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Pentaenolate Activation in the Organocatalytic Allylic Alkylation of Indene-2-carbaldehydes

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Contents

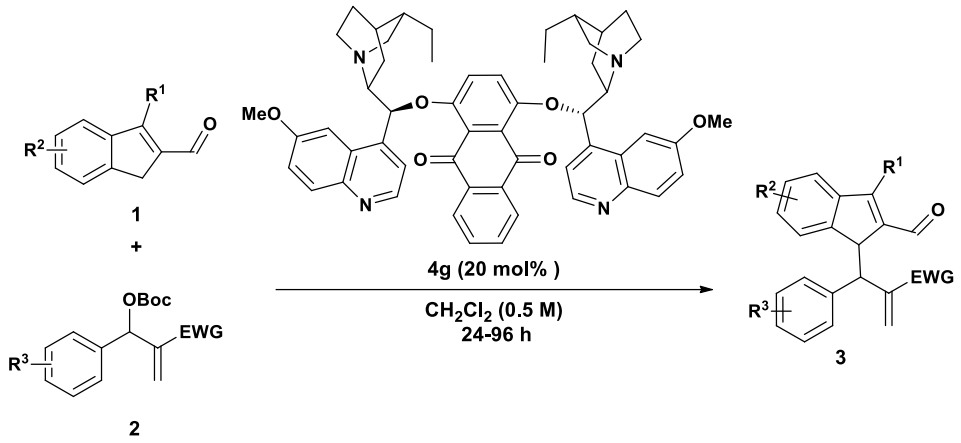
1. General methods

NMR spectra were acquired on a Bruker Ultra Shield 700 instrument, running at 700 MHz for ^{1}H and 176 MHz for ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$: 7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR). High-resolution mass spectra (HRMS) were obtained on Bruker ESI-Q-TOF Impact II spectrometer using electrospray (ESI+) ionization. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or Hanessian's stain. Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. For flash chromatography (FC) silica gel (Silica gel 60, 230-400 mesh, Fluka). The enantiomeric ratio (er) of the products were determined by Ultra Performance Convergence Chromatography (UPC^2) or HPLC using Daicel Chiralpak IA,IB,IC,IG column as chiral stationary phases. Indene-2-carbaldehydes **1** were synthesized according to the literature procedure[1]. MBH carbonates **2** were prepared from the corresponding starting materials following the literature procedure.[2]

[1] B. S. Donslund, N. I. Jessen, G. Bertuzzi, M. Giardinetti, T. A. Palazzo, M. Louise Christensen and K. A. Jørgensen, *Angew. Chem., Int. Ed*., 2018, **57**, 13182–13186.

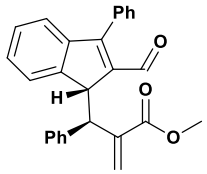
[2] N. S. Camilo, H. Santos, L. A. Zeoly, F. S. Fernandes, M. T. Rodrigues, T. S. Silva, S. R. Lima, J. C. Serafim, A. S. B. de Oliveira, A. G. Carpanez, G. W. Amarante and F. Coelho, *Eur. J. Org. Chem*. 2022, e202101448.

2. Pentaenolate activation in the allylic alkylation of indene-2-carbaldehydes 1 – general procedure



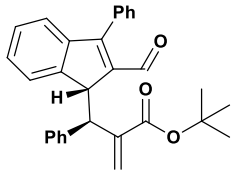
In an ordinary 4 mL glass vial equipped with a magnetic stirring, indene-2-carbaldehyde **1** (0.05 mmol, 1.0 equiv.) and MBH carbonate **2** (0.1 mmol, 2.0 equiv.) were dissolved in CH_2Cl_2 (0.1 mL) and catalyst **4g** (8.6 mg, 0.01 mmol, 0.2 equiv.) was added. The reaction mixture was stirred in room temperature for the indicated time. The progress of the reaction was controlled by ^{1}H NMR spectroscopy. After full conversion of the starting material **1**, the reaction mixture was directly subjected to column chromatography on silica gel (hexanes: diethyl ether 95:5) to afford pure product **3**.

Methyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)acrylate (3a)



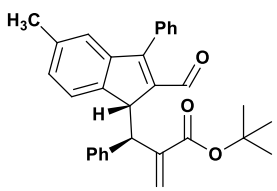
Following the general procedure product **3a** (3.5:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 67% yield (13.3 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.57 – 7.54 (m, 1H), 7.42 (td, *J* = 7.4, 1.3 Hz, 1H), 7.41 – 7.37 (m, 4H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.10 – 7.07 (m, 1H), 7.06 – 7.00 (m, 2H), 6.99 (t, *J* = 7.8 Hz, 2H), 6.46 (d, *J* = 7.2 Hz, 2H), 6.43 – 6.41 (m, 1H), 5.35 – 5.34 (m, 1H), 5.29 – 5.27 (m, 1H), 4.76 (d, *J* = 5.2 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.3, 168.2, 159.9, 146.6, 144.3, 142.6, 142.3, 137.5, 131.9, 129.4 (2C), 129.2, 128.9, 128.6 (2C), 128.6 (2C), 127.8 (2C), 127.7 (2C), 127.2, 125.8, 123.8, 52.5, 49.7, 48.0. The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 4.15 min, τ_{minor} = 3.94 min, (96:4 er). $[\alpha]_D^{21}$ = + 143,6 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{27}H_{23}O_3^+$: 395.1642; found: 395.1629.

***tert*-Butyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)acrylate (3b)**



Following the general procedure product **3b** (5:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 79% yield (17.2 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.63 (dd, *J* = 7.5, 0.6 Hz, 1H), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H), 7.41 – 7.36 (m, 4H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.08 – 7.05 (m, 1H), 7.03 (bs, 2H), 6.97 (t, *J* = 7.8 Hz, 2H), 6.45 (d, *J* = 7.2 Hz, 2H), 6.32 (dd, *J* = 1.5, 1.0 Hz, 1H), 5.27 (dd, *J* = 2.0, 0.9 Hz, 1H), 5.24 – 5.21 (m, 1H), 4.77 (d, *J* = 5.0 Hz, 1H), 1.59 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.1, 166.9, 159.6, 146.6, 144.2, 143.9, 142.6, 137.5, 131.8, 129.3 (2C), 129.0, 128.8, 128.5 (2C), 128.5 (2C) 127.5 (3C), 126.9, 126.1, 125.7, 123.5, 81.5, 49.6, 47.9, 28.2 (3C). The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 3.12 min, τ_{minor} = 3.23 min, (95:5 er). $[\alpha]_D^{21}$ = + 146,7 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{30}H_{28}O_3Na^+$: 459.1931; found: 459.1926.

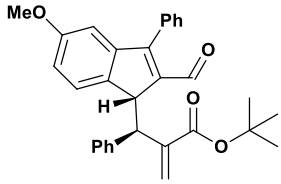
***tert*-Butyl 2-((*R*)-((*R*)-2-formyl-5-methyl-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3c)**



Following the general procedure product **3c** (5.2:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 65% yield (14.7 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.25 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.12 (s, 1H), 7.08 – 7.05 (m, 1H), 7.02 (bs, *J* = 15.6 Hz, 2H), 6.98 (t, *J* = 7.8 Hz, 2H), 6.47 (d,

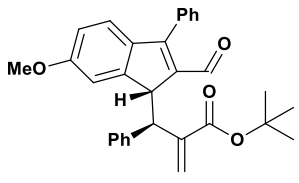
J = 7.2 Hz, 2H), 6.31 (dd, *J* = 1.5, 1.0 Hz, 1H), 5.26 (dd, *J* = 2.0, 1.0 Hz, 1H), 5.21 – 5.19 (m, 1H), 4.72 (d, *J* = 5.0 Hz, 1H), 2.39 (s, 3H), 1.59 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.2, 167.1, 159.9, 144.5, 144.1, 143.9, 143.0, 137.8, 137.5, 132.1, 130.0, 129.4 (2C), 129.1, 128.7 (2C), 128.6 (2C), 127.7 (2C), 127.0, 126.1, 125.6, 124.1, 81.6, 49.3, 48.0, 28.3 (3C), 21.6. The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 3.27 min, τ_{minor} = 3.40 min, (82:18 er). $[\alpha]_D^{21}$ = + 61,8 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{31}H_{30}O_3Na^+$: 473.2087; found: 473.2080

tert-Butyl 2-((*R*)-((*R*)-2-formyl-5-methoxy-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3d)



Following the general procedure product **3d** (6:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 50% yield (11.7 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.42 – 7.36 (m, 3H), 7.10 – 7.04 (m, 1H), 7.02 (bs, 2H), 7.01 – 6.97 (m, 3H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.48 (d, *J* = 7.2 Hz, 2H), 6.30 (dd, *J* = 1.5, 1.1 Hz, 1H), 5.26 (dd, *J* = 2.0, 1.0 Hz, 1H), 5.19 – 5.15 (m, 1H), 4.70 (d, *J* = 5.0 Hz, 1H), 3.80 (s, *J* = 4.1 Hz, 3H), 1.59 (s, *J* = 9.5 Hz, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.0, 167.0, 159.6, 159.4, 145.6, 144.0, 143.7, 138.8, 137.6, 131.8, 129.2 (2C), 129.0, 128.6 (2C), 128.5 (2C), 127.5 (2C), 126.8, 126.3, 125.9, 115.2, 108.3, 81.5, 55.5, 48.8, 47.9, 28.2 (3C). The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 3.32 min, τ_{minor} = 3.44 min, (77:23 er). $[\alpha]_D^{21}$ = + 43,1 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{31}H_{31}O_4^+$: 467.2217; found: 467.2209.

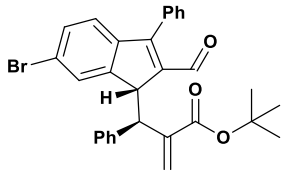
tert-Butyl 2-((*R*)-((*R*)-2-formyl-6-methoxy-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3e)



Following the general procedure product **3e** (4:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 73% yield (17.0 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.41 – 7.35 (m, 3H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.19 (d, *J* = 2.2 Hz, 1H), 7.09 – 7.06 (m, 1H), 7.00 (bs, *J* = 30.3 Hz, 2H), 6.99 (t, *J* = 7.8 Hz, 2H), 6.93 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.48 (d, *J* = 7.2 Hz, 2H), 6.30 (s, 1H), 5.26 – 5.21 (m, 2H), 4.70 (d, *J* = 5.1 Hz, 1H), 3.88 (s, 3H), 1.60 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 188.6, 167.2, 161.0, 159.9, 149.1, 144.2, 141.2, 137.6, 137.3, 132.2, 129.4 (2C), 129.1, 128.7 (2C), 128.6 (2C), 127.7 (2C), 127.0,

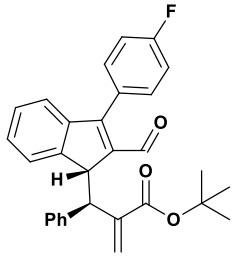
125.9, 124.6, 114.4, 111.2, 81.6, 55.7, 49.6, 48.1, 28.3 (3C). The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 3.27 min, τ_{minor} = 3.39 min, (95:5 er). $[\alpha]_D^{21}$ = + 212,9 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{31}H_{30}O_4Na^+$: 489.2036; found: 489.2034.

***tert*-Butyl 2-((*R*)-((*R*)-6-bromo-2-formyl-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3f)**



Following the general procedure product **3f** (4:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 44% yield (11.4 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.79 – 7.78 (m, 1H), 7.52 – 7.50 (m, 1H), 7.40 (ddd, *J* = 15.5, 7.4, 3.5 Hz, 3H), 7.17 (d, *J* = 8.2 Hz, 1H), 7.10 – 7.07 (m, 1H), 7.00 (t, *J* = 7.8 Hz, 2H), 6.98 (bs, *J* = 23.2 Hz, 2H), 6.48 (d, *J* = 7.1 Hz, 2H), 6.34 (dd, *J* = 1.7, 0.8 Hz, 1H), 5.32 (dd, *J* = 2.1, 0.8 Hz, 1H), 5.22 – 5.19 (m, 1H), 4.75 (d, *J* = 5.1 Hz, 1H), 1.59 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.1, 166.9, 158.7, 148.6, 143.7, 143.3, 142.6, 137.4, 131.5, 131.0, 129.4, 129.3 (2C), 129.2, 128.8 (2C), 128.6 (2C), 127.8 (2C), 127.2, 126.4, 124.7, 123.4, 81.8, 49.7, 47.9, 28.3 (3C). The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 3,27 min, τminor = 3,44 min, (96:4 er). $[\alpha]_D^{21}$ = + 173,8 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{30}H_{27}BrO_3Na^+$: 537.1036; found: 537.1024.

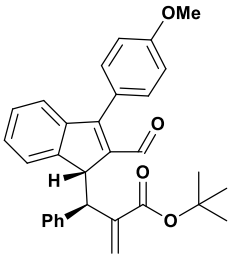
***tert*-Butyl 2-((*R*)-((*R*)-3-(4-fluorophenyl)-2-formyl-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3g)**



Following the general procedure product **3g** (4.5:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 67% yield (15.2 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.63 – 7.61 (m, 1H), 7.44 (td, *J* = 7.5, 1.1 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.11 – 7.04 (m, 3H), 6.99 (bs, *J* = 18.1 Hz, 2H), 6.97 (t, *J* = 7.8 Hz, 2H), 6.43 (d, *J* = 7.2 Hz, 2H), 6.32 (dd, *J* = 1.5, 1.0 Hz, 1H), 5.26 (dd, *J* = 2.0, 0.9 Hz, 1H), 5.21 (dd, *J* = 4.9, 1.9 Hz, 1H), 4.77 (d, *J* = 5.0 Hz, 1H), 1.60 (s, *J* = 6.2 Hz, 9H). ^{13}C NMR (176 MHz, CDCl3) δ 188.9, 167.0, 163.3 (d, *J* = 249.35 Hz), 158.5, 146.7, 144.2, 143.9, 143.0, 137.6, 131.2 (d, *J* = 8.23 Hz, 2C), 129.0, 128.7 (2C), 127.9 (d, J = 3.26 Hz), 127.8, 127.7 (2C), 127.1, 126.3, 125.9, 123.4, 115.8 (d, J = 21.66 Hz, 2C), 81.7, 49.8, 48.0, 28.3 (3C). The er was determined by HPLC using a chiral Chiralpack IA column [hexane: *i*-PrOH, 95:5] τ_{major} = 5.88

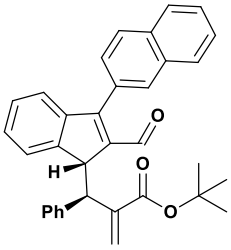
min, τ_{minor} = 5.25 min, (94:6 er); $[\alpha]_D^{21}$ = + 67,5 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{30}H_{27}FO_3Na^+$: 477.1837; found: 477.1824.

***tert*-Butyl 2-((*R*)-((*R*)-2-formyl-3-(4-methoxyphenyl)-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3h)**



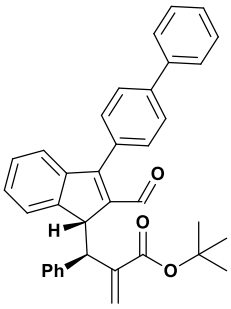
Following the general procedure product **3h** (4.6:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 69% yield (16.1 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.62 (dd, *J* = 7.5, 0.6 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.39 – 7.35 (m, 2H), 7.06 – 7.03 (m, 1H), 6.99 (bs, *J* = 7.6 Hz, 2H), 6.95 (t, *J* = 7.8 Hz, 2H), 6.92 (dd, *J* = 7.5, 1.4 Hz, 2H), 6.44 (d, *J* = 7.2 Hz, 2H), 6.33 – 6.29 (m, 1H), 5.26 (dd, *J* = 2.0, 1.0 Hz, 1H), 5.23 – 5.21 (m, 1H), 4.75 (d, *J* = 5.0 Hz, 1H), 3.83 (s, *J* = 3.4 Hz, 3H), 1.59 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.4, 167.1, 160.5, 159.5, 146.8, 144.4, 144.1, 142.2, 137.8, 130.9 (2C), 128.8, 128.7 (2C), 127.6 (2C), 127.6, 127.0, 126.1, 125.9, 124.2, 123.6, 114.2 (2C), 81.6, 55.5, 49.6, 48.0, 28.3 (3C).). The er was determined by HPLC using a chiral Chiralpack IA column [hexane: *i*-PrOH, 95:5] τ_{major} = 7.67 min, τ_{minor} = 6.94 min, (92:8 er); $[\alpha]_D^{21}$ = + 69,2 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{31}H_{30}O_4Na^+$: 489.2036; found: 489.2029.

***tert*-Butyl 2-((*R*)-((*R*)-2-formyl-3-(naphthalen-2-yl)-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3i)**



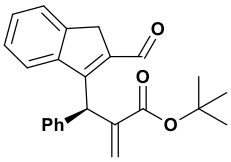
Following the general procedure product **3i** (4:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 52% yield (12.7 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.88 – 7.84 (m, 2H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.65 (dd, *J* = 7.6, 0.7 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.47 – 7.44 (m, 1H), 7.40 – 7.36 (m, 2H), 7.15 (bs, 2H), 7.12 – 7.08 (m, 1H), 7.00 (t, *J* = 7.8 Hz, 2H), 6.49 (d, *J* = 7.2 Hz, 2H), 6.34 (dd, *J* = 1.6, 0.9 Hz, 1H), 5.30 (dd, *J* = 2.0, 0.7 Hz, 1H), 5.27 – 5.24 (m, 1H), 4.83 (d, *J* = 5.0 Hz, 1H), 1.61 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.3, 167.1, 159.7, 146.7, 144.5, 144.0, 143.0, 137.7, 133.5, 133.1, 129.5, 129.2, 128.9, 128.8 (2C), 128.3, 128.3, 127.9, 127.8, 127.7 (2C), 127.1, 127.0, 126.9, 126.6, 126.3, 125.9, 123.8, 81.7, 49.8, 48.1, 28.3 (3C). The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 3.75 min, τ_{minor} = 3.96 min, (95:5 er). $[\alpha]_D^{21}$ = + 57,2 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{34}H_{30}O_3Na^+$: 509.2087; found: 509.2082.

***tert*-Butyl 2-((*R*)-((*R*)-3-([1,1'-biphenyl]-4-yl)-2-formyl-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3j)**



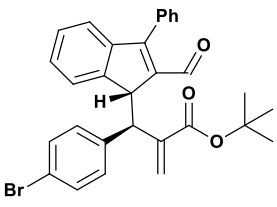
Following the general procedure product **3j** (4.5:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 58% yield (14.9 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.64 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.63 – 7.59 (m, 4H), 7.48 – 7.42 (m, 3H), 7.40 (dd, *J* = 3.7, 0.6 Hz, 2H), 7.39 – 7.36 (m, 1H), 7.12 (bs, *J* = 8.4 Hz, 2H), 7.09 – 7.06 (m, 1H), 6.98 (t, *J* = 7.8 Hz, 2H), 6.47 (d, *J* = 7.2 Hz, 2H), 6.33 (dd, *J* = 1.5, 0.9 Hz, 1H), 5.28 (dd, *J* = 2.0, 0.8 Hz, 1H), 5.26 – 5.23 (m, 1H), 4.80 (d, *J* = 5.0 Hz, 1H), 1.60 (s, *J* = 8.1 Hz, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.2, 167.1, 159.3, 146.8, 144.3, 144.0, 142.8, 142.1, 140.4, 137.7, 130.9, 130.0 (2C), 129.1 (2C), 128.9, 128.7 (2C), 127.9, 127.7, 127.7 (2C), 127.3 (2C), 127.2 (2C), 127.0, 126.2, 125.9, 123.7, 81.7, 49.8, 48.1, 28.3 (3C). The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 3.97 min, τ_{minor} = 4.15 min, (94.5:5.5 er). $[\alpha]_D^{21}$ = + 58,8 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{36}H_{33}O_3^+$: 513.2424; found: 513.2420.

(S)-*tert*-Butyl 2-((2-formyl-1*H*-inden-3-yl)(phenyl)methyl)acrylate (3k')



Following the general procedure product **3k'** was isolated in 48% yield (8.7mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.36 (td, *J* = 7.4, 0.9 Hz, 1H), 7.34 – 7.31 (m, 2H), 7.29 (d, *J* = 7.9 Hz, 3H), 7.28 – 7.24 (m, 1H), 6.39 (s, *J* = 6.4 Hz, 1H), 5.89 (s, 1H), 5.32 (d, *J* = 0.9 Hz, 1H), 3.71 (d, *J* = 2.3 Hz, 2H), 1.31 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 188.5, 165.7, 157.7, 144.4, 144.1, 143.8, 141.2, 139.4, 129.1 (2C), 128.9 (2C), 128.9, 127.6, 127.2, 127.1, 124.7, 123.7, 81.7, 45.9, 36.5, 27.9 (3C). The er was determined by HPLC using a chiral Chiralpack IB column [hexane: *i*-PrOH, 95:5] τ_{major} = 11.99 min, τ_{minor} = 20.45 min, (90:10 er); $[\alpha]_D^{21}$ = + 72,4 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{24}H_{24}O_3Na^+$: 383.1618; found: 383.1611.

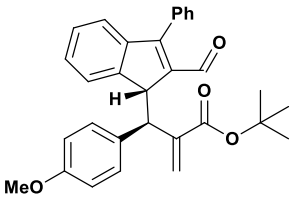
***tert*-Butyl 2-((*R*)-(4-bromophenyl)((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)methyl)acrylate (3l)**



Following the general procedure product **3l** (4.9:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 66% yield (17.0 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.60 (dd, *J* = 7.5, 0.6 Hz, 1H), 7.45 – 7.41 (m, 4H), 7.39 (dd, *J* = 11.1,

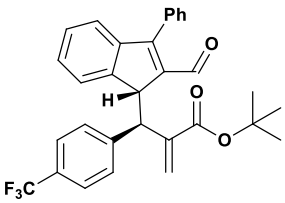
3.7 Hz, 1H), 7.36 (dd, *J* = 4.2, 3.4 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 2H), 7.08 (bs, *J* = 29.4 Hz, 2H), 6.34 (t, *J* = 5.4 Hz, 2H), 6.33 – 6.32 (m, 1H), 5.23 – 5.22 (m, 1H), 5.21 – 5.21 (m, 1H), 4.75 (d, *J* = 4.9 Hz, 1H), 1.59 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.3, 166.8, 160.0, 146.3, 144.2, 143.7, 142.3, 136.8, 131.8, 130.8 (2C), 130.4 (2C), 129.4 (2C), 129.3, 129.1, 128.8 (2C), 127.9, 126.2, 125.8, 123.9, 120.9, 81.8, 49.5, 47.4, 28.3 (3C). The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 3.17 min, τ_{minor} = 3.32 min, (94:6 er). $[\alpha]_D^{21}$ = + 122,6 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{30}H_{27}BrO_3Na^+$: 537.1036; found: 537.1018.

tert-butyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(4-methoxyphenyl)methyl)-acrylate (3m)



Following the general procedure product **3m** (5:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 51% yield (11.9 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.44 – 7.32 (m, 6H), 7.14 – 7.00 (m, 2H), 6.51 (d, *J* = 8.7 Hz, 2H), 6.36 (d, *J* = 8.4 Hz, 2H), 6.30 (s, 1H), 5.23 (s, 1H), 5.19 (d, *J* = 5.0 Hz, 1H), 4.74 (d, *J* = 5.0 Hz, 1H), 3.67 (s, 3H), 1.60 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.3, 167.2, 159.7, 158.6, 146.8, 144.5, 144.3, 142.8, 132.0, 129.9, 129.6 (2C), 129.5 (2C), 129.2, 128.9, 128.6 (2C), 127.6, 126.1, 125.9, 123.7, 113.1 (2C), 81.6, 55.3, 49.9, 47.2, 28.3 (3C). The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 3,27 min, τminor = 3,46 min, (95:5 er). $[\alpha]_D^{21}$ = + 107,5 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{31}H_{31}O_4^+$: 467.2217; found: 467.2218.

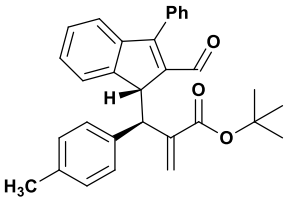
tert-butyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(4-(trifluoromethyl)phenyl)-methyl)acrylate (3n)



Following the general procedure product **3n** (4:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 73% yield (18.4 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.64 – 7.62 (m, 1H), 7.46 (td, *J* = 7.5, 1.2 Hz, 1H), 7.41 (ddd, *J* = 13.7, 9.2, 5.8 Hz, 4H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.00 (bs, *J* = 11.4 Hz, 2H), 6.58 (d, *J* = 8.0 Hz, 2H), 6.35 (d, *J* = 1.2 Hz, 1H), 5.33 (dd, *J* = 4.7, 1.9 Hz, 1H), 5.20 (d, *J* = 1.6 Hz, 1H), 4.79 (d, *J* = 5.0 Hz, 1H), 1.60 (s, 9H) ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.3, 166.6, 160.1, 146.1, 144.2, 143.3, 142.1, 141.9, 131.6, 129.4 129.4 (q, *J* = 32.4 Hz),, 129.3 (2C), 129.2, 129.0 (2C), 128.7 (2C), 128.0, 126.4, 125.8, 124.6 (d, *J* = 3.7 Hz, 2C), 124.2 (q, *J* = 272.0 Hz),

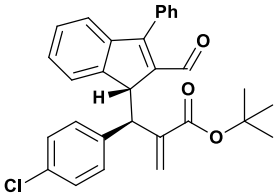
124.0, 82.0, 49.5, 47.7, 28.3 (3C). The er was determined by HPLC using a chiral Chiralpack IA column [hexane: *i*-PrOH, 95:5] τ_{major} = 5.28 min, τ_{minor} = 4.85 min, (95:5 er); $[\alpha]_D^{21}$ = + 89,5 (c = 1.0, CHCl3). HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{31}H_{27}F_3O_3Na^+$: 527.1805; found: 527.1794.

***tert*-Butyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(p-tolyl)methyl)acrylate (3o)**



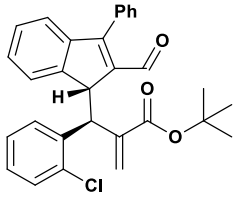
Following the general procedure product **3o** (4:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 55% yield (12.4 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.61 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.43 (td, *J* = 7.4, 1.3 Hz, 1H), 7.41 – 7.36 (m, 4H), 7.35 – 7.32 (m, 1H), 7.05 (bs, *J* = 44.1 Hz, 2H), 6.78 (d, *J* = 7.8 Hz, 2H), 6.32 (d, *J* = 7.9 Hz, 2H), 6.30 – 6.29 (m, 1H), 5.24 (dd, *J* = 2.0, 1.1 Hz, 1H), 5.21 – 5.18 (m, 1H), 4.75 (d, *J* = 5.0 Hz, 1H), 2.18 (s, 3H), 1.61 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.2, 167.2, 159.6, 146.8, 144.3, 144.3, 142.9, 136.5, 134.6, 132.1, 129.5 (2C), 129.1, 128.8, 128.6 (2C), 128.5 (2C), 128.4 (2C), 127.6, 126.2, 125.8, 123.6, 81.6, 49.8, 47.6, 28.3 (3C), 21.05. The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 3.18 min, τ_{minor} = 3.36 min, (96:4 er). $[\alpha]_D^{21}$ = + 120,9 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{31}H_{31}O_3^+$: 451.2268; found: 451.2279.

***tert*-Butyl 2-((*R*)-(4-chlorophenyl)((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)methyl)acrylate (3p)**



Following the general procedure product **3p** (4.9:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 51% yield (12.0 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.61 (dd, J = 7.5, 0.6 Hz, 1H), 7.45 – 7.41 (m, 4H), 7.39 (t, J = 7.2 Hz, 1H), 7.35 (d, J = 7.3 Hz, 1H), 7.08 (bs, J = 22.4 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 6.40 (d, J = 8.4 Hz, 2H), 6.33 (dd, J = 5.0, 4.4 Hz, 1H), 5.24 – 5.23 (m, 1H), 5.22 – 5.21 (m, 1H), 4.75 (d, J = 4.9 Hz, 1H), 1.59 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.3, 166.8, 160.0, 146.3, 144.2, 143.7, 142.3, 136.3, 132.8, 131.8, 130.0 (2C), 129.4(2C), 129.3, 129.1, 128.8 (2C), 127.9, 127.9 (2C), 126.2, 125.8, 123.9, 81.8, 49.6, 47.3, 28.3 (3C). The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 3.04 min, τ_{minor} = 3.20 min, (96:4 er). $[\alpha]_D^{21}$ = + 109,6 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z [M+Na]+ Calcd. for $C_{30}H_{27}ClO_3Na+$: 493.1541; found: 493.1537.

***tert*-Butyl 2-((*S*)-(2-chlorophenyl)((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)methyl)acrylate (3q)**

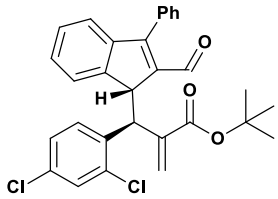


Following the general procedure product **3q** (1.5:1 dr in a crude reaction mixture) was isolated as a 1.4:1 mixture of diastereoisomers (DiaA +DiaB) in 58% yield (13.7 mg) as light-yellow oil.

Major diastereoisomer A ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.64 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.55 – 7.16 (m, 9H), 6.98 (td, *J* = 7.7, 1.6 Hz, 1H), 6.72 (td, *J* = 7.7, 1.2 Hz, 1H), 6.41 (d, *J* = 0.8 Hz, 1H), 6.24 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.77 – 5.74 (m, 1H), 5.34 (d, *J* = 1.3 Hz, 1H), 4.82 (d, *J* = 4.6 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 188.9, 166.5, 158.7, 156.5, 146.7, 144.0, 143.7, 142.6, 134.6, 132.0, 129.8, 129.5 (2C), 129.3, 129.2, 128.9, 128.8 (2C), 127.9, 127.8, 126.1, 126.0, 125.6, 123.8, 81.7, 48.6, 43.4, 28.2 (3C). The er was determined by HPLC using a chiral Chiralpack IG column [hexane: *i*-PrOH, 95:5] τ_{major} = 11.50 min, τ_{minor} = 8.83 min, (94:6 er);

Minor diastereoisomer B (diagnostic signals): ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.88 (s, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 6.12 (s, 1H), 5.89 (d, *J* = 5.4 Hz, 1H), 4.75 (t, *J* = 1.1 Hz, 1H), 4.72 (d, *J* = 5.6 Hz, 1H), 1.29 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.2, 165.7, 159.3, 147.0, 143.5, 140.6, 138.9, 136.8, 134.9, 132.1, 130.6, 130.2, 129.7 (2C), 129.5, 128.9 (2C), 128.9, 128.4, 127.6, 126.3, 125.9, 125.0, 123.8, 81.0, 49.2, 42.6, 27.9 (3C).The er was determined by HPLC using a chiral Chiralpack IG column [hexane: *i*-PrOH, 95:5] τ_{major} = 12.41 min, τ_{minor} = 14.85 min, (93:7 er); HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{30}H_{28}ClO_3^+$: 471.1721; found: 471.1724.

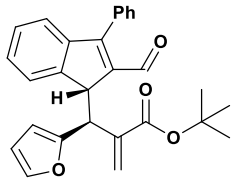
***tert*-Butyl 2-((*S*)-(2,4-dichlorophenyl)((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)methyl)-acrylate (3r)**



Following the general procedure product (**3r**) (1.6:1 dr in a crude reaction mixture) was isolated as a 1.8:1 mixture of diastereoisomers in 77% yield (19.5 mg) as light-yellow oil. Major diastereoisomer A ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.64 – 7.60 (m, 1H), 7.57 – 7.21 (m, 9H), 6.72 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.44 – 6.40 (m, 1H), 6.17 (d, *J* = 8.5 Hz, 1H), 5.74 (dt, *J* = 4.4, 1.7 Hz, 1H), 5.32 – 5.27 (m, 1H), 4.80 (d, *J* = 4.6 Hz, 1H), 1.50 (s. 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 188.9, 166.2, 159.0, 146.4, 143.9, 143.3, 142.2, 137.6, 135.5, 135.40, 133.0, 131.8, 129.9, 129.7, 129.6, 129.5 (2C), 129.0, 128.9(2C), 128.0, 126.1, 126.0, 124.0, 81.9, 48.5, 42.9, 28.2 (3C). The er was determined by HPLC using a chiral Chiralpack IG column [hexane: *i*-PrOH, 95:5] τ_{major} = 9.67 min, τ_{minor} = 7.30 min, (95:5 er);

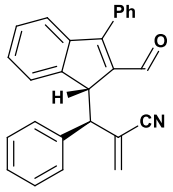
Minor diastereoisomer B (diagnostic signals): ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.87 (s,1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.70 – 6.67 (m, 1H), 6.12 (s, 1H), 5.83 (d, *J* = 5.4 Hz, 1H), 4.75 (t, *J* = 1.1 Hz, 1H), 4.65 (d, *J* = 5.5 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.1, 165.5, 159.5, 146.7, 143.5, 142.2, 140.2, 135.6, 133.4, 131.9, 131.4, 130.0, 129.5, 129.5 (2C), 129.0, 128.9 (2C), 127.8, 126.5, 126.2, 125.7, 125.3, 124.0, 81.2, 49.0, 42.2, 27.9 (3C). The er was determined by HPLC using a chiral Chiralpack IG column [hexane: *i*-PrOH, 95:5] τ_{major} = 22.15 min, τ_{minor} = 7.30 min, (95:5 er). HRMS (ESI) m/z [M+Na]+ Calcd. for $C_{30}H_{26}ClO_3Na^+$: 527.1151; found: 527.1149.

tert-Butyl 2-((*S*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(furan-2-yl)methyl)acrylate (3s)



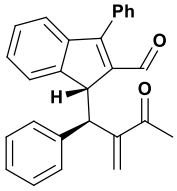
Following the general procedure product **3s** (1.2:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 30% yield (6.4 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.51 (dd, *J* = 5.7, 2.9 Hz, 1H), 7.48 – 7.44 (m, 4H), 7.42 – 7.37 (m, 4H), 7.06 (dd, *J* = 1.8, 0.7 Hz, 1H), 6.38 (t, *J* = 1.0 Hz, 1H), 6.04 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.44 (d, *J* = 4.8 Hz, 1H), 5.29 – 5.28 (m, 1H), 5.26 (d, *J* = 3.0 Hz, 1H), 4.60 (d, *J* = 4.8 Hz, 1H), 1.63 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.0, 166.2, 159.9, 152.3, 146.6, 144.1, 142.0, 142.0, 141.0, 132.0, 129.6 (2C), 129.3, 128.7, 128.7 (2C), 127.7, 127.0, 125.8, 123.6, 109.8, 106.9, 81.8, 49.0, 41.8, 28.4 (3C). The er was determined by HPLC using a chiral Chiralpack IC column [hexane: *i*-PrOH, 95:5] τ_{major} = 11.98 min, τ_{minor} = 13.7 min, (71:29 er); $[\alpha]_D^{21}$ = + 29,6 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{28}H_{26}O_4Na^+$: 449.1723; found:449.1724.

2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)acrylonitrile (3t)



Following the general procedure product **3t** (2.2:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 51% yield (9.2 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.81 (dt, *J* = 3.9, 2.0 Hz, 1H), 7.49 (td, *J* = 7.5, 1.1 Hz, 1H), 7.46 – 7.37 (m, 5H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.00 (dd, *J* = 10.7, 4.9 Hz, 3H), 6.45 (dd, *J* = 8.2, 1.1 Hz, 2H), 6.19 (d, *J* = 2.4 Hz, 1H), 5.57 (d, *J* = 2.5 Hz, 1H), 4.97 (dt, *J* = 4.9, 2.4 Hz, 1H), 4.77 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.3, 160.7, 145.4, 144.3, 141.2, 134.4, 133.0, 131.5, 129.5, 129.4, 129.4 (2C), 128.8 (2C), 128.7 (2C), 128.3, 128.1 (2C), 128.1, 125.7, 125.5, 124.0, 119.1, 50.2, 50.1. The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 3.40 min, τ_{minor} = 3.50 min, (88:12 er). $[\alpha]_D^{21}$ = - 48,9 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{26}H_{20}NO^+$: 362.1539; found: 362.1541.

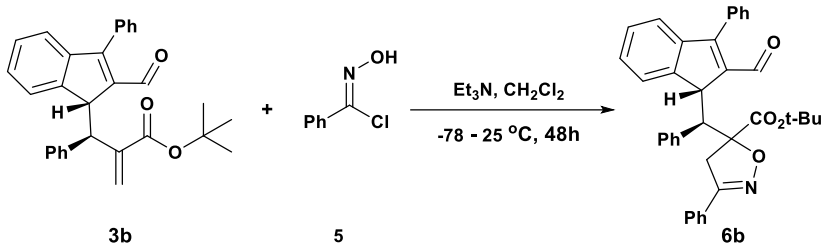
(*R*)-1-((*R*)-2-methylene-3-oxo-1-phenylbutyl)-3-phenyl-1*H*-indene-2-carbaldehyde (3u)



Following the general procedure product **3u** (1.7:1 dr in a crude reaction mixture) was isolated as a single diastereoisomer in 43% yield (9.2 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.42 – 7.34 (m, 7H), 7.09 (s, *J* = 14.9 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.7 Hz, 2H), 6.49 (d, *J* = 7.2 Hz, 2H), 6.29 (d, *J* = 1.1 Hz, 1H), 5.57 (d, *J* = 1.8 Hz, 1H), 5.28 (d, *J* = 5.3 Hz, 1H), 4.74 (d, *J* = 5.4 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 200.0, 189.3, 159.8, 150.4, 146.9, 144.3, 142.9, 138.1, 132.0, 129.5 (2C), 129.2, 128.7 (2C), 128.7, 128.6 (2C), 127.9 (2C), 127.7, 127.7, 127.1, 125.5, 123.8, 49.6, 47.0, 27.3. The er was determined by UPC^2 using a chiral Chiralpack IC column gradient from 100% CO_2 up to 40%; *i*-PrOH, flow rate = 2.2 mL/min τ_{major} = 5.35 min, τ_{minor} = 4.85 min, (94:6 er). $[\alpha]_D^{21}$ = 79,3 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{27}H_{23}O_2^+$: 379.1692; found:379.1699.

