Enantioselective Michael Addition of Malonates to α,β-Unsaturated Ketones Catalyzed by 1,2-Diphenylethanediamine

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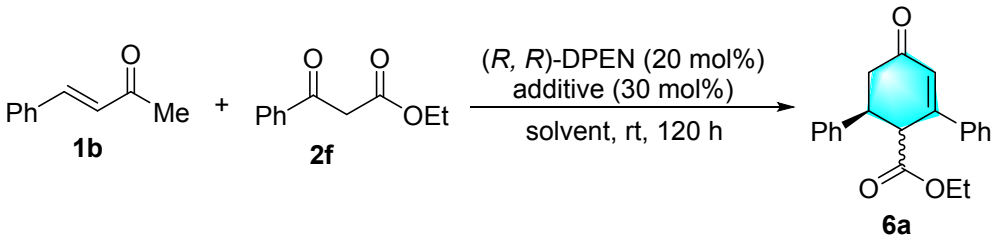
1. General methods

^{1}H and ^{13}C NMR spectra were recorded on Varian 400 MHz spectrometers. Chemical shifts (δ) are reported in ppm and calibrated from residual solvent signal. Coupling constants (*J*) are given in Hz. ESI-HRMS spectrometer was measured with a Bruker Daltonics LCQ^{DECA} ion trap mass spectrometer. Enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AS-H, AD-H, OD-H, OJ-H and IC columns in comparison with the authentic racemates. Optical rotation data were recorded on Rudolph Autopol I automatic polarimeter. Commercial grade solvents were dried and purified by standard procedures. All other reagents were purchased from commercial sources and were used without further purification. PE = petroleum ether.

2. **Table S1** Optimization of reaction conditions.[a]



Entry	Additive	Solvent	Yield (%)[b]	dr[c]	ee (%)[d]
1[e]	SA	DCE	95	52/48	91/82
2	SA	DCE	90	60/40	91/94
3	TFA	DCE	96	61/39	94/94
4	BA	DCE	83	58/42	82/95
5	*o*-Phthalic acid	DCE	93	55/45	90/91
6	OFBA	DCE	91	55/45	92/93
7	TFA	THF	92	55:45	92/96
8	TFA	$CHCl_3$	97	77:23	96/97
9	TFA	MeOH	96	72:28	82/95
10	TFA	EtOH	98	58:42	90/94

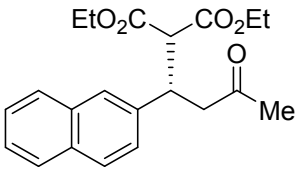
[a] Unless otherwise noted, the reaction was performed with 0.2 mmol of **1b**, 0.4 mmol of malonate **2f**, 20 mol% (*R*, *R*)-DPEN, 30 mol% additive in 1 mL of solvent at room temperature for 120 h. TFA = trifluoroacetic acid, BA = benzoic acid, OFBA = *o*-fluorobenzoic acid, SA = salicylic acid. [b] Isolated yield after flash chromatography on silica gel. [c] Diastereomeric ratio (dr) was determined by ^{1}H NMR analysis of the crude mixture. [d] Determined by chiral stationary-phase HPLC. [e] Carried out with 40 mol% of SA.

3. General procedure for synthesis of racemic adducts 3 and 5

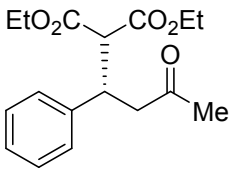
Enone (0.20 mmol) and K_2CO_3 (27.6 mg, 0.2 mmol) were dissolved in EtOH (1 mL). Malonate **2** (2 mmol) was added, and reaction stirred at room temperature until completion (monitored by TLC). The mixture was directly purified by flash chromatography (eluents from PE/ EtOAc) to give racemic products.

4. General procedure for the asymmetric Michael reaction of cinnamones

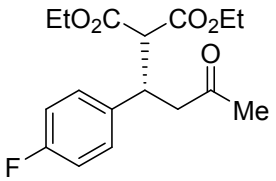
DPEN (8.5 mg, 0.04 mmol), cinnamones **1** (0.2 mmol), malonate **2** (4.0 mmol), and *o*-phthalic acid (13.3 mg, 0.08 mmol) were dissolved in ethanol (1 mL). After stirred at rt for 168 h, the reaction mixture was purified by flash chromatography on silica gel (PE/EtOAc).



Diethyl 2-(1-(naphthalen-2-yl)-3-oxobutyl)malonate (3aa):[22] TLC (PE/EtOAc = 10:1); yellow oil; 95% yield, 94% ee; HPLC: AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 210 nm, t_{major} = 13.103 min, t_{minor} = 16.187 min; $[\alpha]_D^{25}$ = +5.9° (*c* = 0.538, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.78-7.76 (m, 3H), 7.70 (s, 1H), 7.46-7.39 (m, 3H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.17-4.13 (m, 1H), 3.93-3.87 (m, 2H), 3.81 (d, *J* = 10.0 Hz, 1H), 3.03 (d, *J* = 6.8 Hz, 2H), 2.02 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H).

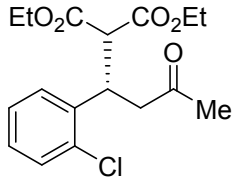


Diethyl 2-(3-oxo-1-phenylbutyl)malonate (3ab):[8a] TLC (PE/EtOAc = 10:1); yellow oil; 75% yield, 91% ee; HPLC: AD-H column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm, t_{minor} = 6.187 min, t_{major} = 8.570 min; $[\alpha]_D^{25}$ = +11.4° (*c* = 0.792, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.29-7.23 (m, 4H), 7.21-7.18 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.99-3.97 (m, 1H), 3.94 (q, *J* = 7.2 Hz, 2H), 3.69 (d, *J* = 9.6 Hz, 1H), 2.96 (ABX, J_{AB} = 16.4 Hz, J_{BX} = 5.2 Hz, 1H), 2.91 (ABX, J_{AB} = 16.6 Hz, J_{AX} = 8.6 Hz, 1H), 2.02 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H).

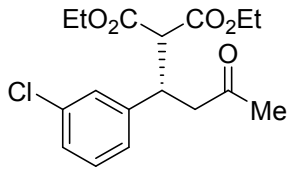


Diethyl 2-(1-(4-fluorophenyl)-3-oxobutyl)malonate (3ac): TLC (PE/EtOAc = 15:1); yellow oil; 99% yield, 95% ee; HPLC: AD-H column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 210 nm, t_{minor} = 6.983 min, t_{major} = 12.983 min; $[\alpha]_D^{25}$ = +18.0° (*c* = 1.276, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.20 (dd, *J* = 8.6, 5.4 Hz, 2H), 6.93 (t, *J* = 8.8 Hz, 2H), 4.16 (dq, *J*

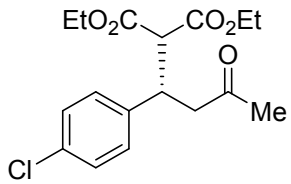
= 7.2, 1.2 Hz, 2H), 3.96-3.91 (m, 3H), 3.64 (d, J = 10.0 Hz, 2H), 2.93 (ABX, J_{AB} = 17.0 Hz, J_{BX} = 4.6 Hz, 1H), 2.86 (ABX, J_{AB} = 17.0 Hz, J_{AX} = 8.2 Hz, 1H), 2.00 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.7, 167.9, 167.5, 161.7 (d, $^1J_{CF}$ = 244.2 Hz), 136.1 (d, $^3J_{CF}$ = 13.2 Hz), 129.7 (d, $^4J_{CF}$ = 8.0 Hz), 115.2 (d, $^2J_{CF}$ = 21.2 Hz), 61.6, 61.3, 57.2, 47.3, 39.6, 30.2, 13.9, 13.7; ESI-HRMS: m/z $[M+H]^+$ calcd for $C_{17}H_{22}FO_5$ 325.1446; found 325.1448.



Diethyl 2-(1-(2-chlorophenyl)-3-oxobutyl)malonate (3ad): TLC (PE/EtOAc = 15:1); yellow oil; 99% yield, 96% ee; HPLC: AD-H column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 210 nm, t_{minor} = 6.577 min, t_{major} = 12.770 min; $[\alpha]_D^{25}$ = +12.9° (c = 0.448, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.33 (dd, J = 7.6, 1.2 Hz, 1H), 7.25 (dd, J = 7.2, 1.2 Hz, 1H), 7.17 (dt, J = 7.6, 1.2 Hz, 1H), 7.13 (dt, J = 7.4, 1.6 Hz, 1H), 4.43 (pseudo q, J = 7.5 Hz,2H), 4.18-4.11 (m, 2H), 4.00 (q, J = 7.2 Hz, 2H), 3.94 (d, J = 9.2 Hz, 1H), 3.07 (ABX, J_{AB} = 17.0 Hz, J_{BX} = 7.8 Hz, 1H), 3.15 (ABX, J_{AB} = 17.0 Hz, J_{AX} = 5.4 Hz, 1H), 2.06 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.9, 168.0, 167.6, 137.7, 133.9, 130.0, 129.3, 128.3, 126.8, 61.5, 61.4, 55.1, 45.5, 36.9, 29.9, 13.9, 13.7; ESI-HRMS: m/z $[M+H]^+$ calcd for $C_{17}H_{22}{}^{35}ClO_5$ 341.1150; found 341.1158; calcd for $C_{17}H_{22}{}^{37}ClO_5$ 343.1121; found 343.1127.

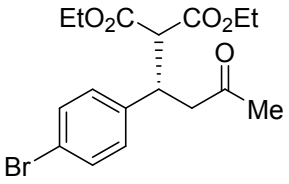


Diethyl 2-(1-(3-chlorophenyl)-3-oxobutyl)malonate (3ae): TLC (PE/EtOAc = 15:1); yellow oil; 99% yield, 94% ee; HPLC: AD-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 9.967 min, t_{major} = 12.463 min; $[\alpha]_D^{25}$ = +14.9° (c = 1.258, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.23 (s, 1H), 7.21-7.14 (m, 3H), 4.18 (q, J = 7.2 Hz, 2H), 3.98 (q, J = 7.2 Hz, 2H), 3.95-3.92 (m, 1H), 3.66 (d, J = 9.6 Hz, 1H), 2.97 (ABX, J_{AB} = 17.2 Hz, J_{BX} = 4.8 Hz, 1H), 2.90 (ABX, J_{AB} = 17.0 Hz, J_{AX} = 9.0 Hz, 1H), 2.05 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.05 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.4, 167.9, 167.4, 142.6, 134.1, 129.6, 128.2, 127.3, 126.5, 61.7, 61.4, 56.9, 46.9, 39.8, 30.2, 13.9, 13.7; ESI-HRMS: m/z $[M+H]^+$ calcd for $C_{17}H_{22}{}^{35}ClO_5$ 341.1150; found 341.1158; calcd for $C_{17}H_{22}{}^{37}ClO_5$ 343.1121; found 341.1128.

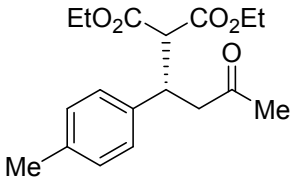


Diethyl 2-(1-(4-chlorophenyl)-3-oxobutyl)malonate (3af):[2b] TLC (PE/EtOAc = 15:1); yellow oil; 99% yield, 95% ee; HPLC: AD-H

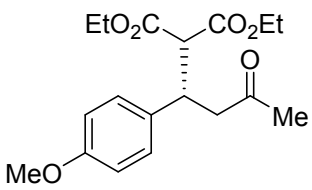
column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 210 nm, t_{minor} = 9.573 min, t_{major} = 13.543 min; $[\alpha]_D^{25}$ = +12.9° (*c* = 0.448, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.22 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 4.17 (pseudo q, *J* = 7.1 Hz, 2H), 3.95 (q, *J* = 7.1 Hz, 2H), 3.92-3.90 (m, 1H), 3.64 (d, *J* = 9.6 Hz, 1H), 2.94 (ABX, J_{AB}= 17.0 Hz, J_{BX} = 4.6 Hz, 1H), 2.86 (ABX, J_{AB}= 17.0 Hz, J_{AX} = 9.0 Hz, 1H), 2.01 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.03 (t, *J* = 7.0 Hz, 3H).



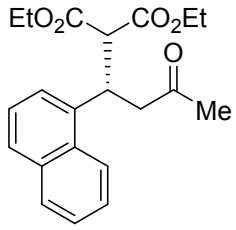
Diethyl 2-(1-(4-bromophenyl)-3-oxobutyl)malonate (3ag):[2b] TLC (PE/EtOAc = 15:1); yellow oil; 70% yield, 93% ee; HPLC: AD-H column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm, t_{minor} = 7.467 min, t_{major} = 10.760 min; $[\alpha]_D^{25}$ = +12.2° (*c* = 0.574, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.37 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H),4.16 (dq, *J* = 7.1, 2.0 Hz, 2H), 3.94 (q, *J* = 7.1 Hz, 2H), 3.92-3.89 (m, 1H), 3.64 (d, *J* = 10.0 Hz, 1H), 2.93 (ABX, J_{AB} = 17.2 Hz, J_{BX} = 4.8 Hz, 1H), 2.93 (ABX, J_{AB} = 17.0 Hz, J_{AX} = 9.0 Hz, 1H), 2.01 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 7.0 Hz, 3H).



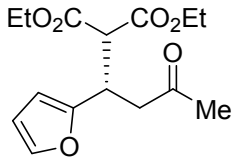
Diethyl 2-(3-oxo-1-(p-tolyl)butyl)malonate (3ah):[2b] TLC (PE/EtOAc = 15:1); yellow oil; 85% yield, 94% ee; HPLC: AD-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 210 nm, t_{minor} = 9.710 min, t_{major} = 14.570 min; $[\alpha]_D^{25}$ = +7.3° (*c* = 0.900, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.11 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.94 (q, *J* = 7.2 Hz, 2H), 3.92-3.88 (m, 1H), 3.65 (d, *J* = 10.0 Hz, 1H), 2.93 (ABX, J_{AB} = 16.4 Hz, J_{BX} = 5.2 Hz, 1H), 2.87 (ABX, J_{AB} = 16.4 Hz, J_{AX} = 8.4 Hz, 1H), 2.27 (s, 3H), 2.00 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 1H).



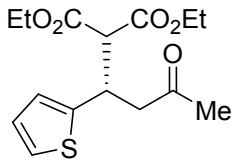
Diethyl 2-(1-(4-methoxyphenyl)-3-oxobutyl)malonate (3ai):[2b] TLC (PE/EtOAc = 15:1); yellow oil; 92% yield, 96% ee; HPLC: AD-H column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm, t_{minor} = 6.520 min, t_{major} = 12.493 min; $[\alpha]_D^{25}$ = +1.4° (*c* = 0.702, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.14 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 4.17 (pseudo q, *J* = 7.2 Hz,2H), 3.93 (q, *J* = 7.2 Hz, 2H), 3.89-3.87 (m, 1H), 3.74 (s, 3H), 3.63 (d, *J* = 10.0 Hz, 1H), 2.90 (ABX, J_{AB} = 16.8 Hz, J_{BX} = 5.2 Hz, 1H), 2.90 (ABX, J_{AB} = 16.8 Hz, J_{BX} = 9.2 Hz, 1H), 2.00 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 1H).



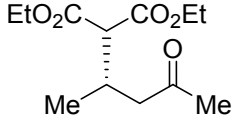
Diethyl 2-(1-(naphthalen-1-yl)-3-oxobutyl)malonate (3aj):[22] TLC (PE/EtOAc = 15:1); yellow oil; 97% yield, 96% ee; HPLC: AD-H column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm, t_{minor} = 6.980 min, t_{major} = 9.190 min; $[\alpha]_D^{25}$ = -3.9° (*c* = 0.134, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 8.31 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.72-7.70 (m, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.41-7.38 (m, 2H), 4.95-4.94 (m, 1H), 4.16 (dq, *J* = 7.2, 2.0 Hz, 2H), 3.94 (d, *J* = 8.4 Hz, 1H), 3.85 (q, *J* = 7.2 Hz, 2H), 3.18 (ABX, J_{AB} = 17.2 Hz, J_{BX} = 5.6 Hz, 1H), 3.11 (ABX, J_{AB} = 17.4 Hz, J_{BX} = 7.8 Hz, 1H), 2.01 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H).



Diethyl 2-(1-(furan-2-yl)-3-oxobutyl)malonate (3ak):[22] TLC (PE/EtOAc = 25:1); yellow oil; 84% yield, 86% ee; HPLC: OJ-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 210 nm, t_{minor} = 13.337 min, t_{major} = 16.950 min; $[\alpha]_D^{25}$ = +3.8° (*c* = 0.338, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.28 (dd, *J* = 1.8, 0.6 Hz, 1H), 6.23 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.09 (d, *J* = 3.2 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.08 (q, *J* = 7.2 Hz, 2H), 4.10-4.05 (m, 1H), 3.76 (d, *J* = 8.0 Hz, 1H), 2.99 (ABX, J_{AB} = 17.2 Hz, J_{BX} = 8.8 Hz, 1H), 2.91 (ABX, J_{AB} = 17.2 Hz, J_{AX} = 4.8 Hz, 1H), 2.10 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 3H).

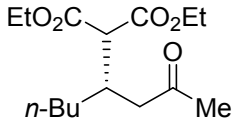


Diethyl 2-(3-oxo-1-(thiophen-2-yl)butyl)malonate (3al):[2b] TLC (PE/EtOAc = 25:1); yellow oil; 97% yield, 92% ee; HPLC: AD-H column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm, t_{minor} = 5.760 min, t_{major} = 7.150 min; $[\alpha]_D^{25}$ = +21.5° (*c* = 0.418, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.12 (d, *J* = 4.8 Hz, 1H), 6.88-6.85 (m, 2H), 4.28 (m, 1H), 4.28 (q, *J* = 7.2 Hz, 1H), 4.16 (dq, *J* = 7.2, 1.6 Hz, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.72 (d, *J* = 8.8 Hz, 1H), 2.98 (d, *J* = 6.4 Hz, 2H), 2.07 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H).

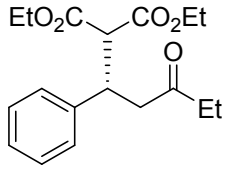


Diethyl 2-(4-oxopentan-2-yl)malonate (3am):[2b] TLC (PE/EtOAc = 25:1); yellow oil; 70% yield, 86% ee; HPLC: IC-H column, hexane/*i*-propanol (80/20), 0.8 mL/min, UV 210 nm, t_{major} = 17.050 min, t_{minor} = 19.150 min; $[\alpha]_D^{25}$ = +8.2° (*c* = 0.316, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 4.17 (q, *J* = 7.2 Hz, 4H),

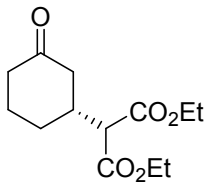
3.33 (d, *J* = 6.8 Hz, 1H), 2.79-2.72 (m, 1H), 2.67 (dd, *J* = 17.2, 4.4 Hz, 1H), 2.40 (dd, *J* = 17.0, 8.2 Hz, 1H), 2.12 (s, 3H), 1.25 (t, *J* = 7.0 Hz, 6H), 1.00 (d, *J* = 6.8 Hz, 3H).



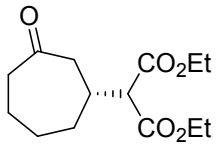
Diethyl 2-(2-oxooctan-4-yl)malonate (3an):[6b] TLC (PE/EtOAc = 20:1); yellow oil; 65% yield, 95% ee; HPLC: IC-H column, hexane/*i*-propanol (1/30), 0.8 mL/min, UV 220 nm, t_{major} = 10.803 min; t_{minor} = 12.127min ; $[\alpha]_D^{25}$ = +7.4° (*c* = 0.940, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 4.17 (q, *J* = 7.2 Hz, 4H), 3.52 (d, *J* = 5.6 Hz, 1H), 2.74 (ABX, J_{AB} = 17.2 Hz, J_{BX} = 5.2 Hz, 1H), 2.66 (pseudo q, *J* = 6.0 Hz, 1H), 2.51 (dd, J_{AB} = 17.2 Hz, J_{AX} = 6.8 Hz, 1H), 2.13 (s, 3H), 1.42-1.24 (m, 6H), 1.26 (t, *J* = 7.0 Hz, 6H), 0.87 (t, *J* = 6.8 Hz, 3H).



Diethyl 2-(3-oxo-1-phenylpentyl)malonate (3ao):[6b] TLC (PE/EtOAc = 20:1); yellow oil; 61% yield, 91% ee; HPLC: IC-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 210 nm, t_{minor} = 10.220 min; t_{major} = 18.073 min; $[\alpha]_D^{25}$ = +4.4° (*c* = 0.450, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.28-7.22 (m, 4H), 7.21-7.17 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.02-3.96 (m, 1H), 3.94 (q, *J* = 7.0 Hz, 2H), 3.70 (d, *J* = 10.0 Hz, 1H), 2.90 (d, *J* = 6.8 Hz, 2H), 2.39-2.29 (m, 1H), 2.27-2.17 (m, 1H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H).

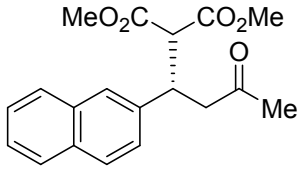


Diethyl 2-(3-oxocyclohexyl)malonate (3ap):[6b] TLC (PE/EtOAc = 25:1); colorless oil; 71% yield, 82% ee; HPLC: IE-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 210 nm, t_{major} = 48.540 min; t_{minor} = 58.187 min; $[\alpha]_D^{25}$ = +2.8° (*c* = 0.216, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 4.18 (q, *J* = 7.0 Hz, 2H), 4.17 (q, *J* = 7.0 Hz, 2H), 3.26 (d, *J* = 8.0 Hz, 1H), 2.54-2.45 (m, 1H), 2.39 (pseudo t, *J* = 16.0 Hz, 2H), 2.27-2.22 (m, 2H), 2.07-2.02 (m, 1H), 1.93 (pseudo d, *J* = 12.8 Hz, 1H), 1.71-1.61 (m, 1H), 1.53-1.3 (m, 1H), 1.24 (t, *J* = 7.2 Hz, 6H).

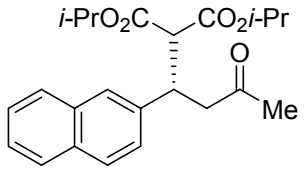


Diethyl 2-(3-oxocycloheptyl)malonate (3aq):[6b] TLC (PE/EtOAc = 10:1); yellow oil; 97% yield, 87% ee; HPLC: IE-H column, hexane/*i*-propanol (80/20), 0.75 mL/min, UV 254 nm, t_{major} = 11.747 min, t_{minor} = 12.743 min; $[\alpha]_D^{25}$ = +17.7° (*c* = 0.260, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) = 4.15 (q, *J* = 7.2 Hz, 4H), 3.26

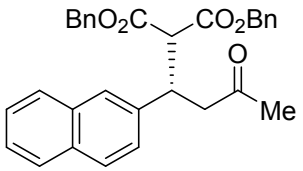
(d, *J* = 5.6 Hz, 1H), 2.57–2.39 (m, 5H), 1.92-1.81 (m, 3H), 1.60–1.34 (m, 3H), 1.22 (t, *J* = 7.2 Hz, 6H).



Dimethyl 2-(1-(naphthalen-2-yl)-3-oxobutyl)malonate (3ba): TLC (PE/EtOAc = 20:1); colorless oil; 81% yield, 90% ee; HPLC: AS-H column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm, t_{major} = 12.603 min, t_{minor} = 16.100 min; $[\alpha]_D^{25}$ = -9.0° (*c* = 0.678, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.79-7.77 (m, 3H), 7.69 (s, 1H), 7.47-7.42 (m, 2H), 7.38 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.19-4.14 (m, 1H), 3.86 (d, *J* = 9.6 Hz, 1H), 3.73 (s, 3H), 3.46 (s, 3H), 3.05 (d, *J* = 6.8 Hz, 2H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.9, 168.5, 167.9, 137.9, 133.2, 132.5, 128.3, 127.8, 127.5, 126.8, 126.1, 125.9, 125.8, 57.0, 52.6, 52.4, 47.1, 40.4, 30.3; ESI-HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{19}H_{21}O_5$ 329.1384; found 329.1389.

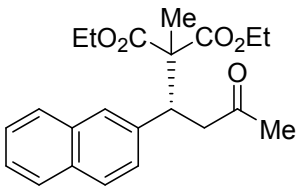


Diisopropyl 2-(1-(naphthalen-2-yl)-3-oxobutyl)malonate (3ca): TLC (PE/EtOAc = 25:1); colorless oil; 65% yield, 93% ee; HPLC: AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 210 nm, t_{major} = 7.893 min, t_{minor} = 9.663 min; $[\alpha]_D^{25}$ = -18.2° (*c* = 1.324, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.78-7.75 (m, 3H), 7.69 (s, 1H), 7.44-7.39 (m, 3H), 5.07 (sep, *J* = 6.4 Hz, 1H), 4.73 (sep, *J* = 6.4 Hz, 1H), 4.16-4.10 (m, 1H), 3.76 (d, *J* = 10.0 Hz, 1H), 3.01 (d, *J* = 6.4 Hz, 2H), 2.01 (s, 3H), 1.24 (d, *J* = 6.4 Hz, 6H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.88 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.0, 167.7, 167.1, 137.9, 133.2, 132.5, 128.1, 127.7, 127.5, 127.2, 126.2, 125.9, 125.7, 69.2, 68.8, 57.6, 47.6, 40.4, 30.3, 21.6, 21.5, 21.3, 21.2; ESI-HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{29}O_5$ 385.2010; found 385.2003.



Dibenzyl 2-(1-(naphthalen-2-yl)-3-oxobutyl)malonate (3da):[8a] TLC (PE/EtOAc = 25:1); yellow oil; 92% yield, 74% ee; HPLC: AS-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 210 nm, t_{major} = 25.450 min, t_{minor} = 33.790 min; $[\alpha]_D^{25}$ = +33.9° (*c* = 0.106, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.69 (dd, *J* = 5.8 , 3.4 Hz, 1H), 7.64-7.62 (m, 2H), 7.57 (s, 1H), 7.36 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.27-7.16 (m, 6H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 2H), 5.08 (AB, *J* = 12.8 Hz, 1H), 5.05 (AB, *J* = 13.6 Hz, 1H), 4.77 (AB, *J* = 12.0 Hz, 1H), 4.74 (AB, *J* = 12.8 Hz, 1H), 4.10 (dt, *J* = 9.0, 5.2 Hz, 1H), 3.86 (d, *J* = 9.6

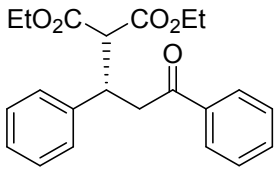
Hz, 1H), 2.92 (ABX, J_{AB} = 17.2 Hz, J_{BX} = 9.2 Hz, 1H), 2.85 (ABX, J_{AB} = 17.2 Hz, J_{BX} = 5.2 Hz, 1H), 1.87 (s, 3H).



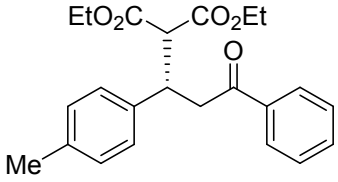
Diethyl 2-methyl-2-(1-(naphthalen-2-yl)-3-oxobutyl)malonate (3ea): TLC (PE/EtOAc = 5:1); color oil; 72% yield, 95% ee; HPLC: AD-H column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 210 nm, t_{minor} = 9.573 min, t_{major} = 13.543 min; $[\alpha]_D^{25}$ = +17.0° (*c* = 0.448, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) = 7.78-7.73 (m, 3H), 7.66 (s, 1H), 7.47–7.40 (m, 2H), 7.34 (d, *J* = 8.6 Hz, 1H), 4.27–4.20 (m, 2H), 4.17 (d, *J* = 11.5 Hz, 1H), 4.13–4.05 (m, 2H), 3.29 (ABX, J_{AB} = 17.0 Hz, J_{BX} = 10.8 Hz, 1H), 3.09 (ABX, J_{AB} = 17.0 Hz, J_{AX} = 1.6 Hz, 1H), 2.03 (s, 3H), 1.40 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.3, 171.4, 171.3, 136.5, 133.1, 132.6, 128.4, 127.81, 127.80, 127.5, 127.2, 126.0, 125.8, 61.49, 61.44, 57.8, 46.2, 45.2, 30.2, 19.1, 13.99, 13.94; ESI-HRMS: *m/z* $[M+H]^+$ calcd for $C_{22}H_{27}O_5$ 371.1853; found 371.1855.

5. General procedure for the asymmetric Michael reaction of chalcones

DPEN (8.5 mg, 0.04 mmol), chalcones **4** (0.2 mmol), diethyl malonate **2a** (0.6 mL, 4.0 mmol), and salicylic acid (11.0 mg, 0.08 mmol) were dissolved in ether (1mL). After stirred at rt for 168 h, the reaction mixture was purified by flash chromatography on silica gel (PE/EtOAc).

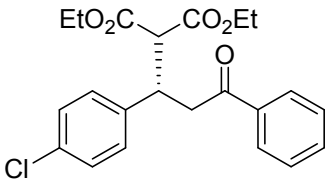


Diethyl 2-(3-oxo-1,3-diphenylpropyl)malonate (5a):[6d] TLC (PE/EtOAc = 20:1); yellow oil; 75% yield, 92% ee; HPLC: AD-H column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm, t_{minor} = 11.973 min, t_{major} = 20.873 min; $[\alpha]_D^{25}$ = +12.6° (*c* = 0.634, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.90 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.26-7.22 (m, 4H), 7.17 (t, *J* = 6.6 Hz, 1H), 4.24-4.16 (m, 3H), 3.96 (q, *J* = 7.2 Hz, 2H), 3.83 (d, *J* = 10.0 Hz, 1H), 3.55 (ABX, J_{AB} = 16.4 Hz, J_{AX} = 4.4 Hz, 1H), 3.46 (ABX, J_{AB} = 16.4 Hz, J_{AX} = 9.2 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H).



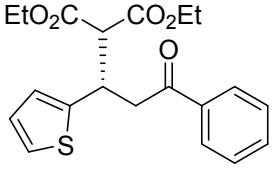
Diethyl 2-(3-oxo-3-phenyl-1-(p-tolyl)propyl)malonate (5b):[6e] TLC (PE/EtOAc = 20:1); yellow oil; 98% yield, 98% ee; HPLC: AD-H column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254

nm, t_{minor} = 9.660 min, t_{major} = 16.310 min; $[\alpha]_D^{25}$ = +16.6° (*c* = 0.626, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.89 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 4.21-4.12 (m, 3H), 3.96 (q, *J* = 7.2 Hz, 2H), 3.80 (d, *J* = 9.6 Hz, 1H), 3.53 (ABX, J_{AB} = 16.6 Hz, J_{AX} = 4.2 Hz, 1H), 3.42 (ABX, J_{AB} = 16.4 Hz, J_{AX} = 9.2 Hz, 1H), 2.25 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H).



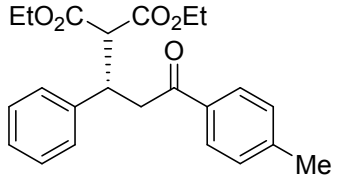
Diethyl 2-(1-(4-chlorophenyl)-3-oxo-3-phenylpropyl)malonate (5c):[6e] TLC (PE/EtOAc = 20:1); yellow oil; 99% yield, 94% ee; HPLC: AD-H column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm, t_{minor} = 10.473 min, t_{major} = 21.103 min; $[\alpha]_D^{25}$ = +26.3° (*c* = 0.3, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.89 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.21 (pseudo s, 4H), 4.21-4.14 (m, 3H), 3.98 (q, *J* = 7.2 Hz, 2H), 3.78 (d, *J* = 9.6 Hz, 1H), 3.53 (ABX, J_{AB} = 16.8 Hz, J_{BX} = 4.0 Hz, 1H), 3.43 (ABX, J_{AB} = 16.8 Hz, J_{AX} = 9.6 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H).

Diethyl 2-(1-(naphthalen-2-yl)-3-oxo-3-phenylpropyl)malonate (5d):[5a] TLC (PE/EtOAc = 20:1); yellow oil; 88% yield, 94% ee; HPLC: AD-H column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm, t_{minor} = 12.440 min, t_{major} = 20.463 min; $[\alpha]_D^{25}$ = +9.8° (*c* = 0.468, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 7.6 Hz, 2H), 7.76-7.73 (m, 3H), 7.70 (s, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.46-7.39 (m, 5H), 4.37 (dt, *J* = 9.0, 5.2 Hz, 1H), 4.27-4.15 (m, 2H), 3.95-3.89 (m, 3H), 3.64 (ABX, J_{AB} = 16.4 Hz, J_{BX} = 4.4 Hz, 1H), 3.58 (ABX, J_{AB} = 16.6 Hz, J_{BX} = 8.2 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H).

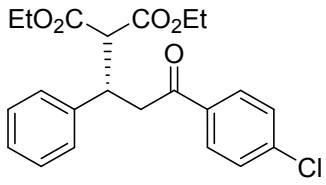


Diethyl 2-(3-oxo-3-phenyl-1-(thiophen-3-yl)propyl)malonate (5e):[5a] TLC (PE/EtOAc = 15:1); yellow oil; 83% yield, 65% ee; HPLC: AD-H column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm, t_{minor} = 8.923 min, t_{major} = 12.197 min; $[\alpha]_D^{25}$ = +17.9° (*c* = 0.876, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 4.8 Hz, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.85 (dd, *J* = 5.2, 3.6 Hz, 1H), 4.53

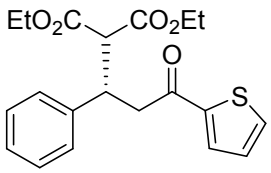
(pseudo q, J = 7.2 Hz, 1H), 4.26-4.13 (m, 2H), 4.06 (q, J = 7.2 Hz, 2H), 3.87 (d, J = 8.4 Hz, 1H), 3.56 (d, J = 6.8 Hz, 2H), 1.24 (t, J = 7.0 Hz, 3H), 1.12 (t, J = 7.0 Hz, 3H).



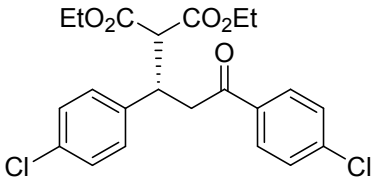
Diethyl 2-(3-oxo-1-phenyl-3-(p-tolyl)propyl)malonate (5f):[6e] TLC (PE/EtOAc = 20:1); yellow oil; 99% yield, 99% ee; HPLC: AD-H column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm, t_{minor} = 13.010 min, t_{major} = 29.877 min; $[\alpha]_D^{25}$ = +12.4° (*c* = 1.320, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, J = 8.0 Hz, 2H), 7.26-7.19 (m, 6H), 7.15 (t, J = 7.0 Hz, 1H), 4.22-4.14 (m, 3H), 3.93 (q, J = 7.2 Hz, 2H), 3.81 (d, J = 9.6 Hz, 1H), 3.50 (ABX, J_{AB} = 16.6 Hz, J_{BX} = 4.6 Hz, 1H), 3.41 (ABX, J_{AB} = 16.4 Hz, J_{AX} = 9.2 Hz, 1H), 2.37 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H), 0.99 (t, J = 7.2 Hz, 3H).



Diethyl 2-(3-(4-chlorophenyl)-3-oxo-1-phenylpropyl)malonate (5g):[6e] TLC (PE/EtOAc = 15:1); yellow oil; 99% yield, >99% ee; HPLC: AD-H column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm, t_{minor} = 13.233 min, t_{major} = 30.840 min; $[\alpha]_D^{25}$ = +23.5° (*c* = 0.310, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.83 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.24-7.23 (m, 4H), 7.19-7.16 (m, 1H), 4.24-4.11 (m, 3H), 3.95 (q, J = 7.2 Hz, 2H), 3.80 (d, J = 10.0 Hz, 1H), 3.52 (ABX, J_{AB} = 16.4 Hz, J_{BX} = 4.4 Hz, 1H), 3.40 (ABX, J_{AB} = 16.6 Hz, J_{AX} = 9.4 Hz, 1H), 1.24 (t, J = 6.8 Hz, 3H), 1.00 (t, J = 7.0 Hz, 3H).



Diethyl 2-(3-oxo-1-phenyl-3-(thiophen-2-yl)propyl)malonate (5h):[5a] TLC (PE/EtOAc = 20:1); yellow oil; 65% yield, 96% ee; HPLC: AD-H column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm, t_{minor} = 10.290 min, t_{major} = 15.050 min; $[\alpha]_D^{25}$ = +25.8° (*c* = 0.240, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.71 (dd, J = 3.8, 1.0 Hz, 1H), 7.56 (dd, J = 5.0, 1.0 Hz, 1H), 7.26-7.20 (m, 4H), 7.17-7.13 (m, 1H), 7.06 (dd, J = 5.0, 3.8 Hz, 1H), 4.22-4.12 (m, 3H), 3.93 (q, J = 7.2 Hz, 2H), 3.82 (d, J = 10.0 Hz, 1H), 3.45 (ABX, J_{AB} = 16.0 Hz, J_{BX} = 4.8 Hz, 1H), 3.35 (ABX, J_{AB} = 16.0 Hz, J_{AX} = 9.2 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H), 0.99 (t, J = 7.2 Hz, 3H).



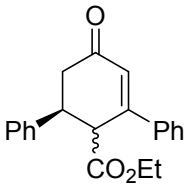
Diethyl 2-(1,3-bis(4-chlorophenyl)-3-oxopropyl)malonate (5i):[23] TLC (PE/EtOAc = 20:1); yellow oil; 99% yield, 93% ee; HPLC: AD-H column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm, t_{minor} = 13.753 min, t_{major} = 34.360 min; $[\alpha]_D^{25}$ = +3.8° (*c* = 0.496, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 9.2 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.24-4.16 (m, 2H), 4.12 (dt, *J* = 9.8, 4.4 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 3.76 (d, *J* = 9.6 Hz, 1H), 3.51 (ABX, J_{AB} = 16.8 Hz, J_{BX} = 4.4 Hz, 1H), 3.37 (ABX, J_{AB} = 16.8 Hz, J_{AX} = 9.6 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.0 Hz, 3H).

6. General procedure for synthesis of racemic adducts 6a-6f

Cinnamones **1** (0.2 mmol), racemic DPEN (8. 5 mg, 0.04 mmol) and TFA (5.0 μL, 0.06 mmol) were dissolved in chloroform (1mL). Ethyl benzoylacetate **2f** (69.3 μL, 0.4 mmol) was added, and reaction stirred at room temperature until completion (monitored by TLC). The mixture was directly purified by flash chromatography (eluents from PE/ethyl ether) to give racemic products.

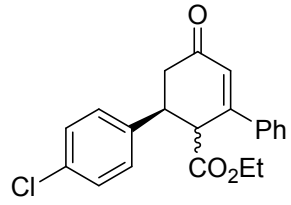
7. General procedure for the synthesis of cyclohexenone 6a-6f

DPEN (8.5 mg, 0.04 mmol), cinnamones **1** (0.2 mmol), ethyl benzoylacetate **2f** (69.3 μL, 0.4 mmol), and TFA (5.0 μL, 0.06 mmol) were dissolved in chloroform (1mL). After stirred at rt for 120 h, the reaction mixture was purified by flash chromatography on silica gel (PE/EtOAc).

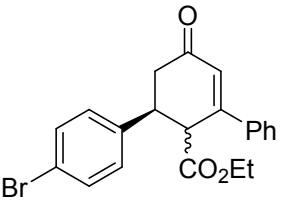


Ethyl 4-oxo-2,6-diphenylcyclohex-2-enecarboxylate (6a):[19b] TLC (PE/EtOAc = 2:1); colorless oil; 97% yield, dr: *trans*/*cis* 77:23; 96% ee/97% ee; HPLC: AD-H column, hexane/*i*-propanol (90/10), 1 mL/min, UV 254 nm, *trans* diastereomer: t_{minor} = 11.297 min, t_{major} = 14.230 min; *cis* diastereomer: t_{major} = 12.720 min, t_{minor} = 14.903 min; $[\alpha]_D^{25}$ = +86.2° (*c* = 0.384, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.44-7.24 (m, 10H; both diastereomers), 6.65 (s, 1H; minor), 6.44 (d, *J* = 1.6 Hz, 1H; major), 4.19 (dd, *J* = 7.6, 1.2 Hz, 1H; major), 4.15 (d, *J* = 4.8 Hz, 1H; minor), 3.88 (q, *J* = 7.2 Hz, 2H; both diastereomers), 3.89-3.78 (m, 1H; both diastereomers), 2.88 (ABX, J_{AB} = 16.8 Hz, J_{BX} = 5.6 Hz, 1H; both diastereomers), 2.83 (ABX, J_{AB} = 16.8 Hz, J_{BX} = 8.8 Hz, 1H; both diastereomers), 0.89 (t, *J* = 7.2 Hz, 3H; major), 0.87 (t, *J* = 7.2 Hz, 3H; minor).

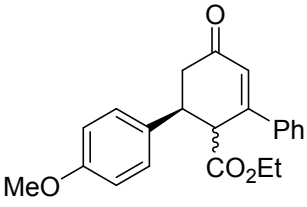
Ethyl 6-(4-chlorophenyl)-4-oxo-2-phenylcyclohex-2-enecarboxylate (6b):[19b] TLC (PE/EtOAc = 2:1); colorless oil; 97% yield, dr: *trans*/*cis* 79:21; 87% ee/87% ee; HPLC: OD-H column, hexane/*i*-propanol (80/20), 0.6 mL/min, UV 254 nm, *trans* diastereomer: t_{major} = 29.077 min, t_{minor} = 36.350 min; *cis* diastereomer: t_{minor} = 22.537 min, t_{major} = 43.003 min; $[\alpha]_D^{25}$ = +82.4° (*c* = 0.376, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.44-7.34 (m, 5H; both diastereomers), 7.30 (d, *J* = 8.0 Hz, 2H; both diastereomers), 7.20 (d, *J* = 8.0 Hz, 2H; both diastereomers), 6.64 (s, 1H; minor), 6.43 (s, 1H; major), 4.15-4.09 (m, 1H; both diastereomers), 3.88 (q, *J* = 7.2 Hz, 2H; both diastereomers), 3.82-3.75 (m, 1H; both diastereomers), 2.85 (ABX, J_{AB} = 17.0 Hz, J_{BX} = 5.4 Hz, 1H; both diastereomers), 2.78 (ABX, J_{AB} = 16.8 Hz, J_{AX} = 9.6 Hz, 1H; both diastereomers), 0.90 (t, *J* = 7.0 Hz, 3H; both diastereomers).



Ethyl 6-(4-bromophenyl)-4-oxo-2-phenylcyclohex-2-enecarboxylate (6c): [19b] TLC (PE/EtOAc = 2:1); colorless oil; 92% yield, dr: *trans*/*cis* 80:20; 95% ee/97% ee; HPLC: IC-H column, hexane/*i*-propanol (95/5), 1 mL/min, UV 254 nm, *trans* diastereomer: t_{minor} = 18.520 min, t_{major} = 23.927 min; *cis* diastereomer: t_{major} = 21.097 min, t_{minor} = 26.050 min; $[\alpha]_D^{25}$ = +24.1° (*c* = 0.646, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ= 7.45 (d, *J* = 8.0 Hz, 2H; both diastereomers), 7.40-7.36 (m, 5H; both diastereomers), 7.15 (d, *J* = 8.0 Hz, 2H; both diastereomers), 6.64 (s, 1H; minor), 6.43 (s, 1H; major), 4.14 (d, *J* = 7.6 Hz, 1H; major), 4.11 (d, *J* = 5.2 Hz, 1H; minor), 3.89 (q, *J* = 7.6 Hz, 2H; both diastereomers), 3.81-3.73 (m, 1H; both diastereomers), 2.86 (ABX, J_{AB} = 17.0 Hz, J_{BX} = 5.0 Hz, 1H; both diastereomers), 2.78 (ABX, J_{AB} = 16.8 Hz, J_{AX} = 9.2 Hz, 1H; both diastereomers), 0.90 (t, *J* = 7.2 Hz, 3H; both diastereomers).

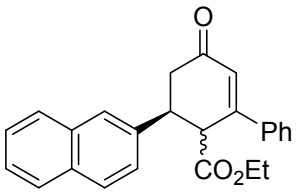


Ethyl 6-(4-methoxyphenyl)-4-oxo-2-phenylcyclohex-2-enecarboxylate (6d):[19b] TLC (PE/EtOAc = 2:1); colorless oil; 99% yield, dr: *trans*/*cis* 66:34; 92% ee/90% ee; HPLC: OD-H column, hexane/*i*-propanol (90/10), 0.6 mL/min, UV 254 nm, *trans* diastereomer: t_{minor} = 29.683 min, t_{major} = 41.330 min; *cis* diastereomer: t_{major} = 26.967 min, t_{minor} = 35.343 min; $[\alpha]_D^{25}$ = +75.3° (*c* = 0.492, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.60-7.58 (m, 1H; both diastereomers), 7.43-7.40 (m, 2H; both diastereomers), 7.37-7.35 (m, 2H; both diastereomers),

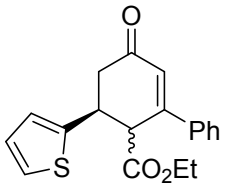


7.19 (d, J = 8.4 Hz, 2H; minor), 7.18 (d, J = 8.4 Hz, 2H; major), 6.90 (d, J = 8.8 Hz, 2H; minor), 6.85 (d, J = 8.4 Hz, 2H; major), 6.64 (s, 1H; minor), 6.43 (d, J = 1.6 Hz, 1H; major), 4.14 (dd, J = 7.6, 1.6 Hz, 1H; major), 4.11 (d, J = 5.2 Hz, 1H; minor), 3.92-3.84 (m, 2H; both diastereomers), 3.81 (s, 3H; minor), 3.78 (s, 3H; major), 3.79-3.71 (m, 1H; both diastereomers), 2.85 (ABX, J_{AB} = 17.0 Hz, J_{BX} = 5.4 Hz, 1H; major), 2.79 (ABX, J_{AB} = 16.8 Hz, J_{AX} = 9.2 Hz, 1H; major), 2.66 (d, J = 4.4 Hz, 1H; minor), 2.61 (d, J = 4.0 Hz, 1H; minor), 0.91 (t, J = 7.0 Hz, 1H; minor), 0.89 (t, J = 7.2 Hz, 1H; major).

