Chiral spiro phosphoric acid-catalysed enantioselective reaction of ketenes with N–H pyrroles

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General Experimental information

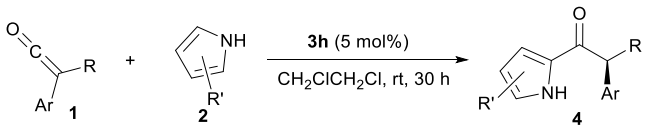
All reactions were performed under a positive pressure of argon atmosphere in flame-dried glassware with magnetic stirring using standard Schlenk techniques. All solvents were dried and distilled before use. Column chromatography was performed using 100−200 mesh silica gel. Visualization on TLC (thin layer chromatography) was achieved by the use of UV light (254 nm) and treatment with aqueous ceric ammonium molybdate staining followed by heating. Melting point (m.p.) were measured using a Buchi melting point apparatus M-560 and are uncorrected. High-resolution mass spectra (HRMS) were measured using electron spray ionization with a LTQ-Orbitrap mass analyzer (ESI-Orbitrap). Optical rotations were measured on an Autopol IV (Rudolph Research Analytical).

Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a 400 MHz (^{1}H NMR at 400 MHz and ^{13}C NMR at 100 MHz), 500 MHz (^{1}H NMR at 500 MHz and ^{13}C NMR at 125 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR, $CDCl_3$ at 7.260 ppm; ^{13}C NMR, $CDCl_3$ at 77.16 ppm). ^{1}H NMR data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet), coupling constant(s) in Hz, and integration. Enantiomeric excess was determined by HPLC with a UV-Visible detector using chiral stationary columns (0.46 cm x 25 cm) from Daicel.

All chiral phosphoric acid catalysts were purchased from Daicel Chiral Technologies (China) Co., LTD and used without further purification. Ketenes[1-8] and α-diazoketones[9-13] were prepared according to the reported procedures.

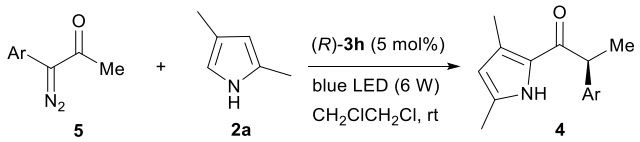
General procedure for the preparation of compound 4

General procedure A:



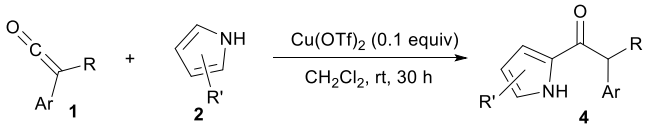
Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with **3h** (0.005 mmol, 5 mol %) and DCE (1.5 mL). To the mixture, pyrrole **2** (0.5 mmol, 5.0 equiv) and ketene **1** (0.1 mmol, 1.0 equiv) in DCE (0.5 mL) were added successively. The resulting solution was stirred for 30 h at room temperature. The solution was evaporated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1) to give the product **4**.

General procedure B:



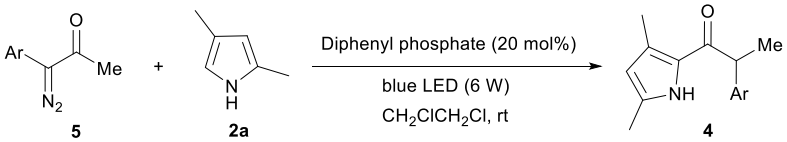
Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with (*R*)-**3h** (0.005 mmol, 5 mol %), diazoketone compound **5** (0.1 mmol, 1.0 equiv), and DCE (2.0 mL). To the mixture, pyrrole **2a** (0.2 mmol, 2.0 equiv) was added. The resulting solution was stirred under the irridation of 6W blue LEDs at room temperature. Upon completion, the solution was evaporated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1) to give the product **4**.

Procedure for the preparation of racemic compound 4 using ketenes:



Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with $Cu(OTf)_2$ (0.03 mmol, 0.1 equiv) and CH_2Cl_2 (3.0 mL). To the mixture, pyrrole **2** (1.5 mmol, 5.0 equiv) and ketene **1** (0.3 mmol, 1.0 equiv.) in CH_2Cl_2 (1.0 ml) were added. The resulting solution was stirred for 30 h at room temperature. The solution was evaporated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1) to give the product **4**.

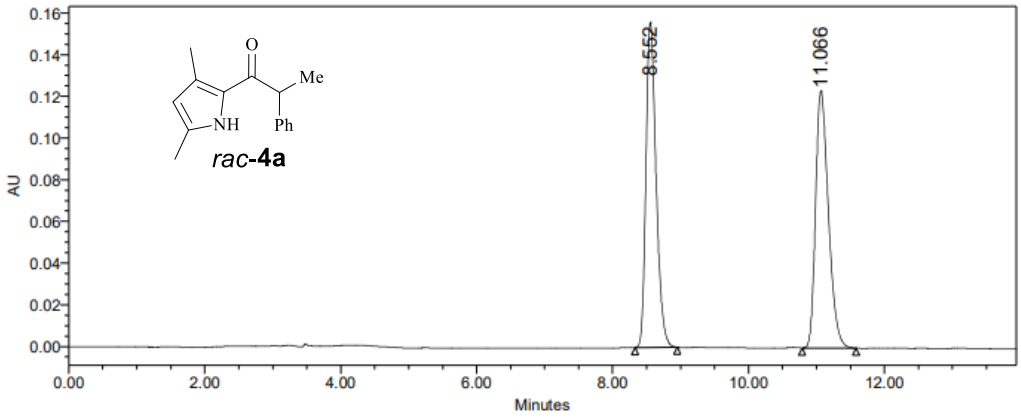
Procedure for preparation of racemic compound 4 using *α*-diazoketones:



Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with diphenyl phosphate (0.06 mmol, 20 mol %), diazo compound **5** (0.3 mmol, 1.0 equiv), and DCE (4.0 mL). To the mixture, pyrrole **2a** (0.6 mmol, 2.0 equiv) were added. The resulting solution was stirred under the irridation of 12W blue LEDs at room temperature. Upon completion, the solution was evaporated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1) to give the product **4**.

Chiral HPLC analysis for reactions in Table 1

Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t

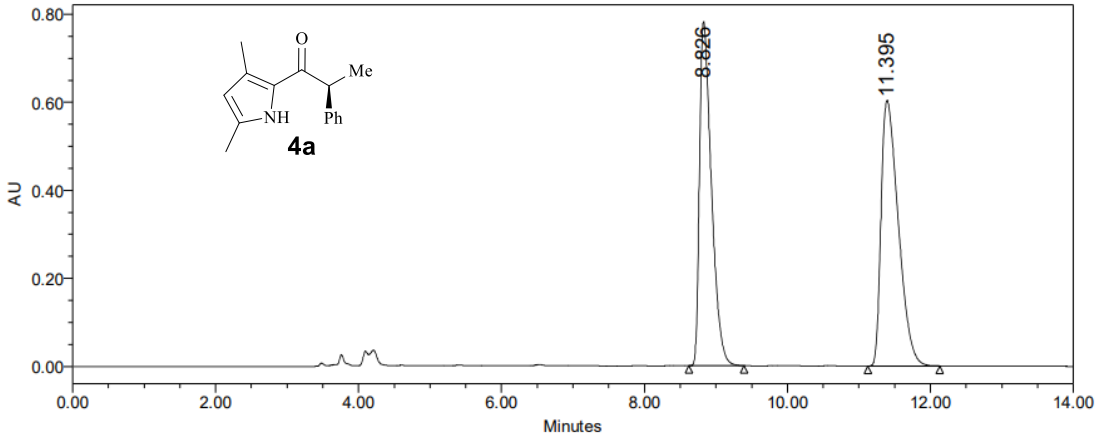


Channel: W2489 ChA; Processed Channel: W2489 ChA 243nm; Result Id: 2603; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 243nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 243nm	8.552	1613054	49.95	155778
2	W2489 ChA 243nm	11.066	1616571	50.05	123367

HPLC of *rac*-**4a**

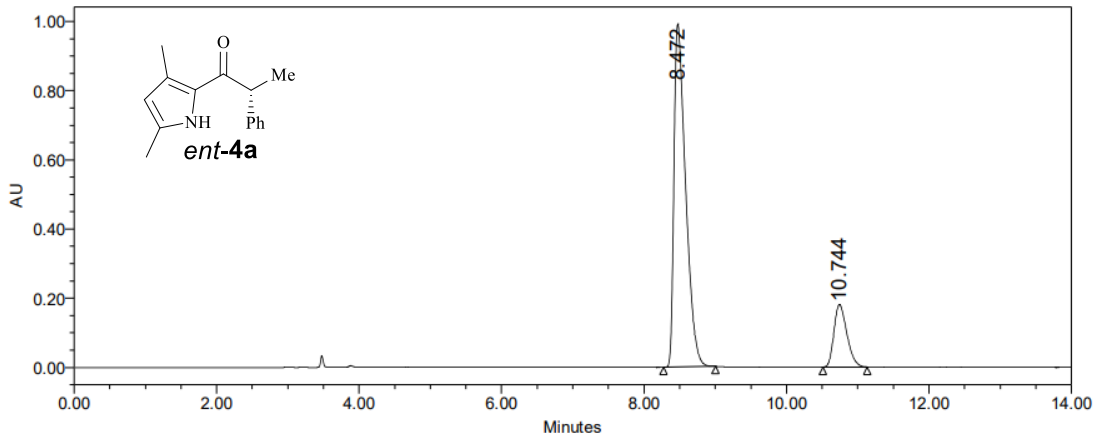


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4337; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.826	9023454	47.18	781029
2	W2489 ChA 254nm	11.395	10100602	52.82	603218

Entry 1 (CPA (*R*)-**3a**/DCM)

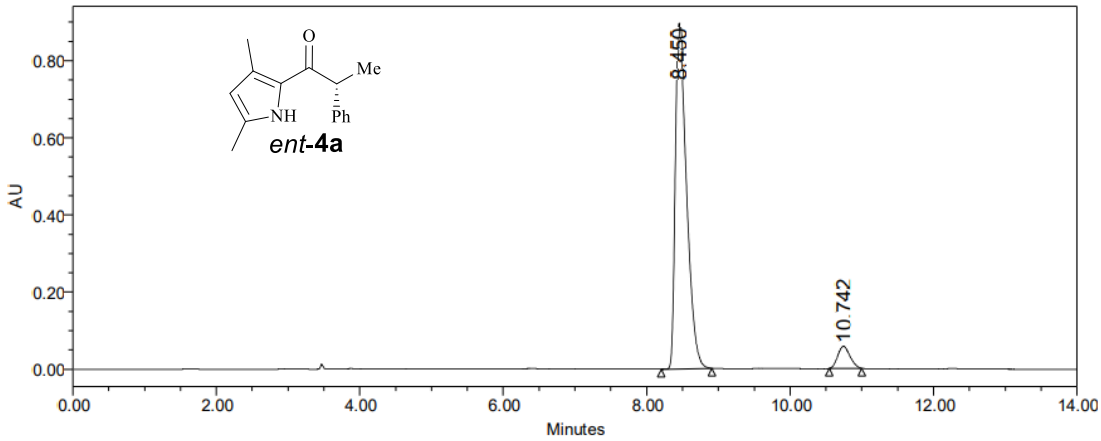


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3884; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.472	11218209	83.08	991364
2	W2489 ChA 254nm	10.744	2284349	16.92	180516

Entry 2 (CPA (*R*)-**3b**/DCM)

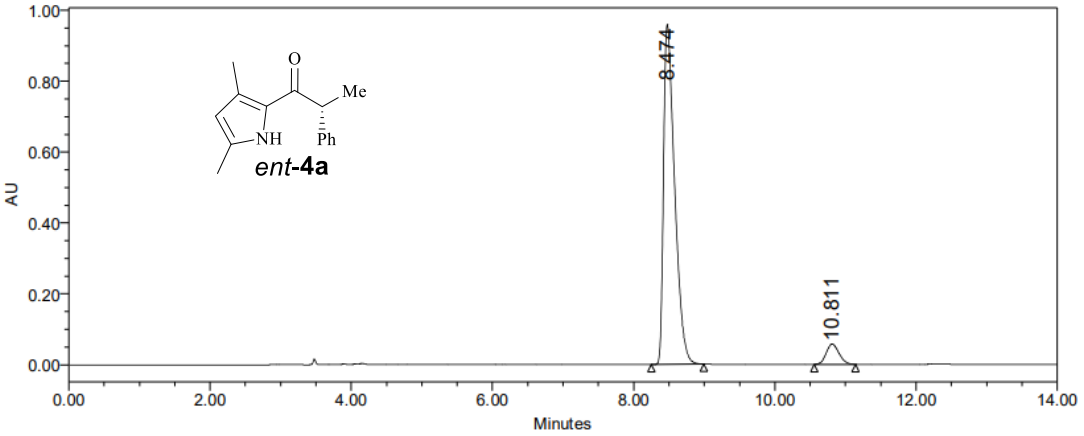


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3886; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.450	9734849	93.48	895468
2	W2489 ChA 254nm	10.742	678742	6.52	57413

Entry 3 (CPA (*R*)-**3c**/DCM)

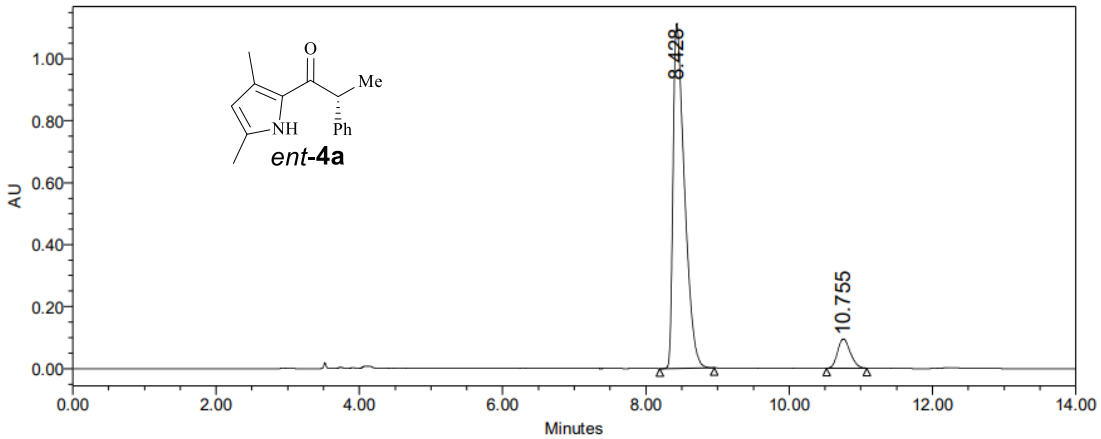


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3870; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.474	10422966	93.48	958063
2	W2489 ChA 254nm	10.811	727413	6.52	57618

Entry 4 (CPA (*R*)-**3d**/DCM)

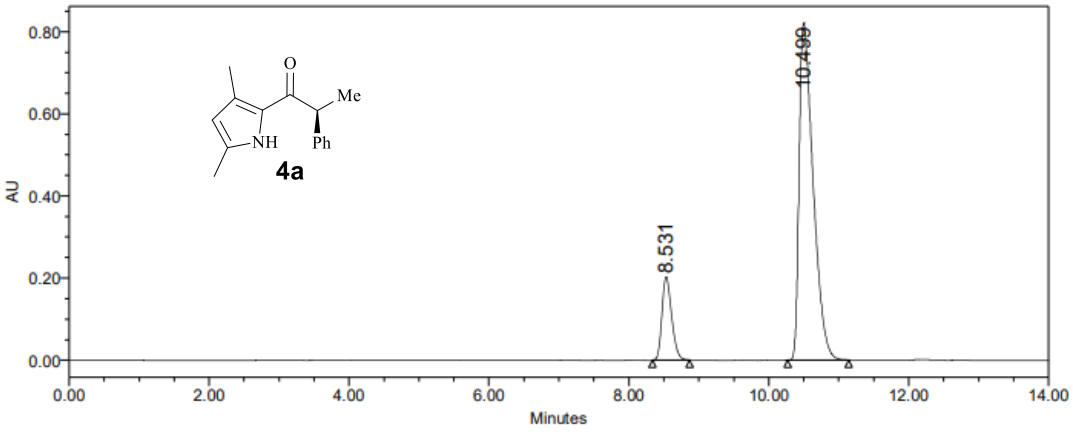


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3889; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.428	12321339	91.34	1112256
2	W2489 ChA 254nm	10.755	1168056	8.66	95087

Entry 5 (CPA (*R*)-**3e**/DCM)

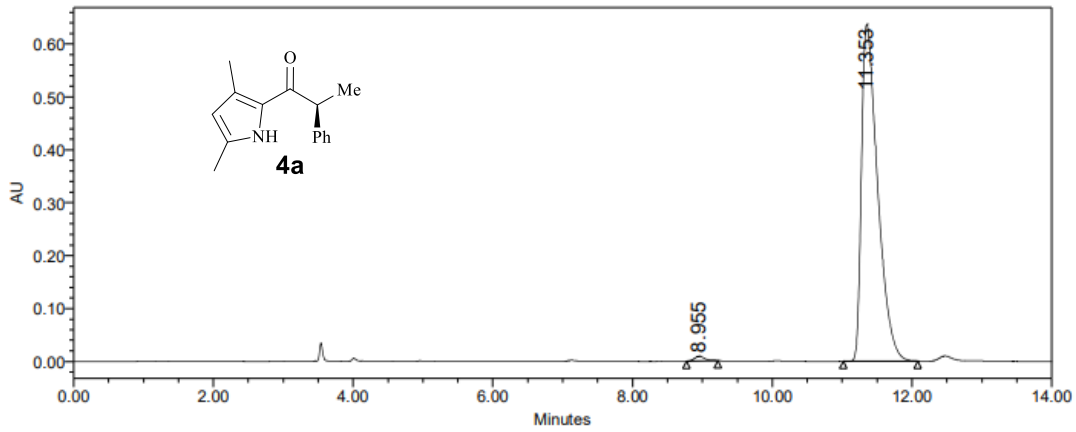


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4327; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.531	1949383	14.55	201710
2	W2489 ChA 254nm	10.499	11446263	85.45	820600

Entry 6 (CPA (*R*)-**3f**/DCM)

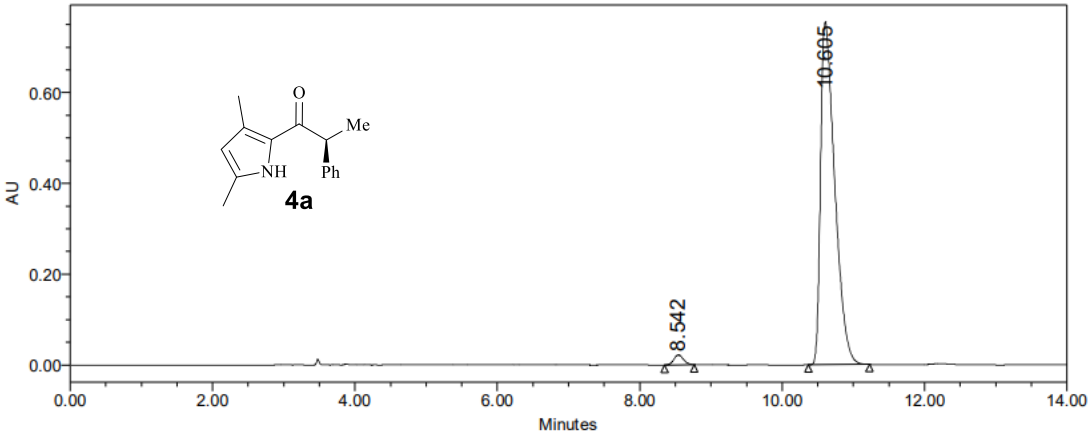


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4343; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.955	92788	0.90	8936
2	W2489 ChA 254nm	11.353	10199965	99.10	636699

Entry 7 (CPA (*R*)-**3g**/DCM)

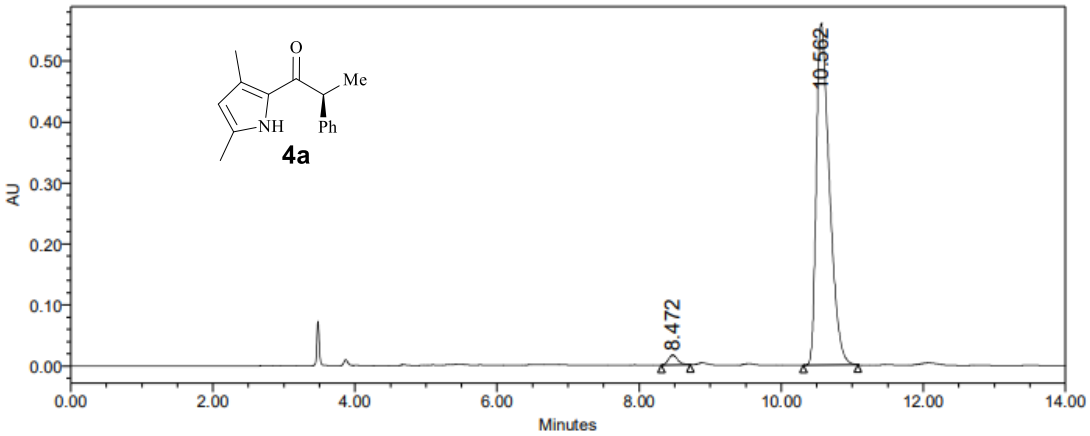


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3891; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.542	203783	1.91	21677
2	W2489 ChA 254nm	10.605	10447232	98.09	754897

Entry 8 (CPA (*R*)-**3h**/DCM)

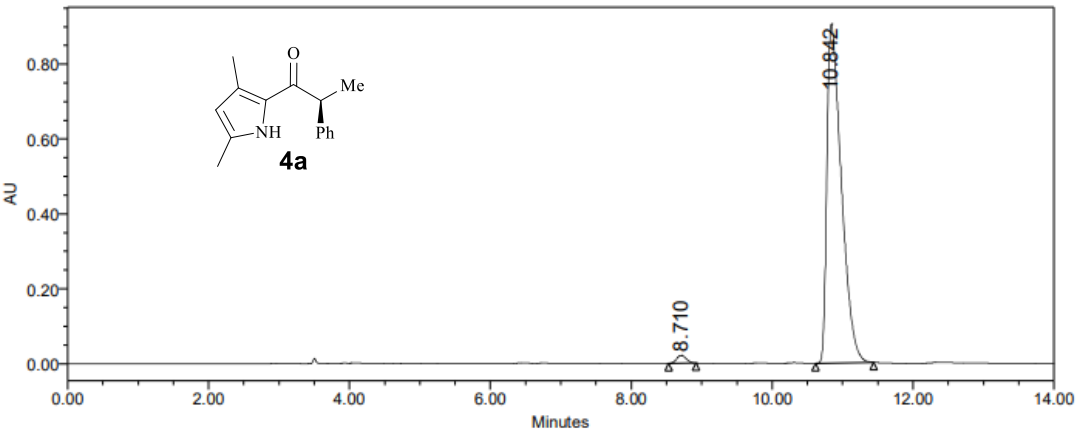


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4041; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.472	145296	1.97	16017
2	W2489 ChA 254nm	10.562	7215970	98.03	559678

Entry 10 (CPA (*R*)-**3h**/THF)

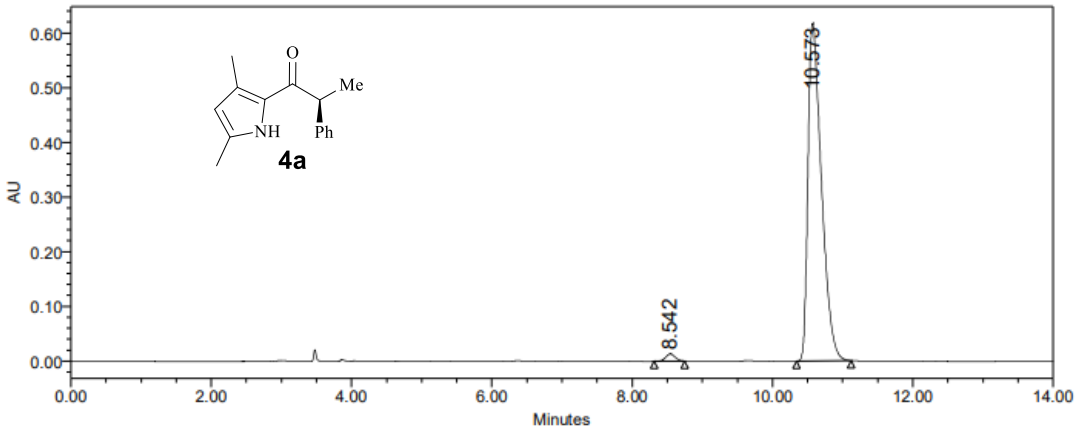


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4062; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.710	205091	1.57	21453
2	W2489 ChA 254nm	10.842	12837516	98.43	904918

Entry 11 (CPA (*R*)-**3h**/Toluene)

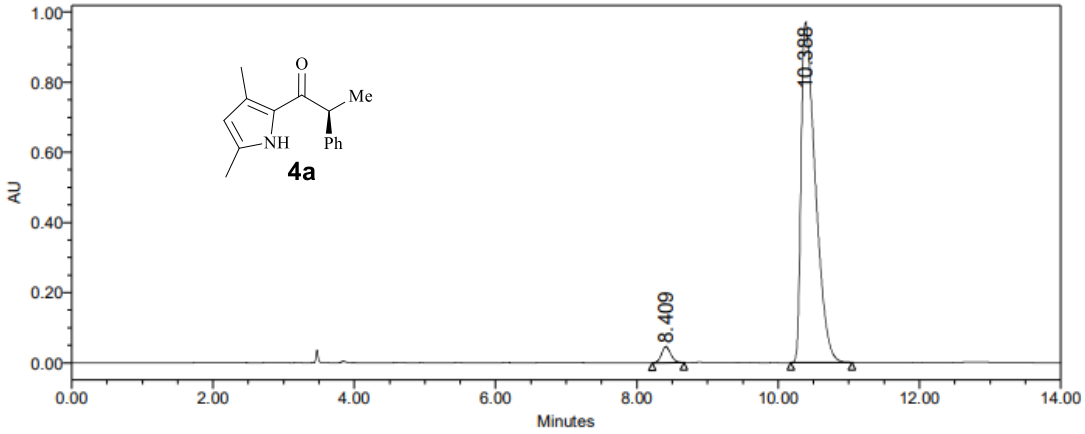


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4051; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.542	124520	1.48	13252
2	W2489 ChA 254nm	10.573	8278899	98.52	617196

Entry 12 (CPA (*R*)-**3h**/Et_2O)

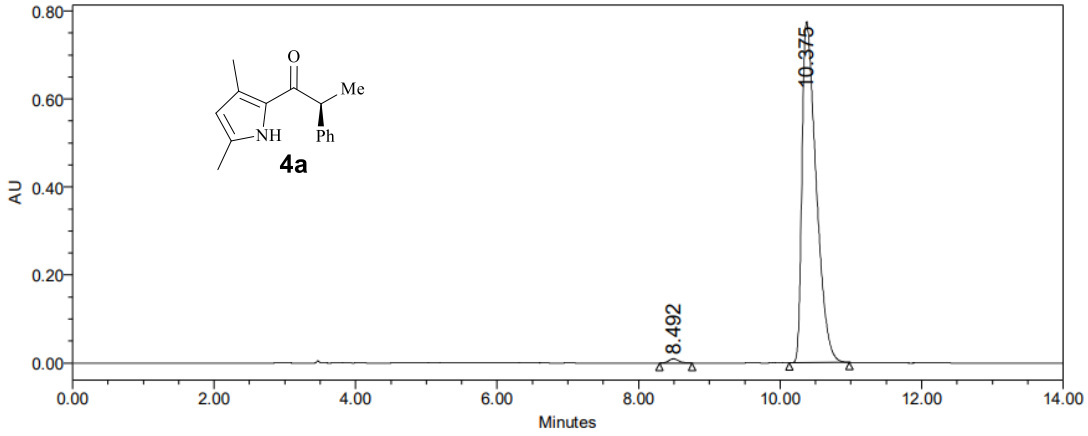


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4044; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.409	417788	2.98	45523
2	W2489 ChA 254nm	10.388	13601288	97.02	969965

Entry 13 (CPA (*R*)-**3h**/$CHCl_3$)

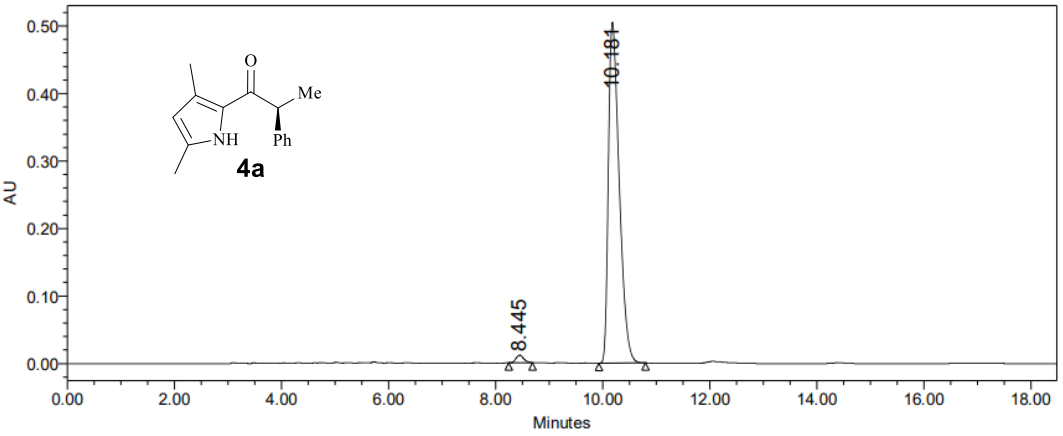


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4331; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.492	90053	0.83	9562
2	W2489 ChA 254nm	10.375	10805130	99.17	774308

Entry 14 (CPA (*R*)-**3h**/DCE, rt)

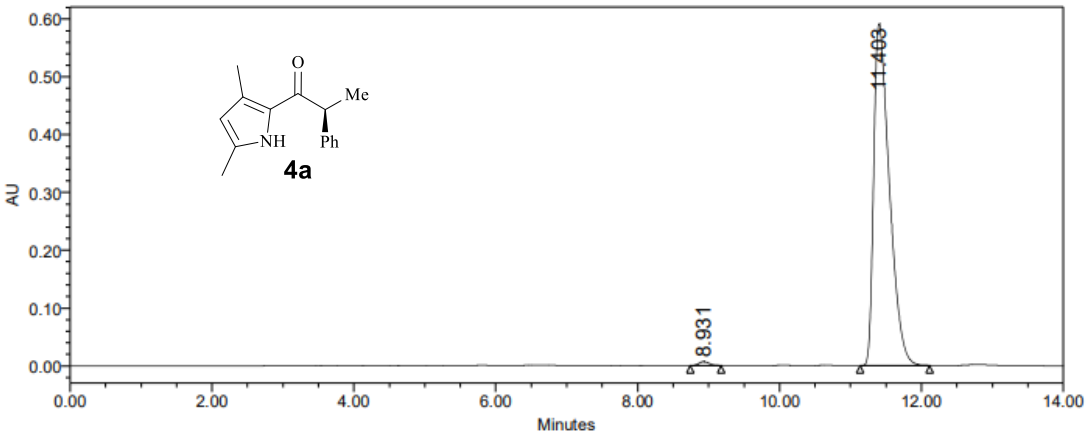


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5606; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.445	110003	1.53	11160
2	W2489 ChA 254nm	10.181	7086266	98.47	504510

Entry 15 (CPA (*R*)-**3h**/DCE, rt, 1 mmol scale)



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4339; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

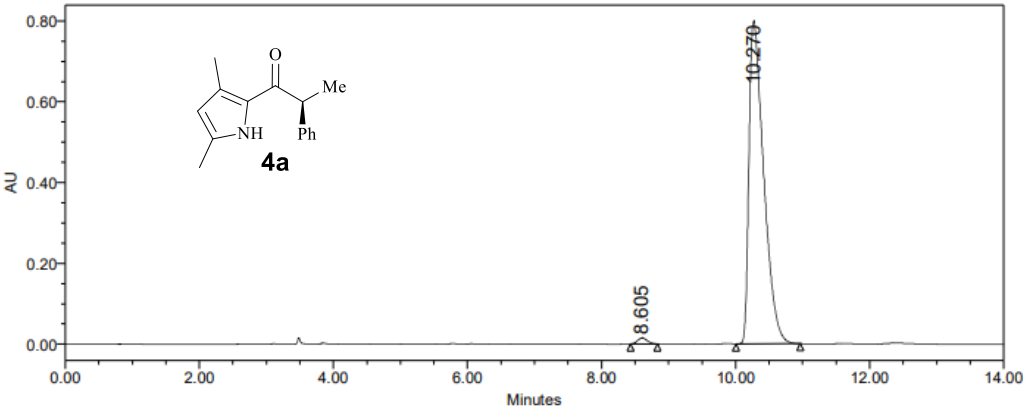
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.931	70752	0.78	6963
2	W2489 ChA 254nm	11.403	9034716	99.22	590956

Entry 16 (CPA (*R*)-**3g**/DCE, rt)

Reactions at low temperatures

Reactions of **1a** with **2a** using CPA **3h** as catalyst in dichloroethane at lower temperatures afforded the desired product **4a** in lower yields with comparable er, comparing to the reaction at room temperature (Table 1, entry 14). Reaction performed at 0 ºC for 30 h afforded the product **4a** in 59% yield with ~99:1 er. Reaction performed at -30 ºC for 30 h gave the product **4a** in 40% yield with ~99:1 er. The corresponding experiments and chiral HPLC analysis for these reactions were provided below.

Reaction at 0 ºC: Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with **3h** (3.5 mg, 0.005 mmol, 5 mol %) and DCE (1.5 mL). To the mixture, pyrrole **2a** (50.4 mg, 0.5 mmol, 5.0 equiv) and ketene **1a** (14 mg, 0.1 mmol, 1.0 equiv) in DCE (0.5 ml) were added successively. The resulting solution was stirred at 0 ºC for 30 h. The reaction was quenched with sat. sol. $NaHCO_3$ and extracted with CH_2Cl_2 (×3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and filtered. The resulting solution was evaporated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1) to give the product **4a** (14.1 mg, 59 % yield). See page S14 for analytical data of the compound **4a**. Chiral HPLC analysis indicated that the enantiomeric ratio of the product **4a** was ~99:1.

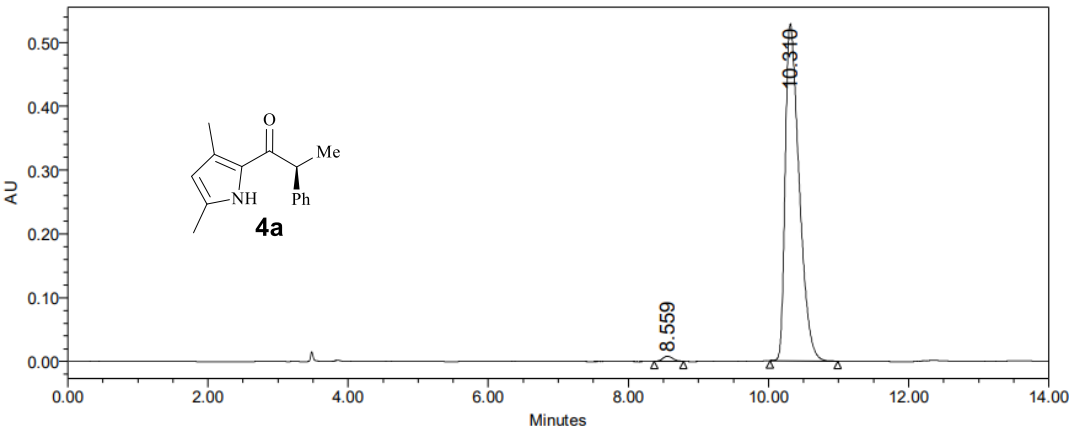


Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.605	152711	1.23	14965
2	W2489 ChA 254nm	10.270	12249990	98.77	798712

CPA (*R*)-**3h**/DCE at 0 ºC

Reaction at -30 ºC: Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with **3h** (3.5 mg, 0.005 mmol, 5 mol %) and DCE (1.5 mL). To the mixture, pyrrole **2a** (50.4 mg, 0.5 mmol, 5.0 equiv) and ketene **1a** (14 mg, 0.1 mmol, 1.0 equiv) in DCE (0.5 ml) were added successively. The resulting solution was stirred at -30 ºC for 30 h. The reaction was quenched with sat. sol. $NaHCO_3$ and extracted with CH_2Cl_2 (×3). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and filtered. The resulting solution was evaporated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1) to give the product **4a** (9.7 mg, 40 % yield). See page S14 for analytical data of the compound **4a**. Chiral HPLC analysis indicated that the enantiomeric ratio of the product **4a** was ~99:1.



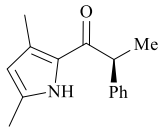
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5557; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.559	83628	1.13	8215
2	W2489 ChA 254nm	10.310	7337367	98.87	527511

CPA (*R*)-**3h**/DCE at -30 ºC

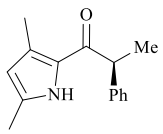
Analytical data for product 4



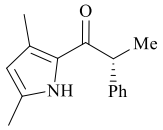
(**4a**) According to the general procedure A, reaction of **1a** (13.2 mg, 0.1 mmol, 1.0 equiv), 2, 4-dimethyl-1*H*-pyrrole **2a** (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5% mmol, 0.05 equiv) afforded **4a** as a white solid (18.4 mg, 81%). Analytical data for compound **4a**: mp 122−123 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +114.0 (c 0.37, $CHCl_3$); enantiomeric ratio: 99:1, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 10.4 min; t_R (minor) = 8.5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.34–7.27 (m, 4H), 7.23–7.19 (m, 1H), 5.77 (d, *J* = 2.0 Hz, 1H), 4.41 (q, *J* = 6.8 Hz, 1H), 2.33 (s, 3H), 2.22 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 141.8, 135.4, 128.7, 128.4, 128.2, 128.0, 126.7, 113.1, 47.3, 19.8, 14.8, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{15}H_{18}NO^+$ 228.1383, found 228.1387.

Scale-up reaction of 1a (1 mmol) with 2a in the presence of CPA catalyst (*R*)-3h:

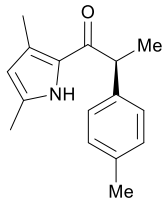
Under argon atmosphere, a flame-dried 100 ml Schlenk flask was charged with (*R*)-**3h** (33.3 mg, 0.05 mmol, 5 mol %) and DCE (15.0 mL). To the mixture, pyrrole **2a** (475.1 mg, 5.0 mmol, 5.0 equiv) and ketene **1a** (132 mg, 1.0 mmol, 1.0 equiv) in DCE (5.0 mL) were added successively. The resulting solution was stirred for 30 h at room temperature. The solution was evaporated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1) to give the product **4a** (167 mg, 74% yield). Chiral HPLC analysis indicated that the enantiomeric ratio of the product was 98.5:1.5 (page S11).



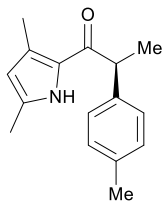
(**4a**) According to the general procedure B, reaction of **5a** (16.0 mg, 0.1 mmol, 1.0 equiv), 2, 4-dimethyl-1*H*-pyrrole **2a** (19.0 mg, 0.2 mmol, 2.0 equiv), and (*R*)-**3h** (3.3 mg, 0.5% mmol, 0.05 equiv) afforded **4a** as a white solid (14.6 mg, 64%). Analytical data for compound **4a** prepared with general procedure B: enantiomeric ratio: 87.5:12.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 11.1 min; t_R (minor) = 9.1 min.



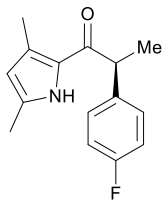
(*ent*-**4a**) According to the general procedure A, reaction of **1a** (13.2 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (47.6 mg, 0.5 mmol, 5.0 equiv), (*S*)-**3h** (3.3 mg, 0.5% mmol, 0.05 equiv) afforded *ent*-**4a** as a white solid (16.6 mg, 73%). Analytical data for compound *ent*-**4a**: mp 123−124 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = −109.3 (c 0.14, $CHCl_3$); enantiomeric ratio: 1.5:98.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 8.4 min; t_R (minor) = 11.4 min; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{15}H_{18}NO^+$ 228.1383, found 228.1385.



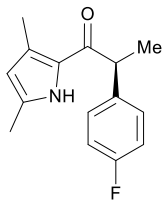
(**4b**) According to the general procedure A, reaction of **1b** (14.6 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5% mmol, 0.05 equiv) afforded **4b** as a white solid (16.4 mg, 68%). Analytical data for compound **4b**: mp 116−117 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +99.3 (c 0.12, $CHCl_3$); enantiomeric ratio: 97:3, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 11.5 min; t_R (minor) = 6.8 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.22 (d, J = 7.5 Hz, 2H), 7.11 (d, J = 7.5 Hz, 2H), 5.77 (s, 1H), 4.37 (q, J = 6.5 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.23 (s, 3H), 1.51 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 138.8, 136.3, 135.2, 129.4, 128.3, 128.2, 127.8, 113.0, 47.0, 21.1, 19.8, 14.7, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{16}H_{20}NO^+$ 242.1539, found 242.1544.



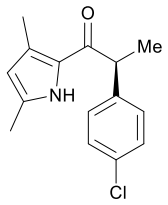
(**4b**) According to the general procedure B, reaction of **5b** (18.0 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (19.7 mg, 0.2 mmol, 2.0 equiv), (*R*)-**3h** (3.4 mg, 0.5% mmol, 0.05 equiv) afforded **4b** as a white solid (15.0 mg, 60%). Analytical data for compound **4b** prepared with general procedure B: enantiomeric ratio: 92:8, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 12.2 min; t_R (minor) = 7.1 min.



(**4c**) According to the general procedure A, reaction of **1c** (15.0 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5% mmol, 0.05 equiv) afforded **4c** as a white solid (16.2 mg, 66%). Analytical data for compound **4c**: mp 146−147 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +85.9 (c 0.09, $CHCl_3$); enantiomeric ratio: 97.5:2.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 9.2 min; t_R (minor) = 7.8 min; ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.4; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.29–7.27 (m, 2H), 7.00–6.95 (m, 2H), 5.78 (d, J = 2.5 Hz, 1H), 4.39 (q, J = 7.0 Hz, 1H), 2.33 (s, 3H), 2.22 (s, 3H), 1.49 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.0, 161.9 (d, J = 243.3 Hz), 137.5 (d, J = 3.1 Hz), 135.5, 129.4 (d, J = 7.9 Hz), 128.4, 128.0, 115.5 (d, J = 21.1 Hz), 113.2, 46.5, 19.9, 14.7, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{15}H_{17}FNO^+$ 246.1289, found 246.1293.

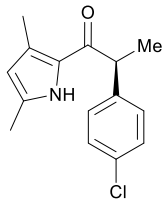


(**4c**) According to the general procedure B, reaction of **5c** (18.0 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (19.2 mg, 0.2 mmol, 2.0 equiv), (*R*)-**3h** (3.4 mg, 0.5% mmol, 0.05 equiv) afforded **4c** as a white solid (19.1 mg, 77%). Analytical data for compound **4c** prepared with general procedure B: enantiomeric ratio: 91:9, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 8.7 min; t_R (minor) = 7.5 min.



(**4d**) According to the general procedure A, reaction of **1d** (16.6 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5% mmol, 0.05 equiv) afforded **4d** as a white solid (18.9 mg, 72%). Analytical data for compound **4d**: mp 125−126 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +75.7 (c 0.10, $CHCl_3$); enantiomeric ratio: 97:3, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 9.7 min; t_R (minor) = 7.8 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.25–7.23 (m, 5H), 5.78 (d,

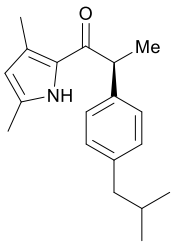
J = 2.5 Hz, 1H), 4.36 (q, J = 7.0 Hz, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 1.49 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.6, 140.2, 135.4, 135.7, 129.3, 128.9, 128.4, 128.0, 113.3, 46.7, 19.8, 14.74, 13.2; HRMS (ESI-Orbitrap) (*m*/z) $[M + Na]^+$ calcd for $C_{15}H_{16}ClNNaO^+$ 284.0813, found 284.0815.



(**4d**) According to the general procedure B, reaction of **5d** (20.0 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (19.6 mg, 0.2 mmol, 2.0 equiv), (*R*)-**3h** (3.4 mg, 0.5% mmol, 0.05 equiv) afforded **4d** as a white solid (18.6 mg, 69%). Analytical data for compound **4d** prepared with general procedure B: enantiomeric ratio: 96:4, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 9.6 min; t_R (minor) = 8.0 min.

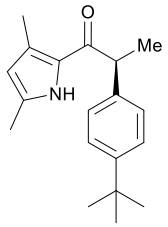
Scale-up reaction of 5d (1.0 mmol) with 2a in the presence of CPA catalyst (*R*)-3h:

Under argon atmosphere, a flame-dried 100 ml Schlenk flask was charged with (*R*)-**3h** (33.3 mg, 0.05 mmol, 5 mol %), diazoketone **5d** (195.0 mg, 1.0 mmol, 1.0 equiv), and DCE (20.0 mL). To the mixture, pyrrole **2a** (190.7 mg, 2.0 mmol, 2.0 equiv) was added. The resulting solution was stirred under the irridation of 6W blue LEDs at room temperature. Upon completion, the solution was evaporated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 15:1) to give the product **4d** (190.4 mg, 73% yield). Chiral HPLC analysis indicated the enantiomeric ratio of the product was 95.5:4.5 (page S77).

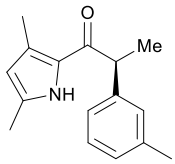


(**4e**) According to the general procedure A, reaction of **1e** (18.8 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5% mmol, 0.05 equiv) afforded **4e** as a white solid (20.7 mg, 73%). Analytical data for compound **4e**: mp 96−97 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +78.7 (c 0.19, $CHCl_3$); enantiomeric ratio: 95.5:4.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 6.8 min; t_R (minor) = 5.4 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.22–7.20 (m, 2H), 7.07–7.06 (m, 2H), 5.76 (d, J = 2.5 Hz, 1H), 4.36 (q, J = 7.0 Hz, 1H), 2.42 (d, J = 7.0 Hz, 2H), 2.32

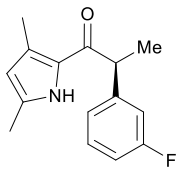
(s, 3H), 2.21 (s, 3H), 1.86–1.78 (m, 1H), 1.50 (d, J = 7.0 Hz, 3H), 0.89 (d, J = 2.5 Hz, 3H), 0.87 (d, J = 2.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 140.1, 139.0, 135.0, 129.5, 128.4, 128.2, 127.6, 113.0, 47.0, 45.2, 30.3, 22.6, 22.5, 19.8, 14.7, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) [M + H]$^+$ calcd for $C_{19}H_{26}NO^+$ 284.2009, found 284.2012.



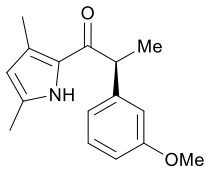
(**4f**) According to the generalprocedure A, reaction of **1f** (18.8 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5% mmol, 0.05 equiv) afforded **4f** as a white solid (21.8 mg, 77%). Analytical data for compound **4f**: mp 152−153 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +75.3 (c 0.21, $CHCl_3$); enantiomeric ratio: 98.5:1.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 8.6 min; t_R (minor) = 5.5 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.32–7.30 (m, 2H), 7.26–7.24 (s, 2H), 5.77 (d, J = 3.0 Hz, 1H), 4.39 (q, J = 6.5 Hz, 1H), 2.35 (s, 3H), 2.21 (s, 3H), 1.51 (d, J = 7.0 Hz, 3H), 1.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 149.5, 138.6, 135.2, 128.4, 128.2, 127.6, 125.6, 113.0, 46.8, 34.5, 31.5, 19.7, 14.8, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) [M + H]$^+$ calcd for $C_{19}H_{26}NO^+$ 284.2009, found 284.2013.



