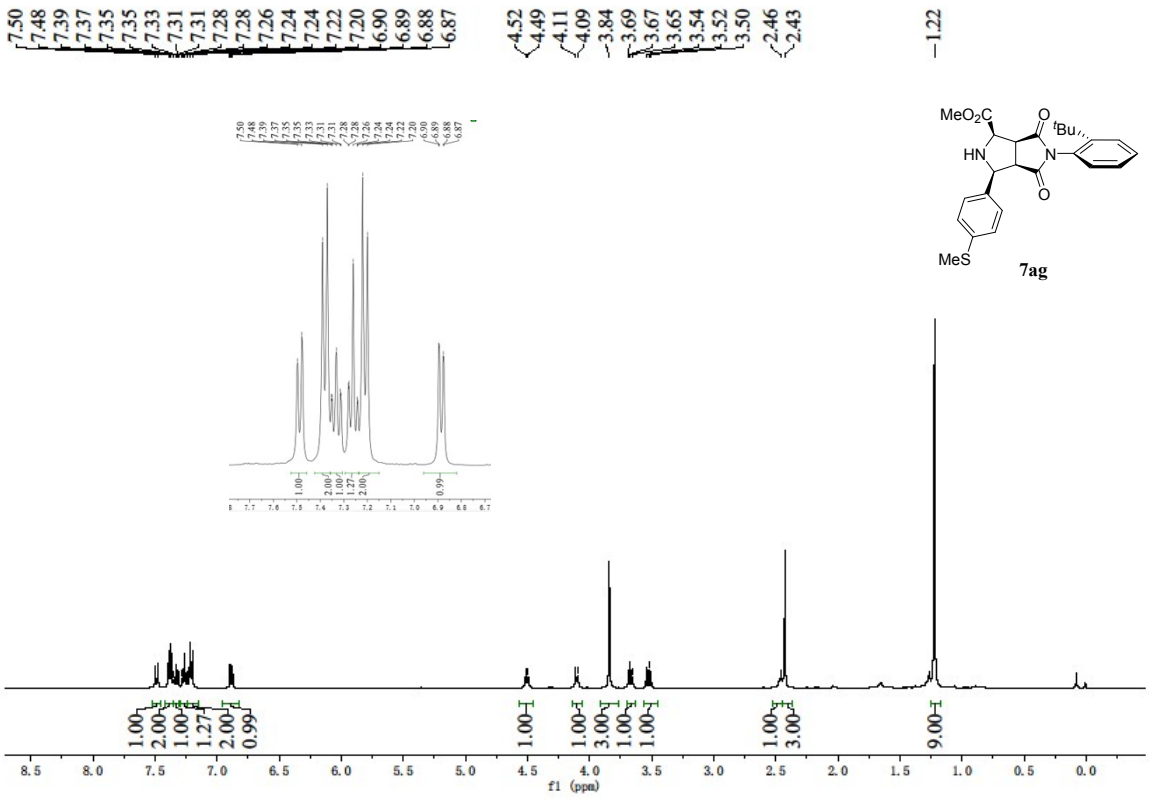
<Chromatogram>



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	8.304	225811	2.310	6312	3.574
2	10.011	9550258	97.690	170279	96.426
Total		9776070	100.000	176591	100.000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7.28
7.28
7.26
7.24
7.24
7.22
7.20
6.90
6.89
6.88
6.87
4.52
4.49
4.11
4.09
3.84
3.69
3.67
3.65
3.54
3.52
3.50
2.46
2.43
1.22
MeO2C
O
tBu
HN
N
O
MeS
7ag
1.00
2.00
1.00
1.27
2.00
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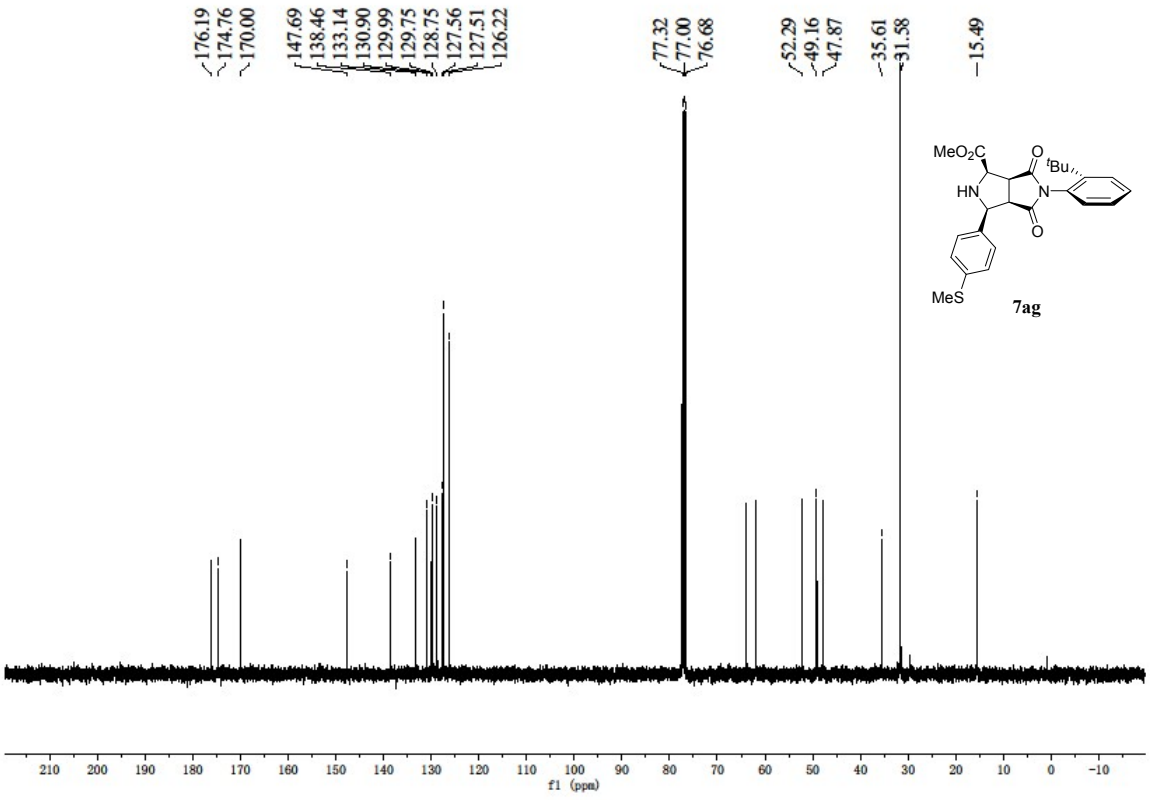
1.00
1.00
3.00
1.00
1.00
1.00
3.00
9.00
f1 (ppm)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128.75
127.56
127.51
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77.32
77.00
76.68
52.29
49.16
47.87
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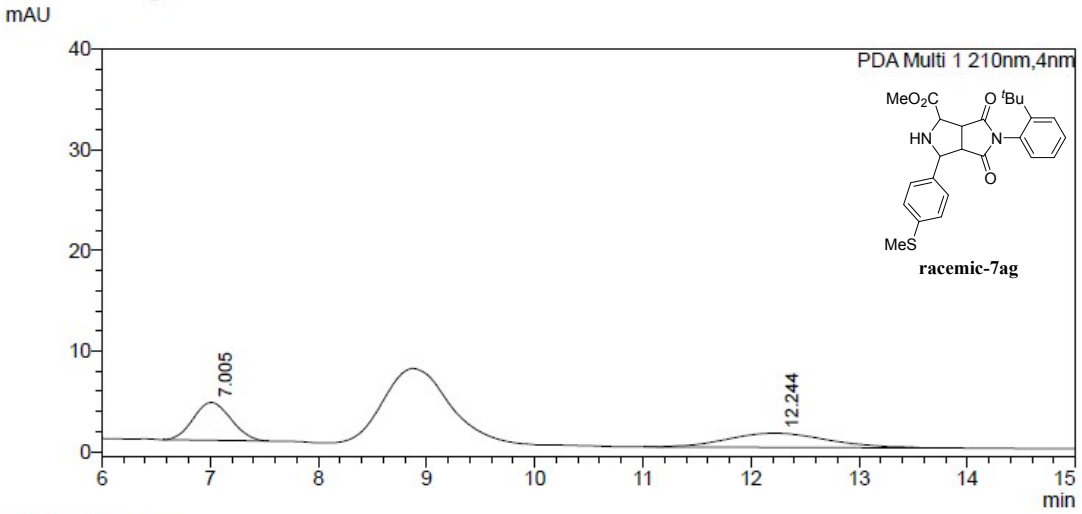
MeO2C
O
tBu
HN
N
O
MeS
7ag
f1 (ppm)

