Supporting Information
for

N-Heterocyclic carbene catalysed redox isomerisation of esters to functionalised benzaldehydes

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I. General experimental

Proton (^{1}H) carbon (^{13}C) and deuterium (^{2}H) NMR spectra were recorded on a Varian Mercury 500 spectrometer operating at 500 MHz for proton and 125 MHz for carbon nuclei and a Bruker DRX400 spectrometer operating at 400 MHz for proton and 100 MHz for carbon nuclei. Infrared spectra (ν_{max}) were recorded on an Agilent Cary 630 FTIR Spectrometer. Low resolution mass spectrometry (ESI) was performed on a Micromass Platform QMS spectrometer. High resolution mass spectra (HRMS) (ESI) were recorded on a Bruker BioApex 47e FTMS fitted with an Analytical electrospray source using NaI for accurate mass calibration.

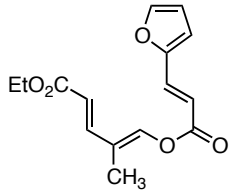
Analytical chiral HPLC was performed with a Perkin Elmer Series 200 HPLC using a Chiralpak AS-H column (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. with visualization at 245 nm.

Flash column chromatography was performed on silica gel (Davisil LC60A, 40-63 μm silica media) using compressed air. Thin layer chromatography (TLC) was performed using aluminum-backed plates coated with 0.2 mm silica (Merck, DC-Platten, Kieselgel; 60 F254 plates). Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable stain followed by heating. Starting materials and reagents were purchased from Sigma-Aldrich or Oakwood and were used as supplied or, in the case of some liquids, distilled. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl and acetonitrile, methylene chloride and benzene were dried by passing over activated alumina. Unless otherwise stated, all reactions were conducted in flame-dried glassware under an N_2 atmosphere.

NHC precatalyst **A·HCl** was prepared following the procedure of Arduengo.[1] Precatalyst **B·HClO$_4$** was prepared following the procedure of Enders.[2] Precatalyst **C1·HBF$_4$** was prepared following the procedure of Lupton.[3] Precatalyst **C3·HBF$_4$** was prepared using the procedure of Glorius.[4] Starting trienes **6** were prepared following the procedure of Lupton.[5] Trienes **6a-e**, **g-p** and **r-s** have been reported previously.[5]

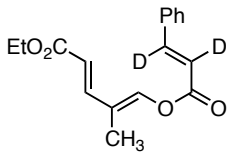
II. Synthesis of trienes 6f, q and t

(2*E*,4*E*)-Ethyl 5-(((*E*)-3-(furan-2-yl)acryloyl)oxy)-4-methylpenta-2,4-dienoate (6f).



Following the reported procedure,[5] the title compound was prepared in 67% yield over two steps. R_f 0.3 (10:1. v/v hexanes : EtOAc) MP 144.1-145.8 °C IR ν_{max} 1723, 1623, 1296, 1137 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.55 (d, *J* = 16.0 Hz, 1H), 7.53 (d, *J* = 1.6 Hz, 1H), 7.37 (d, *J* = 15.6 Hz, 1H), 6.71 (d, *J* = 3.2 Hz, 1H), 6.51 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 5.97 (d, *J* = 15.6 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.90 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.9, 163.1, 150.6, 145.5, 144.4, 141.2, 133.2, 119.1, 117.5, 116.3, 113.5, 112.6, 60.2, 14.3, 10.1 ppm LRMS (ESI) m/z Found: $(M+Na)^+$, $C_{15}H_{16}O_5$, 299.1, requires 299.1 HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{15}H_{16}O_5$, 277.1071, requires 277.1071

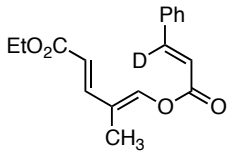
α-D,β-D-(2*E*,4*E*)-Ethyl 5-(cinnamoyloxy)-4-methylpenta-2,4-dienoate (6q).



Deuterium incorporation (by ^{1}H-NMR analysis) α-D = 97% incorporation, β-D = 99% incorporation R_f 0.3 (9:1. v/v EtOAc : hexanes) IR ν_{max} 3090, 2923, 1728, 1704, 1620, 1590, 1310, 1160, 1113 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.59-7.57 (m, 2H), 7.44-7.42 (m, 3H), 7.38 (d, *J* = 15.6 Hz, 1H), 5.94 (d, *J* = 15.6 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.93 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.9, 163.0, 147.0 (t, *J* = 23.4 Hz), 144.4, 141.2, 133.8, 131.0, 129.0, 128.4, 119.3, 117.6, 115.7 (t, *J* = 23.4 Hz), 60.3, 14.3, 10.1 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{17}H_{16}D_2O_4$, 289.1401, requires 289.1404

[1] A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt *Tetrahedron* 1999, **55**, 14523.
[2] D. Enders, K. Breuer, U. Kallfass, T. Balensiefer *Synthesis* 2003, 1292.
[3] L. Candish, C. M. Forsyth, D. W. Lupton *Angew. Chem. Int. Ed.* 2013, **52**, 9149.
[4] F. Liu, X. Bugaut, R. Schedles, R. Froehlich, F. Glorius *Angew. Chem. Int. Ed.* 2011, **50**, 12626.
[5] L. Candish, A. Levens, D. W. Lupton *J. Am. Chem. Soc.* 2014, **136**, 14387.

β-D-(2*E*,4*E*)-Ethyl 5-(cinnamoyloxy)-4-methylpenta-2,4-dienoate (6t).

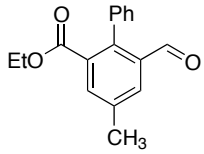


R_f 0.3 (10:1. v/v EtOAc : hexanes) IR ν_{max} 3088, 2979, 1734, 1706, 1621, 1143 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70 (q, *J* = 0.8 Hz, 1H), 7.59-7.56 (m, 2H), 7.44-7.41 (m, 3H), 7.39 (d, *J* = 15.6 Hz, 1H), 6.52 (s, 1H), 5.94 (d, *J* = 15.6 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.92 (d, *J* = 0.8 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.9, 163.0, 147.2 (t, J = 23.5 Hz), 144.4, 141.2, 133.8, 131.0, 129.0, 128.4, 119.3, 117.6, 115.9, 60.3, 14.3, 10.1 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{17}H_{17}DO_4$, 288.1335, requires 288.1341

III. NHC catalyzed redox isomerization

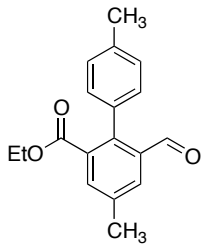
To a magnetically stirred solution of **C3·HBF$_4$** (7.0 mg, 0.015 mmol) in benzene (2 ml) was added potassium hexamethyldisilazide (0.03 ml of a 0.5 M solution in toluene, 0.015 mmol) and the mixture was stirred for 30 minutes. After 30 minutes this solution was added dropwise to a second flask, containing a magnetically stirred mixture of dienyl ester **6** (0.15 mmol) and 4 Å molecular sieves (12 mg) in benzene (2 ml) at room temperature. A reflux condenser was fitted and the reaction was heated to reflux for 42 hours. The reaction was cooled to room temperature, concentrated, and the crude residue purified by flash column chromatography.

Ethyl 6-formyl-4-methyl-[1,1'-biphenyl]-2-carboxylate (5a).



Following the general procedure the title compound was synthesized in 87% yield as a colourless oil. R_f 0.3 (9:1. v/v hexanes : EtOAc) IR ν_{max} 2982, 2864, 2752, 1717, 1690, 1239, 1193 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.94 (dq, *J* = 2.0, 0.8 Hz, 1H). 7.87 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.43-7.40 (m, 3H), 7.27-7.24 (m, 2H), 4.02 (q, *J* = 7.2 Hz, 2H), 2.49 (t, *J* = 0.8 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 191.9, 167.6, 142.6, 138.0, 136.1, 135.2, 134.6, 133.1, 130.3, 129.8, 127.9, 61.1, 20.9, 13.6 ppm (1 peak missing or overlapping) HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{17}H_{16}O_3$, 269.1170, requires 269.1172

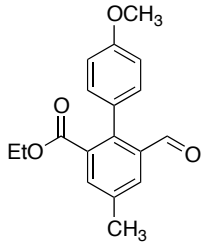
Ethyl 6-formyl-4,4'-dimethyl-[1,1'-biphenyl]-2-carboxylate (5b).



Following the general procedure the title compound was synthesized in 91% yield as a colourless oil. R_f 0.3 (9:1. v/v hexanes : EtOAc) IR ν_{max} 2925, 2856, 1715, 1693, 1239, 1193 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.92 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.84 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.22 (AA'BB', *J* = 8.4 Hz, 2H), 7.14 (AA'BB', *J* = 8.4 Hz, 2H), 4.05 (q, *J* = 7.2 Hz, 2H), 2.48 (t, *J* = 0.8 Hz, 3H), 2.42 (s, 3H), 0.99 (t, *J* = 7.2 Hz, 3H) ppm ^{13}C-NMR

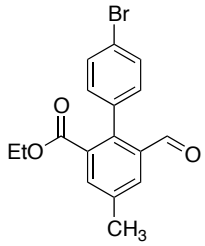
(100 MHz, $CDCl_3$) δ 192.1, 167.7, 142.7, 137.7(0), 137.6(9), 135.1, 134.8, 133.2, 132.9, 130.2, 129.7, 128.6, 61.1, 21.2, 20.9, 13.6 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{18}H_{18}O_3$, 283.1330, requires 283.1329

Ethyl 6-formyl-4'-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxylate (5c).



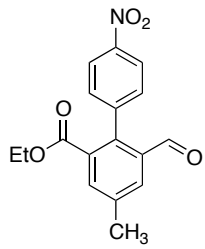
Following the general procedure the title compound was synthesized in 71% yield as a colourless oil. R_f 0.3 (4:1. v/v hexanes : EtOAc) IR ν_{max} 2981, 1719, 1690, 1516, 1306, 1243m 1192 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.91 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.82 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.17 (AA'BB', *J* = 8.8 Hz, 2H), 6.95 (AA'BB', *J* = 8.8 Hz, 2H), 4.06 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 2.47 (t, *J* = 0.8 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 192.2, 167.8, 159.5, 142.2, 137.7, 135.0, 134.9, 133.4, 131.0, 130.2, 128.0, 113.4, 61.1, 55.3, 20.9, 13.8 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{18}H_{18}O_4$, 299.1281, requires 299.1278

Ethyl 4'-bromo-6-formyl-4-methyl-[1,1'-biphenyl]-2-carboxylate (5d).



Following the general procedure the title compound was synthesized in 68% yield as a colourless oil. R_f 0.3 (9:1. v/v hexanes : EtOAc) IR ν_{max} 2983, 2754, 1724, 1692, 1306, 1239, 1194 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.94 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.90 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.56 (AA'BB', *J* = 8.8 Hz, 2H), 7.14 (AA'BB', *J* = 8.8 Hz, 2H), 4.06 (q, *J* = 7.2 Hz, 2H), 2.49 (t, *J* = 0.8 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 191.3, 167.1, 141.3, 138.4, 135.5, 135.1, 134.6, 132.7, 131.4, 131.1, 130.7, 122.3, 61.3, 20.9, 13.7 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{17}H_{15}{}^{79}BrO_3$, 347.0276, requires 347.0278

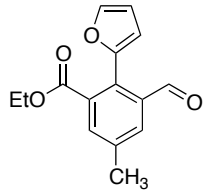
Ethyl 6-formyl-4-methyl-4'-nitro-[1,1'-biphenyl]-2-carboxylate (5e).



Product co-elutes with starting material. Following precipitation and filtration, the product was isolated with ~15% starting material. Yield calculated taking contamination into account. Following the general procedure the title compound was synthesized in 43% yield as a colourless oil. R_f 0.3 4:1. v/v hexanes : EtOAc) IR ν_{max} 2981, 2861, 2753, 2361, 1721, 1692, 1520, 1347, 1238 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 8.31 (AA′BB′, *J* = 8.8 Hz, 2H), 8.02 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.99 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.45 (AA′BB′, *J* = 8.8 Hz, 2H), 4.08 (q, *J* = 7.2 Hz, 2H), 2.53 (t, *J* = 0.8 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 190.4, 166.3, 147.5, 143.7, 140.3, 139.3, 136.0,

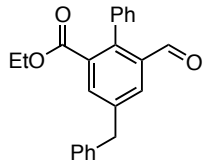
134.4, 131.8, 131.5, 130.6, 123.1, 61.5, 21.0, 13.8 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{17}H_{15}NO_5$, 314.1028, requires 314.1023

Ethyl 3-formyl-2-(furan-2-yl)-5-methylbenzoate (5f).



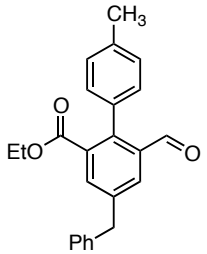
Following the general procedure the title compound was synthesized in 56% yield as a colourless oil. R_f 0.3 (9:1. v/v hexanes : EtOAc) IR ν_{max} 2983, 2868, 2749, 1725, 1693, 1243, 1193 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.92 (dq, *J* = 1.6, 0.8 Hz, 1H), 7.85 (dq, *J* = 1.6, 0.8 Hz, 1H), 7.57 (dd, *J* = 2.0, 0.8 Hz, 1H), 6.55 (dd, *J* = 4.0, 2.0 Hz, 1H), 6.47 (dd, *J* = 4.0, 0.8 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.48 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 191.5, 167.4, 147.1, 143.3, 139.4, 135.3, 135.2, 133.6, 130.6, 130.4, 112.7, 111.3, 61.5, 21.1, 14.0 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{15}H_{14}O_4$, 259.0960, requires 259.0965

Ethyl 4-benzyl-6-formyl-[1,1'-biphenyl]-2-carboxylate (5g).



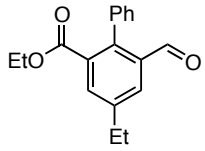
Following the general procedure the title compound was synthesized in 80% yield as a colourless oil. R_f 0.3 (9:1. v/v hexanes : EtOAc) IR ν_{max} 3027, 2980, 2862, 2753, 1716, 1691, 1239, 1189 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.97 (dt, *J* = 2.0, 0.4 Hz, 1H), 7.88 (dt, *J* = 2.0, 0.4 Hz, 1H), 7.43-7.40 (m, 3H), 7.35-7.31 (m, 2H), 7.27-7.23 (m, 5H), 4.10 (brs, 2H), 4.00 (q, *J* = 7.2 Hz, 2H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 192.0, 167.7, 143.3, 141.5, 139.7, 136.1, 135.1, 135.0, 133.6, 130.2, 129.9, 129.1, 128.9, 128.1(3), 128.0(8), 126.8, 61.3, 41.5, 13.7 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{23}H_{20}O_3$, 345.1490, requires 345.1485

Ethyl 4-benzyl-6-formyl-4'-methyl-[1,1'-biphenyl]-2-carboxylate (5h).



