Electronic Supplementary Material (ESI) for ChemComm.

Carbonylative Coupling of Allylic Acetates with Arylboronic Acids

Wei Ma,[a] Ting Yu, Dong Xue,*[a] Chao Wang[a] and Jianliang Xiao*[a,b]

[a] Key Laboratory of Applied Surface and Colloid Chemistry (Shaanxi Normal University), Ministry of Education and School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710062, China

[b] Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD, UK

Contents

1. General information

NMR spectra were recorded on a 400 MHz spectrometer with TMS as the internal standard. All coupling constants (*J* values) were reported in Hertz (Hz). Data are presented as follows: chemical shift in ppm and multiplicity as *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet and *m* = multiplet. Thin layer chromatography (TLC) was performed on glass backed silica gel plates. Column chromatography was performed on silica gel 200-300 mesh. Flash chromatography was performed with freshly distilled solvents. HRMS (ESI) were performed on a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer.

2. Optimization of reaction conditions

2.1 The purification of aryl boronic acids

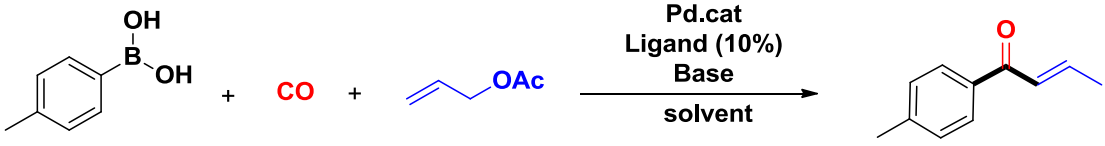
Aryl boronic acids were purified by the following method: 10 mmol of arylboronic acid was dissolved in 15 mL of 1 M NaOH solution and stirred for 20 min. 1 M HCl solution was added dropwise and a white precipitate formed instantly when pH value was adjusted to 7. The white solid was filtered and recrystallised from H_2O/CH_3CN. The solid was filtered, dried under reduced pressure and used directly.

2.2 Typical reaction procedure for the optimization of reaction conditions

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. Pd source (0.02 mmol), ligand (0.05 mmol) and a magnetic stir bar were placed in the tube, which was then capped with a stopper. Then, aryl boronic (0.5 mmol), allyl acetate (1mmol), solvent (3 mL) were added to the tube. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times with CO at room temperature and heated in an oil bath at 120 ℃ for 12 hours. The autoclave was then cooled to room temperature and vented to discharge the excess CO. Water (10 mL) was added, and the product was extracted with EA (3×3 mL). The organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether as eluent to give the desired product. Structures of ligands screened in

this paper are shown in Scheme S1.

Table S1 Screening of ligands and Pd sources



1a 2a 3a

Entry	cat	ligand	Base	solvent	Yield
1	$Pd(PPh_3)_4$	0	KOH	$PhCH_3$	7.5%
2	$Pd(PPh_3)_4$	0	0	$PhCH_3$	trace
3	No	0	KOH	$PhCH_3$	0
4	$Pd(OAc)_2$	0	KOH	$PhCH_3$	0
5	$Pd(dba)_3$	0	KOH	$PhCH_3$	0
6	$Pd(PPh_3)_4$	PPh_3 (2%)	KOH	$PhCH_3$	10%
7	$Pd(OTFA)_2$	PPh_3 (8%)	KOH	$PhCH_3$	0
8	$Pd(OAc)_2$	PPh_3 (8%)	KOH	$PhCH_3$	15%
9	$PdCl_2$	PPh_3 (8%)	KOH	$PhCH_3$	0
10	$Pd(OAc)_2$	$[HP(t\text{-}Bu)_3]BF_4$	KOH	$PhCH_3$	9%
11	$Pd(OAc)_2$	DPPF	KOH	$PhCH_3$	trace
12	$Pd(OAc)_2$	DPPE	KOH	$PhCH_3$	0
13	$Pd(OAc)_2$	DPPP	KOH	$PhCH_3$	0
14	$Pd(OAc)_2$	BINAP	KOH	$PhCH_3$	0
15	$Pd(OAc)_2$	A	KOH	$PhCH_3$	0
16	$Pd(OAc)_2$	B	KOH	$PhCH_3$	0
17	$Pd(OAc)_2$	C	KOH	$PhCH_3$	16%
18	$Pd(OAc)_2$	PCy_3	KOH	$PhCH_3$	30%

Scheme S1 Structures of ligands.

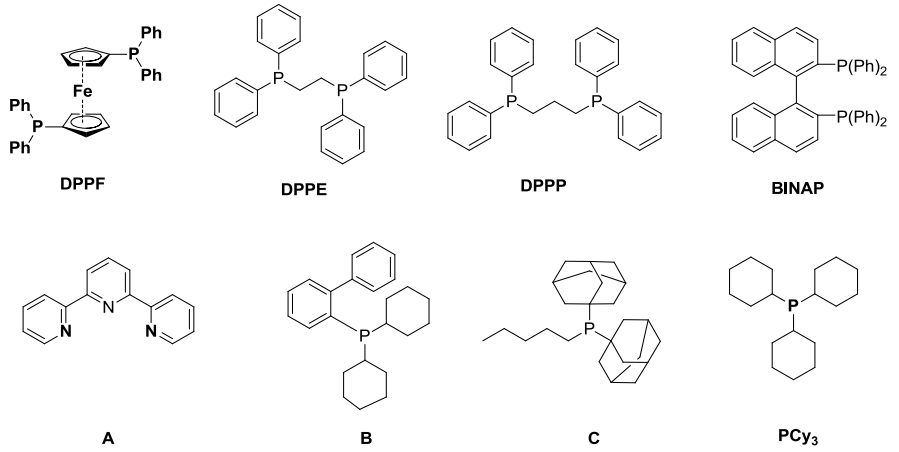
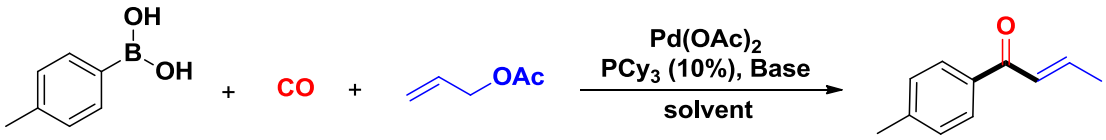


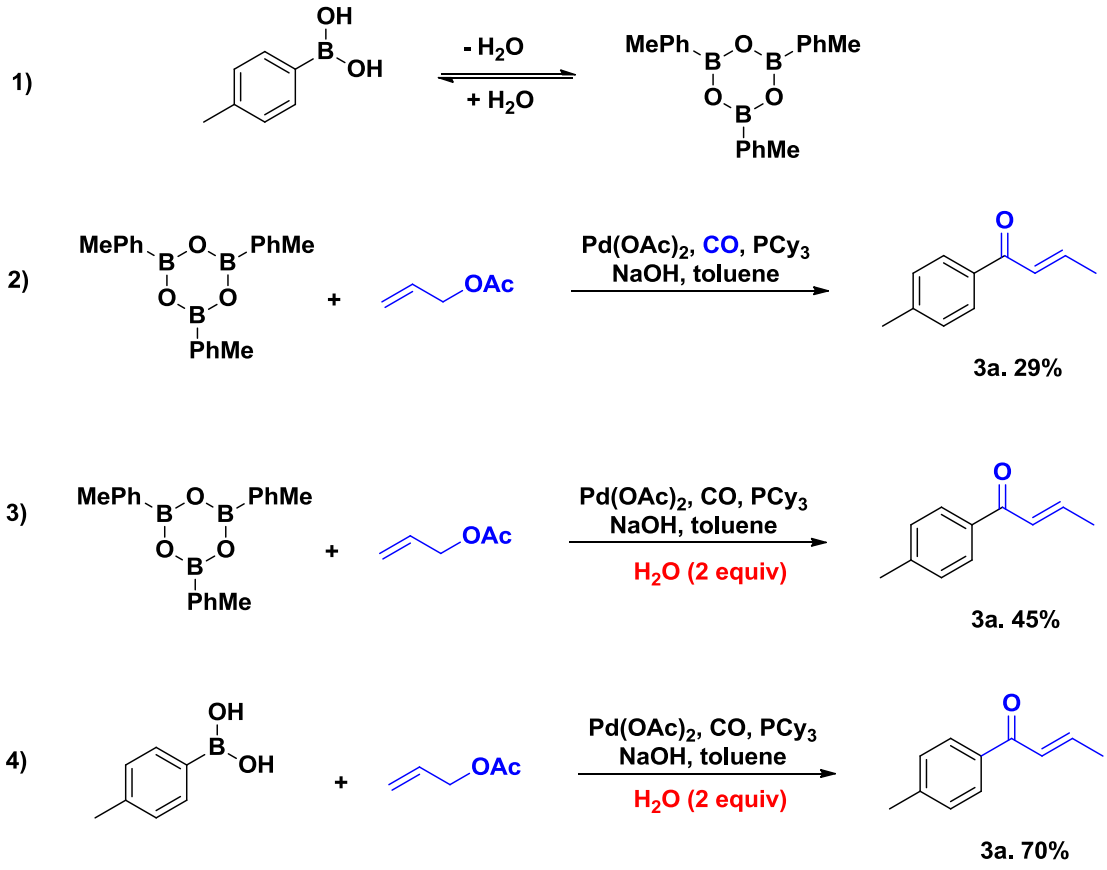
Table S2 Screening of base and additive



1a 2a 3a

Entry	cat	ligand	Base	solvent	additive	Yield
1	$Pd(OAc)_2$	PCy_3	KF $2H_2O$	$PhCH_3$		23%
2	$Pd(OAc)_2$	PCy_3	$NaHCO_3$	$PhCH_3$		0
3	$Pd(OAc)_2$	PCy_3	NEt_3	$PhCH_3$		trace
4	$Pd(OAc)_2$	PCy_3	HCOONa $2H_2O$	$PhCH_3$		trace
5	$Pd(OAc)_2$	PCy_3	NaOH	$PhCH_3$		35%
6	$Pd(OAc)_2$	PCy_3	NaOH	$PhCH_3$	H_2O (2eq)	70%
7	$Pd(OAc)_2$	PCy_3	K_3PO_4	$PhCH_3$		30%
8	$Pd(OAc)_2$	PCy_3	K_3PO_4 $3H_2O$	$PhCH_3$		60%
9	$Pd(OAc)_2$	PCy_3	K_3PO_4 $3H_2O$	$PhCH_3$	H_2O (2eq)	64 %
10	$Pd(OAc)_2$	PCy_3	K_3PO_4 $3H_2O$	$PhCH_3$	H_2O (4eq)	72%
11	$Pd(OAc)_2$	PCy_3	K_3PO_4 $3H_2O$	$PhCH_3$ / dioxane	H_2O (2eq)	81%

Scheme S2 Effect of water



In the case of aryl boroxine (0.17 mmol), a dramatically decreased yield (29%) of **3a** was observed. Therefore, water was added to reduce aryl boroxiane produced. The yield of **3a** increased to 70% (**Sheme S2, eq 4),** when *p*-tolylboronic acid (0.5 mmol) was used as substrate and 2 equiv of water as additive. General reaction conditions for **Scheme S2**: Allylic acetoxy (1mol, 2eq), $Pd(OAc)_2$ (4% mol), PCy_3 (10% mol), NaOH (0.5 mmol), toluene (3 mL), under 5 bar of CO. The reaction was stirred at 120 ^oC for 12 h. The yield of **3a** was detected by NMR.

3. Typical procedure for allylic carbonylation of aryl boronic acids with allyl acetate

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. $Pd(OAc)_2$ (4% mol), PCy_3 (10% mol), and a magnetic stir bar were placed in the tube, which was then capped with a stopper. Then, aryl boronic acid (0.5 mmol), allyl acetate (1.0 mmol), solvent (toluene/dioxane = 1 : 1, 3 mL), K_3PO_4 $3H_2O$ (0.5 mmol)

and H_2O (18mg, 2 eq) were added to the tube. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times and then pressurized to 5 atm with CO at room temperature and heated in an oil bath at 120 ℃ for 12 hours (for substrates **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1i**, **1k**, **1l**, **1o**, **1p**) or 24 hours (for substrates **1g**, **1h**, **1j**, **1m**, **1n**). The autoclave was then cooled to room temperature and vented to discharge the excess CO. Water (10 mL) was added, and the product was extracted with EA (3×3 mL). The organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether as eluent to give α, β-unsaturated aryl ketones.

4. Typical procedure for carbonylation of allyl acetates with *p*-tolylboronic acid

Method A: The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. $Pd(OAc)_2$ (4% mol), PCy_3 (10% mol), and a magnetic stir bar were placed in the tube, which was then capped with a stopper. Then, aryl boronic acid (0.5 mmol), allyl acetate (1.0 mmol), solvent (toluene, 3 mL) and K_3PO_4 (0.5 mmol) were added to the tube. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times and then pressurized to 5 atm with CO at room temperature and heated in an oil bath at 120 ℃ for 24 hours. The autoclave was then cooled to room temperature and vented to discharge the excess CO. Water (10 mL) was added, and the product was extracted with EA (3×3 mL). The organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether as eluent to give the desired products **4b-e**.

Method B: The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. $Pd(OAc)_2$ (4% mol), PCy_3 (10% mol), and a magnetic stir bar were placed in the tube, which was then capped with a stopper. Then, aryl boronic acid (0.5 mmol), allyl acetate (1.0 mmol), solvent (toluene / dioxane = 1:1, 3 mL), K_3PO_4 $3H_2O$ (0.5 mol) and H_2O (18 mg, 2 eq) were added to the tube. The tube was then placed in the autoclave. Once sealed, the autoclave was purged several times and

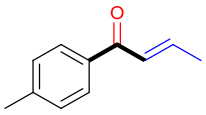
then pressurized to 5 atm with CO at room temperature and heated in an oil bath at 120 ℃ for 24 hours (for substrates **2f, 2g, 2h, 2l, 2m, 2n**) or 12 hours (for substrates **2i, 2j, 2k)**. The autoclave was then cooled to room temperature and vented to discharge the excess CO. Water (10 mL) was added, and the product was extracted with EA (3×3 mL). The organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether as eluent to give the desired products.

5. Procedures for study of reaction mechanism

An autoclave containing a 10 mL Teflon reaction tube was charged with a magnetic stir bar. *p*-Tolylboronic acid (68 mg, 0.5 mmol, 1eq), **2f** (114 mg, 2eq), $Pd(OAc)_2$ (4 mg, 4% mol), PCy_3 (14 mg, 10% mol), K_3PO_4 $3H_2O$ (133 mg, 1 eq), toluene / dioxane = (1 : 1) (3 mL) and water (18 mg, 2 eq.) were added to the tube with a syringe. The tube was placed in the autoclave. Once sealed, the autoclave was pressurized with CO (5 bar) and heated in an oil bath at 120 ℃ for 1 h or 24 h. The yields of **4f** and **4f-a** were determined by NMR.

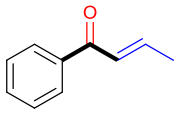
6. Data for products

3a. (E)-1-(p-tolyl)but-2-en-1-one:



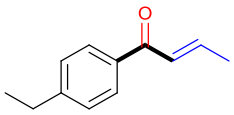
Yield: 81% (12 h, 65 mg); pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.1 Hz, 2 H), 7.24 (d, *J* = 2.8 Hz, 2 H), 7.09 – 7.00 (m, 1H), 6.9 (d, *J* = 15.3 Hz, 1 H), 2.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.2, 144.4, 143.3, 135.3, 129.2, 128.6, 127.5, 21.6, 18.5; IR (KBr): 3082, 1671, 1621, 1443, 966, 799, 742 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{12}O$ [M] + Na^+ = 183.0782, Found = 183.0775.

3b. (E)-1-phenylbut-2-en-1-one:



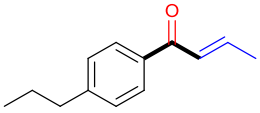
Yield: 71% (52 mg); pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.92 (d, *J* = 7.8 Hz, 2 H), 7.54 (t, *J* = 6.6 Hz, 1 H), 7.46 (t, *J* = 7.5 Hz, 2 H), 7.11–7.01 (m, 1 H), 6.91 (d, *J* = 15.3 Hz, 1 H), 2.00 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.8 145.0, 137.9, 132.6, 128.5, 127.6, 18.6; IR (KBr): 3059, 1671, 1624, 1443, 966, 691 cm^{-1}; HRMS (ESI) Calcd for $C_{10}H_{10}O$ [M] + Na^+ = 169.0629, Found = 169.0666.

3c. (E)-1-(4-ethylphenyl)but-2-en-1-one:



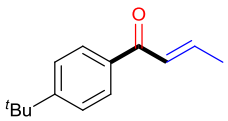
Yield: 73% (63.5 mg); pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.87 (d, *J* = 8.3 Hz, 2 H), 7.28 (d, *J* = 8.3 Hz, 2 H), 7.11-7.02 (m, 1 H), 6.91 (dd, *J* = 15.3 Hz, *J* = 1.5 Hz, 1 H), 2.70 (dd, *J* = 15.2 Hz, *J* = 7.6 Hz, 2 H), 1.99 (dd, J = 6.8 Hz, J = 1.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.3, 149.6, 144.4, 135.6, 128.7, 128.0, 127.5, 28.9, 18.5, 15.1. IR (KBr): 3031, 1671, 1607, 1413, 969, 810 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{14}O$ [M] + Na^+ = 197.0942, Found = 197.0940.

3d. (E)-1-(4-propylphenyl)but-2-en-1-one:



Yield: 71% (66 mg); pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.86 (d, *J* = 8.2 Hz, 2 H), 7.26 (d, *J* = 8.1 Hz, 2 H), 7.11-7.02 (m, 1 H), 6.91 (dd, *J* = 15.3 Hz, *J* = 1.4 Hz, 1 H), 2.64 (t, *J* = 7.5 Hz, 2 H), 1.98 (dd, *J* = 6.8 Hz, *J* = 1.3Hz, 3H), 1.66 (m, 2 H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.3, 148.0, 144.4, 135.6, 128.7, 128.6, 127.5 38.0, 24.2, 18.5, 13.7. IR (KBr): 3036, 1668, 1618, 1440, 1299, 969 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{16}O$ [M] + Na^+ = 211.1094, Found = 211.1087.

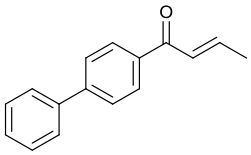
3e. (E)-1-(4-(tert-butyl)phenyl)but-2-en-1-one:



Yield: 85% (86 mg); pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88 (d, *J* = 8.2 Hz, 2 H), 7.48 (d, *J* = 8.2 Hz, 2 H), 7.11-7.02 (m, 1 H), 6.91 (d, *J* = 15.3 Hz, 1

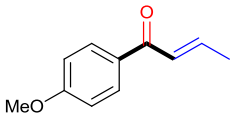
H), 1.99 (d, *J* = 6.8 Hz, 3H), 1.34 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.3, 156.3, 144.5, 135.3, 128.5, 127.5, 125.5, 35.1, 31.1, 18.6; IR (KBr): 3042, 1671, 1621, 1440, 966, 810 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{18}O$ [M]+Na^+ = 225.1251, Found = 225.1240.

3f. (E)-1-([1, 1'-biphenyl]-4-yl)but-2-en-1-one:



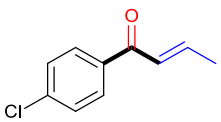
Yield: 60% (67 mg); white solid, Mp (91-92 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.01 (d, *J* = 8.4 Hz, 2 H), 7.68 (d, *J* = 8.4 Hz, 2 H), 7.62 (d, *J* = 7.2 Hz, 2 H), 7.48-7.37 (m, 3 H), 7.15 – 7.06 (m, 1H), 6.95 (dd, *J* = 15.2 Hz, *J* = 1.5 Hz, 1 H), 2.01 (dd, *J* = 6.8 Hz, *J* = 1.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.2, 145.3, 144.9, 140.0, 136.6, 129.1, 128.9, 127.5, 127.3, 127.2, 18.6; IR (KBr): 3056, 1665, 1618, 1440, 919, 760 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{14}O$ [M] + Na^+ = 245.0937, Found = 245.0931.

3g. (E)-1-(4-methoxyphenyl)but-2-en-1-one:



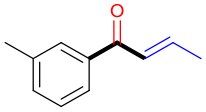
Yield: 62% (54 mg); colorless oil. ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 7.93 (d, *J* = 8.8 Hz, 2 H), 7.09 – 7.00 (m, 1 H), 6.94-6.89 (m, 3 H), 3.85 (s, 3 H), 1.97 (dd, *J* = 6.7 Hz, *J* = 1.2 Hz, 3 H); ^{13}C NMR(100 MHz, CDCl3) δ (ppm): 188.9, 163.3, 143.9, 130.8, 127.2, 113.7, 55.4, 18.5; IR (KBr): 3067, 1665, 1612, 1443, 1027, 1071, 813 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{12}O_2$ [M] + Na = 199.0730, Found = 199.0725.

3h. (E)-1-(4-chlorophenyl)but-2-en-1-one:



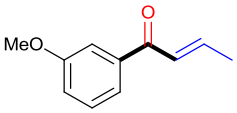
Yield: 30% (27 mg); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.87 (d, *J* = 8.6 Hz, 2 H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.13 – 7.04 (m, 1H), 6.87 (dd, *J* = 15.3 Hz, *J* = 1.6 Hz, 1 H), 2.01(dd, *J* = 6.9 Hz, *J* = 1.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 189.4, 145.6, 139.0, 136.2, 129.9, 128.8, 127.1, 18.6; IR (KBr): 3061, 1668, 1618, 1260, 1091, 805 cm^{-1}; HRMS (ESI) Calcd for $C_{10}H_9ClO$ [M] + Na^+ = 203.0234, Found = 203.0218.

