Supporting Information

Highly enantioselective Michael addition of diethyl malonate to chalcones catalyzed by *cinchona* alkaloids-derivatived bifunctional tertiary amine-thioureas bearing multiple hydrogen-bonding donors

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Contents

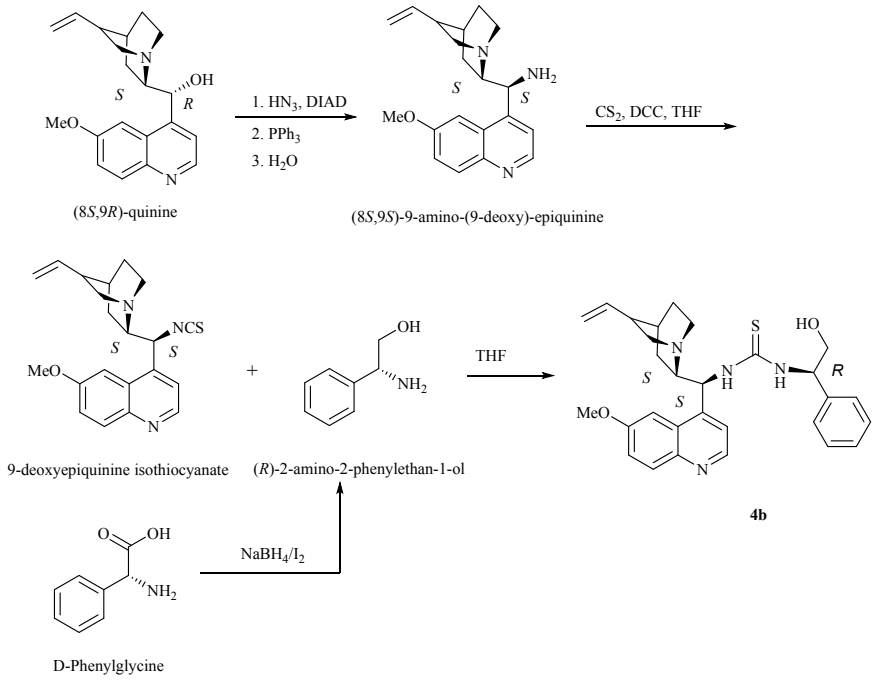
1. General information

Solvents were purified by standard procedures. THF, CH_2Cl_2 and $CHCl_3$ were dried over Na/benzophenone and CaH_2, respectively, and freshly distilled before using. Flash chromatography was done on silica gel (GF_{254}, 200-300 mesh). The reactions were monitored by thin layer chromatography (TLC) and analysis of TLCs was done using UV light (254 nm). Melting points were determined using a standard melting point apparatus and were uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 300 spectrometer in $CDCl_3$. Chemical shifts are expressed in ppm with TMS as internal standard. High-resolution mass spectra (HRMS) were measured with ESI. Optical rotations were determined on a Perkin-Elmer 343 Polarimeter. IR spectra were recorded as KBr disks. Enantiomeric excess (ee) determination was carried out on an Agilent 1260 interfaced to a HP 71 series computer workstation with a Chiralpak AD-H column.

2. General procedure for the preparation of chiral tertiary amine-thioureas 1-7

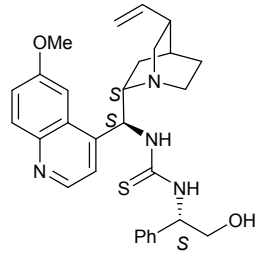
The bifunctional tertiary amine-thioureas **1-7** were synthesized following the similar procedures according to our previous report.[1]

4b as a representative:



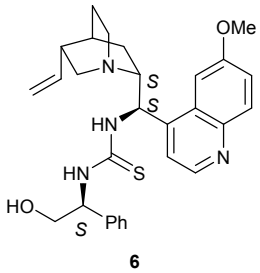
Scheme 1. Procedure for the preparation of **4b**

Among them **5-7** are new compounds.



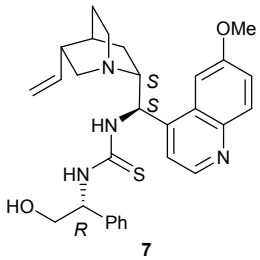
5

White solid, 82% yield; m.p. 167.5-167.8 ºC; $[\alpha]_D^{20}$ -107.2 (*c* 0.25, CH_2Cl_2); IR (KBr): *v* 3272, 3213, 2929, 2864, 2357, 1538, 1509, 1471, 1455, 1359, 1227, 1029, 918, 853, 743, 701 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.65 (s, 1 H), 8.01 (d, *J* = 9.2 Hz, 1 H), 7.78 (s, 2 H), 7.41 - 7.21 (m, 6 H), 5.73 - 5.64 (m, 1 H), 5.02 - 4.97 (m, 2 H), 3.98 (s, 3 H), 3.88 - 3.82 (m, 2 H), 3.26 - 3.20 (m, 2 H), 2.73 - 2.68 (m, 3 H), 2.33 (s, 2 H), 2.13 - 2.07 (m, 1 H), 1.97 (s, 1 H), 1.70 (s, 1 H), 1.65 (s, 2 H), 1.43 - 1.32 (m, 2 H), 0.94 - 0.89 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.8, 182.3, 180.3, 158.3, 147,8. 136.5, 131.4, 128.4, 127.0, 126.9, 126.8, 117.7, 102.6, 65.8, 59.8, 56.1, 53.5, 52.7, 45.9, 36.4, 29.7, 26.7, 24.2, 22.6, 14,1 ppm; HRMS (ESI) calcd for $C_{29}H_{35}N_4O_2S$ [M+H$^+$]: 503.2475, found: 503.2487.



6

White Solid, 80% yield; m.p. 145.7-146.2 ºC; $[\alpha]_D^{20}$ +224.4 (*c* 0.25, CH_2Cl_2); IR (KBr): *v* 3343, 2954, 2924, 2850, 1736, 1622, 1509, 1462, 1377, 1226, 1028, 917, 851, 784, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.63 (s, 1 H), 7.99 (d, *J* = 9.2 Hz, 1 H), 7.69 (s, 2 H), 7.40 - 7.22 (m, 6 H), 5.91 - 5.83 (m, 1 H), 5.19 - 5.11 (m, 2 H), 3.96 (s, 3 H), 3.85 - 3.80 (m, 2 H), 3.00 - 2.94 (m, 3 H), 2.58 (q, *J* = 7.2 Hz, 2 H), 2.31 (d, *J* = 7.2 Hz, 2 H), 2.08 - 2.02 (m, 1 H), 1.97 (s, 1 H), 1.66 (s, 1 H), 1.54 - 1.49 (m, 2 H), 1.26 - 1.21 (m,2 H), 0.97 - 0.85 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.8, 179.3, 158.2, 147.6, 144.5, 138.2, 131.3, 128.7, 128.5, 127.9, 126.7, 122.6, 116.3, 102.1, 66.2, 60.5, 55.9, 48.9, 45.6, 37.7, 37.6, 31.6, 29.7, 26.7, 24.8, 24.7, 24.6, 22.7, 14.1 ppm; HRMS (ESI) calcd for $C_{29}H_{35}N_4O_2S$ [M+H$^+$]: 503.2475, found: 503.2486.



7

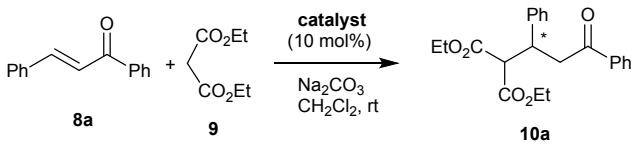
White solid, 76% yield; m.p. 97.4-97.7 ºC; $[\alpha]_D^{20}$ +127.2 (*c* 0.25, CH_2Cl_2); IR (KBr): *v* 3442, 3334, 3267, 2928, 2873, 1658, 1472, 1435, 1227, 1135, 1065, 1029, 852, 701, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.71 (s, 1 H), 7.98 (d, *J* = 9.2 Hz, 1 H), 7.74 (s, 2 H), 7.38 - 7.32 (m, 6 H), 5.86 - 5.78 (m, 1 H), 5.26 - 5.17 (m, 1 H), 4.08 - 4.01 (m, 1 H), 3.94 (s, 3 H), 3.81 - 3.74 (m, 2 H), 3.59 - 3.49 (m, 1 H), 2.79 - 2.74 (m, 3 H), 2.33 (s, 2 H), 2.04 (s, 1 H), 1.70 (s, 1 H), 1.58 (s, 2 H), 1.31 - 1.26 (m, 2 H), 1.12 - 1.04 (m, 2 H), 0.93 - 0.89 (t, 1 H)

ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.0, 158.5, 147.9, 144.7, 139.3, 139.2, 136.7, 131.3, 129.0, 128.5, 127.0, 122.9, 120.1, 117.2, 102.4, 65.3, 60.9, 60.4, 57.7, 56.2, 52.5, 49.5, 47.3, 45.9, 36.5, 29.7, 26.5, 24.4, 14.2 ppm; HRMS (ESI) calcd for $C_{29}H_{35}N_4O_2S$ [M+H$^+$]: 503.2475, found: 503.2488.

3. Optimization of Reaction conditions

The Michael addition of chalcone (**8a**) with diethyl malonate (**9**) was chose as model reaction for the screen of catalysts and reaction conditions.

3.1 Screening of catalysts



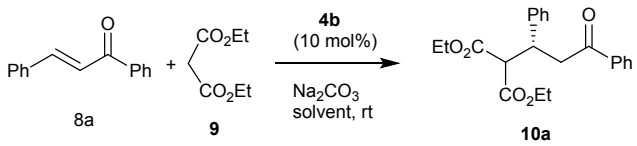
8a **9** **10a**

Entry[a]	Catalyst	Yield (%)[b]	ee (%)[c]	Config.[d]
1	**1a**	30	0	*rac*[e]
2	**1b**	35	0	*rac*
3	**2a**	26	15	*S*
4	**2b**	30	55	*S*
5	**3a**	29	0	*rac*
6	**3b**	37	5	*R*
7	**4a**	24	51	*R*
8	**4b**	35	65	*R*

[a]All reactions were carried out with 0.1 mmol of Chalcone, 0.12 mmol of Diethyl malonate and 100 mol % Na_2CO_3 as base additive in 0.5 mL CH_2Cl_2 at room temperature for 48 h. [b]Isolated yield. [c]Determined by HPLC analysis (Chiralpak AD-H). [d]Absolute configuration was determined by comparison of the optical rotation with the value previously reported.[2] [e] racemic

Catalyst **4b** was defined as the best catalyst for further examination.

3.2 Screening of solvents



Entry[a]	Solvent	Yield (%)[b]	ee (%)[c]
1	CH_2Cl_2	30	65
2	Toluene	45	9
3	MeCN	65	0
4	$CHCl_3$	35	87
5	THF	56	3
6	Et_2O	95	40
7	MeOH	98	0
8	Diethyl malonate	50	5
9	Acetone	69	0
10	DMSO	75	0
11	n-Hexane	35	40
12	n-Heptane	56	50
13	Isopropanol	68	0
14	1,4-Dioxane	60	5
15	Cyclohexane	32	42
16	EtOAc	52	8
17	Liquid petrolatum	35	47

[a]All reactions were carried out with 0.1 mmol of Chalcone, 0.12 mmol of diethyl malonate,10 mol% **4b**, 100 mol % Na_2CO_3 in 0.5 mL solvent at room temperature for 48 h. [b]Isolated yield. [c]Determined by HPLC analysis (Chiralpak AD-H).

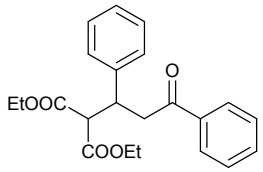
4. General procedure for enantioselective Michael addition

Typical Procedure for Asymmetric Michael Addition of Diethyl Malonate to Chalcones catalyzed by 4b: Reaction of 8a as a Representative. To a solution of Chalcone **8a** (20.83 mg, 0.1 mmol) and thiourea catalyst **4b** (5.2 mg, 0.01 mmol) in $CHCl_3$(0.5 mL) was added NaOH(0.2 mg, 0.005 mmol) and diethyl malonate **9** (19.3 μL, 0.12 mmol) successively at -20 °C. The reaction mixture was stirred at -20 °C for 8 h. The residue was directly purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10/1 as eluant) to afford the adduct **10a**.

Typical Procedure for Asymmetric Michael Addition of Diethyl Malonate to Chalcones

catalyzed by 7: Reaction of 8a as a Representative. To a solution of Chalcone **8a** (20.83 mg, 0.1 mmol) and thiourea catalyst **7** (5.2 mg, 0.01 mmol) in $CHCl_3$(0.5 mL) was added NaOH(0.2 mg, 0.005 mmol) and diethyl malonate **9**(19.3 μL, 0.12 mmol) successively at -50 °C. The reaction mixture was stirred at -50 °C for 10 h. The residue was directly purified by flash column chromatography on silica gel (petroleum ether/ EtOAc = 10/1 as eluant) to afford the adduct **10a**.

Diethyl 2-(3-oxo-1, 3-diphenylpropyl)malonate (10a) [3]



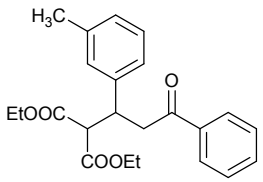
10a

White solid; m.p. 67-69 ºC; IR (KBr): *v* 3062, 3029, 2981, 1733, 1683, 1455, 1367, 1302, 1257, 861, 750, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, *J* = 7.6 Hz, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.42 (t, *J* = 7.2 Hz, 2 H), 7.26 - 7.17 (m, 5 H), 4.23 - 4.16 (m, 3 H), 3.98 - 3.93(q, *J* = 7.2 Hz, 2 H), 3.82 (d, *J* = 10.0 Hz, 1 H), 3.57 - 3.42(m, 2 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.00 (t, *J* = 7.2 Hz, 3 H) ppm.

(*R*)-**10a**: 99% yield; $[\alpha]_D^{20}$ -18.2 (*c* 0.72, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 15.36 min, t_{minor} = 29.28 min, 94% ee.

(*S*)-**10a**: 97% yield; $[\alpha]_D^{20}$ +17.6 (*c* 1.18, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 30.59 min, t_{minor} = 15.53 min, 94% ee.

Diethyl 2-(1-(3-methylphenyl)-3-oxo-3-phenylpropyl)malonate (10b)



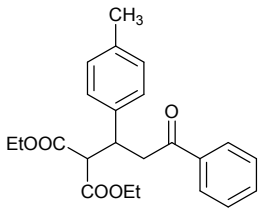
10b

White solid; m.p. 38.3-40.1 ºC; IR (KBr): *v* 2981, 2913, 1748, 1731, 1686, 1448, 1367, 1302, 1257, 1151, 861, 784, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz):δ 7.90 (d, *J* = 7.2 Hz, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.43 (t, *J* = 8.0 Hz, 2 H), 7.14 - 6.97 (m, 4 H), 4.24 - 4.12 (m, 3 H), 3.97 (q, *J* = 7.2 Hz, 2 H), 3.80 (d, *J* = 9.6 Hz, 1 H), 3.56 - 3.42(m, 2 H), 2.28 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.02 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 167.4, 166.7, 139.3, 136.8, 135.8, 131.9, 128.0, 127.5, 127.2, 127.0, 126.8, 124.1, 60.6, 60.2, 56.5, 41.5, 39.6, 20.4, 12.95, 12.69 ppm; HRMS (ESI) calcd for $C_{23}H_{26}O_5$ [M+Na^+]: 405.1672, found: 405.1665.

(*R*)-**10b**: 95% yield; $[\alpha]_D^{20}$ -14.9 (*c* 0.68, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 12.11 min, t_{minor} = 17.96 min, 92% ee.

(*S*)-**10b**: 95% yield; $[\alpha]_D^{20}$ +16.4 (*c* 1.58, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 18.54 min, t_{minor} = 12.26 min, 92% ee.

Diethyl 2-(1-(4-methylphenyl)-3-oxo-3-phenylpropyl)malonate (10c) [4]



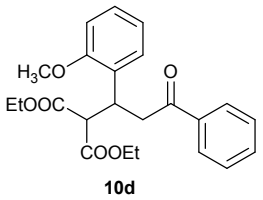
10c

White solid; m.p. 71.4-72.5 ºC; IR (KBr): *v* 2982, 2359, 2332, 1729, 1684, 1447, 1254, 1228, 1178, 1153, 1033, 861, 737, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, *J* = 7.6 Hz, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 7.14 (d, *J* = 7.2 Hz, 2 H),7.04 (d, *J* = 7.2 Hz, 2 H), 4.24 - 4.11 (m, 3 H), 3.97 (q, *J* = 7.2 Hz, 2 H), 3.79 (d, *J* = 9.6 Hz, 1 H), 3.55 - 3.39 (m, 2 H), 2.26 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.03 (t, *J* = 7.2 Hz, 3 H) ppm.

(*R*)-**10c**: 97% yield; $[\alpha]_D^{20}$ -9.1 (*c* 0.76, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 15.36 min, t_{minor} = 29.28 min, 94% ee.

(*S*)-**10c**: 98% yield; $[\alpha]_D^{20}$ +13.8 (*c* 1.27, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 32.98 min, t_{minor} = 16.12 min, 94% ee.

Diethyl 2-(1-(2-methoxyphenyl)-3-oxo-3-phenylpropyl)malonate (10d)



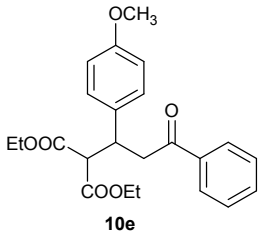
10d

Colorless oil; IR (KBr): *v* 3548, 2982, 1732, 1684, 1599, 1494, 1447, 1246, 1151, 1028, 861, 755, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, *J* = 7.2 Hz, 2 H), 7.52 (t, *J* = 7.2 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 7.14 (t, *J* = 7.6 Hz, 2 H), 6.80 (t, *J* = 7.2 Hz, 2 H), 4.35 - 4.29 (m, 1 H), 4.23 - 4.15 (m, 3 H), 3.92 (q, *J* = 7.2 Hz, 2 H), 3.81 (s, 3 H), 3.68 - 3.62 (dd, J_1 = 6.4 Hz, J_2 = 8.0 Hz, 1 H), 3.48 - 3.43 (dd, J_1 = 4.0 Hz, J_2 = 16.4 Hz, 1 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 0.98 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 167.8, 167.1, 156.4, 136.0, 131.7, 129.7, 127.4, 127.1, 119.3, 109.8, 60.4, 60.1, 54.2, 54.0, 39.6, 37.1, 13.0, 12.7 ppm; HRMS (ESI) calcd for $C_{23}H_{26}NaO_6$ [M+Na^+]: 421.1622, found: 421.1618.

(*R*)-**10d**: 98% yield; $[\alpha]_D^{20}$ -26.5 (*c* 0.61, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 10.47 min, t_{minor} = 13.03 min, 92% ee.

(*S*)-**10d**: 99% yield; $[\alpha]_D^{20}$ +18.9 (*c* 1.33, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 13.10 min, t_{minor} = 10.40 min, 94% ee.

Diethyl 2-(1-(4-methoxyphenyl)-3-oxo-3-phenylpropyl)malonate (10e) [3]



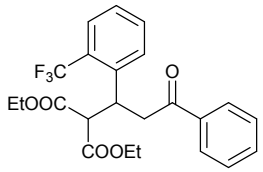
10e

White solid; m.p. 62.2-62.4 ºC; IR (KBr): *v* 2983, 2359, 2334, 1730, 1684, 1448, 1254, 1226, 1153, 10233, 857, 732, 691 cm^{-1} cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.90 (d, *J* = 7.2 Hz, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.43 (t, *J* = 7.2 Hz, 2 H), 7.17 (d, *J* = 8.8 Hz, 2 H), 6.77 (d, *J* = 8.8 Hz, 2 H), 4.24 - 4.10 (m, 3 H), 3.97 (q, *J* = 7.2 Hz, 2 H), 3.78 (d, *J* = 9.6 Hz, 1 H), 3.74 (s, 3 H), 3.54 - 3.49 (dd, J_1 = 4.4 Hz, J_2 = 16.8 Hz, 1 H), 3.44 - 3.37 (dd, J_1 = 9.6 Hz, J_2 = 16.8 Hz, 1 H), 1.25 (t, 3 H), 1.03 (t, 3H) ppm.

(*R*)-**10e**: 94% yield; $[\alpha]_D^{20}$ -16.4 (*c* 0.85, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 24.35 min, t_{minor} = 68.12 min, 94% ee.

(*S*)-**10e**: 93% yield; $[\alpha]_D^{20}$ +11.6 (*c* 0.77, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 69.22 min, t_{minor} = 25.12 min, 90% ee.

Diethyl 2-(1-(2-trifluoromethylphenyl)-3-oxo-3-phenylpropyl)malonate (10f)



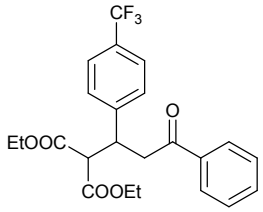
10f

White solid; m.p. 64.3-65.2 ºC; IR (KBr): *v* 2984, 2939, 1733, 1684, 1558, 1494, 1448, 1369, 1311, 1154, 1126, 1037, 861, 770, 749, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, *J* = 8.0 Hz, 2 H), 7.64 (d, *J* = 7.6 Hz, 1 H), 7.53 - 7.49 (m, 2 H), 7.45 - 7.39 (m, 3 H), 7.30 (t, *J* = 7.6 Hz, 1 H), 4.56 (q, *J* = 7.2 Hz, 1 H), 4.19 - 4.01 (m, 5 H), 3.74 - 3.69 (dd, J_1 = 5.2 Hz, J_2 = 16.8 Hz, 1 H), 3.63 - 3.57 (dd, J_1 = 8.0 Hz, J_2 = 16.8 Hz, 1 H), 1.17 (t, *J* = 7.2 Hz, 3 H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 168.3, 167.8, 140.0, 136.8, 133.1, 131.8, 128.7, 128.5, 128.4, 128.1, 127.1, 126.6, 126.5, 61.6, 56.1, 41.3, 35.9, 13.9, 13.7 ppm; HRMS (ESI) calcd for $C_{23}H_{23}F_3NaO_5$ [M+Na^+]: 459.1390, found: 459.1393.

(*R*)-**10f**: 95% yield; $[\alpha]_D^{20}$ -19.5 (*c* 1.35, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 8.32 min, t_{minor} = 14.27 min, 93% ee.

(*S*)-**10f**: 96% yield; $[\alpha]_D^{20}$ +20.6 (*c* 1.07, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 14.62 min, t_{minor} = 8.35 min, 96% ee.

Diethyl 2-(1-(4-trifluoromethylphenyl)-3-oxo-3-phenylpropyl)malonate (10g)



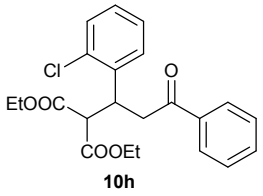
10g

White solid; m.p. 101-102 ºC; IR (KBr): *v* 2917, 2360, 2340, 1729, 1680, 1327, 1243, 1161, 1114, 1069, 846, 749, 668 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, *J* = 8.0 Hz, 2 H), 7.57 - 7.51 (m, 3 H), 7.46 - 7.41 (m, 4 H), 4.28 - 4.17 (m, 3 H), 3.97 (q, *J* = 7.2 Hz, 2 H), 3.83 (d, *J* = 9.6 Hz, 1 H), 3.60 - 3.47 (m, 2 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.02 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 166.9, 166.4, 143.7, 135.4, 132.2, 127.7, 124.3, 60.8, 60.5, 56.0, 41.1, 39.3, 12.9, 12.6 ppm; HRMS (ESI) calcd for $C_{23}H_{23}F_3NaO_5$ [M+Na^+]: 459.1390, found: 459.1400.

(*R*)-**10g**: 98% yield; $[\alpha]_D^{20}$ -18.1 (*c* 0.51, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 15.12 min, t_{minor} = 32.76 min, 95% ee.

(*S*)-**10g**: 98% yield; $[\alpha]_D^{20}$ +17.9 (*c* 0.80, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 33.50 min, t_{minor} = 15.07 min, 94% ee.

Diethyl 2-(1-(2-chlorophenyl)-3-oxo-3-phenylpropyl)malonate (10h) [3]



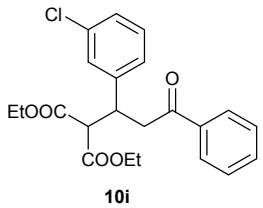
10h

Colorless oil; IR (KBr): *v* 3479, 2982, 2359, 1733, 1687, 1597, 1447, 1368, 1243, 1252, 1227, 1154, 1035, 846, 753, 668 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, *J* = 7.2 Hz, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 7.34 - 7.30 (m, 2 H), 7.17 - 7.10 (m, 2 H), 4.68-4.62 (m, 1 H), 4.21 - 4.11 (m, 2 H), 4.07 (d, J = 8.8 Hz, 1 H), 4.03 (q, *J* = 7.2 Hz, 2 H), 3.72 - 3.58 (m, 2 H), 1.20 (t, *J* = 7.2 Hz, 3 H), 1.08 (t, *J* = 7.2 Hz, 3H).

(*R*)-**10h**: 96% yield; $[\alpha]_D^{20}$ -44.9 (*c* 0.48, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 11.51 min, t_{minor} = 23.93 min, 96% ee.

(*S*)-**10h**: 95% yield; $[\alpha]_D^{20}$ +37.2 (*c* 1.50, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 23.69 min, t_{minor} = 11.46 min, 96% ee.

Diethyl 2-(1-(3-chlorophenyl)-3-oxo-3-phenylpropyl)malonate (10i)



10i

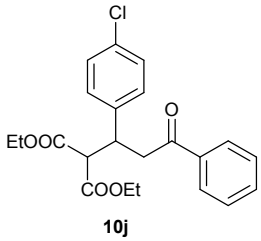
White solid; m.p. 75-77 ºC; IR (KBr): *v* 3488, 2980, 1730, 1685, 1596, 1367, 1255, 1154, 1032, 846, 755, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, *J* = 8.0 Hz, 2 H), 7.55 (t, *J* = 7.2 Hz, 1 H), 7.44 (t, *J* = 7.2 Hz, 2 H), 7.20 - 7.17 (m, 4 H), 4.24 - 4.14 (m, 3 H), 4.00 (q, *J* = 7.2 Hz, 2 H), 3.79 (d, *J* = 9.6 Hz, 1 H), 3.57 - 3.42 (m, 2 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.05 (t, *J* = 7.2

Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 168.1, 167.5, 142.7, 136.6, 134.1, 133.2, 129.6, 128.6, 128.4, 128.1, 127.4, 126.7, 61.8, 61.5, 57.2, 42.2, 40.3, 14.0, 13.8 ppm; HRMS (ESI) calcd for $C_{22}H_{23}ClNaO_5$ [M+Na$^+$]: 425.1126, found: 425.1124.