(**4g**) According to the general procedure A, reaction of **1g** (14.6 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5% mmol, 0.05 equiv) afforded **4g** as a white solid (15.4 mg, 64%). Analytical data for compound **4g**: mp 100−101 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +130.4 (c 0.11, $CHCl_3$); enantiomeric ratio: 97:3, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 10.6 min; t_R (minor) = 7.2 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.13–7.11 (m, 2H), 7.02 (d, J = 7.5 Hz, 1H), 5.77 (d, J = 3.0 Hz, 1H), 4.37 (q, J = 7.0 Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 2.22 (s, 3H), 1.51 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 141.7, 138.3, 135.2, 128.6, 128.5, 128.4, 128.2, 127.6, 125.1, 113.0, 47.3, 21.6, 19.8, 14.8, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) [M + H]$^+$ calcd for $C_{16}H_{20}NO^+$ 242.1539, found 242.1544.

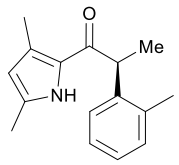


(**4h**) According to the general procedure A, reaction of **1h** (15.0 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5% mmol, 0.05 equiv) afforded **4h** as a white solid (19.6 mg, 80%). Analytical data for compound **4h**: mp 102−103 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +104.4 (c 0.11, $CHCl_3$); enantiomeric ratio: 98:2, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 9.9 min; t_R (minor) = 7.8 min; ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.9; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.30–7.27 (m, 1H), 7.14–7.09 (m, 2H), 6.96–6.92 (m, 1H), 5.83 (s, 1H), 4.46 (q, *J* = 7.0 Hz, 1H), 2.38 (s, 3H), 2.27 (s, 3H), 1.56 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.4, 163.1 (d, *J* = 244.1 Hz), 144.3 (d, *J* = 7.1 Hz), 144.28 , 135.9, 130.0 (d, *J* = 8.3 Hz), 128.7, 128.1, 123.7 (d, *J* = 2.6 Hz), 115.0 (d, *J* = 21.6 Hz), 113.7 (d, *J* = 20.9 Hz), 113.3, 46.9, 19.7, 14.8, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{15}H_{17}FNO^+$ 246.1289, found 246.1293.

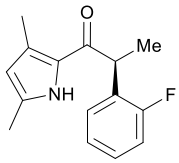


(**4i**) According to the general procedure A, reaction of **1i** (16.2 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5% mmol, 0.05 equiv) afforded **4i** as a colorless oil (16.4 mg, 64%). Analytical data for compound **4i**; R_f = 0.20 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +92.1 (c 0.11, $CHCl_3$); enantiomeric ratio: 97.5:2.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 95:5 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 19.4 min; t_R (minor) = 8.4 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.22–7.19 (m, 1H), 6.91–6.89 (m, 1H), 6.88–6.87(m, 1H), 6.76–6.74 (m, 1H), 5.76 (d, *J* = 3.0 Hz, 1H), 4.36 (q, *J* = 7.0 Hz, 1H), 3.77 (s, 3H), 2.33 (s, 3H), 2.22 (s, 3H), 1.50 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.9, 159.9, 143.3, 135.1, 129.7, 128.5, 128.2, 120.4, 113.8, 113.1, 112.0, 55.30, 47.4, 19.7, 14.7, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{16}H_{20}NO_2^+$ 258.1489, found 258.1492.

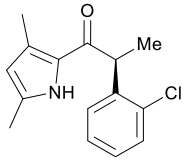
(**4j**) According to the general procedure A, reaction of **1j** (14.6 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5% mmol, 0.05 equiv)



afforded **4j** as a white solid (22.4 mg, 93%). Analytical data for compound **4j**: mp 171−172 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +193.4 (c 0.33, $CHCl_3$); enantiomeric ratio: 98.5:1.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 18.3 min; t_R (minor) = 12.5 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.24–7.21 (m, 1H), 7.19–7.16 (m, 1H), 7.15–7.12 (m, 2H), 5.76 (d, J = 2.5 Hz, 1H), 4.50 (q, J = 7.0 Hz, 1H), 2.40 (s, 3H), 2.21 (s, 3H), 2.20 (s, 3H), 1.51 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5, 140.1, 135.6, 135.3, 130.5, 128.3, 128.2, 127.2, 126.7, 126.6, 112.8, 44.5, 19.5, 17.8, 14.0, 13.0; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{16}H_{20}NO^+$ 242.1539, found 242.1542.

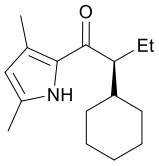


(**4k**) According to the general procedure A, reaction of **1k** (15.0 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5% mmol, 0.05 equiv) afforded **4k** as a white solid (19.8 mg, 81%). Analytical data for compound **4k**: mp 132−133 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +95.1 (c 0.11, $CHCl_3$); enantiomeric ratio: 96:4, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 15.8 min; t_R (minor) = 10.1 min; ^{19}F NMR (471 MHz, $CDCl_3$) δ -118.9; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.34–7.30 (m, 1H), 7.19–7.15 (m, 1H), 7.04–6.99 (m, 2H), 5.77 (d, J = 3.0 Hz, 1H), 4.72 (q, J = 7.0 Hz, 1H), 2.27 (s, 3H), 2.22 (s, 3H), 1.50 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.3, 160.3 (d, J = 243.0 Hz), 135.7, 129.5, 129.0 (d, J = 4.0 Hz), 128.7 (d, J = 15.0 Hz), 128.3 (d, J = 8.4 Hz), 127.9, 124.6 (d, J = 3.4 Hz), 115.2 (d, J = 22.5 Hz), 113.2, 39.7, 18.2, 14.1, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{15}H_{17}FNO^+$ 246.1289, found 246.1295.

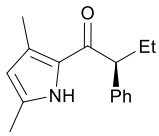


(**4l**) According to the general procedure A, reaction of **1l** (16.6 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole **2a** (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5% mmol, 0.05 equiv) afforded **4l** as a white solid (23.5 mg, 90%)Analytical data for compound **4l**: mp 153−153 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +103.5 (c 0.28, $CHCl_3$); enantiomeric ratio: 97.5:2.5, the er value of the product was

determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 21.5 min; t_R (minor) = 16.9 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.38–7.36 (m, 1H), 7.32–7.30 (m, 1H), 7.20–7.14 (m, 2H), 5.76 (d, J = 3.0 Hz, 1H), 4.77 (q, J = 7.0 Hz, 1H), 2.24 (s, 3H), 2.20 (s, 3H), 1.50 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.3, 139.5, 135.4, 133.8, 129.5, 129.2, 128.9, 128.1, 128.0, 127.4, 113.1, 44.4, 17.6, 14.0, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{15}H_{17}ClNO^+$ 262.0993, found 262.0997.

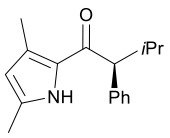


(**4m**) According to the general procedure A, reaction of **1m** (15.2 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4m** as a white solid (17.6 mg, 71%). Analytical data for compound **4m**: mp 106−107 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +49.7 (c 0.11, $CHCl_3$); enantiomeric ratio: 74.5:25.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 6.1 min; t_R (minor) = 5.2 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.88 (s, 1H), 5.81 (s, 1H), 3.04–2.92 (m, 1H), 2.37 (s, 3H), 2.27 (s, 3H), 1.96–1.47 (m, 7H), 1.34–0.79 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.2, 134.7, 128.7, 127.7, 113.0, 46.7, 40.8, 32.3, 29.5, 26.7, 26.6, 26.5, 14.7, 14.0, 13.0; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{15}H_{24}NO^+$ 234.1852, found 234.1853.

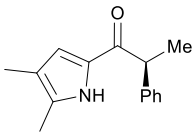


(**4n**) According to the general procedure A, reaction of **1n** (14.6 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4n** as a white solid (19.8 mg, 82%). Analytical data for compound **4n**: mp 113−114 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +93.4 (c 0.14, $CHCl_3$); enantiomeric ratio: 94:6, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 8.9 min; t_R (minor) = 6.7 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.38–7.33 (m, 2H), 7.32–7.27 (m, 2H), 7.24–7.18 (m, 1H), 5.78 (d, J = 2.8 Hz, 1H), 4.19 (t, J = 7.2 Hz, 1H), 2.40 (s, 3H), 2.23 (s, 3H), 2.19 (q, J = 7.2 Hz, 1H), 1.84 (q, J = 7.2 Hz, 1H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 140.2,

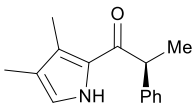
135.3, 128.8, 128.6, 128.4, 128.4, 126.8, 113.2, 55.1, 27.9, 15.0, 13.1, 12.7; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{16}H_{20}NO^+$ 242.1539, found 242.1542.



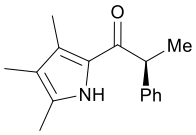
(**4o**) According to the general procedure A, reaction of **1o** (16.0 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4o** as a yellow solid (14.6 mg, 57%). Analytical data for compound **4o**: mp 87−88 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +3.3 (c 0.56, $CHCl_3$); enantiomeric ratio: 53.5:46.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 8.2 min; t_R (minor) = 5.6 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.40–7.36 (m, 2H), 7.29–7.26 (m, 2H), 7.22–7.17 (m, 1H), 5.78 (d, *J* = 2.5 Hz, 1H), 3.90 (d, *J* = 10.5 Hz, 1H), 2.57–2.49 (m, 1H), 2.47 (s, 3H), 2.22 (s, 3H), 1.02 (d, *J* = 6.5 Hz, 3H), 0.75 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 139.3, 134.8, 129.2, 128.9, 128.5, 128.2, 126.9, 113.3, 61.2, 32.5, 22.0, 21.0, 15.3, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{17}H_{22}NO^+$ 256.1696, found 256.1696.



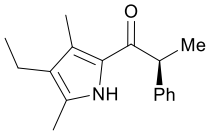
(**4p**) According to the general procedure A, reaction of **1a** (13.2 mg, 0.1 mmol, 1.0 equiv), 2,3-dimethyl-1*H*-pyrrole[14] (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4p** as a white solid (16.1 mg, 71%). Analytical data for compound **4p**: mp 157−158 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +60.3 (c 0.11, $CHCl_3$); enantiomeric ratio: 96:4, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 13.7 min; t_R (minor) = 8.1 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.41–7.34 (m, 2H), 7.33–7.27 (m, 2H), 7.23–7.17 (m, 1H), 6.75 (d, *J* = 2.3 Hz, 1H), 4.40 (q, *J* = 7.0 Hz, 1H), 2.19 (s, 3H), 2.00 (s, 3H), 1.54 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.7, 142.4, 134.8, 128.7, 128.6, 127.8, 126.7, 119.0, 118.1, 46.8, 19.0, 11.4, 11.0; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{15}H_{18}NO^+$ 228.1383, found 228.1385.



(**4q**) According to the general procedure A, reaction of **1a** (13.2 mg, 0.1 mmol, 1.0 equiv), 3,4-dimethyl-1*H*-pyrrole[15] (47.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4q** as a white solid (14.5 mg, 71%). Analytical data for compound **4q**: mp 130−131 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +77.5 (c 0.12, $CHCl_3$); enantiomeric ratio: 95.5:4.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 99:1 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 19.4 min; t_R (minor) = 20.9 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.36–7.27 (m, 4H), 7.25–7.18 (m, 1H), 6.70 (d, J = 3.0 Hz, 1H), 4.41 (q, J = 7.0 Hz, 1H), 2.27 (s, 3H), 1.97 (s, 3H), 1.52 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.8, 141.6, 129.3, 128.9, 127.9, 126.9, 125.7, 122.4, 121.3, 48.0, 19.8, 11.6, 10.1; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{15}H_{18}NO^+$ 228.1383, found 228.1386.

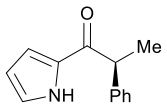


(**4r**) According to the general procedure A, reaction of **1a** (13.2 mg, 0.1 mmol, 1.0 equiv), 2,3,4-trimethyl-1*H*-pyrrole[16] (54.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4r** as a white solid (17.1 mg, 71%). Analytical data for compound **4r**: mp 152−153 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +81.4 (c 0.11, $CHCl_3$); enantiomeric ratio: 94.5:5.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 10.6 min; t_R (minor) = 9.3 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.36–7.27 (m, 4H), 7.24–7.18 (m, 1H), 4.43 (q, J = 7.0 Hz, 1H), 2.27 (s, 3H), 2.17 (s, 3H), 1.89 (s, 3H), 1.53 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.8, 142.1, 132.8, 128.7, 127.9, 127.3, 126.7, 126.6, 118.1, 47.6, 19.8, 12.2, 11.6, 9.0; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{16}H_{20}NO^+$ 242.1539, found 242.1542.

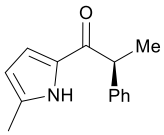


(**4s**) According to the general procedure A, reaction of **1a** (13.2 mg, 0.1 mmol, 1.0 equiv), 3-ethyl-2,4-dimethyl-1*H*-pyrrole (61.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4s** as a white solid (18.9 mg, 74%). Analytical data for compound **4s**: mp 116−117 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +50.3 (c 0.12, $CHCl_3$); enantiomeric ratio: 98:2, the er value of the product

was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 99:1 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 21.4 min; t_R (minor) = 19.4 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.36–7.27 (m, 4H), 7.24–7.17 (m, 1H), 4.41 (q, J = 6.9 Hz, 1H), 2.34 (q, J = 7.5 Hz, 2H), 2.28 (s, 3H), 2.18 (s, 3H), 1.51 (d, J = 6.9 Hz, 3H), 1.01 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 142.0, 132.3, 128.8, 128.0, 127.4, 126.7, 126.0, 124.9, 47.6, 19.9, 17.3, 15.5, 11.9, 11.6; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{17}H_{22}NO^+$ 256.1696, found 256.1696.

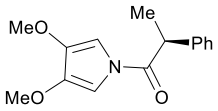


(**4t**) According to the general procedure A, reaction of **1a** (13.2 mg, 0.1 mmol, 1.0 equiv), 1*H*-pyrrole (33.5 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4t** as a white solid (9.0 mg, 45%). Analytical data for compound **4t**: mp 100−106 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +72.5 (c 0.17, $CHCl_3$); enantiomeric ratio: 92.5:7.5, the er value of the product was determined by HPLC on a Daicel Chiralcel AD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 33.4 min; t_R (minor) = 27.1 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.38–7.33 (m, 2H), 7.33–7.27 (m, 2H), 7.25–7.18 (m, 1H), 7.01–6.96 (m, 1H), 6.94–6.89 (m, 1H), 6.26–6.20 (m, 1H), 4.44 (q, J = 6.8 Hz, 1H), 1.54 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 141.9, 131.4, 128.8, 127.8, 127.0, 124.8, 116.8, 110.8, 47.6, 18.8; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{13}H_{14}NO^+$ 200.1070, found 200.1073.

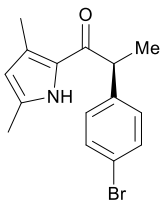


(**4u**) According to the general procedure A, reaction of **1a** (13.2 mg, 0.1 mmol, 1.0 equiv), 2-methyl-1*H*-pyrrole (40.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4u** as a white solid (10.9 mg, 51%). Analytical data for compound **4u**: mp 86−87 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +142.1 (c 0.10, $CHCl_3$); enantiomeric ratio: 93:7, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 12.2 min; t_R (minor) = 8.2 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.40–7.32 (m, 2H), 7.31–7.26 (m, 2H), 7.23–7.15 (m, 1H), 6.90–6.83 (m, 1H), 5.98–5.91 (m, 1H), 4.41 (q, J = 7.0 Hz, 1H), 2.28 (s, 3H), 1.54 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 142.2, 136.9, 130.4, 128.7, 127.8, 126.8, 118.3,

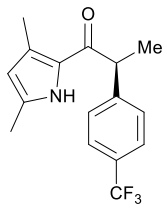
109.7, 47.0, 18.9, 13.3; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{14}H_{16}NO^+$ 214.1226, found 214.1230.



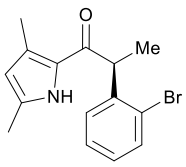
(**4v**) According to the general procedure A, reaction of **1a** (13.2 mg, 0.1 mmol, 1.0 equiv), 3,4-dimethoxy-1*H*-pyrrole[17] (63.6 mg, 0.5 mmol, 5.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4v** as a vesicular solid (14.8 mg, 57%). Analytical data for compound **4v**: R_f = 0.20 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +29.7 (c 0.15, $CHCl_3$); enantiomeric ratio: 86:14, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 11.3 min; t_R (minor) = 15.5 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.28 (m, 4H), 7.26–7.22 (m, 1H), 6.92 (s, 1H), 6.45 (s, 1H), 4.24 (q, *J* = 7.0 Hz, 1H), 3.72 (s, 6H), 1.57 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 143.2, 141.0, 129.2, 127.4, 127.2, 98.5, 58.0, 44.2, 20.2; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{15}H_{18}NO_3^+$ 260.1281, found 260.1286.



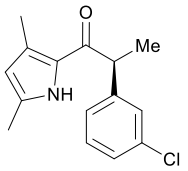
(**4w**) According to the general procedure B, reaction of **5w** (23.9 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole (19.0 mg, 0.2 mmol, 2.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4w** as a white solid (23.0 mg, 75%). Analytical data for compound **4w**: mp 114−115 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +66.3 (c 0.14, $CHCl_3$); enantiomeric ratio: 92:8, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 9.5 min; t_R (minor) = 7.9 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.77 (s, 1H), 4.35 (q, *J* = 7.0 Hz, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 1.48 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 140.8, 135.5, 131.8, 129.7, 128.5, 128.0, 120.8, 113.3, 46.7, 19.7, 14.7, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{15}H_{17}BrNO^+$ 306.0488, found 306.0489



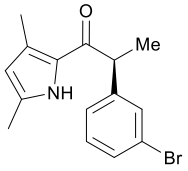
(**4x**) According to the general procedure B, reaction of **5x** (22.8 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole (19.0 mg, 0.2 mmol, 2.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4x** as a white solid (17.4 mg, 59%). Analytical data for compound **4x**: mp 121−122 °C; R_f = 0.25 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +45.7 (c 0.09, $CHCl_3$); enantiomeric ratio: 96.5:3.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 8.6 min; t_R (minor) = 7.2 min; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.48; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 5.78 (d, J = 2.5 Hz, 1H), 4.44 (q, J = 7.0 Hz, 1H), 2.32 (s, 3H), 2.22 (s, 3H), 1.52 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.1, 145.7, 135.4, 129.2 (q, J = 32.1 Hz), 128.40, 128.35, 128.0, 125.7 (q, J = 3.8 Hz), 124.3 (q, J = 270.0 Hz, CF_3), 113.4, 47.1, 19.7, 14.7, 13.2; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{16}H_{17}F_3NO^+$ 296.1257, found 296.1262.



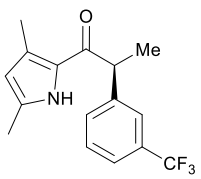
(**4y**) According to the general procedure B, reaction of **5y** (23.9 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole (19.0 mg, 0.2 mmol, 2.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4y** as a white solid (23.3 mg, 76%). Analytical data for compound **4y**: mp 155−156 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +205.4 (c 0.13, $CHCl_3$); enantiomeric ratio: 95.5:4.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 17.6 min; t_R (minor) = 20.7 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.32–7.28 (m, 1H), 7.25–7.20 (m, 1H), 7.13–7.05 (m, 1H), 5.76 (d, J = 2.5 Hz, 1H), 4.71 (q, J = 7.0 Hz, 1H), 2.25 (s, 3H), 2.21 (s, 3H), 1.49 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.2, 141.1, 135.1, 132.9, 129.2, 129.1, 128.4, 128.1, 128.0, 124.7, 113.1, 47.0, 17.8, 14.2, 13.2; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + Na]^+$ calcd for $C_{15}H_{16}BrNNaO^+$ 328.0307, found 328.0309.



(**4z**) According to the general procedure B, reaction of **5z** (19.5 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole (19.0 mg, 0.2 mmol, 2.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4z** as a white solid (19.1 mg, 73%). Analytical data for compound **4z**: mp 116−117 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +104.5 (c 0.16, $CHCl_3$); enantiomeric ratio: 96.5:3.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 9.3 min; t_R (minor) = 7.8 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.34–7.30 (m, 1H), 7.24–7.16 (m, 3H), 5.79 (d, *J* = 2.5 Hz, 1H), 4.38 (q, *J* = 7.0 Hz, 1H), 2.34 (s, 3H), 2.23 (s, 3H), 1.51 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.3, 143.7, 135.8, 134.5, 129.9, 128.6, 128.1, 128.0, 127.0, 126.2, 113.3, 46.9, 19.7, 14.8, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) [M + Na]$^+$ calcd for $C_{15}H_{16}ClNNaO^+$ 284.0813, found 284.0812.

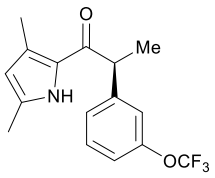


(**4aa**) According to the general procedure B, reaction of **5aa** (23.9 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole (19.0 mg, 0.2 mmol, 2.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4aa** as a white solid (24.8 mg, 81%). Analytical data for compound **4aa**: mp 95−96 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +95.1 (c 0.16, $CHCl_3$); enantiomeric ratio: 95.5:4.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 9.8 min; t_R (minor) = 8.2 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.49–7.45 (m, 1H), 7.36–7.31 (m, 1H), 7.26–7.21 (m, 1H), 7.19–7.12 (m, 1H), 5.79 (d, *J* = 3.0 Hz, 1H), 4.36 (q, *J* = 7.0 Hz, 1H), 2.34 (s, 3H), 2.22 (s, 3H), 1.50 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.3, 144.0, 135.7, 131.0, 130.2, 130.0, 128.6, 128.0, 126.7, 122.8, 113.3, 46.9, 19.8, 14.8, 13.2; HRMS (ESI-Orbitrap) (*m*/*z*) [M + H]$^+$ calcd for $C_{15}H_{17}BrNO^+$ 306.0488, found 306.0488.

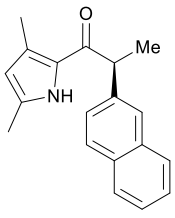


(**4ab**) According to the general procedure B, reaction of **5ab** (22.8 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole (19.0 mg, 0.2 mmol, 2.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4ab** as a yellow solid (22.4 mg, 76%). Analytical data for compound **4ab**: mp 122−123 °C; R_f = 0.25

(petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +48.4 (c 0.11, $CHCl_3$); enantiomeric ratio: 96.5:3.5, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 8.8 min; t_R (minor) = 7.5 min; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.51; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.59 (s, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.44–7.36 (m, 1H), 5.80 (d, J = 2.5 Hz, 1H), 4.48 (q, J = 7.0 Hz, 1H), 2.36 (s, 3H), 2.21 (s, 3H), 1.54 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.2, 142.6, 135.9, 131.5, 131.0 (d, J = 31.9 Hz), 129.1, 128.6, 127.9, 124.9 (q, J = 3.8 Hz), 124.3 (q, J = 270.8 Hz, CF_3), 123.7 (q, J = 3.8 Hz), 113.4, 47.0, 19.8, 14.8, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{16}H_{17}F_3NO^+$ 296.1257, found 296.1261.

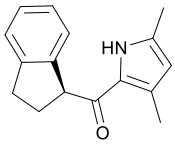


(**4ac**) According to the general procedure B, reaction of **5ac** (24.4 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole (19.0 mg, 0.2 mmol, 2.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4ac** as a yellow solid (21.5 mg, 69%). Analytical data for compound **4ac**: mp 93−94 °C; R_f = 0.25 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +70.7 (c 0.13, $CHCl_3$); enantiomeric ratio: 97:3, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 7.4 min; t_R (minor) = 6.5 min; ^{19}F NMR (471 MHz, $CDCl_3$) δ -55.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.31 (t, J = 8.0 Hz, 1H), 7.26–7.23 (m, 1H), 7.19 (s, 1H), 7.09–7.05 (m, 1H), 5.79 (d, J = 2.5 Hz, 1H), 4.40 (q, J = 7.0 Hz, 1H), 2.33 (s, 3H), 2.22 (s, 3H), 1.51 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.2, 149.5, 144.0, 135.6, 130.0, 128.5, 128.0, 126.3, 120.8, 120.6 (q, J = 255.4 Hz, CF_3),119.2, 113.3, 46.9, 19.7, 14.7, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{16}H_{17}F_3NO_2^+$ 312.1206, found 312.1205.



(**4ad**) According to the general procedure B, reaction of **5ad** (21.0 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole (19.0 mg, 0.2 mmol, 2.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4ab** as a yellow solid (22.5 mg, 81%). Analytical data for compound **4ad**: mp 164−165 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = +95.3 (c 0.15, $CHCl_3$); enantiomeric ratio: 91:9, the er value of

the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 12.8 min; t_R (minor) = 9.4 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.82–7.75 (m, 3H), 7.73 (s, 1H), 7.50–7.46 (m, 1H), 7.46–7.40 (m, 2H), 5.75 (d, J = 3.0 Hz, 1H), 4.55 (q, J = 7.0 Hz, 1H), 2.34 (s, 3H), 2.21 (s, 3H), 1.60 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.0, 139.3, 135.1, 133.7, 132.5, 128.4, 128.3, 127.9, 127.7, 126.6, 126.3, 126.1, 125.7, 113.1, 47.6, 19.8, 14.8, 13.2; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{19}H_{20}NO^+$ 278.1539, found 278.1540.



(**4ae**) According to the general procedure B, reaction of **5ae** (20.0 mg, 0.1 mmol, 1.0 equiv), 2,4-dimethyl-1*H*-pyrrole (19.0 mg, 0.2 mmol, 2.0 equiv), (*R*)-**3h** (3.3 mg, 0.5 % mmol, 0.05 equiv) afforded **4ae** as a white solid (15.3 mg, 64%). Analytical data for compound **4ae**: mp 153−154 °C; R_f = 0.30 (petroleum ether/ethyl acetate = 10:1); $[\alpha]^{25}_D$ = −116.4 (c 0.13, $CHCl_3$); enantiomeric ratio: 99:1, the er value of the product was determined by HPLC on a Daicel Chiralcel OD-3 column; eluent, *n*-hexane/2-propanol = 97:3 (v/v); temp, r.t.; flow rate, 1.0 mL/min; uv-vis detection, λ = 254 nm; t_R (major) = 15.5 min; t_R (minor) = 17.1 min; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.27 (s, 1H), 7.22–7.14 (m, 1H), 7.14–7.07 (m, 2H), 5.88 (d, J = 3.0 Hz, 1H), 4.76 (t, J = 7.8 Hz, 1H), 3.18–3.07 (m, 1H), 3.03–2.93 (m, 1H), 2.56–2.47 (m, 1H), 2.45 (s, 3H), 2.41–2.31 (m, 1H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.9, 144.9, 142.4, 135.3, 128.7, 128.5, 127.2, 126.5, 124.8, 124.5, 113.4, 52.8, 32.2, 29.4, 14.4, 13.1; HRMS (ESI-Orbitrap) (*m*/*z*) $[M + H]^+$ calcd for $C_{16}H_{18}NO^+$ 240.1383, found 240.1389.

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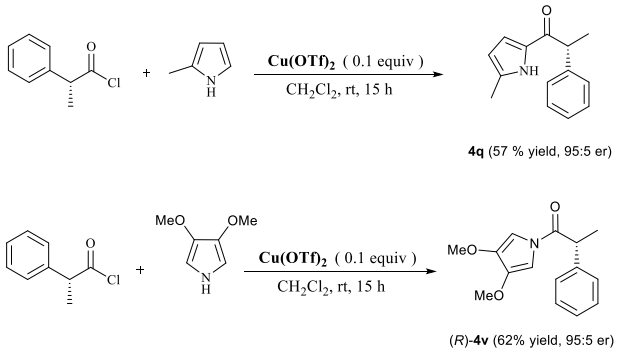
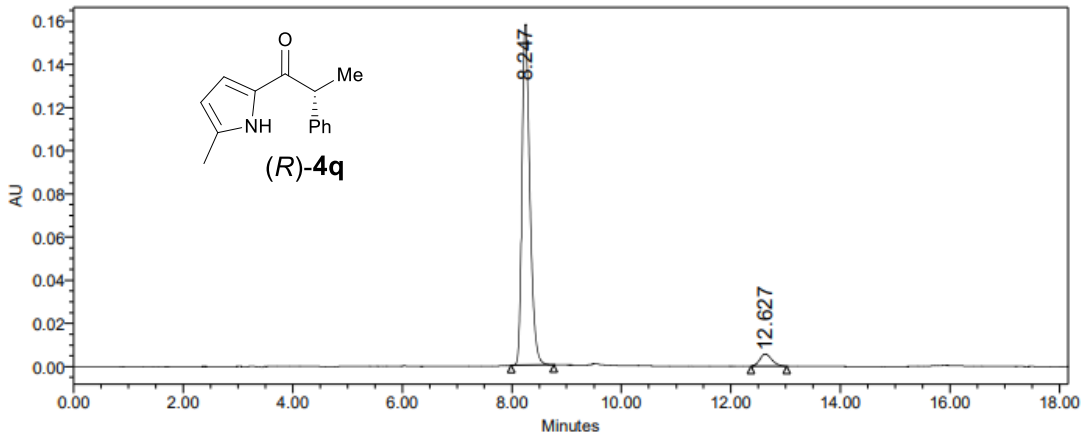
Determination of the configuration of product 4



Under argon atmosphere, a flame-dried 10 ml Schlenk tube was charged with $Cu(OTf)_2$ (0.03 mmol, 0.1 equiv) and CH_2Cl_2 (3.0 mL). Then, 2-methyl-1*H*-pyrrole (0.9 mmol, 3.0 equiv.) and (*R*)-acid chloride (0.3 mmol, 1.0 equiv.) in CH_2Cl_2 (1.0 ml) were added. The resulting solution was stirred for 15 h at room temperature. The solution was evaporated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1 - 15:1) to give the product (*R*)-**4q** (57%). The same procedure was followed for the preparation of (*R*)-**4v** (62%).

Chiral HPLC analysis of (*R*)-4q prepared with (*R*)-2-phenylpropanoyl chloride and pyrroles

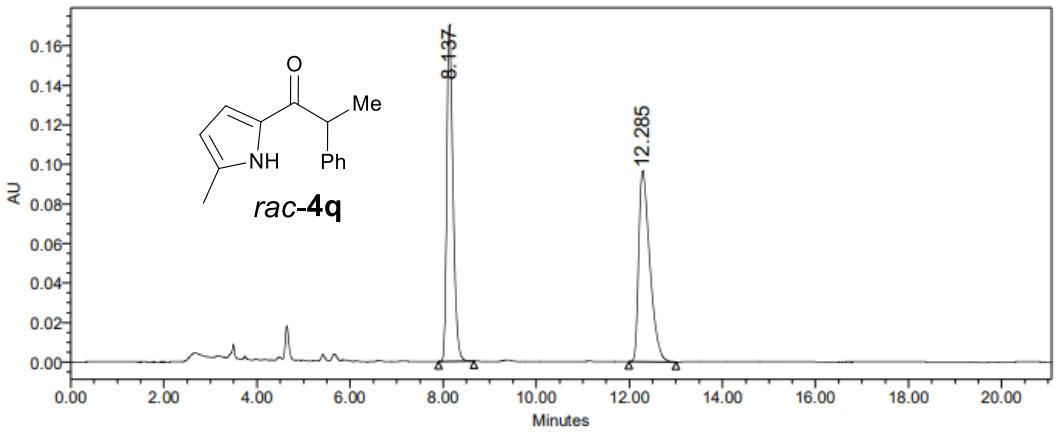
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.247	1573269	94.89	157834
2	W2489 ChA 254nm	12.627	84724	5.11	5612

HPLC of (*R*)-**4q** prepared from (*R*)-2-phenylpropanoyl chloride

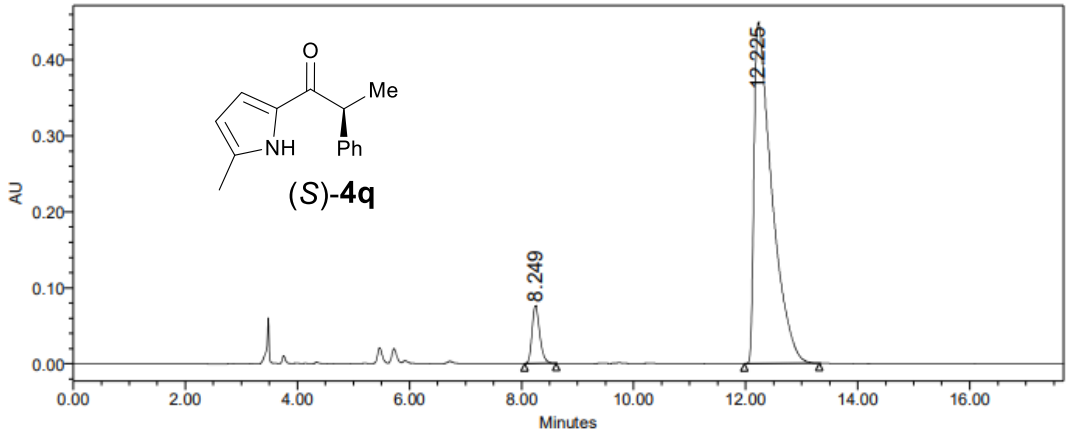


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5197; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.137	1599096	50.06	170342
2	W2489 ChA 254nm	12.285	1595050	49.94	96365

HPLC of *rac*-**4q**



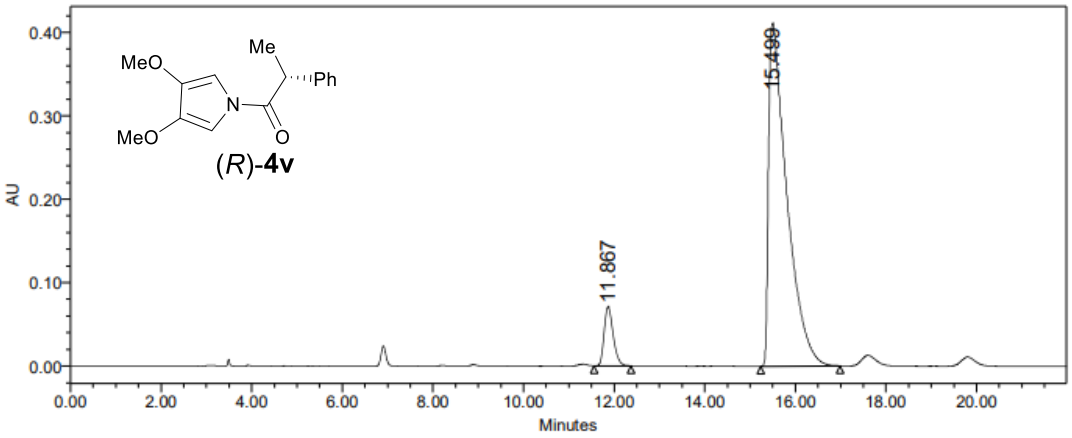
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5176; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.249	719610	6.77	75966
2	W2489 ChA 254nm	12.225	9904893	93.23	448702

HPLC of (*S*)-**4q** prepared from the reaction catalyzed by (*R*)-**3h**

Daicel Chiralcel OD-3 column, n-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t

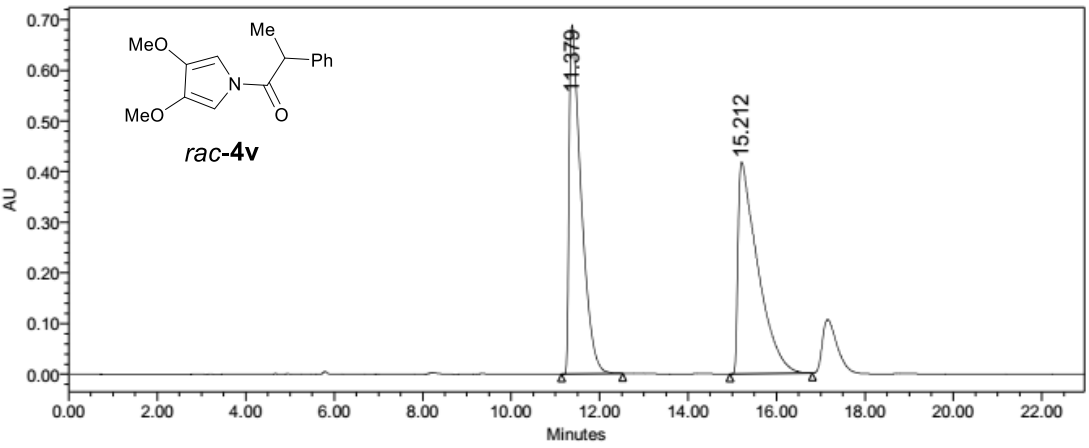


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4325; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.867	985393	7.90	70980
2	W2489 ChA 254nm	15.499	11495425	92.10	410791

HPLC of (*R*)-**4v** prepared from (*R*)-2-phenylpropanoyl chloride

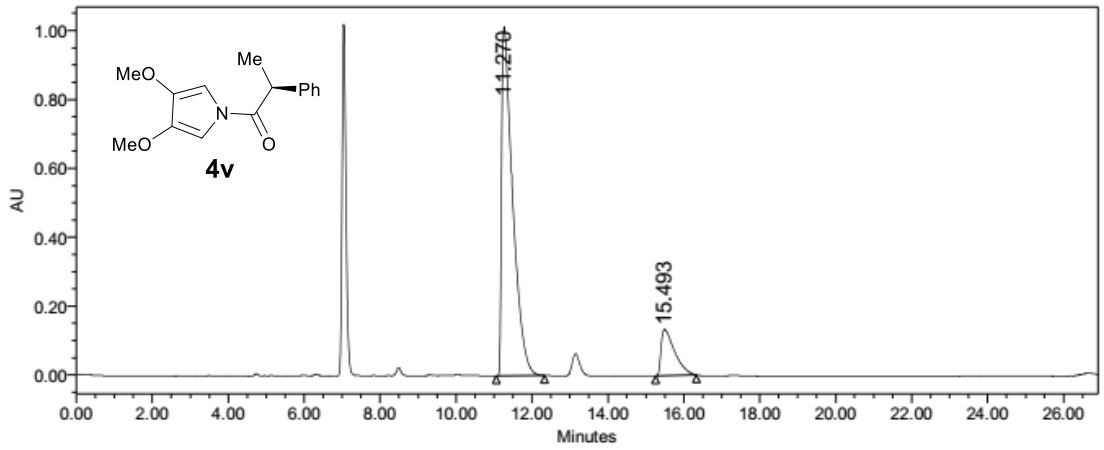


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5018; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.379	13014096	50.05	689246
2	W2489 ChA 254nm	15.212	12986094	49.95	417979

HPLC of *rac*-**4v**

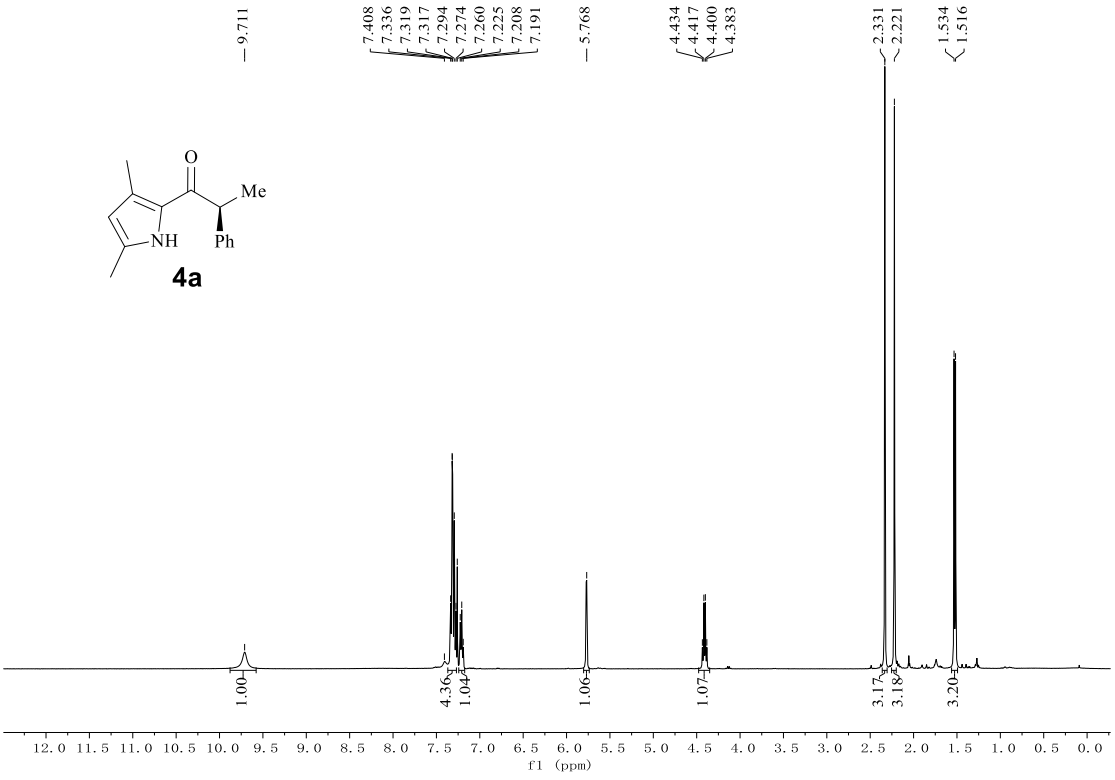


Processed Channel Descr.: W2489 ChA 254nm

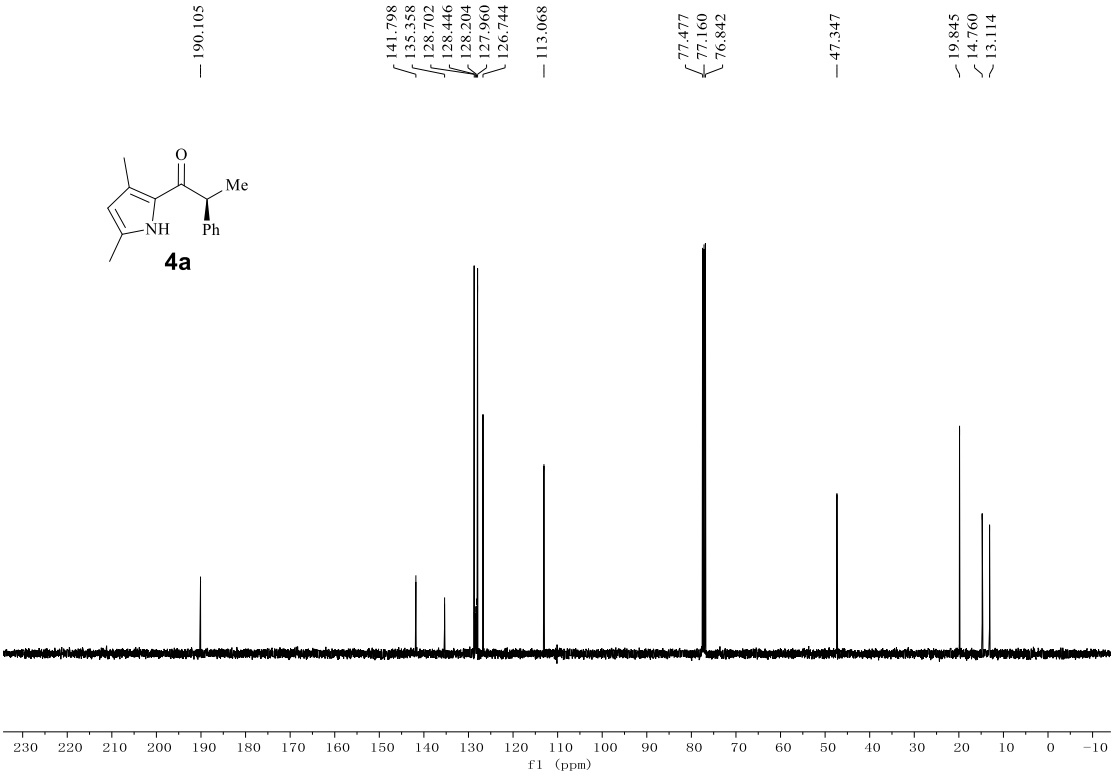
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.270	20417225	85.90	1014136
2	W2489 ChA 254nm	15.493	3352216	14.10	135237

HPLC of (*S*)-**4v** prepared from the reaction catalyzed by (*R*)-**3h**

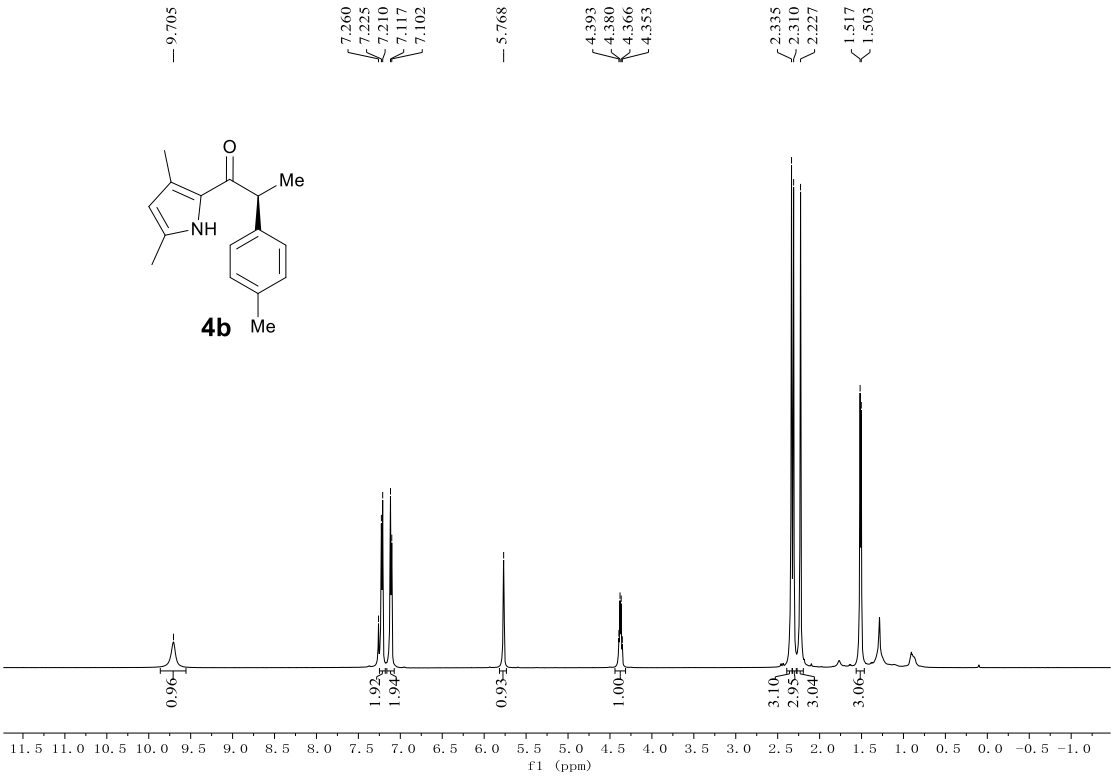
^{1}H NMR and ^{13}C NMR spectra for all of new compounds