3i. (E)-1-(m-tolyl)but-2-en-1-one:



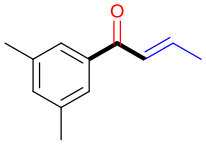
Yield: 88% (70 mg); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.74–7.70 (m, 2 H), 7.37-7.32 (m, 2 H), 7.11-7.02 (m, 1 H), 6.90 (dd, *J* = 15.3 Hz, *J* = 1.5 Hz, 1 H), 2.41 (s, 3 H), 2.00 (dd, *J* = 6.8 Hz, *J* = 1.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.9, 144.7, 138.3, 137.9, 133.3, 129.0, 128.3, 127.7, 125.7, 21.3, 18.5; IR (KBr): 2959, 1651, 1615, 1257, 1099, 802 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{12}O$ [M] + Na^+ = 183.0780, Found=183.0776.

3j. (E)-1-(3-methoxyphenyl)but-2-en-1-one:



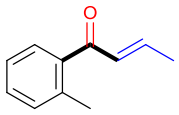
Yield: 78% (69mg); pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 – 7.46 (m, 2 H), 7.36 (t, *J* = 8.0 Hz, 2 H), 7.12-7.03 (m, 2 H), 7.12-7.03 (m, 2H), 6.89 (dd, *J* = 15.3 Hz, *J* = 1.5 Hz, 1 H), 3.86 (s, 3 H), 2.00 (dd, *J* = 6.8 Hz, *J* = 1.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.5, 159.8, 145.1, 139.3, 129.5, 127.6, 121.7, 119.2, 112.8, 55.4, 18.6; IR (KBr): 3003, 1671, 1624, 1460, 1035, 780 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{12}O_2$ [M] + Na^+ = 199.0730, Found = 199.0721.

3k. (E)-1-(3,5-dimethylphenyl)but-2-en-1-one:



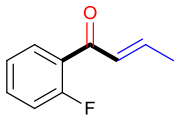
Yield: 86% (75 mg); pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.35 (s, 2 H), 7.17 (s, 1 H), 7.09-7.00 (m, 1 H), 6.90 (dd, *J* = 15.3 Hz, *J* = 1.5 Hz, 1 H), 2.36 (s, 6 H), 1.98 (dd, *J* = 6.8 Hz, *J* = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 191.1, 144.5, 138.1, 138.0, 134.2, 127.8, 129.4, 126.3, 21.2, 18.5; IR (KBr): 3042, 1674, 1601, 1307, 1188, 1043 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{14}O$ [M] + Na^{+} = 197.0938, Found = 197.0931.

3l. (E)-1-(o-tolyl)but-2-en-1-one:



Yield: 63% (50 mg); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37-7.30 (m, 2 H), 7.26-7.20 (m, 2 H), 6.77- 6.68 (m, 1 H), 6.50 (d, *J* = 15.7 Hz, 1 H), 2.38(s, 3 H), 1.94 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 196.9, 146.7, 139.0, 136.6, 132.4, 131.1, 130.1, 127.9, 125.2, 20.0, 18.5; IR (KBr): 3021, 1651, 1621, 1451, 1032, 763 cm^{-1}. HRMS (ESI) Calcd for $C_{11}H_{12}O$ [M] + Na^{+} = 183.0780, Found = 183.0776.

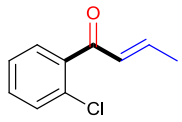
3m. (E)-1-(2-fluorophenyl)but-2-en-1-one:



Yield: 60% (49 mg); pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (td, *J* = 7.5Hz, *J* = 1.8 Hz, 1H), 7.51-7.45 (m, 1 H) ,7.22 (td, *J* = 7.6 Hz, *J* = 1.0 Hz 1 H), 7.14 – 7.09 (m, 1 H), 7.04-6.95 (m, 1 H), 6.77-6.71 (m, 1 H), 1.98 (dd, *J* = 6.9 Hz, *J* = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 188.6 (d, $J_{C\text{-}F}$ = 2.2 Hz), 159.9 (d, $J_{C\text{-}F}$ = 251 Hz), 144.7, 132.5 (d, $J_{C\text{-}F}$ = 8.6 Hz), 130.1 (d, $J_{C\text{-}F}$ = 5.4 Hz), 129.7 (d, $J_{C\text{-}F}$ = 2.8 Hz), 126.0 (d, $J_{C\text{-}F}$ = 13.8 Hz), 123.3 (d, $J_{C\text{-}F}$ = 3.5 Hz), 115.4 (d, $J_{C\text{-}F}$ = 22.8 Hz),

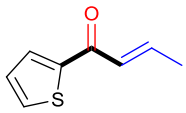
17.5; IR (KBr): 3006, 1674, 1649, 1454, 1035, 777 cm^{-1}. HRMS (ESI) Calcd for $C_{10}H_9FO$ [M] + Na^+ = 187.0530, Found = 187.0524.

3n. (E)-1-(2-chlorophenyl)but-2-en-1-one:



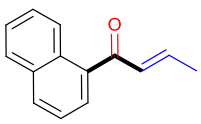
Yield: 68% (61 mg); colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42-7.29 (m, 4 H), 6.76-6.67 (m, 1 H), 6.48 (dd, *J* = 15.7 Hz, *J* = 1.6 Hz, 1 H), 1.96 (dd, *J* = 6.8 Hz, *J* = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 194.2, 148.0, 139.0, 132.0, 131.1, 130.1, 129.0, 126.6, 18.6; IR (KBr): 3059, 1660, 1618, 1435, 1038, 763 cm^{-1}; HRMS (ESI) Calcd for $C_{10}H_9ClO$ [M] + Na^+ = 203.0234, Found = 203.0231.

3o. (E)-1-(thiophen-3-yl)but-2-en-1-one:



Yield: 66% (50 mg); pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.75 (d, *J* = 3.4 Hz, 1 H), 7.63 (d, J = 4.8 Hz, 1 H), 7.17-7.08 (m, 2 H), 6.82 (d, *J* = 15.2 Hz, 1 H), 1.98 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 182.2, 145.1, 144.2, 133.6, 131.8, 128.1, 126.9, 18.4. IR (KBr): 3097, 1665, 1618, 1415, 1293, 1027 cm^{-1}. HRMS (ESI) Calcd for C_8H_8OS [M] + Na^+ = 175.0184, Found = 175.0182.

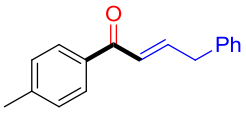
3p. (E)-1-(naphthalen-1-yl)but-2-en-1-one:



Yield: 80% (78 mg); pale yellow oil. ^1H NMR (400M Hz, $CDCl_3$) δ (ppm): 8.25 (d, *J* = 7.8 Hz, 1 H), 7.95 (d, *J* = 8.2 Hz, 1 H), 7.88 (d, *J* = 7.4 Hz, 1 H), 7.65 (d, *J* = 7.0 Hz, 1 H), 7.57-7.47 (m, 3 H), 6.90-6.81 (m, 1 H), 6.68 (d, *J* = 15.6 Hz, 1 H), 1.97 (d, *J* =

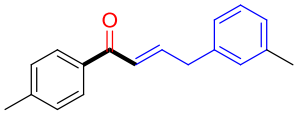
6.8 Hz, 3 H), 7.03 (dd, *J* = 1.4 Hz, *J* = 5.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 196.1, 146.9, 136.9, 133.8, 132.8, 131.3, 130.5, 128.3, 127.3, 126.9, 126.4, 125.6, 124.4, 18.6; IR (KBr): 3056, 1668, 1621, 1296, 1185, 816 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{12}O$ [M] + Na^+ = 219.0782, Found = 219.0772.

4b. (E)-4-phenyl-1-(p-tolyl)but-2-en-1-one



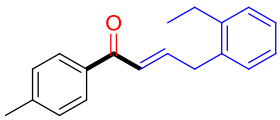
Yield: 55% (65 mg); pale yellow oil. ^{1}H NMR (400M Hz, $CDCl_3$) δ (ppm): 7.90 (d, *J* = 8.2 Hz, 2 H), 7.37 (d, *J* = 7.3 Hz, 2 H), 7.31-7.19 (m, 5 H), 6.56-6.43 (m, 2 H), 3.87 (d, *J* = 6.1 Hz, 3 H), 2.4 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 197.6, 144.0, 137.1, 134.2, 133.4, 129.4, 128.5, 128.4, 127.4, 126.3, 122.8, 42.7, 21.7; IR (KBr): 3028, 1674, 1604, 1257, 1177, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{16}O$ [M] + Na^+ = 259.1099, Found = 259.1096.

4c. (E)-4-(m-tolyl)-1-(p-tolyl)but-2-en-1-one



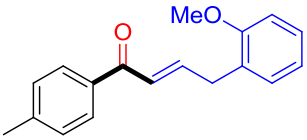
Yield: 56% (70 mg); pale yellow oil; ^{1}H NMR (400M Hz, $CDCl_3$) δ (ppm): 7.91 (d, *J* = 8.1 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.21-7.18 (m, 3 H), 7.04 (d, *J* = 5.7 Hz, 1 H), 6.54 – 6.43 (m, 2 H), 3.88 (d, *J* = 5.9 Hz, 2 H), 2.42 (s, 3 H), 2.34 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 197.7, 144.0, 141.3, 138.0, 137.0, 134.2, 133.5, 129.4, 128.5, 128.4, 128.2, 126.9, 123.5, 122.6, 42.7, 21.7, 21.4; IR (KBr): 3028, 1674, 1607, 1282, 1179, 752 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{18}O$ [M] + H^+ = 251.1430, Found = 251.1424.

4d. (E)-4-(2-ethylphenyl)-1-(p-tolyl)but-2-en-1-one



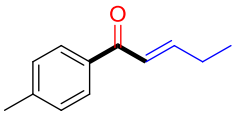
Yield: 45% (60 mg); pale yellow oil. ^{1}H NMR (400M Hz, $CDCl_3$) δ (ppm): 7.92 (d, *J* = 8.0 Hz, 2 H), 7.46 (d, *J* = 7.4 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.18 (m, 3 H), 6.80 (d, *J* = 15.7 Hz, 1H), 6.38-6.30 (m, 1 H), 3.91 (d, *J* = 6.8 Hz, 2 H), 2.68 (q, *J* = 7.6 Hz, 2 H), 2.42 (s, 3 H), 1.18 (t, *J* = 7.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$), δ = 197.7, 144.0, 141.3, 135.6, 134.2, 131.2, 129.3, 128.6, 128.5, 127.6, 126.1, 126.0, 124.3, 43.0, 26.3, 21.6, 15.3; IR (KBr): 3028, 1674, 1607, 1260, 1178, 784 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{20}O$ [M] + Na^+ = 287.1406, Found =287.1404.

4e. (E)-4-(2-methoxyphenyl)-1-(p-tolyl)but-2-en-1-one



Yield: 65% (86 mg); pale yellow oil. ^{1}H NMR (400M Hz, $CDCl_3$) δ (ppm): 7.90 (d, *J* = 8.1 Hz, 2 H), 7.45 (dd, *J* = 7.6 Hz, *J* = 1.4 Hz, 2 H), 7.27 (d, *J* = 8.3 Hz, 2 H), 7.22-7.18 (m, 1 H), 6.92-6.84 (m, 3 H), 6.50-6.43 (m, 1 H), 3.90 (dd, *J* = 6.9 Hz, *J* = 1.4 Hz, 2 H), 3.84 (s, 3 H), 2.42(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 197.8, 156.5, 143.9, 134.3, 129.3, 128.5, 128.4, 128.2, 126.9, 126.2, 123.4, 120.7, 110.8, 55.5, 43.2, 21.6; IR (KBr): 2956, 1671, 1599, 1488, 1243, 1024 cm^{-1}; $C_{18}H_{18}O_2$ [M] + Na^+ = 289.1200, Found = 289.1202.

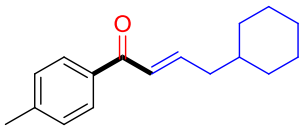
4f. (E)-1-(p-tolyl)pent-2-en-1-one



Yield: 60% (52 mg); pale yellow oil; ^{1}H NMR (400M Hz, $CDCl_3$): δ = 7.84 (d, *J* = 8.2 Hz, 2 H), 7.26 (d, *J* = 7.9 Hz, 2 H), 7.13 – 7.06 (m, 1H), 6.87 (td, *J* = 15.4 Hz, *J* = 1.6 Hz, 1 H), 2.42 (s, 3 H), 2.38-2.30 (m, 3 H) 1.14 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$), δ = 190.6, 150.7, 143.3, 135.5, 129.2, 128.7, 124.9, 25.9, 21.6,

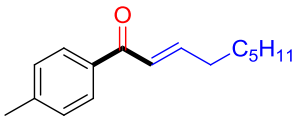
12.4. IR (KBr): 3113, 2920, 1733, 1503, 1389, 1255, 1192, 751 cm^{-1}. $C_{12}H_{14}O$ [M] + Na^+ = 197.0937, Found = 197.0932.

4g. (E)-4-cyclohexyl-1-(p-tolyl)but-2-en-1-one



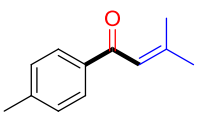
Yield: 56% (68 mg); pale yellow oil. ^1H NMR (400M Hz, $CDCl_3$) δ (ppm): 7.84 (d, *J* = 8.2 Hz, 2 H), 7.26 (d, *J* = 7.9 Hz, 2 H), 7.08-7.00 (m, 1 H), 6.85 (td, *J* = 15.3 Hz, *J* = 1.2 Hz, 1 H), 2.41 (s, 3 H), 2.22-2.18(m, 2 H), 1.77-1.63 (m, 5 H), 1.51 – 1.46 (m, 1 H), 1.29-1.13 (m, 3H), 1.02-0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.3, 148.4, 143.3, 135.5, 129.2, 128.7, 126.9, 40.8, 37.5, 33.2, 26.4, 26.2, 21.6; IR (KBr): 3028, 1668, 1610, 1446, 1263, 1016, 805 cm^{-1}; $C_{17}H_{22}O$ [M] + H^+ = 243.1743, Found = 243.1739.

4h. (E)-1-(p-tolyl)non-2-en-1-one



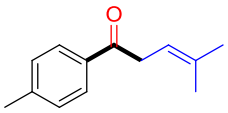
Yield: 43% (50 mg); pale yellow oil. ^1H NMR (400M Hz, $CDCl_3$) δ (ppm): 7.84 (d, *J* = 8.2 Hz, 2 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 7.09-7.02 (m, 1 H), 6.87 (td, *J* = 15.4 Hz, *J* = 1.3 Hz), 2.41 (s, 3 H), 2.33-2.28 (m, 2 H), 1.55-1.48 (m, 2 H), 1.37-1.28 (m, 6 H), 0.89 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.5, 149.6, 143.3, 135.5, 130.2, 129.2, 128.7, 125.8, 32.8, 31.6, 28.9, 28.2, 22.6, 21.6, 14.1; IR (KBr): 2970, 1696, 1649, 1538, 1451, 1041 cm^{-1}; $C_{16}H_{22}O$ [M] + Na^+ = 253.1559, Found = 253.1559.

4i. 3-methyl-1-(p-tolyl)but-2-en-1-one



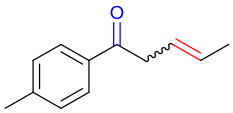
Yield: 84% (73 mg); pale yellow oil. ^{1}H NMR (400M Hz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.2 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 6.72 (t, *J* = 1.2 Hz, 1 H), 2.39 (s, 3 H), 2.19 (d, *J* = 0.8 Hz, 3 H), 2.00 (d, *J* = 0.9 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.3, 154.8, 141.9, 135.7, 128.1, 127.3, 120.2, 26.9, 20.5, 20.1; IR (KBr): 2961, 1660, 1610, 1254, 1013, 805 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{14}O$ [M] + Na^+ = 197.0937, Found = 197.0933.

4j. 4-methyl-1-(p-tolyl)pent-3-en-1-one



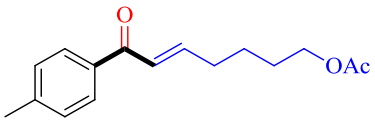
pale yellow oil; ^{1}H NMR (400M Hz, $CDCl_3$) δ (ppm): 7.87 (d, *J* = 8.2 Hz, 2 H), 7.26 (d, *J* = 7.9 Hz, 2 H), 5.45 – 5.41 (m, 1 H), 3.66 (d, *J* = 6.9 Hz, 2 H), 2.41 (s, 3 H), 1.76 (d, *J* = 1.1 Hz, 3 H), 1.69 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.3, 143.7, 135.3, 134.4, 129.2, 128.4, 116.5, 38.4, 25.8, 21.6, 18.2; IR (KBr): 2975, 1665, 1604, 1503, 1293, 1179, 816 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{16}O$ [M] + Na^+ = 211.1093, Found = 211.1107.

4f-a. (Z/E)-1-(p-tolyl)pent-3-en-1-one



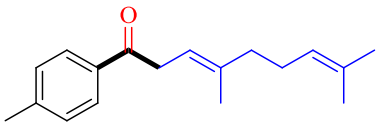
pale yellow oil; ^{1}H NMR (400M Hz, $CDCl_3$) δ (ppm): 7.89 (m, 2 H), 7.28 (m, 2 H), 5.75-5.61 (m, 2 H), 3.76-3.67 (m, 2 H), 2.43 (s, 3 H), 1.75-1,67 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.4, 197.9, 143.8, 134.3, 134.2, 129.4, 129.3, 128.5, 128.4, 127.4, 123.6, 122.5, 42.4, 37.1, 21.7, 18.2, 13.2; IR (KBr): 3036, 1668, 1607, 1279, 1018, 810 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{14}O$ [M] + Na^+ = 197.0937, Found = 197.0932.

4k. (E)-7-oxo-7-(p-tolyl)hept-5-en-1-yl acetate



Yield: 52% (67 mg); pale yellow oil; ^{1}H NMR (400M Hz, $CDCl_3$) δ (ppm): 7.85 (d, *J* = 8.1 Hz, 2 H), 7.27 (d, *J* = 7.1 Hz, 2 H), 7.07-7.00 (m, 1 H), 6.90 (d, *J* = 15.4 Hz), 4.09 (t, *J* = 6.3 Hz, 2 H), 2.42 (s, 3 H), 2.36 (q, *J* = 7.0 Hz, 2 H), 2.06 (s, 3 H), 1.72-1.67 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.3, 143.7, 135.3, 134.4, 129.2, 128.4, 116.5, 38.4, 25.8, 21.6, 18.2; IR (KBr): 2989, 1732, 1662, 1615, 1235, 1038 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{20}O_3$ [M] + Na^+ = 283.1305, Found = 283.1296.

4l. (E)-4, 8-dimethyl-1-(p-tolyl) nona-3, 7-dien-1-one



Yield: 40% (51 mg); pale yellow oil; ^{1}H NMR (400M Hz, $CDCl_3$) δ (ppm): 7.87 (d, *J* = 8.2 Hz, 2 H), 7.26 (d, *J* = 7.9 Hz, 2 H), 5.46-5.41 (m, 1 H), 5.08-5.05 (m, 1 H), 3.67 (d, *J* = 6.8 Hz, 2 H), 2.41 (s, 3 H), 2.08 (m, 4 H), 1.69 (s, 3 H), 1.64 (s, 3 H), 1.58 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 198.3, 143.7, 138.8, 134.4, 131.6, 129.2, 128.5, 124.0, 116.4, 39.7, 38.4, 26.5, 25.6, 21.6, 17.7, 16.6; IR (KBr): 2981, 1676, 1610, 1285, 1105, 813 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{24}O$ [M] + H^+ = 257.1890, Found = 257.1893.

7. References

Entry	Products	Reference
1	**3a**	[S1]
2	**3b**	[S1]
3	**3f**	[S1]
4	**3g**	[S1]
5	**3h**	[S1]

6	**3i**	[S1]
7	**3o**	[S1]
8	**3p**	[S1]
9	**3m**	[S2]

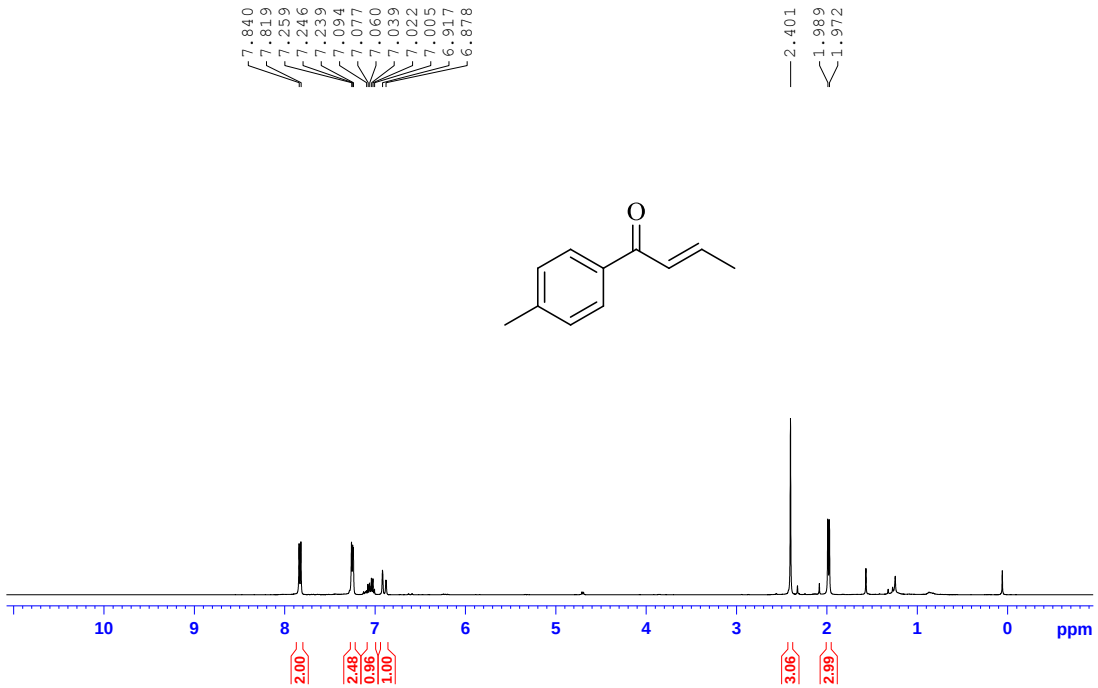
[S1] F. Manjolinho, M. F. Grünberg, N. Rodríguez, L. J. Gooßen, *Eur. J. Org. Chem.* **2012**, 2012, 4680-4683;

[S2] N. Rodríguez, F. Manjolinho, M. F. Grünberg, L. J. Gooßen, *Chem. Eur. J.* **2011**, 17, 13688-13691.

