Supporting Information

Enantioselective Nickel-Catalyzed Electrochemical Reductive Conjugate Alkenylation

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1. General experimental information

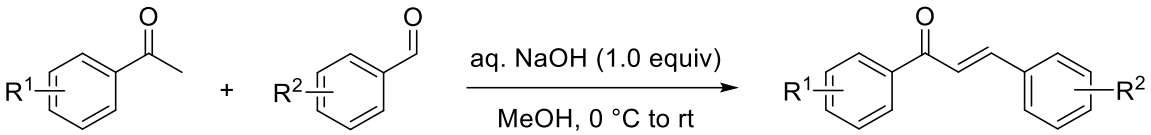
Analytical thin layer chromatography (TLC) was performed using 0.25 mm E. Merk silica plates (60F-254). Compounds were visualised under UV light or by staining with an aqueous Hanessian's stain (Cerium Ammonium Molybdate solution; CAM stain) and potassium permanganate ($KMnO_4$). Purification of the products was carried out by flash column chromatography, using Merck 60 Å 230–400 mesh silica gel. NMR data was collected on a Varian NMR spectrometer (^1H at 400 MHz; ^{13}C at 101 MHz; ^{19}F at 376 MHz) or a Bruker Avance 600 MHz NMR spectrometer (^1H at 600 MHz; ^{13}C at 151 MHz; ^{19}F at 565 MHz) with a 5 mm z-gradient broadband probe. Chemical shifts are reported in parts per million (ppm) relative to the resonance of the residual solvent peak (^1H: $CDCl_3$, δ = 7.26 ppm and ^{13}C: $CDCl_3$, δ = 77.16 ppm). Multiplicity is reported with the usual abbreviations: (brs = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet to doublet, dt = doublet to triplet, and m = multiplet. Coupling constants, *J*, are reported in Hertz (Hz). Please note in some carbon NMR spectra symmetric carbons cannot be discerned and they are listed as one signal. If an apparent multiplicity is observed the actual multiplicity will be noted in brackets. Quantitative ^{13}C NMR spectra were recorded at 151 MHz on a Bruker Avanue 600 MHz NMR spectrometer with inverse-gated decoupling. High resolution mass spectral analysis (HRMS) were recorded on a LTQ Orbitrap XL apparatus in the ESI ionisation mode. Enantiomeric excess (*ee*) was determined a chiral SFC analysis using a Waters Acquity Untra Performance Chromatography (UPC^2) equipped with a PDA detector. Optical rotations were measured using a Schmidt + Haensch polartronic MH8 polarimeter equipped with a sodium vapor lamp at 589.44 nm and path length 100 mm, the concentration of samples was denoted as *c*. Unless otherwise noted, quantitative ^1H NMR conversions and yields were determined from crude reaction mixtures using 1,3,5-trimethoxybenzene as an internal standard.

All electrolysis reactions were performed on ElectraSyn 2.0 with oven-dried vial (5 mL or 10 mL). ElectraSyn 2.0, purchased from IKA, is an all-in-one system that comprehends a potentiostat, a stirring plate and an analytical device to control the reaction parameters. Zinc, stainless steel, nickel foam, aluminium, graphite and RVC (Reticulated vitreous carbon) foam electrodes were purchased from IKA. General procedure to recycle the RVC: after reaction, the RVC was sequentially washed with 2 M HCl, water and acetone. Then the RVC was immersed in acetone and ultrasonic cleaning for 10 minutes. After rinsing with acetone, the RVC was dried before use. The cyclic voltammetries were carried out tetrabutylammonium tetrafluoroborate ($^nBu_4NBF_4$; 0.1 M) in DMF/DMSO (0.1 M) at room temperature, on ElectraSyn 2.0 in a glass cell. All the cyclic voltammograms were recorded with a scan rate of 0.1 V/s. A typical three-electrode cell was employed, which was composed of glassy carbon as working electrode, platinum wire as counter electrode and $Ag/AgNO_3$ as reference electrode. The glass electrochemical cell was kept closed with a stopper connected to the potentiostat. After each series of CV experiments, the electrochemical cell was carefully rinsed with acetone, and de-ionised water.

Unless otherwise indicated, reagents and substrates were purchased from commercial sources and used as received. Bisoxazolines ligands **L7** were synthesised according to the reported literature.[1] Substrate **1b**–**u** were synthesised according to the reported literature procedures. Chemicals, solvents and chiral ligands were purchased from Sigma-Aldrich, TCI and BLDpharm. All reported compounds were characterised by ^1H and ^{13}C NMR and compared with literature data. All compounds were fully characterised by ^1H NMR, ^{13}C NMR and HRMS techniques.

2. Synthesis of *α*,*β*-unsaturated ketones

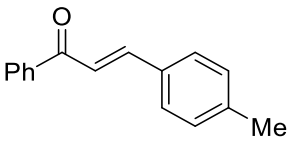
2.1 General procedures



In a round bottom flask equipped with a magnetic stirring bar, the appropriate acetophenone (1.0 equiv.) and the appropriate benzaldehyde (1.0 equiv.) were dissolved in MeOH (1 M). Then, aqueous solution of NaOH (1.0 equiv.) was added dropwise at 0 °C. The reaction mixture was left stirring at room temperature for overnight. After the completion of reaction, the reaction mixture was quenched with water and added CH_2Cl_2. The aqueous phase was then extracted with CH_2Cl_2 (twice). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure in a rotatory evaporator. The product mixture was purified by flash column chromatography to afford the *trans*-chalcone derivatives.[2]

2.2 Specific experimental details for the synthesis of *α*,*β*-unsaturated ketones

(*E*)-1-Phenyl-3-(*p*-tolyl)prop-2-en-1-one (1b)



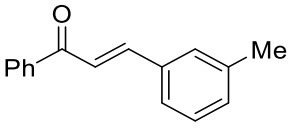
Product **1b** was synthesised following **General procedure** with acetophenone (2.3 mL, 20 mmol, 1.0 equiv.) and *p*-tolualdehyde (2.4 mL, 20 mmol, 1.0 equiv.) in MeOH (20 mL) to obtain **1b** as a pale yellow solid in 4.17 g (94% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.03–8.02 (m, 2H, 2 × C*H*$_{Ar}$), 7.80 (d, *J* = 15.7 Hz, 1H, CH$_α$=C*H*$_β$), 7.59–7.57 (m, 1H, C*H*$_{Ar}$), 7.55–7.49 (m, 5H, C*H*$_α$=CH$_β$ and 4 × C*H*$_{Ar}$), 7.23 (d, *J* = 7.9 Hz, 2H, 2 × C*H*$_{Ar}$), 2.39 (s, 3H, C*H*$_3$). NMR data are in agreement with literature precedents.[3]

^{13}C NMR ($CDCl_3$, 151 MHz): δ 190.7, 145.0, 141.2, 138.5, 132.8, 132.3, 129.8 (2 × C), 128.7 (2 × C), 128.6 (2 × C), 128.6 (2 × C), 121.2, 21.6.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{16}H_{14}OH^+$: 223.1117; found 223.1117.

(*E*)-1-Phenyl-3-(*m*-tolyl)prop-2-en-1-one (1c)



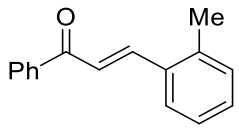
Product **1c** was synthesised following **General procedure** with acetophenone (2.3 mL, 20 mmol, 1.0 equiv.) and *m*-tolualdehyde (2.4 mL, 20 mmol, 1.0 equiv.) in MeOH (20 mL) to obtain **1c** as a pale yellow solid in 4.29 g (97% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.05–8.03 (m, 2H, 2 × C*H*$_{Ar}$), 7.80 (d, *J* = 15.7 Hz, 1H, CH$_α$=C*H*$_β$), 7.59–7.57 (m, 1H, C*H*$_{Ar}$), 7.55–7.44 (m, 5H, C*H*$_α$=CH$_β$ and 4 × C*H*$_{Ar}$), 7.31 (t, *J* = 7.9 Hz, 1H, C*H*$_{Ar}$), 7.23 (d, *J* = 7.5 Hz, 1H, C*H*$_{Ar}$), 2.40 (s, 3H, C*H*$_3$). NMR data are in agreement with literature precedents.[4]

^{13}C NMR ($CDCl_3$, 151 MHz): δ 190.5, 145.0, 138.6, 138.3, 134.9, 132.8, 131.5, 129.1, 128.9, 128.6 (2 × C), 128.5 (2 × C), 125.8, 121.9, 21.4.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{16}H_{14}OH^+$: 223.1117; found 223.1117.

(*E*)-1-Phenyl-3-(*o*-tolyl)prop-2-en-1-one (1d)



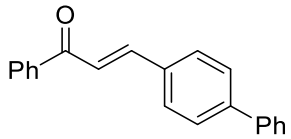
Product **1d** was synthesised following **General procedure** with acetophenone (2.3 mL, 20 mmol, 1.0 equiv.) and o-tolualdehyde (2.4 mL, 20 mmol, 1.0 equiv.) in MeOH (20 mL) to obtain **1d** as a yellow oil in 3.97 g (89% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.13 (d, *J* = 15.6 Hz, 1H, CH_α=C*H*$_\beta$), 8.05–8.03 (m, 2H, 2 × C*H*$_{Ar}$), 7.72–7.70 (m, 1H, C*H*$_{Ar}$), 7.61–7.58 (m, 1H, C*H*$_{Ar}$), 7.53–7.50 (m, 2H, 2 × C*H*$_{Ar}$), 7.47 (d, *J* = 15.6 Hz, 1H, C*H*$_\alpha$=CH_β), 7.31 (td, *J* = 7.4 and 1.4 Hz, 1H, C*H*$_{Ar}$), 7.27–7.23 (m, 2H, 2 × C*H*$_{Ar}$), 2.49 (s, 3H, C*H*$_3$). NMR data are in agreement with literature precedents.[5]

^{13}C NMR ($CDCl_3$, 151 MHz): δ 190.4, 142.4, 138.4, 138.2, 133.9, 132.8, 131.0, 130.3, 128.7 (2 × C), 128.6 (2 × C), 126.5, 126.4, 123.1, 19.9.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{16}H_{14}OH^+$: 223.1117; found 223.1117.

(*E*)-3-([1,1'-Biphenyl]-4-yl)-1-phenylprop-2-en-1-one (1e)



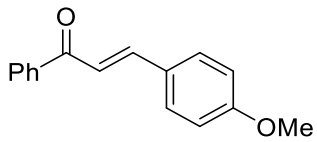
Product **1e** was synthesised following **General procedure** with acetophenone (2.3 mL, 20 mmol, 1.0 equiv.) and 4-phenylbenzaldehyde (3.64 g, 20 mmol, 1.0 equiv.) in MeOH (20 mL) to obtain **1e** as a pale yellow solid in 5.36 g (94% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.06–8.04 (m, 2H, 2 × C*H*$_{Ar}$), 7.87 (d, *J* = 15.7 Hz, 1H, CH_α=C*H*$_\beta$), 7.73 (d, *J* = 8.1 Hz, 2H, 2 × C*H*$_{Ar}$), 7.67 (d, *J* = 8.1 Hz, 2H, 2 × C*H*$_{Ar}$), 7.65–7.57 (m, 4H, C*H*$_\alpha$=CH_β and 3 × C*H*$_{Ar}$), 7.53 (t, *J* = 7.6 Hz, 2H, 2 × C*H*$_{Ar}$), 7.47 (t, *J* = 7.6 Hz, 2H, 2 × C*H*$_{Ar}$), 7.39 (t, *J* = 7.4 Hz, 1H, C*H*$_{Ar}$). NMR data are in agreement with literature precedents.[6]

^{13}C NMR ($CDCl_3$, 151 MHz): δ 190.6, 144.5, 143.4, 140.2, 138.4, 134.0, 132.9, 129.1 (2 × C), 129.1 (2 × C), 128.8 (2 × C), 128.6 (2 × C), 128.0, 127.7 (2 × C), 127.2 (2 × C), 122.0.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{21}H_{16}OH^+$: 285.1274; found 285.1271.

(*E*)-3-(4-Methoxyphenyl)-1-phenylprop-2-en-1-one (1f)



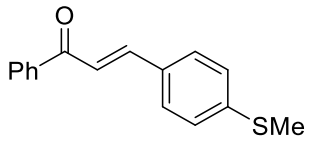
Product **1f** was synthesised following **General procedure** with acetophenone (2.3 mL, 20 mmol, 1.0 equiv.) and *p*-anisaldehyde (2.4 mL, 20 mmol, 1.0 equiv.) in MeOH (20 mL) to obtain **1f** as a pale yellow solid in 4.35 g (91% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.02–8.00 (m, 2H, 2 × CH_{Ar}), 7.79 (d, J = 15.6 Hz, 1H, CH_α=CH_β), 7.62–7.59 (m, 2H, 2 × CH_{Ar}), 7.59–7.56 (m, 1H, CH_{Ar}), 7.51–7.48 (m, 2H, 2 × CH_{Ar}), 7.42 (d, J = 15.6 Hz, 1H, CH_α=CH_β), 6.95–6.93 (m, 2H, 2 × CH_{Ar}), 3.86 (s, 3H, OCH_3). NMR data are in agreement with literature precedents.[7]

^{13}C NMR ($CDCl_3$, 151 MHz): δ 190.5, 161.7, 144.7, 138.5, 132.6, 130.3 (2 × C), 128.6 (2 × C), 128.5 (2 × C), 119.8, 114.5 (2 × C), 121.2, 55.4.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{16}H_{14}O_2H^+$: 239.1067; found 239.1063.

(*E*)-3-(4-(Methylthio)phenyl)-1-phenylprop-2-en-1-one (1g)



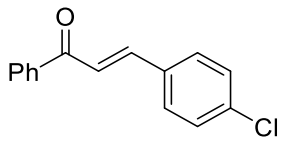
Product **1g** was synthesised following **General procedure** with acetophenone (2.3 mL, 20 mmol, 1.0 equiv.) and 4-(methylthio)benzaldehyde (2.7 mL, 20 mmol, 1.0 equiv.) in MeOH (20 mL) to obtain **1g** as a pale yellow solid in 4.58 g (90% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.02–8.00 (m, 2H, 2 × CH_{Ar}), 7.76 (d, J = 15.6 Hz, 1H, CH_α=CH_β), 7.57–7.54 (m, 1H, CH_{Ar}), 7.54–7.46 (m, 5H, CH_α=CH_β and 4 × CH_{Ar}), 7.23 (d, J = 8.4 Hz, 1H, CH_{Ar}), 2.48 (s, 3H, SCH_3). NMR data are in agreement with literature precedents.[8]

^{13}C NMR ($CDCl_3$, 151 MHz): δ 190.4, 144.3, 142.4, 138.3, 132.7, 131.3, 128.8 (2 × C), 128.6 (2 × C), 128.5 (2 × C), 125.9 (2 × C), 121.0, 15.1.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{16}H_{14}OSH^+$: 255.0838; found 255.0837.

(*E*)-3-(4-Chlorophenyl)-1-phenylprop-2-en-1-one (1h)



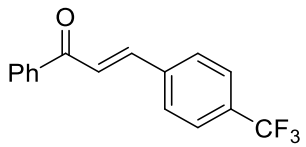
Product **1h** was synthesised following **General procedure** with acetophenone (2.3 mL, 20 mmol, 1.0 equiv.) and *p*-chlorobenzaldehyde (2.81 g, 20 mmol, 1.0 equiv.) in MeOH (20 mL) in MeOH (9.0 mL) to obtain **1h** as a white solid in 4.25 g (88% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.03–8.01 (m, 2H, 2 × CH_{Ar}), 7.76 (d, J = 15.7 Hz, 1H, CH_α=CH_β), 7.61–7.49 (m, 6H, CH_α=CH_β and 5 × CH_{Ar}), 7.41–7.39 (m, 2H, 2 × CH_{Ar}). NMR data are in agreement with literature precedents.[9]

^{13}C NMR ($CDCl_3$, 151 MHz): δ 190.4, 143.4, 138.2 136.6, 133.5, 133.1, 129.7 (2 × C), 129.4 (2 × C), 128.8 (2 × C), 128.6 (2 × C), 122.6.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{15}H_{11}ClOH^+$: 243.0571; found 243.0573.

(*E*)-1-Phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (1i)



Product **1i** was synthesised following **General procedure** with acetophenone (2.3 mL, 20 mmol, 1.0 equiv.) and 4-(trifluoromethyl)benzaldehyde (2.7 mL, 20 mmol, 1.0 equiv.) in MeOH (20 mL) to obtain **1i** as a white solid in 4.91 g (89% yield).

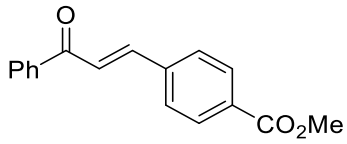
^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.04–8.03 (m, 2H, 2 × C*H*$_{Ar}$), 7.81 (d, *J* = 15.7 Hz, 1H, CH$_\alpha$=C*H*$_\beta$), 7.75 (d, *J* = 8.2 Hz, 2H, 2 × C*H*$_{Ar}$), 7.68 (d, *J* = 8.2 Hz, 2H, 2 × C*H*$_{Ar}$), 7.63–7.59 (m, 2H, C*H*$_\alpha$=CH$_\beta$ and C*H*$_{Ar}$), 7.53–7.51 (m, 2H, 2 × C*H*$_{Ar}$). NMR data are in agreement with literature precedents.[10]

^{13}C NMR (CDCl$_3$, 151 MHz): δ 190.2, 142.9, 138.4, 137.9, 133.3, 132.0 (q, *J* = 32.6 Hz), 128.9 (2 × C), 128.7 (2 × C), 128.7 (2 × C), 126.1 (q, *J* = 3.8 Hz, 2 × C), 124.4, 124.0 (q, *J* = 272.3 Hz).

^{19}F NMR (CDCl$_3$, 565 MHz): δ –62.84.

LC-HRMS (ESI): m/z [M+H]$^+$ calcd. for $C_{16}H_{11}F_3OH^+$: 277.0835; found 277.0832.

Methyl (*E*)-4-(3-oxo-3-phenylprop-1-en-1-yl)benzoate (1j)



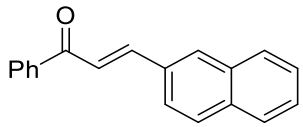
Product **1j** was synthesised following **General procedure** with acetophenone (2.3 mL, 20 mmol, 1.0 equiv.) and methyl 4-formylbenzoate (3.28 g, 20 mmol, 1.0 equiv.) in MeOH (20 mL) to obtain **1j** as a pale yellow solid in 4.83 g (91% yield).

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.07 (dd, *J* = 8.4 and 1.8 Hz, 2H, 2 × C*H*$_{Ar}$), 8.04–8.02 (m, 2H, 2 × C*H*$_{Ar}$), 7.80 (d, *J* = 15.7 Hz, 1H, CH$_\alpha$=C*H*$_\beta$), 7.69 (dd, *J* = 8.4 and 1.8 Hz, 2H, 2 × C*H*$_{Ar}$), 7.61–7.58 (m, 2H, C*H*$_\alpha$=CH$_\beta$ and C*H*$_{Ar}$), 7.53–7.50 (m, 2H, 2 × C*H*$_{Ar}$), 3.93 (s, 3H, OC*H*$_3$). NMR data are in agreement with literature precedents.[11]

^{13}C NMR (CDCl$_3$, 151 MHz): δ 190.2, 166.6, 143.3, 139.2, 138.0, 133.2, 131.6, 130.3 (2 × C), 128.8 (2 × C), 128.7 (2 × C), 128.4 (2 × C), 124.2, 52.41.

LC-HRMS (ESI): m/z [M+H]$^+$ calcd. for $C_{17}H_{14}O_3H^+$: 267.1016; found 267.1015.

(*E*)-3-(Naphthalen-2-yl)-1-phenylprop-2-en-1-one (1k)



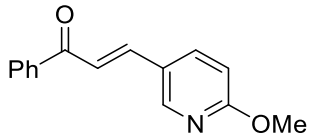
Product **1k** was synthesised following **General procedure** with acetophenone (2.3 mL, 20 mmol, 1.0 equiv.) and 2-naphthaldehyde (3.12 g, 20 mmol, 1.0 equiv.) in MeOH (20 mL) to obtain **1k** as a pale yellow solid in 4.92 g (95% yield).

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.08–8.04 (m, 3H, 3 × C*H*$_{Ar}$), 7.99 (d, *J* = 15.7 Hz, 1H, CH$_\alpha$=C*H*$_\beta$), 7.90–7.85 (m, 3H, 3 × C*H*$_{Ar}$), 7.81 (dd, *J* = 8.5 and 1.7 Hz, 1H, C*H*$_{Ar}$), 7.66 (d, *J* = 15.7 Hz, 1H, C*H*$_\alpha$=CH$_\beta$), 7.62–7.59 (m, 1H, C*H*$_{Ar}$), 7.55–7.52 (m, 4H, 4 × C*H*$_{Ar}$). NMR data are in agreement with literature precedents.[12]

^{13}C NMR (CDCl$_3$, 151 MHz): δ 190.6, 145.0, 138.4, 134.5, 133.5, 132.9, 132.5, 130.8, 128.9, 128.8 (3 × C), 128.7 (2 × C), 127.9, 127.5, 126.9, 123.8, 122.3.

LC-HRMS (ESI): m/z [M+H]$^+$ calcd. for $C_{19}H_{14}OH^+$: 259.1117; found 259.1115.

(*E*)-3-(6-Methoxypyridin-3-yl)-1-phenylprop-2-en-1-one (1l)



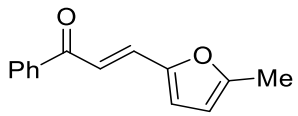
Product **1l** was synthesised following **General procedure** with acetophenone (2.3 mL, 20 mmol, 1.0 equiv.) and 6-methoxy-3-pyridinecarboxaldehyde (3.12 g, 20 mmol, 1.0 equiv.) in MeOH (20 mL) to obtain **1l** as a pale yellow solid in 4.55 g (95% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.37 (d, *J* = 2.5 Hz, 1H, C*H*$_{Py}$), 8.01–7.99 (m, 2H, 2 × C*H*$_{Ar}$), 7.90 (dd, *J* = 8.7 and 2.5 Hz, 1H, C*H*$_{Py}$), 7.76 (d, *J* = 15.7 Hz, 1H, CH$_\alpha$=C*H*$_\beta$), 7.57–7.56 (m, 1H, C*H*$_{Ar}$), 7.51–7.48 (m, 2H, 2 × C*H*$_{Ar}$), 7.43 (d, *J* = 15.7 Hz, 1H, C*H*$_\alpha$=CH$_\beta$), 6.79 (d, *J* = 7.4 Hz, 1H, C*H*$_{Py}$), 3.98 (s, 3H, OC*H*$_3$). NMR data are in agreement with literature precedents.[13]

^{13}C NMR ($CDCl_3$, 151 MHz): δ 190.2, 165.6, 149.2, 141.4, 138.3, 136.6, 132.9, 128.8 (2 × C), 128.6 (2 × C), 124.4, 121.0, 111.7, 54.0.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{15}H_{13}NO_2H^+$: 240.1019; found 240.1018.

(*E*)-3-(5-Methylfuran-2-yl)-1-phenylprop-2-en-1-one (1m)



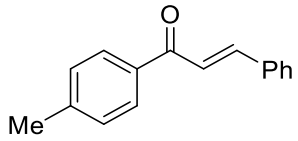
Product **1m** was synthesised following **General procedure** with acetophenone (2.3 mL, 20 mmol, 1.0 equiv.) and 5-methylfurfural (2.0 mL, 20 mmol, 1.0 equiv.) in MeOH (20 mL) to obtain **1m** as a pale yellow solid in 3.60 g (85% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.06–8.01 (m, 2H, 2 × C*H*$_{Ar}$), 7.57–7.47 (m, 4H, CH$_\alpha$=C*H*$_\beta$ and 3 × C*H*$_{Ar}$), 7.38 (d, J = 15.3, 1H, C*H*$_\alpha$=CH$_\beta$), 6.63 (d, *J* = 3.4 Hz, 1H, C*H*$_{Fur}$), 6.13 (dt, *J* = 3.4 and 1.1 Hz, 1H, C*H*$_{Fur}$), 2.39 (s, 3H, C*H*$_3$). NMR data are in agreement with literature precedents.[14]

^{13}C NMR ($CDCl_3$, 151 MHz): δ 190.0, 156.0, 150.5, 138.5, 132.7, 130.9, 128.7 (2 × C), 128.5 (2 × C), 118.4, 117.7, 109.5, 14.1.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{14}H_{12}O_2H^+$: 213.0910; found 213.0910.

(*E*)-3-Phenyl-1-(*p*-tolyl)prop-2-en-1-one (1o)



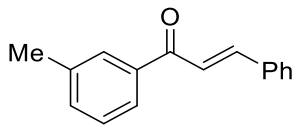
Product **1o** was synthesised following **General procedure** with 4'-methylacetophenone (1.3 mL, 10 mmol, 1.0 equiv.) and benzaldehyde (1.0 mL, 10 mmol, 1.0 equiv.) in MeOH (10 mL) to obtain **1o** as a pale yellow solid in 1.87 g (84% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.96–7.94 (m, 2H, 2 × C*H*$_{Ar}$), 7.81 (d, *J* = 15.7 Hz, 1H, CH$_\alpha$=C*H*$_\beta$), 7.65–7.64 (m, 2H, 2 × C*H*$_{Ar}$), 7.54 (d, *J* = 15.7 Hz, 1H, C*H*$_\alpha$=CH$_\beta$), 7.44–7.40 (m, 3H, 3 × C*H*$_{Ar}$), 7.31 (d, *J* = 8.0 Hz, 1H, C*H*$_{Ar}$), 2.44 (s, 3H, C*H*$_3$). NMR data are in agreement with literature precedents.[15]

^{13}C NMR ($CDCl_3$, 151 MHz): δ 190.1, 144.5, 143.7, 135.7, 135.1, 130.5, 129.4 (2 × C), 129.0 (2 × C), 128.8 (2 × C), 128.5 (2 × C), 122.2, 21.78.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{16}H_{14}OH^+$: 223.1117; found 223.1118.

(*E*)-3-Phenyl-1-(*m*-tolyl)prop-2-en-1-one (1p)



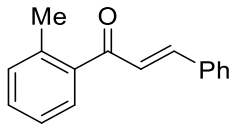
Product **1p** was synthesised following **General procedure** with 3'-methylacetophenone (1.4 mL, 10 mmol, 1.0 equiv.) and benzaldehyde (1.0 mL, 10 mmol, 1.0 equiv.) in MeOH (10 mL) to obtain **1p** as a yellow oil in 1.82 g (82% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.84–7.80 (m, 3H, CH_α=CH_β and 2 × CH_{Ar}), 7.66–7.64 (m, 2H, 2 × CH_{Ar}), 7.54 (d, *J* = 15.7 Hz, 1H, CH_α=CH_β), 7.43–7.39 (m, 5H, 5 × CH_{Ar}), 2.45 (s, 3H, CH_3). NMR data are in agreement with literature precedents.[16]

^{13}C NMR ($CDCl_3$, 151 MHz): δ 190.8, 144.7, 138.5, 138.4, 135.0, 133.7, 130.6, 129.1, 129.0 (2 × C), 128.6, 128.5 (2 × C), 125.8, 122.4, 21.5.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{16}H_{14}OH^+$: 223.1117; found 223.1117.

(*E*)-3-Phenyl-1-(*o*-tolyl)prop-2-en-1-one (1q)



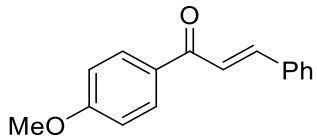
Product **1q** was synthesised following **General procedure** with 2'-methylacetophenone (1.3 mL, 10 mmol, 1.0 equiv.) and benzaldehyde (1.0 mL, 10 mmol, 1.0 equiv.) in MeOH (10 mL) to obtain **1q** as a yellow oil in 1.79 g (81% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.57–7.56 (m, 2H, 2 × CH_{Ar}), 7.51–7.50 (m, 1H, CH_{Ar}), 7.48 (d, *J* = 16.1 Hz, 1H, CH_α=CH_β), 7.41–7.38 (m, 4H, 4 × CH_{Ar}), 7.30–7.26 (m, 2H, 2 × CH_{Ar}), 7.15 (d, *J* = 16.1 Hz, 1H, CH_α=CH_β), 2.46 (s, 3H, CH_3). NMR data are in agreement with literature precedents.[17]

^{13}C NMR ($CDCl_3$, 151 MHz): δ 196.6, 146.0, 139.2, 137.0, 134.7, 131.4, 130.7, 130.6, 129.1 (2 × C), 128.5 (2 × C), 128.2, 126.8, 125.6, 20.3.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{16}H_{14}OH^+$: 223.1117; found 223.1116.

(*E*)-1-(4-Methoxyphenyl)-3-phenylprop-2-en-1-one (1r)



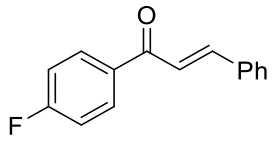
Product **1r** was synthesised following **General procedure** with acetanisole (1.50 g, 10 mmol, 1.0 equiv.) and benzaldehyde (1.0 mL, 10 mmol, 1.0 equiv.) in MeOH (10 mL) to obtain **1r** as a white solid in 2.09 g (88% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.05–8.04 (m, 2H, 2 × CH_{Ar}), 7.81 (d, *J* = 15.6 Hz, 1H, CH_α=CH_β), 7.65–7.64 (m, 2H, 2 × CH_{Ar}), 7.55 (d, *J* = 15.6 Hz, 1H, CH_α=CH_β), 7.44–7.40 (m, 3H, 3 × CH_{Ar}), 6.99–6.98 (m, 2H, 2 × CH_{Ar}), 3.89 (s, 3H, OCH_3). NMR data are in agreement with literature precedents.[18]

^{13}C NMR ($CDCl_3$, 151 MHz): δ 188.9, 163.6, 144.1, 135.2, 131.2, 131.0 (2 × C), 130.5, 129.1 (2 × C), 128.5 (2 × C), 122.0, 114.0 (2 × C), 55.6.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{16}H_{14}O_2H^+$: 239.1067; found 239.1065.

(*E*)-1-(4-Fluorophenyl)-3-phenylprop-2-en-1-one (1s)



Product **1s** was synthesised following **General procedure** with 4'-fluoroacetophenone (1.2 mL, 10 mmol, 1.0 equiv.) and benzaldehyde (1.0 mL, 10 mmol, 1.0 equiv.) in MeOH (10 mL) to obtain **1s** as a white solid in 2.01 g (89% yield).

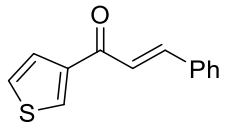
^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.07–8.05 (m, 2H, 2 × C*H*$_{Ar}$), 7.82 (d, *J* = 15.7 Hz, 1H, CH$_\alpha$=C*H*$_\beta$), 7.66–7.64 (m, 2H, 2 × C*H*$_{Ar}$), 7.51 (d, *J* = 15.7 Hz, 1H, C*H*$_\alpha$=CH$_\beta$), 7.44–7.42 (m, 3H, 3 × C*H*$_{Ar}$), 7.20–7.16 (m, 2H, 2 × C*H*$_{Ar}$). NMR data are in agreement with literature precedents.[19]

^{13}C NMR (CDCl$_3$, 151 MHz): δ 189.0, 166.6, 164.9, 145.2, 134.9, 134.7, 134.7, 131.3, 131.2, 129.1 (2 × C), 128.6 (2 × C), 121.7, 116.0, 115.8.

^{19}F NMR (CDCl$_3$, 565 MHz): δ –105.57 (tt, *J* = 8.3 and 5.2 Hz).

LC-HRMS (ESI): m/z [M+H]$^+$ calcd. for $C_{15}H_{11}FOH^+$: 227.0867; found 227.0867.

(*E*)-3-phenyl-1-(thiophen-3-yl)prop-2-en-1-one (1t)



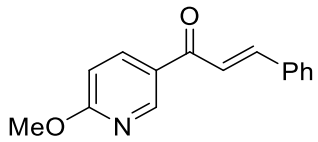
Product **1t** was synthesised following **General procedure** with 3-acetylthiophene (1.26 g, 10 mmol, 1.0 equiv.) and benzaldehyde (1.0 mL, 10 mmol, 1.0 equiv.) in MeOH (10 mL) to obtain **1t** as a white solid in 1.80 g (84% yield).

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.17 (dd, *J* = 2.9 and 1.3 Hz, 1H, C*H*$_{Thio}$), 7.82 (d, *J* = 15.7 Hz, 1H, CH$_\alpha$=C*H*$_\beta$), 7.68 (dd, *J* = 5.1 and 1.3 Hz, 1H, C*H*$_{Thio}$), 7.65–7.62 (m, 2H, 2 × C*H*$_{Ar}$), 7.44–7.39 (m, 4H, C*H*$_\alpha$=CH$_\beta$ and 3 × C*H*$_{Ar}$), 7.37 (dd, *J* = 5.1 and 2.9 Hz, 1H, C*H*$_{Thio}$). NMR data are in agreement with literature precedents.[20]

^{13}C NMR (CDCl$_3$, 151 MHz): δ 184.1, 144.2, 143.2, 134.9, 132.2, 130.6, 129.1 (2 × C), 128.5 (2 × C), 127.6, 126.6, 122.8.

LC-HRMS (ESI): m/z [M+H]$^+$ calcd. for $C_{13}H_{10}OSH^+$: 215.0525; found 215.0524.

(*E*)-1-(6-Methoxypyridin-3-yl)-3-phenylprop-2-en-1-one (1u)



Product **1u** was synthesised following **General procedure** with 5-acetyl-2-methoxypyridine (1.51 g, 10 mmol, 1.0 equiv.) and benzaldehyde (1.0 mL, 10 mmol, 1.0 equiv.) in MeOH (10 mL) to obtain **1u** as a white solid in 2.21 g (92% yield).

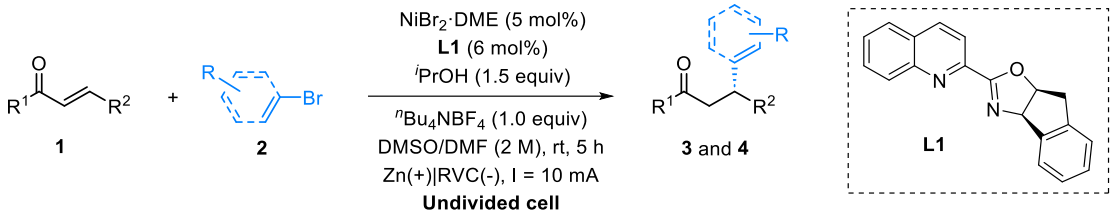
^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.89 (d, *J* = 2.4 Hz, 1H, C*H*$_{Py}$), 8.23 (dd, *J* = 8.7 and 2.4 Hz, 1H, C*H*$_{Py}$), 7.82 (d, *J* = 15.6 Hz, 1H, CH$_\alpha$=C*H*$_\beta$), 7.64–7.63 (m, 2H, 2 × C*H*$_{Ar}$), 7.48 (d, *J* = 15.6 Hz, 1H, C*H*$_\alpha$=CH$_\beta$), 7.43–7.42 (m, 3H, 3× C*H*$_{Ar}$), 6.84 (dd, *J* = 8.6 and 0.8 Hz, 1H, C*H*$_{Py}$), 4.03 (s, 3H, OC*H*$_3$).

^{13}C NMR (CDCl$_3$, 151 MHz): δ 187.9, 166.8, 149.3, 144.9, 138.9, 134.9, 130.8, 129.1 (2 × C), 128.6 (2 × C), 127.9, 121.5, 111.5, 54.22.

LC-HRMS (ESI): m/z [M+H]$^+$ calcd. for $C_{15}H_{13}NO_2H^+$: 240.1019; found 240.1018.

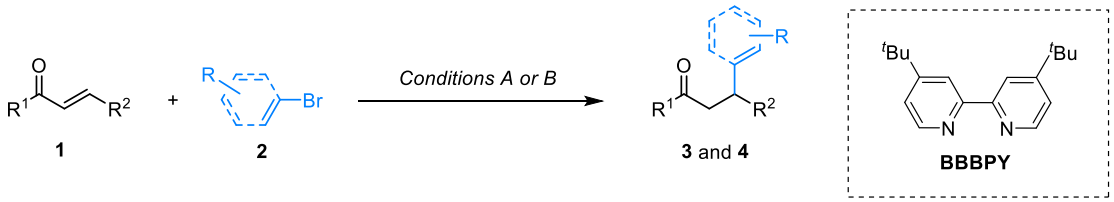
3. Nickel-catalysed electrochemical reductive conjugate addition

3.1 General procedure for asymmetric reductive conjugate addition



3.1.1 General procedure for the enantioselective nickel-catalysed electrochemical reductive conjugate addition

A 5 mL undivided ElectraSyn vial equipped with a magnetic stirring bar, $NiBr_2$·DME (5.0 mol%), and **L1** (6.0 mol%) were dissolved in DMF/DMSO (1:1, 1.0 mL) and stirred for 20 min at room temperature. Then *α*,*β*-unsaturated ketone **1** (1.0 equiv), $^{n}Bu_4NBF_4$ (1.0 equiv), alkenyl bromide (2.0 equiv), and ^{i}PrOH (1.5 equiv) was added, followed by DMF/DMSO (1:1, 1.0 mL). The flask was equipped with zinc as anode and RVC as cathode. The constant current (10 mA) electrolysis was carried out at room temperature under N_2 atmosphere. After stirring for 6 h, the reaction vial was disconnected from ElectraSyn 2.0, gently remove the cap with electrodes from the vial and the resulting reaction mixture was diluted with ethyl acetate and washed with saturated NH_4Cl aqueous solution followed by distilled water washes. The aqueous phase was then extracted with ethyl acetate (2 × 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure in a rotatory evaporator. The product mixture was purified by flash column chromatography to afford the desired product **3** and **4**.



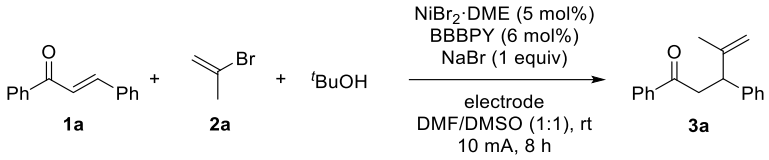
4.1.2 General procedure for the synthesis of racemic alkenylated ketones

Procedure A: A 5 mL flask equipped with a septum and a magnetic stirring bar, $NiBr_2$·DME (5.6 mg, 5.0 mol%), 1.5 mg, 0.005 mmol, 5 mol%) and 4,4-di-*tert*-butyl-2,2-dipyridyl (BBBPY; 6.0 mol%) were dissolved in DMF/DMSO (1:1, 1.0 mL) and stirred under N_2 atmosphere for 20 min at room temperature. Then *α*,*β*-unsaturated ketone **1** (1.0 equiv), $^{n}Bu_4NBF_4$ (1.0 equiv), alkenyl bromide (2.0 equiv), and ^{i}PrOH (1.5 equiv) was added, followed by DMF/DMSO (1:1, 1.0 mL). The flask was equipped with zinc as anode and RVC as cathode. The constant current (10 mA) electrolysis was carried out at room temperature under N_2 atmosphere. After stirring for 6 h, the reaction vial was disconnected from ElectraSyn 2.0, gently remove the cap with electrodes from the vial and the resulting reaction mixture was diluted with ethyl acetate and washed with saturated NH_4Cl aqueous solution followed by distilled water washes. The aqueous phase was then extracted with ethyl acetate (2 × 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure in a rotatory evaporator. The product mixture was purified by flash column chromatography to afford the racemic product **3** and **4**.

Procedure B: In a dried 4 mL vial equipped with a magnetic stirring bar, $NiBr_2$·DME (5.6 mg, 5.0 mol%), 1.5 mg, 0.005 mmol, 5 mol%) and BBBPY (6.0 mol%) were dissolved in DMF/DMSO (1:1, 1.0 mL) and stirred under N_2 atmosphere for 20 min at room temperature. Then *α*,*β*-unsaturated ketone **1** (1.0 equiv), NaBr (1.0 equiv), alkenyl bromide (2.0 equiv), and ^{i}PrOH (1.5 equiv) was added, followed by DMF/DMSO (1:1, 1.0 mL). After stirring for 12 h at room temperature, the resulting reaction mixture was diluted with ethyl acetate and washed with saturated NH_4Cl aqueous solution followed by distilled water washes. The aqueous phase was then extracted with ethyl acetate (2 × 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure in a rotatory evaporator. The product mixture was purified by flash column chromatography to afford the racemic product **3** and **4**.

3.2 Optimisation of the reaction conditions

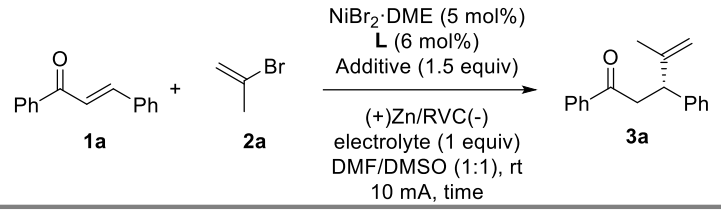
Table S1. Optimised reaction conditions for racemic electrochemical driven nickel-catalysed enantioselective reductive conjugate addition of *trans*-chalcone **1a** and 2-bromopropene **2a**.[a]

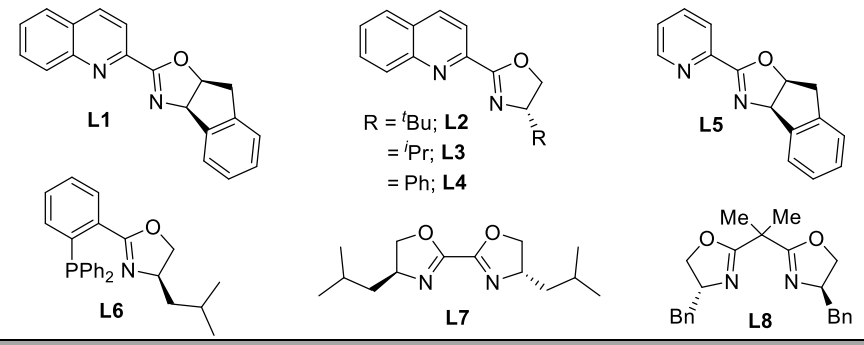


Entry	Anode (+)	Cathode (-)	Yield (%)	Note
1	Zn	Ni	17	
2	SS	Ni	0	
3	RVC	Ni	0	
4	Al	Ni	6	
5	Zn	$C_{graphite}$	4	
6	Zn	RVC	70	
7	RVC	RVC	0	
8	$C_{graphite}$	$C_{graphite}$	0	
9	Zn	RVC	0	No electric
10	Zn	RVC	0	No NiL
11	Zn	RVC	8	DBU (5 eq)

[a] **Reaction conditions: 1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), $NiBr_2$·DME (5 mol%), bbbpy ligand (6 mol%), ^{t}BuOH (0.3 mmol, 1.5 equiv), NaBr (0.2 mmol, 1.0 equiv) in DMSO/DMF (0.1 M, 2 mL, 1:1) under N_2 atmosphere and 10 mA constant current in an undivided cell at room temperature. [b] The yields of **3a** was determined by ^{1}H NMR spectra of the reaction crude using 1,3,5-trimethoxybenzene as an internal standard.

Table S2. Optimised reaction conditions for asymmetric electrochemical driven nickel-catalysed enantioselective reductive conjugate addition of *trans*-chalcone **1a** and 2-bromopropene **2a**.[a]



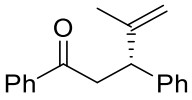


Entry	Electrolyte	Ligand	Additive	Time	Yield (%)	*Ee* (%)	Note
1	NaBr	**L2**	^{t}BuOH	4	46	97	
2	NaBr	**L3**	^{t}BuOH	4	36	72	
3	NaBr	**L4**	^{t}BuOH	4	26	75	
4	NaBr	**L8**	^{t}BuOH	4	0	0	
5	NaBr	**L2**	^{t}BuOH	4	8	nd	I = 6 mA
6	NaBr	**L2**	^{t}BuOH	8	46	97	
7	NaBr	**L1**	^{t}BuOH	4	12	94	
8	TBABr	**L1**	^{t}BuOH	4	12	94	
9	$MgBr_2$	**L1**	^{t}BuOH	4	17	92	
10	$^{n}Bu_4NPF_6$	**L1**	^{t}BuOH	4	55	95	
11	$^{n}Bu_4NBF_4$	**L1**	^{t}BuOH	4	61	94	
12	$^{n}Bu_4NBF_4$	**L2**	^{t}BuOH	6	71	94	
13	$^{n}Bu_4NBF_4$	**L2**	^{t}BuOH	8	23	89	
14	$^{n}Bu_4NBF_4$	**L1**	^{t}BuOH	6	72	96	
15	$^{n}Bu_4NBF_4$	**L1**	^{t}BuOH	8	41	95	
16	$^{n}Bu_4NBF_4$	**L1**	^{i}PrOH	6	74	96	
17	$^{n}Bu_4NBF_4$	**L1**	EtOH	6	40	95	
18	$^{n}Bu_4NBF_4$	**L1**	H_2O	6	71	94	
19	$^{n}Bu_4NBF_4$	**L1**	-	6	14	95	
20	$^{n}Bu_4NBF_4$	**L2**	^{t}BuOH	6	71	94	
21	$^{n}Bu_4NBF_4$	**L3**	^{t}BuOH	6	60	70	
22	$^{n}Bu_4NBF_4$	**L4**	^{t}BuOH	6	59	71	
23	$^{n}Bu_4NBF_4$	**L5**	^{t}BuOH	6	19	60	
24	$^{n}Bu_4NBF_4$	**L6**	^{t}BuOH	6	<5	Nd	
25	$^{n}Bu_4NBF_4$	**L7**	^{t}BuOH	6	<5	Nd	
26	$^{n}Bu_4NBF_4$	**L8**	^{t}BuOH	6	<5	Nd	

[a] **Reaction conditions: 1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), $NiBr_2$·DME (5 mol%), chiral ligand **L*** (6 mol%), additive (0.3 mmol, 1.5 equiv), electrolyte (0.2 mmol, 1.0 equiv) in DMSO/DMF (0.1 M, 2 mL, 1:1) under N_2 atmosphere and 10 mA constant current in an undivided cell at room temperature. [b] The yields of **3a** was determined by ^{1}H NMR spectra of the reaction crude using 1,3,5-trimethoxybenzene as an internal standard. Yield after isolation is reported in parenthesis. [c] Enantiomeric excess (*ee*) was determined by SFC with a chiral stationary phase. [d] In this case **1a** (0.4 mmol, 1.0 equiv) and **2a** (0.8 mmol, 2.0 equiv) were used.

3.3 Specific experimental details and product characterisation

(*R*)-4-Methyl-1,3-diphenylpent-4-en-1-one (3a)



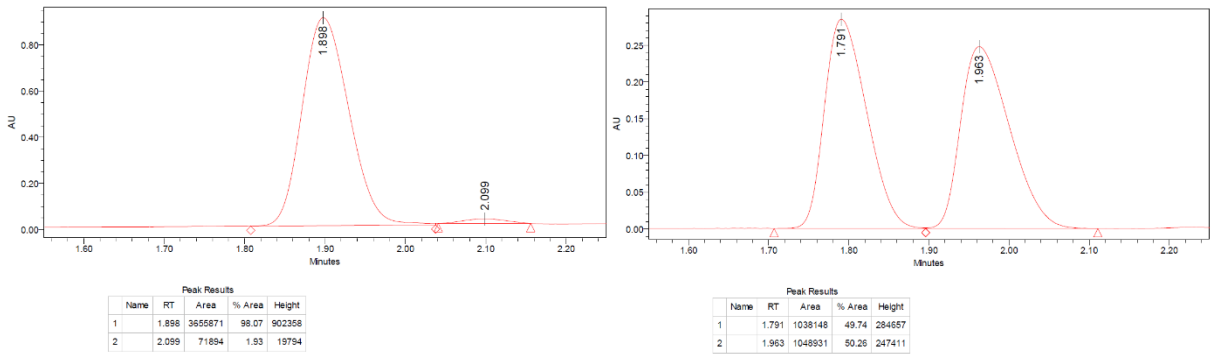
The reaction was performed with **1a** (83.3 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3a** was obtained as a white solid after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 74.2 mg, 74% yield, 96% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.94–7.92 (m, 2H, 2 × C*H*$_{Ar}$), 7.56–7.53 (m, 1H, C*H*$_{Ar}$), 7.44 (t, *J* = 7.7 Hz, 2H, 2 × C*H*$_{Ar}$), 7.30–7.26 (m, 4H, 4 × C*H*$_{Ar}$), 7.21–7.19 (m, 1H, C*H*$_{Ar}$), 4.89–4.86 (m, 2H, C=C*H*$_2$), 4.05 (t, *J* = 7.3 Hz, 1H, C*H*$_\beta$), 3.56 (dd, *J* = 16.7 and 7.8 Hz, 1H, C*H*$_\alpha$H$_\alpha$), 3.36 (dd, *J* = 16.7 and 6.8 Hz, 1H, CH$_\alpha$*H*$_\alpha$), 1.68 (s, 3H, C=CC*H*$_3$).

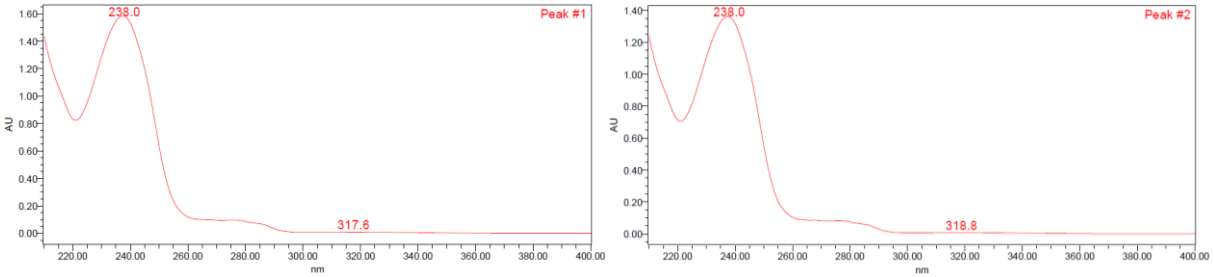
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.6, 147.2, 142.9, 137.4, 133.1, 128.7 (2 × C), 128.6 (2 × C), 128.2 (2 × C), 128.0 (2 × C), 126.7, 110.4, 47.7, 43.3, 22.2.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{18}H_{18}OH^+$: 251.1430; found 251.1429.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 1.90 (major) and 2.10 (minor).

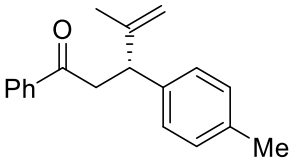


SFC of (*R*)-4-methyl-1,3-diphenylpent-4-en-1-one (**3a**)



UV-visible spectra of (*R*)-4-methyl-1,3-diphenylpent-4-en-1-one (**3a**)

(*R*)-4-Methyl-1-phenyl-3-(*p*-tolyl)pent-4-en-1-one (3b)



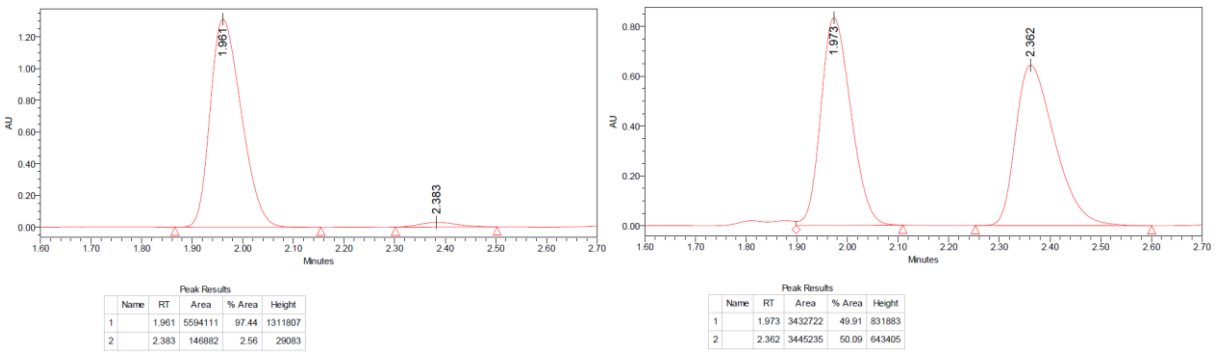
The reaction was performed with **1b** (88.9 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), $^{i}PrOH$ (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3b** was obtained as a white solid after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 92.8 mg, 88% yield, 95% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.96–7.94 (m, 2H, 2 × C*H*$_{Ar}$), 7.57–7.54 (m, 1H, C*H*$_{Ar}$), 7.45 (t, *J* = 7.8 Hz, 2H, 2 × C*H*$_{Ar}$), 7.18 (d, *J* = 8.0 Hz, 2H, 2 × C*H*$_{Ar}$), 7.11 (d, *J* = 8.0 Hz, 2H, 2 × C*H*$_{Ar}$), 4.89–4.87 (m, 2H, C=C*H*$_2$), 4.04 (t, *J* = 7.3 Hz, 1H, C*H*$_\beta$), 3.56 (dd, *J* = 16.7 and 7.8 Hz, 1H, C*H*$_\alpha$H$_\alpha$), 3.35 (dd, *J* = 16.7 and 6.8 Hz, 1H, CH$_\alpha$*H*$_\alpha$), 2.33 (s, 3H, C*H*$_3$), 1.70 (s, 3H, C=CC*H*$_3$).

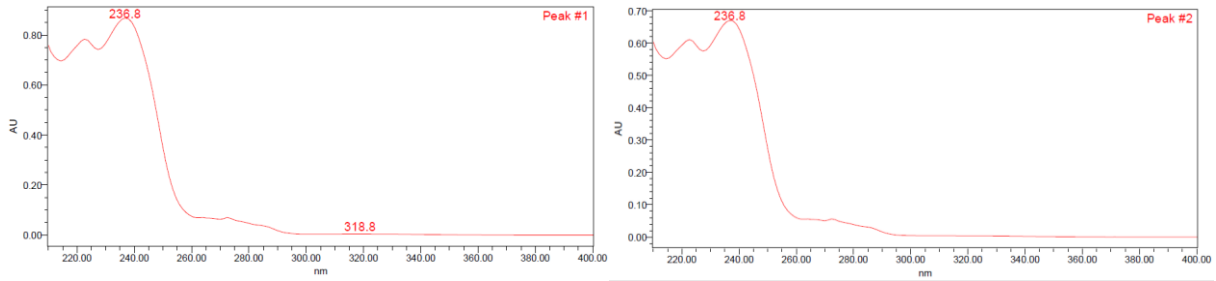
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.6, 147.4, 139.8, 137.4, 136.1, 133.0, 129.3 (2 × C), 128.7 (2 × C), 128.1 (2 × C), 127.8 (2 × C), 110.2, 47.3, 43.3, 22.1, 21.1.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{19}H_{20}OH^+$: 265.1587; found 265.1587.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 1.96 (major) and 2.38 (minor).

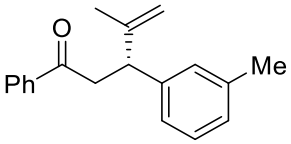


SFC of (*R*)-4-methyl-1-phenyl-3-(*p*-tolyl)pent-4-en-1-one (**3b**)



UV-visible spectra of (*R*)-4-methyl-1-phenyl-3-(*p*-tolyl)pent-4-en-1-one (**3b**)

(*R*)-4-Methyl-1-phenyl-3-(*m*-tolyl)pent-4-en-1-one (3c)



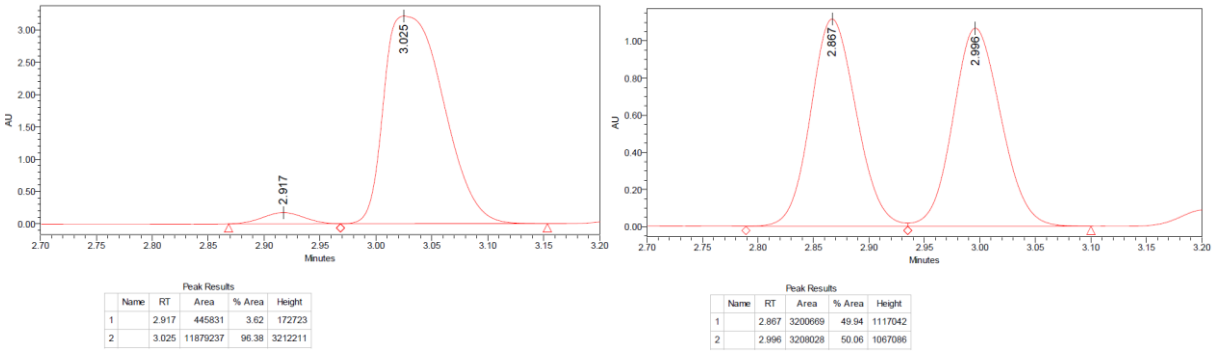
The reaction was performed with **1c** (88.9 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3c** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 44.9 mg, 43% yield, 93% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.95 (dd, *J* = 8.2 and 1.4 Hz, 2H, 2 × CH_{Ar}), 7.57–7.54 (m, 1H, CH_{Ar}), 7.45 (t, *J* = 7.8 Hz, 2H, 2 × CH_{Ar}), 7.19 (t, *J* = 7.5 Hz, 1H, CH_{Ar}), 7.09–7.08 (m, 2H, 2 × CH_{Ar}), 7.03 (d, *J* = 7.6 Hz, 1H, CH_{Ar}), 4.89–4.87 (m, 2H, C=CH_2), 4.03 (t, *J* = 7.3 Hz, 1H, CH_β), 3.57 (dd, *J* = 16.8 and 8.0 Hz, 1H, CH_αH$_\alpha$), 3.35 (dd, *J* = 16.8 and 6.6 Hz, 1H, CH$_\alpha$$H_\alpha$), 2.34 (s, 3H, C$H_3$), 1.69 (s, 3H, C=CC$H_3$).

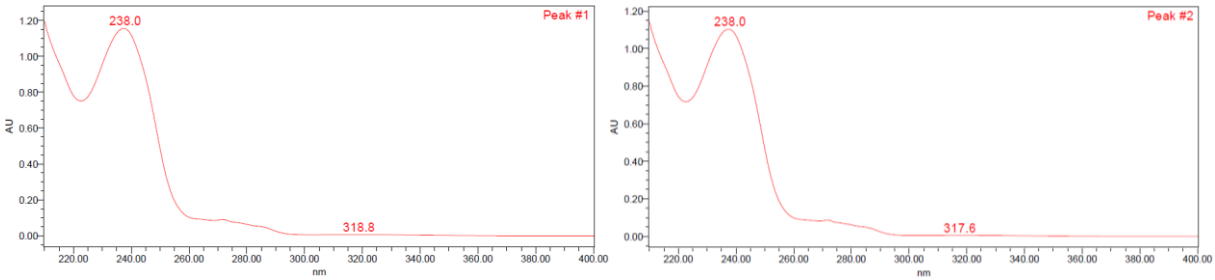
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.6, 147.2, 142.8, 138.1, 137.3, 133.1, 128.7, 128.7 (2 × C), 128.4, 128.1 (2 × C), 127.4, 124.9, 110.3, 47.6, 43.3, 22.2, 21.6.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{19}H_{20}OH^+$: 265.1587; found 265.1586.

SFC: (*R*,*R*)-Whelk-O1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 2.92 (minor) and 3.03 (major).

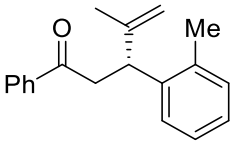


SFC of (*R*)-4-methyl-1-phenyl-3-(*m*-tolyl)pent-4-en-1-one (**3c**)



UV-visible spectra of (*R*)-4-methyl-1-phenyl-3-(*m*-tolyl)pent-4-en-1-one (**3c**)

(*R*)-4-Methyl-1-phenyl-3-(*o*-tolyl)pent-4-en-1-one (3d)



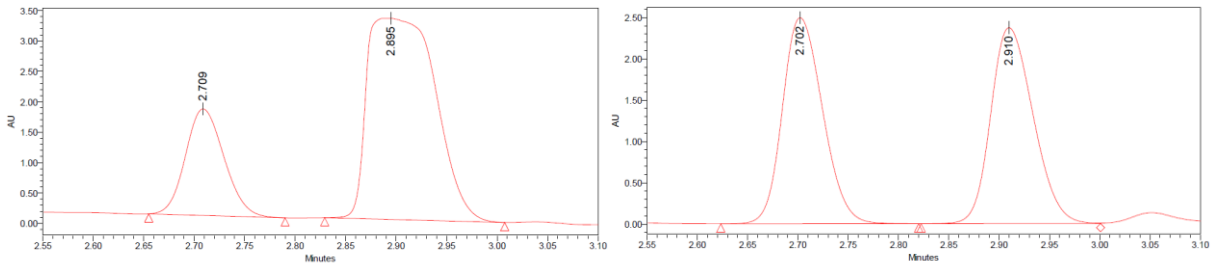
The reaction was performed with **1d** (88.9 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3d** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 12.6 mg, 12% yield, 54% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.95–7.93 (m, 2H, 2 × C*H*$_{Ar}$), 7.57–7.53 (m, 1H, C*H*$_{Ar}$), 7.48–7.43 (m, 2H, 2 × C*H*$_{Ar}$), 7.20–7.09 (m, 4H, 4 × C*H*$_{Ar}$), 4.89–4.77 (m, 2H, C=C*H*$_2$), 4.32 (t, *J* = 7.2 Hz, 1H, C*H*$_\beta$), 3.56 (dd, *J* = 17.0 and 8.1 Hz, 1H, C*H*$_\alpha$H$_\alpha$), 3.29 (dd, *J* = 17.0 and 6.3 Hz, 1H, CH$_\alpha$*H*$_\alpha$), 2.41 (s, 3H, C*H*$_3$), 1.68 (s, 3H, C=CC*H*$_3$).

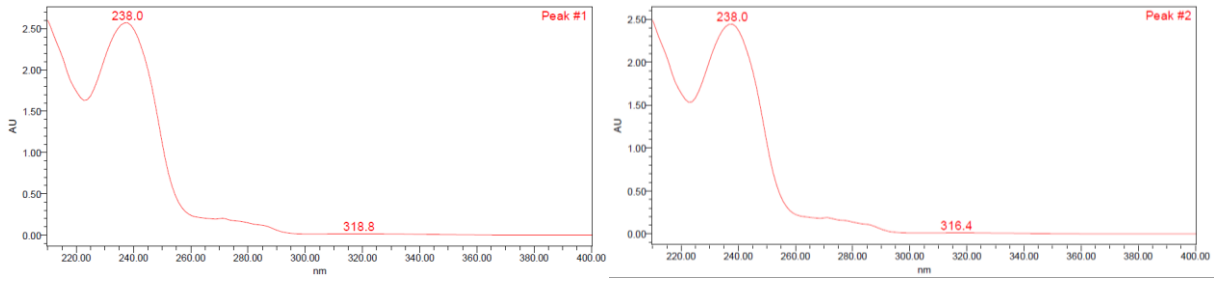
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.7, 146.9, 141.0, 137.3, 136.5, 133.1, 130.7, 128.7 (2 × C), 128.2 (2 × C), 126.6, 126.5, 126.2 110.8, 43.0, 42.9, 22.3, 19.9.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{19}H_{20}OH^+$: 265.1587; found 265.1585.

SFC: (*R*,*R*)-Whelk-O1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 2.71 (minor) and 2.90 (major).

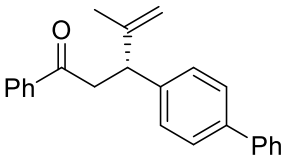


SFC of (*R*)-4-methyl-1-phenyl-3-(*m*-tolyl)pent-4-en-1-one (**3d**)



UV-visible spectra of (*R*)-4-methyl-1-phenyl-3-(*m*-tolyl)pent-4-en-1-one (**3d**)

(*R*)-3-([1,1'-Biphenyl]-4-yl)-4-methyl-1-phenylpent-4-en-1-one (3e)



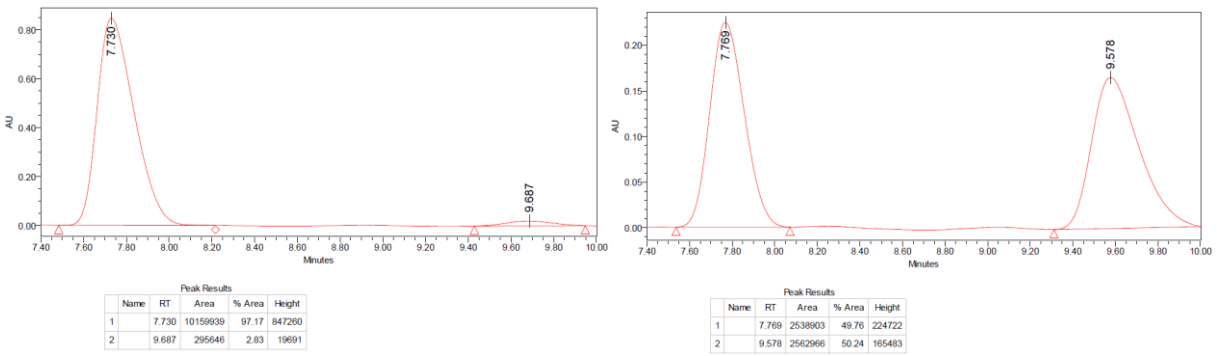
The reaction was performed with **1e** (113.7 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3e** was obtained as a white solid after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 84.8 mg, 65% yield, 95% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.97–7.95 (m, 2H, 2 × C*H*$_{Ar}$), 7.58–7.52 (m, 5H, 5 × C*H*$_{Ar}$), 7.47–7.41 (m, 4H, 4 × C*H*$_{Ar}$), 7.36–7.32 (m, 3H, 3 × C*H*$_{Ar}$), 4.93–4.91 (m, 2H, C=C*H*$_2$), 4.11 (t, *J* = 7.3 Hz, 1H, C*H*$_\beta$), 3.59 (dd, *J* = 16.8 and 7.6 Hz, 1H, C*H*$_\alpha$H$_\alpha$), 3.41 (dd, *J* = 16.8 and 6.9 Hz, 1H, CH$_\alpha$*H*$_\alpha$), 1.73 (s, 3H, C=CC*H*$_3$).

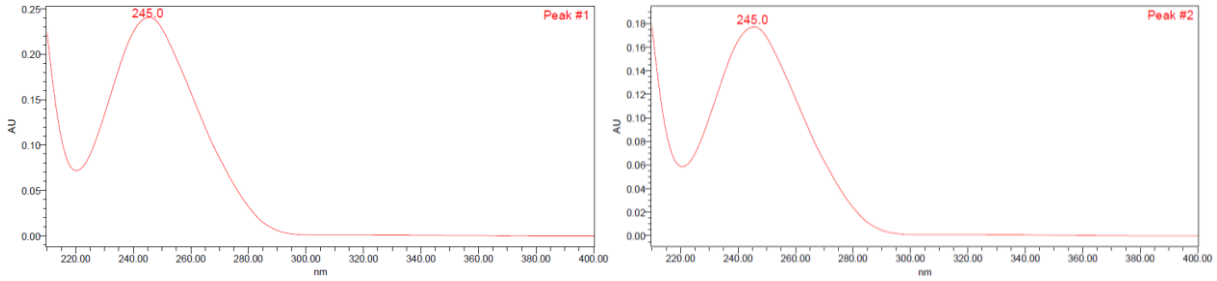
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.6, 147.2, 142.0, 141.0, 139.6, 137.3, 133.2, 128.8 (2 × C), 128.7 (2 × C), 128.4 (2 × C), 128.2 (2 × C), 127.3 (2 × C), 127.2, 127.1 (2 × C), 110.5, 47.4, 43.2, 22.2.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{24}H_{22}OH^+$: 327.1743; found 327.1741.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 10 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 7.73 (major) and 9.69 (minor).

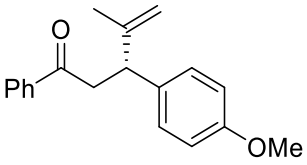


SFC of (*R*)-3-([1,1'-biphenyl]-4-yl)-4-methyl-1-phenylpent-4-en-1-one (**3e**)



UV-visible spectra of (*R*)-3-([1,1'-biphenyl]-4-yl)-4-methyl-1-phenylpent-4-en-1-one (**3e**)

(*R*)-3-(4-Methoxyphenyl)-4-methyl-1-phenylpent-4-en-1-one (3f)



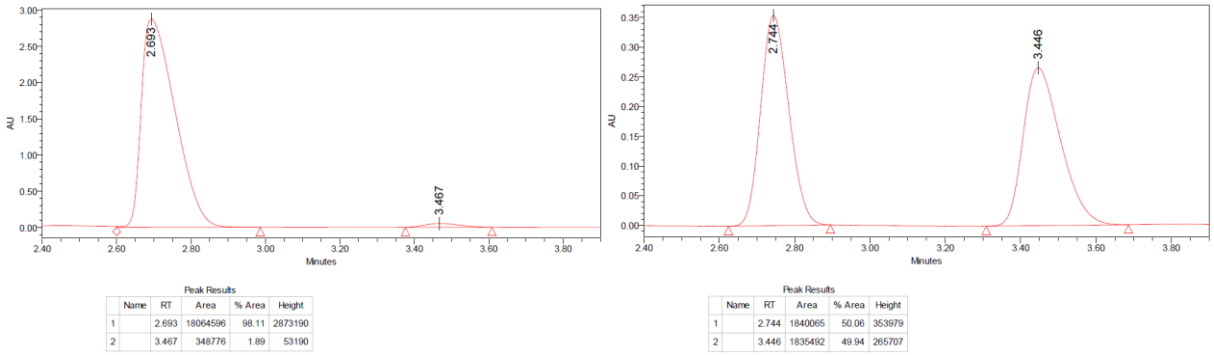
The reaction was performed with **1f** (95.3 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), $^{i}PrOH$ (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3f** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 75.5 mg, 67% yield, 96% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.93 (dd, *J* = 7.9 and 1.5 Hz, 2H, 2 × CH_{Ar}), 7.54 (t, *J* = 7.6 Hz, 1H, CH_{Ar}), 7.44 (t, *J* = 7.6 Hz, 2H, 2 × CH_{Ar}), 7.20–7.17 (m, 2H, 2 × CH_{Ar}), 6.84–6.82 (m, 2H, 2 × CH_{Ar}), 4.87–4.85 (m, 2H, C=CH_2), 4.00 (t, *J* = 7.3 Hz, 1H, CH_β), 3.77 (s, 3H, OCH_3), 3.52 (dd, *J* = 16.6 and 7.5 Hz, 1H, CH_αH$_\alpha$), 3.33 (dd, *J* = 16.8 and 7.1 Hz, 1H, CH$_\alpha$$H_\alpha$), 1.67 (s, 3H, C=CC$H_3$).

