

Supporting information

Enantioselective vinylogous aldol/lactonization cascade reaction between β,γ -unsaturated amides and trifluoromethyl ketones: facile access to chiral trifluoromethyl dihydropyranones

Jun-Hao Fu, Zhen-Guo Zhang, Xue-Ying Zhou, Chun-Wei Fu, Feng Sha, Xin-Yan Wu*

*Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of
Chemistry & Molecular Engineering, East China University of Science and Technology,
Shanghai 200237, P. R. China*

E-mail: xinyanwu@ecust.edu.cn

Table of Contents

1. General Information	S2
2. General Procedure for the Vinylogous Aldol/Lactonization Cascade Reaction	S2
3. References	S8
4. Copies of ^1H NMR and ^{13}C NMR Spectra for products 3	S9
5. Copies of HPLC Spectra of the Products 3	S22

1. General Information

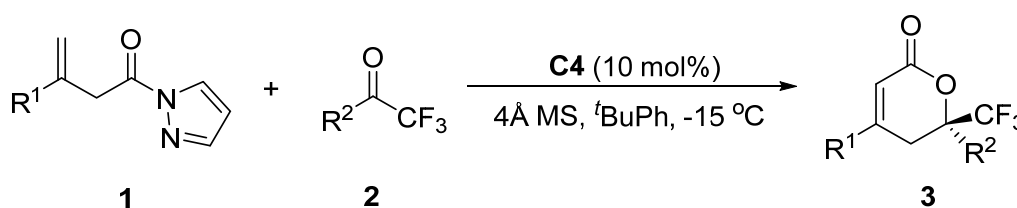
^1H NMR and ^{13}C NMR spectra were recorded on Bruker 400 spectrometer and the chemical shifts are reported in ppm downfield from tetramethylsilane ($\delta = 0.00$ ppm) for ^1H NMR and relative to the central CDCl_3 resonance ($\delta = 77.0$ ppm) for ^{13}C NMR spectroscopy. IR spectra were recorded on Nicolet Magna-I 550 spectrometer. High resolution mass spectra (HRMS) were recorded on Micromass GCT with Electron Spray Ionization (ESI-TOF) resource or Electron Impact Ionization (EI) resource. Optical rotations were measured on a WZZ-2A digital polarimeter at the wavelength of the sodium D-line (589 nm). HPLC analysis was performed on Waters equipment using Daicel Chiralpak AD-H column.

CH_2Cl_2 and ethyl acetate were distilled from CaH_2 . Toluene, *p*-xylene, *o*-xylene, *m*-xylene, mesitylene, *tert*-butylbenzene, ethylbenzene, cumene and (trifluoromethyl)benzene were distilled from sodium-benzophenone. All other chemicals were used without purification as commercially available. Thin-layer chromatography (TLC) was performed on 10-40 μm silica gel plates. Column chromatography was performed using silica gel (300-400 mesh) eluted with ethyl acetate and petroleum ether.

Chiral catalysts **C1-C8**¹, β,γ -unsaturated amides **1**² and the trifluoromethyl acetophenone **2e**³ were prepared according to literature procedure.

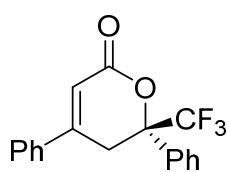
2. General Procedure for the Vinylogous Aldol/Lactonization Cascade

Reaction



To a solution of trifluoromethyl ketone **2** (0.2 mmol) and catalyst **C4** (0.02 mmol, 10 mol%) in 1 mL *t*BuPh was added β,γ -unsaturated amide **1** (0.3 mmol, 1.5 eq.) at $-15\text{ }^\circ\text{C}$, and the resulting mixture was stirred at this temperature until the reaction completed (monitored by TLC). The solvent was removed under reduced pressure, and the residue obtained was purified by column chromatography (petroleum ether/EtOAc) to afford the desired product **3**.

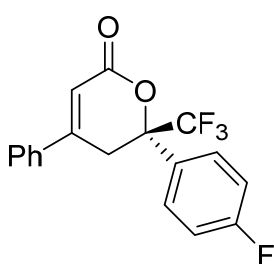
(S)-4,6-diphenyl-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one (3aa)



Colorless oil, 57.2 mg, 90% yield, 99% ee, $[\alpha]_D^{20} +153.9$ (*c* 1.93, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.58-7.52 (m, 2H), 7.51-7.42 (m, 5H), 7.41-7.36 (m, 3H), 6.25 (d, *J* = 2.4 Hz, 1H), 3.63 (d, *J* = 17.2 Hz, 1H), 3.52 (dd, *J*₁ = 17.2 Hz, *J*₂ = 2.4 Hz, 1H); HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): *t*_R = 11.77 min (major), 16.05 min (minor).

(S)-6-(4-fluorophenyl)-4-phenyl-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one (3ab)

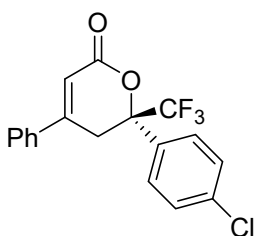
(3ab)



Colorless oil, 55.5 mg, 82% yield, 99% ee, $[\alpha]_D^{20} +158.4$ (*c* 1.22, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.56-7.42 (m, 7H), 7.12-7.04 (m, 2H), 6.26 (d, *J* = 2.4 Hz, 1H), 3.58 (d, *J* = 17.6 Hz, 1H), 3.53 (dd, *J*₁ = 17.6 Hz, *J*₂ = 2.0 Hz, 1H); HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): *t*_R = 16.79 min (major), 24.81 min (minor).

(S)-6-(4-chlorophenyl)-4-phenyl-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one (3ac)

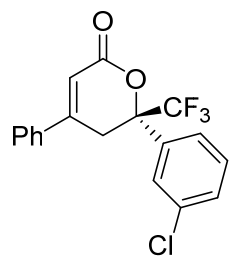
(3ac)



Colorless oil, 70.0 mg, 99% yield, 99% ee, $[\alpha]_D^{20} +207.3$ (*c* 1.59, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.55-7.43 (m, 7H), 7.41 (d, *J* = 8.8 Hz, 2H), 6.26 (d, *J* = 1.2 Hz, 1H), 3.57 (d, *J* = 17.6 Hz, 1H), 3.52 (dd, *J*₁ = 17.6 Hz, *J*₂ = 2.0 Hz, 1H); HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): *t*_R = 15.53 min (major), 21.92 min (minor).

(S)-6-(3-chlorophenyl)-4-phenyl-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one (3ad)

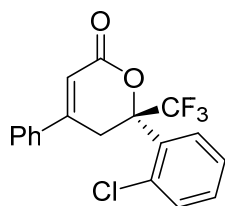
(3ad)



Colorless oil, 69.6 mg, 99% yield, 98% ee, $[\alpha]_D^{20} +166.1$ (*c* 1.60, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.55 (s, 1H), 7.53-7.41 (m, 6H), 7.39 (dt, *J*₁ = 8.0 Hz, *J*₂ = 1.6 Hz, 1H), 7.36-7.31 (m, 1H), 6.29-6.27 (m, 1H), 3.54 (d, *J* = 0.8 Hz, 2H); HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): *t*_R = 11.87 min (major), 13.75 min (minor).

(S)-4-(2-chlorophenyl)-6-phenyl-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one

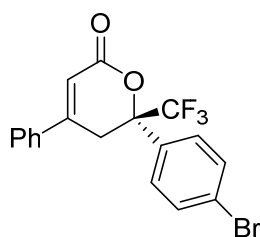
(3ae)



Colorless oil, 20.0 mg, 28% yield, 99% ee, $[\alpha]_{\text{D}}^{20} +160.8$ (c 0.52, CHCl_3); $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.87-7.81 (m, 1H), 7.58 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 2H), 7.51-7.38 (m, 4H), 7.37-7.30 (m, 2H), 6.30 (d, $J = 2.0$ Hz, 1H), 6.30 (d, $J = 2.0$ Hz, 1H), 4.57 (d, $J = 18.0$ Hz, 1H), 3.56 (dd, $J_1 = 18.0$ Hz, $J_2 = 2.4$ Hz, 1H); $^{13}\text{C MNR}$ (100 MHz, CDCl_3): δ 161.7, 152.6, 135.2, 132.8, 132.3, 131.2, 131.1, 131.0, 130.7, 129.2, 127.4, 126.3, 123.6 (q, $J = 283.6$ Hz), 114.0, 83.3 (q, $J = 31.0$ Hz), 29.1; IR (KBr, cm^{-1}): ν 3445, 3064, 2962, 2920, 1734, 1617, 1429, 1259, 1194, 1030, 870, 761, 685; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{16}^{35}\text{ClF}_3\text{NO}_2^+$ and $\text{C}_{18}\text{H}_{16}^{37}\text{ClF}_3\text{NO}_2^+$ ($[\text{M} + \text{NH}_4]^+$): 370.0816 and 372.0787, found: 370.0810 and 372.0792; HPLC analysis (Daicel Chiralpak AD-H column, $\lambda = 254$ nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): $t_{\text{R}} = 12.96$ min (major), 17.52 min (minor).

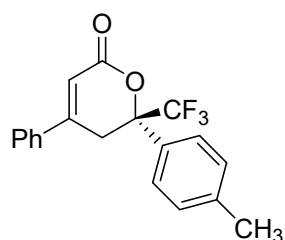
(S)-4-(4-bromophenyl)-6-phenyl-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one

(3af)



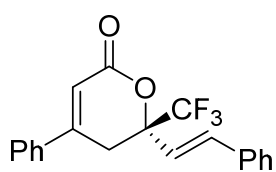
Colorless oil, 76.4 mg, 96% yield, 99% ee, $[\alpha]_{\text{D}}^{20} +187.2$ (c 2.20, CHCl_3); $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.52-7.42 (m, 7 H), 7.36 (dt, $J_1 = 8.8$ Hz, $J_2 = 2.4$ Hz, 2H), 6.26 (d, $J = 1.6$ Hz, 1H), 3.58 (d, $J = 17.6$ Hz, 1H), 3.52 (dd, $J_1 = 17.6$ Hz, $J_2 = 2.0$ Hz, 1H); HPLC analysis (Daicel Chiralpak AD-H column, $\lambda = 254$ nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): $t_{\text{R}} = 17.04$ min (major), 22.82 min (minor).

(S)-4-phenyl-6-(p-tolyl)-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one (3ag)



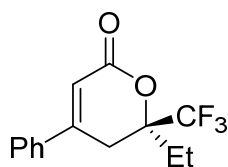
Colorless oil, 40.1 mg, 60% yield, 99% ee, $[\alpha]_{\text{D}}^{20} +163.5$ (c 0.89, CHCl_3); $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.52-7.39 (m, 7H), 7.19 (d, $J = 8.0$ Hz, 2H), 6.24 (d, $J = 2.4$ Hz, 1H), 3.60 (d, $J = 17.6$ Hz, 1H), 3.49 (dd, $J_1 = 17.6$ Hz, $J_2 = 2.4$ Hz, 1H), 2.33 (s, 3H); HPLC analysis (Daicel Chiralpak AD-H column, $\lambda = 254$ nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): $t_{\text{R}} = 13.60$ min (major), 18.25 min (minor).

(*S,E*)-4-phenyl-6-styryl-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one (3ah)



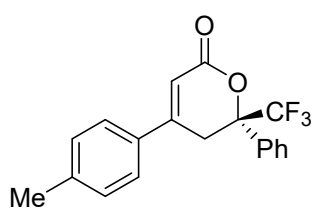
Colorless oil, 60.3 mg, 88% yield, 99% ee, $[\alpha]_{\text{D}}^{20} +147.0$ (*c* 0.30, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.58-7.43 (m, 5H), 7.39-7.26 (m, 5H), 6.92 (d, $J = 16.0$ Hz, 1H), 6.38 (d, $J = 2.0$ Hz, 1H), 6.13 (d, $J = 16.0$ Hz, 1H), 3.39 (dd, $J_1 = 17.2$ Hz, $J_2 = 2.0$ Hz, 1H), 3.16 (d, $J = 17.2$ Hz, 1H); ^{13}C MNR (100 MHz, CDCl_3): δ 161.8, 151.3, 136.4, 135.4, 134.6, 131.2, 129.2, 129.1, 128.7, 127.0, 126.0, 123.3 (q, $J = 282.1$ Hz), 121.1, 114.4, 81.1 (q, $J = 30.3$ Hz), 29.6; IR (KBr, cm^{-1}): ν 3029, 1720, 1625, 1448, 1230, 1172, 1021, 970, 748, 689; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{15}\text{F}_3\text{O}_2^+$ ($[\text{M}]^+$): 344.1019, found: 344.1027; HPLC analysis (Daicel Chiralpak AD-H column, $\lambda = 254$ nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): $t_{\text{R}} = 25.10$ min (major), 18.73 min (minor).

(*R*)-6-ethyl-4-phenyl-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one (3ai)



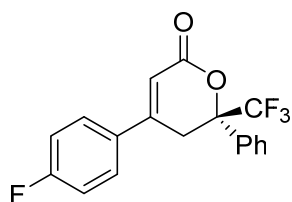
Colorless oil, 11.8 mg, 22% yield, 99% ee, $[\alpha]_{\text{D}}^{20} +48.3$ (*c* 0.06, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.57-7.44 (m, 5H), 6.39 (s, 1H), 3.13 (dd, $J_1 = 18.4$ Hz, $J_2 = 1.6$ Hz, 1H), 2.97 (d, $J = 18.4$ Hz, 1H), 2.18-2.06 (m, 1H), 2.05-1.93 (m, 1H), 1.08 (t, $J = 7.2$ Hz, 3H); HPLC analysis (Daicel Chiralpak AD-H column, $\lambda = 254$ nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): $t_{\text{R}} = 20.86$ min (major), 28.26 min (minor).

(*S*)-6-phenyl-4-(*p*-tolyl)-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one (3ba)



Colorless oil, 40.6 mg, 61% yield, 99% ee, $[\alpha]_{\text{D}}^{20} +173.2$ (*c* 0.71, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.57-7.50 (m, 2H), 7.42-7.35 (m, 5H), 7.25 (d, $J = 8.4$ Hz, 2H), 6.22 (d, $J = 2.4$ Hz, 1H), 3.62 (d, $J = 17.6$ Hz, 1H), 3.49 (dd, $J_1 = 17.6$ Hz, $J_2 = 2.4$ Hz, 1H), 2.39 (s, 3H); HPLC analysis (Daicel Chiralpak AD-H column, $\lambda = 254$ nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): $t_{\text{R}} = 16.63$ min (major), 27.04 min (minor).

(*S*)-4-(4-fluorophenyl)-6-phenyl-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one (3ca)

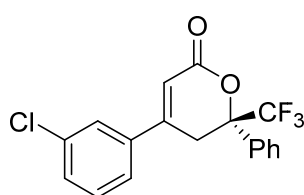


Colorless oil, 56.5 mg, 84% yield, 99% ee, $[\alpha]_{\text{D}}^{20} +190.2$ (*c* 1.92, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.56-7.46 (m, 4H), 7.43-7.36 (m, 3H), 7.17-7.11 (m, 2H), 6.21 (d, $J = 2.0$ Hz, 1H), 3.58 (d, $J = 17.2$ Hz, 1H), 3.51 (dd, $J_1 = 17.6$ Hz, $J_2 = 2.4$ Hz, 1H);

^{13}C MNR (100 MHz, CDCl_3): δ 163.4 (d, $J = 248.7$ Hz), 161.5, 151.9, 135.3, 131.3, 129.5 (d, $J = 3.4$ Hz), 129.2, 128.6 (d, $J = 8.4$ Hz), 125.9, 123.1 (q, $J = 282.0$ Hz), 115.9 (d, $J = 21.7$ Hz), 114.8, 82.1 (q, $J = 40.0$ Hz), 29.6; IR (KBr, cm^{-1}): ν 3438, 3083, 2975, 2925, 1729, 1606, 1511, 1448, 1241, 1174, 1049, 995, 767, 688, 522; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{12}\text{F}_4\text{O}_2\text{Na}^+$ ($[\text{M} + \text{Na}]^+$): 359.0666, found: 359.0670; HPLC analysis (Daicel Chiralpak AD-H column, $\lambda = 254$ nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): $t_{\text{R}} = 15.01$ min (major), 22.47 min (minor).

(S)-4-(3-chlorophenyl)-6-phenyl-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one

(3da)

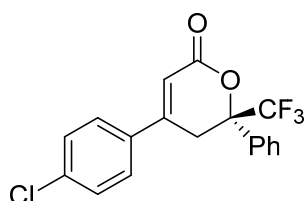


Colorless oil, 56.4 mg, 80% yield, 99% ee, $[\alpha]_{\text{D}}^{20} +153.6$ (c 1.65, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.56-7.50 (m, 2H), 7.47-7.43 (m, 2H), 7.43-7.34 (m, 5H), 6.25 (d, $J = 1.6$ Hz, 1H), 3.57 (d, $J = 17.6$ Hz, 1H), 3.51 (dd, $J_1 = 17.6$ Hz, $J_2 = 2.4$ Hz, 1H); HPLC analysis (Daicel Chiralpak AD-H column, $\lambda = 254$

nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): $t_{\text{R}} = 9.56$ min (major), 11.48 min (minor).

(S)-4-(4-chlorophenyl)-6-phenyl-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one

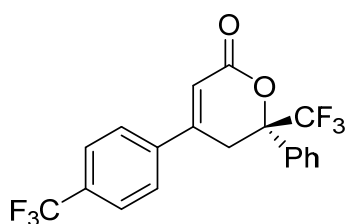
(3ea)



Colorless oil, 55.8 mg, 79% yield, 99% ee, $[\alpha]_{\text{D}}^{20} +139.2$ (c 1.49, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.55-7.49 (m, 2H), 7.46-7.36 (m, 7H), 6.23 (d, $J = 2.4$ Hz, 1H), 3.57 (d, $J = 17.6$ Hz, 1H), 3.51 (dd, $J_1 = 17.6$ Hz, $J_2 = 2.4$ Hz, 1H); HPLC analysis

(Daicel Chiralpak AD-H column, $\lambda = 254$ nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): $t_{\text{R}} = 22.48$ min (major), 34.26 min (minor).

(S)-6-phenyl-6-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-5,6-dihydro-2H-pyran-2-one (3fa)

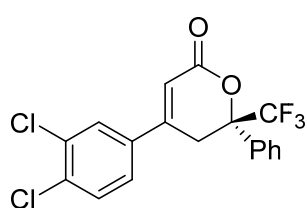


Colorless oil, 71.2 mg, 92% yield, 99% ee, $[\alpha]_{\text{D}}^{20} +187.2$ (c 1.49, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.71 (d, $J = 8.0$ Hz, 2H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.56-7.50 (m, 2H), 7.44-7.37 (m, 3H), 6.30 (s, 1H), 3.64-3.53 (m, 2H); ^{13}C MNR

(100 MHz, CDCl_3): δ 161.2, 150.4, 139.0, 133.4, 132.7 (q, $J = 32.8$ Hz), 129.9, 128.9, 126.4, 126.4, 126.2 (q, $J = 3.8$ Hz), 123.5 (q, $J = 270.7$ Hz),

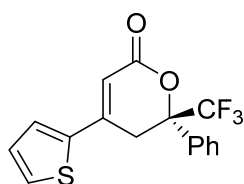
123.2 (q, $J = 281.9$ Hz), 116.9, 82.6 (q, $J = 40.0$ Hz), 29.8; IR (KBr, cm^{-1}): ν 2927, 1729, 1415, 1326, 1170, 1126, 1070, 1049, 844, 719; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{12}\text{F}_6\text{O}_2^+$ ($[\text{M}]^+$): 386.0736, found: 386.0740; HPLC analysis (Daicel Chiralpak AD-H column, $\lambda = 254$ nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): $t_{\text{R}} = 15.46$ min (major), 18.58 min (minor).