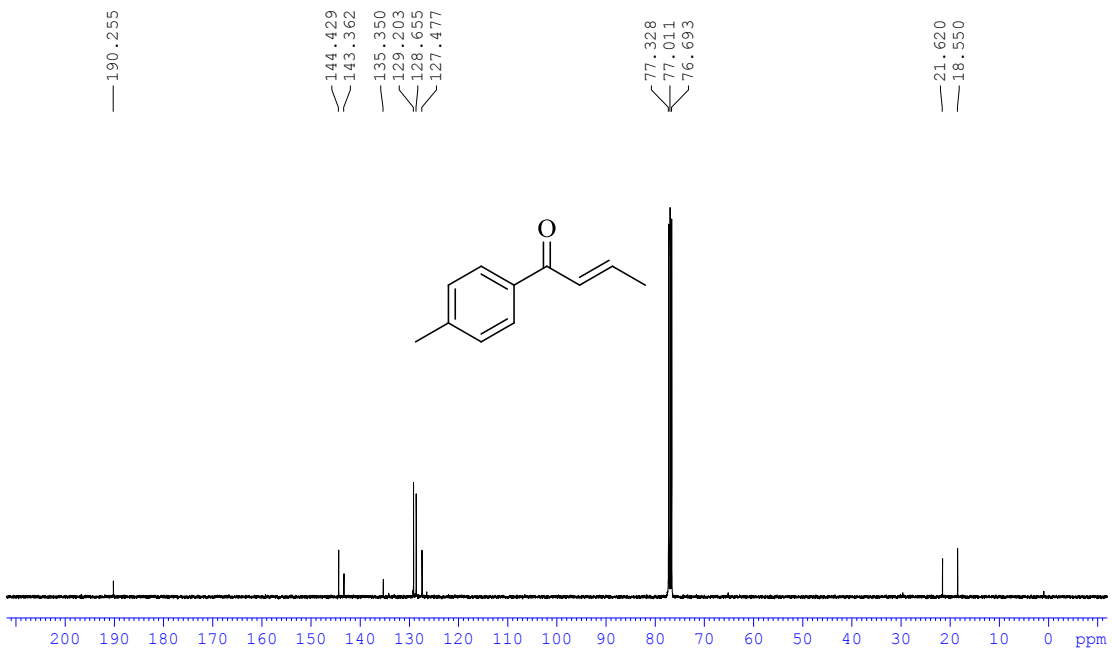
8. Copies of the ^{1}H NMR and ^{13}C NMR spectra of products

3a. (E)-1-(p-tolyl)but-2-en-1-one

^{1}H NMR (400 MHz, $CDCl_3$)

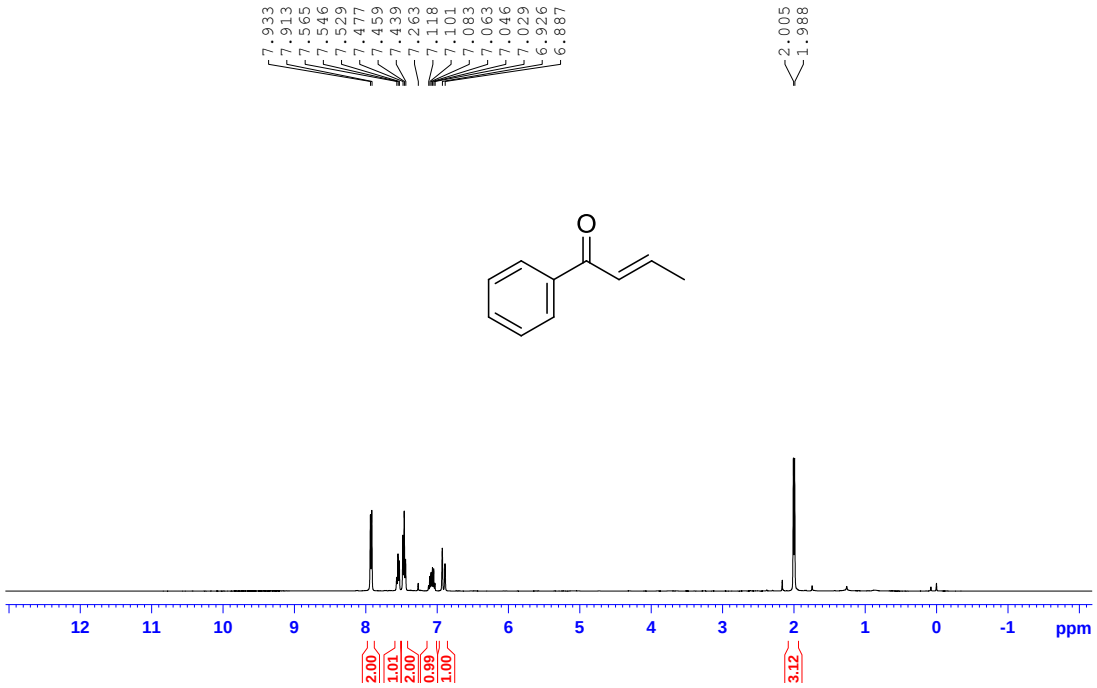


^{13}C NMR (100 MHz, $CDCl_3$)

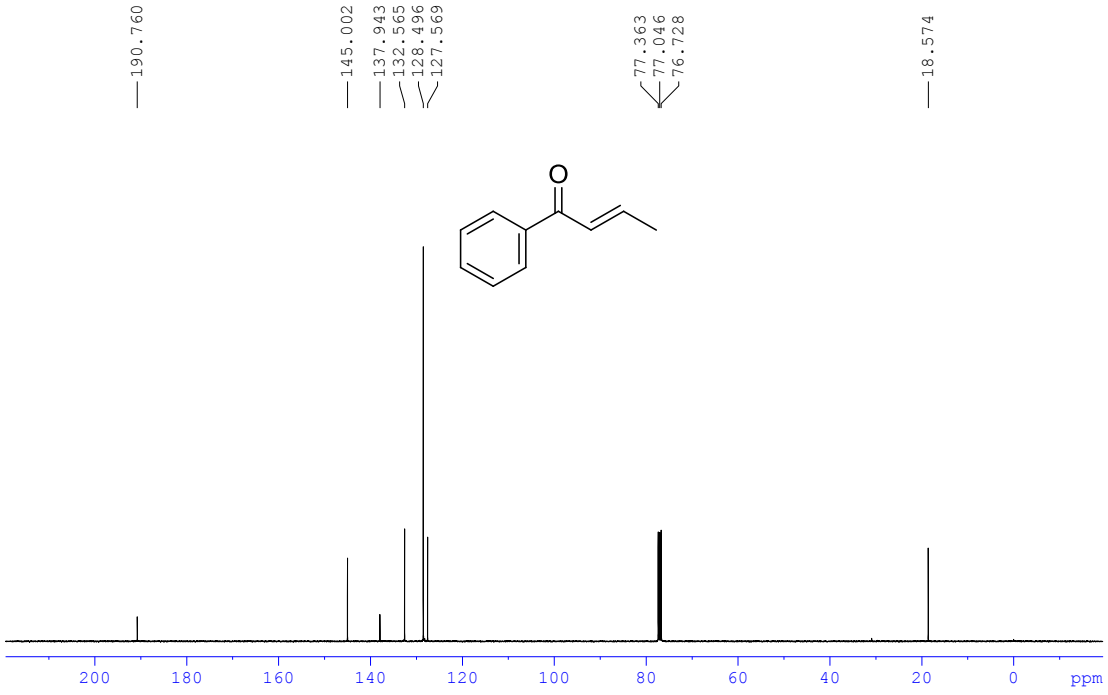


3b. (E)-1-phenylbut-2-en-1-one:

^{1}H NMR (400 MHz, $CDCl_3$)

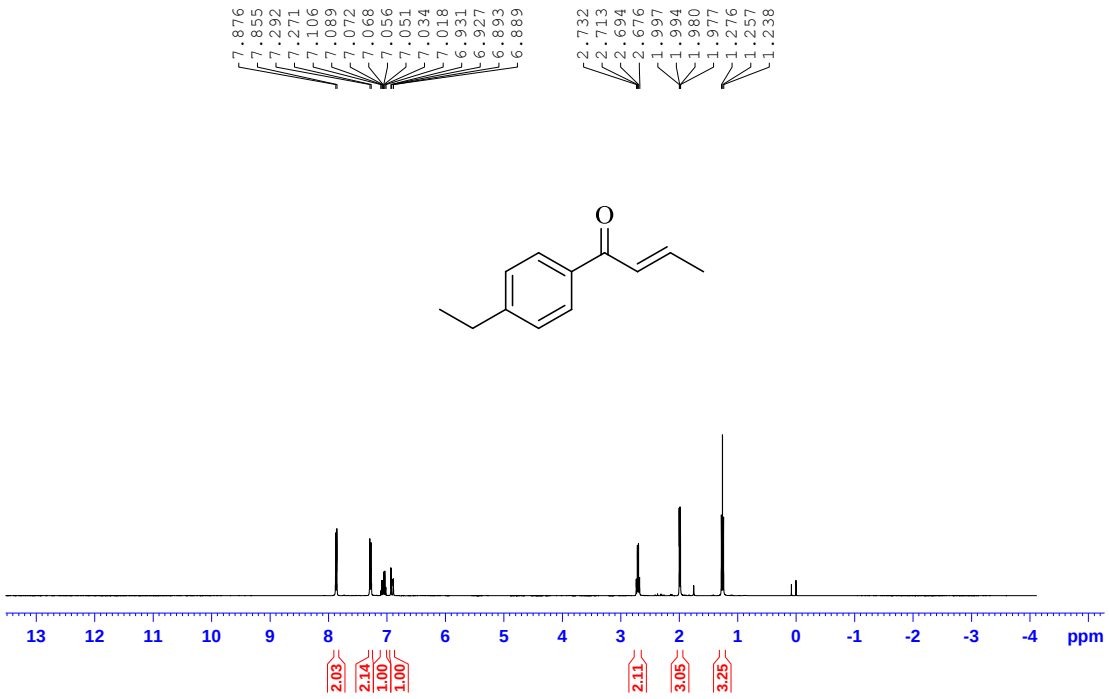


^{13}C NMR (100 MHz, $CDCl_3$)

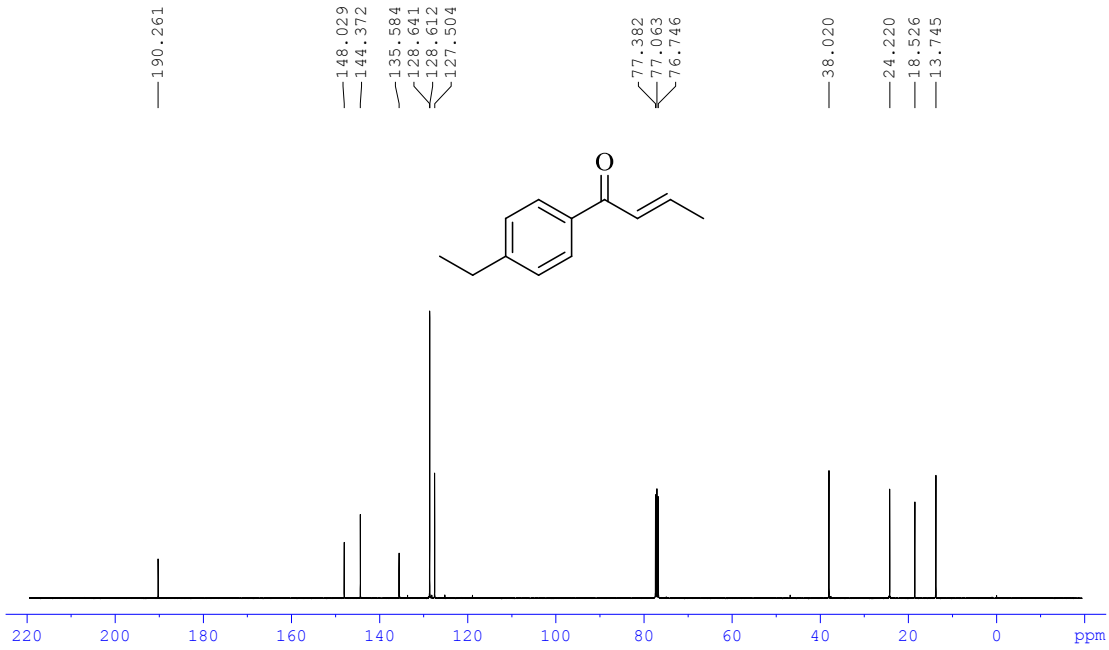


3c. (E)-1-(4-ethylphenyl)but-2-en-1-one:

^{1}H NMR (400 MHz, $CDCl_3$)

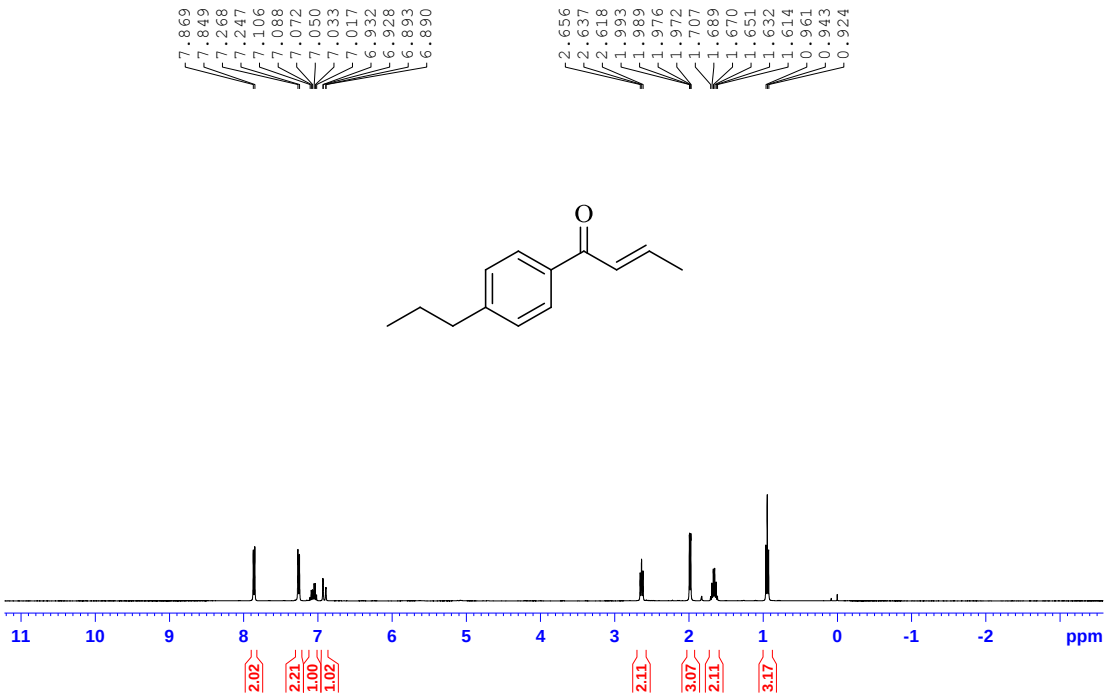


^{13}C NMR (100 MHz, $CDCl_3$)

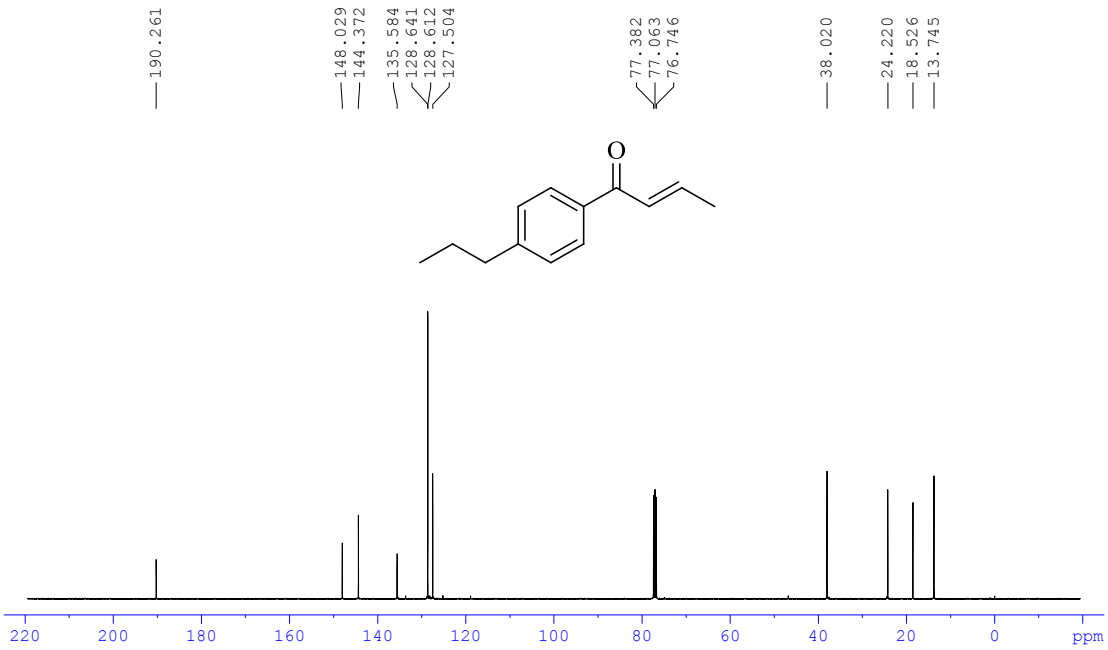


3d. (E)-1-(4-propylphenyl)but-2-en-1-one:

^{1}H NMR (400 MHz, $CDCl_3$)

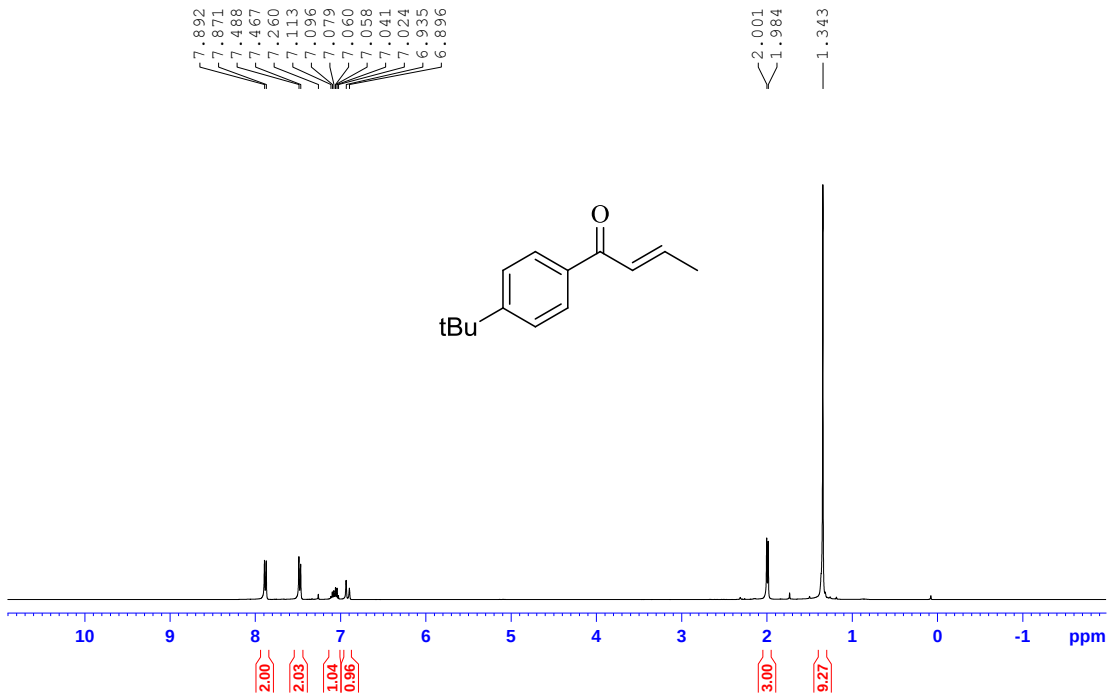


^{13}C NMR (100 MHz, $CDCl_3$)