<Chromatogram>

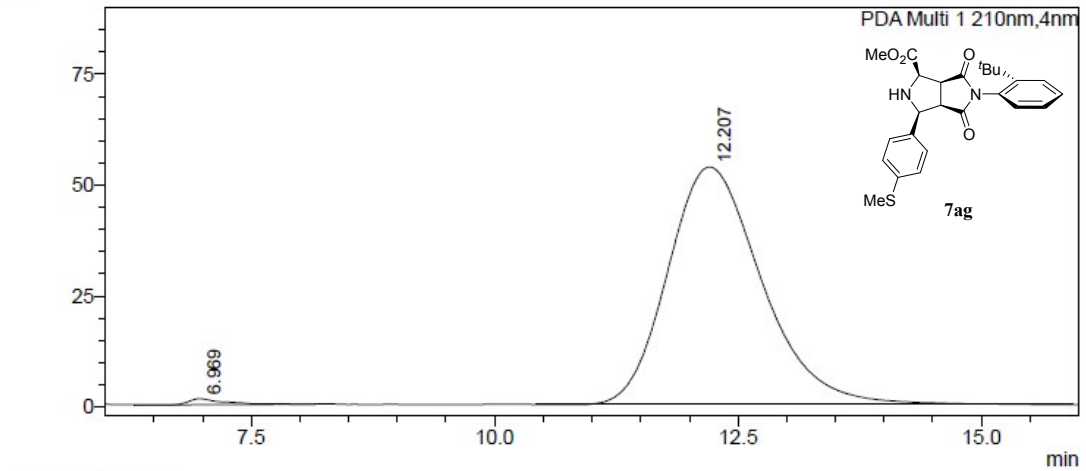


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	7.005	90813	50.043	3753	72.744
2	12.244	90656	49.957	1406	27.256
Total		181469	100.000	5159	100.000

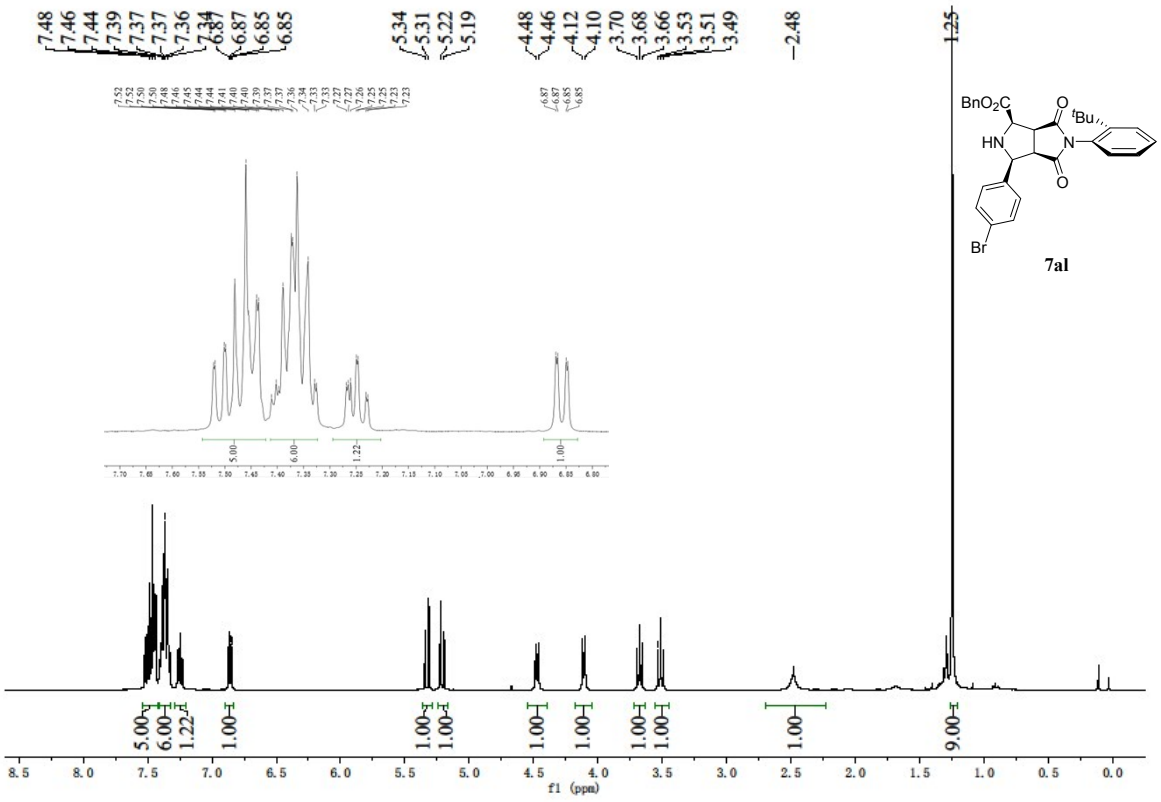
<Chromatogram>



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	6.969	31167	0.857	1329	2.421
2	12.207	3603659	99.143	53548	97.579
Total		3634826	100.000	54877	100.000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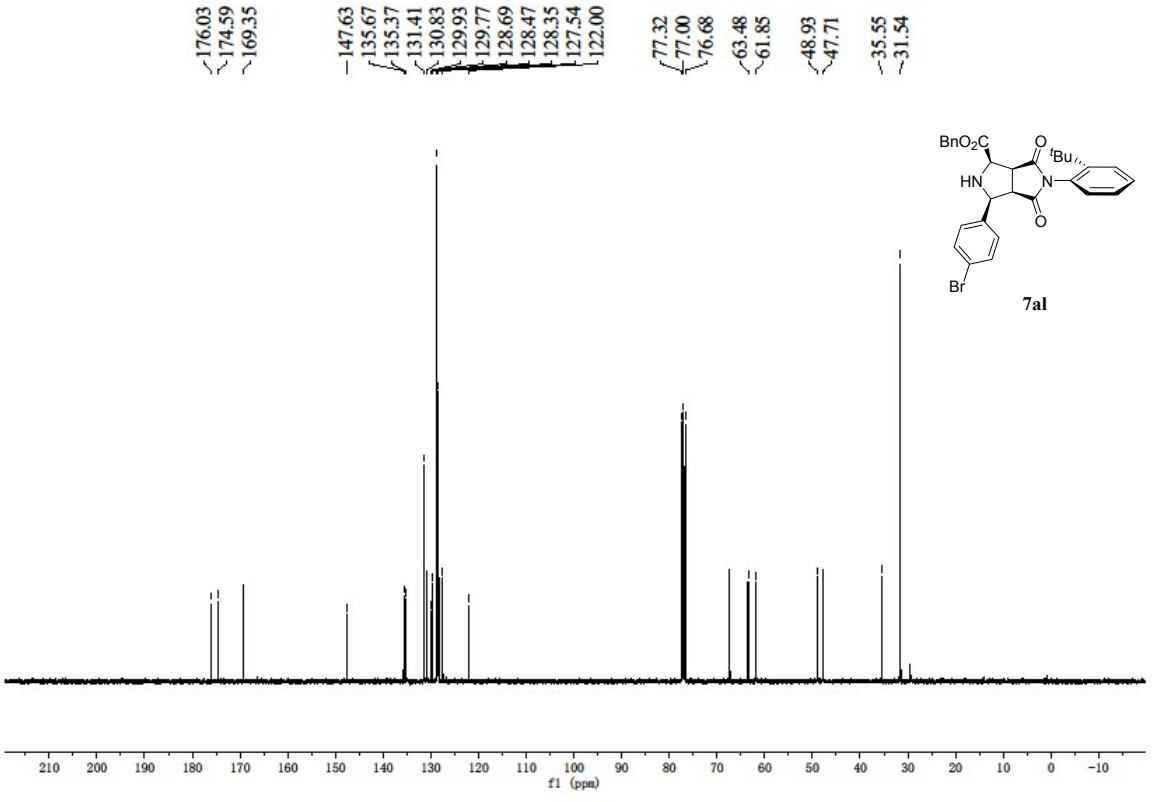
7.44
7.39
7.37
7.37
7.36
6.87
6.87
6.85
6.85
5.34
5.31
5.22
5.19
4.48
4.46
4.12
4.10
3.70
3.68
3.66
3.53
3.51
3.49
2.48
1.25
BnO2C
O
tBu
HN
N
O
O
Br
7al
5.00
6.00
1.22
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
9.00
f1 (ppm)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174.59
169.35
147.63
135.67
135.37
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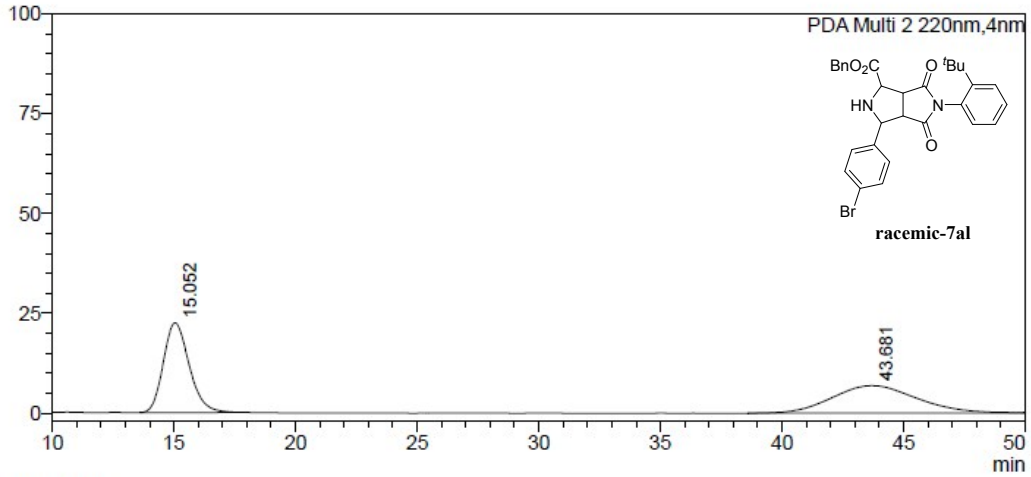
130.83
129.93
129.77
128.69
128.47
128.35
127.54
122.00
77.32
77.00
76.68
63.48
61.85
48.93
47.71
35.55
31.54
BnO2C
O
tBu
HN
N
O
O
Br
7al
f1 (ppm)