Ethyl 6-(naphthalen-2-yl)-4-oxo-2-phenylcyclohex-2-enecarboxylate (6e):[19b] TLC (PE/EtOAc = 2:1); colorless oil; 99% yield, dr: *trans*/*cis* 53:47; 89% ee/87% ee; HPLC: OD-H column, hexane/*i*-propanol (80/20), 0.75 mL/min, UV 254 nm, *trans* diastereomer: t_{major} = 21.860 min, t_{minor} = 27.543 min; *cis* diastereomer: t_{minor} = 17.337 min, t_{major} = 32.870 min; $[\alpha]_D^{25}$ = +30.8° (c = 0.552, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ= 7.88-7.78 (m, 3H; both diastereomers), 7.69 (s, 1H; minor), 7.67 (s, 1H; major), 7.62 (dd, J = 6.8, 2.8 Hz, 1H; both diastereomers), 7.51-7.42 (m, 6H; both diastereomers), 7.38-7.36 (m, 1H; both diastereomers), 6.70 (s, 1H; minor), 6.48 (s, 1H; major), 4.33 (d, J = 7.6 Hz, 1H; major), 4.26 (d, J = 4.8 Hz, 1H; minor), 4.03-3.69 (m, 3H; both diastereomers), 2.97-2.75 (m, 2H; both diastereomers), 0.85 (t, J = 7.0 Hz, 3H; major), 0.69 (t, J = 7.2 Hz, 3H; minor).



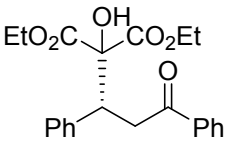
Ethyl 6-(thiophen -2-yl)-4-oxo-2-phenylcyclohex-2-enecarboxylate (6f): TLC (PE/EtOAc = 1:1); yellow oil; 94% yield, dr: *trans*/*cis* 60:40; 92% ee/90% ee; HPLC: OD-H column, hexane/*i*-propanol (80/20), 0.75 mL/min, UV 254 nm, *trans* diastereomer: t_{major} = 15.183 min, t_{minor} = 20.427 min; *cis* diastereomer: t_{minor} = 13.797 min, t_{major} = 17.387 min; $[\alpha]_D^{25}$ = +27.4° (c = 0.518, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.61-7.59 (m, 1H; both diastereomers), 7.46-7.39 (m, 3H; both diastereomers), 7.38-7.36 (m, 1H; both diastereomers), 7.26-7.15 (m, 1H; both diastereomers), 7.00-6.88 (m, 2H; both diastereomers), 6.62 (s, 1H; minor), 6.44 (s, 1H; major), 4.22-4.21 (m, 1H; both diastereomers), 4.06-3.89 (m, 3H; both diastereomers), 3.02 (ABX, J_{AB} = 17.0 Hz, J_{BX} = 4.6 Hz, 1H; major), 2.87-2.77 (m, 1H; both diastereomers), 1.02 (t, J = 7.2 Hz, 3H; major), 0.96 (t, J = 7.2 Hz, 3H; minor); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.0, 196.5, 170.5, 169.3, 154.7, 154.2,



144.7, 143.3, 138.0, 136.6, 130.4, 129.9, 128.9, 128.7, 127.8, 126.8, 126.7, 126.6, 126.5, 126.4, 124.9, 124.5, 124.3, 124.2, 61.4, 61.3, 52.3, 51.3, 41.9, 39.3, 38.7, 38.4, 13.73, 13.70; ESI-HRMS: *m*/*z* $[M+H]^+$ calcd for $C_{19}H_{19}O_3S^+$ 327.1049; found 327.1051.

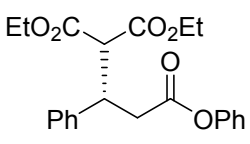
8. Synthetic transformation of adduct 5a

Diethyl 2-hydroxy-2-(3-oxo-1,3-diphenylpropyl)malonate (7):[21] A mixture of **5a** (73.6 mg, 0.2mmol), I_2 (50.4 mg, 0.2 mmol), and NaOAc (16.4 mg, 0.2 mmol) were stirred in 2mL of THF. Upon exposure to air at 35 °C for 48 h, most of the solvent was removed *in vacuo*, and 10 mL of water was added. To the mixture was added saturated $Na_2S_2O_3$ until the disappearance of umber, and then the mixture was extracted with dichloromethane (3×10 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (PE/EtOAc = 6:1) to provide the corresponding *α*-hydroxylmalonates **7** (72.0 mg**,** 96% yield, 94% ee) as yellow oil.



HPLC: AD-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 254 nm, t_{minor} = 20.550 min, t_{major} = 23.740 min; $[\alpha]_D^{25}$ = +43.1° (*c* = 0.320, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.43-7.39 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 2H), 7.17 (t, *J* = 7.0 Hz, 1H), 4.45 (dd, *J* = 10.2, 2.6 Hz, 1H), 4.28 (q, *J* = 6.8 Hz, 2H), 4.08-3.94 (m, 3H), 3.73 (ABX, J_{AB} = 17.4 Hz, J_{BX} = 10.2 Hz, 1H), 3.37 (dd, J_{AB} = 17.6 Hz, J_{AX} = 2.8 Hz, 1H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H).

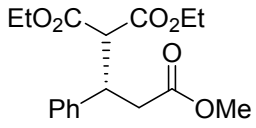
1,1-diethyl 3-phenyl 2-phenylpropane-1,1,3-tricarboxylate (8): 5a (73.6 mg, 0.2 mmol) was dissolved in dry 1,2-dichloroethane (2 mL). Subsequently, *m*-CPBA (313.0 mg, 2.0 mmol) was added, followed by warm up to 60°C. The reaction mixture was stirred for 72 h, then quenched with a saturated solution of $NaHSO_3$, and stirred for 1 h. The organic phases were separated and washed with saturated aqueous $NaHCO_3$ solution (3 x 50 mL), then dried over anhydrous Na_2SO_4, to provide **8** (PE/EtOAc = 10:1) (69.7 mg, 91% yield, 95% ee) as colorless oil.



HPLC: AD-H column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm, t_{minor} = 9.573 min, t_{major} = 13.540 min; $[\alpha]_D^{25}$ = +10.4° (*c* = 0.546, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) : δ = 7.32-7.25 (m, 7H), 7.15 (t, *J* =

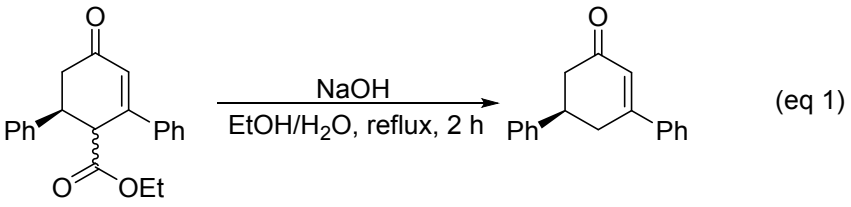
7.4 Hz, 1H), 6.75 (d, J = 7.6 Hz, 2H), 4.24 (q, J = 7.2 Hz, 2H), 4.04 (dt, J = 6.8, 4.8 Hz, 1H), 3.95 (q, J = 7.2 Hz, 2H), 3.80 (d, J = 10.4 Hz, 1H), 3.14 (ABX, J_{AB} = 15.4 Hz, J_{BX} = 4.6 Hz, 1H), 2.97 (ABX, J_{AB} = 15.6 Hz, J_{AX} = 10.4 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H), 1.00 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 167.9, 167.4, 150.4, 139.4, 129.2, 128.5, 128.3, 127.5, 125.7, 121.3, 61.8, 61.4, 57.3, 41.6, 38.8, 14.0, 13.7; ESI-HRMS: *m/z* $[M+H]^+$ calcd for $C_{22}H_{25}O_6^+$ 385.1646; found 385.1647.

1,1-diethyl 3-methyl 2-phenylpropane-1,1,3-tricarboxylate (9): 8 (76.8 mg, 0.2 mmol) was dissolved in dry MeOH (1 mL), and $NaBH_4$ (15.1 mg, 0.4 mmol) was added at 0°C. After stirring for 5 h at rt, the mixture was diluted with diethyl ether and quenched with brine, then the organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by flash silica gel (PE/DCM = 50:1) to provide the corresponding **9** (55.4 mg, 86% yield, 89% ee) as colorless oil.



HPLC: AD-H column, hexane/*i*-propanol (90/10), 1.0 mL/min, UV 210 nm, t_{minor} = 9.787 min, t_{major} = 12.010 min; $[\alpha]_D^{25}$ = +12.8° (*c* = 0.601, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.32-7.19 (m, 5H), 4.21 (q, J = 7.2 Hz, 2H), 3.95-3.89 (m, 3H), 3.74 (d, J = 10.4 Hz, 1H), 3.53 (s, 3H), 2.86 (ABX, J_{AB} = 15.6 Hz, J_{BX} = 4.8 Hz, 1H), 2.74 (ABX, J_{AB} = 15.8 Hz, J_{AX} = 9.8 Hz, 1H), 1.26 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.6, 168.0, 167.5, 139.7, 128.3, 128.0, 127.3, 61.7, 61.3, 57.2, 51.5, 41.4, 38.5, 13.9, 13.6; ESI-HRMS: *m/z* $[M+H]^+$ calcd for $C_{17}H_{23}O_6^+$ 323.1489; found 323.1490.

9. General procedure for decarboxylation of 6a



6a
58:42 dr
90% ee/94% ee

10
93% yield, 87% ee

(eq 1)

To a reaction tube was added **6a** (64.0 mg, 0.2 mmol) and NaOH (28.0 mg, 0.7 mmol). After the mixture was dissolved in ethanol (0.5 mL), then 1.5 mL of water was added. The resulting

solution was refluxed with vigorous stirring until TLC indicated complete disappearance of the starting material (2 h). Once cooling a period of time, the solution was rinsed with saturated aqueous $NaHCO_3$ solution to neutral, subsequently dried over anhydrous Na_2SO_4. The crude product was purified by flash column chromatography to yield 3,5-diphenylcyclohexenone **10** as a white solid (46.0 mg, 93% yield, 87% ee).

HPLC: AD-H column, hexane/*i*-propanol (80/20), 0.75 mL/min, UV 254 nm, t_{major} = 11.747 min, t_{minor} = 12.743 min; $[\alpha]_D^{23}$ = -26.6° (*c* = 0.124, CH_2Cl_2) (lit,[24] *S*-configuration, $[\alpha]_D^{23}$ = +36.9° (*c* = 2, CH_2Cl_2)); ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.58-7.55 (m, 2H), 7.43-7.41 (m, 3H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.33-7.28 (m, 3H), 6.53 (d, *J* = 2.4 Hz, 1H), 3.51-3.43 (m, 1H), 3.07 (ABX, J_{AB} = 17.6 Hz, J_{AX} = 4.0 Hz, 1H), 2.98-2.90 (m, 1H), 2.79 (ABX, J_{AB} = 16.8 Hz, J_{AX} = 5.6 Hz, 1H), 2.73 (ABX, J_{AB} = 16.4 Hz, J_{BX} = 12.8 Hz, 1H).

10. Reference

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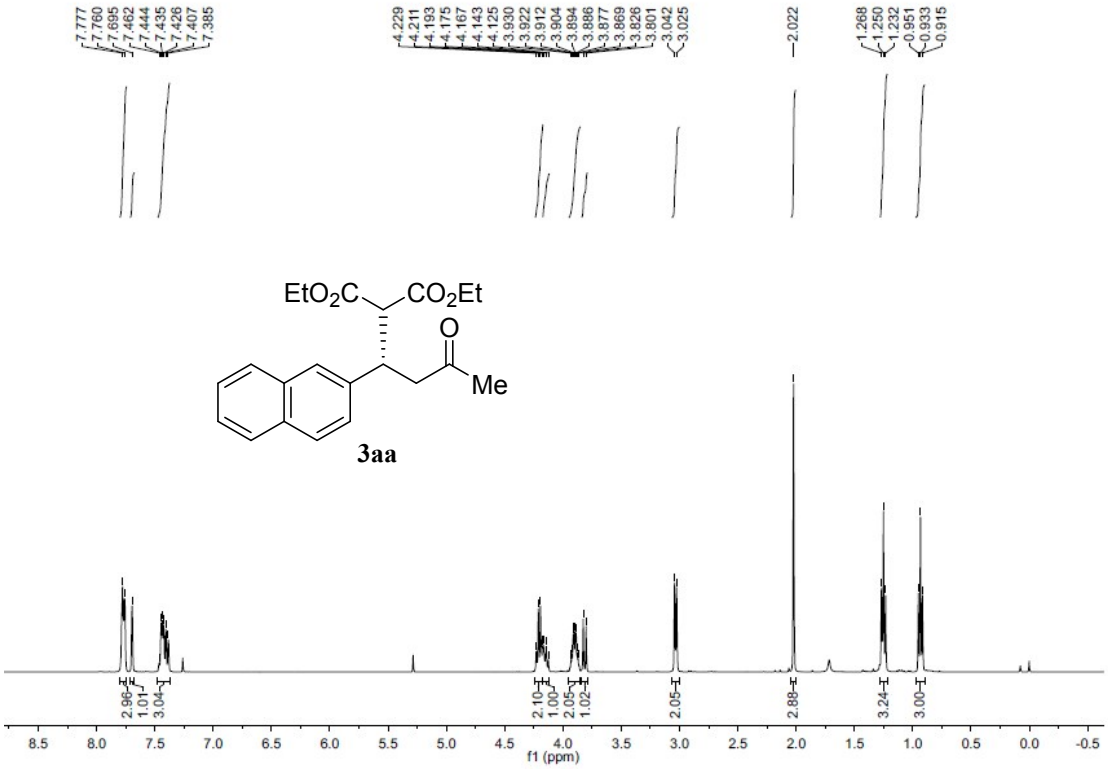
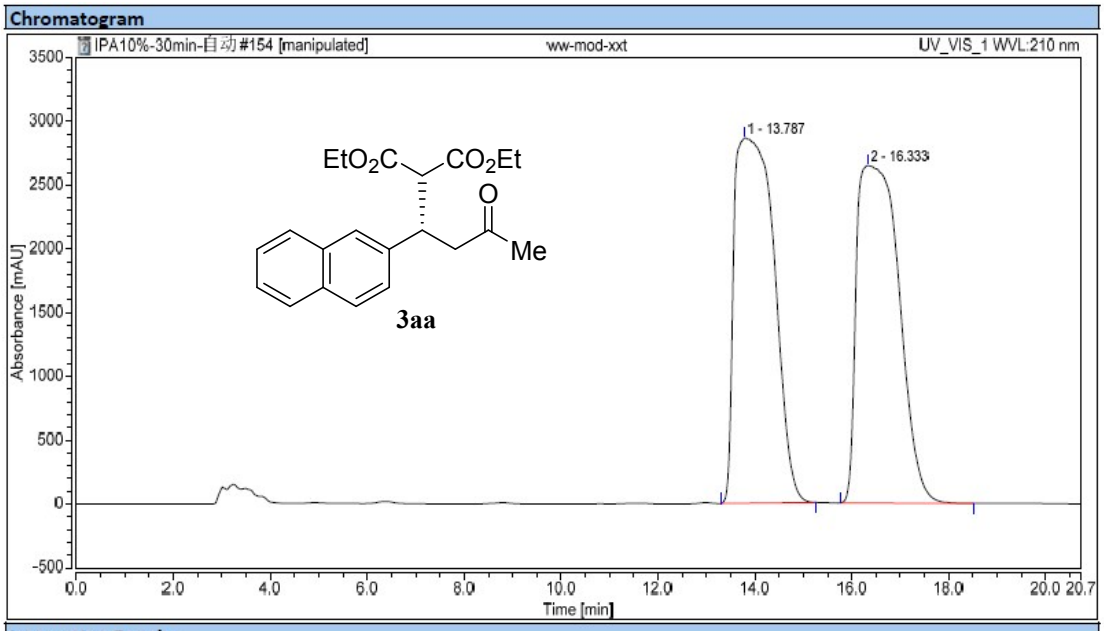
11. NMR spectra and HPLC chromatograms

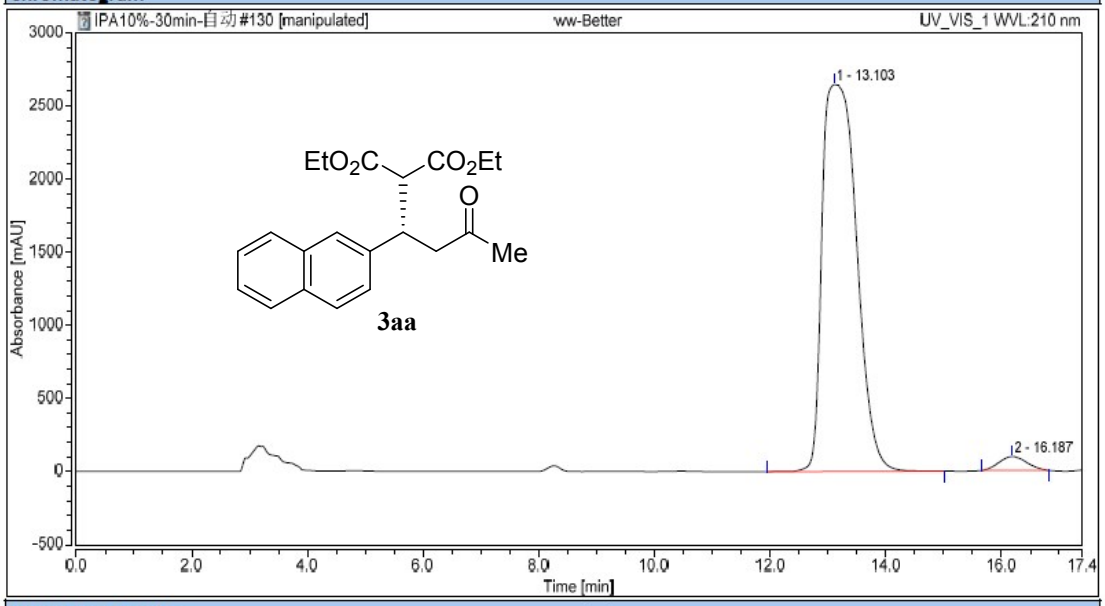




Integration Results

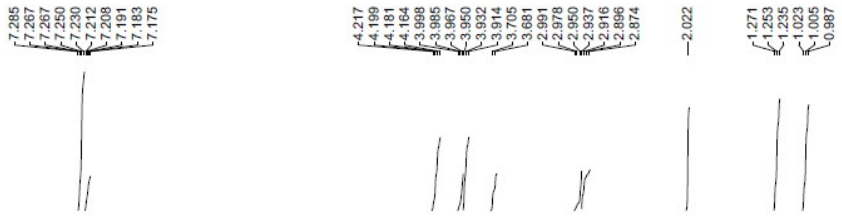
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.787	2727.717	2864.620	50.45	51.99	n.a.
2		16.333	2678.832	2645.475	49.55	48.01	n.a.
Total:			**5406.549**	**5510.096**	**100.00**	**100.00**	

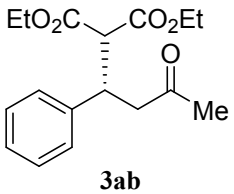
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.103	1823.513	2643.395	97.21	96.55	n.a.
2		16.187	52.267	94.393	2.79	3.45	n.a.
Total:			**1875.780**	**2737.788**	**100.00**	**100.00**	





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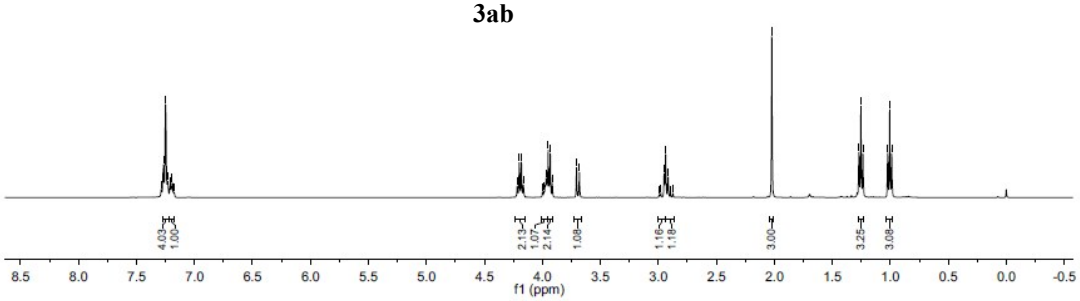

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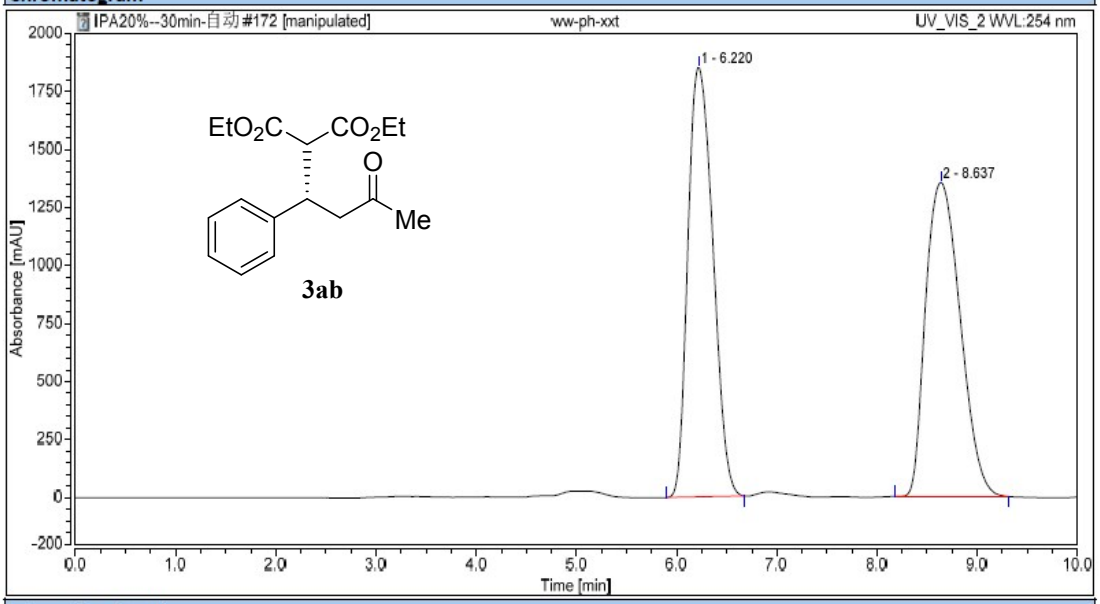
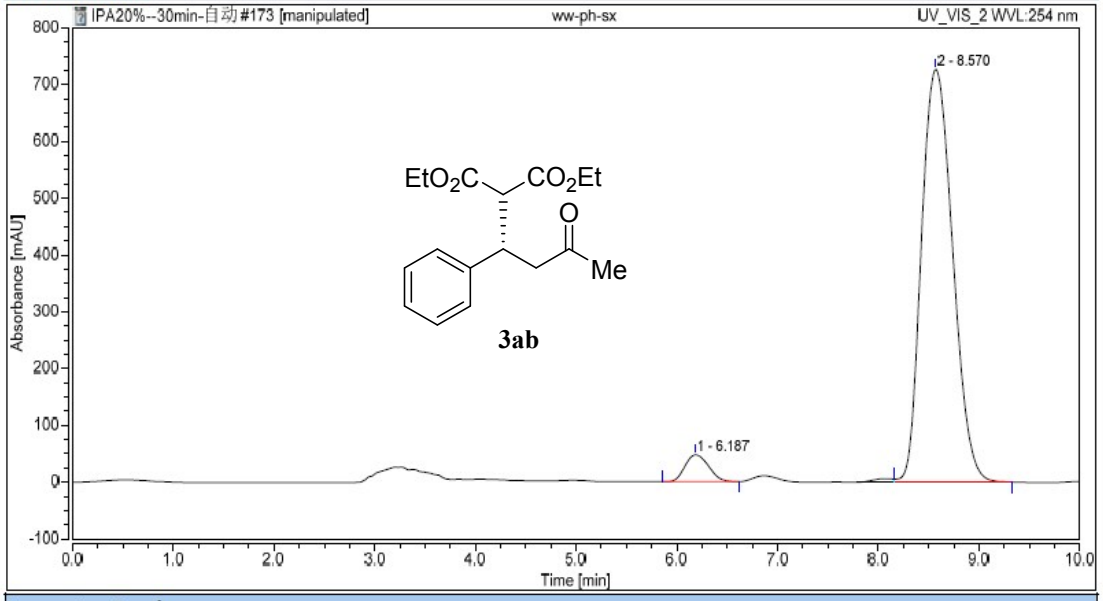


Integration Results

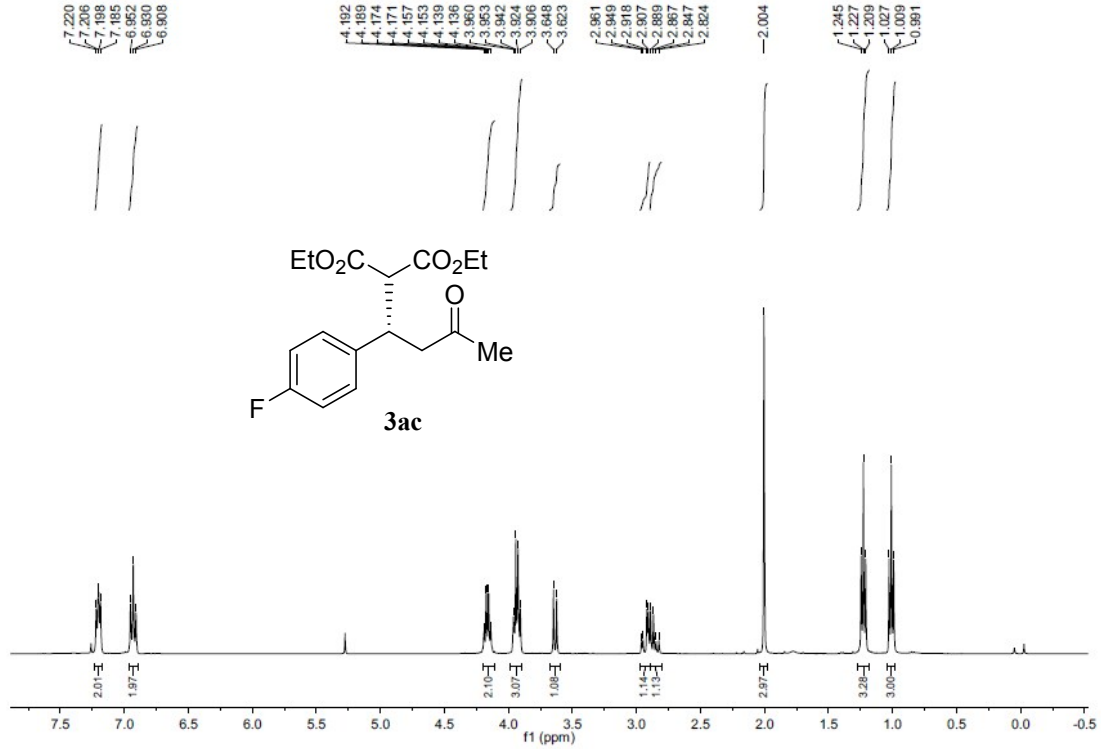
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.220	535.764	1850.582	49.75	57.76	n.a.
2		8.637	541.149	1353.365	50.25	42.24	n.a.
Total:			**1076.912**	**3203.947**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.187	12.776	47.120	4.67	6.09	n.a.
2		8.570	260.925	727.005	95.33	93.91	n.a.
Total:			**273.701**	**774.124**	**100.00**	**100.00**	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4.192
4.189
4.174
4.171
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4.153
4.139
4.136
3.960
3.953
3.942
3.924
3.906
3.648
3.623
2.961
2.949
2.918
2.907
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2.847
2.824
2.004
1.245
1.227
1.209
1.027
1.009
0.991
EtO2C
CO2Et
O
Me
F
3ac
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2.10
3.07
1.08
1.14
1.13
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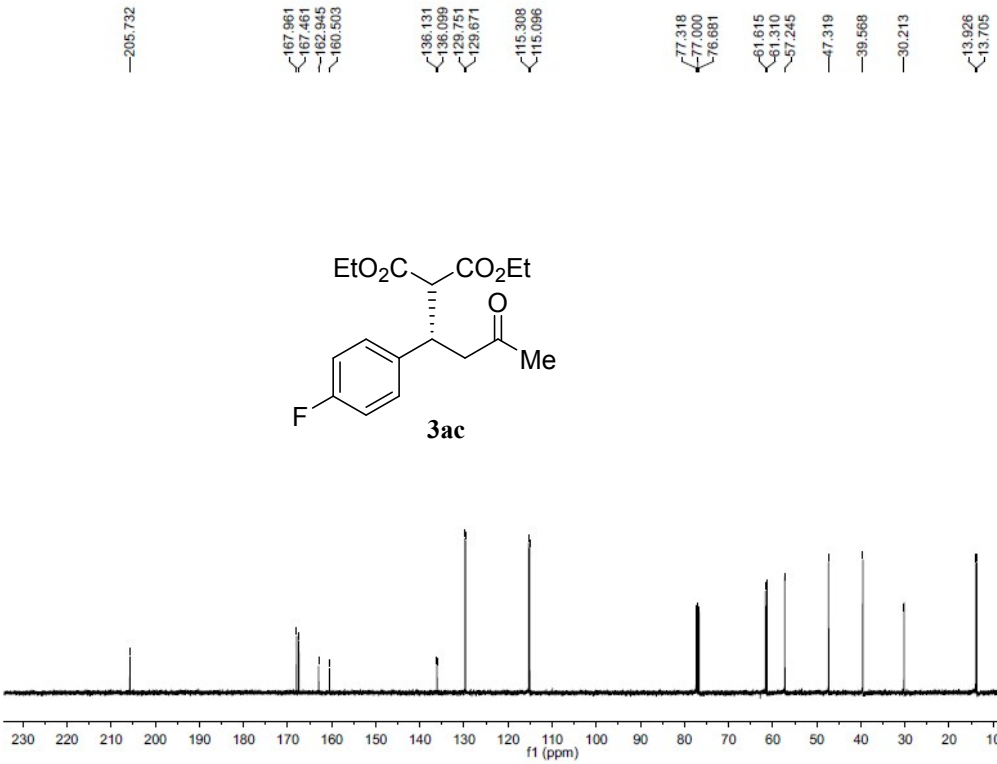
3.28
3.00
f1 (ppm)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76.681
61.615
61.310
57.245
47.319
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13.926
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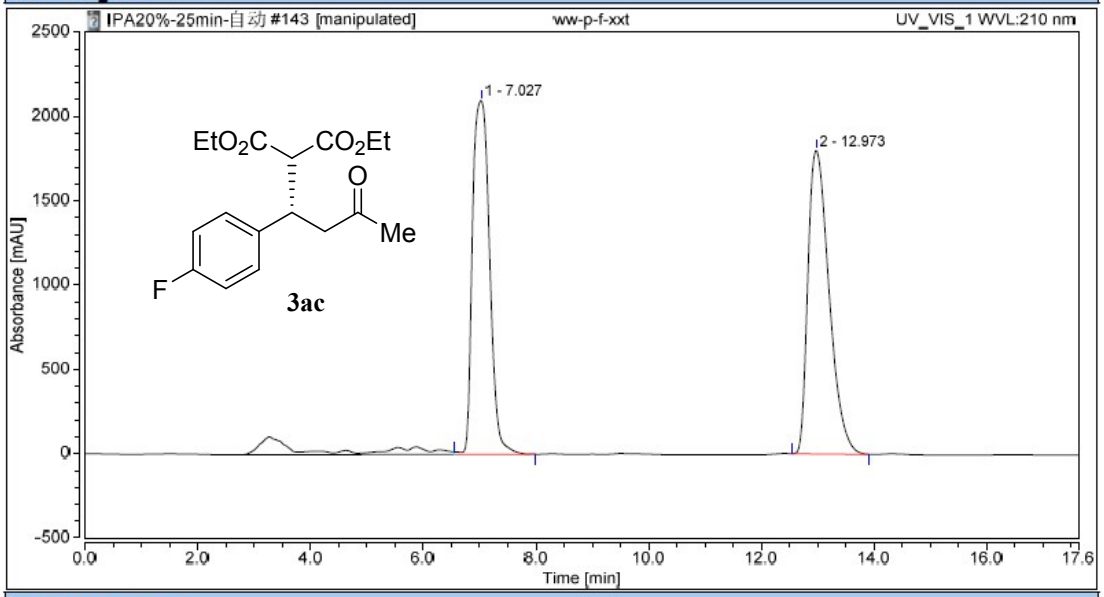
EtO2C
CO2Et
O
Me
F
3ac
f1 (ppm)

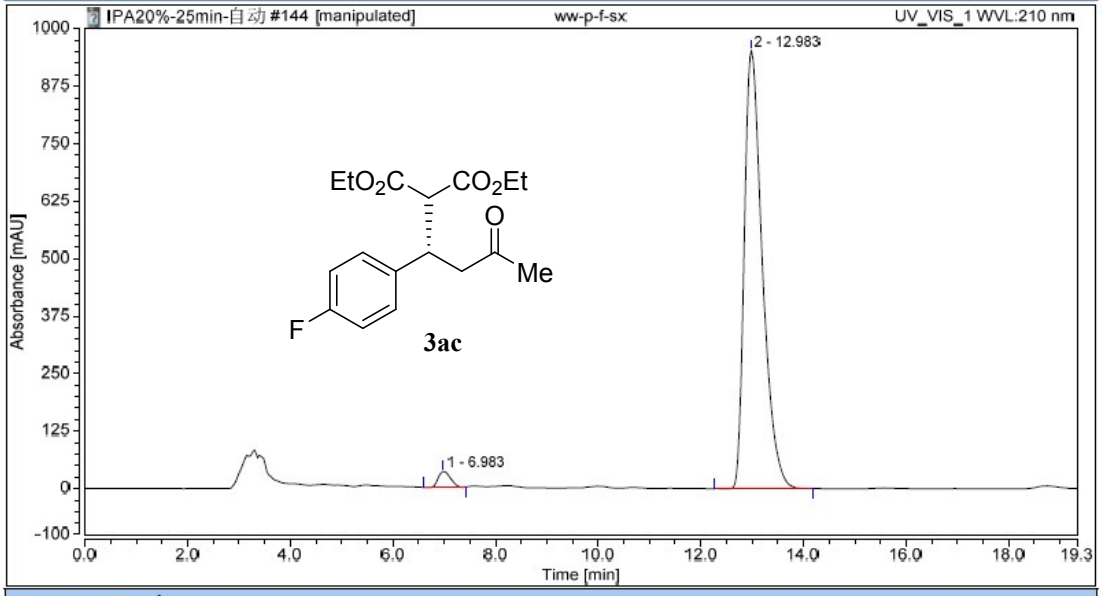
Chromatogram



Integration Results

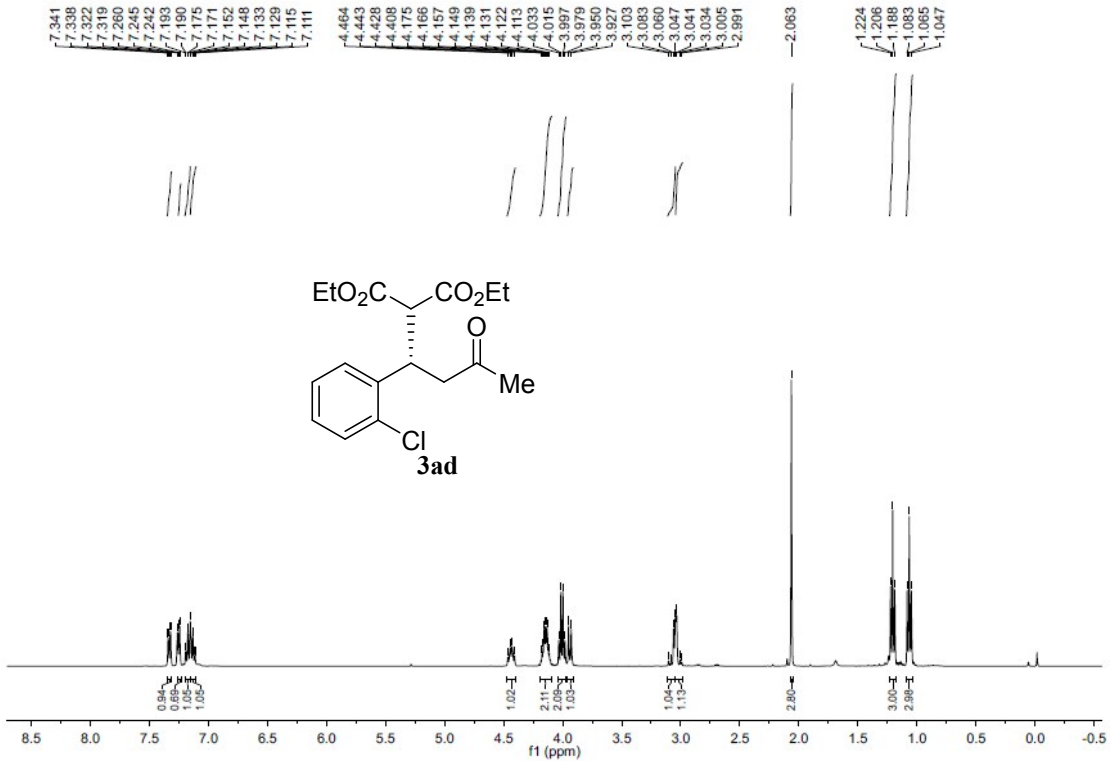
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.027	736.019	2101.054	48.53	53.82	n.a.
2		12.973	780.630	1802.696	51.47	46.18	n.a.
Total:			**1516.649**	**3903.749**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.983	9.139	33.999	2.30	3.45	n.a.
2		12.983	388.560	952.540	97.70	96.55	n.a.
Total:			**397.699**	**986.538**	**100.00**	**100.00**	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7.115
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4.408
4.175
4.166
4.157
4.149
4.139
4.131
4.122
4.113
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4.015
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CO2Et
O
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Cl
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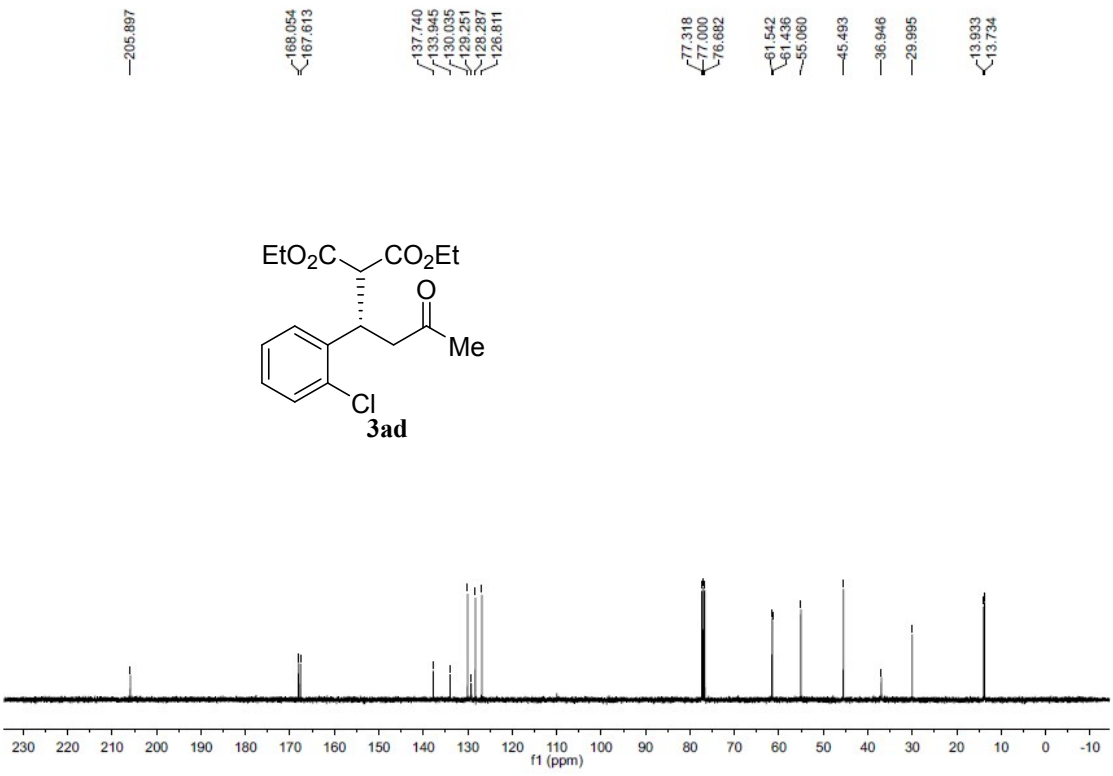
0.69
1.05
1.05
1.02
2.11
2.09
1.03
1.04
1.13
2.80
3.00
2.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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61.436
55.060
45.493
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29.995
13.933
13.734
EtO2C
CO2Et
O
Me
Cl
3ad
230
220
210
200
190
180
170
160
150
140
130
120
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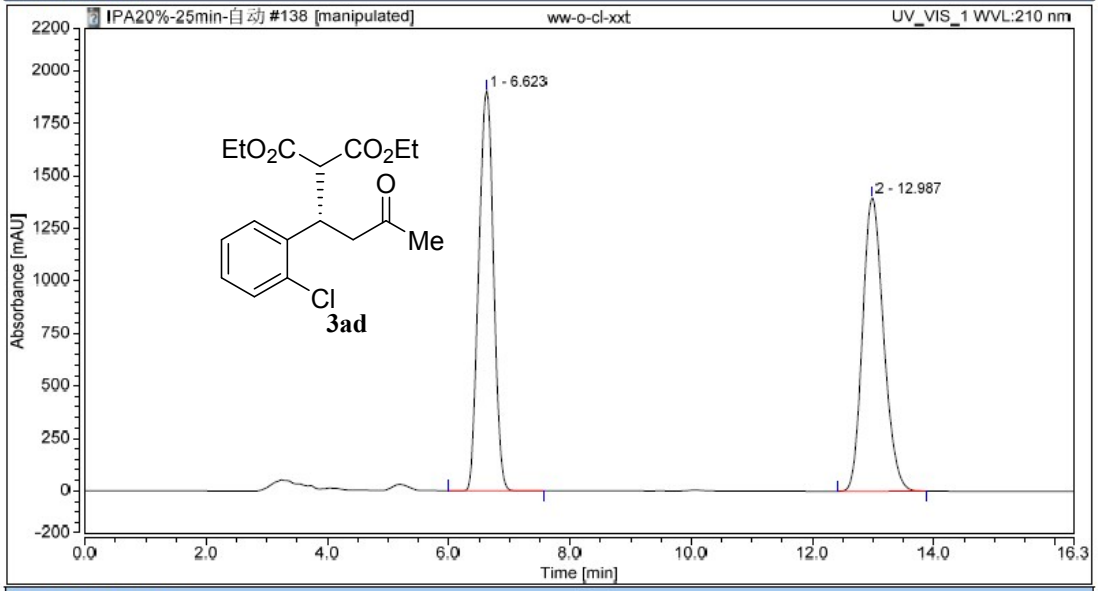
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

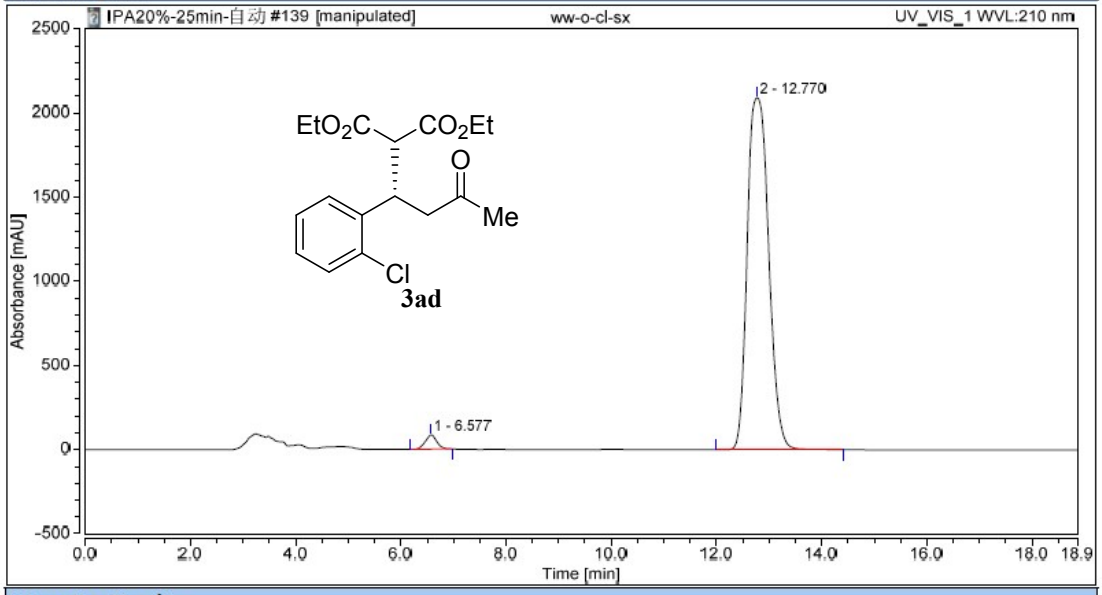
Chromatogram



Integration Results

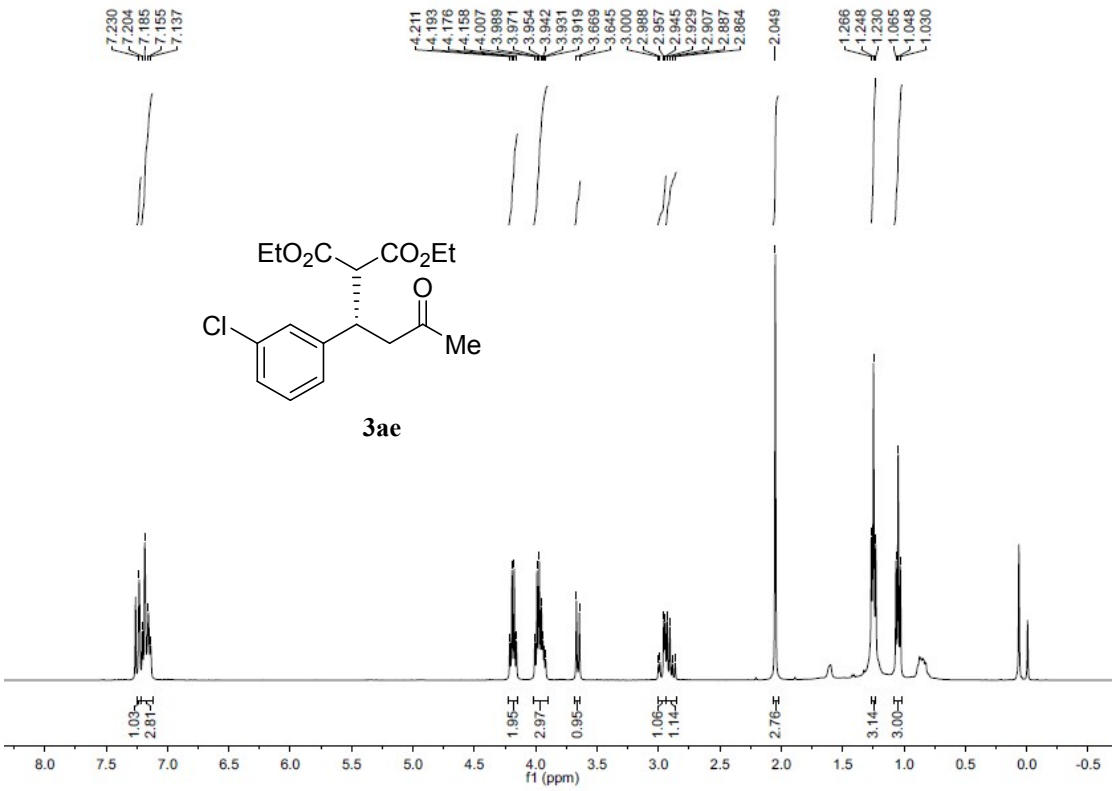
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.623	537.928	1905.908	48.90	57.69	n.a.
2		12.987	562.098	1397.834	51.10	42.31	n.a.
Total:			**1100.026**	**3303.742**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.577	21.287	84.916	2.11	3.90	n.a.
2		12.770	986.901	2093.270	97.89	96.10	n.a.
Total:			**1008.188**	**2178.187**	**100.00**	**100.00**	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6.0
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4.5
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1.5
1.0
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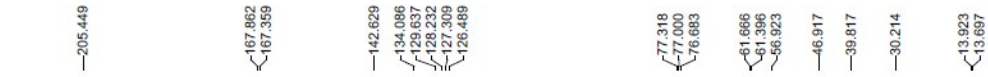
0.0
-0.5
f1 (ppm)