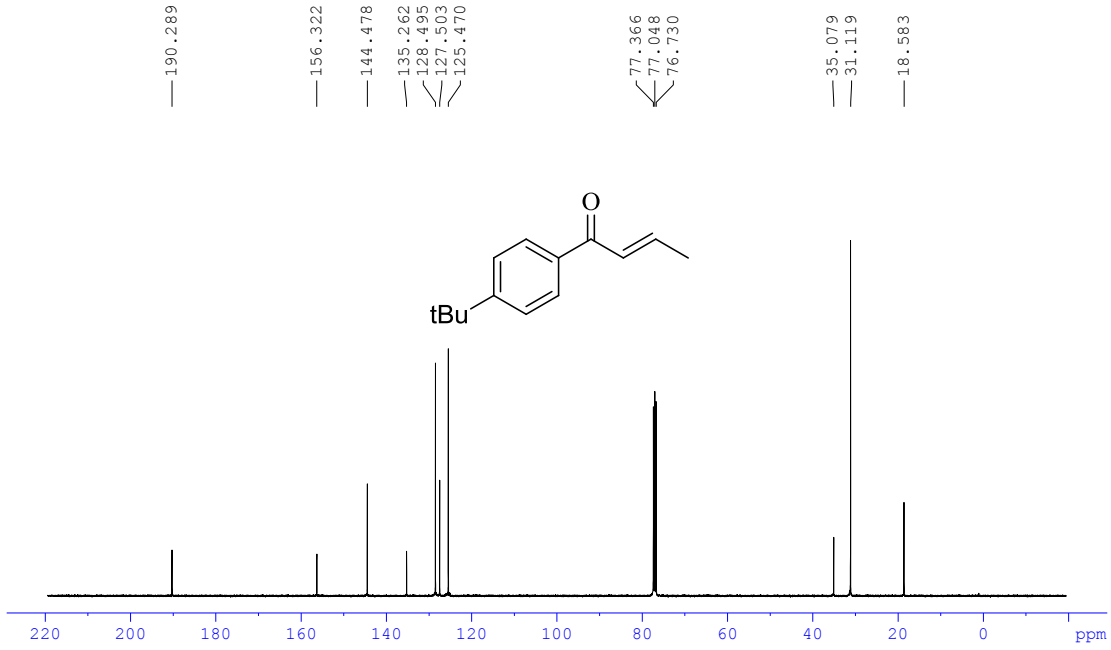


3e. (E)-1-(4-(tert-butyl)phenyl)but-2-en-1-one:

^{1}H NMR (400 MHz, $CDCl_3$)

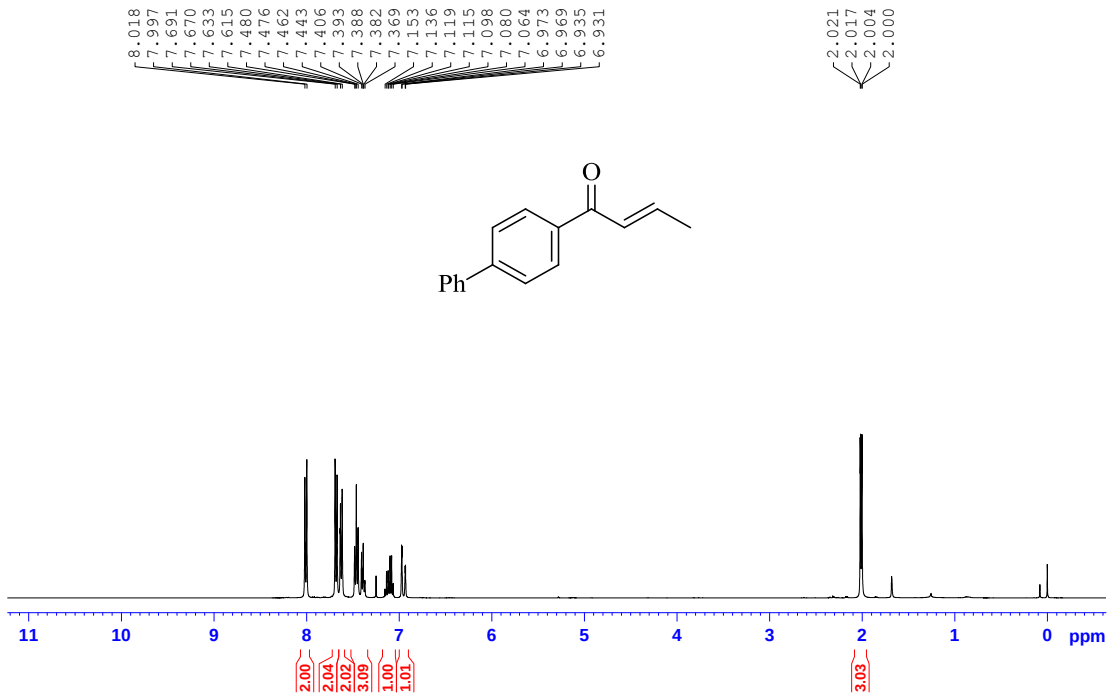


^{13}C NMR (100 MHz, $CDCl_3$)

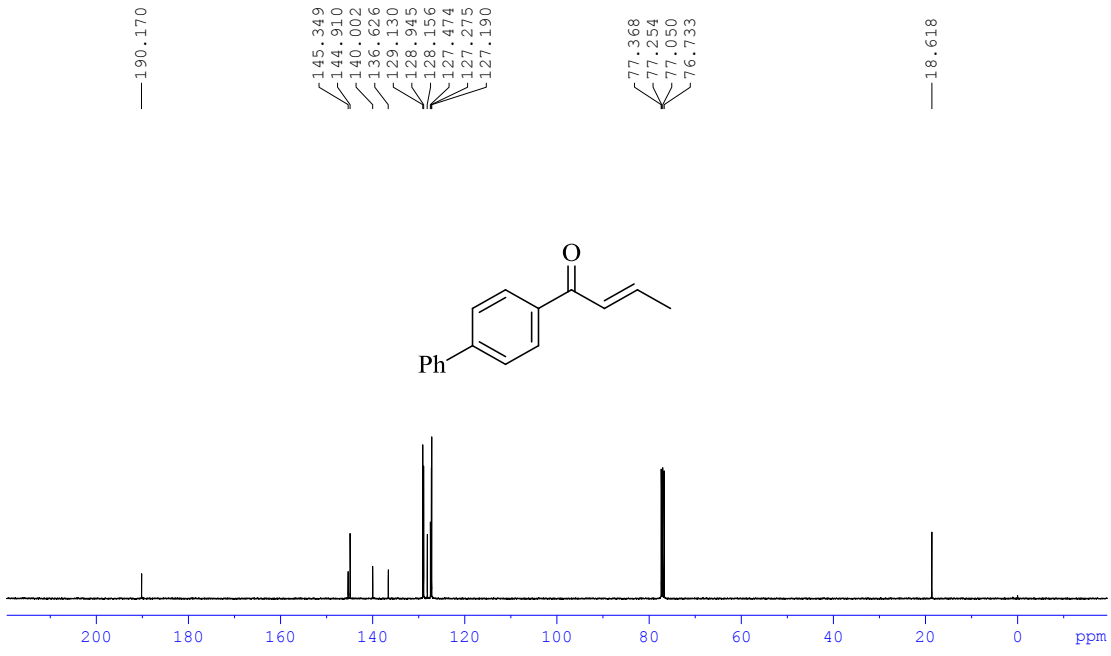


3f. (E)-1-([1,1'-biphenyl]-4-yl)but-2-en-1-one:

^{1}H NMR (400 MHz, $CDCl_3$)

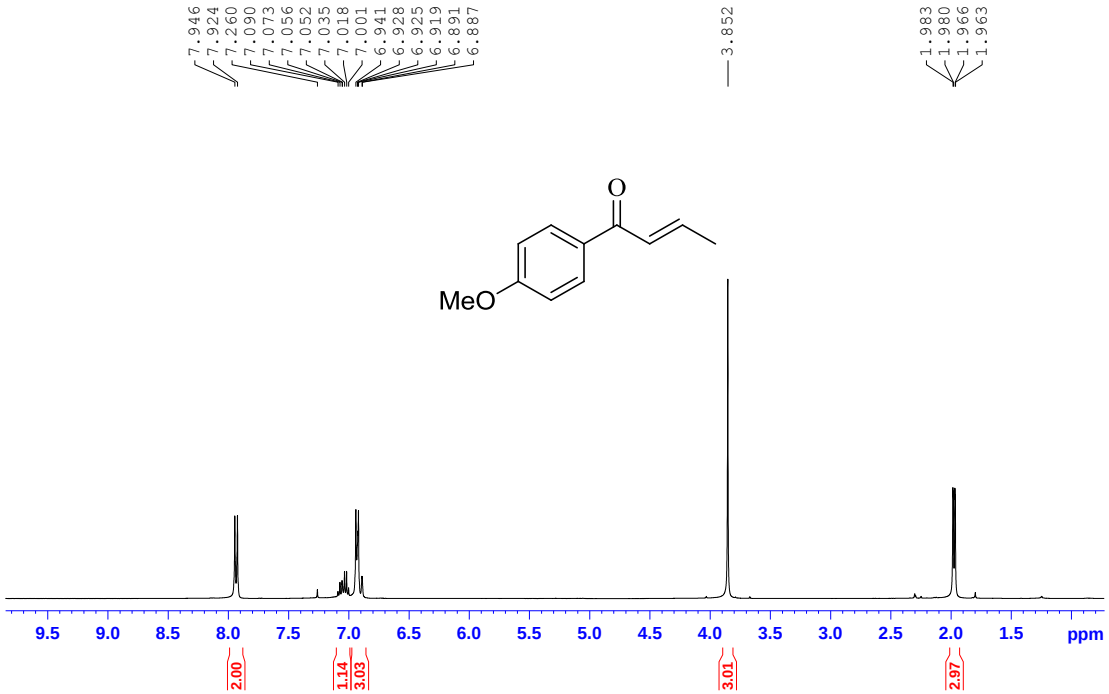


^{13}C NMR (100 MHz, $CDCl_3$)

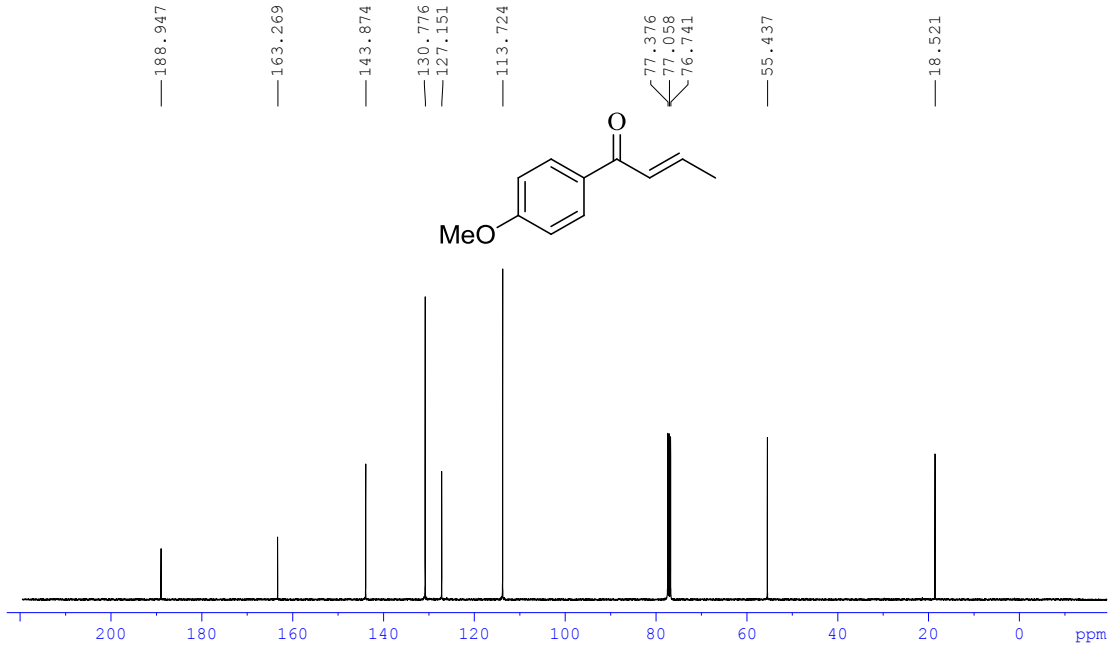


3g. (E)-1-(4-methoxyphenyl)but-2-en-1-one

^{1}H NMR (400 MHz, $CDCl_3$)

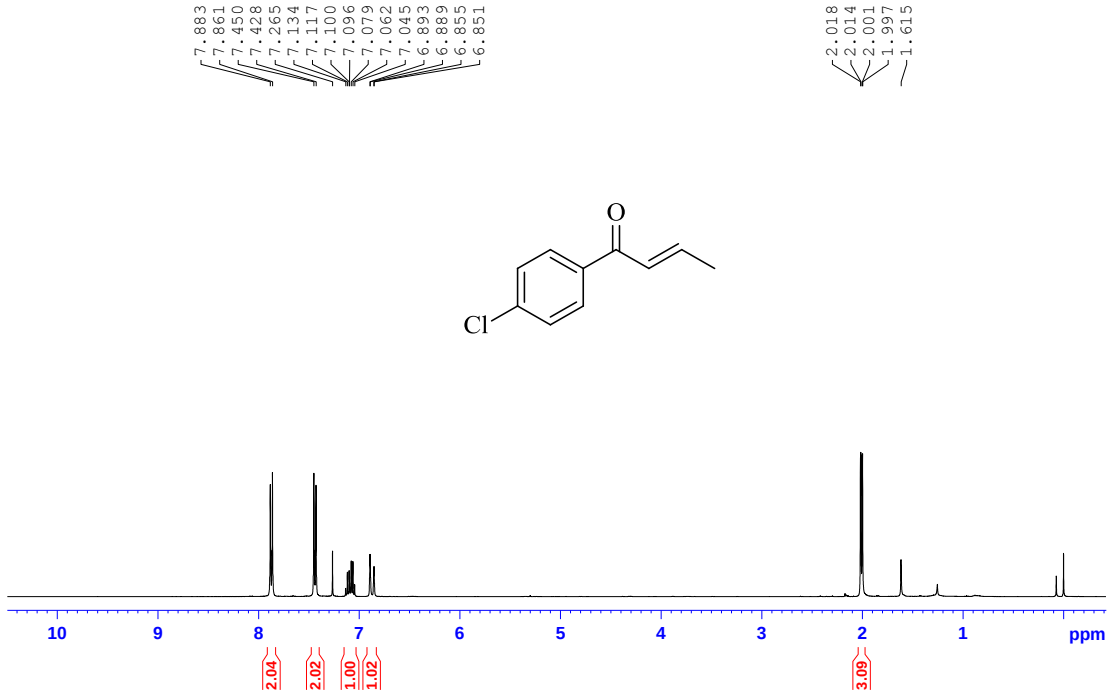


^{13}C NMR (100 MHz, $CDCl_3$)

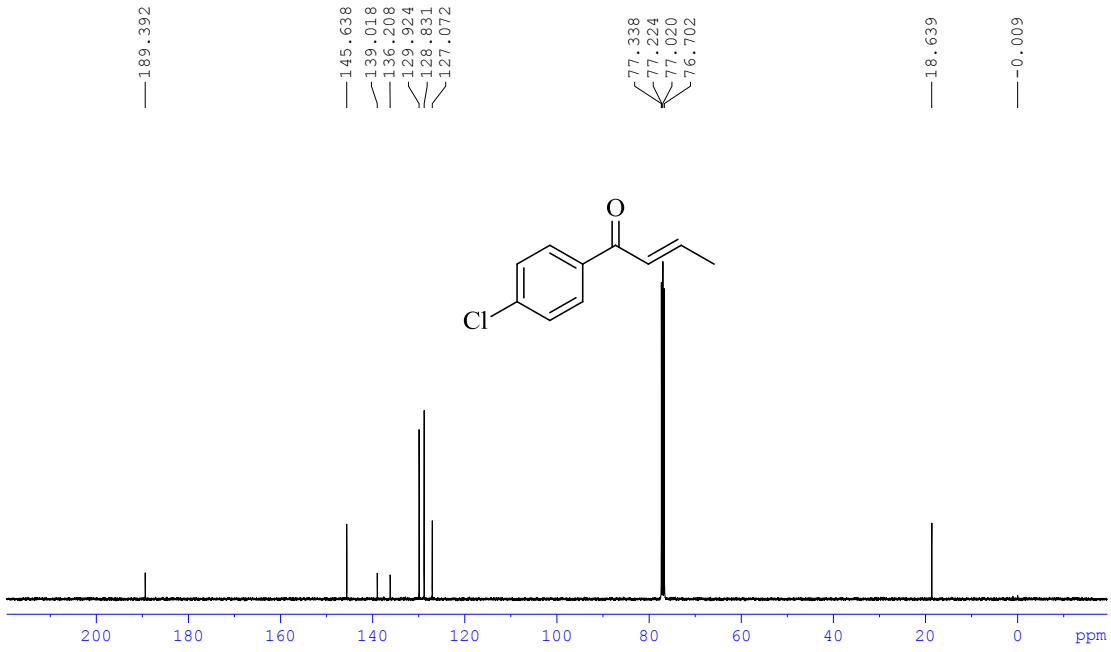


3h. (E)-1-(4-chlorophenyl)but-2-en-1-one:

^{1}H NMR (400 MHz, $CDCl_3$)

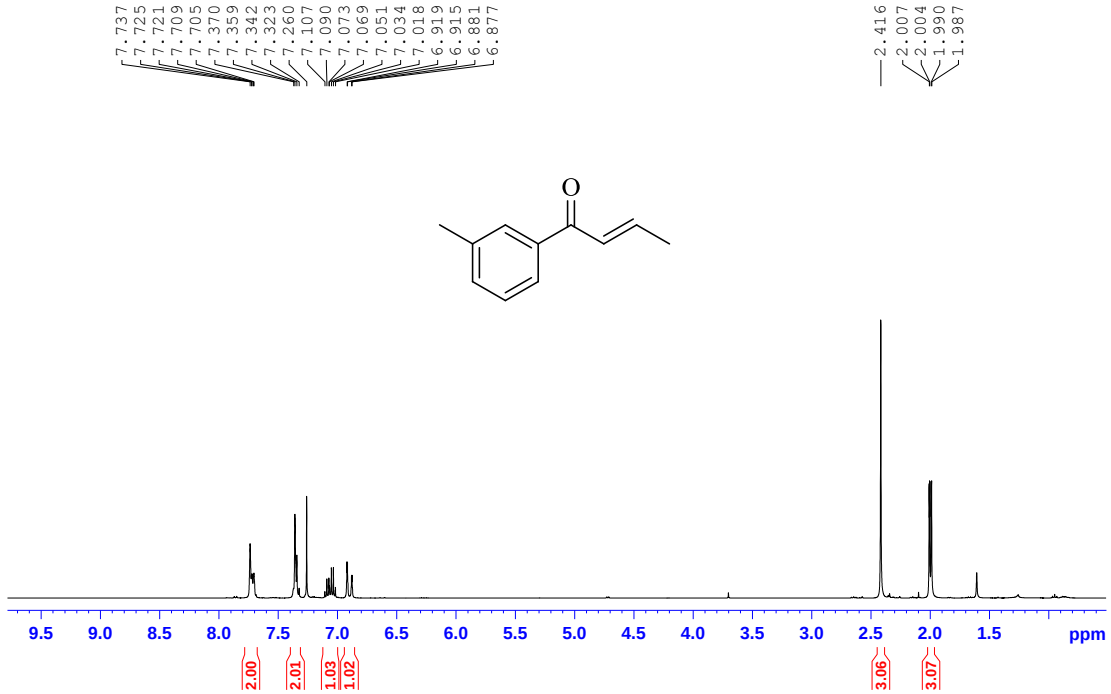


^{13}C NMR (100 MHz, $CDCl_3$)

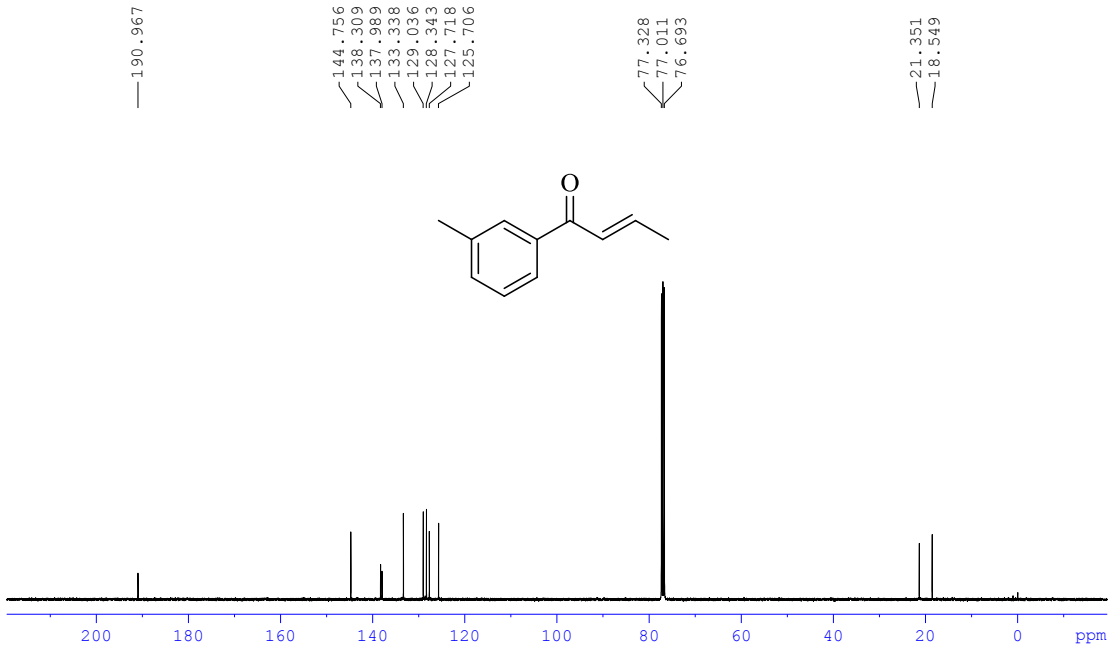


3i. (E)-1-(m-tolyl)but-2-en-1-one:

^{1}H NMR (400 MHz, $CDCl_3$)

