Electronic Supplementary Material (ESI) for Chemical Communications

Tertiary Amine Catalyzed Carbocyclization Sequence to Spirocyclo Hexene Systems Having Vicinal Quaternary Stereocenters

Jindian Duan, Fangyi Cao, Xiaoqin Wang, and Cheng Ma*
Department of Chemistry Zhejiang University 20 Yugu Road, Hangzhou 310027, P.R. China
E-mail: mcorg@zju.edu.cn

Contents

Experimental section

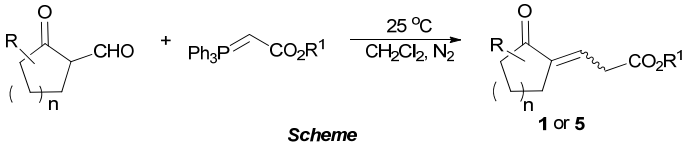
General

All reactions were carried out under nitrogen atmosphere, with dry, freshly distilled solvents in anhydrous conditions. 1,4-Dioxane and THF was distilled from sodium, while dichloromethane and DMF distilled from CaH_2 immediately prior to use. All chemicals were used without further purification as commercially available unless otherwise noted. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (300–400 mesh). NMR (400 MHz or 500 MHz for ^{1}H NMR, 100 MHz or 125 MHz for ^{13}C NMR) spectra were recorded in $CDCl_3$ with TMS as the internal standard. High resolution mass spectral (HRMS) analyses were measured using EI techniques. UV detection was monitored at 254 nm. Melting points were obtained in open capillary tubes and were uncorrected.

Cyclic β-oxoaldehydealdehydes,[1] β,γ-unsaturated α-keto esters,[2,3] substituted 2-alkylidene cyclopentanones **9**[4] and **10**[5] were synthesized according to the literature procedures.

General procedure for the synthesis of cyclic ketone derivatives 1 and 5

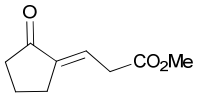
2-Alkylidene cyclic ketone derivatives **1** and **5** were prepared by the Wittig reaction of the corresponding cyclic β-oxoaldehyde and triphenylphosphorane as shown as following.



Scheme

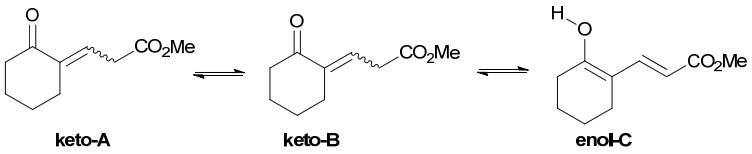
To a solution of cyclic β-oxoaldehyde (2 mmol) in anhydrous CH_2Cl_2 (5 mL), the triphenylphosphorane (2.2 mmol) was added under nitrogen atmosphere and the mixture was stirred at 25 °C for several hours until complete consumption of the aldehyde (as observed by TLC). Then the resulting mixture was concentrated under reduced pressure and purified by column chromatography on silica gel (300–400 mesh) to afford the product **1** or **5**.

(*E*)-Methyl 3-(2-oxocyclopentylidene)propanoate (1a)



Prepared according to general procedure with *n*-hexane/EtOAc 10:1 as an eluent to afford **1a** (302 mg, 90 %) as a colorless oil. The *E*-configuration of double double was detected accordingly to the NOESY and COSY spectrums; **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 6.67–6.63 (m, 1H), 3.72 (s, 3H), 3.20 (d, J = 7.2 Hz, 2H), 2.64–2.60 (m, 2H), 2.38–2.34 (m, 2H), 2.01–1.93 ppm (m, 2H); **HRMS (EI)**: $[C_9H_{12}O_3]^+$, Calc: 168.0786, Found: 168.0788.

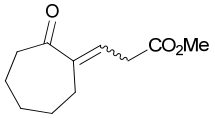
Methyl 3-(2-oxocyclohexylidene)propanoate (keto-A)



Prepared according to general procedure with *n*-hexane /EtOAc 10:1 as an eluent to afford the desired compound as a colorless oil (291 mg, 80 %); this compound existed as a mixture of three unisolatable isomers according to

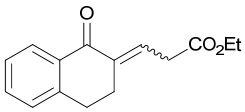
the ^{1}H NMR spectra (keto-**A**/keto-**B**/enol-**C** = 1 : 0.28 : 0.33), the configuration of double bond in keto-A was not detected; **HRMS (EI)**: $[C_{10}H_{14}O_3]^+$, Calc: 182.0943, Found: 182.0944; for keto-**A** form: **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 6.72 (t, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 3.16 (d, *J* = 7.2 Hz, 2H), 2.51–2.44 (m, 4H), 1.99–1.82 (m, 2H), 1.78–1.70 ppm (m, 2H).

Methyl 3-(2-oxocycloheptylidene)propanoate



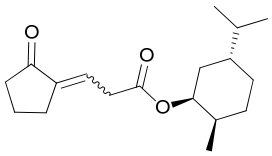
Prepared according to general procedure with *n*-hexane /EtOAc 10:1 as an eluent to afford the desired compound (314 mg, 80 %) as a colorless oil; the configuration of double bond was not detected; **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): δ 6.67 (t, *J* = 7.5 Hz, 1H), 3.71 (s, 3H), 3.20 (d, *J* = 7.0 Hz, 2H), 2.63–2.60 (m, 2H), 2.44–2.42 (m, 2H), 1.76–1.66 ppm (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): δ 204.0, 170.9, 143.2, 129.0, 52.1, 43.2, 33.5, 31.2, 29.3, 27.4, 25.1 ppm; **HRMS (EI)**: $[C_{11}H_{16}O_3]^+$, Calc: 196.1099, Found: 196.1101.

Ethyl 3-(1-oxo-3,4-dihydronaphthalen-2(1*H*)-ylidene)propanoate



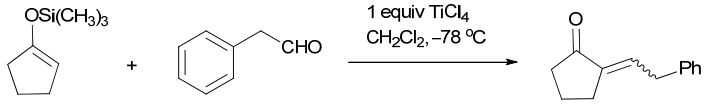
Prepared according to general procedure with *n*-hexane /EtOAc 10:1 as an eluent to afford the desired compound (366 mg, 75 %) as a pale sticky oil; the configuration of double bond was not detected; **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): δ 8.10 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.27–7.24 (m, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 3.30 (d, *J* = 7.5 Hz, 2H), 3.00–2.97 (m, 2H), 2.82–2.80 (m, 2H), 1.28 ppm (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): δ 186.9, 170.4, 143.6, 137.7, 133.3, 133.2, 130.1, 128.3, 128.2, 127.0, 61.2, 34.0, 28.8, 26.0, 14.2 ppm; **HRMS (EI)**: $[C_{15}H_{16}O_3]^+$, Calc: 244.1099, Found: 244.1103.

((1*S*,2*R*,5*R*)-5-isopropyl-2-methylcyclohexyl) 3-(2-oxocyclopentylidene)propanoate (5)



Prepared according to general procedure with *n*-hexane /EtOAc 20:1 as an eluent to afford **5** (496 mg, 85 %) as a pale sticky oil; the configuration of double bond was not detected; **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): δ 6.69–6.66 (m, 1H), 4.74–4.69 (m, 1H), 3.17 (d, *J* = 7.5 Hz, 2H), 2.63–2.60 (m, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.99–1.94 (m, 3H), 1.86–1.80 (m, 1H), 1.69–1.67 (m, 1H), 1.49–1.48 (m, 1H), 1.41–1.36 (m, 1H), 1.09–0.97 (m, 2H), 0.91–0.88 (m, 8H), 0.76–0.74 ppm (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): δ 201.2, 164.4, 134.5, 121.5, 69.9, 41.7, 35.6, 33.3, 30.3, 28.9, 26.1, 21.7, 21.1, 18.2, 16.8, 15.5, 14.4, 11.1 ppm; **HRMS (EI)**: $[C_{18}H_{28}O_3]^+$, Calc: 292.2038, Found: 292.2042.

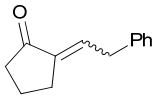
Preparation of 2-(2-phenylethylidene)cyclopentanone (9)



Scheme **9**

To a solution of phenylacetaldehyde (2.9 g, 24 mmol) in anhydrous CH_2Cl_2 (50 mL), titanium chloride (2.6 mL, 24 mmol) was added at ⁻78˚C for 1h. Then (cyclopent-1-en-1-yloxy)trimethylsilane[5] (3.1g, 20 mmol) was added over 1h. The reaction mixture was stirred for 8 h at ⁻78˚C, and worked up using saturated $NaHCO_3$ and ether. Organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and evaporated under vacuuo. The crude residue obtained was purified by column chromatography (*n*-hexane/EtOAc 10:1) to yield product **9** (2.2 g, 60%) as a sticky oil.

2-(2-Phenylethylidene)cyclopentanone (**9**)

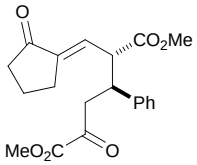


The configuration of double bond was not detected; **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.30–7.26 (m, 2H), 7.25–7.17 (m, 3H), 6.70 (t, *J* = 3 Hz, 1H), 3.48 (d, *J* = 7.2 Hz, 2H), 2.69–2.66 (m, 2H), 2.35 (t, *J* = 8 Hz, 2H), 2.00–1.92 ppm (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): δ 207.0, 137.7, 133.7, 129.0, 128.6, 128.4, 128.4, 38.5, 35.7, 26.7, 19.7 ppm; **HRMS (EI)**: $[C_{13}H_{14}O]^+$, Calc: 186.1045, Found: 186.1049.

Procedure for the preparation of 3a

To a solution of *α*-keto ester **2a** (57.0 mg, 0.30 mmol) in anhydrous 1,4-dioxane (3 mL), 2-alkylidene cyclopentanone **1a** (55.4 mg, 0.33 mmol) and Na_2CO_3 (6.4 mg, 0.06 mmol) were added successively under nitrogen atmosphere. The reaction was stirred at 25 °C for 12 h, quenched with H_2O (10 mL) and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting oil was purified by column chromatography (*n*-hexane/EtOAc 10:1) to afford compound **3a** (91.3 mg, 85%) as a white solid.

Dimethyl 5-oxo-2-((2-oxocyclopentylidene)methyl)-3-phenylhexanedioate (*anti*-3a)

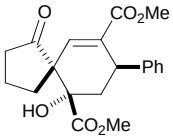


White solid, m.p. 145–148 °C (ether/*n*-hexane); **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.29–7.19 (m, 5H), 6.53 (d, *J* = 10.8 Hz, 1H), 3.85–3.81 (m, 1H), 3.79 (s, 3H), 3.55–3.52 (m, 1H), 3.50 (s, 3H), 3.34–3.18 (m, 2H), 2.63–2.56 (m, 1H), 2.37–2.29 (m, 3H), 1.94–1.88 ppm (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$, TMS): δ 206.1, 191.4, 170.9, 160.7，141.5, 133.9, 128.7, 128.5, 127.8, 127.7, 127.4, 53.0, 52.3, 52.0, 42.7, 41.7, 38.4, 29.6, 26.8, 19.5 ppm; **IR** (KBr): *v* 3029, 2952, 1742, 1735, 1715, 1647, 1454, 1437, 1266, 1246, 1213, 1178, 1085; **HRMS (EI)**: $[C_{20}H_{22}O_6]^+$, Calc: 358.1416, Found: 358.1418.

General procedure for the preparation of 4, 6, 8, and 11

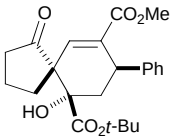
To a solution of α-keto ester **2** (0.30 mmol) in anhydrous 1,4-dioxane (3 mL), 2-alkylidene cyclopentanone **1** (0.33 mmol) and DABCO·$6H_2O$ (0.06 mmol, 20 mol %) were added successively under nitrogen atmosphere. The reaction was stirred at 25 ^oC or 40 ^oC until completely consumption of the intermediate. The resulting mixture was concentrated under reduced pressure and purified by column chromatography to afford the products.

Dimethyl 6-hydroxy-1-oxo-8-phenylspiro[4.5]dec-9-ene-6,9-dicarboxylate (4a)



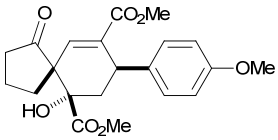
Prepared according to general procedure with *n*-hexane /acetone 10:1 as an eluent to afford **4a** (103 mg, 96 %) as a pale sticky oil; **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): δ 7.28–7.25 (m, 2H), 7.19–7.16 (m, 1H), 7.12–7.11 (m, 2H), 6.71 (d, J = 2 Hz, 1H), 5.18 (d, J = 2.5 Hz, 1H), 4.10–4.06 (m, 1H), 3.67 (s, 3H), 3.49 (s, 3H), 2.63–2.55 (m, 3H), 2.24–2.20 (m, 1H), 2.15–2.03 (m, 2H), 1.97–1.96 (m, 1H), 1.84–1.79 ppm (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): δ 221.7, 173.0, 167.0, 144.1, 136.1, 134.2, 128.7,127.3, 126.5, 78.5, 53.5, 52.5, 51.7, 39.7, 38.9, 38.1, 36.1, 18.9 ppm; **IR** (thin film): v 3434, 2952, 2914, 1722, 1596, 1493, 1435, 1269, 1223, 1163, 1067; **HRMS (EI)**: $[C_{20}H_{22}O_6]^+$, Calc: 358.1416, Found: 358.1420.

6-*tert*-Butyl 9-methyl 6-hydroxy-1-oxo-8-phenylspiro[4.5]dec-9-ene-6,9-dicarboxylate (4b)



Prepared according to general procedure with *n*-hexane/acetone 10:1 as an eluent to afford **4b** (110 mg, 92 %) as a pale sticky oil; **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.30–7.27 (m, 2H), 7.21–7.17 (m, 1H), 7.14–7.12 (m, 2H), 6.71(s, 1H), 5.27(s, 1H), 4.05 (t, J = 8.8 Hz, 1H), 3.49 (s, 3H), 2.61 (t, J = 7.2 Hz, 1H), 2.53 (dd, J_1 = 6.4 Hz, J_2 = 8.0 Hz, 1H), 2.22–2.19 (m, 1H), 2.13–2.03 (m, 3H), 1.73–1.66 (m, 1H), 1.44 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, TMS): δ 222.0, 171.4, 166.9, 144.2, 135.9, 134.1, 128.5, 127.1, 126.3, 82.7, 78.9, 53.2, 51.5, 39.7, 38.8, 37.8, 36.1, 27.7, 18.7 ppm; **IR** (thin film): v 3396, 3028, 2976, 1720, 1642, 1493, 1452, 1394, 1265, 1225, 1161, 1072; **HRMS (EI)**: $[C_{23}H_{28}O_6]^+$, Calc: 400.1886, Found: 400.1888.

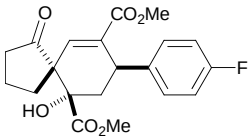
Dimethyl 6-hydroxy-8-(4-methoxyphenyl)-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (4c)



Prepared according to general procedure with *n*-hexane /acetone 10:1 as an eluent to afford **4c** (110 mg, 95 %) as a white solid, m.p. 143–147 ^oC (ether/*n*-hexane); **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): δ 7.04–7.03 (m, 2H), 6.82–6.80 (m, 2H), 6.66 (d, J = 1 Hz, 1H), 5.16 (d, J = 2 Hz, 1H), 4.03 (t, J = 8.0 Hz, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 3.51 (s, 3H), 2.60–2.56 (m, 3H), 2.23–2.18 (m, 1H), 2.11–2.03 (m, 2H), 2.00–1.94 (m, 1H), 1.82–1.77 ppm (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): δ 221.7, 173.0, 167.0, 158.1, 135.9, 135.6, 134.5, 128.2, 114.1, 78.5,

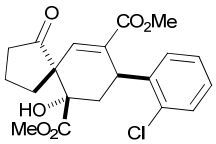
55.2, 53.4, 52.4, 51.7, 38.8, 38.7, 38.0, 36.1, 18.9 ppm; **IR** (KBr): *v* 3489, 2966, 2945, 1742, 1730, 1712, 1608, 1509, 1350, 1214, 1178, 1084, 1033; **HRMS (EI)**: $[C_{21}H_{24}O_7]^+$, Calc: 388.1522, Found: 388.1517.

Dimethyl 8-(4-fluorophenyl)-6-hydroxy-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (4d)



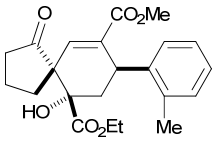
Prepared according to general procedure with *n*-hexane/acetone 10:1 as an eluent to afford **4d** (109 mg, 97 %) as a pale sticky oil; **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.08–7.07 (m, 2H)，6.98–6.94 (m, 2H)，6.70 (s, 1H), 5.17 (s, 1H), 4.09–4.05 (m, 1H), 3.69 (s, 3H), 3.51 (s, 3H), 2.61–2.56 (m, 3H), 2.23–2.17 (m, 1H), 2.12–1.97 (m, 3H), 1.81–1.75 ppm (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, TMS): δ 221.4, 172.7, 166.6, 162.5($J_{C\text{-}F}$ = 240 Hz)**,** 139.5 ($J_{C\text{-}F}$ = 2.7 Hz), 136.1, 133.9, 128.5 ($J_{C\text{-}F}$ = 8.5 Hz), 115.3 ($J_{C\text{-}F}$ = 21.1 Hz), 78.2, 53.3, 52.3, 51.6, 38.8, 38.7, 37.9, 35.9, 18.8 ppm; **IR** (thin film): *v* 3434, 2954, 2899, 1722, 1645, 1508, 1435, 1270, 1222, 1159, 1069; **HRMS (EI)**: $[C_{20}H_{21}FO_6]^+$, Calc: 376.1322, Found: 376.1324.

Dimethyl 8-(2-chlorophenyl)-6-hydroxy-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (4e)



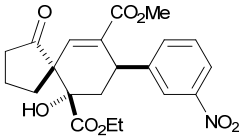
Prepared according to general procedure with *n*-hexane/acetone 10:1 as an eluent to afford **4e** (112 mg, 95 %) as a white solid, m.p. 135–138 °C (ether/*n*-hexane); **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): δ 7.36 (s, 1H), 7.14–7.12 (m, 2H), 6.94 (s, 1H), 6.79 (s, 1H), 5.12 (s, 1H), 4.64 (s, 1H), 3.70 (s, 3H), 3.51 (s, 3H), 2.72 (s, 1H), 2.59–2.56 (m, 2H), 2.20 (s, 1H), 2.08–2.03 (m, 2H), 2.00–1.97 (m, 1H), 1.67–1.66 ppm (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): δ 221.3, 172.9, 166.6, 141.7, 137.1, 133.6, 129.7, 127.6, 127.2, 127.0, 78.3, 53.5, 52.4, 51.8, 38.8, 36.1, 35.9, 35.8, 35.7, 18.9 ppm; **IR** (KBr): *v* 3441, 3065, 2954, 1724, 1641, 1474, 1432, 1269, 1227, 1190, 1166, 1071; **HRMS (EI)**: $[C_{20}H_{21}ClO_6]^+$, Calc: 392.1027, Found: 392.1028.

6-Ethyl 9-methyl 6-hydroxy-1-oxo-8-o-tolylspiro[4.5]dec-9-ene-6,9-dicarboxylate (4f)



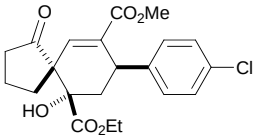
Prepared according to general procedure with *n*-hexane /acetone 10:1 as an eluent to afford **4f** (101 mg, 87 %) as a pale sticky oil ; **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.15–7.14 (m, 1H), 7.10–7.08 (m, 2H), 6.88 (s, 1H), 6.71 (s, 1H), 5.28 (s, 1H), 4.32 (t, *J* = 8.0 Hz, 1H), 4.17 (q, *J* = 6.8 Hz, 2H), 3.49 (s, 3H), 2.62–2.53 (m, 3H), 2.45 (s, 3H), 2.25–2.20 (m, 1H), 2.12–1.99 (m, 3H), 1.70 (t, *J* = 12 Hz, 1H), 1.26 ppm (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, TMS): δ 222.1, 172.4, 166.8, 142.3, 135.7, 135.5, 134.8, 130.3, 126.4, 126.2, 125.4, 78.4, 61.6, 53.2, 51.6, 38.8, 36.2, 36.0, 35.0, 19.3, 18.8, 13.9 ppm; **IR** (thin film): *v* 3404, 2975, 2928, 1716, 1634, 1596, 1495, 1431, 1378, 1266, 1089, 1048; **HRMS (EI)**: $[C_{22}H_{26}O_6]^+$, Calc: 386.1729, Found: 386.1731.