3ae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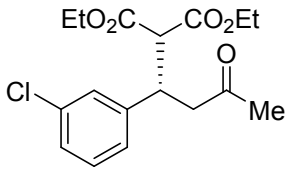
13.923
13.697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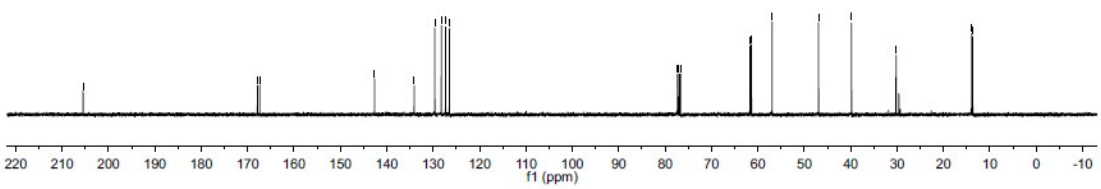
CO2Et
O
Cl
Me

3ae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180
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150
140
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120
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100
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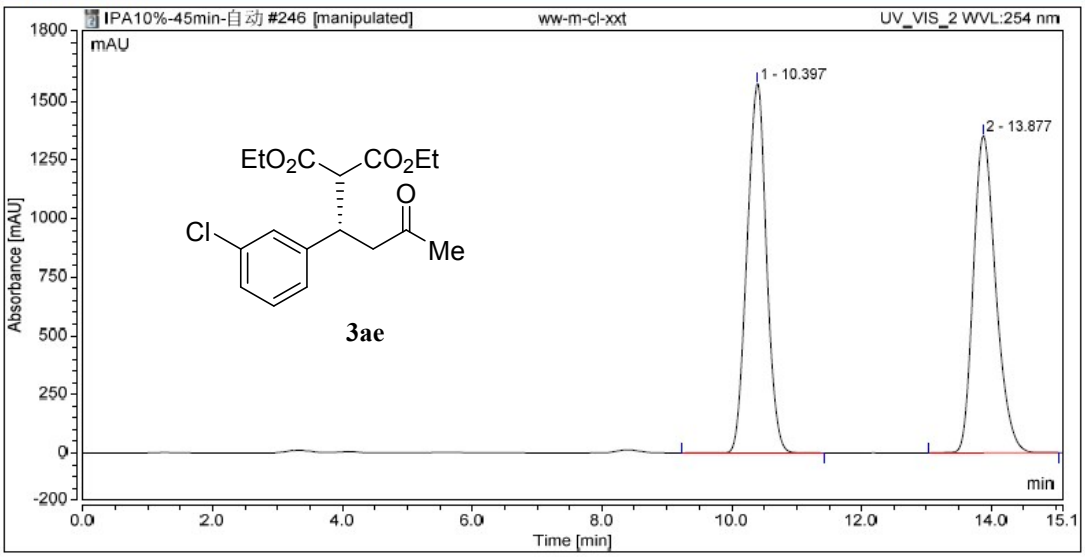
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

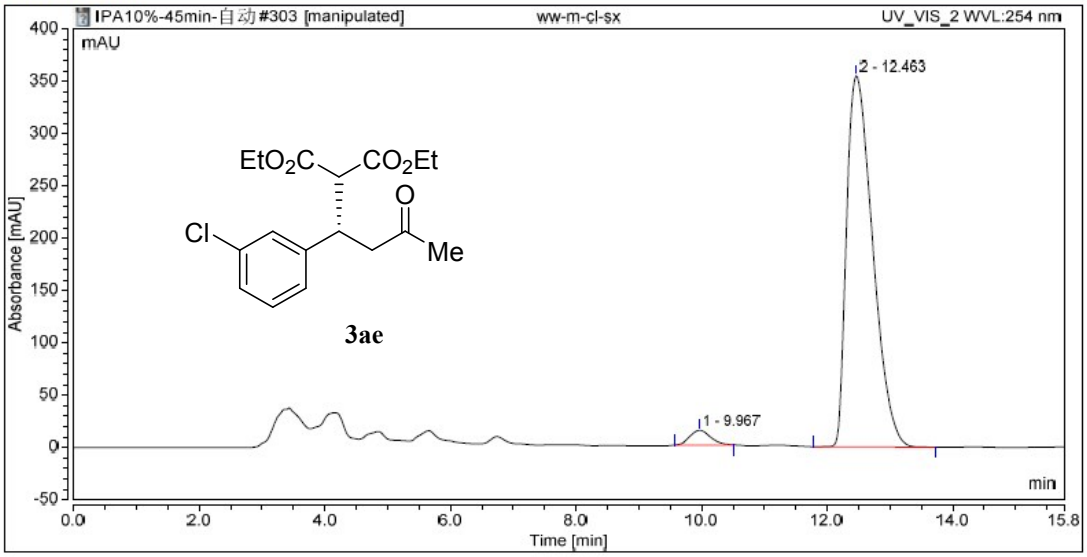
Chromatogram



Integration Results

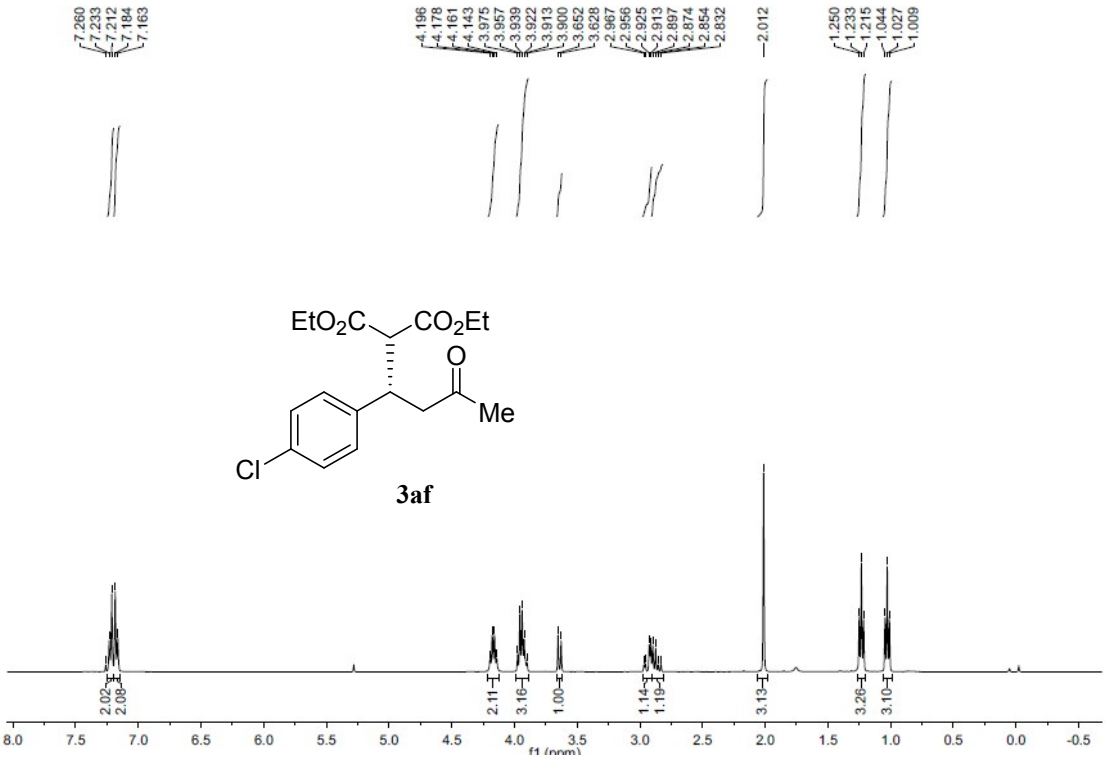
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.397	541.840	1574.273	49.94	53.78	n.a.
2		13.877	543.059	1352.975	50.06	46.22	n.a.
Total:			**1084.898**	**2927.248**	**100.00**	**100.00**	

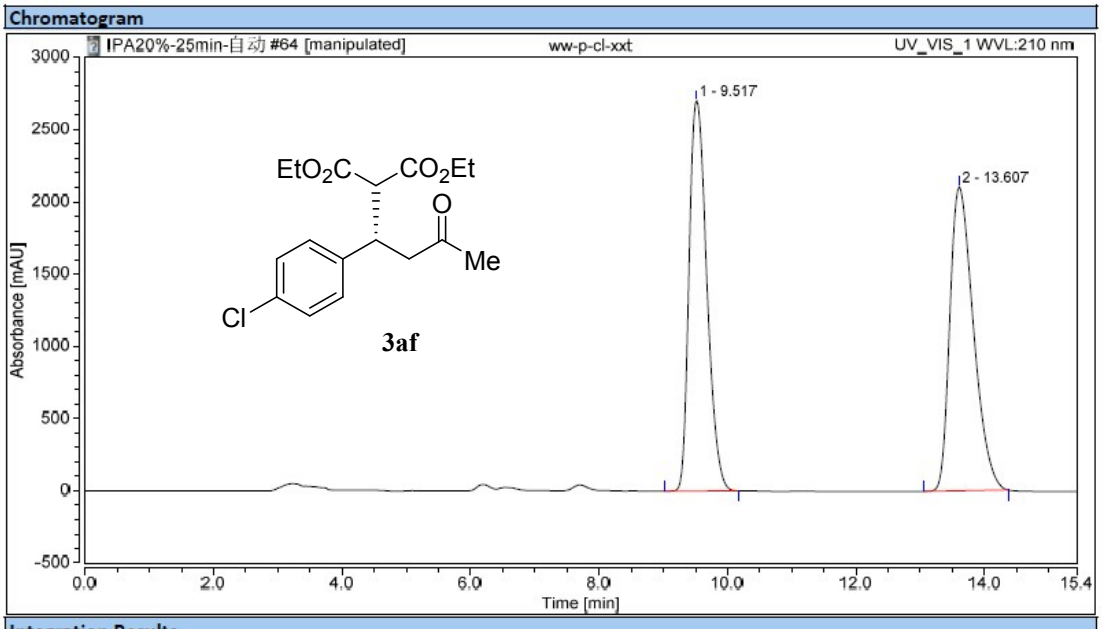
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.967	5.363	14.065	3.05	3.81	n.a.
2		12.463	170.573	354.688	96.95	96.19	n.a.
Total:			**175.936**	**368.753**	**100.00**	**100.00**	

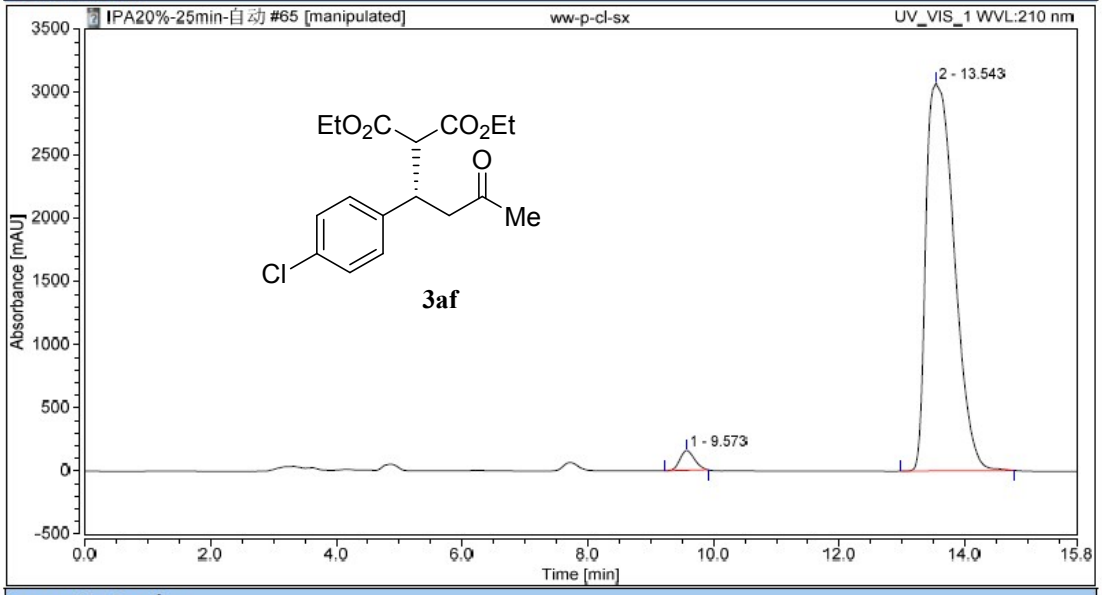




Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.517	864.926	2701.827	49.11	56.21	n.a.
2		13.607	896.133	2104.801	50.89	43.79	n.a.
Total:			**1761.059**	**4806.628**	**100.00**	**100.00**	

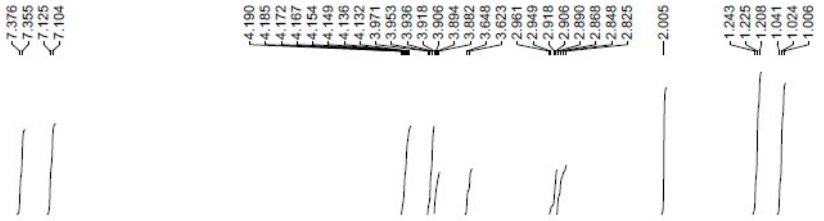
Chromatogram

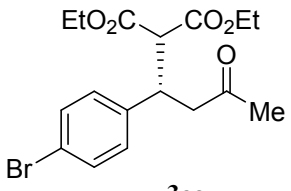


3af

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.573	42.447	157.704	2.58	4.88	n.a.
2		13.543	1602.750	3073.590	97.42	95.12	n.a.
Total:			**1645.197**	**3231.295**	**100.00**	**100.00**	





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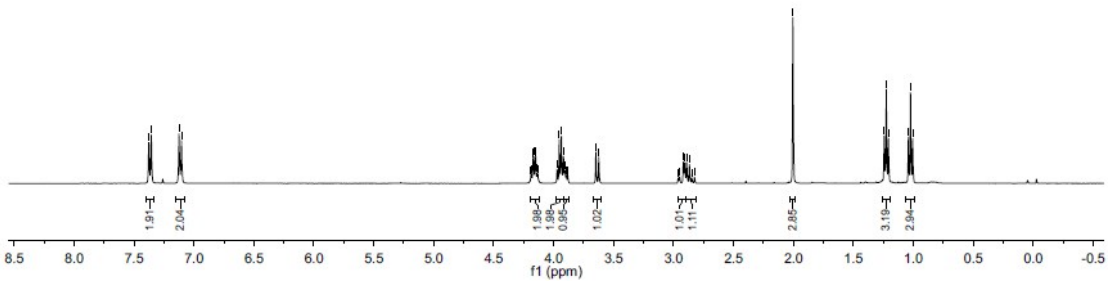
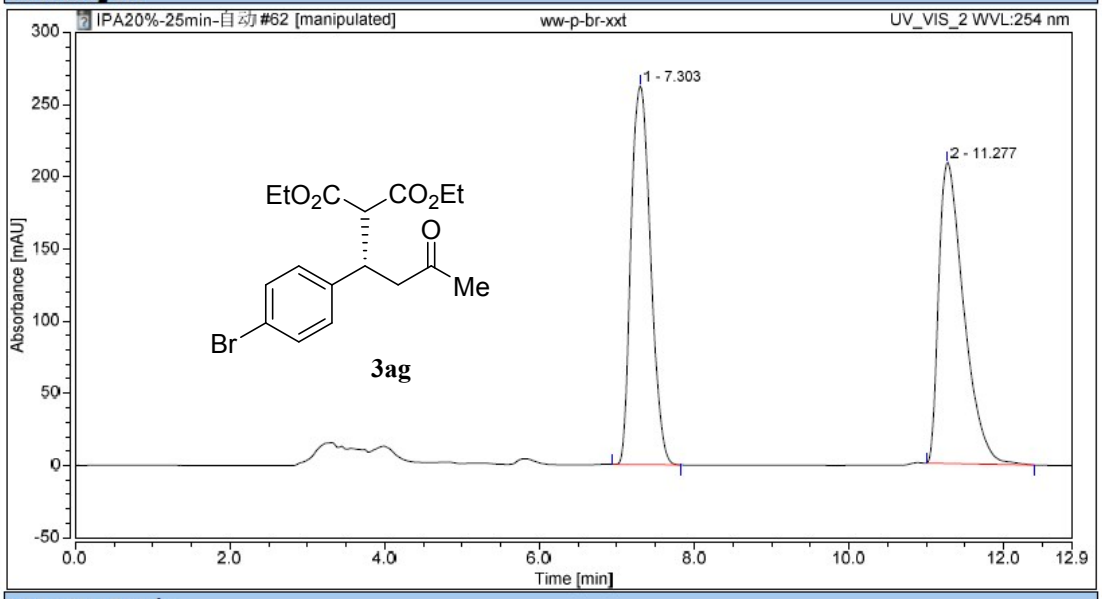


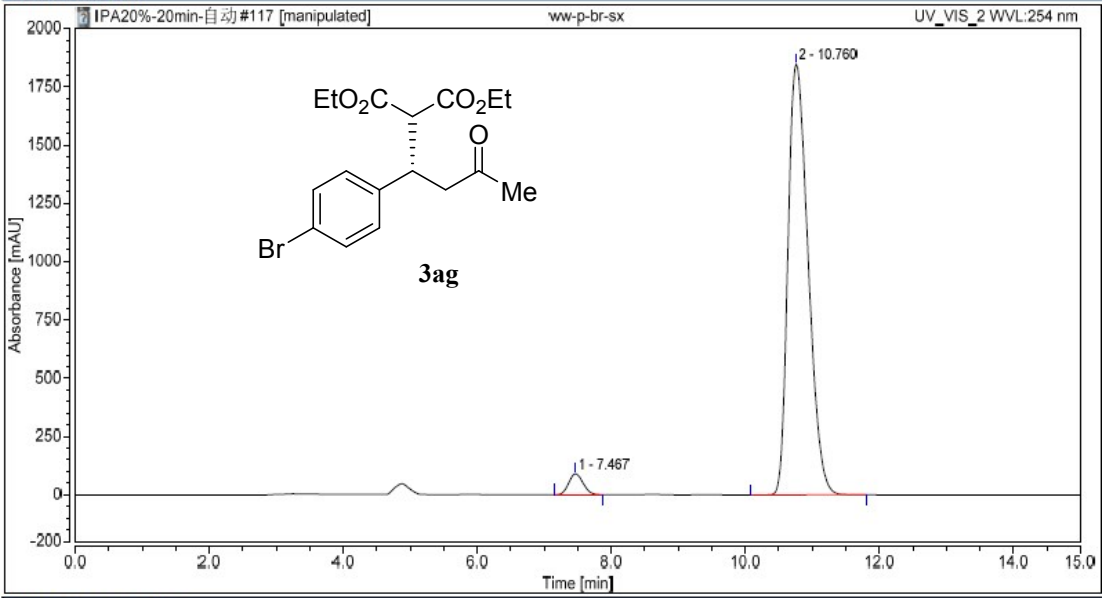
Chromatogram



Integration Results

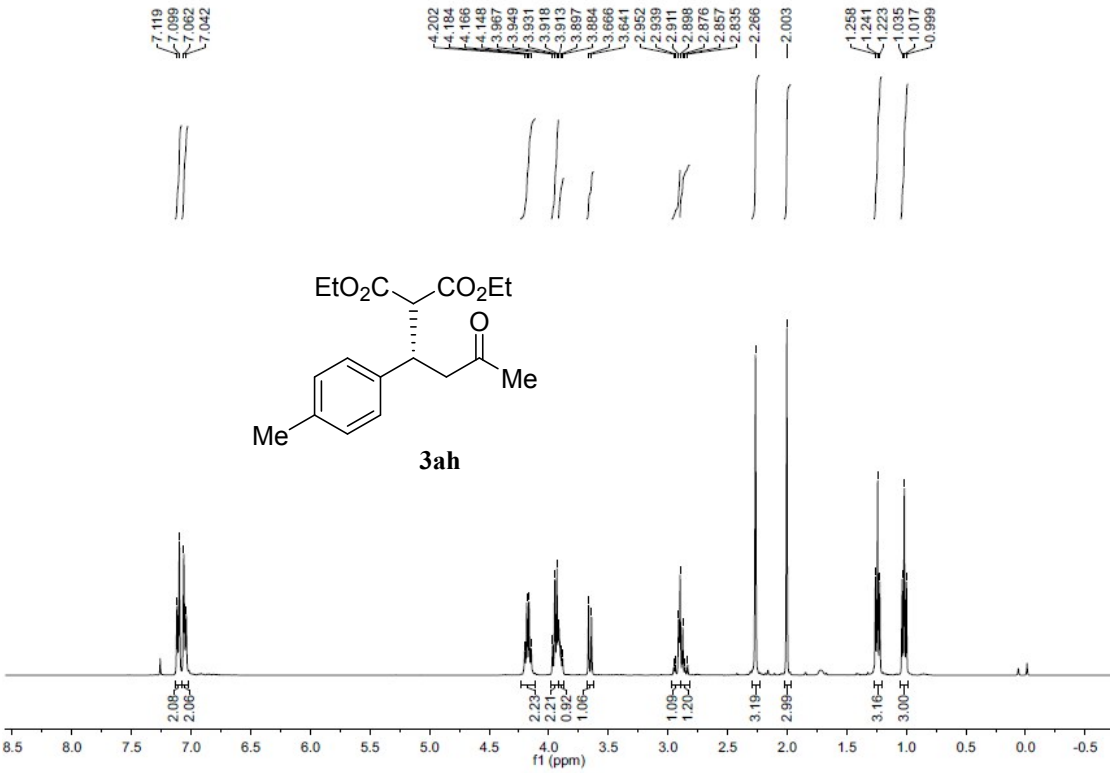
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.303	76.778	262.373	49.52	55.72	n.a.
2		11.277	78.262	208.495	50.48	44.28	n.a.
Total:			**155.040**	**470.868**	**100.00**	**100.00**	

Chromatogram

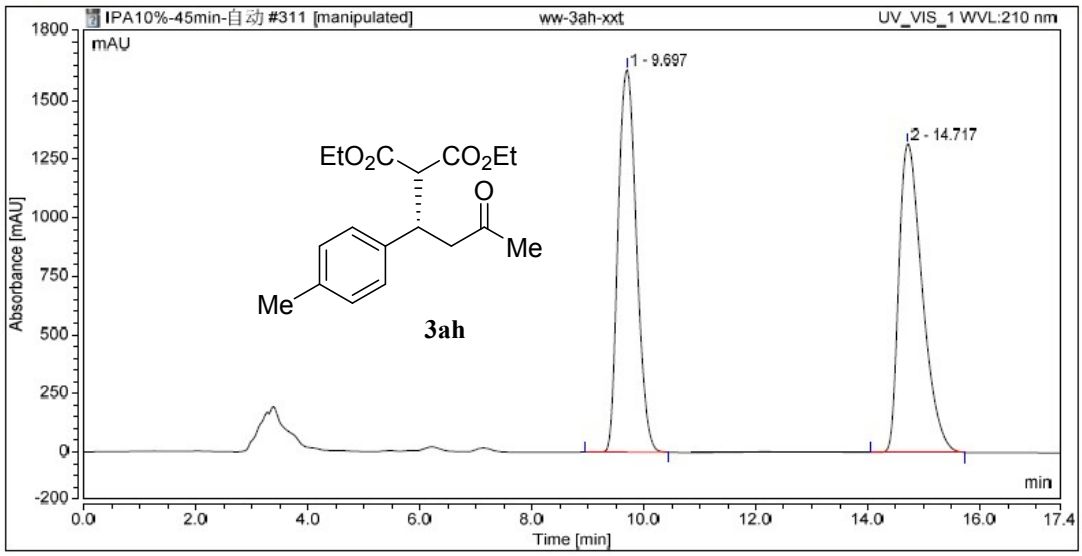


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.467	22.380	89.971	3.37	4.64	n.a.
2		10.760	642.517	1847.551	96.63	95.36	n.a.
Total:			**664.897**	**1937.522**	**100.00**	**100.00**	



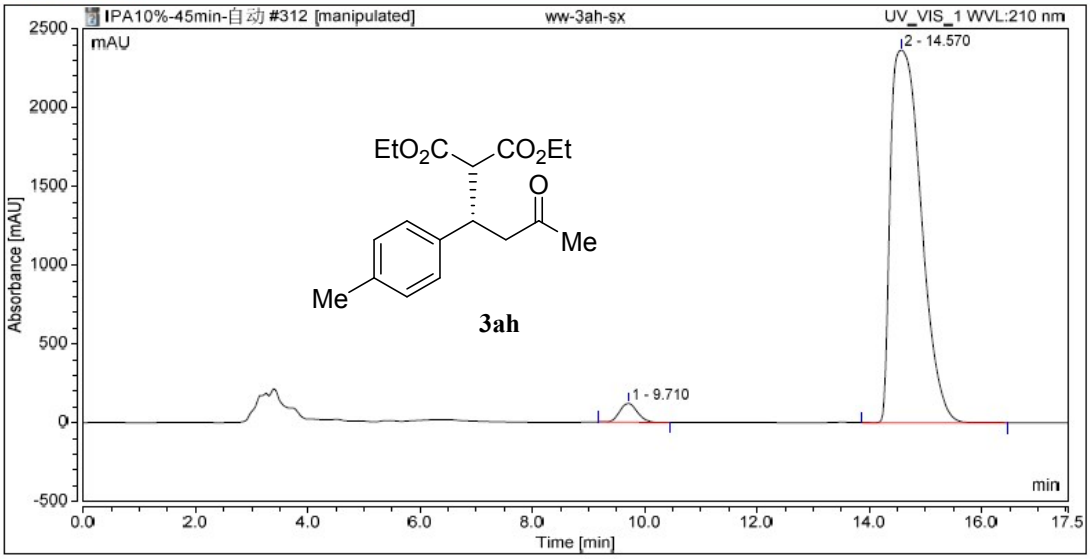
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.697	616.864	1632.770	49.15	55.34	n.a.
2		14.717	638.092	1317.559	50.85	44.66	n.a.
Total:			**1254.956**	**2950.329**	**100.00**	**100.00**	

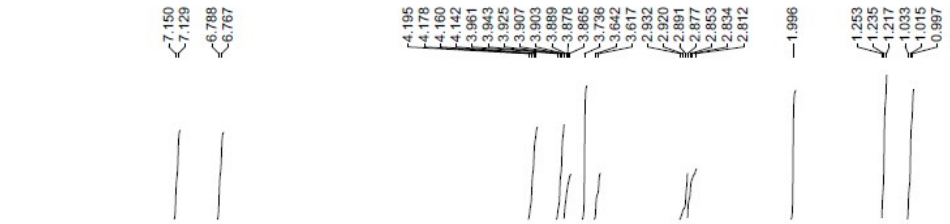
Chromatogram

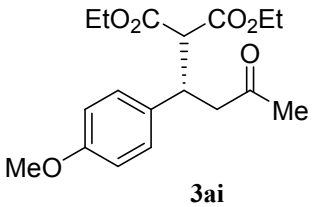


3ah

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.710	43.615	119.421	2.84	4.81	n.a.
2		14.570	1494.336	2365.025	97.16	95.19	n.a.
Total:			**1537.951**	**2484.446**	**100.00**	**100.00**	





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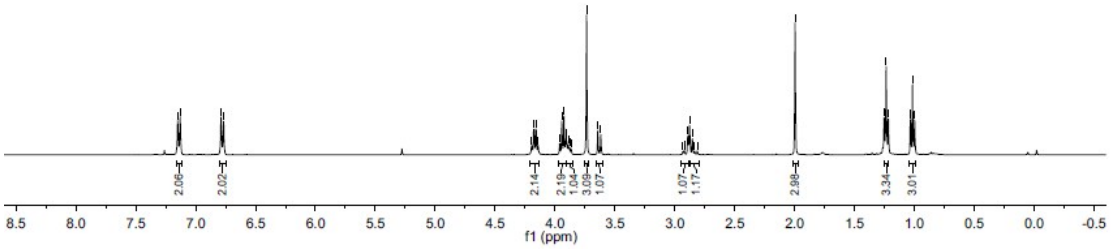
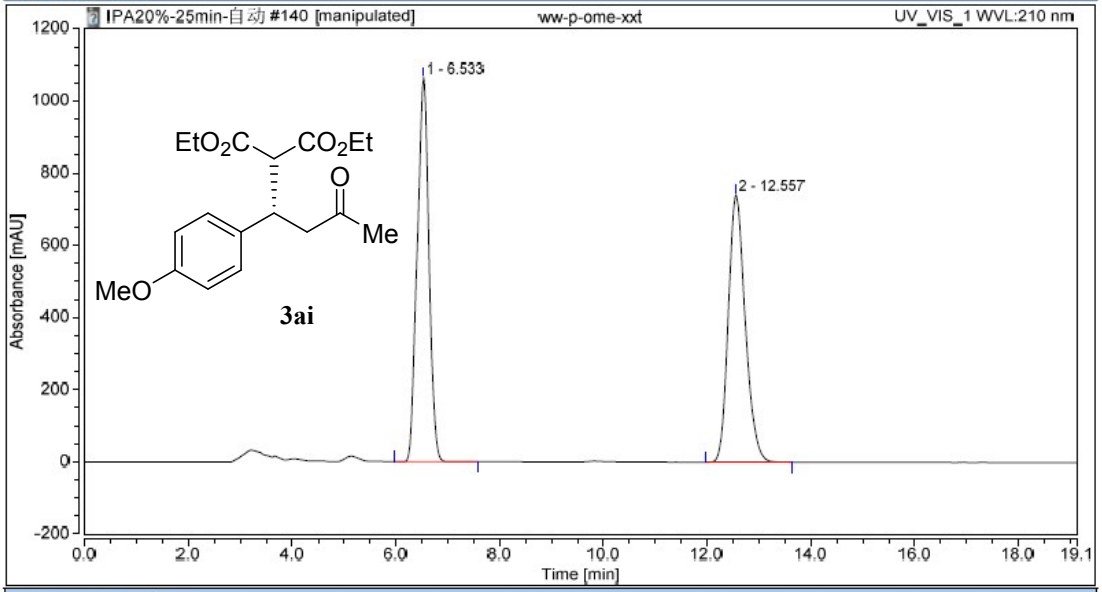


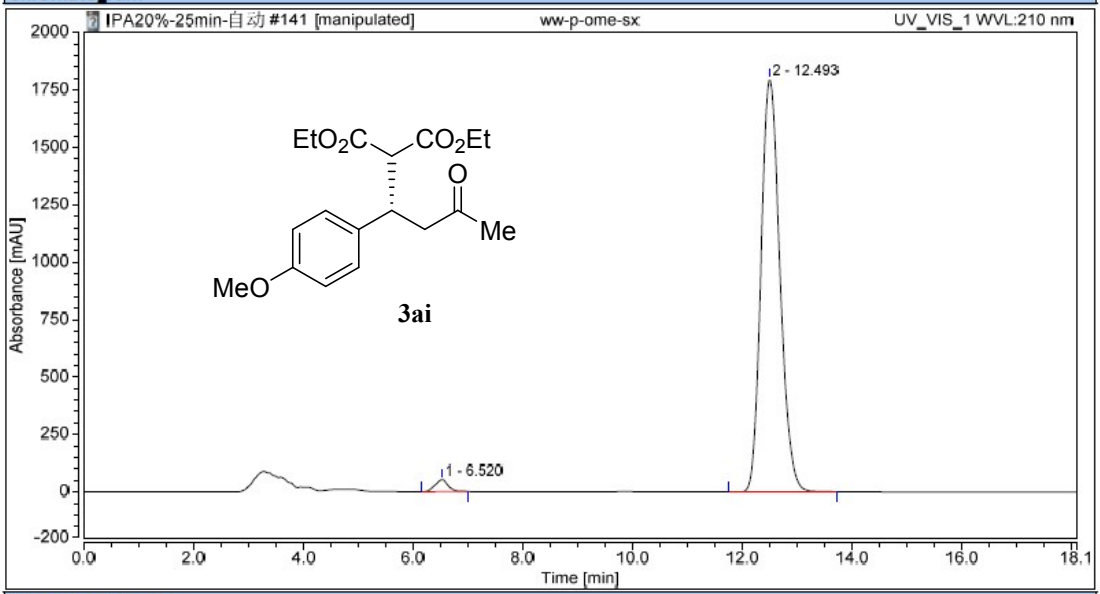
Chromatogram



Integration Results

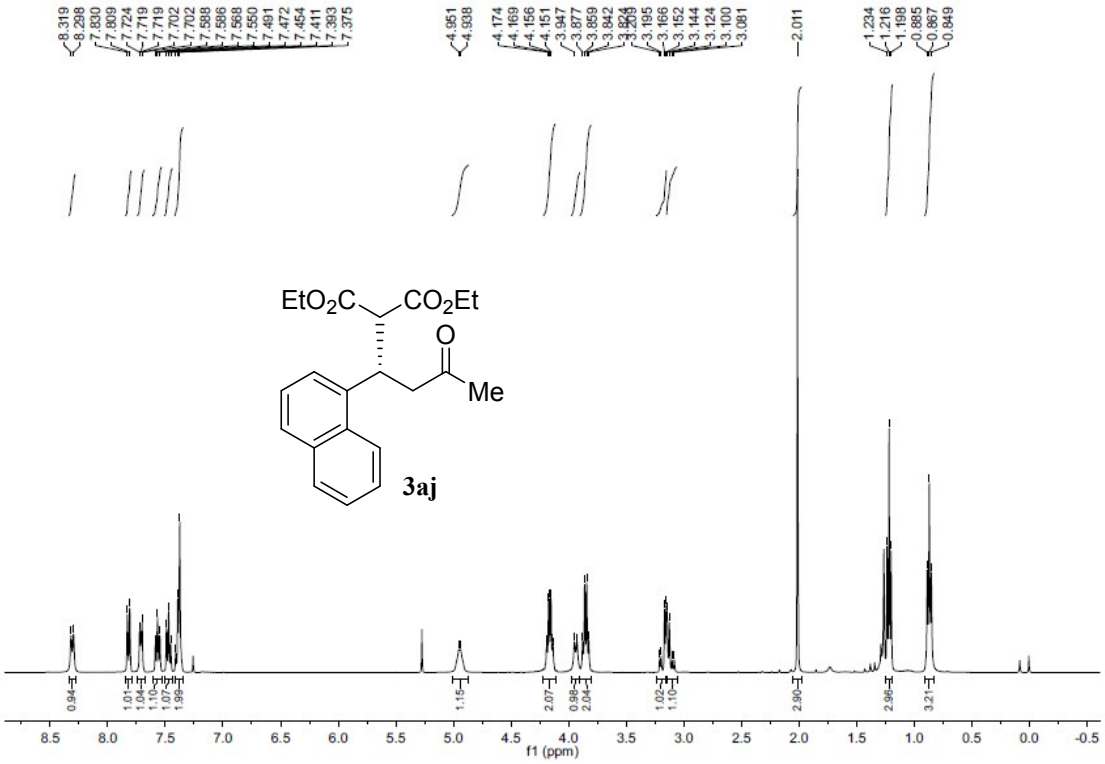
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.533	278.403	1063.381	49.89	58.98	n.a.
2		12.557	279.686	739.723	50.11	41.02	n.a.
Total:			**558.089**	**1803.104**	**100.00**	**100.00**	

Chromatogram

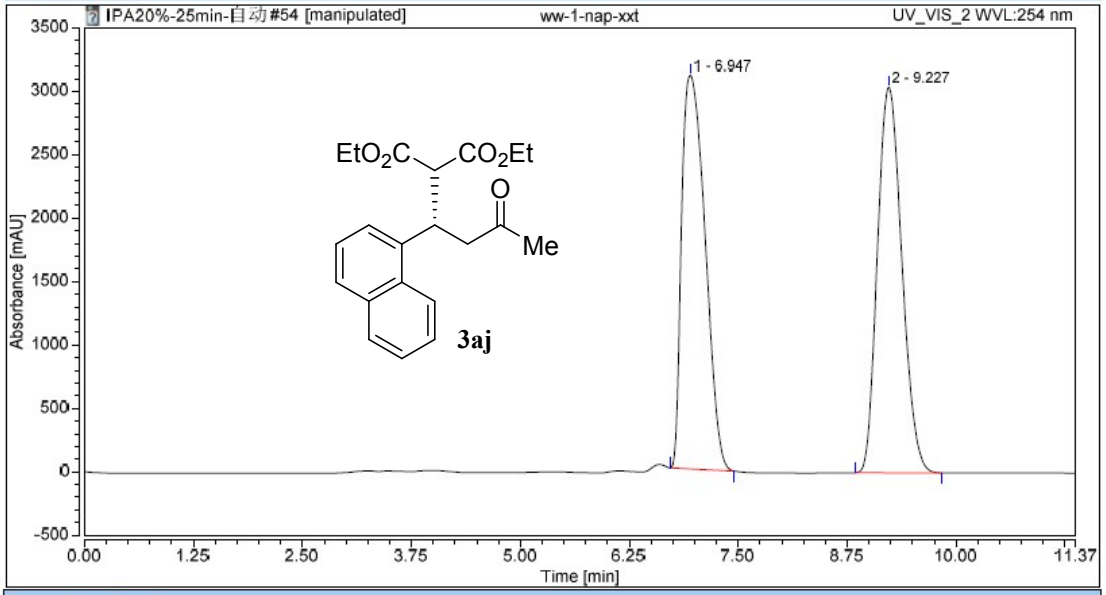


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.520	14.017	52.293	1.92	2.83	n.a.
2		12.493	716.172	1797.033	98.08	97.17	n.a.
Total:			**730.188**	**1849.325**	**100.00**	**100.00**	



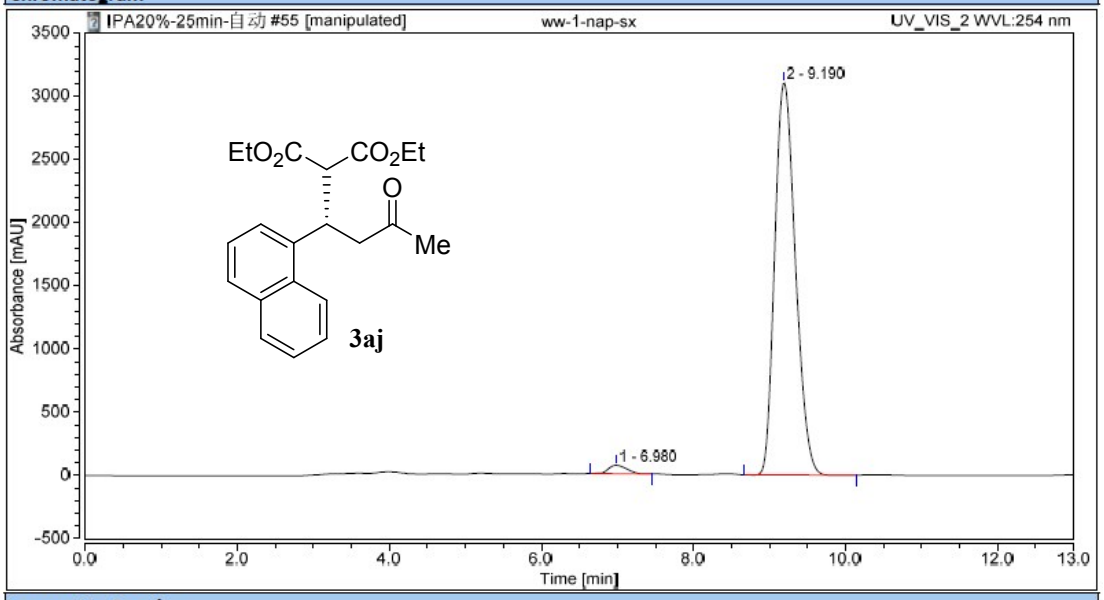
Chromatogram



Integration Results

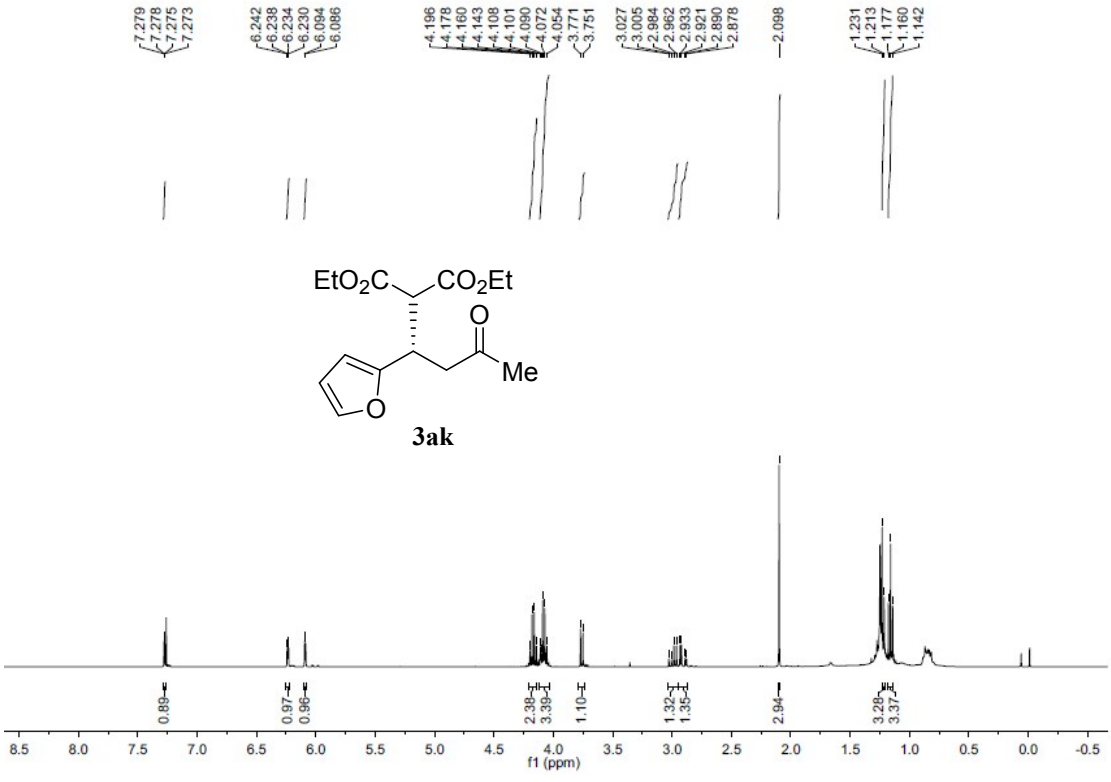
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.947	964.311	3104.544	49.38	50.51	n.a.
2		9.227	988.381	3041.341	50.62	49.49	n.a.
Total:			**1952.692**	**6145.885**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.980	17.749	66.180	1.78	2.09	n.a.
2		9.190	978.519	3106.899	98.22	97.91	n.a.
Total:			**996.268**	**3173.079**	**100.00**	**100.00**	