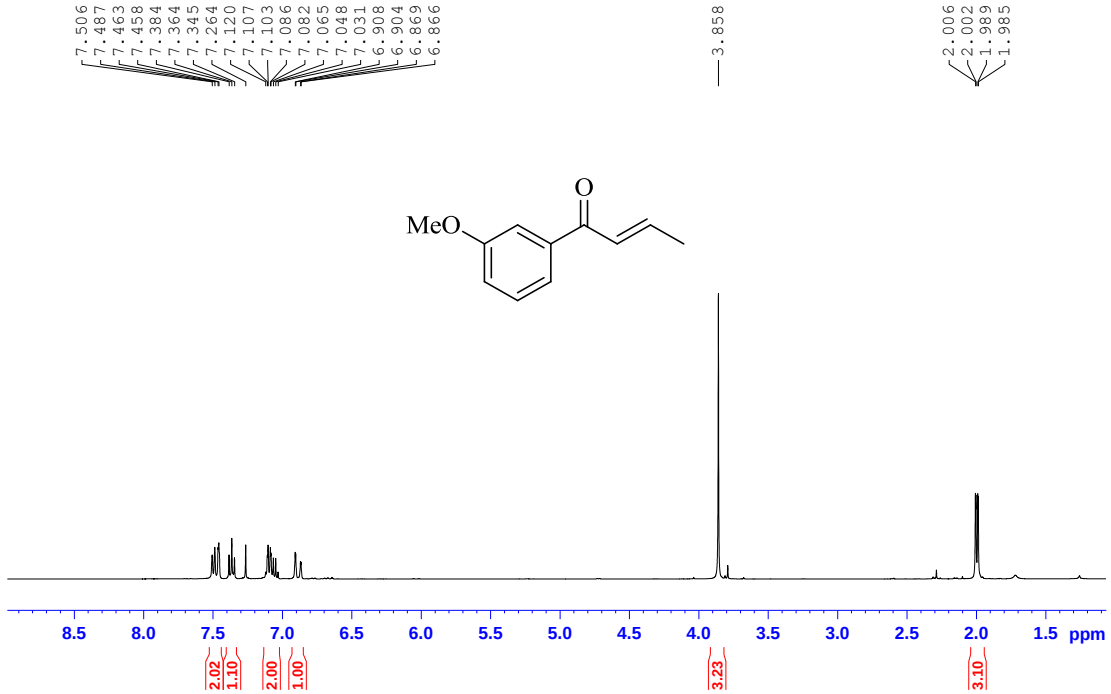


^{13}C NMR (100 MHz, $CDCl_3$)

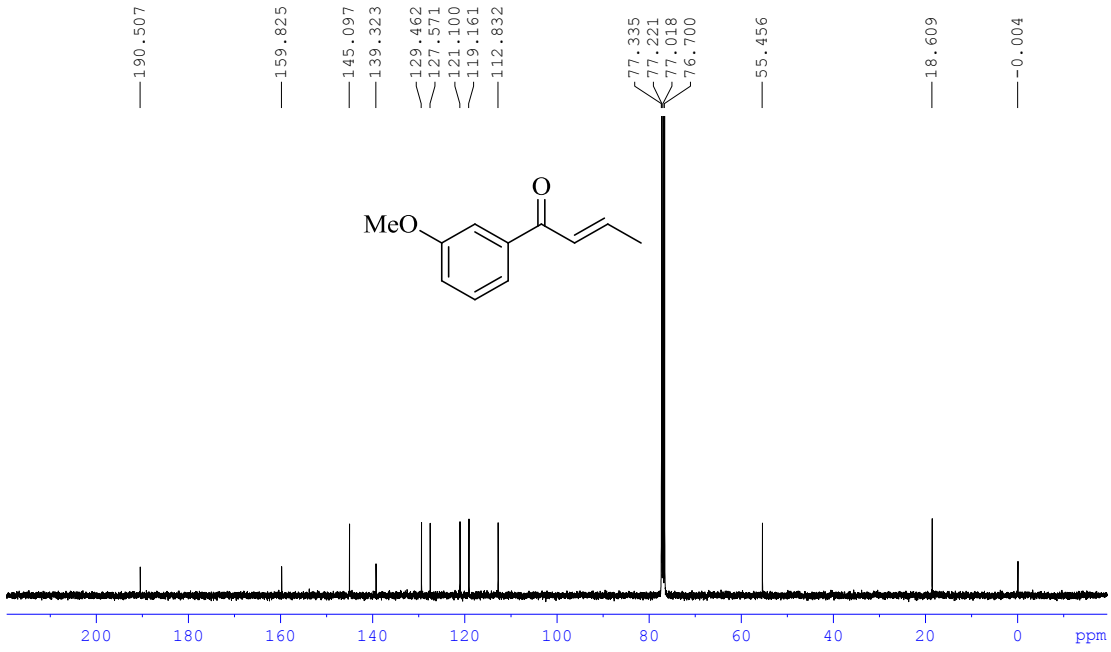


3j. (E)-1-(3-methoxyphenyl)but-2-en-1-one:

^{1}H NMR (400 MHz, $CDCl_3$)

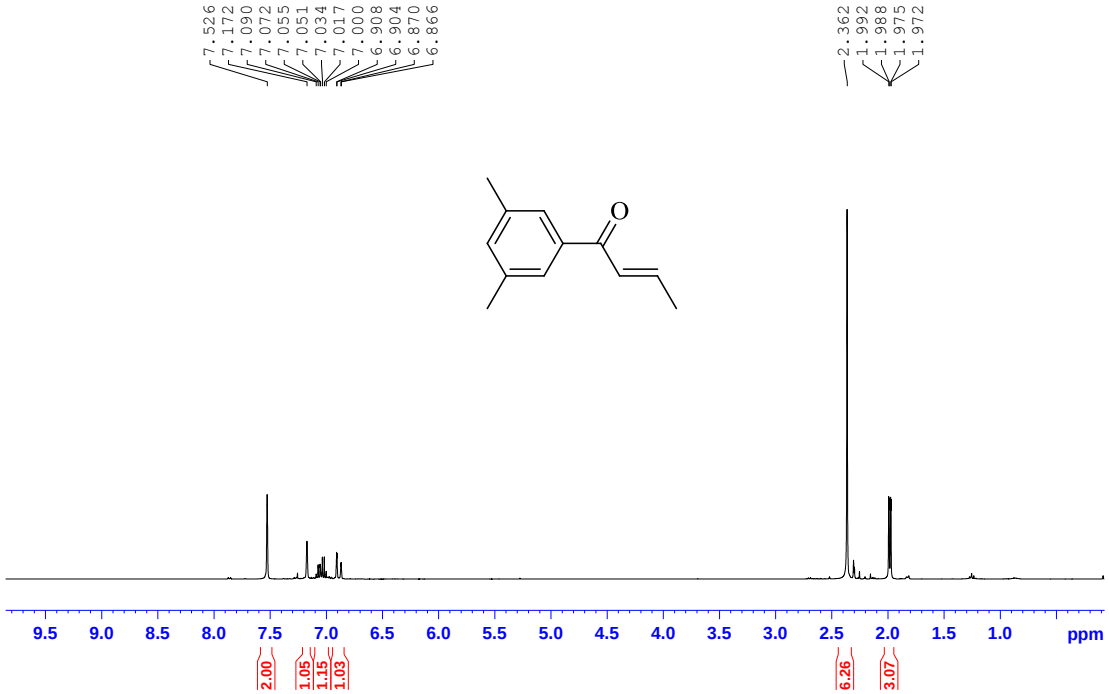


^{13}C NMR (100 MHz, $CDCl_3$)

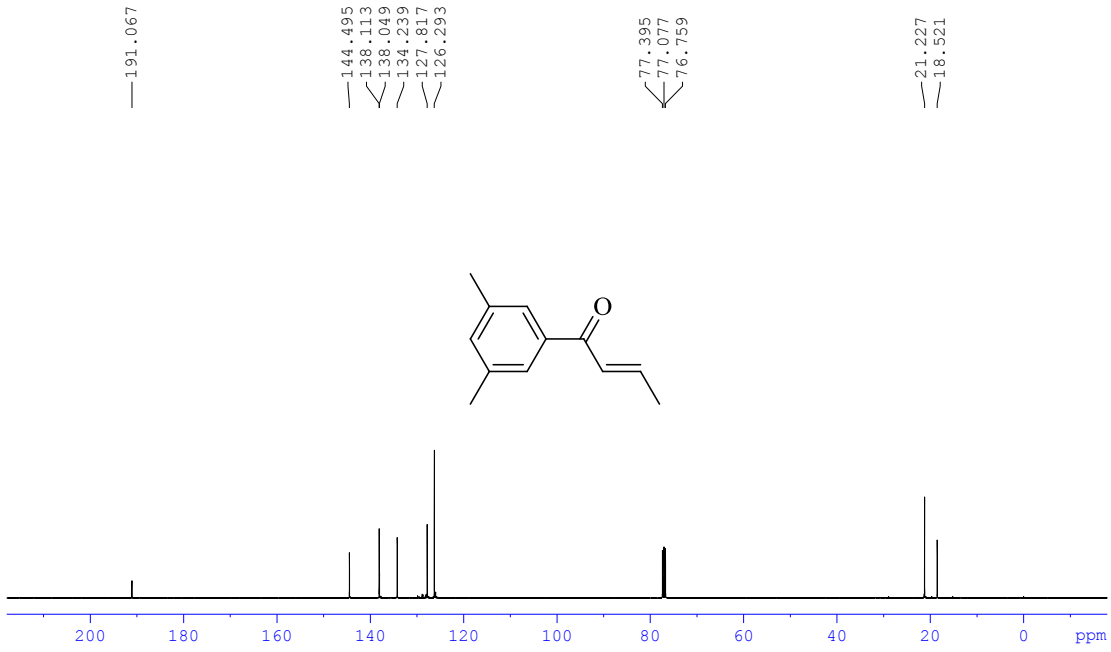


3k. (E)-1-(3,5-dimethylphenyl)but-2-en-1-one

^{1}H NMR (400 MHz, $CDCl_3$)

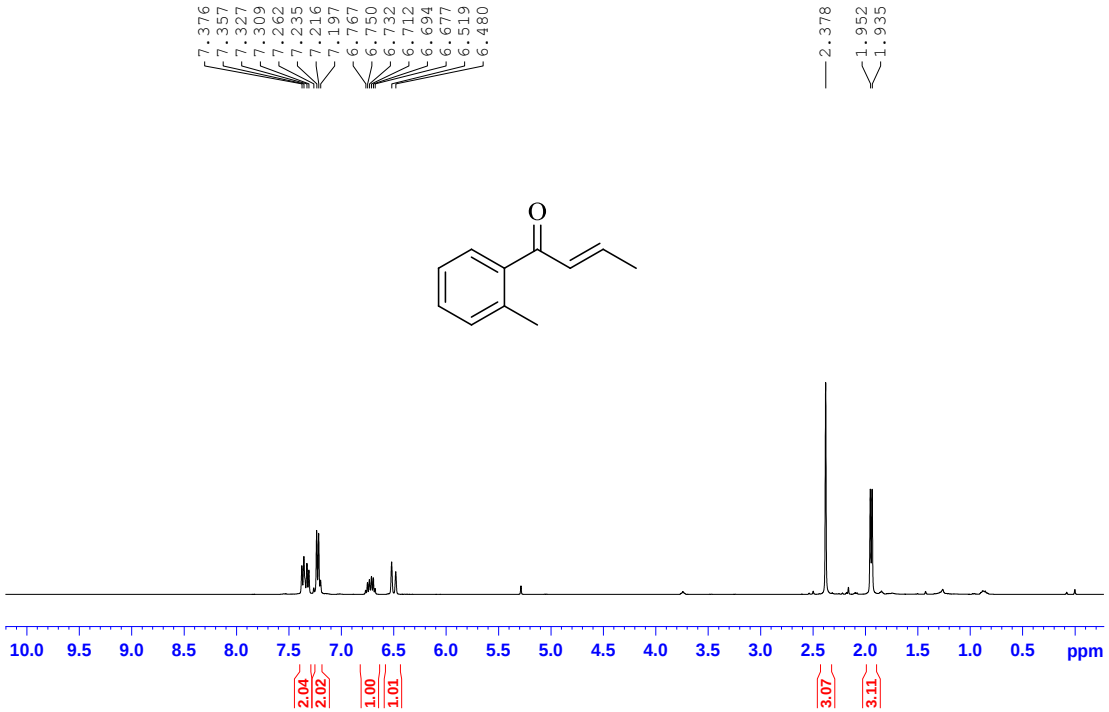


^{13}C NMR (100 MHz, $CDCl_3$)

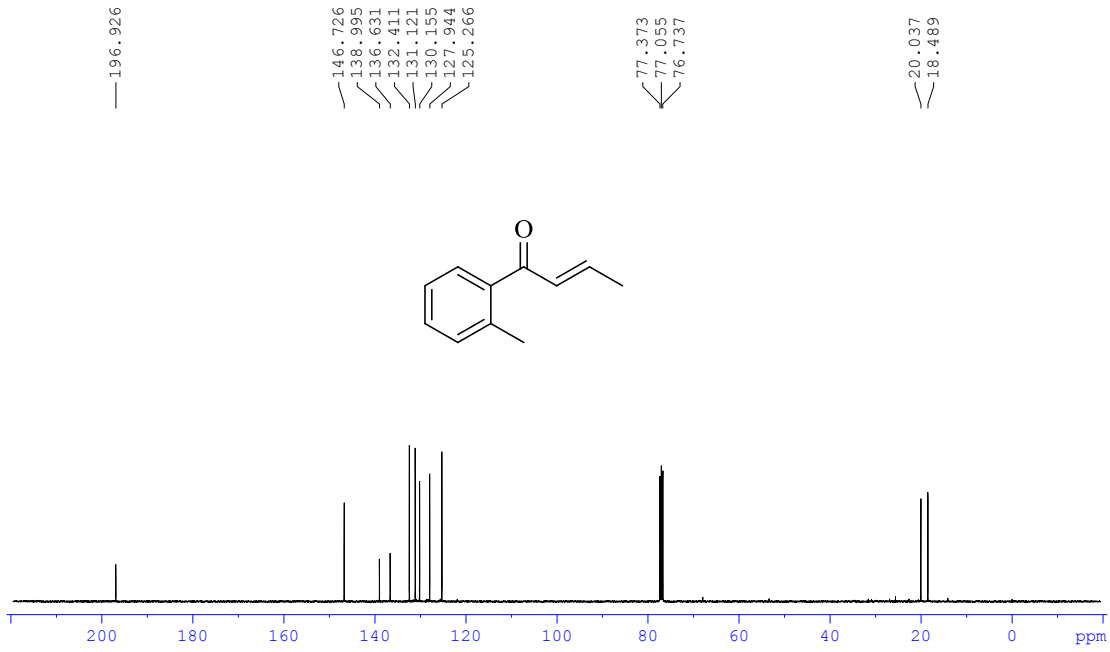


3l. (E)-1-(o-tolyl)but-2-en-1-one:

^{1}H NMR (400 MHz, $CDCl_3$)

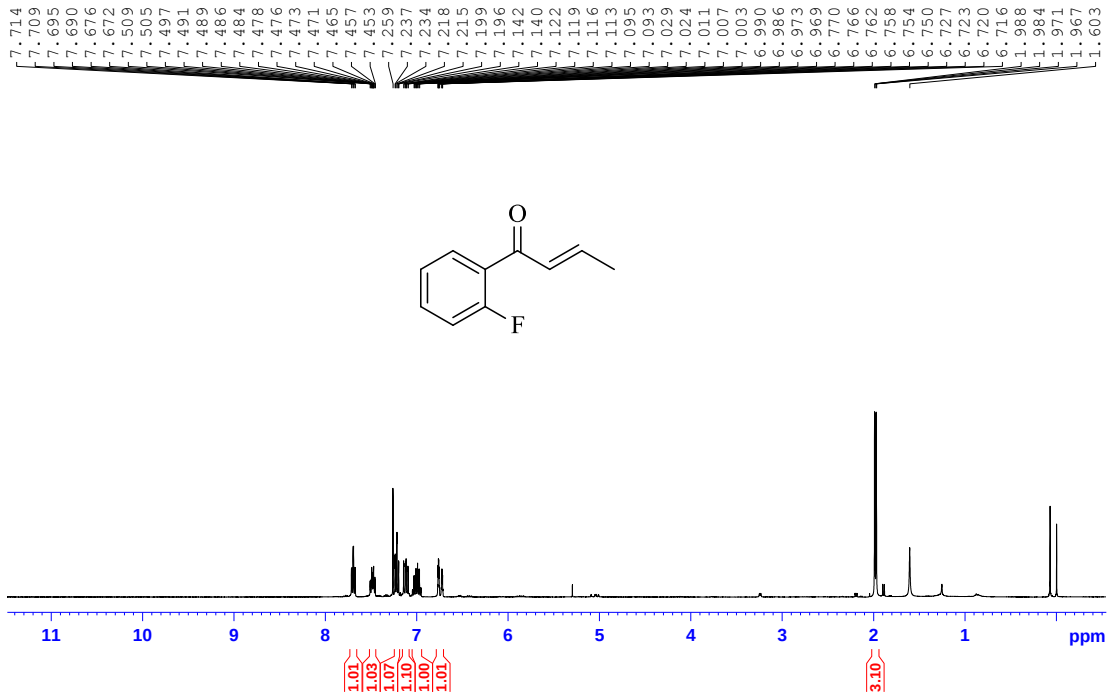


^{13}C NMR (100 MHz, $CDCl_3$)

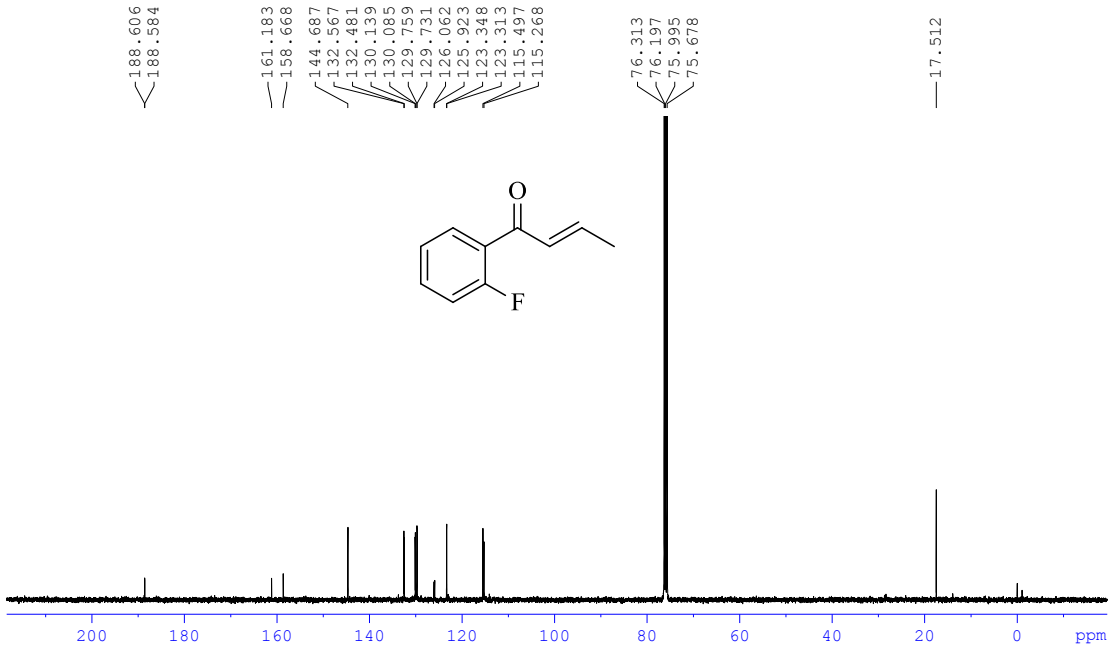


3m. (E)-1-(2-fluorophenyl)but-2-en-1-one:

^{1}H NMR (400 MHz, $CDCl_3$)

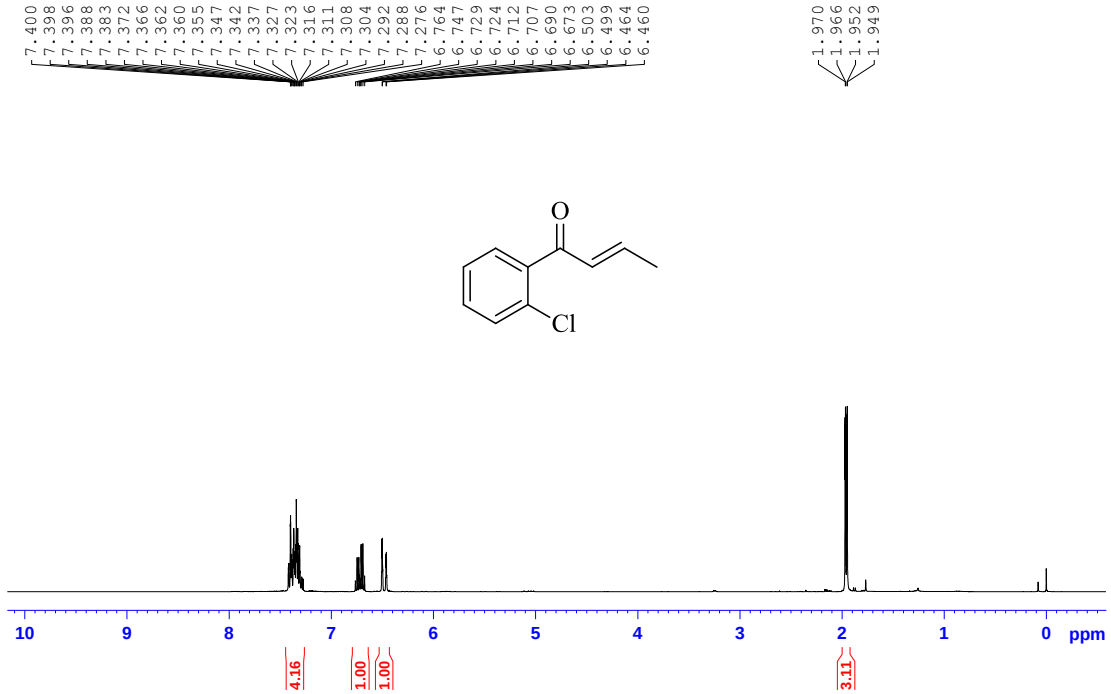


^{13}C NMR (100 MHz, $CDCl_3$)