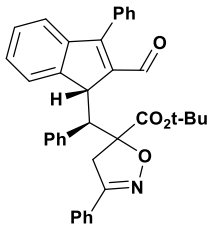
3. Selective transformations of products 3

3.1 Selective dipolar [3+2]-cycloaddition of the aldehyde 3b with imidoyl chloride 5



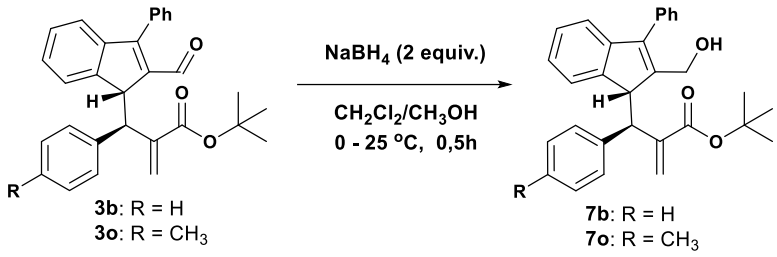
In an ordinary 4 mL glass, flame-dried vial equipped with a magnetic stirring bar the *N*-hydroxybenzimidoyl chloride **7** (0.065 mmol, 1.0 equiv.) was dissolved in anhydrous CH_2Cl_2 (0.5 mL) and cooled to –78 °C via a dry ice/acetone bath. Then Et_3N (0.065 mmol, 1.0 equiv.) was added and the reaction mixture was stirred for 10 minutes at this temperature. Next, **3b** (34 mg, 0.078 mmol) dissolved in CH_2Cl_2 (150 μl) was added dropwise via syringe, and the reaction was warmed slowly to room temperature and stirred for 48h. After full conversion of the starting material **3b** (as confirmed by ^{1}H NMR spectroscopy), the reaction mixture was directly subjected to column chromatography on silica gel (eluent: hexanes/diethyl ether 80:20) to afford pure product **6b** in 90% yield (32.5 mg) as light-yellow oil.

***tert*-Butyl 5-((*R*)-((*R*)-2-formyl-3-phenyl-1H-inden-1-yl)(phenyl)methyl)-3-phenyl-4,5-dihydroisoxazole-5-carboxylate (6b)**



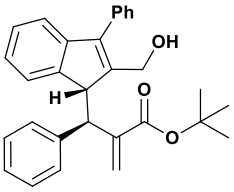
^{1}H NMR (700 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.38 (ddd, *J* = 199.3, 7.7, 0.9 Hz, 1H), 7.83 (ddd, *J* = 5.8, 3.0, 1.4 Hz, 2H), 7.49 – 7.42 (m, 6H), 7.38 (td, *J* = 7.5, 1.2 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.14 (td, *J* = 7.5, 1.2 Hz, 1H), 7.05 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.94 – 6.90 (m, 3H), 4.62 (d, *J* = 18.2 Hz, 1H), 4.48 (d, *J* = 1.4 Hz, 1H), 4.32 (s, 1H), 3.98 (d, *J* = 18.2 Hz, 1H), 1.06 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 189.6, 170.2, 161.6, 156.5, 146.2, 143.2, 141.7, 136.0, 131.7, 130.4, 129.5 (2C), 129.4 (2C), 129.3, 129.3, 129.0, 128.9, 128.8 (2C), 128.6 (2C), 127.2, 127.0 (2C), 126.8 (2C), 126.6, 123.0, 91.6, 82.3, 51.7, 47.6, 46.0, 27.3 (3C). $[\alpha]_D^{21}$ = -173,5 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+H]^+$ Calcd. For $C_{37}H_{34}NO_4^+$: 556.2482; found:556.2481.

3.2. Selective reduction of aldehydes 3b,o



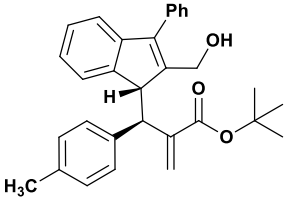
In an ordinary 4 mL glass vial equipped with a magnetic stirring bar, the aldehyde **3b** or **3o** (0.05 mmol, 1.0 equiv.) was dissolved in the mixture of CH_2Cl_2 (0.1 mL) and MeOH (0.1 mL). Then $NaBH_4$ (0,1 mmol, 2.0 equiv.) was added and the reaction mixture was stirred in room temperature for 30 minutes. After full conversion of the starting material **3b** or **3o** (as confirmed by TLC analysis), the reaction mixture was directly subjected to column chromatography on silica gel (eluent: hexanes/ethyl acetate 80:20) to afford pure product **7b** or **7o.**

***tert*-Butyl 2-((*R*)-((*R*)-2-(hydroxymethyl)-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (7b)**



Following the general procedure product **7b** was isolated as a single diastereoisomer in 87% yield (19.1 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.4, 0.6 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.33 – 7.30 (m, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.22 – 7.17 (m, 2H)., 7.13 – 7.10 (m, 1H), 7.09 – 7.05 (m, 4H), 6.74 – 6.69 (m, 2H), 6.32 (d, *J* = 1.0 Hz, 1H), 5.23 – 5.21 (m, 1H), 4.81 (d, *J* = 5.2 Hz, 1H), 4.52 (d, *J* = 5.2 Hz, 1H), 4.41 (d, *J* = 13.1 Hz, 1H), 4.31 (d, *J* = 13.1 Hz, 1H), 1.62 (s, *J* = 9.0 Hz, 1H), 1.57 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 167.0, 145.7, 144.9, 144.9, 144.2, 142.1, 138.8, 134.5, 129.1 (2C), 128.8 (2C), 128.5 (2C), 128.1 (2C), 127.7, 127.1, 127.0, 126.5, 125.1, 124.9, 120.8, 81.6, 58.4, 50.7, 47.8, 28.3 (3C). $[\alpha]_D^{21}$ = 123,7 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. $C_{30}H_{30}O_3Na^+$: 461.2087; found:461.2096.

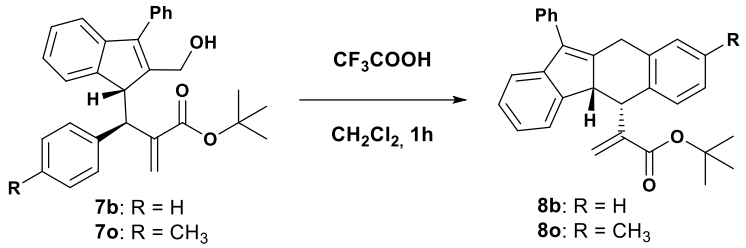
***tert*-Butyl 2-((*R*)-((*R*)-2-(hydroxymethyl)-3-phenyl-1H-inden-1-yl)(*p*-tolyl)methyl)-acrylate (7o)**



Following the general procedure product **7o** was isolated as a single diastereoisomer in 89% yield (20.1 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 10.8, 3.6 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.33 (ddt, *J* = 5.9, 4.7, 2.4 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.24 – 7.20 (m, 2H), 7.11 (d, *J* = 7.1 Hz, 2H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.62 (d, *J* = 8.1 Hz, 2H), 6.32

(d, *J* = 1.0 Hz, 1H), 5.24 – 5.22 (m, 1H), 4.80 (d, *J* = 5.2 Hz, 1H), 4.51 (d, *J* = 5.2 Hz, 1H), 4.42 (d, *J* = 13.1 Hz, 1H), 4.33 (d, *J* = 13.1 Hz, 1H), 2.24 (s, 3H), 1.83 (s, 1H), 1.57 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 167.0, 145.6, 145.1, 145.0, 144.3, 142.0, 136.5, 135.7, 134.5, 129.1 (2C), 128.8 (2C), 128.6 (2C), 128.5 (2C), 127.6, 126.9, 126.5, 125.0, 124.8, 120.8, 81.6, 58.3, 50.8, 47.3, 28.3 (3C), 21.1. $[\alpha]_D^{21}$ = 176,8 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. $C_{31}H_{32}O_3Na^+$: 475.2244; found:475.2243.

3.3. Selective cyclization of alcohols 7b,o

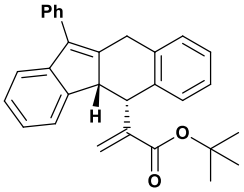


7b: R = H
7o: R = CH_3

8b: R = H
8o: R = CH_3

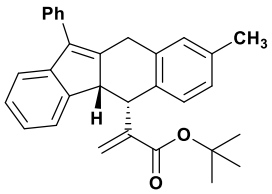
In an ordinary 4 mL glass vial equipped with a magnetic stirring bar, the alcohol **7b** or **7o** (0.05 mmol, 1.0 equiv.) was dissolved in the CH_2Cl_2 (2.5 mL). Then CF_3COOH (0.13 mmol, 2.6 equiv.) was added and the reaction mixture was stirred in room temperature for 1 hour. After full conversion of the starting material **7b** or **7o** (as confirmed by TLC analysis), the reaction mixture was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: hexanes/ diethyl ether 95:5) to afford pure product **8b** or **8o.**

***tert*-Butyl 2-((4b*S*,5*R*)-11-phenyl-5,10-dihydro-4bH-benzo[b]fluoren-5-yl)acrylate (8b)**



Following the general procedure product **8b** was isolated as a single diastereoisomer in 60% yield (12.6 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.56 (dq, *J* = 7.4, 0.9 Hz, 1H), 7.50 (tt, *J* = 7.4, 1.6 Hz, 2H), 7.47 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.25 – 7.19 (m, 5H), 7.17 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.13 (td, *J* = 7.3, 1.2 Hz, 1H), 5.66 – 5.63 (m, 1H), 5.26 (d, *J* = 7.0 Hz, 1H), 4.58 (d, *J* = 1.7 Hz, 1H), 4.09 (s, 2H), 3.88 (d, *J* = 6.9 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 166.7, 146.3, 143.3, 141.8, 140.1, 139.6, 138.7, 135.2, 135.1, 129.9, 129.5, 129.1 (2C), 128.7 (2C), 127.5, 127.0, 126.7, 126.6, 125.3, 124.7, 124.3, 119.4, 80.4, 50.9, 42.2, 30.6, 28.2 (3C). $[\alpha]_D^{21}$ = 139,1 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. $C_{30}H_{28}O_2Na^+$: 443.1982; found:443.1980.

***tert-Butyl* 2-((4b*S*,5*R*)-8-methyl-11-phenyl-4b,10-dihydro-5H-benzo[b]fluoren-5-yl)-acrylate (8o)**



Following the general procedure product **8o** was isolated as a single diastereoisomer in 72% yield (15.6 mg) as light-yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.57 (dq, *J* = 7.4, 0.9 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.47 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.25 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.21 (td, *J* = 7.4, 1.4 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.07 – 7.04 (m, 1H), 7.00 (ddd, *J* = 7.8, 1.9, 0.8 Hz, 1H), 5.66 – 5.63 (m, 1H), 5.23 (d, *J* = 7.0 Hz, 1H), 4.60 (d, *J* = 1.7 Hz, 1H), 4.06 (s, 2H), 3.87 (d, *J* = 7.0 Hz, 1H), 2.32 (s, 3H), 1.32 f(s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 166.6, 146.1, 143.2, 141.8, 140.2, 139.4, 136.4, 135.6, 135.1, 134.8, 129.8, 129.5, 129.0 (2C), 128.5 (2C), 127.4, 127.3, 126.5, 125.2, 124.5, 124.1, 119.2, 80.2, 51.0, 41.7, 30.4, 28.0 (3C), 21.0. $[\alpha]_D^{21}$ = 146,1 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z $[M+Na]^+$ Calcd. $C_{31}H_3O_2Na^+$: 457.2138; found:457.2140.

4. Crystal and X-ray data for *tert*-Butyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)acrylate (3b)

The crystal structure of the compound **3b**, ($C_{30}H_{28}O_3$), was established by single-crystal X-ray diffraction at 100 K. The compound crystallizes in the non-centrosymmetric triclinic space group P1 (Z = 1) (**Figure 1**).

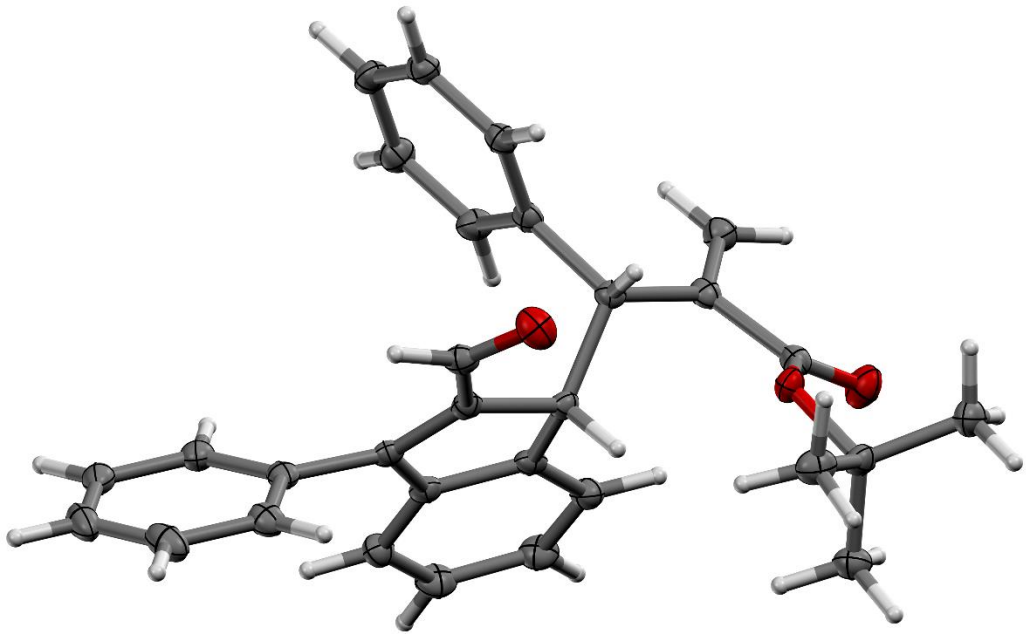


Figure 1. Crystal structure of the compound **3b** at 100 K, showing 50% probability displacement ellipsoids. Hydrogen atoms are drawn with an arbitrary radius.

Single crystal X-ray diffraction data were collected at 100 K by the ω-scan technique using a RIGAKU XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer[3] with PhotonJet micro-focus X-ray Source Cu-Kα (λ = 1.54184 Å). Data collection, cell refinement, data reduction and absorption correction were performed using CrysAlis PRO software[3]. The crystal structure was solved by using direct methods with the SHELXT 2018/2 program[4]. Atomic scattering factors were taken from the International Tables for X-ray Crystallography. Positional parameters of non-H-atoms were refined by a full-matrix least-squares method on F^2 with anisotropic thermal parameters by using the SHELXL 2018/3 program[5]. All hydrogen atoms were found from the difference Fourier maps and for further calculations they were positioned geometrically in

[3] Rigaku OD. CrysAlis PRO. Rigaku Oxford Diffraction Ltd, Yarnton, Oxfordshire, England, **2019**.
[4] Sheldrick, G.M. "SHELXT - integrated space-group and crystal-structure determination", *Acta Cryst*. **2015**, *A71*, 3-8.
[5] Sheldrick, G.M. "Crystal structure refinement with SHELXL", *Acta Cryst*. **2015**, *C71*, 3-8.

calculated positions (C–H = 0.95–1.00 Å) and constrained to ride on their parent atoms with isotropic displacement parameters set to 1.2-1.5 times the U_{eq} of the parent atom.

3b: Formula $C_{30}H_{28}O_3$, triclinic, space group P1, Z = 1, unit cell constants a = 8.0220(1), b = 8.2914(1), c = 10.1712(1) Å, α = 76.898(1), β = 85.404(1), γ = 62.195(1)°, V = 582.577(13) $Å^3$. The integration of the data yielded a total of 20203 reflections with θ angles in the range of 4.47 to 66.58°, of which 3917 were unique (R_{int} = 1.44%). The final anisotropic full-matrix least-squares refinement on F^2 with 302 parameters converged at final R_1 = 0.0219 for the observed data and wR_2 = 0.0573 for all data. The goodness-of-fit was 1.033. The largest peak in the final difference electron density synthesis was 0.158 $eÅ^{-3}$ and the largest hole was -0.120 $eÅ^{-3}$. The absolute configuration was unambiguously established from anomalous scattering, by calculating the x Flack parameter[6] of 0.01(4) using 1845 quotients.

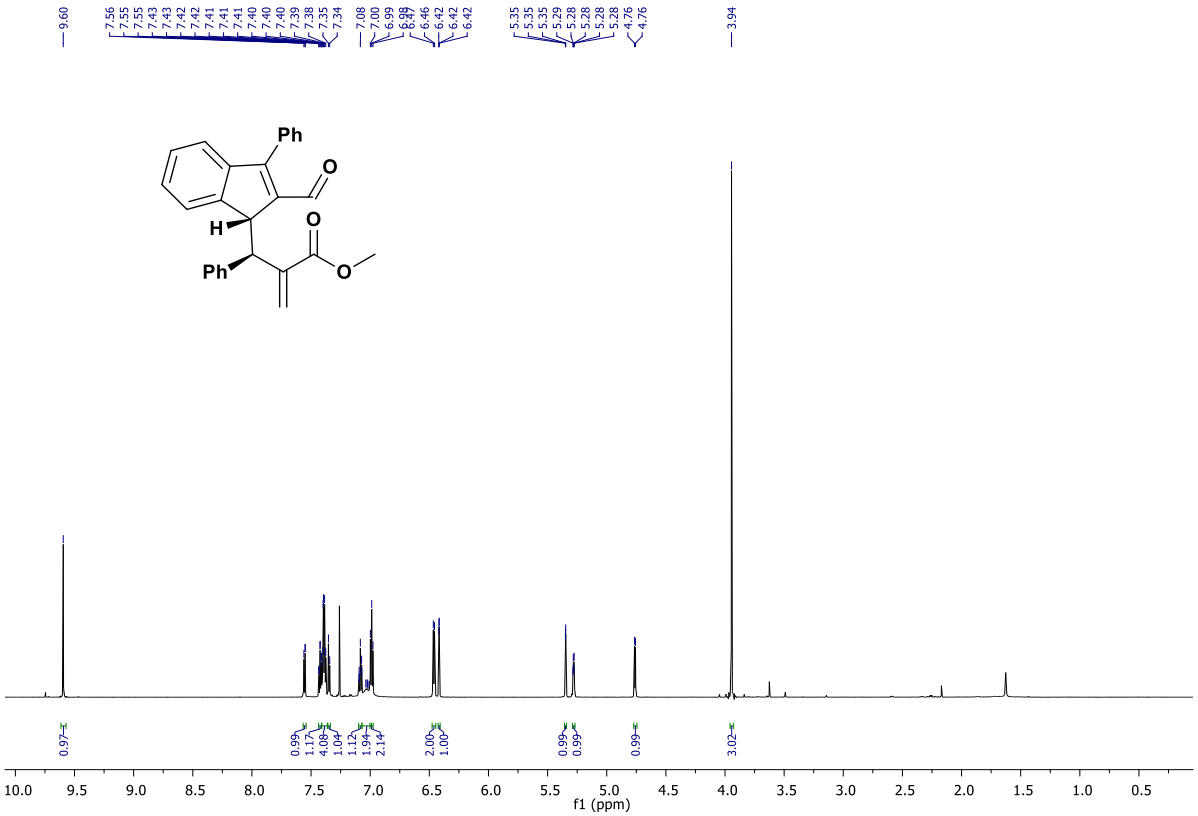
CCDC 2192825 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

[6] Parsons, S.; Flack, H.D.; Wagner, T. "Use of intensity quotients and differences in absolute structure refinement" *Acta Cryst*. **2013**, *B69*, 249-259.

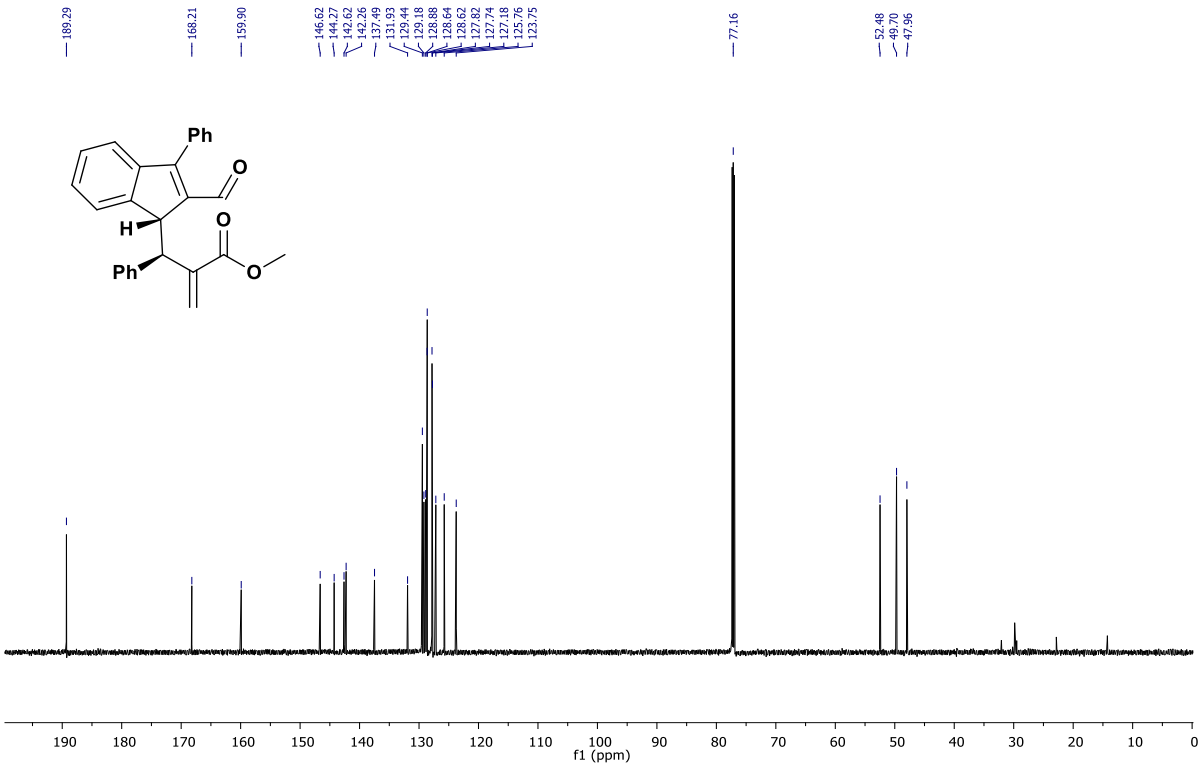
5. NMR Data

Methyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1H-inden-1-yl)(phenyl)methyl)acrylate (3a)

^{1}H NMR (700 MHz, $CDCl_3$)

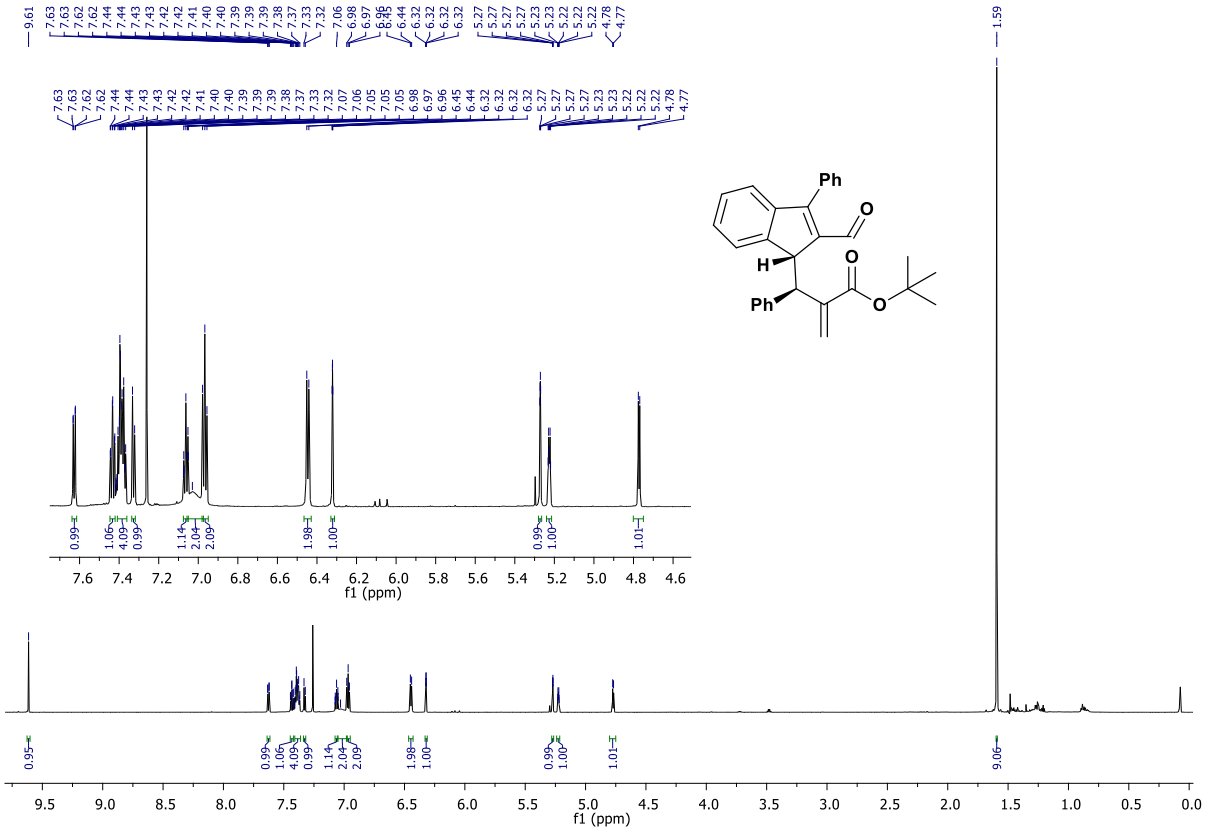


^{13}C NMR (176 MHz, $CDCl_3$)

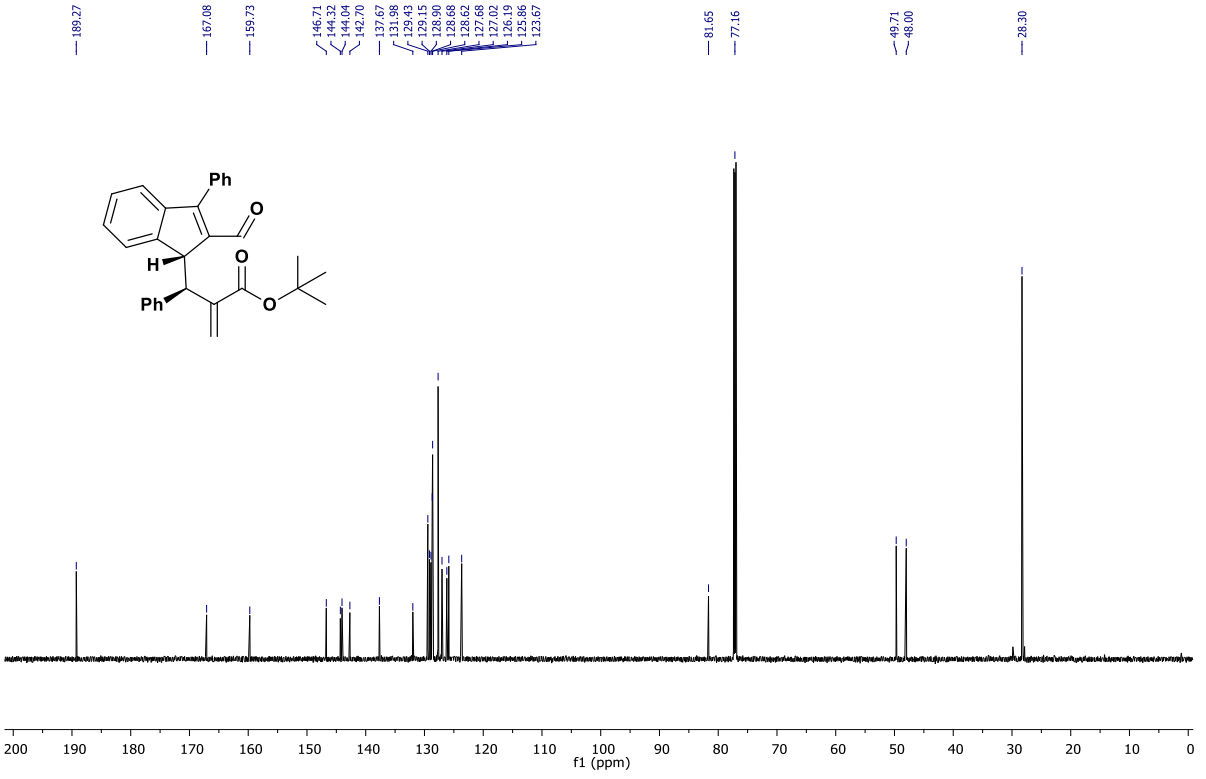


tert-Butyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)acrylate (3b)

^{1}H NMR (700 MHz, $CDCl_3$)

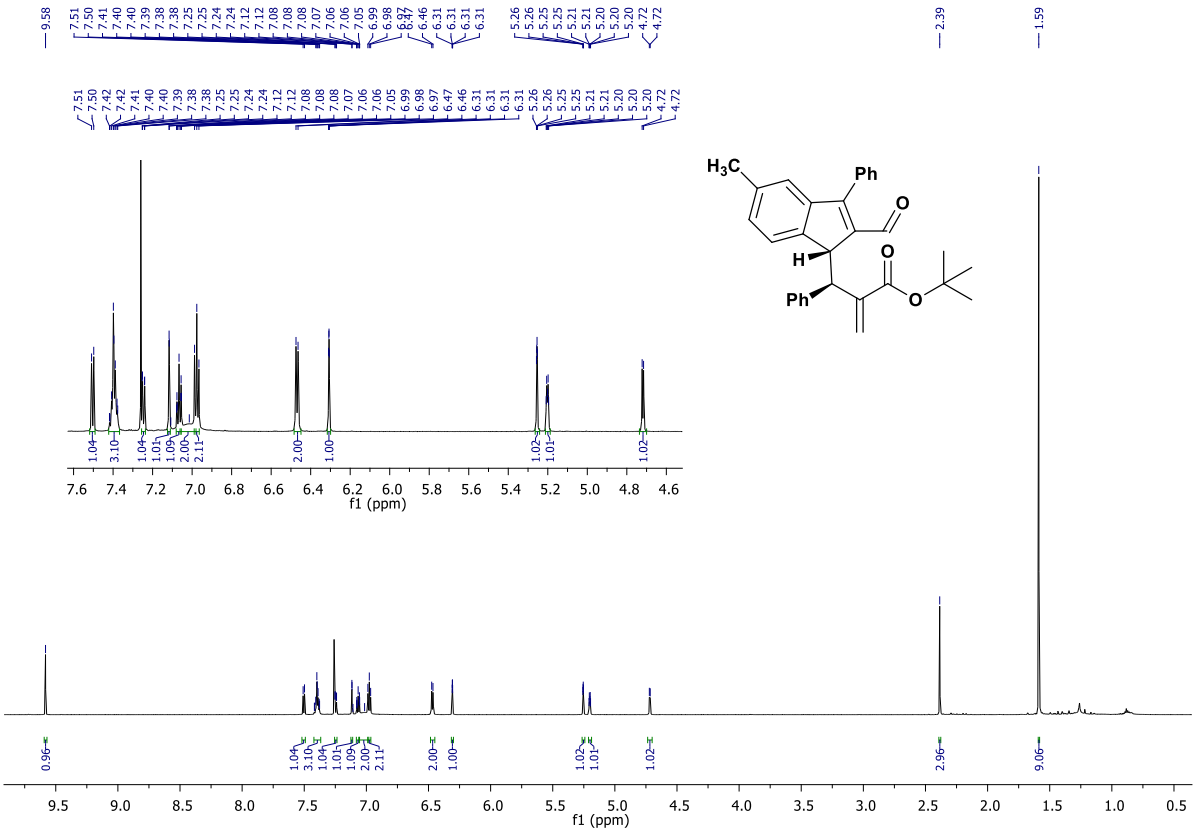


^{13}C NMR (176 MHz, $CDCl_3$)

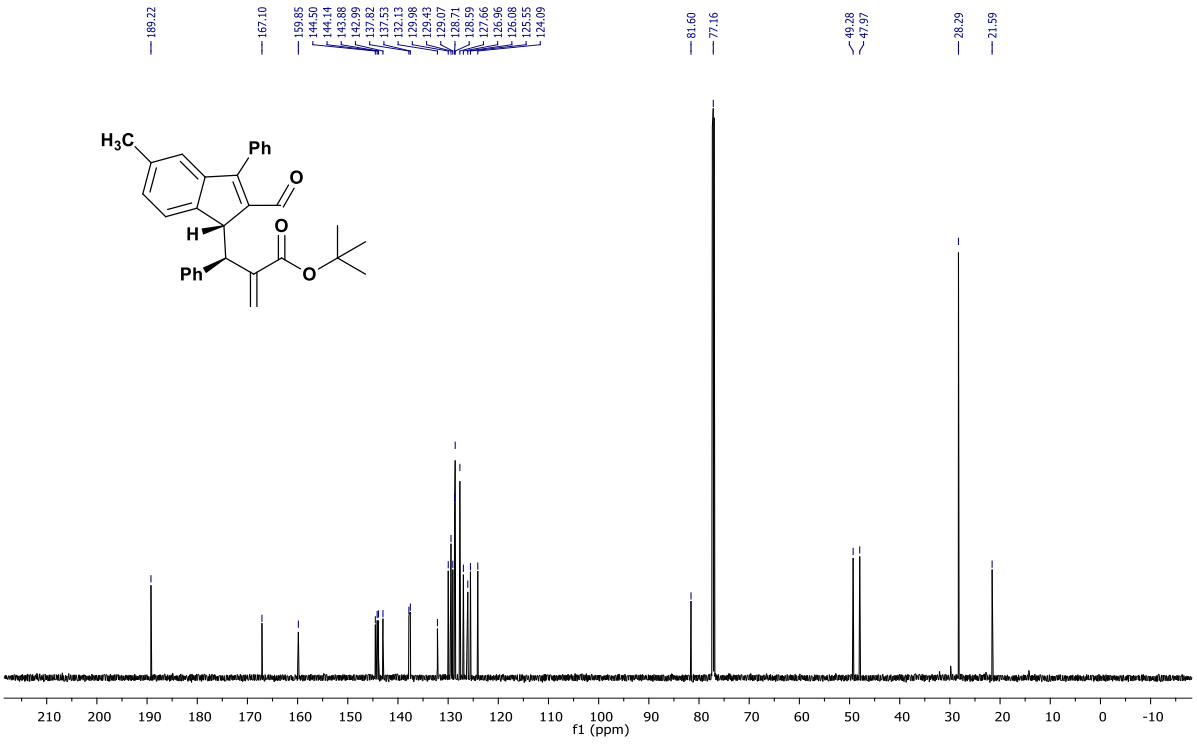


tert-Butyl 2-((*R*)-((*R*)-2-formyl-5-methyl-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3c)

^{1}H NMR (700 MHz, $CDCl_3$)

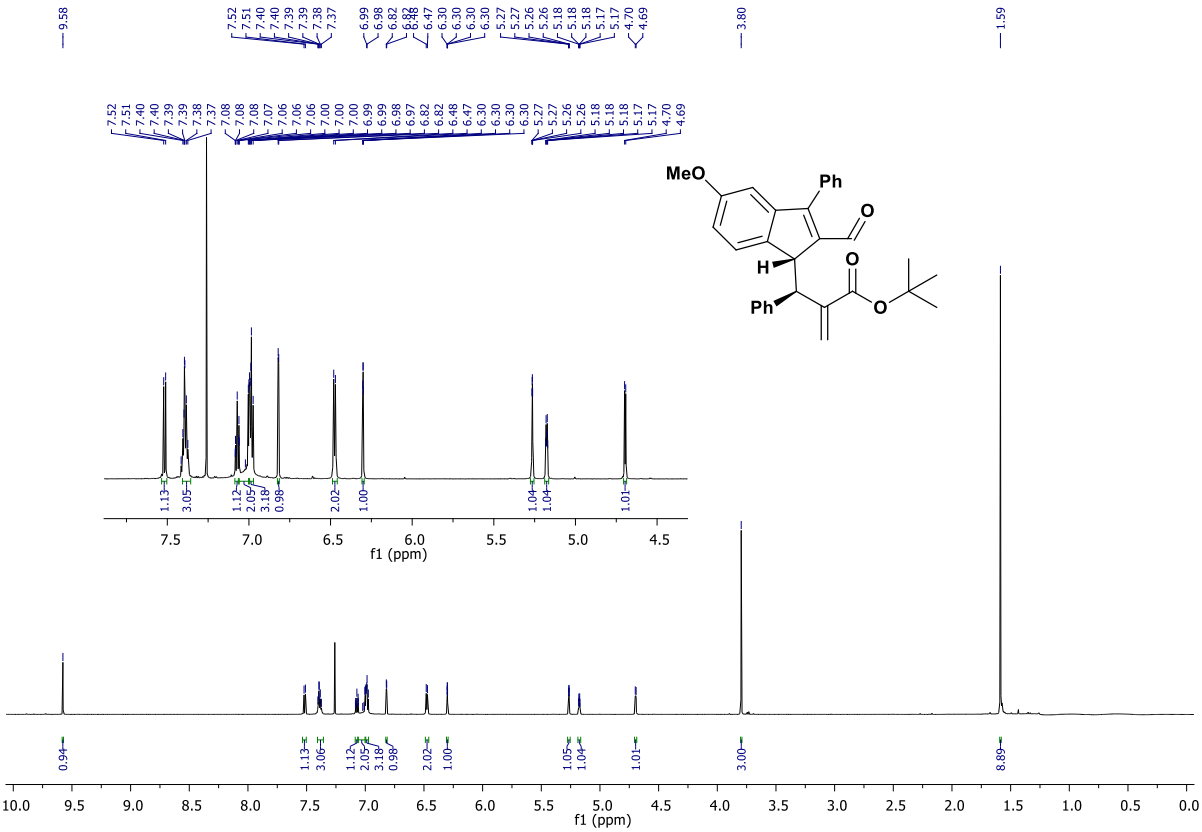


^{13}C NMR (176 MHz, $CDCl_3$)