<Chromatogram>

mAU



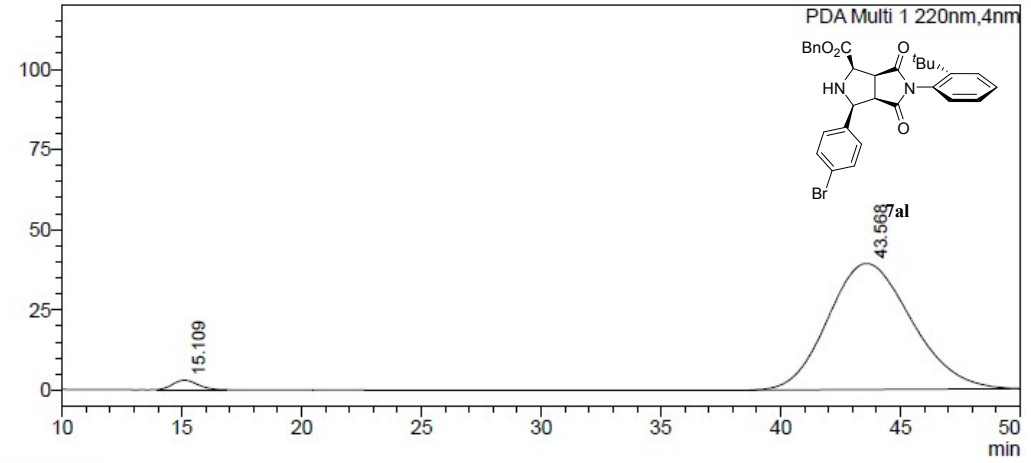
<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.052	1661034	50.188	22453	76.632
2	43.681	1648558	49.812	6847	23.368
Total		3309593	100.000	29299	100.000

<Chromatogram>

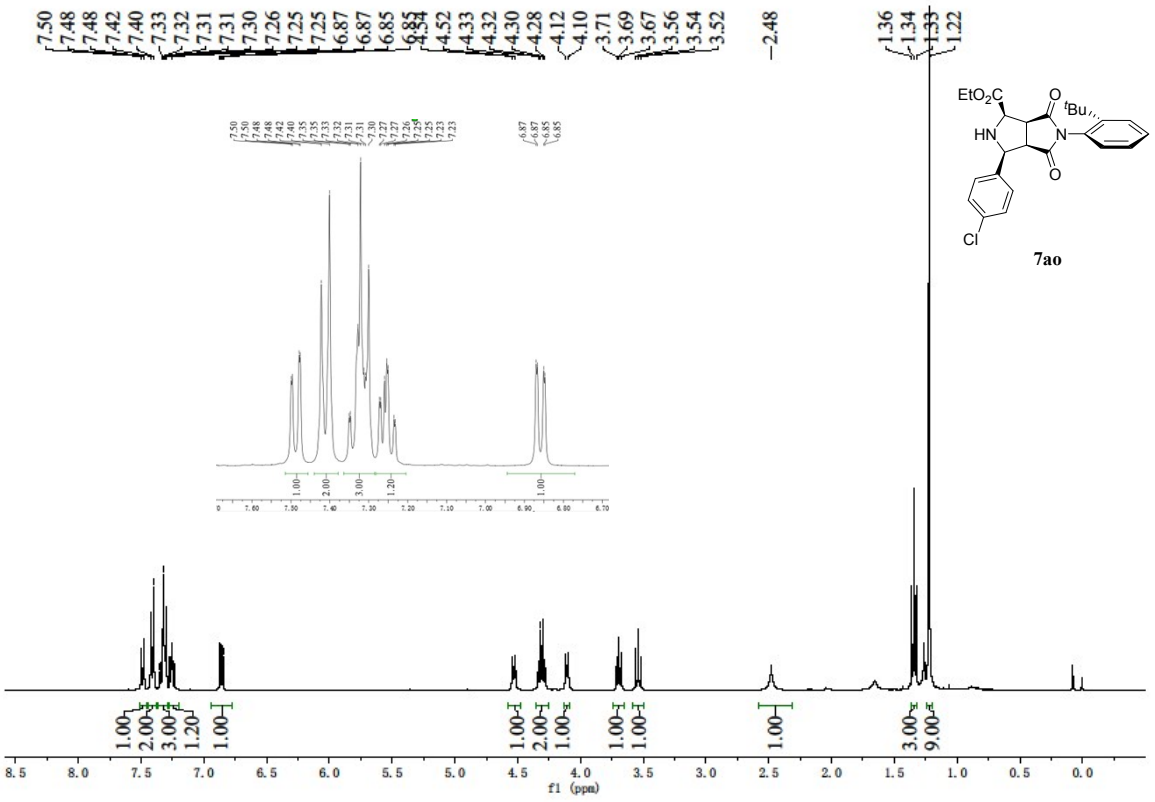
mAU



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	15.109	212186	2.171	2953	6.991
2	43.568	9563055	97.829	39286	93.009
Total		9775241	100.000	42239	100.000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7.48
7.48
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7.32
7.31
7.31
7.30
7.26
7.25
7.25
6.87
6.87
6.85
6.85
4.54
4.52
4.33
4.32
4.30
4.28
4.12
4.10
3.71
3.69
3.67
3.56
3.54
3.52
2.48
1.36
1.34
1.33
1.22
EtO2C
HN
O
tBu
N
O
O
Cl
7ao
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2.00
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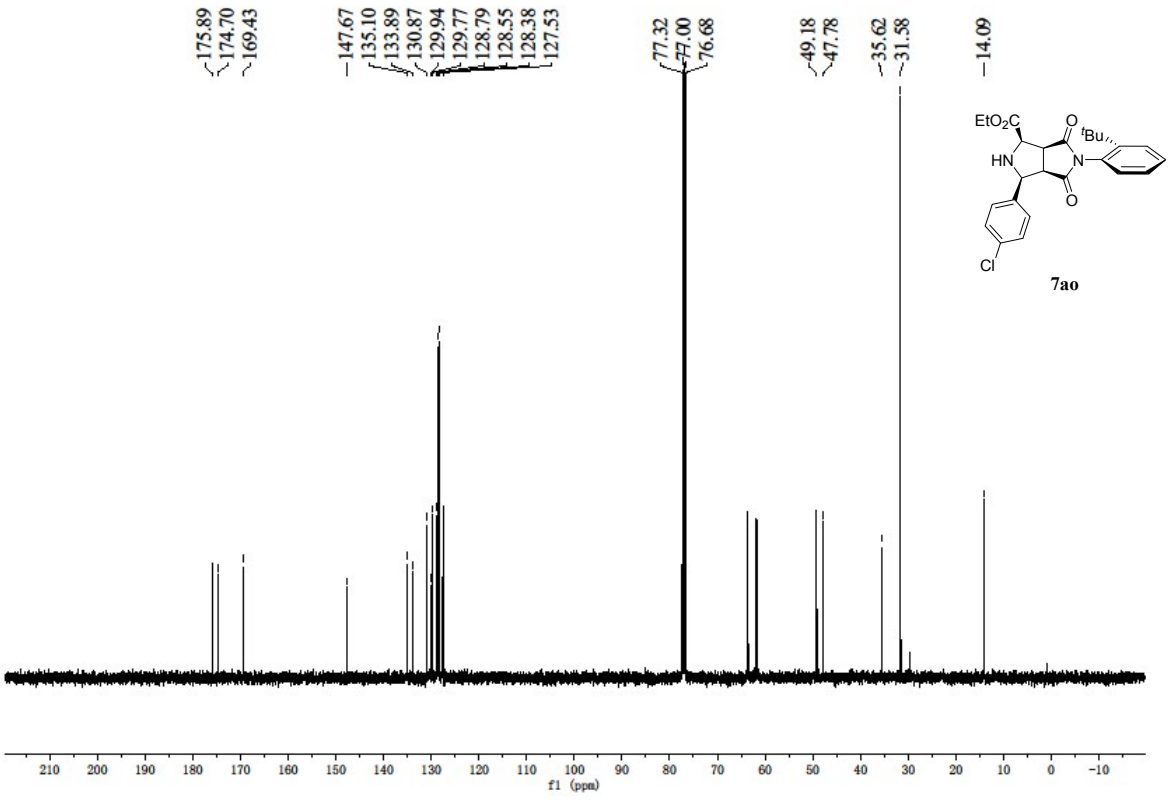
1.00
1.00
3.00
9.00
f1 (ppm)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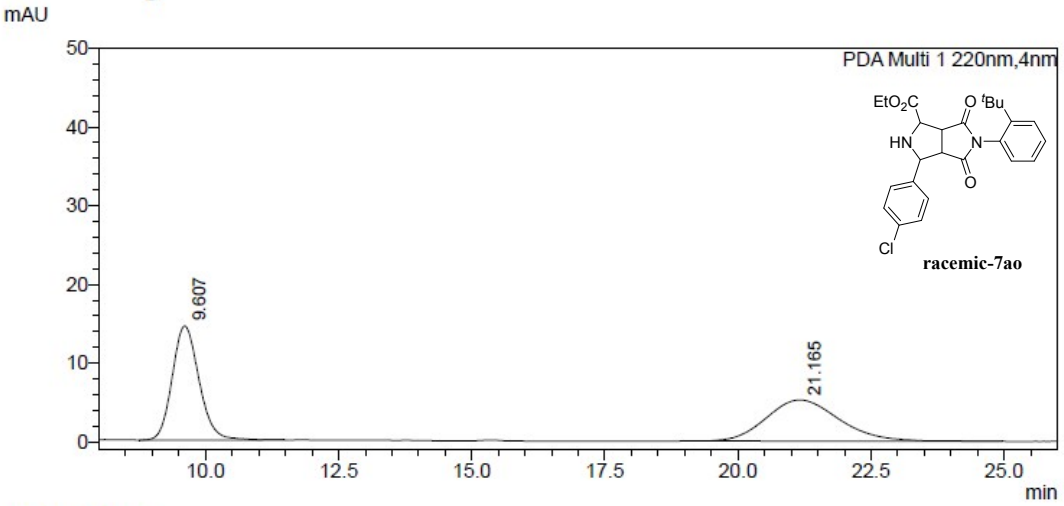
128.79
128.55
128.38
127.53
77.32
77.00
76.68
49.18
47.78
35.62
31.58
14.09
EtO2C
HN
O
tBu
N
O
O
Cl
7ao
f1 (ppm)

