Supporting information

Paired Electrolysis Enables Decarboxylative Coupling of Alkenyl Acids with Diazo Compounds

Jingchao Jiao, Yapeng Yan, Qiumin Ke, Yusen Zhang, Hang Huang, Qianwen Gao, Jie Liu,* and Xi Wang*

[a]*College of Chemistry and Chemical Engineering, State Key Laboratory of Chemo/Biosensing and Chemometrics, Advanced Catalytic Engineering Research Center of the Ministry of Education, Hunan University, Changsha 410082, P. R. China.*

[b]*Greater Bay Area Institute for Innovation, Hunan University, Guangzhou 511300, P. R. China.*

E-mail: cccewangxi@hnu.edu.cn

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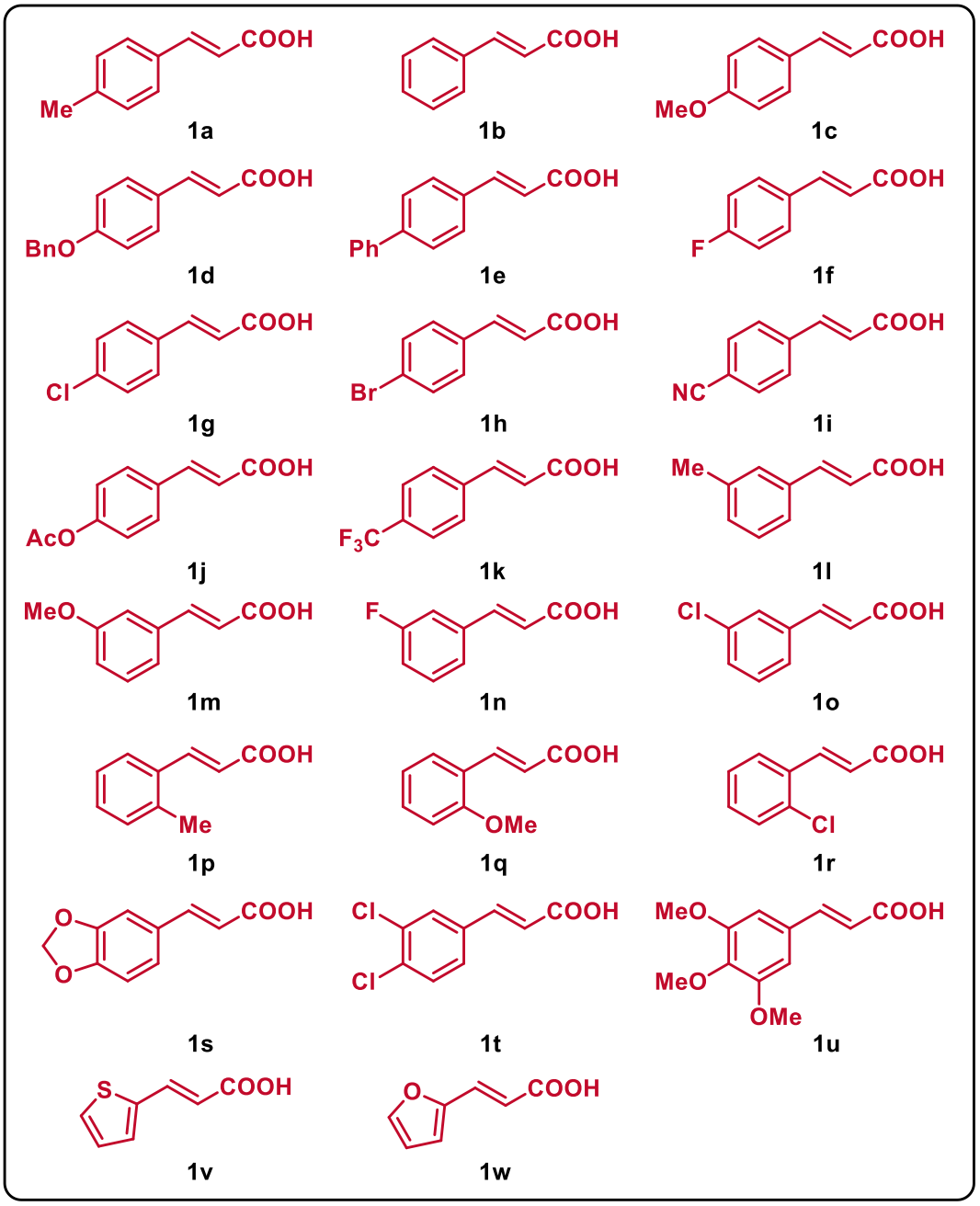
1. General

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in flame-dried glassware under an argon atmosphere using standard Schlenk techniques. All solvents were freshly distilled and degassed according to the handbook Purification of Laboratory Chemicals (4th Edition, Butterworth Heinemann, W. L. F. Armarego and Douglas Dalzell Perrin). The boiling point of petroleum ether (PE) was between 60 and 90 ºC. Commercially available reagents were used as received from Energy Chemical, Aladdin, Leyan, Alfa Aesar China, TCI China. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. Analytical thin layer chromatography (TLC) was performed using silica gel plates (Qingdao, China). Visualisation was by ultraviolet fluorescence, and/or phosphomolybdic acid, and/or $KMnO_4$ (1.5 g in 400 mL H_2O, 5.0 g $NaHCO_3$). The electrochemical reactions were performed on a IT6720 potentiostat in constant current mode. ^{1}H-Nuclear Magnetic Resonance (^{1}H-NMR), ^{13}C Nuclear Magnetic Resonance (^{13}C-NMR) spectra and ^{19}F-Nuclear Magnetic Resonance (^{19}F-NMR) were recorded on Bruker 400 MHz and JEOL JNM-ECZ400S/L1 400 MHz at 20 °C with $CDCl_3$, DMSO-*d6* as solvent. Chemical shifts (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^{1}H NMR) and 77.16 ppm (^{13}C NMR); references for DMSO-*d6* were 2.50 ppm (^{1}H NMR) and 39.5 ppm (^{13}C NMR); reference for D_2O was 4.79 ppm (^{1}H NMR). The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q= quartet, m = multiplet, br = broad), coupling constant J(Hz), and integration. High resolution mass spectra were recorded on Thermo Oribtrap Exploris 120, Thermo Finnigan MAT95XP, JEOL AccuTOF LC-plus 4G, Agilent 7250 Accurate-Mass Q-TOF GC/MS. IR spectra were recorded on SHIMADZU IRSpirit-T and reported in unit of cm-1. GC and GCMS data were recorded on SHIMADZU Nexis GC-2030 and SHIMADZU GCMS-QP2020NX respectively. The data of cyclic voltammetry was measured using BAS Epsilon electrochemical analyzer.

2. Preparation of starting materials

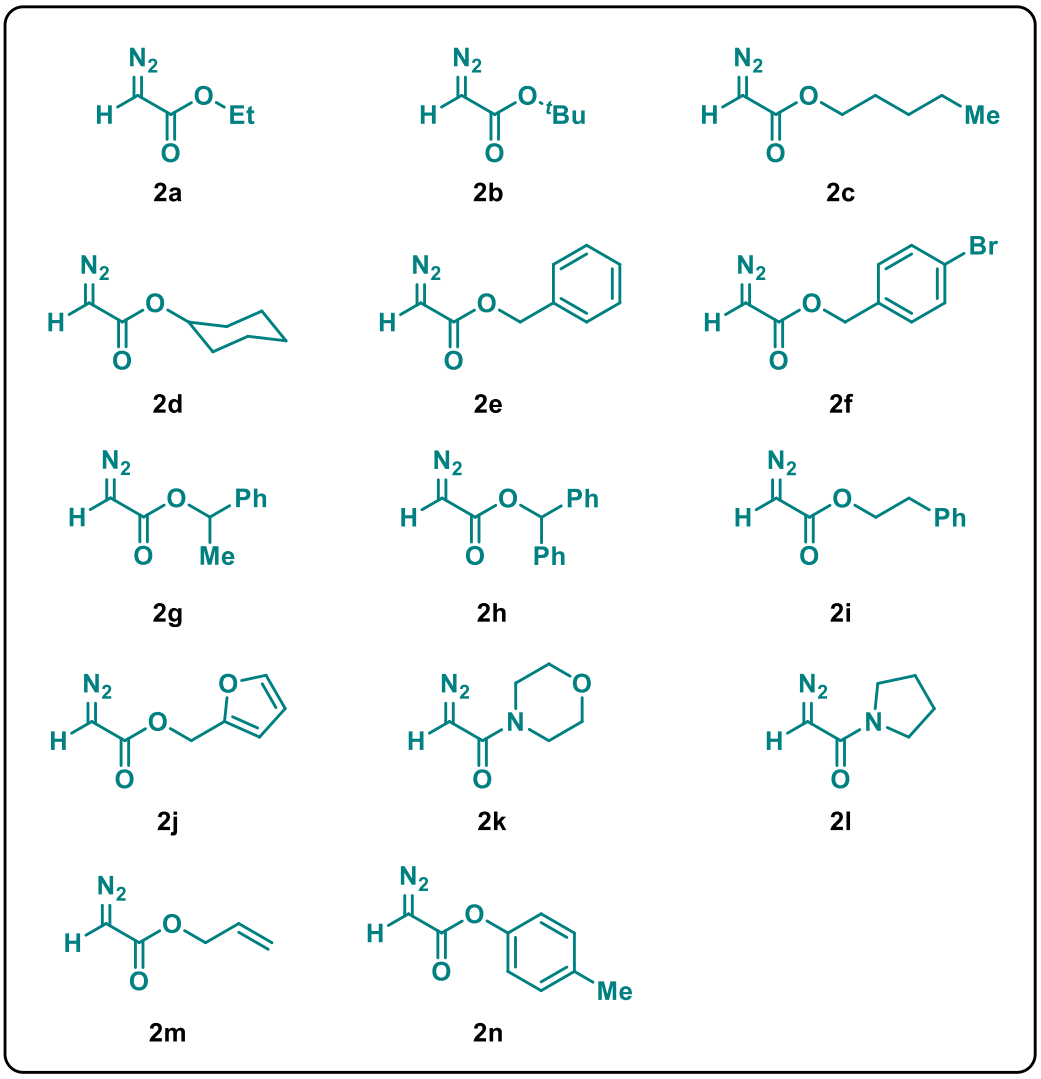
2.1 Preparation of alkenyl acids 1

Alkenyl acids **1a** – **1c, 1f** – **1h, 1j** – **1w** are commercially available from Energy Chemical, Aladdin, Leyan. All commercially available alkenyl acids were used as received. Alkenyl acids **1d**,[1] **1e**,[2] **1i**,[3] were prepared according to previously reported literature procedures.

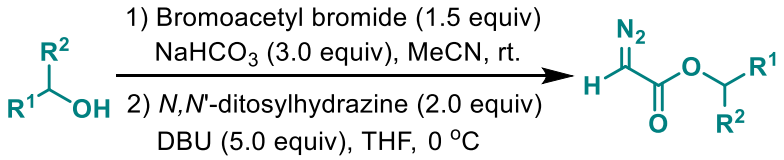


2.2 Preparation of diazo compounds 2

The diazo compounds **2a**,[4] **2b**,[4] **2d**,[4] **2e**,[4] **2g**,[4] **2i**,[4] **2j**,[4] **2k**,[5] **2l**,[5] **2m**,[4] **2n**,[4] were prepared according to the previously reported literature procedures. The diazo compounds **2c**, **2f**, **2h** were prepared according to the following procedure.

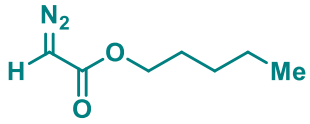


Procedure for the preparation of diazo compounds from alcohols (GP1)

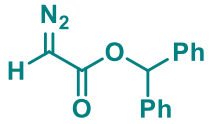


A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with $NaHCO_3$ (2.520 g, 30.00 mmol, 3.0 equiv) before a solution of alcohol (10.00 mmol, 1.0 equiv) in MeCN (50 mL) was added. Bromoacetyl bromide (3.028 g, 15.00 mmol, 1.5 equiv) was slowly added to the result solution at 0 °C and the mixture was stirred at the same temperature for 30 min. Then the reaction was quenched with H_2O. The

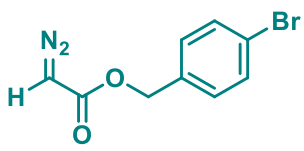
solution was extracted with DCM. The organic phase was washed with brine, dried over Na_2SO_4. The solvent was evaporated, and the residue was used in the next reaction without purification. The obtained bromoacetate and *N, N'*-ditosylhydrazine[4] (6.810 g, 20.00 mmol, 2.0 equiv) were dissolved in THF (50 mL). DBU (7.612 g, 50.00 mmol, 5.0 equiv) was added dropwise at 0 °C and stirred at the same temperature for 30 minutes. After the reaction was complete, the reaction was quenched with saturated $NaHCO_3$ solution. The solution was extracted with Et_2O. The organic phase was washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography to give the corresponding diazo compounds **2**.



Pentyl 2-diazoacetate (2c): The title compound was prepared according to general procedure (**GP1**) with 1-pentanol (0.882 g, 10.00 mmol, 1.0 equiv), $NaHCO_3$ (2.520 g, 30.00 mmol, 3.0 equiv), bromoacetyl bromide (3.028 g, 15.00 mmol, 1.5 equiv), *N, N'*-ditosylhydrazine (6.810 g, 20.00 mmol, 2.0 equiv), and DBU (7.612 g, 50.00 mmol, 5.0 equiv) in MeCN and THF (50 mL + 50 mL). Purification via silica gel chromatography (PE:EtOAc = 30:1) gave the desired product **2c** as a yellow liquid in 49% yield (0.765 g); **TLC R_f** = 0.3 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 4.71 (s, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 1.64 – 1.57 (m, 2H), 1.32 – 1.27 (m, 4H), 0.92 – 0.81 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.8, 64.9, 46.0, 28.4, 27.8, 22.2, 13.8; **IR** (neat, cm^{-1}): 2958*w*, 2107*s*, 1684*s*, 1399*m*, 1182*s*, 1050*w*, 988*w*, 908*s*, 651*w*, 468*w*.



Benzhydryl 2-diazoacetate (2h): The title compound was prepared according to general procedure (**GP1**) with benzhydrol (1.840 mg, 10.0 mmol, 1.0 equiv), $NaHCO_3$ (2.520 g, 30.00 mmol, 3.0 equiv), bromoacetyl bromide (3.028 g, 15.00 mmol, 1.5 equiv), *N, N'*-ditosylhydrazine (6.810 g, 20.00 mmol, 2.0 equiv), and DBU (7.612 g, 50.00 mmol, 5.0 equiv) in MeCN and THF (50 mL + 50 mL). Purification via silica gel chromatography (PE:EtOAc = 20:1) gave the desired product **2h** as a yellow liquid in 56% yield (1.412 g); **TLC R_f** = 0.3 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.25 – 7.16 (m, 10H), 6.87 (s, 1H), 4.72 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 139.9, 128.4, 127.9, 126.9, 76.7, 46.5; **IR** (neat, cm^{-1}): 2107*s*, 1684*s*, 1496*w*, 1450*w*, 1376*s*, 1239*m*, 1170*s*, 993*m*, 908*m*, 731*s*, 696*s*, 645*w*.



4-bromobenzyl 2-diazoacetate (2f): The title compound was prepared according to general procedure (**GP1**) with 4-bromobenzyl alcohol (1.870 mg, 10.00 mmol, 1.0 equiv), $NaHCO_3$ (2.520 g, 30.00 mmol, 3.0 equiv), bromoacetyl bromide (3.028 g, 15.00 mmol, 1.5 equiv), *N, N*'-ditosylhydrazine (6.810 g, 20.00 mmol, 2.0 equiv), and DBU (7.612 g, 50.00 mmol, 5.0 equiv) in MeCN and THF (50 mL + 50 mL). Purification via silica gel chromatography (PE:EtOAc = 20:1) gave the desired product **2f** as a yellow liquid in 55% yield (1.403 g); **TLC R_f** = 0.3 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.46 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 5.12 (s, 2H), 4.80 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.2, 134.7, 131.5, 129.7, 122.1, 65.4, 46.2; **IR** (neat, cm^{-1}): 2107*s*, 1684*s*, 1490*w*, 1382*m*, 1347*m*, 1107*s*, 1010*m*, 908*m*, 799*m*, 731*s*, 651*w*, 474*w*.

3 Paired electrolysis enables decarboxylative coupling of alkenyl acids with diazo compounds

3.1 General procedure for synthesis of β, γ-alkenyl esters and amides (GP2)

GP2-1, for liquid diazo compounds

The electrocatalytic reaction was carried out in an undivided cell with a graphite felt anode (20 mm × 10 mm × 5 mm) and a Pt plate cathode (15 mm × 10 mm × 0.10 mm). A flame-dried undivided electrochemical cell equipped with a magnetic stir bar was charged with the alkenyl acids **1** (0.300 mmol, 1.0 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before MeCN/H_2O (3:1, 4 mL) was added. The corresponding diazo compounds **2** (0.750 mmol, 2.5 equiv), and DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv) were added to the mixture by micro-syringe successively. The reaction mixture was then stirred under constant current of 5 mA at 50 ℃ for 4 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford the desired product **3**.

GP2-2, for solid diazo compounds

The electrocatalytic reaction was carried out in an undivided cell with a graphite felt anode (20 mm × 10 mm × 5 mm) and a Pt plate cathode (15 mm × 10 mm × 0.10 mm). A flame-dried undivided electrochemical cell equipped with a magnetic stir bar was charged with alkenyl acids **1** (0.300 mmol, 1.0 equiv), diazo compounds **2** (0.750 mmol, 2.5 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before MeCN/H_2O (3:1, 4 mL) was added. DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv)

was added to the mixture by micro-syringe successively. The reaction mixture was then stirred under constant current of 5 mA at 50 ℃ for 4 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford the desired product **3**.

3.2 General procedure for synthesis of dideuterated β, γ-alkenyl esters and amides (GP3)

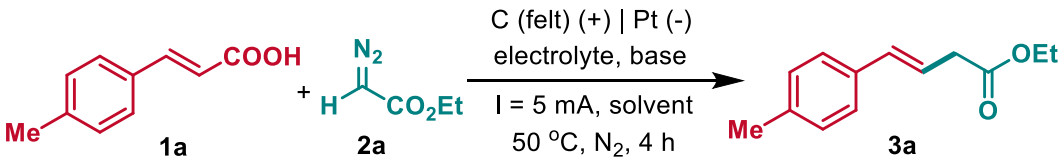
GP3-1, for liquid diazo compounds

The electrocatalytic reaction was carried out in an undivided cell with a graphite felt anode (20 mm × 10 mm × 5 mm) and a Pt plate cathode (15 mm × 10 mm × 0.10 mm). A flame-dried undivided electrochemical cell equipped with a magnetic stir bar was charged with the alkenyl acids **1** (0.300 mmol, 1.0 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before MeCN/D_2O (3:1, 4 mL) was added. The corresponding diazo compounds **2** (0.750 mmol, 2.5 equiv), and DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv) were added to the mixture by micro-syringe successively. The reaction mixture was then stirred under constant current of 5 mA at 50 ℃ for 4 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford the desired product **3'**.

GP3-2, for solid diazo compounds

The electrocatalytic reaction was carried out in an undivided cell with a graphite felt anode (20 mm × 10 mm × 5 mm) and a Pt plate cathode (15 mm × 10 mm × 0.10 mm). A flame-dried undivided electrochemical cell equipped with a magnetic stir bar was charged with alkenyl acids **1** (0.300 mmol, 1.0 equiv), diazo compounds **2** (0.750 mmol, 2.5 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before MeCN/D_2O (3:1, 4 mL) was added. DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv) was added to the mixture by micro-syringe successively. The reaction mixture was then stirred under constant current of 5 mA at 50 ℃ for 4 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford the desired product **3'**.

3.3 Screening of reaction conditions



Entry[a]	Electrolyte	Base	Solvent	Yield (%)[b]
1	$LiClO_4$	Cs_2CO_3	MeCN/H_2O (3:1)	15
2	$LiClO_4$	Na_2CO_3	MeCN/H_2O (3:1)	9
3	$LiClO_4$	DABCO	MeCN/H_2O (3:1)	27
4	$LiClO_4$	Et_3N	MeCN/H_2O (3:1)	38
5	**$LiClO_4$**	**DIPEA**	**MeCN/H_2O (3:1)**	**74 (72)[c]**
6	$LiClO_4$	$^nPr_3N$	MeCN/H_2O (3:1)	51
7	$TBABF_4$	DIPEA	MeCN/H_2O (3:1)	46
8	TBAI	DIPEA	MeCN/H_2O (3:1)	35
9	$TBAClO_4$	DIPEA	MeCN/H_2O (3:1)	27
10	LiCl	DIPEA	MeCN/H_2O (3:1)	28
11	$LiClO_4$	DIPEA	Acttone/H_2O (3:1)	48
12	$LiClO_4$	DIPEA	DMF/H_2O (3:1)	19
13	$LiClO_4$	DIPEA	DMA/H_2O (3:1)	23
14	$LiClO_4$	DIPEA	Dioxane/H_2O (3:1)	29
15	$LiClO_4$	DIPEA	NMP/H_2O (3:1)	26
16	$LiClO_4$	DIPEA	MeCN/H_2O (1:1)	62
17	$LiClO_4$	DIPEA	MeCN/H_2O (1:3)	46
18	$LiClO_4$	DIPEA	MeCN	trace
19	$LiClO_4$	DIPEA	H_2O	trace
20[d]	$LiClO_4$	DIPEA	MeCN/H_2O (3:1)	60
21[e]	$LiClO_4$	DIPEA	MeCN/H_2O (3:1)	57
22[f]	$LiClO_4$	DIPEA	MeCN/H_2O (3:1)	8
23[g]	$LiClO_4$	DIPEA	MeCN/H_2O (3:1)	62
24[h]	$LiClO_4$	DIPEA	MeCN/H_2O (3:1)	49
25[i]	$LiClO_4$	DIPEA	MeCN/H_2O (3:1)	52
26[j]	$LiClO_4$	DIPEA	MeCN/H_2O (3:1)	nd.

[a]Reaction conditions: graphite felt anode (20 mm * 10 mm * 5 mm), Pt plate cathode (15 mm * 10mm* 0.1 mm), undivided cell, **1a** (48.7 mg, 0.30 mmol, 1.0 equiv), **2a** (85.6 mg, 0.75 mmol, 2.5 equiv), electrolyte (0.30 mmol, 1.0 equiv), base (0.36 mmol, 1.2 equiv), the solvent 4 mL, I = 5 mA, 50 °C, N_2, 4 h (2.5 F/mol). [b]Yield determined by ^1H NMR analysis using dibromomethane as an internal standard. [c]Isolated yield. [d]The reaction time was extended to 6 h. [e]The reaction was conducted under constant current of 10 mA for 2 h. [f]The reaction was conducted under room temperature. [g]Ni plate (20 mm * 10 mm * 5 mm) was used the cathode. [h]graphite felt (20 mm * 10 mm * 5 mm) was used the cathode. [i]Pt plate (15 mm * 10mm* 0.1 mm) was used the anode. [j]The reaction was conducted under no electric current. "nd." stands for "not detected".

General procedure for screening of reaction conditions of 3a (GP-4)

GP4-1, for solid base

The electrocatalytic reaction was carried out in an undivided cell with a graphite felt anode (20 mm × 10 mm × 5 mm) and a Pt plate cathode (15 mm × 10 mm × 0.10 mm). A flame-dried undivided electrochemical cell equipped with a magnetic stir bar was charged with the 4-methylcinnamic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), electrolyte (0.300 mmol, 1.0 equiv), and base (0.360 mmol, 1.2 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before solvent (4 mL) was added. The ethyl diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv) was added to the mixture by micro-syringe successively. The reaction mixture was then stirred under constant current of 5 mA for 4 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The yield of **3a** was determined by ^{1}H NMR analysis of the crude residue using dibromomethane as an internal standard.

GP4-2, for liquid base

The electrocatalytic reaction was carried out in an undivided cell with a graphite felt anode (20 mm × 10 mm × 5 mm) and a Pt plate cathode (15 mm × 10 mm × 0.10 mm). A flame-dried undivided electrochemical cell equipped with a magnetic stir bar was charged with 4-methylcinnamic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), and electrolyte (0.300 mmol, 1.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before solvent (4 mL) was added. The ethyl diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), and base (0.360 mmol, 1.2 equiv) were added to the mixture by micro-syringe successively. The reaction mixture was then stirred under constant current of 5 mA for 4 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The yield of **3a** was determined by ^{1}H NMR analysis of the crude residue using dibromomethane as an internal standard.

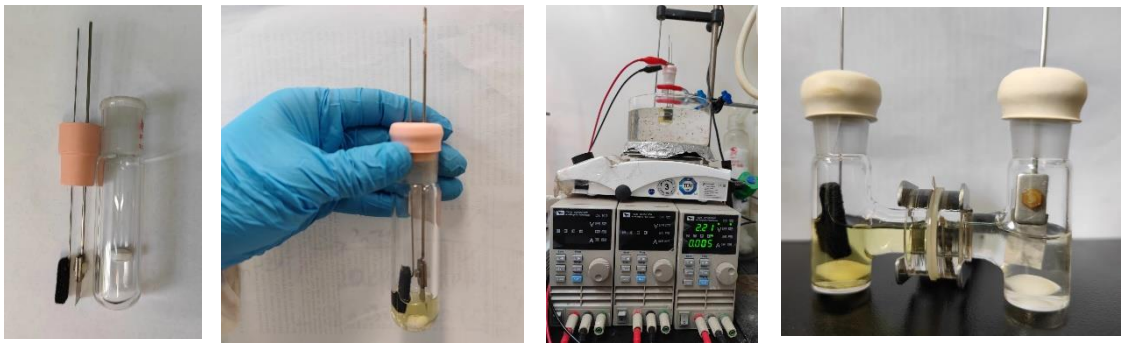
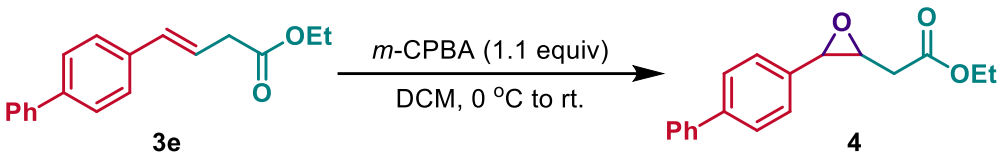


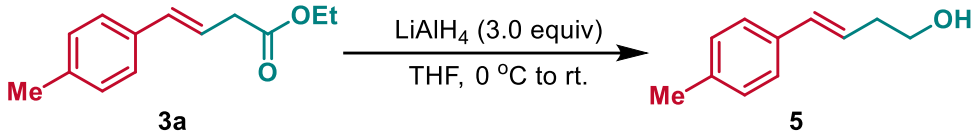
Figure S1 reaction setup

4 Follow-up transformation of β, γ-alkenyl esters



3e **4**

A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with *m*-CPBA (38.0 mg, 0.220 mmol, 1.1 equiv) before DCM (2 mL) was added. The reaction mixture was cooled to 0 °C, and a solution of **3e** (53.3 mg, 0.200 mmol, 1.0 equiv) in DCM (1 mL) was solely added at 0 °C (ice bath). The reaction mixture was allowed to warm to room temperature and stirred for 29 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography (PE:EtOAc = 15:1) to afford the desired product **4** as a white solid in 60% yield (33.9

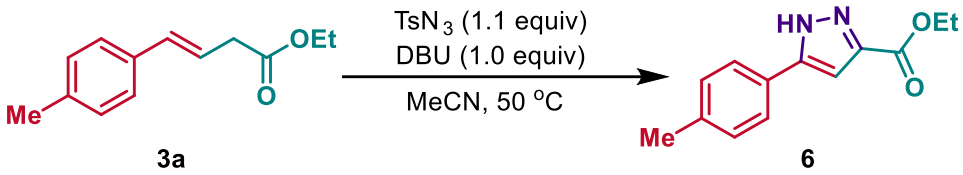


3a **5**

mg); **MP**: 70 – 72 °C; **TLC R**$_f$ = 0.3 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.59 – 7.57 (m, 4H), 7.47 – 7.42 (m, 2H), 7.37 – 7.33 (m, 3H), 4.21 (q, J = 7.1 Hz, 2H), 3.77 (s, 1H), 3.41 – 3.37 (m, 1H), 2.79 – 2.69 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.1, 141.3, 140.6, 135.7, 128.8, 127.4, 127.3, 127.1, 126.1, 61.0, 58.1, 58.0, 38.0, 14.2; **HRMS** (EI) *m*/*z* = 282.1256 calcd. for $C_{18}H_{18}O_3$ $[M]^+$, found: 282.1259; **IR** (neat, cm^{-1}): 3752*w*, 1736*s*, 1570*w*, 1491*w*, 1370*w*, 11182*m*, 1028*m*, 696*w*.

A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with **3a** (40.9 mg, 0.200 mmol, 1.0 equiv) before dry THF (2 mL) was added. The reaction mixture was cooled to 0 °C, and a solution of $LiAlH_4$ (11.4 mg, 0.600 mmol, 3.0 equiv) in dry THF (1 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. After the reaction was complete, the reaction mixture was quenched with saturated NH_4Cl solution and extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography (PE:EtOAc = 5:1) to afford the desired product **5** as a colorless liquid in quantitative yield (32.1 mg). **TLC R**$_f$ = 0.3 (PE:EtOAc = 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.30 (d, J = 7.9 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 6.50 (d, J = 15.9 Hz, 1H), 6.18 (dt, J^1 = 15.8, J^2 = 7.1 Hz, 1H), 3.77 (t, J = 6.3 Hz, 2H), 2.50 (td, J^1 = 7.2, J^2 = 6.5 Hz, 2H), 2.37 (s, 3H), 1.99 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 136.9, 134.4, 132.5, 129.2, 125.9, 125.2, 62.0, 36.3, 21.1. The spectral

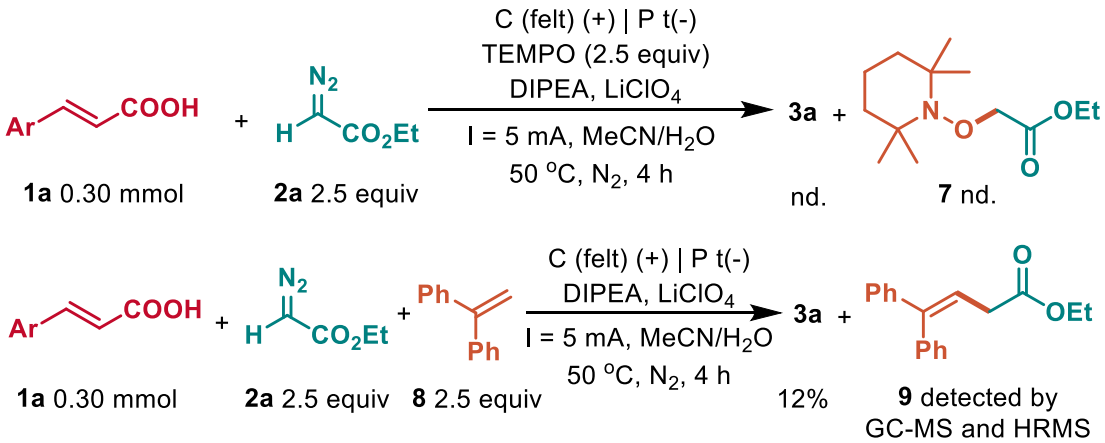
data are in accordance with previous reported literature.[6]



A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with **3a** (40.9 mg, 0.200 mmol, 1.0 equiv), and TsN_3 (43.4 mg, 0.220 mmol, 1.1 equiv) before MeCN (2 mL) was added. The DBU (30.4 mg, 0.200 mmol, 1.0 equiv) was slowly added. The reaction mixture was then stirred at 50 °C for 12 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography (PE:EtOAc = 5:1) to afford the desired product **6** as a white solid in 72% yield (33.2 mg). **TLC Rf** = 0.3 (PE:EtOAc = 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.57 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.92 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 161.3, 147.0, 141.0, 138.3, 129.4, 127.0, 125.5, 104.6, 60.8, 21.2, 13.9; The spectral data are in accordance with previous reported literature.[7]

5. Mechanistic studies

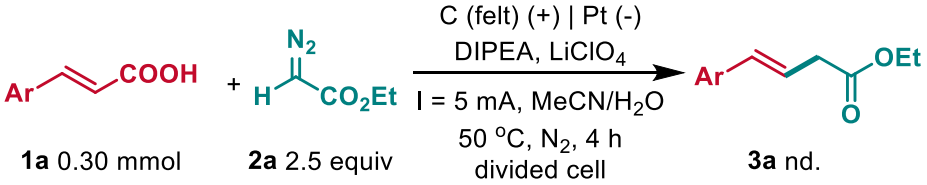
5.1 Control experiments



The electrocatalytic reaction was carried out in an undivided cell with a graphite felt anode (20 mm × 10 mm × 5 mm) and a Pt plate cathode (15 mm × 10 mm × 0.10 mm). A flame-dried undivided electrochemical cell equipped with a magnetic stir bar was charged with the 4-methylcinnamic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), $LiClO_4$ (31.9 mg, 0.360 mmol, 1.2 equiv), and radical scavenger TEMPO (117.2 mg, 0.750 mmol, 2.5 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before the mixture solvent MeCN/H_2O (3:1, 4 mL) was added. The ethyl diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv),

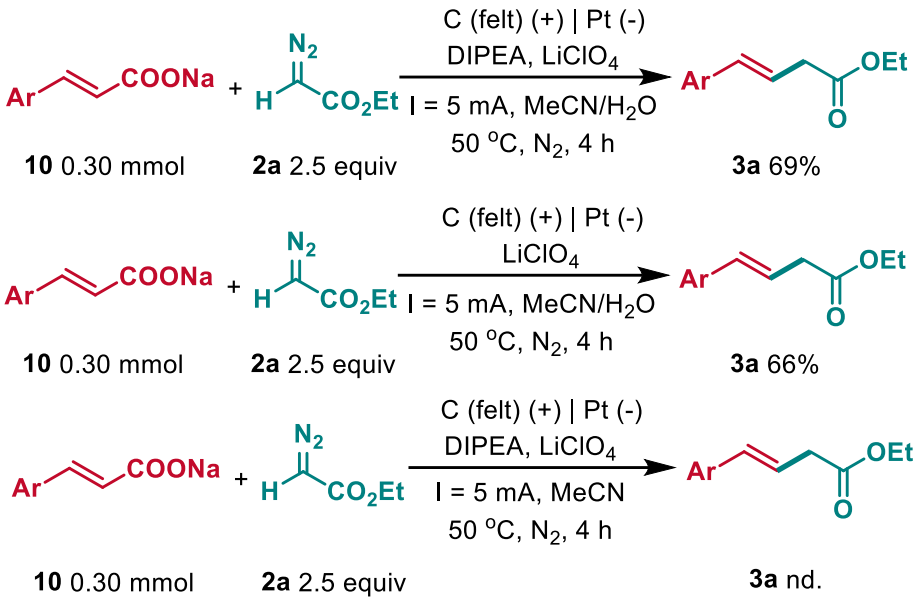
and DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv) were added to the mixture by micro-syringe successively. The reaction mixture was then stirred under constant current of 5 mA at 50 ℃ for 4 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. Trace amount of desired product **3a** was detected, whereas TEMPO adduct **7** was not detected by TLC, GC-MS and ^{1}H NMR analysis.

The electrocatalytic reaction was carried out in an undivided cell with a graphite felt anode (20 mm × 10 mm × 5 mm) and a Pt plate cathode (15 mm × 10 mm × 0.10 mm). A flame-dried undivided electrochemical cell equipped with a magnetic stir bar was charged with the 4-methylcinnamic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), and $LiClO_4$ (31.9 mg, 0.360 mmol, 1.2 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before the mixture solvent MeCN/H_2O (3:1, 4 mL) was added. The ethyl diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and 1,1-diphenylethylene **8** (135.2 mg, 0.75 mmol, 2.5 equiv) were added to the mixture by micro-syringe successively. The reaction mixture was then stirred under constant current of 5 mA at 50 ℃ for 4 h. Only 12% yield of desired product **3a** was isolated, and the adduct **9** was detected by GC-MS (found: 266.150) and HRMS (EI) *m*/*z* = 266.1306 calcd. for $C_{18}H_{18}O_2$ $[M]^+$, found: 266.1307).



The electrocatalytic reaction was carried out in the anode chamber of a divided cell with a graphite felt anode (20 mm × 10 mm × 5 mm) and a Pt plate cathode (15 mm × 10 mm × 0.10 mm). A flame-dried divided electrochemical cell equipped with a magnetic stir bar in each chamber. The cathodic chamber was charged with the 4-methylcinnamic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), and $LiClO_4$ (31.9 mg, 0.360 mmol, 1.2 equiv). The anothade was charged with $LiClO_4$ (31.9 mg, 0.360 mmol, 1.2 equiv). Two chambers sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before the mixture solvent MeCN/H_2O (3:1, 4 mL) was added. The ethyl diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), and DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), were added to the anode chamber by micro-syringe successively, and the DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv) was added to the cathodic chamber by micro-syringe successively. The reaction mixture was then stirred under constant current of 5 mA at 50 ℃ for 4 h. After the reaction was

complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The desired product **3a** was not detected by TLC and GC-MS.



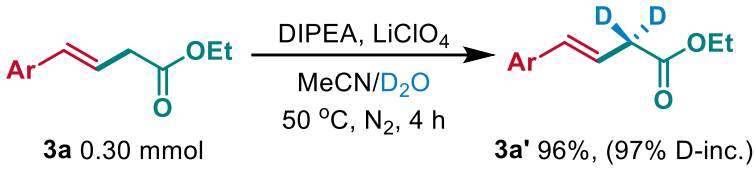
The electrocatalytic reaction was carried out in an undivided cell with a graphite felt anode (20 mm × 10 mm × 5 mm) and a Pt plate cathode (15 mm × 10 mm × 0.10 mm). A flame-dried undivided electrochemical cell equipped with a magnetic stir bar was charged with the sodium cinnamate **10** (55.3 mg, 0.300 mmol, 1.0 equiv), and $LiClO_4$ (31.9 mg, 0.360 mmol, 1.2 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before the mixture solvent MeCN/H_2O (3:1, 4 mL) was added. The ethyl diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), and DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), were added to the mixture by micro-syringe successively. The reaction mixture was then stirred under constant current of 5 mA at 50 ℃ for 4 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford the desired product **3a** in 69% yield.

The electrocatalytic reaction was carried out in an undivided cell with a graphite felt anode (20 mm × 10 mm × 5 mm) and a Pt plate cathode (15 mm × 10 mm × 0.10 mm). A flame-dried undivided electrochemical cell equipped with a magnetic stir bar was charged with the sodium cinnamate **10** (55.3 mg, 0.300 mmol, 1.0 equiv), and $LiClO_4$ (31.9 mg, 0.360 mmol, 1.2 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before the mixture solvent MeCN/H_2O (3:1, 4 mL) was added. The ethyl diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv) was added to the mixture by micro-syringe successively. The reaction mixture was then stirred under constant current of 5 mA at 50 ℃ for 4 h. After the

reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford the desired product **3a** in 66% yield.

The electrocatalytic reaction was carried out in an undivided cell with a graphite felt anode (20 mm × 10 mm × 5 mm) and a Pt plate cathode (15 mm × 10 mm × 0.10 mm). A flame-dried undivided electrochemical cell equipped with a magnetic stir bar was charged with the sodium cinnamate **10** (55.3 mg, 0.300 mmol, 1.0 equiv), and $LiClO_4$ (31.9 mg, 0.360 mmol, 1.2 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before the solvent MeCN (4 mL) was added. The ethyl diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), and DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv) were added to the mixture by micro-syringe successively. The reaction mixture was then stirred under constant current of 5 mA at 50 ℃ for 4 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The desired product **3a** was not detected.

5.2 H/D kinetic isotope experiments



3a 0.30 mmol

3a' 96%, (97% D-inc.)

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before the mixture solvent MeCN/D_2O (3:1, 4 mL) was added. The β, γ-alkenyl esters **3a** (61.3 mg, 0.300 mmol, 1.0 equiv), and DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv) were added to the mixture by micro-syringe successively. The reaction mixture was then stirred at 50 ℃ for 4 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography (PE:EtOAc = 50:1) to afford the desired product **3a'** as a colorless liquid in 96% yield (59.4 mg, 97% D-inc.); **TLC Rf** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.28 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.26 (d, *J* = 15.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); The characteristic peak of **3a** (3.22 (d, *J* = 9.4 Hz, 0.06H)) was observed; **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.6, 137.2, 134.0, 133.2, 129.1, 126.1, 120.6, 60.6, 38.3 – 37.7 (m, 1C), 21.1, 14.1; **HRMS** (EI) *m/z* = 206.1276 calcd. for $C_{13}H_{14}D_2O_2$ $[M]^+$, found: 206.1278; **IR** (neat, cm^{-1}):

2981*w*, 1730*s*, 1513*w*, 1444*w*, 1364*w*, 1273*m*, 1245*s*, 1136*m*, 1050*m*, 1022*m*, 970*m*, 816*m*, 771*w*, 742*w*, 502*w*.

5.3 Electrochemical measurements

The cyclic voltammograms were recorded in a mixed solvent of MeCN/H_2O (3:1) with $LiClO_4$ (0.06 M) as supporting electrolyte using a glassy carbon disk working electrode (diameter, 1 mm), a Pt wire auxiliary electrode and a SCE reference electrode. The scan rate was 50 mv/s unless other mentioned. Before CV test, the solution was stirred for ten minutes.

