Organocatalytic Enantioselective Desymmetrization of Cyclic Enones *via* Phosphine Promoted [3+2] Annulations

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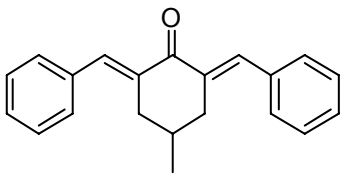
1) General methods

All reactions were run under argon by using standard techniques for manipulating air-sensitive compounds. Anhydrous solvents were obtained by filtration through drying columns (THF, Et_2O, CH_2Cl_2). All reagents were of commercial quality and were used without further purification. Flash column chromatography was performed using 40-63 mesh silica. Nuclear magnetic resonance spectra (^1H, ^{13}C, ^{31}P) were recorded either on Brucker AV 500 or AV 300 spectrometers. IR spectra were recorded with a Perkin-Elmer FT-IR spectrophotometer. High resolution mass spectra (HRMS-ESI) were obtained on LCT Waters equipment. Optical rotations were determined with a JASCO P-1010 polarimeter. HPLC was performed at a column temperature of 30°C on a Waters 2695 Separations Module equipped with a diode array UV detector. Data are reported as follows: column type, eluent, flow rate, retention time.

2) Substrates

4-methylcyclohexanone, 4-*tert*-butylcyclohexanone, 4-phenylcyclohexanone and 4-isopropylcyclohexanone are commercially available. The diarylidenecyclohexanones **1a,c,d,f,e** are known compounds.[1,2] They have been prepared as shown hereafter. 2,4-dibenzylidenebicyclo[3.1.0]hexan-3-one **4a** and 2,4-dibenzylidene-6-methylbicyclo[3.1.0]hexan-3-one **4b** were prepared according to literature procedure.[3]

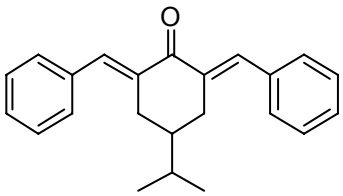


(2*E*,6*E*)-2,6-dibenzylidene-4-methylcyclohexanone **1a**. *Method A:* 4-methylcyclohexanone (10 mmol, 1.12 g) was dissolved in a mixture of ethanol (20 mL) and water (10 mL). Benzaldehyde (20 mmol, 2 mL) and NaOH [1M] (10 mL) were then added at 0°C. The mixture was stirred at room temperature overnight. The yellow precipitate was filtrated and the desired compound was obtained as a yellow solid (2.27 g, 79%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (bs, 2H, C=*CH*C_6H_5), 7.50-7.25 (m, 10H), 3.07

[1] Frey, H. *Synthesis* **1992**, 387-390.
[2] Dimmock, J. R.; Padmanilayam, M. P.; Zello, G. A.; Nienaber, K. H.; Allen, T. M.; Santos, C. L.; De Clercq, E.; Balzarini, J.; Manavathu E. K. ; Stables, J. P. *Eur. J. Med. Chem.*, **2003**, *38*, 169-177
[3] Kearley, M. L.; Lahti, P. M. *Tetrahedron Lett.***1991**, *32*, 5869-5872 ; Kearley, M. L.; Ichimura, A. S.; Lahti, P. M. *J. Am. Chem. Soc.* **1995**, *117*, 5235-5244; Flaugh, M. E.; Crowell, T. A.; Farlow, D. S. *J. Org. Chem.* **1980**, *45*, 5399-5400.

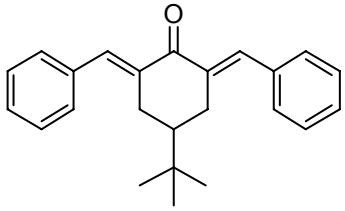
(dd, $^2J_{AB}$ = 16.0, ^3J = 3.5 Hz, 2H, C*H*H), 2.52 (m, 2H, 2C*H*H), 1.89 (m, 1H, C*H*CH_3), 1.08 (d, ^3J = 6.5 Hz, 3H, CHC*H*$_3$); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.3 (Cq), 137.3 (C=*CH*C_6H_5), 136.1 (Cq), 135.5 (Cq), 130.5 (CH), 128.7 (CH), 128.5 (CH), 36.6 (*C*H_2), 29.6 (*CH*CH_3), 21.8 (CH*CH*$_3$); **IR**: ν_{max}= 2957, 1660, 1603, 1568, 1444, 1288, 1240, 1142, 931, 770, 755, 692 cm^{-1}; **MS (ESI)** *m/z* : 289 $[M+H]^+$; **Melting point**: 96-97°C.

(2*E*,6*E*)-2,6-dibenzylidene-4-isopropylcyclohexanone **1b**.

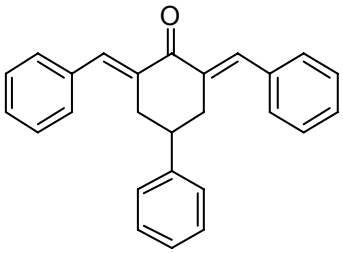


Method A was employed, starting from 4-isopropyl-cyclohexanone (1.6 mmol, 0.25 mL) and benzaldehyde (3.2 mmol, 0.35 mL). The product was obtained as a yellow solid (330 mg, 65%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.8 (br, 2H), 7.50-7.30 (m, 10H), 3.06 (dd, *J* = 15.5, 3.0 Hz, 2H, CH_2), 2.60-2.55 (m, 2H, CH_2), 1.64 (m, *J* = 6.5 Hz, 1H, CH), 1.60-1.50 (m, 1H, CH), 0.91 (d, ^3J = 7.0 Hz, 6H, CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.7 (Cq), 137.3 (C_6H_5C*H*=C), 136.2 (Cq), 135.8 (Cq), 130.5 (CH), 128.7 (CH), 128.6 (CH), 40.4 (CH), 31.7 (CH), 31.6 (CH_2), 19.9 (CH_3); **IR**: ν_{max}= 1661, 1570, 1444, 1291, 1154, 775, 693 cm^{-1}; **MS (ESI)** *m/z* : 339 $[M+Na]^+$; **Melting point**: 102-103°C.

(2*E*,6*E*)-2,6-dibenzylidene-4-*tert*-butylcyclohexanone **1c**. *Method A*: 4-*tert*-butylcyclohexanone (10 mmol, 1.54 g), was dissolved in a mixture of ethanol (20 mL) and water (10 mL). Benzaldehyde (20 mmol, 2 mL) and NaOH [1M] (10 mL) were then added and the resulting mixture was heated at 50°C and stirred overnight. The yellow precipitate was filtrated and the desired compound was obtained as a yellow solid after crystallization in ethanol (1.79 g, 54%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80-7.75 (m, 2H), 7.50-7.30 (m, 10H), 3.17 (dd, *J* = 15.5, 2.0 Hz, 2H, CH_2), 2.50-2.40 (m, 2H, CH_2), 1.49 (m, 1H, CH), 0.95 (s, 9H, CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.8 (Cq), 137.0 (CH), 136.3 (Cq), 136.2 (Cq), 130.4 (CH), 128.7 (CH), 128.6 (CH), 44.5 (CH), 32.7 (Cq), 29.7 (CH_2), 27.4 (CH_3); **IR**: ν_{max}= 2959, 1660, 1603, 1445, 1244, 1157, 983, 776, 693 cm^{-1}; **MS (ESI)** *m/z* : 353 $[M+Na]^+$; **Melting point**: 137-138°C.



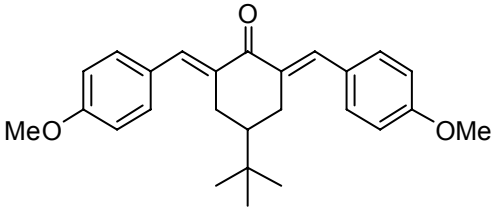
(2*E*,6*E*)-2,6-dibenzylidene-4-phenylcyclohexanone **1d**.



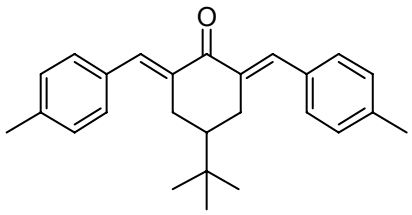
Method A was employed starting from 4-phenylcyclohexanone (2.87 mmol, 500 mg) and benzaldehyde (5.74 mmol, 0.9 mL). The product was obtained as a yellow solid from the crude

reaction mixture by filtration (958 mg, 96%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90-7.85 (m, 2H), 7.45-7.25 (m, 15H), 3.35-3.30 (m, 2H), 3.10-3.00 (m, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 189.7 (Cq), 144.8 (Cq), 138.0 (CH), 135.9 (Cq), 135.2 (Cq), 130.6 (CH), 128.89 (CH), 128.87 (CH), 128.6 (CH), 126.99 (CH), 126.97 (CH), 41.0 (CH), 36.1 (CH_2); **IR**: ν_{max}= 1733, 1660, 1598, 1443, 1288, 1146, 983, 750 691 cm^{-1}; **MS (ESI)** *m/z* : 373 $[M+Na]^+$;**Melting point**: 134-135°C.

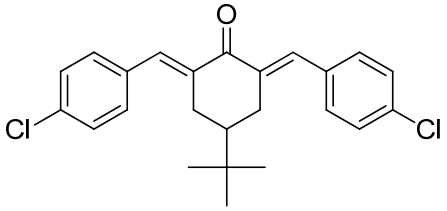
(2*E*,6*E*)-4-*tert*-butyl-2,6-bis(4-methoxybenzylidene) cyclohexanone **1e**. *Method A* was employed starting from 4-*tert*-butylcyclohexanone (10 mmol, 1.54 g) and 4-methoxybenzaldehyde (20 mmol, 2.4 mL). The product was obtained as a yellow solid (2.42 g, 62%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (m, 2H), 7.45 (d, *J* = 8.5 Hz, 4H), 6.95 (d, *J* = 8.5 Hz, 4H), 3.85 (s, 6H, OMe), 3.15 (dd, *J* = 15.5, 2.5 Hz, 2H, CH_2), 2.44 (t, *J* ~ 14 Hz, 2H), 1.48 (tt, *J* = 13.0, 3.0 Hz, 1H), 0.97 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.5 (Cq), 160.0 (2Cq), 136.5 (CH), 134.4 (Cq), 132.3 (CH), 128.9 (Cq), 114.1 (CH), 55.4 (OCH_3), 44.5 (Cq), 32.6 (Cq), 29.7 (CH_2), 27.5 (CH_3); **IR**: ν_{max}= 2951, 1664, 1507, 1291, 1254, 1169, 1029, 830, 770 cm^{-1}; **MS (ESI)** *m/z* : 413 $[M+Na]^+$; **Melting point**: 171-172°C.



(2*E*,6*E*)-4-*tert*-butyl-2,6-bis(4-methylbenzylidene)cyclo-hexanone **1f**. *Method A* was employed with 4-*tert*-butylcyclohexanone (10 mmol, 1.54 g) and 4-methylbenzaldehyde (20 mmol, 2.35 mL)). The product was obtained as a yellow solid (3.10 g, 87%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (m, 2H), 7.41 (d, *J* = 7.5 Hz, 4H), 7.25 (d, *J* = 7.5 Hz, 4H), 3.19 (d, *J* = 15.0 Hz, 2H), 2.46 (t, *J* ~ 14 Hz, 2H), 2.41 (s, 6H), 1.51 (t, *J* = 12.5 Hz, 1H), 0.99 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.7 (Cq), 138.9 (Cq), 136.9 (CH), 135.6 (Cq), 133.4 (Cq), 130.5 (CH), 129.3 (CH), 44.5 (CH), 32.7 (Cq), 29.7 (CH_2), 27.4 ($C(CH_3)_3$), 21.5 (CH_3); **IR**: ν_{max}= 2961, 2358, 1663, 1573, 1315, 1174, 930, 817, 666 cm^{-1}; **MS (ESI)** *m/z* : 381 $[M+Na]^+$; **Melting point**: 156-157°C.

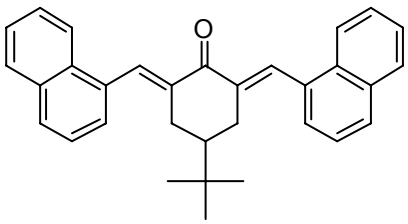


(2*E*,6*E*)-4-*tert*-butyl-2,6-bis(4-chlorobenzylidene)cyclo-hexanone **1g**. *Method A* was employed starting from 4-*tert*-butylcyclohexanone (10 mmol, 1.54 g) and 4-chlorobenzaldehyde (20 mmol, 2.8 g). The product was obtained as a yellow solid (3.25 g, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (bs, 2H), 7.39

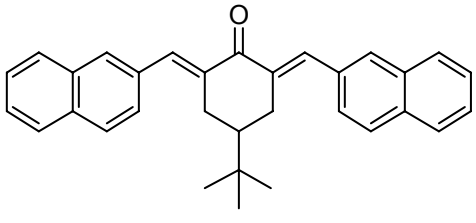


(bs, 8H), 3.09 (m, 2H), 2.41 (m, 2H), 1.47 (m, 1H), 0.94 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.2 (Cq), 136.6 (Cq), 135.8 (CH), 134.7 (Cq), 134.5 (Cq), 131.6 (CH), 128.9 (CH), 44.5 (CH), 32.7 (Cq), 29.6 (CH_2), 27.4 (CH_3); **IR**: ν_{max}= 2958, 1663, 1577, 1558, 1404, 1241, 1092, 983, 928, 823, 704 cm^{-}1; **MS (ESI)** *m/z* : 421 $[M+Na]^+$; **Melting point**: 177-178°C.

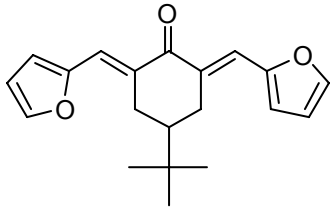
(2*E*,6*E*)-4-*tert*-butyl-2,6-bis(naphthalen-1-ylmethylene)-cyclohexanone **1h**. *Method A* was employed starting from 4-*tert*-butylcyclohexanone (10 mmol, 1.54 g) and 1-naphthaldehyde (20 mmol, 2.7 mL). The product was obtained as a yellow solid (1.98 g, 46%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.43 (m, 2H), 8.10-8.05 (m, 2H), 7.95-7.85 (m, 4H), 7.60-7.45 (m, 8H), 3.06 (dd, *J* = 15.0, 2.4 Hz, 2H), 2.38 (m, 2H), 1.53 (tt, *J* = 12.6, 3.3 Hz, 1H), 0.78 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.5 (Cq), 138.3 (Cq), 135.4 (CH), 133.7 (Cq), 133.3 (Cq), 132.2 (Cq), 129.0 (CH), 128.7 (CH), 126.9 (CH), 126.6 (CH), 126.3 (CH), 125.2 (CH), 124.9 (CH), 45.1 (CH), 32.7 (Cq), 29.9 (CH_2), 27.2 (CH_3); **IR**: ν_{max}= 2955, 1593, 1231, 1196, 1156, 968, 861, 778 cm^{-1}; **MS (ESI)** *m/z* : 453 $[M+Na]^+$; **Melting point**: 146-148°C.



(2*E*,6*E*)-4-*tert*-butyl-2,6-bis(naphthalen-2-ylmethylene)cyclohexanone **1i**. *Method A* was employed with 4-*tert*-butylcyclohexanone (5 mmol, 770 mg) and 2-naphthaldehyde (10 mmol, 1.56 g). The product was obtained as a yellow solid (1.79 g, 83%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (bs, 4H), 7.90-7.80 (m, 6H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.55-7.45 (m, 4H), 3.31 (d, *J* = 15.5 Hz, 2H), 2.58 (t, *J* ~14 Hz, 2H), 1.55-1.50 (m, 1H), 0.97 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.7 (Cq), 137.1 (CH), 136.6 (Cq), 133.8 (2Cq), 133.3 (Cq), 133.2 (Cq), 130.4 (CH), 128.6 (CH), 128.2 (CH), 127.8 (CH), 127.7 (CH), 127.0 (CH), 126.6 (CH), 44.7 (CH), 32.7 (Cq), 29.8 (CH_2), 27.4 (CH_3): **IR**: ν_{max}= 2356, 1692, 1595, 1563, 1429, 1297, 992, 747, 724 cm^{-1}; **MS (ESI)** *m/z* : 453 $[M+Na]^+$; **Melting point**: 191-193°C.



(2*E*,6*E*)-4-*tert*-butyl-2,6-bis(furan-2-ylmethylene)cyclohexanone **1j**. *Method A* was employed starting from 4-*tert*-butylcyclohexanone (10 mmol, 1.54 g) and 2-furaldehyde (20 mmol, 1.65 mL). The product (2.45g, 79%) was obtained as a yellow solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 1.8 Hz, 2H), 7.53 (d, *J* = 2.4 Hz,

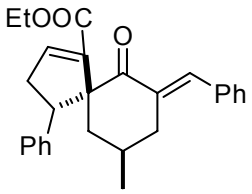


2H), 6.67 (d, *J* = 3.4 Hz, 2H), 6.53 (dd, *J* = 3.4, 1.8 Hz, 2H), 3.38 (dd, *J* = 16.5, 3.0 Hz, 2H), 2.41 (m, 2H), 1.65-1.55 (tt, *J* = 12.9, 3.6 Hz, 1H), 1.06 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 189.5 (Cq), 152.9 (Cq), 144.7 (CH), 133.3 (Cq), 123.4 (CH), 116.2 (CH), 112.4 (CH), 43.3 (CH), 32.2 (Cq), 29.4 (CH_2), 27.5 (CH_3); **IR**: ν_{max}= 2959, 1596, 1477, 1307, 1239, 730 cm^{-1}; **MS (ESI)** *m/z* : 333 $[M+Na]^+$; **Melting point**: 136-138°C.

3) Phosphine promoted [3+2] cyclisations on enones 1.

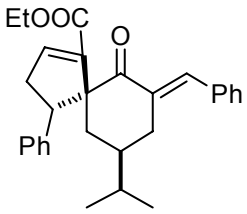
***Procedure a*:** Ethyl 2,3 butadienoate (0,40 mmol) was added to a mixture of enones **1** (0.20 mmol) and cyclohexyldiphenyl phosphine (10 mol %, 0.020 mmol, 5.4 mg) in degazed toluene (0.7 mL) under argon atmosphere. The solution was stirred at 40°C until completion. The crude mixture was concentrated *in vacuo*. Diastereomeric ratios were measured by NMR on the crude mixture, based on integration of the C=CHPh signals at about 7.5 ppm. The final product was purified by flash chromatography on silica gel (5% EtOAc / heptanes).
***Procedure b*:** Ethyl 2,3 butadienoate (0,30 mmol) was added to a mixture of enones **1** (0.15 mmol) and either FerroPHANE, **A**, or *t*-Bu-Binepine, **B** (10 mol %, 0.015 mmol) in degazed toluene (0.5 mL) under argon atmosphere. The solution was stirred at 80°C until completion. The crude mixture was concentrated *in vacuo*. Diastereomeric ratios were measured by NMR on the crude mixture, based on integration of the C=CHPh signals at about 7.5 ppm. The final product was purified by flash chromatography on silica gel (5% EtOAc / heptanes).

(*E*)-ethyl 7-benzylidene-9-methyl-6-oxo-4-phenylspiro[4.5]dec-1-ene-1-carboxylate **2a**. ***Procedure a*** (catalyst $CyPPh_2$): 95% yield, 90/10 dr; Procedure b (catalyst (S,S)-FerroPHANE): 91% yield, 76% ee, 80/20 dr**;** Pale yellow oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 (bs, 1H, C_6H_5CH=C), 7.35-7.10 (m, 10H), 6.91 (m, 1H, CH_2CH=C), 4.15-4.00 (m, 3H, CH_2CH_3, $CH_2CHC_6H_5$), 2.88 (ddd, $^2J_{AB}$ = 18.0 Hz, ^3J = 10,2, 1.8 Hz, 1H, CH_2CH=C), 2.75-2.65 (m, 2H, CH_2CH=C, CH_2CHCH_3), 2.13 (ddd, $^2J_{AB}$ = 15.3 Hz, ^3J = 12.6, 3.0 Hz, 1H, CH_2CHCH_3), 1.85 (dt, $^2J_{AB}$ = 13.8, $^3J \approx {}^4J$ = 3.0 Hz, 1H, CH_2CHCH_3), 1.60 (t, $^2J \approx {}^3J$ = 13 Hz, 1H, CH_2CHCH_3), 1.18 (t, ^3J = 6.9 Hz, 3H, CH_2CH_3), 0.54 (d, ^3J = 6.6 Hz, 3H, $CHCH_3$), 0.40-0.25 (m, 1H, $CHCH_3$); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.2 (Cq), 163.8 (Cq), 143.4 (Cq), 143.3 (CH_2CH=C), 139.1 (Cq), 136.7 (Cq), 136.1 (Cq), 136.0 (C_6H_5CH=C), 130.5 (2CH), 128.6 (2CH), 128.5 (CH), 128.4 (2CH), 128.4 (2CH), 127.5 (CH), 62.9 (Cq), 60.7 (CH_2CH_3), 56.1 ($CH_2CHC_6H_5$), 37.5 (CH_2), 36.6 (CH_2), 35.7 (CH_2), 26.5 ($CHCH_3$), 22.0 ($CHCH_3$), 14.3 (CH_2CH_3); **IR**: ν_{max}= 2924, 1706, 1592, 1491, 1445, 1242, 1075, 1026, 904,

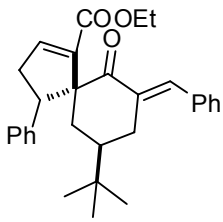


750, 696 cm^{-1}; **HRMS (ESI)** calcd. For $C_{27}H_{28}NaO_3$ $[M+Na]^+$: 423.1936, found: 423.1921; **HPLC Analysis**: 76% ee [Daicel CHIRACEL IC, 10% *i*PrOH/*n*-heptane, 1mL/min, 300 nm, retention times: 19.8 min (major) and 34.8 min (minor)]. Minor diastereoisomer: selected **^{1}H NMR** data (300 MHz, $CDCl_3$) δ 7.67 (bs), 6.99 (dd, *J* = 3.0, 2.0 Hz), 4.21 (dd, *J* = 11.1, 7.5 Hz), 1.40 (t, *J* = 13.0 Hz), 0.75 (d, *J* = 6.6 Hz).

(*E*)-ethyl 7-benzylidene-9-isopropyl-6-oxo-4-phenylspiro[4.5]dec-1-ene-1-carboxylate **2b**. ***Procedure a*** (catalyst $CyPPh_2$): 93% yield, 85/15 dr; ***Procedure b*** (catalyst (*S*,*S*)-FerroPHANE): 44% yield, 82% ee, 80/20 dr; Pale yellow oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2.5 Hz, 1H), 7.40-7.15 (m, 10H), 7.00 (t, *J* = 2.0 Hz, 1H), 4.25-4.10 (m, 3H), 2.96 (ddd, *J* = 18.0, 10.0, 2.0 Hz, 1H), 2.80-2.75 (m, 2H), 2.24 (ddd, *J* = 15.5, 12.2, 3.0 Hz, 1H), 1.93 (dt, *J* = 13.5, 3.0 Hz, 1H), 1.69 (t, *J* = 13.0 Hz, 1H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.20-1.10 (m, 1H), 0.57 (d, *J* = 6.5 Hz, 3H), 0.54 (d, *J* = 6.5 Hz, 3H), 0.30-0.20 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.4 (Cq), 163.8 (Cq), 143.5 (CH), 143.3 (Cq), 139.1 (Cq), 136.9 (Cq), 136.2 (Cq), 136.1 (CH), 130.4 (2CH), 128.9 (2CH), 128.5 (2CH), 128.4 (3CH), 127.4 (CH), 62.8 (Cq), 60.6 (CH_2), 55.9 (CH), 36.6 (CH), 35.8 (CH_2), 32.3 (CH), 31.8 (CH_2), 31.7 (CH_2), 19.6 (CH_3), 18.9 (CH_3), 14.2 (CH_3); **IR**: ν_{max}= 2956, 2360, 1708, 1592, 1446, 1326, 1244, 1091, 1027, 911, 865 cm^{-1}; **HRMS (ESI)** calcd. For $C_{29}H_{32}NaO_3$ $[M+Na]^+$: 451.2249, found: 451.2259; **HPLC Analysis**: 82% ee [Daicel CHIRACEL IA, 10% *i*PrOH/*n*-heptane, 1mL/min, 300 nm, retention times: 7.7 min (minor) and 10.2 min (major)]; Minor diastereoisomer: selected **^{1}H NMR** data (500 MHz, $CDCl_3$) δ 7.68 (br), 7.04 (dd, *J* = 2.9, 1.95 Hz), 0.73 (dd, *J* = 7.0, 5.5 Hz).