(S)-4-(3,4-dichlorophenyl)-6-phenyl-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one (3ga)



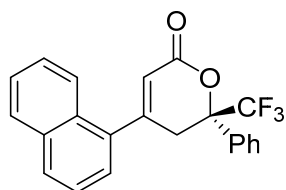
Colorless oil, 76.1 mg, 99% yield, 99% ee, $[\alpha]_{\text{D}}^{20} +193.4$ (c 2.17, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.56 (d, $J = 2.0$ Hz, 1H), 7.55-7.47 (m, 3H), 7.44-7.37 (m, 3H), 7.33 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H); 6.25 (s, 1H), 3.52 (s, 2H); ^{13}C MNR (100 MHz, CDCl_3): δ 161.1, 149.3, 135.5, 135.3, 133.8, 133.3, 131.2, 129.9, 128.9, 127.8, 126.4, 125.0, 123.1 (q, $J = 282.1$ Hz), 116.2, 82.5 (q, $J = 30.0$ Hz), 29.5; IR (KBr, cm^{-1}): ν 2921, 1747, 1245, 1178, 1101, 1045, 1031, 991, 804, 777, 701; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{11}\text{O}_2\text{F}_3^{35}\text{Cl}_2^+$, $\text{C}_{19}\text{H}_{11}\text{O}_2\text{F}_3^{35}\text{Cl}^{37}\text{Cl}^+$ and $\text{C}_{19}\text{H}_{11}\text{O}_2\text{F}_3^{37}\text{Cl}_2^+$ ($[\text{M}]^+$): 386.0083, 388.0053 and 390.0024, found: 386.0086, 388.0063 and 390.0022; HPLC analysis (Daicel Chiralpak AD-H column, $\lambda = 254$ nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): $t_{\text{R}} = 17.23$ min (major), 20.06 min (minor).

(S)-6-phenyl-4-(thiophen-2-yl)-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one (3ha)



Colorless oil, 54.1 mg, 83% yield, 99% ee, $[\alpha]_{\text{D}}^{20} +189.7$ (c 1.67, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.59-7.53 (m, 2H), 7.52 (d, $J = 5.2$ Hz, 1H), 7.46 (d, $J = 3.6$ Hz, 1H), 7.42-7.34 (m, 3H), 7.15 (dd, $J_1 = 4.8$ Hz, $J_2 = 4.0$ Hz, 1H), 6.17 (d, $J = 2.0$ Hz, 1H), 3.62 (d, $J = 17.2$ Hz, 1H), 3.50 (dd, $J_1 = 17.2$ Hz, $J_2 = 2.0$ Hz, 1H); HPLC analysis (Daicel Chiralpak AD-H column, $\lambda = 254$ nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): $t_{\text{R}} = 21.51$ min (major), 26.18 min (minor).

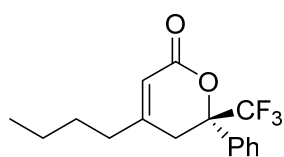
(S)-4-(naphthalen-1-yl)-6-phenyl-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one (3ia)



Colorless oil, 37.7 mg, 51% yield, 96% ee, $[\alpha]_{\text{D}}^{20} +171.2$ (c 0.87, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.88 (d, $J = 8.0$ Hz, 2H), 7.62-7.56 (d, $J = 8.0$ Hz, 2H), 7.54-7.37 (m, 7H), 7.20 (d, $J = 6.8$ Hz, 1H), 6.12 (d, $J = 2.4$ Hz, 1H), 3.74 (dd, $J_1 = 17.6$ Hz, $J_2 = 2.4$

Hz, 1H), 3.45 (d, $J = 17.6$ Hz, 1H); ^{13}C MNR (100 MHz, CDCl_3): δ 161.2, 153.7, 135.5, 133.8, 133.7, 130.0, 129.8, 129.5, 128.9, 128.7, 127.0, 126.8, 126.6, 125.1, 124.5, 124.3, 123.3 (q, $J = 282.0$ Hz), 120.0, 82.9 (q, $J = 30.5$ Hz), 33.6; IR (KBr, cm^{-1}): ν 2923, 1727, 1398, 1255, 1174, 1051, 869, 819, 700; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{15}\text{F}_3\text{O}_2^+$ ($[\text{M}]^+$): 368.1019, found: 368.1026; HPLC analysis (Daicel Chiralpak AD-H column, $\lambda = 254$ nm, eluent: 90/10 hexane/2-propanol, flow rate: 0.9 mL/min): $t_{\text{R}} = 8.41$ min (major), 11.25 min (minor).

(S)-4-butyl-6-phenyl-6-(trifluoromethyl)-5,6-dihydro-2H-pyran-2-one (3ja)

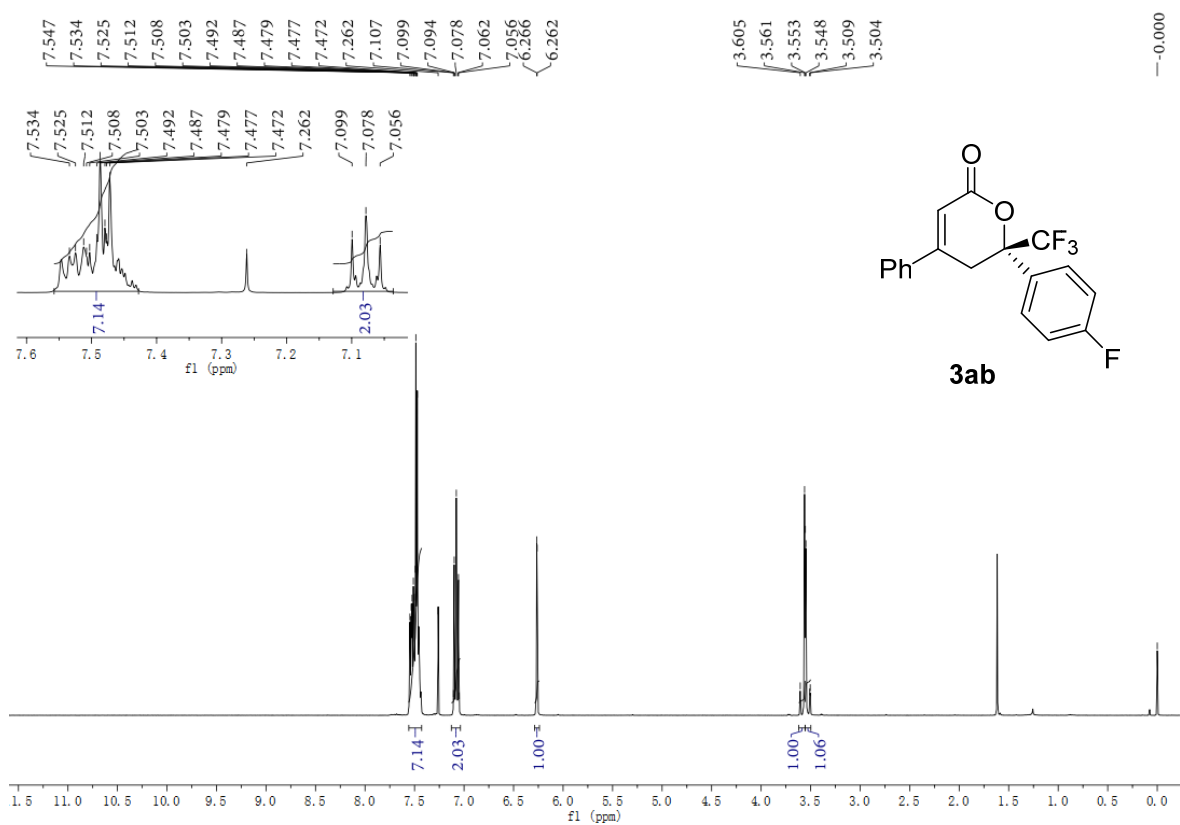
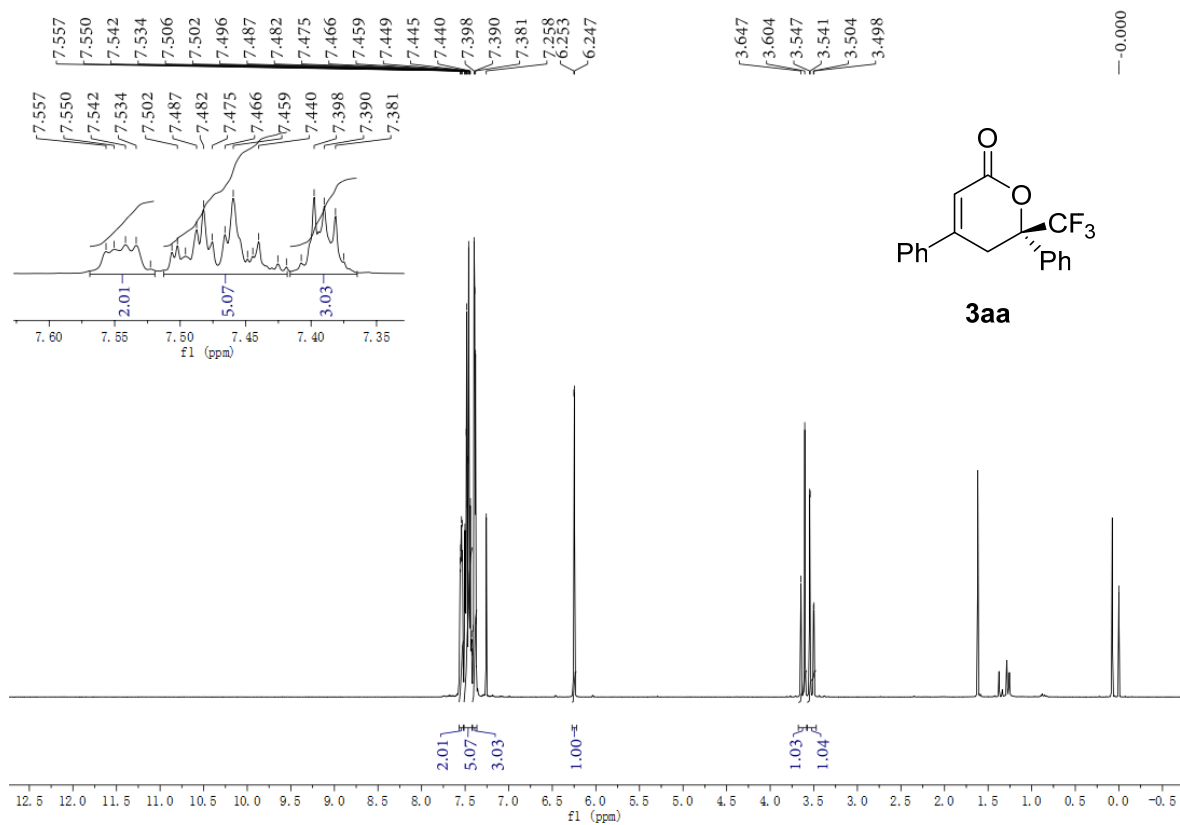


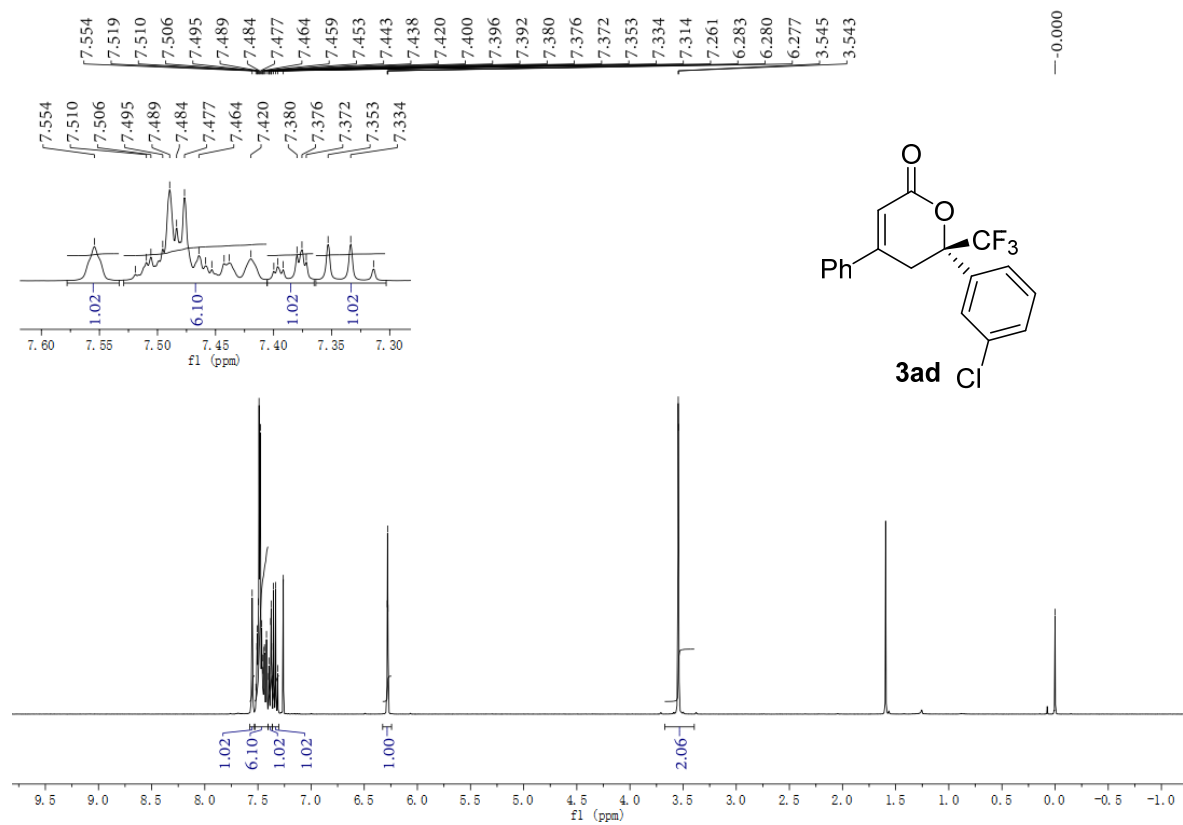
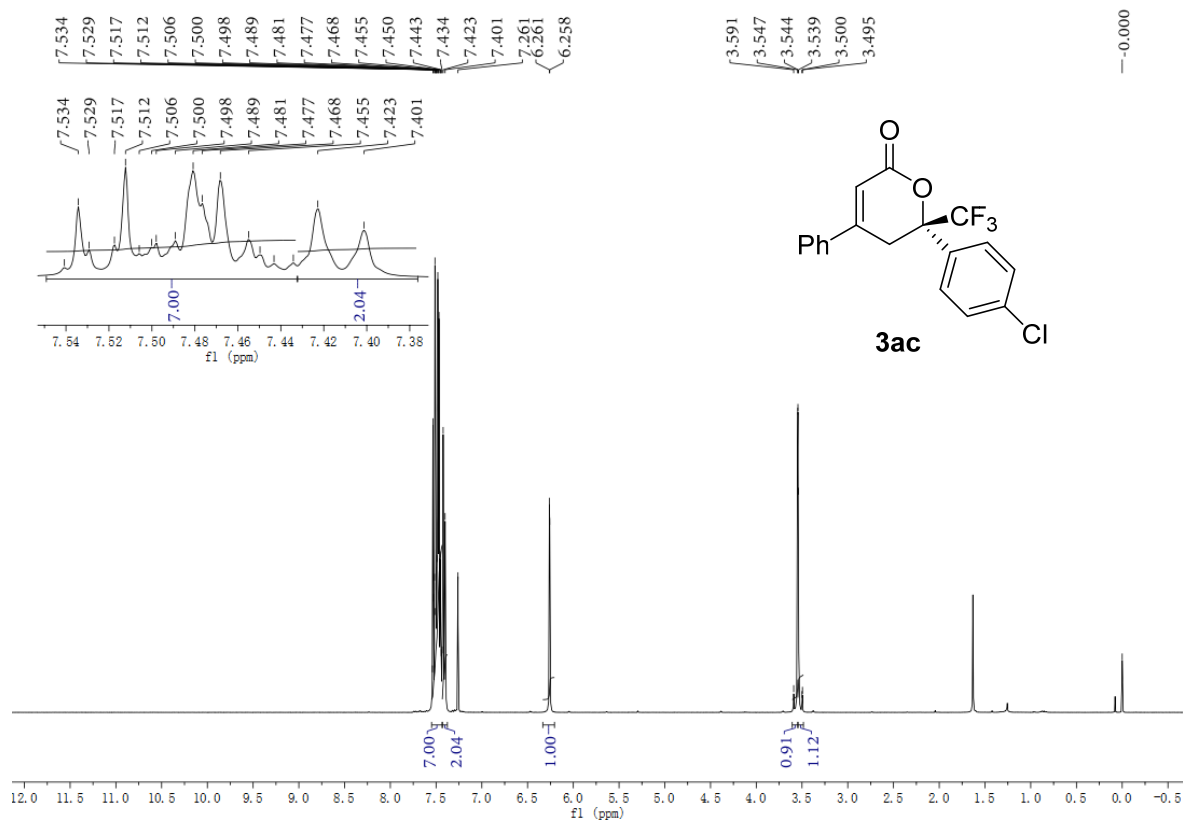
Colorless oil, 34.1 mg, 57% yield, 99% ee, $[\alpha]_{\text{D}}^{20} +118.8$ (c 0.55, CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.54-7.47 (m, 2H), 7.44-7.38 (m, 3H), 5.74 (s, 1H), 3.15 (dd, $J_1 = 18.0$ Hz, $J_2 = 1.6$ Hz, 1H), 3.01 (d, $J = 17.6$ Hz, 1H), 2.20 (t, $J = 7.6$ Hz, 2H), 1.51-1.33 (m, 2H), 1.30-1.10 (m, 2H), 0.86 (t, $J = 7.6$ Hz, 3H); ^{13}C MNR (100 MHz, CDCl_3): δ 161.5, 157.8, 134.0, 129.6, 128.7, 126.4, 123.2 (q, $J = 281.8$ Hz), 115.7, 82.3 (q, $J = 30.4$ Hz), 36.6, 31.3, 28.0, 22.0, 13.7; IR (KBr, cm^{-1}): ν 2933, 1741, 1452, 1238, 1172, 1047, 993, 871, 759, 719; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{O}_2^+$ ($[\text{M}]^+$): 298.1175, found: 298.1182; HPLC analysis (Daicel Chiralpak AD-H column, $\lambda = 254$ nm, eluent: 95/5 hexane/2-propanol, flow rate: 0.9 mL/min): $t_{\text{R}} = 11.39$ min (major), 12.45 min (minor).