6-Ethyl 9-methyl 6-hydroxy-8-(3-nitrophenyl)-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (4g)



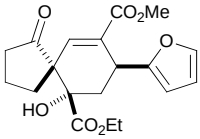
Prepared according to general procedure with *n*-hexane/acetone 8:1 as an eluent to afford **4g** (120 mg, 96 %) as a white solid, m.p. 146–150 °C (ether/*n*-hexane); **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): δ 8.09–8.07 (m, 1H), 7.96 (s, 1H), 7.52–7.46 (m, 2H), 6.84 (s, 1H), 5.23 (s, 1H), 4.22–4.15 (m, 3H), 3.53 (s, 3H), 2.64–2.60 (m, 3H), 2.27–2.22 (m, 1H), 2.15–2.01 (m, 3H), 1.80-1.75 (m, 1H), 1.26 ppm (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): δ 221.3, 172.1, 166.1, 148.5, 146.5, 137.9, 133.9, 132.5, 129.6, 121.9, 121.7, 78.0, 61.9, 53.4, 51.9, 39.5, 38.9, 37.8, 36.1, 18.9, 14.0 ppm; **IR** (KBr): *v* 3409, 3098, 2977, 2952, 1743, 1713, 1523, 1440, 1349, 1273, 1227, 1068; **HRMS (EI)**: $[C_{21}H_{23}NO_8]^+$, Calc: 417.1424, Found: 417.1439.

6-Ethyl 9-methyl 8-(4-chlorophenyl)-6-hydroxy-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (4h)



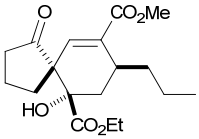
Prepared according to general procedure with *n*-hexane/acetone 10:1 as an eluent to afford **4h** (114 mg, 94 %) as a pale sticky oil; **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.28–7.24 (m, 2H)，7.08–7.06 (m, 2H)，6.73 (s, 1H), 5.22 (d, *J* = 1.2 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 4.08–4.04 (m, 1H), 3.52 (s, 3H), 2.59–2.55 (m, 3H), 2.19–2.00 (m, 4H), 1.77–1.71 (m, 1H), 1.26 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, TMS): δ 221.6, 172.2, 166.6, 142.5, 136.5, 133.5, 132.0, 128.7, 128.5, 78.1, 61.7, 53.3, 51.7, 39.0, 38.8, 37.7, 36.0, 18.8, 13.9 ppm; **IR** (thin film): *v* 3424, 2975, 2899, 1722, 1644, 1490, 1435, 1407, 1268, 1222, 1091, 1051; **HRMS (EI)**: $[C_{21}H_{23}ClO_6]^+$, Calc: 406.1183, Found: 406.1186.

6-Ethyl 9-methyl 8-(furan-2-yl)-6-hydroxy-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (4i)



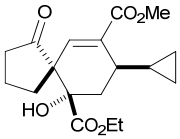
Prepared according to general procedure with *n*-hexane/acetone 10:1 as an eluent to afford **4i** (105 mg, 97 %) as a pale sticky oil; **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): δ 7.29–7.26 (m, 1H), 6.66–6.65 (m, 1H), 6.27–6.26 (m, 1H), 6.00 (d, *J* = 3.0 Hz, 1H), 4.81 (s, 1H), 4.25–4.22 (m, 1H), 4.16–4.10 (m, 1H), 4.07–4.00(m, 1H), 3.63 (s, 3H), 2.63 (q, *J* = 7.0 Hz, 1H), 2.53 (t, *J* = 8.0 Hz, 2H), 2.25–2.20 (m, 1H), 2.12–2.05 (m, 2H), 2.03–1.97 (m, 2H), 1.23 ppm (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): δ 220.4, 172.5, 166.7, 155.5, 141.0, 136.5, 131.6, 110.3, 105.5, 77.5, 61.8, 53.7, 51.8, 39.0, 35.2, 34.3, 33.2, 18.9, 13.9 ppm; **IR** (thin film): *v* 3430, 2974, 2938, 1728, 1441, 1381, 1269, 1084, 1053; **HRMS (EI)**: $[C_{19}H_{22}O_7]^+$, Calc: 362.1366, Found: 362.1361.

6-Ethyl 9-methyl 6-hydroxy-1-oxo-8-propylspiro[4.5]dec-9-ene-6,9-dicarboxylate (4j)



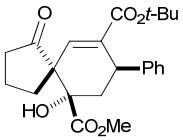
Prepared according to general procedure with *n*-hexane/acetone 15:1 as an eluent to afford **4j** (88 mg, 87 %) as a pale sticky oil; **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): δ 6.46 (d, *J* = 1.5 Hz, 1H), 4.89 (d, *J* = 1.5 Hz, 1H), 4.22-4.17 (m, 2H), 3.74 (s, 3H), 2.89-2.87 (m, 1H), 2.53–2.49 (m, 2H), 2.41 (q, *J* = 7.0 Hz 1H), 2.04–1.92 (m, 4H), 1.68–1.57 (m, 2H), 1.36–1.28 (m, 6H), 0.91 ppm (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): δ 219.1, 170.4, 164.9, 133.2, 132.0, 75.5, 59.1, 51.0, 49.2, 36.3, 33.2, 33.1, 30.7, 29.5, 17.0, 16.3, 11.6, 11.5 ppm; **IR** (thin film): *v* 3439, 2959, 2872, 1732, 1642, 1435, 1403, 1262, 1191, 1129, 1073; **HRMS (EI)**: $[C_{18}H_{26}O_6]^+$, Calc: 338.1729, Found: 338.1721.

6-Ethyl 9-methyl 8-cyclopropyl-6-hydroxy-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (4k)



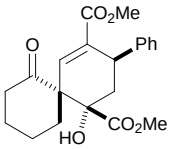
Prepared according to general procedure with *n*-hexane/acetone 15:1 as an eluent to afford **4k** (76 mg, 75 %) as a pale sticky oil; **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): δ 6.31 (d, *J* = 1.0 Hz, 1H), 4.82 (d, *J* = 1.5 Hz,1H), 4.24–4.17 (m, 2H), 3.76 (s, 3H), 2.50 (t, *J* = 7.5 Hz, 2H), 2.43 (q, *J* = 7.0 Hz, 1H), 2.27–2.23 (m, 1H), 2.10–1.93 (m, 4H), 1.69–1.64 (m, 1H), 1.29 (t, *J* = 7.0 Hz, 3H), 0.62-0.58 (m, 1H), 0.54–0.50 (m, 2H), 0.43–0.39 (m, 1H), 0.16–0.13 ppm (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): δ 218.8, 170.6, 166.0, 133.9, 130.7, 75.6, 59.3, 51.3, 49.3, 36.6, 34.2, 33.2, 31.8, 16.5, 13.0, 11.7, 3.7 ppm; **IR** (thin film): *v* 3444, 2977, 2899, 1731, 1642, 1435, 1403, 1264, 1191, 1157, 1045; **HRMS (EI)**: $[C_{18}H_{24}O_6]^+$, Calc: 336.1573, Found: 336.1576.

9-*tert*-Butyl 6-methyl 6-hydroxy-1-oxo-8-phenylspiro[4.5]dec-9-ene-6,9-dicarboxylate (4l)



Prepared according to general procedure with *n*-hexane/acetone 10:1 as an eluent to afford **4l** (97 mg, 81 %) as a white solid, m.p. 148–152 ^{o}C (ether/*n*-hexane); **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): δ 7.29–7.26 (m, 2H), 7.21–7.18 (m, 1H)，7.13–7.11 (m, 2H), 6.62 (d, *J* = 2 Hz, 1H), 5.36 (d, *J* = 2 Hz,1H), 4.01–3.98 (m, 1H), 3.70 (s, 3H), 2.60–2.53 (m, 3H), 2.21–2.17 (m, 1H), 2.10–1.94 (m, 3H), 1.80–1.75 (m, 1H), 1.10 ppm (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): δ 222.1, 173.0, 166.1, 144.5, 135.8, 134.5, 128.5, 127.4, 126.3, 81.0, 78.5, 53.3, 52.4, 39.9, 38.8, 38.0, 36.2, 27.5, 18.8 ppm; **IR** (KBr): *v* 3456, 2985, 2935, 1745, 1705, 1647, 1453, 1437, 1369, 1285, 1239, 1159, 1115, 1068; **HRMS (EI)**: $[C_{23}H_{28}O_6]^+$, Calc: 400.1886, Found: 400.1891.

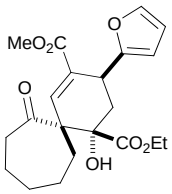
Dimethyl 1-hydroxy-7-oxo-3-phenylspiro[5.5]undec-4-ene-1,4-dicarboxylate (4m)



Prepared according to general procedure with *n*-hexane/acetone 10:1 as an eluent to afford **4m** (81 mg, 73 %) from the corresponding propanoate mixtures (60.0 mg, 0.33 mmol) as a white solid, m.p. 130–133 ^{o}C (ether/*n*-hexane); **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.30–7.27 (m, 2H), 7.21–7.18 (m, 1H), 7.14–7.13 (m, 3H), 5.55 (d, *J* = 2 Hz, 1H), 4.10–4.05 (m, 1H), 3.73 (s, 3H), 3.51 (s, 3H), 2.84–2.76 (m, 1H), 2.58–2.54 (m, 1H), 2.40–2.35 (m, 1H), 2.15–2.14 (m, 3H), 2.01–1.94 (m, 2H), 1.86–1.80 ppm (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$, TMS): δ 215.1, 173.4, 166.9, 144.0, 138.0, 134.3，128.6, 126.9, 126.3, 78.5, 55.9, 52.4, 51.6, 39.6, 39.4, 39.1, 37.5, 25.7, 21.0 ppm; **IR** (KBr): *v* 3332, 2948, 1731, 1715, 1494, 1454, 1437, 1272, 1237, 1138, 1116, 1054; **HRMS (EI)**: $[C_{21}H_{24}O_6]^+$, Calc: 372.1573, Found: 372.1575.

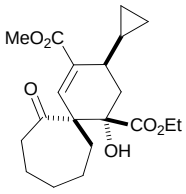
Product **4m** was obtained from the propanoate mixtures (81.9 mg, 0.45 mmol, 1.5 equiv) in 75 % yield (84 mg).

1-Ethyl 4-methyl 3-(furan-2-yl)-1-hydroxy-7-oxospiro[5.6]dodec-4-ene-1,4-dicarboxylate (4n)



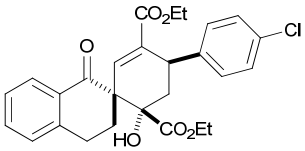
Prepared according to general procedure with *n*-hexane/acetone 10:1 as an eluent to afford **4n** (81 mg, 69 %) as a white solid, m.p. 133–136 ^{o}C (ether/*n*-hexane); **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): δ 7.28–7.27 (m, 1H), 6.95–6.94 (m, 1H), 6.28–6.27 (m, 1H), 6.03 (d, *J* = 3.0 Hz, 1H), 4.25–4.15 (m, 4H), 3.64 (s, 3H), 2.67–2.64 (m, 2H), 2.41–2.36 (m, 1H), 2.28(q, *J* = 7.5 Hz 1H), 2.15–2.03 (m, 2H), 1.91–1.74 (m, 3H), 1.61–1.47 (m, 3H), 1.29 ppm (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): δ 215.4, 173.2, 166.7, 155.7, 141.1, 139.5, 131.1, 110.3, 105.4, 77.3, 62.1, 58.8, 51.8, 43.2, 34.8, 34.2,32.8, 30.2, 26.1, 24.8, 14.1 ppm; **IR** (KBr): *v* 3422, 2976, 2935, 1722, 1439, 1369, 1266, 1088, 1049; **HRMS (EI)**: $[C_{21}H_{26}O_7]^+$, Calc: 390.1679, Found: 390.1682.

Ethyl 4-methyl 3-cyclopropyl-1-hydroxy-7-oxospiro[5.6]dodec-4-ene-1,4-dicarboxylate (4o)



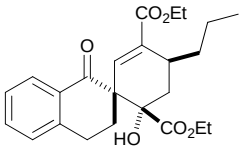
Prepared according to general procedure with *n*-hexane/acetone 15:1 as an eluent to afford **4o** (77 mg, 71 %) as a pale sticky oil; **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): δ 6.60 (s, 1H), 4.28–4.23 (m, 2H), 4.19 (s, 1H), 3.76 (s, 3H), 2.64–2.60 (m, 2H), 2.21–2.14 (m, 1H), 2.10–2.00 (m, 3H), 1.90–1.85 (m, 2H), 1.80–1.78 (m, 1H), 1.70–1.67 (m, 1H), 1.59–1.47 (m, 3H), 1.32 (t, *J* = 7.0 Hz, 3H), 0.62–0.59 (m, 1H), 0.54–0.51 (m, 2H), 0.43–0.39 (m, 1H), 0.14–0.11 ppm (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): δ 213.5, 171.4, 166.2, 133.6, 75.3, 59.7, 56.5, 49.4, 40.9, 33.7, 32.9, 31.7, 28.0, 23.8, 22.6, 13.5, 11.9, 3.6 ppm; **IR** (thin film): *v* 3497, 2934, 1720, 1715, 1438, 1366, 1259, 1155, 1117, 1045; **HRMS (EI)**: $[C_{20}H_{28}O_6]^+$, Calc: 364.1886, Found: 364.1889.

Diethyl 4-(4-chlorophenyl)-6-hydroxy-1'-oxo-3',4'-dihydro-1'H-spiro[cyclohex[2]ene-1,2'-naphthalene]- 3,6-dicarboxylate (4p)



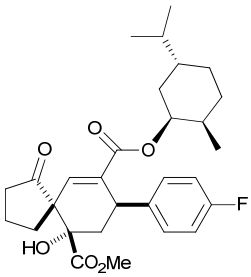
Prepared according to general procedure with *n*-hexane/acetone 10:1 as an eluent to afford **4p** (128 mg, 89 %) as a white solid, m.p. 145–148 °C (ether/*n*-hexane); **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 8.13–8.11 (d, J = 8 Hz, 1H)，7.60–7.56 (m, 1H)，7.42–7.38 (m, 1H)，7.32–7.27 (m, 3H), 7.13–7.11 (m, 2H), 6.91 (d, J = 1.6 Hz, 1H), 6.71 (d, J = 2.4 Hz, 1H), 4.17–4.07 (m, 3H), 4.02–3.85 (m, 2H), 3.37–3.28 (m, 1H), 2.98–2.93 (m, 1H), 2.47 (dd, J_1 = 6.8 Hz, J_2 = 8.4 Hz 1H), 2.36–2.22 (m, 2H), 2.06–2.00 (m, 1H), 1.10 (t, J = 7.2 Hz, 3H), 0.88 ppm (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, TMS): δ 201.7, 172.4, 166.2, 143.2, 142.9, 136.0, 135.9, 134.5, 132.0, 131.3, 128.7, 128.6, 128.6, 128.5, 127.3, 78.9, 61.4, 60.6, 50.3, 39.4, 36.9, 35.0, 25.4, 13.8, 13.7 ppm; **IR** (KBr): v 3373, 2976, 2937, 1720, 1660, 1598, 1489, 1455, 1409, 1363, 1226, 1093, 1046; **HRMS (EI)**: $[C_{27}H_{27}ClO_6]^+$, Calc: 482.1496, Found: 482.1498.

Diethyl 6-hydroxy-1'-oxo-4-propyl-3',4'-dihydro-1'H-spiro[cyclohex[2]ene-1,2'-naphthalene]-3,6-di-carboxylate (4q)



Prepared according to general procedure with *n*-hexane/acetone 15:1 as an eluent to afford **4q** (92 mg, 74 %) as a pale sticky oil; **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ8.08 (d, J = 7.6 Hz, 1H)，7.55 (t, J = 7.2 Hz, 1H)，7.37 (t, J = 7.6 Hz, 1H), 7.28–7.26 (m, 1H), 6.63 (s, 1H), 6.39 (d, J = 2.4 Hz, 1H), 4.21–4.15 (m, 2H), 4.10 (q, J = 7.2 Hz, 2H), 3.17–3.13 (m, 1H), 2.99–2.97 (m, 1H), 2.87–2.83 (m, 1H), 2.34–2.22 (m, 2H), 2.11–2.06 (m, 1H), 1.90–1.84 (m, 1H), 1.75–1.72 (m, 1H), 1.43–1.34 (m, 3H), 1.27 (t, J = 7.2 Hz, 3H), 1.11 (t, J = 7.2 Hz, 3H), 0.94 ppm (t, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, TMS): δ 202.3, 173.0, 167.0, 143.4, 138.1, 134.3, 133.7, 131.5, 128.5, 128.4, 127.1, 78.9, 61.2, 60.6, 50.5, 36.2, 34.8, 32.5, 31.9, 25.4, 19.4, 14.1, 14.0, 13.8 ppm; **IR** (thin film): v 3366, 2958, 1735, 1717, 1660, 1599, 1455, 1261, 1229, 1157, 1114, 1045; **HRMS (EI)**: $[C_{24}H_{30}O_6]^+$, Calc: 414.2042, Found: 414.2044.

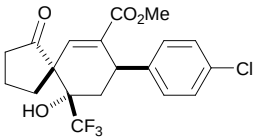
9-((1S,2R,5R)-5-isopropyl-2-methylcyclohexyl)6-methyl8-(4-fluorophenyl)-6-hydroxy-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (6)



Prepared according to general procedure with *n*-hexane/acetone 25:1 as an eluent to afford **6** (142 mg, 95 %) as a

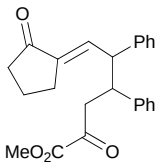
pale sticky oil (d. r. = 3:1); For major diastereomer: **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.09–7.05 (m, 2H), 6.97–6.91 (m, 2H), 6.73 (s, 1H), 5.22 (s, 1H), 4.61–4.55 (m, 1H), 4.07–4.03 (m, 1H), 3.69 (s, 3H), 2.58–2.54 (m, 3H), 2.18–2.13 (m, 1H), 2.09–1.95 (m, 3H), 1.86–1.41 (m, 6H), 1.04–0.69 (m, 8H), 0.62–0.55 (m, 3H), 0.41–0.40 ppm (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$, TMS): δ 221.5, 172.8, 166.4, 162.6 ($J_{C\text{-}F}$ = 242.8 Hz), 140.1, 136.2, 134.1, 128.4 ($J_{C\text{-}F}$ = 7.4 Hz), 115.5 ($J_{C\text{-}F}$ = 20.1 Hz), 78.2, 74.8, 53.3，52.3, 46.6, 40.7, 38.7, 38.6, 38.4, 35.9, 33.9, 31.3, 24.6, 22.4, 21.8, 20.9, 18.7, 15.1 ppm; **IR** (thin film): *v* 3440, 2952, 1732, 1709, 1640，1506, 1450，1262, 1221, 1185, 1063; **HRMS (EI)**: $[C_{29}H_{37}FO_6]^+$, Calc: 500.2574, Found: 500.2578.