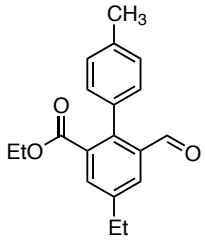
Following the general procedure the title compound was synthesized in 85% yield as a colourless oil. R_f 0.3 (9:1. v/v hexanes : EtOAc) IR ν_{max} 3028, 2982, 2863, 2753, 1719, 1692, 1239, 1189 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.95 (dt, *J* = 2.0, 0.4 Hz, 1H), 7.86 (dt, *J* = 2.0, 0.4 Hz, 1H), 7.34-7.30 (m, 2H), 7.26-7.21 (m, 5H), 7.15-7.13 (m, 2H), 4.09 (brs, 2H), 4.02 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 0.96 (t, *J* = 7.2 Hz, 3H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 192.2, 167.8, 143.4, 141.2, 139.7, 137.9, 135.1, 135.0, 133.7, 132.9, 130.2, 129.8, 129.1, 128.9, 128.8, 126.7, 61.3, 41.5, 21.4, 13.7 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{24}H_{22}O_3$, 359.1650, requires 359.1642

Ethyl 4-ethyl-6-formyl-[1,1'-biphenyl]-2-carboxylate (5i).



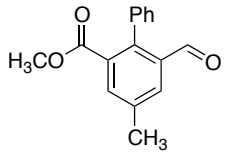
Following the general procedure the title compound was synthesized in 52% yield as a colourless oil. R_f 0.4 (9:1. v/v hexanes : EtOAc) IR ν_{max} 2969, 2935, 2870, 2755, 1716, 1690, 1300, 1232, 1190, 1131 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.97 (dt, *J* = 2.0, 0.8 Hz, 1H), 7.89 (dt, *J* = 2.0, 0.8 Hz, 1H), 7.43-7.41 (m, 3H), 7.28-7.26 (m, 2H), 4.02 (q, *J* = 7.2 Hz, 2H), 2.79 (qt, *J* = 7.2, 0.8 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 192.2, 167.9, 144.3, 142.9, 136.3, 134.9, 134.4, 133.3, 130.0, 129.3, 128.1, 61.3, 28.5, 15.3, 13.7 ppm (1 peak missing or overlapping) HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{18}H_{18}O_3$, 283.1328, requires 283.1329

Ethyl 4-ethyl-6-formyl-4'-methyl-[1,1'-biphenyl]-2-carboxylate (5j).



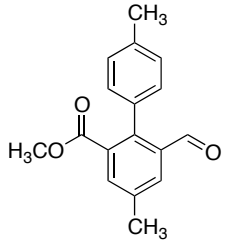
Following the general procedure the title compound was synthesized in 59% yield as a colourless oil. R_f 0.3 (9:1. v/v hexanes : EtOAc) IR ν_{max} 2968, 2933, 2868, 2753, 1717, 1689, 1300, 1232, 1189, 1127 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.95 (dt, *J* = 2.0, 0.8 Hz, 1H), 7.86 (dt, *J* = 2.0, 0.8 Hz, 1H), 7.22 (AA'BB', *J* = 8.0 Hz, 2H), 7.15 (AA'BB', *J* = 8.0 Hz, 2H), 4.05 (q, *J* = 7.2 Hz, 2H), 2.78 (brq, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 192.4, 168.0, 144.1, 143.1, 137.9, 135.0, 134.2, 133.5, 133.1, 129.9, 129.2, 128.8, 61.3, 28.5, 21.4, 15.3, 13.8 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{19}H_{20}O_3$, 297.1484, requires 297.1485

Methyl 6-formyl-4-methyl-[1,1'-biphenyl]-2-carboxylate (5l).



Following the general procedure the title compound was synthesized in 77% yield as a colourless oil. R_f 0.3 (9:1. v/v hexanes : EtOAc) IR ν_{max} 2951, 2863, 2753, 1731, 1691, 1312, 1240, 1129 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.95 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.88 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.44-7.41 (m, 3H), 7.27-7.24 (m, 2H), 3.58 (s, 3H), 2.49 (t, *J* = 0.8 Hz, 3H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 191.9, 167.8, 142.8, 137.9, 135.8, 135.3, 134.7, 132.5, 130.4, 129.7, 128.0, 127.9, 52.1, 20.9 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{16}H_{14}O_3$, 255.1017, requires 255.1016

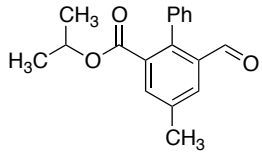
Methyl 6-formyl-4,4'-dimethyl-[1,1'-biphenyl]-2-carboxylate (5m).



Following the general procedure the title compound was synthesized in 72% yield as a colourless oil. R_f 0.3 (9:1. v/v hexanes : EtOAc) IR ν_{max} 2952, 2866, 2752, 1732, 1691, 1312, 1240, 1130 cm^{-1} ^{1}H-NMR (400

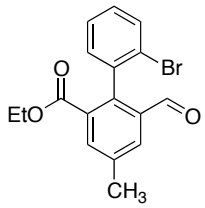
MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.93 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.87 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.23 (AA'BB', *J* = 7.6 Hz, 2H), 7.14 (AA'BB', *J* = 7.6 Hz, 2H), 3.61 (s, 3H), 2.48 (t, *J* = 0.8 Hz, 3H), 2.42 (s, 3H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 192.1, 167.8, 142.9, 137.7(2), 137.7(0), 135.2, 134.8, 132.7, 132.6, 130.4, 129.6, 128.7, 52.1, 21.3, 20.9 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{17}H_{16}O_3$, 269.1172, requires 269.1172

Isopropyl 6-formyl-4-methyl-[1,1'-biphenyl]-2-carboxylate (5n).



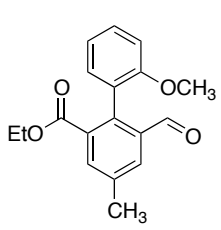
Following the general procedure the title compound was synthesized in 81% yield as a colourless oil. R_f 0.3 (9:1. v/v hexanes : EtOAc) IR ν_{max} 2982, 2936, 2866, 1714, 1692, 1305, 1241, 1106 cm^{-1} ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.93 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.84 (dq, *J* = 2.0, 0.8 Hz, 1H), 7.42-7.40 (m, 3H), 7.28-7.25 (m, 2H), 4.91 (sept, *J* = 6.0 Hz, 1H), 2.49 (t, *J* = 0.8 Hz, 3H), 0.95 (d, *J* = 6.0 Hz, 6H) ppm ^{13}C-NMR (100 MHz, $CDCl_3$) δ 192.0, 167.3, 142.3, 137.9, 136.1, 135.1, 134.5, 133.6, 130.0, 129.9, 127.9(0), 127.8(8), 68.8, 21.2, 20.9 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{18}H_{18}O_3$, 305.1152, requires 305.1148

Ethyl 2'-bromo-6-formyl-4-methyl-[1,1'-biphenyl]-2-carboxylate (5o).



Following the general procedure the title compound was synthesized in 46% yield as a colourless oil. R_f 0.3 (9:1. v/v hexanes : EtOAc) IR ν_{max} 2980, 2859, 2752, 1716, 1694, 1240, 1195 cm^{-1} HPLC Diacel AS-H, hexane : *i*PrOH 90:10, 1 ml/min λ = 245 nm, fraction tr = 7.11 (major enantiomer) and 7.70 (minor enantiomer); er = 67:33 ^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.06 (dq, *J* = 2.0, 0.5 Hz, 1H), 7.99 (dq, *J* = 2.0, 0.5 Hz, 1H), 7.67 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.37 (td, *J* = 7.5, 1.5 Hz, 1H), 7.29 (td, *J* = 7.5, 1.5 Hz, 1H), 7.22 (dd, *J* = 7.5, 1.5 Hz, 1H), 4.11-4.04 (m, 2H), 2.51 (t, *J* = 0.5 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3H) ppm ^{13}C-NMR (150 MHz, $CDCl_3$) δ 191.2, 166.3, 141.7, 138.8, 137.6, 136.2, 134.4, 132.2, 131.8, 131.2, 131.0, 129.6, 127.0, 124.1, 61.2, 21.0, 13.6 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{17}H_{15}{}^{79}BrO_3$, 347.0281, requires 347.0277

Ethyl 6-formyl-2'-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxylate (5p).

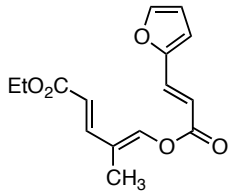


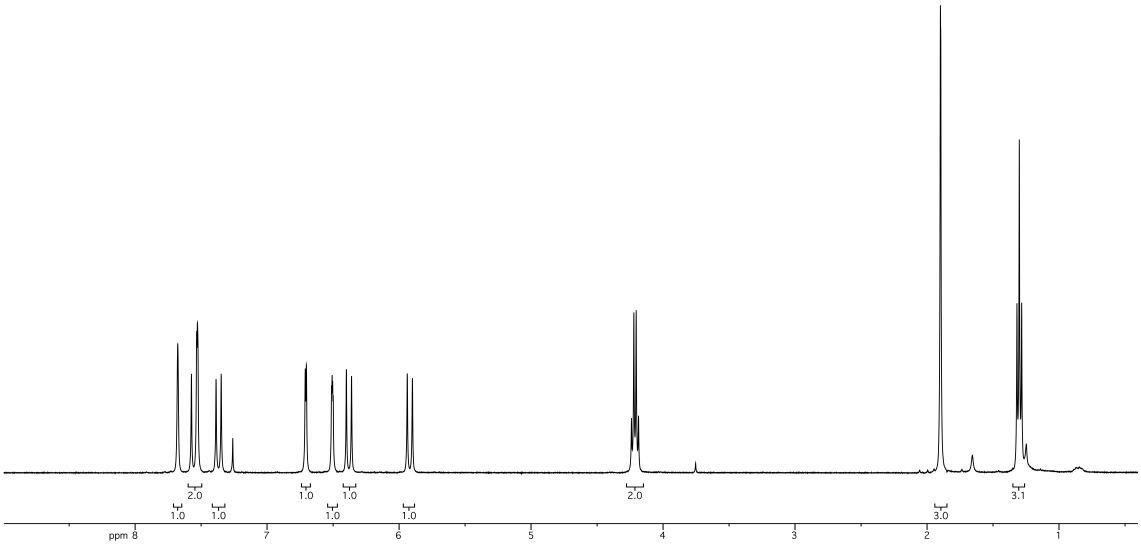
Following the general procedure the title compound was synthesized in 41% yield as a colourless oil. R_f 0.2 (9:1. v/v hexanes : EtOAc) IR ν_{max} 2925, 2852, 2751, 1717, 1691, 1236, 1191 cm^{-1} HPLC Diacel AS-H, hexane : *i*PrOH 90:10, 1 ml/min λ = 245 nm, fraction tr = 6.86 (minor enantiomer) and 9.67 (major enantiomer); er = 65:35 ^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.96 (dq, *J* = 2.0, 0.5 Hz, 1H), 7.93 (dq, *J* = 2.0, 0.5 Hz, 1H),

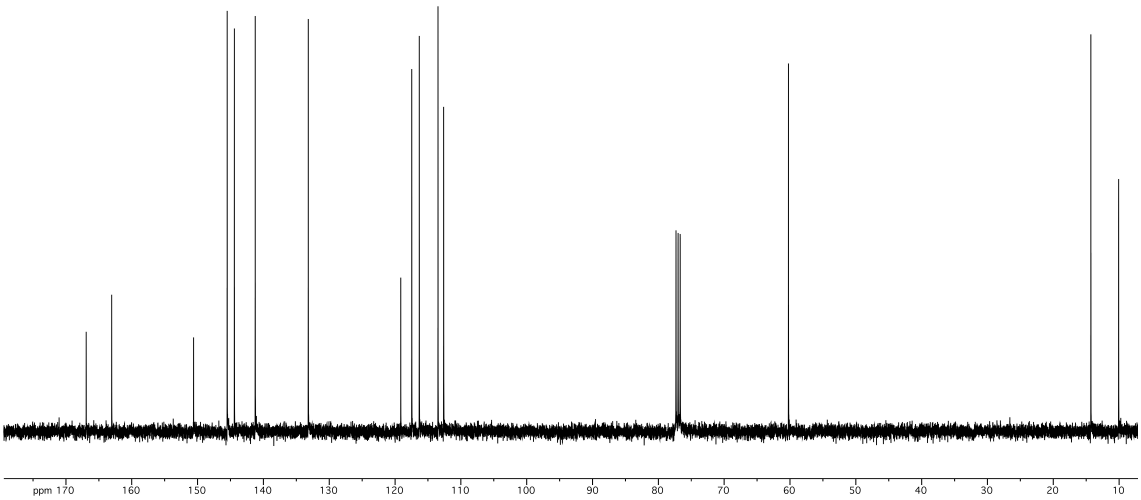
7.42 (td, J = 7.5, 1.0 HZ, 1H), 7.10 (dd, J = 7.5, 1.0 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 7.5 Hz, 1H), 4.05 (ABX_3, J = 7.5, 7.0 Hz, 2H), 2.49 (t, J = 0.5 Hz, 3H), 0.98 (t, J = 7.0 Hz, 3H) ppm ^{13}C-NMR (150 MHz, $CDCl_3$) δ 192.4, 167.5, 156.8, 139.2, 137.8, 135.5, 134.7, 133.1, 131.2, 130.3, 129.7, 125.0, 120.4, 110.3, 60.9, 55.5, 20.9, 13.6 ppm HRMS (ESI) *m/z* Found: $(M+H)^+$, $C_{18}H_{18}O_4$, 299.1278, requires 299.1278

IV. ^{1}H- and ^{13}C-NMR spectra

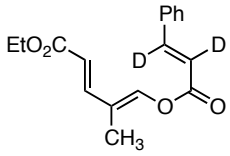
(2*E*,4*E*)-Ethyl 5-(((*E*)-3-(furan-2-yl)acryloyl)oxy)-4-methylpenta-2,4-dienoate (6f)