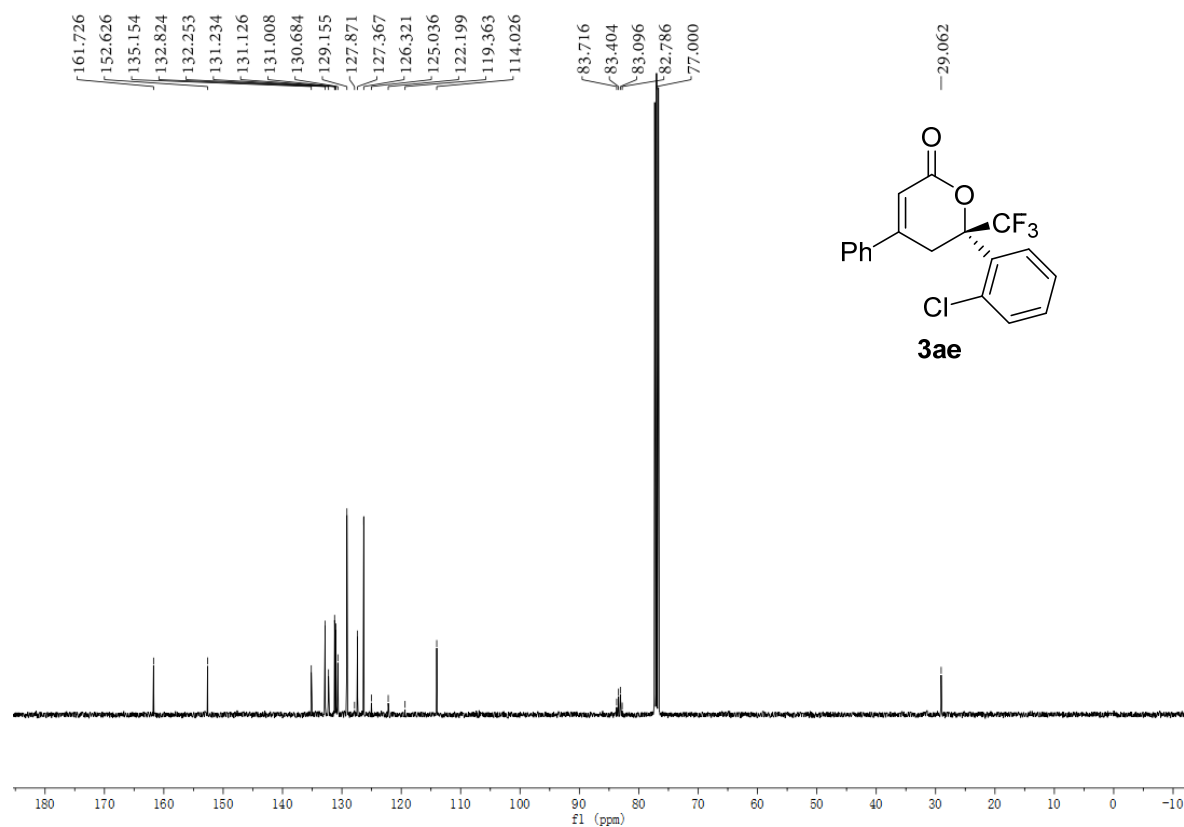
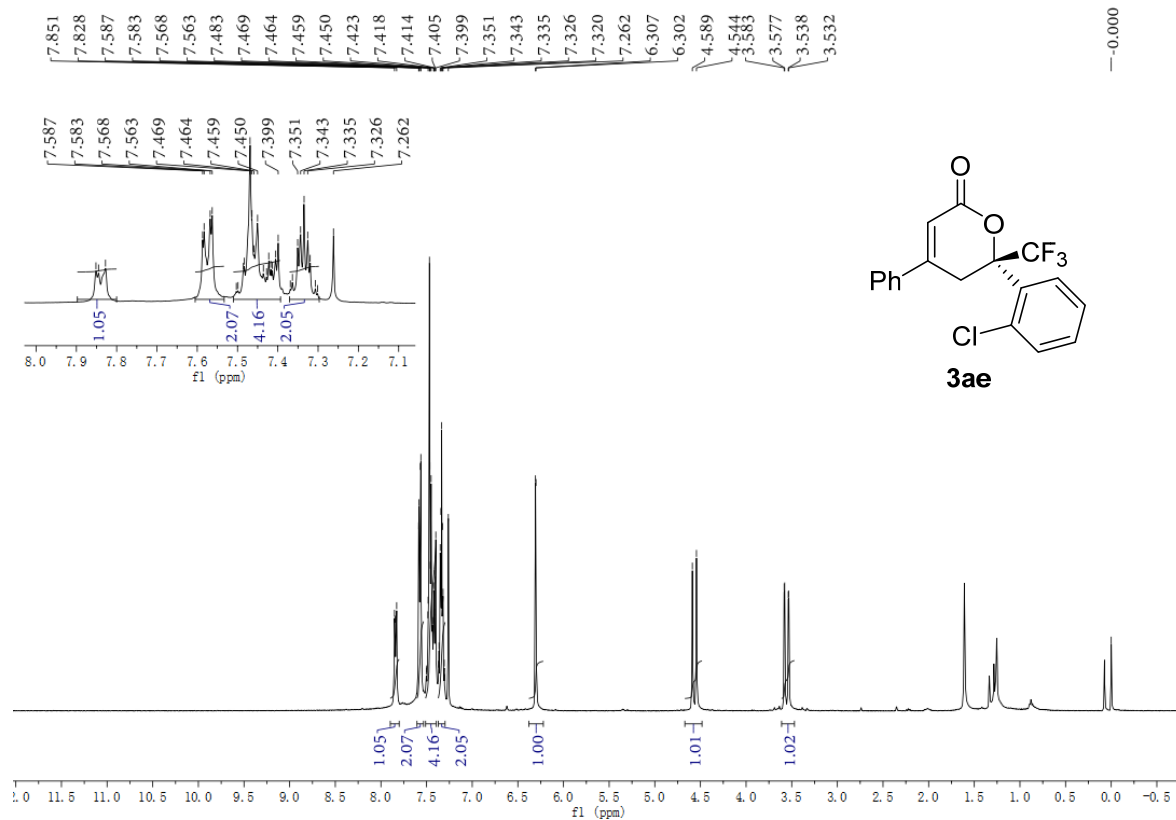
3. References

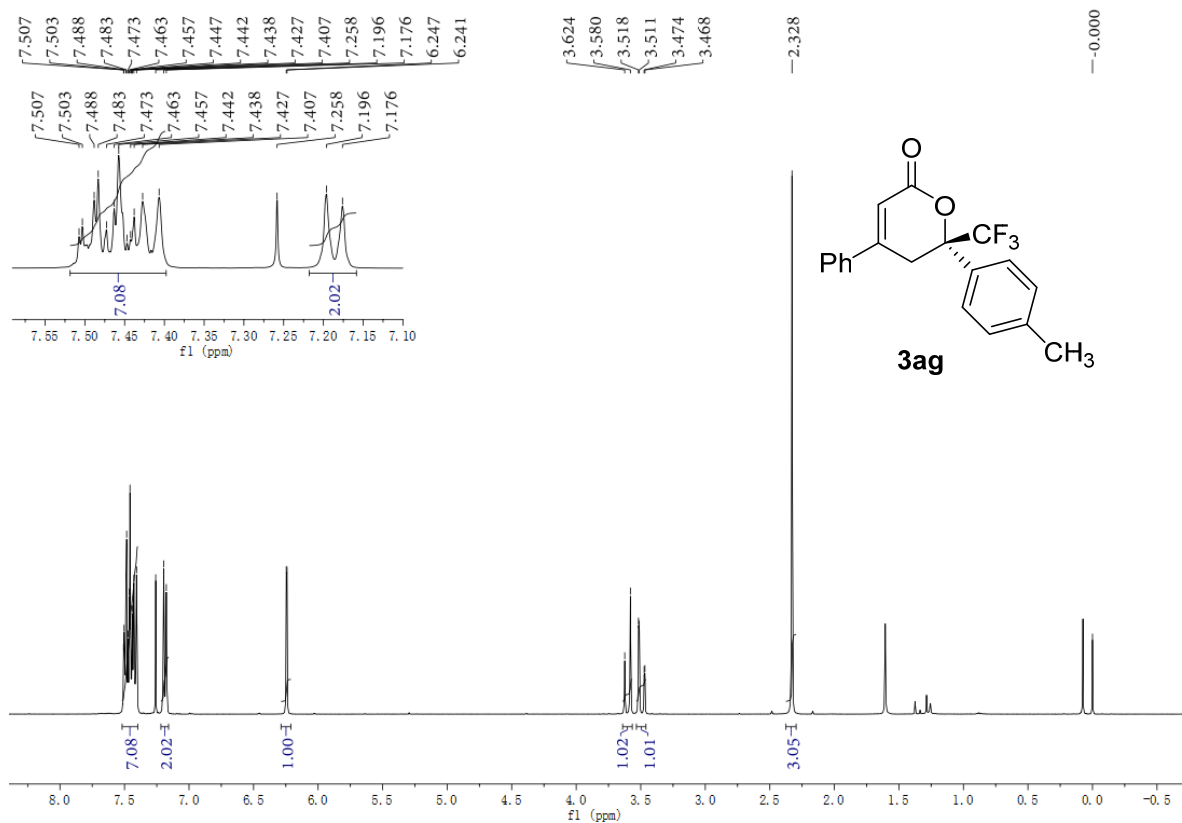
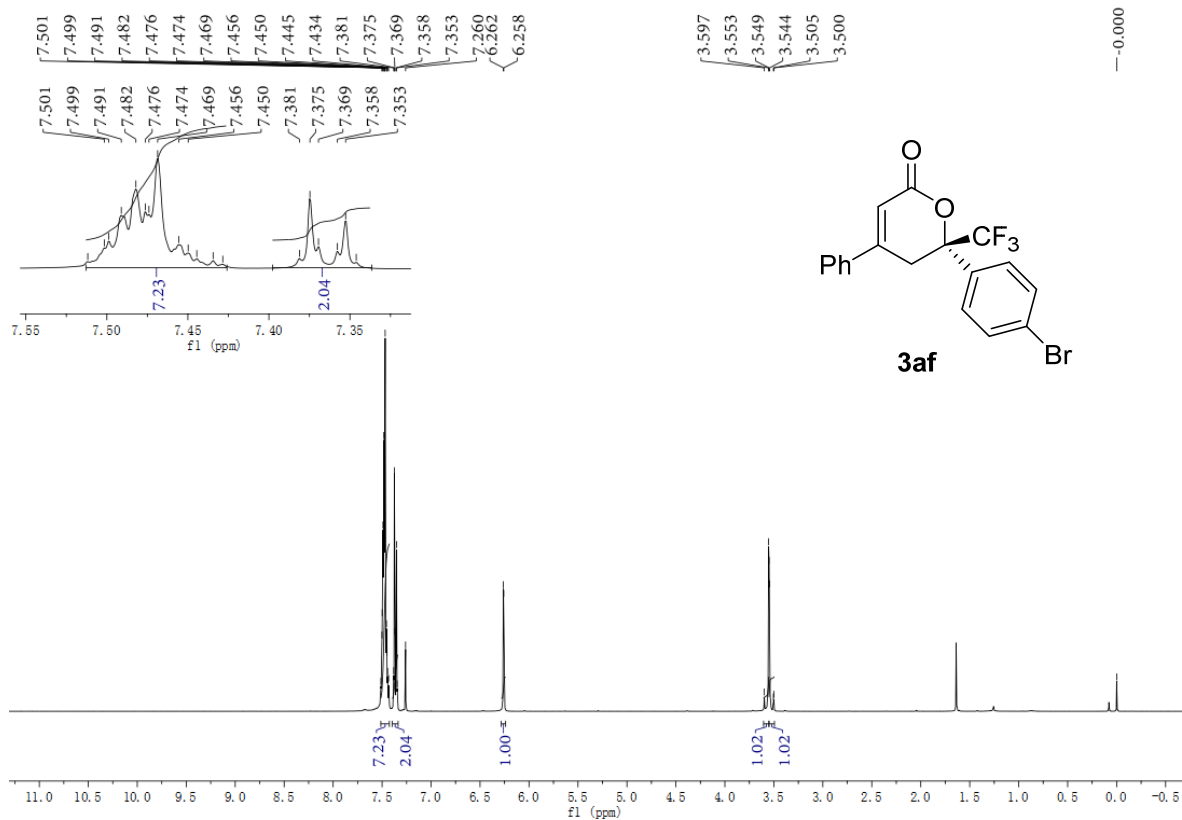
1. (a) B. Vakulya, S. Varga, A. Csámpai, T. Soós, *Org. Lett.*, 2005, **7**, 1967-1969; (b) T. Okino, Y. Hoashi, T. Furukawa, X. Xu, Y. Takemoto, *J. Am. Chem. Soc.*, 2005, **127**, 119-125; (c) A. Berkessel, S. Mukherjee, T. N. Müller, F. Cleemann, K. Roland, M. Brandenburg, J.-M. Neudörfl, J. Lex, *Org. Biomol. Chem.*, 2006, **4**, 4319-4330; (d) S.-Z. Nie, Z.-P. Hu, Y.-N. Xuan, J.-J. Wang, X.-M. Li, M. Yan, *Tetrahedron: Asymmetry*, 2010, **21**, 2055-2059; (e) W. Yang, D.-M. Du, *Adv. Synth. Catal.*, 2011, **353**, 1241-1246; (f) H. Wang, Y. Wang, H. Song, Z. Zhou, C. Tang, *Eur. J. Org. Chem.*, 2013, 4844-4851.
2. T.-Z. Li, Y. Jiang, Y.-Q. Guan, F. Sha and X.-Y. Wu, *Chem. Commun.*, 2014, **50**, 10790-10792.
3. H. Cheng, Y. Pei, F. Leng, J. Li, A. Liang, D. Zou, Y. Wu, Y. Wu, *Tetrahedron Lett.*, 2013, **54**, 4483-4486.

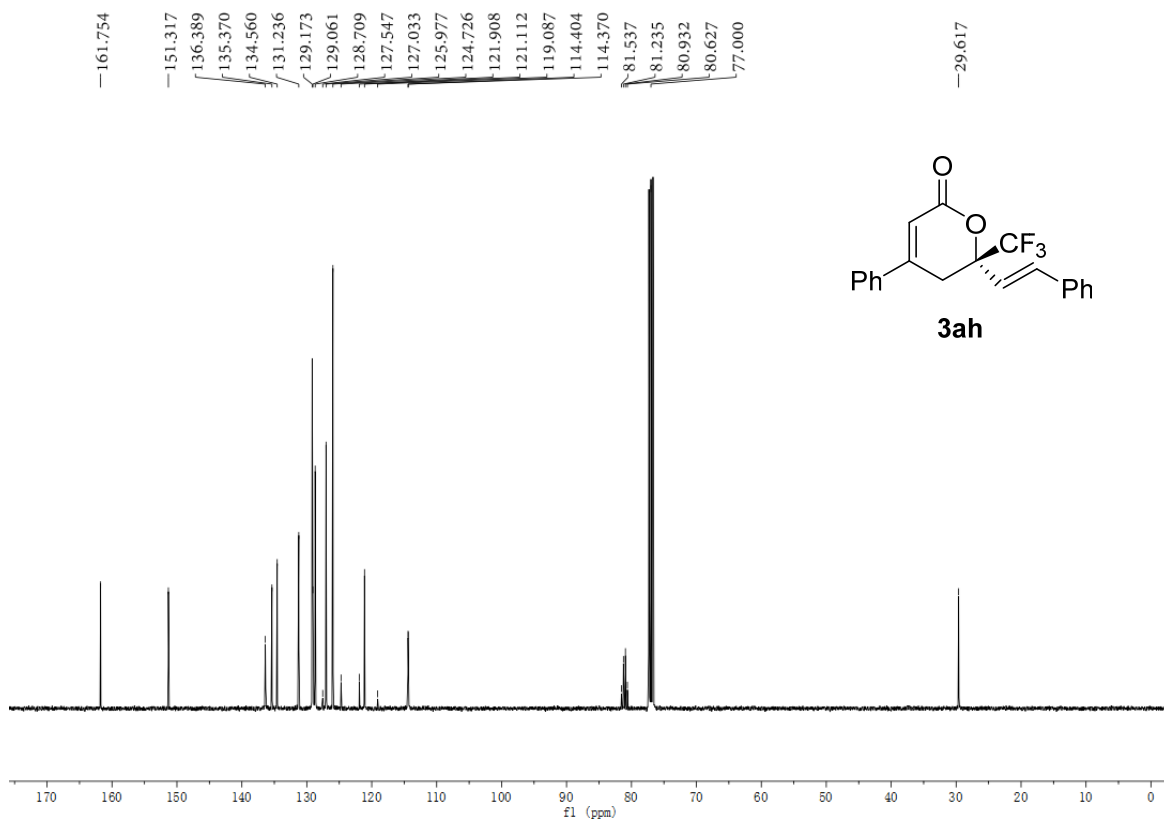
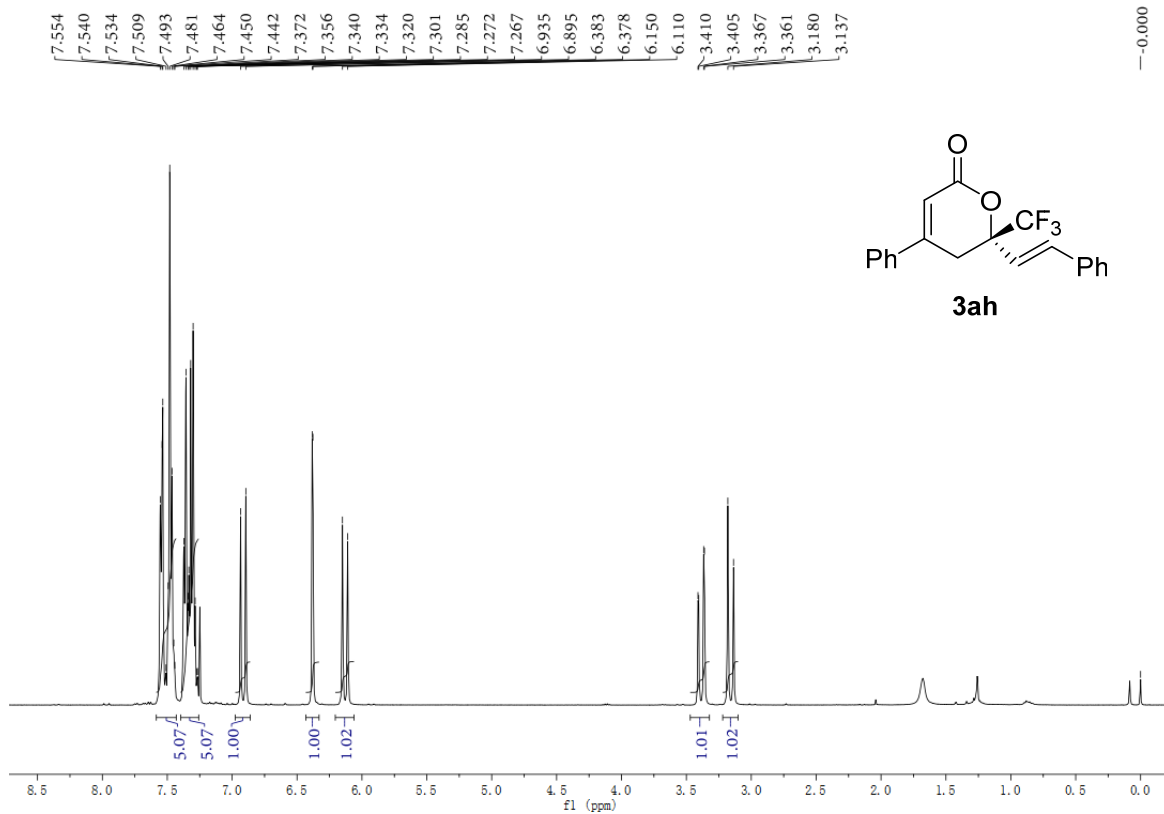
4. Copies of ^1H NMR and ^{13}C NMR Spectra for products 3