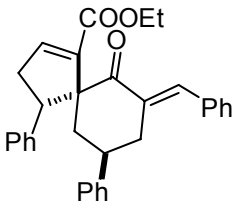


(*E*)-ethyl 7-benzylidene-9-*tert*-butyl-6-oxo-4-phenylspiro[4.5]dec-1-ene-1-carboxylate **2c**. ***Procedure a*** (catalyst $CyPPh_2$): 92% yield, >95/5 dr; ***Procedure b*** (catalyst (*S*,*S*)-FerroPHANE): 98% yield, 92% ee, >95/5 dr; White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.4 Hz, 1H), 7.30-7.10 (m, 10H), 6.95 (t, *J* = 2.7 Hz, 1H), 4.15-4.00 (m, 3H), 2.90 (ddd, *J* = 18.3, 9.6, 2.1 Hz, 1H), 2.83 (dt, *J* = 14.4, 3.0 Hz, 1H), 2.71 (ddd, *J* = 18.3, 8.1, 3.0 Hz, 1H), 2.15 (td, *J* = 15.0, 2.7 Hz, 1H), 1.92 (dt, *J* = 13.8, 2.7 Hz, 1H), 1.65 (t, *J* = 13.2 Hz, 1H), 1.18 (t, *J* = 6.9 Hz, 3H), 0.49 (s, 9H), 0.27 (tt, *J* = 13.0, 3.5 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.4 (Cq), 163.8 (Cq), 143.6 (CH), 143.3 (Cq), 139.0 (Cq), 137.4 (Cq), 136.2 (Cq), 135.9 (CH), 130.2 (2CH), 129.1 (2CH), 128.5 (2CH), 128.4 (2CH), 128.3 (CH), 127.4 (CH), 63.0 (Cq), 60.6 (CH_2), 55.8 (CH), 40.2 (CH), 35.8 (CH_2), 32.2 (Cq), 29.9 (CH_2), 29.2 (CH_2), 27.0

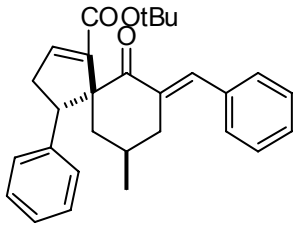


(3CH_3), 14.2 (CH_3); **IR**: ν_{max}= 2946, 1697, 1667, 1588, 1370, 1327, 1243, 1232, 1162, 1095, 1027, 754, 697 cm^{-1}; **HRMS (ESI)** calcd. For $C_{30}H_{34}NaO_3$ $[M+Na]^+$: 465.2406, found: 465.2397; **HPLC Analysis**: 92% ee [Daicel CHIRACEL IC, 10% *i*PrOH/*n*-heptane, 1mL/min, 300 nm, retention times: 16.4 min (major) and 40.0 min (minor)]; $[\alpha]_D^{24}$ = + 290 (c = 0.91, $CHCl_3$); **Melting point**: 128-130°C.

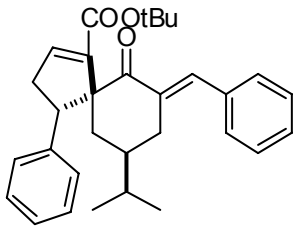
(*E*)-ethyl 7-benzylidene-6-oxo-1,9-diphenylspiro[4.5]dec-1-ene-2-carboxylate **2d**. ***Procedure a*** (catalyst $CyPPh_2$): 86% yield, 90/10 dr; ***Procedure b*** (catalyst (*S*,*S*)-FerroPHANE): 98% yield, 92% ee, 85/15 dr; White solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (bs, 1H), 7.40-7.15 (m, 13H), 7.02 (bs, 1H), 6.80 (d, *J* = 7.5 Hz, 2H), 4.30-4.20 (m, 3H), 3.05-2.90 (m, 2H), 2.85-2.75 (m, 2H), 2.24 (dd, *J* = 14.0, 13.0 Hz, 1H), 2.18 (d, *J* = 13.0 Hz, 1H), 1.65-1.60 (m, 1H), 1.33 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 204.7 (Cq), 163.8 (Cq), 145.1 (Cq), 143.4 (Cq), 143.1 (CH), 138.9 (Cq), 136.9 (CH), 136.4 (Cq), 135.8 (Cq), 130.5 (2CH), 128.9 (2CH), 128.8 (2CH), 128.6 (2CH), 128.5 (3CH), 127.7 (CH), 126.8 (2CH), 126.5 (CH), 63.3 (Cq), 60.8 (CH_2), 56.2 (CH), 37.8 (CH), 37.2 (CH_2), 35.5 (CH_2), 35.2 (CH_2), 14.3 (CH_3); **IR**: ν_{max}= 2932, 1697, 1592, 1371, 1327, 1240, 1151, 760, 747, 693 cm^{-1}; **HRMS (ESI)** calcd. For $C_{32}H_{30}NaO_3$ $[M+Na]^+$: 485.2093, found: 485.2073; **HPLC Analysis**: 92% ee [Daicel CHIRACEL IA, 5% *i*PrOH/*n*-heptane, 1ml/min, 270 nm, retention times: 13.8 min (minor) and 18.4 min (major)]; **Melting point**: 165-166°C.



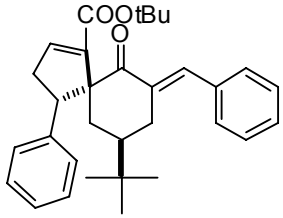
(*E*)-tert-butyl 7-benzylidene-9-methyl-6-oxo-4-phenylspiro[4.5]dec-1-ene-1-carboxylate **3a**. ***Procedure a*** (catalyst $CyPPh_2$): 90% yield, 85/15 dr; ***Procedure b*** (catalyst (S,S)-FerroPHANE): 86% yield, 90% ee, 80/20 dr; White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.4 Hz, 1H), 7.35-7.05 (m, 10H), 6.85 (t, *J* = 2.4 Hz, 1H), 3.98 (m, 1H), 2.86 (ddd, *J* = 17.7, 10.2, 2.1 Hz, 1H), 2.70-2.60 (m, 1H), 2.08 (ddd, *J* = 15.3, 12.6, 3.0 Hz, 1H), 1.83 (dt, *J* = 13.8, 3.0 Hz, 1H), 1.59 (t, *J* = 12.6 Hz, 2H), 1.37 (s, 9 H), 0.54 (d, *J* = 6.6 Hz, 3H), 0.35-0.25 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.1 (Cq), 163.1 (Cq), 144.6 (Cq), 142.8 (CH), 139.3 (Cq), 136.8 (Cq), 136.2 (Cq), 135.9 (CH), 130.4 (2CH), 128.6 (2CH), 128.44 (CH), 128.41 (4CH), 127.43 (CH), 81.2 (Cq), 62.9 (Cq), 56.5 (CH), 37.5 (CH_2), 36.7 (CH_2), 35.4 (CH_2), 28.2 (CH_3), 26.3 (CH), 22.0 (CH_3); **IR**: ν_{max}= 2919, 1693, 1671, 1590, 1445, 1332, 1244, 1148, 1076, 1022, 847 cm^{-1}; **Melting point**: 142-144°C; **HRMS (ESI)** calcd. For $C_{29}H_{32}NaO_3$ $[M+Na]^+$: 451.2249, found:



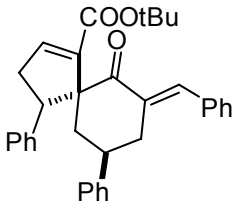
451.2256; **HPLC Analysis**: 90% ee [Daicel CHIRACEL IA, 5% *i*PrOH/*n*-heptane, 1mL/min, 300 nm, retention times: 7.4 min (minor) and 12.1 min (major)].



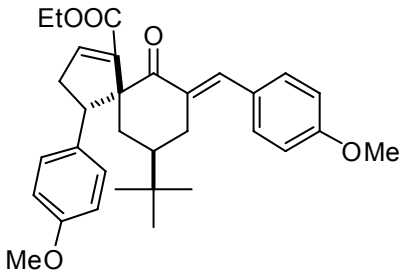
(*E*)-*tert*-butyl 7-benzylidene-9-isopropyl-6-oxo-4-phenylspiro[4.5]-dec-1-ene-1-carboxylate **3b**. ***Procedure a*** (catalyst $CyPPh_2$): 91% yield, 70/30 dr; ***Procedure b*** (catalyst (S,S)-FerroPHANE): 43% yield, 86% ee, 70/30 dr; Pale yellow oil; *Selected data from the mixture of two diastereoisomers:* **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.5 Hz, 1H), 7.45-7.15 (m, 10H), 6.98 (m, 1H), 4.09 (dd, *J* = 9.0, 8.5 Hz, 1H), 3.00-2.90 (m, 1H), 2.80-2.70 (m, 2H), 2.24 (td, *J* = 15.5, 2.5 Hz, 1H), 1.95 (broad d, *J* = 13.5 Hz, 1H), 1.73 (t, *J* = 13.5 Hz, 1H), 1.46 (s, 9H), 1.25-1.15 (m, 1H), 0.62 (d, *J* = 7.0 Hz, 3H), 0.58 (d, *J* = 6.5 Hz, 3H), 0.30-0.20 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.4 (Cq), 163.1 (Cq), 144.5 (Cq), 142.9 (CH), 137.1 (Cq), 136.3 (Cq), 135.9 (CH), 130.3 (2CH), 129.0 (2CH), 128.4 (4CH), 128.3 (CH), 127.3 (CH), 81.1 (Cq), 62.8 (Cq), 56.4 (CH), 36.3 (CH_2), 35.5 (CH), 32.3 (CH_2), 31.85 (CH), 31.78 (CH), 28.2 (CH_3), 19.6 (CH_3), 18.9 (CH_3); **IR**: ν_{max}= 2927, 1702, 1674, 1591, 1366, 1161, 935, 754, 696 cm^{-1}; **HRMS (ESI)** calcd. For $C_{31}H_{36}NaO_3$ $[M+Na]^+$: 479.2562, found: 479.2581; **HPLC Analysis**: 86% ee [Daicel CHIRACEL IA, 2% EtOH/*n*-heptane, 1mL/min, 300 nm, retention times: 11.3 min (minor) and 15.4 min (major)].



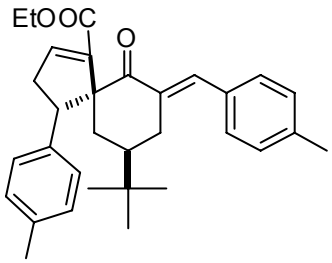
(*E*)-*tert*-butyl 7-benzylidene-9-tert-butyl-6-oxo-4-phenylspiro[4.5]-dec-1-ene-1-carboxylate **3c**. ***Procedure a*** (catalyst $CyPPh_2$): 87% yield, 90/10 dr; ***Procedure b*** (catalyst (S,S)-FerroPHANE): 71% yield, 95% ee, 90/10 dr; Pale yellow solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 1.5 Hz, 1H), 7.45-7.15 (m, 10H), 6.99 (br, 1H), 4.06 (t, *J* = 9.0 Hz, 1H), 2.95 (ddd, *J* = 18.0, 9.5, 2.0 Hz, 1H), 2.91 (m, 1H), 2.78 (ddd, *J* = 18.0, 8.0, 3.0 Hz, 1H), 2.21 (m, 1H), 1.99 (m, 1H), 1.75 (t, *J* = 13.0 Hz, 1H), 1.47 (s, 9H), 0.60 (s, 9H), 0.33 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.4 (Cq), 163.2 (Cq), 144.6 (Cq), 143.0 (CH), 139.3 (Cq), 137.6 (Cq), 136.3 (Cq), 135.8 (CH), 130.2 (2CH), 129.2 (2CH), 128.5 (4CH), 128.4 (CH), 127.4 (CH), 81.2 (Cq), 62.9 (Cq), 56.3 (CH), 39.9 (CH), 35.6 (CH_2), 32.3 (Cq), 29.9 (CH_2), 29.2 (CH_2), 28.3 (CH_3), 27.0 (CH_3); **IR**: ν_{max}= 2965, 1701, 1586, 1365, 1253, 1161, 1105, 758, 691 cm^{-1}; **Melting point**: 123-126°C; **HRMS (ESI)** calcd. For $C_{32}H_{38}NaO_3$ $[M+Na]^+$: 493.2719, found: 493.2713; **HPLC Analysis**: 95% ee [Daicel CHIRACEL IA, 5% *i*PrOH/*n*-heptane, 1ml/min, 300 nm, retention times: 6.5 min (minor) and 8.4 min (major)].



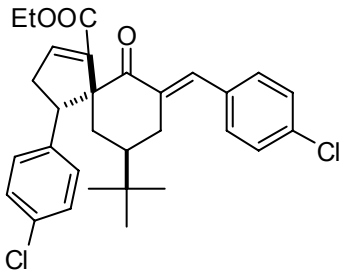
(*E*)-tert-butyl 7-benzylidene-6-oxo-4,9-diphenylspiro[4.5]dec-1-ene-1-carboxylate **3d**. ***Procedure a*** (catalyst $CyPPh_2$): 64% yield, 85/15 dr; White solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (m, 1H), 7.40-6.95 (m, 15H), 6.82 (d, *J* = 7.5 Hz, 1H), 4.23 (dd, *J* = 10.0, 8.0 Hz, 1H), 3.00-2.90 (m, 2H), 2.90-2.70 (m, 2H), 2.25 (t, *J* = 13.5 Hz, 1H), 2.15-2.10 (m, 1H), 1.65-1.55 (m, 1H), 1.53 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 204.6 (Cq), 163.0 (Cq), 145.2 (Cq), 144.4 (Cq), 142.9 (CH), 139.1 (Cq), 136.8 (CH), 136.5 (Cq), 135.9 (Cq), 130.4 (CH), 128.9 (CH), 128.8 (CH), 128.6 (CH), 128.5 (CH), 127.7 (CH), 126.7 (CH), 126.5 (CH), 81.3 (Cq), 63.2 (Cq), 56.6 (CH), 37.6 (CH), 37.1 (CH_2), 35.3 (CH_2), 35.2 (CH_2), 28.3 (CH_3); **IR**: ν_{max}= 3060, 2979, 1695, 1591, 1338, 1243, 1157, 1122, 945, 750, 692 cm^{-1}; **HRMS (ESI)** calcd. For $C_{34}H_{34}NaO_3$ $[M+Na]^+$: 513.2406, found: 513.2406; HPLC Analysis: 90% ee [Daicel CHIRACEL IA, 5% EtOH/*n*-heptane, 1mL/min, 300 nm, retention times: 6.3 min and 7.3 min]; **Melting point**: 130-131°C.



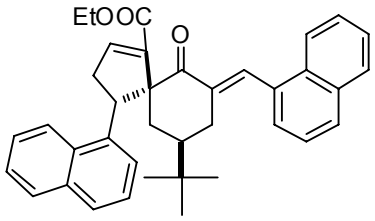
(*E*)-ethyl 9-*tert*-butyl-7-(4-methoxybenzylidene)-4-(4-methoxyphenyl)-6-oxospiro[4.5]dec-1-ene-1-carboxylate **2e**. ***Procedure b*** (catalyst (*S,S*)-FerroPHANE): 91% yield, 93% ee, >95/5 dr; Colorless oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 2.1 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.99 (t, *J* = 2.4 Hz, 1H), 6.92 (d, *J* = 6.9 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 4.20-4.05 (m, 3H), 3.83 (s, 3H), 3.75 (s, 3H), 2.95-2.85 (m, 2H), 2.76 (ddd, *J* = 18.3, 8.1, 3.0 Hz, 1H), 2.30-2.20 (m, 1H), 1.96 (dt, *J* = 13.5, 3.0 Hz, 1H), 1.70 (t, *J* = 13.2 Hz, 1H), 1 .24 (t, *J* = 6.9 Hz, 3H), 0.61 (s, 9H), 0.43 (tt, *J* = 12.6, 3.0 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.2 (Cq), 163.9 (Cq), 159.9 (Cq), 158.9 (Cq), 143.5 (CH), 143.4 (Cq), 136.1 (C*H*), 135.2 (Cq), 132.2 (2CH), 131.3 (Cq), 130.1 (2CH), 128.8 (Cq), 114.0 (2CH), 113.9 (2CH), 62.7 (Cq), 60.5 (CH_2), 55.5 (CH_3), 55.4 (CH_3), 55.0 (CH), 40.0 (CH), 36.1 (CH_2), 32.2 (Cq), 29.8 (CH_2), 29.3 (CH_2), 27.2 ($3CH_3$), 14.2 (CH_3); **IR**: ν_{max}= 2953, 2358, 1709, 1604, 1509, 1366, 1248, 1162, 1030, 830, 730 cm^{-1}; **HRMS (ESI)** calcd. For $C_{32}H_{38}NaO_5$ $[M+Na]^+$: 525.2617, found: 555.2601; **HPLC Analysis**: 94% ee [Daicel CHIRACEL IA, 5% *i*PrOH/*n*-heptane, 1mL/min, 300 nm, retention times: 22.4 min (minor) and 43.8 min major)]; **$[\alpha]_D^{24}$ =** +355 (c = 1.23, $CHCl_3$).



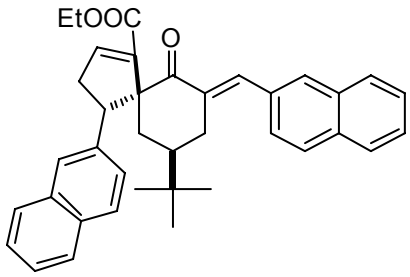
(*E*)-ethyl 9-*tert*-butyl-7-(4-methylbenzylidene)-6-oxo-4-p-tolyl-spiro[4.5]dec-1-ene-1-carboxylate **2f**. ***Procedure b*** (catalyst (*S,S*)-FerroPHANE)**:** 77% yield, 90% ee, 95/5 dr; White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.1 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 7.01 (t, *J* = 2.4 Hz, 1H), 4.30-4.00 (m, 3H), 3.00-2.85 (m, 2H), 2.76(ddd, *J* = 18.0, 7.8, 3.0 Hz, 1H), 2.37 (s, 3H), 2.29 (s, 3H), 2.25-2.15 (m, 1H), 1.97 (dt, *J* = 13.5, 3.0 Hz, 1H), 1.70 (t, *J* = 13.2 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.58 (s, 9H), 0.37 (tt, *J* = 12.9, 3.0 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.5 (Cq), 163.9 (Cq), 143.5 (CH), 143.4 (Cq), 138.6 (Cq), 137.0 (Cq), 136.5 (Cq), 136.1 (CH), 136.0 (Cq), 133.4 (Cq), 130.4 (2CH), 129.2 (2CH), 129.1 (2CH), 129.0 (2CH), 62.8 (Cq), 60.6 (CH_2), 55.5 (CH), 40.0 (CH), 35.9 (CH_2), 32.3 (Cq), 29.9 (CH_2), 29.3 (CH_2), 27.1 ($3CH_3$), 21.5 (CH_3), 21.1 (CH_3), 14.2 (CH_3); **IR**: ν_{max}= 2945, 1701, 1670, 1597, 1435, 1367, 1233, 1160, 1093, 1029, 813, 755 cm^{-1}; **Melting point**: 172-173°C; **HRMS (ESI)** calcd. For $C_{32}H_{38}NaO_3$ $[M+Na]^+$: 493.2719, found: 493.2735; **HPLC Analysis**: 90% ee [Daicel CHIRACEL IA, 5% *i*PrOH/*n*-heptane, 1mL/min, 300 nm, retention times: 11.5 min (minor) and 17.9 min major)]; **$[\alpha]_D^{24}$** = +320 (c = 0.87, $CHCl_3$).



(*E*)-ethyl 9-tert-butyl-7-(4-chlorobenzylidene)-4-(4-chloro phenyl)-6-oxospiro[4.5]dec-1-ene-1-carboxylate **2g**. ***Procedure b*** (catalyst (*S,S*)-FerroPHANE): 86% yield, 86% ee, >95/5 dr; White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 (d, J = 2.4 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.00 (t, ^3J = 2.5 Hz, 1H, CH_2CH=C), 4.20-4.00 (m, 3H), 2.95-2.75 (m, 3H), 2.25 (m, 1H), 1.95 (dt, *J* = 13.8, 2.7 Hz, 1H), 1.72 (t, *J* = 13.2 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.59 (s, 9H), 0.29 (tt, *J* = 12.9, 2.7 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 204.8 (Cq), 163.7 (Cq), 143.3 (CH, Cq), 137.7 (Cq), 137.5 (Cq), 134.9 (CH), 134.5 (Cq), 134.4 (Cq), 133.2 (Cq), 131.5 (2CH), 130.4 (2CH), 128.8 (2CH), 128.6 (2CH), 62.8 (Cq), 60.7 (CH_2), 54.9 (CH), 40.5 (CH), 35.9 (CH_2), 32.3 (Cq), 29.8 (CH_2), 29.2 (CH_2), 27.1 (CH_3), 14.3 (CH_3); **IR**: ν_{max}= 2942, 1704, 1587, 1491, 1369, 1235, 1163, 1089, 1013, 831, 760 cm^{-1}; **Melting point**: 145-147°C; **HRMS (ESI)** calcd. For $C_{30}H_{32}NaCl_2O_3$ $[M+Na]^+$: 533.1626, found: 533.1608; **HPLC Analysis**: 86% ee [Daicel CHIRACEL IA, 5% *i*PrOH/*n*-heptane, 1mL/min, 300 nm, retention times: 11.6 min (minor) and 15.8 min major)]; **$[\alpha]_D^{24}$** = +280 (c = 1.0, $CHCl_3$).

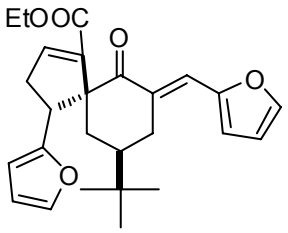


(*E*)-ethyl 9-*tert*-butyl-4-(naphthalen-1-yl)-7-(naphthalen-1-ylmethylene)-6-oxospiro[4.5]dec-1-ene-1-carboxylate **2h** ***Procedure b*** (catalyst (*S,S*)-FerroPHANE): 95% yield, 85% ee, 95/5 dr; Pale yellow oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 1H), 7.95 (br, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.79 (dd, *J* = 12.5, 8.5 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.55-7.20 (m, 7H), 7.13 (t, *J* = 2.5 Hz, 1H), 6.95 (d, *J* = 7.0 Hz, 1H), 5.02 (t, *J* = 9.0 Hz, 1H), 4.30-4.20 (m, 2H), 3.22 (ddd, *J* = 18.5, 10.0, 2.0 Hz, 1H), 2.96 (ddd, *J* = 18.0, 7.5, 3.0 Hz, 1H), 2.28 (dt, *J* = 14.5, 2.8 Hz, 1H), 2.19 (dt, *J* = 14.0, 2.5 Hz, 1H), 1.97 (m, 1H), 1.75 (t, *J* = 13.0 Hz, 1H), 1.33 (t, *J* = 7.0 Hz, 3H), 0.37 (s, 9H), -0.1 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 206.4 (Cq), 163.9 (Cq), 143.5 (Cq), 143.2 (CH), 139.4 (Cq), 135.4 (Cq), 134.9 (CH), 134.1 (Cq), 133.6 (Cq), 133.4 (Cq), 132.7 (Cq), 131.6 (Cq), 128.9 (CH), 128.3 (CH), 128.2 (CH), 126.7 (CH), 126.3 (CH), 126.2 (CH), 126.1 (CH), 126.0 (CH), 125.9 (CH), 125.4 (CH), 125.3 (CH), 125.0 (CH), 124.5 (CH), 63.5 (Cq), 60.7 (CH_2), 50.0 (CH), 40.9 (CH), 37.8 (CH_2), 32.2 (Cq), 31.0 (CH_2), 29.1 (CH_2), 26.9 (CH_3), 14.4 (CH_3); **IR**: ν_{max}= 2954, 1704, 1597, 1440, 1366, 1246, 1160, 1046, 907, 777, 728 cm^{-1}; **HRMS (ESI)** calcd. For $C_{38}H_{38}KO_3$ $[M+K]^+$: 581.2458, found: 581.2482; **HPLC Analysis**: 81% ee [Daicel CHIRACEL IA, 5% *i*PrOH/*n*-heptane, 1mL/min, 300 nm, retention times: 10.9 min (minor) and 18.4 min major)]; **$[\alpha]_D^{24}$** = -20 (c = 1.2, $CHCl_3$).