<Chromatogram>

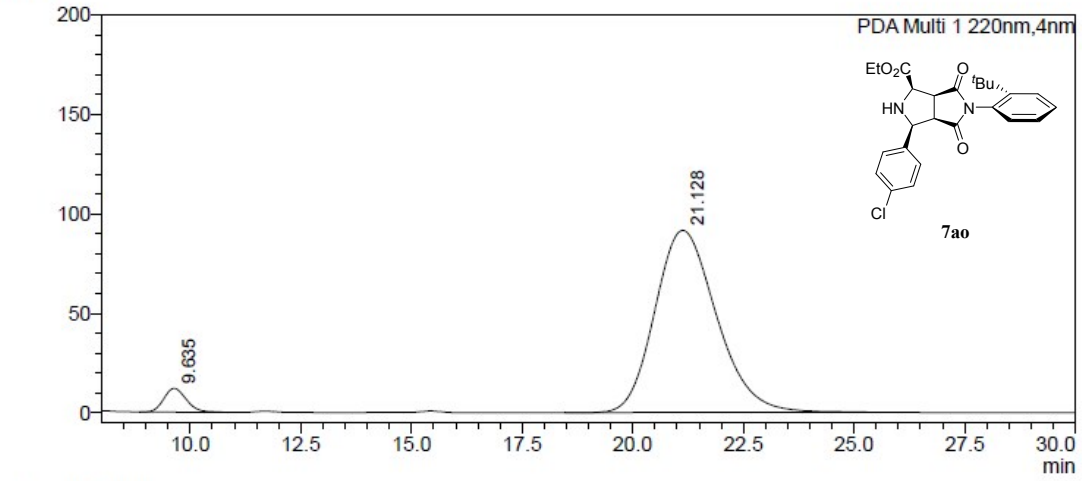


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	9.607	510483	50.423	14512	73.468
2	21.165	501912	49.577	5241	26.532
Total		1012395	100.000	19752	100.000

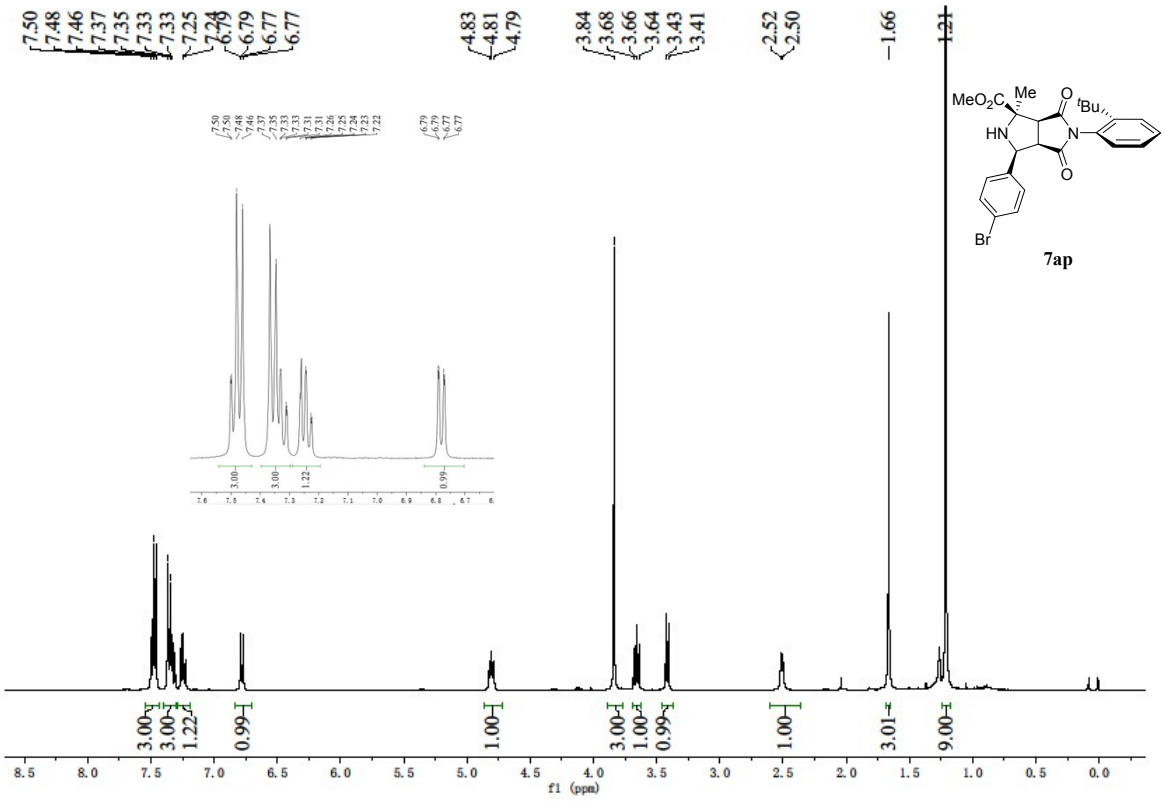
<Chromatogram>



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	9.635	423990	4.555	11964	11.558
2	21.128	8883597	95.445	91551	88.442
Total		9307588	100.000	103515	100.000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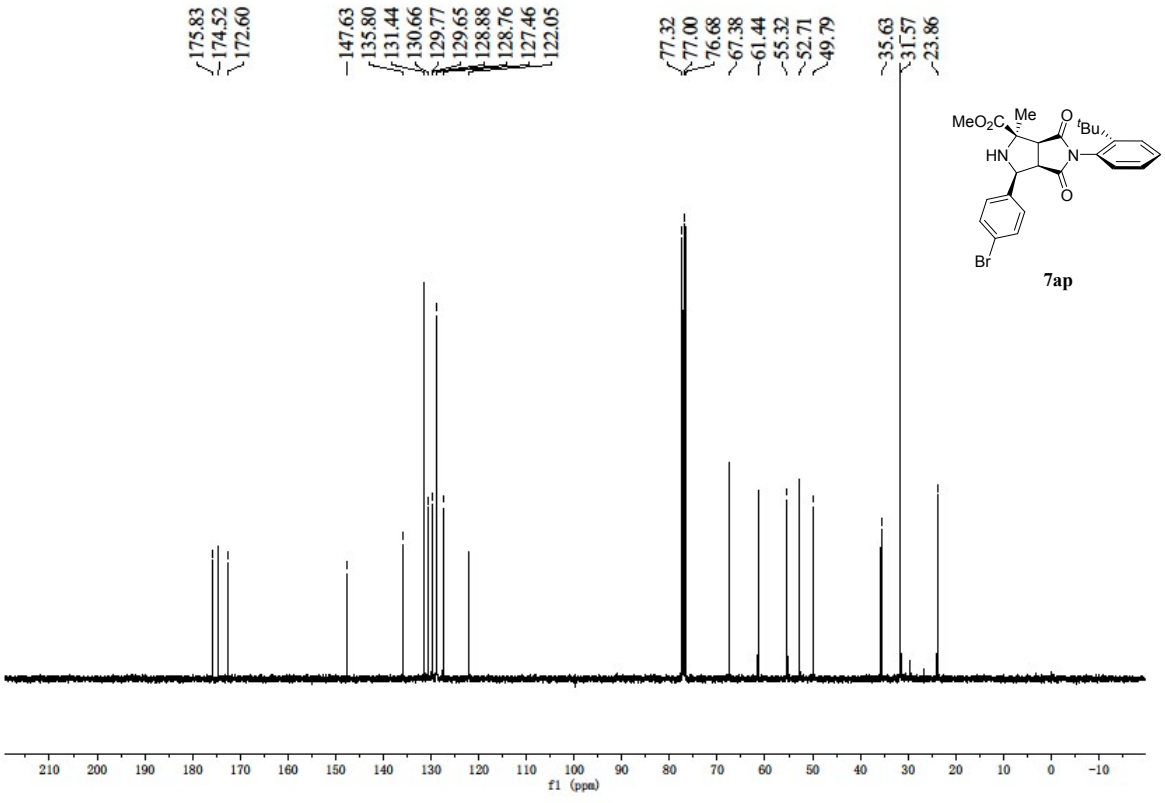
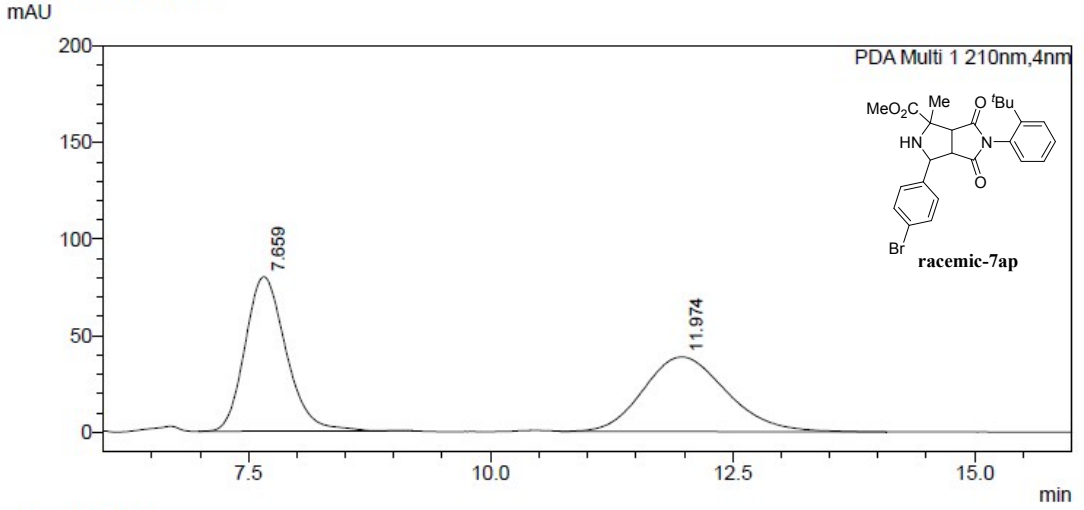
7.48
7.46
7.37
7.35
7.33
7.33
7.25
6.79
6.77
6.77
4.83
4.81
4.79
3.84
3.68
3.66
3.64
3.43
3.41
2.52
2.50
1.66
1.21
MeO2C
Me
HN
O
tBu
N
O
Br
7ap
3.00
3.00
1.22
0.99
1.00
3.00
1.00
0.99
1.00
3.01
9.00
f1 (ppm)