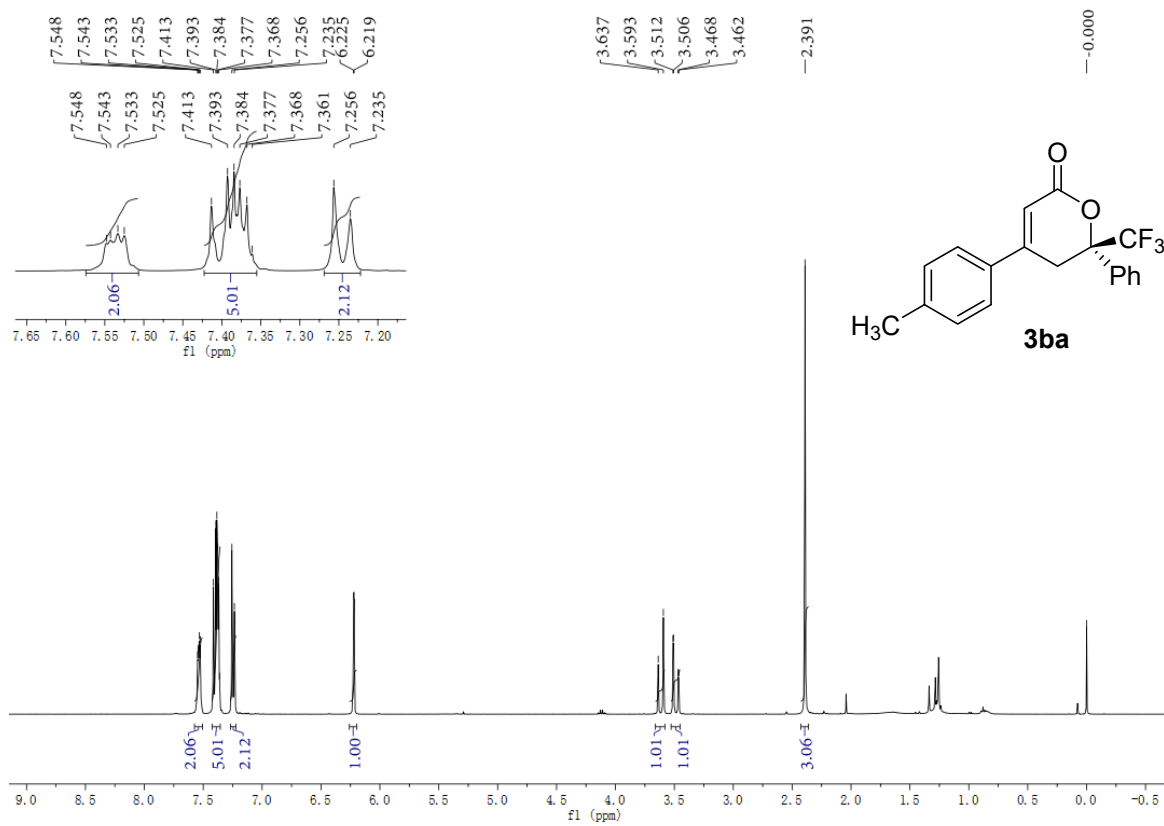
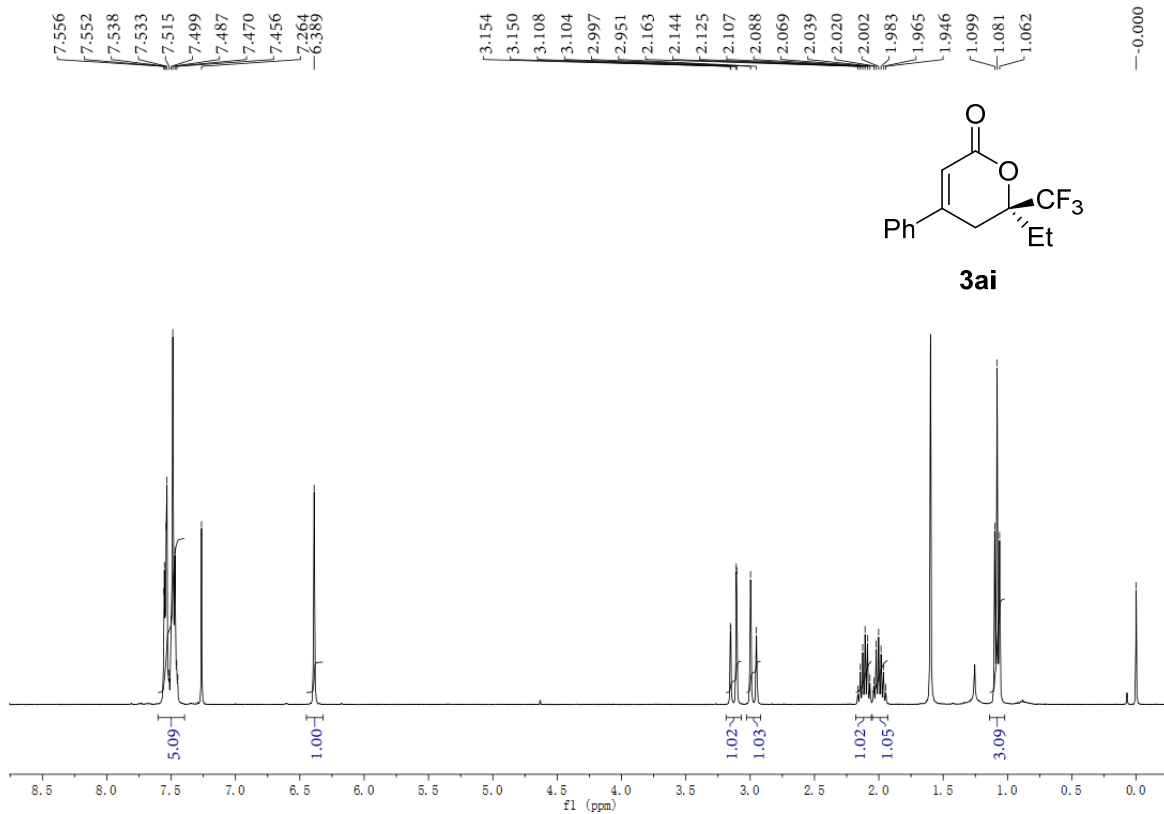


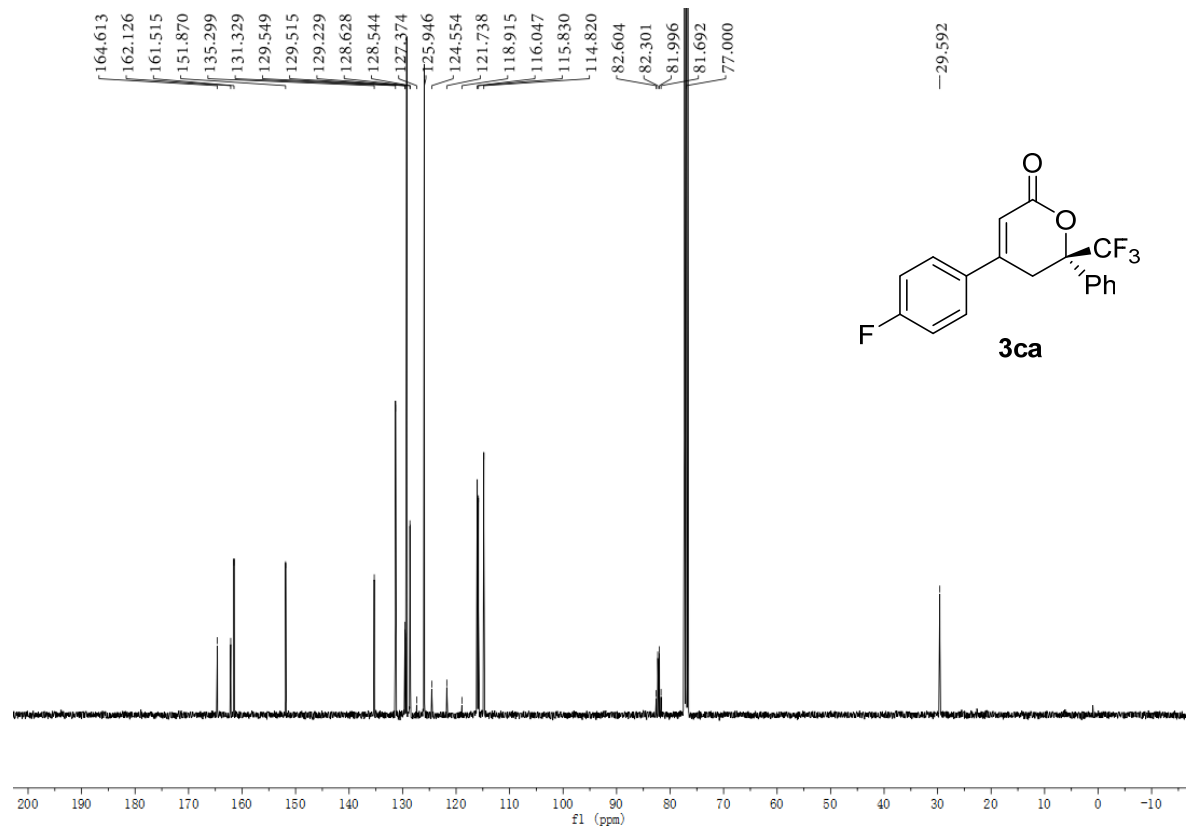
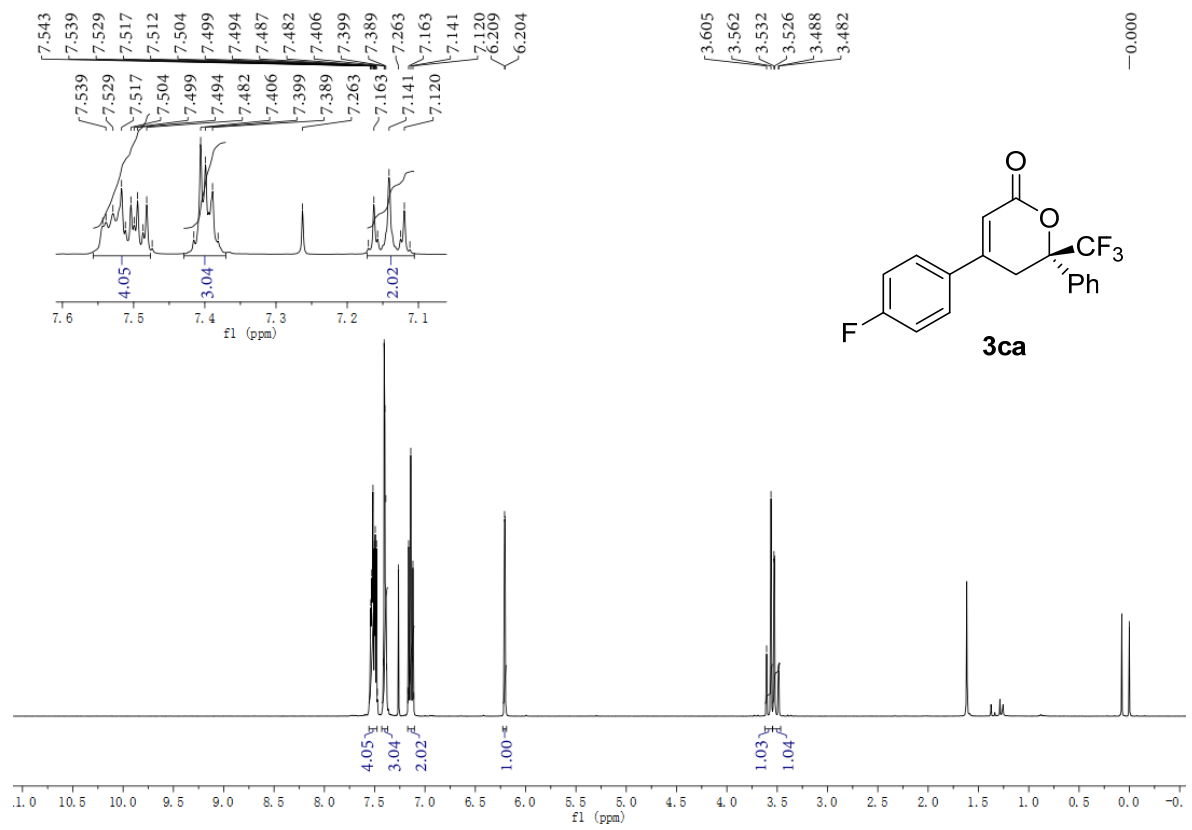


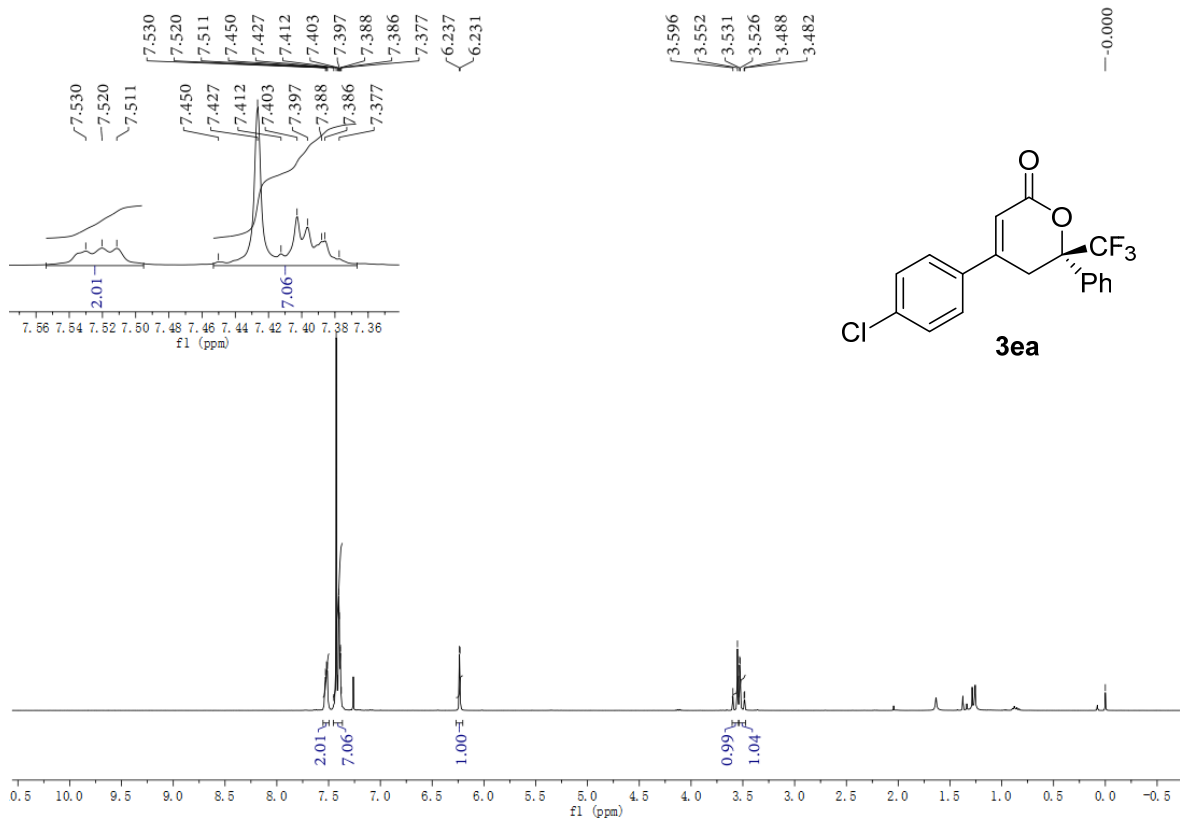
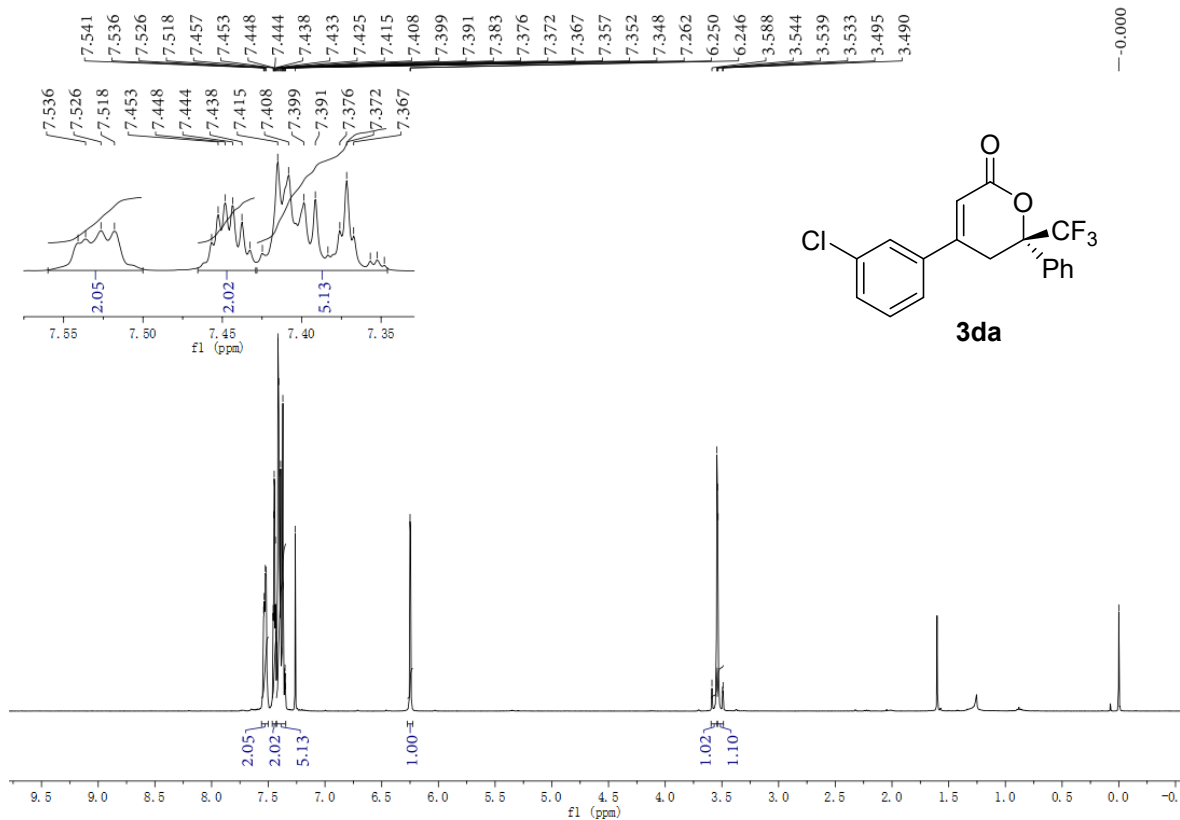