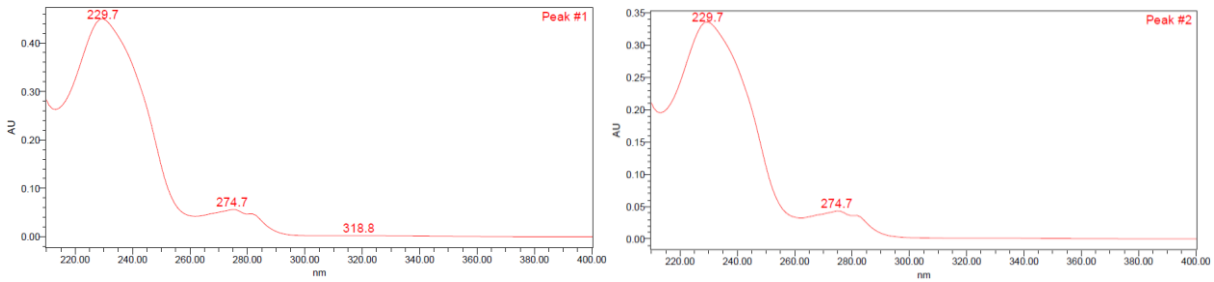
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.8, 158.3, 147.5, 137.3, 134.9, 133.1, 128.9 (2 × C), 128.7 (2 × C), 128.1 (2 × C), 113.9 (2 × C), 110.0, 55.3, 46.9, 43.4, 22.1.

LC-HRMS (ESI): m/z $[M+Na]^+$ calcd. for $C_{19}H_{20}O_2Na^+$: 303.1356; found 303.1358.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 2.69 (major) and 3.47 (minor).

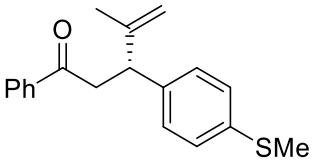


SFC of (*R*)-3-(4-methoxyphenyl)-4-methyl-1-phenylpent-4-en-1-one (**3f**)



UV-visible spectra of (*R*)-3-(4-methoxyphenyl)-4-methyl-1-phenylpent-4-en-1-one (**3f**)

(*R*)-4-Methyl-3-(4-(methylthio)phenyl)-1-phenylpent-4-en-1-one (3g)



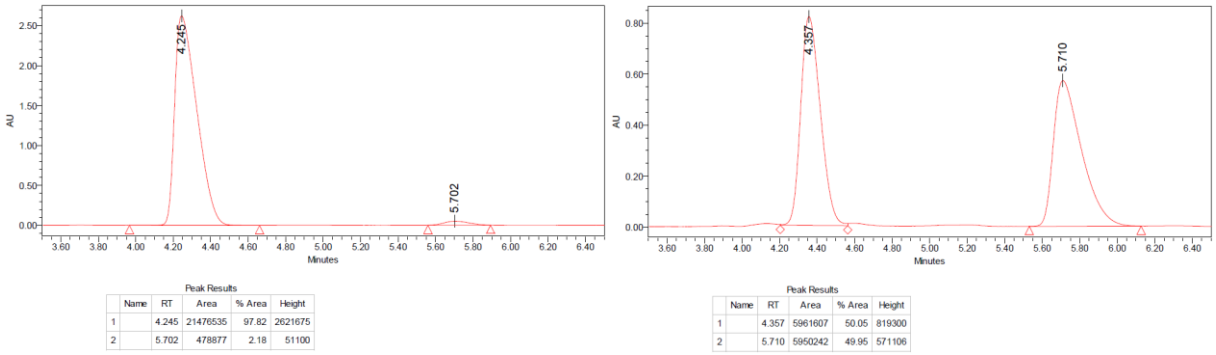
The reaction was performed with **1g** (101.7 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 μL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), $^{i}PrOH$ (46 μL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3g** was obtained as a yellow oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 59.3 mg, 50% yield, 96% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.93 (dd, *J* = 8.1 and 1.5 Hz, 2H, 2 × C*H*$_{Ar}$), 7.56–7.53 (m, 1H, C*H*$_{Ar}$), 7.44 (t, *J* = 7.6 Hz, 2H, 2 × C*H*$_{Ar}$), 7.21–7.17 (m, 4H, 4 × C*H*$_{Ar}$), 4.89–4.86 (m, 2H, C=C*H*$_2$), 4.02 (t, *J* = 7.3 Hz, 1H, C*H*$_β$), 3.52 (dd, *J* = 16.8 and 7.4 Hz, 1H, C*H*$_α$H$_α$), 3.34 (dd, *J* = 16.8 and 7.2 Hz, 1H, CH$_α$*H*$_α$), 2.45 (s, 3H, SC*H*$_3$), 1.67 (s, 3H, C=CC*H*$_3$).

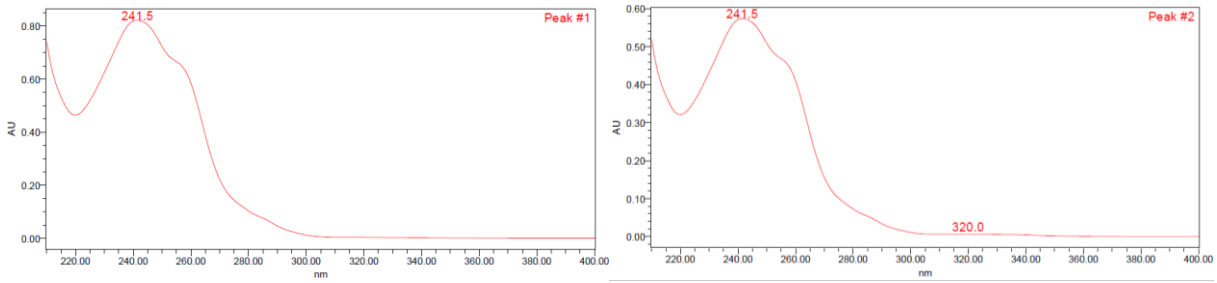
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.4, 147.1, 139.9, 137.2, 136.4, 133.1, 128.7 (2 × C), 128.5 (2 × C), 128.1 (2 × C), 127.0 (2 × C), 110.4, 47.1, 43.1, 22.1, 16.1.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{19}H_{20}OSH^+$: 297.1308; found 297.1308.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 10 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 4.25 (major) and 5.70 (minor).

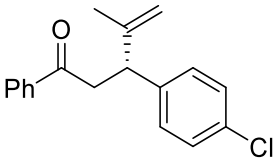


SFC of (*R*)-4-methyl-3-(4-(methylthio)phenyl)-1-phenylpent-4-en-1-one (**3g**)



UV-visible spectra of (*R*)-4-methyl-3-(4-(methylthio)phenyl)-1-phenylpent-4-en-1-one (**3g**)

(*R*)-3-(4-Chlorophenyl)-4-methyl-1-phenylpent-4-en-1-one (3h)



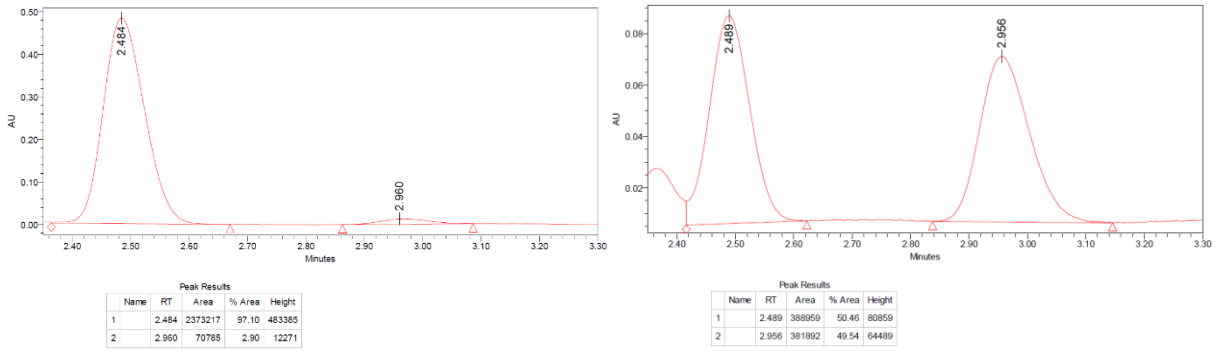
The reaction was performed with **1h** (97.1 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 μL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), $^{i}PrOH$ (46 μL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3h** was obtained as a white solid after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 75.9 mg, 67% yield, 94% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.92–7.91 (m, 2H, 2 × CH_{Ar}), 7.56–7.54 (m, 1H, CH_{Ar}), 7.45 (t, *J* = 7.8 Hz, 2H, 2 × CH_{Ar}), 7.25–7.24 (m, 2H, 2 × CH_{Ar}), 7.21–7.19 (m, 2H, 2 × CH_{Ar}), 4.90–4.87 (m, 2H, C=CH_2), 4.03 (t, *J* = 7.2 Hz, 1H, CH_β), 3.51 (dd, *J* = 16.8 and 7.1 Hz, 1H, CH_αH$_\alpha$), 3.34 (dd, *J* = 16.8 and 7.4 Hz, 1H, CH$_\alpha$$H_\alpha$), 1.66 (s, 3H, C=CC$H_3$).

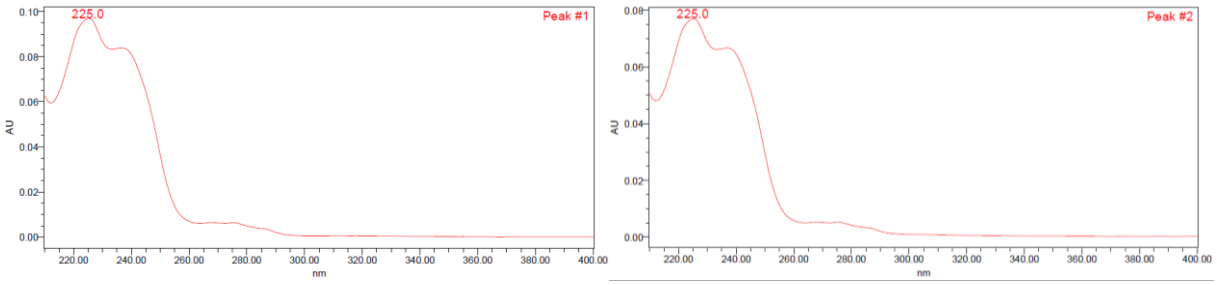
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.3, 146.9, 141.4, 137.2, 133.3, 132.4, 129.4 (2 × C), 128.8 (2 × C), 128.7 (2 × C), 128.1 (2 × C), 110.8, 47.0, 43.1, 22.2.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{18}H_{17}ClOH^+$: 285.1041; found 285.1040.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 2.48 (major) and 2.96 (minor).

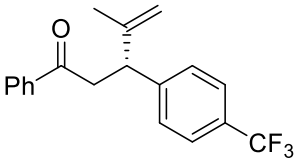


SFC of (*R*)-3-(4-Chlorophenyl)-4-methyl-1-phenylpent-4-en-1-one (**3h**)



UV-visible spectra of (*R*)-3-(4-Chlorophenyl)-4-methyl-1-phenylpent-4-en-1-one (**3h**)

(*R*)-4-Methyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (3i)



The reaction was performed with **1i** (110.5 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 μL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 μL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3i** was obtained as a white solid after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 57.1 mg, 45% yield, 91% *ee*, (*R*)-configuration].

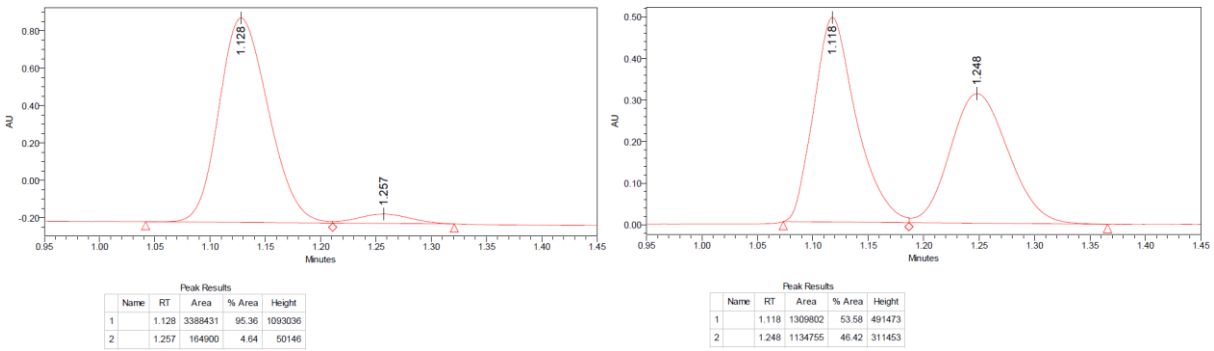
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.93–7.92 (m, 2H, 2 × C*H*$_{Ar}$), 7.59–7.53 (m, 3H, 3 × C*H*$_{Ar}$), 7.45 (t, *J* = 7.8 Hz, 2H, 2 × C*H*$_{Ar}$), 7.39 (d, *J* = 8.0 Hz, 2H, 2 × C*H*$_{Ar}$), 4.94–4.90 (m, 2H, C=C*H*$_2$), 4.12 (t, *J* = 7.2 Hz, 1H, C*H*$_β$), 3.56 (dd, *J* = 17.0 and 7.0 Hz, 1H, C*H*$_α$H$_α$), 3.39 (dd, *J* = 17.0 and 7.5 Hz, 1H, CH$_α$*H*$_α$), 1.67 (s, 3H, C=CC*H*$_3$).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.0, 147.0, 146.5, 137.1, 133.4, 129.0 (q, *J* = 32.3 Hz), 128.8 (2 × C), 128.4 (2 × C), 128.1 (2 × C), 155.6 (q, *J* = 3.8 Hz, 2 × C), 124.4 (q, *J* = 271.9 Hz), 111.2, 47.1, 43.1, 22.1, 16.1.

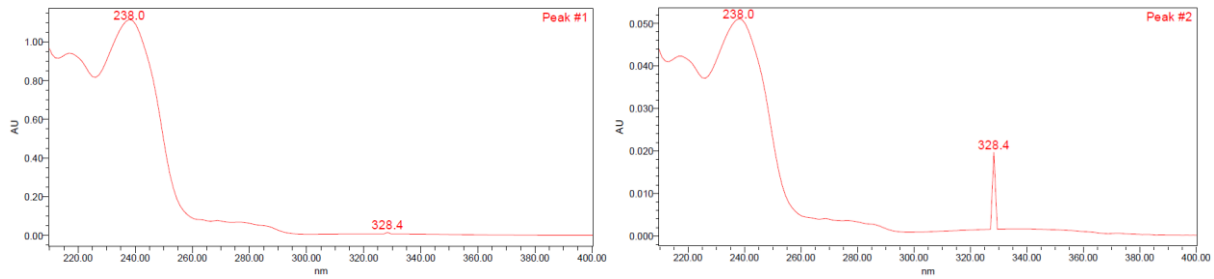
^{19}F NMR ($CDCl_3$, 565 MHz): δ –62.40.

LC-HRMS (ESI): m/z $[M-H]^-$ calcd. for $C_{19}H_{16}F_3O^-$: 317.1159; found 317.1164.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 1.13 (major) and 1.26 (minor).

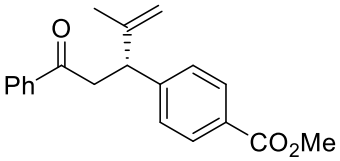


SFC of (*R*)-4-methyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (**3i**)



UV-visible spectra of (*R*)-4-methyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (**3i**)

Methyl (*R*)-4-(2-methyl-5-oxo-5-phenylpent-1-en-3-yl)benzoate (3j)



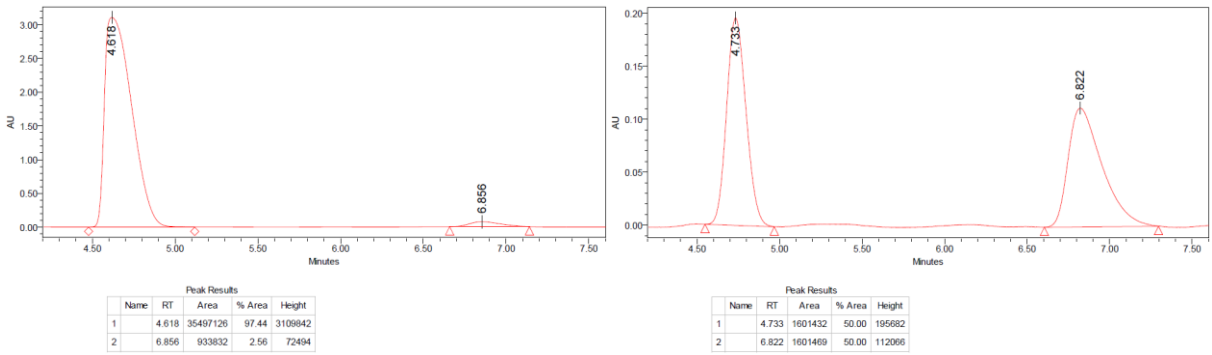
The reaction was performed with **1j** (106.5 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), $^{i}PrOH$ (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3j** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 81.5 mg, 66% yield, 95% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.95 (d, *J* = 8.3 Hz, 2H, 2 × CH_{Ar}), 7.92 (d, *J* = 7.1 Hz, 2H, 2 × CH_{Ar}), 7.55–7.53 (m, 1H, CH_{Ar}), 7.43 (t, *J* = 7.8 Hz, 2H, 2 × CH_{Ar}), 7.34 (d, *J* = 8.3 Hz, 2H, 2 × CH_{Ar}), 4.92–4.89 (m, 2H, C=CH_2), 4.11 (t, *J* = 7.3 Hz, 1H, CH_β), 3.88 (s, 3H, OCH_3).3.55 (dd, *J* = 16.9 and 7.2 Hz, 1H, CH_αH$_\alpha$), 3.38 (dd, *J* = 16.8 and 7.3 Hz, 1H, CH$_\alpha$$H_\alpha$), 1.66 (s, 3H, C=CC$H_3$).

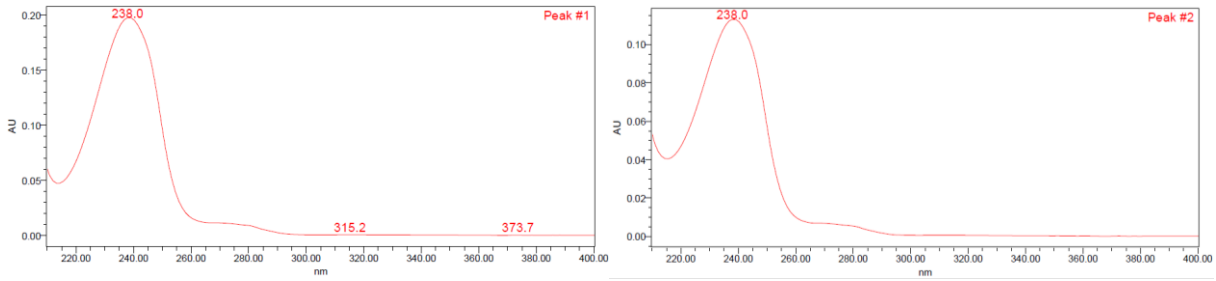
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.1, 167.1, 148.3, 146.5, 137.1, 133.3, 129.9 (2 × C), 128.7 (2 × C), 128.7, 128.1 (2 × C), 128.1 (2 × C), 111.1, 52.1, 47.6, 42.8, 22.1.

LC-HRMS (ESI): m/z [M+Na]$^+$ calcd. for $C_{20}H_{20}O_3Na^+$: 331.1305; found 331.1304.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 10 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 4.62 (major) and 6.86 (minor).

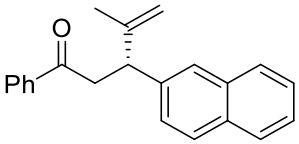


SFC of methyl (*R*)-4-(2-methyl-5-oxo-5-phenylpent-1-en-3-yl)benzoate (**3j**)



UV-visible spectra of methyl (*R*)-4-(2-methyl-5-oxo-5-phenylpent-1-en-3-yl)benzoate (**3j**)

(*R*)-4-Methyl-3-(naphthalen-2-yl)-1-phenylpent-4-en-1-one (3k)



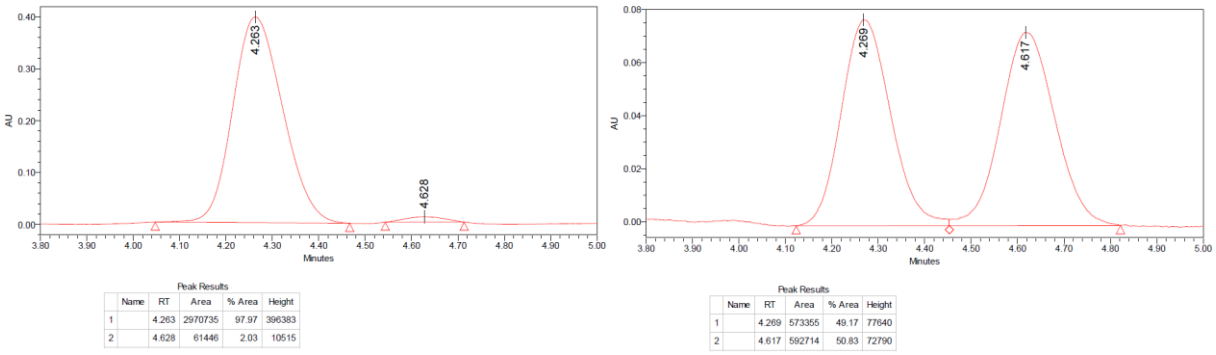
The reaction was performed with **1k** (103.3 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 μL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 μL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3k** was obtained as a white solid after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 83.8 mg, 70% yield, 96% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.97–7.95 (m, 2H, 2 × C*H*$_{Ar}$), 7.82–7.79 (m, 3H, 3 × C*H*$_{Ar}$), 7.73 (s, 1H, C*H*$_{Ar}$), 7.56–7.53 (m, 1H, C*H*$_{Ar}$), 7.48–7.43 (m, 5H, 5 × C*H*$_{Ar}$), 4.97 (s, 2H, C=C*H*$_2$), 4.26 (t, *J* = 7.2 Hz, 1H, C*H*$_\beta$), 3.66 (dd, *J* = 16.8 and 7.6 Hz, 1H, C*H*$_\alpha$H$_\alpha$), 3.48 (dd, *J* = 16.8 and 6.9 Hz, 1H, CH$_\alpha$*H*$_\alpha$), 1.72 (s, 3H, C=CC*H*$_3$).

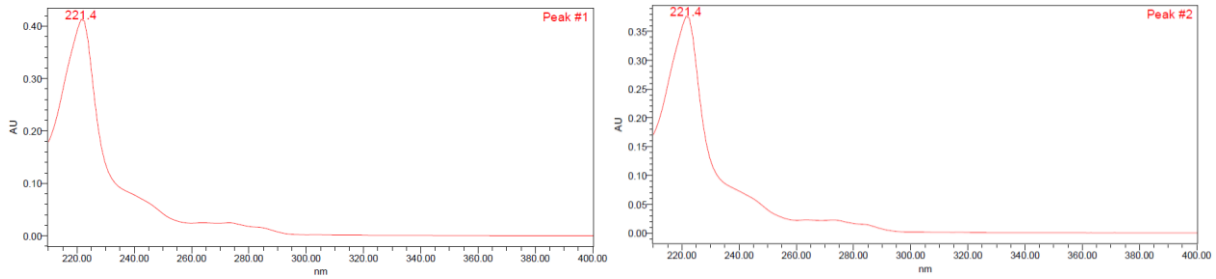
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.5, 147.1, 140.3, 137.3, 133.6, 133.1, 132.5, 128.7 (2 × C), 128.3, 128.2 (2 × C), 127.8, 127.7, 126.4, 126.4, 126.1, 125.6, 110.7, 47.8, 43.1, 22.3.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{22}H_{20}OH^+$: 301.1587; found 301.1588.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 4.26 (major) and 4.63 (minor).

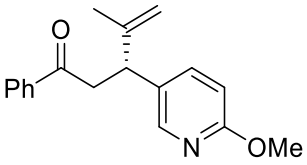


SFC of (*R*)-4-methyl-3-(naphthalen-2-yl)-1-phenylpent-4-en-1-one (**3k**)



UV-visible spectra of (*R*)-4-methyl-3-(naphthalen-2-yl)-1-phenylpent-4-en-1-one (**3k**)

(*R*)-3-(6-Methoxypyridin-3-yl)-4-methyl-1-phenylpent-4-en-1-one (3l)



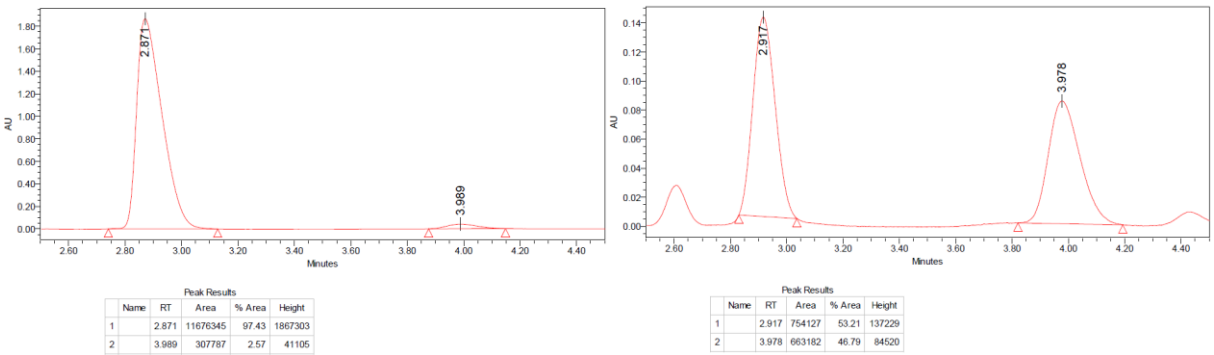
The reaction was performed with **1l** (95.7 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3l** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 101.3 mg, 90% yield, 95% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.05 (d, *J* = 2.5 Hz, 1H, C*H*$_{Py}$), 7.92–7.90 (m, 2H, 2 × C*H*$_{Ar}$), 7.53–7.52 (m, 1H, C*H*$_{Ar}$), 7.46 (dd, *J* = 8.6 and 2.5 Hz, 1H, 2 × C*H*$_{Py}$), 7.43 (t, *J* = 7.8 Hz, 2H, 2 × C*H*$_{Ar}$), 6.66 (d, *J* = 8.5 Hz, 2H, 2 × C*H*$_{Py}$), 4.89–4.87 (m, 2H, C=C*H*$_2$), 3.98 (t, *J* = 7.3 Hz, 1H, C*H*$_\beta$), 3.89 (s, 3H, OC*H*$_3$), 3.51 (dd, *J* = 16.8 and 6.9 Hz, 1H, C*H*$_\alpha$H$_\alpha$), 3.33 (dd, *J* = 16.8 and 7.6 Hz, 1H, CH$_\alpha$*H*$_\alpha$), 1.66 (s, 3H, C=CC*H*$_3$).

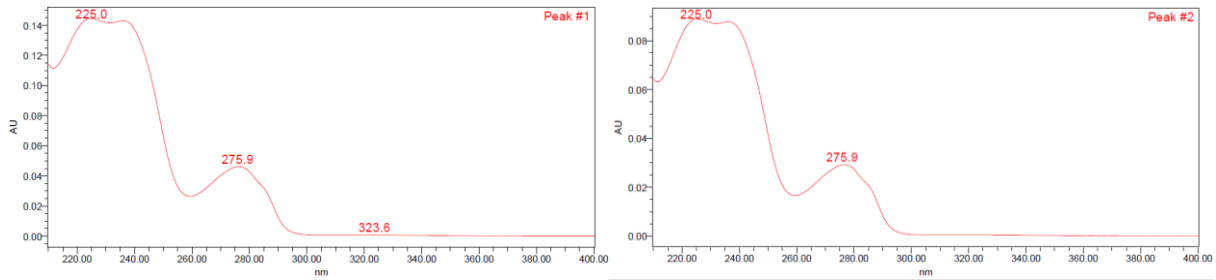
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.1, 163.2, 146.7, 146.1, 138.3, 137.1, 133.2, 130.7, 128.7 (2 × C), 128.1 (2 × C), 110.8, 110.7, 53.4, 44.3, 42.9, 22.0.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{18}H_{18}NO_2H^+$: 282.1489; found 282.1486.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 2.87 (major) and 3.99 (minor).

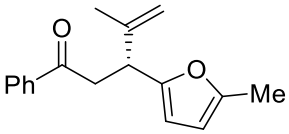


SFC of (*R*)-3-(6-methoxypyridin-3-yl)-4-methyl-1-phenylpent-4-en-1-one (**3l**)



UV-visible spectra of (*R*)-3-(6-methoxypyridin-3-yl)-4-methyl-1-phenylpent-4-en-1-one (**3l**)

(*R*)-4-Methyl-3-(5-methylfuran-2-yl)-1-phenylpent-4-en-1-one (3m)



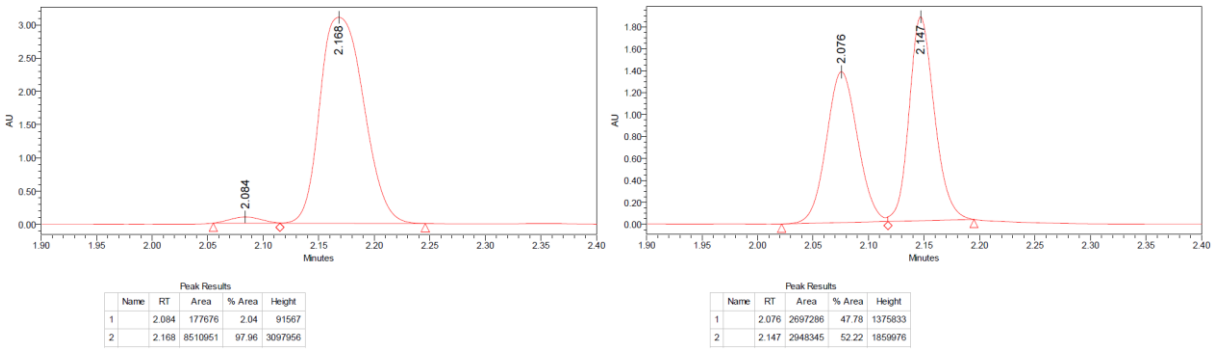
The reaction was performed with **1m** (84.9 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3m** was obtained as a yellow oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 80.2 mg, 79% yield, 96% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.00 (d, *J* = 7.3 Hz, 2H, 2 × CH_{Ar}), 7.58 (t, *J* = 7.4 Hz, 1H, CH_{Ar}), 7.49 (t, *J* = 7.7 Hz, 2H, 2 × CH_{Ar}), 5.95 (d, *J* = 3.0 Hz, 1H, CH_{Fur}), 5.86 (d, *J* = 3.0 Hz, 1H, CH_{Fur}), 4.90–4.88 (m, 2H, C=CH_2), 4.16 (t, *J* = 7.3 Hz, 1H, CH_{β}), 3.52 (dd, *J* = 16.6 and 7.1 Hz, 1H, CH_{α}H$_{\alpha}$), 3.40 (dd, *J* = 16.6 and 7.5 Hz, 1H, CH$_{\alpha}$H$_{\alpha}$), 2.25 (s, 3H, CH_3), 1.79 (s, 3H, C=CCH_3).

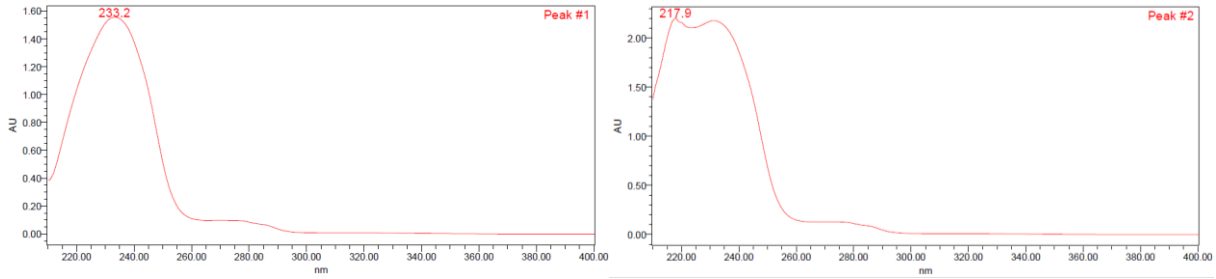
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.3, 154.1, 151.0, 145.2, 137.2, 133.2, 128.7 (2 × C), 128.2 (2 × C), 112.0, 106.4, 106.1, 41.9, 40.9, 21.0 13.7.

LC-HRMS (ESI): m/z [M-H]$^-$ calcd. for $C_{17}H_{17}O^-$: 253.1234; found 253.1236.

SFC: (*R*,*R*)-Whelk-O1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 2.08 (minor) and 2.17 (major).

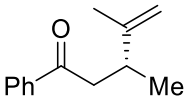


SFC of (*R*)-4-methyl-3-(5-methylfuran-2-yl)-1-phenylpent-4-en-1-one (**3m**)



UV-visible spectra of (*R*)-4-methyl-3-(5-methylfuran-2-yl)-1-phenylpent-4-en-1-one (**3m**)

(*R*)-3,4-Dimethyl-1-phenylpent-4-en-1-one (3n)



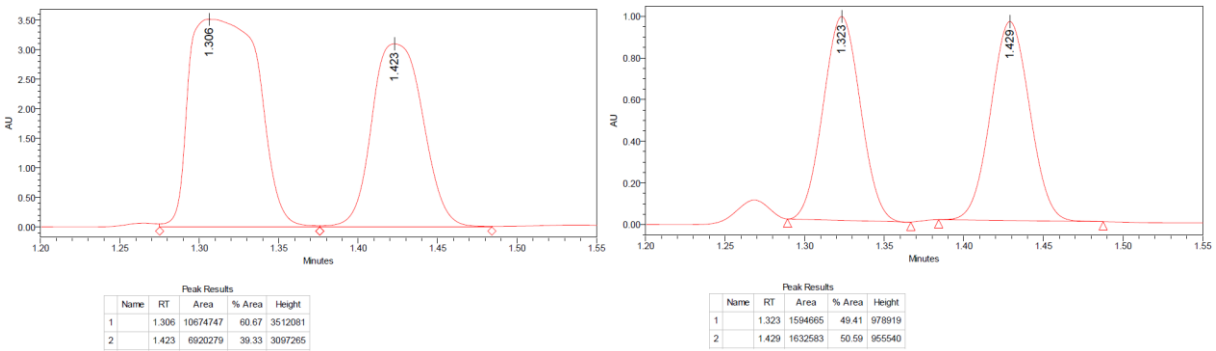
The reaction was performed with **1n** (58.5 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3n** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 68.9 mg, 92% yield, 21% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.96–7.94 (m, 2H, 2 × C*H*$_{Ar}$), 7.56–7.53 (m, 1H, C*H*$_{Ar}$), 7.45 (t, *J* = 7.8 Hz, 2H, 2 × C*H*$_{Ar}$), 4.74–4.72 (m, 2H, C=C*H*$_2$), 3.13–3.10 (m, 1H, C*H*$_α$H$_α$), 2.93 – 2.84 (m, 2H, C*H*$_β$ and CH$_α$*H*$_α$) 1.76 (s, 3H, C=CC*H*$_3$), 1.10 (d, *J* = 6.6 Hz, 3H, C*H*$_3$).

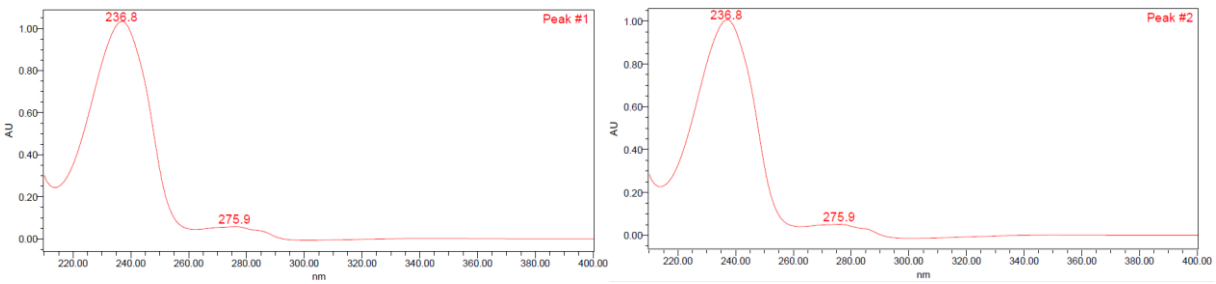
^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.7, 149.4, 137.4, 133.0, 128.7 (2 × C), 128.2 (2 × C), 109.6, 44.4, 37.0, 20.4, 19.7.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{13}H_{16}OH^+$: 189.1274; found 189.1275.

SFC: (*R*,*R*)-Whelk-O1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 1.31 (minor) and 1.42 (major).

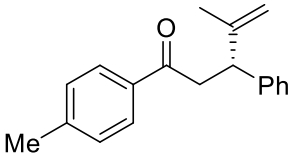


SFC of (*R*)-3,4-dimethyl-1-phenylpent-4-en-1-one (**3n**)



UV-visible spectra of (*R*)-3,4-dimethyl-1-phenylpent-4-en-1-one (**3n**)

(*R*)-4-Methyl-3-phenyl-1-(*p*-tolyl)pent-4-en-1-one (3o)



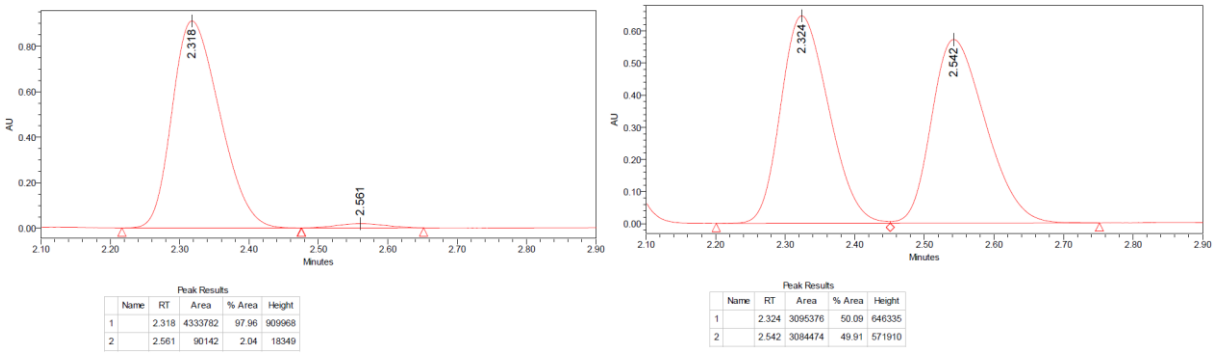
The reaction was performed with **1n** (88.9 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 μL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), $^{i}PrOH$ (46 μL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3o** was obtained as a white solid after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 91.8 mg, 87% yield, 97% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.84 (d, *J* = 8.1 Hz, 2H, 2 × C*H*$_{Ar}$), 7.30–7.27 (m, 4H, 4 × C*H*$_{Ar}$), 7.24 (d, *J* = 8.1 Hz, 2H, 2 × C*H*$_{Ar}$), 7.22 – 7.19 (m, 1H, C*H*$_{Ar}$), 4.89–4.87 (m, 2H, C=C*H*$_2$), 4.06 (t, *J* = 7.3 Hz, 1H, C*H*$_\beta$), 3.54 (dd, *J* = 16.6 and 7.8 Hz, 1H, C*H*$_\alpha$H$_\alpha$), 3.32 (dd, *J* = 16.7 and 6.7 Hz, 1H, CH$_\alpha$*H*$_\alpha$), 2.40 (s, 3H, C*H*$_3$), 1.68 (s, 3H, C=CC*H*$_3$).

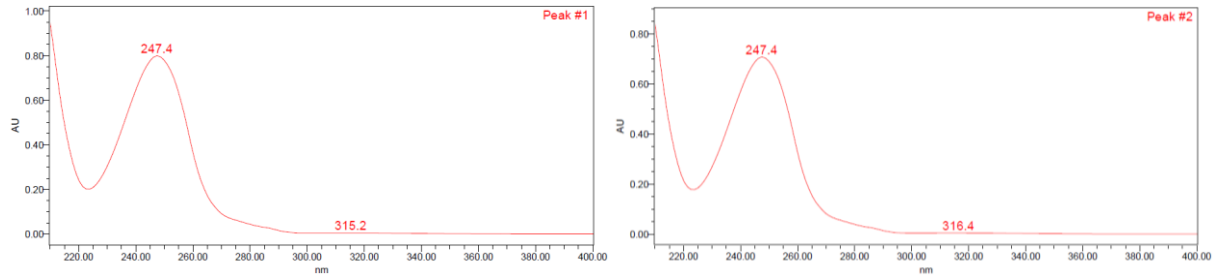
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.2, 147.2, 143.9, 143.0, 134.8, 129.4 (2 × C), 128.6 (2 × C), 128.3 (2 × C), 128.0 (2 × C), 126.6, 110.3, 47.7, 43.1, 22.2, 21.7.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{19}H_{20}OH^+$: 265.1587; found 265.1586.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 2.32 (major) and 2.56 (minor).

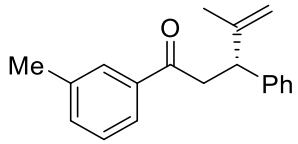


SFC of (*R*)-4-methyl-3-phenyl-1-(*p*-tolyl)pent-4-en-1-one (**3o**)



UV-visible spectra of (*R*)-4-methyl-3-phenyl-1-(*p*-tolyl)pent-4-en-1-one (**3o**)

(*R*)-4-Methyl-3-phenyl-1-(*m*-tolyl)pent-4-en-1-one (3p)



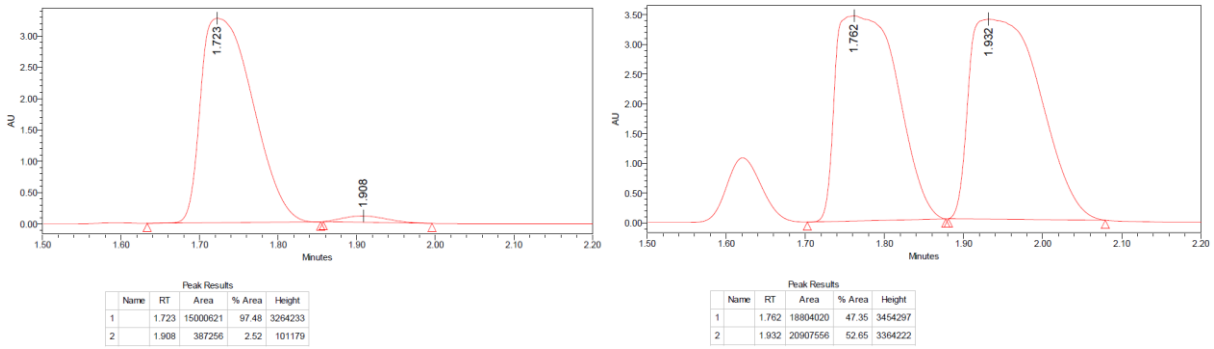
The reaction was performed with **1p** (88.9 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3p** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 81.1 mg, 77% yield, 96% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.75–7.74 (m, 2H, 2 × CH_{Ar}), 7.38–7.28 (m, 6H, 6 × CH_{Ar}), 7.23–7.20 (m, 1H, CH_{Ar}), 4.91–4.88 (m, 2H, C=CH_2), 4.07 (t, *J* = 7.3 Hz, 1H, CH_β), 3.56 (dd, *J* = 16.7 and 7.8 Hz, 1H, CH_αH$_\alpha$), 3.35 (dd, *J* = 16.8 and 6.8 Hz, 1H, CH$_\alpha$$H_\alpha$), 2.40 (s, 3H, C$H_3$), 1.69 (s, 3H, C=CC$H_3$).

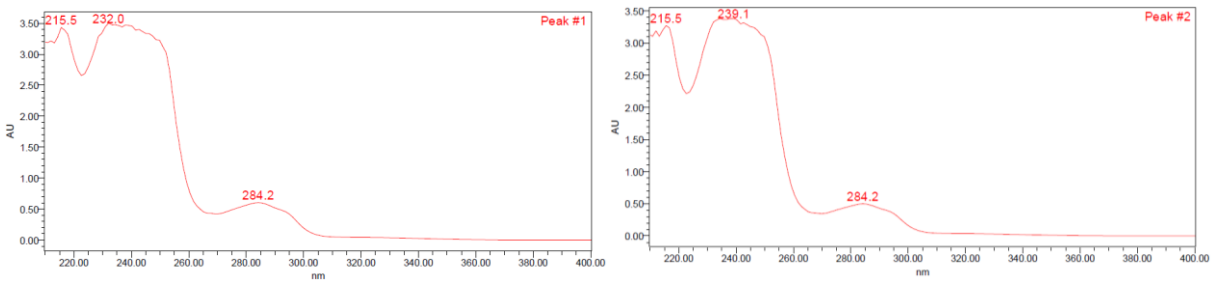
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.7, 147.2, 142.9, 138.5, 137.3, 133.8, 128.7, 128.6 (2 × C), 128.5, 128.0 (2 × C), 126.6, 125.3, 110.3, 47.7, 43.3, 22.2, 21.5.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{19}H_{20}OH^+$: 265.1587; found 265.1587.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 1.72 (major) and 1.91 (minor).

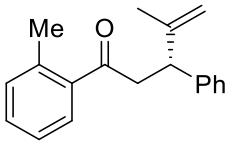


SFC of (*R*)-4-methyl-3-phenyl-1-(*m*-tolyl)pent-4-en-1-one (**3p**)



UV-visible spectra of (*R*)-4-methyl-3-phenyl-1-(*m*-tolyl)pent-4-en-1-one (**3p**)

(*R*)-4-Methyl-3-phenyl-1-(*o*-tolyl)pent-4-en-1-one (3q)



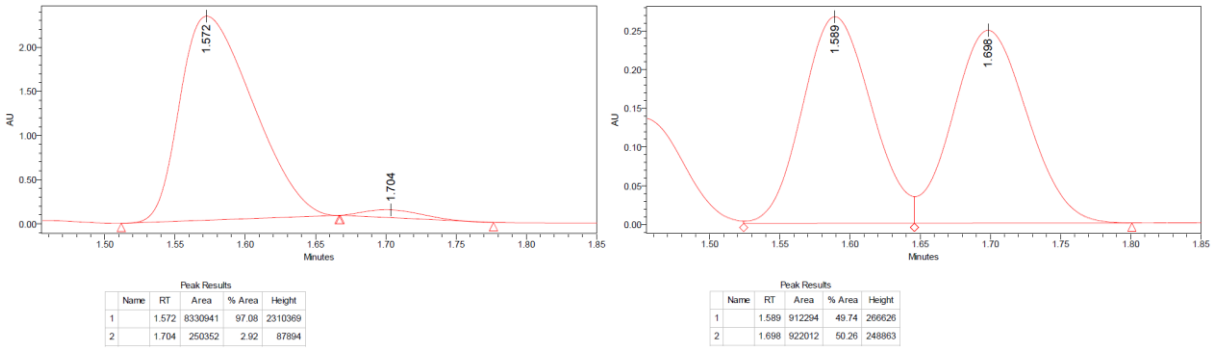
The reaction was performed with **1q** (88.9 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3q** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 74.9 mg, 71% yield, 94% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.54 (dd, *J* = 7.7 and 1.4 Hz, 1H, CH_{Ar}), 7.35 (td, *J* = 7.5 and 1.4 Hz, 1H, CH_{Ar}), 7.30 (t, *J* = 7.5 Hz, 2H, 2 × CH_{Ar}), 7.26–7.21 (m, 5H, 5 × CH_{Ar}), 4.91–4.88 (m, 2H, C=CH_2), 4.00 (t, *J* = 7.5 Hz, 1H, CH_β), 3.45 (dd, *J* = 16.3 and 7.7 Hz, 1H, CH_αH$_\alpha$), 3.33 (dd, *J* = 16.3 and 7.3 Hz, 1H, CH$_\alpha$$H_\alpha$), 2.35 (s, 3H, C$H_3$), 1.67 (s, 3H, C=CC$H_3$).

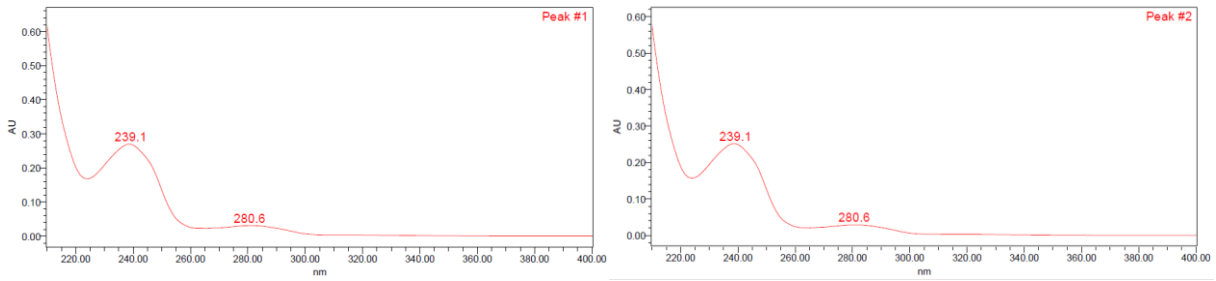
^{13}C NMR ($CDCl_3$, 151 MHz): δ 203.0, 147.1, 142.6, 138.6, 137.9, 131.9, 131.1, 128.5 (2 × C), 128.0, 128.0 (2 × C), 126.7, 125.6, 110.5, 48.1, 46.3, 22.1, 20.8.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{19}H_{20}OH^+$: 265.1587; found 265.1586.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 1.57 (major) and 1.70 (minor).

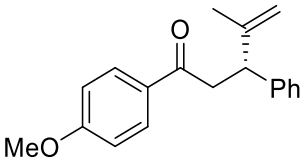


SFC of (*R*)-4-methyl-3-phenyl-1-(*o*-tolyl)pent-4-en-1-one (**3q**)



UV-visible spectra of (*R*)-4-methyl-3-phenyl-1-(*o*-tolyl)pent-4-en-1-one (**3q**)

(*R*)-1-(4-Methoxyphenyl)-4-methyl-3-phenylpent-4-en-1-one (3r)



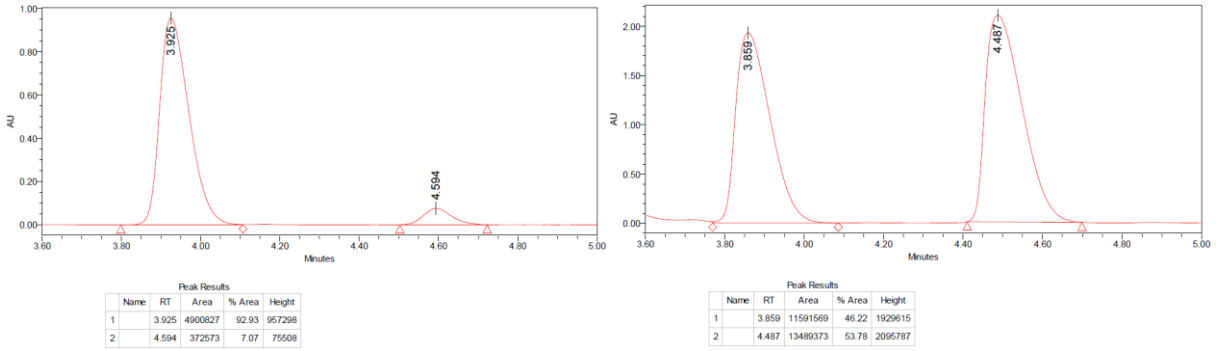
The reaction was performed with **1r** (95.3 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 μL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), $^{i}PrOH$ (46 μL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3r** was obtained as a white solid after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 79.5 mg, 71% yield, 86% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.93–7.92 (m, 2H, 2 × CH_{Ar}), 7.31–7.27 (m, 4H, 4 × CH_{Ar}), 7.22–7.19 (m, 1H, CH_{Ar}), 6.93–6.91 (m, 2H, 2 × CH_{Ar}), 4.89–4.87 (m, 2H, C=CH_2), 4.05 (t, *J* = 7.3 Hz, 1H, CH_{β}), 3.86 (s, 3H, OCH_3), 3.51 (dd, *J* = 16.5 and 7.8 Hz, 1H, CH_{α}H$_{\alpha}$), 3.30 (dd, *J* = 16.5 and 6.8 Hz, 1H, CH$_{\alpha}H_{\alpha}$), 1.68 (s, 3H, C=CCH_3).

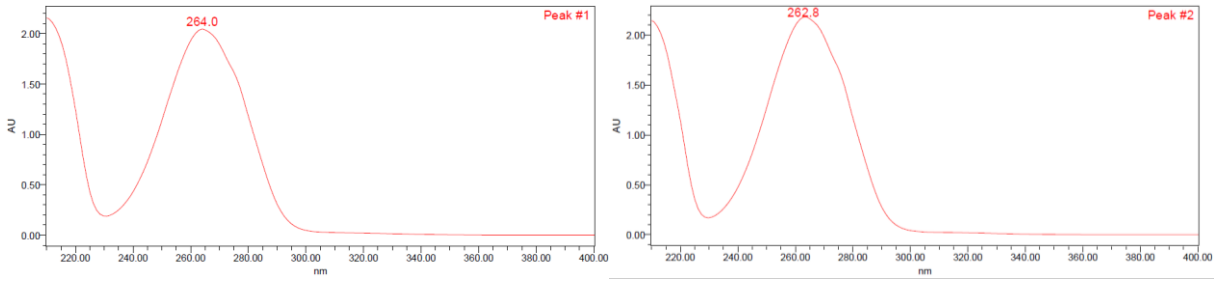
^{13}C NMR ($CDCl_3$, 151 MHz): δ 197.1, 163.5, 147.3, 143.0, 130.4 (2 × C), 130.4, 128.6 (2 × C), 128.0 (2 × C), 126.6, 113.8 (2 × C), 110.3, 55.6, 47.8, 42.8, 22.0

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{19}H_{20}O_2H^+$: 281.1536; found 281.1534.

SFC: Chiralcel OJ-3, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 260 nm. Retention time (min.): 3.93 (major) and 4.59 (minor).

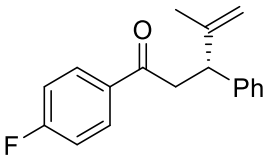


SFC of (*R*)-1-(4-methoxyphenyl)-4-methyl-3-phenylpent-4-en-1-one (**3r**)



UV-visible spectra of (*R*)-1-(4-methoxyphenyl)-4-methyl-3-phenylpent-4-en-1-one (**3r**)

(*R*)-1-(4-Fluorophenyl)-4-methyl-3-phenylpent-4-en-1-one (3s)



The reaction was performed with **1s** (90.5 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3s** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 83.0 mg, 77% yield, 96% *ee*, (*R*)-configuration].

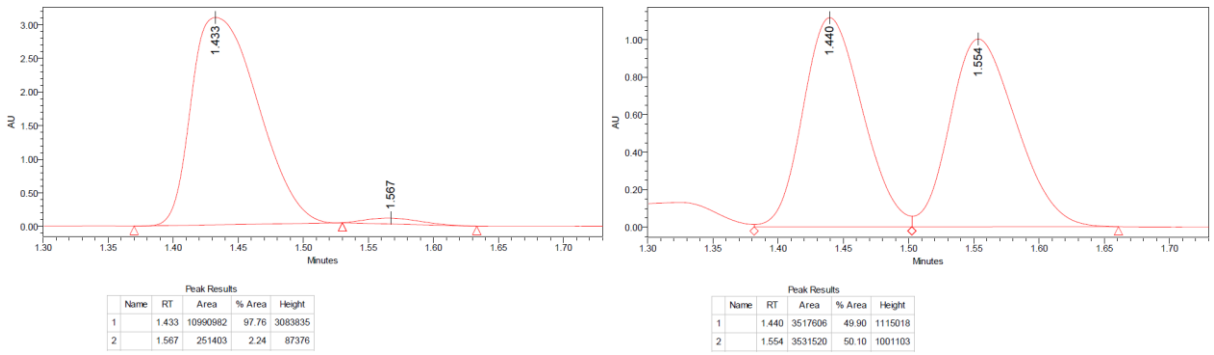
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.96–7.93 (m, 2H, 2 × C*H*$_{Ar}$), 7.30–7.25 (m, 4H, 4 × C*H*$_{Ar}$), 7.21–7.19 (m, 1H, C*H*$_{Ar}$), 7.12–7.08 (m, 2H, 2 × C*H*$_{Ar}$), 4.89–4.85 (m, 2H, C=C*H*$_2$), 4.02 (t, *J* = 7.3 Hz, 1H, C*H*$_\beta$), 3.51 (dd, *J* = 16.7 and 7.7 Hz, 1H, C*H*$_\alpha$H$_\alpha$), 3.32 (dd, *J* = 16.7 and 6.9 Hz, 1H, CH$_\alpha$*H*$_\alpha$), 1.67 (s, 3H, C=CC*H*$_3$).

^{13}C NMR ($CDCl_3$, 151 MHz): δ 197.1, 166.7, 165.0, 147.1, 142.7, 133.7, 133.7, 130.8, 130.8, 128.6 (2 × C), 127.9 (2 × C), 126.8, 115.9, 115.7, 110.4, 47.8, 43.2, 22.2

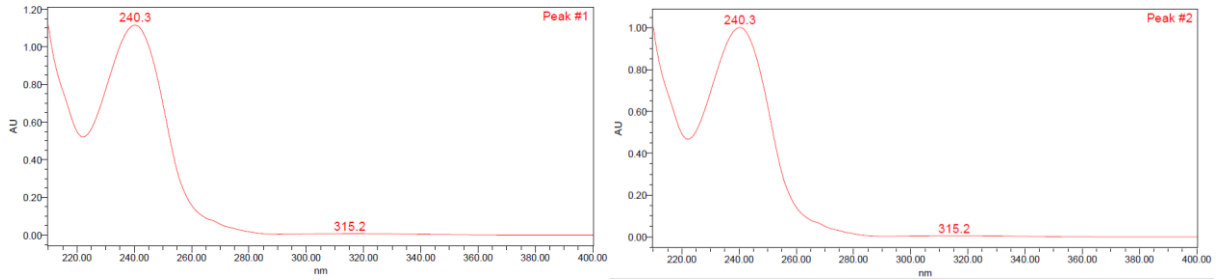
^{19}F NMR ($CDCl_3$, 565 MHz): δ –105.40 (m).

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{18}H_{17}FOH^+$: 269.1336; found 269.1336.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 1.43 (major) and 1.57 (minor).

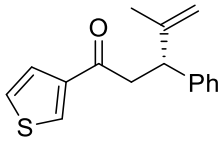


SFC of (*R*)-1-(4-fluorophenyl)-4-methyl-3-phenylpent-4-en-1-one (**3s**)



UV-visible spectra of (*R*)-1-(4-fluorophenyl)-4-methyl-3-phenylpent-4-en-1-one (**3s**)

(*R*)-4-Methyl-3-phenyl-1-(thiophen-3-yl)pent-4-en-1-one (3t)



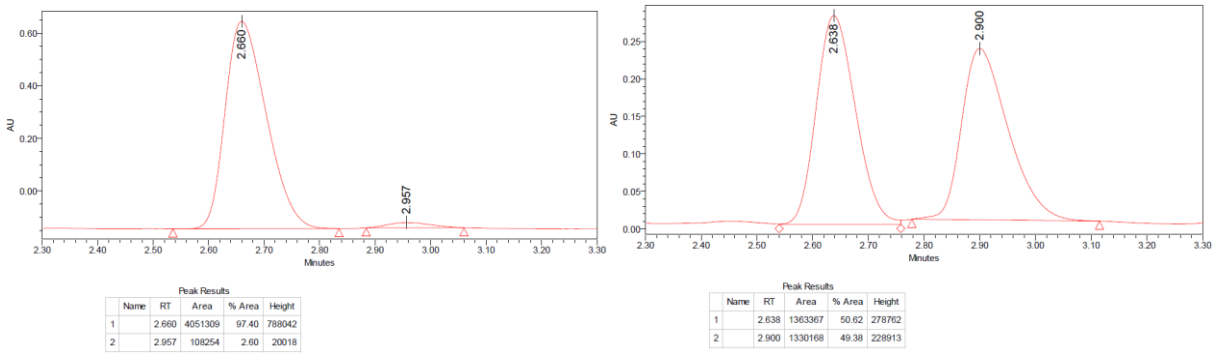
The reaction was performed with **1t** (85.7 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 μL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 μL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3t** was obtained as a white solid after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 78.2 mg, 76% yield, 95% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.02 (dd, *J* = 3.0 and 1.2 Hz, 1H, C*H*$_{Thio}$), 7.52 (dd, *J* = 5.1 and 1.2 Hz, 1H, C*H*$_{Thio}$), 7.30–7.26 (m, 5H, C*H*$_{Thio}$ and 4 × C*H*$_{Ar}$), 7.22–7.19 (m, 1H, C*H*$_{Ar}$), 4.90–4.89 (m, 2H, C=C*H*$_2$), 4.03 (t, *J* = 7.3 Hz, 1H, C*H*$_\beta$), 3.46 (dd, *J* = 16.4 and 7.7 Hz, 1H, C*H*$_\alpha$H$_\alpha$), 3.26 (dd, *J* = 16.4 and 7.7 Hz, 1H, CH$_\alpha$*H*$_\alpha$), 1.68 (s, 3H, C=CC*H*$_3$).

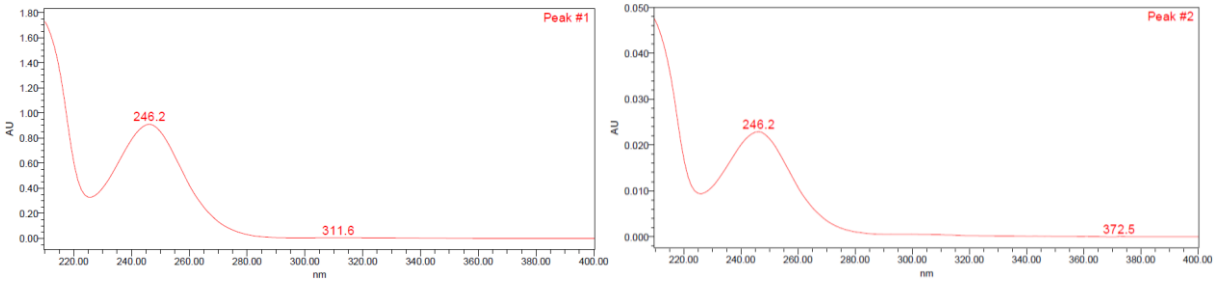
^{13}C NMR ($CDCl_3$, 151 MHz): δ 192.9, 147.1, 142.8, 142.6, 131.9, 128.6 (2 × C), 127.9 (2 × C), 127.1, 126.7, 126.4 110.4, 47.6, 44.6, 22.2.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{16}H_{16}OSH^+$: 257.0995; found 257.0992.

SFC: Trefoil AMY1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 2.66 (major) and 2.96 (minor).

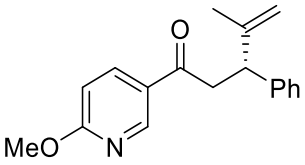


SFC of (*R*)-4-methyl-3-phenyl-1-(thiophen-3-yl)pent-4-en-1-one (**3t**)



UV-visible spectra of (*R*)-4-methyl-3-phenyl-1-(thiophen-3-yl)pent-4-en-1-one (**3s**)

(*R*)-1-(6-Methoxypyridin-3-yl)-4-methyl-3-phenylpent-4-en-1-one (3u)



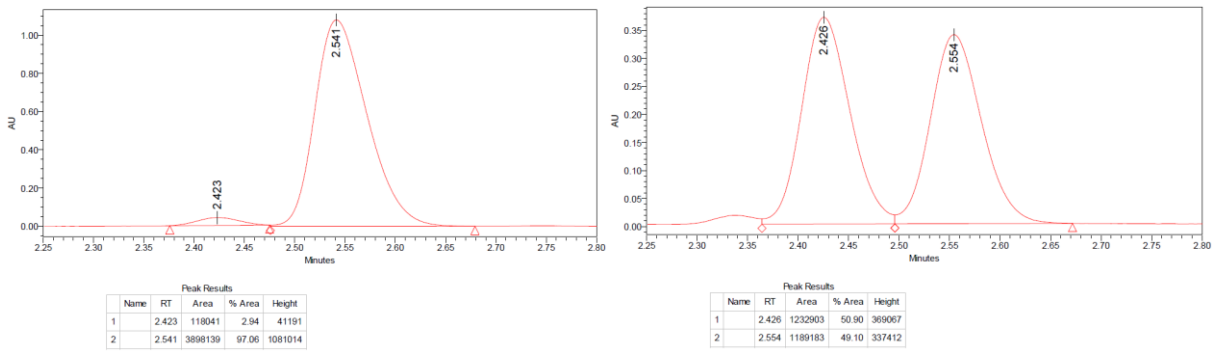
The reaction was performed with **1u** (95.7 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 2-bromopropene (71 μL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 μL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 16 h. Product **3u** was obtained as a white solid after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 94.2 mg, 84% yield, 94% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.77 (d, *J* = 2.4 Hz, 1H, C*H*$_{Py}$), 8.08 (dd, *J* = 8.8 and 2.4 Hz, 1H, C*H*$_{Py}$), 7.30 – 7.25 (m, 4H, 4 × C*H*$_{Ar}$), 7.21–7.18 (m, 1H, C*H*$_{Ar}$), 6.75 (d, *J* = 8.8 Hz, 1H, C*H*$_{Py}$), 4.89–4.87 (m, 2H, C=C*H*$_2$), 4.03 (t, *J* = 7.3 Hz, 1H, C*H*$_β$), 3.99 (s, 3H, OC*H*$_3$), 3.47 (dd, *J* = 16.4 and 7.6 Hz, 1H, C*H*$_α$H$_α$), 3.30 (dd, *J* = 16.4 and 7.1 Hz, 1H, CH$_α$*H*$_α$), 1.67 (s, 3H, C=CC*H*$_3$).

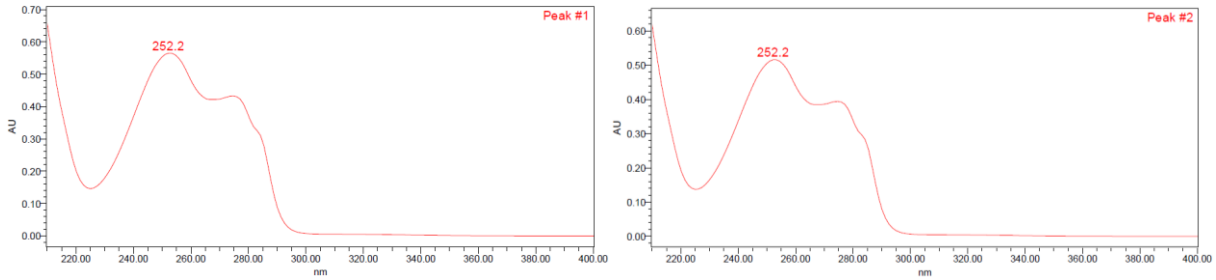
^{13}C NMR ($CDCl_3$, 151 MHz): δ 196.4, 166.8, 149.0, 147.1, 142.6, 138.3, 128.6 (2 × C), 127.9 (2 × C), 127.0, 126.8, 111.2, 110.4, 54.2, 47.7, 43.0, 22.1.

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{18}H_{19}NO2H^+$: 282.1489; found 282.1486.

SFC: Trefoil CEL2, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 2.42 (minor) and 2.54 (major).