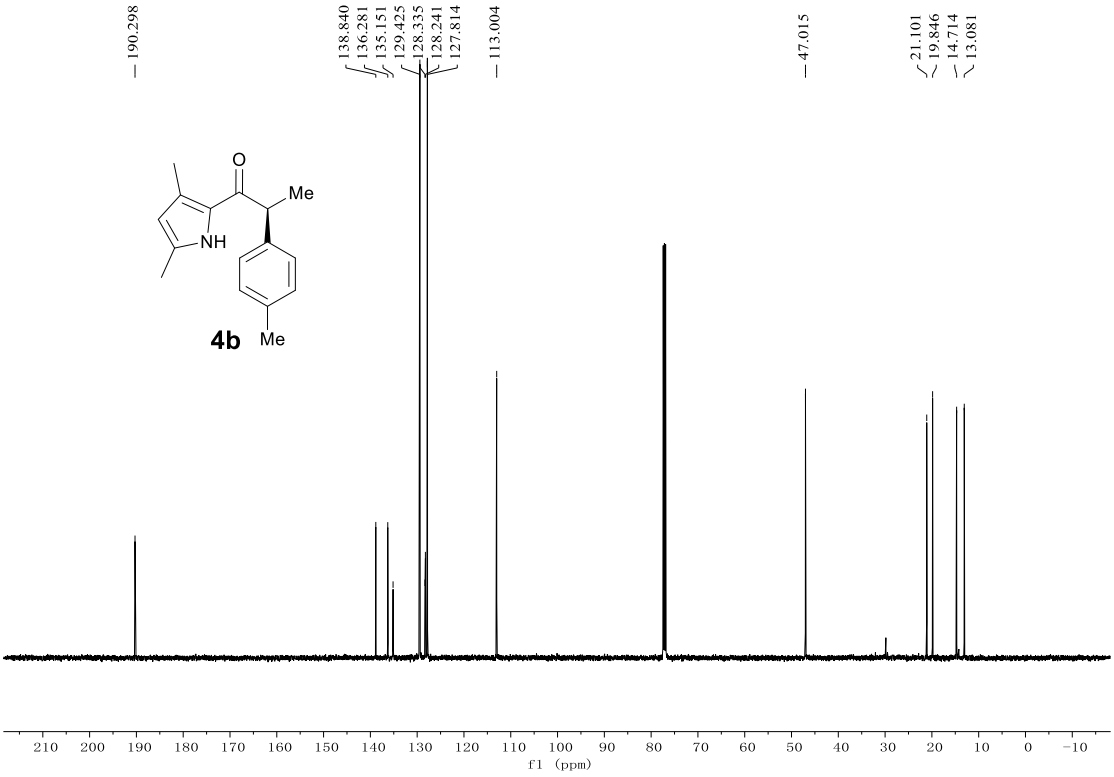
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4a**



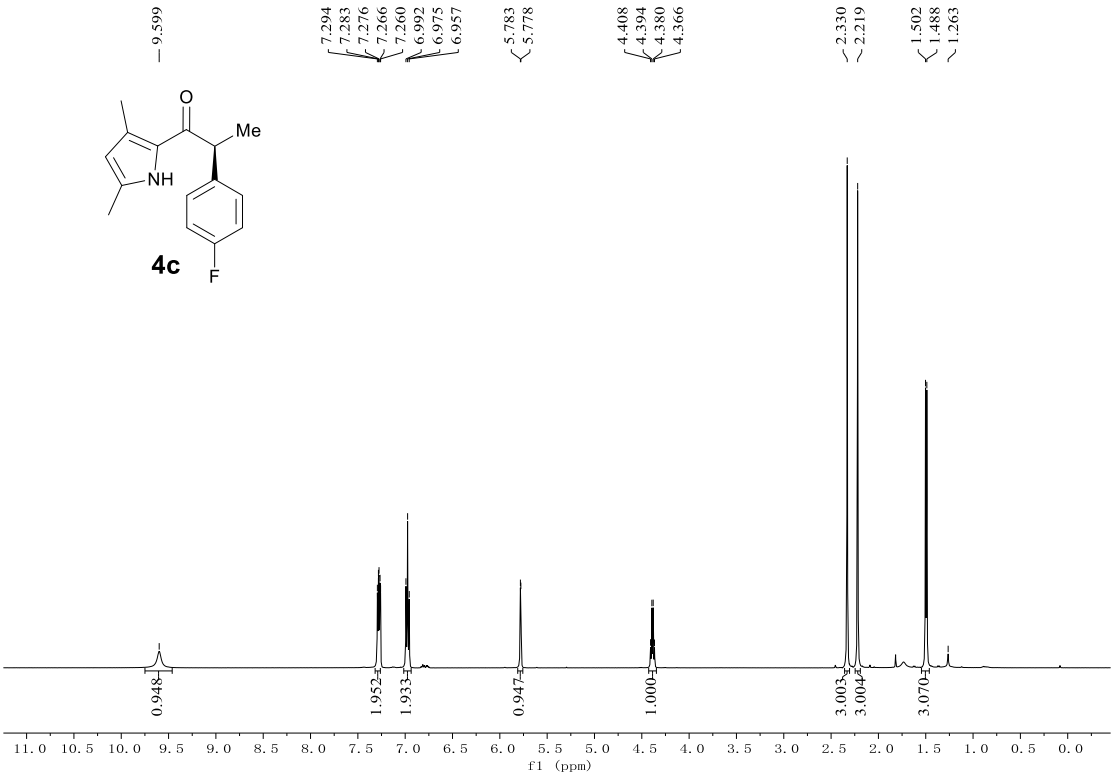
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **4a**



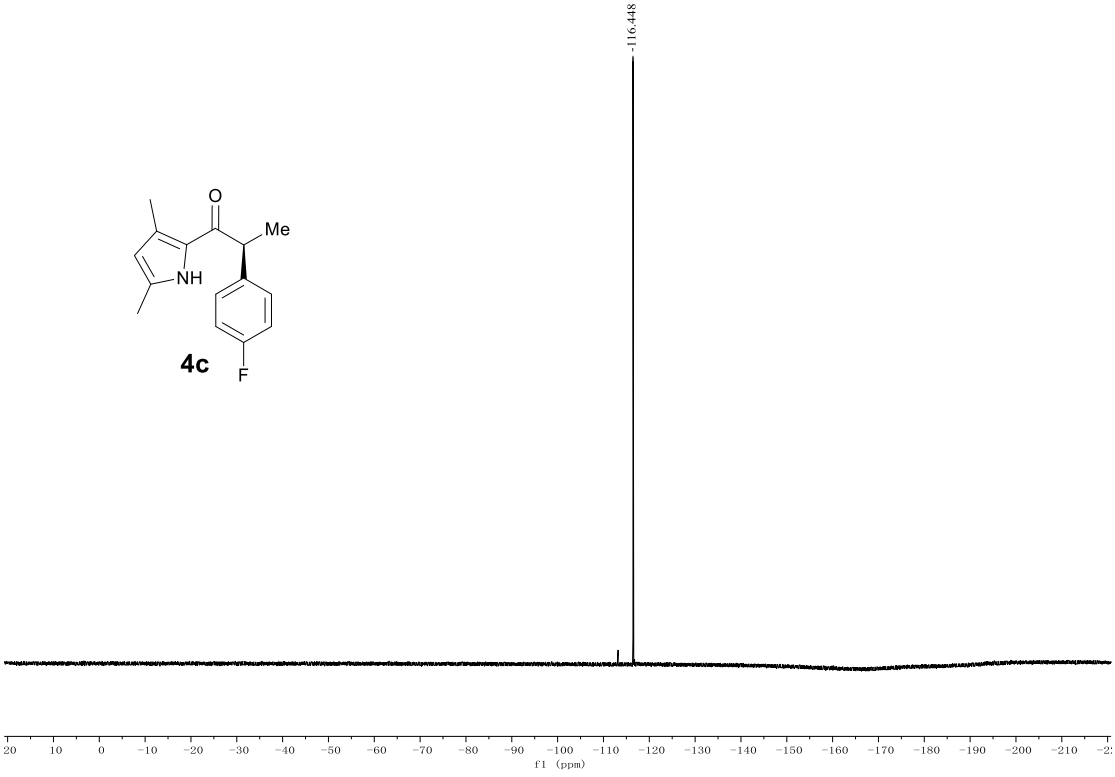
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4b**



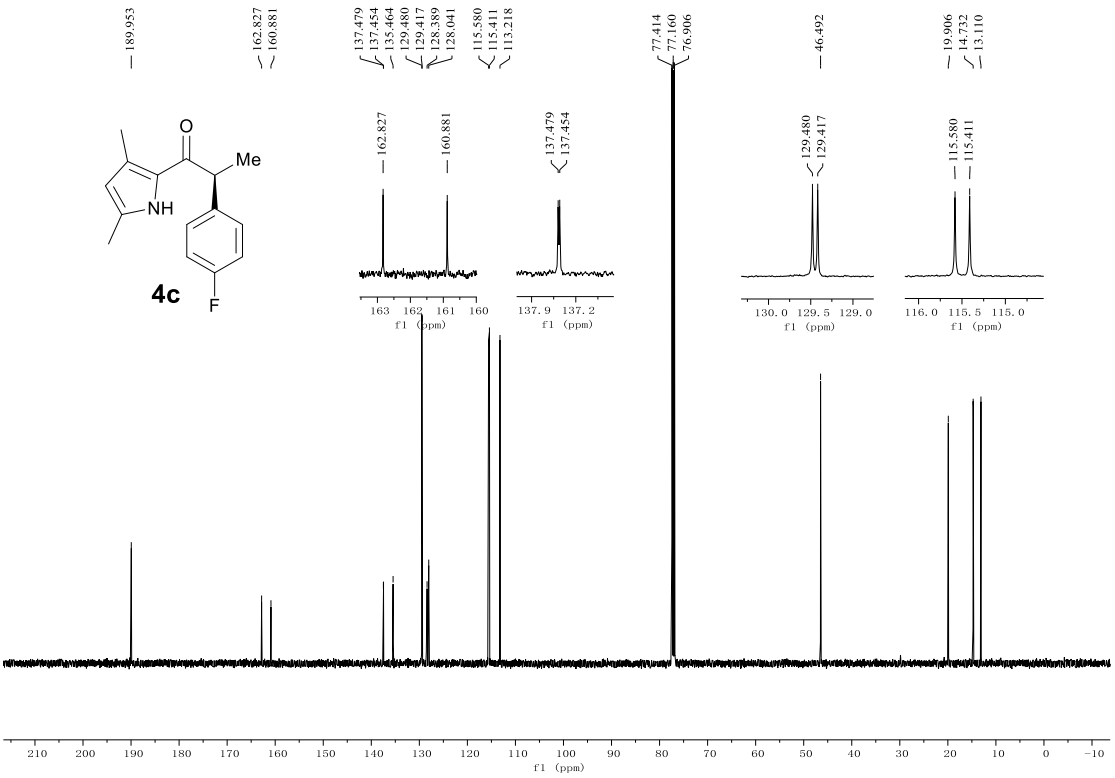
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4b**



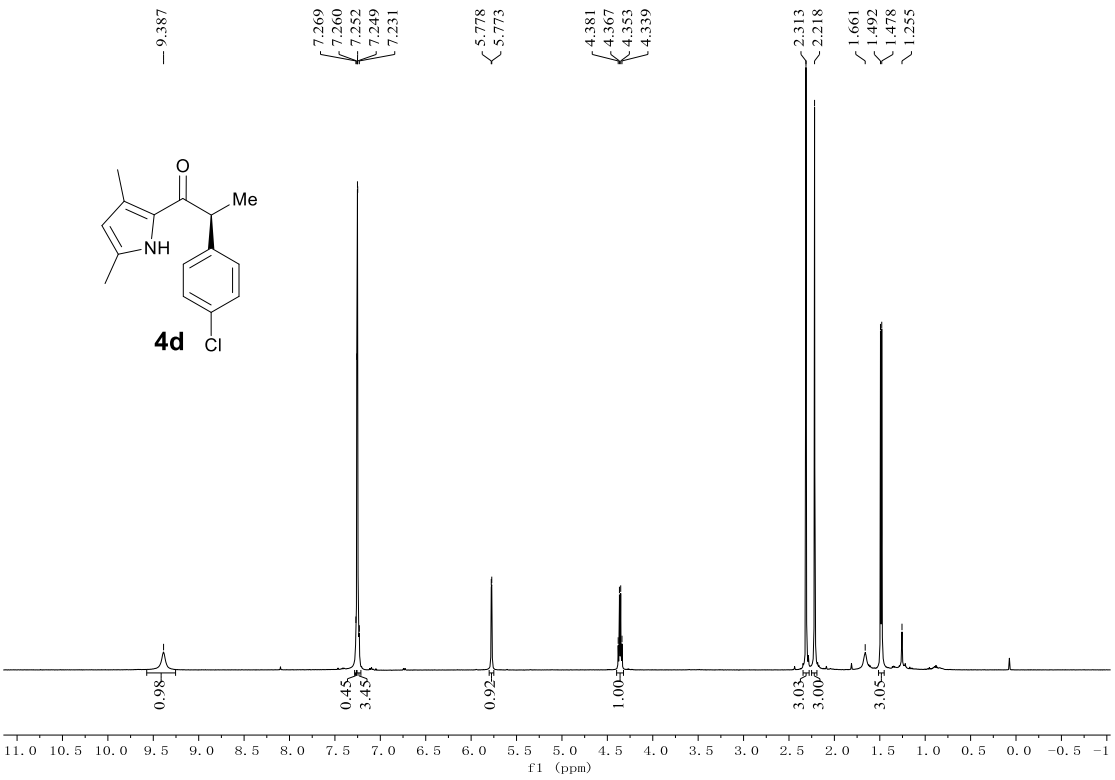
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4c**



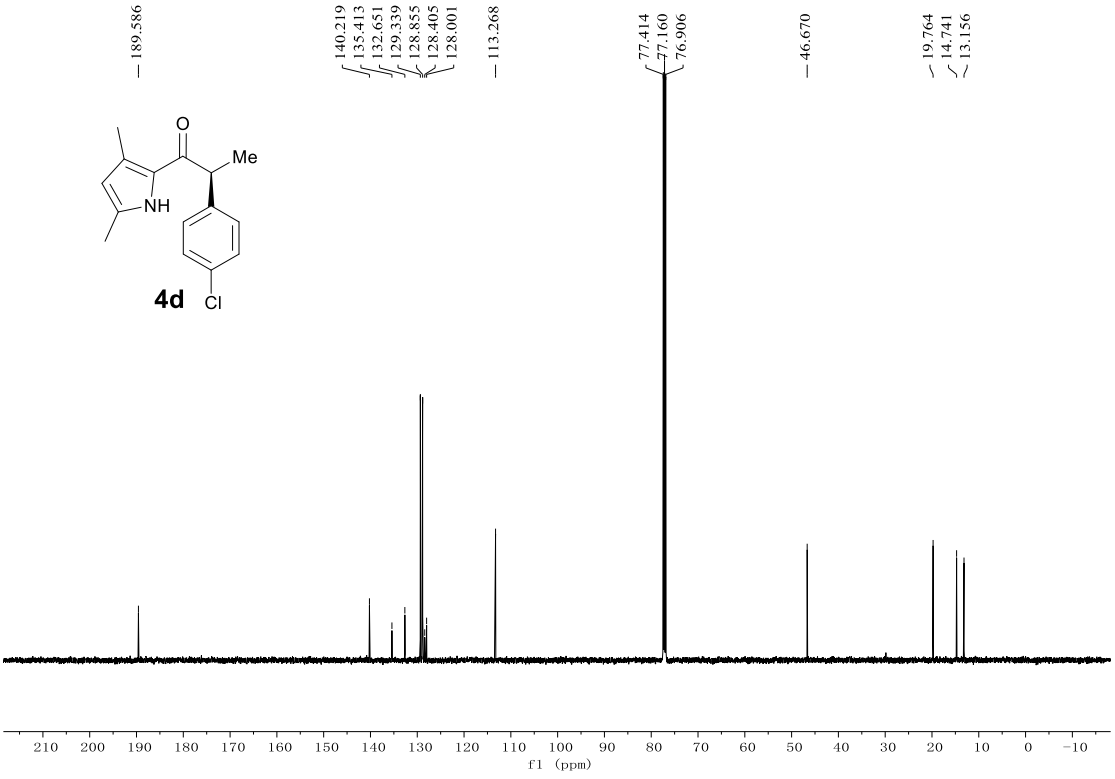
^{19}F NMR spectrum ($CDCl_3$, 471 MHz) of **4c**



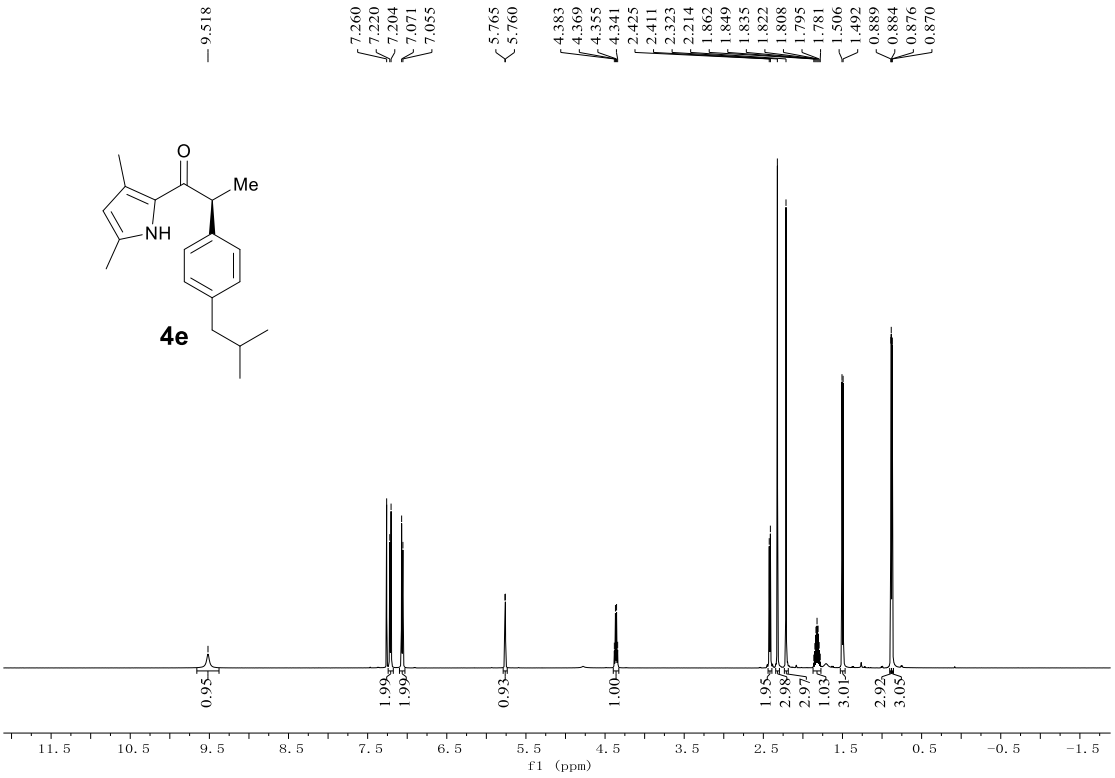
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4c**



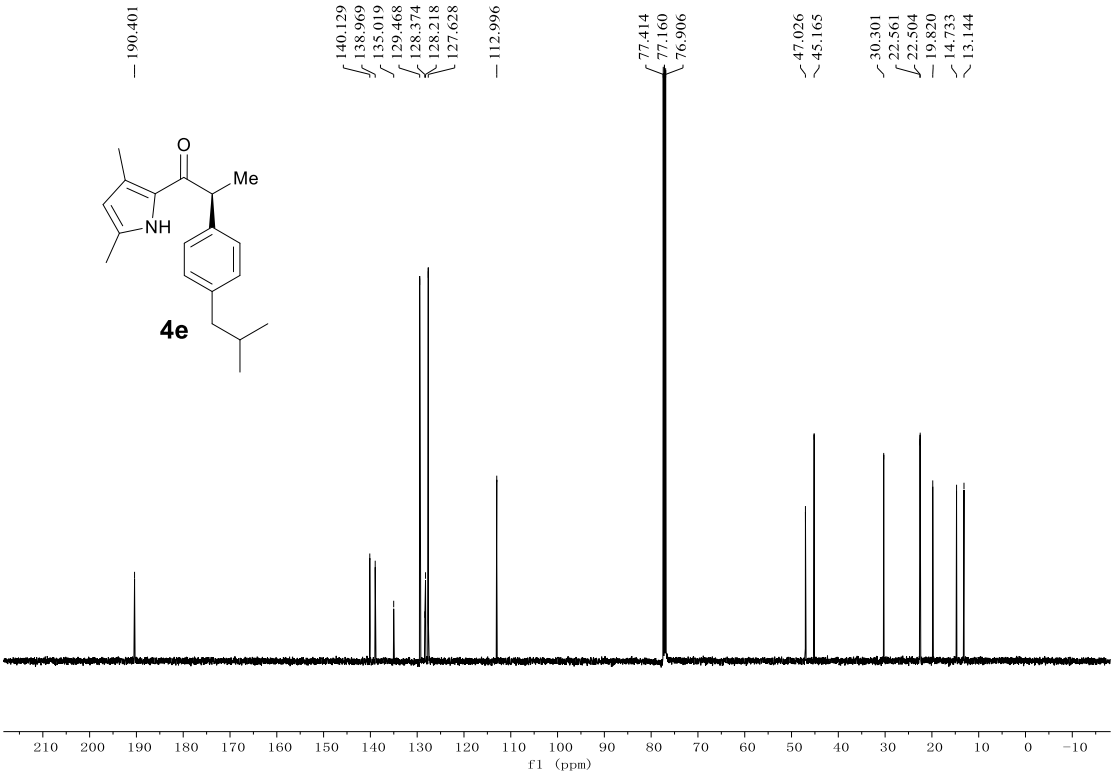
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4d**



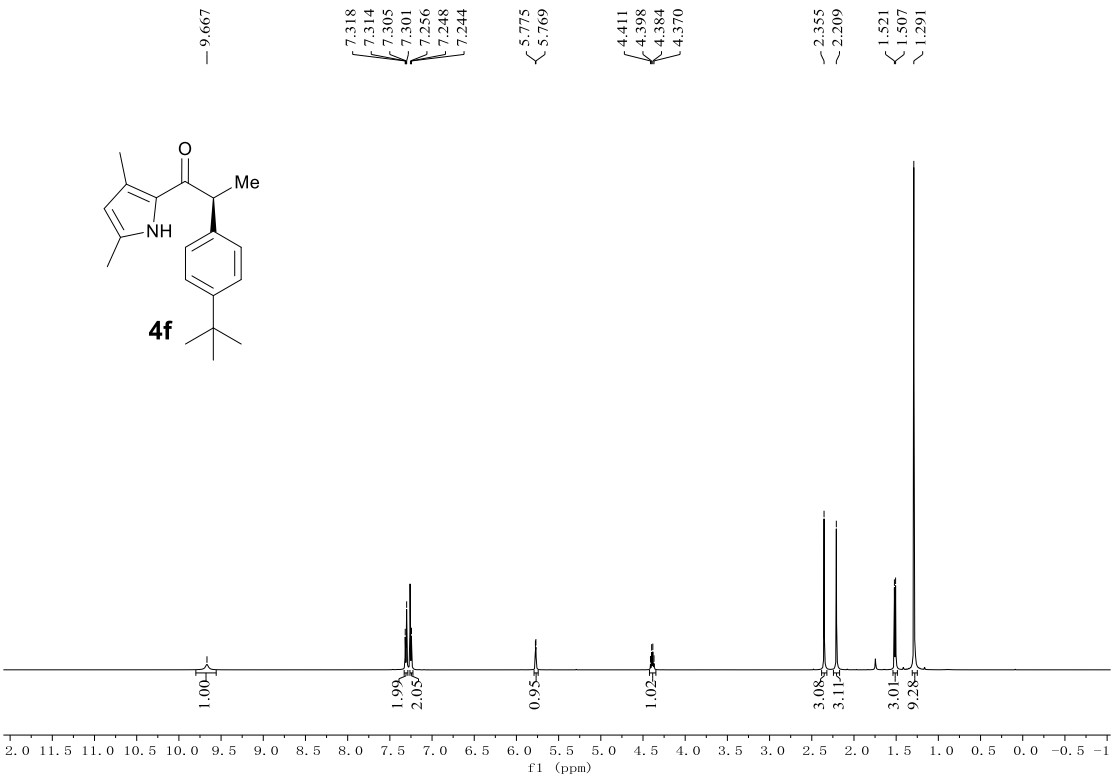
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4d**



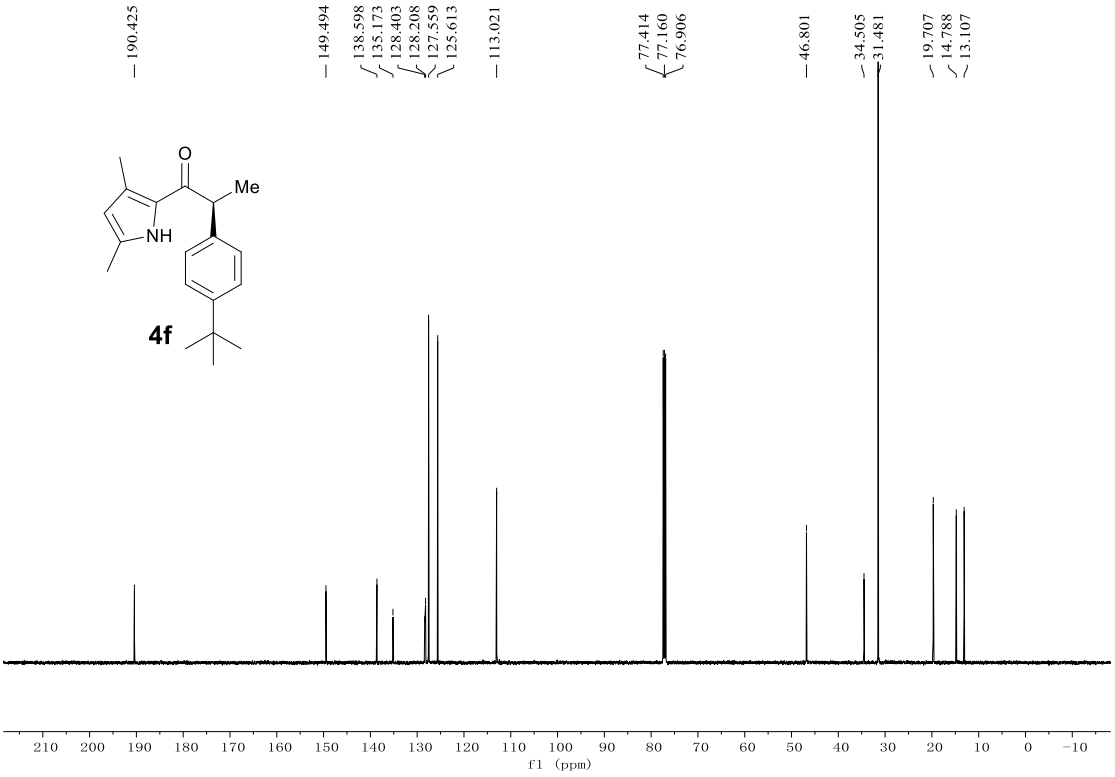
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4e**



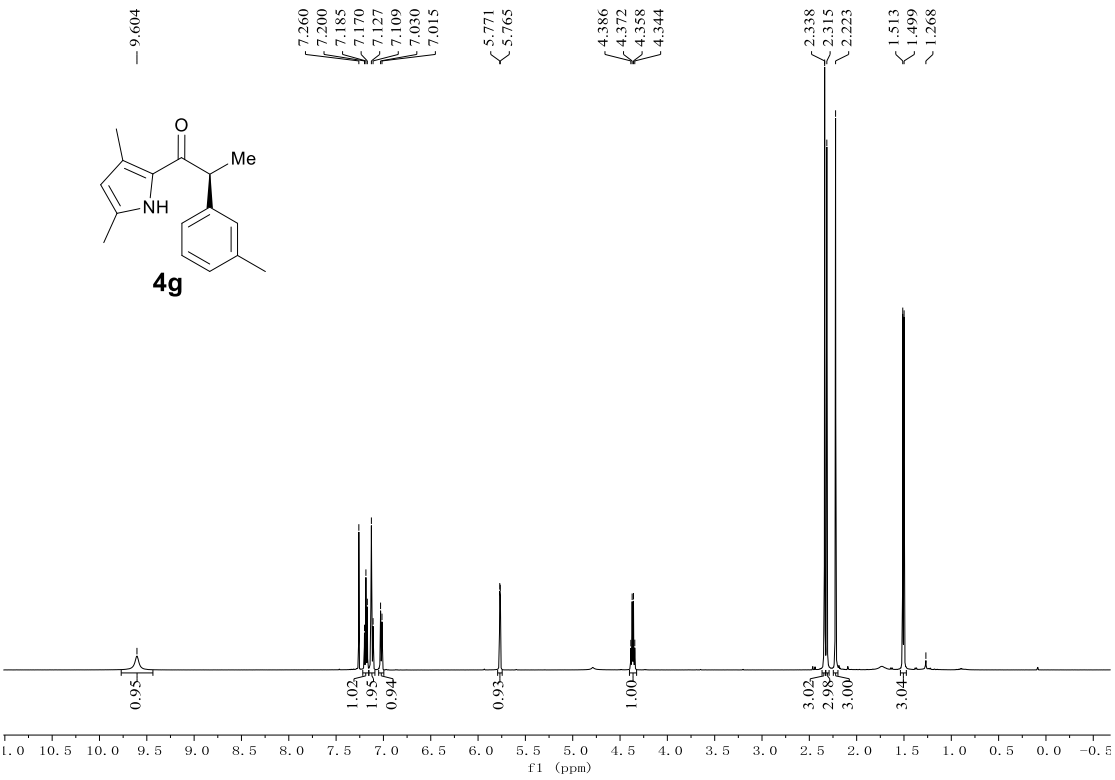
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4e**



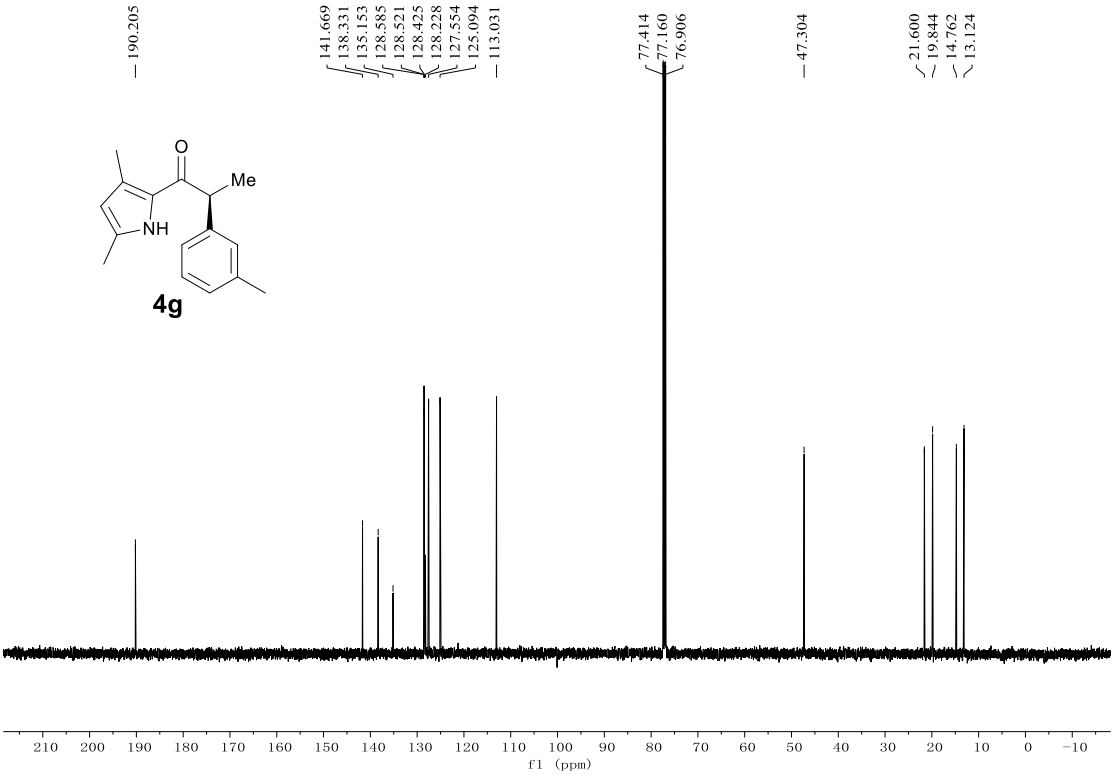
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4f**



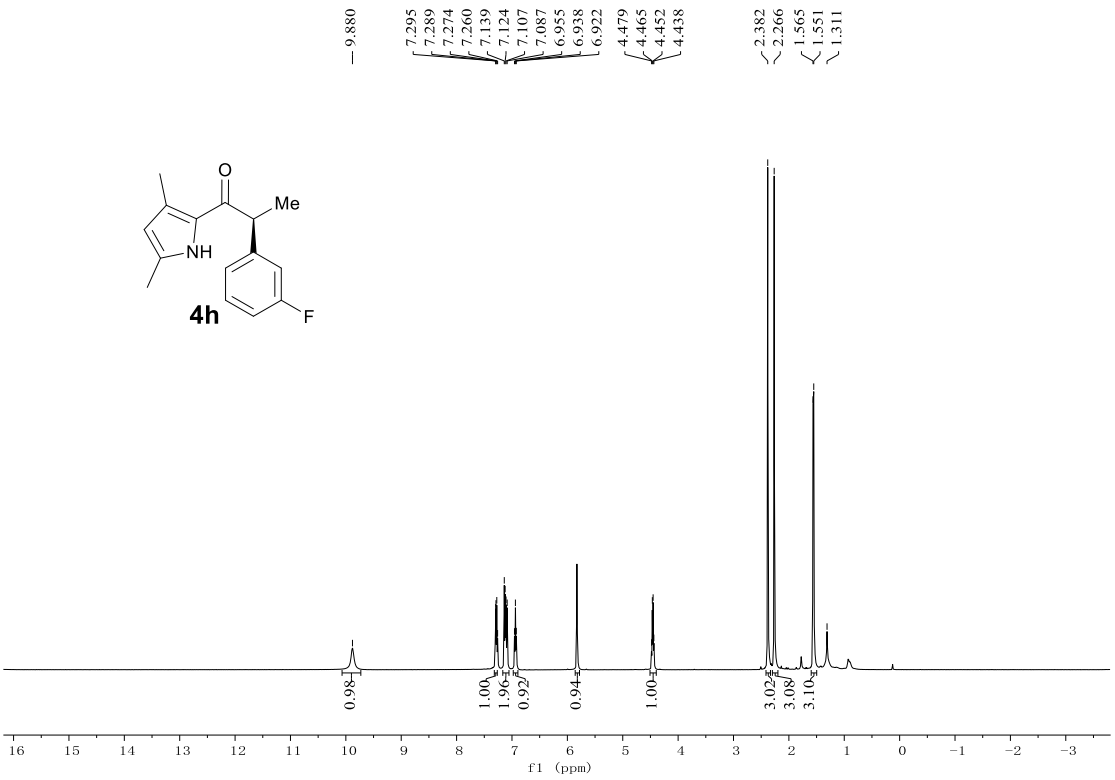
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4f**



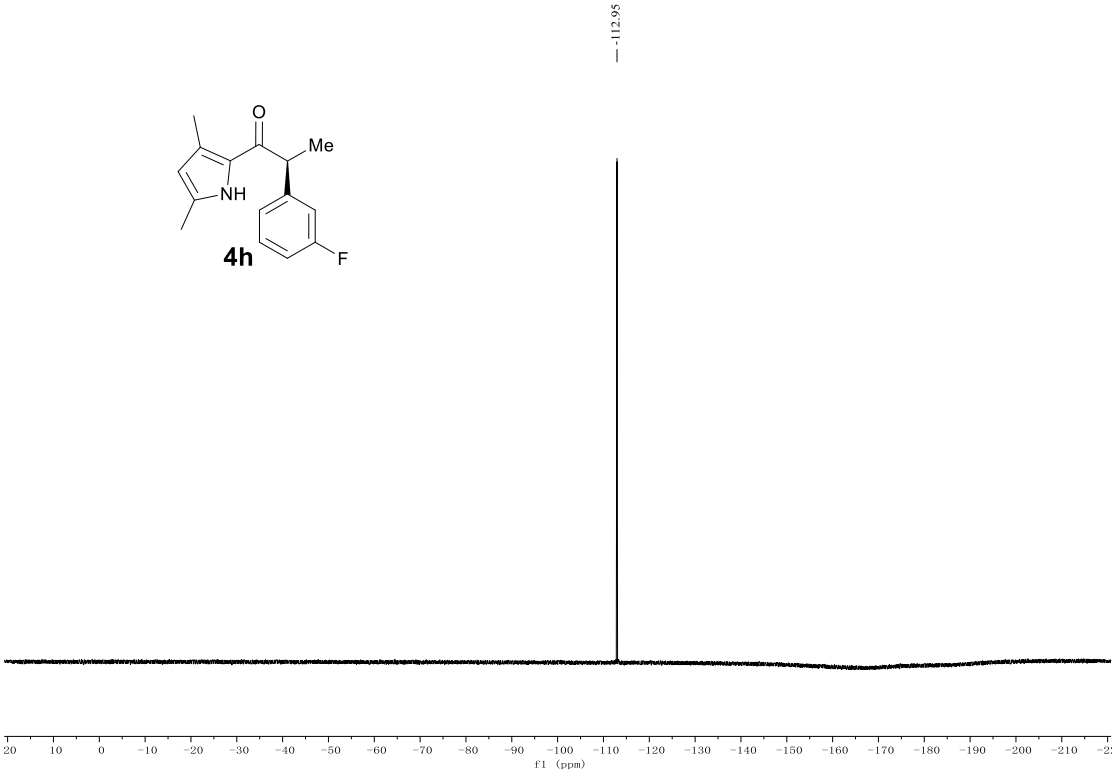
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4g**



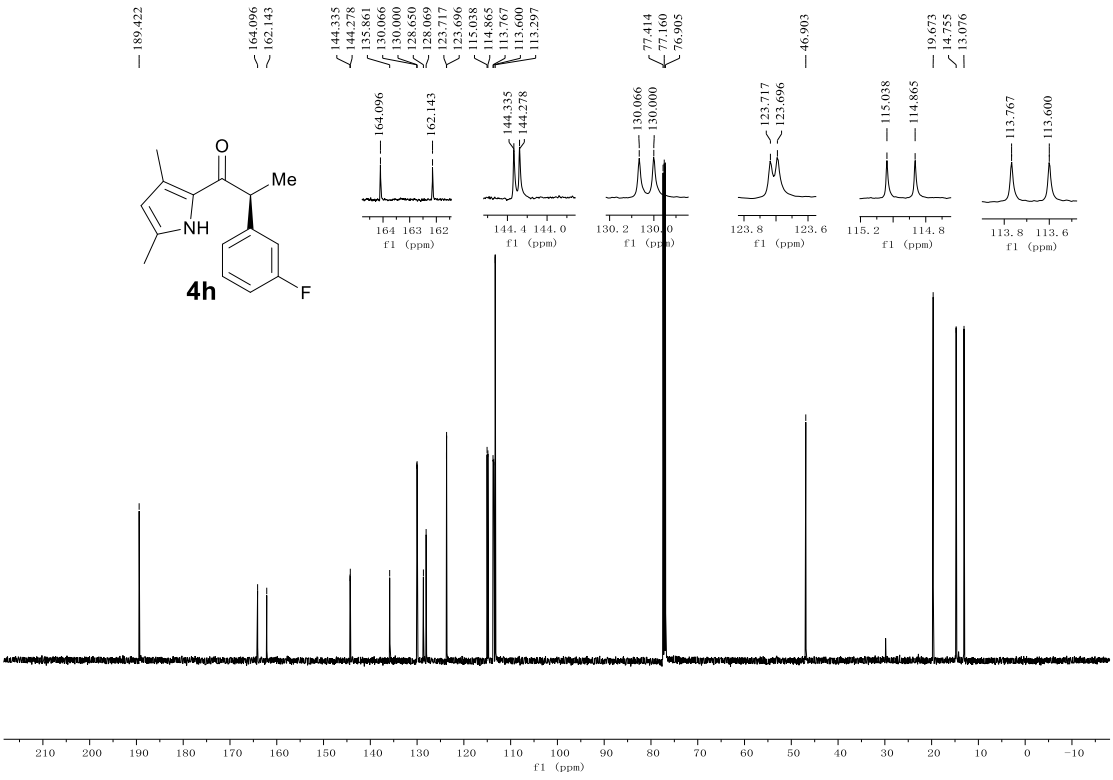
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4g**



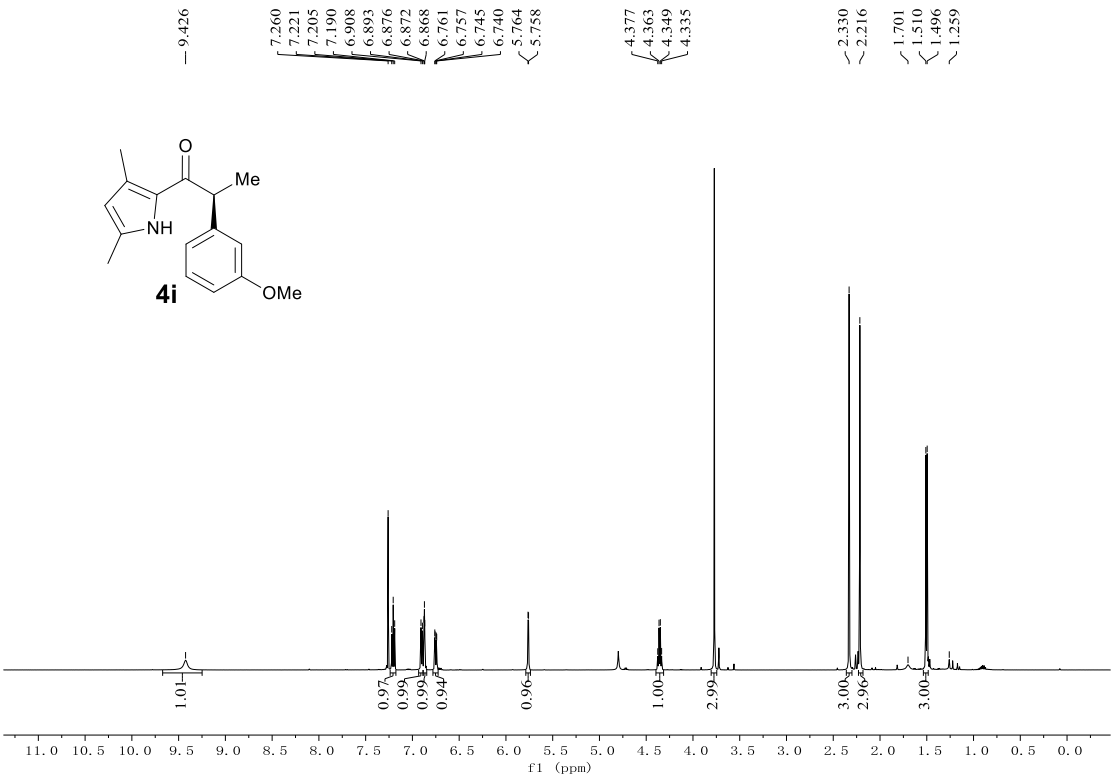
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4h**



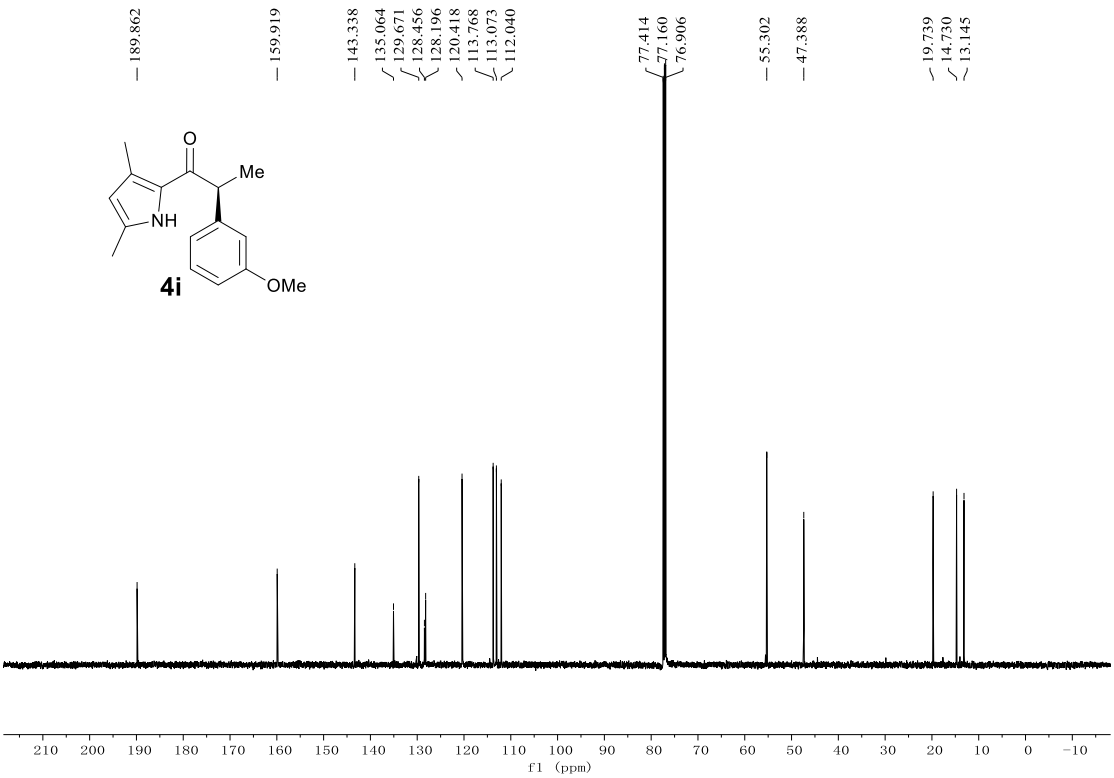
^{19}F NMR spectrum ($CDCl_3$, 471 MHz) of **4h**



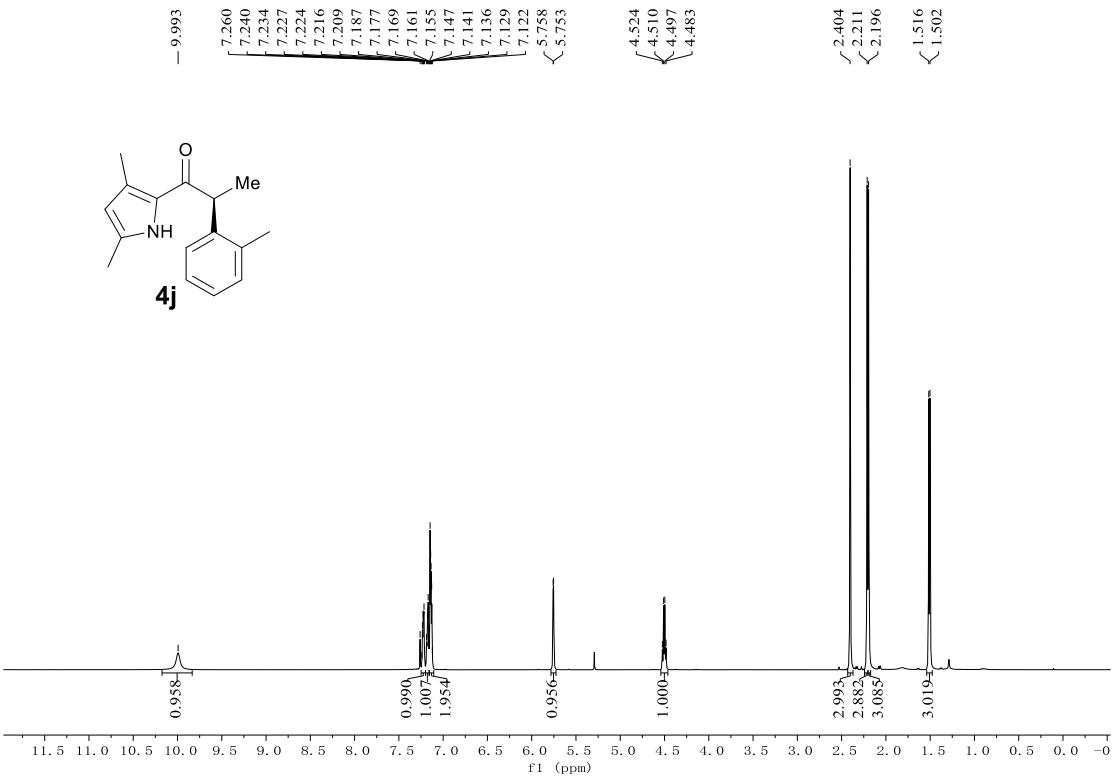
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4h**