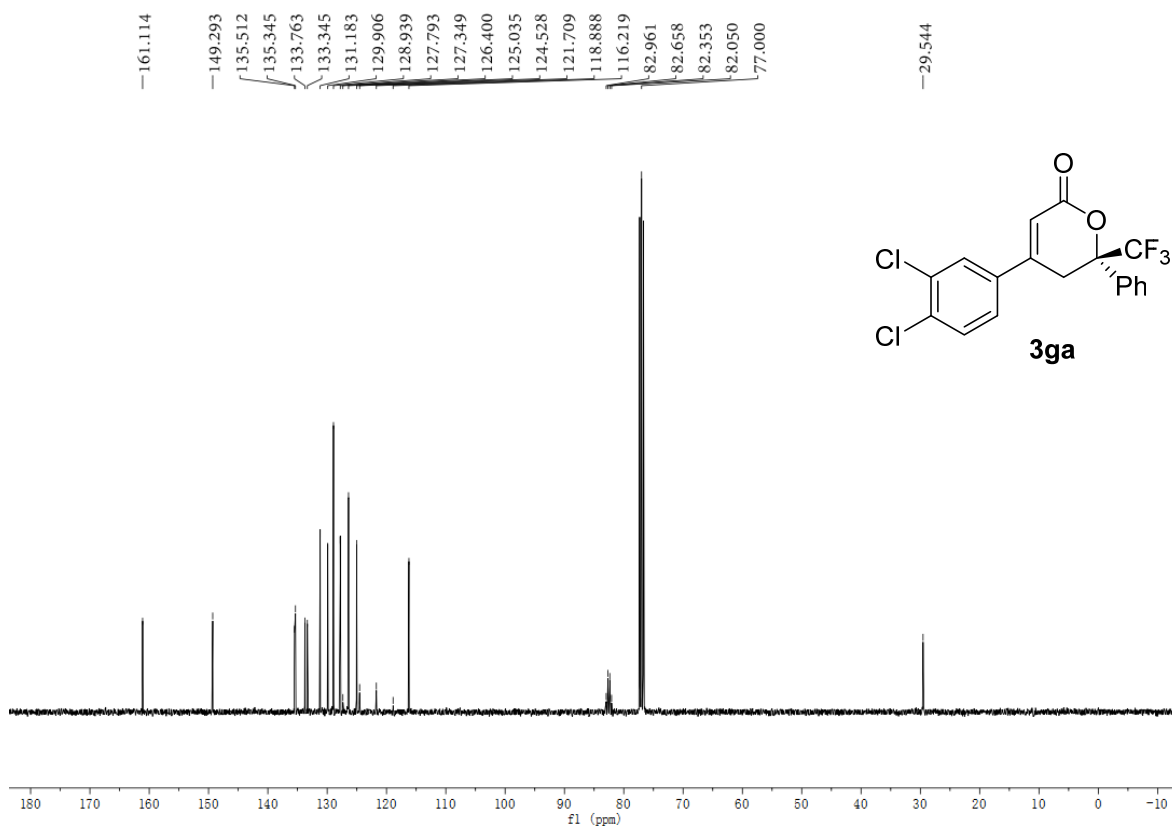
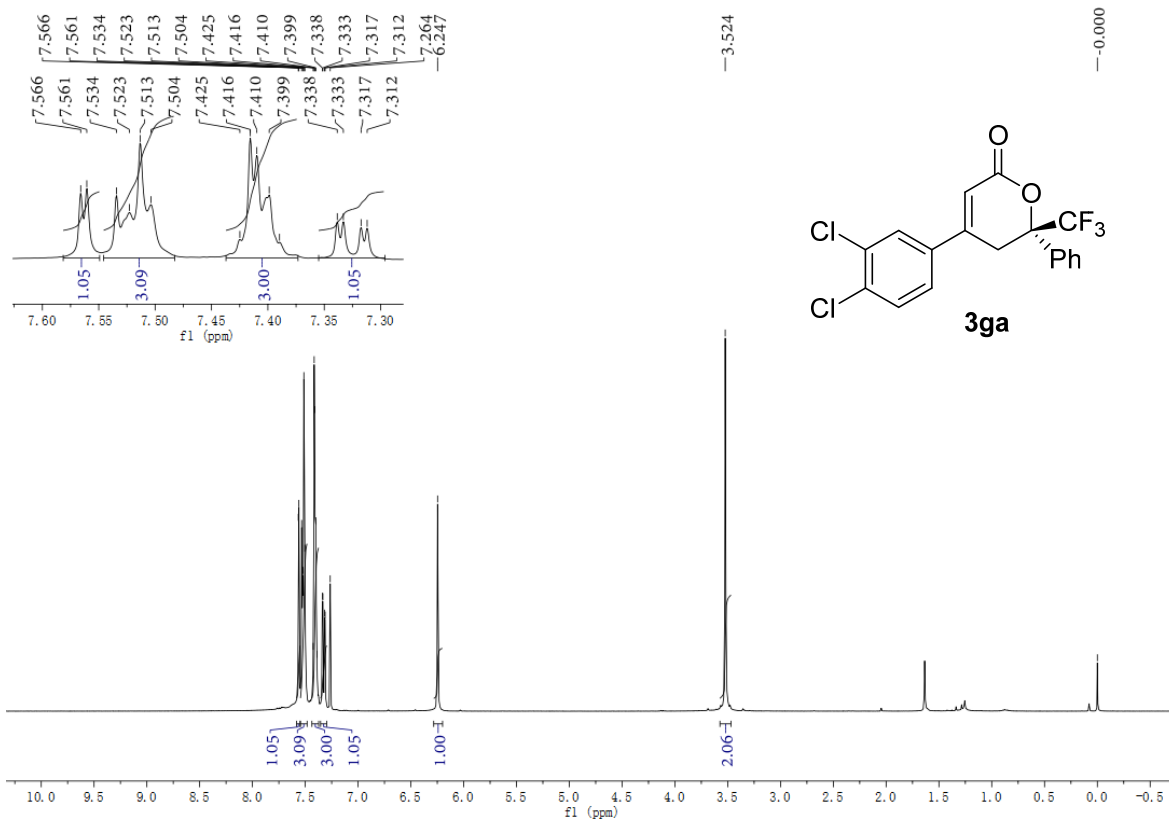


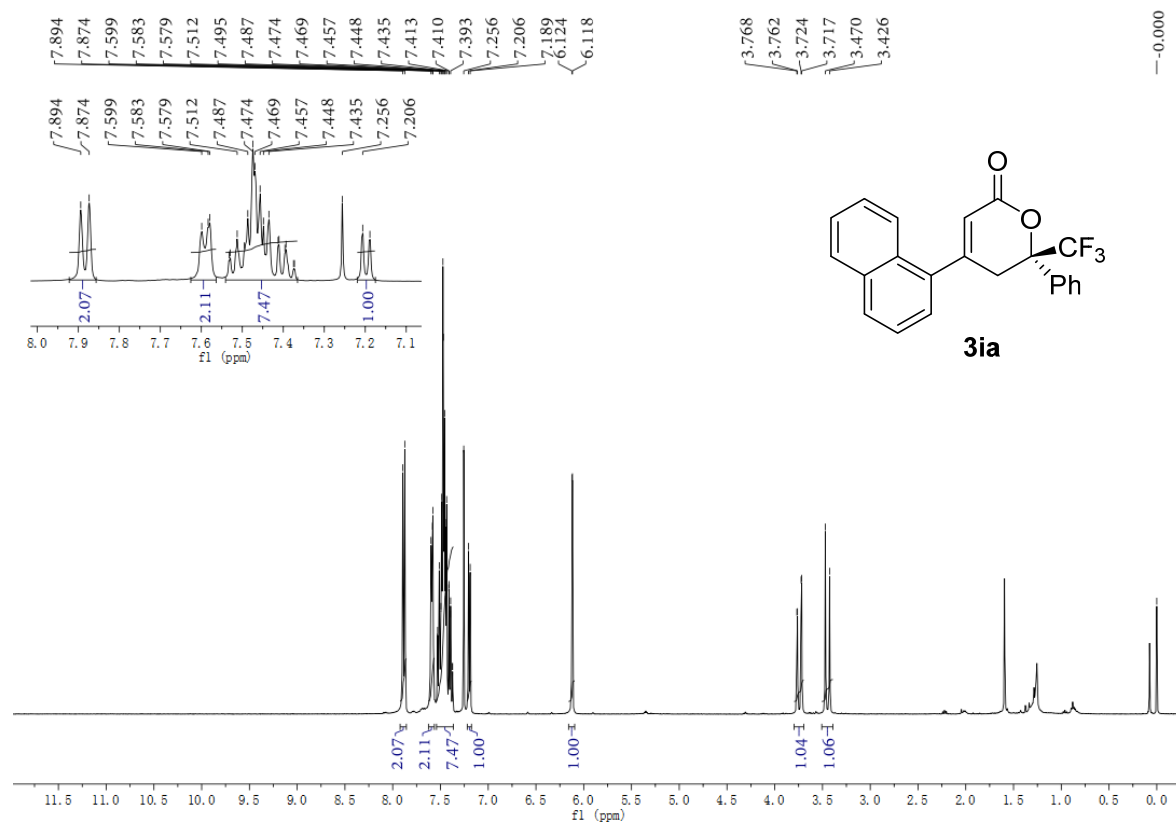
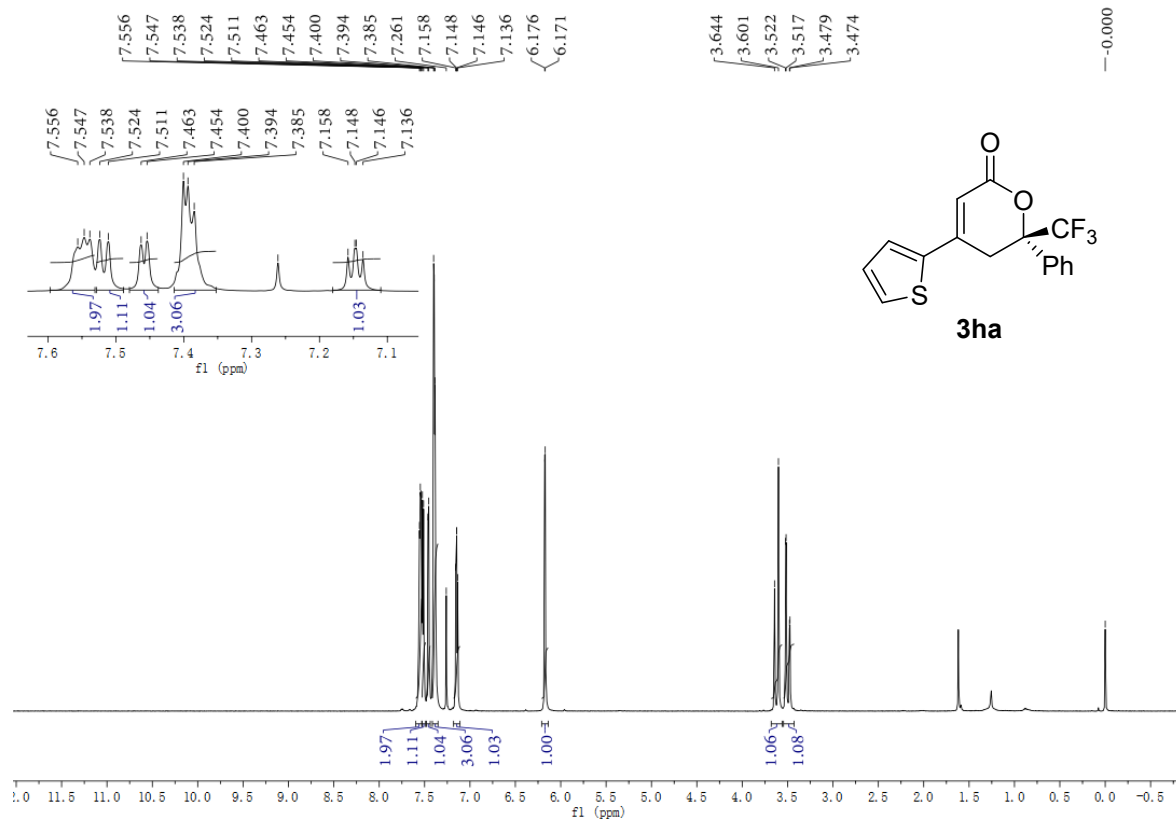


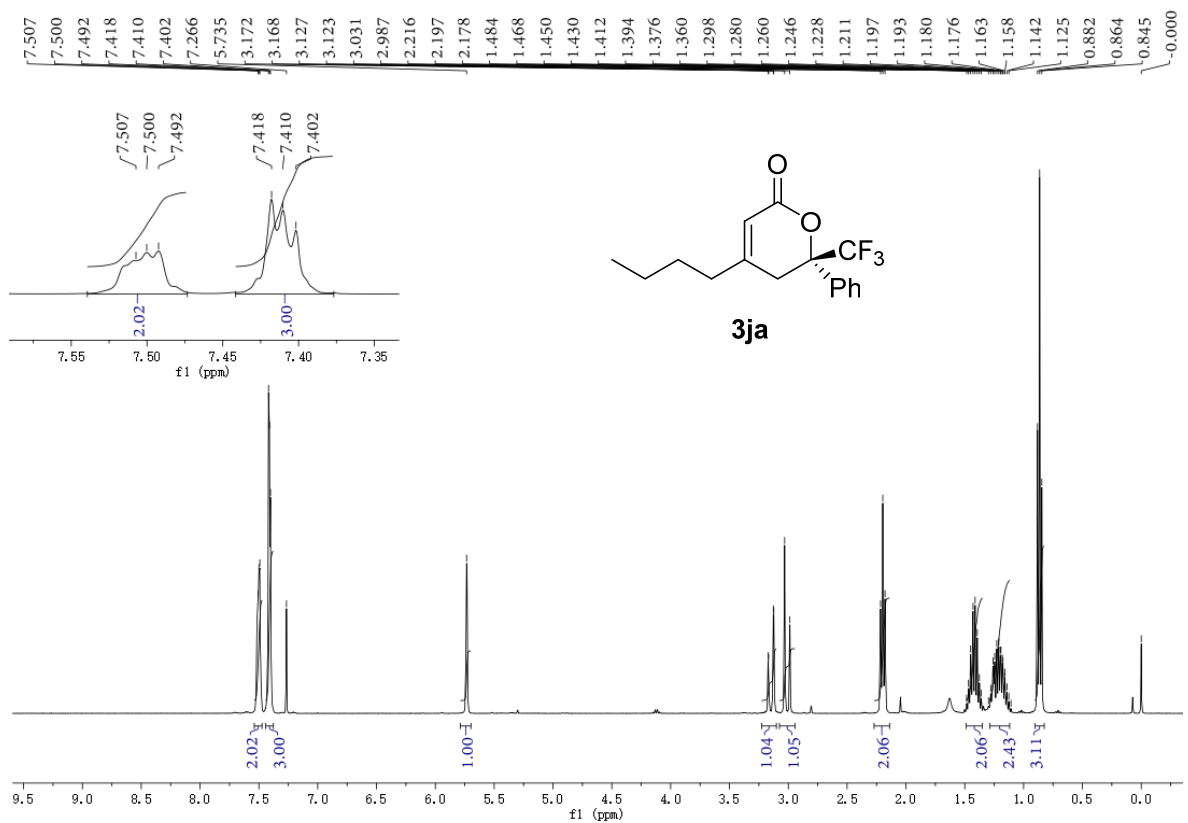
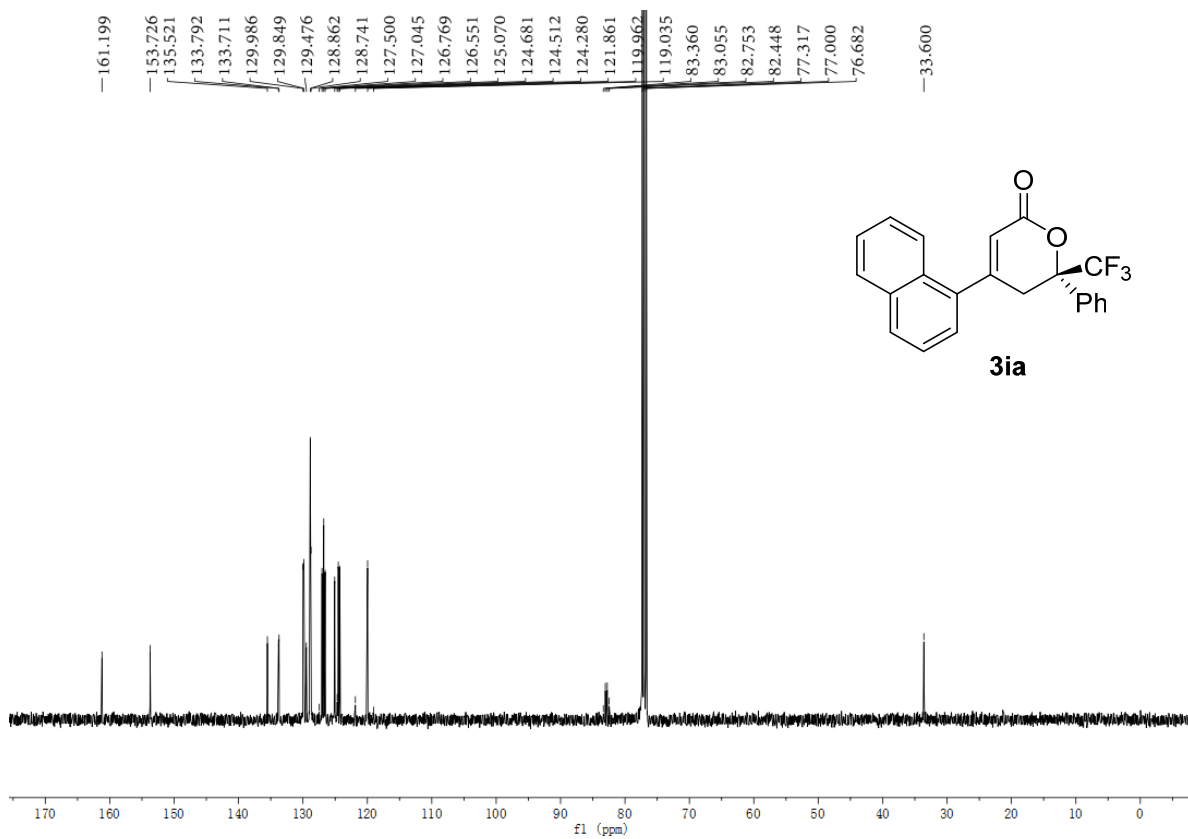