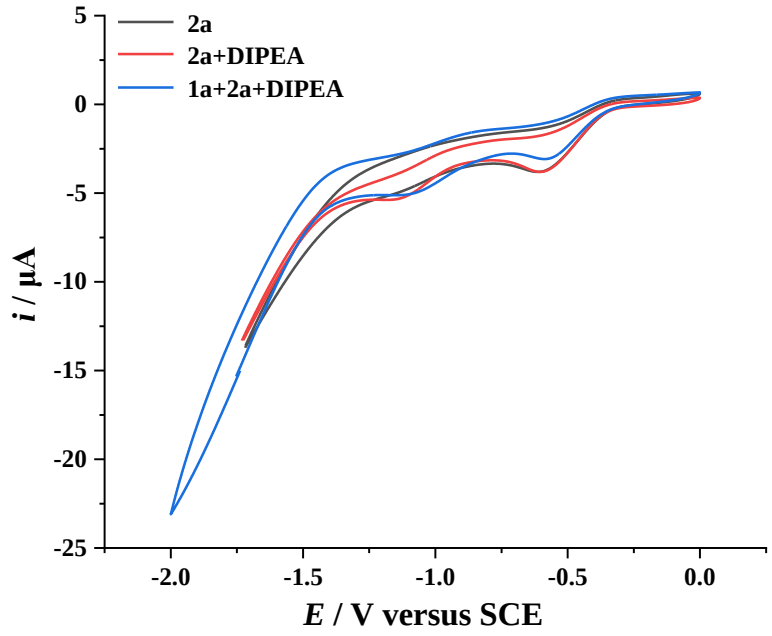


Figure S2. **1a** (0.05 M), **2a** (0.30 M), DIPEA (0.06 M).

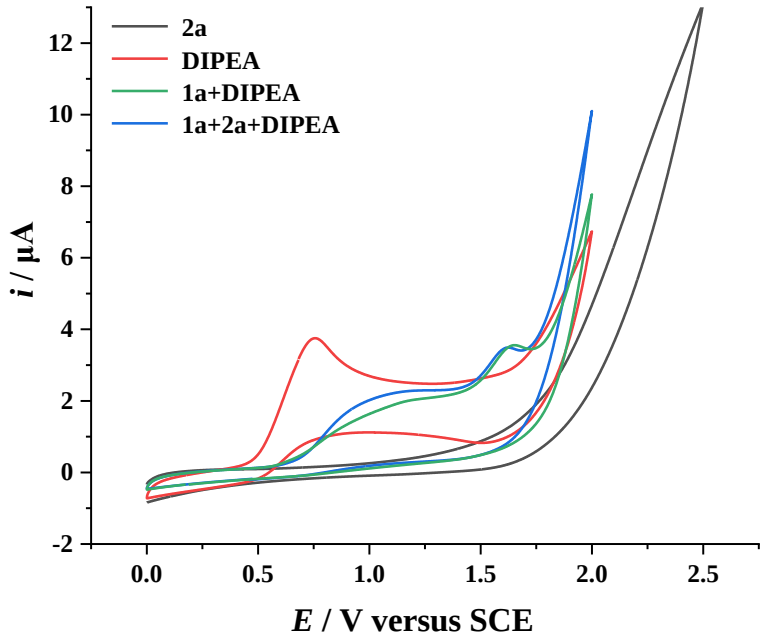


Figure S3. **1a** (0.05 M), **2a** (0.30 M), DIPEA (0.06 M).

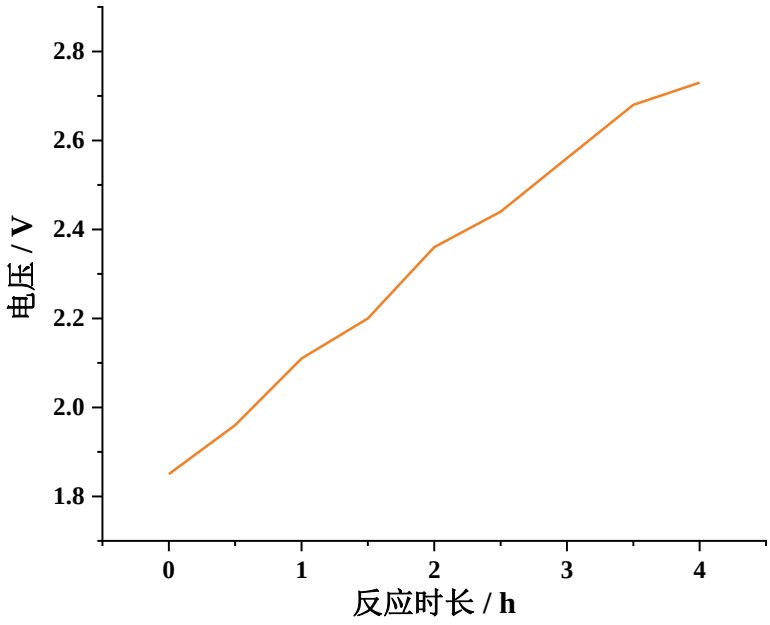
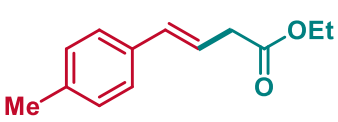
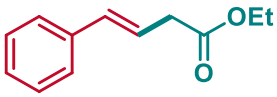


Figure S4 voltage over the course of electrolysis.

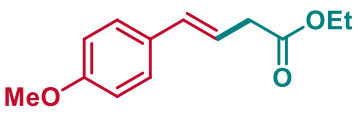
6. Spectral data



Ethyl (*E*)-4-(*p*-tolyl)but-3-enoate (3a): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3a** as a colorless liquid in 72% yield (44.1 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.28 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.28 (dt, J^1 = 15.8 Hz, J^2 = 7.2 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.24 (dd, J^1 = 7.1 Hz, J^2 = 1.0 Hz, 2H), 2.34 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.6, 137.2, 134.0, 133.1, 129.1, 126.1, 120.7, 60.7, 38.4, 21.1, 14.1. The spectral data are in accordance with literature.[8]

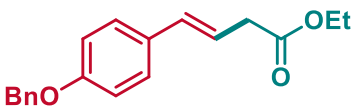


Ethyl (*E*)-4-phenylbut-3-enoate (3b): The title compound was prepared according to general procedure (**GP2-1**) with cinnamic acid **1b** (44.4 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3b** as a colorless liquid in 62% yield (41.2 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.43 (d, *J* = 6.9 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.27 (m, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.36 (dt, J^1 = 15.9 Hz, J^2 = 7.1 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.29 (dd, J^1 = 7.1 Hz, J^2 = 1.4 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.6, 136.8, 133.3, 128.5, 127.5, 126.2, 121.8, 60.8, 38.5, 14.2. The spectral data are in accordance with literature.[8]

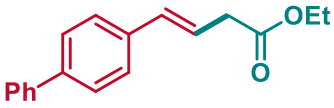


Ethyl (*E*)-4-(4-methoxyphenyl)but-3-enoate (3c): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(4-methoxyphenyl) acrylic acid **1c** (53.5 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3c** as a colorless liquid in 82% yield (53.9 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.30 (d, *J* = 8.7 Hz,

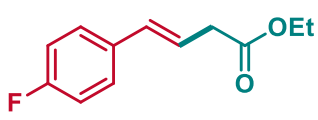
2H), 6.84 (d, J = 8.7 Hz, 2H), 6.43 (d, J = 15.9 Hz, 1H), 6.16 (dt, J^1 = 15.8 Hz, J^2 = 7.1 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H) 3.80 (s, 3H), 3.21 (dd, J^1 = 7.1 Hz, J^2 = 1.5 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.8, 159.1, 132.7, 129.7, 127.4, 119.5, 113.9, 60.7, 55.2, 38.4, 14.2. The spectral data are in accordance with literature.[8]



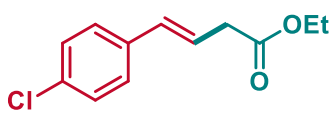
Ethyl (*E*)-4-(4-(benzyloxy)phenyl)but-3-enoate (3d): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(4-(benzyloxy)phenyl) acrylic acid **1d** (76.3 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 30:1) gave the desired product **3d** as a white solid in 69% yield (62.3 mg); **MP**: 65 – 67 °C; **TLC R_f** = 0.3 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.45 – 7.38 (m, 4H), 7.35 – 7.31 (m, 3H), 6.94 (d, J = 8.8 Hz, 2H), 6.45 (d, J = 15.9 Hz, 1H), 6.18 (dt, J^1 = 15.9 Hz, J^2 = 7.1 Hz, 1H), 5.07 (s, 2H), 4.19 (q, J = 7.2 Hz, 2H), 3.23 (dd, J^1 = 7.2 Hz, J^2 = 1.5 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.7, 158.3, 136.9, 132.7, 129.9, 128.5, 127.9, 127.4, 119.7, 114.8, 69.9, 60.7, 38.4, 14.2. The spectral data are in accordance with literature.[9]



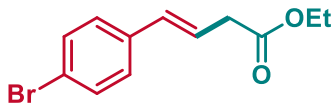
Ethyl (*E*)-4-([1,1'-biphenyl]-4-yl)but-3-enoate (3e): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-([1,1'-biphenyl]-4-yl) acrylic acid **1e** (79.9 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3e** as a white solid in 66% yield (52.8 mg); **MP**: 85 – 87 °C; **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.62 – 7.56 (m, 4H), 7.47 – 7.43 (m, 4H), 7.35 (t, J = 7.3 Hz, 1H), 6.55 (d, J = 15.8 Hz, 1H), 6.37 (dt, J^1 = 15.9 Hz, J^2 = 7.1 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.28 (dd, J^1 = 7.1 Hz, J^2 = 1.4 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.5, 140.6, 140.2, 135.9, 132.9, 128.7, 127.2, 127.2, 126.9, 126.7, 121.9, 60.8, 38.5, 14.2; **HRMS** (EI) m/z = 266.1307 calcd. for $C_{18}H_{18}O_2$ $[M]^+$, found: 266.1305; **IR** (neat, cm^{-1}): 2924*w*, 1730*s*, 1484*w*, 1404*m*, 1370*m*, 1324*w*, 1290*m*, 1199*s*, 1176*s*, 1119*w*, 1028*m*, 976*m*, 908*m*, 839*w*, 810*w*, 759*s*, 736*s*, 685*m*, 479*w*.



Ethyl (*E*)-4-(4-fluorophenyl)but-3-enoate (3f): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(4-fluorophenyl)acrylic acid **1f** (49.8 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3f** as a colorless liquid in 60% yield (37.6 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.34 – 7.26 (m, 2H), 7.01 – 6.97 (m, 2H), 6.44 (d, J = 15.9 Hz, 1H), 6.21 (dt, J^1 = 15.9, J^2 = 7.1 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.22 (dd, J^1 = 7.1, J^2 = 1.5 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.5, 162.2 (d, J = 246.6 Hz), 133.0 (d, J = 3.4 Hz), 132.1, 127.7 (d, J = 7.9 Hz), 121.6 (d, J = 2.3 Hz), 115.4 (d, J = 21.6 Hz), 60.77, 38.30, 14.15. The spectral data are in accordance with literature.[8]

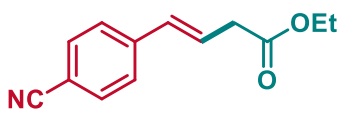


Ethyl (*E*)-4-(4-chlorophenyl)but-3-enoate (3g): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(4-chlorophenyl)acrylic acid **1g** (54.8 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3g** as a colorless liquid in 69% yield (46.7 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.31 – 7.26 (m, 4H), 6.45 (d, J = 15.9 Hz, 1H), 6.29 (dt, J^1 = 16.0 Hz, J^2 = 7.0 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.24 (dd, J^1 = 7.1 Hz, J^2 = 1.4 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.4, 135.3, 133.1, 132.1, 128.6, 127.4, 122.5, 60.8, 38.3, 14.1. The spectral data are in accordance with literature.[8]

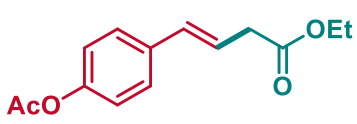


Ethyl (*E*)-4-(4-bromophenyl)but-3-enoate (3h): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(4-bromophenyl)acrylic acid **1h** (83.1 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3h** as a colorless liquid in 50% yield (40.3 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.42 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 6.42 (d, J = 16.0 Hz, 1H), 6.29 (dt, J^1 = 15.9 Hz, J^2 = 7.0 Hz, 1H), 4.17 (q, J = 7.1 Hz,

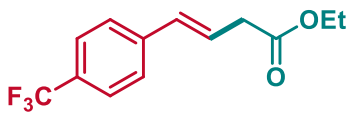
2H), 3.23 (dd, J^1 = 7.0 Hz, J^2 =1.3 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.4, 135.8, 132.2, 131.6, 127.8, 122.7, 121.3, 60.8, 38.4, 14.2. The spectral data are in accordance with literature.[8]



Ethyl (*E*)-4-(4-cyanophenyl)but-3-enoate (3i): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(4-cyanophenyl)acrylic acid **1i** (64.6 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 5 h. Purification via silica gel chromatography (PE:EtOAc = 20:1) gave the desired product **3i** as a colorless liquid in 32% yield (20.7 mg); **TLC R_f** = 0.3 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.59 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 6.53 – 6.40 (m, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.28 (d, J = 6.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H).; **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.0, 141.3, 132.4, 131.8, 126.7, 126.1, 118.9, 110.8, 61.0, 38.3, 14.2; **HRMS** (EI) *m/z* = 215.0946 calcd. for $C_{13}H_{13}NO_2$ $[M]^+$, found: 215.0950; **IR** (neat, cm^{-1}): 2924*w*, 2227*w*, 1730*s*, 1604*w*, 1296*w*, 1256*w*, 1165*s*, 1028*m*, 970*m*, 850*w*, 548*w*.

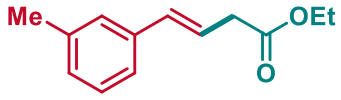


Ethyl (*E*)-4-(4-acetoxyphenyl)but-3-enoate (3j): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(4-acetoxyphenyl)acrylic acid **1j** (61.9 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5mA at 50 °C for 5 h. Purification via silica gel chromatography (PE:EtOAc = 15:1) gave the desired product **3j** as a colorless liquid in 39% yield (29.1 mg); **TLC R_f** = 0.3 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.37 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 8.6 Hz, 2H), 6.47 (d, J = 15.9 Hz, 1H), 6.25 (dt, J^1 = 15.9 Hz, J^2 = 7.1 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 3.23 (dd, J^1 = 7.1 Hz, J^2 = 1.5 Hz, 2H), 2.29 (s, 3H), 1.27 (d, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.5, 169.4, 149.9, 134.7, 132.3, 127.2, 122.1, 121.6, 60.8, 38.4, 21.1, 14.2. The spectral data are in accordance with literature.[8]

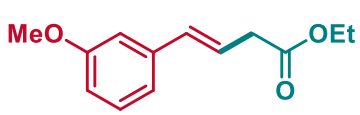


Ethyl (*E*)-4-(4-(trifluoromethyl)phenyl)but-3-enoate (3k): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(4-(trifluoromethyl)phenyl)acrylic acid **1k** (64.8 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2

equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3k** as a colorless liquid in 45% yield (34.6 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.56 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 6.52 (d, J = 16.0 Hz, 1H), 6.41 (dt, J^1 = 15.9 Hz, J^2 = 6.9 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.27 (dd, J^1 = 7.0 Hz, J^2 = 1.2 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.2, 140.3, 132.1, 129.4 (q, J = 32.3 Hz, 1C), 126.4, 125.5 (q, J = 3.8 Hz, 1C), 124.7, 124.2 (q, J = 272.0 Hz, 1C), 61.0, 38.4, 14.2. The spectral data are in accordance with literature.[10]

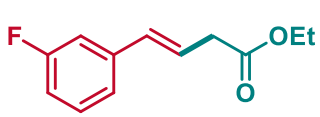


Ethyl (*E*)-4-(*m*-tolyl)but-3-enoate (3l): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(m-tolyl)acrylic acid **1l** (48.7 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current at of 5 mA 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3l** as a colorless liquid in 66% yield (40.4 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.23 – 7.17 (m, 3H), 7.06 (d, J = 6.5 Hz, 1H), 6.47 (d, J = 15.9 Hz, 1H), 6.30 (dt, J^1 = 15.9 Hz, J^2 = 7.1 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.24 (dd, J^1 = 7.1 Hz, J^2 = 1.4 Hz, 2H), 2.35 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.6, 138.0, 136.8, 133.4, 128.4, 128.3, 126.9, 123.4, 121.6, 60.7, 38.4, 21.3, 14.2. The spectral data are in accordance with literature.[8]

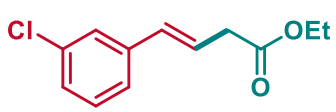


Ethyl (*E*)-4-(3-methoxyphenyl)but-3-enoate (3m): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(3-methoxyphenyl) acrylic acid **1m** (53.5 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3m** as a colorless liquid in 45% yield (29.9 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.22 (t, J = 7.9 Hz, 1H), 6.97 (d, J = 7.7 Hz, 1H), 6.91 (s, 1H), 6.79 (d, J = 8.2 Hz, 1H), 6.47 (d, J = 15.9 Hz, 1H), 6.30 (dt, J^1 = 15.8 Hz, J^2 = 7.0 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 3.24 (dd, J^1 = 7.0 Hz, J^2 = 1.4 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.5, 159.7, 138.3, 133.2, 129.5, 122.2, 118.9, 113.2, 111.5,

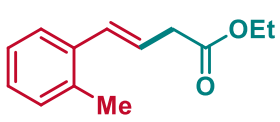
60.8, 55.2, 38.4, 14.2. The spectral data are in accordance with literature.[8]



Ethyl (*E*)-4-(3-fluorophenyl)but-3-enoate (3n): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(3-fluorophenyl)acrylic acid **1n** (49.8 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3n** as a colorless liquid in 45% yield (28.1 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.24 – 7.21 (m, 1H), 7.10 (d, J = 7.8 Hz, 1H), 7.06 – 7.03 (m, 1H), 6.92 – 6.87 (m, 1H), 6.43 (d, J = 16.0 Hz, 1H), 6.29 (dt, J^1 = 15.9 Hz, J^2 = 7.0 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.21 (dd, J^1 = 7.0 Hz, J^2 = 1.4 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.3, 163.0 (d, J = 245.2 Hz, 1C), 139.2 (d, J = 7.6 Hz, 1C), 132.2 (d, J = 2.5 Hz, 1C), 129.9 (d, J = 8.4 Hz, 1C), 123.3, 122.1 (d, J = 2.8 Hz, 1C), 114.3 (d, J = 21.4 Hz, 1C), 112.7 (d, J = 21.8 Hz, 1C), 60.8, 38.3, 14.2. The spectral data are in accordance with literature.[8]

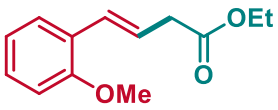


Ethyl (*E*)-4-(3-chlorophenyl)but-3-enoate (3o): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(3-chlorophenyl)acrylic acid **1o** (54.8 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3o** as a colorless liquid in 41% yield (27.6 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.35 (s, 1H), 7.25 – 7.17 (m, 3H), 6.43 (d, J = 15.9 Hz, 1H), 6.32 (dt, J^1 = 15.9 Hz, J^2 = 6.9 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.24 (dd, J^1 = 6.9 Hz, J^2 = 1.2 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.3, 138.7, 134.4, 132.0, 129.7, 127.4, 126.2, 124.5, 123.5, 60.9, 38.3, 14.2. The spectral data are in accordance with literature.[8]

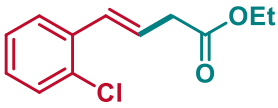


Ethyl (*E*)-4-(o-tolyl)but-3-enoate (3p): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(*o*-tolyl)acrylic acid **1p** (48.7 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3p** as a colorless liquid

in 79% yield (48.7 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.46 – 7.44 (m, 1H), 7.18 – 7.13 (m, 3H), 6.71 (d, *J* = 15.8 Hz, 1H), 6.26 – 6.13 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.27 (dd, J^1 = 7.1 Hz, J^2 = 1.6 Hz, 2H), 2.35 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.6, 136.0, 135.2, 131.2, 130.2, 127.4, 126.0, 125.7, 123.1, 60.7, 38.7, 19.7, 14.2; **HRMS** (EI) *m*/*z* = 204.1150 calcd. for $C_{13}H_{16}O_2$ $[M]^+$, found: 204.1155; **IR** (neat, cm^{-1}): 2981*w*, 1736*s*, 1462*w*, 1371*w*, 1296*w*, 1245*w*, 1154*s*, 1028*m*, 965*m*, 862*w*, 748.1*m*.

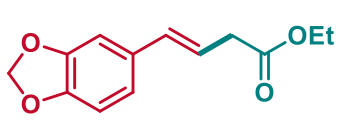


Ethyl (*E*)-4-(2-methoxyphenyl)but-3-enoate (3q): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(2-methoxyphenyl)acrylic acid **1q** (53.5 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3q** as a colorless liquid in 71% yield (46.7 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.45 (dd, J^1 = 7.6 Hz, J^2 = 1.7 Hz, 1H), 7.24 – 7.19 (m, 1H), 6.94 – 6.90 (m, 1H), 6.87 – 6.80 (m, 2H), 6.31 (dt, J^1 = 16.0 Hz, J^2 = 7.2 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.26 (dd, J^1 = 7.2 Hz, J^2 = 1.6 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.8, 156.5, 128.5, 128.1, 126.8, 125.9, 122.4, 120.6, 110.7, 60.7, 55.4, 38.9, 14.2; **HRMS** (EI) *m*/*z* = 220.1099 calcd. for $C_{13}H_{16}O_3$ $[M]^+$, found: 220.1102; **IR** (neat, cm^{-1}): 2929*w*, 1736*s*, 1599*w*, 1490*m*, 1462*w*, 1370*w*, 1296*w*, 1245*s*, 1176*m*, 1159*m*, 1113*w*, 1028*m*, 970*w*, 753*m*.

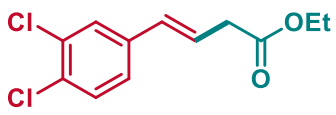


Ethyl (*E*)-4-(2-chlorophenyl)but-3-enoate (3r): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(2-chlorophenyl)acrylic acid **1r** (54.8 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3r** as a colorless liquid in 43% yield (28.8 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.55 (dd, J^1 = 7.6 Hz, J^2 = 1.9 Hz, 1H), 7.35 – 7.33 (m, 1H), 7.24 – 7.16 (m, 2H), 6.88 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, J^1 = 15.8 Hz, J^2 = 7.1 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.30 (dd, J^1 = 7.1 Hz, J^2 = 1.6 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.4, 134.9, 132.8, 129.6, 129.5, 128.5, 126.8, 126.8, 124.7, 60.8, 38.5, 14.2; **HRMS** (EI) *m*/*z* = 224.0604 calcd. for $C_{12}H_{13}ClO_2$ $[M]^+$, found: 224.0608; **IR** (neat, cm^{-1}): 2924*w*, 1736*s*, 1473*w*,

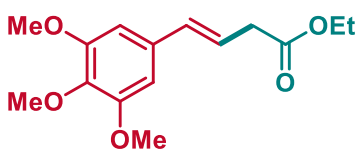
1370*w*, 1262*w*, 1159*m*, 1033*m*, 965*m*, 753*m*.



Ethyl (*E*)-4-(benzo[*d*][1,3]dioxol-5-yl)but-3-enoate (3s): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl) acrylic acid **1s** (57.7 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3s** as a colorless liquid in 81% yield (57.1 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 6.91 (s, 1H), 6.79 – 6.72 (m, 2H), 6.38 (d, J = 15.8 Hz, 1H), 6.12 (dt, J^1 = 15.8 Hz, J^2 = 5.93 Hz, 1H), 5.93 (s, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.19 (dd, J^1 = 7.2 Hz, J^2 = 1.5 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.6, 147.9, 147.1, 132.8, 131.3, 120.8, 120.0, 108.1, 105.5, 100.9, 60.7, 38.3, 14.1. The spectral data are in accordance with literature.[8]

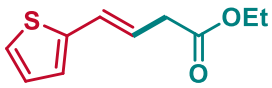


Ethyl (*E*)-4-(3,4-dichlorophenyl)but-3-enoate (3t): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(3,4-dichlorophenyl)acrylic acid **1t** (65.1 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 5 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3t** as a colorless liquid in 37% yield (28.8 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.44 (d, J = 2.0 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.18 (dd, J^1 = 8.3 Hz, J^2 = 2.1 Hz, 1H), 6.39 (d, J = 16.0 Hz, 1H), 6.30 (dt, J^1 = 15.9 Hz, J^2 = 6.7 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.23 (dd, J^1 = 6.7, J^2 = 1.0 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.2, 136.9, 132.6, 131.1, 131.0, 130.4, 128.0, 125.4, 124.0, 60.9, 38.2, 14.2; **HRMS** (EI) m/z = 258.0214 calcd. for $C_{12}H_{12}Cl_2O_2$ $[M]^+$, found: 258.0215; **IR** (neat, cm^{-1}): 2929*w*, 1736*s*, 1473*m*, 1370*w*, 1290*w*, 1256*w*, 1193*m*, 1153*m*, 1136*m*, 1028*m*, 965*w*, 731*w*.

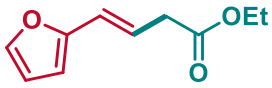


Ethyl (*E*)-4-(3,4,5-trimethoxyphenyl)but-3-enoate (3u): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(3,4,5-trimethoxyphenyl) acrylic acid **1u** (71.5 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg,

0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 20:1) gave the desired product **3u** as a colorless liquid in 76% yield (63.8 mg); **TLC R_f** = 0.4 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 6.57 (s, 2H), 6.39 (d, J = 15.7 Hz, 1H), 6.20 (dt, J^1 = 15.8 Hz, J^2 = 7.1 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.84 (s, 6H), 3.81 (s, 3H), 3.21 (dd, J^1 = 7.2Hz, J^2 = 1.4 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.5, 153.2, 137.6, 133.1, 132.5, 121.2, 103.2, 60.8, 60.7, 55.9, 38.2, 14.1; **HRMS** (EI) m/z = 280.1311 calcd. for $C_{15}H_{20}O_5$ $[M]^+$, found: 280.1313; **IR** (neat, cm^{-1}): 2941*w*, 1730*s*, 1581*s*, 1507*m*, 1456*m*, 1416*m*, 1370*w*, 1347*w*, 1324*w*, 1239*m*, 1153*m*, 1125*s*, 1028*w*, 1005*w*, 965*w*, 908*w*, 782*w*, 731*s*, 645*w*.

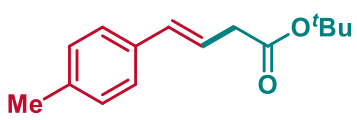


Ethyl (*E*)-4-(thiophen-2-yl)but-3-enoate (3v): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(thiophen-2-yl)acrylic acid **1v** (46.3 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3v** as a colorless liquid in 34% yield (20.1 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.14 (d, J = 4.8 Hz, 1H), 6.96 – 6.93 (m, 2H), 6.62 (d, J = 15.7 Hz, 1H), 6.13 (dt, J^1 = 22.8 Hz, J^2 = 7.2 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.20 (dd, J^1 = 7.2 Hz, J^2 = 1.6 Hz, 2H), 1.30 – 1.26 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.3, 141.8, 127.2, 126.8, 125.8, 124.1, 121.4, 60.8, 38.2, 14.2. The spectral data are in accordance with literature.[11]

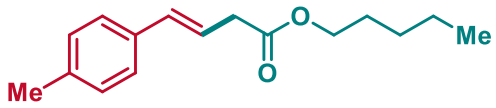


Ethyl (*E*)-4-(furan-2-yl)but-3-enoate (3w): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(furan-2-yl)acrylic acid **1w** (41.4 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3w** as a colorless liquid in 43% yield (21.6 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.33 (d, J = 1.6 Hz, 1H), 6.36 – 6.29 (m, 2H), 6.26 – 6.18 (m, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.20 (dd, J^1 = 6.9 Hz, J^2 = 1.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.4, 152.3, 141.9, 121.8, 120.5, 111.1, 107.5, 60.8, 38.2, 14.2; **HRMS** (EI) m/z = 180.0786 calcd. for $C_{10}H_{12}O_3$ $[M]^+$, found: 180.0788; **IR** (neat, cm^{-1}): 2981*w*, 2924*w*, 1736*s*, 1370*w*, 1273*w*, 1256*w*, 1182*w*,

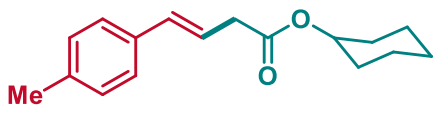
1159*m*, 1028*m*, 959*m*, 856*w*, 696*w*.



***Tert*-butyl (*E*)-4-(*p*-tolyl)but-3-enoate (3ab):** The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), *tert*-butyl 2-diazoacetate **2b** (106.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3ab** as a colorless liquid in 69% yield (47.9 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.19 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H), 6.35 (d, J = 16.0 Hz, 1H), 6.15 (dt, J^1 = 15.9 Hz, J^2 = 7.1 Hz, 1H), 3.06 (dd, J^1 = 7.1 Hz, J^2 = 1.5 Hz, 2H), 2.25 (s, 3H), 1.39 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.0, 137.1, 134.3, 132.8, 129.2, 126.1, 121.4, 80.7, 39.7, 28.1, 21.1. The spectral data are in accordance with literature.[12]

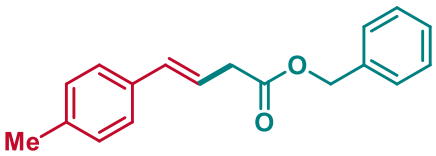


Pentyl (*E*)-4-(*p*-tolyl)but-3-enoate (3ac): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), pentyl 2-diazoacetate **2c** (117.1 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3ac** as a colorless liquid in 68% yield (50.2 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.27 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 6.47 (d, J = 15.8 Hz, 1H), 6.26 (dt, J^1 = 15.9 Hz, J^2 = 7.1 Hz, 1H), 4.12 (t, J = 6.8 Hz, 2H), 3.24 (dd, J^1 = 7.2 Hz, J^2 = 1.4 Hz, 2H), 2.34 (s, 3H), 1.69 – 1.62 (m, 2H), 1.37 – 1.33 (m, 4H), 0.93 – 0.90 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.7, 137.2, 134.1, 133.1, 129.2, 126.1, 120.8, 64.9, 38.4, 28.2, 28.0, 22.3, 21.1, 13.9; **HRMS** (EI) m/z = 246.1620 calcd. for $C_{16}H_{22}O_2$ $[M]^+$, found: 246.1621; **IR** (neat, cm^{-1}): 2929*w*, 1730*m*, 1513*w*, 1462*w*, 1256*w*, 1159*w*, 965*m*, 908*s*, 793*w*, 731*s*, 651*w*, 502*w*.

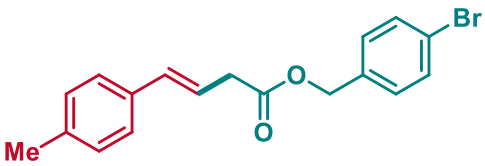


Cyclohexyl (*E*)-4-(*p*-tolyl)but-3-enoate (3ad): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), cyclohexyl 2-diazoacetate **2d** (126.1 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant

current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3ad** as a colorless liquid in 49% yield (37.6 mg); **TLC** $\mathbf{R_f}$ = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.19 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.17 (dt, J^1 = 15.9 Hz, J^2 = 7.1 Hz, 1H), 4.75 – 4.68 (m, 1H), 3.13 (dd, J^1 = 7.1 Hz, J^2 = 1.4 Hz, 2H), 2.25 (s, 3H), 1.80 – 1.77 (m, 2H), 1.68 – 1.63 (m, 2H), 1.35 – 1.18 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.1, 137.2, 134.2, 133.0, 129.2, 126.1, 121.0, 73.0, 38.8, 31.6, 25.3, 23.7, 21.1; **HRMS** (EI) *m*/*z* = 258.1620 calcd. for $C_{17}H_{22}O_2$ $[M]^+$, found: 258.1624; **IR** (neat, cm^{-1}): 2935*s*, 2861*m*, 1730*s*, 1513*w*, 1450*w*, 1262*w*, 1165*w*, 1039*w*, 1016*w*, 965*m*, 793*w*, 736*w*.

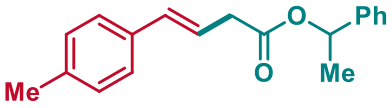


Benzyl (*E*)-4-(*p*-tolyl)but-3-enoate (3ae): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), benzyl 2-diazoacetate **2e** (132.1 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3ae** as a colorless liquid in 57% yield (44.6 mg); **TLC** $\mathbf{R_f}$ = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.39 – 7.35 (m, 5H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, J^1 = 15.8 Hz, J^2 = 7.1 Hz, 1H), 5.18 (s, 2H), 3.30 (dd, J^1 = 7.1 Hz, J^2 = 1.4 Hz, 2H), 2.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.5, 137.3, 135.8, 134.0, 133.4, 129.2, 128.5, 128.2, 128.2, 126.2, 120.4, 66.5, 38.3, 21.1. The spectral data are in accordance with literature.[8]

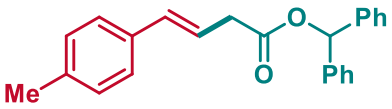


4-bromobenzyl (*E*)-4-(*p*-tolyl)but-3-enoate (3af): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), 4-bromobenzyl 2-diazoacetate **2f** (191.3 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3af** as a white solid in 74% yield (76.3 mg); **MP**: 66 – 70 °C; **TLC** $\mathbf{R_f}$ = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.39 (d, *J* = 8.2 Hz, 2H), 7.17 – 7.12 (m, 4H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.15 (dt, J^1 = 15.3 Hz, J^2 = 7.1 Hz, 1H), 5.00 (s, 2H), 3.18 (d, *J* = 7.1 Hz, 2H), 2.24 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.3, 137.4, 134.8, 133.9, 133.5, 131.7, 129.9, 129.2, 126.1,

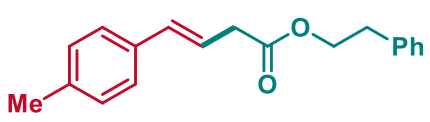
122.3, 120.2, 65.6, 38.5, 21.1; **HRMS** (EI) *m*/*z* = 344.0412 calcd. for $C_{18}H_{17}BrO_2$ $[M]^+$, found: 344.0413; **IR** (neat, cm^{-1}): 1736*s*, 1490*m*, 1376*w*, 1233*m*, 1147*s*, 1067*w*, 1010*m*, 965*m*, 908*m*, 828*m*, 799*m*, 731*m*, 502*w*.



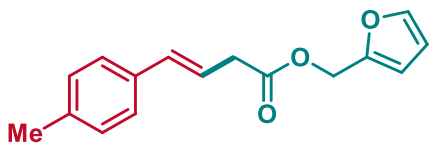
1-phenylethyl (*E*)-4-(*p*-tolyl)but-3-enoate (3ag): The title compound was prepared according to general procedure (**GP2-2**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), 1-phenylethyl 2-diazoacetate **2g** (142.7 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3ag** as a colorless liquid in 59% yield (49.4 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.31 – 7.26 (m, 5H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.18 (dt, J^1 = 15.8, J^2 = 7.0 Hz, 1H), 5.87 (q, *J* = 6.6 Hz, 1H), 3.19 (d, *J* = 7.0 Hz, 2H), 2.27 (s, 3H), 1.50 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.9, 141.5, 137.3, 134.1, 133.3, 129.2, 128.5, 127.8, 126.1, 126.0, 120.6, 72.6, 38.6, 22.2, 21.1; **HRMS** (EI) *m*/*z* = 280.1463 calcd. for $C_{19}H_{20}O_2$ $[M]^+$, found: 280.1467; **IR** (neat, cm^{-1}): 2981*w*, 1736*s*, 1541*w*, 1507*w*, 1456*w*, 1245*m*, 1159*w*, 1062*m*, 965*w*, 759*m*, 696*m*.



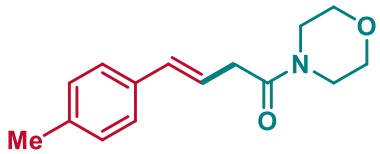
Benzhydryl (*E*)-4-(*p*-tolyl)but-3-enoate (3ah): The title compound was prepared according to general procedure (**GP2-2**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), benzhydryl 2-diazoacetate **2h** (189.2 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3ah** as a colorless liquid in 82% yield (84.4 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.43 – 7.39 (m, 10H), 7.35 – 7.31 (m, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.00 (s, 1H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.34 (dt, J^1 = 15.9, J^2 = 7.0 Hz, 1H), 3.40 (dd, J^1 = 7.1, J^2 = 1.4 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.5, 140.0, 137.3, 134.0, 133.5, 129.2, 128.4, 127.9, 127.0, 126.1, 120.3, 76.8, 38.5, 21.1; **HRMS** (EI) *m*/*z* = 342.1620 calcd. for $C_{24}H_{22}O_2$ $[M]^+$, found: 342.1622; **IR** (neat, cm^{-1}): 1736*s*, 1496*w*, 1450*w*, 1233*m*, 1182*w*, 1147*m*, 1022*w*, 965*m*, 908*m*, 793*w*, 759*w*, 736*m*, 696*s*, 645*w*, 599*w*, 548*w*, 502*w*.



Phenethyl (*E*)-4-(*p*-tolyl)but-3-enoate (3ai): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), phenethyl 2-diazoacetate **2i** (142.7 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3ai** as a white solid in 67% yield (52.9 mg); MP: 49 – 50 °C; **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.36 – 7.27 (m, 7H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.26 (dt, J^1 = 15.8, J^2 = 7.1 Hz, 1H), 4.38 (t, *J* = 7.0 Hz, 2H), 3.26 (dd, J^1 = 7.2, J^2 = 1.4 Hz, 2H), 3.00 (t, *J* = 6.9 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.5, 137.7, 137.3, 134.0, 133.2, 129.2, 128.9, 128.4, 126.5, 126.1, 120.6, 65.1, 38.4, 35.0, 21.1; **HRMS** (EI) *m*/*z* = 280.1463 calcd. for $C_{19}H_{20}O_2$ $[M]^+$, found: 280.1464; **IR** (neat, cm^{-1}): 2924*w*, 1736*s*, 1513*w*, 1456*w*, 1239*s*, 1153*m*, 793*w*, 748*m*, 702*m*, 502*w*.

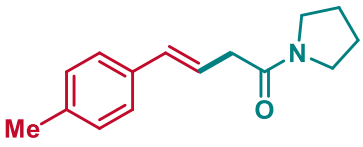


Furan-2-ylmethyl (*E*)-4-(*p*-tolyl)but-3-enoate (3aj): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), furan-2-ylmethyl 2-diazoacetate **2j** (124.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3aj** as a colorless liquid in 51% yield (38.9 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.43 (d, *J* = 1.8 Hz, 1H), 7.25 (d, *J* = 5.7 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.46 – 6.36 (m, 3H), 6.23 (dt, J^1 = 15.8, J^2 = 7.0 Hz, 1H), 5.10 (s, 2H), 3.26 (dd, J^1 = 7.1, J^2 = 1.4 Hz, 2H), 2.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.3, 149.3, 143.3, 137.4, 134.0, 133.5, 129.2, 126.2, 120.3, 110.8, 110.6, 58.3, 38.2, 21.2; **HRMS** (EI) *m*/*z* = 256.1099 calcd. for $C_{16}H_{16}O_3$ $[M]^+$, found: 256.1102; **IR** (neat, cm^{-1}): 2924*w*, 1736*w*, 1513*s*, 1245*m*, 1153*m*, 965*m*, 748*m*, 599*s*, 502*s*.

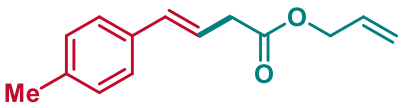


(*E*)-1-morpholino-4-(*p*-tolyl)but-3-en-1-one (3ak): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), 2-diazo-1-morpholinoethan-1-one **2k** (116.4 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1

(4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 2:1) gave the desired product **3ak** as a white solid in 82% yield (60.4 mg); **MP**: 72 – 75 °C; **TLC R_f** = 0.3 (PE:EtOAc = 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.18 (d, *J* = 7.7 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.18 (dt, J^1 = 15.9 Hz, J^2 = 6.7 Hz, 1H), 3.59 – 3.57 (m, 6H), 3.46 – 3.39 (m, 2H), 3.21 (dd, J^1 = 6.7, J^2 = 1.6 Hz, 2H), 2.25 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 169.6, 137.3, 133.9, 132.7, 129.2, 126.0, 121.5, 66.8, 66.6, 46.2, 42.0, 37.7, 21.1; **HRMS** (EI) *m*/*z* = 245.1416 calcd. for $C_{15}H_{19}NO_2$ $[M]^+$, found: 245.1418; **IR** (neat, cm^{-1}): 2855*w*, 1650*s*, 1639*w*, 1541*w*, 1507*m*, 1456*m*, 1433*w*, 1273*w*, 1227*s*, 1113*w*, 1033*w*, 965*w*, 748*w*.

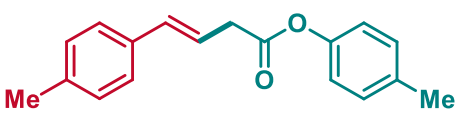


(*E*)-1-(pyrrolidin-1-yl)-4-(*p*-tolyl)but-3-en-1-one (3al): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), 2-diazo-1-(pyrrolidin-1-yl)ethan-1-one **2l** (104.4 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 2:1) gave the desired product **3al** as a white solid in 85% yield (58.6 mg); MP: 89 – 91 °C **TLC R_f** = 0.3 (PE:EtOAc = 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.19 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 7.7 Hz, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.23 (dt, J^1 = 15.9 Hz, J^2 = 6.7 Hz, 1H), 3.42 – 3.38 (m, 4H), 3.15 (d, *J* = 6.7 Hz, 2H), 2.24 (s, 3H), 1.88 – 1.83 (m, 2H), 1.80 – 1.75 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 169.4, 137.0, 134.2, 132.4, 129.1, 126.0, 121.9, 46.6, 45.7, 39.4, 26.0, 24.3, 21.1; **HRMS** (EI) *m*/*z* = 229.1467 calcd. for $C_{15}H_{19}NO$ $[M]^+$, found: 229.1468; **IR** (neat, cm^{-1}): 2969*w*, 2872*w*, 1650*s*, 1633*s*, 1541*w*, 1513*w*, 1439*s*, 1342*w*, 1187*w*, 970*w*, 810*w*, 771*w*, 502*w*.