Methyl 8-(4-chlorophenyl)-10-hydroxy-1-oxo-10-(trifluoromethyl)spiro[4.5]dec-6-ene-7-carboxylate (8)



Prepared according to general procedure with *n*-hexane/acetone 20:1 as an eluent to afford **8** (67 mg, 56 %) as a white solid, m.p. 146–148 ^{o}C (ether/*n*-hexane); **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.27–7.26 (m, 2H)，7.08–7.06 (m, 2H)，6.69 (s, 1H), 5.77 (s, 1H), 4.09–4.05 (m, 1H), 3.52 (s, 3H), 2.70–2.47 (m, 3H), 2.38–2.33 (m, 1H), 2.25–2.09 (m, 3H), 1.71–1.64 ppm (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, TMS): δ 221.7, 166.3, 141.7, 135.5, 133.6, 132.3, 128.9, 128.4, 127.3, 124.4, 76.4, 51.9, 51.8, 38.4, 38.3, 35.7, 34.5, 18.5 ppm; **IR** (KBr): *v* 3361, 2966, 1720, 1650, 1491, 1432, 1273, 1245, 1160, 1123, 1102, 1013; **HRMS (EI)**: $[C_{19}H_{18}ClF_3O_4]^+$, Calc: 402.0846, Found: 402.0845.

Methyl 2-oxo-6-(2-oxocyclopentylidene)-4,5-diphenylhexanoate (11)



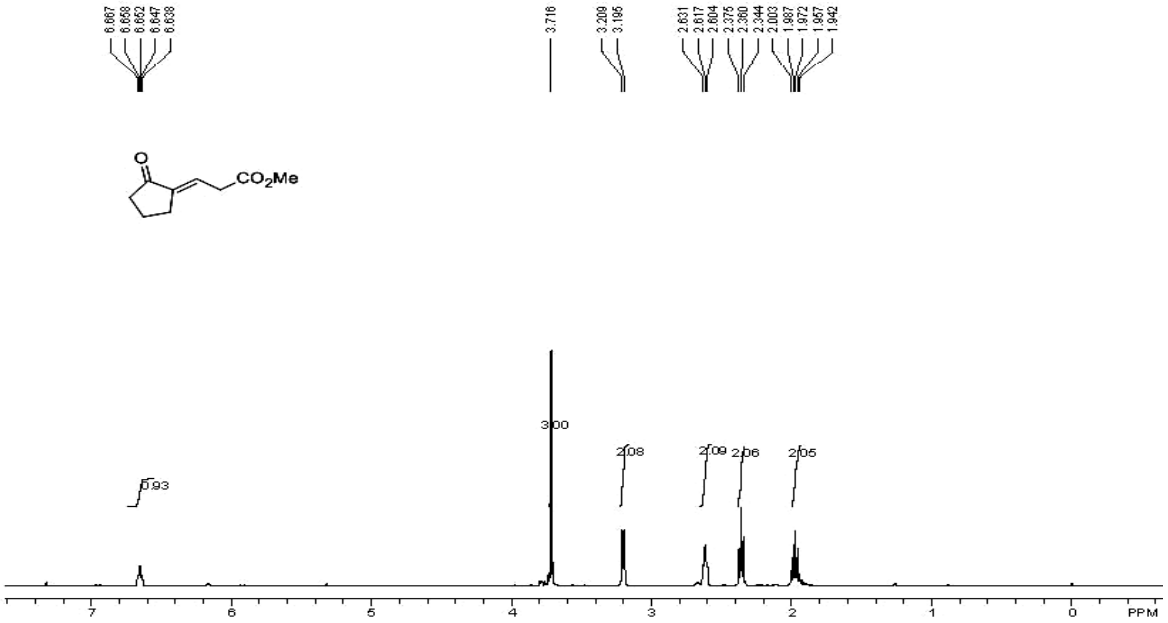
Prepared according to the general procedure with *n*-hexane/acetone 5:1 as an eluent to afford **11** (67 mg, 61 %) as a colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): δ 7.17–7.11 (m, 4H), 7.10–7.06 (m, 2H), 7.03–7.00 (m, 4H), 6.79 (d, J = 10.5 Hz, 1H), 3.75 (s, 3H), 3.74–3.67 (m, 2H), 3.35 (dd, J_1 = 9.0 Hz, J_2 = 17.5 Hz, 1H), 3.17 (dd, J_1 = 4.5 Hz, J_2 = 18.0 Hz, 1H), 2.57-2.53 (m, 2H), 2.36–2.26 (m, 2H), 1.93–1.87 ppm (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$, TMS): δ 206.8, 192.2, 161.1, 140.6, 140.1, 138.6, 135.0, 128.5, 128.3, 128.2, 128.2, 126.9, 126.8, 53.0, 52.1, 46.4, 42.7, 38.5, 27.0, 19.6 ppm; **HRMS (EI)**: $[C_{24}H_{24}O_4]^+$, Calc: 376.1675, Found: 376.1674.

Reference

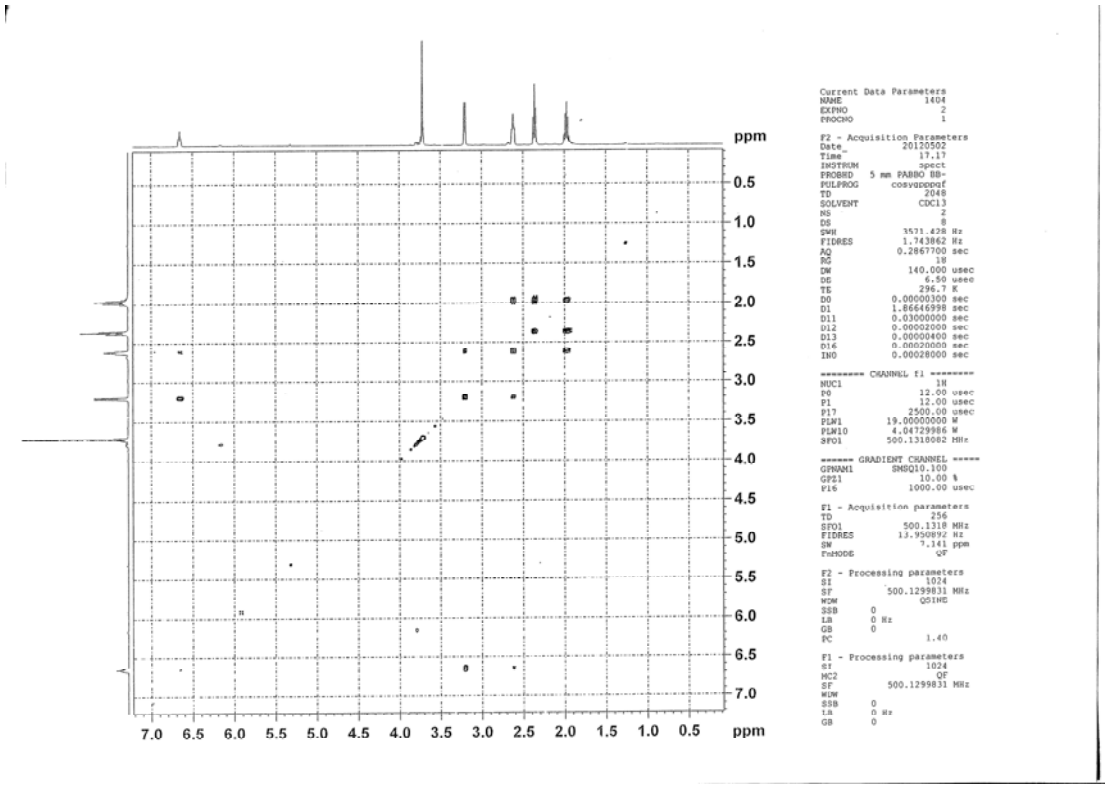
1. W. J. Yao, L. J. Pan, Y. H. Wu and C. Ma, *Org. Lett.* 2010, **12**, 2422.
2. W. J. Yao, Y. H. Wu, G. Wang, Y. P. Zhang and C. Ma, *Angew. Chem. Int. Ed.* 2009, **48**, 9713.
3. X. Q. Wang, W. J. Yao, Z. H. Yao and C. Ma, *J. Org. Chem*. 2012, **77**, 2959.
4. T. Mukaiyama, K. Banno and K. Narasak, *J. Am. Chem. Soc.* 1974, **96**, 7503.
5. S. D. Yang, L. Y. Wu, Z. Y. Yan, Z. L. Pan and Y. M. Liang, *Journal of Molecular Catalysis A: Chemical* 2007, **268**, 107.

^{1}H NMR and ^{13}C NMR spectra

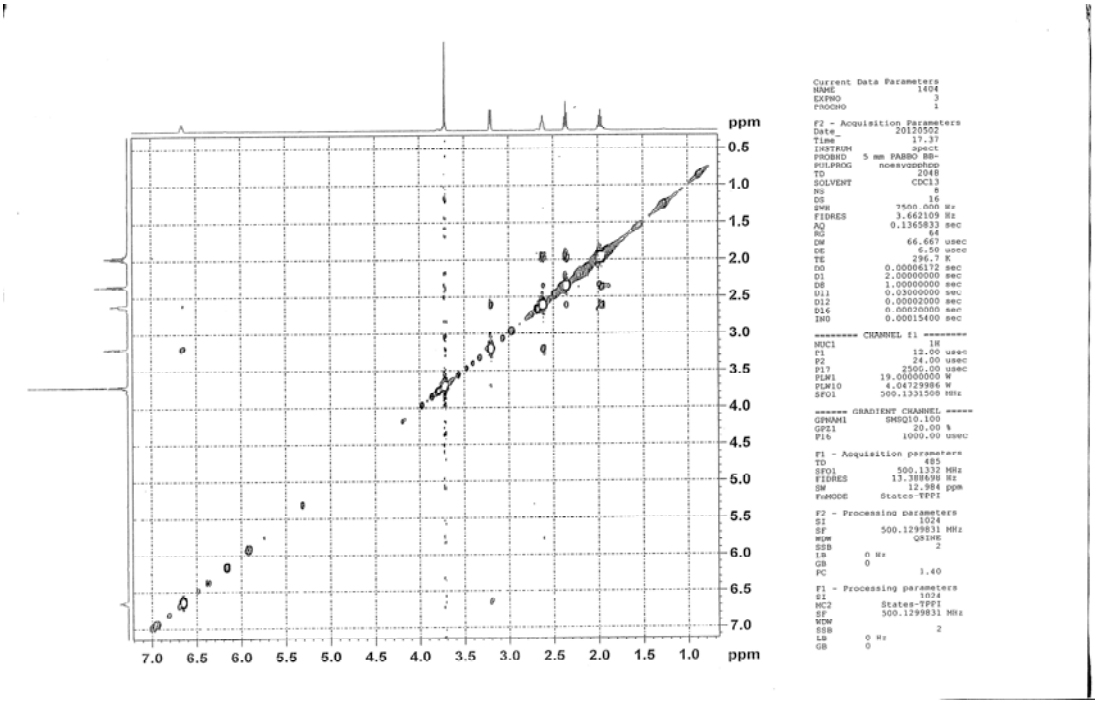
Methyl 3-(2-oxocyclopentylidene)propanoate (1a)



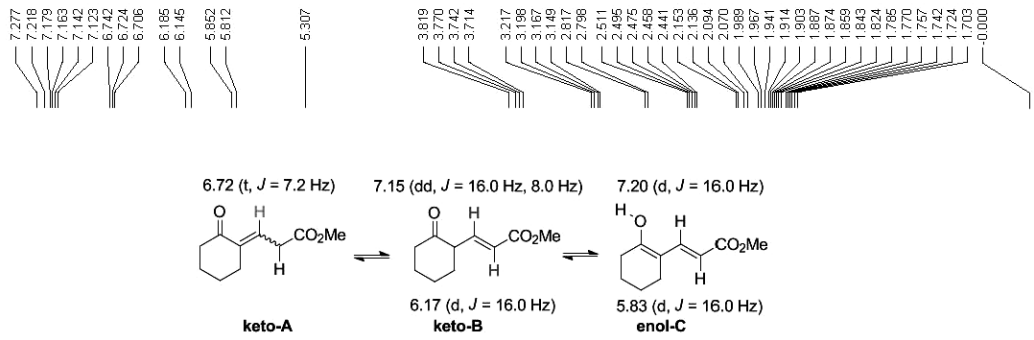
^{1}H-^{1}H COSY

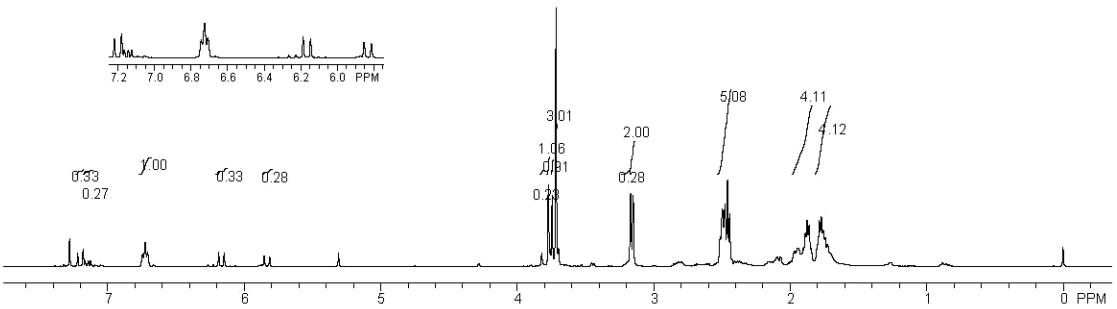


Methyl 3-(2-oxocyclopentylidene)propanoate (1a) ^{1}H-^{1}H NOESY

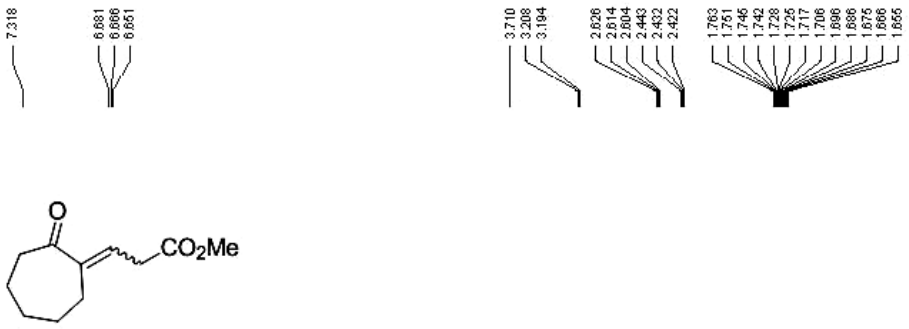


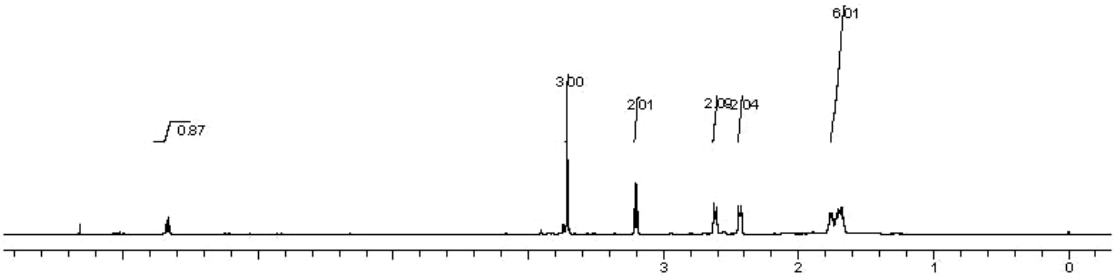
Methyl 3-(2-oxocyclohexylidene)propanoate (keto-A)

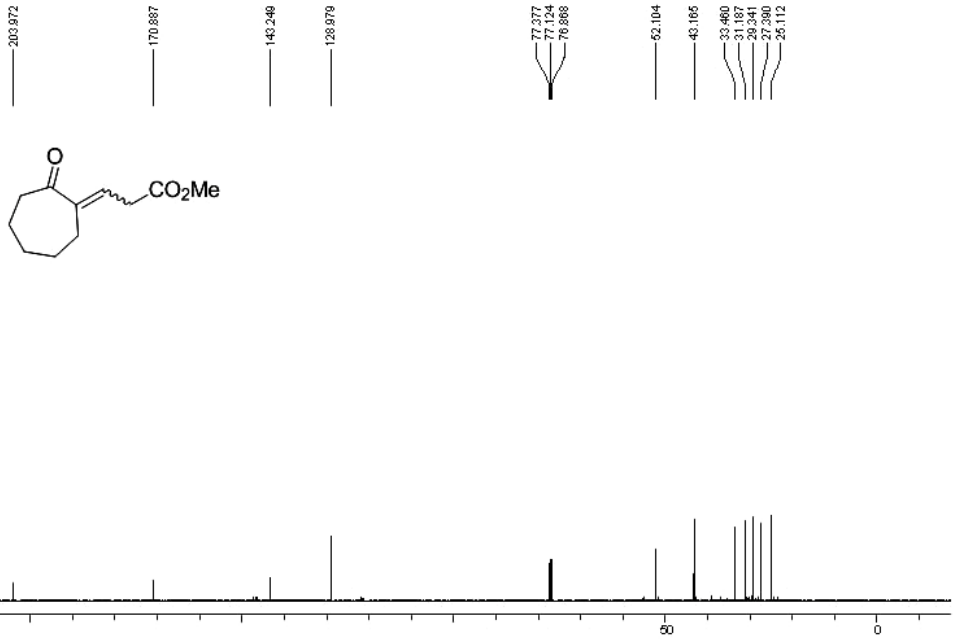




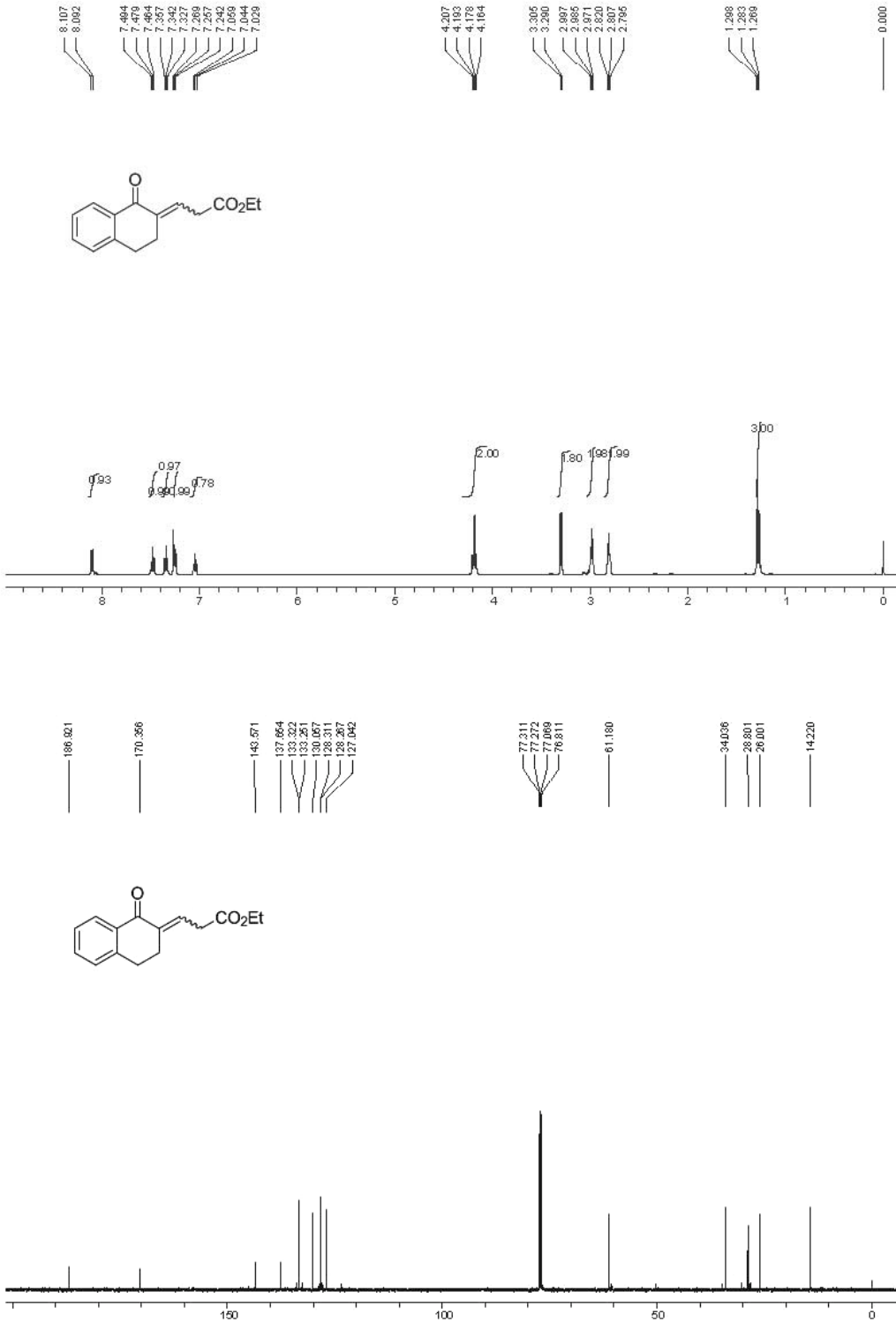
Methyl 3-(2-oxocycloheptylidene)propanoate