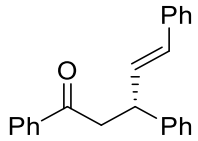


SFC of (*R*)-1-(6-methoxypyridin-3-yl)-4-methyl-3-phenylpent-4-en-1-one (**3u**)



UV-visible spectra of (*R*)-1-(6-methoxypyridin-3-yl)-4-methyl-3-phenylpent-4-en-1-one (**3u**)

(*R*,*E*)-1,3,5-Triphenylpent-4-en-1-one (4a)



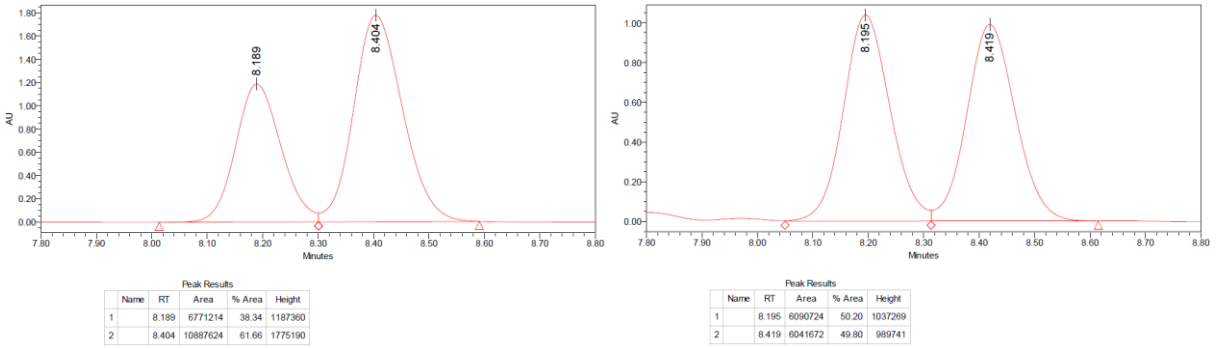
The reaction was performed with **1a** (83.3 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), *β*-bromostyrene (103 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 6 h. Product **4a** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 82.1 mg, 66% yield, 23% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.99–7.97 (m, 2H, 2 × C*H*$_{Ar}$), 7.57–7.56 (m, 1H, C*H*$_{Ar}$), 7.47 (t, *J* = 7.7 Hz, 2H, 2 × C*H*$_{Ar}$), 7.37–7.33 (m, 6H, 6 × C*H*$_{Ar}$), 7.30–7.28 (m, 2H, 2 × C*H*$_{Ar}$), 7.27–7.24 (m, 1H, C*H*$_{Ar}$), 7.23–7.20 (m, 1H, C*H*$_{Ar}$), 6.48–6.41 (m, 2H, C*H*=C*H*), 4.35 (td, *J* = 7.1 and 5.6 Hz, 1H, C*H*$_{β}$), 3.58–3.49 (m, 2H, C*H*$_{α}$*H*$_{α}$).

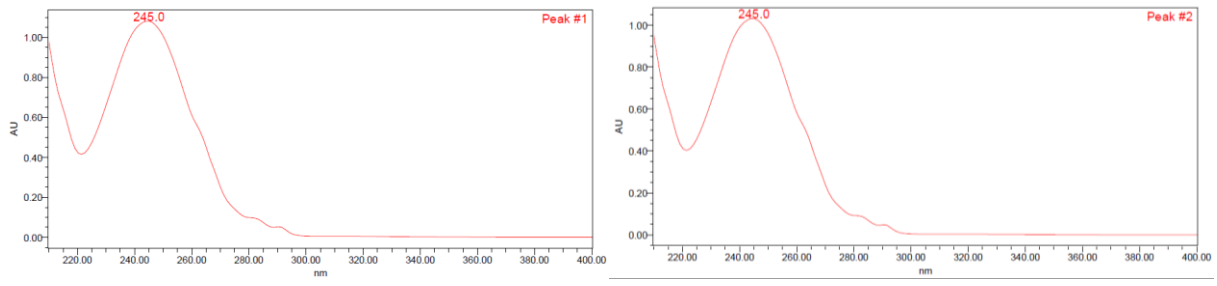
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.2, 143.4, 137.3, 137.2, 133.2, 132.7, 130.2, 128.8 (2 × C), 128.7 (2 × C), 128.6 (2 × C), 128.2 (2 × C), 127.9 (2 × C), 127.4, 126.7, 126.4 (2 × C), 44.6, 44.0.

LC-HRMS (ESI): m/z $[M+Na]^+$ calcd. for $C_{23}H_{20}ONa^+$: 335.1406; found 335.1407.

SFC: (*R*,*R*)-Whelk-O1, CO_2/MeOH with gradient from 97% to 90% in 10 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 8.19 (minor) and 8.40 (major).

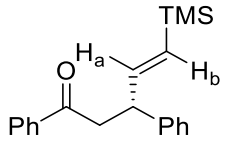


SFC of (*R*,*E*)-1,3,5-triphenylpent-4-en-1-one (**4a**)



UV-visible spectra of (*R*,*E*)-1,3,5-triphenylpent-4-en-1-one (**4a**)

(*R*,*E*)-1,3-Diphenyl-5-(trimethylsilyl)pent-4-en-1-one (4b)



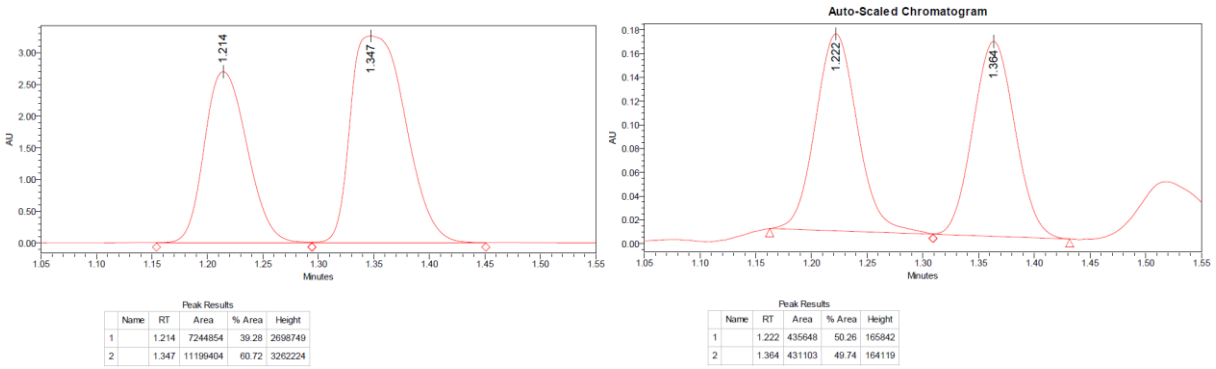
The reaction was performed with **1a** (83.3 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), (2-bromovinyl)trimethylsilane (123 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 6 h. Product **4a** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 89.6 mg, 72% yield, 21% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.92–7.90 (m, 2H, 2 × C*H*$_{Ar}$), 7.54–7.51 (m, 1H, C*H*$_{Ar}$), 7.43 (t, *J* = 7.8 Hz, 2H, 2 × C*H*$_{Ar}$), 7.31–7.28 (m, 2H, 2 × C*H*$_{Ar}$), 7.25–7.23 (m, 2H, 2 × C*H*$_{Ar}$), 7.21–7.18 (m, 1H, C*H*$_{Ar}$), 6.21 (dd, *J* = 18.7 and 6.2 Hz, 1H, C*H*$_a$=CH$_b$), 5.64 (dd, *J* = 18.7 and 1.5 Hz, 1H, CH$_a$=C*H*$_b$), 4.16–4.12 (m, 1H, C*H*$_\beta$), 3.44 (dd, *J* = 16.3 and 7.3 Hz, 1H, C*H*$_\alpha$H$_\alpha$), 3.34 (dd, *J* = 16.3 and 7.0 Hz, 1H, CH$_\alpha$*H*$_\alpha$), 0.01 (s, 9H, 3 × C*H*$_3$).

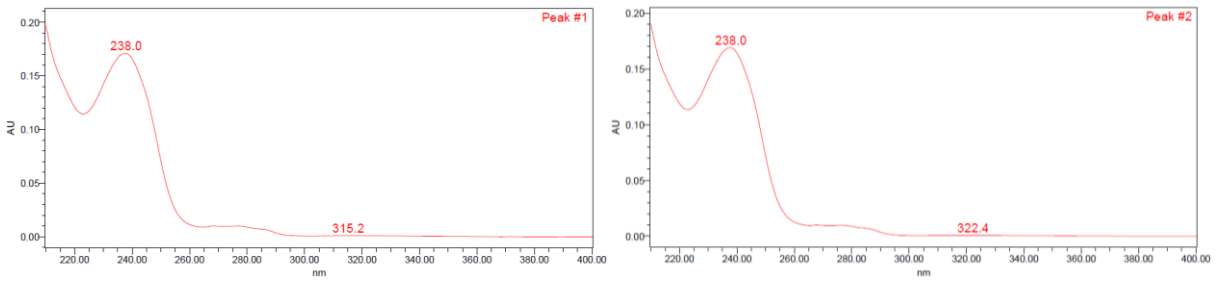
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.6, 148.0, 143.3, 137.4, 133.1, 129.9, 128.7 (4 × C), 128.2 (2 × C), 128.0 (2 × C), 126.6, 47.1, 44.2, –1.1 (3 × C).

LC-HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{20}H_{24}OSiH^+$: 309.1669; found 309.1672.

SFC: Trefoilk CEL2, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 1.21 (minor) and 1.35 (major).

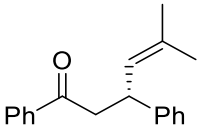


SFC of (*R*,*E*)-1,3-diphenyl-5-(trimethylsilyl)pent-4-en-1-one (**4b**)



UV-visible spectra of (*R*,*E*)-1,3-diphenyl-5-(trimethylsilyl)pent-4-en-1-one (**4b**)

(*R*)-5-Methyl-1,3-diphenylhex-4-en-1-one (4c)



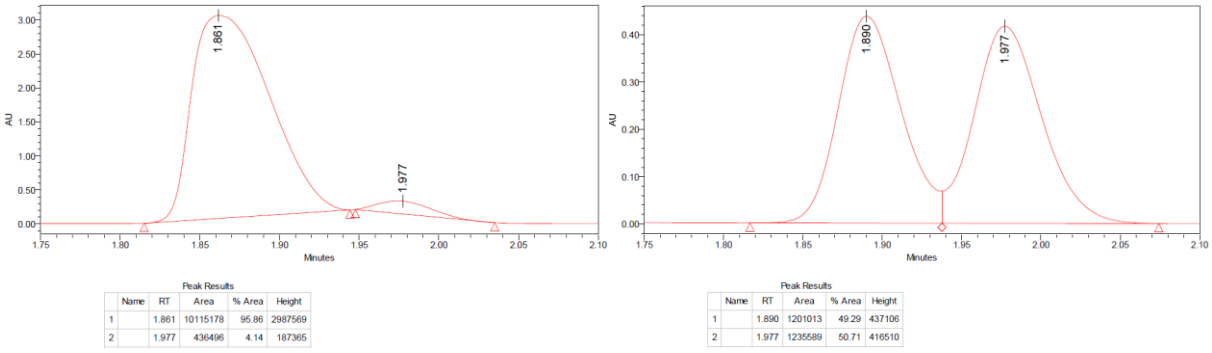
The reaction was performed with **1a** (83.3 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 1-bromo-2-methyl-1-propene (82 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 6 h. Product **4a** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 54.1 mg, 51% yield, 92% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.93 (dd, *J* = 8.3 and 1.4 Hz, 2H, 2 × C*H*$_{Ar}$), 7.56–7.53 (m, 1H, C*H*$_{Ar}$), 7.45 (t, *J* = 7.8 Hz, 2H, 2 × C*H*$_{Ar}$), 7.31–7.26 (m, 4H, 4 × C*H*$_{Ar}$), 7.20–7.17 (m, 1H, C*H*$_{Ar}$), 5.33 (dt, *J* = 9.6 and 1.5 Hz, 1H, C=C*H*), 4.32–4.28 (m, 1H, C*H*$_{\beta}$), 3.37 (dd, *J* = 16.1 and 6.3 Hz, 1H, C*H*$_{\alpha}$H$_{\alpha}$), 3.30 (dd, *J* = 16.1 and 7.9 Hz, 1H, CH$_{\alpha}$*H*$_{\alpha}$), 1.67 (dd, 6H, 2 × C*H*$_3$).

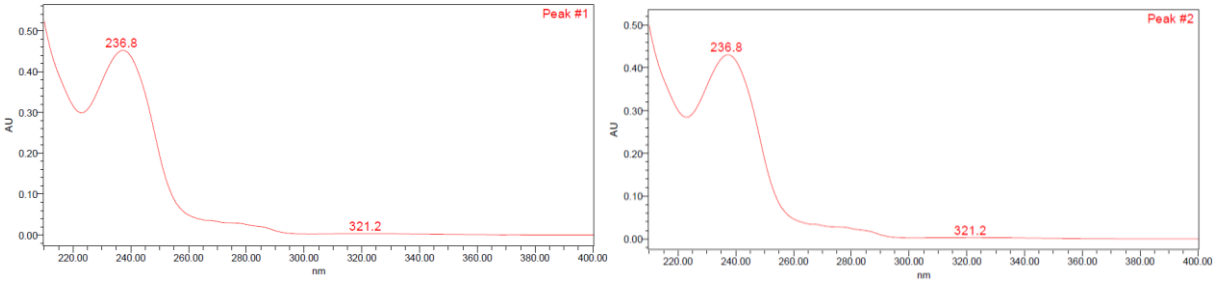
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.9, 145.2, 137.4, 133.0, 132.8, 128.7 (2 × C), 128.7 (2 × C), 128.2 (2 × C), 127.4 (3 × C), 126.3, 46.1, 40.2, 26.0, 18.3.

LC-HRMS (ESI): m/z $[M+Na]^+$ calcd. for $C_{19}H_{20}ONa^+$: 287.1406; found 287.1405.

SFC: Chiralcel OJ-3, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 1.86 (major) and 1.98 (minor).

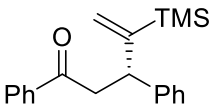


SFC of (*R*)- 5-methyl-1,3-diphenylhex-4-en-1-one (**4c**)



UV-visible spectra of (*R*)-5-methyl-1,3-diphenylhex-4-en-1-one (**4c**)

(*S*)-1,3-Diphenyl-4-(trimethylsilyl)pent-4-en-1-one (4d)



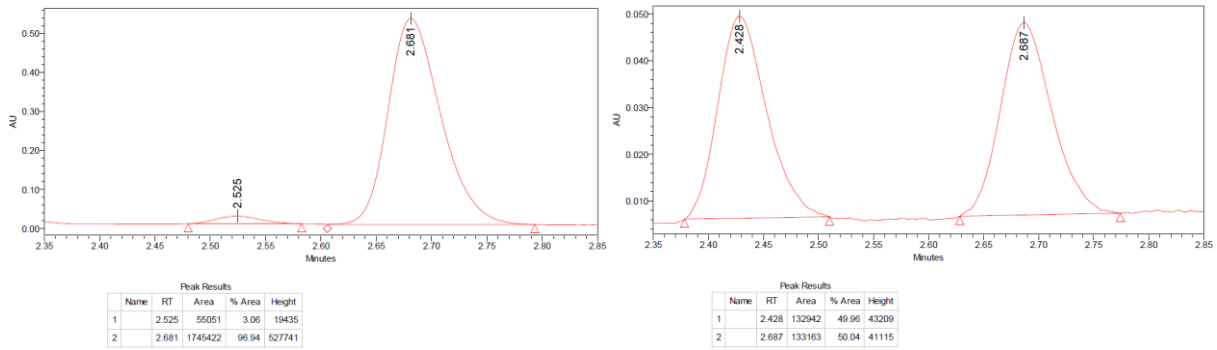
The reaction was performed with **1a** (83.3 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), (1-bromovinyl)trimethylsilane (124 µL, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 6 h. Product **4a** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 67.1 mg, 54% yield, 93% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.92 (d, *J* = 7.4 Hz, 2H, 2 × CH_{Ar}), 7.54 (t, *J* = 7.3 Hz, 1H, CH_{Ar}), 7.44 (t, *J* = 7.7 Hz, 2H, 2 × CH_{Ar}), 7.30–7.24 (m, 4H, 4 × CH_{Ar}), 7.20–7.17 (m, 1H, CH_{Ar}), 5.75 (s, 1H, C=C*H*H), 5.56 (s, 1H, C=CH*H*),4.38 (t, *J* = 7.2 Hz, 1H, CH_{β}), 3.57 (dd, *J* = 16.6 and 7.2 Hz, 1H, CH_{α}H$_{\alpha}$), 3.36 (dd, *J* = 16.6 and 7.2 Hz, 1H, CH$_{\alpha}$$H_{\alpha}$), –0.04 (s, 9H, 3 × C$H_3$).

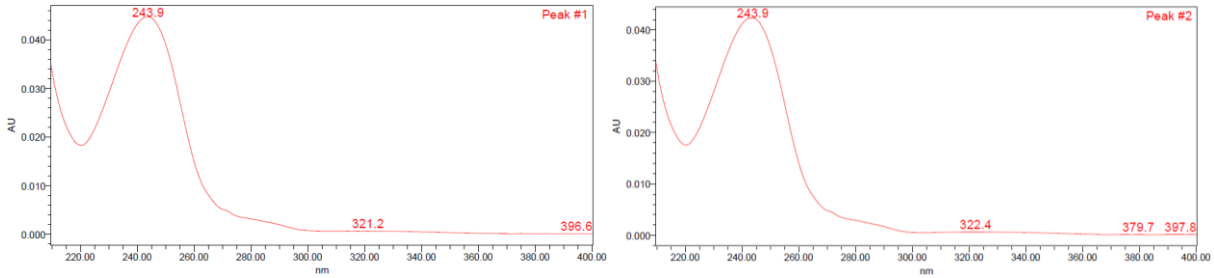
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.7, 153.9, 143.2, 137.4, 133.0, 128.6 (2 × C), 218.6 (2 × C), 128.4 (2 × C), 128.1 (2 × C), 126.6, 123.2, 45.4, 44.3, –1.1 (3 × C).

LC-HRMS (ESI): m/z [M+Na]$^+$ calcd. for $C_{20}H_{24}OSiNa^+$: 331.1489; found 331.1487.

SFC: Chiralcel OJ-3, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 2.53 (minor) and 2.68 (major).

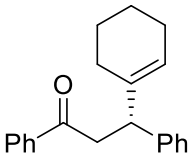


SFC of (*S*)-1,3-diphenyl-4-(trimethylsilyl)pent-4-en-1-one (**4d**)



UV-visible spectra of (*S*)-1,3-diphenyl-4-(trimethylsilyl)pent-4-en-1-one (**4d**)

(*R*)-3-(Cyclohex-1-en-1-yl)-1,3-diphenylpropan-1-one (4e)



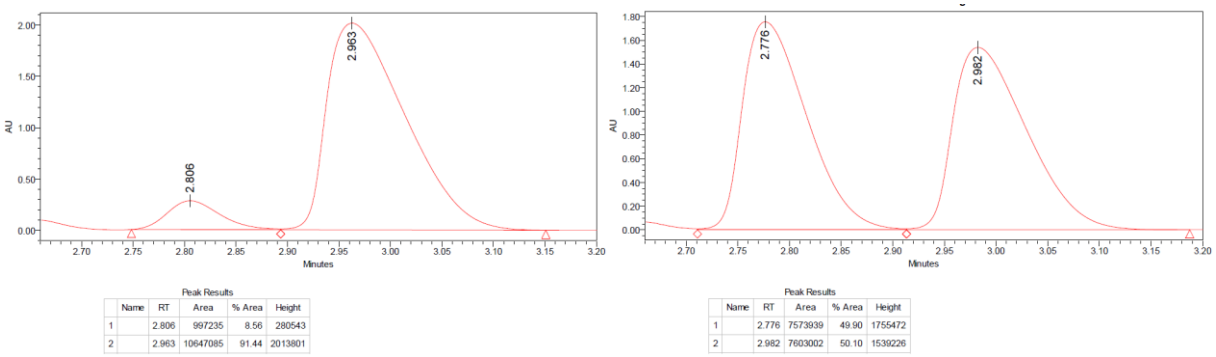
The reaction was performed with **1a** (83.3 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 1-bromocyclohexene (128.8 mg, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 6 h. Product **4e** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 103.1 mg, 89% yield, 83% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.95–7.93 (m, 2H, 2 × C*H*$_{Ar}$), 7.56–7.53 (m, 1H, C*H*$_{Ar}$), 7.45 (t, *J* = 7.7 Hz, 2H, 2 × C*H*$_{Ar}$), 7.30–7.26 (m, 4H, 4 × C*H*$_{Ar}$), 7.21–7.18 (m, 1H, C*H*$_{Ar}$), 5.60 (td, *J* = 3.9 and 1.9 Hz, 1H, C=C*H*), 3.99 (t, *J* = 7.4 Hz, 1H, C*H*$_{\beta}$), 3.54 (dd, *J* = 16.4 and 7.5 Hz, 1H, C*H*$_{\alpha}$H$_{\alpha}$), 3.35 (dd, *J* = 16.4 and 7.2 Hz, 1H, CH$_{\alpha}$*H*$_{\alpha}$), 2.06–2.03 (m, 2H, C*H*$_2$), 1.89–1.87 (m, 2H, C*H*$_2$), 1.60–1.51 (m, 4H, 2 × C*H*$_2$).

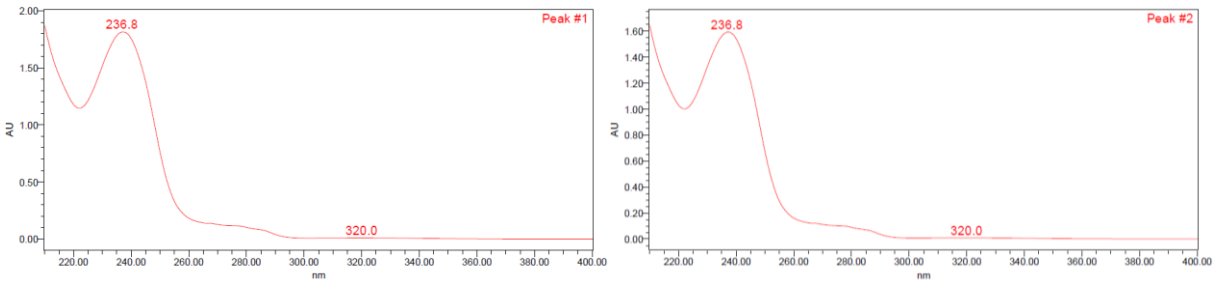
^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.0, 143.6, 139.2, 137.4, 132.9, 128.6 (2 × C), 128.4 (2 × C), 128.1 (2 × C), 127.9 (2 × C), 126.3, 121.5, 47.9, 42.7, 27.6, 25.4, 23.0, 22.5.

LC-HRMS (ESI): m/z [M+Na]$^+$ calcd. for $C_{21}H_{22}ONa^+$: 313.1563; found 313.1561.

SFC: Chiralcel OJ-3, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 2.81 (minor) and 2.96 (major).

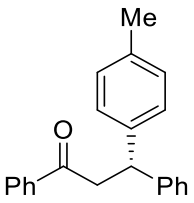


SFC of (*R*)-3-(cyclohex-1-en-1-yl)-1,3-diphenylpropan-1-one (**4e**)



UV-visible spectra of (*R*)-3-(cyclohex-1-en-1-yl)-1,3-diphenylpropan-1-one (**4e**)

(*S*)-1,3-Diphenyl-3-(*p*-tolyl)propan-1-one (4f)



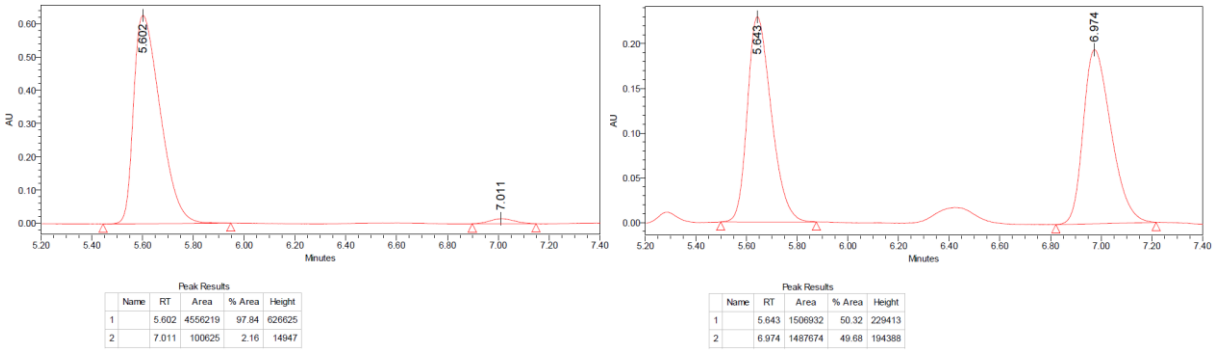
The reaction was performed with **1a** (83.3 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 4-iodotoluene (174.4 mg, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), $^{i}PrOH$ (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 6 h. Product **4f** was obtained as a white solid after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 111.6 mg, 93% yield, 96% *ee*, (*S*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.98–7.97 (m, 2H, 2 × CH_{Ar}), 7.58–7.56 (m, 1H, CH_{Ar}), 7.47 (t, *J* = 7.8 Hz, 2H, 2 × CH_{Ar}), 7.32–7.29 (m, 4H, 4 × CH_{Ar}), 7.22–7.18 (m, 3H, 3 × CH_{Ar}), 7.12 (d, *J* = 7.9 Hz, 2H, 2 × CH_{Ar}), 4.84 (t, *J* = 7.3 Hz, 1H, CH_{β}), 3.76 (d, *J* = 7.3 Hz, 2H, C$H_{\alpha}H_{\alpha}$), 2.33 (s, 3H, CH_3).

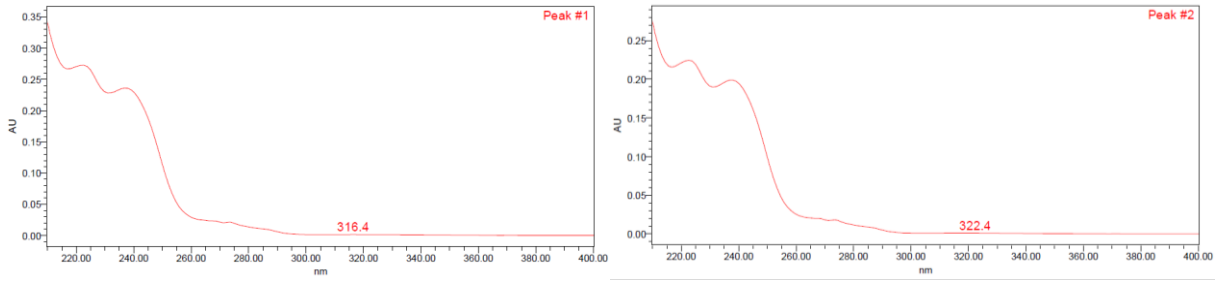
^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.2, 144.5, 141.3, 137.2, 136.0, 133.1, 129.4 (2 × C), 128.7 (2 × C), 128.6 (2 × C), 128.2 (2 × C), 127.9 (2 × C), 127.8 (2 × C), 126.4, 45.7, 44.9, 21.1.

LC-HRMS (ESI): m/z $[M+Na]^+$ calcd. for $C_{22}H_{20}ONa^+$: 323.1406; found 323.1404.

SFC: Chiralcel OJ-3, CO_2/MeOH with gradient from 97% to 90% in 10 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 5.60 (major) and 7.01 (minor).

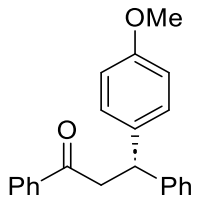


SFC of (*S*)-1,3-diphenyl-3-(*p*-tolyl)propan-1-one (**4f**)



UV-visible spectra of (*S*)-1,3-diphenyl-3-(*p*-tolyl)propan-1-one (**4f**)

(*S*)-3-(4-Methoxyphenyl)-1,3-diphenylpropan-1-one (4g)



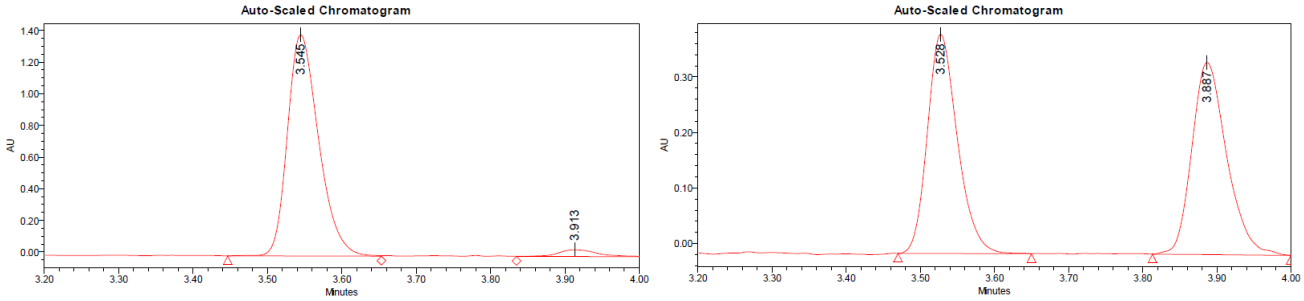
The reaction was performed with **1a** (83.3 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 4-iodoanisole (187.2 mg, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 6 h. Product **4g** was obtained as a white solid after column chromatography (SiO_2, pentane:ether = 15:1) [>99% conversion, 105 mg, 83% yield, 92% *ee*, (*S*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.05–7.84 (m, 2H, 2 × C*H*$_{Ar}$), 7.60–7.54 (m, 1H, C*H*$_{Ar}$), 7.46 (t, *J* = 7.8 Hz, 2H, 2 × C*H*$_{Ar}$), 7.37–7.26 (m, 4H, 4 × C*H*$_{Ar}$), 7.27–7.16 (m, 3H, 3 × C*H*$_{Ar}$), 6.88–6.82 (m, 2H, 2 × C*H*$_{Ar}$), 4.83 (t, *J* = 7.3 Hz, 1H, C*H*$_{\beta}$), 3.82–3.66 (m, 5H, C*H*$_{\alpha}$*H*$_{\alpha}$ and OC*H*$_3$).

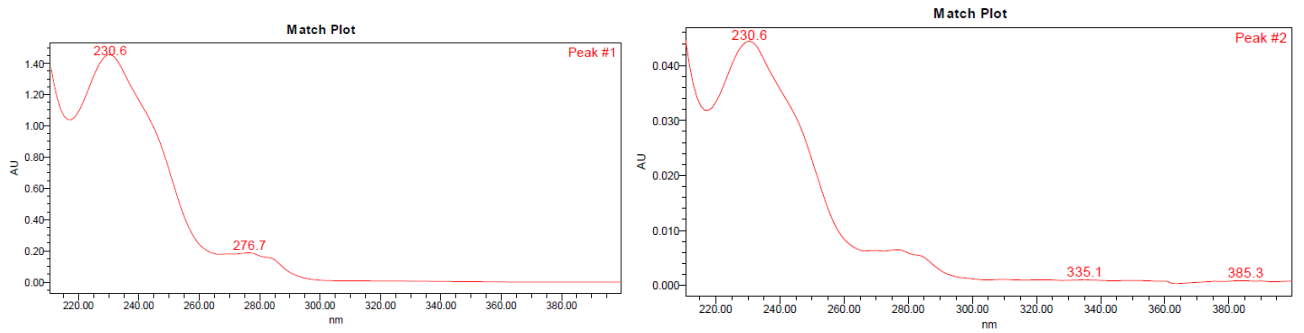
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.2, 158.1, 144.6, 144.6, 137.5, 136.3, 133.1, 128.8, 128.6 (2 × C), 128.1, 127.8, 126.4, 114.0, 55.2, 45.2, 45.0.

LC-HRMS (ESI): m/z [M+Na]$^+$ calcd. for $C_{22}H_{20}O2Na^+$: 339.1356; found 339.1355.

SFC: Chiralcel OJ-3, CO_2/MeOH with gradient from 97% to 50% in 4.5 min, 1.8 mL/min., 40 °C, detection at 227 nm. Retention time (min.): 3.54 (major) and 3.91 (minor).

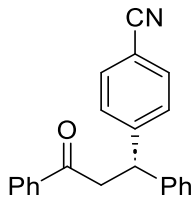


SFC of (*S*)-3-(4-methoxyphenyl)-1,3-diphenylpropan-1-one (**4g**)



UV-visible spectra of (*S*)-3-(4-methoxyphenyl)-1,3-diphenylpropan-1-one (**4g**)

(*S*)-4-(3-Oxo-1,3-diphenylpropyl)benzonitrile (4h)



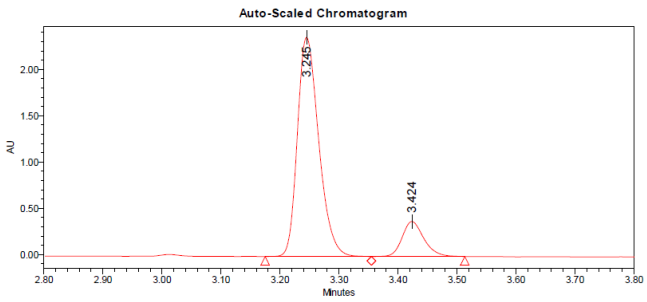
The reaction was performed with **1a** (83.3 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 4-iodobenzonitrile (183.2 mg, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 6 h. Product **4h** was obtained as a white solid after column chromatography (SiO_2, pentane:ether = 10:1) [>99% conversion, 106 mg, 84% yield, 72% *ee*, (*S*)-configuration].

^{1}H NMR (CDCl$_3$, 600 MHz) δ 8.00–7.95 (m, 2H, 2 × C*H*$_{Ar}$), 7.63–7.56 (m, 3H, 3 × C*H*$_{Ar}$), 7.55–7.46 (m, 2H, 2 × C*H*$_{Ar}$), 7.45–7.38 (m, 2H, 2 × C*H*$_{Ar}$), 7.37–7.32 (m, 2H, 2 × C*H*$_{Ar}$), 7.31–7.23 (m, 3H, 3 × C*H*$_{Ar}$), 4.98 –4.86 (m, 1H, C*H*$_{\beta}$), 3.86–3.74 (m, 2H, C*H*$_{\alpha}$*H*$_{\alpha}$).

^{13}C NMR (151 MHz, CDCl$_3$) δ 197.2, 149.7, 142.8, 136.7, 133.5, 132.4, 128.9, 128.8, 128.7, 128.1, 127.8, 127.0, 118.9, 110.3, 46.0, 44.2.

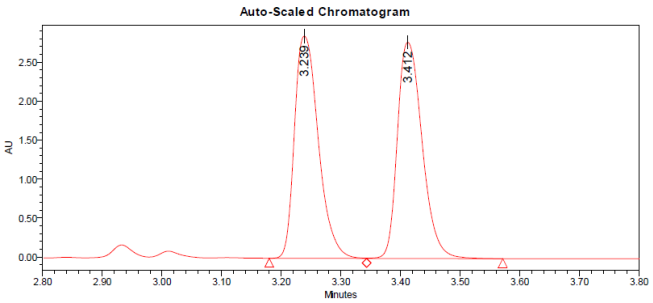
LC-HRMS (ESI): m/z [M+Na]$^+$ calcd. for $C_{22}H_{18N}O^+$: 312.1383; found 312.1383.

SFC: Chiralcel OJ-3, CO_2/MeOH with gradient from 97% to 50% in 4.5 min, 1.8 mL/min., 40 °C, detection at 236 nm. Retention time (min.): 3.24 (major) and 3.42 (minor).



Peak Results

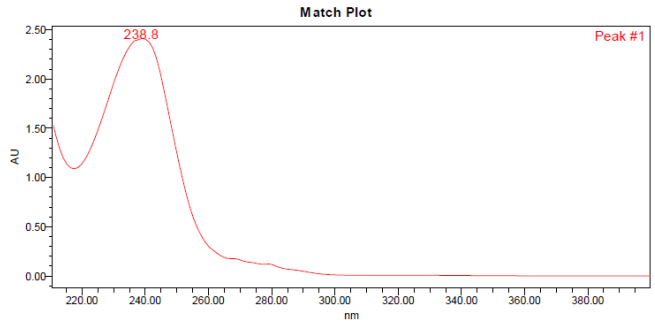
	Name	RT	Area	% Area	Height
1		3.245	5941722	86.04	2367594
2		3.424	964370	13.96	378122

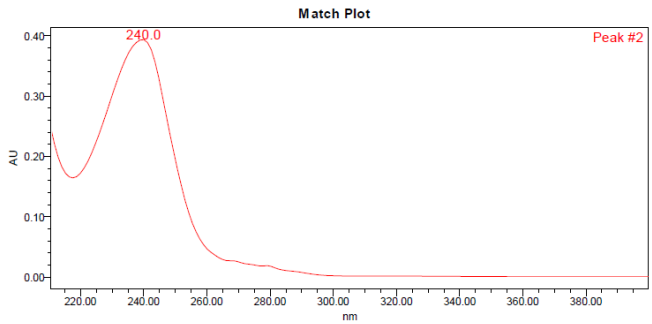


Peak Results

	Name	RT	Area	% Area	Height
1		3.239	7927146	49.80	2852287
2		3.412	7989466	50.20	2775309

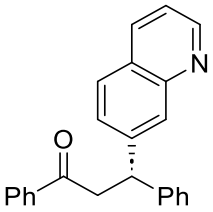
SFC of (*S*)-(3-oxo-1,3-diphenylpropyl)benzonitrile (**4h**)





UV-visible spectra of (*S*)-(3-oxo-1,3-diphenylpropyl)benzonitrile (**4h**)

(*S*)-1,3-Diphenyl-3-(quinolin-7-yl)propan-1-one (4i)



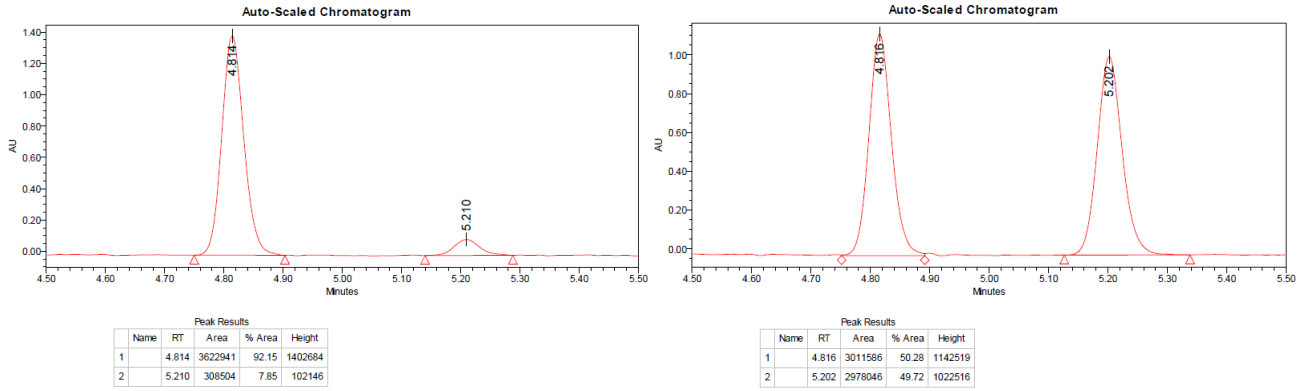
The reaction was performed with **1a** (83.3 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%), 6-iodoquinoline (204 mg, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), ^{i}PrOH (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 6 h. Product **4i** was obtained as a white solid after column chromatography (SiO_2, pentane:ether = 2:1) [>99% conversion, 27 mg, 20% yield, 84% *ee*, (*S*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.89–8.81 (m, 1H, C*H*$_{Ar}$), 8.12–8.06 (m, 1H, C*H*$_{Ar}$), 8.04 (d, *J* = 8.8 Hz, 1H, C*H*$_{Ar}$), 7.98–7.93 (m, 2H, 2 × C*H*$_{Ar}$), 7.71 (d, *J* = 2.1 Hz, 1H, C*H*$_{Ar}$), 7.65 (dd, *J* = 8.7 and 2.0 Hz, 1H, C*H*$_{Ar}$), 7.58–7.53 (m, 1H, C*H*$_{Ar}$), 7.47–7.42 (m, 2H, 2 × C*H*$_{Ar}$), 7.37 (dd, *J* = 8.3 and 4.2 Hz, 1H, C*H*$_{Ar}$), 7.34–7.27 (m, 4H, 4 × C*H*$_{Ar}$), 7.23–7.16 (m, 1H, C*H*$_{Ar}$), 5.04 (t, *J* = 7.2 Hz, 1H, C*H*$_{\beta}$), 3.92–3.79 (m, 2H, C*H*$_{\alpha}$*H*$_{\alpha}$).

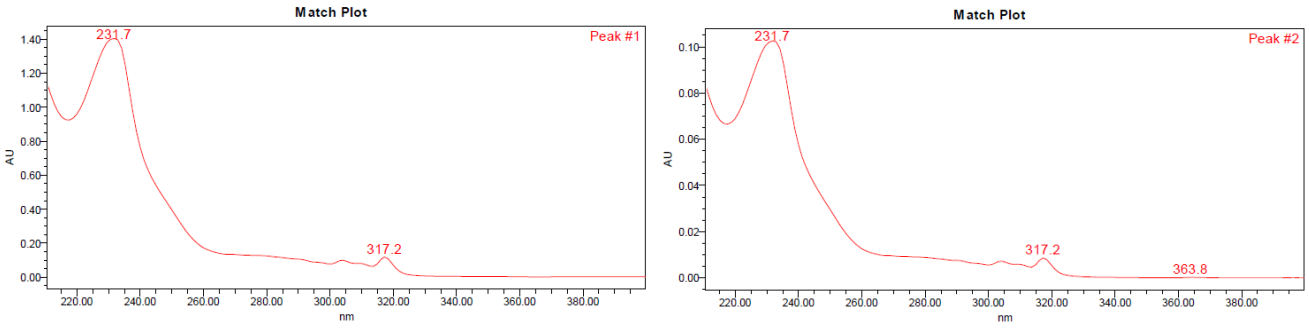
^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 149.9, 147.0, 143.7, 142.7, 137.0, 136.4, 133.4, 130.6, 129.6, 128.9, 128.8, 128.4, 128.2, 128.0, 126.8, 125.9, 121.3, 45.9, 44.6.

LC-HRMS (ESI): m/z [M+Na]$^+$ calcd. for $C_{24}H_{20}NO^+$: 338.1539; found 338.1536.

SFC: (R,R)whelk-O1, CO_2/MeOH with gradient from 97% to 50% in 4.5 min, 1.8 mL/min., 40 °C, detection at 231 nm. Retention time (min.): 4.81 (major) and 5.21 (minor).

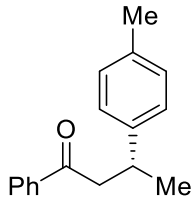


SFC of (*S*)-1,3-diphenyl-3-(quinolin-7-yl)propan-1-one (**4i**)



UV-visible spectra of (*S*)-1,3-diphenyl-3-(quinolin-7-yl)propan-1-one (**4i**)

(*R*)-1-Phenyl-3-(p-tolyl)butan-1-one (4j)



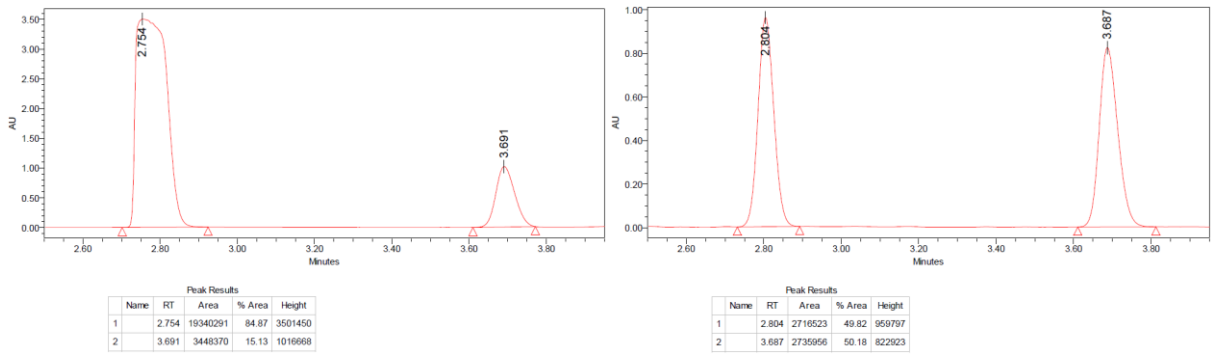
The reaction was performed with **1m** (58.5 mg, 0.4 mmol, 1.0 equiv.), $NiBr_2$·DME (5.6 mg, 5.0 mol%), (*R*)-**L1** (6.9 mg, 6.0 mol%),4-iodotoluene (174.4 mg, 0.8 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (131.7 mg, 0.4 mmol, 1.0 equiv.), $^{i}PrOH$ (46 µL, 0.6 mmol, 1.5 equiv.) in DMSO (1.0 mL) and DMF (1.0 mL) at room temperature for 6 h. Product **4j** was obtained as a colourless oil after column chromatography (SiO_2, pentane:EtOAc = 50:1) [>99% conversion, 91.8 mg, 96% yield, 70% *ee*, (*R*)-configuration].

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.98–7.97 (m, 2H, 2 × CH_{Ar}), 7.58–7.56 (m, 1H, CH_{Ar}), 7.47 (t, *J* = 7.8 Hz, 2H, 2 × CH_{Ar}), 7.22 (d, *J* = 8.0 Hz, 2H, 2 × CH_{Ar}), 7.16 (d, *J* = 8.0 Hz, 2H, 2 × CH_{Ar}), 4.54–4.50 (m, 1H, CH_{β}), 3.32 (dd, *J* = 16.4 and 5.8 Hz, 1H, CH_{α}H$_{\alpha}$), 3.21 (dd, *J* = 16.4 and 8.3 Hz, 1H, CH$_{\alpha}$$H_{\alpha}$), 2.36 (s, 3H, C$H_3$), 1.37 (d, *J* = 6.9 Hz, 3H, CH_3).

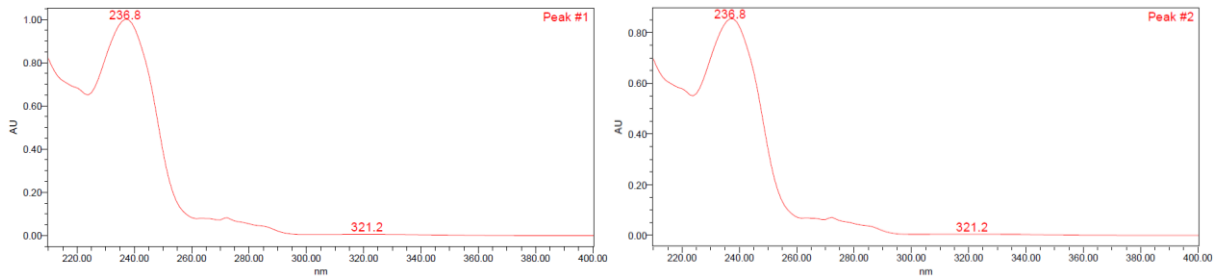
^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.2, 143.7, 137.3, 135.8, 133.0, 129.3 (2 × C), 128.6 (2 × C), 128.1 (2 × C), 126.8 (2 × C), 47.2, 35.2, 22.1, 21.1.

LC-HRMS (ESI): m/z [M+Na]$^+$ calcd. for $C_{17}H_{18}ONa^+$: 261.1250; found 261.1249.

SFC: (*R*,*R*)-Whelk-O1, CO_2/MeOH with gradient from 97% to 90% in 5 min, 1.8 mL/min., 40 °C, detection at 240 nm. Retention time (min.): 2.75 (major) and 3.69 (minor).



SFC of (*R*)-1-phenyl-3-(*p*-tolyl)butan-1-one (**4j**)



UV-visible spectra of (*R*)-1-phenyl-3-(*p*-tolyl)butan-1-one (**4j**)

3.4. Determination of absolute configuration

The absolute configuration was determined by comparison of the optical rotation for compound **3a** and **3b** with the reported data for these same compounds.

*Compound **3a**:*

Reported data: 94% *ee*, $[\alpha]^{28}_{D}$ = 152.8˚ (c = 0.5, $CHCl_3$), *R*-configuration[21] and 98% *ee*, $[\alpha]^{25}_{D}$ = -150.4˚ (c = 0.5, $CHCl_3$), *S*-configuration.[22]

Obtained data: 96% *ee*, $[\alpha]^{20}_{D}$ = 153.4˚ (c = 0.037, $CHCl_3$), *R*-configuration.

*Compound **3b**:*

Reported data: 94% *ee*, $[\alpha]^{28}_{D}$ = 325.2˚ (c = 0.5, $CHCl_3$), *R*-configuration.

Obtained data: 96% *ee*, $[\alpha]^{20}_{D}$ = 328.6˚ (c = 0.038, $CHCl_3$), *R*-configuration.

The absolute configuration of other compounds was assigned by analogy.

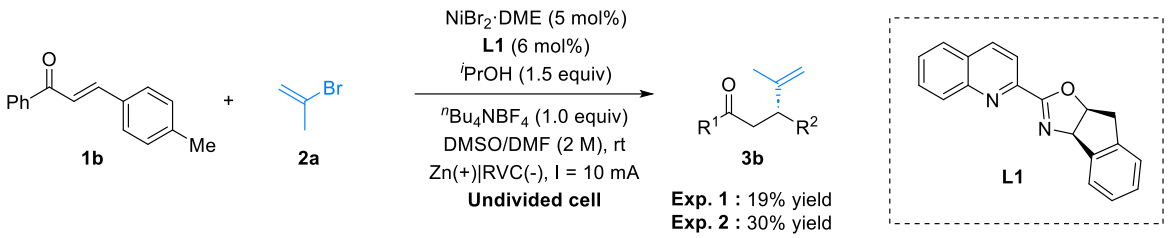
4. Corroboration of the mechanistic proposal via quantitative KIE studies

With a general mechanistic picture of this transformation, we took a step further and attempted to confirm our proposal by studying the KIE. The accurate determination of KIEs can provide powerful information on the bonding changes occurring at those atoms actively participating in the rate-determining step of a reaction. As a result, it has constituted a key tool in physical-organic chemistry for the past several decades. In 1995, Singleton introduced quantitative ^{13}C NMR methodology for the determination of ^{13}C KIEs at natural abundance with high precision, in a strategy that avoids the necessity of enriching substrates with a specific isotope. In this regard, due to the intrinsic difficulties of labelling the *α*,*β*-unsaturated ketones scaffold or even alkenyl halides, we decided to take advantage of the natural abundance of the ^{13}C isotope in our substrates and study the quantitative kinetic isotope effects.

The ^{13}C NMR KIEs study of enantioselective nickel-catalysed electrochemical reductive conjugate alkenylation between *trans*-4-methylchalcone 1b and 2-bromopropene 2a (product analysis)

Low conversion reaction

The reaction of **1b** with **2a** catalysed by $NiBr_2$-**L1** catalyst was chosen as a model reaction for the product analysis of experimental ^{13}C KIEs at natural abundance. The study of ^{13}C NMR KIEs at natural abundance, the reactions have to be carried to low conversion for product analysis. Due to kinetic resolution, the product is enriched in the faster reacting isotope (^{12}C) at low conversion, whereas the remaining starting material becomes enriched in the slower reacting isotope (^{13}C) at high conversions. Two identical reactions were taken to 19 and 30% yields of the product **3b** (each of these two KIE measurements require 5 mmol of **1b** and **2a**), and the dihydropyridine product **3b** was isolated. The desired product **3b** was analysed by quantitative ^{13}C NMR composition with a standard sample from the same commercial lot of starting materials. The relative changes in ^{13}C composition from **1a** and **2a** were calculated using Me (from **1b**) and Me (from **2a**) as internal standards, respectively with the assumption that its isotopic composition does not change.



Quantitative ^{13}C NMR of product

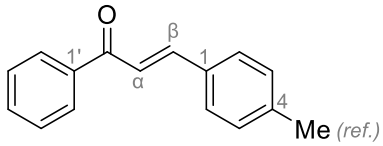
1b and **2a** were chosen as an initial starting material to study ^{13}C NMR KIEs. The quantitative ^{13}C NMR spectra were taken at 151 MHz on a Bruker Avance 600 MHz NMR spectrometer with inverse-gated decoupling. The chosen acquisition parameters were: acquisition time 6.0 s; size of fid 300k; recovery delays 60 s; transmitter frequency offset 100 ppm; number of scans 256. ^{13}C NMR measurements were carried out for the KIE values of product **3b**. ^{13}C NMR data were processed using 1 Hz exponential multiplication. For the KIE determination, the integration of methyl group (from **1b**) and methyl group (from **2a**) were set to 100 which assumed as an internal standard. The average integration values for the other carbons were used to calculate the KIE values following:

$$KIE_{calc} = \frac{ln(1-F)}{ln[1-\left(F\frac{R_P}{R_0}\right)]}$$

where F is the fraction of reaction and R_P and R_0 are the isotope ratio of product and initial starting substrate, respectively.

KIEs calculation from 1b (dihydrochalcone moiety from the product 3b)

Table S3.1: ^{13}C Integrations of initial **1a** (standard)



C	ppm	#1	#2	#3	#4	#5	average	SD
Me (ref)	**21.6**	100	100	100	100	100	100	0
α	**121.2**	94.3	94.61	93.29	93.82	93.2	93.844	0.61581653
1	**132.3**	94.18	94.5	94.56	94.42	94.34	94.4	0.14832397
1'	**138.5**	94.91	94.65	94.78	94.52	94.7	94.712	0.14549914
4	**141.2**	94.77	94.96	93.47	94.72	94.86	94.556	0.61394625
β	**145**	95.35	95.19	93.95	95.36	94.36	94.842	0.64720167
CO	**190.7**	93.93	94.78	93.32	94.74	93.56	94.066	0.66991044

Table S3.2: ^{13}C Integrations of dihydrochalcone from **3b** (19% yield of **3b**)

C	ppm	#1	#2	#3	#4	#5	#6	#7	average	SD
Me	**21.1**	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.0000	0
α	**43.3**	93.55	93.41	93.53	93.26	93.38	93.44	93.69	100.0000	0.138426532
β	**47.3**	92.39	92.99	92.97	92.41	92.74	92.59	92.38	92.6386	0.26673511
1'	**136.1**	94.61	94.58	94.86	94.70	94.76	94.57	94.28	94.6229	0.184093661
4	**137.4**	94.50	94.38	94.60	94.63	94.39	94.36	94.34	94.4571	0.11954278
1	**139.8**	94.17	94.49	94.45	94.45	94.24	94.49	94.00	94.3271	0.192588879
CO	**198.6**	94.21	94.56	94.17	93.83	94.10	94.07	93.78	94.1029	0.259725129

Table S3.3: Calculated ^{13}C KIEs of dihydrochalcone from **3b** (19% yield of **3b**)

C	ppm	#1	#2	#3	#4	#5	#6	#7	average	SD
Me	**21.1**	1	1	1	1	1	1	1	1	0
α	**43.3**	1.003498313	1.005171884	1.003737089	1.00697055	1.005531157	1.004812841	1.001829723	1.004507365	0.001654872
β	**47.3**	1.029539975	1.022168209	1.022412407	1.029292713	1.025228231	1.027072145	1.029663646	1.026482475	0.003277824
1'	**136.1**	1.001200112	1.001553577	0.998263231	1.000141056	0.999436132	1.001671448	1.005100547	1.0010523	0.002170486
4	**137.4**	1.000659653	1.002075822	0.999482246	0.999129508	1.001957671	1.002312199	1.002548675	1.001166539	0.00140942
1	**139.8**	1.002718765	0.998939724	0.999410709	0.999410709	1.001889915	0.998939724	1.004736802	1.000863764	0.002277463
CO	**198.6**	0.998298512	0.994184466	0.998770628	1.002799797	0.999597792	0.999952666	1.003394776	0.999571234	0.003067772

Table S3.4: ^{13}C Integrations of dihydrochalcone from **3b** (30% yield of **3b**)

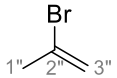
C	ppm	#1	#2	#3	#4	#5	#6	#7	average	SD
Me	**21.1**	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.0000	0
α	**43.3**	93.42	93.26	93.40	93.49	93.35	93.55	93.32	93.3986	0.099570506
β	**47.3**	92.88	92.79	92.69	92.63	92.87	92.62	92.69	92.7386	0.108386434
1'	**136.1**	94.69	94.86	94.78	94.82	94.76	94.66	94.60	94.7386	0.092453334
4	**137.4**	94.54	94.55	94.57	94.38	94.60	94.56	94.43	94.5186	0.081123069
1	**139.8**	94.20	94.47	94.45	94.52	94.37	94.56	94.41	94.4257	0.118160504
CO	**198.6**	94.18	93.97	94.00	94.16	94.09	94.23	94.05	94.0971	0.096904469

Table S3.5: Calculated ^{13}C KIEs of dihydrochalcone from **3b** (30% yield of **3b**)

C	ppm	#1	#2	#3	#4	#5	#6	#7	average	SD
Me	**21.1**	1	1	1	1	1	1	1	1	0
α	**43.3**	1.005453203	1.007523739	1.005711637	1.004549544	1.0063582	1.003776042	1.006746467	1.005731262	0.001286708
β	**47.3**	1.025375447	1.026564882	1.027889153	1.028685072	1.025507494	1.028817824	1.027889153	1.027247004	0.00143493
1'	**136.1**	1.000279169	0.998125274	0.999137922	0.998631387	0.999391347	1.000660062	1.001422561	0.99966396	0.001172474
4	**137.4**	1.000203355	1.00007625	0.99982212	1.002240645	0.999441125	0.999949172	1.001603259	1.000476561	0.001032383
1	**139.8**	1.002551044	0.999109654	0.999363906	0.99847449	1.000381976	0.997966836	0.999872728	0.999674376	0.001504769
CO	**198.6**	0.998545534	1.001227516	1.000843651	0.998800452	0.999693508	0.997908707	1.000204414	0.999603397	0.001237006

KIEs calculation from 2a (propenyl moiety from the product 3b)

Table S4.1: ^{13}C Integrations of initial 2-bromopropene (standard)



C	ppm	#1	#2	#3	#4	#5	average	SD
1"	**28.9**	100	100	100	100	100	100	0
2"	**129.9**	100.12	100.94	100.57	100.44	100.03	100.42	0.365855163
3"	**117.4**	100.91	101.65	100.99	100.77	101.24	101.112	0.345861244

Table S4.2: ^{13}C Integrations of propenyl moiety from product **3b** (19% yield of **3b**)

C	ppm	#1	#2	#3	#4	#5	#6	#7	average	SD
1"	**22.1**	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.0000	0
2"	**147.4**	98.78	98.63	98.98	98.83	99.08	99.09	98.87	98.8943	0.167218135
3"	**110.2**	101.01	101	101.12	101.26	101.2	101.12	101.28	101.1414	0.111718183

Table S4.3: Calculated ^{13}C KIEs of propenyl moiety from product **3b** (19% yield of **3b**)

C	ppm	#1	#2	#3	#4	#5	#6	#7	average	SD
1"	**22.1**	1	1	1	1	1	1	1	1	0
2"	**147.4**	1.018480188	1.020201001	1.016193851	1.01790774	1.015054131	1.014940285	1.017450196	1.017175342	0.001911698
3"	**110.2**	1.001124073	1.001234398	0.999911933	0.998373002	0.999032024	0.999911933	0.9981535	0.999677266	0.001229319

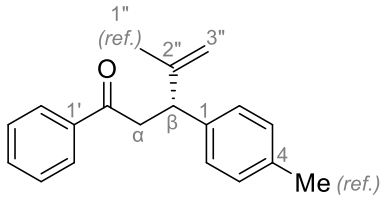
Table S4.4: ^{13}C Integrations of propenyl moiety from product **3b** (30% yield of **3b**)

C	ppm	#1	#2	#3	#4	#5	#6	#7	average	SD
1"	**22.1**	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.0000	0
2"	**147.4**	99.15	99.17	99.14	98.95	98.92	99.03	99	99.0514	0.101886959
3"	**110.2**	100.89	101.19	100.93	100.98	101.07	101.17	101.16	101.0557	0.123268966

Table S4.5: Calculated ^{13}C KIEs of propenyl moiety from product **3b** (30% yield of **3b**)

C	ppm	#1	#2	#3	#4	#5	#6	#7	average	SD
1"	**22.1**	1	1	1	1	1	1	1	1	0
2"	**147.4**	1.015388347	1.015142995	1.01551106	1.017847261	1.018216946	1.016862519	1.017231613	1.016600106	0.001252649
3"	**110.2**	1.00264389	0.999073785	1.002166665	1.001570659	1.000499316	0.999311141	0.999429855	1.000670759	0.001466795

Table S5: Experimental ^{13}C KIEs at natural abundance from Product analysis



C	Experimental [a]	
	Exp. 1	**Exp. 2**
Me	1.000 (Reference)	
α	1.005 (2)	1.006 (1)
β	***1.026 (3)***	***1.027 (1)***
1'	1.001 (2)	1.000 (1)
4	1.001 (1)	1.000 (1)
1	1.001 (2)	1.000 (2)
CO	1.000 (3)	1.000 (1)
1"	1.000 (Reference)	
2"	***1.017 (2)***	***1.017 (1)***
3"	1.000 (1)	1.001 (1)

[a] Two experiments were carried to 19 and 30% yield to determine the KIEs for incoming dihydrochalcone and propenyl group. The numbers in parenthesis represent the standard deviation in the last digit as determined from five independent measurements.

5. Cyclic voltammetry studies

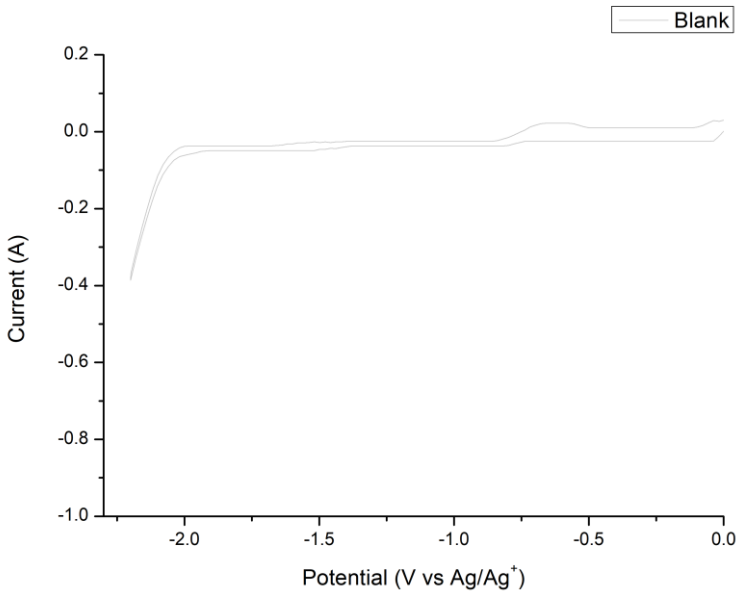


Figure S1. Cyclic voltammogram of 0.1 M ^{t}BuNBF$_4$ in DMF/DMSO (1:1). Sweep rate: 100 mV/s. Glassy carbon electrode as working electrode, Ag/AgNO$_3$ (1.0 M) as reference electrode, Pt wire as auxiliary electrode.

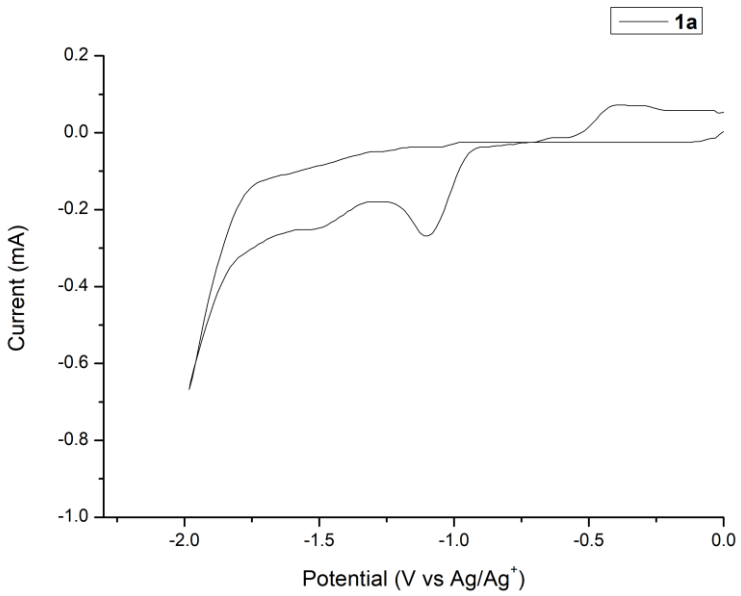


Figure S2. Cyclic voltammogram of *trans*-chalcone **1a** in 0.1 M ^{t}BuNBF$_4$ in DMF/DMSO (1:1). Sweep rate: 100 mV/s. Glassy carbon electrode as working electrode, Ag/AgNO$_3$ (1.0 M) as reference electrode, Pt wire as auxiliary electrode.

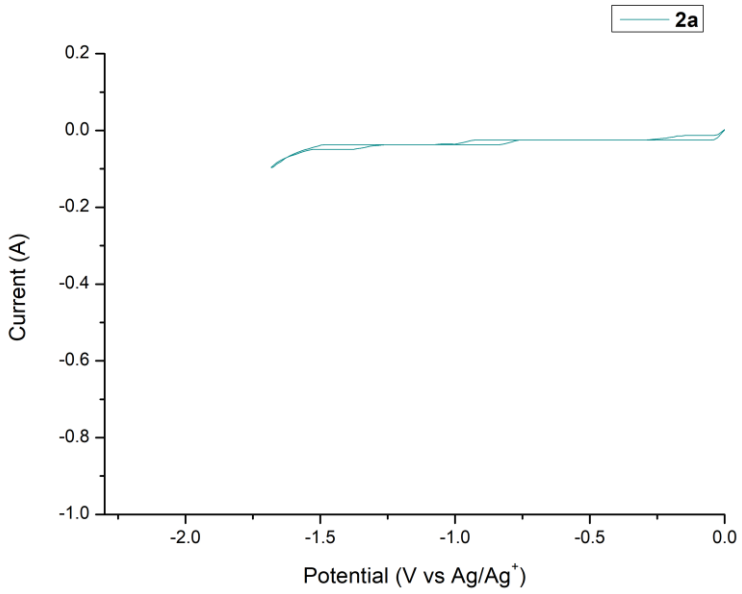


Figure S3. Cyclic voltammogram of 2-bromopropene **2a** in 0.1 M ^{t}BuNBF$_4$ in DMF/DMSO (1:1). Sweep rate: 100 mV/s. Glassy carbon electrode as working electrode, Ag/Ag NO$_3$ (1.0 M) as reference electrode, Pt wire as auxiliary electrode.

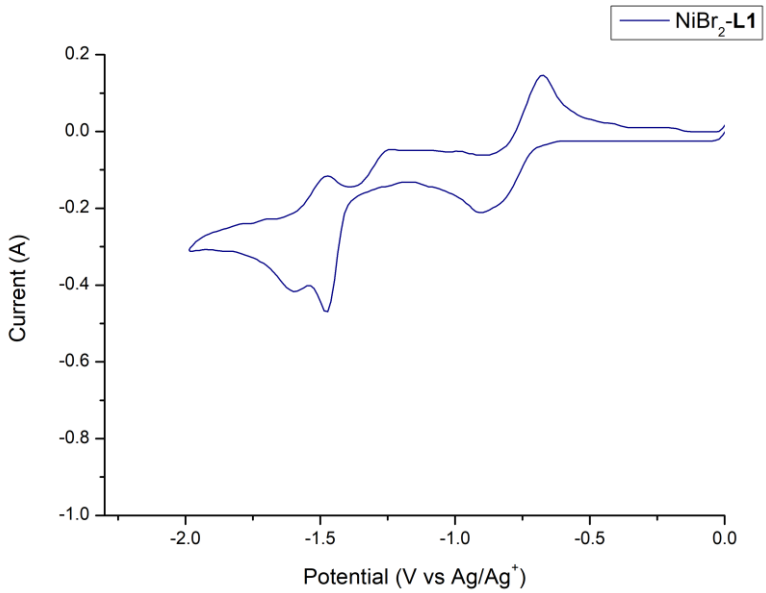


Figure S4. Cyclic voltammogram of NiBr$_2$·DME and **L1** (1:1) in 0.1 M ^{t}BuNBF$_4$ in DMF/DMSO (1:1). Sweep rate: 100 mV/s. Glassy carbon electrode as working electrode, Ag/AgNO$_3$ (1.0 M) as reference electrode, Pt wire as auxiliary electrode.