175.83
174.52
172.60
147.63
135.80
131.44
130.66
129.77
129.65
128.88
128.76
127.46
122.05
77.32
77.00
76.68
67.38
61.44
55.32
52.71
49.79
35.63
31.57
23.86
MeO2C
Me
HN
O
tBu
N
O
Br
7ap
f1 (ppm)

<Chromatogram>

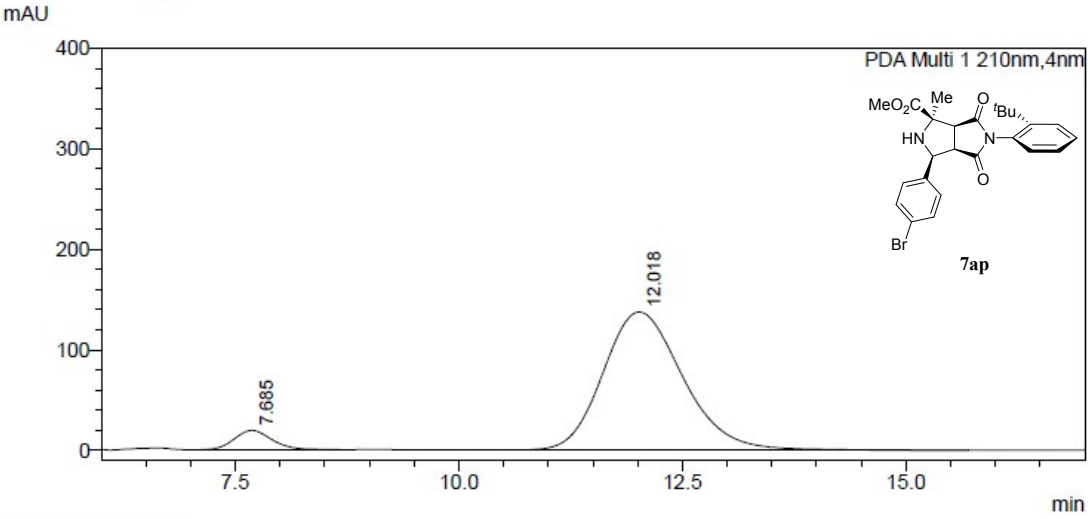


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	7.659	2364001	50.624	80021	67.463
2	11.974	2305712	49.376	38594	32.537
Total		4669712	100.000	118615	100.000