(*R*)-**10i**: 98% yield; $[\alpha]_D^{20}$ -30.2 (*c* 0.37, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 14.64 min, t_{minor} = 17.73 min, 92% ee.

(*S*)-**10i**: 99% yield; $[\alpha]_D^{20}$ +24.7 (*c* 1.62, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 17.66 min, t_{minor} = 14.62 min, 99% ee.

Diethyl 2-(1-(4-chlorophenyl)-3-oxo-3-phenylpropyl)malonate (10j) [3]



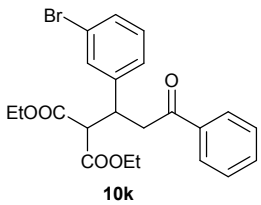
10j

White solid; m.p. 97-98.8 ºC; IR (KBr): *v* 3062, 2982, 1748, 1731, 1686, 1486, 1450, 1367, 1250, 1225, 1028, 860, 750, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, *J* = 7.2 Hz, 2 H), 7.56 (t, 1 H), 7.45 (t, 2 H), 7.24 (s, 4 H), 4.27 - 4.15 (m, 3 H), 4.00 (q, *J* = 7.2 H, 2 H), 3.80 (d, *J* = 9.6 Hz, 1 H), 3.58 - 3.42 (m, 2 H), 1.27 (t, *J* = 7.2 Hz, 3 H), 1.07 (t, *J* = 7.2 Hz, 3H) ppm.

(*R*)-**10j**: 99% yield; $[\alpha]_D^{20}$ -9.4 (*c* 0.67, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 18.47 min, t_{minor} = 45.98 min, 94% ee.

(*S*)-**10j**: 94% yield; $[\alpha]_D^{20}$ +6.3 (*c* 0.64, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 42.85 min, t_{minor} = 17.83 min, 90% ee.

Diethyl 2-(1-(3-bromophenyl)-3-oxo-3-phenylpropyl)malonate (10k)



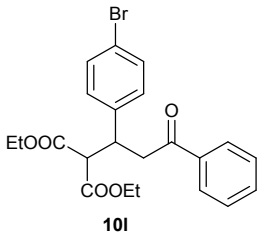
10k

White solid; m.p. 59.6-60.7 ºC; IR (KBr): *v* 2922, 2850, 1733, 1687, 1579, 1447, 1367, 1254, 1223, 1150, 1027, 887, 784, 750, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, *J* = 8.0 Hz, 2 H), 7.55 (t, *J* = 7.2 Hz, 1 H), 7.44 (t, *J* = 7.6 Hz, 2 H), 7.31 (d, *J* = 7.6 Hz, 1 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 7.13 (t, *J* = 8.0 Hz, 1 H), 4.22 - 4.13 (m, 3 H), 4.00 (q, *J* = 7.2 Hz, 2 H), 3.78 (d, *J* = 9.6 Hz, 1 H), 3.57 - 3.42 (m, 2 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.06 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 167.0, 166.5, 142.0, 135.5, 132.2, 130.2, 129.2, 128.9, 127.5, 127.0, 126.1, 121.3, 60.7, 60.5, 56.1, 41.1, 39.2, 13.0, 12.7 ppm; HRMS (ESI) calcd for $C_{22}H_{23}BrNaO_5$ [M+Na$^+$]: 469.0621, found: 469.0616.

(*R*)-**10k**: 97% yield; $[\alpha]_D^{20}$ -24.9 (*c* 0.50, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 14.73 min, t_{minor} = 17.81 min, 90% ee.

(*S*)-**10k**: 99%yield; $[\alpha]_D^{20}$ +25.1 (*c* 1.76, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 18.42 min, t_{minor} = 15.07 min, 90% ee.

Diethyl 2-(1-(4-bromophenyl)-3-oxo-3-phenylpropyl)malonate (10l)



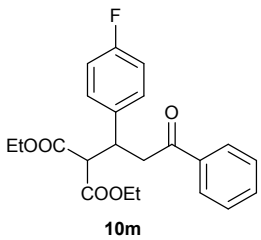
10l

White solid; m.p. 105-106 ºC; IR (KBr): *v* 3062, 2981, 1747, 1729, 1684, 1487, 1447, 1367, 1250, 1225, 1151, 1028, 861, 750, 668 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, *J* = 7.6 Hz, 2 H), 7.55 (t, *J* = 7.2 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 4.24 - 4.12 (m, 3 H), 4.04 (q, *J* = 7.2 Hz, 2 H), 3.78 (d, *J* = 9.6 Hz, 1 H), 3.55 - 3.40 (m, 2 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.05 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.1, 167.0, 166.5, 138.5, 135.5, 132.2, 130.4, 129.0, 127.6, 127.0, 120.0, 60.7, 60.5, 56.2, 42.3, 39.1, 13.0, 12.8 ppm; HRMS (ESI) calcd for $C_{22}H_{23}BrNaO_5$ [M+Na^+]: 469.0621, found: 469.0615.

(*R*)-**10l**: 89% yield; $[\alpha]_D^{20}$ -5.9 (*c* 0.36, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 19.58 min, t_{minor} = 48.46 min, 93% ee.

(*S*)-**10l**: 90% yield; $[\alpha]_D^{20}$ +6.6 (*c* 0.58, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 47.18 min, t_{minor} = 19.98 min, 90% ee.

Diethyl 2-(1-(4-fluorophenyl)-3-oxo-3-phenylpropyl)malonate (10m)



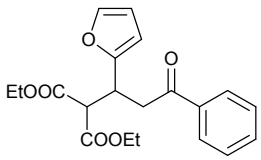
10m

White solid; m.p. 77-79 ºC; IR (KBr): *v* 3473, 3415, 2982, 2849, 1732, 1684, 1618, 1151, 1223, 1178, 1097, 847, 739, 612 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, *J* = 7.2 Hz, 2 H), 7.54 (t, *J* = 7.2 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 7.24 (t, *J* = 7.2 Hz, 2 H), 6.93 (t, *J* = 8.8 Hz, 2 H), 4.27 - 4.14 (m, 3 H), 3.97 (q, *J* = 7.2 Hz, 2 H), 3.78 (d, *J* = 9.6 Hz, 1 H), 3.56 - 3.51 (dd, J_1 = 4.4 Hz, J_2 = 16.8 Hz, 1 H), 3.45 - 3.39 (dd, J_1 = 9.6 Hz, J_2 = 16.8 Hz, 1 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.03 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 167.1, 166.6, 161.9, 159.5, 135.6, 135.1, 132.1, 128.9, 128.8, 127.5, 127.0, 114.2, 114.0, 60.7, 60.4, 56.5, 41.6, 39.0, 13.0, 12.7 ppm; HRMS (ESI) calcd for $C_{22}H_{23}FNaO_5$ [M+Na^+]: 409.1422, found: 409.1411.

(*R*)-**10m**: 99% yield; $[\alpha]_D^{20}$ -22.5 (*c* 0.43, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 16.48 min, t_{minor} = 44.42 min, 92% ee.

(*S*)-**10m**: 99% yield; $[\alpha]_D^{20}$ +20.3 (*c* 1.69, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 41.96 min, t_{minor} = 16.31 min, 90% ee.

Diethyl 2-(1-(furan-2-yl)-3-oxo-3-phenylpropyl)malonate (10n) [5]



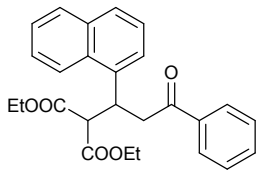
10n

White solid; m.p. 39-40 ºC; IR (KBr): *v* 1732, 1684, 1596, 1451, 1367, 1255, 1225, 1154, 1096, 1013, 859, 737, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, *J* = 7.2 Hz, 2 H), 7.57 (t, *J* = 7.2 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 2 H), 7.29 (s, 1 H), 6.25 -6.24 (m, 1 H), 6.13 (d, *J* = 3.2 Hz, 1 H), 4.38 - 4.32 (m, 1 H), 4.26-4.18 (m, 2 H), 4.13 (q, *J* = 7.2 Hz, 2 H), 3.93 (d, *J* = 8.0 Hz, 1 H), 3.63 - 3.46 (m, 2 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 1.19 (t, *J* = 7.2 Hz, 3 H) ppm.

(*R*)-**10n**: 87% yield; $[\alpha]_D^{20}$ -16.9 (*c* 0.47, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 11.80 min, t_{minor} = 14.76 min, 91% ee.

(*S*)-**10n**: 85% yield; $[\alpha]_D^{20}$ +14.6 (*c* 0.89, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 14.87 min, t_{minor} = 11.95 min, 91% ee.

Diethyl 2-(1-(naphthalen-1-yl)-3-oxo-3-phenylpropyl)malonate (10o) [6]



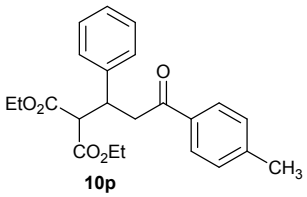
10o

White solid; m.p. 75.6-77.3 ºC; IR (KBr): *v* 3419, 2982, 2359, 1730, 1687, 1597, 1448, 1367, 1248, 1219, 1152, 1030, 860, 779, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.30 (d, *J* = 8.4 Hz, 1 H), 7.88 (d, *J* = 7.6 Hz, 2 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.56 - 7.34 (m, 7 H), 5.16 (d, *J* = 6.4 Hz, 1 H), 4.20 - 4.10 (m, 2 H), 4.03 (d, *J* = 8.4 Hz, 1 H), 3.90 - 3.84 (m, 2 H), 3.73 (d, *J* = 6.4 Hz, 2 H), 1.18 (t, *J* = 7.2 Hz, 3 H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm.

(*R*)-**10o**: 80% yield; $[\alpha]_D^{20}$ -80.9 (*c* 0.31, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 15.14 min, t_{minor} = 22.25 min, 94% ee.

(*S*)-**10o**: 83% yield; $[\alpha]_D^{20}$ +56.3 (*c* 1.89, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 23.43 min, t_{minor} = 15.24 min, 95% ee.

Diethyl 2-(1-phenyl-3-oxo-3-(4-methylphenyl) propyl)malonate (10p)



10p

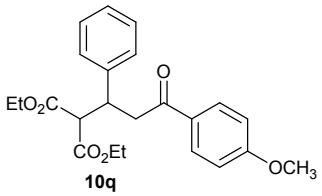
White solid; m.p. 86.5-88.4 ºC; IR (KBr): *v* 2981, 2928, 1728, 1685, 1607, 1465, 1368, 1179, 1148, 1029, 865, 818, 699 cm^{-1}; ^1H NMR

($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 8.0 Hz, 2 H), 7.27 - 7.14 (m, 7 H), 4.25 - 4.13 (m, 3 H), 3.97 - 3.92(q, *J* = 7.2 Hz, 2 H), 3.82 (d, *J* = 9.6 Hz, 1 H), 3.53 - 3.39(m, 2 H), 2.38 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.00 (t, *J* = 7.2 Hz, 3 H) ppm.

(*R*)-**10p**: 96% yield; $[\alpha]_D^{20}$ -17.0 (*c* 1.24, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 22.77 min, t_{minor} = 44.48 min, 94% ee.

(*S*)-**10p**: 95% yield; $[\alpha]_D^{20}$ +22.4 (*c* 1.20, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 44.14 min, t_{minor} = 22.02 min, 94% ee.

Diethyl 2-(1-phenyl-3-oxo-3-(4-methoxyphenyl) propyl)malonate (10q) [3]



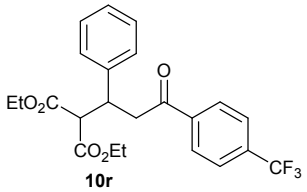
10q

White solid; m.p. 70.1-70.5 ºC; IR (KBr): *v* 2979, 2926, 2841, 1736, 1673, 1598, 1369, 1249, 1225, 1168, 1021, 841, 763, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, *J* = 9.2 Hz, 2 H), 7.27 - 7.14 (m, 5 H), 6.89 (d, *J* = 8.8 Hz, 2 H) 4.25 - 4.14 (m, 3 H), 3.97 - 3.92(q, *J* = 7.2 Hz, 2 H), 3.85 (s, 3 H), 3.82 (d, *J* = 10.0 Hz, 1 H), 3.51 - 3.35(m, 2 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.00 (t, *J* = 7.2 Hz, 3 H) ppm.

(*R*)-**10q**: 98% yield; $[\alpha]_D^{20}$ -11.8 (*c* 1.25, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 35.15 min, t_{minor} = 61.07 min, 96% ee.

(*S*)-**10q**: 96% yield; $[\alpha]_D^{20}$ +18.7 (*c* 1.01, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 60.61 min, t_{minor} = 34.10 min, 94% ee.

Diethyl 2-(1-phenyl-3-oxo-3-(4-trifluoromethylphenyl) propyl)malonate (10r)



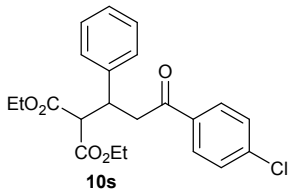
10r

White solid; m.p. 49.7-50.2 ºC; IR (KBr): *v* 2981, 2920, 1732, 1694, 1461, 1324, 1257, 1167, 1129, 1066, 1014, 852, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, *J* = 8.4 Hz, 2 H), 7.69 (d, *J* = 8.0 Hz, 2 H), 7.27 - 7.16 (m, 5 H), 4.27 - 4.13 (m, 3 H), 3.99 - 3.93(q, *J* = 7.2 Hz, 2 H), 3.82 (d, *J* = 9.6 Hz, 1 H), 3.62 - 3.37(m, 2 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.01 (t, *J* = 7.2 Hz, 3 H) ppm.

(*R*)-**10r**: 99% yield; $[\alpha]_D^{20}$ -12.7 (*c* 1.80, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 18.23 min, t_{minor} = 28.86 min, 95% ee.

(*S*)-**10r**: 98% yield; $[\alpha]_D^{20}$ +14.3 (*c* 1.71, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 29.09 min, t_{minor} = 18.15 min, 90% ee.

Diethyl 2-(1-phenyl-3-oxo-3-(4-chlorophenyl) propyl)malonate (10s) [3]



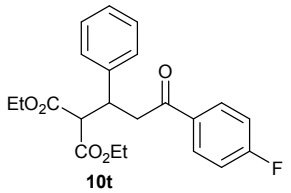
10s

White solid; m.p. 54.6-55.2 ºC; IR (KBr): *v* 2981, 2920, 1733, 1689, 1589, 1400, 1256, 1152, 1093, 1031, 829, 764, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.84 (d, *J* = 8.4 Hz, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 7.24 - 7.15 (m, 5 H), 4.26 - 4.11 (m, 3 H), 3.98 - 3.93(q, *J* = 7.2 Hz, 2 H), 3.80 (d, *J* = 9.6 Hz, 1 H), 3.55 - 3.37(m, 2 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.00 (t, *J* = 7.2 Hz, 3 H) ppm.

(*R*)-**10s**: 96% yield; $[\alpha]_D^{20}$ -14.0 (*c* 1.98, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 20.75 min, t_{minor} = 46.50 min, 96% ee.

(*S*)-**10s**: 97% yield; $[\alpha]_D^{20}$ +15.4 (*c* 1.75, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 46.45 min, t_{minor} = 20.47 min, 92% ee.

Diethyl 2-(1-phenyl-3-oxo-3-(4-fluorophenyl) propyl)malonate (10t)



10t

White solid; m.p. 68.6-69.7 ºC; IR (KBr): *v* 2982, 2930, 1729, 1689, 1597, 1507, 1254, 1230, 1156, 1031, 840, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.95 - 7.91 (m, 2 H), 7.25 - 7.06 (m, 7 H), 4.26 - 4.12 (m, 3 H), 3.98 - 3.93(q, *J* = 7.2 Hz, 2 H), 3.81 (d, *J* = 9.6 Hz, 1 H), 3.55 - 3.37(m, 2 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.01 (t, *J* = 7.2 Hz, 3 H) ppm.

(*R*)-**10t**: 99% yield; $[\alpha]_D^{20}$ -16.4 (*c* 1.78, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 17.74 min, t_{minor} = 39.34 min, 95% ee.

(*S*)-**10t**: 99% yield; $[\alpha]_D^{20}$ +14.7 (*c* 1.95, $CHCl_3$); chiral HPLC Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm, t_{major} = 39.44 min, t_{minor} = 17.57 min, 90% ee.

5. Reference

1 H. Li, X. Zhang, X. Shi, W. He, S. Zhang and B. Zhang, *Adv. Synth. Catal.*, 2012, **354**, 2264.

2 M. Agostinho and S. Kobayashi, *J. Am. Chem. Soc.*, 2008, **130**, 2430..

3 J. Wang, H. Li, L. Zu, W. Jiang, H. Xie, W. Duan and W. Wang, *J. Am. Chem. Soc.*, 2006, **128**, 12652

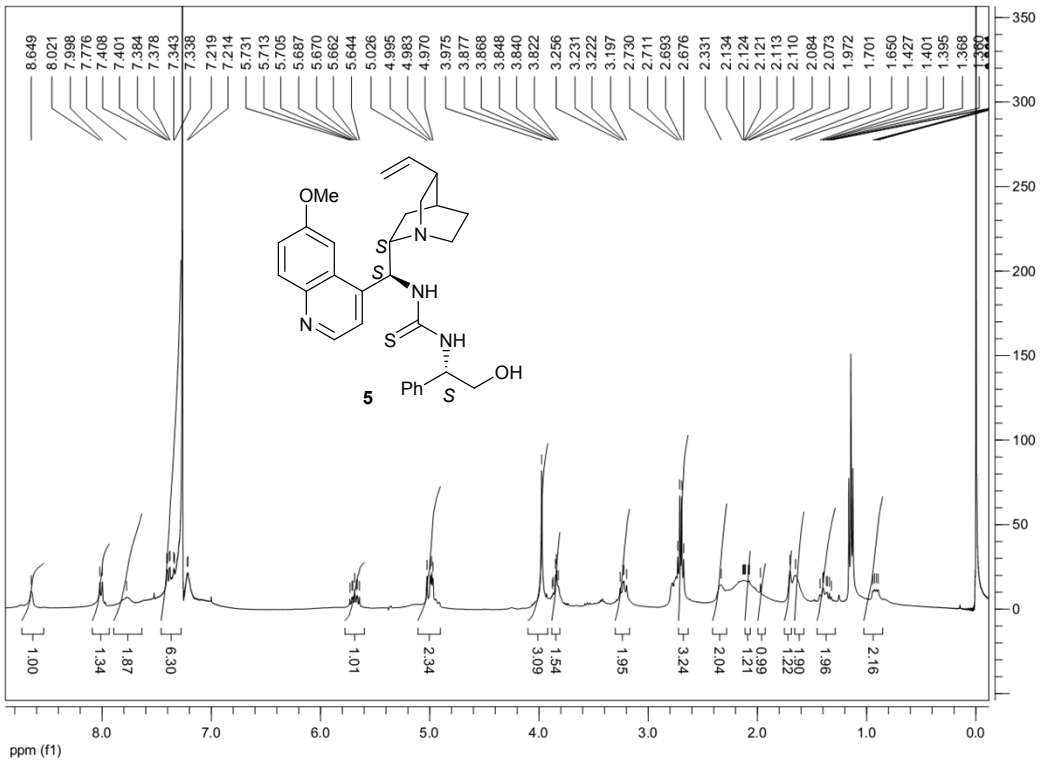
4 S. Saravanan and S. Muthusubramanian, *Indian J. Chem., Sec. B*, 2010, **49B**, 917.

5 T. Ooi, D. Ohara, K. Fukumoto and K. Maruoka, *Org. Lett.*, 2005, **7**, 3195.

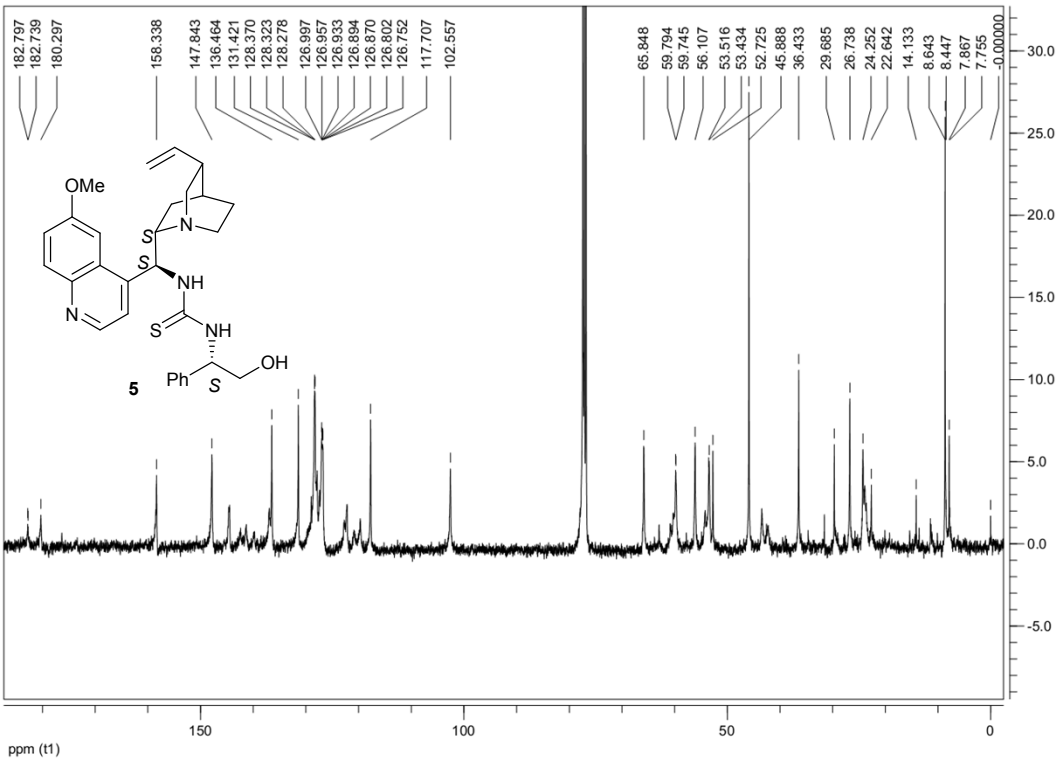
6 Y. Suzuki, J. Wakatsuki, M. Tsubaki and M. Sato, *Tetrahedron*, 2013, **69**, 9690.

6. Spectra of organocatalysts 5-7

^{1}H NMR of **5**



^{13}C NMR of **5**



HRMS of **5**

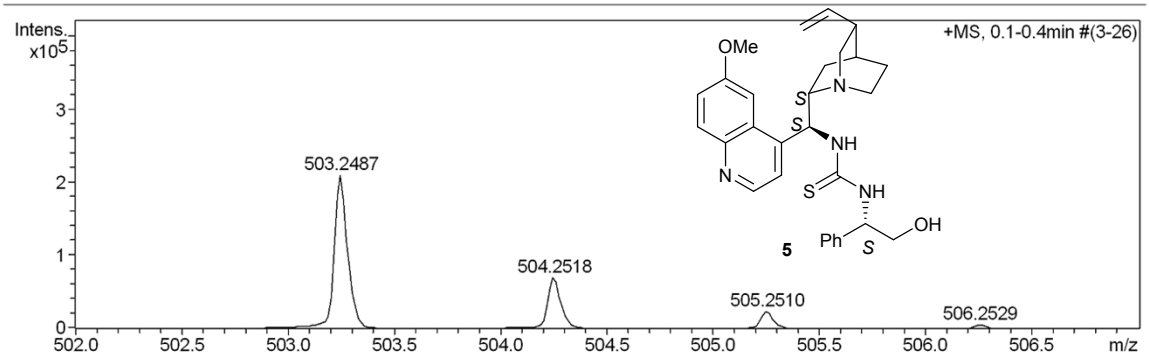
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	C:\Documents and Settings\Administrator\×ÀÃæ\ÁõÓñÁú\gzh-lyl-a.d	Acquisition Date	2013-5-13 16:17:19
Method	tune_low 50-500.m	Operator	NWU
Sample Name	Sample	Instrument / Ser#	micrOTOF-Q II 10280
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	110.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule
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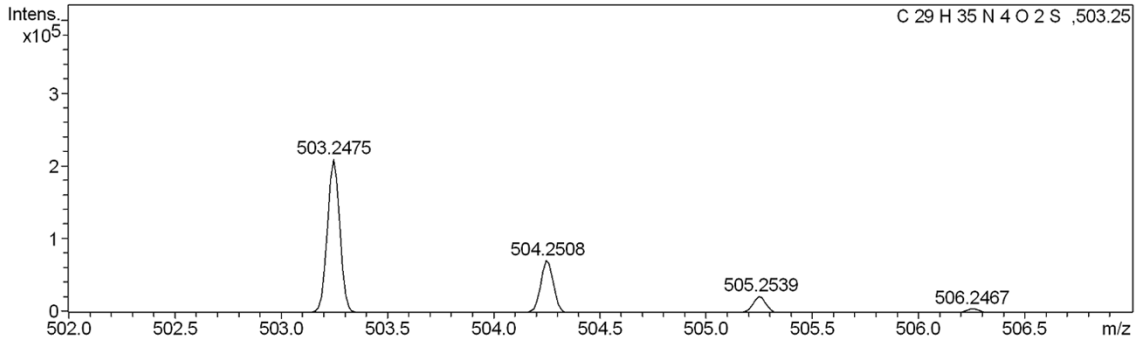
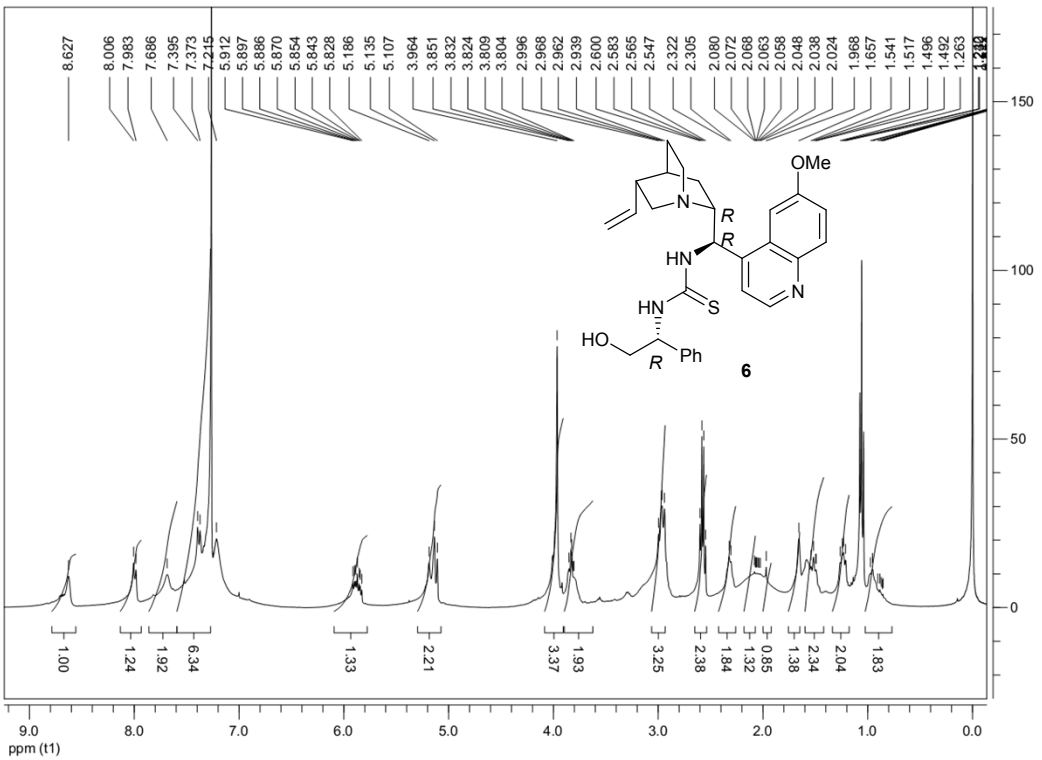
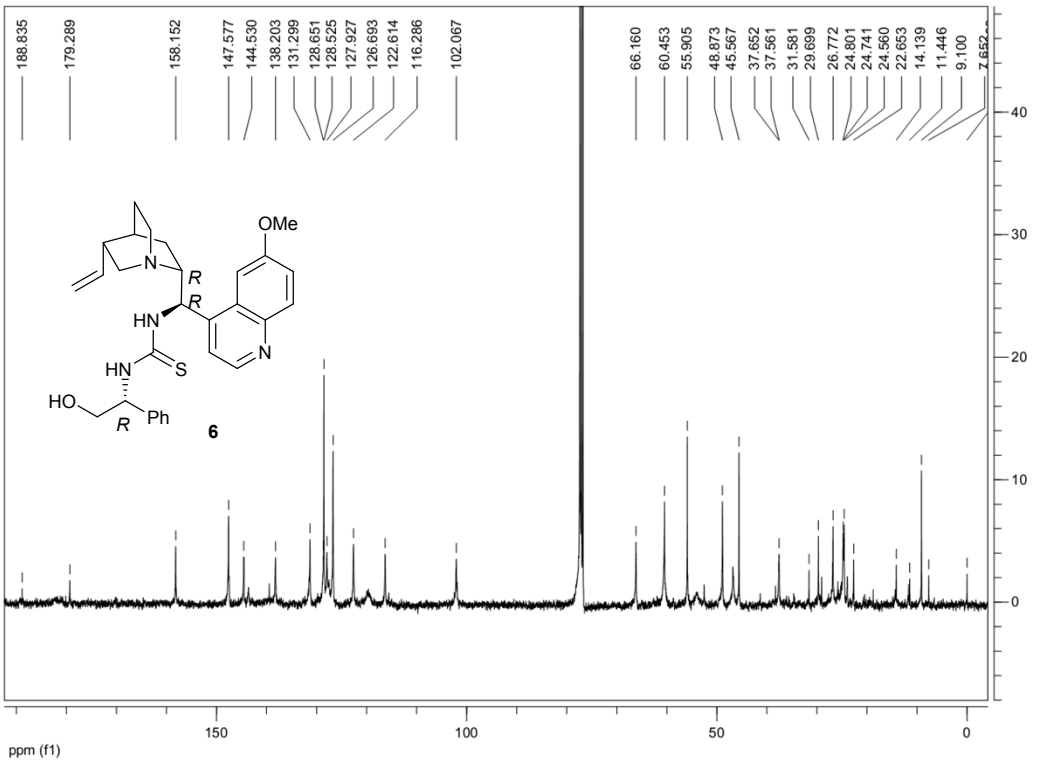