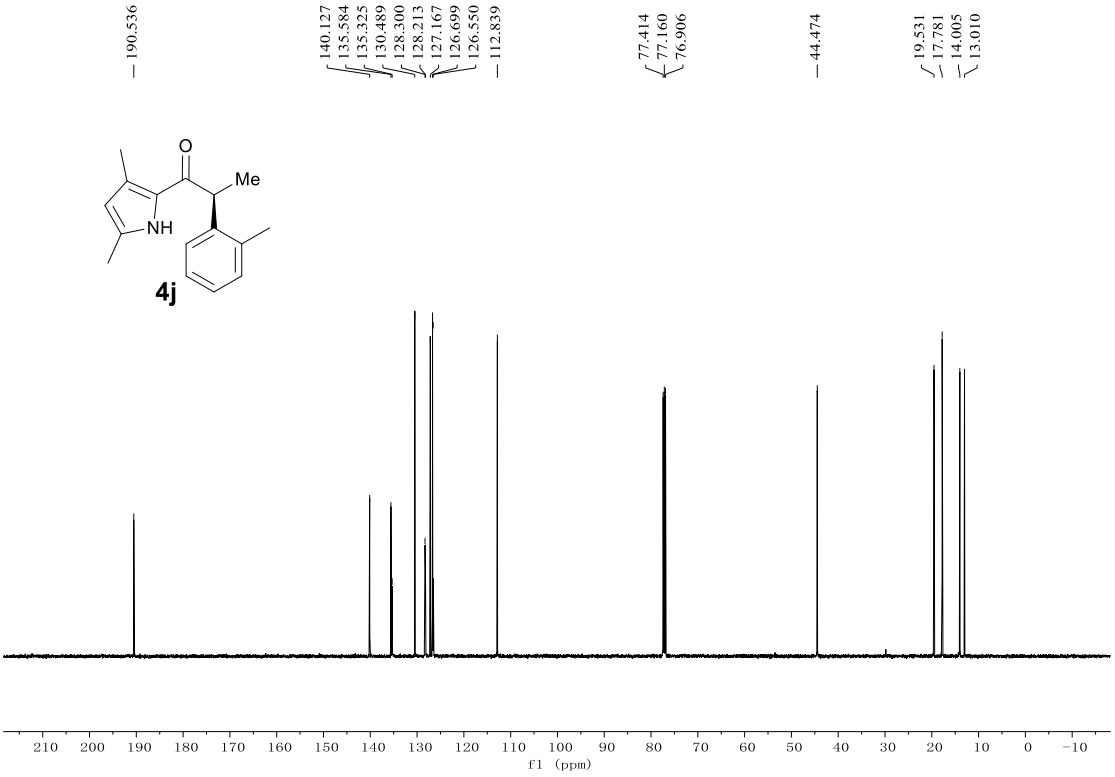
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4i**



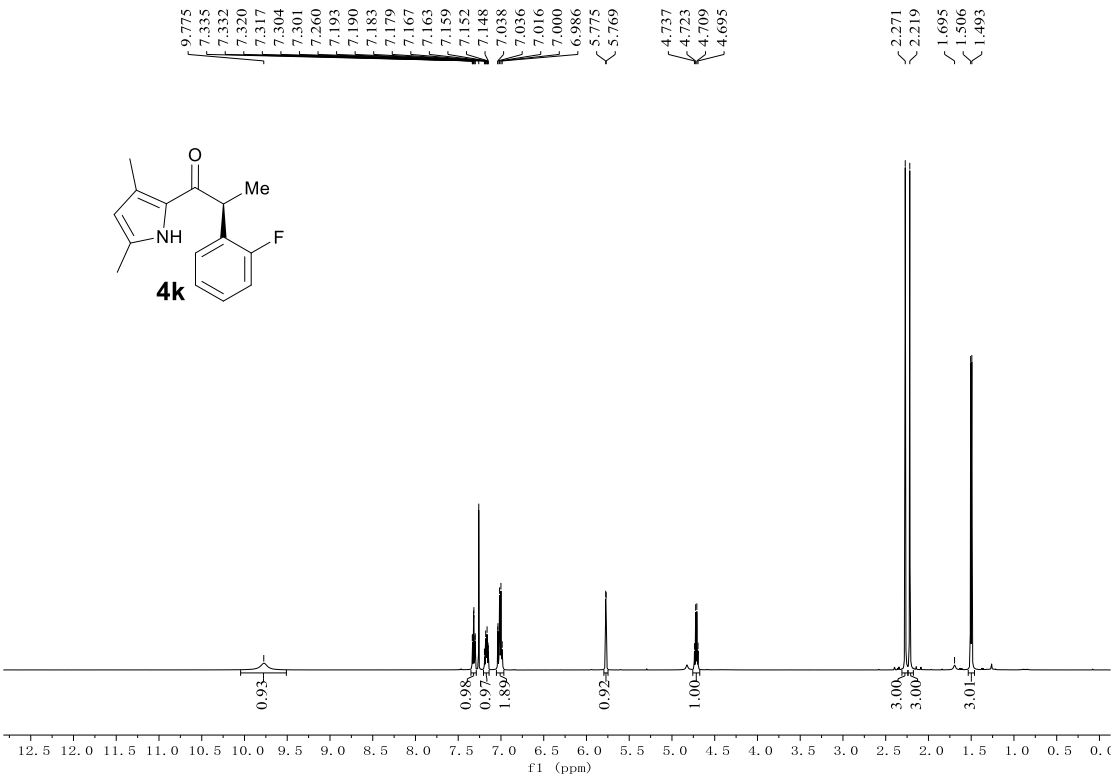
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4i**



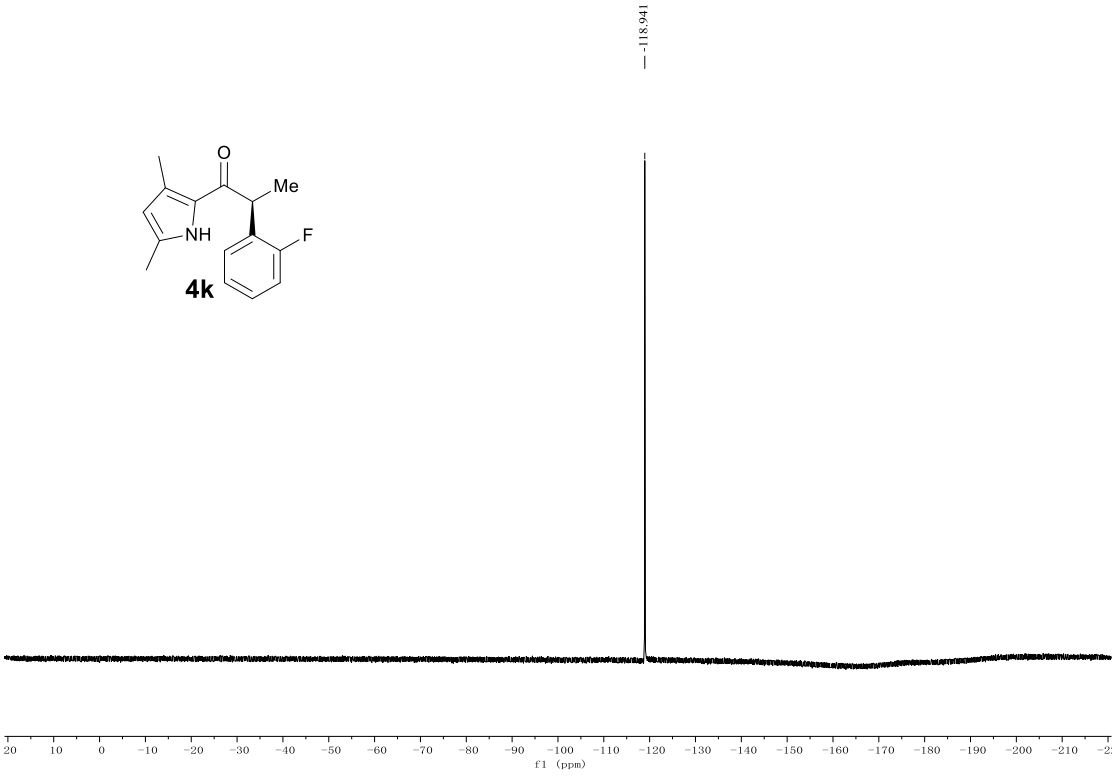
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4j**



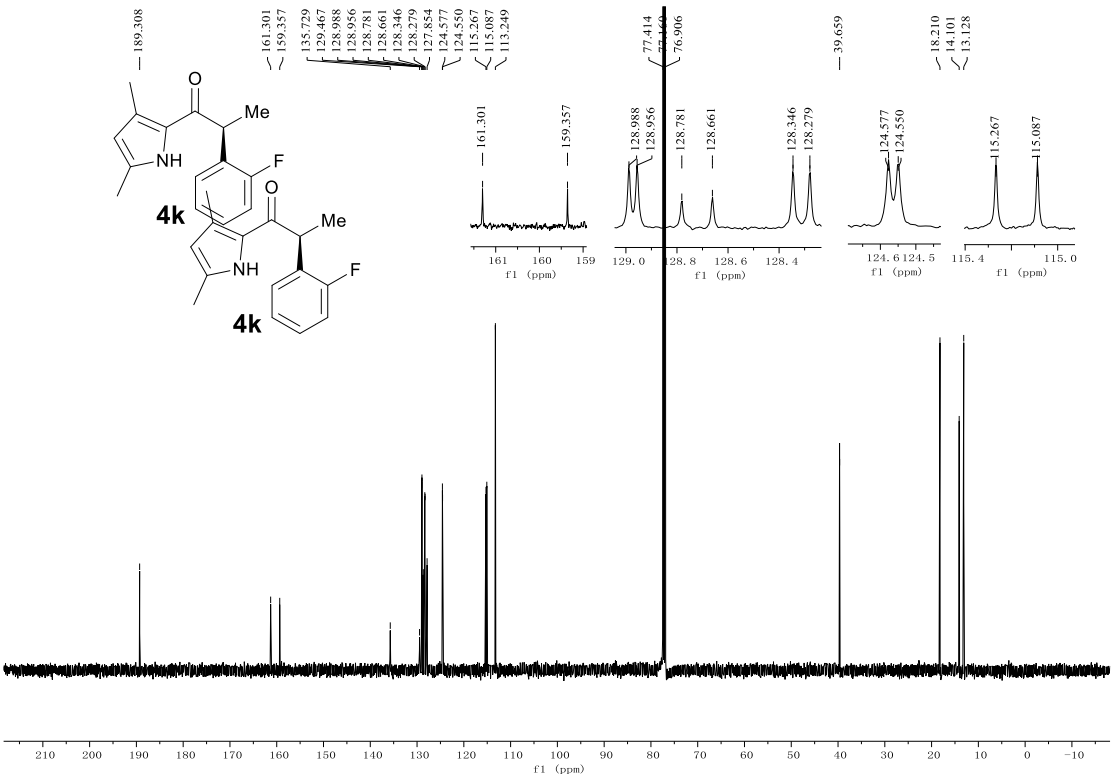
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4j**



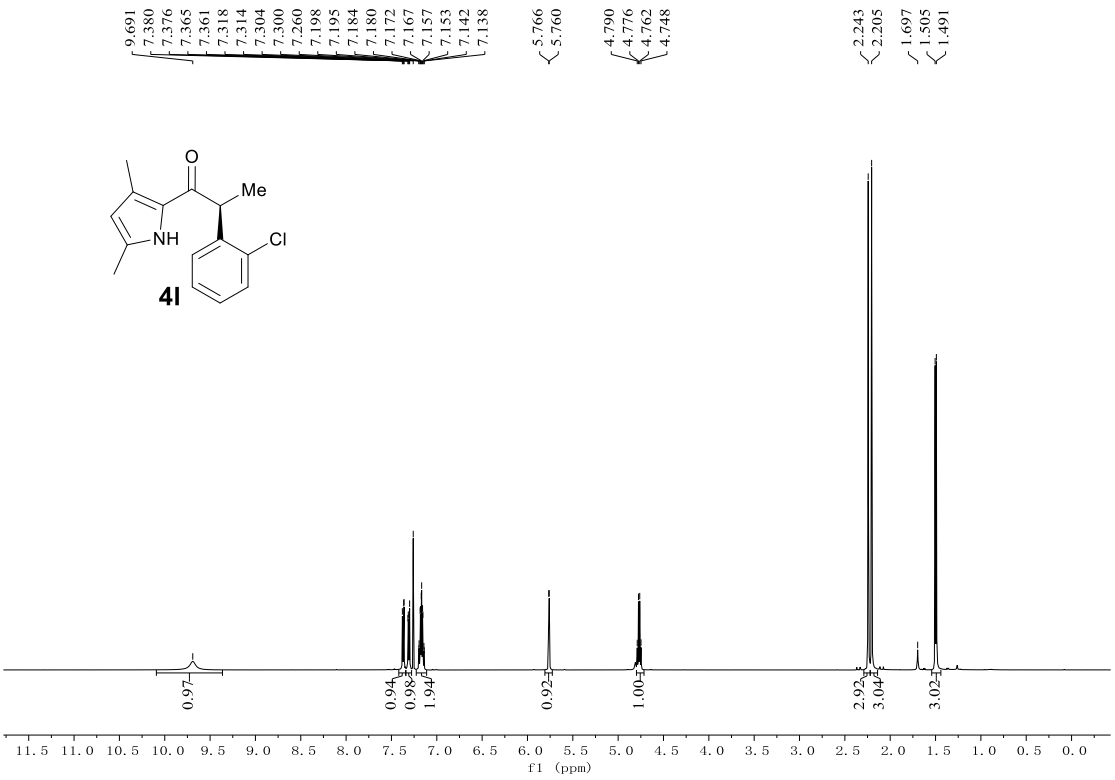
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4k**



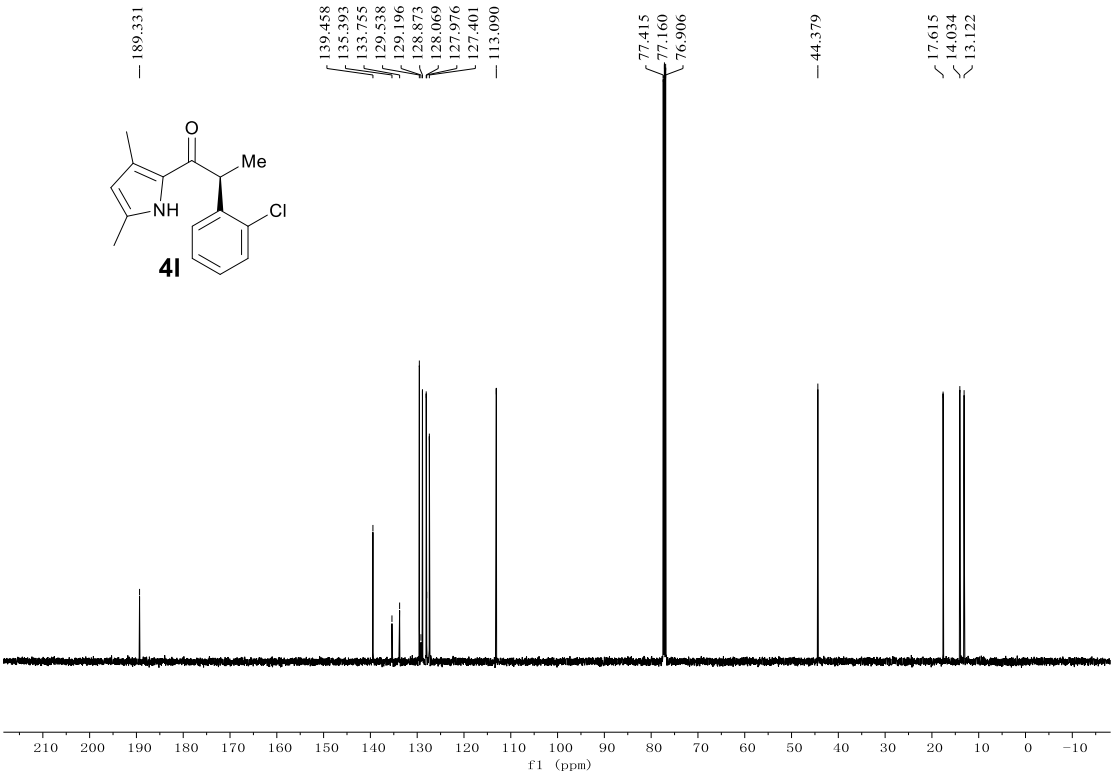
^{19}F NMR spectrum ($CDCl_3$, 471 MHz) of **4k**



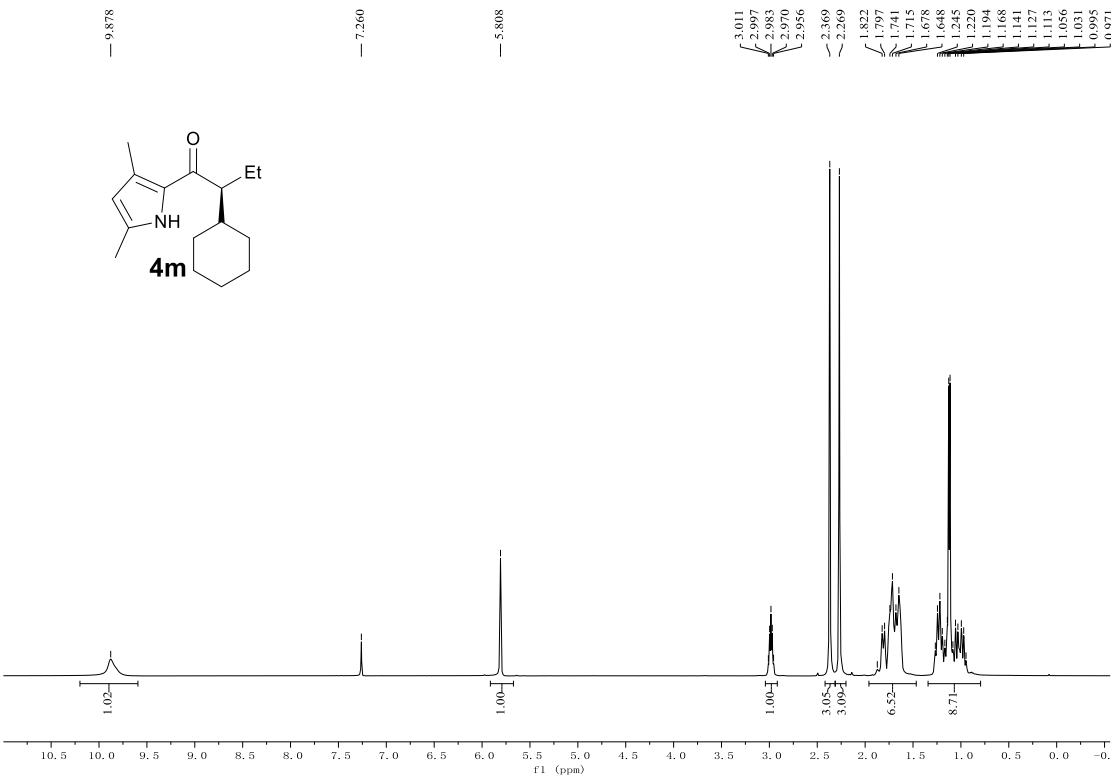
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4k**



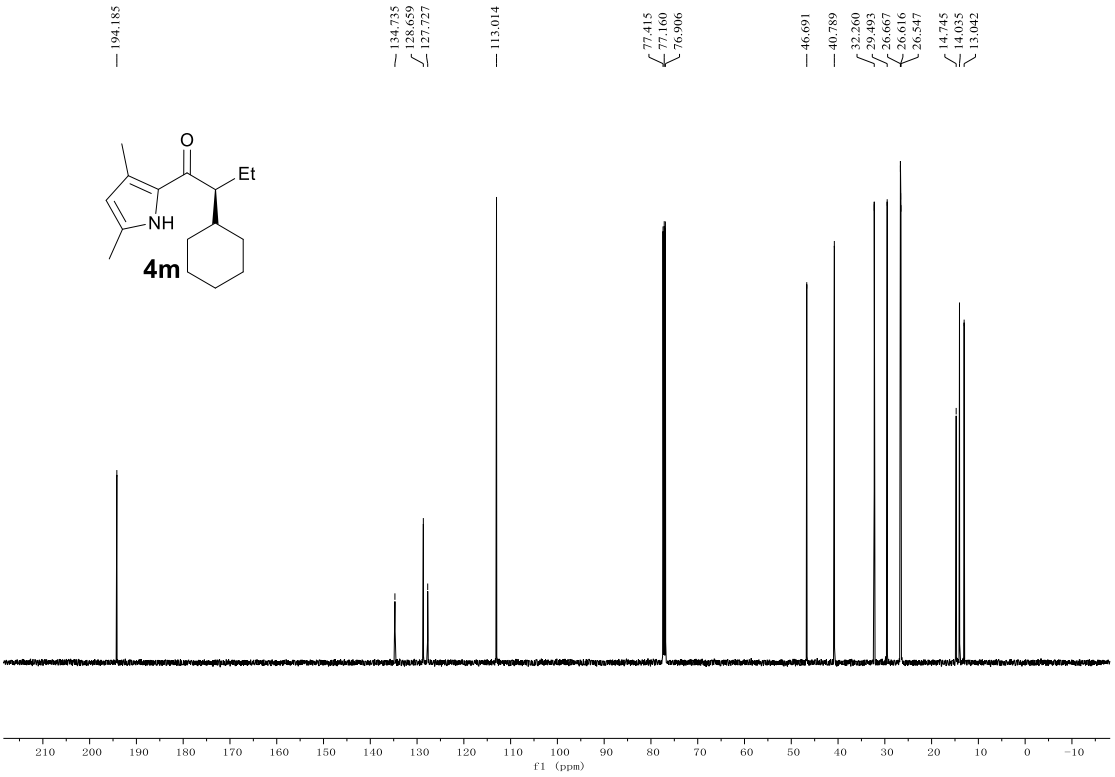
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4l**



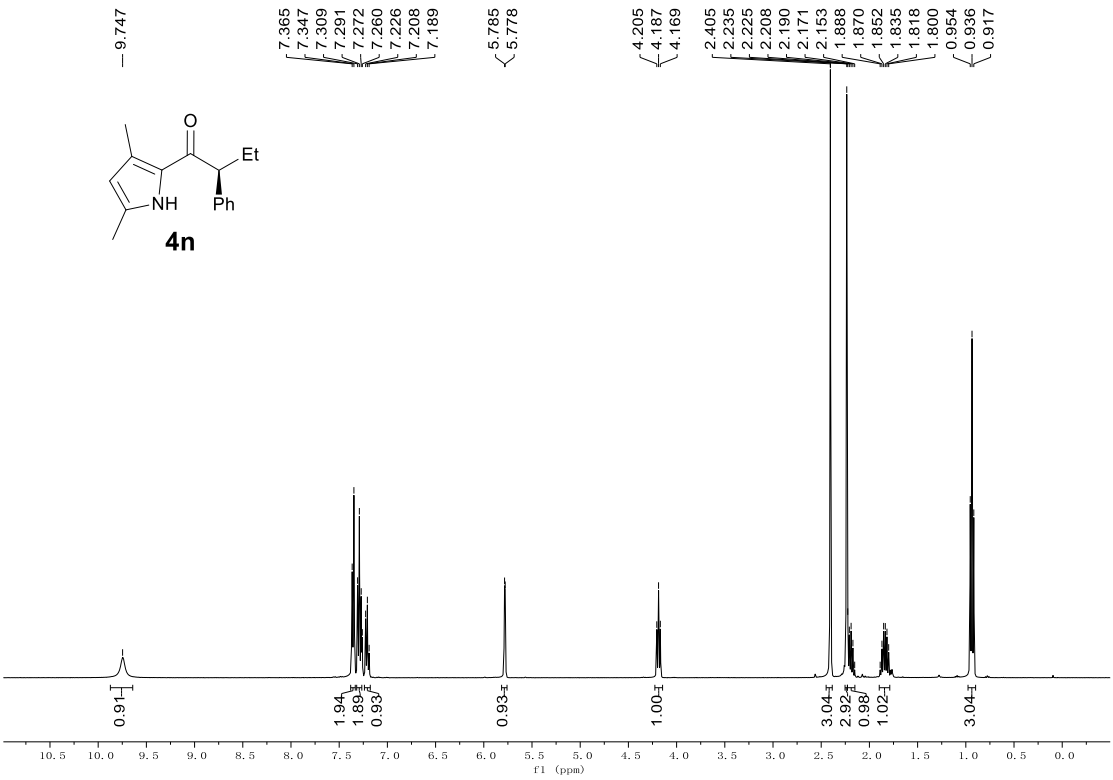
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4l**



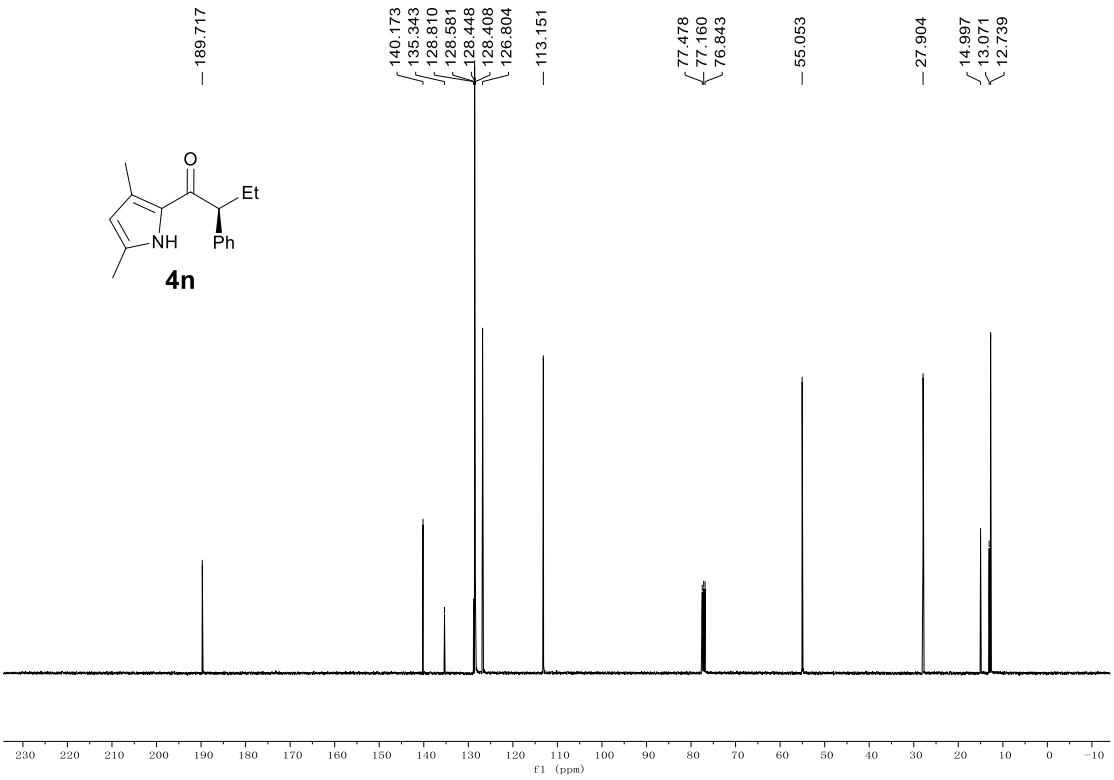
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4m**



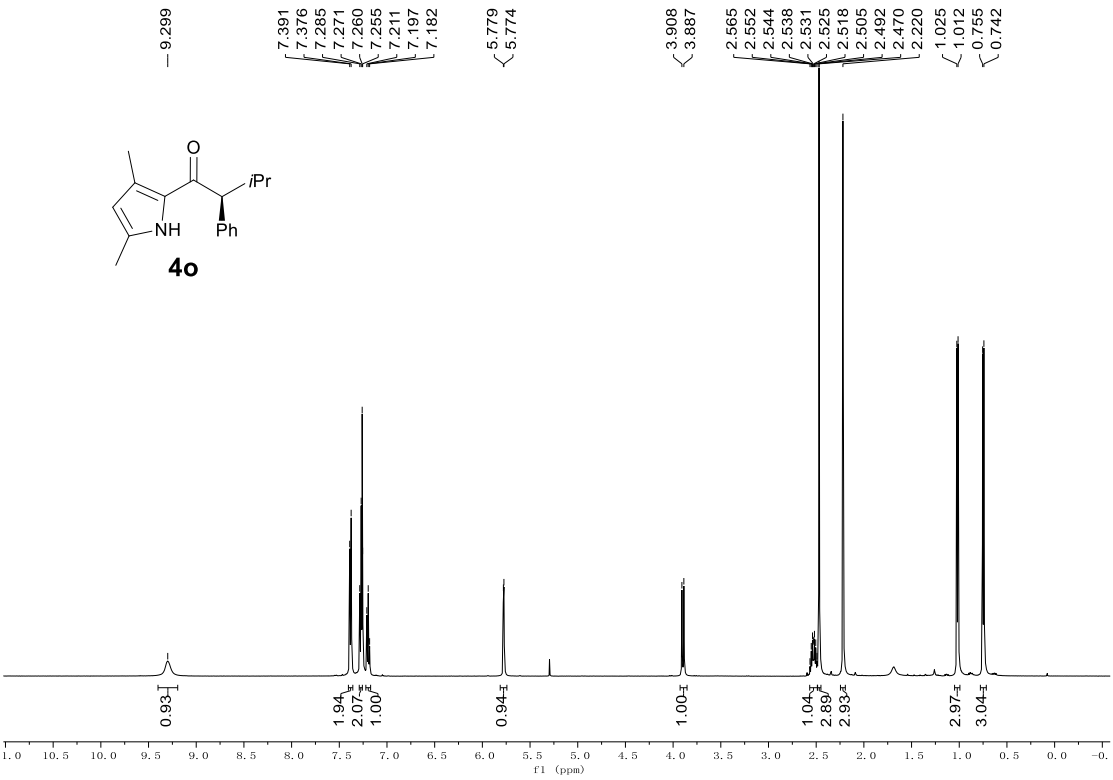
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4m**



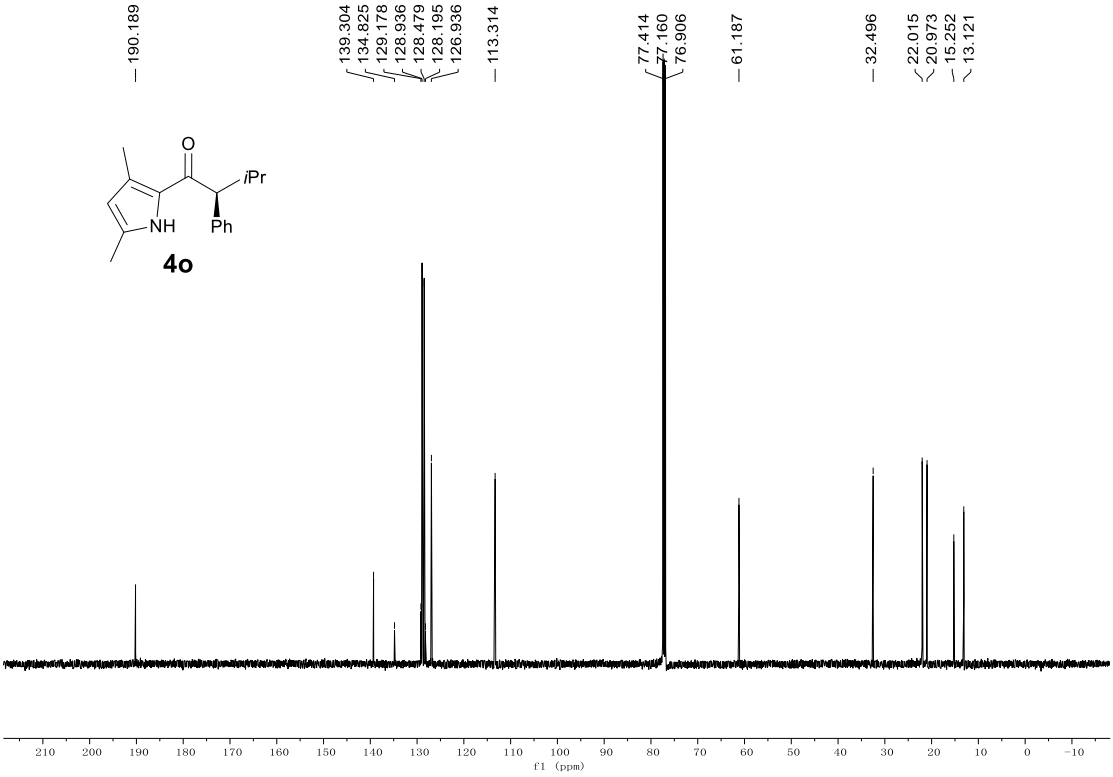
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4n**



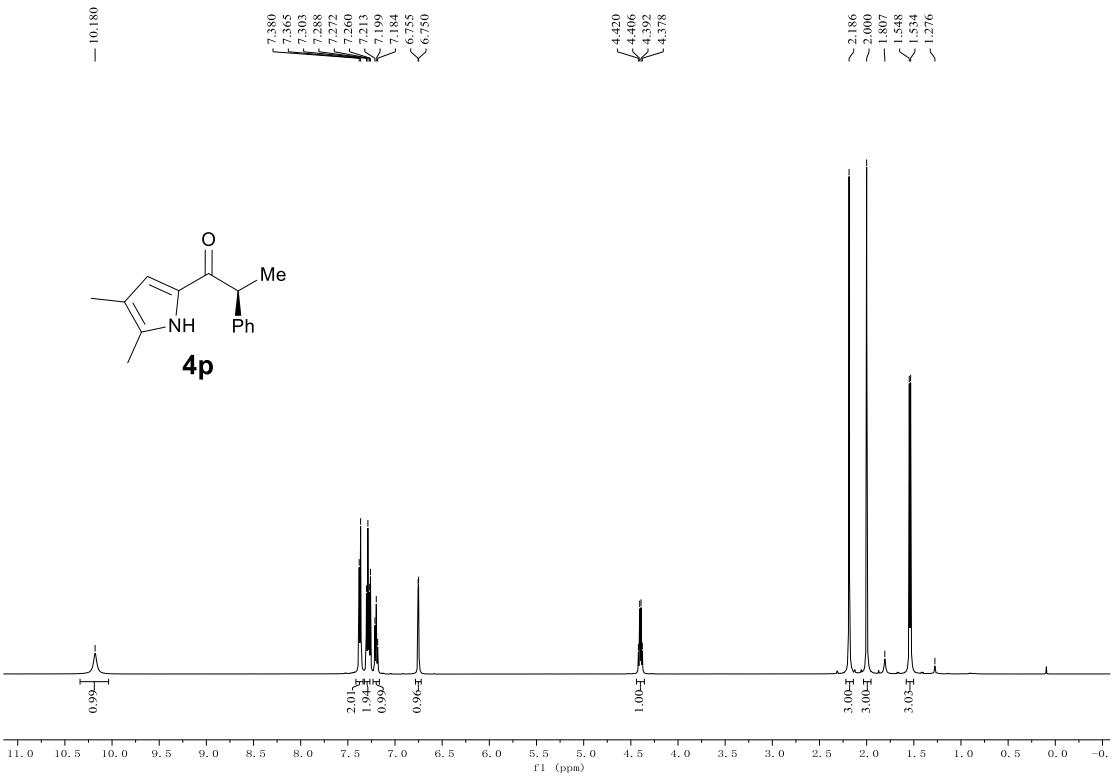
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **4n**



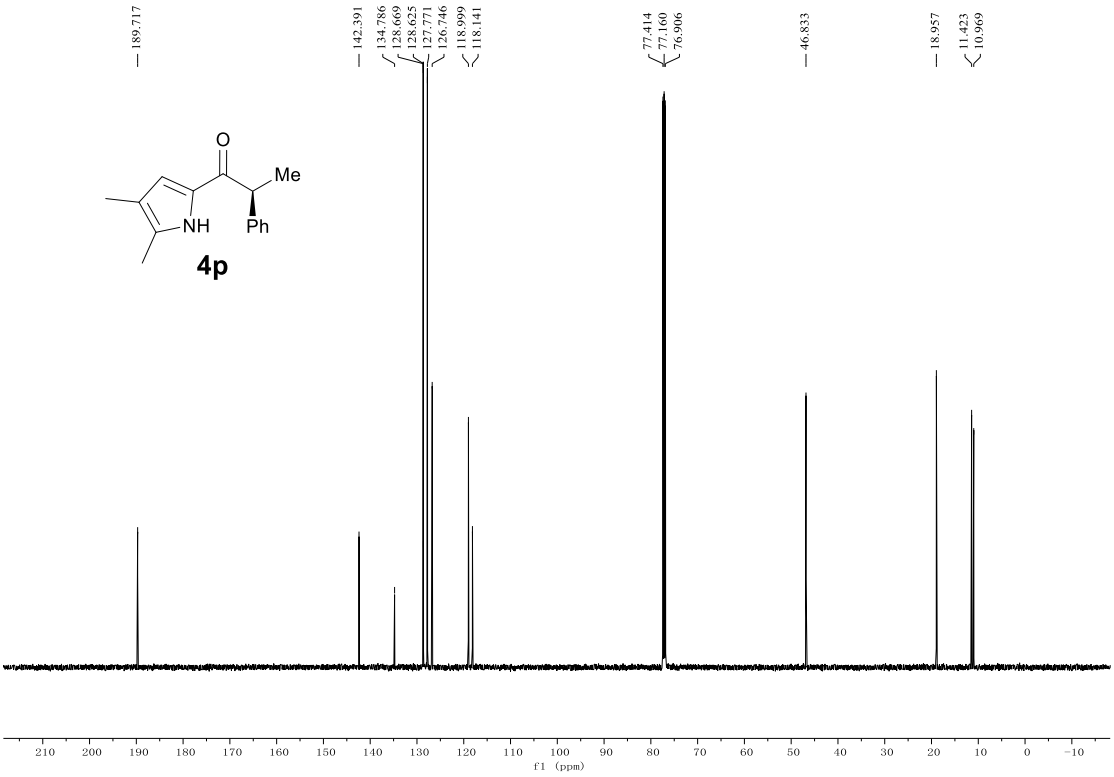
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4o**



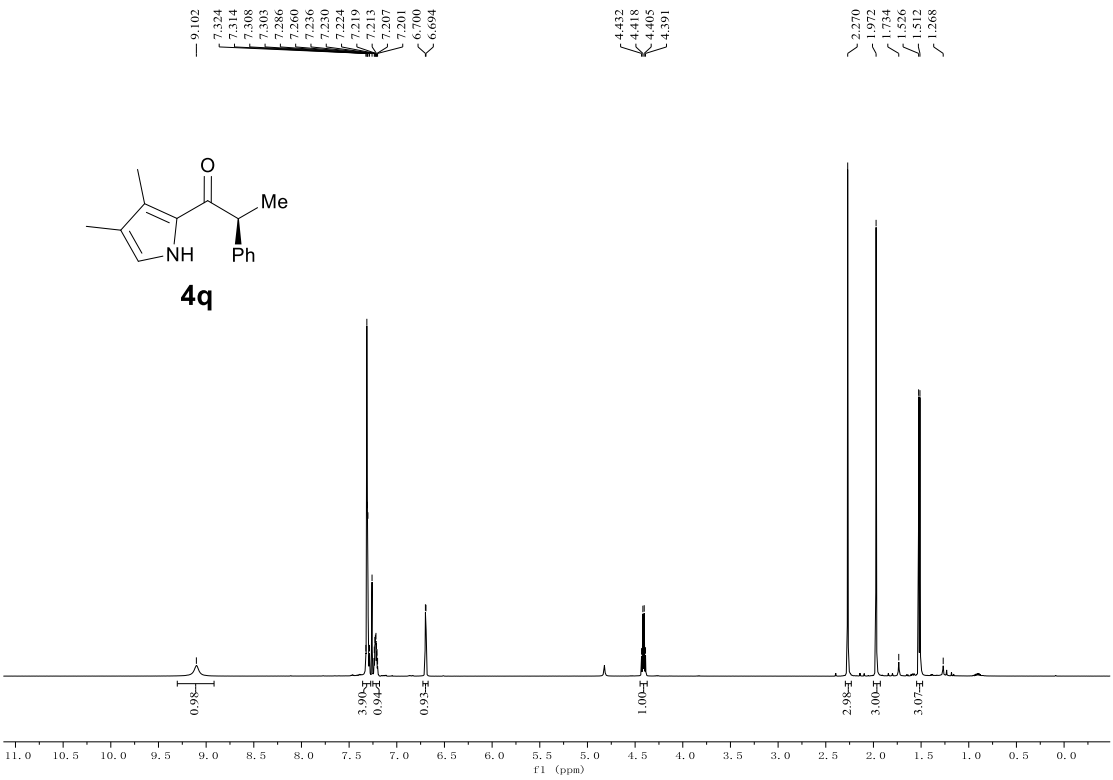
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4o**



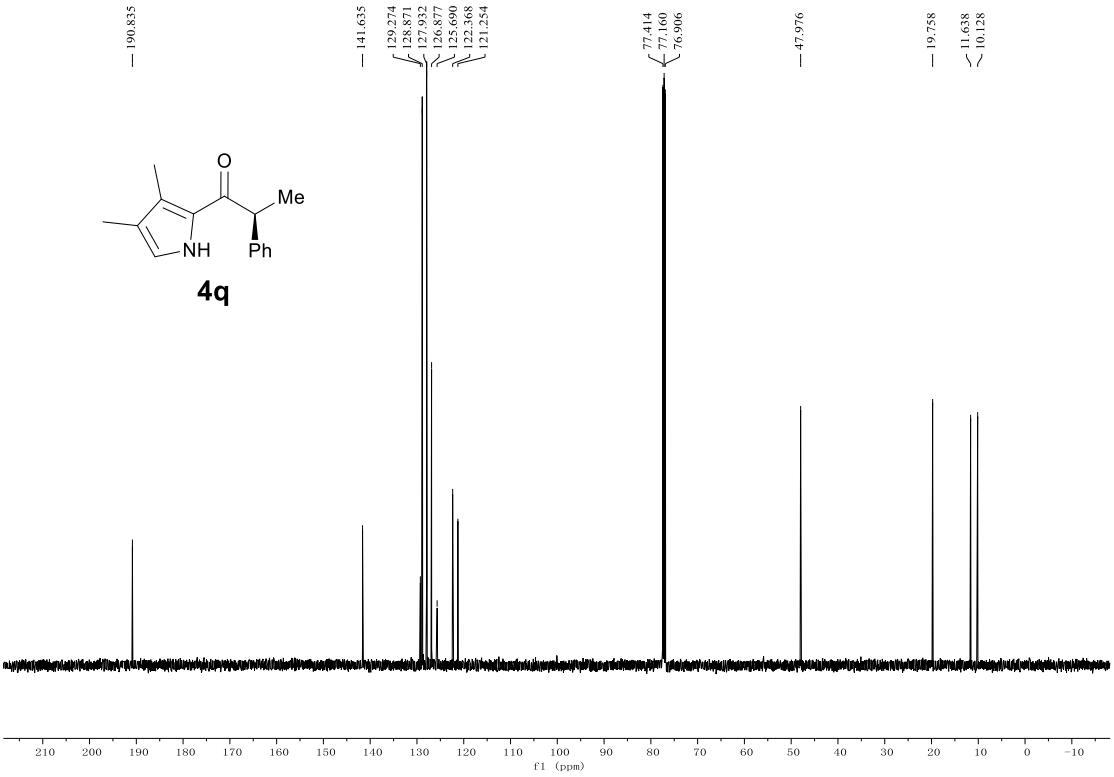
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4p**



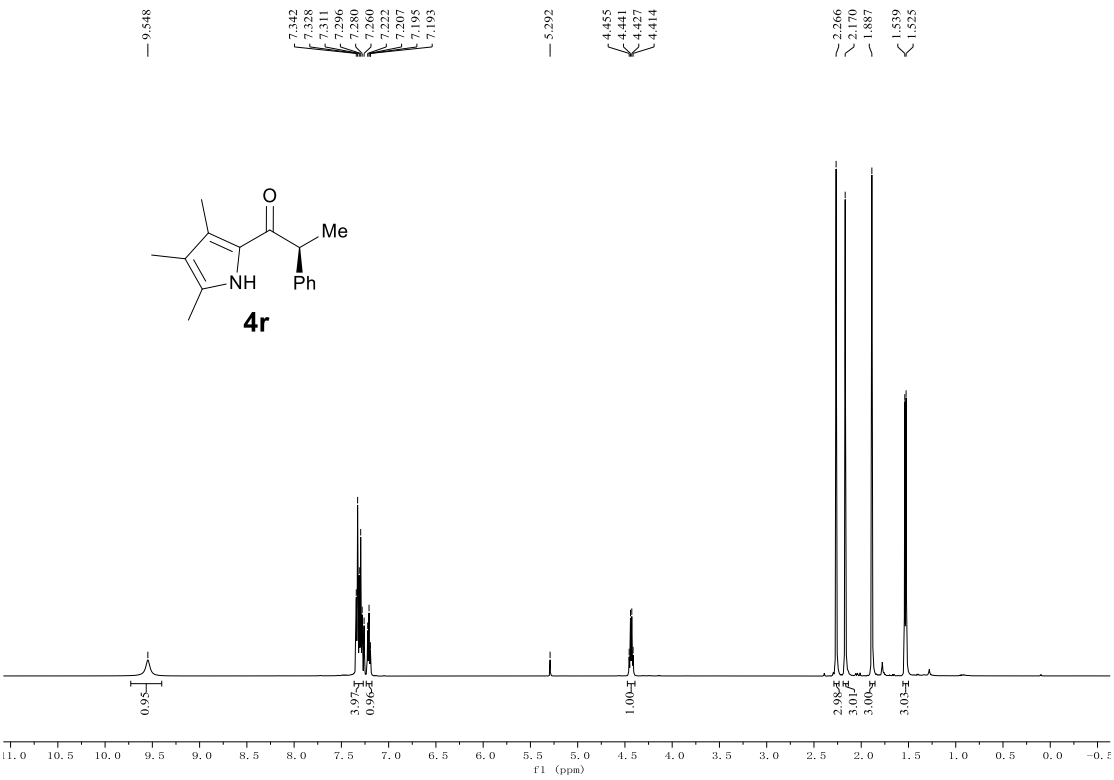
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4p**