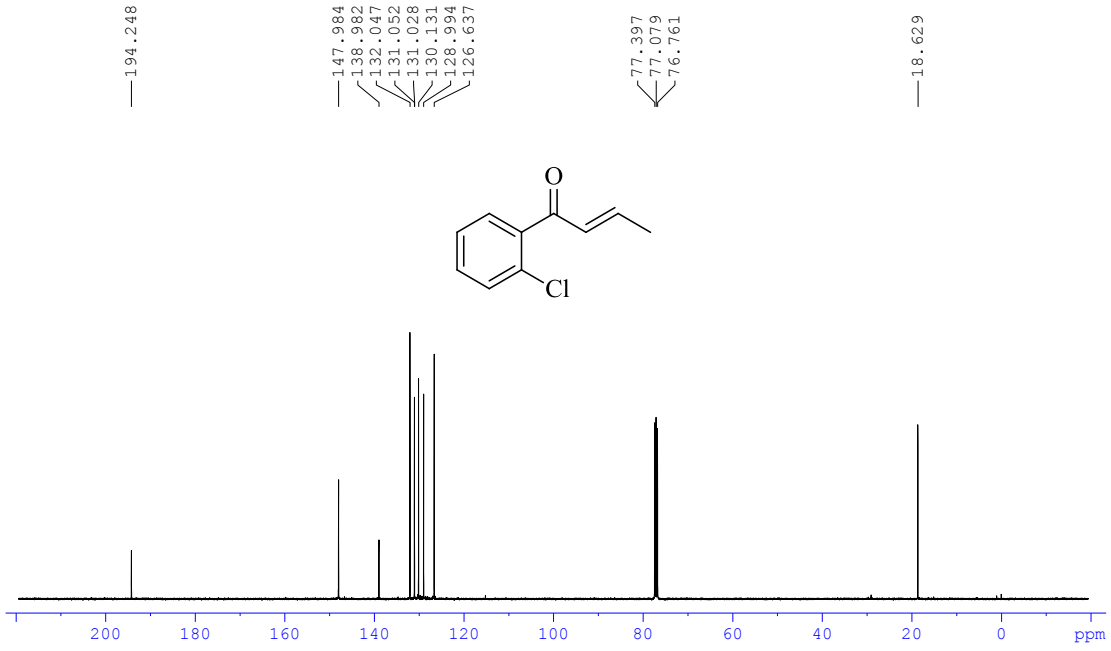


3n. (E)-1-(2-chlorophenyl)but-2-en-1-one:

^{1}H NMR (400 MHz, $CDCl_3$)

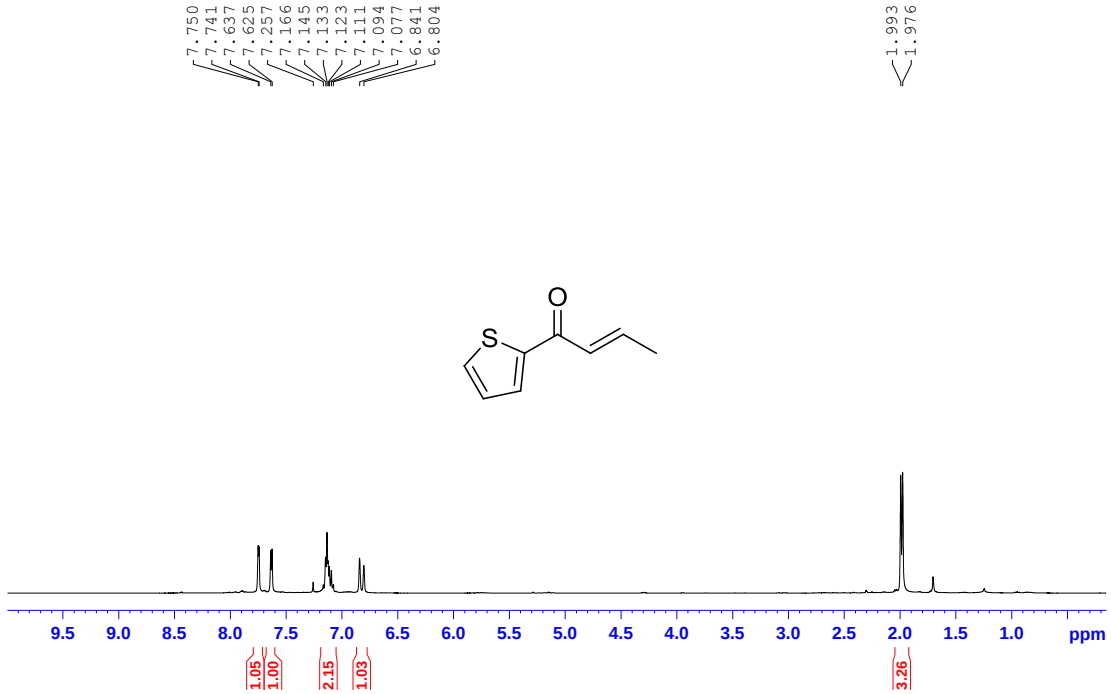


^{13}C NMR (100 MHz, $CDCl_3$)

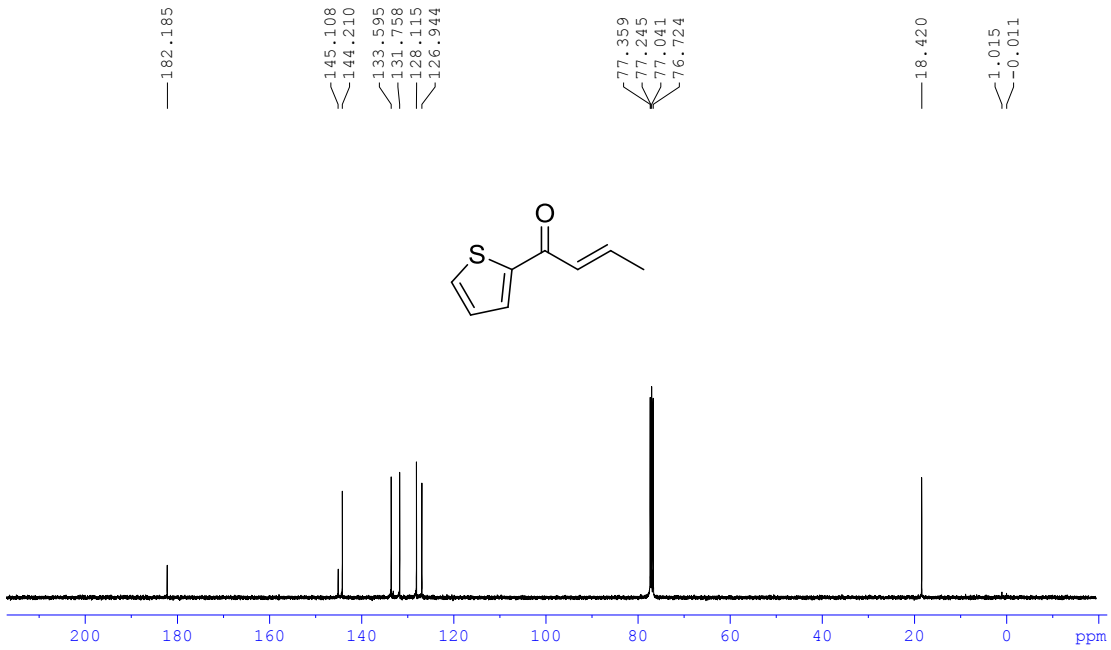


3o. (E)-1-(thiophen-3-yl)but-2-en-1-one:

^{1}H NMR (400 MHz, $CDCl_3$)

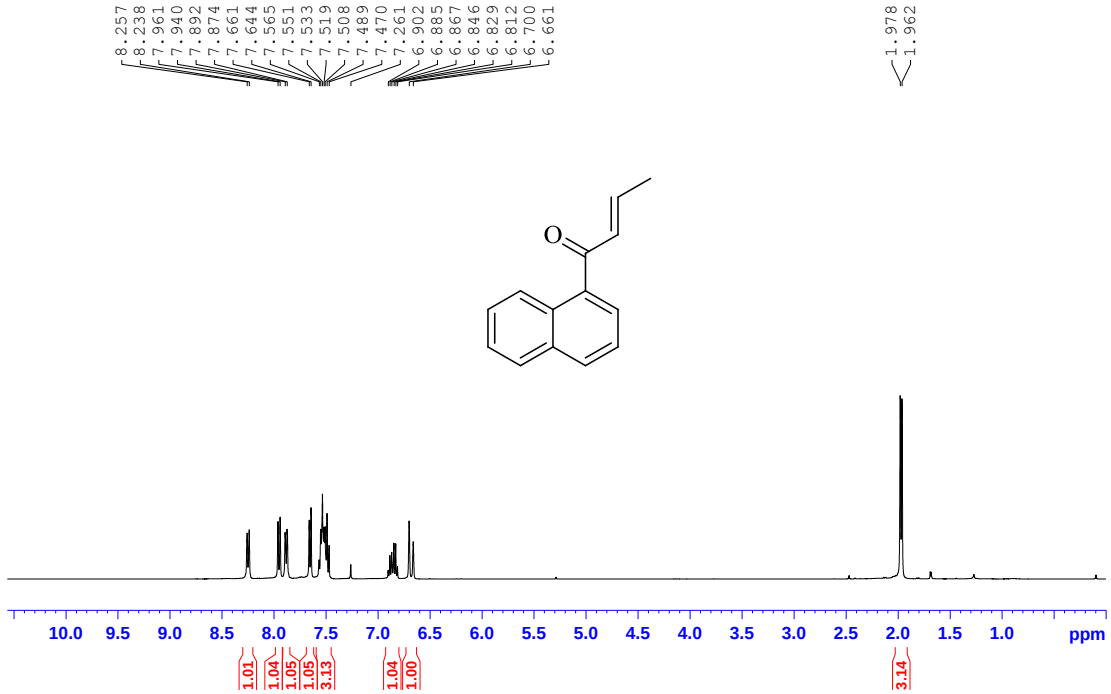


^{13}C NMR (100 MHz, $CDCl_3$)

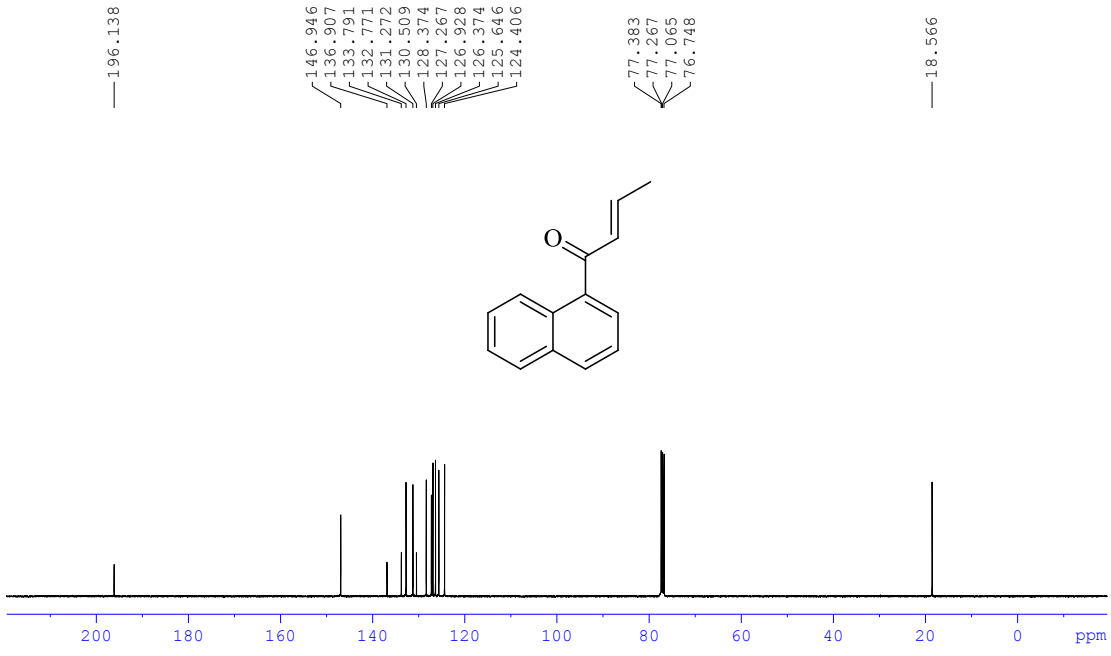


3p. (E)-1-(naphthalen-1-yl)but-2-en-1-one:

^{1}H NMR (400 MHz, $CDCl_3$)

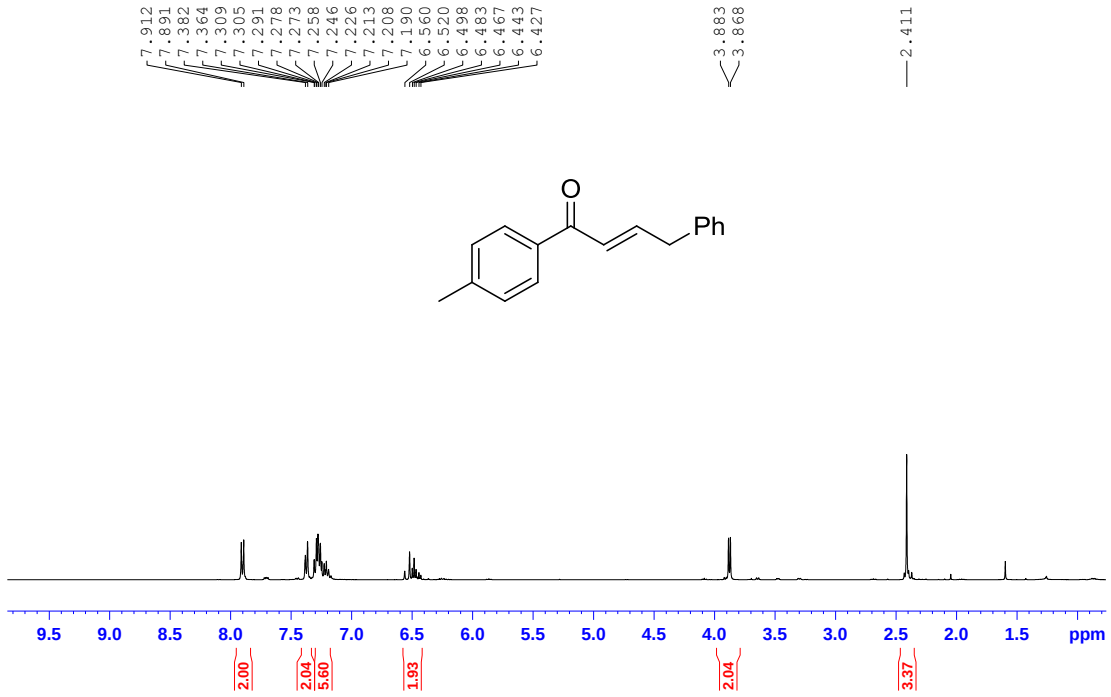


^{13}C NMR (100 MHz, $CDCl_3$)

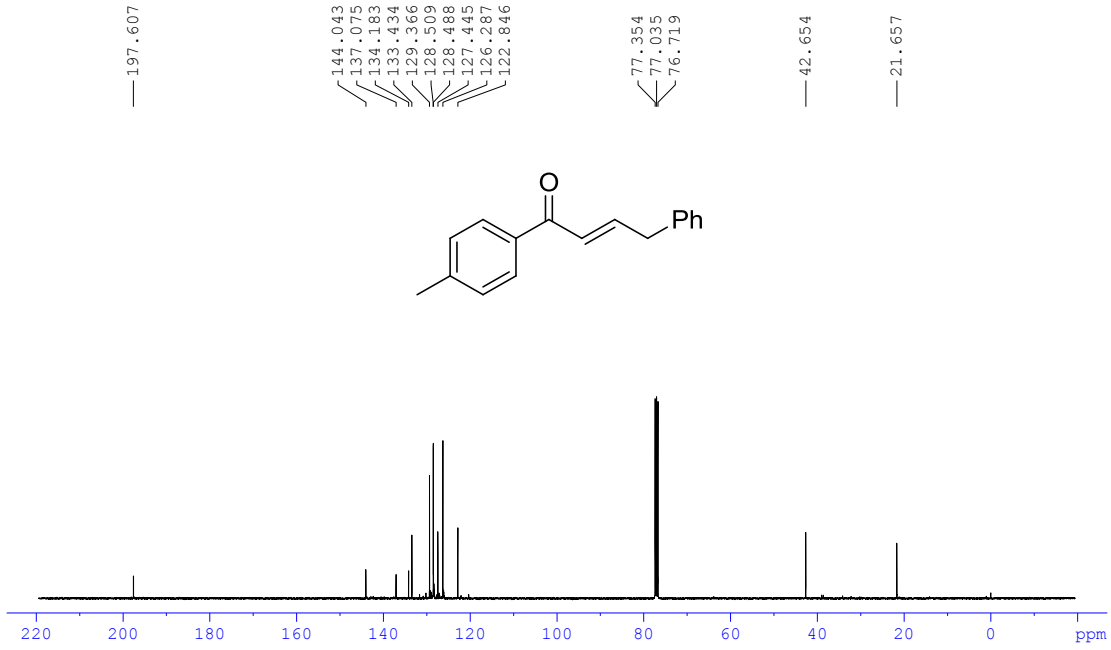


4b. (E)-4-phenyl-1-(p-tolyl)but-2-en-1-one

^{1}H NMR (400 MHz, $CDCl_3$)

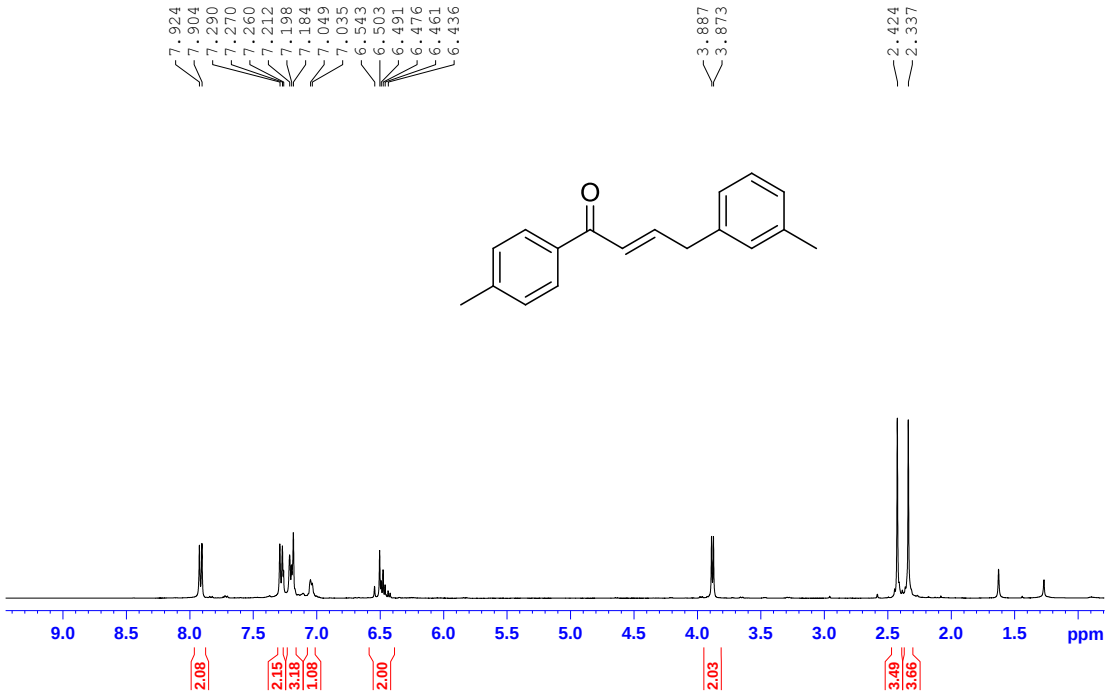


^{13}C NMR (100 MHz, $CDCl_3$)

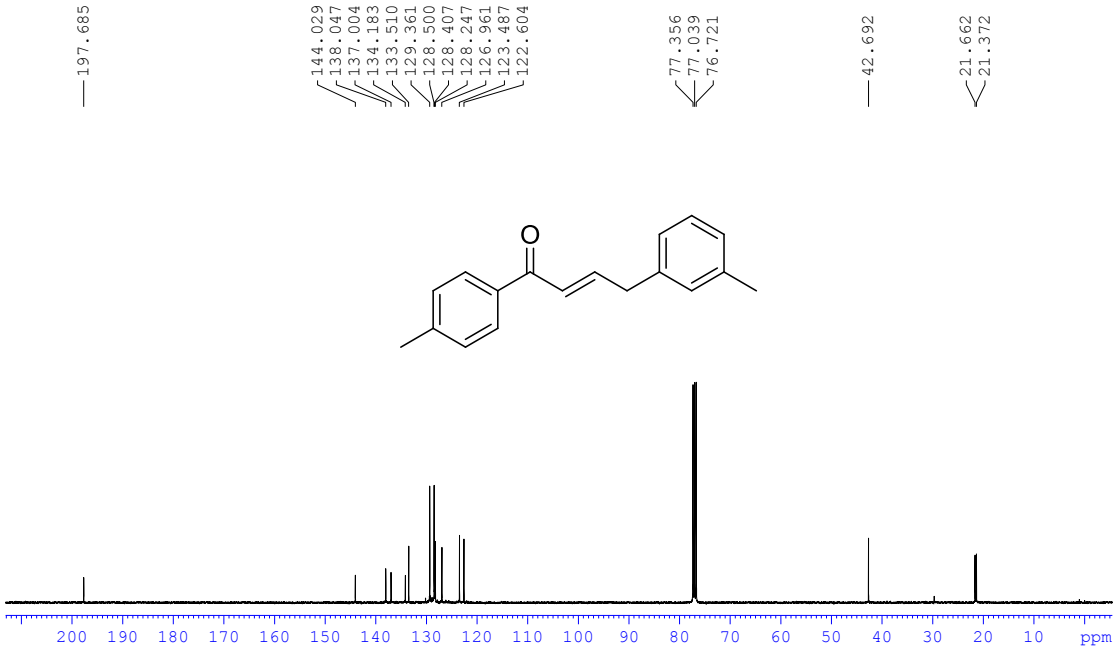


4c. (E)-4-(m-tolyl)-1-(p-tolyl)but-2-en-1-one

^{1}H NMR (400 MHz, $CDCl_3$)