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule

^{1}H NMR of **6**



^{13}C NMR of **6**



HRMS of **6**

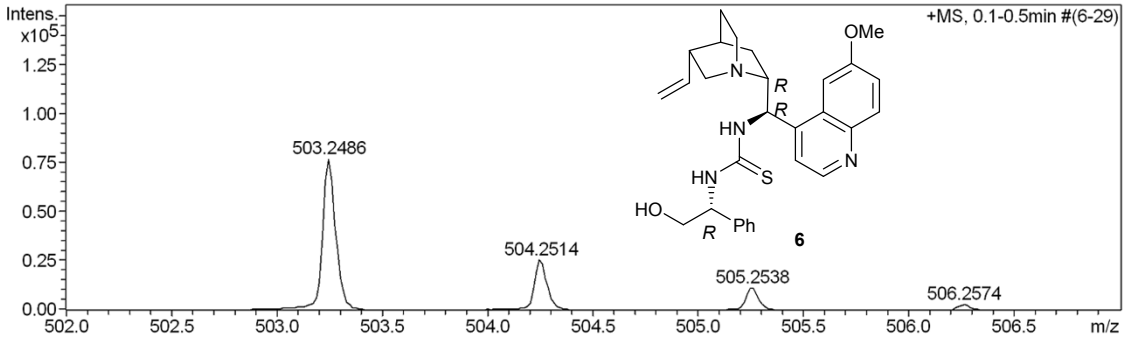
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	C:\Documents and Settings\Administrator\×ÀÃæ\ÁõÓñÁú\gzh-lyl-b.d	Acquisition Date	2013-5-13 16:18:40
Method	tune_low 50-500.m	Operator	NWU
Sample Name	Sample	Instrument / Ser#	micrOTOF-Q II 10280
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	110.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule
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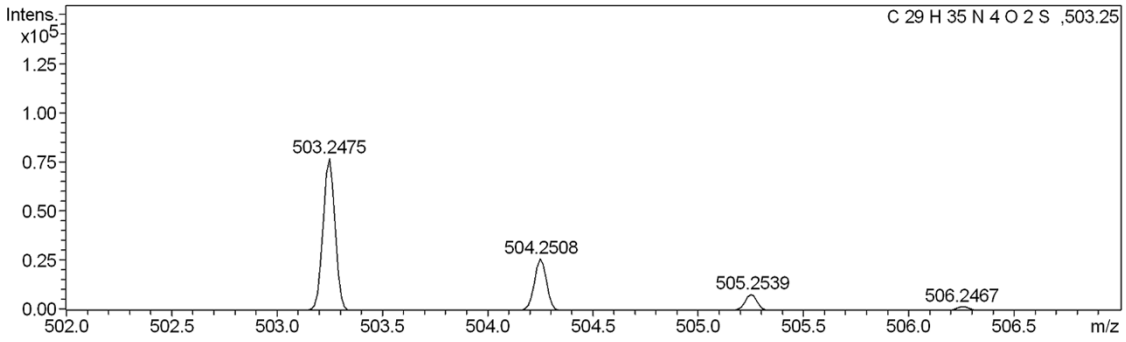
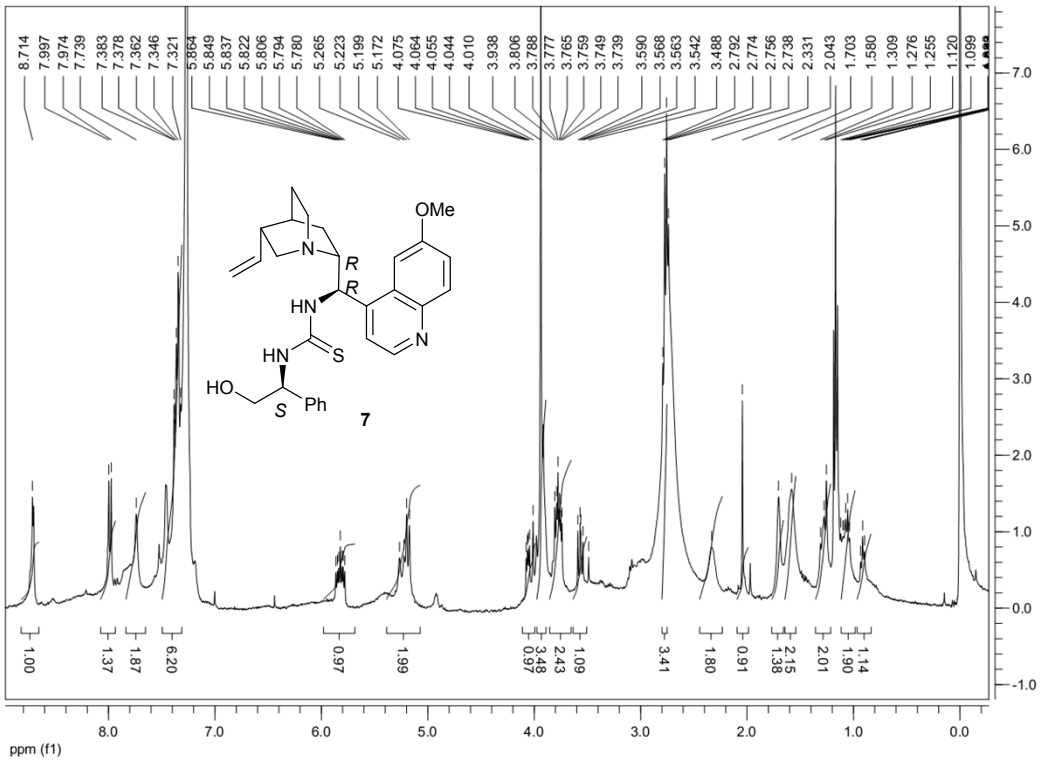
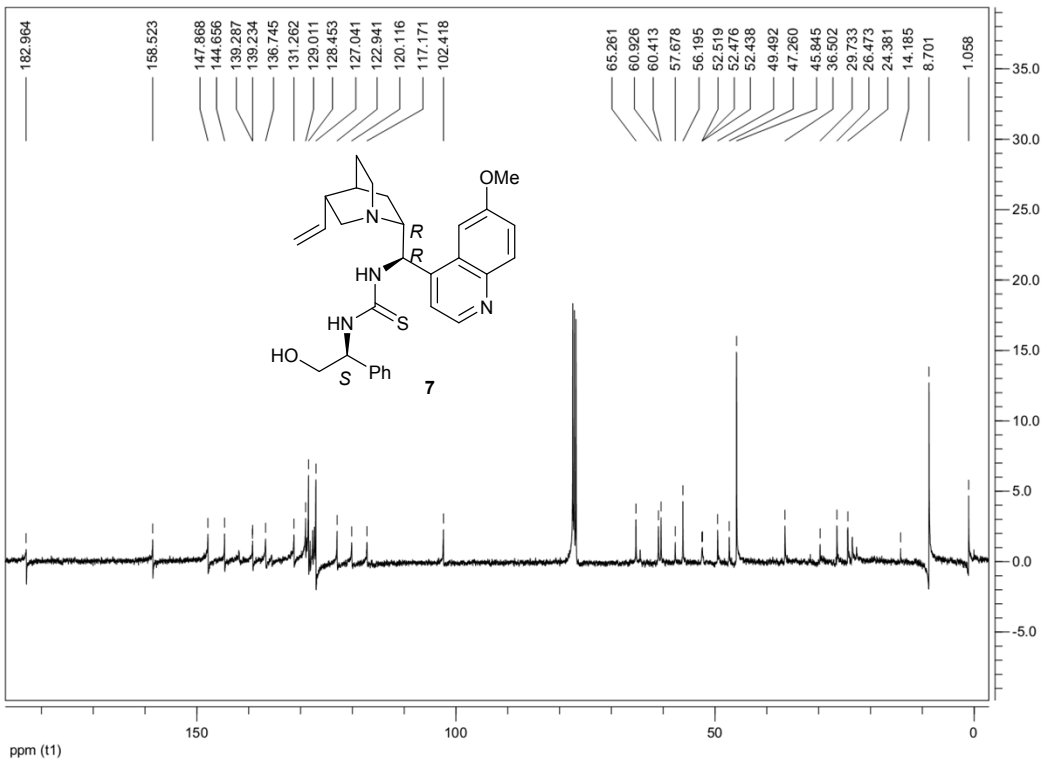


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule

^{1}H NMR of **7**



^{13}C NMR of **7**



^{1}H NMR of **7**

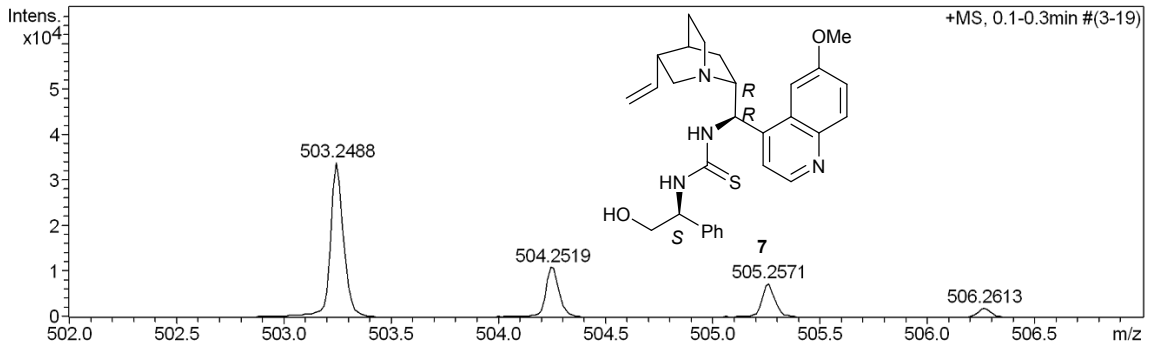
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	C:\Documents and Settings\Administrator\×ÀÃæ\ÁõÓñÁú\gzh-lyl-c.d	Acquisition Date	2013-5-13 16:20:36
Method	tune_low 50-500.m	Operator	NWU
Sample Name	Sample	Instrument / Ser#	micrOTOF-Q II 10280
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	110.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡Ÿ Conf	N-Rule
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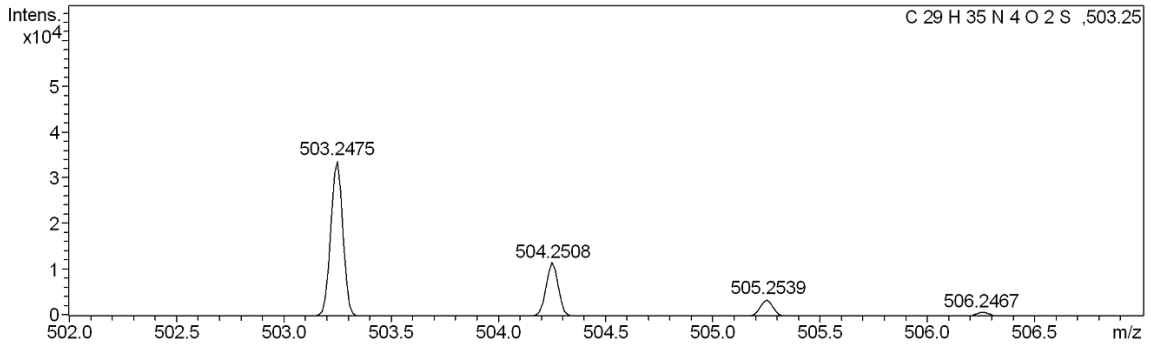
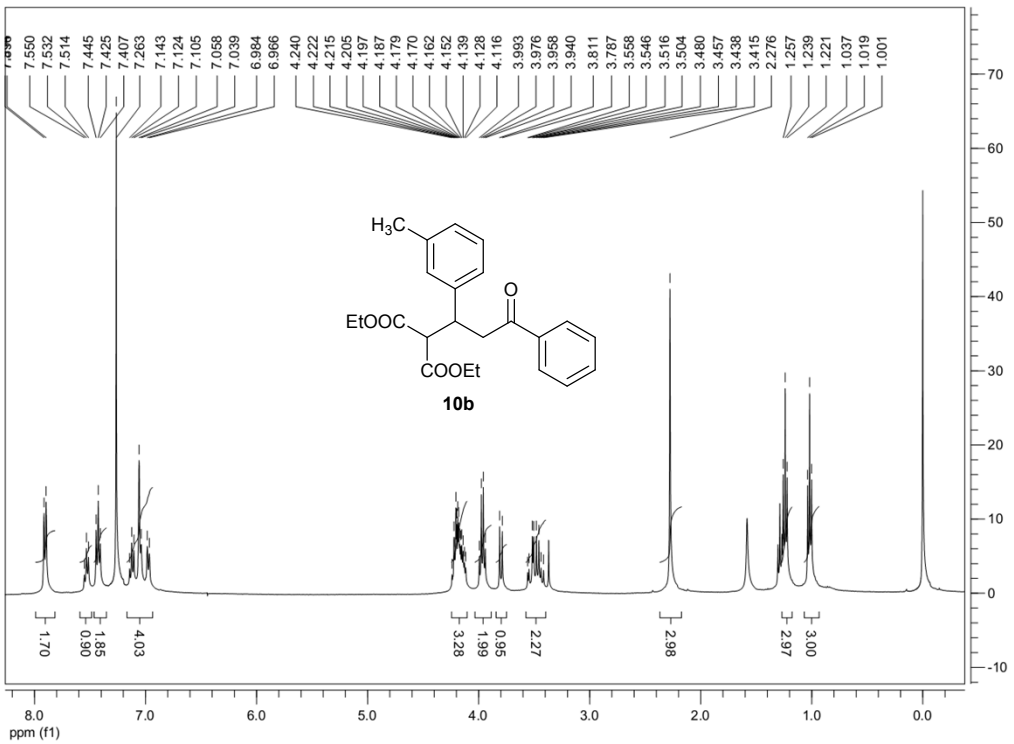


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡Ÿ Conf	N-Rule

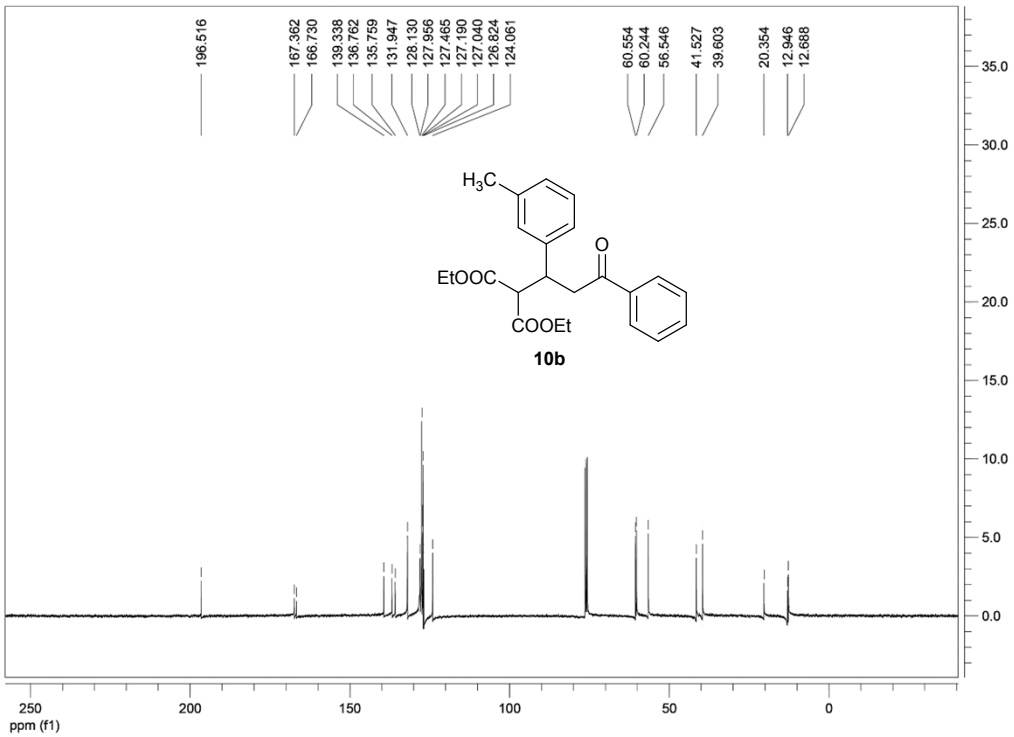
7. Spectra of new compounds of Michael adducts

Michael adducts **10a**, **10c**, **10e**, **10h**, **10j**, **10n**, **10o**, **10p**, **10q**, **10r**, **10s** and **10t** are known compounds, and their spectra are in accordance with those reported in the literature.

^{1}H NMR of **10b**



^{13}C NMR of **10b**



HRMS of **10b**

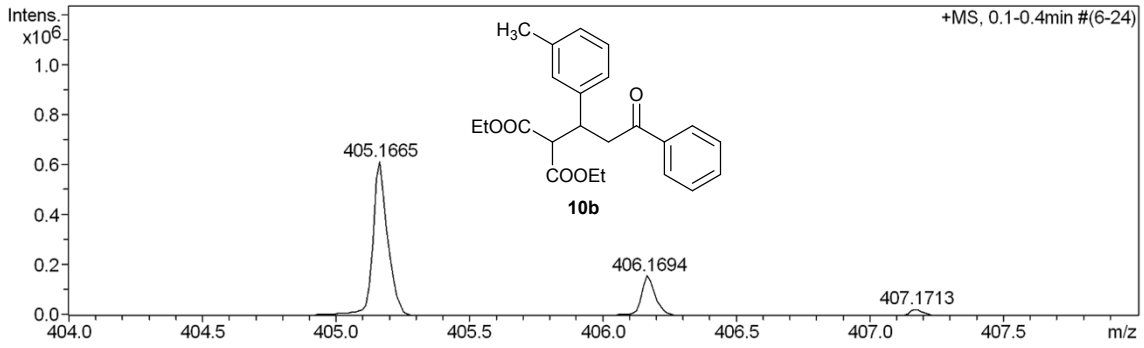
Mass Spectrum SmartFormula Report

Analysis Info

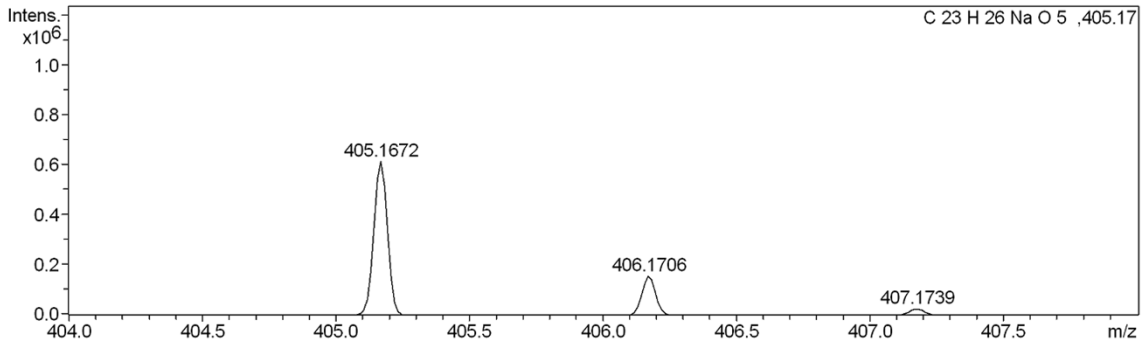
Analysis Name	H:\gzh_lianghao_2.d	Acquisition Date	2013-5-9 15:42:27
Method	tune_low 50-500.m	Operator	NWU
Sample Name	Sample	Instrument / Ser#	micrOTOF-Q II 10280
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	110.0 Vpp	Set Divert Valve	Source

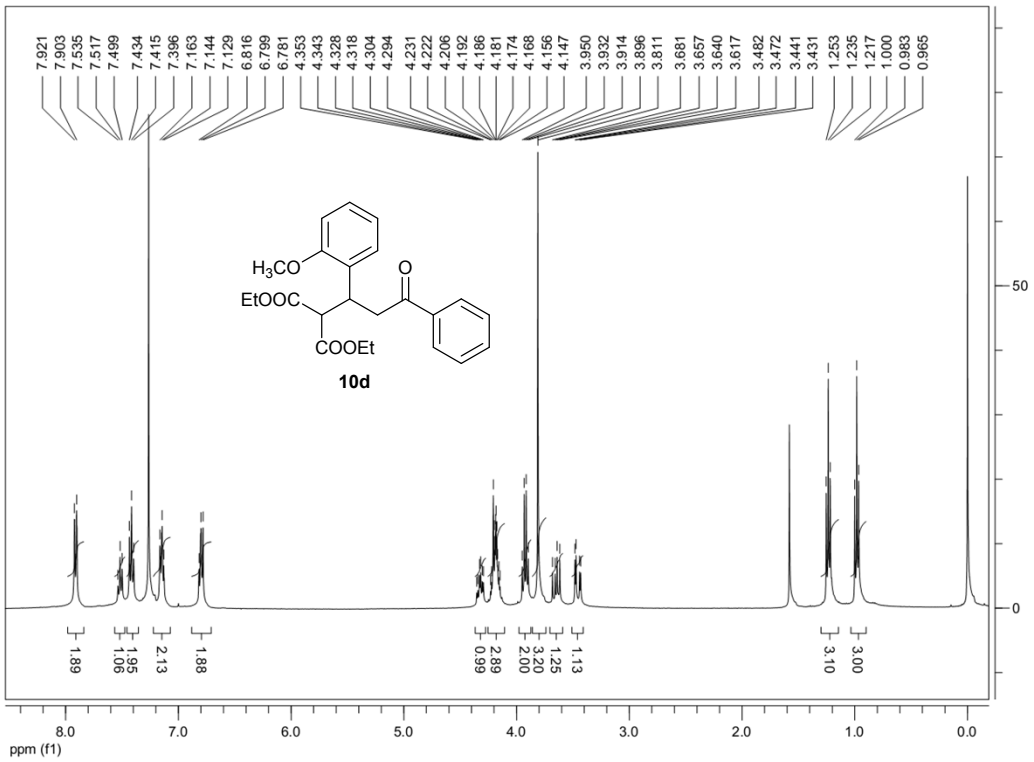


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule
405.1665	1	C 23 H 26 Na O 5	100.00	405.1672	0.7	1.7	5.4	10.5	even	ok