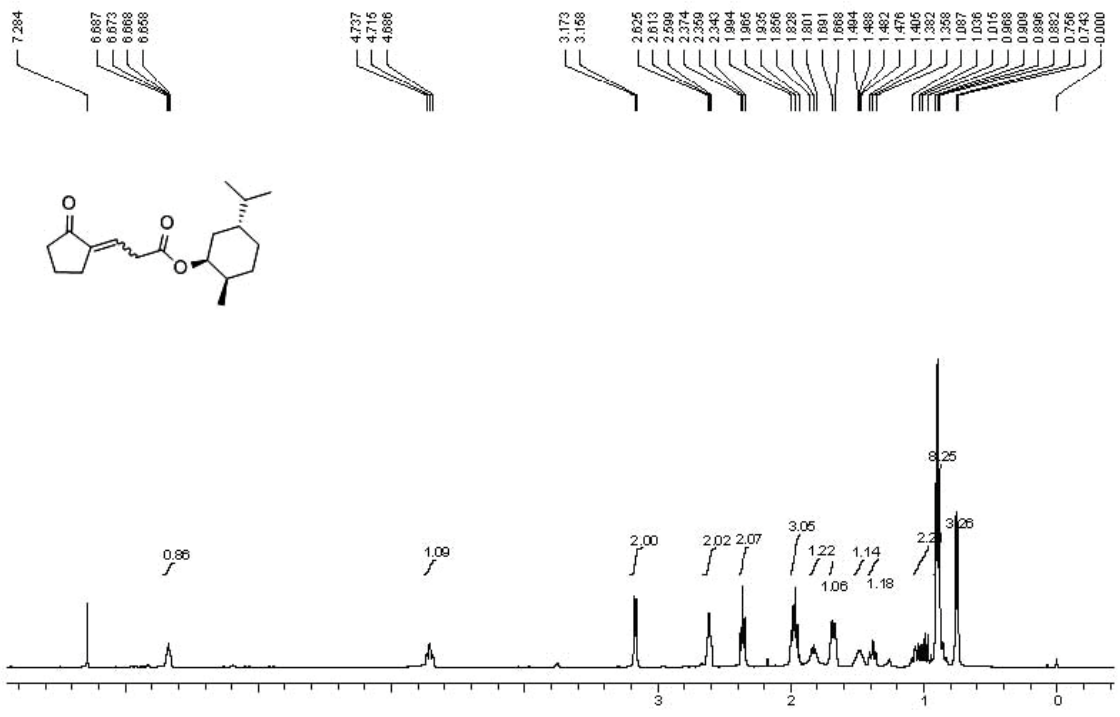


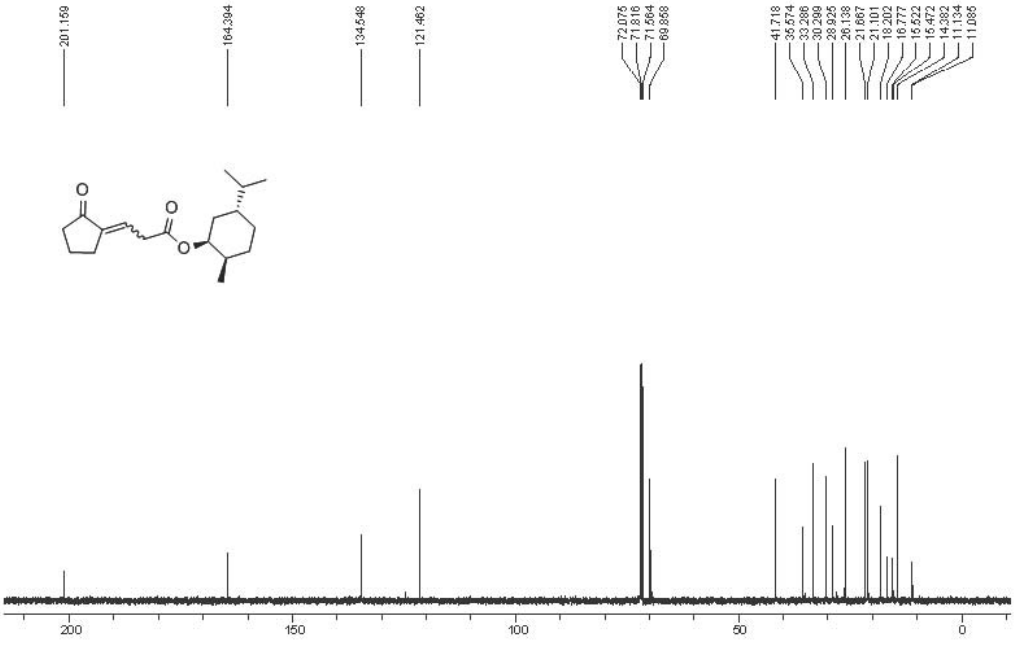


Ethyl 3-(1-oxo-3,4-dihydronaphthalen-2(1H)-ylidene)propanoate

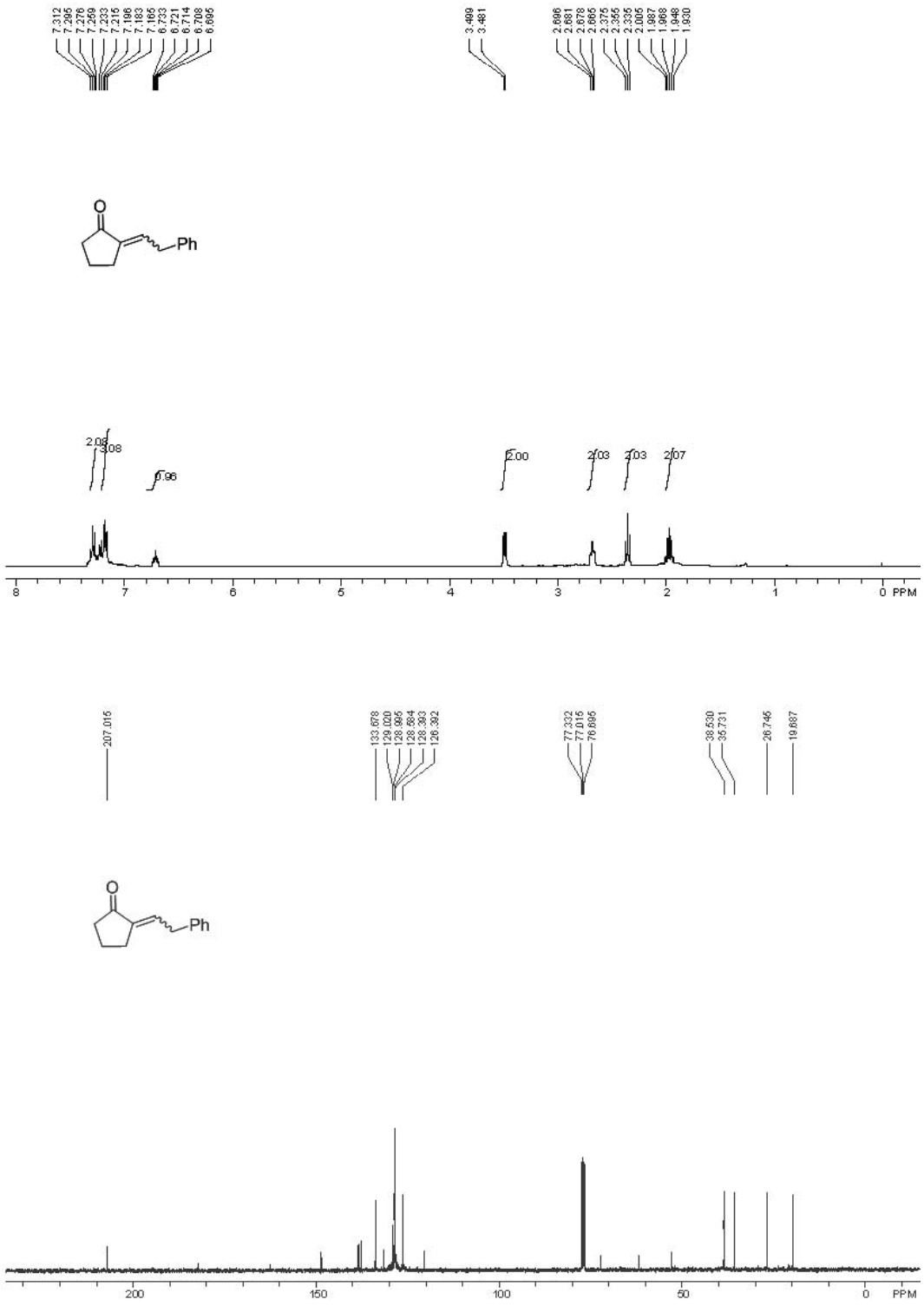


((1*S*,2*R*,5*R*)-5-isopropyl-2-methylcyclohexyl) 3-(2-oxocyclopentylidene)propanoate (5)

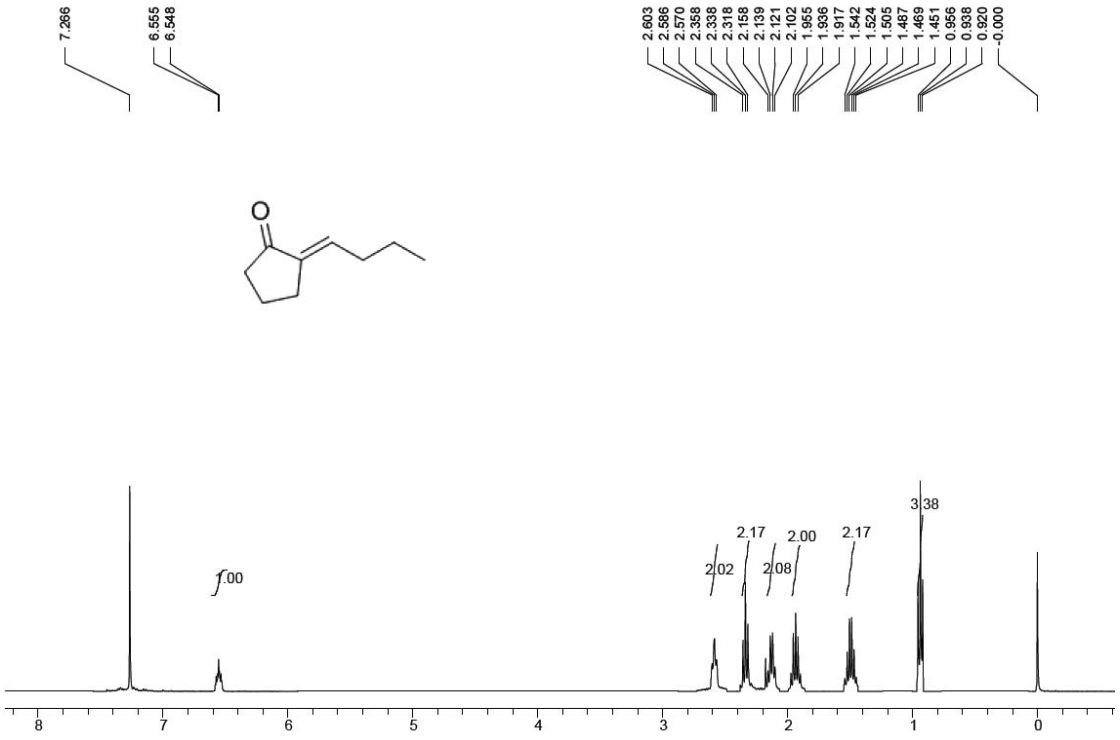




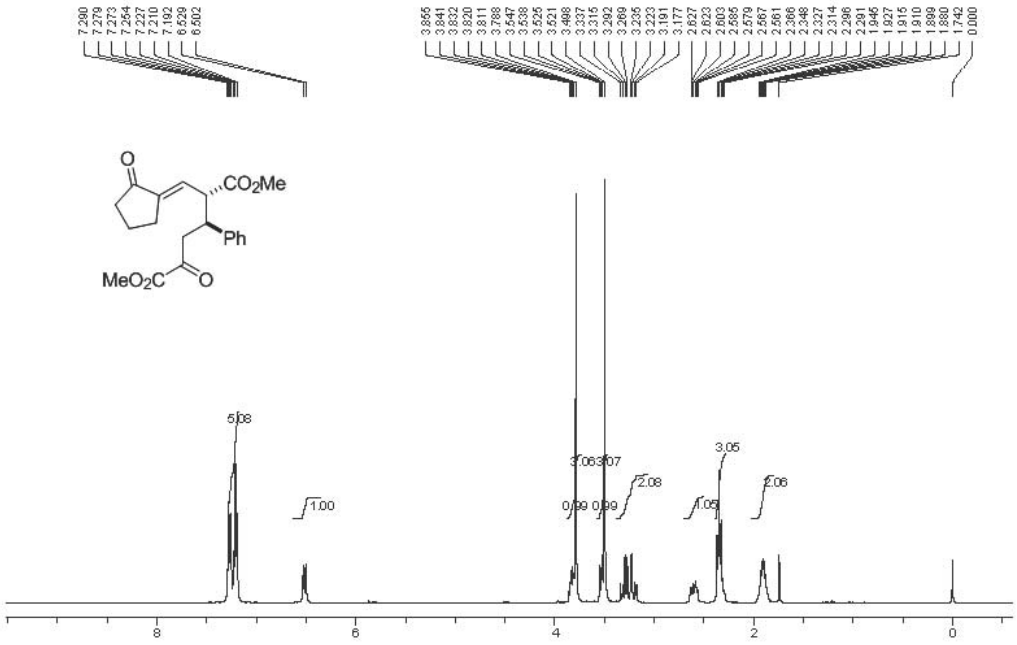
2-(2-Phenylethylidene)cyclopentanone (**9**)

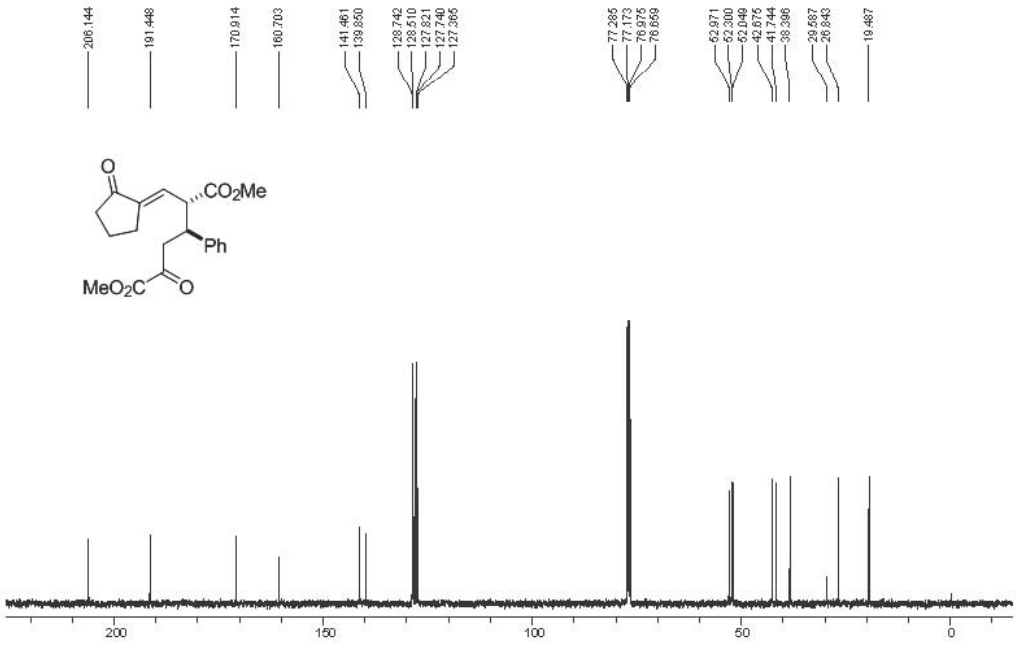


2-Butylidenecyclopentanone (10)

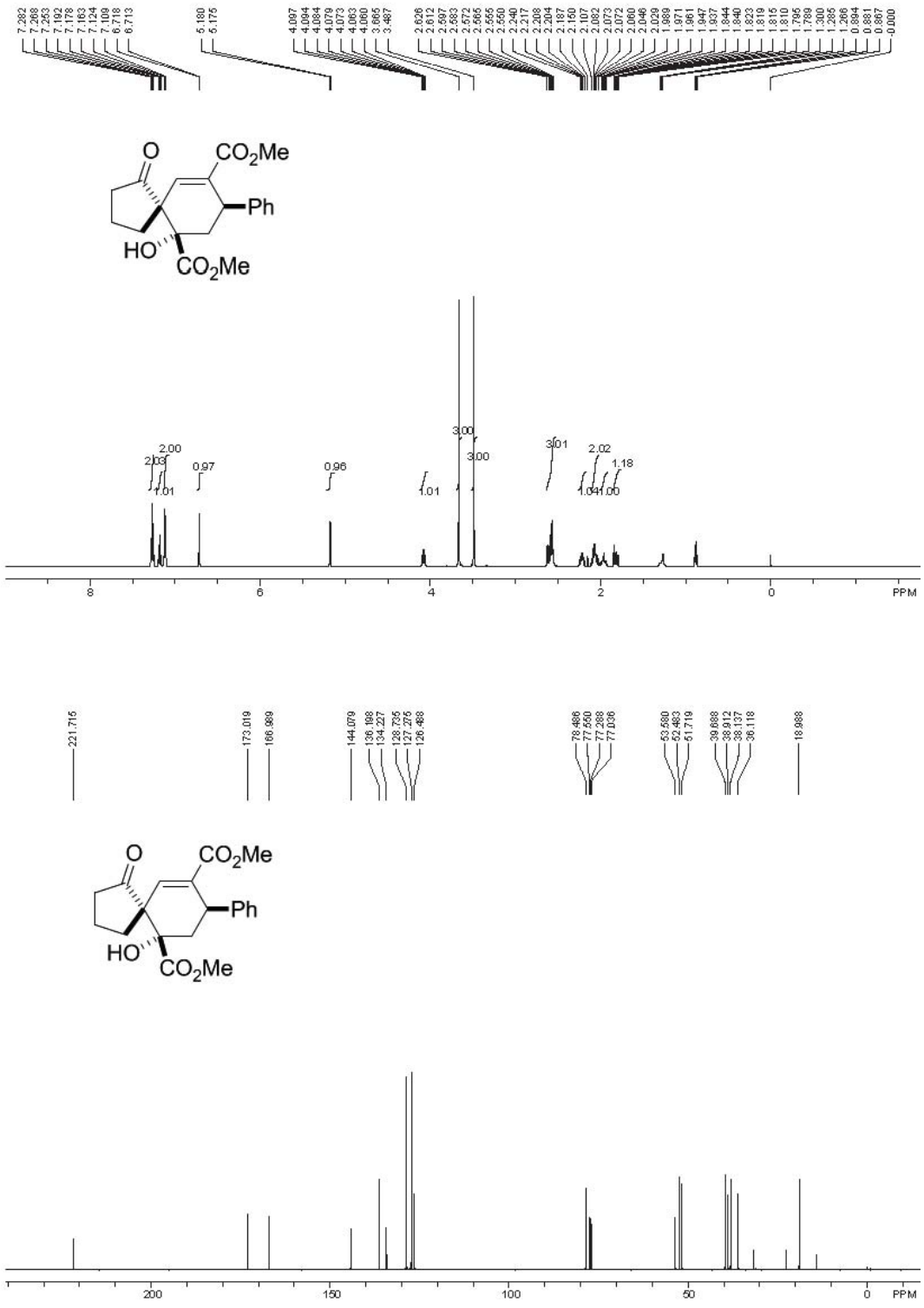


Dimethyl 5-oxo-2-((2-oxocyclopentylidene)methyl)-3-phenylhexanedioate (3a)