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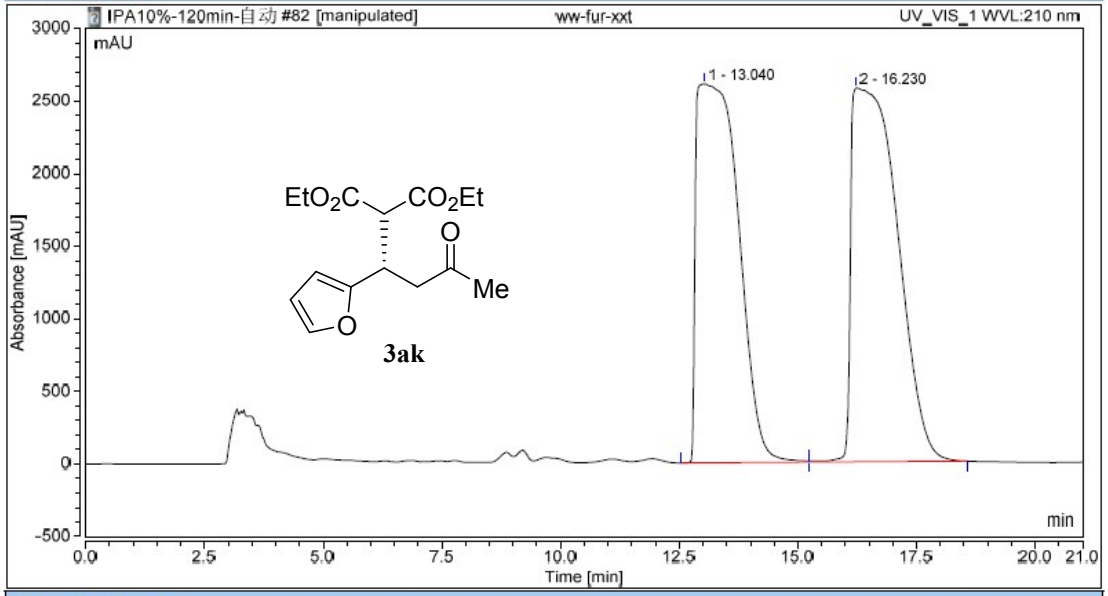
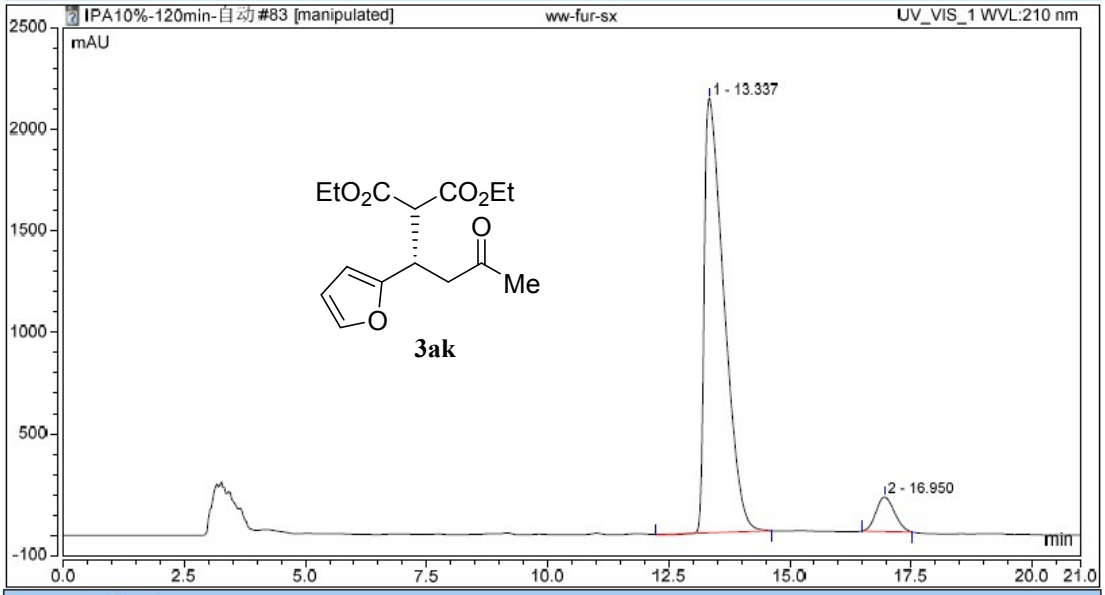


Integration Results

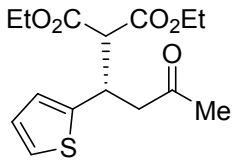
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.040	2691.320	2612.380	48.10	50.34	n.a.
2		16.230	2903.548	2577.329	51.90	49.66	n.a.
Total:			**5594.868**	**5189.709**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.337	1003.616	2139.896	93.03	92.64	n.a.
2		16.950	75.204	169.968	6.97	7.36	n.a.
Total:			**1078.820**	**2309.864**	**100.00**	**100.00**	



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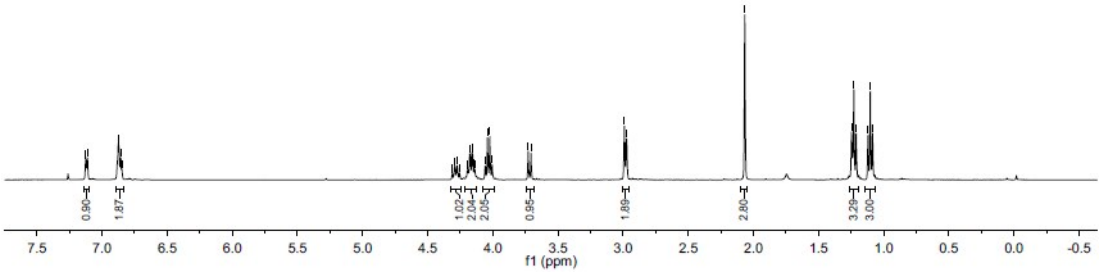

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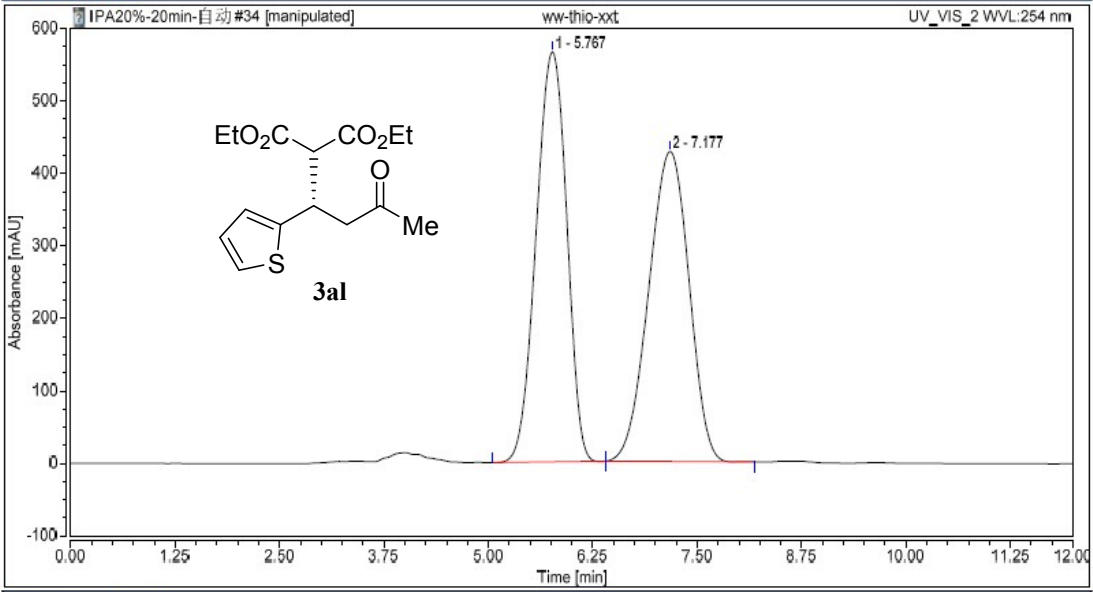
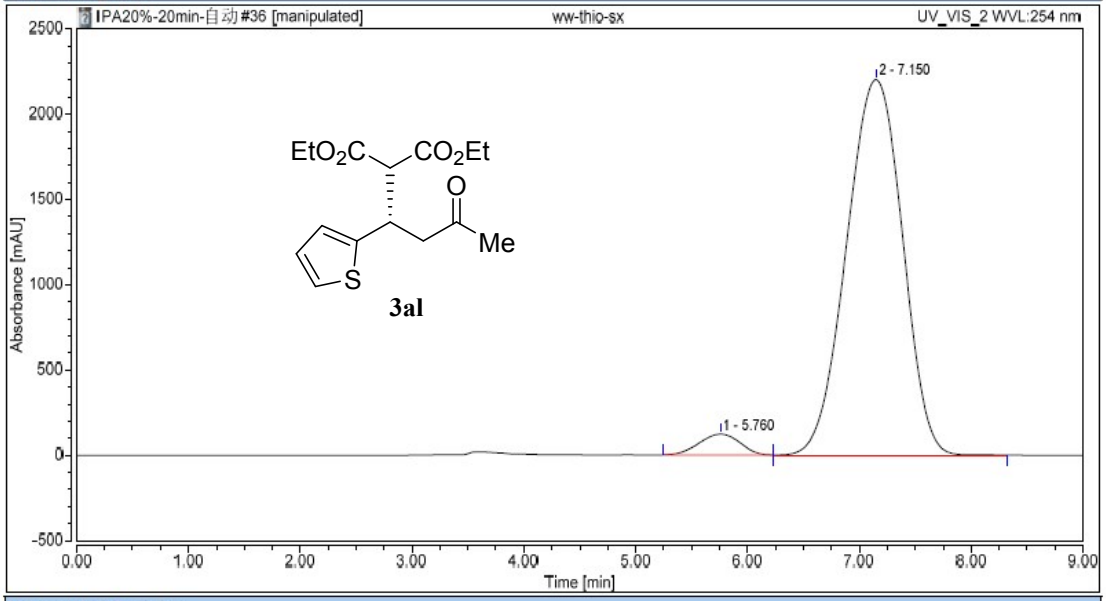


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.767	240.271	565.982	50.15	56.95	n.a.
2		7.177	238.831	427.759	49.85	43.05	n.a.
Total:			**479.102**	**993.741**	**100.00**	**100.00**	

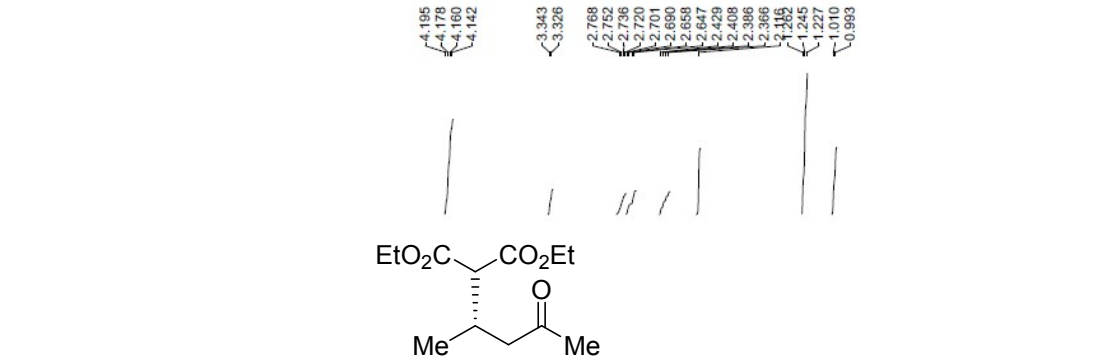
Chromatogram



3al

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.760	51.634	122.290	3.89	5.26	n.a.
2		7.150	1274.557	2200.749	96.11	94.74	n.a.
Total:			**1326.190**	**2323.039**	**100.00**	**100.00**	



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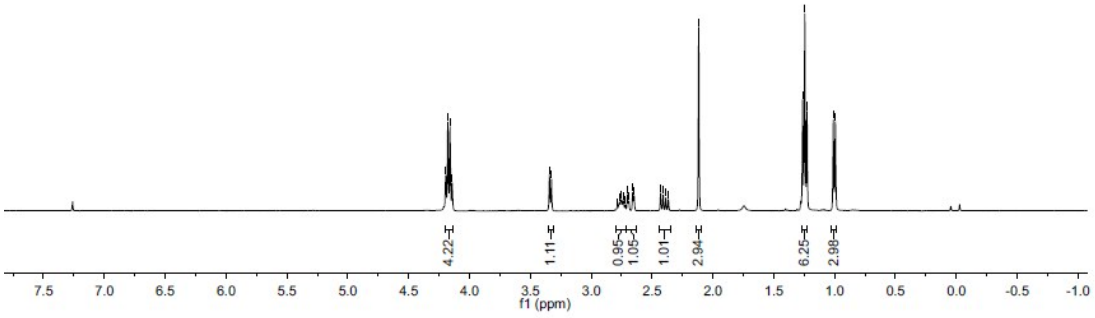

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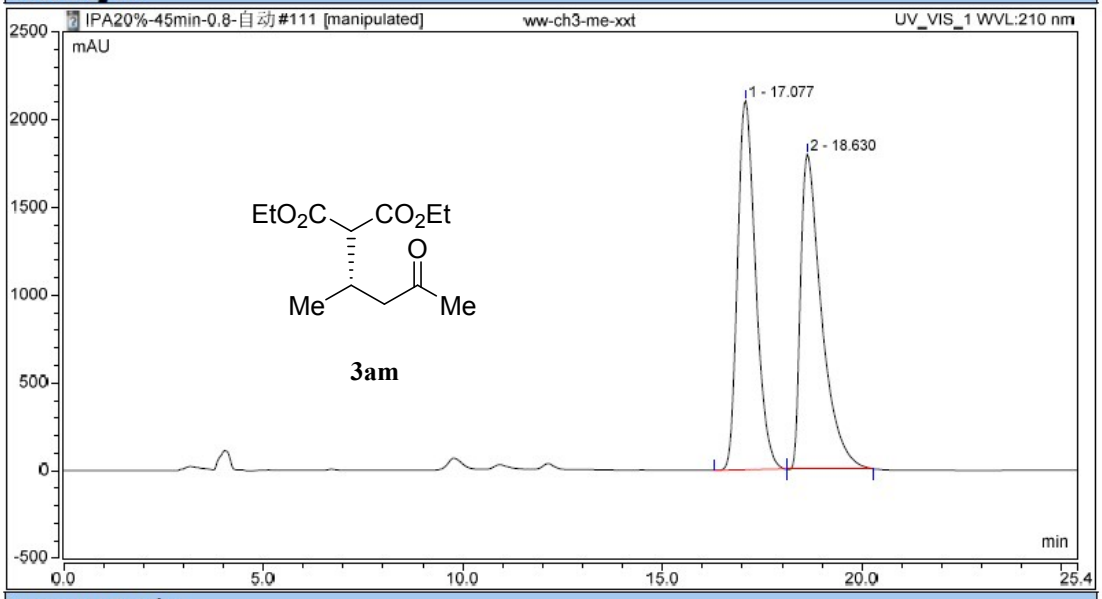
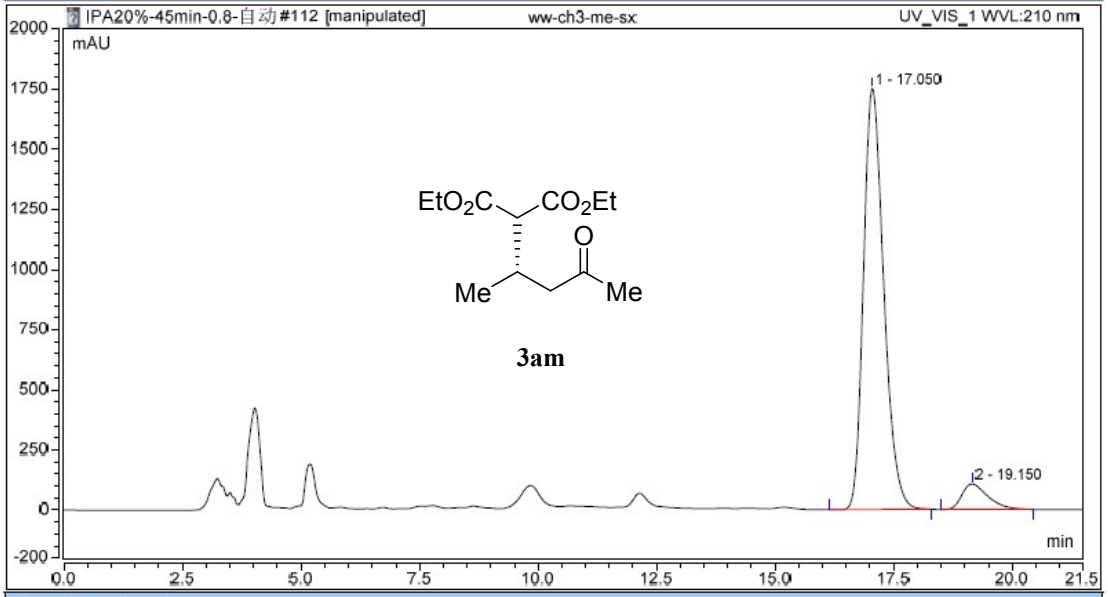


3am

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.077	1101.608	2104.644	50.21	54.00	n.a.
2		18.630	1092.513	1793.043	49.79	46.00	n.a.
Total:			**2194.121**	**3897.687**	**100.00**	**100.00**	

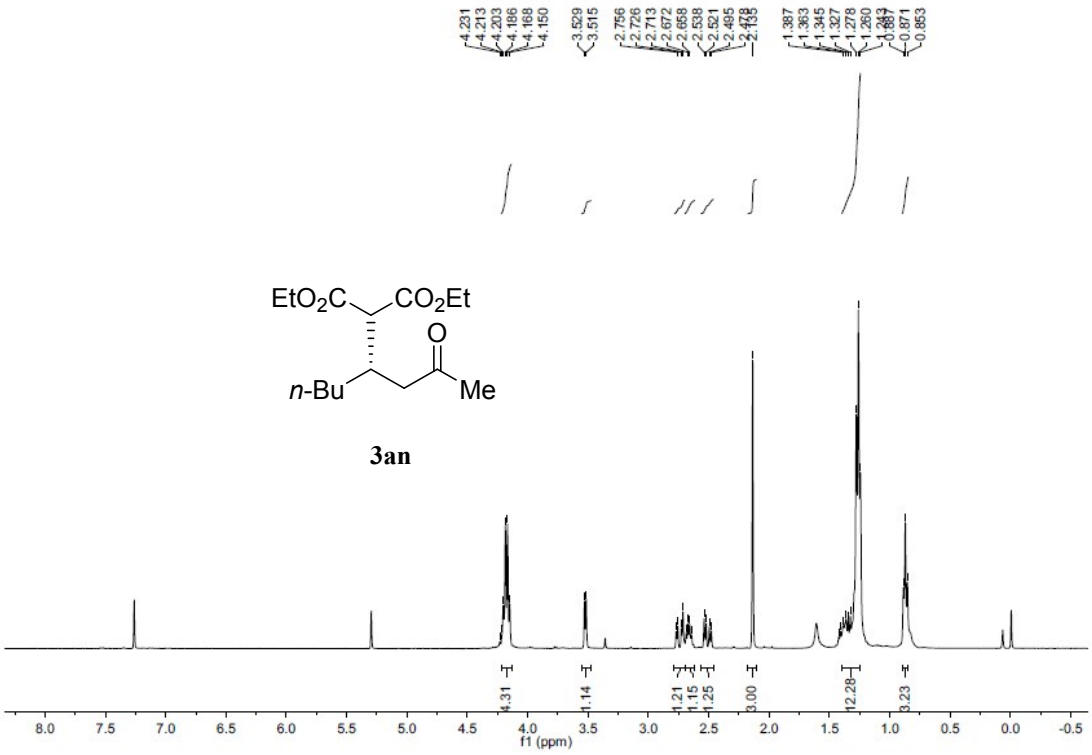
Chromatogram



3am

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.050	866.554	1751.339	92.75	94.29	n.a.
2		19.150	67.722	106.068	7.25	5.71	n.a.
Total:			**934.276**	**1857.407**	**100.00**	**100.00**	



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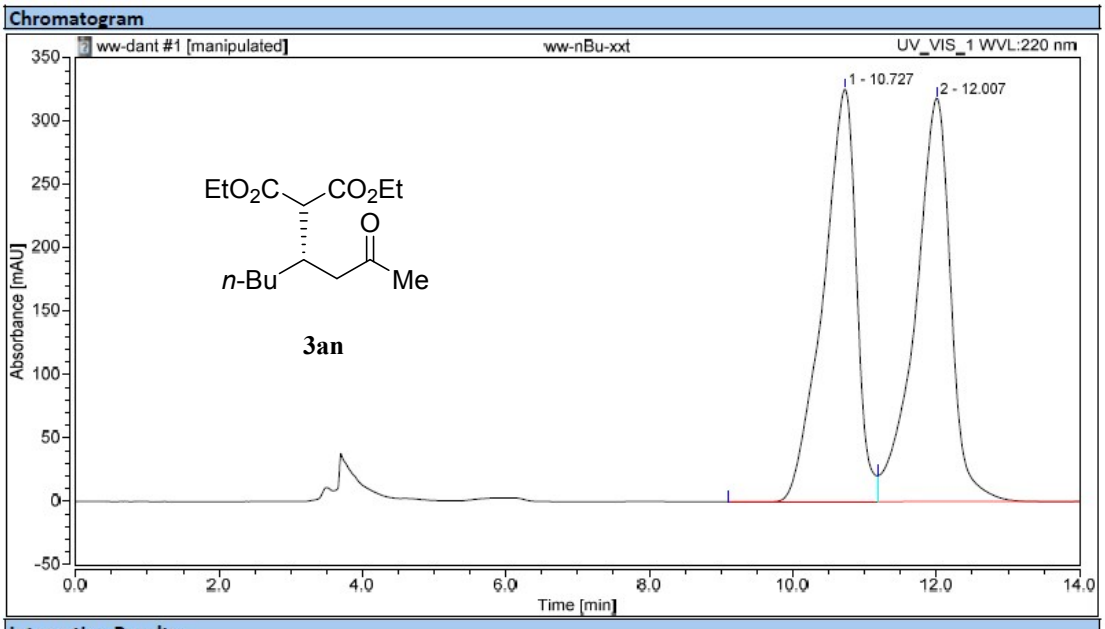
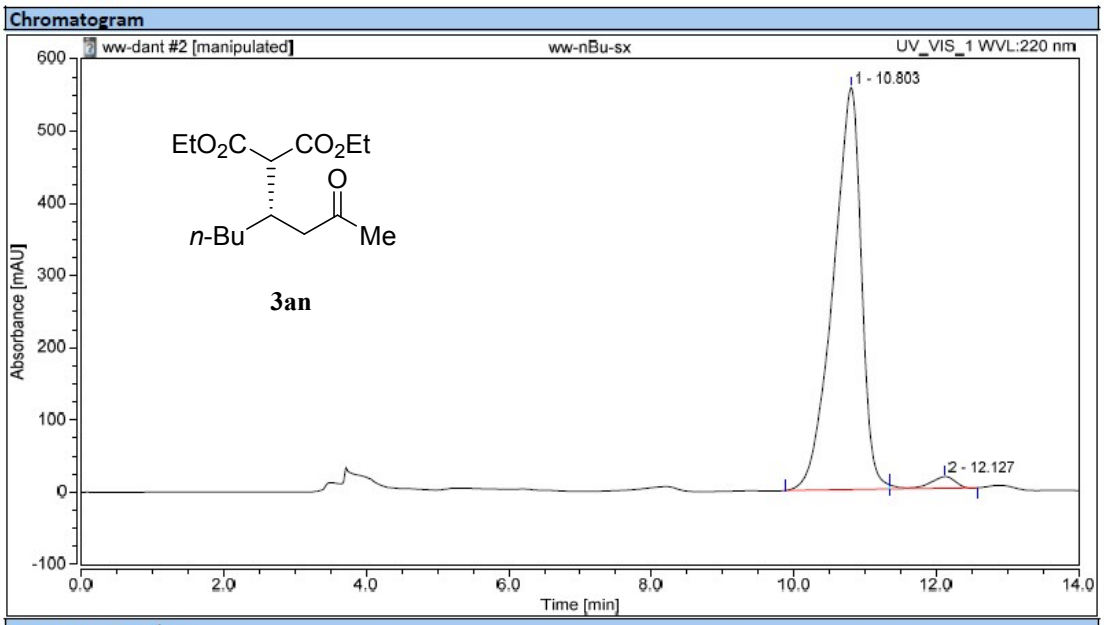


3an

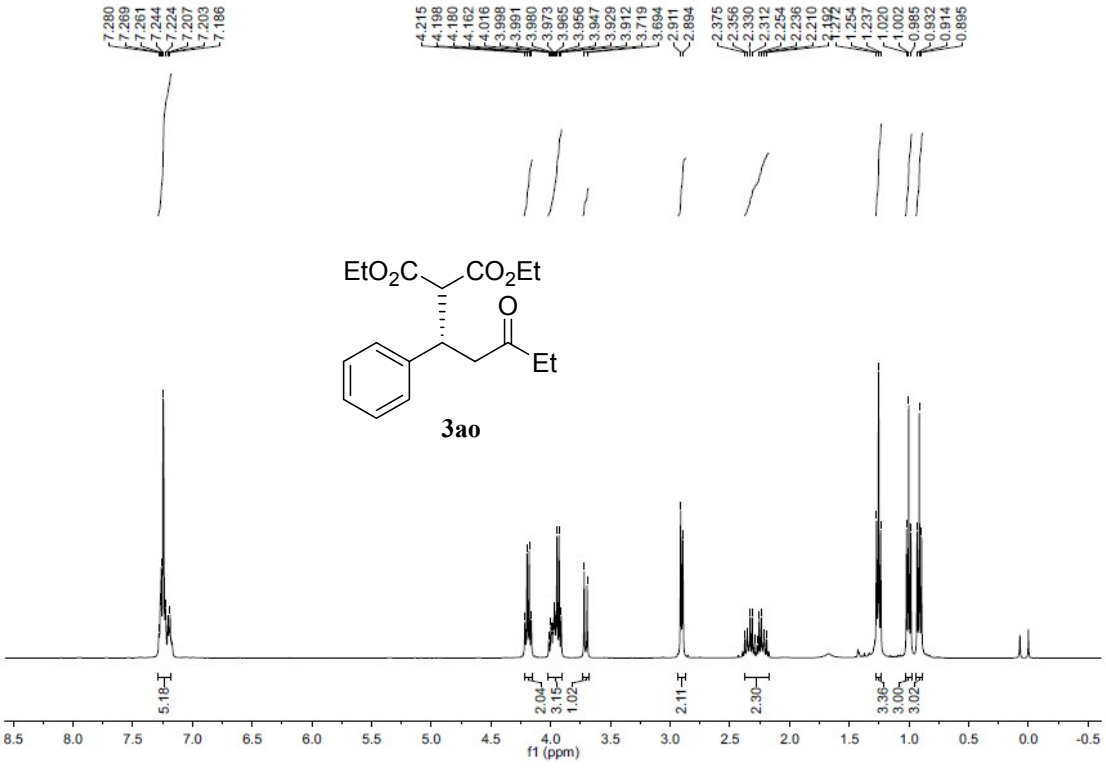
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.727	175.255	325.555	49.18	50.56	n.a.
2		12.007	181.102	318.384	50.82	49.44	n.a.
Total:			**356.357**	**643.939**	**100.00**	**100.00**	

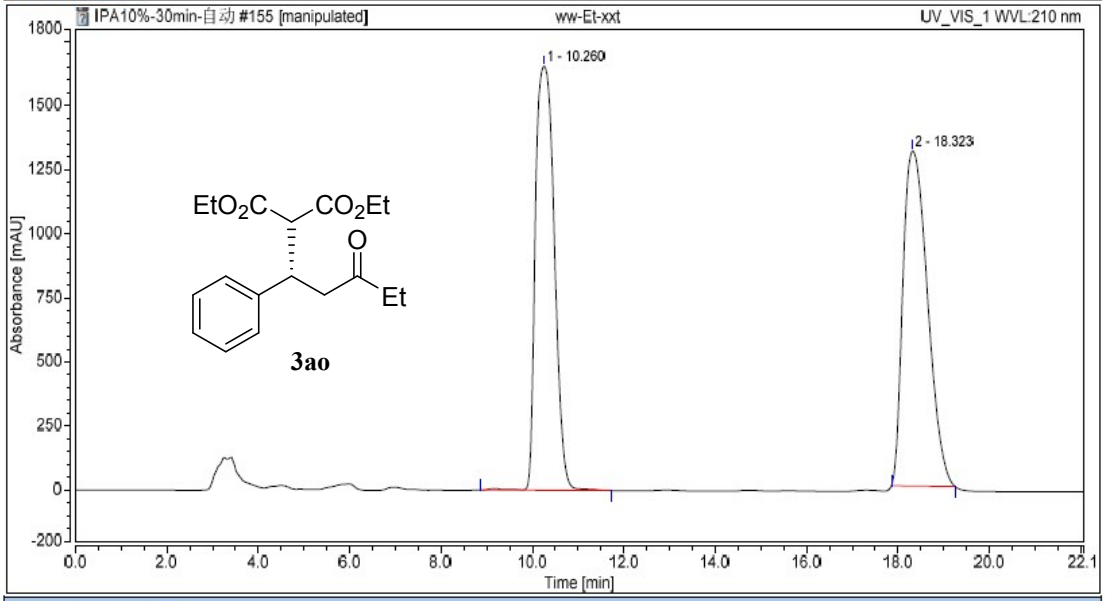


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.803	255.351	556.774	97.35	97.19	n.a.
2		12.127	6.962	16.111	2.65	2.81	n.a.
Total:			262.313	572.885	100.00	100.00	



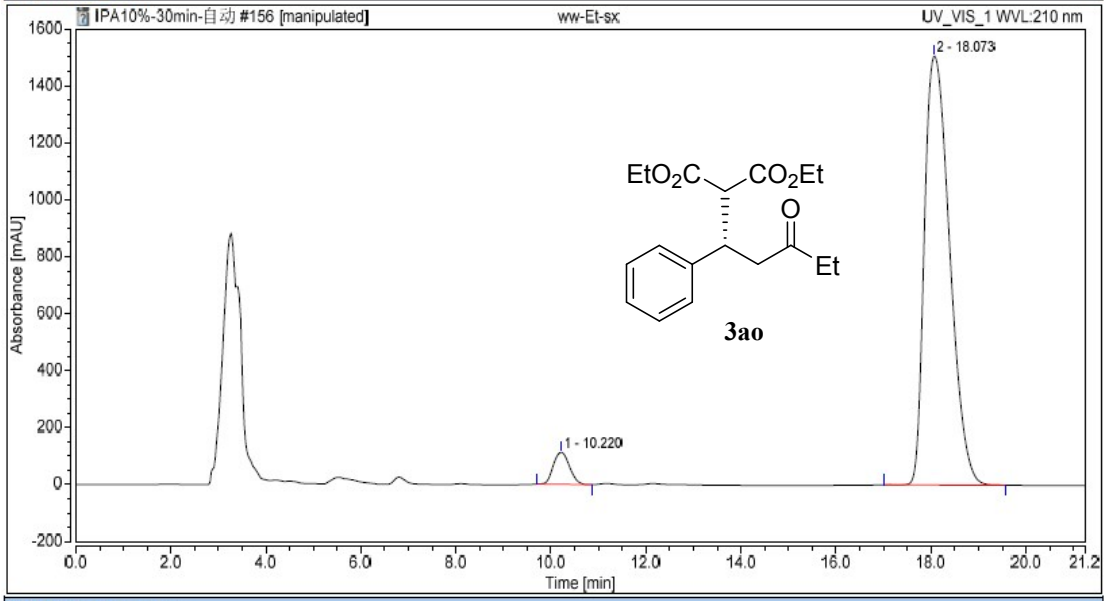
Chromatogram



Integration Results

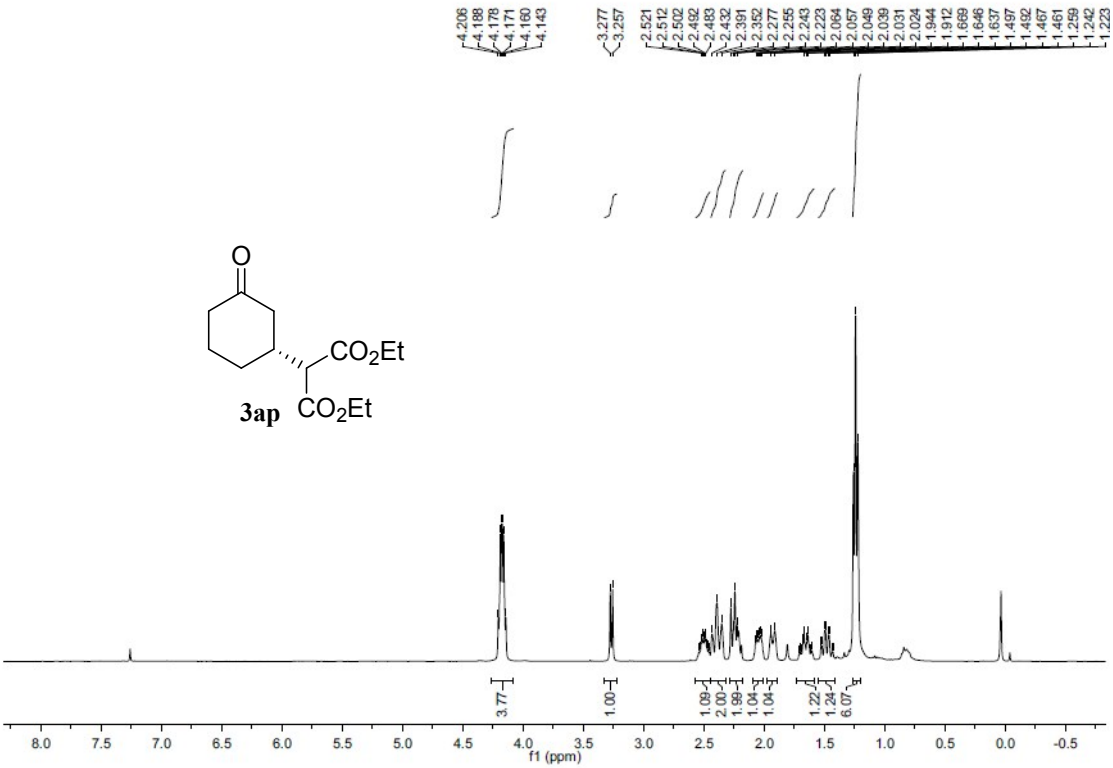
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.260	794.201	1656.000	49.40	55.89	n.a.
2		18.323	813.416	1307.023	50.60	44.11	n.a.
Total:			**1607.617**	**2963.023**	**100.00**	**100.00**	

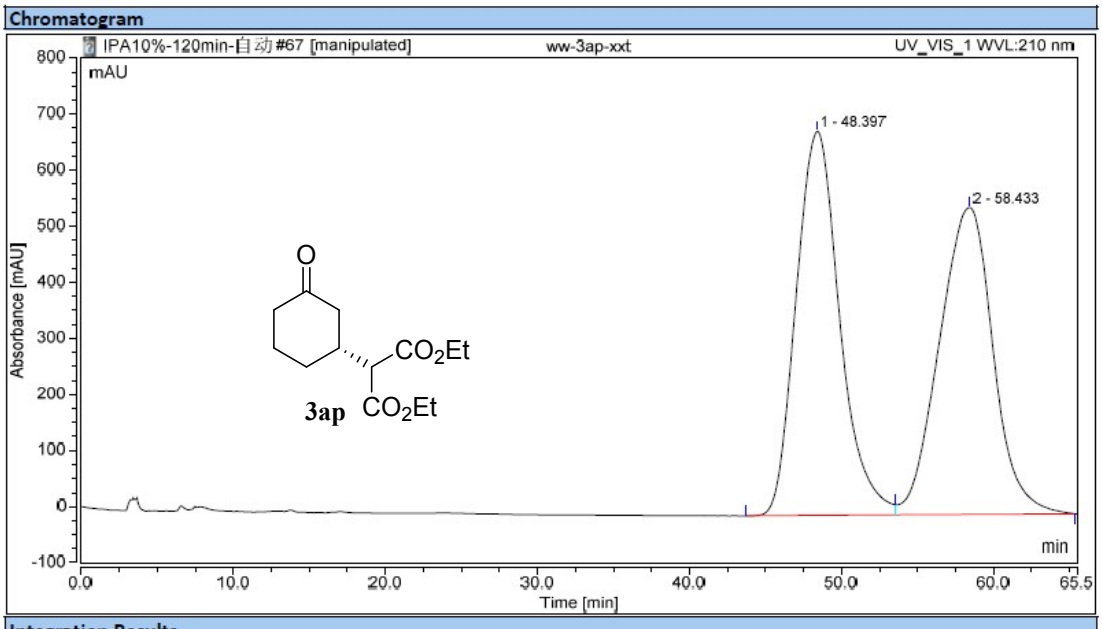
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.220	44.329	112.847	4.56	6.97	n.a.
2		18.073	927.191	1505.943	95.44	93.03	n.a.
Total:			**971.520**	**1618.790**	**100.00**	**100.00**	

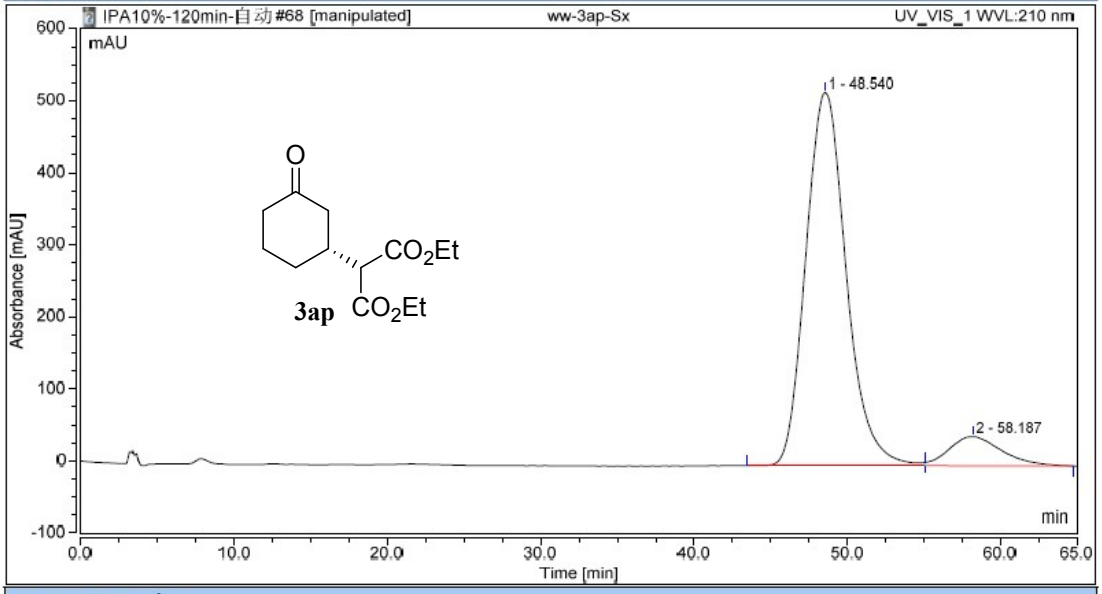




Integration Results

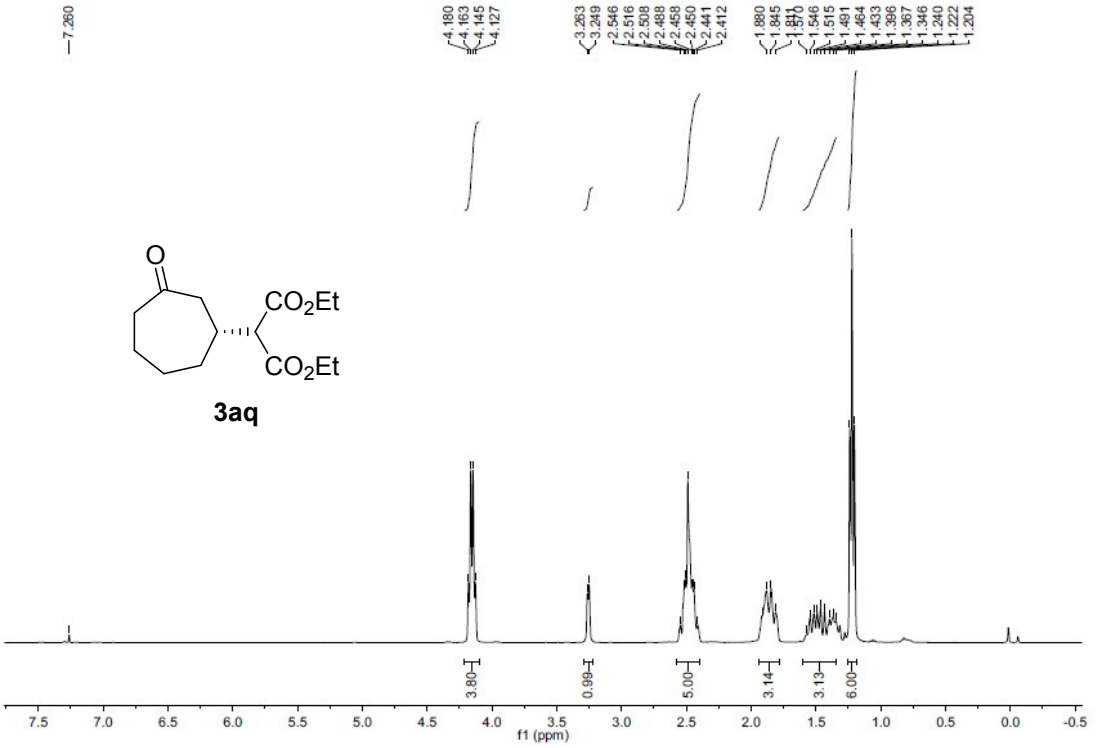
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		48.397	2271.765	684.662	50.31	55.57	n.a.
2		58.433	2243.967	547.412	49.69	44.43	n.a.
Total:			**4515.733**	**1232.074**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		48.540	1581.277	517.846	90.75	92.76	n.a.
2		58.187	161.112	40.447	9.25	7.24	n.a.
Total:			**1742.388**	**558.293**	**100.00**	**100.00**	



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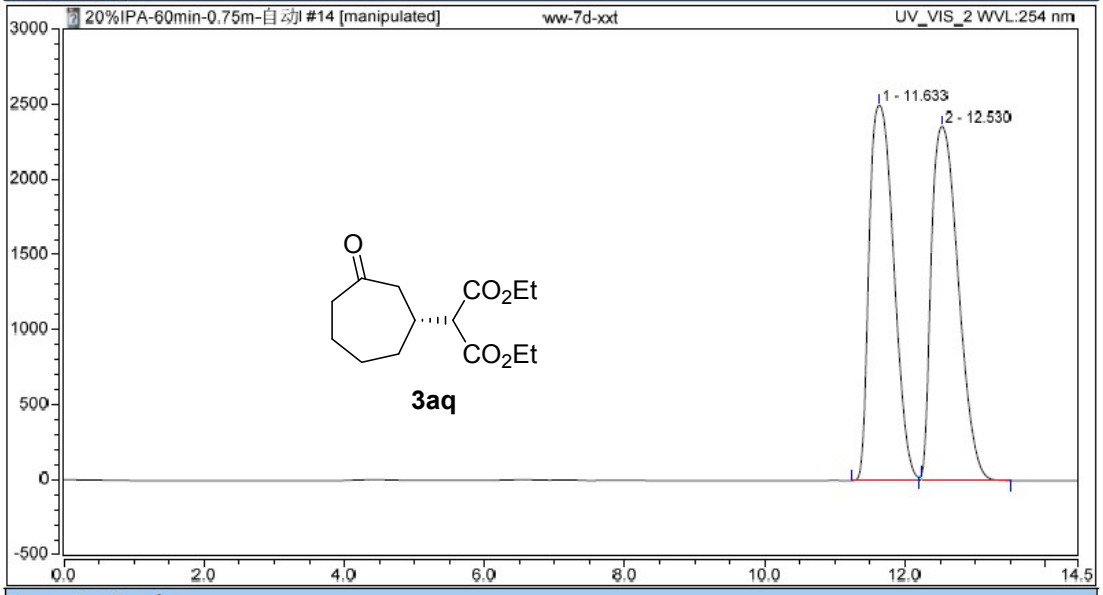
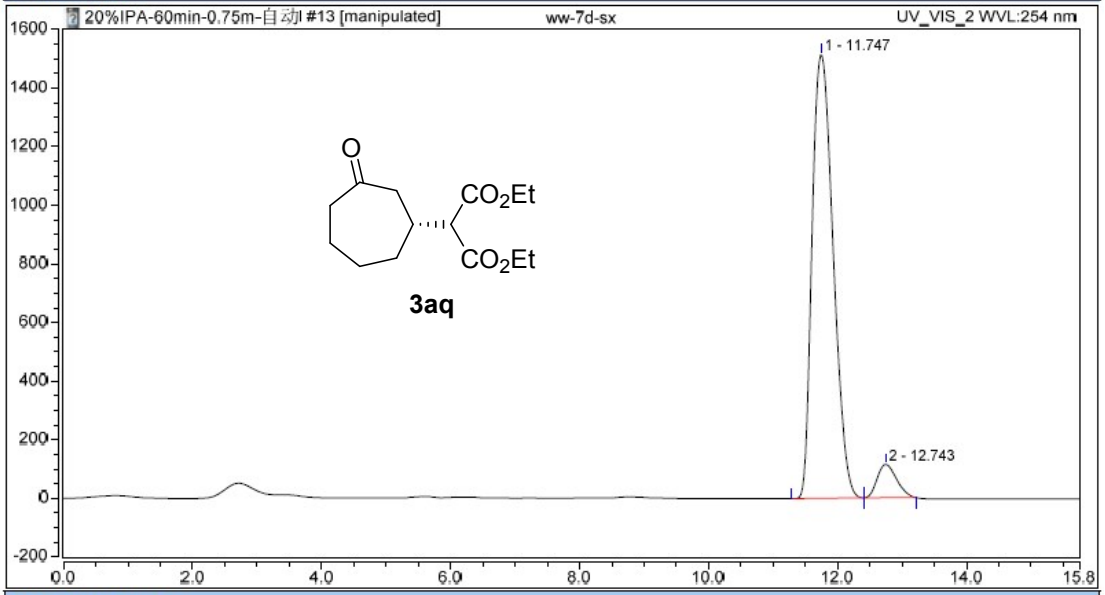