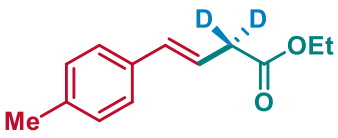


Allyl (*E*)-4-(*p*-tolyl)but-3-enoate (3am): The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), allyl 2-diazoacetate **2m** (94.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3am** as a colorless liquid in 38% yield (24.7 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.19 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.18 (dt, J^1 = 15.8 Hz, J^2 = 7.1 Hz, 1H), 5.86 (ddt, J^1 = 16.4 Hz, J^2 = 10.9 Hz, J^3 = 5.8 Hz, 1H), 5.26 (dd, J^1 = 17.2 Hz, J^2 = 1.6 Hz,

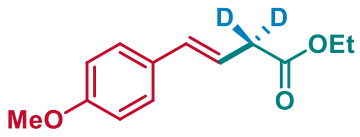
1H), 5.17 (dd, J^1 = 10.4 Hz, J^2 = 1.5 Hz, 1H), 4.54 (d, J = 5.8 Hz, 2H), 3.19 (dd, J^1 = 7.2 Hz, J^2 = 1.4 Hz, 2H), 2.26 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.3, 137.4, 134.0, 133.4, 132.0, 129.2, 126.2, 120.5, 118.4, 65.4, 38.4, 21.2; **HRMS** (EI) *m*/*z* = 216.1150 calcd. for $C_{14}H_{16}O_2$ $[M]^+$, found: 216.1153; **IR** (neat, cm^{-1}): 2924*w*, 1736*s*, 1262*w*, 1153*m*, 970*w*, 908*m*, 731*s*, 502*w*.



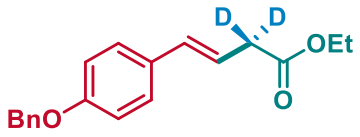
***P*-tolyl (*E*)-4-(*p*-tolyl)but-3-enoate (3an):** The title compound was prepared according to general procedure (**GP2-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), *p*-tolyl 2-diazoacetate **2n** (132.1 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:H_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3an** as a white solid in 48% yield (38.7 mg); **MP**: 73 – 75 °C; **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.30 (d, J = 7.9 Hz, 2H), 7.18 – 7.13 (m, 4H), 6.98 (d, J = 8.3 Hz, 2H), 6.57 (d, J = 15.9 Hz, 1H), 6.34 (dt, J^1 = 15.8 Hz, J^2 = 7.1 Hz, 1H), 3.47 (dd, J^1 = 7.1 Hz, J^2 = 1.4 Hz, 2H), 2.34 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.3, 148.4, 137.5, 135.5, 134.0, 133.8, 129.9, 129.3, 126.2, 121.2, 120.0, 38.4, 21.2, 20.8; **HRMS** (EI) *m*/*z* = 266.1307 calcd. for $C_{18}H_{18}O_2$ $[M]^+$, found: 266.1309; **IR** (neat, cm^{-1}): 2918*w*, 1758*s*, 1507*m*, 1199*s*, 1130*s*, 965*w*, 496*w*.



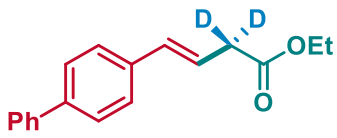
Ethyl (*E*)-4-(*p*-tolyl)but-3-enoate-2,2-D_2 (3a'): The title compound was prepared according to general procedure (**GP3-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:D_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3a'** as a colorless liquid in 73% yield (44.3 mg, 94% D-inc.); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.31 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 7.7 Hz, 2H), 6.50 (d, J^1 = 16.3 Hz, 1H), 6.28 (d, J = 15.6 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H); The characteristic peak of **3a** (3.25 (d, J = 7.1 Hz, 0.12H)) was observed; **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.6, 137.2, 134.0, 133.2, 129.1, 126.1, 120.6, 60.6, 38.3 – 37.7 (m, 1C), 21.1, 14.1; **HRMS** (EI) *m*/*z* = 206.1276 calcd. for $C_{13}H_{14}D_2O_2$ $[M]^+$, found: 206.1278; **IR** (neat, cm^{-1}): 2981*w*, 1730*s*, 1513*w*, 1444*w*, 1364*w*, 1273*m*, 1245*s*, 1136*m*, 1050*m*, 1022*m*, 970*m*, 816*m*, 771*w*, 742*w*, 502*w*.



Ethyl (*E*)-4-(4-methoxyphenyl)but-3-enoate-2,2-D$_2$ (3c'): The title compound was prepared according to general procedure (**GP3-1**) with (*E*)-3-(4-methoxyphenyl)acrylic acid **1c** (53.5 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:D_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3c'** as a colorless liquid in 78% yield (53.9 mg, 95% D-inc.); **TLC R$_f$** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.30 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 7.0 Hz, 2H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.15 (d, *J* = 15.9 Hz, 1H), 4.17 (q, *J* = 6.5 Hz, 2H), 3.79 (s, 3H), 1.28 (t, *J* = 6.7 Hz, 3H); The characteristic peak of **3c** (3.19 (d, *J* = 7.0 Hz, 0.10H).) was observed; **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.8, 159.0, 132.7, 129.6, 127.4, 119.4, 113.8, 60.6, 55.2, 38.3 – 37.7 (m, 1C), 14.1; **HRMS** (EI) *m*/*z* = 222.1225 calcd. for $C_{13}H_{14}D_2O_3$ $[M]^+$, found: 222.1224; **IR** (neat, cm^{-1}): 2981*w*, 1730*s*, 1604*m*, 1507*s*, 1462*w*, 1245*s*, 1176*m*, 1136*m*, 1028*m*, 970*m*, 908*s*, 828*m*, 731*s*, 651*w*, 519*w*.

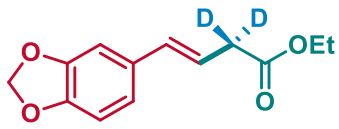


Ethyl (*E*)-4-(4-(benzyloxy)phenyl)but-3-enoate-2,2-D$_2$ (3d'): The title compound was prepared according to general procedure (**GP3-1**) with (*E*)-3-(4-(benzyloxy)phenyl) acrylic acid **1d** (76.3 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:D_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 30:1) gave the desired product **3d'** as a white solid in 68% yield (61.3 mg, 95% D-inc.); **MP**: 68 – 70 °C; **TLC R$_f$** = 0.3 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.47 – 7.37 (m, 4H), 7.37 – 7.28 (m, 3H), 6.94 (d, *J* = 7.4 Hz, 2H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.17 (d, *J* = 15.8 Hz, 1H), 5.07 (s, 2H), 4.19 (q, *J* = 7.0 Hz, 2H), 1.30 (t, *J* = 7.0 Hz, 3H); The characteristic peak of **3d** (3.21 (d, *J* = 7.1 Hz, 0.11H)) was observed; **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.7, 158.2, 136.8, 132.7, 129.8, 128.5, 127.9, 127.4, 119.5, 114.8, 69.9, 60.6, 38.3 – 37.6 (m, 1C), 14.1; **HRMS** (EI) *m*/*z* = 298.1538 calcd. for $C_{19}H_{18}D_2O_3$ $[M]^+$, found: 298.1541; **IR** (neat, cm^{-1}): 1730*w*, 1607*w*, 1245*m*, 1022*w*, 902*s*, 828*w*, 725*s*, 696*m*, 645*w*, 519*w*.

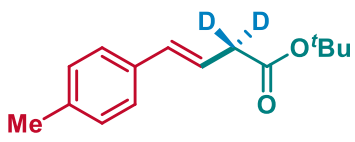


Ethyl (*E*)-4-([1,1'-biphenyl]-4-yl)but-3-enoate-2,2-D$_2$ (3e'): The title compound was prepared according to general procedure (**GP3-1**) with (*E*)-3-([1,1'-biphenyl]-4-yl)acrylic acid **1e** (79.9 mg, 0.300 mmol, 1.0 equiv), ethyl

2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:D_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3e'** as a white solid in 65% yield (51.6 mg, 99% D-inc.); **MP**: 92 – 94 °C; **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.61 – 7.55(m, 4H), 7.47 – 7.43 (m, 4H), 7.35 (t, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); The characteristic peak of **3e** (3.26 (d, *J* = 5.6 Hz, 0.03H)) was observed;**^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.6, 140.6, 140.2, 135.9, 132.9, 128.7, 127.3, 127.2, 126.9, 126.7, 121.8, 60.8, 38.0 – 37.6 (m, 1C), 14.2; **HRMS** (EI) *m/z* = 268.1432 calcd. for $C_{18}H_{16}D_2O_2$ $[M]^+$, found: 268.1434; **IR** (neat, cm^{-1}): 2986*w*, 1730*s*, 1490*w*, 1273*m*, 1256*m*, 1142*m*, 1056*w*, 976*m*, 748*s*, 686*w*.

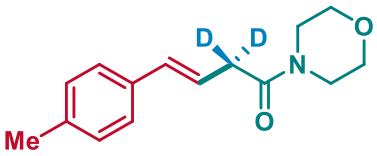


Ethyl (*E*)-4-(benzo[*d*][1,3]dioxol-5-yl)but-3-enoate-2,2-D_2 (3s'): The title compound was prepared according to general procedure (**GP3-1**) with (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)acrylic acid **1s** (57.7 mg, 0.300 mmol, 1.0 equiv), ethyl 2-diazoacetate **2a** (85.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:D_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3s'** as a colorless liquid in 72% yield (50.7 mg, 95% D-inc.); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 6.92 (s, 1H), 6.82 – 6.69 (m, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.11 (d, *J* = 15.8 Hz, 1H), 5.93 (s, 2H), 4.16 (q, *J* = 6.4 Hz, 2H), 1.27 (t, *J* = 6.5 Hz, 3H); The characteristic peak of **3s'** (3.18 (d, *J* = 7.1 Hz, 1H)) was observed; **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.7, 147.9, 147.6, 132.9, 131.3, 120.8, 119.9, 108.1, 105.5, 101.0, 60.7, 38.2 – 37.5 (m, 1C), 14.1; **HRMS** (EI) *m/z* = 236.1018 calcd. for $C_{13}H_{12}D_2O_4$ $[M]^+$, found: 236.1019; **IR** (neat, cm^{-1}): 2298*w*, 1730*s*, 1491*m*, 1449*m*, 1365*w*, 1296*s*, 1193*w*, 1136*w*, 1033*s*, 965*m*, 931*m*.

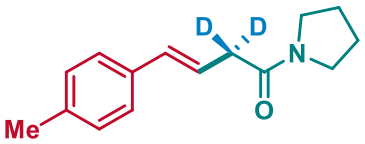


***T*ert-butyl (*E*)-4-(*p*-tolyl)but-3-enoate-2,2-D_2 (3ab'):** The title compound was prepared according to general procedure (**GP3-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), *tert*-butyl 2-diazoacetate **2b** (106.6 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:D_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3ab'** as a colorless liquid in 69% yield (48.3 mg, 94% D-inc.); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$,

300 K): δ (ppm) = 7.18 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.35 (d, *J* = 15.8 Hz, 1H), 6.14 (d, *J* = 15.9 Hz, 1H), 2.25 (s, 3H), 1.39 (s, 9H); The characteristic peak of **3ab** (3.04 (d, *J* = 7.0 Hz, 0.12H)) was observed; **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.1, 137.1, 134.2, 132.8, 129.1, 126.1, 121.3, 80.7, 39.5 – 38.9 (m, 1C); 28.0, 21.1; **HRMS** (EI) *m*/*z* = 234.1589 calcd. for $C_{15}H_{18}D_2O_2$ $[M]^+$, found: 234.1590; **IR** (neat, cm^{-1}): 2981*w*, 1730*s*, 1514*w*, 1456*w*, 1370*m*, 1279*m*, 1256*s*, 1165*s*, 1136*m*, 971*m*, 502*m*.



(*E*)-1-morpholino-4-(p-tolyl)but-3-en-1-one-2,2-D_2 (3ak'): The title compound was prepared according to general procedure (**GP3-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), 2-diazo-1-morpholinoethan-1-one **2k** (116.4 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:D_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 2:1) gave the desired product **3ak'** as a white solid in 84% yield (62.1 mg, 93% D-inc.); **MP**: 78 – 80 °C; **TLC R_f** = 0.3 (PE:EtOAc = 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.18 (d, *J* = 7.5 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.17 (d, *J* = 15.9 Hz, 1H), 3.62 – 3.55 (m, 6H), 3.44 – 3.42 (m, 2H), 2.25 (s, 3H); The characteristic peak of **3ak** (3.20 (d, *J* = 6.1 Hz, 0.15H)) was observed; **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 169.7, 137.3, 134.0, 132.8, 129.2, 126.1, 121.4, 66.8, 66.6, 46.2, 42.0, 37.5 – 37.2 (m, 1C), 21.1; **HRMS** (EI) *m*/*z* = 247.1541 calcd. for $C_{15}H_{17}D_2NO_2$ $[M]^+$, found: 247.1543; **IR** (neat, cm^{-1}): 2855*w*, 1633*s*, 1513*w*, 1433*m*, 1273*m*, 1250*m*, 1113*s*, 1022*w*, 970*w*, 916*w*, 571*w*, 502*w*.

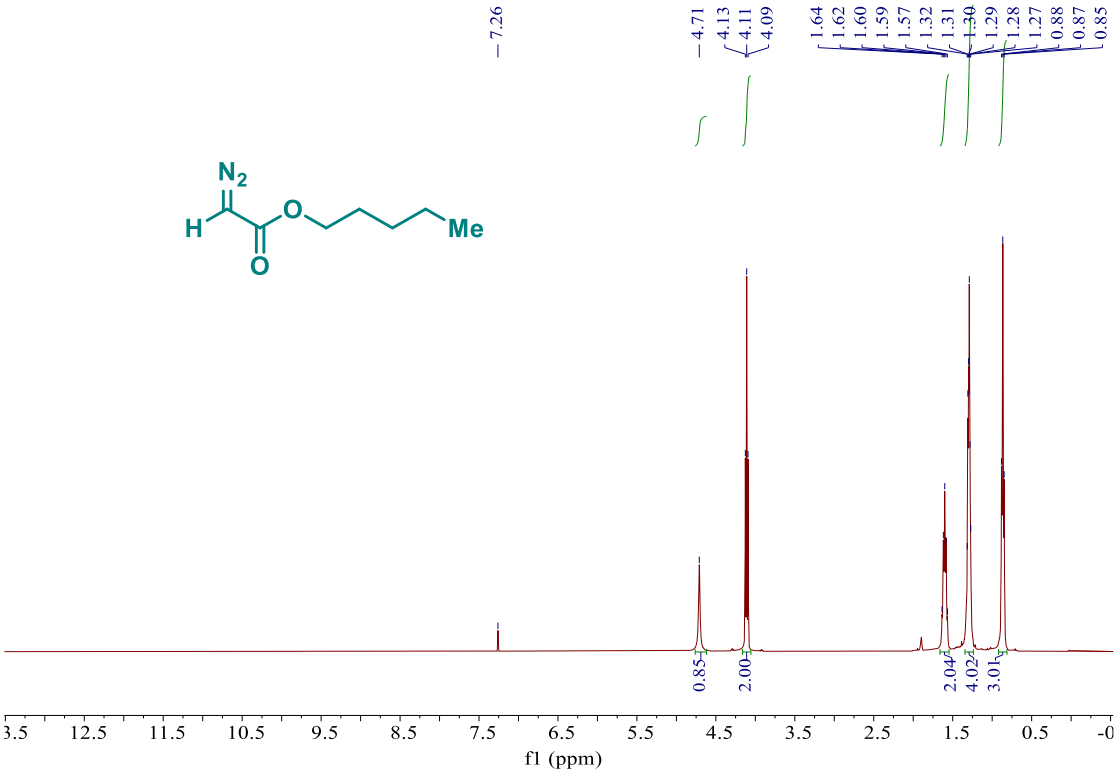


(*E*)-1-(pyrrolidin-1-yl)-4-(*p*-tolyl)but-3-en-1-one-2,2-D_2 (3al'): The title compound was prepared according to general procedure (**GP3-1**) with (*E*)-3-(*p*-tolyl)acrylic acid **1a** (48.7 mg, 0.300 mmol, 1.0 equiv), 2-diazo-1-(pyrrolidin-1-yl)ethan-1-one **2l** (104.4 mg, 0.750 mmol, 2.5 equiv), DIPEA (46.5 mg, 0.360 mmol, 1.2 equiv), and $LiClO_4$ (31.9 mg, 0.300 mmol, 1.0 equiv) in MeCN:D_2O = 3:1 (4 mL) under constant current of 5 mA at 50 °C for 4 h. Purification via silica gel chromatography (PE:EtOAc = 2:1) gave the desired product **3al'** as a white solid in 85% yield (59.1 mg, 95% D-inc.); MP: 96 – 98 °C; **TLC R_f** = 0.3 (PE:EtOAc = 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.27 (d, *J* = 7.5Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 3.51 – 3.47 (m, 4H), 2.33 (s, 3H), 1.98 – 1.93 (m, 2H), 1.88 – 1.84 (m, 2H); The characteristic peak of **3al** (3.22 (d, *J* = 6.8 Hz, 0.11H)) was observed; **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) =

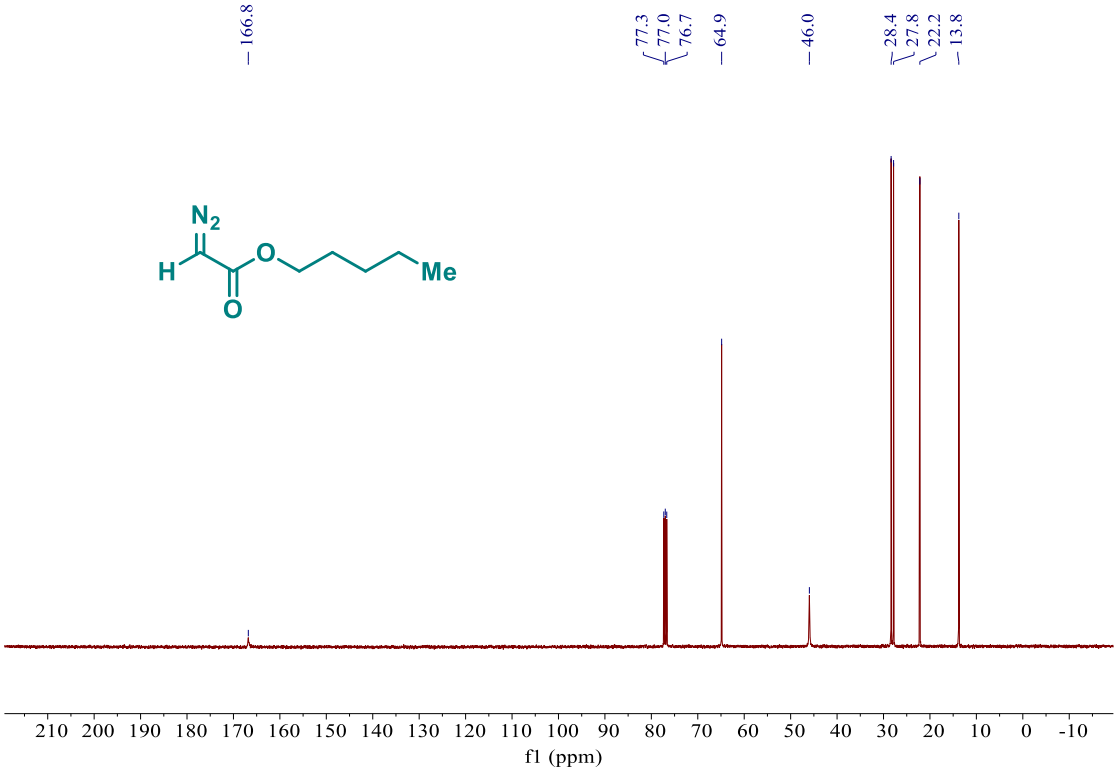
169.5, 137.1, 134.2, 132.6, 129.2, 126.1, 121.9, 46.6, 45.8, 38.7 – 38.1, (m, 1C), 26.1, 24.3, 21.1; **HRMS** (EI) *m*/*z* = 231.1592 calcd. for $C_{15}H_{17}D_2NO$ $[M]^+$, found: 231.1594; **IR** (neat, cm^{-1}): 2969*w*, 2872*w*, 1633*s*, 1633*s*, 1427*s*, 1342*w*, 1193*w*, 970*w*, 816*w*, 736*w*, 508*w*.

7. Spectra

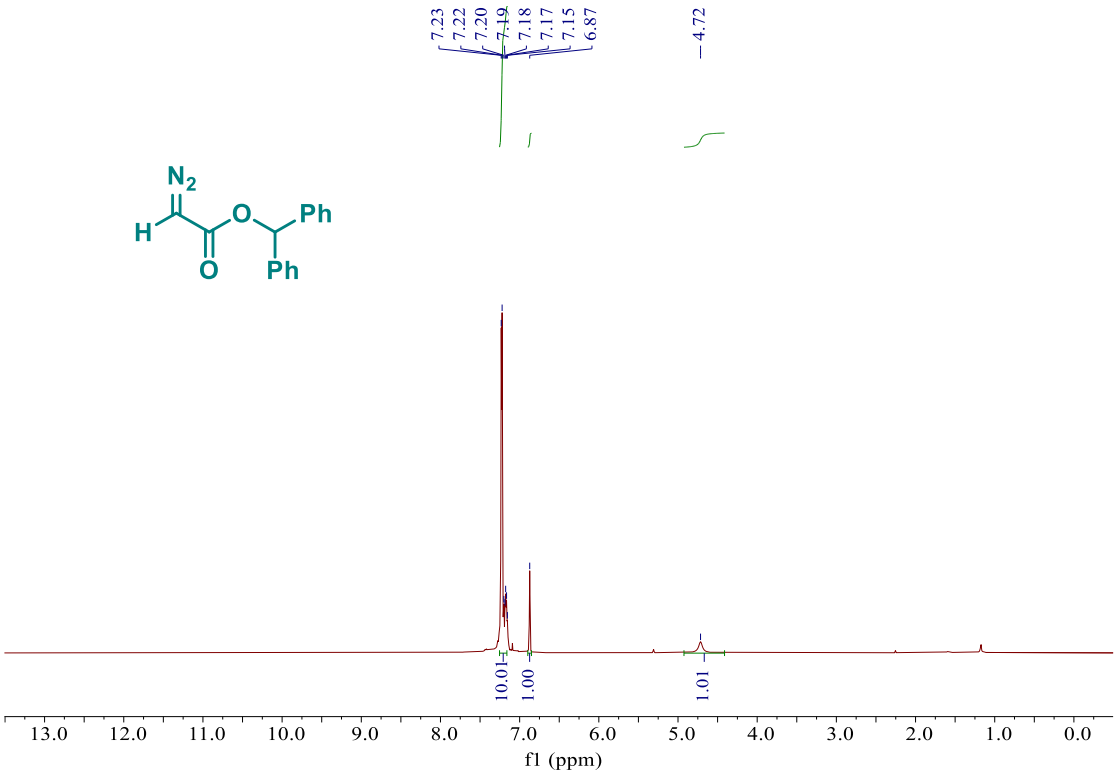
^{1}H NMR Spectrum of pentyl 2-diazoacetate 2c



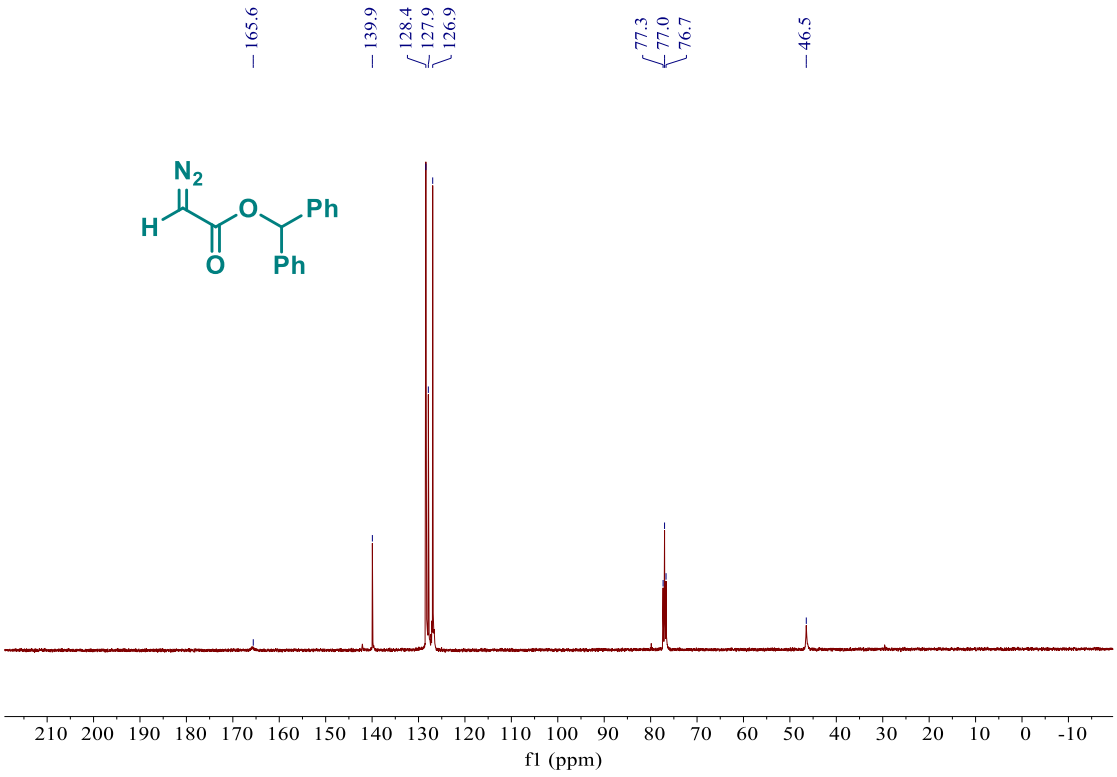
^{13}C NMR Spectrum of pentyl 2-diazoacetate 2c



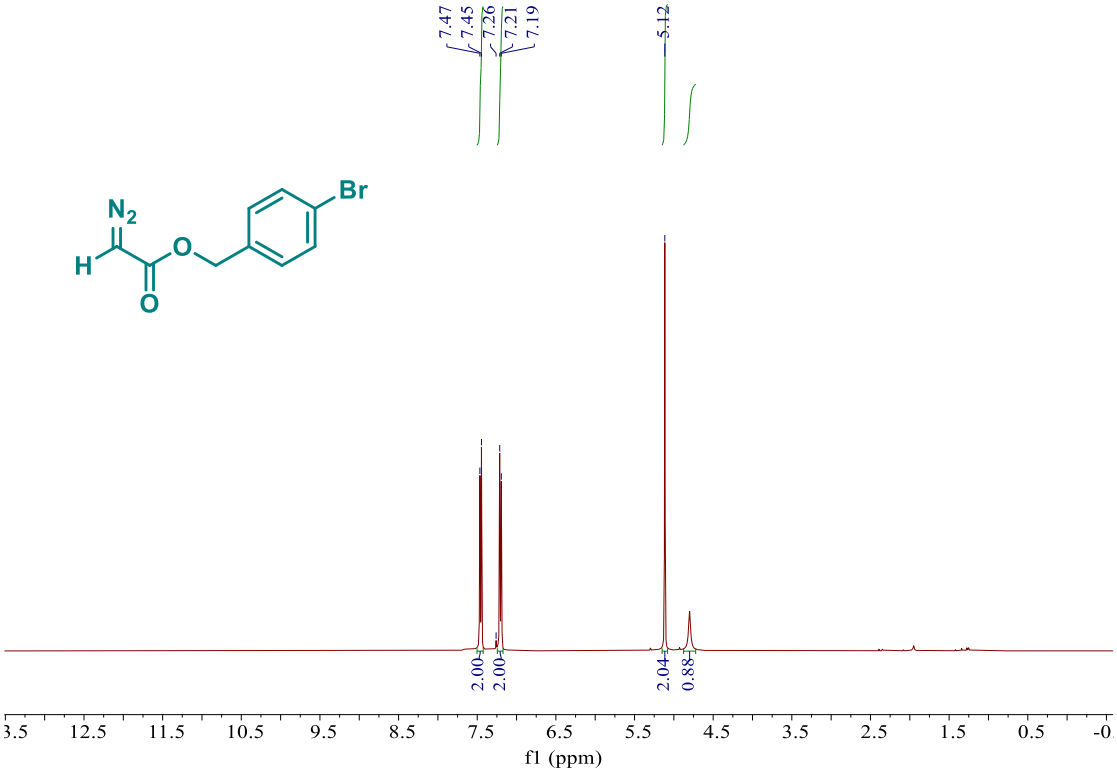
^{1}H NMR Spectrum of benzhydryl 2-diazoacetate 2h



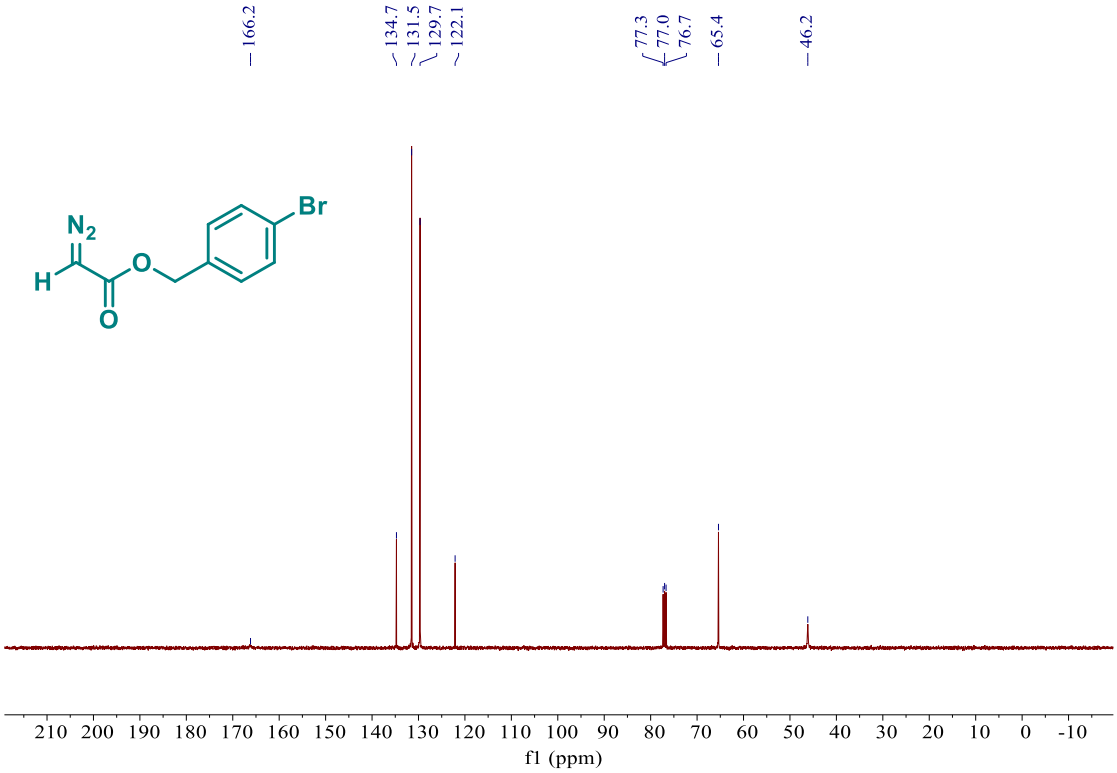
^{13}C NMR Spectrum of benzhydryl 2-diazoacetate 2h



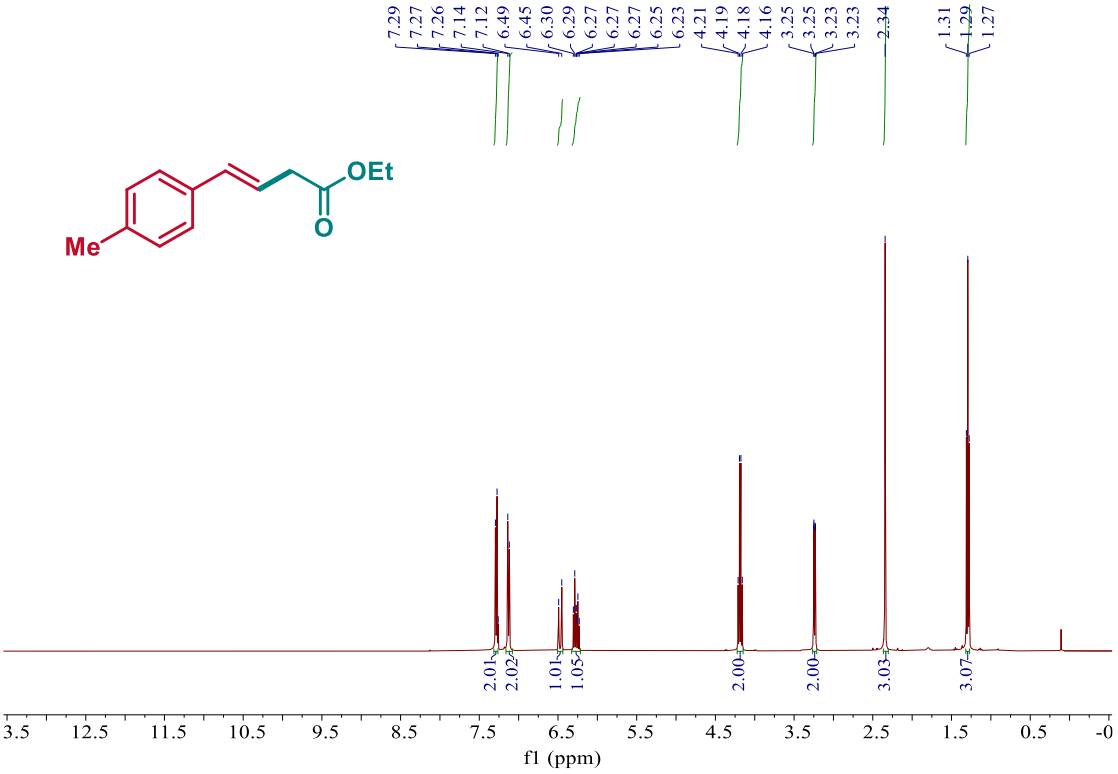
^{1}H NMR Spectrum of 4-bromobenzyl 2-diazoacetate 2f



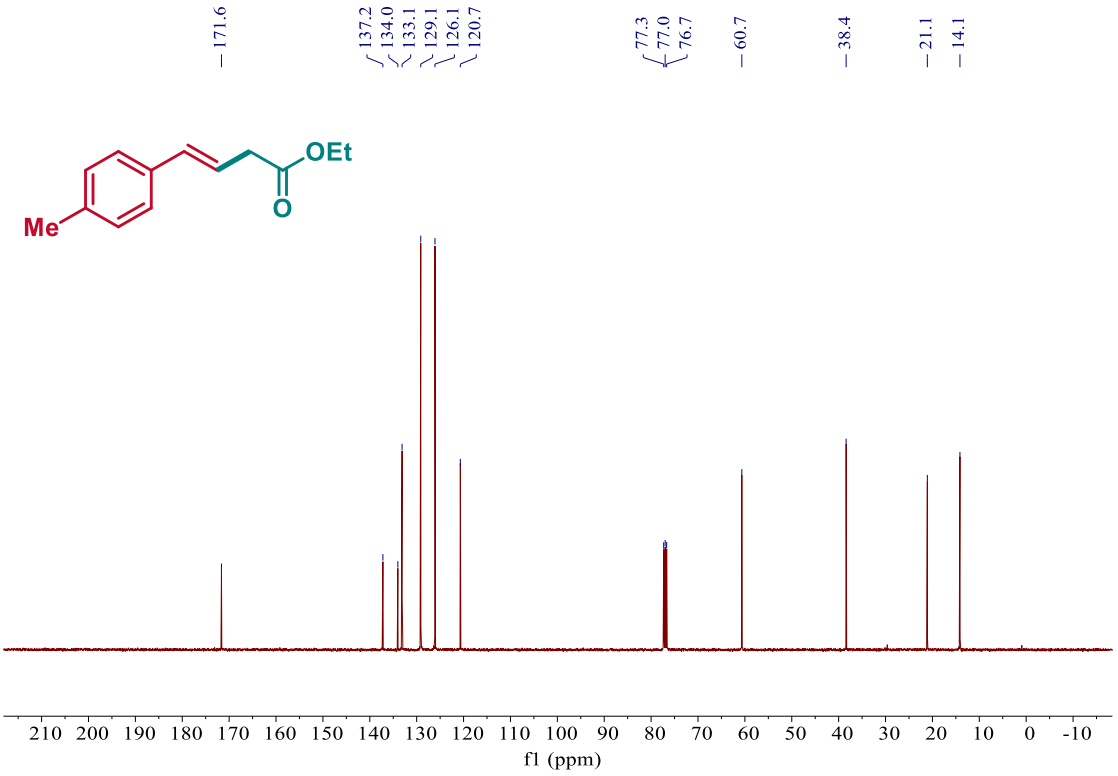
^{13}C NMR Spectrum of 4-bromobenzyl 2-diazoacetate 2f



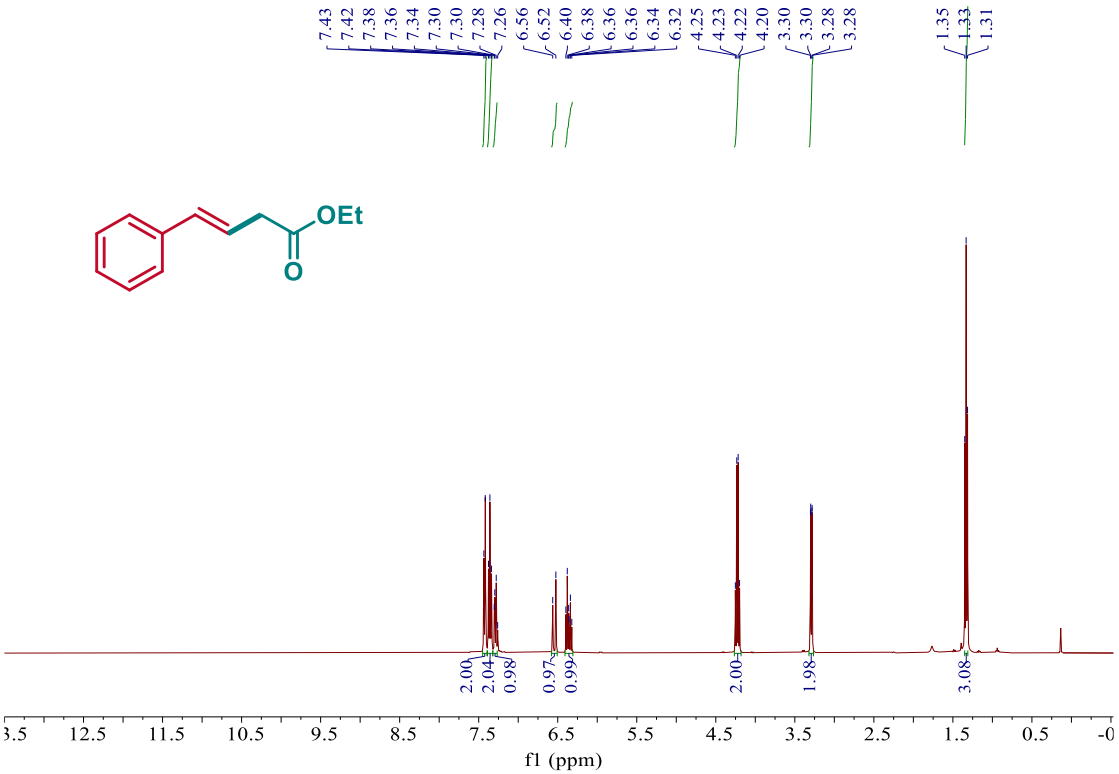
^{1}H NMR Spectrum of ethyl (*E*)-4-(*p*-tolyl)but-3-enoate 3a



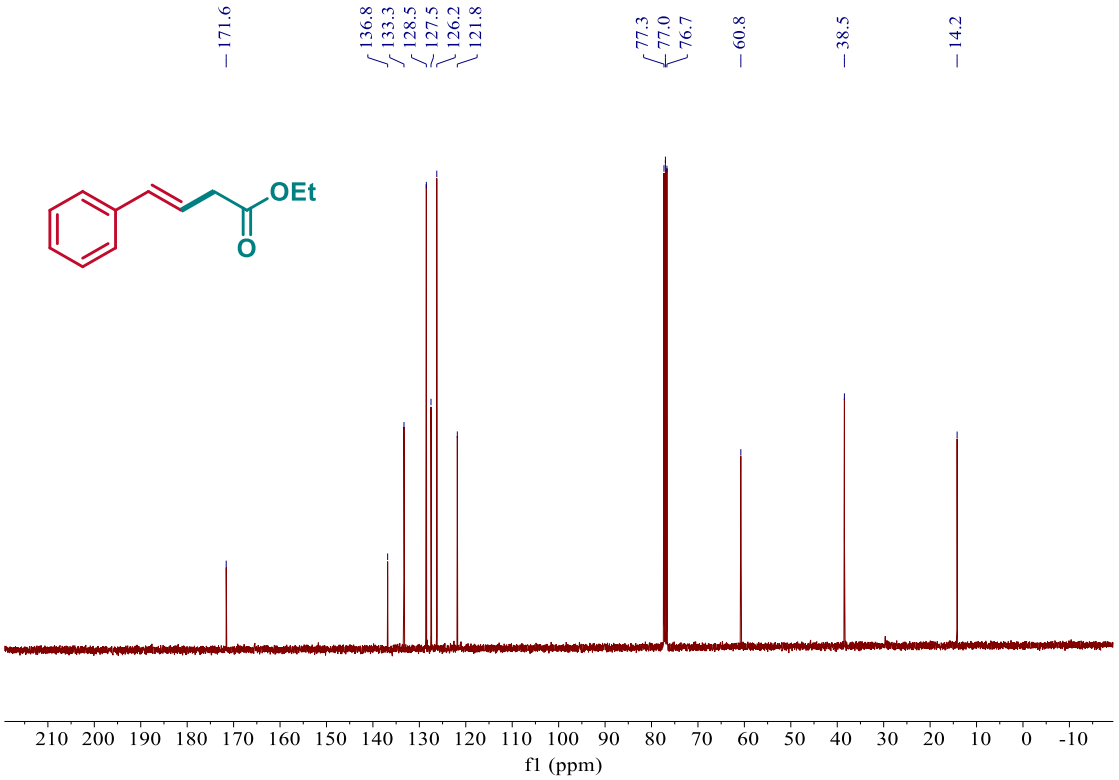
^{13}C NMR Spectrum of ethyl (*E*)-4-(*p*-tolyl)but-3-enoate 3a