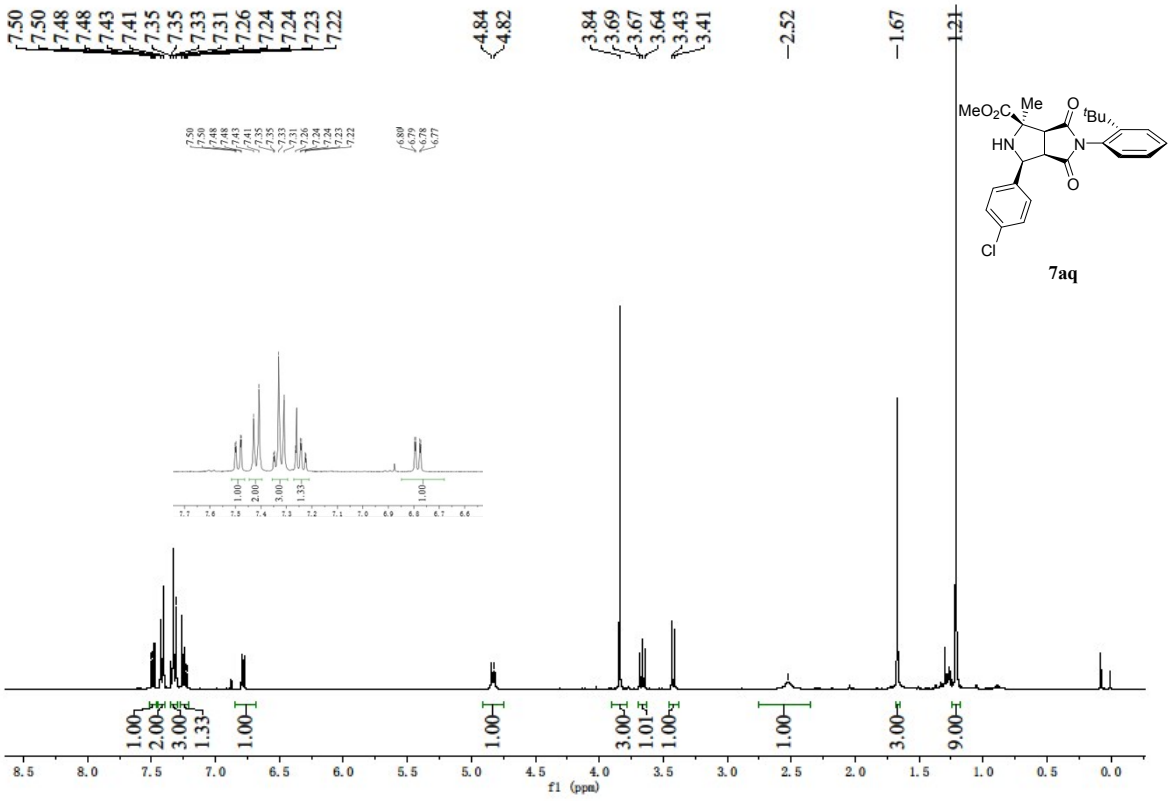
<Chromatogram>



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	7.685	566185	6.230	19298	12.319
2	12.018	8522134	93.770	137354	87.681
Total		9088319	100.000	156653	100.000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7.48
7.48
7.43
7.41
7.35
7.35
7.33
7.31
7.26
7.24
7.24
7.23
7.22
4.84
4.82
3.84
3.69
3.67
3.64
3.43
3.41
2.52
1.67
1.21
MeO2C
Me
HN
O
tBu
N
O
Cl
7aq
1.00
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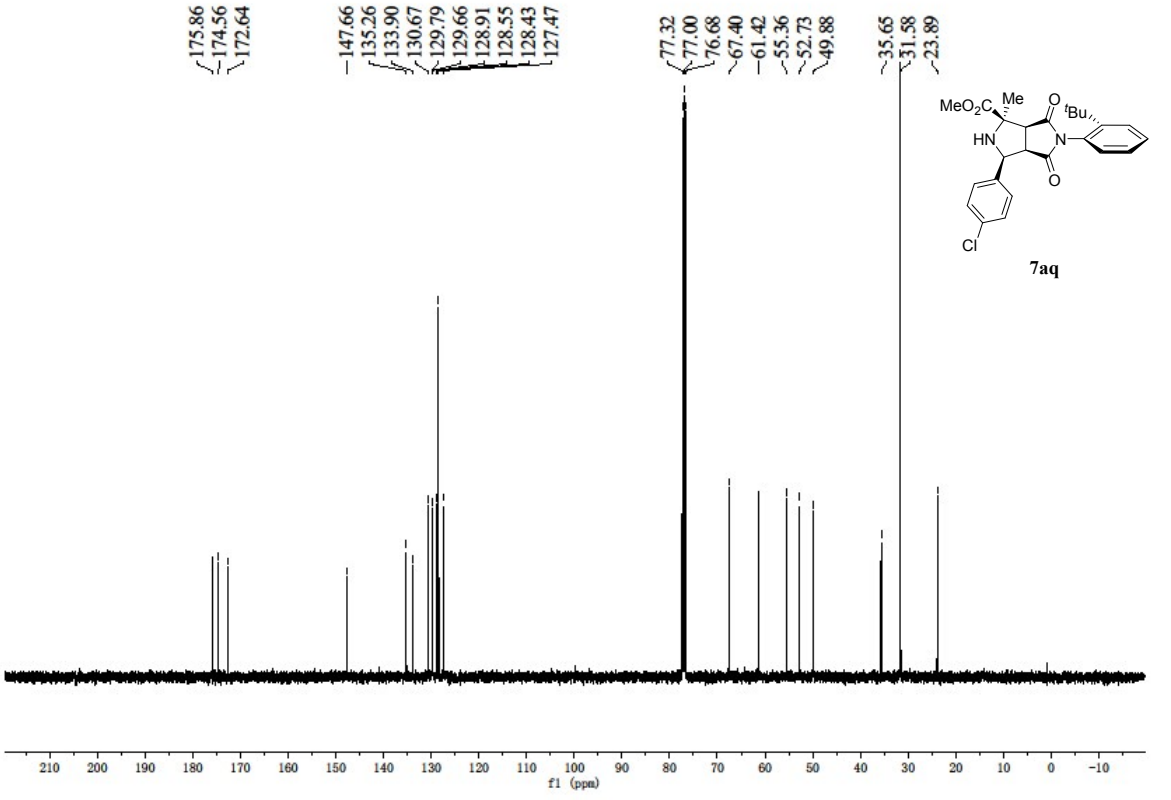
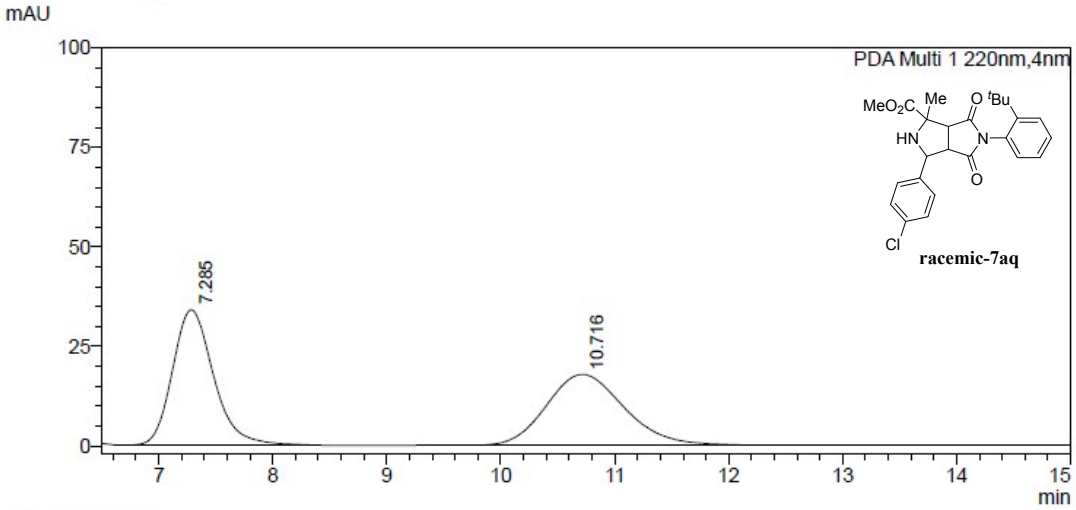
1.00
1.00
3.00
9.00
f1 (ppm)


175.86
174.56
172.64
147.66
135.26
133.90
130.67
129.79
129.66
128.91
128.55
128.43
127.47
77.32
77.00
76.68
67.40
61.42
55.36
52.73
49.88
35.65
31.58
23.89
MeO2C
Me
HN
O
tBu
N
O
Cl
7aq
f1 (ppm)

<Chromatogram>



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	7.285	848337	50.173	33951	65.614
2	10.716	842497	49.827	17793	34.386
Total		1690833	100.000	51743	100.000

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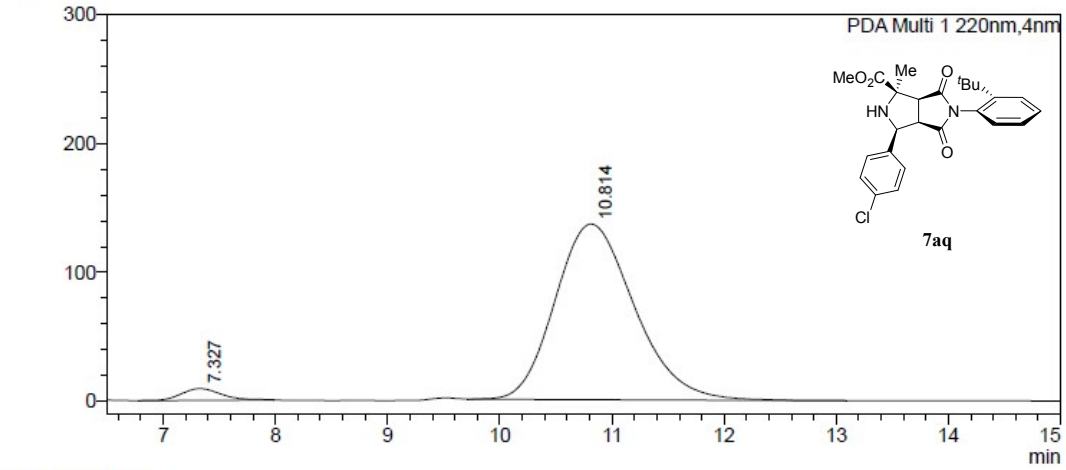
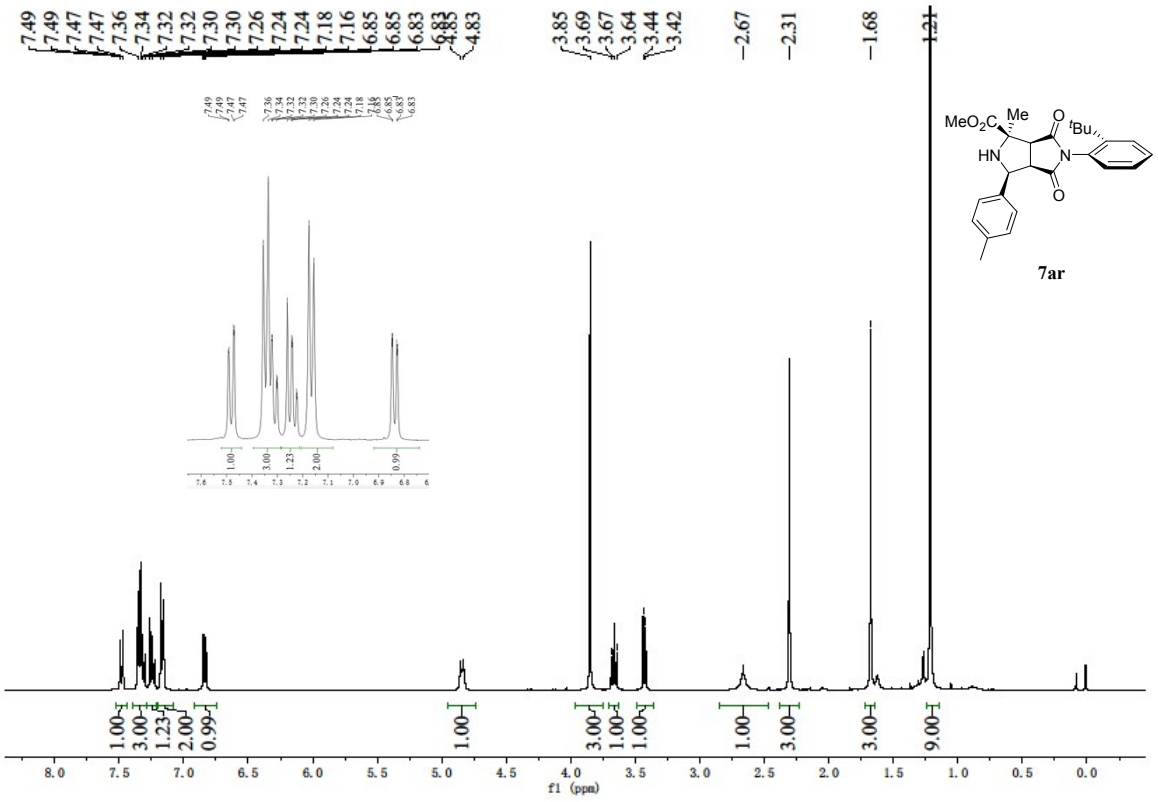