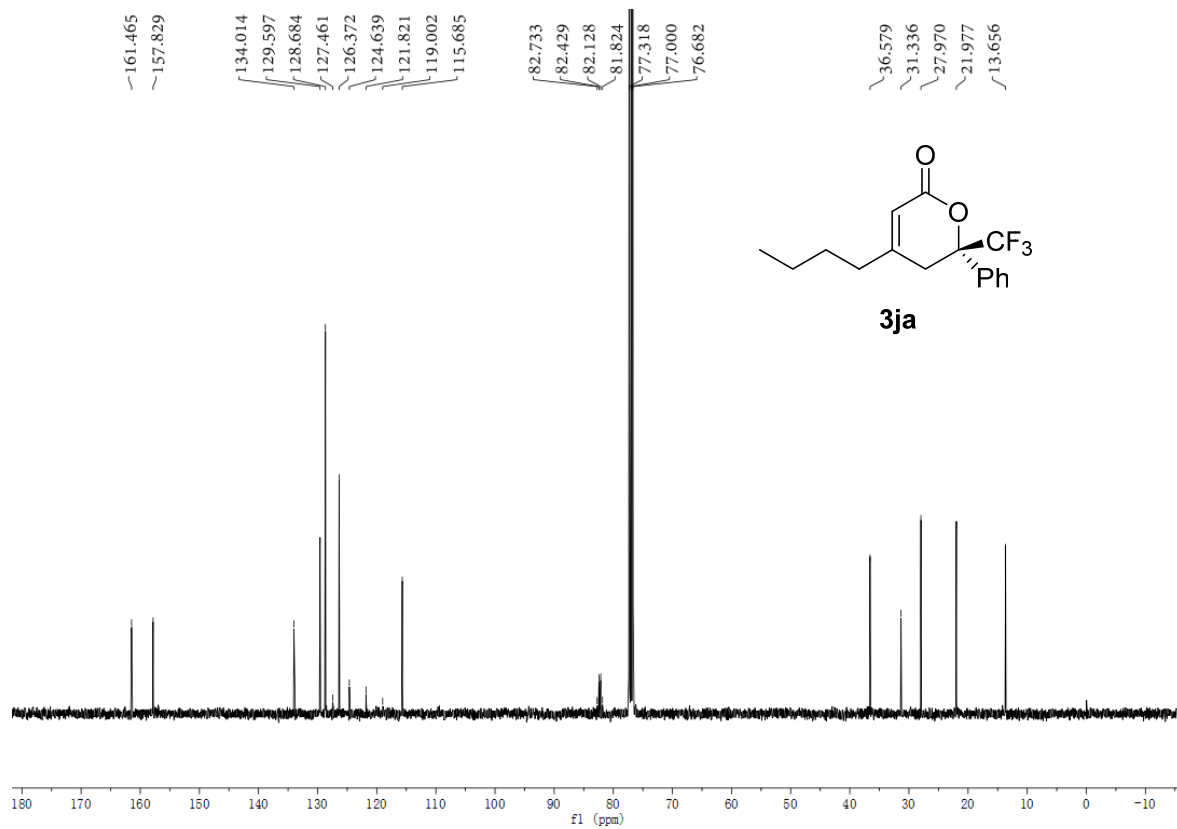




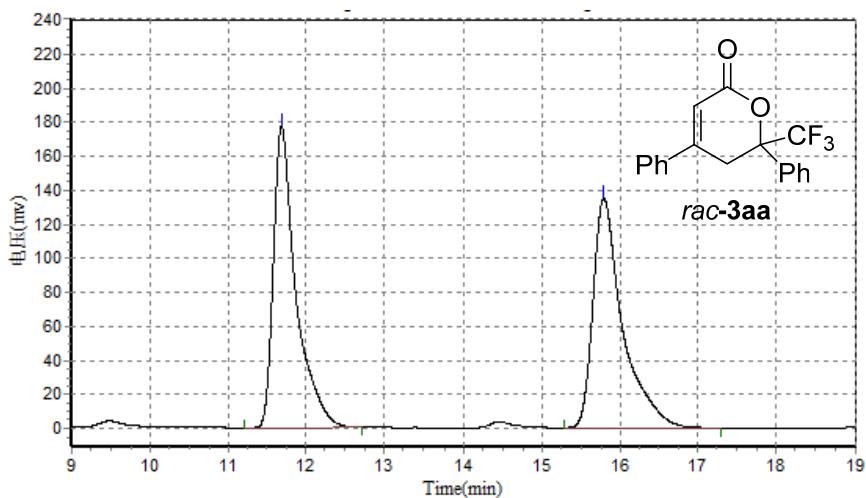






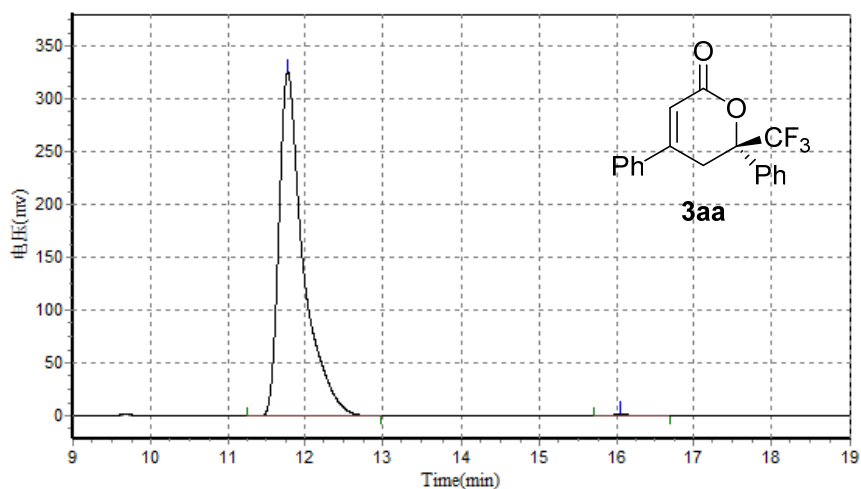


5. Copies of HPLC Spectra of the Products 3



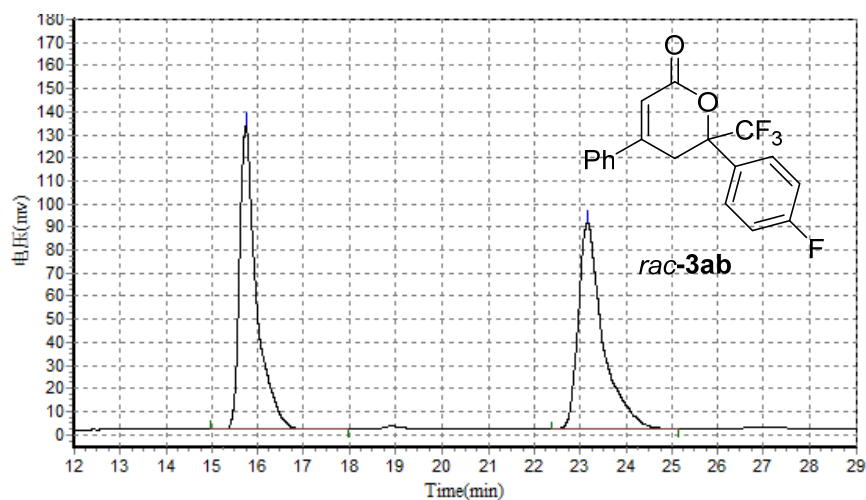
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.687	176956.625	3525965.750	49.8998
2		15.793	134924.000	3540124.750	50.1002
Total			311880.625	7066090.500	100.0000



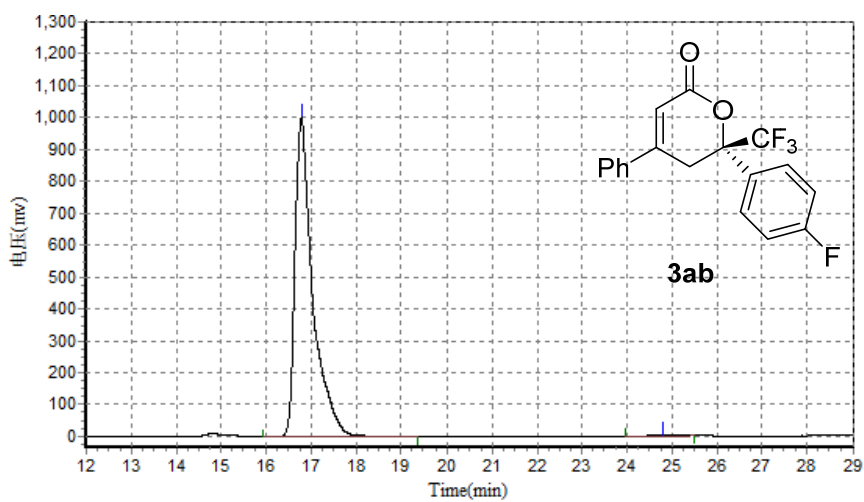
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.772	325611.875	7091776.500	99.5413
2		16.048	1353.322	32678.002	0.4587
Total			326965.197	7124454.502	100.0000



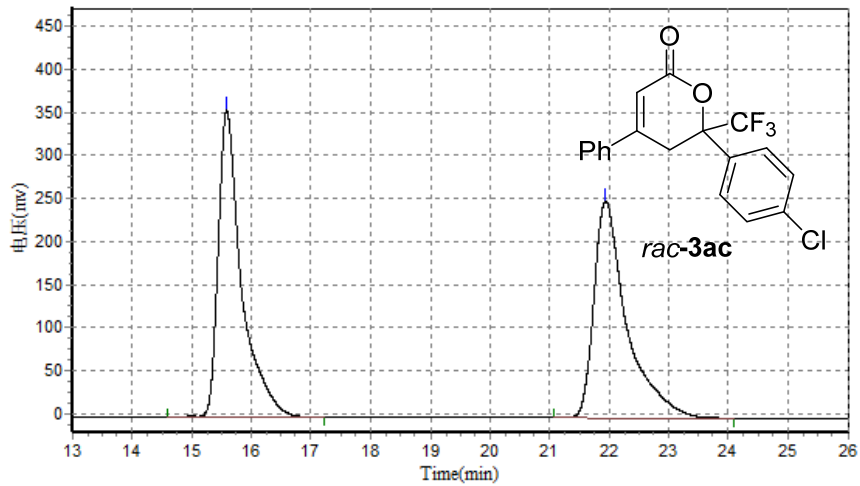
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.743	131733.047	3350922.250	50.3672
2		23.163	89150.500	3302065.000	49.6328
Total			220883.547	6652987.250	100.0000



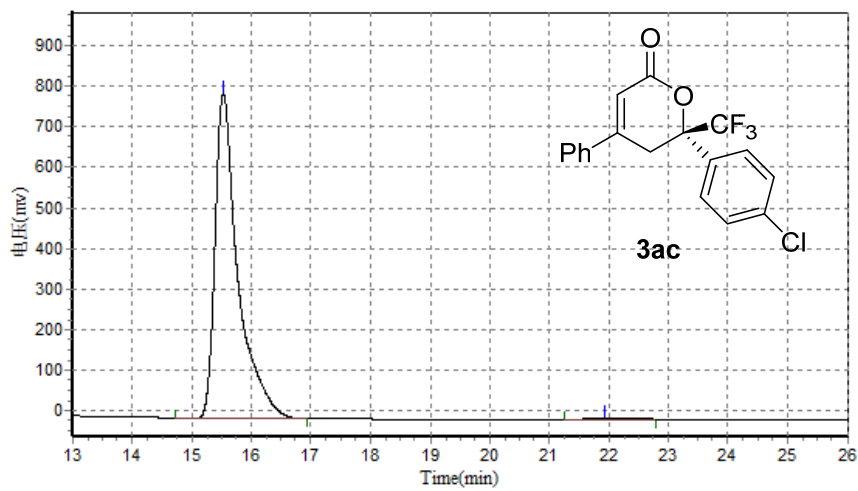
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.787	998433.375	27177788.000	99.8056
2		24.810	1777.917	52927.410	0.1944
Total			1000211.292	27230715.410	100.0000



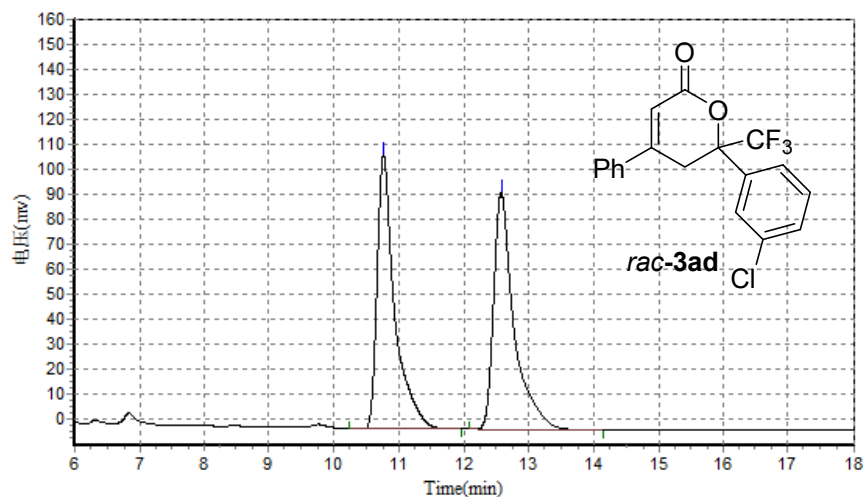
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.588	356577.625	9659311.000	50.1484
2		21.940	251944.203	9602132.000	49.8516
Total			608521.828	19261443.000	100.0000



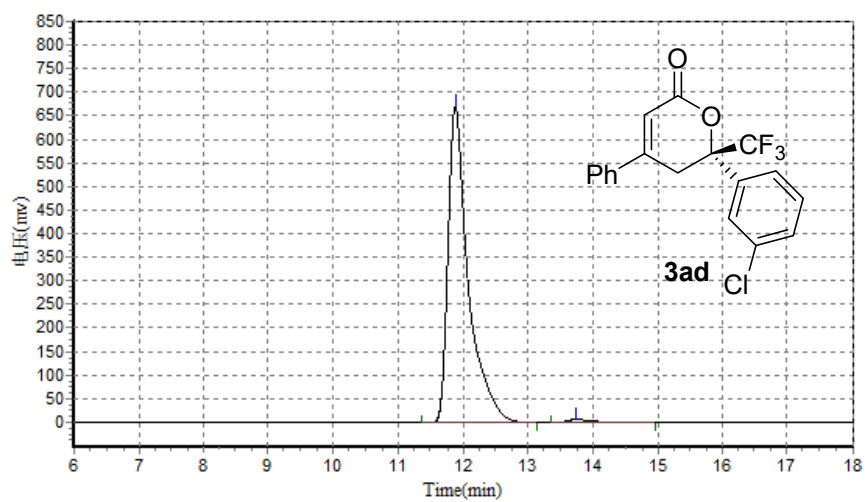
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.532	798678.625	21308082.000	99.5746
2		21.920	2942.826	91027.516	0.4254
Total			801621.451	21399109.516	100.0000



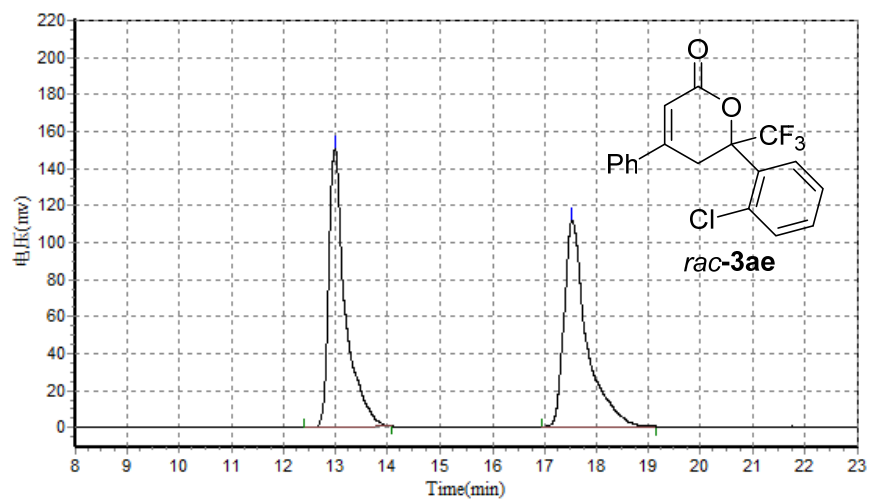
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.770	109468.711	2062802.625	49.7551
2		12.567	94835.844	2083111.375	50.2449
Total			204304.555	4145914.000	100.0000



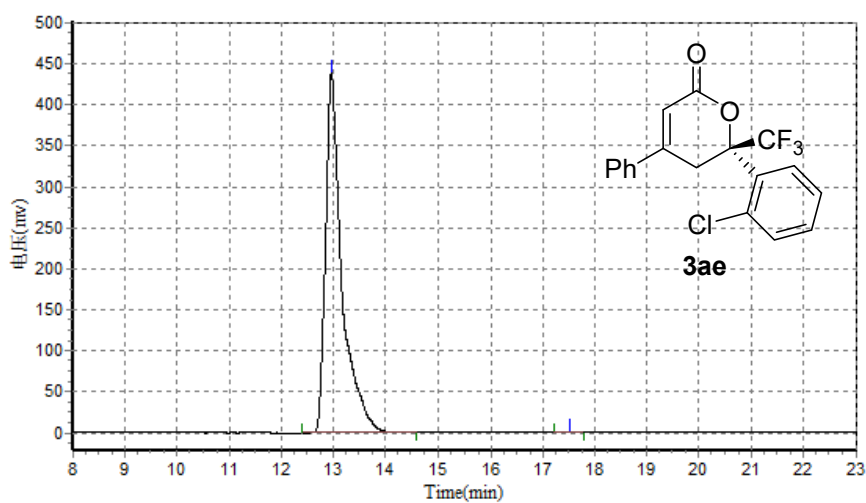
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.872	670408.625	14579587.000	98.9015
2		13.747	6687.911	161932.547	1.0985
Total			677096.536	14741519.547	100.0000



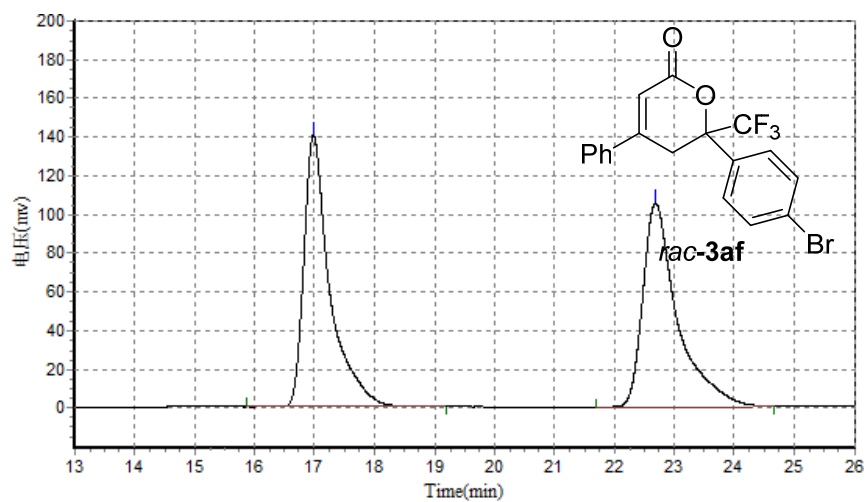
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.997	150040.906	3339293.750	49.9181
2		17.527	111622.758	3350249.750	50.0819
Total			261663.664	6689543.500	100.0000



