Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Table of Contents

1. General Information

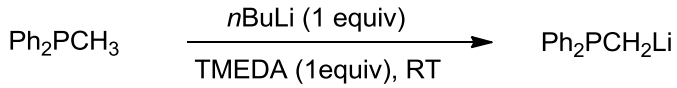
Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere; materials obtained from commercial suppliers were used directly without further purification. The $[\alpha]_D$ was recorded using PolAAr 3005 High Accuracy Polarimeter. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker 400 (or 500) MHz spectrometer in chloroform-d_3. ^{31}P NMR were recorded on a Bruker 300 MHz spectrometer in chloroform-d_3. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). Noteworthy, splitting signals between ^{13}C nucleus and ^{13}P nucleus in some Peng-Phoses were difficult to distinguish and these ^{13}C NMR signals were reported as singlet entirely. Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer.

Trichloromethane ($CHCl_3$), carbon tetrachlorid，dichloromethane, dichloroethane and ethyl acetate were freshly distilled from CaH_2; tetrahydrofuran (THF), toluene and ether were dried with sodium benzophenone and distilled before use; Ph_2PCH_3 was purchased from Acros Company.

Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate.

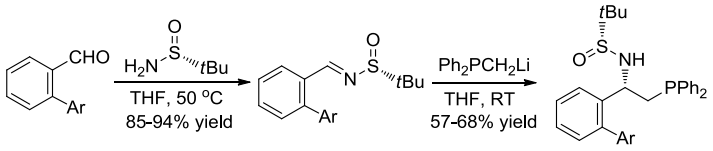
2. Typical Synthetic Procedure and Datas for Peng-Phoses.

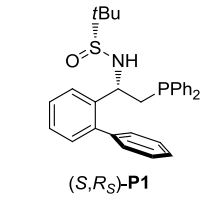
Typical Procedure for the Preparation of Methylphosphonic Lithium



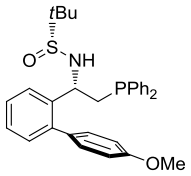
The diphenyl methyl phosphonic lithium was prepared according to the literature[1]: According to Peterson's method, 5 mmol *n*BuLi (1.6 M in hexane) was slowly added to a Schlenk tube that containing TMEDA (5.0 mmol), the mixture was stirred for 30 minutes. Then methyldiphenylphosphane (5 mmol) was added slowly to the solution of *n*BuLi and TMEDA. The mixture was stirred until a bright yellow precipitate was generated. At last, a solution of methyl phosphonic lithium was formed by the addition of few milliliters of THF.

Typical Procedure for the Synthesis of Phosphines (S,R_S)-P1~8.

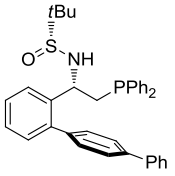




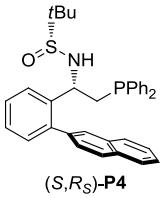
(S,R_S)-**P1**
d.r. = 14:1
68%



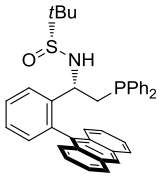
(S,R_S)-**P2**
d.r. = 12:1
56%



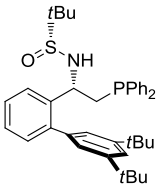
(S,R_S)-**P3**
d.r. = 15:1
63%



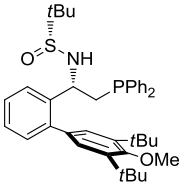
(S,R_S)-**P4**
d.r. = 9:1
54%



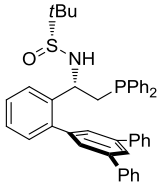
(S,R_S)-**P5**
d.r. = 8:1
57%



(S,R_S)-**P6**
d.r. = 12:1
56%



(S,R_S)-**P7**
d.r. = 15:1
53%

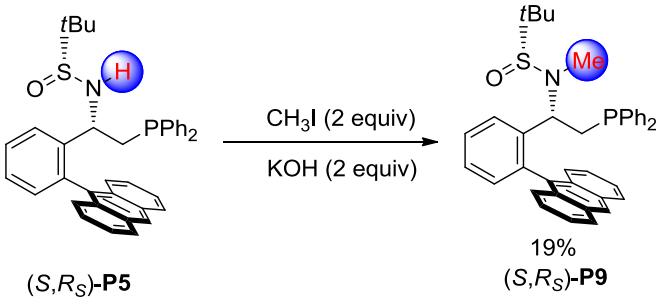


(S,R_S)-**P8**
d.r. = 14:1
52%

A solution of diphenyl methyl phosphonic lithium (1.5 mmol) that containing TMEDA (1.5 mmol) in anhydrous THF was added to the solution of corresponding chiral sulfinyl imines[2] (1.0 mmol chiral sulfinyl imines in 2 mL anhydrous THF) at

room temperature. The mixture was stirred until completion of imine as indicated by TLC, followed by hydrolysis with 10 mL of water and diluted with EtOAc. The organic layer was separated, the aqueous phase was extracted three times with EtOAc (3X10 mL). The combined organic phases were dried over $MgSO_4$ and the solvents were removed in vacuo. The residue was purified by silica gel chromatography using petroleum ether/EtOAc as the eluent to afford the desired Peng-Phoses.

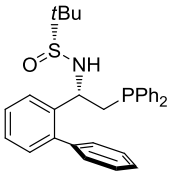
Procedure for the Synthesis (S,R_S)-P9.



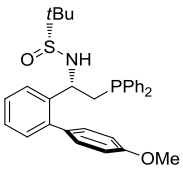
(S,R_S)-**P5** (S,R_S)-**P9**

A stirred solution of (S,R_S)-**P5** (0.3 mmol), KOH (0.6 mmol), tetrabutyl ammonium bromidein (0.12 mmol) in ether (2 mL) was added CH_3I (0.6 mmol) slowly. The mixture was stirred at 25 ^oC until completion of (S,R_S)-**P5** as indicated by TLC, after completion of the reaction, the reaction mixture was directly purified by silica gel chromatography using petroleum ether/EtOAc as the eluent to afford the desired (S,R_S)-**P9** in 19% yield (noteworthy, a great deal of phosphonium salts were obtained during the methylation process).

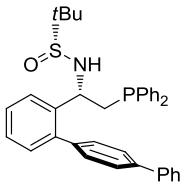
General Data for (S,R_S)-P1~9



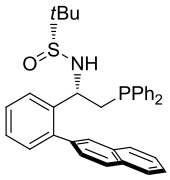
(S,R_S)-**P1**; White solid. m.p. = 159-161 °C; $[\alpha]_D^{20}$ = + 20.9 (*c* = 0.33, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.38–7.35 (m, 1H), 7.31–7.10 (m, 17H), 4.71–4.64 (m, 1H), 3.82 (d, *J* = 6.0 Hz, 1H), 2.61–2.55 (m, 1H), 2.47–2.41 (m, 1H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.06, 140.41, 141.09 (d, J_{CP}= 4.9 Hz), 137.90 (d, J_{CP}= 12.5 Hz), 137.35 (d, J_{CP}= 12.8 Hz), 132.64 (d, J_{CP}= 19.2 Hz), 132.26 (d, J_{CP}= 18.9 Hz), 130.23, 129.36, 128.55, 128.43, 128.40, 128.33, 128.12, 128.00, 127.36, 127.01, 126.56, 56.25, 54.30 (d, J_{CP}= 16.8 Hz), 38.52 (d, J_{CP}= 15.4 Hz), 22.41; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ = -24.36 ppm; HRMS (ESI) m/z calcd. for $C_{30}H_{32}NNaOPS$ $[M+Na]^+$ = 508.1834, found = 508.1845; IR (neat): υ 3231, 3051, 2961, 2922, 1476, 1430, 1398, 1366, 1181, 1065, 1044, 1031, 894, 771, 744, 695 cm^{-1}.



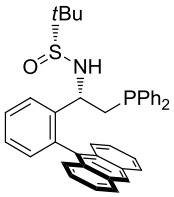
(S,R_S)-**P2**; White solid. m.p. = 127-129 °C; $[\alpha]_D^{20}$ = + 17.6 (*c* = 0.33, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.36–7.33 (m, 1H), 7.28–7.12 (m, 14H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.74–4.67 (m, 1H), 3.83–3.82 (m, 4H), 2.61–2.55 (m, 1H), 2.45–2.40 (m, 1H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.56, 140.72, 140.36 (d, J_{CP}= 5.0 Hz), 137.89 (d, J_{CP}= 12.5 Hz), 137.41 (d, J_{CP}= 13.1 Hz), 132.72 (d, J_{CP}= 19.5 Hz), 132.23 (d, J_{CP}= 18.7 Hz), 130.43, 128.53, 128.36, 128.29, 127.79, 127.35, 126.44, 113.55, 56.25, 55.13, 54.11 (d, J_{CP}= 16.7 Hz), 38.60 (d, J_{CP}= 15.2 Hz), 22.46; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ = -24.36 ppm; HRMS (ESI) m/z calcd. for $C_{31}H_{34}NNaO_2PS$ $[M+Na]^+$ = 538.1940, found = 538.1954; IR (neat): υ 3224, 2950, 2927, 1607, 1512, 1478, 1431, 1391, 1290, 1243, 1176, 1061, 1042, 999, 897, 834, 778, 738 cm^{-1}.



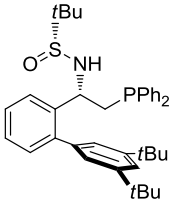
(*S*,*R*$_S$)-**P3**; White solid. m.p. = 160-162 ^{o}C; $[\alpha]_D^{20}$ = + 8.3 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.49–7.46 (m, 2H), 7.41–7.35 (m, 2H), 7.32–7.28 (m, 3H), 7.23–7.20 (m, 6H), 7.17–7.10 (m, 5H), 4.77–4.70 (m, 1H), 3.86 (d, *J* = 5.6 Hz, 1H), 2.64–2.59 (m, 1H), 2.48–2.43 (m, 1H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.62 (d, J_{CP}= 7.3 Hz), 140.22 (d, J_{CP}= 4.7 Hz), 139.66, 139.36, 137.77 (d, J_{CP}= 12.5 Hz), 132.27 (d, J_{CP}= 13.0 Hz), 132.69 (d, J_{CP}= 19.5 Hz), 132.21 (d, J_{CP}= 18.5 Hz), 130.27, 129.83, 128.73, 128.58, 128.38, 128.30, 128.11, 127.47, 127.25, 126.96, 126.77, 126.58, 56.28, 54.09 (d, J_{CP}= 16.5 Hz), 38.74 (d, J_{CP}= 15.3 Hz), 22.46; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ = -24.55 ppm; HRMS (ESI) m/z calcd. for $C_{36}H_{36}NNaOPS$ $[M+Na]^+$ = 584.2147, found = 584.2152; IR (neat): υ 3212, 3054, 3024, 2955, 2921, 1477, 1451, 1430, 1392, 1367, 1180, 1042, 1029, 900, 841, 753, 740 cm^{-1}.



(*S*,*R*$_S$)-**P4**; White solid. m.p. = 212-214 ^{o}C; $[\alpha]_D^{20}$ = + 5.3 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86–7.62 (m, 5H), 7.52–7.27 (m, 6H), 7.11–6.85 (m, 9H), 4.71 (br, 1H), 3.90 (br, 1H), 2.54–2.43 (m, 2H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.90, 140.44 (d, J_{CP}= 4.9 Hz), 137.96, 137.74 (d, J_{CP}= 12.4 Hz), 136.95 (d, J_{CP}= 12.9 Hz), 133.16, 132.51 (d, J_{CP}= 19.5 Hz), 132.36, 132.13 (d, J_{CP}= 18.8 Hz), 130.47, 128.47, 128.32, 128.28, 128.22, 128.18, 128.16, 128.10, 127.75, 127.63, 127.48, 126.60, 126.16, 125.95, 56.37, 54.41 (d, J_{CP}= 16.0 Hz), 38.82 (d, J_{CP}= 15.2 Hz), 22.48; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ = -24.46 ppm; HRMS (ESI) m/z calcd. for $C_{34}H_{34}NNaOPS$ $[M+Na]^+$ = 558.1991, found = 558.2004; IR (neat): υ 3224, 3050, 2957, 1483, 1468, 1429, 1391, 1366, 1265, 1233, 1179, 1155, 1042, 1030, 900, 860, 826, 754, 737 cm^{-1}.

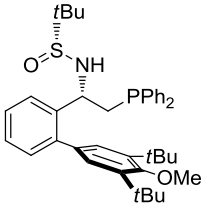


(*S*,*R*$_S$)-**P5**; White solid. m.p. = 82-84 ^{o}C; $[\alpha]_D^{20}$ = + 96.8 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.66–7.60 (m, 2H), 7.51–7.43 (m, 4H), 7.37–7.29 (m, 2H), 7.25–7.18 (m, 4H), 7.09–7.04 (m, 3H), 6.87–6.84 (m, 2H), 6.36–6.33 (m, 2H), 4.07–4.05 (m, 1H), 3.91–3.84 (m, 1H), 2.29–2.17 (m, 2H), 0.78 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.26 (d, J_{CP}= 6.1 Hz), 137.53 (d, J_{CP}= 11.5 Hz), 136.62, 135.82 (d, J_{CP}= 12.1 Hz), 134.56, 132.58, 132.39, 132.04, 131.84, 131.53, 131.35, 131.29, 130.64, 129.94, 128.78, 128.70, 128.44, 128.37, 128.34, 128.21, 128.17, 128.10, 127.61, 127.37, 127.12, 127.03, 126.64, 125.72, 125.70, 125.40, 125.20, 56.68, 55.94 (d, J_{CP}= 12.1 Hz), 38.31 (d, J_{CP}= 16.2 Hz), 21.94; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ = -24.19 ppm; HRMS (ESI) m/z calcd. for $C_{38}H_{36}NNaOPS$ $[M+Na]^+$ = 608.2147, found = 608.2152; IR (neat): υ 3050, 2864, 2348, 1725, 1432, 1356, 1047, 885, 844, 792, 736 cm^{-1}.

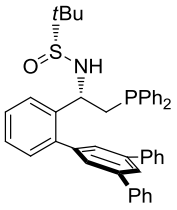


(*S*,*R*$_S$)-**P6**; White solid. m.p. = 58-60 ^{o}C; $[\alpha]_D^{20}$ = + 36.8 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.46–7.47 (m, 1H), 7.39–7.35 (m, 1H), 7.29–7.26 (m, 1H), 7.23–7.11 (m, 11H), 7.05–7.02 (m, 2H), 4.79–4.72 (m, 1H), 3.84 (d, *J* = 6.8 Hz, 1H), 2.48–2.36 (m, 2H), 1.32 (s, 18H), 1.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.54, 141.94, 140.64 (d, J_{CP}= 5.0 Hz), 139.92, 138.52 (d, J_{CP}= 13.0 Hz), 136.79 (d, J_{CP}= 12.5 Hz), 132.53 (d, J_{CP}= 19.4 Hz), 132.23 (d, J_{CP}= 18.9 Hz), 130.31, 128.48, 128.41, 128.38, 128.31, 127.73, 127.14, 126.51, 123.93, 120.77, 56.32, 54.84 (d, J_{CP}= 15.5 Hz), 38.77 (d, J_{CP}= 15.6 Hz), 34.89, 31.46, 22.33; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ = -24.72 ppm; HRMS (ESI) m/z calcd. for $C_{38}H_{48}NNaOPS$ $[M+Na]^+$ = 620.3086, found = 620.3099; IR (neat): υ 2957, 2902,

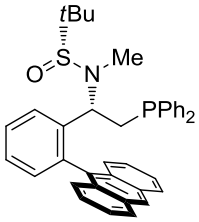
2866, 1592, 1476, 1432, 1392, 1361, 1246, 1053, 899, 879, 739 cm^{-1}.



(*S*,R_S)-**P7**; White solid. m.p. = 54-56 ^oC; $[\alpha]_D^{20}$ = + 34.2 (*c* = 0.33, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.37–7.33 (m, 1H), 7.28–7.15 (m, 12H), 7.09–7.06 (m, 2H), 4.82–4.78 (m, 1H), 3.80–3.73 (m, 4H), 2.53–2.48 (m, 1H), 2.41–2.36 (m, 1H), 1.41 (s, 18H), 1.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.45, 143.28, 141.60, 140.58 (d, J_{CP}= 4.9 Hz), 138.45 (d, J_{CP}= 13.2 Hz), 137.05, 134.92, 132.55 (d, J_{CP}= 19.5 Hz), 132.19 (d, J_{CP}= 19.8 Hz), 128.59, 128.49, 128.41, 128.34, 127.90, 127.61, 127.14, 126.61, 64.12, 56.27, 54.87 (d, J_{CP}= 16.3 Hz), 38.64 (d, J_{CP}= 15.6 Hz), 35.80, 32.15, 22.34; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ = -24.49 ppm; HRMS (ESI) m/z calcd. for $C_{39}H_{50}NnaO_2PS$ $[M+Na]^+$ = 650.3192, found = 650.3212; IR (neat): υ 2957, 2867, 1411, 1391, 1360, 1257, 1220, 1115, 1053, 1010, 888, 764, 738, cm^{-1}.



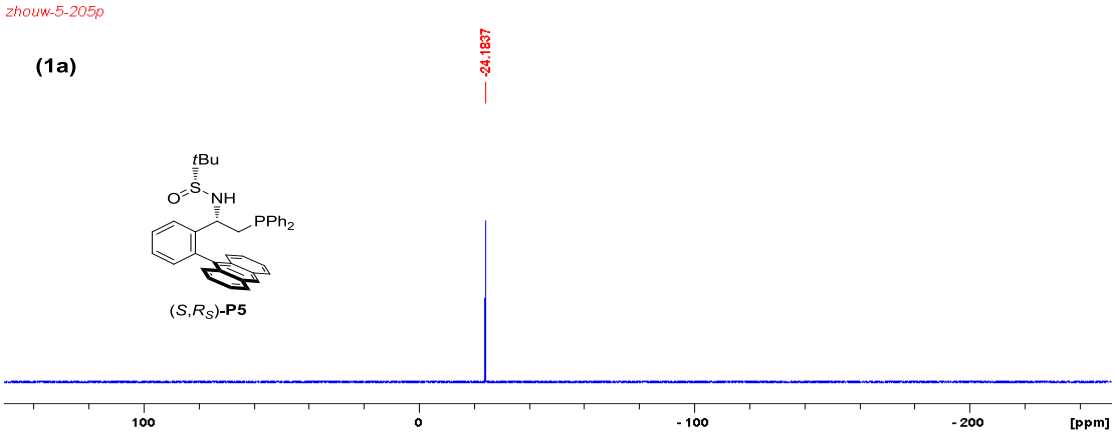
(*S*,R_S)-**P8**; White solid. m.p. = 71-73 ^oC; $[\alpha]_D^{20}$ = + 42.6 (*c* = 0.33, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.65–7.63 (m, 5H), 7.52 (s, 2H), 7.45–7.40 (m, 5H), 7.37–7.25 (m, 4H), 7.23–7.15 (m, 5H), 7.11–7.00 (m, 5H), 4.81–4.74 (m, 1H), 3.91 (d, *J* = 6.0 Hz, 1H), 2.65–2.59 (m, 1H), 2.49–2.44 (m, 1H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.63, 141.54, 140.73, 140.61, 140.26 (d, J_{CP}= 5.1 Hz), 137.79 (d, J_{CP}= 12.4 Hz), 137.00 (d, J_{CP}= 12.9 Hz), 132.48 (d, J_{CP}= 19.3 Hz), 132.22 (d, J_{CP}= 18.9 Hz), 130.30, 128.70, 128.58, 128.46, 128.37, 128.34, 128.31, 128.27, 128.16, 127.44, 127.41, 127.25, 127.16, 126.94, 124.71, 56.31, 54.92 (d, J_{CP}= 16.2 Hz), 38.78 (d, J_{CP}= 15.5 Hz), 22.32; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ = -24.07 ppm; HRMS (ESI) m/z calcd. for $C_{42}H_{40}NNaOPS$ $[M+Na]^+$ = 660.2460, found = 660.2480; IR (neat): υ 3054, 3031, 2951, 1592, 1575, 1432, 1411, 1361, 1182, 1052, 882 cm^{-1}.

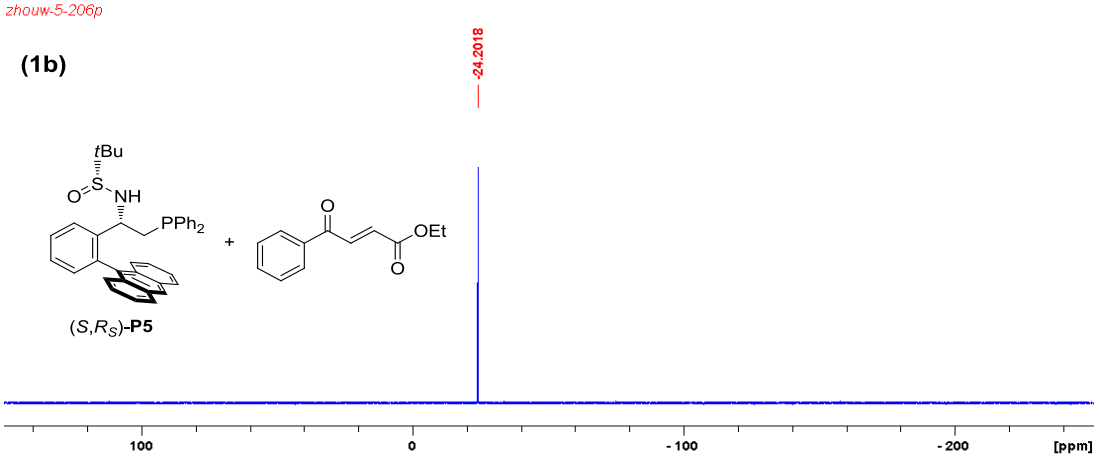


(*S*,*R*$_S$)-**P9**; White solid. m.p. = 184-186 ^{o}C; $[\alpha]_D^{20}$ = + 59.5 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.09–8.04 (m, 2H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.57–7.52 (m, 2H), 7.48–7.42 (m, 3H), 7.32–7.26 (m, 3H), 7.14–7.02 (m, 4H), 6.93–6.90 (m, 2H), 6.80–6.77 (m, 2H), 6.52–6.48 (m, 2H), 3.88–3.83 (m, 1H), 2.66–2.60 (m, 1H), 2.39–2.33 (m, 4H), 0.83 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.92 (d, J_{CP}= 4.7 Hz), 138.58 (d, J_{CP}= 13.7 Hz), 137.36, 136.78 (d, J_{CP}= 13.8 Hz), 135.08, 132.68, 132.48, 132.14, 132.06, 131.87, 131.47, 131.22, 130.65, 130.07, 128.46, 128.41, 128.21, 128.15, 128.09, 128.03, 127.57, 127.54, 127.03, 126.90, 125.83, 125.33, 125.27, 62.25 (d, J_{CP}= 15.3 Hz), 58.54, 33.92 (d, J_{CP}= 17.4 Hz), 29.68, 23.36; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ = -22.55 ppm; HRMS (ESI) m/z calcd. for $C_{39}H_{38}NNaOPS$ $[M+Na]^+$ = 622.2304, found = 622.2311; IR (neat): υ 2921, 2851, 1648, 1632, 1468, 1432, 1357, 1237, 1195, 1068, 1027, 902, 847, 735, 697 cm^{-1}.

3. ^{31}P NMR Experiments of (*S*,*R*$_S$)-P5 in the Cross RC Reaction

For better understanding of the catalytic process of (*S*,*R*$_S$)-**P5** in the cross RC reaction, series of ^{31}P NMR experiments were carried out (Figure 1). The ^{31}P NMR spectrum containing 3-aroyl acrylates (Figure 1b) hardly had any difference compared with the ^{31}P NMR spectrum of the pure (*S*,*R*$_S$)-**P5** (Figure 1a) demonstrated a fact that (*S*,*R*$_S$)-**P5** had no interaction with 3-aroyl acrylates. Noteworthy, a newly formed ^{31}P peaks was observed by the addition of acrolein to the (*S*,*R*$_S$)-**P5** solution (Figure 1c).





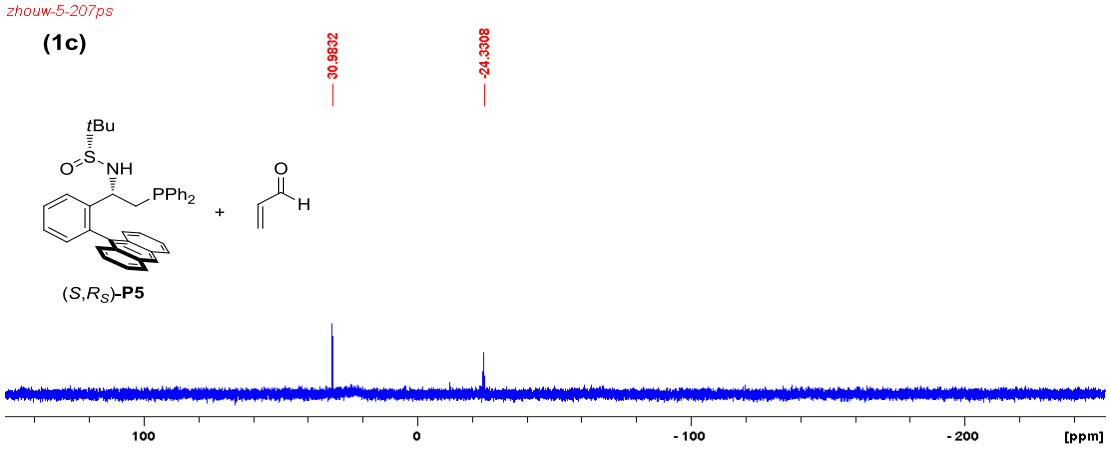


Figure S1. (a) ^{31}P NMR spectrum of pure (S,R_S)-**P5**; (b) ^{31}P NMR spectrum of (S,R_S)-**P5** containing 3-aroyl acrylates; (c) ^{31}P NMR spectrum of (S,R_S)-**P5** containing acrolein.

4. Optimization of Xiao-Phoses and Wei-Phoses in the Cross R-C Reaction

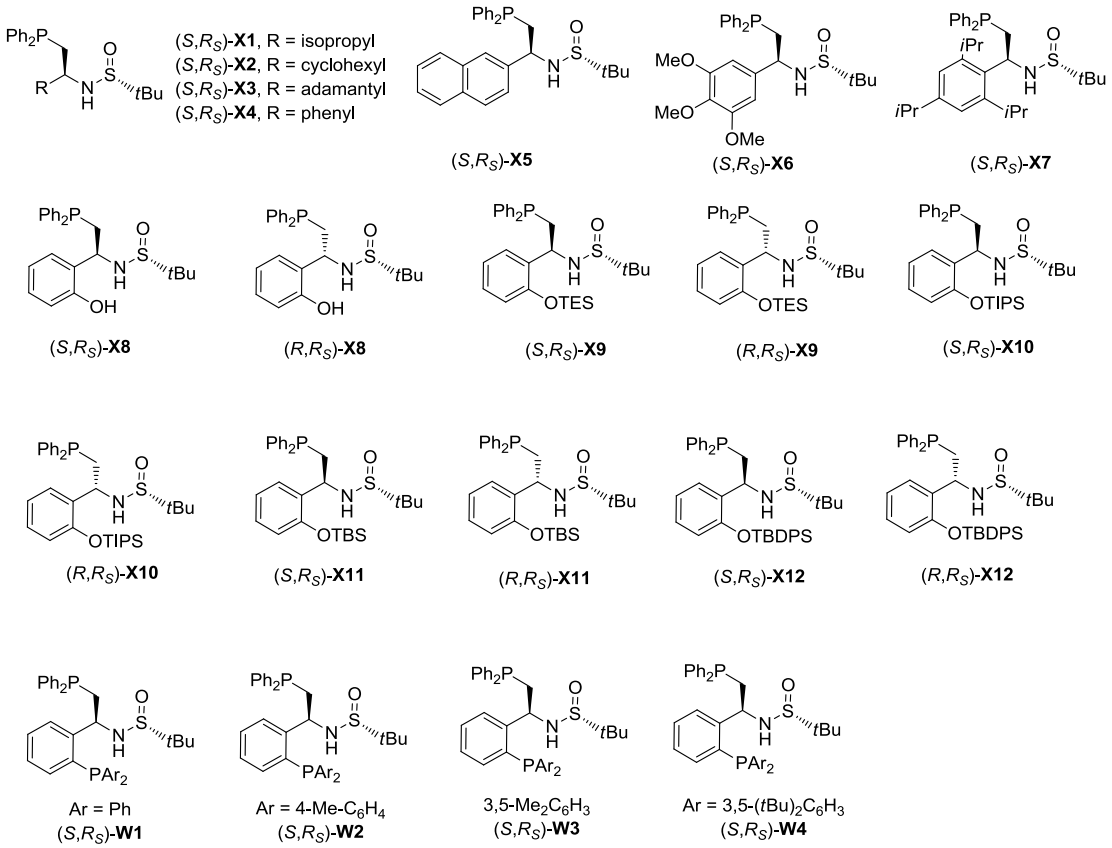
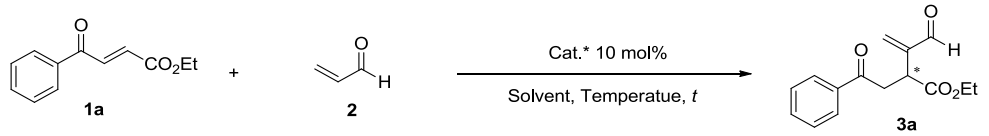


Figure S2. Screened Xiao-Phoses and Wei-Phoses.

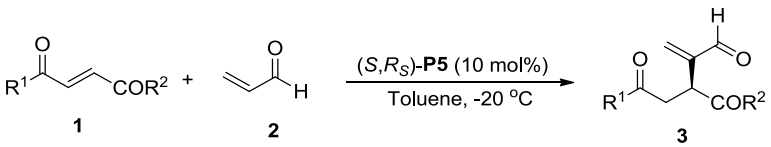
Table S1: Optimization of Xiao-phoses and Wei-Phoses for the cross R-C reaction of 3-aroyl acrylates and acrolein[a].



Entry	Cat.*	Tem. [°C]	Solvent	*t* [h]	Yield [%][b]	ee [%][c]
1	(*S*,R_S)-**X4**	25	$CHCl_3$	12	49	46
2	(*S*,R_S)-**X4**	25	DCM	12	24	51
3	(*S*,R_S)-**X4**	25	DCE	12	42	40
4	(*S*,R_S)-**X4**	25	Et_2O	12	<5	--
5	(*S*,R_S)-**X4**	25	THF	12	13	54
6	(*S*,R_S)-**X4**	25	CH_3CO_2Et	12	12	53
7	(*S*,R_S)-**X4**	25	Acetone	12	63	39
8	(*S*,R_S)-**X4**	25	Toluene	12	41	36
9	(*S*,R_S)-**X1**	25	Acetone	12	27	36
10	(*S*,R_S)-**X2**	25	Acetone	12	34	35
11	(*S*,R_S)-**X3**	25	Acetone	12	21	17
12	(*S*,R_S)-**X5**	25	Acetone	12	39	36
13	(*S*,R_S)-**X6**	25	Acetone	12	42	38
14	(*S*,R_S)-**X7**	25	Acetone	12	33	27
15	(*S*,R_S)-**X8**	25	Acetone	12	15	23
16	(*R*,R_S)-**X8**	25	Acetone	12	18	-47
17	(*S*,R_S)-**X9**	25	Acetone	12	37	28
18	(*R*,R_S)-**X9**	25	Acetone	12	24	-55
19	(*S*,R_S)-**X10**	25	Acetone	12	62	34
20	(*R*,R_S)-**X10**	25	Acetone	12	60	-67
21	(*R*,R_S)-**X10**	0	Acetone	14	57	78
22	(*R*,R_S)-**X10**	-10	Acetone	14	45	85
23	(*R*,R_S)-**X10**	-20	Acetone	24	<10	--
21	(*S*,R_S)-**X11**	25	Acetone	12	58	36
22	(*R*,R_S)-**X11**	25	Acetone	12	42	-65
23	(*S*,R_S)-**X12**	25	Acetone	12	40	32
24	(*R*,R_S)-**X12**	25	Acetone	12	53	-64
25	(*S*,R_S)-**W1**	25	Acetone	12	69	58
26	(*S*,R_S)-**W2**	25	Acetone	12	64	50
27	(*S*,R_S)-**W3**	25	Acetone	12	68	45
28	(*S*,R_S)-**W4**	25	Acetone	12	67	44
29	(*S*,R_S)-**W1**	0	Acetone	12	55	61
30	(*S*,R_S)-**W1**	-10	Acetone	12	49	65
31	(*S*,R_S)-**W1**	-20	Acetone	16	37	67

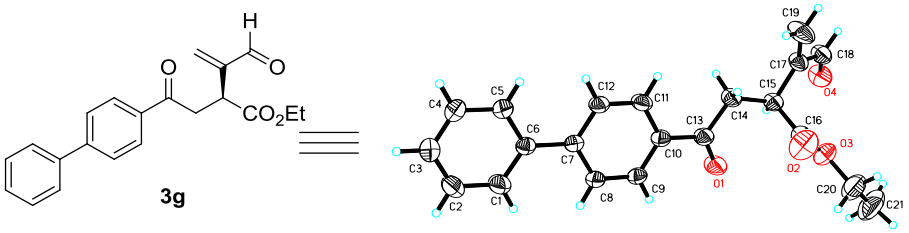
[a] Unless otherwise specified, all reactions were carried out with **1a** (0.1 mmol), **2** (0.3 mmol) , Xiao-Phos OR Wei-Phos (10 mol%) in solvent (2 mL). [b] Yield of isolated products. [c] Determined by HPLC analysis using a chiral stationary phase.

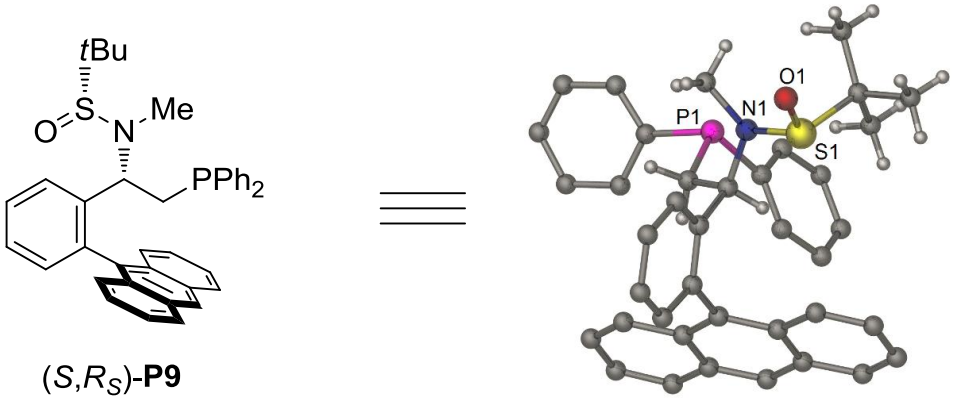
5. Typical Procedure for the Peng-Phos Catalyzed Cross R-C Reaction of Active Alkenes and Acrolein.



A stirred solution of **1**[3] (0.2 mmol) and (S,R_S)-**P5** (0.02 mmol) in toluene (2 mL) was cooled to -20 °C. Subsequently, **2** (0.6 mmol) in toluene (2 mL) added slowly over 4 h. The mixture was stirred for another 8 h, the solvents were removed in vacuo and the residue was directly purified by silica gel chromatography using petroleum ether/EtOAc as the eluent to afford the desired RC product.

6. X-ray crystal structure for 3g and (S,R_S)-P9





The H-atoms on the aryl ring have been removed for claritry.

7. Experimental Procedure for the Transformations of 3a

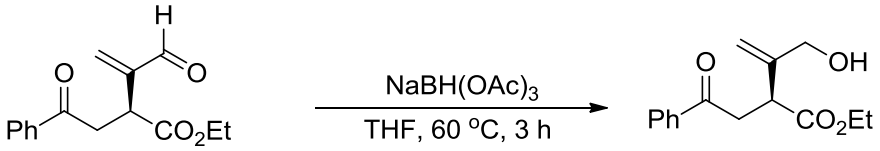
Experimental procedure for the Wittig reaction of 3a

3a
92% *ee*

4
81%, 92% *ee*

A stirred solution of **3a** (0.2 mmol) in toluene (2 mL) was added (1-phenyl-2-(triphenylphosphoranylidene)-ethanone (0.6 mmol). The mixture was stirred at 100 °C for 12 h. After completion of the reaction, the reaction mixture was directly applied to a silica gel chromatography column to afford the desired **4** in 81% yield without loss of enantiopurity.

Experimental procedure for the selective reduction of 3a

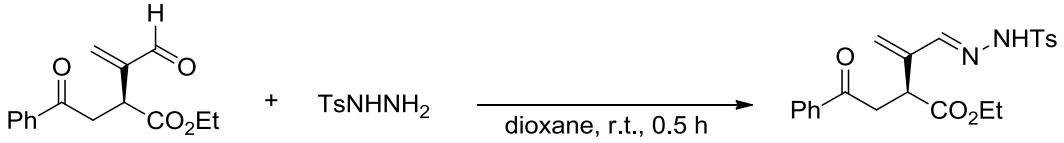


3a
92% *ee*

5
74%, 92% *ee*

Under Ar, a stirred solution of **3a** (0.2 mmol) in THF (2 mL) was added $NaBH(OAc)_3$ (0.6 mmol). The mixture was stirred at 60 °C for 3 h. After completion of the reaction, the reaction mixture was directly applied to a silica gel chromatography column to afford the desired **5** in 74% yield without loss of enantiopurity.

Experimental procedure for the condensation reaction of 3a with $TsNHNH_2$

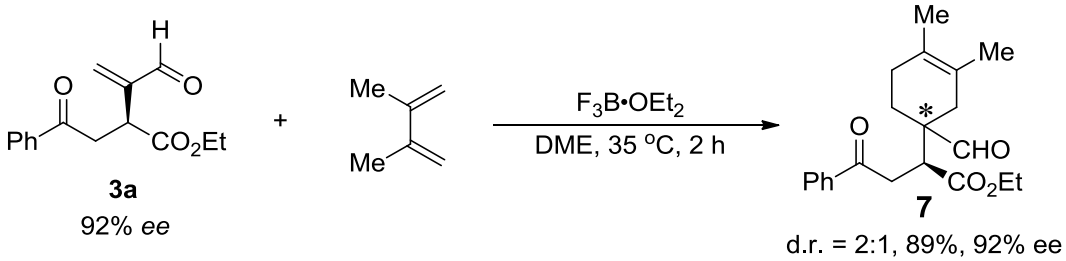


3a
92% *ee*

6
94%, 92% *ee*

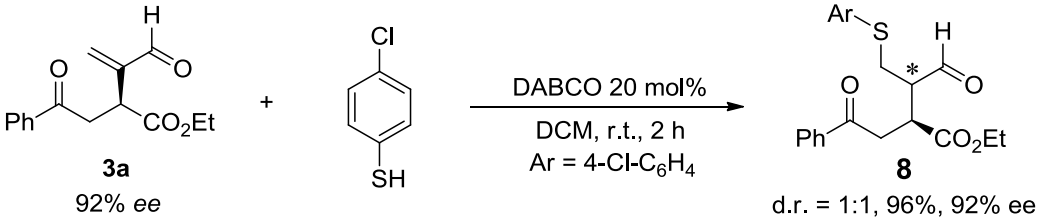
A stirred solution of **3a** (0.2 mmol) in dioxane (2 mL) was added $TsNHNH_2$ (0.24 mmol). The mixture was stirred at r.t. for 0.5 h. After completion of the reaction, the reaction mixture was directly applied to a silica gel chromatography column to afford the desired **6** in 94% yield without loss of enantiopurity.

Experimental procedure for the Diels-Alder reaction of 3a



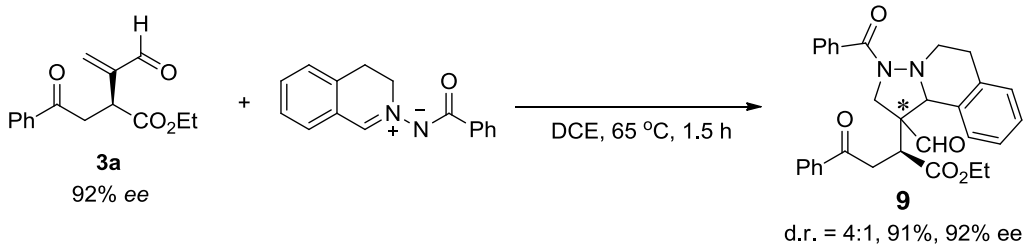
A stirred solution of **3a** (0.2 mmol) and 2,3-dimethyl-1,3-butadiene (0.6 mmol) in DME (2 mL) was added boron fluoride ethyl ether (0.08 mmol). The mixture was stirred at 35 ^{o}C for 2 h. After completion of the reaction, the reaction mixture was directly applied to a silica gel chromatography column to afford the desired **7** in 89% yield without loss of enantiopurity (d.r. = 2:1, the diastereoisomers of **7** were inseparable through silica gel chromatography).

Experimental procedure for the Michael addition of 3a with 4-Chlorothiophenol



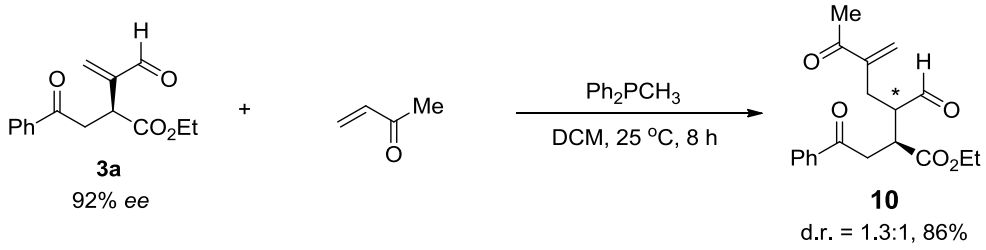
A stirred solution of **3a** (0.2 mmol) in DCM (2 mL) was added 4-chlorothiophenol (0.24 mmol), DABCO (0.04 mmol). The mixture was stirred at r.t. for 2 h. After completion of the reaction, the reaction mixture was directly applied to a silica gel chromatography column to afford the desired **8** in 96% yield without loss of enantiopurity (d.r. = 1:1).

Experimental procedure for the dipolar cycloaddition of 3a



A stirred solution of **3a** (0.2 mmol) in DCE (2 mL) was added benzoyl(3,4-dihydroisoquinolin-2-ium-2-yl)amide[4] (0.4 mmol). The mixture was stirred at 65 ^{o}C for 1.5 h. After completion of the reaction, the reaction mixture was directly applied to a silica gel chromatography column to afford the desired **9** in 91% yield without loss of enantiopurity (d.r. = 4:1).

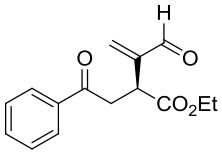
Experimental procedure for the R-C of 3a with methyl vinyl ketone



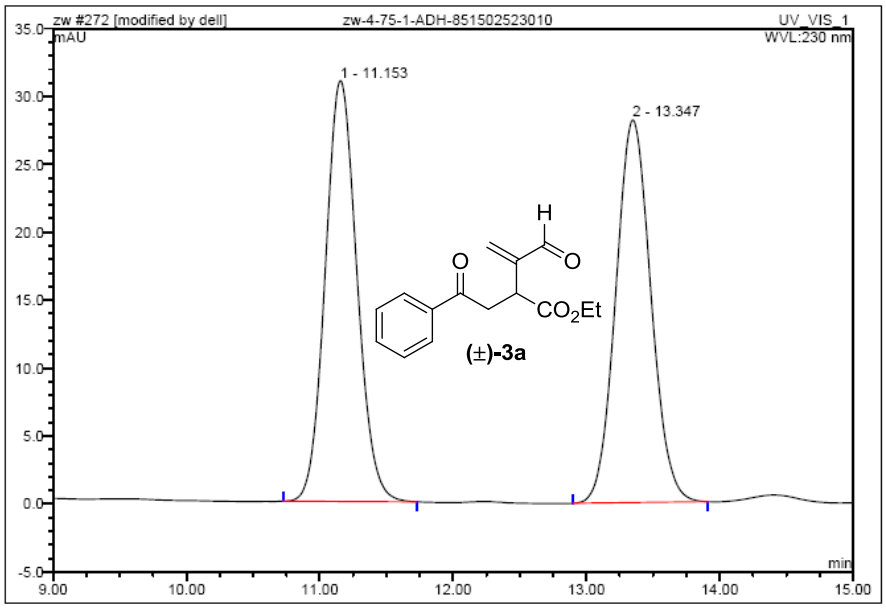
A stirred solution of **3a** (0.2 mmol) and methyl vinyl ketone (0.6 mmol) in DCM (2 mL) was added Ph_2PCH_3 (0.04 mmol). The mixture was stirred at 25 ^{o}C for 8 h. After completion of the reaction, the reaction mixture was directly applied to a silica gel chromatography column to afford the desired **10** in 86% yield. (d.r. = 1.3:1, the diastereoisomers of **10** were inseparable through silica gel chromatography and we have not found suitable chiral stationary for determining the ee).

8 General Datas and HPLC Spectra for 3, 4, 5, 6, 7, 8, 9

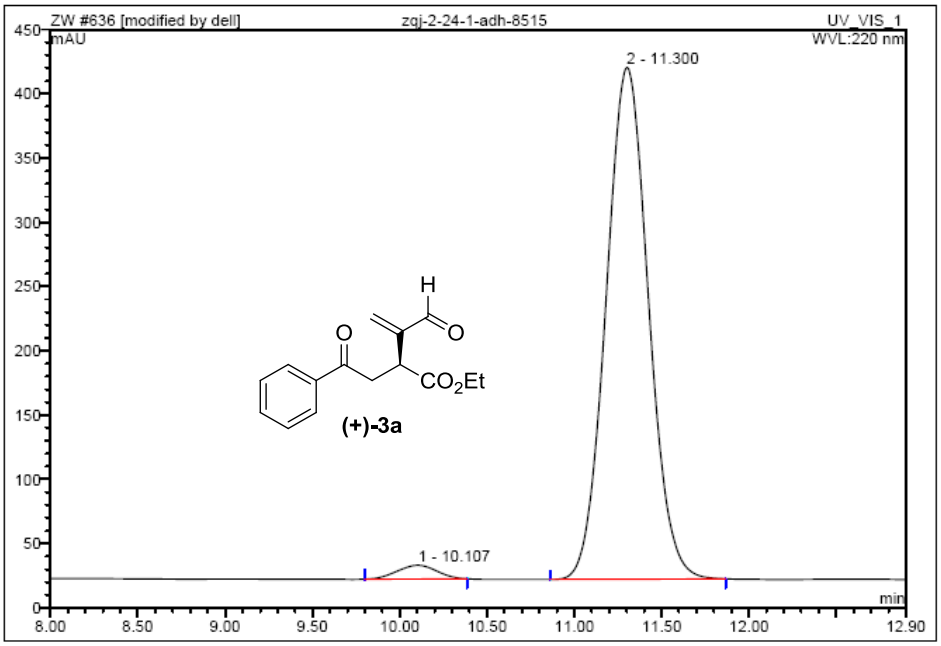
3a (*S*)-ethyl 3-formyl-2-(2-oxo-2-phenylethyl)but-3-enoate



3a; Colorless oil; $[\alpha]_D^{20}$ = + 127.1 (*c* = 0.33, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 9.55 (s, 1H), 7.96–7.93 (m, 2H), 7.59–7.54 (m, 1H), 7.47–7.44 (m, 2H), 6.49 (d, *J* = 0.8 Hz, 1H), 6.20 (s, 1H), 4.23 (dd, *J* = 8.0, 5.6 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.69 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.22 (dd, *J* = 17.6, 5.6 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.06, 192.68, 172.08, 147.31, 136.37, 136.18, 133.30, 128.59, 128.03, 61.26, 39.77, 39.70, 13.98; Enantiomeric excess: 95%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 85/15; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 10.10 min, second peak: t_R = 11.30 min; HRMS (ESI) m/z calcd. for $C_{15}H_{16}NaO_4$ $[M+Na]^+$ = 283.0941, found = 283.0950; IR (neat): υ 2983, 2939, 2907, 2824, 1727, 1691, 1679, 1594, 1448, 1401, 1362, 1325, 1211, 1174, 1159, 1096, 1022, 975, 753, cm^{-1}.

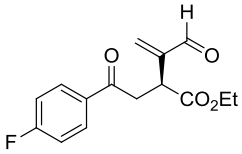


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.15	n.a.	30.976	8.536	49.77	n.a.	BMB*
2	13.35	n.a.	28.161	8.616	50.23	n.a.	BMB*
Total:			59.137	17.152	100.00	0.000	

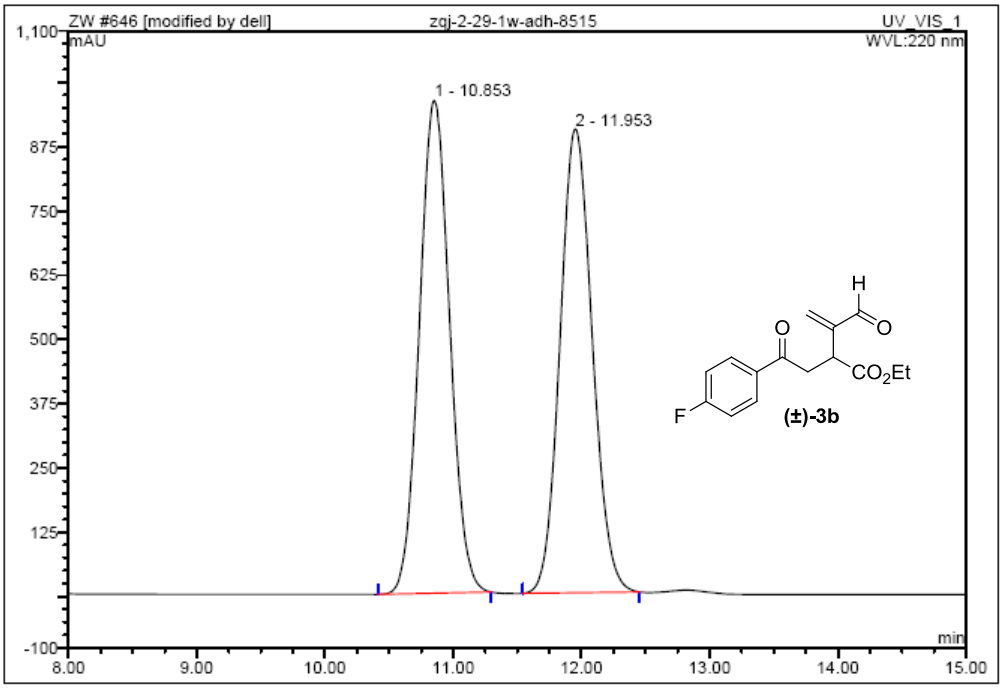


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.11	n.a.	10.643	2.811	2.45	n.a.	BMB*
2	11.30	n.a.	398.288	111.844	97.55	n.a.	BMB*
Total:			408.931	114.655	100.00	0.000	

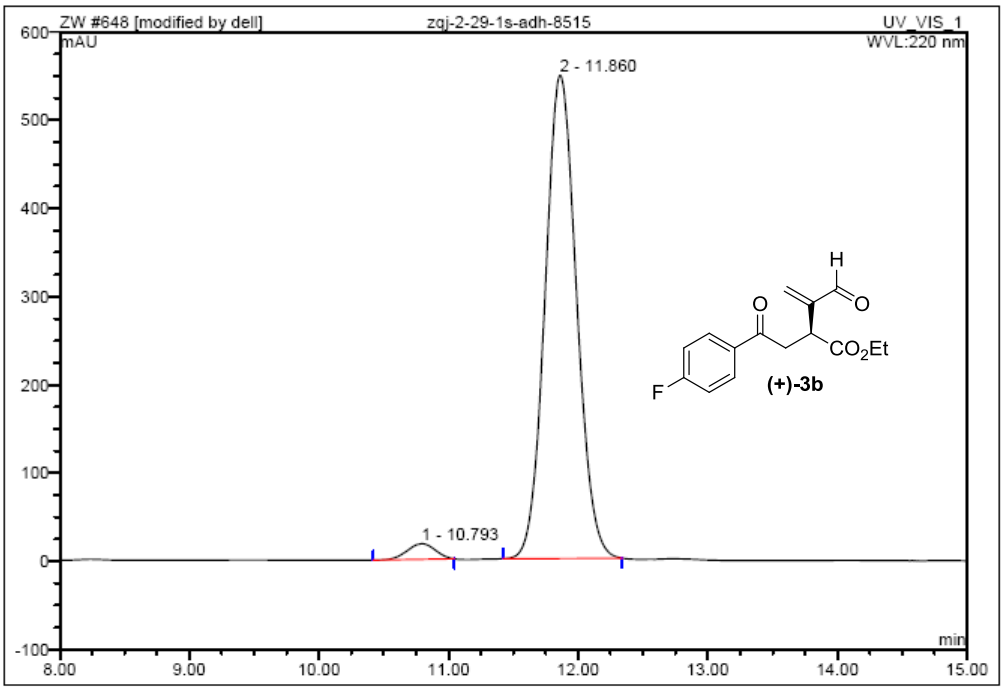
3b (*S*)-ethyl 2-(2-(4-fluorophenyl)-2-oxoethyl)-3-formylbut-3-enoate



3b; Colorless oil; $[\alpha]_D^{20}$ = + 167.2 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.56 (s, 1H), 8.00–7.97 (m, 2H), 7.15–7.12 (m, 2H), 6.50 (s, 1H), 6.22 (s, 1H), 4.22 (dd, *J* = 8.5, 5.5 Hz, 1H), 4.17 (q, *J* = 7.0 Hz, 2H), 3.68 (dd, *J* = 18.0, 8.5 Hz, 1H), 3.17 (dd, *J* = 18.0, 5.5 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.50, 192.69, 172.02, 165.84 (d, J_{CF} = 253.63 Hz), 147.19, 136.30, 132.78 (d, J_{CF} = 3.0 Hz), 130.69 (d, J_{CF} = 9.4 Hz), 115.71 (d, J_{CF} = 21.8 Hz), 61.31, 39.79, 39.58, 13.97; Enantiomeric excess: 94%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 85/15; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 10.79 min, second peak: t_R = 11.86 min; HRMS (ESI) m/z calcd. for $C_{15}H_{15}FNaO_4$ $[M+Na]^+$ = 301.0847, found = 301.0855; IR (neat): υ 2982, 2918, 2848, 1729, 1684, 1648, 1628, 1595, 1507, 1409, 1363, 1322, 1212, 1173, 1156, 1096, 1024, 972, 821 cm^{-1}.

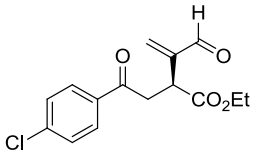


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.85	n.a.	958.757	262.172	49.99	n.a.	BMB*
2	11.95	n.a.	902.274	262.317	50.01	n.a.	BMB*
Total:			1861.031	524.490	100.00	0.000	

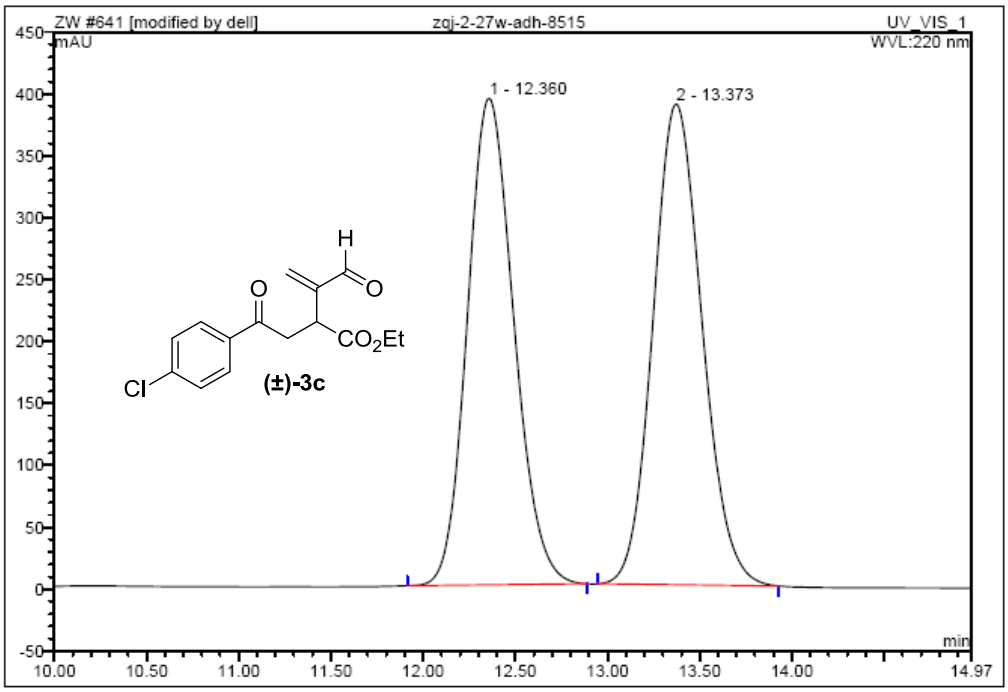


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.79	n.a.	17.841	4.472	2.83	n.a.	BMB*
2	11.86	n.a.	547.665	153.823	97.17	n.a.	BMB*
Total:			565.506	158.295	100.00	0.000	

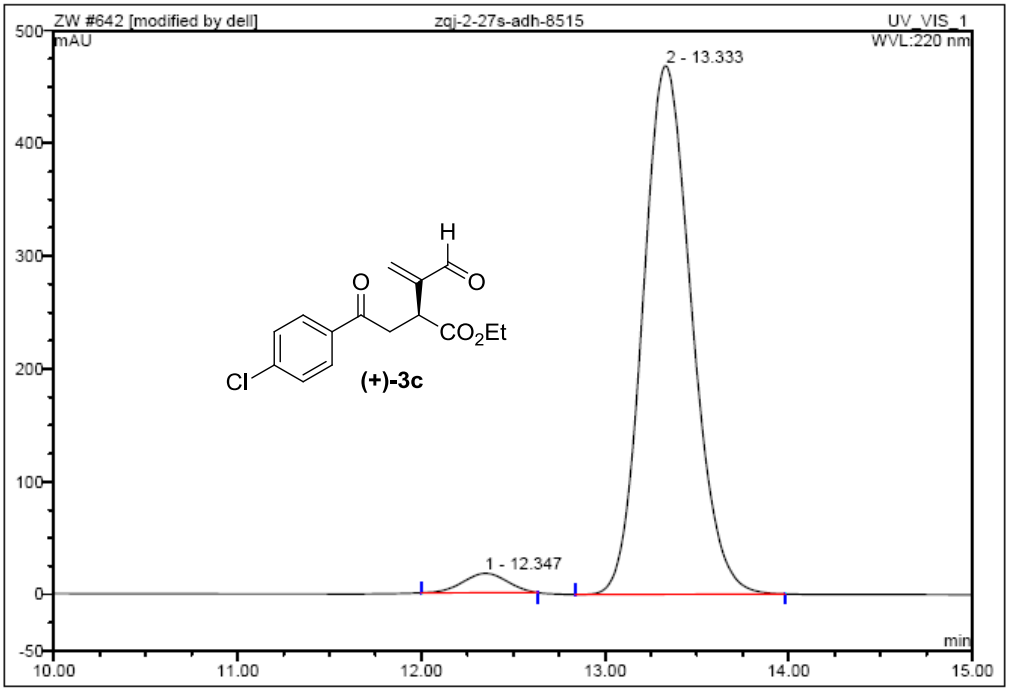
3c (*S*)-ethyl 2-(2-(4-chlorophenyl)-2-oxoethyl)-3-formylbut-3-enoate



3c; Colorless oil; $[\alpha]_D^{20}$ = + 130.2 (*c* = 0.33, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.91–7.89 (m, 2H), 7.46–7.43 (m, 2H), 6.51 (s, 1H), 6.22 (s, 1H), 4.22 (dd, *J* = 8.0, 5.0 Hz, 1H), 4.18 (q, *J* = 7.5 Hz, 2H), 3.68 (dd, *J* = 18.0, 8.5 Hz, 1H), 3.16 (dd, *J* = 18.0, 5.5 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.92, 192.69, 171.98, 147.15, 139.79, 136.35, 134.66, 129.46, 128.93, 61.35, 39.79, 39.64, 13.98; Enantiomeric excess: 94%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 85/15; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 12.34 min, second peak: t_R = 13.33 min; HRMS (ESI) m/z calcd. for $C_{15}H_{15}ClNaO_4$ $[M+Na]^+$ = 317.0551, found = 317.0557; IR (neat): υ 2981, 2921, 2823, 2703, 1730, 1685, 1627, 1588, 1571, 1400, 1306, 1246, 1213, 1173, 1090, 991, 827 cm^{-1}.