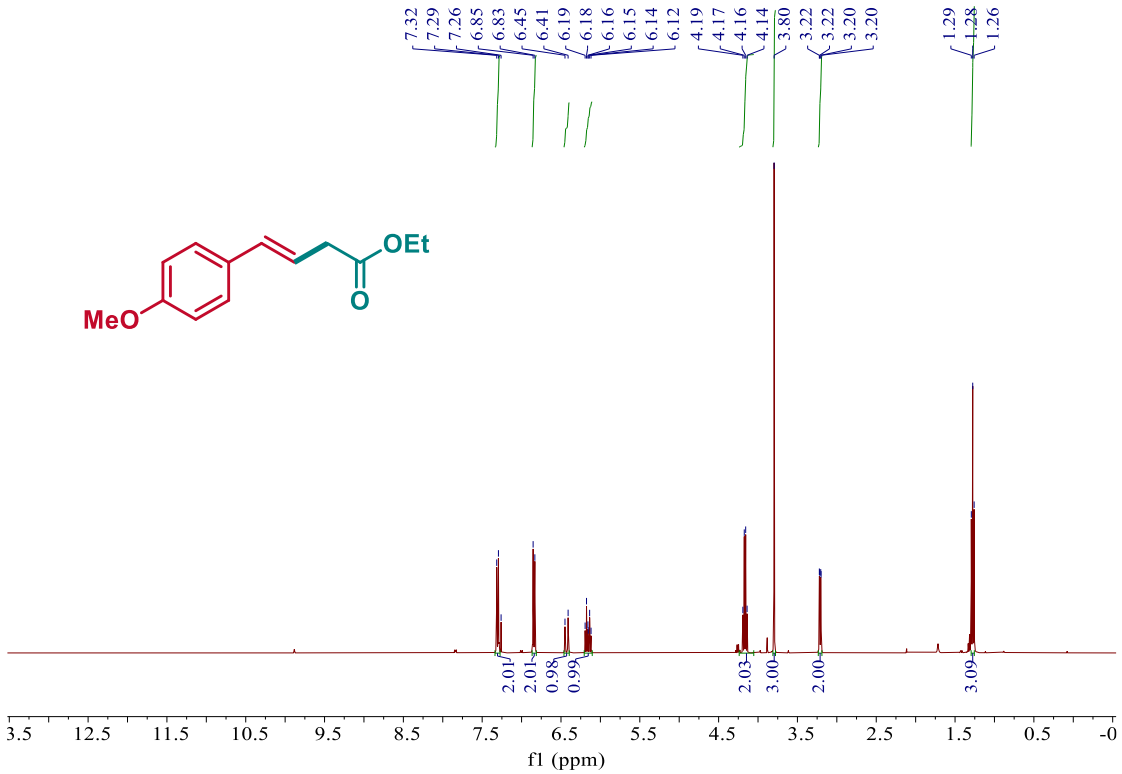
^{1}H NMR Spectrum of ethyl (*E*)-4-phenylbut-3-enoate 3b



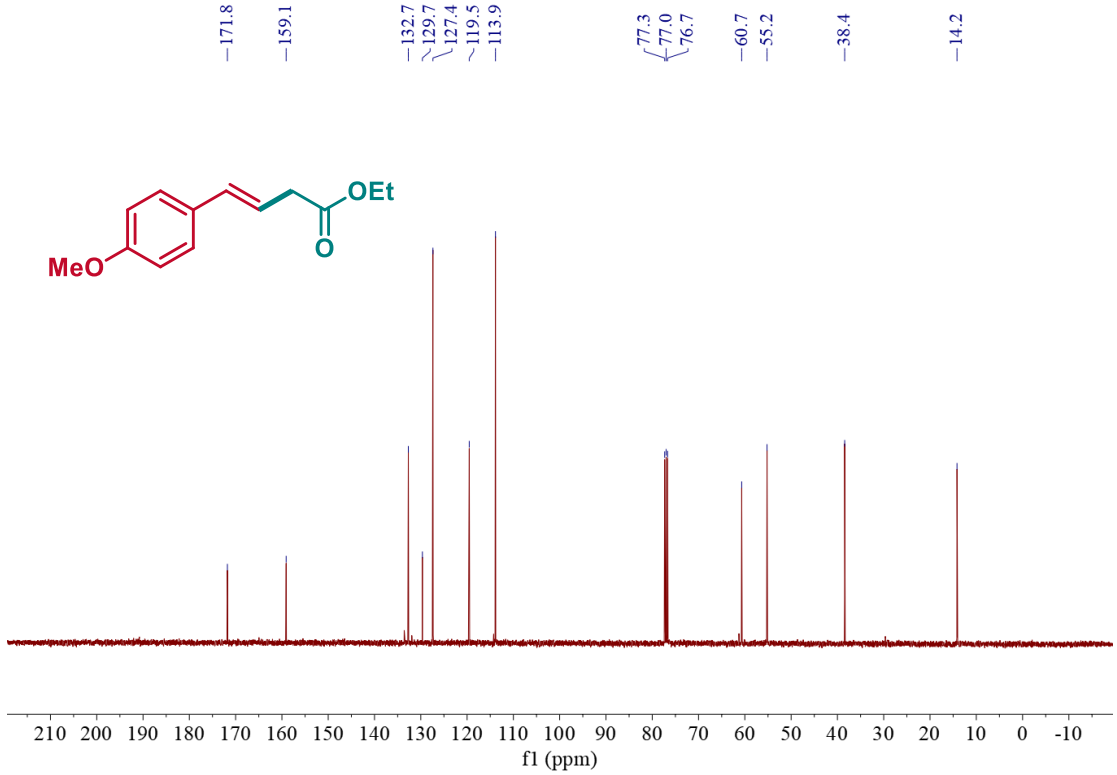
^{13}C NMR Spectrum of ethyl (*E*)-4-phenylbut-3-enoate 3b



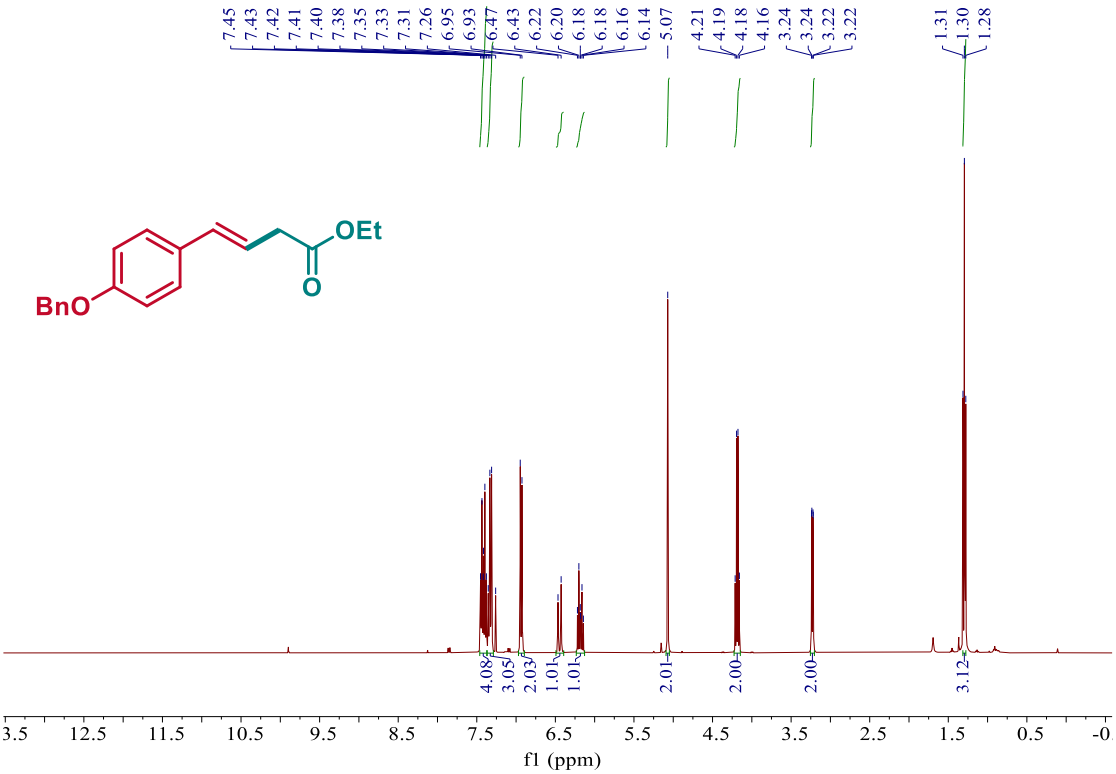
^{1}H NMR Spectrum of ethyl (*E*)-4-(4-methoxyphenyl)but-3-enoate 3c



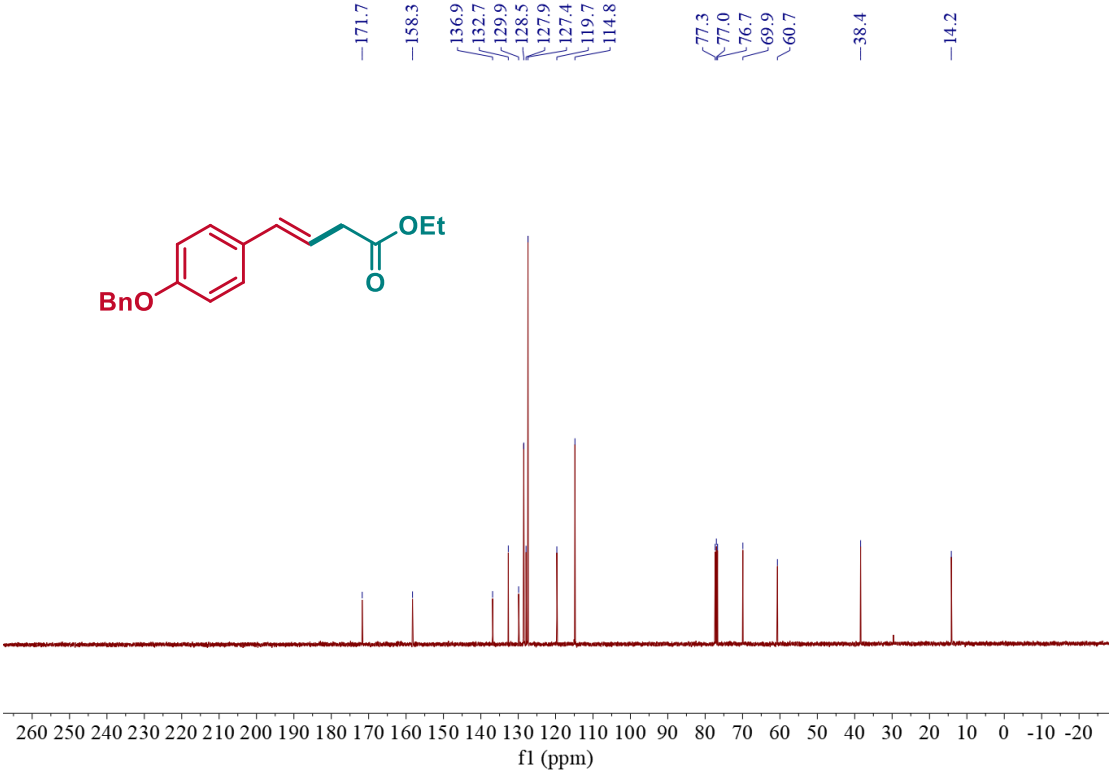
^{13}C NMR Spectrum of ethyl (*E*)-4-(4-methoxyphenyl)but-3-enoate 3c



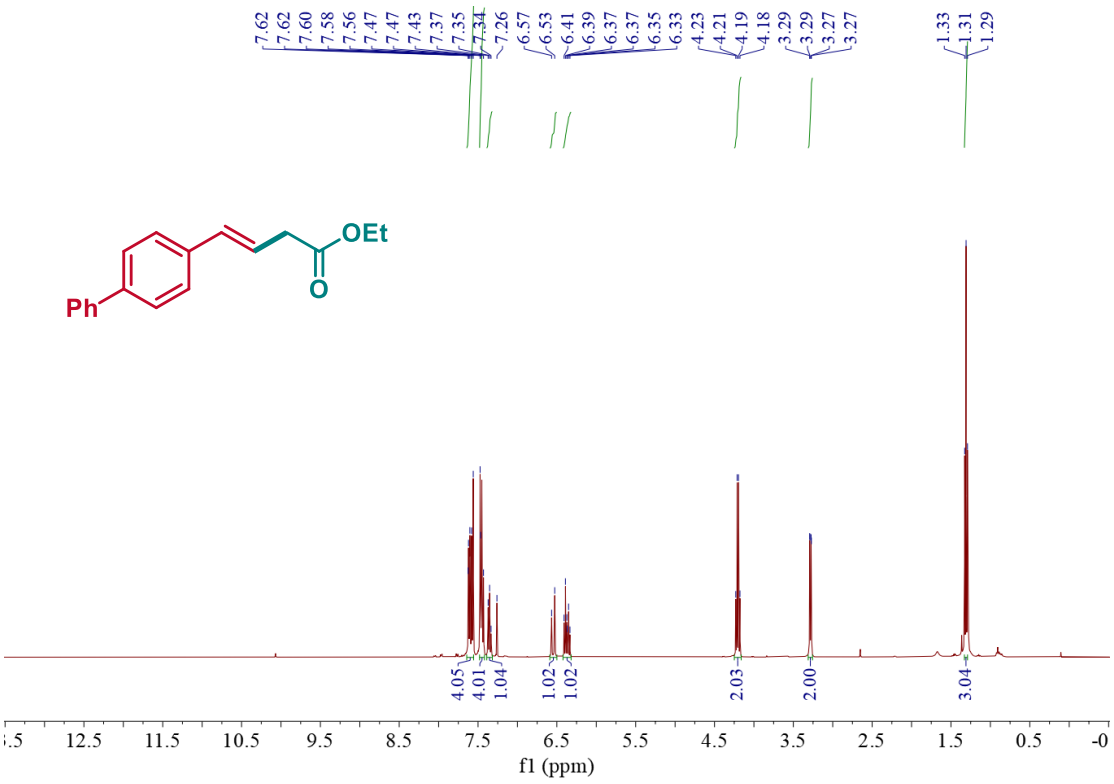
^{1}H NMR Spectrum of ethyl (*E*)-4-(4-(benzyloxy)phenyl)but-3-enoate 3d



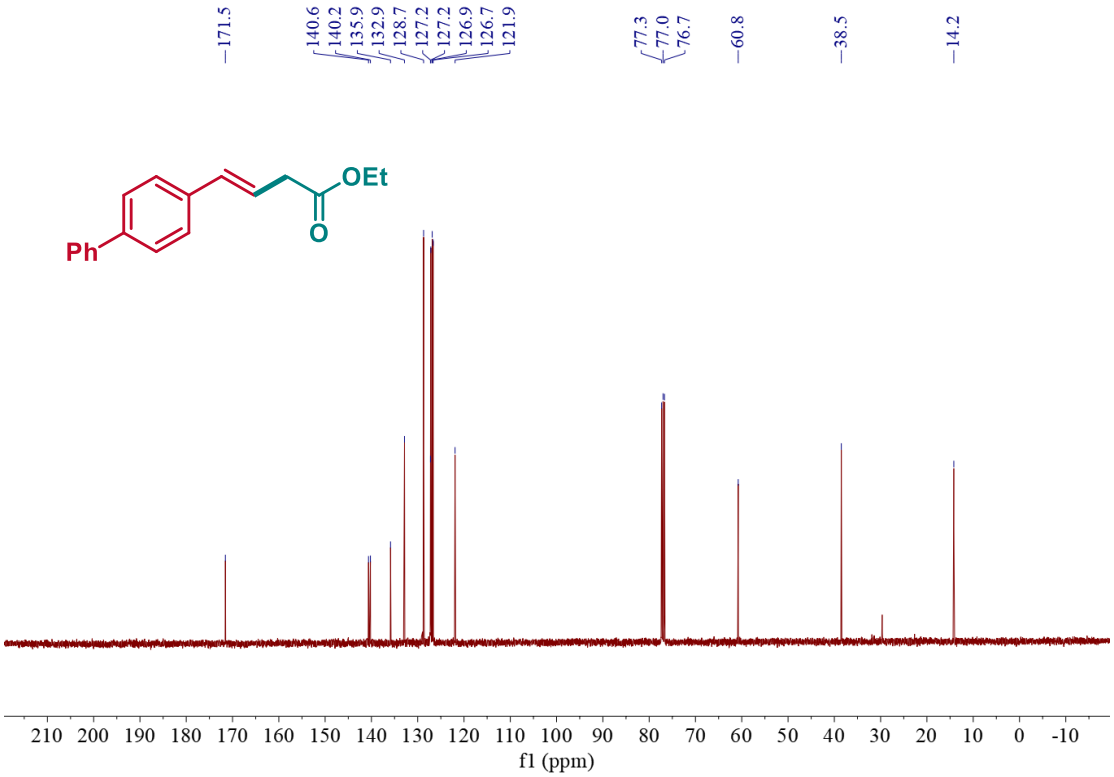
^{13}C NMR Spectrum of ethyl (*E*)-4-(4- (benzyloxy)phenyl)but-3-enoate 3d



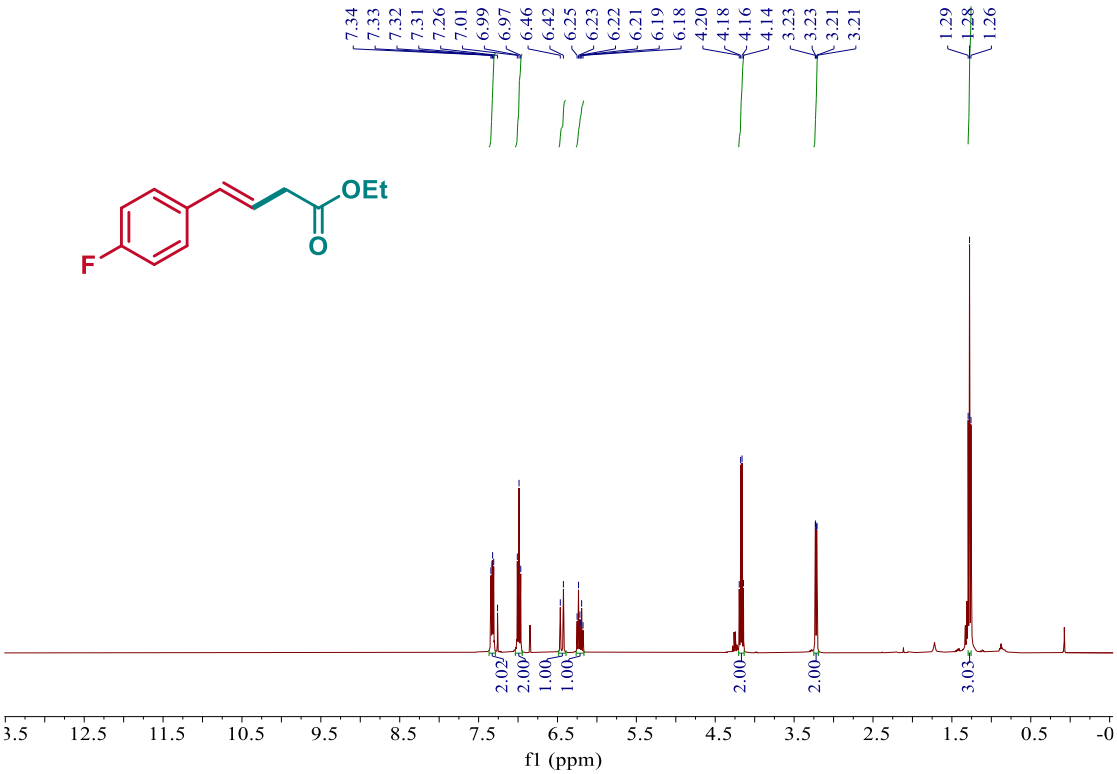
^{1}H NMR Spectrum of ethyl (*E*)-4-([1,1'-biphenyl]-4-yl)but-3-enoate 3e



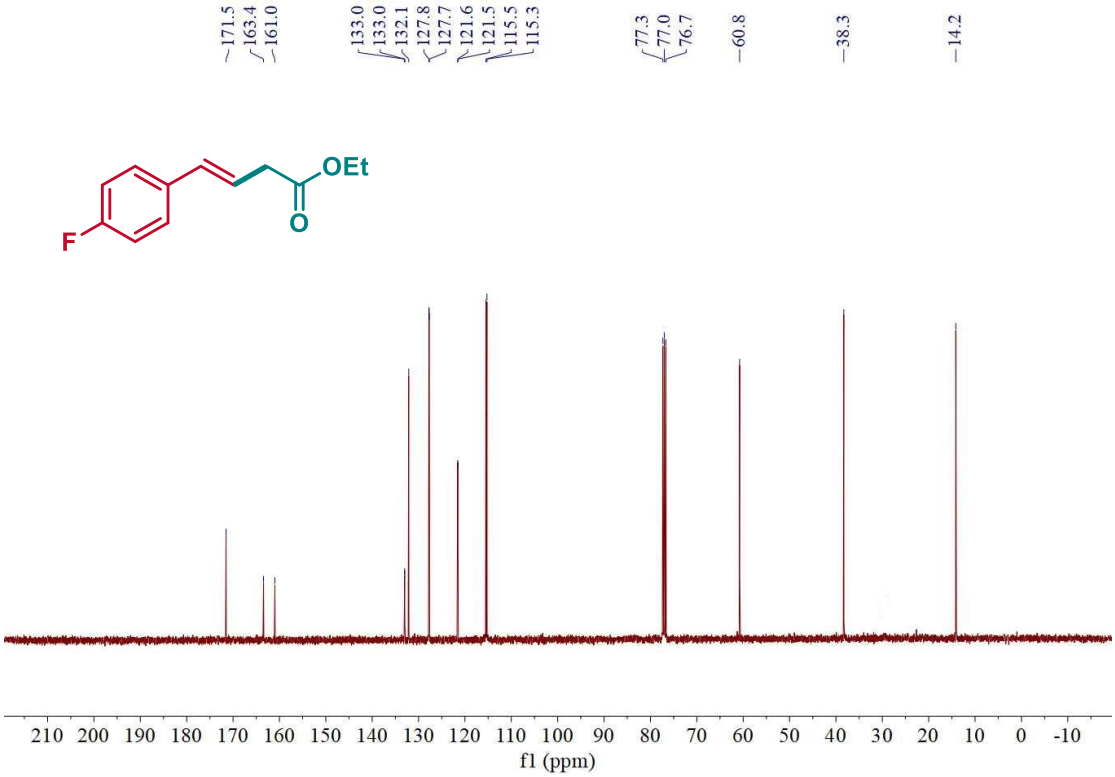
^{13}C NMR Spectrum of ethyl (*E*)-4-([1,1'-biphenyl]-4-yl)but-3-enoate 3e



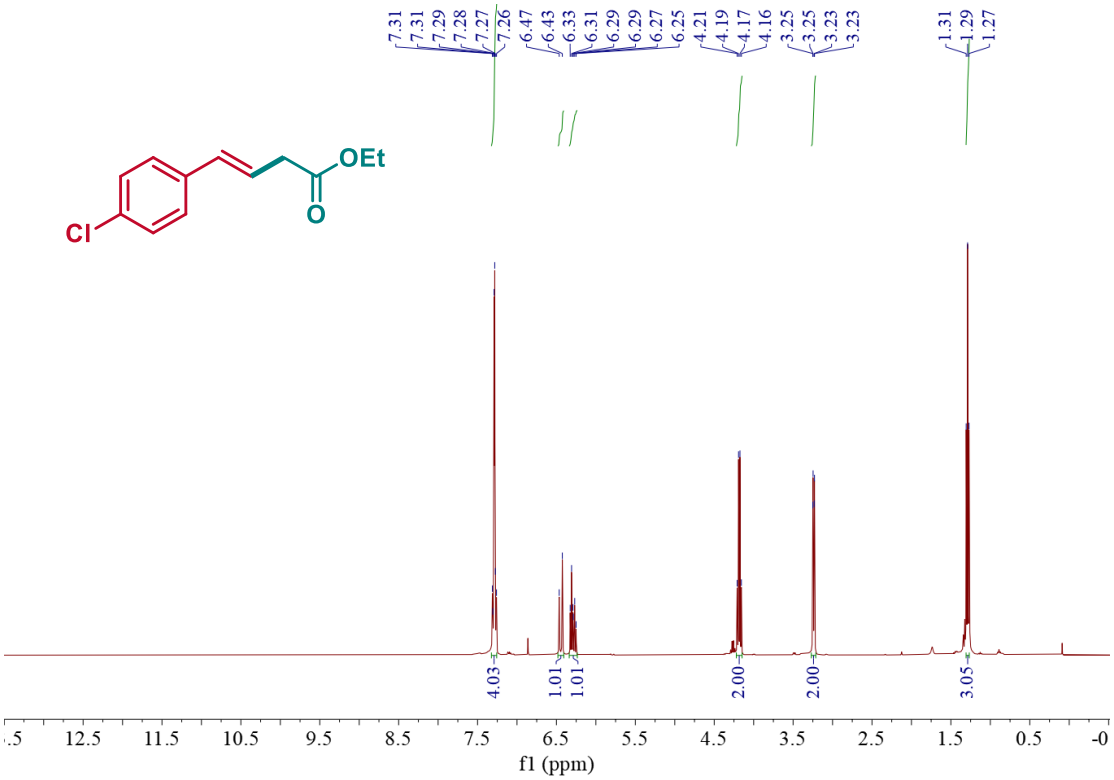
^{1}H NMR Spectrum of ethyl (*E*)-4-(4-fluorophenyl)but-3-enoate 3f



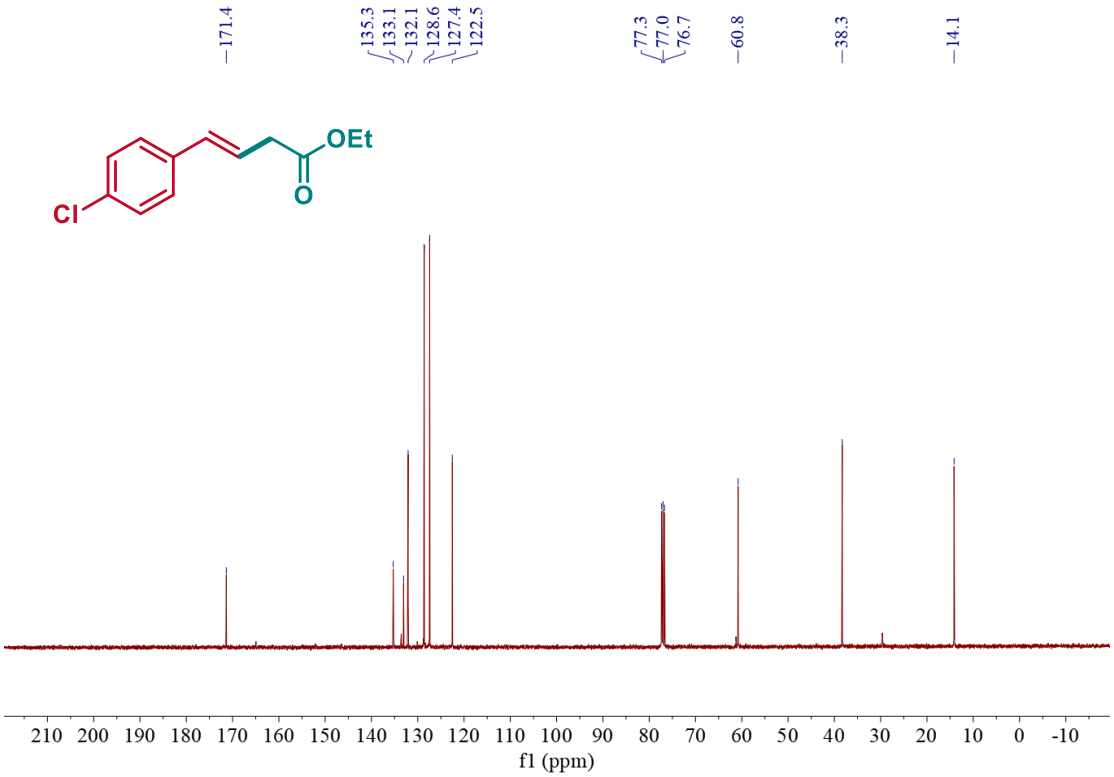
^{13}C NMR Spectrum of ethyl (*E*)-4-(4-fluorophenyl)but-3-enoate 3f



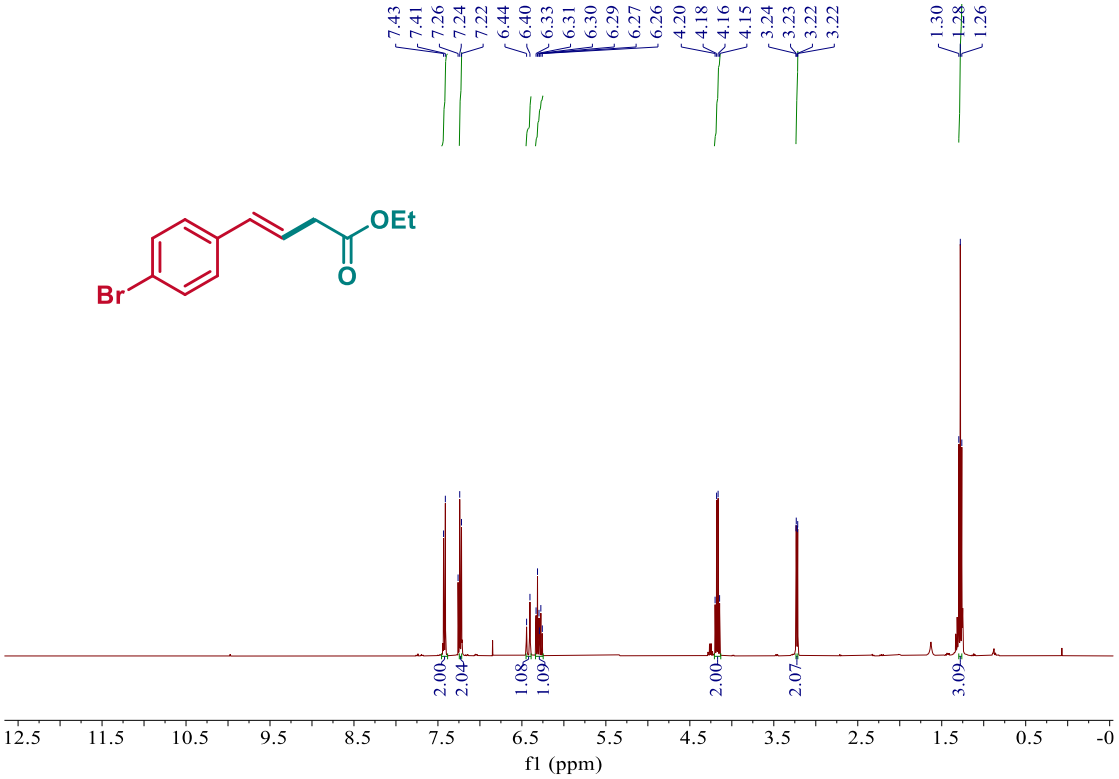
^{1}H NMR Spectrum of ethyl (*E*)-4-(4-chlorophenyl)but-3-enoate 3g



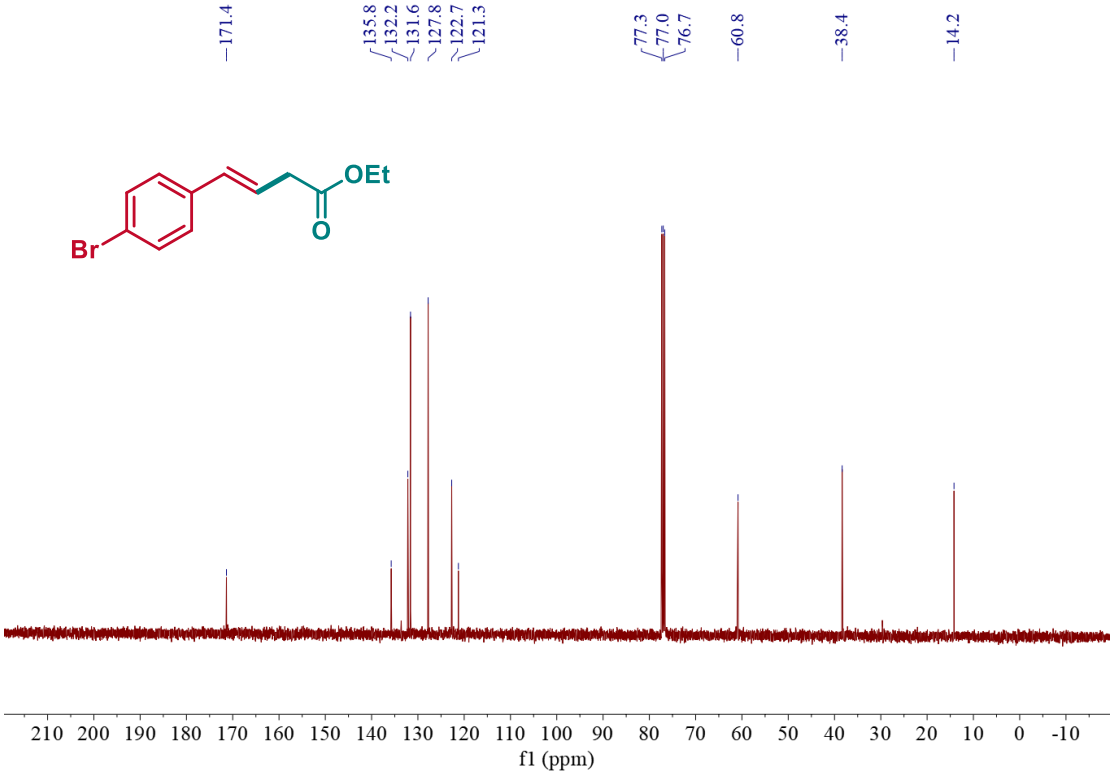
^{13}C NMR Spectrum of ethyl (*E*)-4-(4-chlorophenyl)but-3-enoate 3g



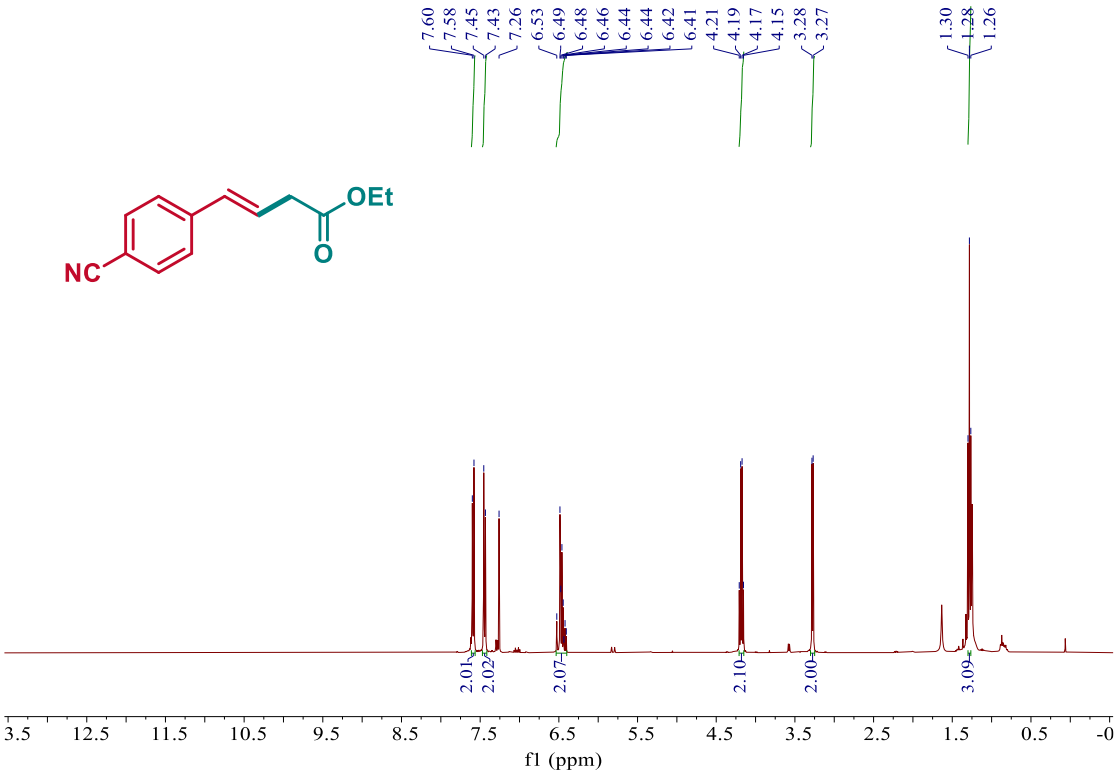
^{1}H NMR Spectrum of ethyl (*E*)-4-(4-bromophenyl)but-3-enoate 3h



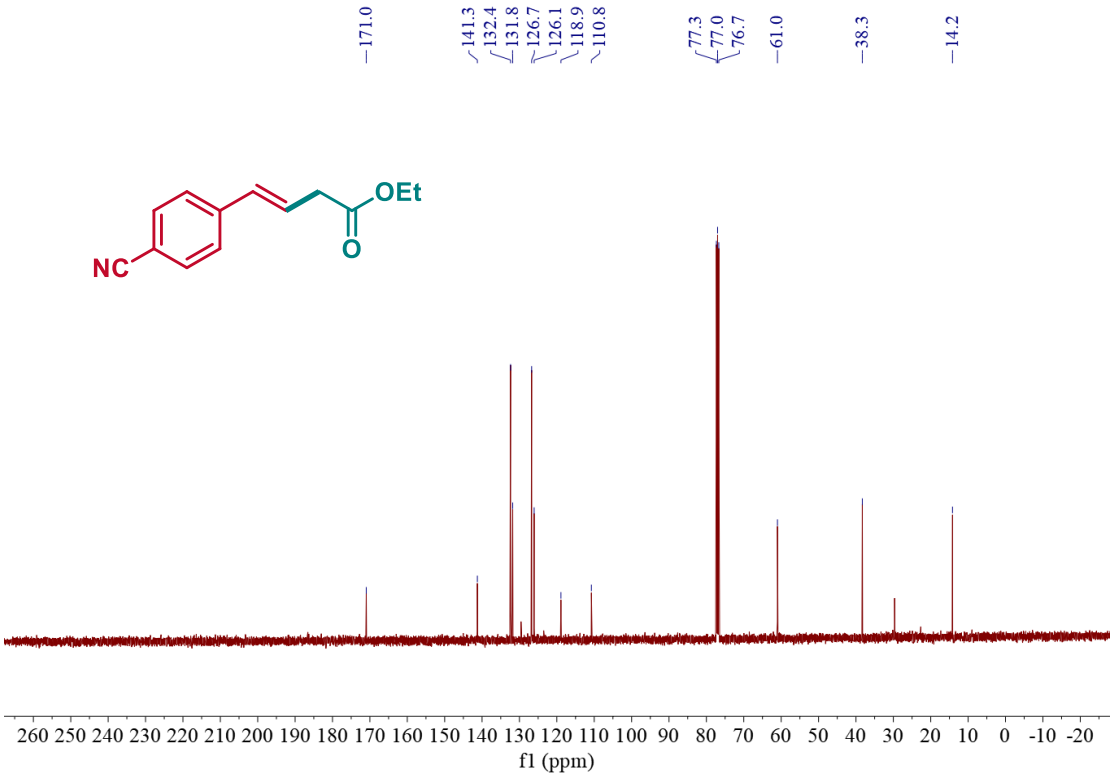
^{13}C NMR Spectrum of ethyl (*E*)-4-(4-bromophenyl)but-3-enoate 3h



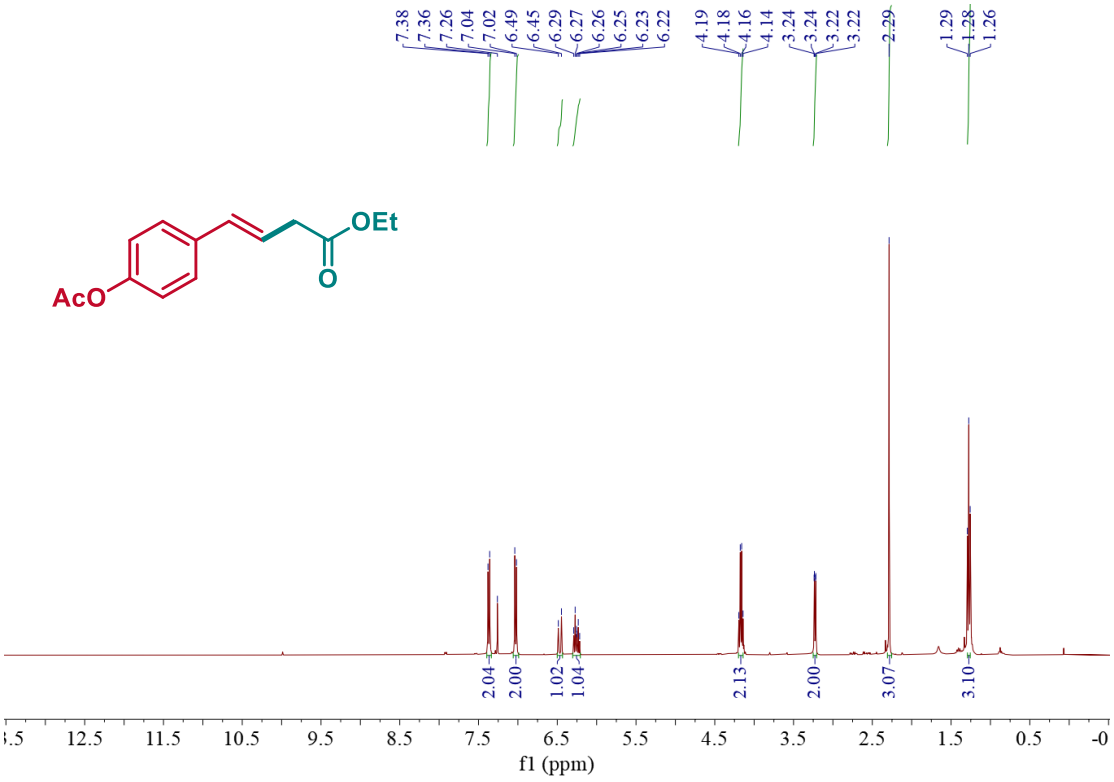
^{1}H NMR Spectrum of ethyl (*E*)-4-(4-cyanophenyl)but-3-enoate 3i