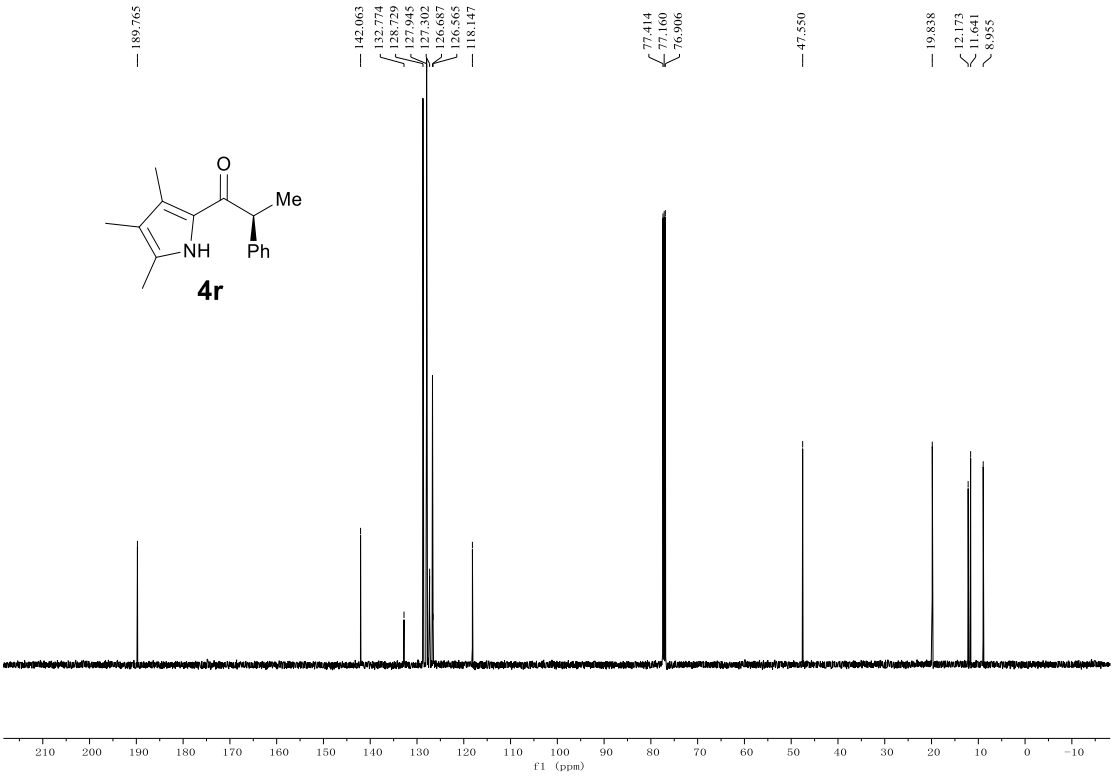
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4q**



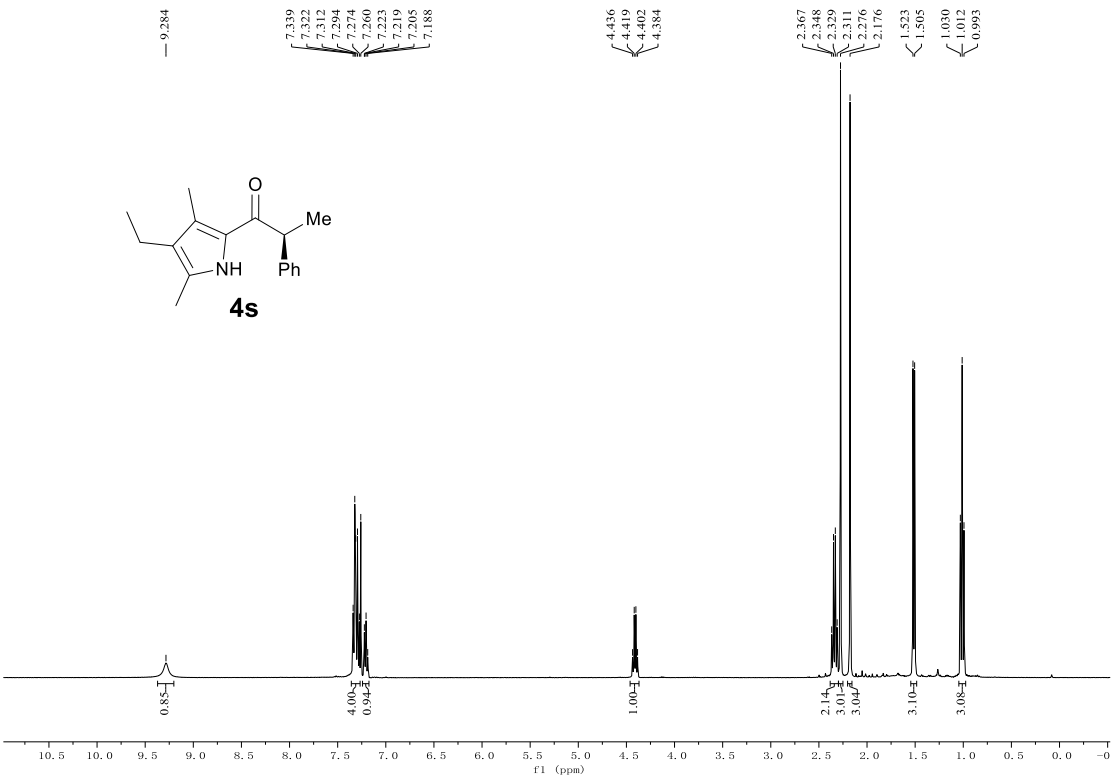
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4q**



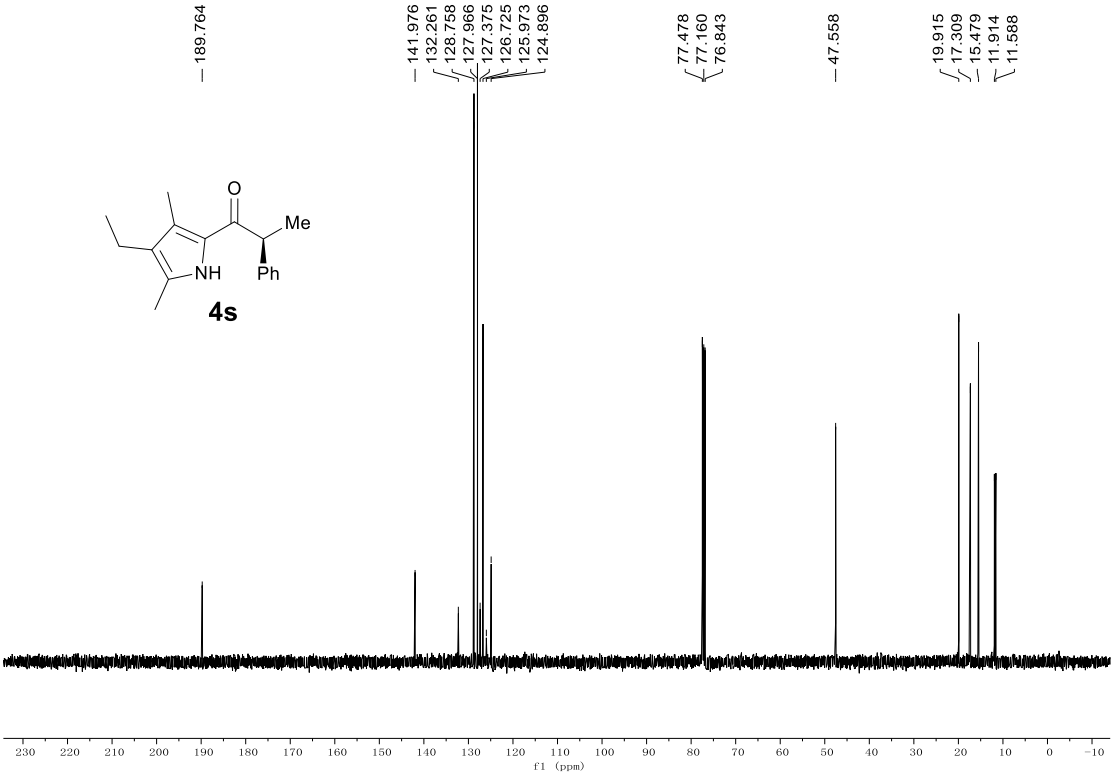
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4r**



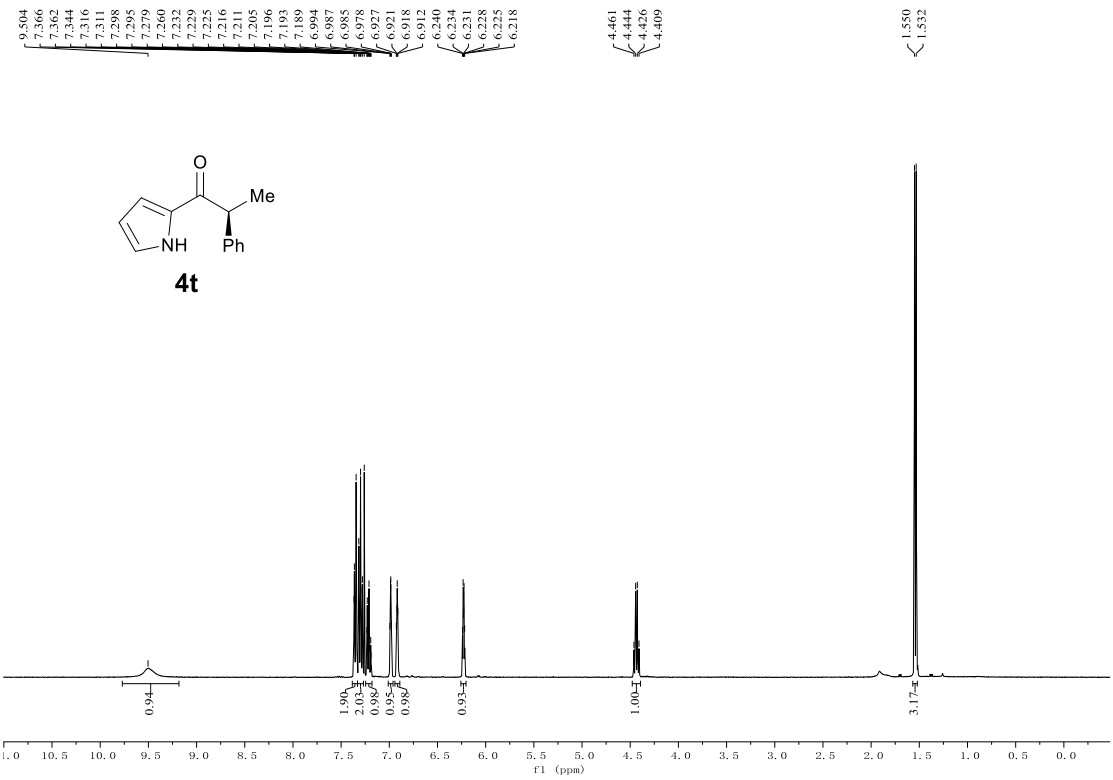
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4r**



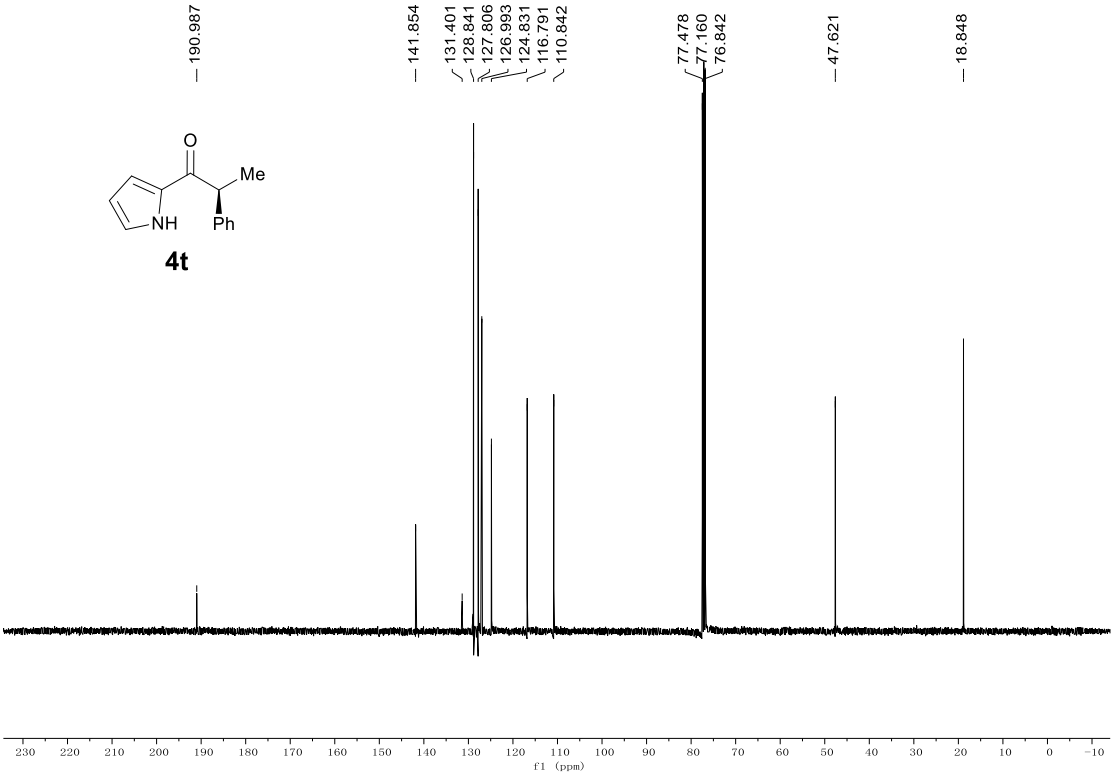
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4s**



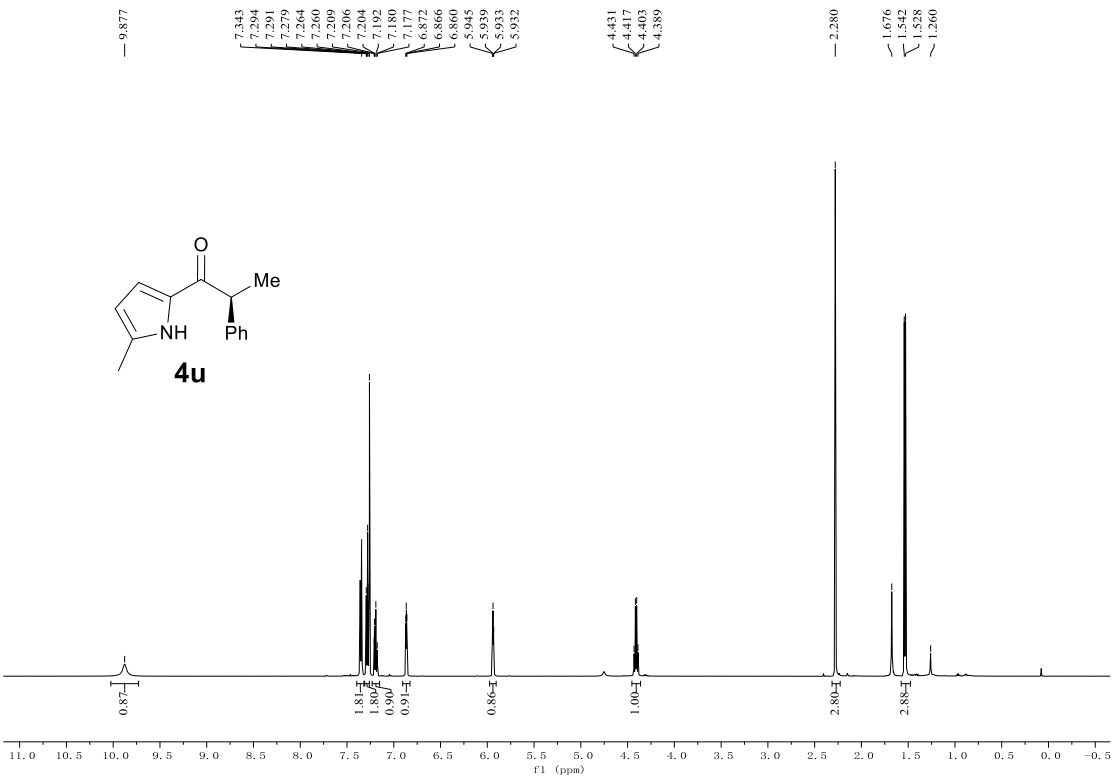
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **4s**



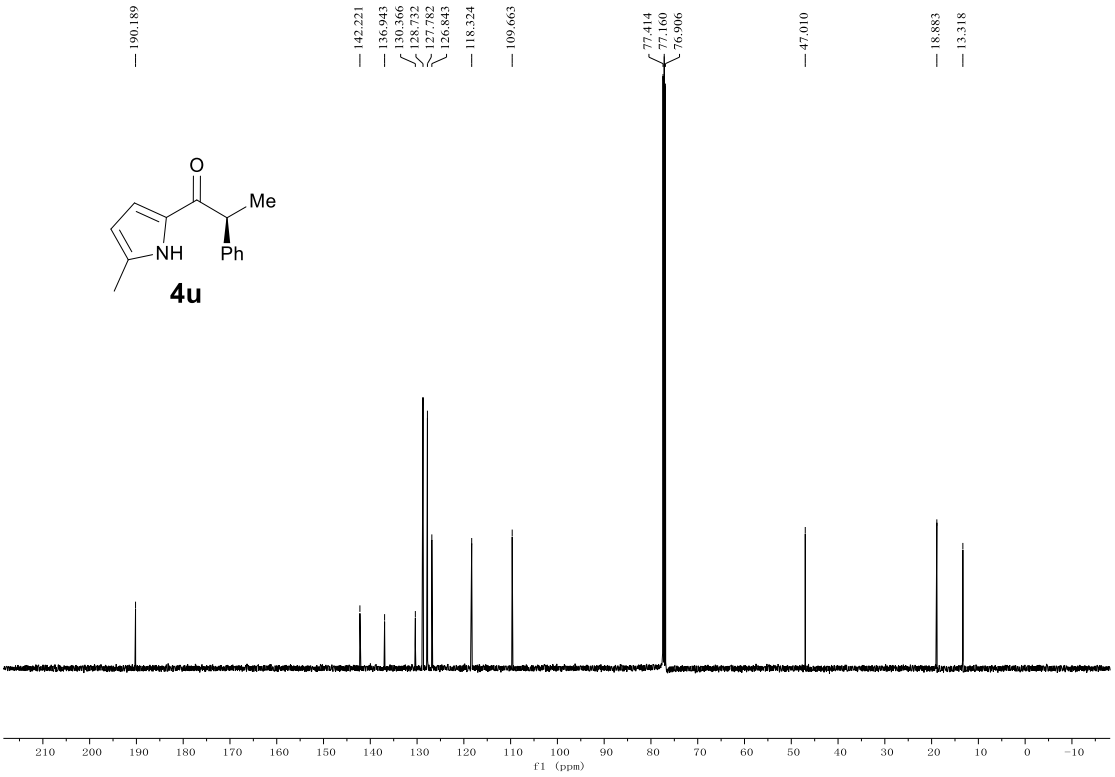
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4t**



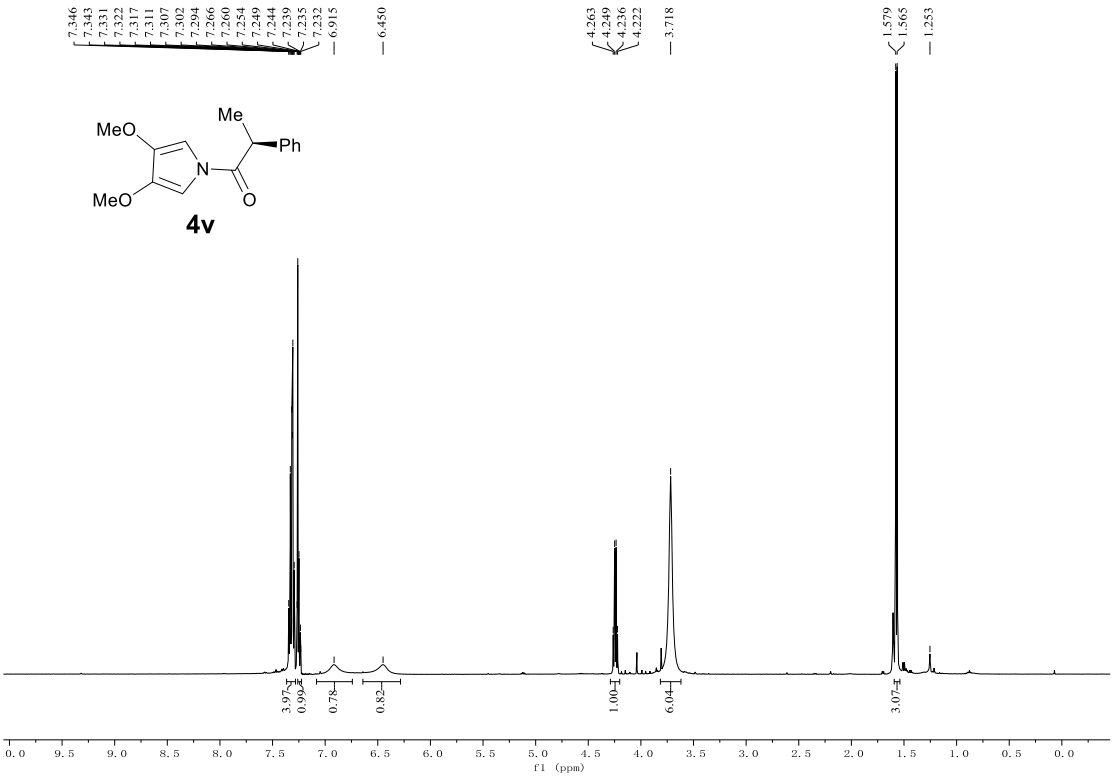
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **4t**



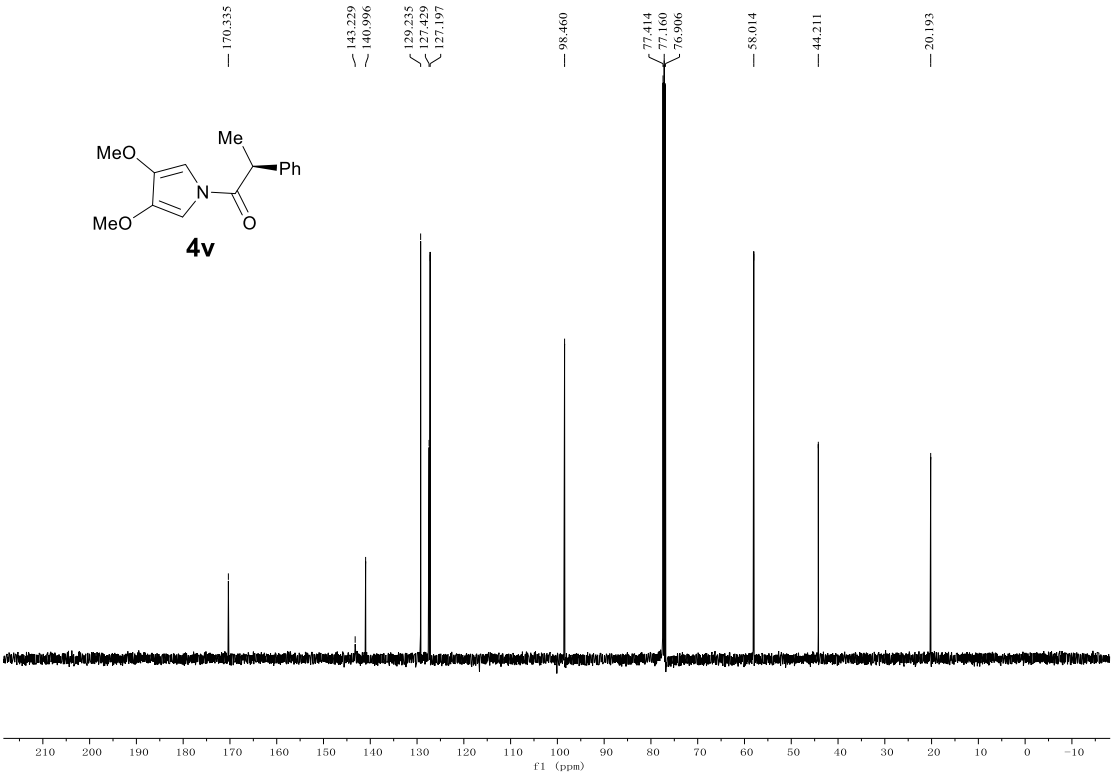
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4u**



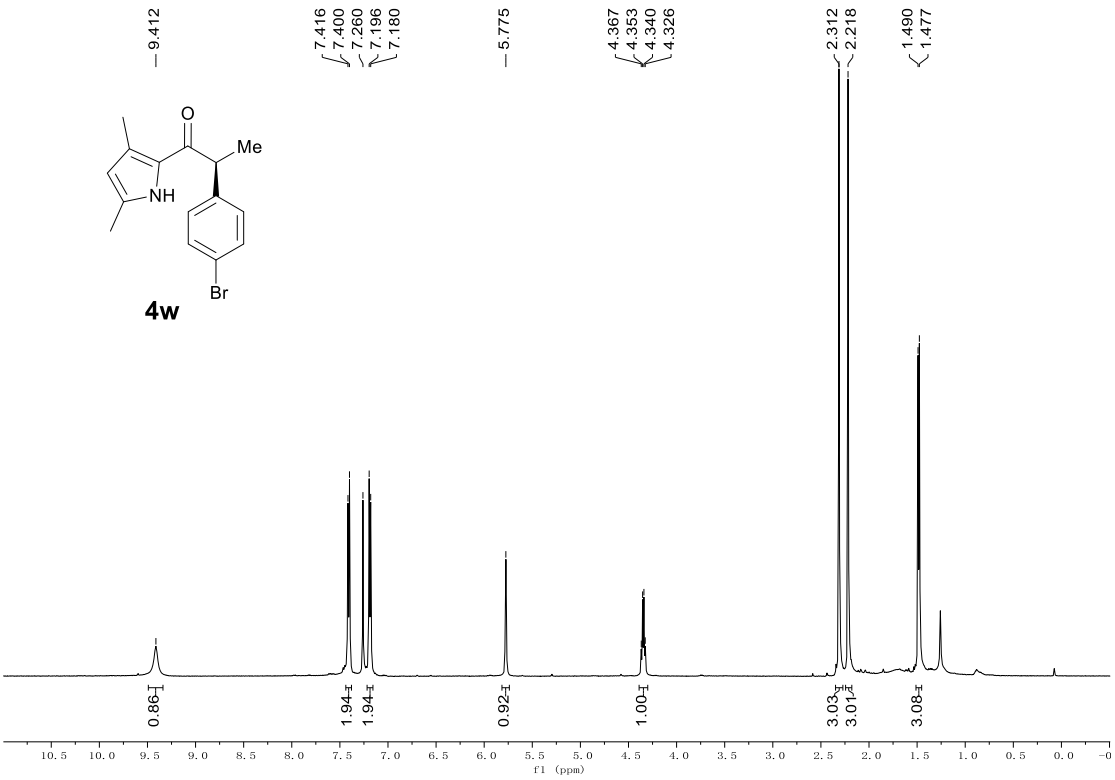
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4u**



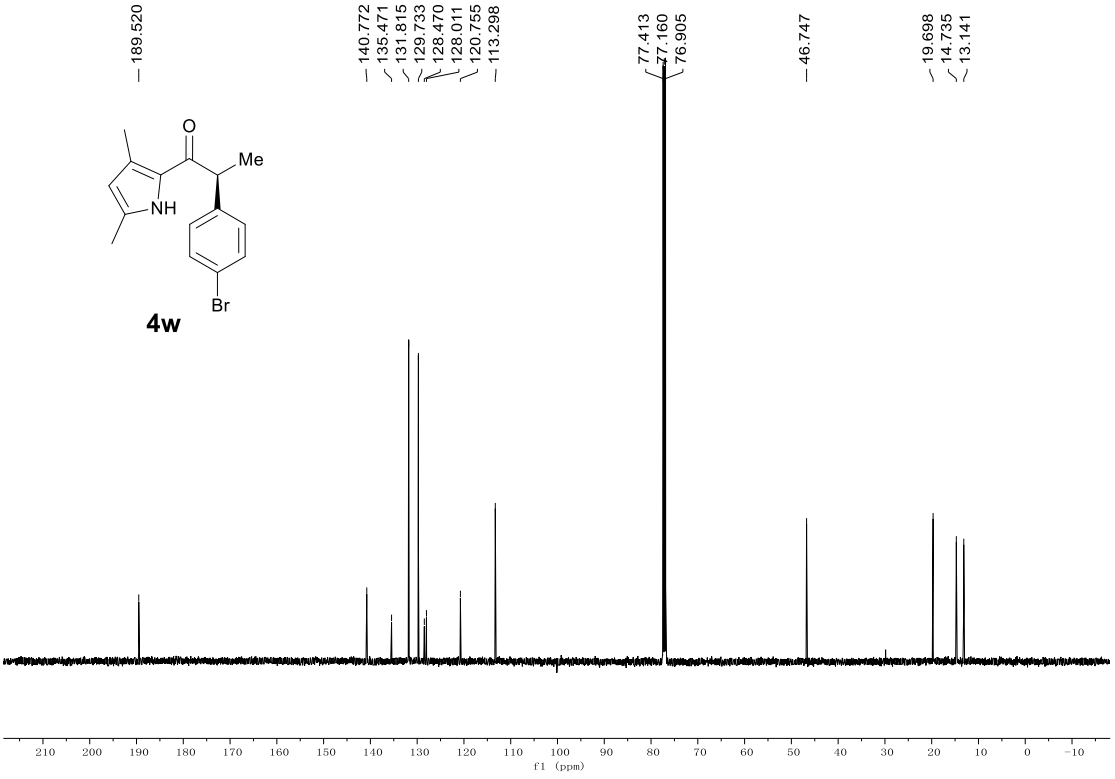
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4v**



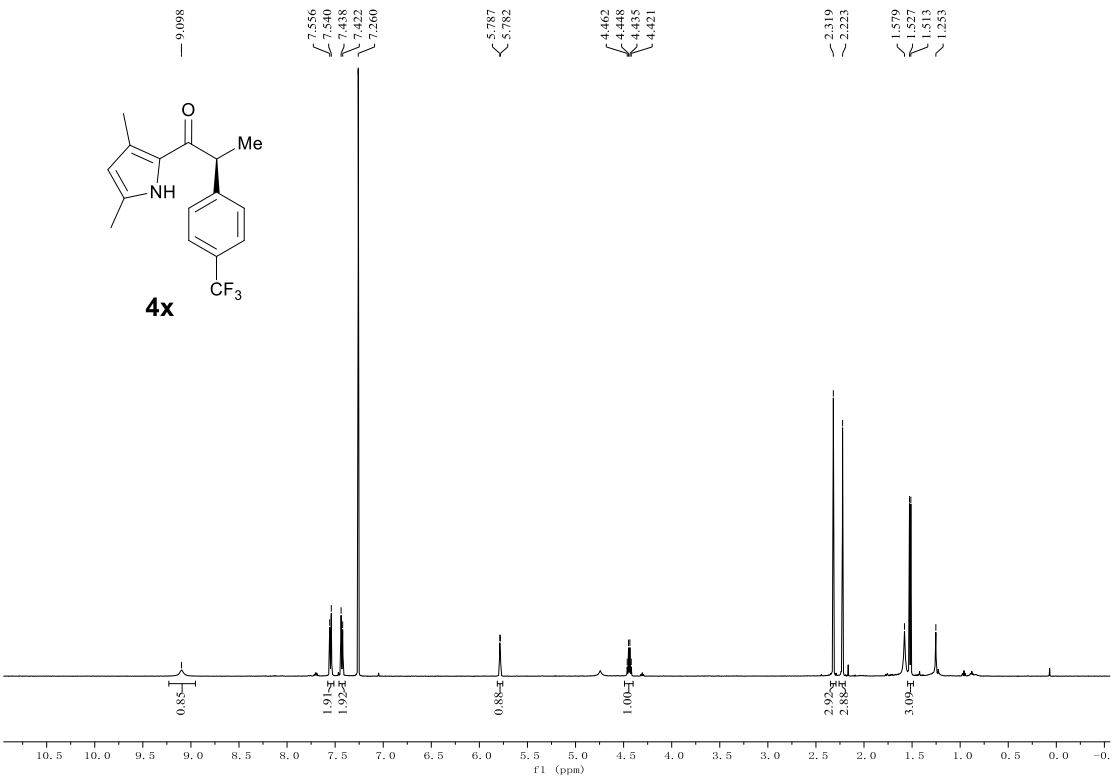
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4v**



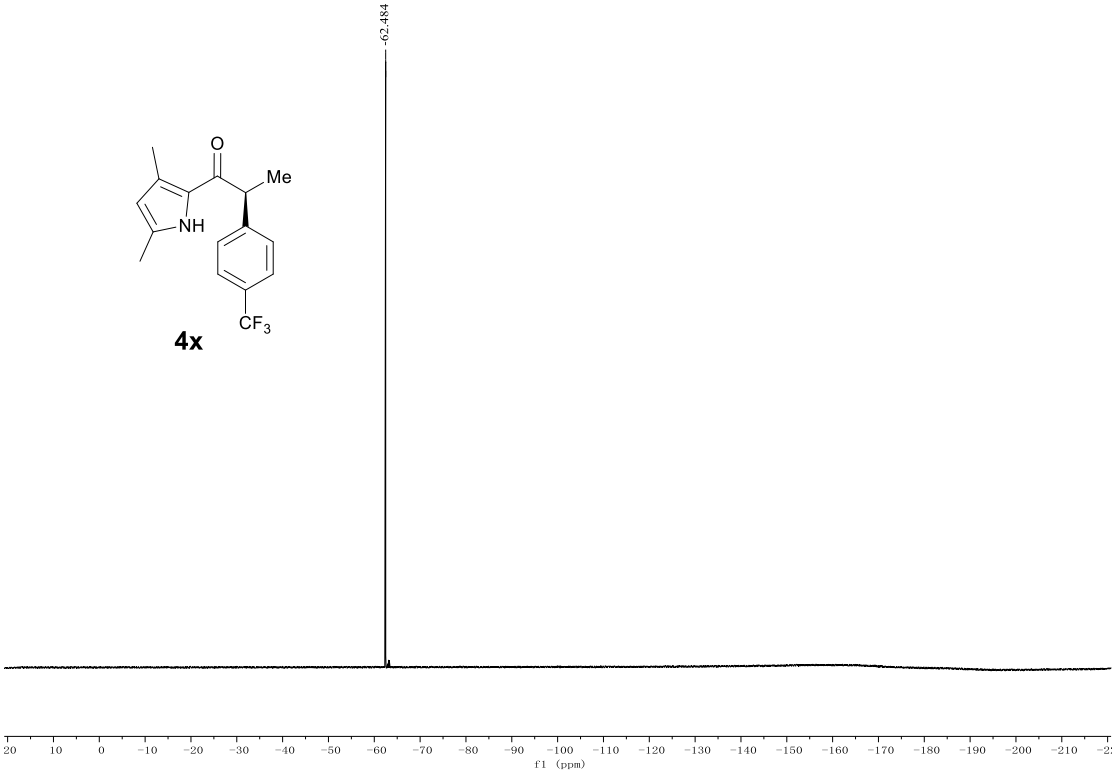
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4w**



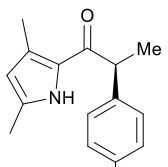
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4w**

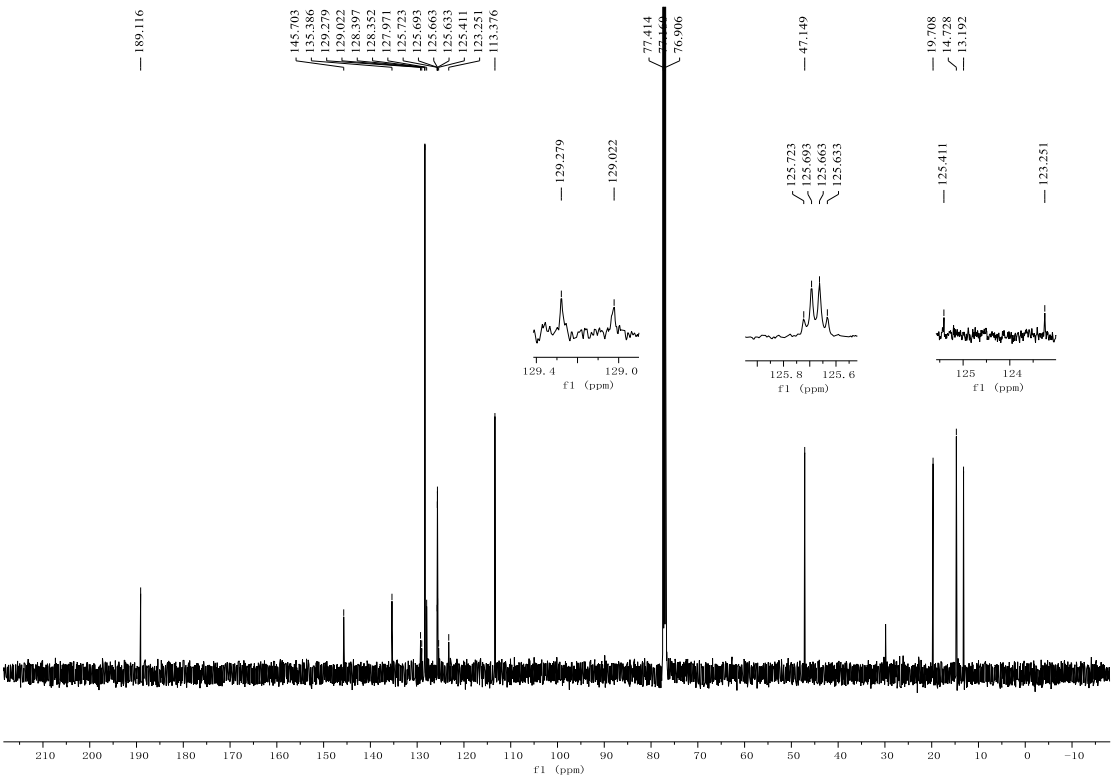


^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4x**

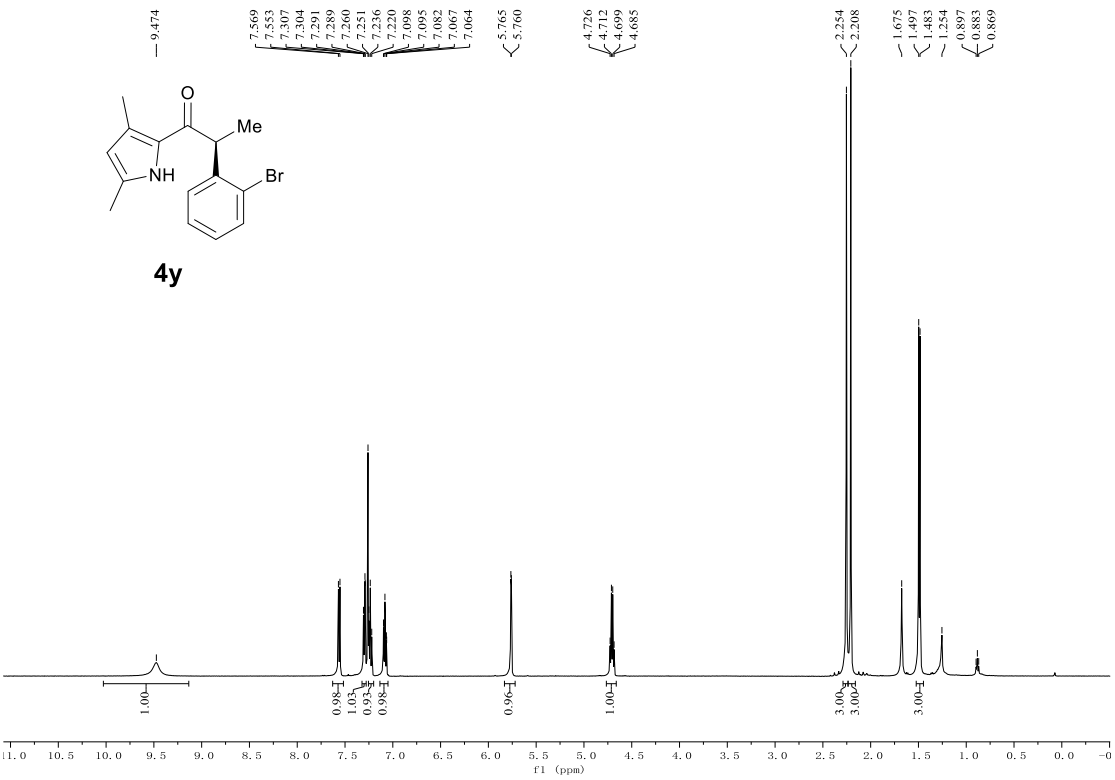


^{19}F NMR spectrum ($CDCl_3$, 471 MHz) of **4x**

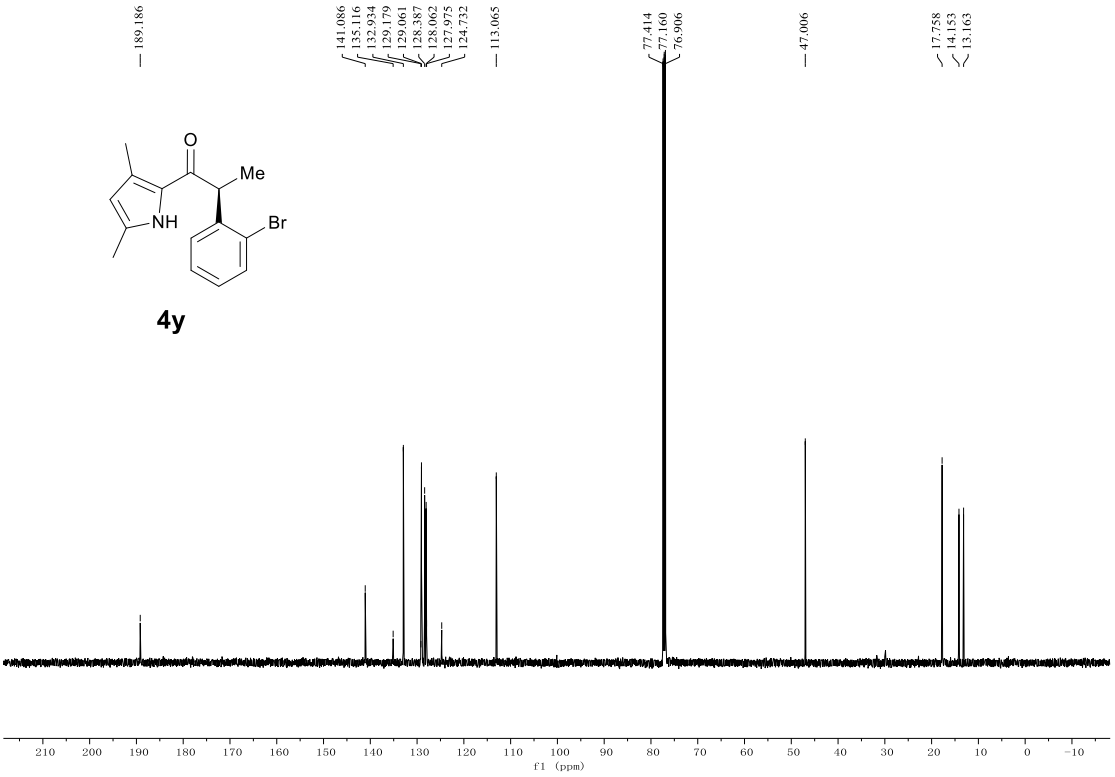




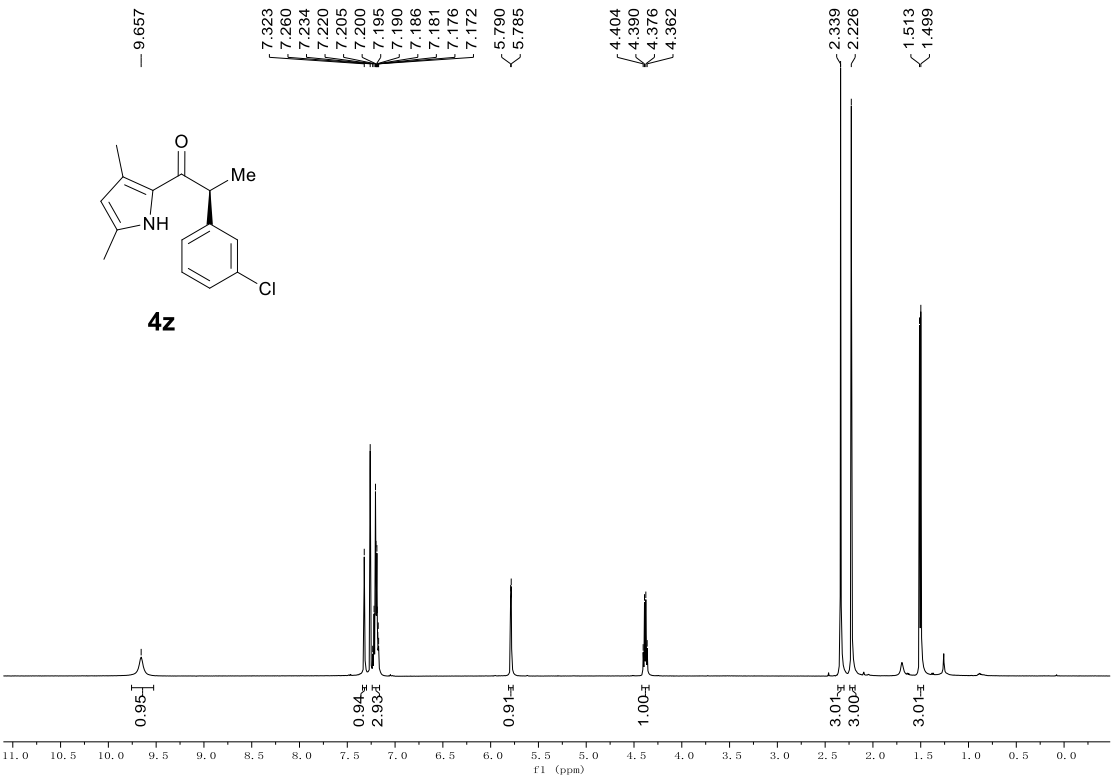
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4x**



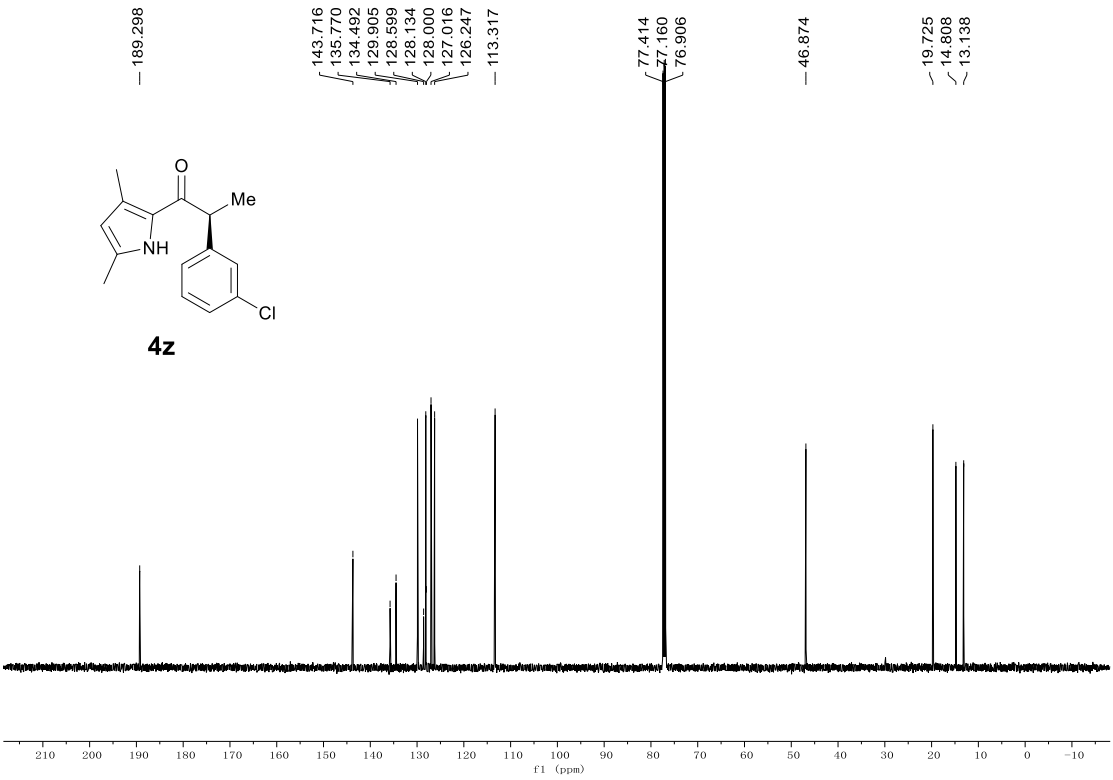
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4y**