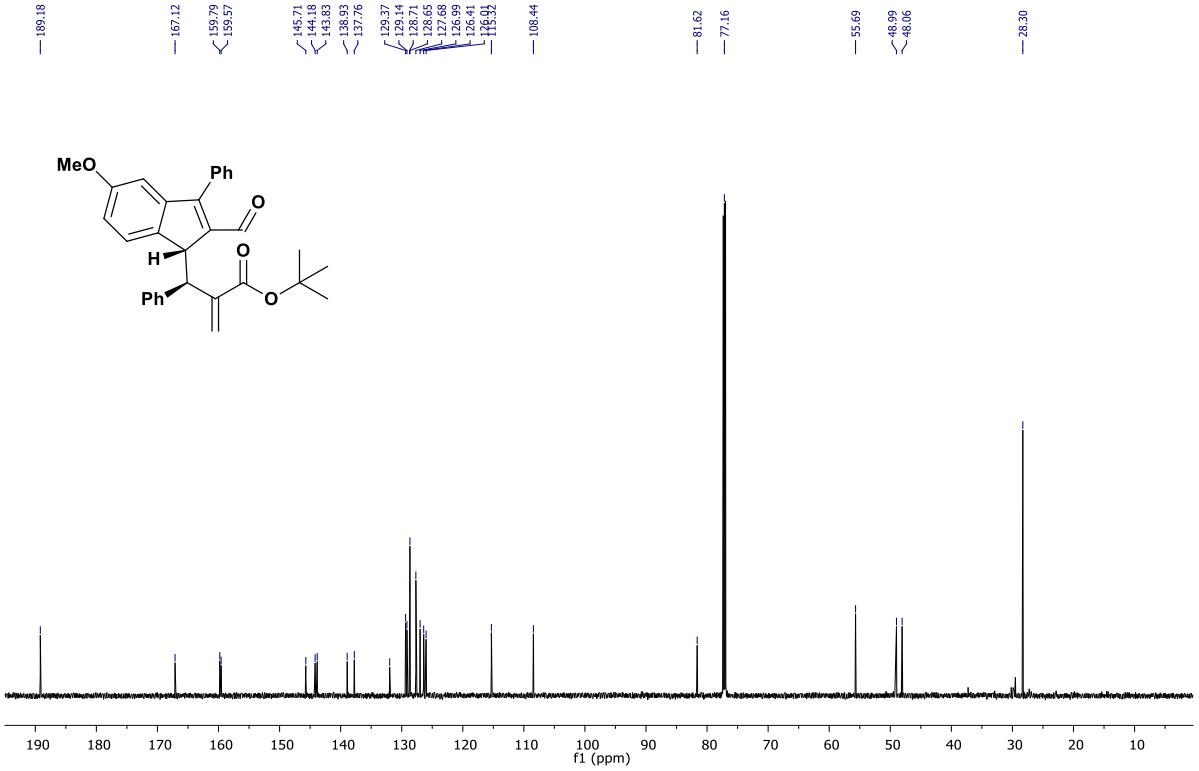


tert-Butyl 2-((*R*)-((*R*)-2-formyl-5-methoxy-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3d)

^{1}H NMR (700 MHz, $CDCl_3$)

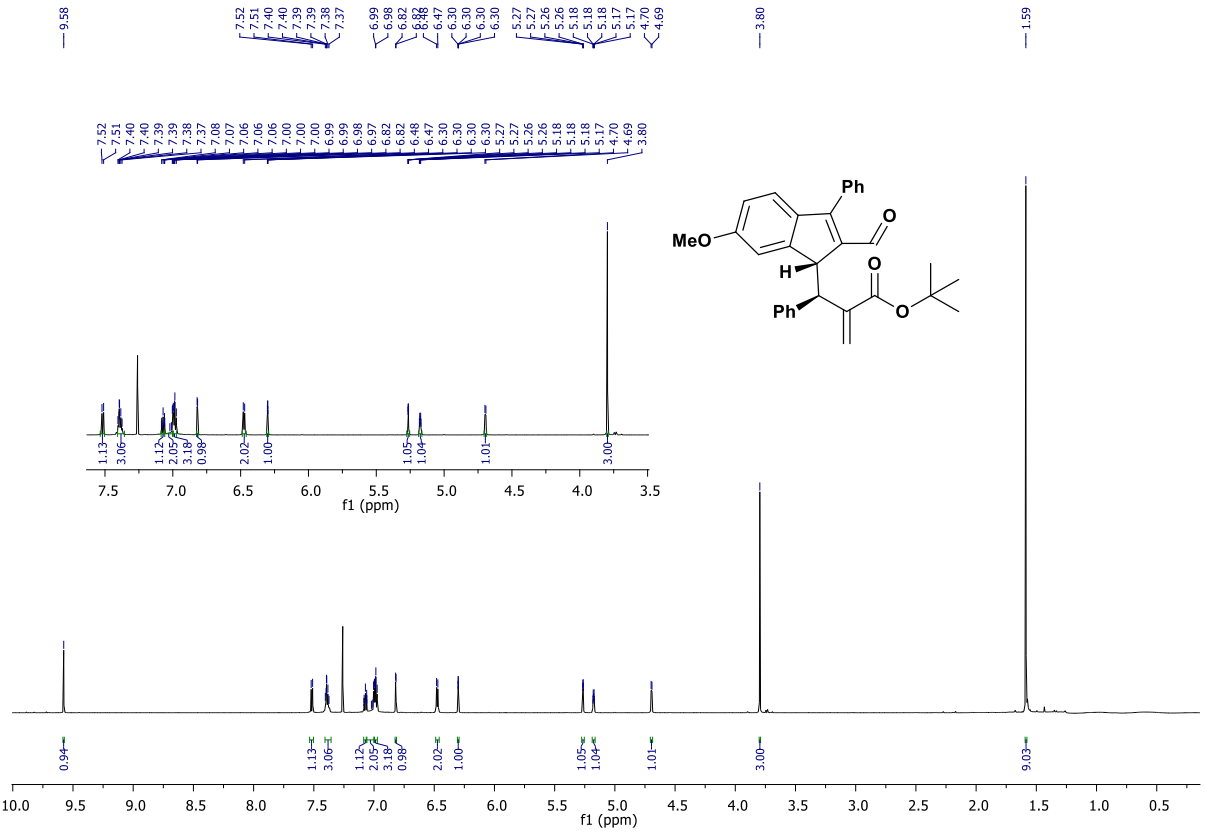


^{13}C NMR (176 MHz, $CDCl_3$)

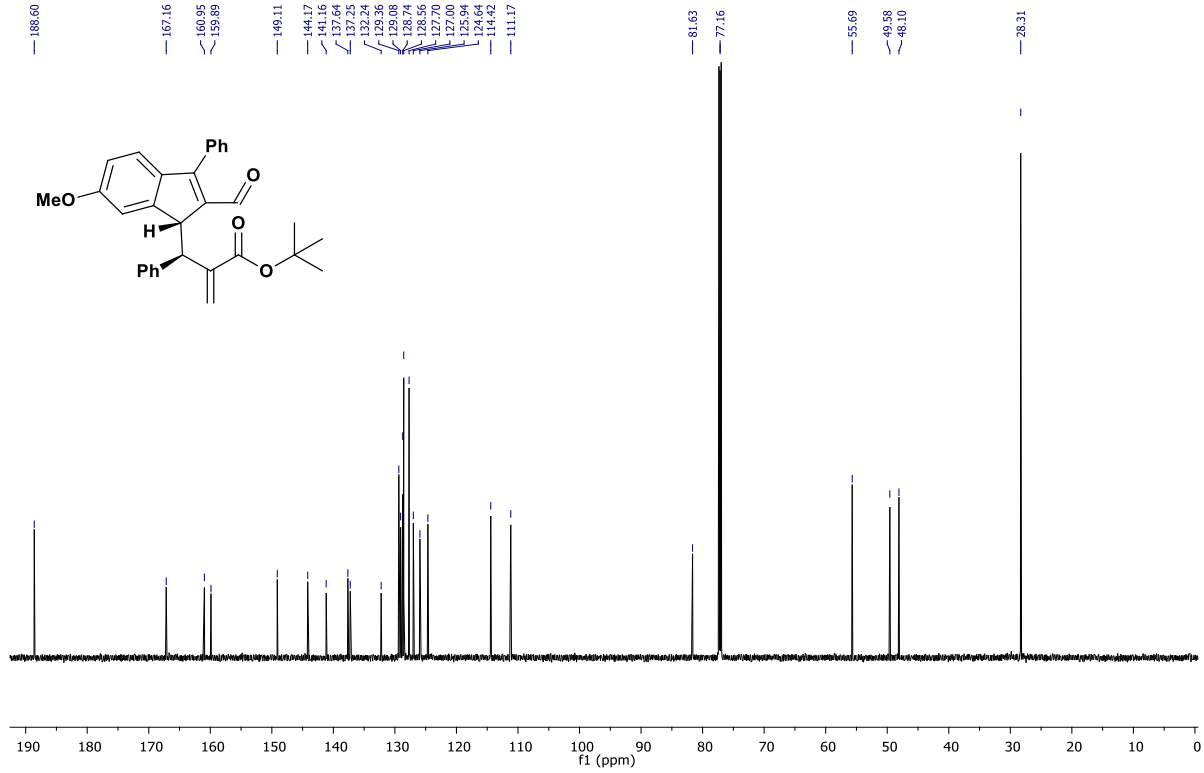


tert-Butyl 2-((*R*)-((*R*)-2-formyl-6-methoxy-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3e)

^{1}H NMR (700 MHz, $CDCl_3$)

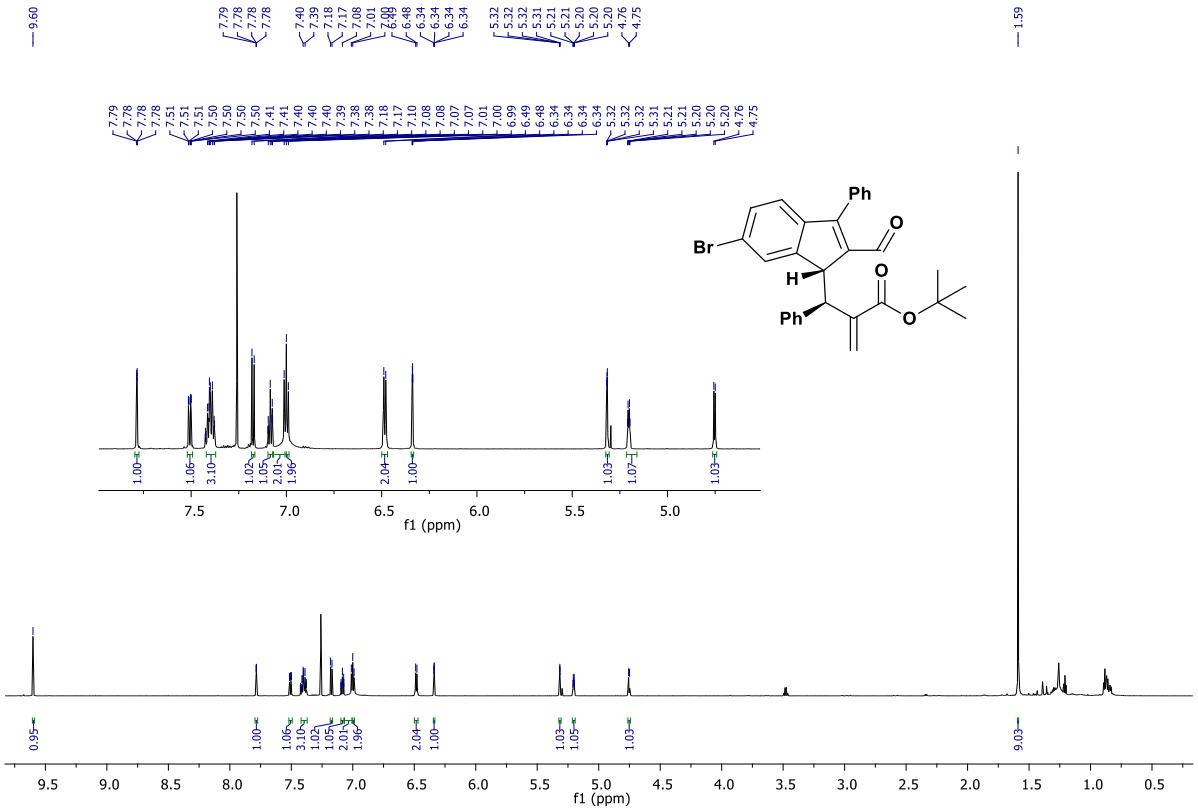


^{13}C NMR (176 MHz, $CDCl_3$)

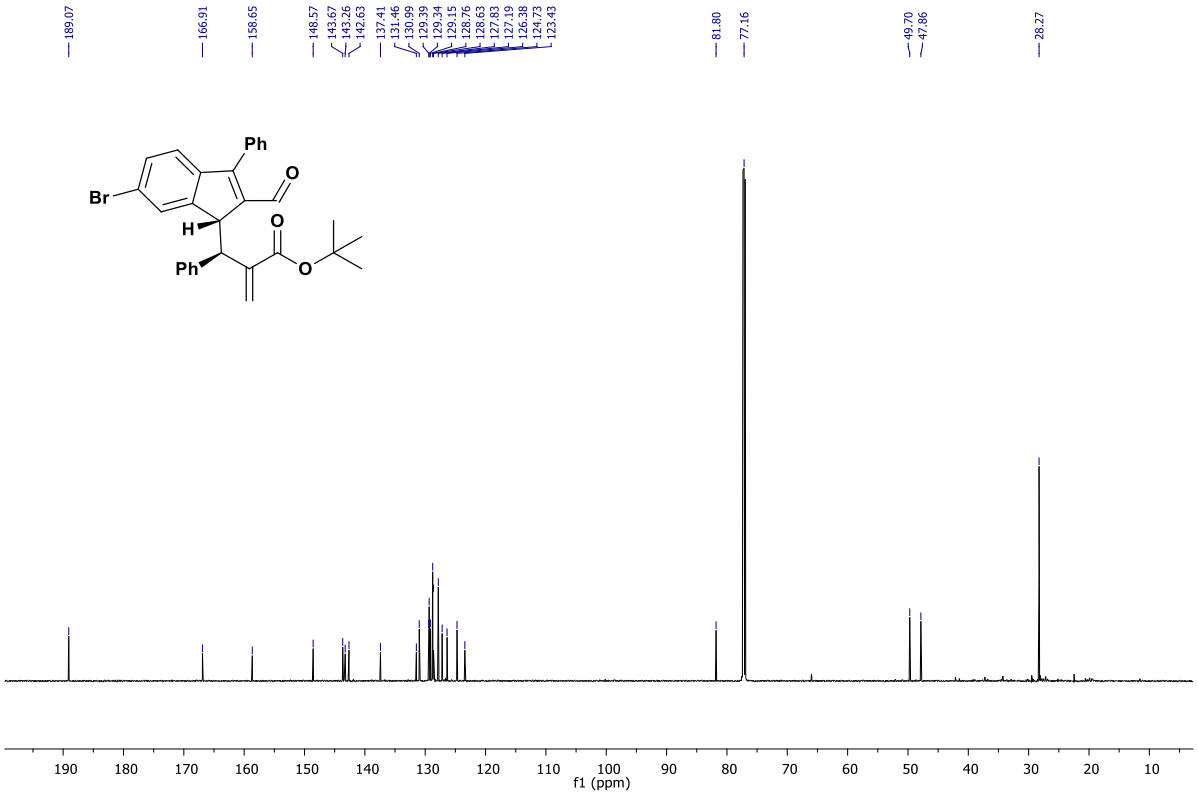


tert-Butyl 2-((_R_)-((_R_)-6-bromo-2-formyl-3-phenyl-1_H_-inden-1-yl)(phenyl)methyl)-acrylate (3f)

^{1}H NMR (700 MHz, $CDCl_3$)

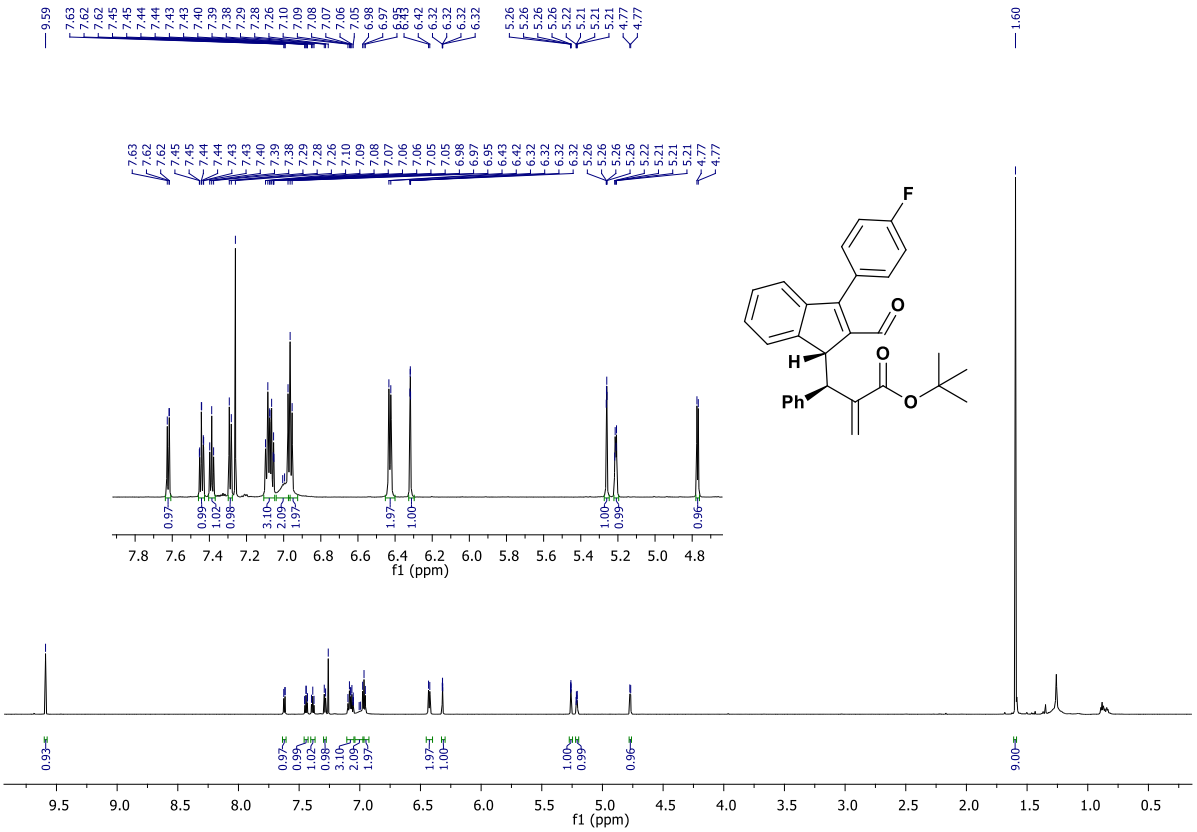


^{13}C NMR (176 MHz, $CDCl_3$)

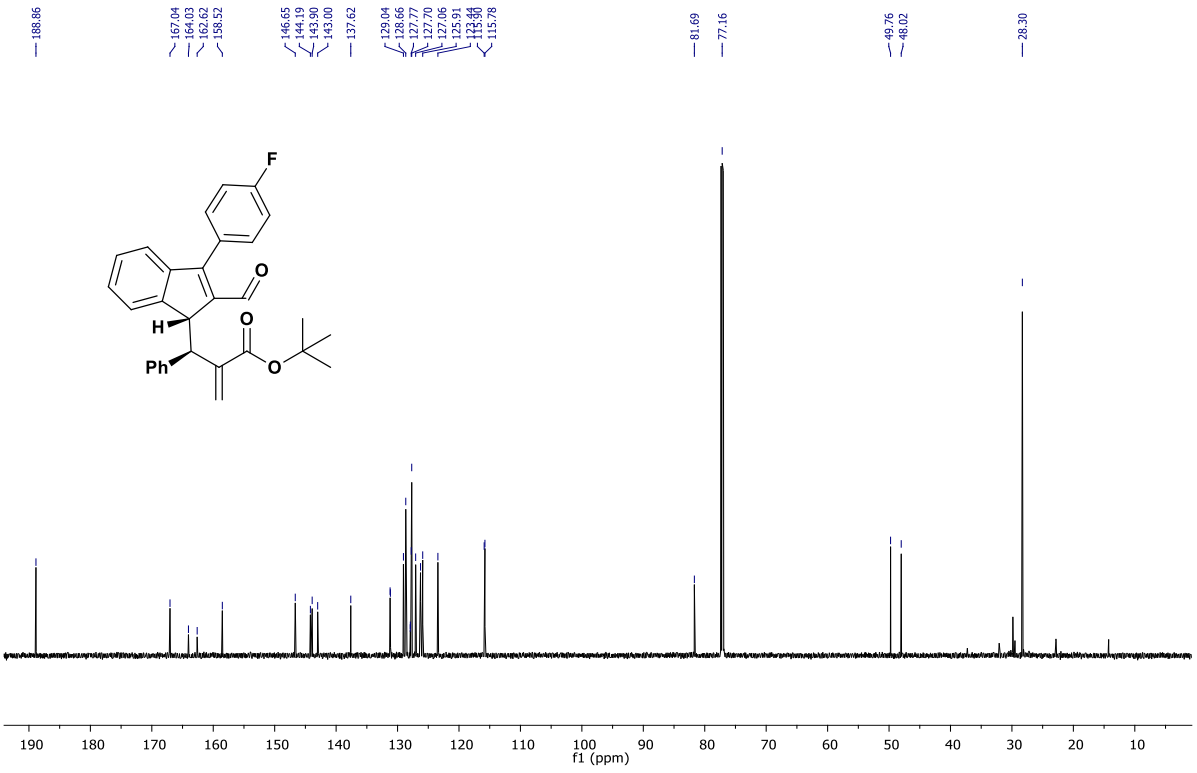


tert-Butyl 2-((_R_)-((_R_)-3-(4-fluorophenyl)-2-formyl-1_H_-inden-1-yl)(phenyl)methyl)-acrylate (3g)

^{1}H NMR (700 MHz, $CDCl_3$)

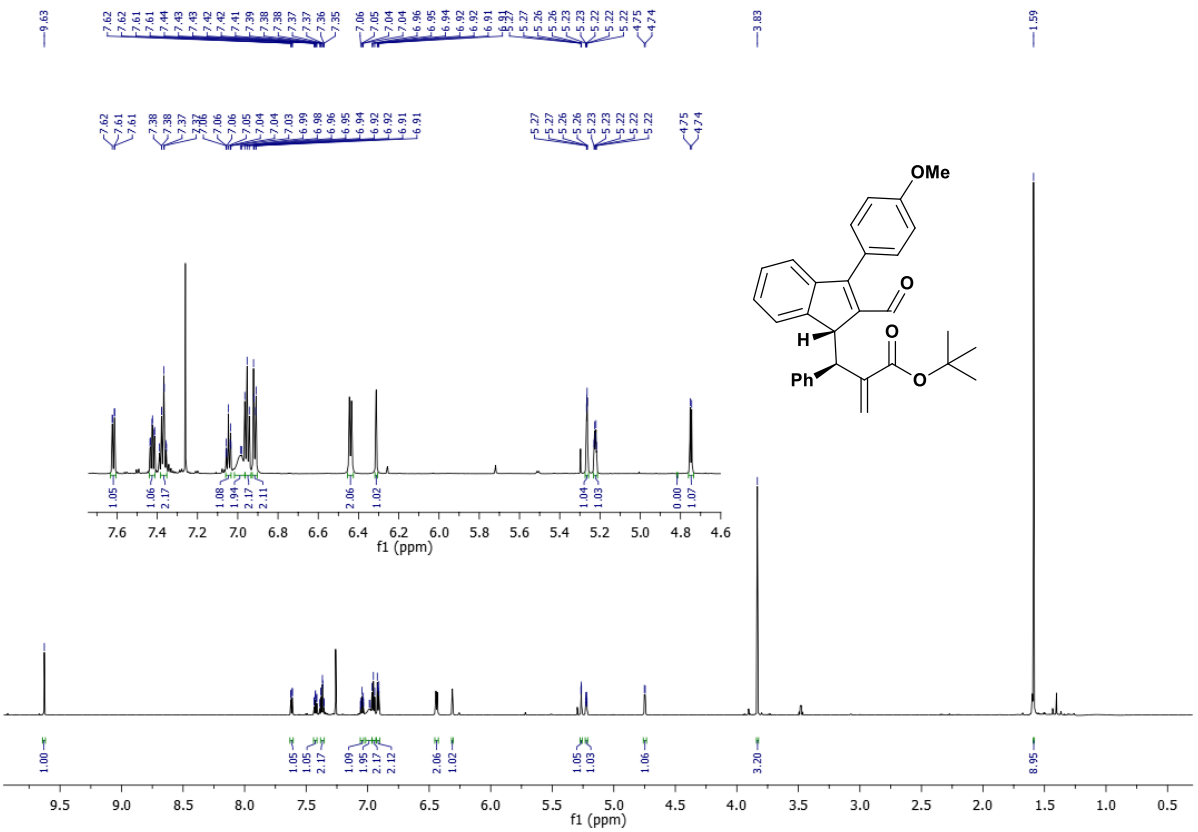


^{13}C NMR (176 MHz, $CDCl_3$)

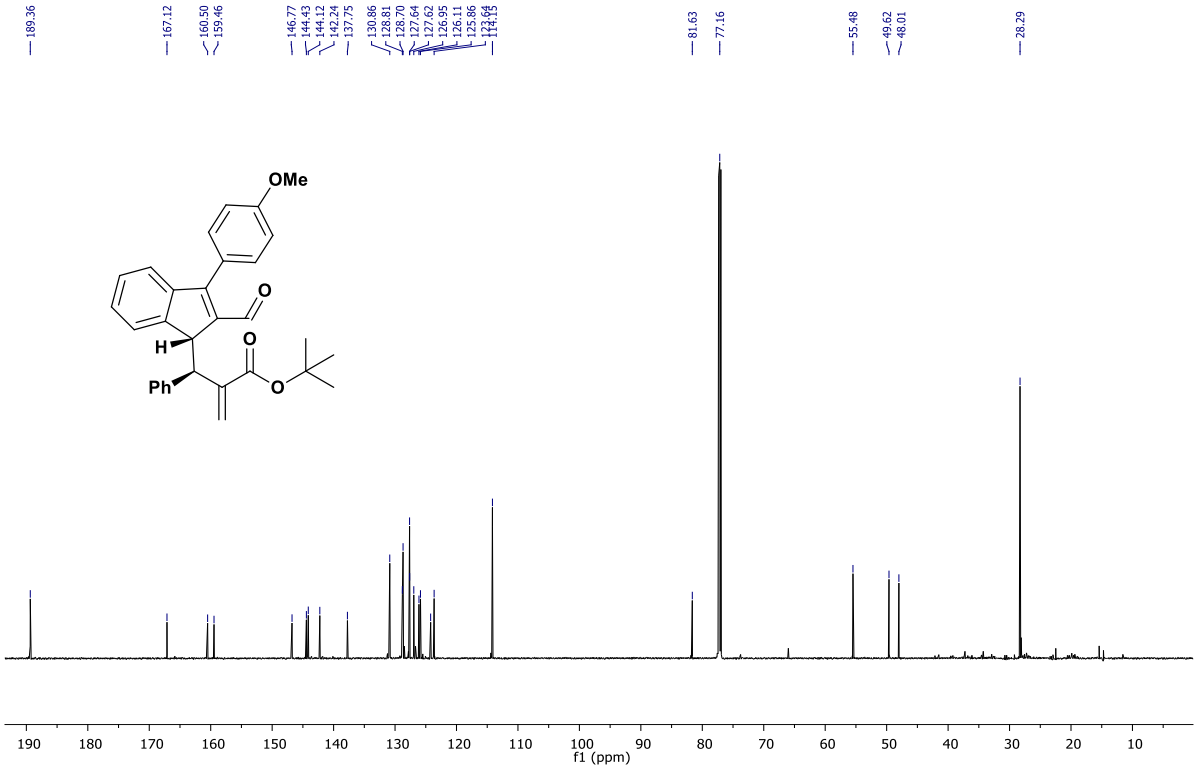


***tert*-Butyl 2-((*R*)-((*R*)-2-formyl-3-(4-methoxyphenyl)-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3h)**

^{1}H NMR (700 MHz, $CDCl_3$)

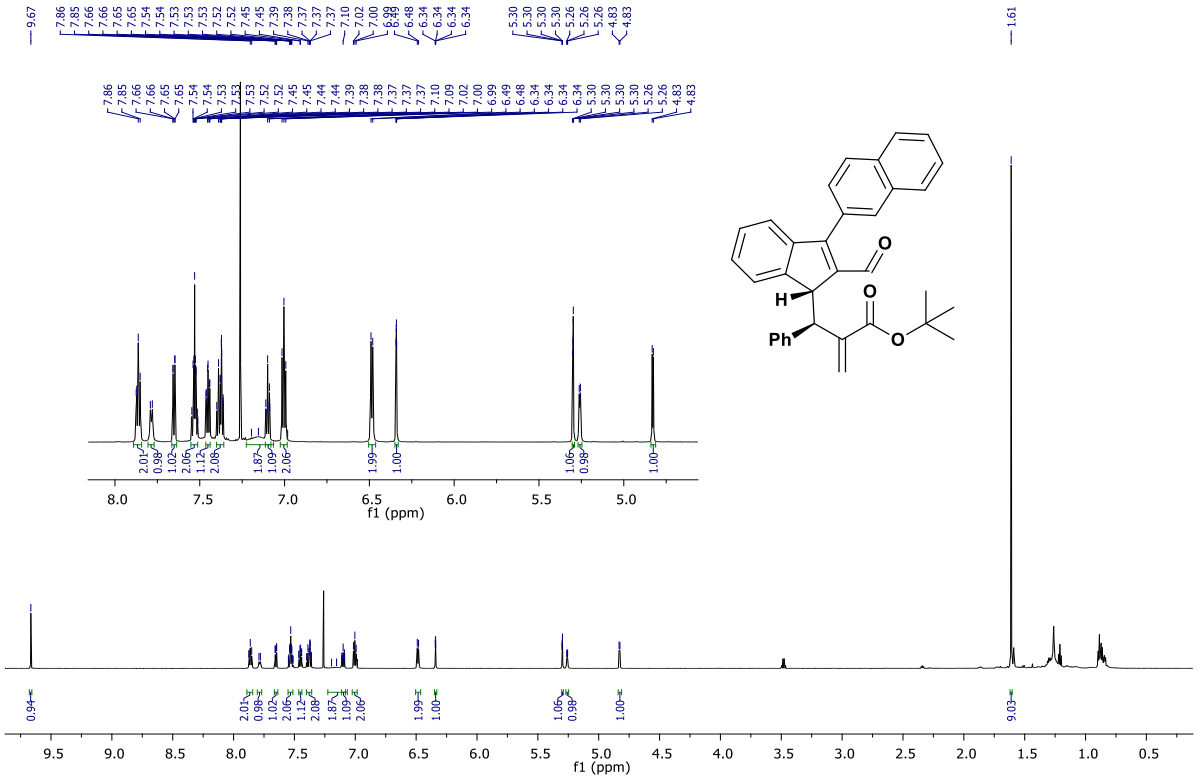


^{13}C NMR (176 MHz, $CDCl_3$)

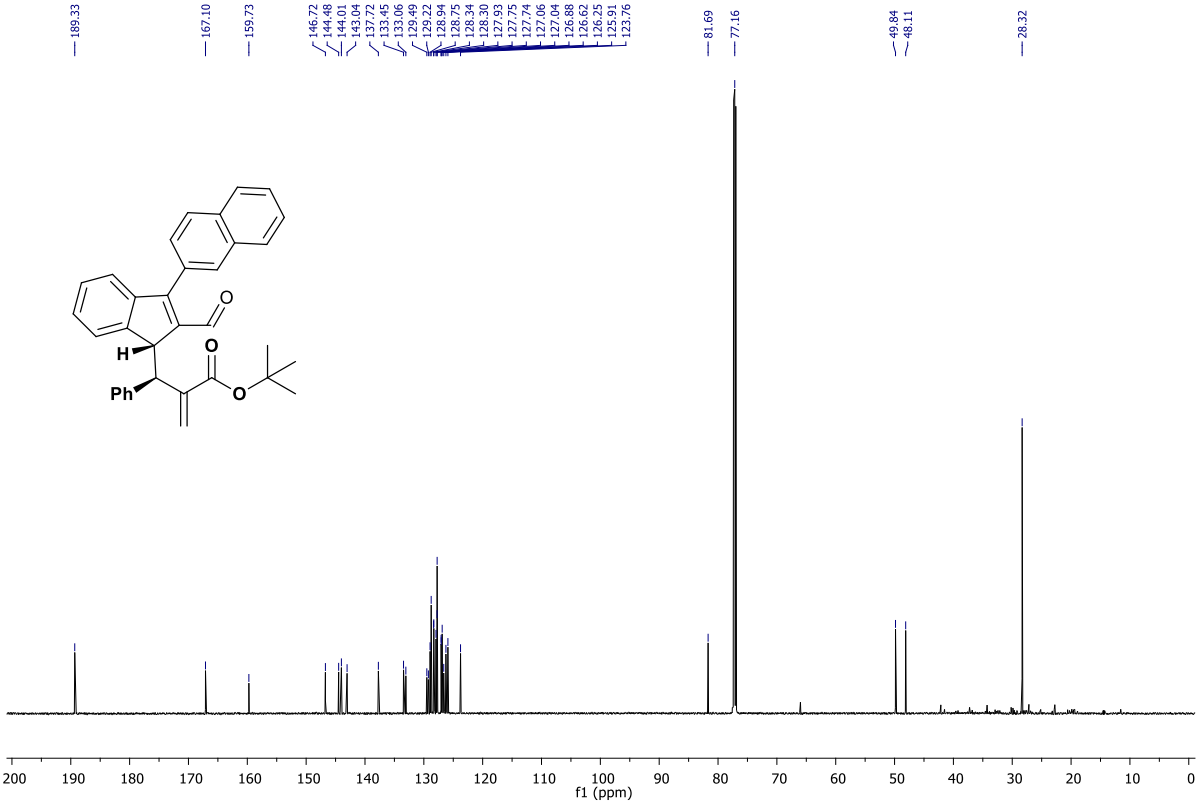


tert-Butyl 2-((*R*)-((*R*)-2-formyl-3-(naphthalen-2-yl)-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3i)

^{1}H NMR (700 MHz, $CDCl_3$)

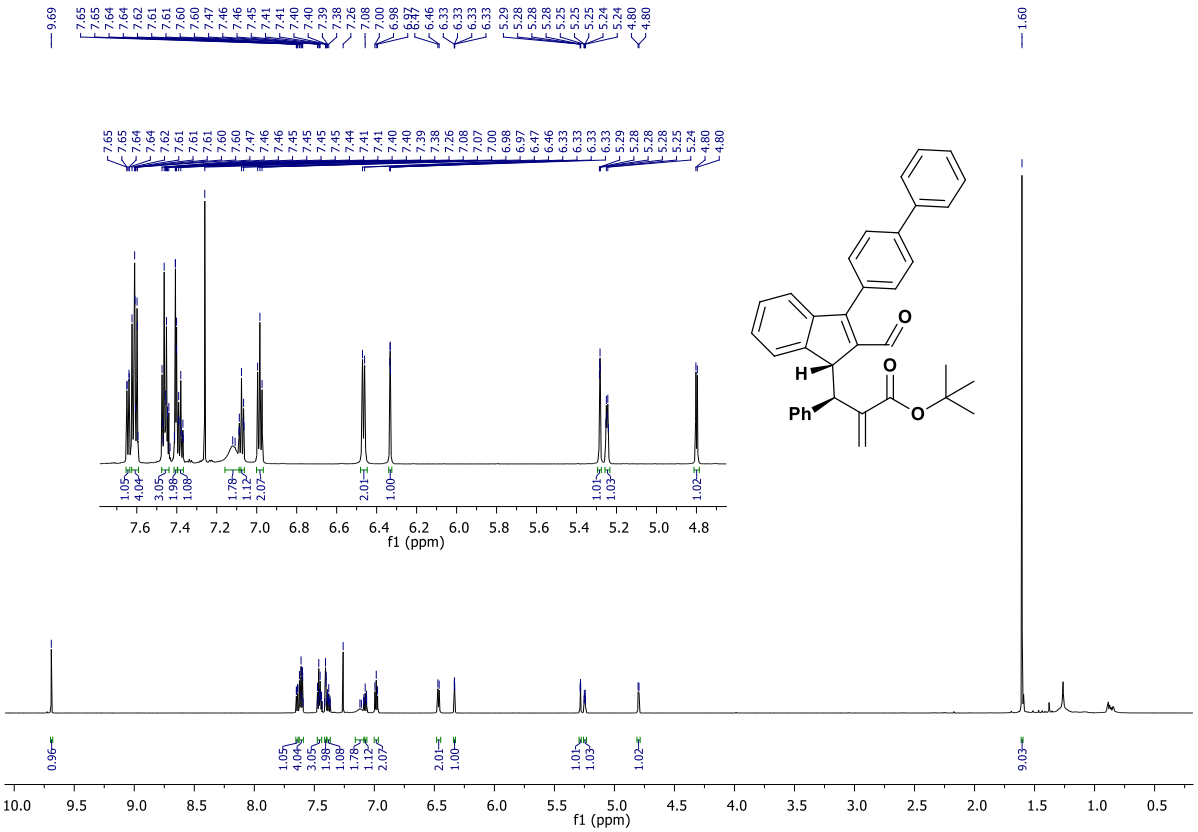


^{13}C NMR (176 MHz, $CDCl_3$)