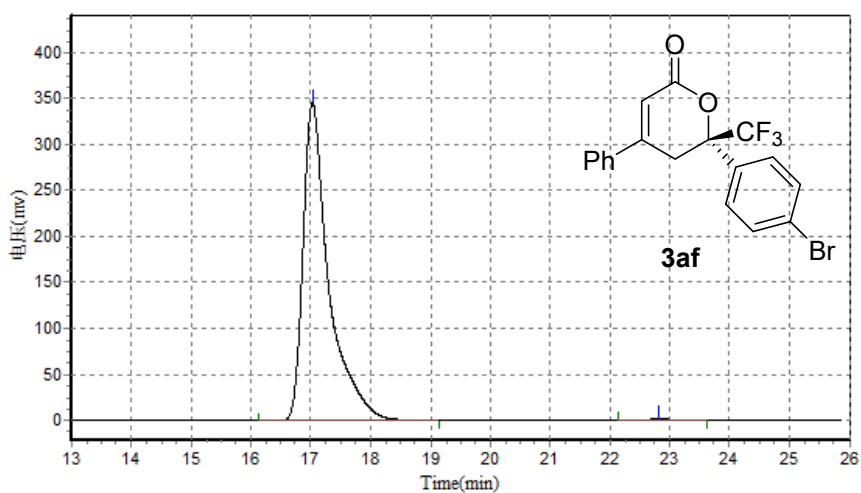
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.962	438120.031	9558516.000	99.8415
2		17.518	819.023	15175.950	0.1585
Total			438939.054	9573691.950	100.0000



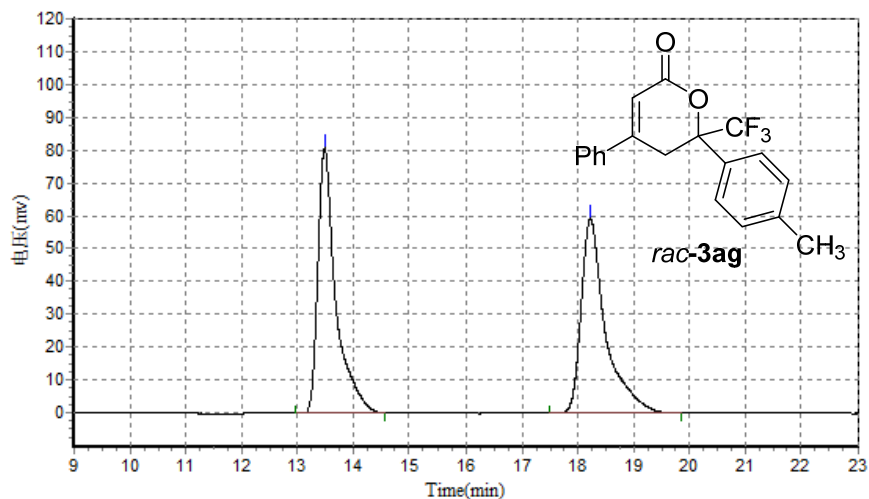
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.988	140142.141	4232241.000	50.2405
2		22.687	105120.523	4191714.750	49.7595
Total			245262.664	8423955.750	100.0000



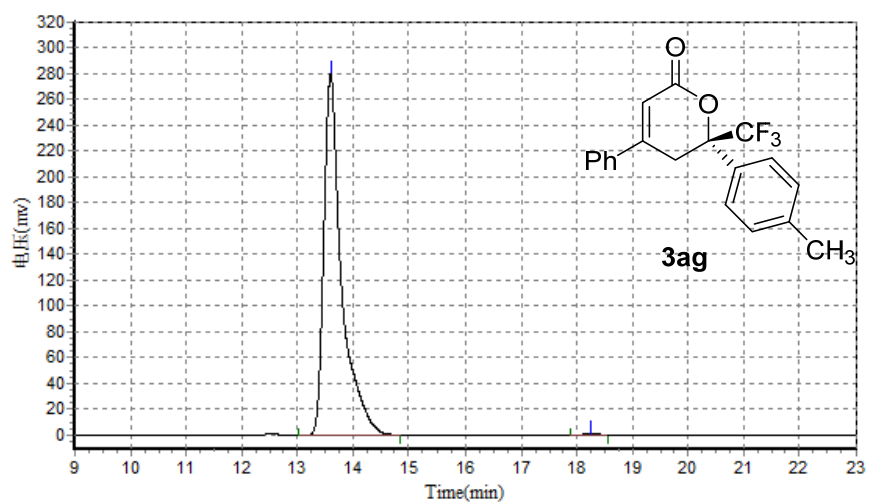
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.037	344927.906	10318541.000	99.6145
2		22.820	1224.653	39927.602	0.3855
Total			346152.559	10358468.602	100.0000



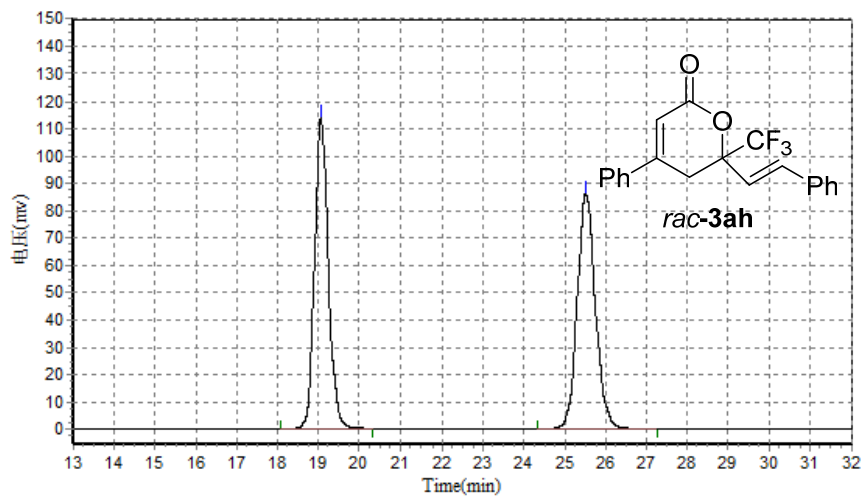
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.488	80731.836	1802093.625	50.0225
2		18.222	59215.820	1800471.125	49.9775
Total			139947.656	3602564.750	100.0000



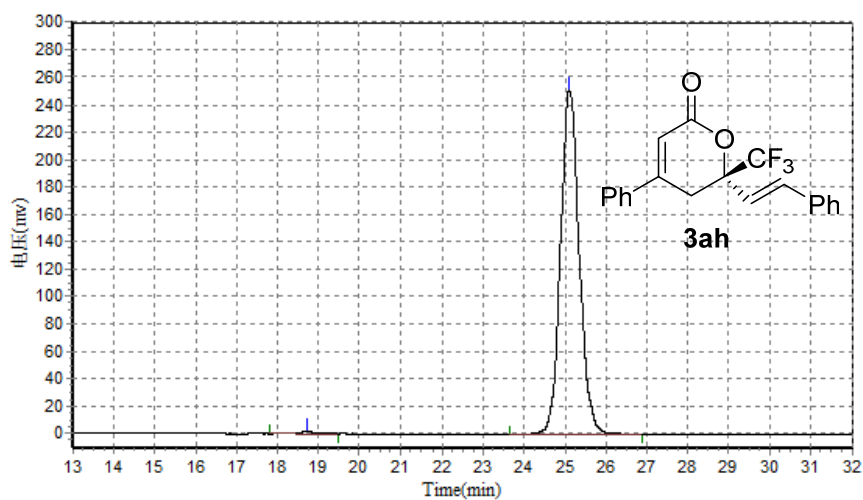
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.597	279737.750	6185282.000	99.8194
2		18.245	559.227	11193.000	0.1806
Total			280296.977	6196475.000	100.0000



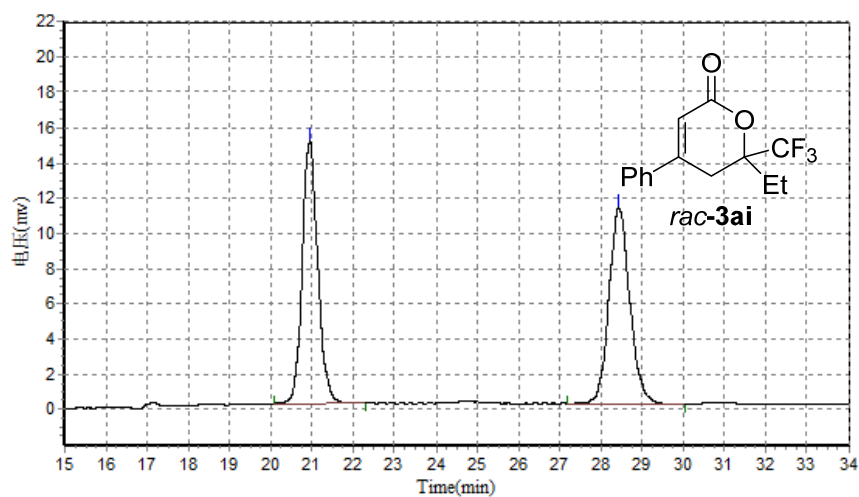
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.053	113714.773	2666137.500	49.9611
2		25.507	86113.391	2670287.500	50.0389
Total			199828.164	5336425.000	100.0000



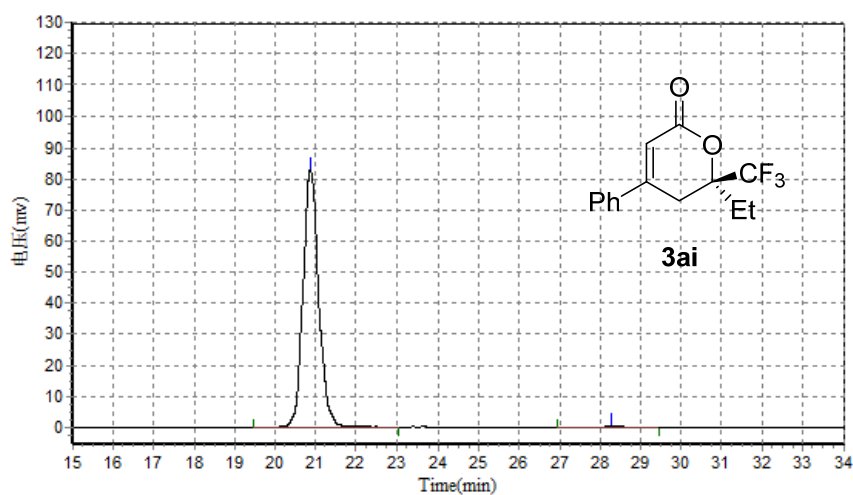
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.728	1608.469	40082.301	0.5005
2		25.098	251175.906	7968642.500	99.4995
Total			252784.375	8008724.801	100.0000



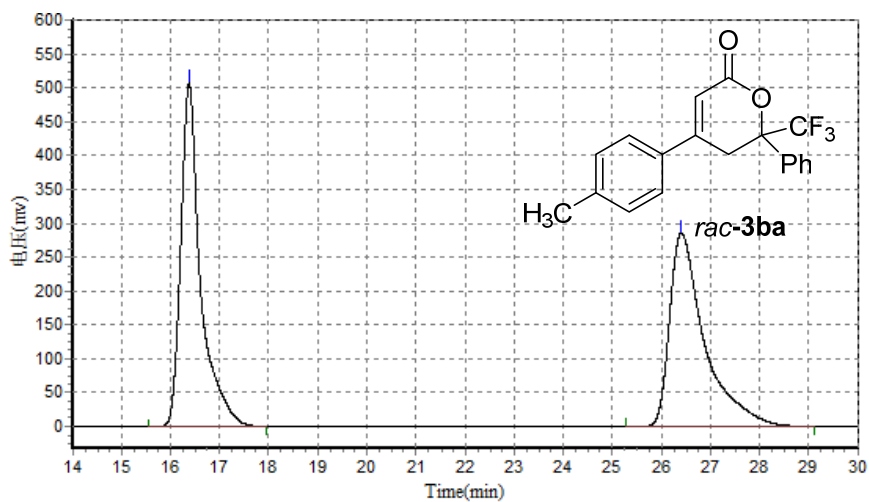
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.958	14925.946	391908.344	49.8716
2		28.422	11158.030	393925.969	50.1284
Total			26083.977	785834.313	100.0000



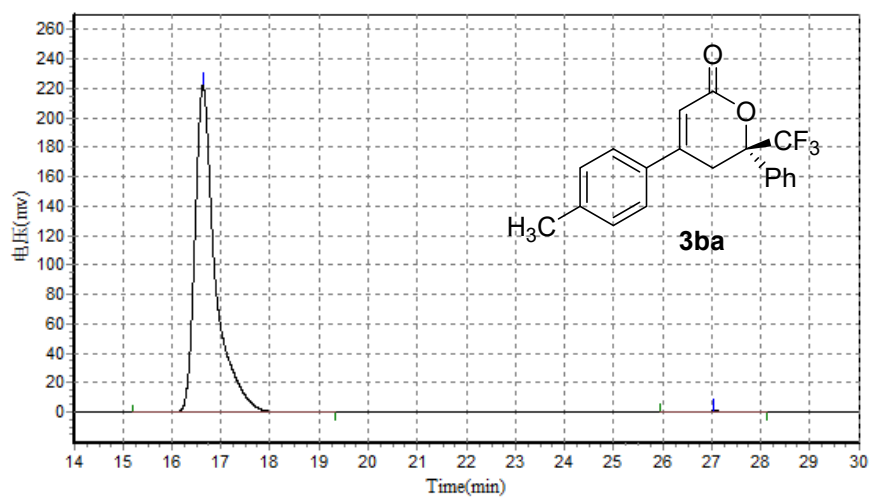
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.862	82819.188	2224088.000	99.4840
2		28.258	246.535	11535.000	0.5160
Total			83065.722	2235623.000	100.0000



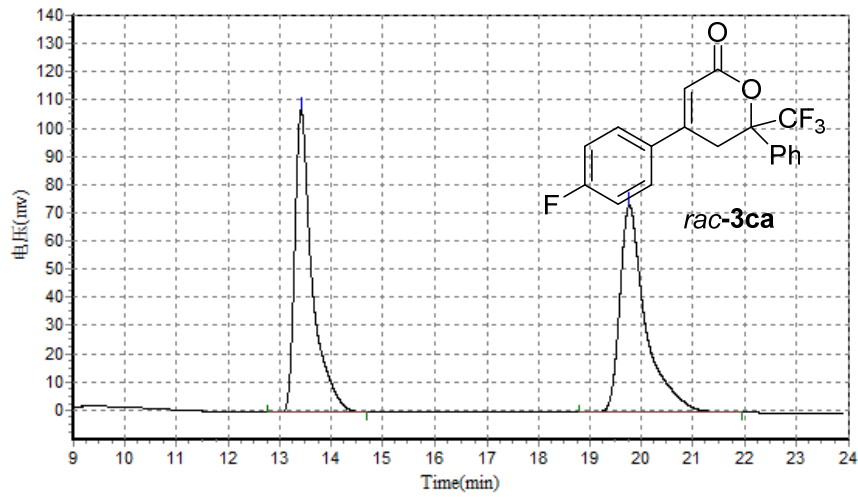
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.372	506154.406	14178490.000	50.0639
2		26.412	285633.594	14142320.000	49.9361
Total			791788.000	28320810.000	100.0000



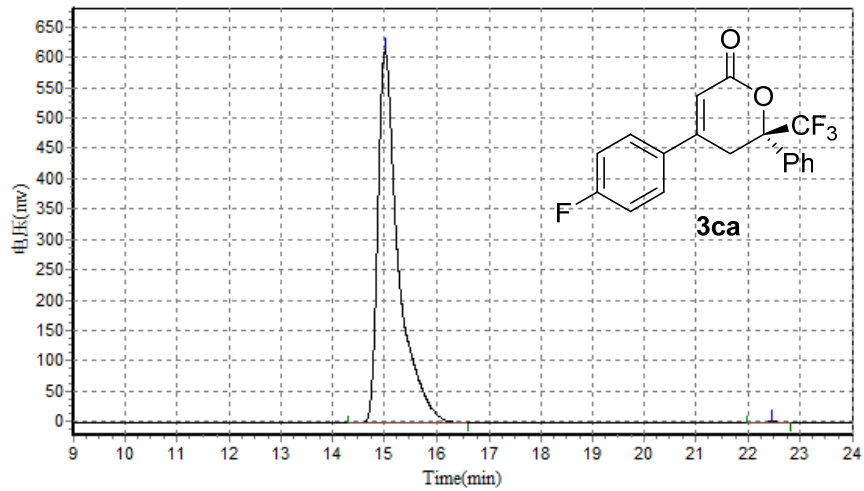
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.627	222027.406	6378714.000	99.5913
2		27.040	670.343	26177.498	0.4087
Total			222697.750	6404891.498	100.0000



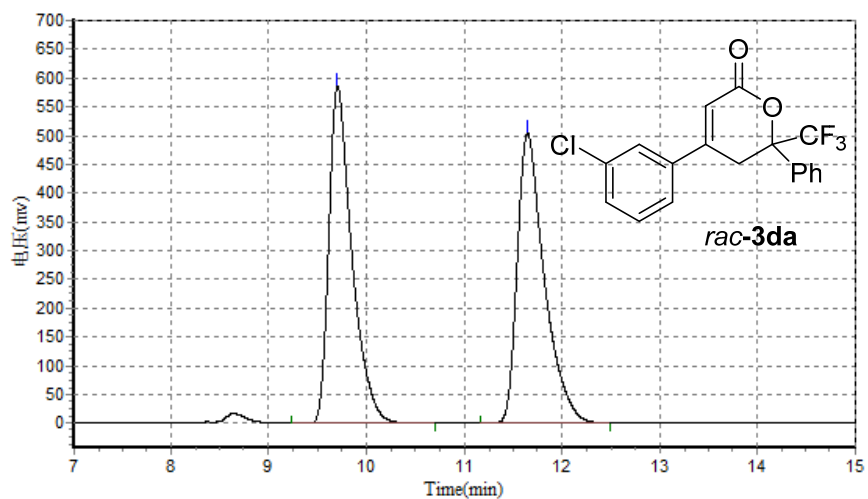
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.420	107273.883	2520516.250	49.7671
2		19.765	73518.211	2544103.250	50.2329
Total			180792.094	5064619.500	100.0000



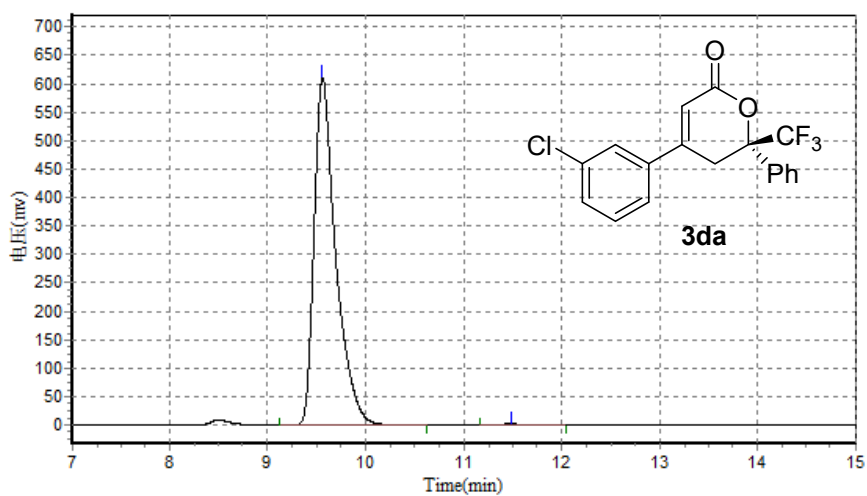
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.015	611238.938	16811072.000	99.8837
2		22.467	792.086	19581.701	0.1163
Total			612031.024	16830653.701	100.0000