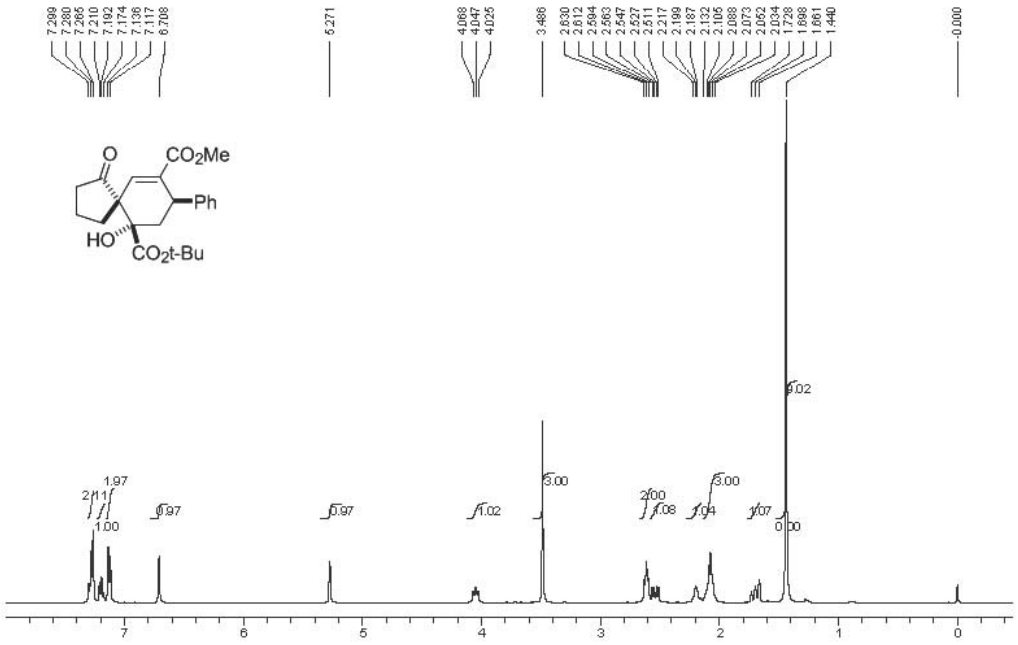


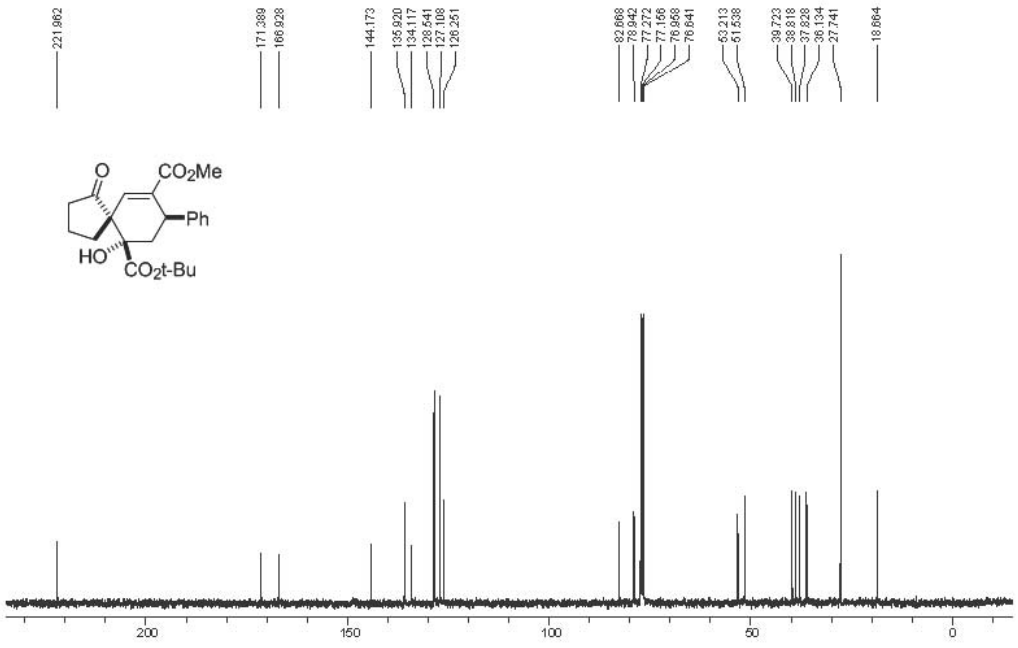


Dimethyl 6-hydroxy-1-oxo-8-phenylspiro[4.5]dec-9-ene-6,9-dicarboxylate (4a)

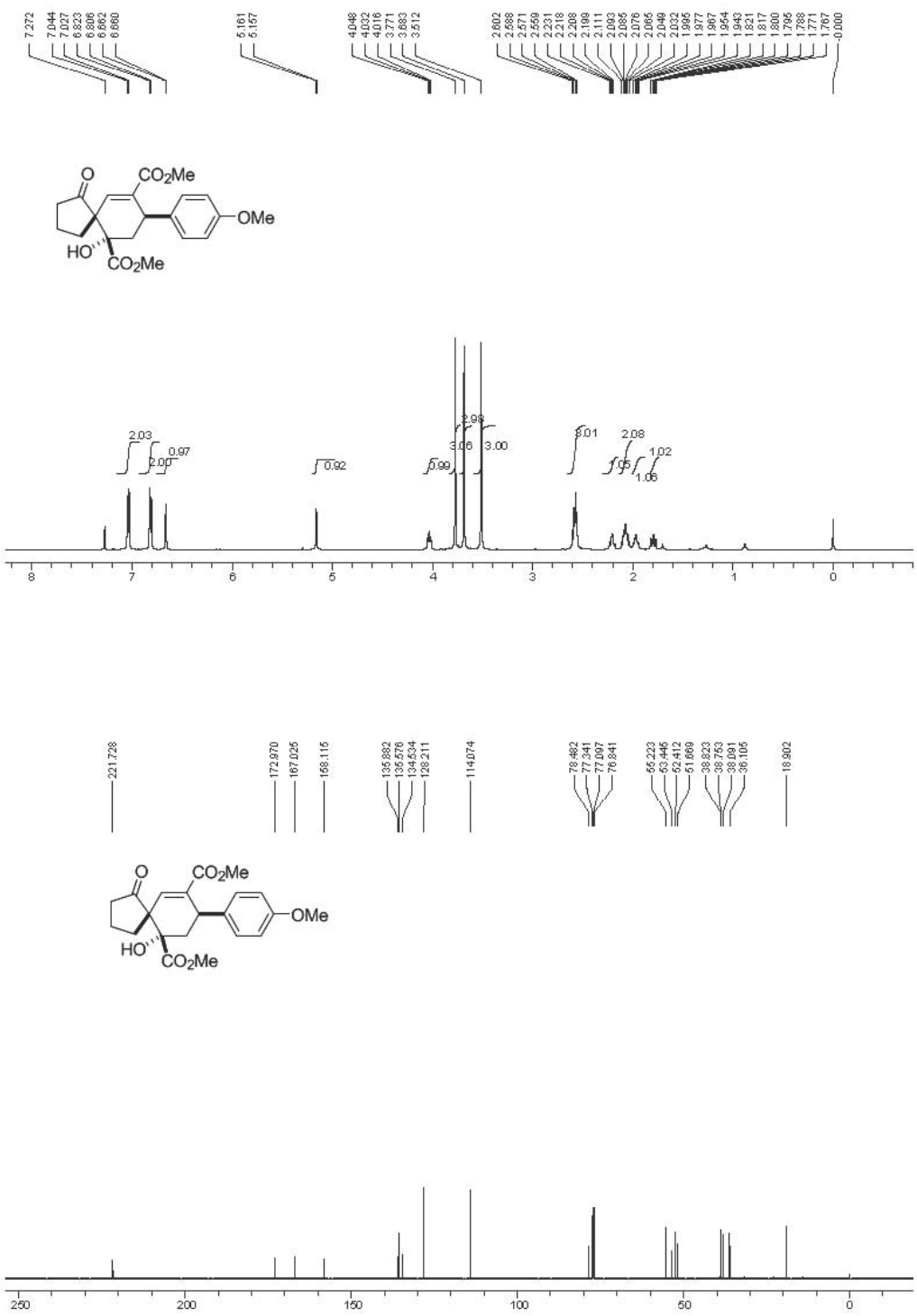


6-*tert*-Butyl 9-methyl 6-hydroxy-1-oxo-8-phenylspiro[4.5]dec-9-ene-6,9-dicarboxylate (4b)

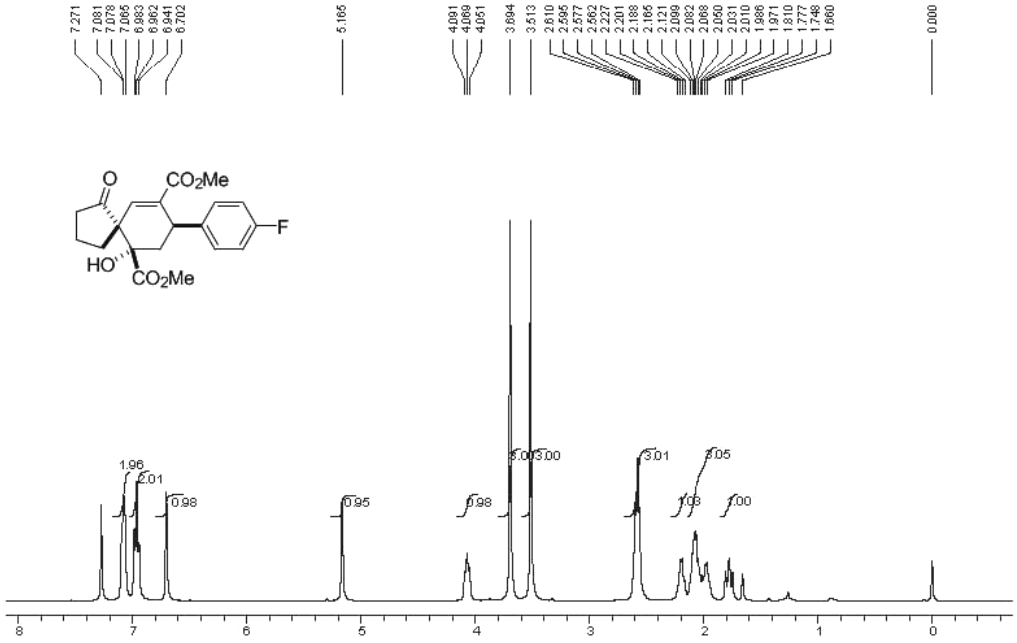


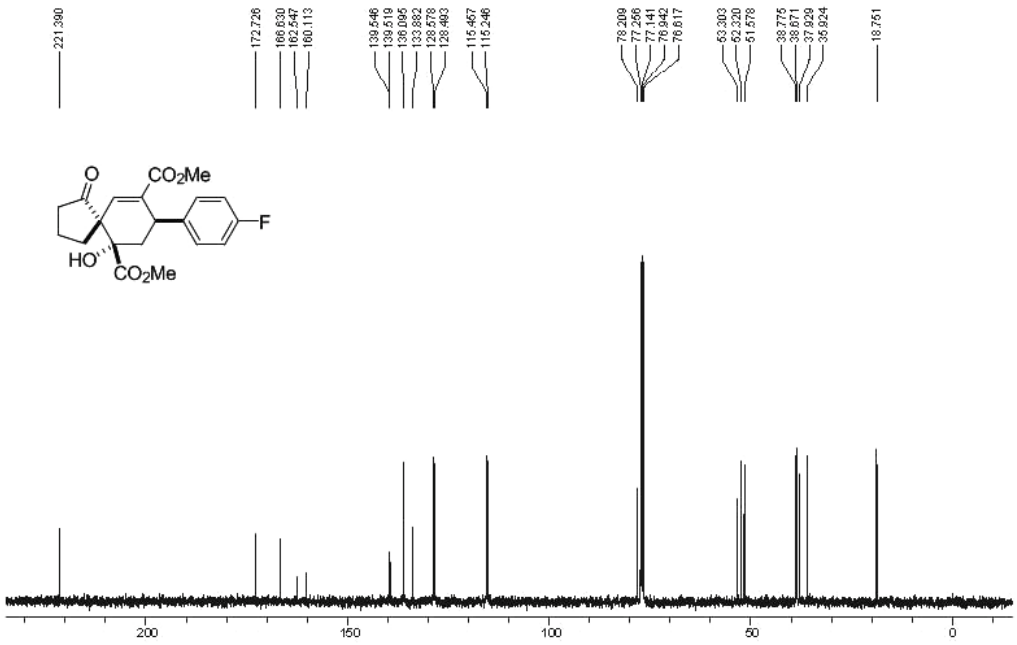


Dimethyl 6-hydroxy-8-(4-methoxyphenyl)-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (4c)

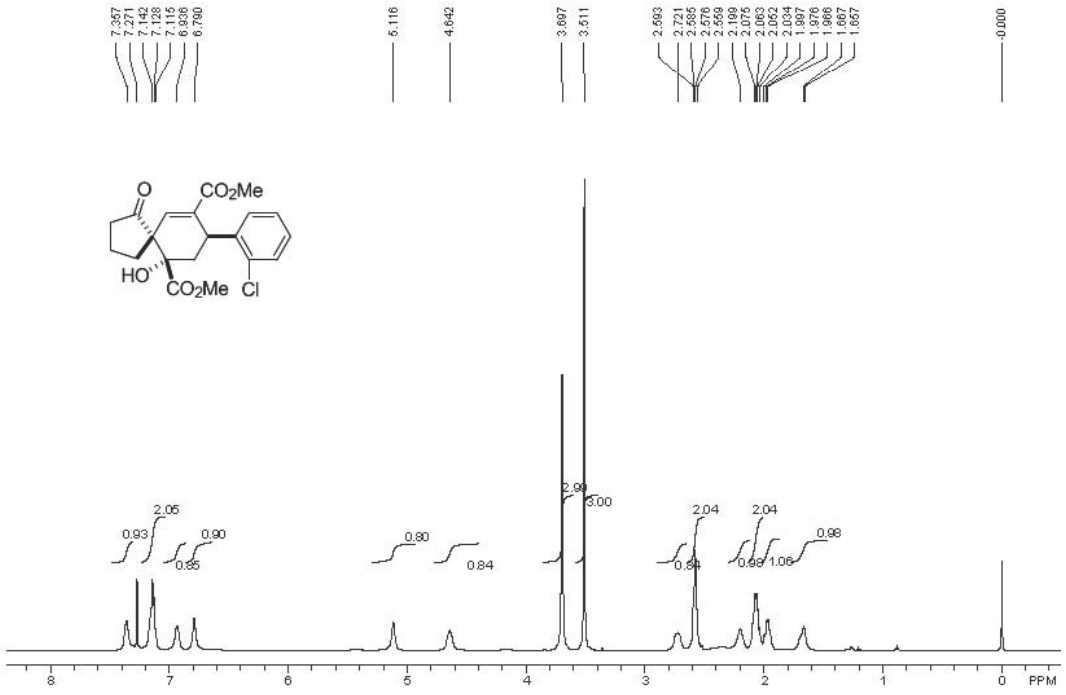


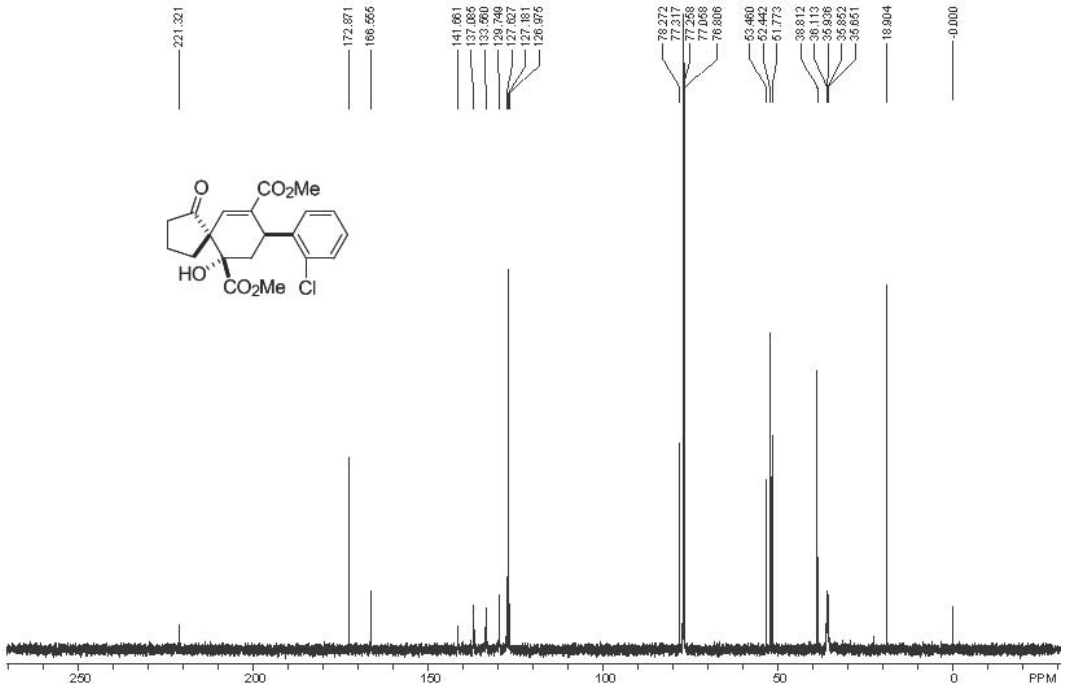
Dimethyl 8-(4-fluorophenyl)-6-hydroxy-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (4d)