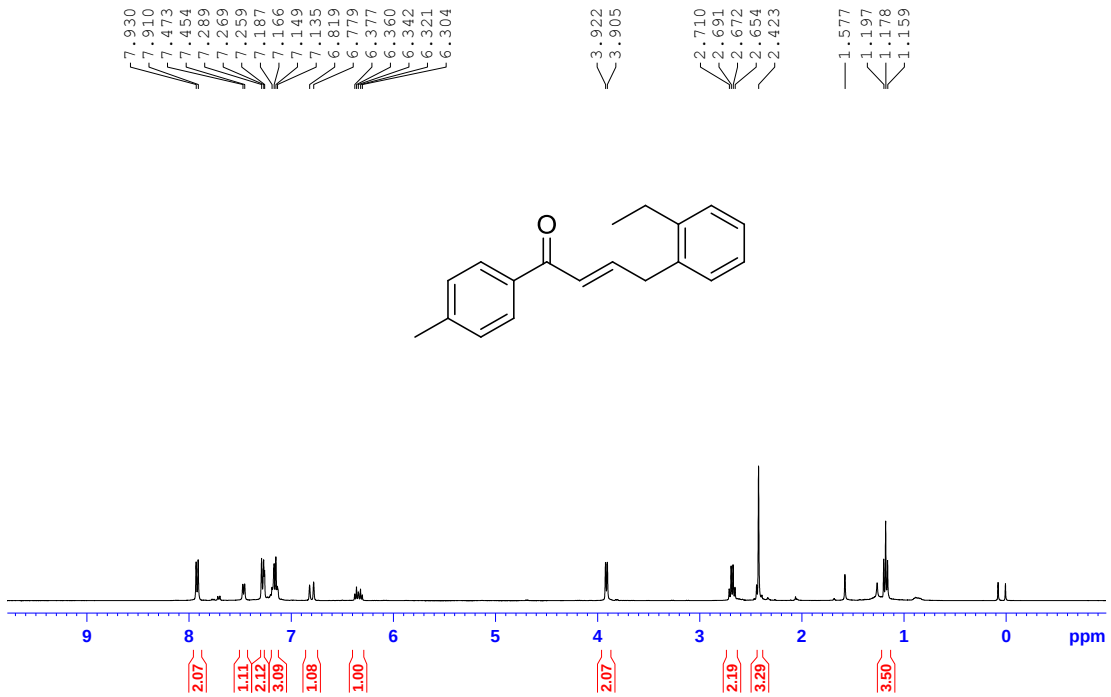


^{13}C NMR (100 MHz, $CDCl_3$)

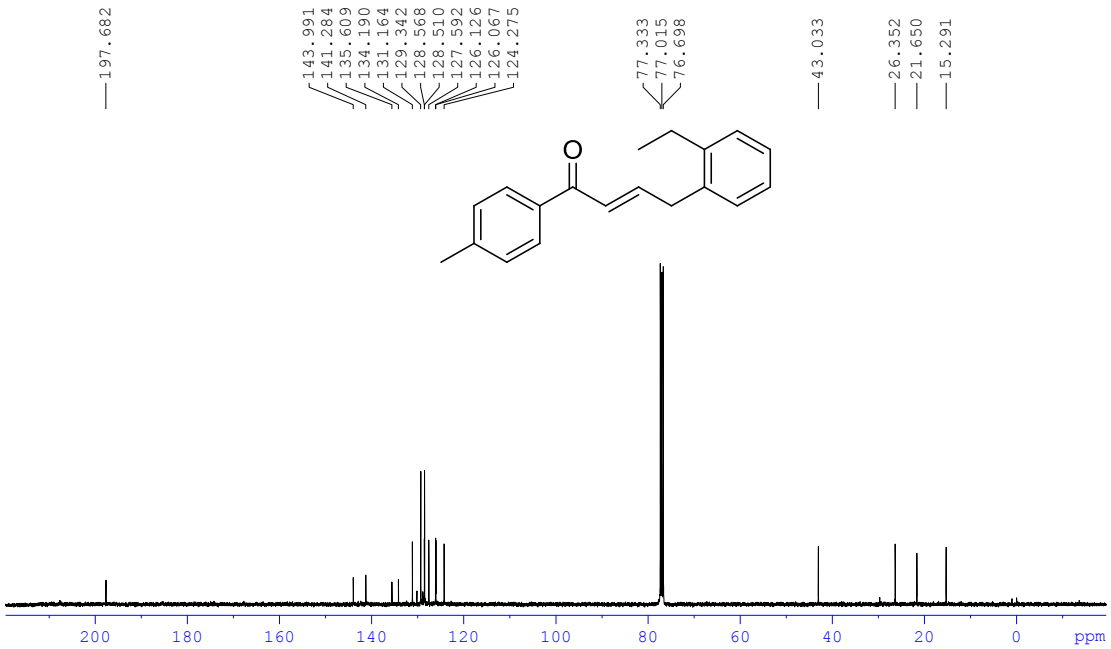


4d. (E)-4-(2-ethylphenyl)-1-(p-tolyl)but-2-en-1-one

^{1}H NMR (400 MHz, $CDCl_3$)

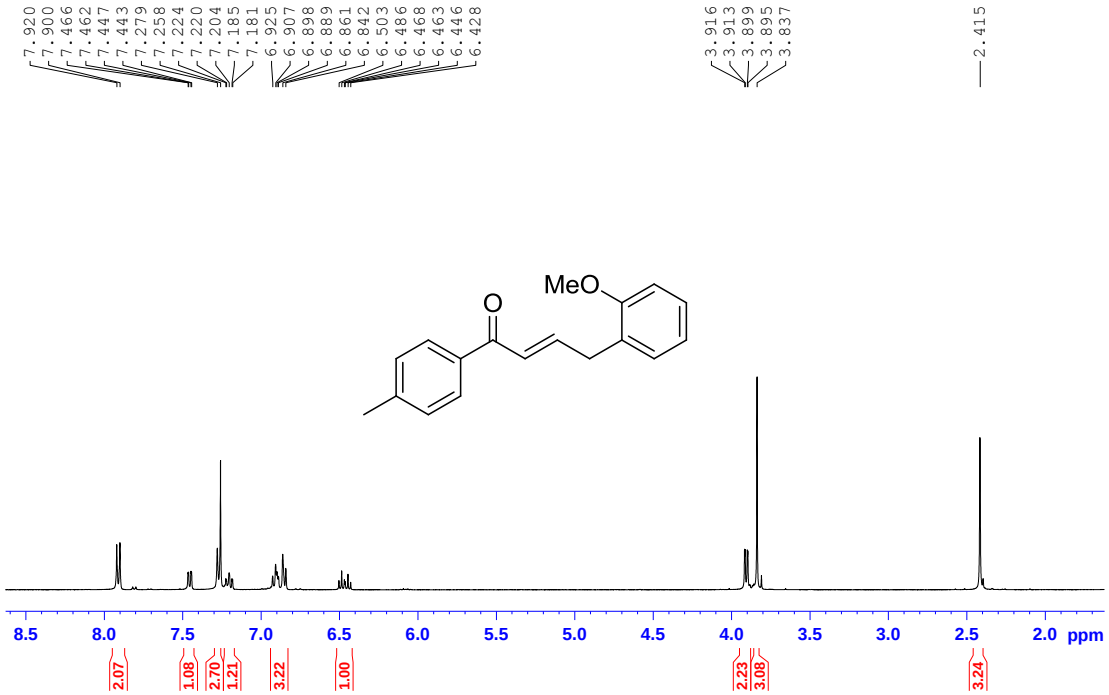


^{13}C NMR (100 MHz, $CDCl_3$)

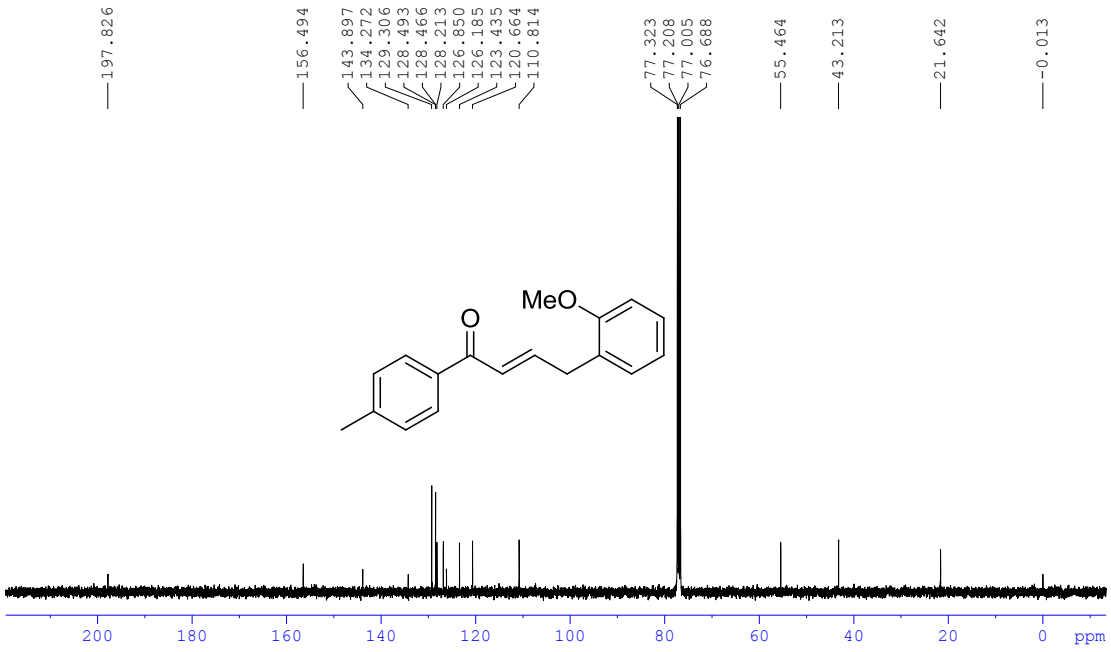


4e. (E)-4-(2-methoxyphenyl)-1-(p-tolyl)but-2-en-1-one

^{1}H NMR (400 MHz, $CDCl_3$)

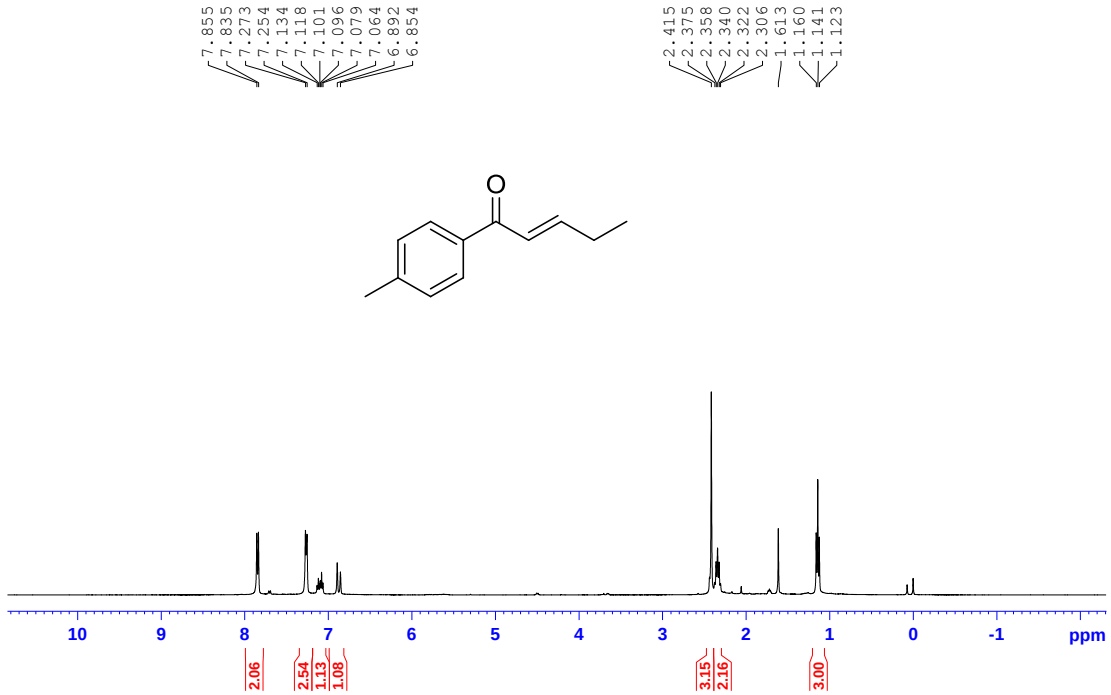


^{13}C NMR (100 MHz, $CDCl_3$)



4f. (E)-1-(p-tolyl)pent-2-en-1-one

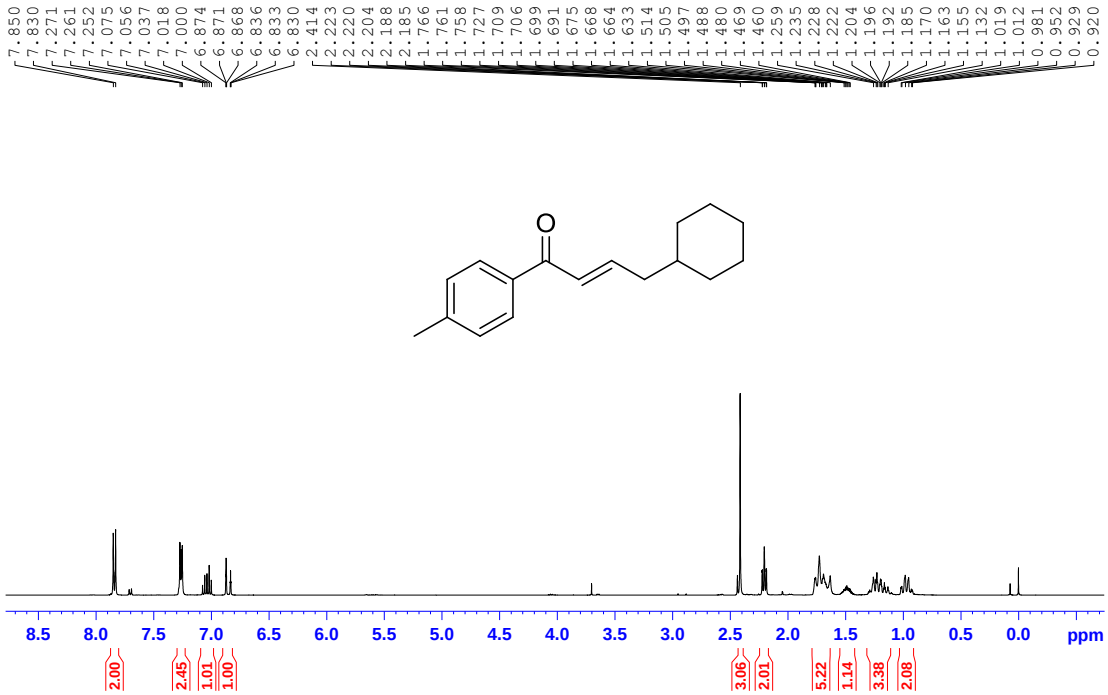
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

4g. (E)-4-cyclohexyl-1-(p-tolyl)but-2-en-1-one

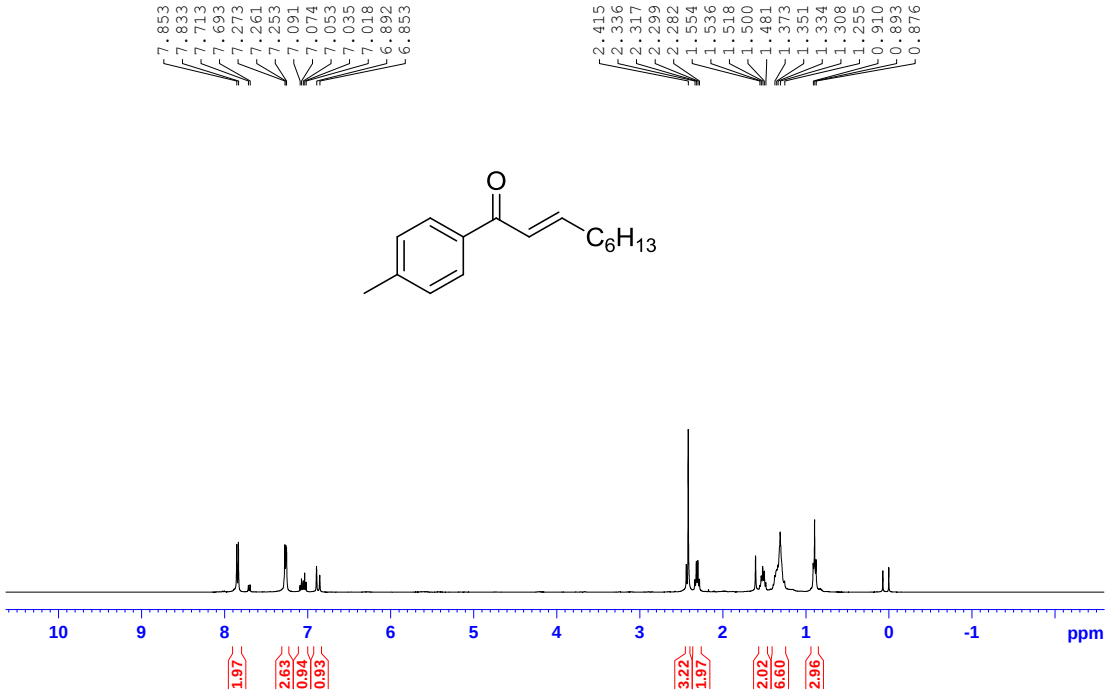
^{1}H NMR (400 MHz, $CDCl_3$)



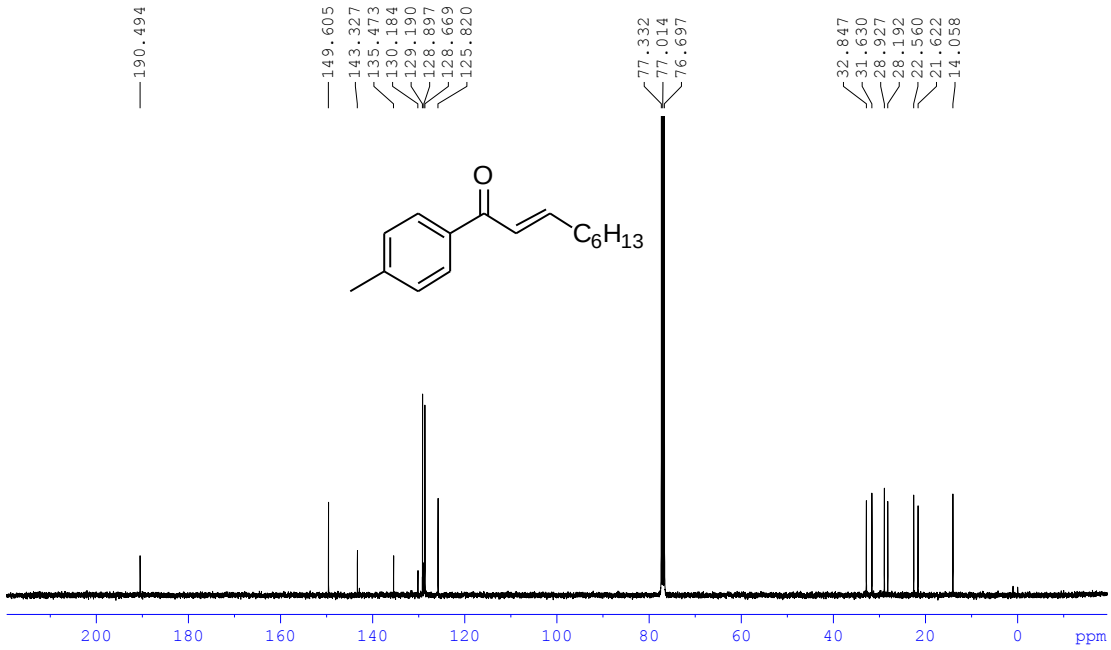
^{13}C NMR (100 MHz, $CDCl_3$)

4h. (E)-1-(p-tolyl)non-2-en-1-one

^{1}H NMR (400 MHz, $CDCl_3$)