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	7.327	223301	3.224	9065	6.237
2	10.814	6703686	96.776	136264	93.763
Total		6926987	100.000	145329	100.000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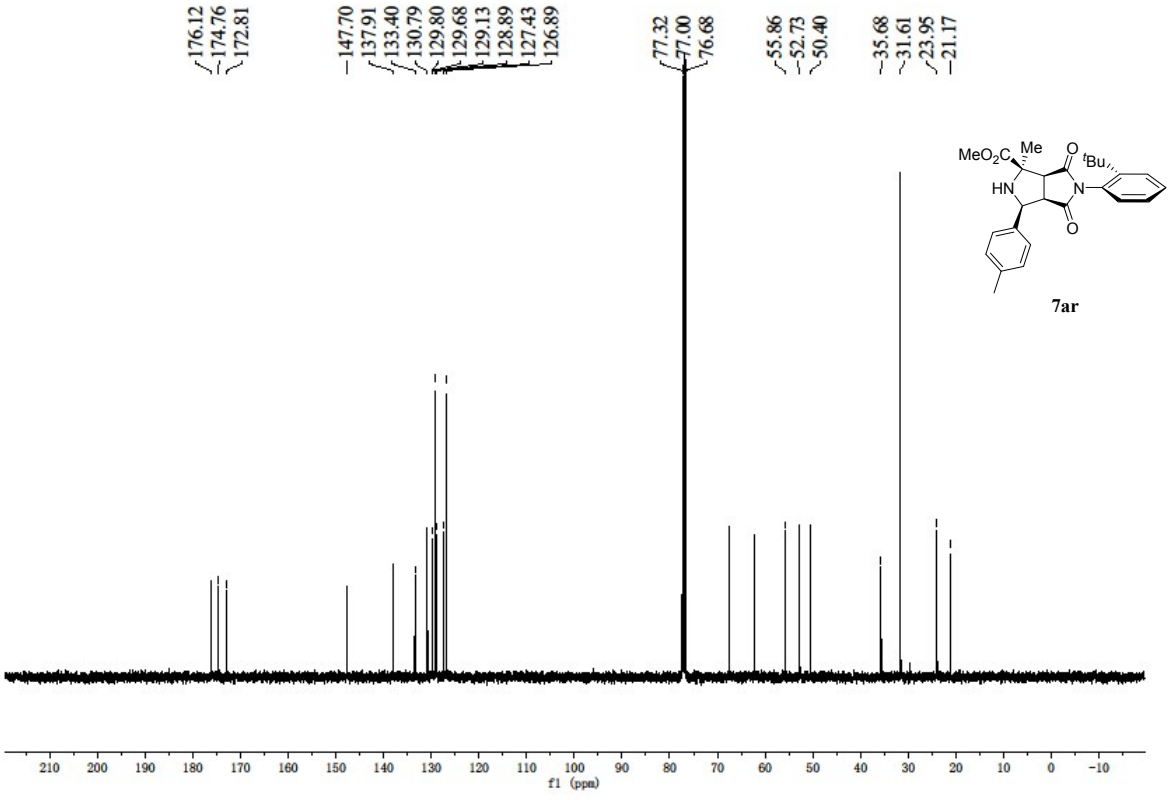
7.49
7.47
7.47
7.36
7.34
7.32
7.32
7.30
7.30
7.26
7.24
7.24
7.18
7.16
6.85
6.85
6.83
6.83
4.85
4.83
3.85
3.69
3.67
3.64
3.44
3.42
2.67
2.31
1.68
1.21
MeO2C
Me
O
tBu
HN
N
O
O
7ar
1.00
3.00
1.23
2.00
0.99
1.00
3.00
1.00
1.00
1.00
3.00
3.00
9.00
f1 (ppm)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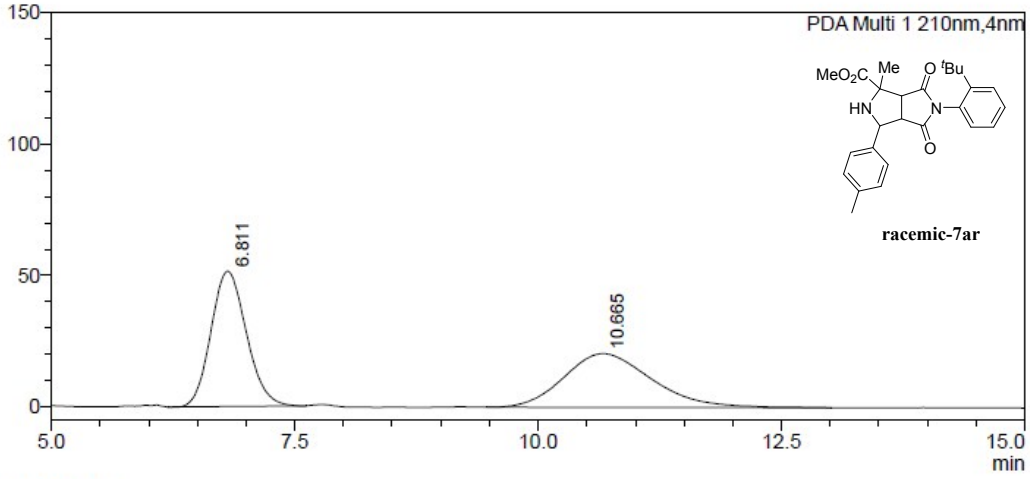
174.76
172.81
147.70
137.91
133.40
130.79
129.80
129.68
129.13
128.89
127.43
126.89
77.32
77.00
76.68
55.86
52.73
50.40
35.68
31.61
23.95
21.17
MeO2C
Me
O
tBu
HN
N
O
O
7ar
f1 (ppm)

<Chromatogram>

mAU



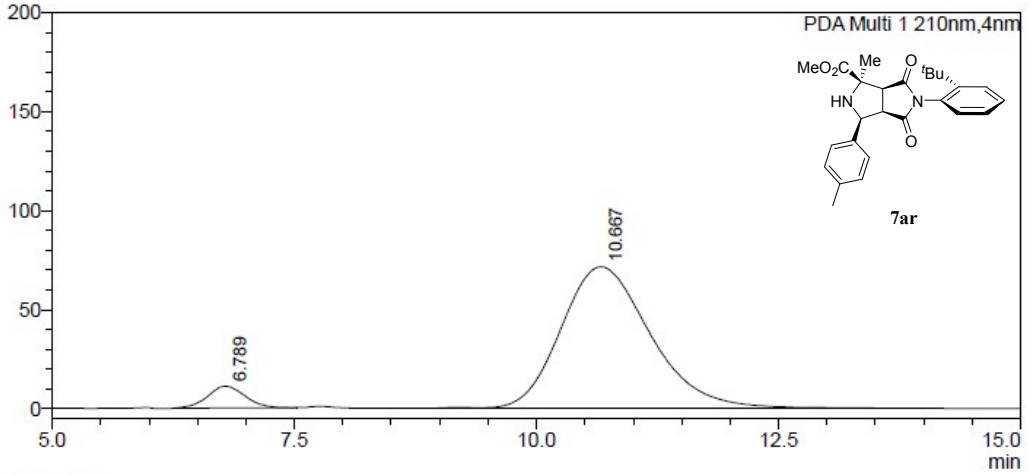
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	6.811	1302116	50.395	51403	71.559
2	10.665	1281715	49.605	20430	28.441
Total		2583831	100.000	71833	100.000