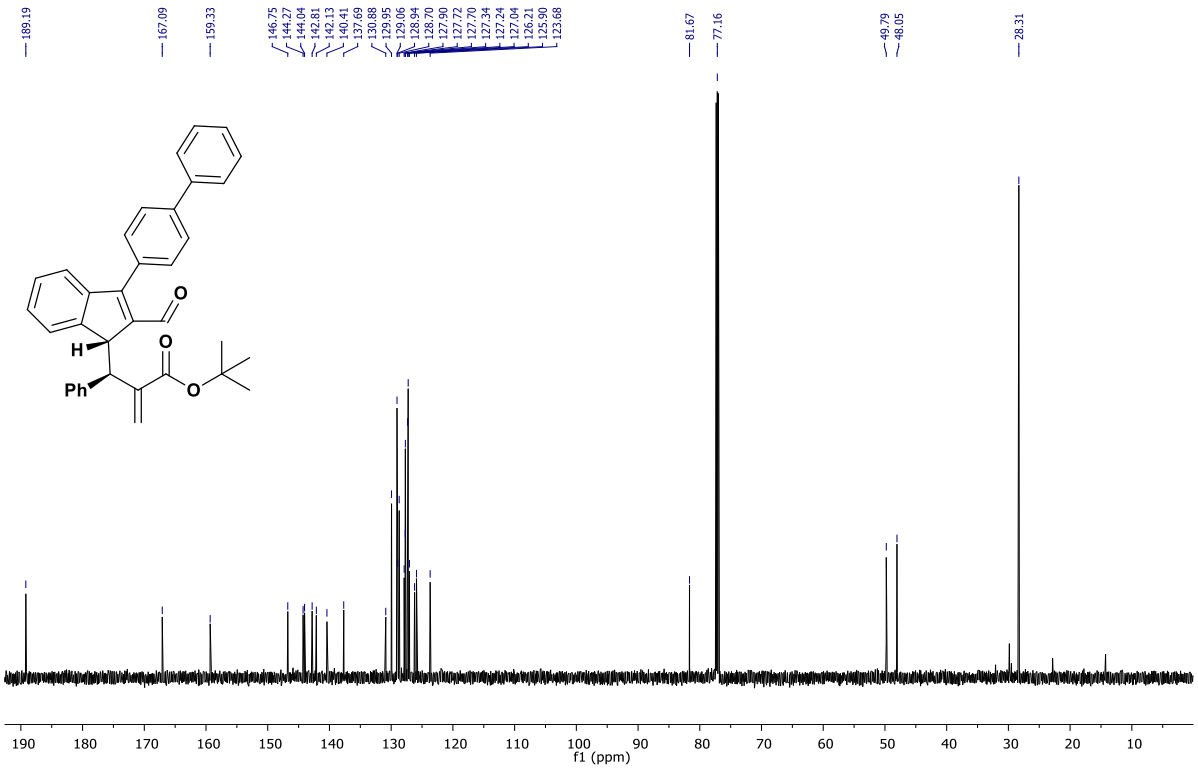


tert-Butyl 2-((_R_)-((_R_)-3-([1,1'-biphenyl]-4-yl)-2-formyl-1_H_-inden-1-yl)(phenyl)methyl)-acrylate (3j)

^{1}H NMR (700 MHz, $CDCl_3$)

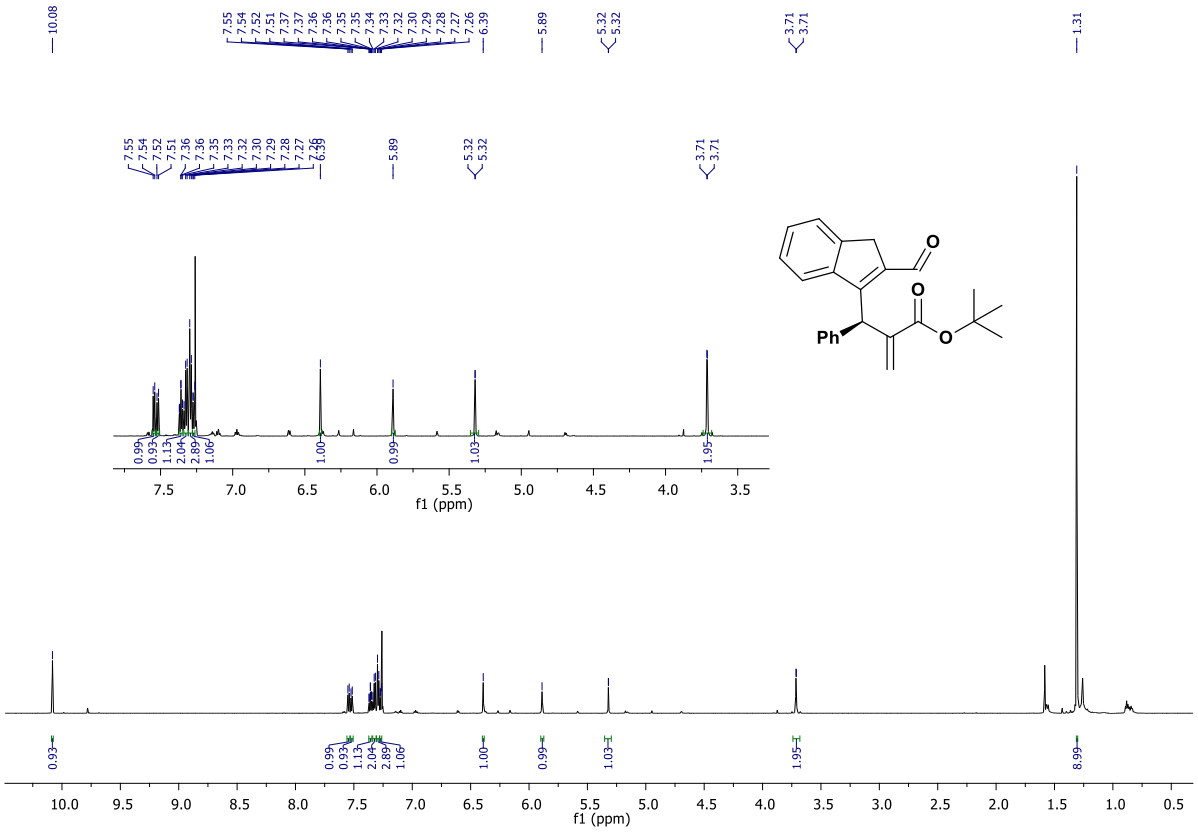


^{13}C NMR (176 MHz, $CDCl_3$)

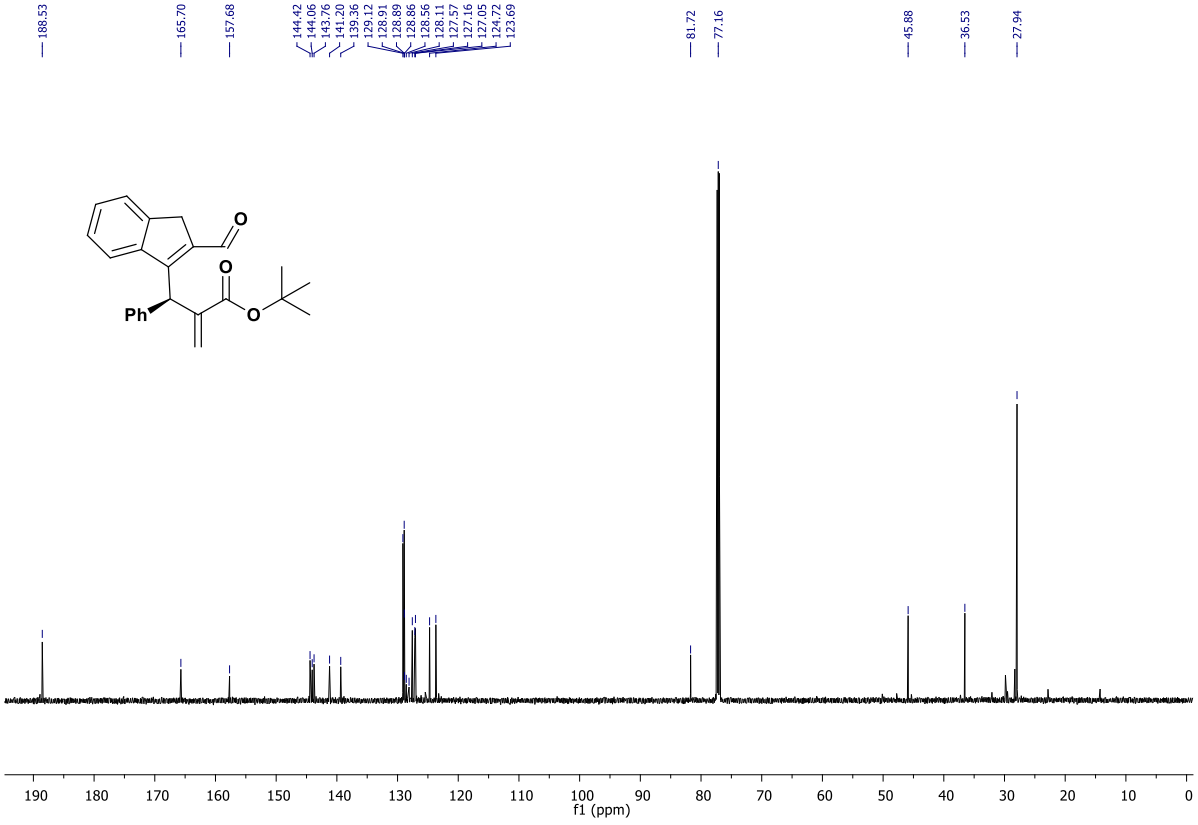


(S)-*tert*-Butyl 2-((2-formyl-1*H*-inden-3-yl)(phenyl)methyl)acrylate (3k')

^{1}H NMR (700 MHz, $CDCl_3$)

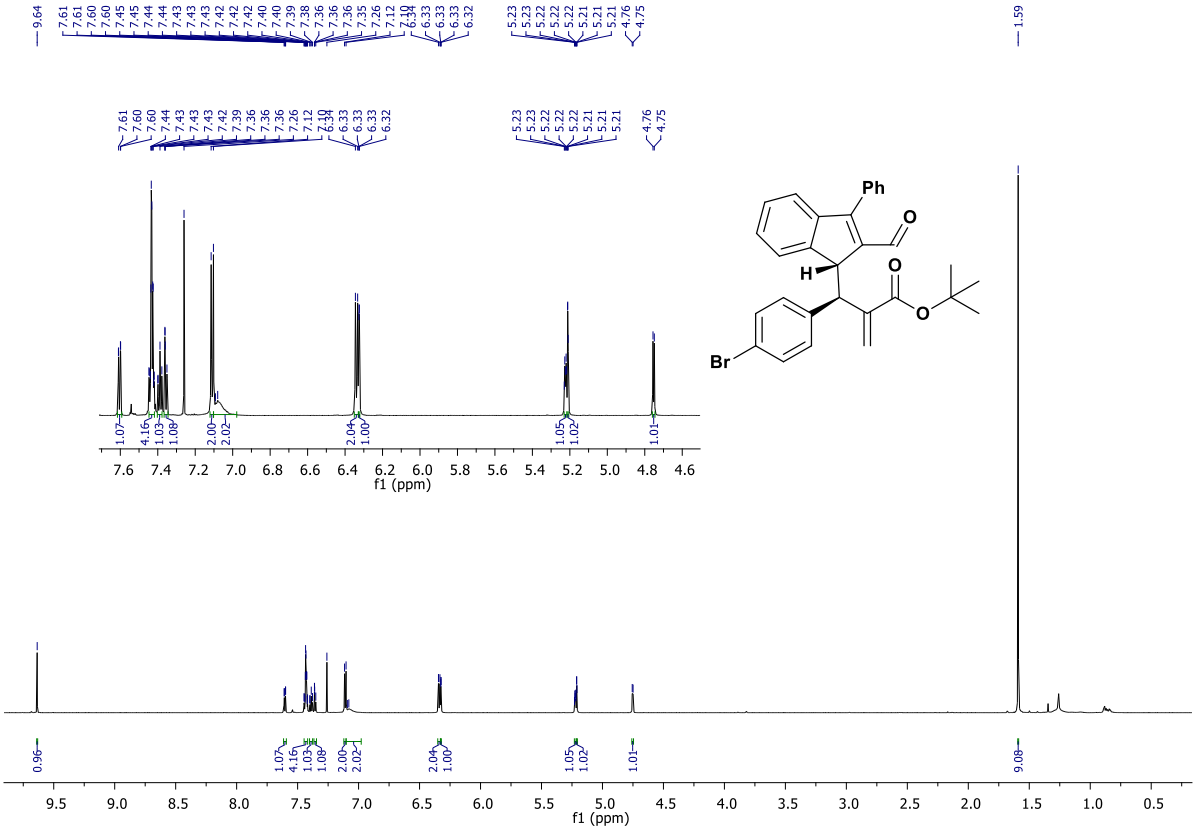


^{13}C NMR (176 MHz, $CDCl_3$)

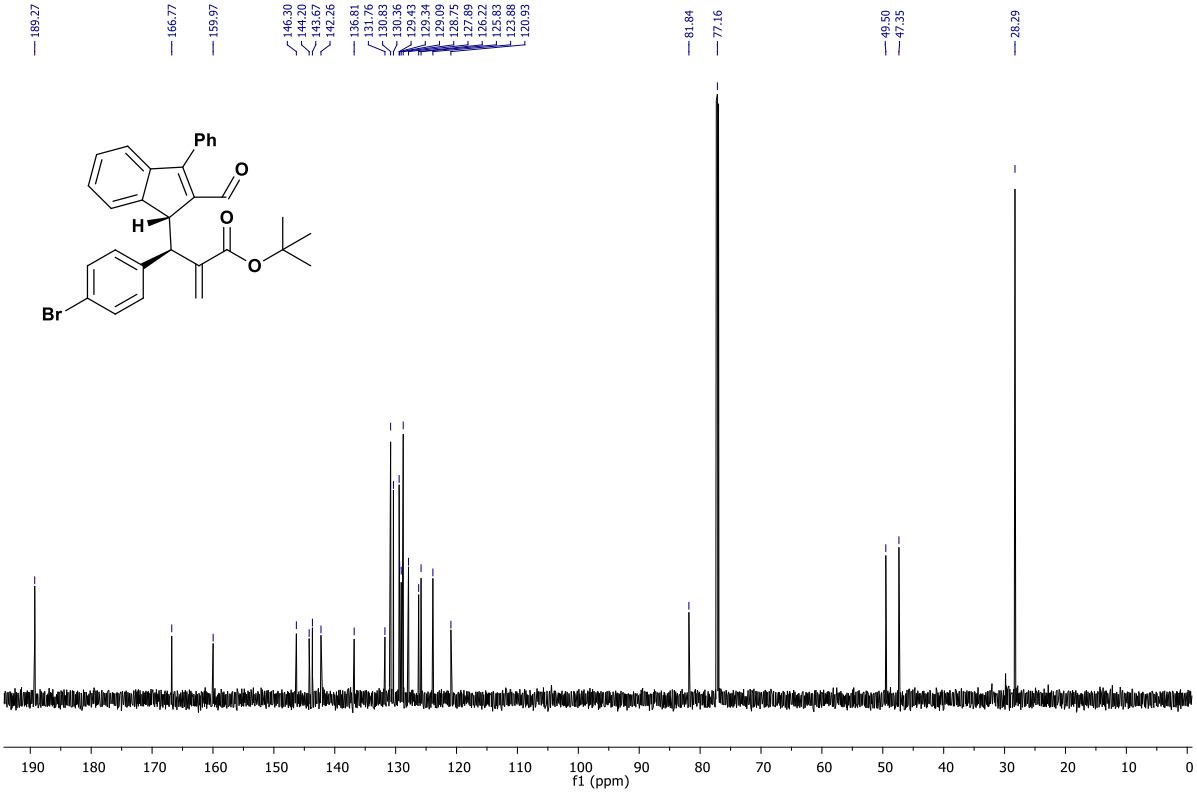


tert-Butyl 2-((*R*)-(4-bromophenyl)((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)methyl)acrylate (3l)

^{1}H NMR (700 MHz, $CDCl_3$

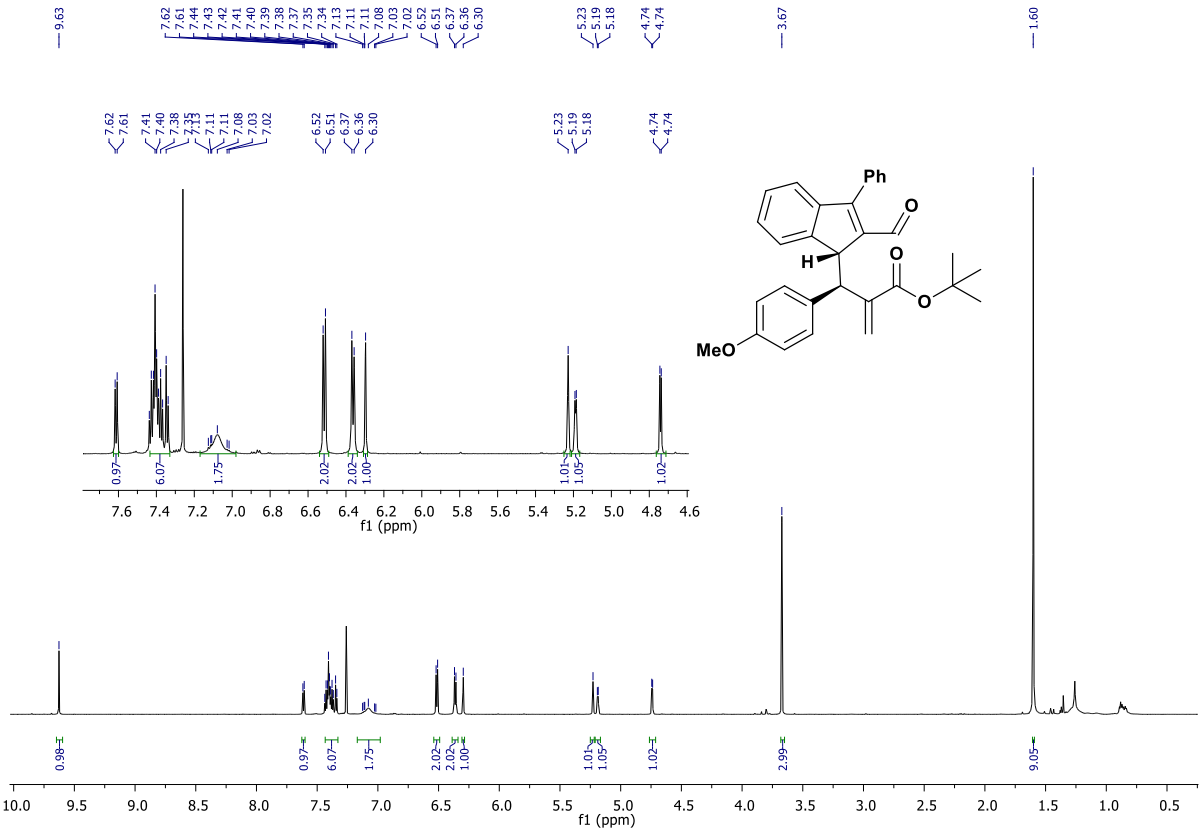


^{13}C NMR (176 MHz, $CDCl_3$)

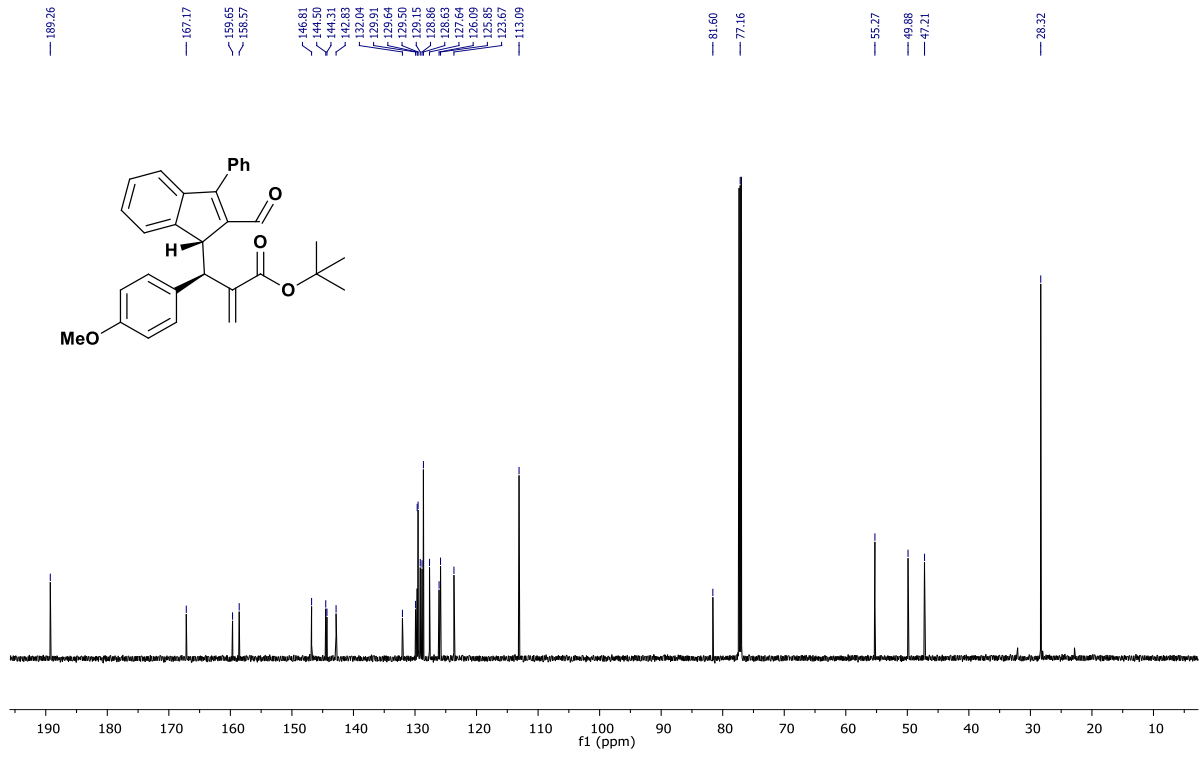


tert-Butyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(4-methoxyphenyl)methyl)-acrylate (3m)

^{1}H NMR (700 MHz, $CDCl_3$)

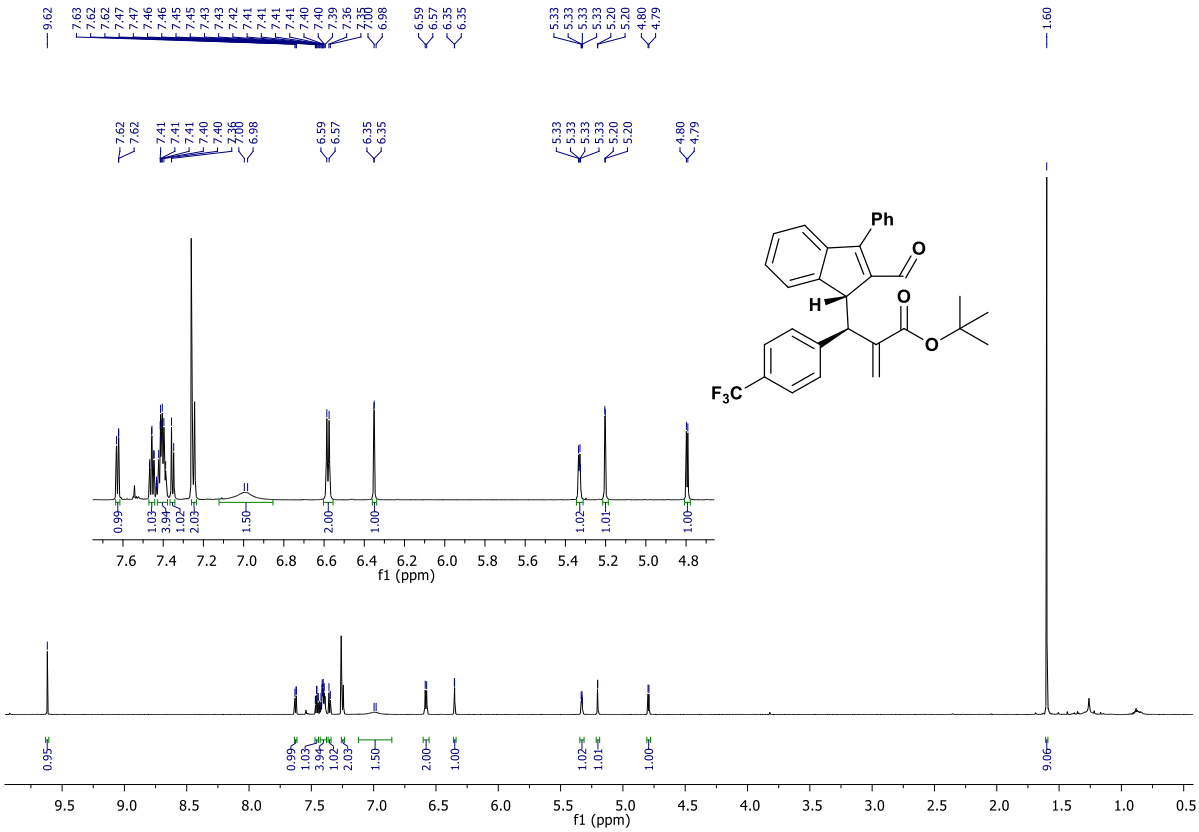


^{13}C NMR (176 MHz, $CDCl_3$)

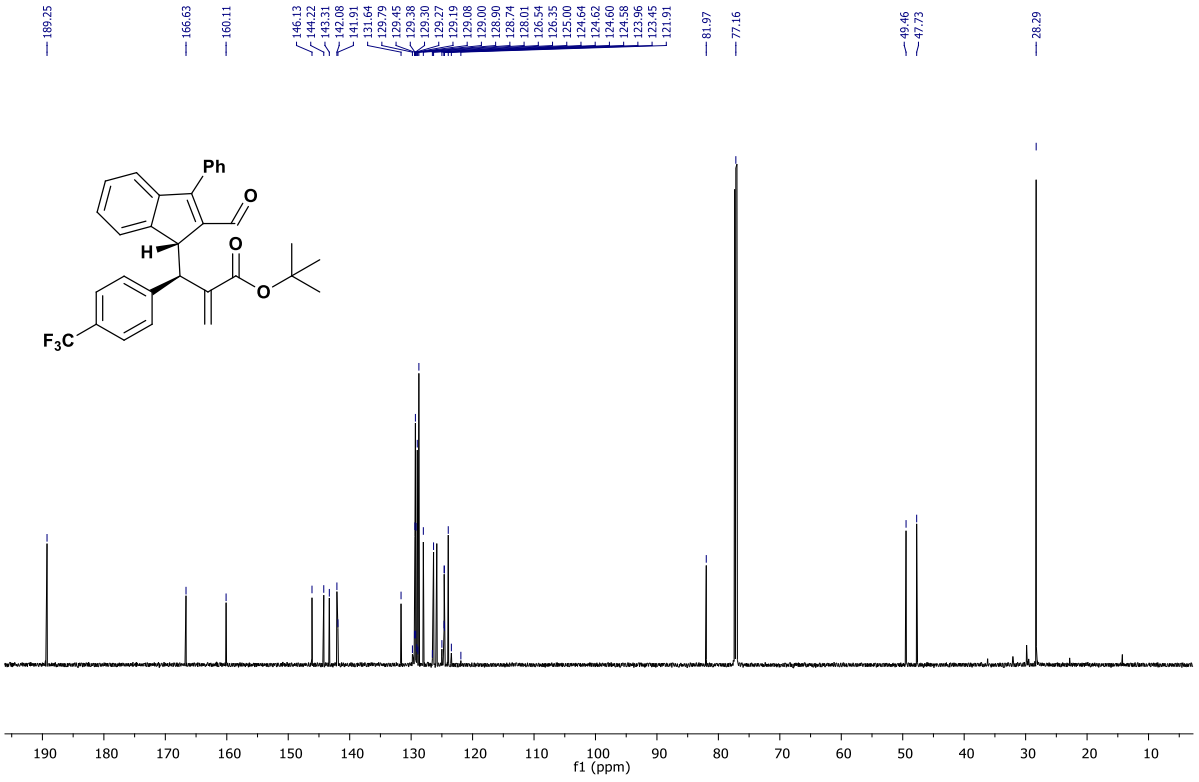


***tert*-Butyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(4-(trifluoromethyl)phenyl)-methyl)acrylate (3n)**

^{1}H NMR (700 MHz, $CDCl_3$)

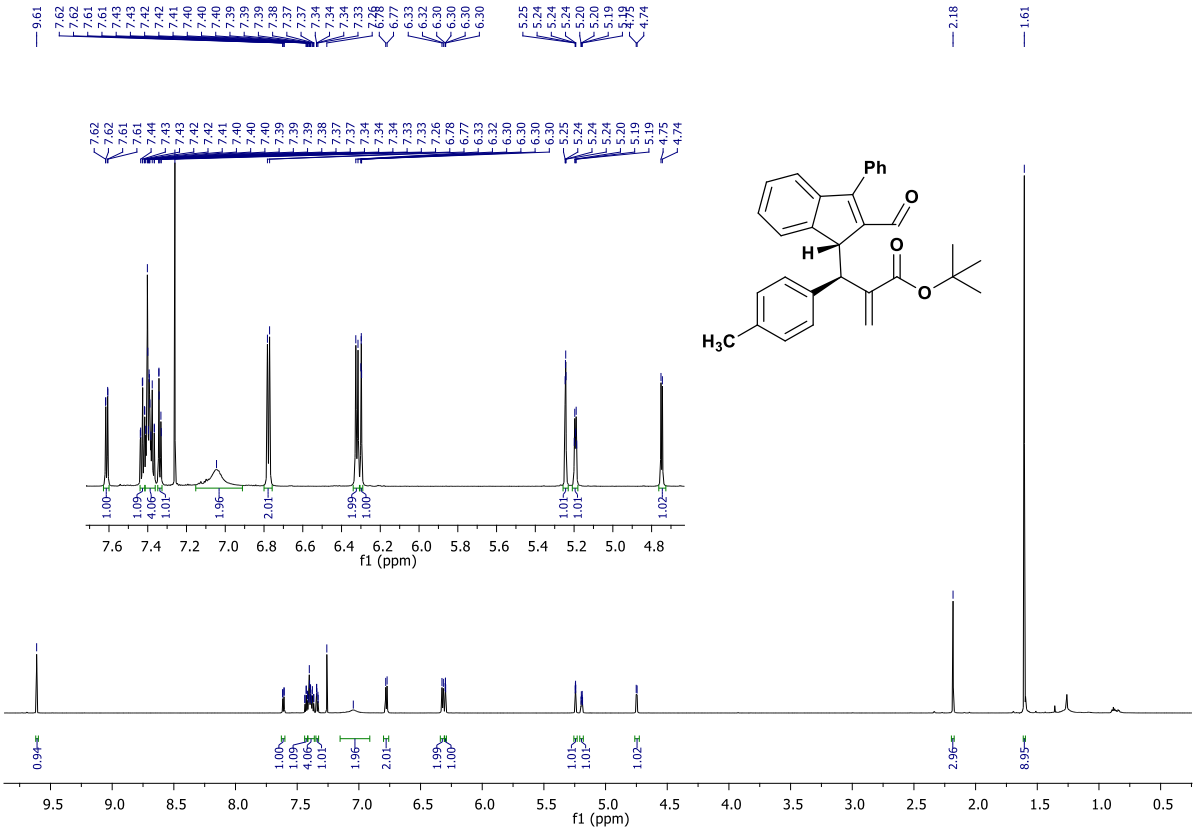


^{13}C NMR (176 MHz, $CDCl_3$)

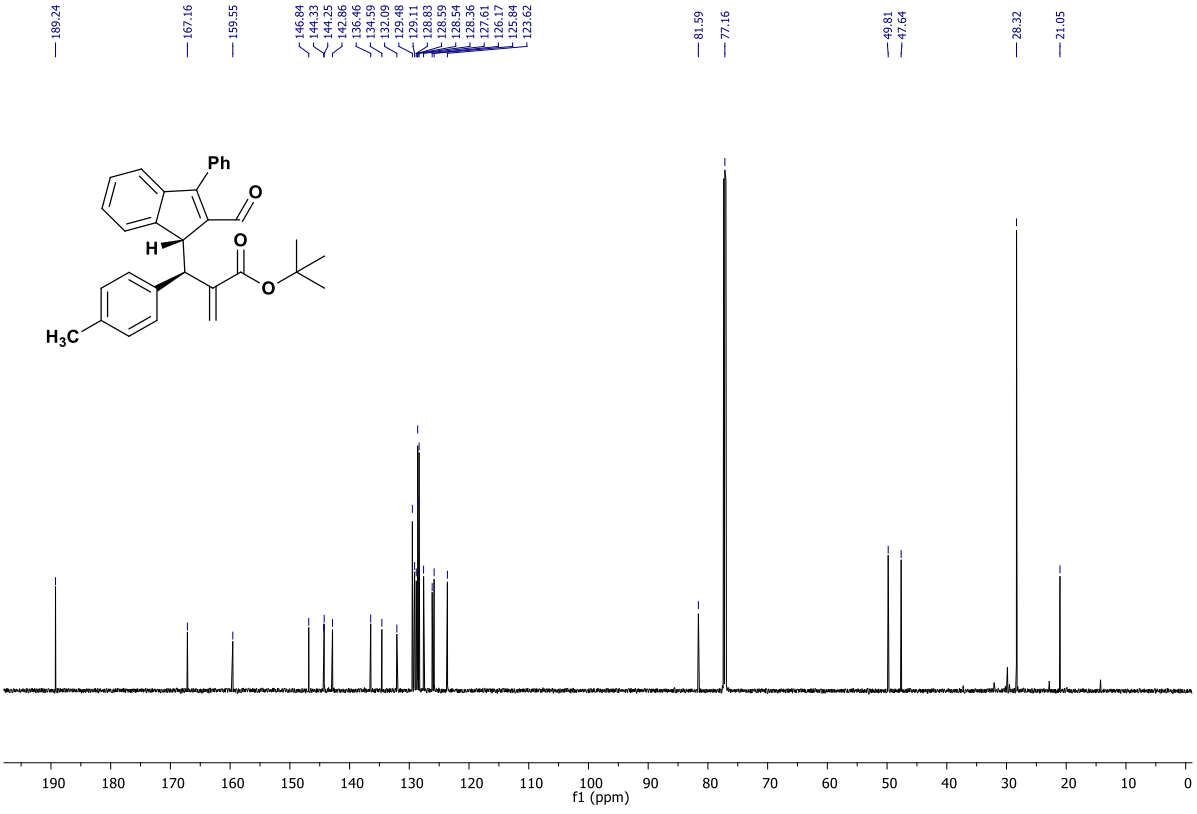


tert-Butyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(p-tolyl)methyl)acrylate (3o)

^{1}H NMR (700 MHz, $CDCl_3$)

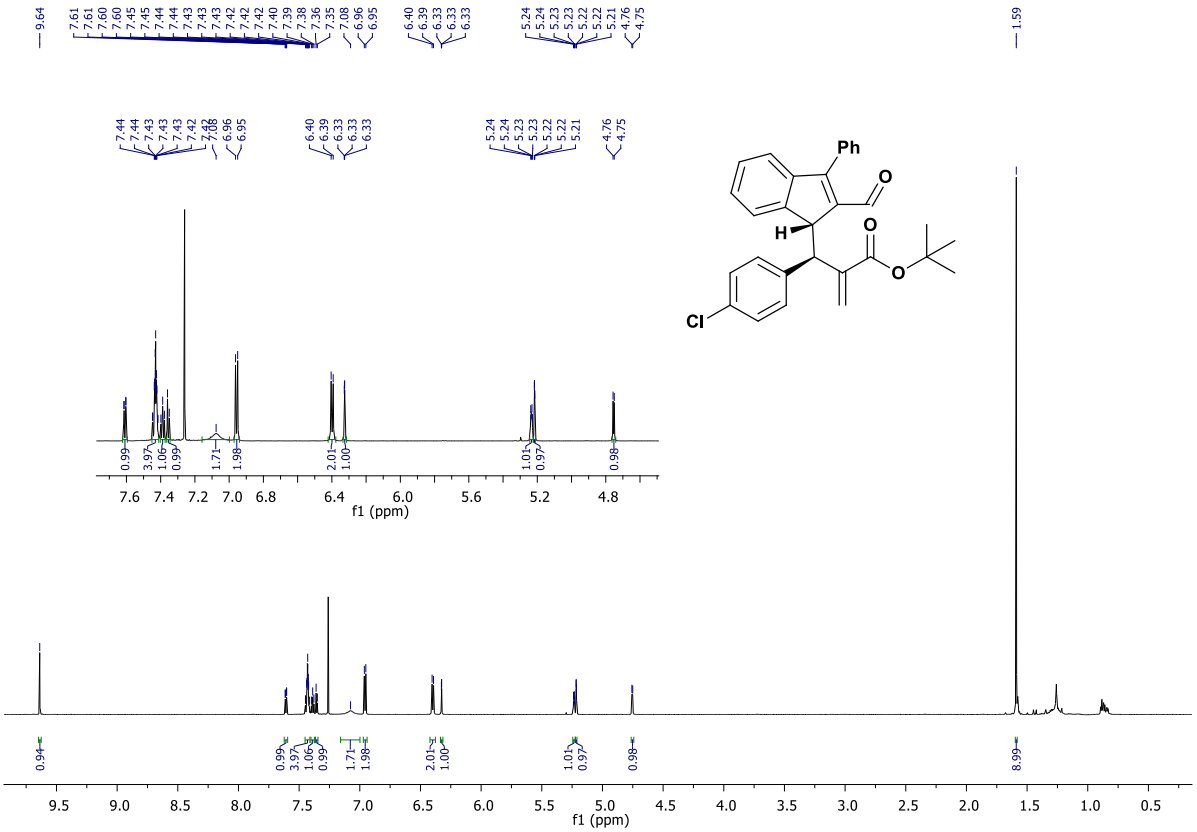


^{13}C NMR (176 MHz, $CDCl_3$)

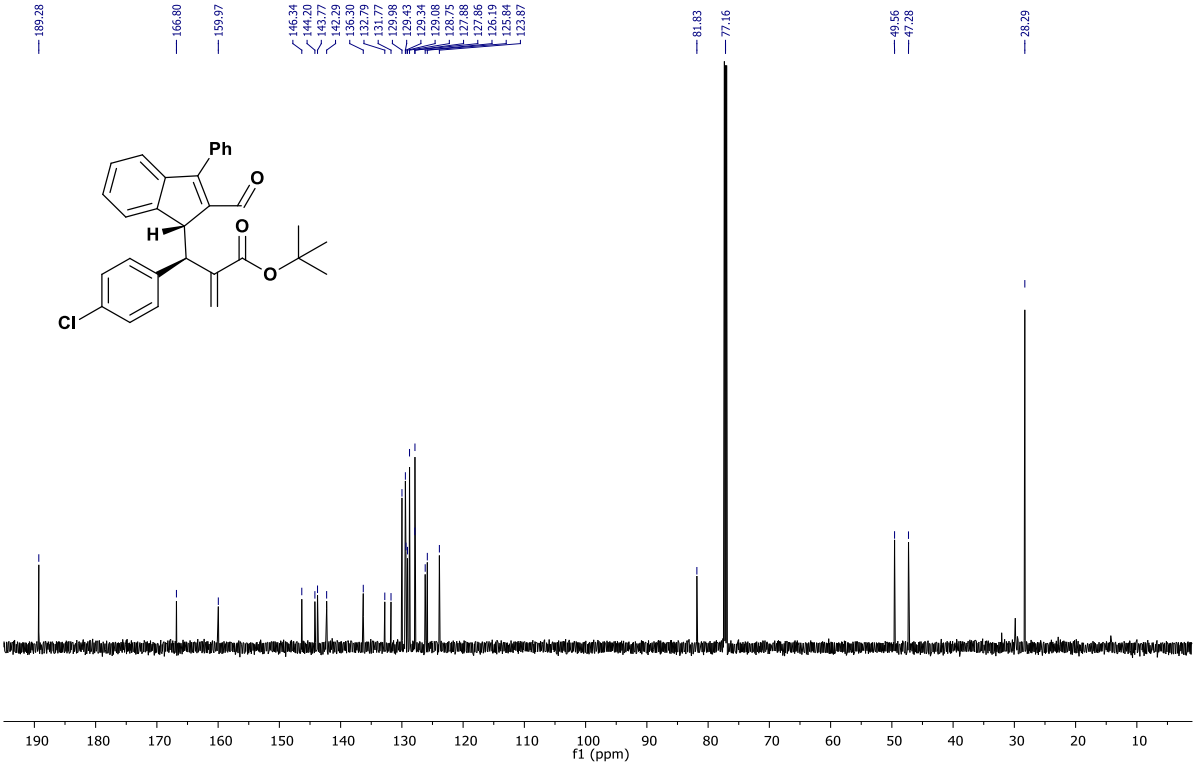


tert-Butyl 2-((*R*)-(4-chlorophenyl)((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)methyl)acrylate (3p)