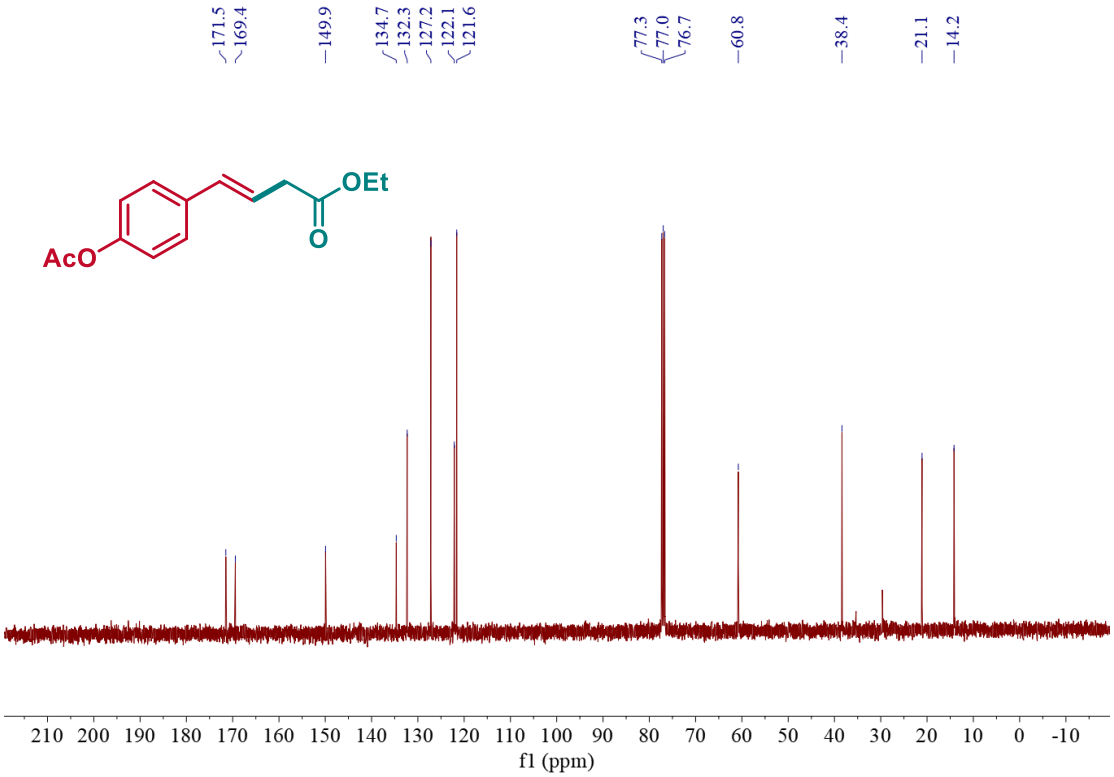
^{13}C NMR Spectrum of ethyl (*E*)-4-(4-cyanophenyl)but-3-enoate 3i



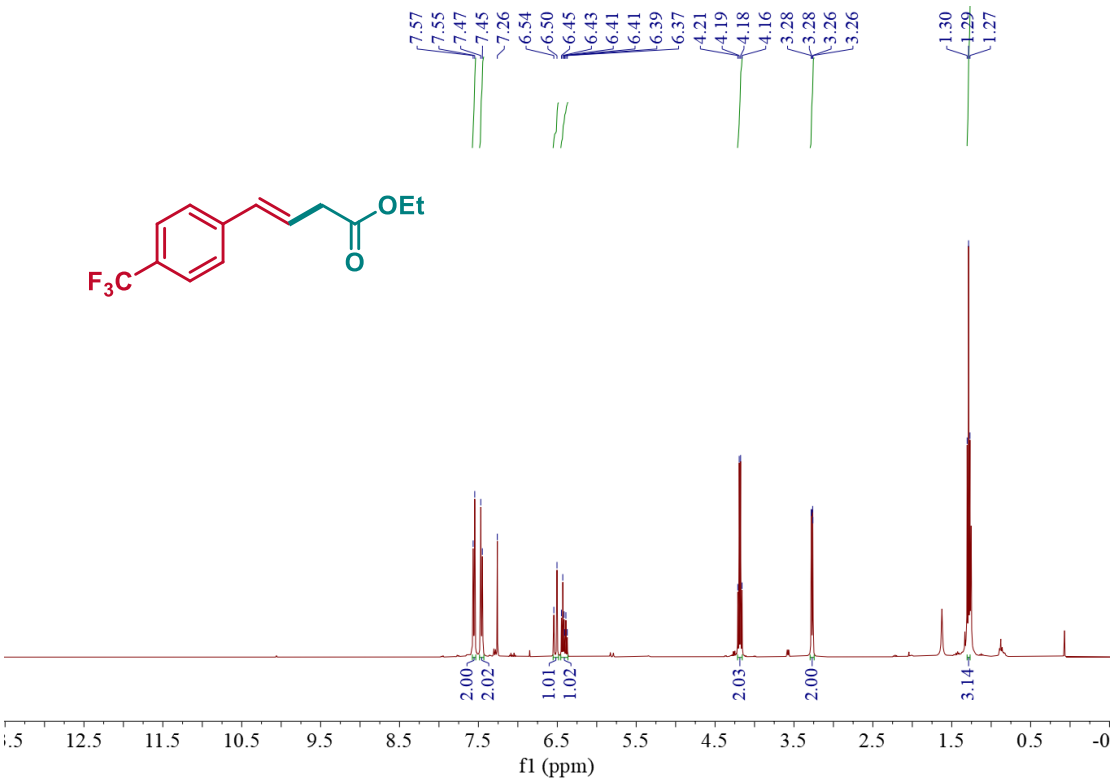
^{1}H NMR Spectrum of ethyl (*E*)-4-(4-acetoxyphenyl)but-3-enoate 3j



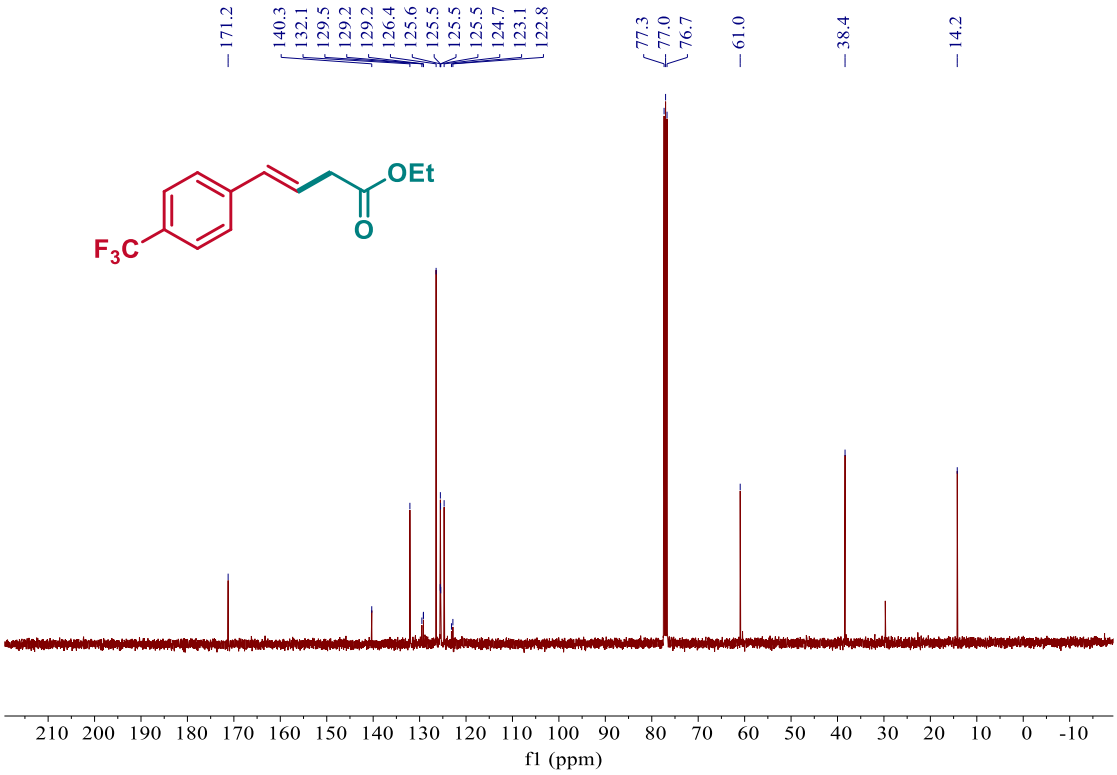
^{13}C NMR Spectrum of ethyl (*E*)-4-(4-acetoxyphenyl)but-3-enoate 3j



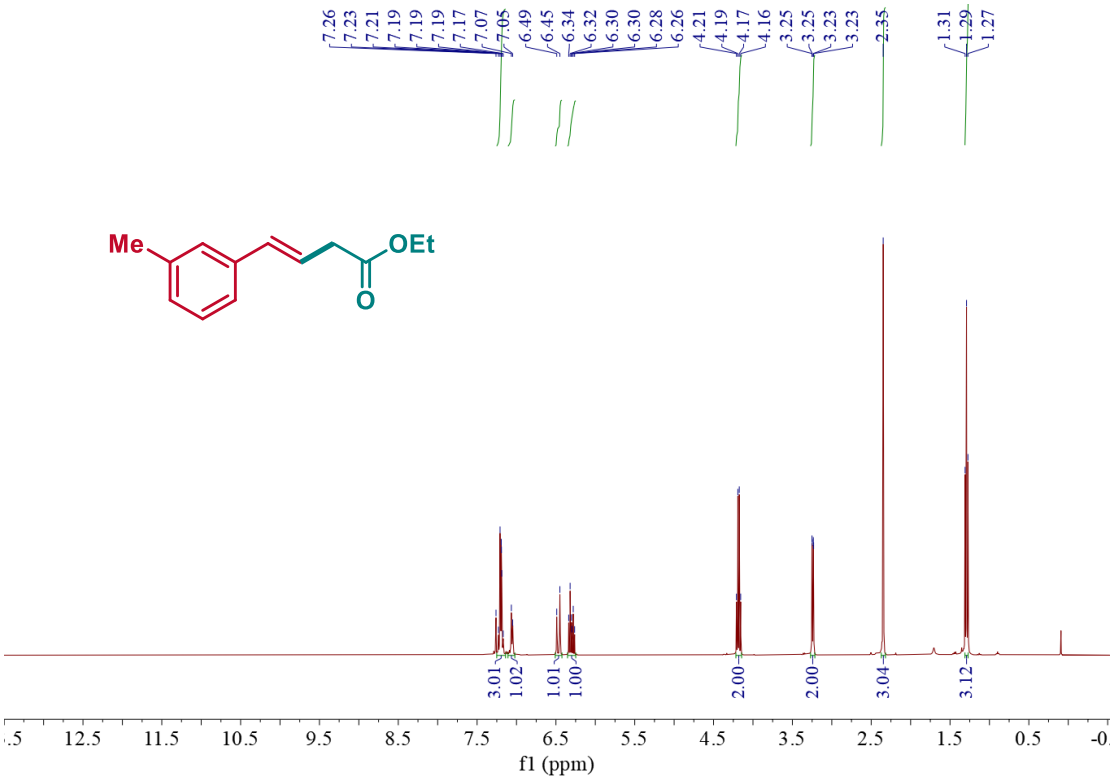
^{1}H NMR Spectrum of ethyl (*E*)-4-(4-(trifluoromethyl)phenyl)but-3-enoate 3k



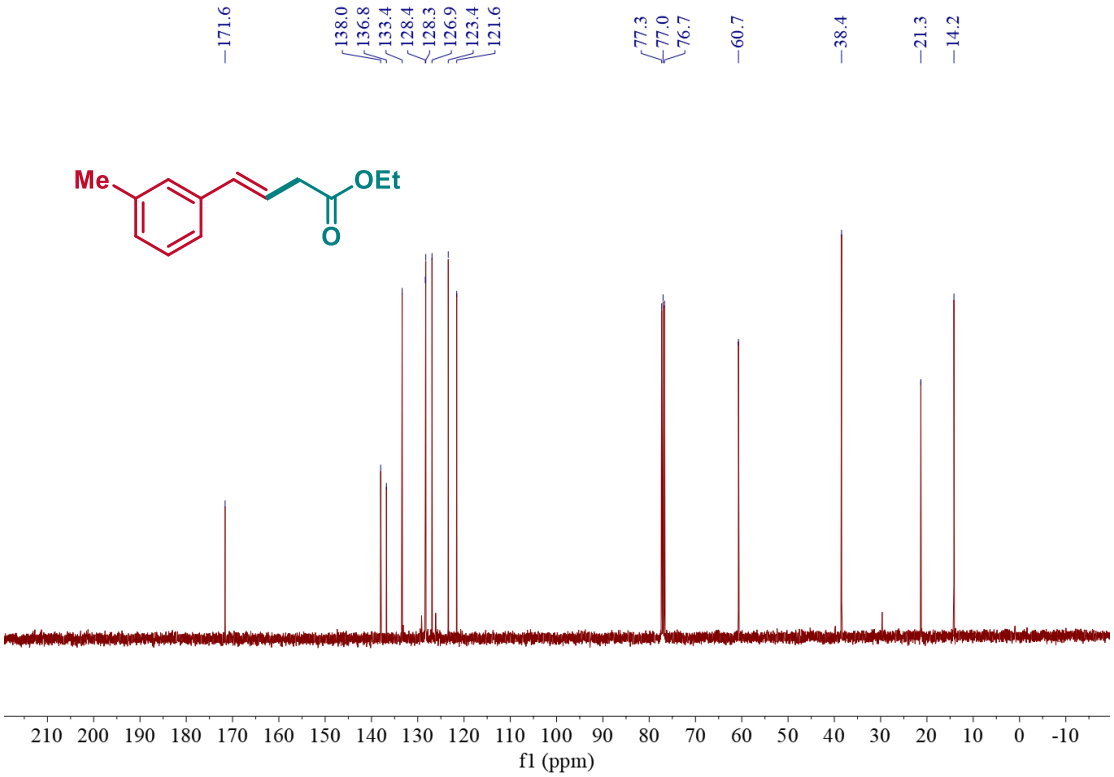
^{13}C NMR Spectrum of ethyl (*E*)-4-(4-(trifluoromethyl)phenyl)but-3-enoate 3k



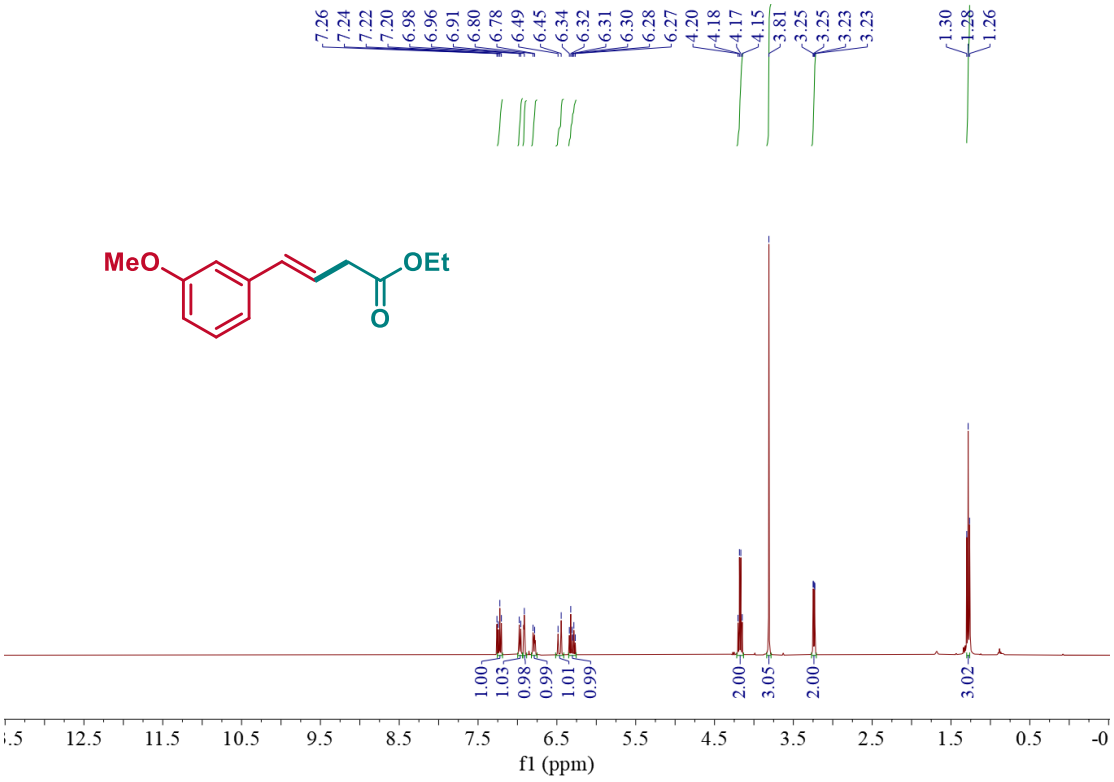
^{1}H NMR Spectrum of ethyl (*E*)-4-(*m*-tolyl)but-3-enoate 3l



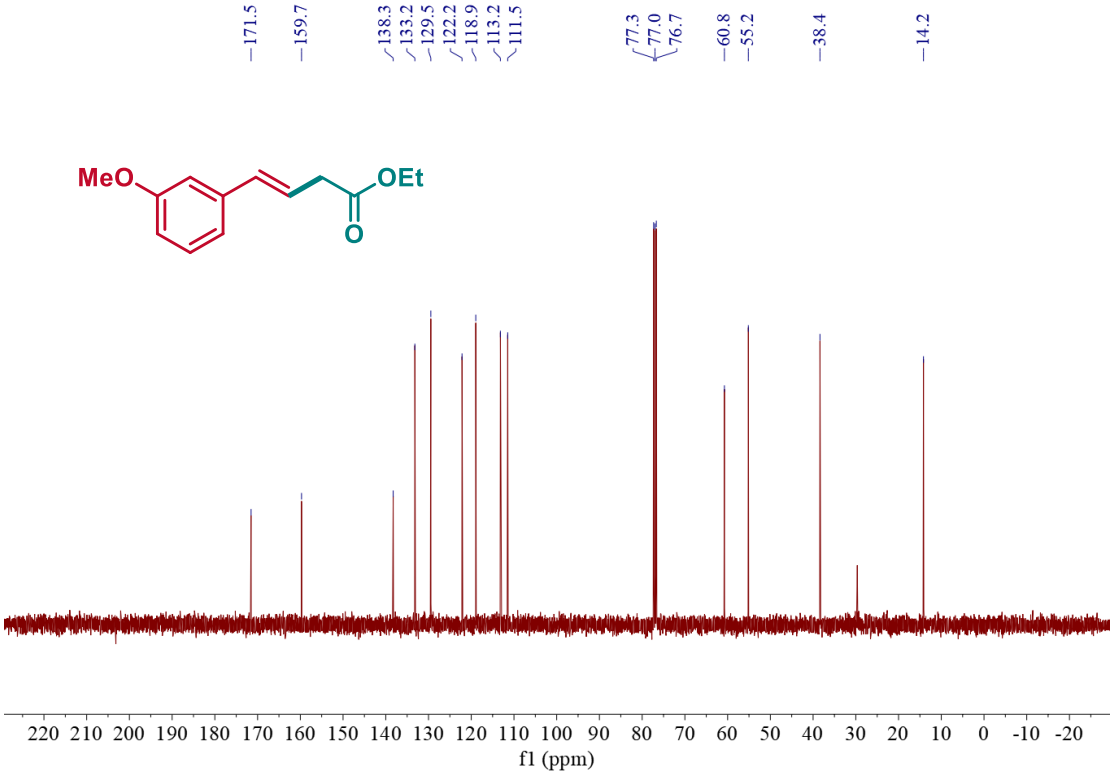
^{13}C NMR Spectrum of ethyl (*E*)-4-(*m*-tolyl)but-3-enoate 3l



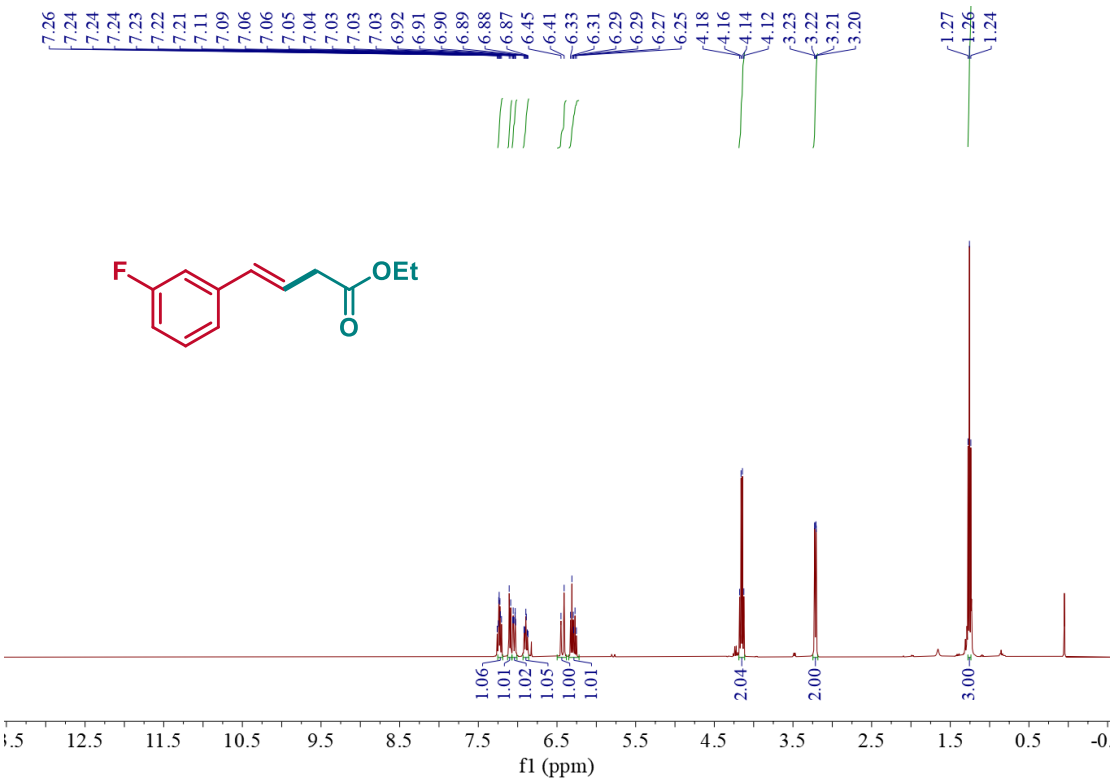
^{1}H NMR Spectrum of ethyl (*E*)-4-(3-methoxyphenyl)but-3-enoate 3m



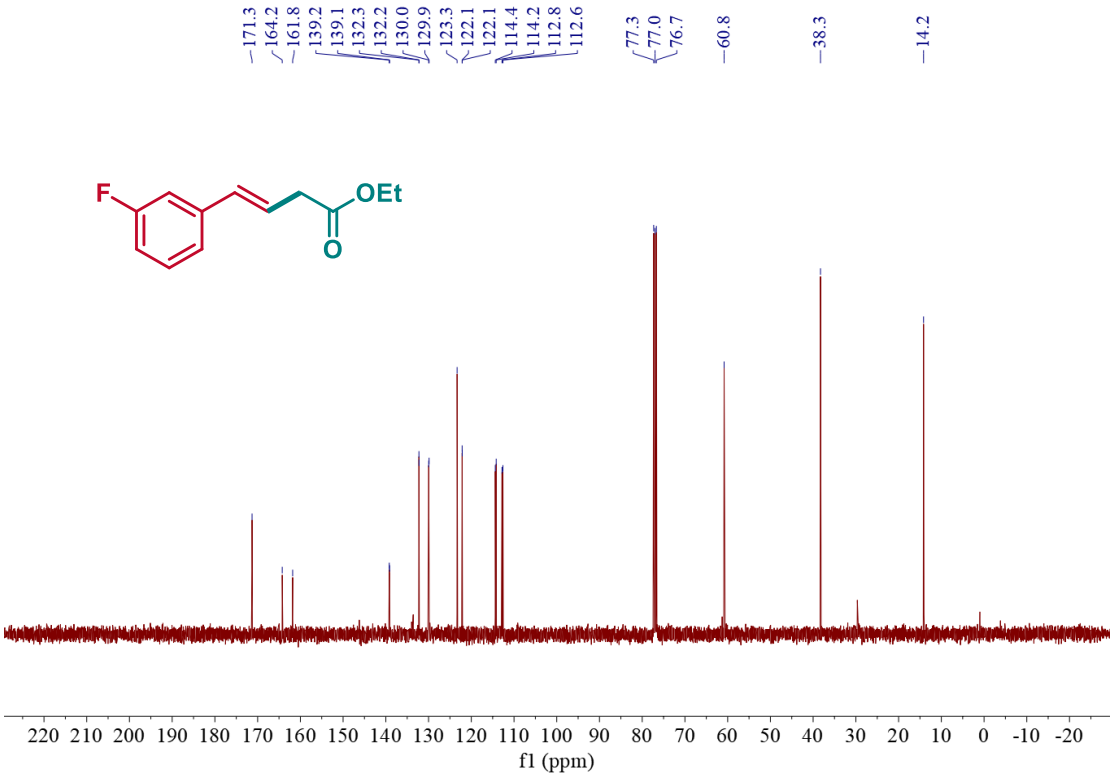
^{13}C NMR Spectrum of ethyl (*E*)-4-(3-methoxyphenyl)but-3-enoate 3m



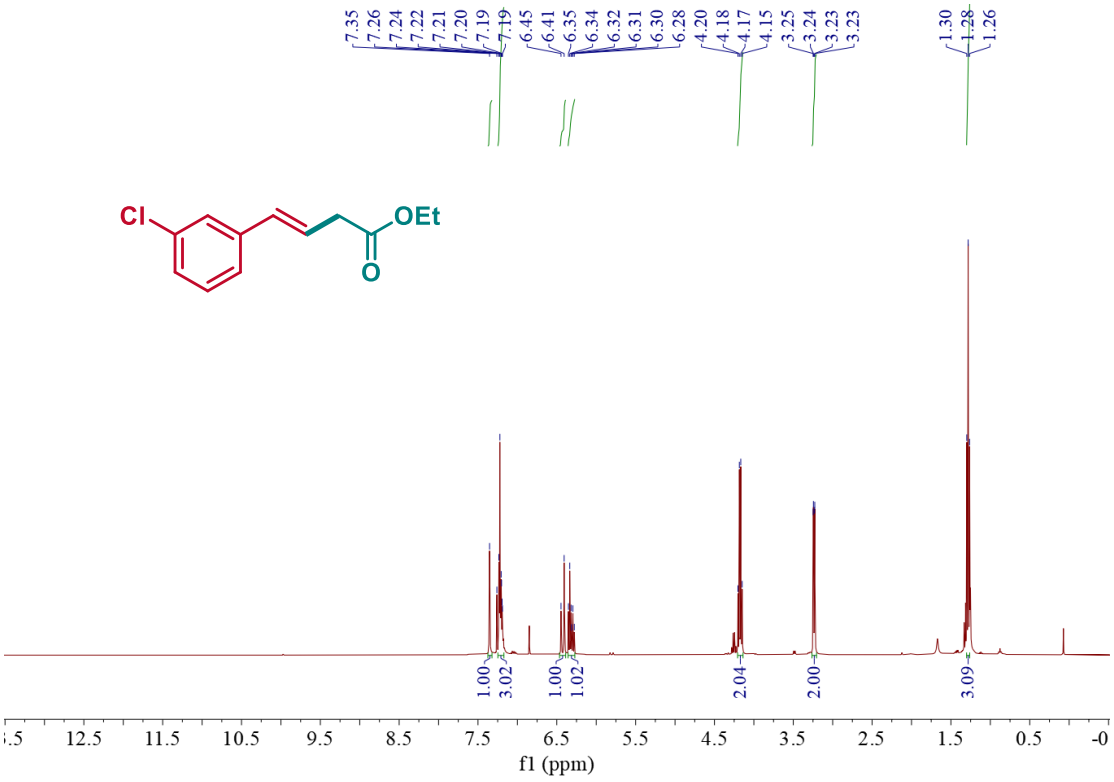
^{1}H NMR Spectrum of ethyl (*E*)-4-(3-fluorophenyl)but-3-enoate 3n



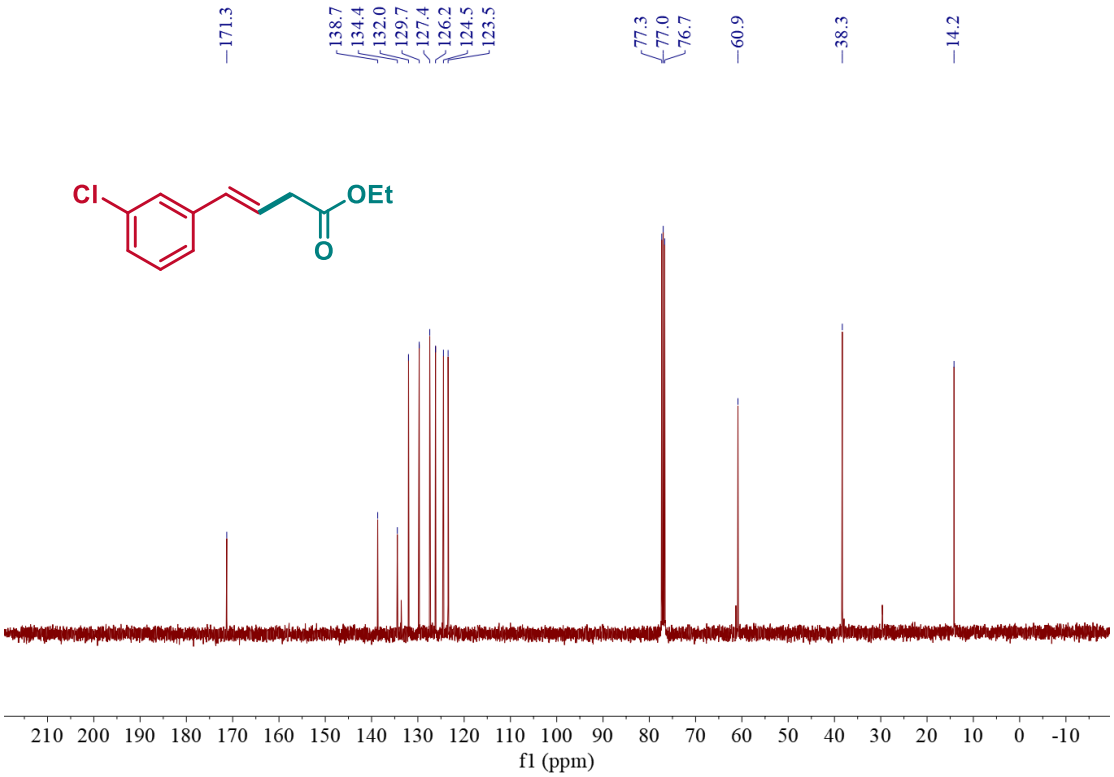
^{13}C NMR Spectrum of ethyl (*E*)-4-(3-fluorophenyl)but-3-enoate 3n



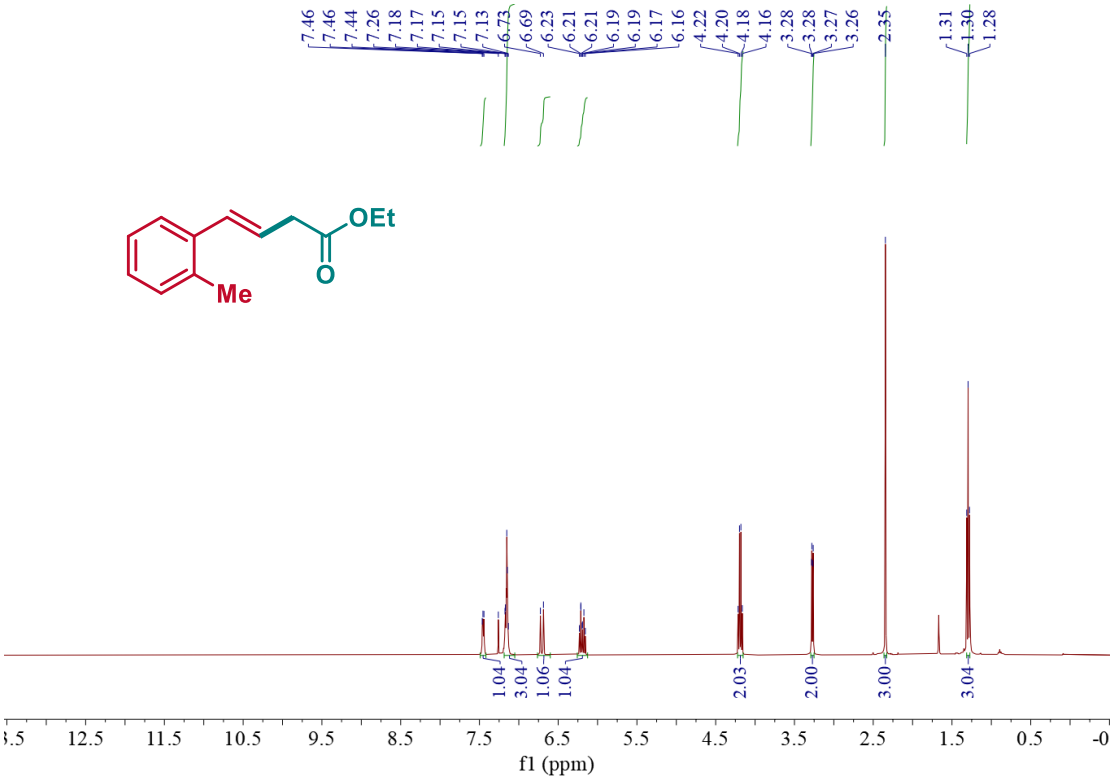
^{1}H NMR Spectrum of ethyl (*E*)-4-(3-chlorophenyl)but-3-enoate 3o



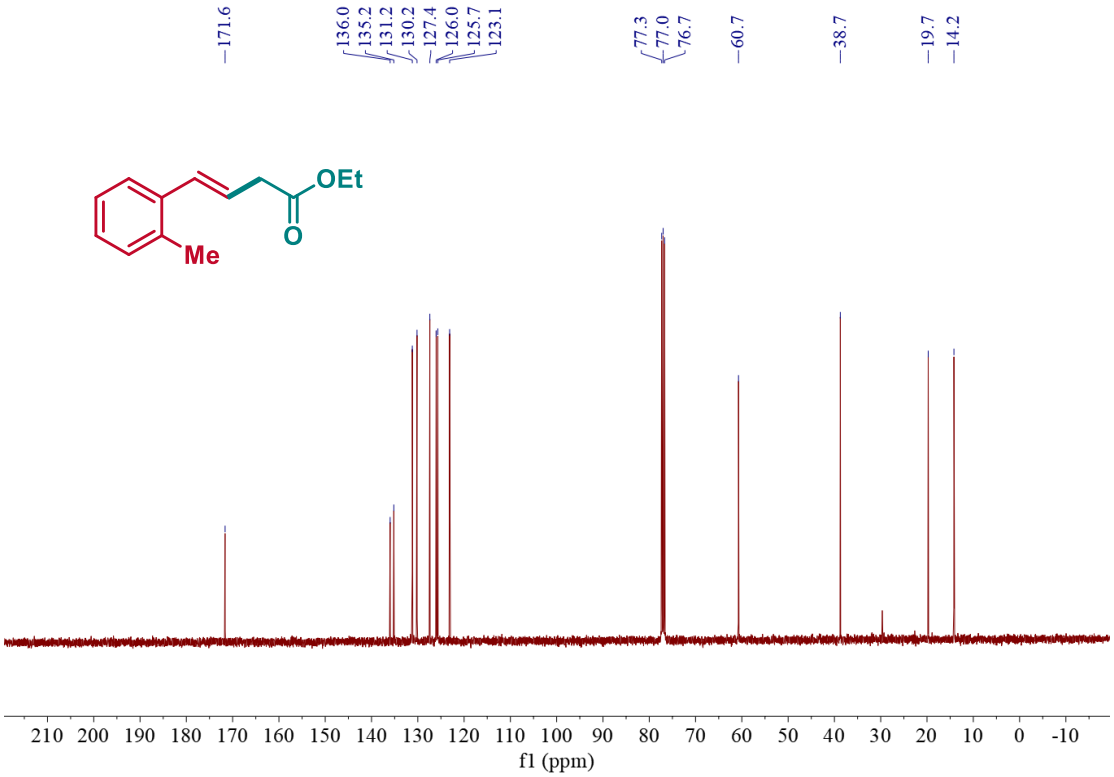
^{13}C NMR Spectrum of ethyl (*E*)-4-(3-chlorophenyl)but-3-enoate 3o



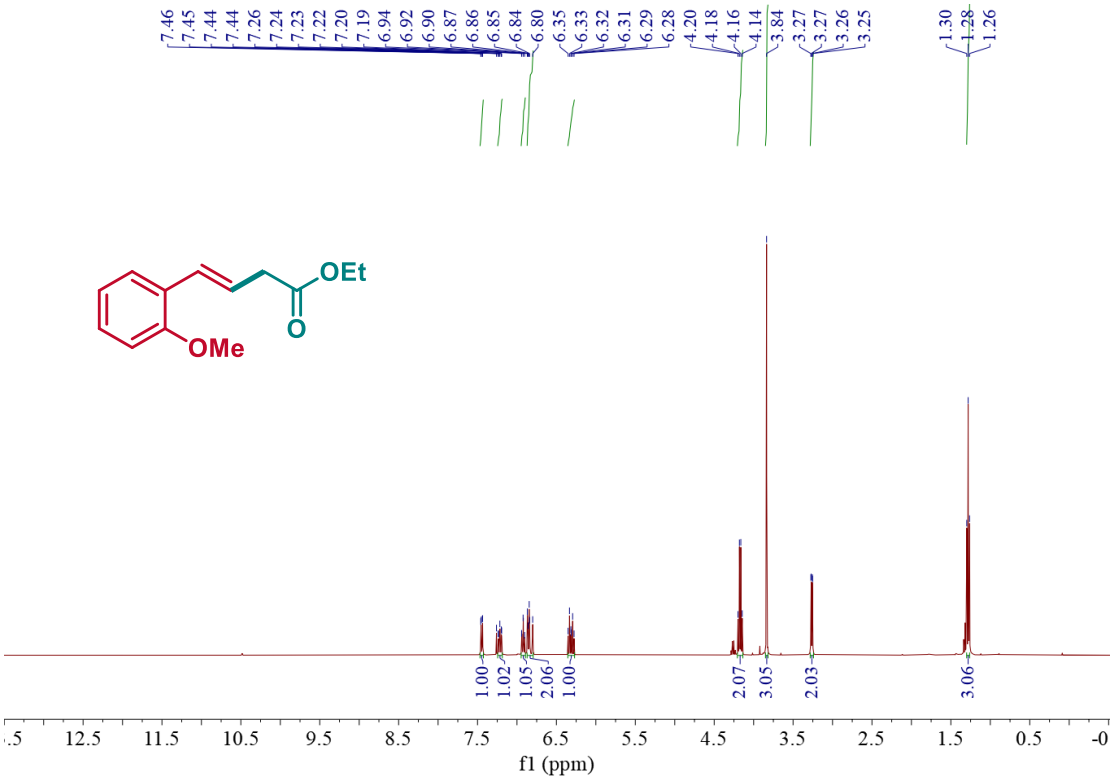
^{1}H NMR Spectrum of ethyl (*E*)-4-(o-tolyl)but-3-enoate 3p