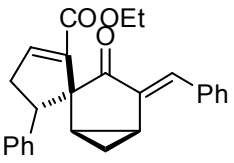


(*E*)-ethyl 9-tert-butyl-4-(naphthalen-2-yl)-7-(naphthalen-2-ylmethylene)-6-oxospiro[4.5]dec-1-ene-1-carboxylate **2i**. ***Procedure b*** (catalyst (*S,S*)-FerroPHANE): 72% yield, 90% ee, 95/5 dr; White solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.90-7.70 (m, 9H), 7.55-7.40 (m, 5H), 7.31 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.10 (t, *J* = 2.7 Hz, 1H), 4.35-4.15 (m, 3H), 3.14 (ddd, *J* = 18.0, 9.6, 2.1 Hz, 1H), 2.98 (m, 1H), 2.90 (ddd, *J* =18.3, 7.8, 3.0 Hz, 1H), 2.40-2.30 (m, 1H), 2.11 (dt, *J* = 13.8, 2.7 Hz, 1H), 1.80 (t, *J* = 12.9 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.41 (s, 9H), 0.31 (dt, *J* = 12.9, 3.0 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.4 (Cq), 163.9 (Cq), 143.6 (CH), 143.4 (Cq), 137.7 (Cq), 136.6 (Cq), 136.2 (CH), 133.7 (Cq), 133.4 (Cq), 133.2 (Cq), 133.1 (Cq), 132.8 (Cq), 130.1 (CH), 128.4 (CH), 128.0 (3CH), 127.79 (CH), 127.75 (CH), 127.62 (CH), 127.59 (CH), 127.3 (CH), 126.8 (CH), 126.5 (CH), 126.3 (CH), 125.9 (CH), 63.2 (Cq), 60.7 (CH_2), 56.0 (CH), 40.3 (CH), 36.0 (CH_2), 32.1 (Cq), 30.1 (CH_2), 29.4 (CH_2), 26.9 (CH_3), 14.3 (CH_3); **IR**: ν_{max}= 2956, 2359, 1706, 1585, 1366, 1241, 1162, 1097, 855, 818, 746, 668 cm^{-1}; **Melting point**: 165-166°C; **HRMS (ESI)** calcd. For $C_{38}H_{38}NaO_3$ $[M+Na]^+$: 565.2719, found: 565.2736; **HPLC Analysis**: 90% ee [Daicel

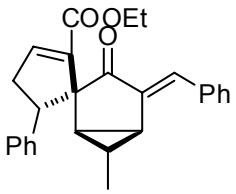
CHIRACEL IA, 5% *i*PrOH/*n*-heptane, 1mL/min, 300 nm, retention times: 14.8 min (minor) and 27.8 min (major)]; $[\alpha]_D^{24}$ = +343 (c = 0.88, $CHCl_3$).



(*E*)-ethyl 9-tert-butyl-4-(furan-2-yl)-7-(furan-2-ylmethylene)-6-oxospiro[4.5]dec-1-ene-1-carboxylate **2j**. ***Procedure b*** (catalyst (*S,S*)-FerroPHANE): 57% yield, 92% ee, 75/25 dr; Yellow oil; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 1.5 Hz, 1H), 7.49 (d, *J* = 2.4 Hz, 1H), 7.29 (dd, *J* = 1.5, 0.6 Hz, 1H), 6.91 (t, *J* = 2.4 Hz, 1H), 6.62 (d, *J* = 3.3 Hz, 1H), 6.49 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.28 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.11 (d, *J* = 3.0 Hz, 1H), 4.20-4.00 (m, 3H), 3.18 (dt, *J* = 16.5, 3.0 Hz, 1H), 2.88 (ddd, *J* = 18.0, 10.5, 3.0 Hz, 1H), 2.77 (ddd, *J* = 18.0, 8.1, 3.0 Hz, 1H), 2.31 (ddd, *J* = 15.9, 13.2, 2.7 Hz, 1H), 2.03 (dt, *J* = 13.8, 2.7 Hz, 1H), 1.65 (t, *J* = 13.2 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.76 (s, 9H), 0.44 (tt, *J* = 12.9, 3.6 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 203.6 (Cq), 163.5 (Cq), 153.5 (Cq), 152.9 (Cq), 144.6 (CH), 143.8 (Cq), 142.6 (CH), 141.4 (CH), 133.1 (Cq), 123.5 (CH), 116.2 (CH), 112.4 (CH), 110.6 (CH), 108.1 (CH), 62.2 (Cq), 60.6 (CH_2), 49.0 (CH), 39.4 (CH), 34.7 (CH_2), 32.3 (Cq), 30.0 (CH_2), 29.4 (CH_2), 27.2 (CH_3), 14.1 (CH_3); **IR**: ν_{max}= 2960, 1709, 1670, 1591, 1243, 1103, 735 cm^{-1}; **HRMS (ESI)** calcd. For $C_{26}H_{30}NaO_5$ $[M+Na]^+$: 423.2171, found: 423.2176; **HPLC Analysis**: 92% ee [Daicel CHIRACEL IA, 5% *i*PrOH/*n*-heptane, 1mL/min, 330 nm, retention times: 22.3 min (minor) and 35.8 min (major)]; $[\alpha]_D^{24}$ = +166 (c = 0.62, $CHCl_3$).



(*E*)-ethyl 4-benzylidene-3-oxo-5'-phenylspiro[bicyclo[3.1.0]hexane-2,1'-cyclopent[2]ene]-2'-carboxylate **5a.** ***Procedure b*** (catalyst (*S,S*)-FerroPHANE): 63% yield, 83% ee, 95/5 dr; Orange oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (m, 2H), 7.65-7.45 (m, 9H), 7.38 (t, *J* = 2.7 Hz, 1H), 4.33 (m, 2H), 4.08 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.46 (ddd, *J* = 18.6, 8.4, 2.7 Hz, 1H), 3.06 (ddd, *J* = 18.9, 6.3, 2.7 Hz, 1H), 2.75-2.60 (m, 1H), 1.85-1.75 (m, 1H), 1.39 (t, *J* = 6.9 Hz, 3H), 1.17-1.10 (m, 1H), 0.03 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 209.1 (Cq), 163.9 (Cq), 146.2 (CH), 142.6 (Cq), 140.4 (Cq), 139.3 (Cq), 135.9 (Cq), 131.1 (CH), 130.1 (2CH), 129.1 (CH), 128.8 (2CH), 128.7 (2CH), 128.4 (2CH), 126.9 (CH), 67.0 (Cq), 60.6 (CH_2), 52.5 (CH), 40.0 (CH_2), 22.3 (CH), 20.2 (CH), 15.9 (CH_2), 14.1 (CH_3); **IR**: ν_{max}= 2928, 1708, 1625, 1493, 1325, 1263, 1177, 1112, 1028, 755, 692 cm^{-1}; **HRMS (ESI)** calcd. For $C_{26}H_{24}NaO_3$ $[M+Na]^+$: 407.1623, found: 407.1634; **HPLC Analysis**: 86% ee [Daicel CHIRACEL IA, 10% *i*PrOH/ *n*-heptane, 1mL/min, 300 nm, retention times: 6.8 min (major) and 7.8 min (minor)]; $[\alpha]_D^{24}$ = +11 (c = 1.6, $CHCl_3$).

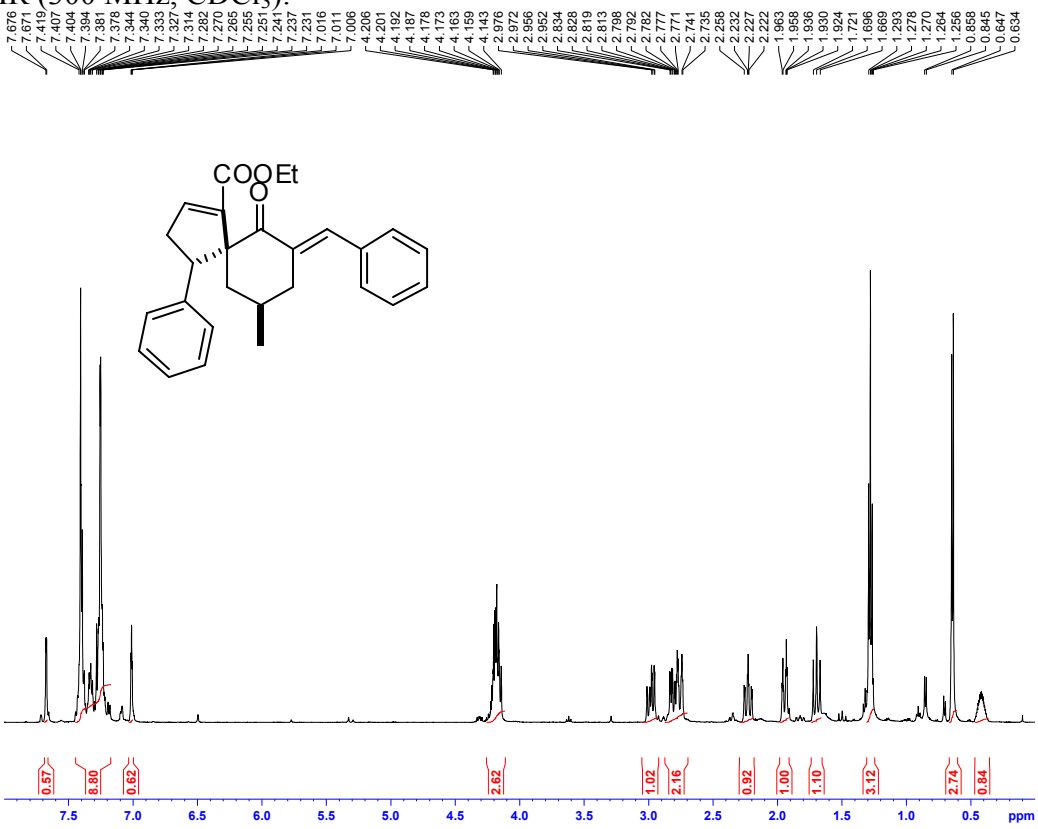


(*E*)-ethyl 4-benzylidene-6-methyl-3-oxo-5'-phenylspiro[bicyclo[3.1.0] hexane-2,1'-cyclopent[2]ene]-2'-carboxylate **5b**. ***Procedure b*** (catalyst (*S,S*)-FerroPHANE): 66% yield, 83% ee, 95/5 dr; Orange oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 2H), 7.40-7.20 (m, 9H), 7.11 (t, *J* = 2.5 Hz, 1H), 4.08 (m, 2H), 3.77 (dd, *J* = 9.0, 5.5 Hz, 1H), 3.24 (ddd, *J* = 19.0, 9.0, 2.5 Hz, 1H), 2.79 (ddd, *J* = 19.0, 5.5, 2.5 Hz, 1H), 2.23 (m, 1H), 1.25 (m, 1H), 1.14 (t, *J* = 7.0 Hz, 3H), 0.69 (d, *J* = 6.0 Hz, 3H), 0.13 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 209.8 (Cq), 163.9 (Cq), 146.0 (CH), 143.5 (Cq), 140.3 (Cq), 138.9 (Cq), 135.9 (Cq), 130.7 (CH), 130.1 (2CH), 129.1 (CH), 128.7 (4CH), 128.4 (2CH), 126.9 (CH), 67.9 (Cq), 60.6 (CH_2), 52.4 (CH), 40.5 (CH_2), 30.9 (CH), 29.0 (CH), 25.1 (CH) 16 9 (CH_3), 14.1 (CH_3); **IR**: ν_{max}= 2924, 1711, 1627, 1448, 1264, 1176, 1102, 1027, 732 cm^{-1}; **HRMS (ESI)** calcd. For $C_{27}H_{26}NaO_3$ $[M+Na]^+$: 421.1780, found: 421.1786; **HPLC Analysis**: 83% ee [Daicel CHIRACEL IA, 10% *i*PrOH/ *n*-heptane, 1mL/min, 270 nm, retention times: 7.9 min (major) and 10.9 min (minor)]; **$[\alpha]_D^{24}$** = +16 (c = 1.5, $CHCl_3$).

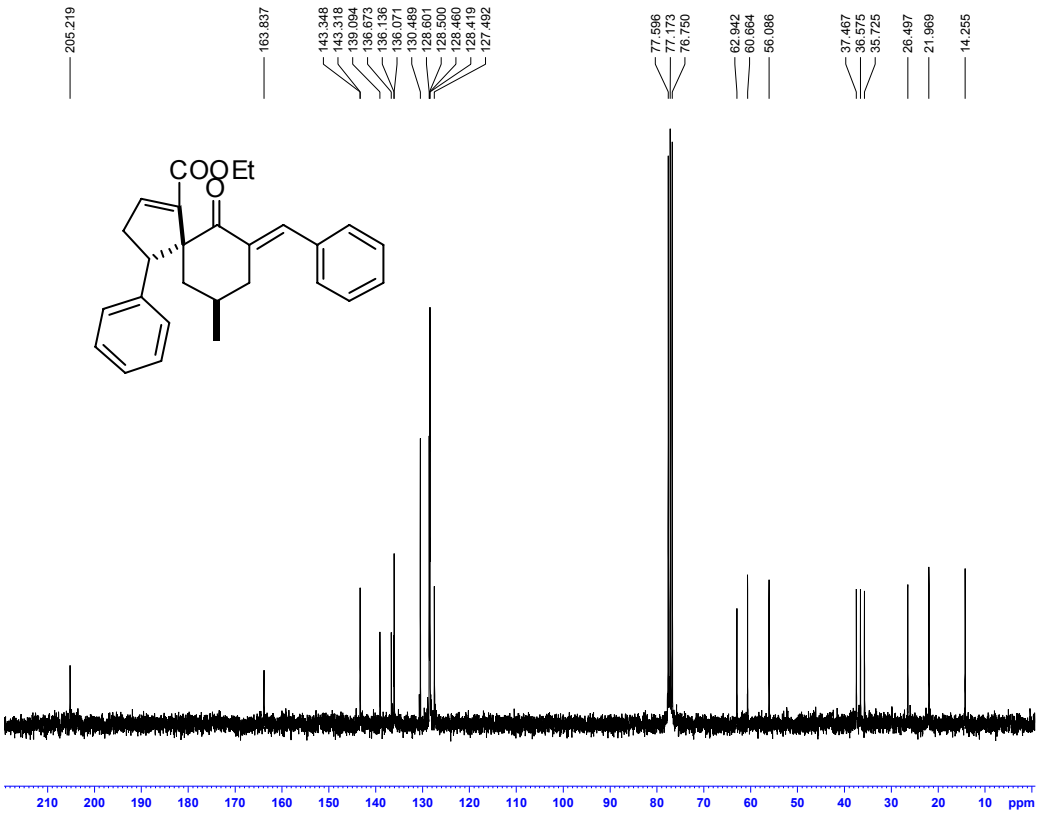
4) NMR spectra and HPLC analysis

(*E*)-ethyl 7-benzylidene-9-methyl-6-oxo-4-phenylspiro[4.5]dec-1-ene-1-carboxylate **2a**

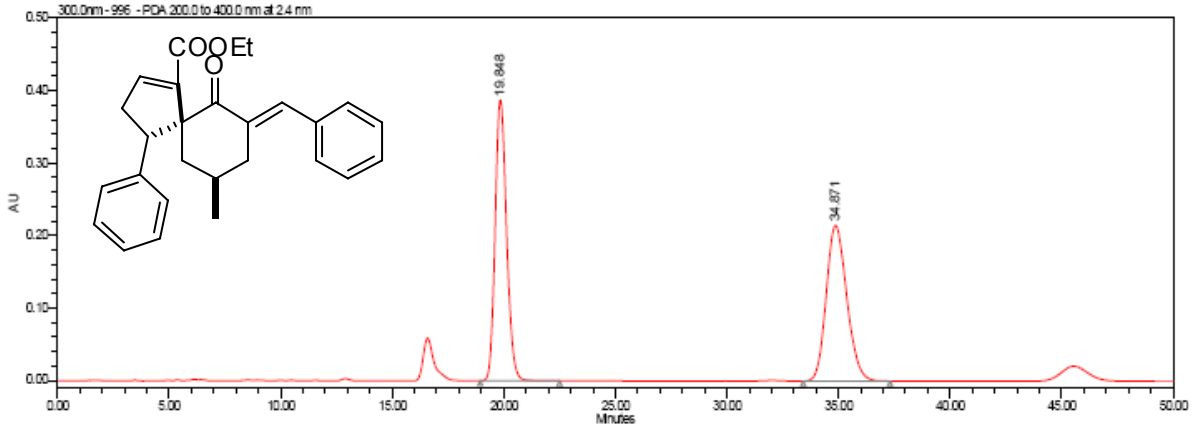
^{1}H NMR (300 MHz, $CDCl_3$):



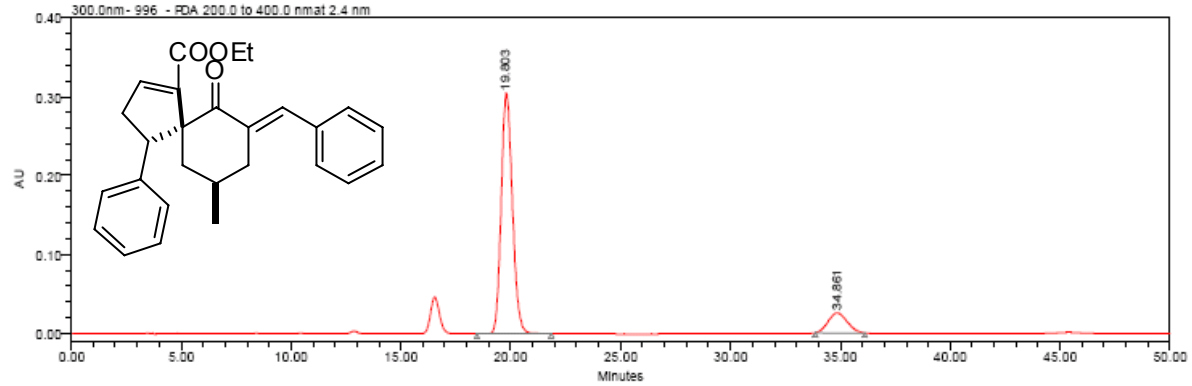
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: Table 2, entry 1: 76% ee [Daicel CHIRACEL IC, 10% *i*PrOH/*n*-heptane, 1 mL/min, 300 nm]:



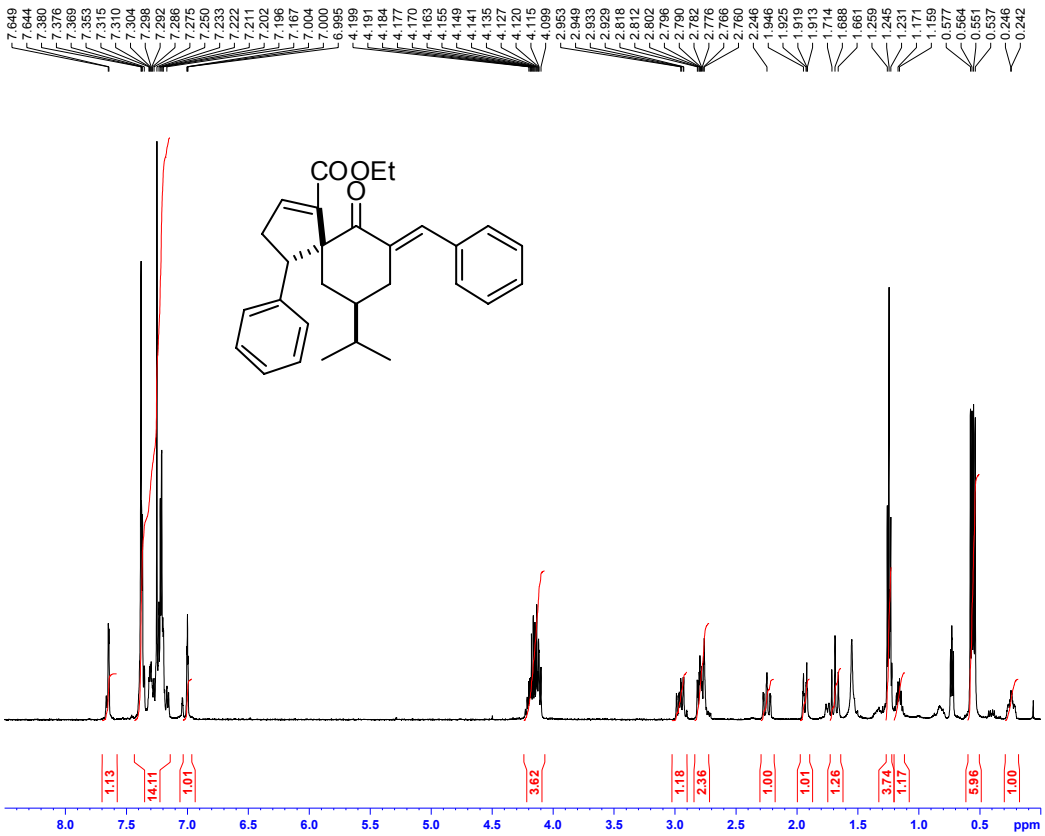
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	19.848	13812283	50.14
2	PDA 200.0 to 400.0 nm at 2.4 nm	34.871	13736399	49.86



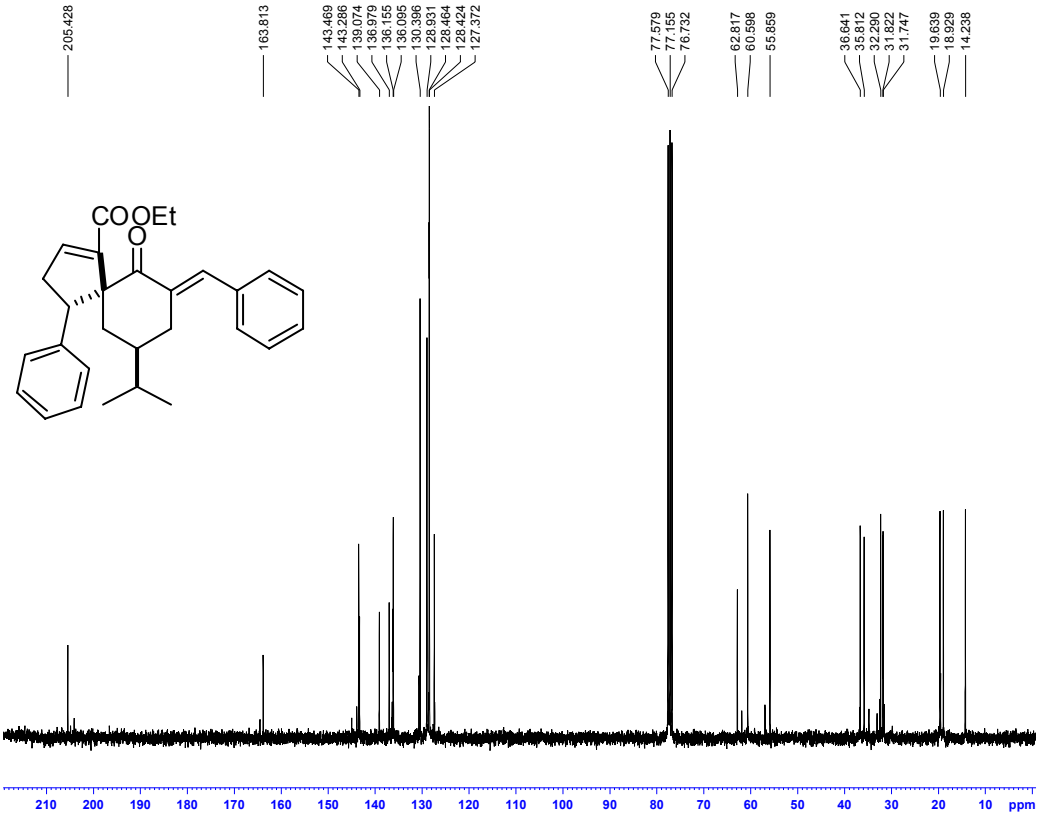
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	19.803	10794621	87.66
2	PDA 200.0 to 400.0 nm at 2.4 nm	34.861	1520031	12.34

(*E*)-ethyl 7-benzylidene-9-isopropyl-6-oxo-4-phenylspiro[4.5]dec-1-ene-1-carboxylate **2b**

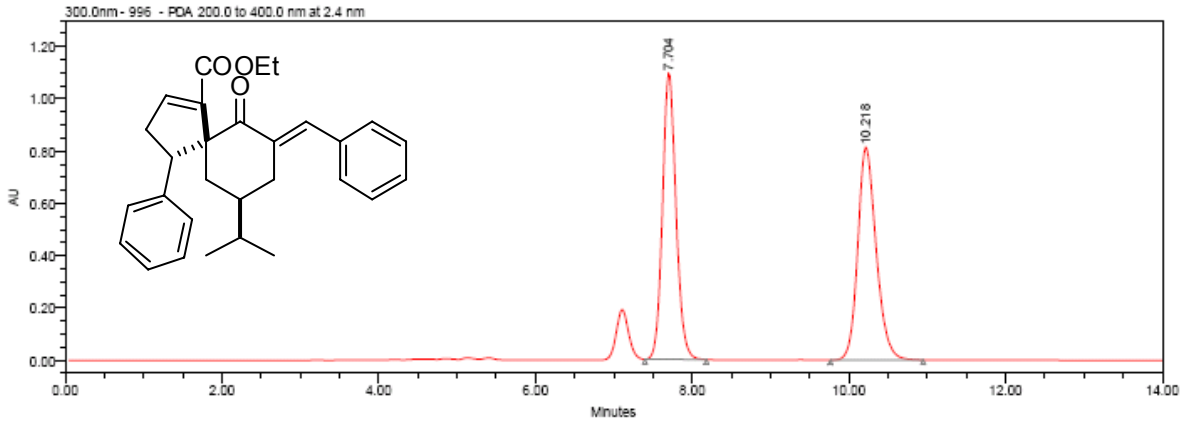
^{1}H NMR (300 MHz, $CDCl_3$):