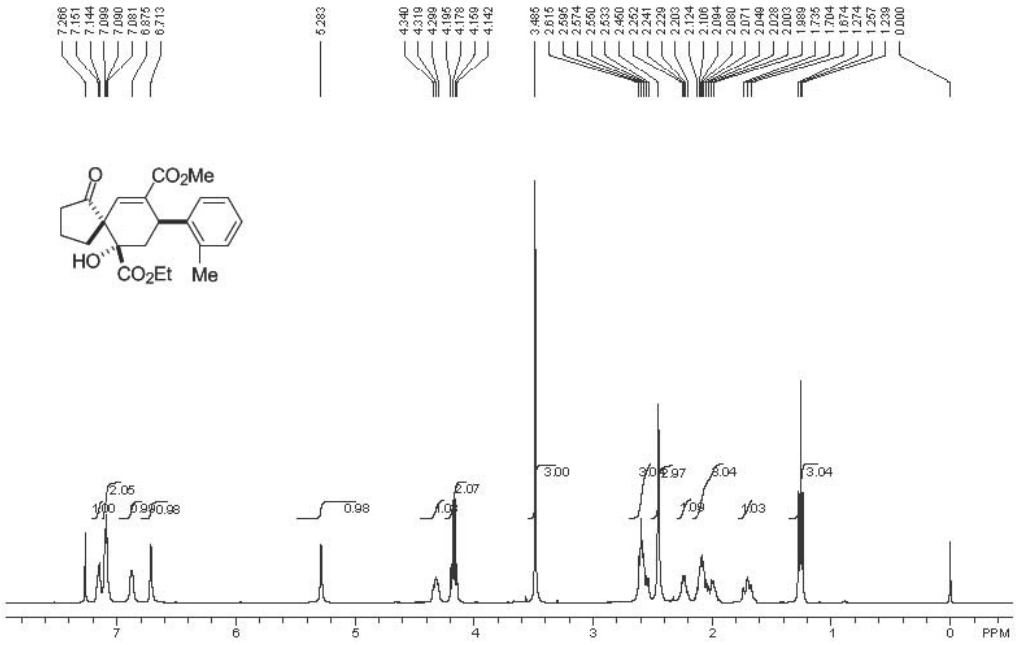


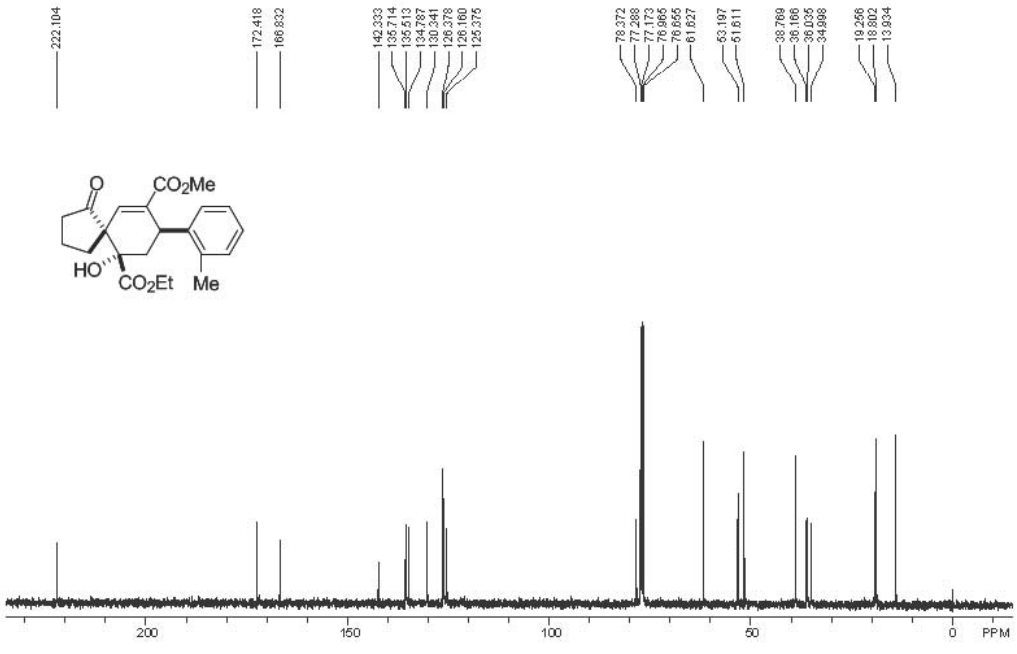
Dimethyl 8-(2-chlorophenyl)-6-hydroxy-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (4e)



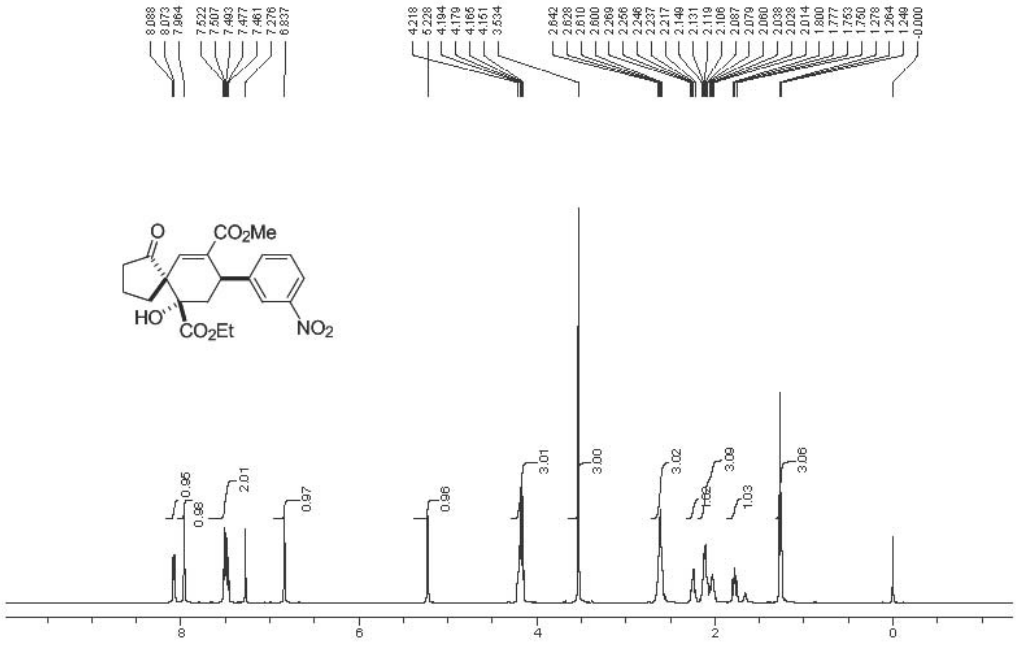


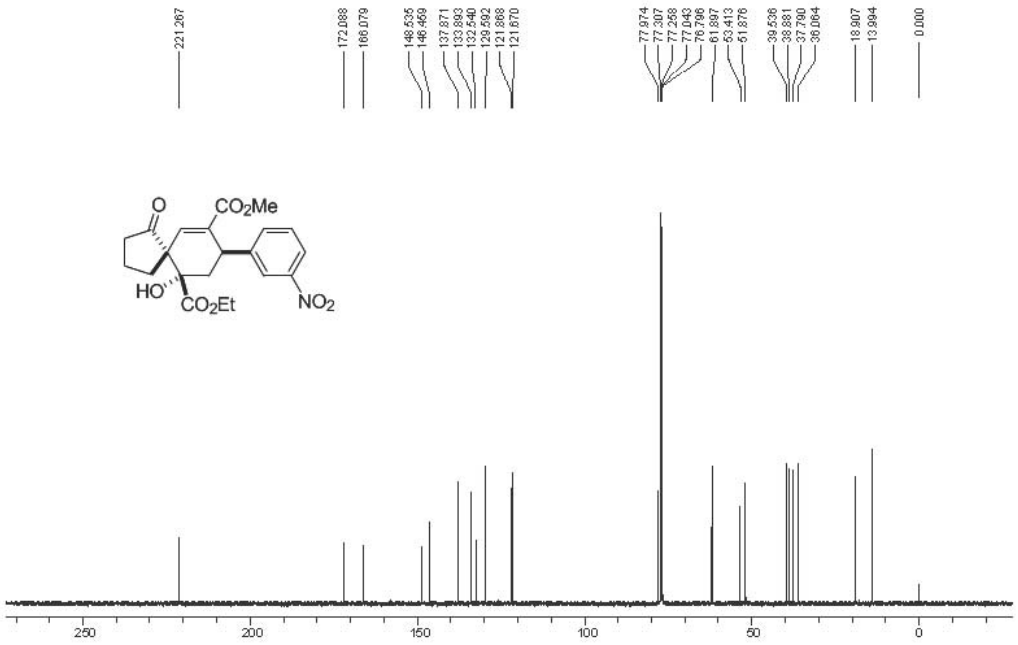
6-Ethyl 9-methyl 6-hydroxy-1-oxo-8-o-tolylspiro[4.5]dec-9-ene-6,9-dicarboxylate (4f)



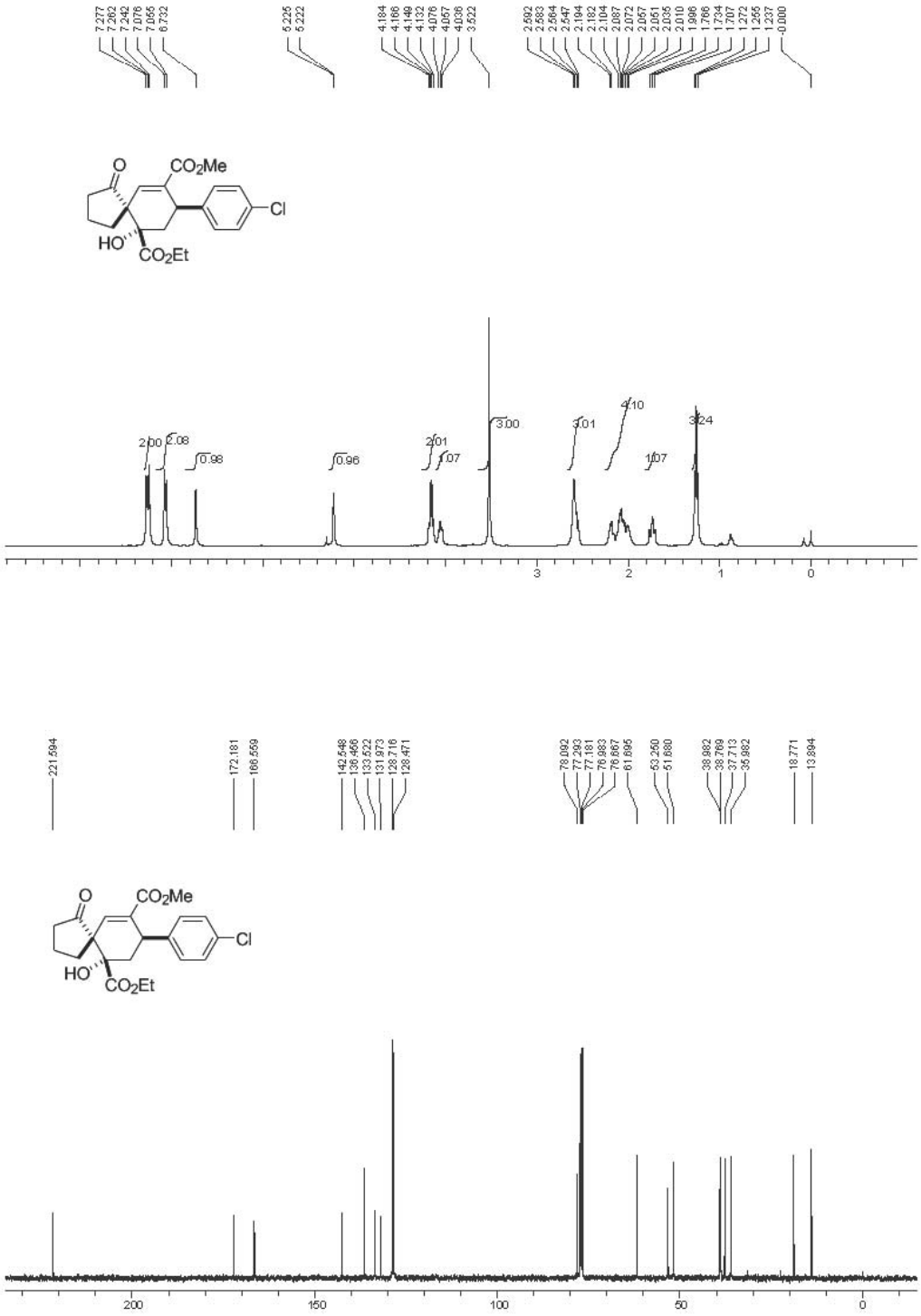


6-Ethyl 9-methyl 6-hydroxy-8-(3-nitrophenyl)-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (4g)

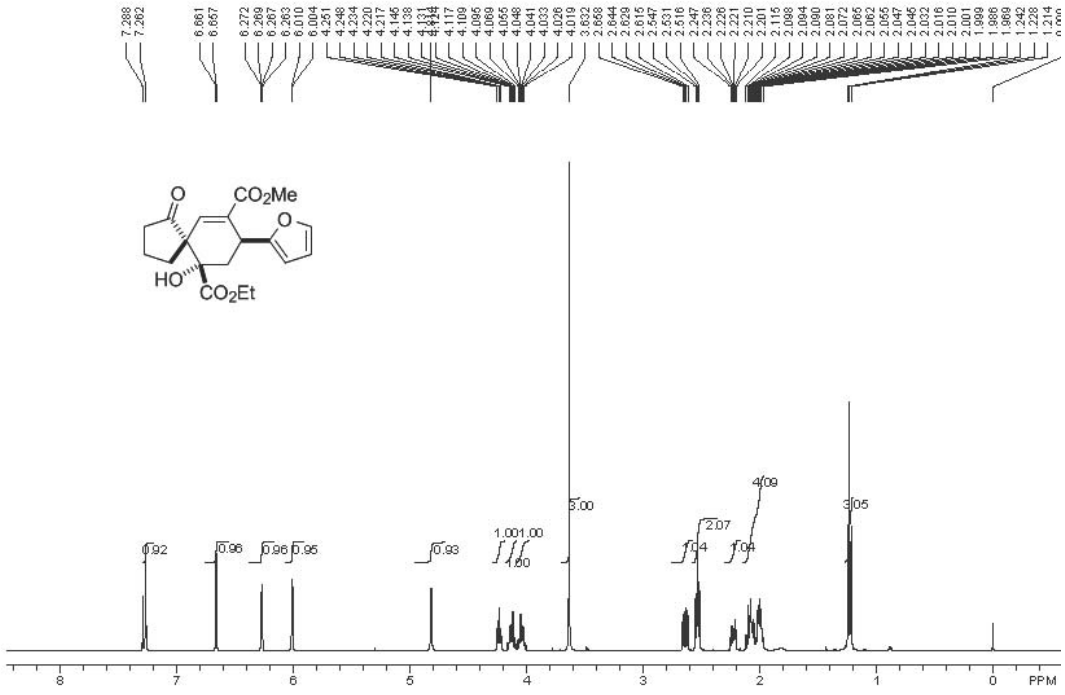


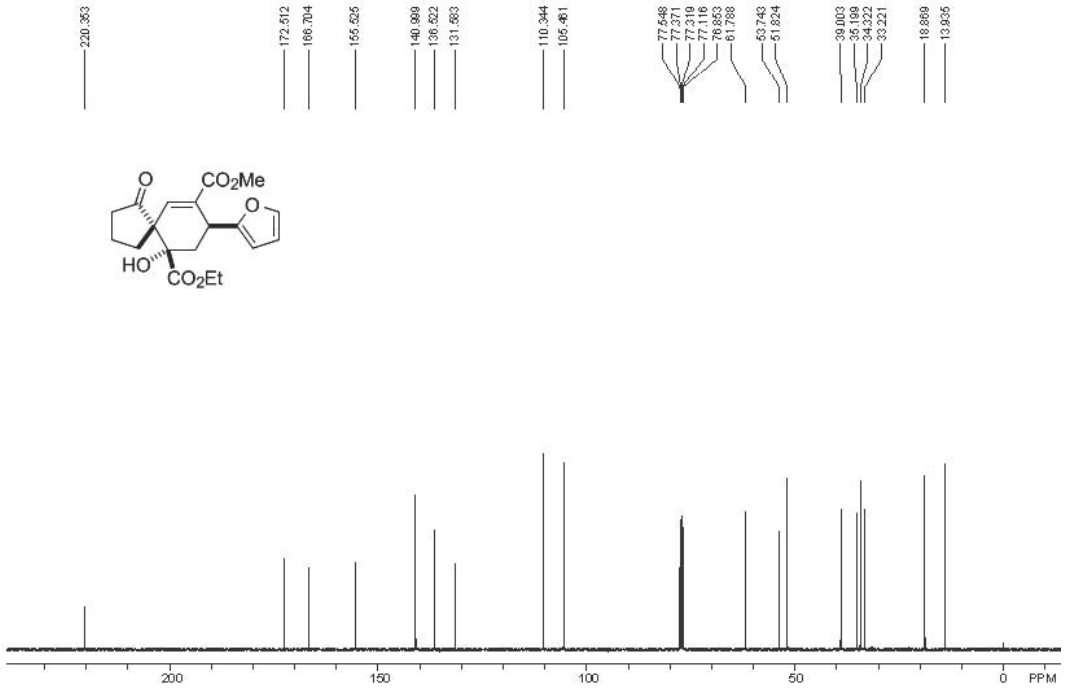


6-Ethyl 9-methyl 8-(4-chlorophenyl)-6-hydroxy-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (4h)

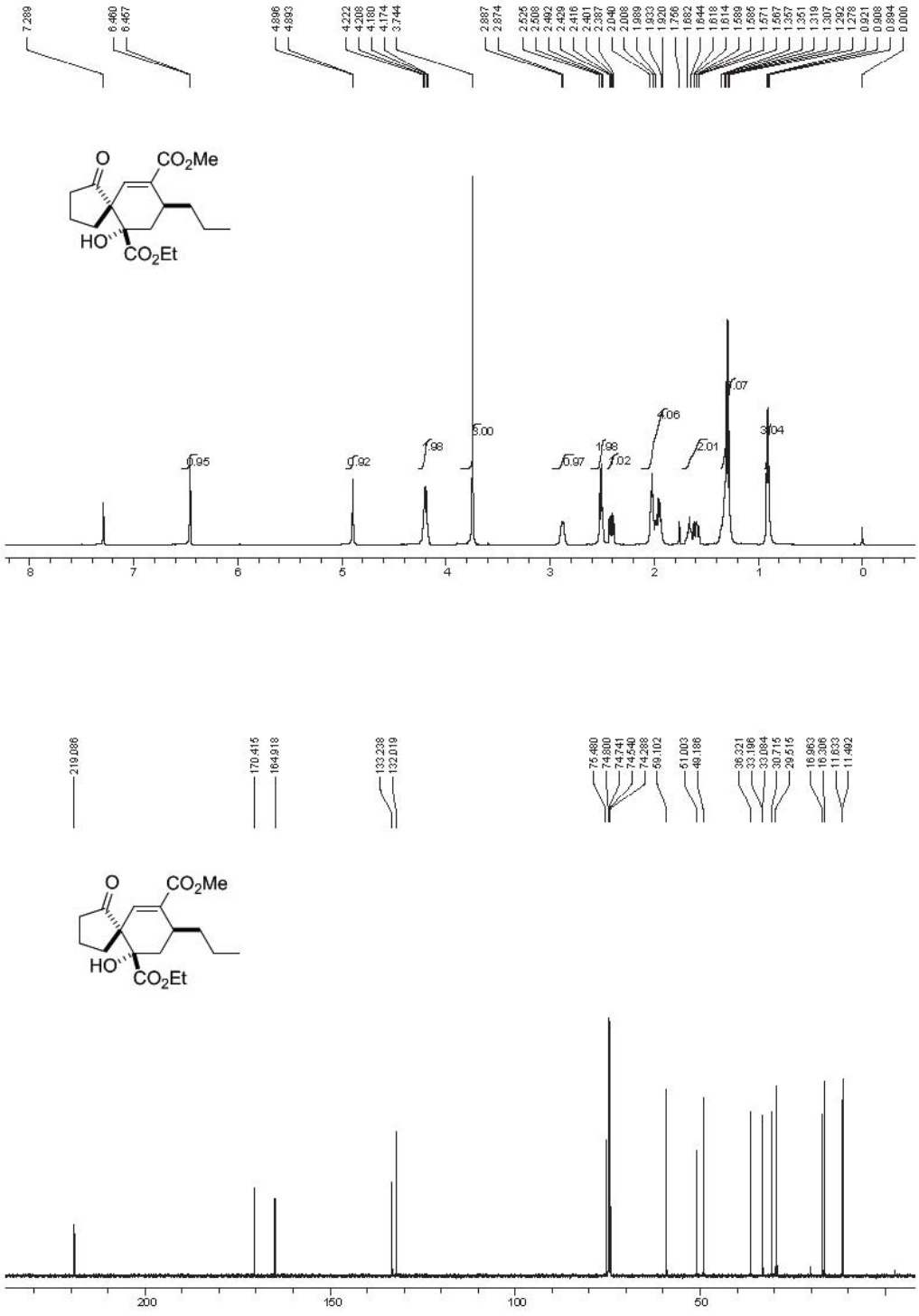


6-Ethyl 9-methyl 8-(furan-2-yl)-6-hydroxy-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (4i)