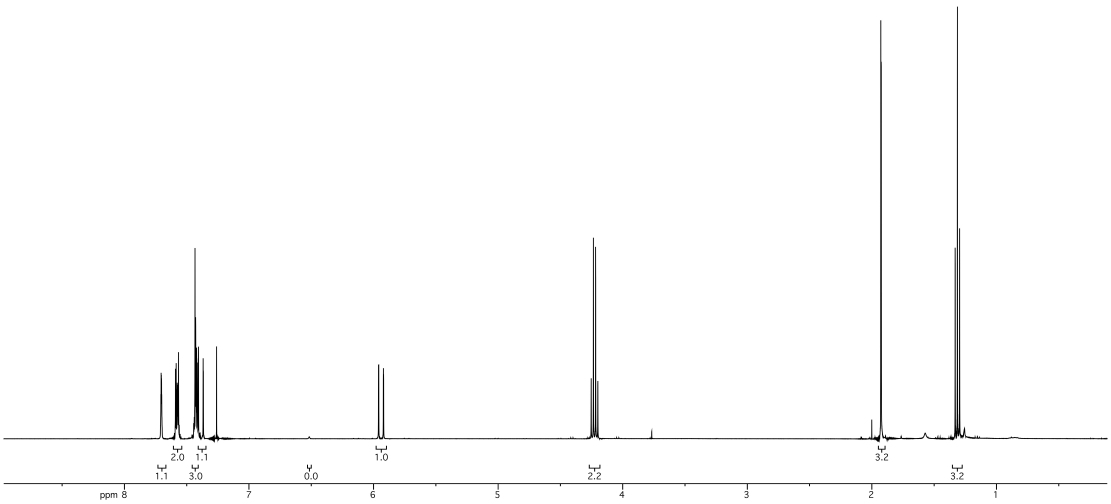


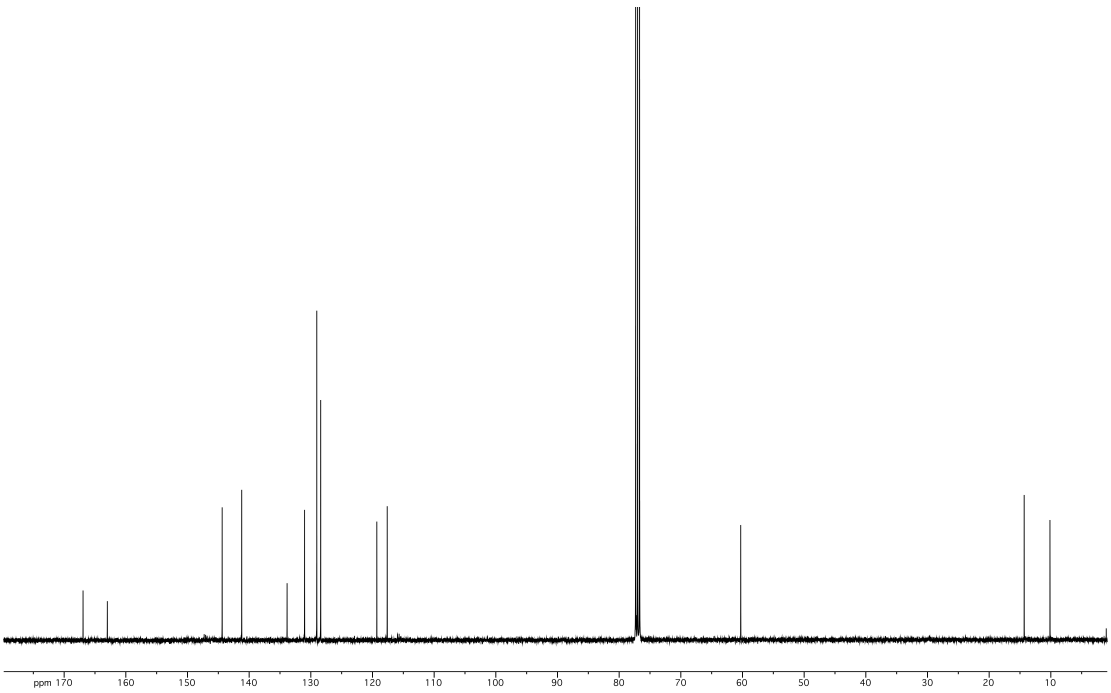




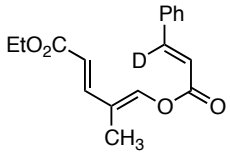
α-D,β-D-(2*E*,4*E*)-Ethyl 5-(cinnamoyloxy)-4-methylpenta-2,4-dienoate (6q)

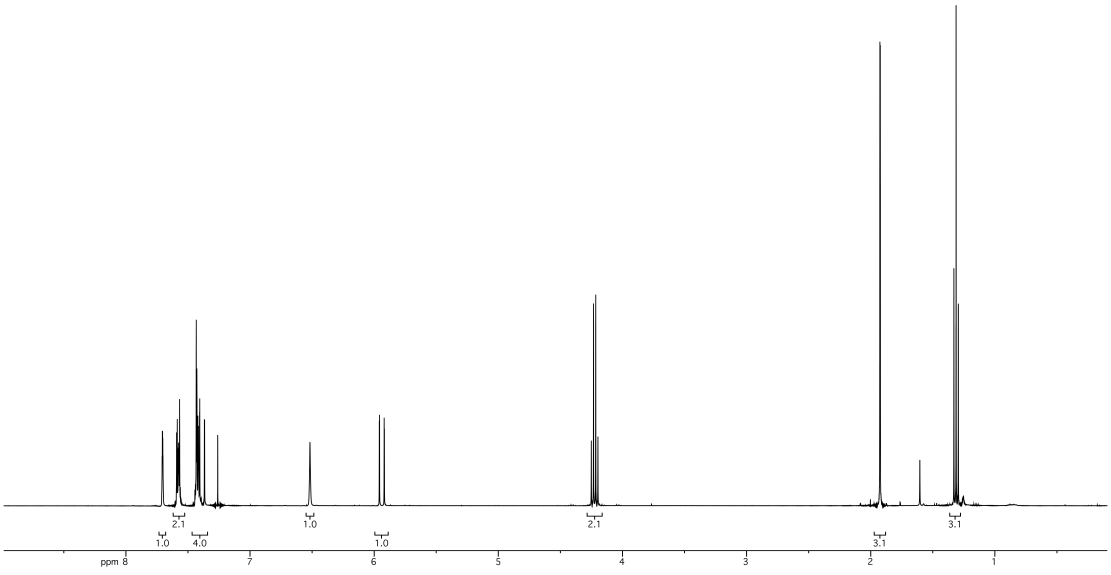


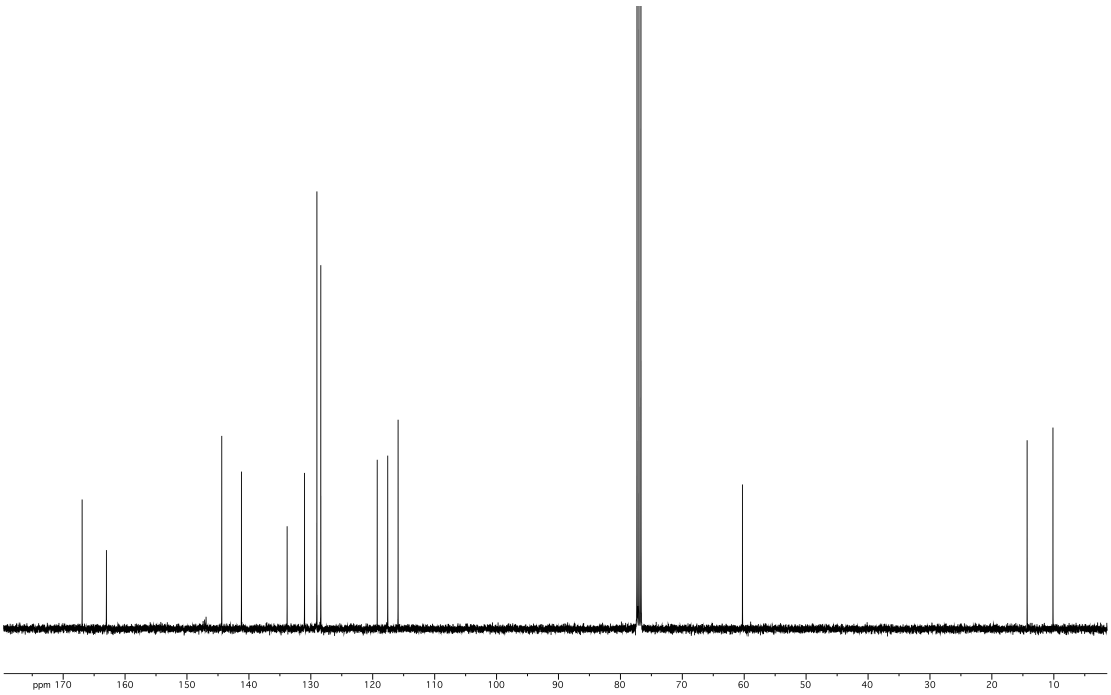




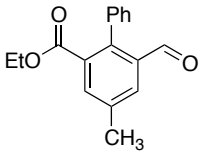
β-D-(2*E*,4*E*)-Ethyl 5-(cinnamoyloxy)-4-methylpenta-2,4-dienoate (6t)

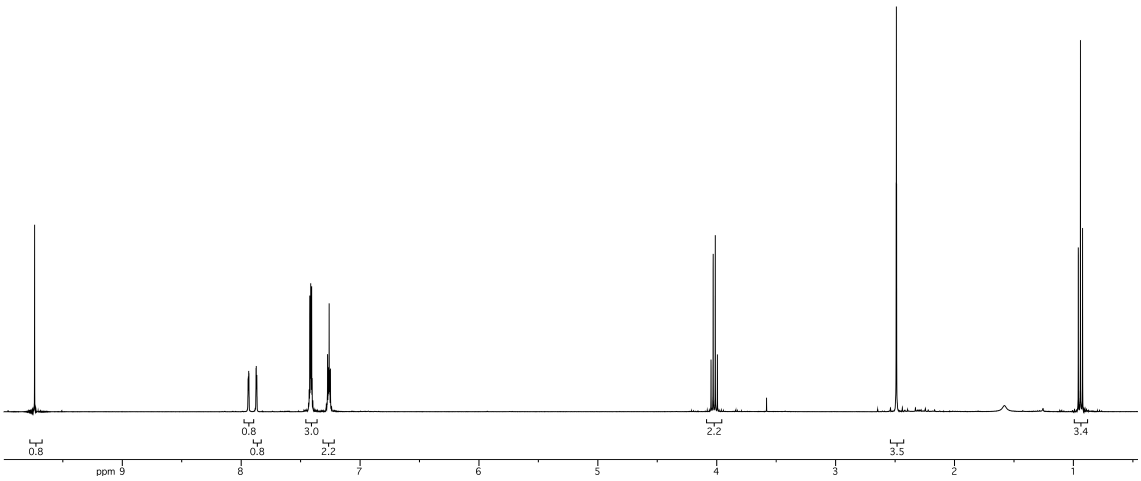


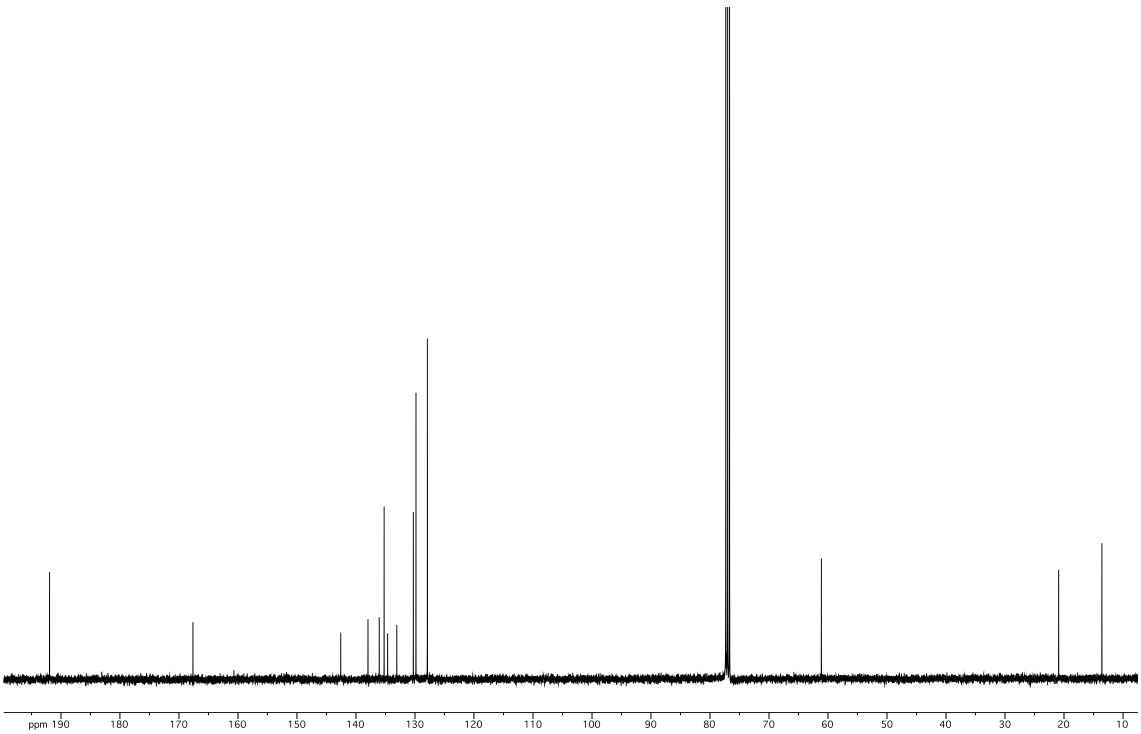




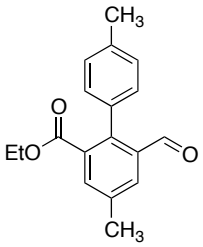
Ethyl 6-formyl-4-methyl-[1,1'-biphenyl]-2-carboxylate (5a)