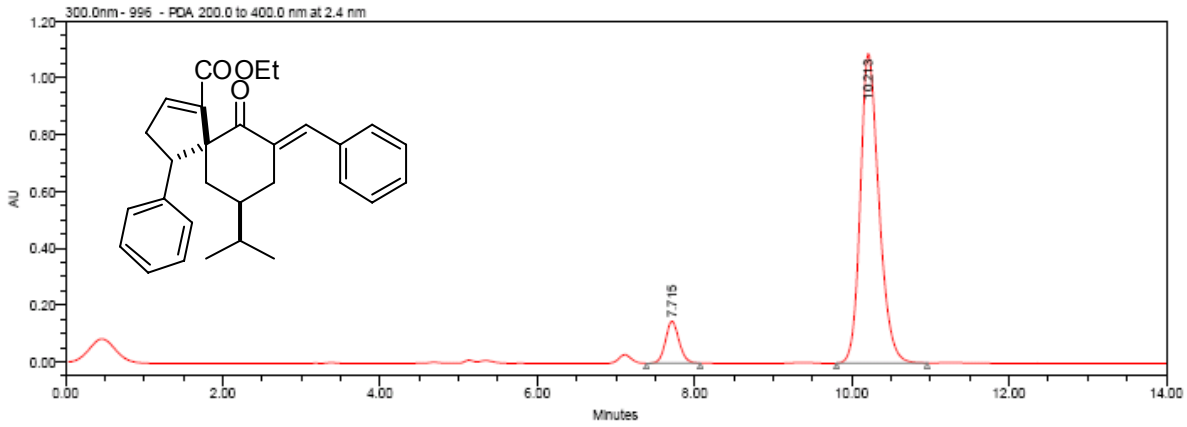
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: Table 2, entry 2: 82% ee [Daicel CHIRACEL IA, 10% *i*PrOH/*n*-heptane, 1 mL/min, 300 nm]:



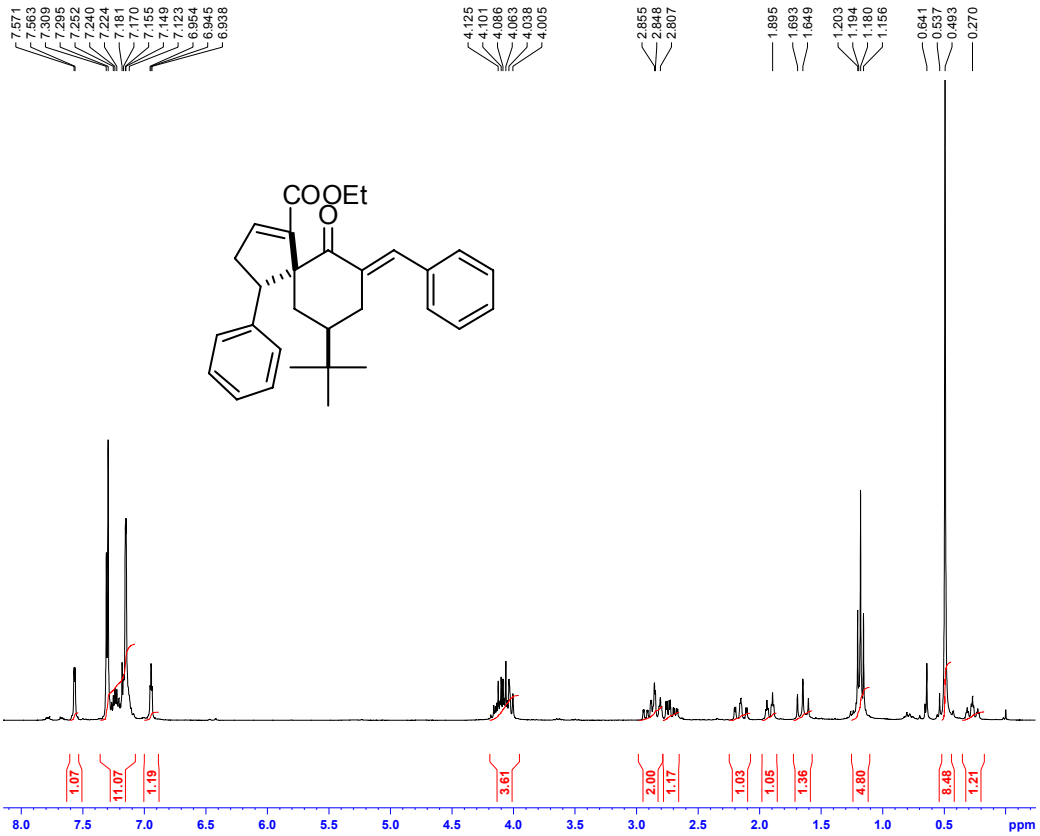
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	7.704	13158655	49.77
2	PDA 200.0 to 400.0 nm at 2.4 nm	10.218	13278547	50.23



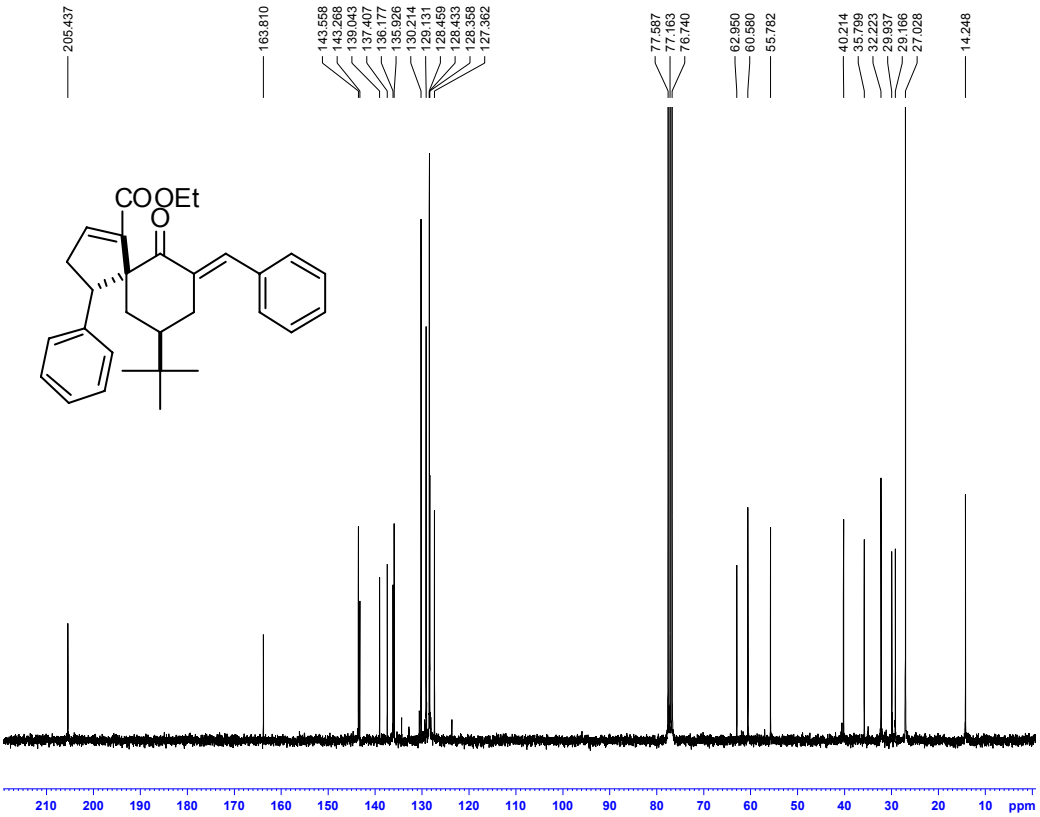
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	7.715	1782482	9.02
2	PDA 200.0 to 400.0 nm at 2.4 nm	10.213	17989088	90.98

(*E*)-ethyl 7-benzylidene-9-tert-butyl-6-oxo-4-phenylspiro[4.5]dec-1-ene-1-carboxylate **2c**

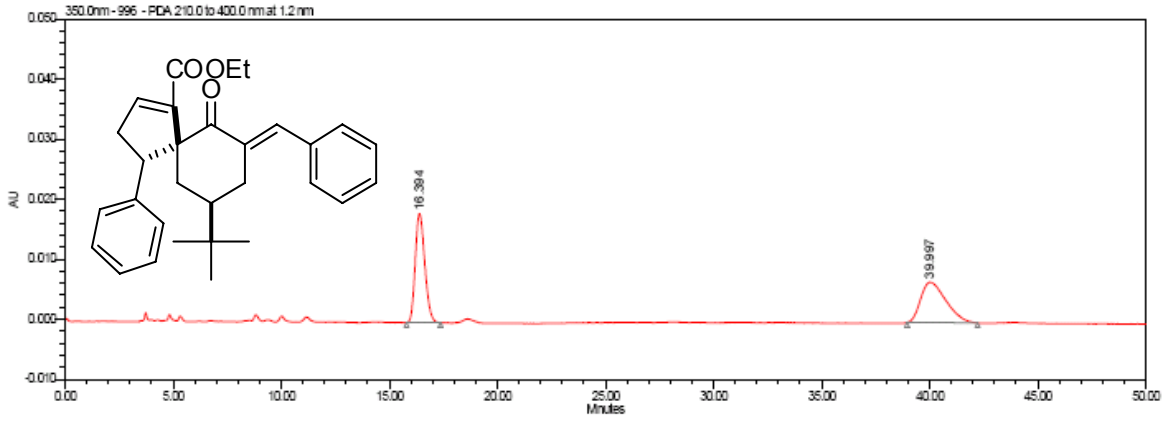
^{1}H NMR (300 MHz, $CDCl_3$):



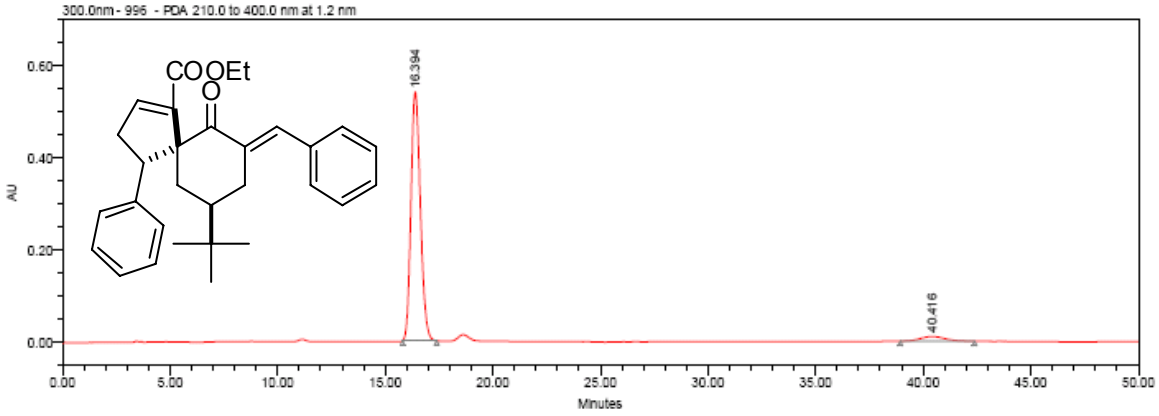
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: Table 2, entry 3: 92% ee [Daicel CHIRACEL IC, 10% *i*PrOH/*n*-heptane, 1 mL/min, 300 nm]:



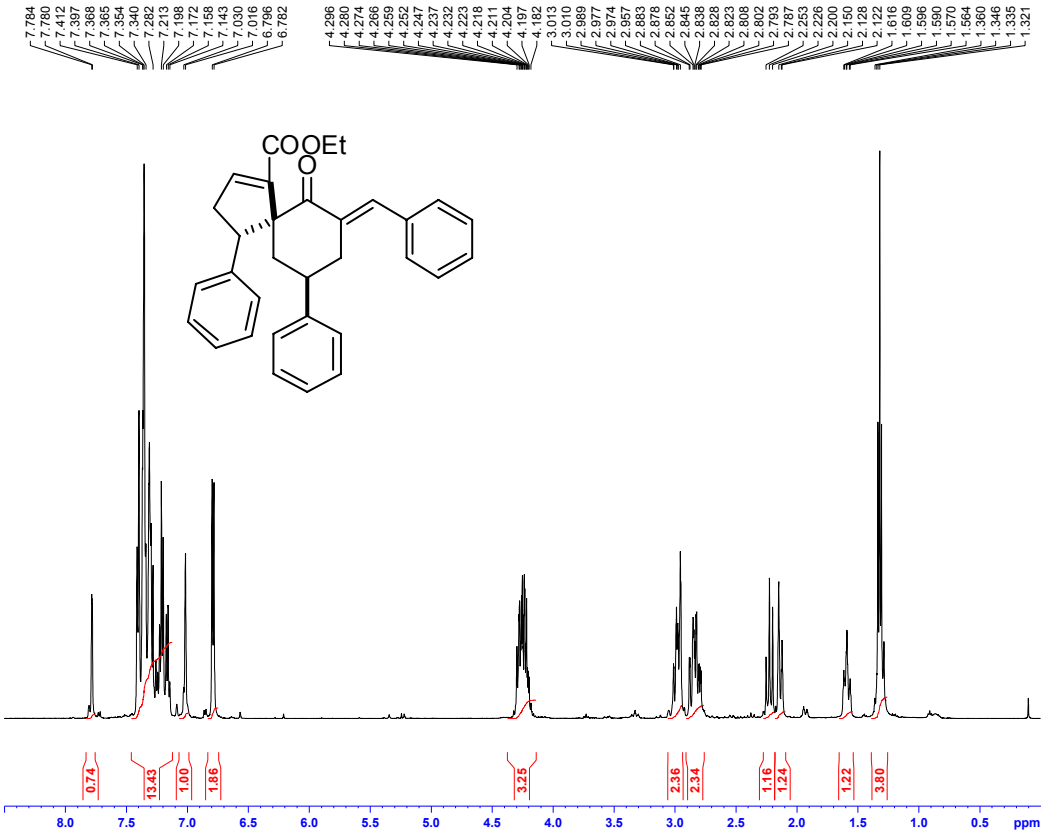
	Channel Description	RT	Area	% Area
1	PDA 210.0 to 400.0 nm at 1.2 nm	16.394	555836	50.48
2	PDA 210.0 to 400.0 nm at 1.2 nm	39.997	545179	49.52



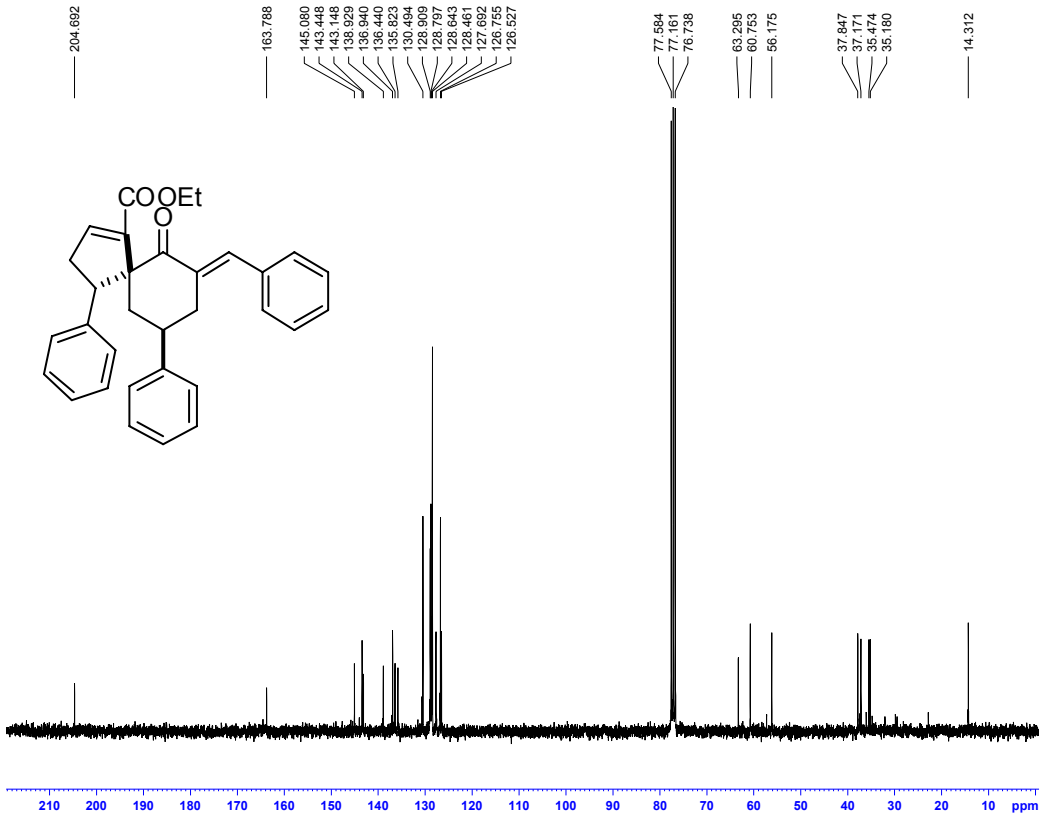
	Channel Description	RT	Area	% Area
1	PDA 210.0 to 400.0 nm at 1.2 nm	16.394	16351895	95.28
2	PDA 210.0 to 400.0 nm at 1.2 nm	40.416	810224	4.72

(*E*)-ethyl 7-benzylidene-6-oxo-1,9-diphenylspiro[4.5]dec-1-ene-2-carboxylate **2d**

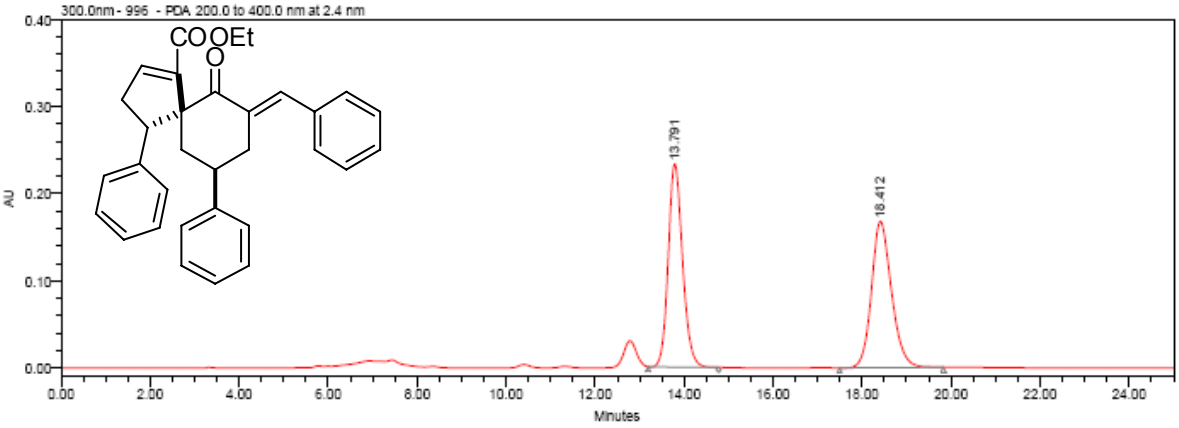
^{1}H NMR (300 MHz, $CDCl_3$):



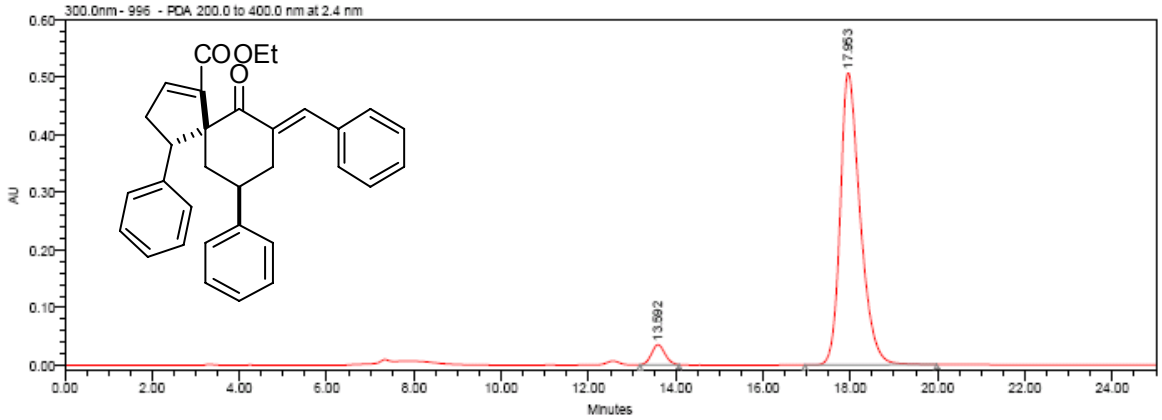
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: Table 2, entry 4: 92% ee [Daicel CHIRACEL IA, 5% *i*PrOH/*n*-heptane, 1 mL/min, 300 nm]:



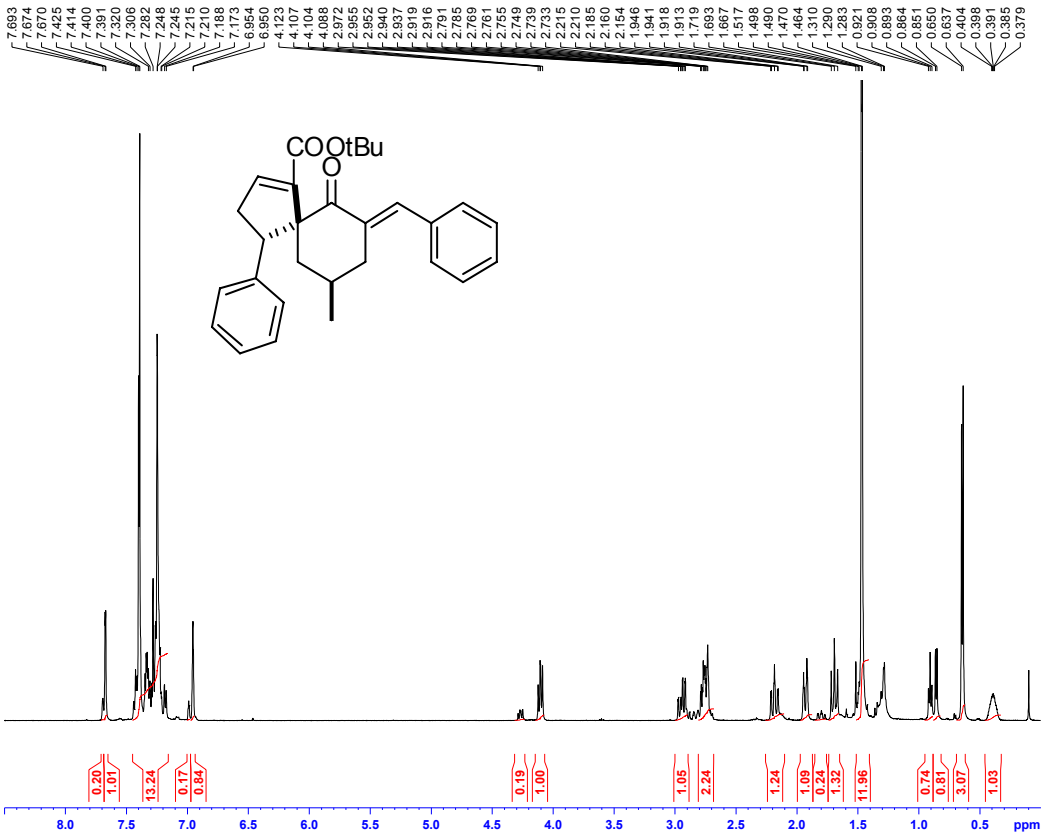
	Channel Description	RT	Area	%Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	13.791	5201765	49.79
2	PDA 200.0 to 400.0 nm at 2.4 nm	18.412	5245481	50.21



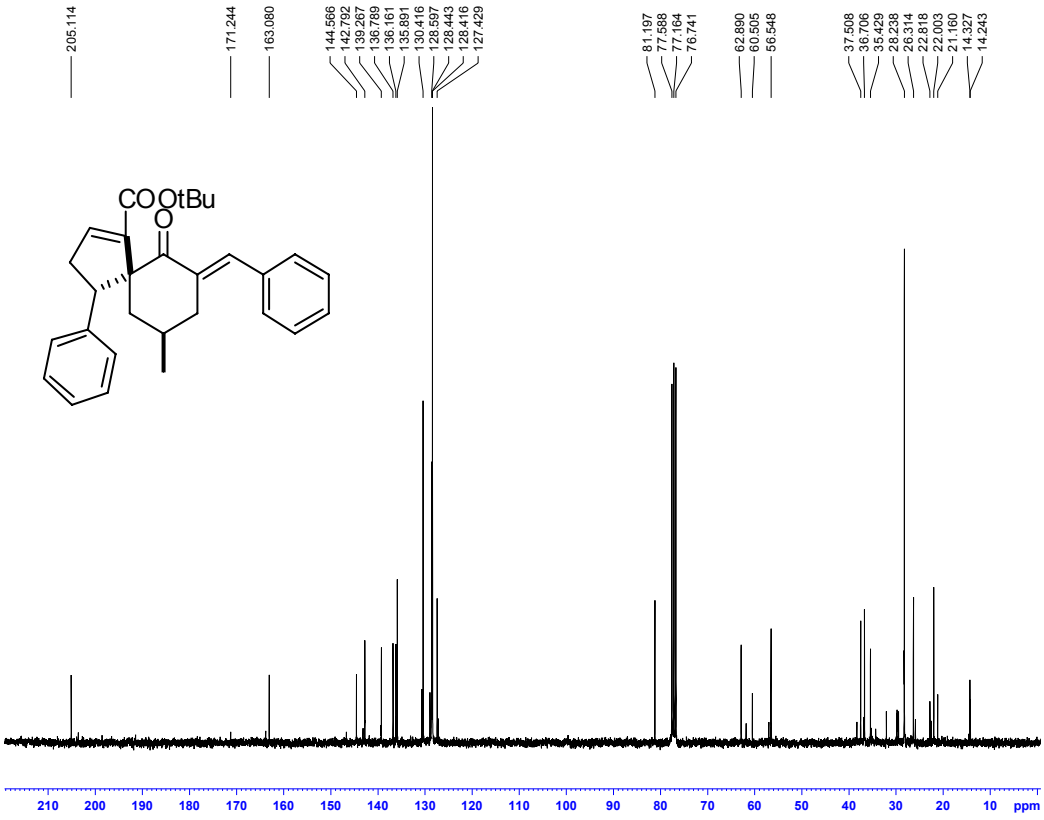
	Channel Description	RT	Area	%Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	13.592	737717	4.40
2	PDA 200.0 to 400.0 nm at 2.4 nm	17.953	16040392	95.60