Integration Results

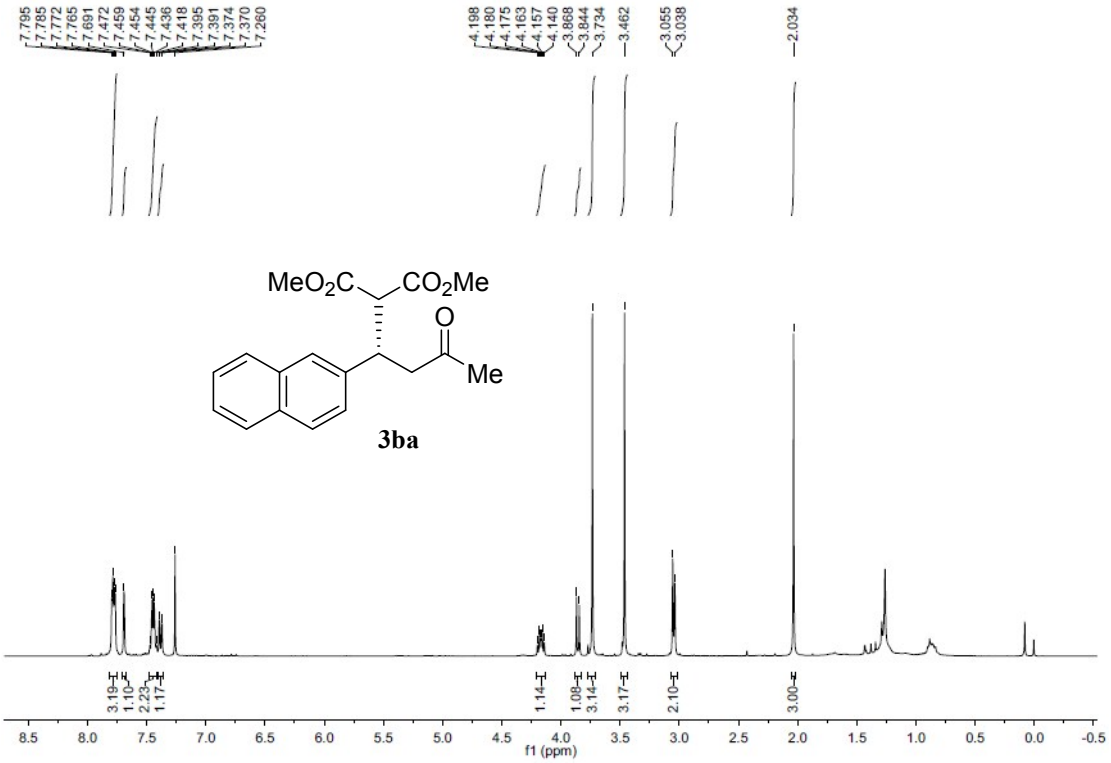
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.633	1014.357	2501.650	49.12	51.45	n.a.
2		12.530	1050.520	2360.347	50.88	48.55	n.a.
Total:			**2064.877**	**4861.996**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.747	570.328	1514.715	93.49	93.01	n.a.
2		12.743	39.684	113.845	6.51	6.99	n.a.
Total:			**610.011**	**1628.560**	**100.00**	**100.00**	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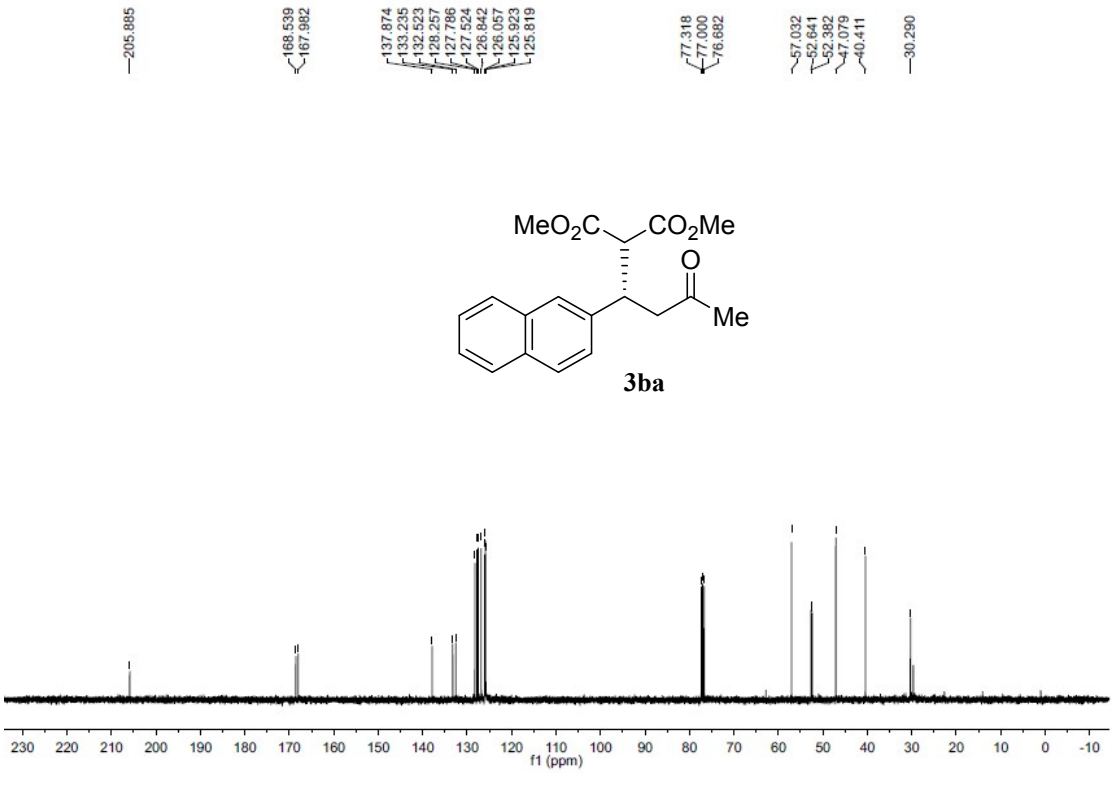
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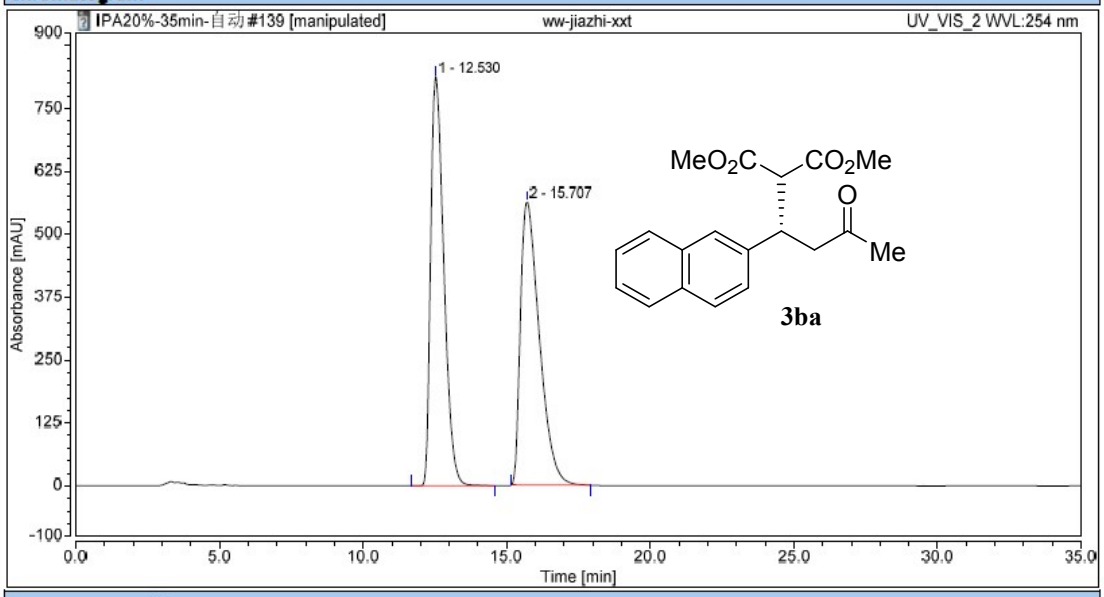
f1 (ppm)

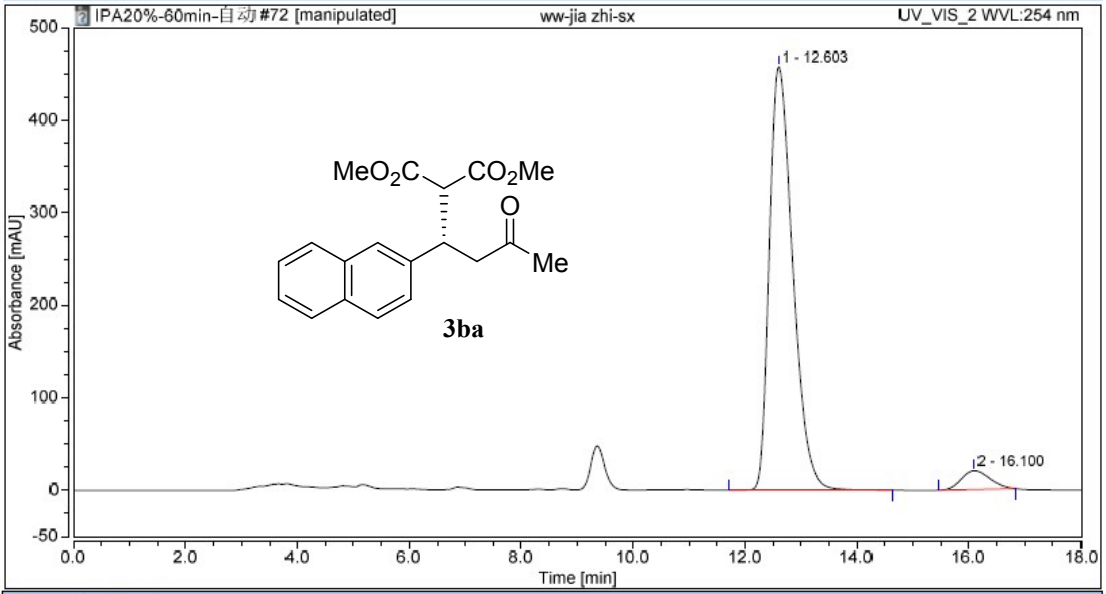
Chromatogram



Integration Results

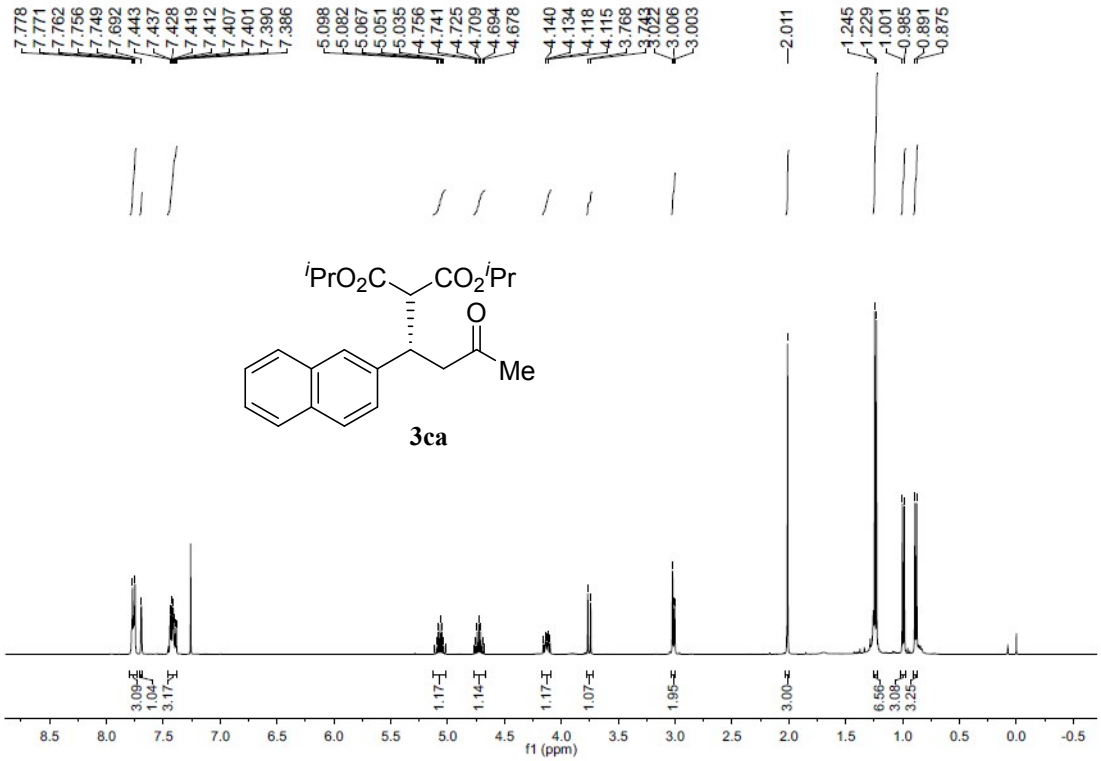
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.530	431.468	812.980	50.16	59.07	n.a.
2		15.707	428.680	563.244	49.84	40.93	n.a.
Total:			**860.148**	**1376.224**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.603	222.364	458.214	94.83	95.73	n.a.
2		16.100	12.126	20.446	5.17	4.27	n.a.
Total:			**234.490**	**478.660**	**100.00**	**100.00**	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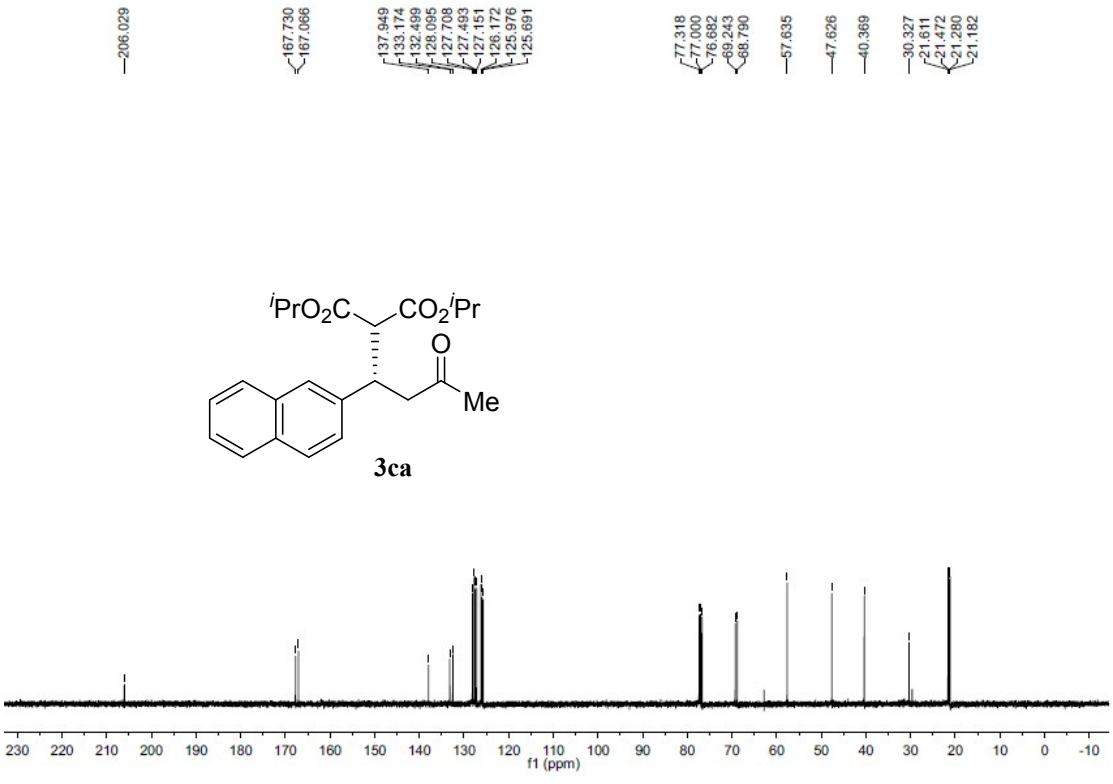
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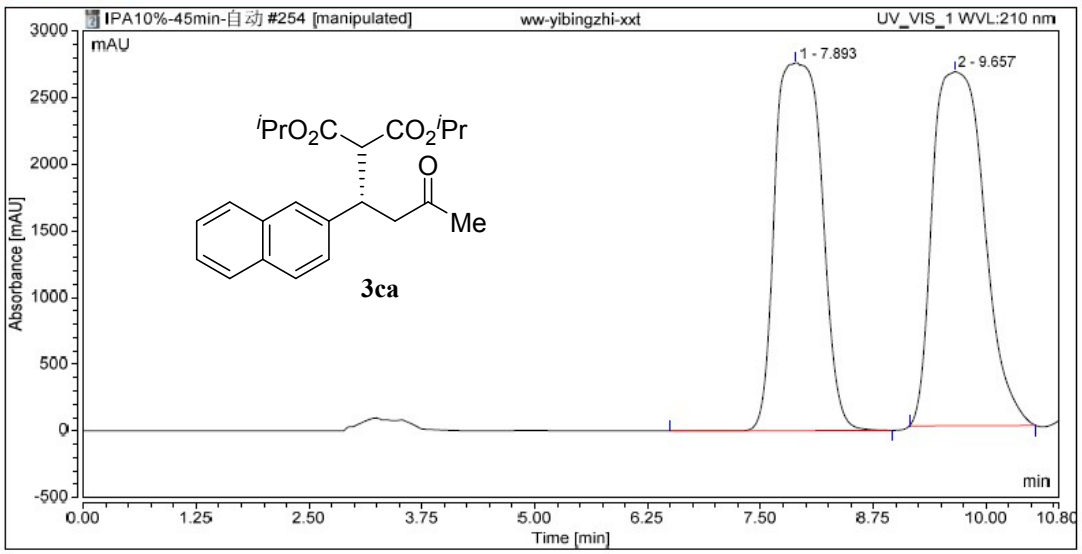
f1 (ppm)

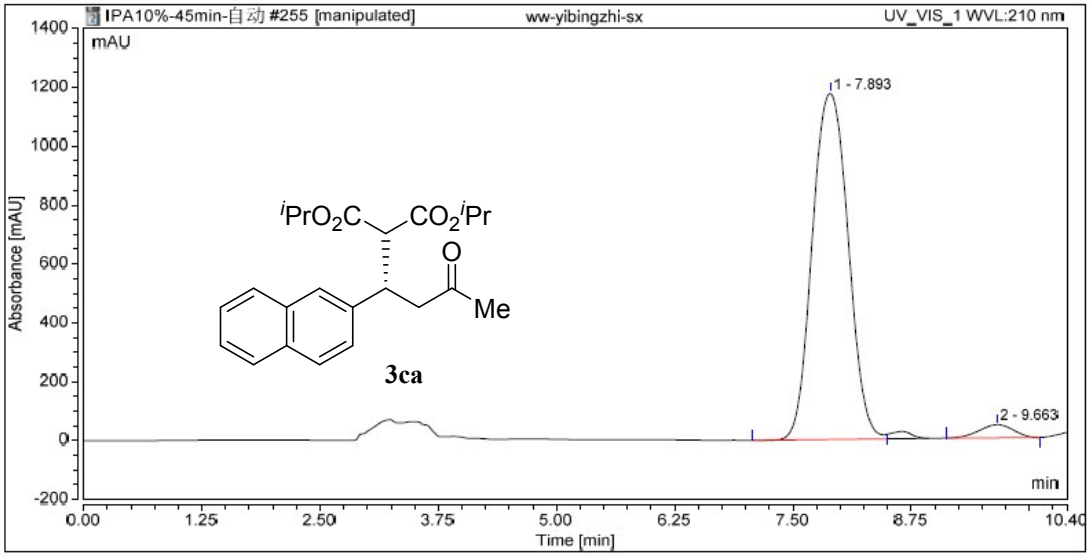
Chromatogram



Integration Results

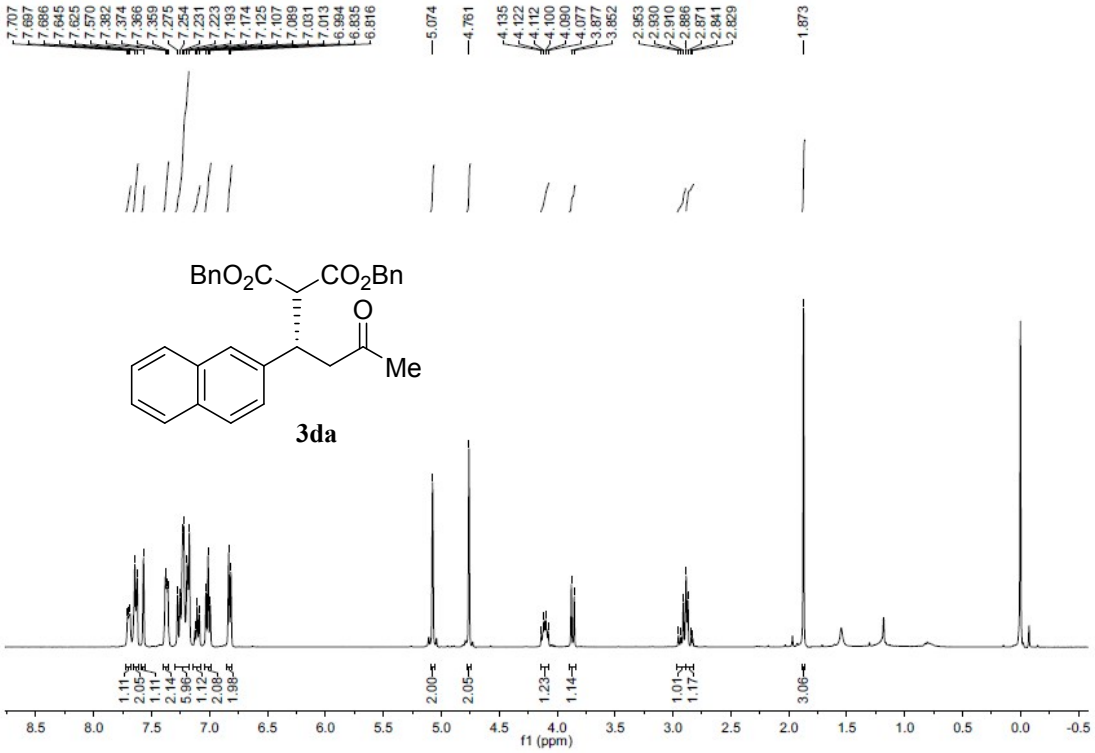
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.893	1657.413	2759.267	48.45	50.95	n.a.
2		9.657	1763.415	2656.510	51.55	49.05	n.a.
Total:			**3420.828**	**5415.777**	**100.00**	**100.00**	

Chromatogram

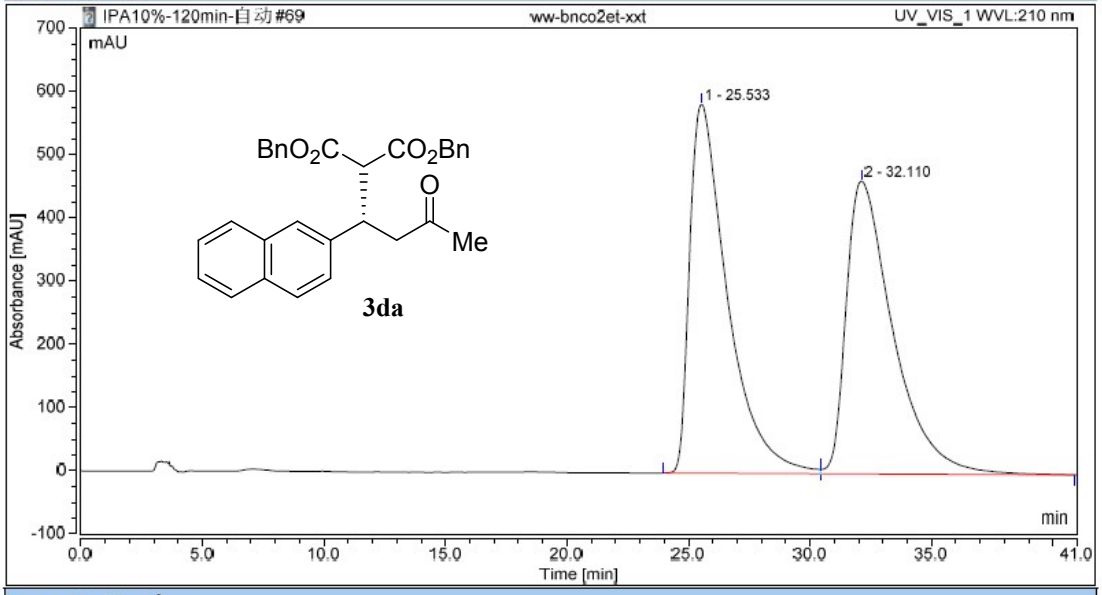


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.893	516.201	1175.119	96.54	96.37	n.a.
2		9.663	18.477	44.254	3.46	3.63	n.a.
Total:			**534.678**	**1219.374**	**100.00**	**100.00**	



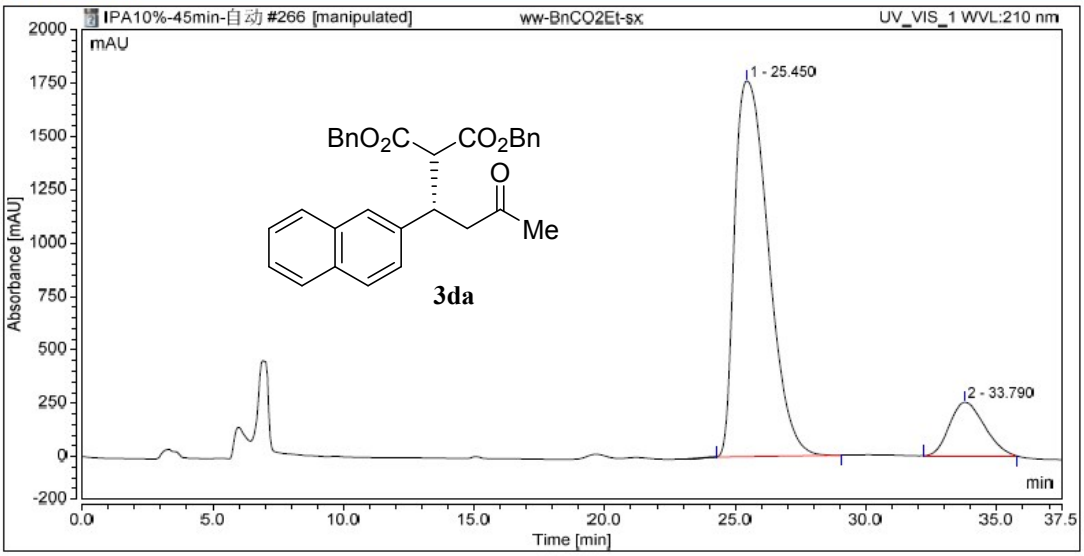
Chromatogram



Integration Results

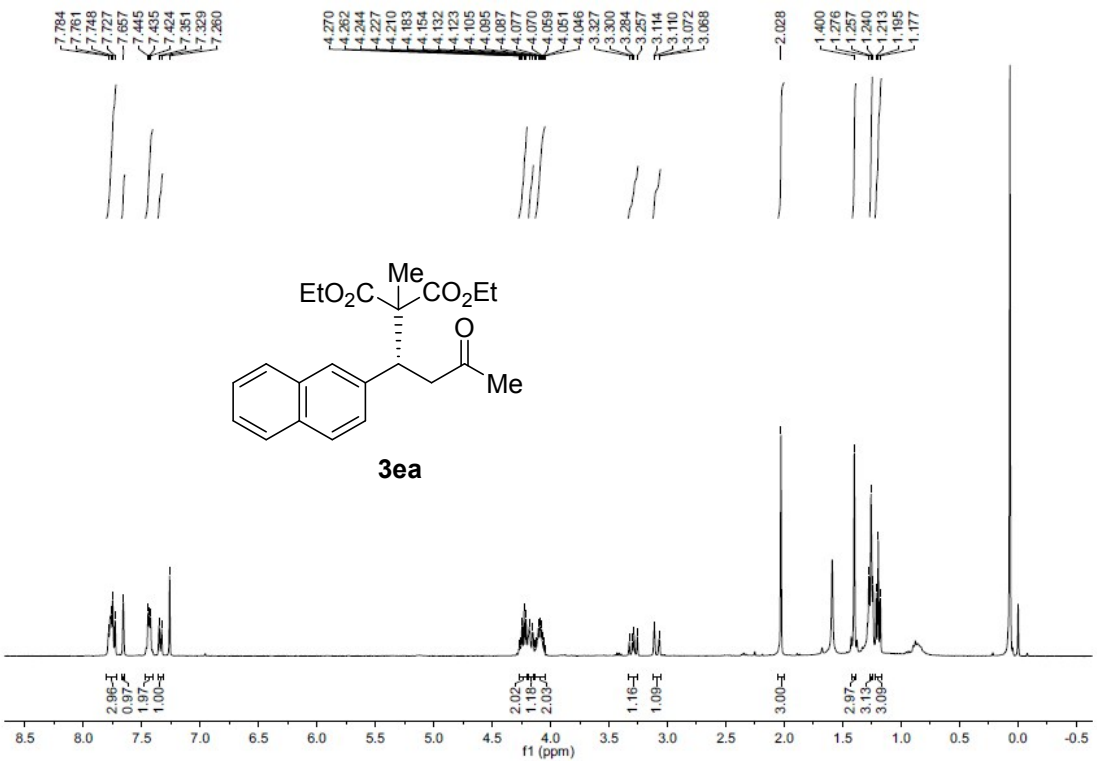
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		25.533	1050.156	584.036	50.39	55.75	n.a.
2		32.110	1033.896	463.470	49.61	44.25	n.a.
Total:			**2084.053**	**1047.506**	**100.00**	**100.00**	

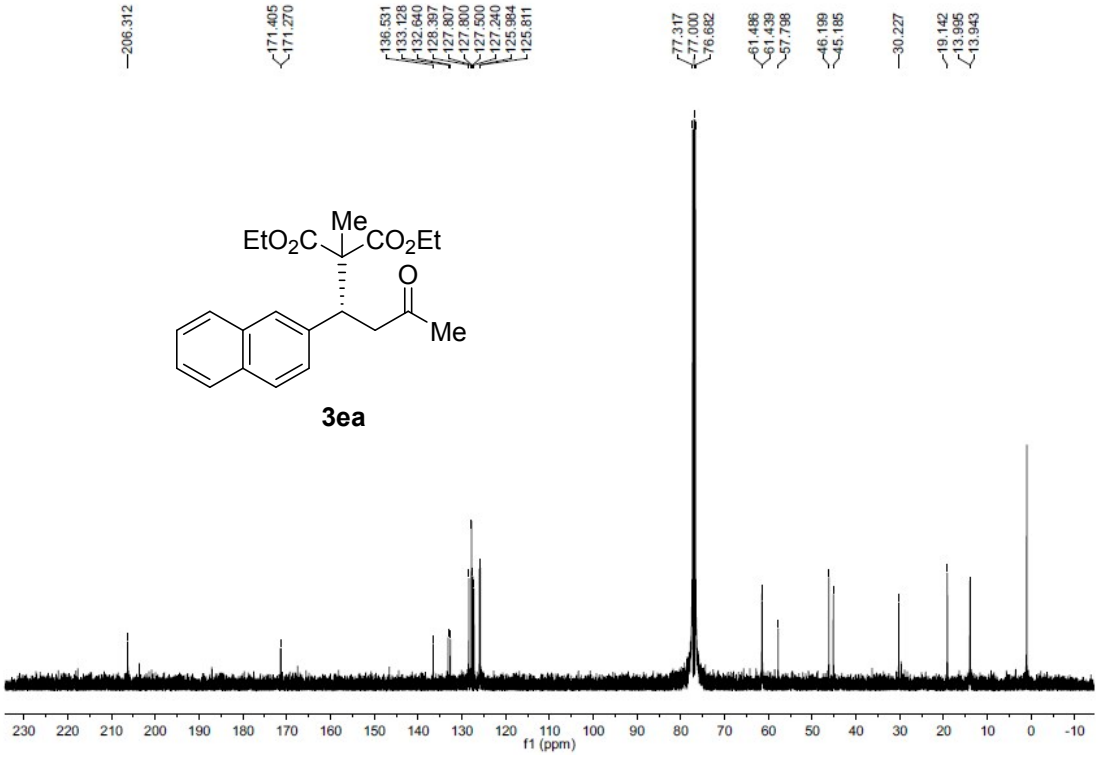
Chromatogram

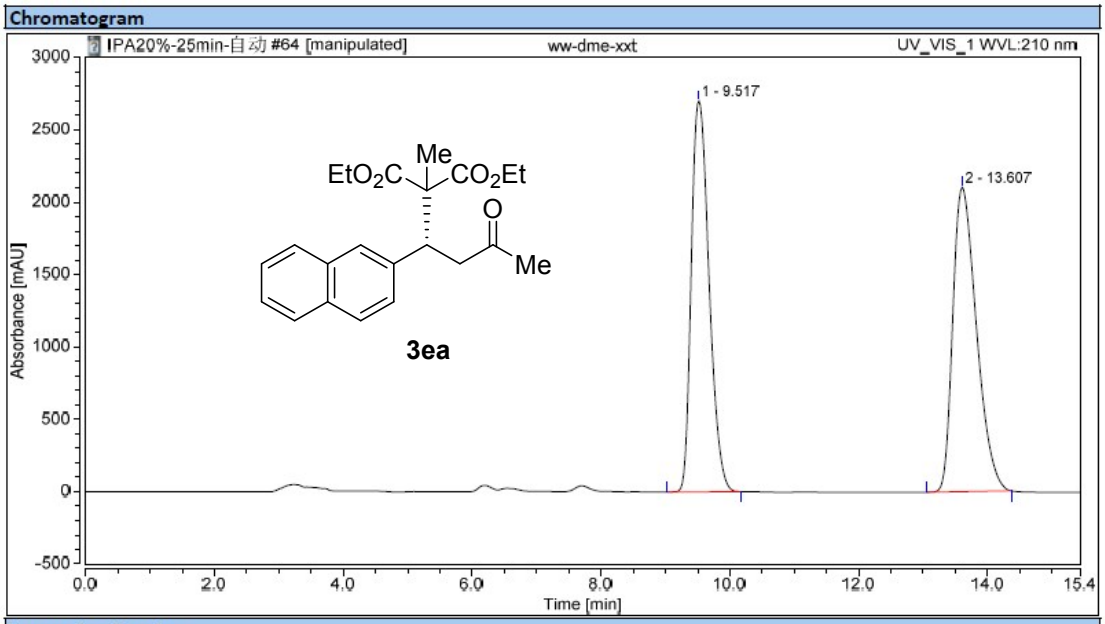


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		25.450	2634.109	1760.901	87.17	87.52	n.a.
2		33.790	387.604	251.008	12.83	12.48	n.a.
Total:			**3021.712**	**2011.910**	**100.00**	**100.00**	



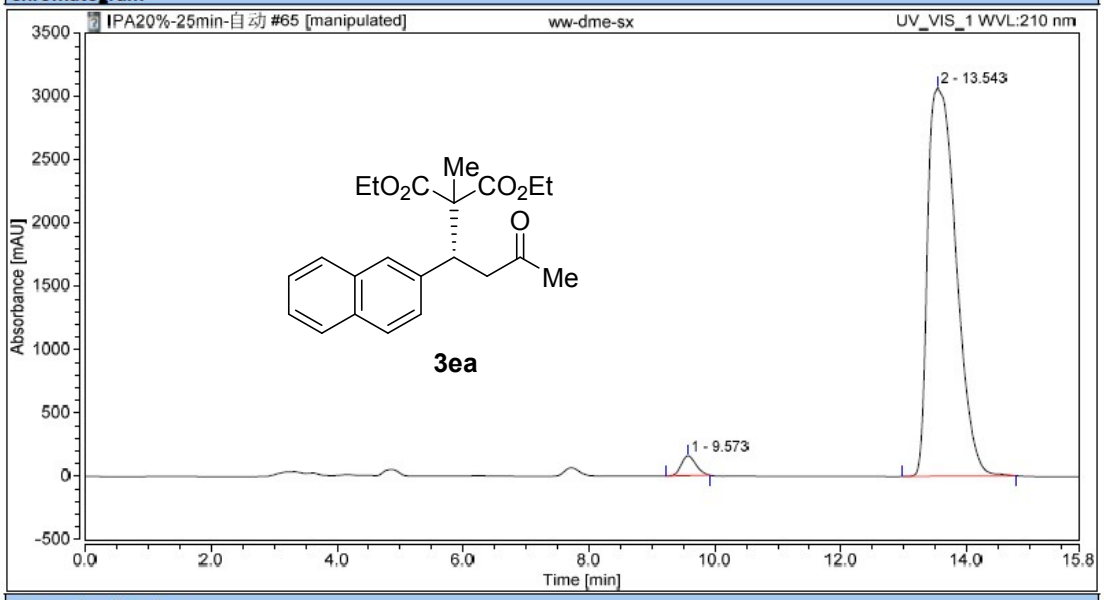




Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.517	864.926	2701.827	49.11	56.21	n.a.
2		13.607	896.133	2104.801	50.89	43.79	n.a.
Total:			**1761.059**	**4806.628**	**100.00**	**100.00**	

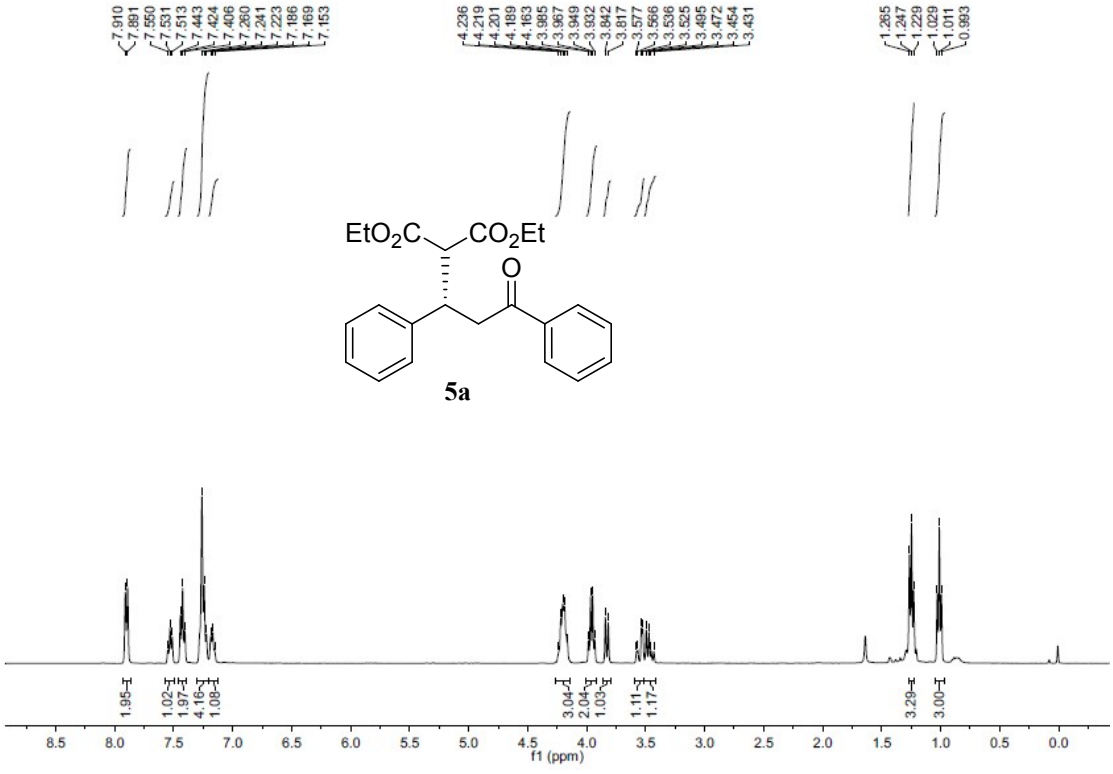
Chromatogram



3ea

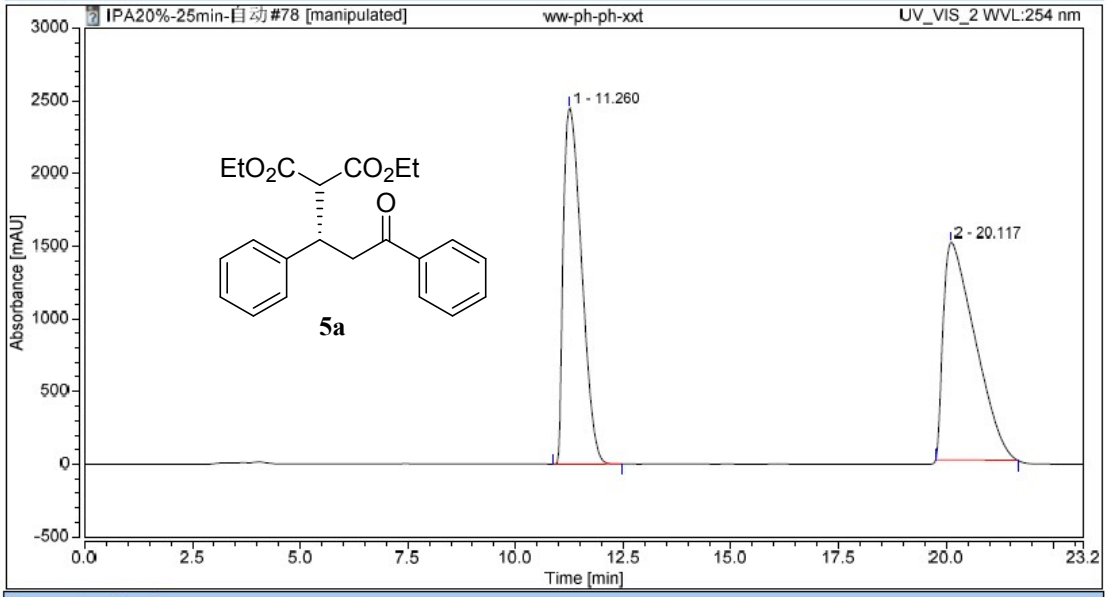
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.573	42.447	157.704	2.58	4.88	n.a.
2		13.543	1602.750	3073.590	97.42	95.12	n.a.
Total:			**1645.197**	**3231.295**	**100.00**	**100.00**	



5a

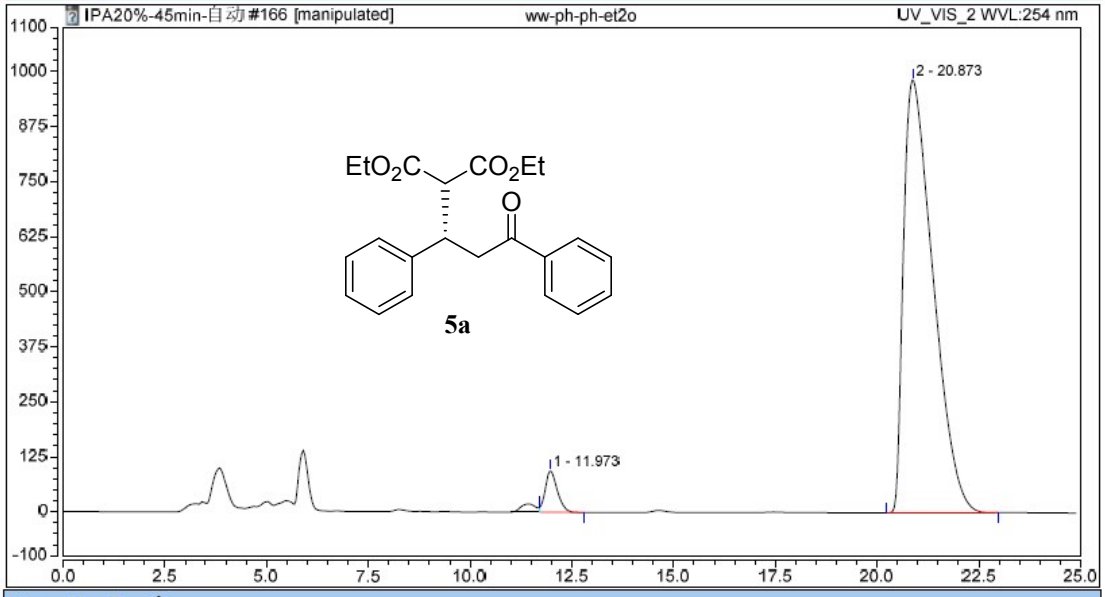
Chromatogram



Integration Results

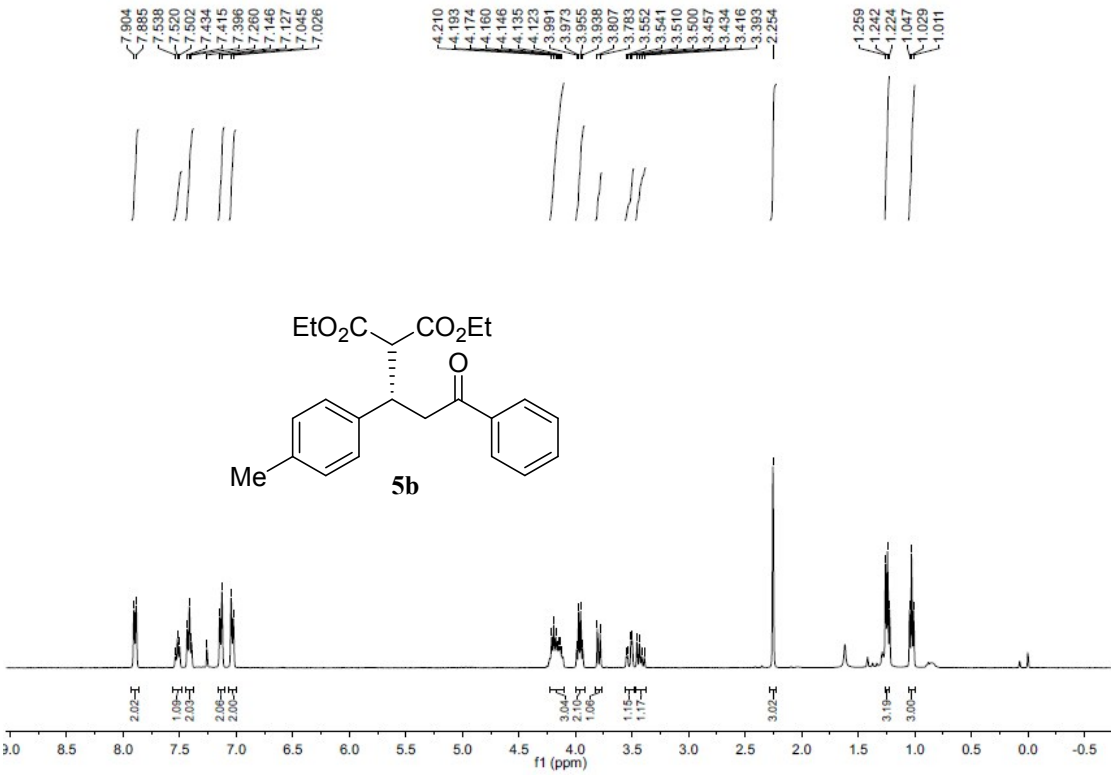
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.260	1199.402	2450.919	48.31	62.09	n.a.
2		20.117	1283.242	1496.690	51.69	37.91	n.a.
Total:			**2482.643**	**3947.610**	**100.00**	**100.00**	