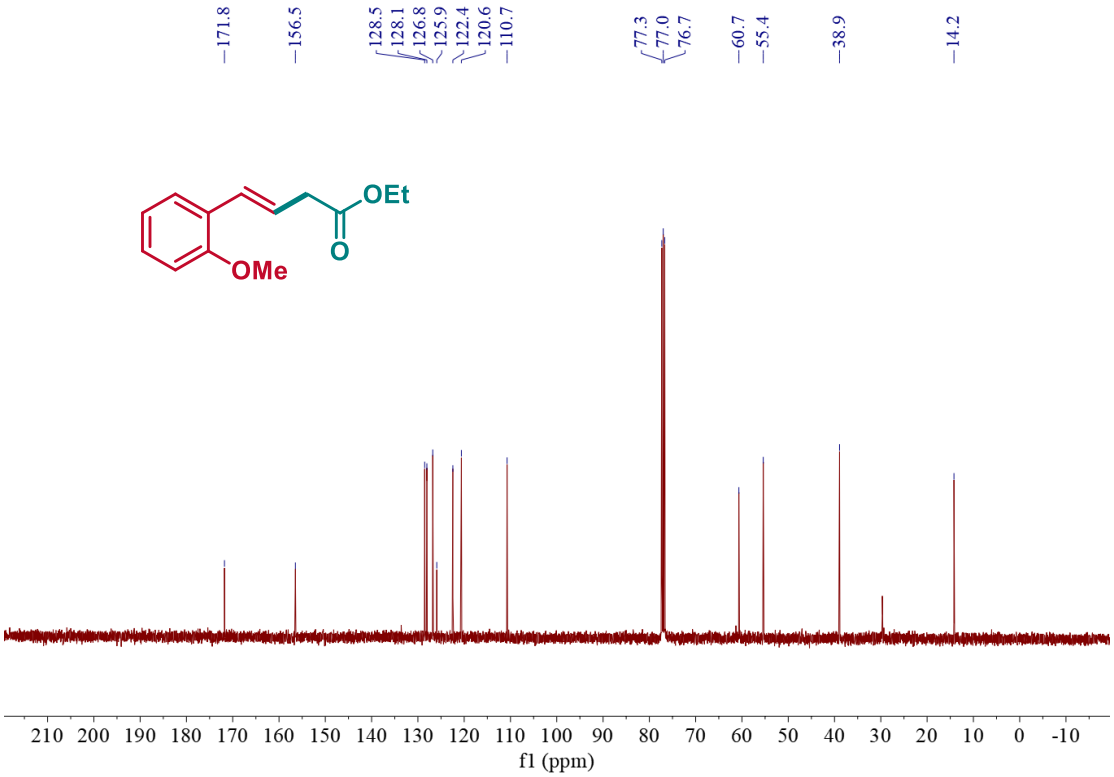
^{13}C NMR Spectrum of ethyl (*E*)-4-(o-tolyl)but-3-enoate 3p



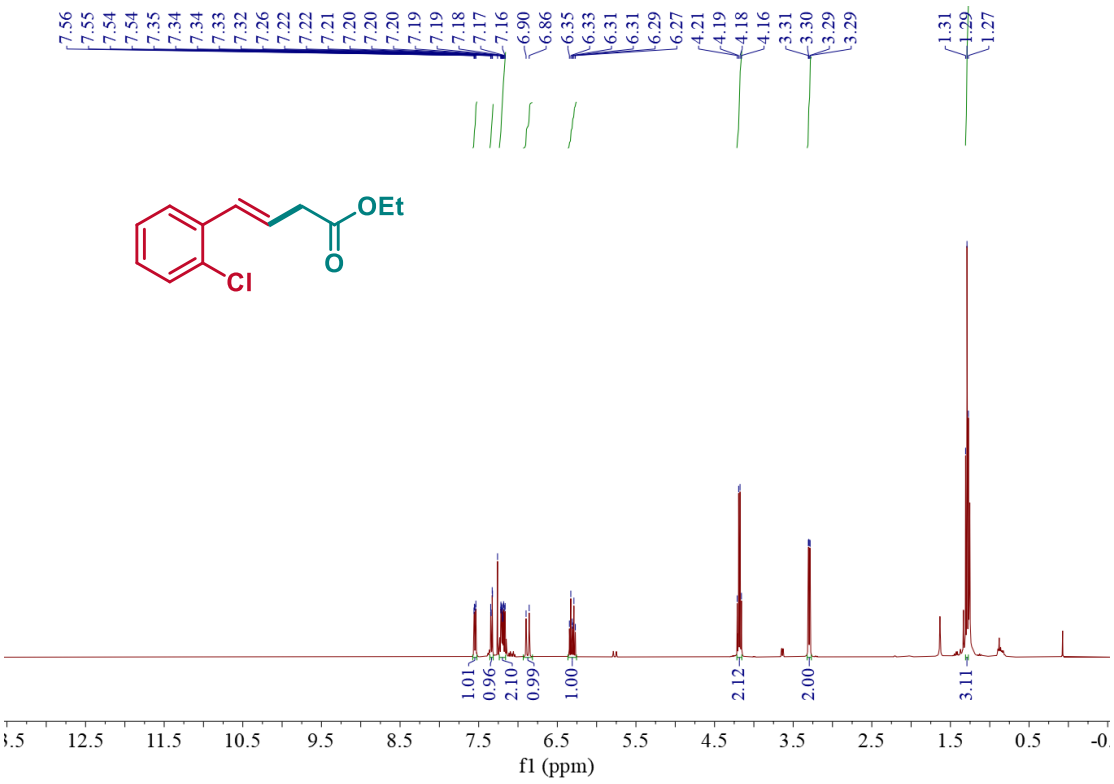
^{1}H NMR Spectrum of ethyl (*E*)-4-(2-methoxyphenyl)but-3-enoate 3q



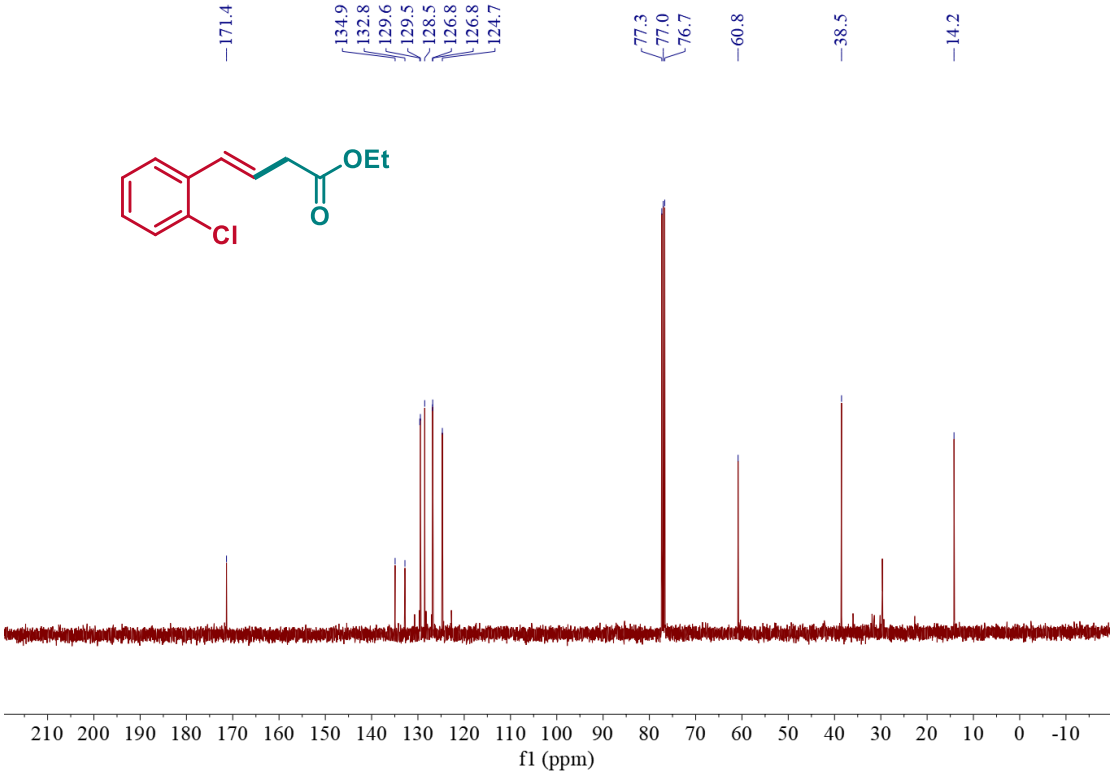
^{13}C NMR Spectrum of ethyl (*E*)-4-(2-methoxyphenyl)but-3-enoate 3q



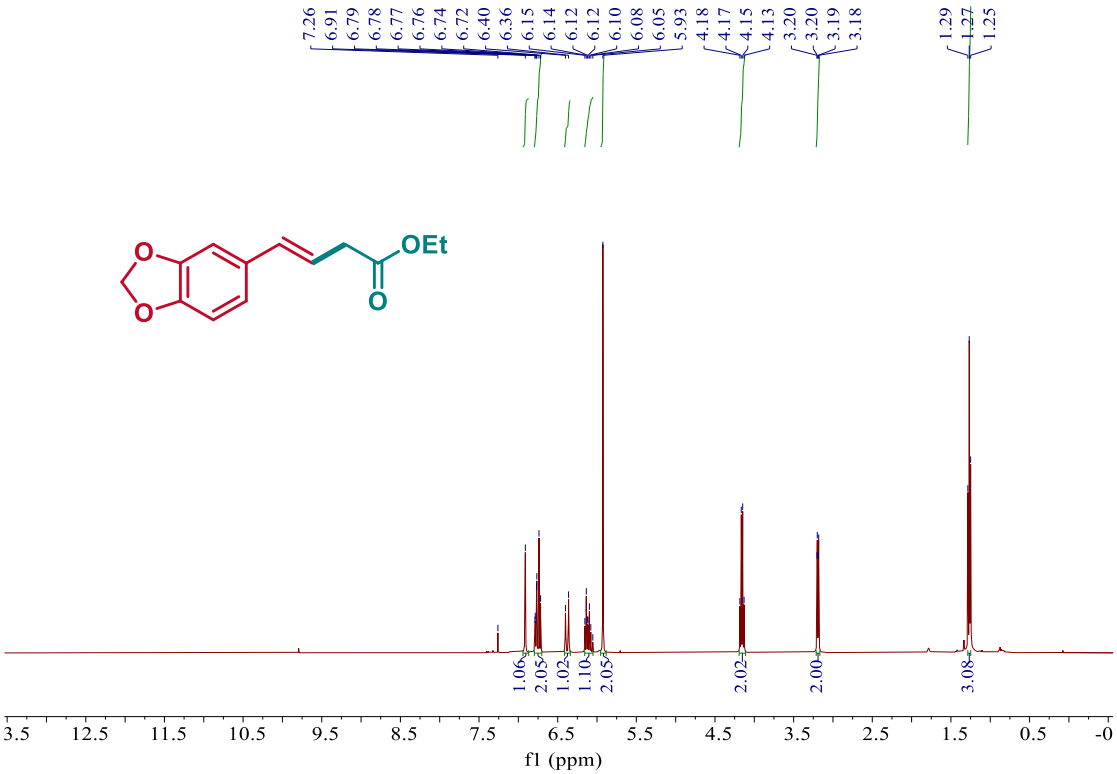
^{1}H NMR Spectrum of ethyl (*E*)-4-(2-chlorophenyl)but-3-enoate 3r



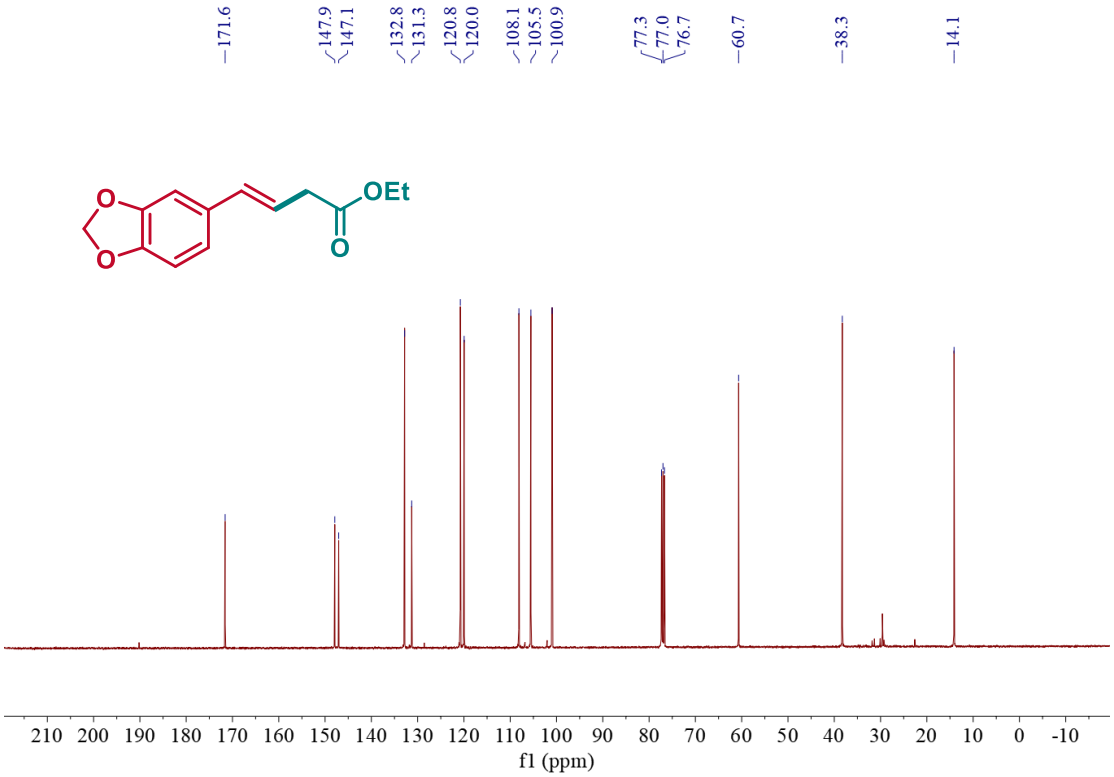
^{13}C NMR Spectrum of ethyl (*E*)-4-(2-chlorophenyl)but-3-enoate 3r



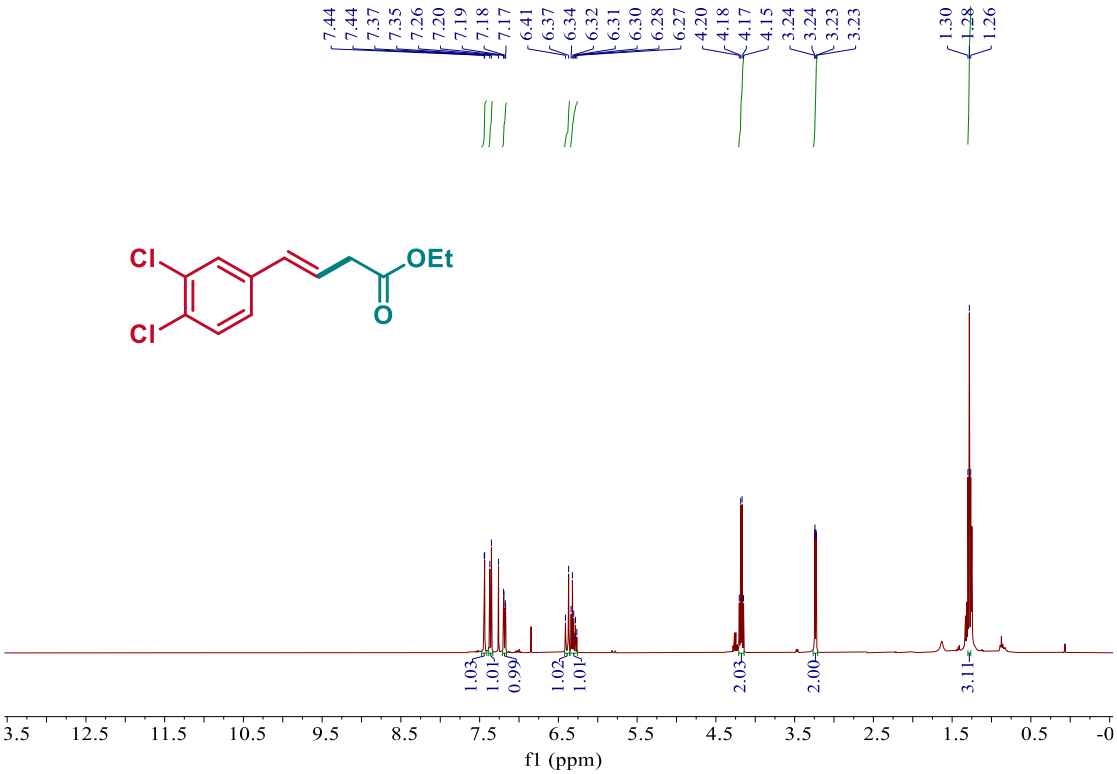
^{1}H NMR Spectrum of ethyl (*E*)-4-(benzo[*d*][1,3]dioxol-5-yl)but-3-enoate 3s



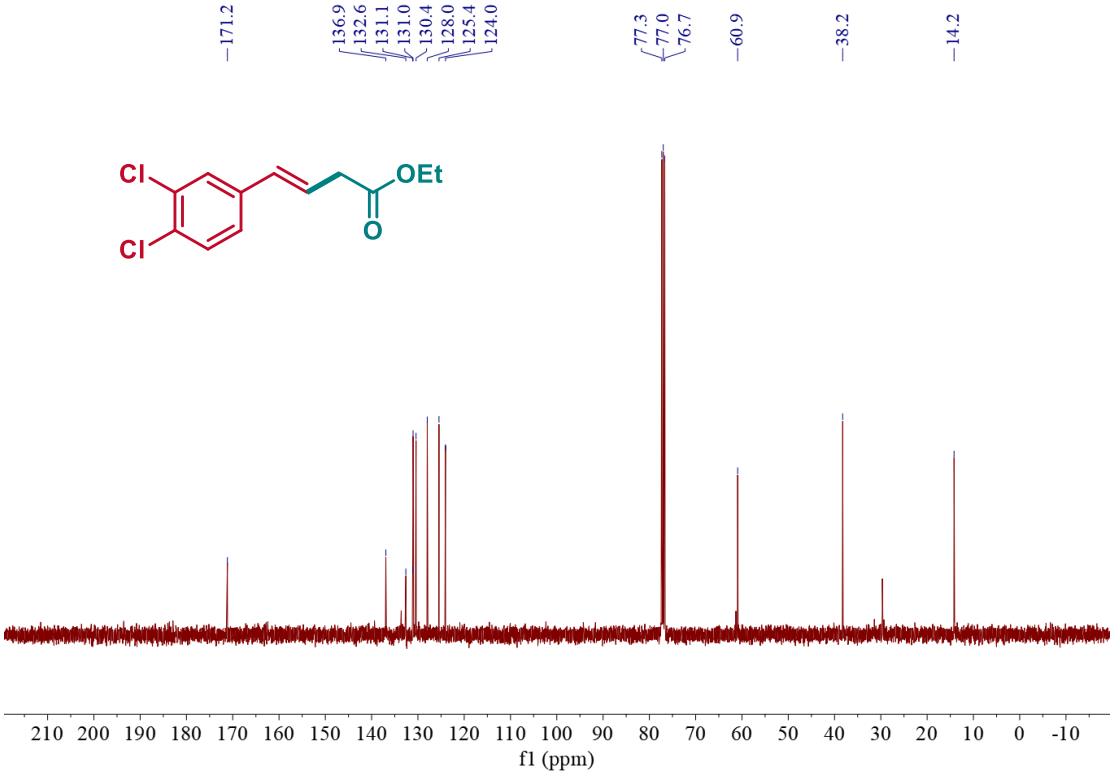
^{13}C NMR Spectrum of ethyl (*E*)-4-(benzo[*d*][1,3]dioxol-5-yl)but-3-enoate 3s



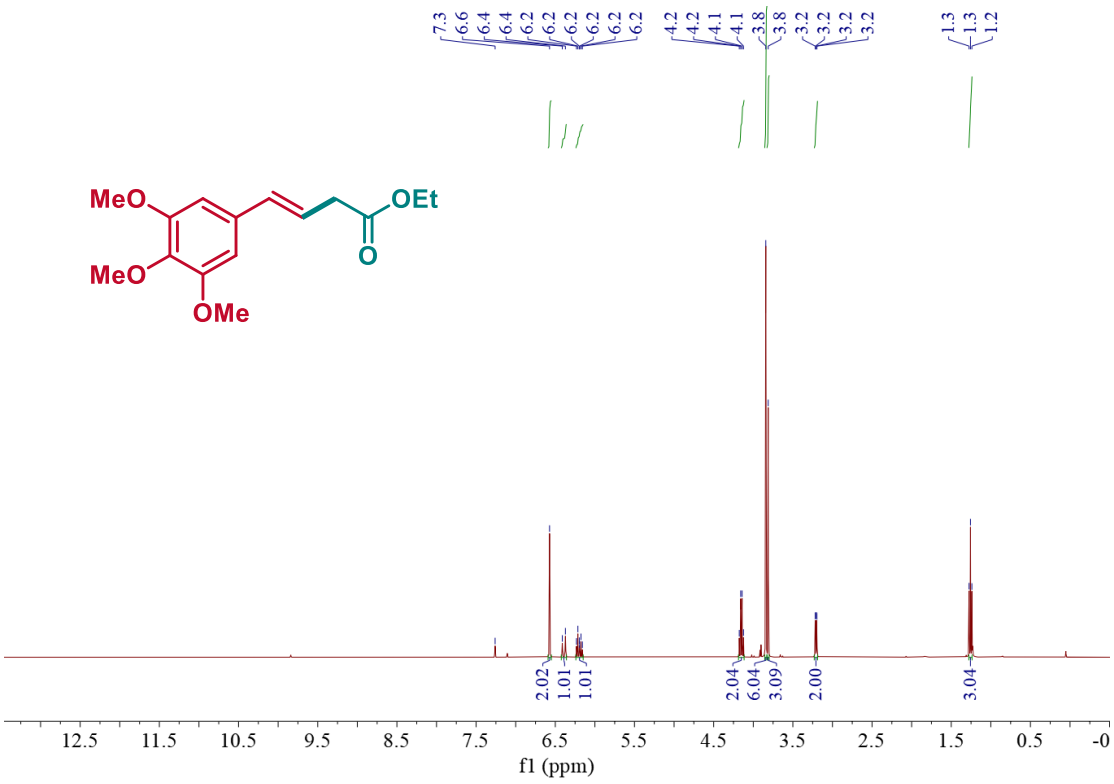
^{1}H NMR Spectrum of ethyl (*E*)-4-(3,4-dichlorophenyl)but-3-enoate 3t



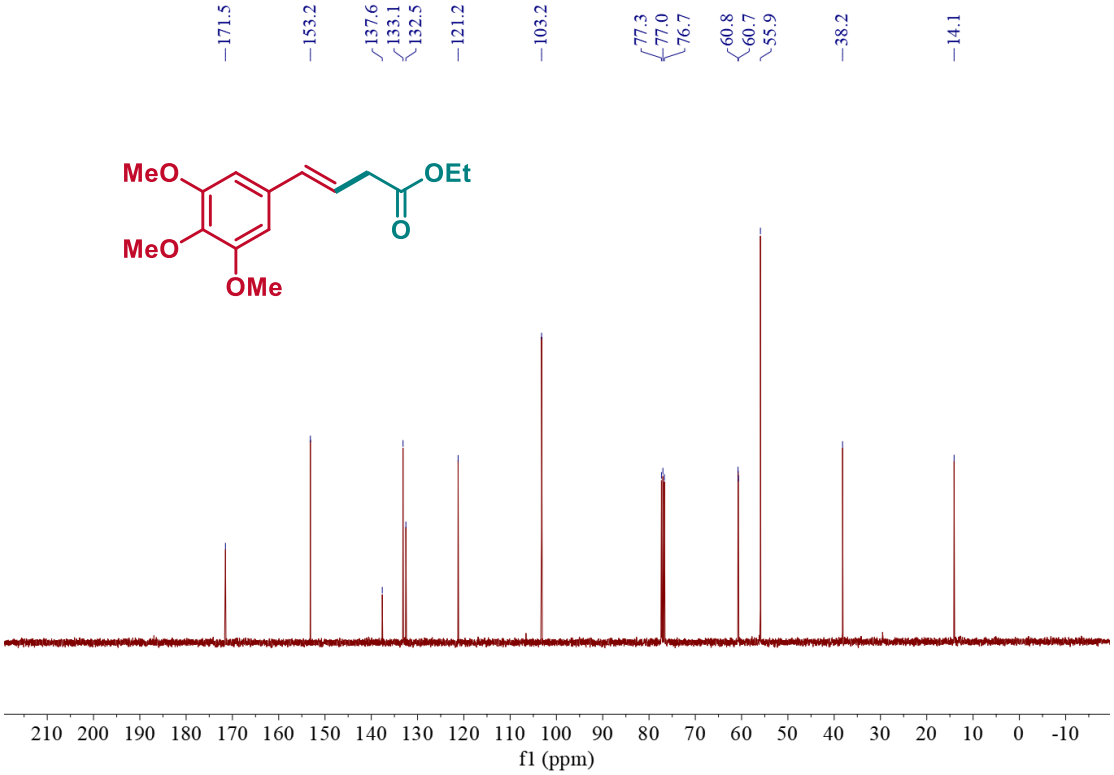
^{13}C NMR Spectrum of ethyl (*E*)-4-(3,4-dichlorophenyl)but-3-enoate 3t



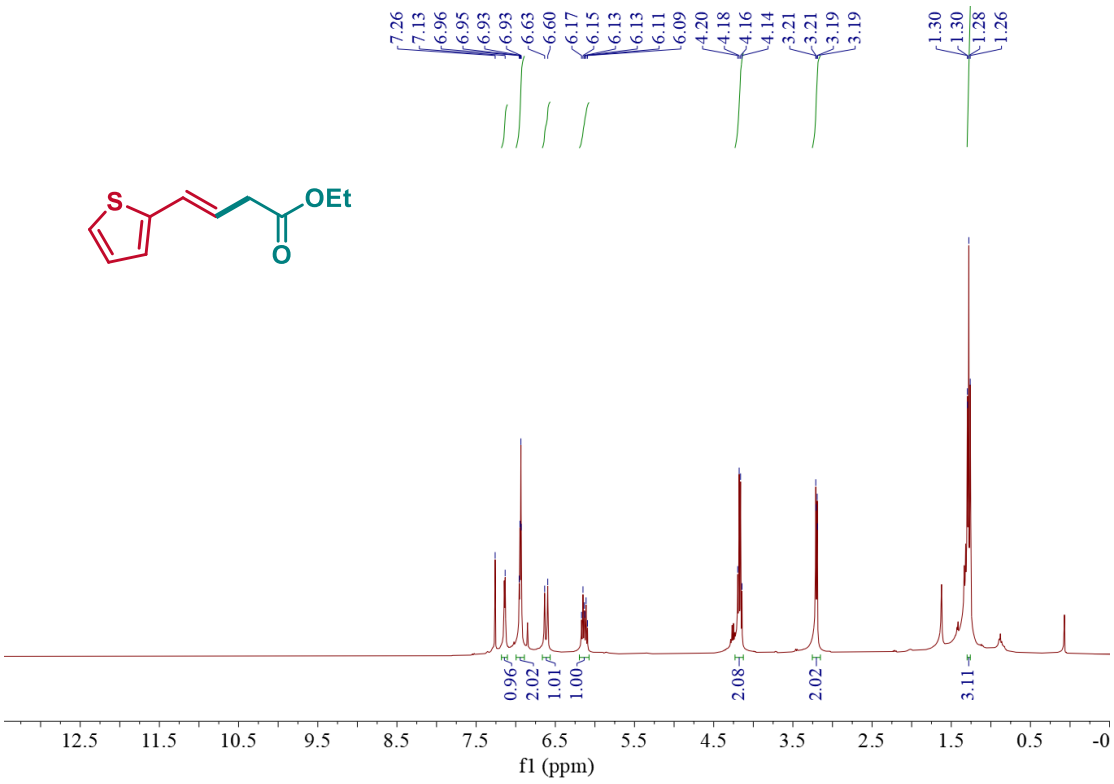
^{1}H NMR Spectrum of ethyl (*E*)-4-(3,4,5-trimethoxyphenyl)but-3-enoate 3u



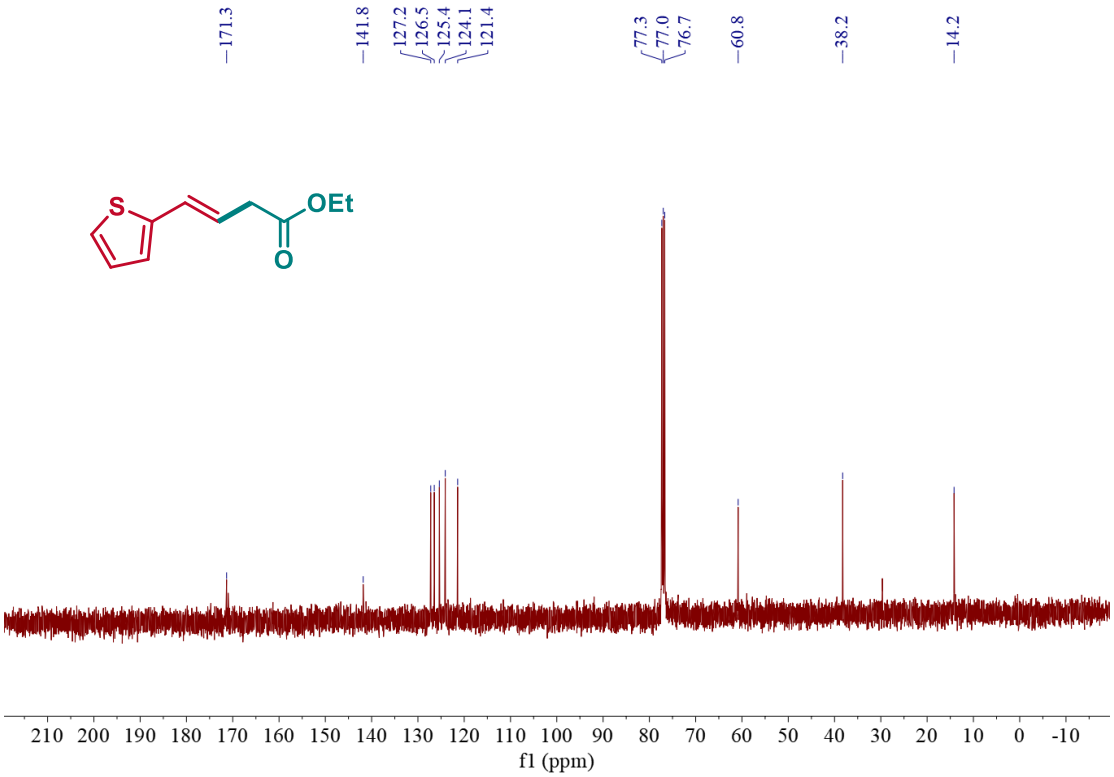
^{13}C NMR Spectrum of ethyl (*E*)-4-(3,4,5-trimethoxyphenyl)but-3-enoate 3u



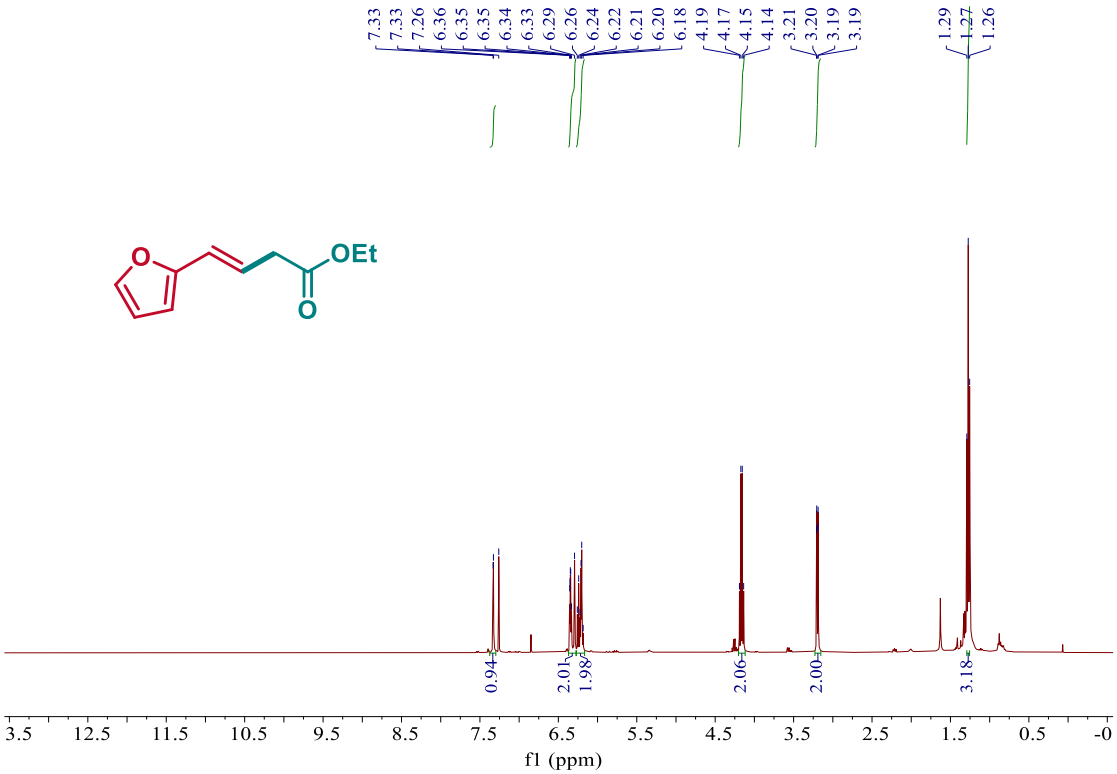
^{1}H NMR Spectrum of ethyl (*E*)-4-(thiophen-2-yl)but-3-enoate 3v



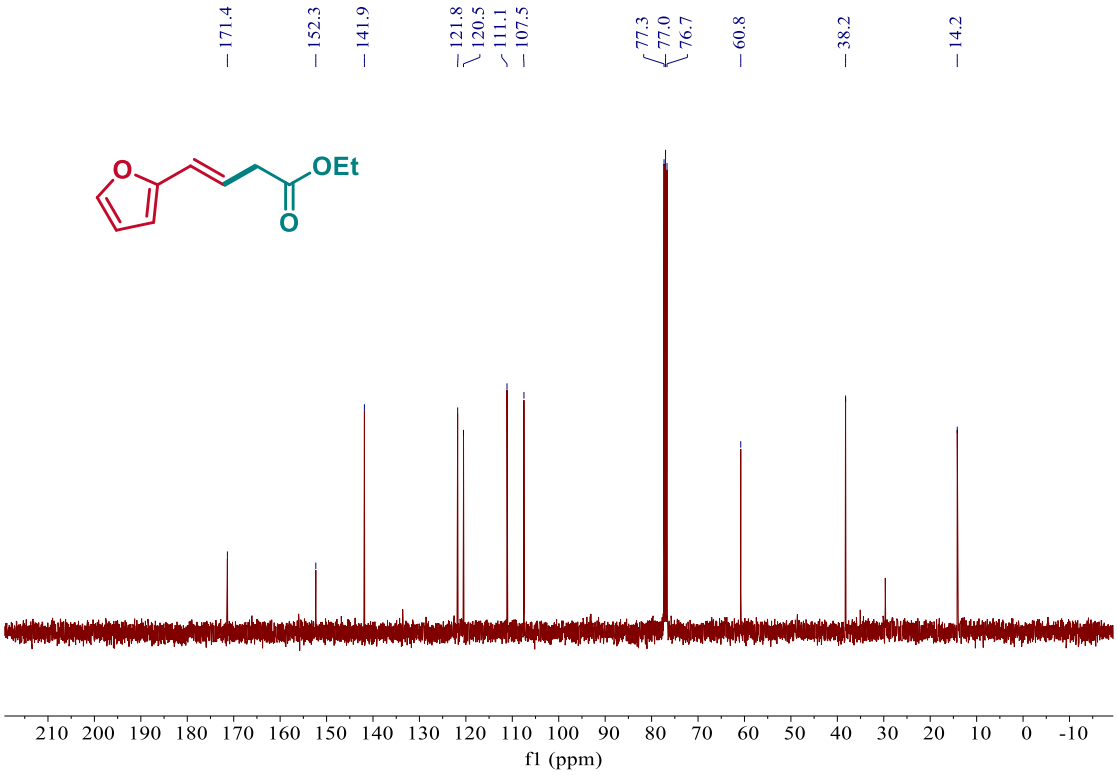
^{13}C NMR Spectrum of ethyl (*E*)-4-(thiophen-2-yl)but-3-enoate 3v



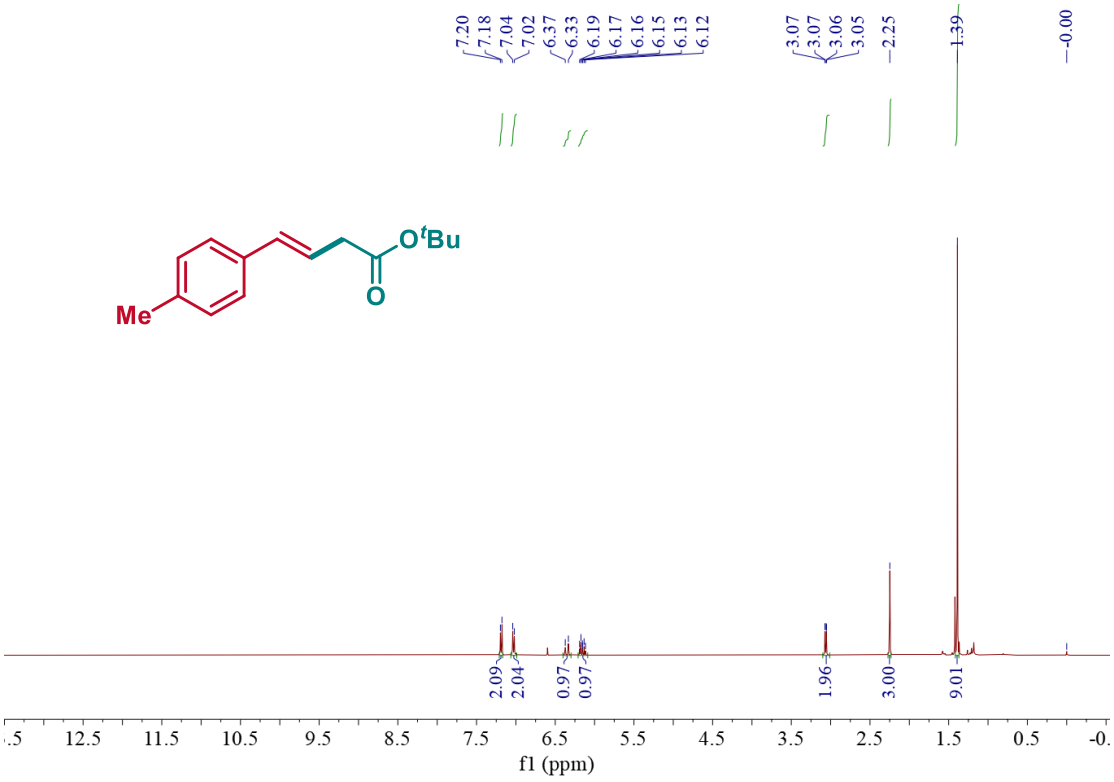
^{1}H NMR Spectrum of ethyl (*E*)-4-(furan-2-yl)but-3-enoate 3w



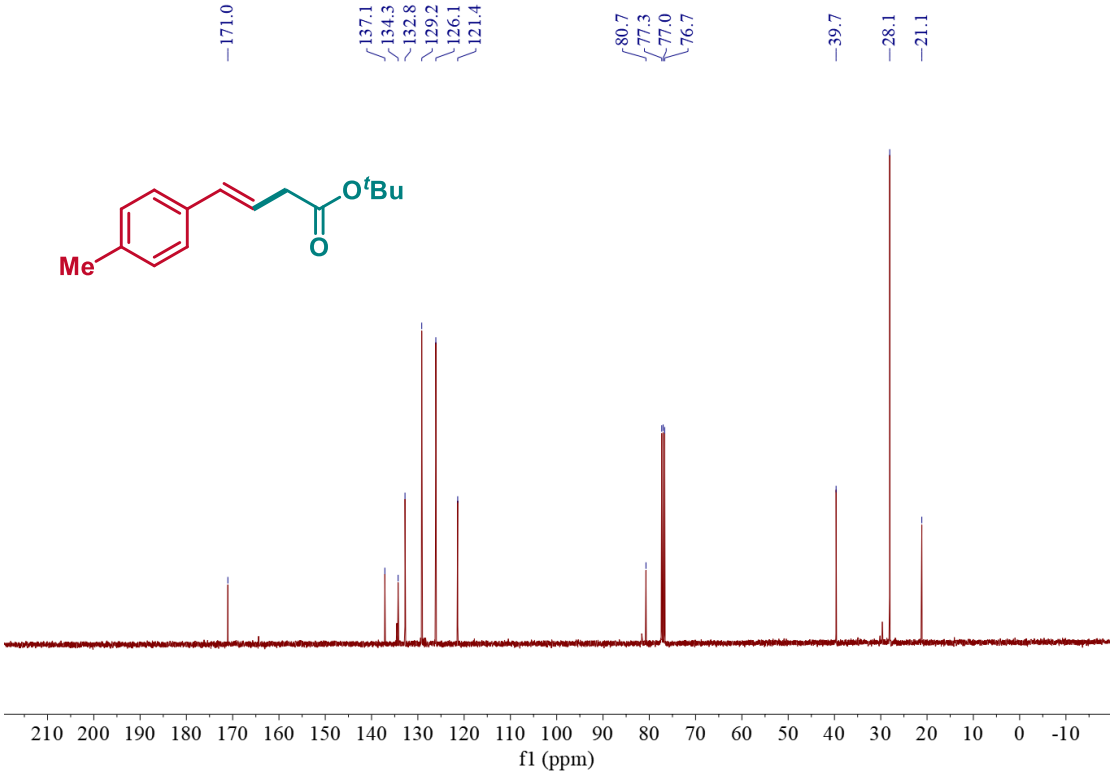
^{13}C NMR Spectrum of ethyl (*E*)-4-(furan-2-yl)but-3-enoate 3w