<Chromatogram>

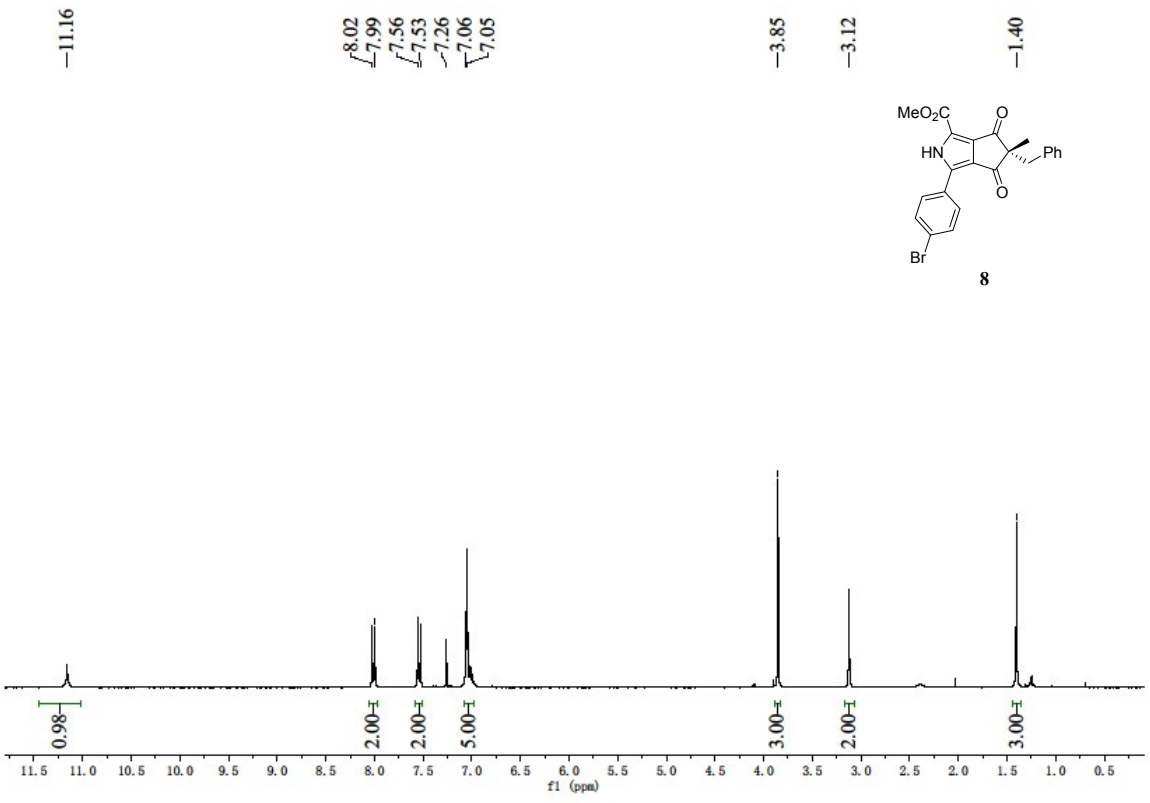
mAU



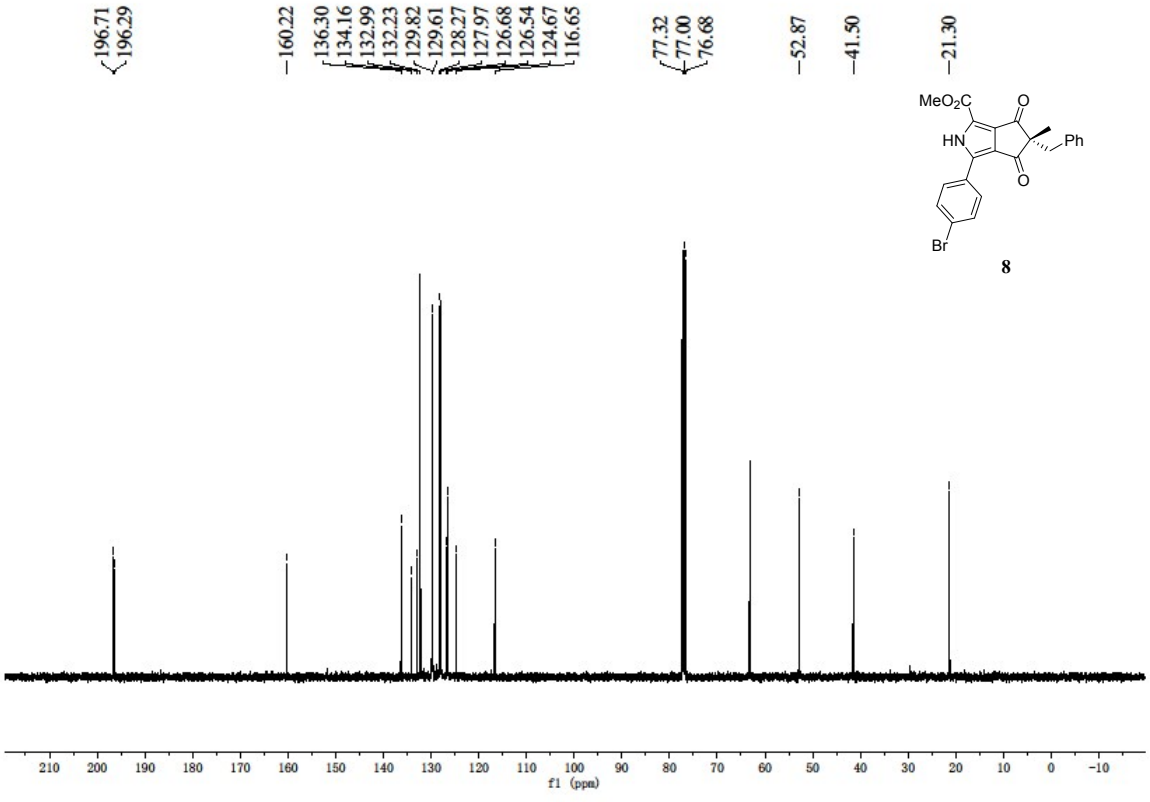
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	6.789	295418	6.038	11034	13.381
2	10.667	4597057	93.962	71429	86.619
Total		4892475	100.000	82463	100.000

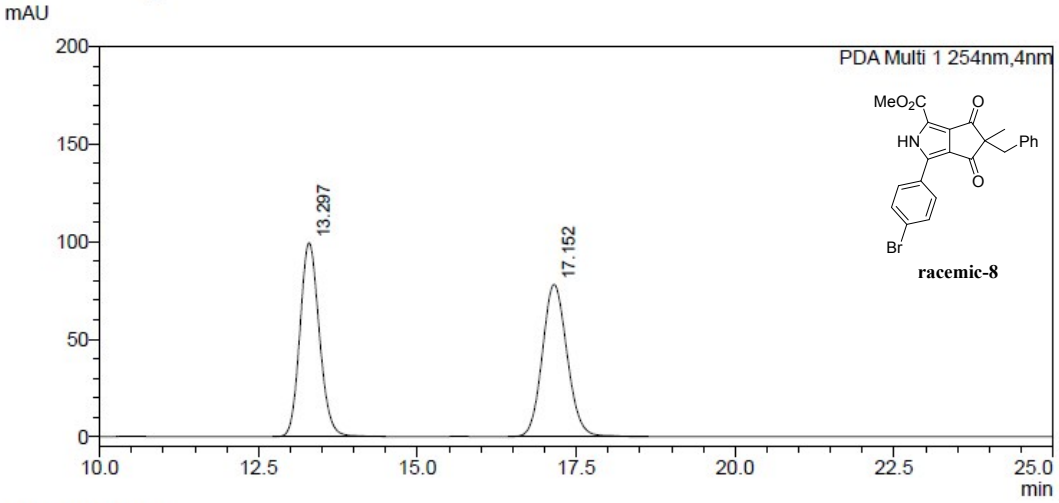

11.16
8.02
7.99
7.56
7.53
7.26
7.06
7.05
3.85
3.12
1.40
MeO2C
O
HN
Ph
O
Br
0.98
2.00
2.00
5.00
3.00
2.00
3.00
f1 (ppm)

8


196.71
196.29
160.22
136.30
134.16
132.99
132.23
129.82
129.61
128.27
127.97
126.68
126.54
124.67
116.65
77.32
77.00
76.68
52.87
41.50
21.30
MeO2C
O
HN
Ph
O
Br
f1 (ppm)

8

<Chromatogram>

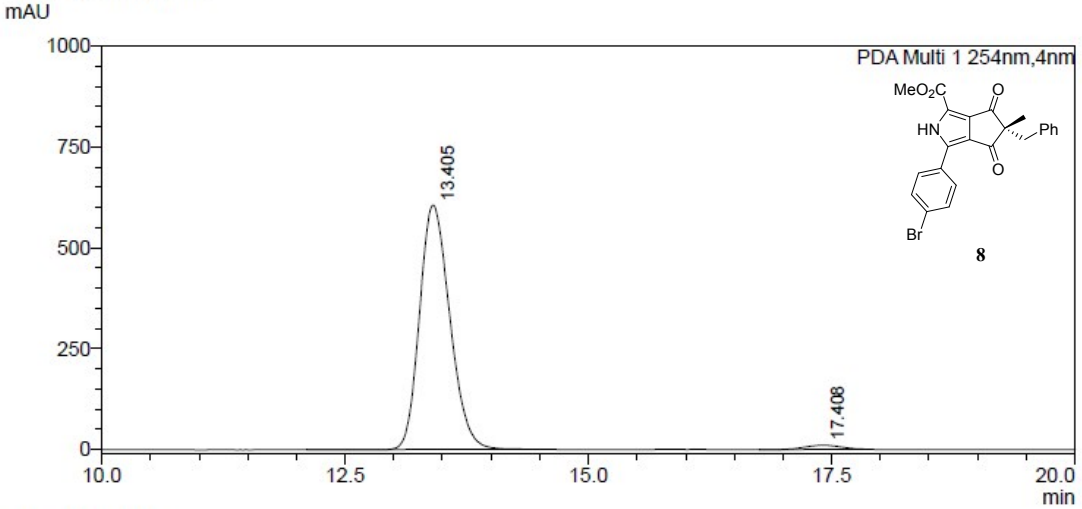


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	13.297	2109789	49.869	99461	56.007
2	17.152	2120835	50.131	78125	43.993
Total		4230624	100.000	177586	100.000

<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	13.405	13143644	97.938	605564	98.273
2	17.408	276755	2.062	10642	1.727
Total		13420399	100.000	616206	100.000

4. References

[1] Z.-M. Zhang, P. Chen, W.-B. Li, Y.-F. Niu, X.-L. Zhao, and J.-L. Zhang, *Angew. Chem. Int. Ed*., 2014, **53**, 4350; (b) Z.-M. Zhang, B. Xu, S. Xu, H.-H. Wu, and J.-L. Zhang, *Angew. Chem. Int. Ed*., 2016, **55**, 6324; (c) B. Xu, Z.-M. Zhang, S. Xu, B. Liu, Y.-J. Xiao, and J.-L. Zhang, *ACS Catal*., 2017, **7**, 210.

[2] D. Kalia, S. P. Pawar, and J. S. Thopate, *Angew. Chem*., 2017, **129**, 1.

[3] (a) S. Cabrera, R. G. Arrayás, J. C. Carretero, *J. Am. Chem. Soc*. 2005, **127**, 16394. (b) C. Nájera, M. Retamosa, J. M. Sansano, *Org. Lett*., 2007, **9**, 4025; (c) A. López-Pérez, J. Adrio, J. C. Carretero, *J. Am. Chem. Soc*., 2008, **130**, 10084.

[4] T. Das, P. Saha, and V. K. Singh, *Org. Lett*., 2015, **17**, 5088.

[5] H.-C. Liu, H.-Y. Tao, H. Cong, and C.-J. Wang, *J. Org. Chem.,* 2016, **81**, 3752.