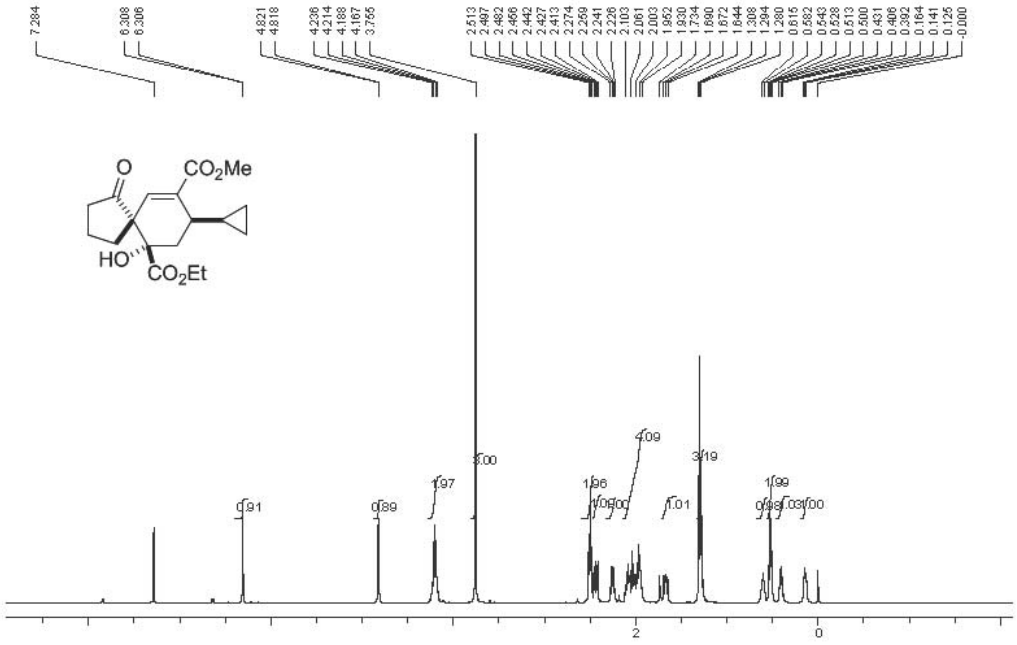


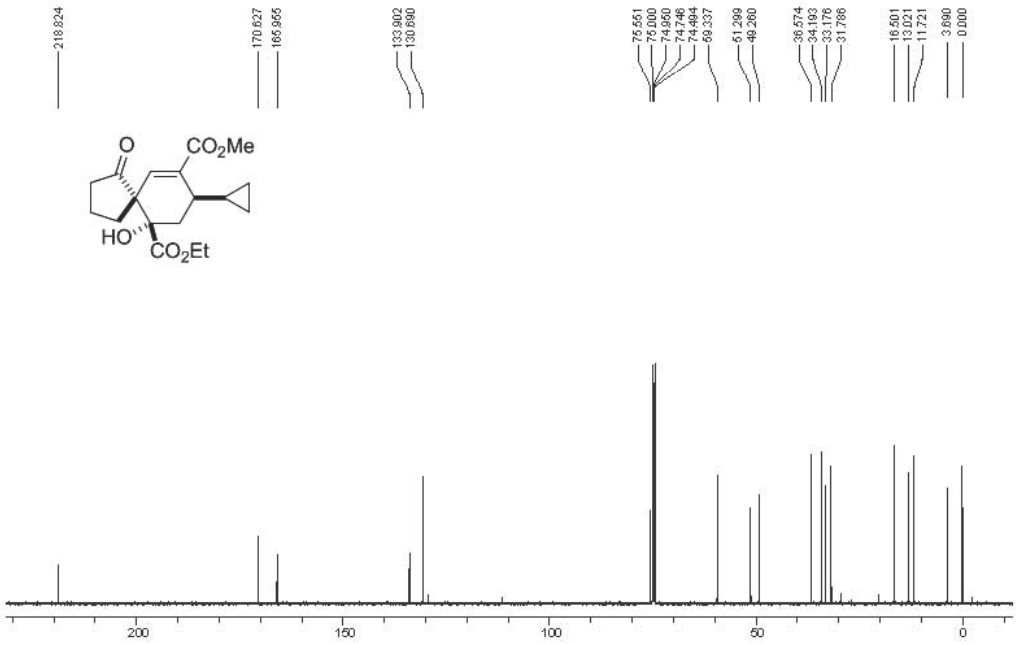


6-Ethyl 9-methyl 6-hydroxy-1-oxo-8-propylspiro[4.5]dec-9-ene-6,9-dicarboxylate (4j)

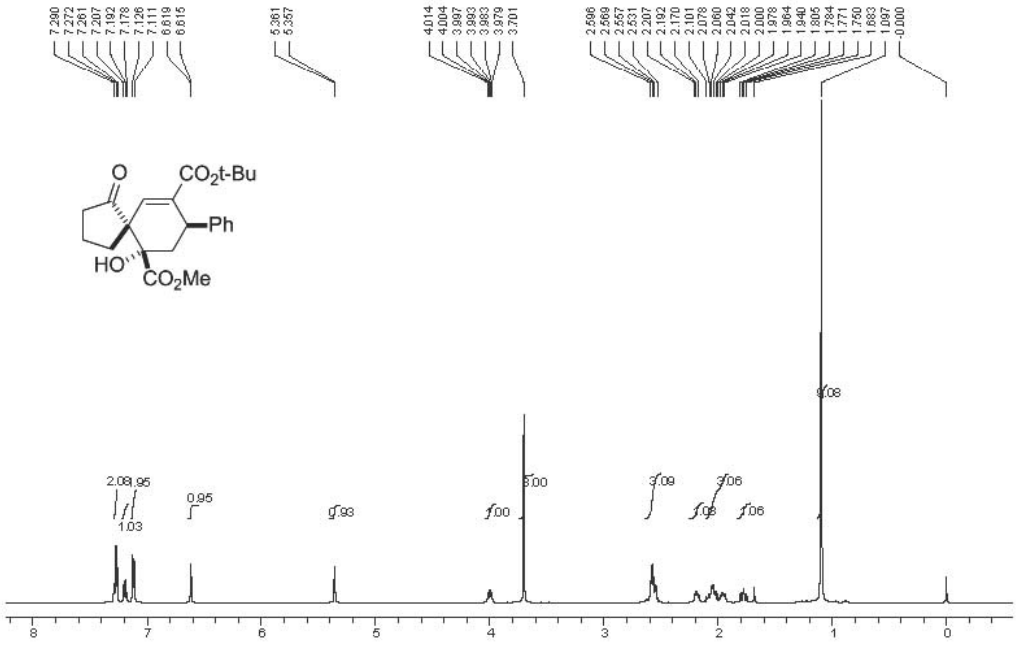


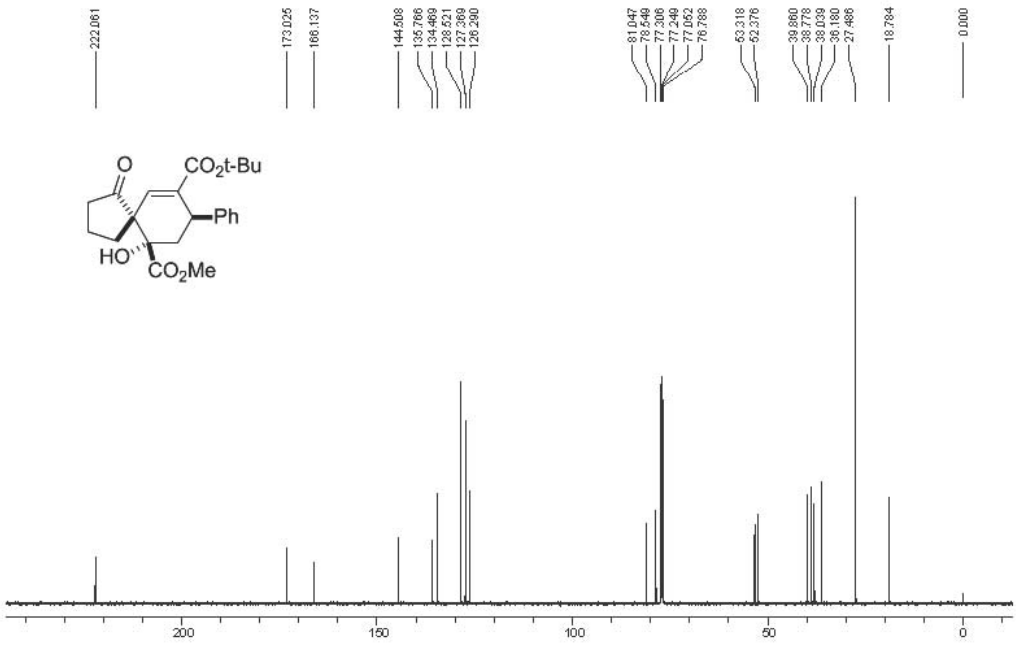
6-Ethyl 9-methyl 8-cyclopropyl-6-hydroxy-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (4k)



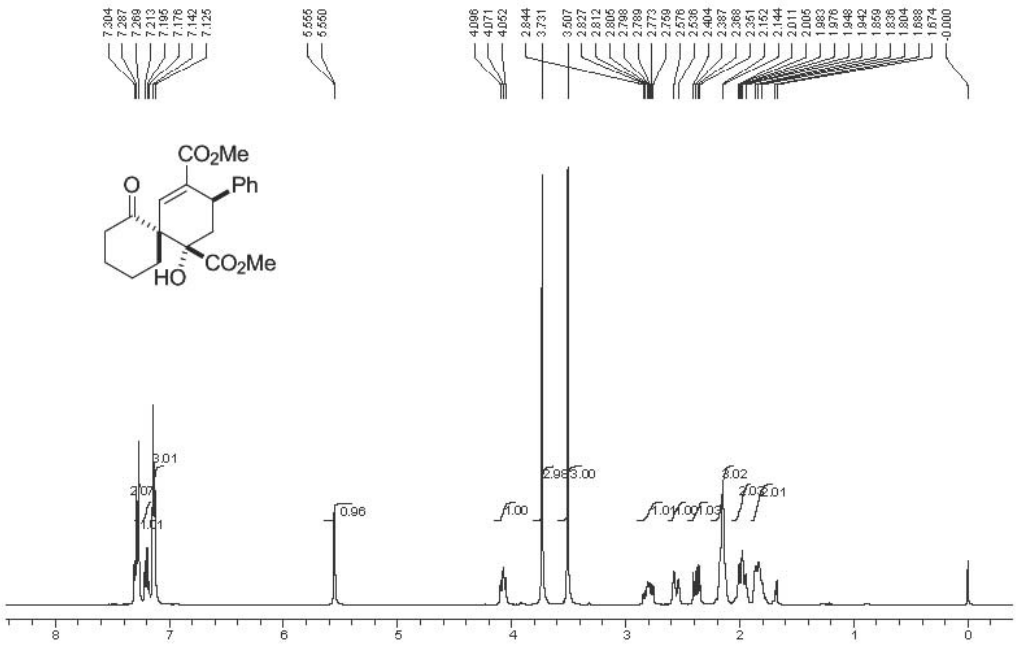


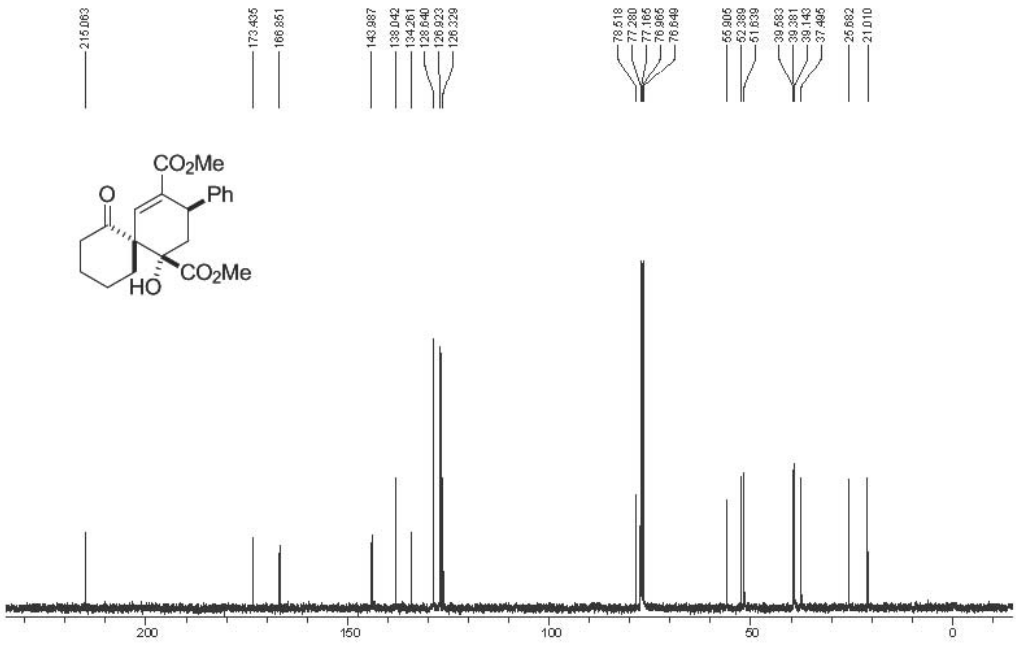
9-*tert*-Butyl 6-methyl 6-hydroxy-1-oxo-8-phenylspiro[4.5]dec-9-ene-6,9-dicarboxylate (4l)



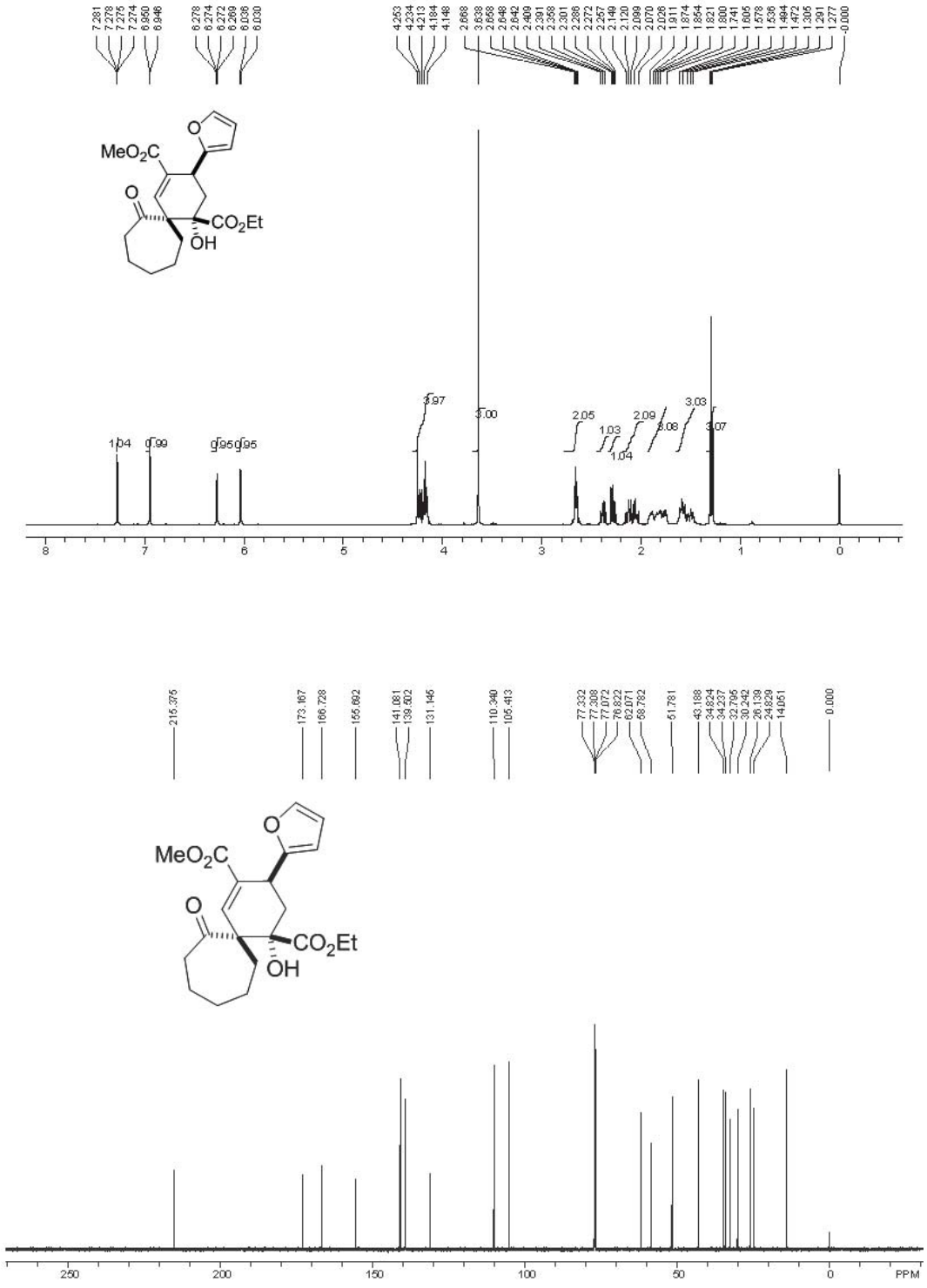


Dimethyl 1-hydroxy-7-oxo-3-phenylspiro[5.5]undec-4-ene-1,4-dicarboxylate (4m)