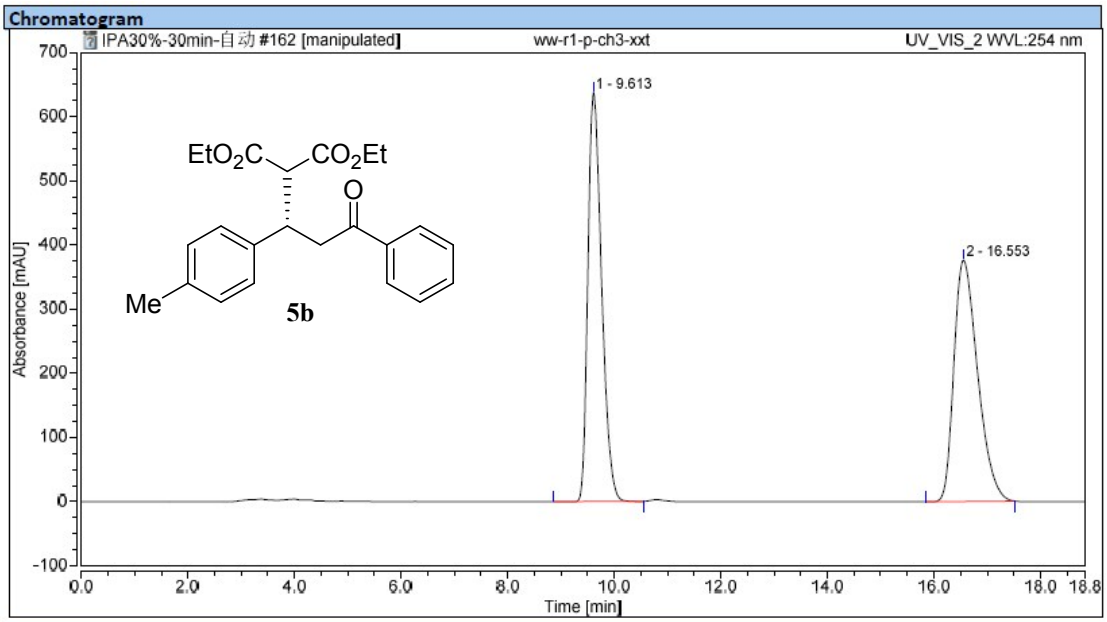
Chromatogram



Integration Results

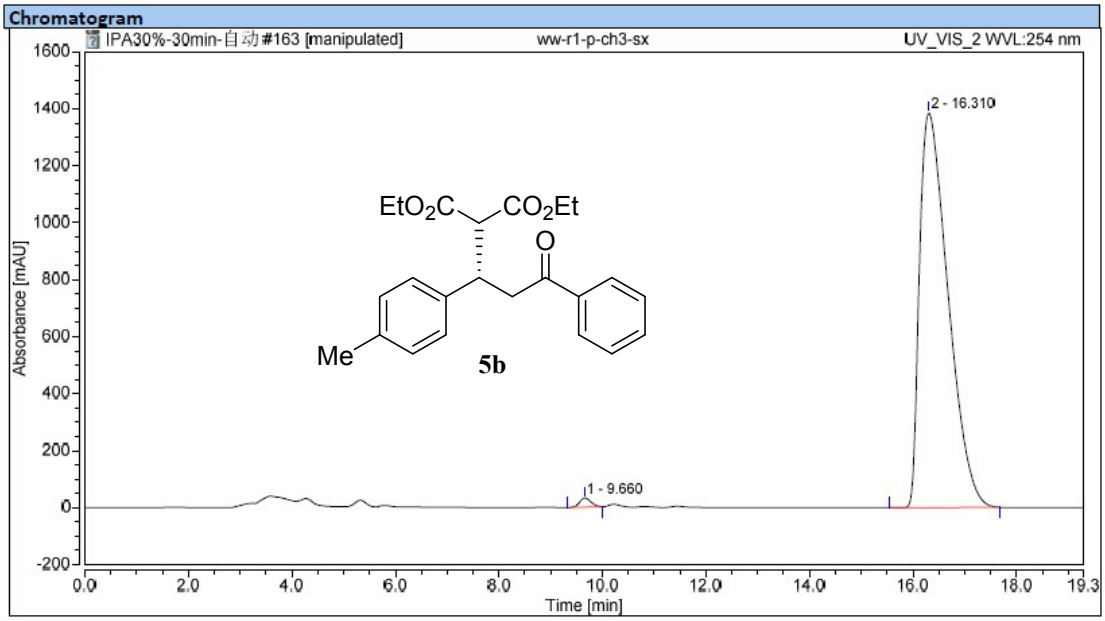
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.973	32.504	94.187	3.78	8.74	n.a.
2		20.873	827.580	983.888	96.22	91.26	n.a.
Total:			**860.084**	**1078.075**	**100.00**	**100.00**	





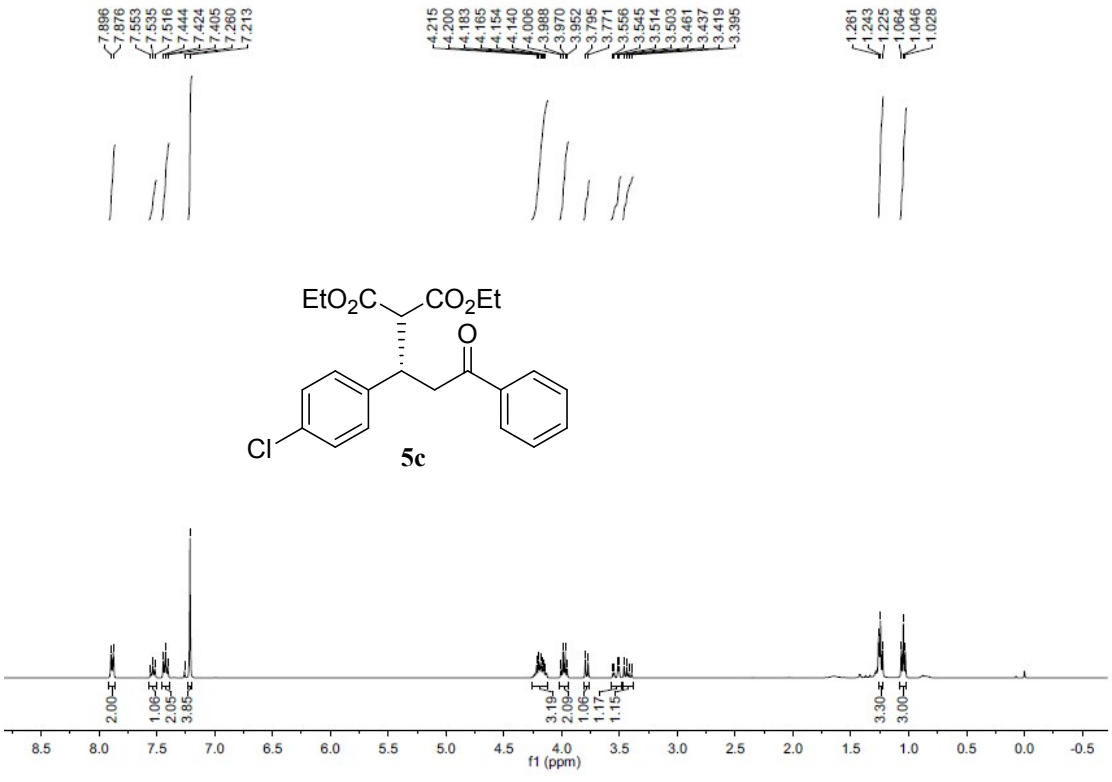
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.613	189.814	637.260	49.49	62.86	n.a.
2		16.553	193.700	376.492	50.51	37.14	n.a.
Total:			**383.514**	**1013.752**	**100.00**	**100.00**	

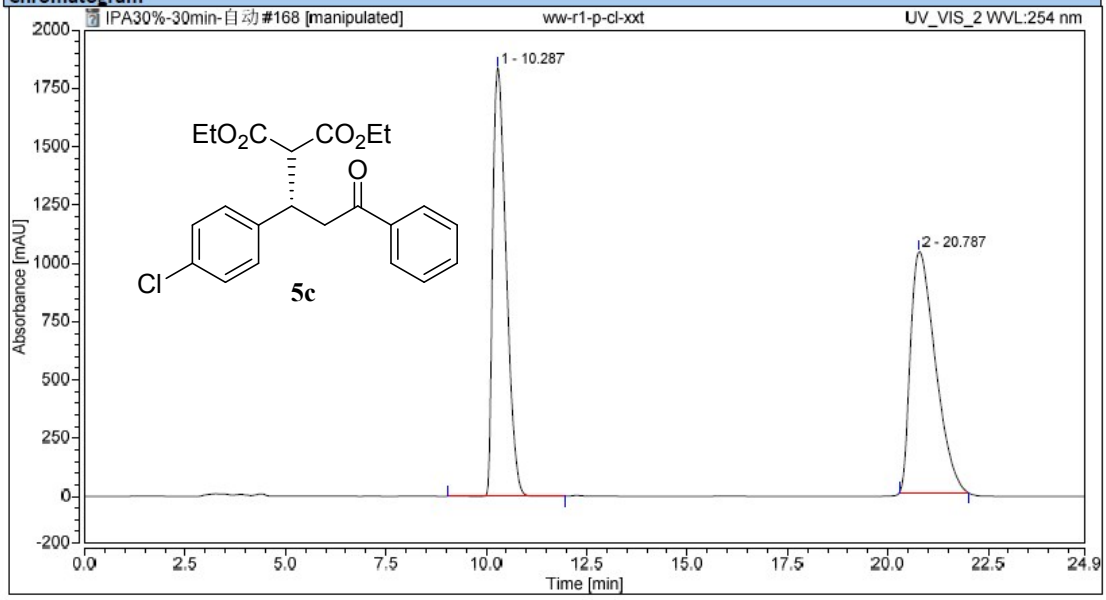


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.660	8.291	32.371	0.93	2.28	n.a.
2		16.310	882.435	1385.347	99.07	97.72	n.a.
Total:			**890.726**	**1417.717**	**100.00**	**100.00**	



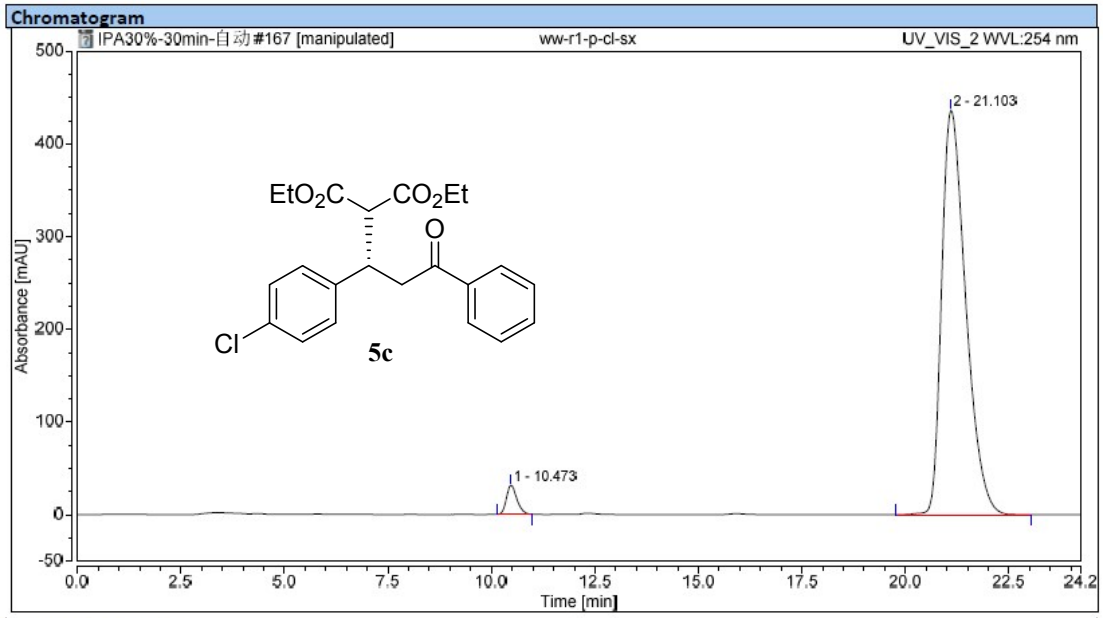
Chromatogram



Integration Results

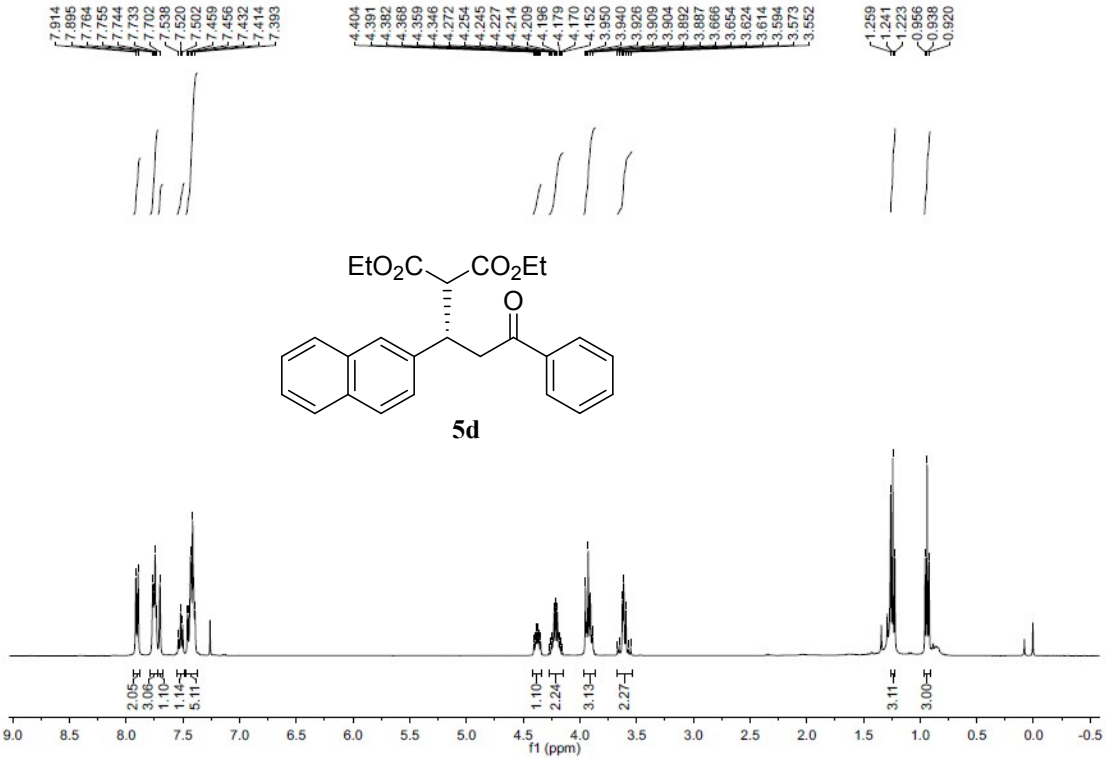
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.287	712.030	1836.884	48.90	63.94	n.a.
2		20.787	744.198	1035.799	51.10	36.06	n.a.
Total:			**1456.228**	**2872.683**	**100.00**	**100.00**	

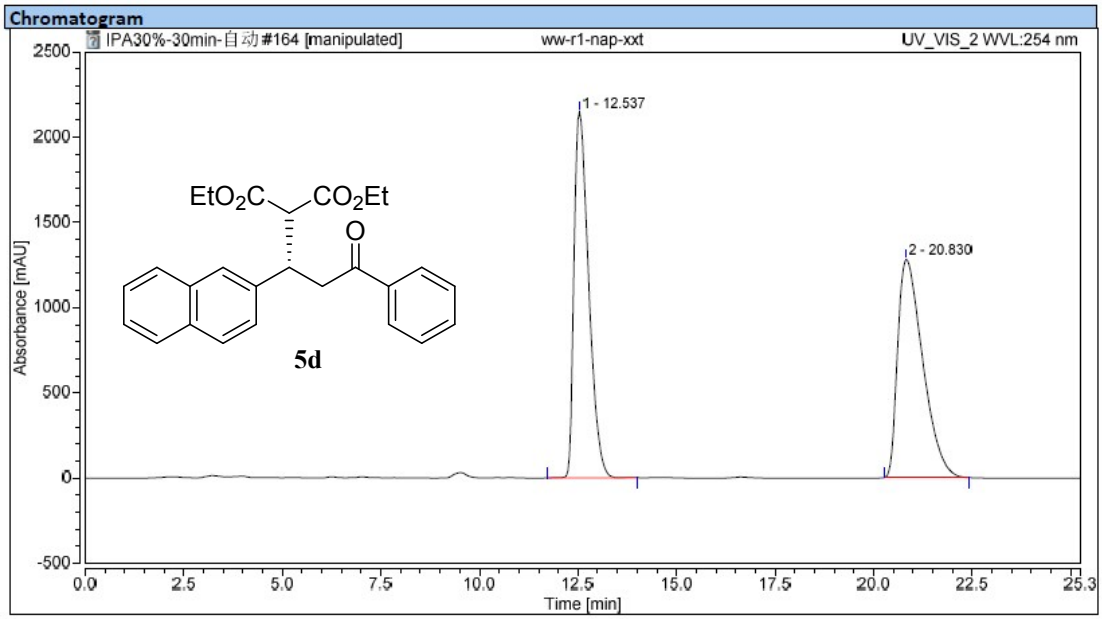
Chromatogram



Integration Results

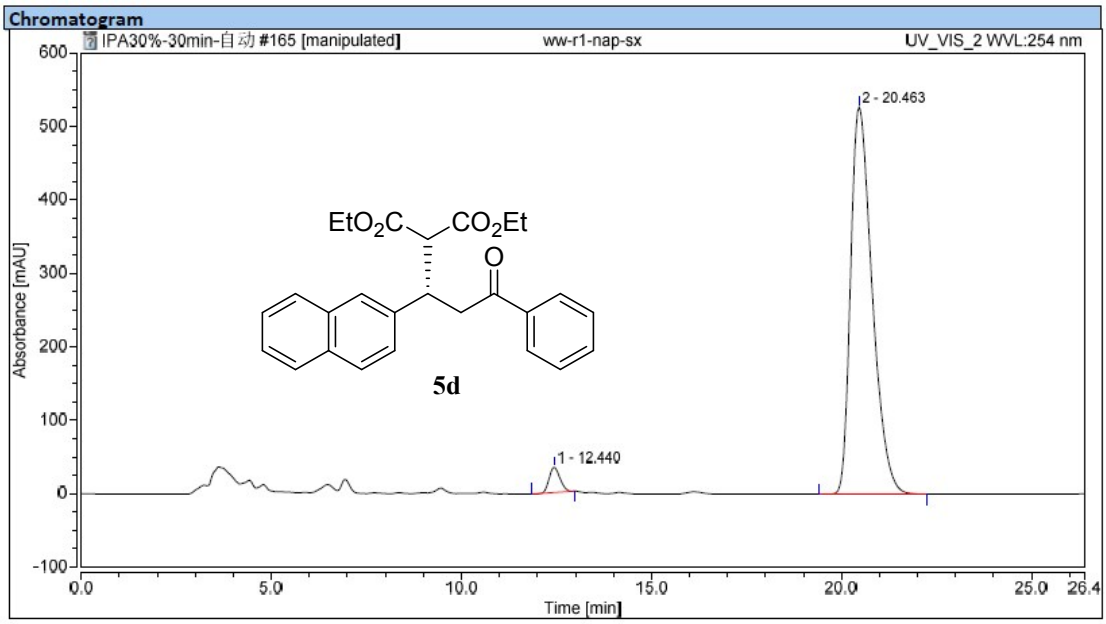
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.473	9.250	31.771	3.05	6.78	n.a.
2		21.103	294.319	436.527	96.95	93.22	n.a.
Total:			**303.569**	**468.298**	**100.00**	**100.00**	





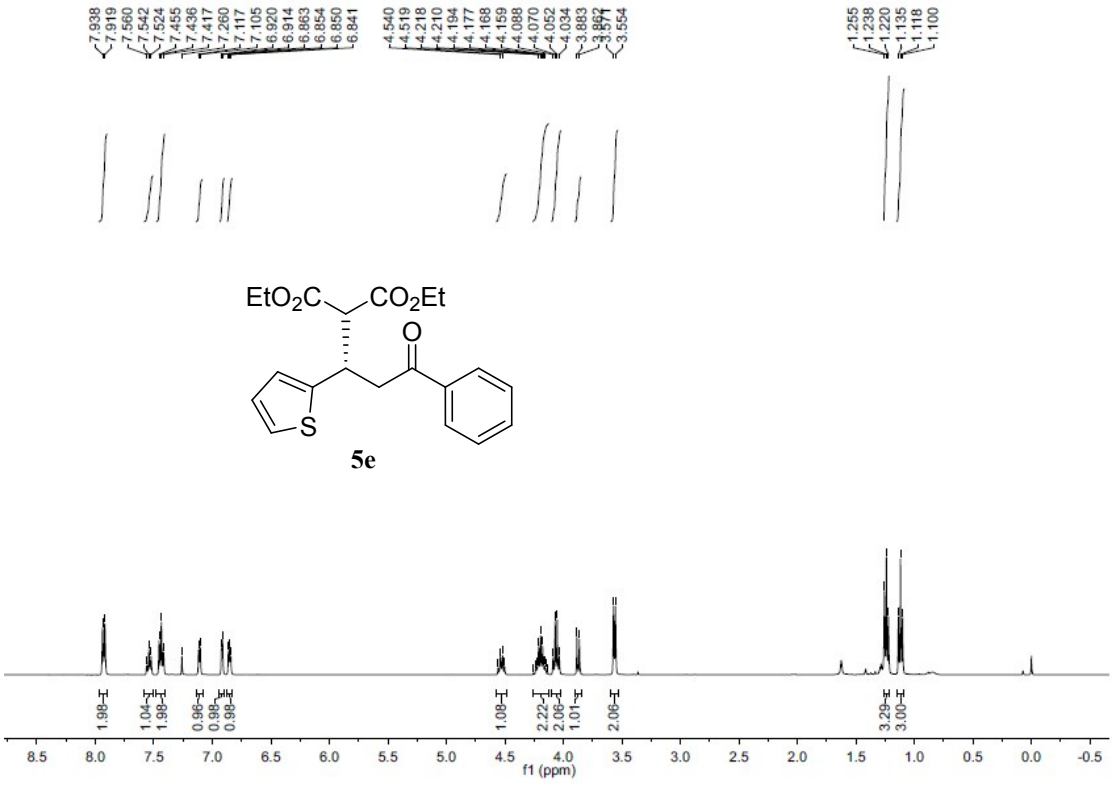
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.537	925.585	2147.229	49.49	62.64	n.a.
2		20.830	944.669	1280.886	50.51	37.36	n.a.
Total:			**1870.254**	**3428.114**	**100.00**	**100.00**	

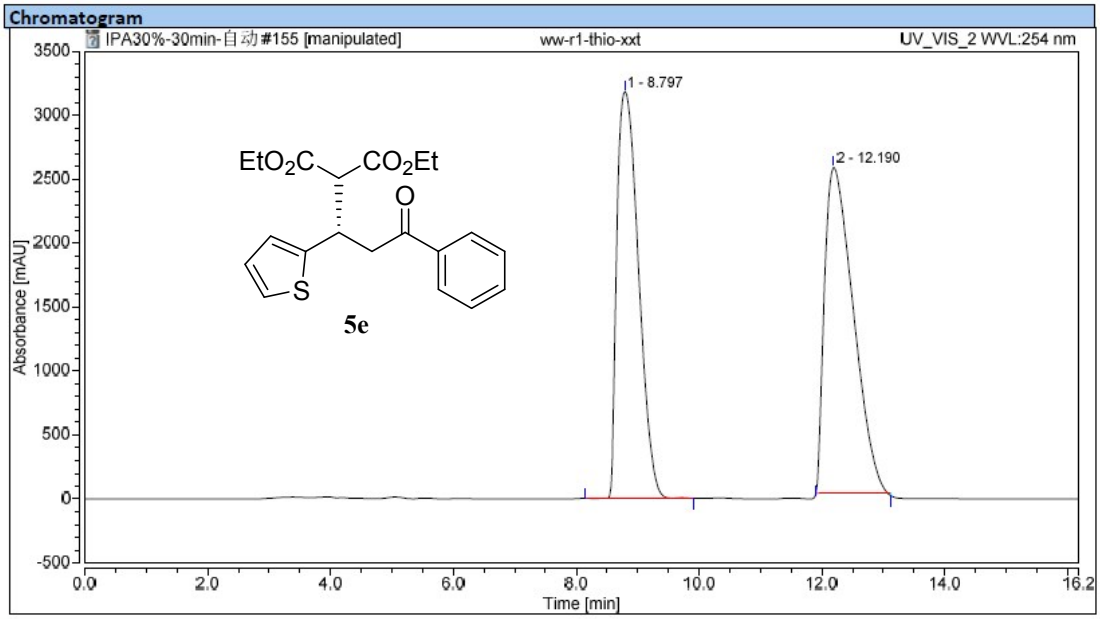


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.440	11.215	34.340	3.13	6.12	n.a.
2		20.463	346.846	527.161	96.87	93.88	n.a.
Total:			**358.060**	**561.501**	**100.00**	**100.00**	



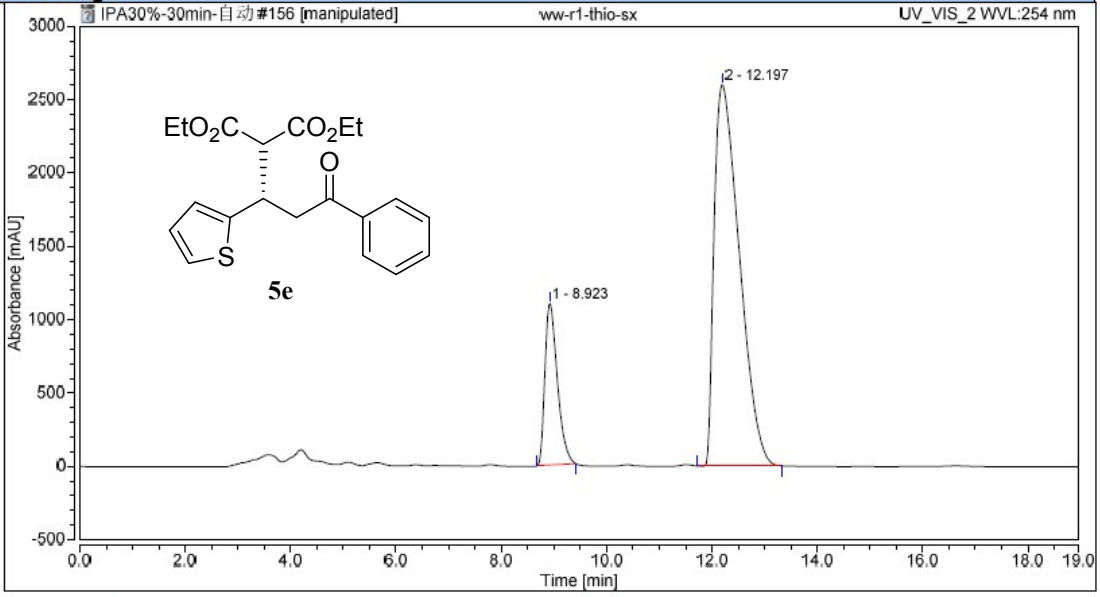
Chromatogram



Integration Results

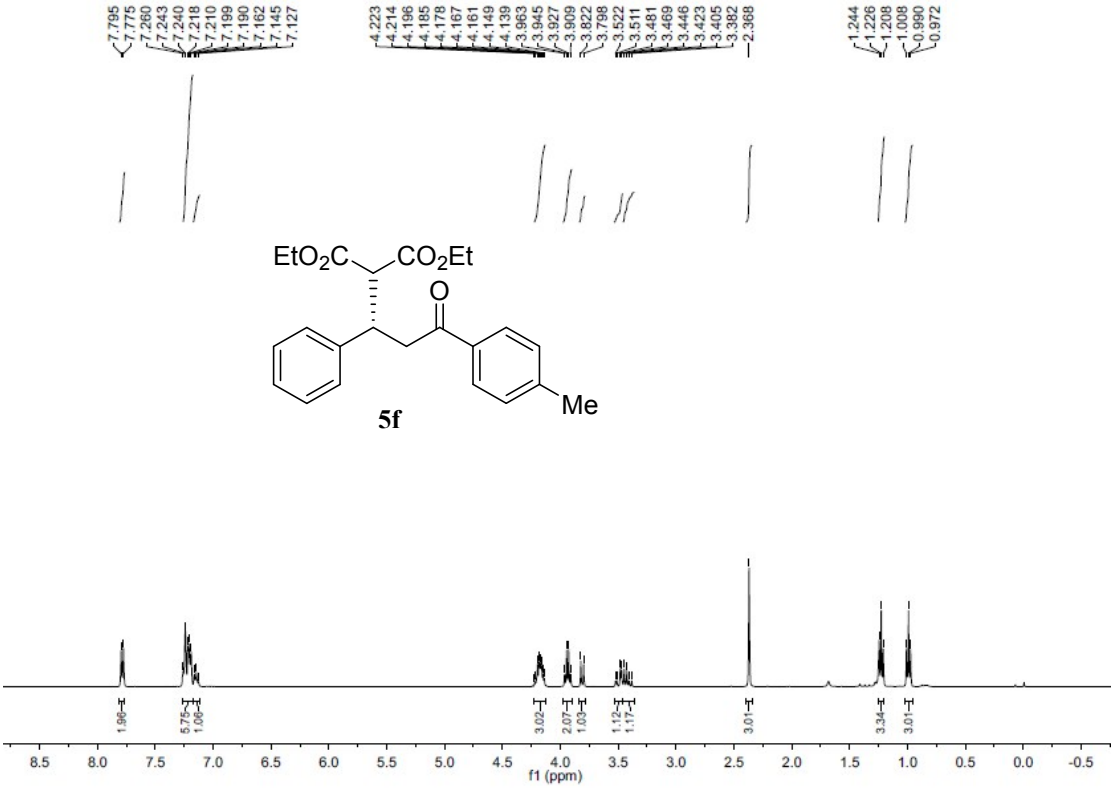
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.797	1294.325	3181.227	48.46	55.54	n.a.
2		12.190	1376.496	2547.071	51.54	44.46	n.a.
Total:			**2670.820**	**5728.298**	**100.00**	**100.00**	

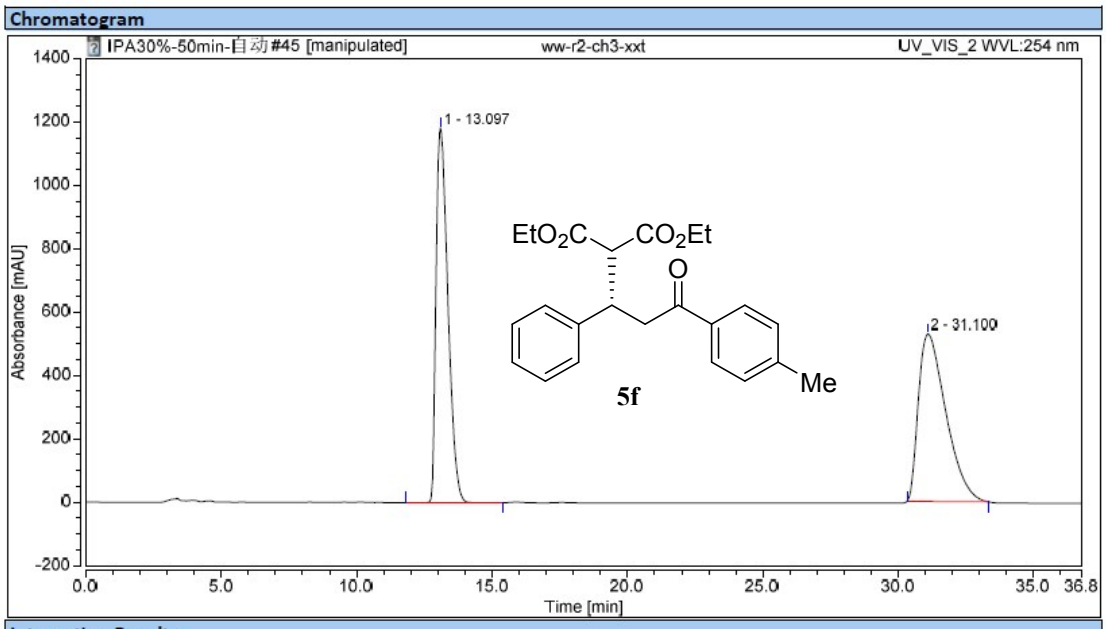
Chromatogram



Integration Results

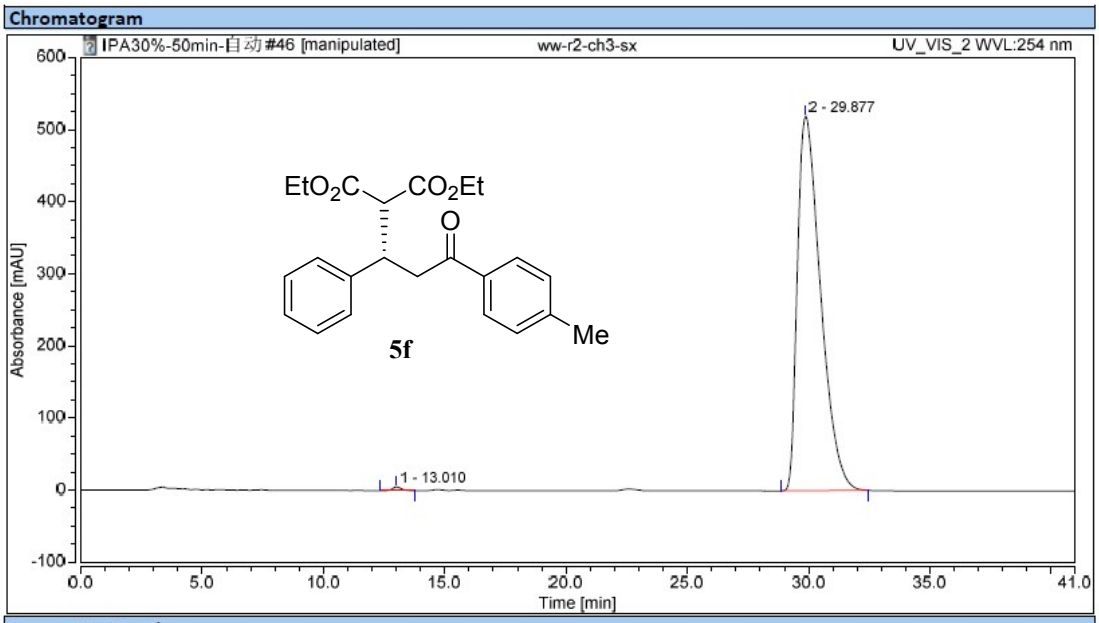
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.923	300.944	1105.090	17.30	29.83	n.a.
2		12.197	1438.842	2599.745	82.70	70.17	n.a.
Total:			**1739.787**	**3704.834**	**100.00**	**100.00**	





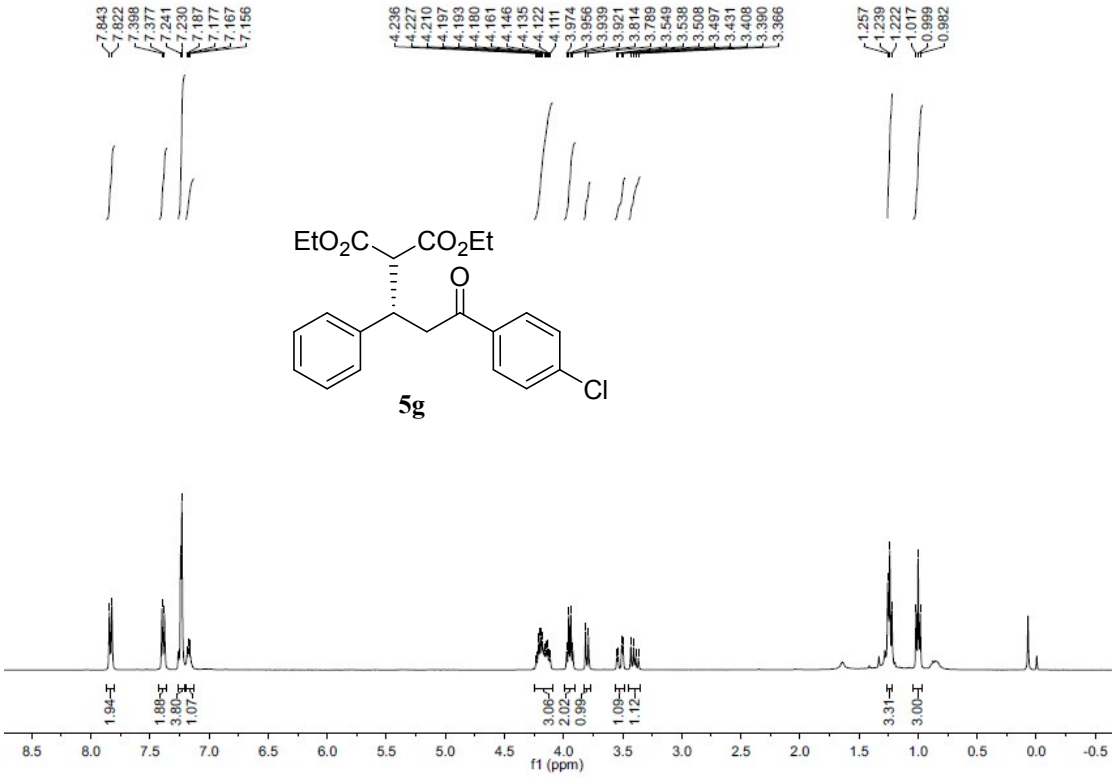
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.097	599.447	1181.131	49.16	69.09	n.a.
2		31.100	619.814	528.347	50.84	30.91	n.a.
Total:			**1219.261**	**1709.478**	**100.00**	**100.00**	

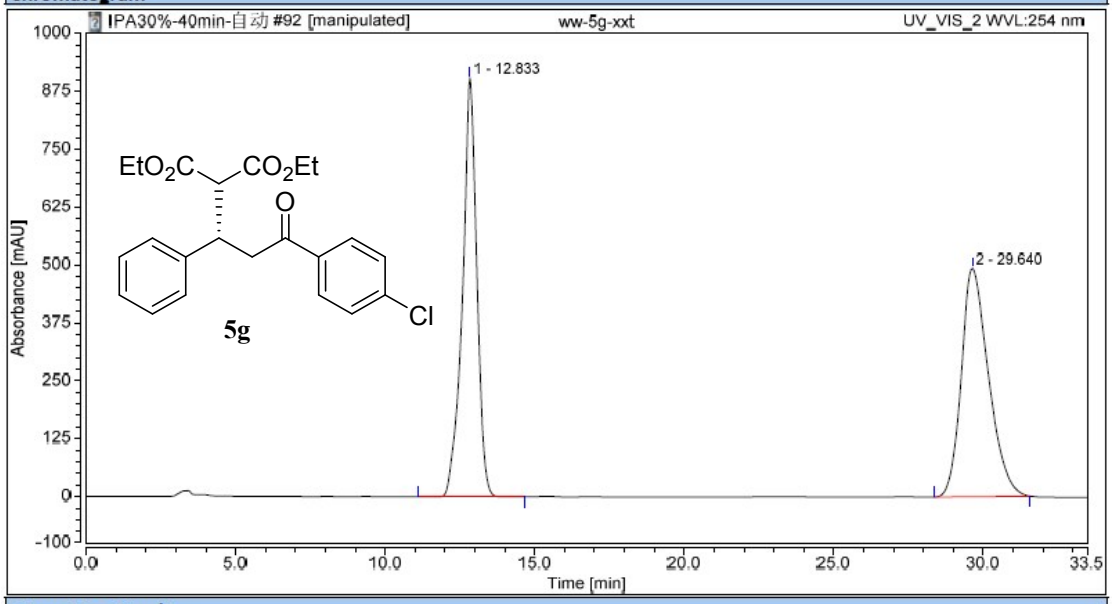


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.010	2.052	5.145	0.36	0.98	n.a.
2		29.877	574.035	519.766	99.64	99.02	n.a.
Total:			**576.087**	**524.911**	**100.00**	**100.00**	



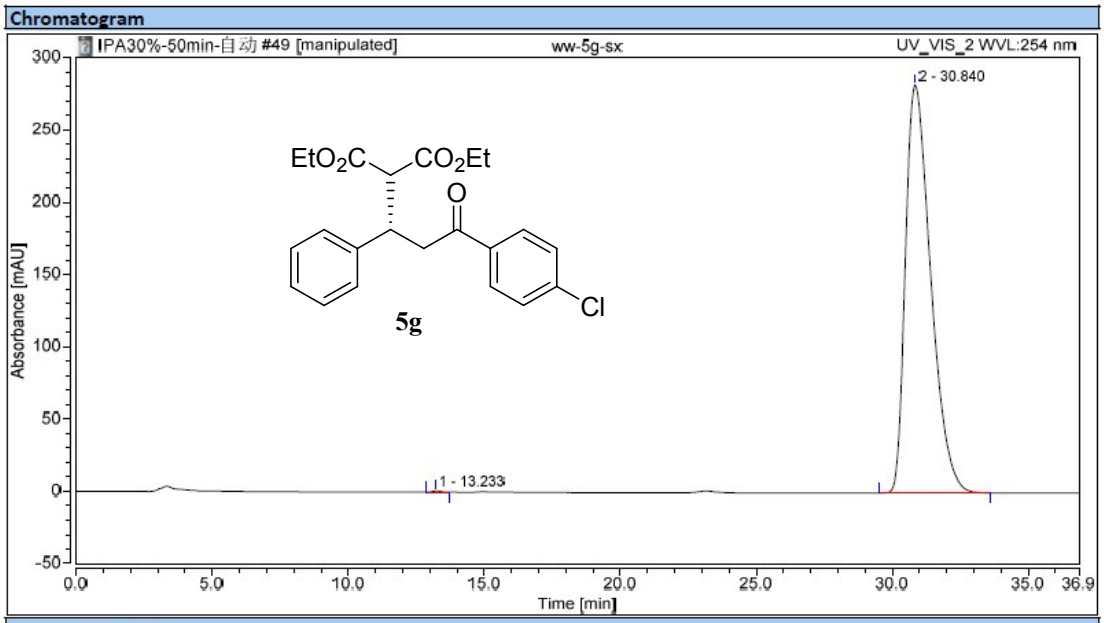
Chromatogram



Integration Results

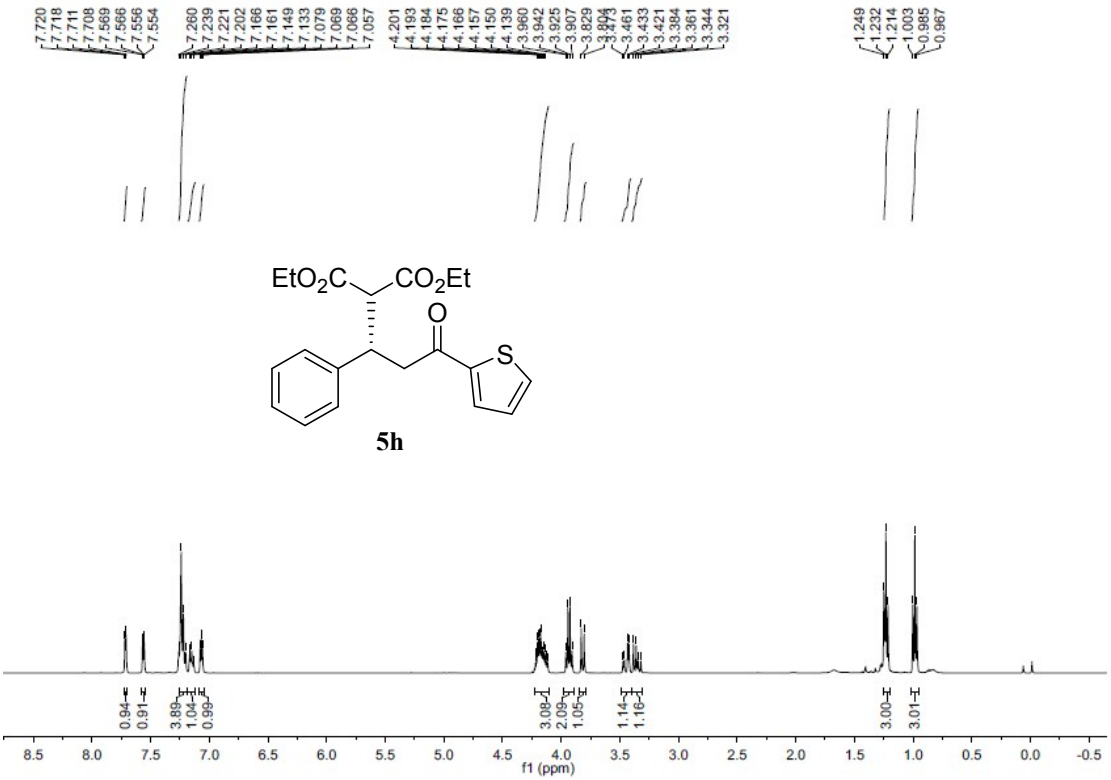
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.833	503.877	903.552	49.24	64.69	n.a.
2		29.640	519.453	493.236	50.76	35.31	n.a.
Total:			**1023.331**	**1396.788**	**100.00**	**100.00**	