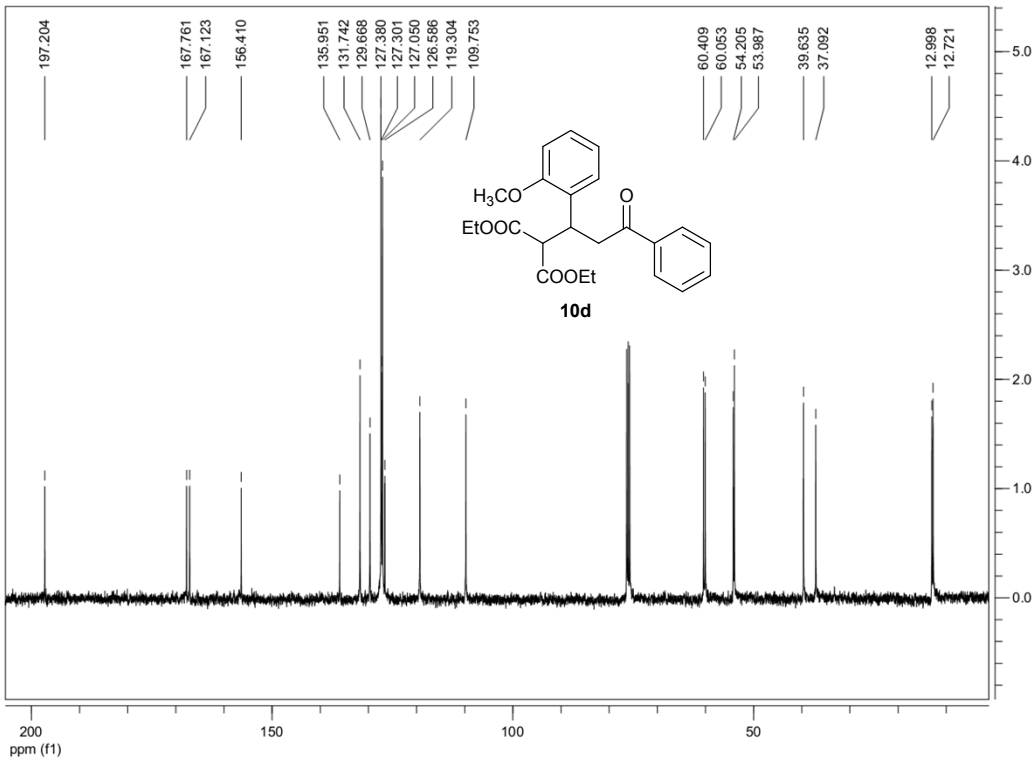


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule

^{1}H NMR of **10d**



^{13}C NMR of **10d**



HRMS of **10d**

Mass Spectrum SmartFormula Report

Analysis Info

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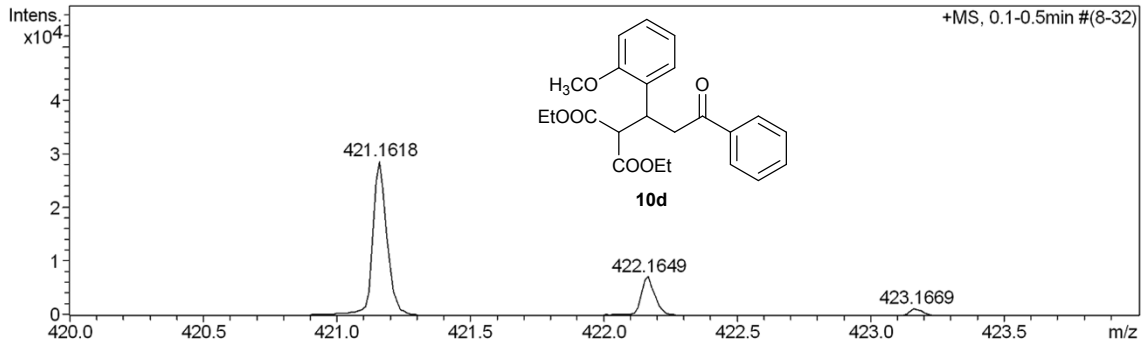
Method	tune_low 50-500.m	Operator	NWU
Sample Name	Sample	Instrument / Ser#	micrOTOF-Q II 10280
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	110.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule
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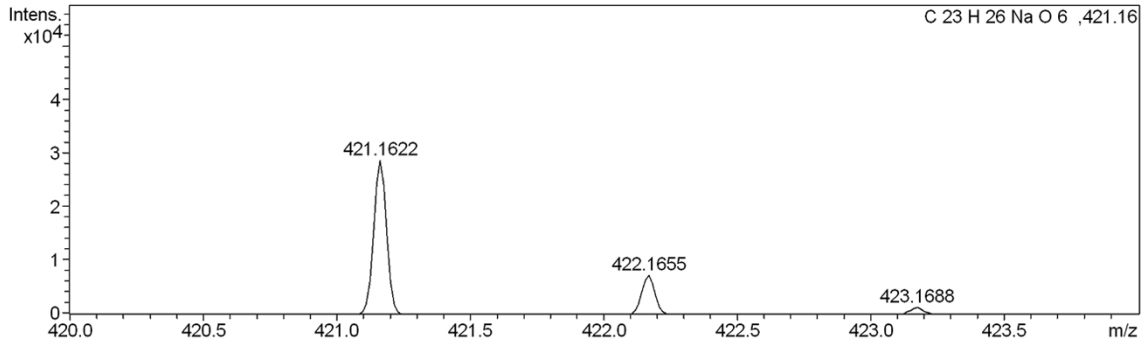
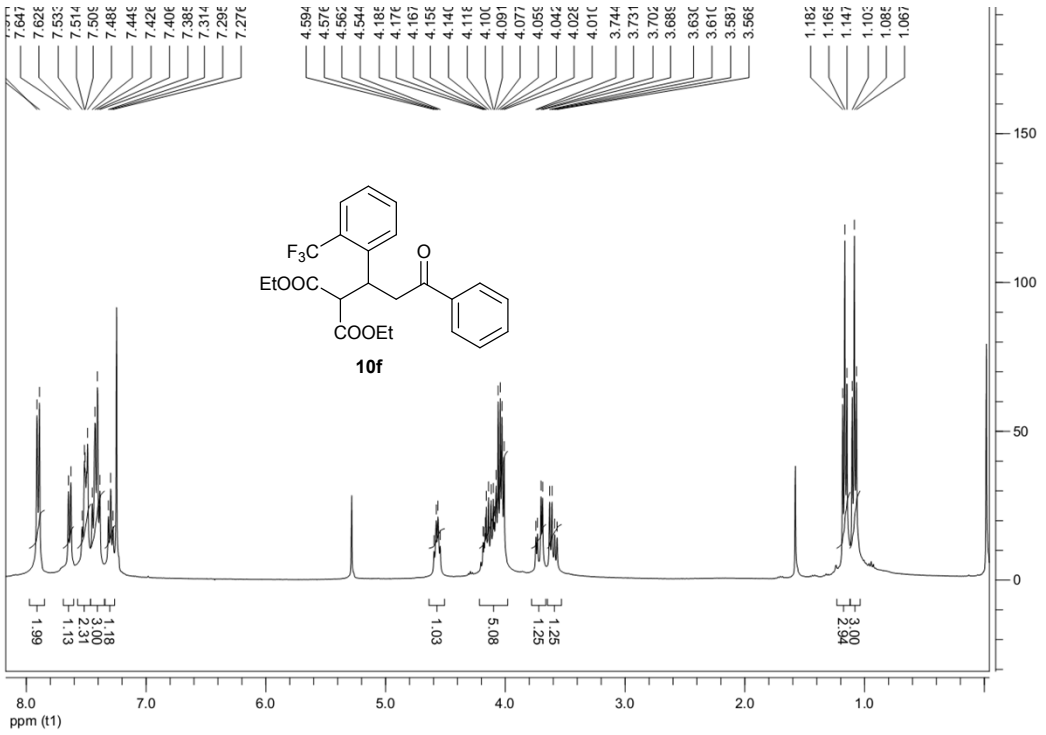
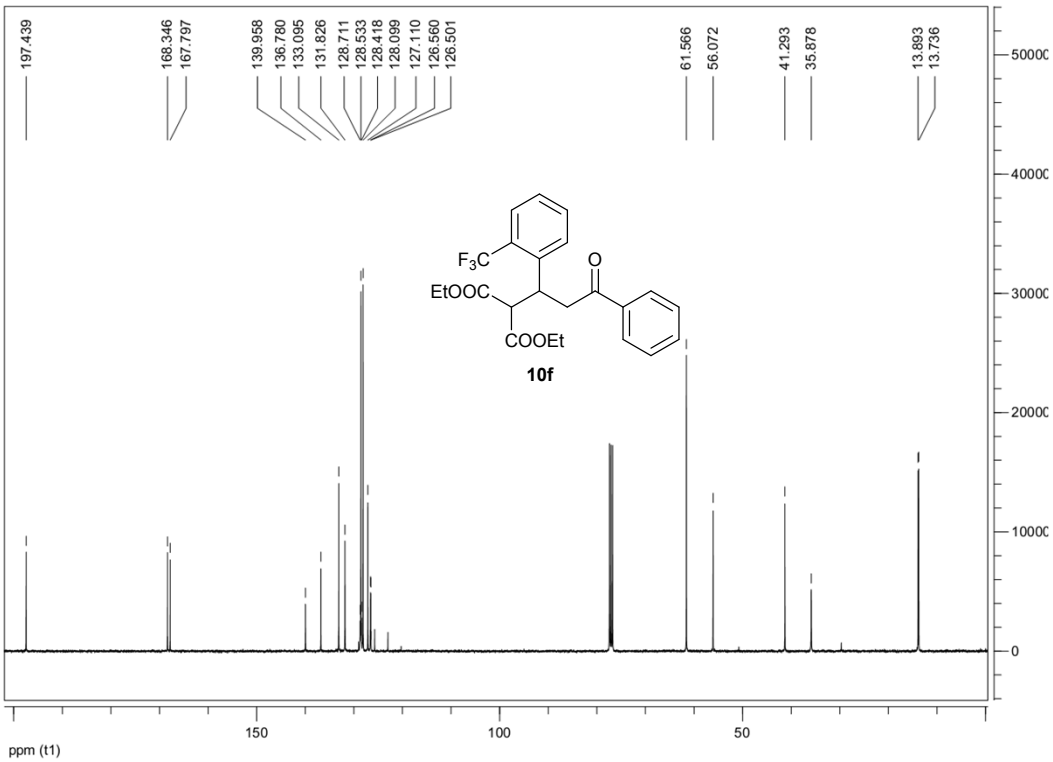


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule

^{1}H NMR of **10f**



^{13}C NMR of **10f**



HRMS of **10f**

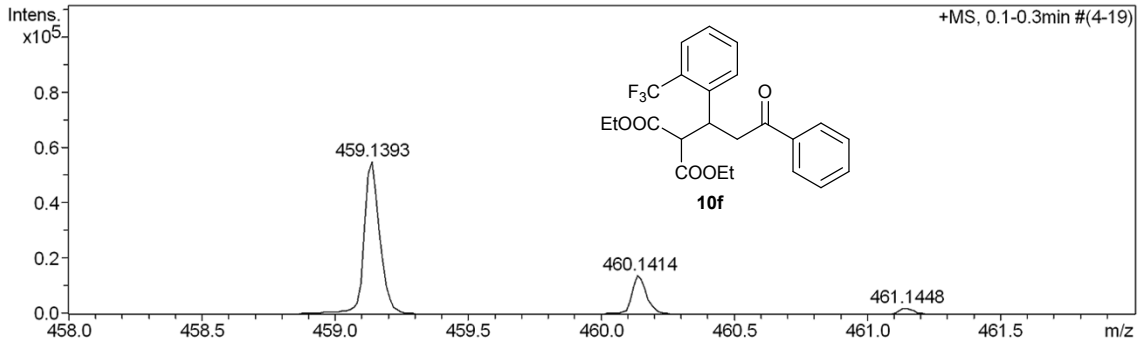
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	C:\Documents and Settings\Administrator\×ÀÃæ\ÁõÓñÁú\gzh_lianghao_6.d	Acquisition Date	2013-5-9 15:50:01
Method	tune_low 50-500.m	Operator	NWU
Sample Name	Sample	Instrument / Ser#	micrOTOF-Q II 10280
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	110.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule
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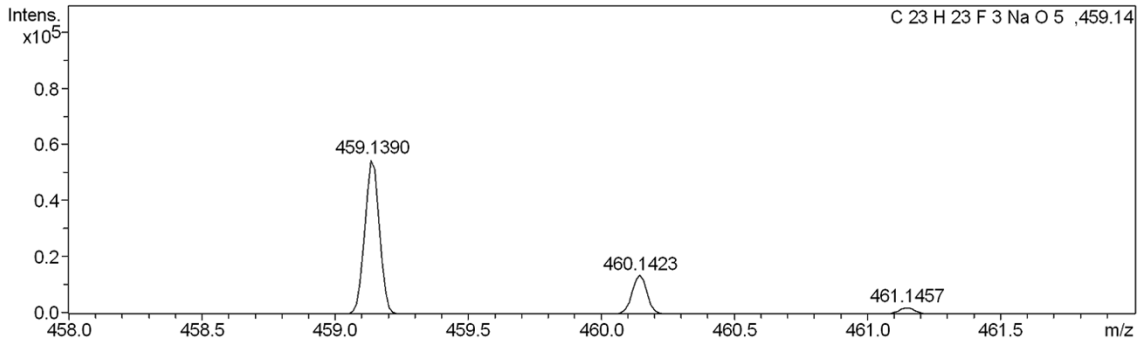
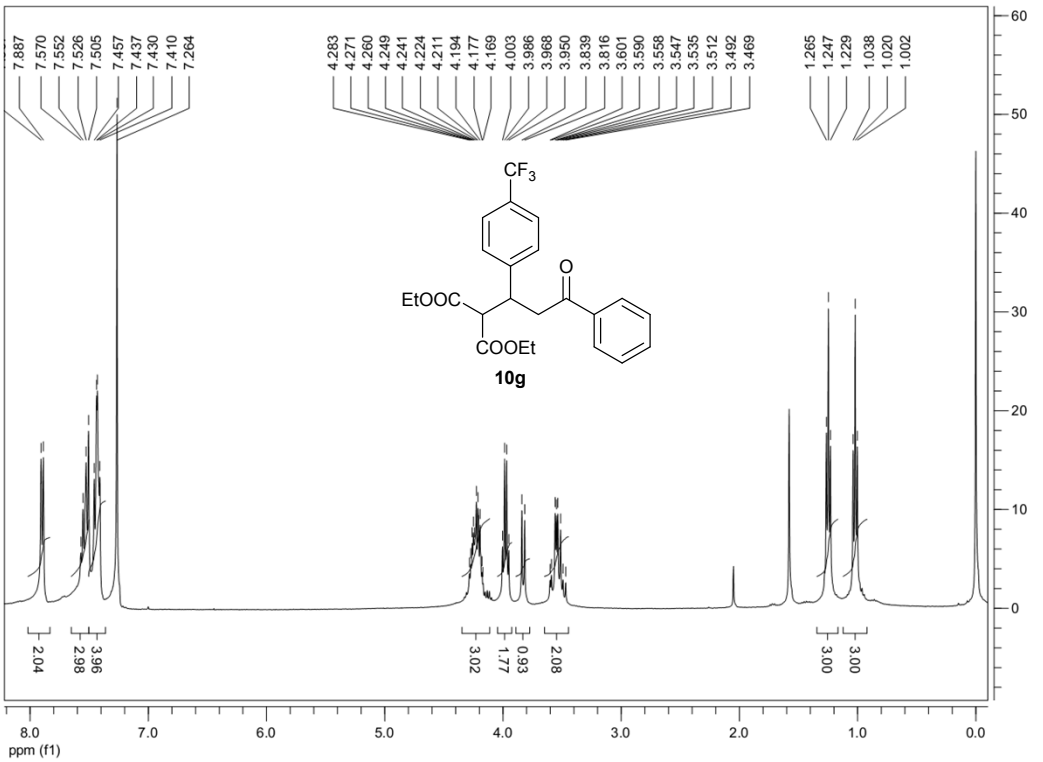
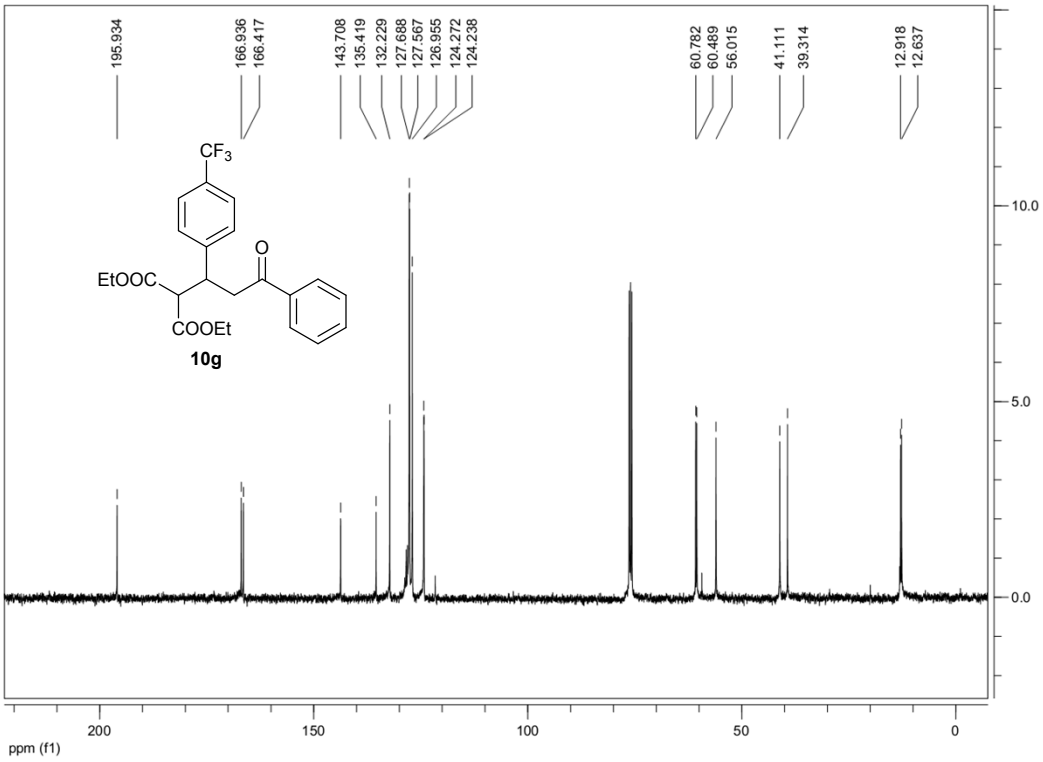


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule

^{1}H NMR of **10g**



^{13}C NMR of **10g**



HRMS of **10g**

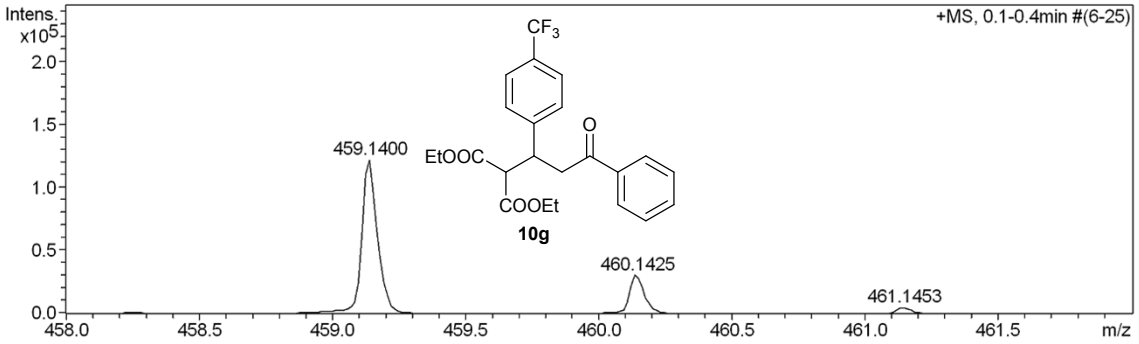
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	C:\Documents and Settings\Administrator\×ÀÃæ\ÁõÓñÁú\gzh_lianghao_7.d	Acquisition Date	2013-5-9 15:53:00
Method	tune_low 50-500.m	Operator	NWU
Sample Name	Sample	Instrument / Ser#	micrOTOF-Q II 10280
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	110.0 Vpp	Set Divert Valve	Source



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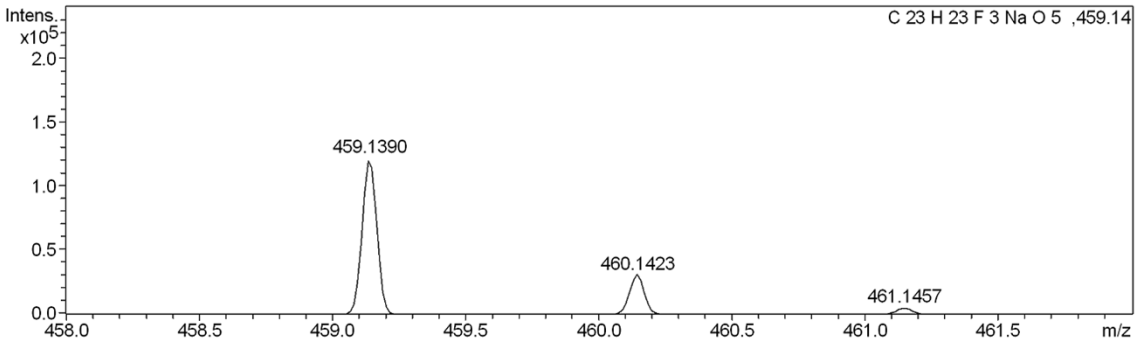
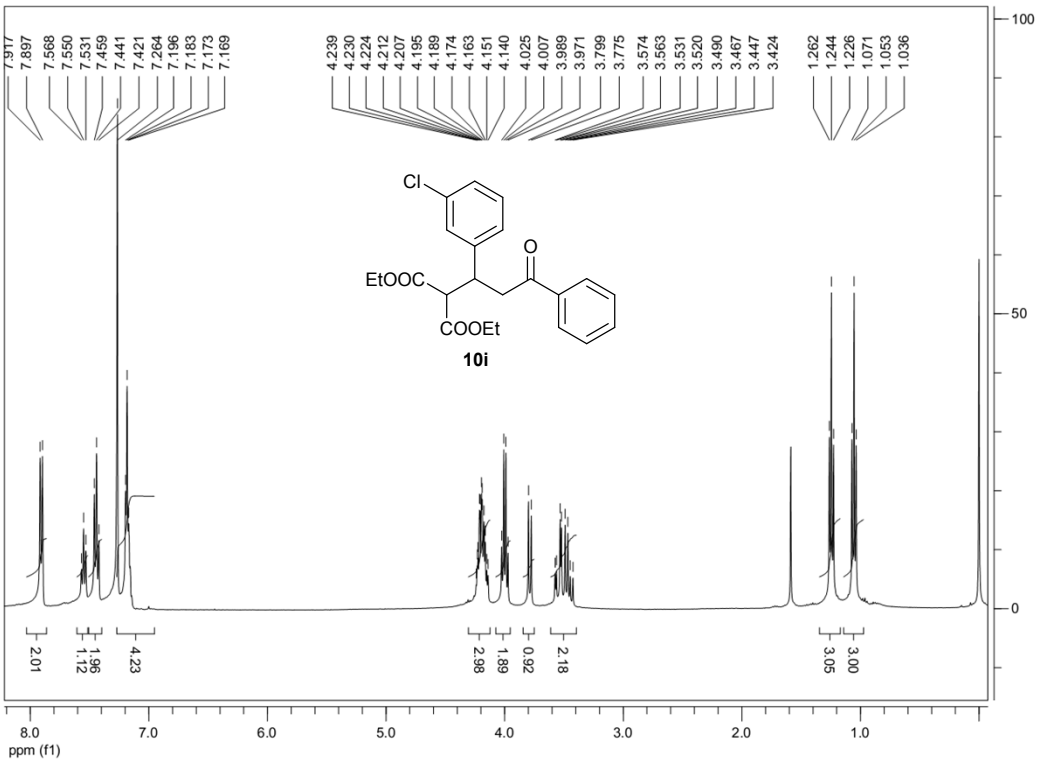
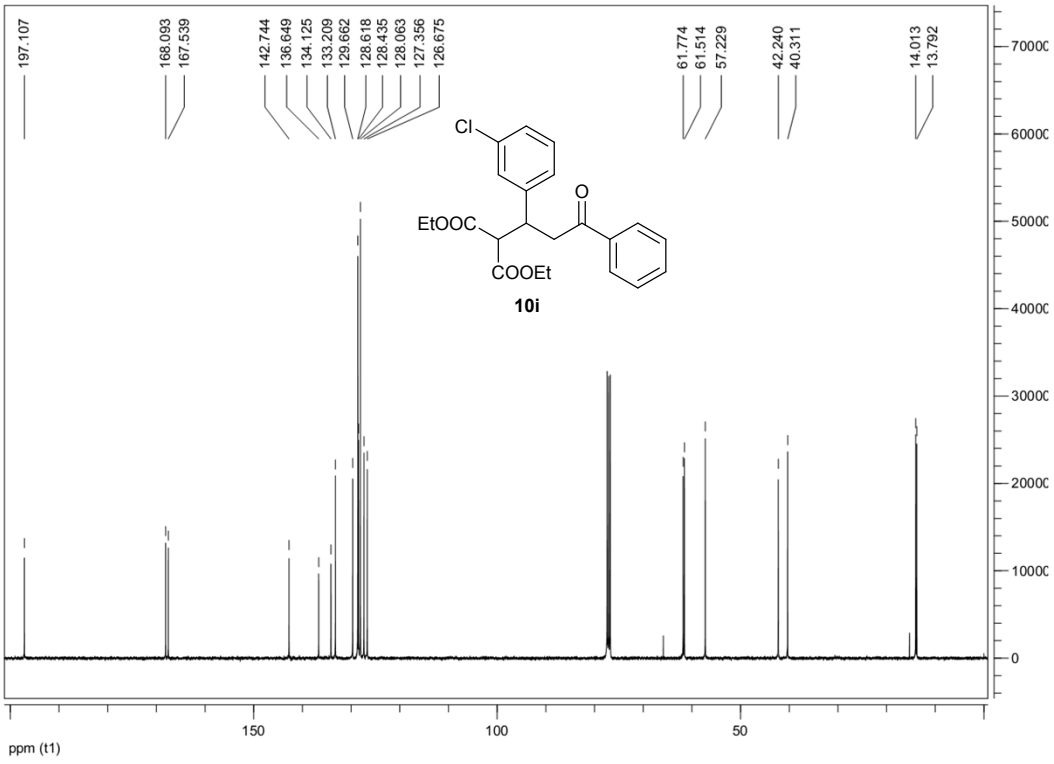