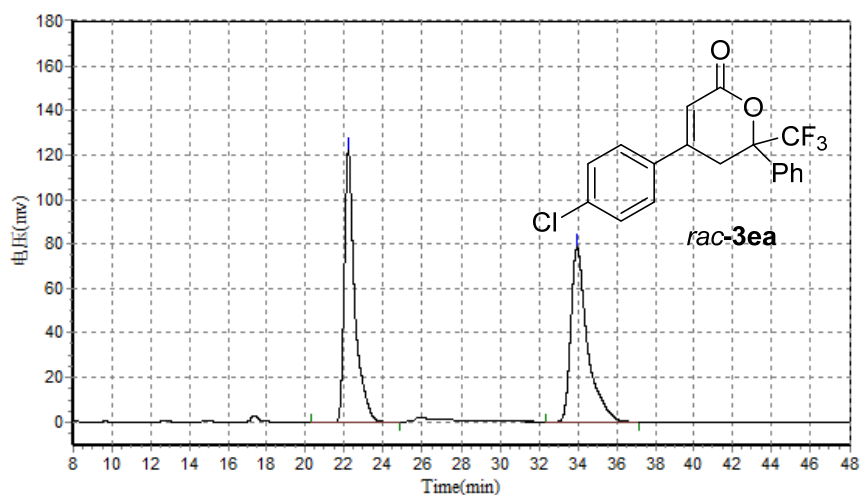
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.707	584823.938	9657408.000	49.7771
2		11.645	504012.844	9743881.000	50.2229
Total			1088836.781	19401289.000	100.0000



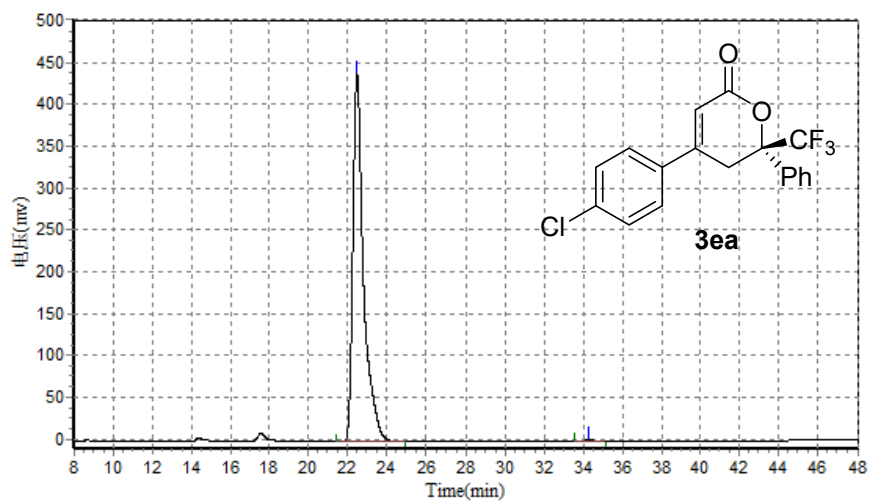
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.562	609451.125	9425343.000	99.6215
2		11.482	2061.542	35812.250	0.3785
Total			611512.667	9461155.250	100.0000



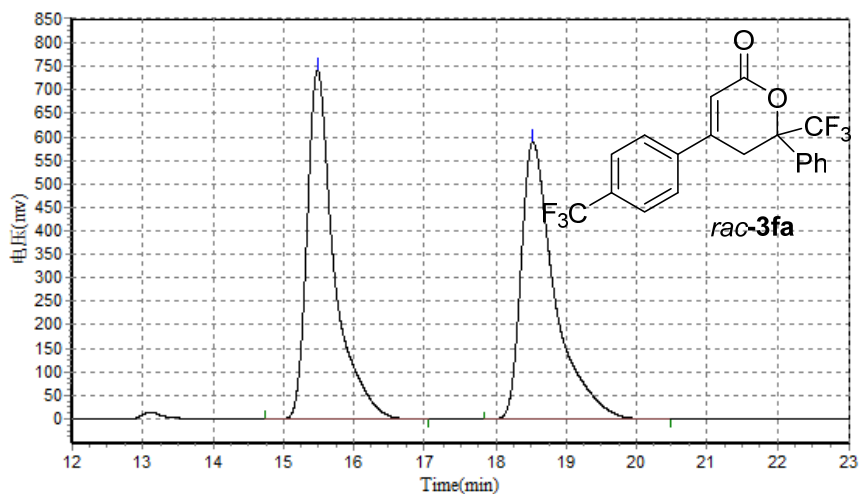
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.212	121940.164	4591132.500	49.5659
2		33.953	78561.008	4671544.500	50.4341
Total			200501.172	9262677.000	100.0000



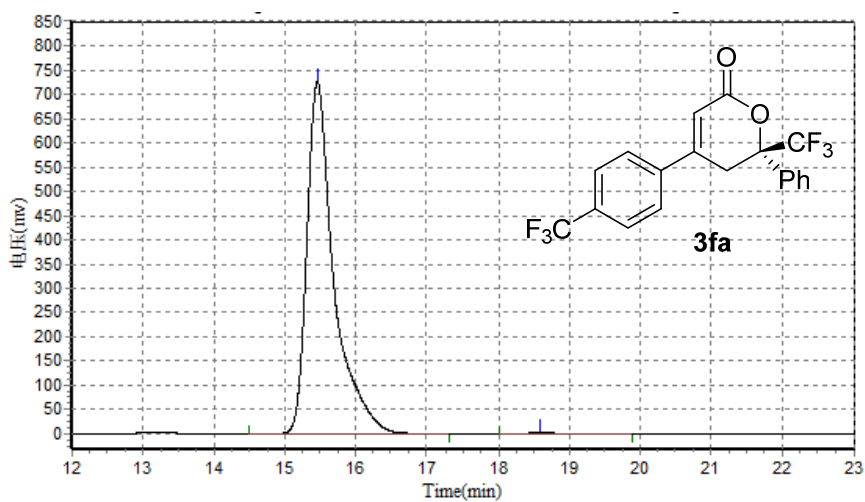
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.478	439185.938	16603243.000	99.7899
2		34.257	791.459	34963.742	0.2101
Total			439977.396	16638206.742	100.0000



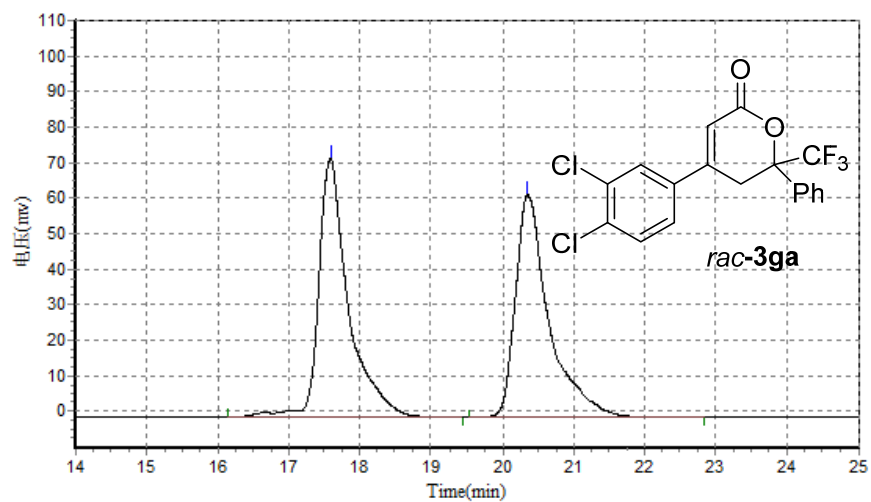
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.483	742989.313	19838678.000	50.3645
2		18.525	588889.250	19551558.000	49.6355
Total			1331878.563	39390236.000	100.0000



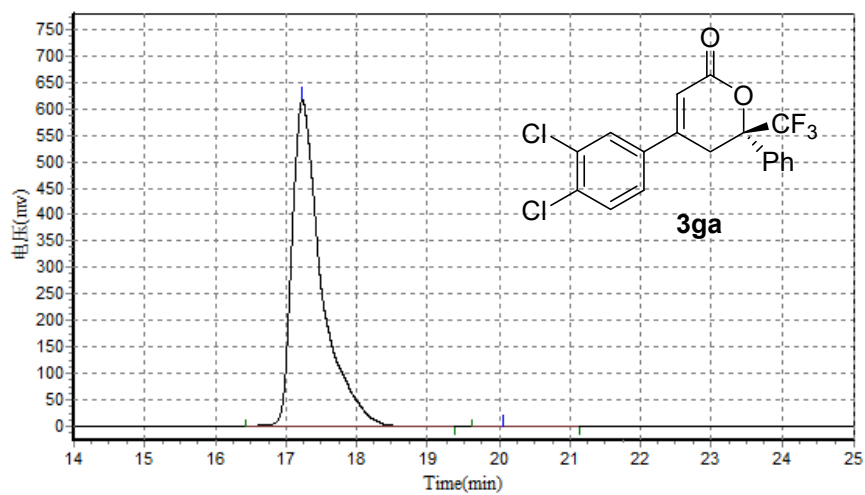
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.460	725878.250	19139862.000	99.7769
2		18.583	1357.914	42789.102	0.2231
Total			727236.164	19182651.102	100.0000



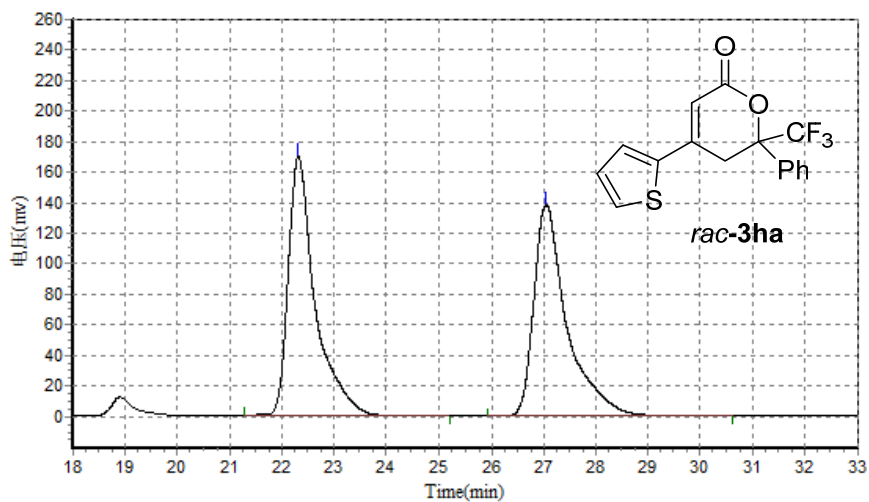
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.590	72745.117	2112629.250	50.8934
2		20.347	62397.746	2038453.625	49.1065
Total			135142.863	4151082.875	100.0000



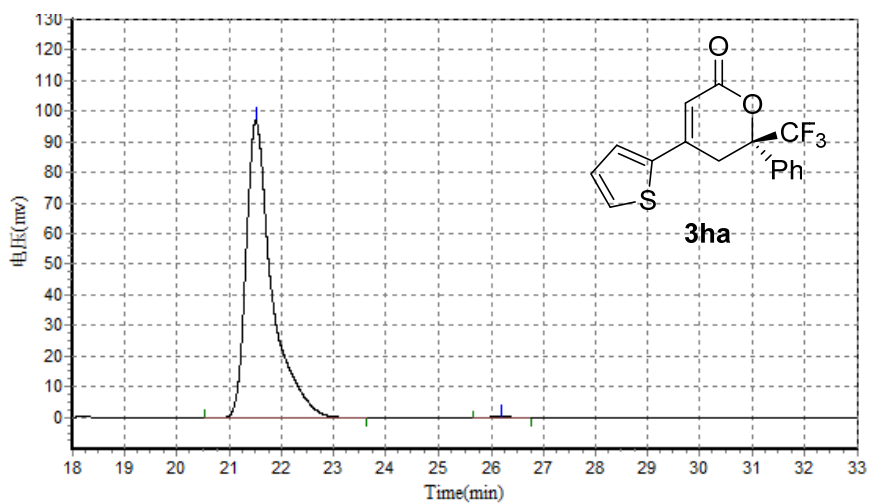
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.232	619805.313	17907792.000	99.8231
2		20.062	1042.927	31737.453	0.1769
Total			620848.240	17939529.453	100.0000



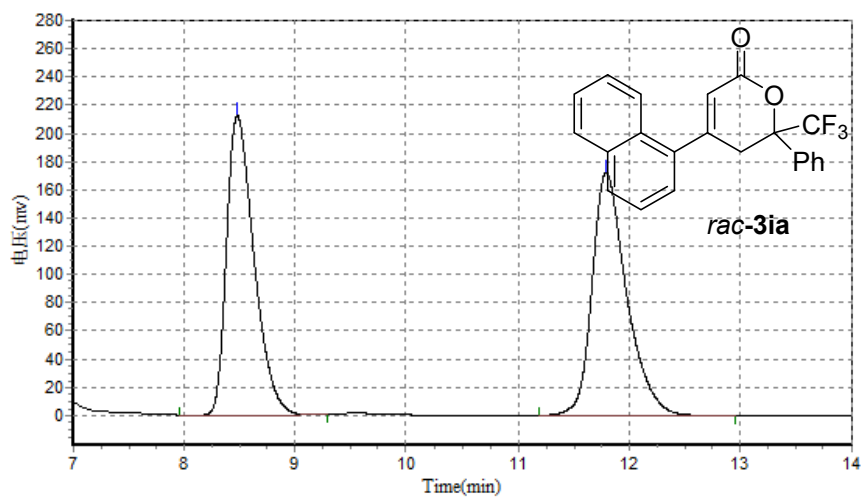
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.318	170028.375	6071396.000	50.0078
2		27.050	138478.719	6069495.000	49.9922
Total			308507.094	12140891.000	100.0000



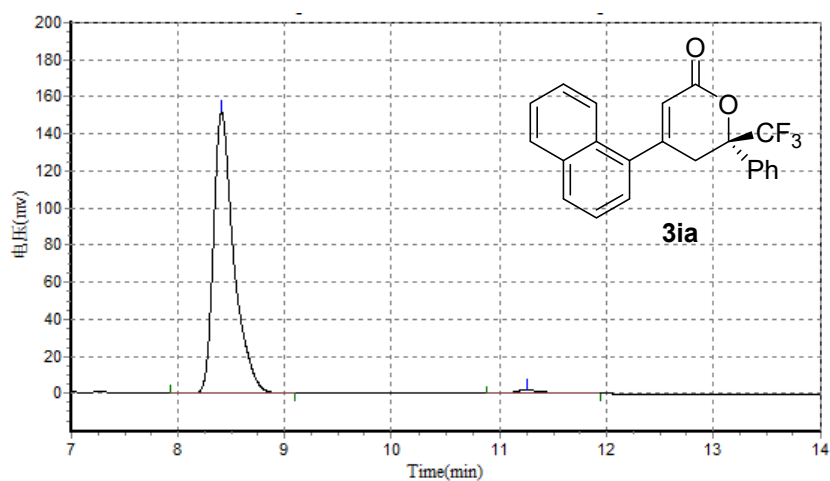
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.510	97177.414	3326105.250	99.7797
2		26.182	240.176	7344.000	0.2203
Total			97417.590	3333449.250	100.0000



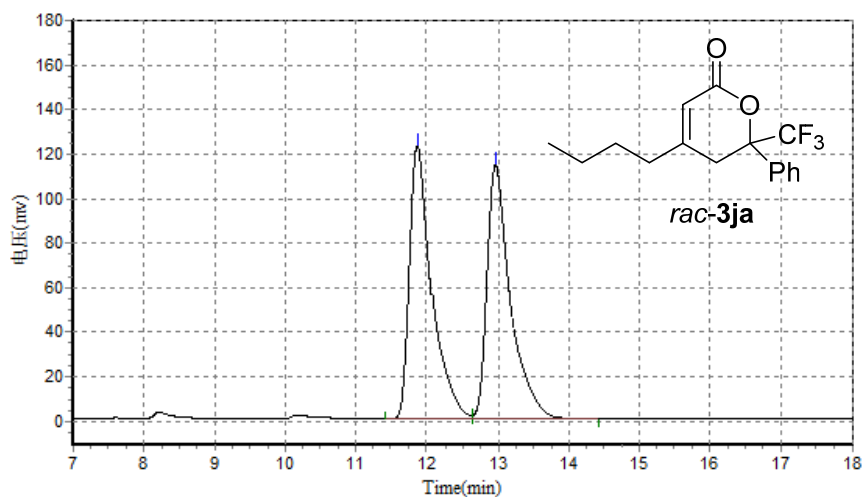
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.478	212068.547	3650695.250	49.7112
2		11.795	171910.984	3693113.250	50.2888
Total			383979.531	7343808.500	100.0000



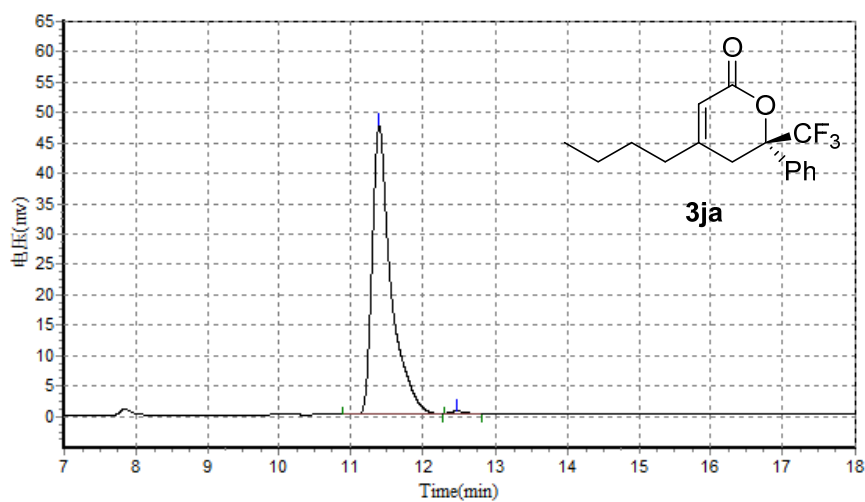
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.408	151692.000	2009086.875	98.1803
2		11.253	1984.644	37237.051	1.8197
Total			153676.644	2046323.926	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.872	122414.383	2609203.000	49.8990
2		12.958	113711.742	2619767.000	50.1010
Total			236126.125	5228970.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.393	47385.227	862194.375	99.3053
2		12.453	416.542	6031.899	0.6947
Total			47801.769	868226.274	100.0000