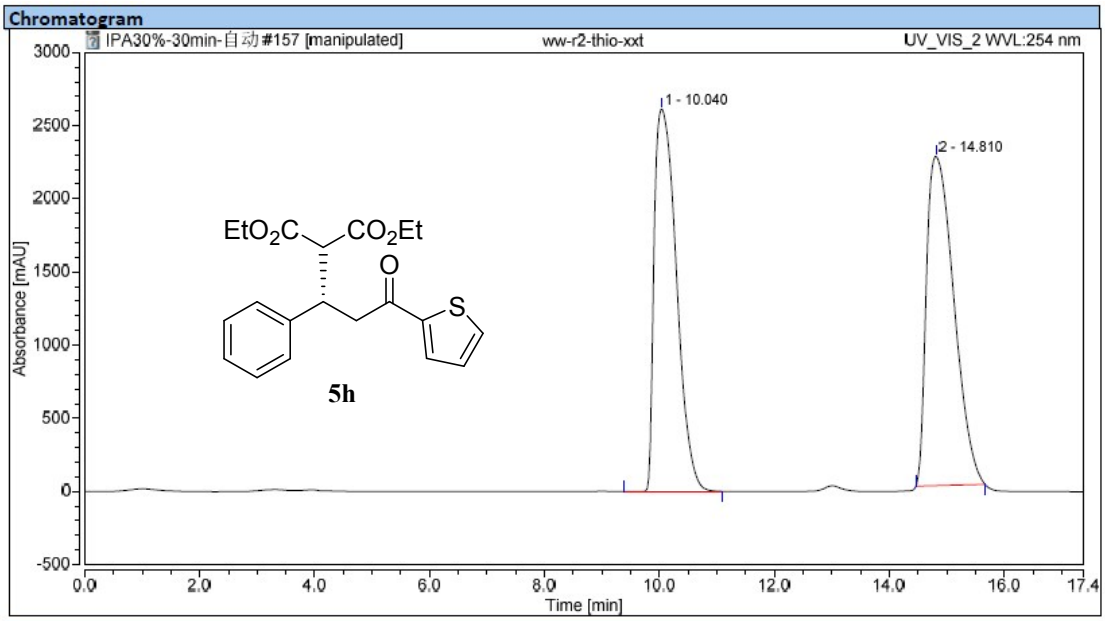
Chromatogram



Integration Results

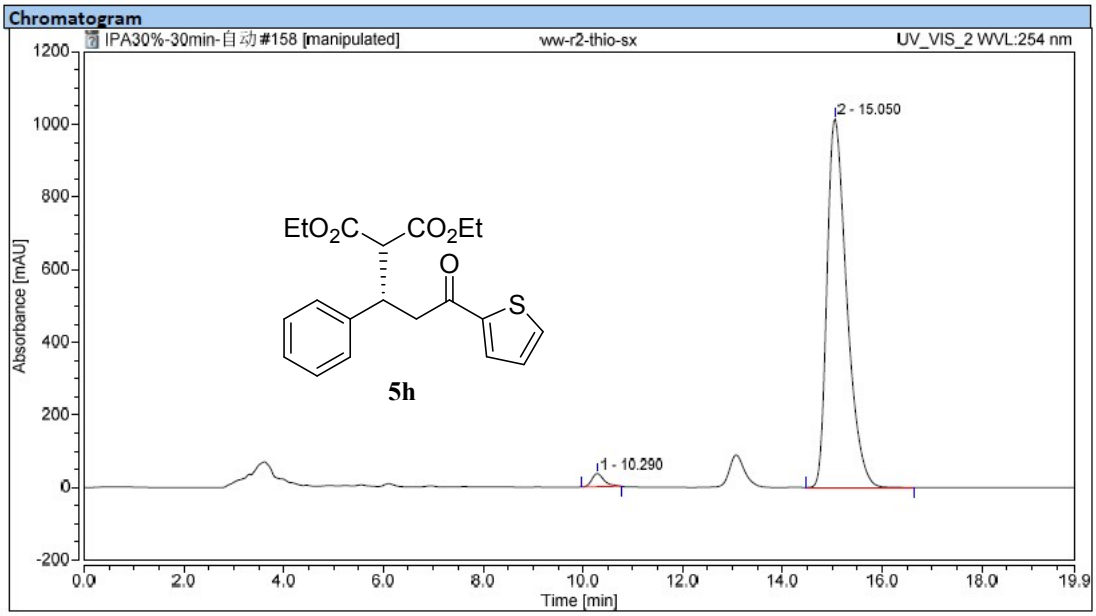
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.233	0.327	0.867	0.11	0.31	n.a.
2		30.840	303.968	282.399	99.89	99.69	n.a.
Total:			**304.295**	**283.265**	**100.00**	**100.00**	





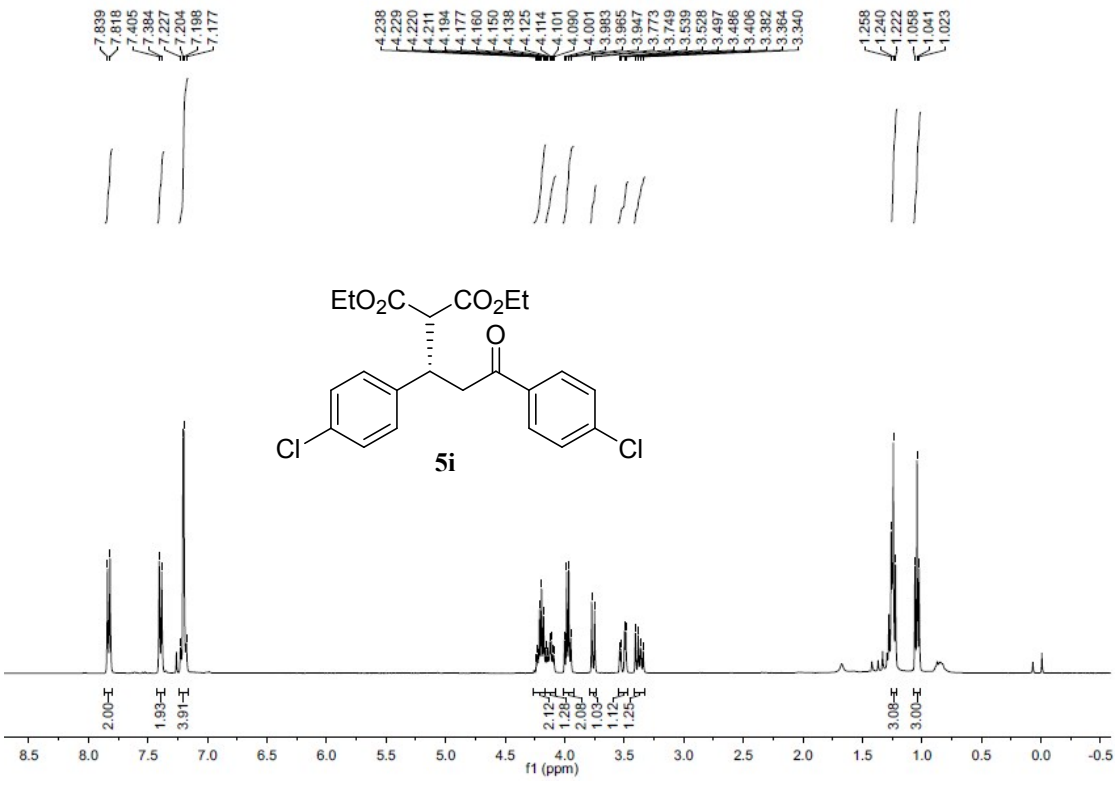
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.040	1169.906	2614.604	48.48	53.74	n.a.
2		14.810	1243.401	2251.066	51.52	46.26	n.a.
Total:			**2413.307**	**4865.670**	**100.00**	**100.00**	

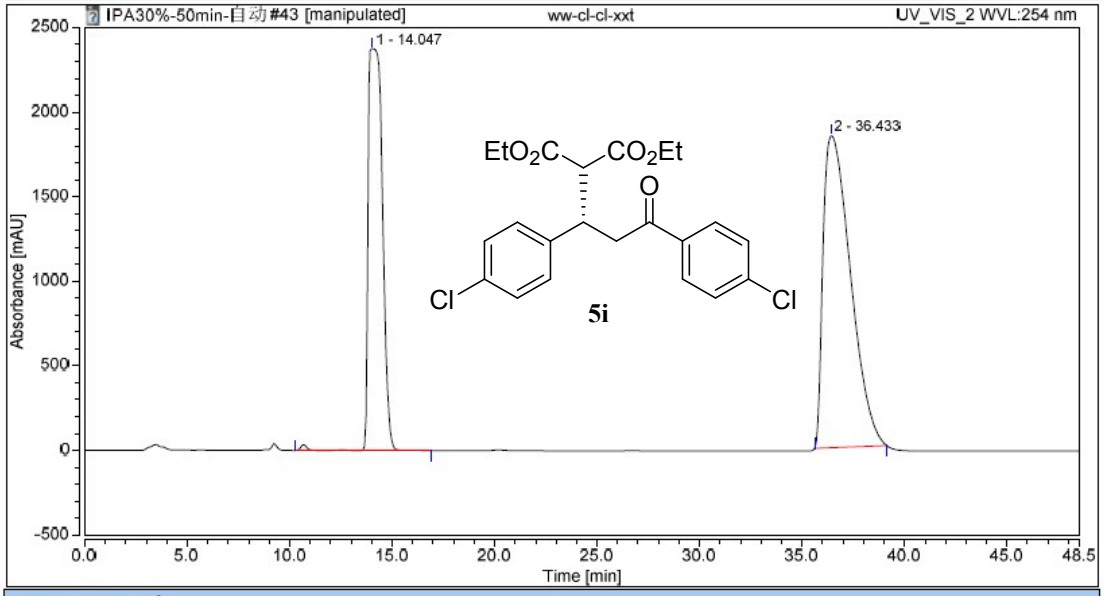


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.290	10.418	36.735	2.20	3.49	n.a.
2		15.050	463.574	1015.478	97.80	96.51	n.a.
Total:			**473.991**	**1052.213**	**100.00**	**100.00**	



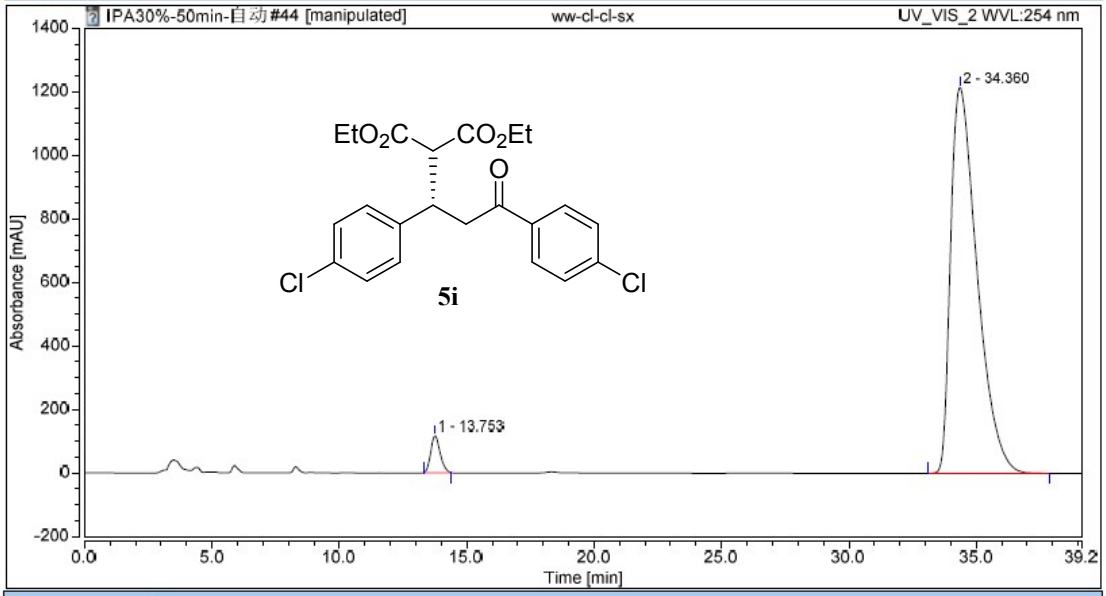
Chromatogram



Integration Results

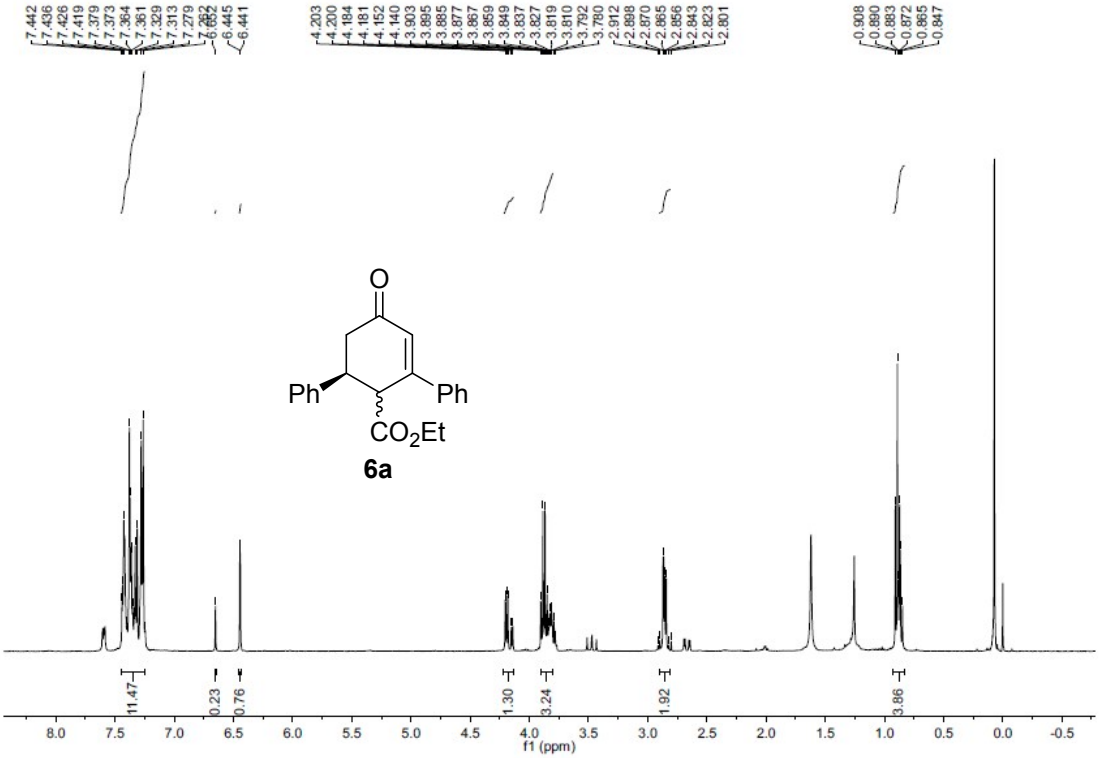
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.047	1907.711	2377.296	40.09	56.30	n.a.
2		36.433	2850.576	1844.996	59.91	43.70	n.a.
Total:			**4758.286**	**4222.293**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.753	49.397	116.499	3.27	8.75	n.a.
2		34.360	1462.244	1215.410	96.73	91.25	n.a.
Total:			**1511.640**	**1331.908**	**100.00**	**100.00**	



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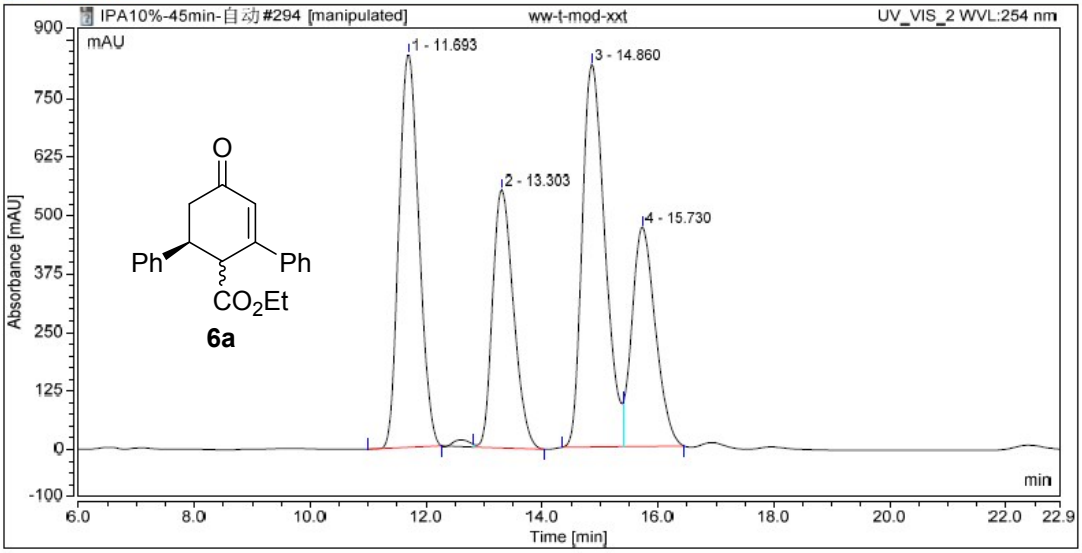
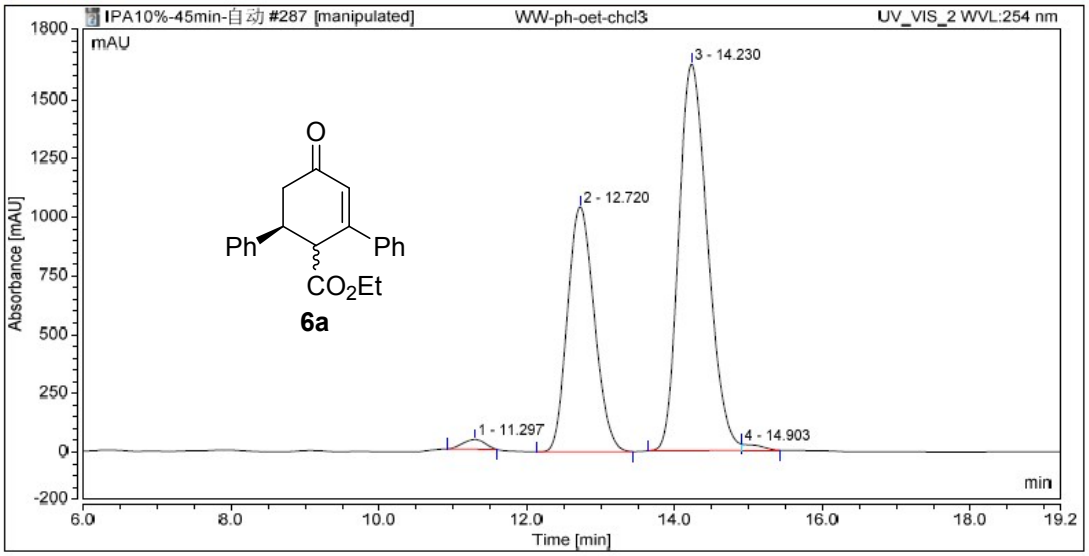


Integration Results

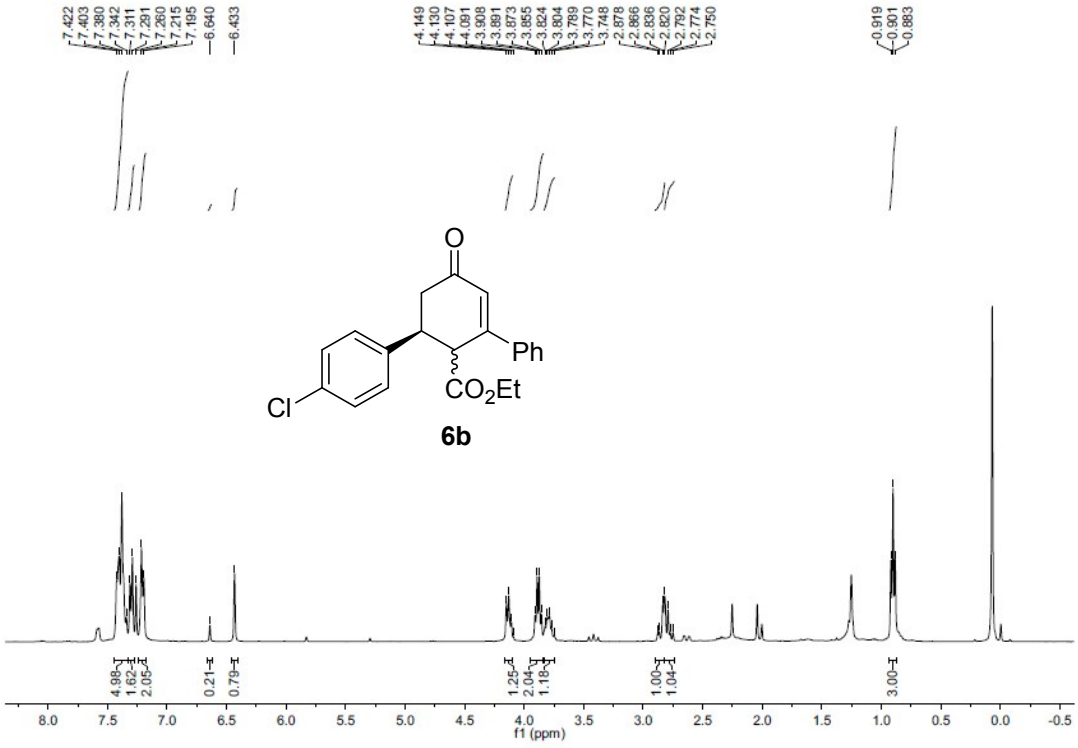
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.693	336.407	840.030	29.05	31.36	n.a.
2		13.303	231.382	552.044	19.98	20.61	n.a.
3		14.860	370.280	817.914	31.97	30.53	n.a.
4		15.730	220.037	469.027	19.00	17.51	n.a.
Total:			**1158.105**	**2679.016**	**100.00**	**100.00**	

Chromatogram

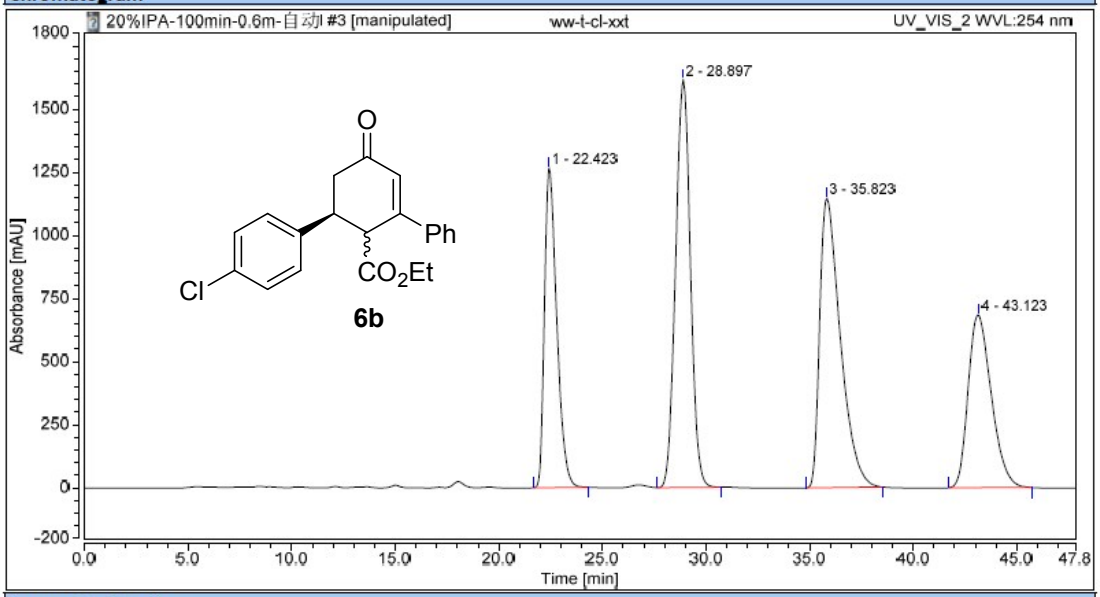


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.297	13.987	40.542	1.16	1.47	n.a.
2		12.720	438.597	1042.741	36.38	37.84	n.a.
3		14.230	745.444	1644.948	61.83	59.70	n.a.
4		14.903	7.690	27.121	0.64	0.98	n.a.
Total:			**1205.717**	**2755.352**	**100.00**	**100.00**	



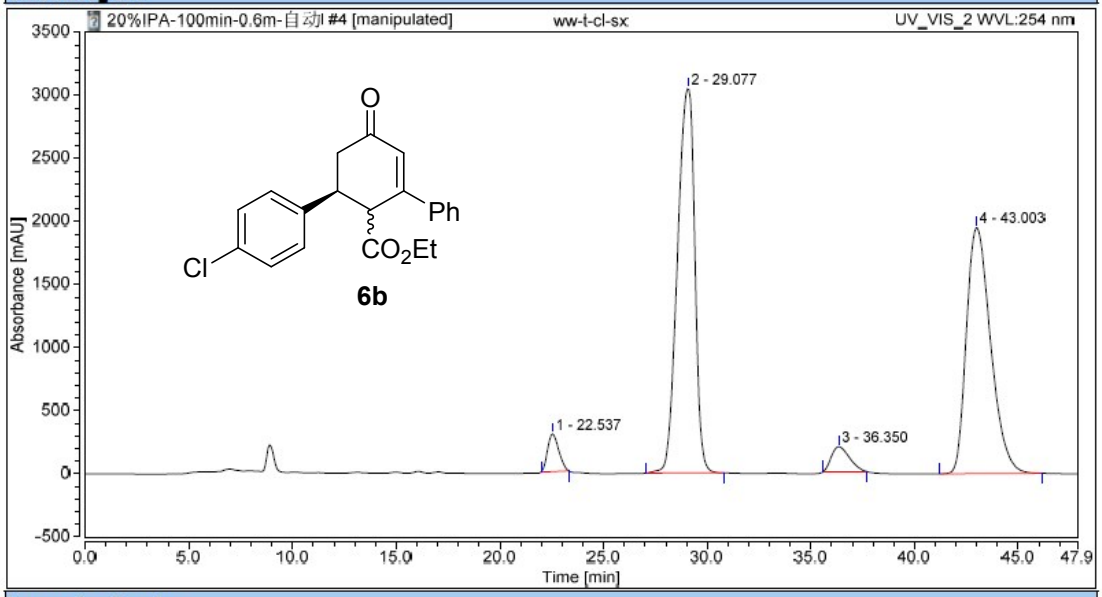
Chromatogram



Integration Results

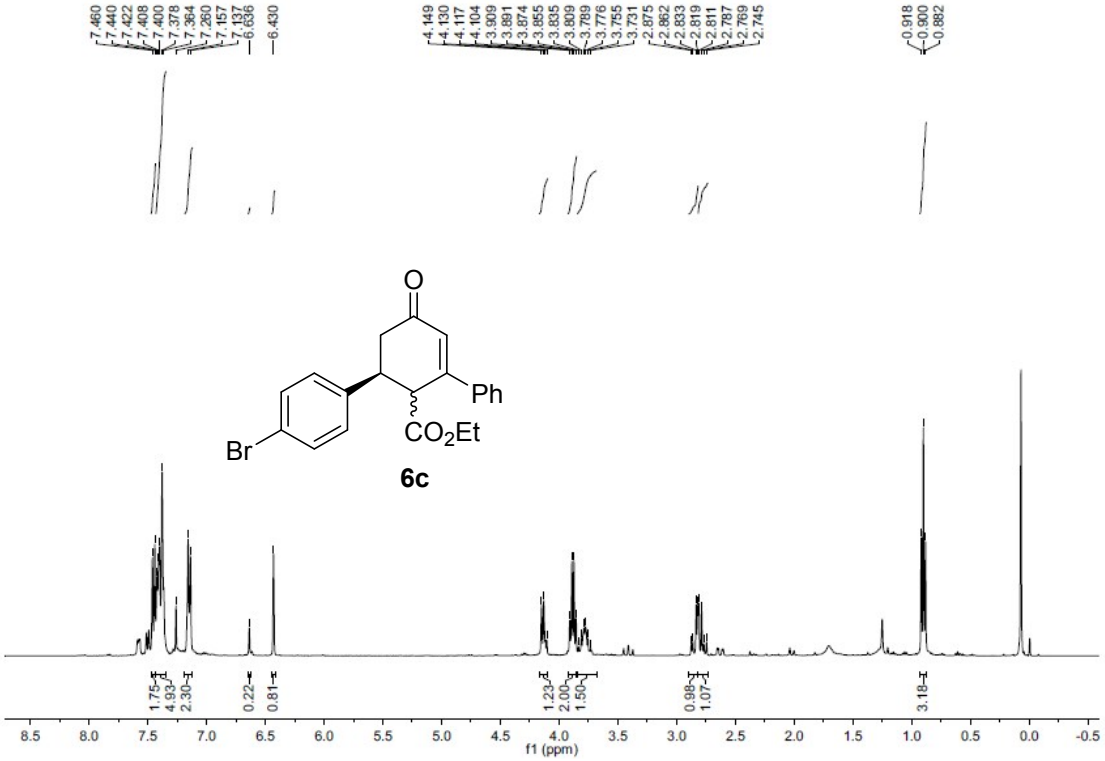
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.423	867.116	1264.062	19.66	26.86	n.a.
2		28.897	1338.573	1612.609	30.35	34.27	n.a.
3		35.823	1318.600	1145.579	29.90	24.34	n.a.
4		43.123	885.853	683.498	20.09	14.52	n.a.
Total:			**4410.143**	**4705.749**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.537	187.026	298.711	3.13	5.43	n.a.
2		29.077	2948.006	3047.957	49.32	55.46	n.a.
3		36.350	199.825	198.124	3.34	3.60	n.a.
4		43.003	2642.462	1951.316	44.21	35.50	n.a.
Total:			**5977.318**	**5496.108**	**100.00**	**100.00**	



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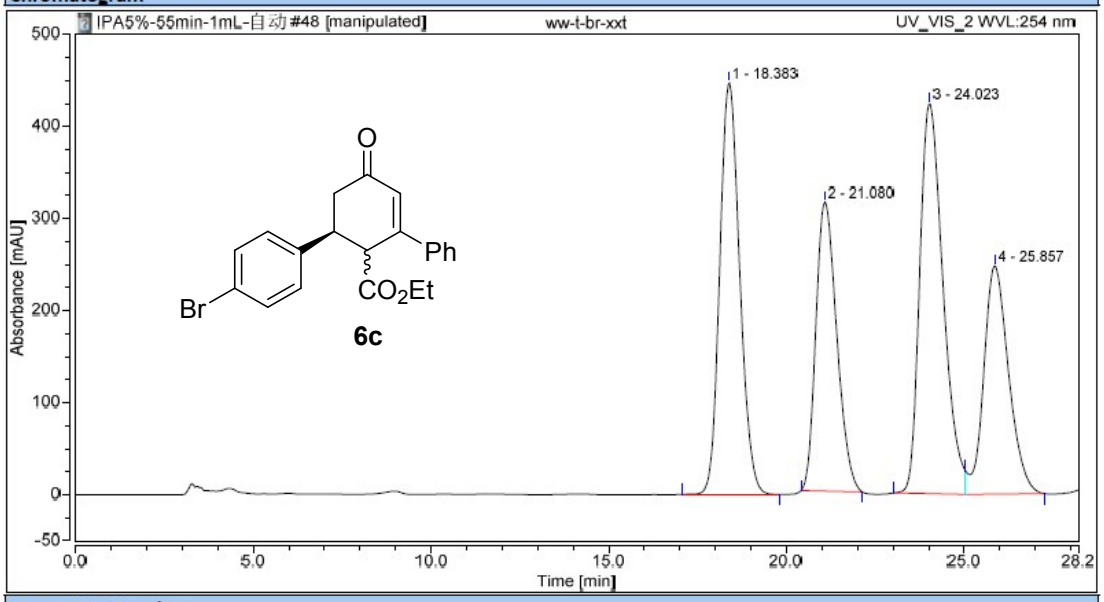
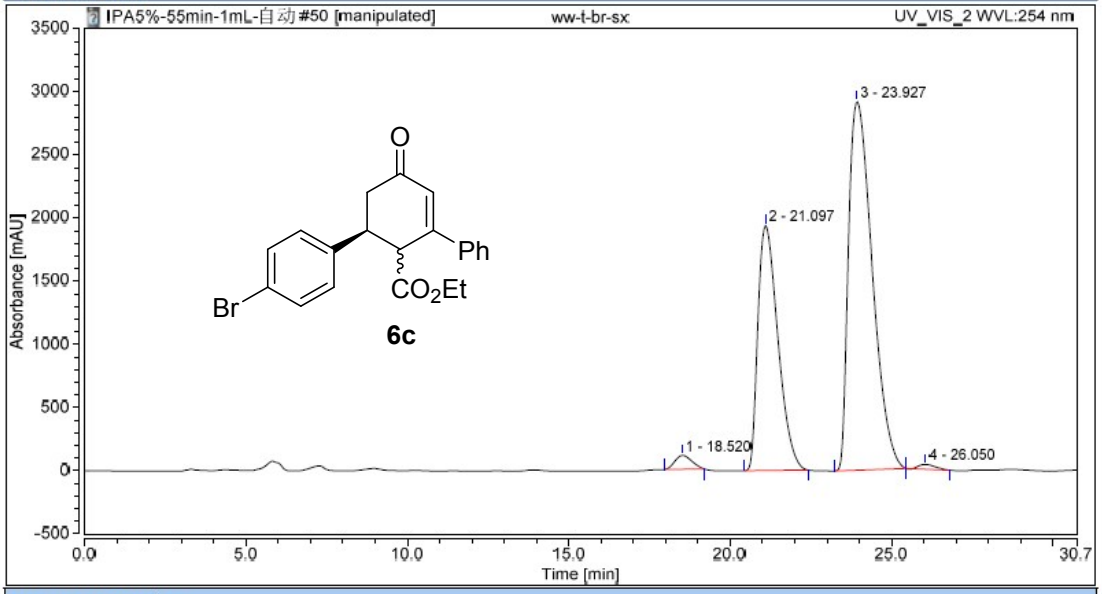


Integration Results

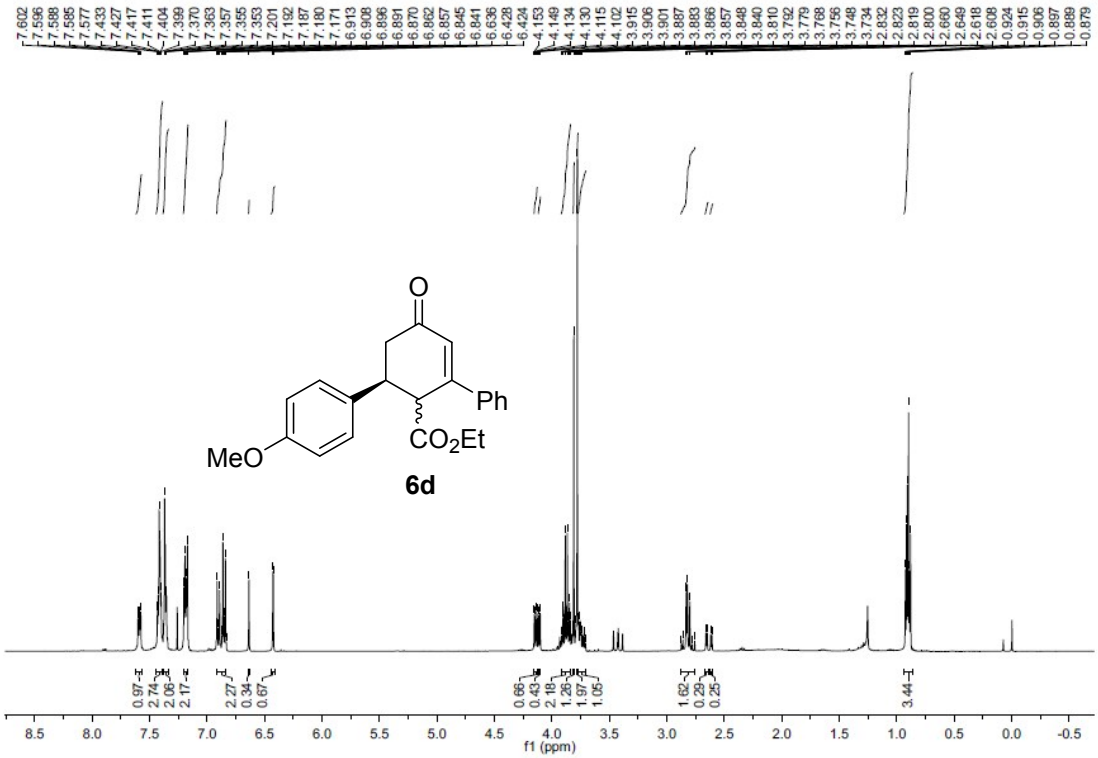
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.383	290.606	447.465	28.28	31.22	n.a.
2		21.080	213.279	314.086	20.76	21.91	n.a.
3		24.023	321.931	423.876	31.33	29.57	n.a.
4		25.857	201.731	247.924	19.63	17.30	n.a.
Total:			**1027.548**	**1433.352**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.520	66.965	110.023	1.69	2.20	n.a.
2		21.097	1391.412	1939.403	35.05	38.73	n.a.
3		23.927	2488.991	2918.848	62.69	58.29	n.a.
4		26.050	22.724	38.813	0.57	0.78	n.a.
Total:			**3970.092**	**5007.087**	**100.00**	**100.00**	



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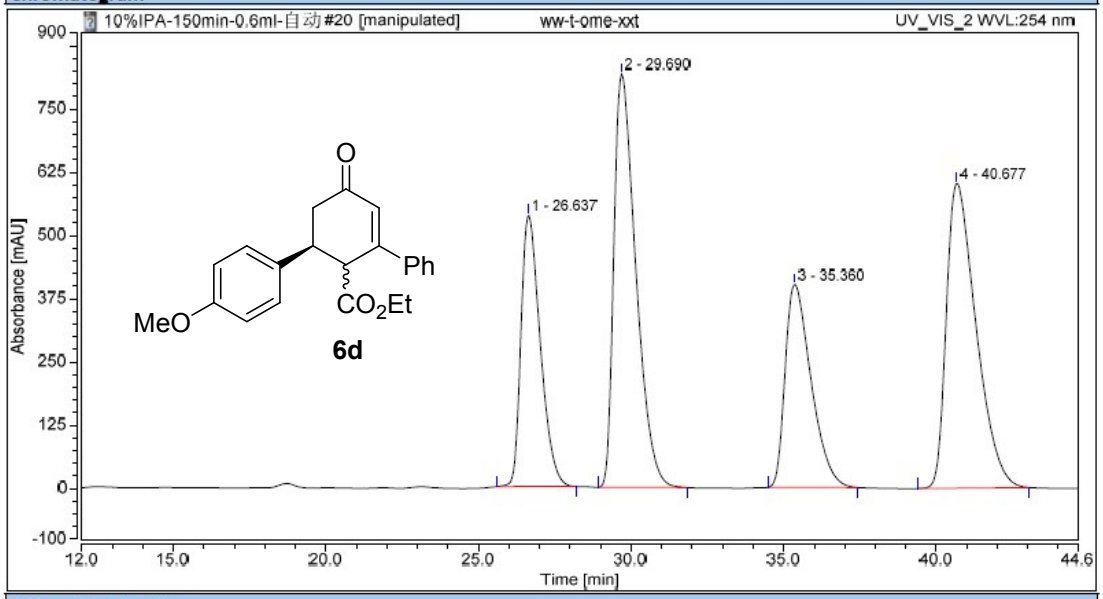
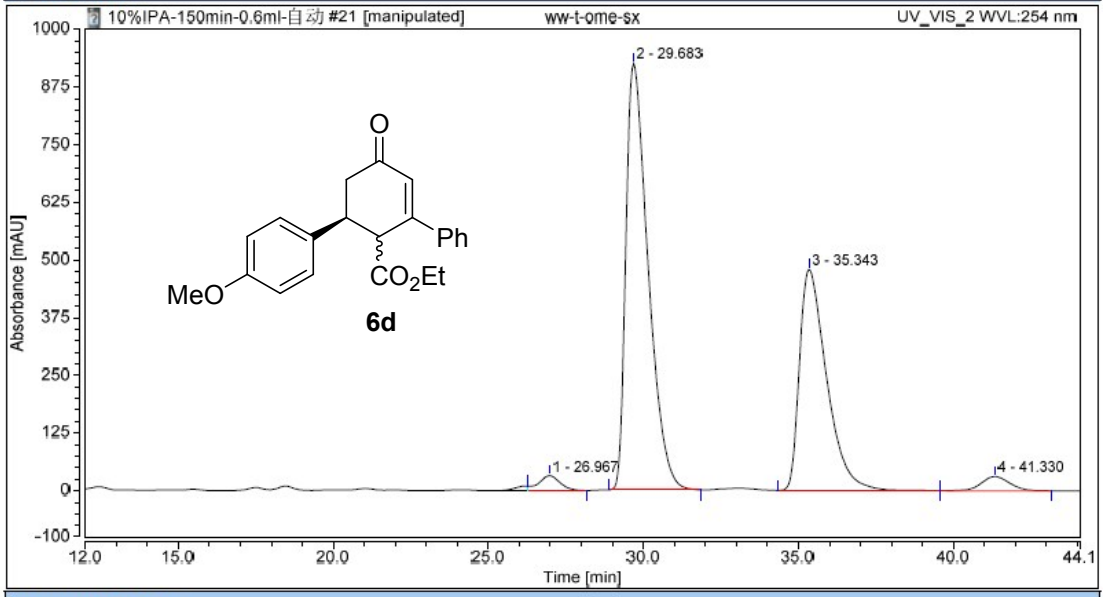


Integration Results

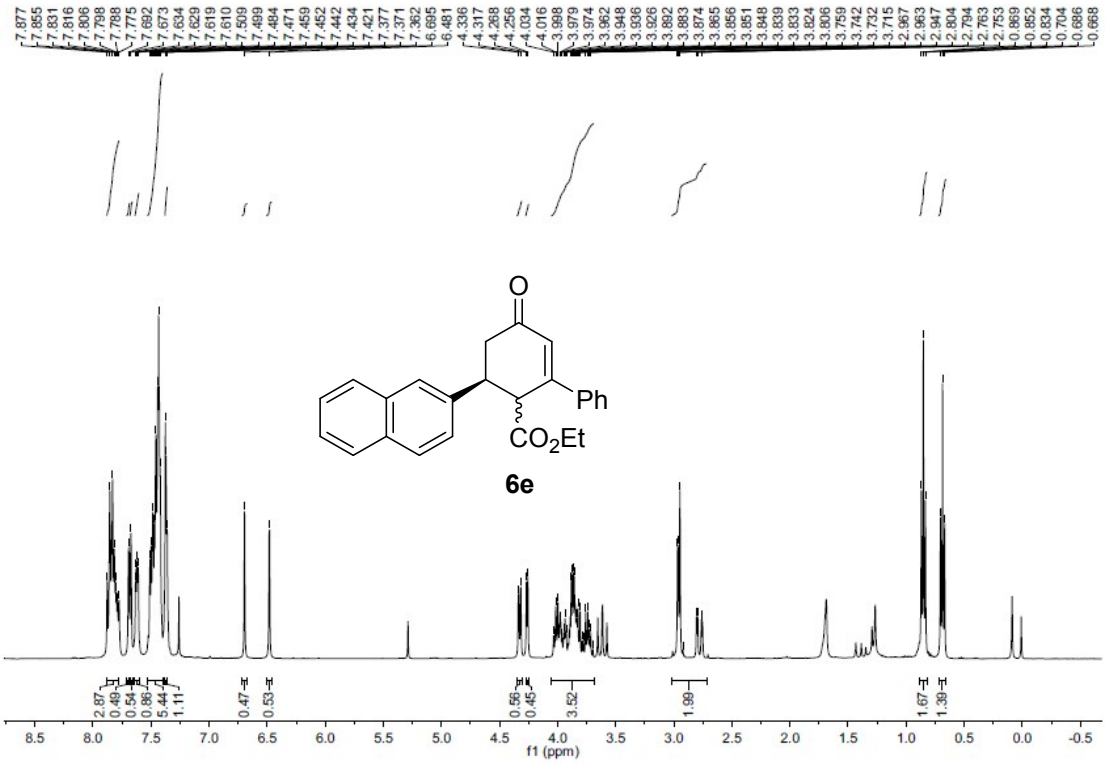
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		26.637	393.221	536.128	18.33	22.75	n.a.
2		29.690	679.929	816.595	31.69	34.65	n.a.
3		35.360	394.418	401.411	18.38	17.03	n.a.
4		40.677	678.110	602.561	31.60	25.57	n.a.
Total:			**2145.678**	**2356.695**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		26.967	25.319	32.242	1.93	2.20	n.a.
2		29.683	766.563	924.739	58.47	63.05	n.a.
3		35.343	486.216	478.805	37.09	32.65	n.a.
4		41.330	32.888	30.880	2.51	2.11	n.a.
Total:			**1310.986**	**1466.667**	**100.00**	**100.00**	



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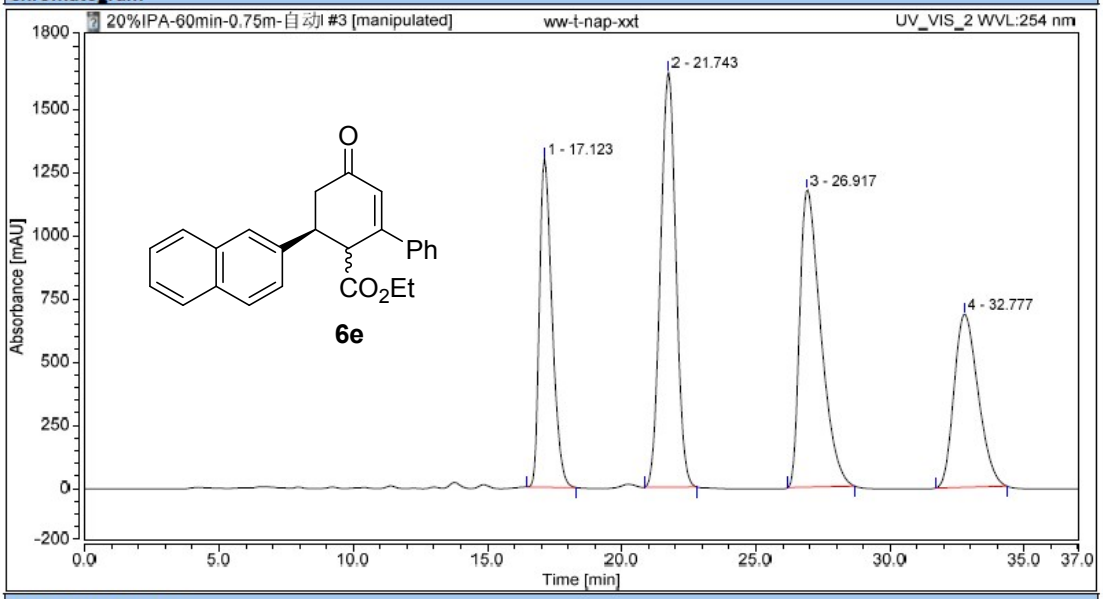
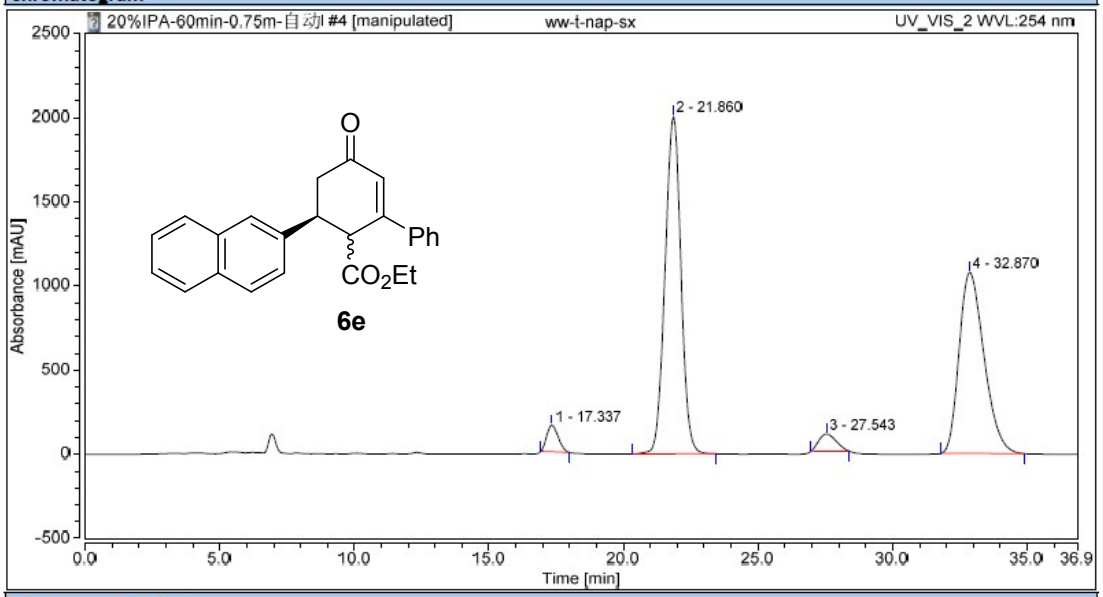