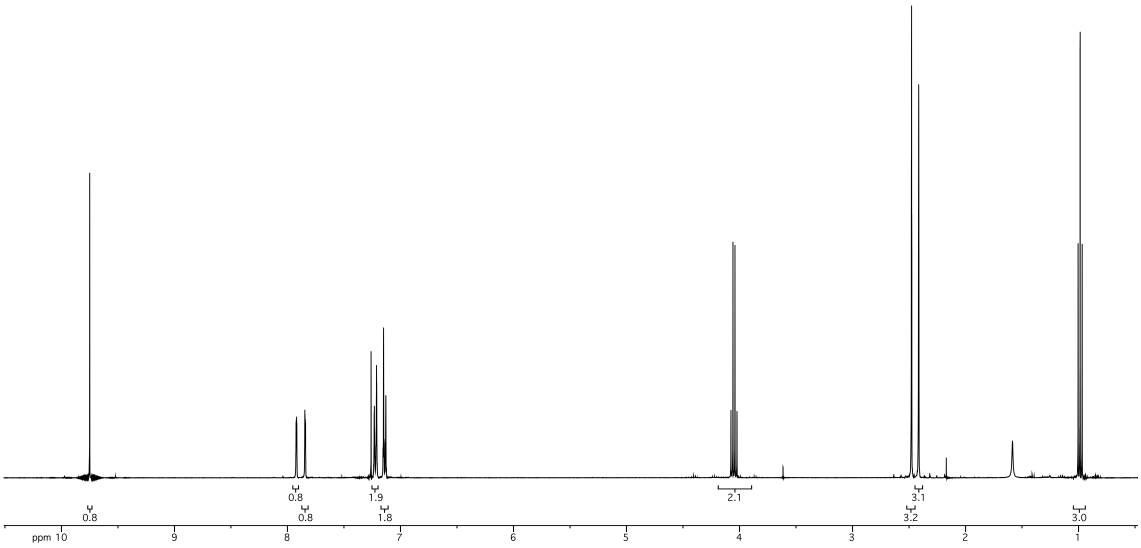


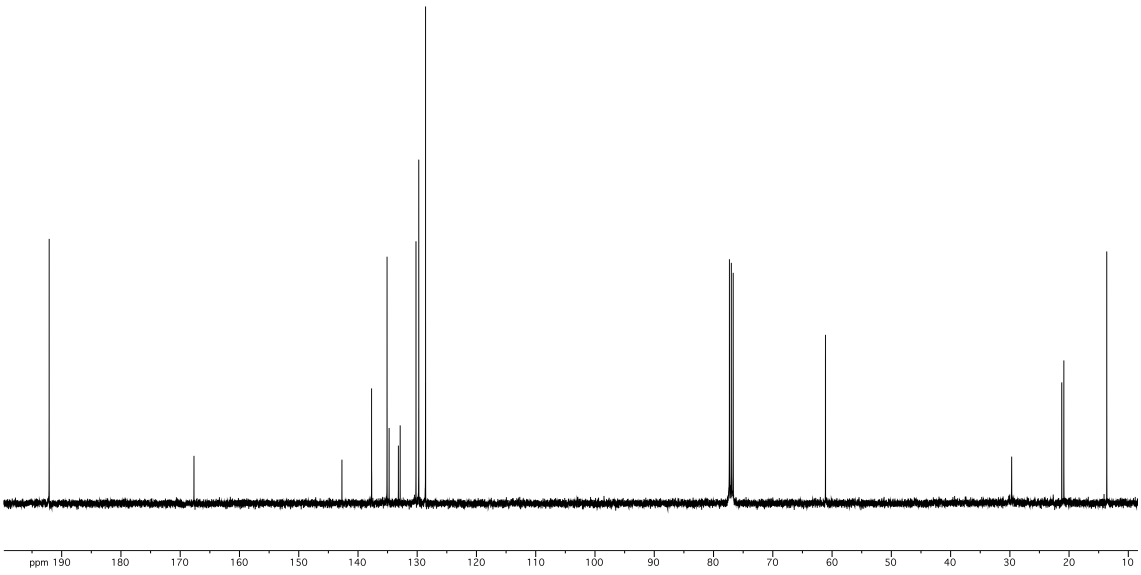




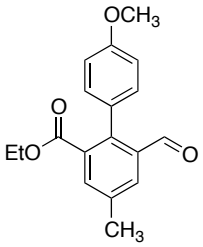
Ethyl 6-formyl-4,4'-dimethyl-[1,1'-biphenyl]-2-carboxylate (5b)

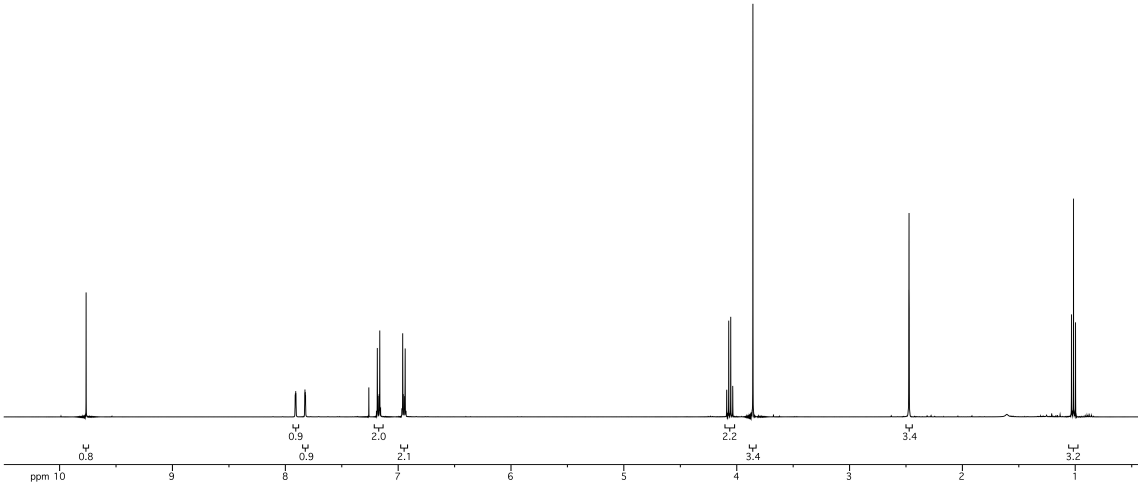


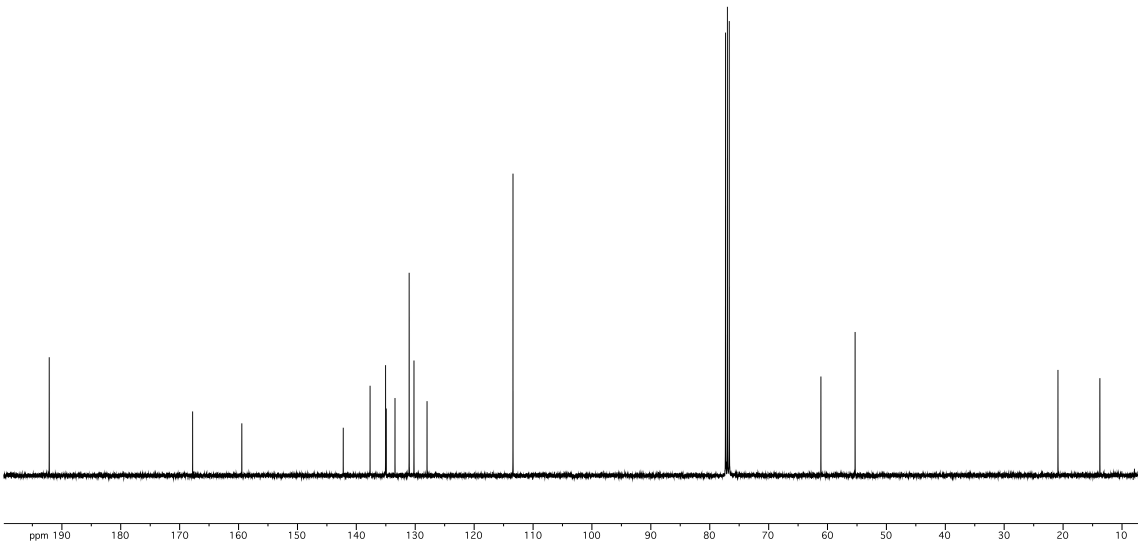




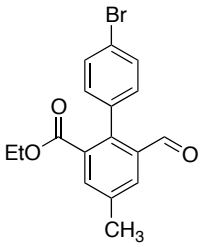
Ethyl 6-formyl-4'-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxylate (5c)

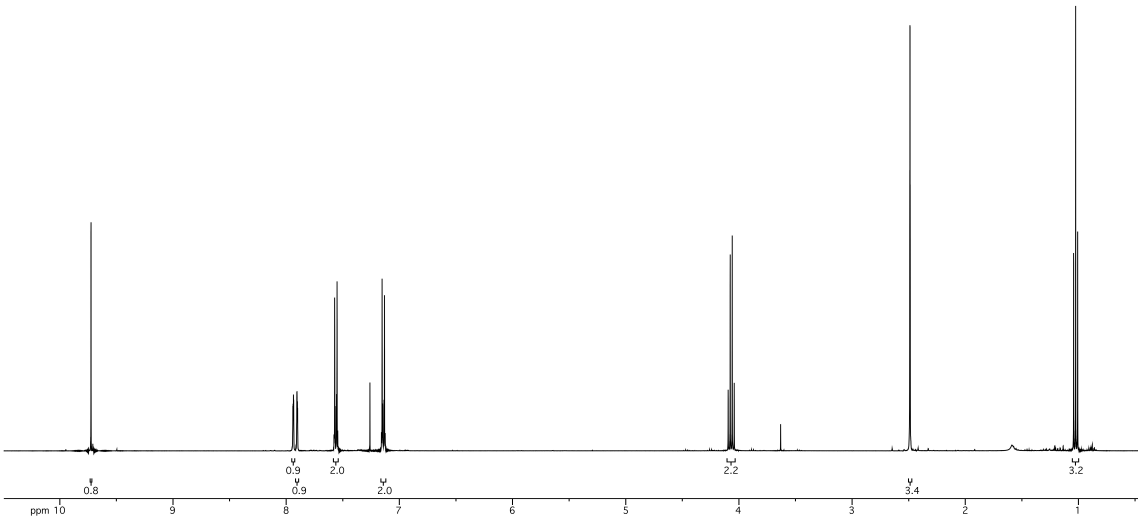


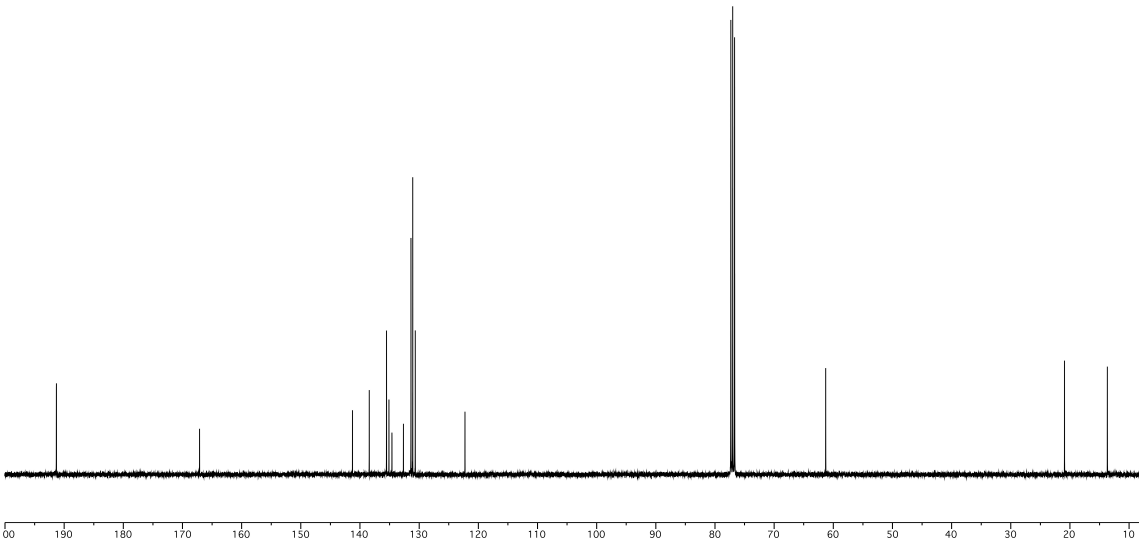




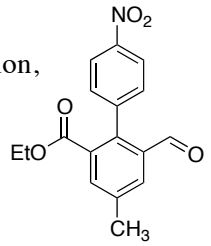
Ethyl 4'-bromo-6-formyl-4-methyl-[1,1'-biphenyl]-2-carboxylate (5d)



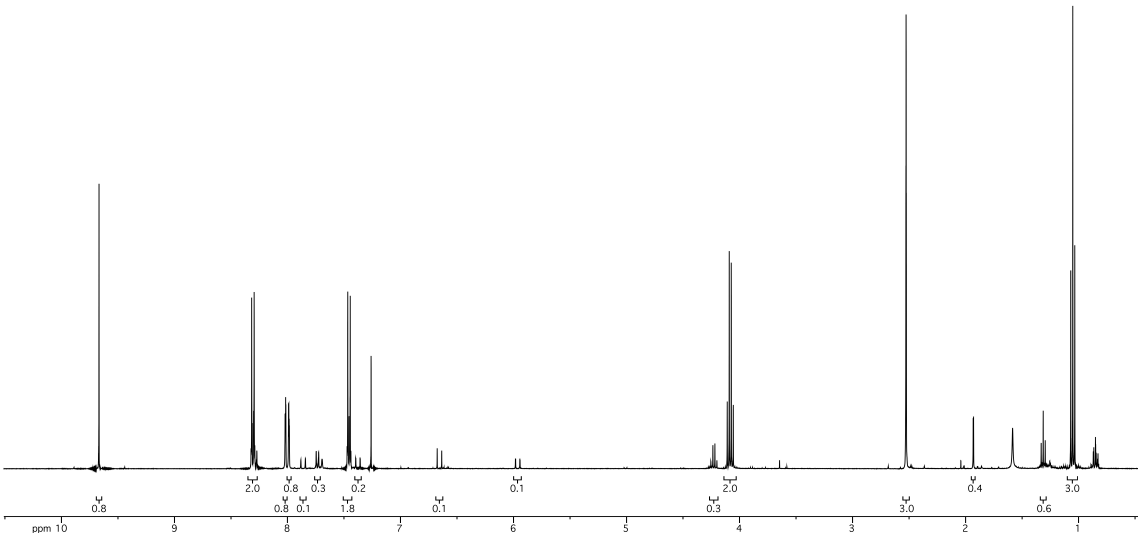


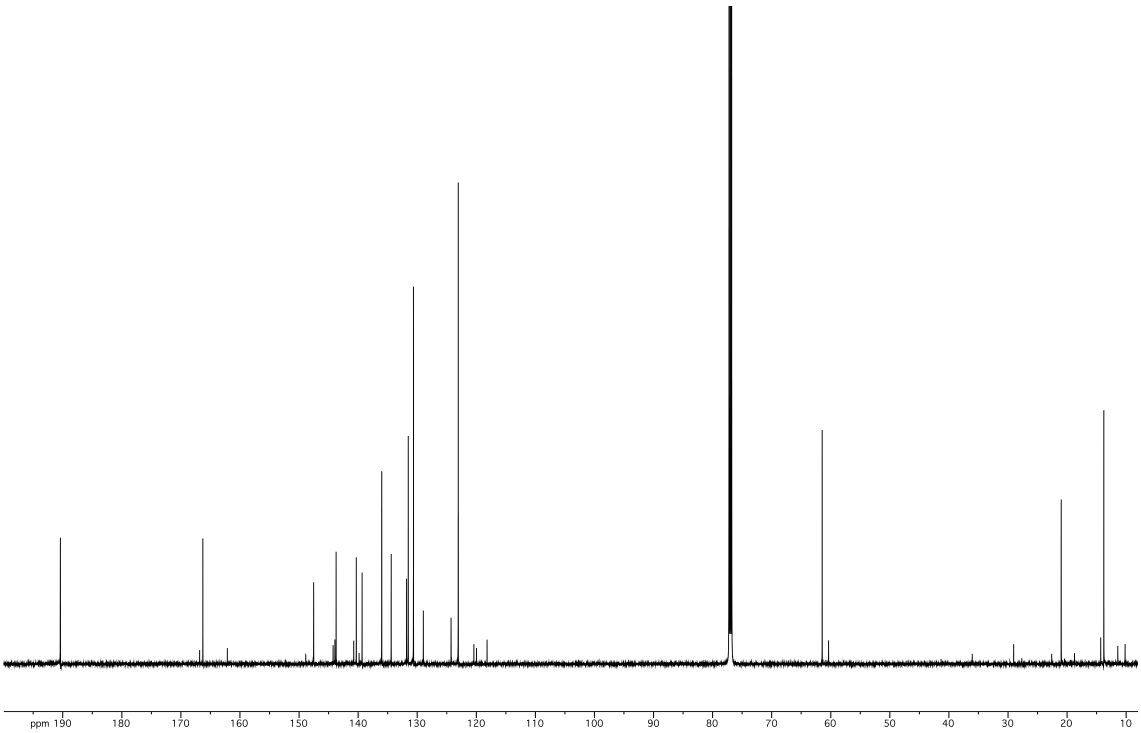


Ethyl 6-formyl-4-methyl-4'-nitro-[1,1'-biphenyl]-2-carboxylate (5e)