(*E*)-tert-butyl 7-benzylidene-9-methyl-6-oxo-4-phenylspiro[4.5]dec-1-ene-1-carboxylate **3a**

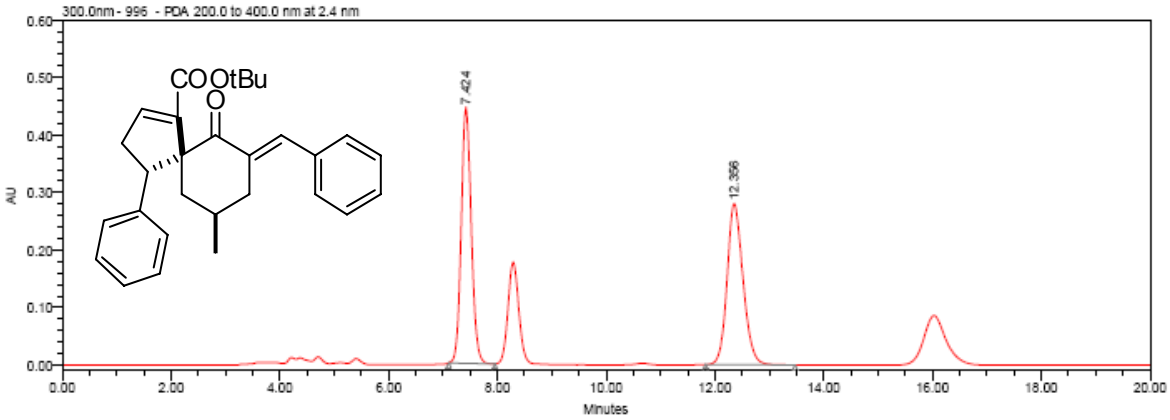
^{1}H NMR (300 MHz, $CDCl_3$):



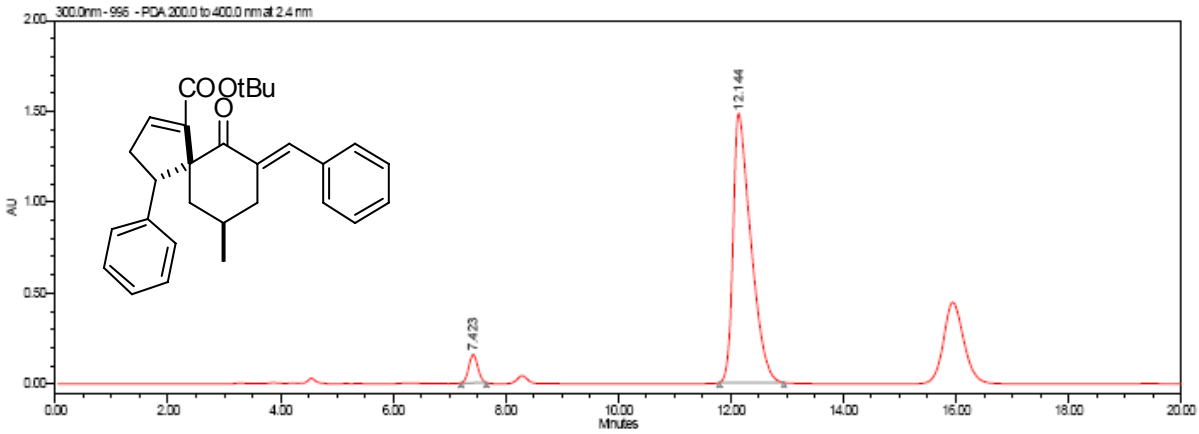
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: Table 2, entry 5: 90% ee [Daicel CHIRACEL IA, 5% *i*PrOH/*n*-heptane, 1 mL/min, 300 nm]:



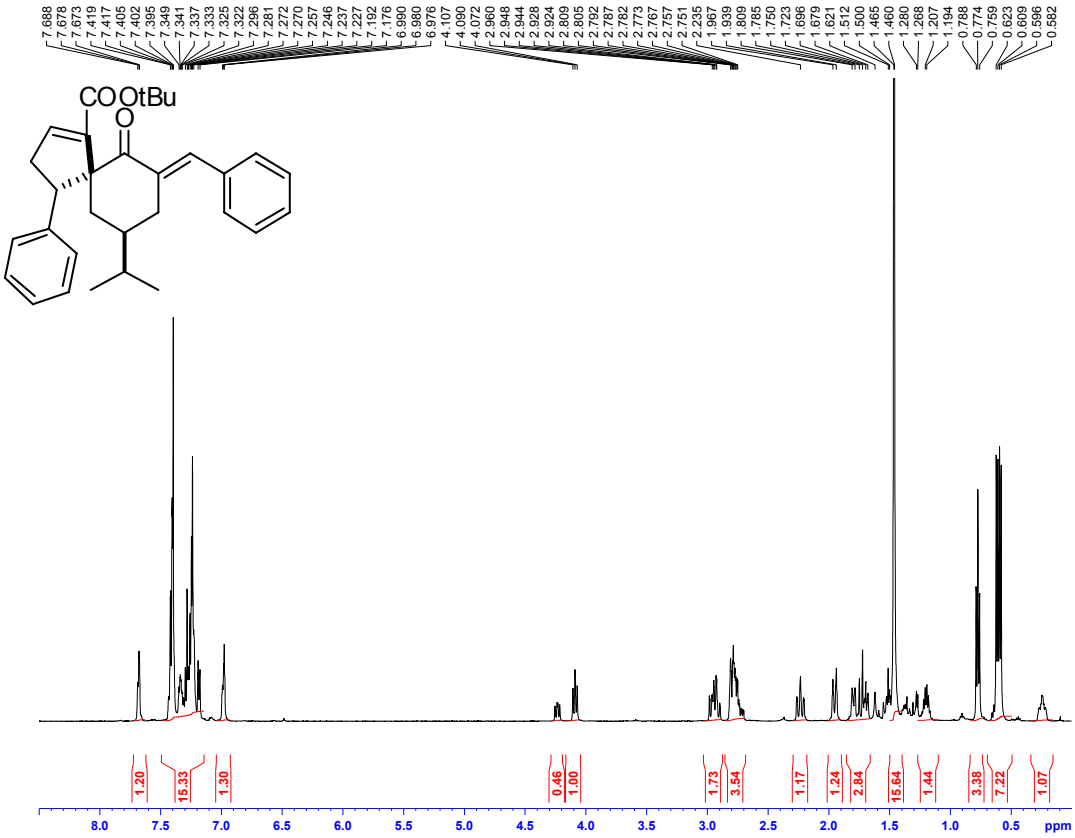
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	7.424	5664385	49.88
2	PDA 200.0 to 400.0 nm at 2.4 nm	12.356	5691881	50.12



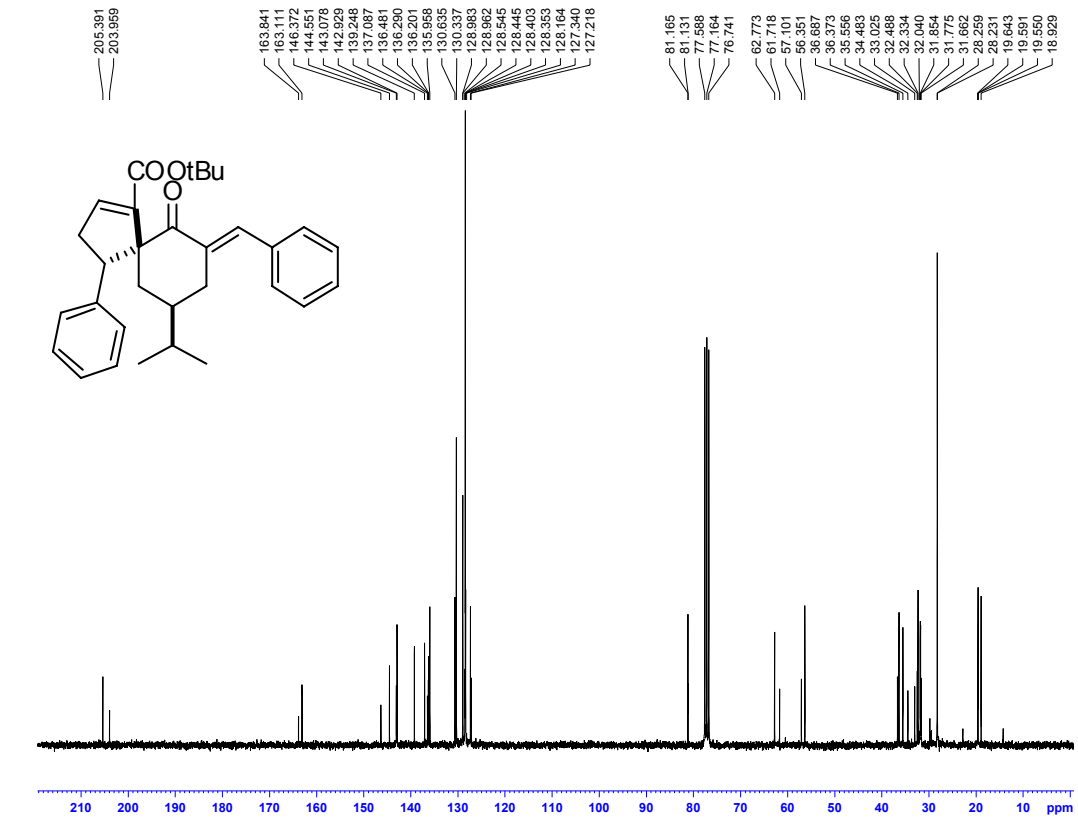
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	7.423	1728420	5.05
2	PDA 200.0 to 400.0 nm at 2.4 nm	12.144	32512520	94.95

(*E*)-tert-butyl 7-benzylidene-9-isopropyl-6-oxo-4-phenylspiro[4.5]dec-1-ene-1-carboxylate **3b**

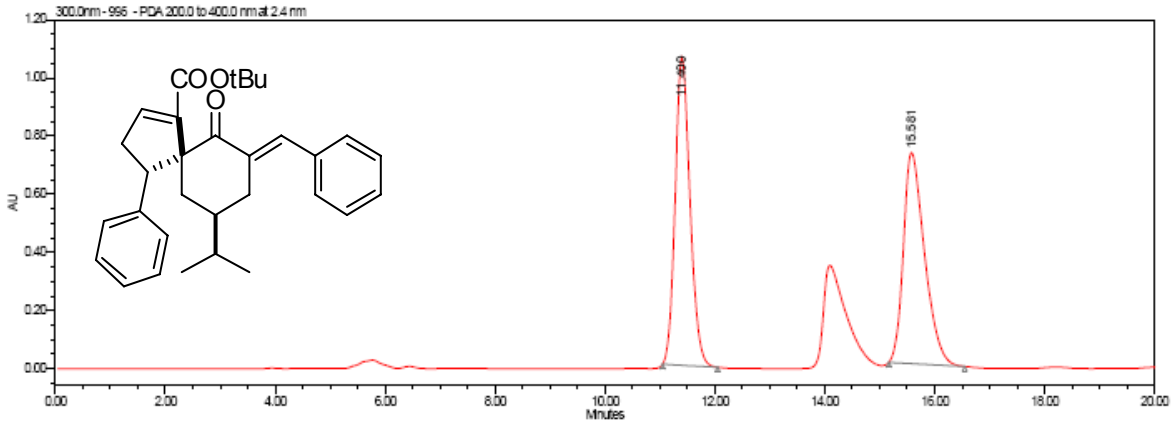
^{1}H NMR (300 MHz, $CDCl_3$):



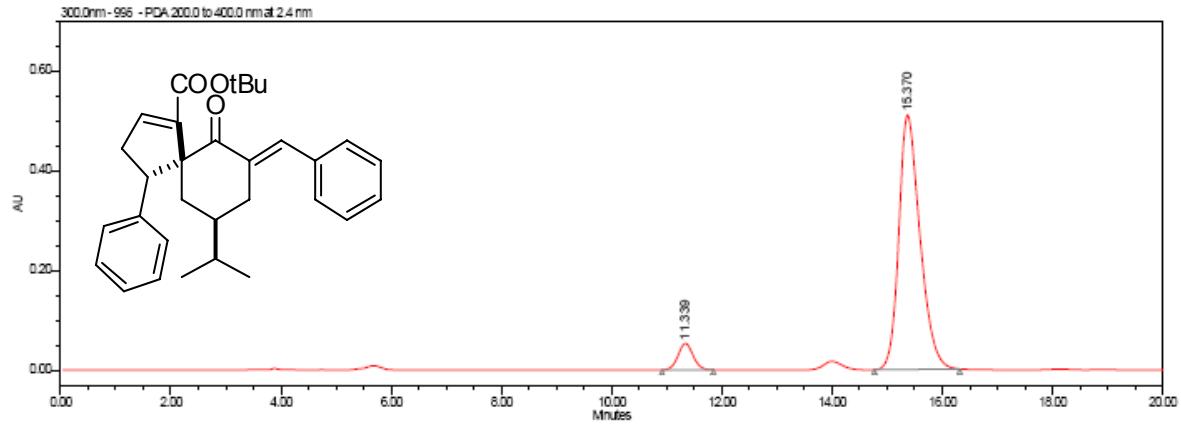
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: Table 2, entry 6: 86% ee [Daicel CHIRACEL IA, 2% EtOH/*n*-heptane, 1 mL/min, 300 nm]:



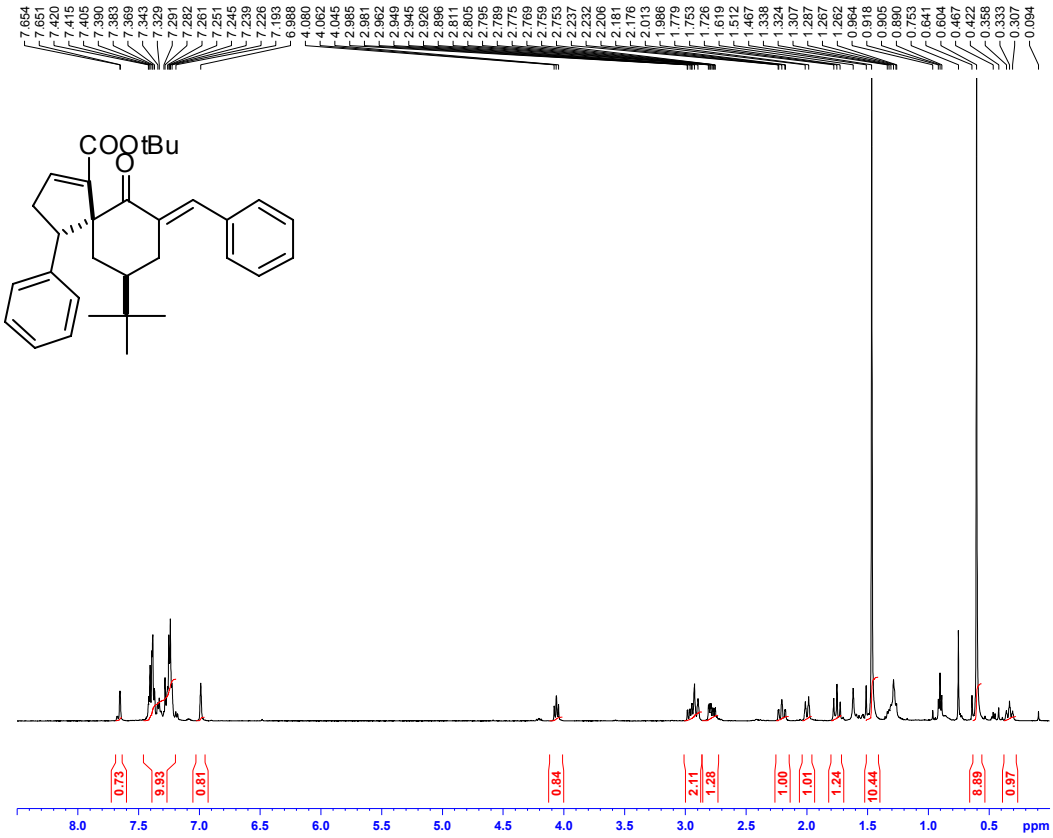
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	11.400	19913108	50.65
2	PDA 200.0 to 400.0 nm at 2.4 nm	15.581	19405567	49.35



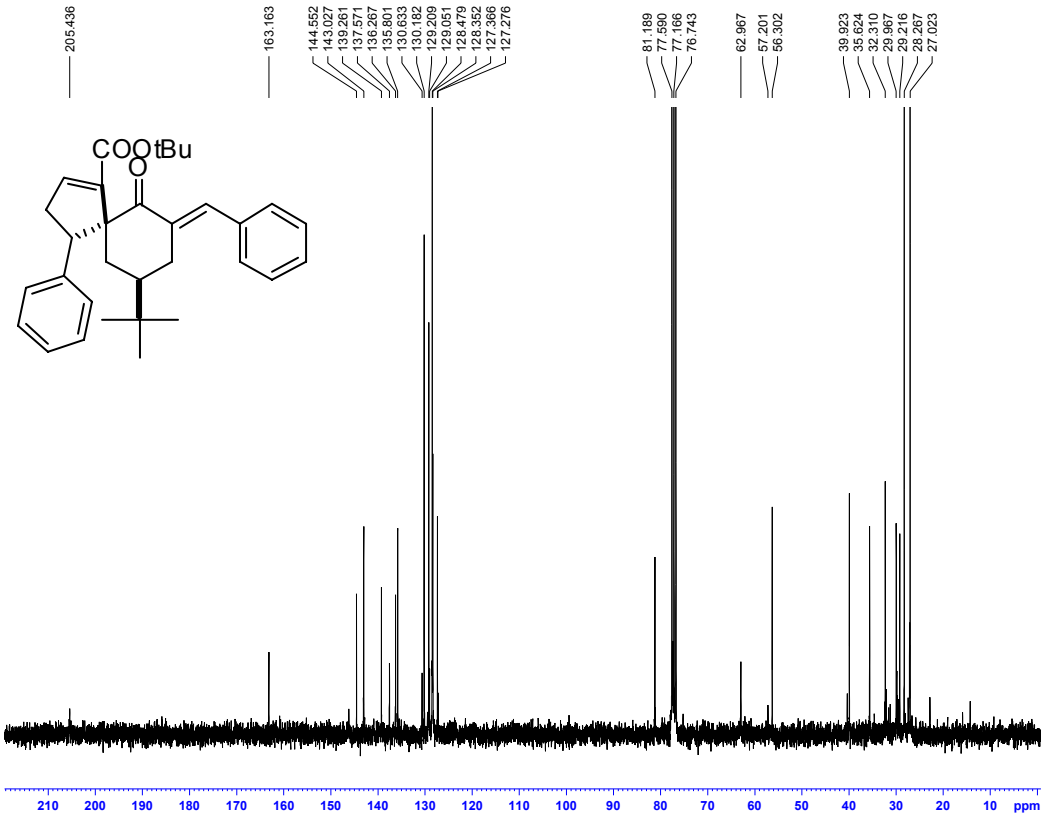
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	11.339	1005994	6.88
2	PDA 200.0 to 400.0 nm at 2.4 nm	15.370	13608619	93.12

(*E*)-tert-butyl 7-benzylidene-9-tert-butyl-6-oxo-4-phenylspiro[4.5]dec-1-ene-1-carboxylate **3c**

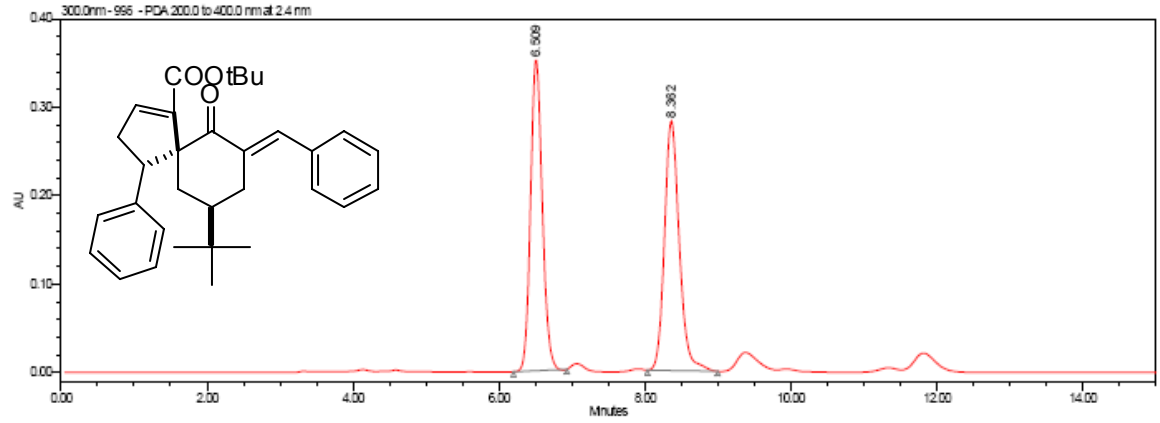
^{1}H NMR (300 MHz, $CDCl_3$):



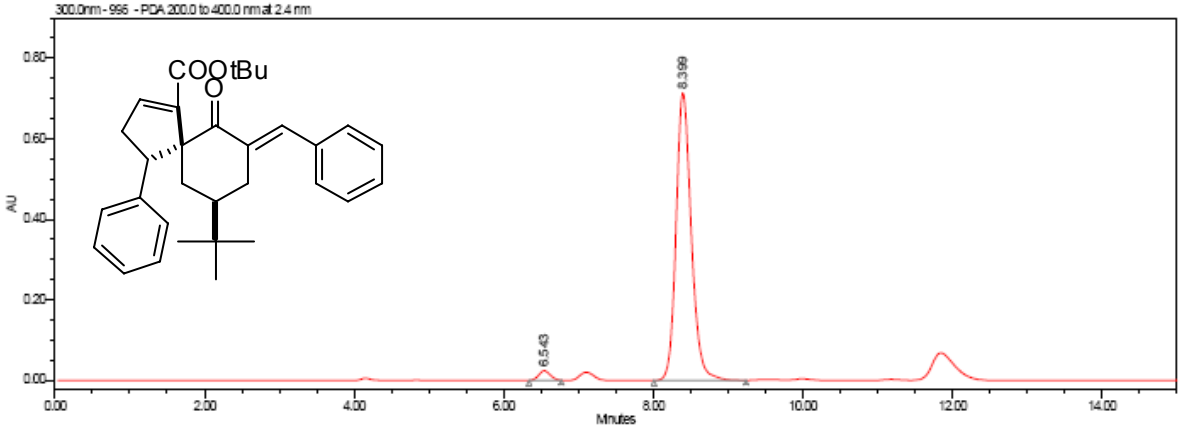
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: Table 2, entry 7: 95% ee [Daicel CHIRACEL IA, 5% *i*PrOH /*n*-heptane, 1 mL/min, 300 nm]:



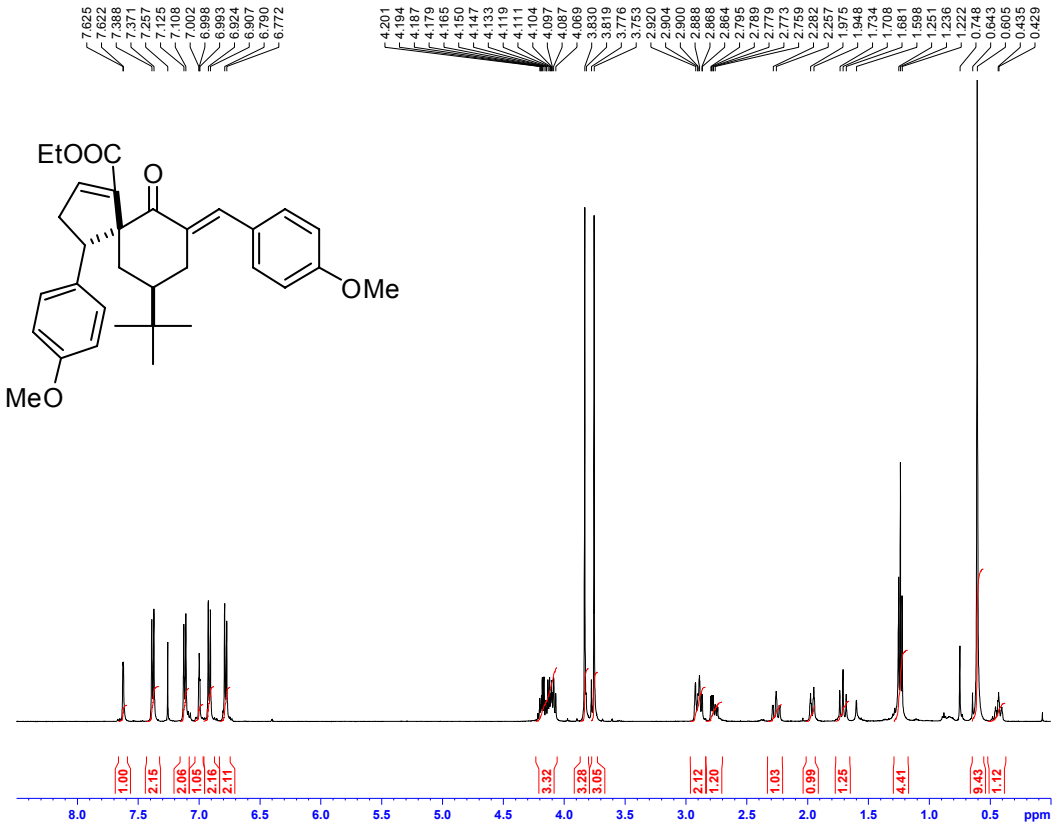
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	6.509	3933986	49.64
2	PDA 200.0 to 400.0 nm at 2.4 nm	8.362	3990623	50.36



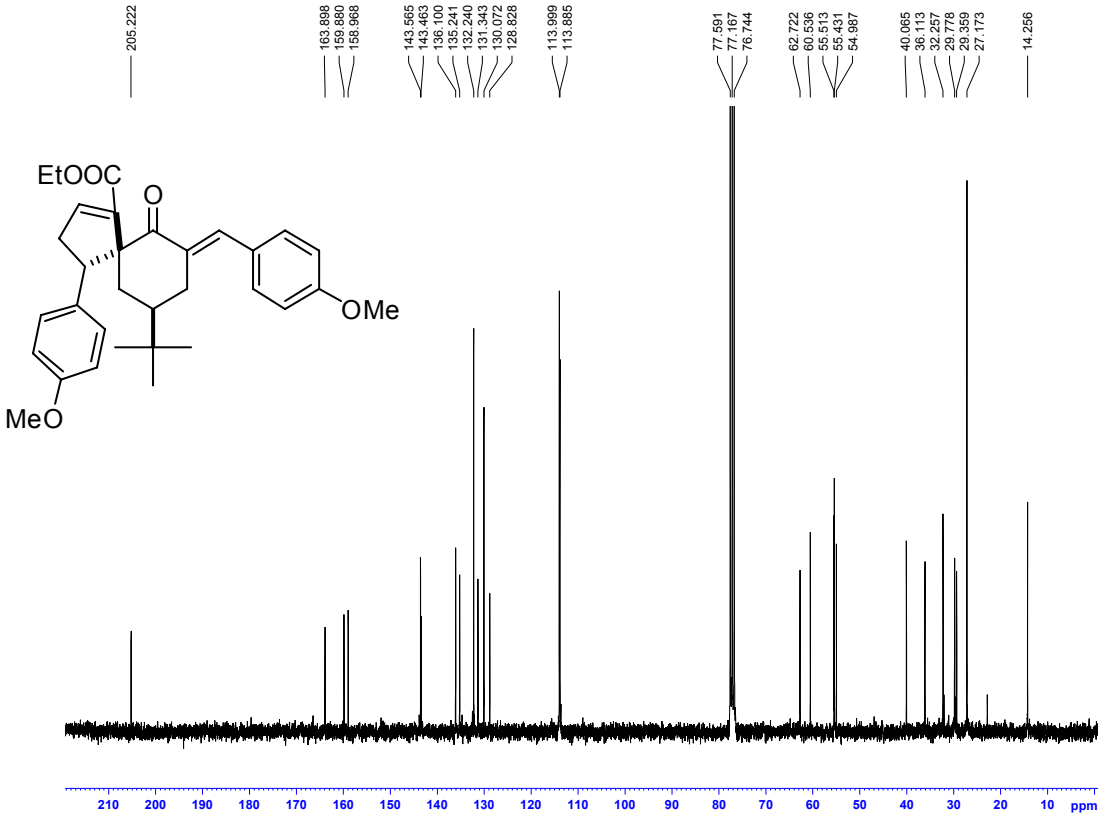
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	6.543	251937	2.44
2	PDA 200.0 to 400.0 nm at 2.4 nm	8.399	10086251	97.56

(*E*)-ethyl 9-tert-butyl-7-(4-methoxybenzylidene)-4-(4-methoxyphenyl)-6-oxospiro[4.5]dec-1-ene-1-carboxylate **2e**

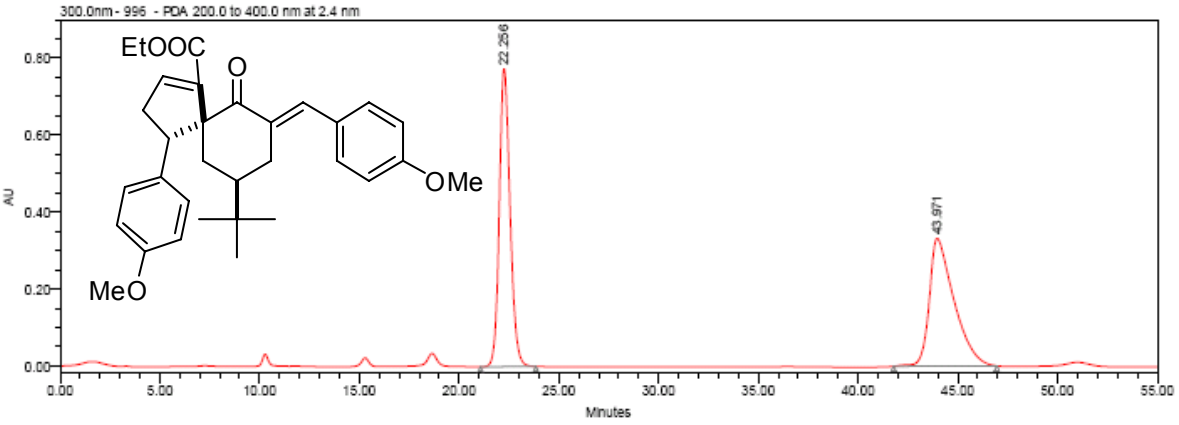
^{1}H NMR (300 MHz, $CDCl_3$):



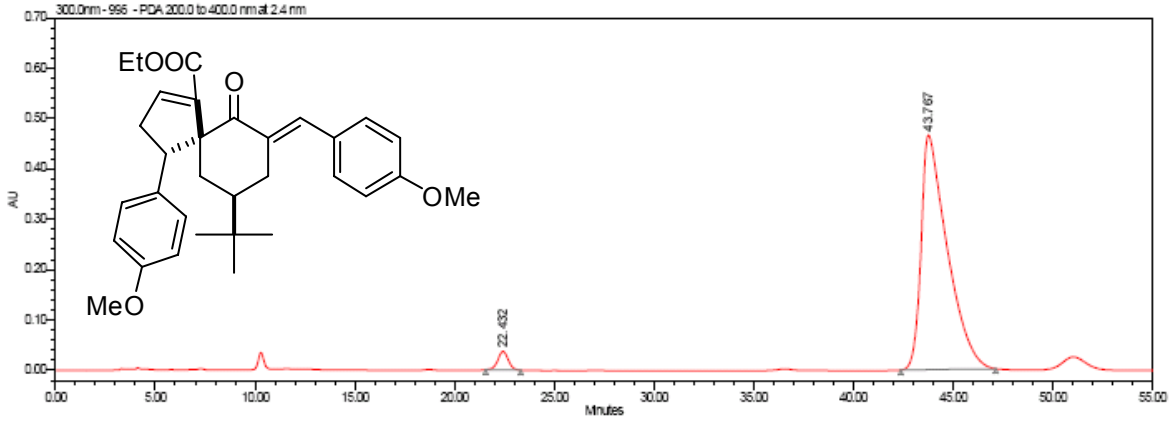
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: Table 3, entry 1: 94% ee [Daicel CHIRACEL IA, 5% *i*PrOH /*n*-heptane, 1 mL/min, 300 nm]:



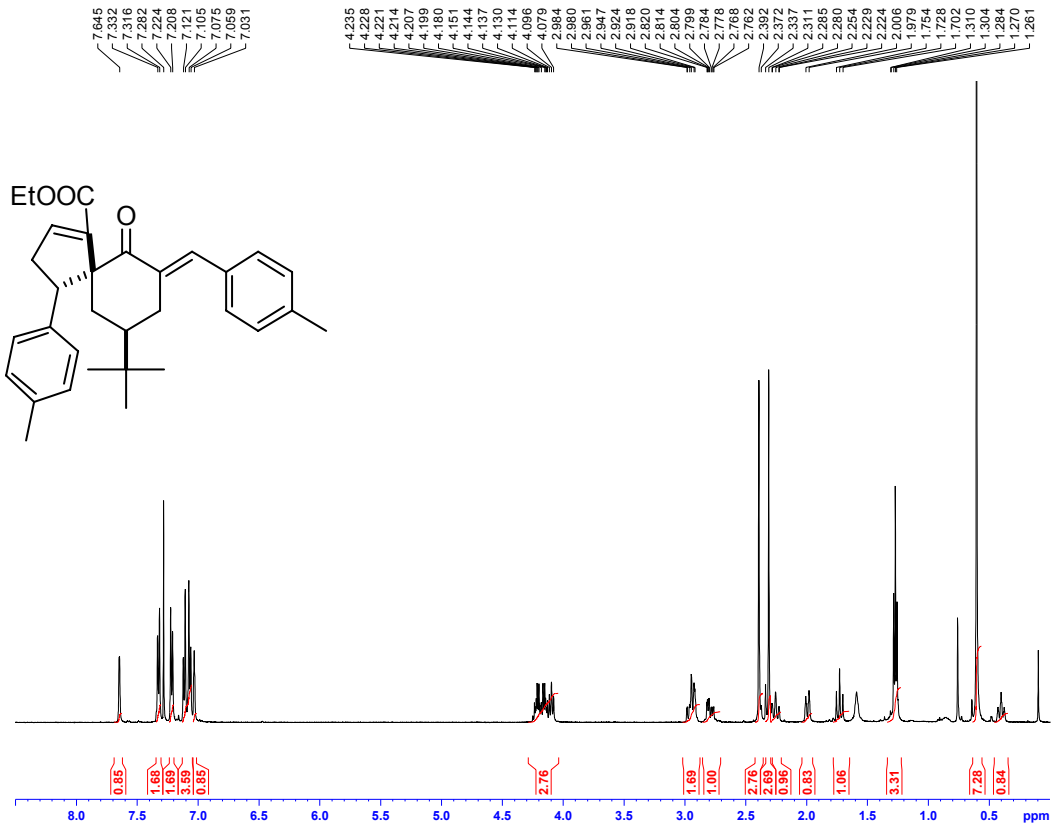
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	22.256	29014291	50.35
2	PDA 200.0 to 400.0 nm at 2.4 nm	43.971	28607837	49.65



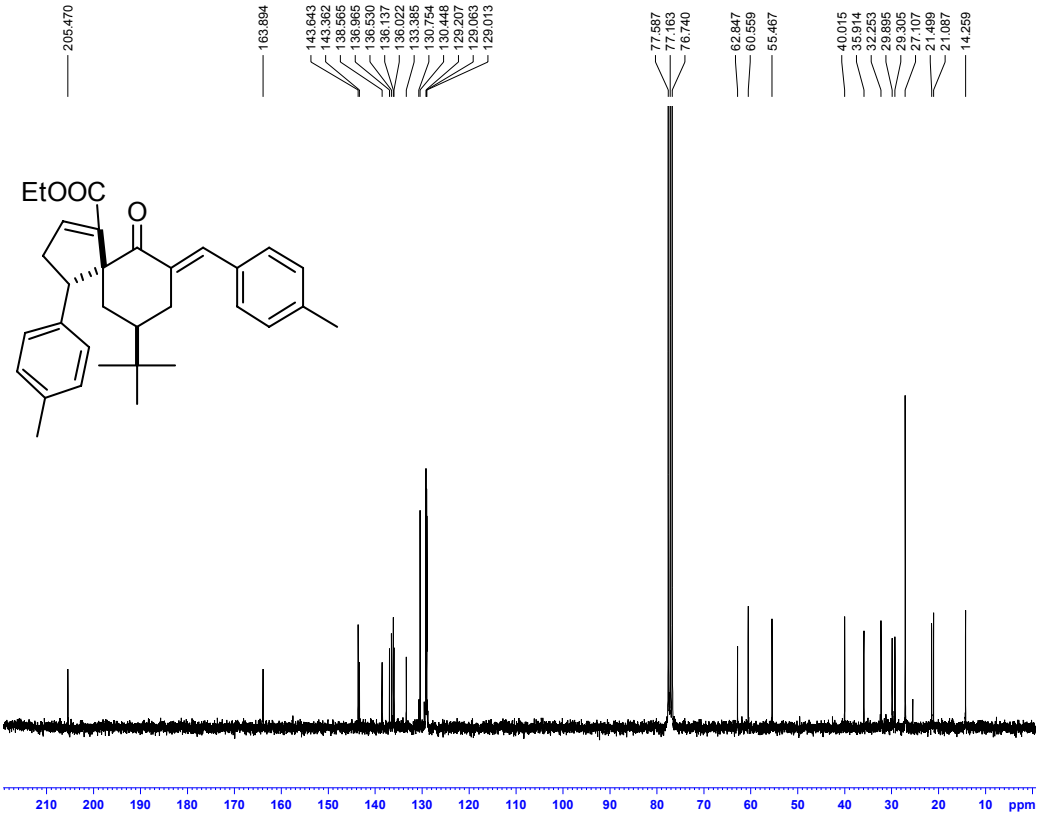
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	22.432	1345075	3.07
2	PDA 200.0 to 400.0 nm at 2.4 nm	43.767	42473611	96.93

(*E*)-ethyl 9-tert-butyl-7-(4-methylbenzylidene)-6-oxo-4-p-tolylspiro[4.5]dec-1-ene-1-carboxylate **2f**

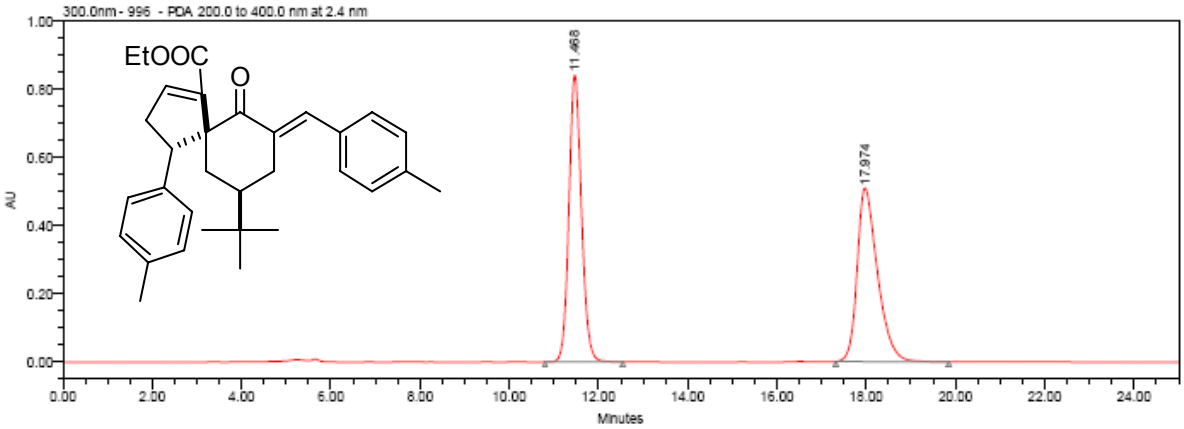
^{1}H NMR (300 MHz, $CDCl_3$):



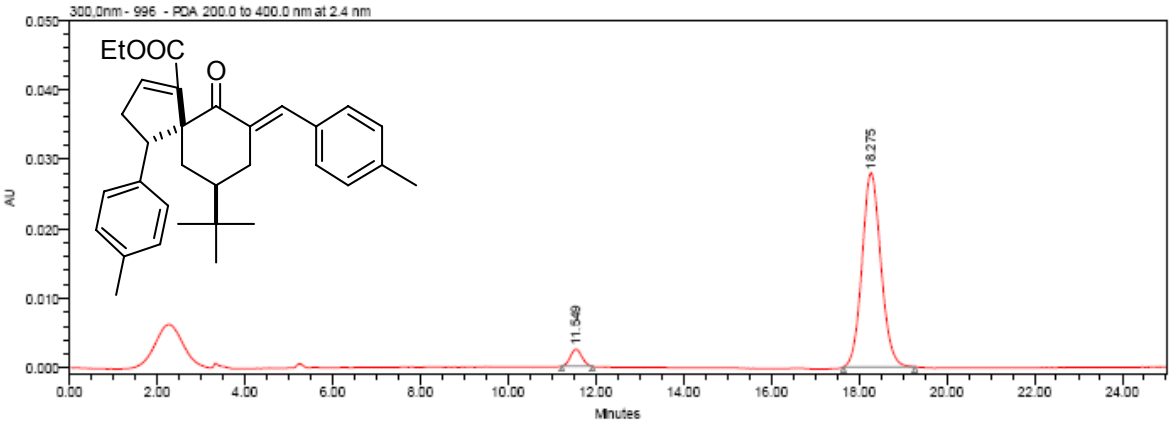
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: Table 3, entry 2: 90% ee [Daicel CHIRACEL IA, 5% *i*PrOH /*n*-heptane, 1 mL/min, 300 nm]:



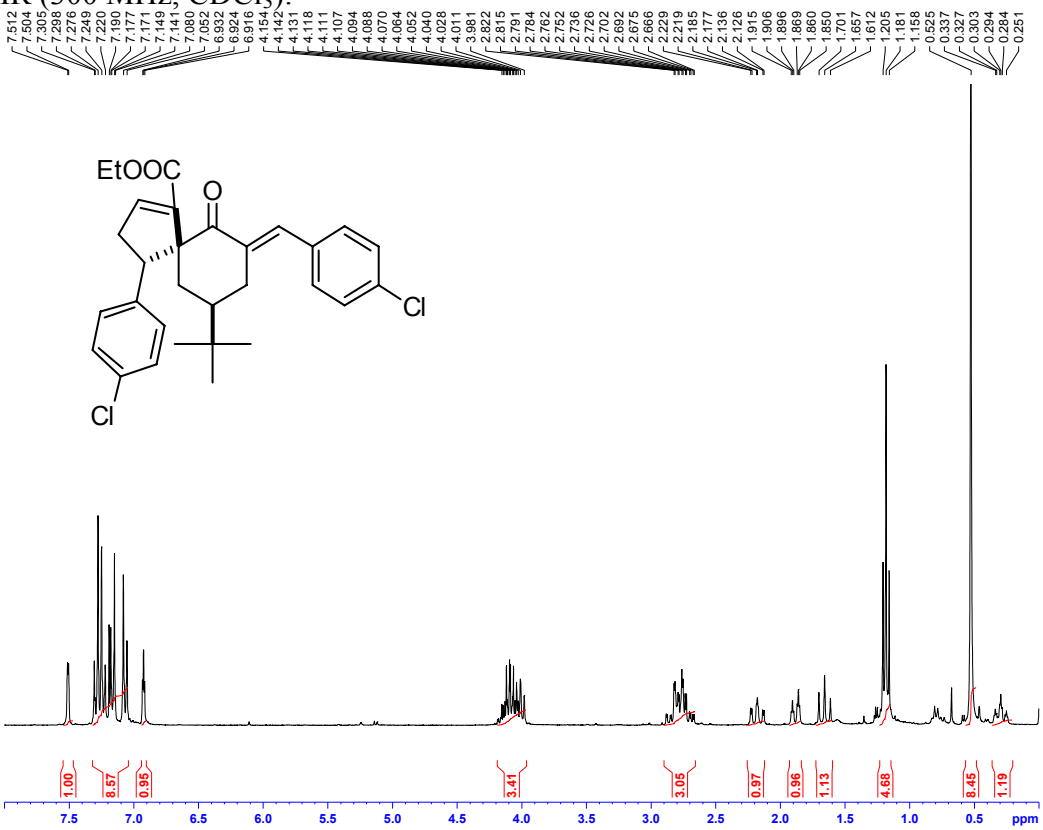
	Channel Description	RT	Area	%Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	11.468	16380182	50.51
2	PDA 200.0 to 400.0 nm at 2.4 nm	17.974	16048850	49.49



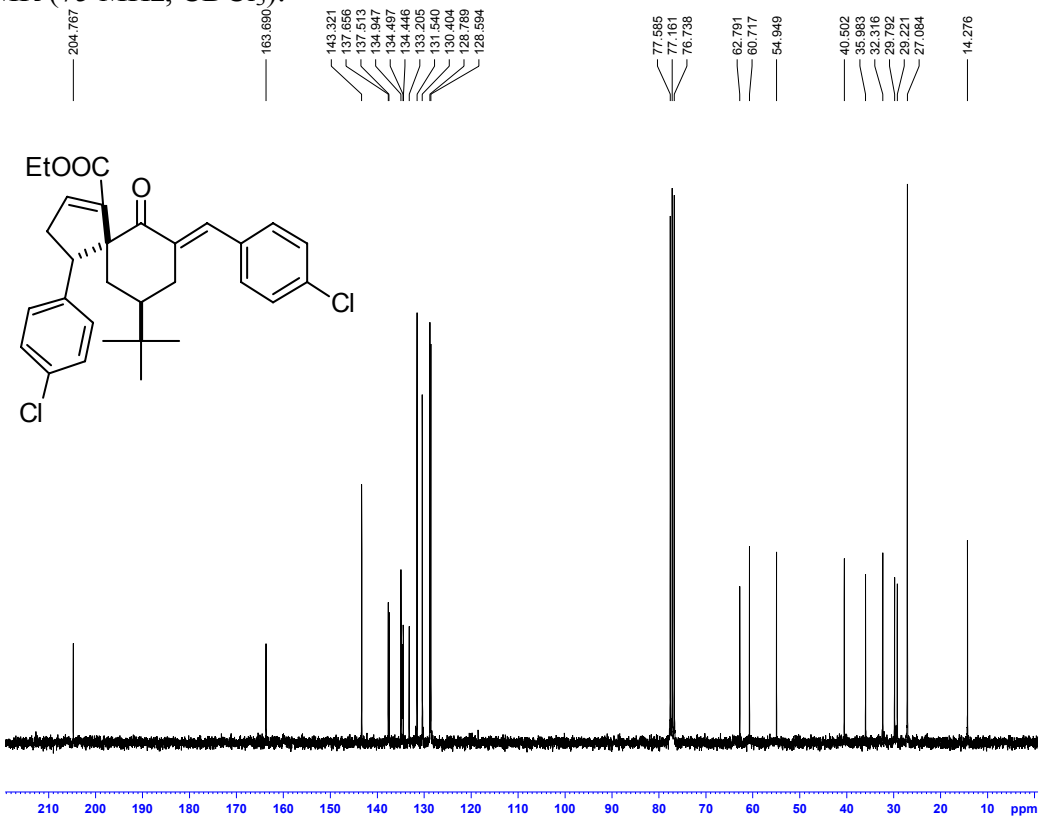
	Channel Description	RT	Area	%Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	11.549	44337	5.06
2	PDA 200.0 to 400.0 nm at 2.4 nm	18.275	832682	94.94

(*E*)-ethyl 9-tert-butyl-7-(4-chlorobenzylidene)-4-(4-chlorophenyl)-6-oxospiro[4.5]dec-1-ene-1-carboxylate **2g**

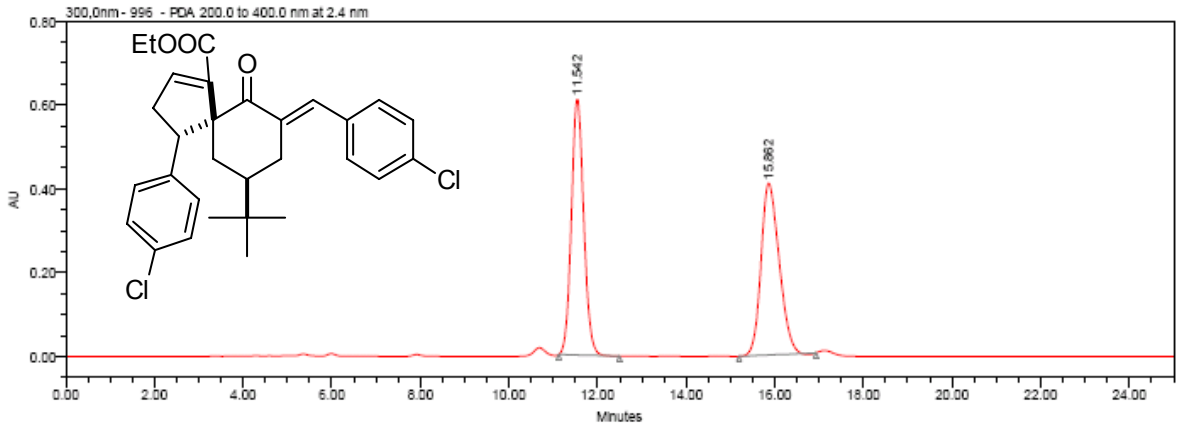
^{1}H NMR (300 MHz, $CDCl_3$):