^{1}H NMR (700 MHz, $CDCl_3$)

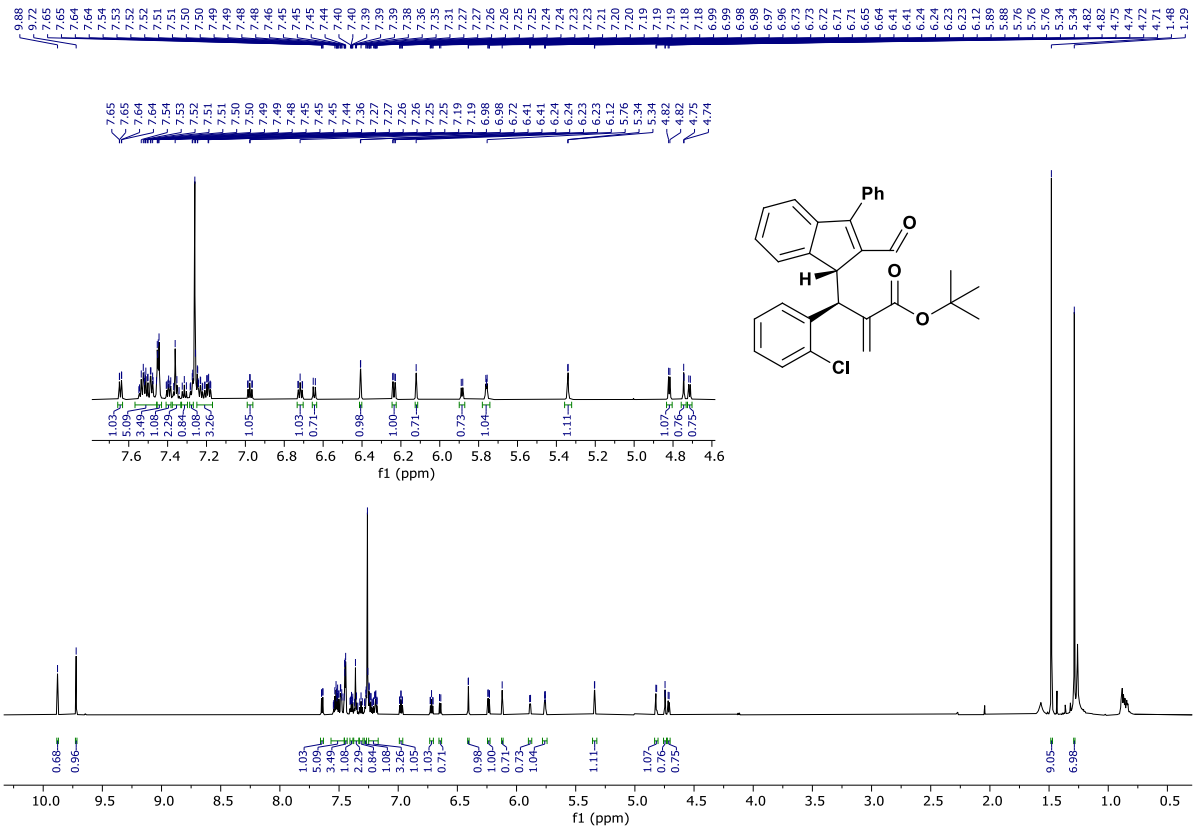


^{13}C NMR (176 MHz, $CDCl_3$)

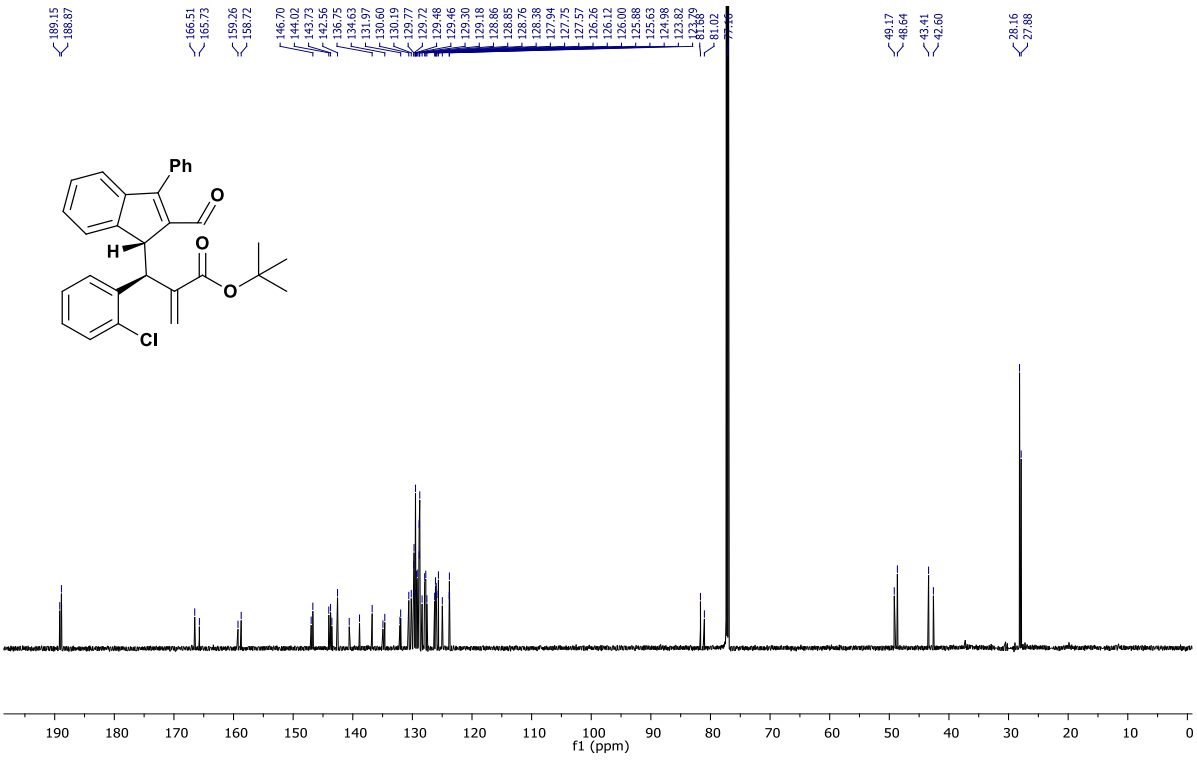


tert-Butyl 2-((*S*)-(2-chlorophenyl)((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)methyl)acrylate (3q)

^{1}H NMR mixture of diastereomers (700 MHz, $CDCl_3$)

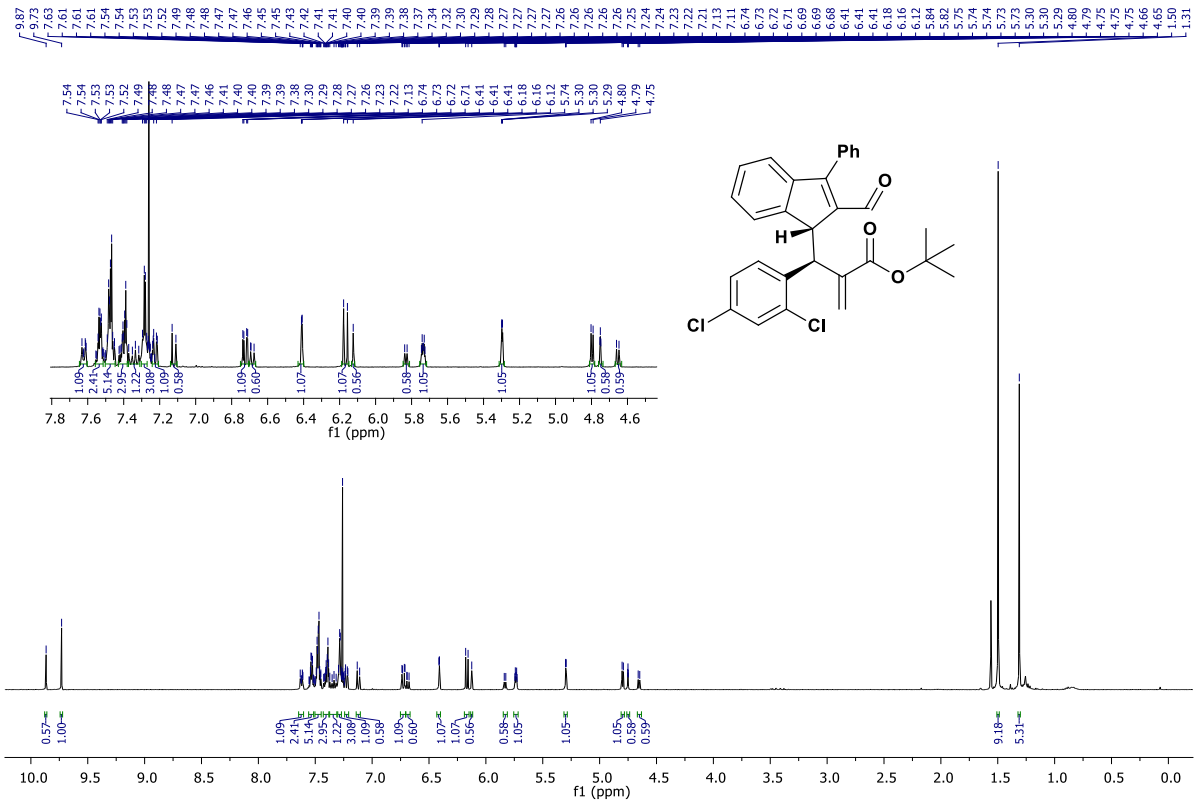


^{13}C NMR mixture of diastereomers (176 MHz, $CDCl_3$)

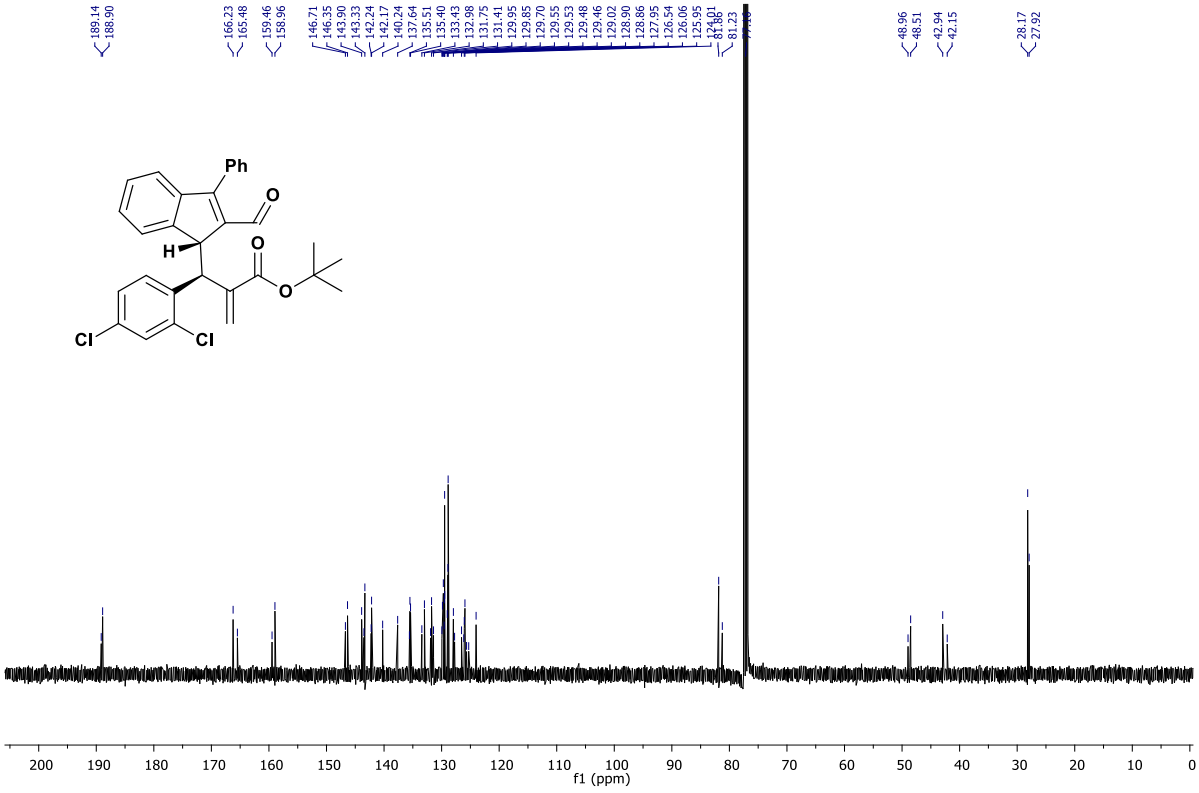


tert-Butyl 2-((*S*)-(2,4-dichlorophenyl)((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)methyl)-acrylate (3r)

^{1}H NMR mixture of diastereomers (700 MHz, $CDCl_3$)

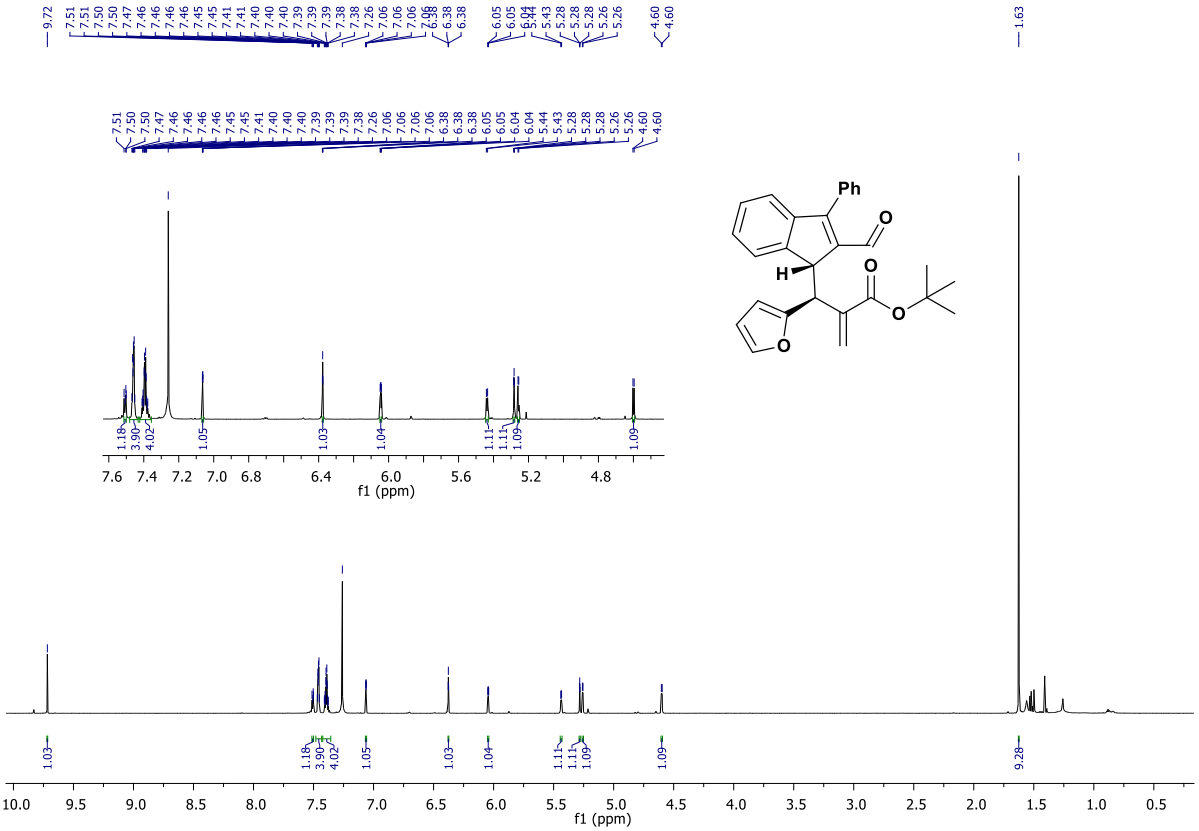


^{13}C NMR mixture of diastereomers (176 MHz, $CDCl_3$)

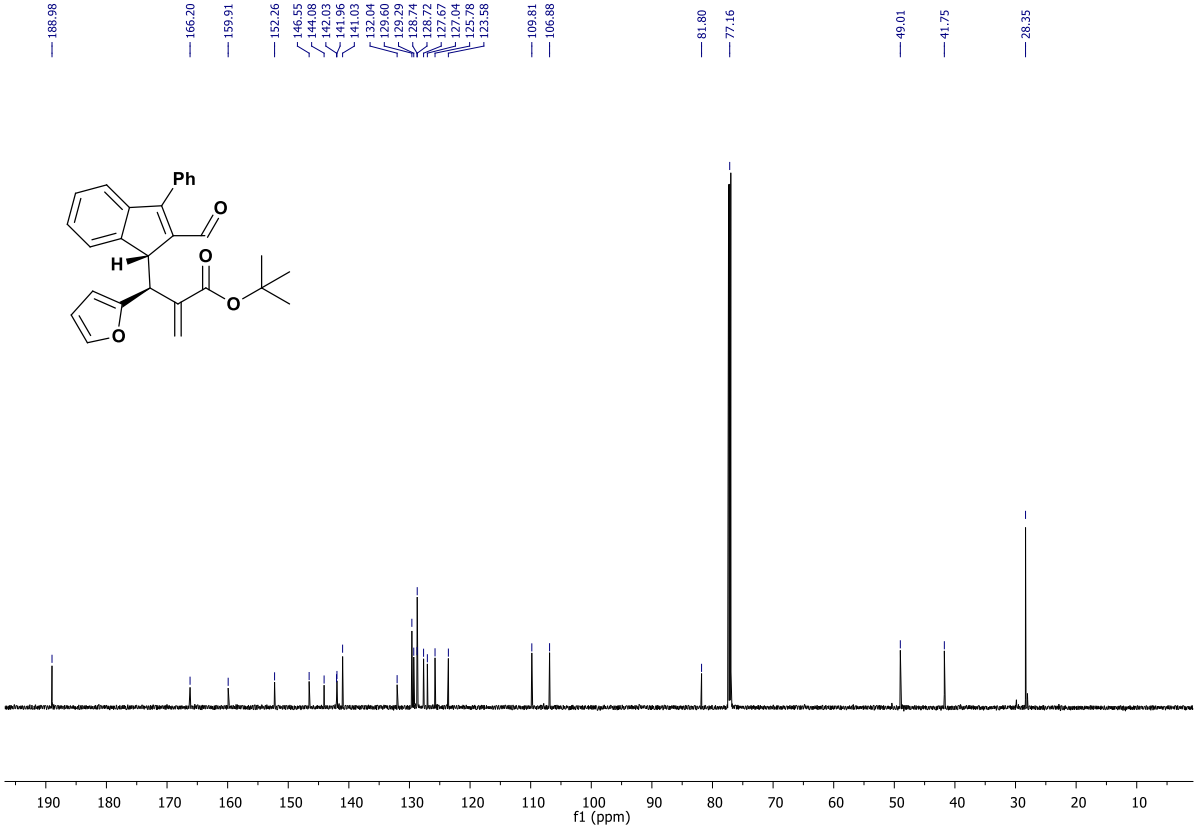


tert-Butyl 2-((*S*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(furan-2-yl)methyl)acrylate (3s)

^{1}H NMR (700 MHz, $CDCl_3$)

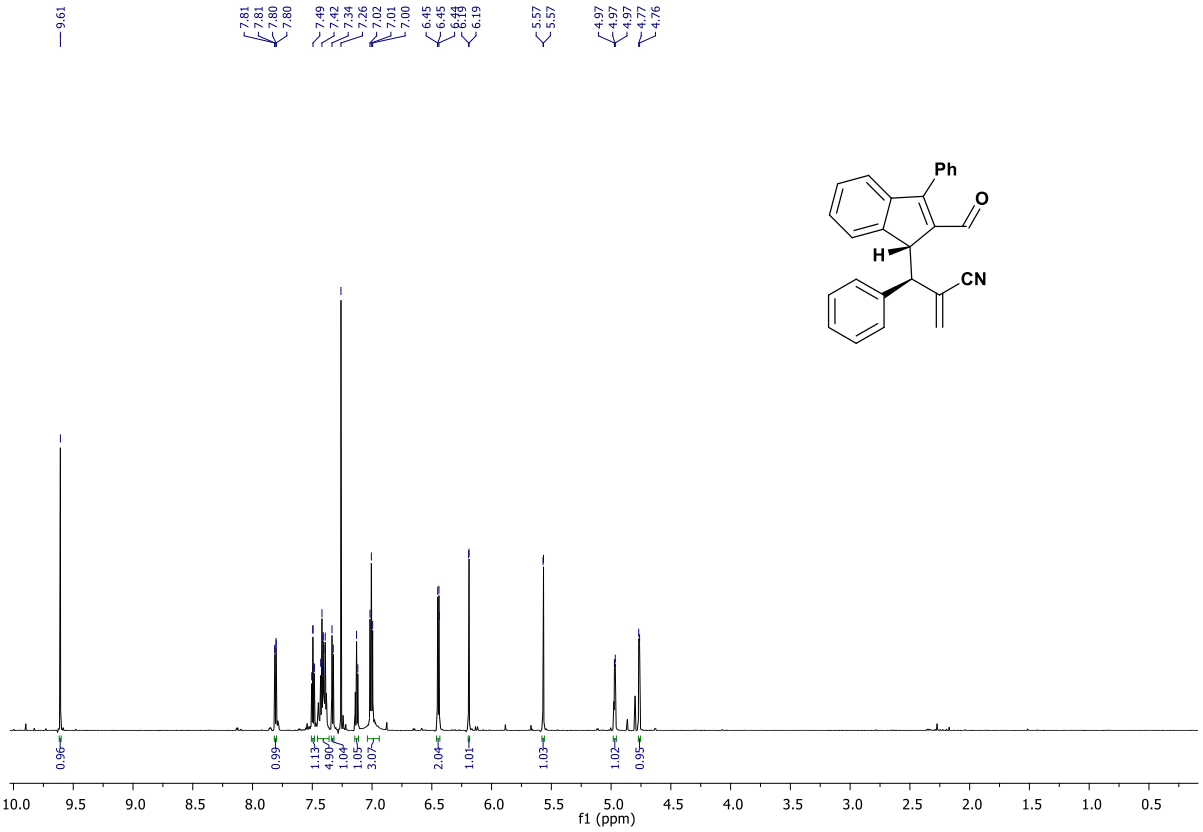


^{13}C NMR (176 MHz, $CDCl_3$)

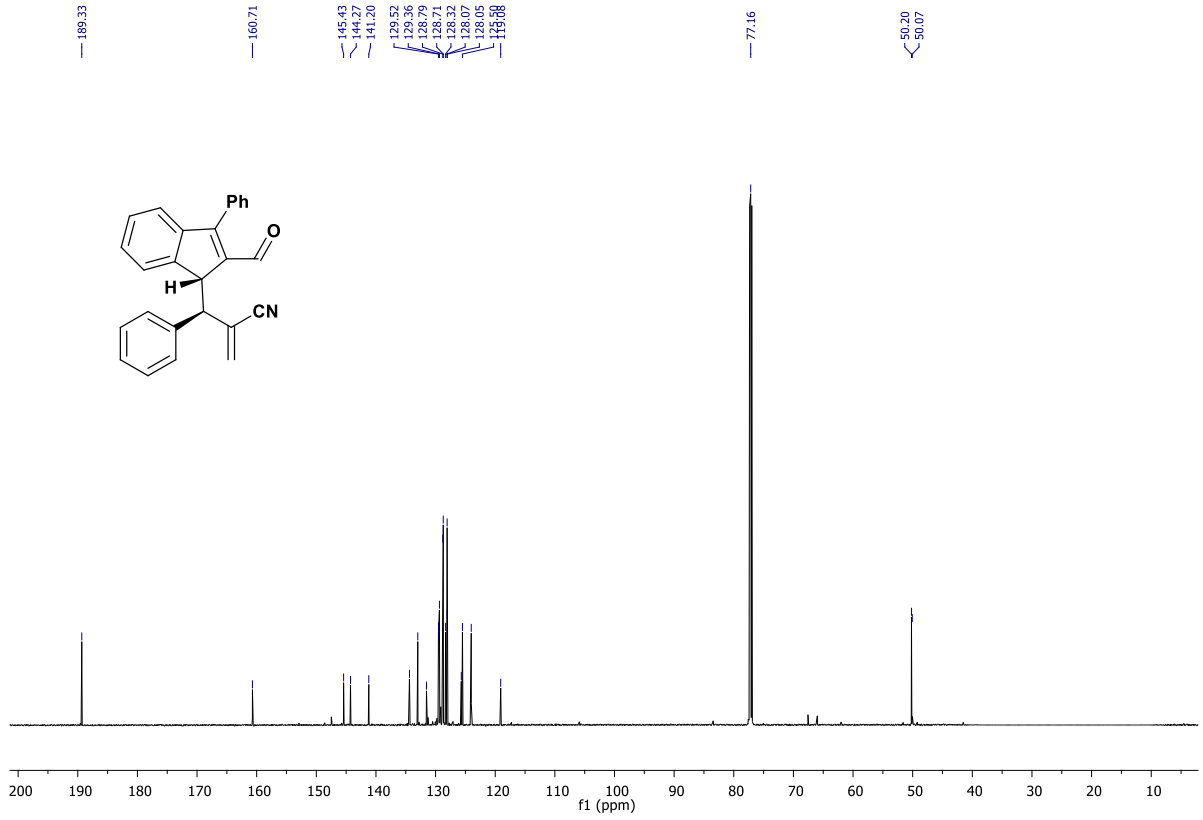


2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)acrylonitrile (3t)

^{1}H NMR (700 MHz, $CDCl_3$)

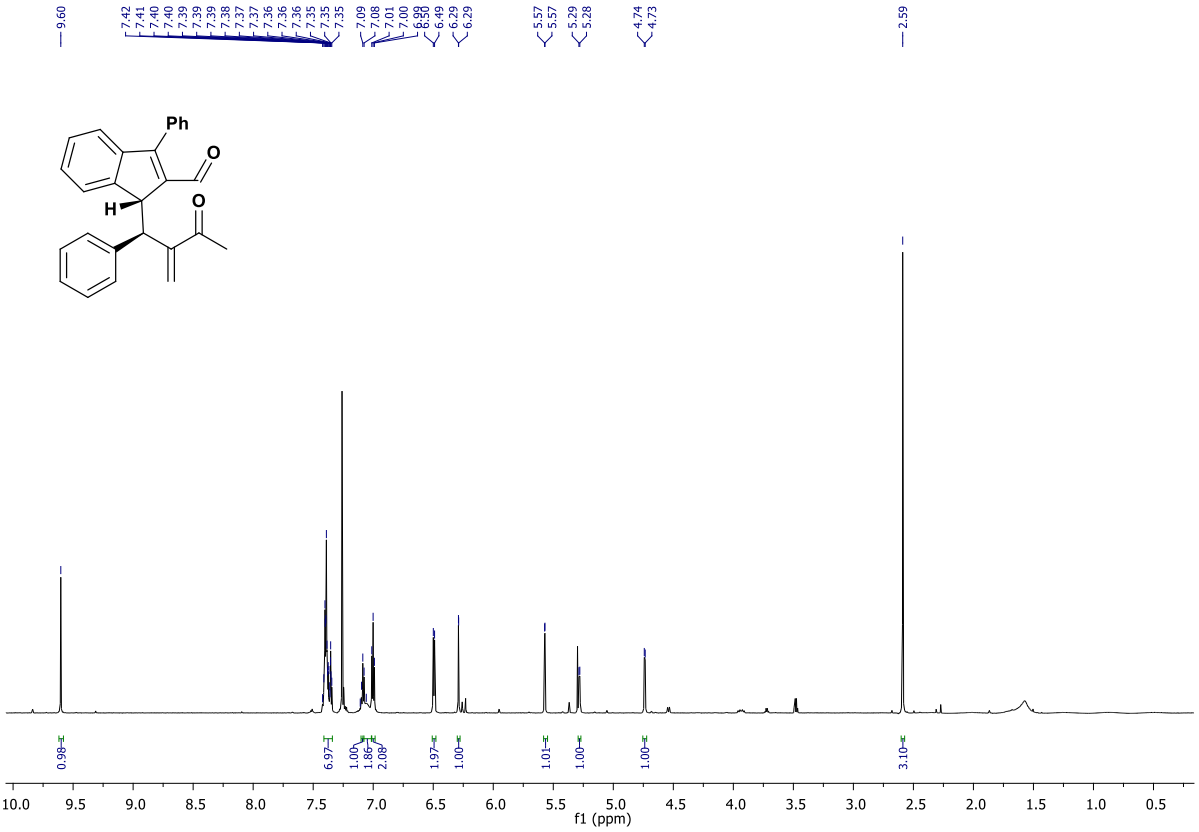


^{13}C NMR (176 MHz, $CDCl_3$)

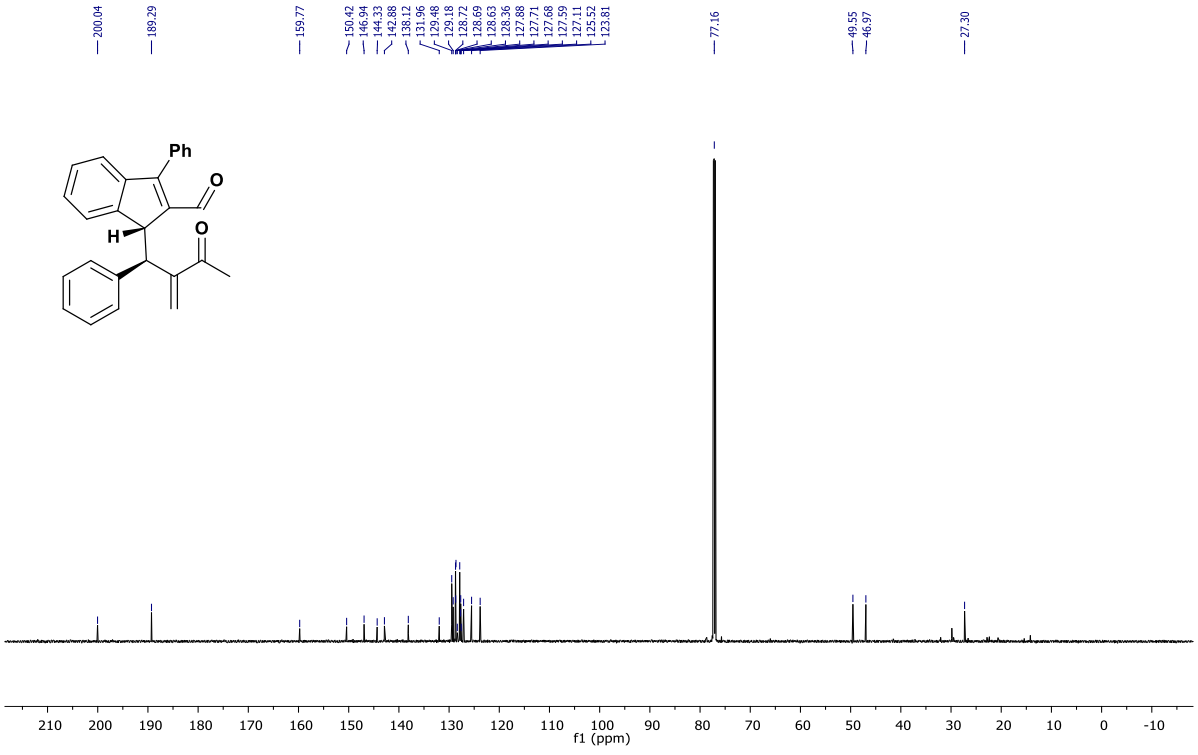


(*R*)-1-((*R*)-2-methylene-3-oxo-1-phenylbutyl)-3-phenyl-1*H*-indene-2-carbaldehyde (3u)

^{1}H NMR (700 MHz, $CDCl_3$)

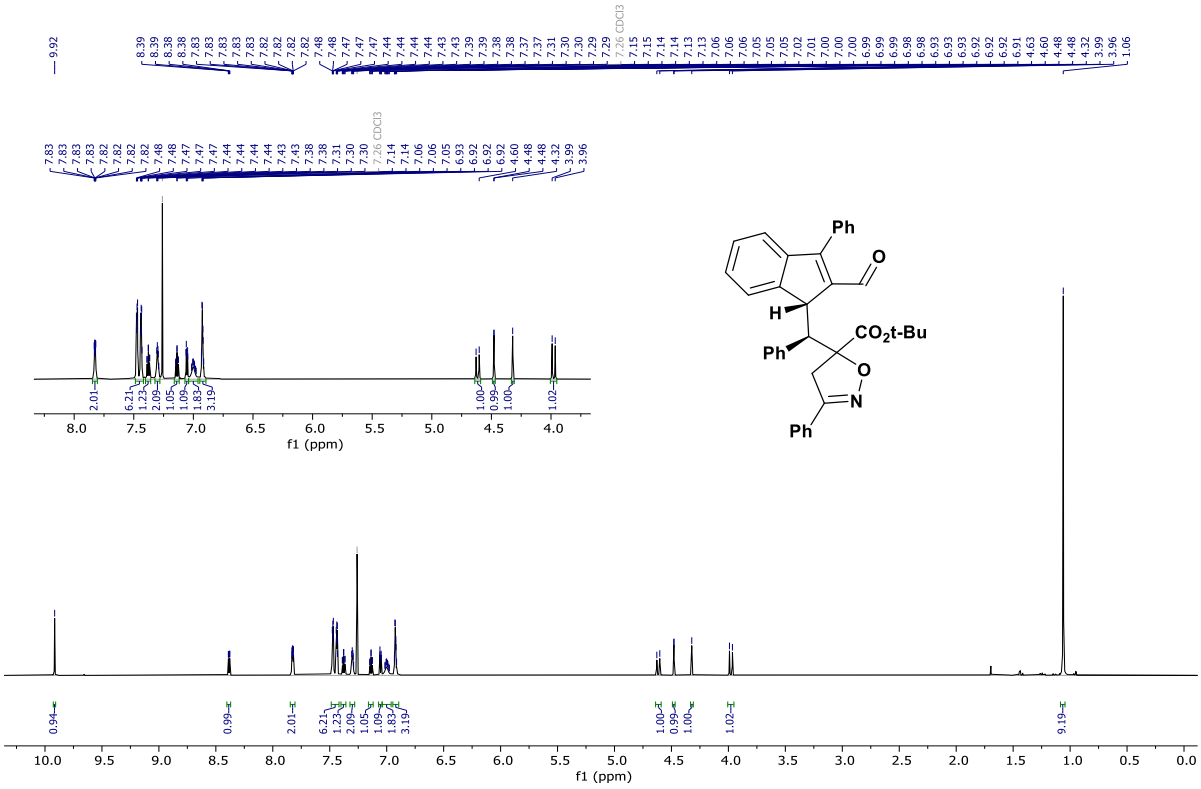


^{13}C NMR (176 MHz, $CDCl_3$)

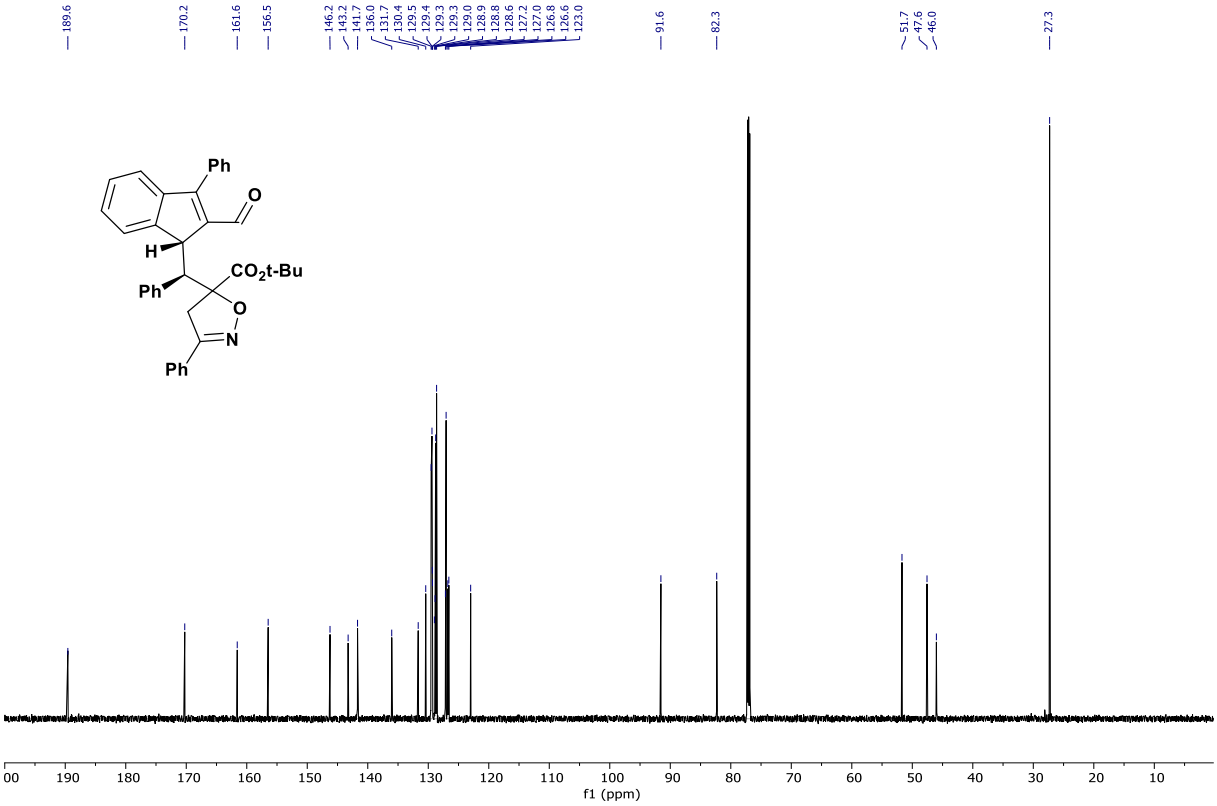


tert-Butyl 5-((R)-((R)-2-formyl-3-phenyl-1H-inden-1-yl)(phenyl)methyl)-3-phenyl-4,5-dihydroisoxazole-5-carboxylate (6b)