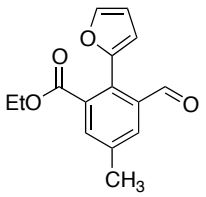


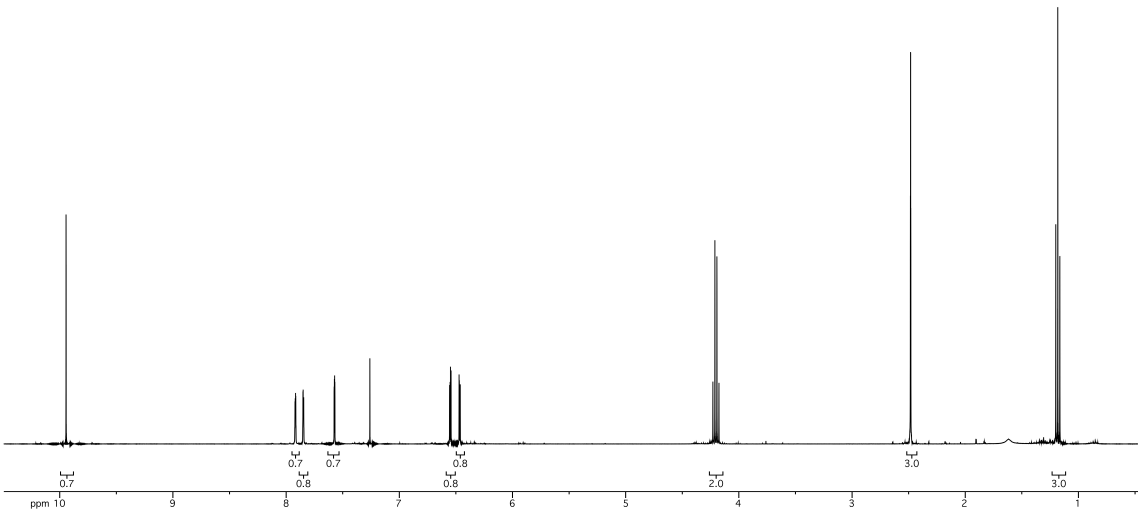
Product co-elutes with starting material. Following precipitation and filtration, the product was isolated with ~15% starting material. Yield calculated taking contamination into account.

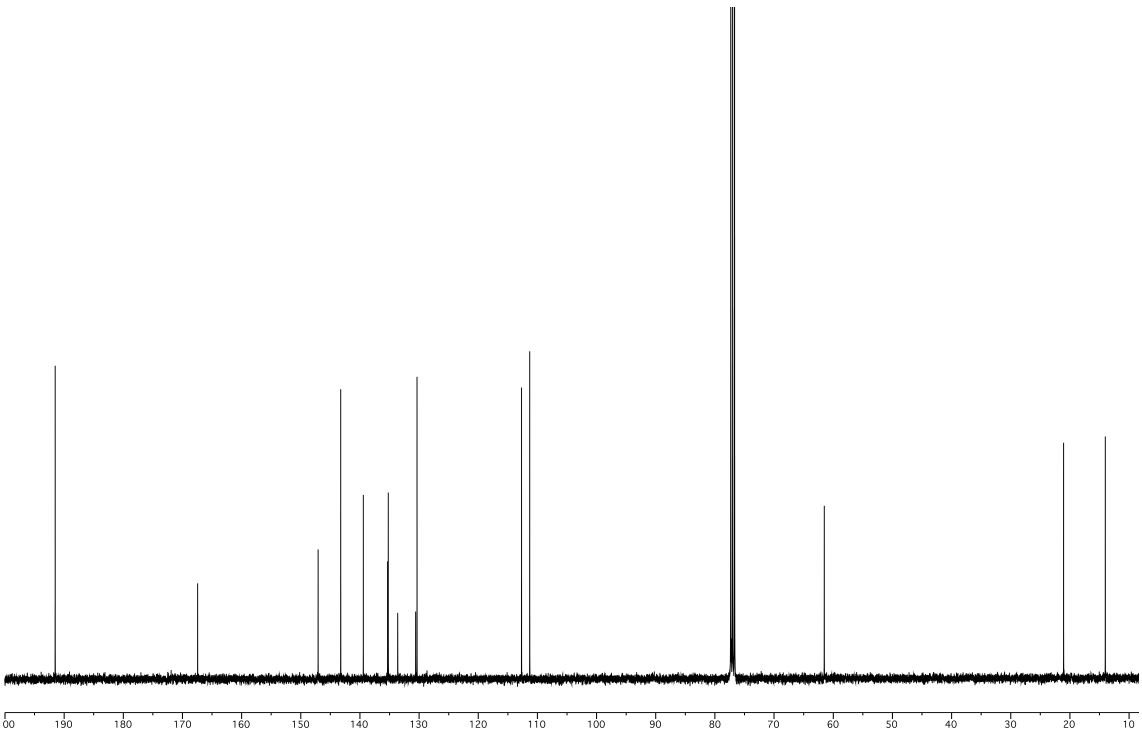




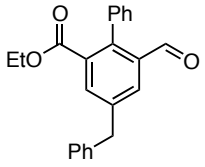
Ethyl 3-formyl-2-(furan-2-yl)-5-methylbenzoate (5f)

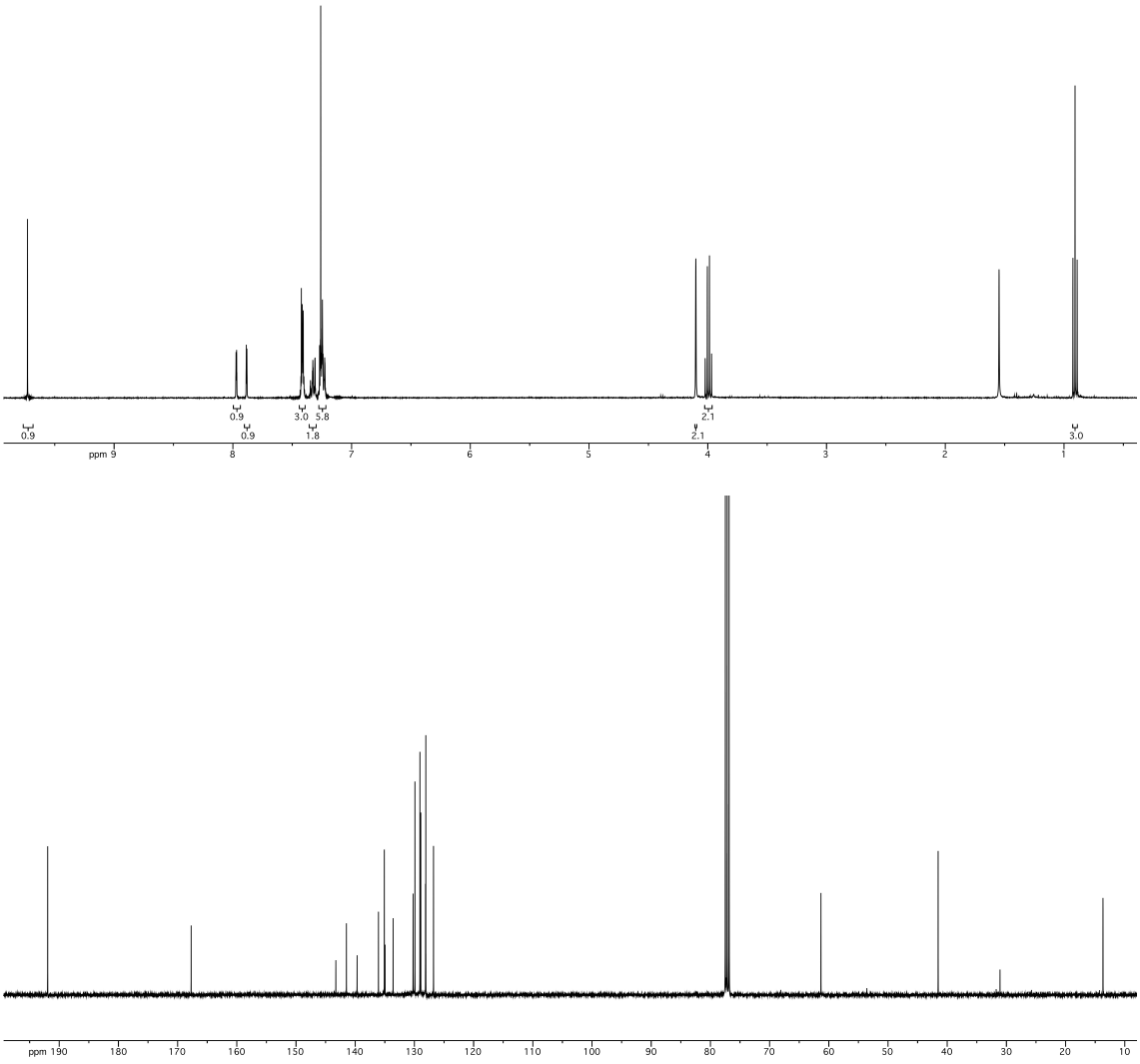




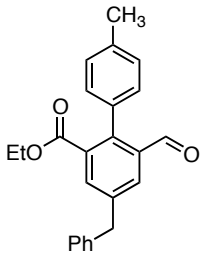


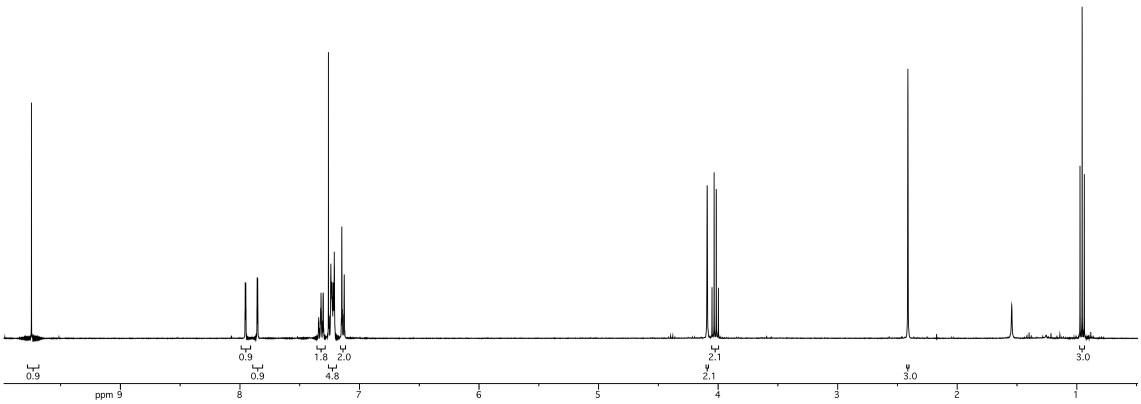
Ethyl 4-benzyl-6-formyl-[1,1'-biphenyl]-2-carboxylate (5g)

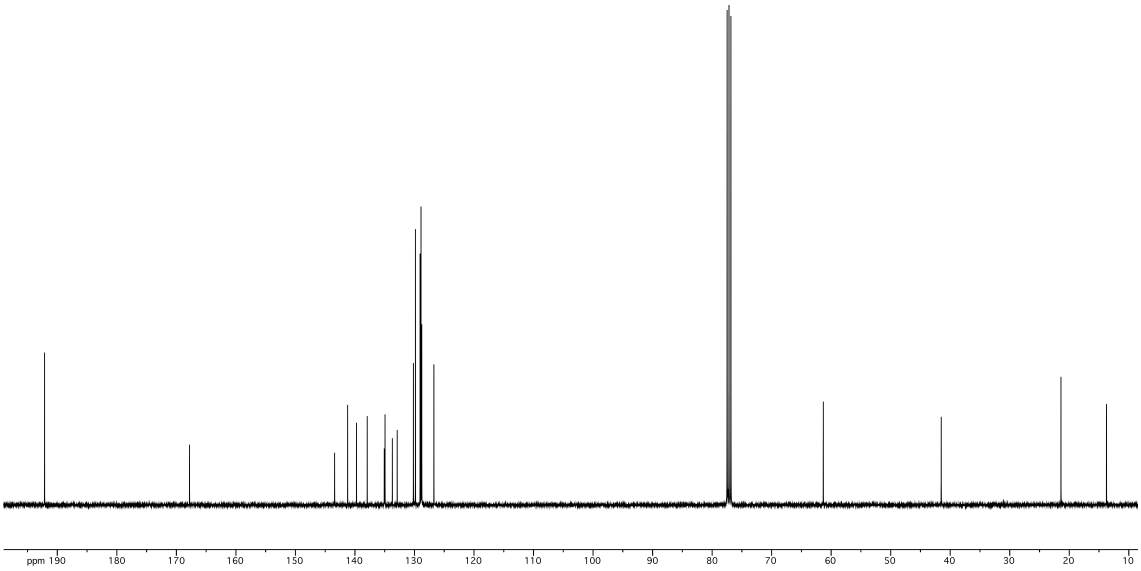




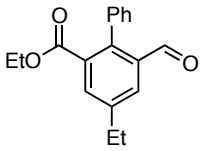
Ethyl 4-benzyl-6-formyl-4'-methyl-[1,1'-biphenyl]-2-carboxylate (5h)