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.123	709.023	1296.860	19.82	27.05	n.a.
2		21.743	1090.302	1638.462	30.47	34.17	n.a.
3		26.917	1066.778	1174.855	29.81	24.50	n.a.
4		32.777	711.915	684.516	19.90	14.28	n.a.
Total:			**3578.019**	**4794.693**	**100.00**	**100.00**	

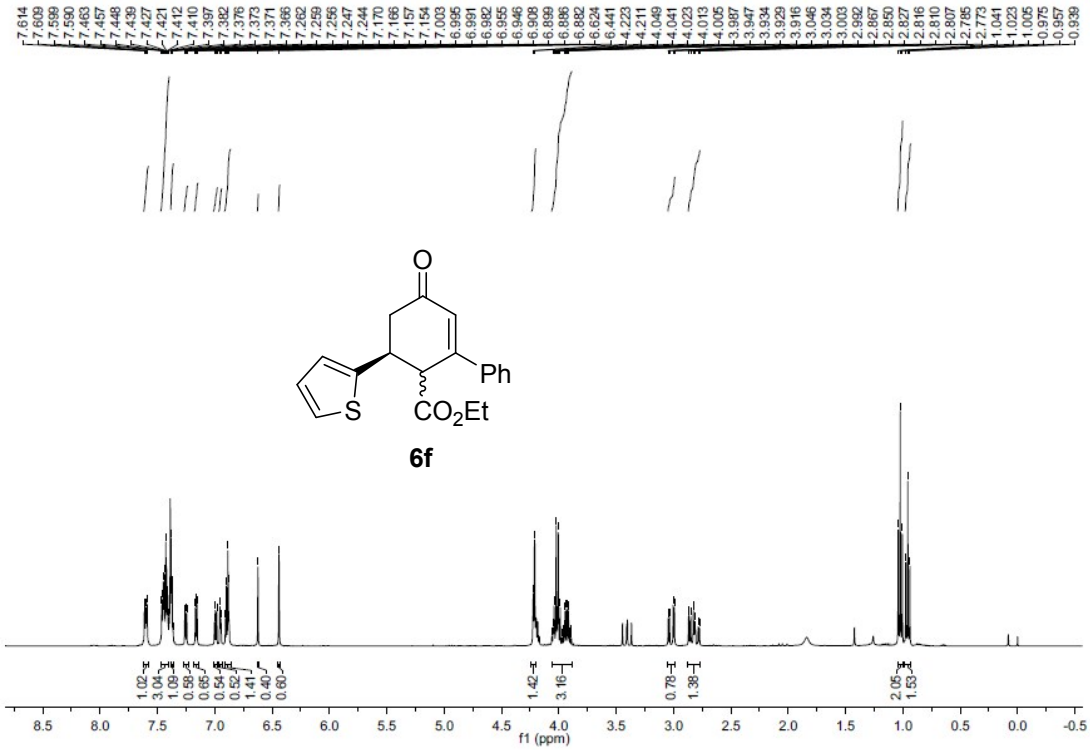
Chromatogram



6e

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.337	77.517	157.007	2.89	4.70	n.a.
2		21.860	1373.136	2005.731	51.20	60.03	n.a.
3		27.543	76.483	101.855	2.85	3.05	n.a.
4		32.870	1154.980	1076.725	43.06	32.22	n.a.
Total:			**2682.116**	**3341.318**	**100.00**	**100.00**	



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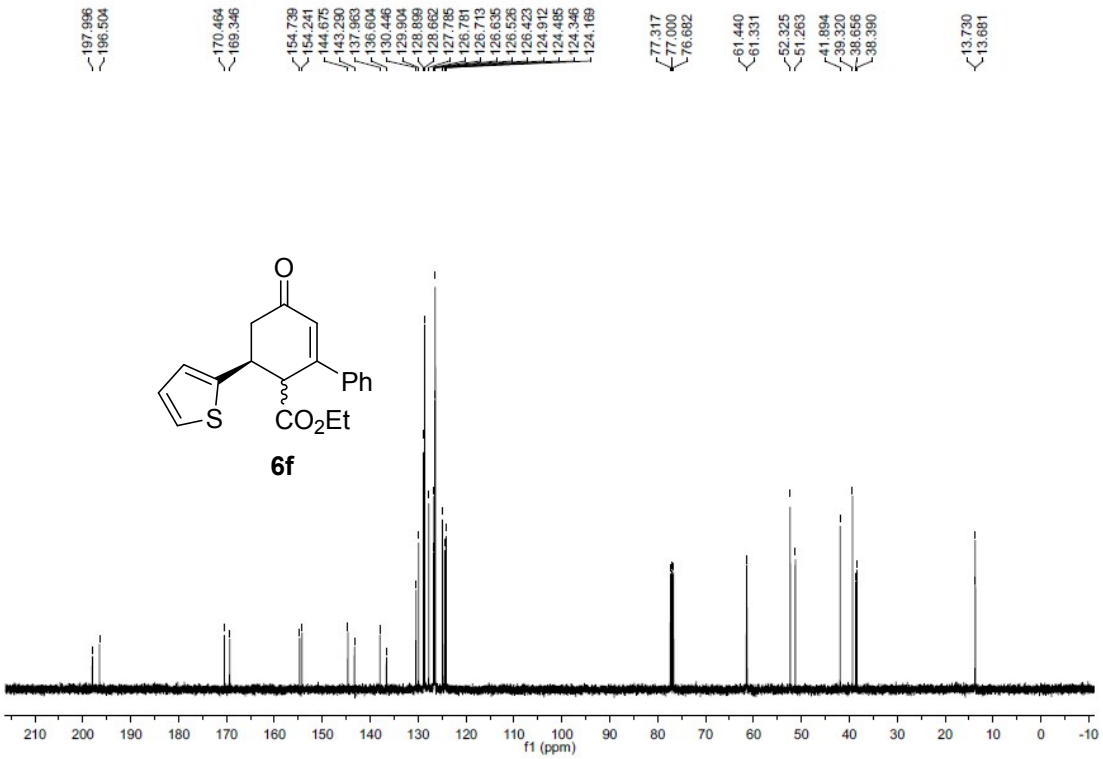
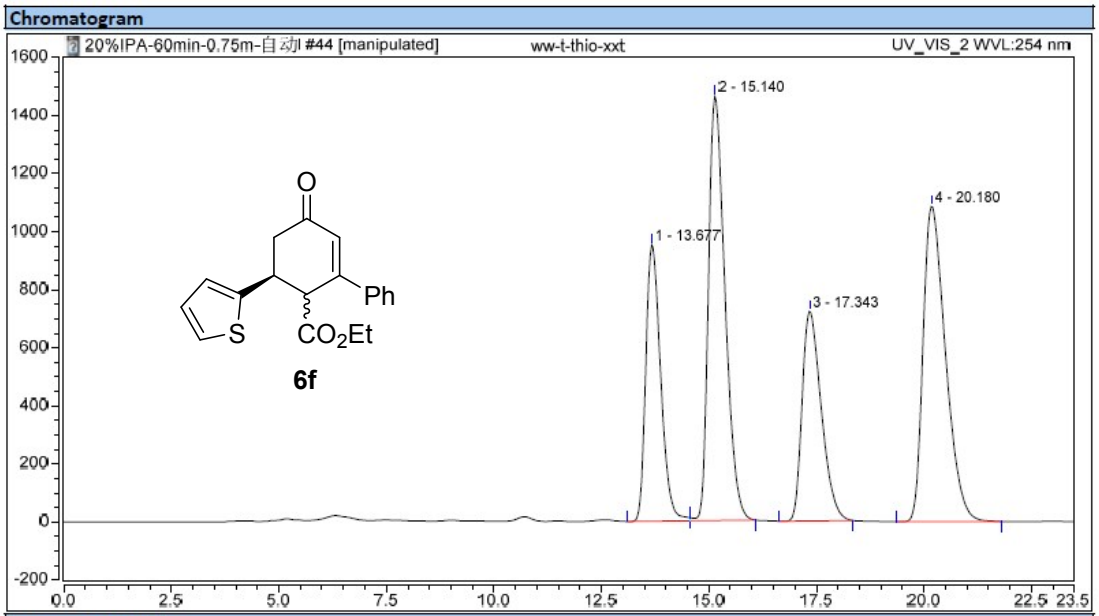
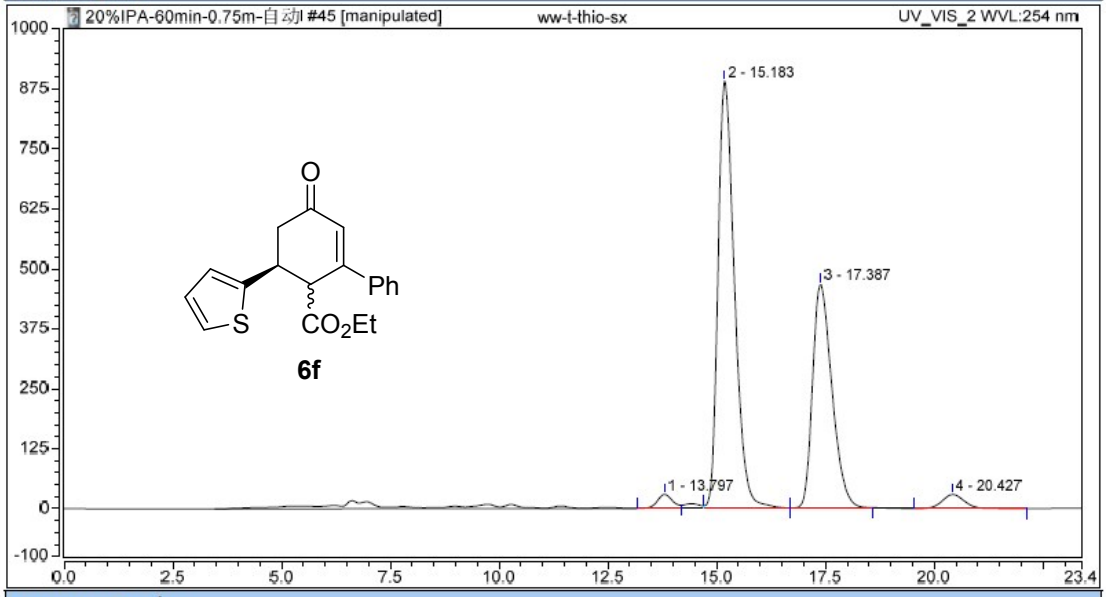




Integration Results

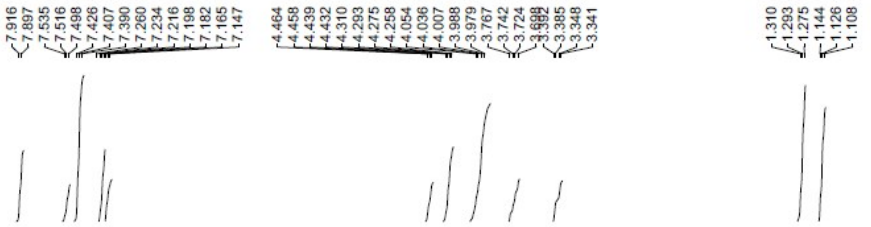
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.677	381.017	952.699	18.50	22.56	n.a.
2		15.140	650.720	1461.546	31.60	34.61	n.a.
3		17.343	373.031	722.154	18.11	17.10	n.a.
4		20.180	654.796	1086.482	31.79	25.73	n.a.
Total:			**2059.565**	**4222.881**	**100.00**	**100.00**	

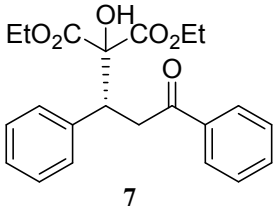
Chromatogram



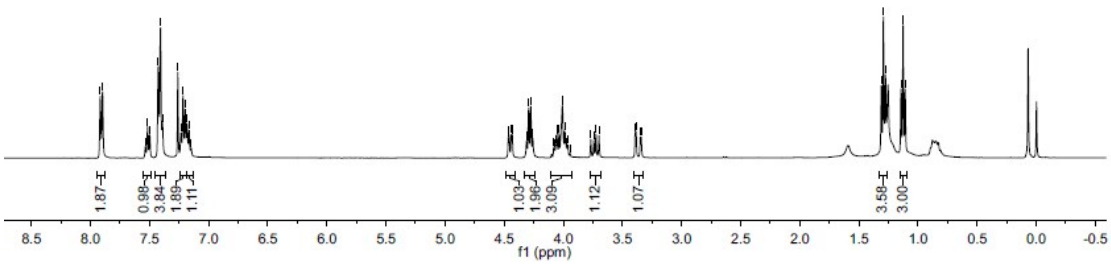
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.797	12.538	29.686	1.88	2.09	n.a.
2		15.183	392.591	891.177	58.96	62.85	n.a.
3		17.387	243.245	467.715	36.53	32.99	n.a.
4		20.427	17.445	29.360	2.62	2.07	n.a.
Total:			**665.819**	**1417.937**	**100.00**	**100.00**	





7



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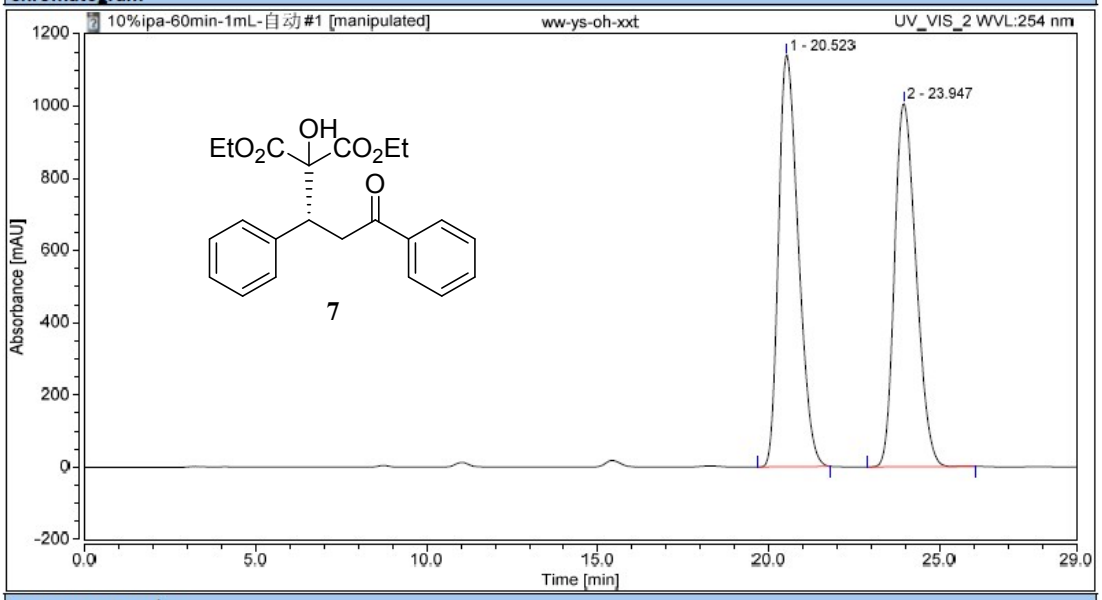
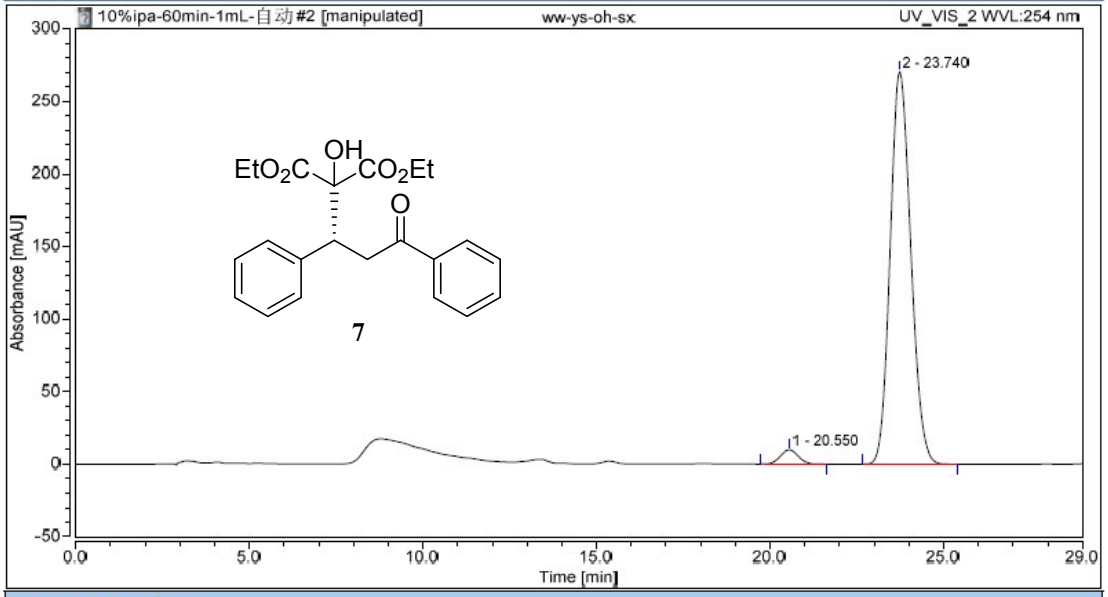


Integration Results

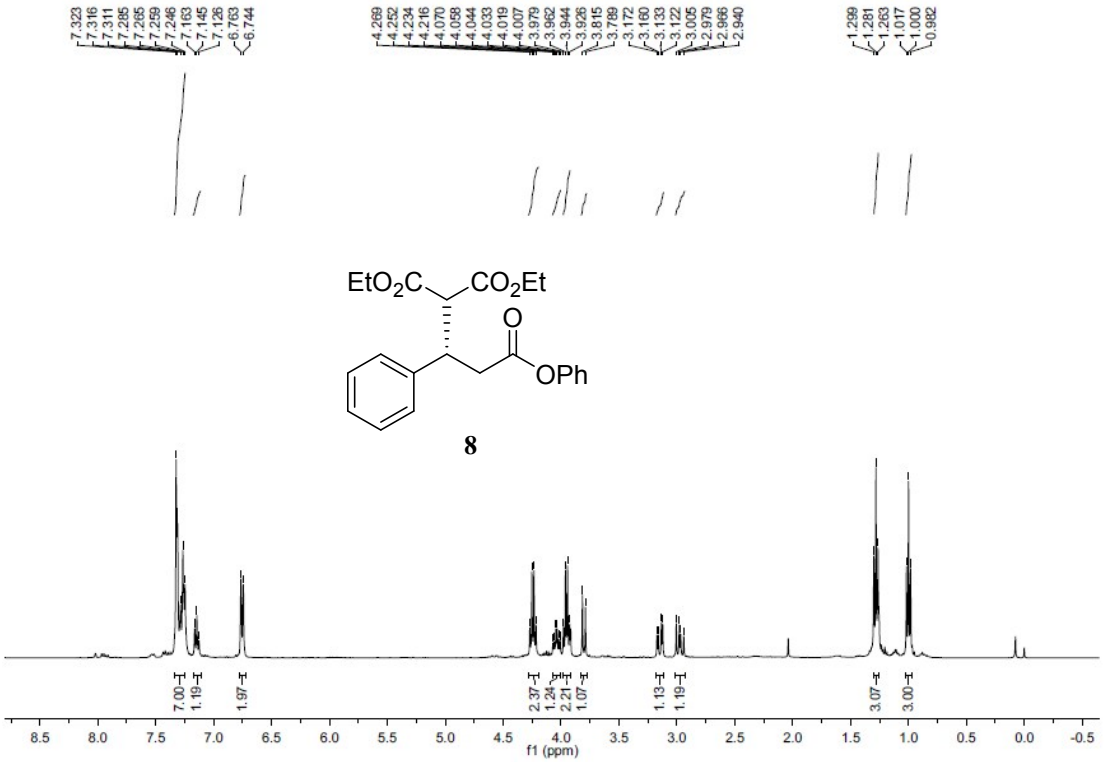
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.523	763.331	1139.880	50.94	53.11	n.a.
2		23.947	735.183	1006.382	49.06	46.89	n.a.
Total:			**1498.514**	**2146.261**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.550	5.965	9.928	3.09	3.54	n.a.
2		23.740	187.028	270.657	96.91	96.46	n.a.
Total:			**192.994**	**280.585**	**100.00**	**100.00**	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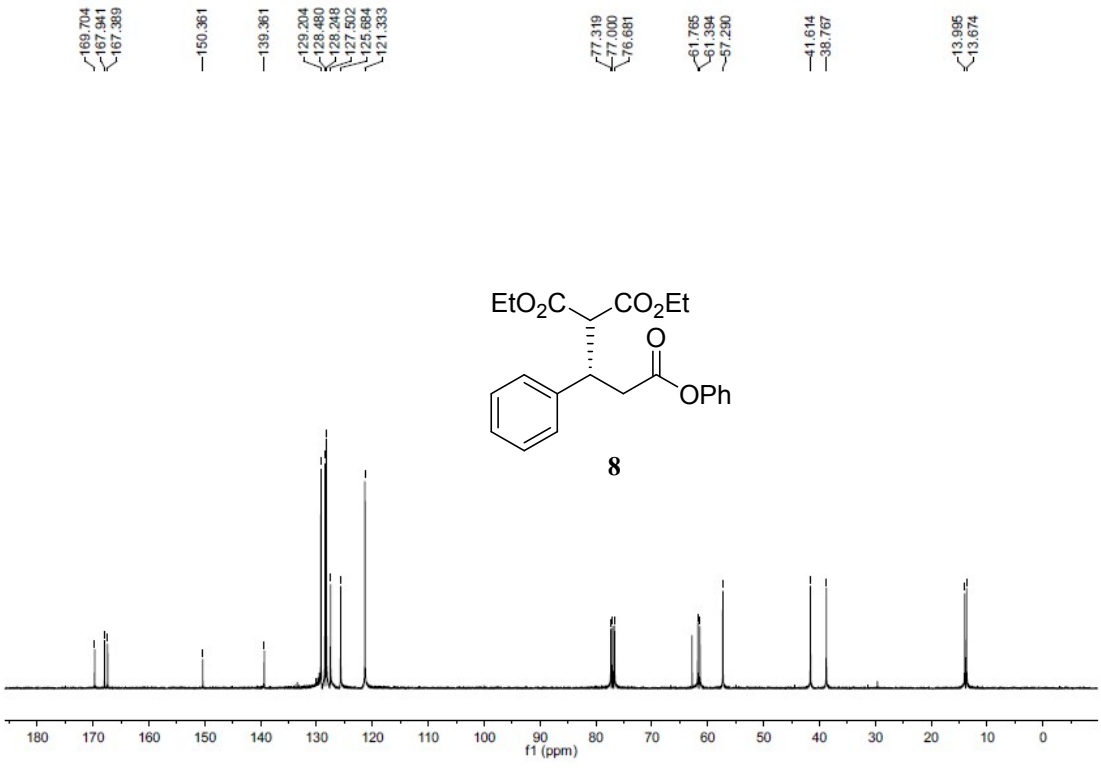
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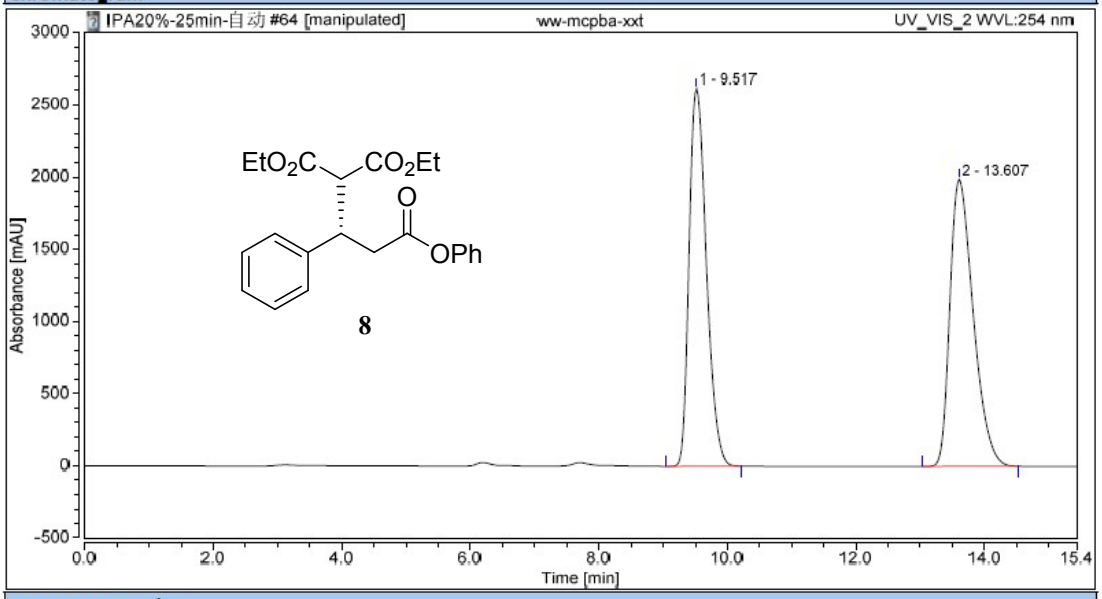
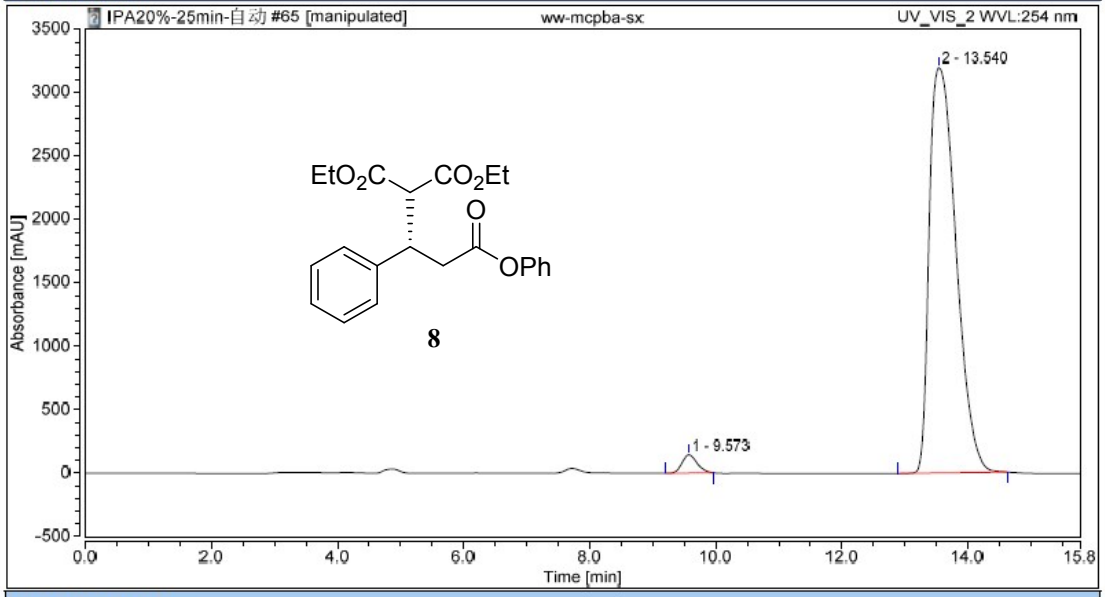
Chromatogram



Integration Results

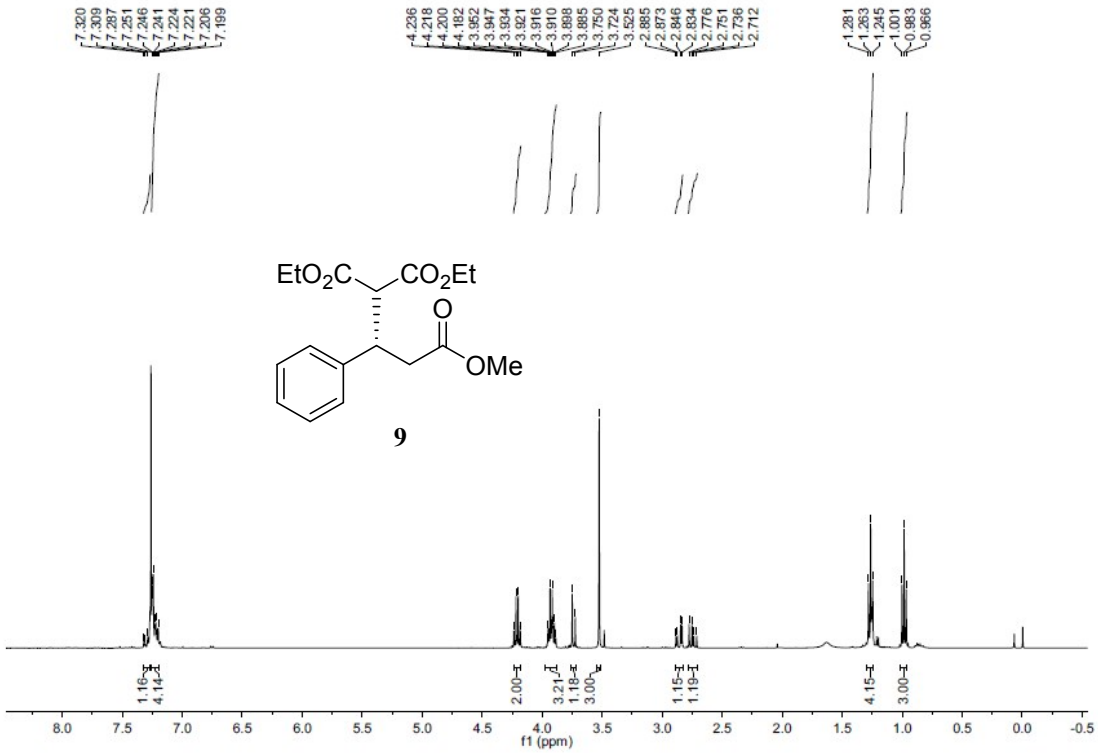
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.517	814.884	2615.938	49.34	56.83	n.a.
2		13.607	836.669	1987.432	50.66	43.17	n.a.
Total:			**1651.553**	**4603.370**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.573	40.304	145.342	2.51	4.35	n.a.
2		13.540	1566.924	3196.046	97.49	95.65	n.a.
Total:			**1607.227**	**3341.388**	**100.00**	**100.00**	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7.309
7.287
7.251
7.246
7.241
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7.221
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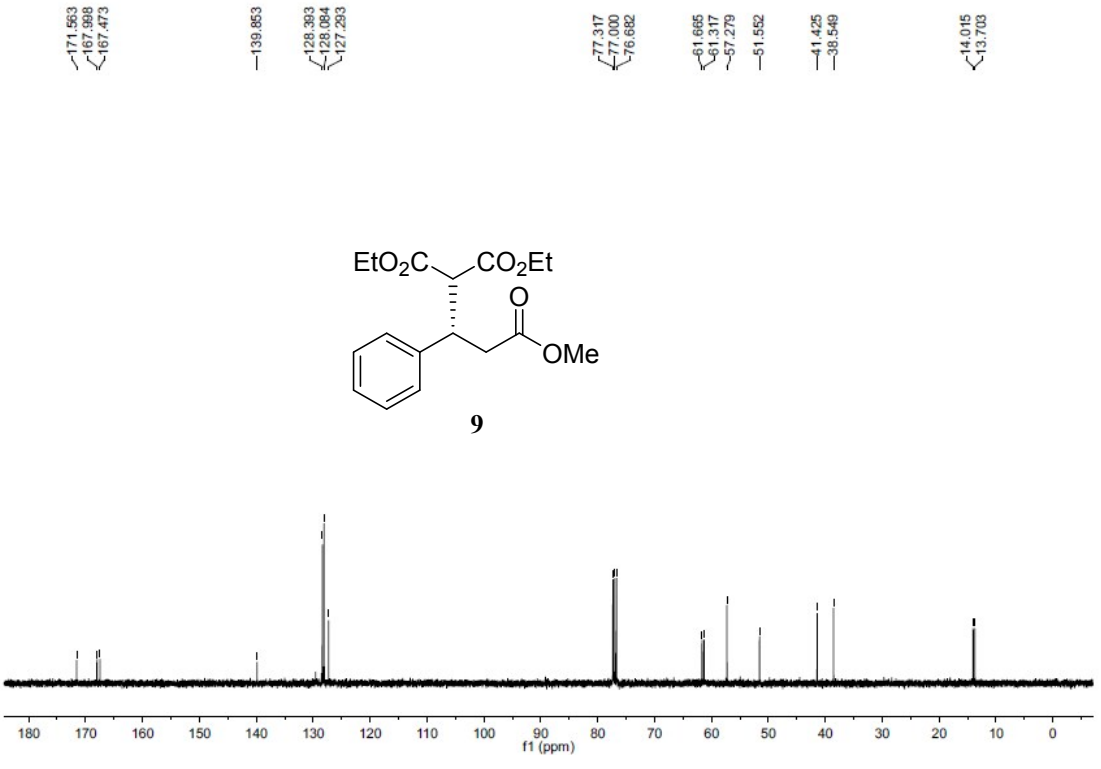
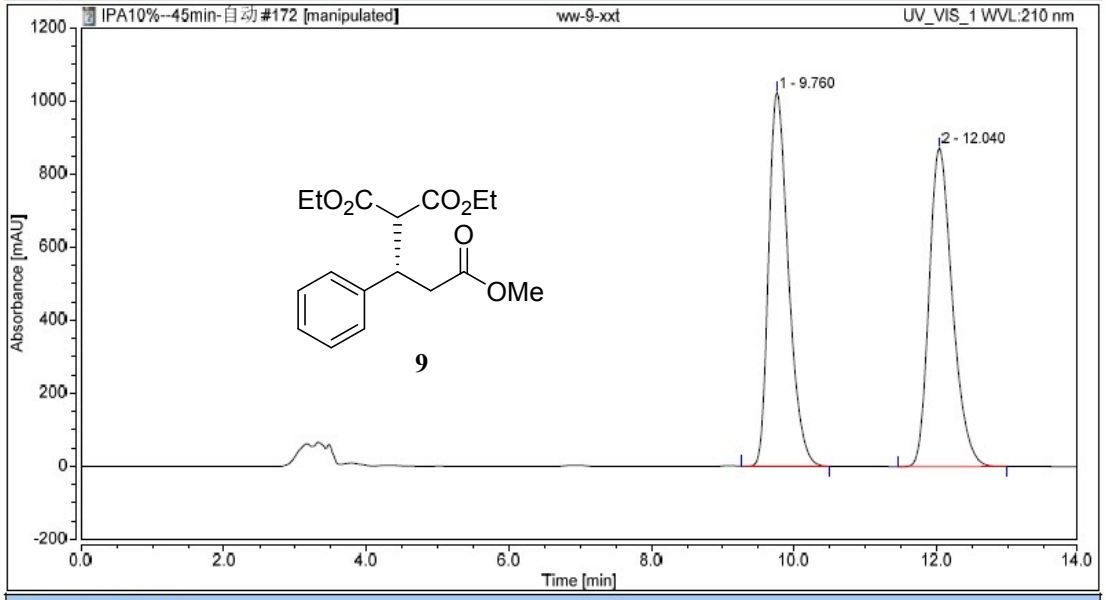
7.199
4.236
4.218
4.200
4.182
3.952
3.947
3.934
3.921
3.916
3.910
3.898
3.885
3.750
3.724
3.525
2.885
2.873
2.846
2.834
2.776
2.751
2.736
2.712
1.281
1.263
1.245
1.001
0.983
0.966
EtO2C
CO2Et
O
OMe
1.16
4.14
2.00
3.21
1.18
3.00
1.15
1.19
4.15
3.00
f1 (ppm)

9


171.563
167.998
167.473
139.853
128.393
128.084
127.293
77.317
77.000
76.682
61.665
61.317
57.279
51.552
41.425
38.549
14.015
13.703
EtO2C
CO2Et
O
OMe
f1 (ppm)

9

Chromatogram

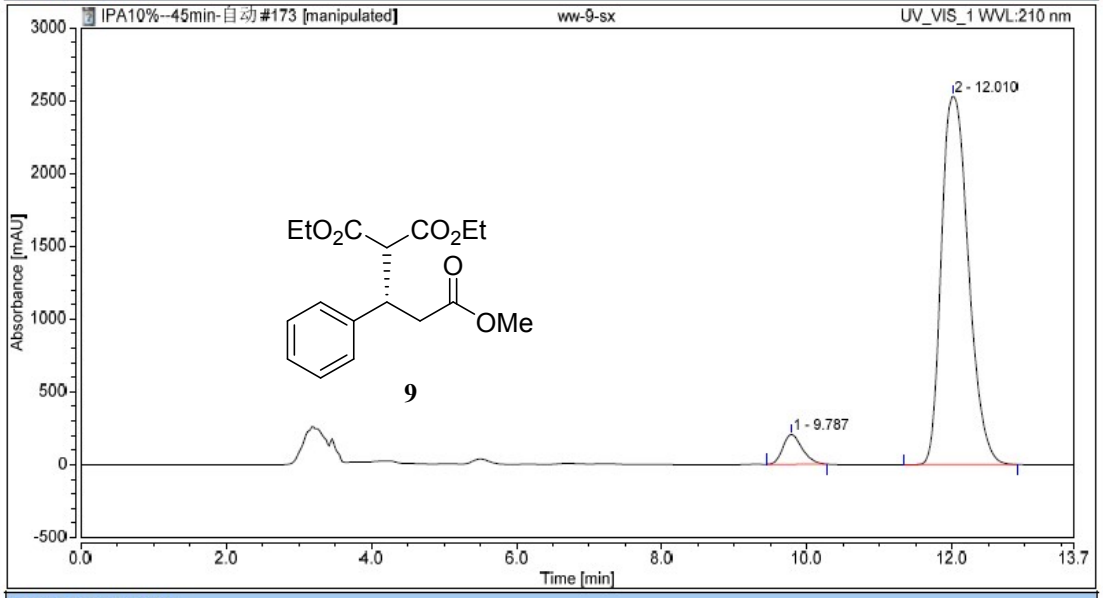


9

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.760	328.666	1023.429	49.85	53.99	n.a.
2		12.040	330.614	872.134	50.15	46.01	n.a.
Total:			**659.281**	**1895.562**	**100.00**	**100.00**	

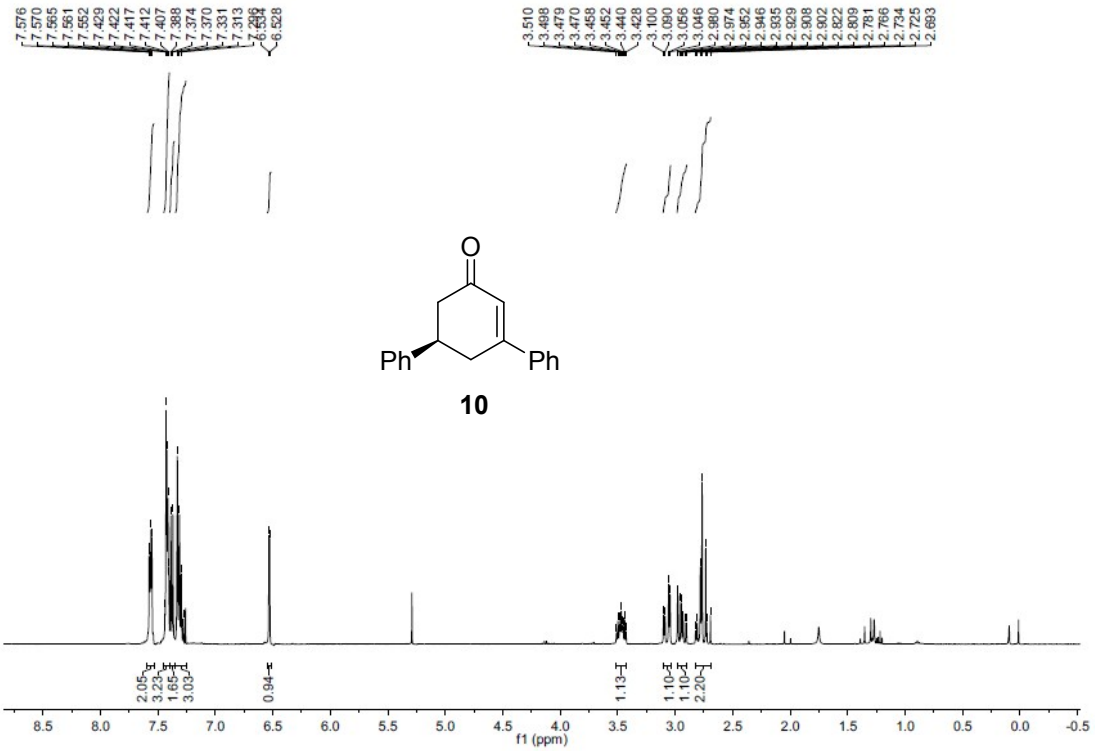
Chromatogram



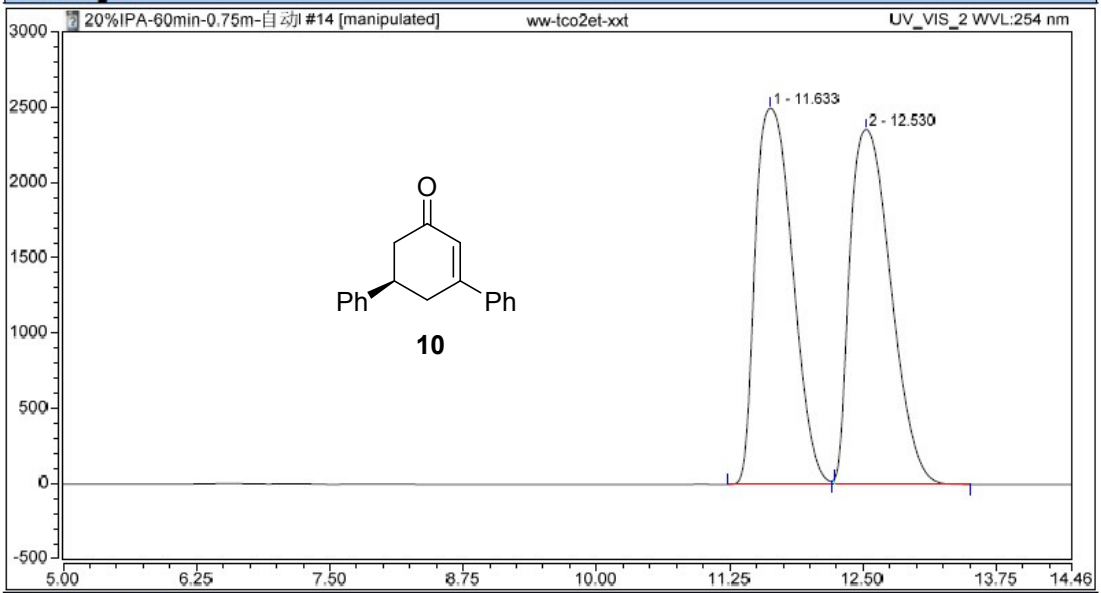
9

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.787	63.146	204.796	5.46	7.48	n.a.
2		12.010	1094.074	2532.660	94.54	92.52	n.a.
Total:			**1157.220**	**2737.456**	**100.00**	**100.00**	



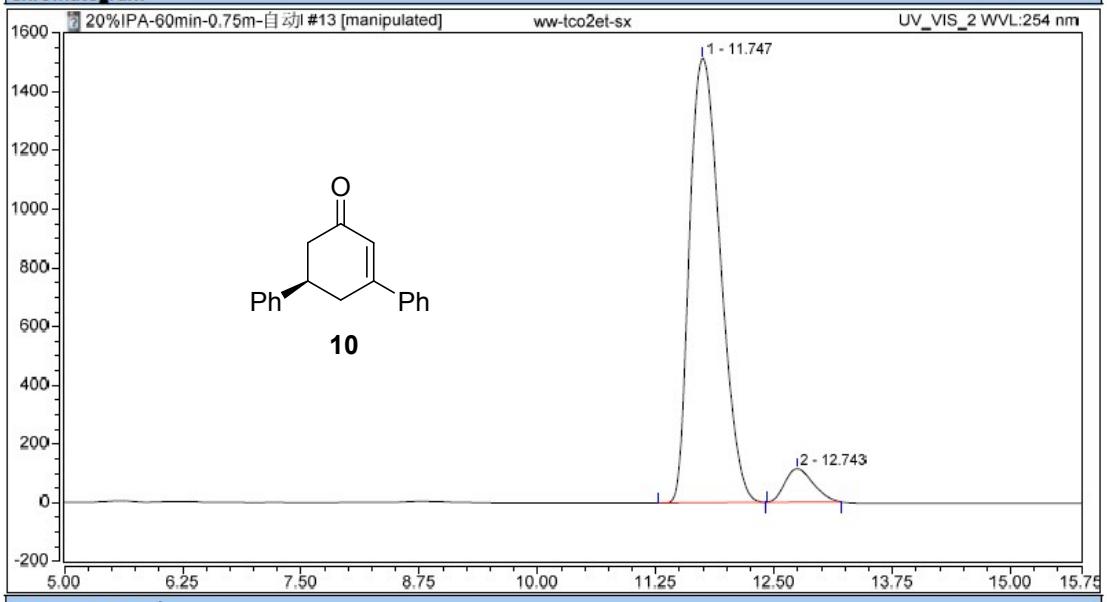
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.633	1014.357	2501.650	49.12	51.45	n.a.
2		12.530	1050.520	2360.347	50.88	48.55	n.a.
Total:			**2064.877**	**4861.996**	**100.00**	**100.00**	

Chromatogram



10

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.747	570.328	1514.715	93.49	93.01	n.a.
2		12.743	39.684	113.845	6.51	6.99	n.a.
Total:			**610.011**	**1628.560**	**100.00**	**100.00**	