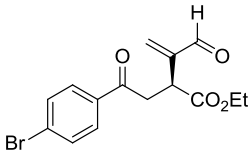


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.36	n.a.	392.890	114.485	48.87	n.a.	BMB*
2	13.37	n.a.	388.201	119.773	51.13	n.a.	BMB*
Total:			781.091	234.259	100.00	0.000	

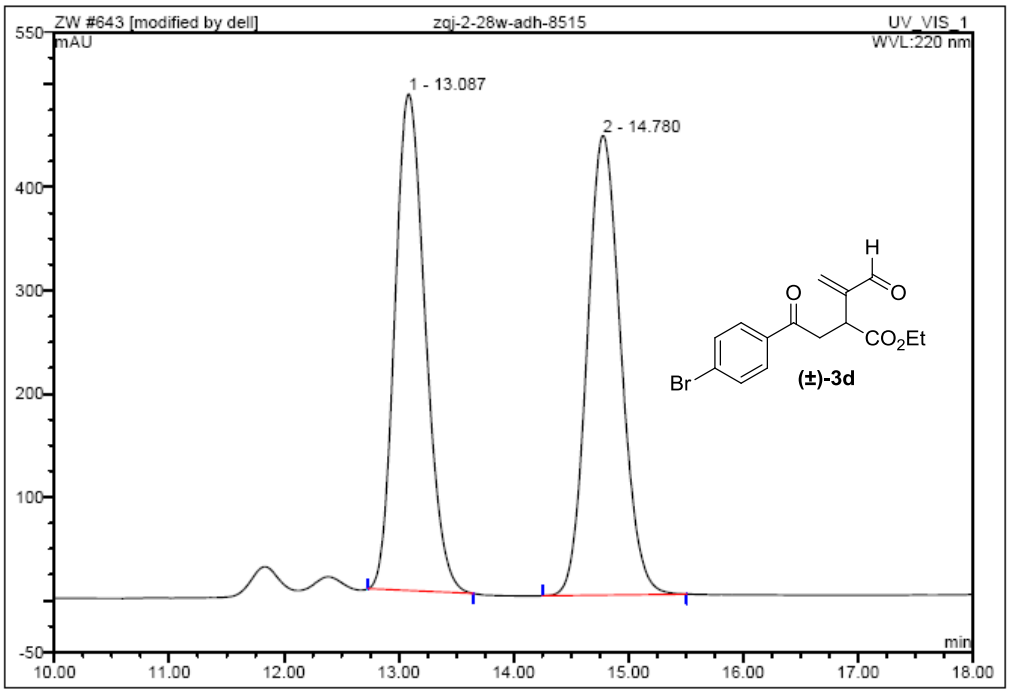


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.35	n.a.	17.151	4.798	3.23	n.a.	BMB*
2	13.33	n.a.	468.642	143.877	96.77	n.a.	BMB*
Total:			485.793	148.676	100.00	0.000	

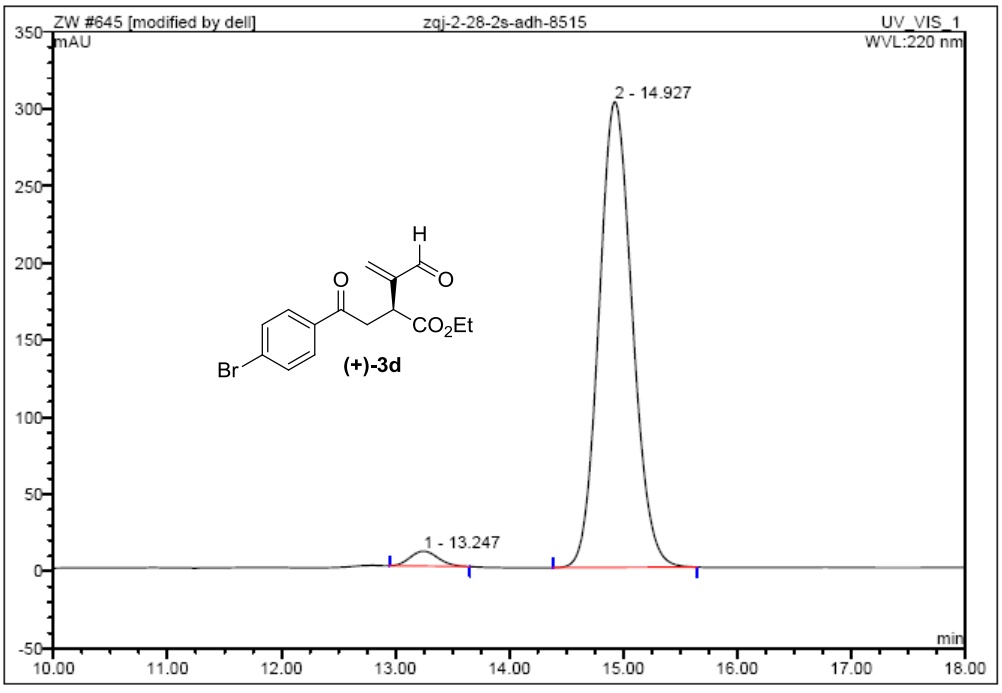
3d (*S*)-ethyl 2-(2-(4-bromophenyl)-2-oxoethyl)-3-formylbut-3-enoate



3d[5]; Colorless oil; $[\alpha]_D^{20}$ = + 119.1 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.56 (s, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 6.50 (s, 1H), 6.22 (s, 1H), 4.22 (dd, *J* = 8.0, 5.5 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 3.67 (dd, *J* = 18.0, 8.5 Hz, 1H), 3.15 (dd, *J* = 18.0, 5.5 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.10, 192.67, 171.95, 147.12, 136.33, 135.04, 131.91, 129.55, 128.51, 61.33, 39.76, 39.60, 13.97; Enantiomeric excess: 95%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 85/15; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 13.24 min, second peak: t_R = 14.92 min; HRMS (ESI) m/z calcd. for $C_{15}H_{15}BrNaO_4$ $[M+Na]^+$ = 361.0046, found = 361.0054; IR (neat): υ 2981, 2921, 2849, 1730, 1685, 1628, 1584, 1568, 1396, 1307, 1246, 1213, 1173, 1069, 990, 822, 786 cm^{-1}.

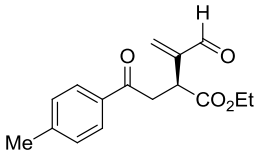


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.09	n.a.	480.415	147.772	49.44	n.a.	BMB*
2	14.78	n.a.	444.732	151.112	50.56	n.a.	BMB*
Total:			925.147	298.884	100.00	0.000	

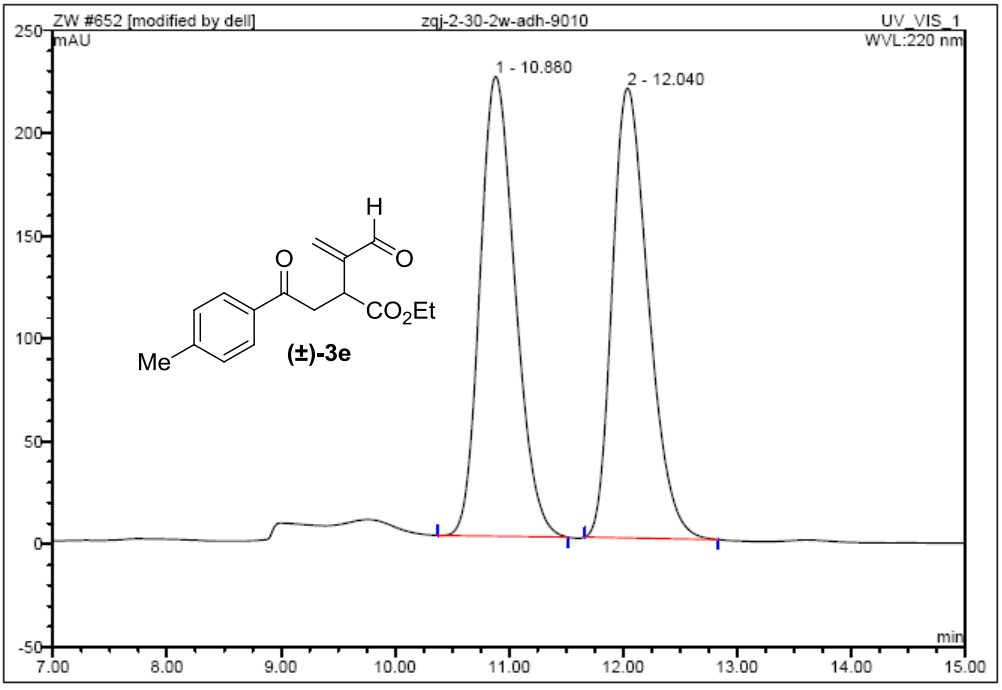


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.25	n.a.	9.742	2.775	2.64	n.a.	BMB*
2	14.93	n.a.	302.169	102.297	97.36	n.a.	BMB*
Total:			311.911	105.072	100.00	0.000	

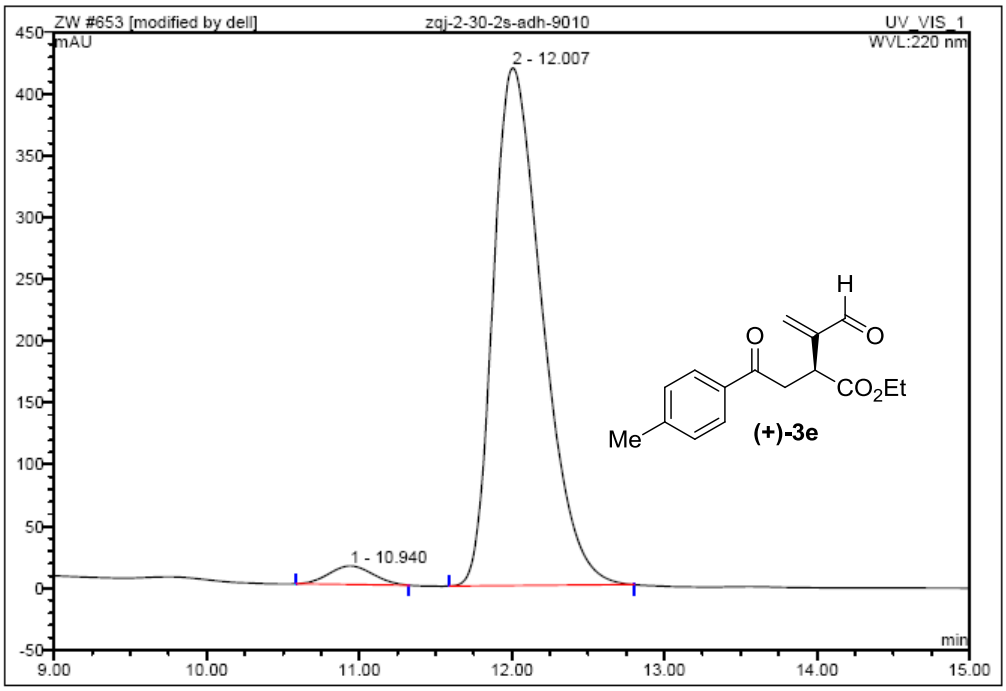
3e (*S*)-ethyl 3-formyl-2-(2-oxo-2-(p-tolyl)ethyl)but-3-enoate



3e; White solid. m.p. = 48-50 °C; $[\alpha]_D^{20}$ = + 117.6 (*c* = 0.33, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 9.56 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.50 (s, 1H), 6.20 (s, 1H), 4.23 (dd, *J* = 8.0, 5.5 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 3.67 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.21 (dd, *J* = 18.0, 5.5 Hz, 1H), 2.42 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.65, 192.73, 172.15, 147.32, 144.13, 136.22, 133.86, 129.25, 128.14, 61.22, 39.74, 39.55, 21.61, 13.98; Enantiomeric excess: 94%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 10.94 min, second peak: t_R = 12.00 min; HRMS (ESI) m/z calcd. for $C_{16}H_{18}NaO_4$ $[M+Na]^+$ = 297.1097, found = 297.1109; IR (neat): υ 2987, 2908, 2850, 1732, 1682, 1672, 1605, 1404, 1364, 1325, 1244, 1210, 1173, 1158, 1022, 976, 913, 813 cm^{-1}.

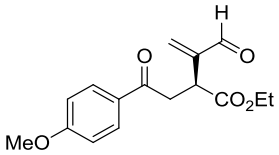


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.88	n.a.	223.649	79.934	49.90	n.a.	BMB*
2	12.04	n.a.	218.894	80.240	50.10	n.a.	BMB*
Total:			442.543	160.174	100.00	0.000	

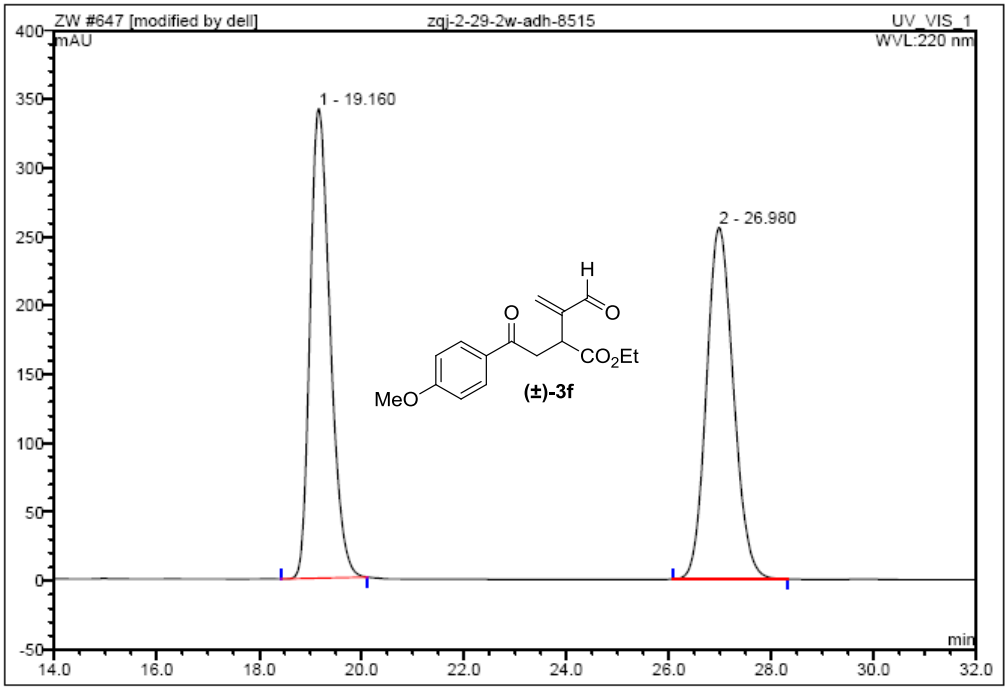


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.94	n.a.	14.959	4.980	3.08	n.a.	BMB*
2	12.01	n.a.	418.821	156.459	96.92	n.a.	BMB*
Total:			433.780	161.438	100.00	0.000	

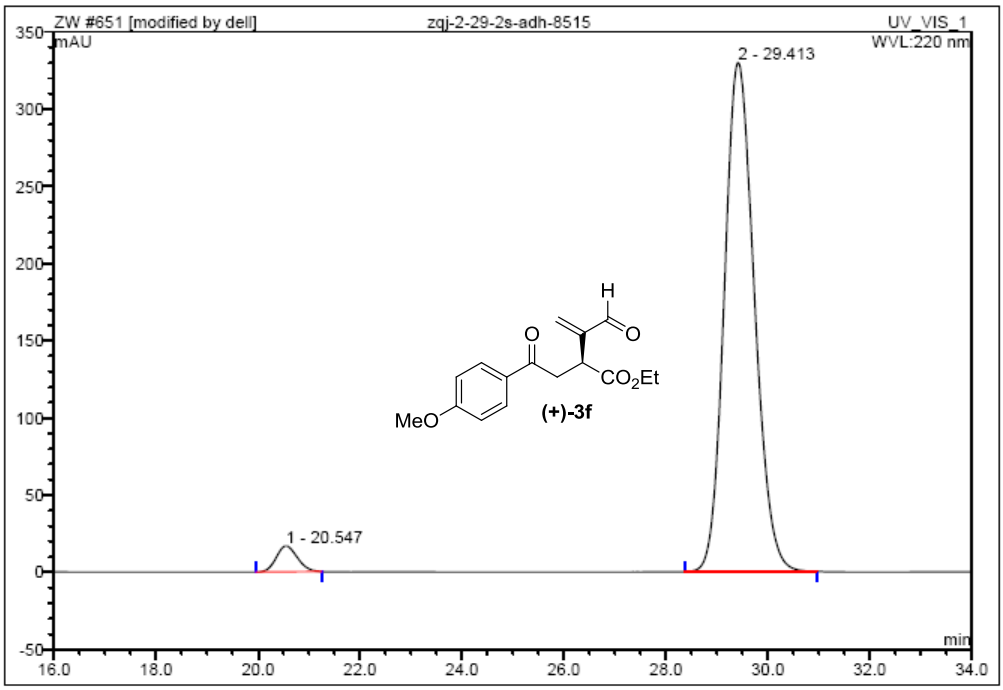
3f (*S*)-ethyl 3-formyl-2-(2-(4-methoxyphenyl)-2-oxoethyl)but-3-enoate



3f; Colorless oil; $[\alpha]_D^{20}$ = + 123.6 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.56 (s, 1H), 7.95–7.93 (m, 2H), 6.95–6.92 (m, 2H), 6.50 (s, 1H), 6.20 (s, 1H), 4.22 (dd, *J* = 7.5, 5.5 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 3.64 (dd, *J* = 17.5, 8.0 Hz, 1H), 3.20 (dd, *J* = 17.5, 6.0 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.52, 192.77, 172.21, 163.63, 147.36, 136.22, 130.32, 129.44, 113.72, 61.21, 55.44, 39.81, 39.30, 13.99; Enantiomeric excess: 93%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 85/15; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 20.54 min, second peak: t_R = 29.41 min; HRMS (ESI) m/z calcd. for $C_{16}H_{18}NaO_5$ $[M+Na]^+$ = 313.1046, found = 313.1057; IR (neat): υ 2980, 2935, 2841, 1730, 1674, 1598, 1574, 1510, 1420, 1363, 1307, 1252, 1217, 1164, 1095, 1027, 989, 833 cm^{-1}.

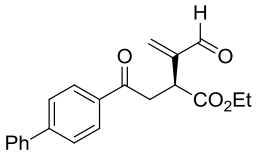


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.16	n.a.	341.322	154.839	49.77	n.a.	BMB*
2	26.98	n.a.	255.491	156.258	50.23	n.a.	BMB*
Total:			596.813	311.097	100.00	0.000	

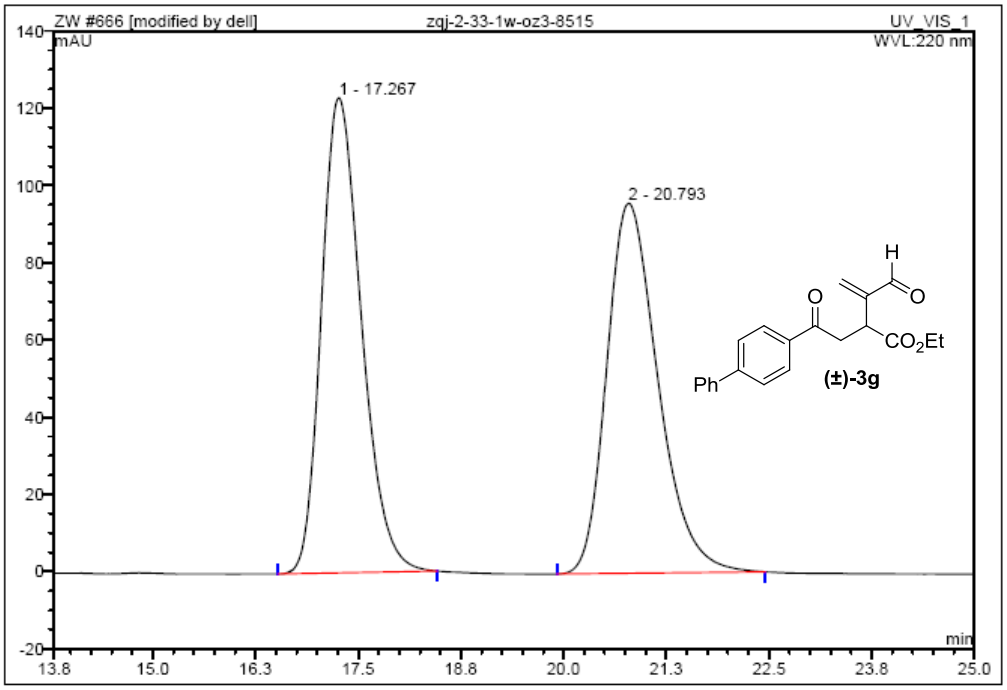


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.55	n.a.	16.692	7.975	3.43	n.a.	BMB*
2	29.41	n.a.	329.643	224.846	96.57	n.a.	BMB*
Total:			346.335	232.821	100.00	0.000	

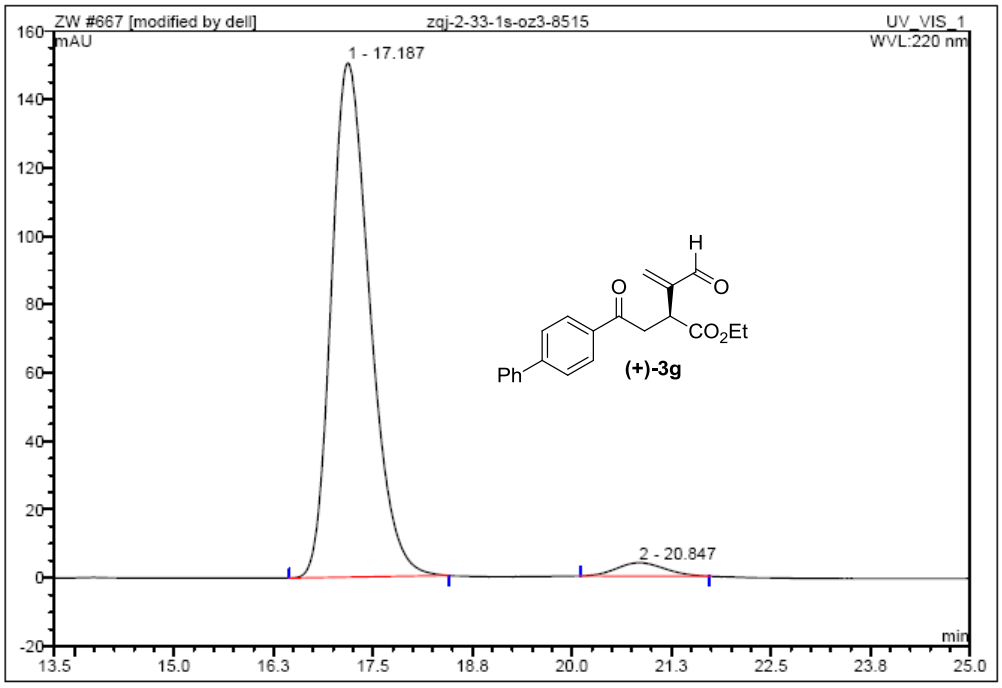
3g (*S*)-ethyl 2-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-3-formylbut-3-enoate



3g; White solid. m.p. = 101-103 °C; $[\alpha]_D^{20}$ = + 82.1 (*c* = 0.33, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 9.59 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.65–7.63 (m, 2H), 7.50–7.47 (m, 2H), 7.44–7.41 (m, 1H), 6.53 (s, 1H), 6.23 (s, 1H), 4.27 (dd, *J* = 8.0, 6.0 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.75 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.27 (dd, *J* = 18.0, 5.5 Hz, 1H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.63, 192.73, 172.10, 147.27, 145.96, 139.74, 136.28, 135.02, 128.91, 128.63, 128.23, 127.22, 61.28, 39.80, 39.69, 13.99; Enantiomeric excess: 94%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 85/15; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 17.18 min, second peak: t_R = 20.84 min; HRMS (ESI) m/z calcd. for $C_{21}H_{20}NaO_4$ $[M+Na]^+$ = 359.1254, found = 359.1267; IR (neat): υ 2979, 2921, 2902, 2850, 2818, 1735, 1687, 1676, 1600, 1445, 1401, 1324, 1244, 1215, 1158, 1092, 973, 832, 760 cm^{-1}.

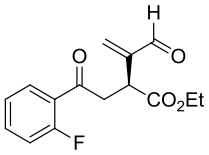


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.27	n.a.	123.023	69.455	50.09	n.a.	BMB*
2	20.79	n.a.	95.806	69.192	49.91	n.a.	BMB*
Total:			218.829	138.646	100.00	0.000	

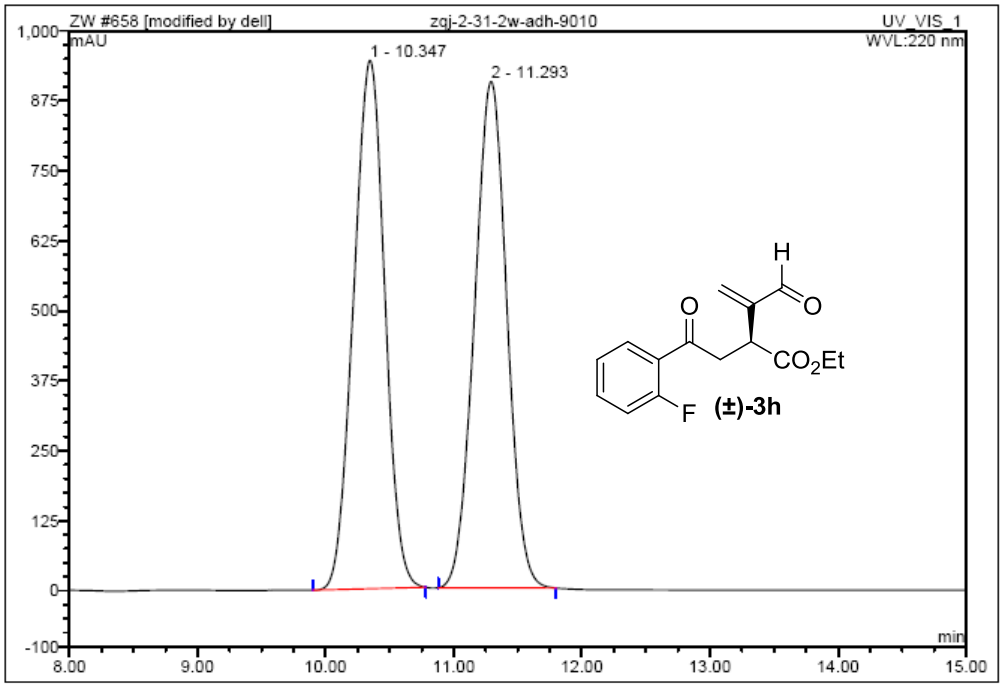


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.19	n.a.	150.532	84.393	96.86	n.a.	BMB*
2	20.85	n.a.	3.909	2.735	3.14	n.a.	BMB*
Total:			154.441	87.128	100.00	0.000	

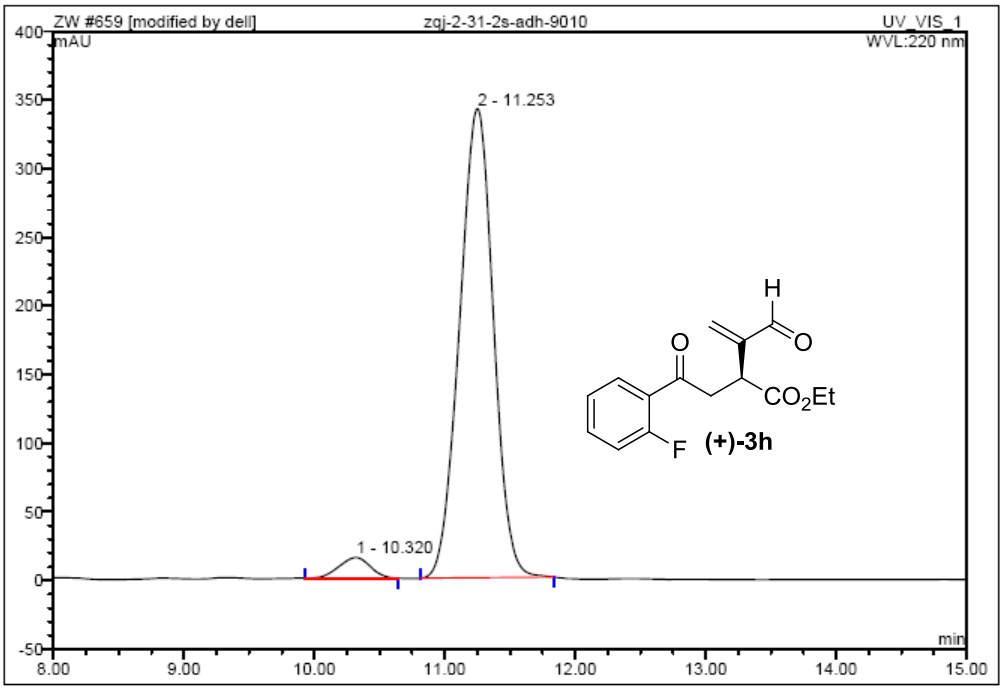
3h (*S*)-ethyl 2-(2-(2-fluorophenyl)-2-oxoethyl)-3-formylbut-3-enoate



3h; White solid. m.p. = 33-35 ^{o}C; $[\alpha]_D^{20}$ = + 95.6 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.90–7.86 (m, 1H), 7.56–7.51 (m, 1H), 7.25–7.22 (m, 1H), 7.16–7.12 (m, 1H), 6.48 (s, 1H), 6.21 (s, 1H), 4.25 (dd, *J* = 8.5, 5.0 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 3.69–3.63 (m, 1H) , 3.24–3.19 (m, 1H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.31, 192.59, 172.14, 162.10 (d, J_{CF} = 253.25 Hz), 147.27, 135.94, 134.90 (d, J_{CF} = 9.13 Hz), 130.65 (d, J_{CF} = 2.38 Hz), 124.93 (d, J_{CF} = 12.75 Hz), 124.50 (d, J_{CF} = 3.13 Hz), 116.71 (d, J_{CF} = 23.50 Hz), 61.28, 44.59, 39.39, 14.02; Enantiomeric excess: 92%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 10.32 min, second peak: t_R = 11.25 min; HRMS (ESI) m/z calcd. for $C_{15}H_{15}NaO_4$ $[M+Na]^+$ = 301.0847, found = 301.0854; IR (neat): υ 2979, 2925, 2814, 2694, 1732, 1686, 1676, 1606, 1478, 1449, 1396, 1324, 1269, 1204, 1159, 1089, 974, 912 cm^{-1}.

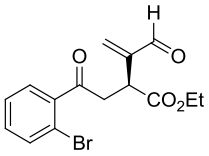


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.35	n.a.	943.588	266.131	50.07	n.a.	BMB*
2	11.29	n.a.	904.609	265.381	49.93	n.a.	BMB*
Total:			1848.197	531.512	100.00	0.000	

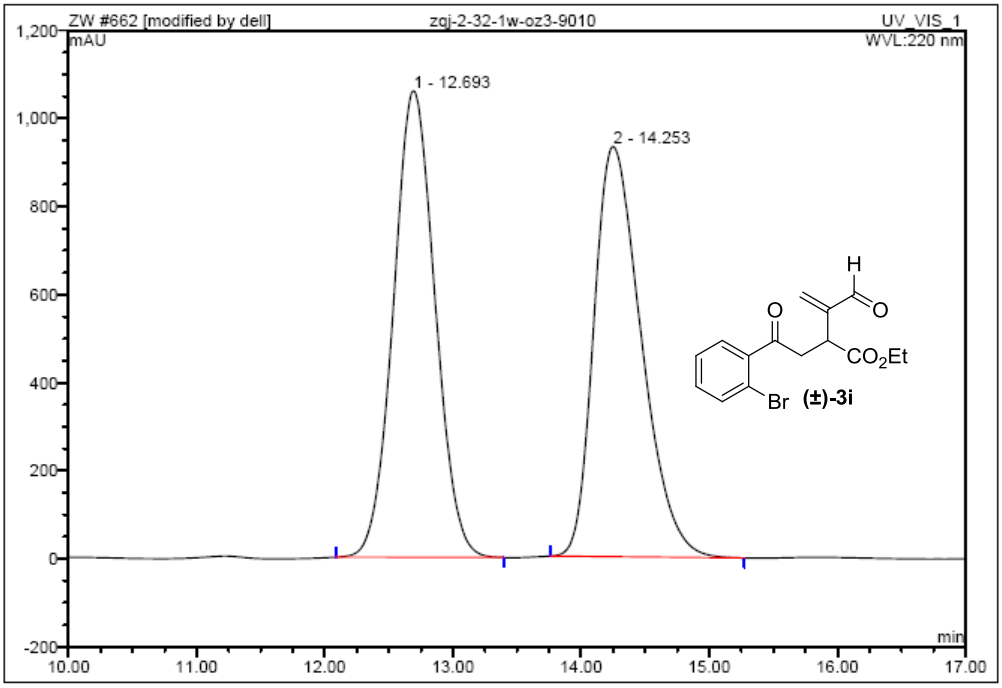


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.32	n.a.	14.962	4.164	3.91	n.a.	BMB*
2	11.25	n.a.	341.803	102.462	96.09	n.a.	BMB*
Total:			356.765	106.626	100.00	0.000	

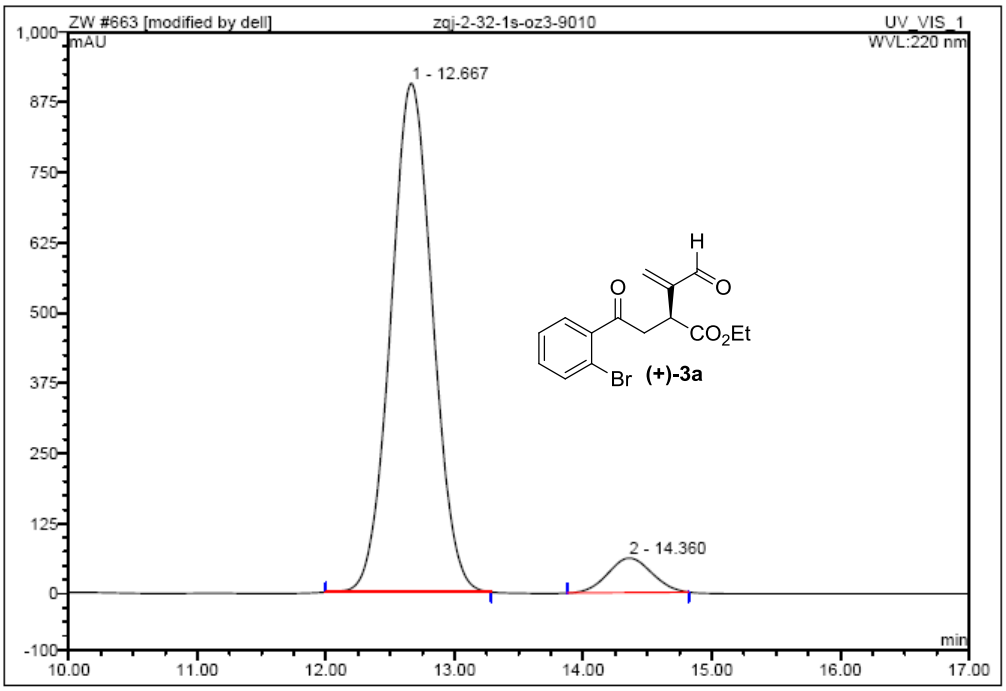
3i (*S*)-ethyl 2-(2-(2-bromophenyl)-2-oxoethyl)-3-formylbut-3-enoate



3i; Colorless oil; $[\alpha]_D^{20}$ = + 79.8 (*c* = 0.33, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 9.55 (s, 1H), 7.62–7.60 (m, 1H), 7.50–7.48 (m, 1H), 7.40–7.37 (m, 1H), 7.32–7.29 (m, 1H), 6.51 (s, 1H), 6.22 (s, 1H), 4.22 (dd, *J* = 8.5, 5.5 Hz, 1H), 4.17 (q, *J* = 7.0 Hz, 2H), 3.63 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.16 (dd, *J* = 18.0, 5.5 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.70, 192.57, 171.72, 146.91, 140.67, 136.41, 133.73, 131.80, 128.89, 127.40, 118.67, 61.38, 43.33, 40.07, 13.98; Enantiomeric excess: 87%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 90/10; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 12.66 min, second peak: t_R = 14.36 min; HRMS (ESI) m/z calcd. for $C_{15}H_{15}BrNaO_4$ $[M+Na]^+$ = 361.0046, found = 361.0058; IR (neat): υ 2918, 2849, 1730, 1688, 1649, 1629, 1587, 1467, 1428, 1211, 1171, 1093, 1024, 971 cm^{-1}.

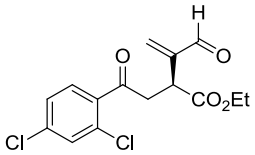


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.69	n.a.	1059.166	399.435	50.00	n.a.	BMB*
2	14.25	n.a.	931.543	399.447	50.00	n.a.	BMB*
Total:			1990.709	798.882	100.00	0.000	

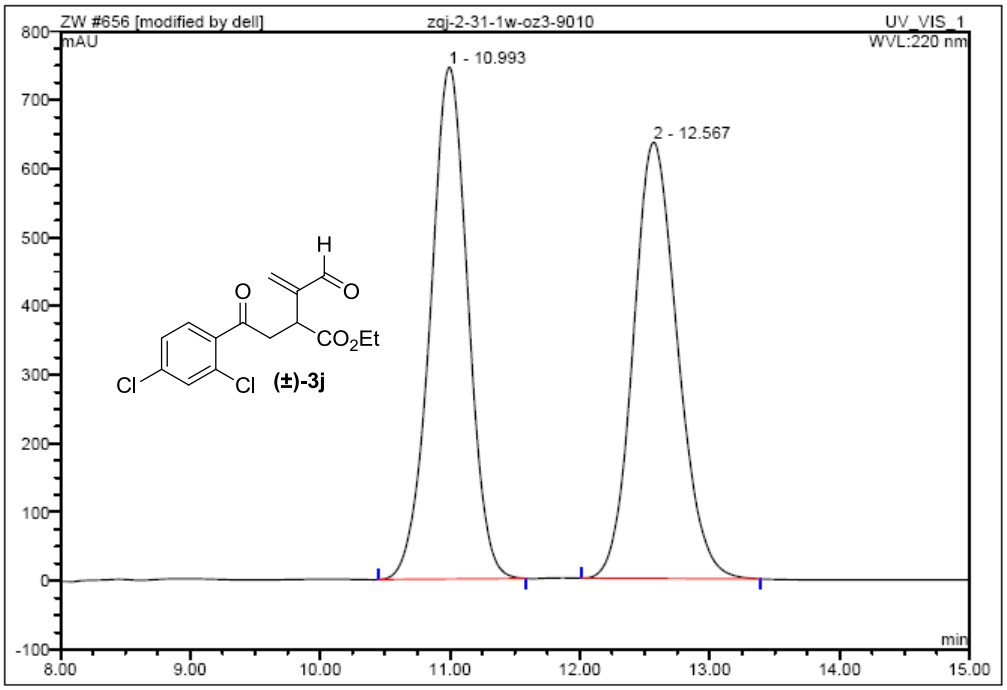


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.67	n.a.	905.790	342.116	93.36	n.a.	BMB*
2	14.36	n.a.	61.314	24.319	6.64	n.a.	BMB*
Total:			967.104	366.435	100.00	0.000	

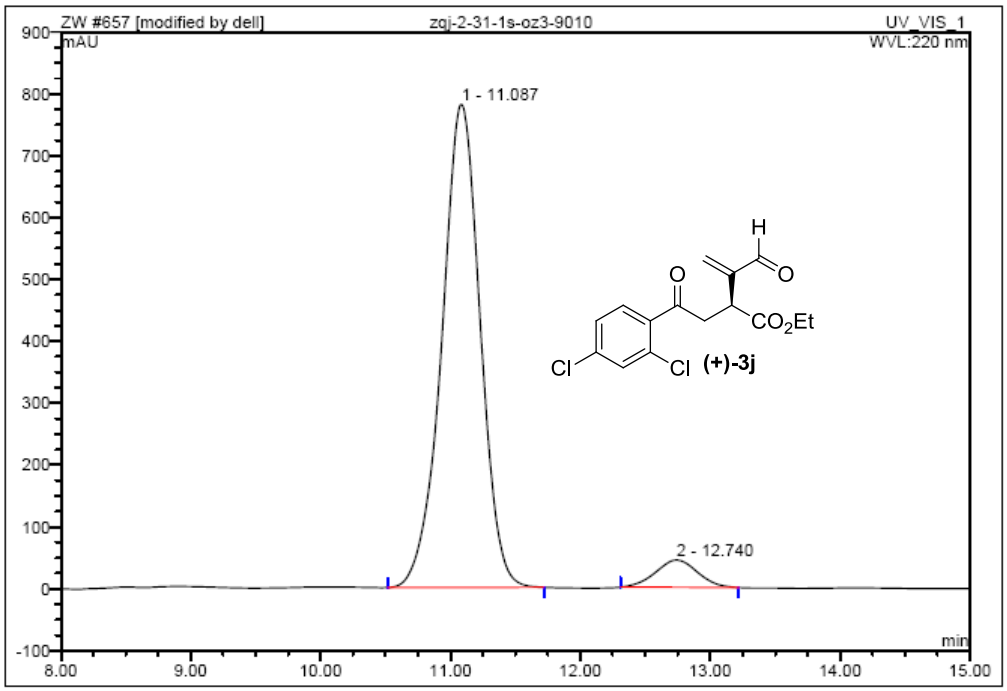
3j (*S*)-ethyl 2-(2-(2,4-dichlorophenyl)-2-oxoethyl)-3-formylbut-3-enoate



3j; Colorless oil; $[\alpha]_D^{20}$ = + 85.5 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.55 (s, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.34–7.32 (m, 1H), 6.48 (s, 1H), 6.22 (s, 1H), 4.21 (dd, *J* = 8.5, 5.0 Hz, 1H), 4.16 (q, *J* = 7.5 Hz, 2H), 3.63 (dd, *J* = 18.0, 8.5 Hz, 1H), 3.12 (dd, *J* = 18.0, 5.0 Hz, 1H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.62, 192.53, 171.72, 146.91, 137.67, 136.57, 136.33, 132.16, 130.60, 130.46, 127.33, 61.41, 40.22, 29.64, 13.96; Enantiomeric excess: 88%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 90/10; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 11.08 min, second peak: t_R = 12.74 min; HRMS (ESI) m/z calcd. for $C_{15}H_{14}Cl_2NaO_4$ $[M+Na]^+$ = 351.0161, found = 351.0168; IR (neat): υ 2981, 2916, 2847, 1730, 1690, 1628, 1581, 1552, 1464, 1371, 1209, 1171, 1092, 990, 957 cm^{-1}.

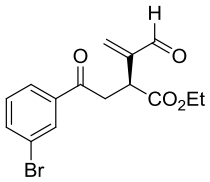


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.99	n.a.	745.192	249.813	49.89	n.a.	BMB*
2	12.57	n.a.	635.325	250.922	50.11	n.a.	BMB*
Total:			1380.517	500.735	100.00	0.000	

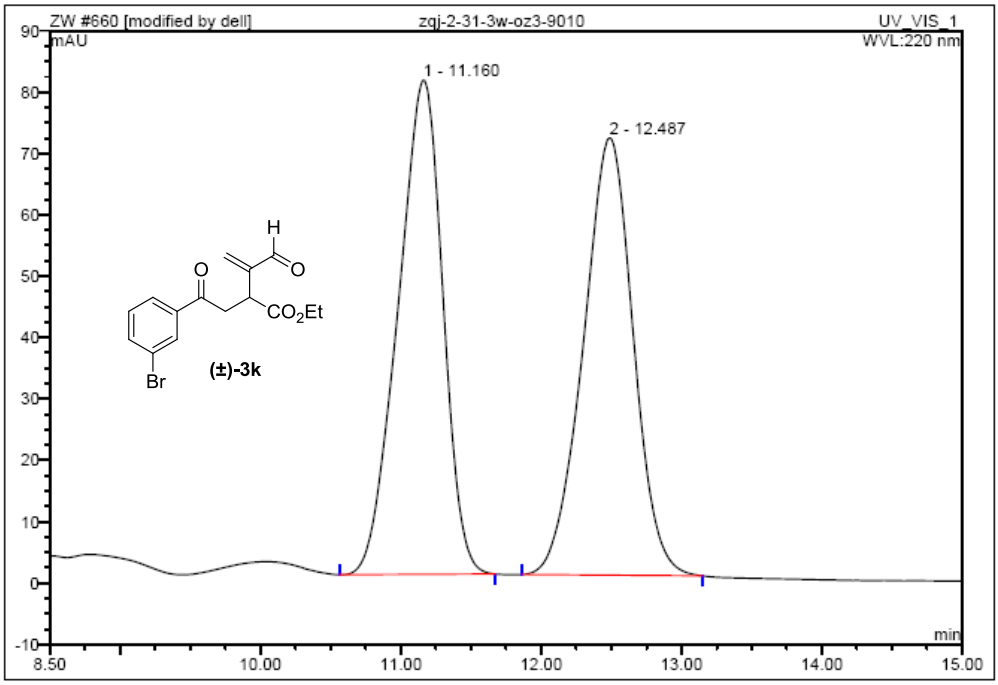


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.09	n.a.	780.877	266.630	94.19	n.a.	BMB*
2	12.74	n.a.	43.922	16.452	5.81	n.a.	BMB*
Total:			824.798	283.082	100.00	0.000	

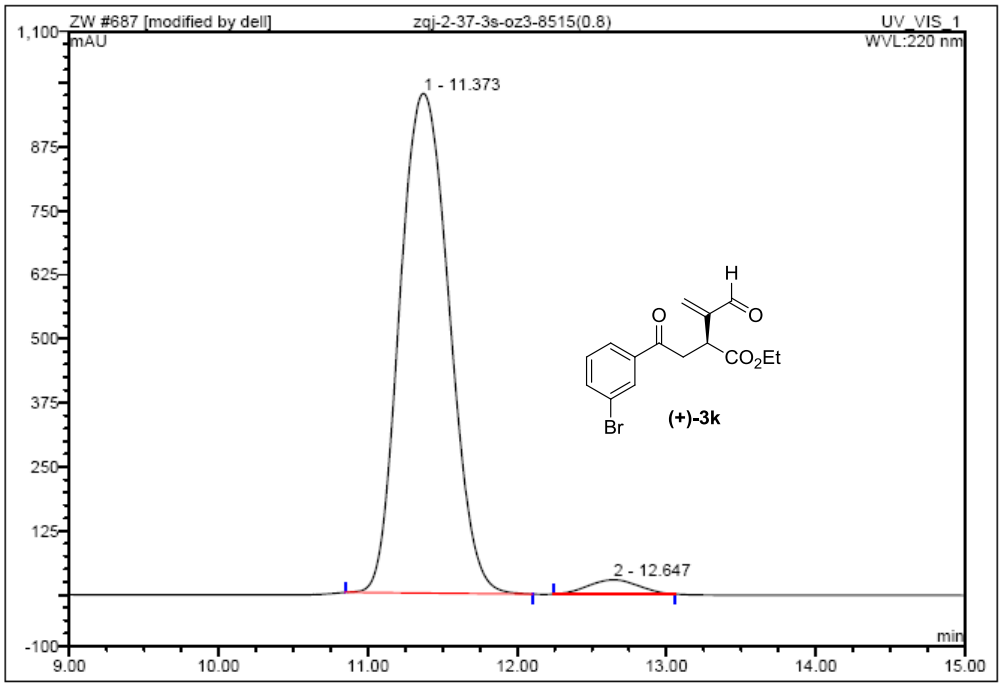
3k (*S*)-ethyl 2-(2-(3-bromophenyl)-2-oxoethyl)-3-formylbut-3-enoate



3k; Colorless oil; $[\alpha]_D^{20}$ = + 110.6 (*c* = 0.33, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 9.57 (s, 1H), 8.09–8.08 (m, 1H), 7.89–7.87 (m, 1H), 7.71–7.69 (m, 1H), 7.37–7.34 (m, 1H), 6.51 (s, 1H), 6.23 (s, 1H), 4.22 (dd, *J* = 8.0, 5.0 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 3.68 (dd, *J* = 18.0, 8.5 Hz, 1H), 3.16 (dd, *J* = 18.0, 5.5 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.79, 192.66, 171.91, 147.08, 138.02, 136.36, 136.15, 131.11, 130.21, 126.57, 122.96, 61.37, 39.75, 39.72, 13.98; Enantiomeric excess: 94%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 90/10; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 11.37 min, second peak: t_R = 12.64 min; HRMS (ESI) m/z calcd. for $C_{15}H_{15}BrNaO_4$ $[M+Na]^+$ = 361.0046, found = 361.0053; IR (neat): υ 2981, 2923, 2823, 1730, 1687, 1627, 1566, 1420, 1303, 1242, 1209, 1163, 1094, 1029, 956 cm^{-1}.

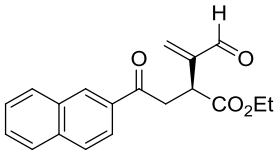


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.16	n.a.	80.527	29.727	50.31	n.a.	BMB*
2	12.49	n.a.	71.253	29.366	49.69	n.a.	BMB*
Total:			151.780	59.093	100.00	0.000	

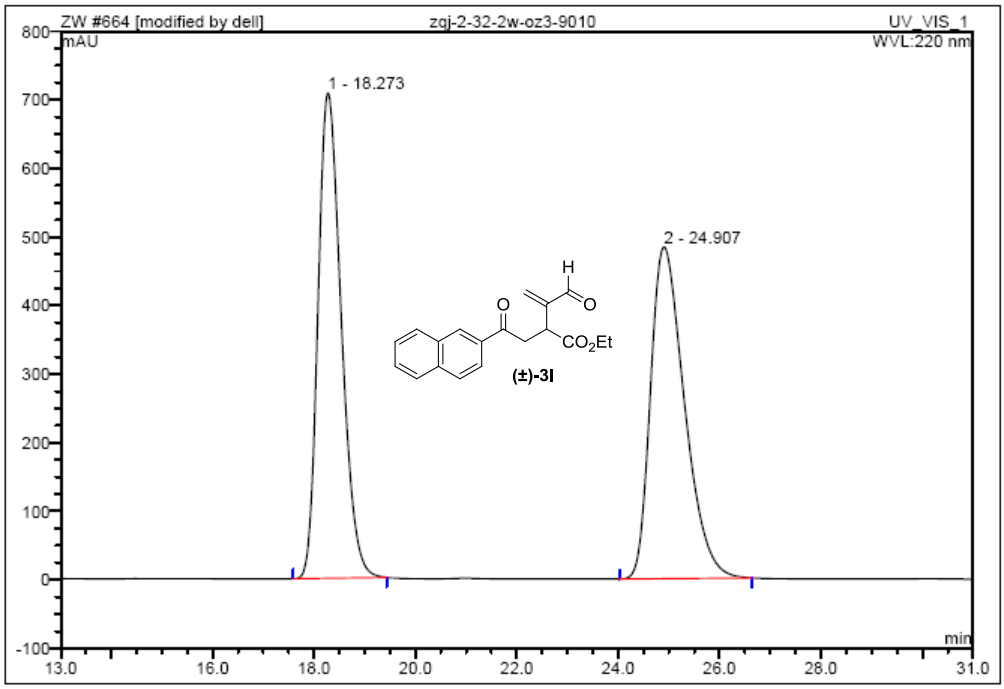


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.37	n.a.	975.108	373.218	97.17	n.a.	BMB*
2	12.65	n.a.	27.849	10.865	2.83	n.a.	BMB*
Total:			1002.957	384.083	100.00	0.000	

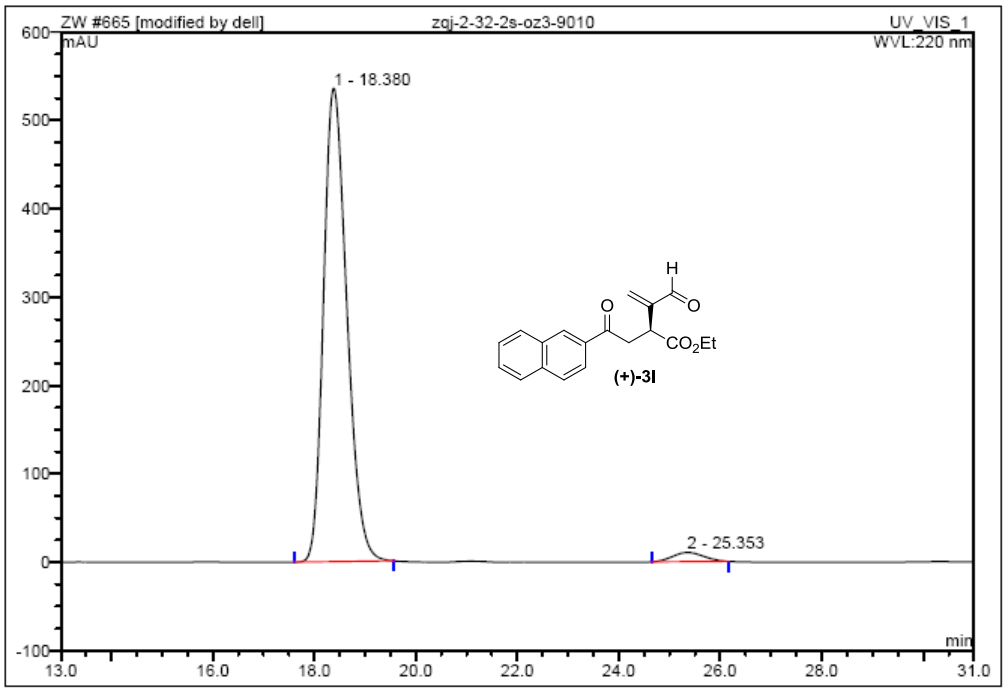
3l (*S*)-ethyl 3-formyl-2-(2-(naphthalen-2-yl)-2-oxoethyl)but-3-enoate



3l; White solid. m.p. = 44-46 ^{o}C; $[\alpha]_D^{20}$ = + 108.6 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.60 (s, 1H), 8.49 (s, 1H), 8.04–8.02 (m, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.92–7.88 (m, 2H), 7.64–7.56 (m, 2H), 6.56 (s, 1H), 6.24 (s, 1H), 4.31 (dd, *J* = 8.0, 5.5 Hz, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 3.85 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.38 (dd, *J* = 18.0, 6.0 Hz, 1H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.99, 192.80, 172.15, 147.32, 136.38, 135.67, 133.66, 132.43, 129.86, 129.56, 128.55, 128.47, 127.75, 126.81, 123.66, 61.31, 39.91, 39.72, 14.01; Enantiomeric excess: 95%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 90/10; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 18.38 min, second peak: t_R = 25.35 min; HRMS (ESI) m/z calcd. for $C_{19}H_{18}NaO_4$ $[M+Na]^+$ = 333.1097, found = 333.1105; IR (neat): υ 2957, 2922, 2852, 1730, 1688, 1675, 1624, 1593, 1467, 1372, 1317, 1258, 1226, 1170, 1093, 1016, 972 cm^{-1}.