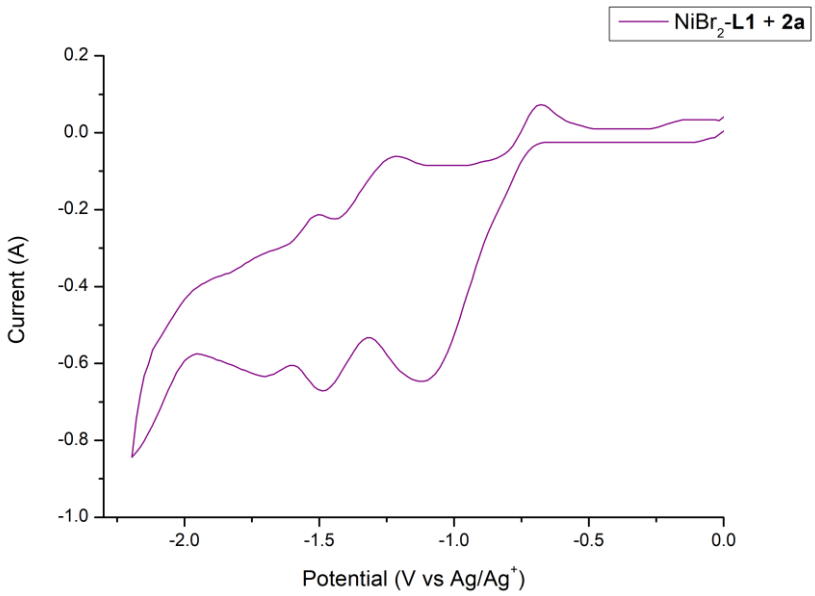
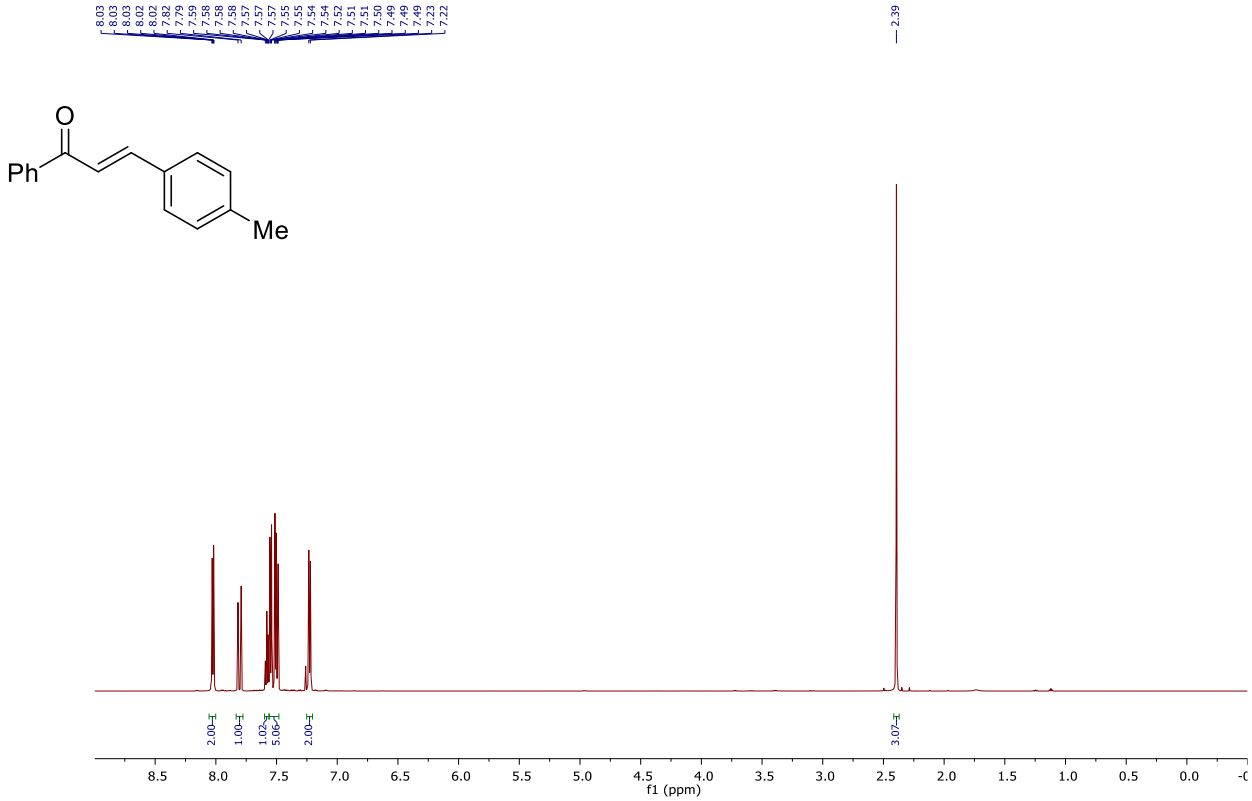


Figure S5. Cyclic voltammogram of **2a**, $NiBr_2$·DME and **L1** (1:1) in 0.1 M $^tBuNBF_4$ in DMF/DMSO (1:1). Sweep rate: 100 mV/s. Glassy carbon electrode as working electrode, $Ag/AgNO_3$ (1.0 M) as reference electrode, Pt wire as auxiliary electrode.

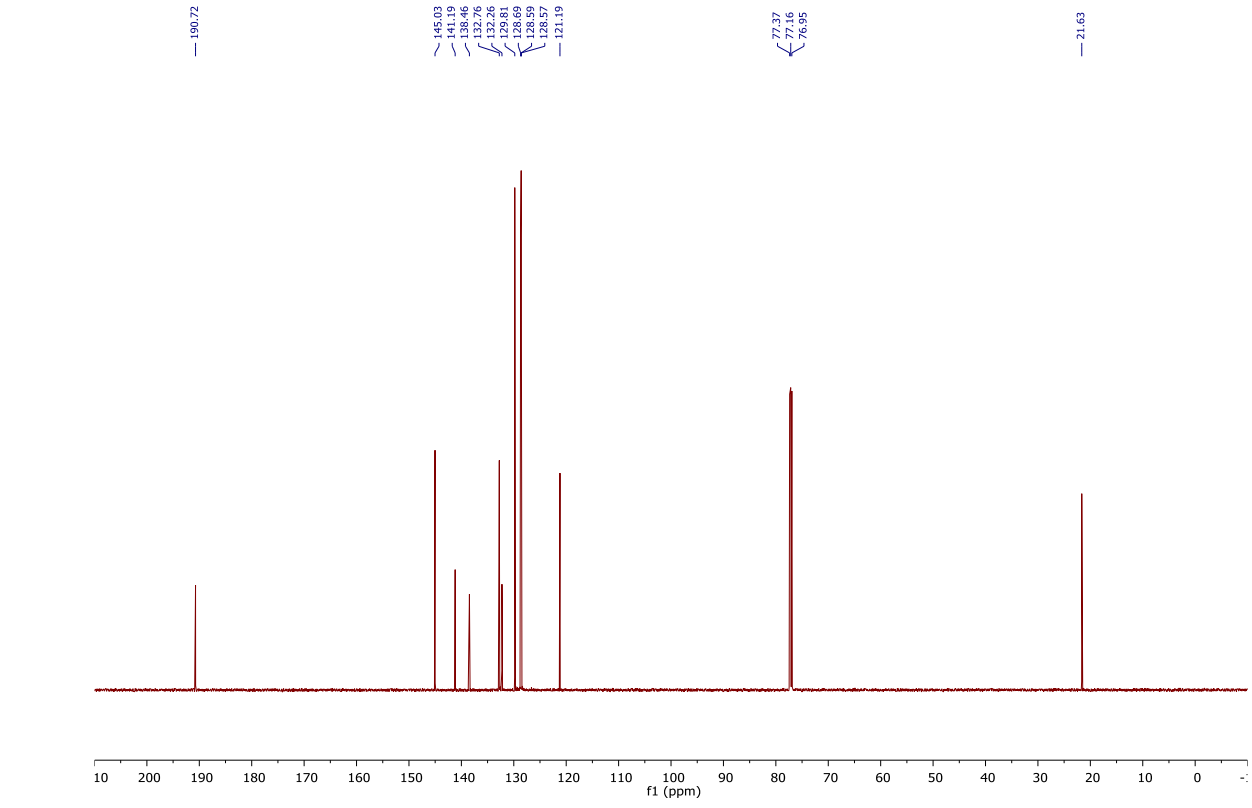
6. NMR spectra

NMR spectra of (*E*)-1-phenyl-3-(*p*-tolyl)prop-2-en-1-one (1b)

^{1}H NMR with $CDCl_3$, 600 MHz

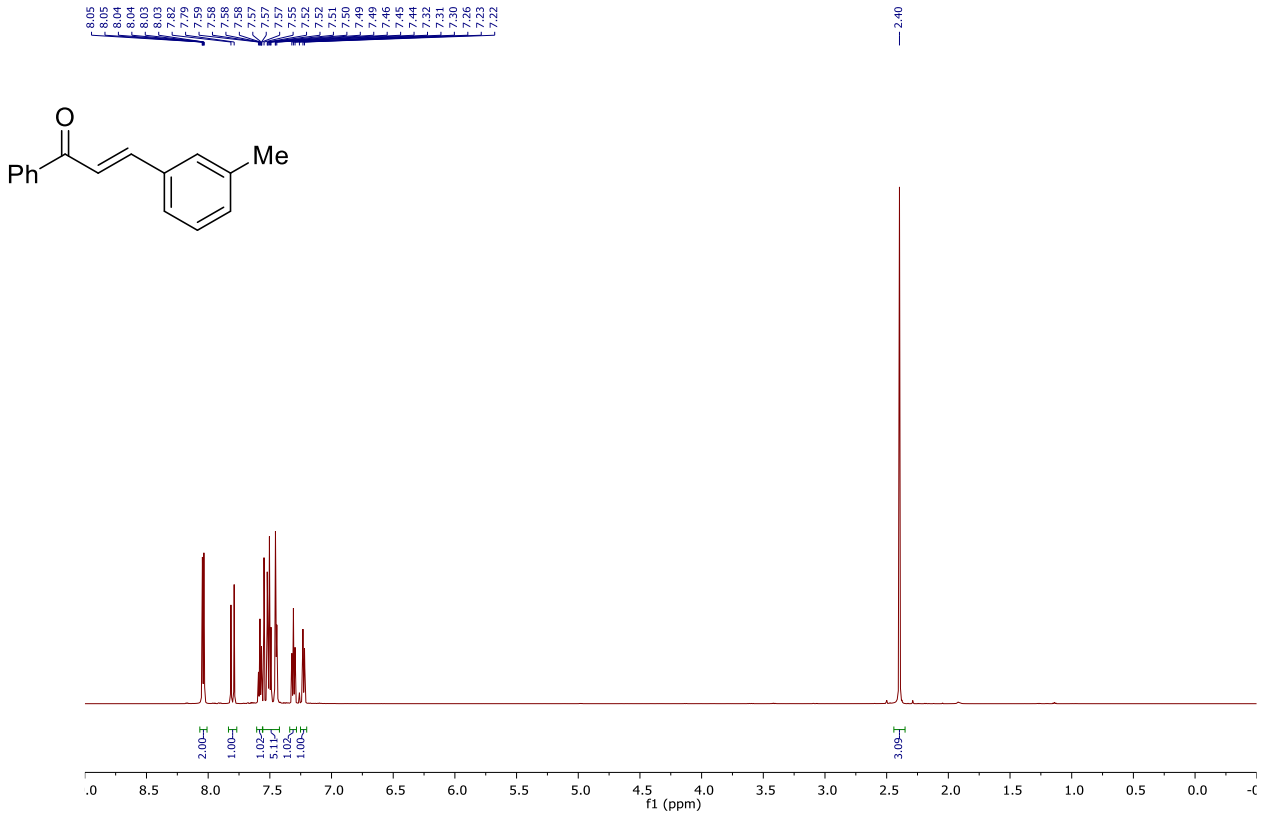


^{13}C NMR with $CDCl_3$, 151 MHz

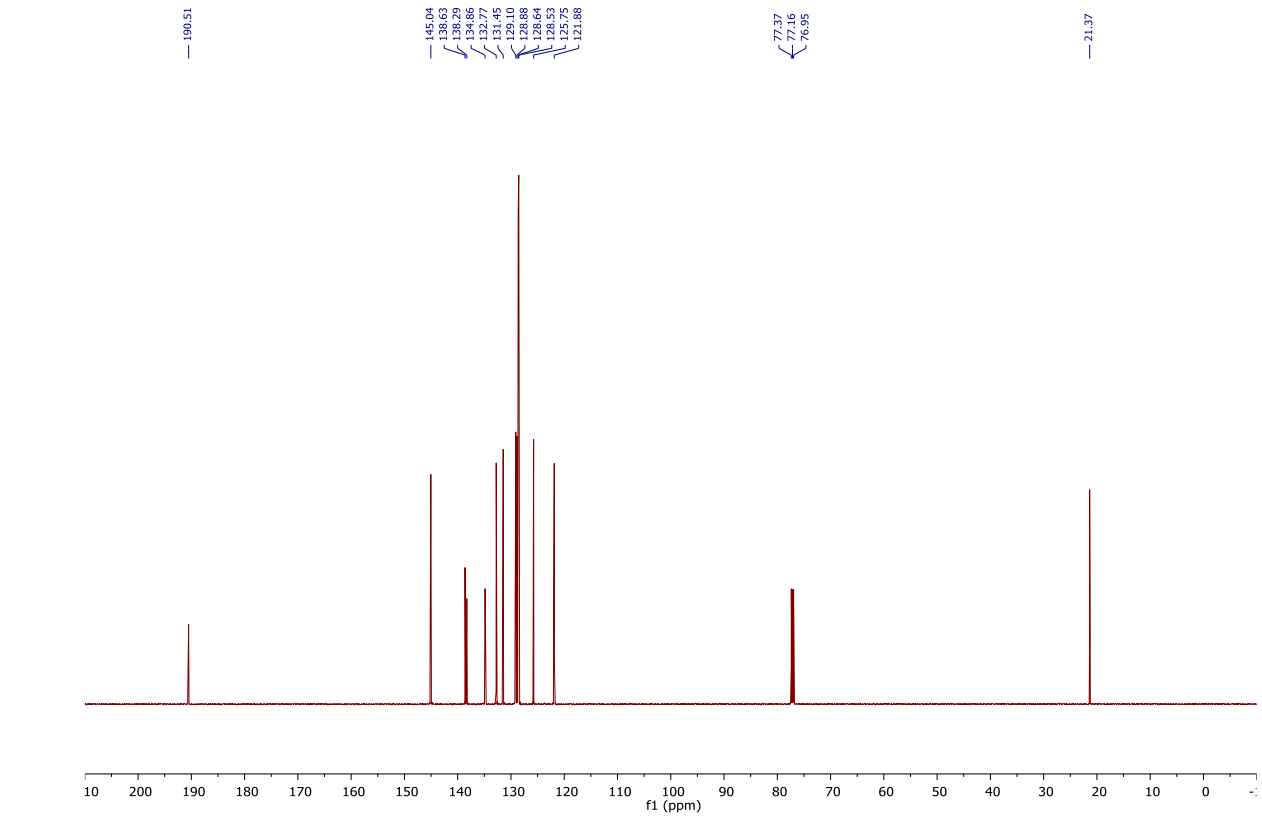


NMR spectra of (*E*)-1-phenyl-3-(*m*-tolyl)prop-2-en-1-one (1c)

^{1}H NMR with $CDCl_3$, 600 MHz

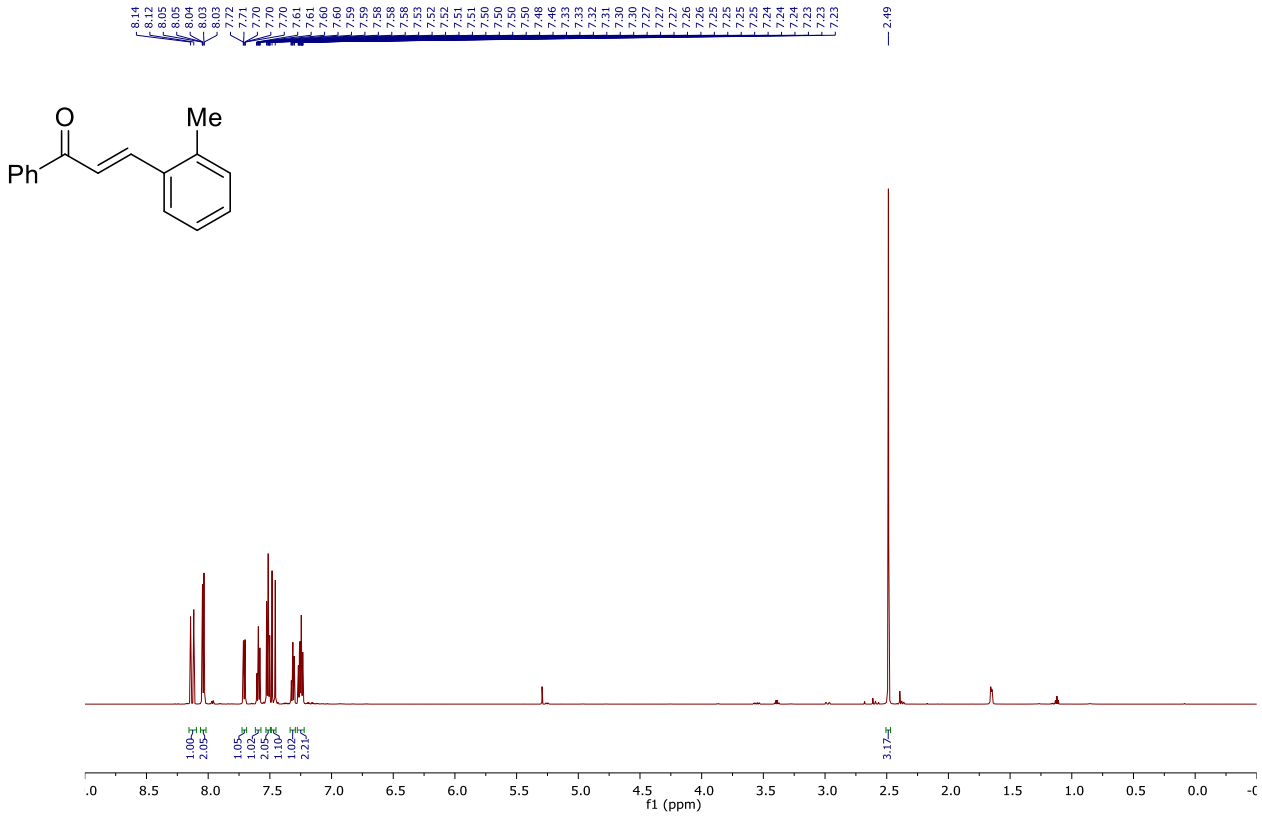


^{13}C NMR with $CDCl_3$, 151 MHz

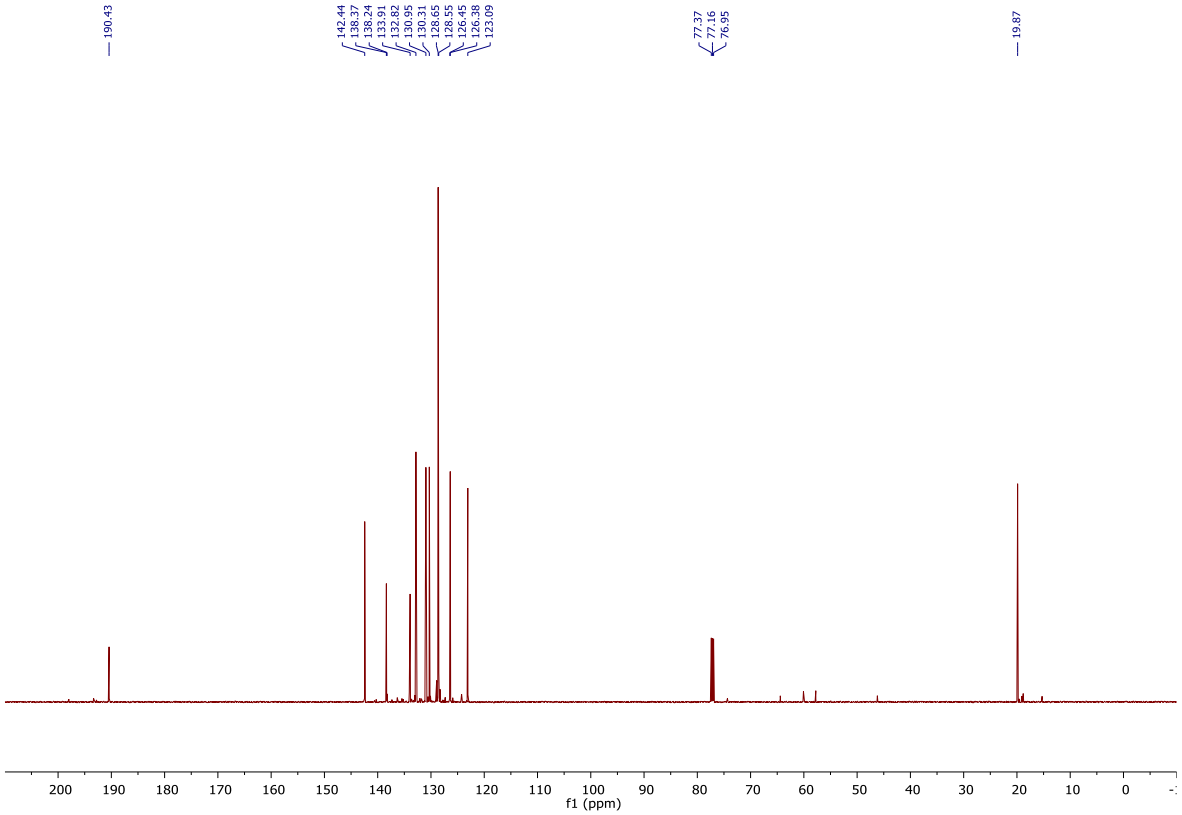


NMR spectra of (*E*)-1-phenyl-3-(*m*-tolyl)prop-2-en-1-one (1d)

^{1}H NMR with $CDCl_3$, 600 MHz

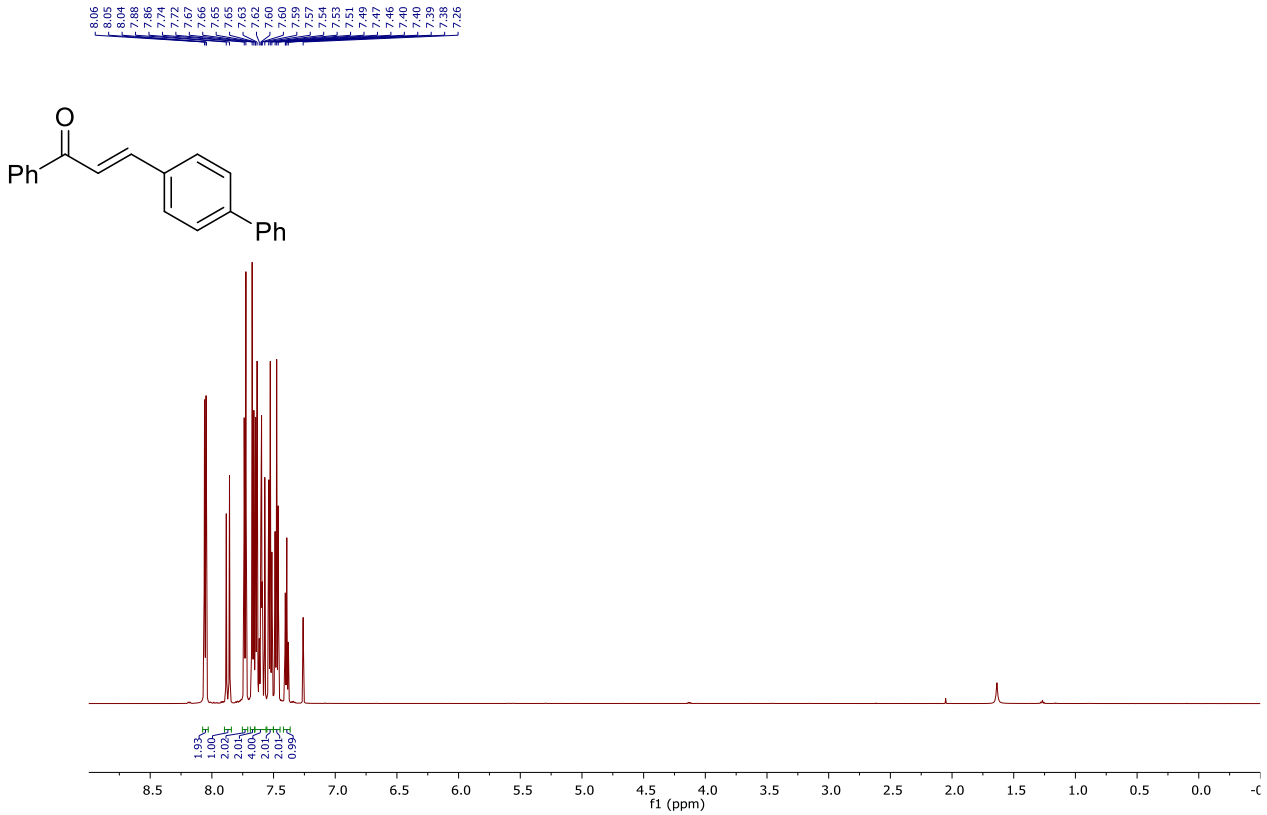


^{13}C NMR with $CDCl_3$, 151 MHz

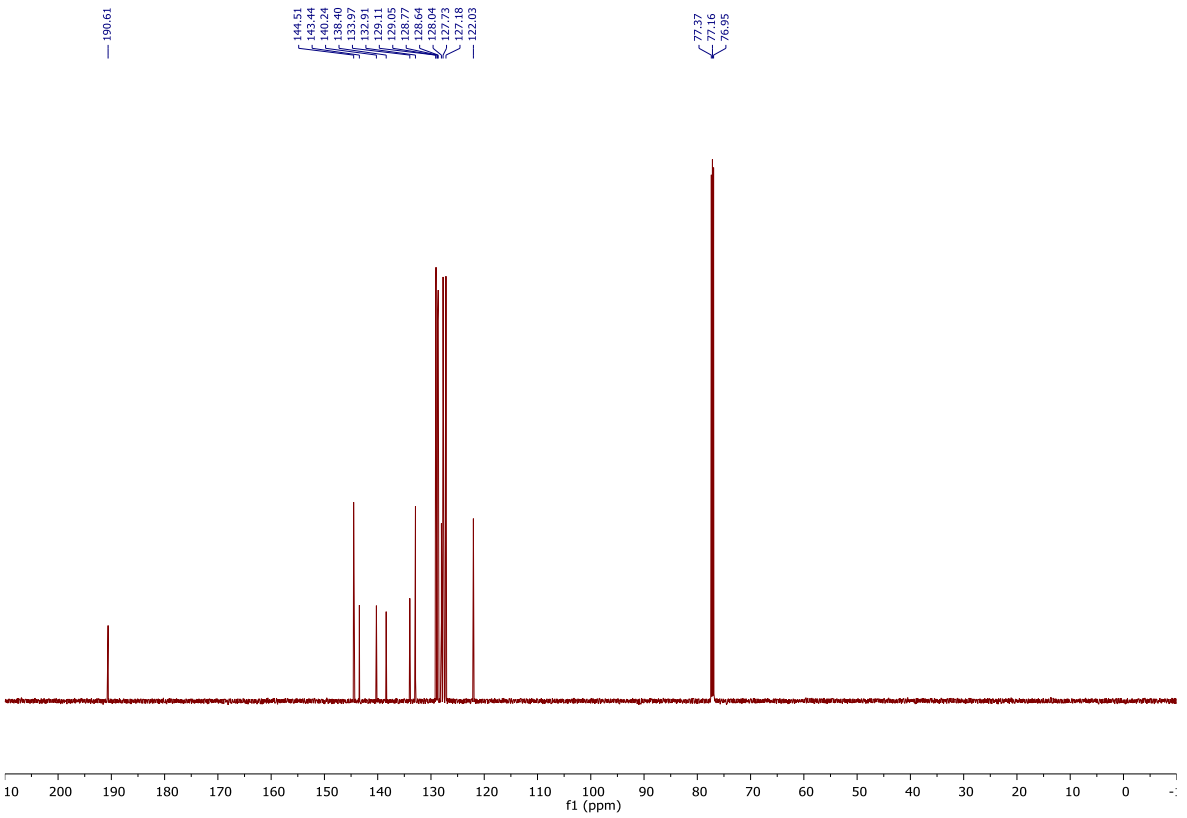


NMR spectra of (*E*)-3-([1,1'-biphenyl]-4-yl)-1-phenylprop-2-en-1-one (1e)

^{1}H NMR with $CDCl_3$, 600 MHz

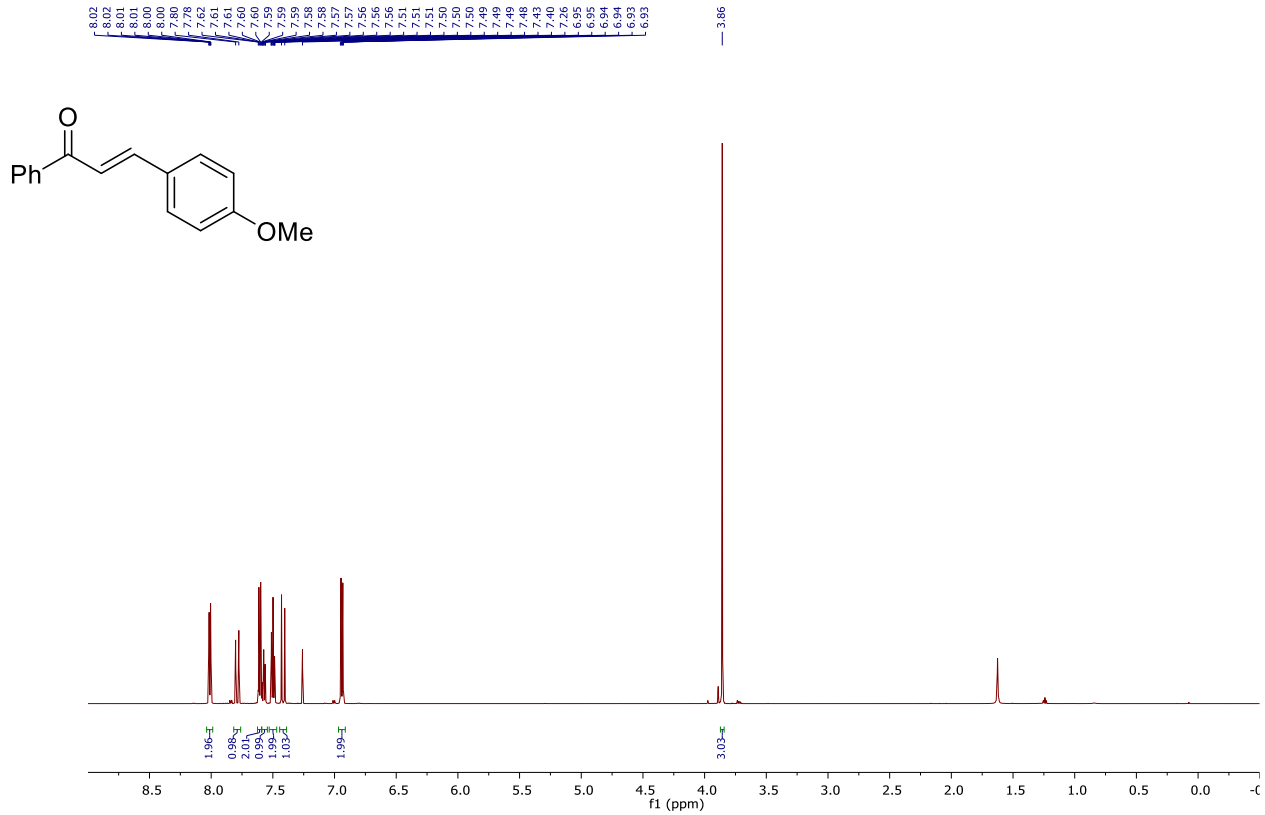


^{13}C NMR with $CDCl_3$, 151 MHz

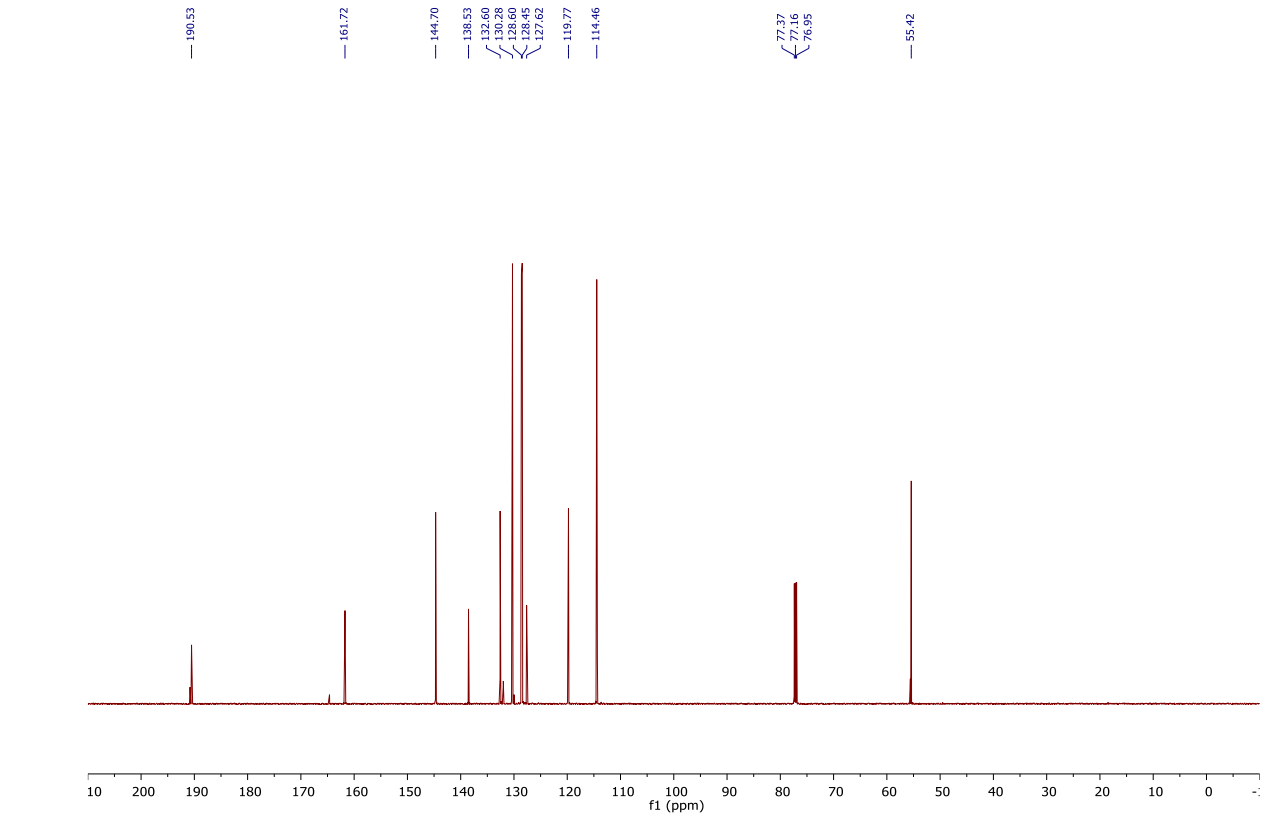


NMR spectra of (*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (1f)

^{1}H NMR with $CDCl_3$, 600 MHz

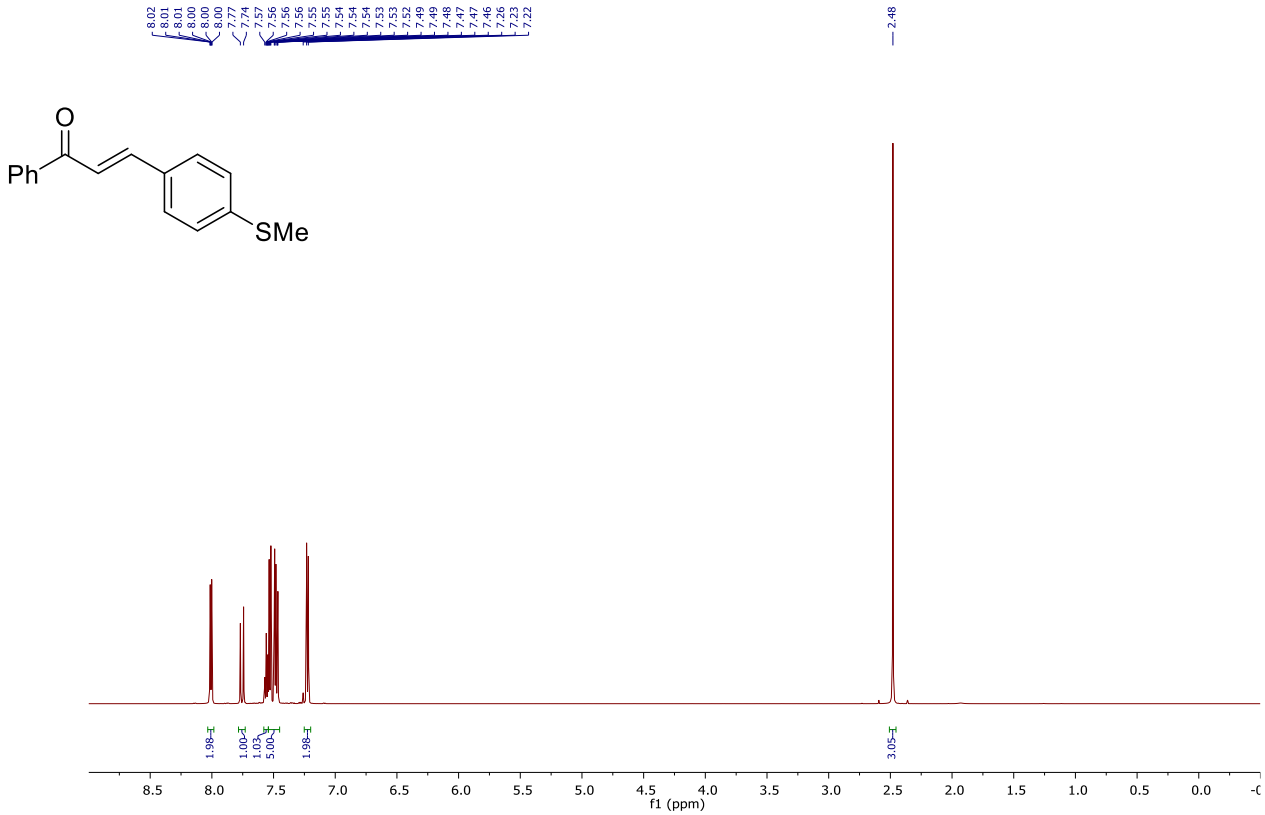


^{13}C NMR with $CDCl_3$, 151 MHz

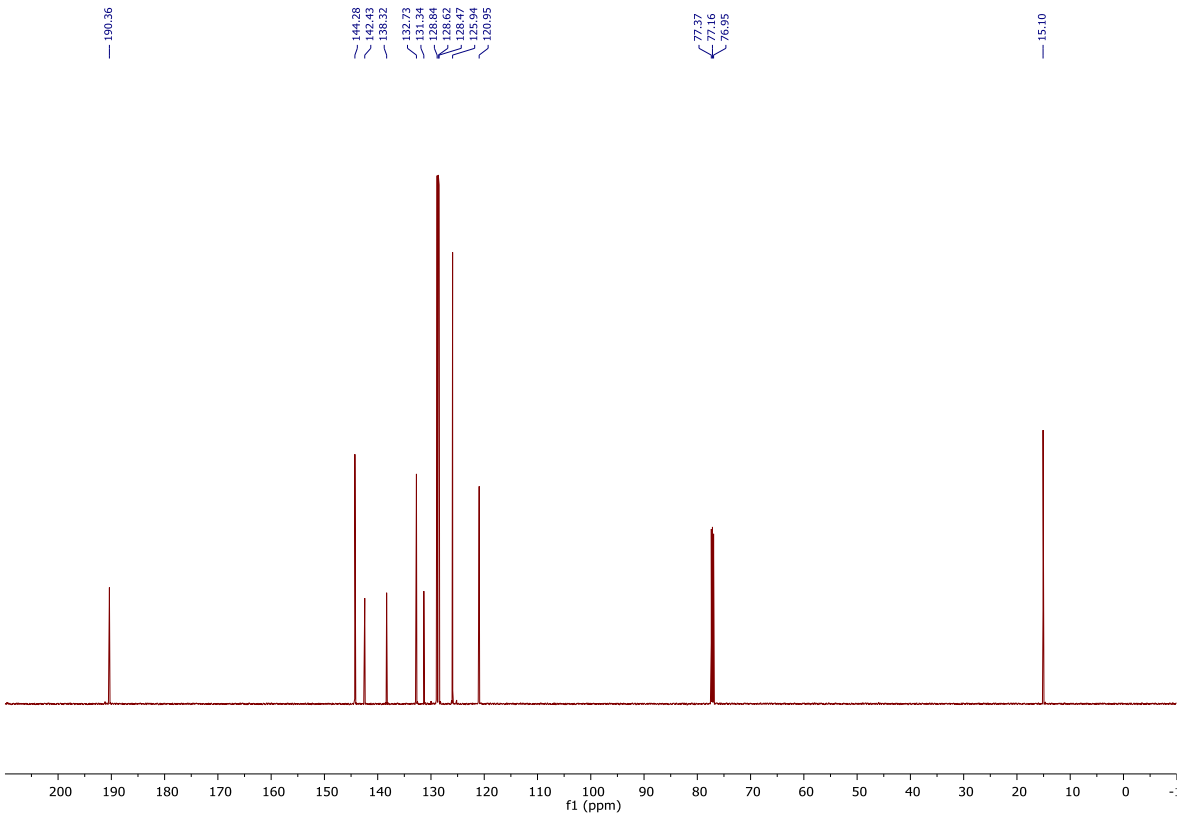


NMR spectra of (*E*)-3-(4-(methylthio)phenyl)-1-phenylprop-2-en-1-one (1g)

^{1}H NMR with $CDCl_3$, 600 MHz

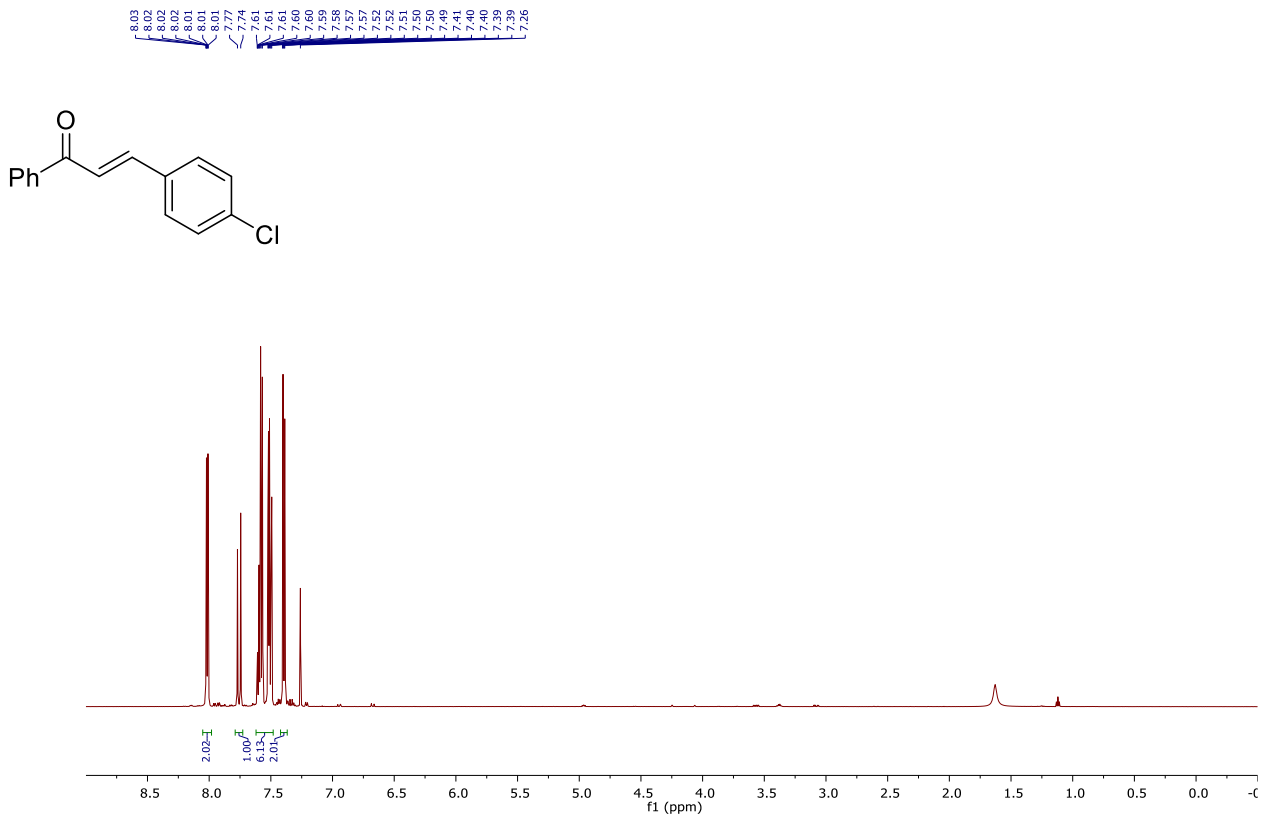


^{13}C NMR with $CDCl_3$, 151 MHz

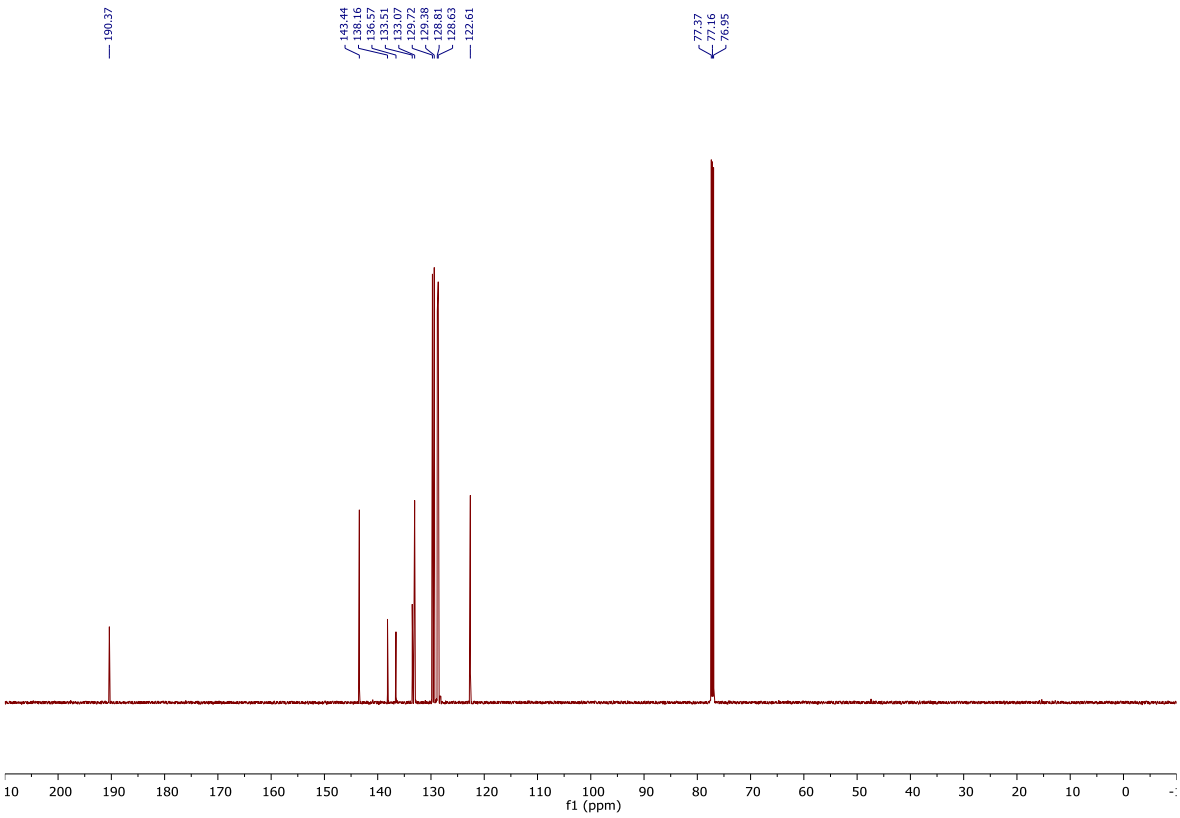


NMR spectra of (*E*)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (1h)

^{1}H NMR with $CDCl_3$, 600 MHz

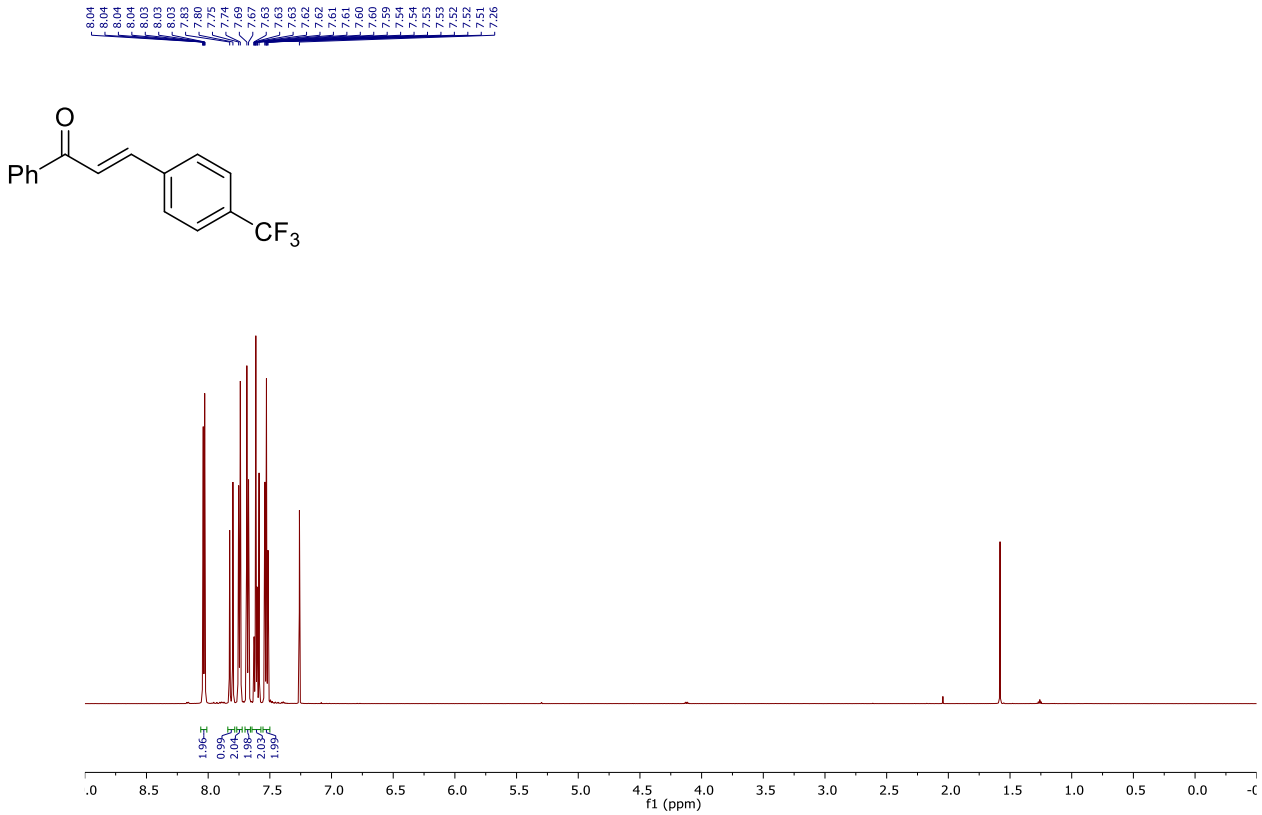


^{13}C NMR with $CDCl_3$, 151 MHz

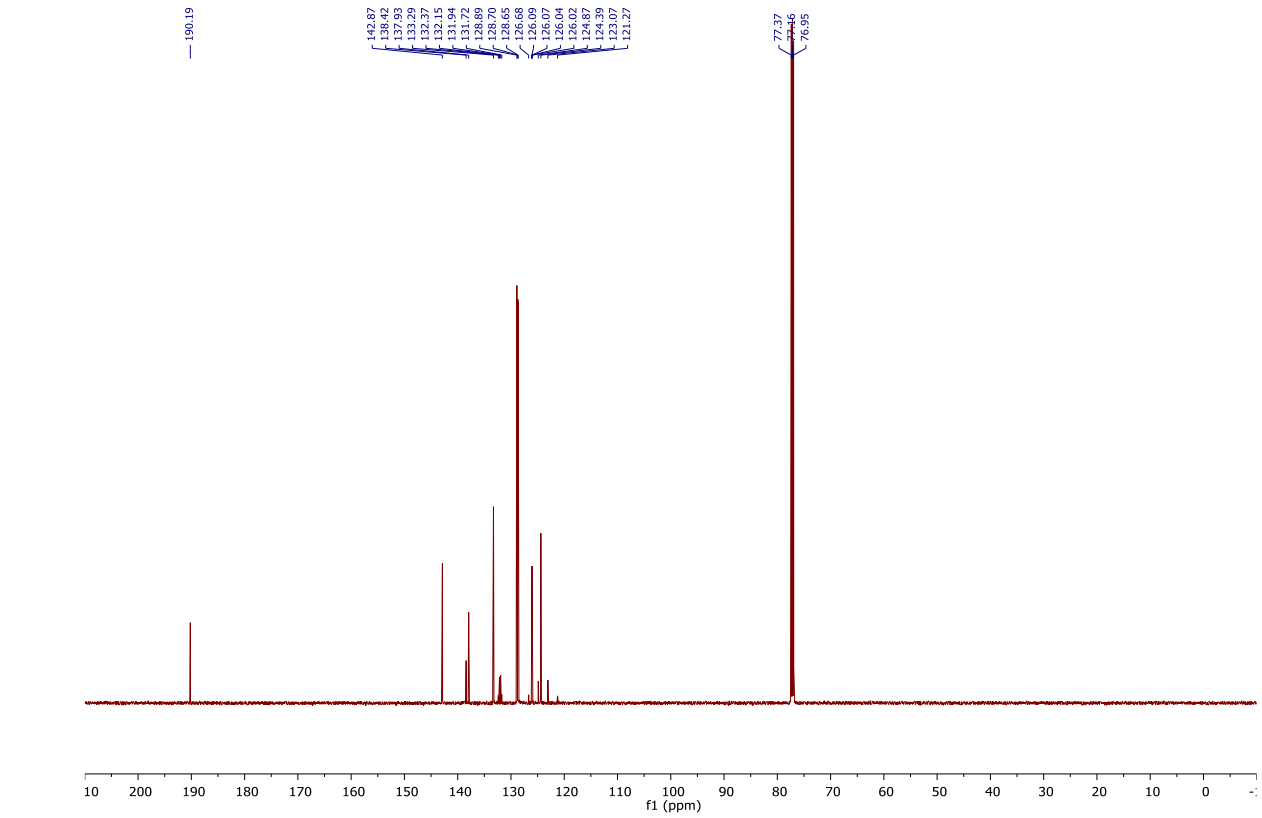


NMR spectra of (*E*)-1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (1i)

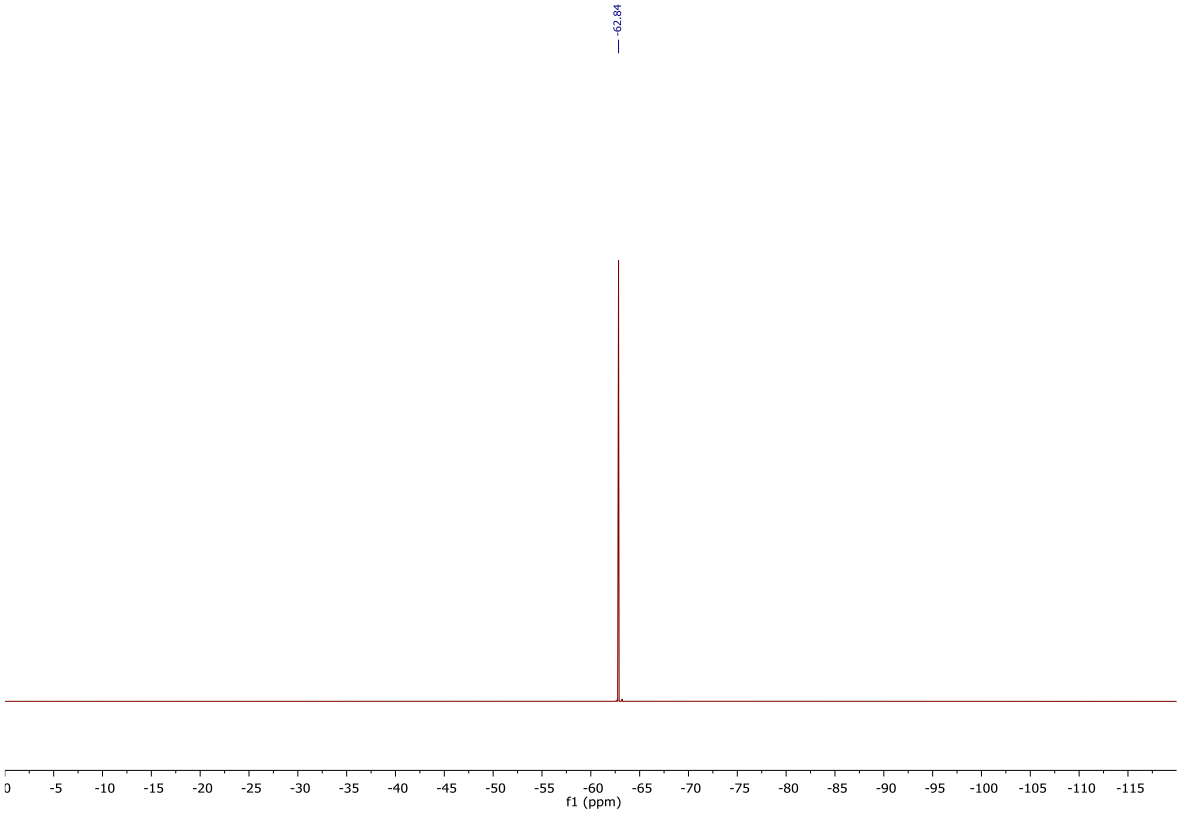
^{1}H NMR with $CDCl_3$, 600 MHz



^{13}C NMR with $CDCl_3$, 151 MHz

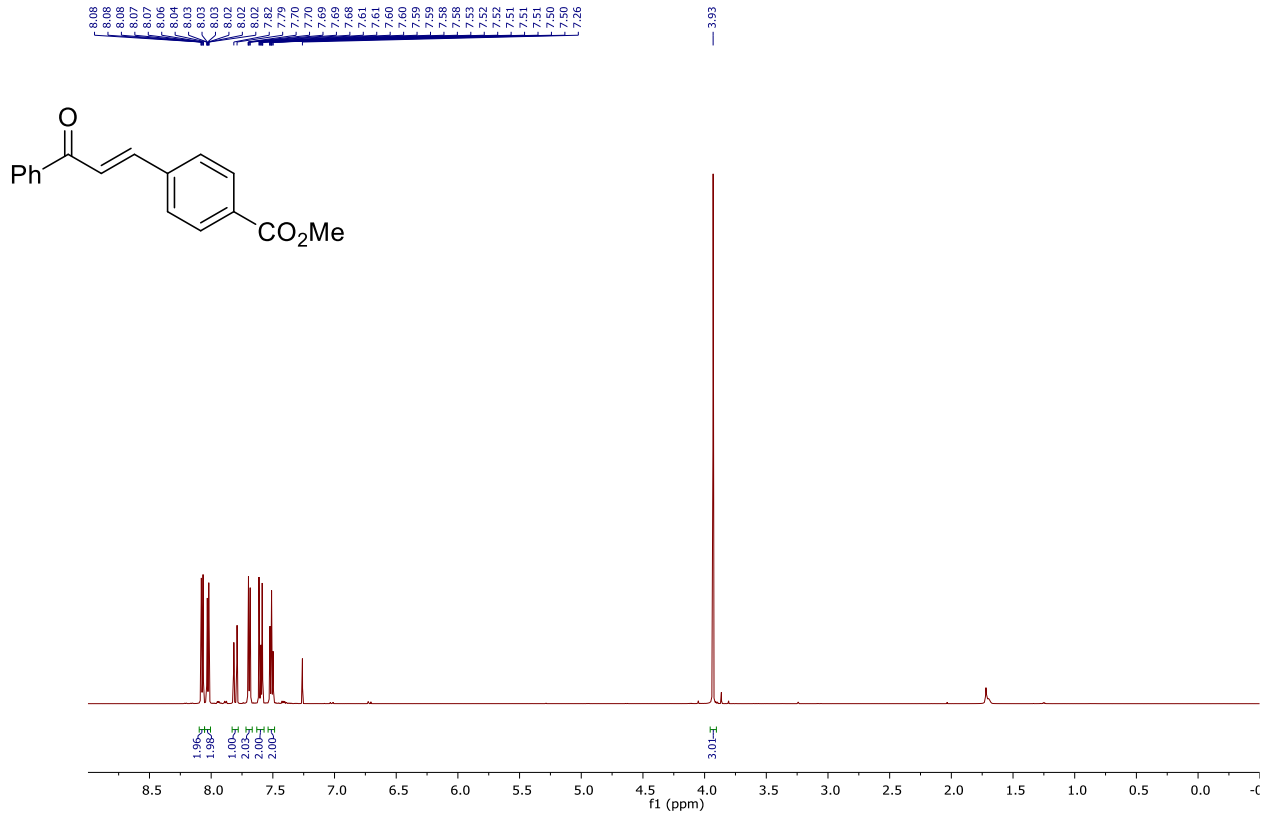


^{19}F NMR with $CDCl_3$, 565 MHz

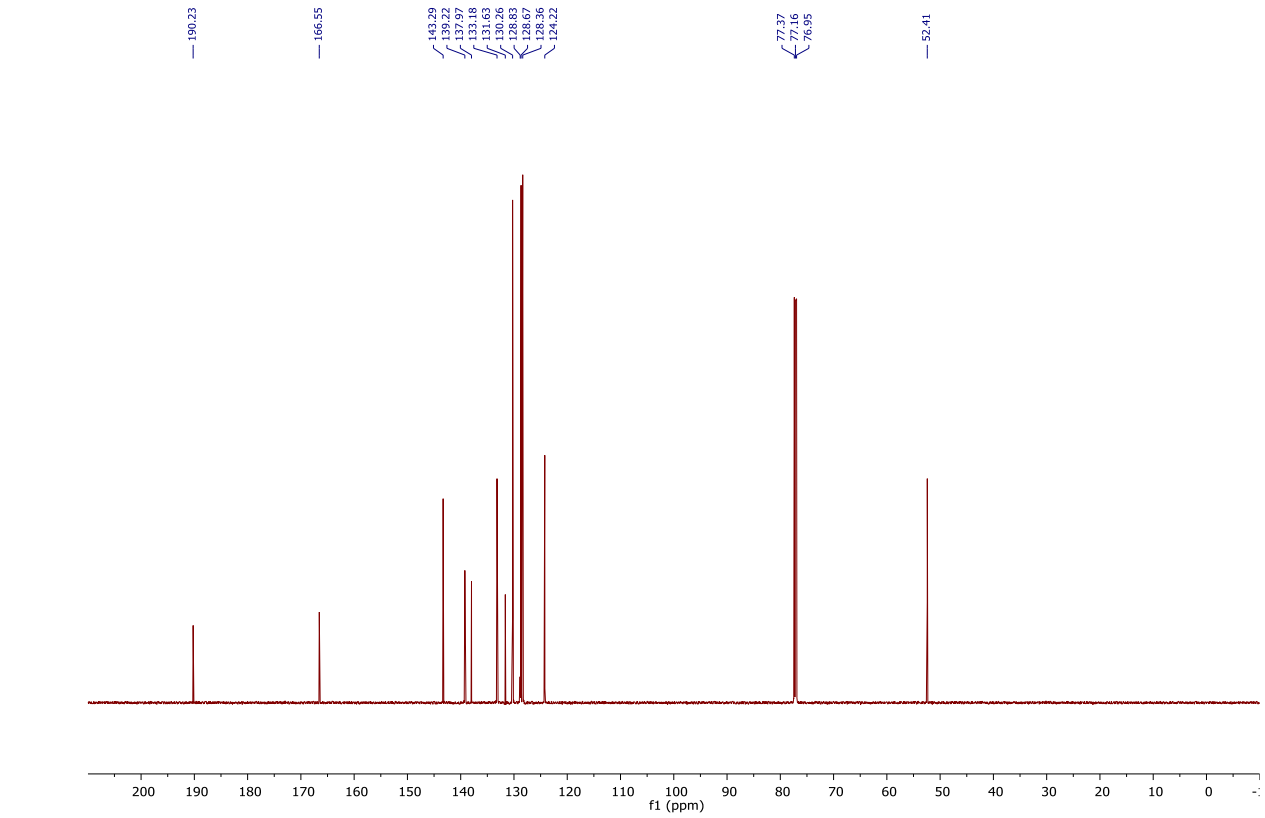


NMR spectra of methyl (*E*)-4-(3-oxo-3-phenylprop-1-en-1-yl)benzoate (1j)

^{1}H NMR with $CDCl_3$, 600 MHz

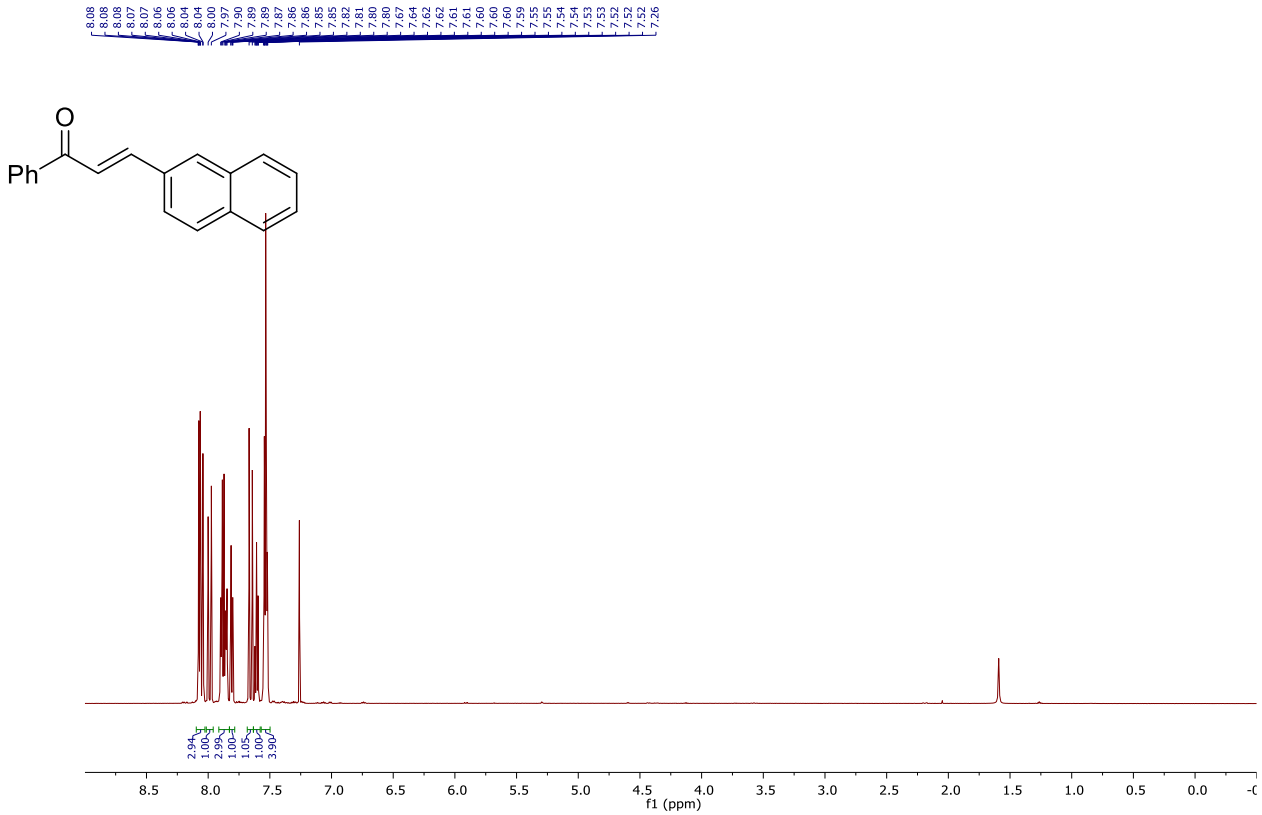


^{13}C NMR with $CDCl_3$, 151 MHz

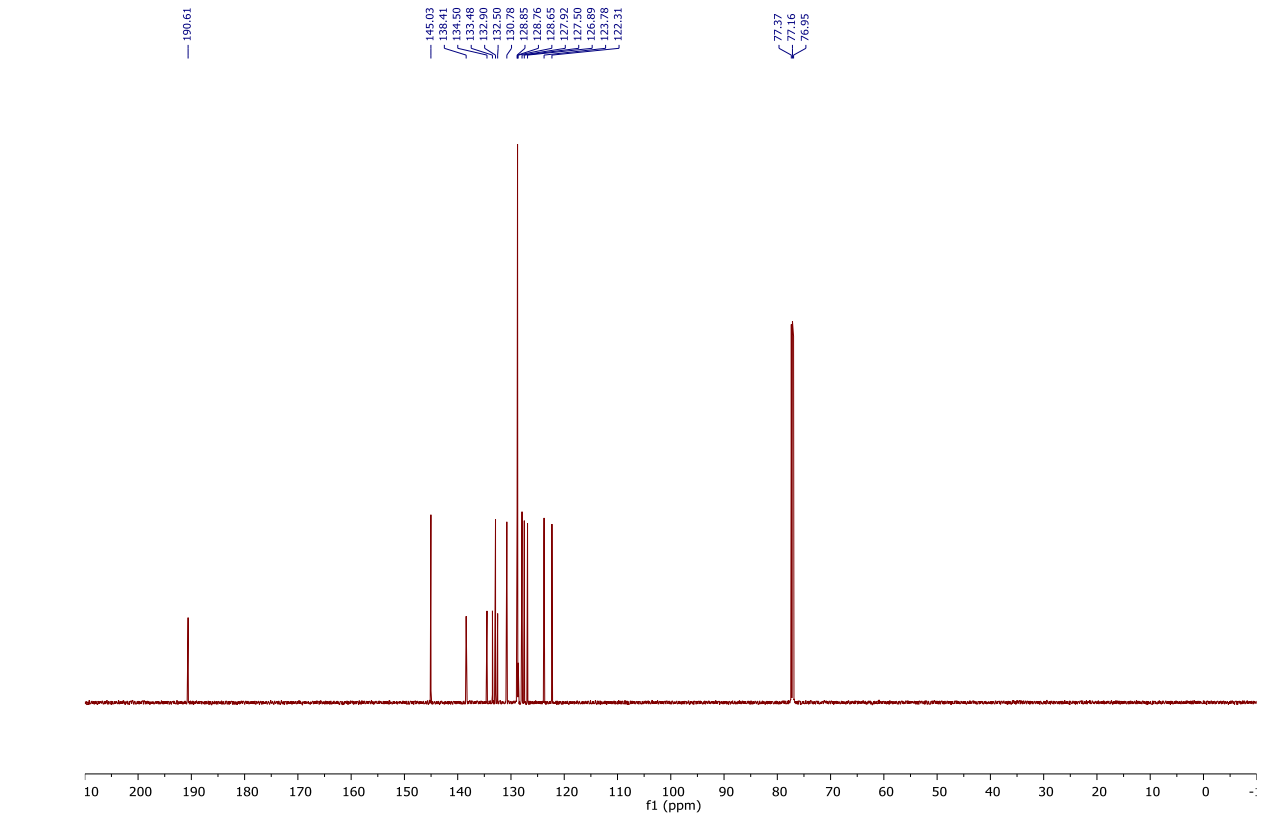


NMR spectra of (*E*)-3-(naphthalen-2-yl)-1-phenylprop-2-en-1-one (1k)