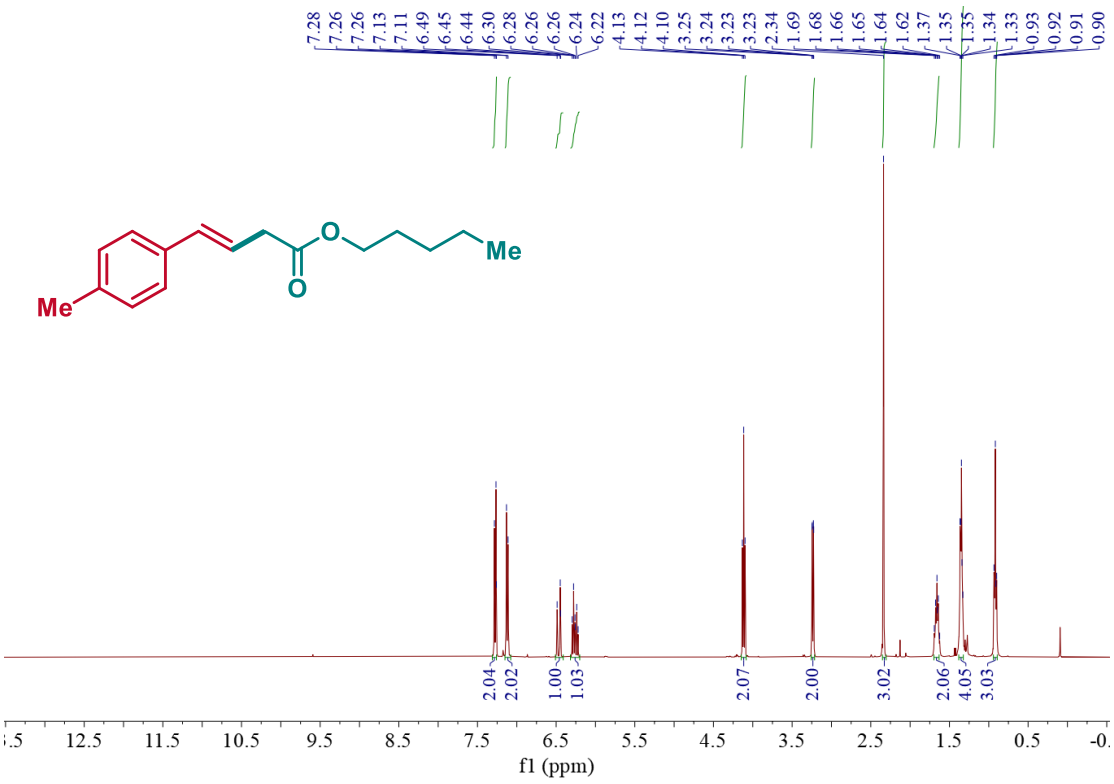
^{1}H NMR Spectrum of *tert*-butyl (*E*)-4-(*p*-tolyl)but-3-enoate 3ab



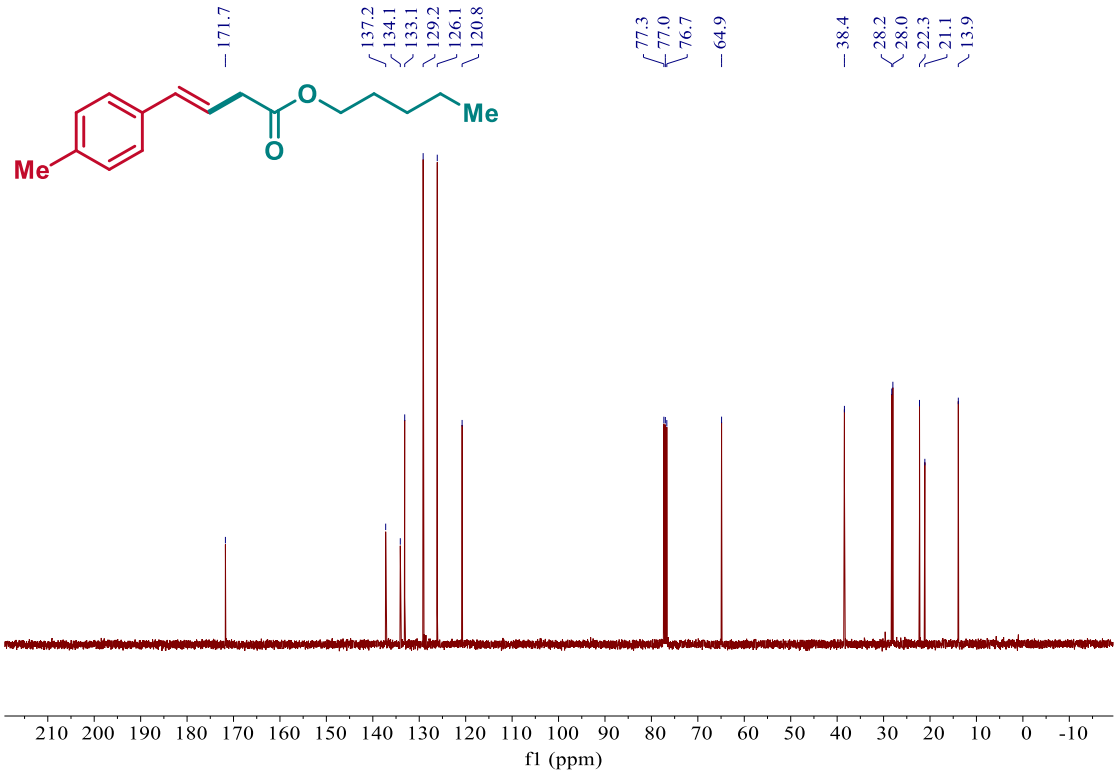
^{13}C NMR Spectrum of *tert*-butyl (*E*)-4-(*p*-tolyl)but-3-enoate 3ab



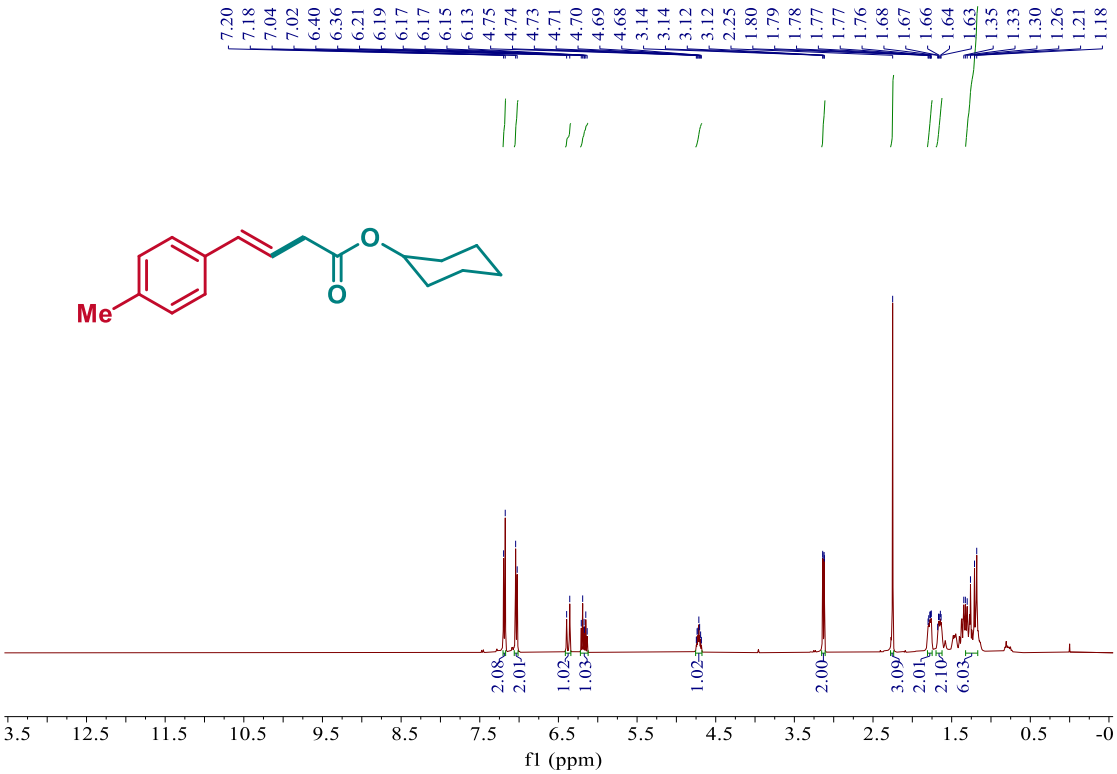
^{1}H NMR Spectrum of pentyl (*E*)-4-(*p*-tolyl)but-3-enoate 3ac



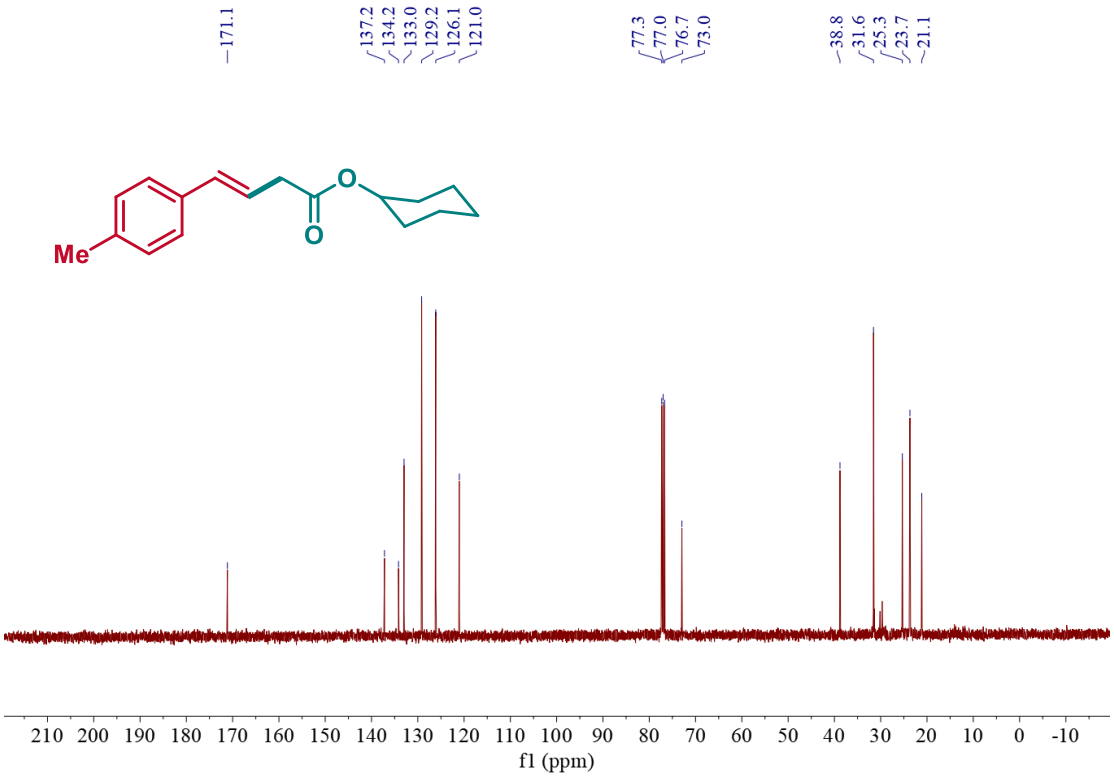
^{13}C NMR Spectrum of pentyl (*E*)-4-(*p*-tolyl)but-3-enoate 3ac



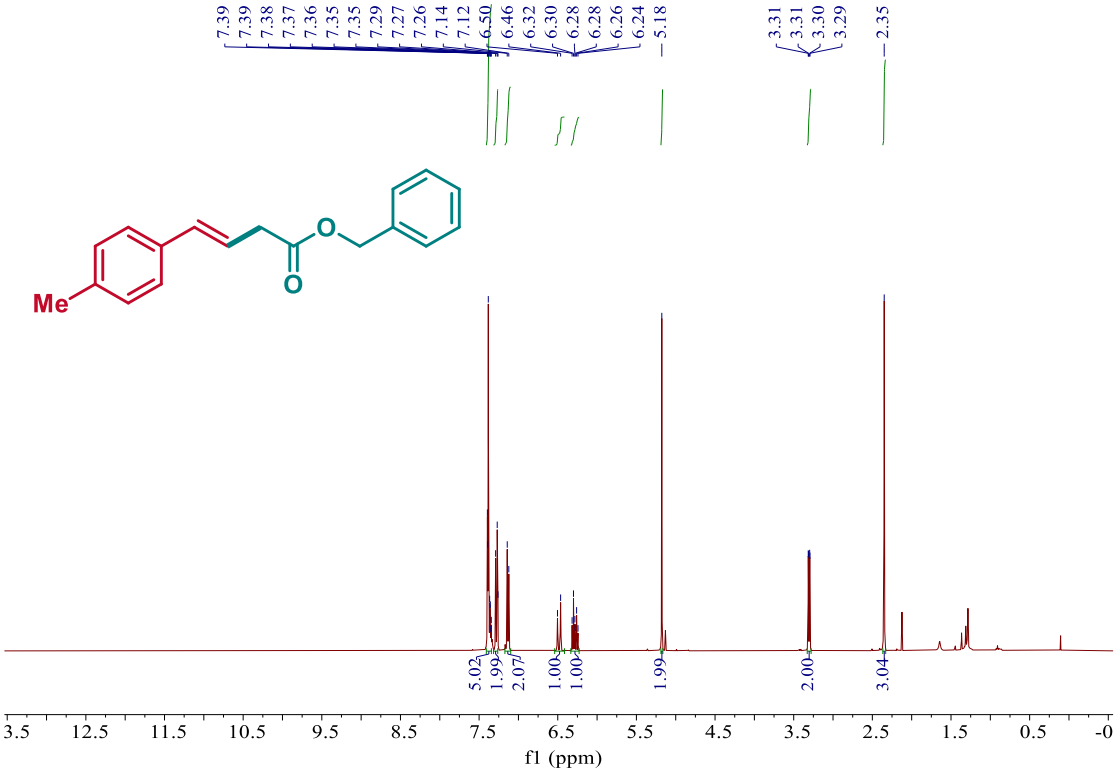
^{1}H NMR Spectrum of cyclohexyl (*E*)-4-(*p*-tolyl)but-3-enoate 3ad



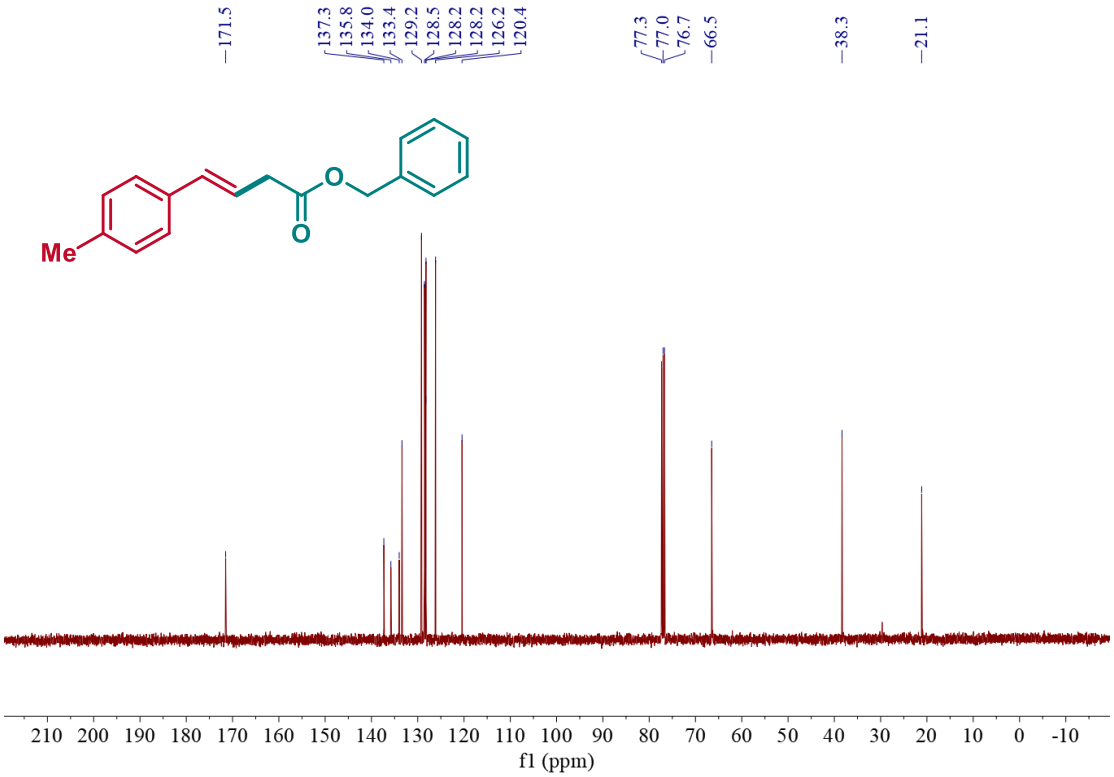
^{13}C NMR Spectrum of cyclohexyl (*E*)-4-(p-tolyl)but-3-enoate 3ad



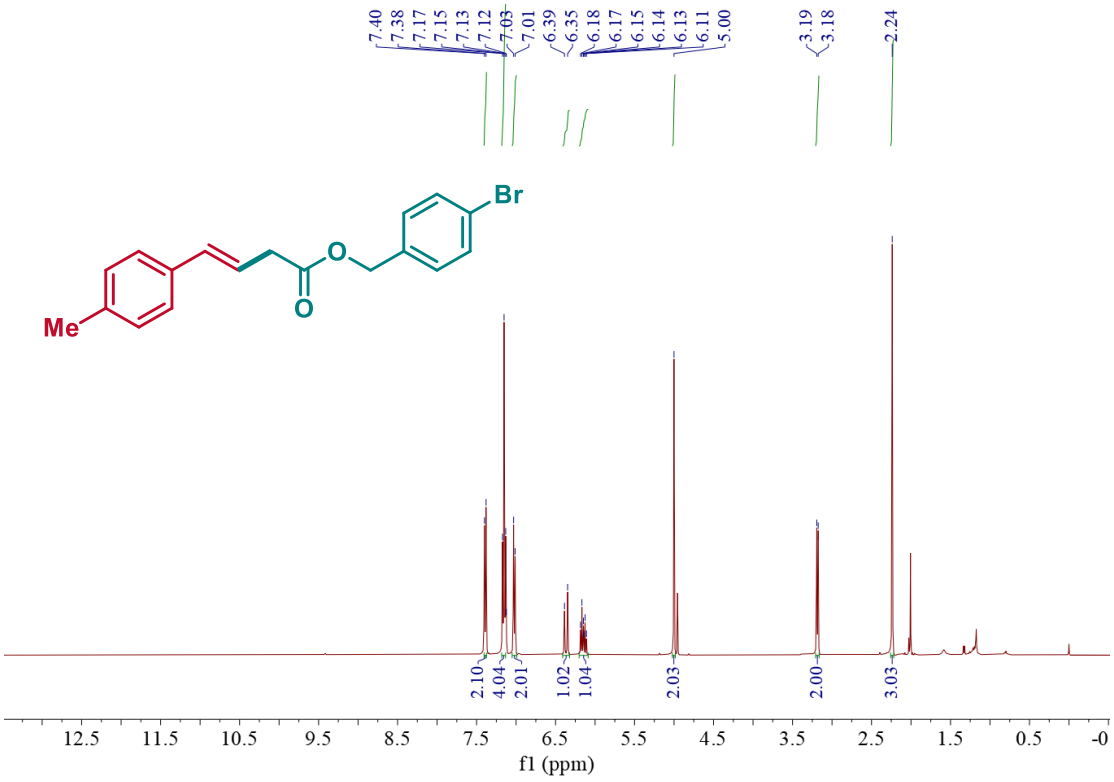
^{1}H NMR Spectrum of benzyl (*E*)-4-(*p*-tolyl)but-3-enoate 3ae



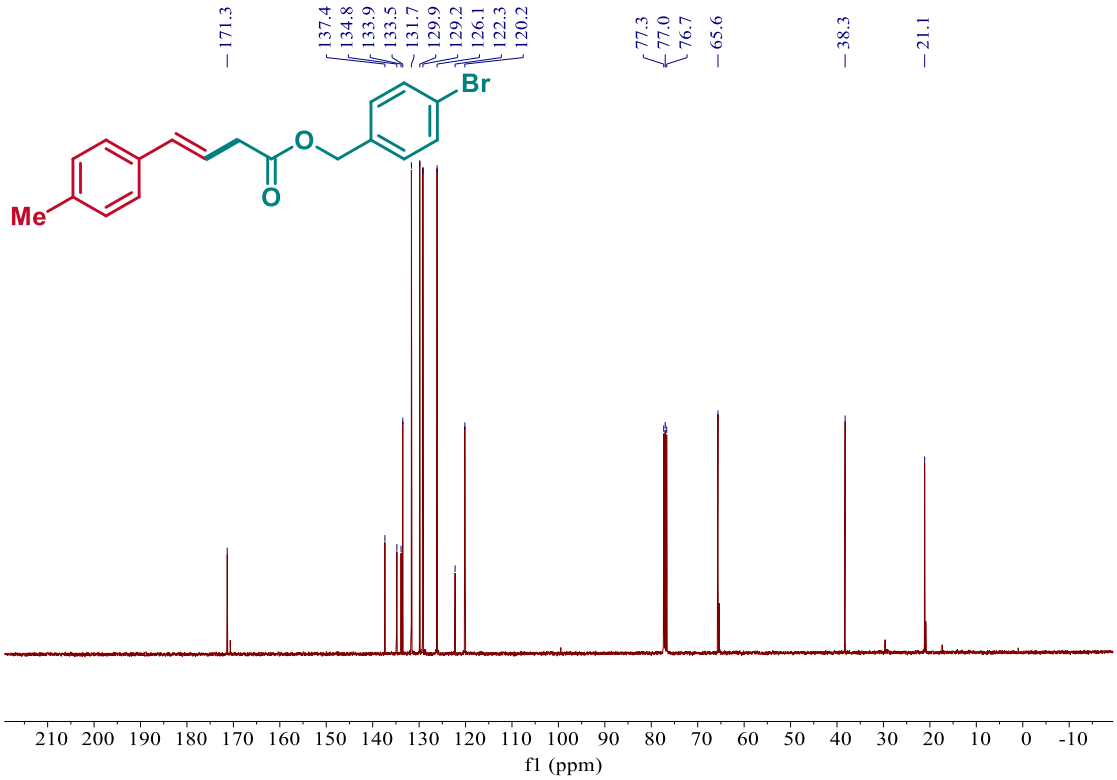
^{13}C NMR Spectrum of benzyl (*E*)-4-(*p*-tolyl)but-3-enoate 3ae



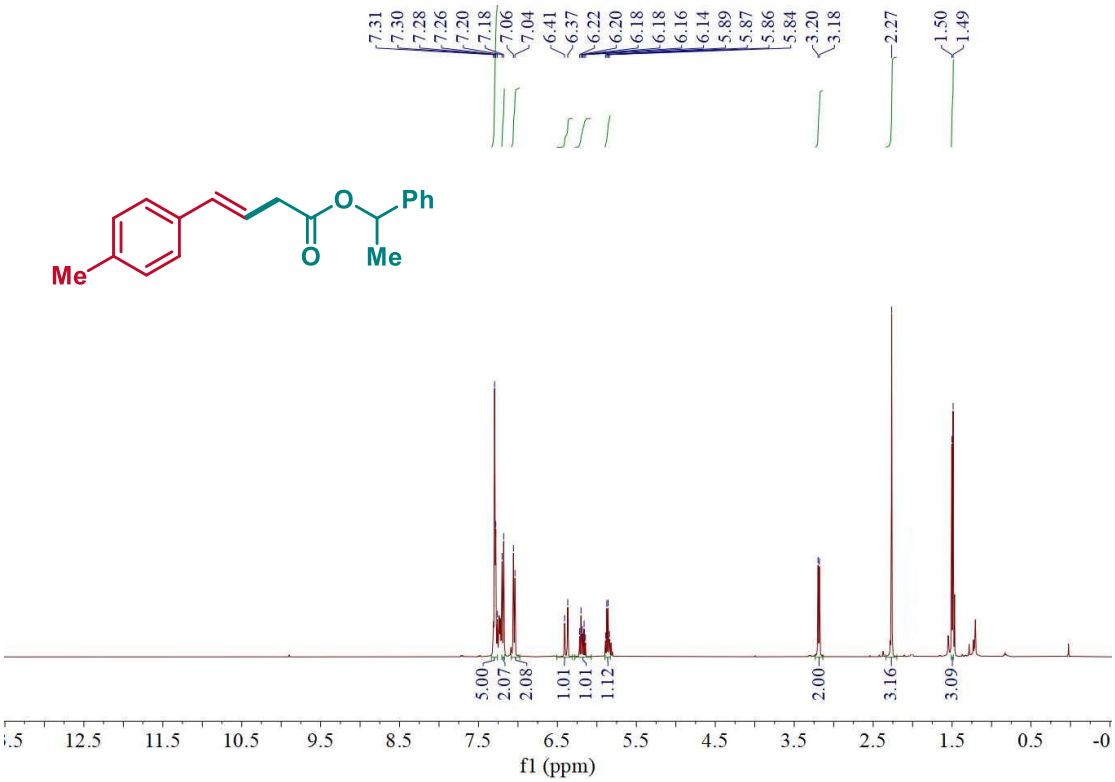
^{1}H NMR Spectrum of 4-bromobenzyl (*E*)-4-(*p*-tolyl)but-3-enoate 3af



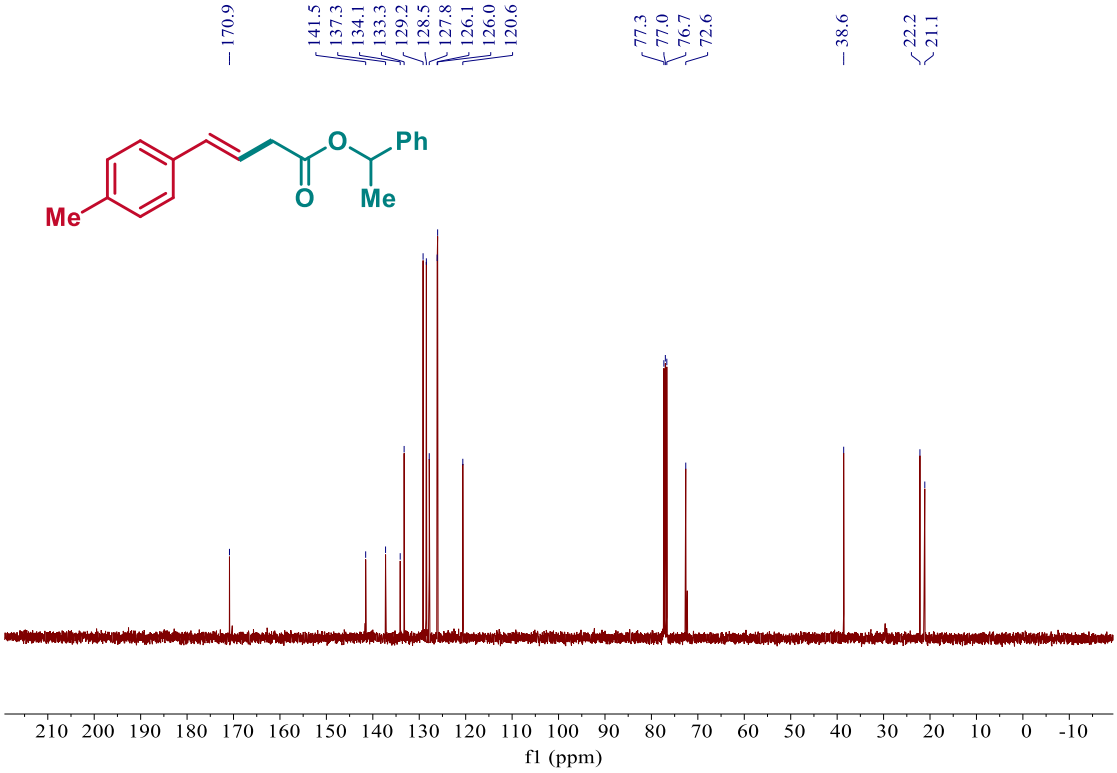
^{13}C NMR Spectrum of 4-bromobenzyl (*E*)-4-(*p*-tolyl)but-3-enoate 3af



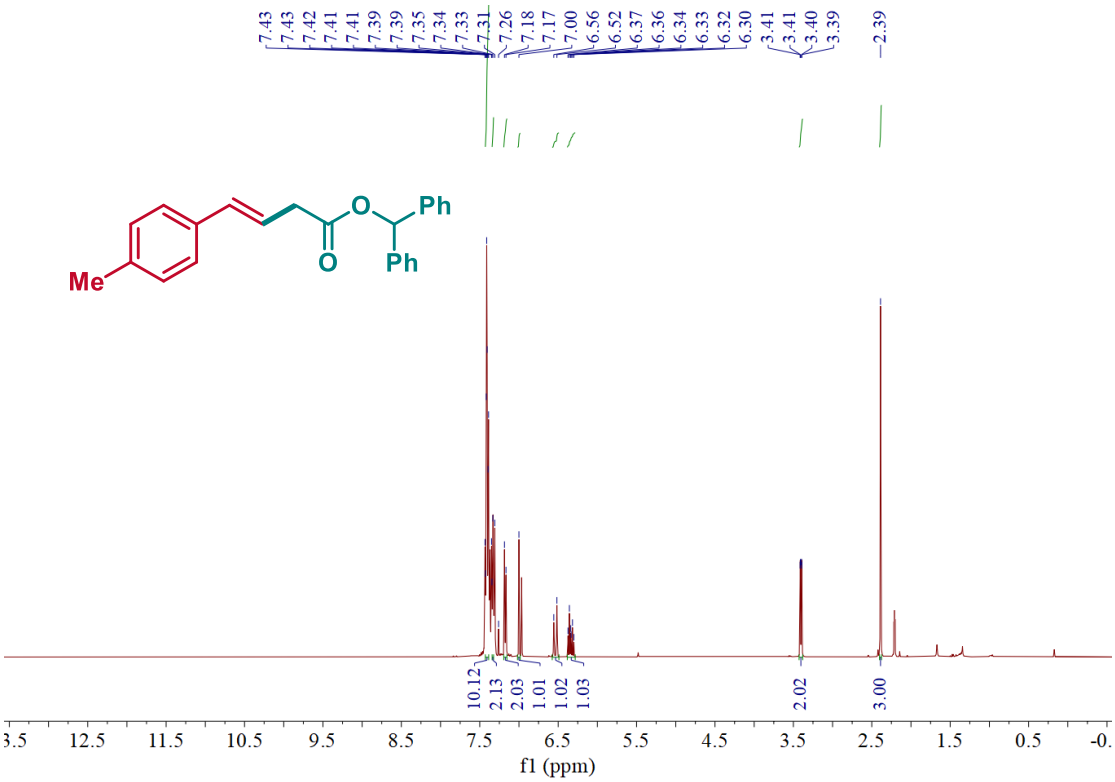
^{1}H NMR Spectrum of 1-phenylethyl (*E*)-4-(*p*-tolyl)but-3-enoate 3ag



^{13}C NMR Spectrum of 1-phenylethyl (*E*)-4-(*p*-tolyl)but-3-enoate 3ag



^{1}H NMR Spectrum of benzhydryl (*E*)-4-(*p*-tolyl)but-3-enoate 3ah



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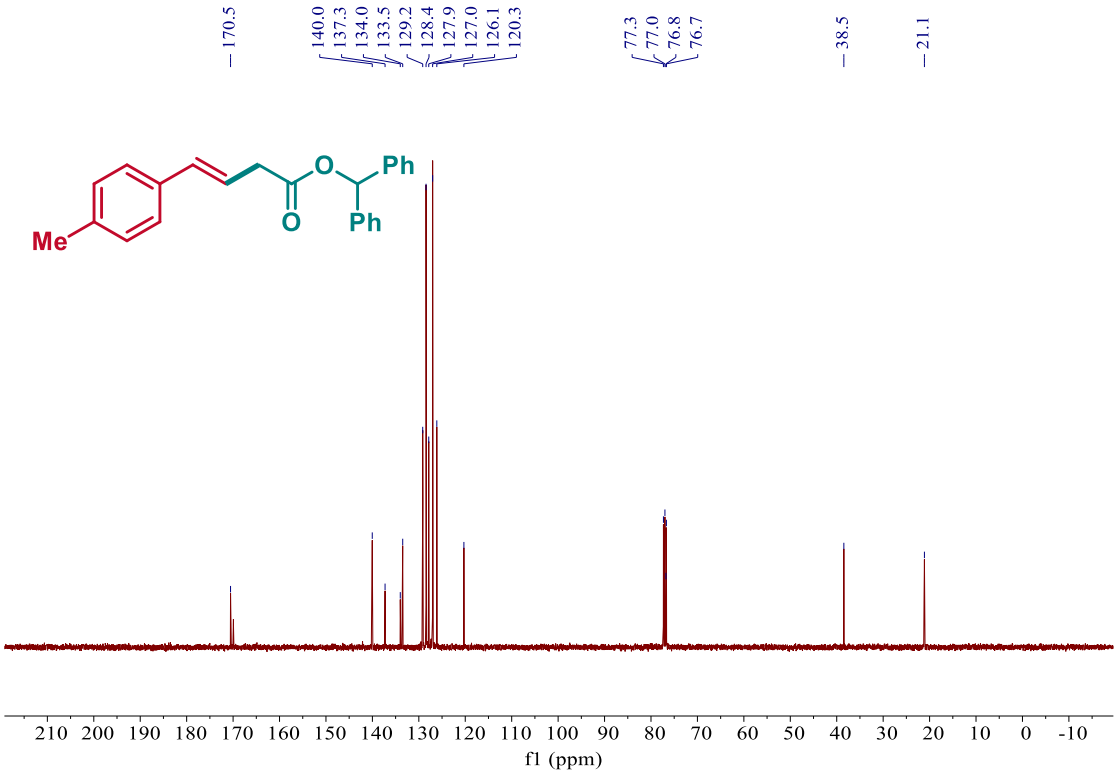
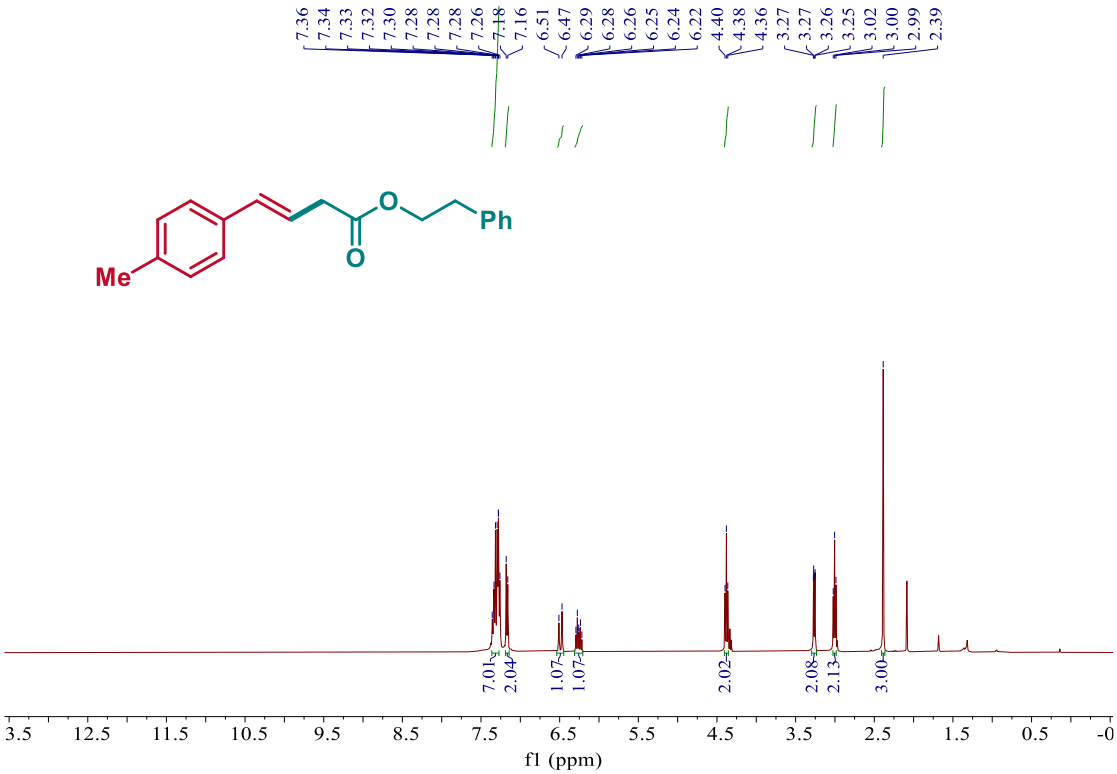


^{1}H NMR Spectrum of phenethyl (*E*)-4-(*p*-tolyl)but-3-enoate 3ai



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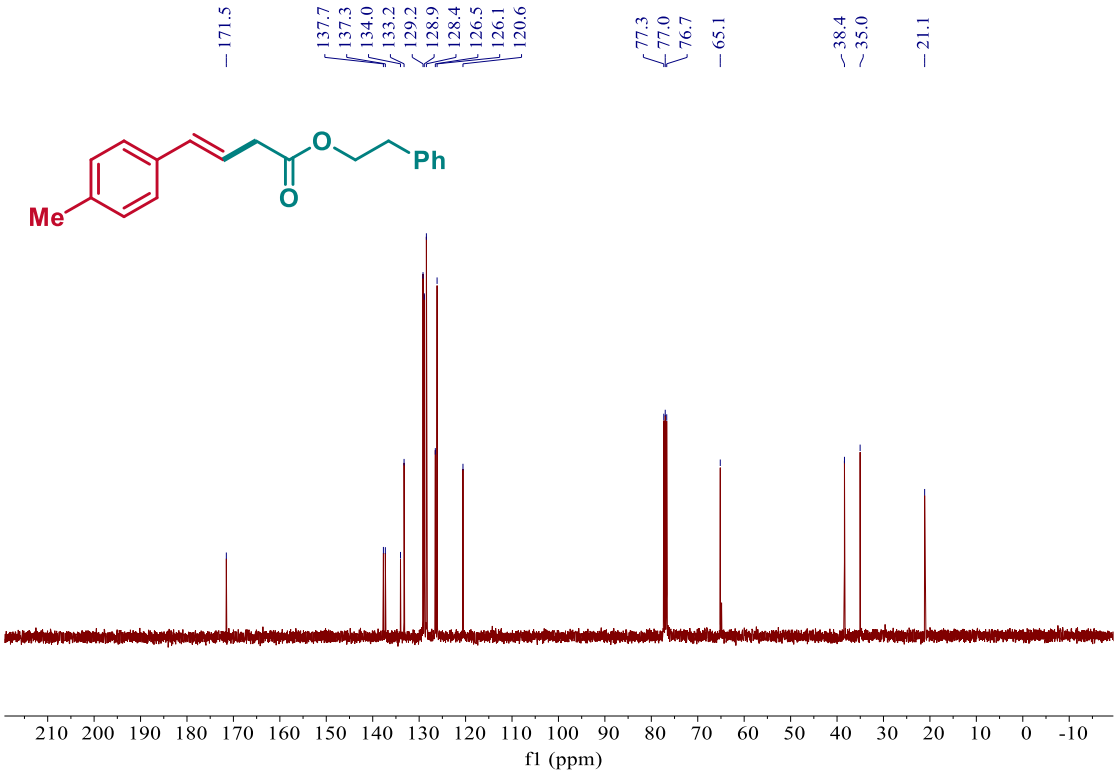
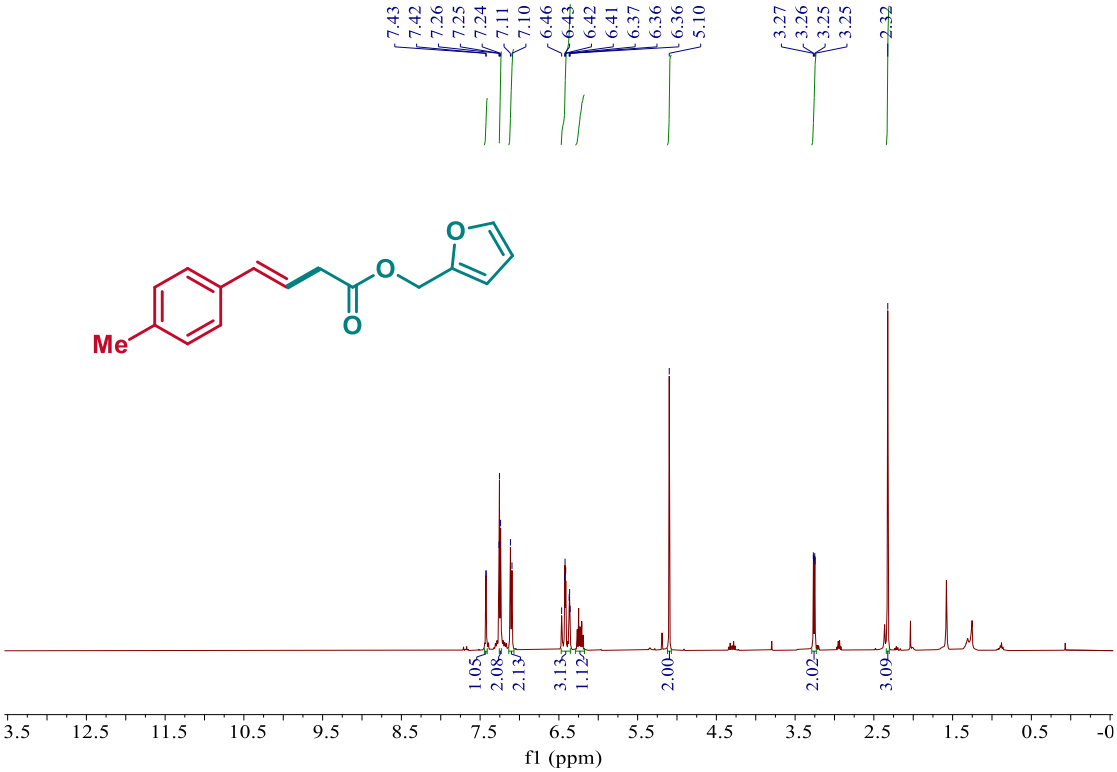
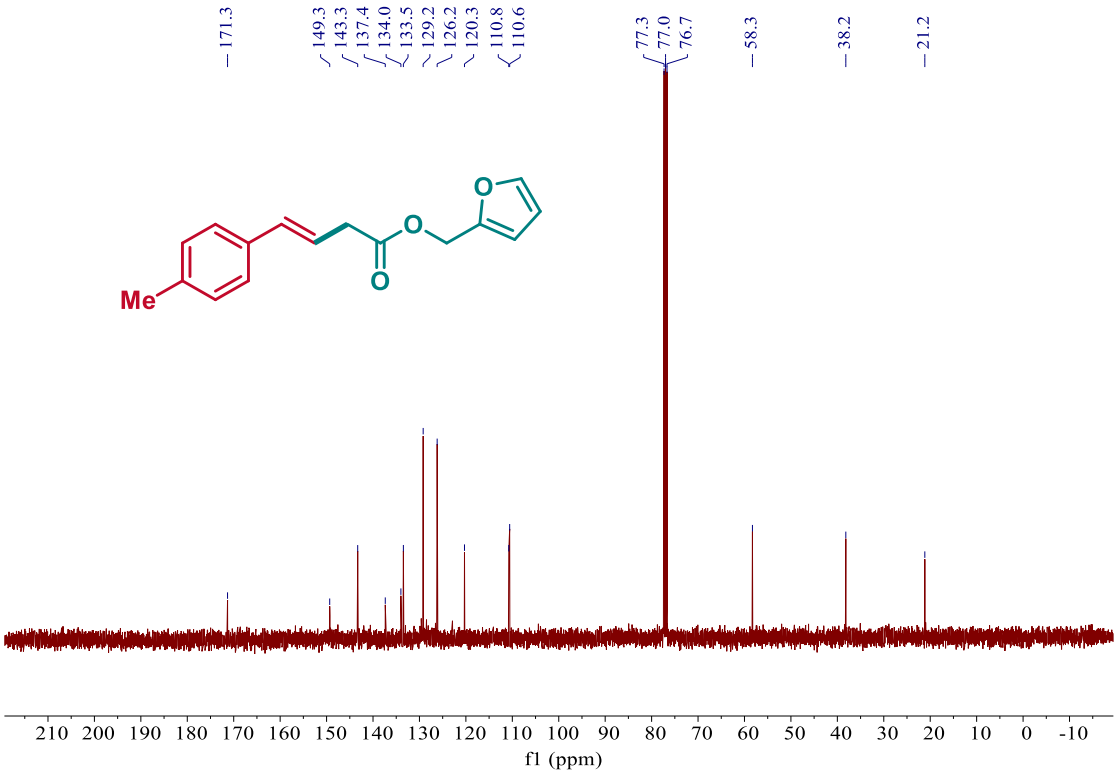