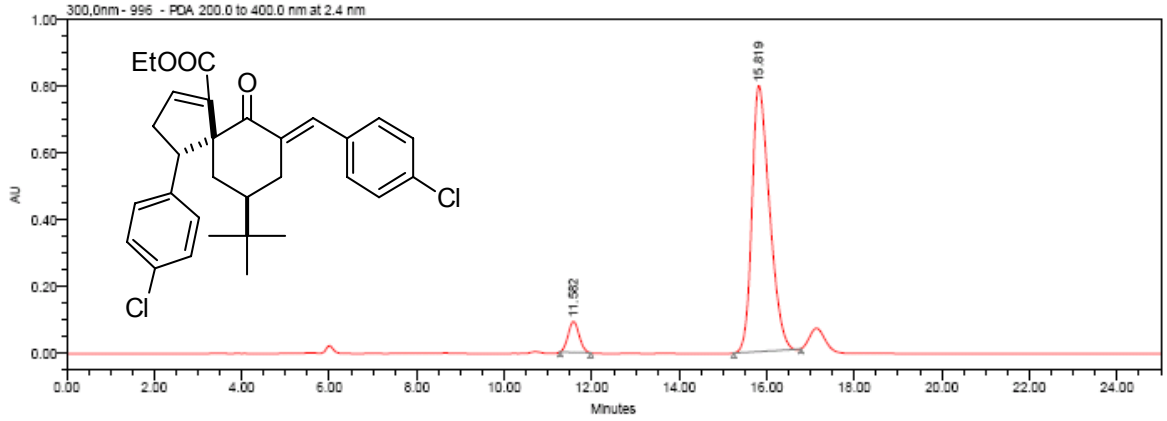
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: Table 3, entry 3: 86% ee [Daicel CHIRACEL IA, 5% *i*PrOH /*n*-heptane, 1 mL/min, 300 nm]:



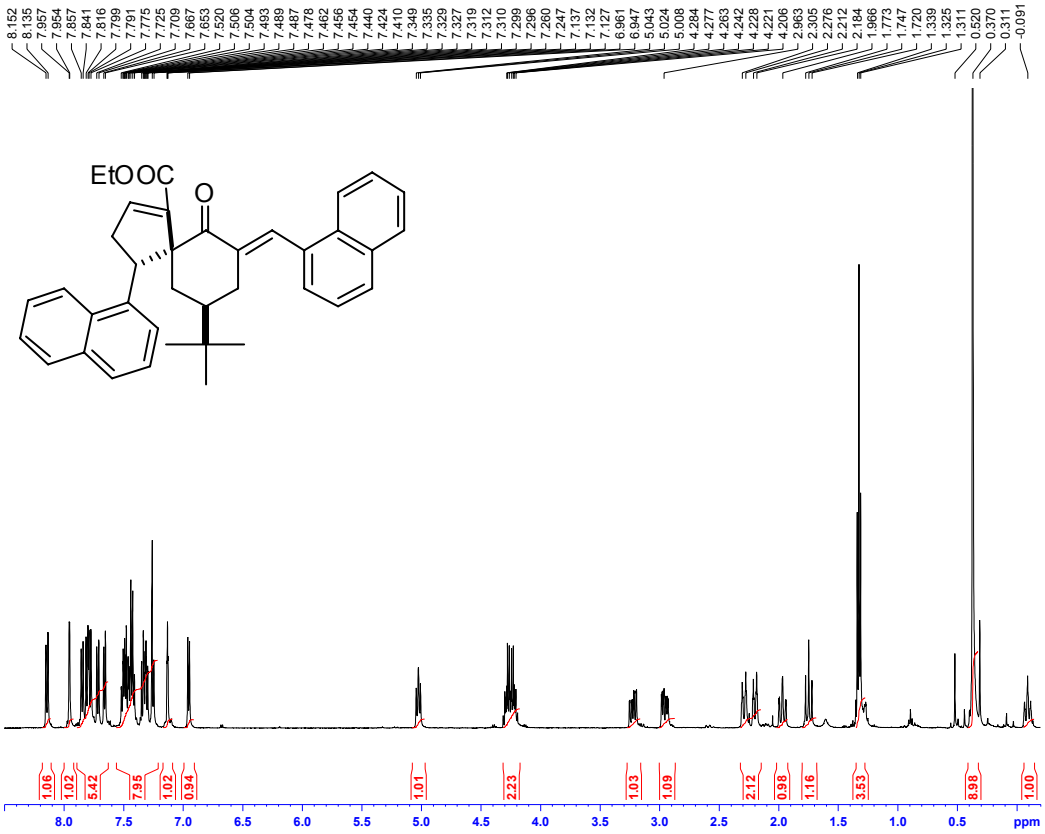
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	11.542	11815306	50.25
2	PDA 200.0 to 400.0 nm at 2.4 nm	15.862	11695825	49.75



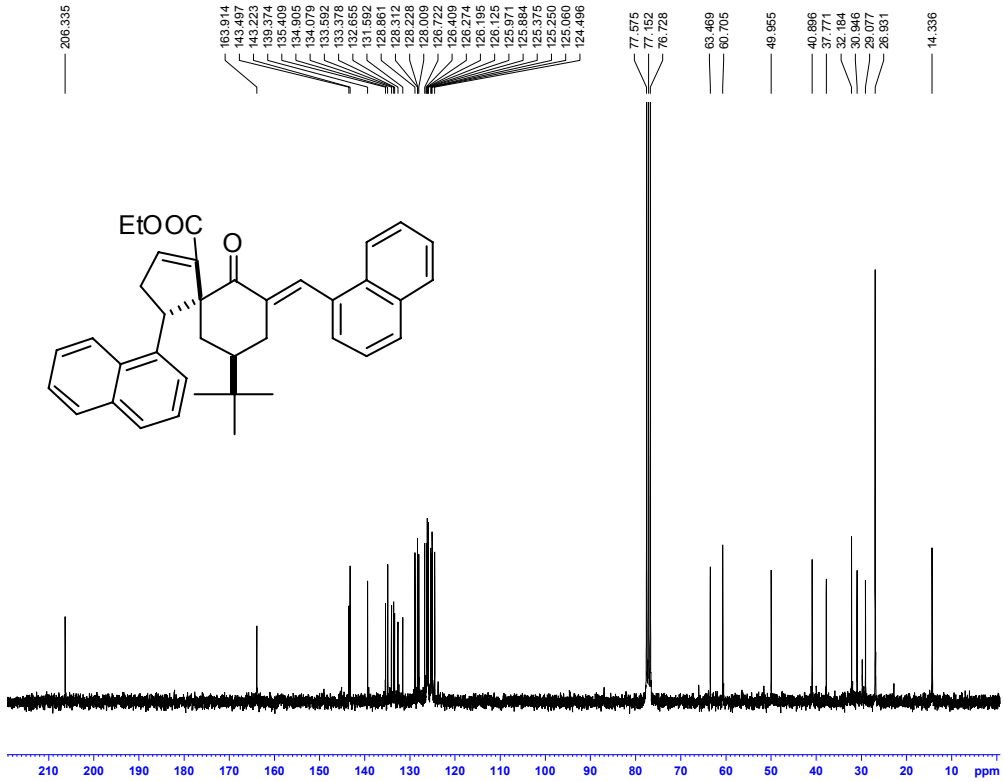
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	11.582	1611840	6.77
2	PDA 200.0 to 400.0 nm at 2.4 nm	15.819	22179564	93.23

(*E*)-ethyl 9-tert-butyl-4-(naphthalen-1-yl)-7-(naphthalen-1-ylmethylene)-6-oxospiro[4.5]dec-1-ene-1-carboxylate **2h**

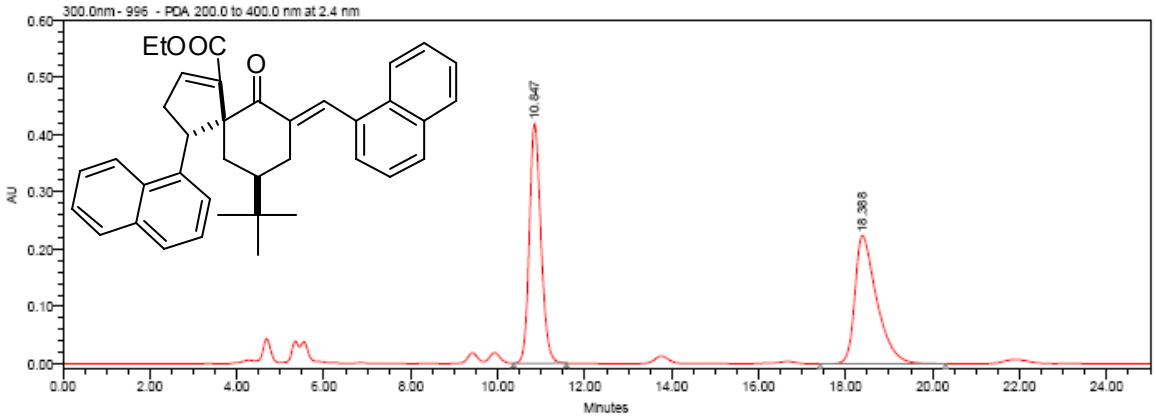
^{1}H NMR (300 MHz, $CDCl_3$):



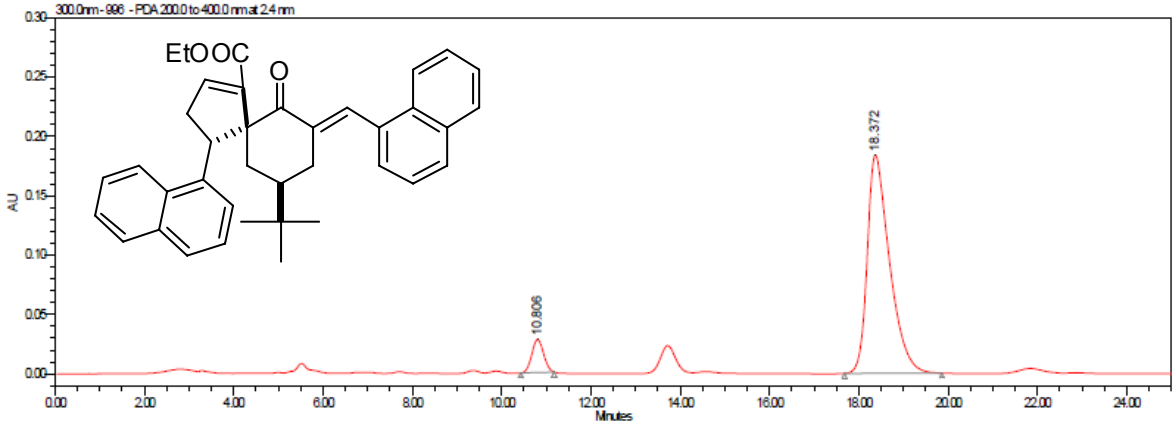
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: Table 3, entry 4: 85% ee [Daicel CHIRACEL IA, 5% *i*PrOH /*n*-heptane, 1 mL/min, 300 nm]:



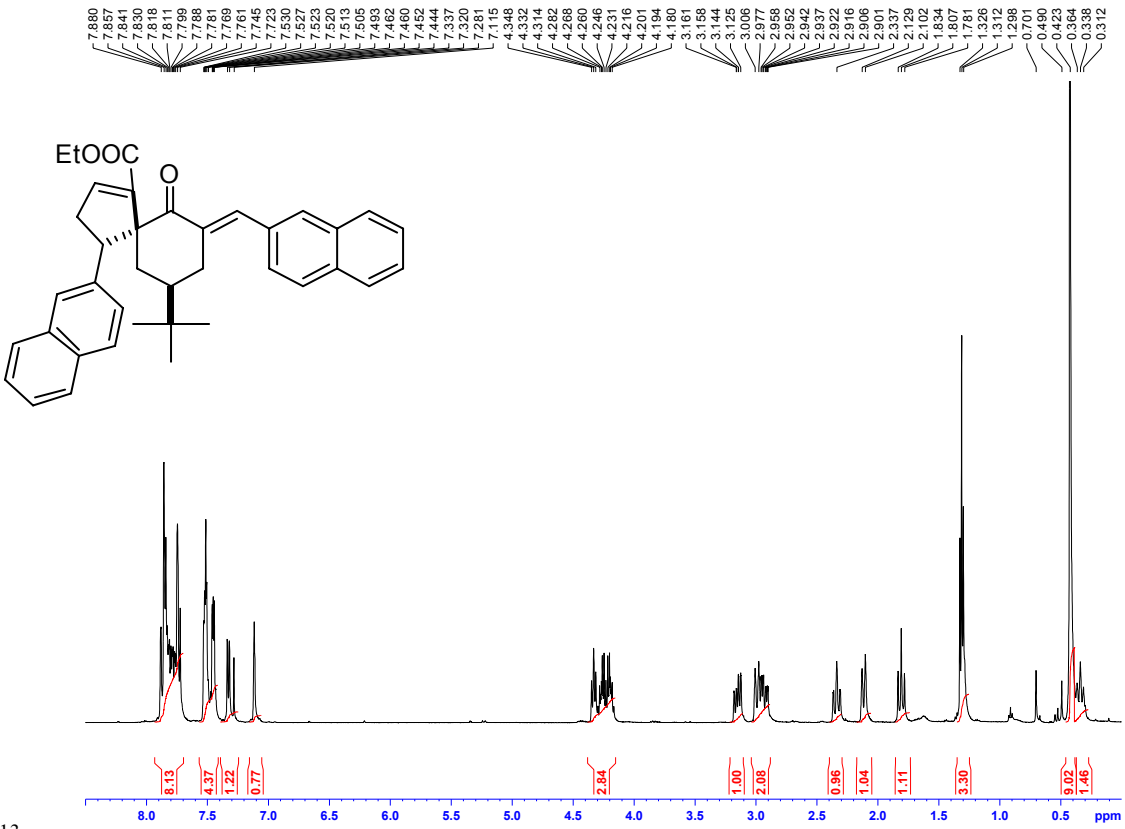
	Channel Description	RT	Area	%Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	10.847	7717662	49.77
2	PDA 200.0 to 400.0 nm at 2.4 nm	18.388	7790542	50.23



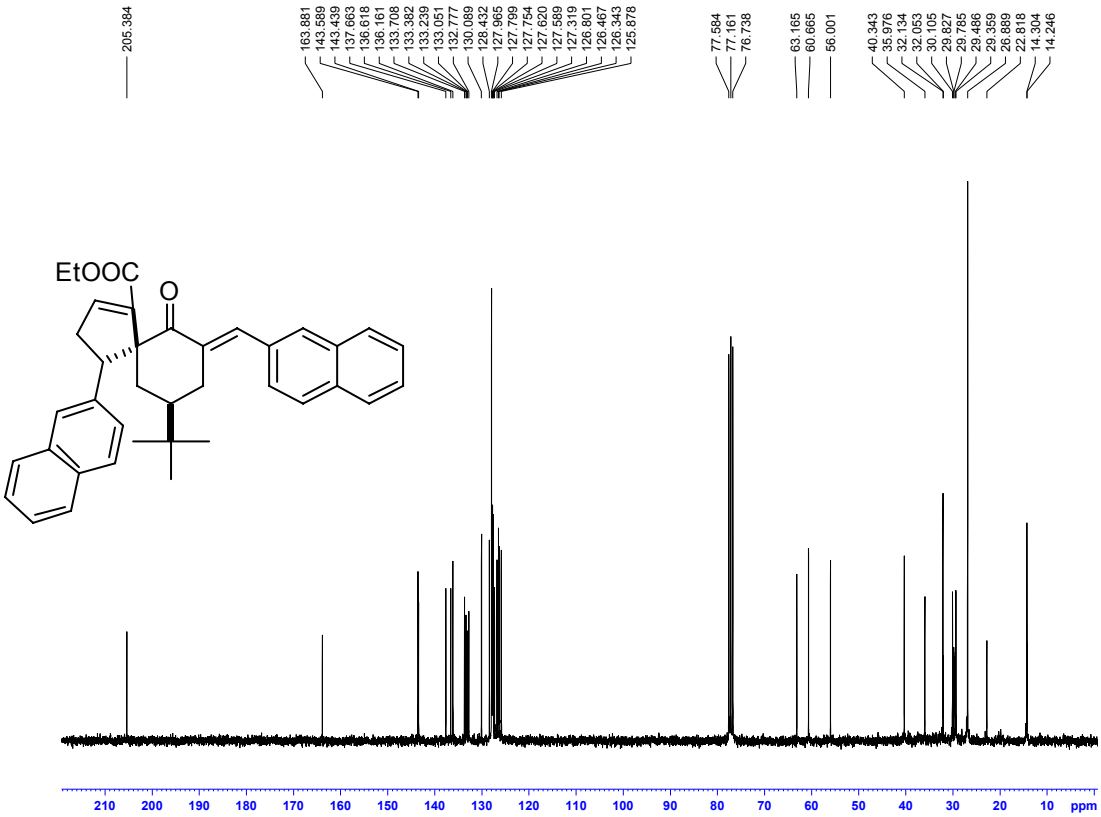
	Channel Description	RT	Area	%Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	10.806	511957	7.43
2	PDA 200.0 to 400.0 nm at 2.4 nm	18.372	6382117	92.57

(*E*)-ethyl 9-tert-butyl-4-(naphthalen-2-yl)-7-(naphthalen-2-ylmethylene)-6-oxospiro[4.5]dec-1-ene-1-carboxylate **2i**

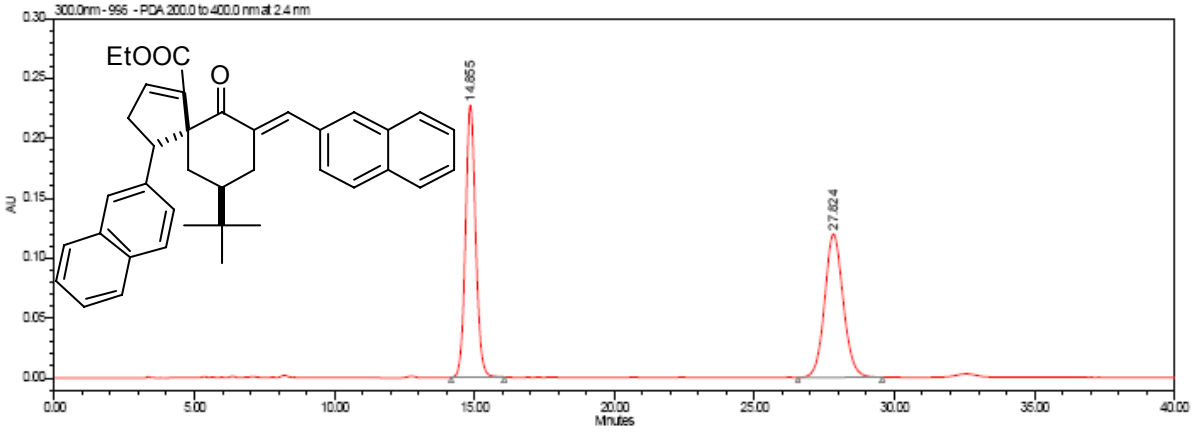
^{1}H NMR (300 MHz, $CDCl_3$):



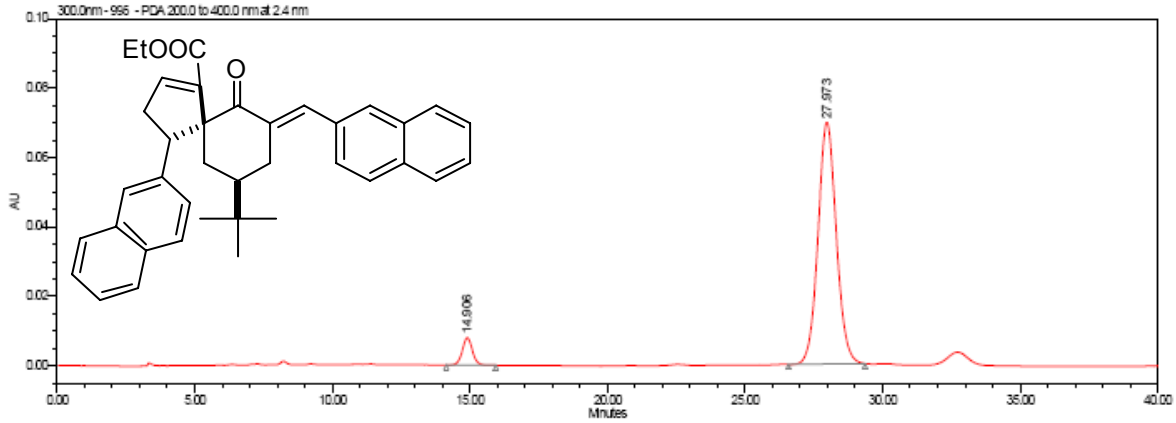
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: Table 3, entry 5: 90% ee [Daicel CHIRACEL IA, 5% *i*PrOH /*n*-heptane, 1 mL/min, 300 nm]:



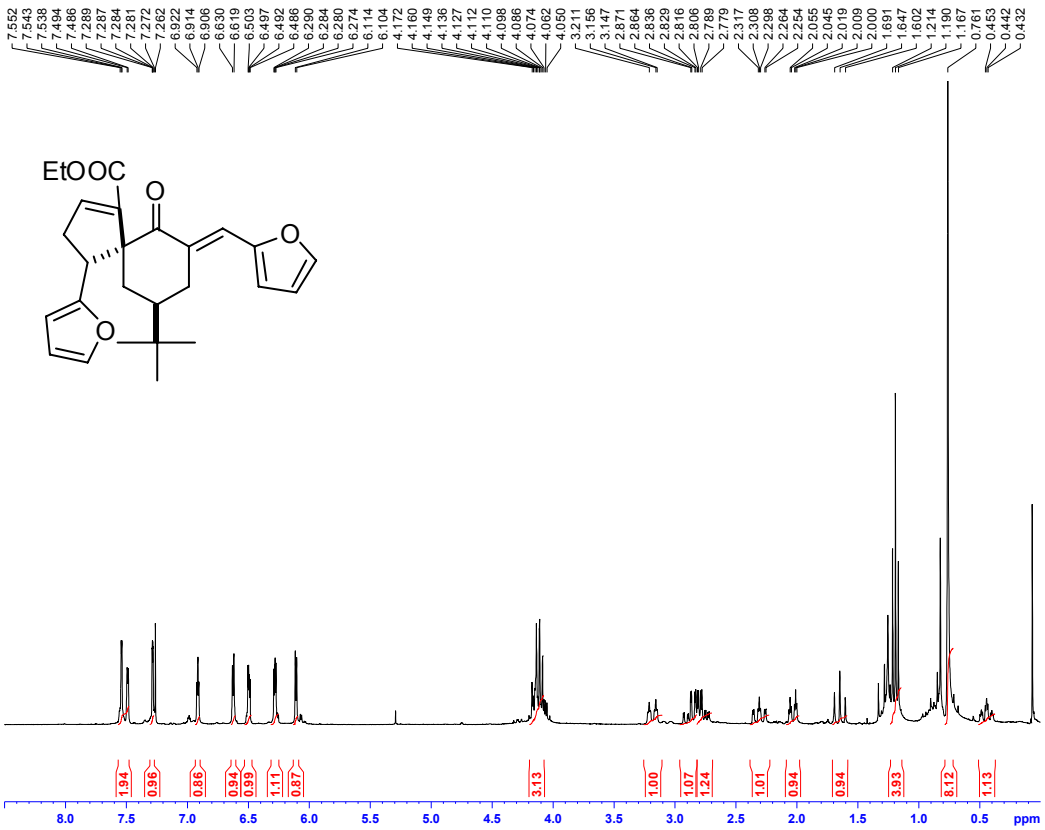
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	14.855	5707426	50.87
2	PDA 200.0 to 400.0 nm at 2.4 nm	27.824	5511560	49.13