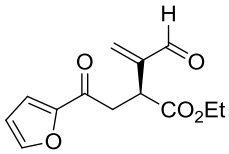


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.27	n.a.	708.044	375.491	50.02	n.a.	BMB*
2	24.91	n.a.	484.003	375.158	49.98	n.a.	BMB*
Total:			1192.047	750.649	100.00	0.000	

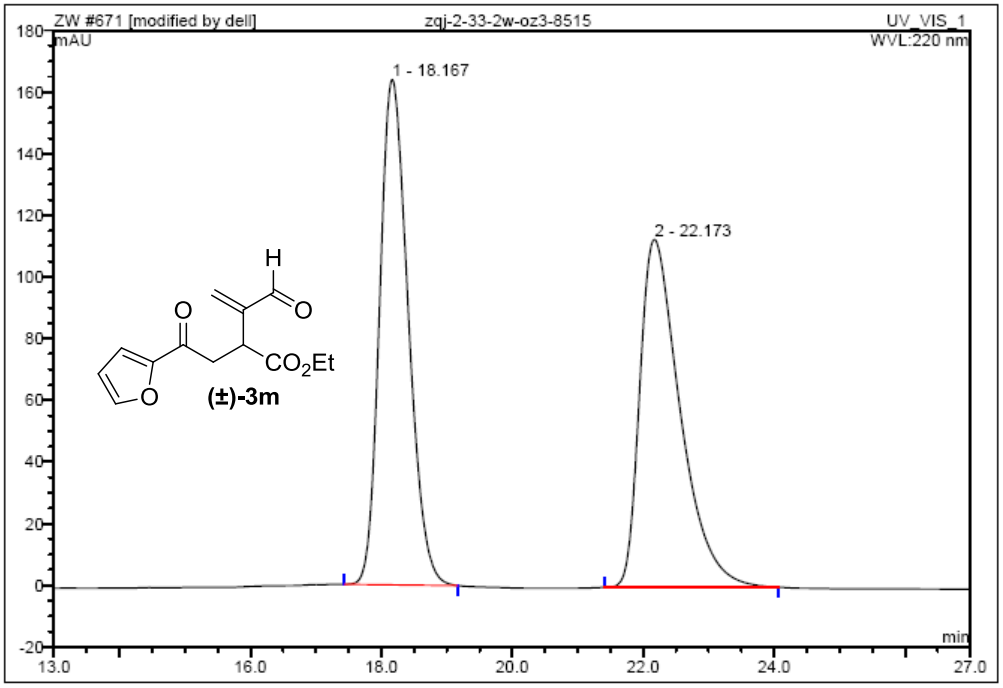


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.38	n.a.	535.615	284.860	97.49	n.a.	BMB*
2	25.35	n.a.	10.342	7.328	2.51	n.a.	BMB*
Total:			545.957	292.188	100.00	0.000	

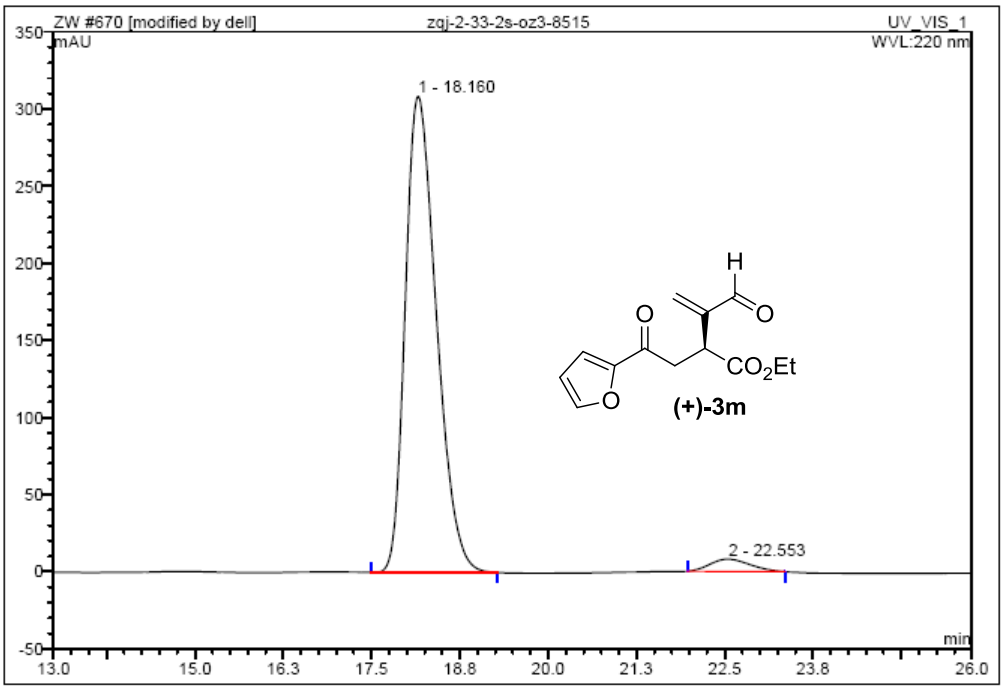
3m (*S*)-ethyl 3-formyl-2-(2-(furan-2-yl)-2-oxoethyl)but-3-enoate



3m; White solid. m.p. = 34-36 ^{o}C; $[\alpha]_D^{20}$ = + 146.5 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.54 (s, 1H), 7.59–7.58 (m, 1H), 7.20 (d, *J* = 4.0 Hz, 1H), 6.54 (dd, *J* = 3.5, 1.5 Hz, 1H), 6.49 (s, 1H), 6.20 (s, 1H), 4.20–4.13 (m, 3H), 3.56 (dd, *J* = 17.5, 8.0 Hz, 1H), 3.08 (dd, *J* = 17.5, 6.0 Hz, 1H), 1.22 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.61, 186.11, 171.80, 152.18, 146.97, 146.48, 136.39, 117.29, 112.26, 61.28, 39.45, 39.16, 13.93; Enantiomeric excess: 94%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 85/15; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 18.16 min, second peak: t_R = 22.55 min; HRMS (ESI) m/z calcd. for $C_{13}H_{14}NaO_5$ $[M+Na]^+$ = 273.0733, found = 273.0739; IR (neat): υ 3122, 2981, 2930, 2812, 1724, 1692, 1650, 1561, 1468, 1407, 1325, 1273, 1220, 1168, 1095, 1016, 979 cm^{-1}.

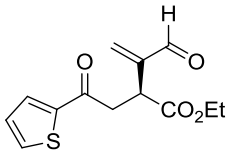


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.17	n.a.	163.892	82.611	50.58	n.a.	BMB*
2	22.17	n.a.	112.851	80.703	49.42	n.a.	BMB*
Total:			276.743	163.315	100.00	0.000	

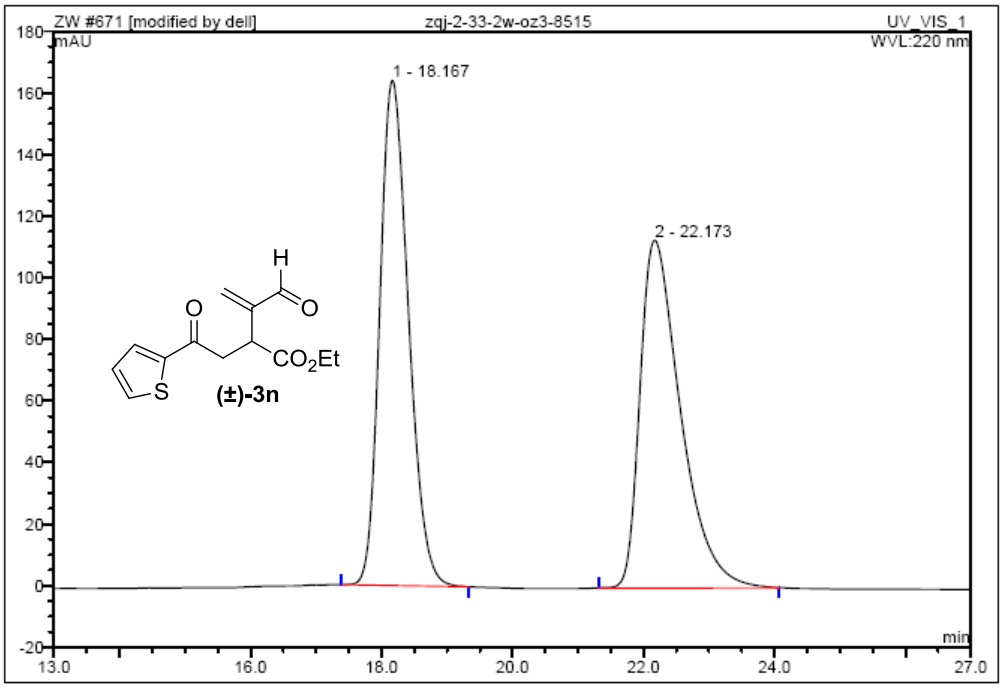


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.16	n.a.	308.703	157.632	96.79	n.a.	BMB*
2	22.55	n.a.	7.969	5.227	3.21	n.a.	BMB*
Total:			316.673	162.859	100.00	0.000	

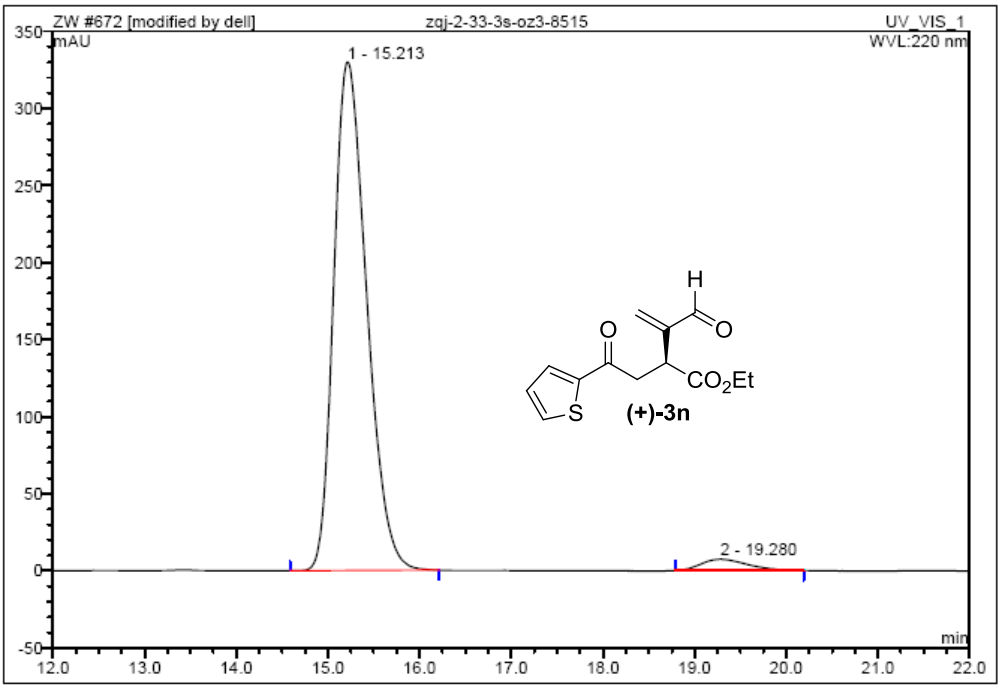
3n (*S*)-ethyl 3-formyl-2-(2-oxo-2-(thiophen-2-yl)ethyl)but-3-enoate



3n; Colorless oil; $[\alpha]_D^{20}$ = + 158.1 (*c* = 0.33, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 9.55 (s, 1H), 7.74–7.73 (m, 1H), 7.66–7.64 (m, 1H), 7.14–7.12 (m, 1H), 6.50 (s, 1H), 6.21 (s, 1H), 4.21–4.14 (m, 3H), 3.63 (dd, *J* = 17.5, 8.0 Hz, 1H), 3.18 (dd, *J* = 17.5, 6.0 Hz, 1H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.75, 189.98, 171.88, 147.00, 143.49, 136.60, 133.92, 132.20, 128.17, 61.37, 40.04, 39.96, 13.99; Enantiomeric excess: 94%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 85/15; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 15.21 min, second peak: t_R = 19.28 min; HRMS (ESI) m/z calcd. for $C_{13}H_{14}NaO_4S$ $[M+Na]^+$ = 289.0505, found = 289.0510; IR (neat): υ 3095, 2981, 2921, 2849, 2703, 1729, 1688, 1658, 1518, 1414, 1366, 1304, 1218, 1163, 1093, 1024, 957, 940 cm^{-1}.

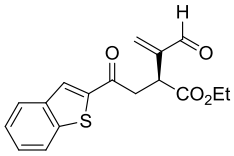


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.17	n.a.	164.010	82.863	50.63	n.a.	BMB*
2	22.17	n.a.	112.897	80.792	49.37	n.a.	BMB*
Total:			276.907	163.654	100.00	0.000	

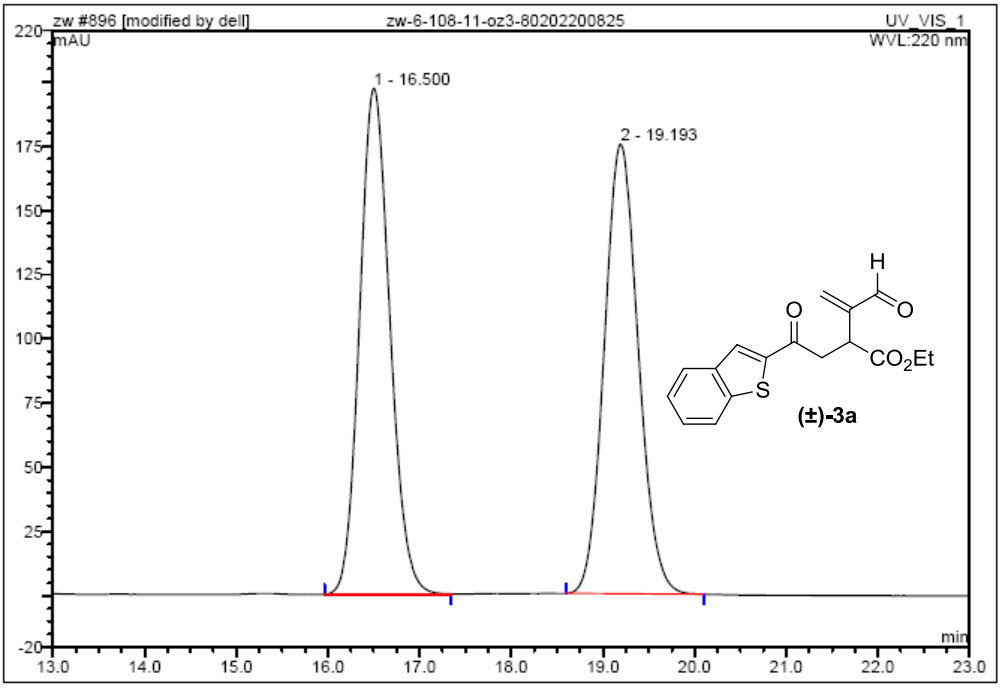


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.21	n.a.	329.952	137.119	96.96	n.a.	BMB*
2	19.28	n.a.	7.324	4.301	3.04	n.a.	BMB*
Total:			337.277	141.420	100.00	0.000	

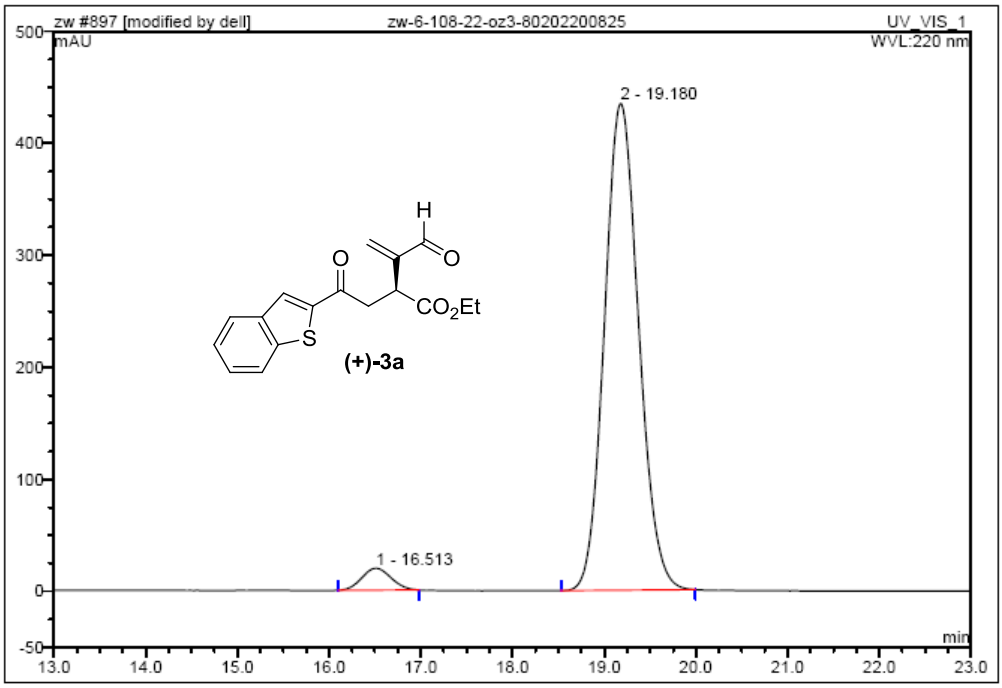
3o (*S*)-ethyl 2-(2-(benzo[b]thiophen-2-yl)-2-oxoethyl)-3-formylbut-3-enoate



3o; Colorless oil; $[\alpha]_D^{20}$ = + 117.7 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.58 (s, 1H), 8.01 (s, 1H), 7.91–7.88 (m, 2H), 7.50–7.47 (m, 1H), 7.44–7.41 (m, 1H), 6.55 (s, 1H), 6.24 (s, 1H), 4.25 (dd, *J* = 7.5, 6.5 Hz, 1H), 4.19 (q, *J* = 6.0 Hz, 2H), 3.76 (dd, *J* = 17.5, 8.0 Hz, 1H), 3.30 (dd, *J* = 17.5, 6.0 Hz, 1H), 1.24 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.75, 191.56, 171.75, 146.91, 142.85, 142.51, 139.01, 136.72, 129.43, 127.53, 126.00, 125.04, 122.95, 61.42, 40.14, 39.90, 13.98; Enantiomeric excess: 93%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 80/20; flow rate 0.8 ml/min; 25 ℃; 220 nm), first peak: t_R = 16.51 min, second peak: t_R = 19.18 min; HRMS (ESI) m/z calcd. for $C_{17}H_{16}NaO_4S$ $[M+Na]^+$ = 339.0662, found = 339.0670; IR (neat): υ 2981, 2923, 2851, 2814, 2694, 1732, 1690, 1657, 1592, 1514, 1401, 1330, 1214, 1156, 1095, 975 cm^{-1}.

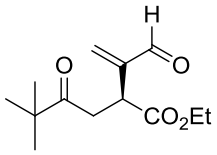


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.50	n.a.	196.921	75.333	50.05	n.a.	BMB*
2	19.19	n.a.	174.989	75.197	49.95	n.a.	BMB*
Total:			371.909	150.530	100.00	0.000	

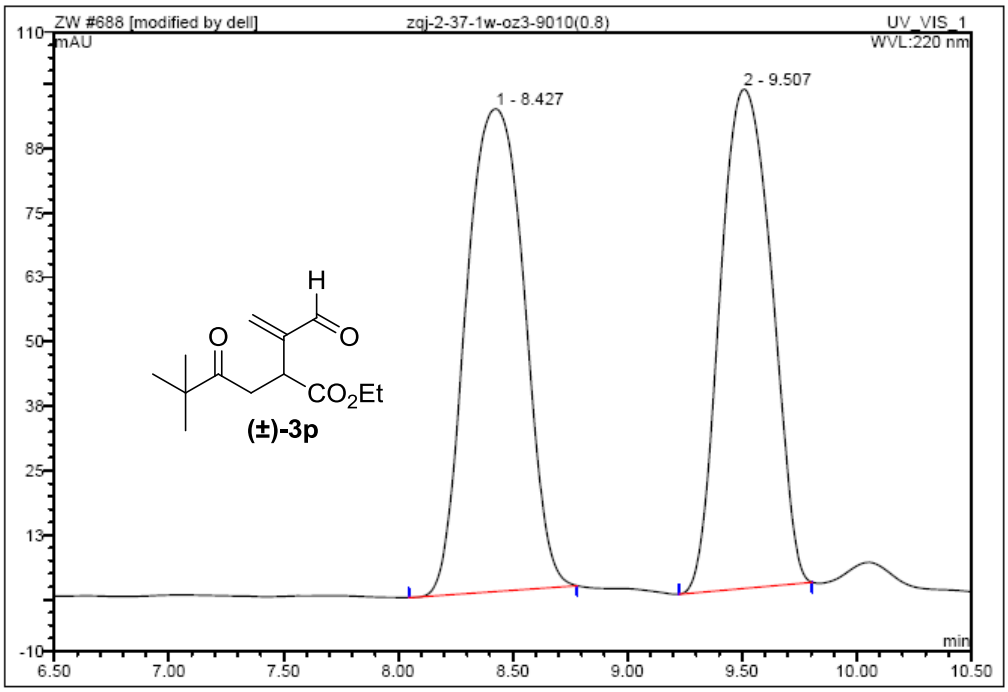


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.51	n.a.	19.609	7.244	3.72	n.a.	BMB*
2	19.18	n.a.	434.796	187.555	96.28	n.a.	BMB*
Total:			454.406	194.799	100.00	0.000	

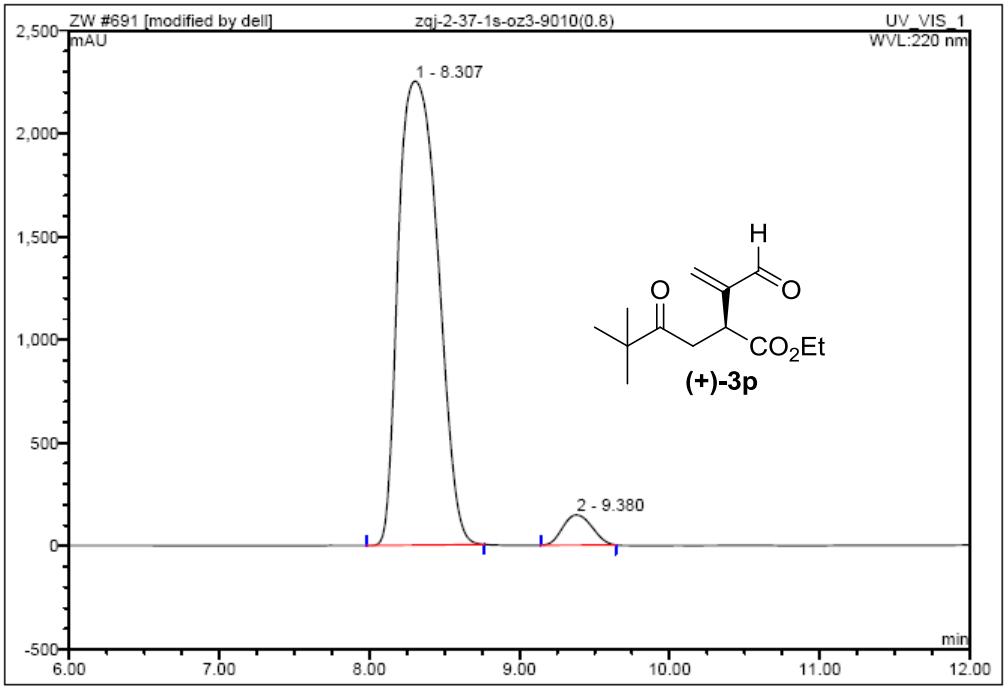
3p (*S*)-ethyl 5,5-dimethyl-4-oxo-2-(3-oxoprop-1-en-2-yl)hexanoate



3p; Colorless oil; $[\alpha]_D^{20}$ = + 67.1 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.54 (s, 1H), 6.42 (s, 1H), 6.16 (s, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 4.04 (dd, *J* = 8.0, 5.0 Hz, 1H), 3.19 (dd, *J* = 18.0, 8.5 Hz, 1H), 2.73 (dd, *J* = 18.0, 5.0 Hz, 1H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 212.96, 192.72, 172.20, 147.49, 135.97, 61.16, 43.86, 39.62, 38.17, 26.36, 14.00; Enantiomeric excess: 91%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 90/10; flow rate 0.8 ml/min; 25 ℃; 220 nm), first peak: t_R = 8.30 min, second peak: t_R = 9.38 min; HRMS (ESI) m/z calcd. for $C_{13}H_{20}NaO_4$ $[M+Na]^+$ = 263.1254 found = 263.1260; IR (neat): υ 2959, 2922, 2852, 2704, 1734, 1693, 1628, 1478, 1462, 1396, 1366, 1304, 1233, 1190, 1165, 1098 ,1035, 959 cm^{-1}.

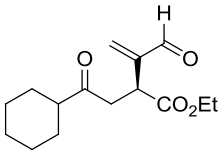


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.43	n.a.	93.538	27.400	52.03	n.a.	BMB*
2	9.51	n.a.	96.771	25.267	47.97	n.a.	BMB*
Total:			190.309	52.666	100.00	0.000	

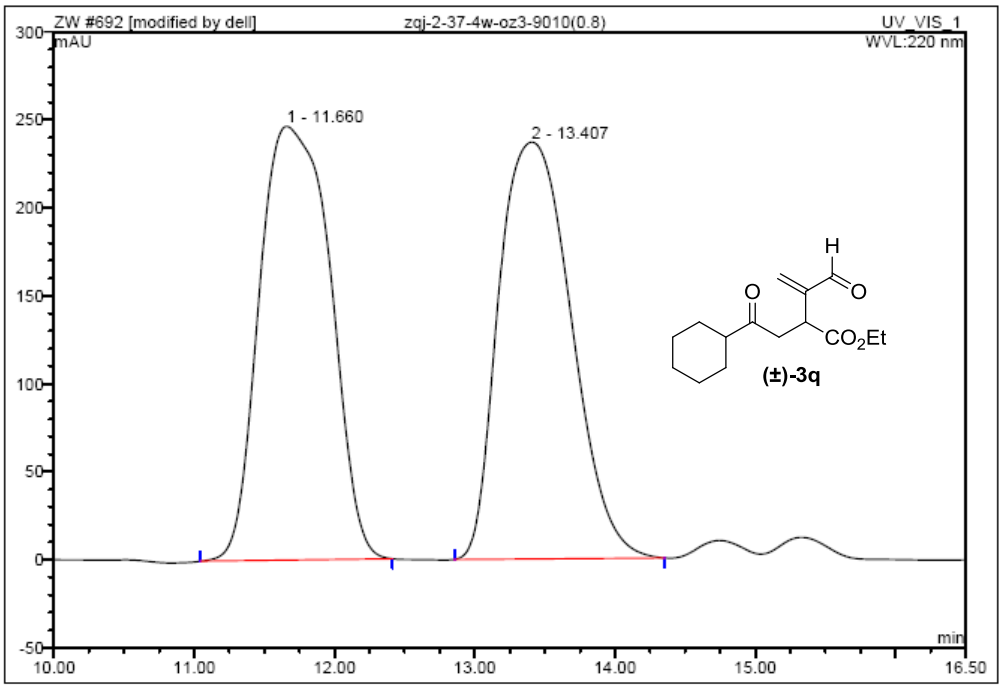


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.31	n.a.	2249.768	689.615	95.42	n.a.	BMB*
2	9.38	n.a.	146.794	33.132	4.58	n.a.	BMB*
Total:			2396.562	722.747	100.00	0.000	

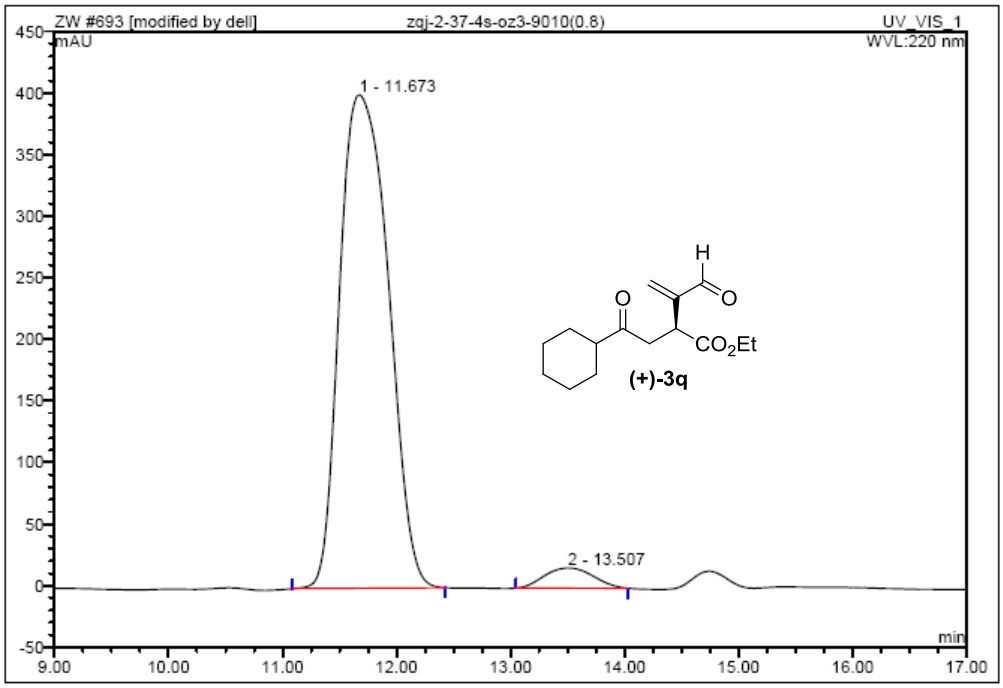
3q (*S*)-ethyl 2-(2-cyclohexyl-2-oxoethyl)-3-formylbut-3-enoate



3q; Colorless oil; $[\alpha]_D^{20}$ = + 20.3 (*c* = 0.33, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 9.53 (s, 1H), 6.42 (s, 1H), 6.16 (s, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 4.04 (dd, *J* = 8.5, 5.0 Hz, 1H), 3.16 (dd, *J* = 18.0, 8.5 Hz, 1H), 2.64 (dd, *J* = 18.0, 5.5 Hz, 1H), 2.39–2.33 (m, 1H), 1.91–1.77 (m, 4H), 1.69–1.66 (m, 1H), 1.39–1.22 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 210.89, 192.71, 172.10, 147.42, 135.99, 61.20, 50.63, 41.49, 39.56, 28.33, 28.30, 25.78, 25.58, 25.53, 13.99; Enantiomeric excess: 92%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 90/10; flow rate 0.8 ml/min; 25 ℃; 220 nm), first peak: t_R = 11.67 min, second peak: t_R = 13.51 min; HRMS (ESI) m/z calcd. for $C_{15}H_{22}NaO_4$ $[M+Na]^+$ = 289.1410, found = 289.1418; IR (neat): υ 2927, 2853, 1732, 1692, 1627, 1448, 1370, 1297, 1228, 1164, 1097, 1024, 956, 922 cm^{-1}.

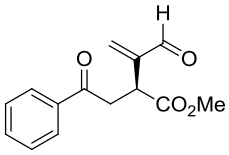


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.66	n.a.	246.587	144.626	50.45	n.a.	BMB*
2	13.41	n.a.	236.939	142.072	49.55	n.a.	BMB*
Total:			483.526	286.698	100.00	0.000	

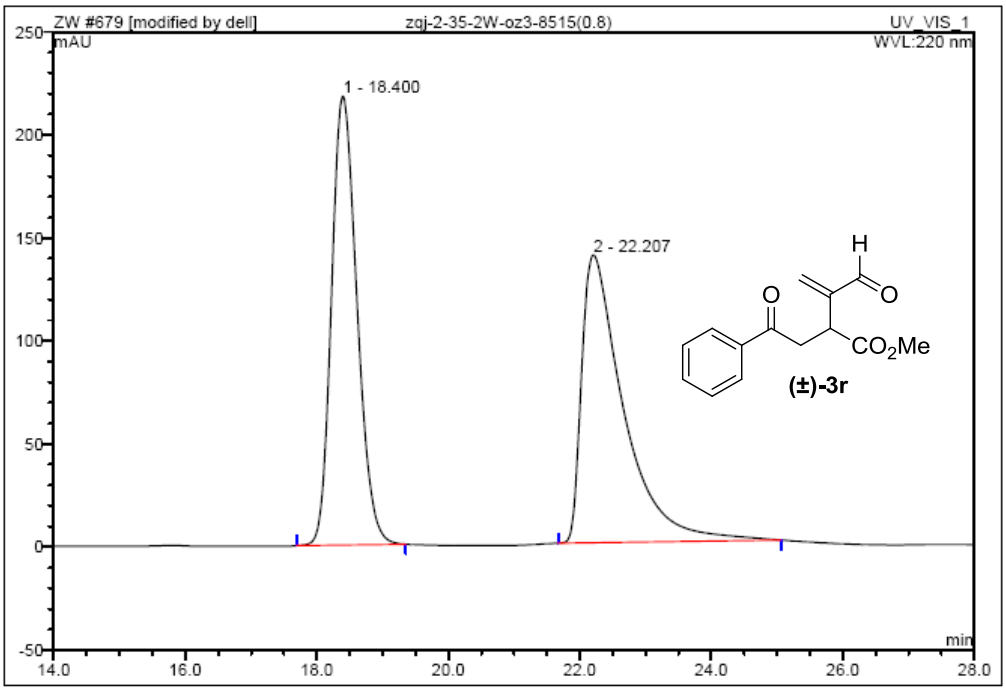


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.67	n.a.	400.635	198.462	96.07	n.a.	BMB*
2	13.51	n.a.	16.327	8.121	3.93	n.a.	BMB*
Total:			416.962	206.584	100.00	0.000	

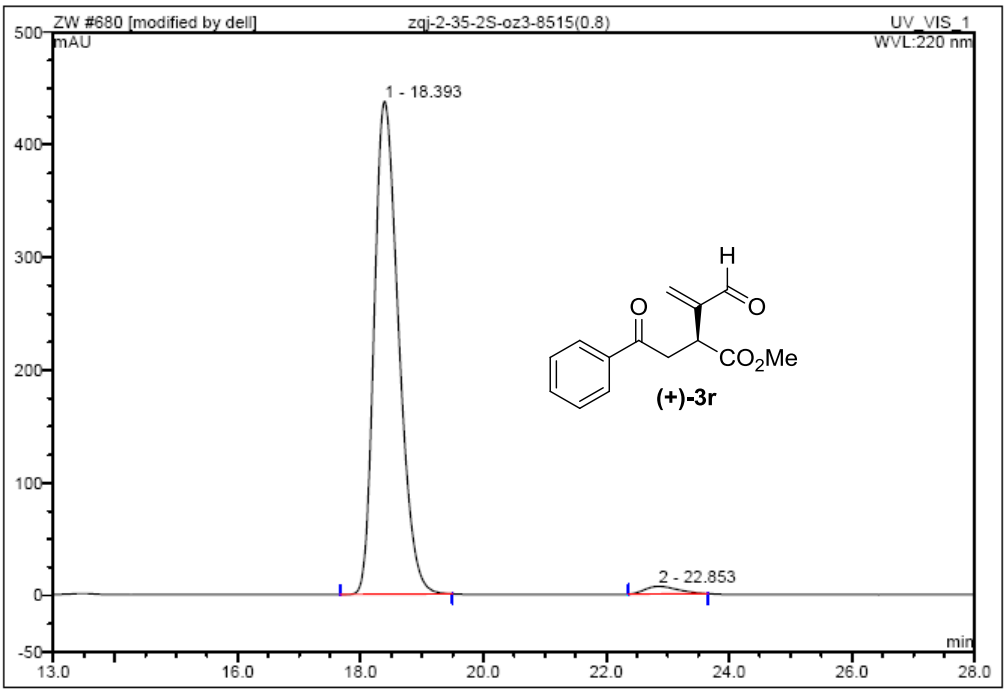
3r (*S*)-methyl 3-formyl-2-(2-oxo-2-phenylethyl)but-3-enoate



3r; Colorless oil; $[\alpha]_D^{20}$ = + 108.6 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.97–7.95 (m, 2H), 7.60–7.57 (m, 1H), 7.49–7.46 (m, 2H), 6.51 (s, 1H), 6.22 (s, 1H), 4.27 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.74–3.69 (m, 4H), 3.25 (dd, *J* = 18.0, 5.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.98, 192.68, 172.62, 147.11, 136.37, 136.25, 133.36, 128.61, 128.04, 52.41, 39.73, 39.48; Enantiomeric excess: 96%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 85/15; flow rate 0.8 ml/min; 25 ℃; 220 nm), first peak: t_R = 18.39 min, second peak: t_R = 22.85 min; HRMS (ESI) m/z calcd. for $C_{14}H_{14}NaO_4$ $[M+Na]^+$ = 269.0784, found = 269.0789; IR (neat): υ 2953, 2922, 2851, 1734, 1683, 1627, 1596, 1448, 1358, 1306, 1246, 1164, 1001 cm^{-1}.

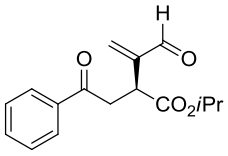


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.40	n.a.	217.893	97.729	48.66	n.a.	BMB*
2	22.21	n.a.	139.679	103.129	51.34	n.a.	BMB*
Total:			357.571	200.857	100.00	0.000	

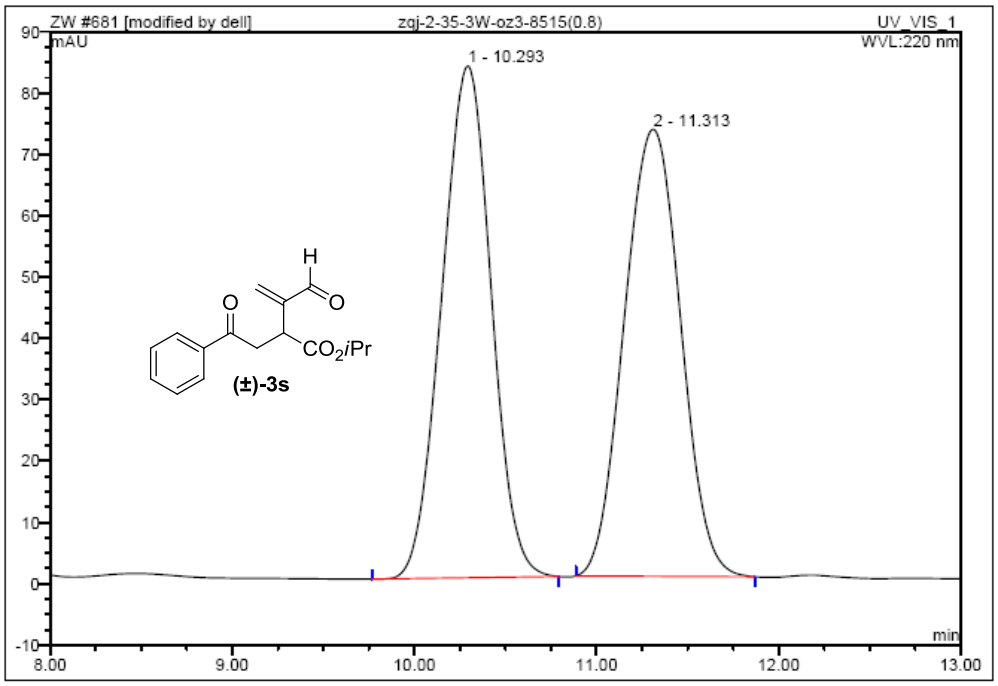


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.39	n.a.	437.509	200.413	97.92	n.a.	BMB*
2	22.85	n.a.	6.825	4.255	2.08	n.a.	BMB*
Total:			444.333	204.668	100.00	0.000	

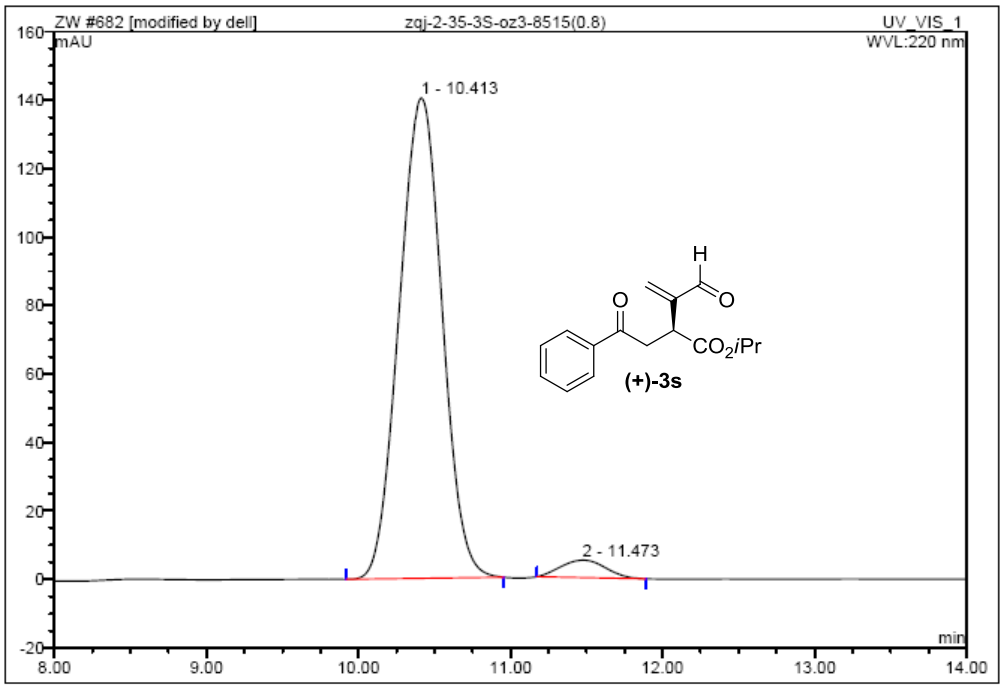
3s (*S*)-isopropyl 3-formyl-2-(2-oxo-2-phenylethyl)but-3-enoate



3s; White solid. m.p. = 61-63 °C; $[\alpha]_D^{20}$ = + 127.1 (*c* = 0.33, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 9.56 (s, 1H), 7.97–7.95 (m, 2H), 7.59–7.56 (m, 1H), 7.48–7.45 (m, 2H), 6.50 (s, 1H), 6.20 (s, 1H), 5.08–5.01 (m, 1H), 4.20 (dd, *J* = 8.0, 5.5 Hz, 1H), 3.69 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.20 (dd, *J* = 18.0, 5.5 Hz, 1H), 1.26 (d, *J* = 6.5 Hz, 3H), 1.17 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.12, 192.73, 171.53, 147.42, 136.39, 136.12, 133.25, 128.57, 128.02, 68.69, 40.03, 39.64, 21.64, 21.39; Enantiomeric excess: 93%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 85/15; flow rate 0.8 ml/min; 25 ℃; 220 nm), first peak: t_R = 10.41 min, second peak: t_R = 11.47 min; HRMS (ESI) m/z calcd. for $C_{16}H_{18}NaO_4$ $[M+Na]^+$ = 297.1097, found = 297.1106; IR (neat): υ 2983, 2935, 2902, 2814, 2697, 1725, 1689, 1677, 1595, 1448, 1377, 1326, 1246, 1211, 1179, 1101, 979 cm^{-1}.

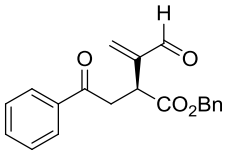


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.29	n.a.	83.457	26.250	50.13	n.a.	BMB*
2	11.31	n.a.	72.860	26.117	49.87	n.a.	BMB*
Total:			156.317	52.367	100.00	0.000	

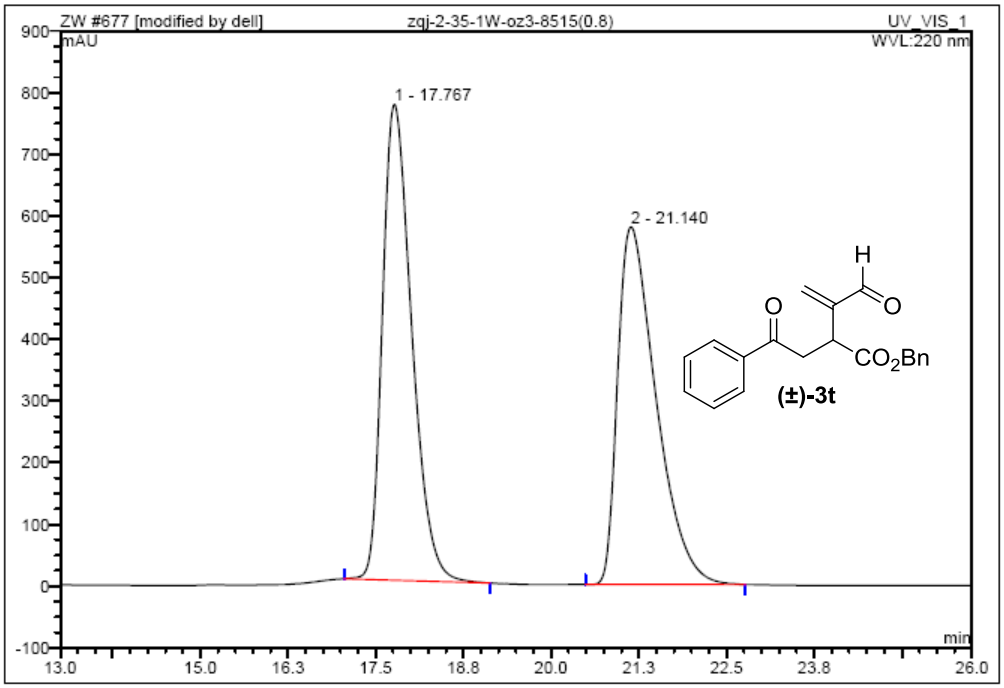


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.41	n.a.	140.475	45.912	96.37	n.a.	BMB*
2	11.47	n.a.	5.077	1.730	3.63	n.a.	BMB*
Total:			145.552	47.642	100.00	0.000	

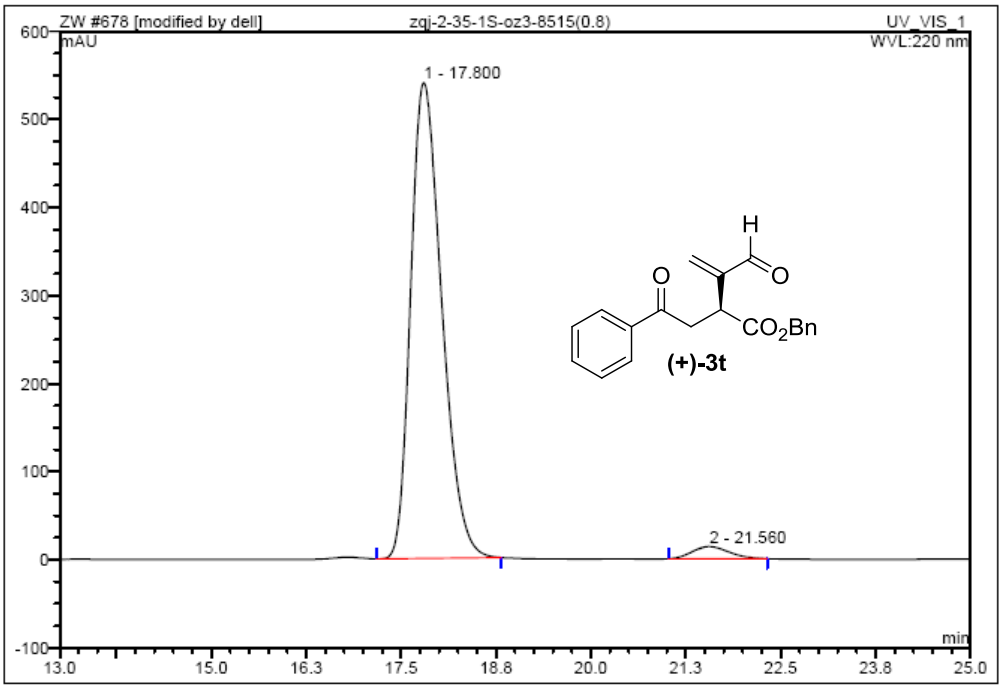
3t (*S*)-benzyl 3-formyl-2-(2-oxo-2-phenylethyl)but-3-enoate



3t; Colorless oil; $[\alpha]_D^{20}$ = + 85.8 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.55 (s, 1H), 7.97–7.95 (m, 2H), 7.60–7.57 (m, 1H), 7.49–7.46 (m, 2H), 7.38–7.32 (m, 5H), 6.45 (s, 1H), 6.19 (s, 1H), 5.17 (q, *J* = 7.5 Hz, 2H), 4.32 (dd, *J* = 7.5, 5.5 Hz, 1H), 3.72 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.27 (dd, *J* = 18.0, 5.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.94, 192.67, 171.96, 146.99, 136.40, 136.26, 135.53, 133.33, 128.59, 128.44, 128.16, 128.08, 128.03, 66.99, 39.72, 39.65; Enantiomeric excess: 94%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 85/15; flow rate 0.8 ml/min; 25 ℃; 220 nm), first peak: t_R = 17.80 min, second peak: t_R = 21.56 min; HRMS (ESI) m/z calcd. for $C_{20}H_{18}NaO_4$ $[M+Na]^+$ = 345.1097, found = 345.1108; IR (neat): υ 3063, 3033, 2924, 1732, 1684, 1596, 1580, 1449, 1305, 1212, 1157, 1088, 1001, 957 cm^{-1}.

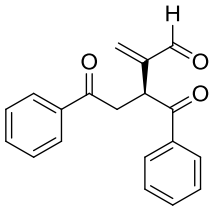


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.77	n.a.	771.143	373.431	50.44	n.a.	BMB*
2	21.14	n.a.	579.566	366.917	49.56	n.a.	BMB*
Total:			1350.709	740.348	100.00	0.000	

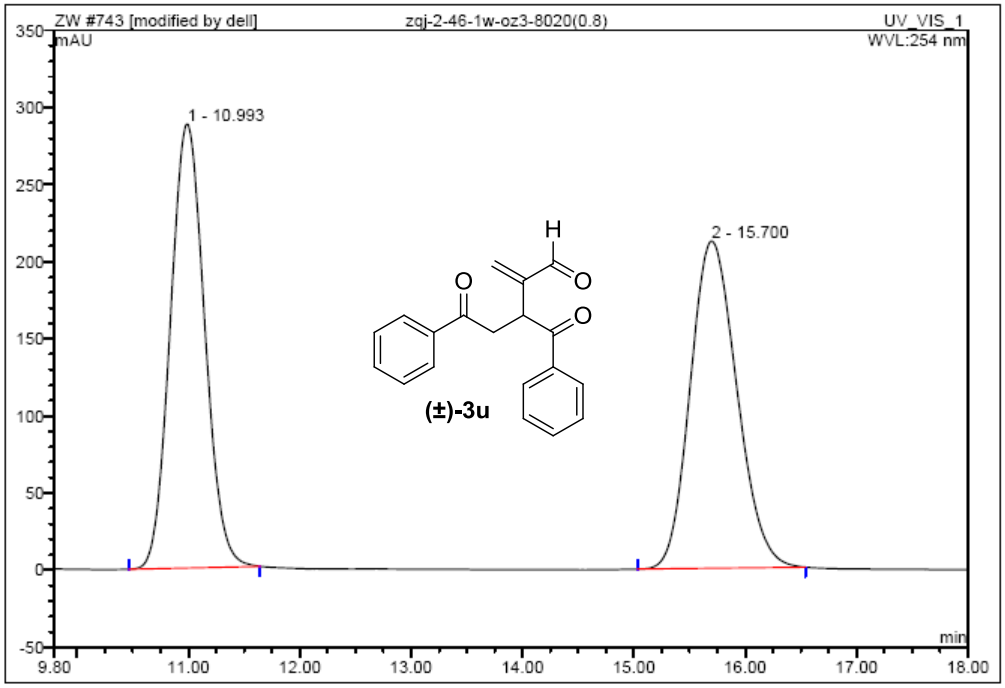


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.80	n.a.	540.050	256.136	97.05	n.a.	BMB*
2	21.56	n.a.	13.833	7.779	2.95	n.a.	BMB*
Total:			553.883	263.915	100.00	0.000	

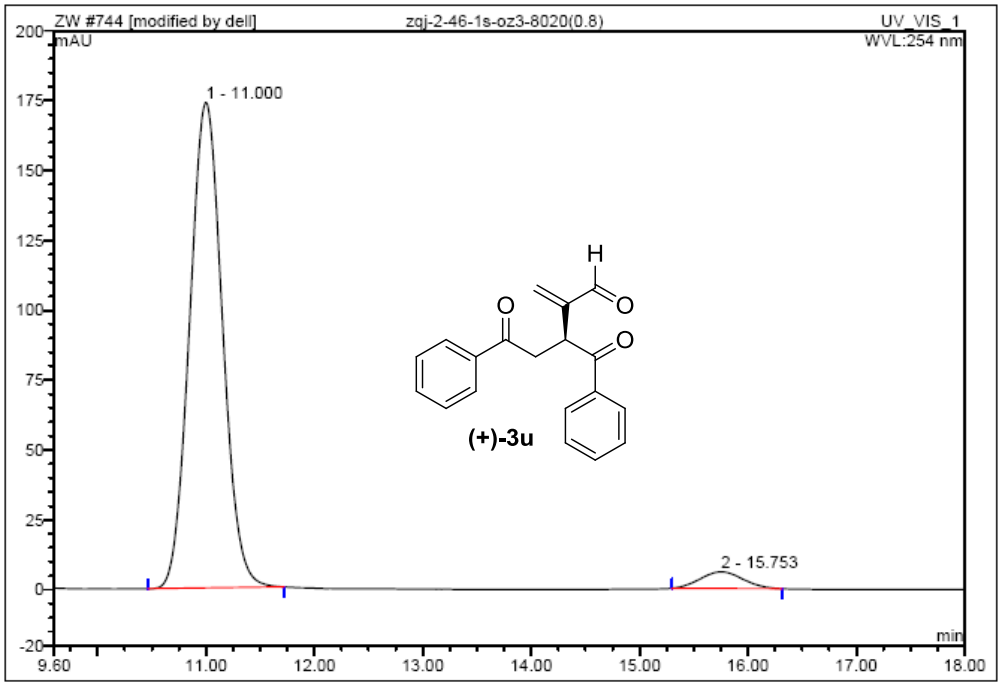
3u (*S*)-3-benzoyl-2-methylene-5-oxo-5-phenylpentanal



3u; Colorless oil; $[\alpha]_D^{20}$ = + 254.2 (*c* = 0.33, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 9.59 (s, 1H), 8.00–7.94 (m, 4H), 7.58–7.54 (m, 2H), 7.47–7.43 (m, 4H), 6.40 (s, 1H), 6.19 (s, 1H), 5.35 (dd, *J* = 9.6, 4.0 Hz, 1H), 3.86 (dd, *J* = 18.0, 9.6 Hz, 1H), 3.24 (dd, *J* = 18.0, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.53, 197.15, 192.47, 147.29, 136.97, 136.18, 135.74, 133.35, 133.31, 128.67, 128.58, 128.09, 41.40, 39.20; Enantiomeric excess: 92%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 80/20; flow rate 0.8 ml/min; 25 ℃; 220 nm), first peak: t_R = 11.00 min, second peak: t_R = 15.75 min; HRMS (ESI) m/z calcd. for $C_{19}H_{16}NaO_3$ $[M+Na]^+$ = 315.0992, found = 315.1001; IR (neat): υ 3060, 2916, 2822, 1676, 1595, 1579, 1447, 1250, 1217, 1178, 999, 949 cm^{-1}.

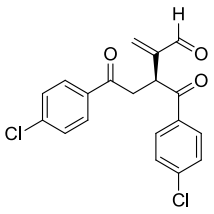


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.99	n.a.	287.810	102.627	49.97	n.a.	BMB*
2	15.70	n.a.	212.155	102.765	50.03	n.a.	BMB*
Total:			499.966	205.392	100.00	0.000	

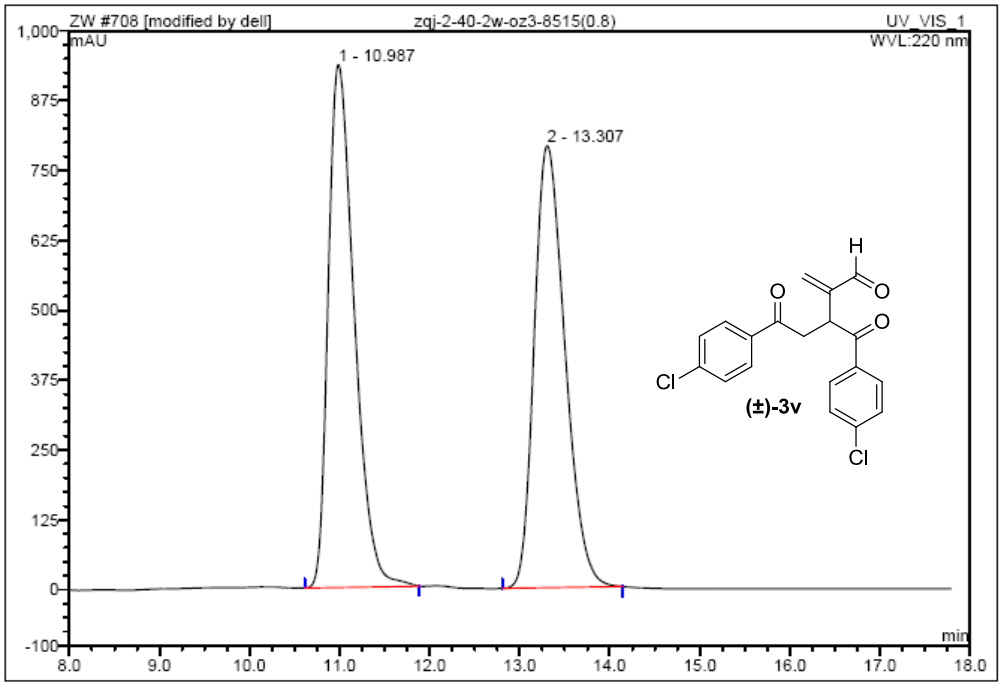


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.00	n.a.	173.758	60.873	95.73	n.a.	BMB*
2	15.75	n.a.	5.940	2.717	4.27	n.a.	BMB*
Total:			179.698	63.590	100.00	0.000	

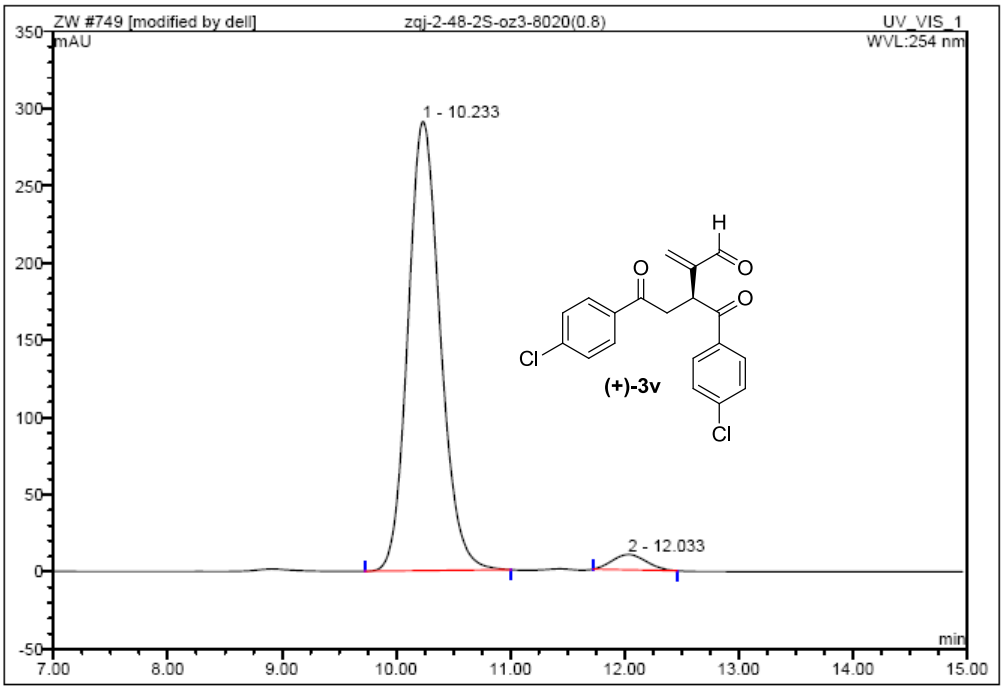
3v (*S*)-3-(4-chlorobenzoyl)-5-(4-chlorophenyl)-2-methylene-5-oxopentanal



3v; Colorless oil; $[\alpha]_D^{20}$ = + 217.2 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (s, 1H), 7.94–7.86 (m, 4H), 7.44–7.41 (m, 4H), 6.40 (s, 1H), 6.21 (s, 1H), 5.27 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.82 (dd, *J* = 18.0, 10.4 Hz, 1H), 3.18 (dd, *J* = 18.0, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.30, 195.94, 192.32, 146.87, 139.95, 139.88, 137.17, 134.38, 134.00, 130.07, 129.49, 129.02, 128.95, 41.39, 39.07; Enantiomeric excess: 93%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 80/20; flow rate 0.8 ml/min; 25 ℃; 220 nm), first peak: t_R = 10.23 min, second peak: t_R = 12.03 min; HRMS (ESI) m/z calcd. for $C_{19}H_{14}Cl_2NaO_3$ $[M+Na]^+$ = 383.0212, found = 383.0215; IR (neat): υ 3074, 2920, 2851, 2699, 1676, 1589, 1506, 1399, 1313, 1216, 1155, 1090, 995 cm^{-1}.