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule

^{1}H NMR of **10i**



^{13}C NMR of **10i**



HRMS of **10i**

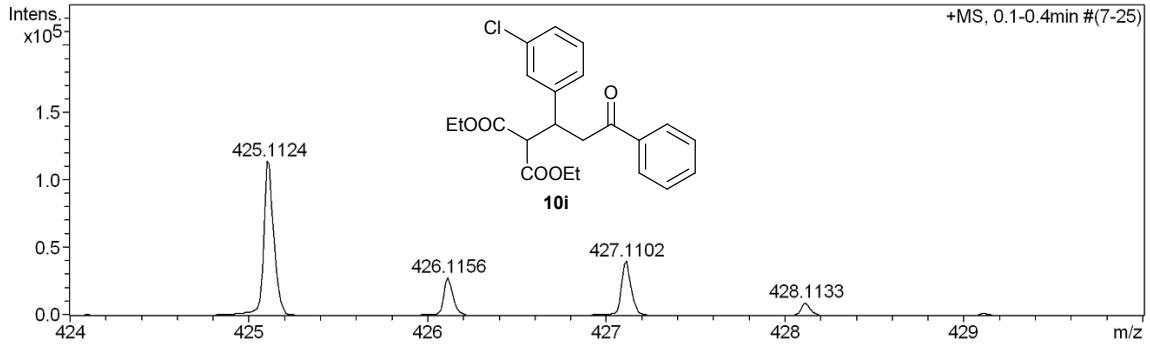
Mass Spectrum SmartFormula Report

Analysis Info

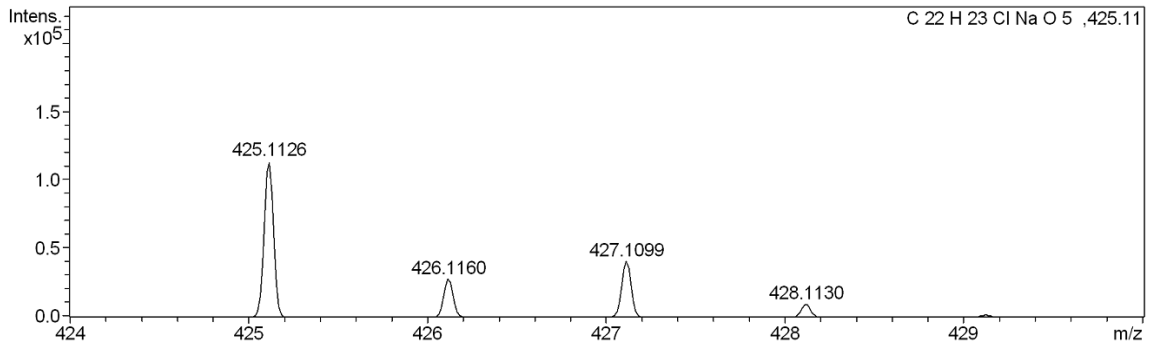
Analysis Name	C:\Documents and Settings\Administrator\×ÀÃæ\ÁõÓñÁú\gzh-lyl-9.d	Acquisition Date	2013-5-13 16:22:42
Method	tune_low 50-500.m	Operator	NWU
Sample Name	Sample	Instrument / Ser#	micrOTOF-Q II 10280
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	110.0 Vpp	Set Divert Valve	Source

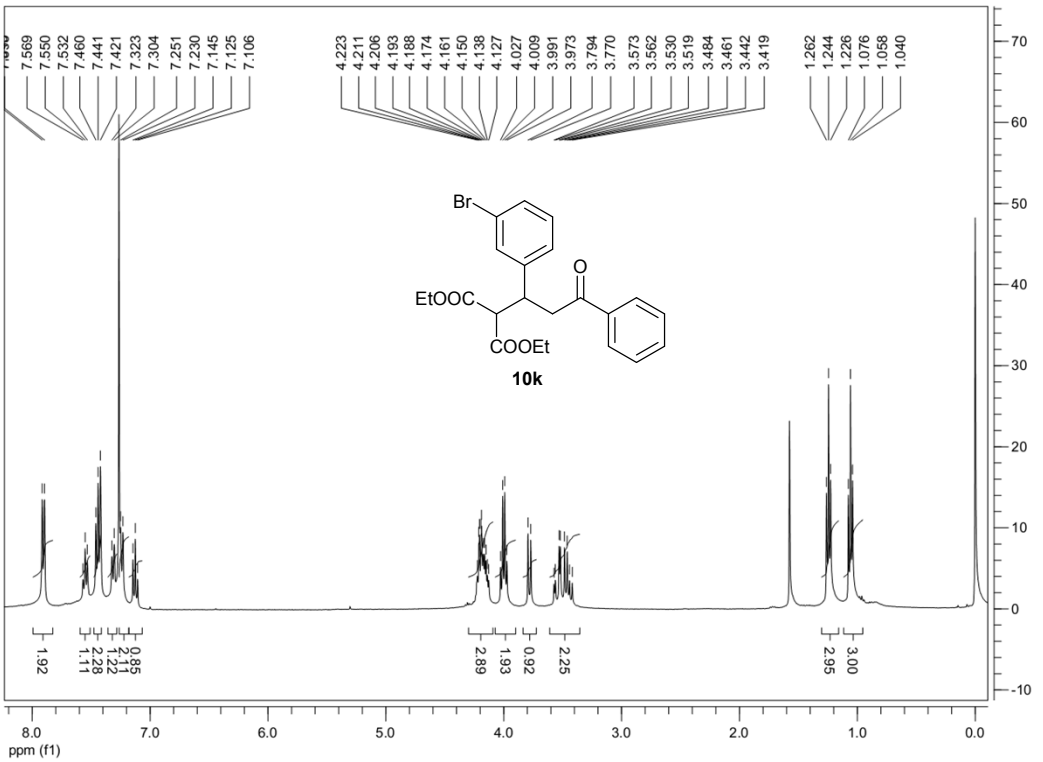


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule
425.1124	1	C 22 H 23 Cl Na O 5	100.00	425.1126	0.2	0.5	6.0	10.5	even	ok

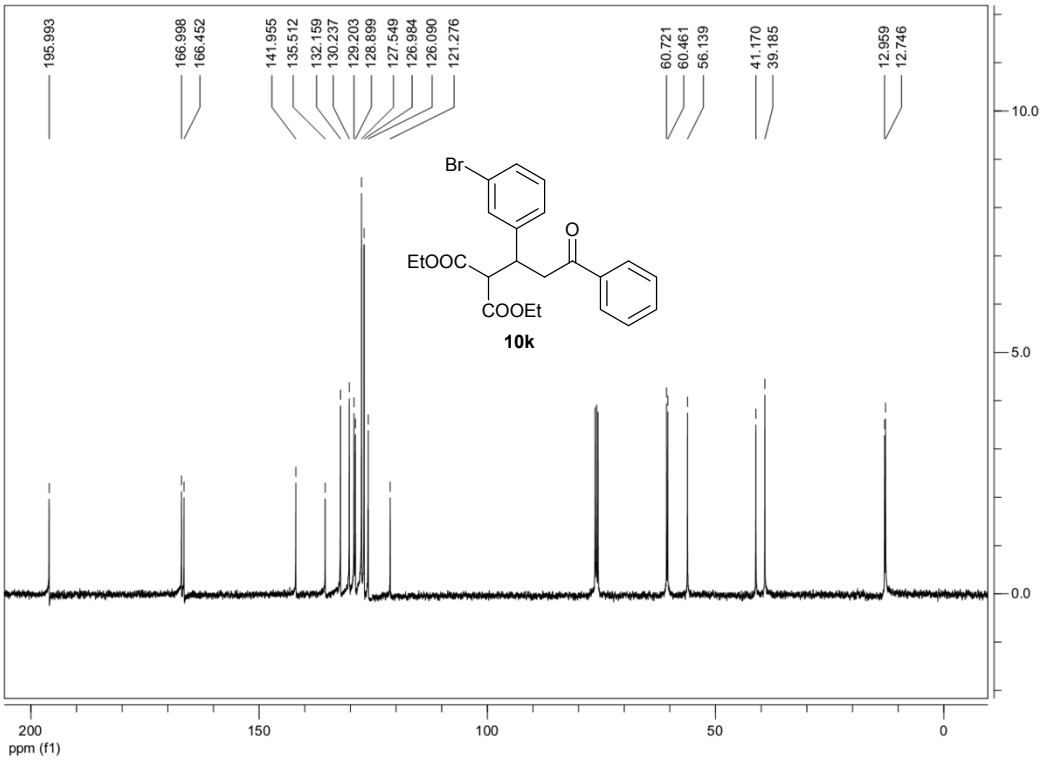


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule

^{1}H NMR of **10k**



^{13}C NMR of **10k**



HRMS of **10k**

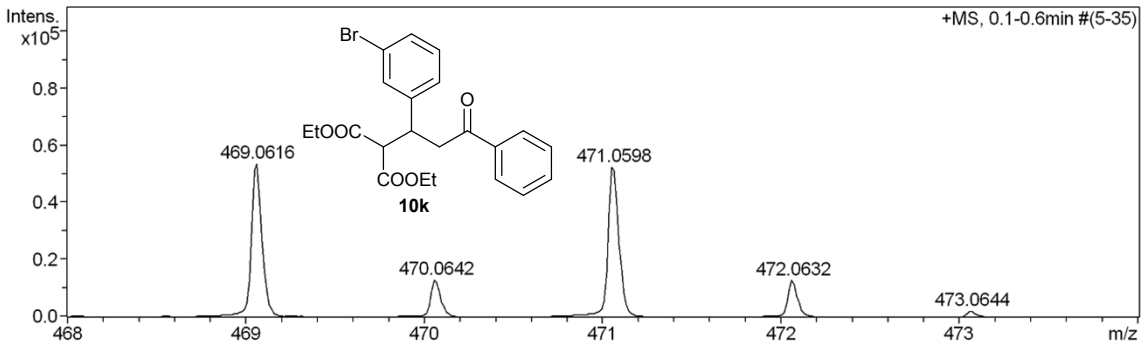
Mass Spectrum SmartFormula Report

Analysis Info

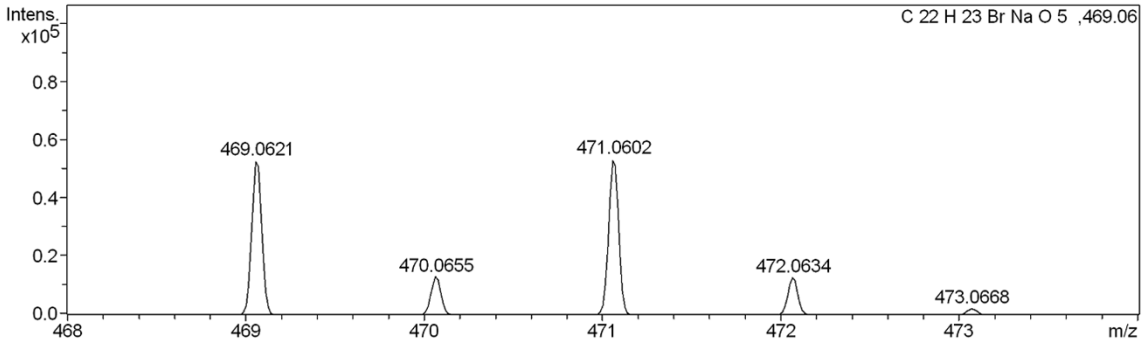
Analysis Name	C:\Documents and Settings\Administrator\×ÀÃæ\ÁõÓñÁú\gzh-lyl-11.d	Acquisition Date	2013-5-13 16:25:12
Method	tune_low 50-500.m	Operator	NWU
Sample Name	Sample	Instrument / Ser#	micrOTOF-Q II 10280
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	110.0 Vpp	Set Divert Valve	Source

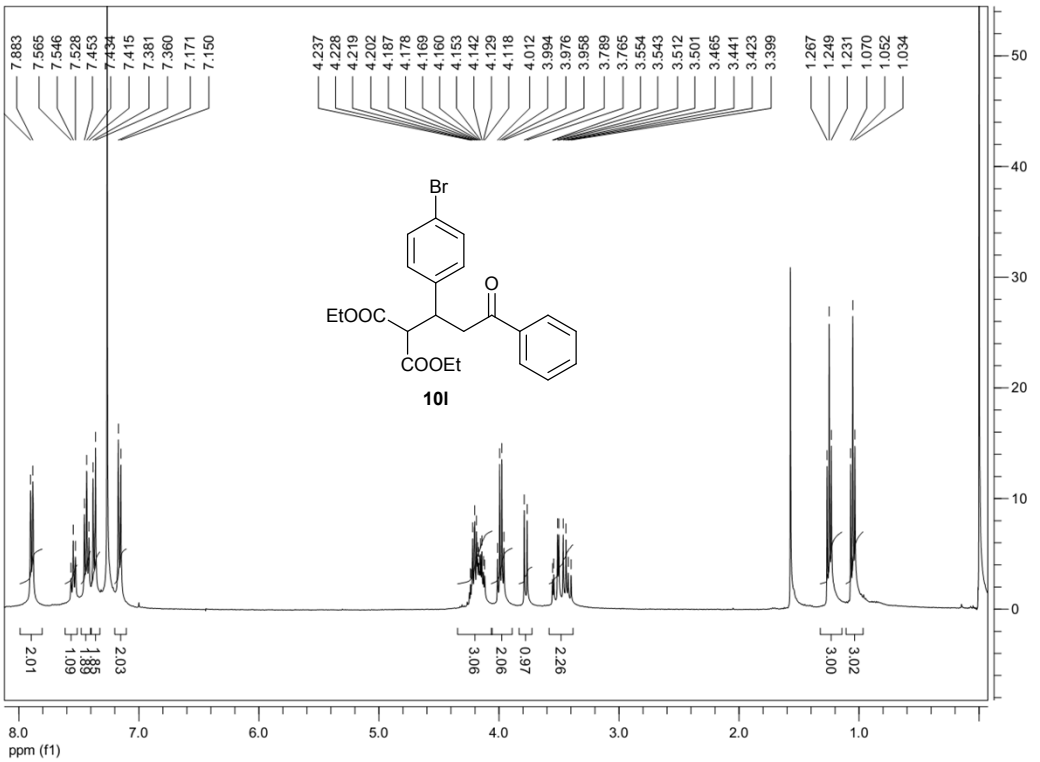


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule
469.0616	1	C 22 H 23 Br Na O 5	100.00	469.0621	0.5	1.0	11.2	10.5	even	ok

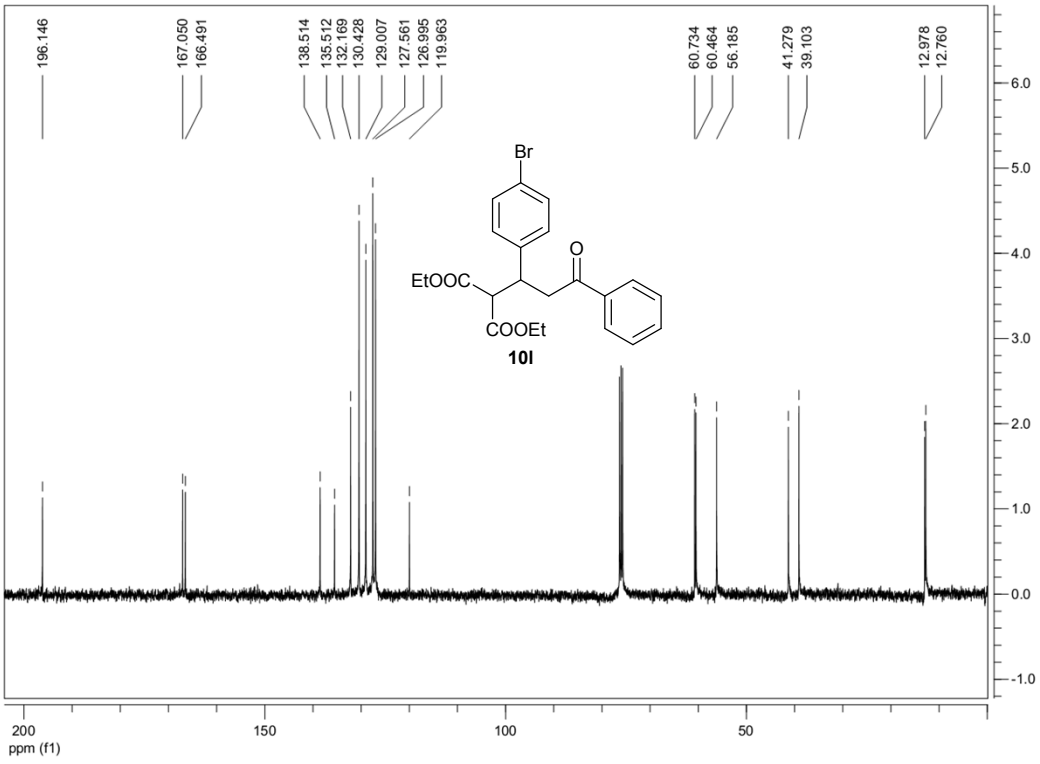


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule

^{1}H NMR of **10l**



^{13}C NMR of **10l**



HRMS of **10l**

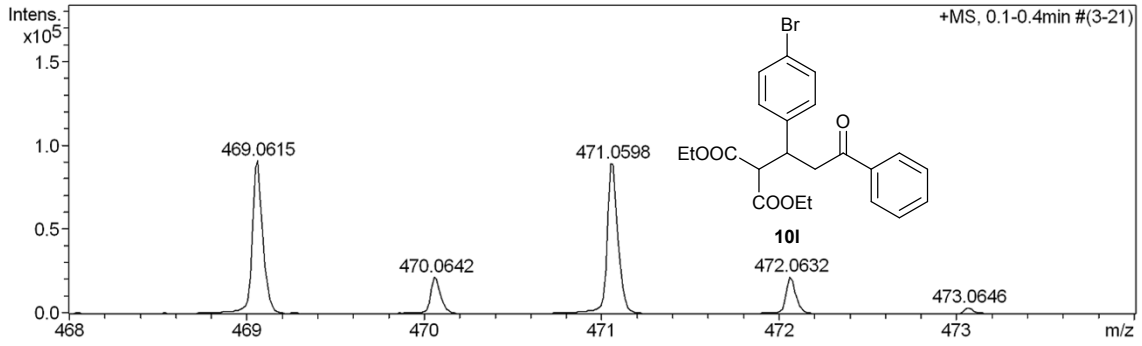
Mass Spectrum SmartFormula Report

Analysis Info

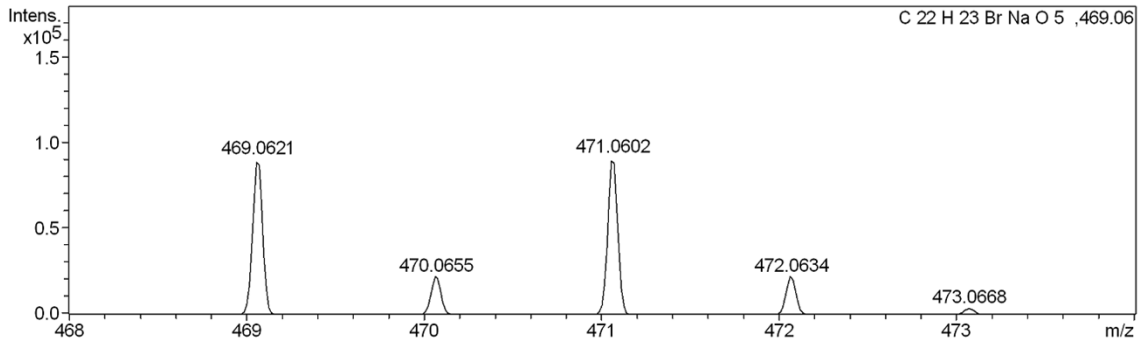
Analysis Name	C:\Documents and Settings\Administrator\×ÀÃæ\ÁõÓñÁú\gzh-lyl-12.d	Acquisition Date	2013-5-13 16:27:23
Method	tune_low 50-500.m	Operator	NWU
Sample Name	Sample	Instrument / Ser#	micrOTOF-Q II 10280
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	110.0 Vpp	Set Divert Valve	Source

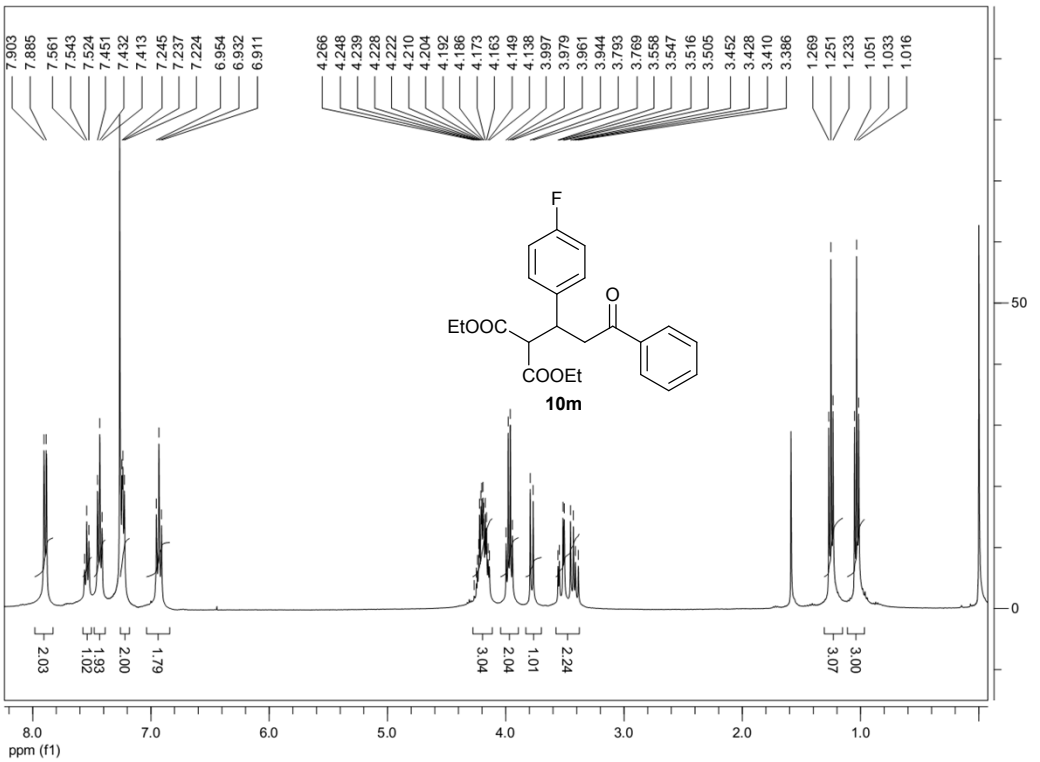


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule
469.0615	1	C 22 H 23 Br Na O 5	100.00	469.0621	0.6	1.3	11.0	10.5	even	ok

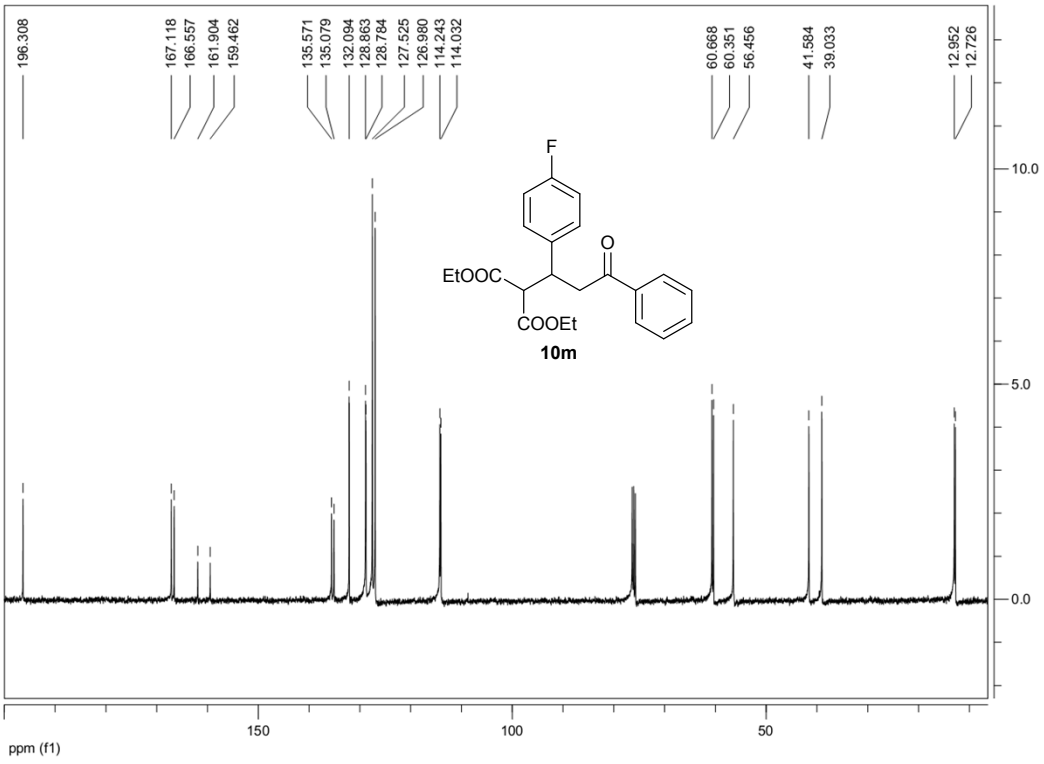


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule

^{1}H NMR of **10m**



^{13}C NMR of **10m**



^{13}C NMR of **10m**

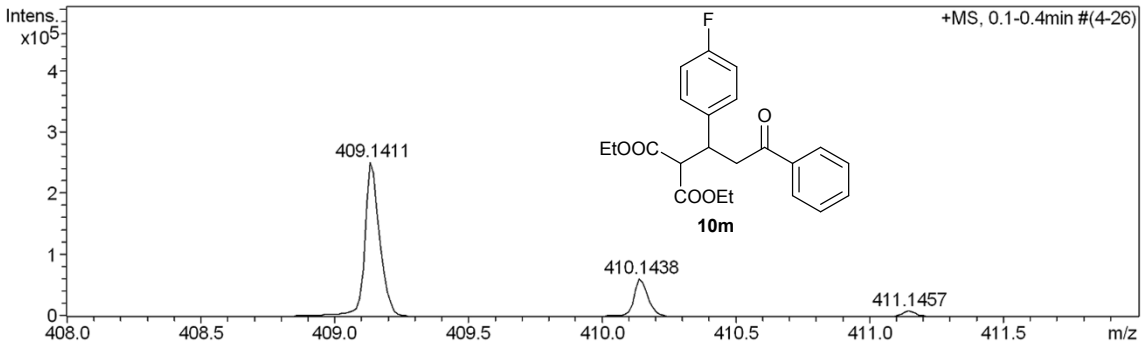
Mass Spectrum SmartFormula Report

Analysis Info

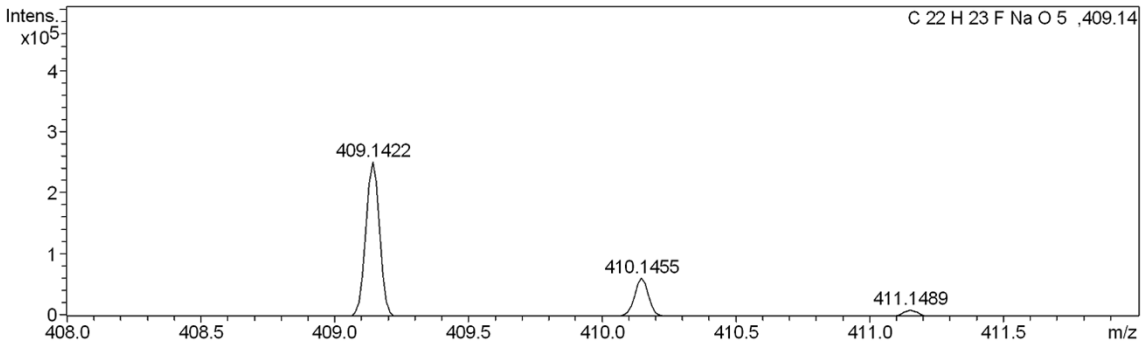
Analysis Name	C:\Documents and Settings\Administrator\×ÀÃæ\ÁõÓñÁú\gzh-lyl-14.d	Acquisition Date	2013-5-13 16:29:42
Method	tune_low 50-500.m	Operator	NWU
Sample Name	Sample	Instrument / Ser#	micrOTOF-Q II 10280
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	110.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule
409.1411	1	C 22 H 23 F Na O 5	100.00	409.1422	1.1	2.6	3.1	10.5	even	ok

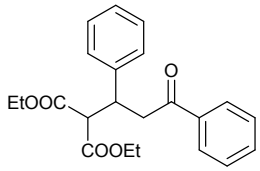


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule

8. Copies of HPLC analysis

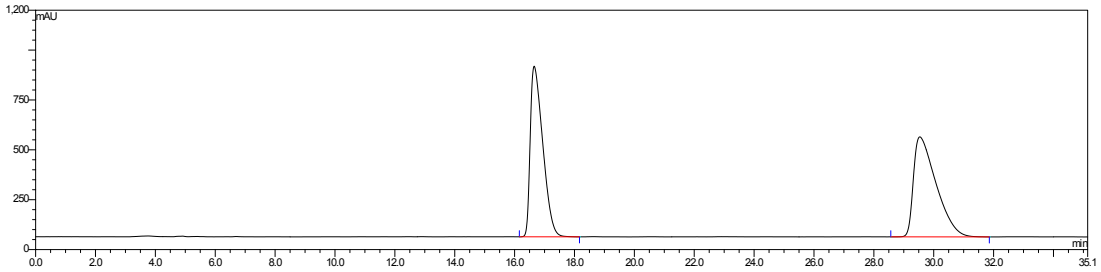
Enantiomeric excesses of Michael adducts were determined by HPLC analysis using chiral column (φ 4.6 mm × 250 mm, DAICEL CHIRALPAK AD-H).