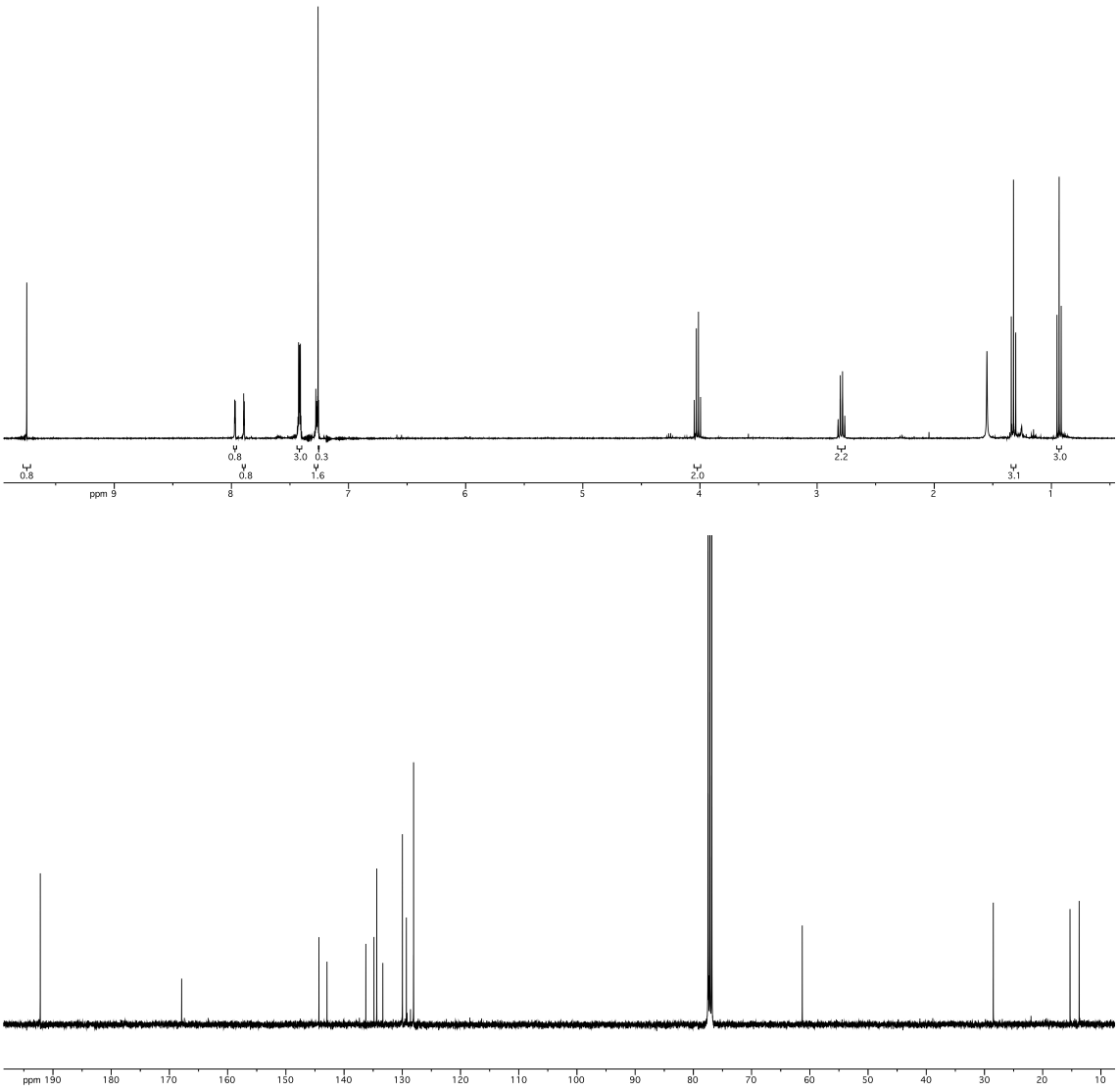




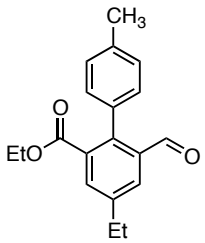


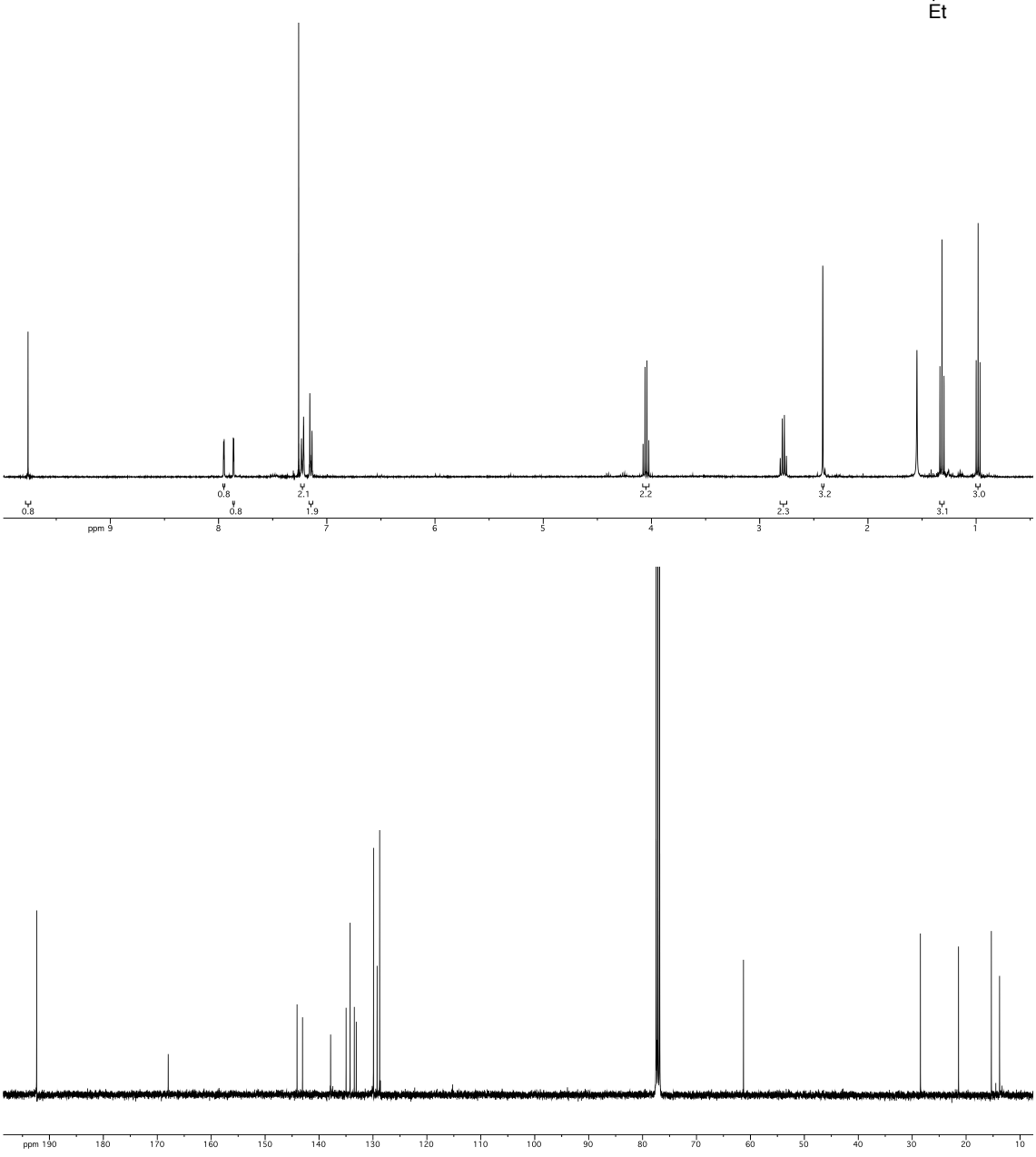
Ethyl 4-ethyl-6-formyl-[1,1'-biphenyl]-2-carboxylate (5i)



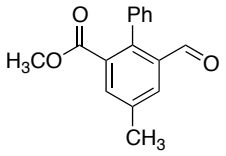


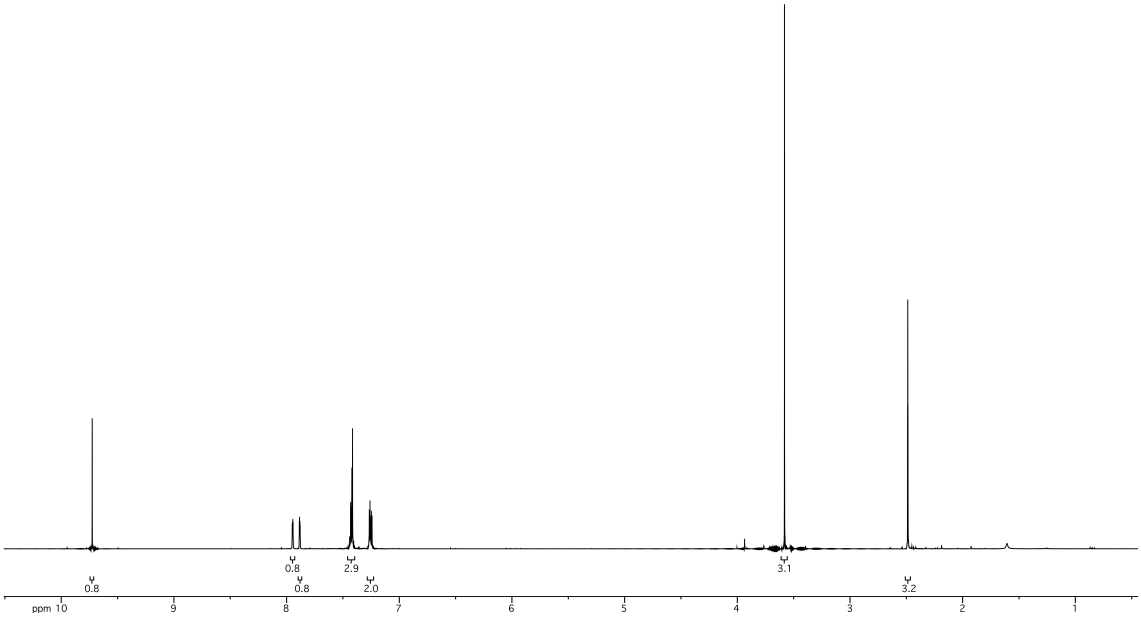
Ethyl 4-ethyl-6-formyl-4'-methyl-[1,1'-biphenyl]-2-carboxylate (5j)

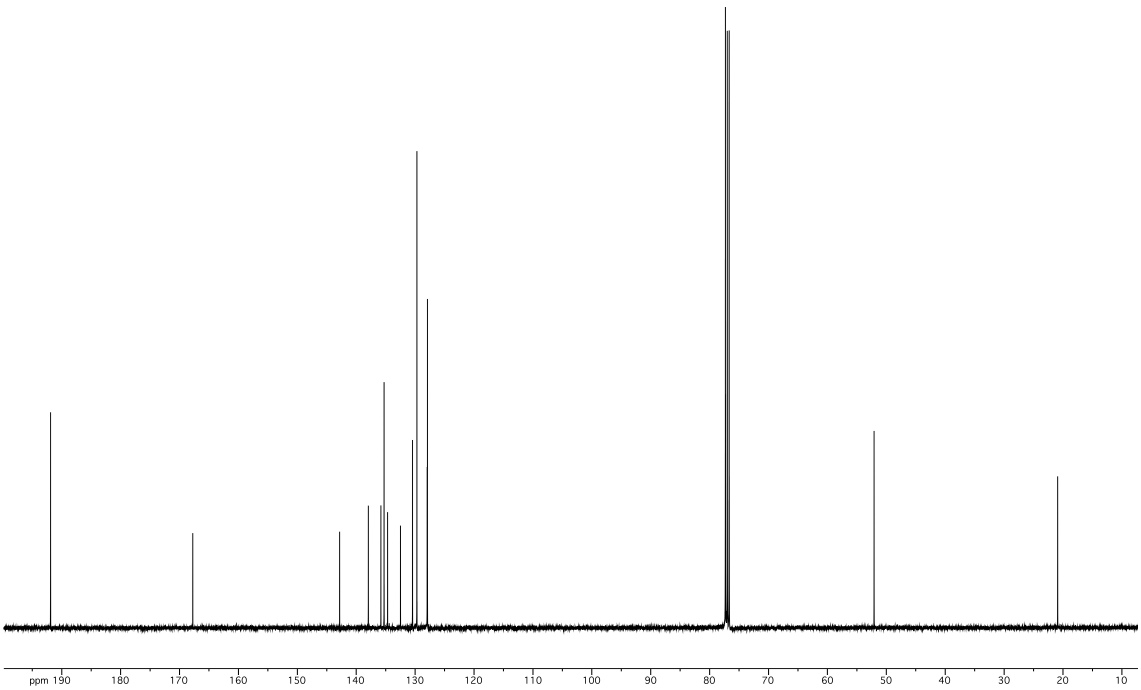




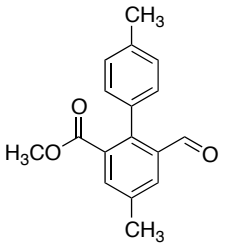
Methyl 6-formyl-4-methyl-[1,1'-biphenyl]-2-carboxylate (5l)