^{1}H NMR with $CDCl_3$, 600 MHz

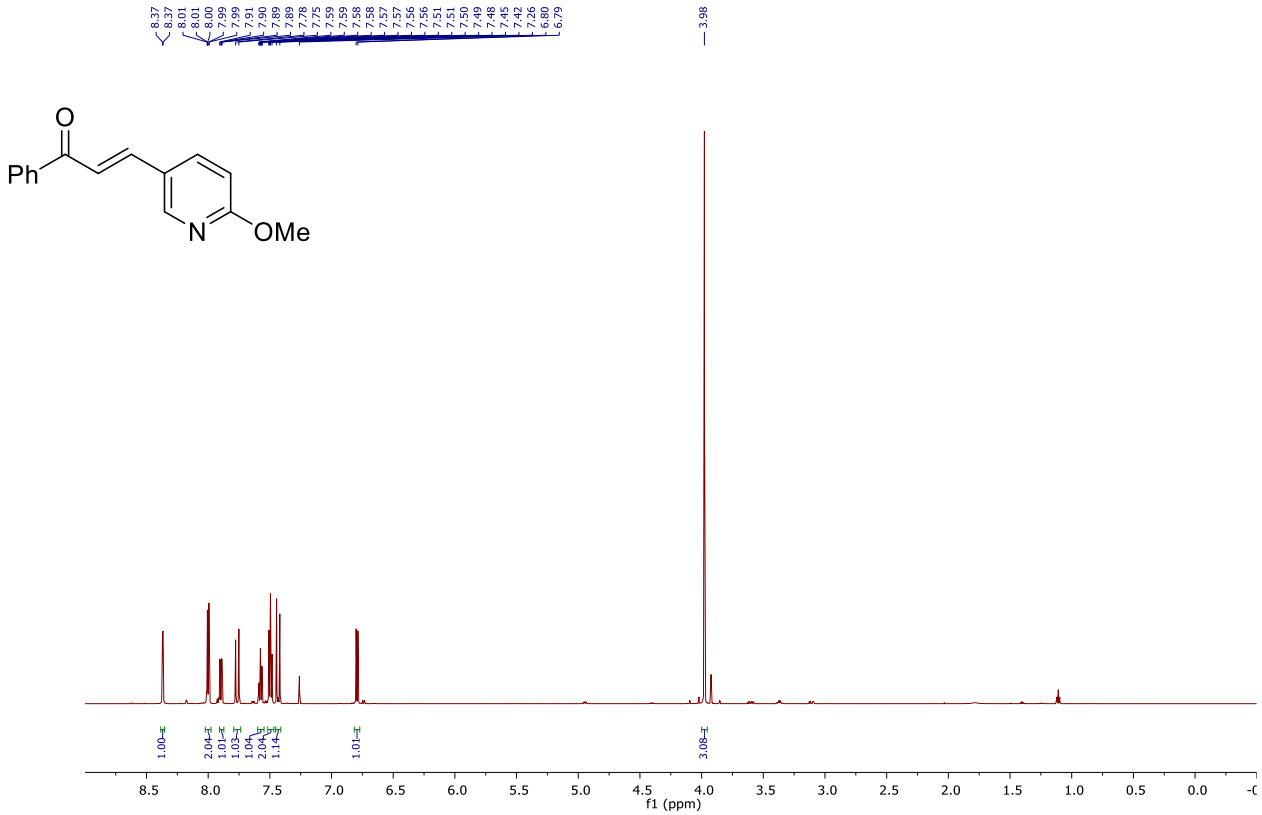


^{13}C NMR with $CDCl_3$, 151 MHz

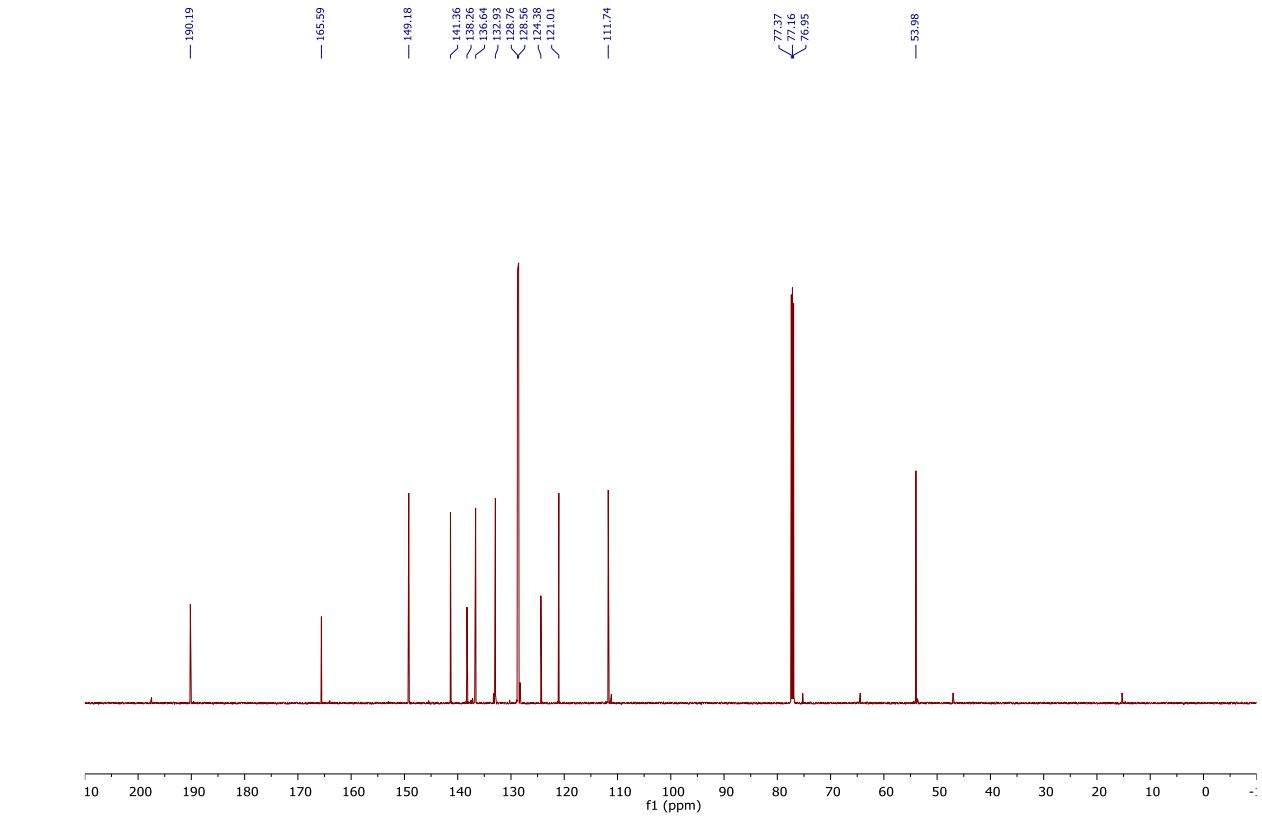


NMR spectra of (*E*)-3-(6-methoxypyridin-3-yl)-1-phenylprop-2-en-1-one (1l)

^{1}H NMR with $CDCl_3$, 600 MHz

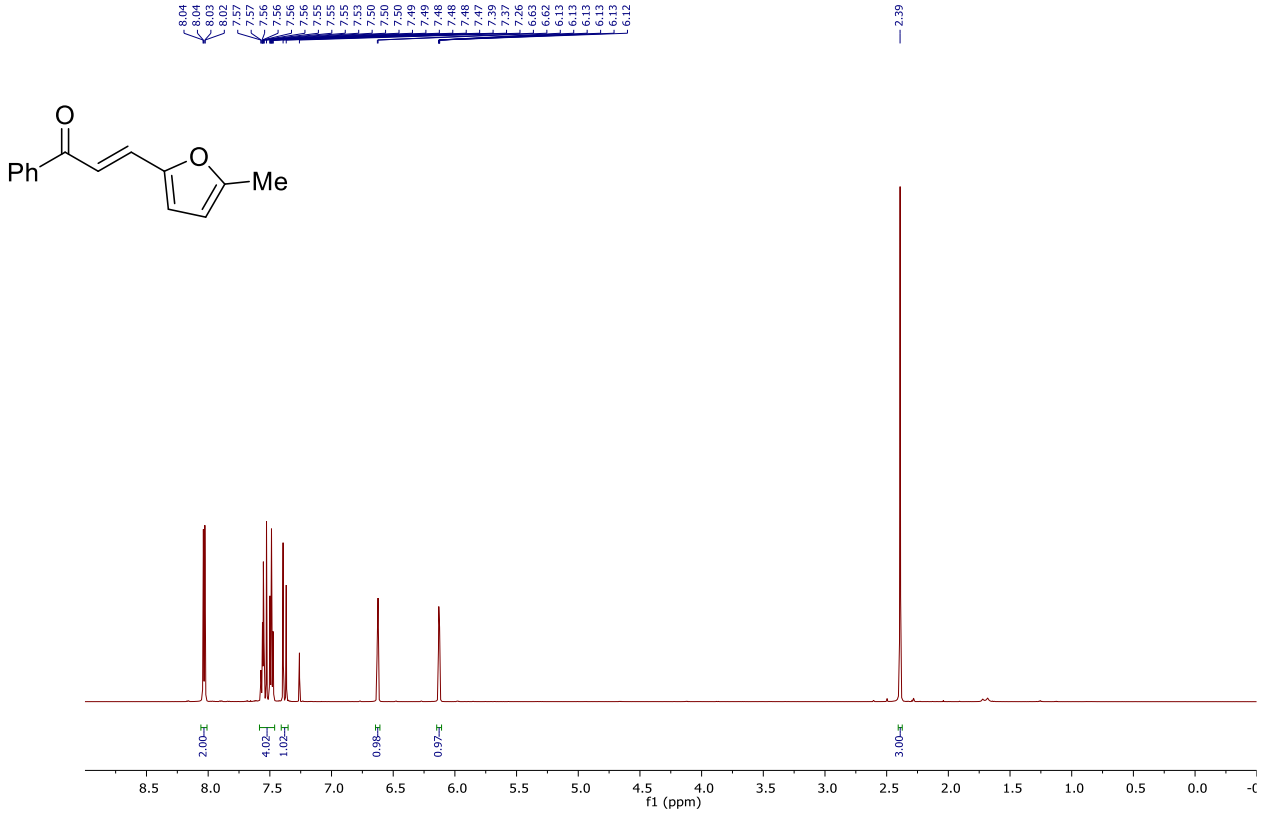


^{13}C NMR with $CDCl_3$, 151 MHz

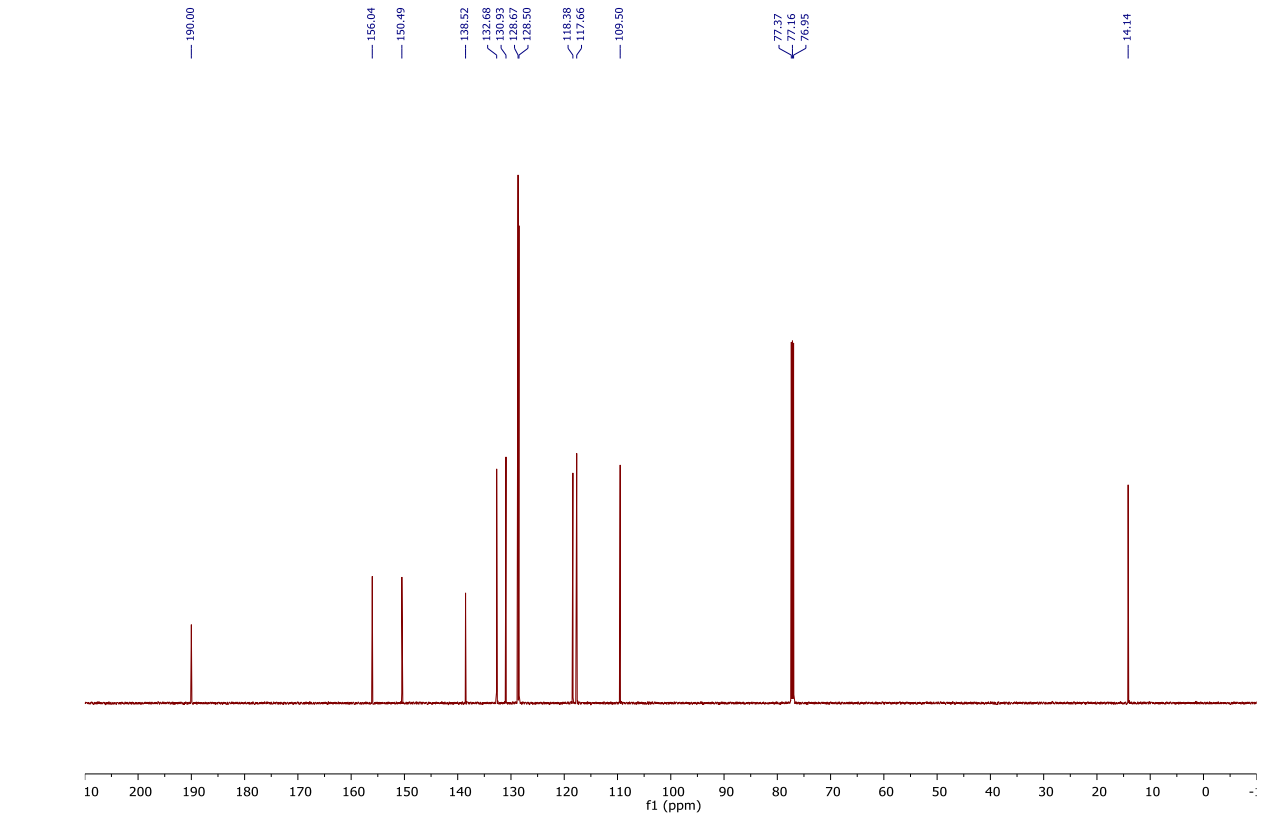


NMR spectra of (*E*)-3-(5-methylfuran-2-yl)-1-phenylprop-2-en-1-one (1m)

^{1}H NMR with $CDCl_3$, 600 MHz

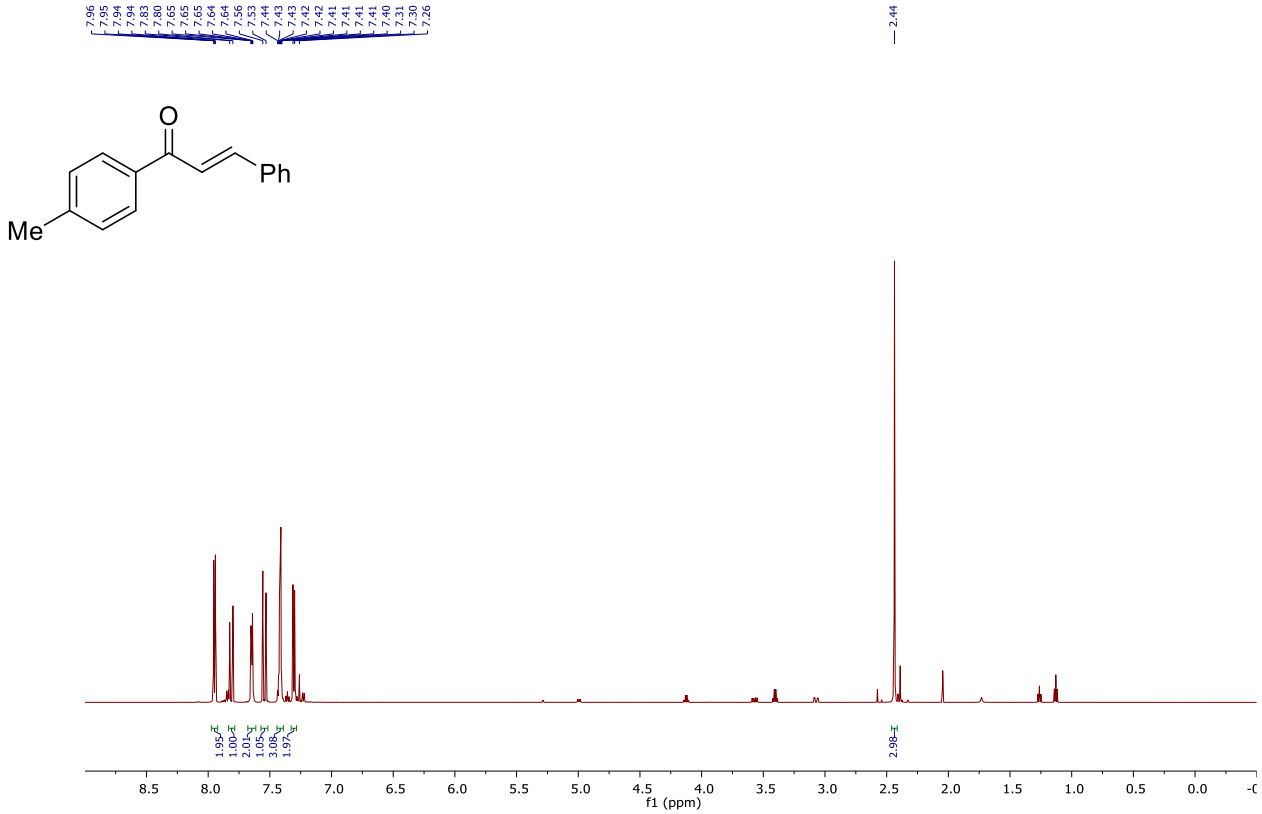


^{13}C NMR with $CDCl_3$, 151 MHz

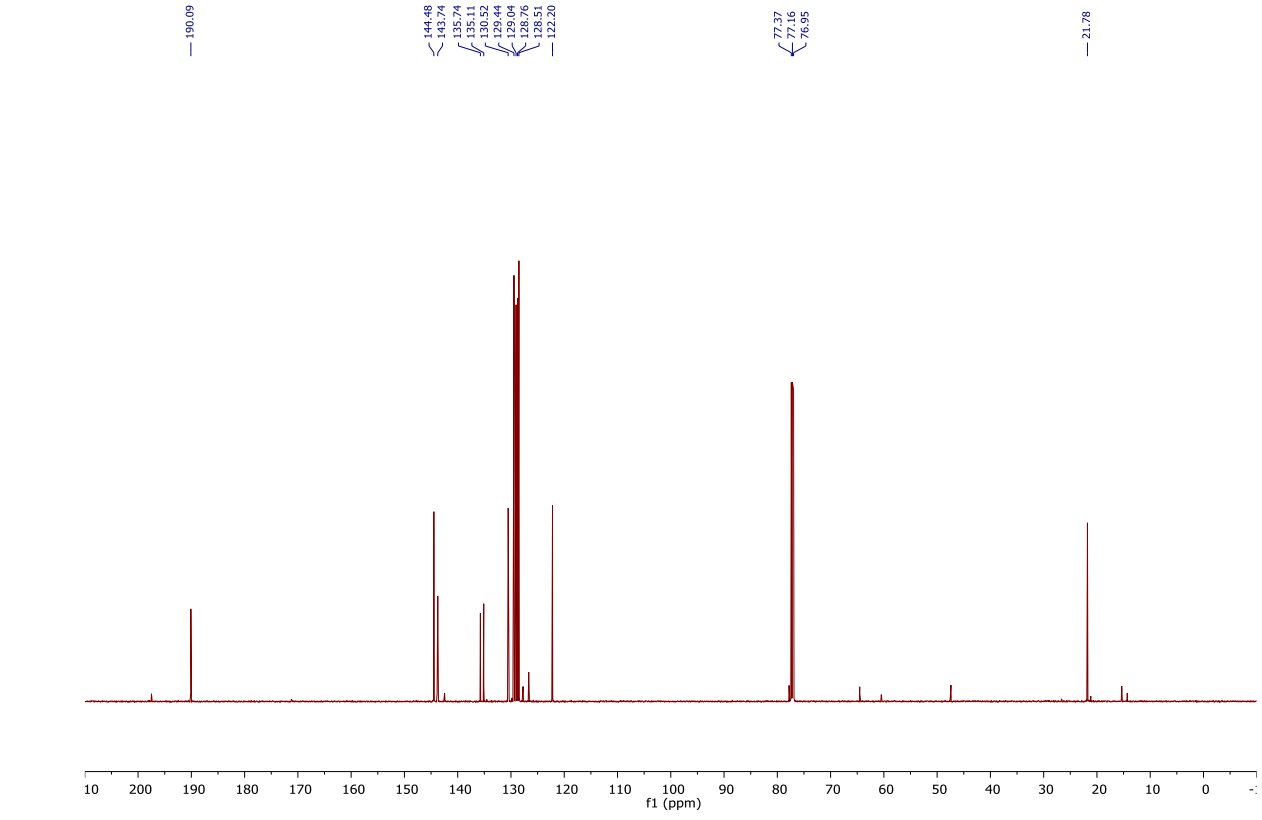


NMR spectra of (*E*)-3-phenyl-1-(*p*-tolyl)prop-2-en-1-one (1o)

^{1}H NMR with $CDCl_3$, 600 MHz

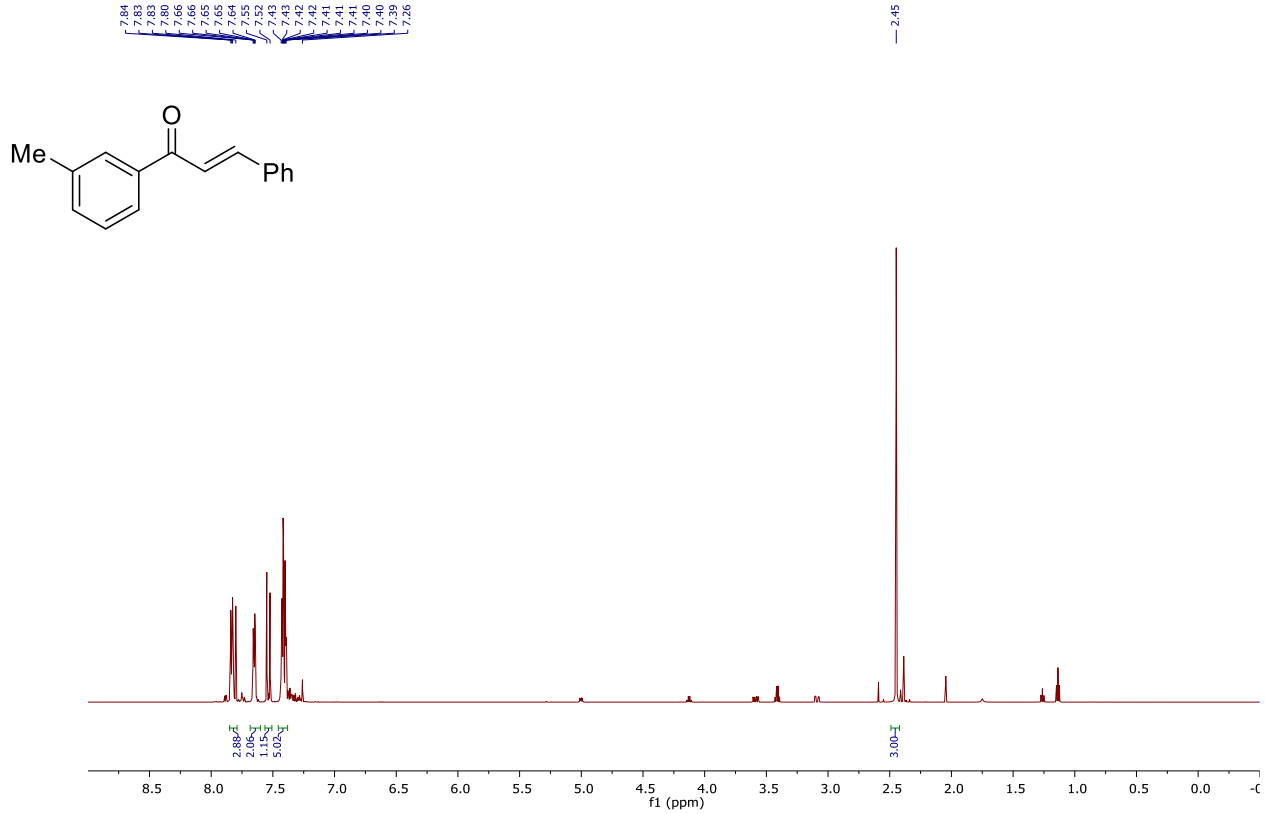


^{13}C NMR with $CDCl_3$, 151 MHz

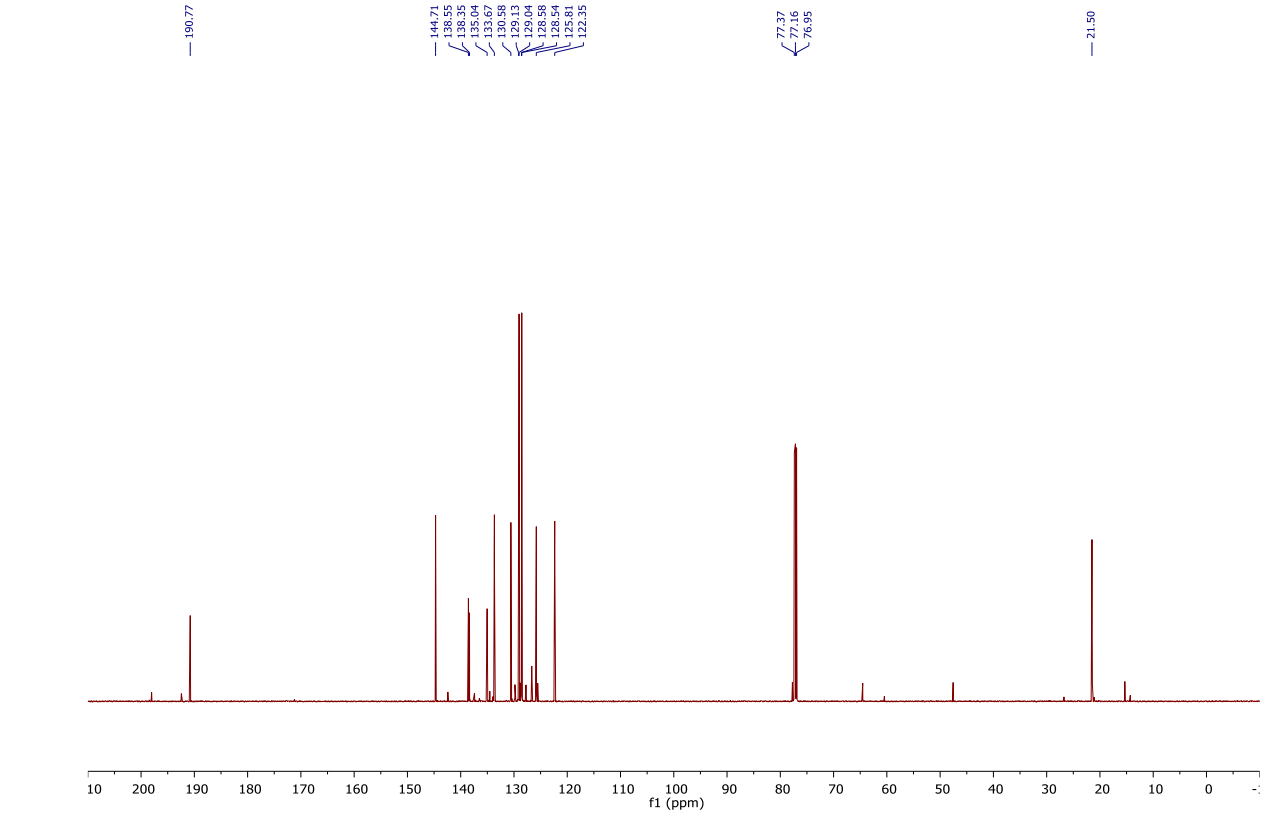


NMR spectra of (*E*)-3-phenyl-1-(*m*-tolyl)prop-2-en-1-one (1p)

^{1}H NMR with $CDCl_3$, 600 MHz

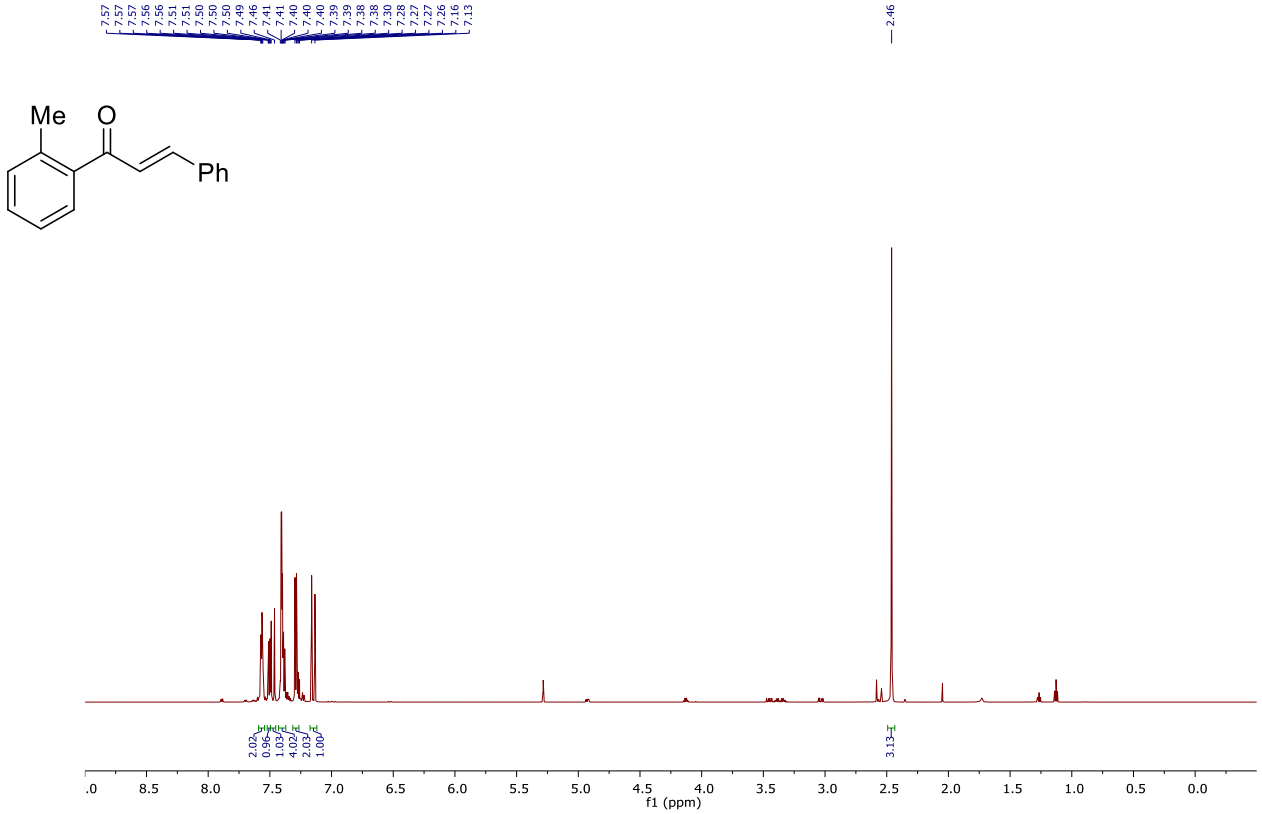


^{13}C NMR with $CDCl_3$, 151 MHz

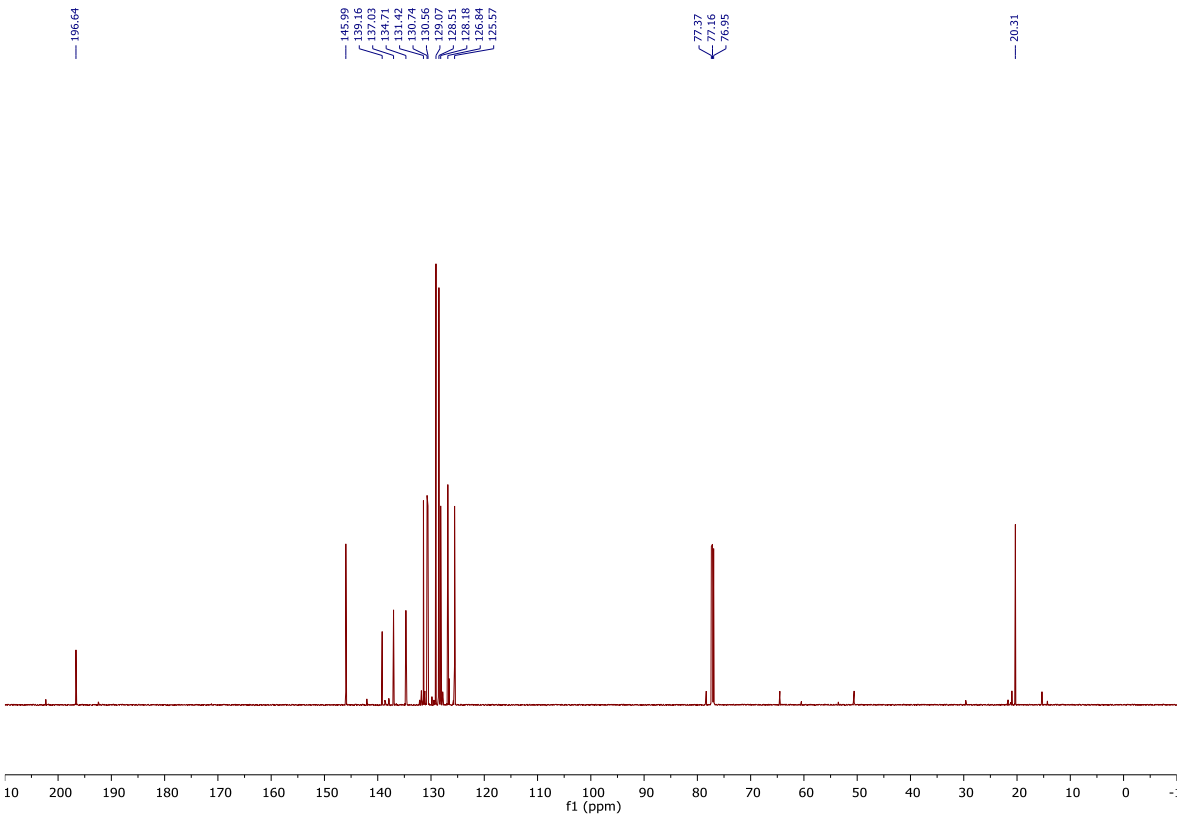


NMR spectra of (*E*)-3-phenyl-1-(*o*-tolyl)prop-2-en-1-one (1q)

^{1}H NMR with $CDCl_3$, 600 MHz

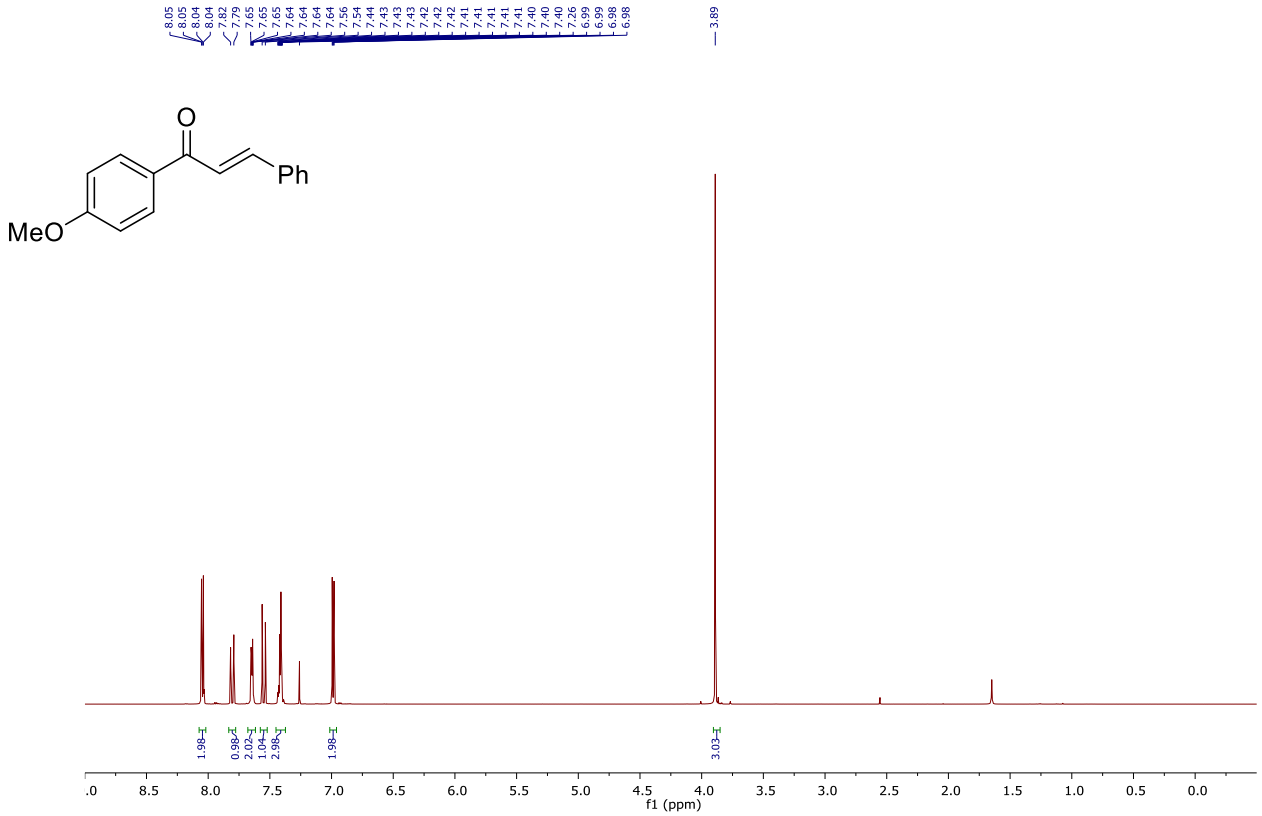


^{13}C NMR with $CDCl_3$, 151 MHz

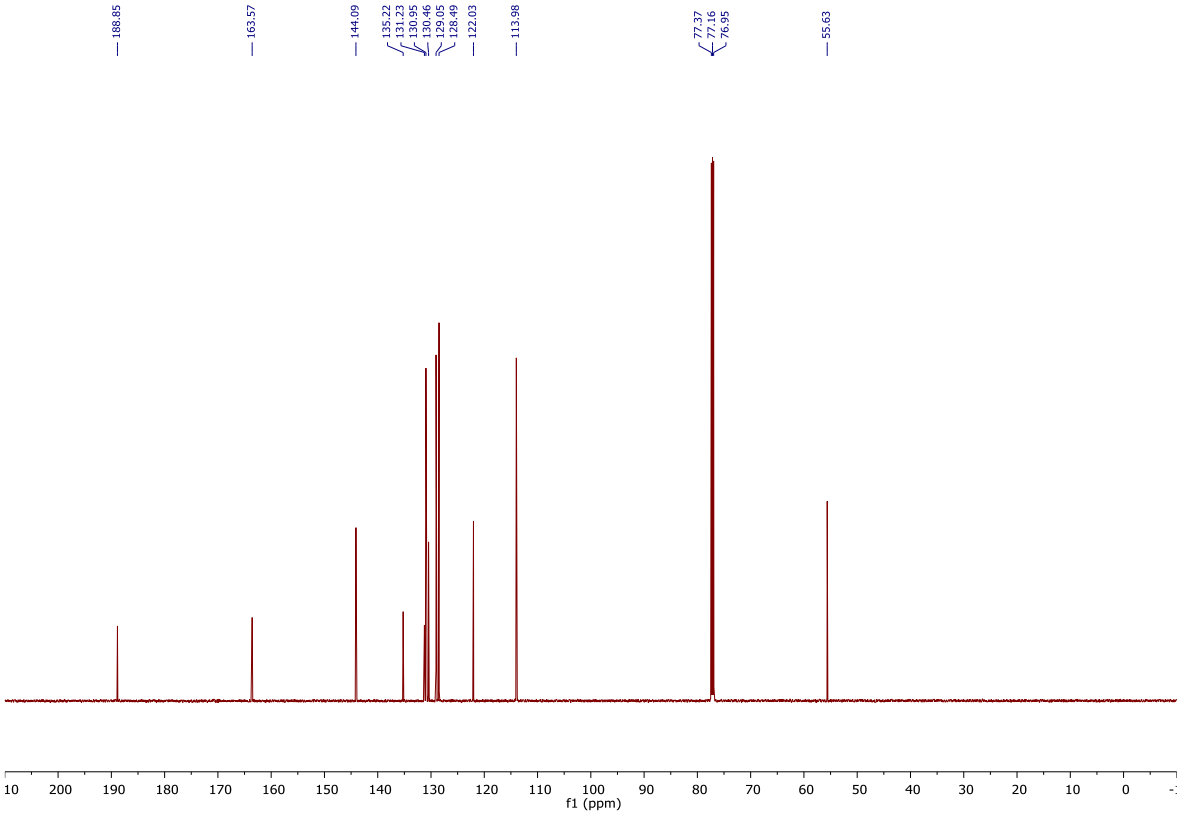


NMR spectra of (*E*)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (1r)

^{1}H NMR with $CDCl_3$, 600 MHz

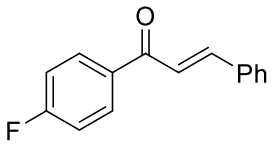


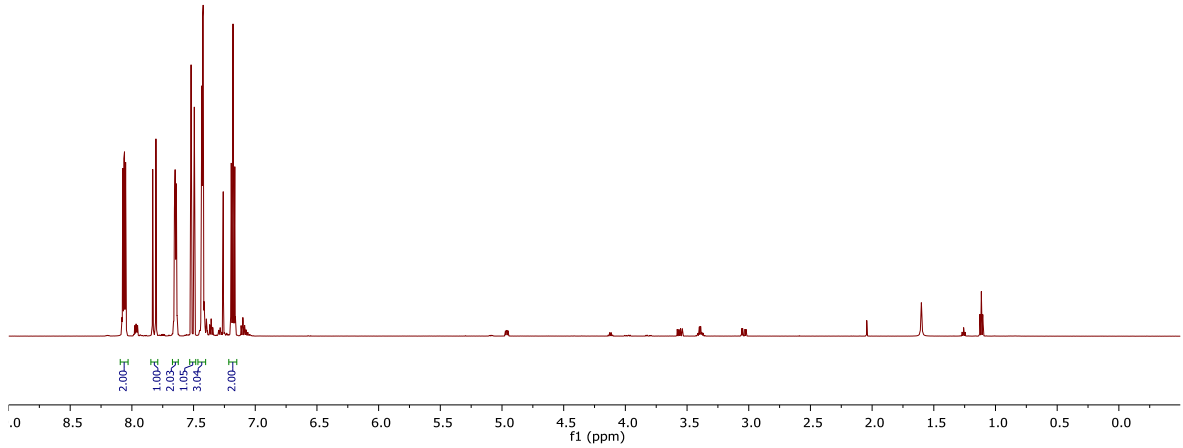
^{13}C NMR with $CDCl_3$, 151 MHz



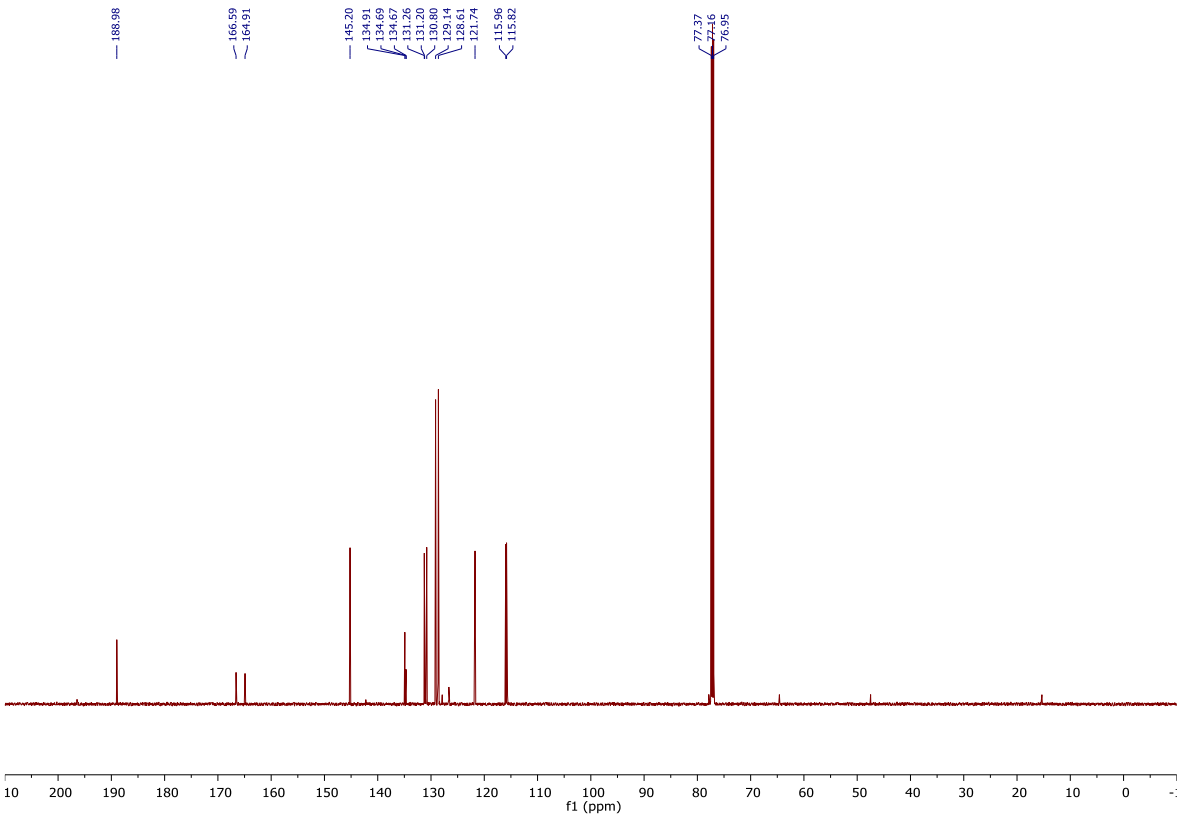
NMR spectra of (*E*)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-one (1s)

^{1}H NMR with $CDCl_3$, 600 MHz

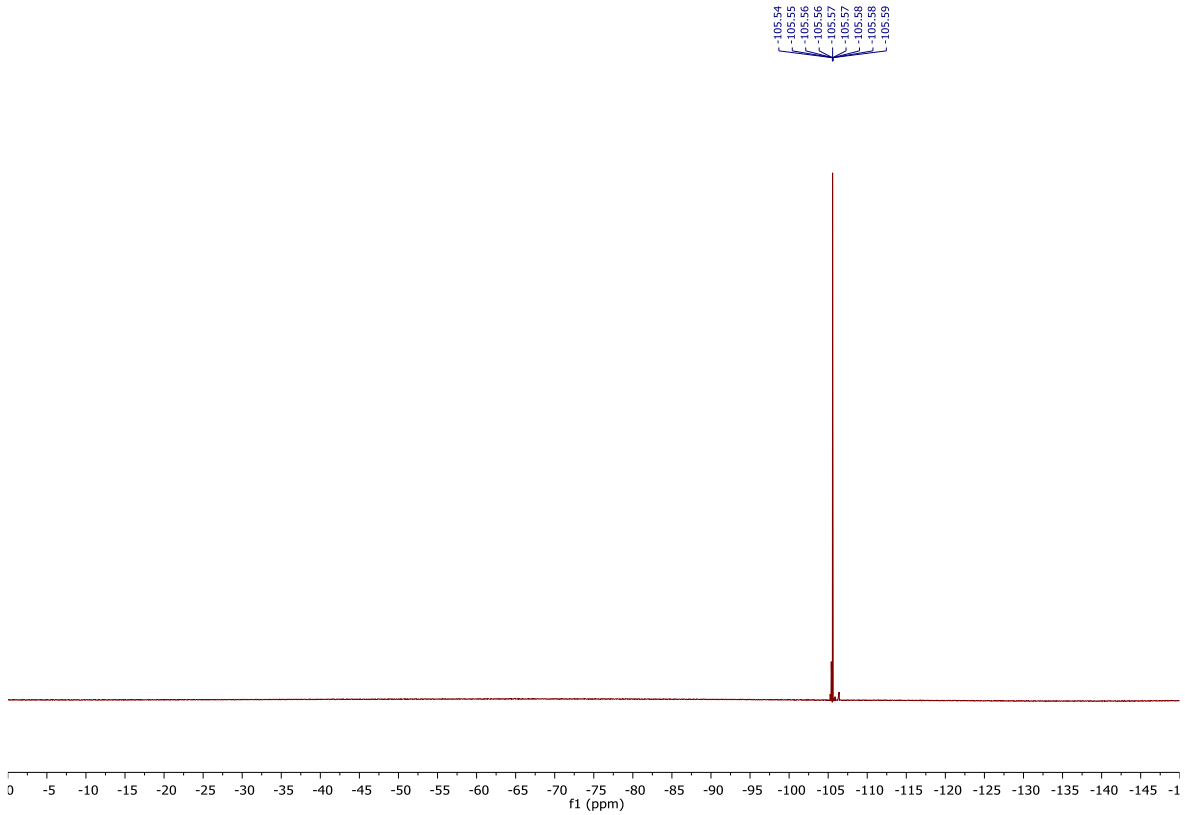




^{13}C NMR with $CDCl_3$, 151 MHz

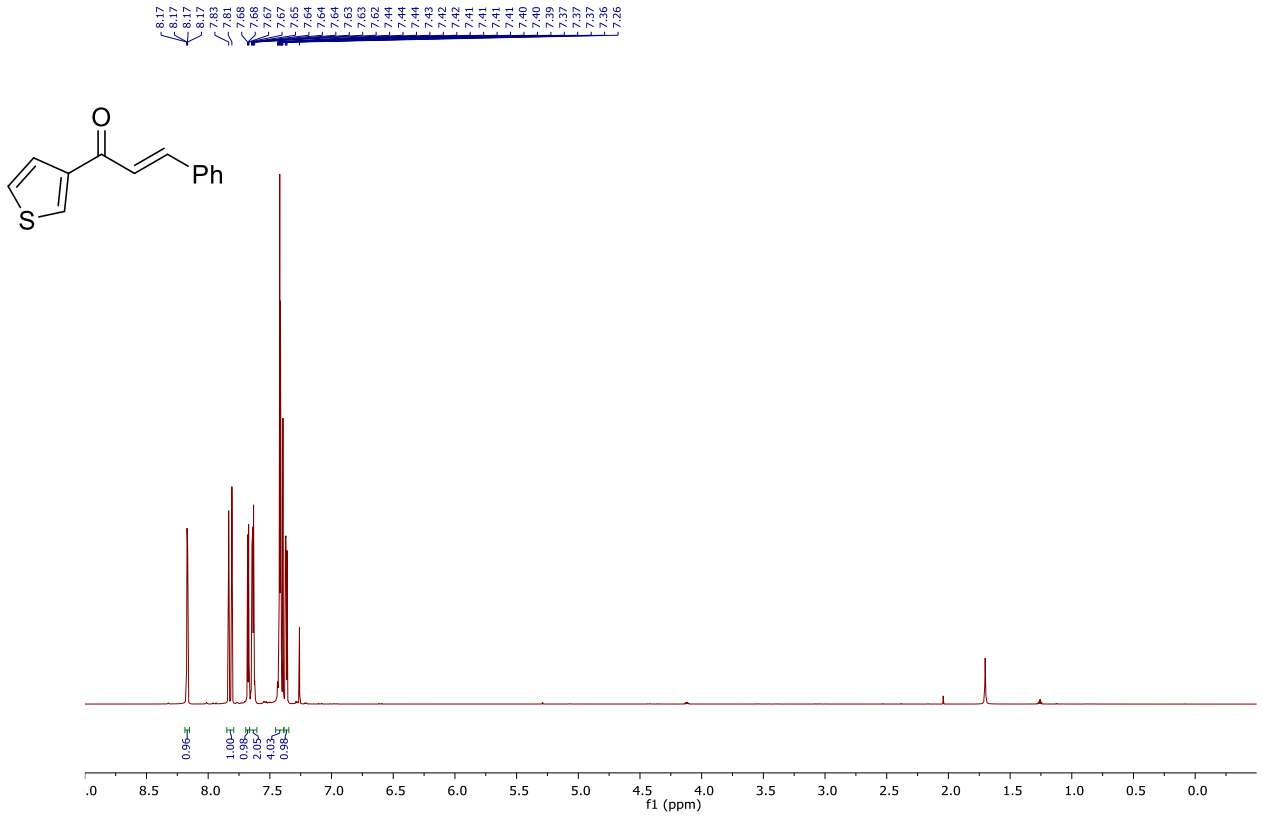


^{19}F NMR with $CDCl_3$, 565 MHz

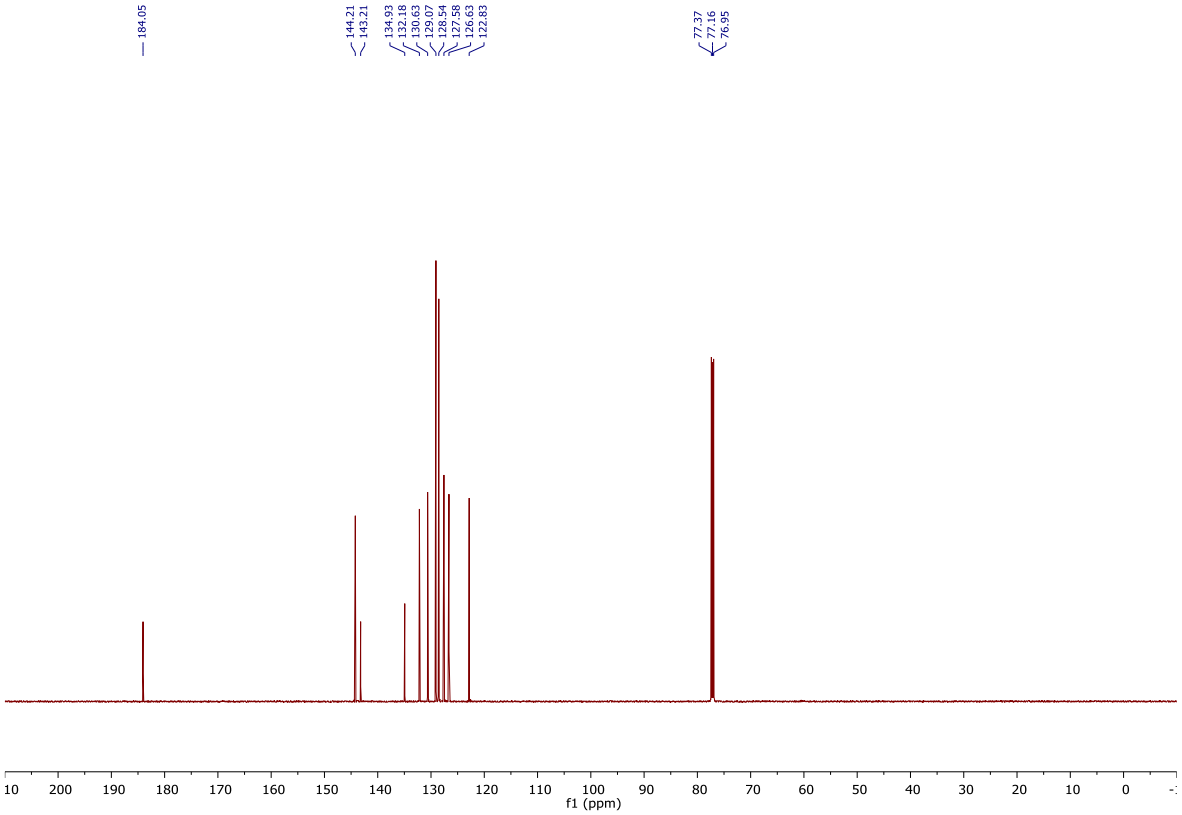


NMR spectra of (*E*)-3-phenyl-1-(thiophen-3-yl)prop-2-en-1-one (1t)

^{1}H NMR with $CDCl_3$, 600 MHz

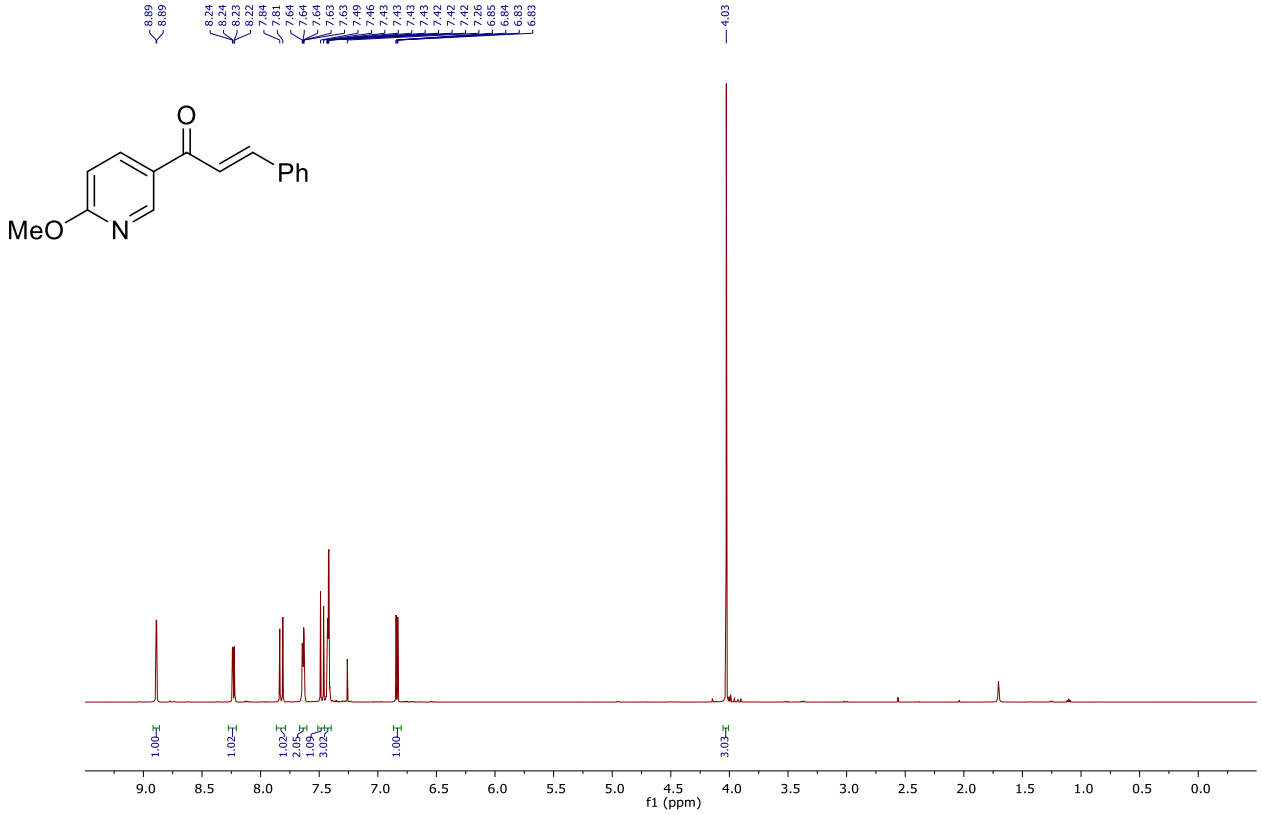


^{13}C NMR with $CDCl_3$, 151 MHz

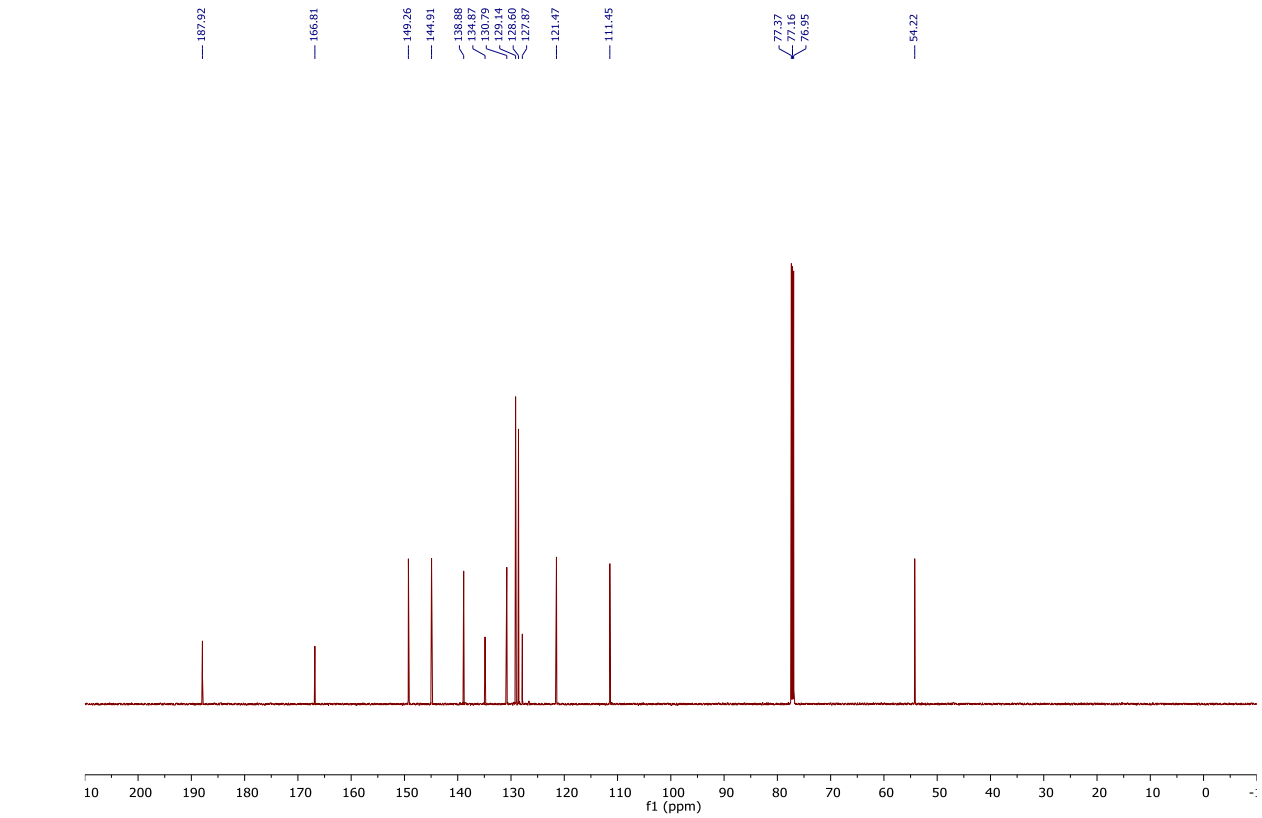


NMR spectra of (*E*)-1-(6-methoxypyridin-3-yl)-3-phenylprop-2-en-1-one (1u)

^{1}H NMR with $CDCl_3$, 600 MHz

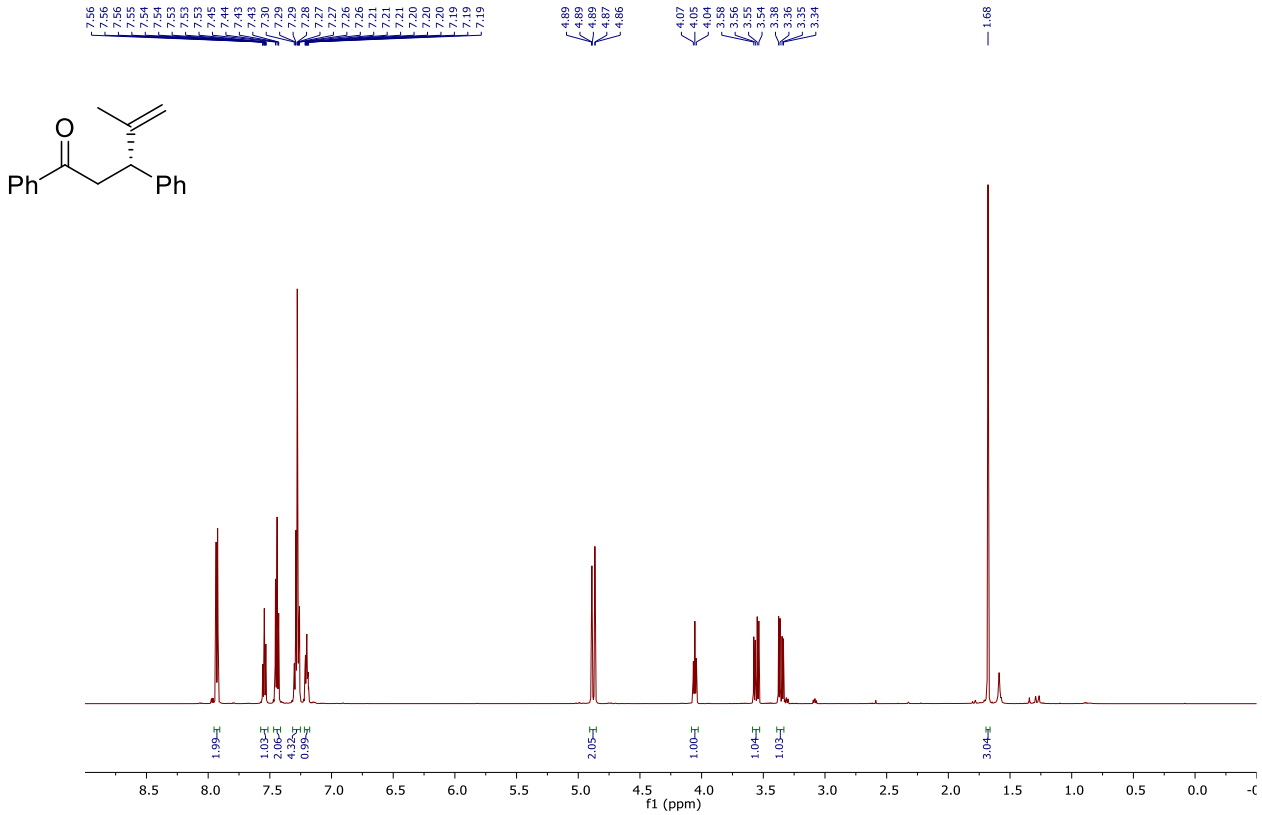


^{13}C NMR with $CDCl_3$, 151 MHz

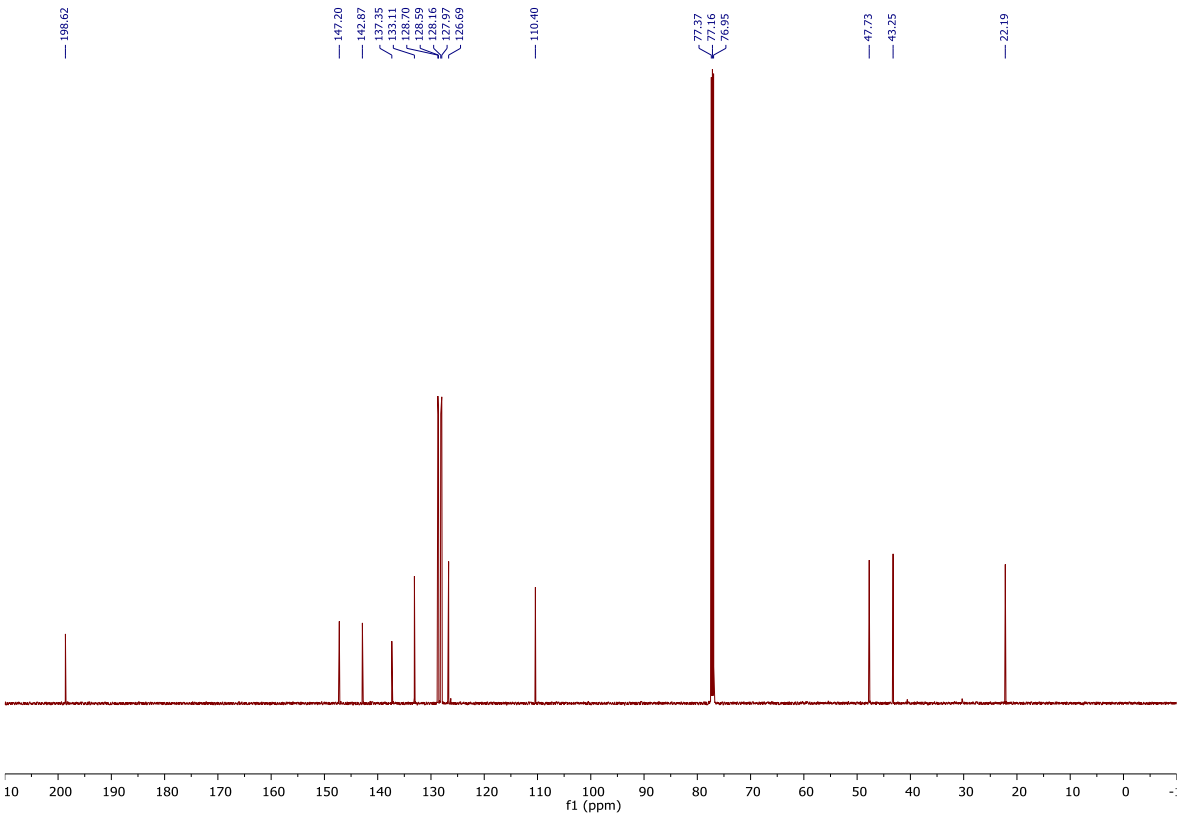


NMR spectra of (*R*)-4-methyl-1,3-diphenylpent-4-en-1-one (3a)