^{1}H NMR (700 MHz, $CDCl_3$)

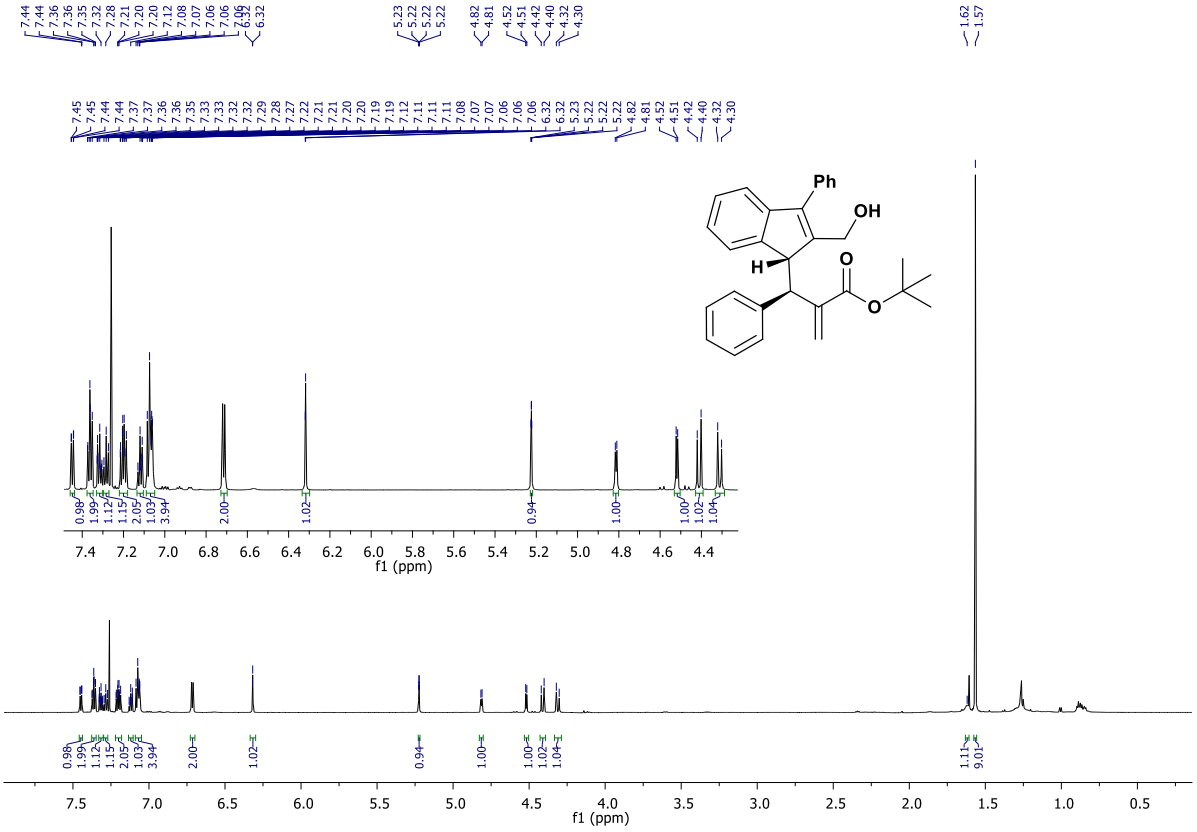


^{13}C NMR (176 MHz, $CDCl_3$)

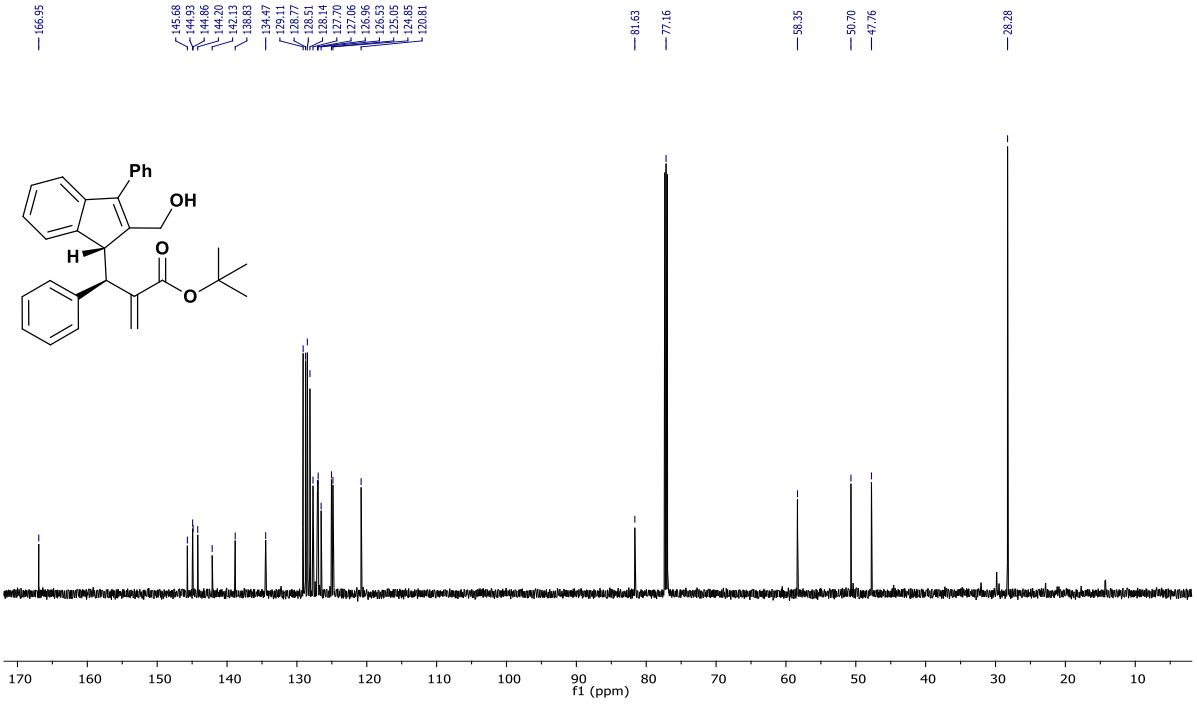


tert-Butyl 2-((*R*)-((*R*)-2-(hydroxymethyl)-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (7b)

^{1}H NMR (700 MHz, $CDCl_3$)

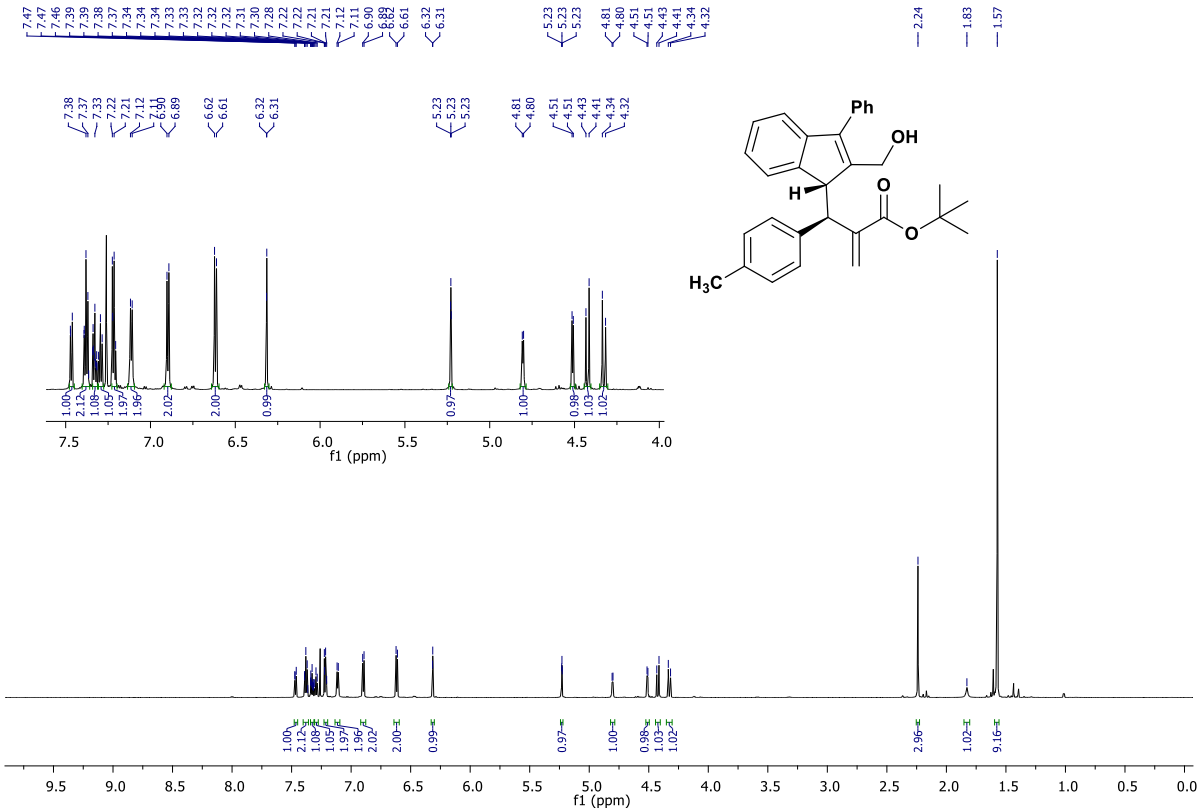


^{13}C NMR (176 MHz, $CDCl_3$)

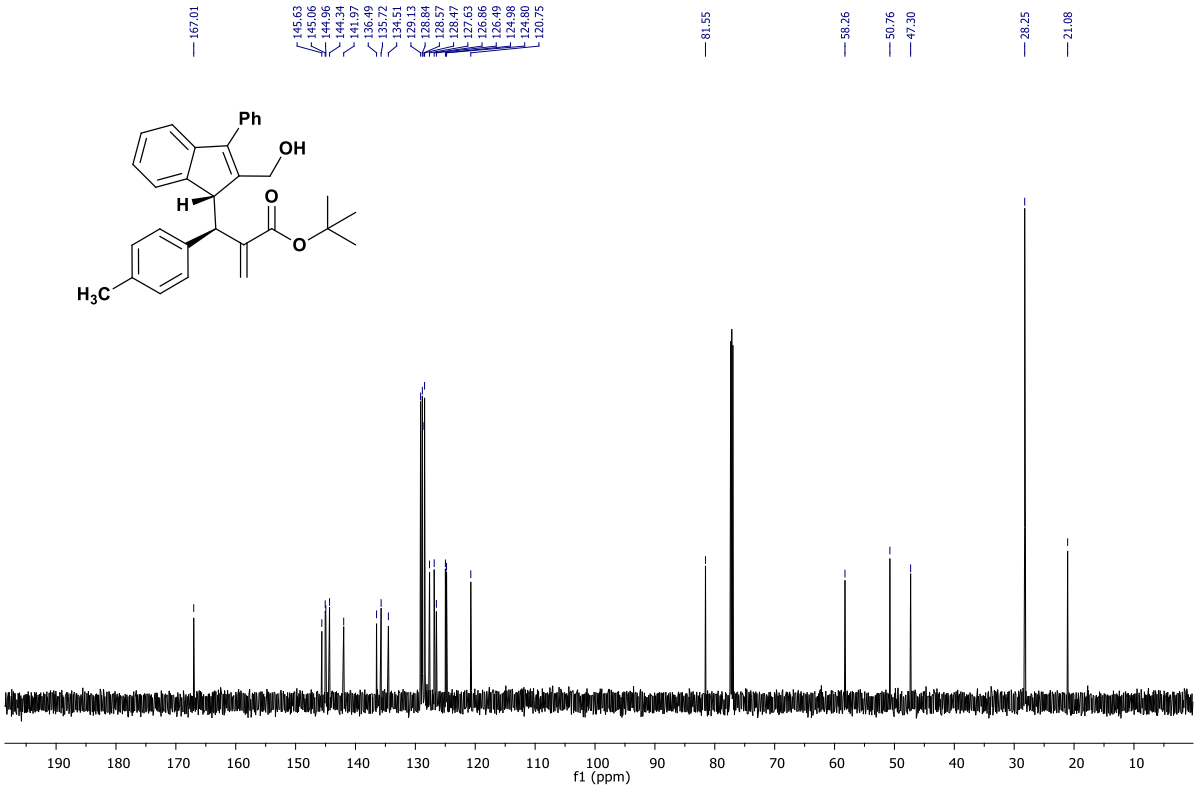


tert-Butyl 2-((R)-((R)-2-(hydroxymethyl)-3-phenyl-1H-inden-1-yl)(p-tolyl)methyl)-acrylate (7o)

^{1}H NMR (700 MHz, $CDCl_3$)

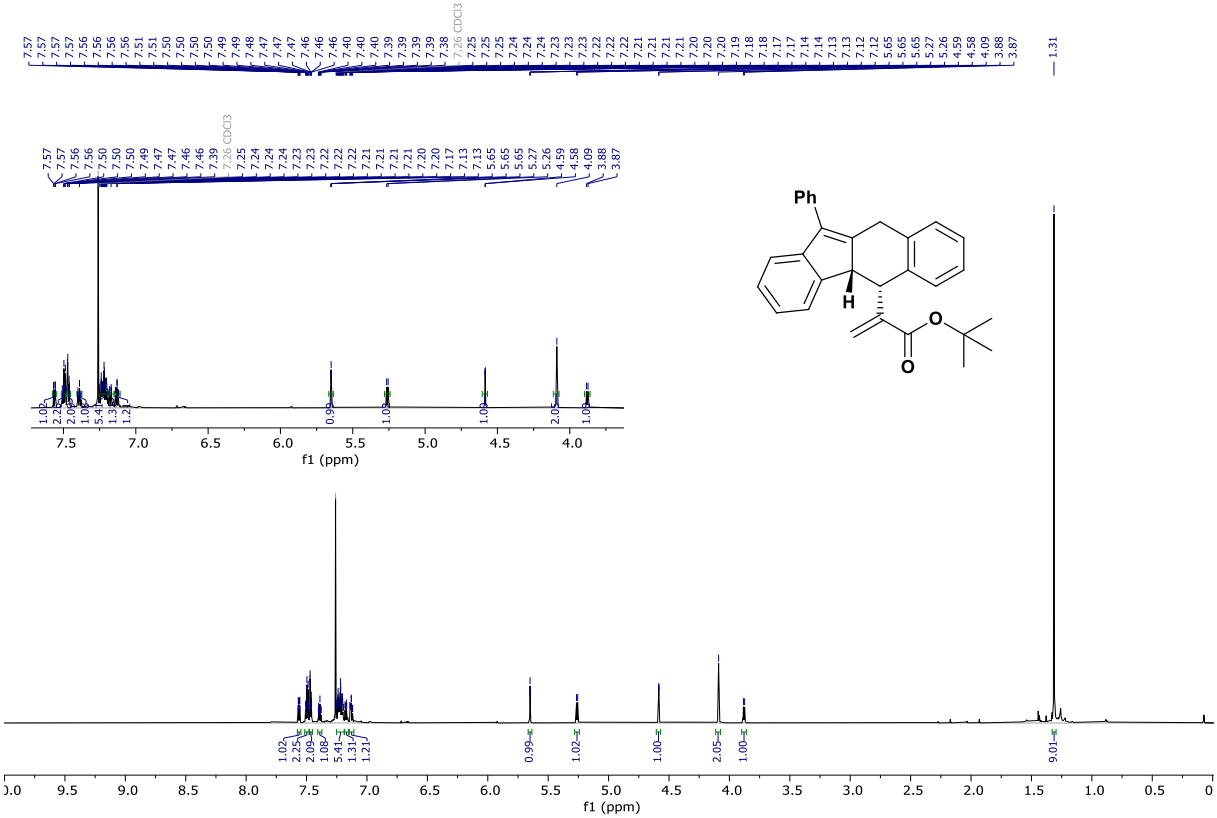


^{13}C NMR (176 MHz, $CDCl_3$)

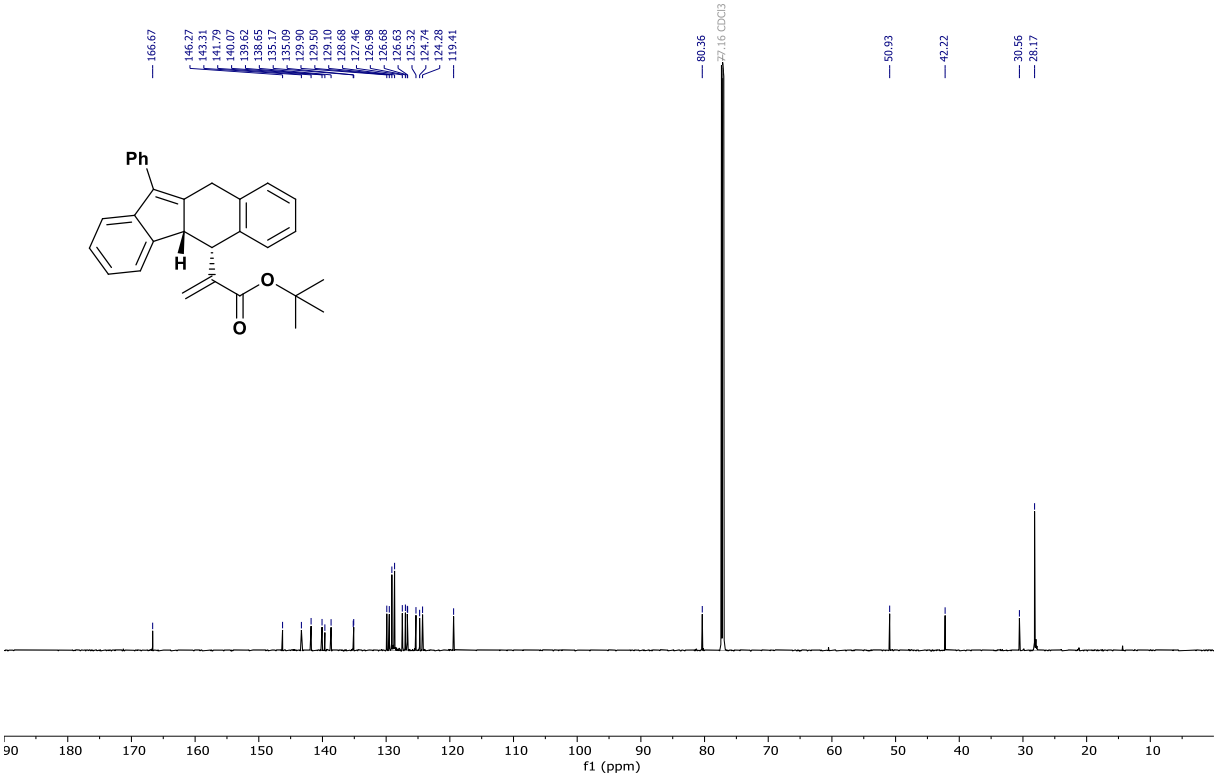


tert-Butyl 2-((4bS,5R)-11-phenyl-5,10-dihydro-4bH-benzo[b]fluoren-5-yl)acrylate (8b)

^{1}H NMR (700 MHz, $CDCl_3$)

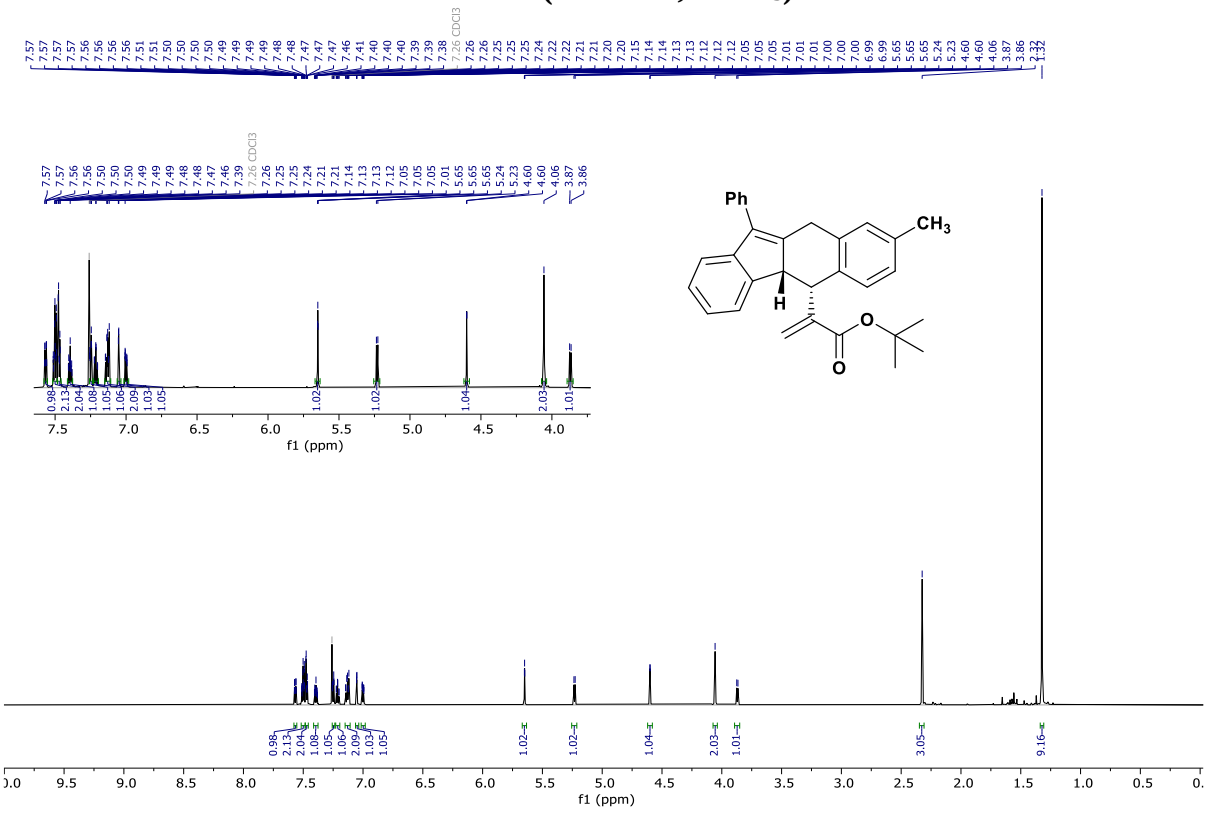


^{13}C NMR (176 MHz, $CDCl_3$)

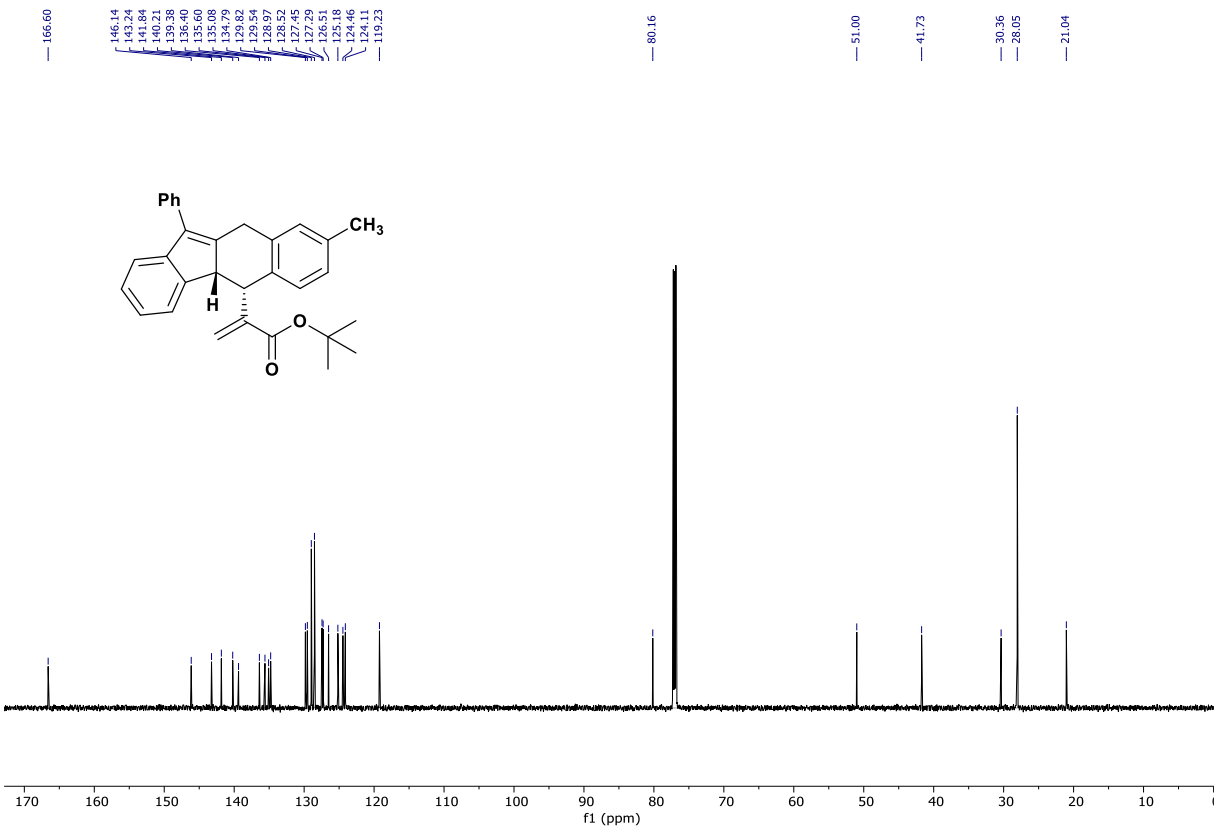


tert-Butyl 2-((4bS,5R)-8-methyl-11-phenyl-4b,10-dihydro-5H-benzo[b]fluoren-5-yl)-acrylate (8o)

^{1}H NMR (700 MHz, $CDCl_3$)

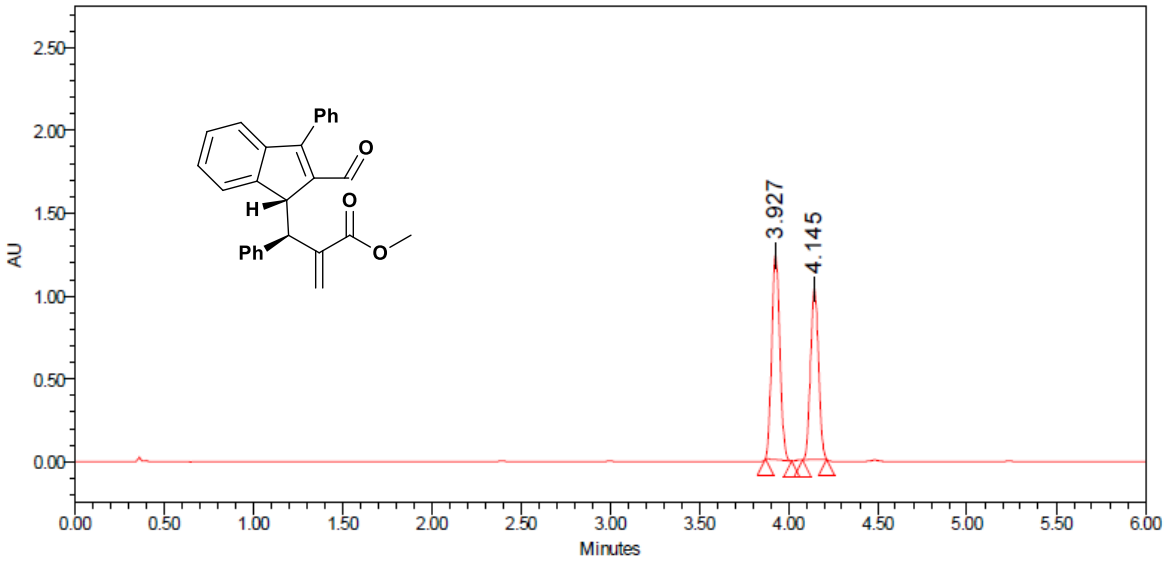


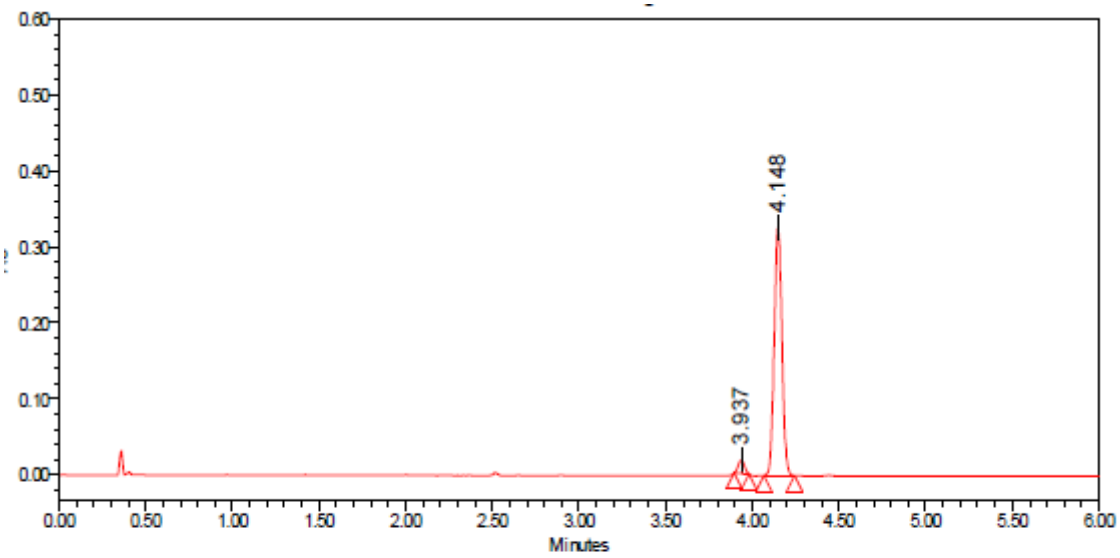
^{13}C NMR (176 MHz, $CDCl_3$)



UPCC, HPLC data

Methyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1H-inden-1-yl)(phenyl)methyl)acrylate (3a)

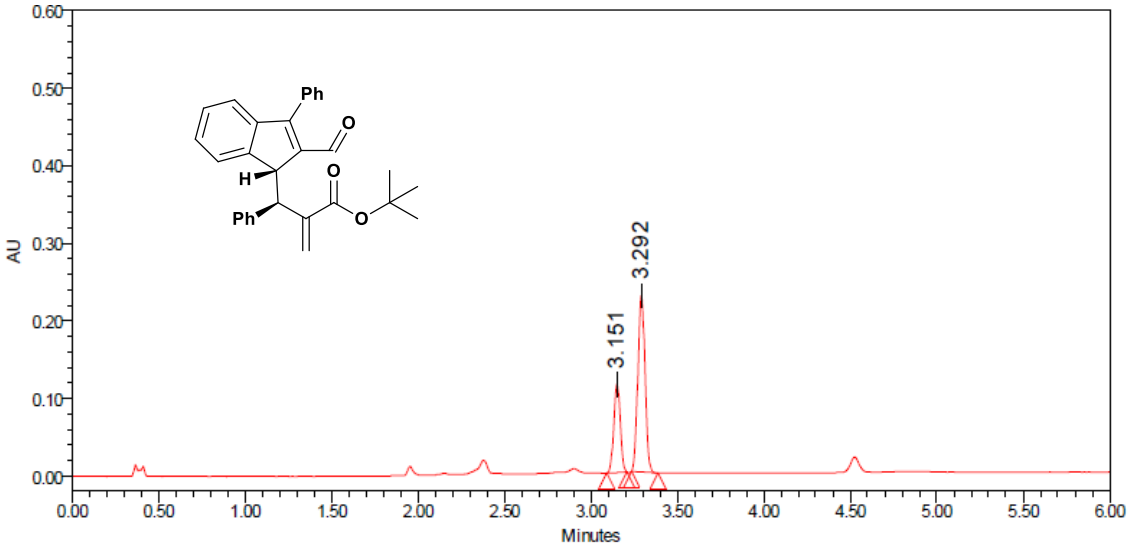


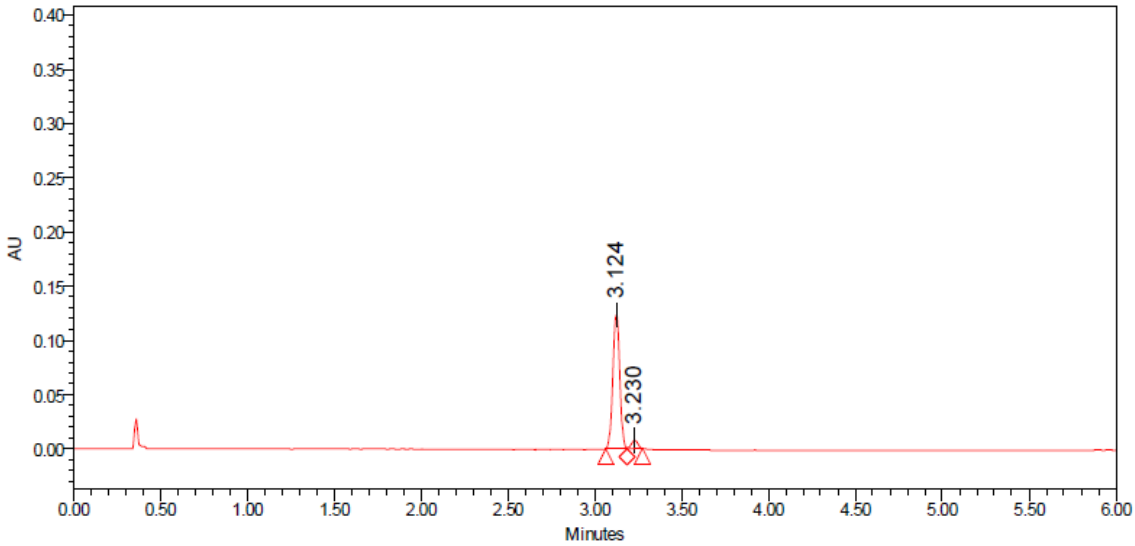


Peak Results

	RT	% Area
1	3.937	4.24
2	4.148	95.76

***tert*-Butyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)acrylate (3b)**

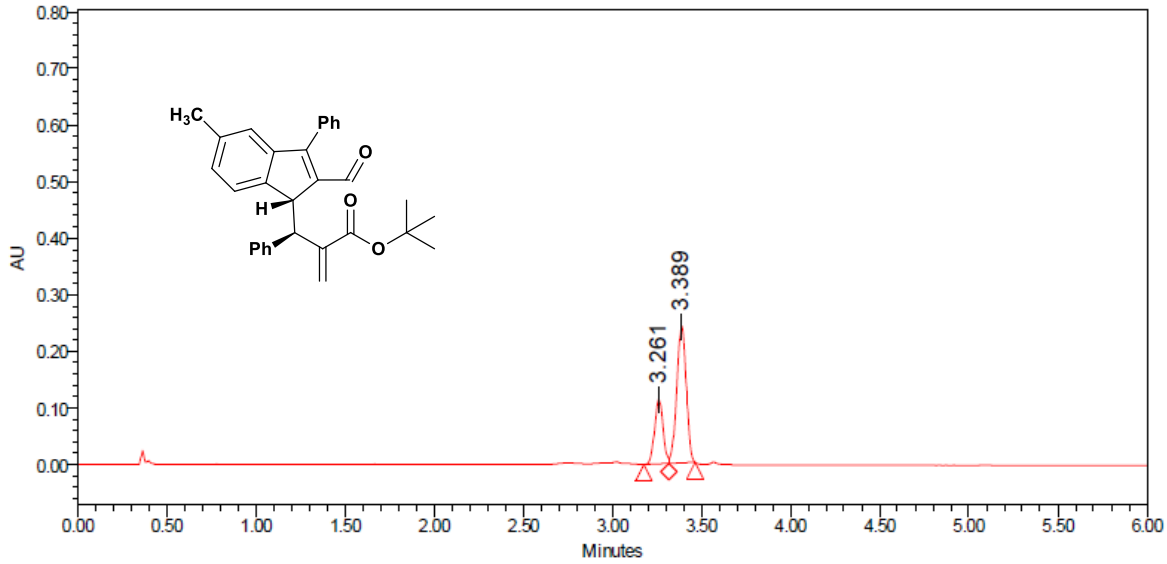


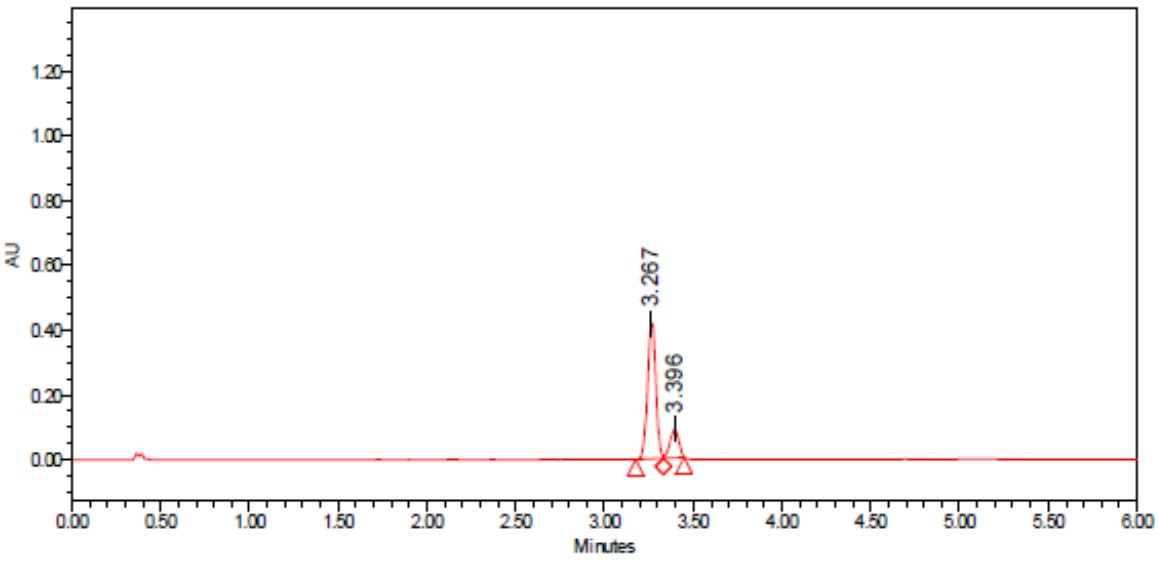


Peak Results

	RT	% Area
1	3.124	94.64
2	3.230	5.36

tert-Butyl 2-((_R_)-((_R_)-2-formyl-5-methyl-3-phenyl-1_H_-inden-1-yl)(phenyl)methyl)-acrylate (3c)