HPLC data of Michael Reaction



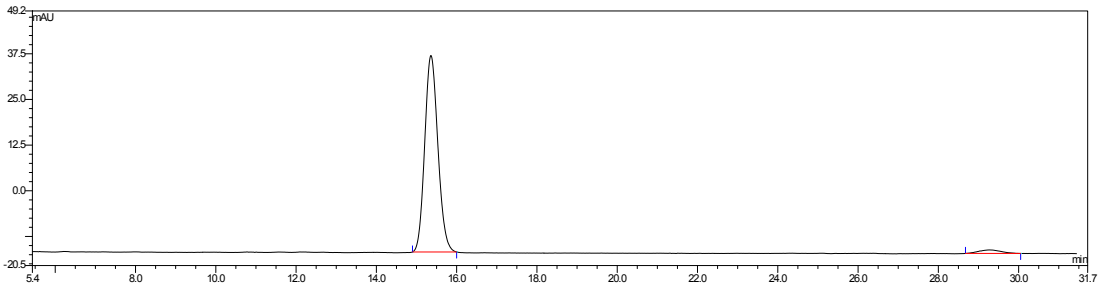
10a

Diethyl 2-(3-oxo-1, 3-diphenylpropyl)malonate (10a). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	16.650	413.9912	n.a.	BMB	855.070	48.61	11.95
2	n.a.	29.533	437.6329	n.a.	BMB	501.193	51.39	n.a.
Total :			851.6241	0.0000		1356.263	100.00	

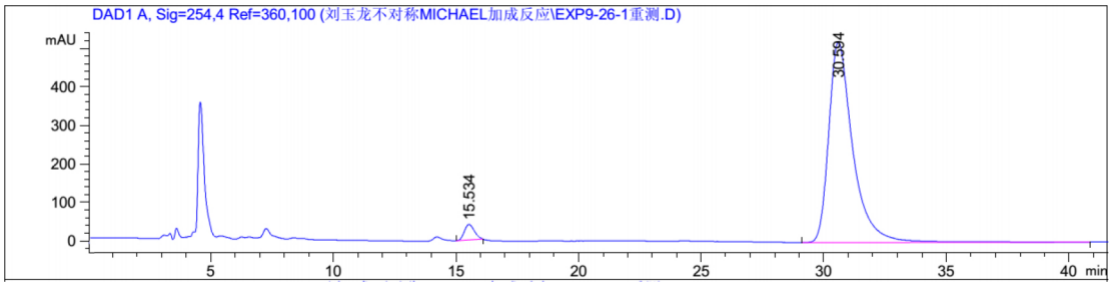
(*R*)-**10a**



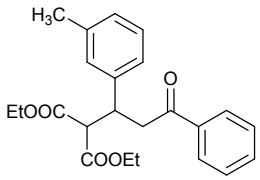
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	15.358	20.4152	n.a.	BMB*	53.787	97.09	16.78

2	n.a.	29.275	0.6128	n.a.	BMB*	0.950	2.91	n.a.
Total :			21.0279	0.0000		54.737	100.00	

(*S*)-**10a**

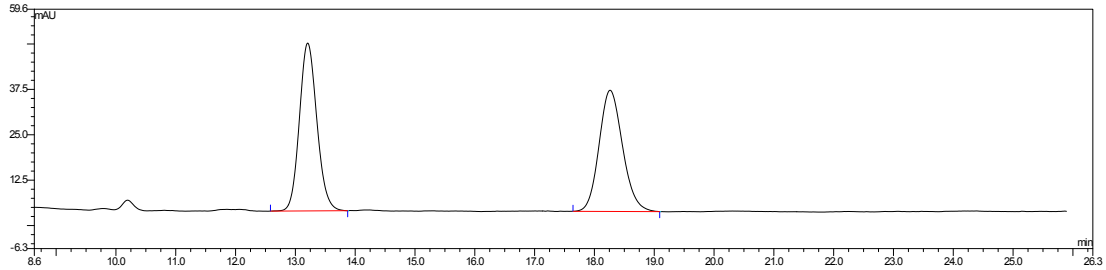


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.534	BBA	0.4417	53.66717	1.89898	3.0866
2	30.594	BB	1.0255	1685.02466	24.52580	96.9134
总量 :				1738.69183	26.42478	



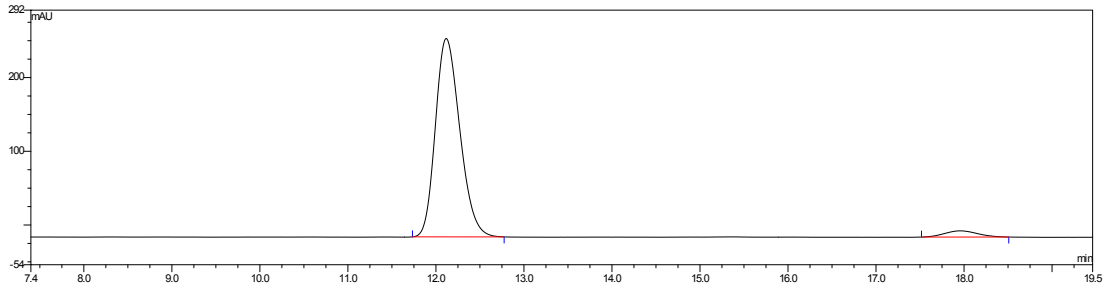
10b

Diethyl 2-(1-(3-methylphenyl)-3-oxo-3-phenylpropyl)malonate (10b). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



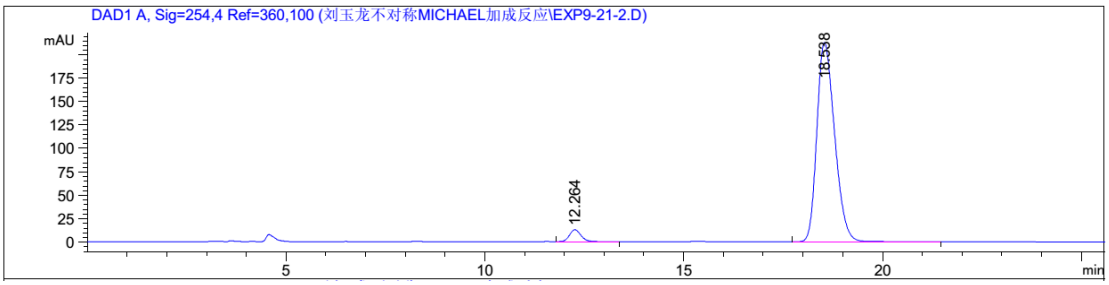
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	13.208	15.6786	n.a.	BMB	46.211	50.80	8.13
2	n.a.	18.258	15.1855	n.a.	BMB	33.372	49.20	n.a.
Total :			30.8642	0.0000		79.583	100.00	

(*R*)-**10b**

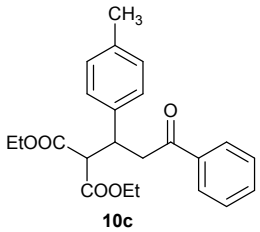


No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	12.117	168.5480	n.a.	BMB	518.781	95.90	9.69
2	n.a.	17.958	7.2021	n.a.	BMB*	16.560	4.10	n.a.
Total:			175.7500	0.0000		535.341	100.00	

(*S*)-**10b**

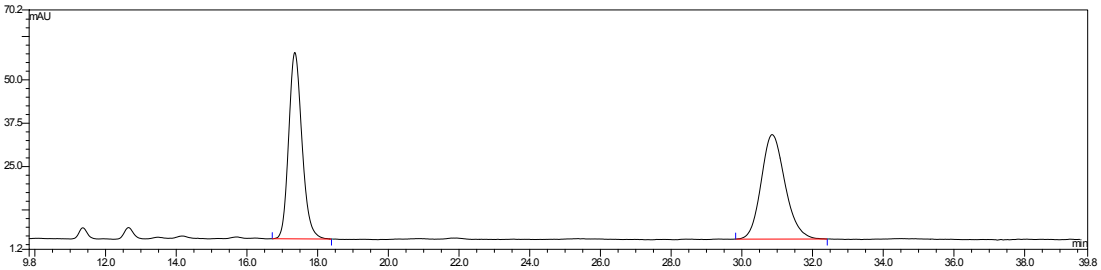


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.264	BB	0.3111	256.25427	12.71763	3.7375
2	18.538	BB	0.4817	6600.03271	212.87347	96.2625
总量：				6856.28699	225.59110	



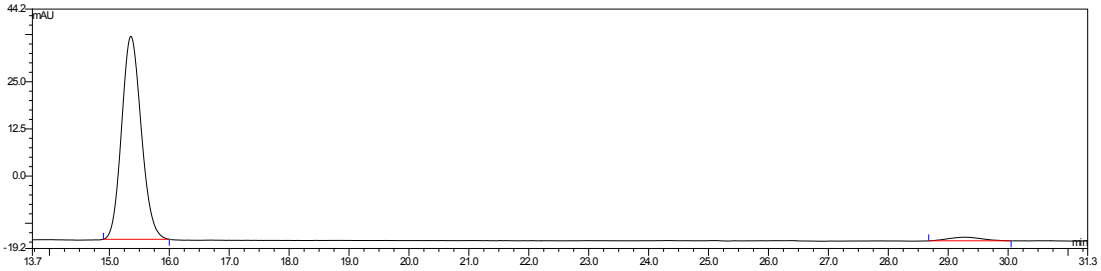
10c

Diethyl 2-(1-(4-methylphenyl)-3-oxo-3-phenylpropyl)malonate (10c). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



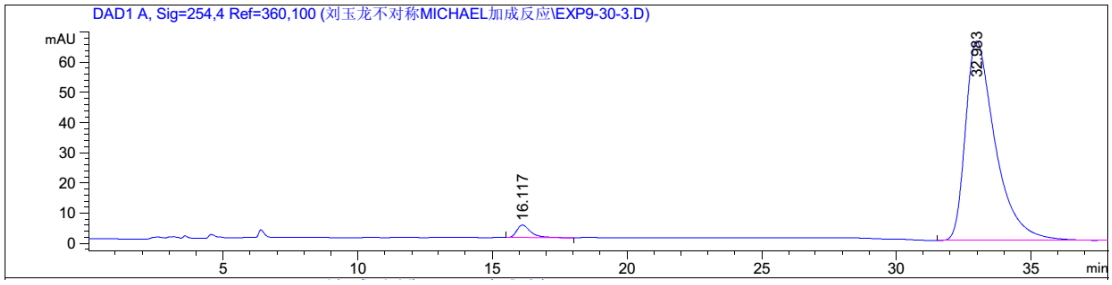
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	17.350	23.4333	n.a.	BMB	53.731	49.82	14.29
2	n.a.	30.858	23.6072	n.a.	BMB	30.108	50.18	n.a.
Total:			47.0405	0.0000		83.839	100.00	

(*R*)-**10c**

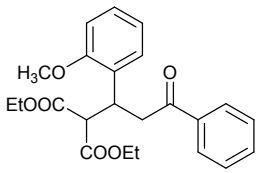


No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	15.358	20.4152	n.a.	BMB*	53.787	97.09	16.78
2	n.a.	29.275	0.6128	n.a.	BMB*	0.950	2.91	n.a.
Total:			21.0279	0.0000		54.737	100.00	

(*S*)-**10c**

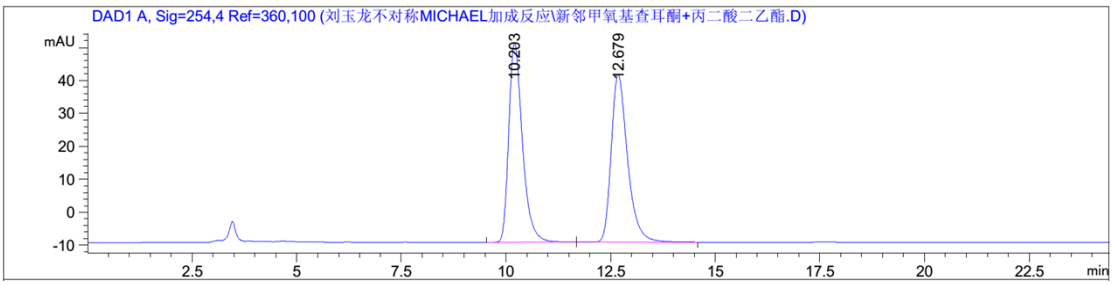


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.117	BB	0.5294	149.76488	4.18617	2.8489
2	32.983	BBA	1.1629	5107.18604	66.13708	97.1511
总量：				5256.95091	70.32325	



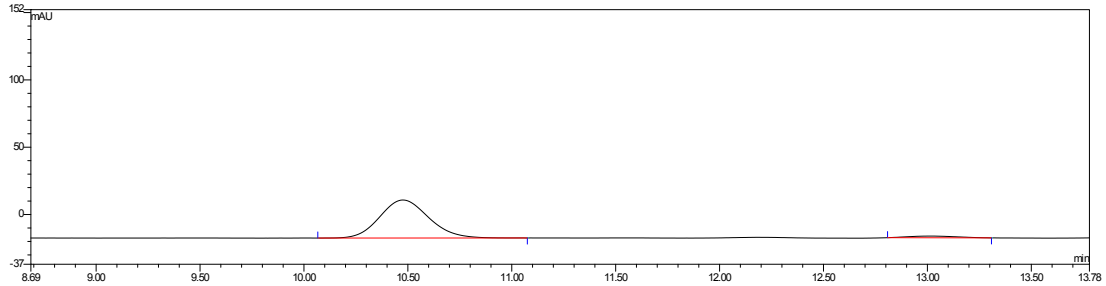
10d

Diethyl 2-(1-(2-methoxyphenyl)-3-oxo-3-phenylpropyl)malonate (10d). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.203	BB	0.3475	1376.61414	60.48577	49.9361
2	12.679	BB	0.4104	1380.13660	50.89090	50.0639
总量：				2756.75073	111.37666	

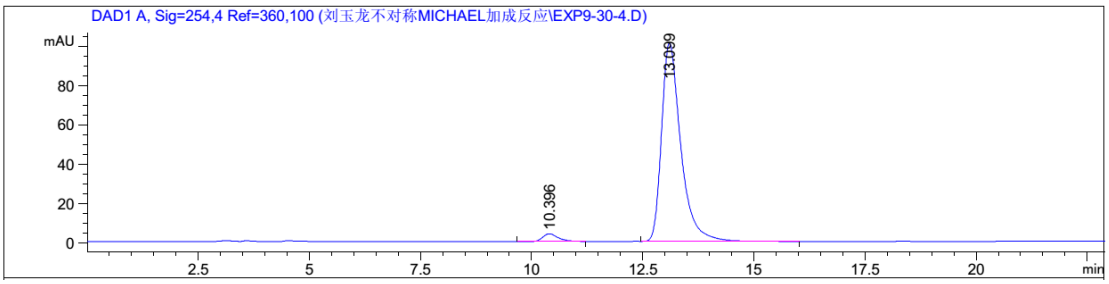
(*R*)-**10d**



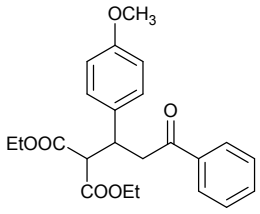
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	10.475	15.3548	n.a.	BMB	56.765	95.81	5.86
2	n.a.	13.025	0.6715	n.a.	BMB	2.543	4.19	n.a.
Total			16.0262	0.0000		59.308	100.00	

:								

(*S*)-**10d**

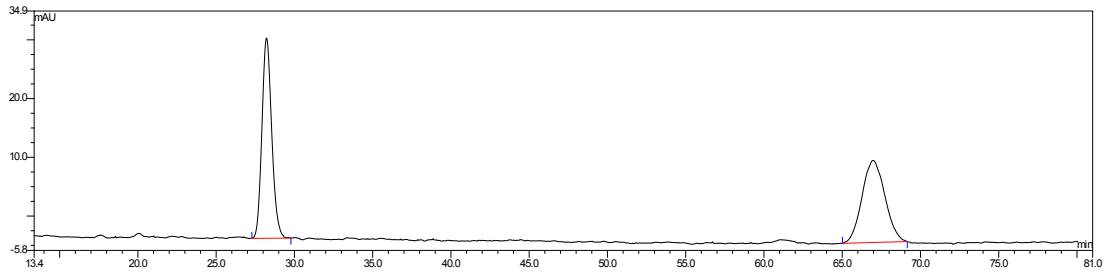


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.396	BB	0.3646	92.65488	3.85224	2.9696
2	13.099	BB	0.4524	3027.44360	100.80955	97.0304
总量 :				3120.09848	104.66178	



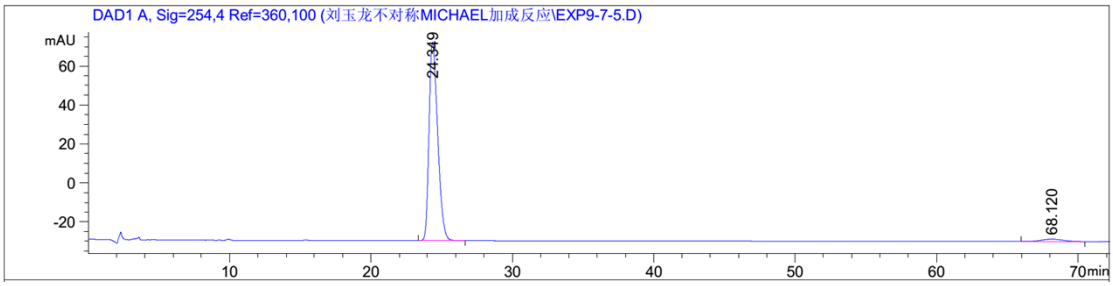
10e

Diethyl 2-(1-(4-methoxyphenyl)-3-oxo-3-phenylpropyl)malonate (10e). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



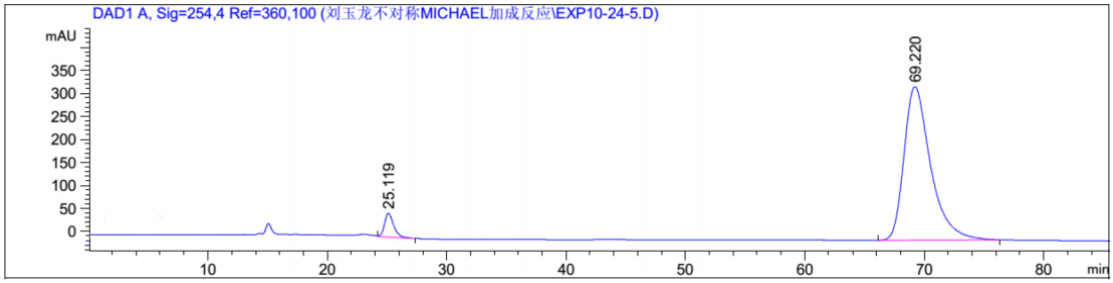
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	28.217	24.7966	n.a.	BMB	34.088	51.17	20.13
2	n.a.	66.983	23.6616	n.a.	BMB	13.962	48.83	n.a.
Total :			48.4581	0.0000		48.050	100.00	

(*R*)-**10e**

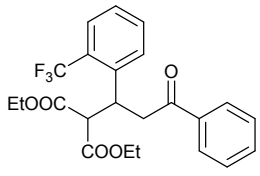


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	24.349	BB	0.6574	4330.48389	101.98273	96.8067
2	68.120	BBA	1.2947	142.84593	1.29925	3.1933
总量 :				4473.32982	103.28197	

(*S*)-**10e**

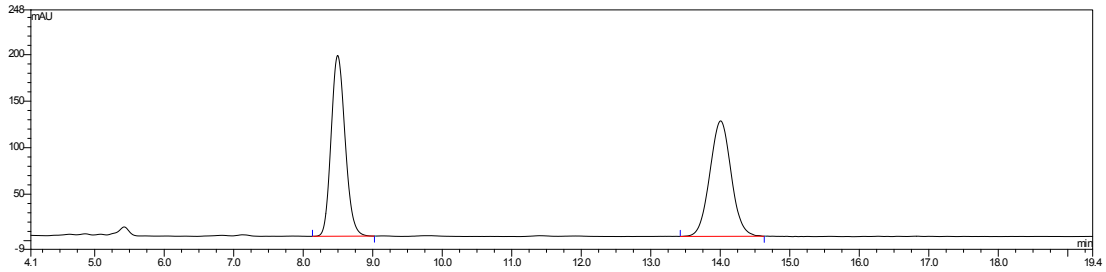


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.119	VB	0.7840	276.74765	5.17456	5.1093
2	69.220	VV	2.2344	5139.83203	33.23292	94.8907
总量 :				5416.57968	38.40749	



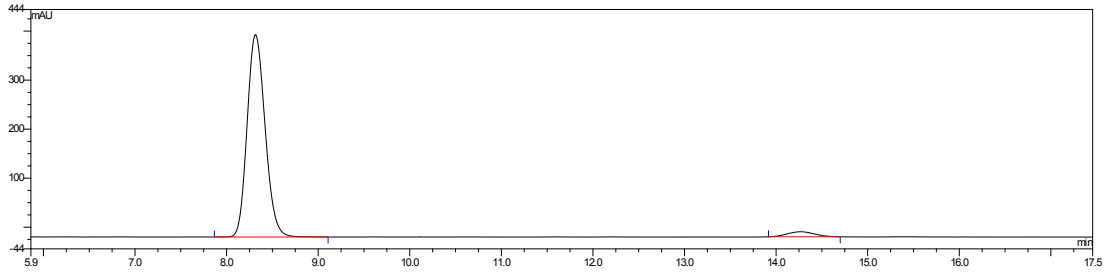
10f

Diethyl 2-(1-(2-trifluoromethylphenyl)-3-oxo-3-phenylpropyl)malonate (10f). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



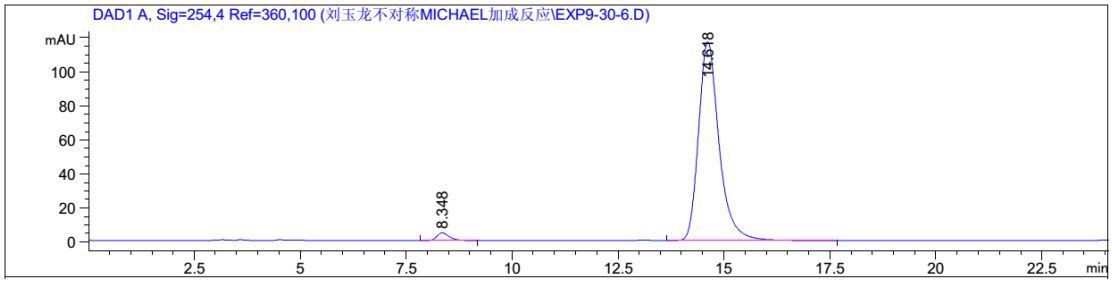
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	8.492	45.4058	n.a.	BMB	194.270	50.69	11.92
2	n.a.	14.008	44.1640	n.a.	BMB	124.071	49.31	n.a.
Total :			89.5698	0.0000		318.341	100.00	

(*R*)-**10f**

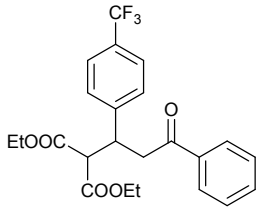


No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	8.317	93.7649	n.a.	BMB	412.909	96.38	13.07
2	n.a.	14.267	3.5253	n.a.	BMB*	10.290	3.62	n.a.
Total :			97.2902	0.0000		423.199	100.00	

(*S*)-**10f**

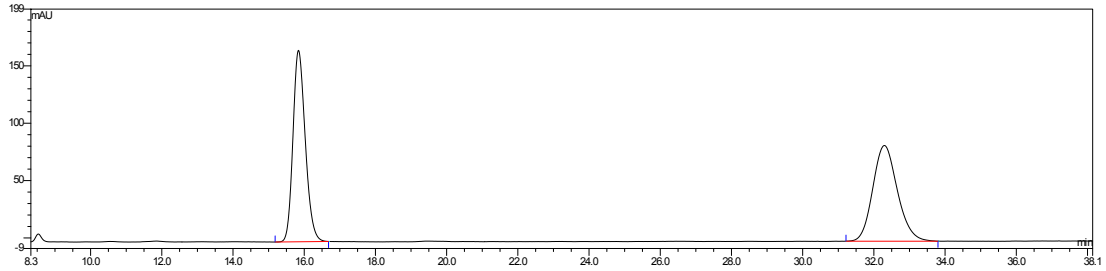


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.348	BB	0.3054	90.24258	4.47210	2.2469
2	14.618	BB	0.5106	3926.08447	116.66838	97.7531
总量：				4016.32705	121.14048	