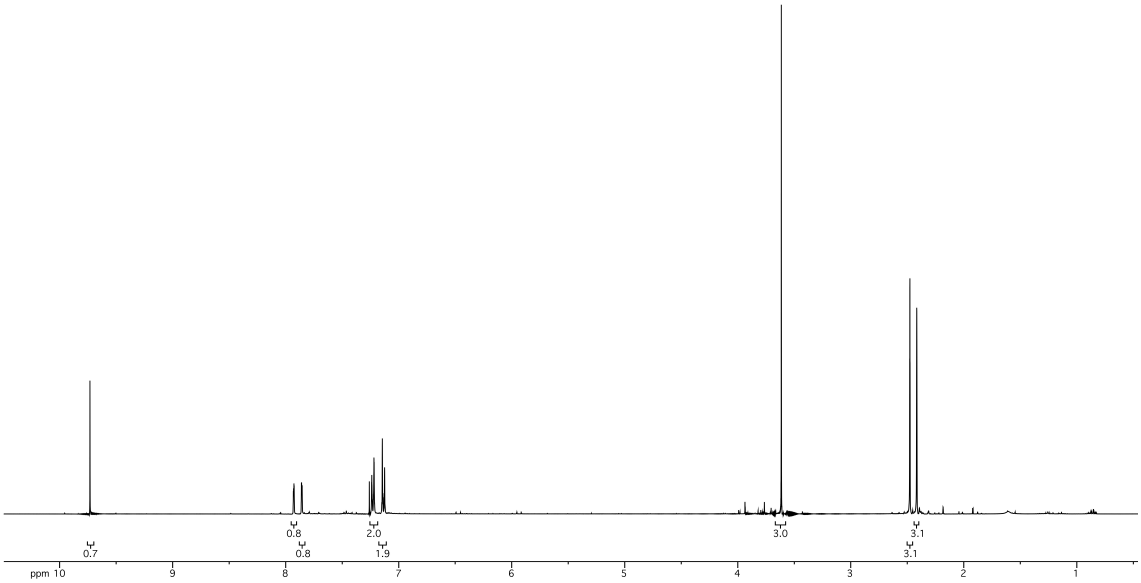


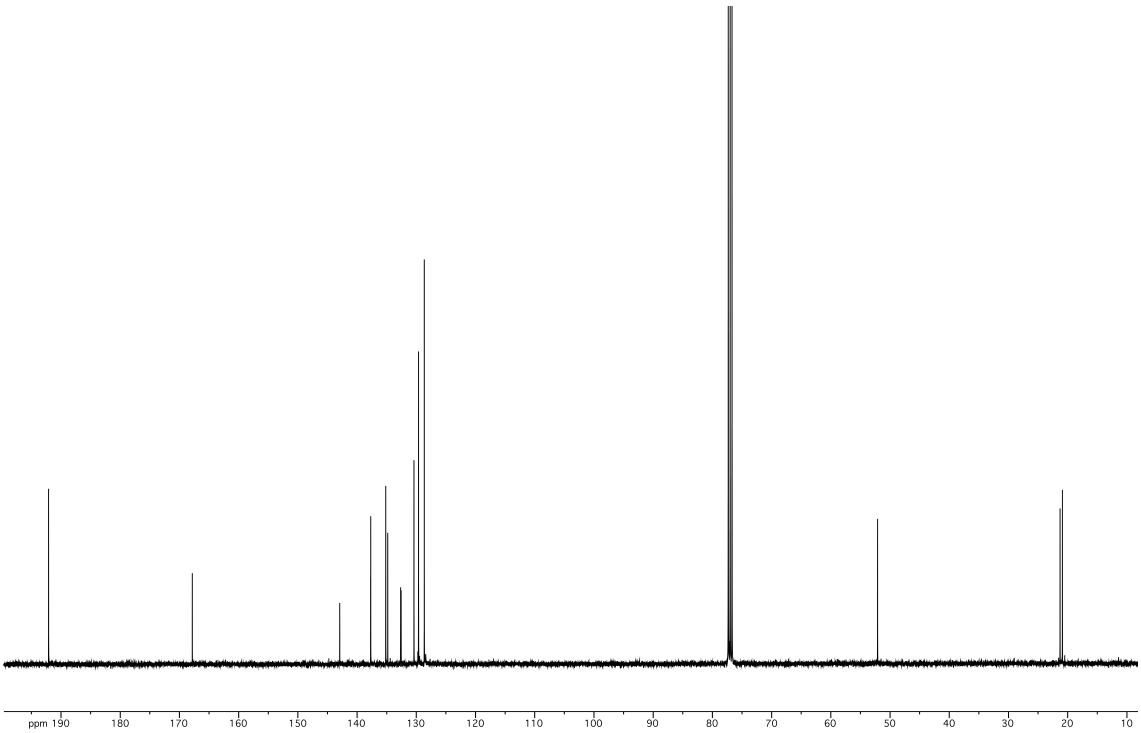




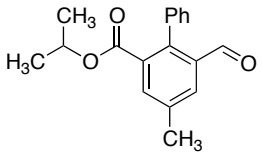
Methyl 6-formyl-4,4'-dimethyl-[1,1'-biphenyl]-2-carboxylate (5m)

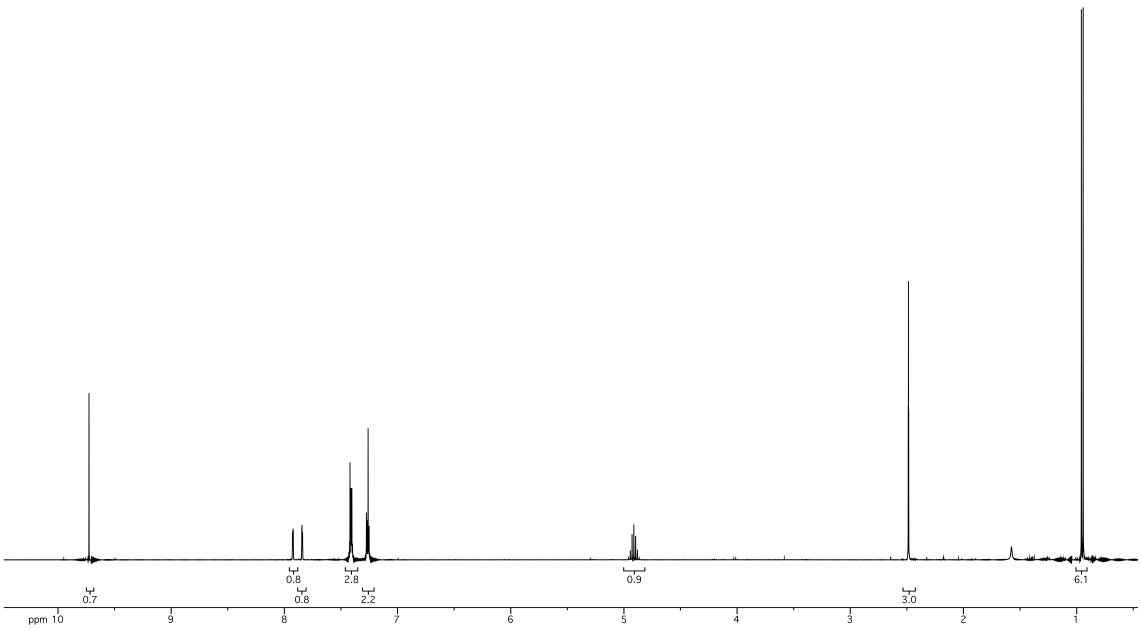


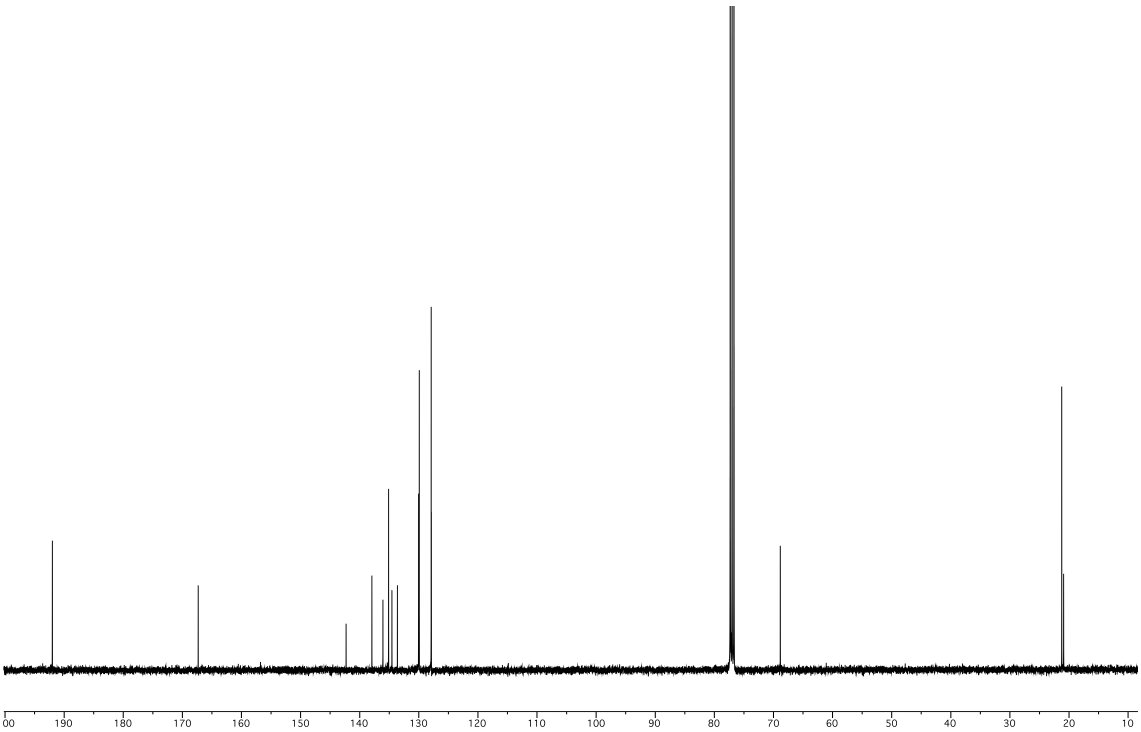




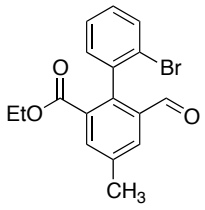
Isopropyl 6-formyl-4-methyl-[1,1'-biphenyl]-2-carboxylate (5n)

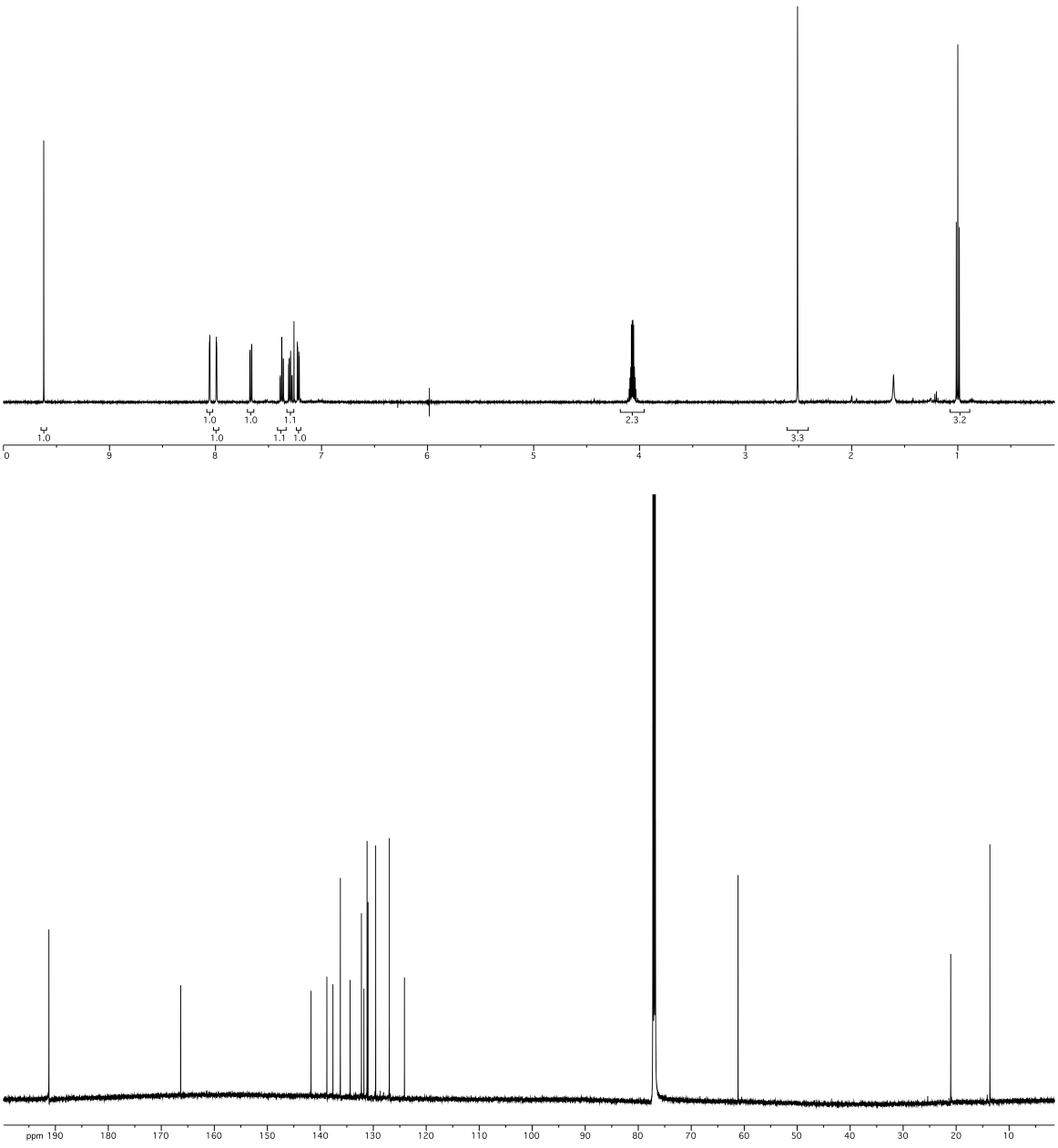


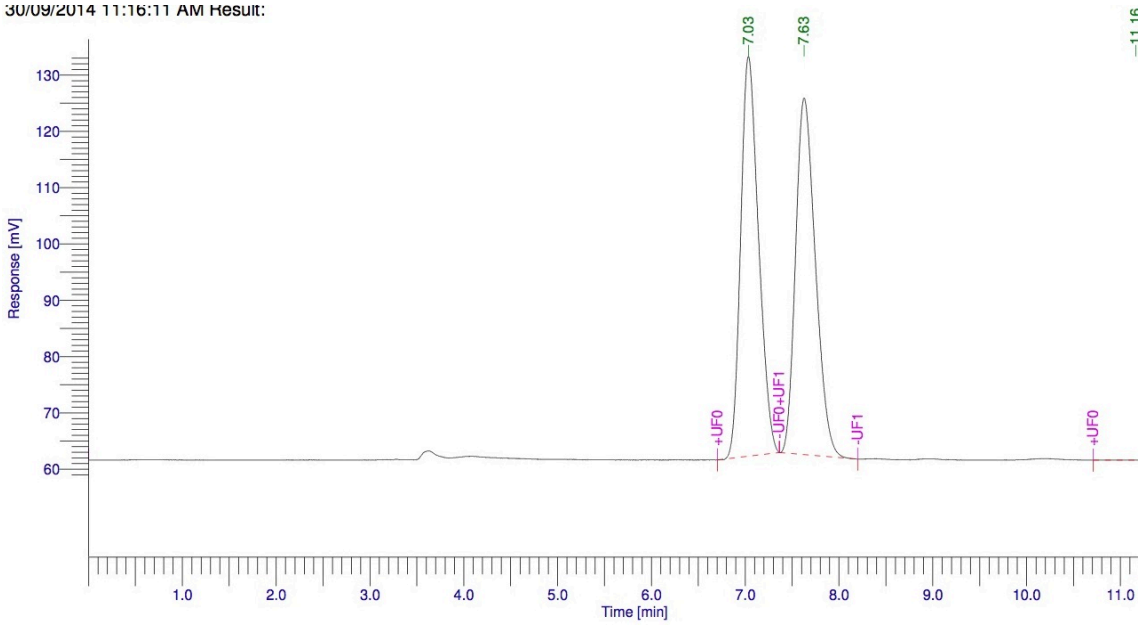




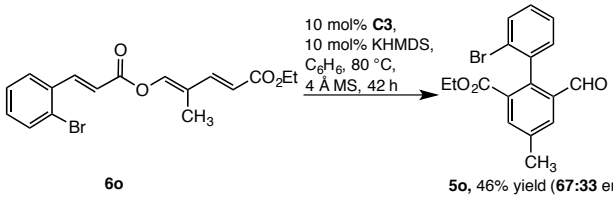
Ethyl 2'-bromo-6-formyl-4-methyl-[1,1'-biphenyl]-2-carboxylate (5o)