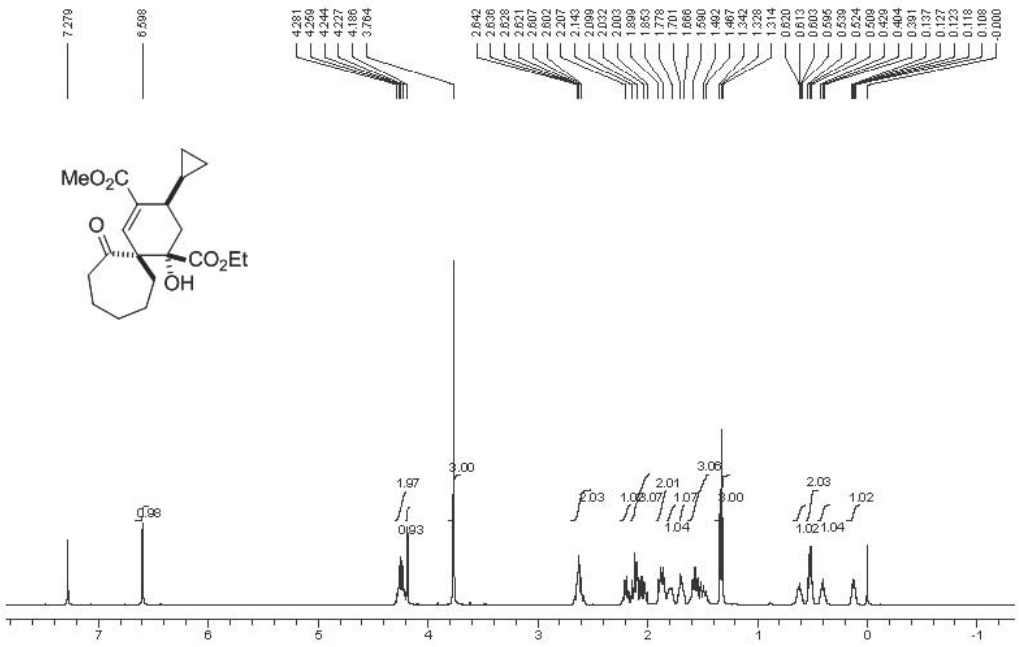


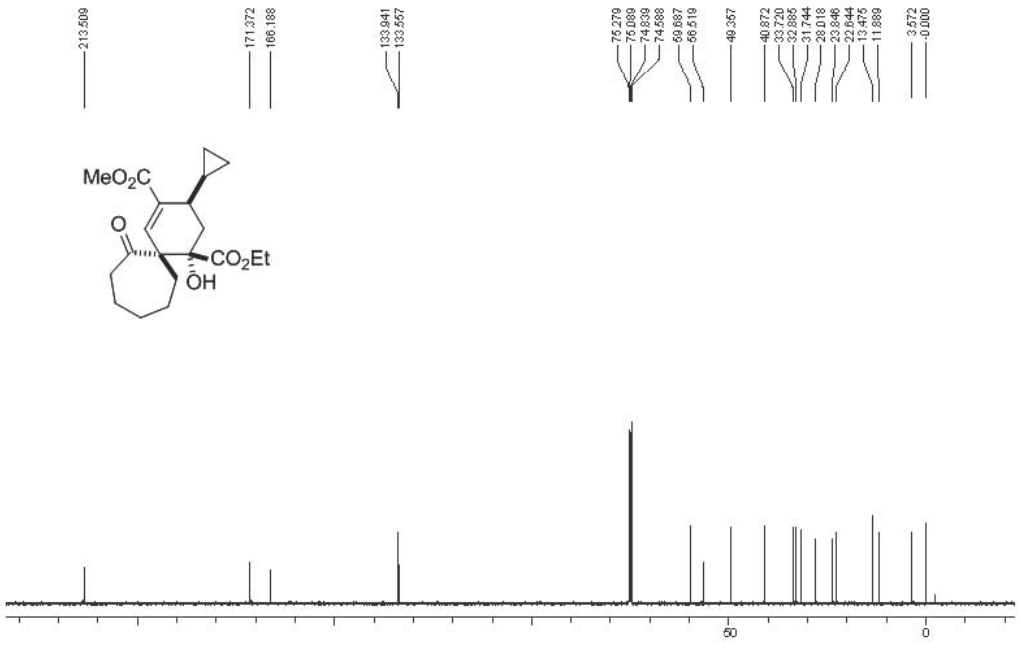


1-Ethyl 4-methyl 3-(furan-2-yl)-1-hydroxy-7-oxospiro[5.6]dodec-4-ene-1,4-dicarboxylate (4n)

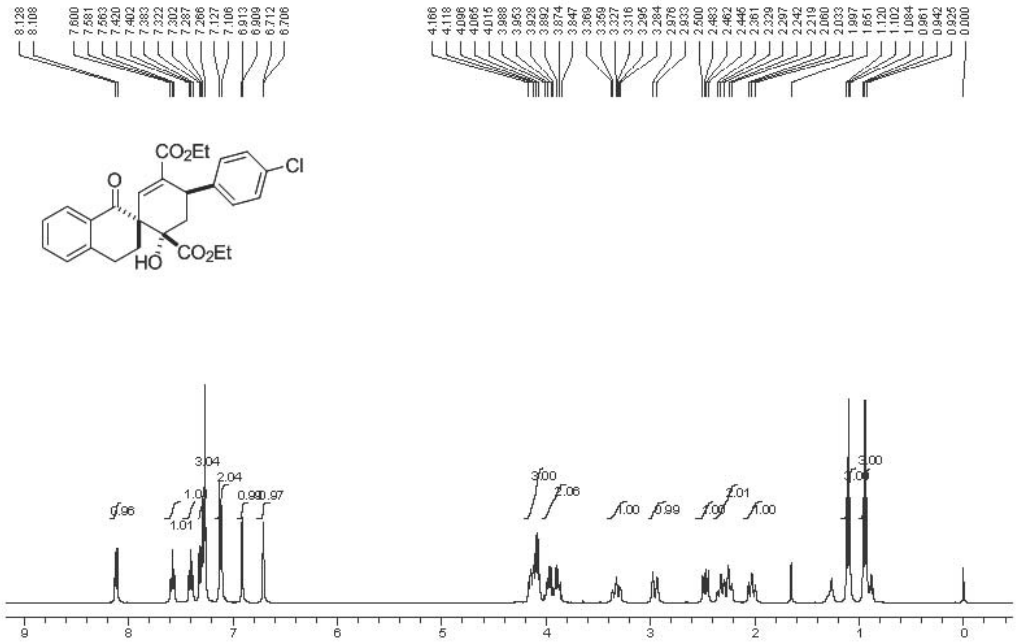


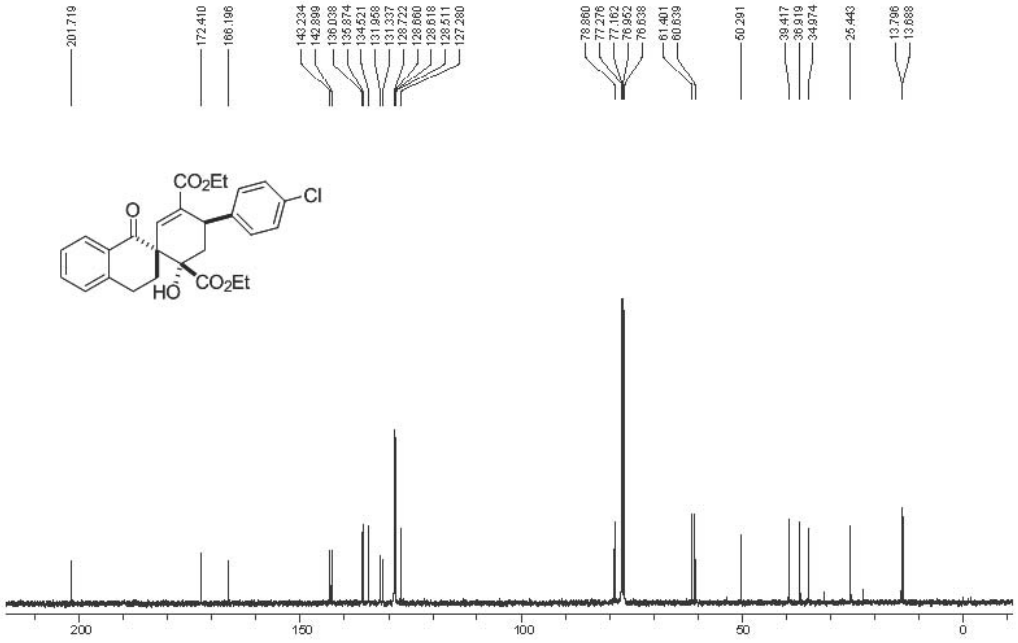
Ethyl 4-methyl 3-cyclopropyl-1-hydroxy-7-oxospiro[5.6]dodec-4-ene-1,4-dicarboxylate (4o)



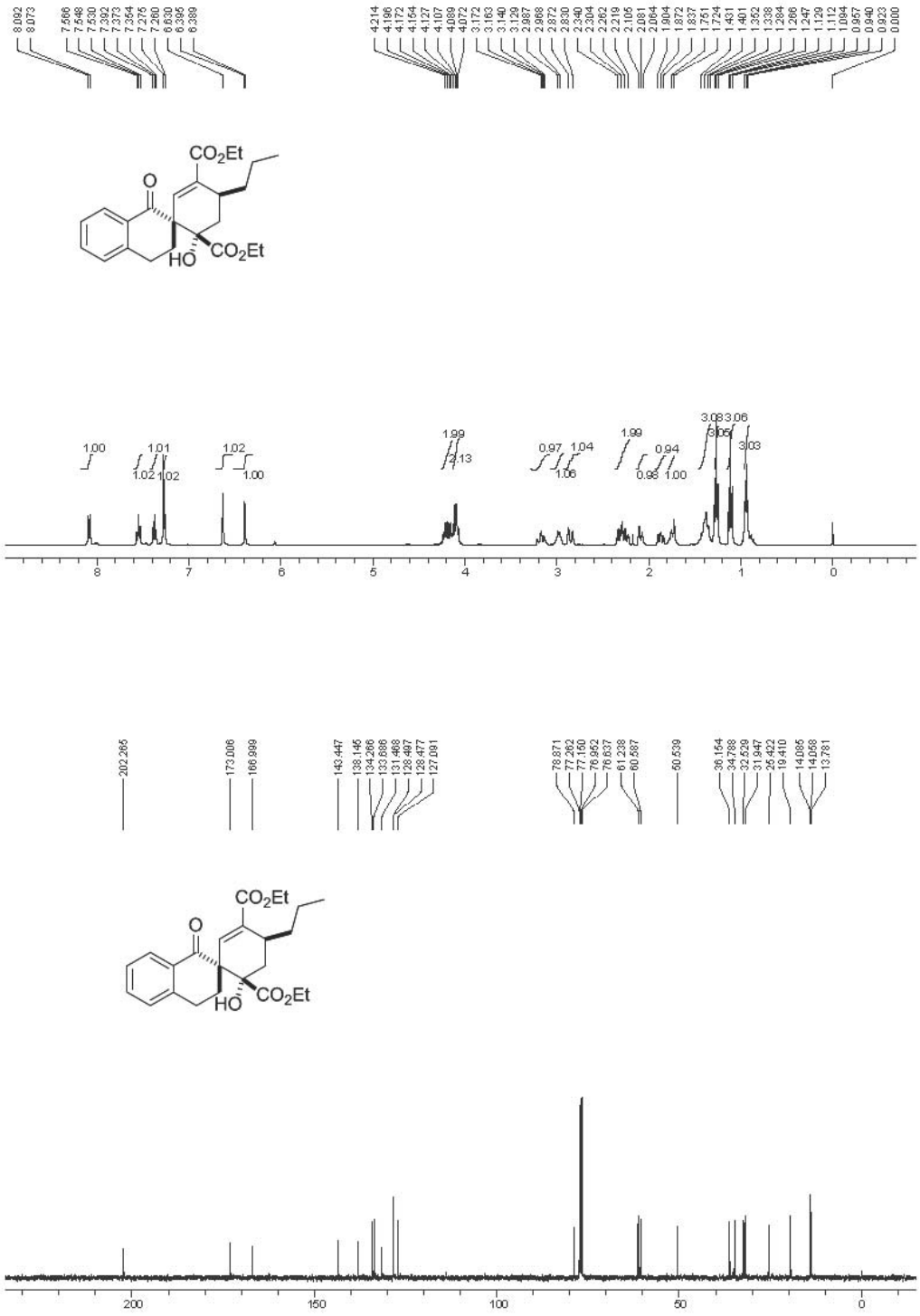


Diethyl 4-(4-chlorophenyl)-6-hydroxy-1'-oxo-3',4'-dihydro-1'H-spiro[cyclohex[2]ene-1,2'-naphthalene]-3,6-dicarboxylate (4p)

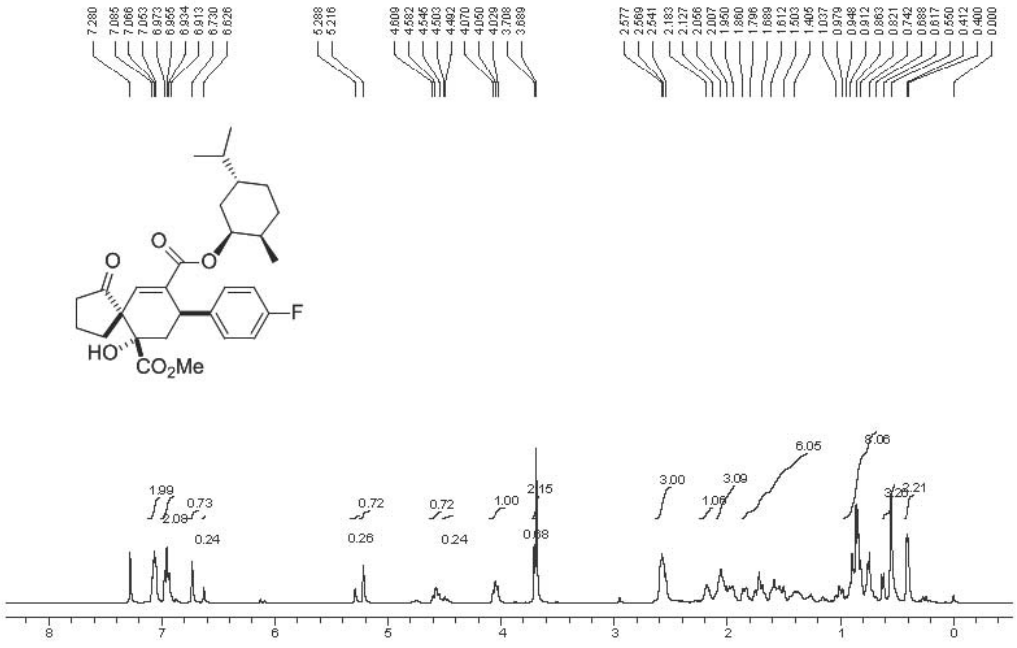


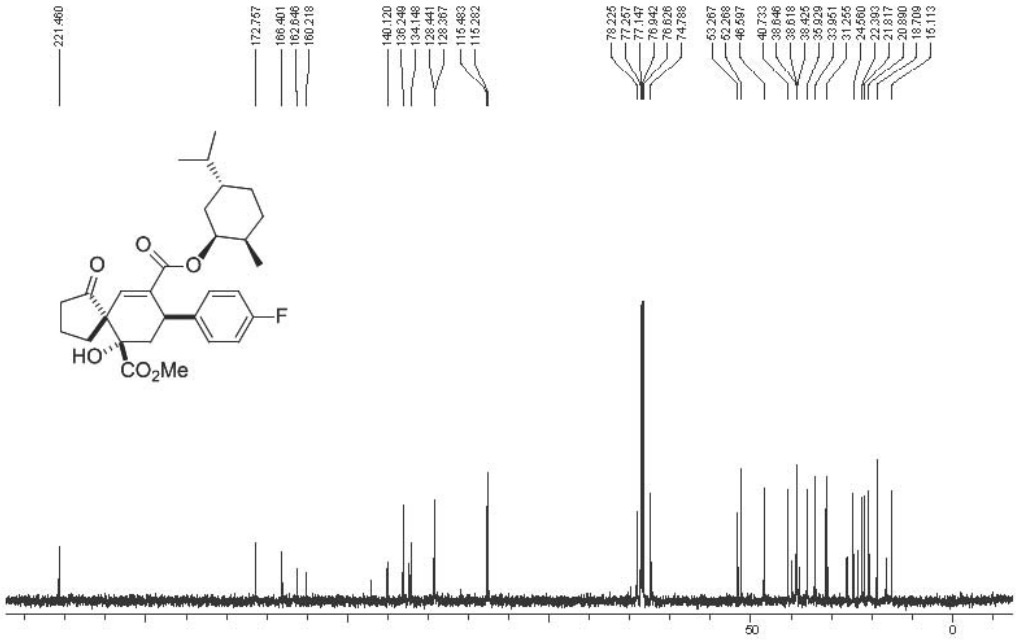


Diethyl 6-hydroxy-1'-oxo-4-propyl-3',4'-dihydro-1'H-spiro[cyclohex[2]ene-1,2'-naphthalene]-3,6-Dicarboxylate (4q)

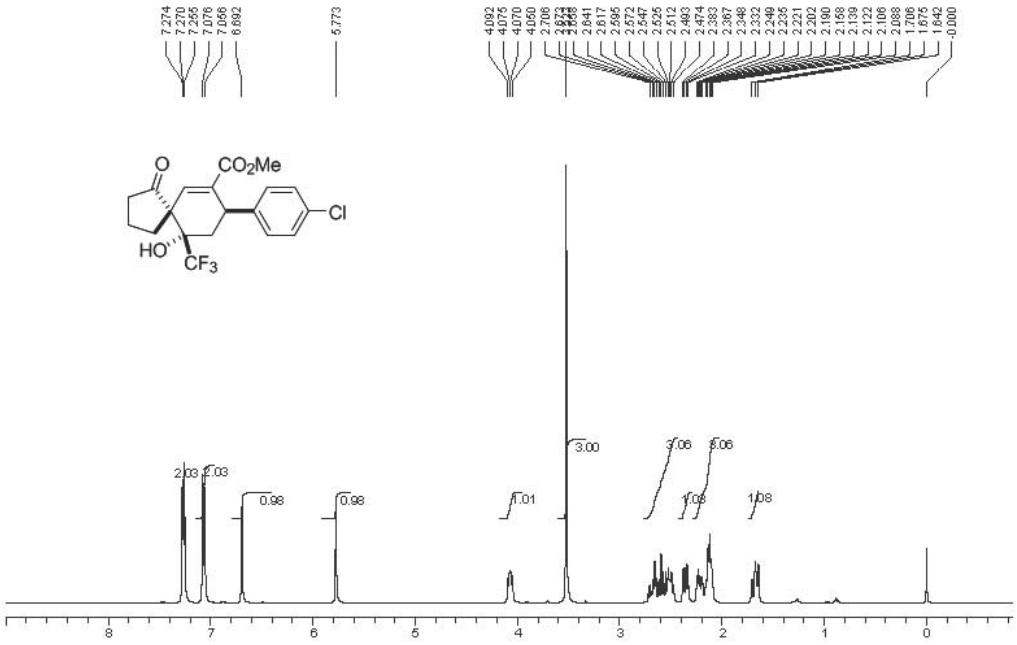


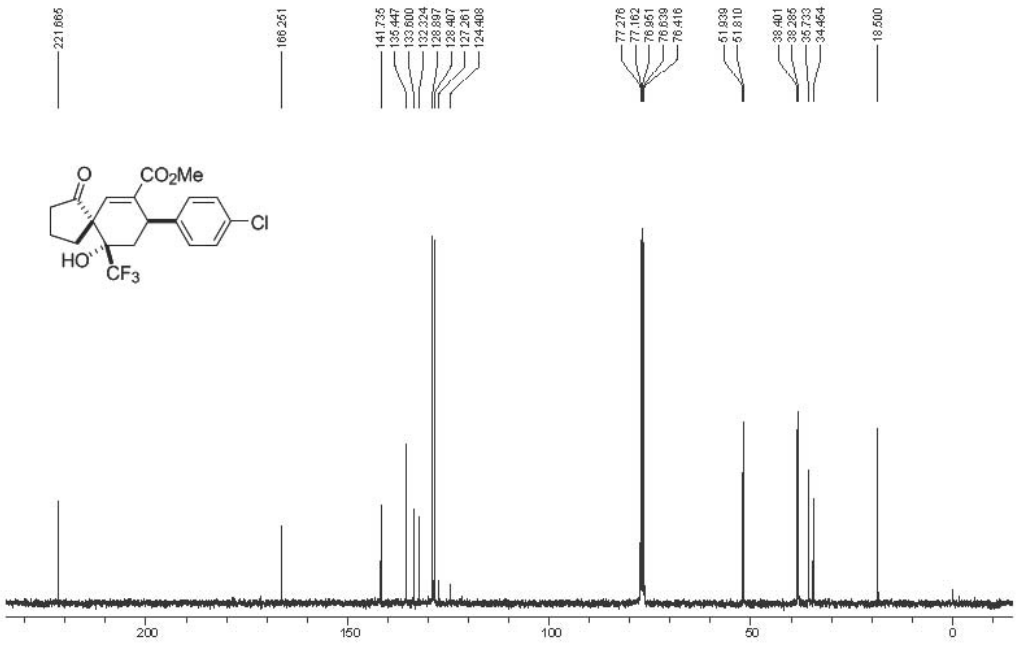
9-((1S,2R,5R)-5-isopropyl-2-methylcyclohexyl)6-methyl8-(4-fluorophenyl)-6-hydroxy-1-oxospiro[4.5]dec-9-ene-6,9-dicarboxylate (6)





Methyl 8-(4-chlorophenyl)-10-hydroxy-1-oxo-10-(trifluoromethyl)spiro[4.5]dec-6-ene-7-carboxylate (8)





Methyl 2-oxo-6-(2-oxocyclopentylidene)-4,5-diphenylhexanoate (11)