^{1}H NMR with $CDCl_3$, 600 MHz

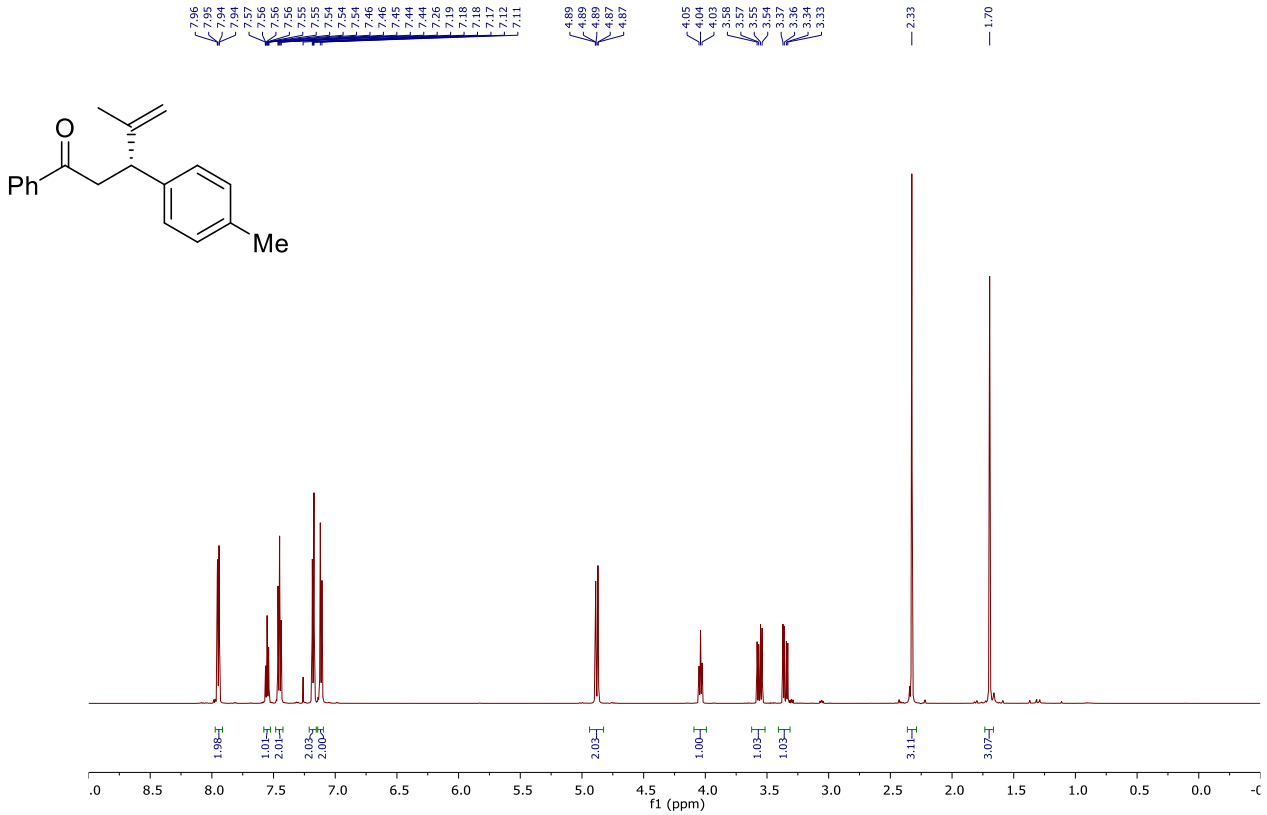


^{13}C NMR with $CDCl_3$, 151 MHz

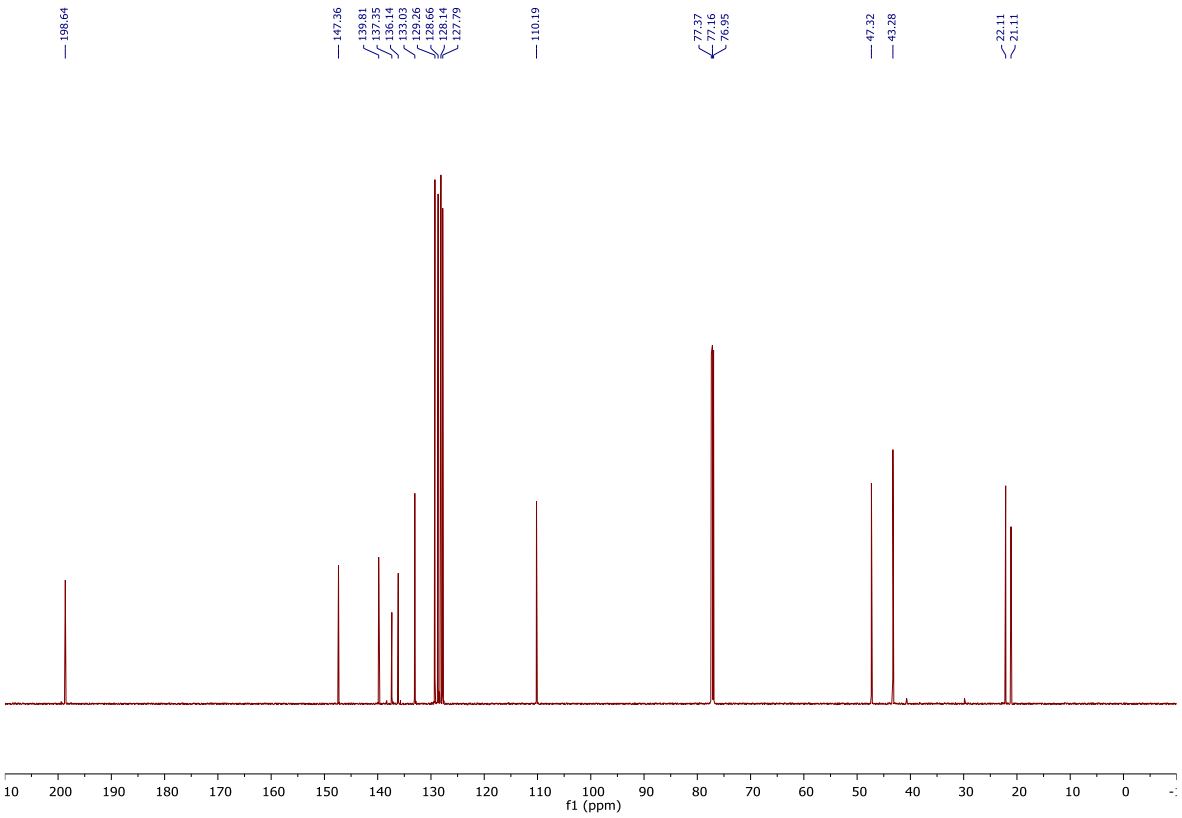


NMR spectra of (*R*)-4-methyl-1-phenyl-3-(*p*-tolyl)pent-4-en-1-one (3b)

^{1}H NMR with $CDCl_3$, 600 MHz

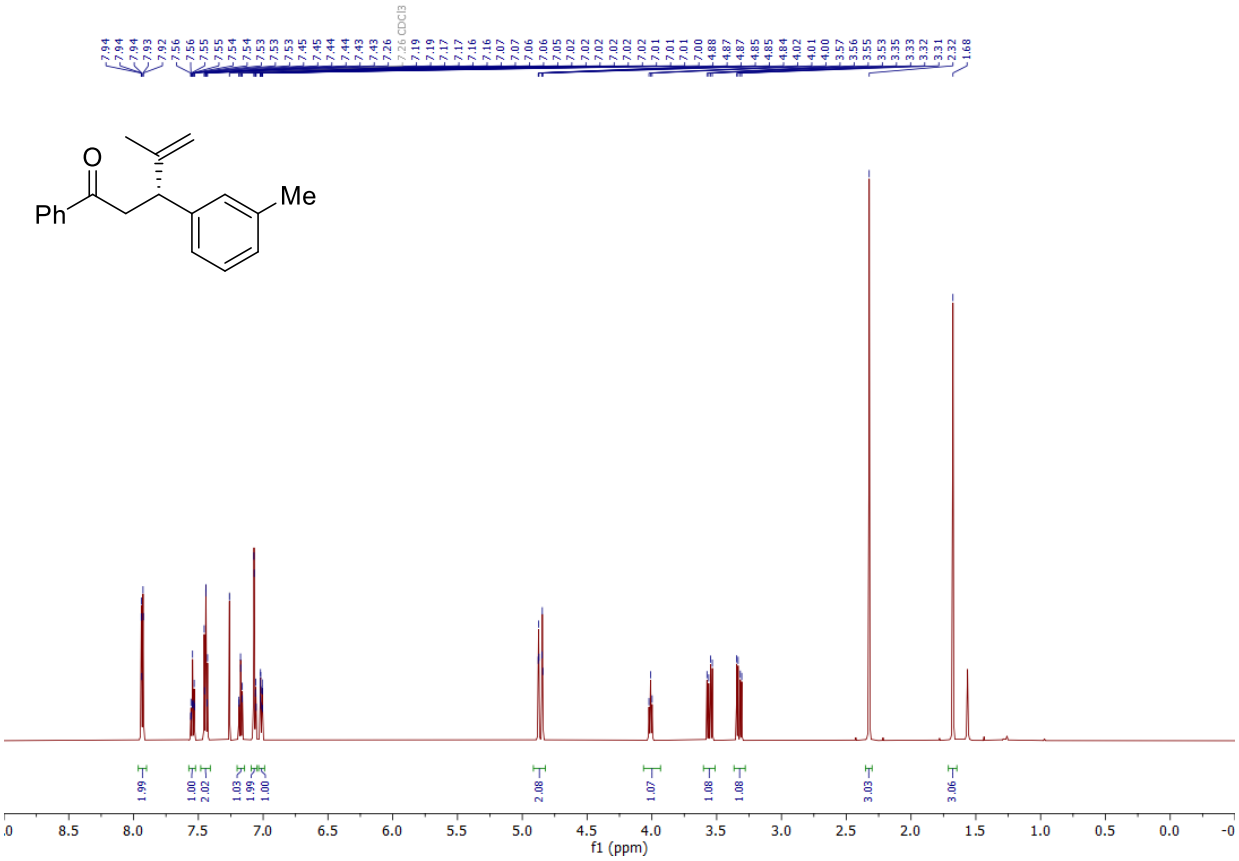


^{13}C NMR with $CDCl_3$, 151 MHz

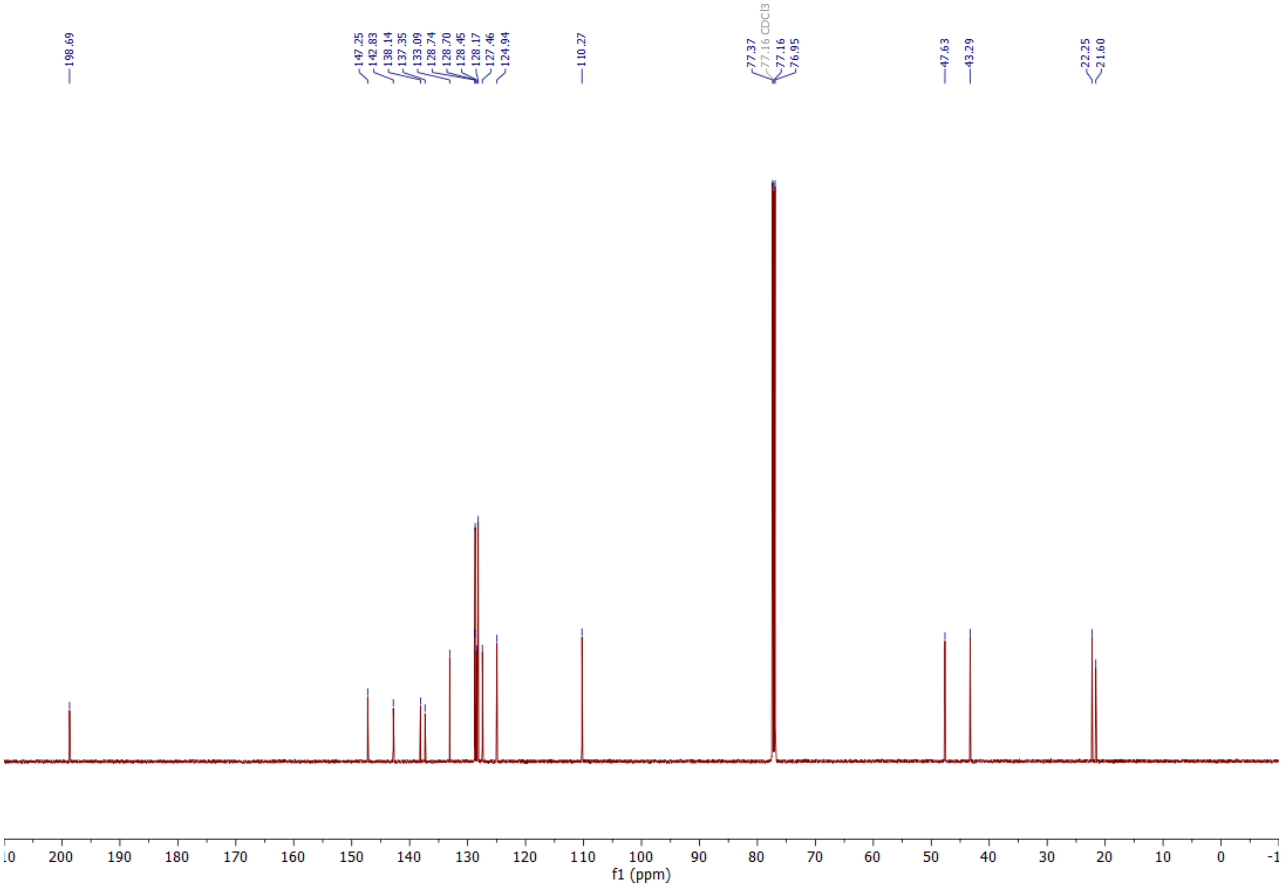


NMR spectra of (*R*)-4-methyl-1-phenyl-3-(*m*-tolyl)pent-4-en-1-one (3c)

^{1}H NMR with $CDCl_3$, 600 MHz

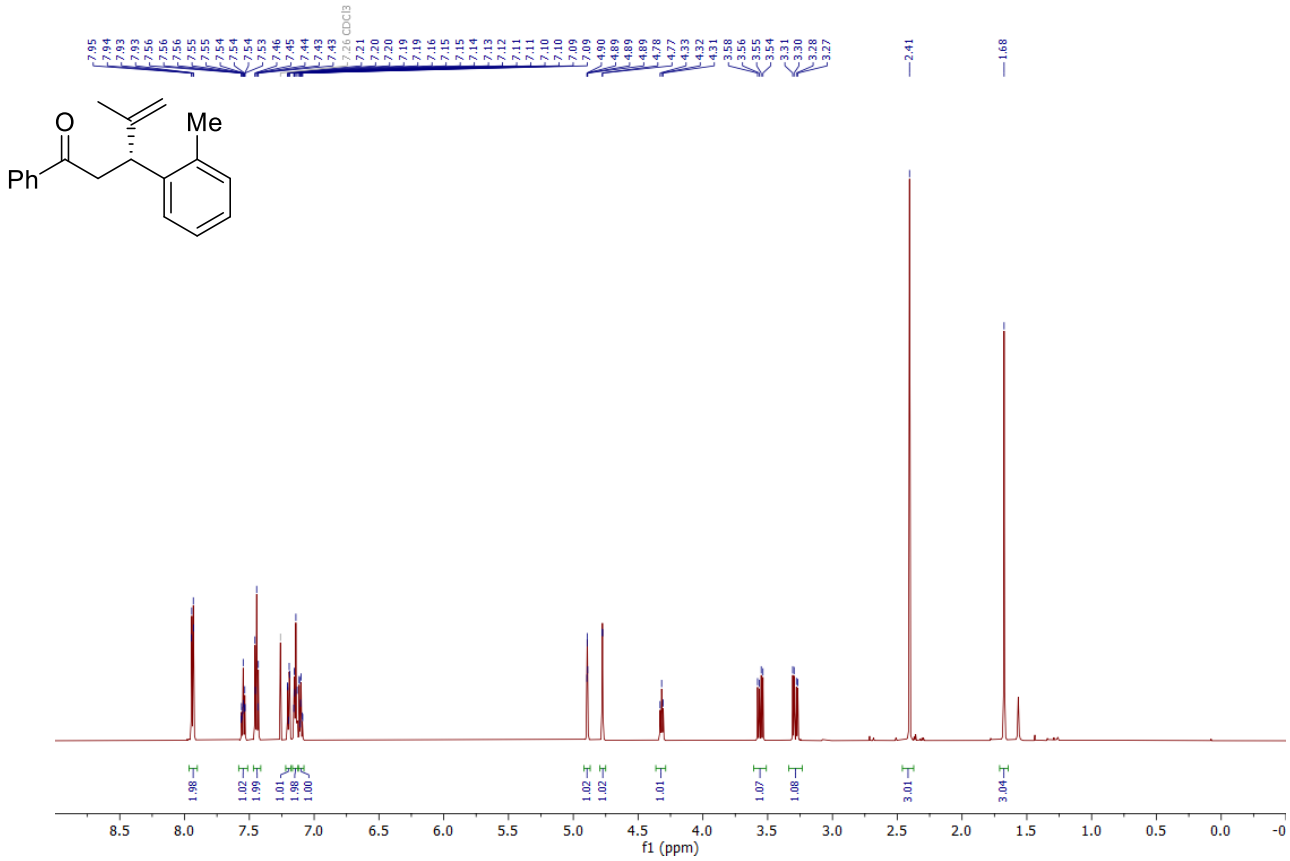


^{13}C NMR with $CDCl_3$, 151 MHz

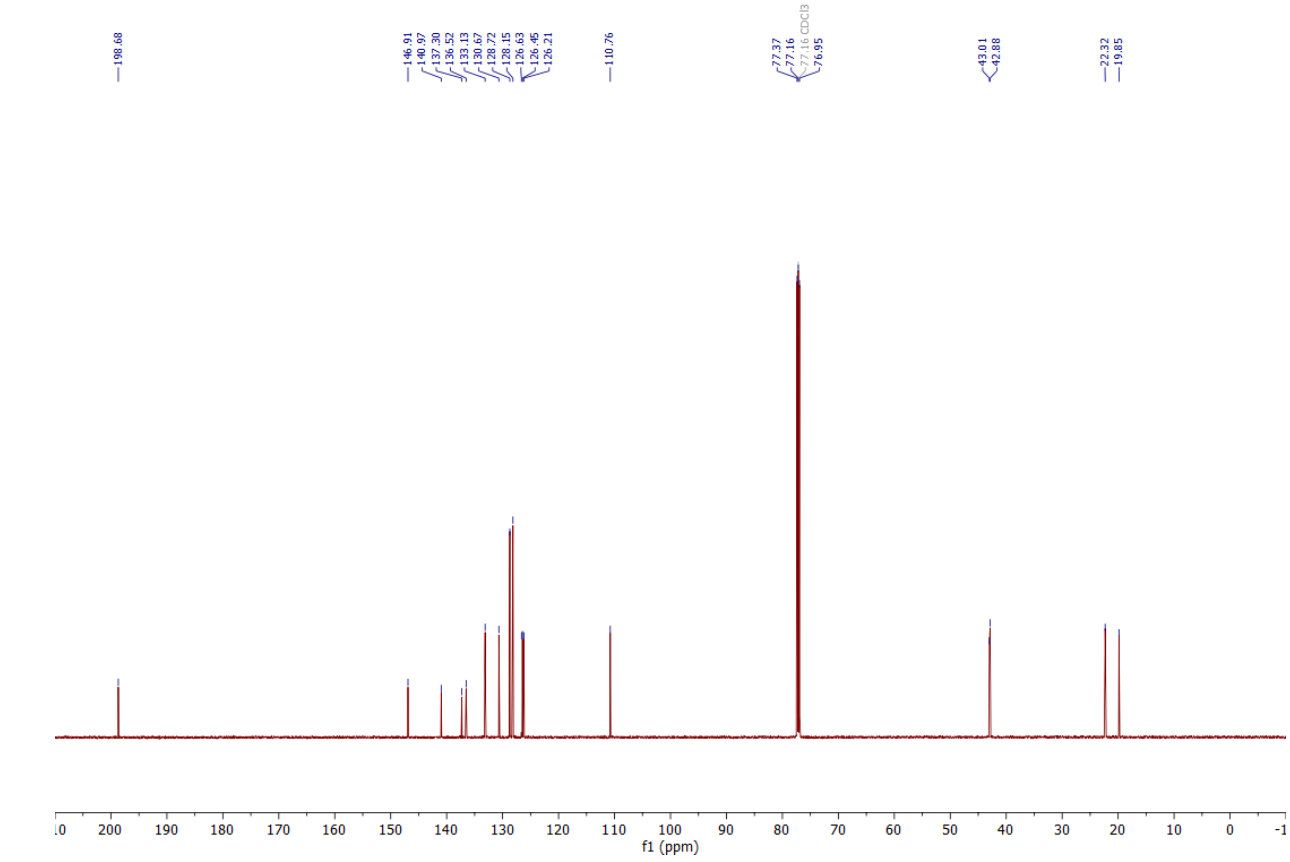


NMR spectra of (*R*)-4-methyl-1-phenyl-3-(*m*-tolyl)pent-4-en-1-one (3d)

^{1}H NMR with $CDCl_3$, 600 MHz

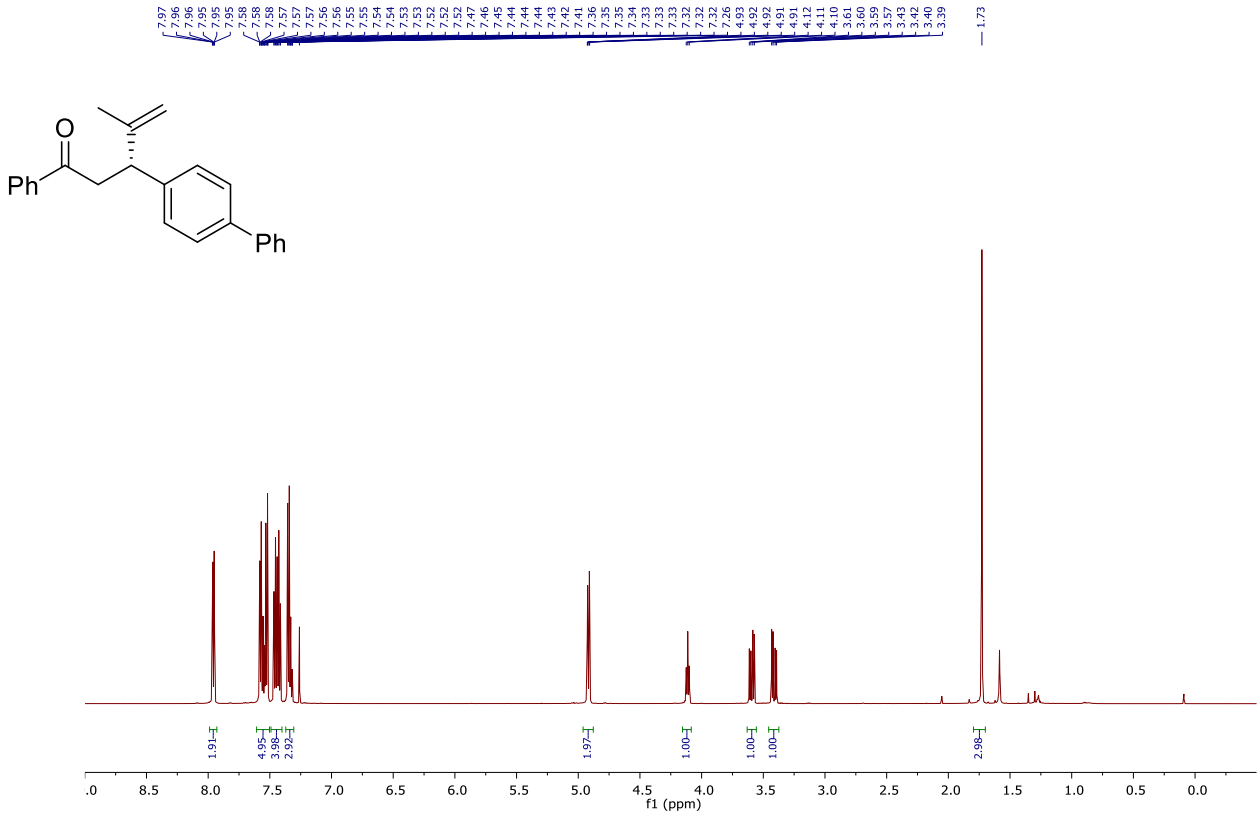


^{13}C NMR with $CDCl_3$, 151 MHz

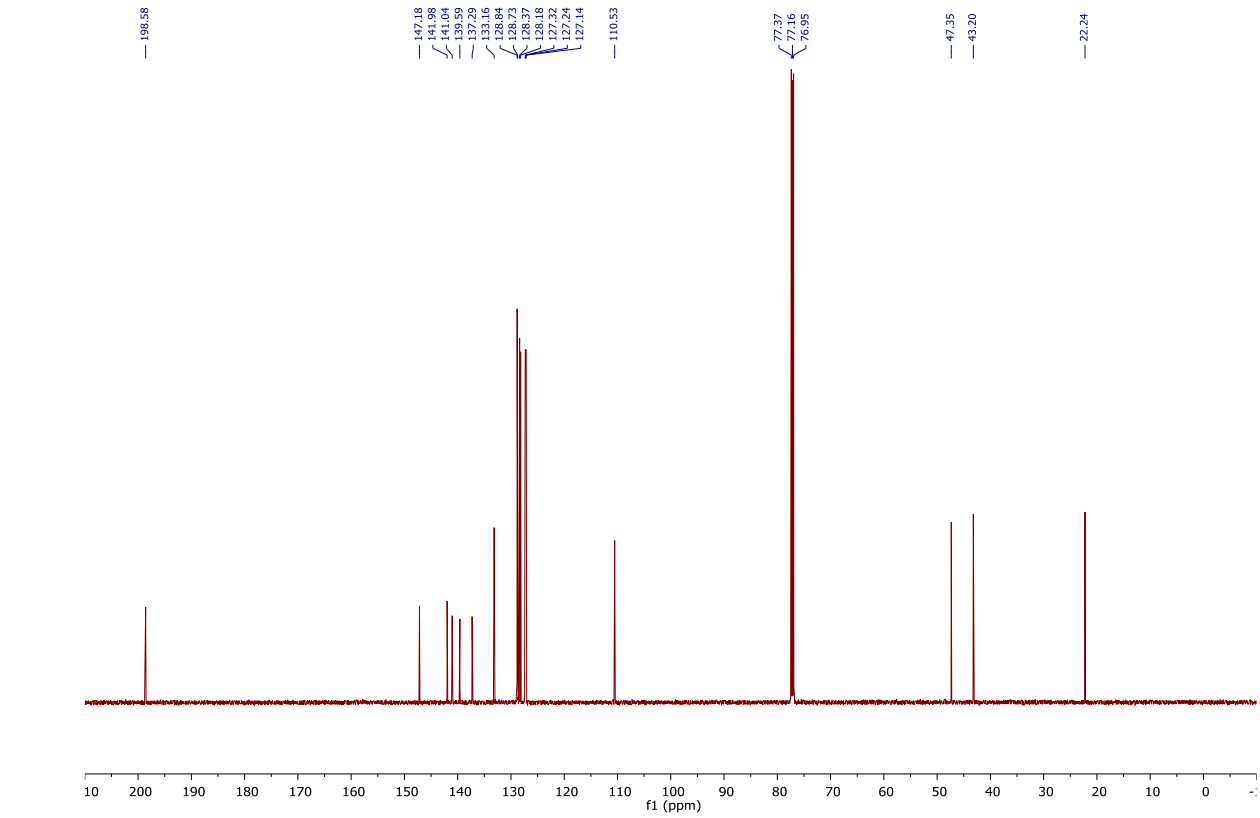


NMR spectra of (*R*)-3-([1,1'-biphenyl]-4-yl)-4-methyl-1-phenylpent-4-en-1-one (3e)

^{1}H NMR with $CDCl_3$, 600 MHz

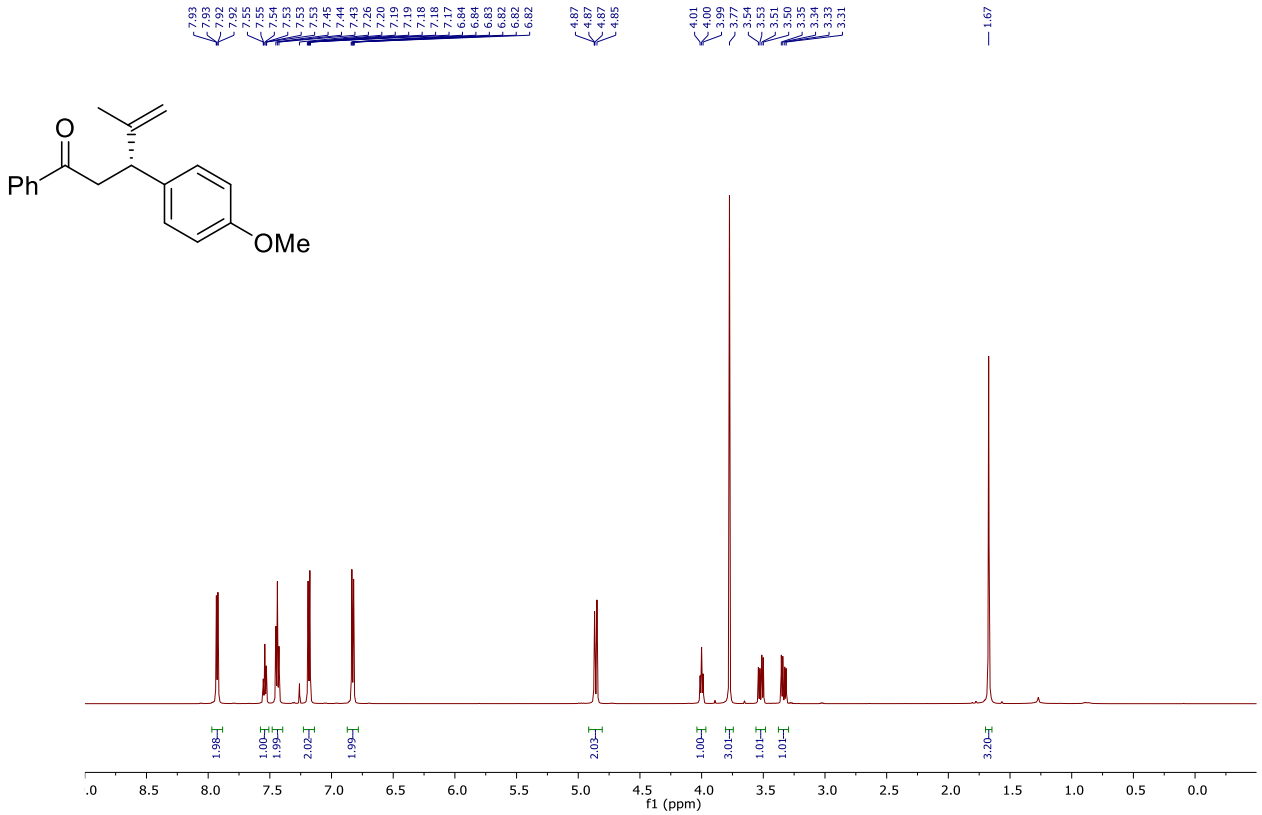


^{13}C NMR with $CDCl_3$, 151 MHz

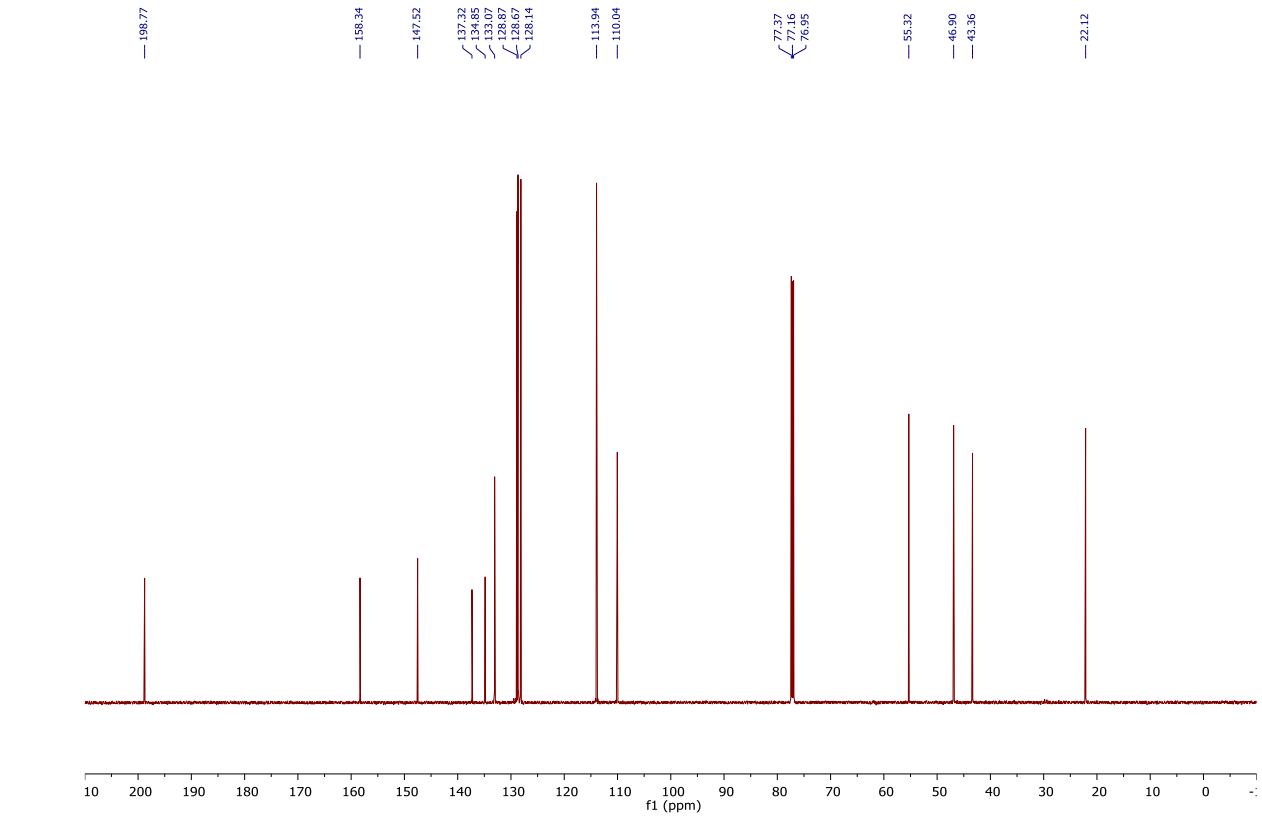


NMR spectra of (*R*)-4-methyl-1,3-diphenylpent-4-en-1-one (3f)

^{1}H NMR with $CDCl_3$, 600 MHz

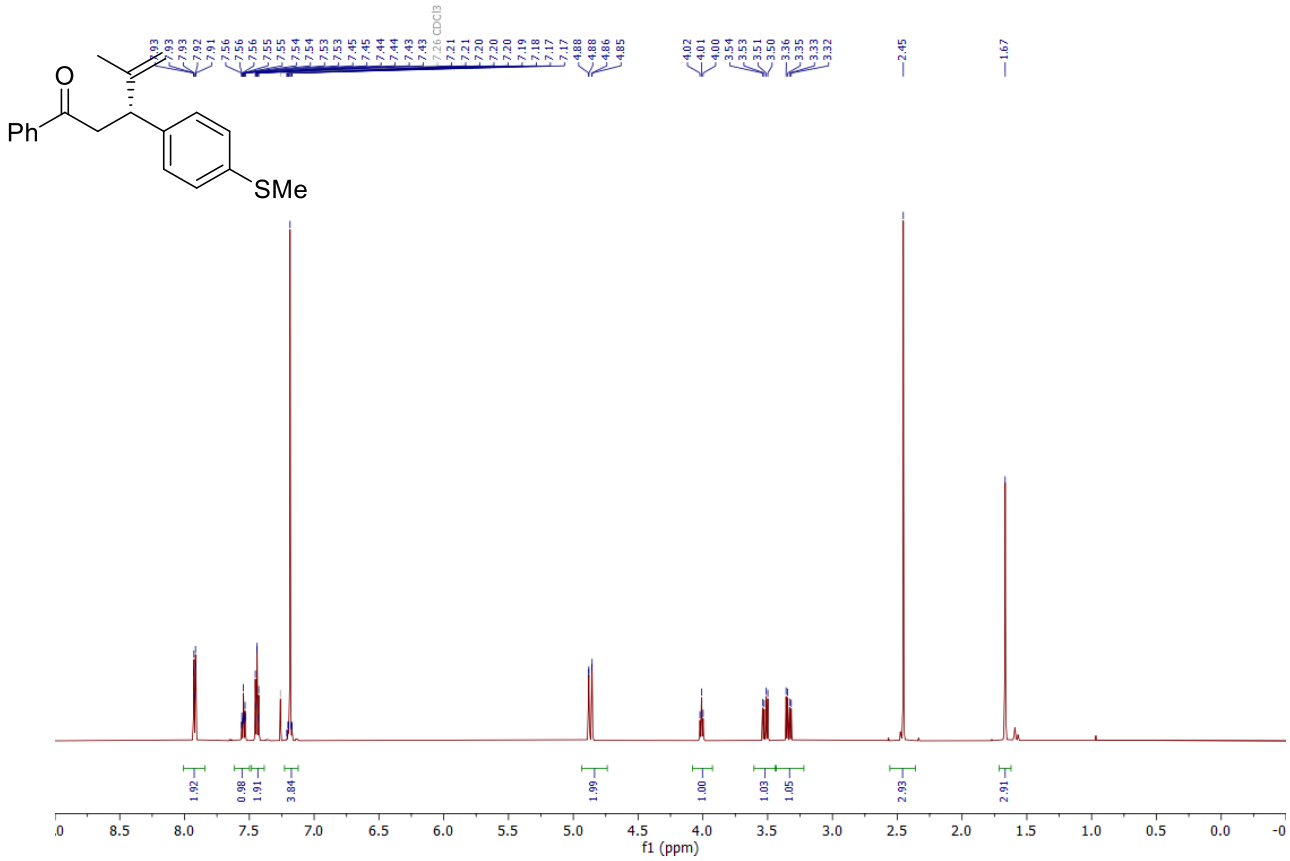


^{13}C NMR with $CDCl_3$, 151 MHz

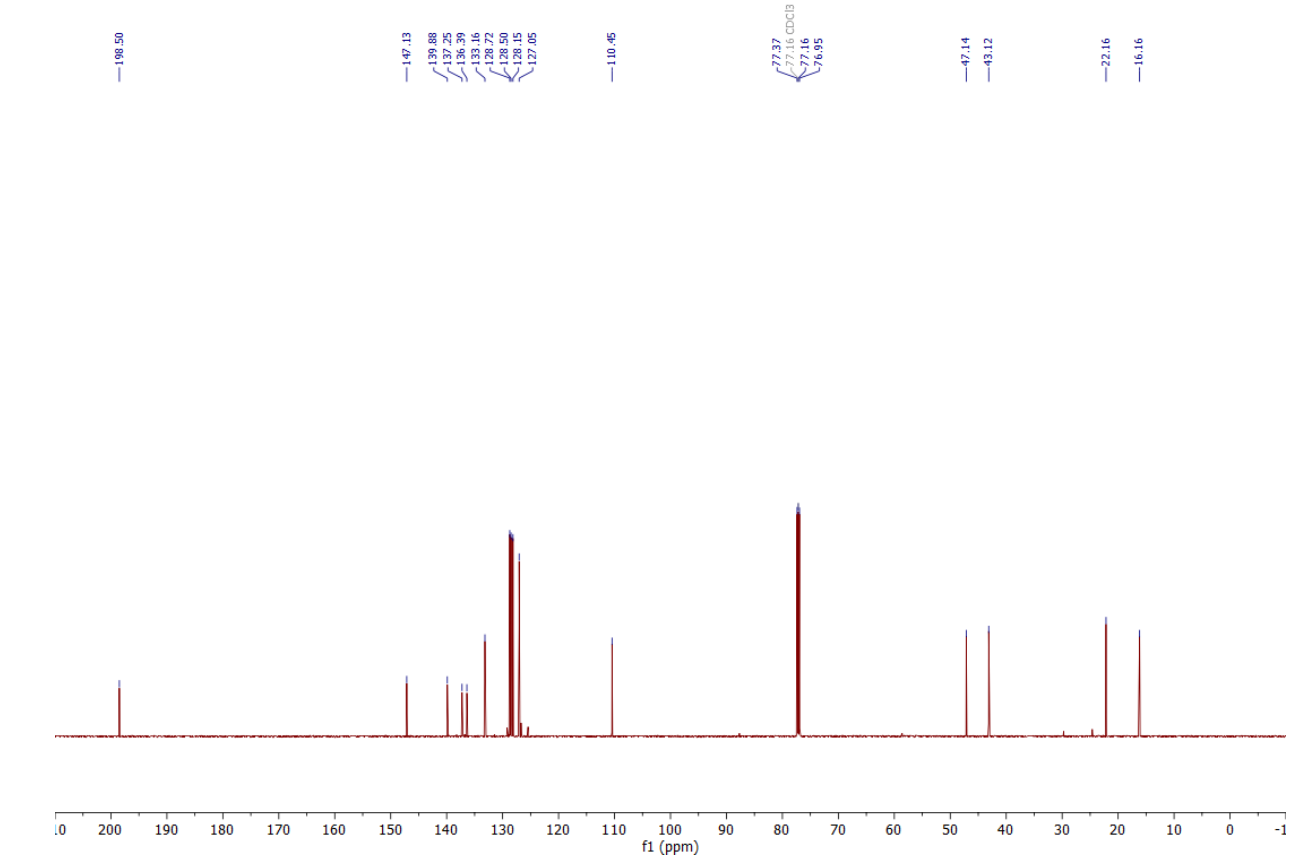


NMR spectra of (*R*)-4-methyl-3-(4-(methylthio)phenyl)-1-phenylpent-4-en-1-one (3g)

^{1}H NMR with $CDCl_3$, 600 MHz

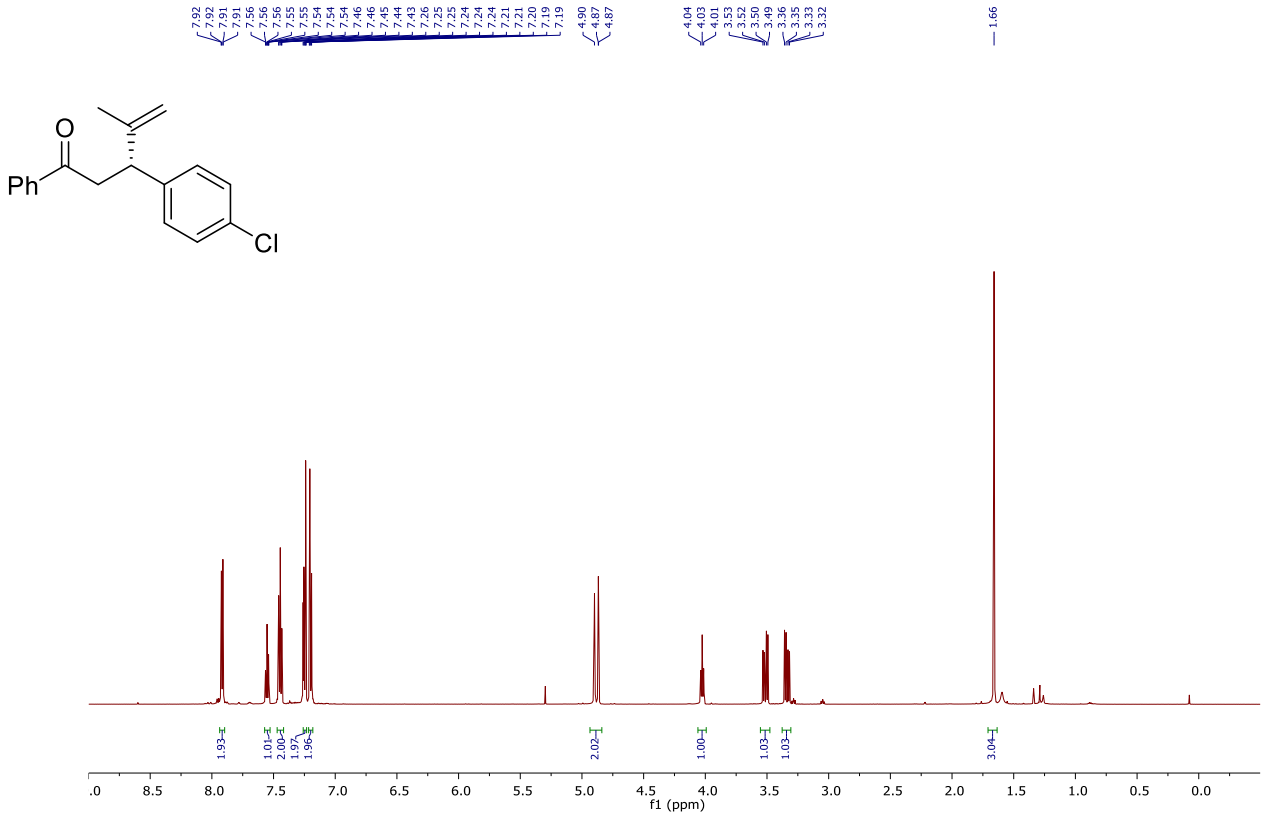


^{13}C NMR with $CDCl_3$, 151 MHz

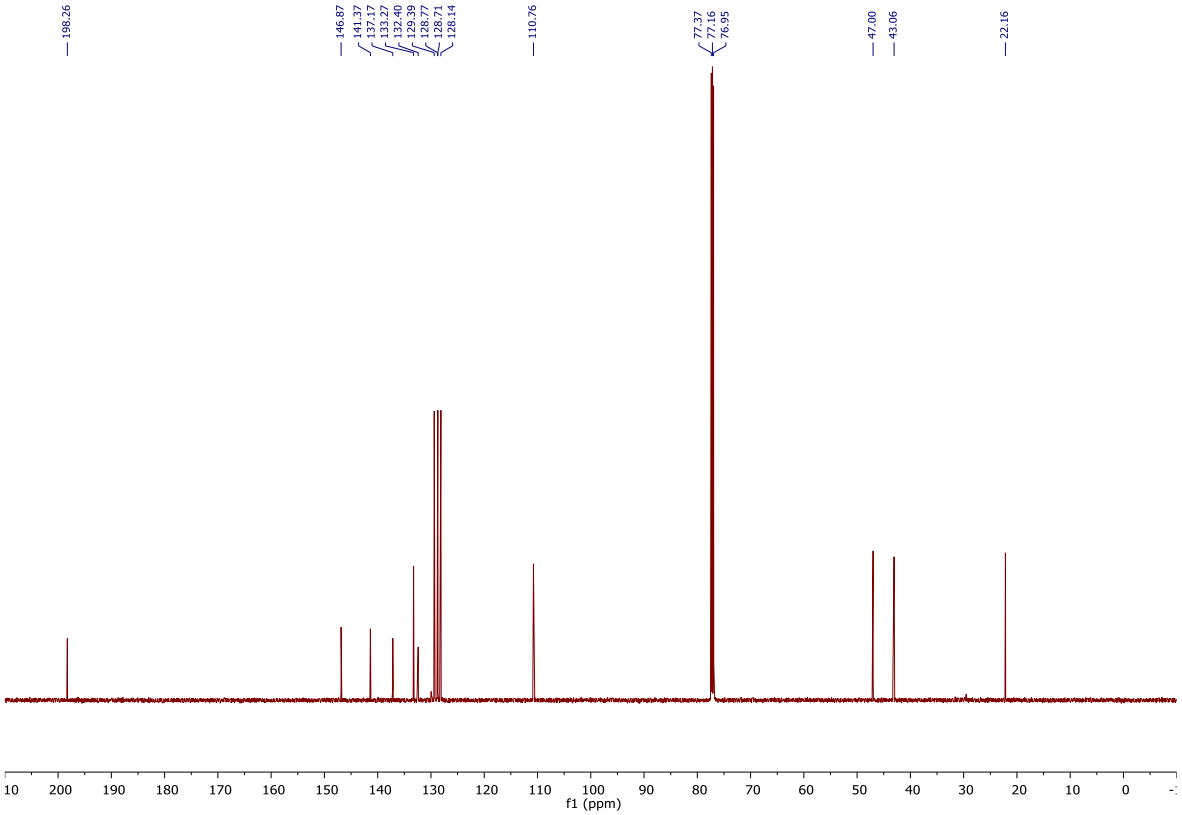


NMR spectra of (*R*)-3-(4-Chlorophenyl)-4-methyl-1-phenylpent-4-en-1-one (3h)

^{1}H NMR with $CDCl_3$, 600 MHz

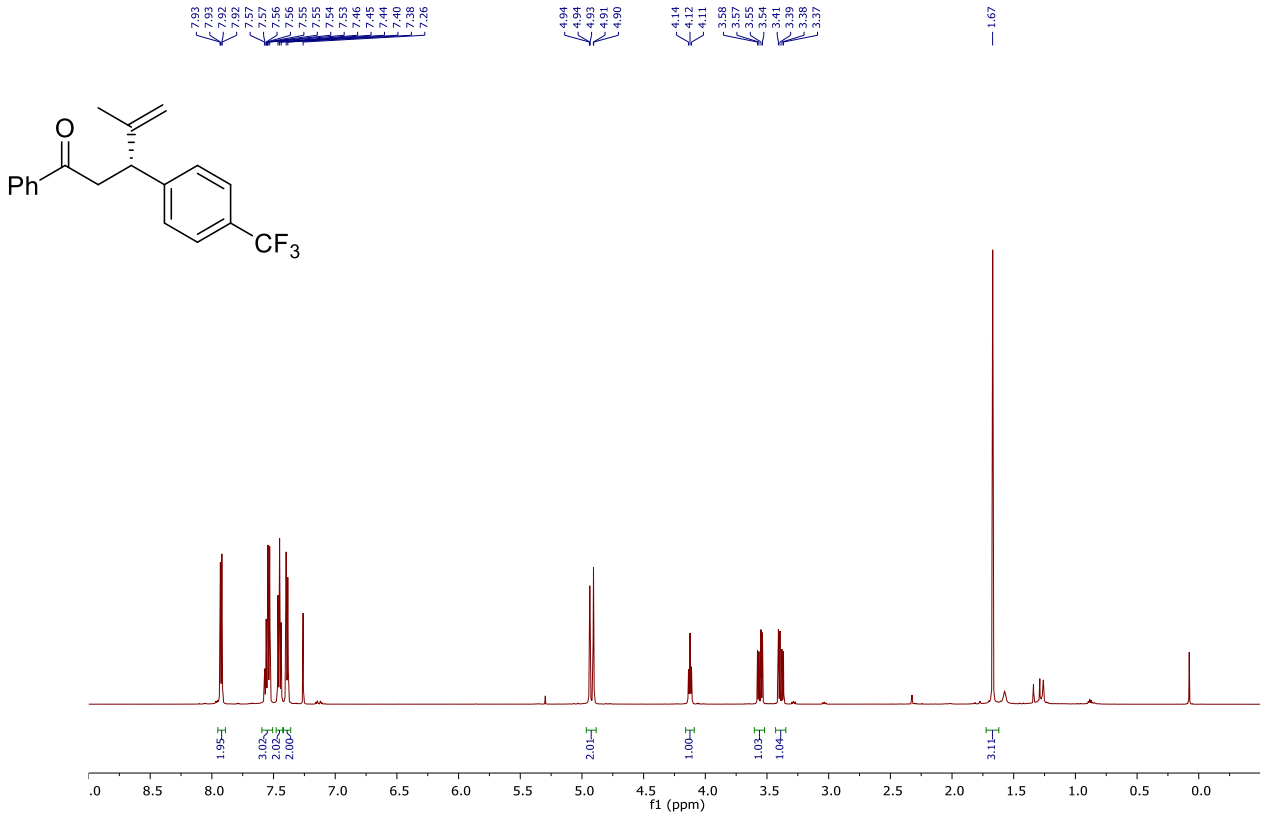


^{13}C NMR with $CDCl_3$, 151 MHz

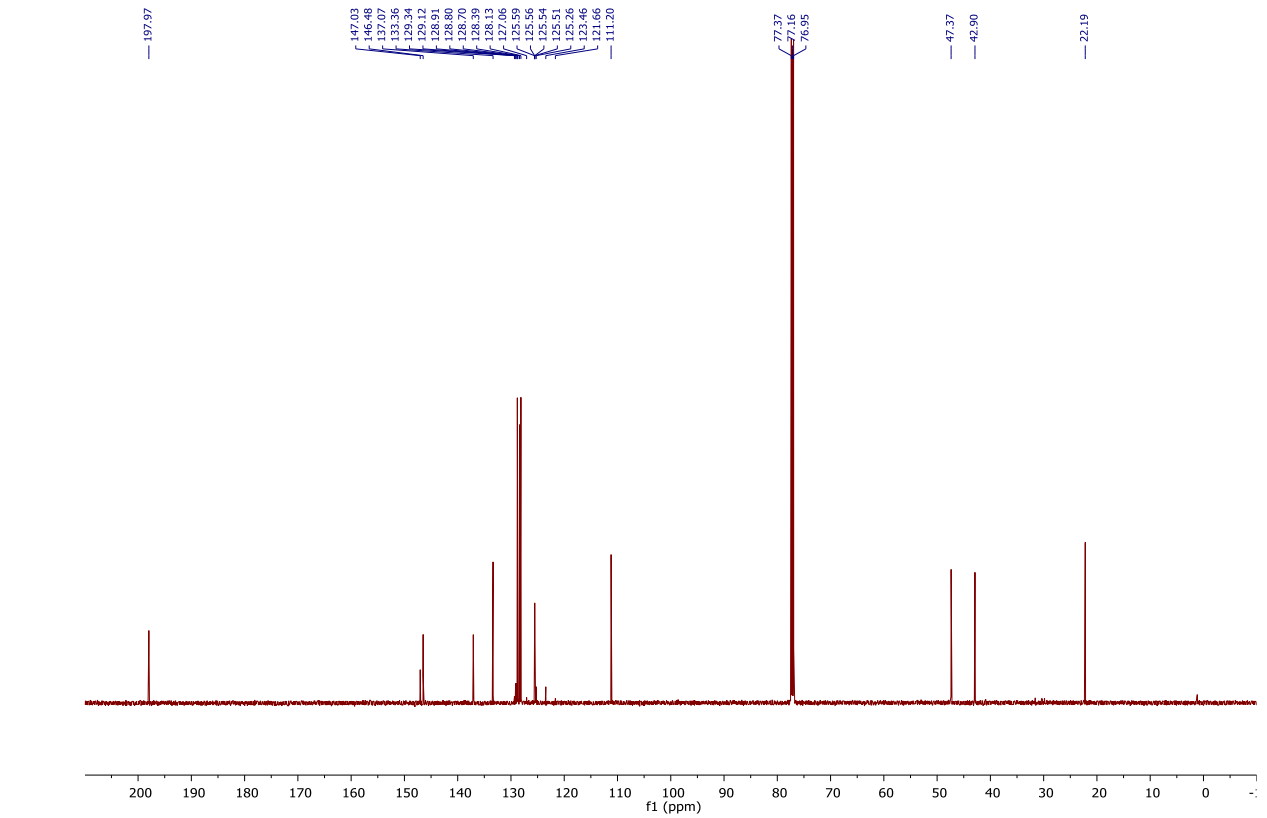


NMR spectra of (*R*)-4-methyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (3i)

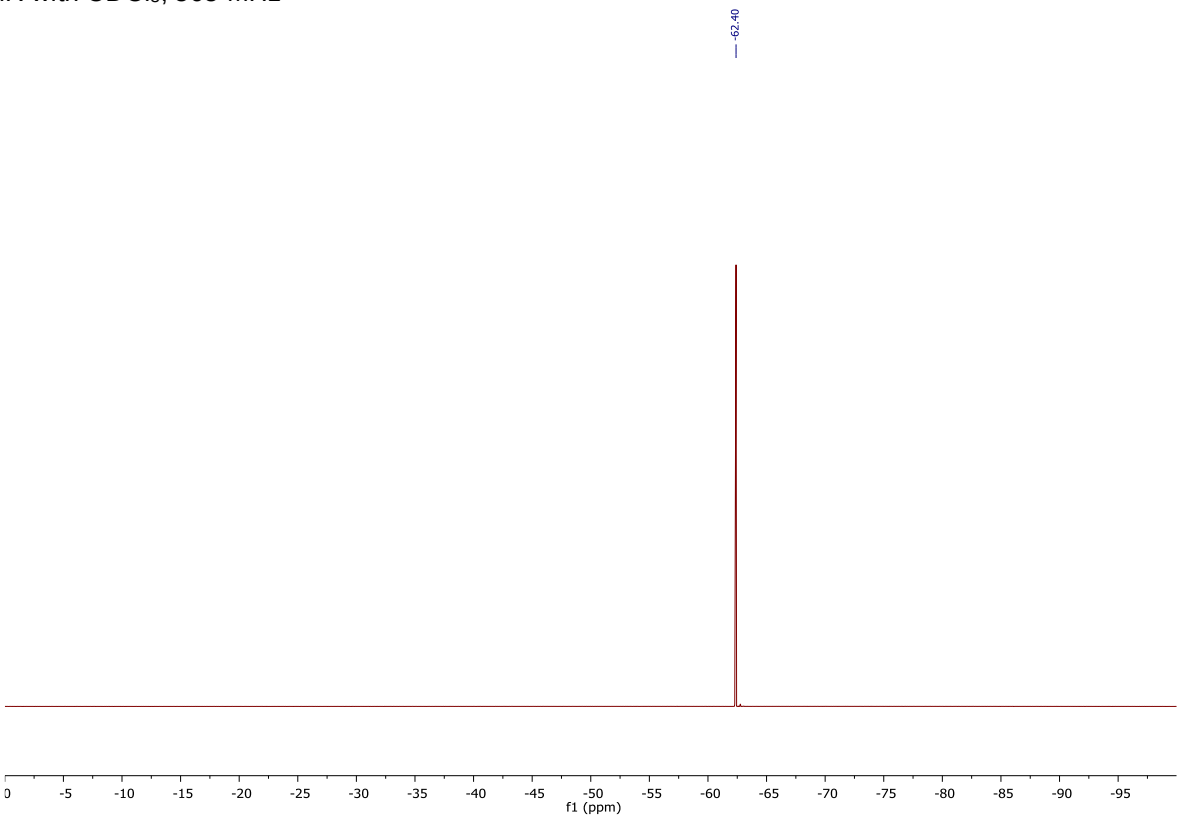
^{1}H NMR with $CDCl_3$, 600 MHz



^{13}C NMR with $CDCl_3$, 151 MHz

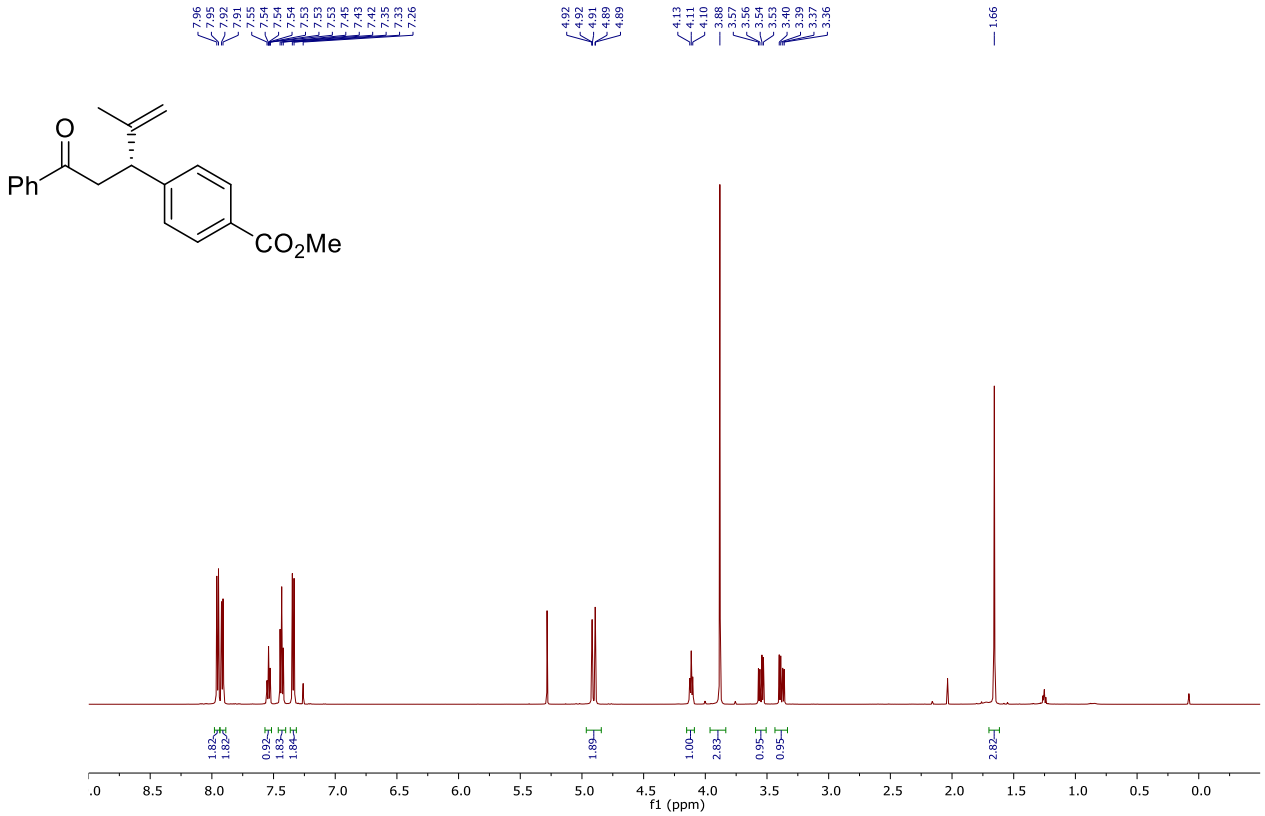


^{19}F NMR with $CDCl_3$, 565 MHz

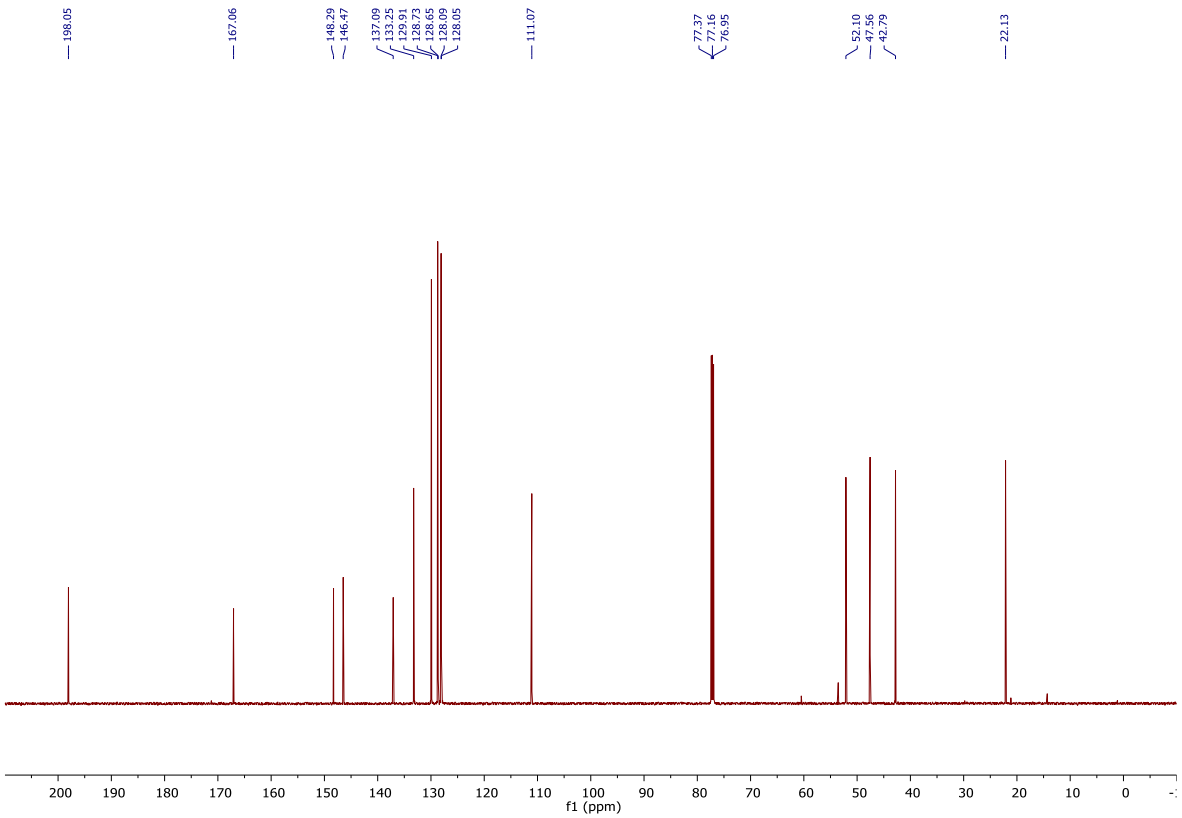


NMR spectra of methyl (*R*)-4-(2-methyl-5-oxo-5-phenylpent-1-en-3-yl)benzoate (3j)

^{1}H NMR with $CDCl_3$, 600 MHz

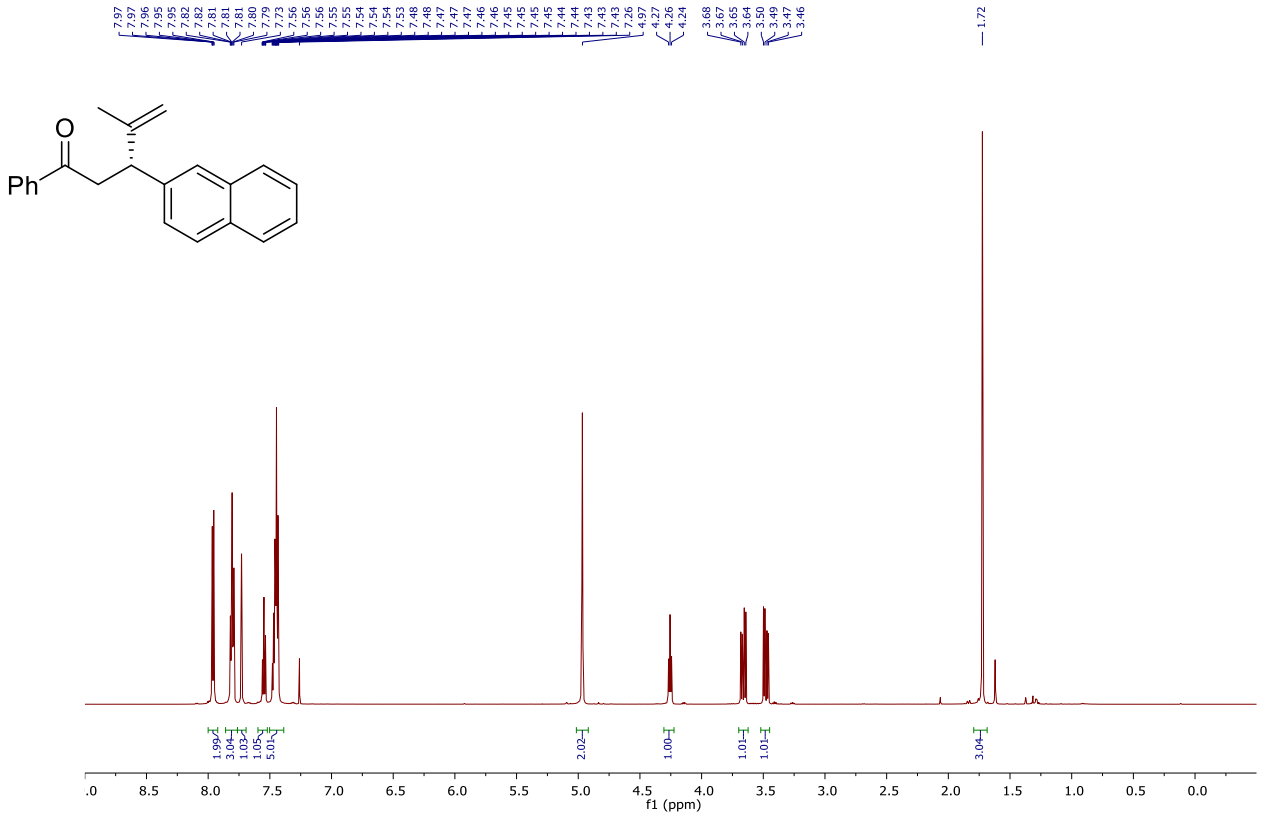


^{13}C NMR with $CDCl_3$, 151 MHz

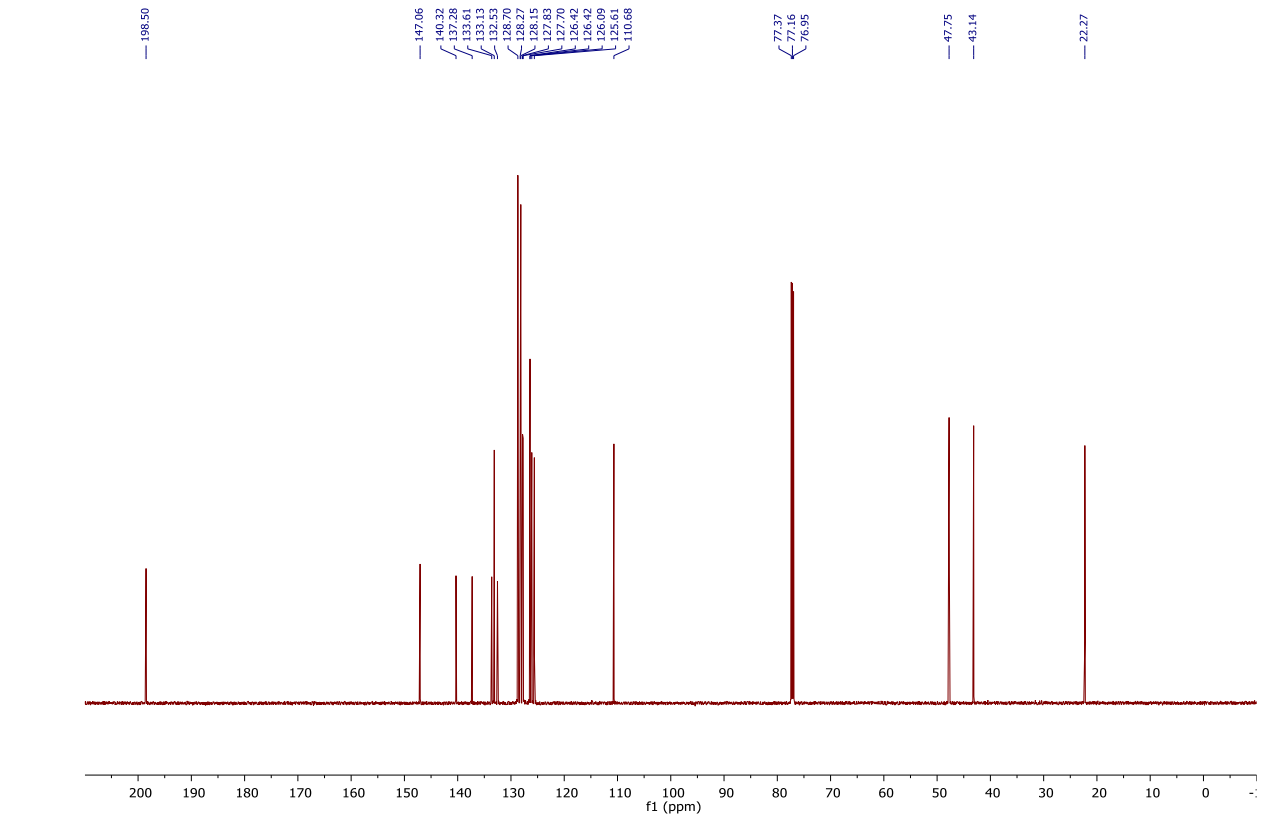


NMR spectra of (*R*)-4-methyl-3-(naphthalen-2-yl)-1-phenylpent-4-en-1-one (3k)