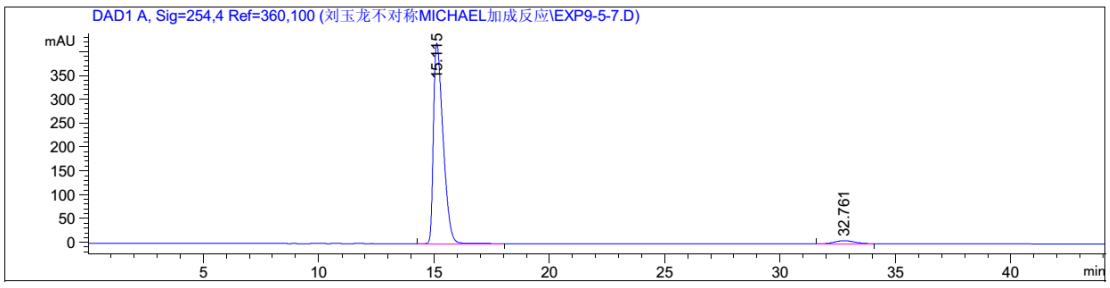
10g

Diethyl 2-(1-(4-trifluoromethylphenyl)-3-oxo-3-phenylpropyl)malonate (10g). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



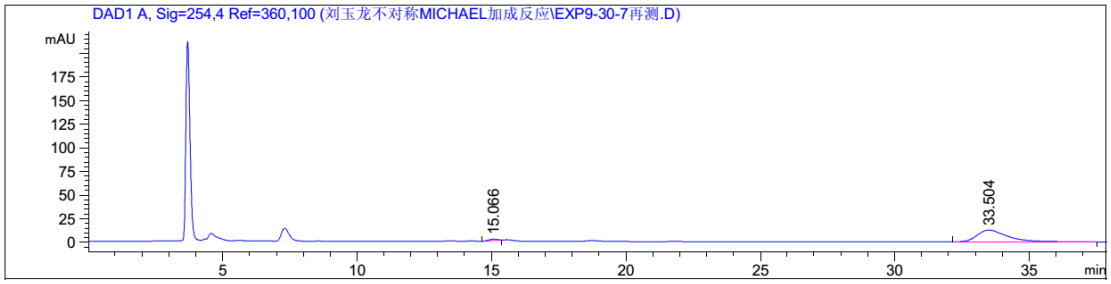
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	15.842	66.7600	n.a.	BMB	166.843	50.07	17.58
2	n.a.	32.300	66.5778	n.a.	BMB	83.403	49.93	n.a.
Total:			133.3379	0.0000		250.247	100.00	

(*R*)-**10g**

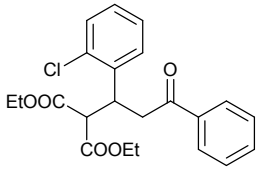


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.115	BB	0.4382	1.20377e4	420.27466	97.2936
2	32.761	BBA	0.8586	334.85385	6.02273	2.7064
总量：				1.23726e4	426.29739	

(*S*)-**10g**

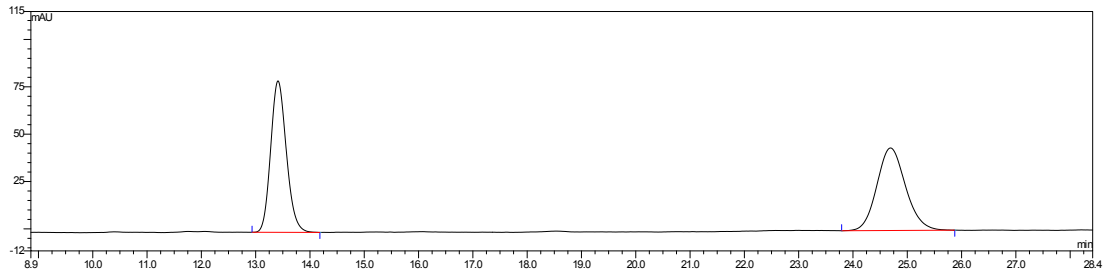


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.066	BB	0.3480	28.86505	1.33644	2.9315
2	33.504	BB	1.1466	955.77594	12.27279	97.0685
总量 :				984.64099	13.60923	



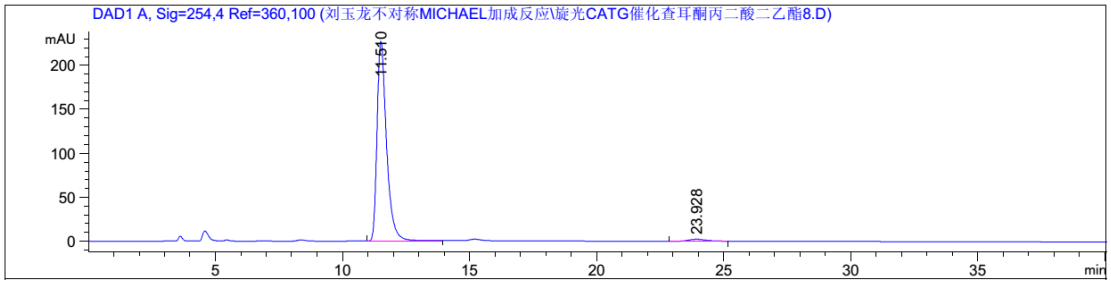
10h

Diethyl 2-(1-(2-chlorophenyl)-3-oxo-3-phenylpropyl)malonate (10h). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



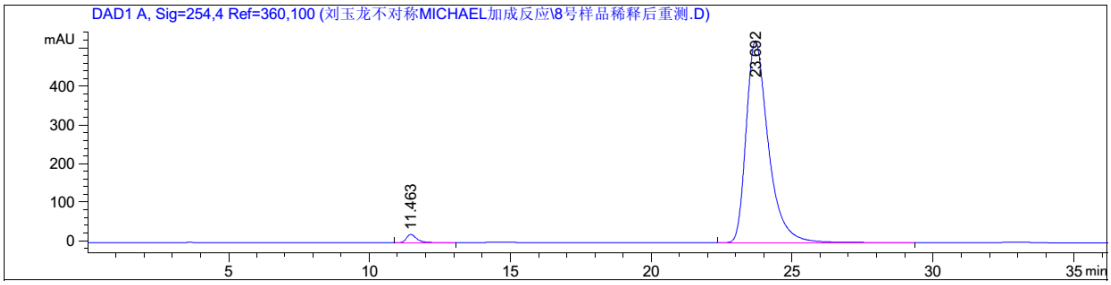
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	13.408	26.7492	n.a.	BMB	79.931	50.07	15.28
2	n.a.	24.692	26.6727	n.a.	BMB	43.569	49.93	n.a.
Total :			53.4220	0.0000		123.499	100.00	

(*R*)-**10h**

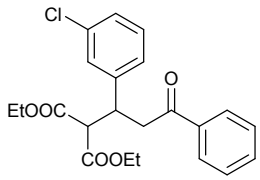


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.510	BV	0.3946	5922.13477	226.84277	97.9198
2	23.928	BV	0.7654	125.80910	2.41645	2.0802
总量 :				6047.94387	229.25922	

(*S*)-**10h**

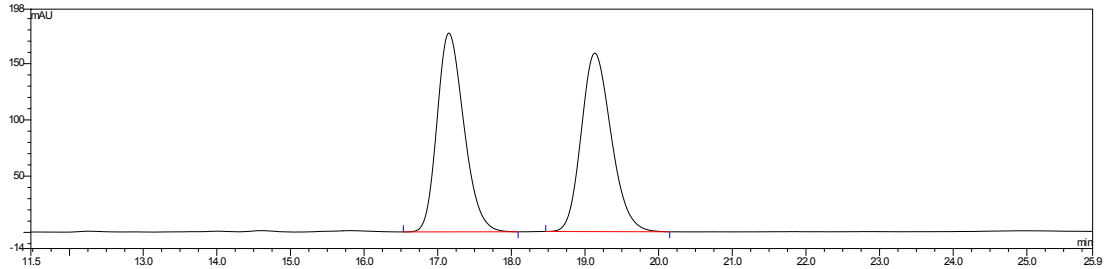


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.463	BB	0.3798	541.72778	21.50977	1.8650
2	23.692	BB	0.8305	2.85056e4	520.87469	98.1350
总量 :				2.90473e4	542.38447	



10i

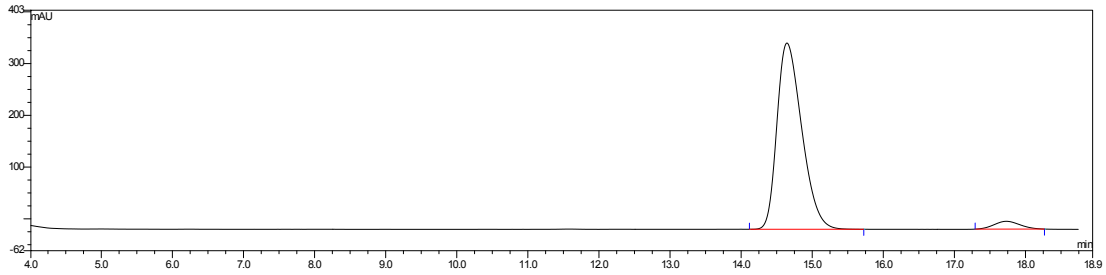
Diethyl 2-(1-(3-chlorophenyl)-3-oxo-3-phenylpropyl)malonate (10i). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



No.	Peakname	Ret.Tim	Area	Amount	Type	Height	Rel.Area	Resolution

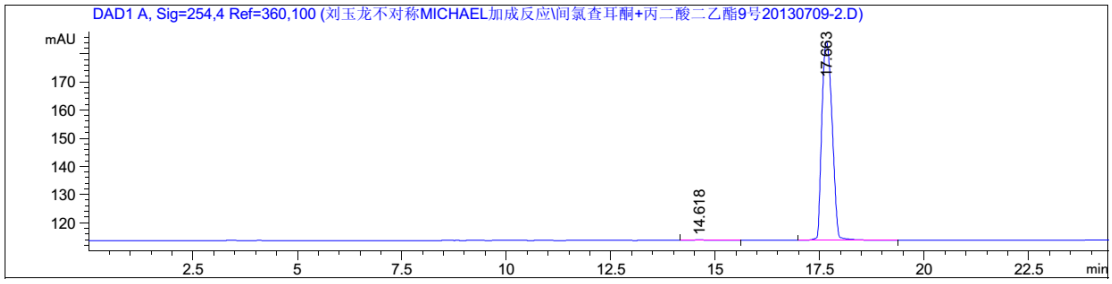
		e min	mAU*min			mAU	%	
1	n.a.	17.150	74.7607	n.a.	BMB	176.692	49.94	2.82
2	n.a.	19.133	74.9432	n.a.	BMB	158.639	50.06	n.a.
Total :			149.7039	0.0000		335.331	100.00	

(*R*)-**10i**

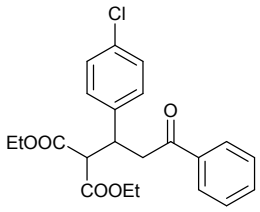


No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	14.642	145.4153	n.a.	BMB	359.866	95.82	4.70
2	n.a.	17.733	6.3423	n.a.	BMB*	15.061	4.18	n.a.
Total :			151.7577	0.0000		374.927	100.00	

(*S*)-**10i**

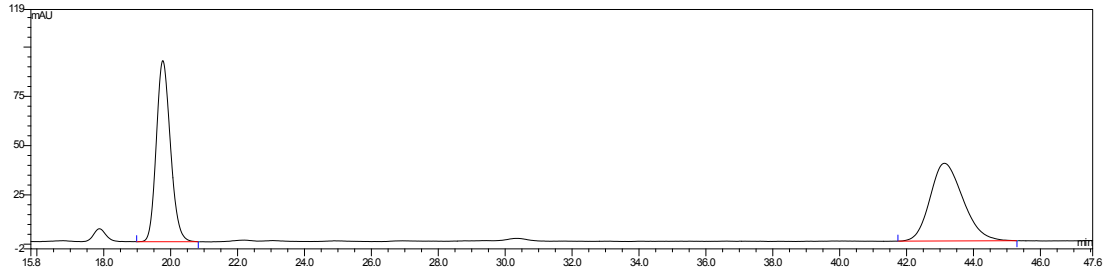


峰 #	保留时间 [min]	类型	峰宽 [mAU*s]	峰面积 [mAU]	峰高 %	峰面积
1	14.618	BB	0.3793	5.30831	1.71404e-1	0.4347
2	17.663	BB	0.2865	1215.87598	70.73312	99.5653
总量 :				1221.18429	70.90452	



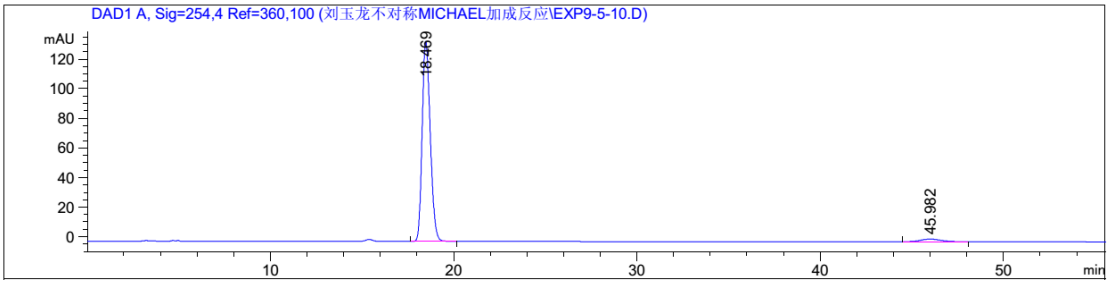
10j

Diethyl 2-(1-(4-chlorophenyl)-3-oxo-3-phenylpropyl)malonate (10j). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



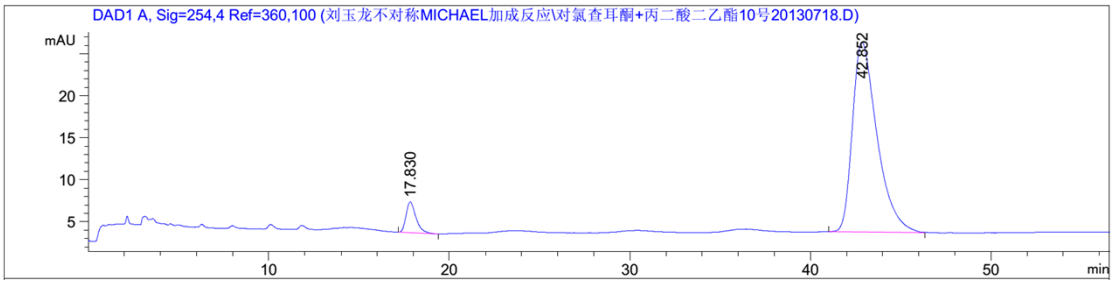
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	19.767	44.9388	n.a.	BMB	91.879	50.02	18.28
2	n.a.	43.133	44.8956	n.a.	BMB	39.407	49.98	n.a.
Total :			89.8344	0.0000		131.286	100.00	

(*R*)-**10j**

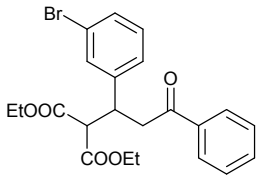


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.469	BB	0.4751	4140.06055	135.26331	96.7624
2	45.982	BB	0.9244	138.52345	1.80701	3.2376
总量 :				4278.58400	137.07031	

(*S*)-**10j**

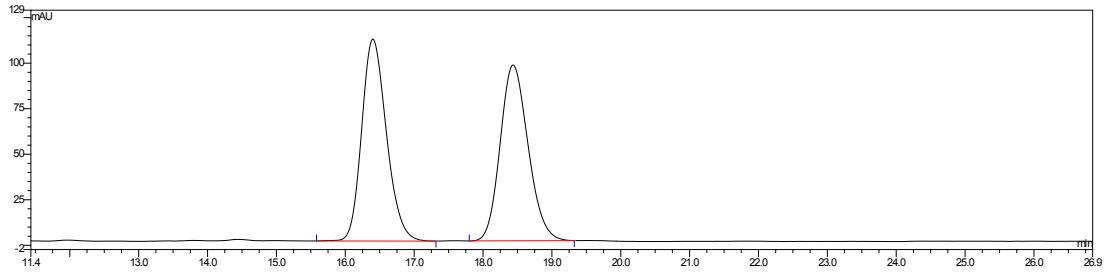


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.830	BBA	0.5207	117.61896	3.45878	5.2181
2	42.852	BB	1.4198	2136.42505	22.58013	94.7819
总量 :				2254.04401	26.03891	



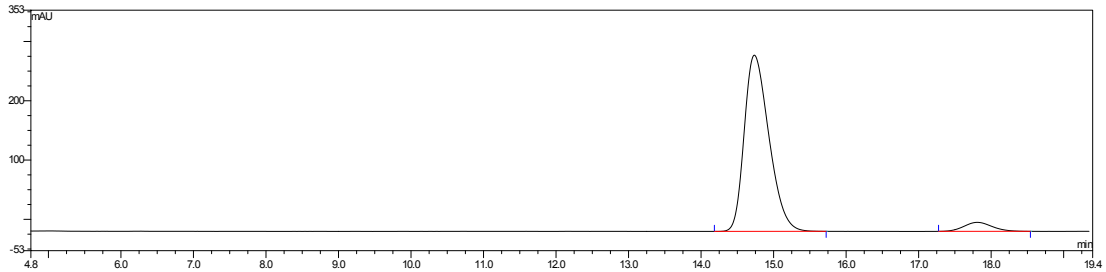
10k

Diethyl 2-(1-(3-bromophenyl)-3-oxo-3-phenylpropyl)malonate (10k). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	16.400	46.2073	n.a.	BMB	110.896	50.47	2.92
2	n.a.	18.433	45.3432	n.a.	BMB	96.528	49.53	n.a.
Total :			91.5505	0.0000		207.424	100.00	

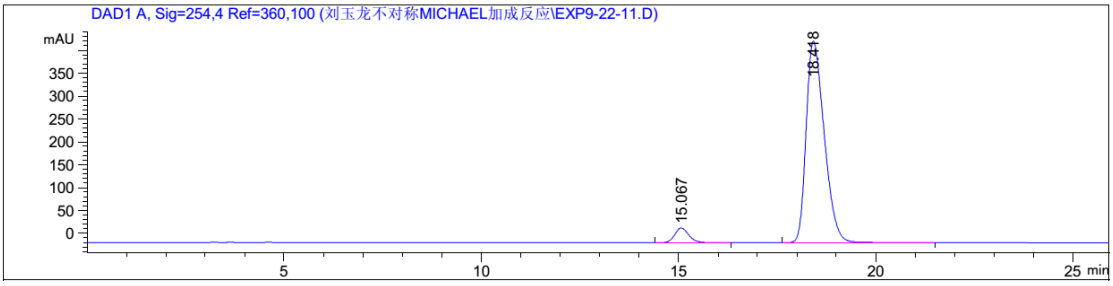
(*R*)-**10k**



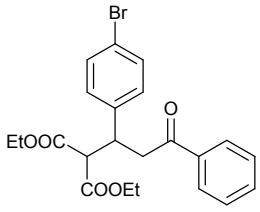
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	14.733	117.3051	n.a.	BMB	297.215	94.87	4.67
2	n.a.	17.808	6.3473	n.a.	BMB*	14.733	5.13	n.a.
Total			123.6524	0.0000		311.947	100.00	

:								

(*S*)-**10k**

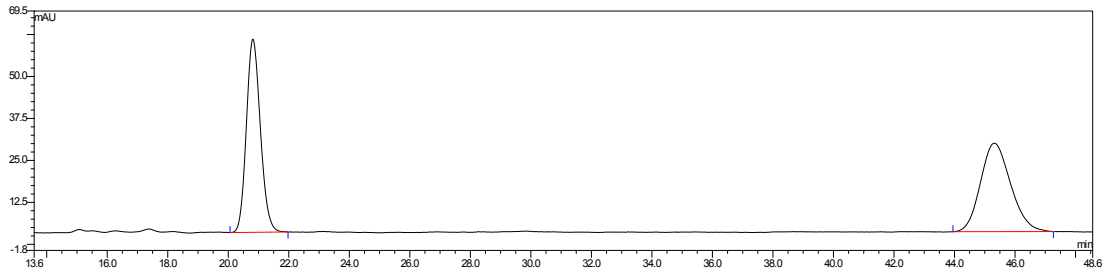


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.067	BB	0.3776	770.50568	31.70139	5.2221
2	18.418	BB	0.4929	1.39842e4	439.90903	94.7779
总量 :				1.47548e4	471.61042	



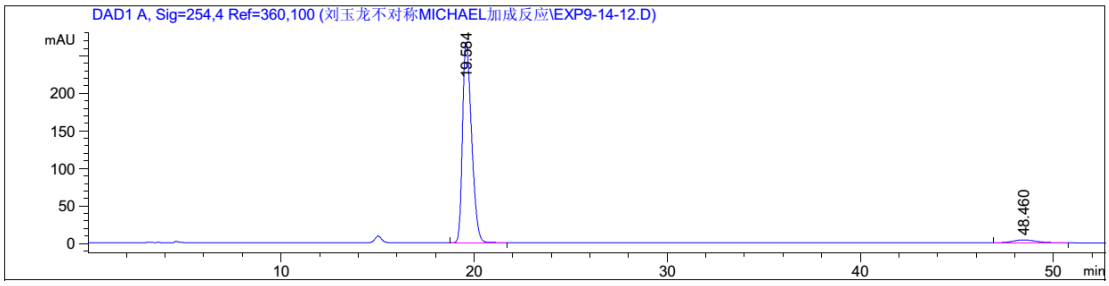
10l

Diethyl 2-(1-(4-bromophenyl)-3-oxo-3-phenylpropyl)malonate (10l). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



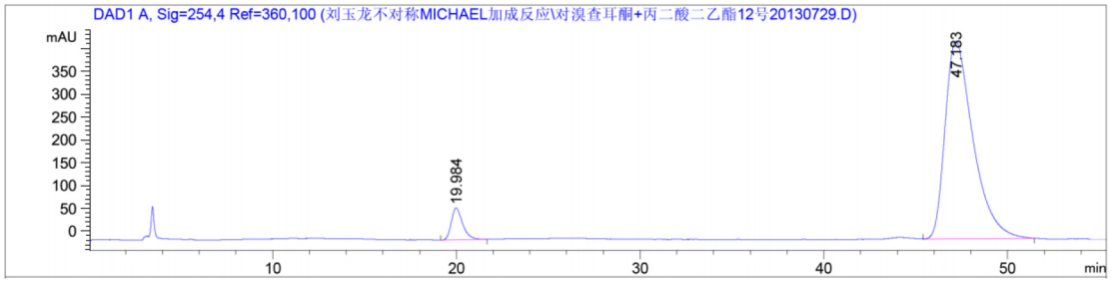
No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	20.817	30.8878	n.a.	BMB	57.525	50.42	18.43
2	n.a.	45.317	30.3714	n.a.	BMB	26.342	49.58	n.a.
Total :			61.2592	0.0000		83.867	100.00	

(*R*)-**10l**

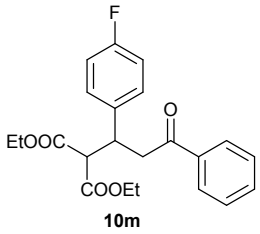


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.584	BB	0.5035	8691.88965	267.23639	96.6274
2	48.460	BB	1.0941	303.37488	3.79737	3.3726
总量 :				8995.26453	271.03376	

(*S*)-**10l**

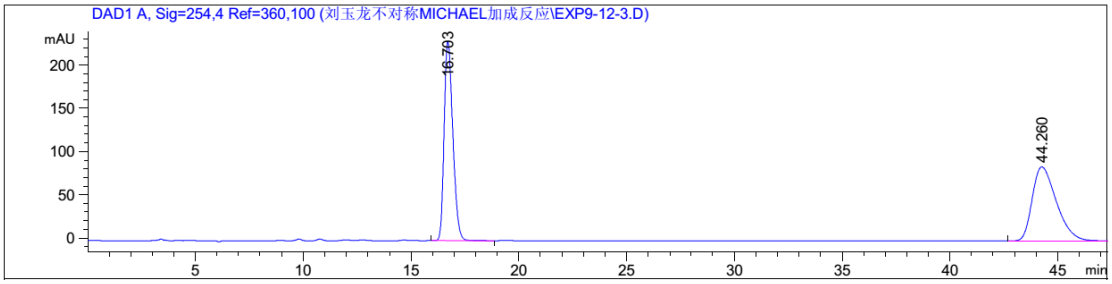


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.984	BBA	0.5499	227.54240	6.63763	5.2097
2	47.183	BB	1.5558	4140.08838	39.14755	94.7903
总量 :				4367.63078	45.78518	



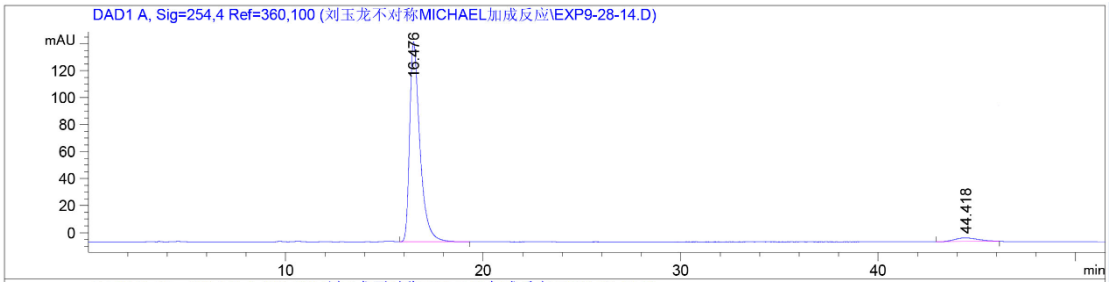
10m

Diethyl 2-(1-(4-fluorophenyl)-3-oxo-3-phenylpropyl)malonate (10m). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



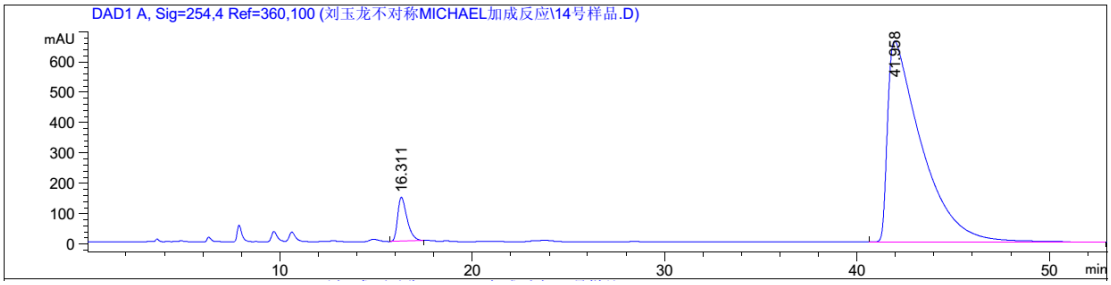
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.703	BB	0.4347	6452.30664	230.38689	49.2792
2	44.260	BBA	1.2002	6641.06201	85.49921	50.7208
总量 :				1.30934e4	315.88610	