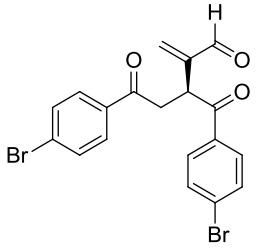


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.99	n.a.	935.629	313.698	50.09	n.a.	BMB*
2	13.31	n.a.	790.761	312.580	49.91	n.a.	BMB*
Total:			1726.390	626.277	100.00	0.000	

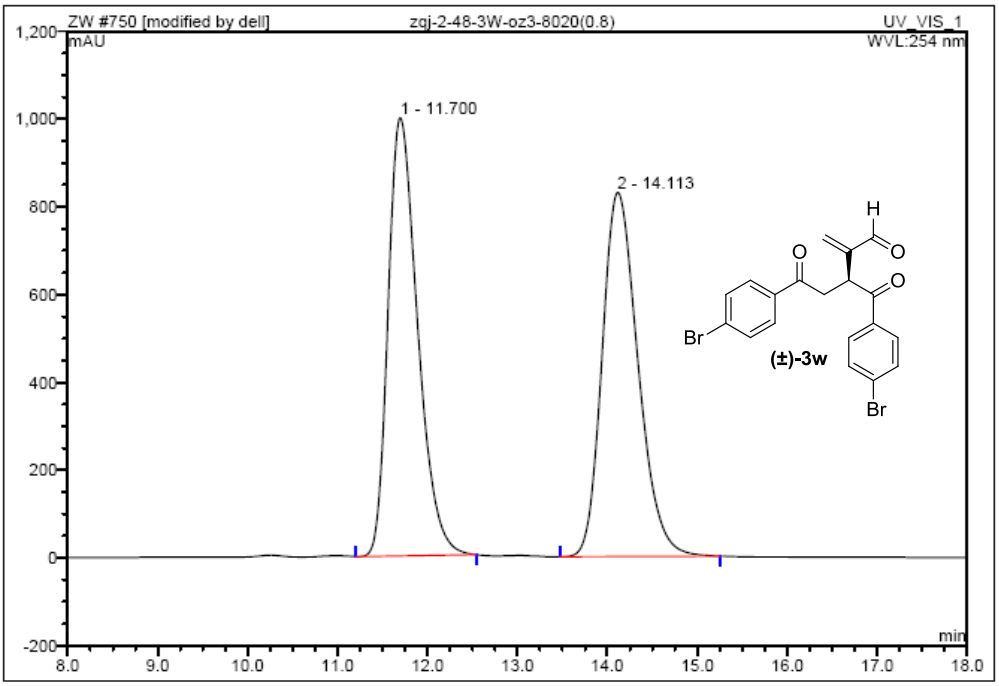


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.23	n.a.	290.864	95.364	96.56	n.a.	BMB*
2	12.03	n.a.	9.888	3.401	3.44	n.a.	BMB*
Total:			300.752	98.766	100.00	0.000	

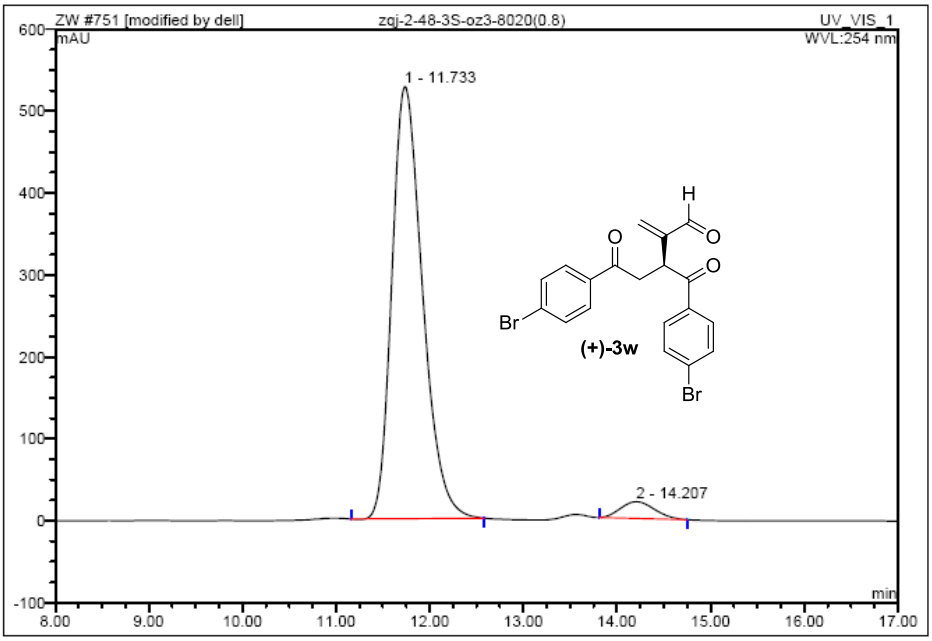
3w (*S*)-3-(4-bromobenzoyl)-5-(4-bromophenyl)-2-methylene-5-oxopentanal



3w; Colorless oil; $[\alpha]_D^{20}$ = + 185.0 (*c* = 0.33, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 9.58 (s, 1H), 7.86–7.79 (m, 4H), 7.61–7.59 (m, 4H), 6.39 (s, 1H), 6.21 (s, 1H), 5.26 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.81 (dd, *J* = 18.0, 10.0 Hz, 1H), 3.17 (dd, *J* = 18.0, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.49, 196.12, 192.32, 146.79, 137.22, 134.74, 134.37, 132.02, 131.94, 130.16, 129.58, 128.73, 128.64, 41.36, 39.02; Enantiomeric excess: 92%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 80/20; flow rate 0.8 ml/min; 25 ℃; 220 nm), first peak: t_R = 11.73 min, second peak: t_R = 14.20 min; HRMS (ESI) m/z calcd. for $C_{19}H_{14}Br_2NaO_3$ $[M+Na]^+$ = 470.9202, found = 470.9209; IR (neat): υ 3089, 2921, 2850, 1676, 1583, 1567, 1483, 1396, 1249, 1214, 1174, 1068, 992 cm^{-1}.

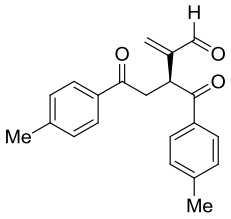


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.70	n.a.	997.971	379.131	49.70	n.a.	BMB*
2	14.11	n.a.	829.624	383.646	50.30	n.a.	BMB*
Total:			1827.595	762.777	100.00	0.000	

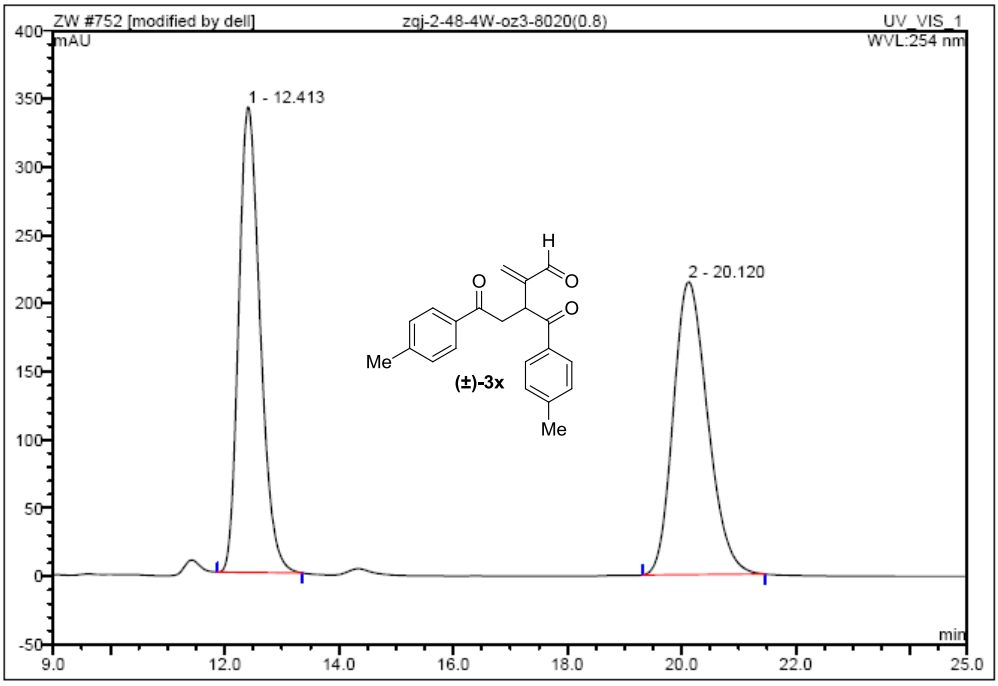


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.73	n.a.	527.073	199.789	95.88	n.a.	BMB*
2	14.21	n.a.	20.487	8.590	4.12	n.a.	BMB*
Total:			547.560	208.379	100.00	0.000	

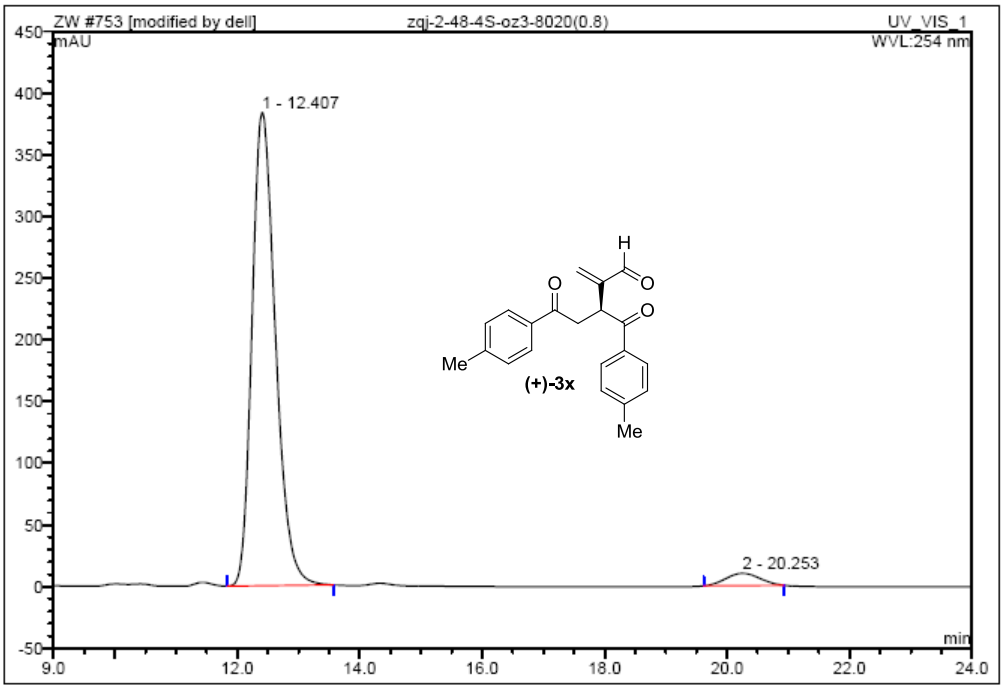
3x (*S*)-3-(4-methylbenzoyl)-2-methylene-5-oxo-5-(p-tolyl)pentanal



3x; Colorless oil; $[\alpha]_D^{20}$ = + 264.2 (*c* = 0.33, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.91–7.83 (m, 4H), 7.25–7.23 (m, 4H), 6.40 (s, 1H), 6.16 (s, 1H), 5.31 (dd, *J* = 9.6, 4.4 Hz, 1H), 3.81 (dd, *J* = 18.0, 9.6 Hz, 1H), 3.21 (dd, *J* = 18.0, 4.4 Hz, 1H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.21, 196.79, 192.55, 147.57, 144.20, 144.07, 136.84, 133.79, 133.28, 129.35, 129.23, 128.82, 128.20, 41.27, 39.07, 21.64; Enantiomeric excess: 93%, determined by HPLC (Chiralpak OZ-3, hexane/*i*-PrOH = 80/20; flow rate 0.8 ml/min; 25 ℃; 220 nm), first peak: t_R = 12.40 min, second peak: t_R = 20.25 min; HRMS (ESI) m/z calcd. for $C_{21}H_{20}NaO_3$ $[M+Na]^+$ = 343.1305, found = 343.1314; IR (neat): υ 2919, 2852, 1674, 1605, 1571, 1398, 1317, 1253, 1223, 1177, 999, 941 cm^{-1}.

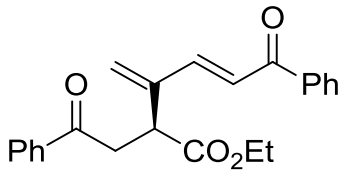


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.41	n.a.	341.274	148.851	49.84	n.a.	BMB*
2	20.12	n.a.	214.723	149.822	50.16	n.a.	BMB*
Total:			555.998	298.673	100.00	0.000	

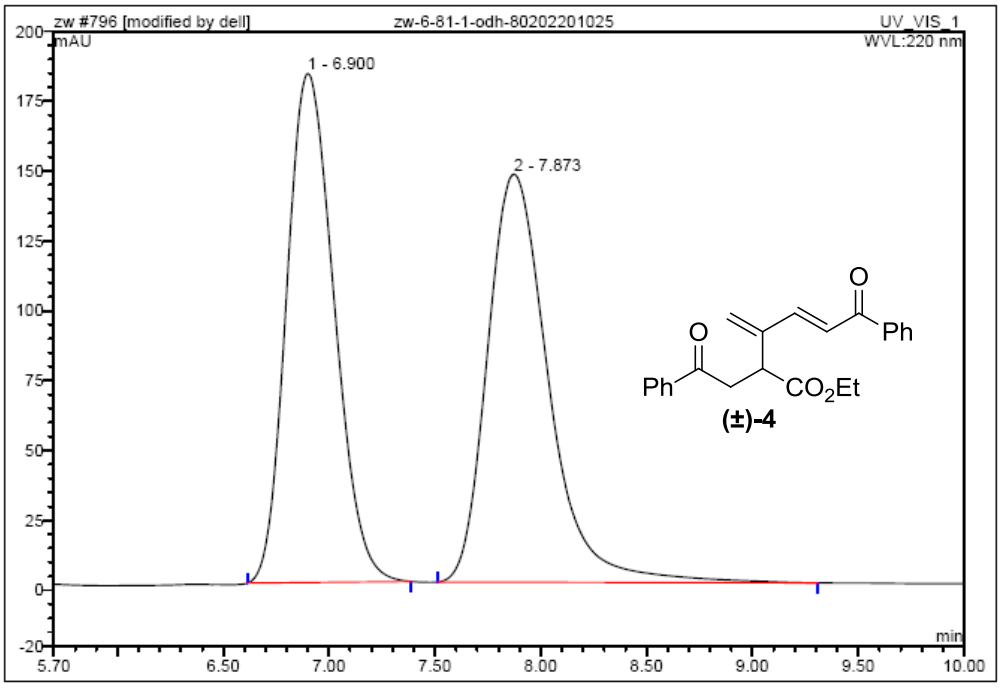


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.41	n.a.	383.584	169.656	96.38	n.a.	BMB*
2	20.25	n.a.	9.937	6.381	3.62	n.a.	BMB*
Total:			393.521	176.036	100.00	0.000	

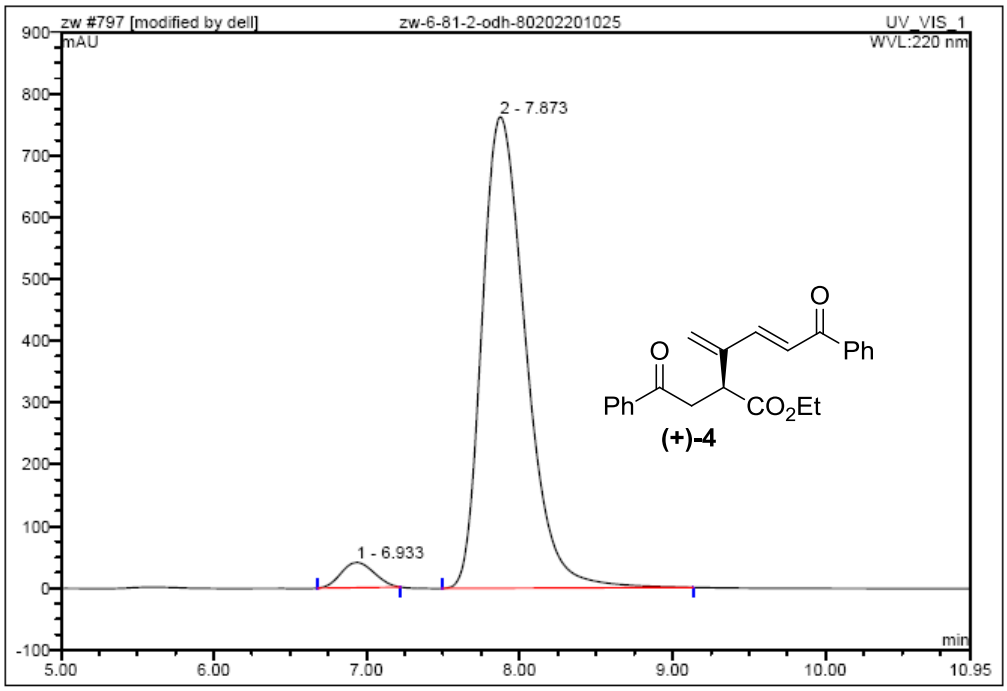
4 (*S*,*E*)-ethyl 3-methylene-6-oxo-2-(2-oxo-2-phenylethyl)-6-phenylhex-4-enoate



4; Colorless oil; $[\alpha]_D^{20}$ = + 92.3 (*c* = 0.33, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.00–7.97 (m, 4H), 7.59–7.56 (m, 2H), 7.50–7.45 (m, 5H), 7.28 (d, *J* = 15.6 Hz, 1H), 5.71 (s, 1H), 5.65 (s, 1H), 4.27–4.18 (m, 3H), 3.85 (dd, *J* = 18.0, 9.6 Hz, 1H), 3.21 (dd, *J* = 18.0, 3.6 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.44, 190.08, 172.57, 144.49, 142.62, 137.73, 136.16, 133.41, 132.95, 128.61, 128.44, 128.04, 126.02, 122.59, 61.34, 42.16, 40.57, 14.01; Enantiomeric excess: 92%, determined by HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 80/20; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 6.93 min, second peak: t_R = 7.87 min; HRMS (ESI) m/z calcd. for $C_{23}H_{22}NaO_4$ $[M+Na]^+$ = 385.1410, found = 385.1425; IR (neat): υ 3058, 2923, 2852, 1725, 1681, 1596, 1447, 1282, 1212, 1173, 1018, 987 cm^{-1}.

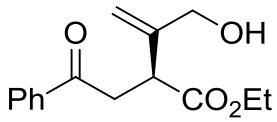


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.90	n.a.	182.176	47.416	49.21	n.a.	BMB*
2	7.87	n.a.	146.053	48.947	50.79	n.a.	BMB*
Total:			328.229	96.363	100.00	0.000	

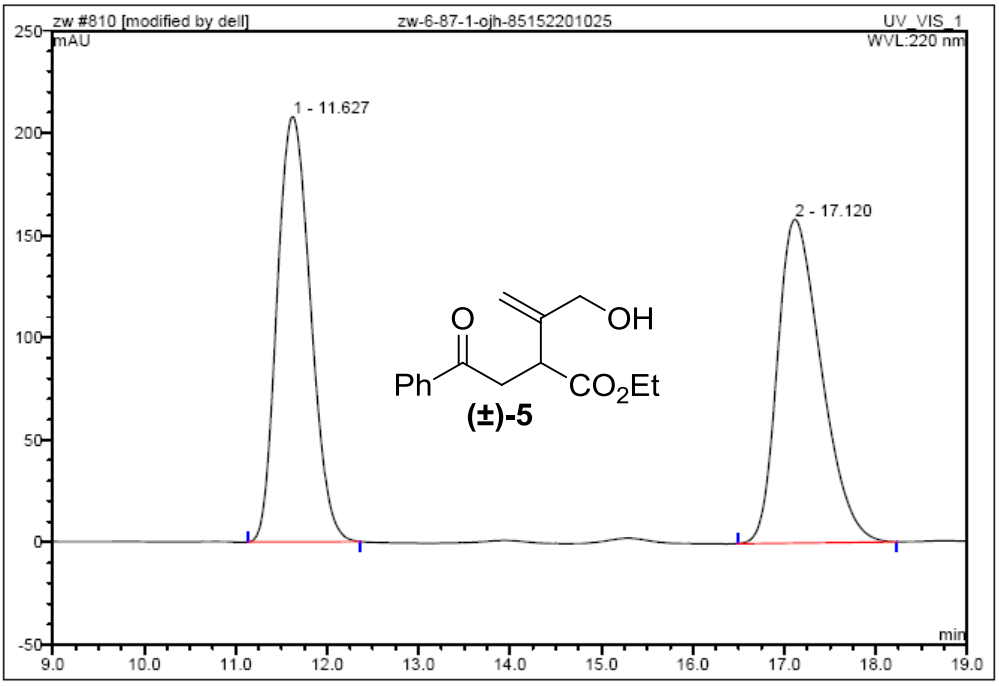


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.93	n.a.	40.838	10.250	3.90	n.a.	BMB*
2	7.87	n.a.	762.710	252.396	96.10	n.a.	BMB*
Total:			803.548	262.645	100.00	0.000	

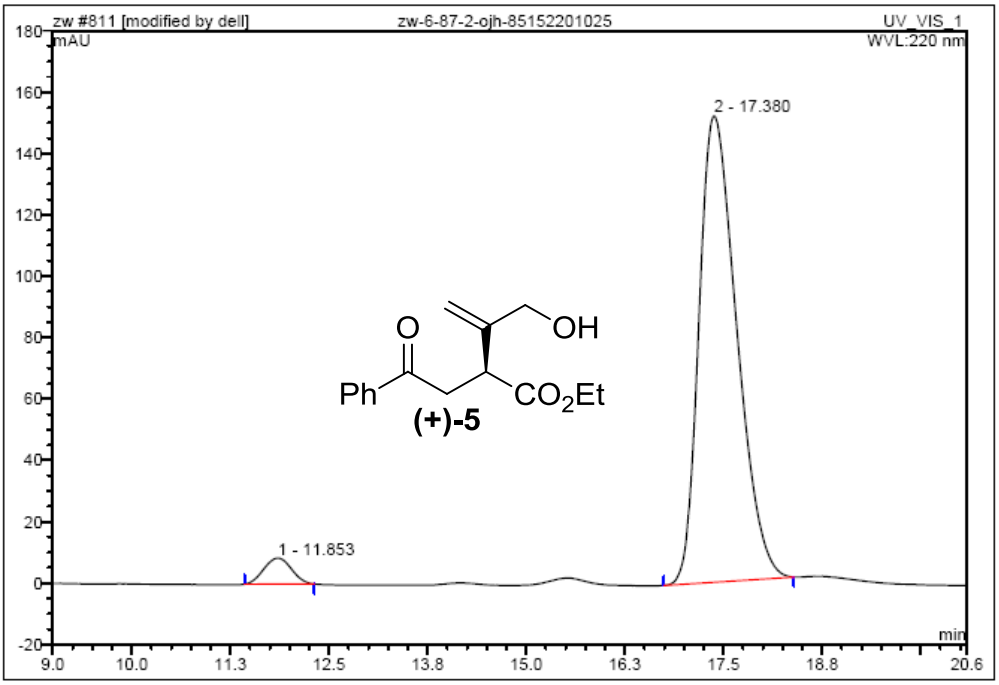
5 (*S*)-ethyl 3-(hydroxymethyl)-2-(2-oxo-2-phenylethyl)but-3-enoate



5; Colorless oil; $[\alpha]_D^{20}$ = + 32.0 (*c* = 0.33, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.60–7.56 (m, 1H), 7.49–7.45 (m, 2H), 5.25 (s, 1H), 5.13 (s, 1H), 4.26 (s, 2H), 4.21–4.14 (m, 2H), 3.82 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.71 (dd, *J* = 17.6, 8.4 Hz, 1H), 3.32 (dd, *J* = 17.6, 5.2 Hz, 1H), 2.24 (s, 1H), 1.26 (t, *J* =7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.89, 173.10, 145.90, 136.37, 133.38, 128.62, 128.06, 113.17, 65.73, 61.19, 43.05, 40.35, 14.04; Enantiomeric excess: 92%, determined by HPLC (Chiralpak OJ-H, hexane/*i*-PrOH = 85/15; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 11.85 min, second peak: t_R = 17.38 min; HRMS (ESI) m/z calcd. for $C_{15}H_{18}NaO_4$ $[M+Na]^+$ = 285.1097, found = 285.1100; IR (neat): υ 3456, 2976, 2924, 2870, 1725, 1681, 1596, 1448, 1212, 1171, 1020, 1001 cm^{-1}.

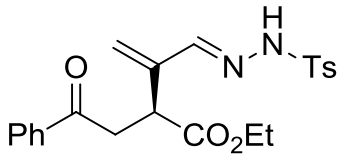


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.63	n.a.	207.782	87.856	49.94	n.a.	BMB*
2	17.12	n.a.	158.157	88.070	50.06	n.a.	BMB*
Total:			365.939	175.925	100.00	0.000	

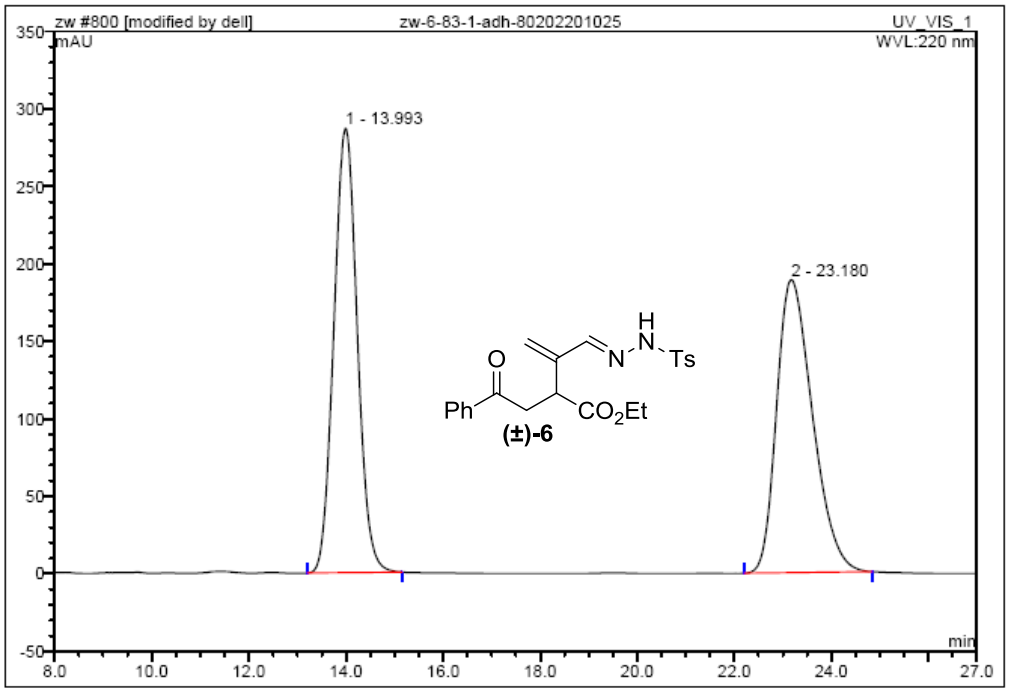


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.85	n.a.	8.468	3.436	3.93	n.a.	BMB*
2	17.38	n.a.	151.954	83.958	96.07	n.a.	BMB*
Total:			160.421	87.394	100.00	0.000	

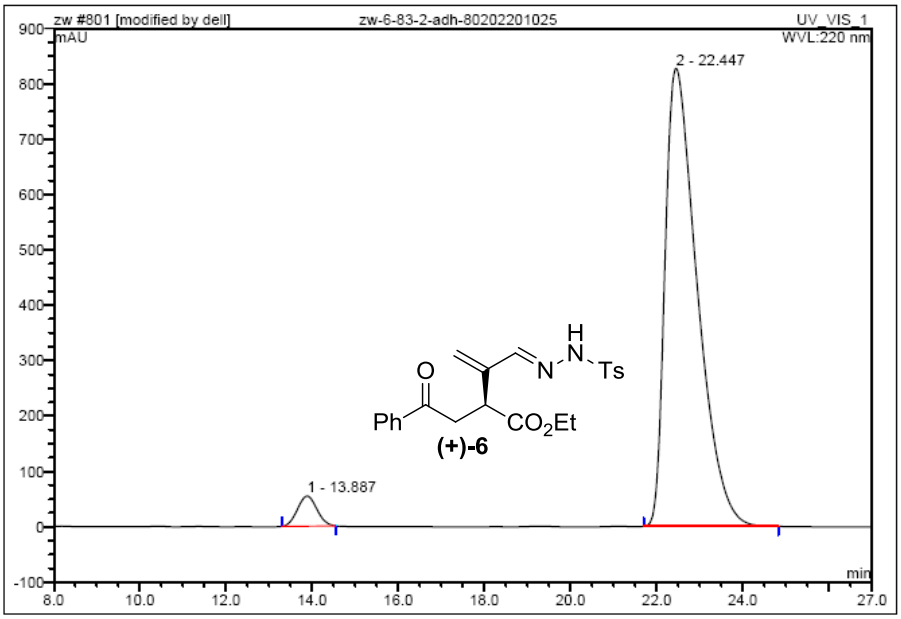
6 (*S*,*E*)-ethyl 2-(2-oxo-2-phenylethyl)-3-((2-tosylhydrazono)methyl)but-3-enoate



6; Colorless oil; $[\alpha]_D^{20}$ = + 60.2 (*c* = 0.33, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.60–7.57 (m, 1H), 7.48–7.44 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.57 (s, 1H), 5.40 (s, 1H), 4.26 (dd, *J* = 9.2, 4.0 Hz, 1H), 4.13–4.05 (m, 2H), 3.59 (dd, *J* = 18.0, 9.6 Hz, 1H), 2.93 (dd, *J* = 18.0, 4.0 Hz, 1H), 2.21 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.81, 172.61, 147.57, 144.09, 141.75, 136.34, 134.79, 133.18, 129.45, 128.52, 128.02, 127.96, 124.41, 61.02, 41.78, 40.09, 21.33, 13.90; Enantiomeric excess: 92%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 80/20; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 13.88 min, second peak: t_R = 22.44 min; HRMS (ESI) m/z calcd. for $C_{22}H_{24}N_2NaO_5S$ $[M+Na]^+$ = 451.1298, found = 451.1308; IR (neat): υ 3229, 2904, 1726, 1681, 1596, 1448, 1359, 1309, 1210, 1161, 1086, 884 cm^{-1}.

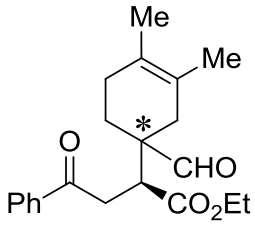


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.99	n.a.	286.751	159.826	49.65	n.a.	BMB*
2	23.18	n.a.	189.078	162.065	50.35	n.a.	BMB*
Total:			475.829	321.891	100.00	0.000	

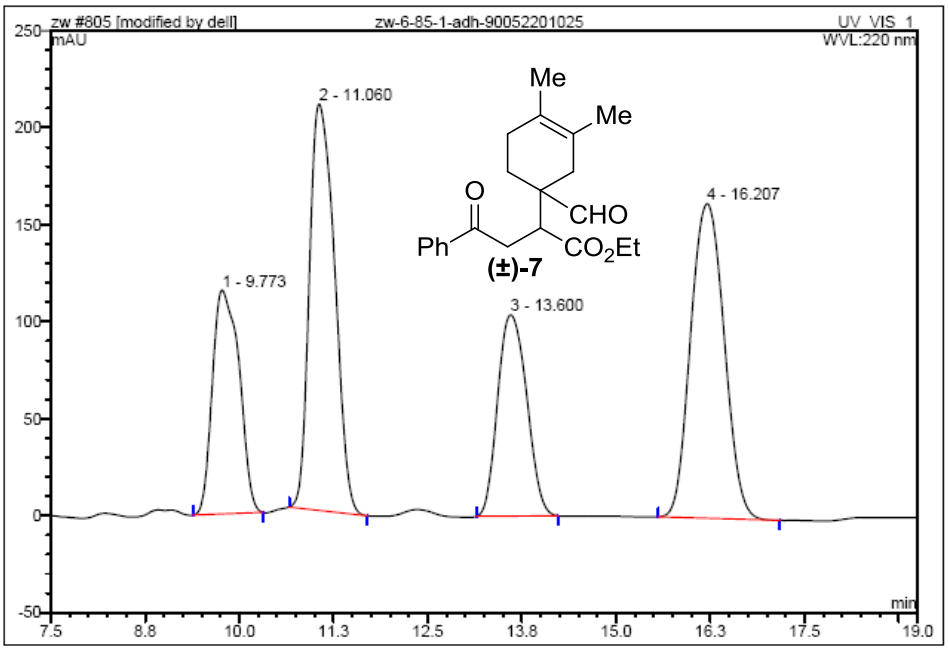


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.89	n.a.	54.098	28.256	3.81	n.a.	BMB*
2	22.45	n.a.	827.134	713.750	96.19	n.a.	BMB*
Total:			881.232	742.005	100.00	0.000	

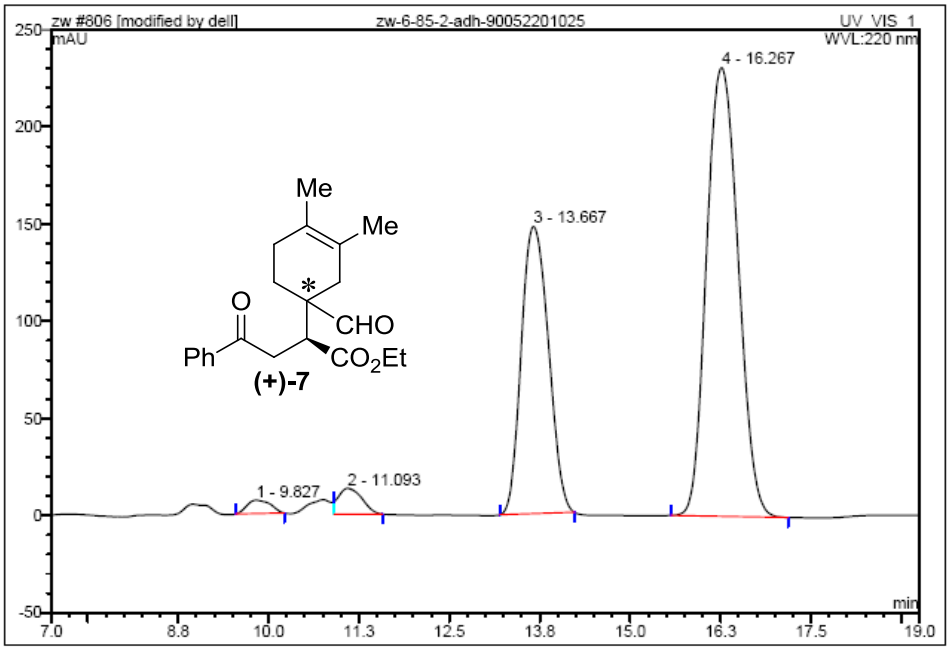
7(2*S*)-ethyl 2-(1-formyl-3,4-dimethylcyclohex-3-en-1-yl)-4-oxo-4-phenylbutanoate



3ia; Colorless oil; $[\alpha]_D^{20}$ = + 13.1 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.54 (s, 1H), 7.96–7.93 (m, 2H), 7.59–7.55 (m, 1H), 7.48–7.44 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.55–3.44 (m, 1H), 3.34–3.21 (m, 1H), 3.09–3.02 (m, 1H), 2.27 (s, 1H), 2.11–1.93 (m, 4H), 1.72–1.66 (m, 4H), 1.57 (s, 3H), 1.25 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.85, 197.80, 172.58, 136.34, 133.32, 128.56, 127.98, 125.49, 123.06, 61.01, 49.28, 45.61, 35.83, 34.17, 28.41, 26.49, 19.21, 18.70, 14.07; Enantiomeric excess: 92% and 92%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 95/05; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 9.82 min, second peak: t_R = 11.09 min, third peak: t_R = 13.66 min, forth peak: t_R = 16.26 min; HRMS (ESI) m/z calcd. for $C_{21}H_{26}NaO_4$ $[M+Na]^+$ = 365.1723, found = 365.1734; IR (neat): υ 2979, 2914, 2721, 1722, 1685, 1597, 1447, 1363, 1216, 1175, 1023, 857 cm^{-1}.

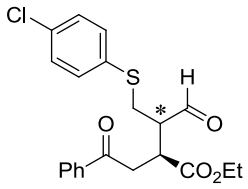


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.77	n.a.	115.466	47.407	18.32	n.a.	BMB*
2	11.06	n.a.	209.621	81.163	31.36	n.a.	BMB*
3	13.60	n.a.	103.879	46.402	17.93	n.a.	BMB*
4	16.21	n.a.	162.196	83.829	32.39	n.a.	BMB*
Total:			591.162	258.801	100.00	0.000	

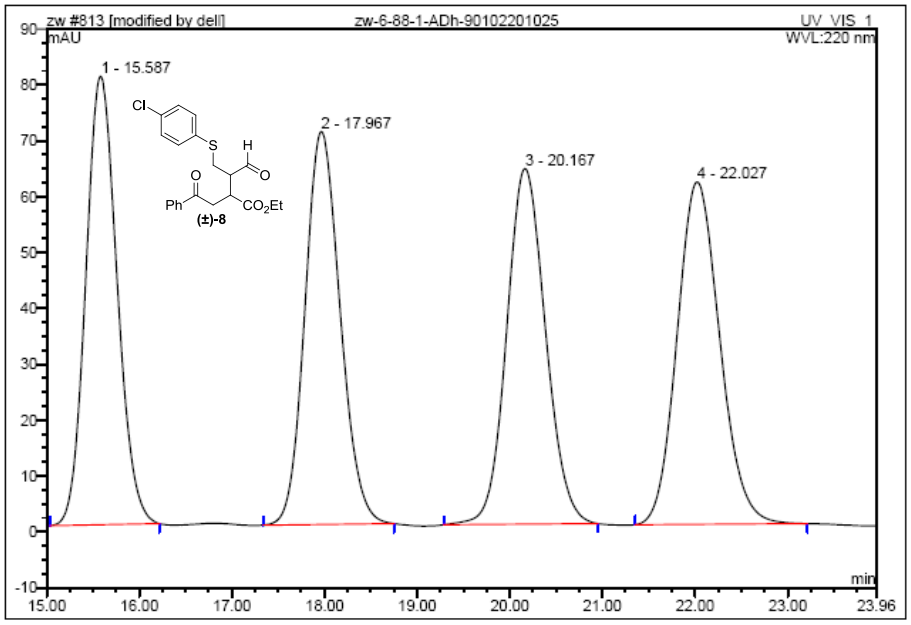


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.83	n.a.	6.871	2.608	1.38	n.a.	BMB*
2	11.09	n.a.	13.329	4.988	2.63	n.a.	MB*
3	13.67	n.a.	147.768	64.260	33.93	n.a.	BMB*
4	16.27	n.a.	230.876	117.520	62.06	n.a.	BMB*
Total:			398.845	189.377	100.00	0.000	

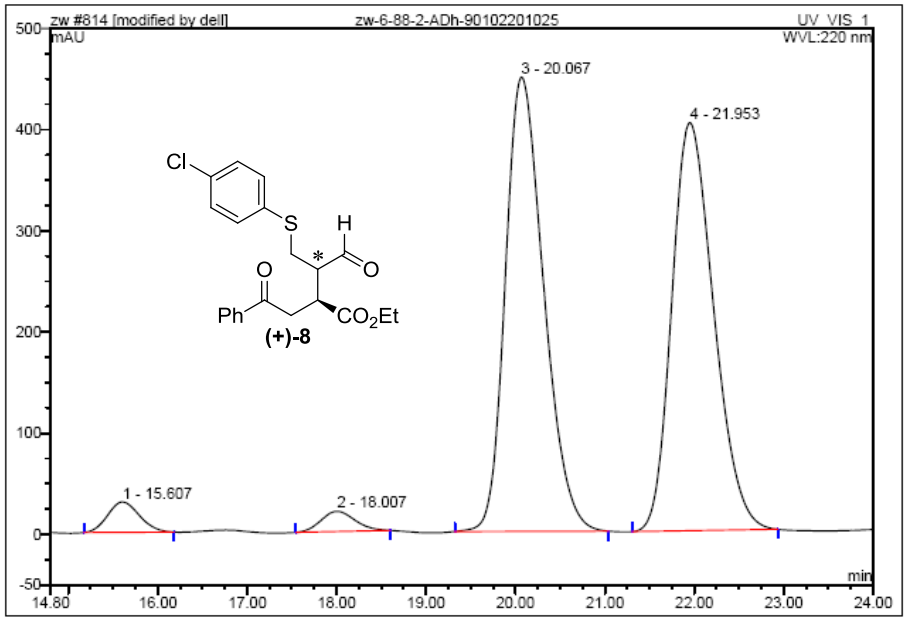
8



8; Colorless oil; $[\alpha]_D^{20}$ = + 4.9 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.60–7.57 (m, 1H), 7.49–7.45 (m, 2H), 7.31–7.26 (m, 4H), 4.20–4.06 (m, 2H), 3.67–3.63 (m, 1H), 3.55 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.37 (dd, *J* = 18.0, 8.8 Hz, 1H), 3.17–3.07 (m, 2H), 2.95–2.90 (m, 1H), 1.21 (t, *J* =6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.87, 197.02, 172.61, 136.15, 133.54, 133.18, 133.04, 131.58, 129.31, 128.67, 128.05, 61.51, 51.22, 40.14, 37.18, 31.58, 14.00; Enantiomeric excess: 92% and 92%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 90/10; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 15.60 min, second peak: t_R = 18.00 min, third peak: t_R = 20.06 min, forth peak: t_R = 21.95 min; HRMS (ESI) m/z calcd. for $C_{21}H_{21}ClNaO_4S$ $[M+Na]^+$ = 427.0741, found = 427.0744; IR (neat): υ 3060, 2980, 2927, 2834, 2739, 1721, 1683, 1596, 1476, 1448, 1365, 1261, 1218, 1176, 1094, 1010 cm^{-1}.

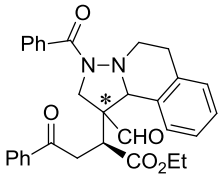


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.59	n.a.	80.241	31.364	24.90	n.a.	BMB*
2	17.97	n.a.	70.300	30.950	24.57	n.a.	BMB*
3	20.17	n.a.	63.627	30.944	24.56	n.a.	BMB*
4	22.03	n.a.	61.251	32.715	25.97	n.a.	BMB*
Total:			275.418	125.973	100.00	0.000	

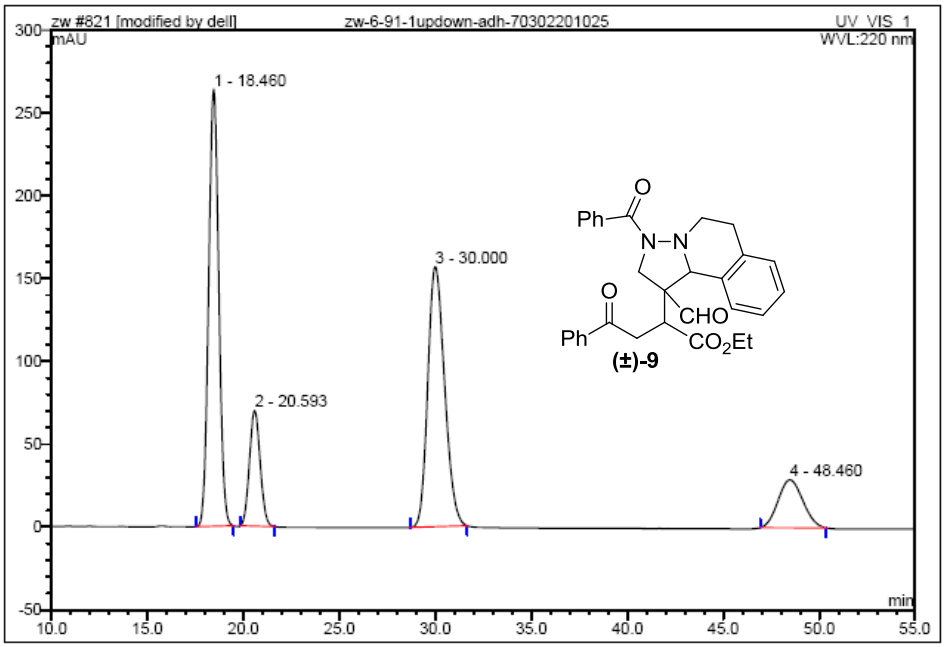


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.61	n.a.	30.076	12.403	2.68	n.a.	BMB*
2	18.01	n.a.	19.936	8.766	1.89	n.a.	BMB*
3	20.07	n.a.	448.940	222.957	48.12	n.a.	BMB*
4	21.95	n.a.	403.282	219.203	47.31	n.a.	BMB*
Total:			902.233	463.328	100.00	0.000	

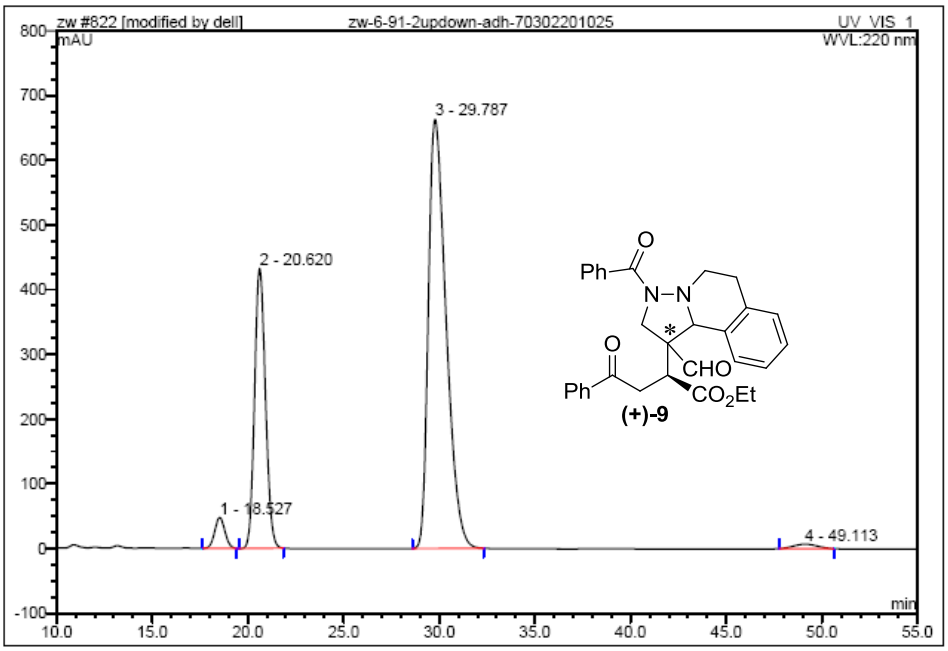
9 (2S)-ethyl 2-(3-benzoyl-1-formyl-1,2,3,5,6,10b-hexahydropyrazolo[5,1-a] isoquinolin-1-yl)-4-oxo-4-phenylbutanoate



9; Colorless oil; $[\alpha]_D^{20}$ = + 159.2 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.60–7.56 (m, 1H), 7.48–7.39 (m, 3H), 7.36–7.29 (m, 3H), 7.27–7.23 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 4.90 (s, 1H), 4.67 (br, 1H), 4.43 (d, *J* = 12.4 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.96 (d, *J* = 8.8 Hz, 1H), 3.58 (br, 1H), 2.92–2.66 (m, 5H), 1.26 (t, *J* =10.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.20, 196.65, 170.90, 167.99, 135.63, 134.32, 133.65, 132.94, 130.44, 128.95, 128.63, 128.25, 128.08, 127.94, 127.61, 127.03, 126.86, 66.45, 63.31, 61.86, 47.77, 43.44, 41.30, 38.52, 28.46, 14.02; Enantiomeric excess: 92% and 92%, determined by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 70/30; flow rate 1.0 ml/min; 25 ℃; 220 nm), first peak: t_R = 18.53 min, second peak: t_R = 20.62 min, third peak: t_R = 29.78 min, forth peak: t_R = 49.11 min; HRMS (ESI) m/z calcd. for $C_{31}H_{30}N_2NaO_5$ $[M+Na]^+$ = 533.2047, found = 533.2052; IR (neat): υ 3061, 2976, 2934, 1720, 1683, 1632, 1577, 1448, 1407, 1363, 1264, 1218, 1172, 1095, 1027, 932 cm^{-1}.

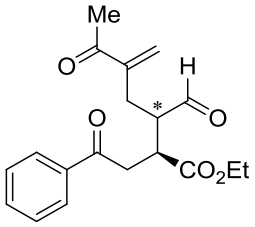


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.46	n.a.	263.798	160.502	39.31	n.a.	BMB*
2	20.59	n.a.	69.757	45.323	11.10	n.a.	BMB*
3	30.00	n.a.	156.946	159.093	38.96	n.a.	BMB*
4	48.46	n.a.	29.025	43.399	10.63	n.a.	BMB*
Total:			519.527	408.318	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.53	n.a.	47.290	29.039	2.81	n.a.	BMB*
2	20.62	n.a.	432.524	285.543	27.58	n.a.	BMB*
3	29.79	n.a.	663.325	710.779	68.66	n.a.	BMB*
4	49.11	n.a.	6.906	9.843	0.95	n.a.	BMB*
Total:			1150.045	1035.203	100.00	0.000	

10 Ethyl 3-formyl-5-methylene-6-oxo-2-(2-oxo-2-phenylethyl)heptanoate



10; Colorless oil; $[\alpha]_D^{20}$ = + 13.7 (*c* = 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.12 (d, *J* = 1.6 Hz, 1H), 7.97–7.95 (m, 2H), 7.61–7.55 (m, 1H), 7.50–7.45 (m, 2H), 6.17 (s, 1H), 5.97 (s, 1H), 4.18 (d, *J* = 7.2 Hz, 1H), 3.75–3.51 (m, 2H), 3.11–3.05 (m, 1H), 2.90–2.84 (m, 2H), 2.56–2.51 (m, 1H), 2.37 (s, 3H), 1.26 (t, *J* =7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.92, 199.12, 197.34, 172.90, 145.34, 136.28, 133.34, 128.57, 128.48, 128.01, 61.22, 51.15, 39.49, 37.35, 28.31, 25.70, 14.03; HRMS (ESI) m/z calcd. for $C_{19}H_{22}NaO_5$ $[M+Na]^+$ = 353.1359, found = 533.1364; IR (neat): υ 2981, 2925, 2853, 2733, 1722, 1676, 1597, 1448, 1365, 1217, 1175, 1022 cm^{-1}. (Noteworthy, diastereoisomers of **10** were inseparable through silica gel chromatography and we have not found suitable chiral stationary for its resolution)

9. References

[1] a) D. J. Peterson, *J. Organomet. Chem*. **1967**, *8*, 199; b) J.-M. Camus, J. Andrieu, P. Richard, R. Poli, *Eur. J. Inorg. Chem*. **2004**, 1081.

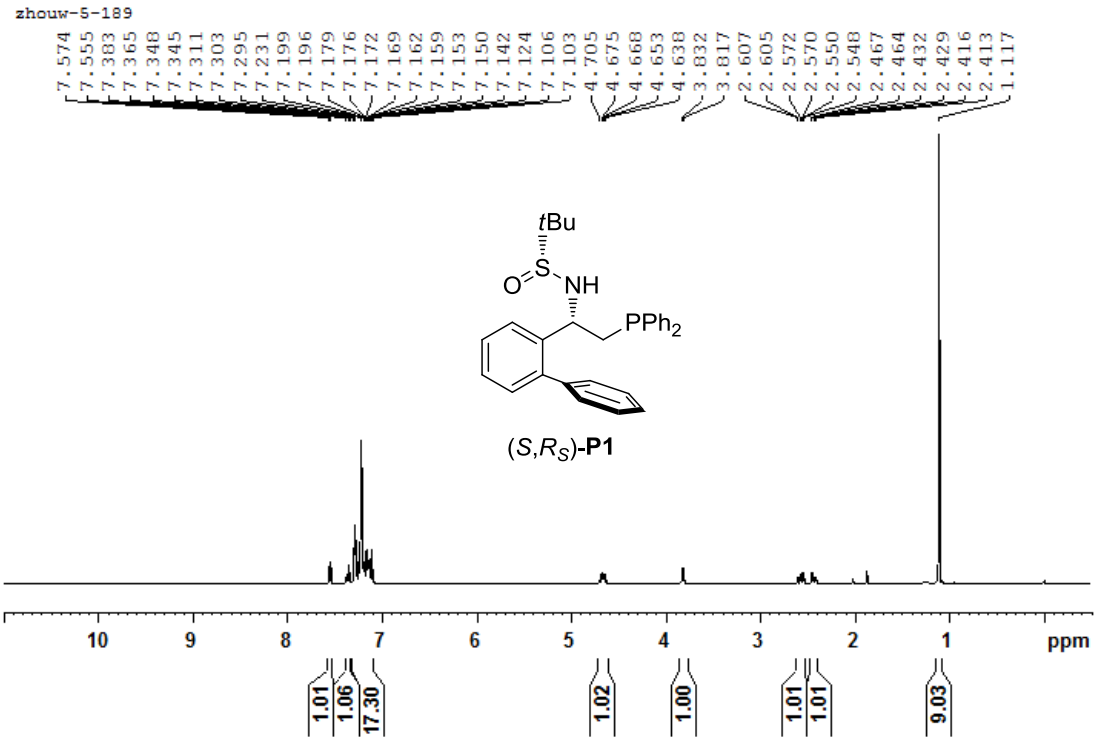
[2] a) L. B. Schenken, J. A. Ellman, *Org. Lett*. **2003**, *5*, 545; b) Z.-M. Zhang, P. Chen, W. Li, Y. Niu, X.-L. Zhao, J. Zhang, *Angew. Chem. Int. Ed*. **2014**, *53*, 4350; c) X. Su, W. Zhou, Y. Li, J. Zhang, *Angew. Chem. Int. Ed*. **2015**, *54*, 6874; d) W. Zhou, X. Su. M. Tao, C. Zhu, Q. Zhao, J. Zhang, *Angew. Chem. Int. Ed*. **2015**, *54*, 14853; e) P. Chen, X. Su, W. Zhou, Y. Xiao, J. Zhang, *Tetrahedron* **2016**, 10.1016/ j.tet.2015. 12.002.

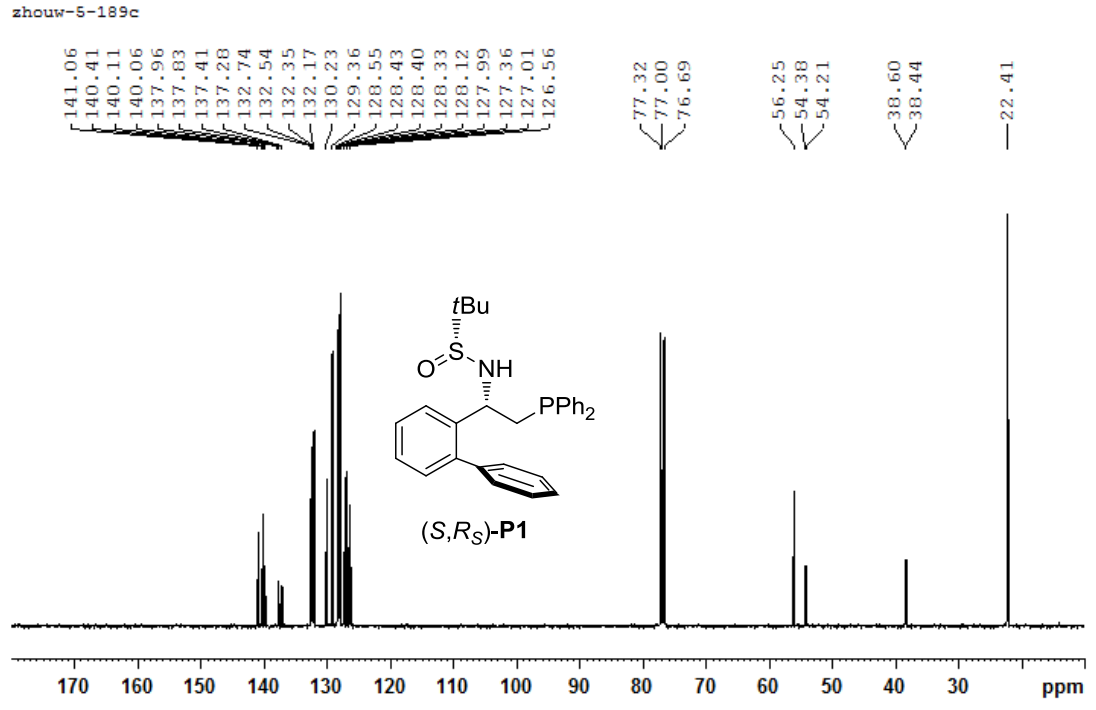
[3] H.-H. Lu, X.-F. Wang, C.-J. Yao, J.-M. Zhang, H. Wu, W.-J. Xiao, *Chem. Commun*. **2009**, 4251.

[4] R. Na, H. Liu, Z. Li, B. Wang, J. Liu, M.-A. Wang, M. Wang, J. Zhong, H. Guo, *Tetrahedron*, **2012**, *68*, 2349.

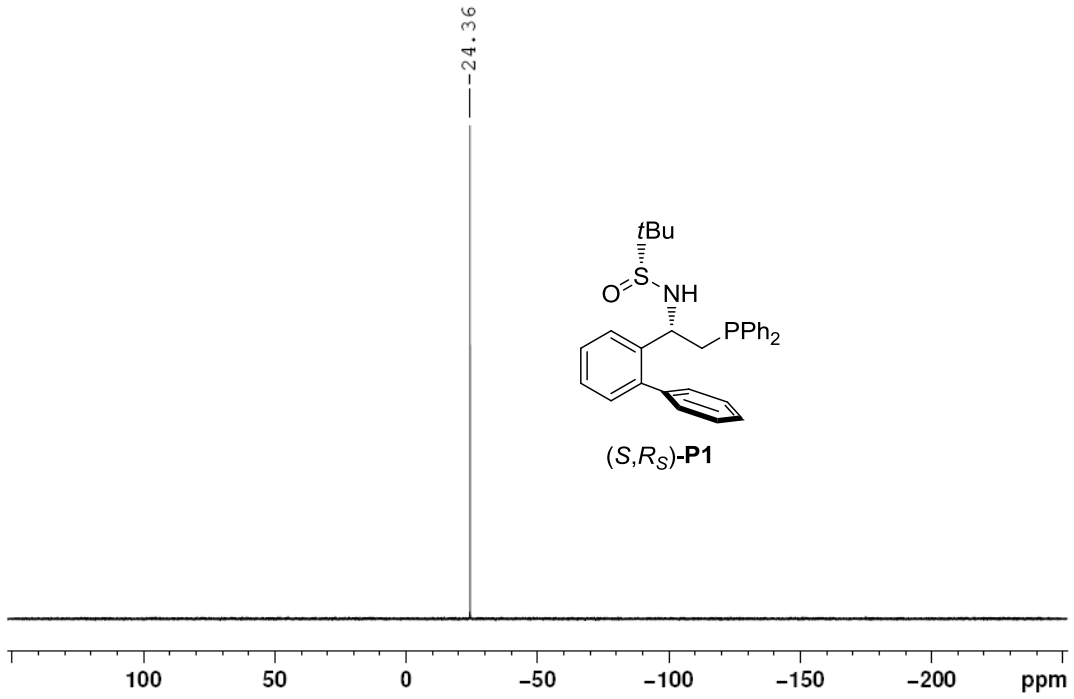
[5] X. Dong, L. Liang, E. Li, Y. Huang, *Angew. Chem.* **2015**, *127*, 1641; *Angew. Chem. Int. Ed*. **2015**, *54*, 1621.