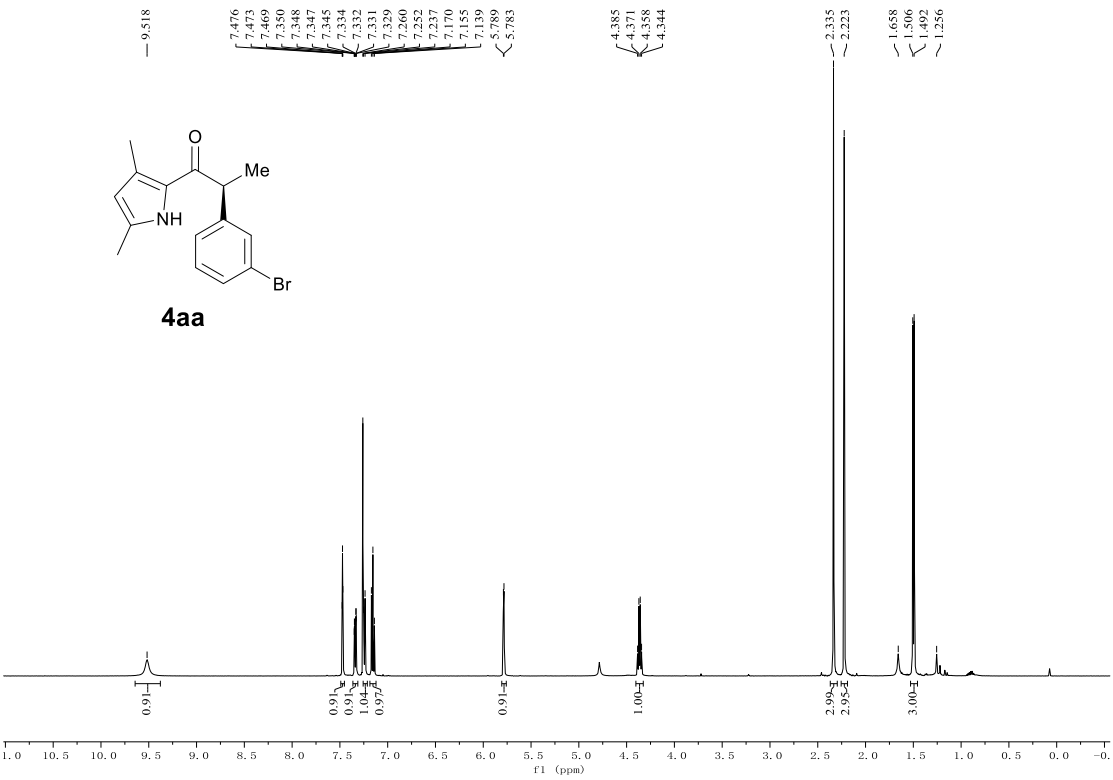
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4y**



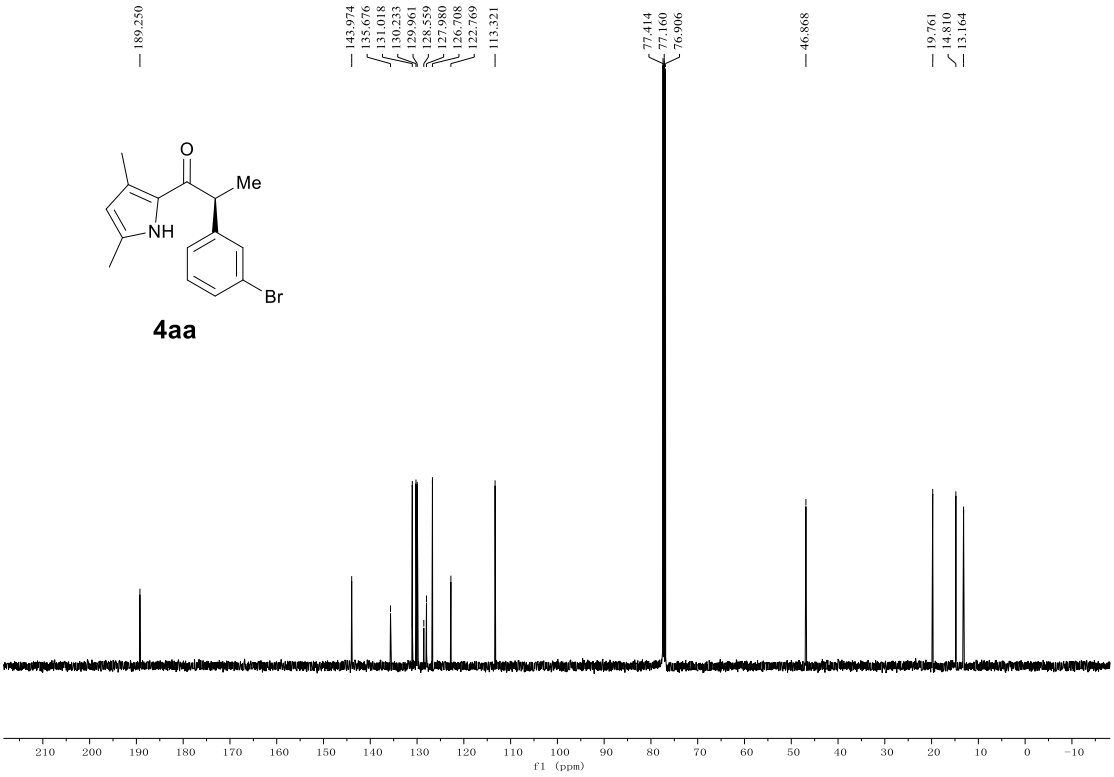
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4z**



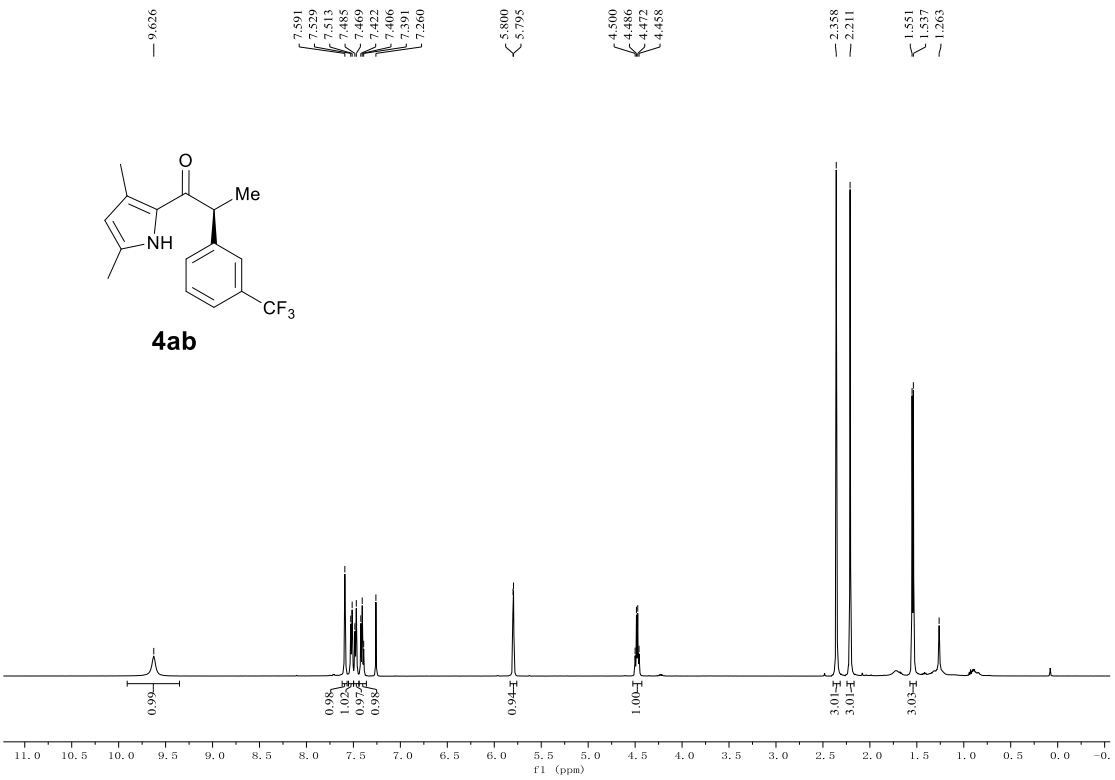
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4z**



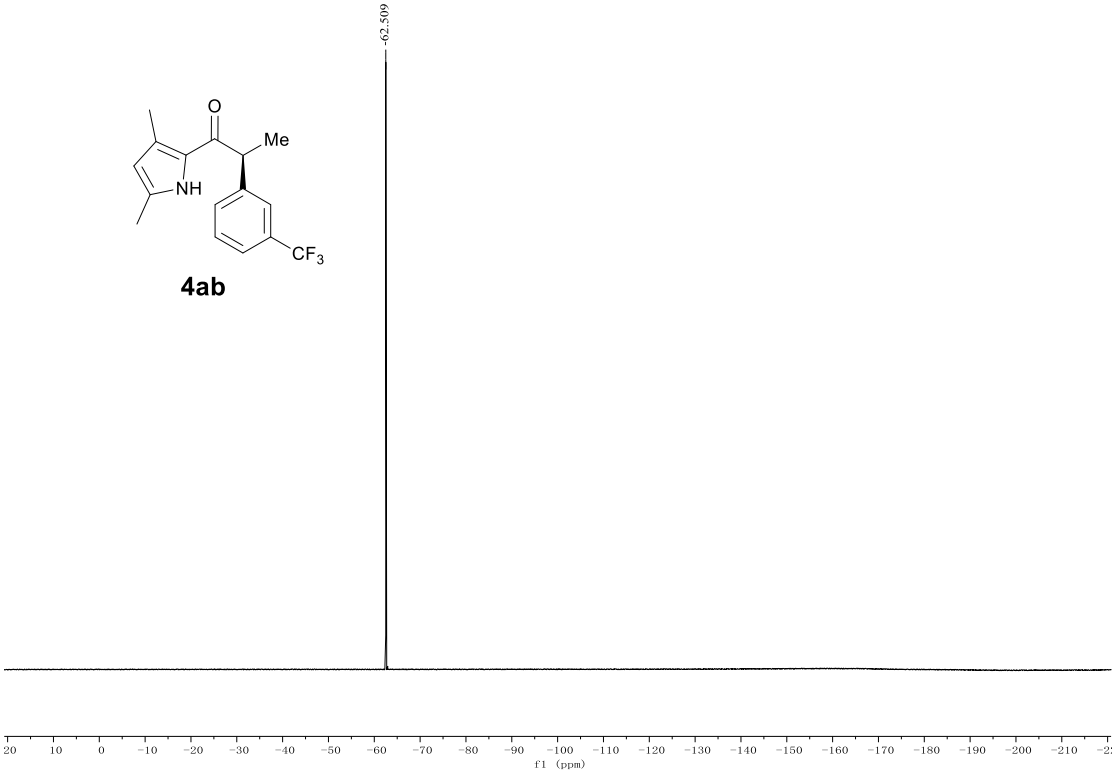
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4aa**



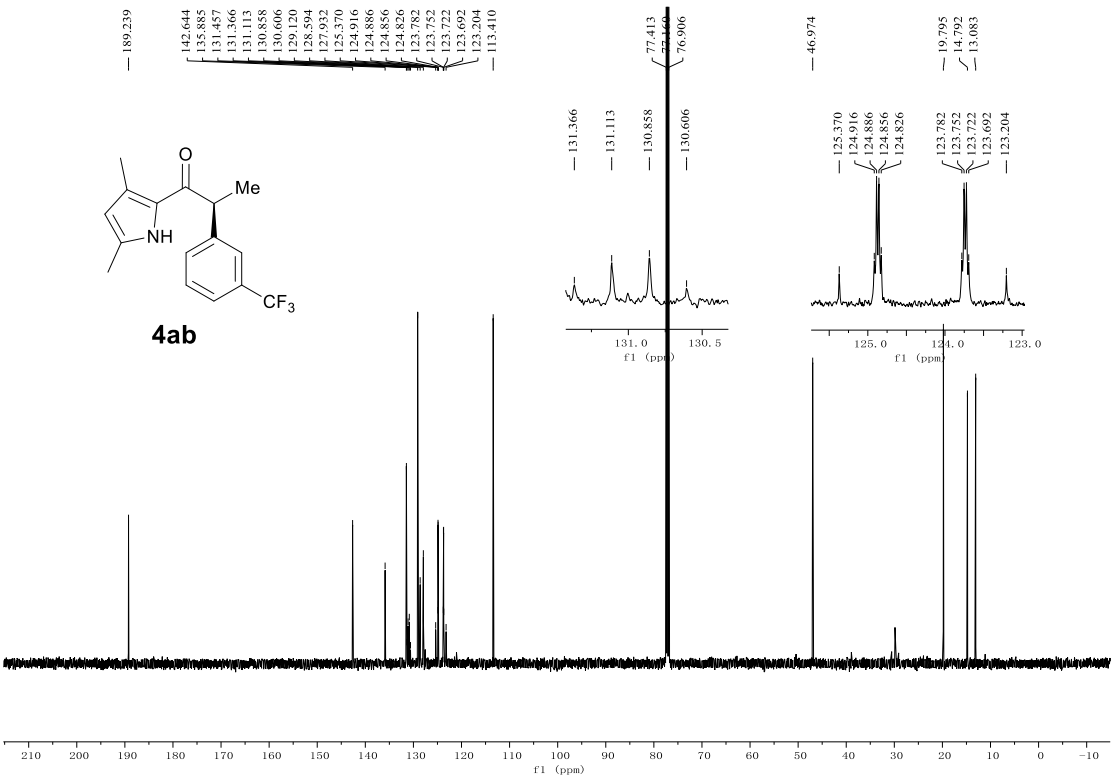
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4aa**



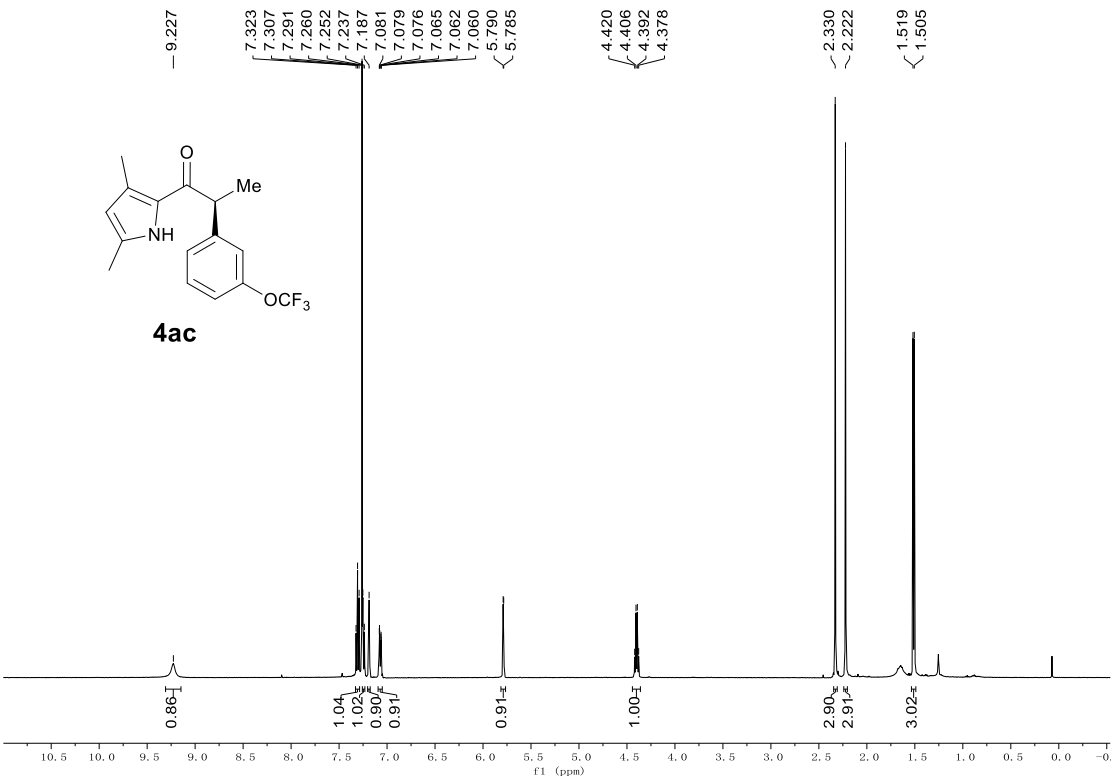
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4ab**



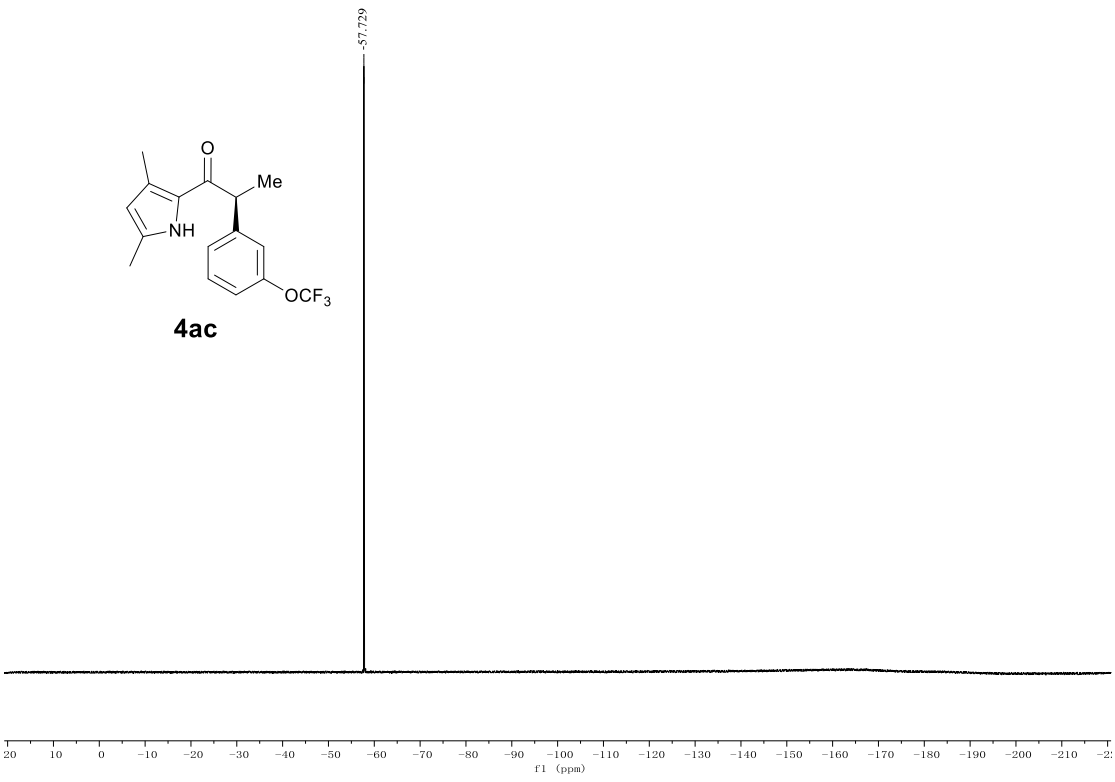
^{19}F NMR spectrum ($CDCl_3$, 471 MHz) of **4ab**



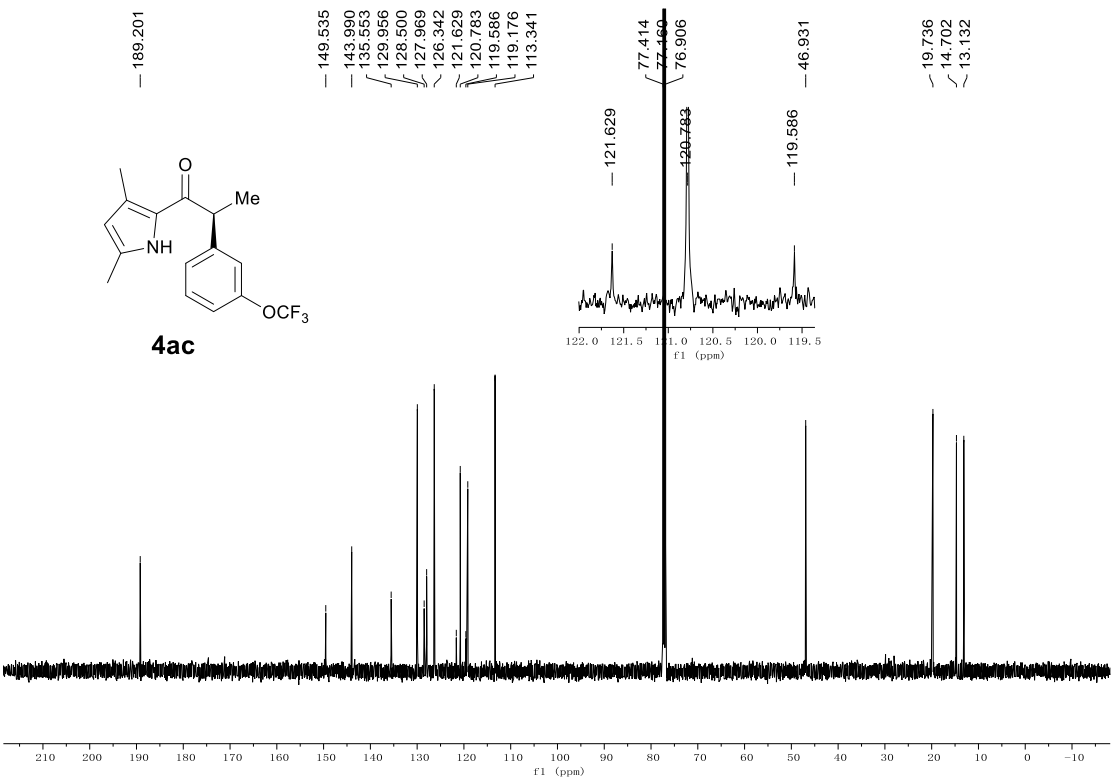
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4ab**



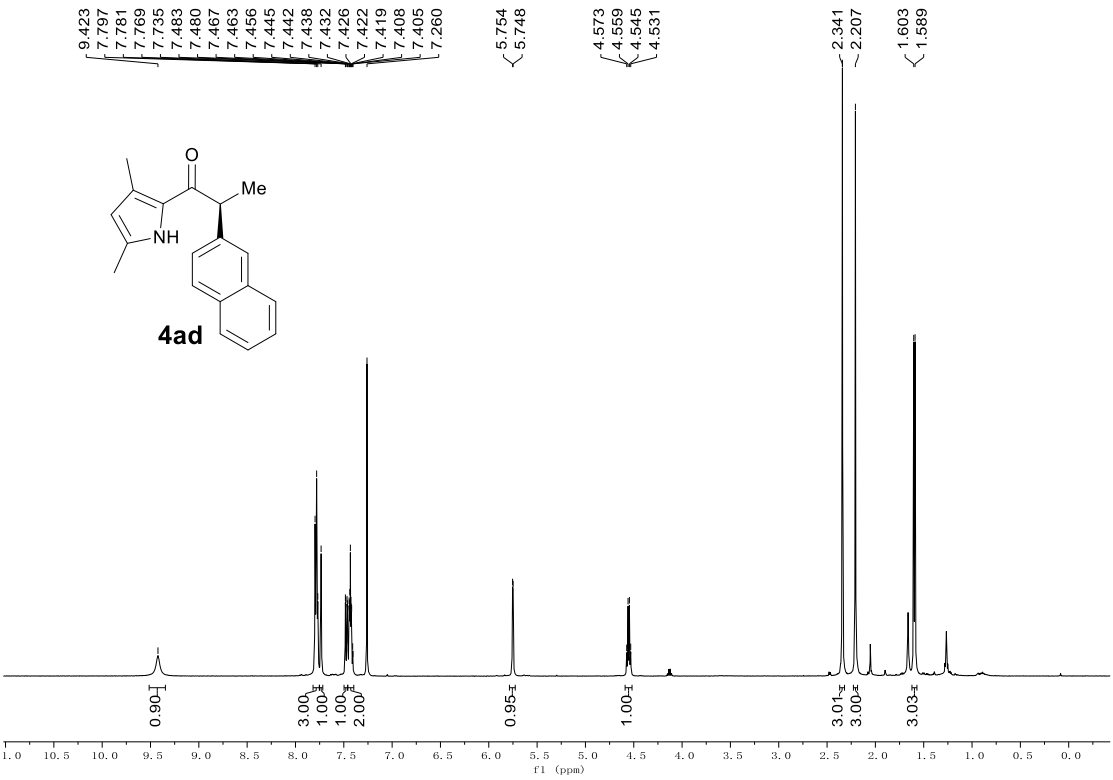
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4ac**



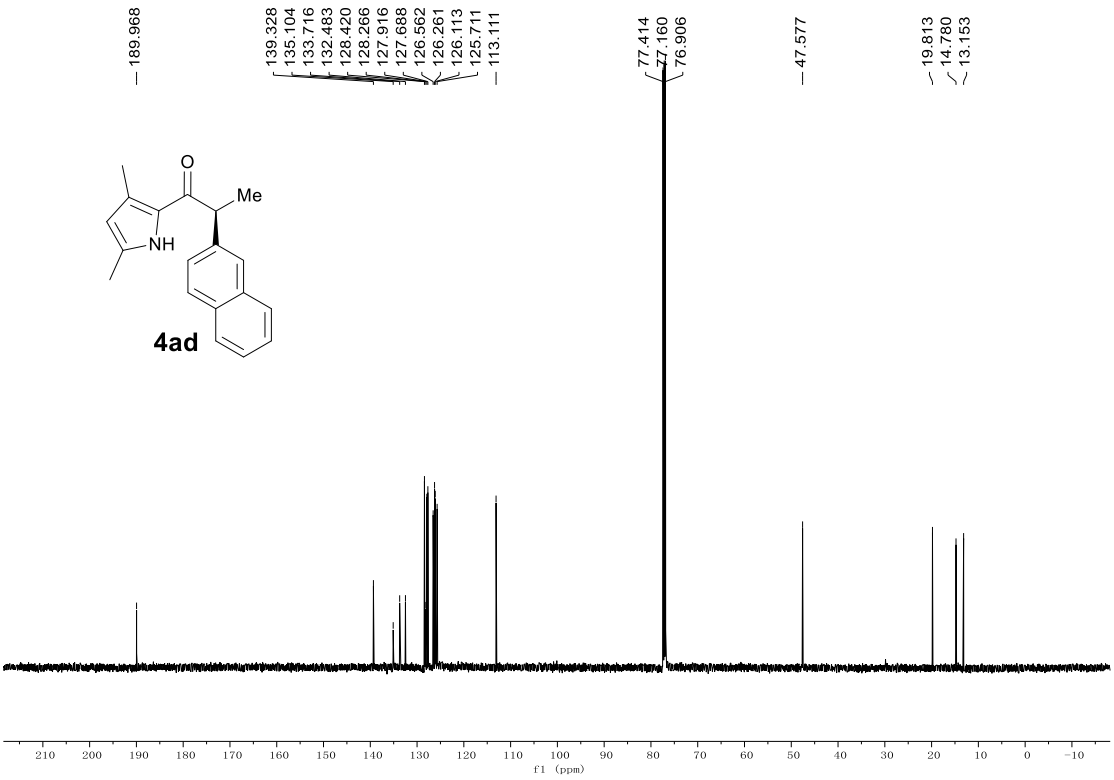
^{19}F NMR spectrum ($CDCl_3$, 471 MHz) of **4ac**



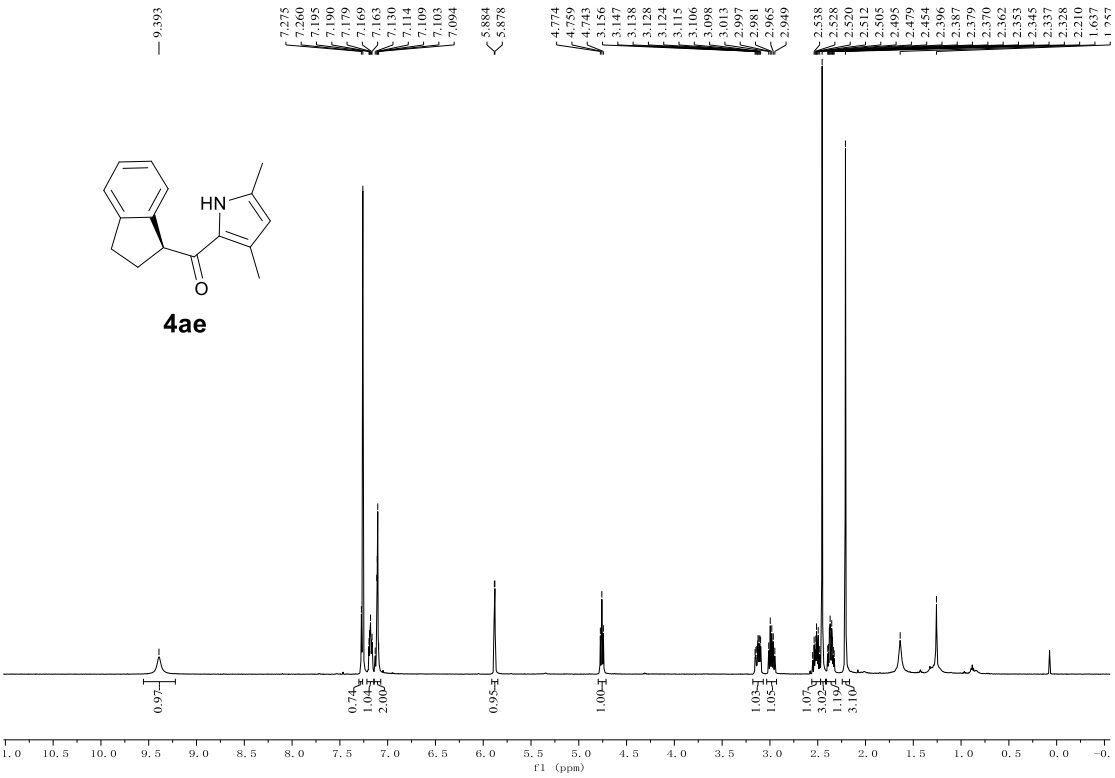
^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4ac**



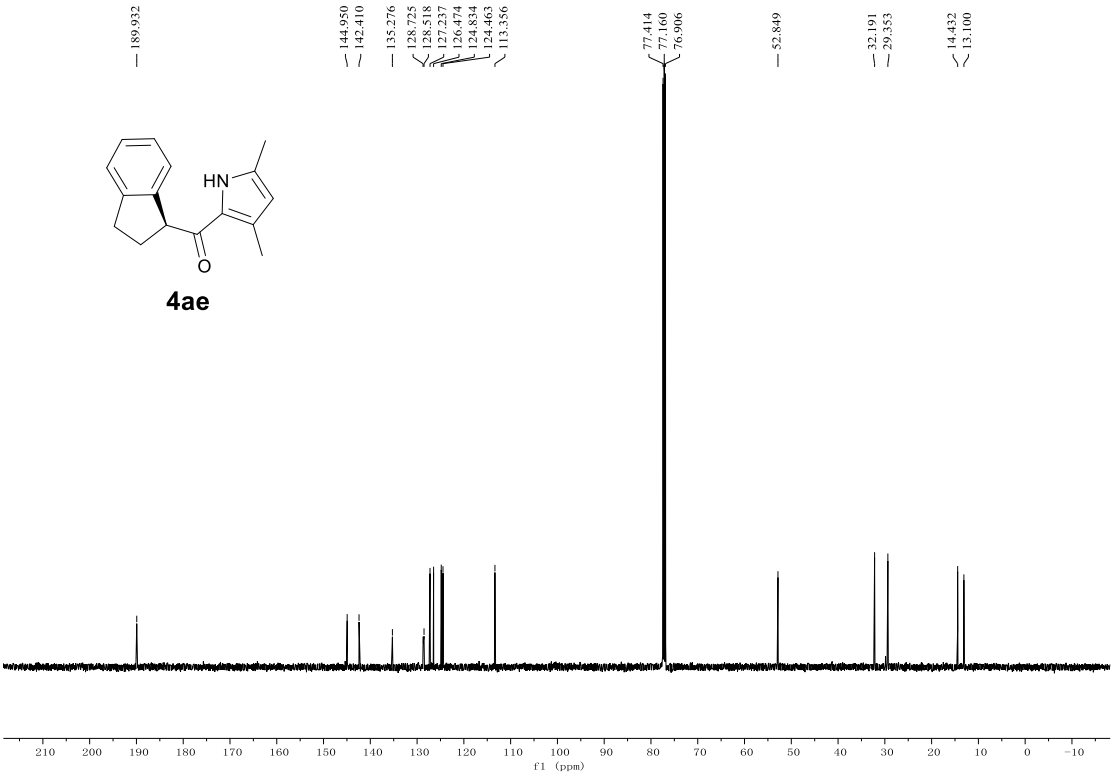
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4ad**



^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4ad**



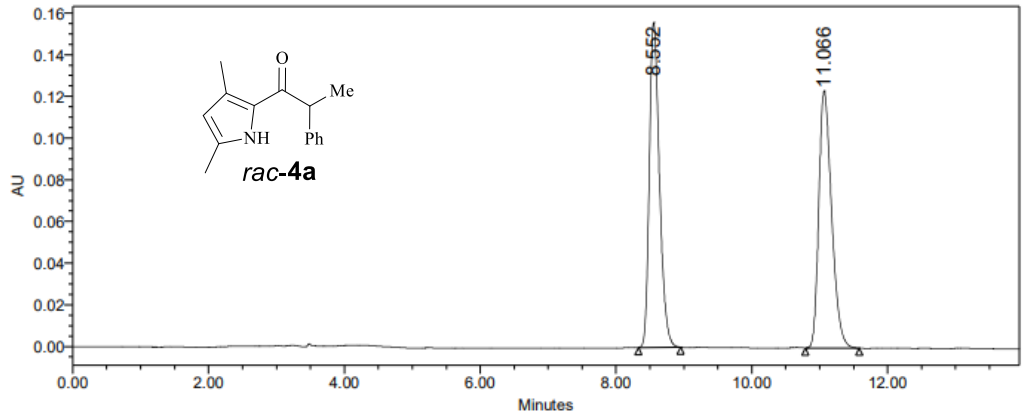
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4ae**



^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of **4ae**

Chiral HPLC analysis of 4a-4z, 4aa-4ae

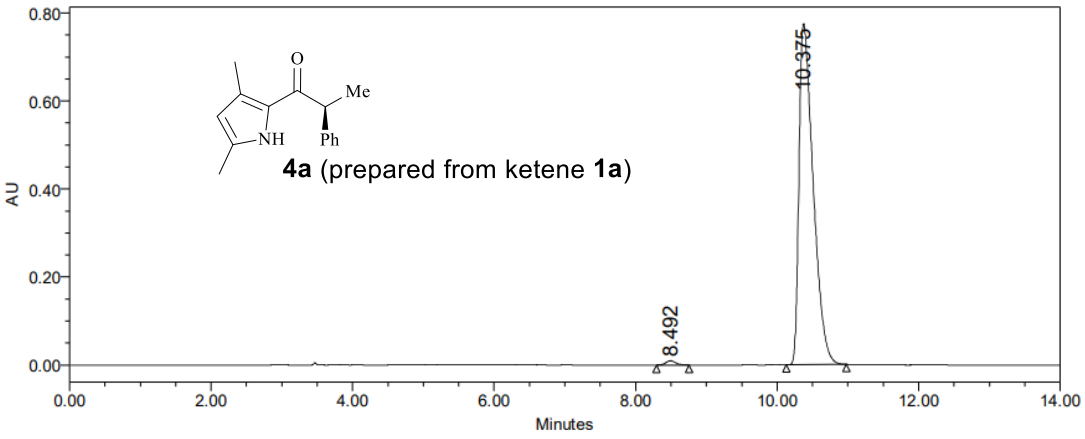
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 243nm; Result Id: 2603; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 243nm

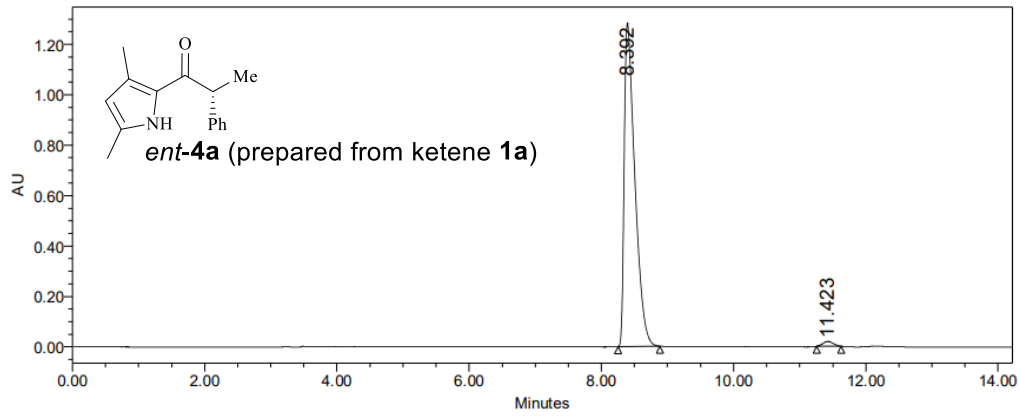
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 243nm	8.552	1613054	49.95	155778
2	W2489 ChA 243nm	11.066	1616571	50.05	123367



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4331; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

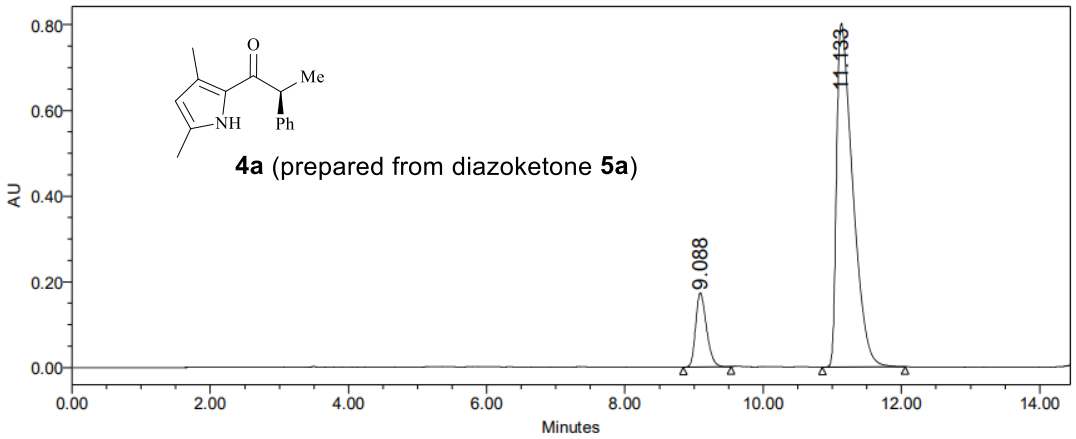
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.492	90053	0.83	9562
2	W2489 ChA 254nm	10.375	10805130	99.17	774308



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2369; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.392	14280833	98.53	1282417
2	W2489 ChA 254nm	11.423	213109	1.47	19263

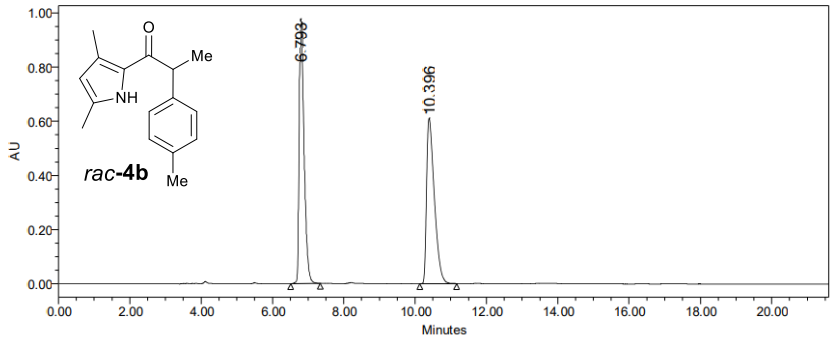


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5218; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.088	1883527	12.58	172372
2	W2489 ChA 254nm	11.133	13086677	87.42	801186

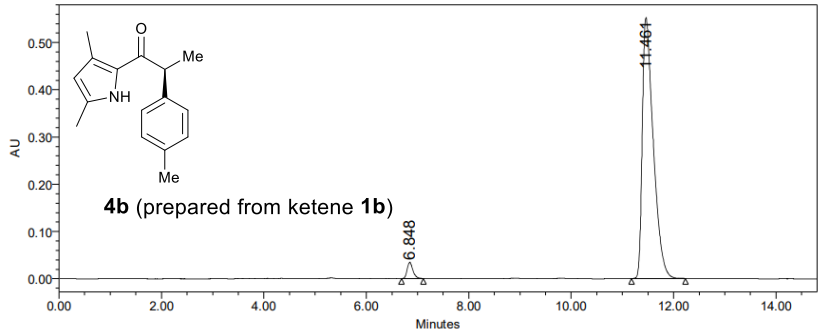
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4934; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

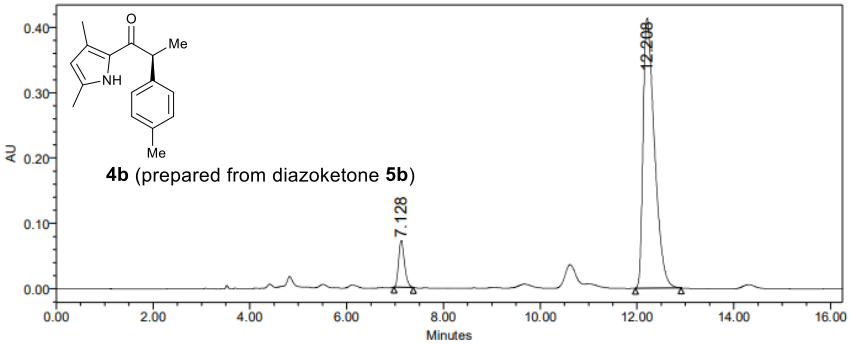
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.793	9294808	50.22	976648
2	W2489 ChA 254nm	10.396	9214921	49.78	611416



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4993; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.848	267085	3.14	34291
2	W2489 ChA 254nm	11.461	8245459	96.86	551902

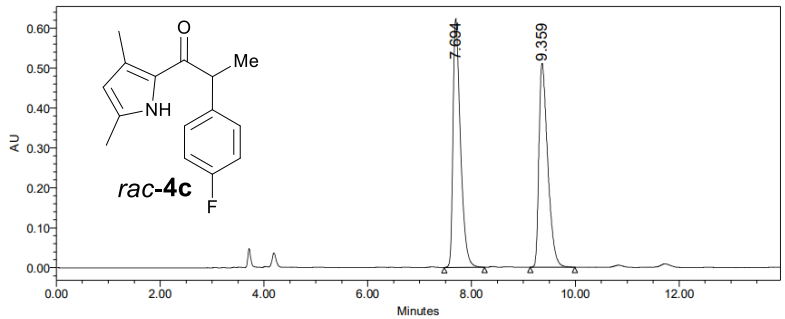


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1956; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.128	601228	8.15	71013
2	W2489 ChA 254nm	12.208	6780090	91.85	412485

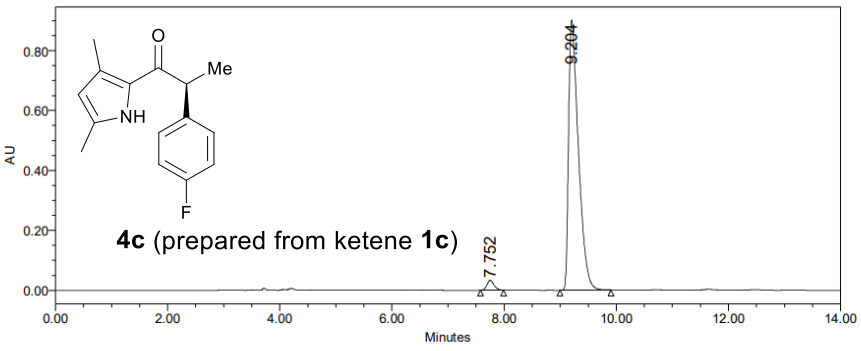
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4976; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

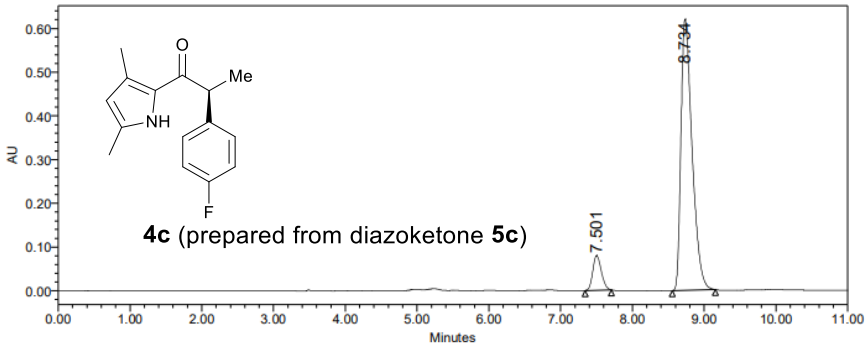
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.694	6191793	50.75	622562
2	W2489 ChA 254nm	9.359	6009101	49.25	510008



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4979; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.752	285102	2.53	32780
2	W2489 ChA 254nm	9.204	10977336	97.47	900420

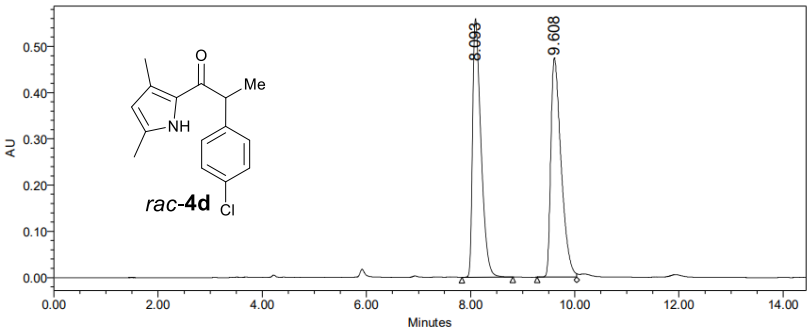


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2626; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.501	658096	8.99	79474
2	W2489 ChA 254nm	8.734	6662586	91.01	619962

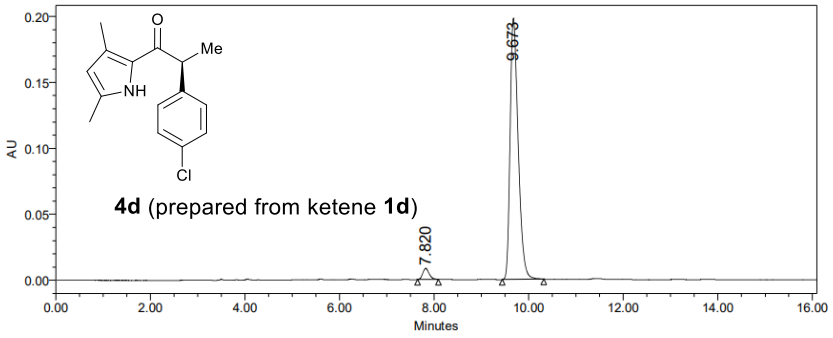
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4943; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

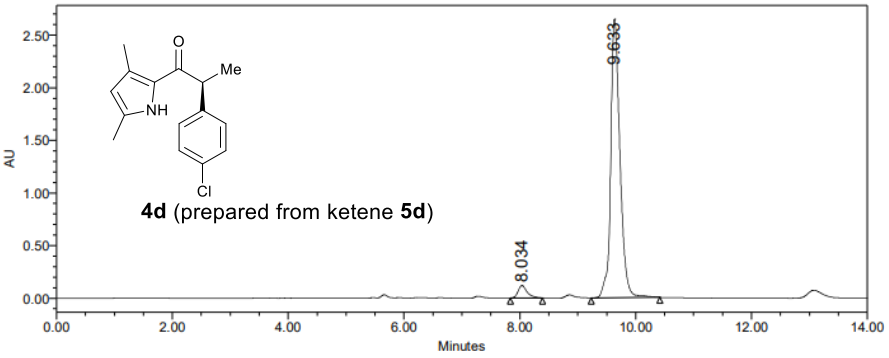
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.093	6238217	48.85	558447
2	W2489 ChA 254nm	9.608	6532246	51.15	474054