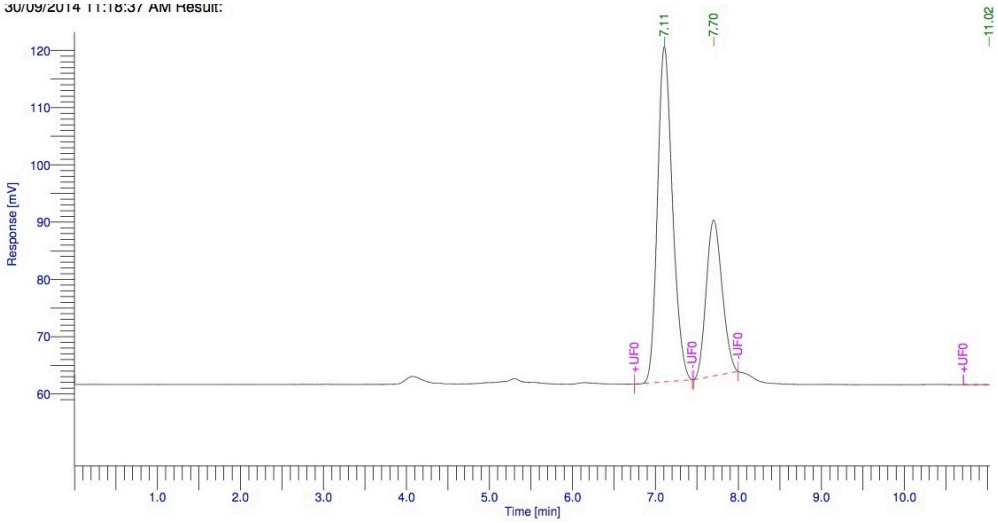


Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
7.033	937565.51	71008.55	50.20	50.20
7.627	929849.26	63305.40	49.79	49.79
11.163	116.65	16.21	0.01	0.01
	1867531.41	134330.16	100.00	100.00



6o

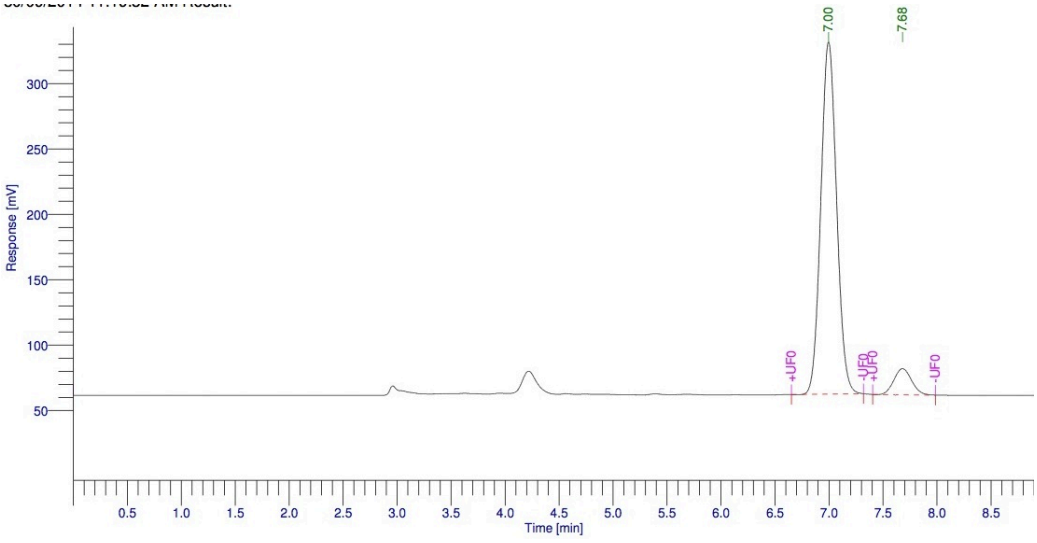
5o, 46% yield (**67:33** er)



Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
7.107	734872.93	58607.42	66.89	66.89
7.700	363511.47	27243.27	33.09	33.09
11.017	163.97	13.91	0.01	0.01
	1098548.37	85864.60	100.00	100.00

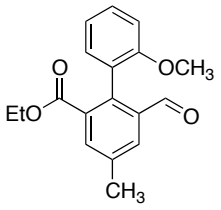
7o (**92:8** er)

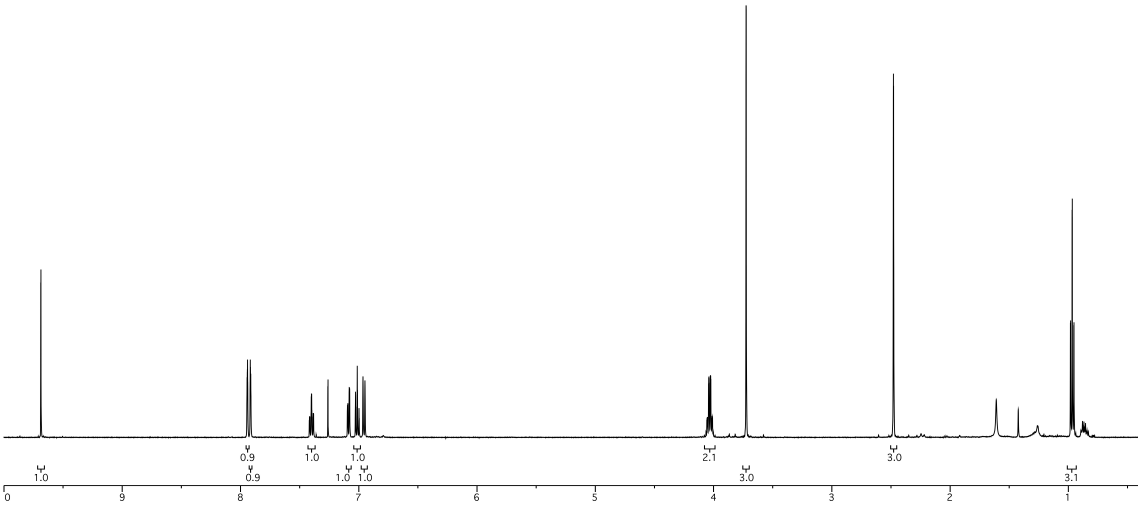
5o, 45% yield (**92:8** er)

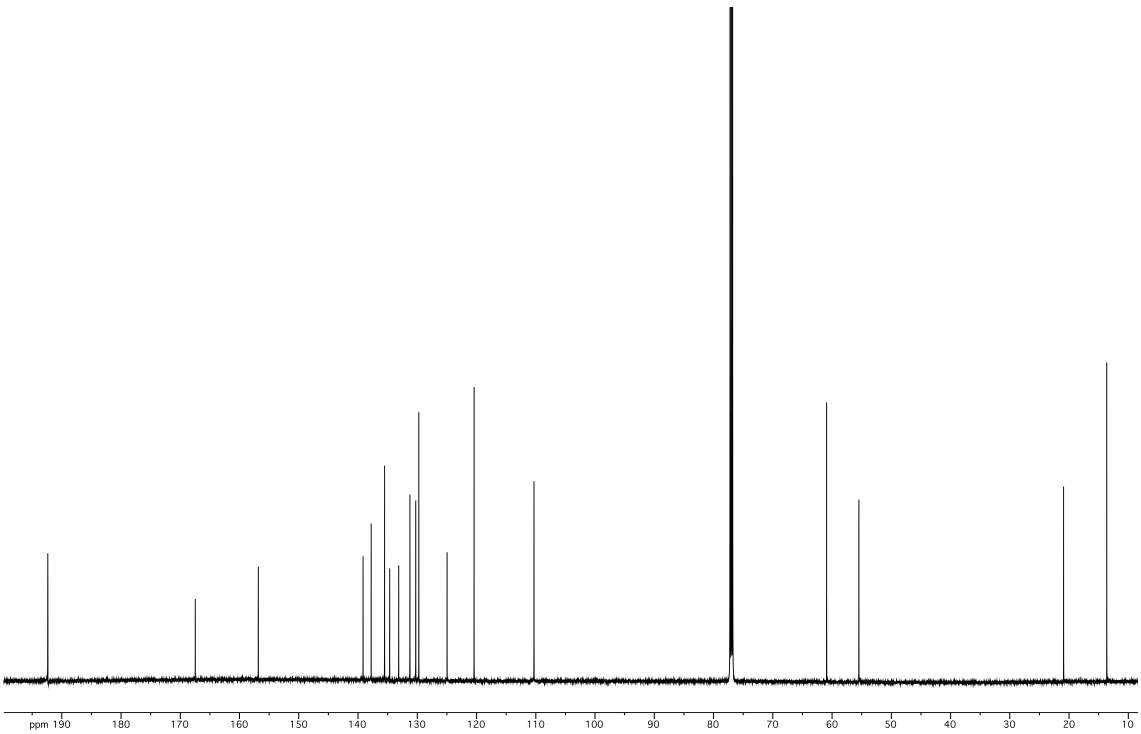


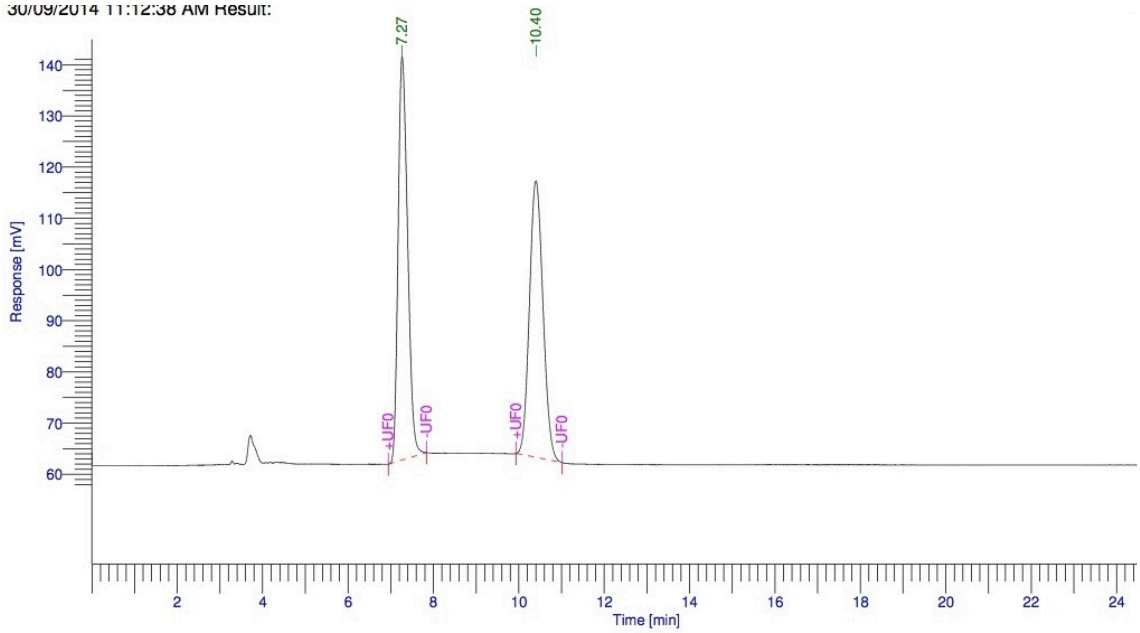
Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
6.995	2736626.39	269269.86	92.27	92.27
7.680	229180.77	20077.21	7.73	7.73
	2965807.16	289347.07	100.00	100.00

Ethyl 6-formyl-2'-methoxy-4-methyl-[1,1'-biphenyl]-2-carboxylate (5p)

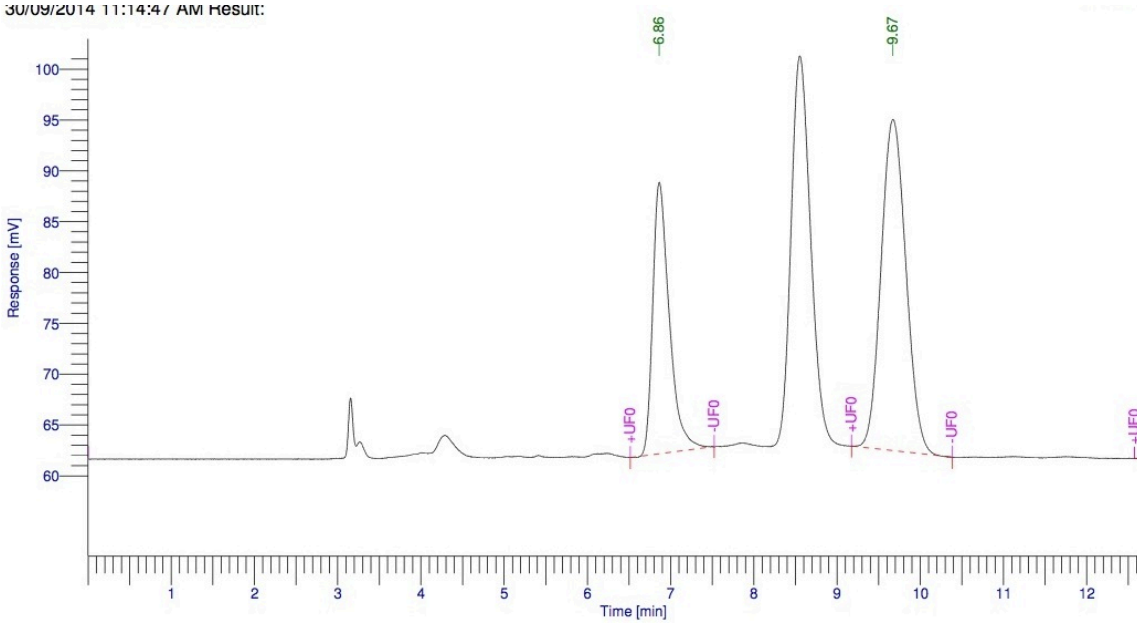








Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
7.265	1215922.11	78769.15	50.61	50.61
10.402	1186749.77	54002.24	49.39	49.39
	2402671.88	132771.39	100.00	100.00



Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
6.862	368259.71	26698.25	35.27	35.27
9.670	675737.48	32590.82	64.72	64.72
12.890	38.72	14.25	0.00	0.00
	1044035.91	59303.32	100.00	100.00