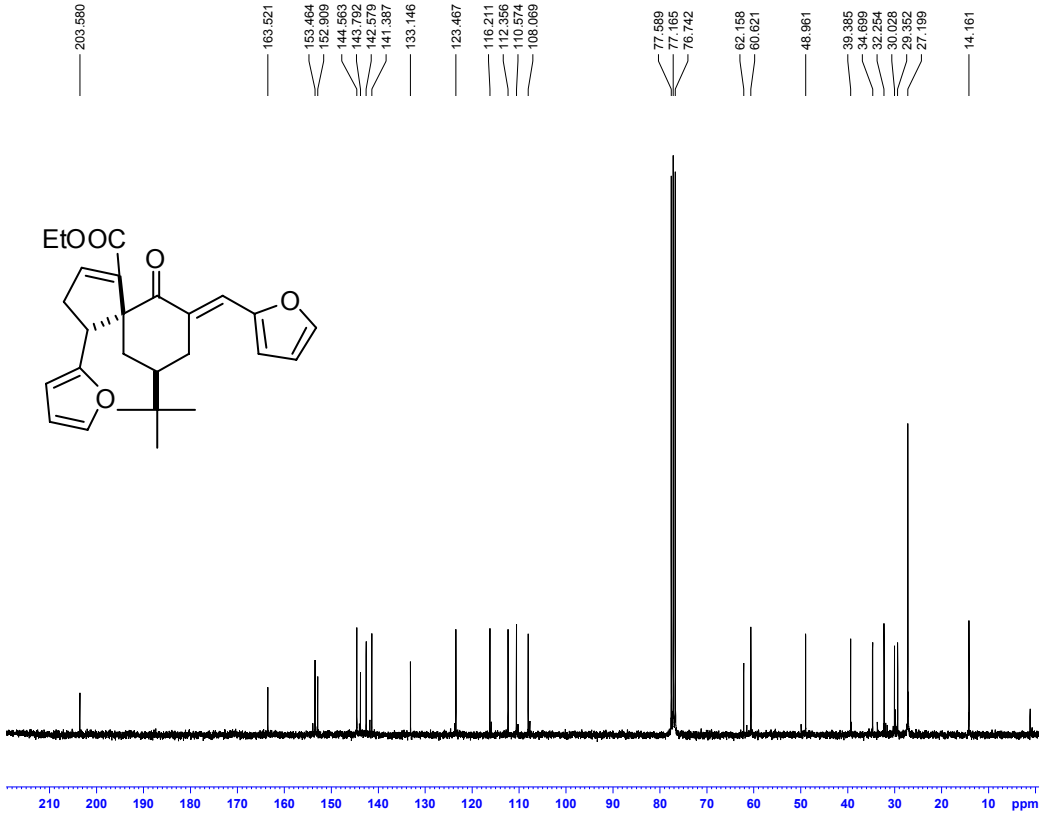
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	14.906	200421	5.86
2	PDA 200.0 to 400.0 nm at 2.4 nm	27.973	3217497	94.14

(*E*)-ethyl 9-tert-butyl-4-(furan-2-yl)-7-(furan-2-ylmethylene)-6-oxospiro[4.5]dec-1-ene-1-carboxylate **2j**

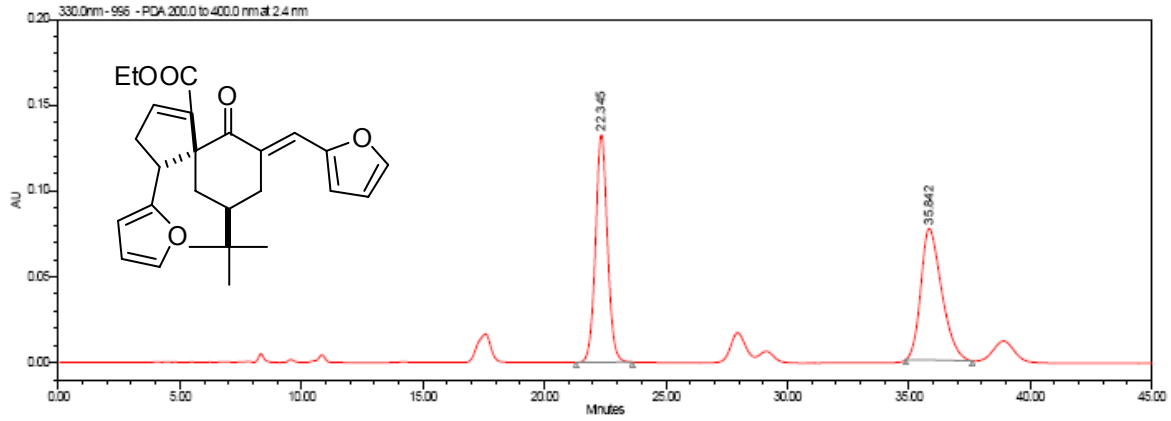
^{1}H NMR (300 MHz, $CDCl_3$):



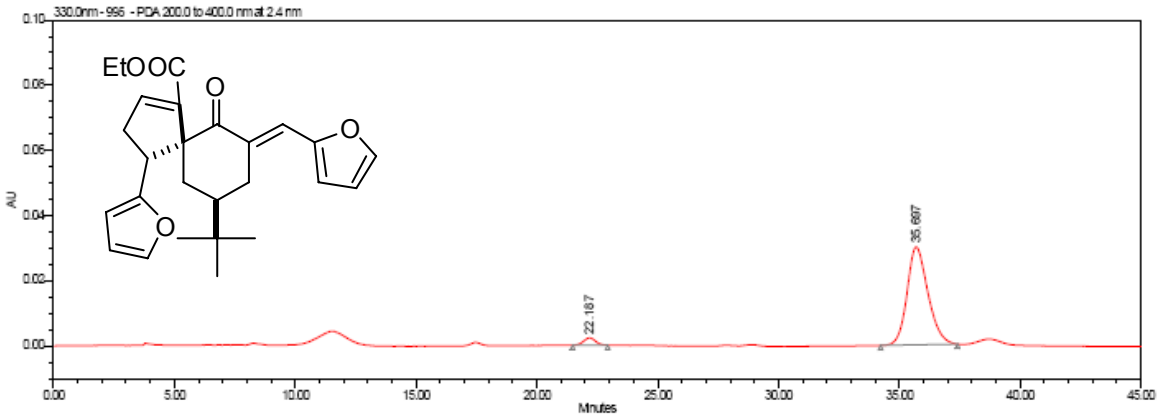
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: Table 3, entry 6: 92% ee [Daicel CHIRACEL IA, 5% *i*PrOH /*n*-heptane, 1 mL/min, 330 nm]:



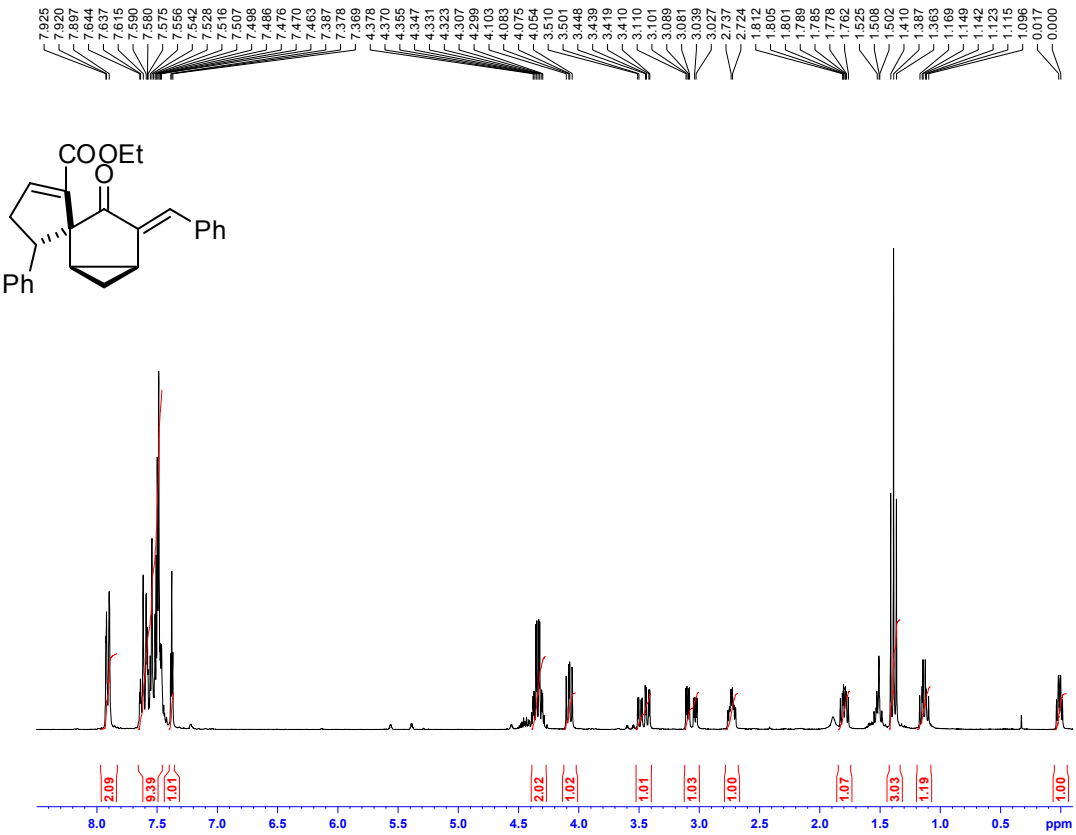
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	22.345	4527780	49.71
2	PDA 200.0 to 400.0 nm at 2.4 nm	35.842	4580185	50.29



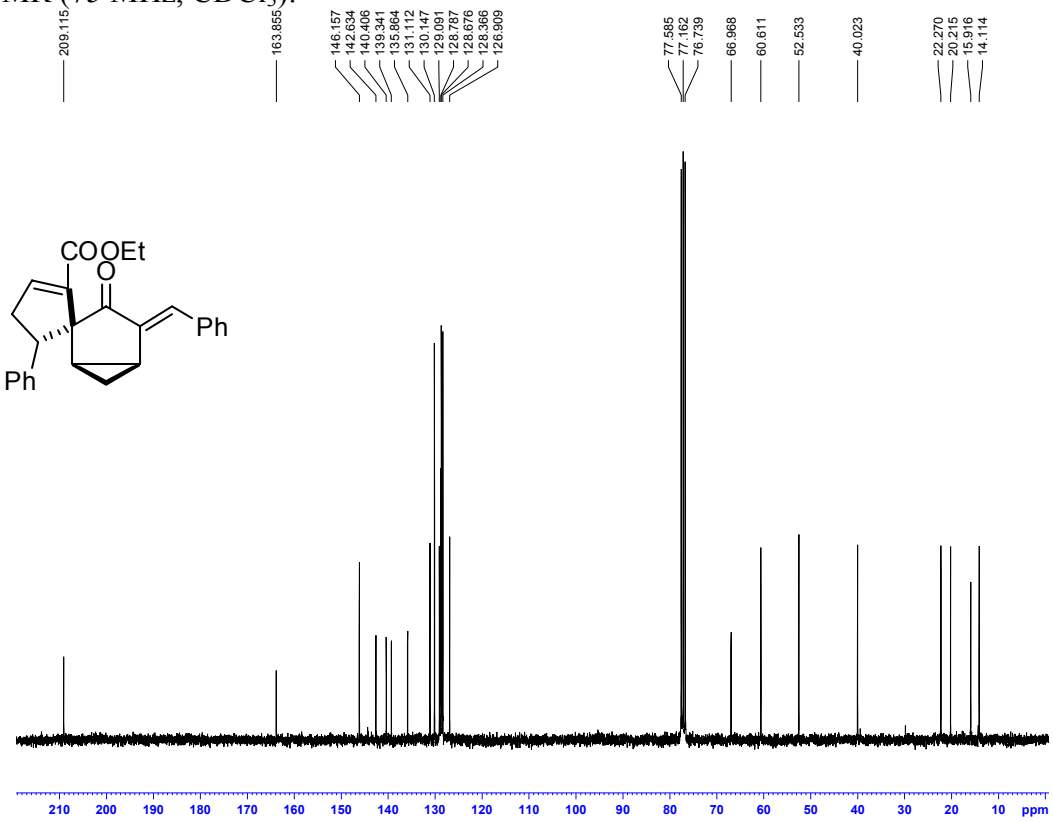
	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	22.187	76848	4.07
2	PDA 200.0 to 400.0 nm at 2.4 nm	35.697	1805197	95.93

(*E*)-ethyl 4-benzylidene-3-oxo-5'-phenylspiro[bicyclo[3.1.0]hexane-2,1'-cyclopent[2]ene]-2'-carboxylate **5a**

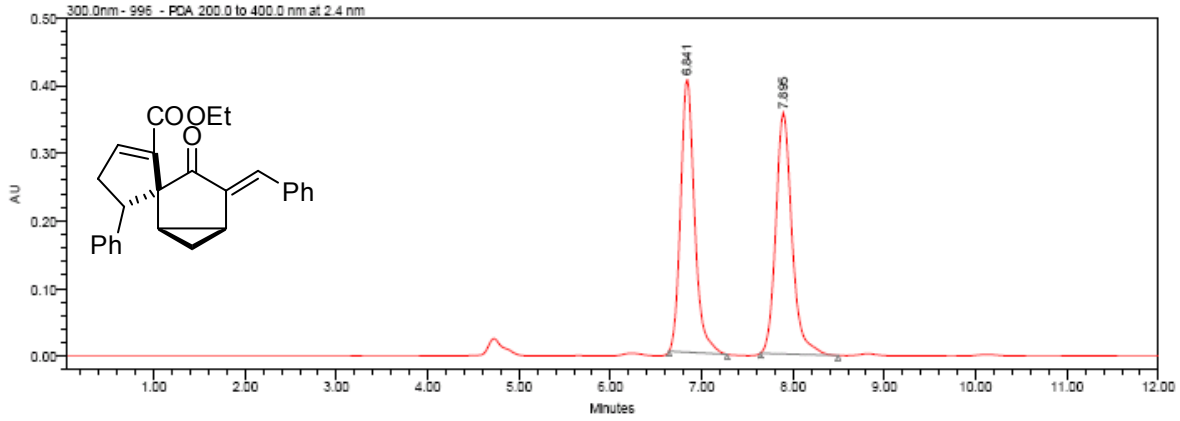
^{1}H NMR (300 MHz, $CDCl_3$):



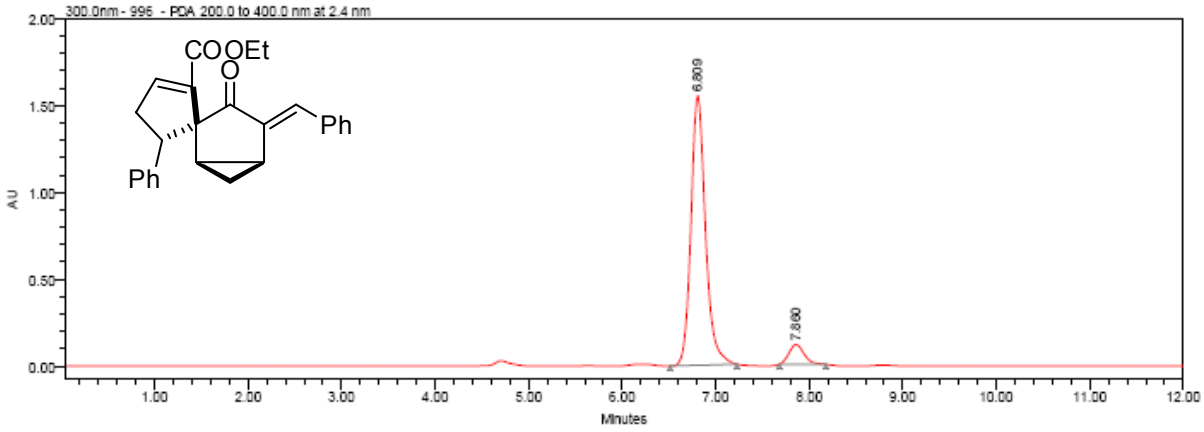
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: product **5a**: 86% ee [Daicel CHIRACEL IA, 10% *i*PrOH /*n*-heptane, 1 mL/min, 300 nm]:



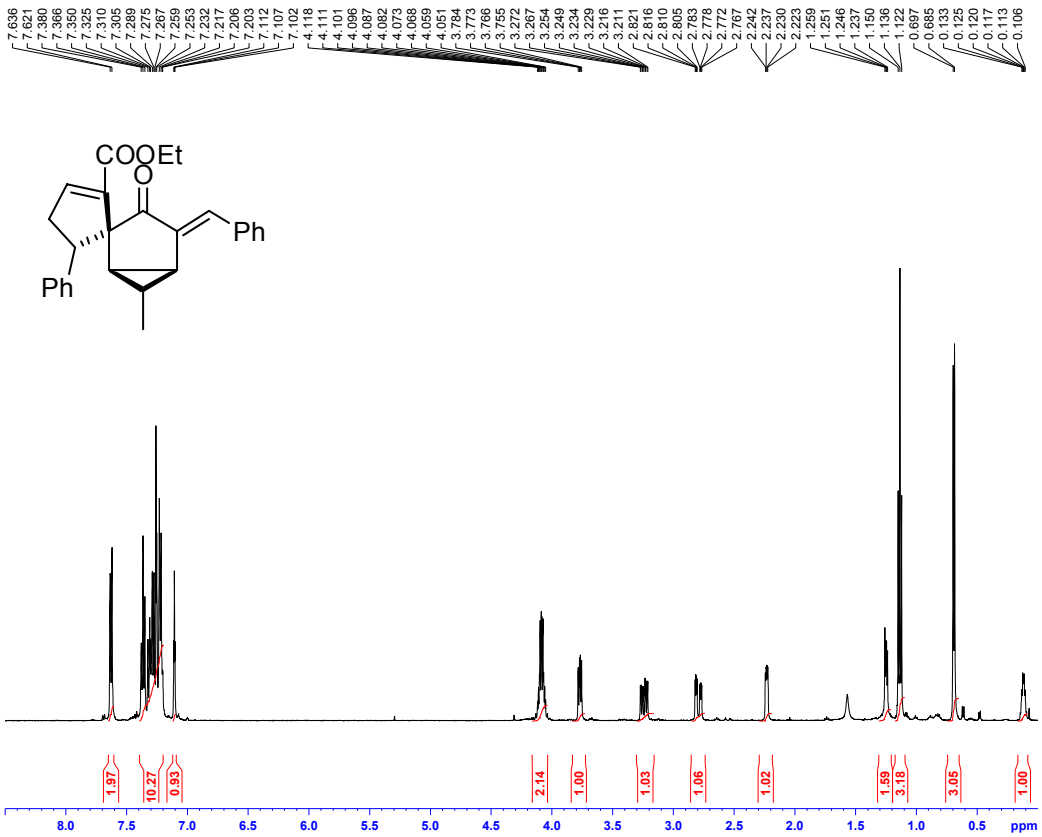
	Channel Description	RT	Area	%Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	6.841	4288494	49.46
2	PDA 200.0 to 400.0 nm at 2.4 nm	7.895	4382077	50.54



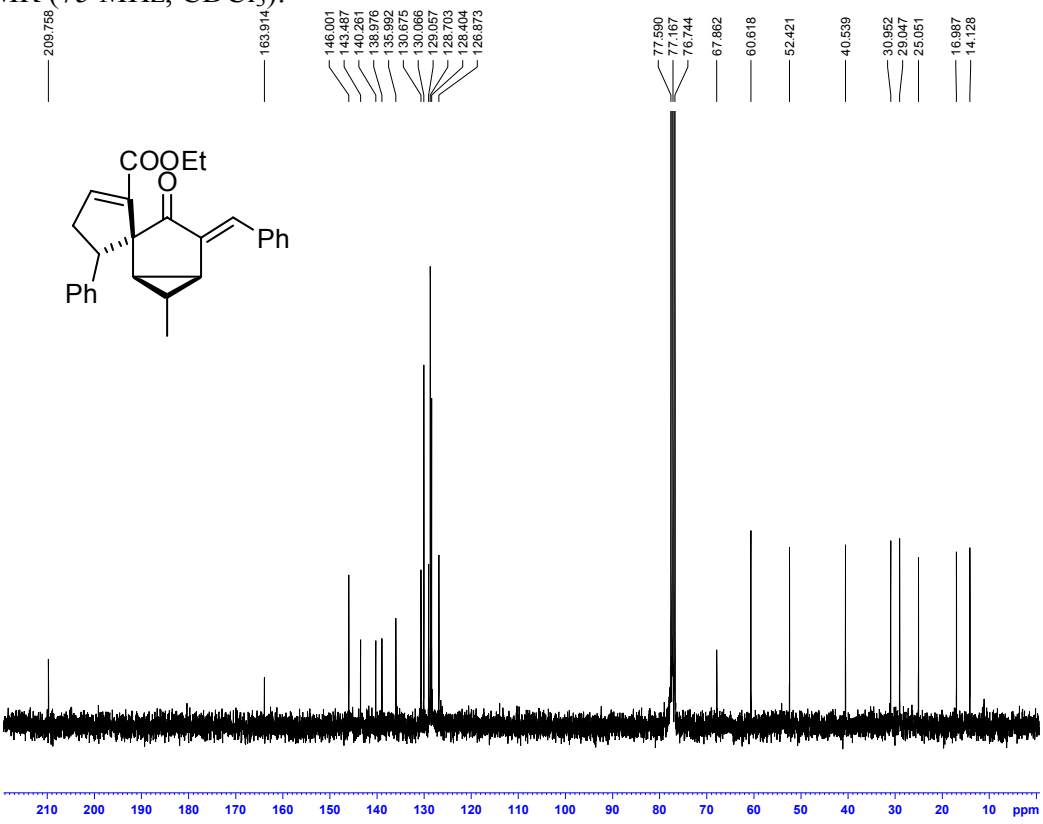
	Channel Description	RT	Area	%Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	6.809	16734953	92.83
2	PDA 200.0 to 400.0 nm at 2.4 nm	7.860	1293277	7.17

(*E*)-ethyl 4-benzylidene-6-methyl-3-oxo-5'-phenylspiro[bicyclo[3.1.0]hexane-2,1'-cyclopent[2]ene]-2'-carboxylate **5b**

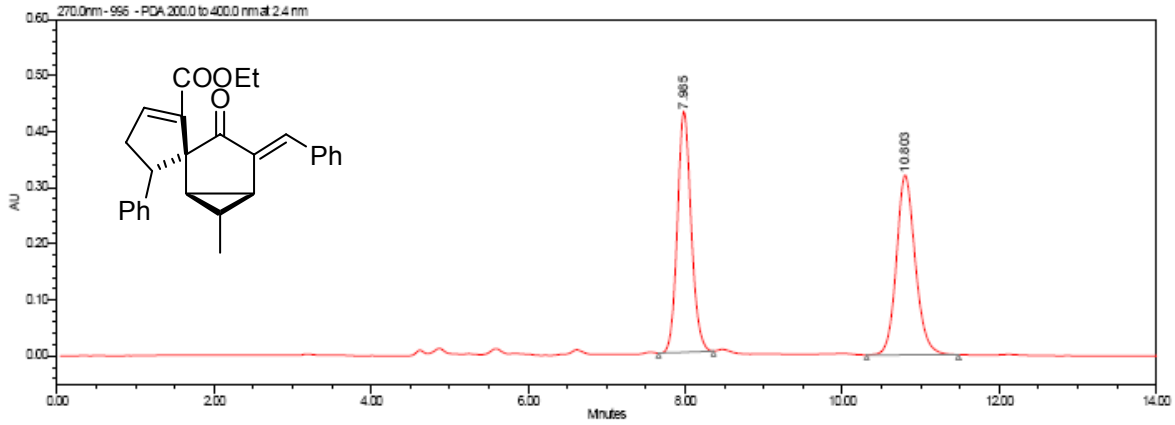
^{1}H NMR (300 MHz, $CDCl_3$):



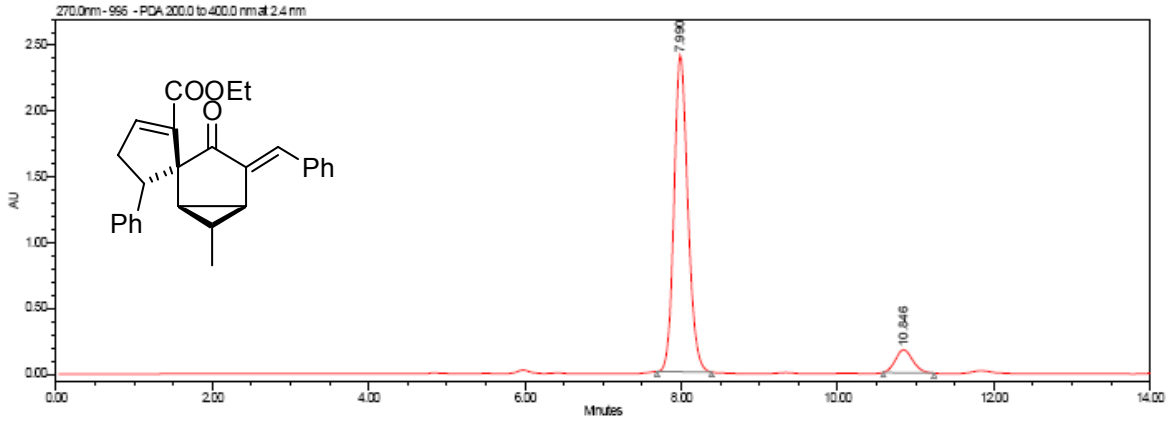
^{13}C NMR (75 MHz, $CDCl_3$):



HPLC Analysis: product **5b**: 83% ee [Daicel CHIRACEL IA, 10% *i*PrOH /*n*-heptane, 1 mL/min, 270 nm]:



	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	7.985	5244967	49.50
2	PDA 200.0 to 400.0 nm at 2.4 nm	10.803	5350856	50.50



	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	7.990	29404753	91.61
2	PDA 200.0 to 400.0 nm at 2.4 nm	10.846	2691328	8.39