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4995; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.820	77514	3.20	8325
2	W2489 ChA 254nm	9.673	2344470	96.80	197900

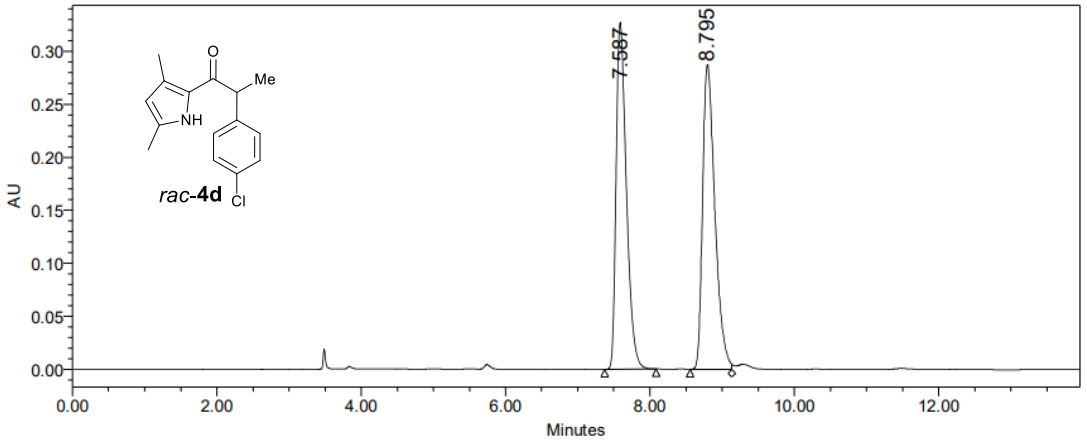


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5216; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.034	1298052	4.22	118403
2	W2489 ChA 254nm	9.633	29489647	95.78	2644554

Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t

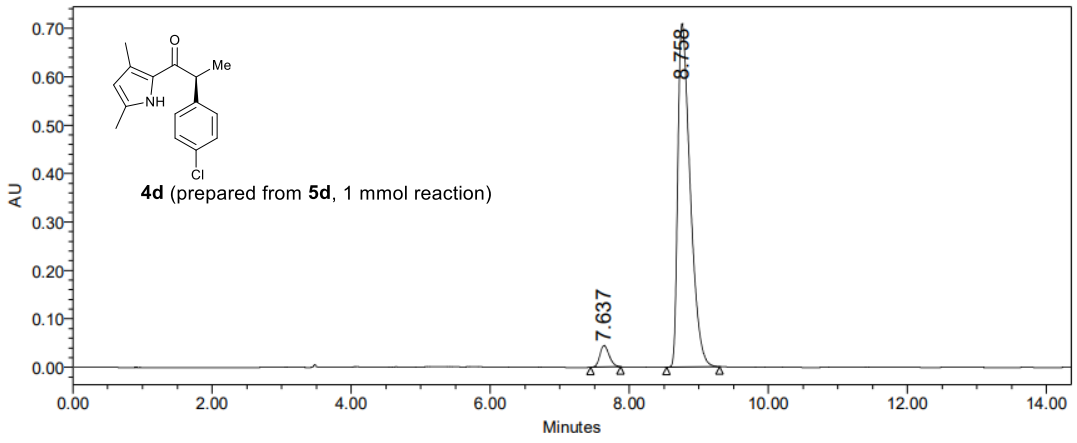


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5615; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.587	3230363	48.75	326911
2	W2489 ChA 254nm	8.795	3395758	51.25	287074

HPLC analysis for 1 mmol reaction of **5d** with **2a**

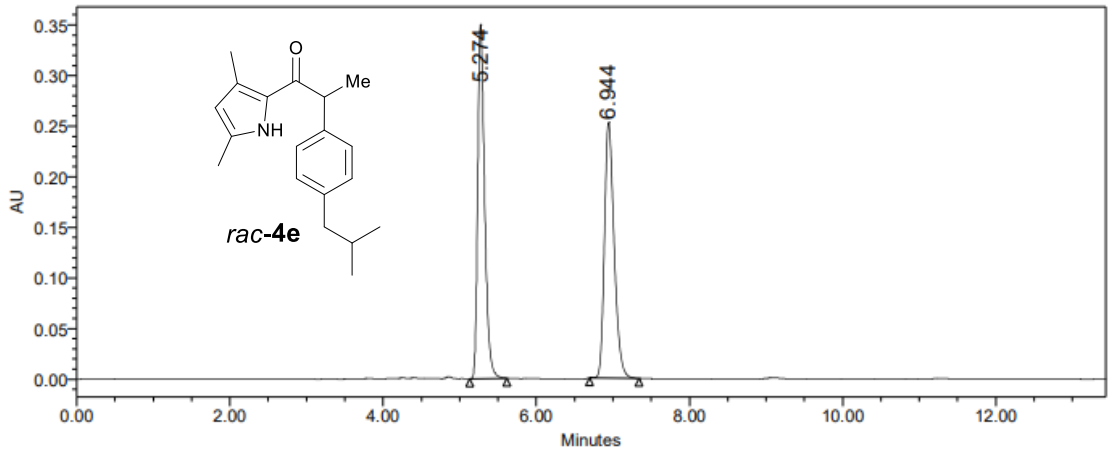


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5610; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.637	417851	4.56	44917
2	W2489 ChA 254nm	8.758	8753694	95.44	708744

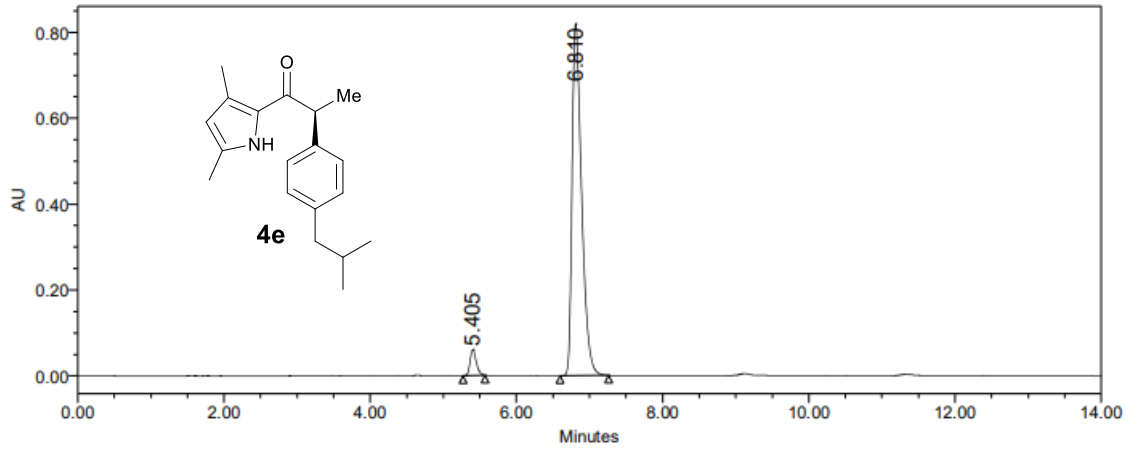
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5214; Processing Method: 9703 OD 3 243

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.274	2215009	49.94	349873
2	W2489 ChA 254nm	6.944	2220677	50.06	252435

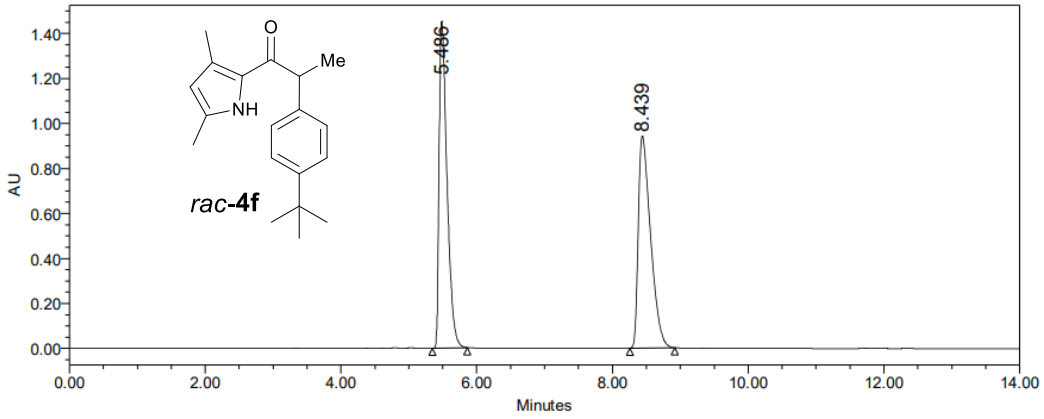


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5212; Processing Method: 9703 OD 3 243

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.405	358967	4.63	60372
2	W2489 ChA 254nm	6.810	7386938	95.37	819183

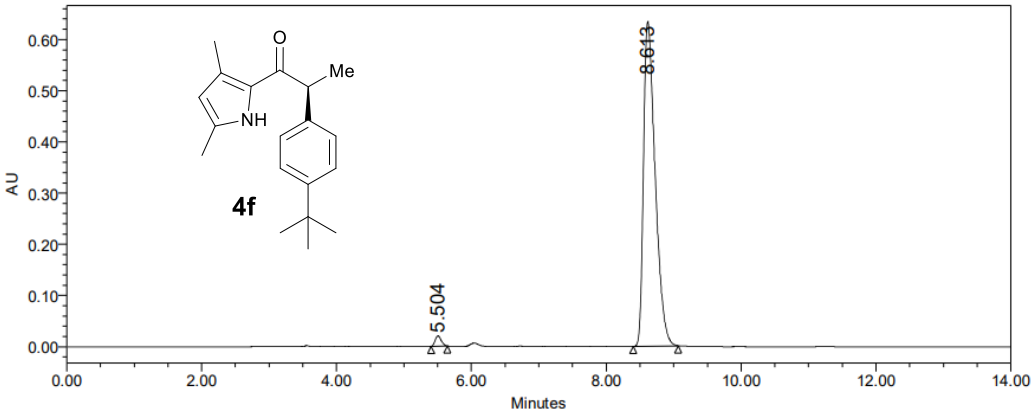
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4622; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.486	11791631	49.93	1451832
2	W2489 ChA 254nm	8.439	11827051	50.07	942572

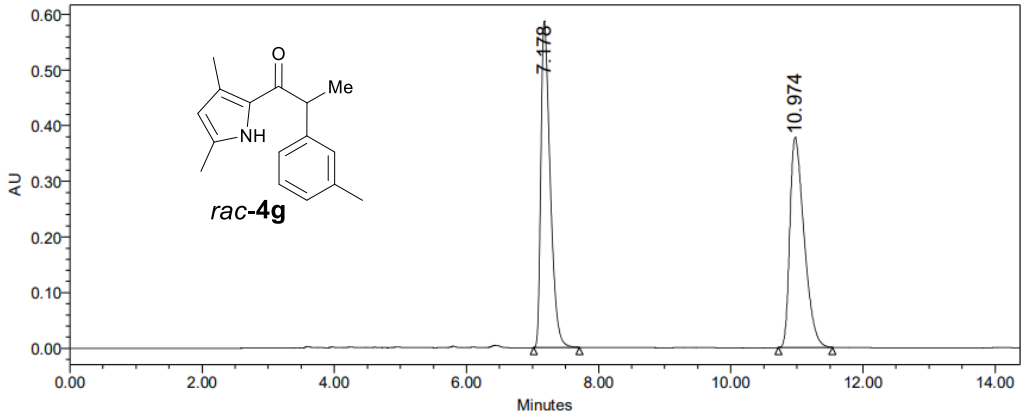


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4609; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.504	126108	1.63	20108
2	W2489 ChA 254nm	8.613	7602735	98.37	633704

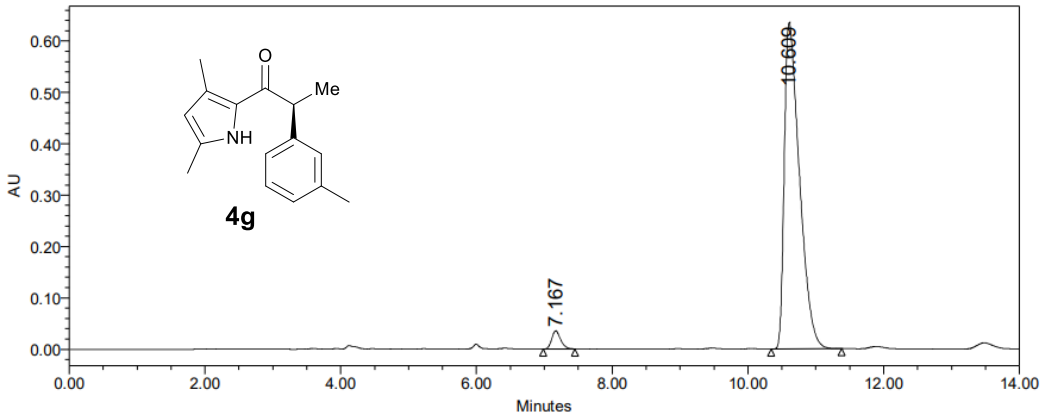
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1900; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.178	5715077	50.14	586375
2	W2489 ChA 254nm	10.974	5682916	49.86	377495

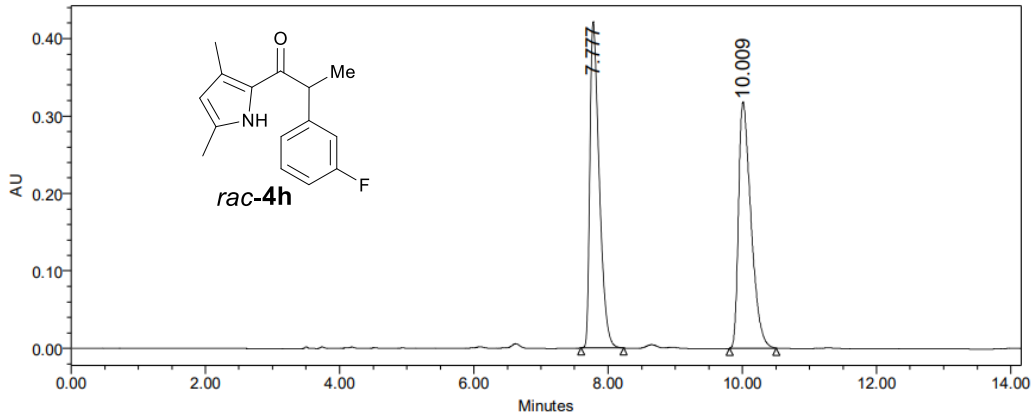


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4957; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.167	324713	3.19	35453
2	W2489 ChA 254nm	10.609	9863358	96.81	635795

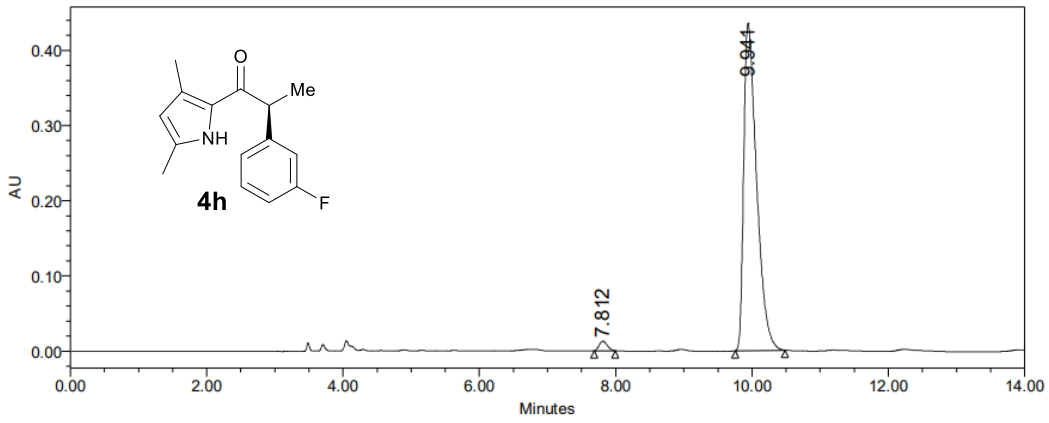
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 243nm; Result Id: 2586; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 243nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 243nm	7.777	4069258	49.84	420645
2	W2489 ChA 243nm	10.009	4094593	50.16	317890

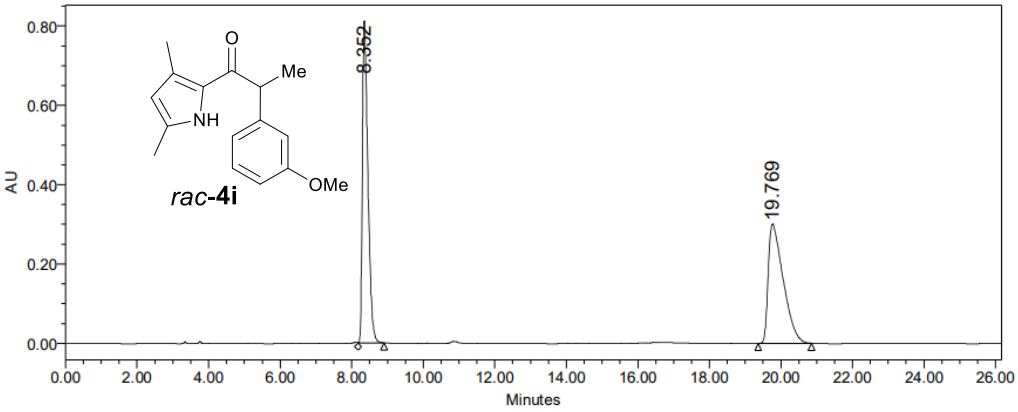


Channel: W2489 ChA; Processed Channel: W2489 ChA 243nm; Result Id: 2590; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 243nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 243nm	7.812	104108	1.79	12616
2	W2489 ChA 243nm	9.941	5698539	98.21	435055

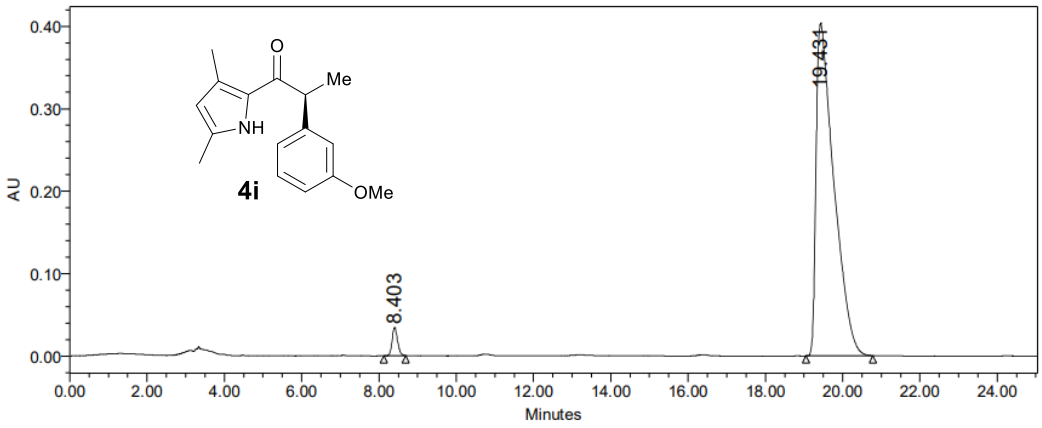
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 95:5 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2235; Processing Method: 9505 254 OD 3

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.352	8656147	49.73	811074
2	W2489 ChA 254nm	19.769	8751490	50.27	301267

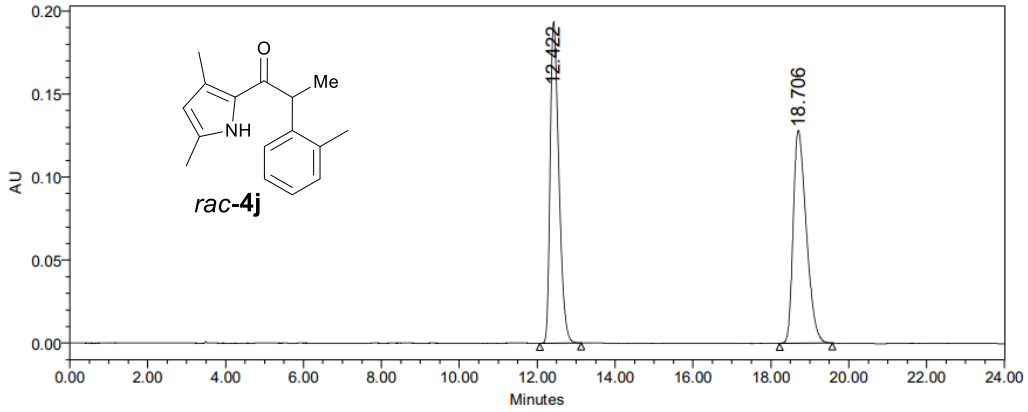


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2245; Processing Method: 9505 254 OD 3

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.403	330836	2.51	33889
2	W2489 ChA 254nm	19.431	12874931	97.49	403566

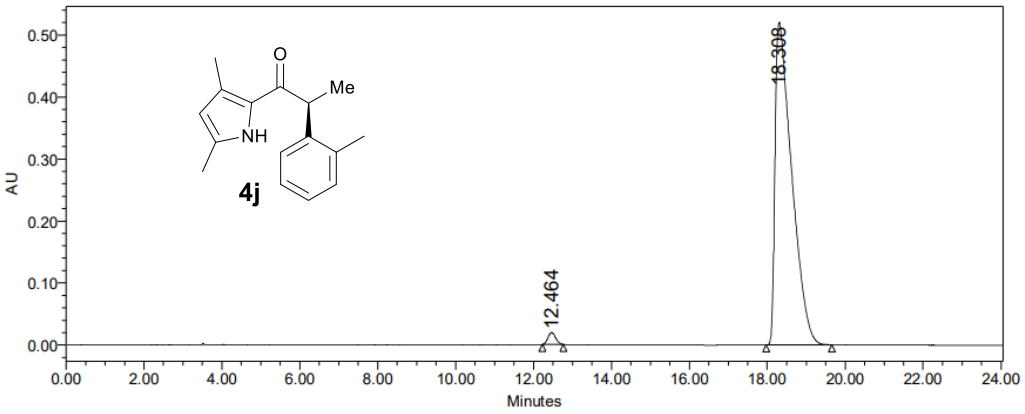
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4997; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	12.422	2994202	50.00	193343
2	W2489 ChA 254nm	18.706	2994640	50.00	128058

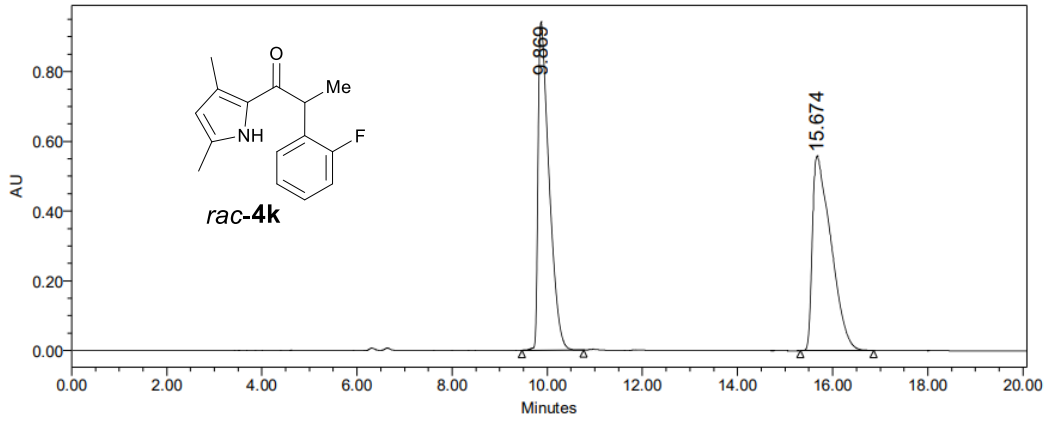


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5001; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	12.464	271105	1.73	19321
2	W2489 ChA 254nm	18.308	15420049	98.27	519946

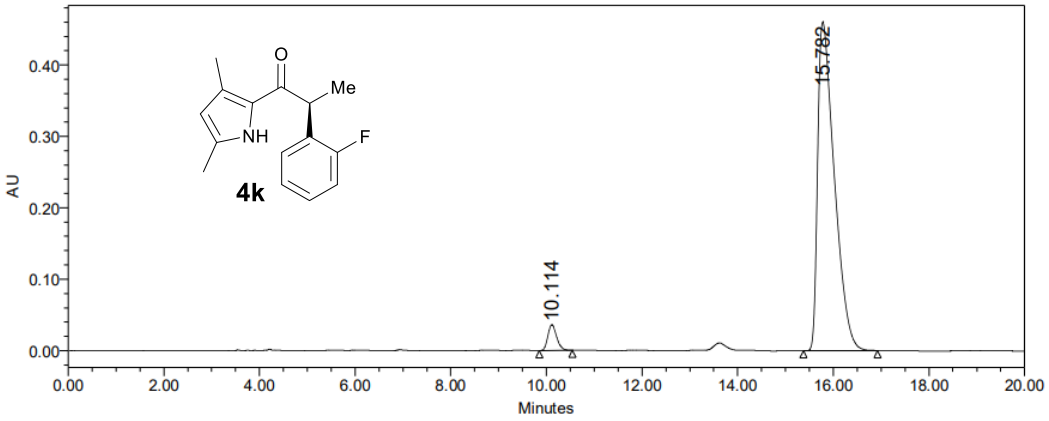
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4953; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.869	15155960	49.97	941677
2	W2489 ChA 254nm	15.674	15176797	50.03	558223

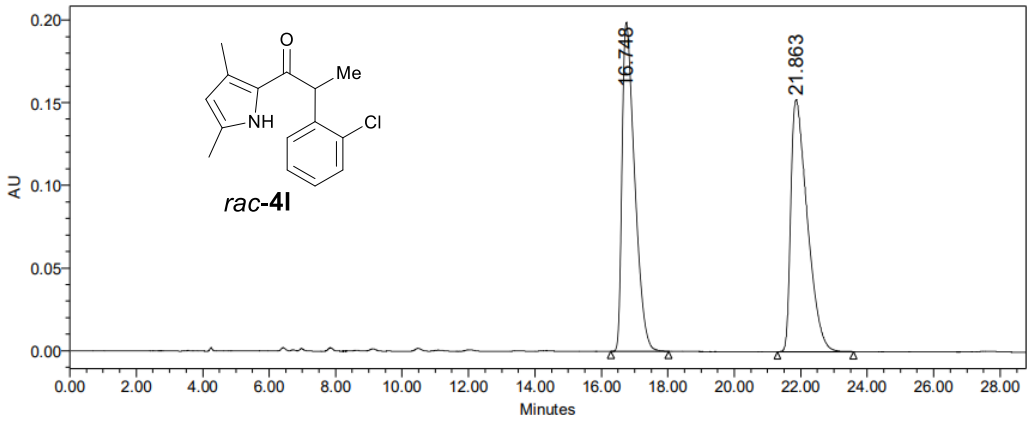


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4955; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	10.114	464872	4.01	36176
2	W2489 ChA 254nm	15.782	11121322	95.99	460505

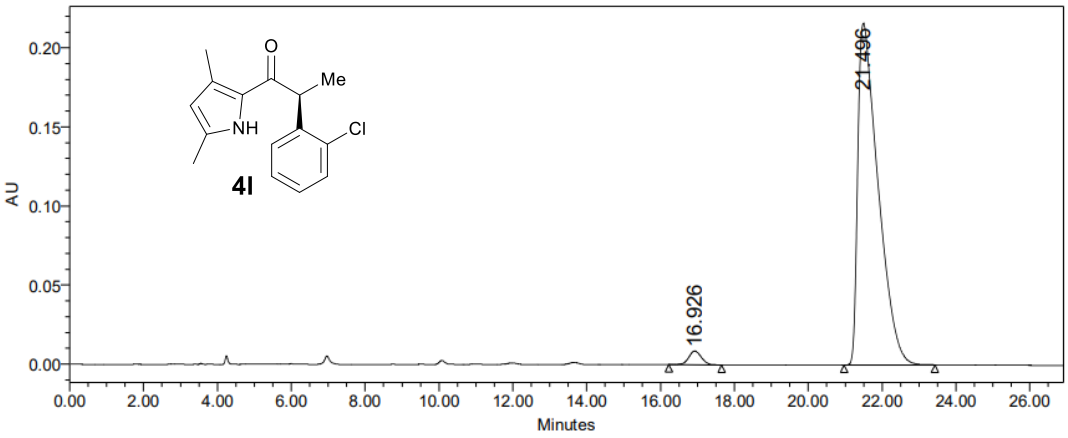
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4947; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	16.748	5231924	49.94	198813
2	W2489 ChA 254nm	21.863	5245068	50.06	152491

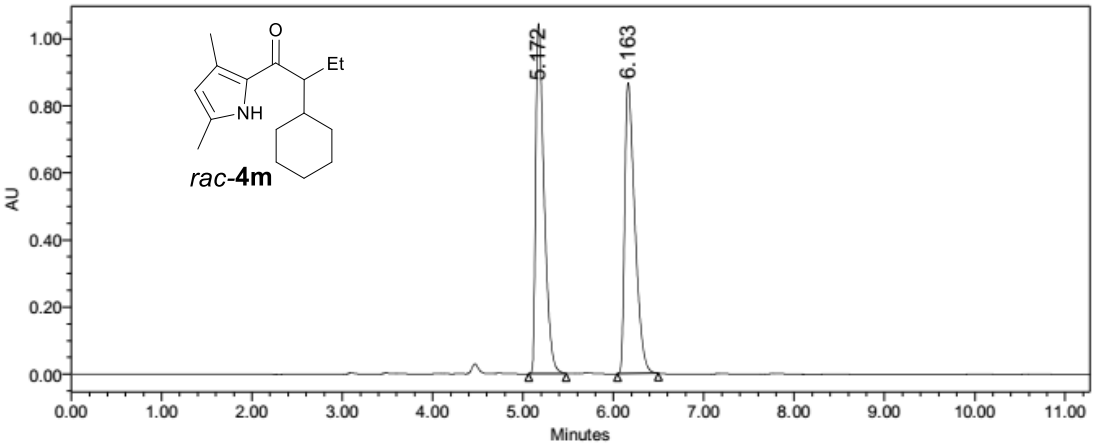


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4950; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	16.926	208543	2.47	8716
2	W2489 ChA 254nm	21.496	8226521	97.53	216030

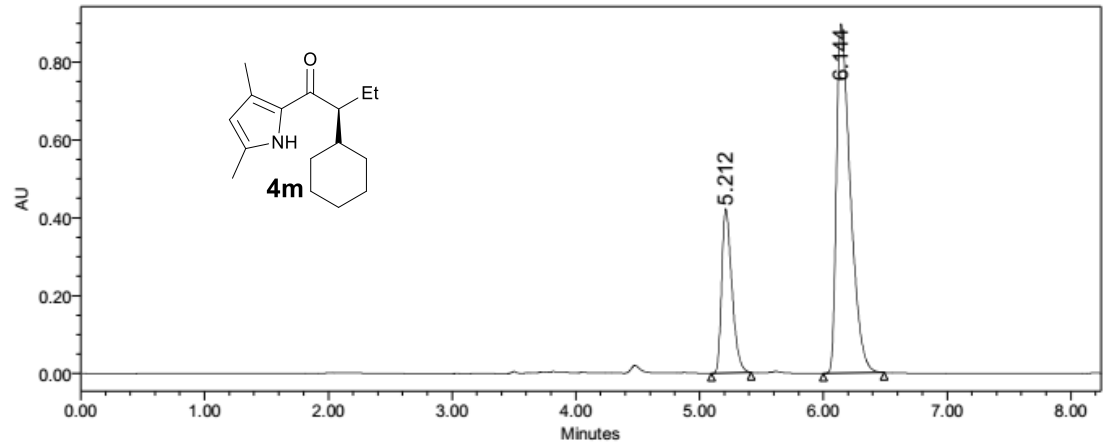
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 243nm; Result Id: 2595; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 243nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 243nm	5.172	6727462	50.04	1043629
2	W2489 ChA 243nm	6.163	6716129	49.96	867711

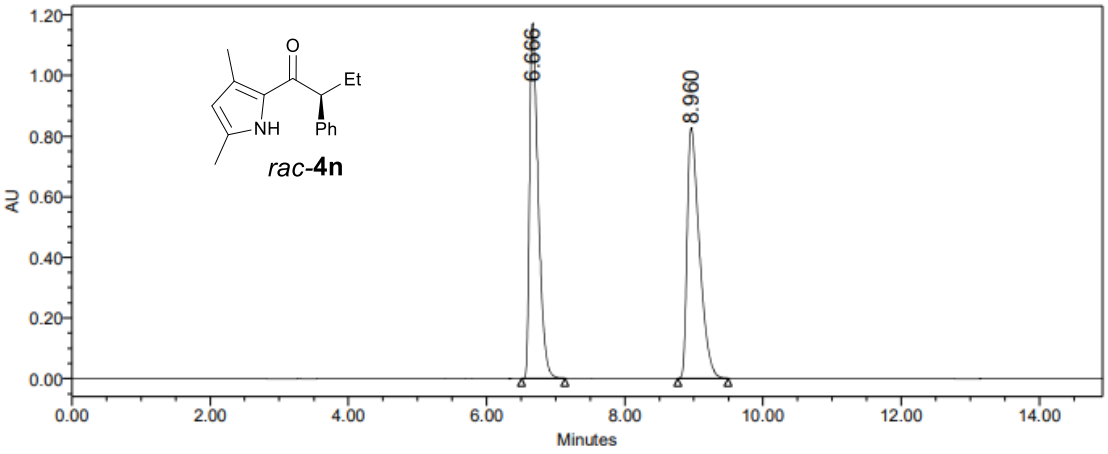


Channel: W2489 ChA; Processed Channel: W2489 ChA 243nm; Result Id: 2599; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 243nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 243nm	5.212	2417970	25.62	421302
2	W2489 ChA 243nm	6.144	7018640	74.38	896529

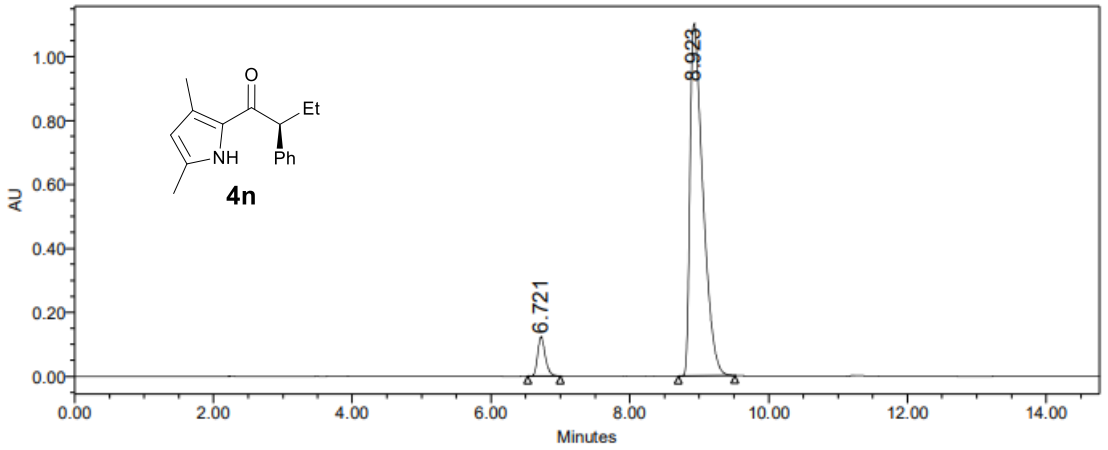
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5204; Processing Method: 9703 OD 3 243

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.666	10141090	49.92	1170336
2	W2489 ChA 254nm	8.960	10172279	50.08	826857

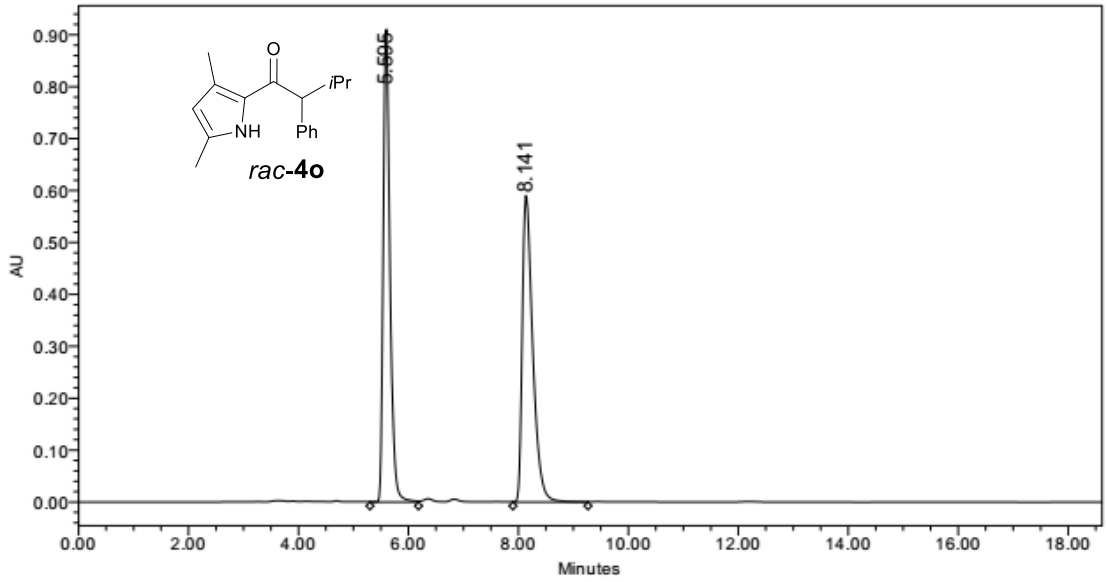


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5199; Processing Method: 9703 OD 3 254

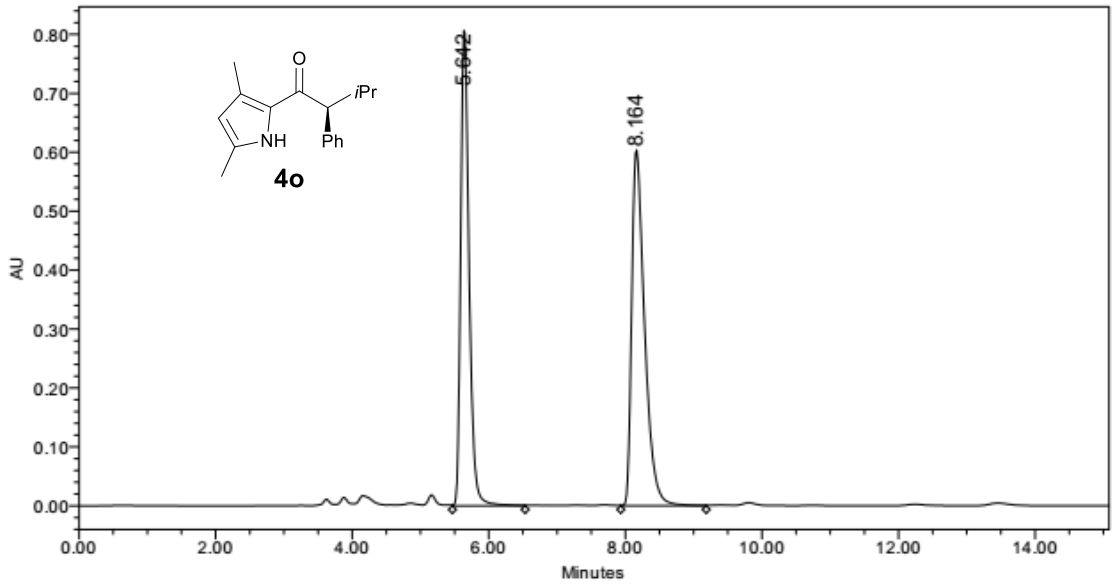
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.721	935374	6.16	123127
2	W2489 ChA 254nm	8.923	14243407	93.84	1101217

Daicel Chiralcel AD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t

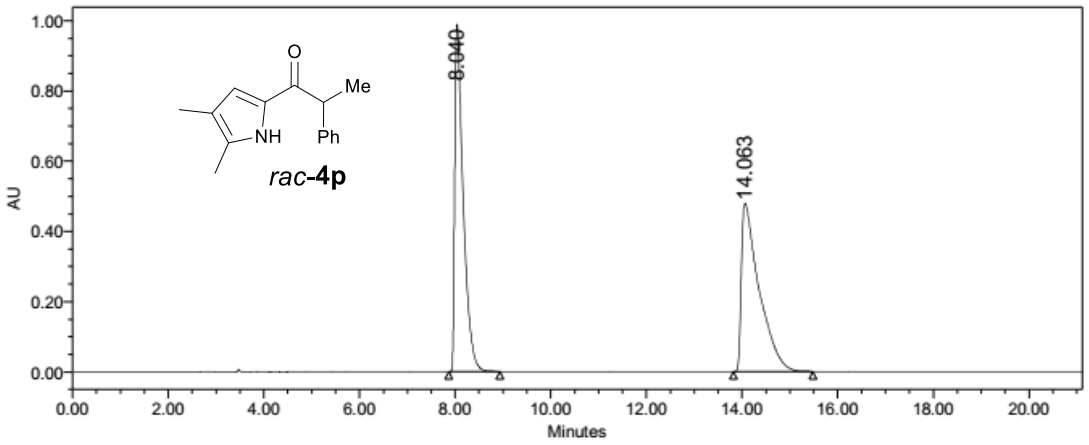


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	5.595	7774213	49.93	911558	60.59
2	8.141	7794681	50.07	593024	39.41



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	5.642	6891583	46.56	813756	57.40
2	8.164	7910243	53.44	603995	42.60

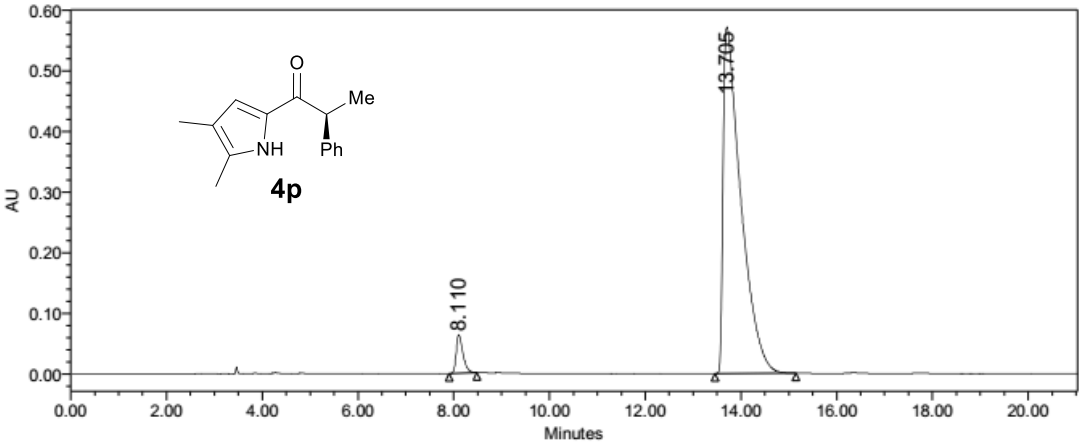
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3281; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.040	12384154	49.91	988624
2	W2489 ChA 254nm	14.063	12427905	50.09	479660

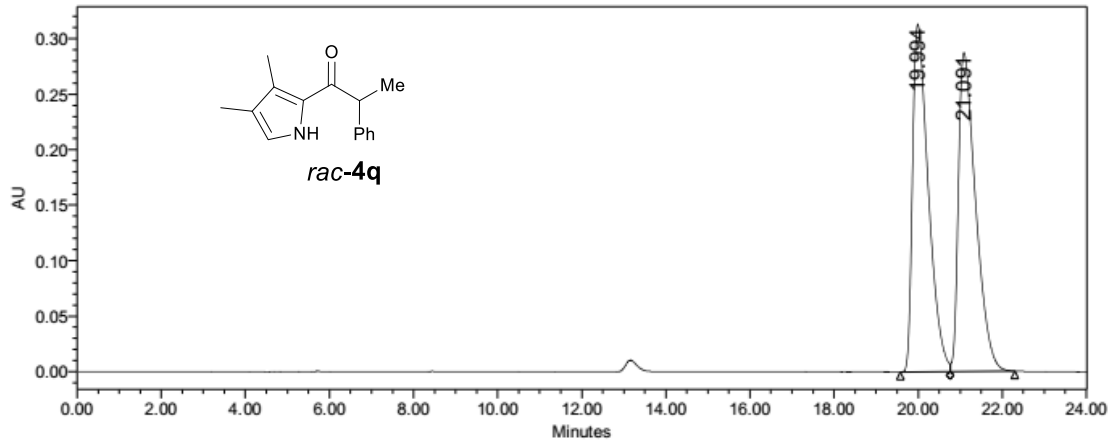


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3284; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.110	632973	4.13	63302
2	W2489 ChA 254nm	13.705	14679875	95.87	571502

Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 99:1 (v/v), 1.0 mL/min, 254 nm, r.t

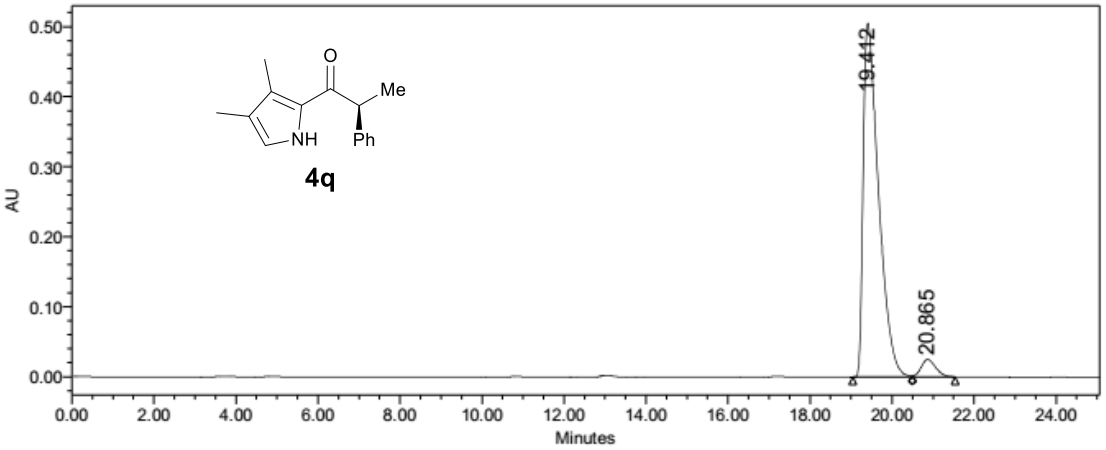


rac-**4q**

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5014; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	19.994	8158517	49.96	313431
2	W2489 ChA 254nm	21.091	8171415	50.04	287417



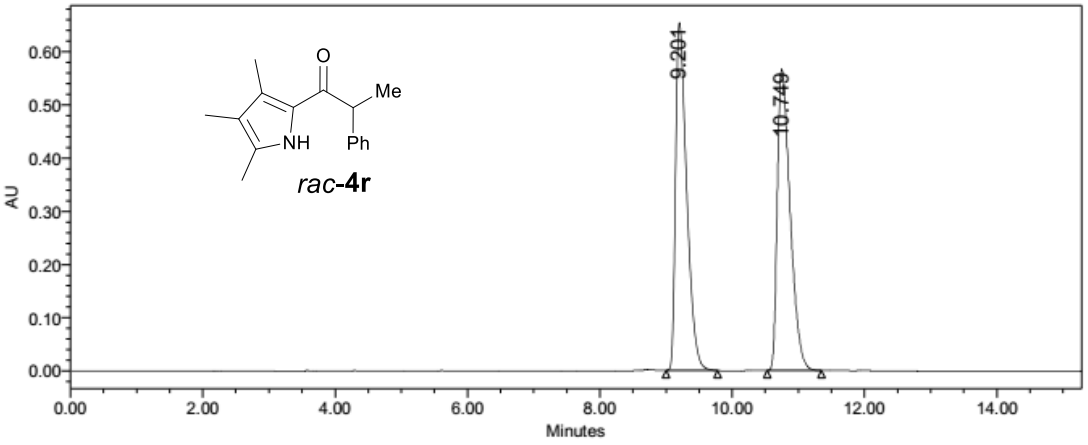
4q

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5016; Processing Method: 9901 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	19.412	13123373	95.51	505198
2	W2489 ChA 254nm	20.865	616629	4.49	24975