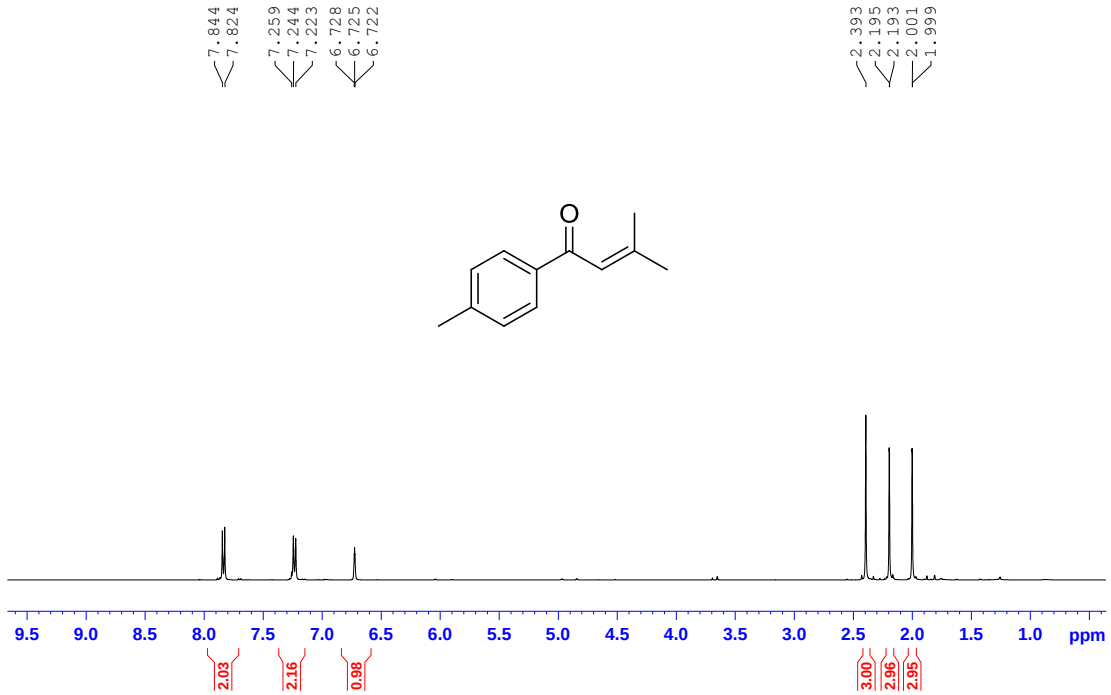


^{13}C NMR (100 MHz, $CDCl_3$)

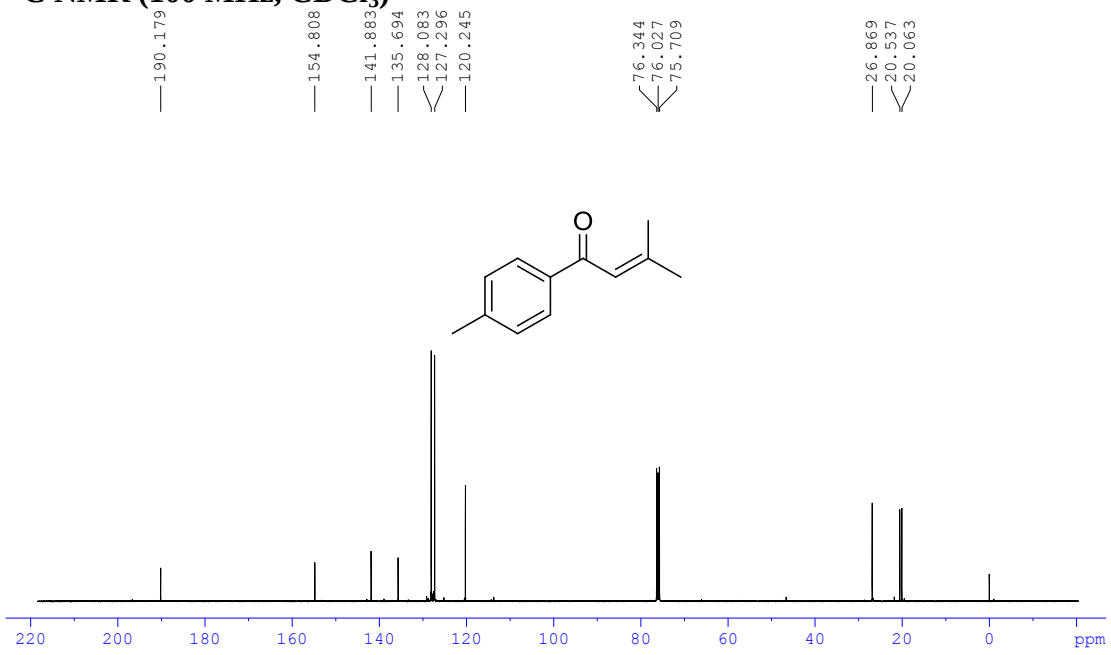


4i. 3-methyl-1-(p-tolyl)but-2-en-1-one

^{1}H NMR (400 MHz, $CDCl_3$)

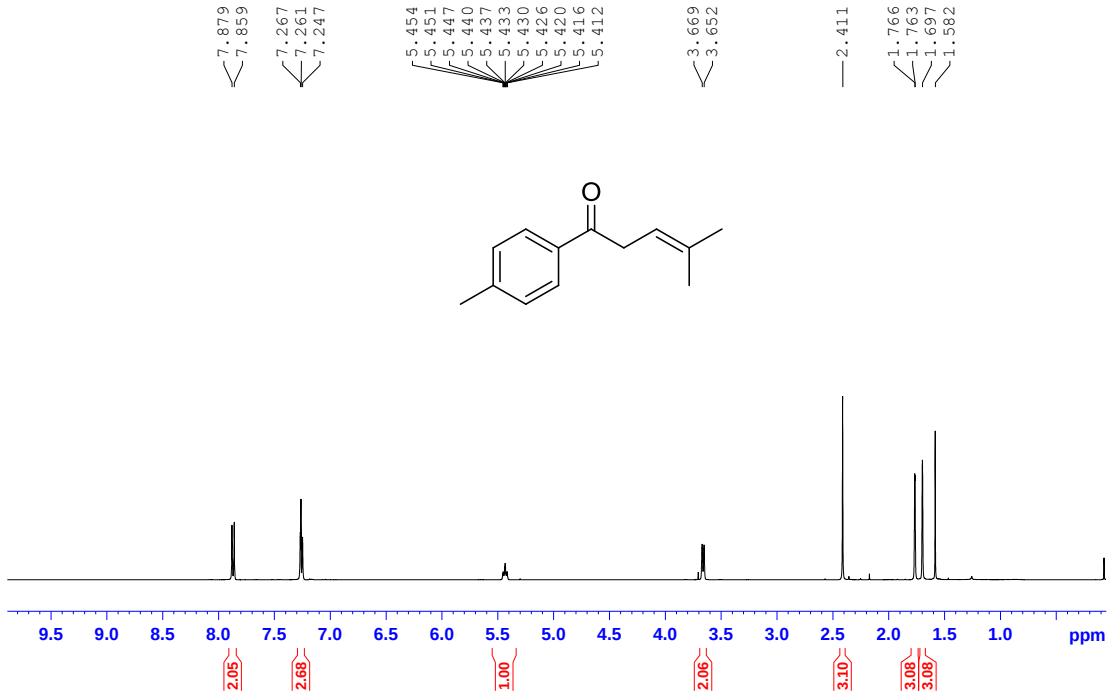


^{13}C NMR (100 MHz, $CDCl_3$)

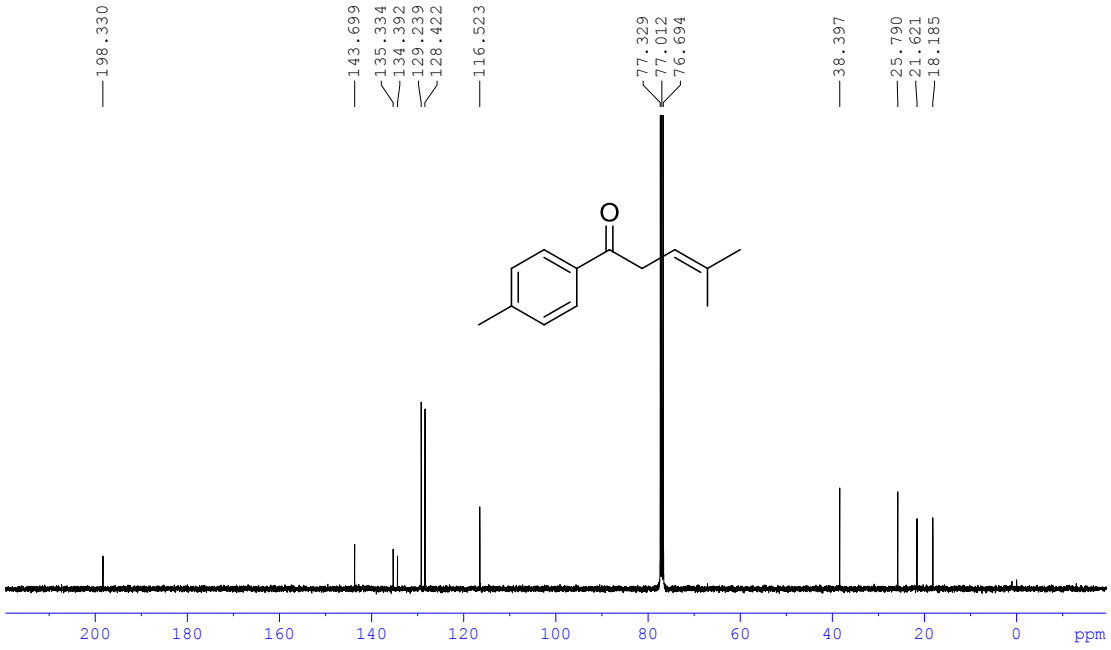


4j. 4-methyl-1-(p-tolyl)pent-3-en-1-one

^{1}H NMR (400 MHz, $CDCl_3$)

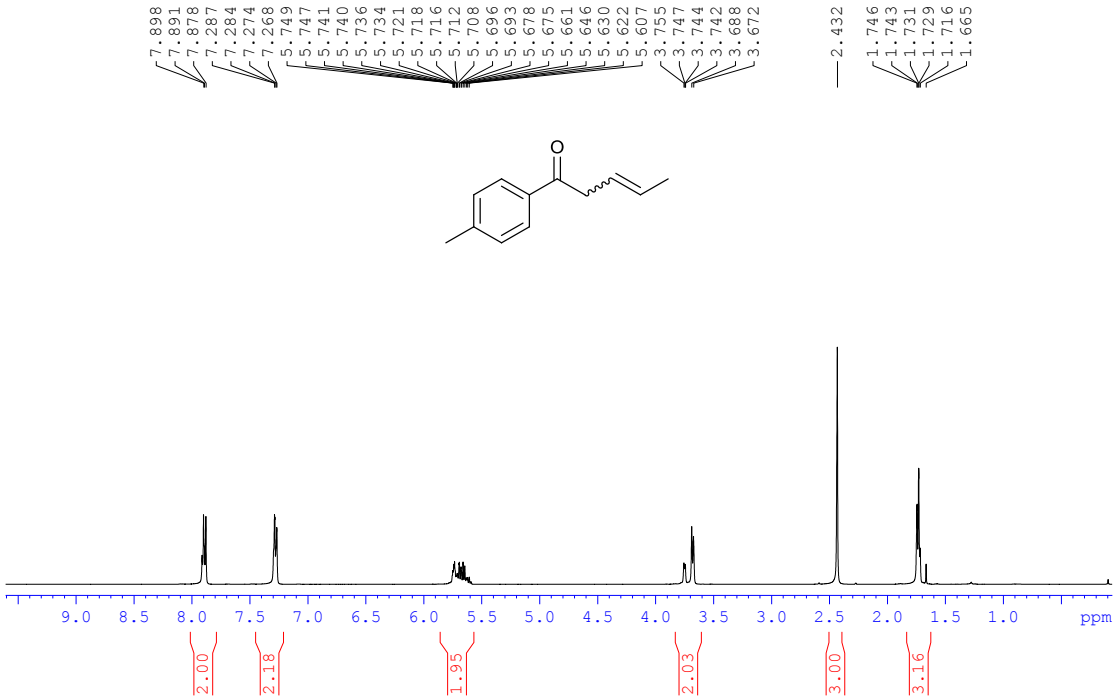


^{13}C NMR (100 MHz, $CDCl_3$)

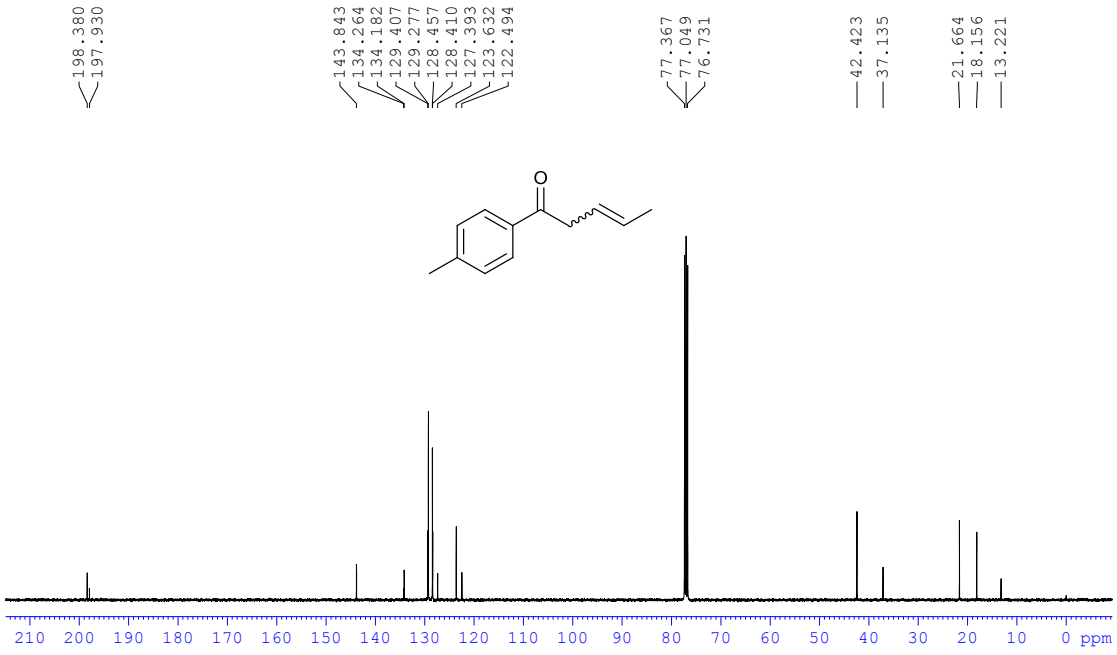


4f-a. (Z/E)-1-(p-tolyl)pent-3-en-1-one

^{1}H NMR (400 MHz, $CDCl_3$)

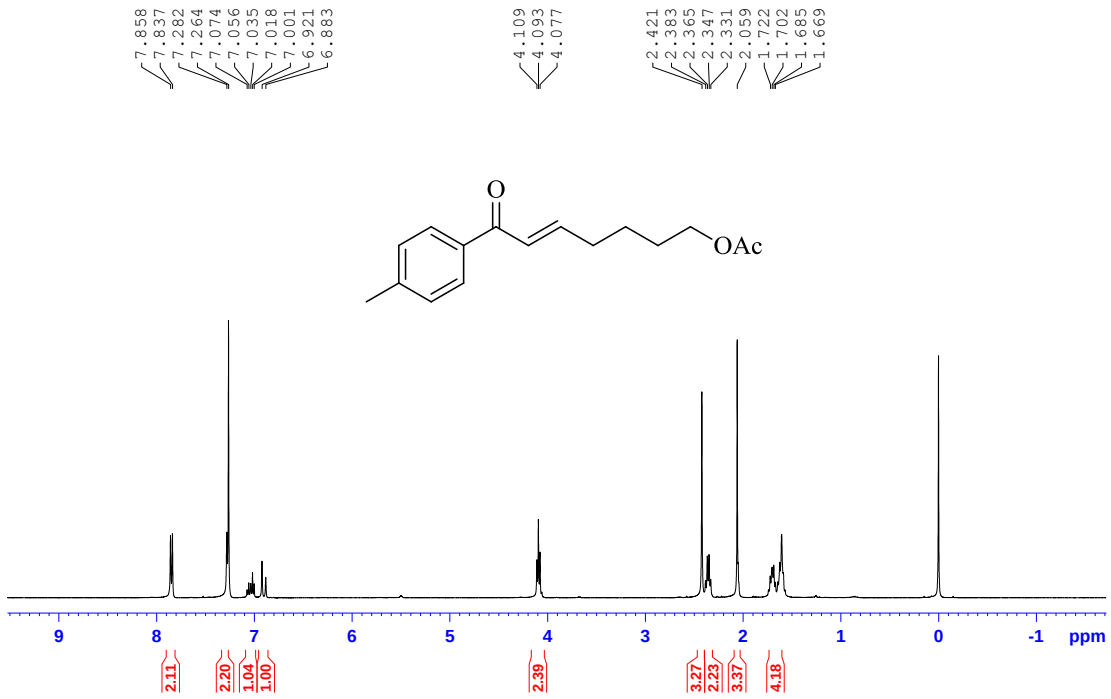


^{13}C NMR (100 MHz, $CDCl_3$)

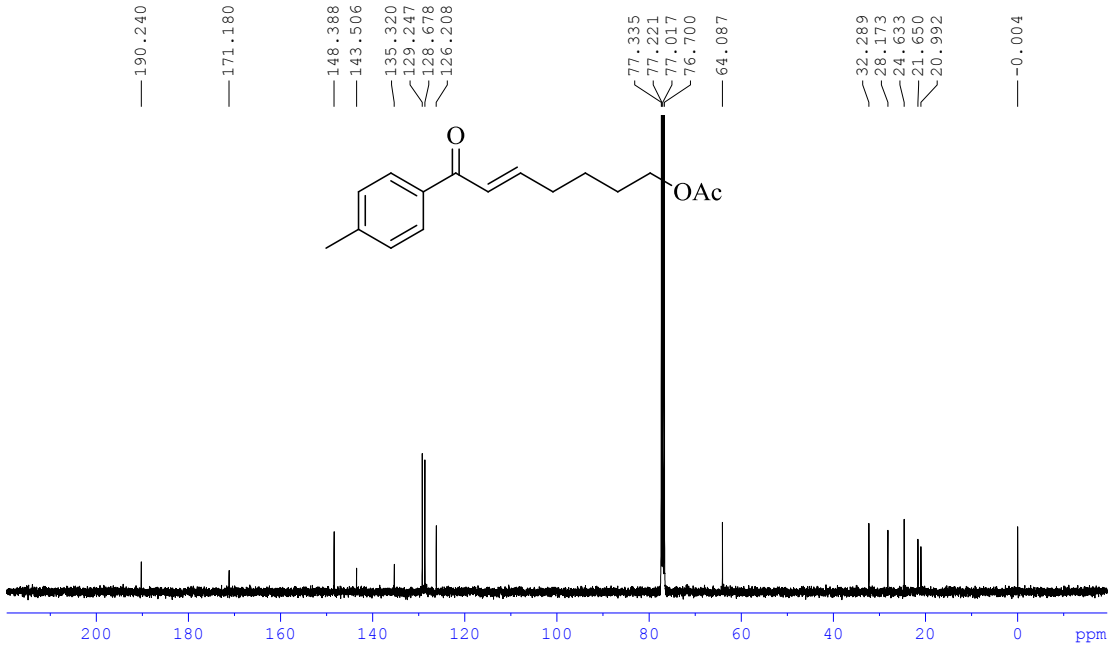


4k. (E)-7-oxo-7-(p-tolyl)hept-5-en-1-yl acetate

^{1}H NMR (400 MHz, $CDCl_3$)

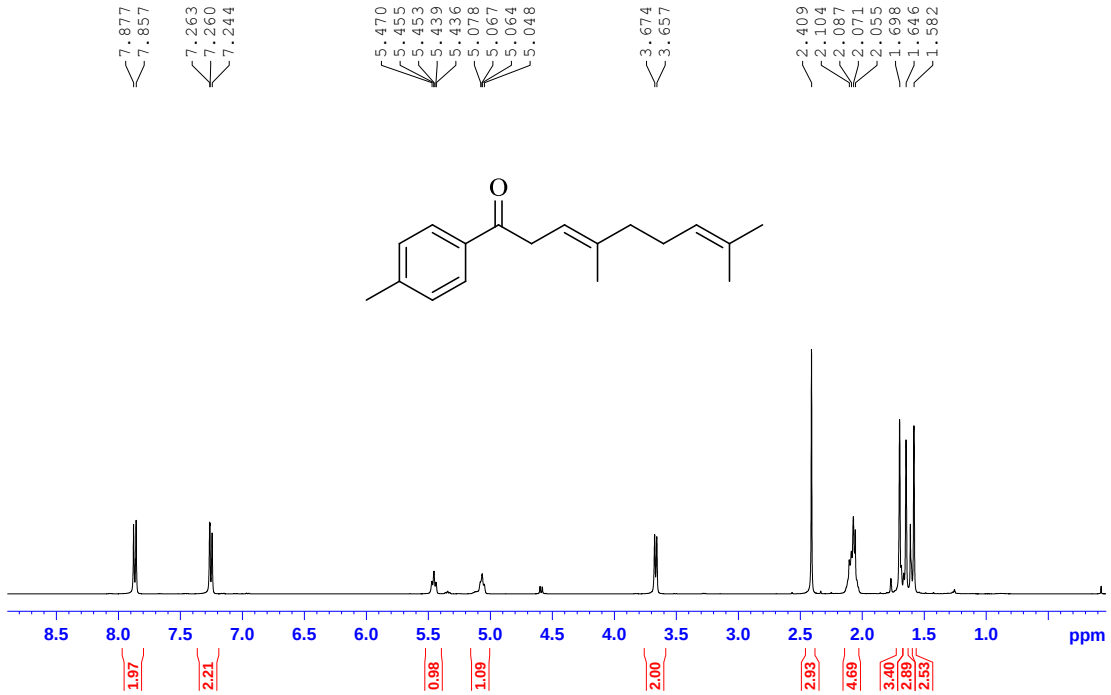


^{13}C NMR (100 MHz, $CDCl_3$)



4l. (E)-4, 8-dimethyl-1-(p-tolyl) nona-3, 7-dien-1-one

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)