10. 1H, 13C, 31P Spectra



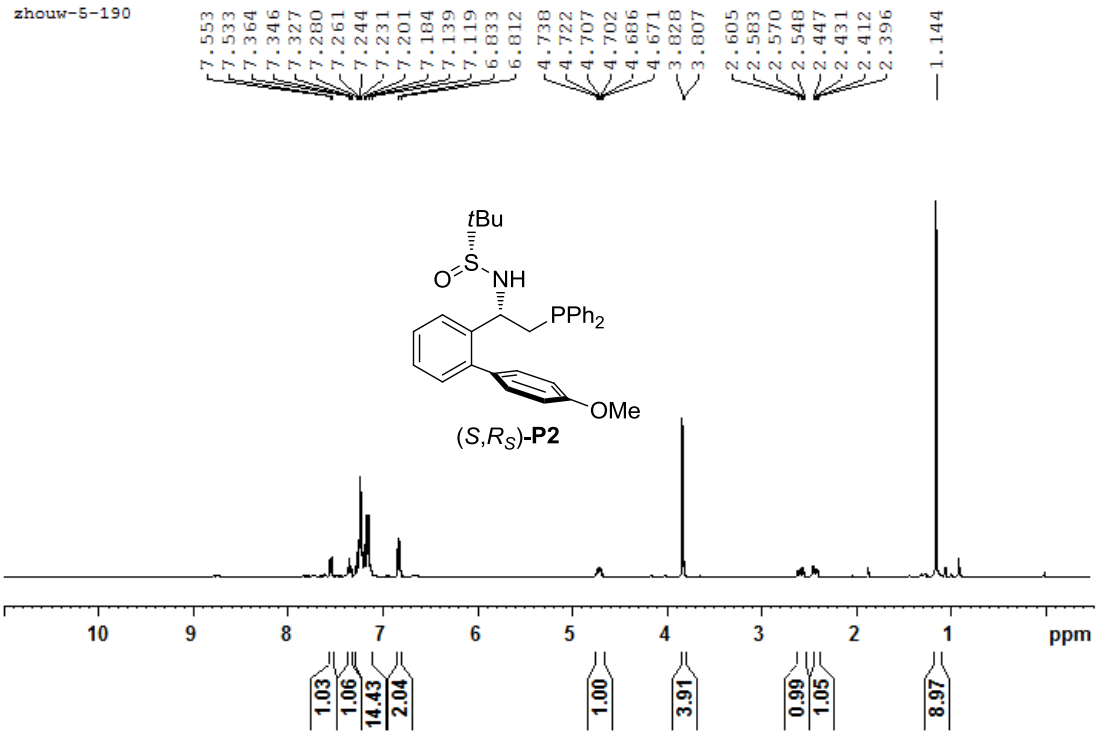


zhouw-5-189p

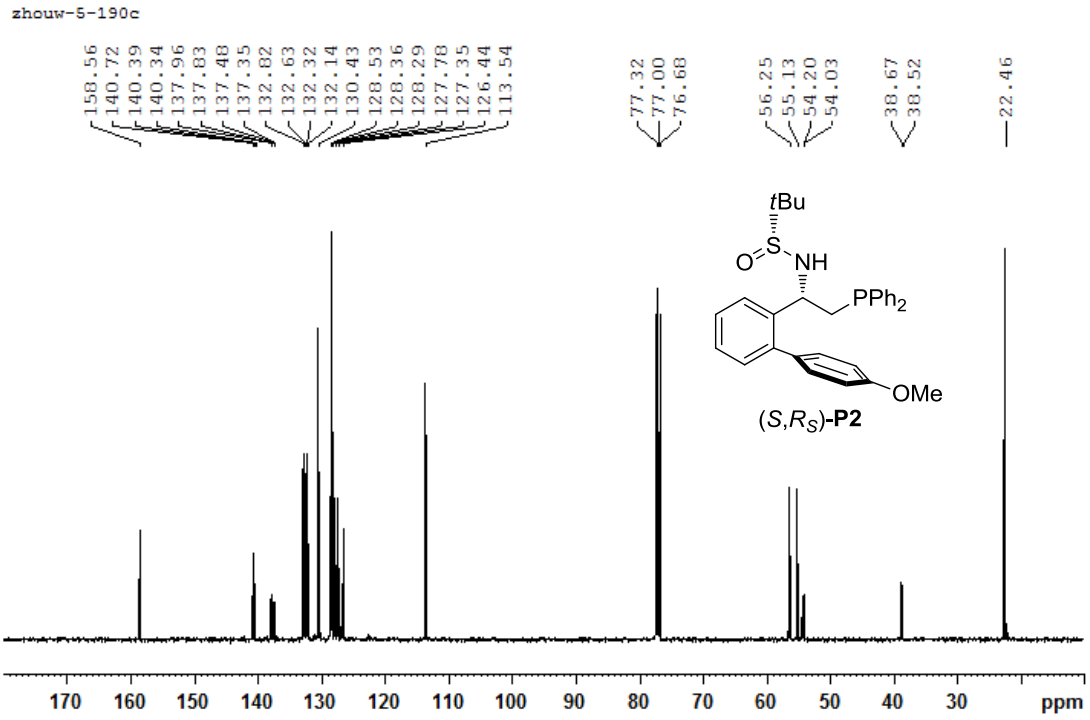


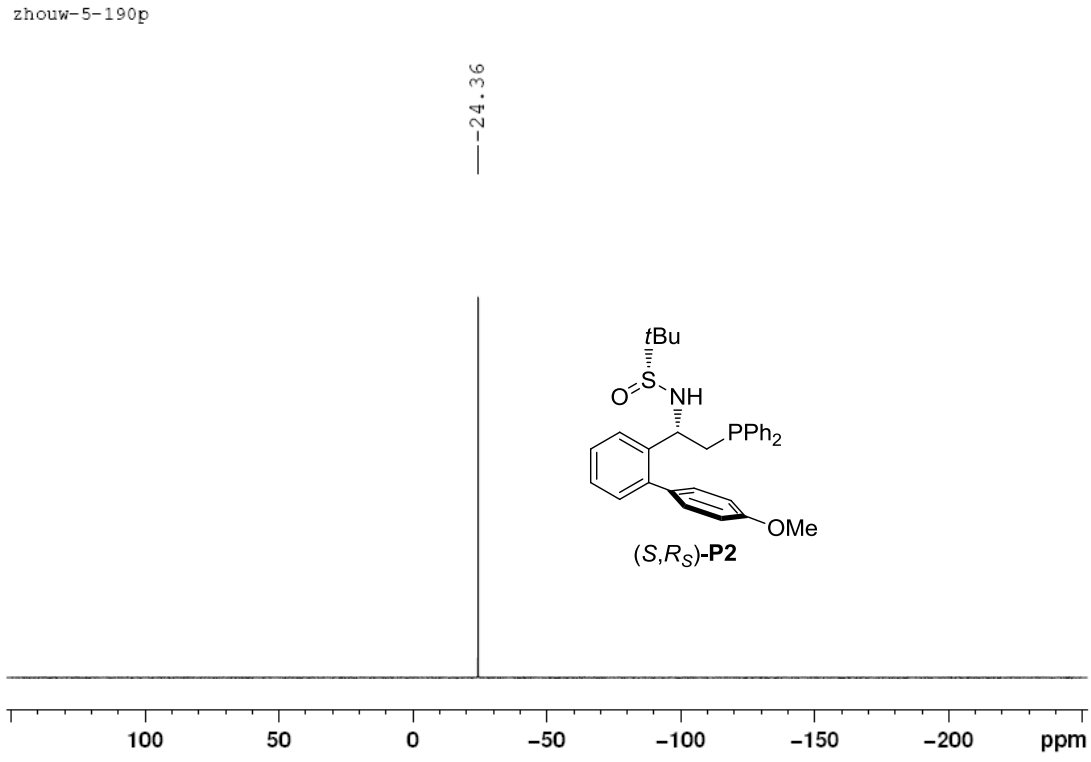
(S,R_S)-**P1**

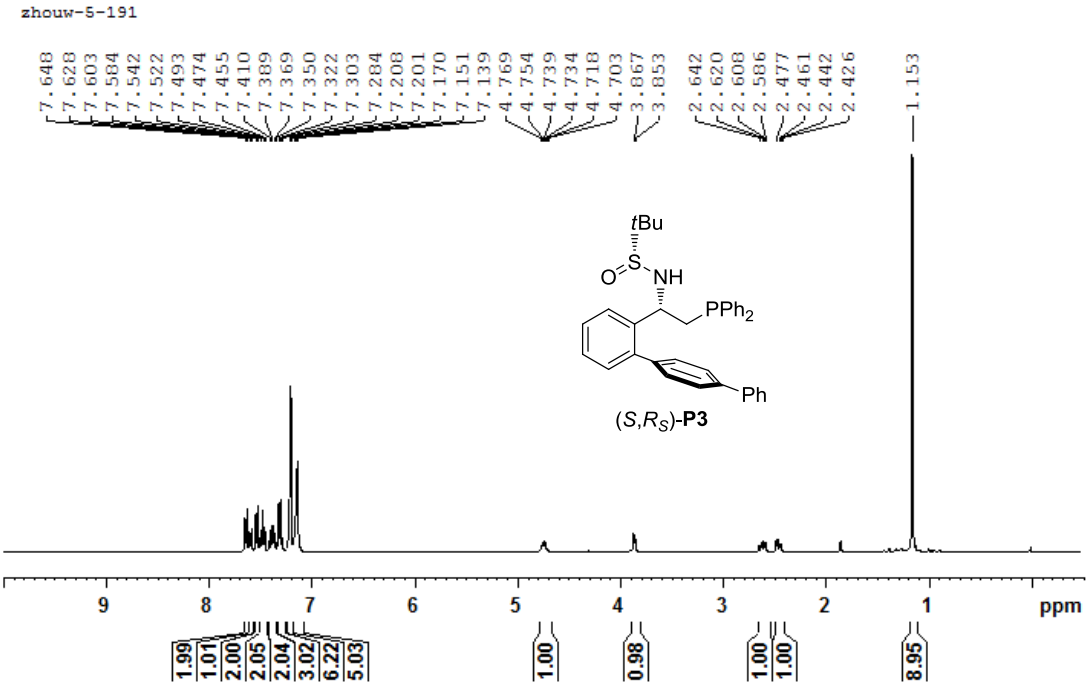
zhouw-5-190

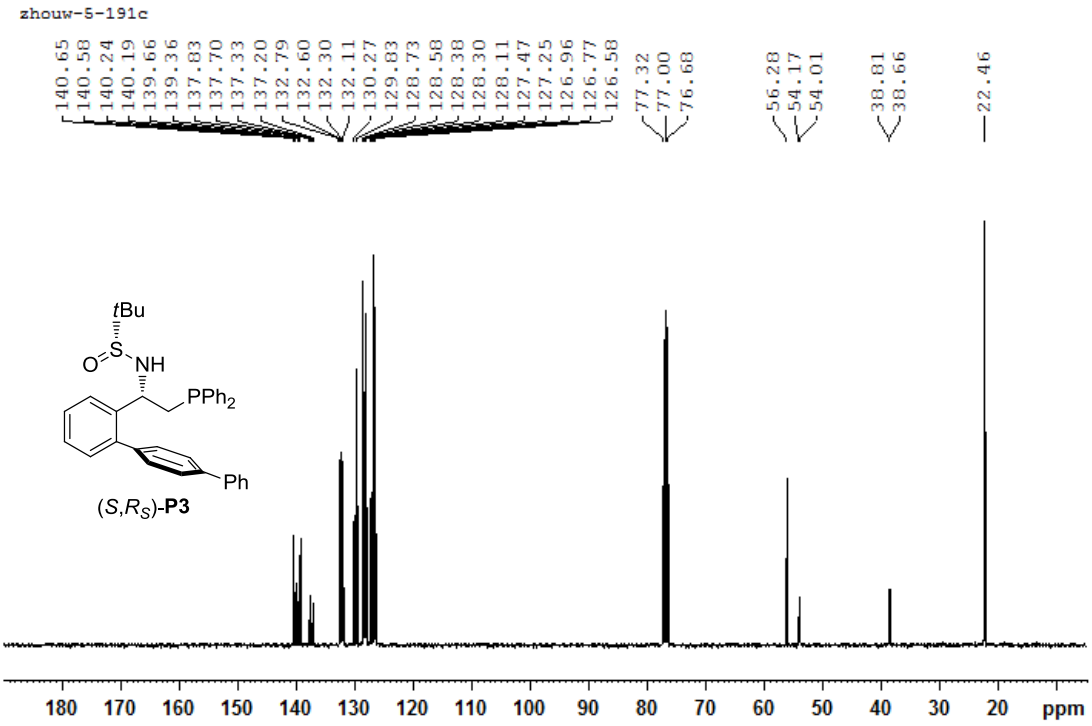


(S,R_S)-**P2**

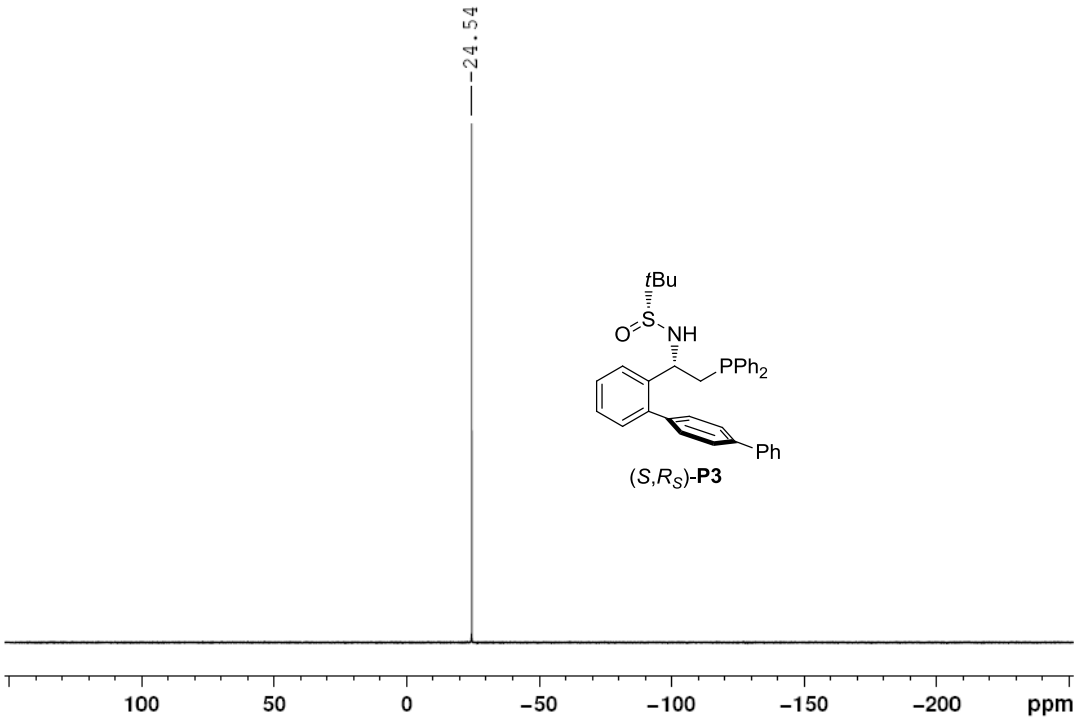

zhouw-5-190c
158.56
140.72
140.39
140.34
137.96
137.83
137.48
137.35
132.82
132.63
132.32
132.14
130.43
128.53
128.36
128.29
127.78
127.35
126.44
113.54
77.32
77.00
76.68
56.25
55.13
54.20
54.03
38.67
38.52
22.46
tBu
S
O
NH
PPh2
OMe
(S,RS)-P2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


zhouw-5-190p
24.36
tBu
S
O
NH
PPh2
OMe
(S,RS)-P2
100
50
0
-50
-100
-150
-200
ppm


zhouw-5-191
7.648
7.628
7.603
7.584
7.542
7.522
7.493
7.474
7.455
7.410
7.389
7.369
7.350
7.322
7.303
7.284
7.208
7.201
7.170
7.151
7.139
4.769
4.754
4.739
4.734
4.718
4.703
3.867
3.853
2.642
2.620
2.608
2.586
2.477
2.461
2.442
2.426
1.153
tBu
O
S
NH
PPh2
Ph
(S,RS)-P3
9
8
7
6
5
4
3
2
1
ppm
1.99
1.01
2.00
2.05
2.04
3.02
6.22
5.03
1.00
0.98
1.00
1.00
8.95

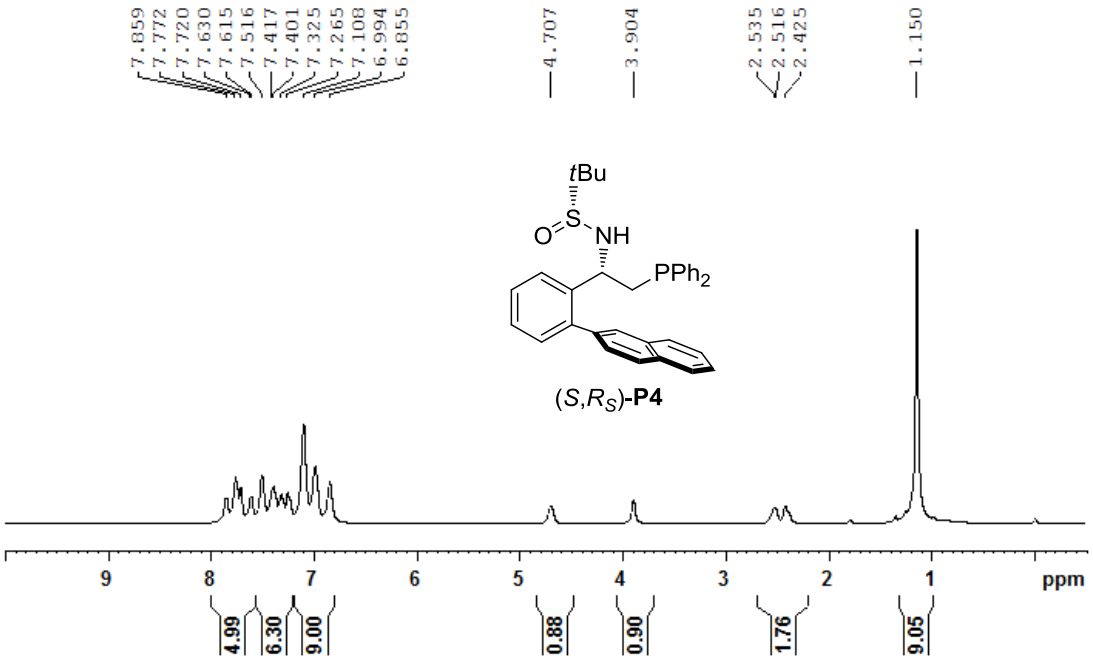

zhouw-5-191c
140.65
140.58
140.24
140.19
139.66
139.36
137.83
137.70
137.33
137.20
132.79
132.60
132.30
132.11
130.27
129.83
128.73
128.58
128.38
128.30
128.11
127.47
127.25
126.96
126.77
126.58
77.32
77.00
76.68
56.28
54.17
54.01
38.81
38.66
22.46
tBu
O
S
NH
PPh2
Ph
(S,RS)-P3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

zhouw-5-191p



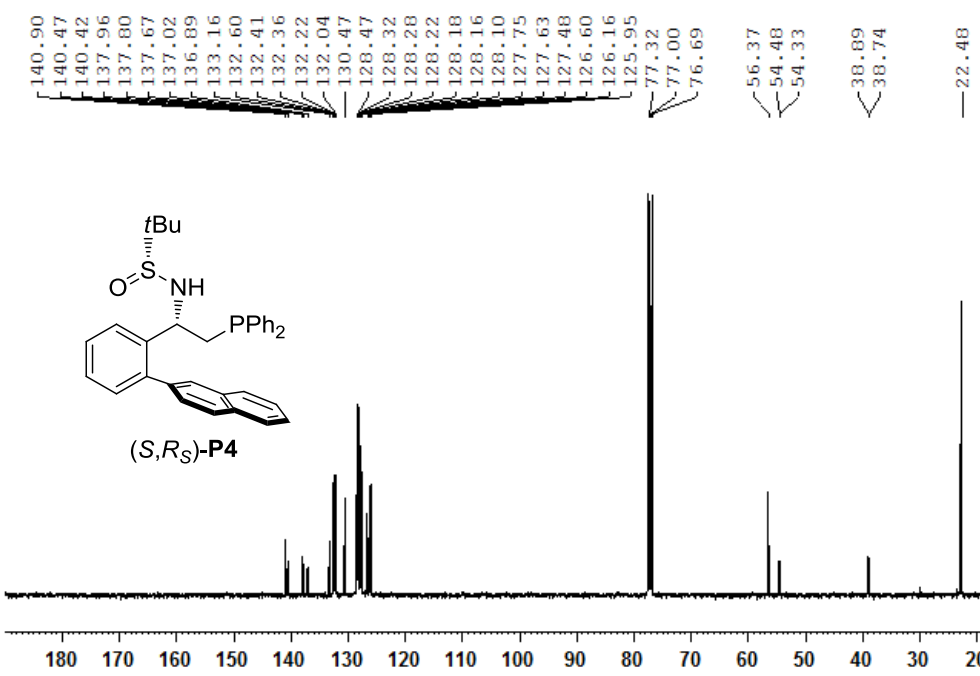
(S,R_S)-**P3**

zhouw-5-201

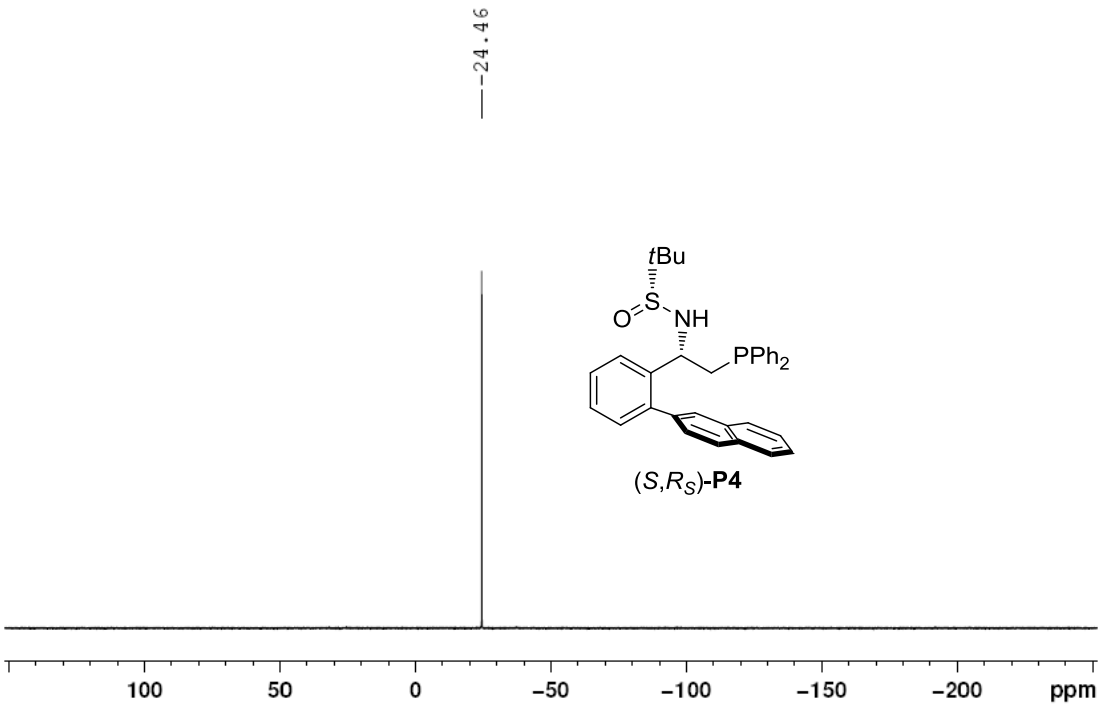


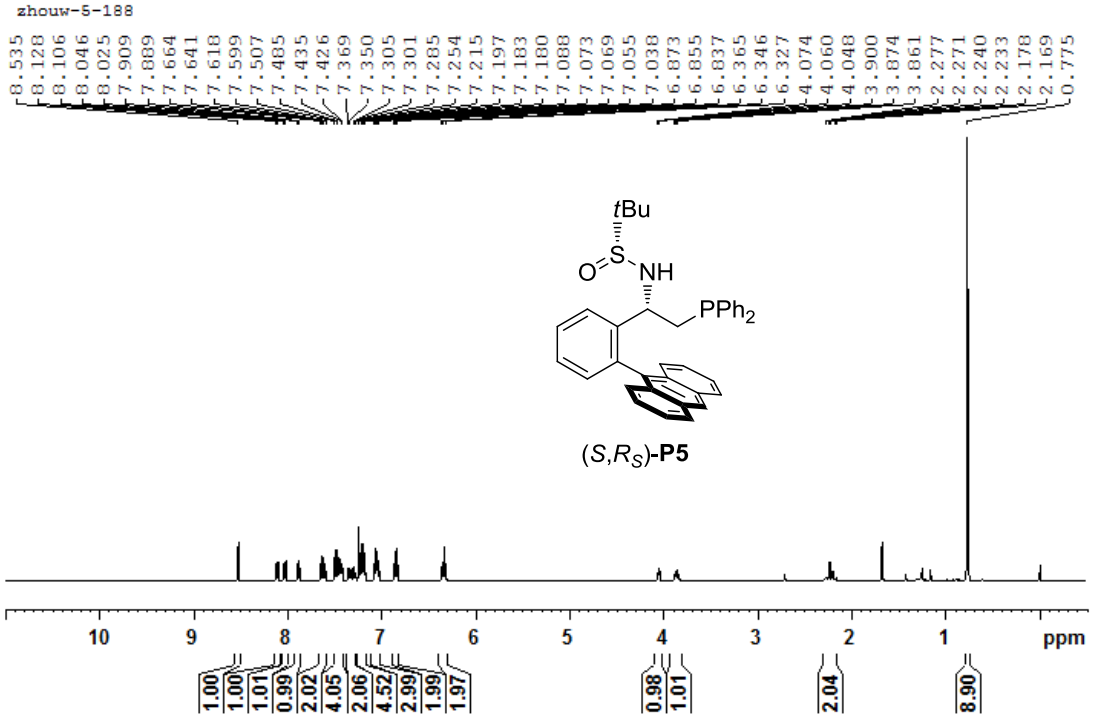
(S,R_S)-**P4**

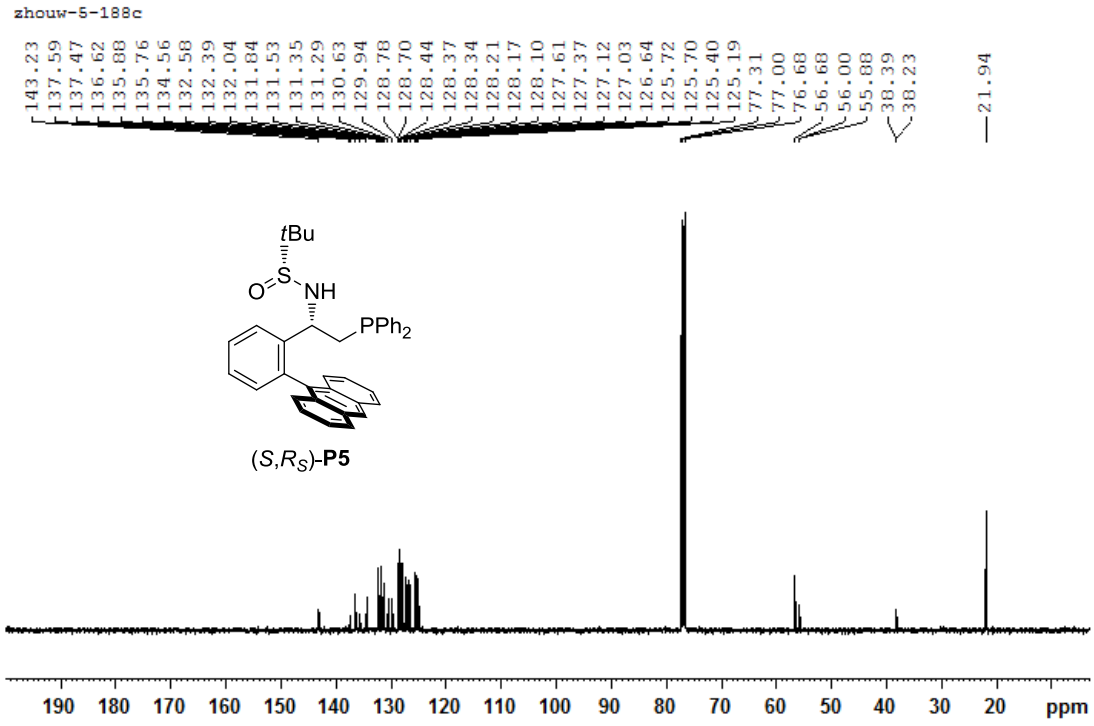
zhouw-5-201cs



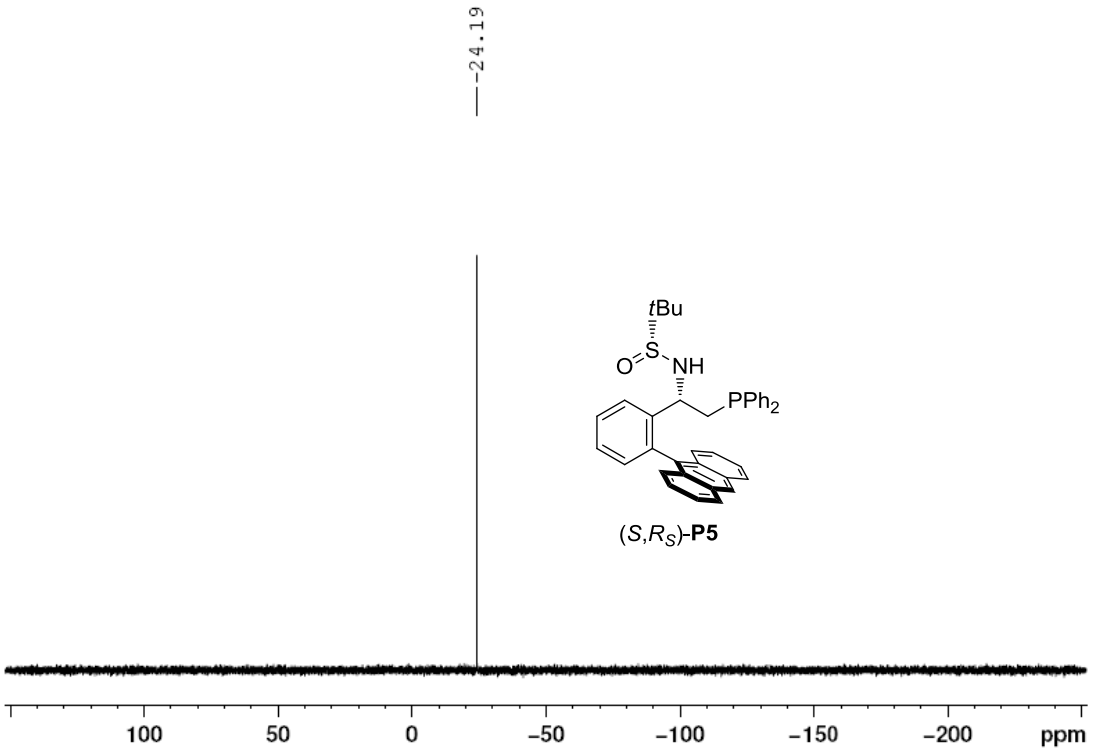
zhouw-5-201p




zhouw-5-188
8.535
8.128
8.106
8.046
8.025
7.909
7.889
7.664
7.641
7.618
7.599
7.507
7.485
7.435
7.426
7.369
7.350
7.305
7.301
7.285
7.254
7.215
7.197
7.183
7.180
7.088
7.073
7.069
7.055
7.038
6.873
6.855
6.837
6.365
6.346
6.327
4.074
4.060
4.048
3.900
3.874
3.861
2.277
2.271
2.240
2.233
2.178
2.169
0.775
tBu
O
S
NH
PPh2
(S,RS)-P5
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.01
0.99
2.02
4.05
2.06
4.52
2.99
1.99
1.97
0.98
1.01
2.04
8.90

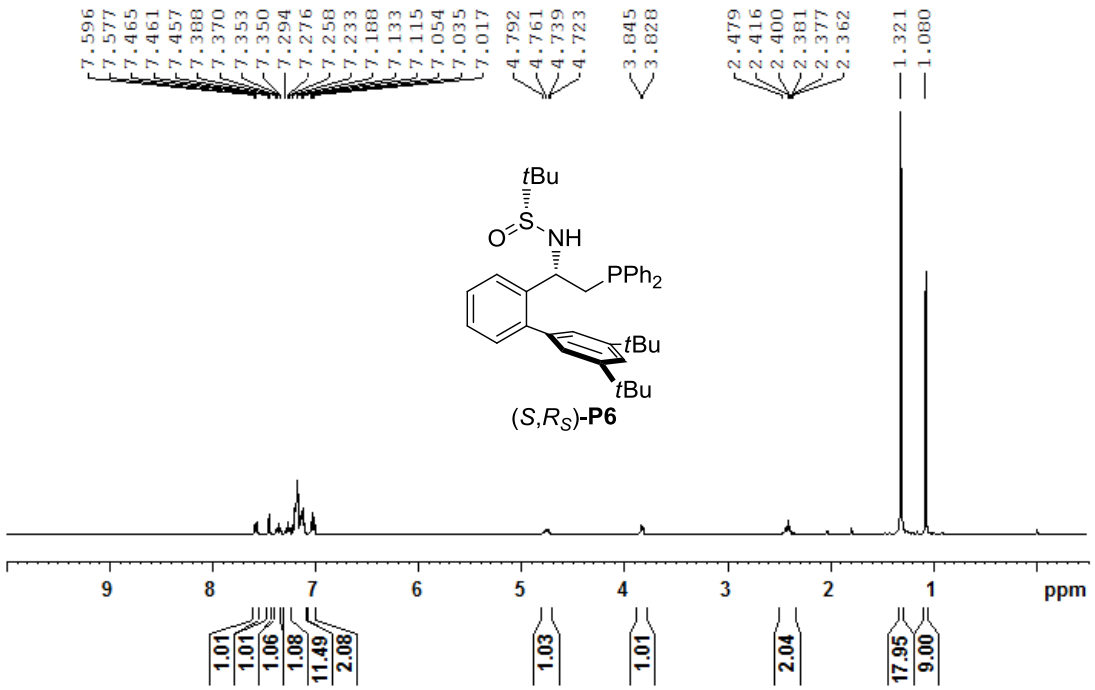

zhouw-5-188c
143.23
137.59
137.47
136.62
135.88
135.76
134.56
132.58
132.39
132.04
131.84
131.53
131.35
131.29
130.63
129.94
128.78
128.70
128.44
128.37
128.34
128.21
128.17
128.10
127.61
127.37
127.12
127.03
126.64
125.72
125.70
125.40
125.19
77.31
77.00
76.68
56.68
56.00
55.88
38.39
38.23
21.94
tBu
O
S
NH
PPh2
(S,RS)-P5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

zhouw-5-188p



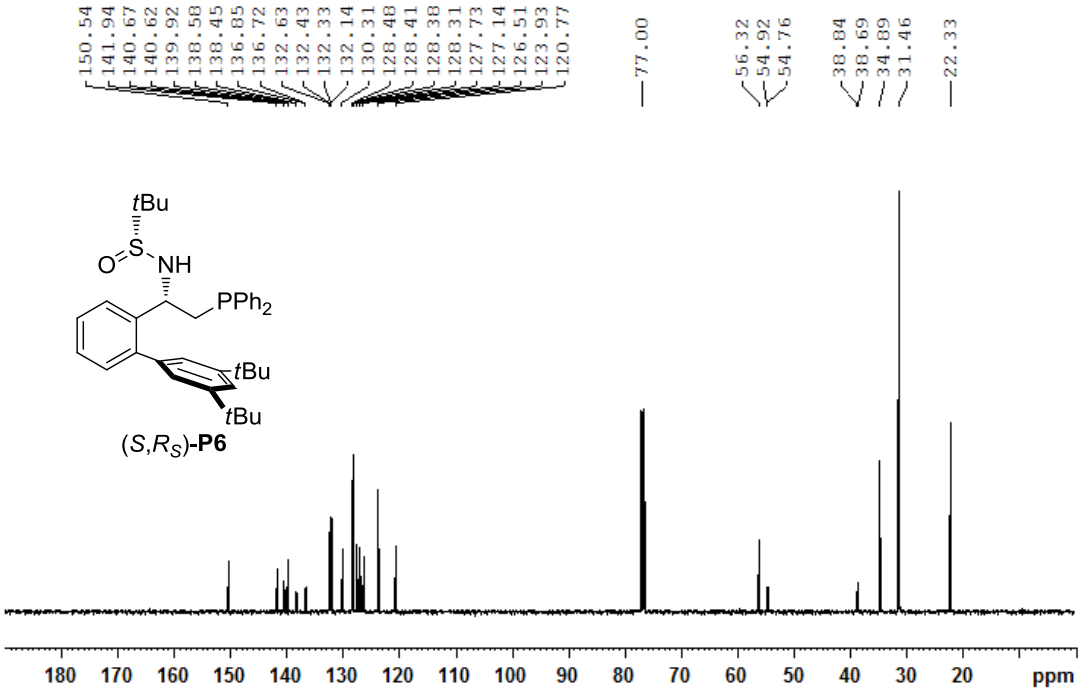
(S,R_S)-**P5**

zhouw-5-193



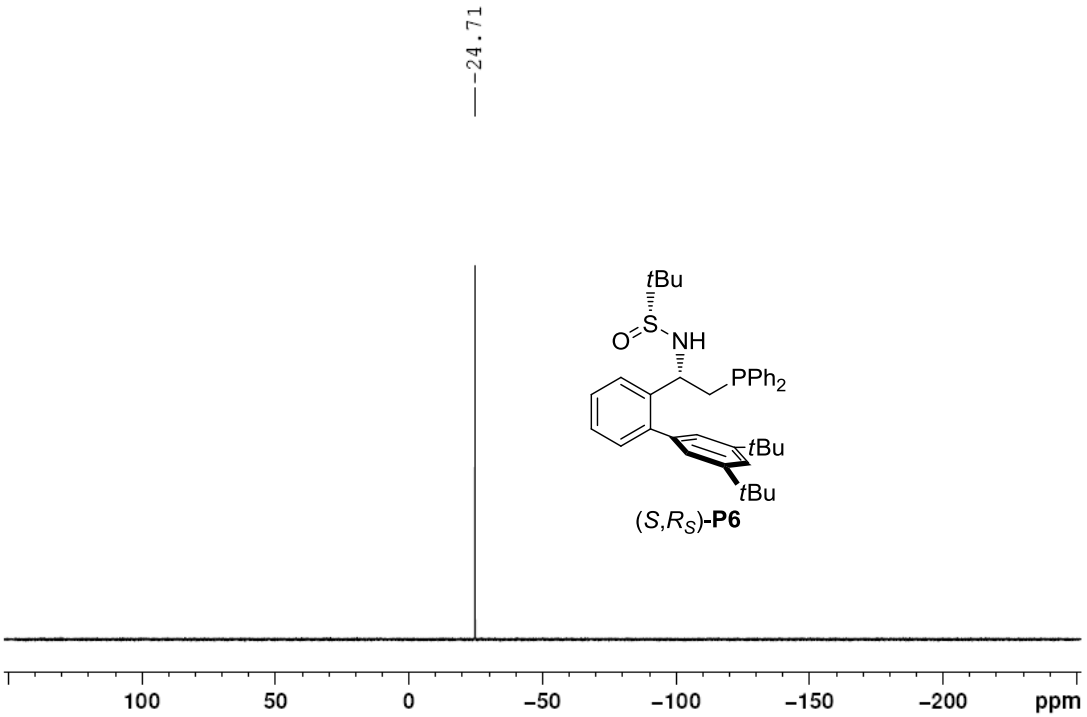
(S,R_S)-**P6**

zhouw-5-193c

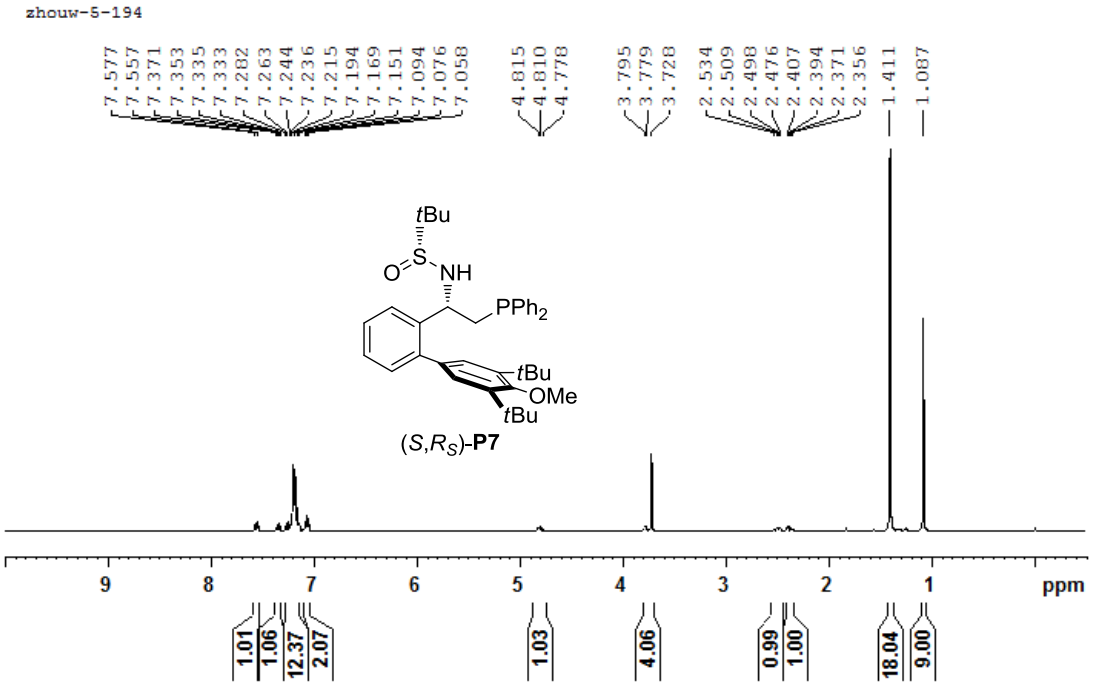


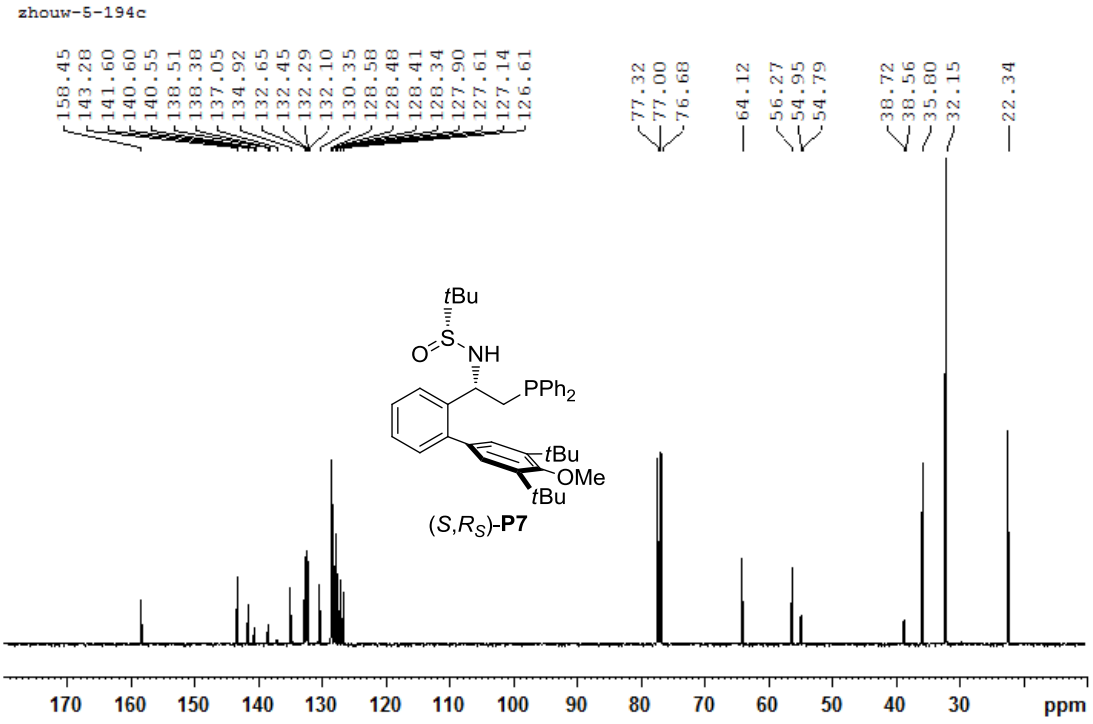
(S,R_S)-**P6**

zhouw-5-193p

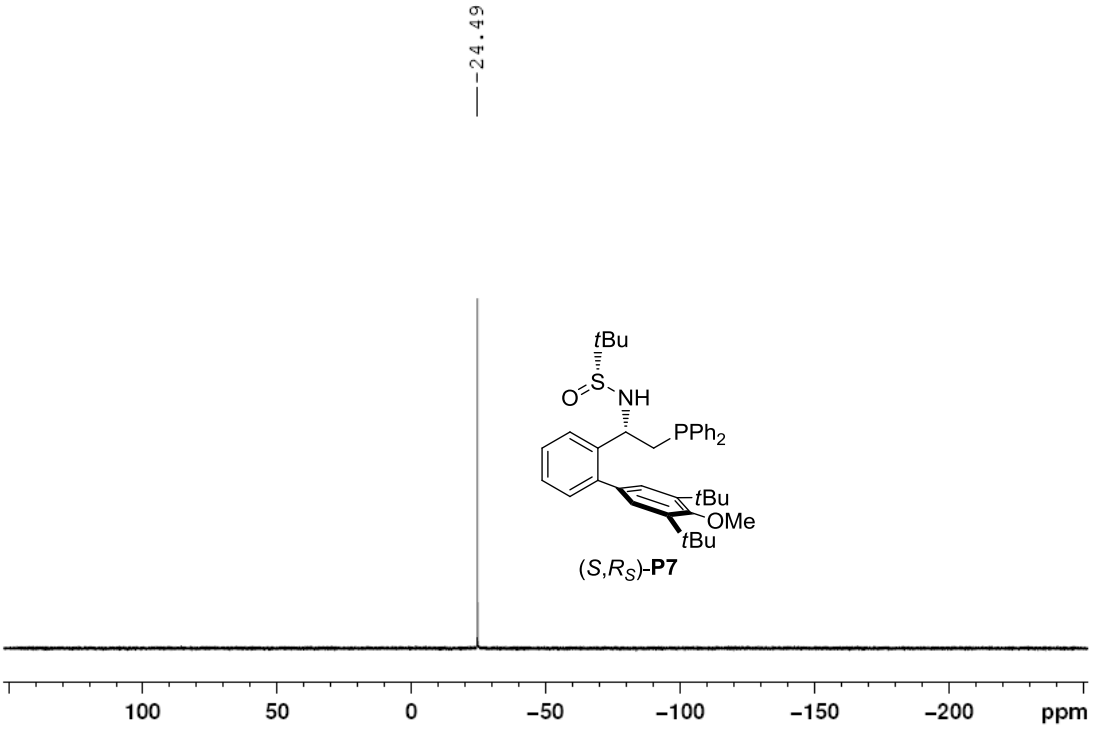


(S,R_S)-**P6**


zhouw-5-194
7.577
7.557
7.371
7.353
7.335
7.333
7.282
7.263
7.244
7.236
7.215
7.194
7.169
7.151
7.094
7.076
7.058
4.815
4.810
4.778
3.795
3.779
3.728
2.534
2.509
2.498
2.476
2.407
2.394
2.371
2.356
1.411
1.087
tBu
S
O
NH
PPh2
tBu
OMe
tBu
(S,RS)-P7
9
8
7
6
5
4
3
2
1
ppm
1.01
1.06
12.37
2.07
1.03
4.06
0.99
1.00
18.04
9.00

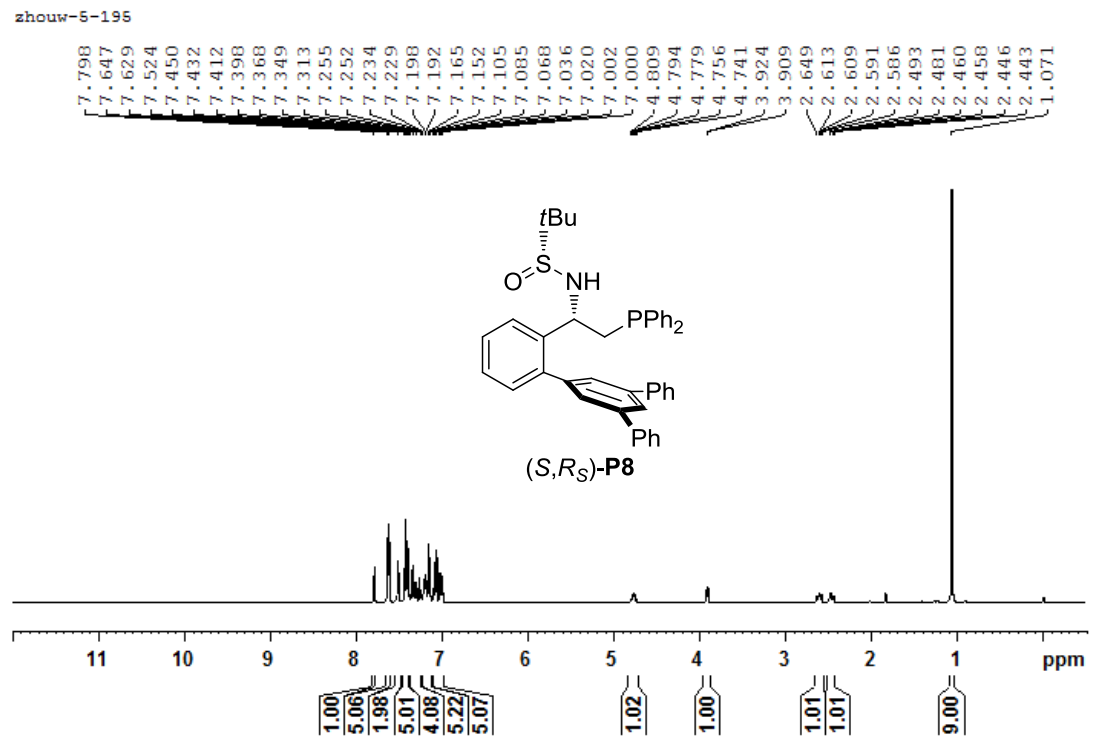

zhouw-5-194c
158.45
143.28
141.60
140.60
140.55
138.51
138.38
137.05
134.92
132.65
132.45
132.29
132.10
130.35
128.58
128.48
128.41
128.34
127.90
127.61
127.14
126.61
77.32
77.00
76.68
64.12
56.27
54.95
54.79
38.72
38.56
35.80
32.15
22.34
tBu
S
O
NH
PPh2
tBu
OMe
tBu
(S,RS)-P7
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

zhouw-5-194p

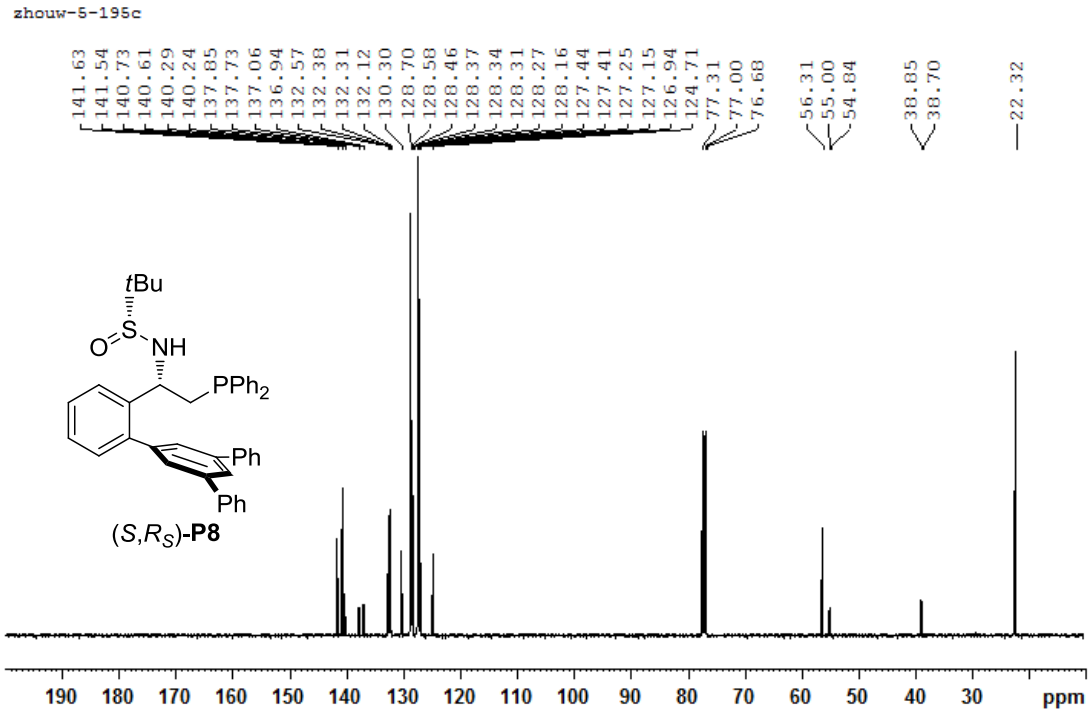


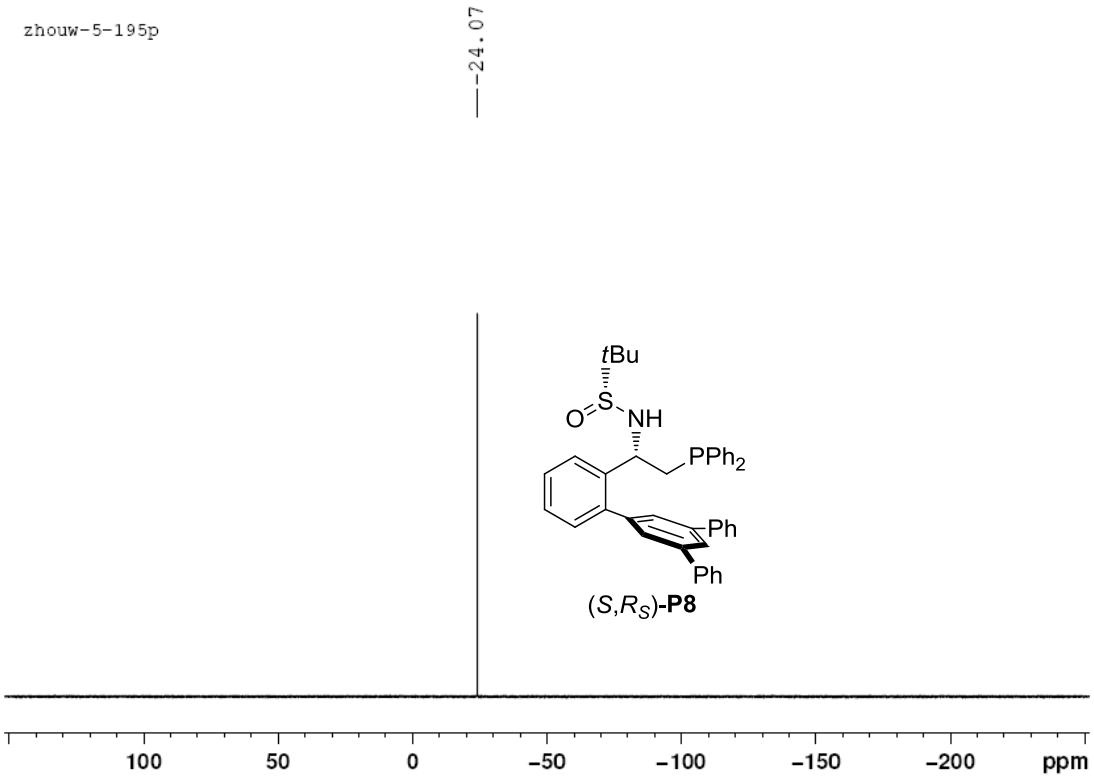
(S,R_S)-**P7**

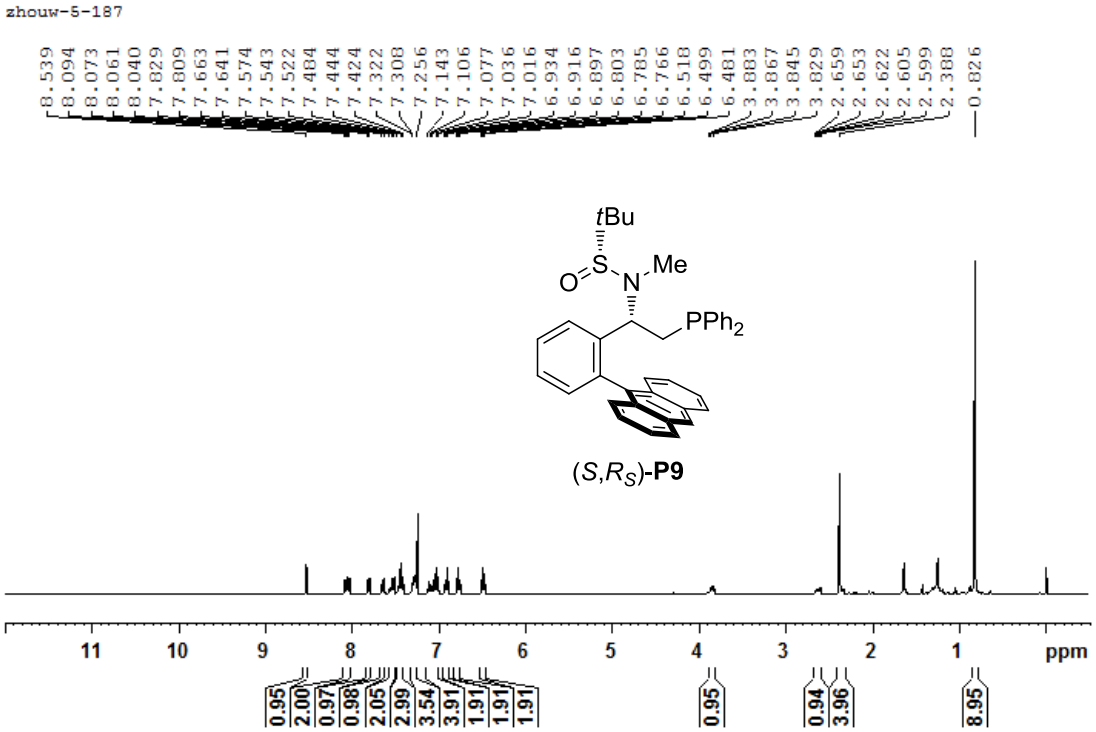
zhouw-5-195

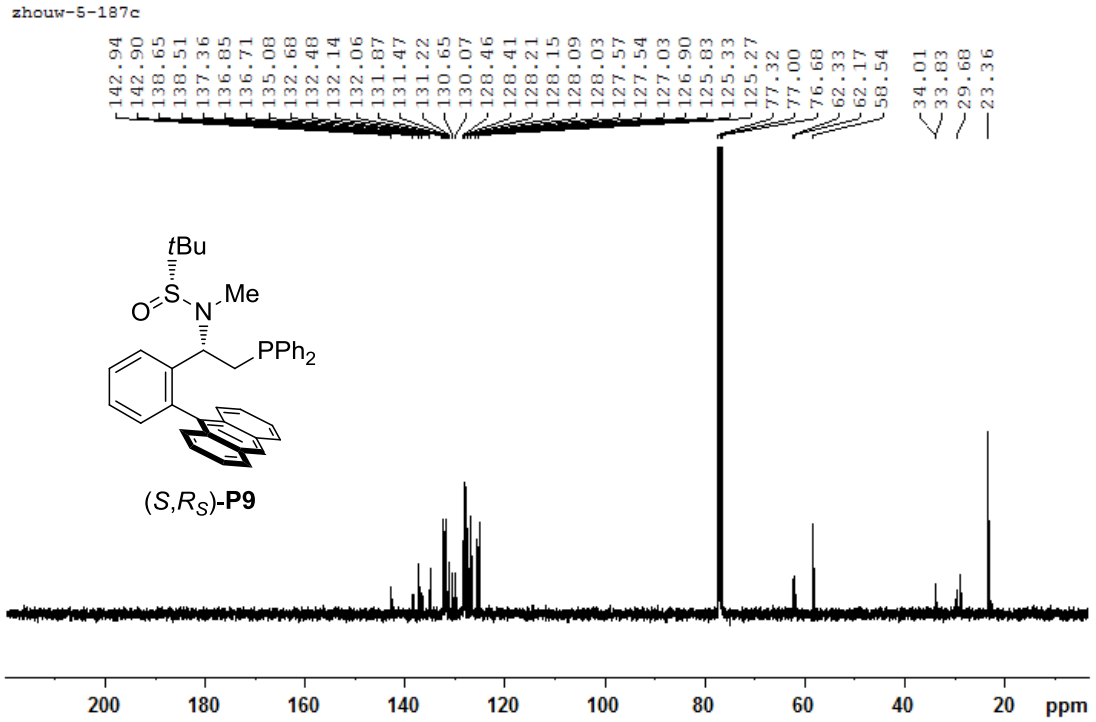


(S,R_S)-**P8**

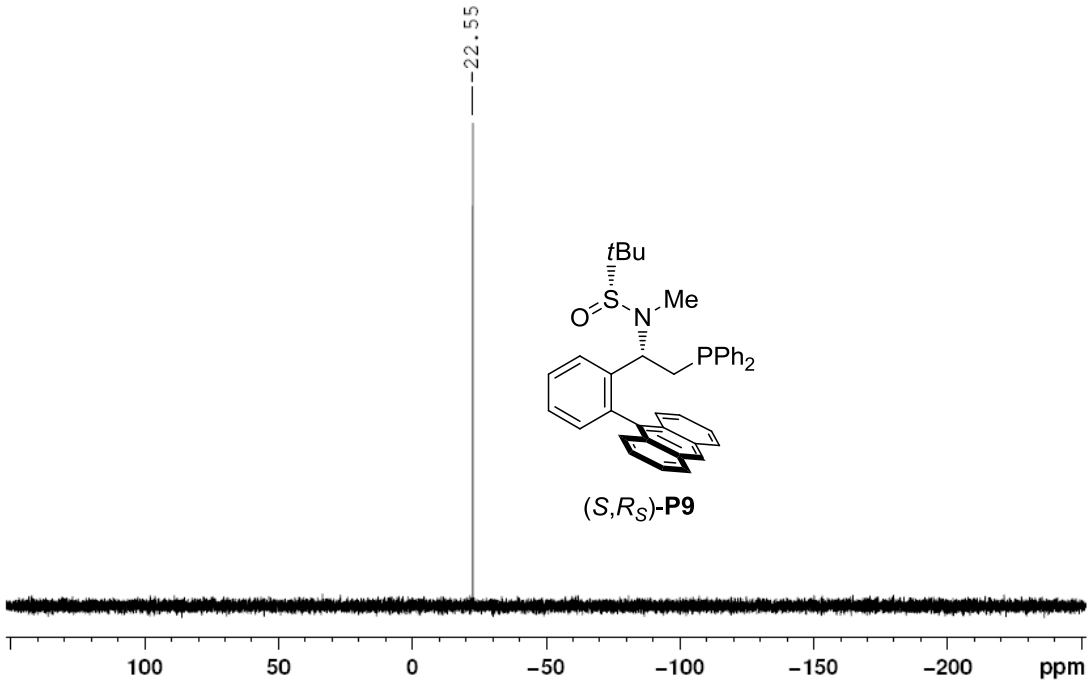

zhouw-5-195c
141.63
141.54
140.73
140.61
140.29
140.24
137.85
137.73
137.06
136.94
132.57
132.38
132.31
132.12
130.30
128.70
128.58
128.46
128.37
128.34
128.31
128.27
128.16
127.44
127.41
127.25
127.15
126.94
124.71
77.31
77.00
76.68
56.31
55.00
54.84
38.85
38.70
22.32
tBu
S
O
NH
PPh2
Ph
Ph
(S,RS)-P8
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


zhouw-5-195p
-24.07
tBu
S
O
NH
PPh2
Ph
Ph
(S,RS)-P8
100
50
0
-50
-100
-150
-200
ppm