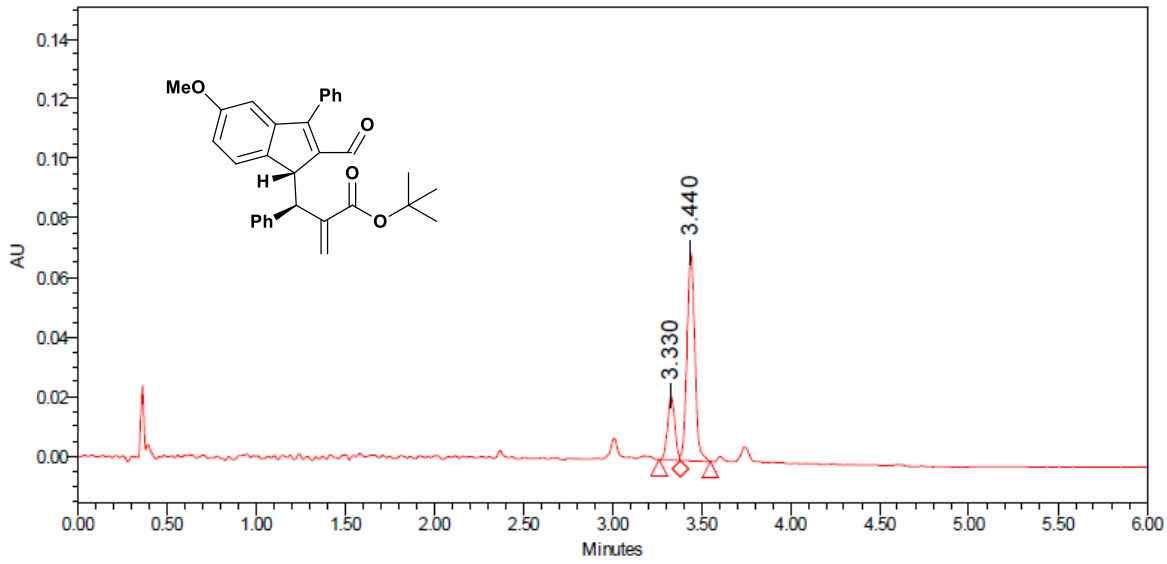


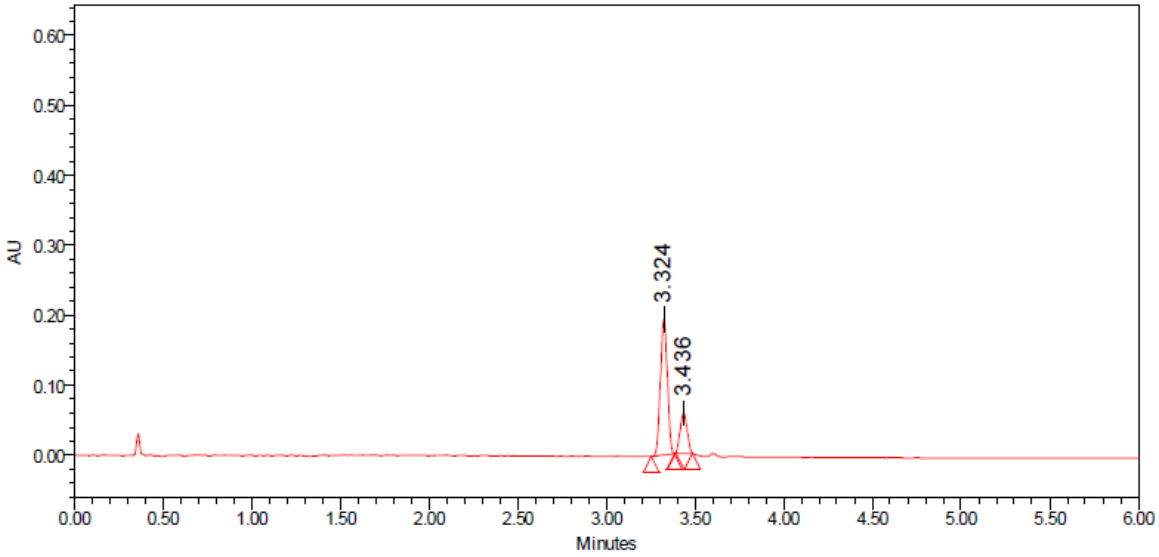


Peak Results

	RT	% Area
1	3.267	81.97
2	3.396	18.03

tert-Butyl 2-((_R_)-((_R_)-2-formyl-5-methoxy-3-phenyl-1_H_-inden-1-yl)(phenyl)methyl)-acrylate (3d)

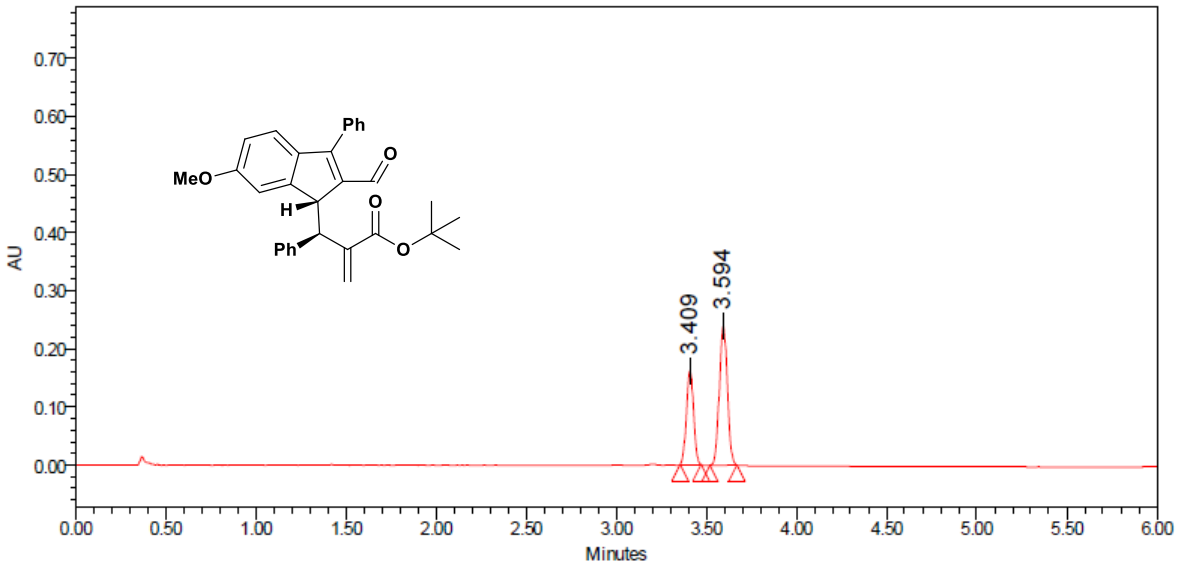


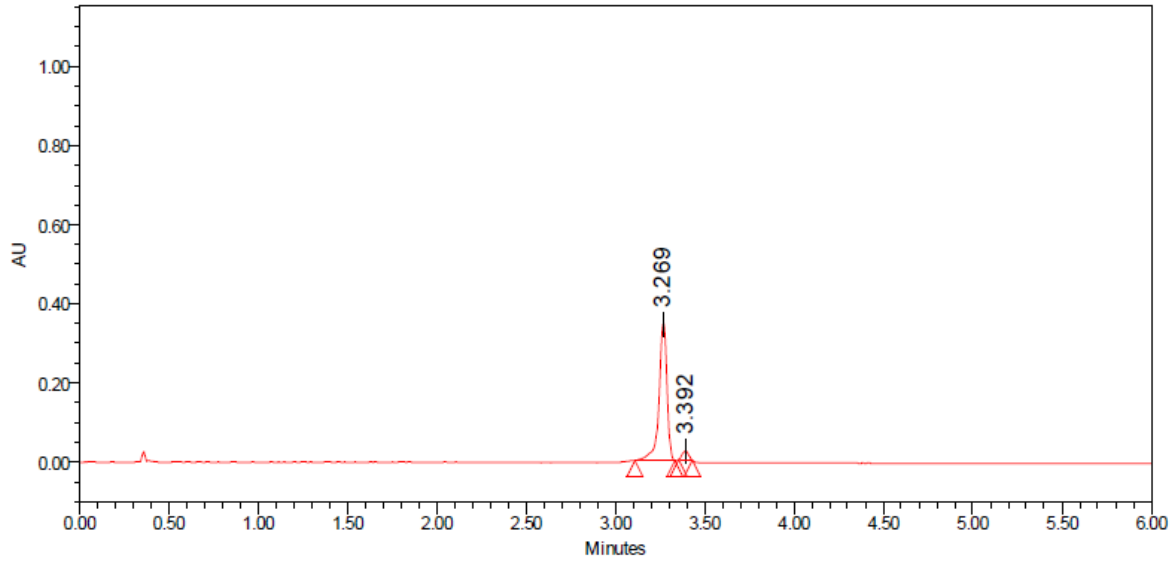


Peak Results

	RT	% Area
1	3.324	77.04
2	3.436	22.96

tert-Butyl 2-((_R_)-((_R_)-2-formyl-6-methoxy-3-phenyl-1_H_-inden-1-yl)(phenyl)methyl)-acrylate (3e)

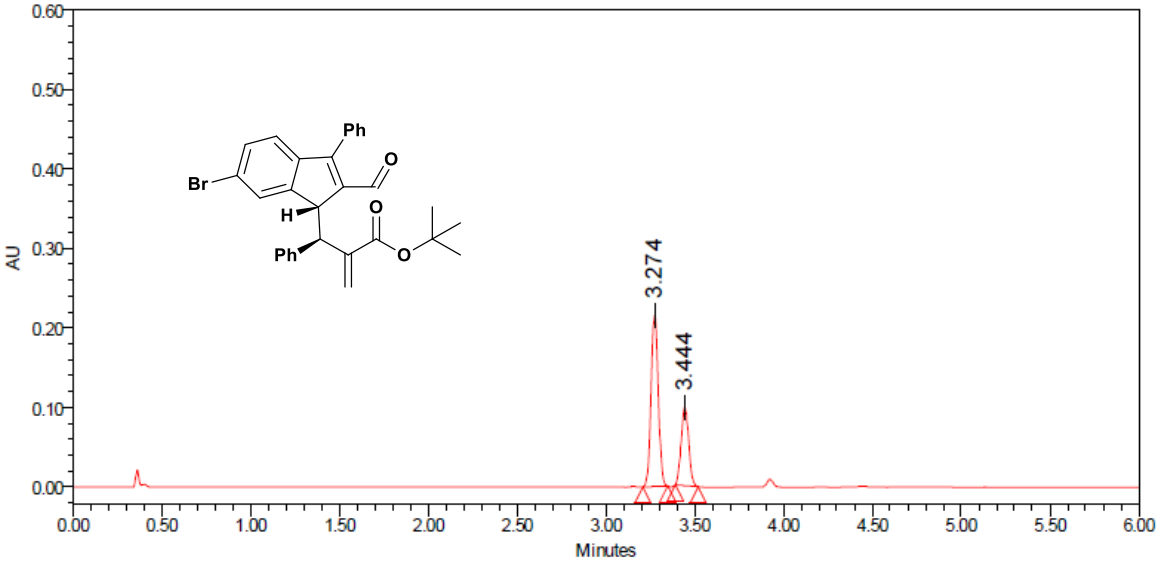


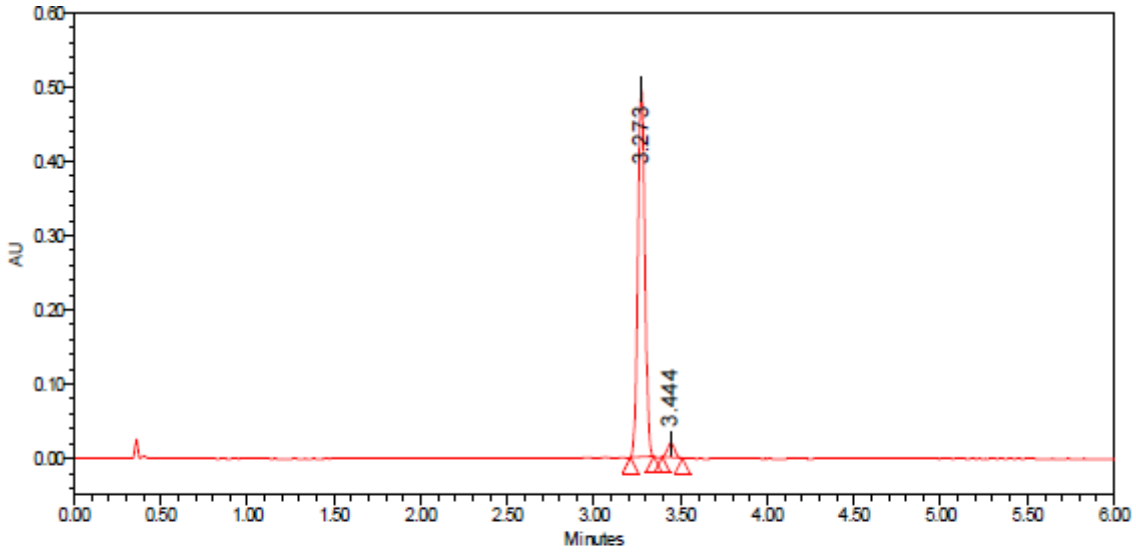


Peak Results

	RT	% Area
1	3.269	94.96
2	3.392	5.04

tert-Butyl 2-((_R_)-((_R_)-6-bromo-2-formyl-3-phenyl-1_H_-inden-1-yl)(phenyl)methyl)-acrylate (3f)

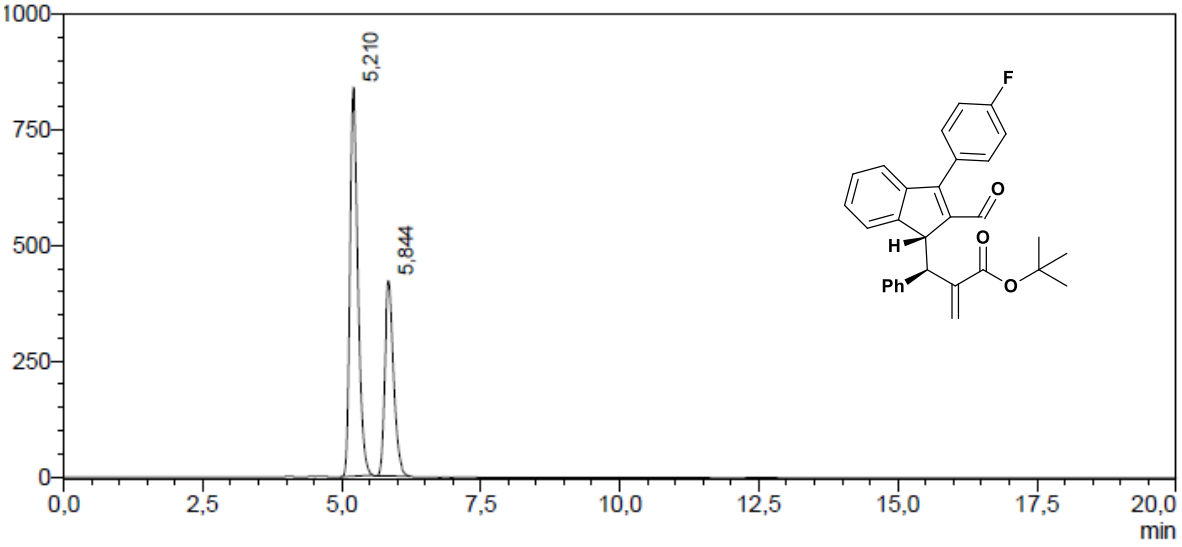


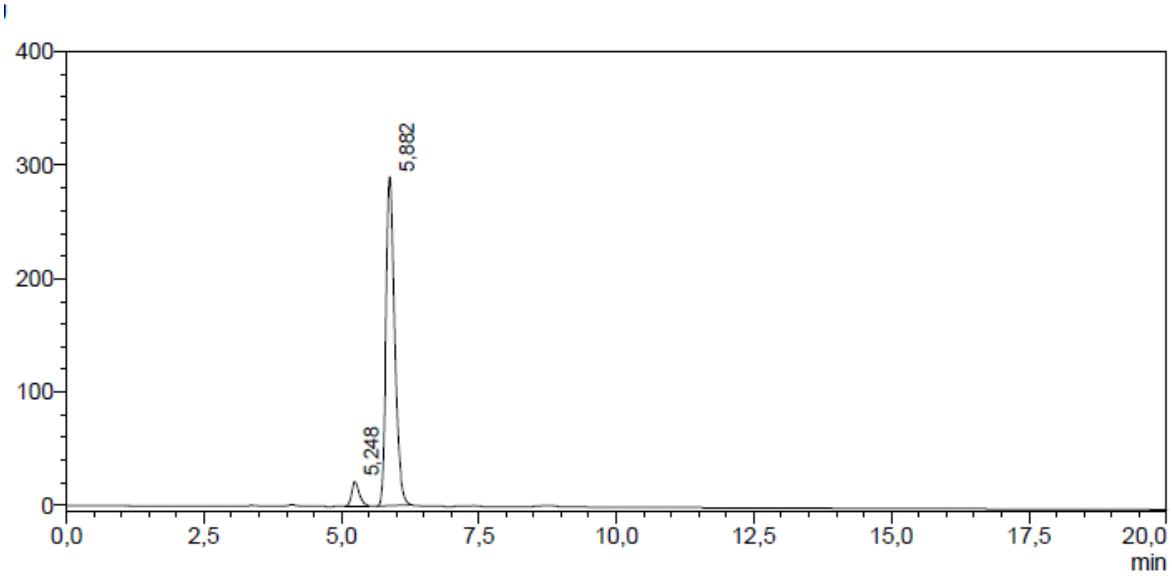


Peak Results

	RT	% Area
1	3.273	96.09
2	3.444	3.91

tert-Butyl 2-((_R_)-((_R_)-3-(4-fluorophenyl)-2-formyl-1_H_-inden-1-yl)(phenyl)methyl)-acrylate (3g)

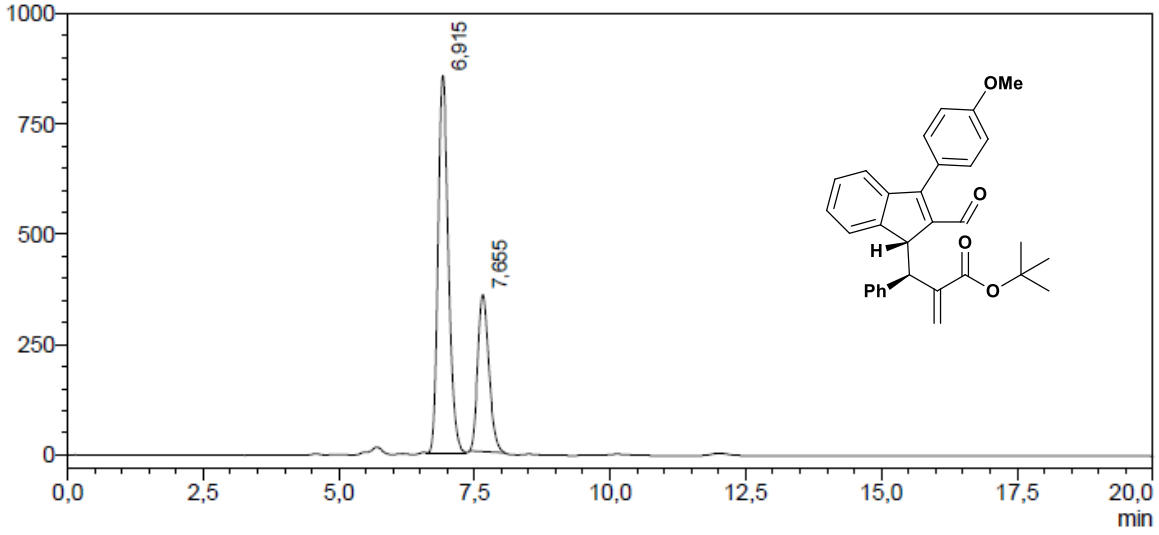


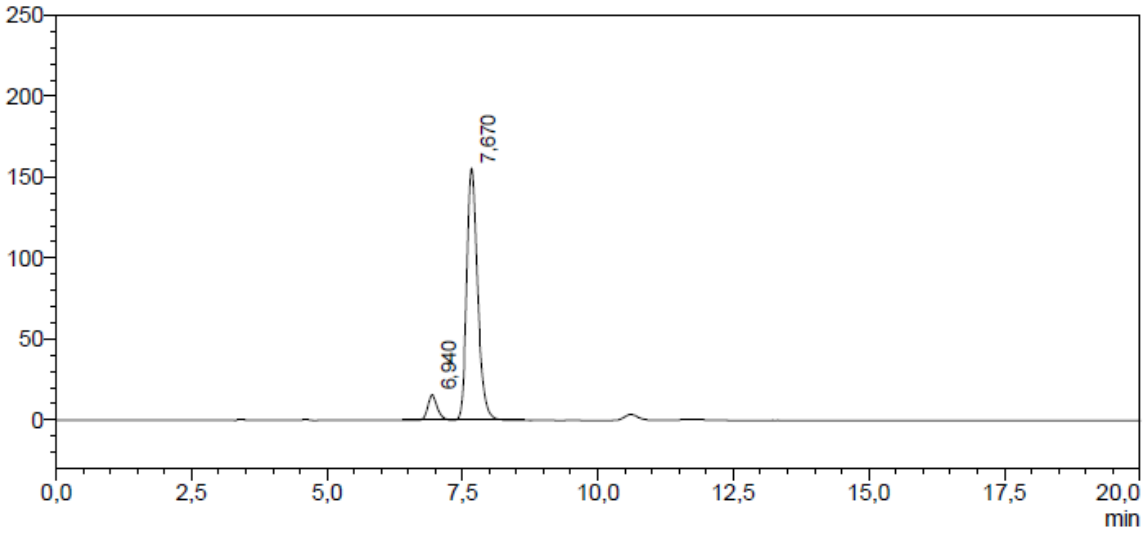


PDA Ch2 268nm

Peak#	Ret. Time	Area%
1	5,248	6,134
2	5,882	93,866
Total		100,000

tert-Butyl 2-((*R*)-((*R*)-2-formyl-3-(4-methoxyphenyl)-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3h)

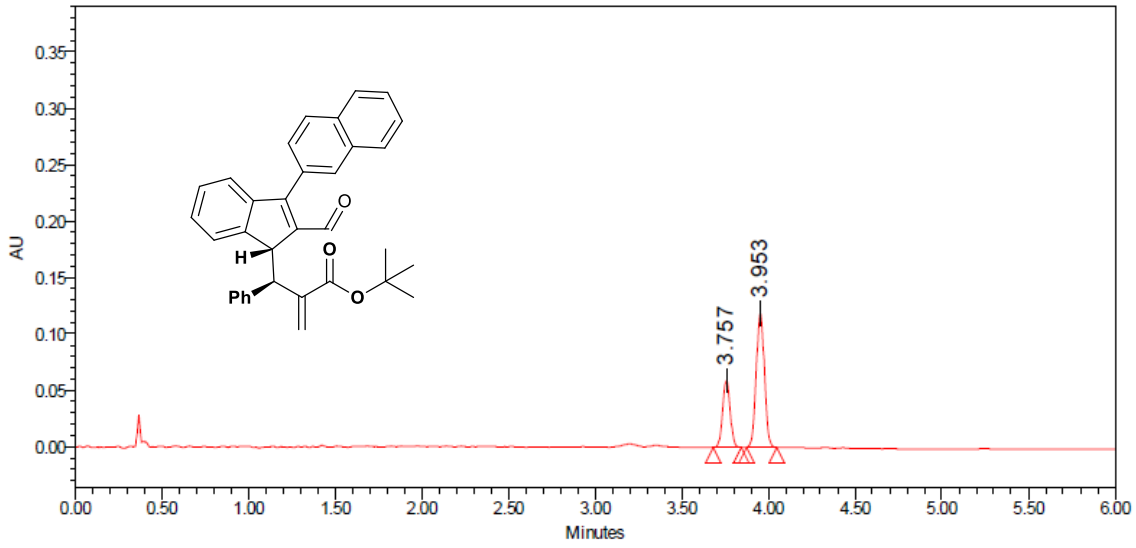


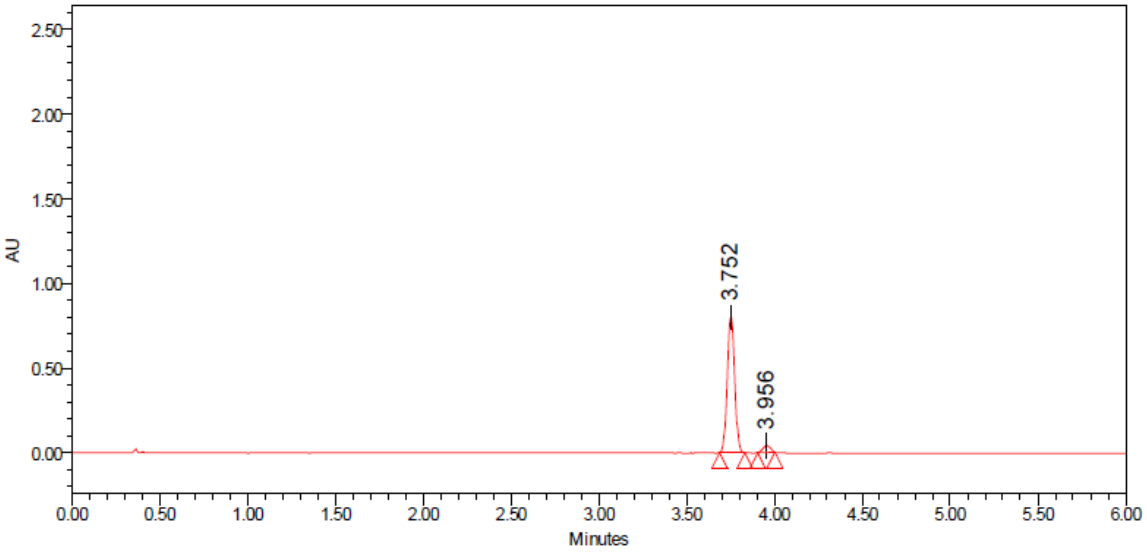


PDA Ch2 310nm

Peak#	Ret. Time	Area%
1	6,940	8,082
2	7,670	91,918
Total		100,000

tert-Butyl 2-((*R*)-((*R*)-2-formyl-3-(naphthalen-2-yl)-1*H*-inden-1-yl)(phenyl)methyl)-acrylate (3i)

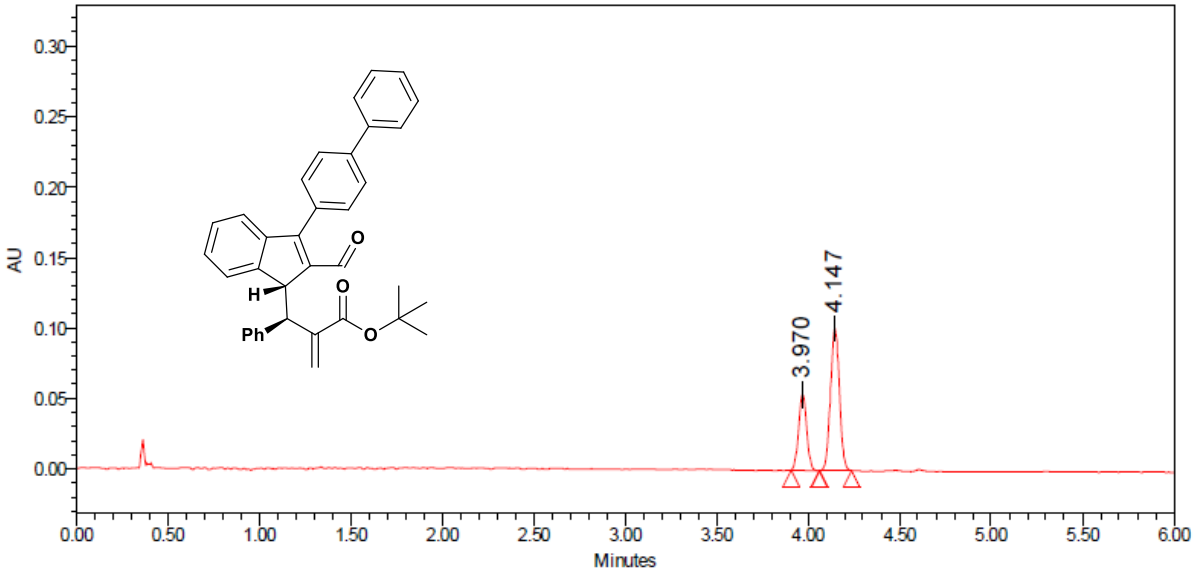


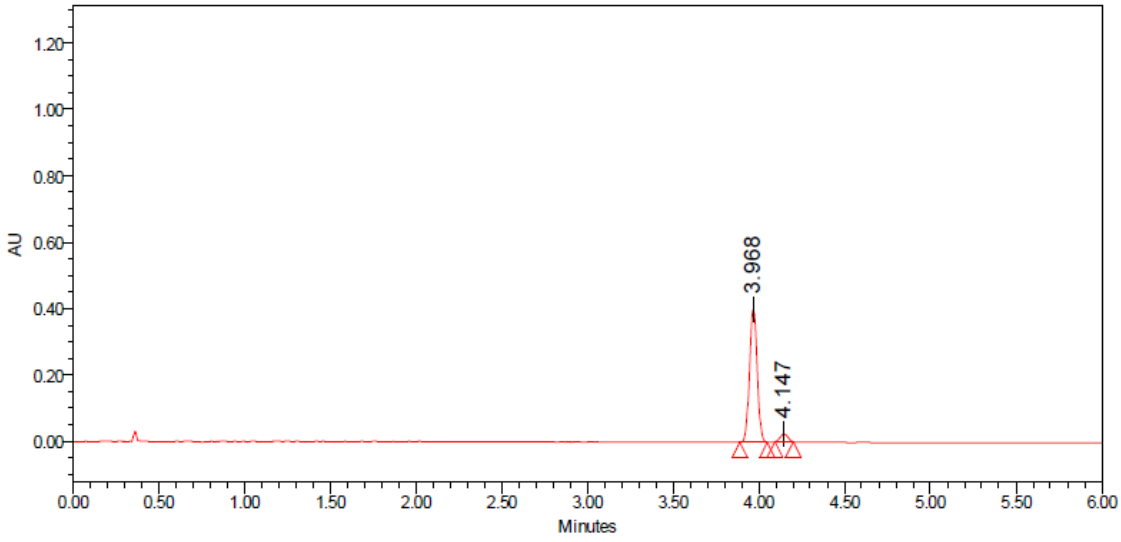


Peak Results

	RT	% Area
1	3.752	95.05
2	3.956	4.95

tert-Butyl 2-((_R_)-((_R_)-3-([1,1'-biphenyl]-4-yl)-2-formyl-1_H_-inden-1-yl)(phenyl)methyl)-acrylate (3j)

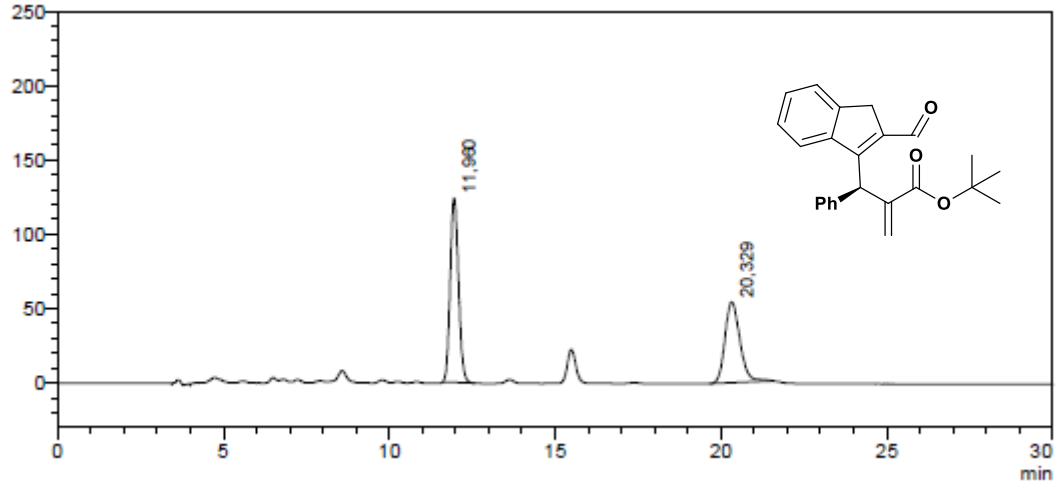


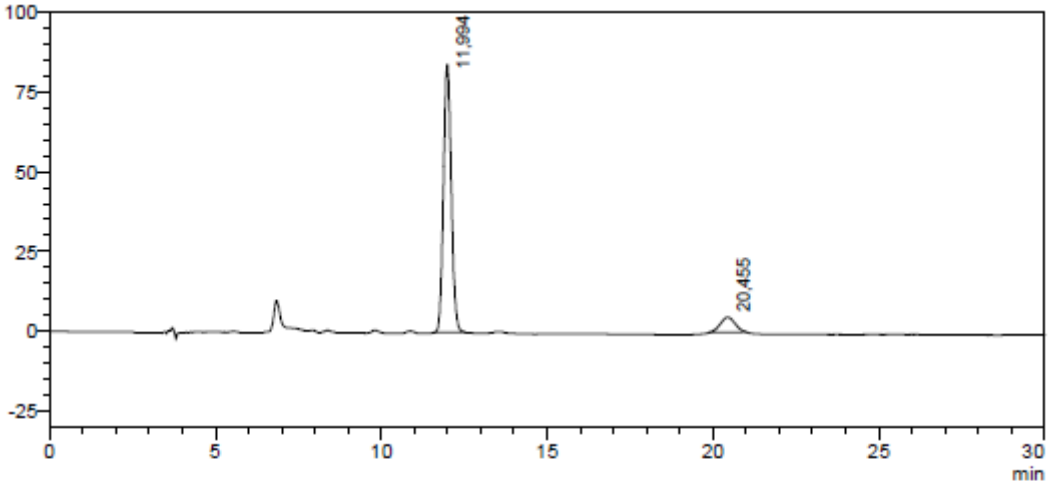


Peak Results

	RT	% Area
1	3.968	94.49
2	4.147	5.51

(S)-*tert*-Butyl 2-((2-formyl-1*H*-inden-3-yl)(phenyl)methyl)acrylate (3k')

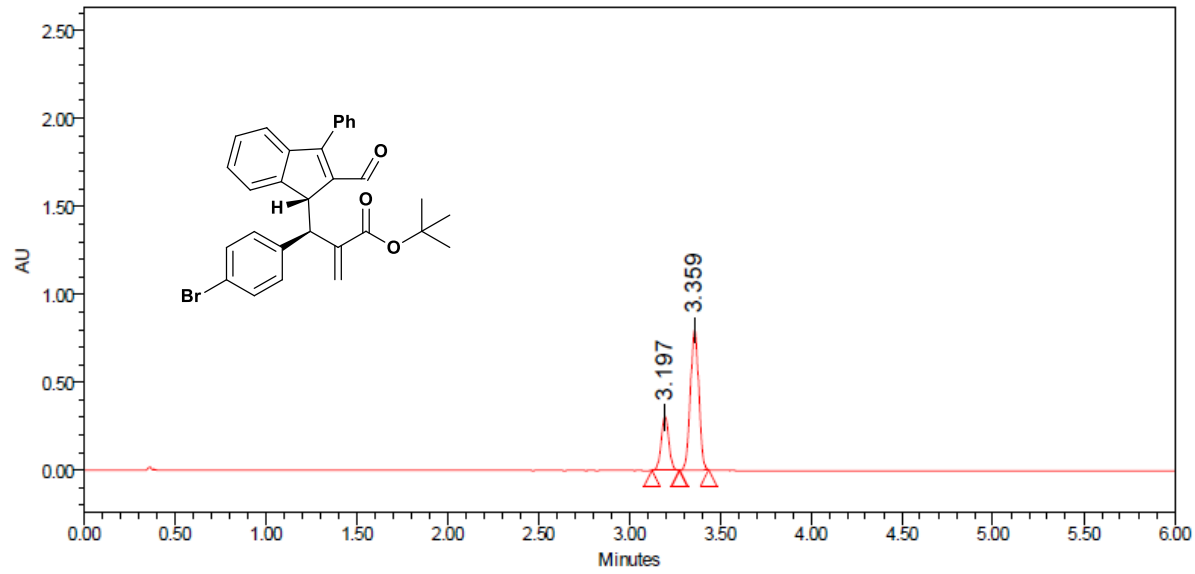


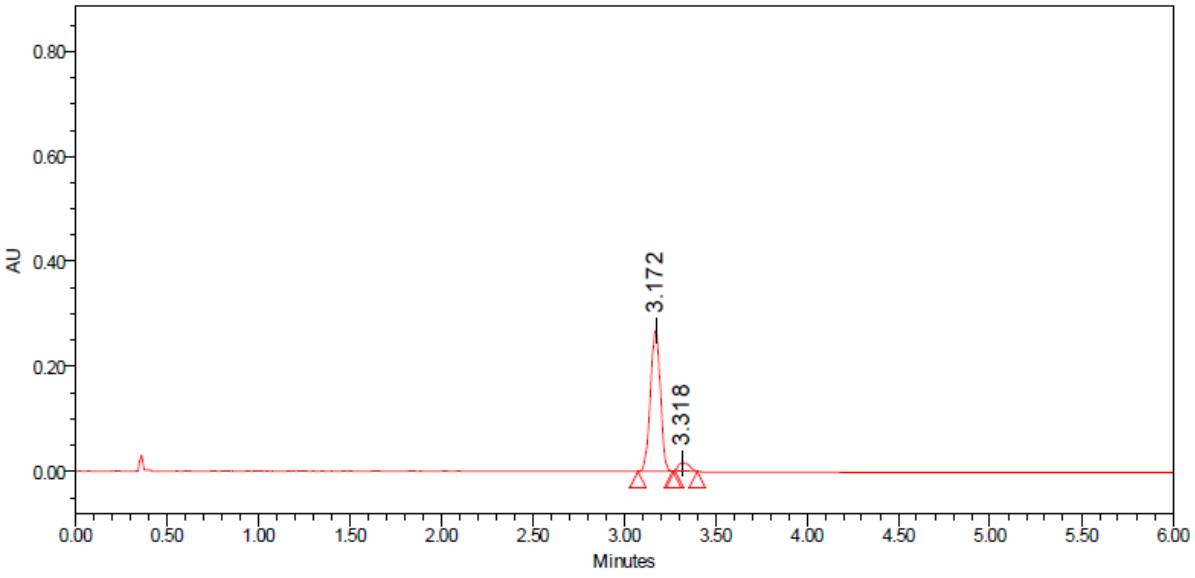


PDA Ch2 301nm

Peak#	Ret. Time	Area%
1	11,994	90,256
2	20,455	9,744
Total		100,000

tert-Butyl 2-((_R_)-(4-bromophenyl)((_R_)-2-formyl-3-phenyl-1_H_-inden-1-yl)methyl)acrylate (3l)