^{1}H NMR with $CDCl_3$, 600 MHz

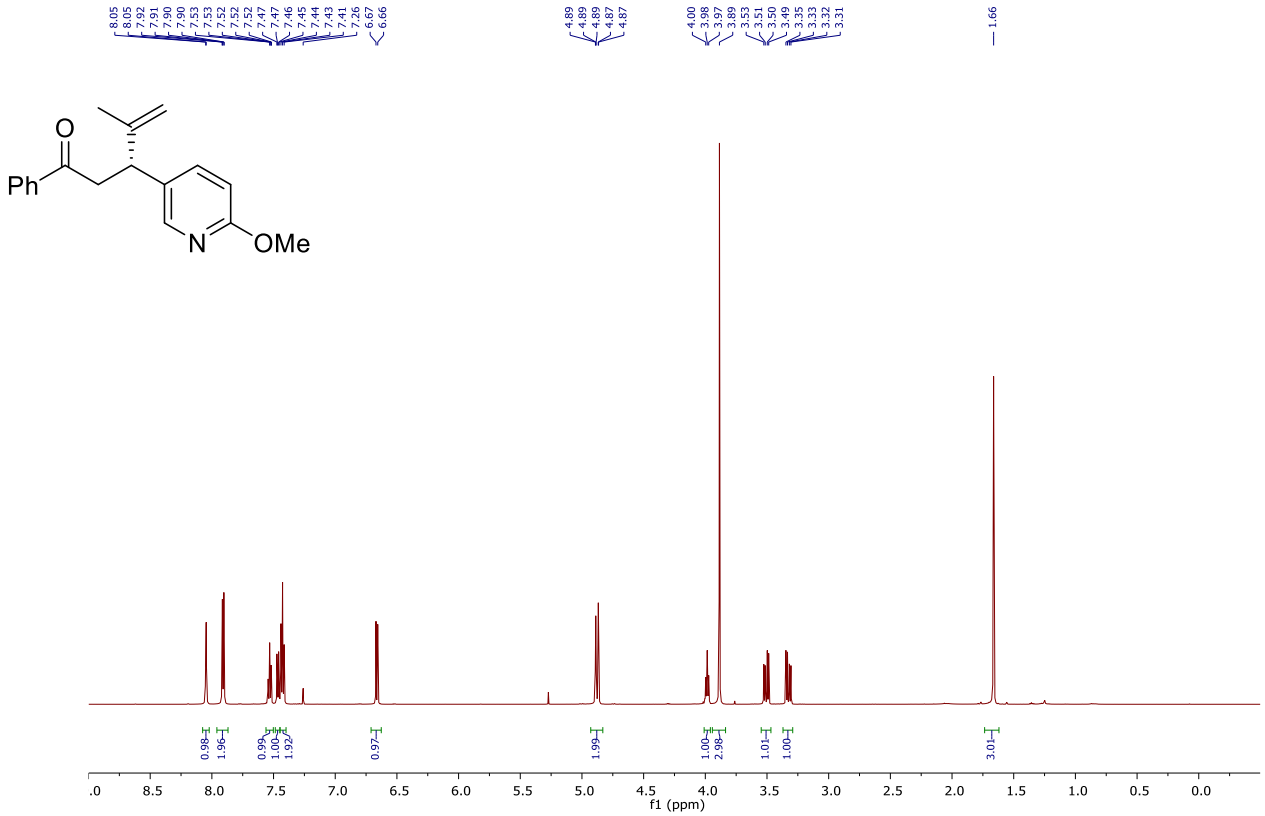


^{13}C NMR with $CDCl_3$, 151 MHz

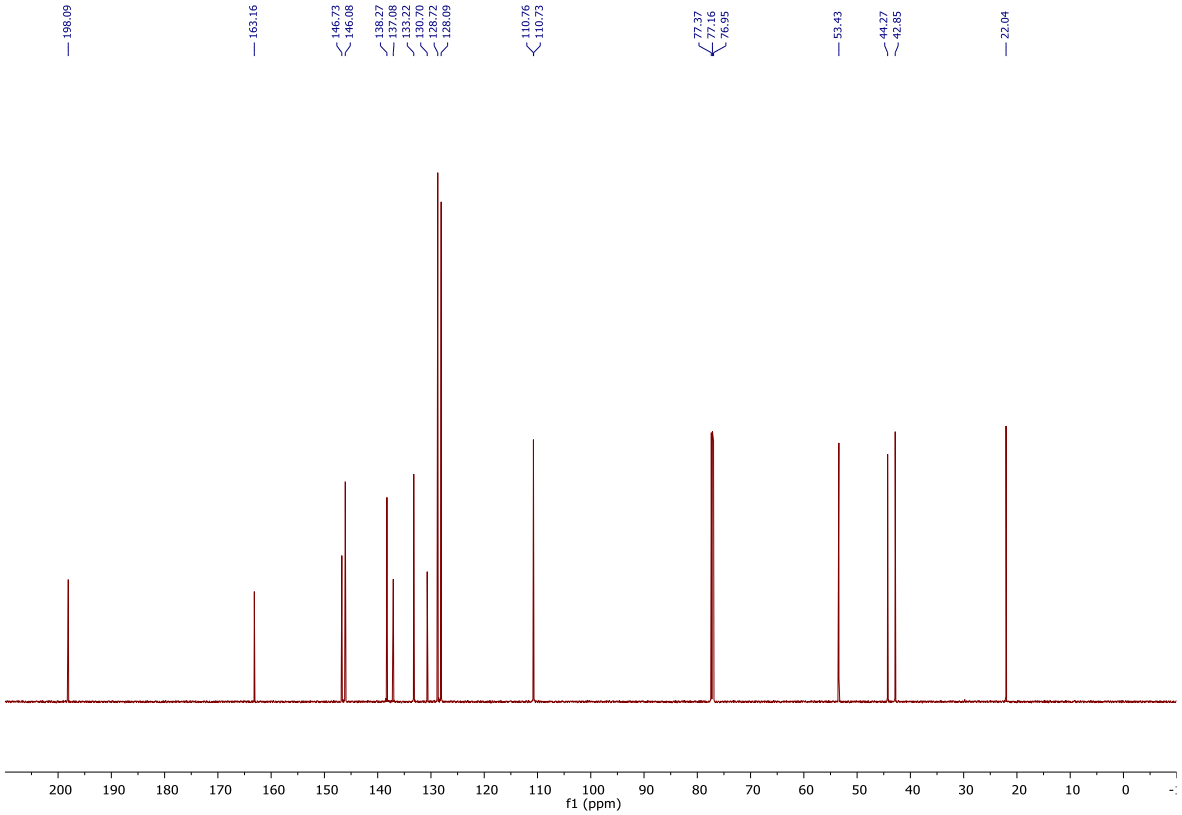


NMR spectra of (*R*)-3-(6-Methoxypyridin-3-yl)-4-methyl-1-phenylpent-4-en-1-one (3l)

^{1}H NMR with $CDCl_3$, 600 MHz

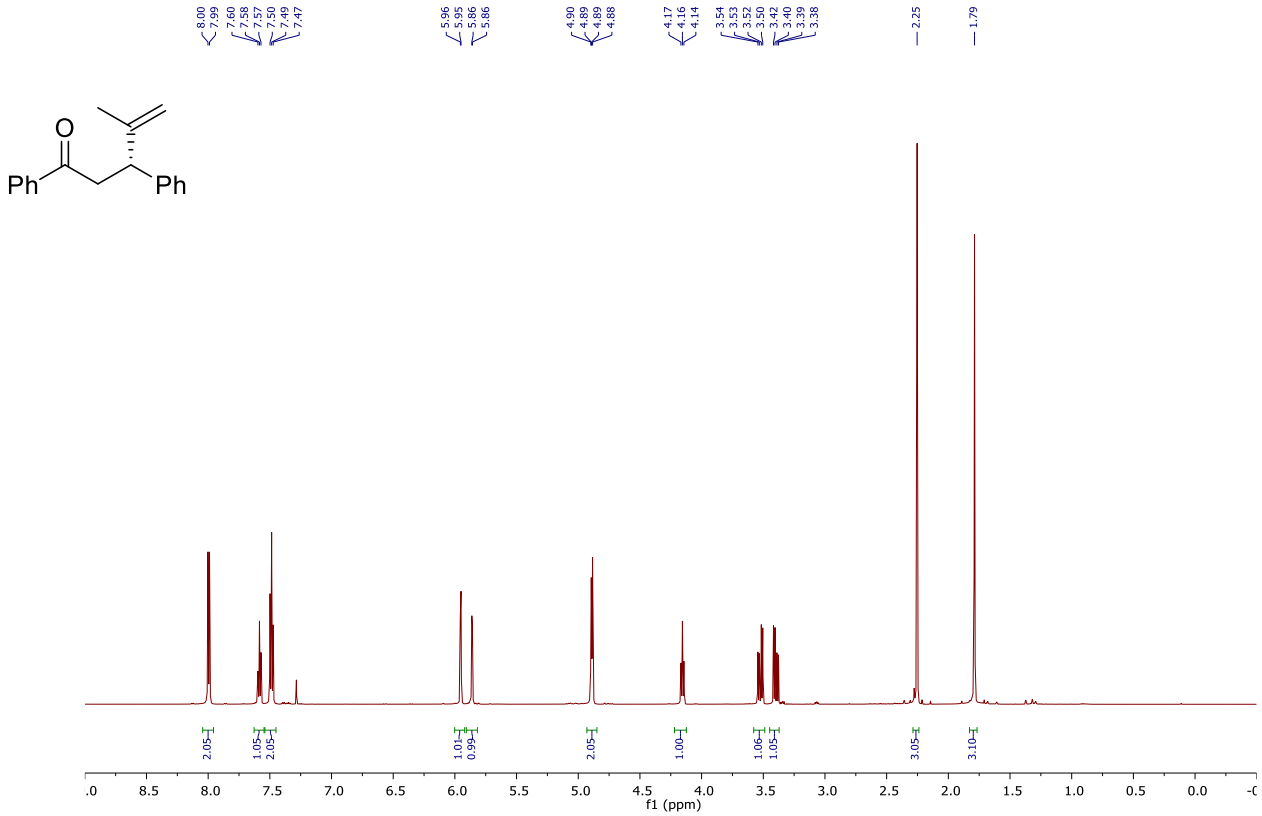


^{13}C NMR with $CDCl_3$, 151 MHz

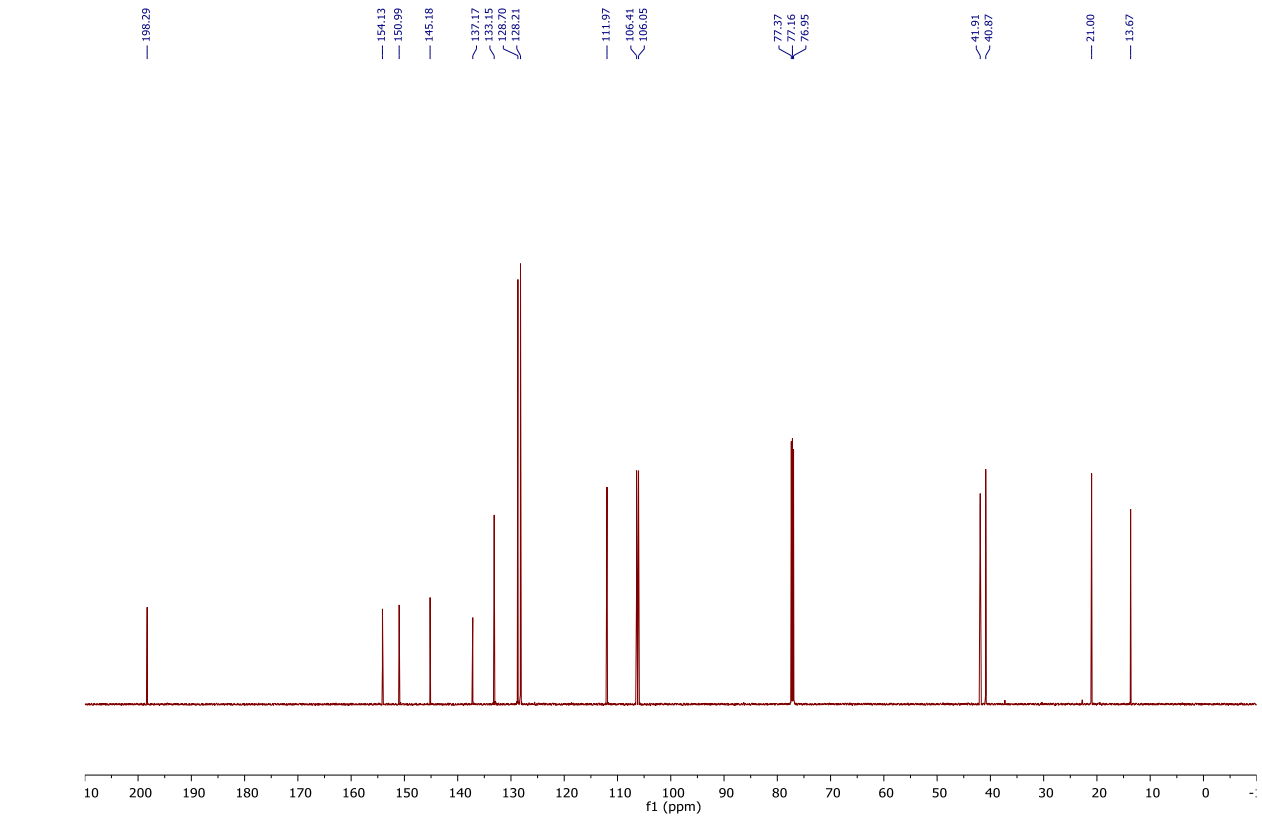


NMR spectra of (*R*)-4-methyl-3-(5-methylfuran-2-yl)-1-phenylpent-4-en-1-one (3m)

^{1}H NMR with $CDCl_3$, 600 MHz

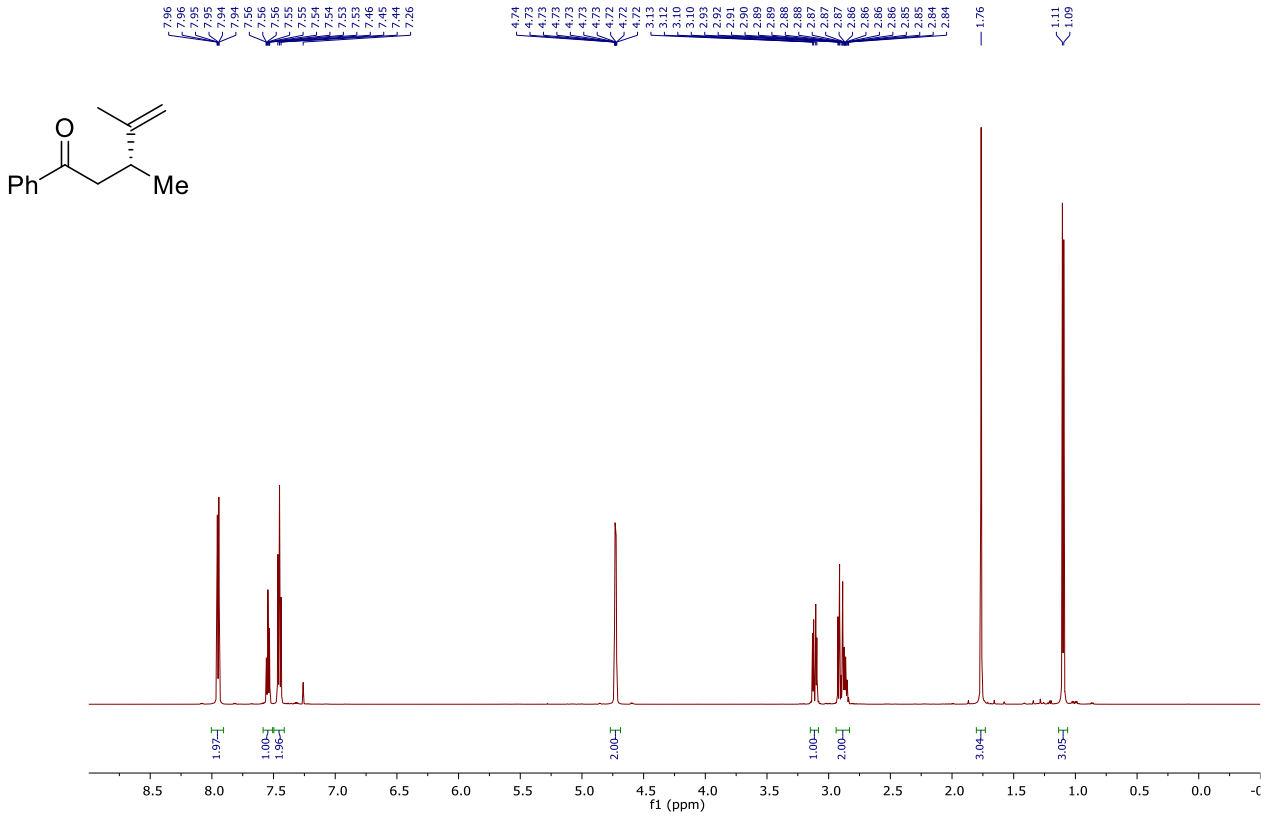


^{13}C NMR with $CDCl_3$, 151 MHz

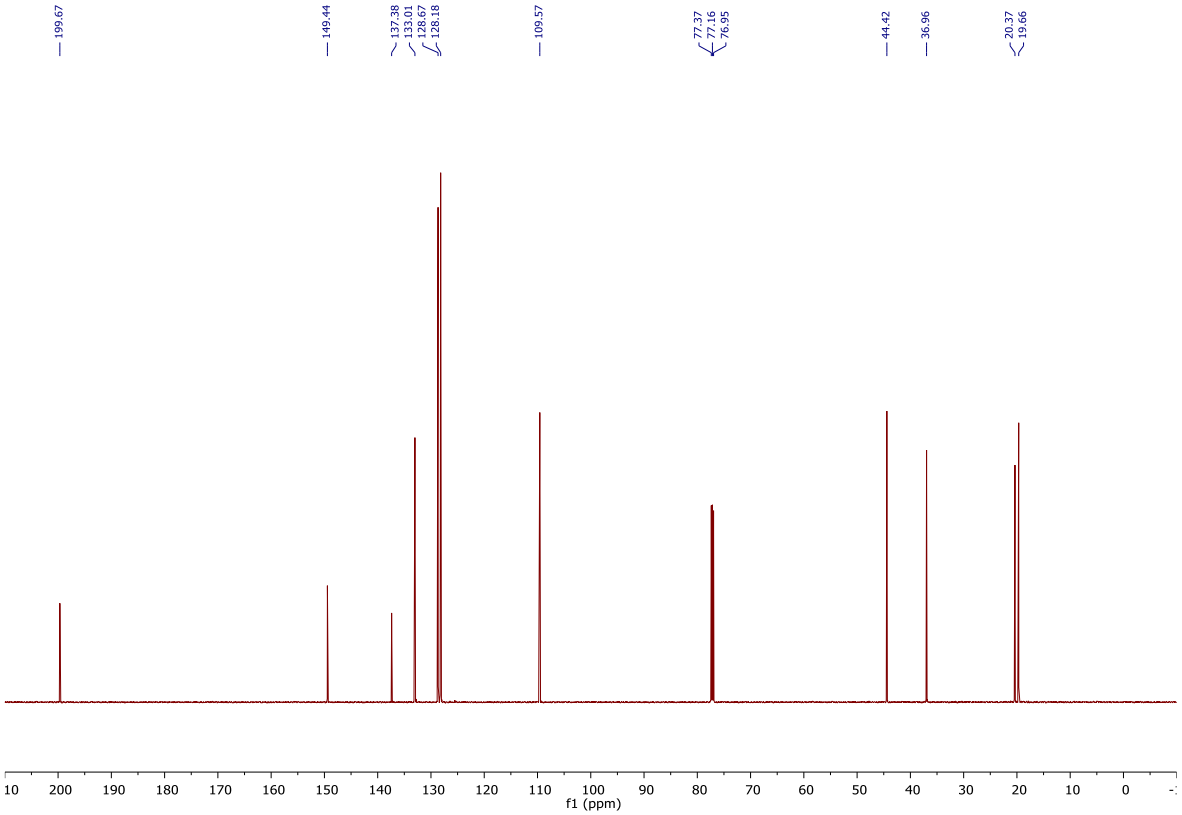


NMR spectra of (*R*)-3,4-dimethyl-1-phenylpent-4-en-1-one (3n)

^{1}H NMR with $CDCl_3$, 600 MHz

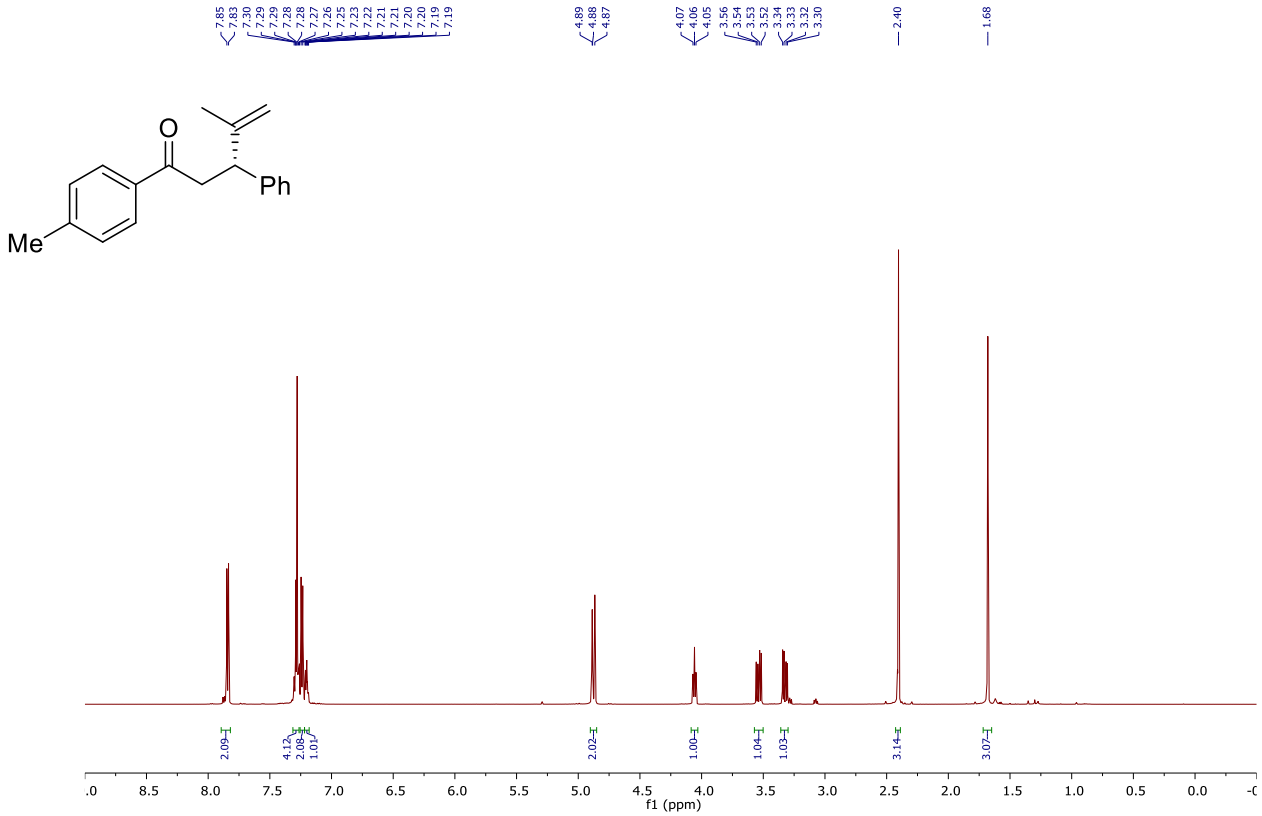


^{13}C NMR with $CDCl_3$, 151 MHz

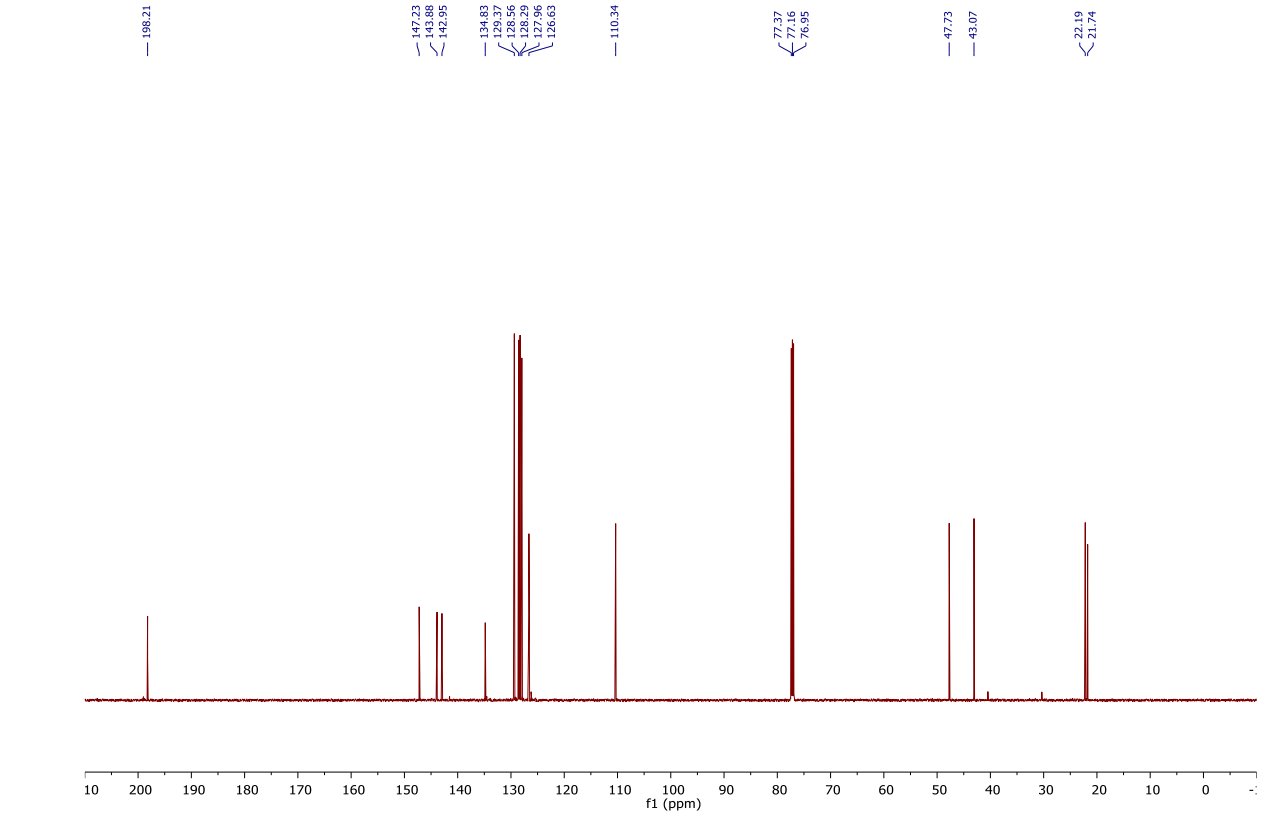


NMR spectra of (*R*)-4-methyl-3-phenyl-1-(*p*-tolyl)pent-4-en-1-one (3o)

^{1}H NMR with $CDCl_3$, 600 MHz

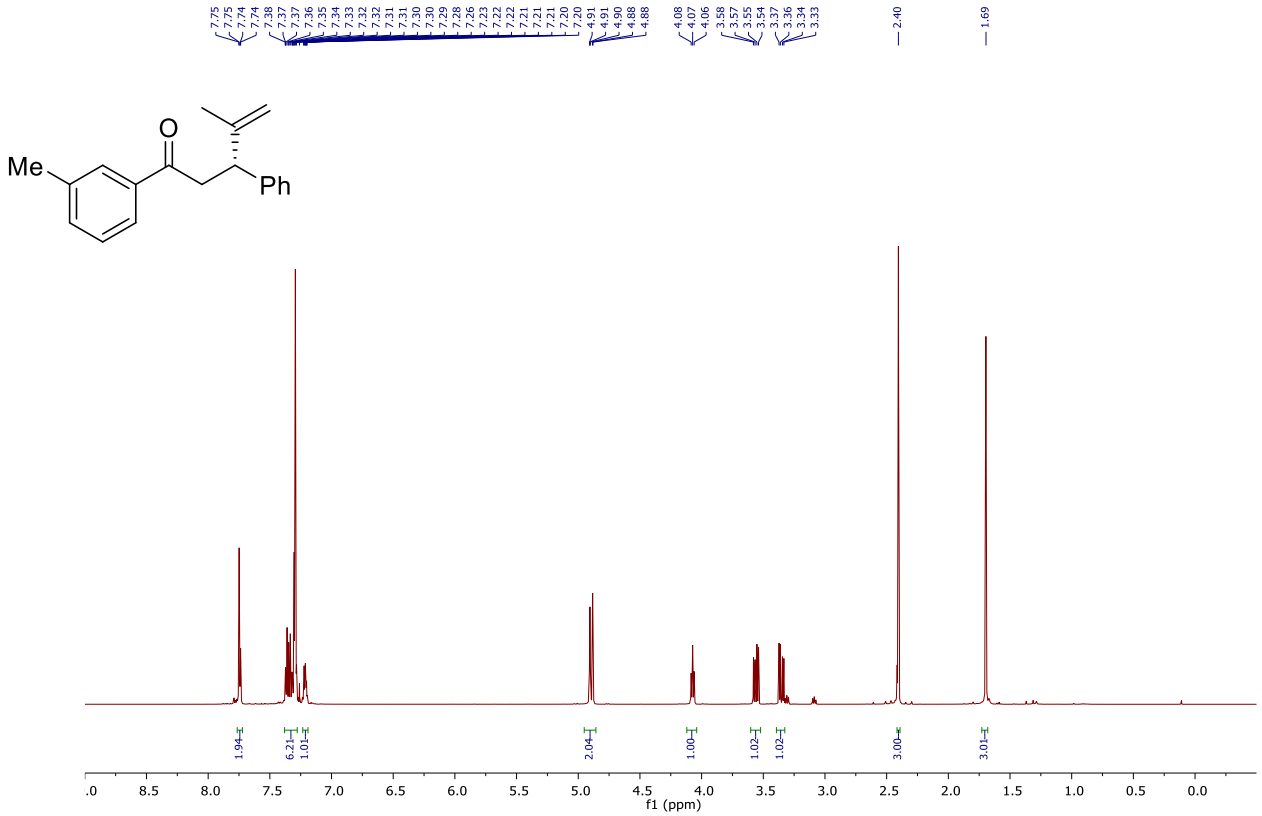


^{13}C NMR with $CDCl_3$, 151 MHz

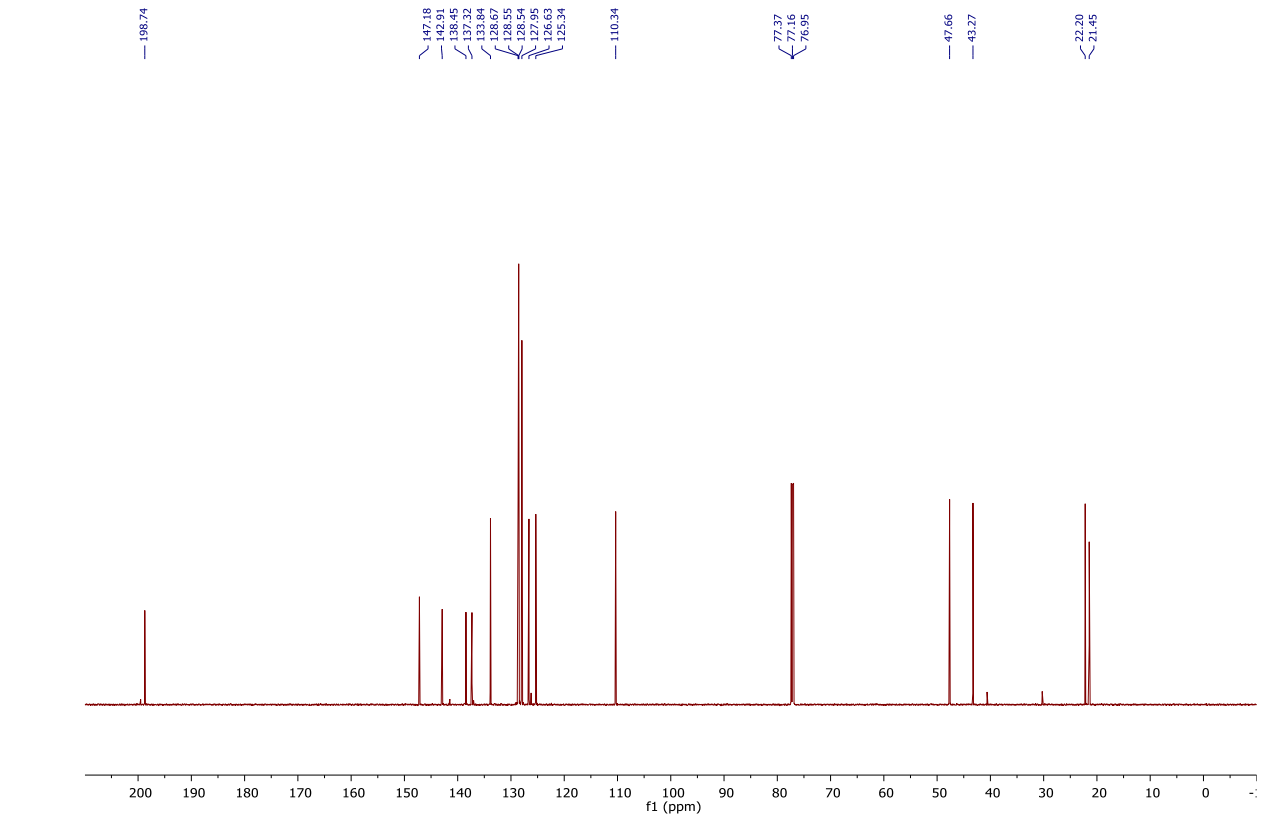


NMR spectra of (*R*)-4-methyl-3-phenyl-1-(*m*-tolyl)pent-4-en-1-one (3p)

^{1}H NMR with $CDCl_3$, 600 MHz

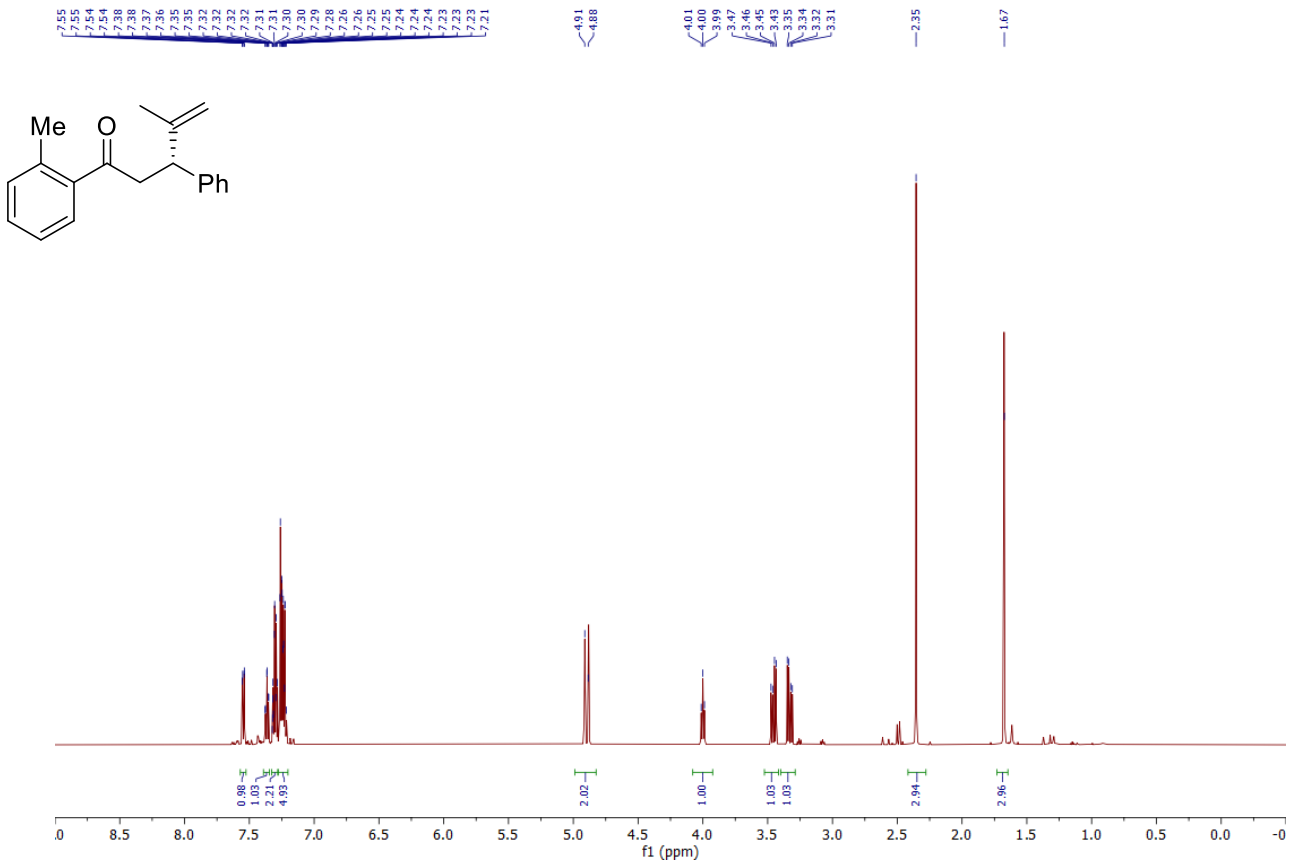


^{13}C NMR with $CDCl_3$, 151 MHz

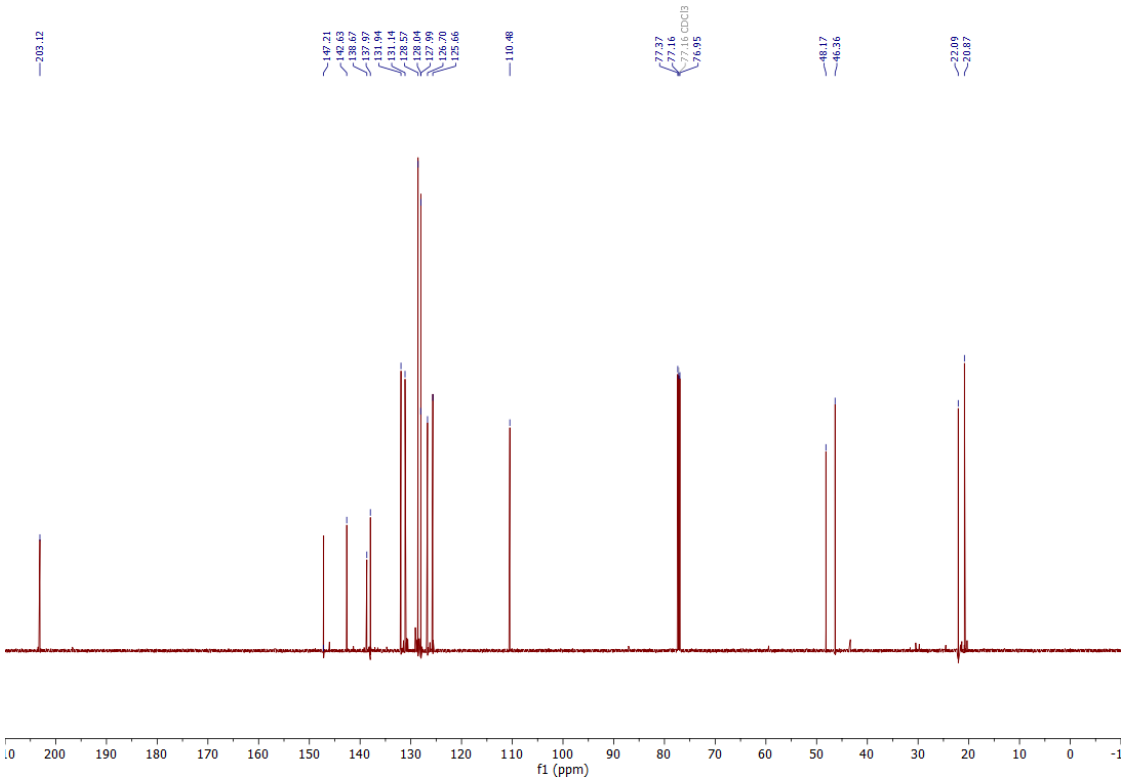


NMR spectra of (*R*)-4-methyl-3-phenyl-1-(*o*-tolyl)pent-4-en-1-one (3q)

^{1}H NMR with $CDCl_3$, 600 MHz

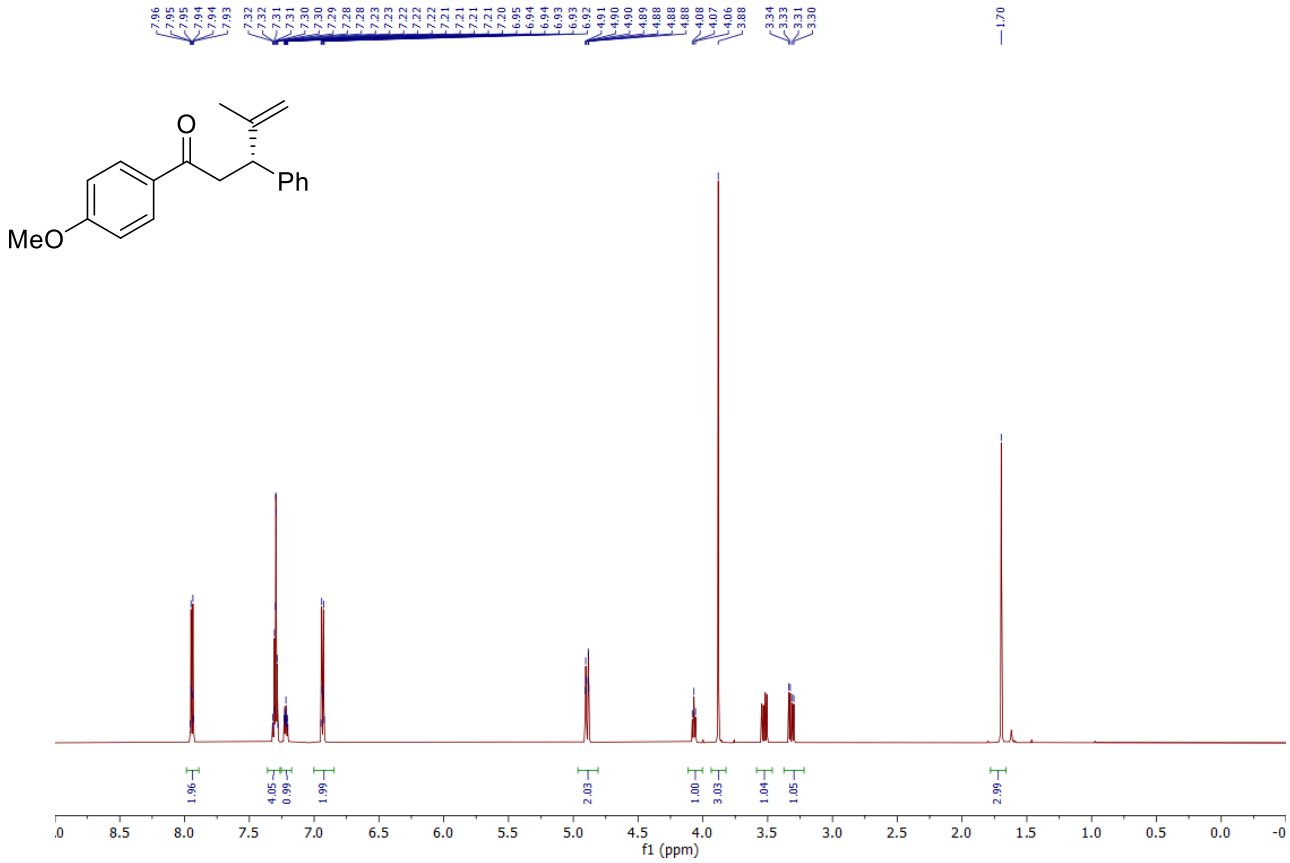


^{13}C NMR with $CDCl_3$, 151 MHz

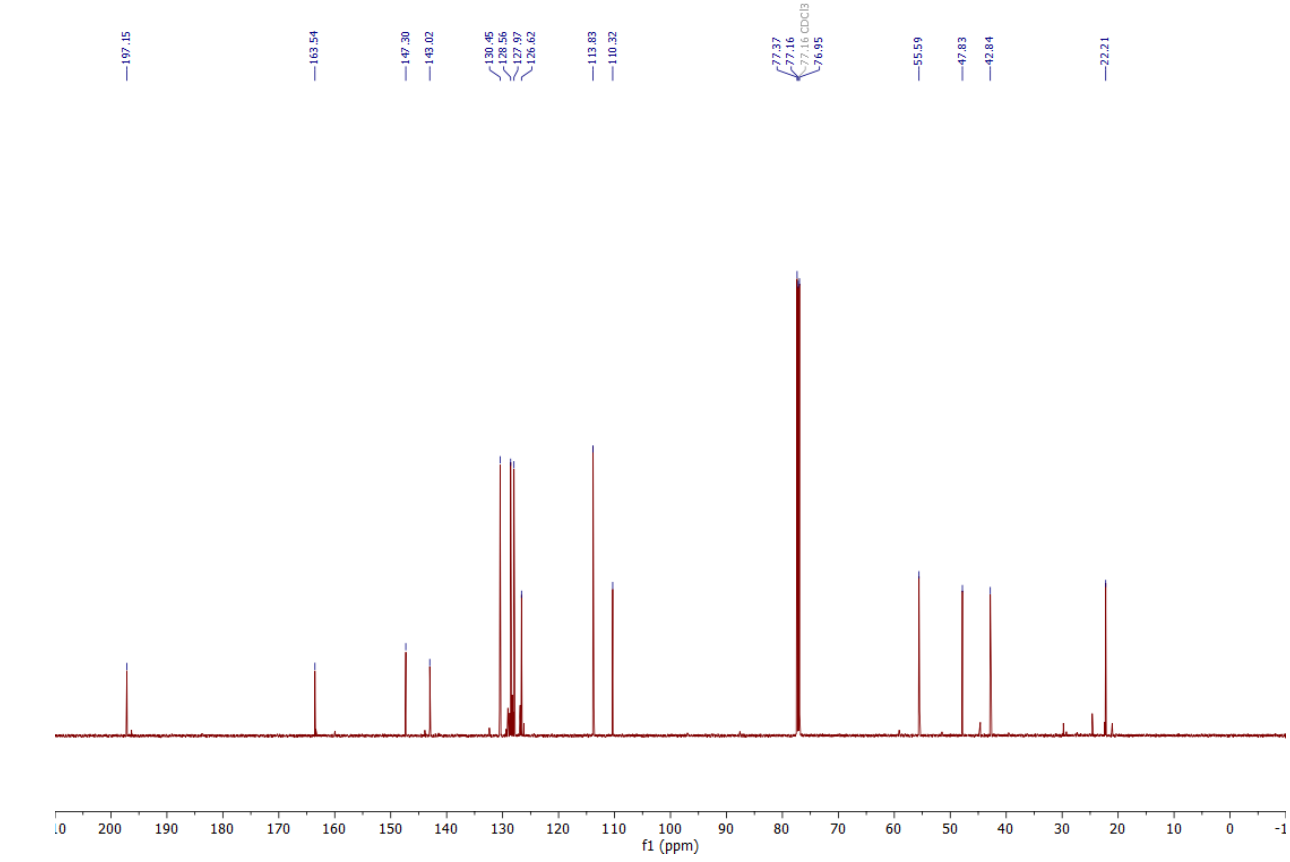


NMR spectra of (*R*)-1-(4-methoxyphenyl)-4-methyl-3-phenylpent-4-en-1-one (3r)

^{1}H NMR with $CDCl_3$, 600 MHz

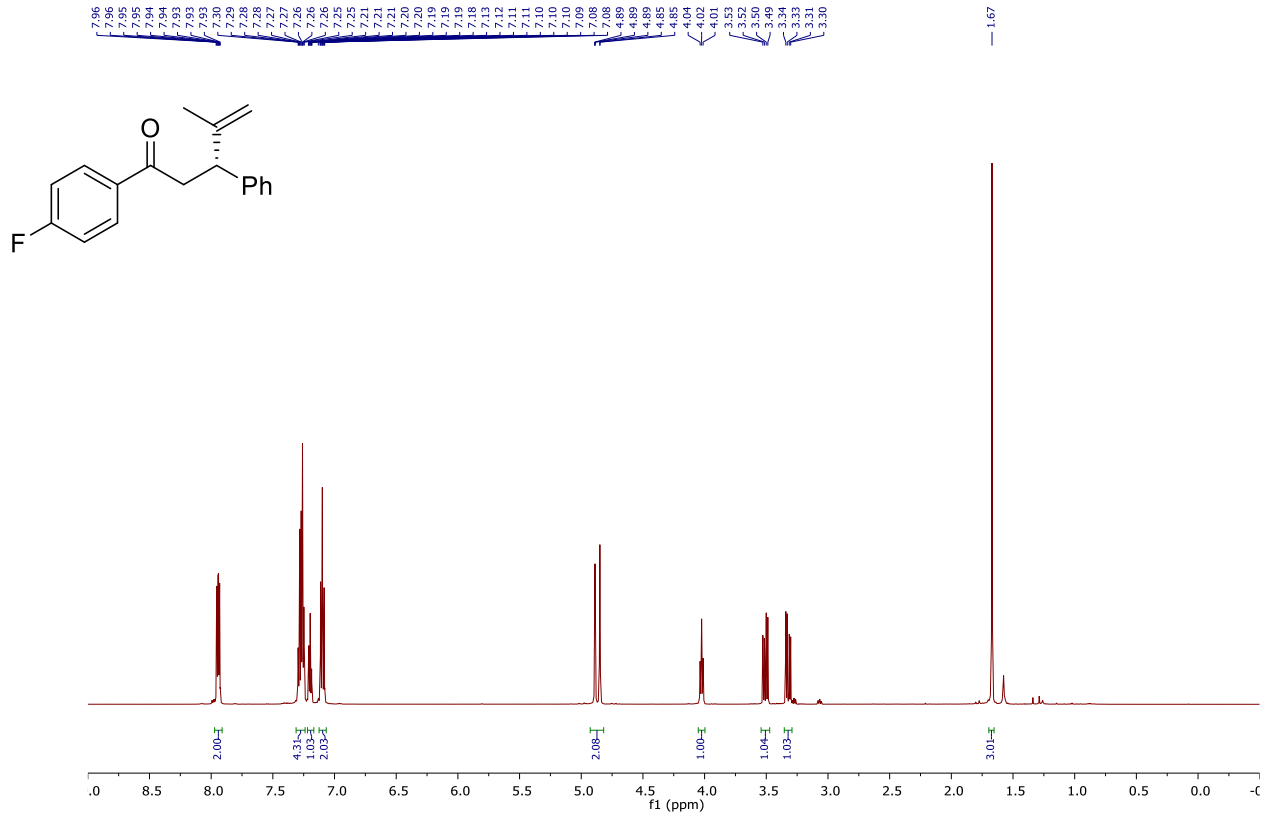


^{13}C NMR with $CDCl_3$, 151 MHz

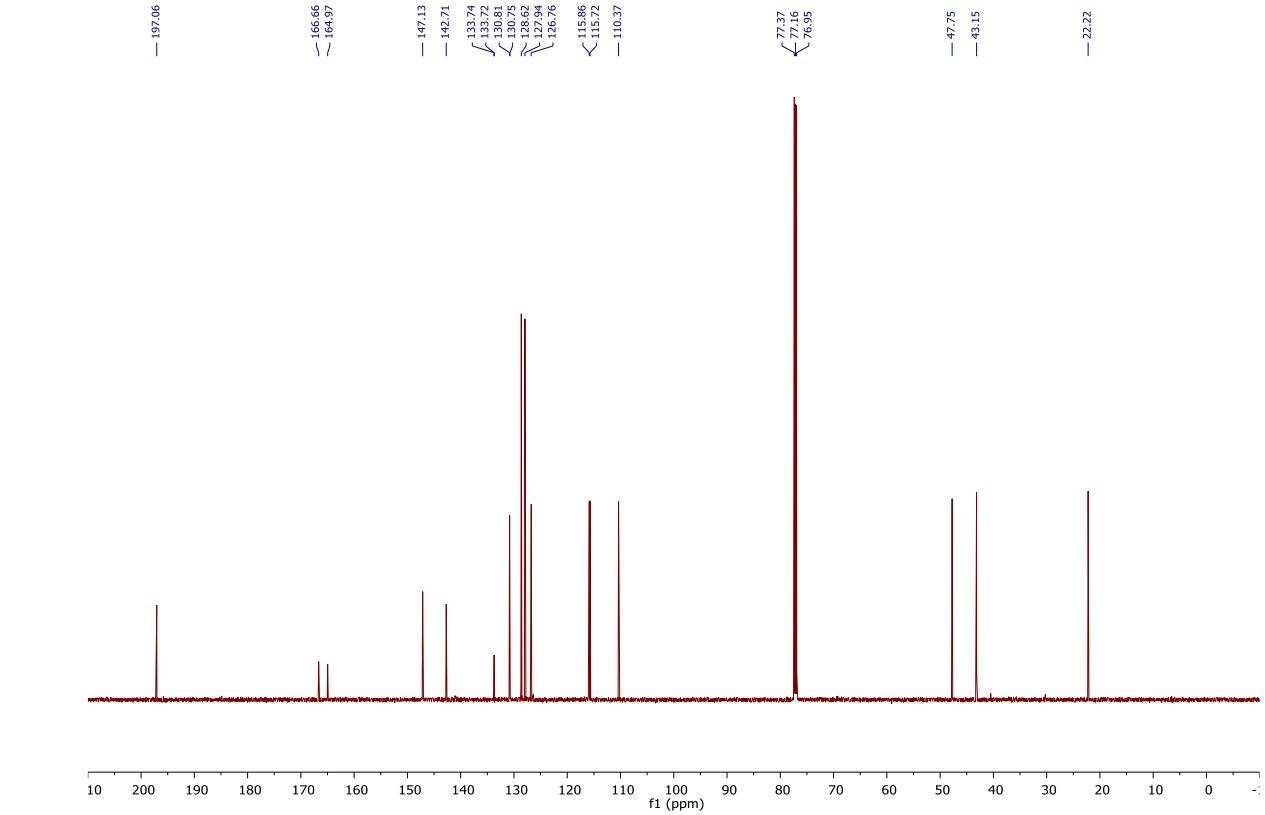


NMR spectra of (*R*)-1-(4-fluorophenyl)-4-methyl-3-phenylpent-4-en-1-one (3s)

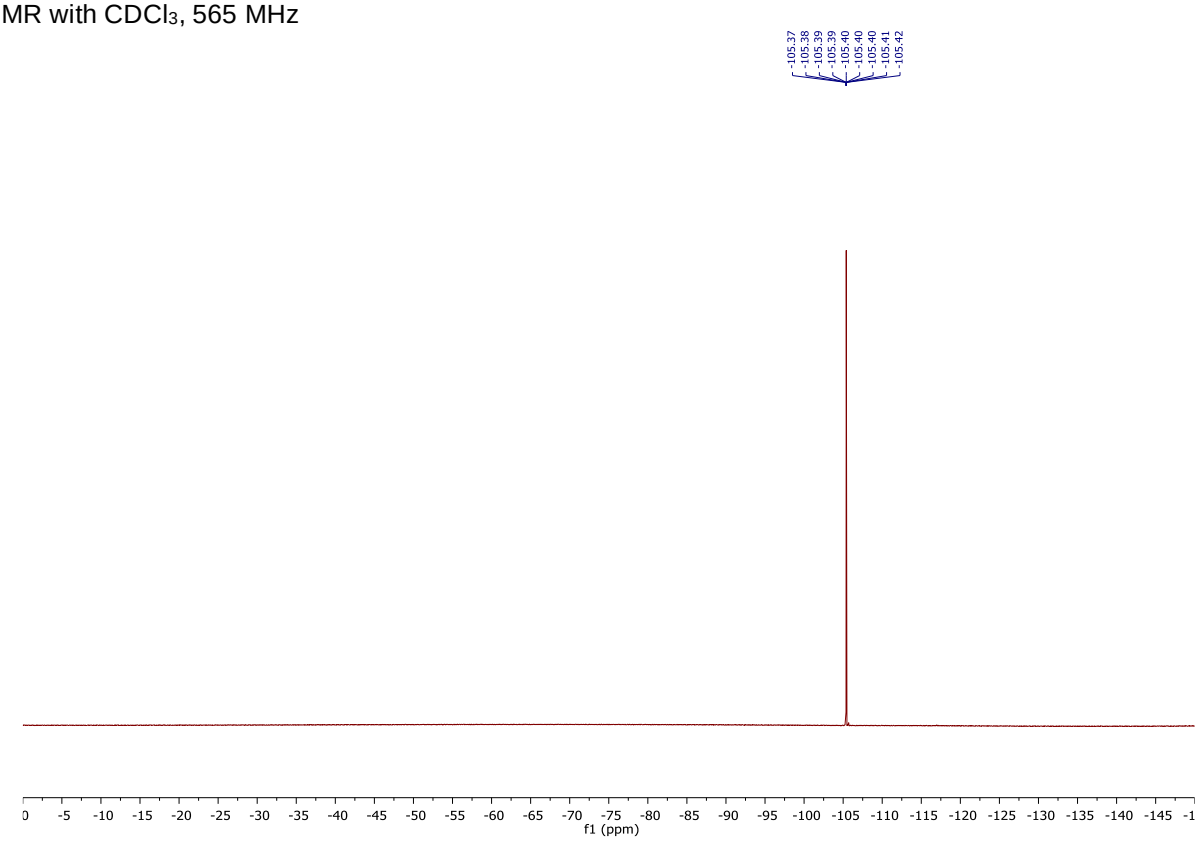
^{1}H NMR with $CDCl_3$, 600 MHz



^{13}C NMR with $CDCl_3$, 151 MHz

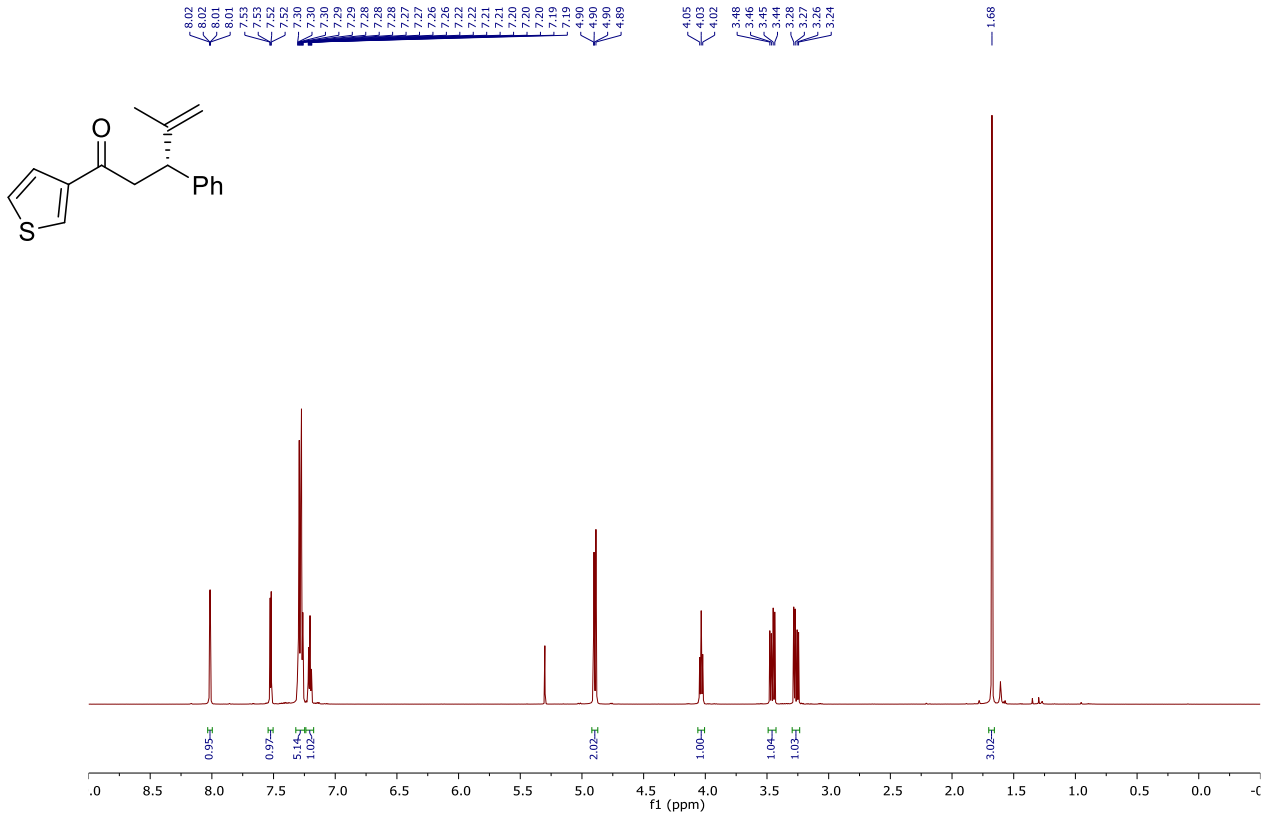


^{19}F NMR with $CDCl_3$, 565 MHz

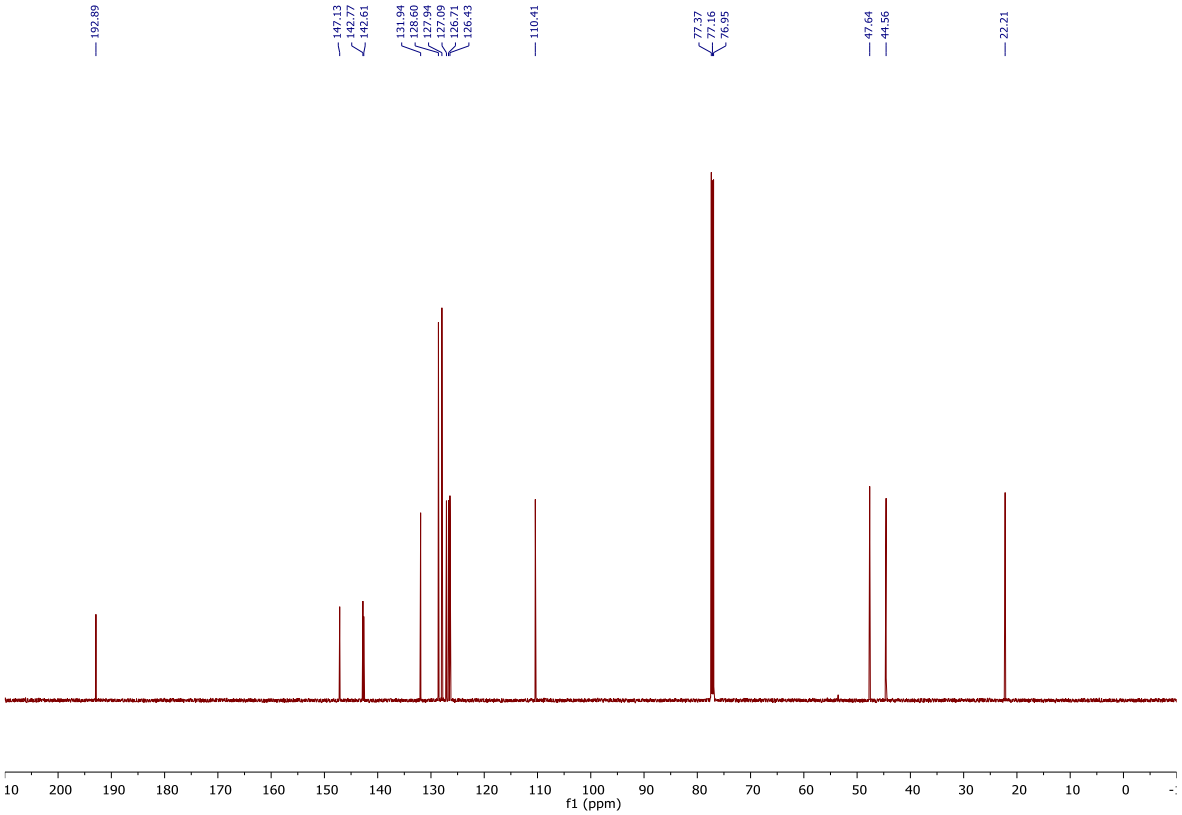


NMR spectra of (*R*)-4-methyl-3-phenyl-1-(thiophen-3-yl)pent-4-en-1-one (3t)