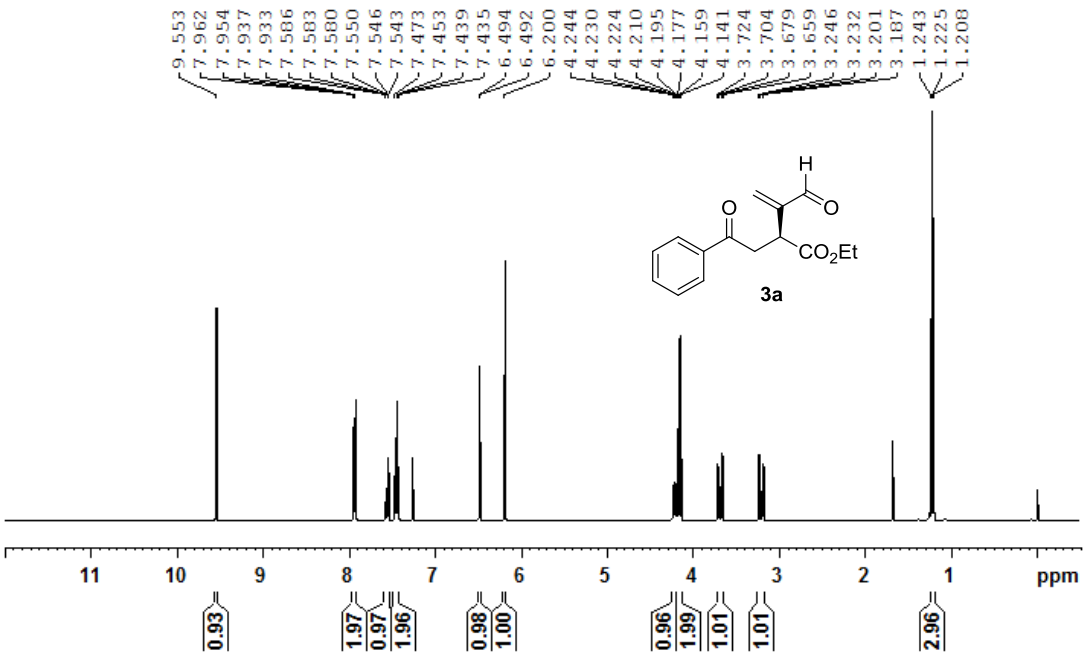

zhouw-5-187
8.539
8.094
8.073
8.061
8.040
7.829
7.809
7.663
7.641
7.574
7.543
7.522
7.484
7.444
7.424
7.322
7.308
7.256
7.143
7.106
7.077
7.036
7.016
6.934
6.916
6.897
6.803
6.785
6.766
6.518
6.499
6.481
3.883
3.867
3.845
3.829
2.659
2.653
2.622
2.605
2.599
2.388
0.826
tBu
S
O
N
Me
PPh2
(S,RS)-P9
11
10
9
8
7
6
5
4
3
2
1
ppm
0.95
2.00
0.97
0.98
2.05
2.99
3.54
3.91
1.91
1.91
1.91
0.95
0.94
3.96
8.95

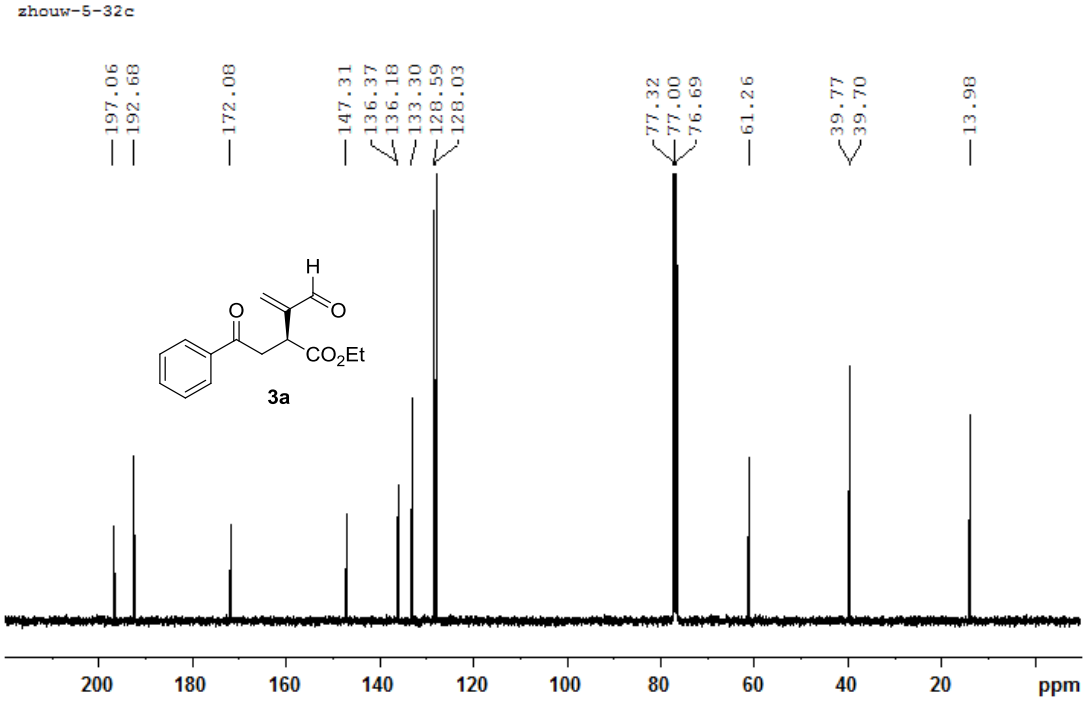

zhouw-5-187c
142.94
142.90
138.65
138.51
137.36
136.85
136.71
135.08
132.68
132.48
132.14
132.06
131.87
131.47
131.22
130.65
130.07
128.46
128.41
128.21
128.15
128.09
128.03
127.57
127.54
127.03
126.90
125.83
125.33
125.27
77.32
77.00
76.68
62.33
62.17
58.54
34.01
33.83
29.68
23.36
tBu
S
O
N
Me
PPh2
(S,RS)-P9
200
180
160
140
120
100
80
60
40
20
ppm

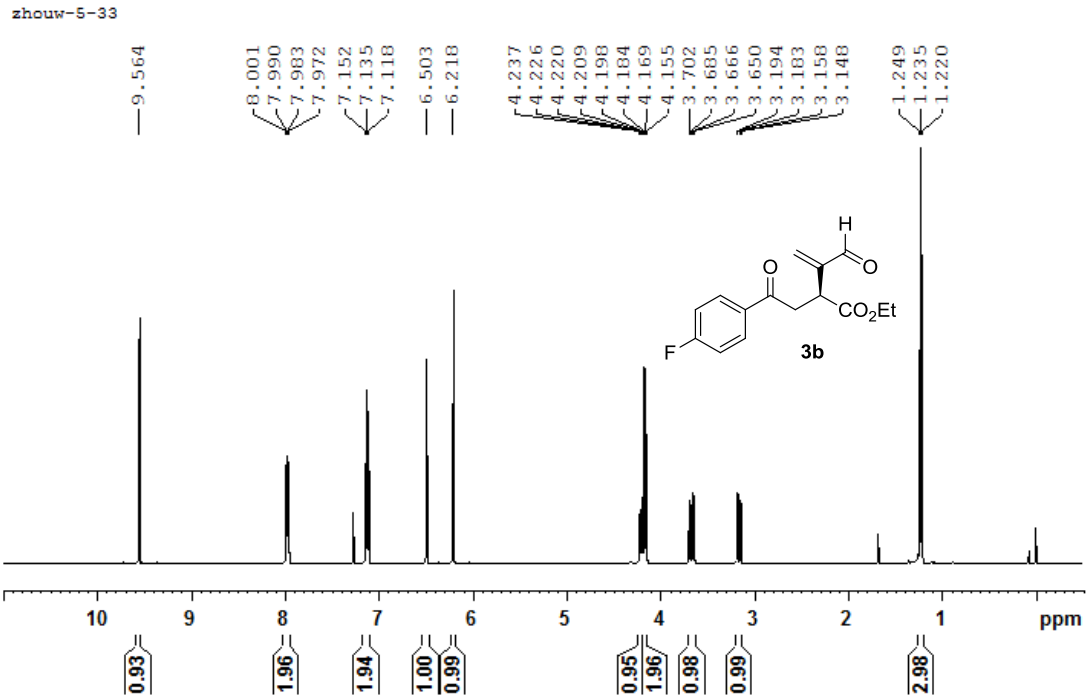
zhouw-5-187p

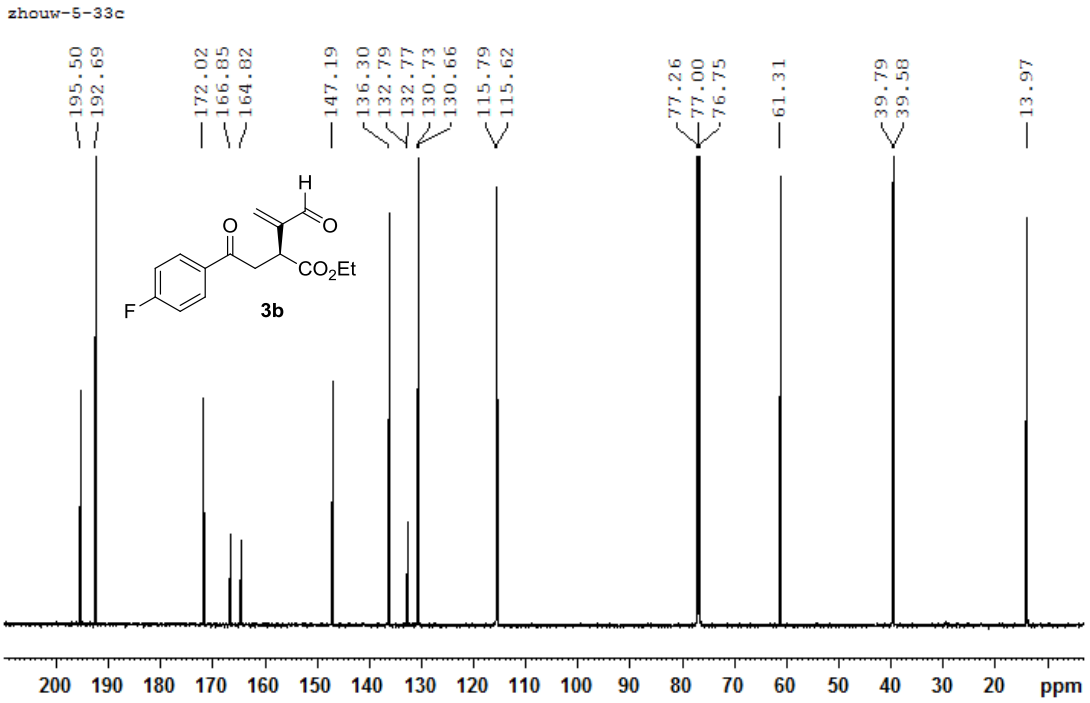


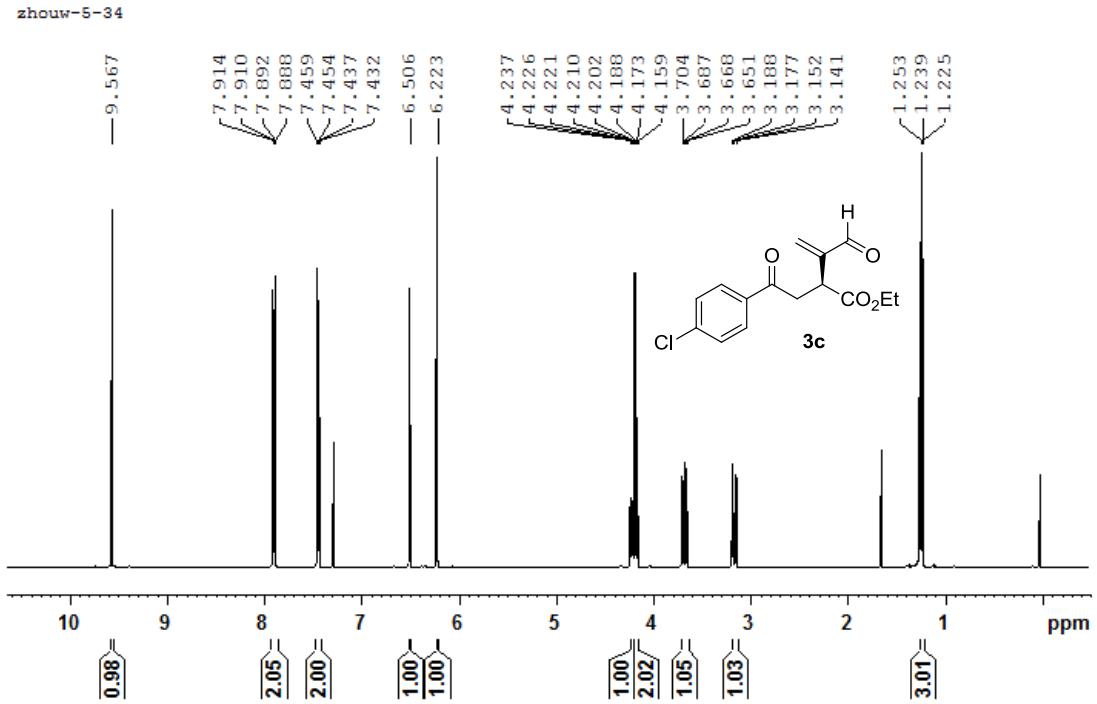
zhouw-5-32

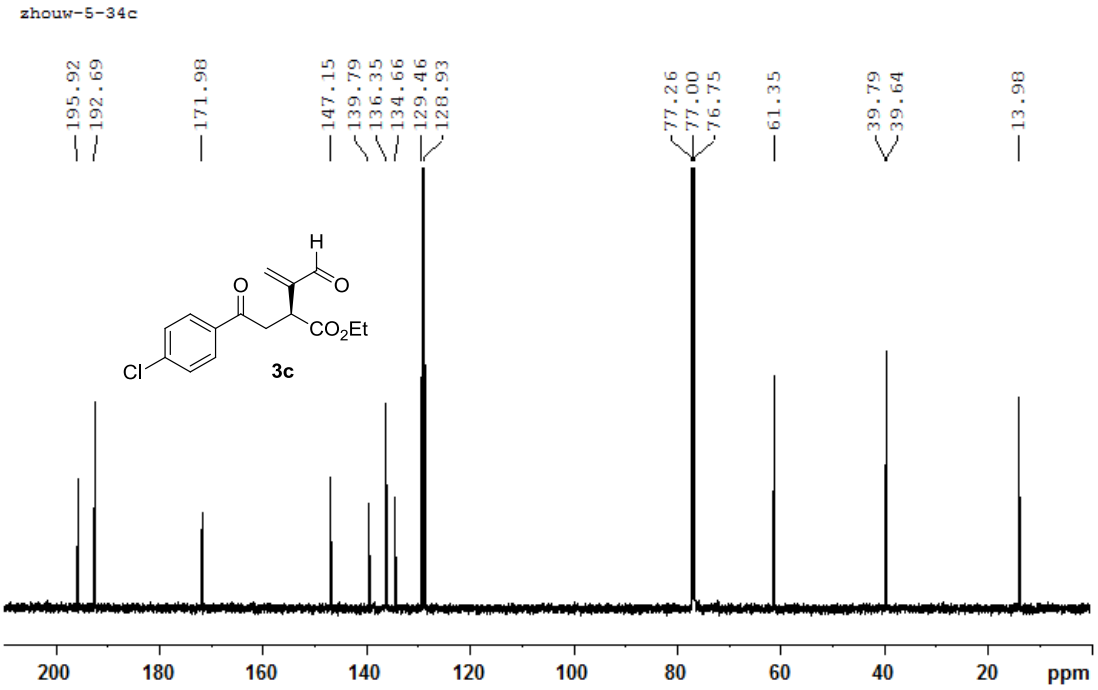


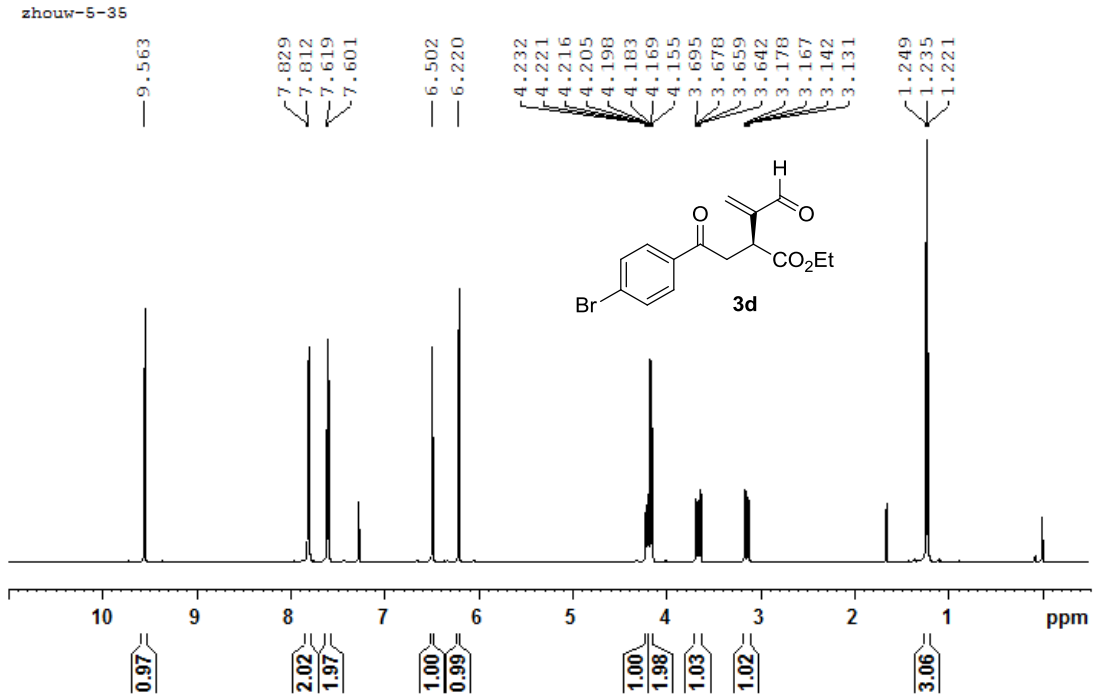

zhouw-5-32c
197.06
192.68
172.08
147.31
136.37
136.18
133.30
128.59
128.03
77.32
77.00
76.69
61.26
39.77
39.70
13.98
H
O
O
CO2Et
3a
200
180
160
140
120
100
80
60
40
20
ppm


zhouw-5-33
9.564
8.001
7.990
7.983
7.972
7.152
7.135
7.118
6.503
6.218
4.237
4.226
4.220
4.209
4.198
4.184
4.169
4.155
3.702
3.685
3.666
3.650
3.194
3.183
3.158
3.148
1.249
1.235
1.220
H
O
O
CO2Et
F
3b
10
9
8
7
6
5
4
3
2
1
ppm
0.93
1.96
1.94
1.00
0.99
0.95
1.96
0.98
0.99
2.98

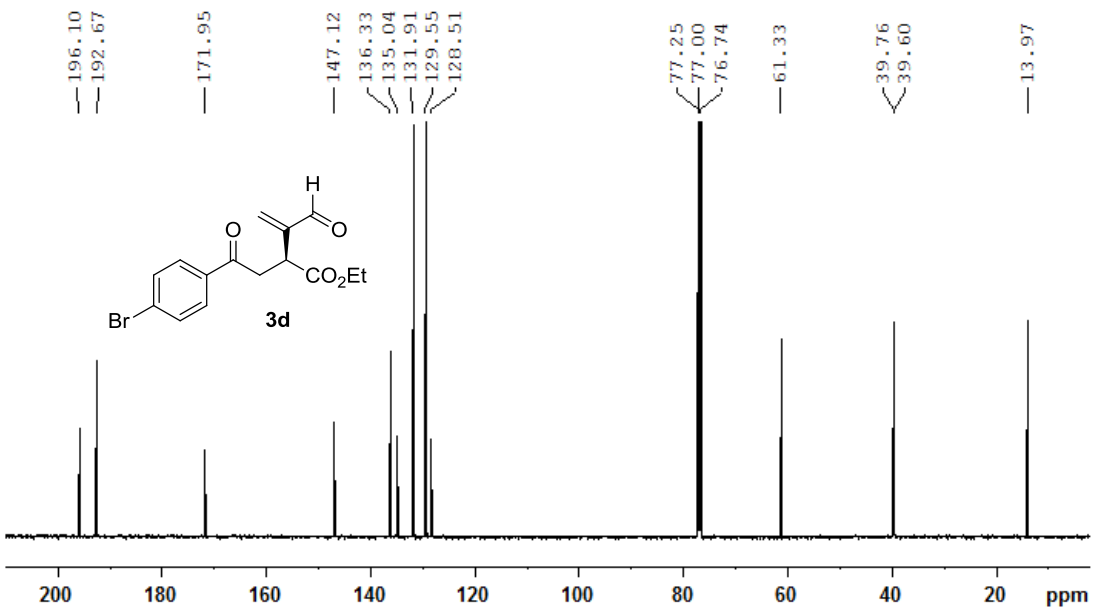

zhouw-5-33c
195.50
192.69
172.02
166.85
164.82
147.19
136.30
132.79
132.77
130.73
130.66
115.79
115.62
77.26
77.00
76.75
61.31
39.79
39.58
13.97
H
O
O
CO2Et
F
3b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


zhouw-5-34
9.567
7.914
7.910
7.892
7.888
7.459
7.454
7.437
7.432
6.506
6.223
4.237
4.226
4.221
4.210
4.202
4.188
4.173
4.159
3.704
3.687
3.668
3.651
3.188
3.177
3.152
3.141
1.253
1.239
1.225
H
O
O
CO2Et
Cl
3c
10 9 8 7 6 5 4 3 2 1 ppm
0.98
2.05
2.00
1.00
1.00
1.00
2.02
1.05
1.03
3.01

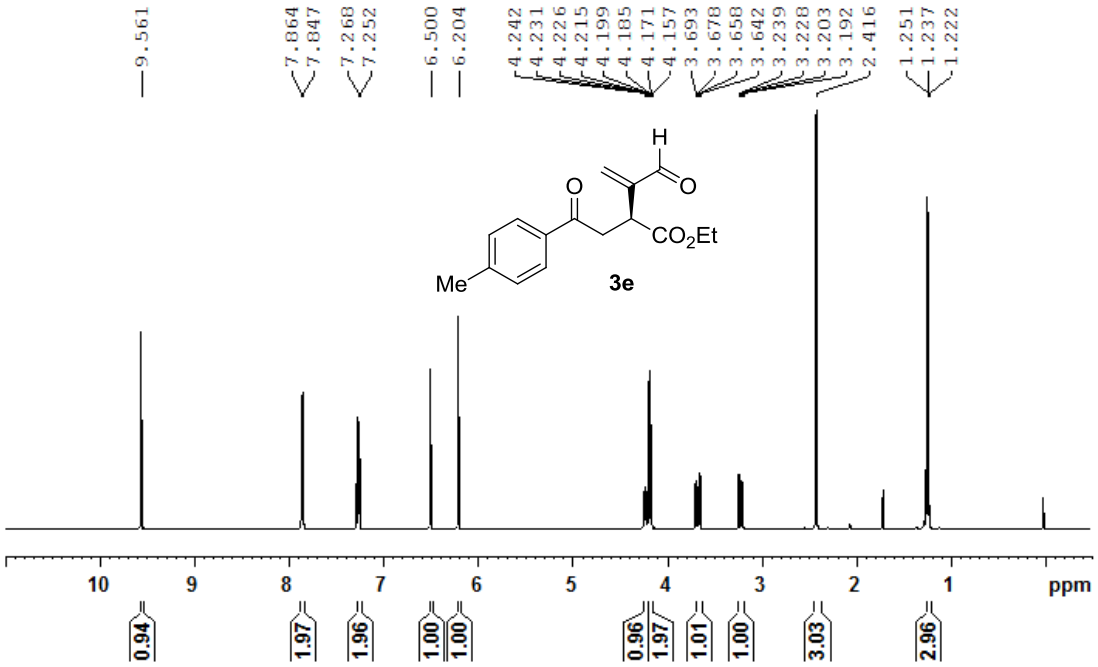

zhouw-5-34c
195.92
192.69
171.98
147.15
139.79
136.35
134.66
129.46
128.93
77.26
77.00
76.75
61.35
39.79
39.64
13.98
H
O
O
CO2Et
Cl
3c
200
180
160
140
120
100
80
60
40
20
ppm

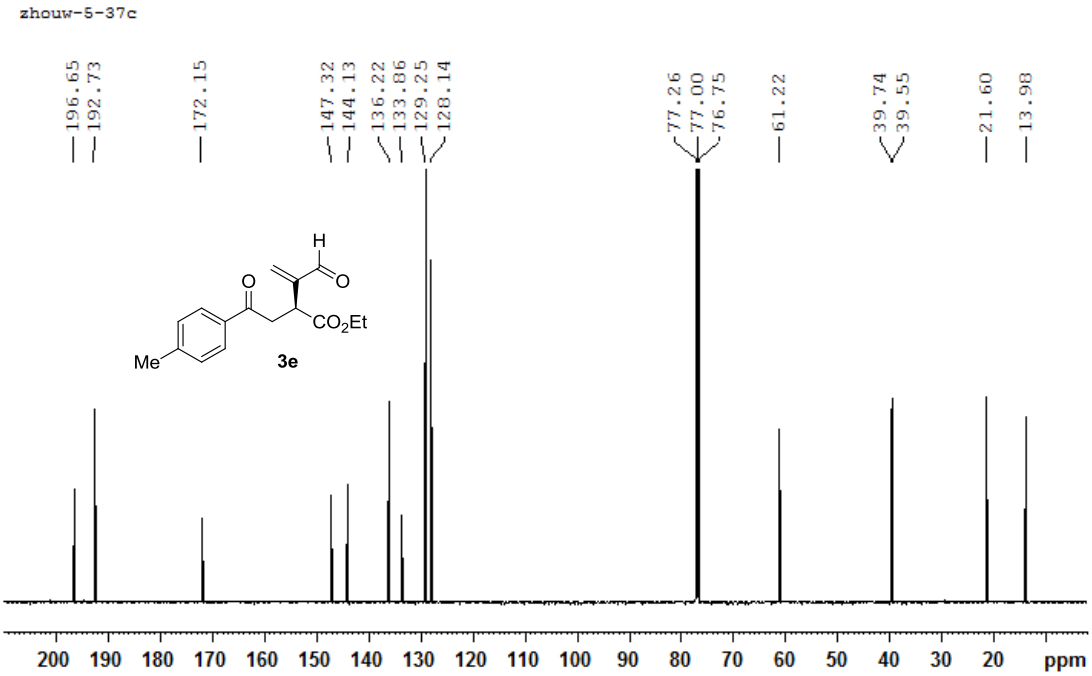

zhouw-5-35
9.563
7.829
7.812
7.619
7.601
6.502
6.220
4.232
4.221
4.216
4.205
4.198
4.183
4.169
4.155
3.695
3.678
3.659
3.642
3.178
3.167
3.142
3.131
1.249
1.235
1.221
H
O
O
CO2Et
Br
3d
10
9
8
7
6
5
4
3
2
1
ppm
0.97
2.02
1.97
1.00
0.99
1.00
1.98
1.03
1.02
3.06

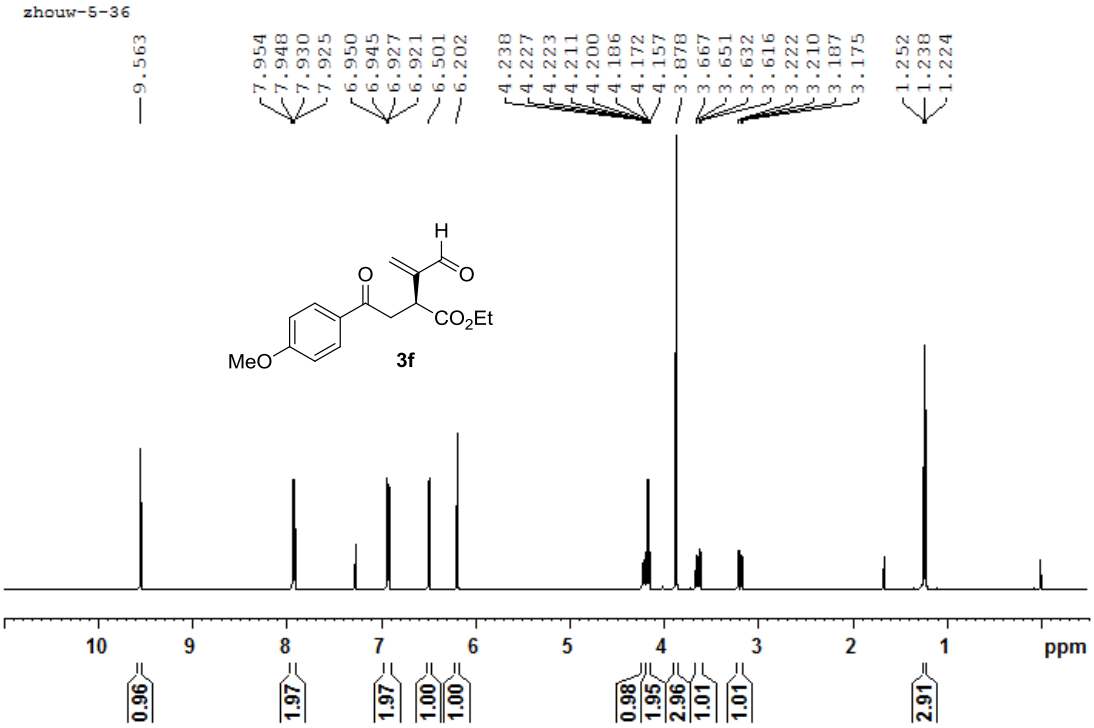
zhouw-5-35c

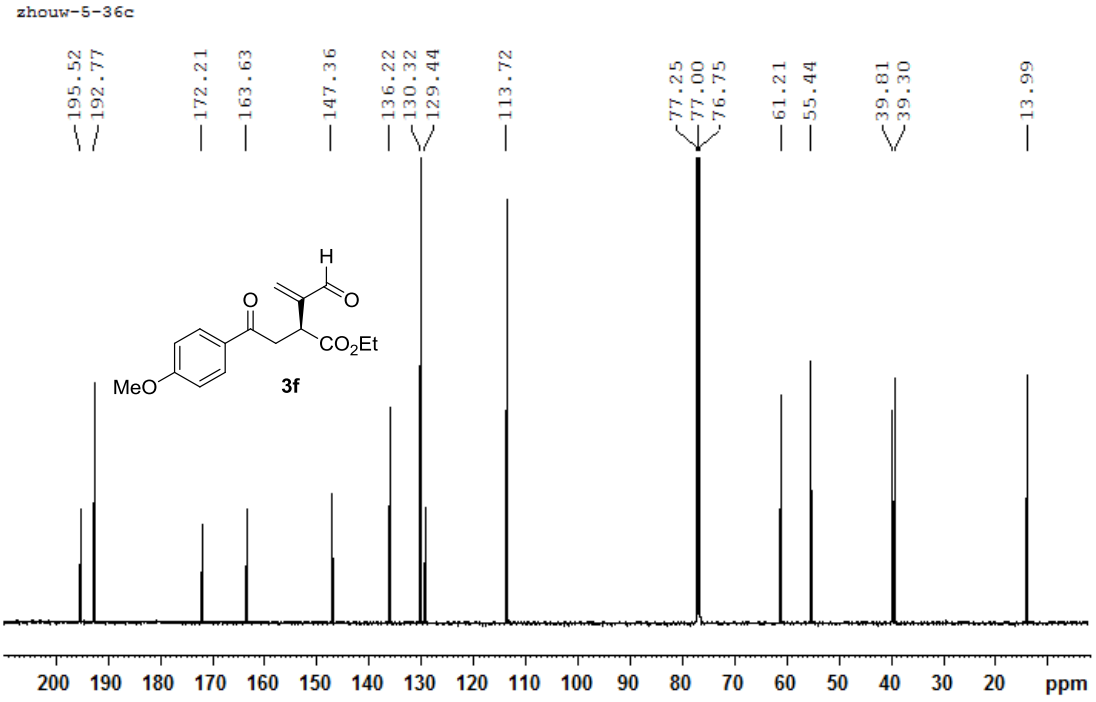


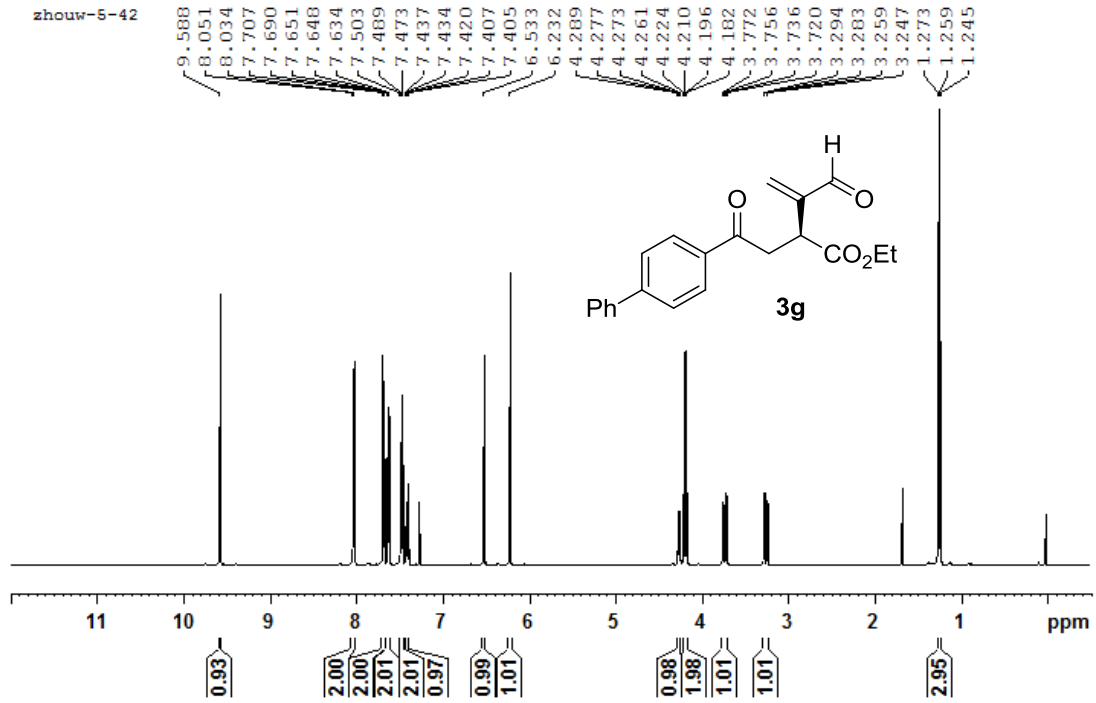
zhouw-5-37



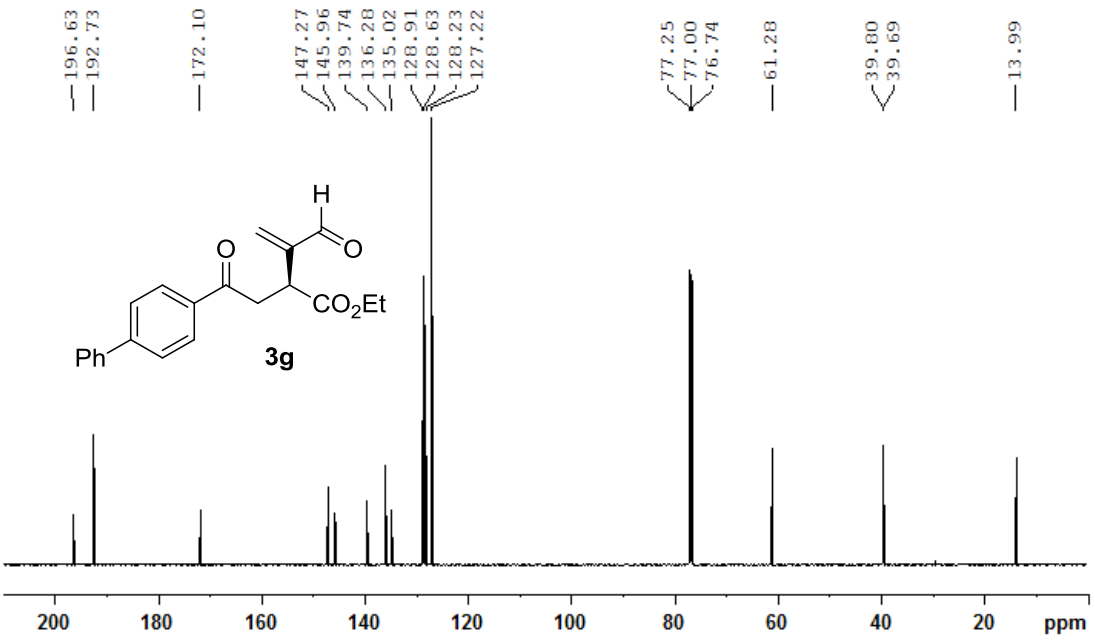

zhouw-5-37c
196.65
192.73
172.15
147.32
144.13
136.22
133.86
129.25
128.14
77.26
77.00
76.75
61.22
39.74
39.55
21.60
13.98
H
O
O
CO2Et
Me
3e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


zhouw-5-36
9.563
7.954
7.948
7.930
7.925
6.950
6.945
6.927
6.921
6.501
6.202
4.238
4.227
4.223
4.211
4.200
4.186
4.172
4.157
3.878
3.667
3.651
3.632
3.616
3.222
3.210
3.187
3.175
1.252
1.238
1.224
H
O
O
CO2Et
MeO
3f
10 9 8 7 6 5 4 3 2 1 ppm
0.96
1.97
1.97
1.00
1.00
0.98
1.95
2.96
1.01
1.01
2.91

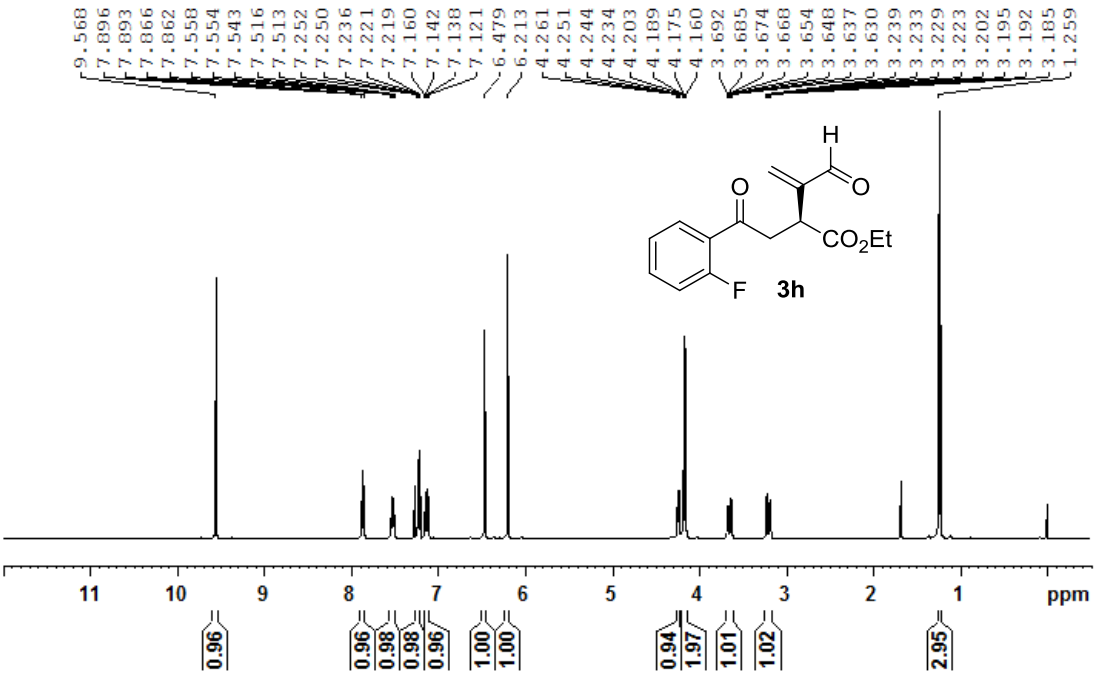

zhouw-5-36c
195.52
192.77
172.21
163.63
147.36
136.22
130.32
129.44
113.72
77.25
77.00
76.75
61.21
55.44
39.81
39.30
13.99
H
O
O
CO2Et
MeO
3f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

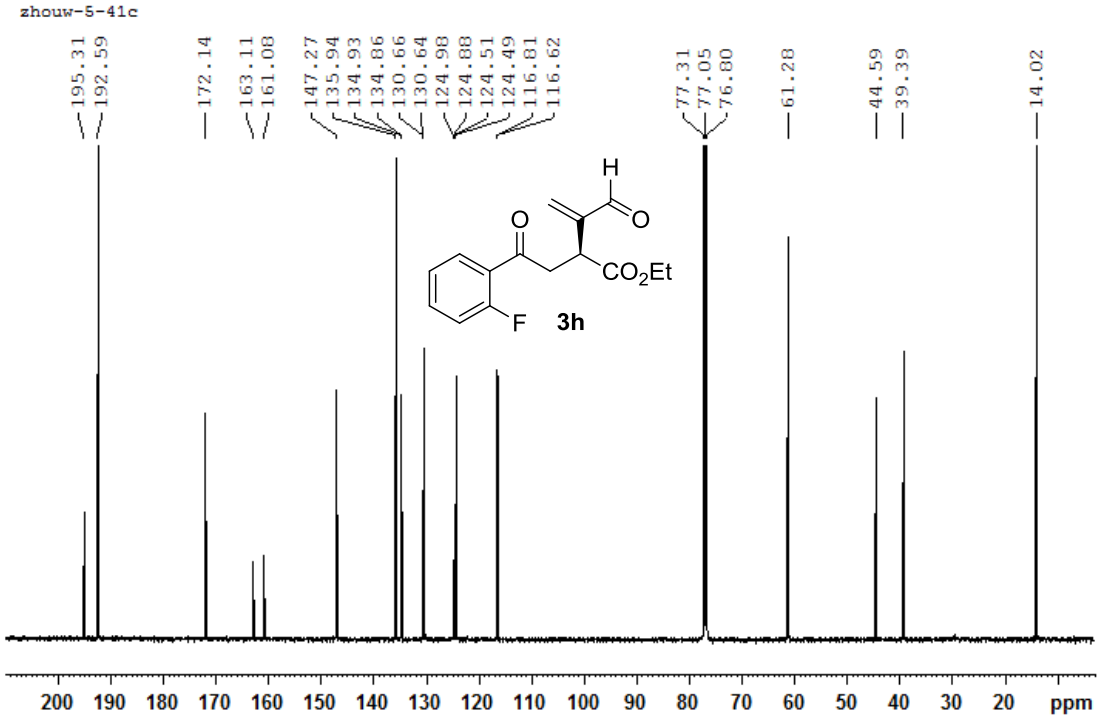

zhouw-5-42
9.588
8.051
8.034
7.707
7.690
7.651
7.648
7.634
7.503
7.489
7.473
7.437
7.434
7.420
7.407
7.405
6.533
6.232
4.289
4.277
4.273
4.261
4.224
4.210
4.196
4.182
3.772
3.756
3.736
3.720
3.294
3.283
3.259
3.247
1.273
1.259
1.245
H
O
O
CO2Et
Ph
3g
11 10 9 8 7 6 5 4 3 2 1 ppm
0.93
2.00
2.00
2.01
2.01
0.97
0.99
1.01
0.98
1.98
1.01
1.01
2.95

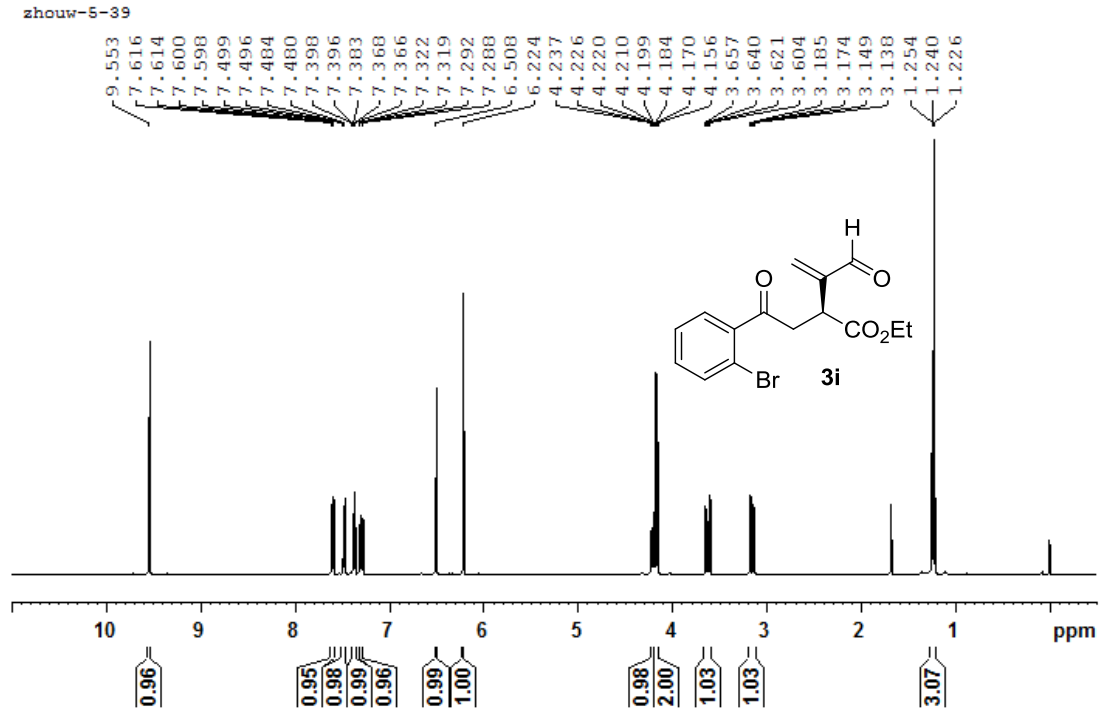
zhouw-5-42c

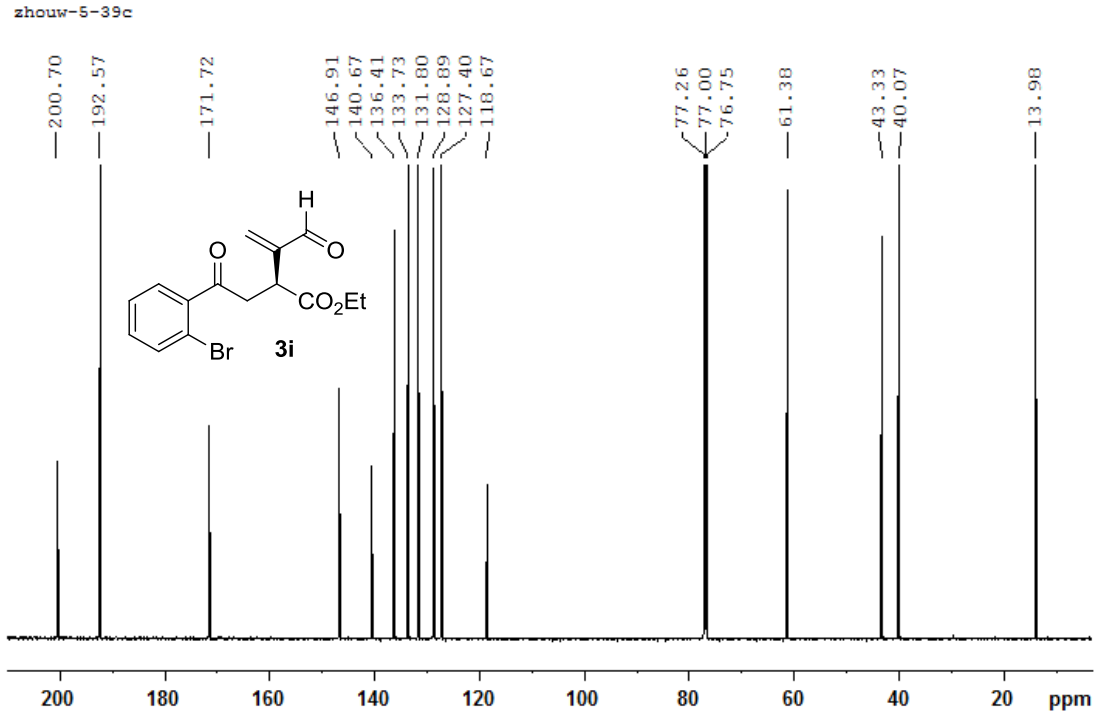


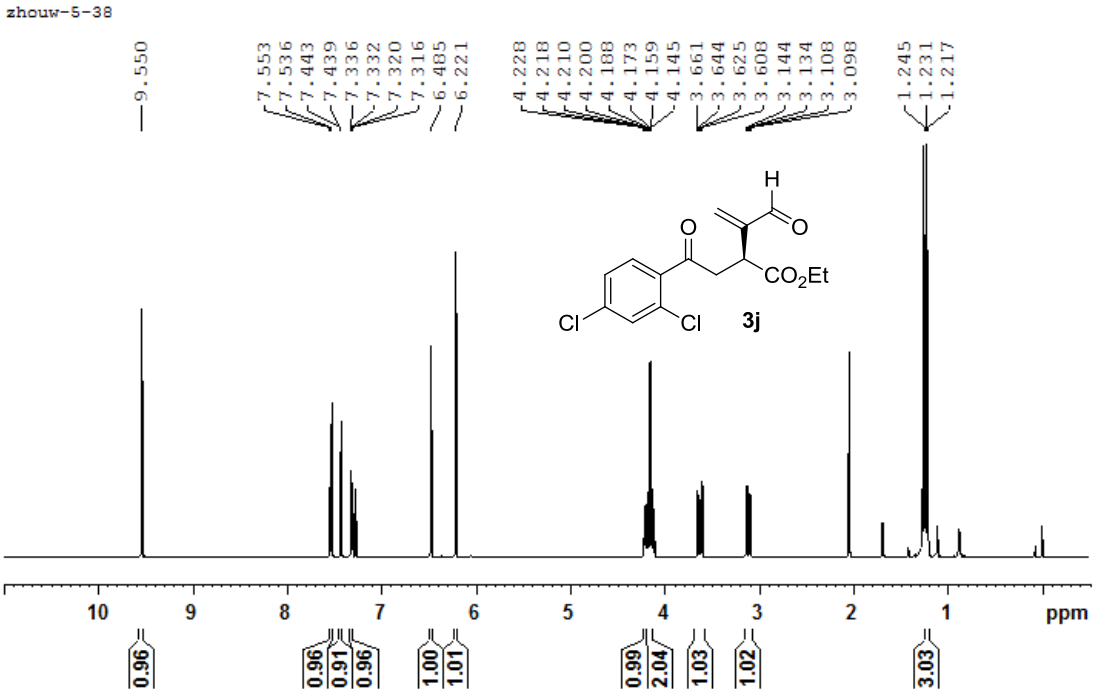
zhouw-5-41

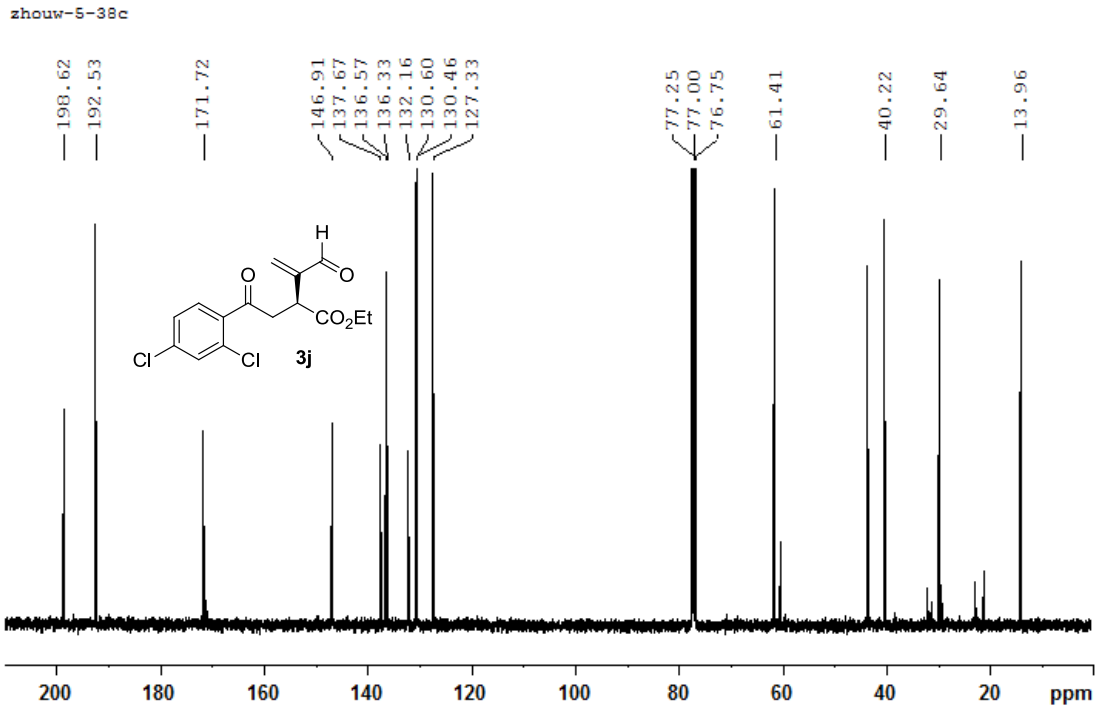


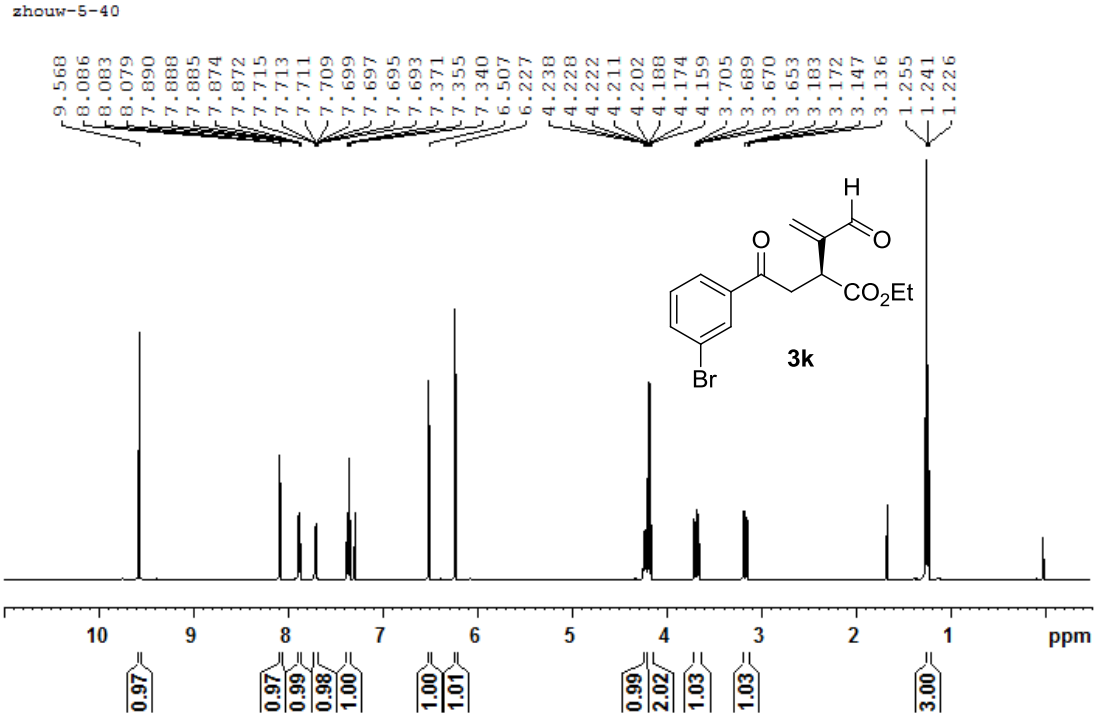

zhouw-5-41c
195.31
192.59
172.14
163.11
161.08
147.27
135.94
134.93
134.86
130.66
130.64
124.98
124.88
124.51
124.49
116.81
116.62
77.31
77.05
76.80
61.28
44.59
39.39
14.02
H
O
O
CO2Et
F
3h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