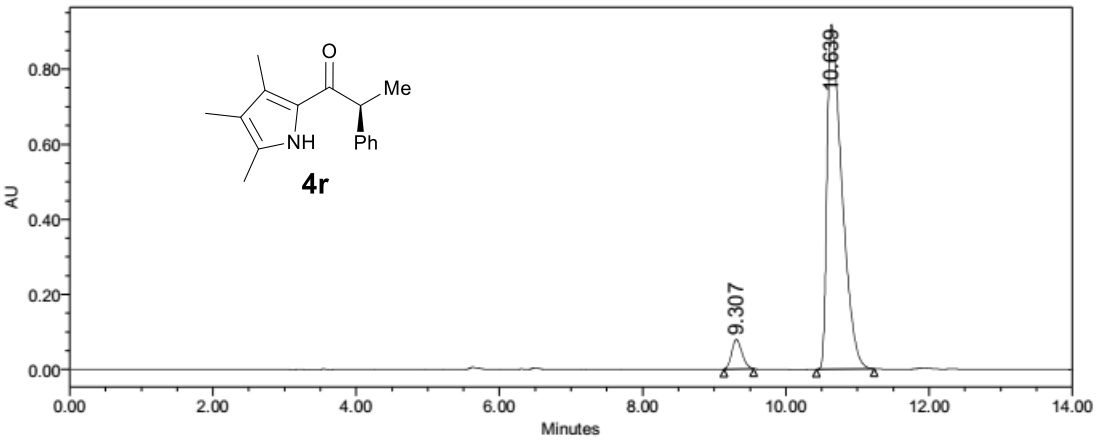
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2360; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.201	7609197	50.07	653735
2	W2489 ChA 254nm	10.749	7586917	49.93	567170

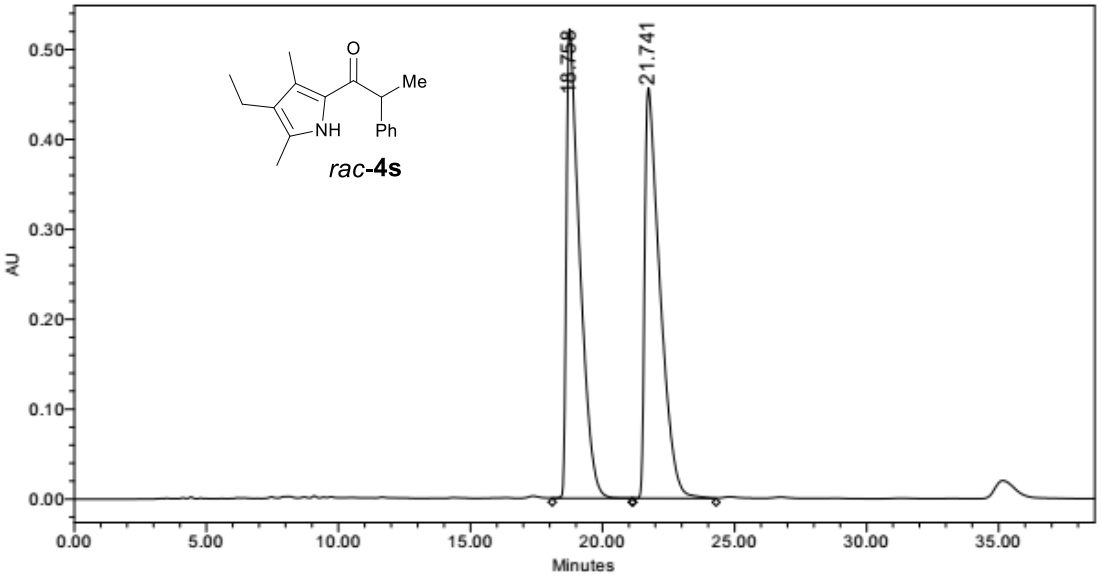


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2363; Processing Method: 9703 OD3 254

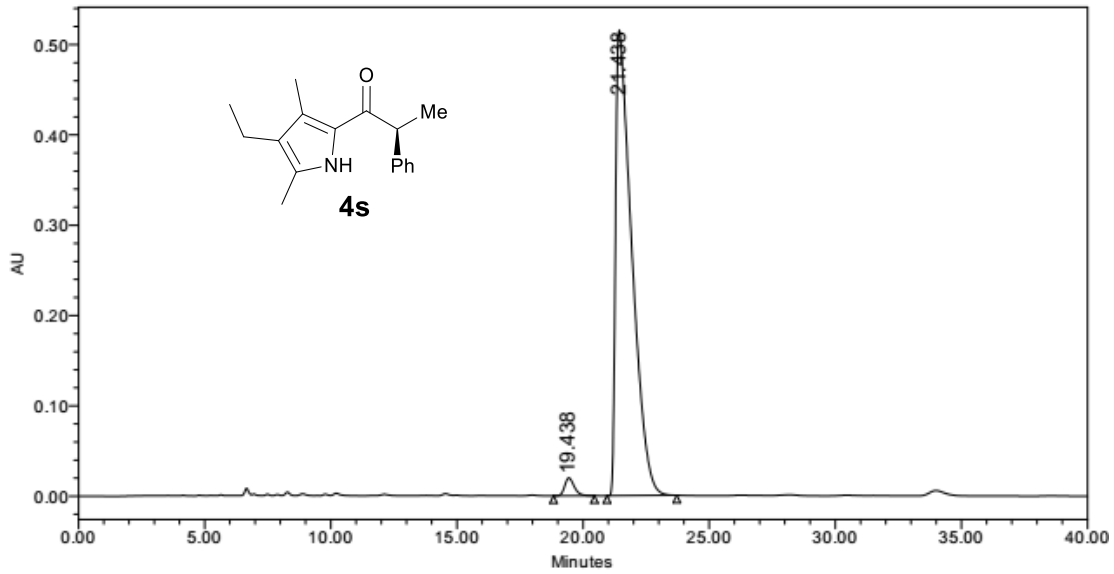
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.307	787435	5.59	78342
2	W2489 ChA 254nm	10.639	13288176	94.41	918483

Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 99:1 (v/v), 1.0 mL/min, 254 nm, r.t

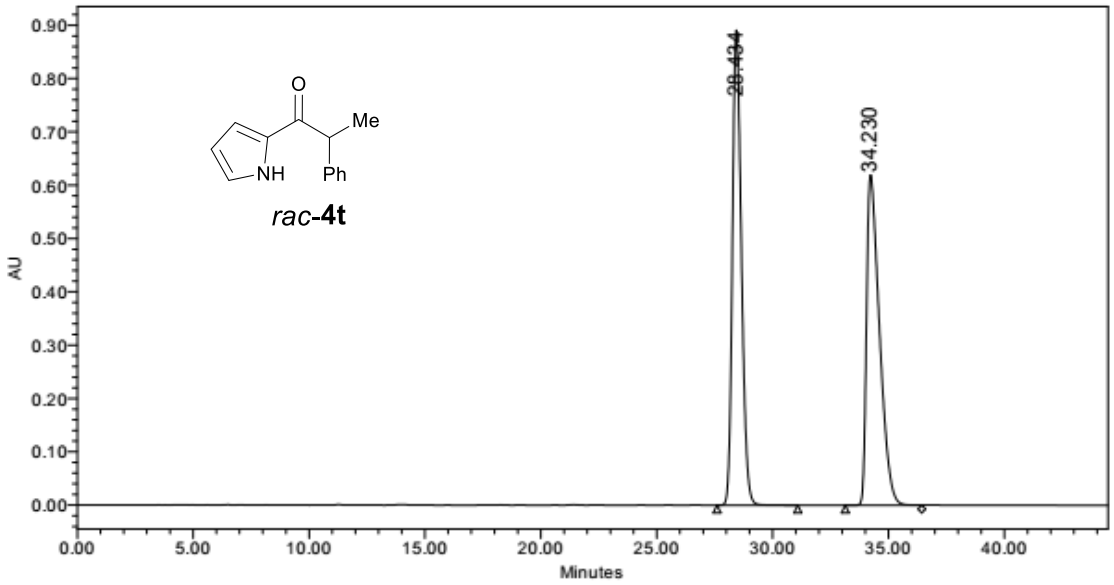


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	18.758	18296022	49.97	522500	53.37
2	21.741	18319879	50.03	456513	46.63

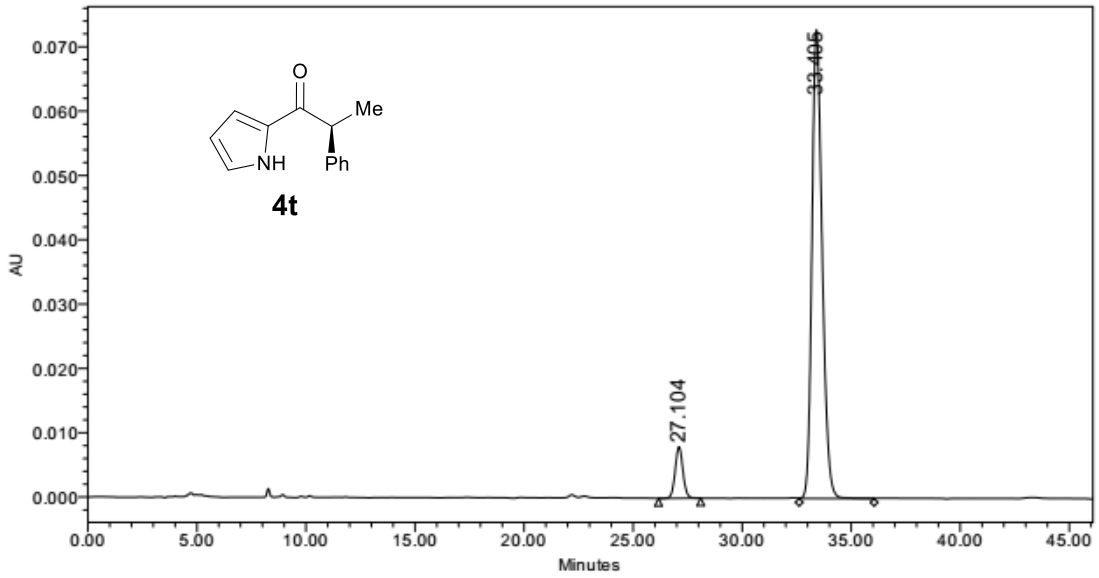


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	19.438	519288	2.21	19779	3.70
2	21.438	23006321	97.79	515216	96.30

Daicel Chiralcel AD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t

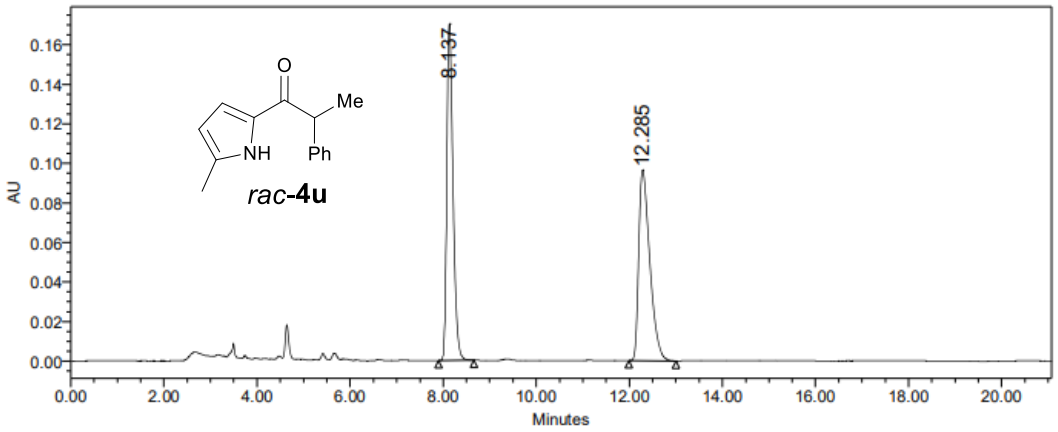


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	28.434	23975815	49.98	890673	58.99
2	34.230	23994033	50.02	619162	41.01



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	27.104	199401	7.73	7996	9.89
2	33.405	2378576	92.27	72843	90.11

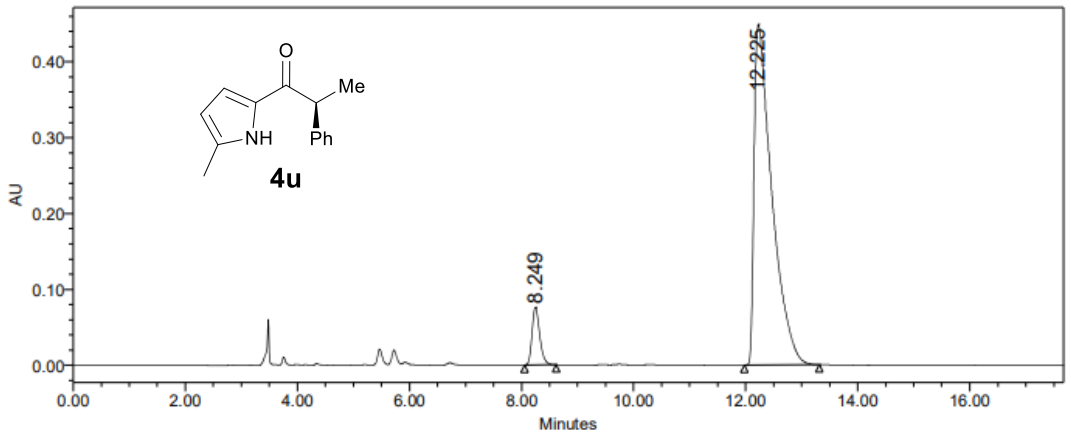
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5197; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.137	1599096	50.06	170342
2	W2489 ChA 254nm	12.285	1595050	49.94	96365

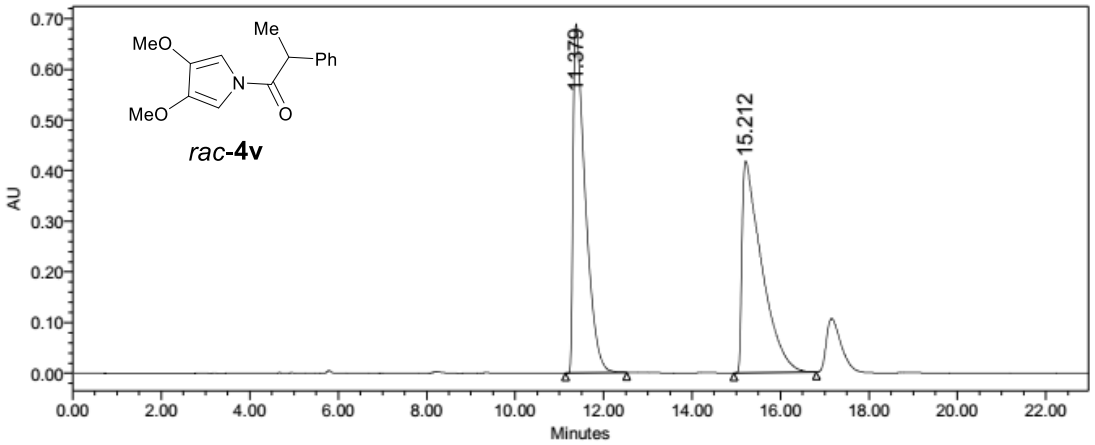


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5176; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.249	719610	6.77	75966
2	W2489 ChA 254nm	12.225	9904893	93.23	448702

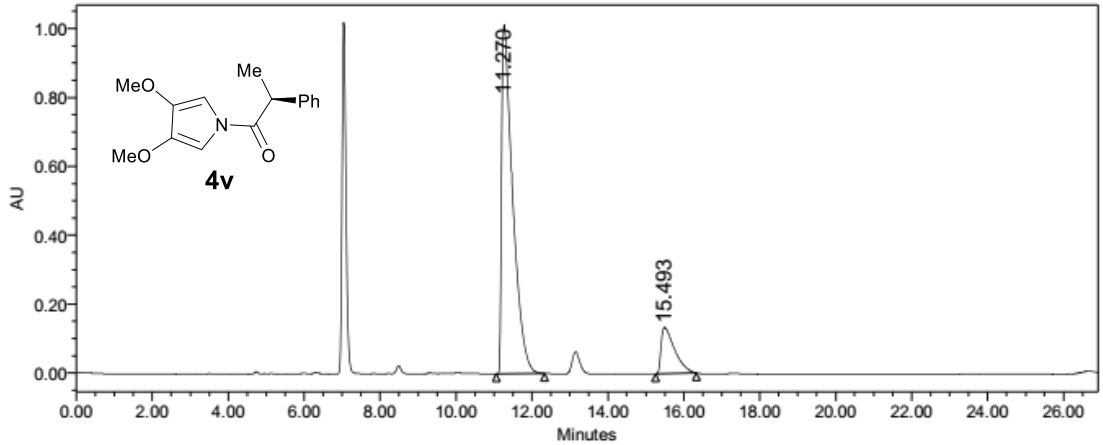
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5018; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.379	13014096	50.05	689246
2	W2489 ChA 254nm	15.212	12986094	49.95	417979

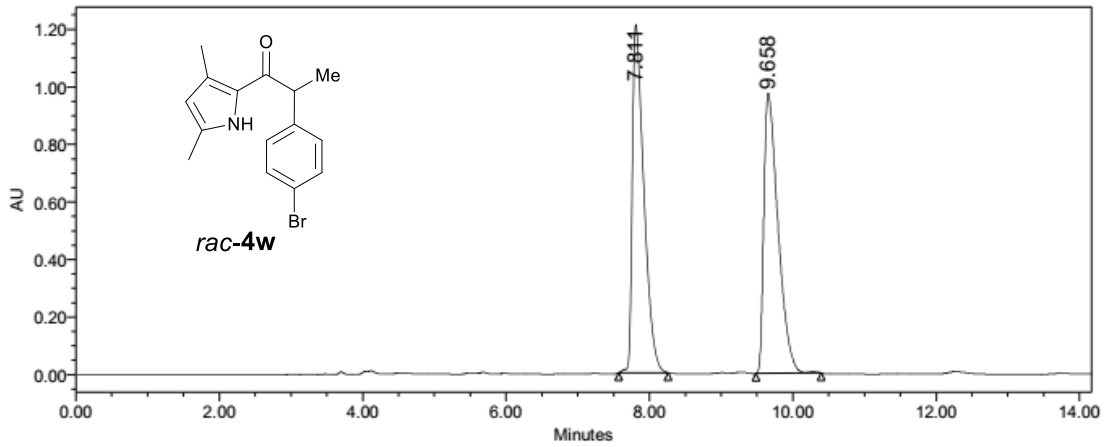


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5022; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.270	20417225	85.90	1014136
2	W2489 ChA 254nm	15.493	3352216	14.10	135237

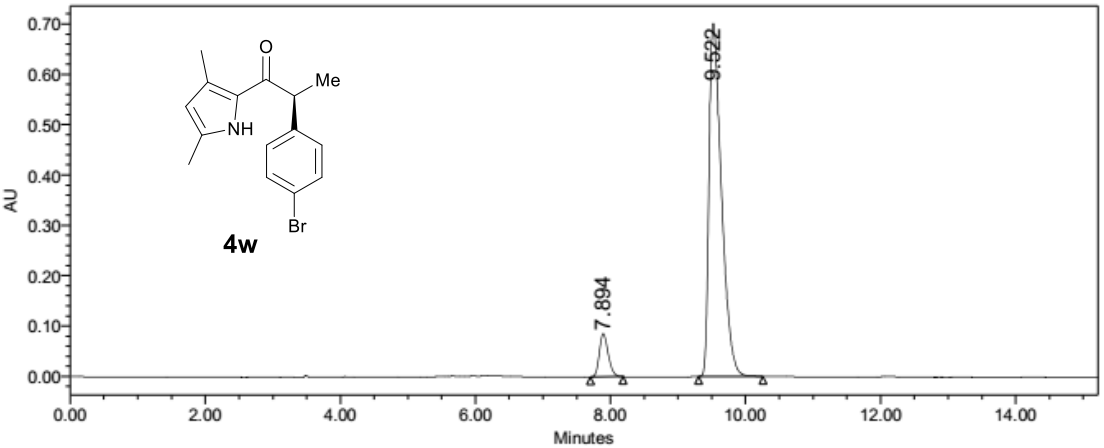
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2692; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.811	13485719	50.26	1210223
2	W2489 ChA 254nm	9.658	13346097	49.74	974093

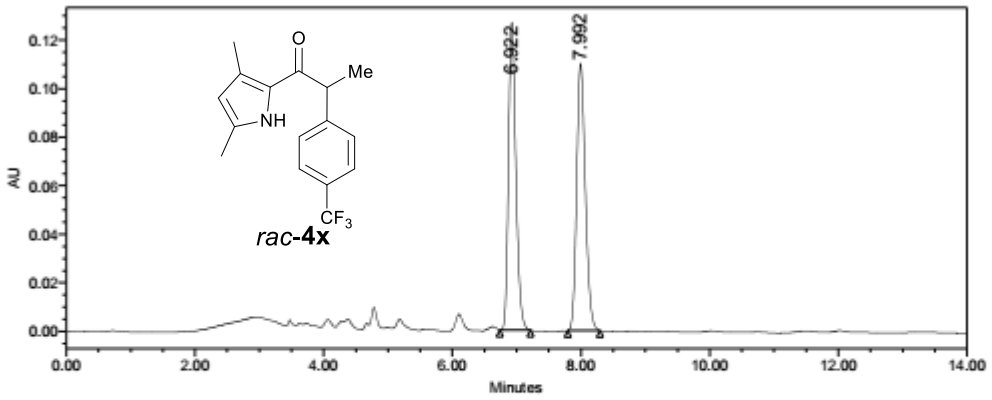


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5008; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.894	786403	8.04	85875
2	W2489 ChA 254nm	9.522	8990647	91.96	701320

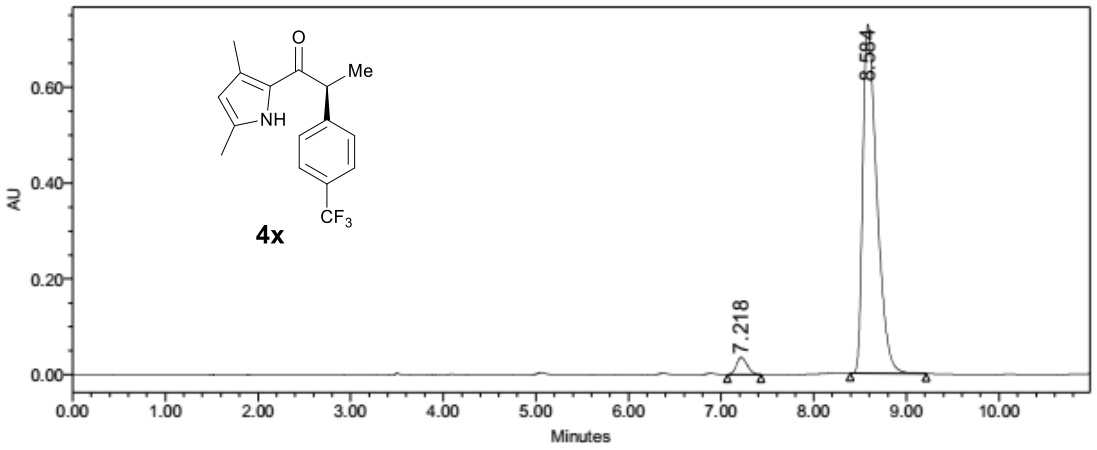
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2698; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.922	1014626	49.72	126568
2	W2489 ChA 254nm	7.992	1026039	50.28	109914

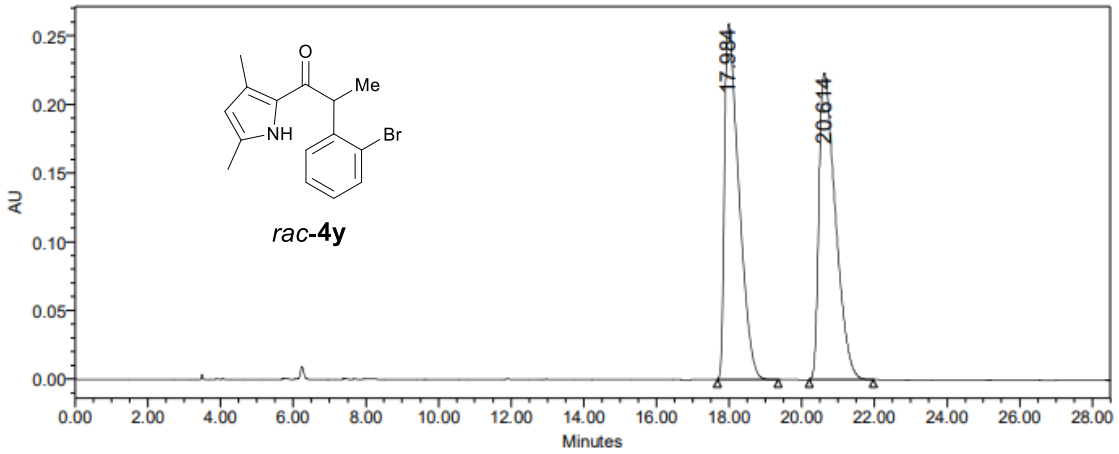


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4966; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.218	294721	3.71	35860
2	W2489 ChA 254nm	8.584	7645257	96.29	727962

Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t

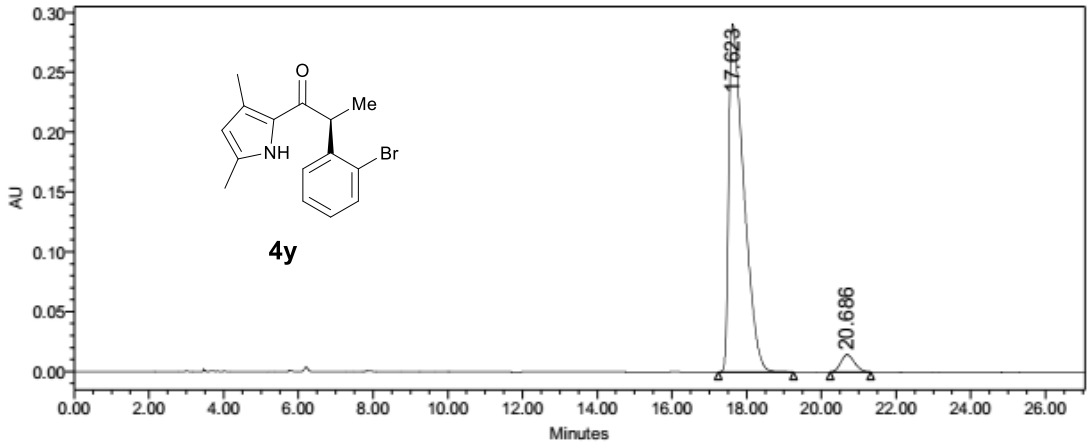


rac-**4y**

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2855; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	17.984	7076565	49.96	258360
2	W2489 ChA 254nm	20.614	7087377	50.04	222833



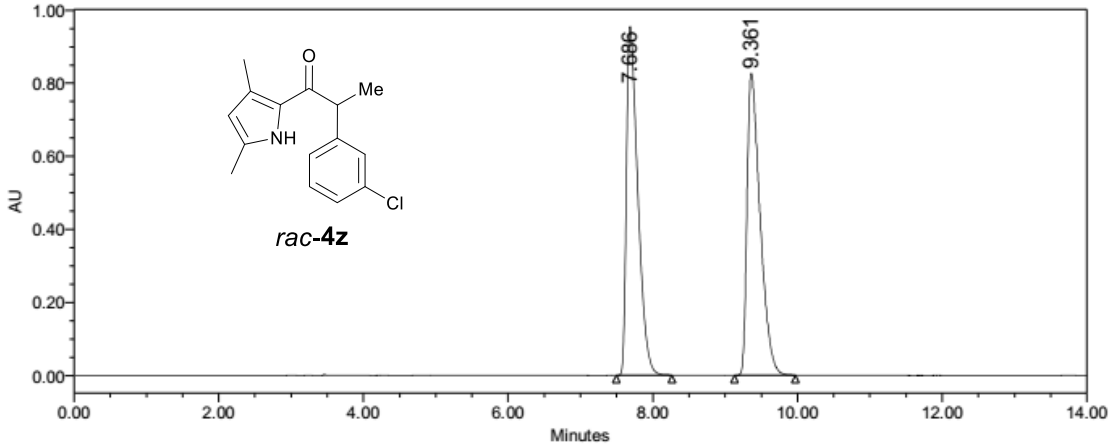
4y

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2861; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	17.623	8134182	95.71	290737
2	W2489 ChA 254nm	20.686	364349	4.29	14296

Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t

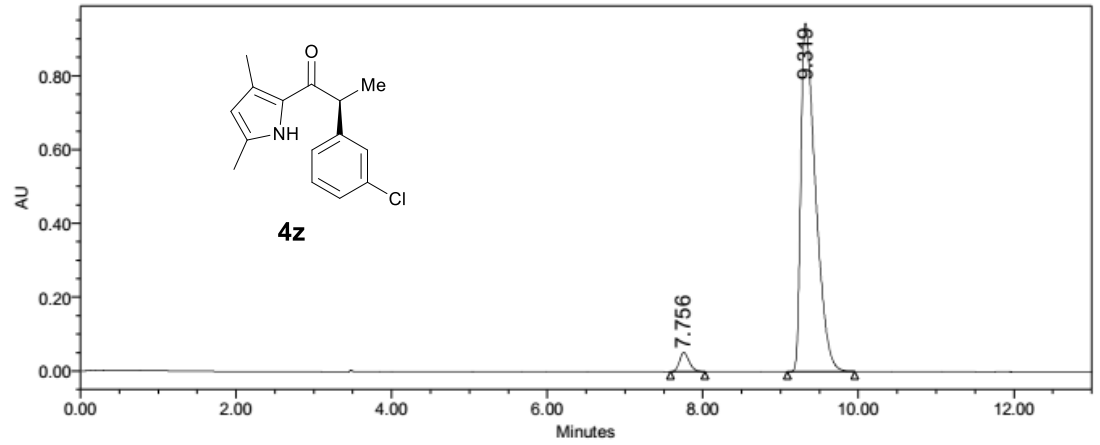


rac-**4z**

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3056; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.686	10421630	50.00	954023
2	W2489 ChA 254nm	9.361	10420153	50.00	827159



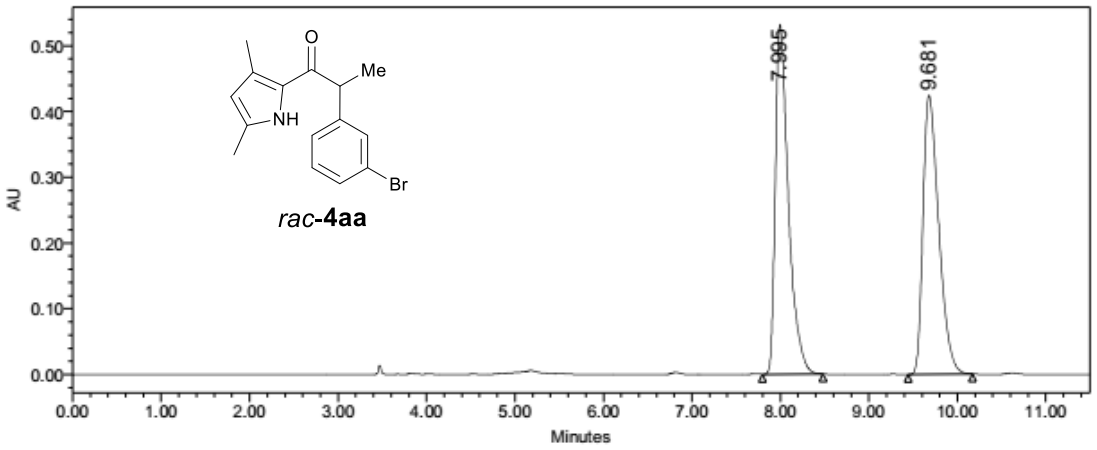
4z

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3046; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.756	457583	3.56	52190
2	W2489 ChA 254nm	9.319	12379284	96.44	944066

Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t

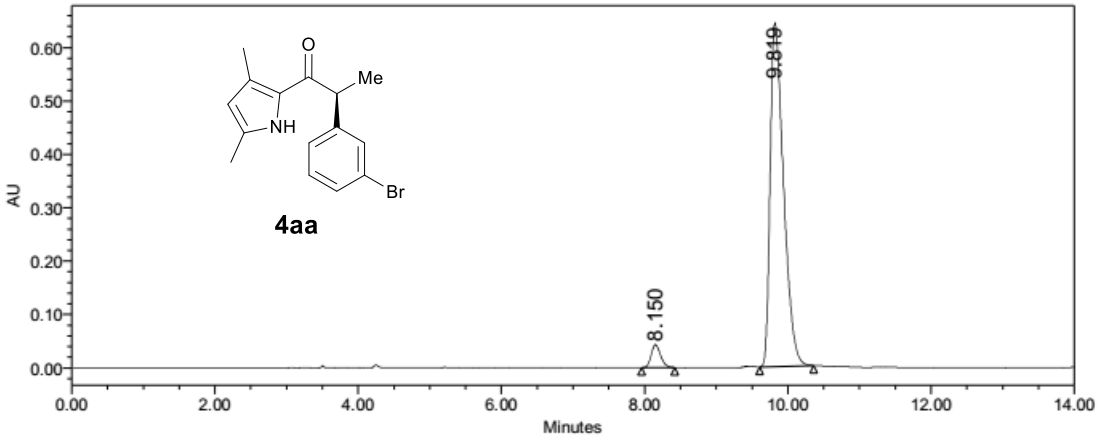


rac-**4aa**

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4873; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.995	5463122	50.97	531680
2	W2489 ChA 254nm	9.681	5254302	49.03	424445



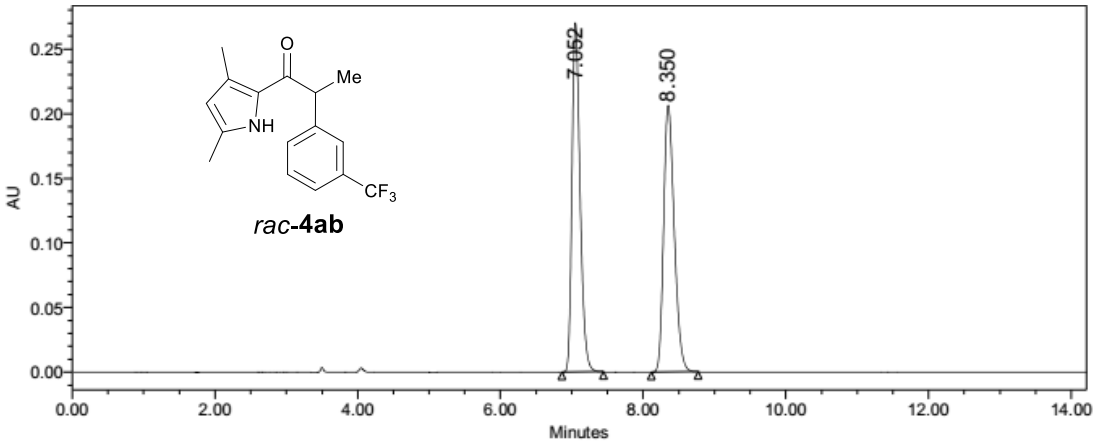
4aa

Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4681; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.150	395786	4.54	43039
2	W2489 ChA 254nm	9.819	8315375	95.46	643888

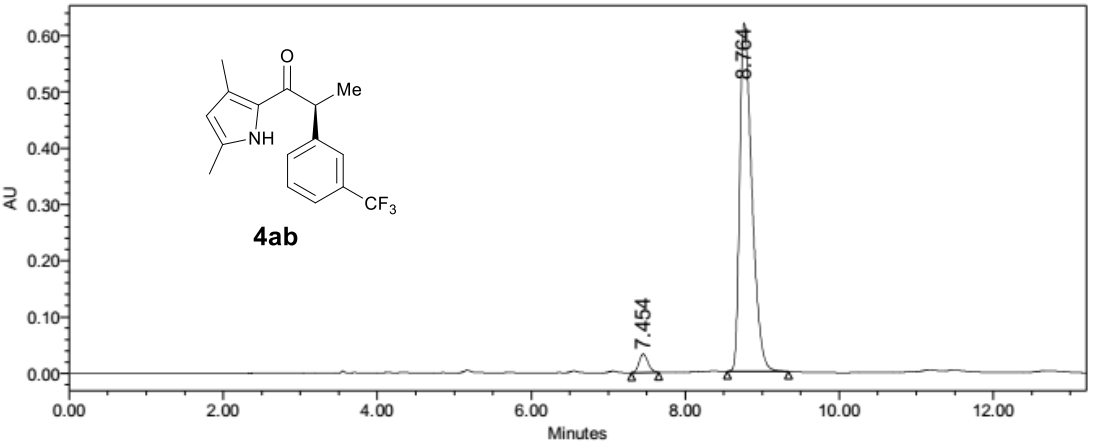
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4991; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.052	2126331	49.95	270119
2	W2489 ChA 254nm	8.350	2130758	50.05	206400

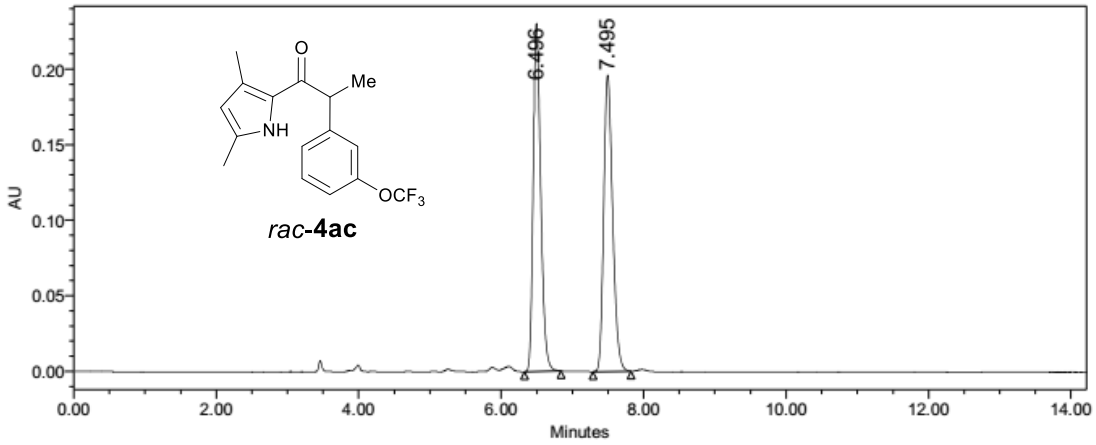


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4960; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.454	264429	3.73	32857
2	W2489 ChA 254nm	8.764	6816660	96.27	619111

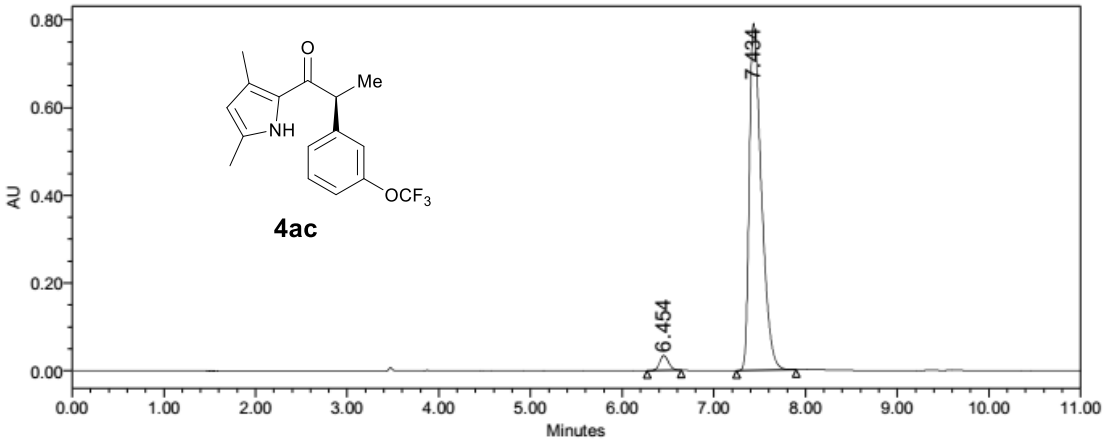
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3940; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.496	1691977	49.85	230375
2	W2489 ChA 254nm	7.495	1702174	50.15	196403

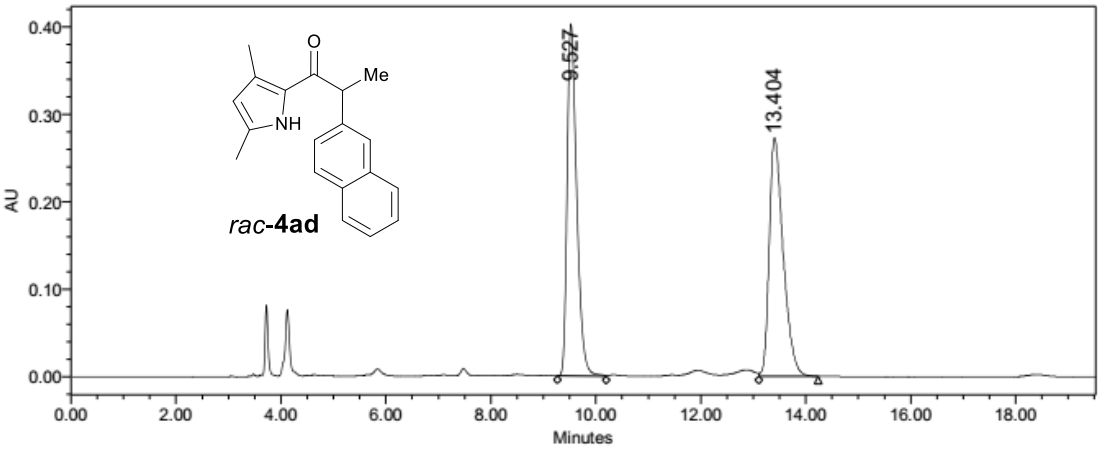


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3807; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.454	230174	3.07	34152
2	W2489 ChA 254nm	7.434	7256722	96.93	791134

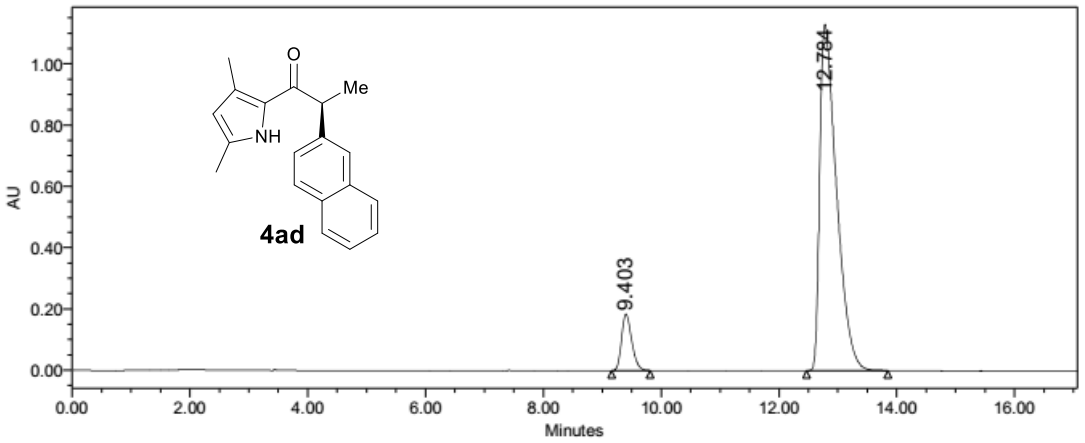
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3048; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.527	5064902	50.09	402546
2	W2489 ChA 254nm	13.404	5046747	49.91	272794

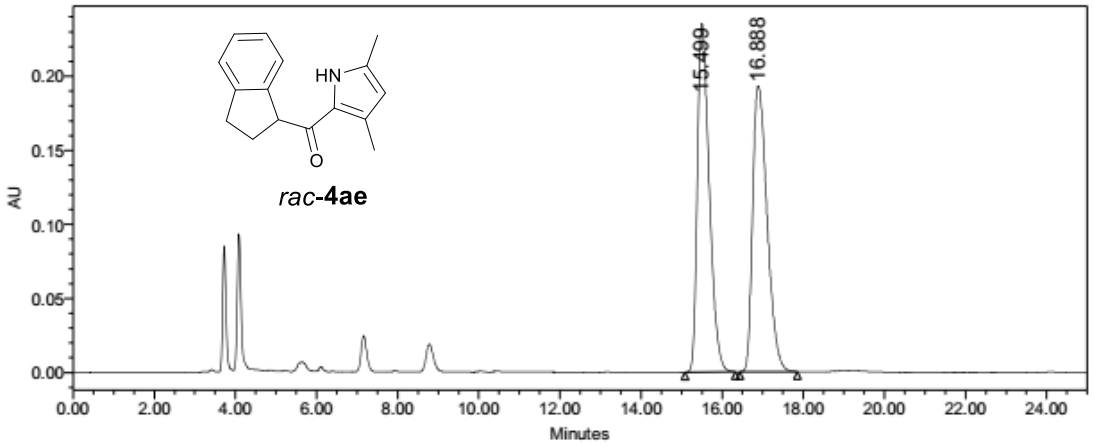


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3052; Processing Method: 9703 OD 3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.403	2228008	9.10	184025
2	W2489 ChA 254nm	12.784	22254779	90.90	1130150

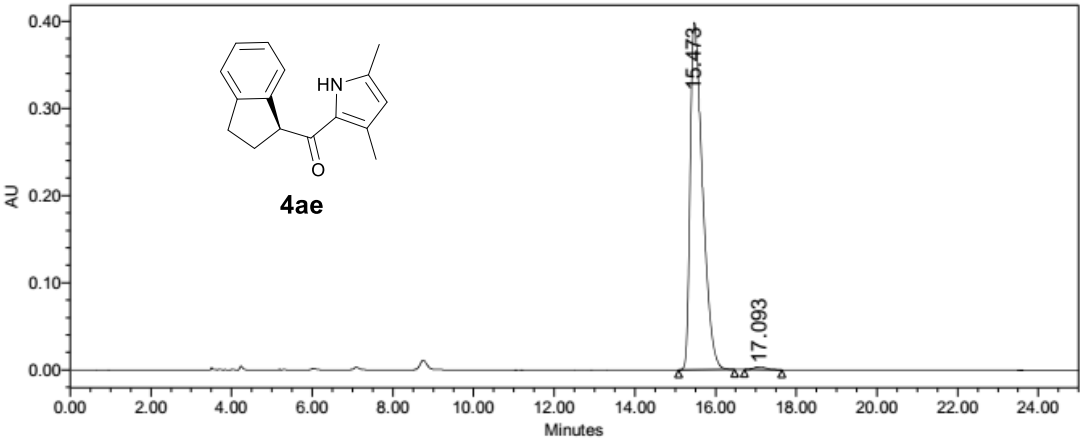
Daicel Chiralcel OD-3 column, *n*-hexane/2-propanol = 97:3 (v/v), 1.0 mL/min, 254 nm, r.t



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4853; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	15.499	4787706	50.00	235248
2	W2489 ChA 254nm	16.888	4786754	50.00	193095



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4857; Processing Method: 9703 OD3 254

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	15.473	8500372	99.16	398515
2	W2489 ChA 254nm	17.093	72363	0.84	3449