^{1}H NMR with $CDCl_3$, 600 MHz

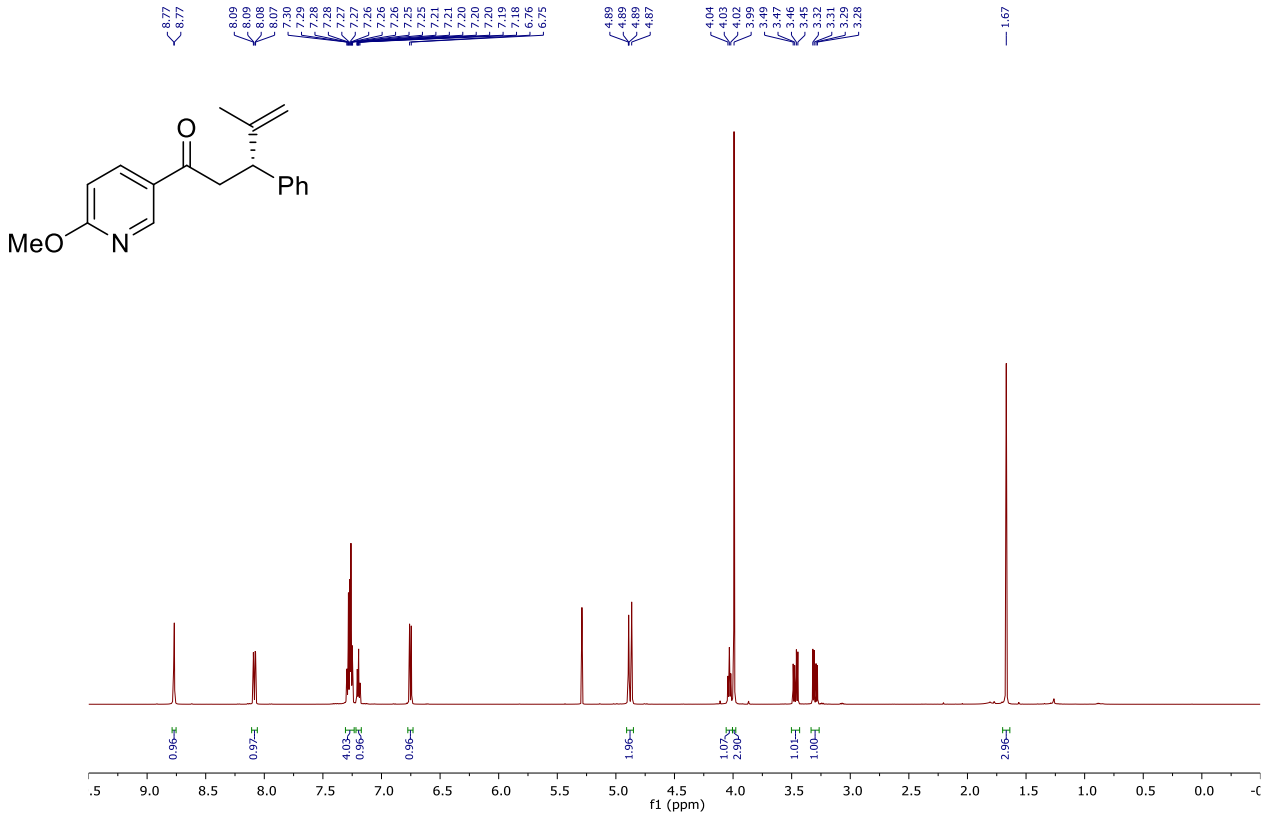


^{13}C NMR with $CDCl_3$, 151 MHz

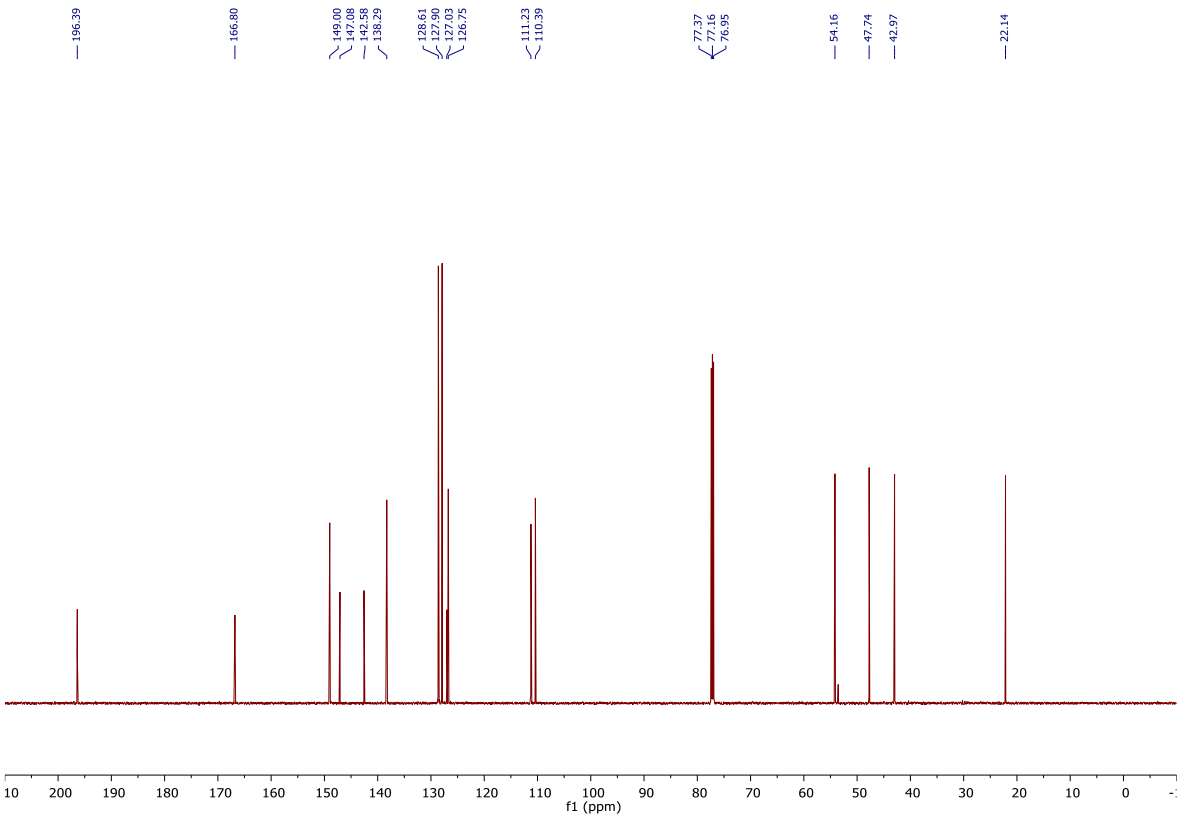


NMR spectra of (*R*)-1-(6-methoxypyridin-3-yl)-4-methyl-3-phenylpent-4-en-1-one (3u)

^{1}H NMR with $CDCl_3$, 600 MHz

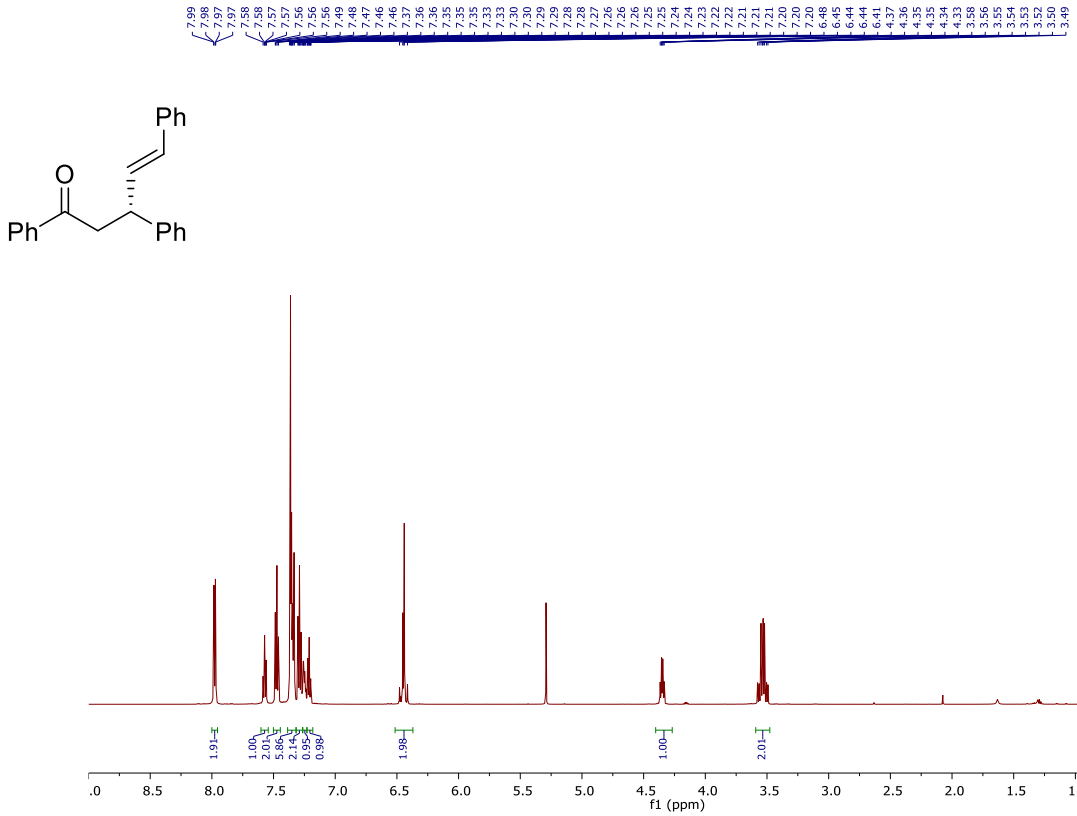


^{13}C NMR with $CDCl_3$, 151 MHz

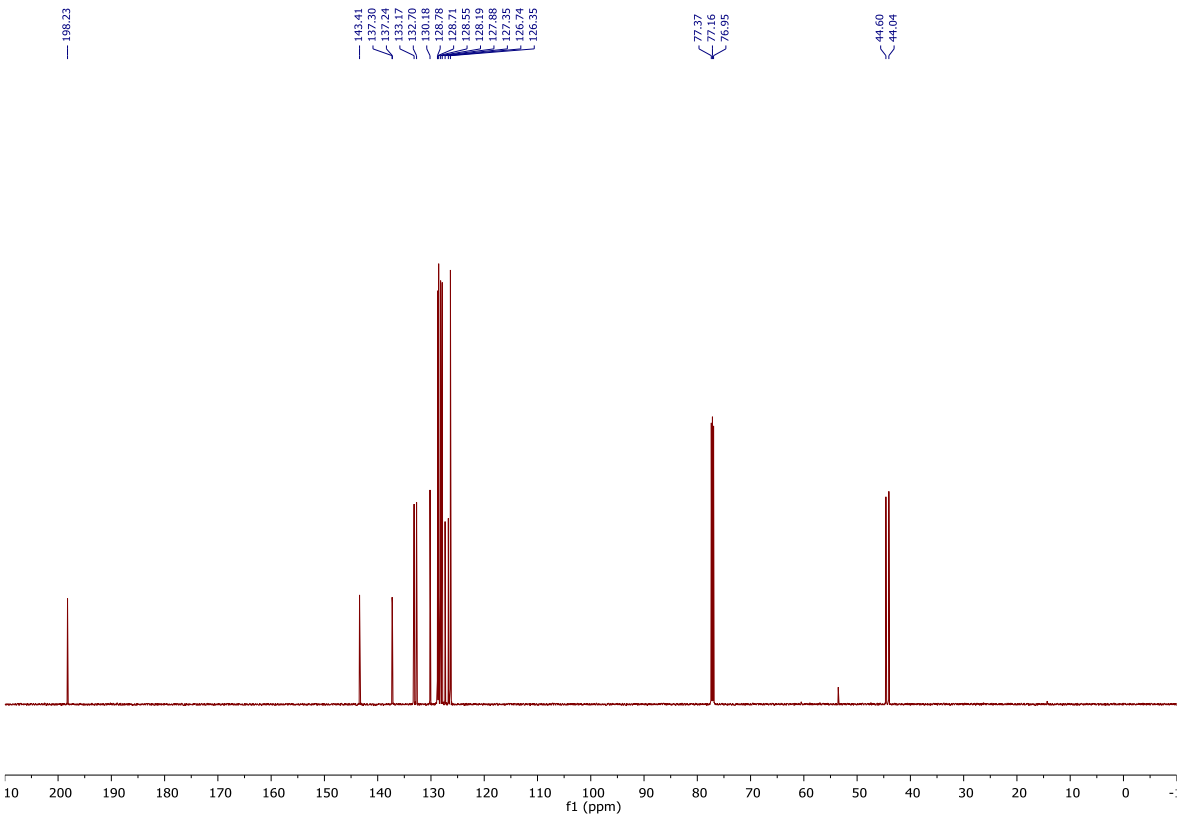


NMR spectra of (*R*,*E*)-1,3,5-triphenylpent-4-en-1-one (4a)

^{1}H NMR with $CDCl_3$, 600 MHz

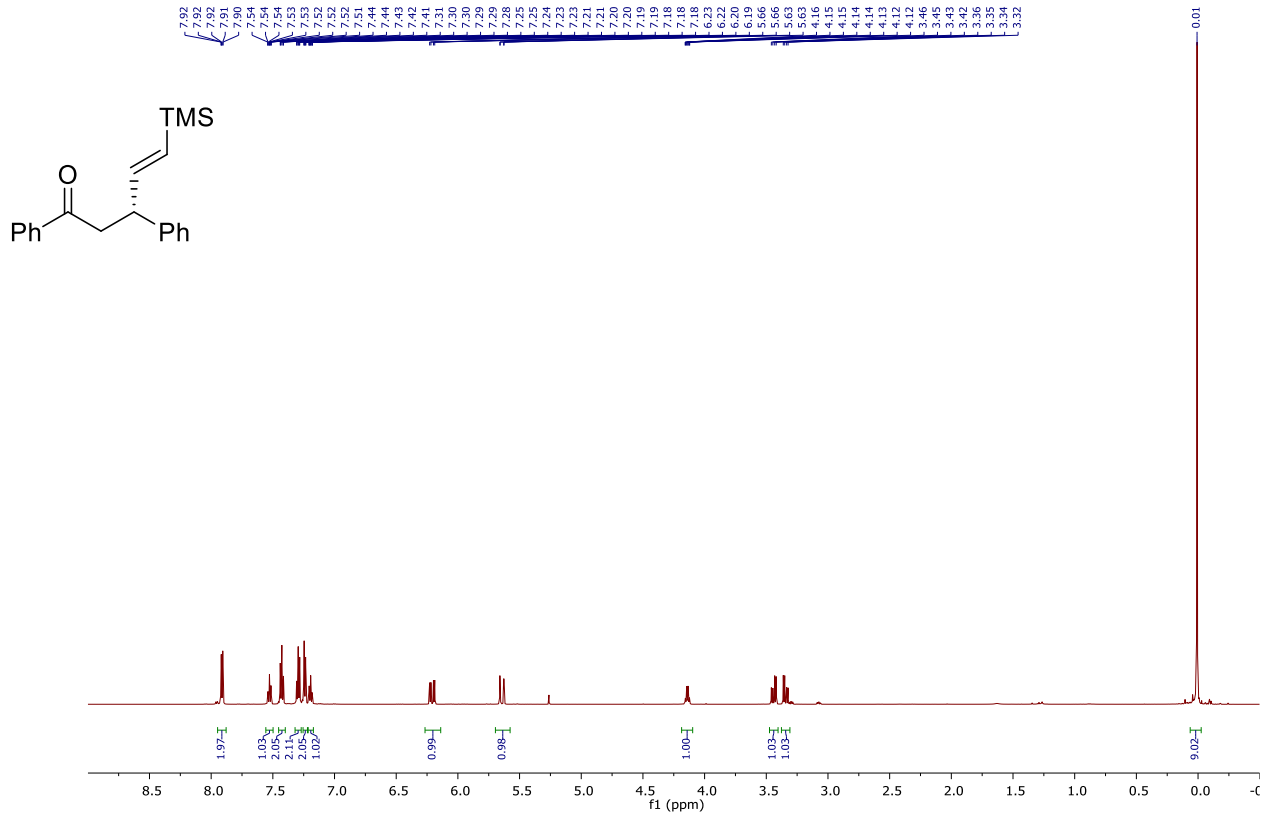


^{13}C NMR with $CDCl_3$, 151 MHz

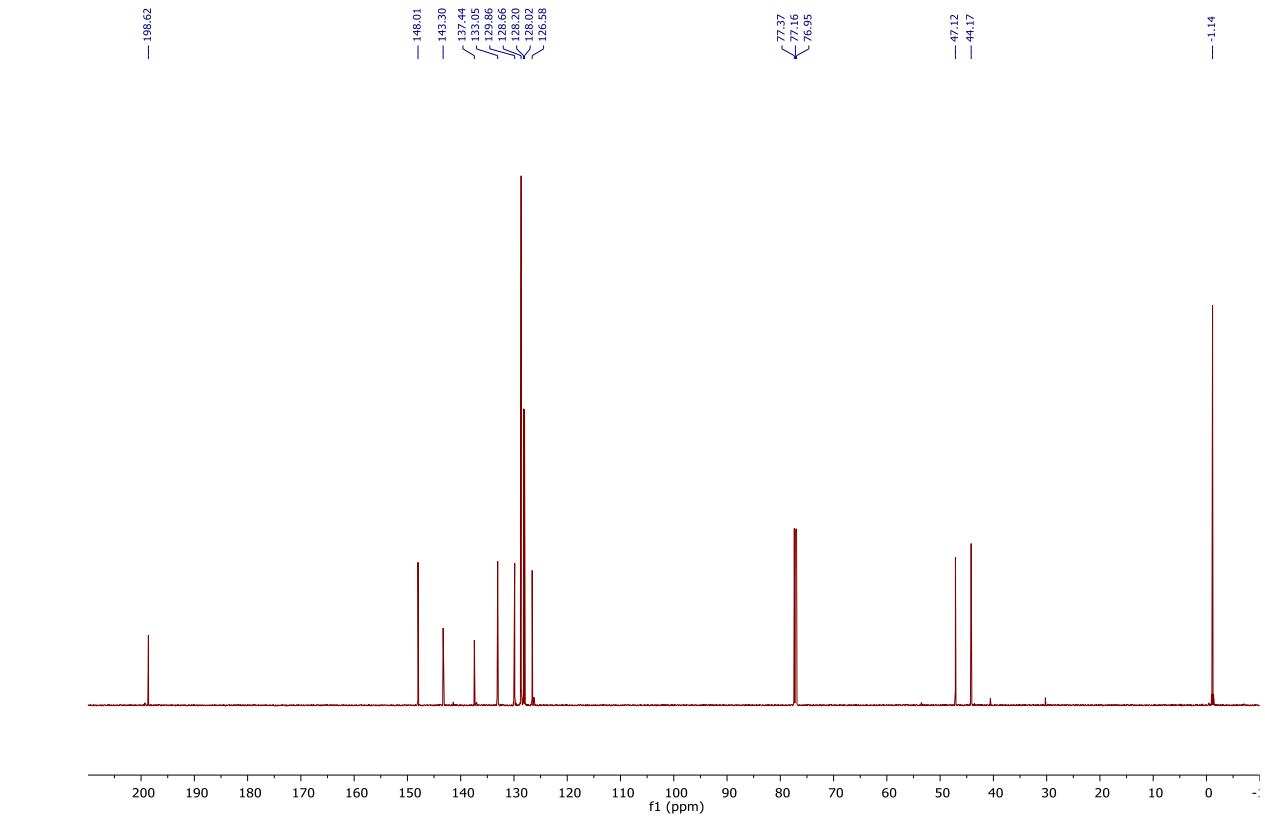


NMR spectra of (*R*,*E*)-1,3-diphenyl-5-(trimethylsilyl)pent-4-en-1-one (4b)

^{1}H NMR with $CDCl_3$, 600 MHz

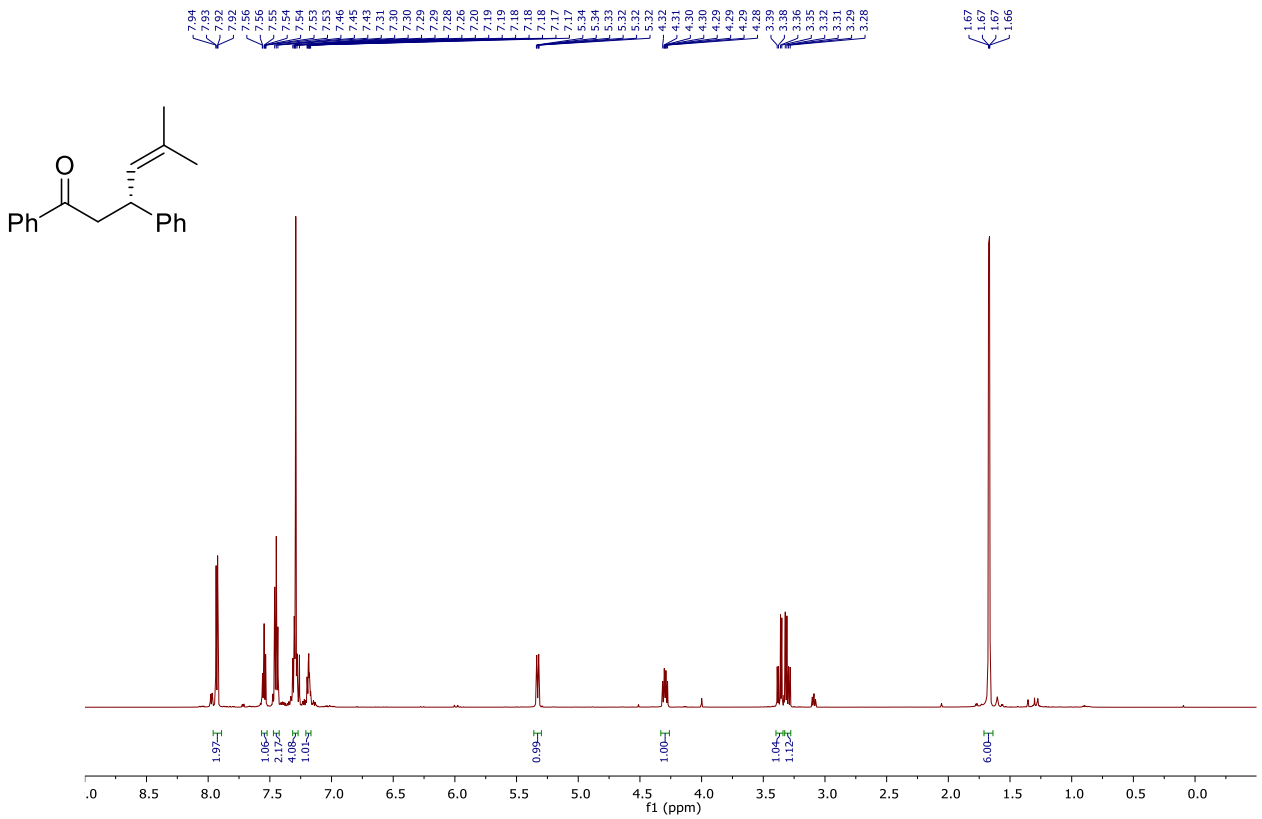


^{13}C NMR with $CDCl_3$, 151 MHz

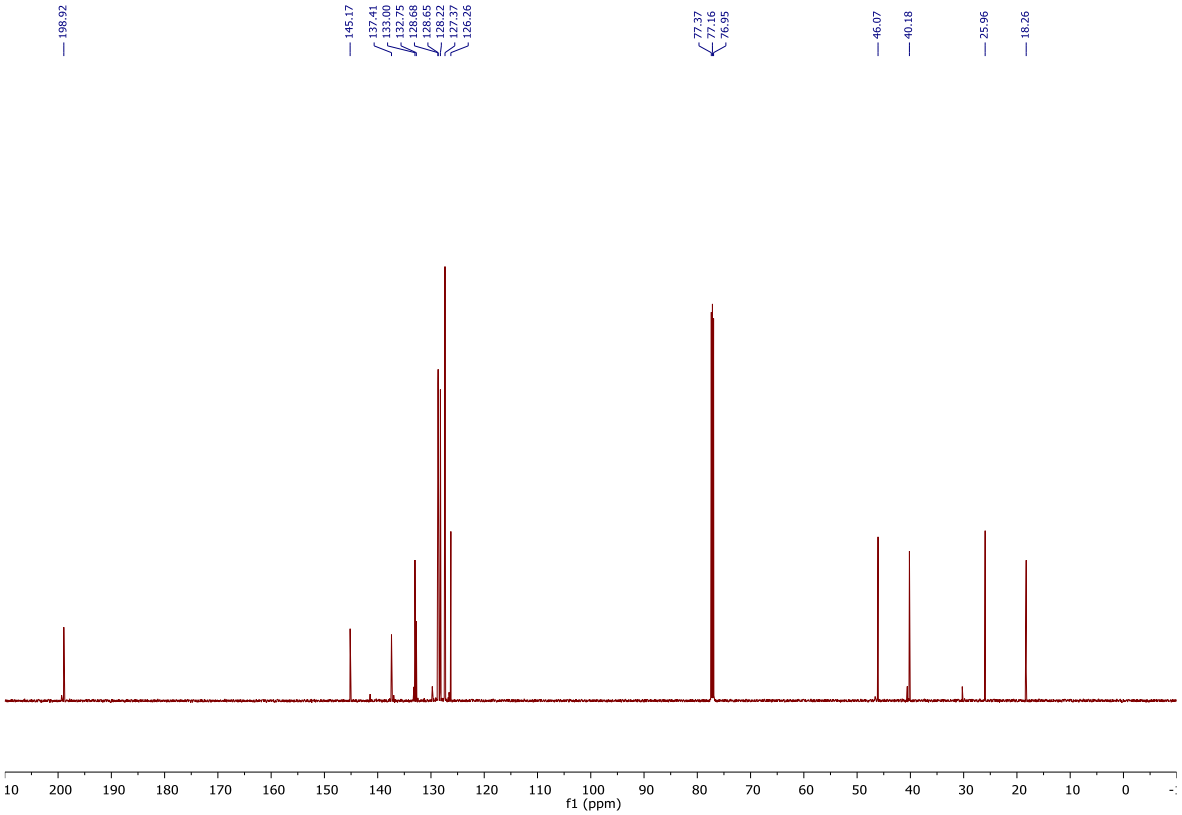


NMR spectra of (*R*)-5-methyl-1,3-diphenylhex-4-en-1-one (4c)

^{1}H NMR with $CDCl_3$, 600 MHz

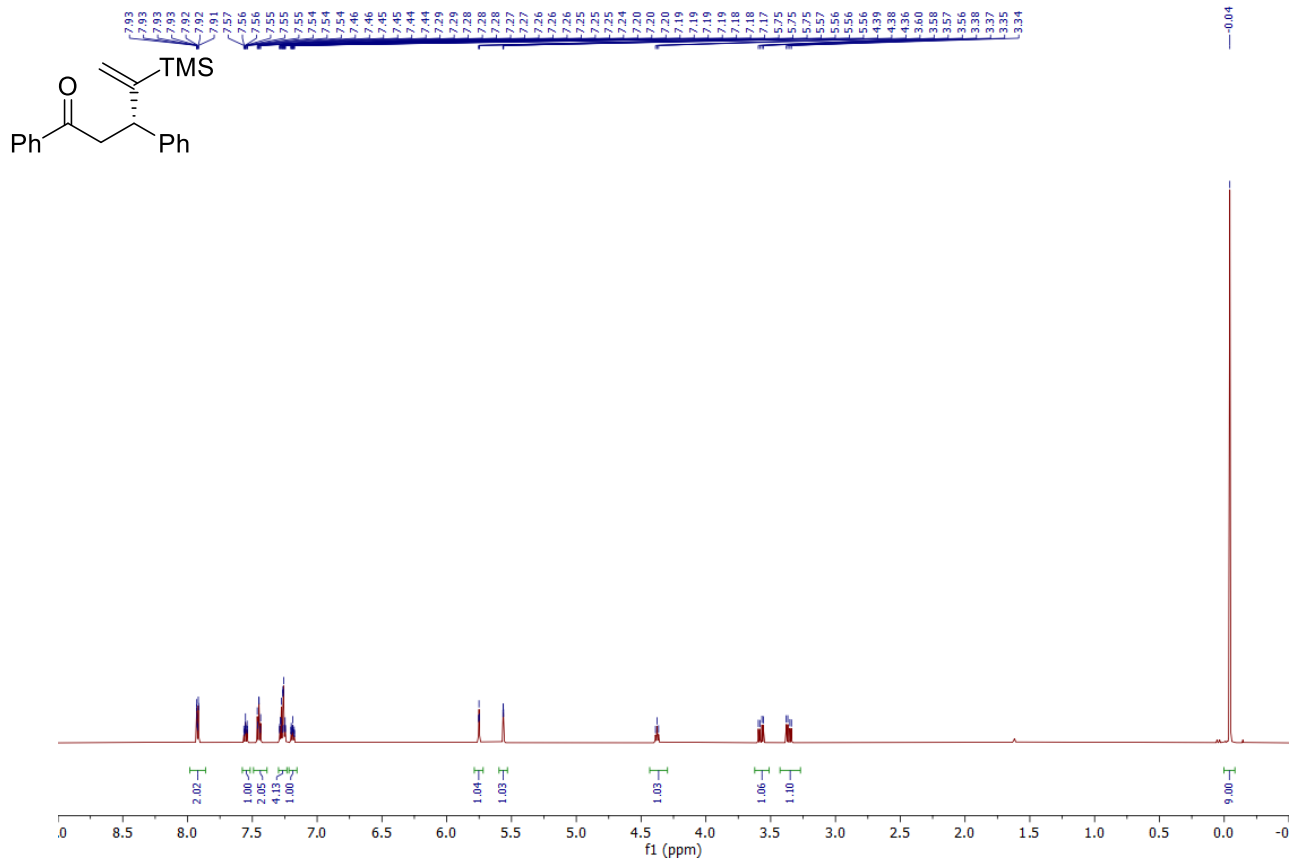


^{13}C NMR with $CDCl_3$, 151 MHz

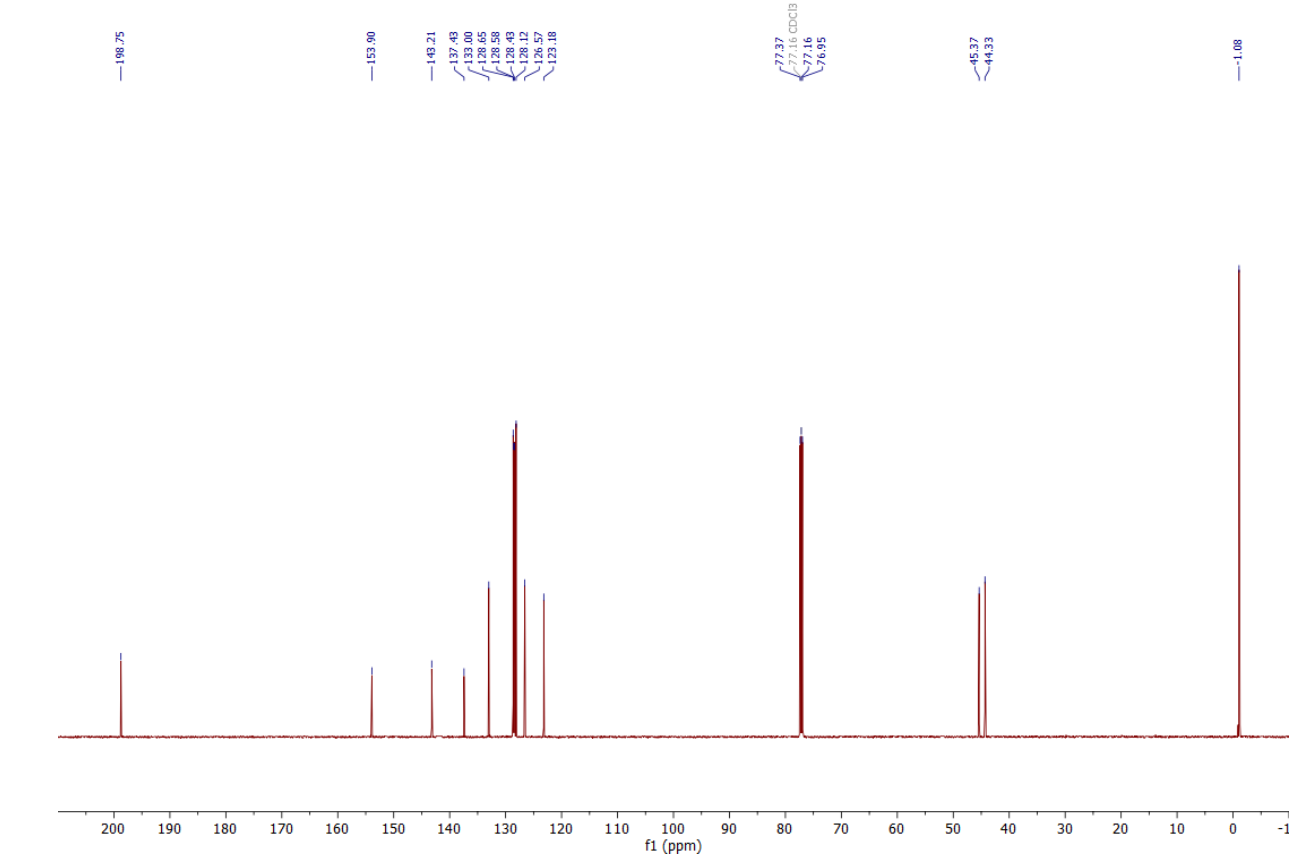


NMR spectra of (*S*)-1,3-diphenyl-4-(trimethylsilyl)pent-4-en-1-one (4d)

^{1}H NMR with $CDCl_3$, 600 MHz

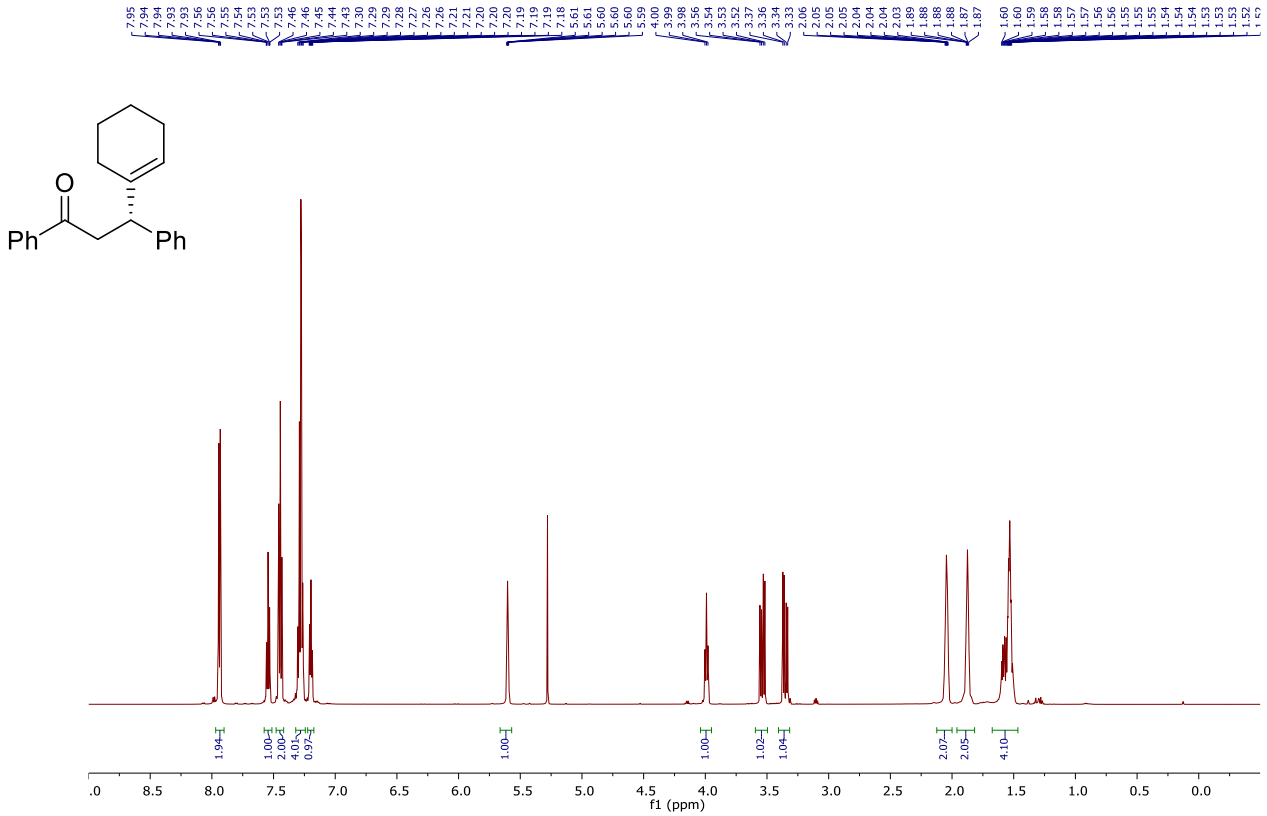


^{13}C NMR with $CDCl_3$, 151 MHz

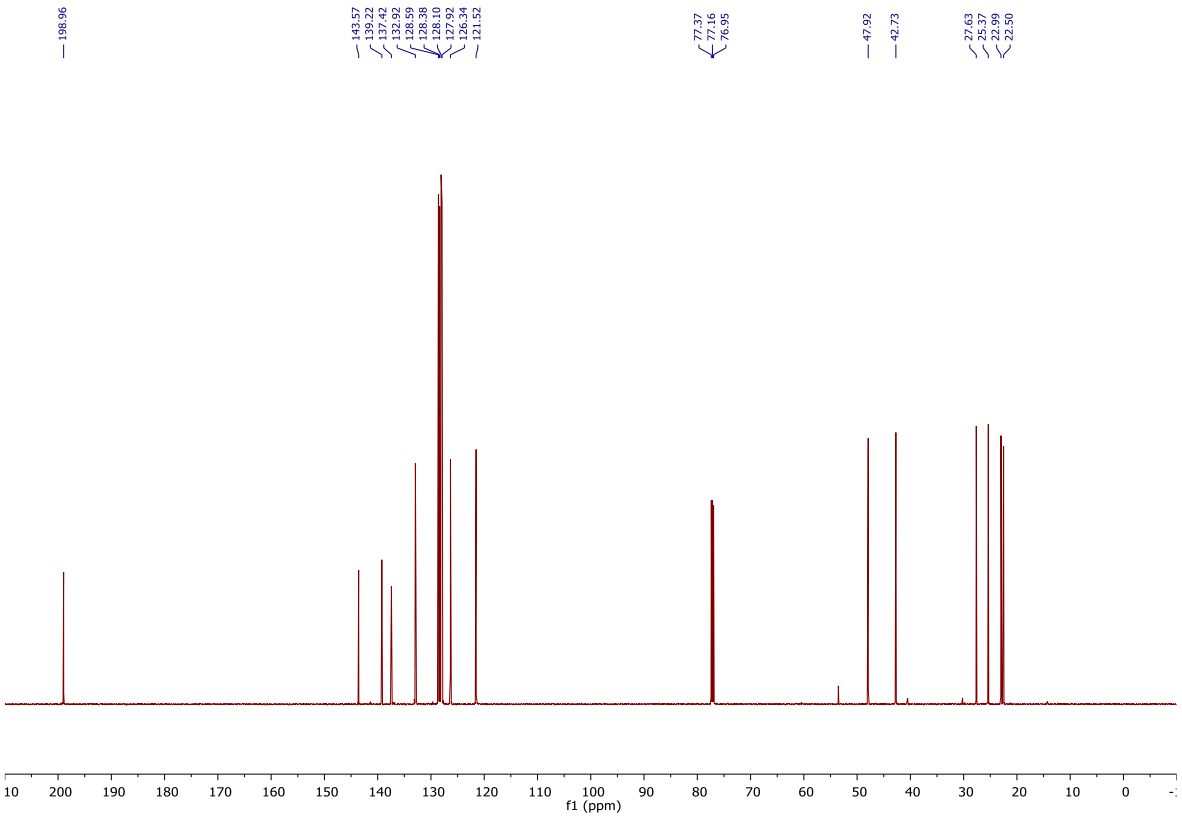


NMR spectra of (*R*)-3-(cyclohex-1-en-1-yl)-1,3-diphenylpropan-1-one (4e)

^{1}H NMR with $CDCl_3$, 600 MHz

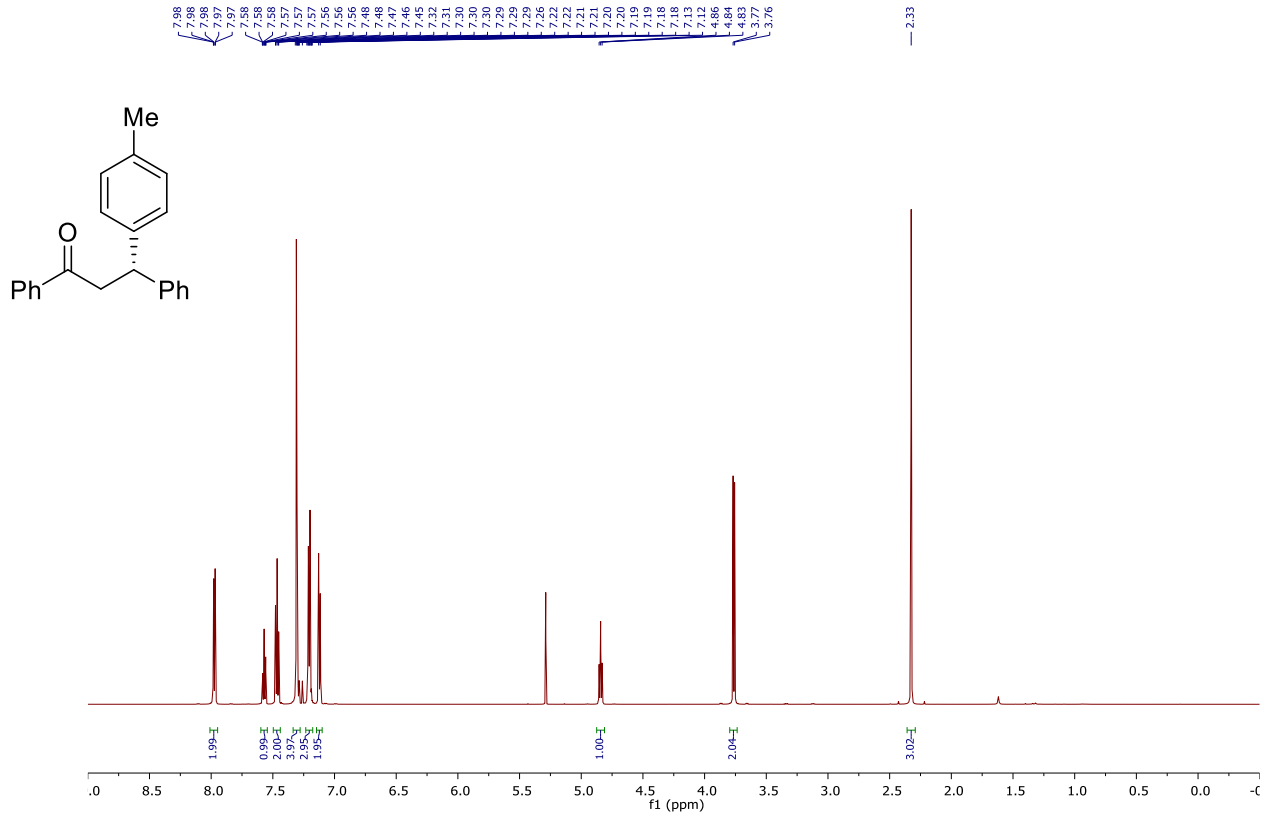


^{13}C NMR with $CDCl_3$, 151 MHz

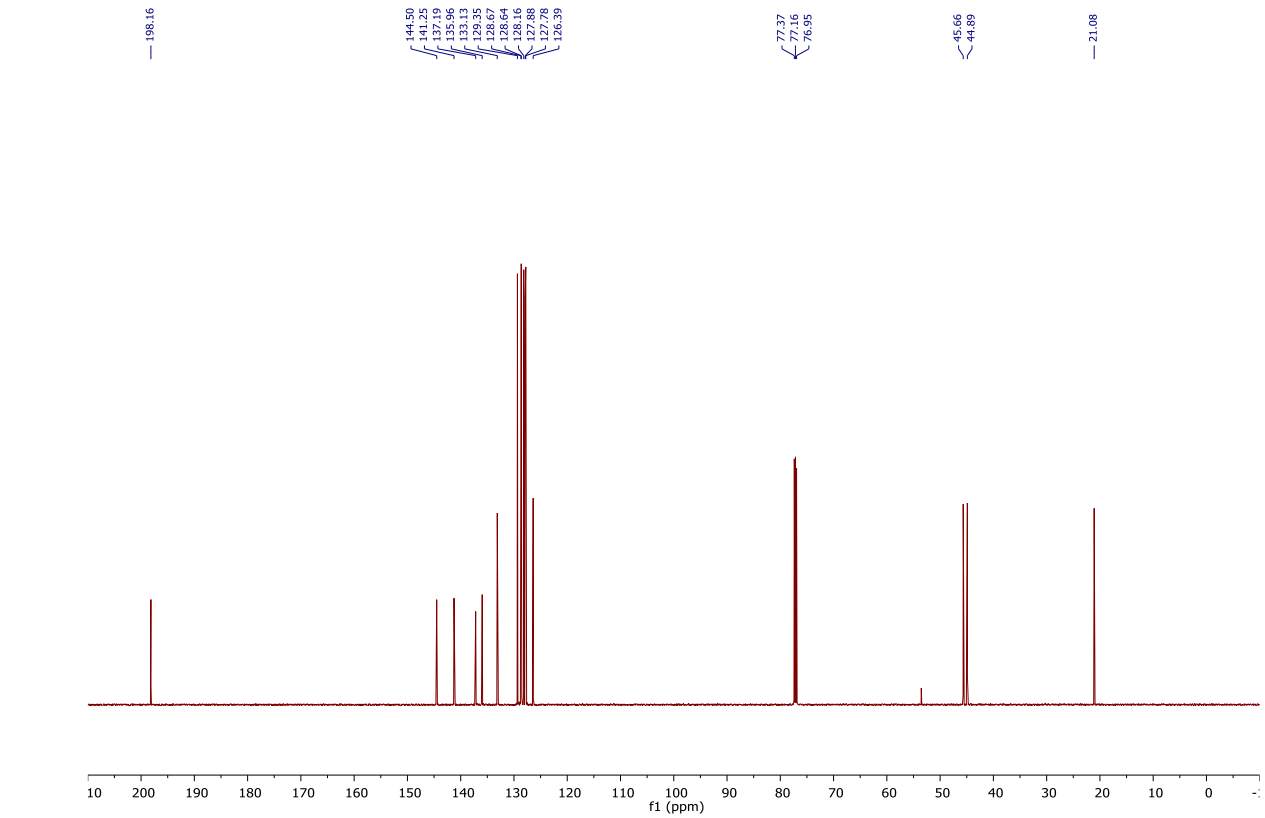


NMR spectra of (*S*)-1,3-diphenyl-3-(p-tolyl)propan-1-one (4f)

^{1}H NMR with $CDCl_3$, 600 MHz

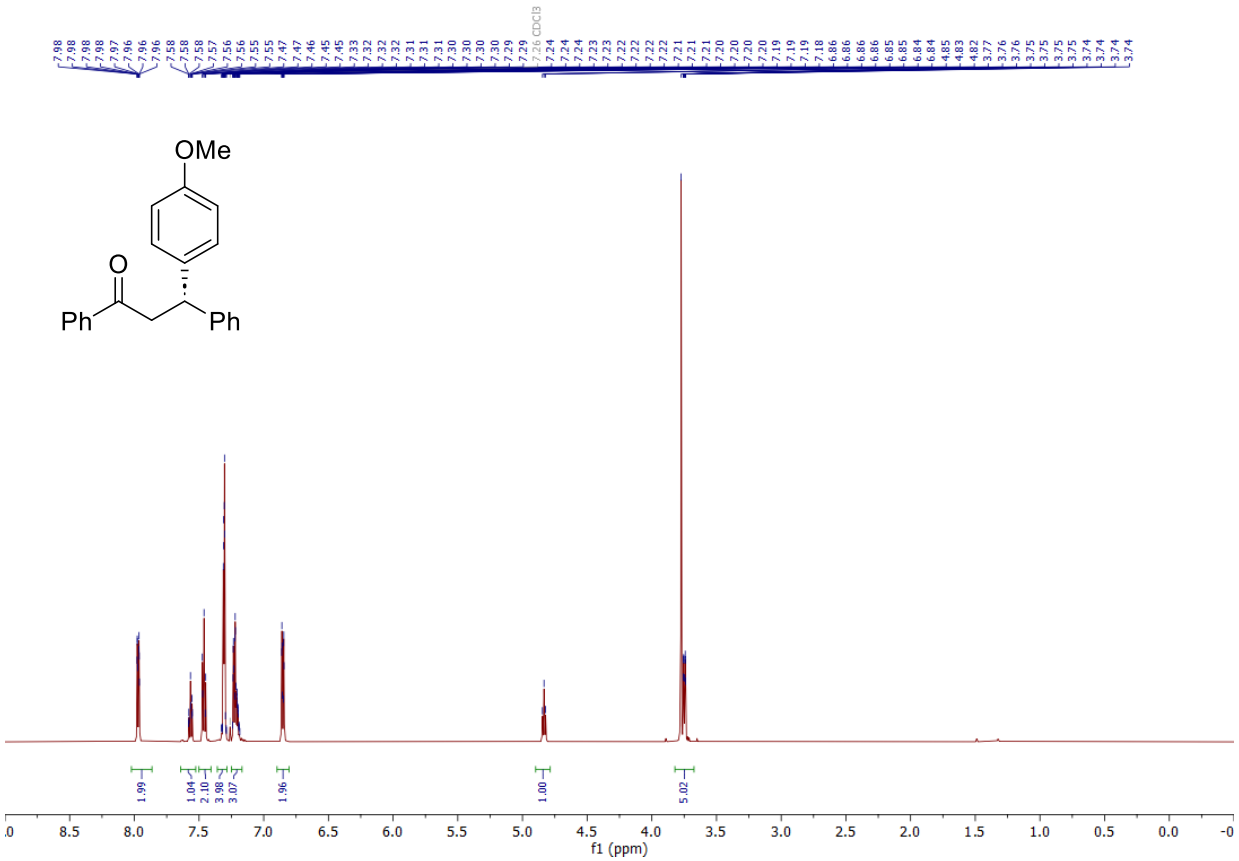


^{13}C NMR with $CDCl_3$, 151 MHz

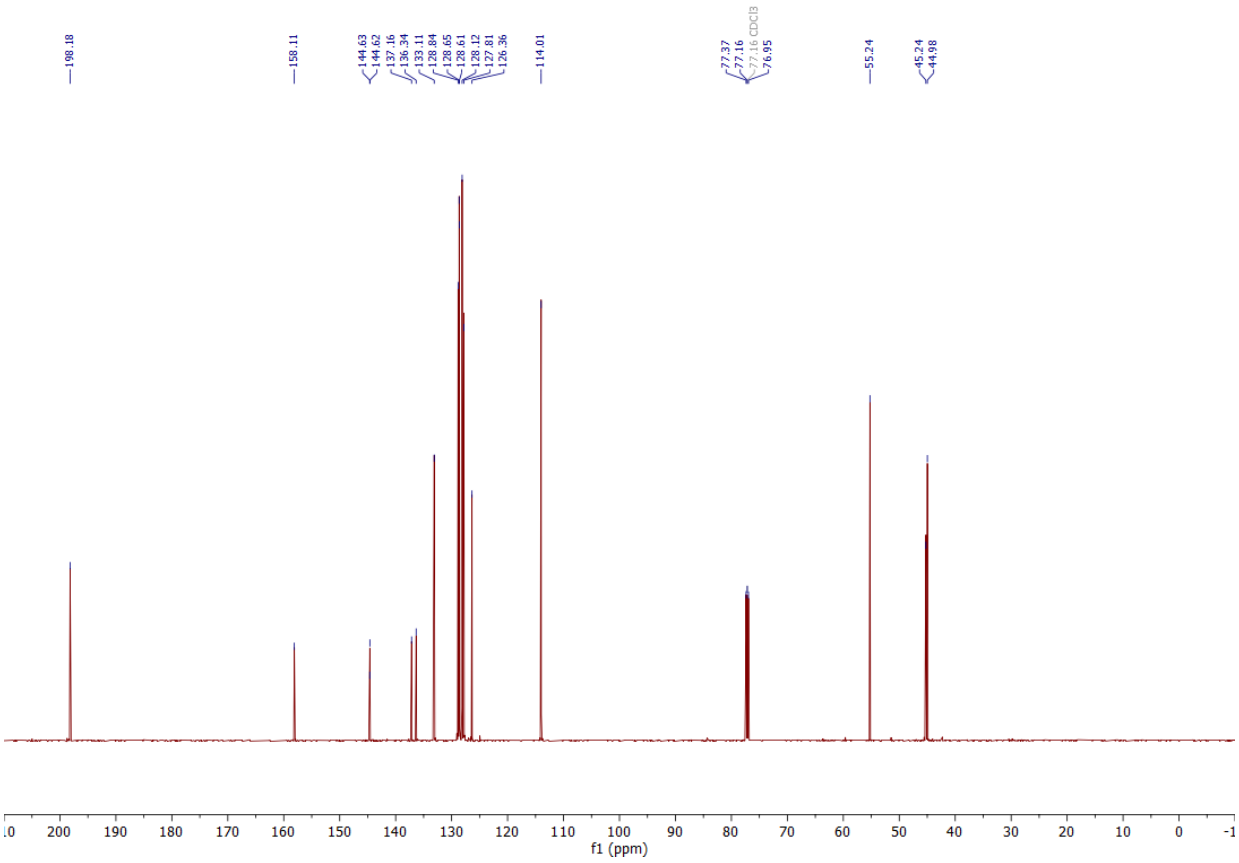


NMR spectra of (*S*)-3-(4-methoxyphenyl)-1,3-diphenylpropan-1-one (4g)

^{1}H NMR with $CDCl_3$, 600 MHz

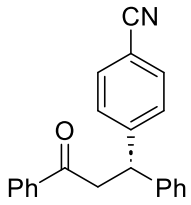


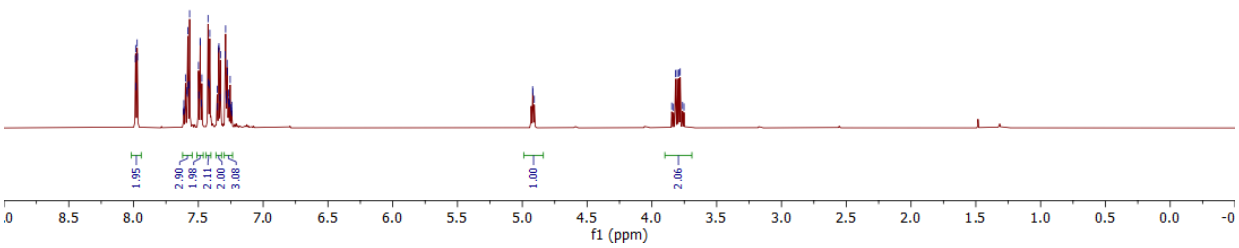
^{13}C NMR with $CDCl_3$, 151 MHz



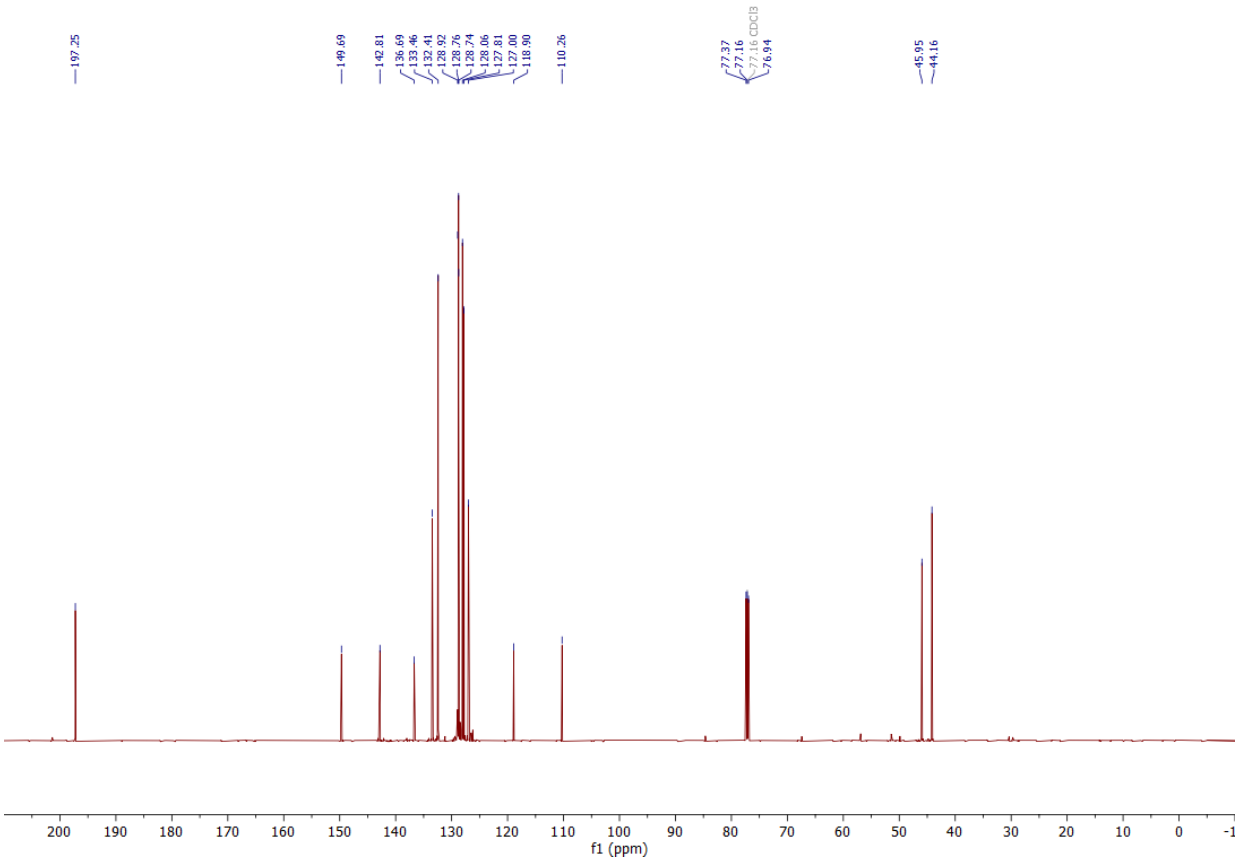
NMR spectra of (*S*)-4-(3-oxo-1,3-diphenylpropyl)benzonitrile (4h)

^{1}H NMR with $CDCl_3$, 600 MHz



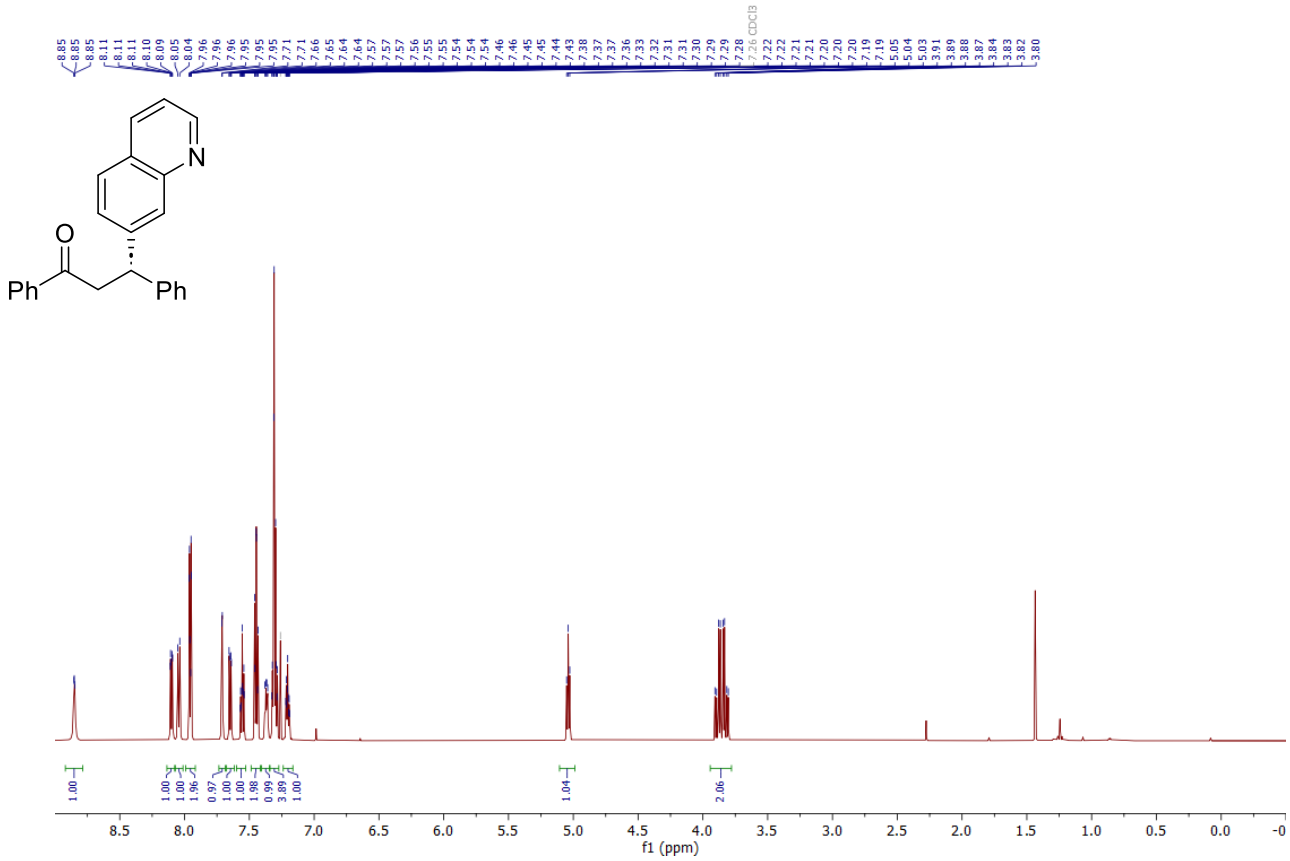


^{13}C NMR with $CDCl_3$, 151 MHz

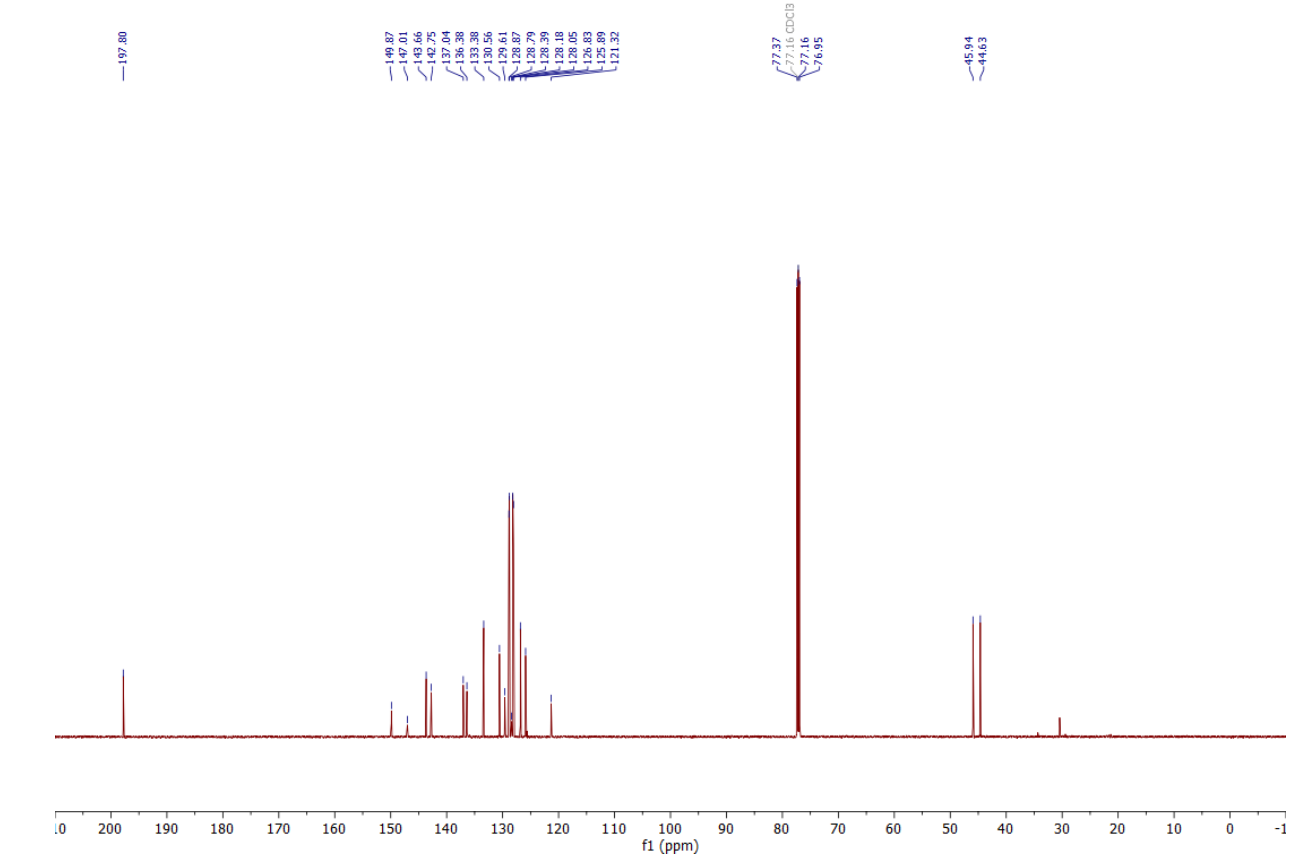


NMR spectra of (*S*)-1,3-diphenyl-3-(quinolin-7-yl)propan-1-one (4i)

^{1}H NMR with $CDCl_3$, 600 MHz

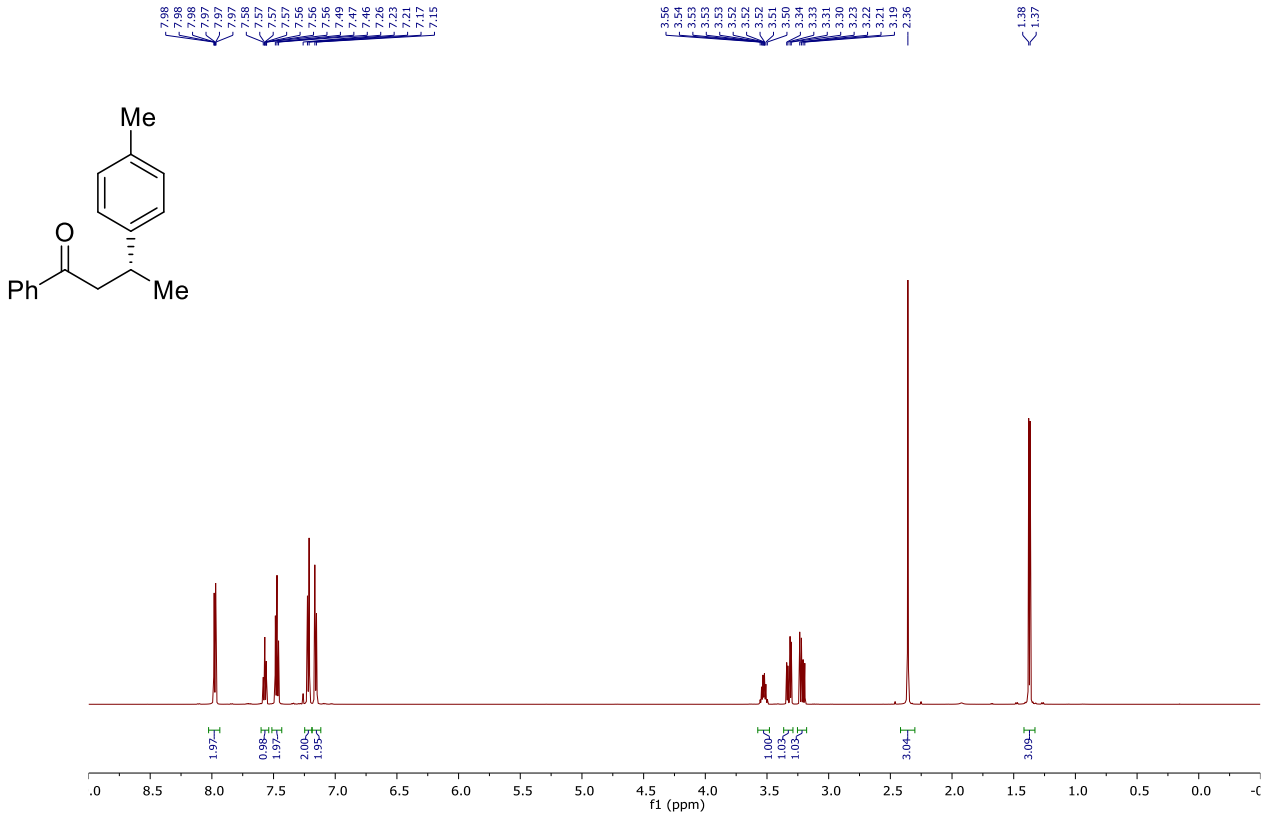


^{13}C NMR with $CDCl_3$, 151 MHz

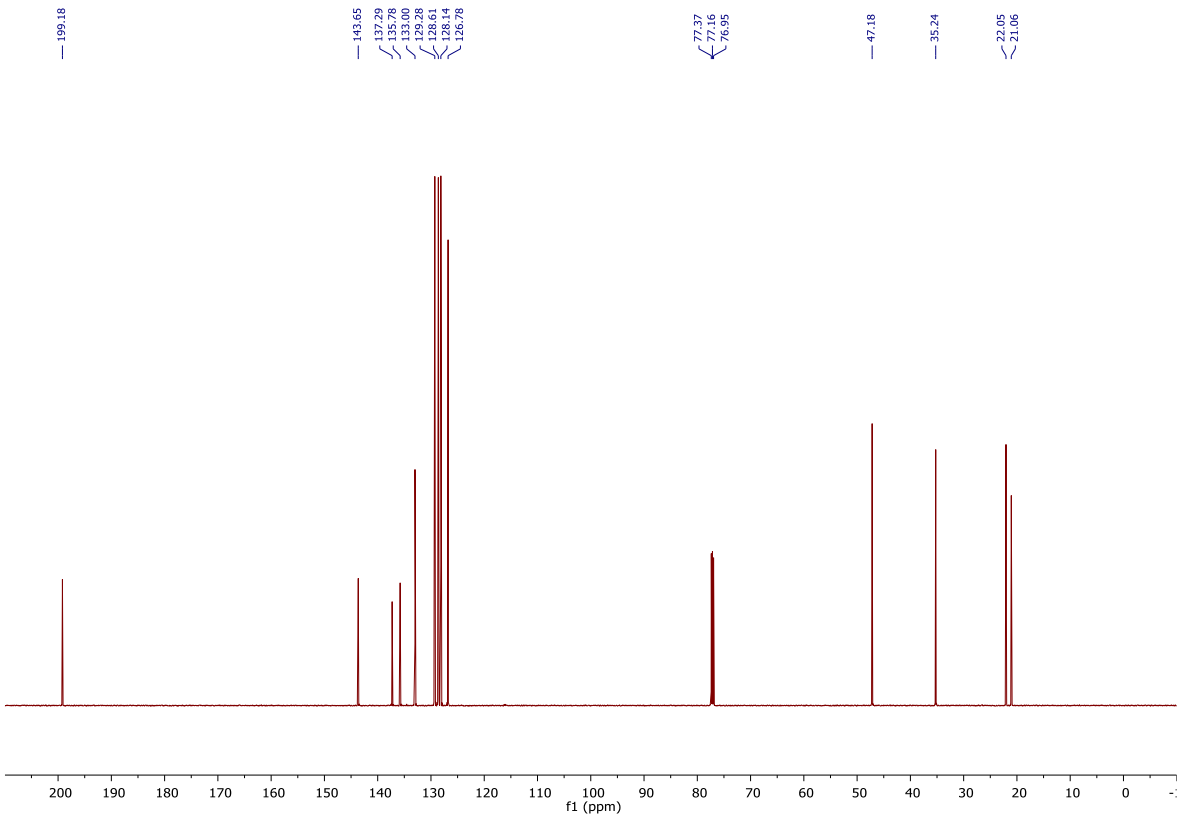


NMR spectra of (*R*)-1-phenyl-3-(p-tolyl)butan-1-one (4j)

^{1}H NMR with $CDCl_3$, 600 MHz



^{13}C NMR with $CDCl_3$, 151 MHz



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