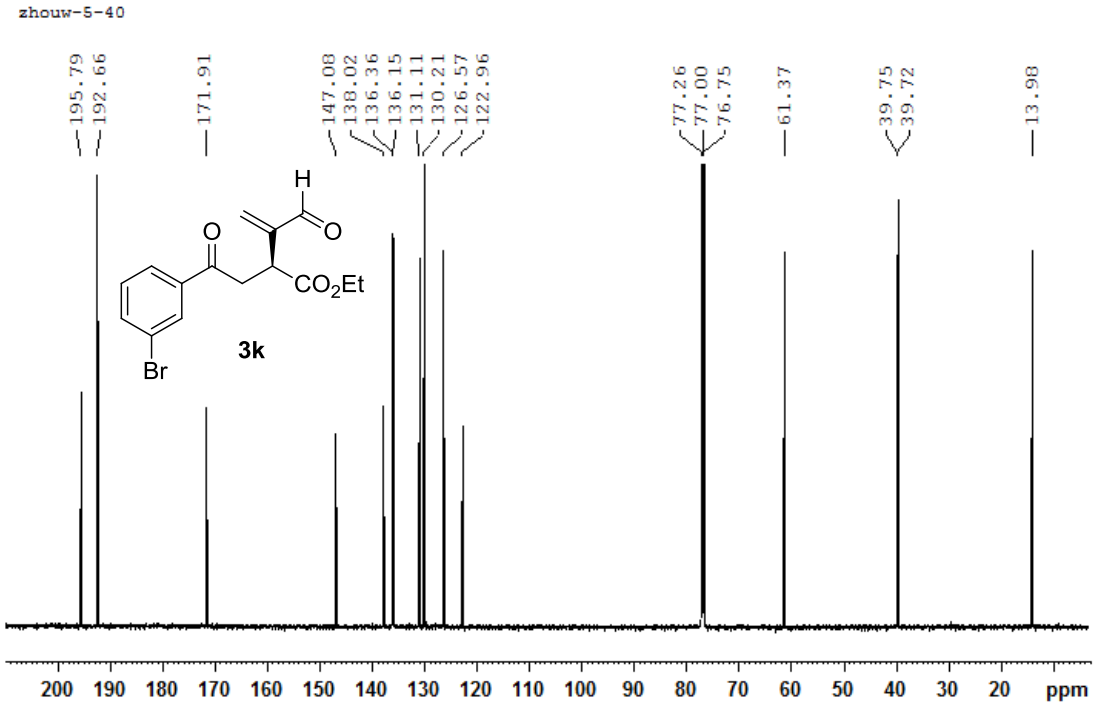

zhouw-5-39
9.553
7.616
7.614
7.600
7.598
7.499
7.496
7.484
7.480
7.398
7.396
7.383
7.368
7.366
7.322
7.319
7.292
7.288
6.508
6.224
4.237
4.226
4.220
4.210
4.199
4.184
4.170
4.156
3.657
3.640
3.621
3.604
3.185
3.174
3.149
3.138
1.254
1.240
1.226
H
O
O
CO2Et
Br
3i
10 9 8 7 6 5 4 3 2 1 ppm
0.96
0.95
0.98
0.99
0.96
0.99
1.00
0.98
2.00
1.03
1.03
3.07

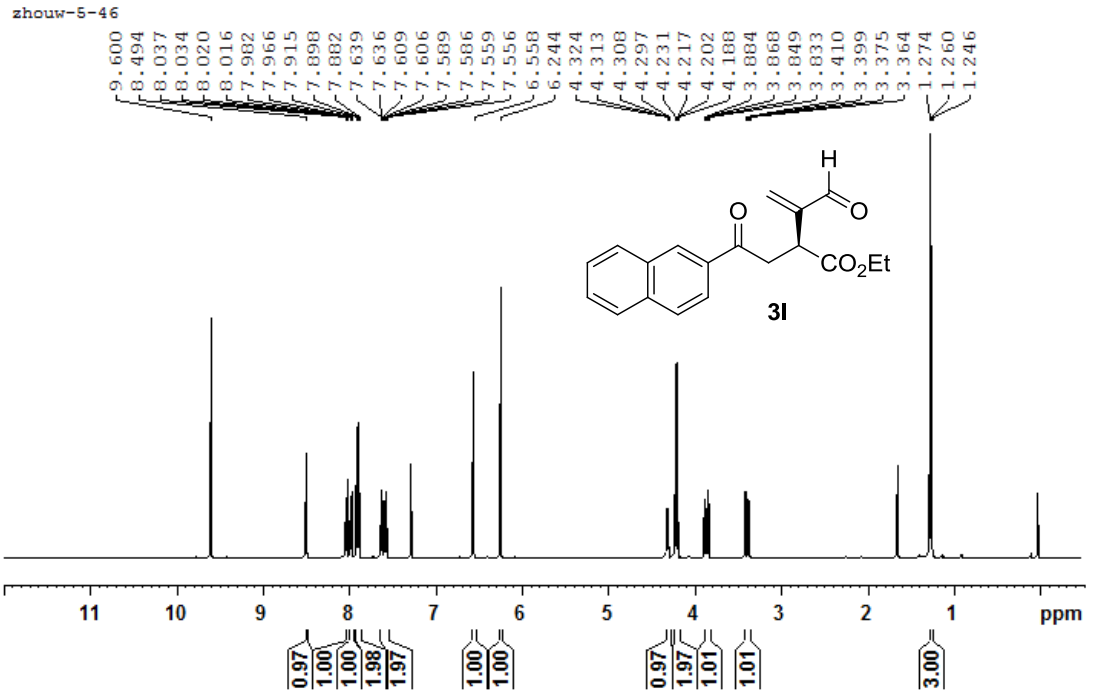

zhouw-5-39c
200.70
192.57
171.72
146.91
140.67
136.41
133.73
131.80
128.89
127.40
118.67
77.26
77.00
76.75
61.38
43.33
40.07
13.98
H
O
O
CO2Et
Br
3i
200
180
160
140
120
100
80
60
40
20
ppm

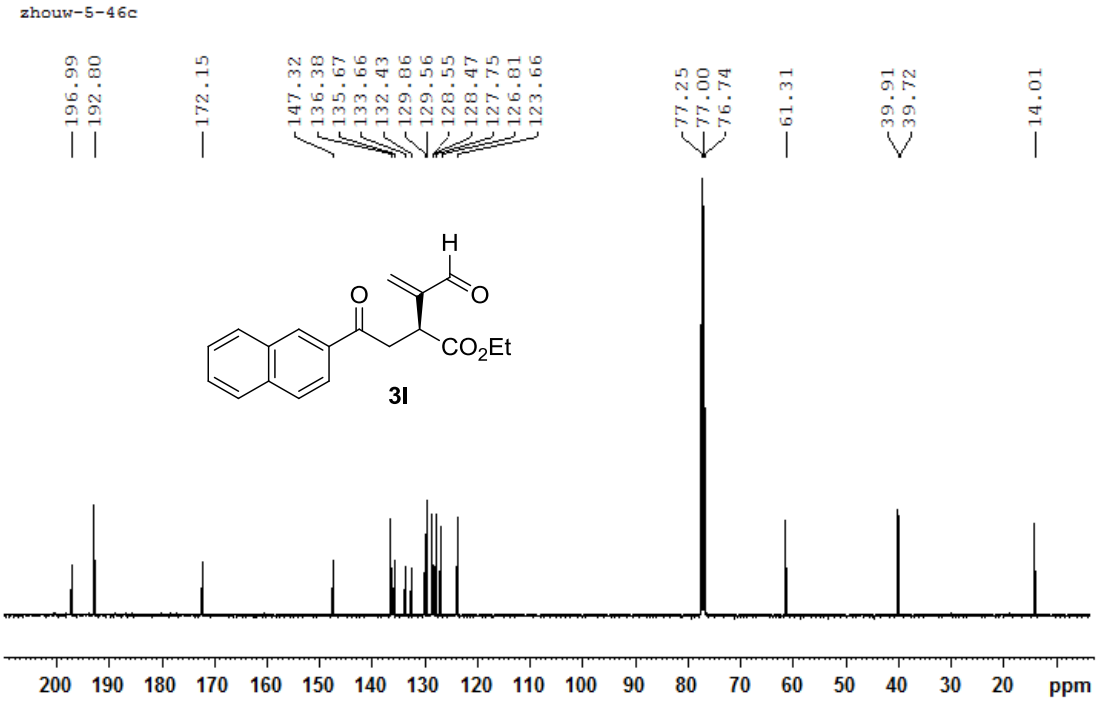

zhouw-5-38
9.550
7.553
7.536
7.443
7.439
7.336
7.332
7.320
7.316
6.485
6.221
4.228
4.218
4.210
4.200
4.188
4.173
4.159
4.145
3.661
3.644
3.625
3.608
3.144
3.134
3.108
3.098
1.245
1.231
1.217
H
O
O
CO2Et
Cl
Cl
3j
10
9
8
7
6
5
4
3
2
1
ppm
0.96
0.96
0.91
0.96
1.00
1.01
0.99
2.04
1.03
1.02
3.03

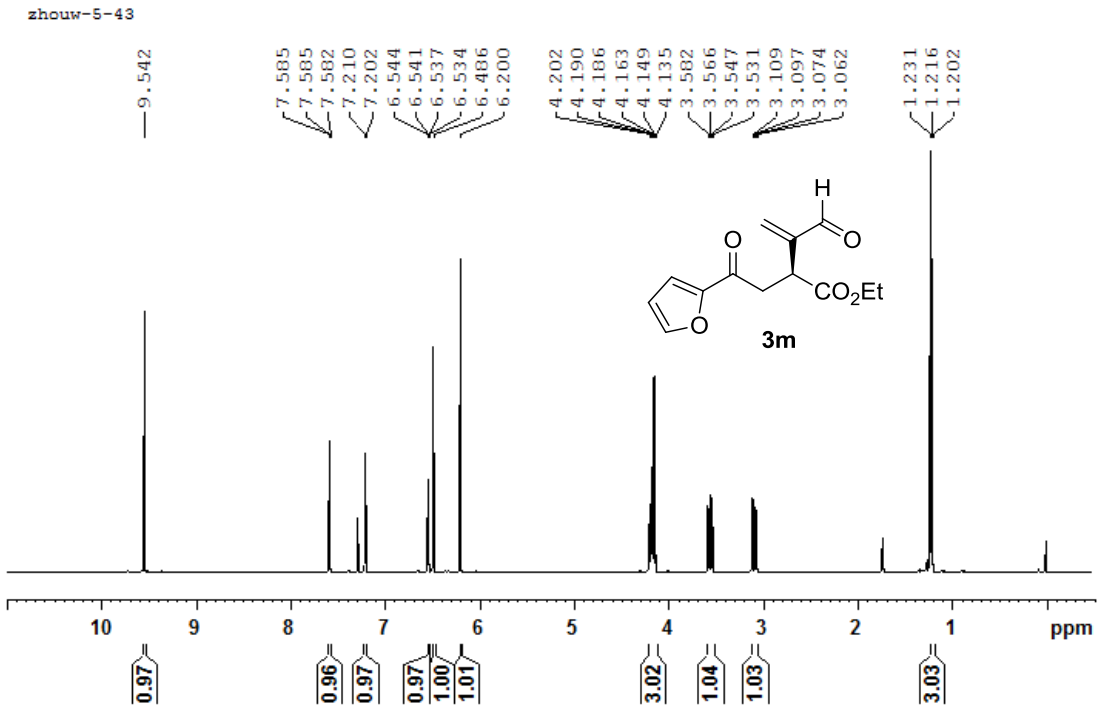

zhouw-5-38c
198.62
192.53
171.72
146.91
137.67
136.57
136.33
132.16
130.60
130.46
127.33
77.25
77.00
76.75
61.41
40.22
29.64
13.96
H
O
O
CO2Et
Cl
Cl
3j
200
180
160
140
120
100
80
60
40
20
ppm

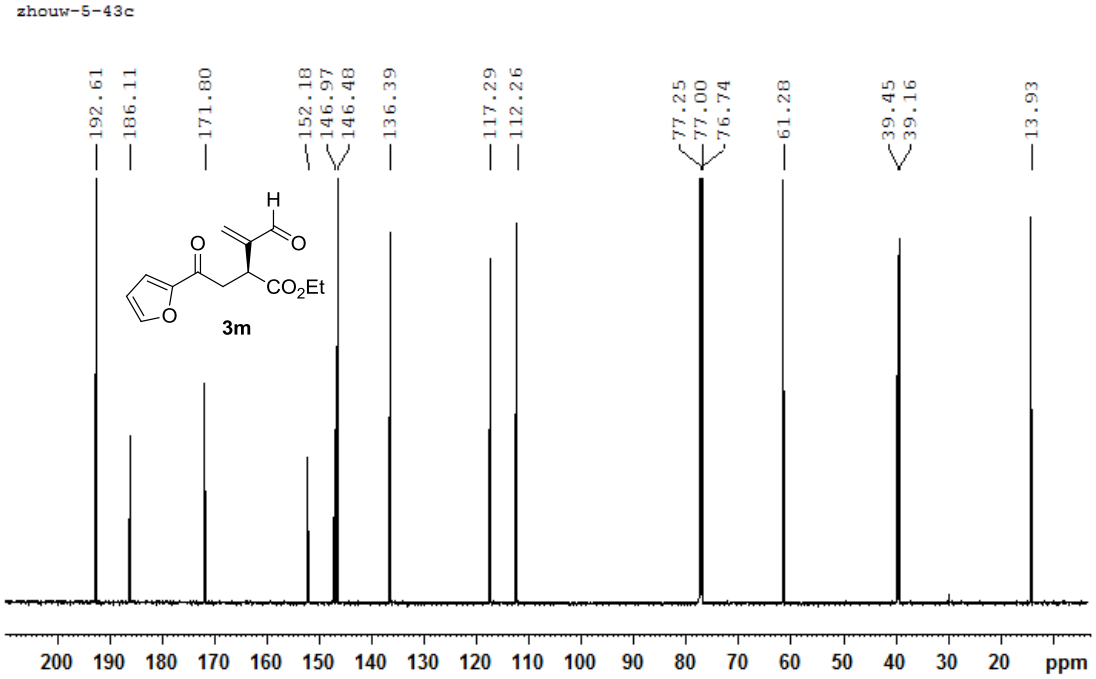

zhouw-5-40
9.568
8.086
8.083
8.079
7.890
7.888
7.885
7.874
7.872
7.715
7.713
7.711
7.709
7.699
7.697
7.695
7.693
7.371
7.355
7.340
6.507
6.227
4.238
4.228
4.222
4.211
4.202
4.188
4.174
4.159
3.705
3.689
3.670
3.653
3.183
3.172
3.147
3.136
1.255
1.241
1.226
H
O
O
CO2Et
Br
3k
10
9
8
7
6
5
4
3
2
1
ppm
0.97
0.97
0.99
0.98
1.00
1.00
1.01
0.99
2.02
1.03
1.03
3.00

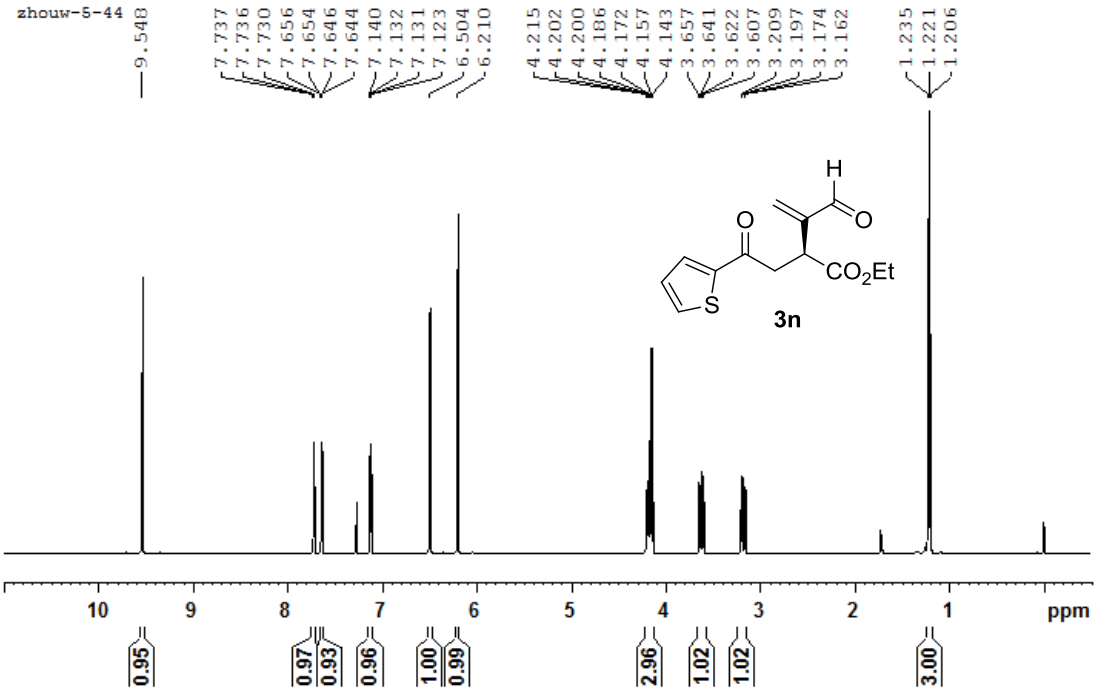

zhouw-5-40
195.79
192.66
171.91
147.08
138.02
136.36
136.15
131.11
130.21
126.57
122.96
77.26
77.00
76.75
61.37
39.75
39.72
13.98
H
O
O
CO2Et
Br
3k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

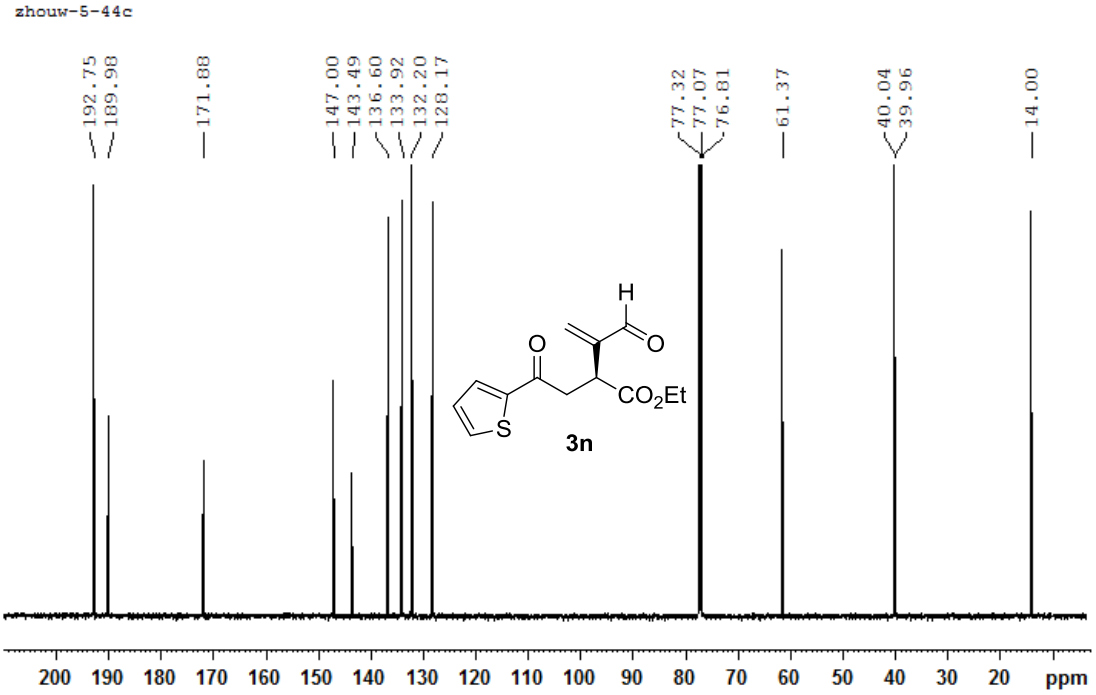

zhouw-5-46
9.600
8.494
8.037
8.034
8.020
8.016
7.982
7.966
7.915
7.898
7.882
7.639
7.636
7.609
7.606
7.589
7.586
7.559
7.556
6.558
6.244
4.324
4.313
4.308
4.297
4.231
4.217
4.202
4.188
3.884
3.868
3.849
3.833
3.410
3.399
3.375
3.364
1.274
1.260
1.246
H
O
O
CO2Et
3l
11 10 9 8 7 6 5 4 3 2 1 ppm
0.97
1.00
1.00
1.98
1.97
1.00
1.00
0.97
1.97
1.01
1.01
3.00

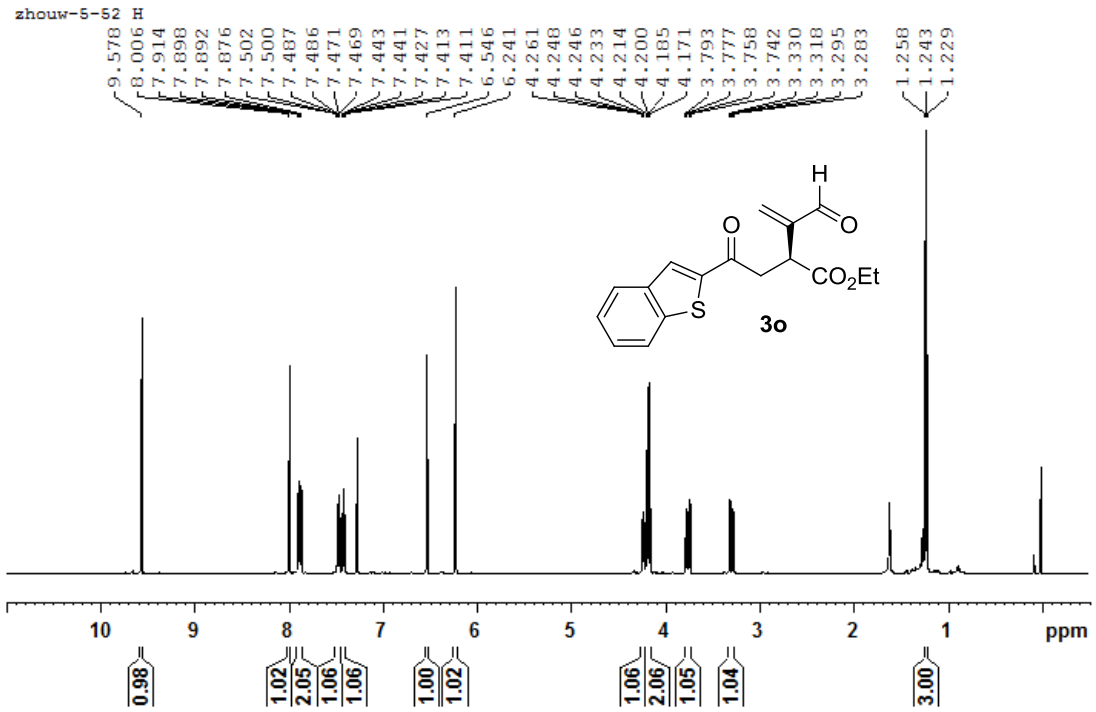

zhouw-5-46c
196.99
192.80
172.15
147.32
136.38
135.67
133.66
132.43
129.86
129.56
128.55
128.47
127.75
126.81
123.66
77.25
77.00
76.74
61.31
39.91
39.72
14.01
H
O
O
CO2Et
3l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

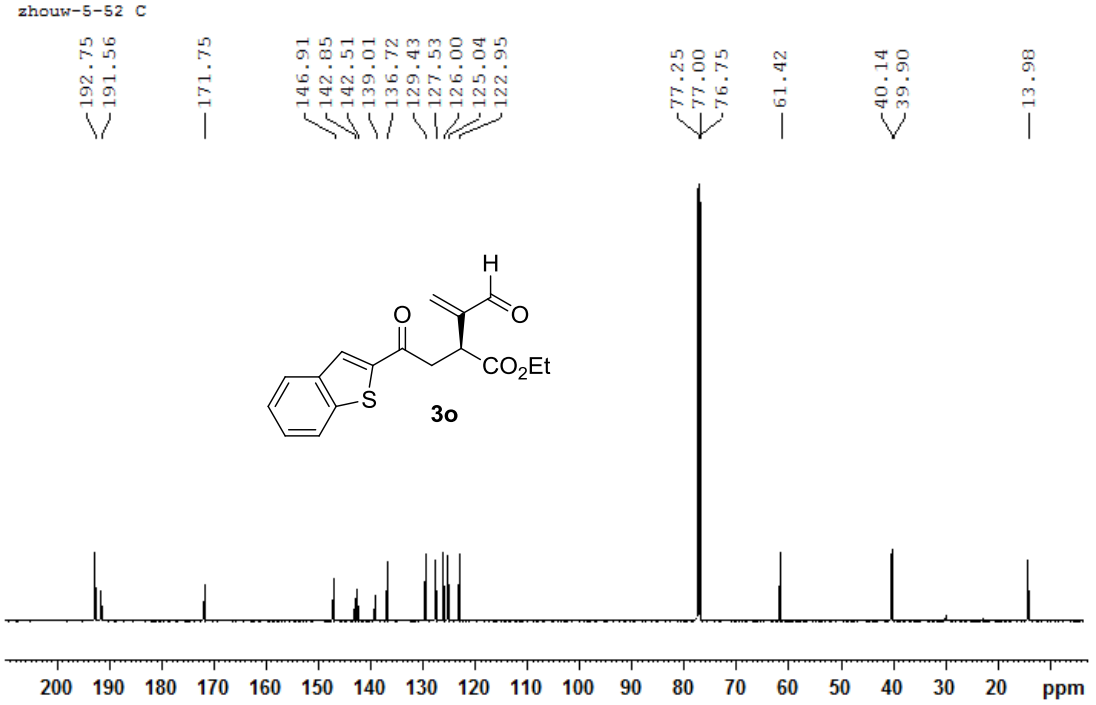

zhouw-5-43
9.542
7.585
7.585
7.582
7.210
7.202
6.544
6.541
6.537
6.534
6.486
6.200
4.202
4.190
4.186
4.163
4.149
4.135
3.582
3.566
3.547
3.531
3.109
3.097
3.074
3.062
1.231
1.216
1.202
H
O
O
CO2Et
O
3m
10 9 8 7 6 5 4 3 2 1 ppm
0.97
0.96
0.97
0.97
1.00
1.01
3.02
1.04
1.03
3.03

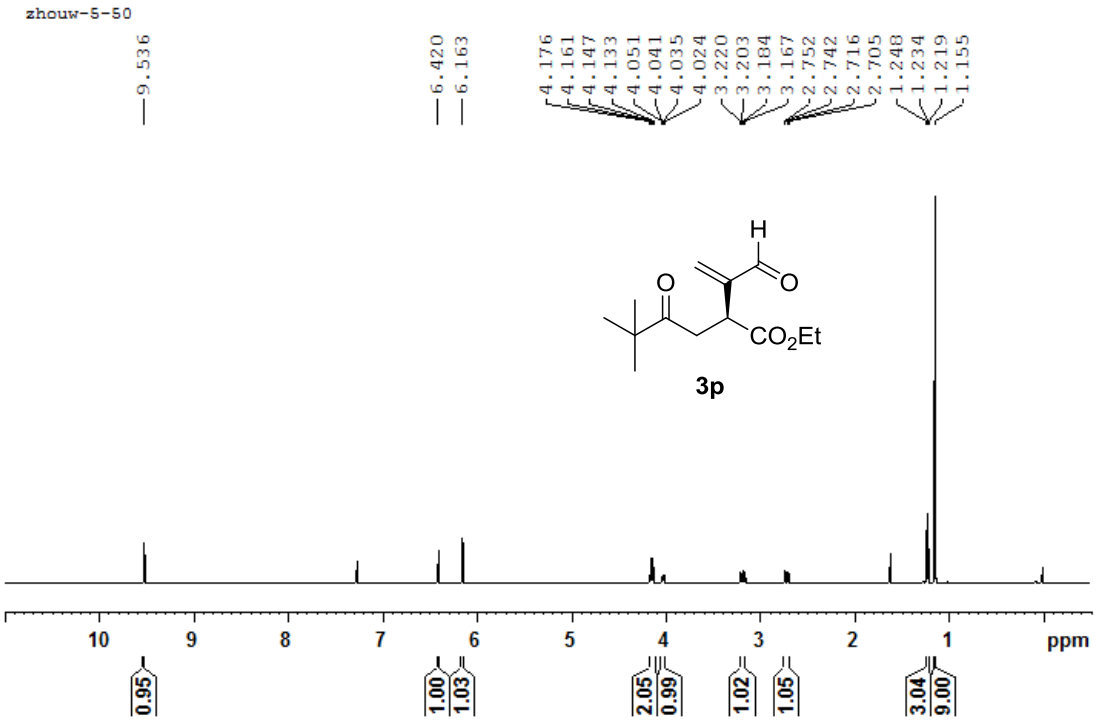

zhouw-5-43c
192.61
186.11
171.80
152.18
146.97
146.48
136.39
117.29
112.26
77.25
77.00
76.74
61.28
39.45
39.16
13.93
H
O
O
CO2Et
O
3m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

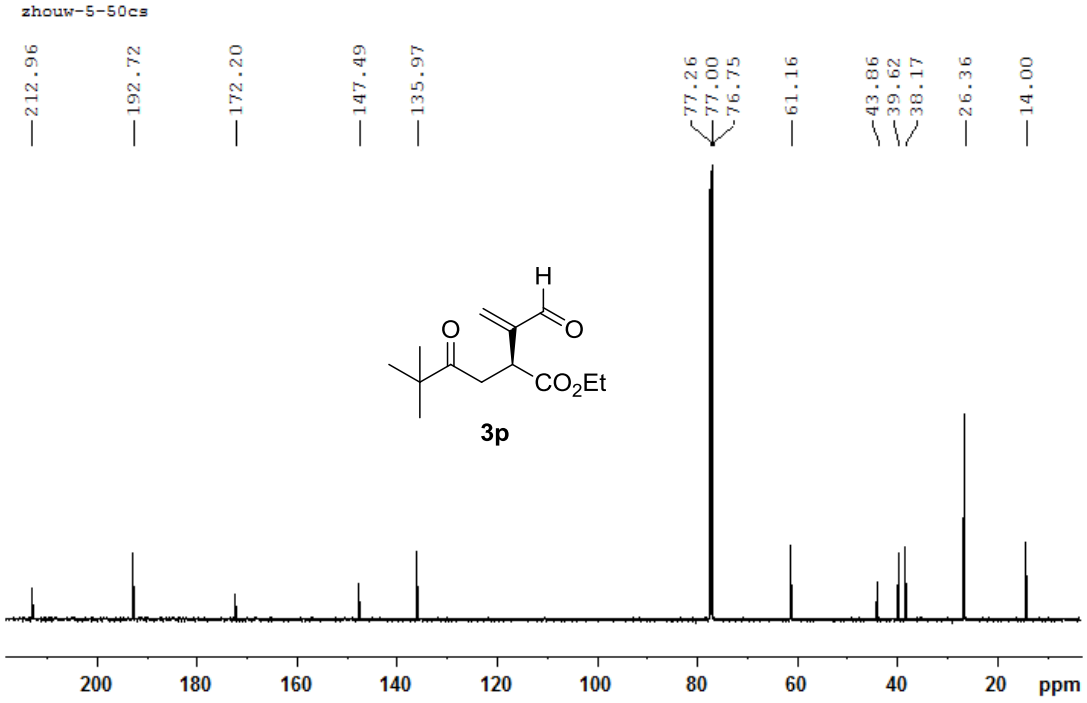

zhouw-5-44
9.548
7.737
7.736
7.730
7.656
7.654
7.646
7.644
7.140
7.132
7.131
7.123
6.504
6.210
4.215
4.202
4.200
4.186
4.172
4.157
4.143
3.657
3.641
3.622
3.607
3.209
3.197
3.174
3.162
1.235
1.221
1.206
H
O
O
CO2Et
S
3n
10 9 8 7 6 5 4 3 2 1 ppm
0.95
0.97
0.93
0.96
1.00
0.99
2.96
1.02
1.02
3.00

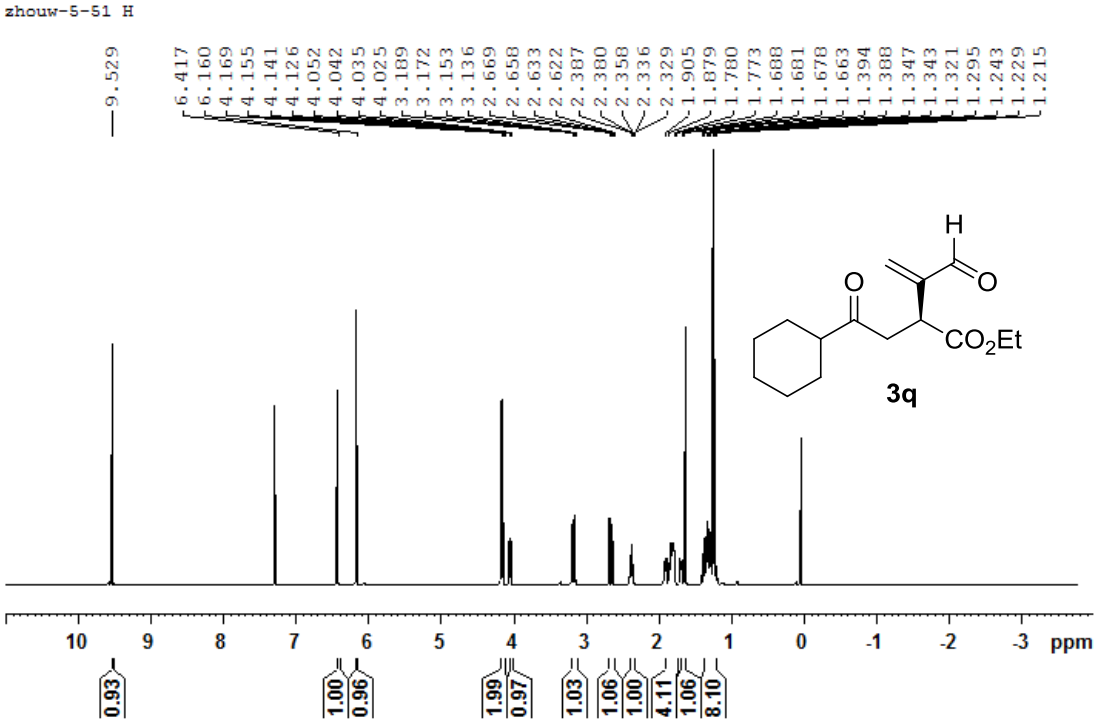

zhouw-5-44c
192.75
189.98
171.88
147.00
143.49
136.60
133.92
132.20
128.17
77.32
77.07
76.81
61.37
40.04
39.96
14.00
H
O
O
CO2Et
S
3n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

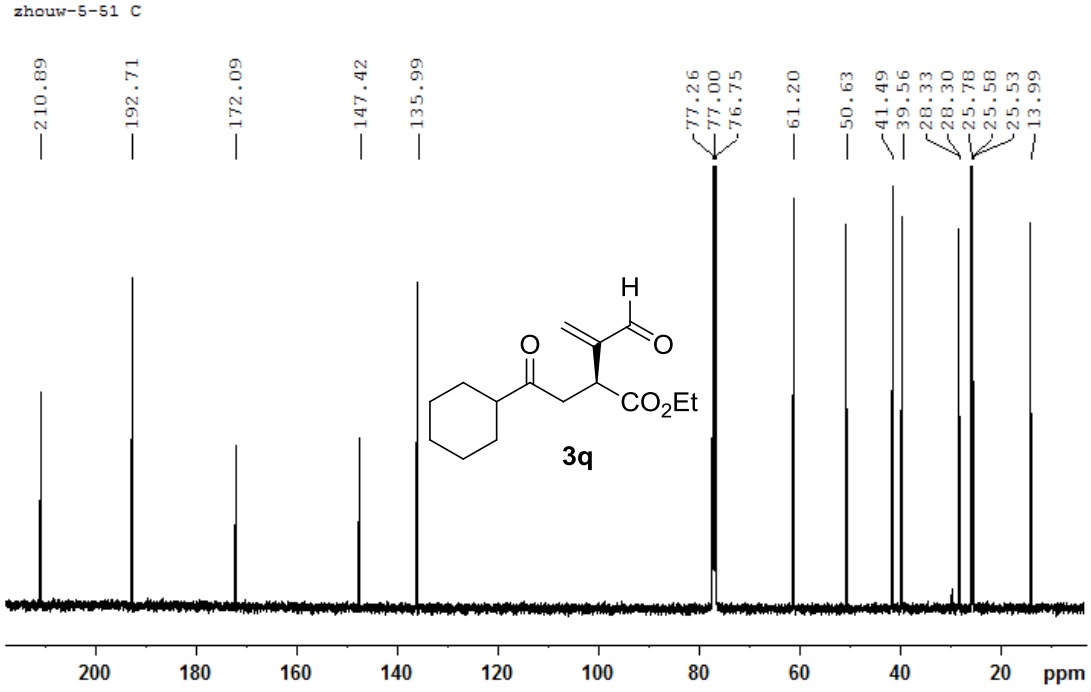

zhouw-5-52 H
9.578
8.006
7.914
7.898
7.892
7.876
7.502
7.500
7.487
7.486
7.471
7.469
7.443
7.441
7.427
7.413
7.411
6.546
6.241
4.261
4.248
4.246
4.233
4.214
4.200
4.185
4.171
3.793
3.777
3.758
3.742
3.330
3.318
3.295
3.283
1.258
1.243
1.229
H
O
O
CO2Et
S
3o
10 9 8 7 6 5 4 3 2 1 ppm
0.98
1.02
2.05
1.06
1.06
1.00
1.02
1.06
2.06
1.05
1.04
3.00

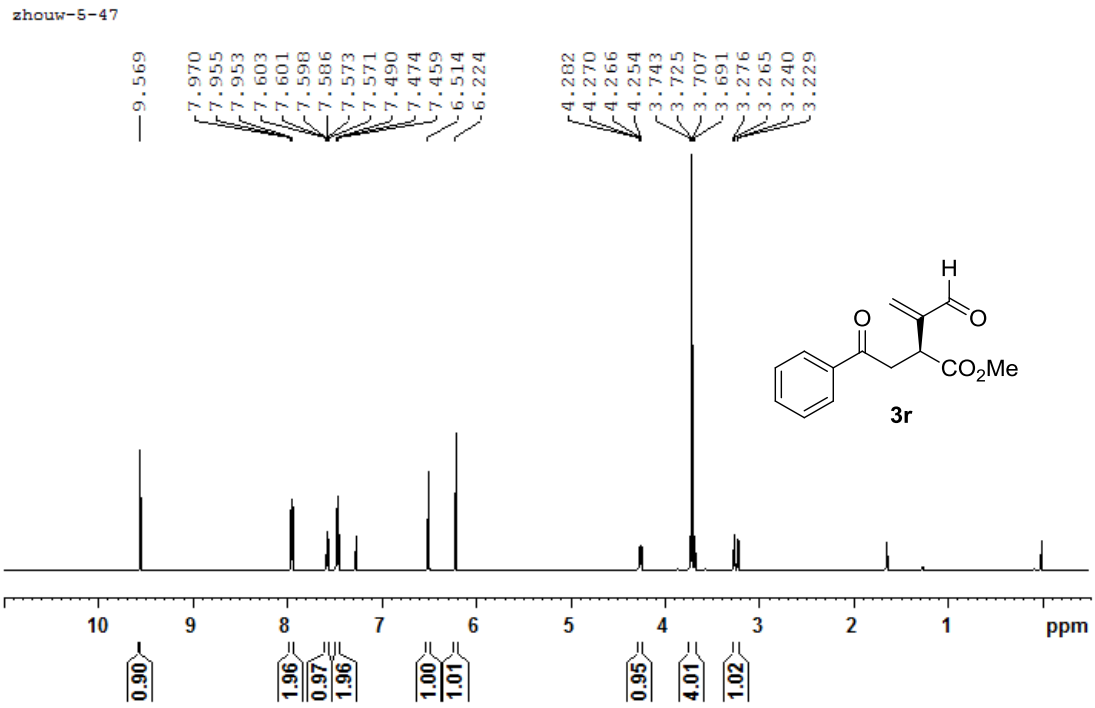

zhouw-5-52 C
192.75
191.56
171.75
146.91
142.85
142.51
139.01
136.72
129.43
127.53
126.00
125.04
122.95
77.25
77.00
76.75
61.42
40.14
39.90
13.98
H
O
O
CO2Et
S
3o
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

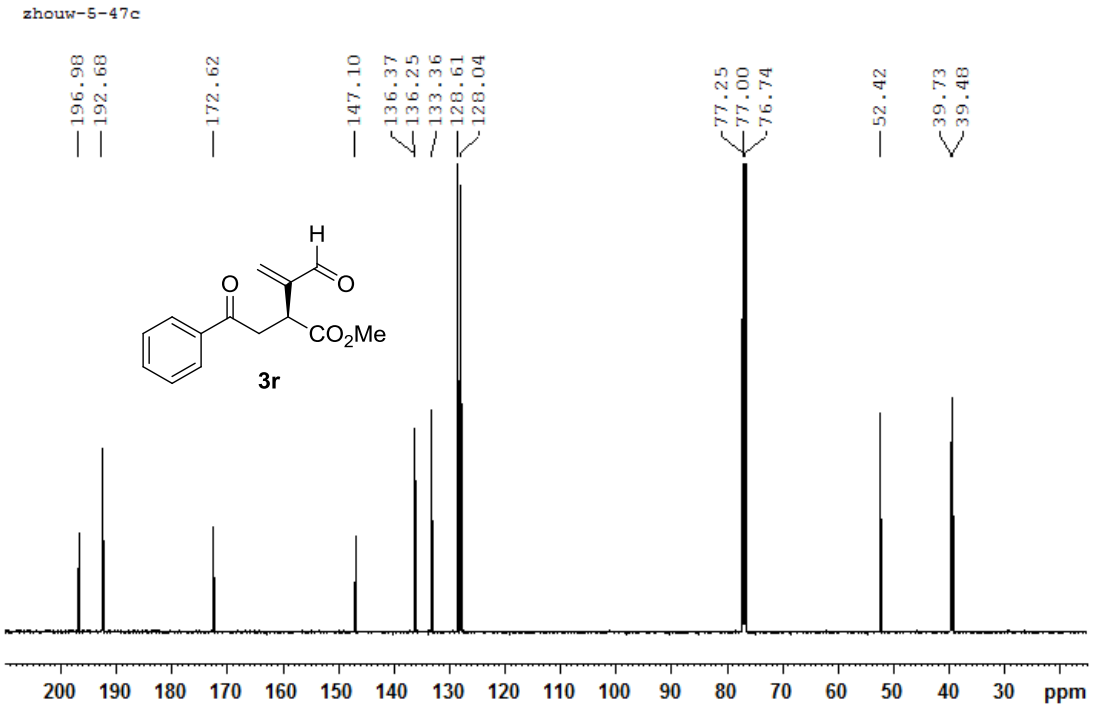

zhouw-5-50
9.536
6.420
6.163
4.176
4.161
4.147
4.133
4.051
4.041
4.035
4.024
3.220
3.203
3.184
3.167
2.752
2.742
2.716
2.705
1.248
1.234
1.219
1.155
H
O
O
CO2Et
3p
10 9 8 7 6 5 4 3 2 1 ppm
0.95
1.00
1.03
2.05
0.99
1.02
1.05
3.04
9.00

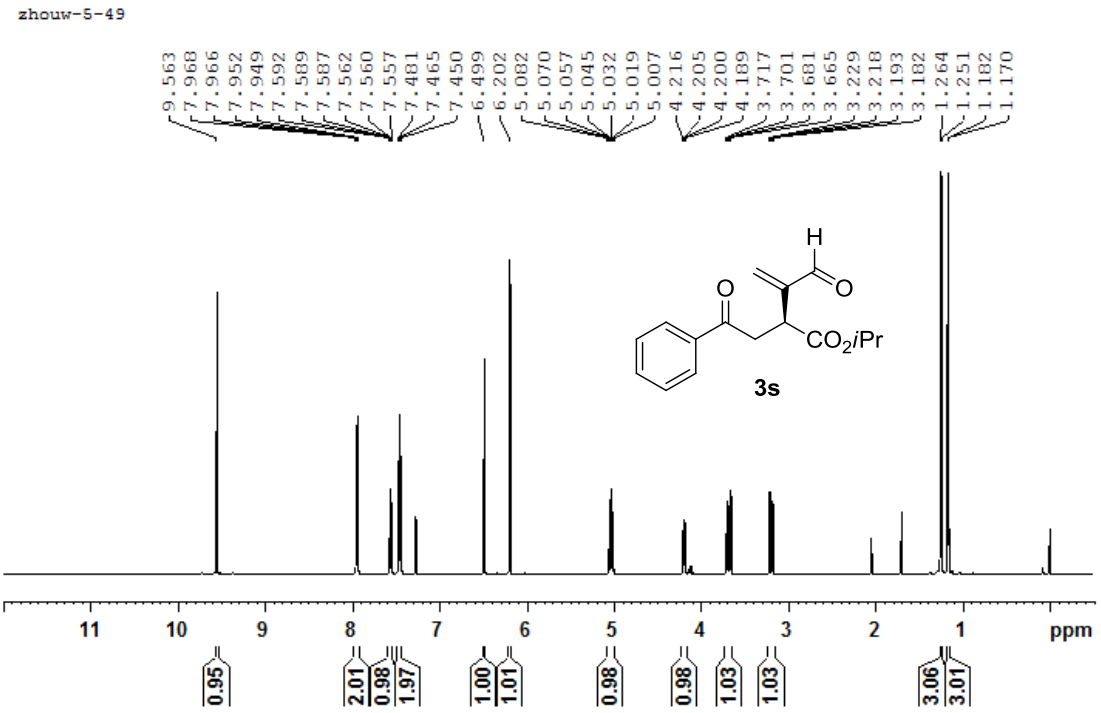

zhouw-5-50cs
212.96
192.72
172.20
147.49
135.97
77.26
77.00
76.75
61.16
43.86
39.62
38.17
26.36
14.00
H
O
O
CO2Et
3p
200
180
160
140
120
100
80
60
40
20
ppm


zhouw-5-51 H
9.529
6.417
6.160
4.169
4.155
4.141
4.126
4.052
4.042
4.035
4.025
3.189
3.172
3.153
3.136
2.669
2.658
2.633
2.622
2.387
2.380
2.358
2.336
2.329
1.905
1.879
1.780
1.773
1.688
1.681
1.678
1.663
1.394
1.388
1.347
1.343
1.321
1.295
1.243
1.229
1.215
H
O
O
CO2Et
3q
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm
0.93
1.00
0.96
1.99
0.97
1.03
1.06
1.00
4.11
1.06
8.10

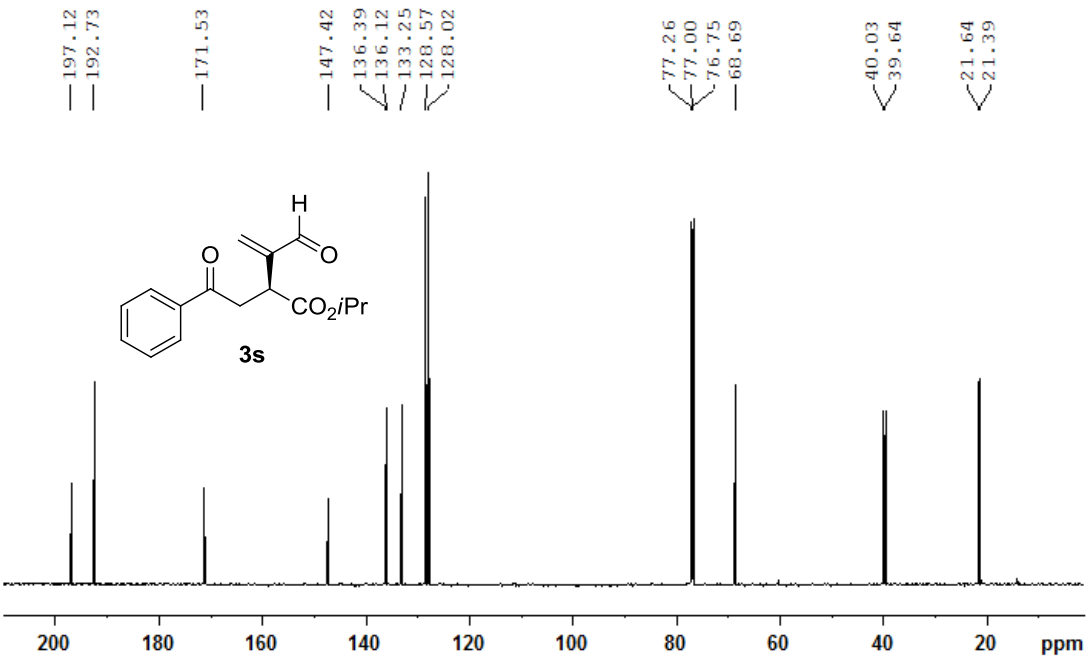

zhouw-5-51 C
210.89
192.71
172.09
147.42
135.99
77.26
77.00
76.75
61.20
50.63
41.49
39.56
28.33
28.30
25.78
25.58
25.53
13.99
H
O
O
CO2Et
3q
200
180
160
140
120
100
80
60
40
20
ppm


zhouw-5-47
9.569
7.970
7.955
7.953
7.603
7.601
7.598
7.586
7.573
7.571
7.490
7.474
7.459
6.514
6.224
4.282
4.270
4.266
4.254
3.743
3.725
3.707
3.691
3.276
3.265
3.240
3.229
H
O
O
CO2Me
3r
10
9
8
7
6
5
4
3
2
1
ppm
0.90
1.96
0.97
1.96
1.00
1.01
0.95
4.01
1.02

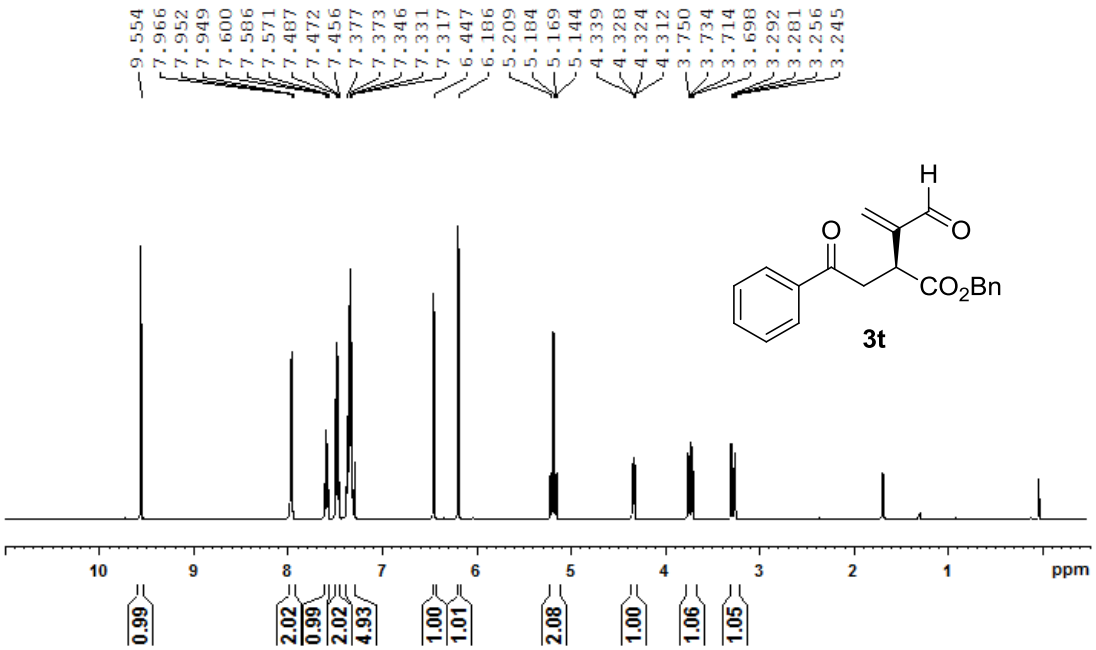

zhouw-5-47c
196.98
192.68
172.62
147.10
136.37
136.25
133.36
128.61
128.04
77.25
77.00
76.74
52.42
39.73
39.48
H
O
O
CO2Me
3r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm


zhouw-5-49
9.563
7.968
7.966
7.952
7.949
7.592
7.589
7.587
7.562
7.560
7.557
7.481
7.465
7.450
6.499
6.202
5.082
5.070
5.057
5.045
5.032
5.019
5.007
4.216
4.205
4.200
4.189
3.717
3.701
3.681
3.665
3.229
3.218
3.193
3.182
1.264
1.251
1.182
1.170
H
O
O
CO2iPr
3s
11 10 9 8 7 6 5 4 3 2 1 ppm
0.95
2.01
0.98
1.97
1.00
1.01
0.98
0.98
1.03
1.03
3.06
3.01