(*R*)-**10m**

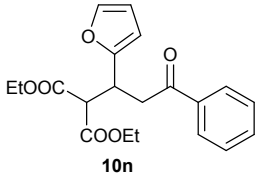


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.476	BB	0.5402	5361.76563	148.17935	95.8502
2	44.418	BBA	1.0379	232.13522	2.73041	4.1498
总量 :				5593.90085	150.90977	

(*S*)-**10m**

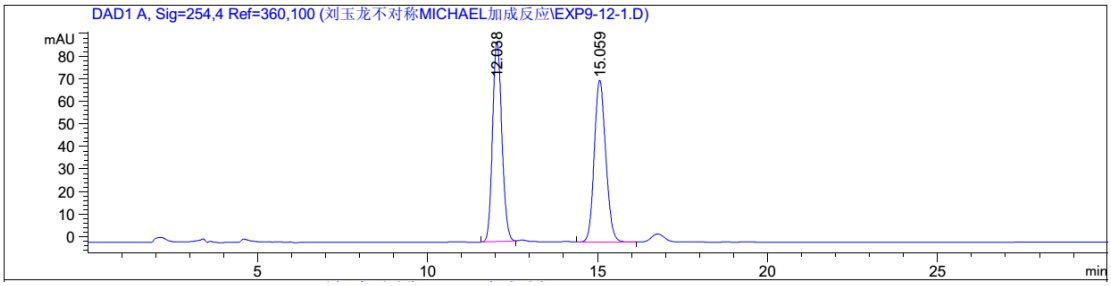


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.311	BBA	0.4868	4439.25781	140.41568	5.2301
2	41.958	BB	1.7340	8.04390e4	660.86523	94.7699
总量 :				8.48782e4	801.28091	



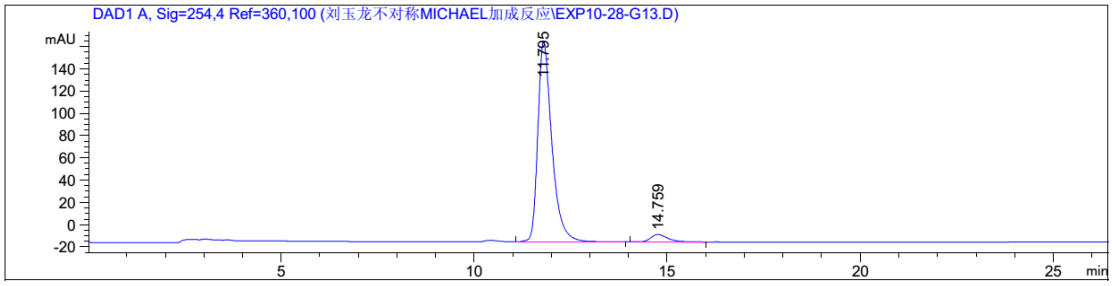
10n

Diethyl 2-(1-(furan-2-yl)-3-oxo-3-phenylpropyl)malonate (10n). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



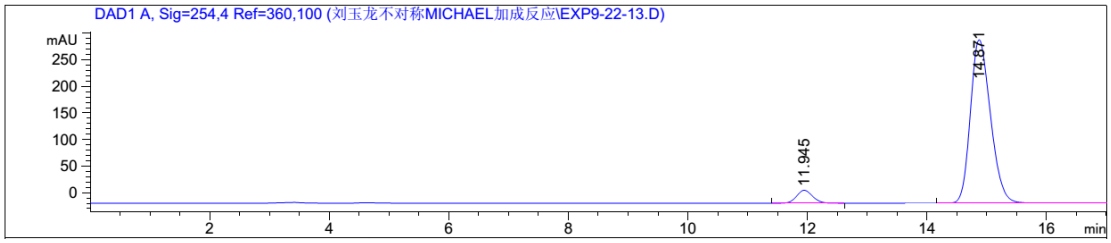
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.038	BB	0.2929	1677.15320	88.58865	49.8443
2	15.059	BB	0.3645	1687.62793	71.71877	50.1557
总量 :				3364.78113	160.30743	

(*R*)-10n

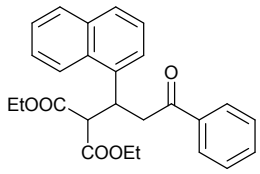


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.795	BB	0.3819	4565.66992	180.01645	95.5960
2	14.759	VB	0.4655	210.33310	6.75129	4.4040
总量 :				4776.00302	186.76774	

(*S*)-10n

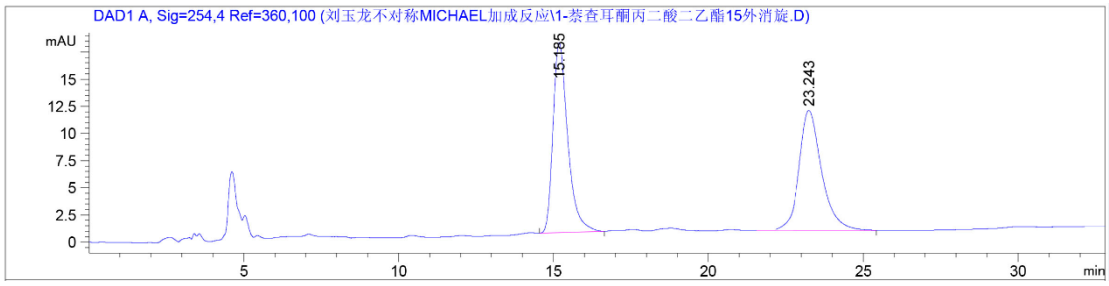


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.945	MF	0.2435	334.28809	22.87820	4.4591
2	14.871	VBA	0.3615	7162.54590	307.73297	95.5409
总量 :				7496.83398	330.61117	

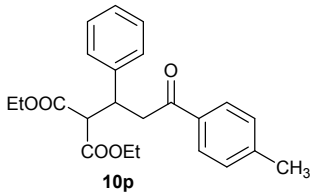


10o

Diethyl 2-(1-(naphthalen-1-yl)-3-oxo-3-phenylpropyl)malonate (10o). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.

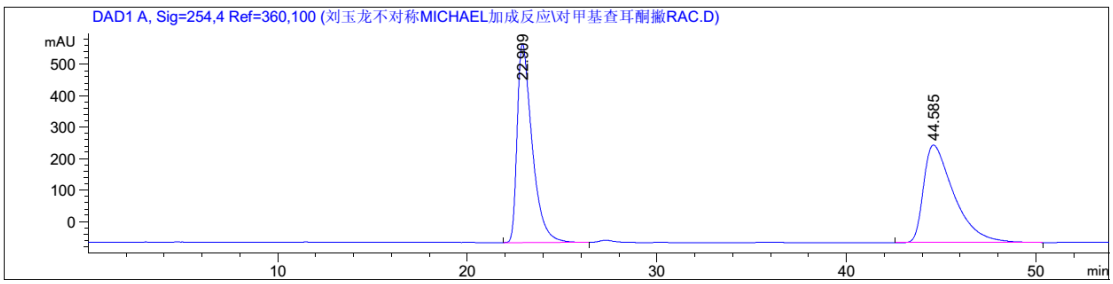


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.185	BB	0.5017	578.23468	17.48882	50.7800
2	23.243	VV	0.7598	560.47076	11.04870	49.2200
总量 :				1138.70544	28.53752	



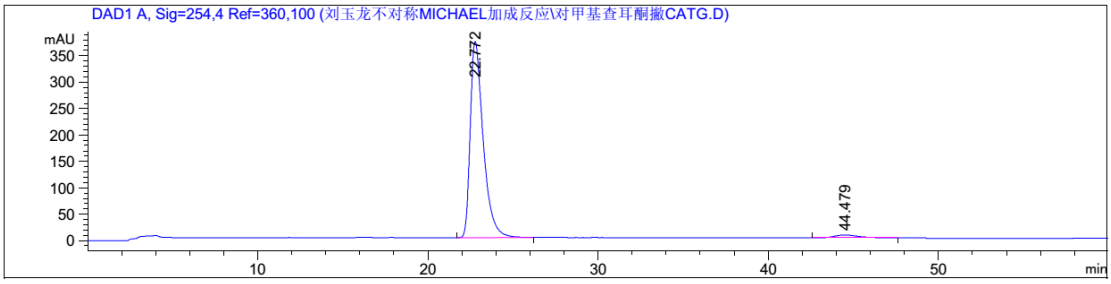
10p

Diethyl 2-(1-phenyl-3-oxo-3-(4-methylphenyl) propyl)malonate (10p). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



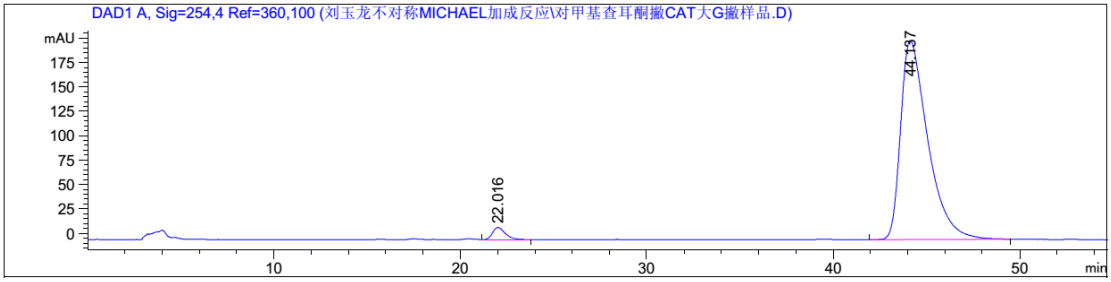
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.909	BB	0.8231	3.46400e4	632.31329	50.0226
2	44.585	BB	1.6518	3.46087e4	310.64136	49.9774
总量 :				6.92486e4	942.95465	

(*R*)-**10p**

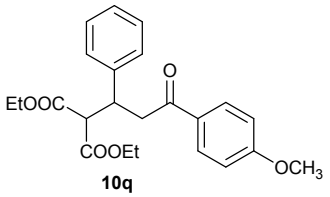


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.772	BB	0.7935	1.96572e4	371.38565	97.1105
2	44.479	BB	1.1959	584.89990	5.74463	2.8895
总量：				2.02421e4	377.13028	

(*S*)-**10p**

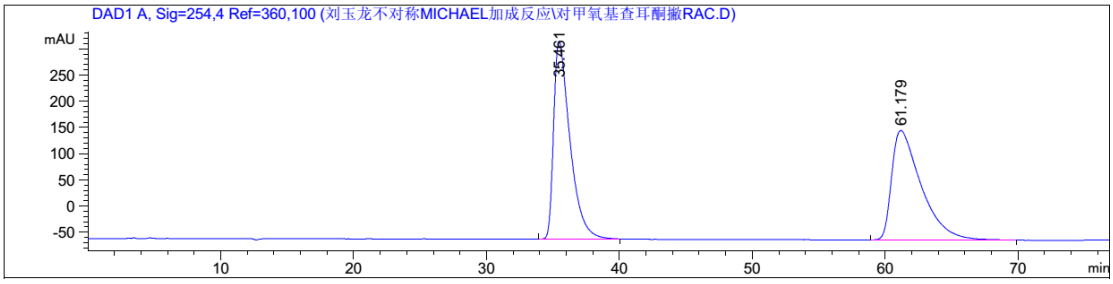


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.016	BB	0.7204	584.67456	12.34935	2.7527
2	44.137	BB	1.5106	2.06556e4	203.77536	97.2473
总量：				2.12403e4	216.12471	



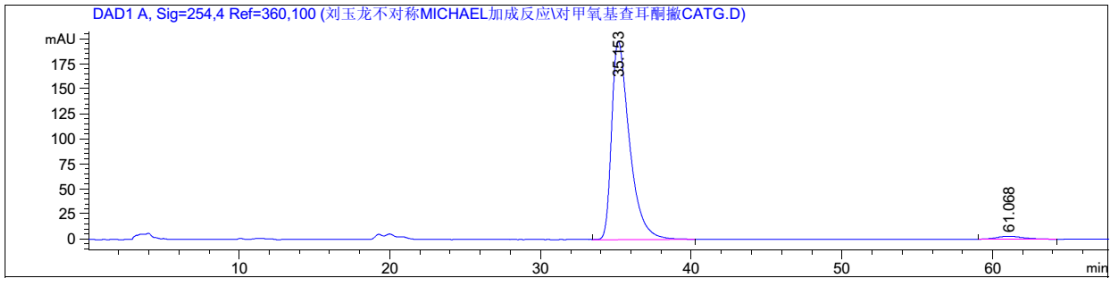
10q

Diethyl 2-(1-phenyl-3-oxo-3-(4-methoxyphenyl) propyl)malonate (10q). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



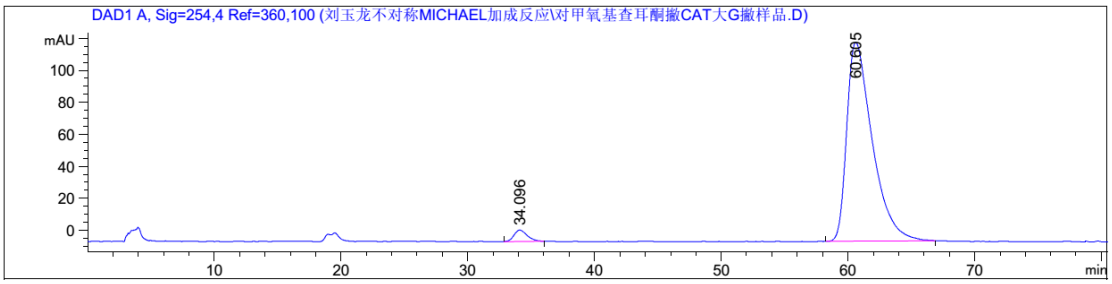
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	35.461	BB	1.3001	3.22527e4	377.76276	49.9490
2	61.179	BB	2.2349	3.23185e4	209.14067	50.0510
总量 :				6.45713e4	586.90343	

(*R*)-**10q**

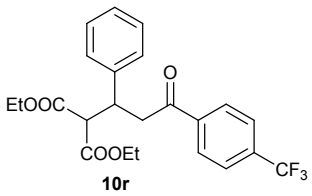


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	35.153	BB	1.2456	1.62681e4	198.19156	97.7618
2	61.068	BB	1.5263	372.44531	2.86952	2.2382
总量 :				1.66405e4	201.06108	

(*S*)-**10q**

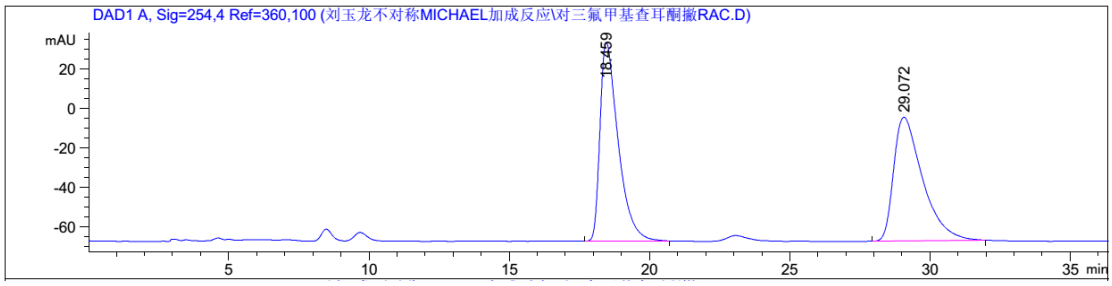


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	34.096	BB	1.0406	510.25381	7.04788	2.8519
2	60.605	BB	2.0206	1.73818e4	124.21184	97.1481
总量 :				1.78920e4	131.25972	



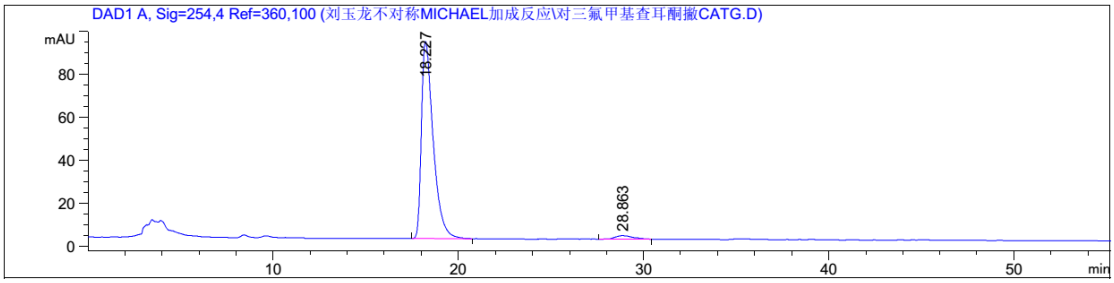
10r

Diethyl 2-(1-phenyl-3-oxo-3-(4-trifluoromethylphenyl) propyl)malonate (10r). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



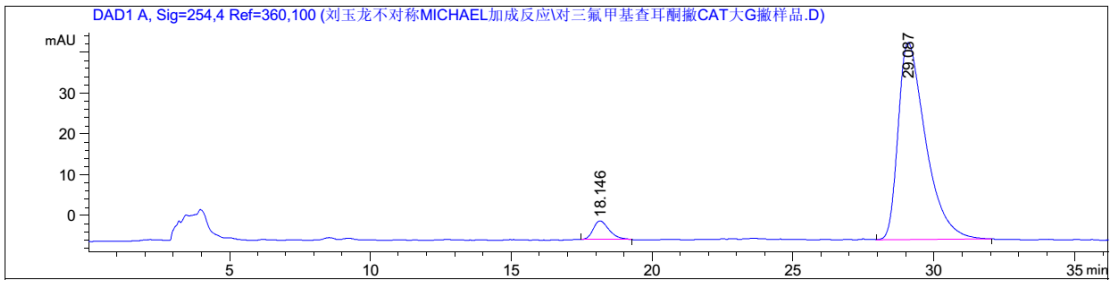
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.459	BB	0.6768	4530.88281	100.71526	50.1559
2	29.072	BB	1.0761	4502.71436	62.68071	49.8441
总量 :				9033.59717	163.39597	

(*R*)-**10r**

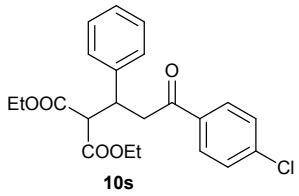


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.227	BB	0.6664	4049.25049	91.83716	97.3205
2	28.863	BB	0.8023	111.48539	1.63742	2.6795
总量 :				4160.73588	93.47458	

(*S*)-**10r**

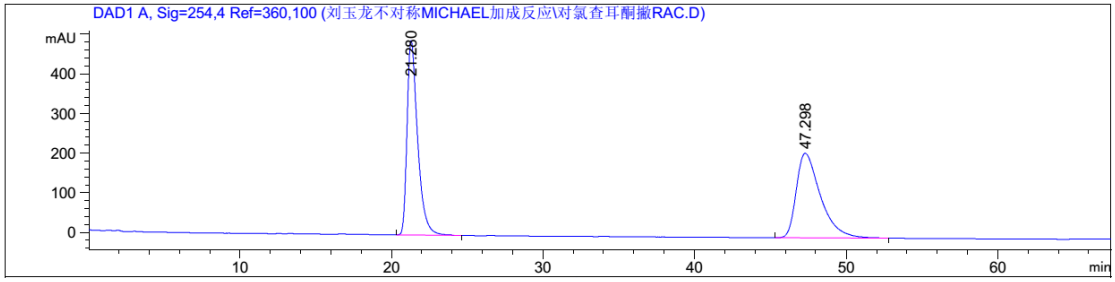


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.146	BBA	0.6050	179.29201	4.53731	5.2008
2	29.087	BB	1.0324	3268.08765	48.23912	94.7992
总量 :				3447.37965	52.77643	



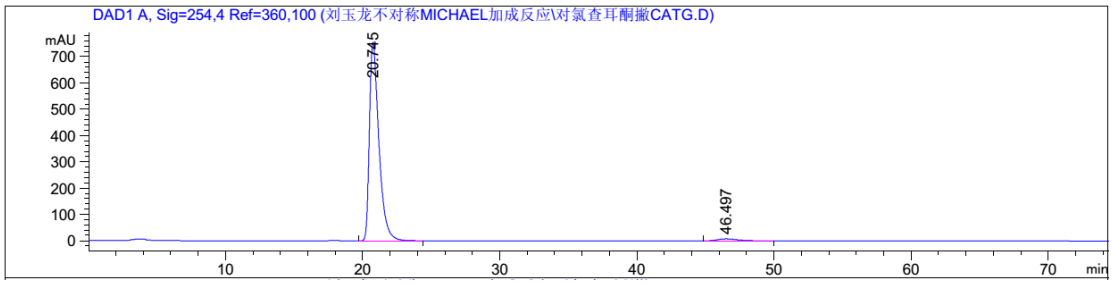
10s

Diethyl 2-(1-phenyl-3-oxo-3-(4-chlorophenyl) propyl)malonate (10s). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



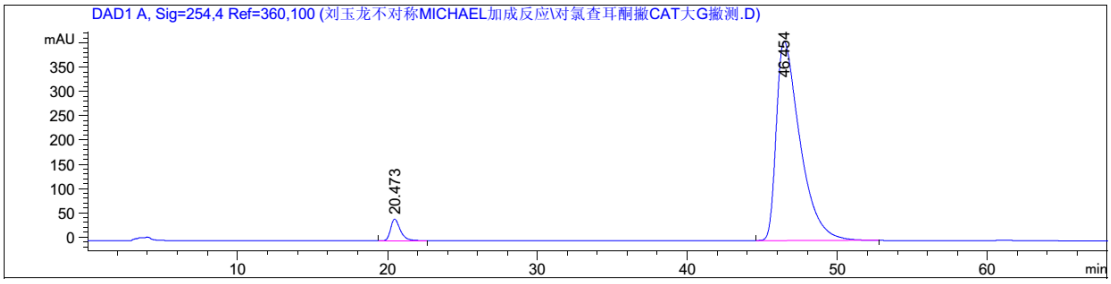
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.280	BB	0.7303	2.37602e4	491.19012	50.1124
2	47.298	BB	1.6561	2.36536e4	213.24799	49.8876
总量 :				4.74138e4	704.43811	

(*R*)-**10s**

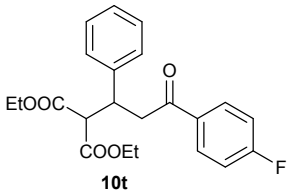


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.745	BB	0.7219	3.62755e4	755.90344	97.7935
2	46.497	BB	1.2749	818.47736	7.89913	2.2065
总量 :				3.70940e4	763.80257	

(*S*)-**10s**

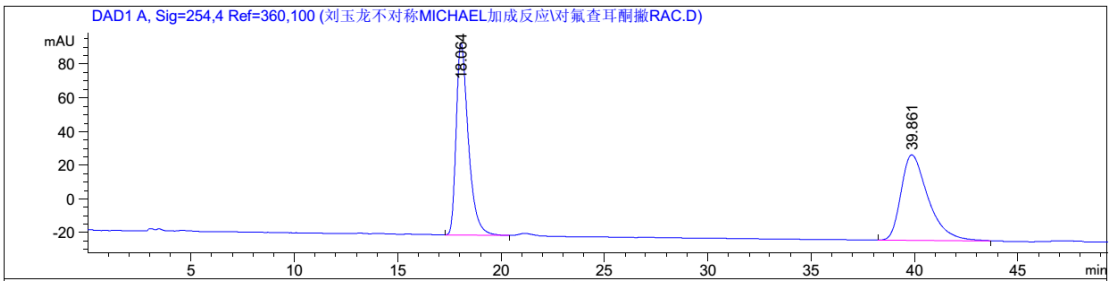


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.473	BB	0.6768	1983.65479	44.27040	4.2166
2	46.454	BB	1.6327	4.50607e4	409.84174	95.7834
总量 :				4.70443e4	454.11214	



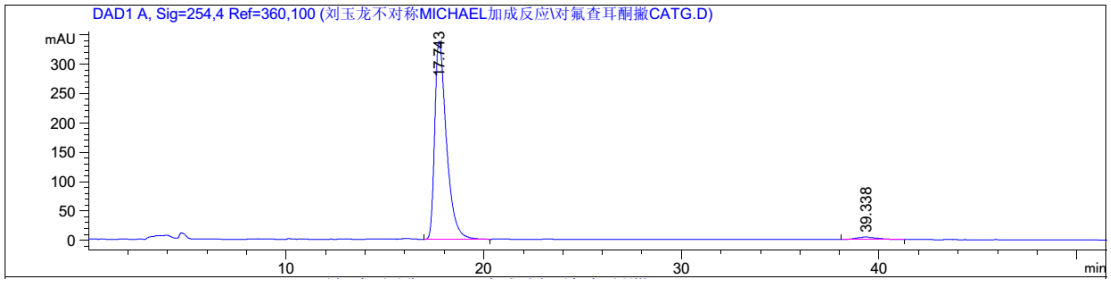
10t

Diethyl 2-(1-phenyl-3-oxo-3-(4-fluorophenyl) propyl)malonate (10t). Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 254 nm.



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.064	BB	0.6200	4655.13672	114.09566	50.0485
2	39.861	BB	1.3559	4646.11719	50.85120	49.9515
总量 :				9301.25391	164.94687	

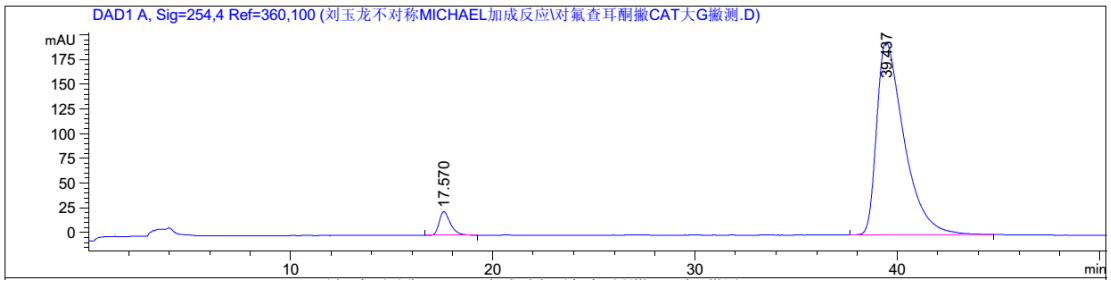
(*R*)-**10t**



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.743	BB	0.6203	1.38780e4	337.11984	97.6997
2	39.338	BB	0.9817	326.75610	3.93923	2.3003

总量 : 1.42047e4 341.05907

(*S*)-**10t**



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.570	BB	0.5859	933.57733	24.10439	4.8448
2	39.437	BB	1.4153	1.83361e4	194.60355	95.1552

总量 : 1.92697e4 218.70793