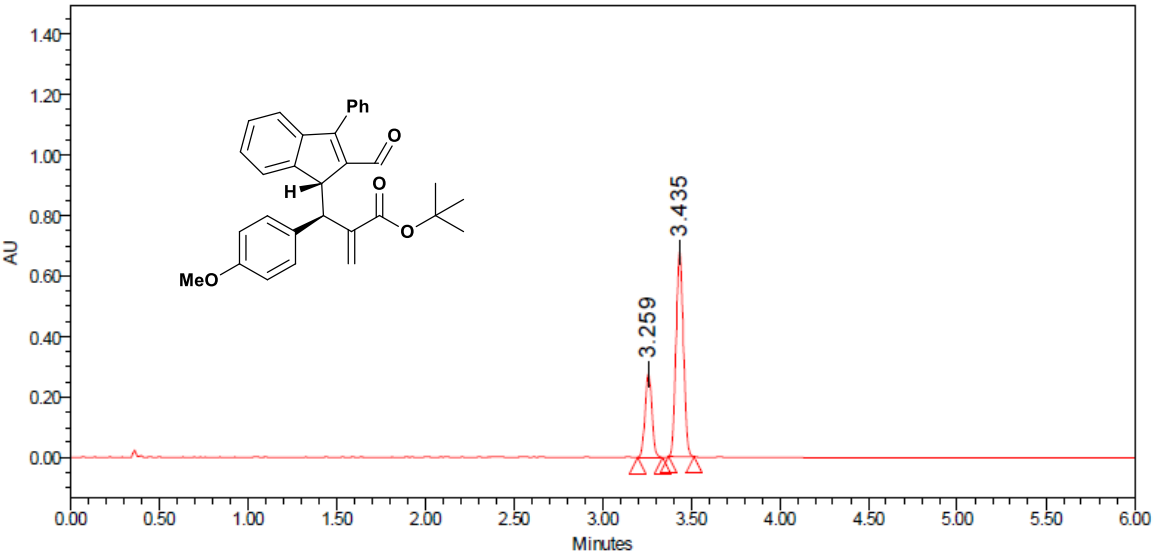


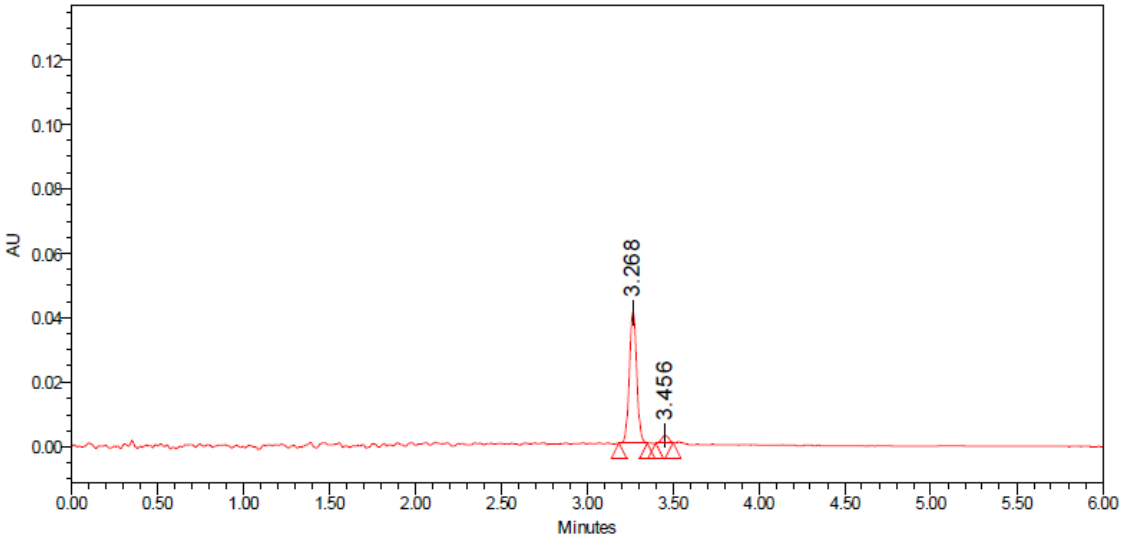


Peak Results

	RT	% Area
1	3.172	94.23
2	3.318	5.77

tert-Butyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(4-methoxyphenyl)methyl)-acrylate (3m)

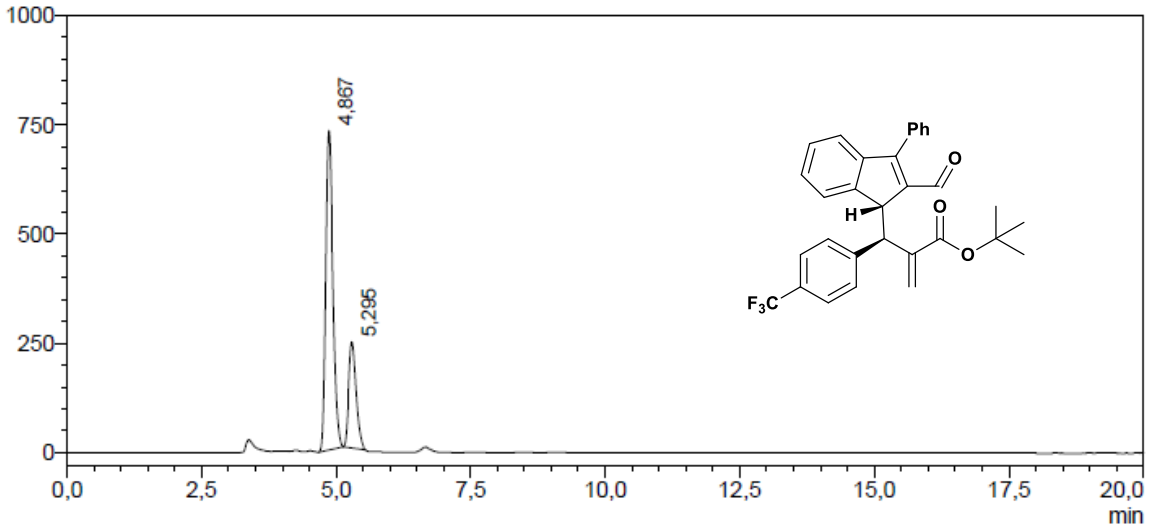


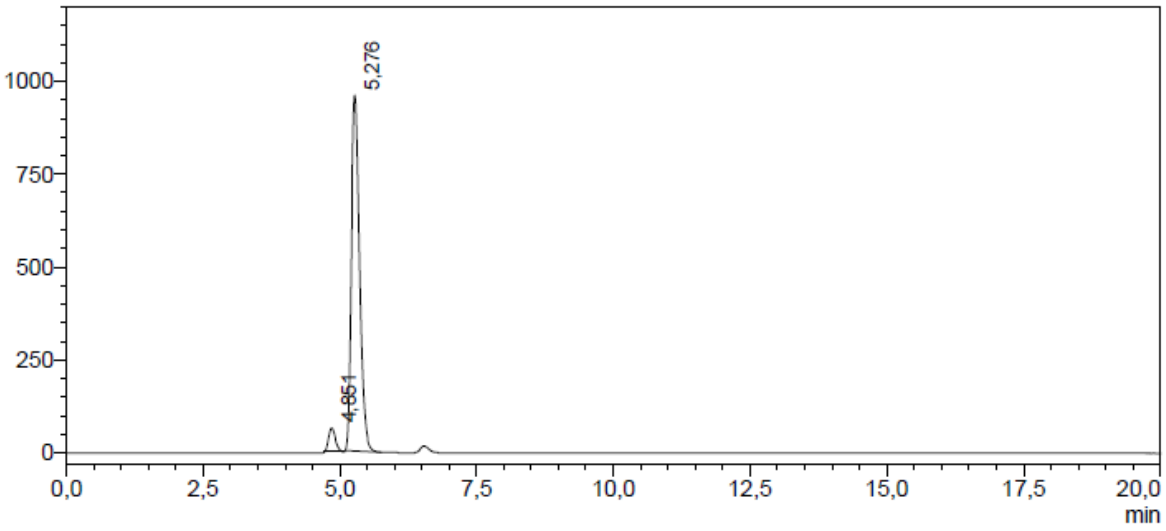


Peak Results

	RT	% Area
1	3.268	94.82
2	3.456	5.18

tert-Butyl 2-((_R_)-((_R_)-2-formyl-3-phenyl-1_H_-inden-1-yl)(4-(trifluoromethyl)phenyl)-methyl)acrylate (3n)

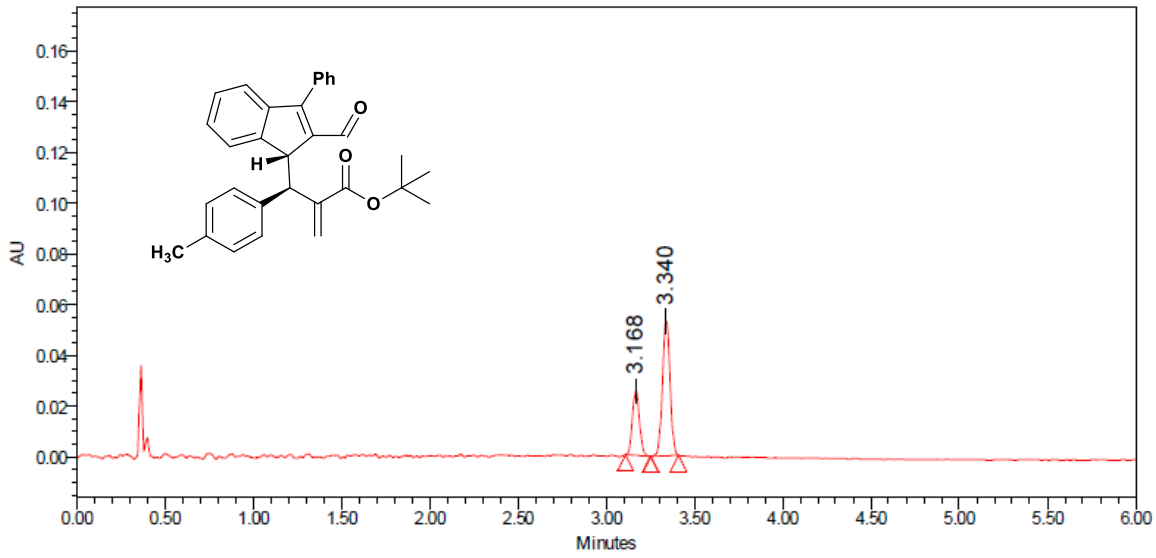


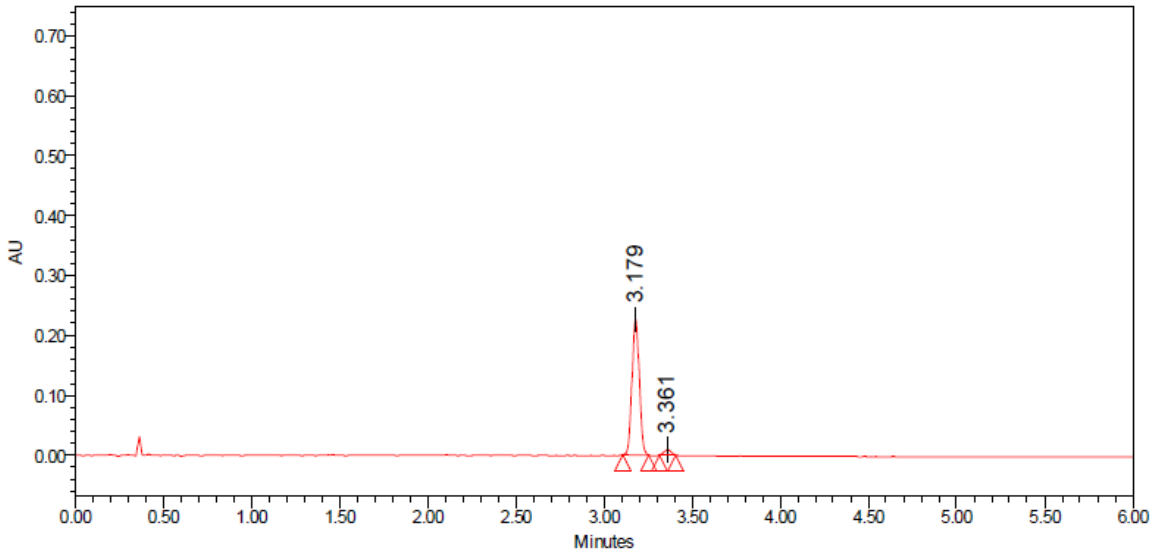


PDA Ch2 306nm

Peak#	Ret. Time	Area%
1	4,851	5,252
2	5,276	94,748
Total		100,000

***tert*-Butyl 2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(p-tolyl)methyl)acrylate (3o)**

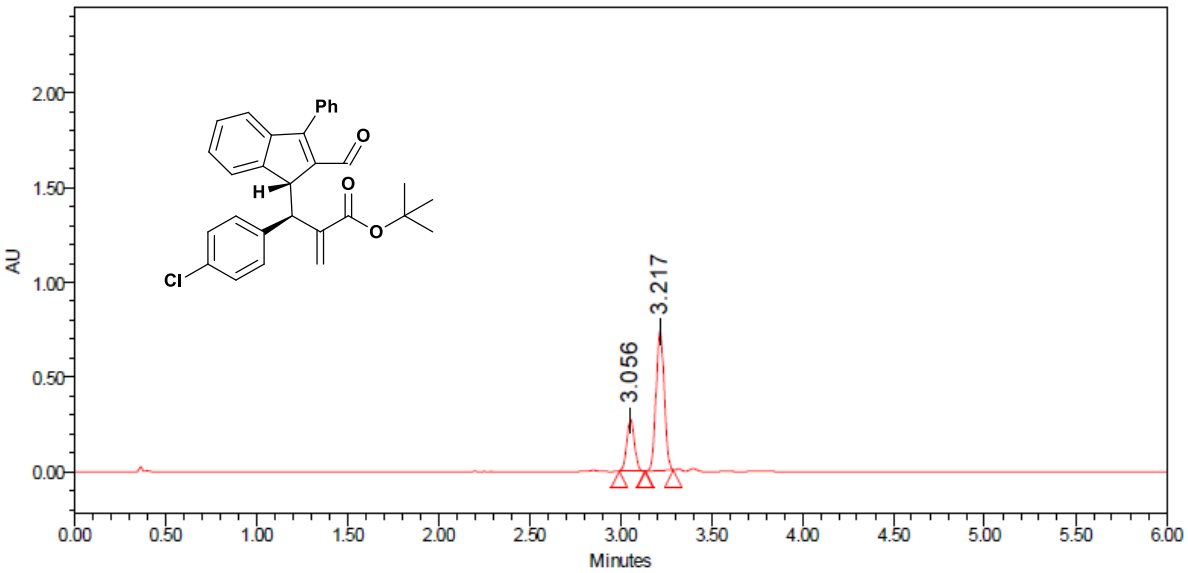


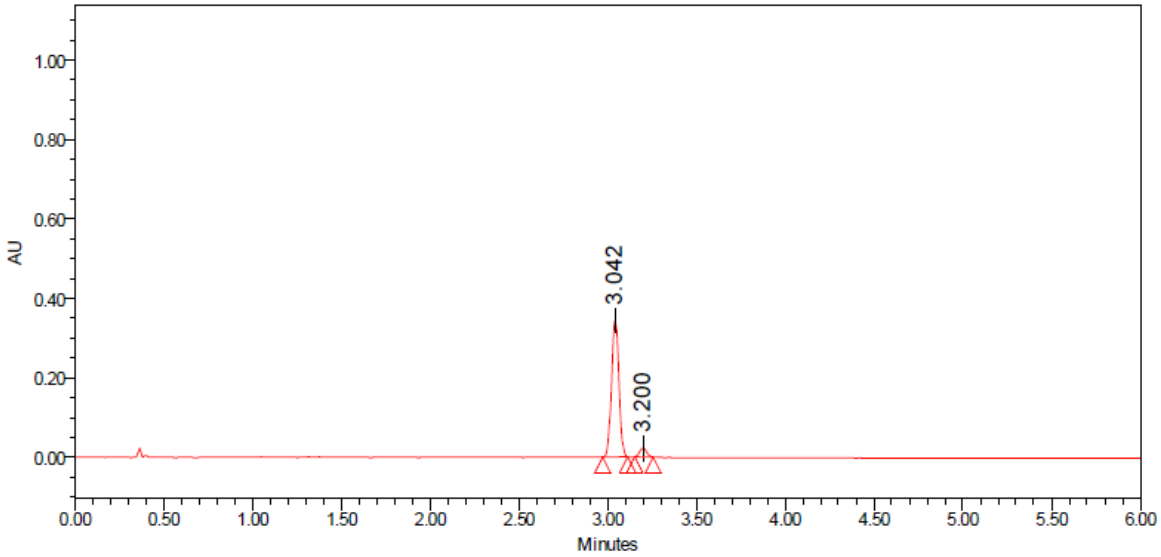


Peak Results

	RT	% Area
1	3.179	96.25
2	3.361	3.75

tert-Butyl 2-((_R_)-(4-chlorophenyl)((_R_)-2-formyl-3-phenyl-1_H_-inden-1-yl)methyl)acrylate (3p)

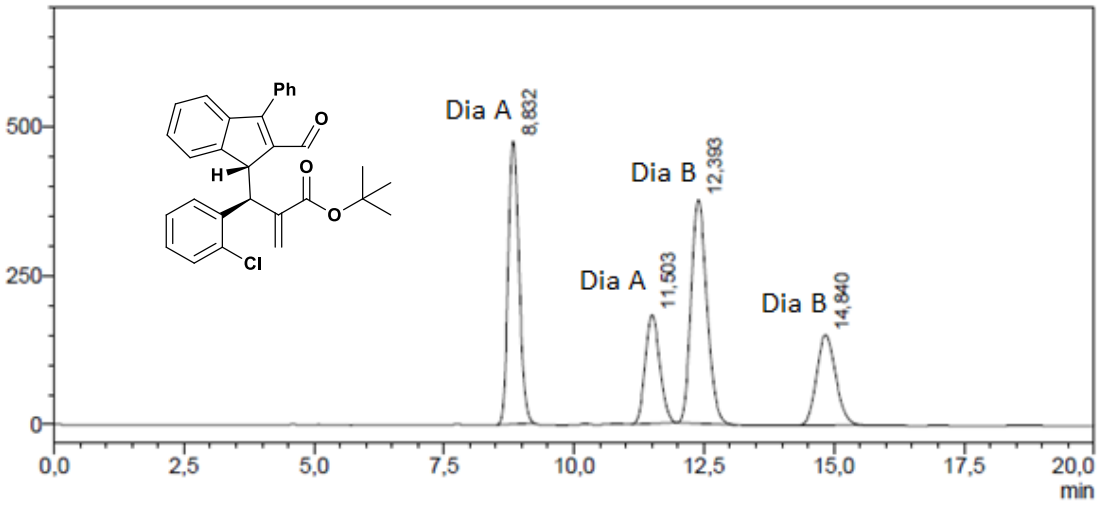


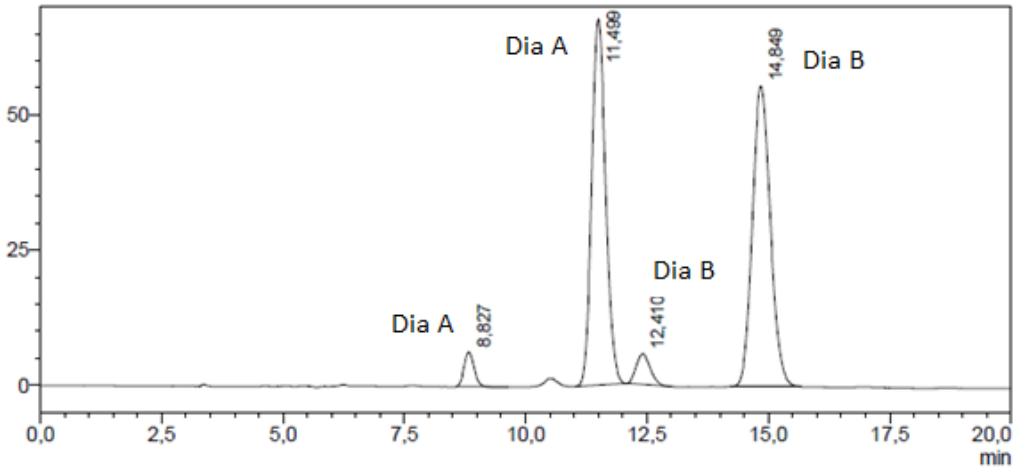


Peak Results

	RT	% Area
1	3.042	94.11
2	3.200	5.89

tert-Butyl 2-((*S*)-(2-chlorophenyl)((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)methyl)acrylate (3q)

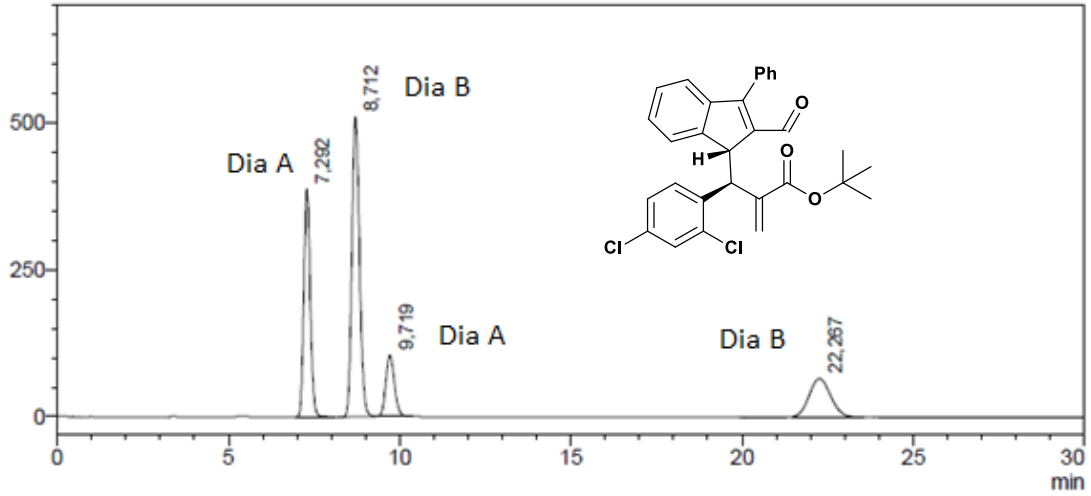


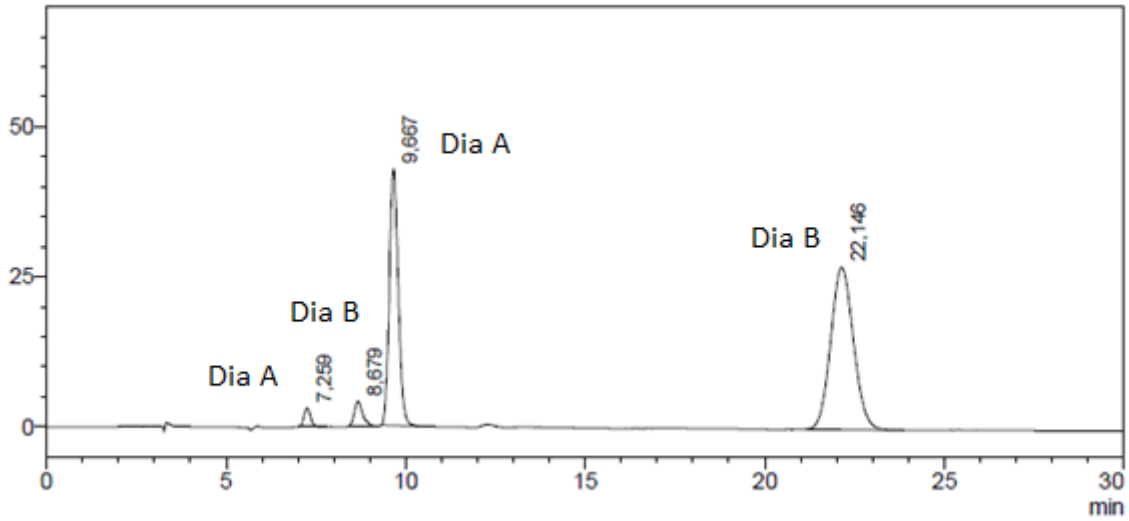


PDA Ch2 309nm

Peak#	Ret. Time	Area%
1	8,827	6,318
2	11,499	93,682
3	12,410	7,338
4	14,849	92,662
Total		200,000

tert-Butyl 2-((*S*)-(2,4-dichlorophenyl)((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)methyl)-acrylate (3r)

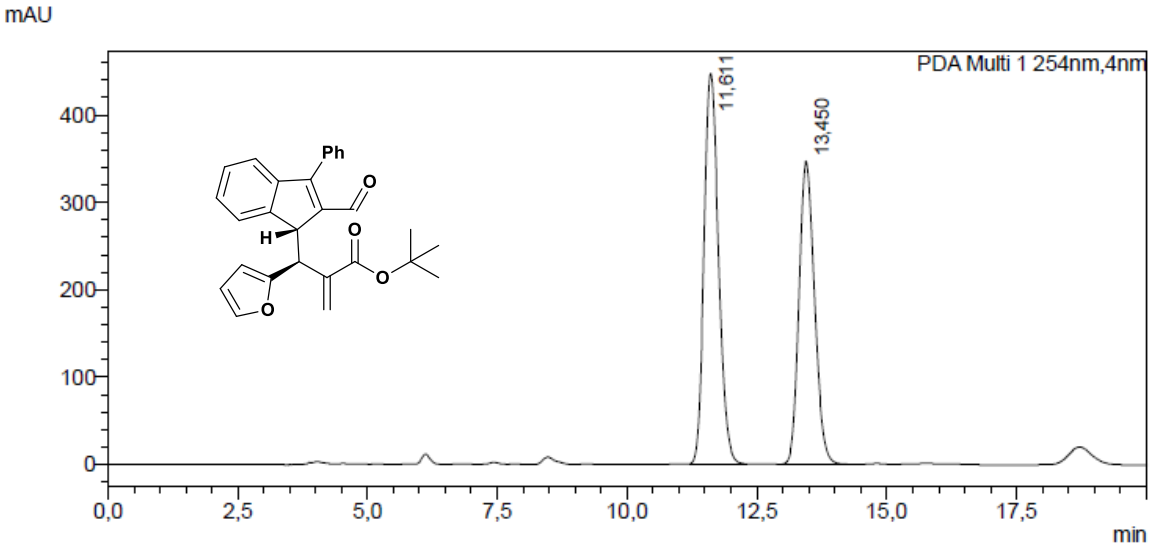


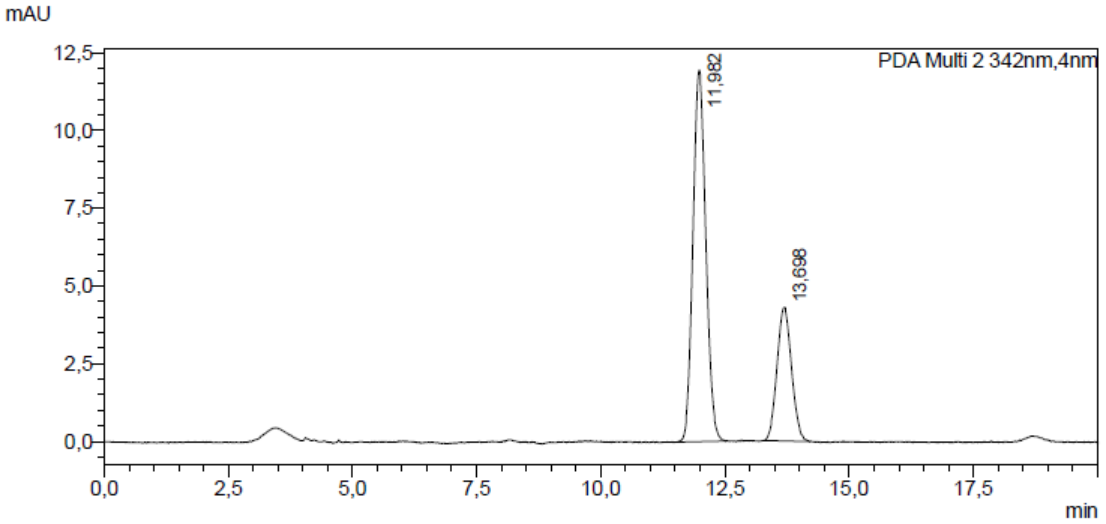


PDA Ch2 309nm

Peak#	Ret. Time	Area%
1	7,295	4,896
2	8,679	5,340
3	9,667	95,104
4	22,146	94,660
Total		200,00

***tert*-Butyl 2-((*S*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(furan-2-yl)methyl)acrylate (3s)**

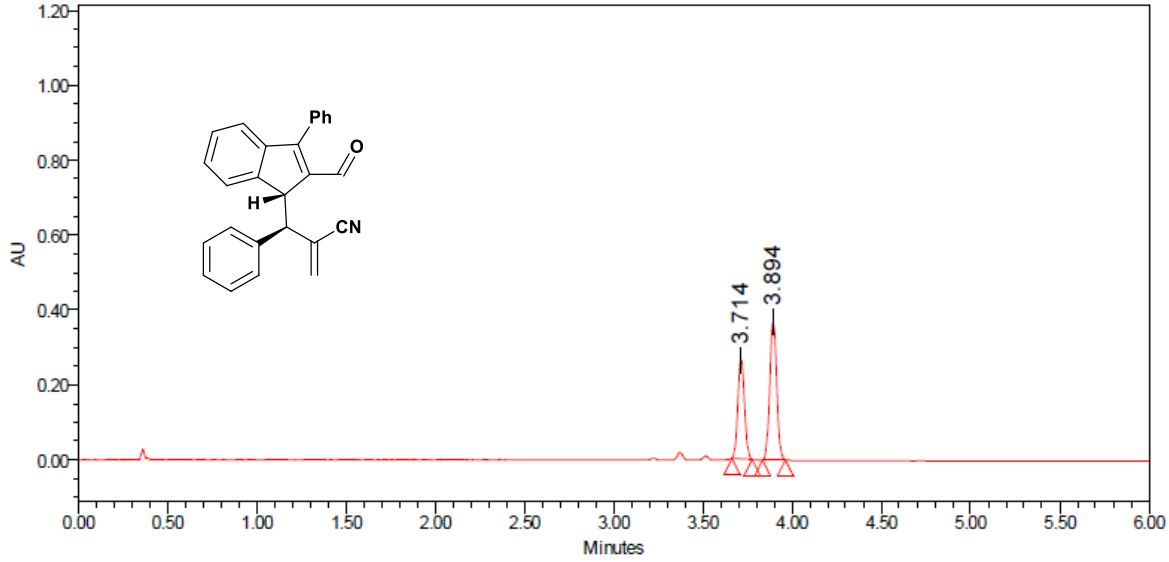


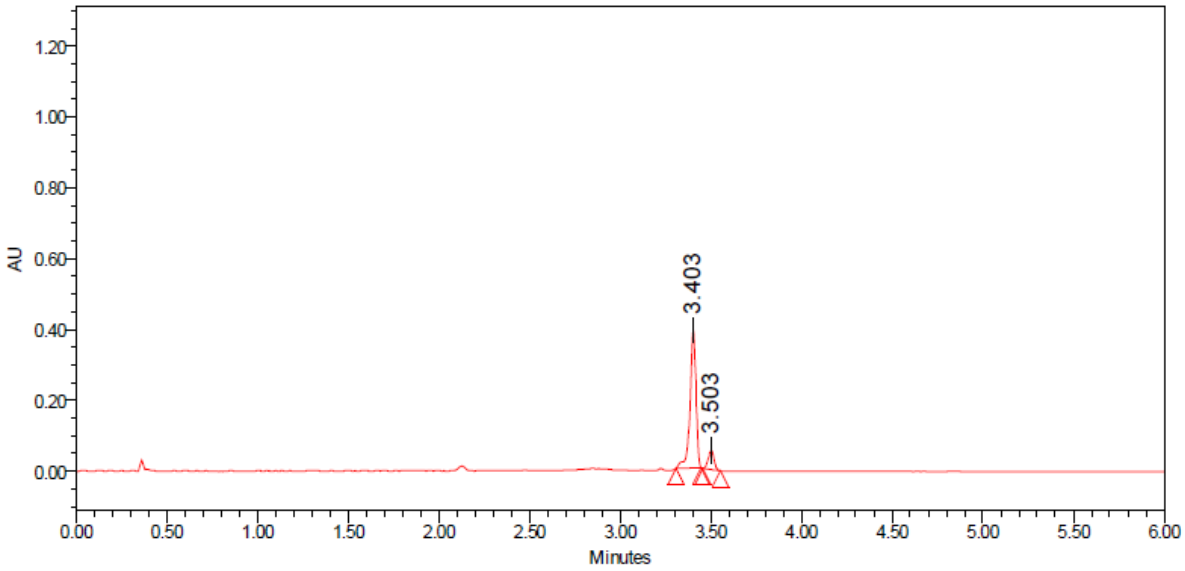


PDA Ch2 342nm

Peak#	Ret. Time	Area%
1	11,982	71,074
2	13,698	28,926
Total		100,000

2-((*R*)-((*R*)-2-formyl-3-phenyl-1*H*-inden-1-yl)(phenyl)methyl)acrylonitrile (3t)

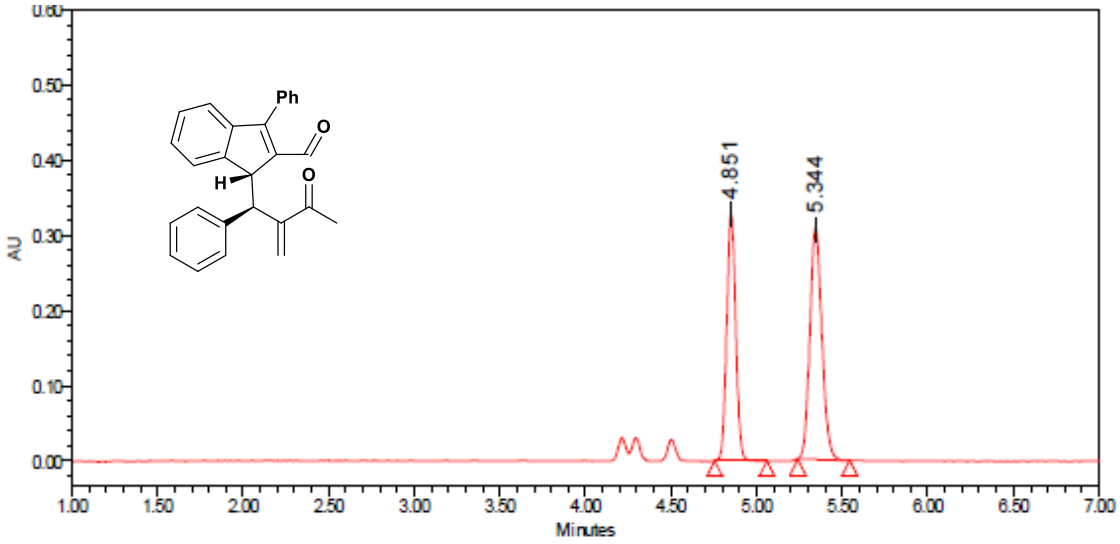


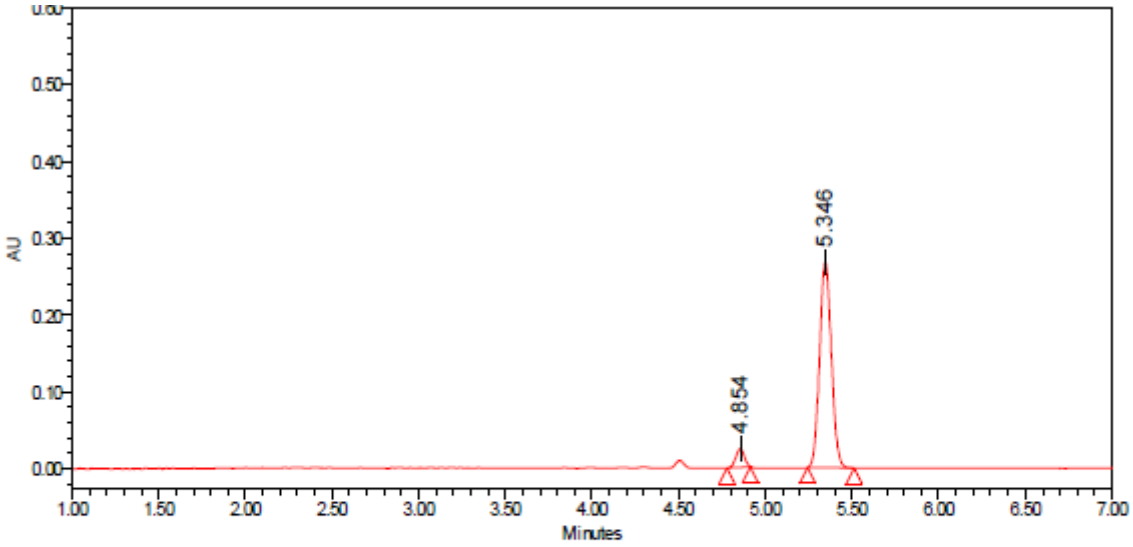


Peak Results

	RT	% Area
1	3.403	88.20
2	3.503	11.80

(*R*)-1-((*R*)-2-methylene-3-oxo-1-phenylbutyl)-3-phenyl-1*H*-indene-2-carbaldehyde (3u)





Peak Results

	RT	% Area
1	4.854	6.11
2	5.346	93.89