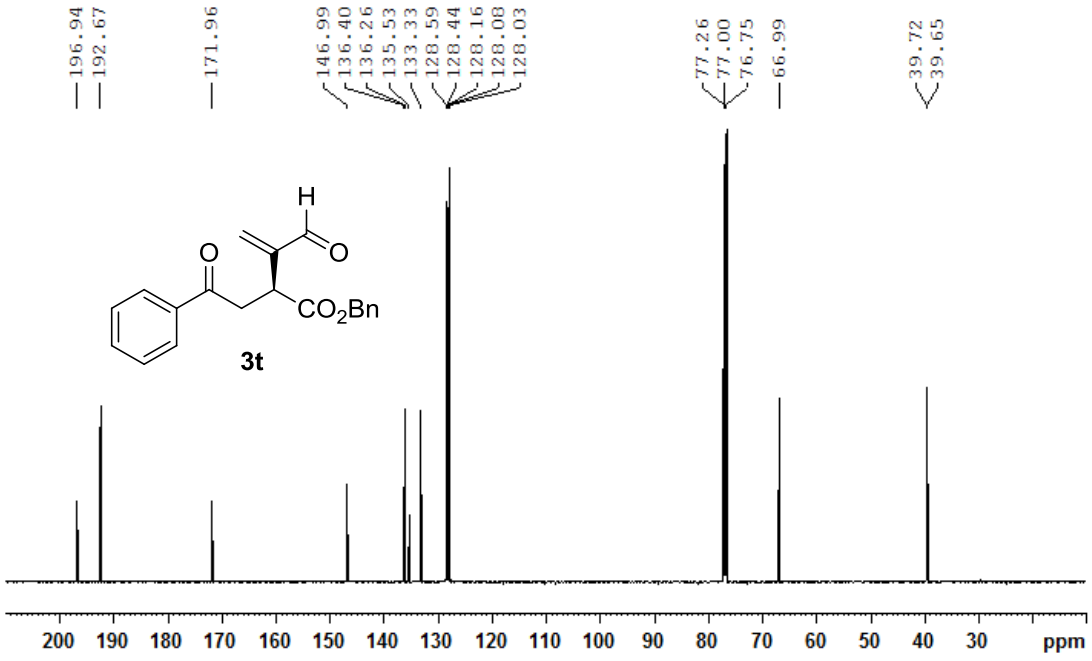
zhouw-5-49c



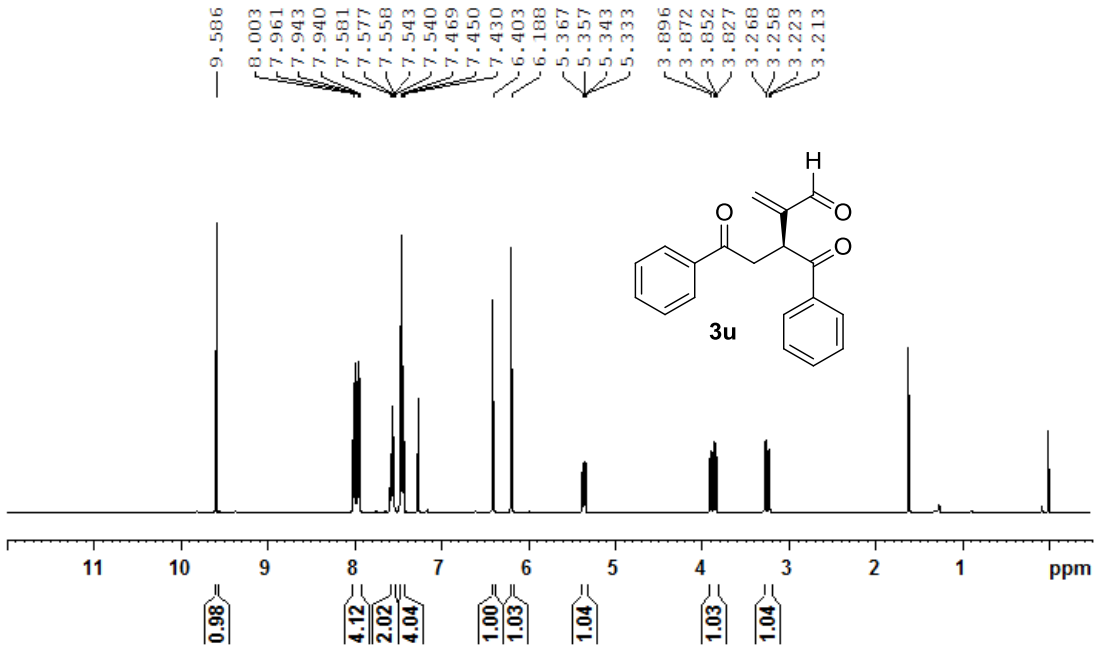
zhouw-5-48

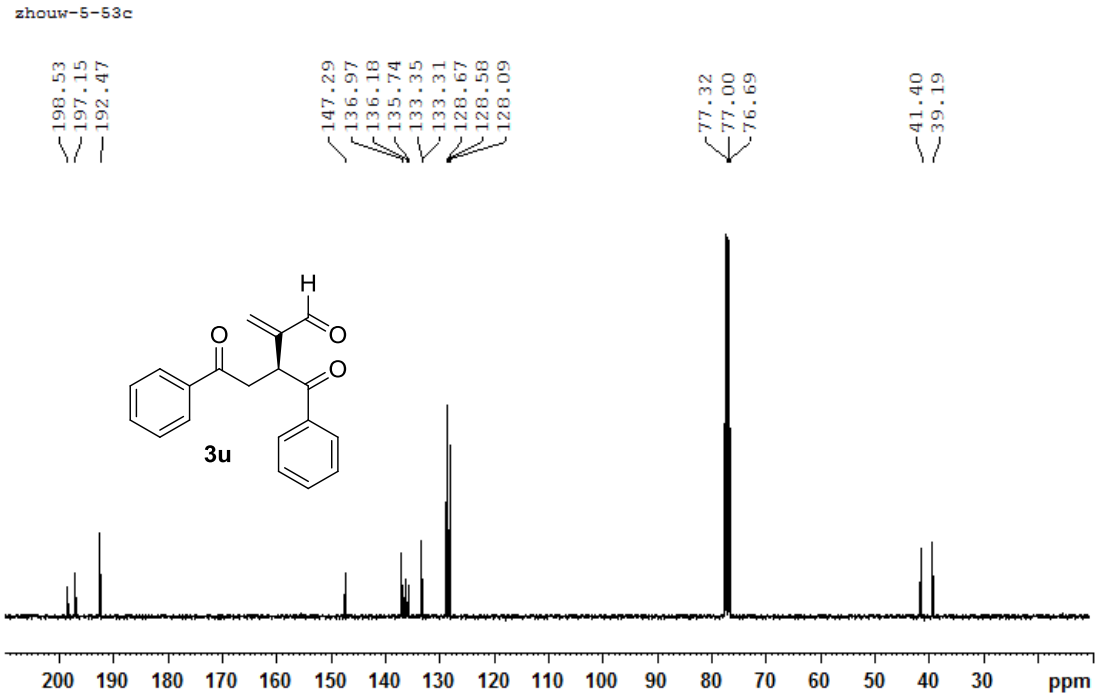


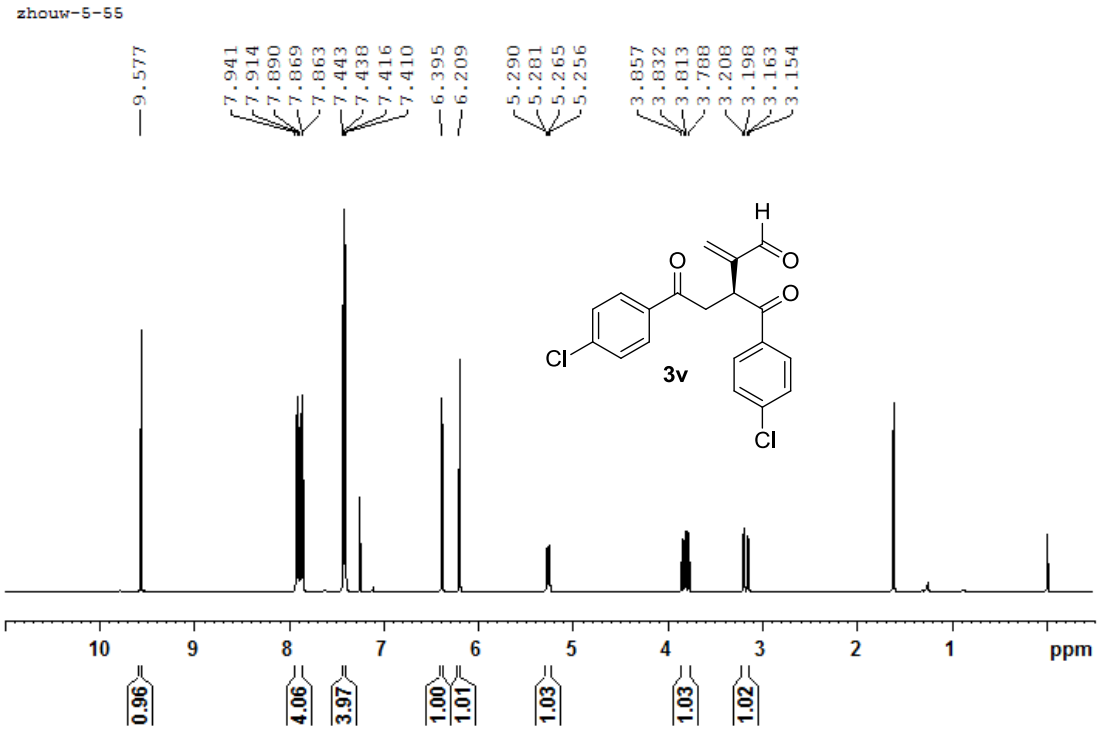
zhouw-5-48c

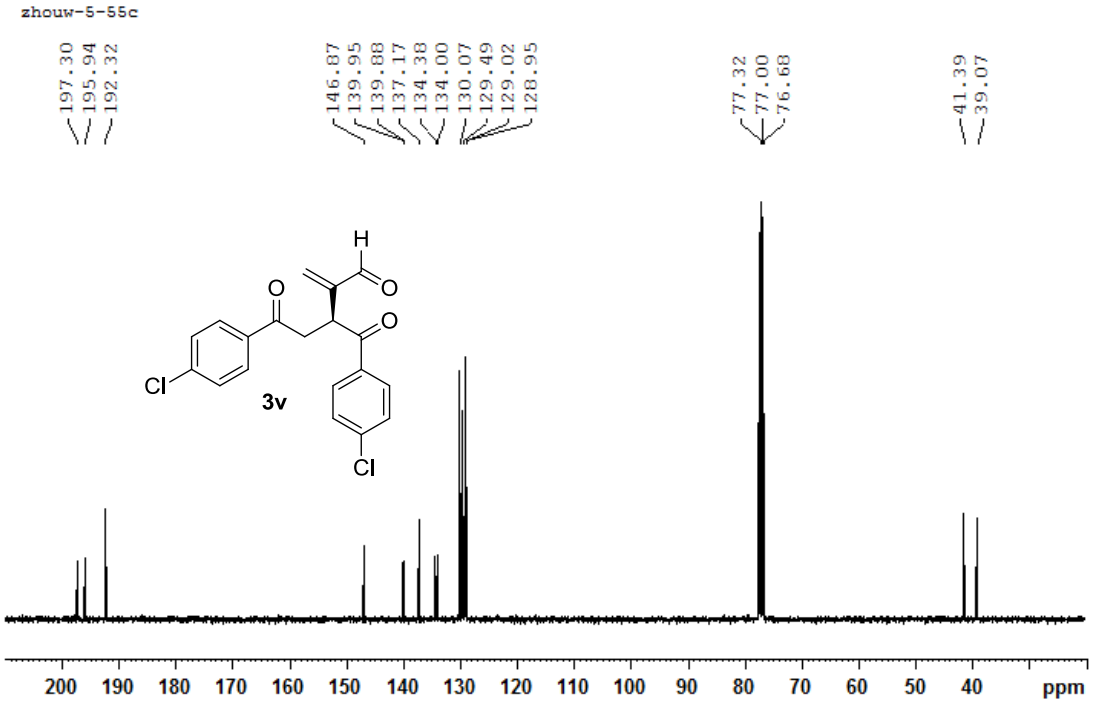


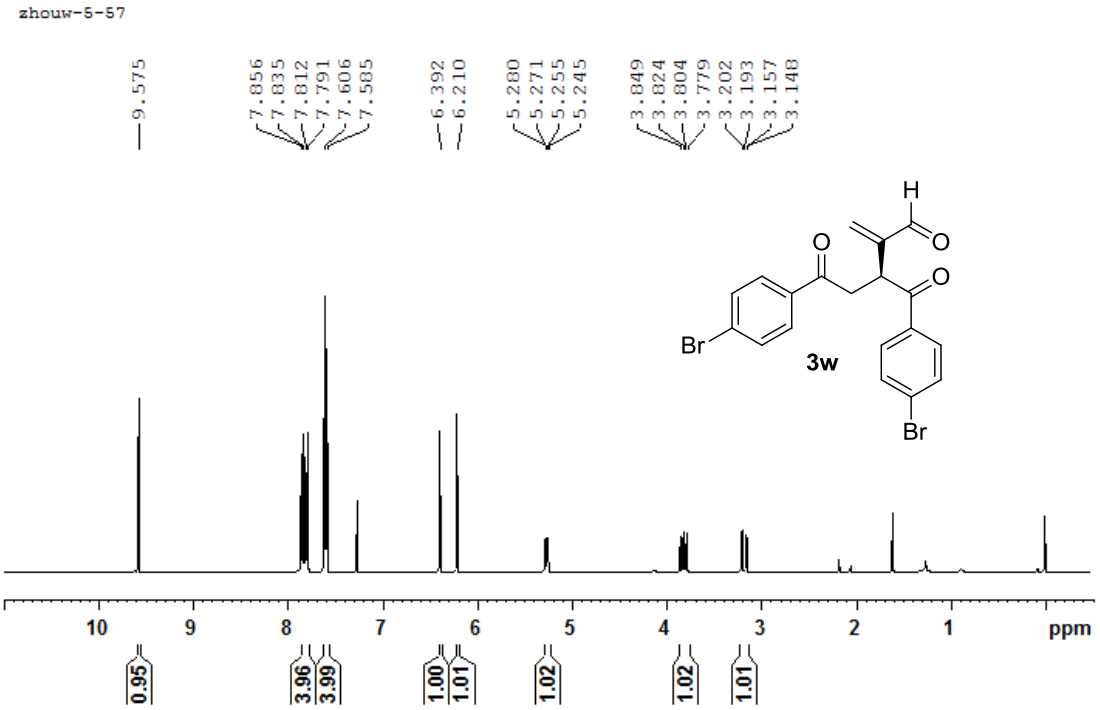
zhouw-5-53s

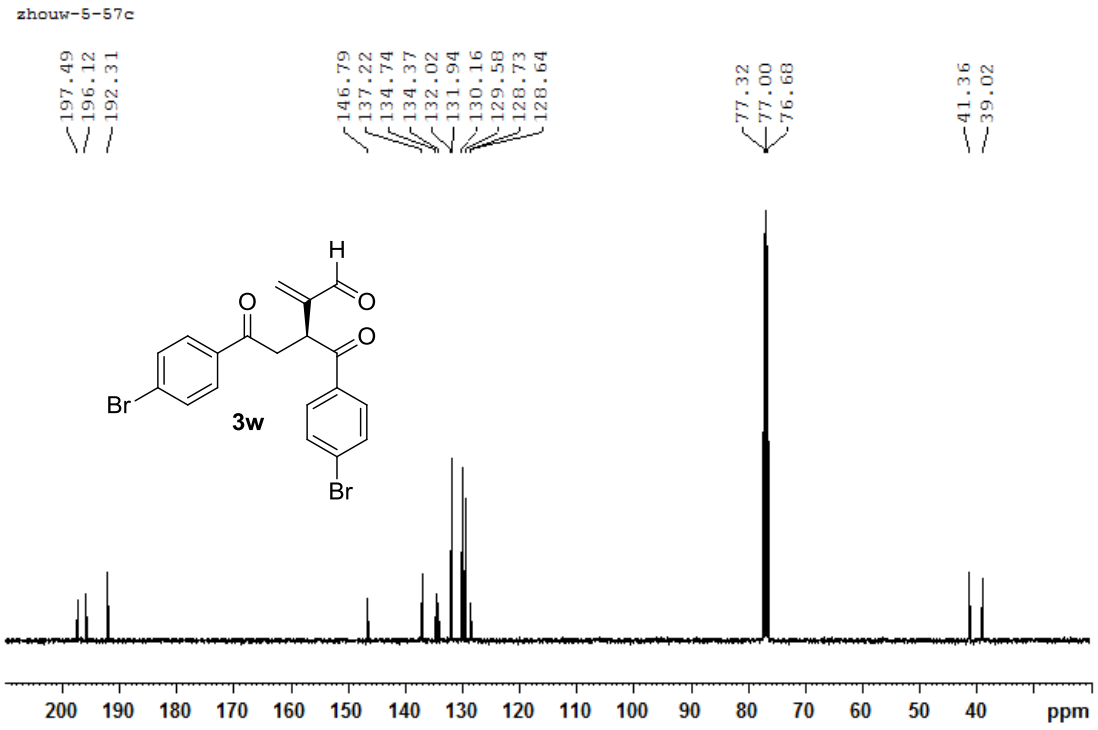


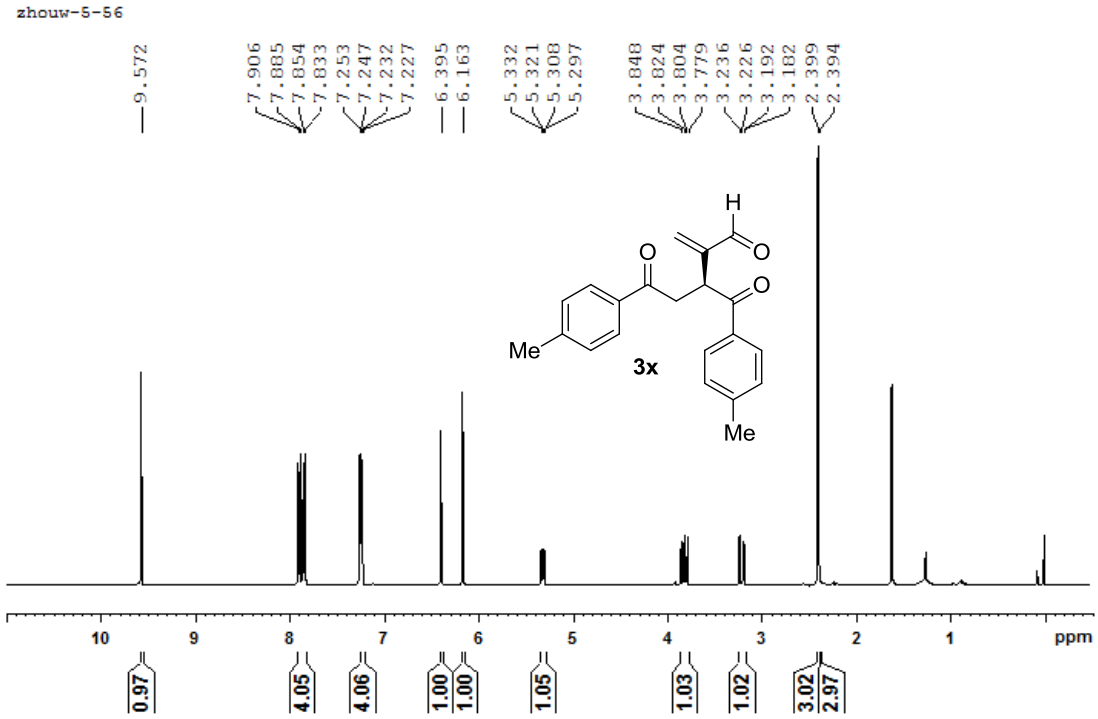

zhouw-5-53c
198.53
197.15
192.47
147.29
136.97
136.18
135.74
133.35
133.31
128.67
128.58
128.09
77.32
77.00
76.69
41.40
39.19
H
O
O
O
3u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

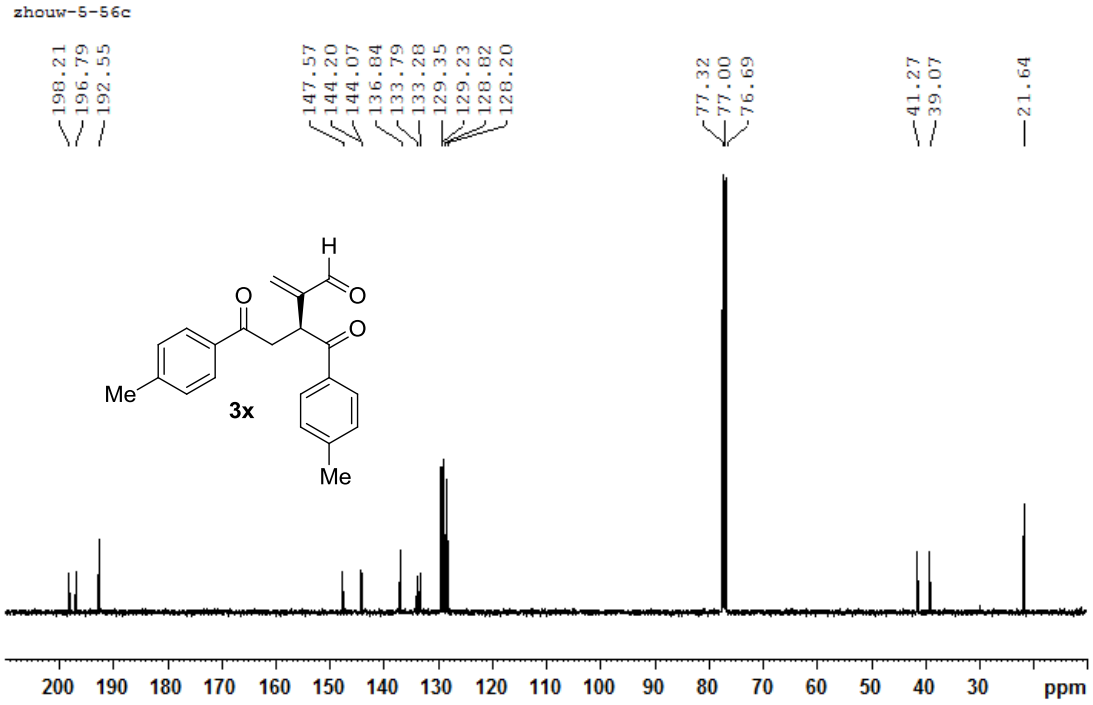

zhouw-5-55
9.577
7.941
7.914
7.890
7.869
7.863
7.443
7.438
7.416
7.410
6.395
6.209
5.290
5.281
5.265
5.256
3.857
3.832
3.813
3.788
3.208
3.198
3.163
3.154
H
O
O
O
Cl
Cl
3v
10 9 8 7 6 5 4 3 2 1 ppm
0.96
4.06
3.97
1.00
1.01
1.03
1.03
1.02

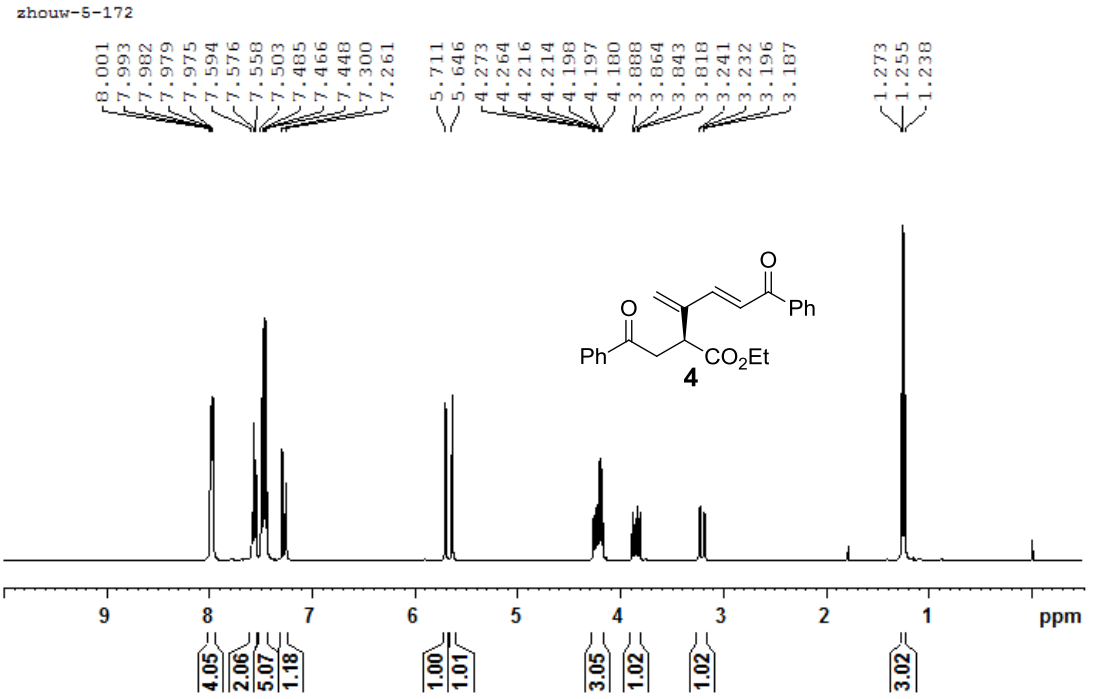

zhouw-5-55c
197.30
195.94
192.32
146.87
139.95
139.88
137.17
134.38
134.00
130.07
129.49
129.02
128.95
77.32
77.00
76.68
41.39
39.07
H
O
O
O
Cl
3v
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm


zhouw-5-57
9.575
7.856
7.835
7.812
7.791
7.606
7.585
6.392
6.210
5.280
5.271
5.255
5.245
3.849
3.824
3.804
3.779
3.202
3.193
3.157
3.148
H
O
O
O
Br
3w
Br
10 9 8 7 6 5 4 3 2 1 ppm
0.95
3.96
3.99
1.00
1.01
1.02
1.02
1.01

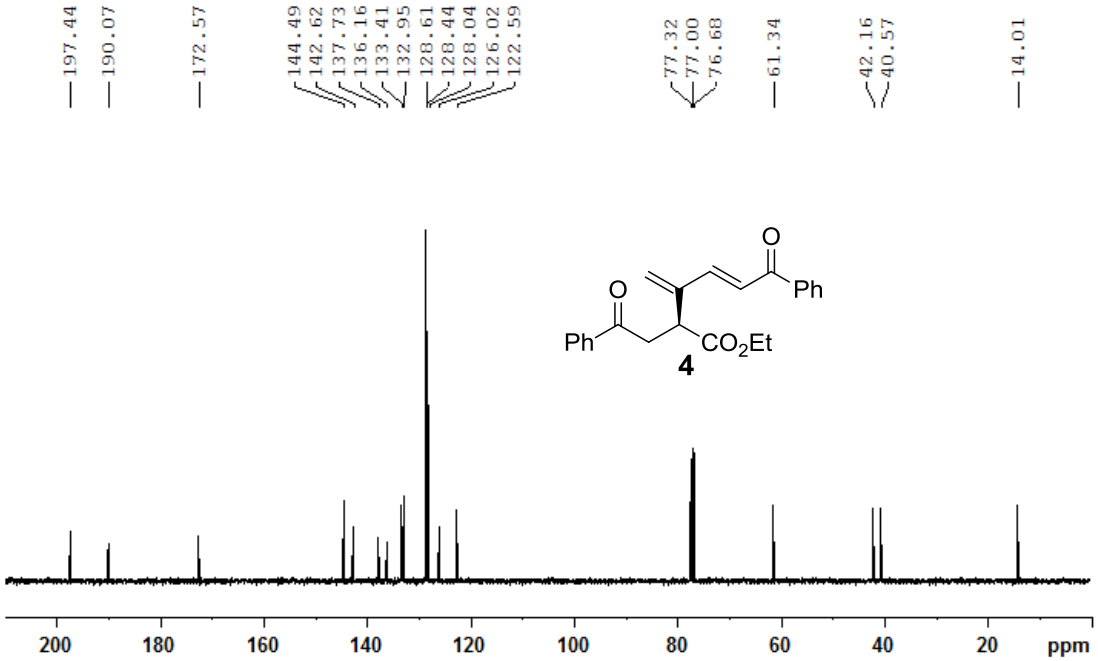

zhouw-5-57c
197.49
196.12
192.31
146.79
137.22
134.74
134.37
132.02
131.94
130.16
129.58
128.73
128.64
77.32
77.00
76.68
41.36
39.02
H
O
O
O
Br
3w
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm


zhouw-5-56
9.572
7.906
7.885
7.854
7.833
7.253
7.247
7.232
7.227
6.395
6.163
5.332
5.321
5.308
5.297
3.848
3.824
3.804
3.779
3.236
3.226
3.192
3.182
2.399
2.394
H
O
O
O
Me
3x
Me
10 9 8 7 6 5 4 3 2 1 ppm
0.97
4.05
4.06
1.00
1.00
1.05
1.03
1.02
3.02
2.97

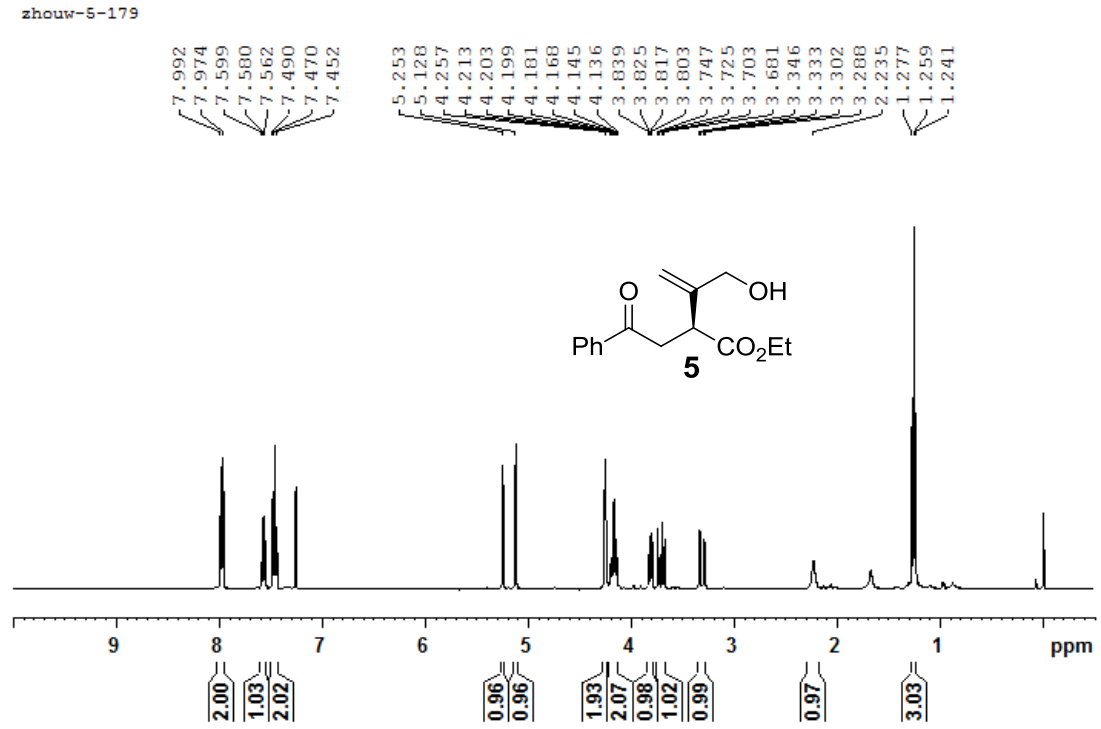

zhouw-5-56c
198.21
196.79
192.55
147.57
144.20
144.07
136.84
133.79
133.28
129.35
129.23
128.82
128.20
77.32
77.00
76.69
41.27
39.07
21.64
H
O
O
O
Me
3x
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm


zhouw-5-172
8.001
7.993
7.982
7.979
7.975
7.594
7.576
7.558
7.503
7.485
7.466
7.448
7.300
7.261
5.711
5.646
4.273
4.264
4.216
4.214
4.198
4.197
4.180
3.888
3.864
3.843
3.818
3.241
3.232
3.196
3.187
1.273
1.255
1.238
O
Ph
O
Ph
CO2Et
4
9 8 7 6 5 4 3 2 1 ppm
4.05
2.06
5.07
1.18
1.00
1.01
3.05
1.02
1.02
3.02

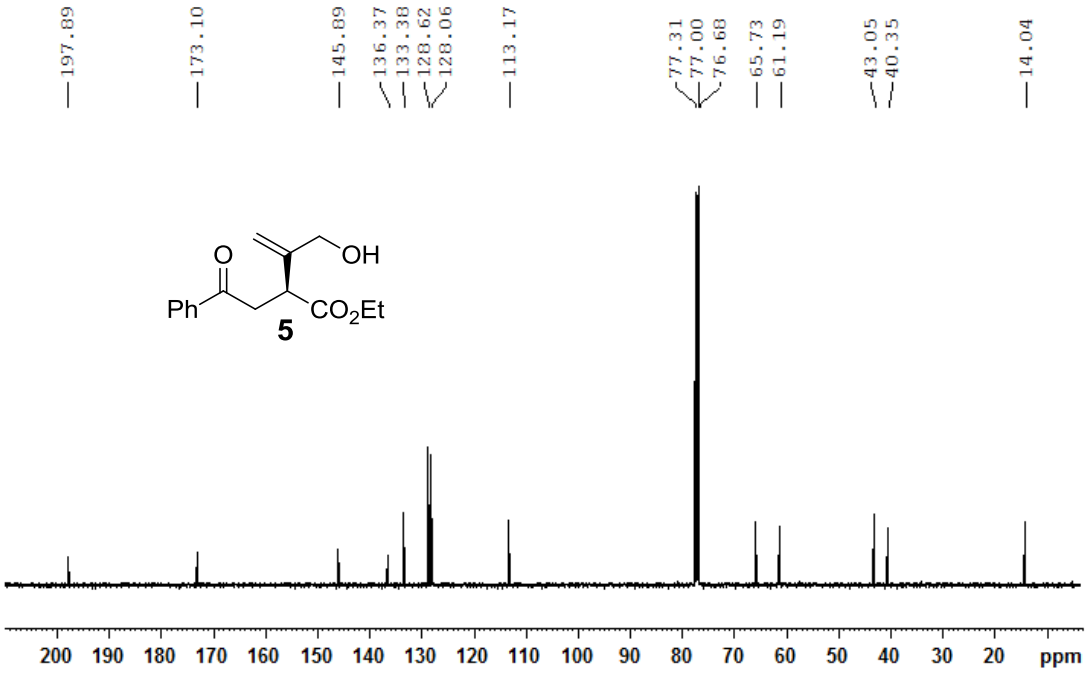
zhouw-5-172c



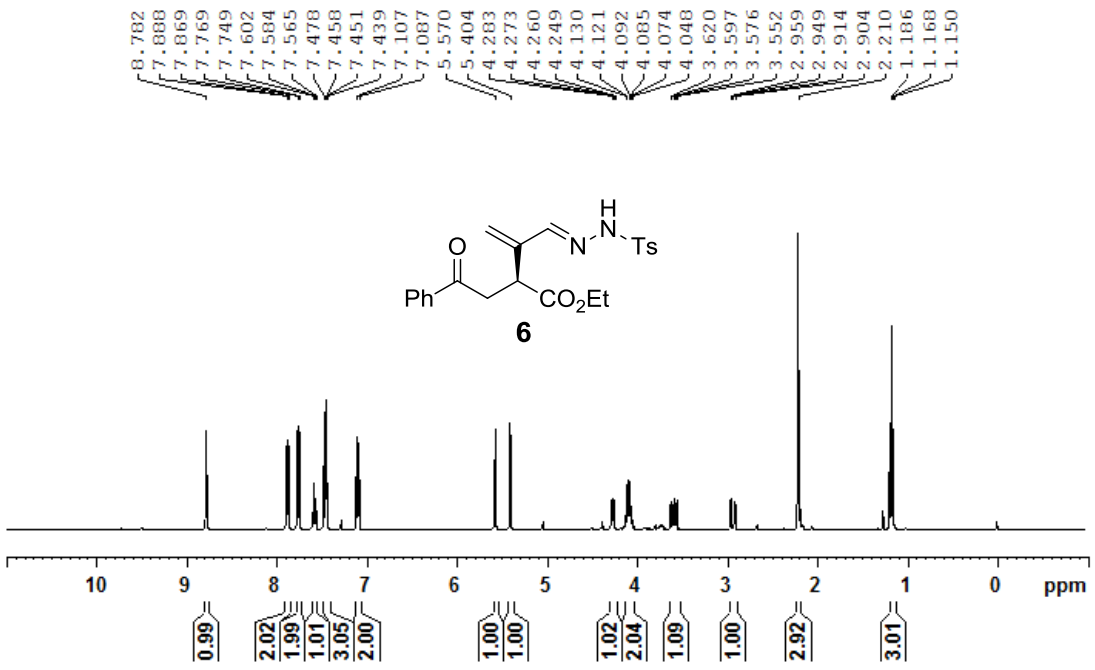
zhouw-5-179

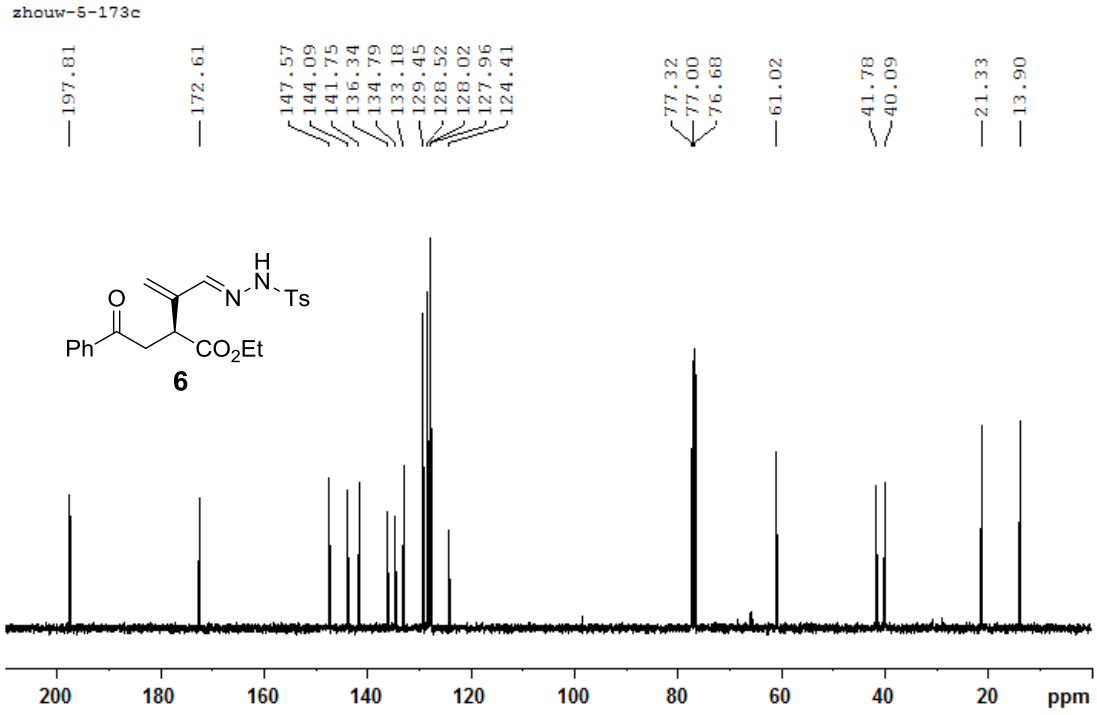


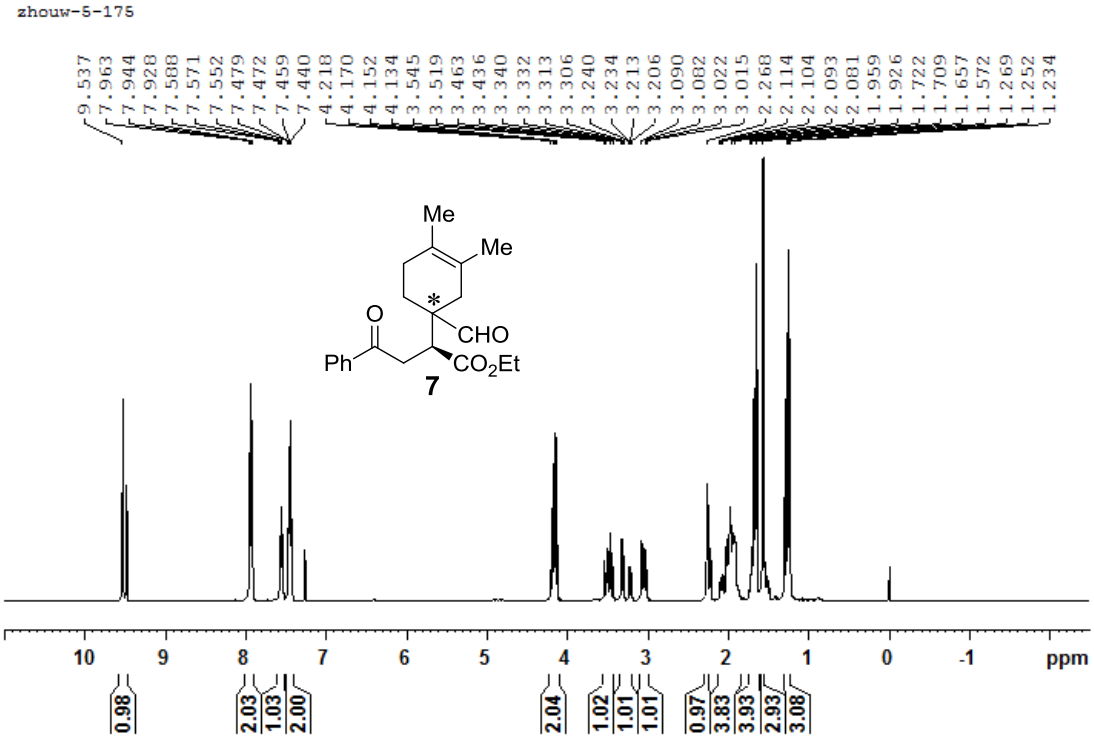
zhouw-5-179c

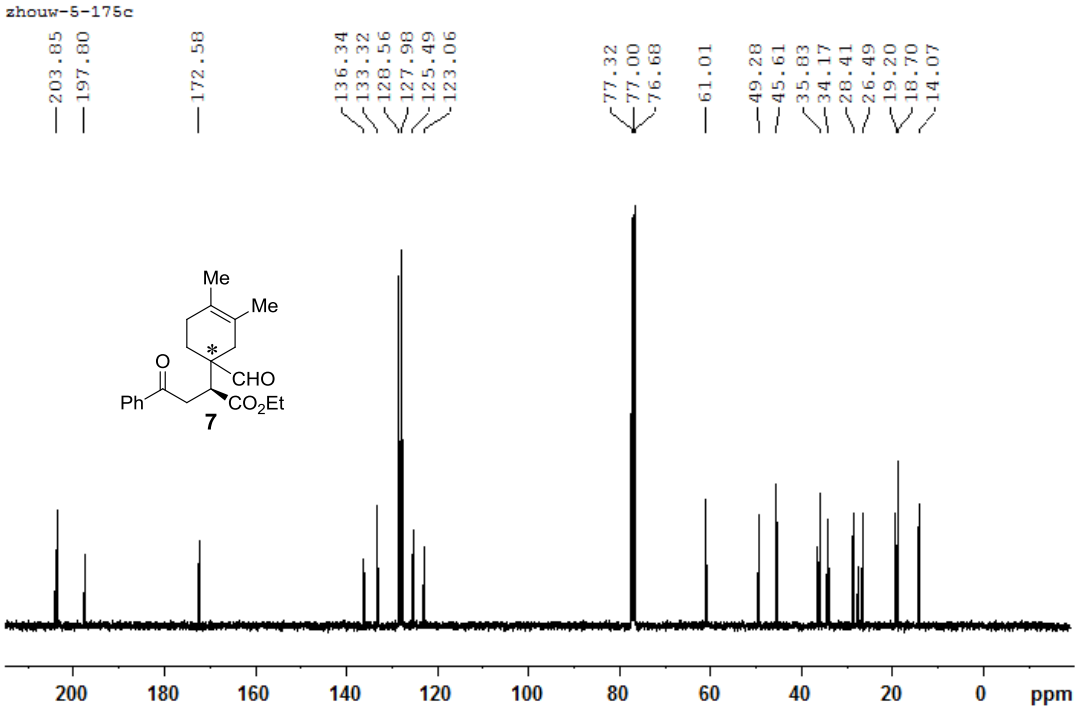


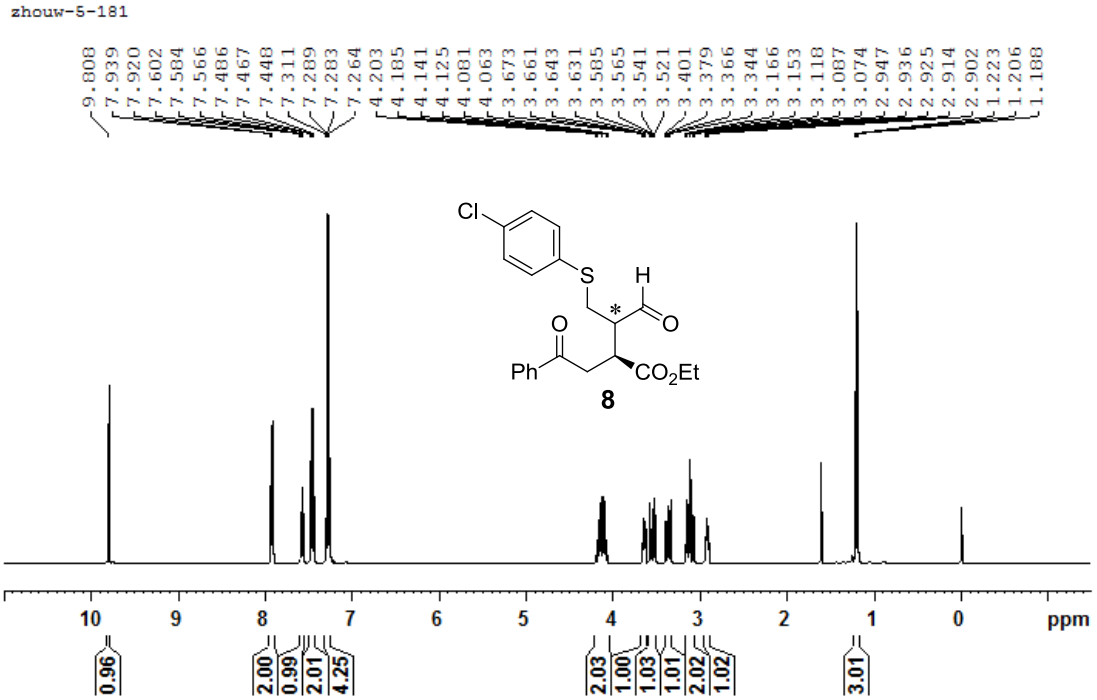
zhouw-5-173

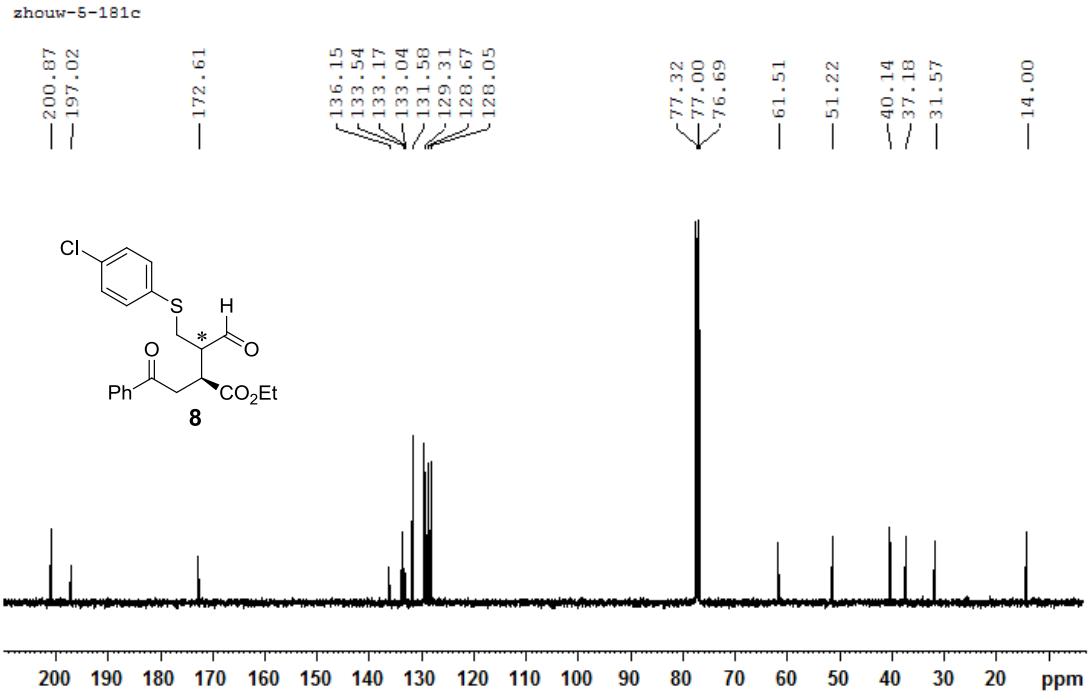


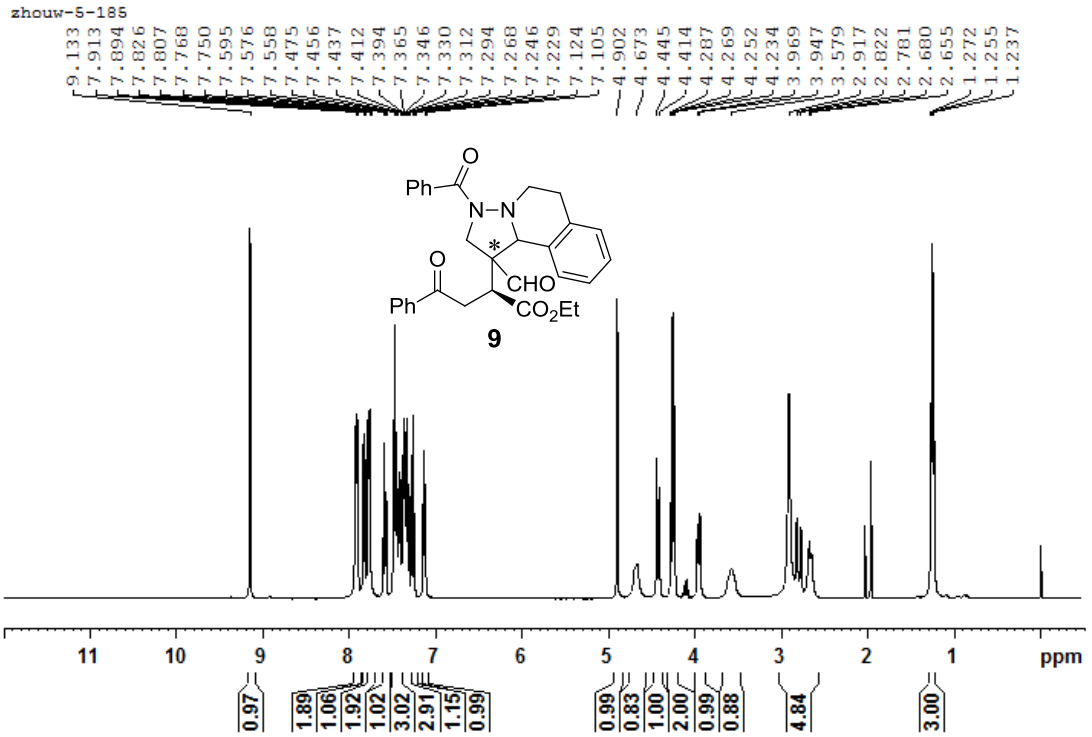

zhouw-5-173c
197.81
172.61
147.57
144.09
141.75
136.34
134.79
133.18
129.45
128.52
128.02
127.96
124.41
77.32
77.00
76.68
61.02
41.78
40.09
21.33
13.90
Ph
O
N
H
N
Ts
CO2Et
6
200
180
160
140
120
100
80
60
40
20
ppm

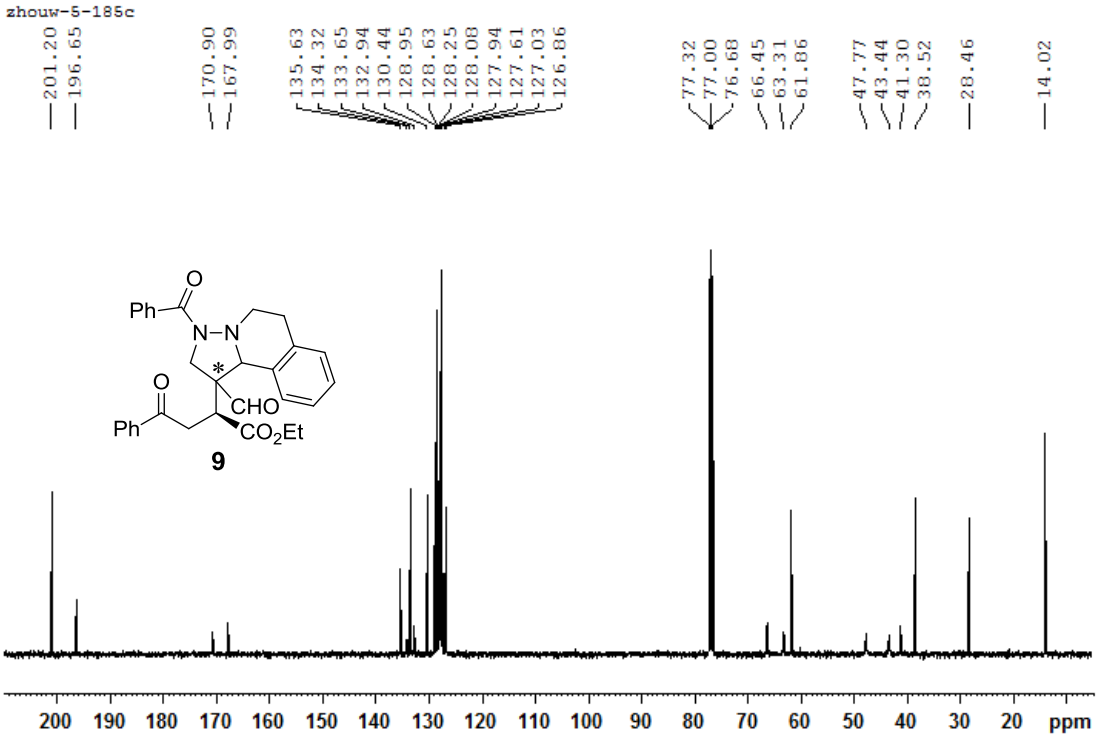

zhouw-5-175
9.537
7.963
7.944
7.928
7.588
7.571
7.552
7.479
7.472
7.459
7.440
4.218
4.170
4.152
4.134
3.545
3.519
3.463
3.436
3.340
3.332
3.313
3.306
3.240
3.234
3.213
3.206
3.090
3.082
3.022
3.015
2.268
2.114
2.104
2.093
2.081
1.959
1.926
1.722
1.709
1.657
1.572
1.269
1.252
1.234
Me
Me
*
CHO
O
Ph
CO2Et
7
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.98
2.03
1.03
2.00
2.04
1.02
1.01
1.01
0.97
3.83
3.93
2.93
3.08

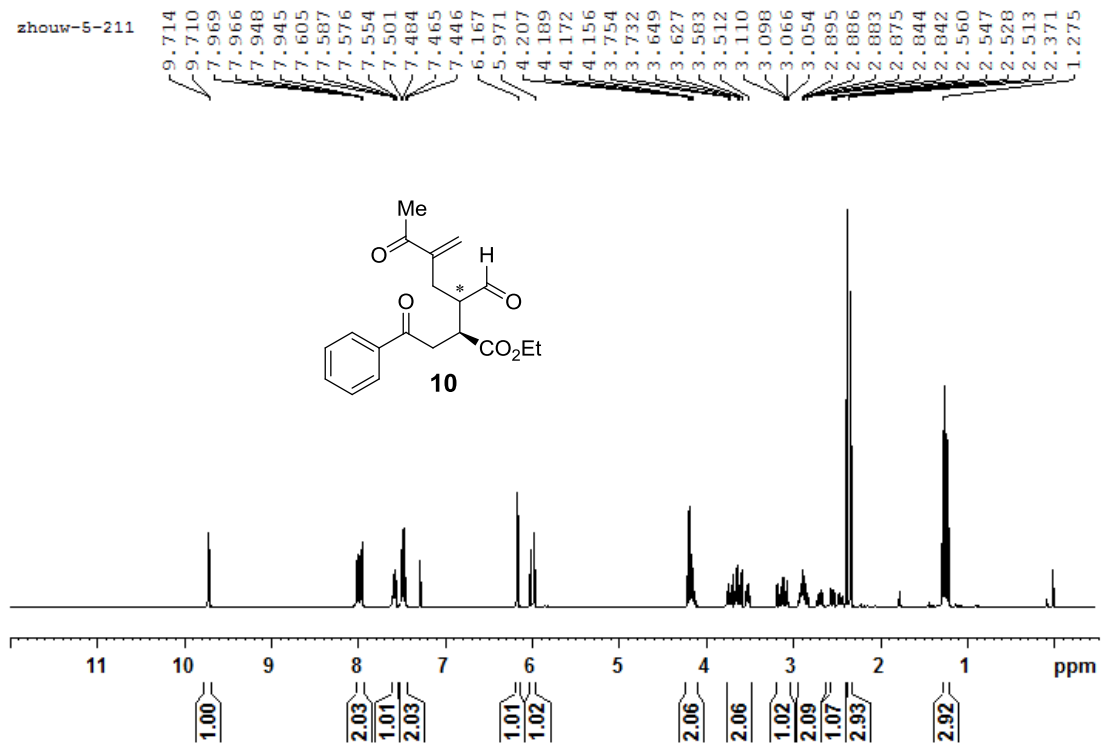

zhouw-5-175c
203.85
197.80
172.58
136.34
133.32
128.56
127.98
125.49
123.06
77.32
77.00
76.68
61.01
49.28
45.61
35.83
34.17
28.41
26.49
19.20
18.70
14.07
Me
Me
O
CHO
Ph
CO2Et
7
200
180
160
140
120
100
80
60
40
20
0
ppm

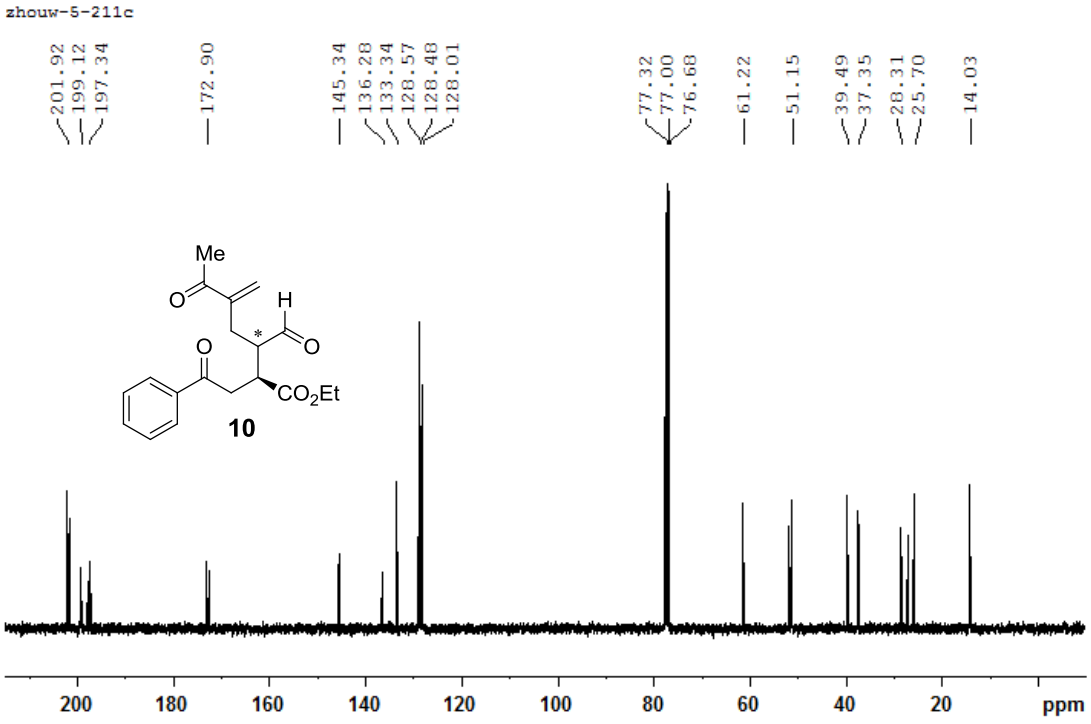

zhouw-5-181
9.808
7.939
7.920
7.602
7.584
7.566
7.486
7.467
7.448
7.311
7.289
7.283
7.264
4.203
4.185
4.141
4.125
4.081
4.063
3.673
3.661
3.643
3.631
3.585
3.565
3.541
3.521
3.401
3.379
3.366
3.344
3.166
3.153
3.118
3.087
3.074
2.947
2.936
2.925
2.914
2.902
1.223
1.206
1.188
Cl
S
H
O
O
Ph
CO2Et
8
10
9
8
7
6
5
4
3
2
1
0
ppm
0.96
2.00
0.99
2.01
4.25
2.03
1.00
1.03
1.01
2.02
1.02
3.01


zhouw-5-181c
200.87
197.02
172.61
136.15
133.54
133.17
133.04
131.58
129.31
128.67
128.05
77.32
77.00
76.69
61.51
51.22
40.14
37.18
31.57
14.00
Cl
S
H
O
O
Ph
CO2Et
8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


zhouw-5-185
9.133
7.913
7.894
7.826
7.807
7.768
7.750
7.595
7.576
7.558
7.475
7.456
7.437
7.412
7.394
7.365
7.346
7.330
7.312
7.294
7.268
7.246
7.229
7.124
7.105
4.902
4.673
4.445
4.414
4.287
4.269
4.252
4.234
3.969
3.947
3.579
2.917
2.822
2.781
2.680
2.655
1.272
1.255
1.237
Ph
O
N–N
O
CHO
Ph
CO2Et
9
11 10 9 8 7 6 5 4 3 2 1 ppm
0.97
1.89
1.06
1.92
1.02
3.02
2.91
1.15
0.99
0.99
0.83
1.00
2.00
0.99
0.88
4.84
3.00


zhouw-5-185c
201.20
196.65
170.90
167.99
135.63
134.32
133.65
132.94
130.44
128.95
128.63
128.25
128.08
127.94
127.61
127.03
126.86
77.32
77.00
76.68
66.45
63.31
61.86
47.77
43.44
41.30
38.52
28.46
14.02
Ph
O
N–N
*
CHO
CO2Et
9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


zhouw-5-211
9.714
9.710
7.969
7.966
7.948
7.945
7.605
7.587
7.576
7.554
7.501
7.484
7.465
7.446
6.167
5.971
4.207
4.189
4.172
4.156
3.754
3.732
3.649
3.627
3.583
3.512
3.110
3.098
3.066
3.054
2.895
2.886
2.883
2.875
2.844
2.842
2.560
2.547
2.528
2.513
2.371
1.275
Me
O
H
*
O
O
CO2Et
10
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
2.03
1.01
2.03
1.01
1.02
2.06
2.06
1.02
2.09
1.07
2.93
2.92


zhouw-5-211c
201.92
199.12
197.34
172.90
145.34
136.28
133.34
128.57
128.48
128.01
77.32
77.00
76.68
61.22
51.15
39.49
37.35
28.31
25.70
14.03
Me
O
H
O
O
CO2Et
10
200
180
160
140
120
100
80
60
40
20
ppm