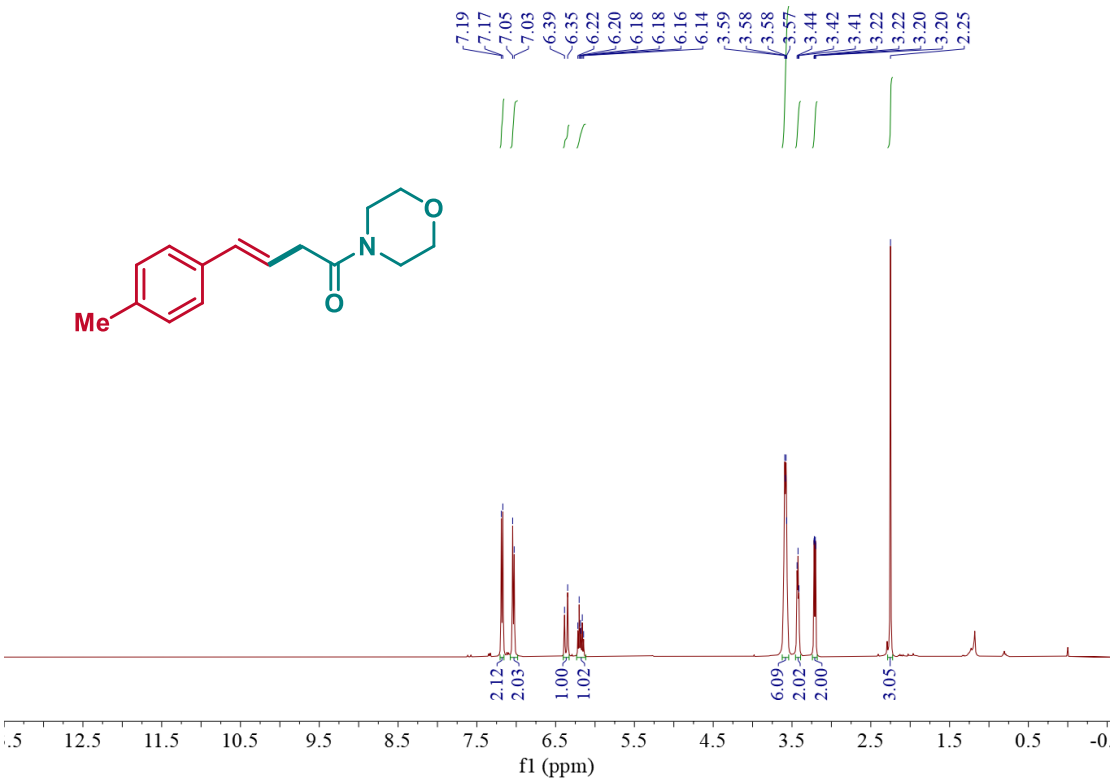
^{1}H NMR Spectrum of furan-2-ylmethyl (*E*)-4-(*p*-tolyl)but-3-enoate 3aj



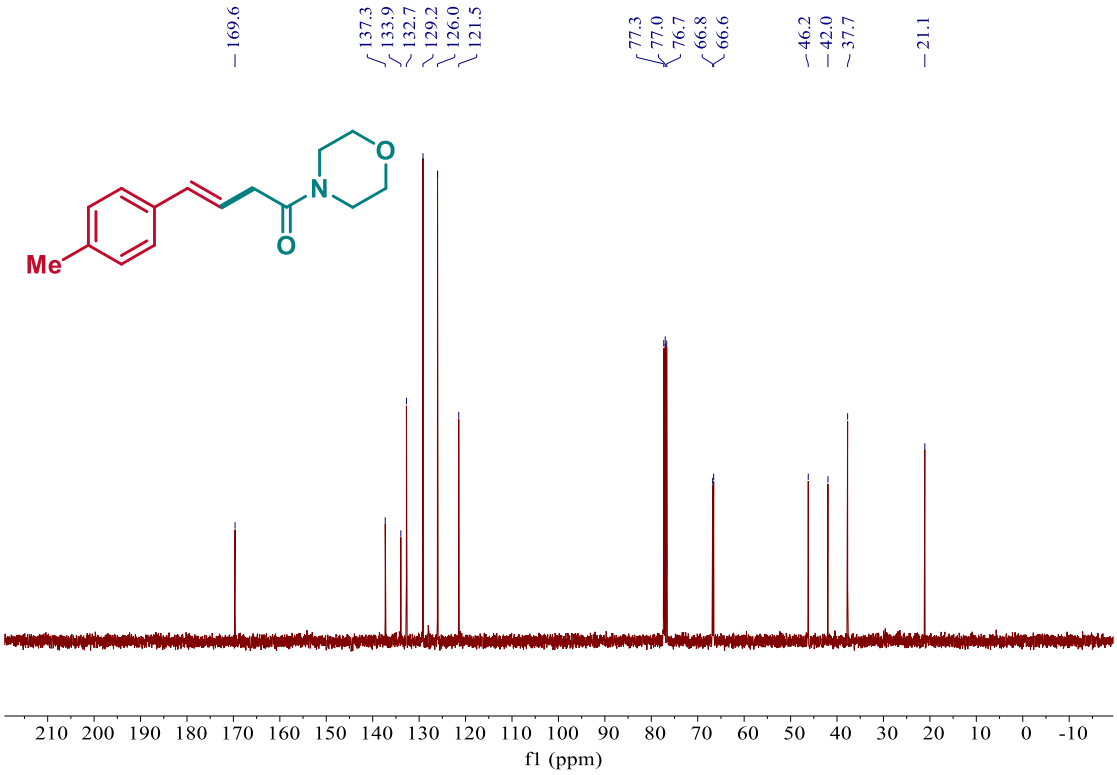
^{13}C NMR Spectrum of furan-2-ylmethyl (*E*)-4-(*p*-tolyl)but-3-enoate 3aj



^{1}H NMR Spectrum of (*E*)-1-morpholino-4-(*p*-tolyl)but-3-en-1-one 3ak



^{13}C NMR Spectrum of (*E*)-1-morpholino-4-(*p*-tolyl)but-3-en-1-one 3ak



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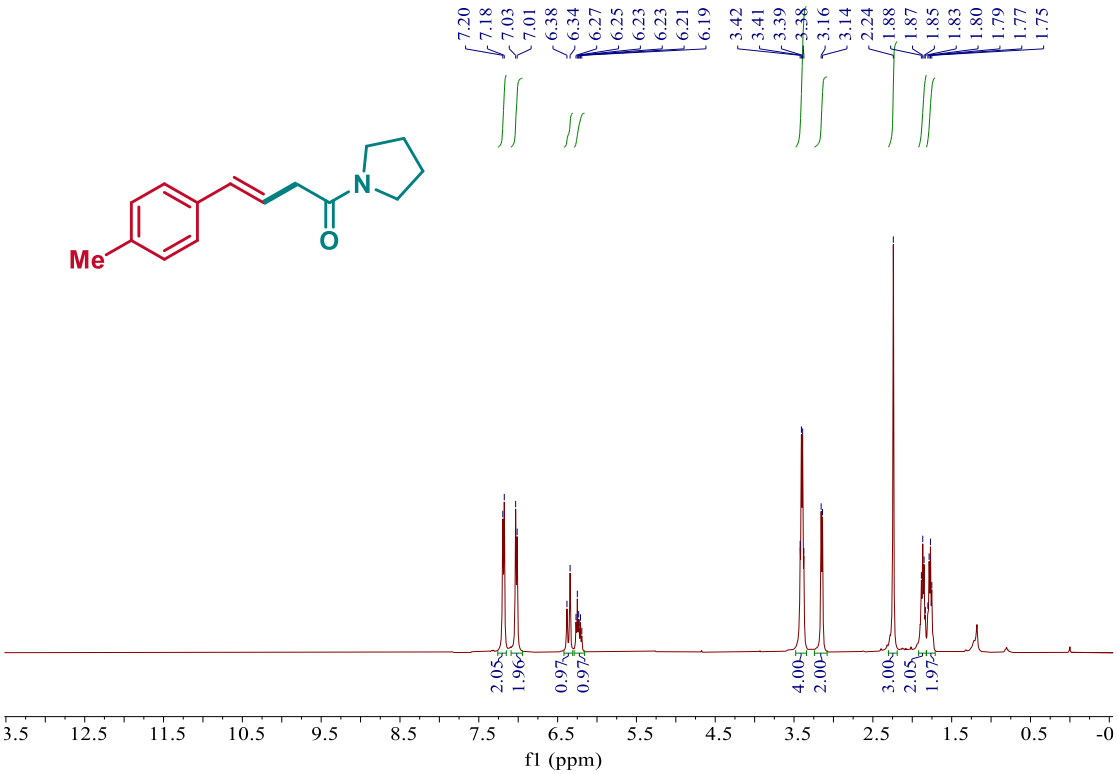
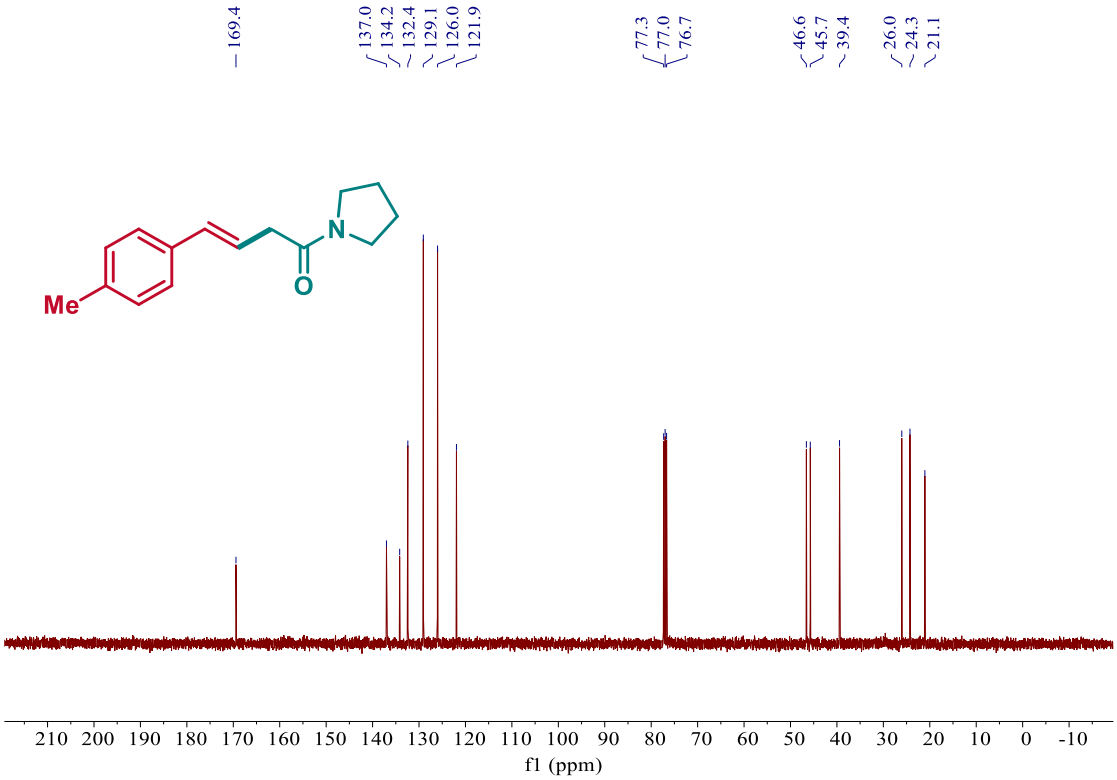
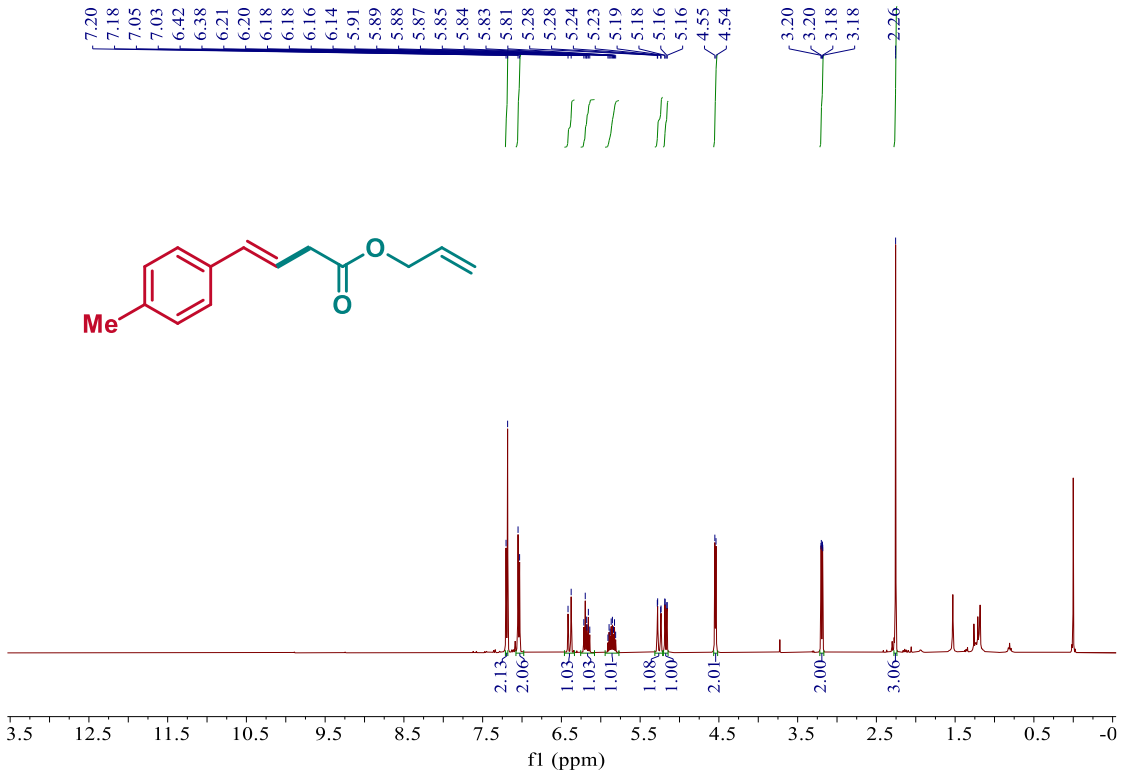


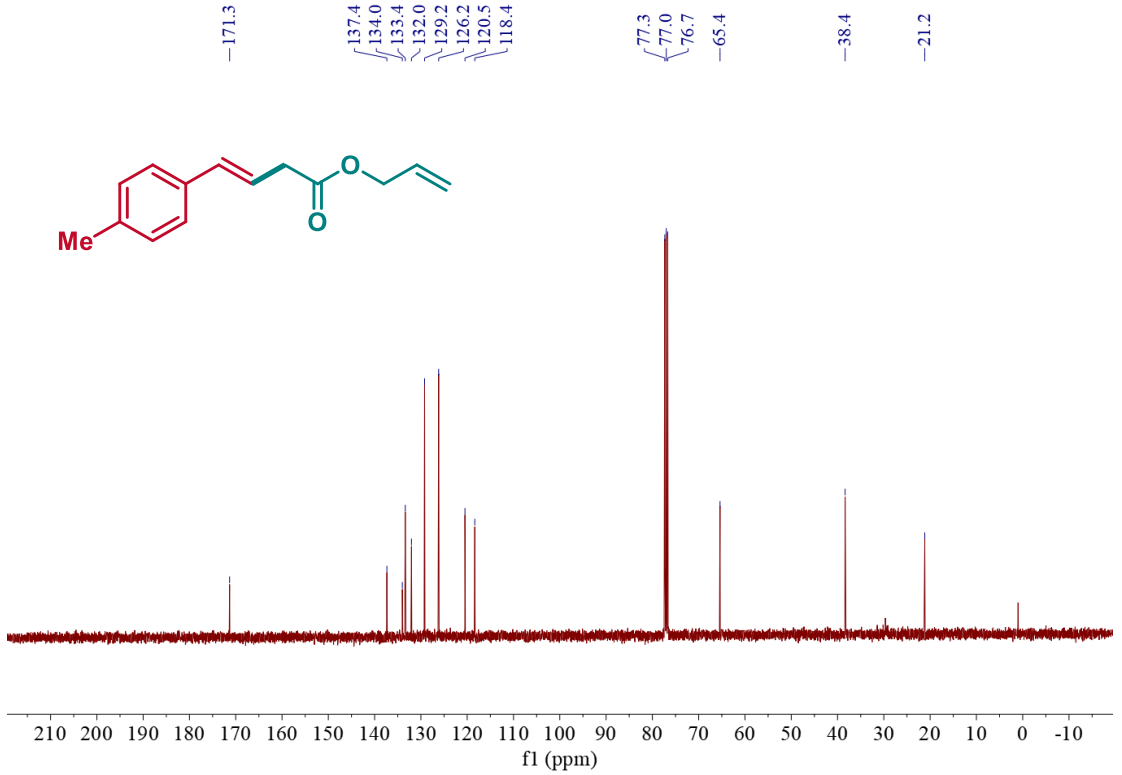
^{13}C NMR Spectrum of (*E*)-1-(pyrrolidin-1-yl)-4-(*p*-tolyl)but-3-en-1-one 3al



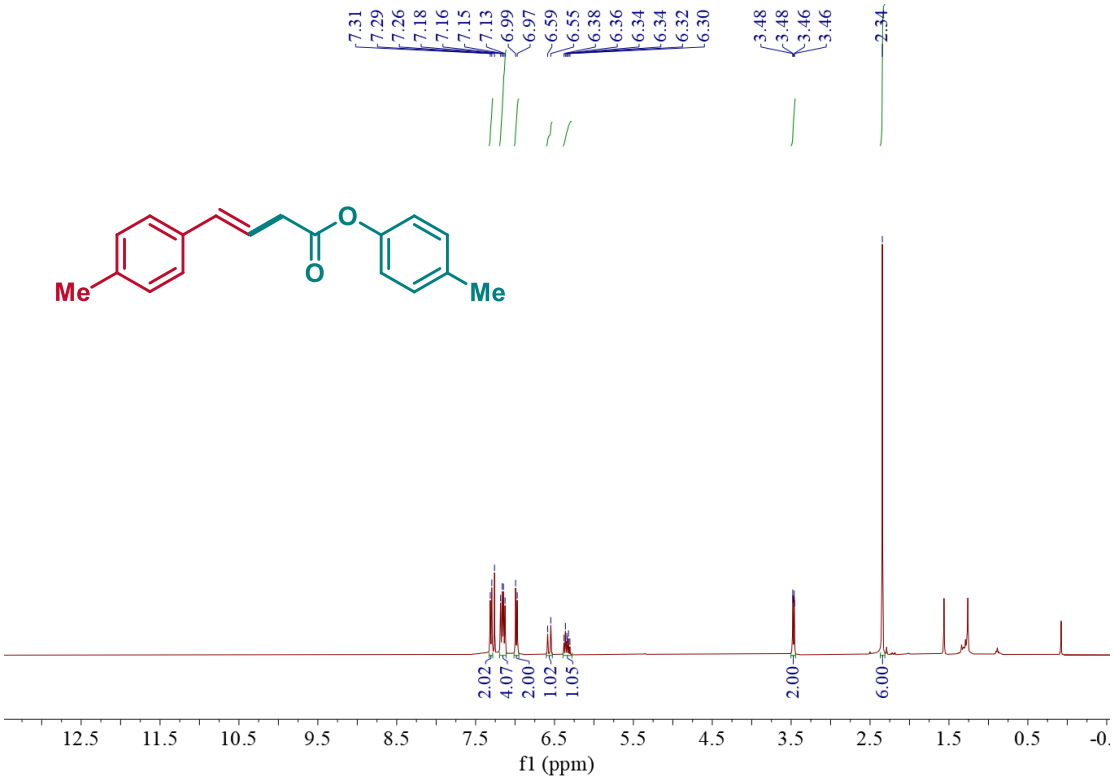
^{1}H NMR Spectrum of allyl (*E*)-4-(*p*-tolyl)but-3-enoate 3am



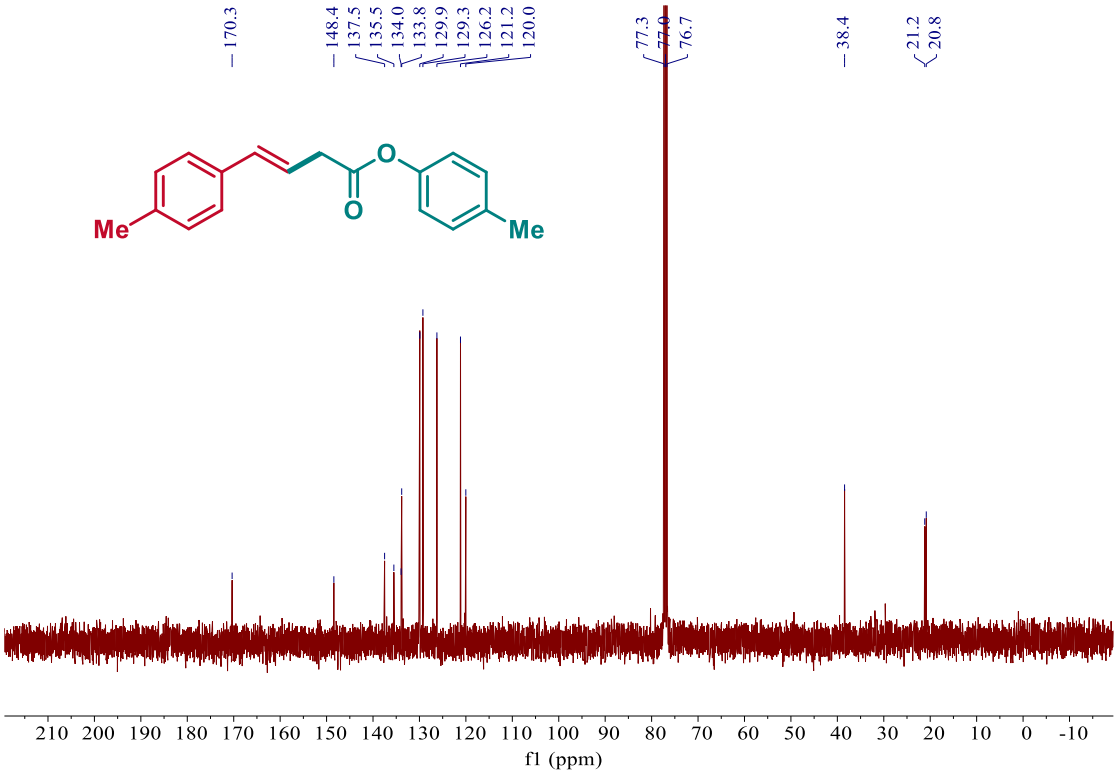
^{13}C NMR Spectrum of allyl (*E*)-4-(*p*-tolyl)but-3-enoate 3am



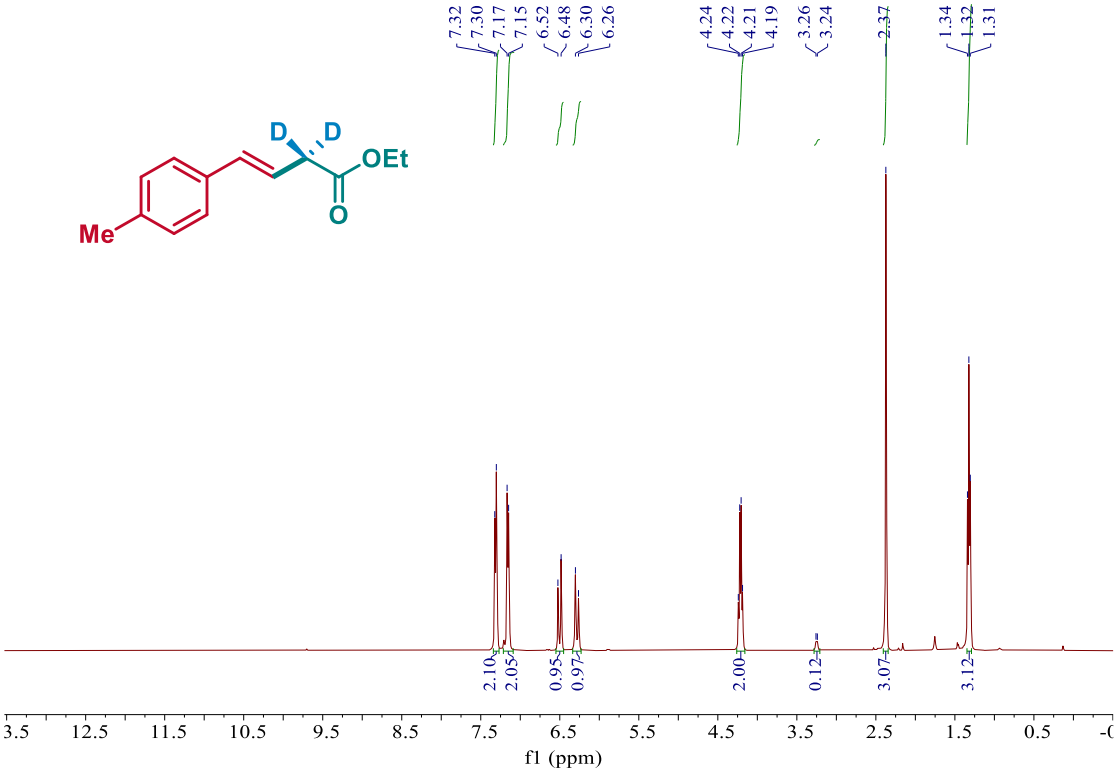
^{1}H NMR Spectrum of *p*-tolyl (*E*)-4-(*p*-tolyl)but-3-enoate 3an



^{13}C NMR Spectrum of *p*-tolyl (*E*)-4-(*p*-tolyl)but-3-enoate 3an



^{1}H NMR Spectrum of ethyl (*E*)-4-(*p*-tolyl)but-3-enoate-2,2-D$_2$ 3a'



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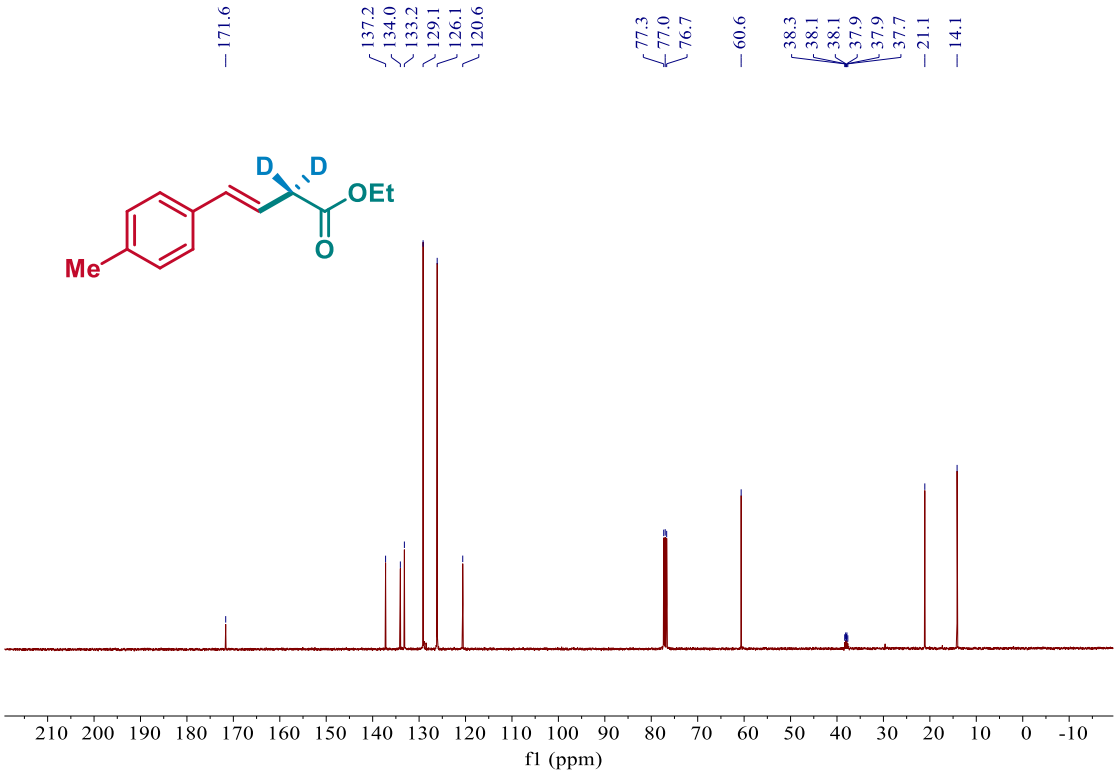
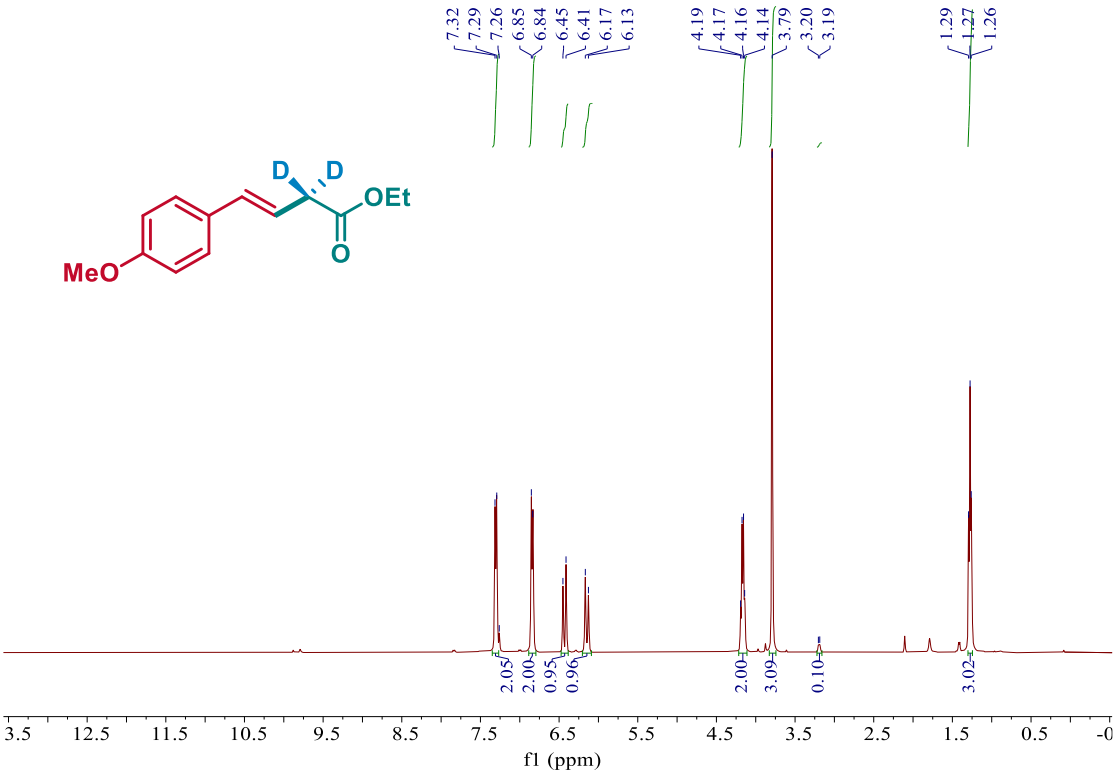


^{1}H NMR Spectrum of ethyl (*E*)-4-(4-methoxyphenyl)but-3-enoate-2,2-D$_2$ 3c'



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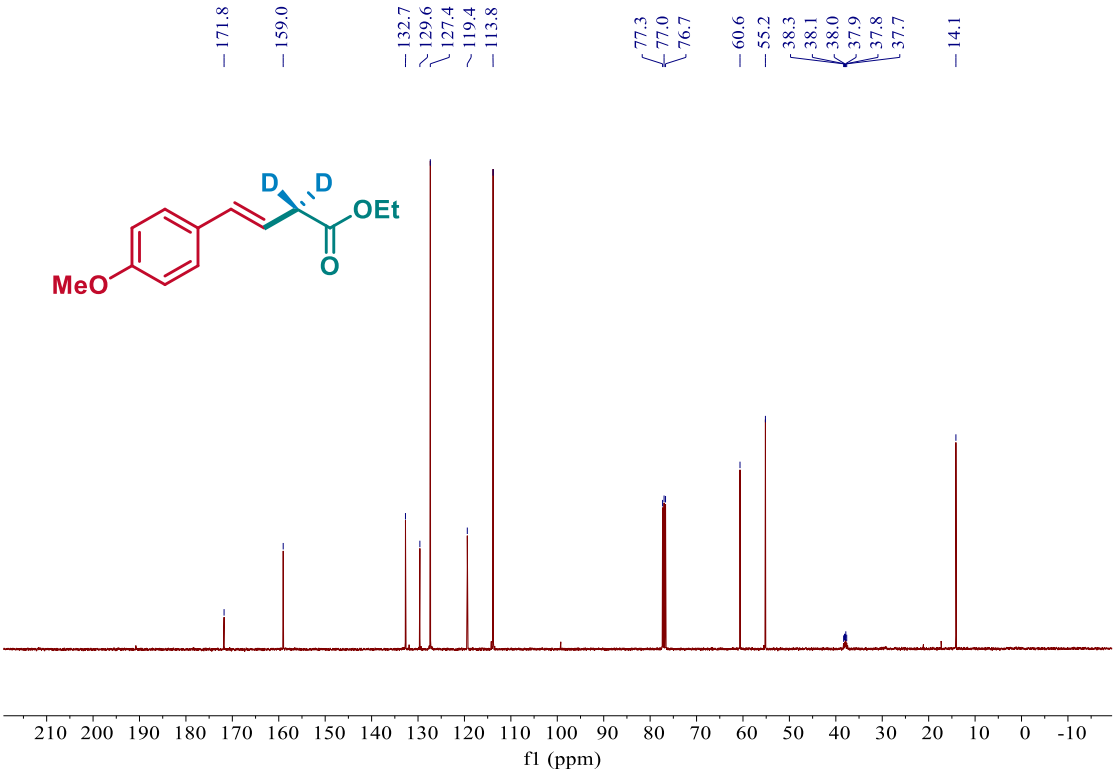
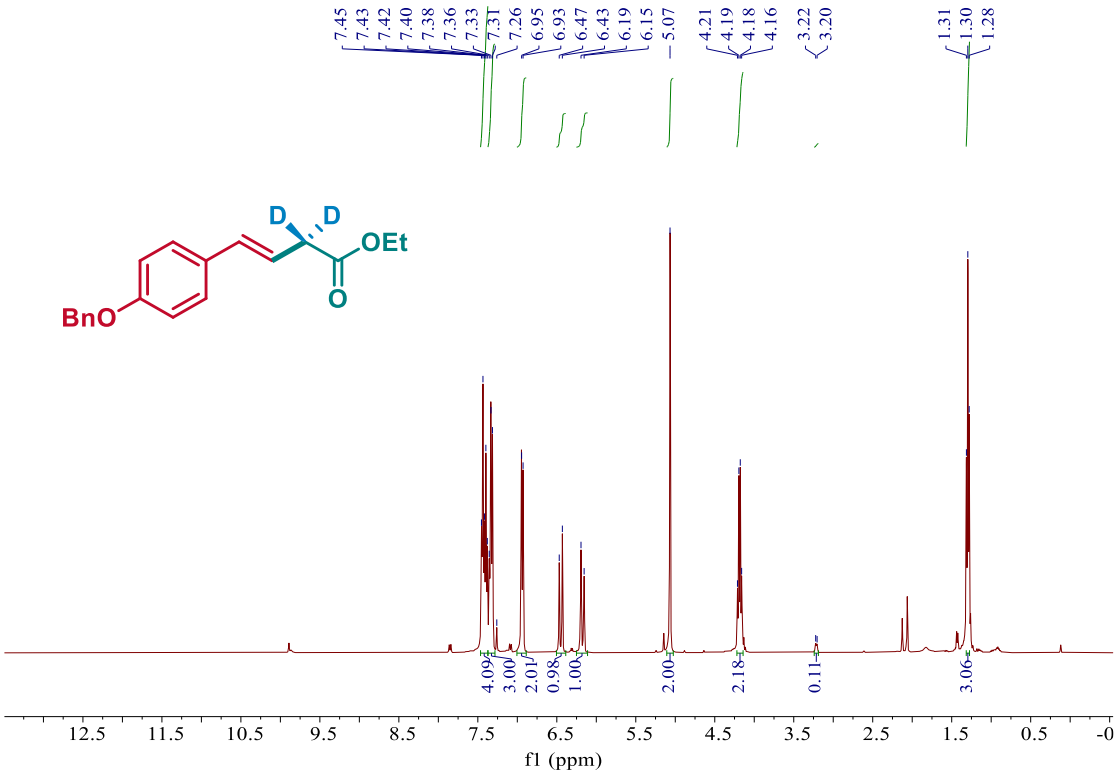


^{1}H NMR Spectrum of ethyl (*E*)-4-(4-(benzyloxy)phenyl)but-3-enoate-2,2-D$_2$ 3d'



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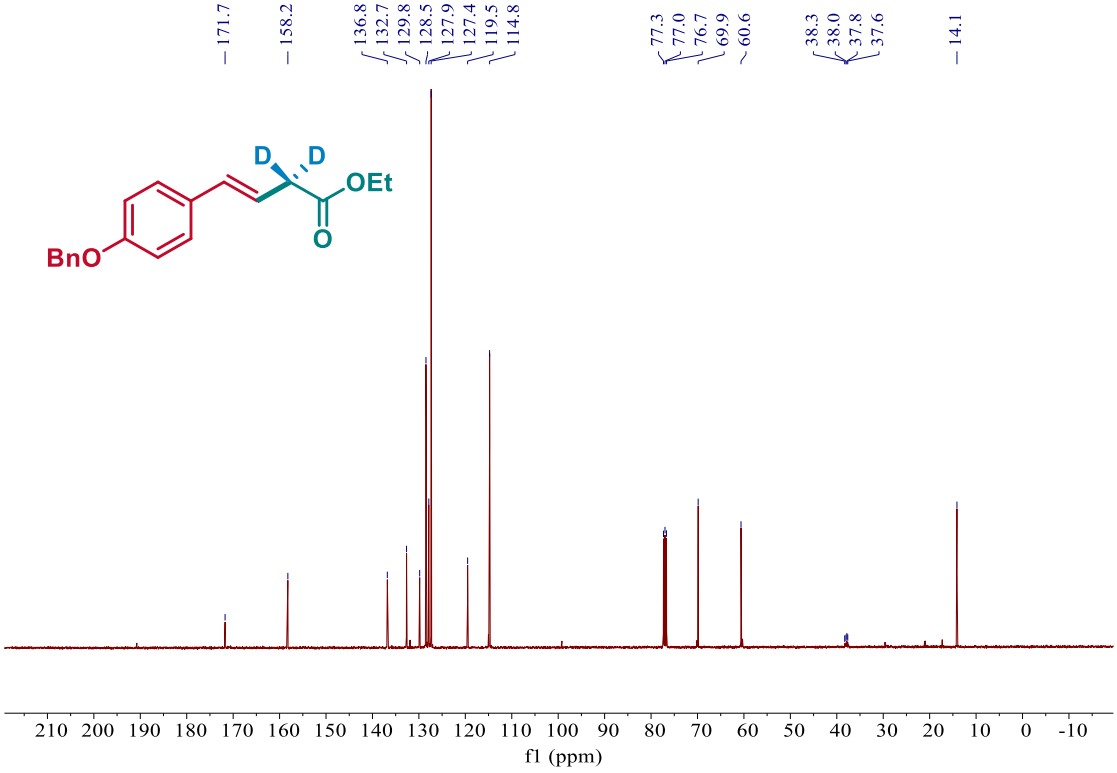
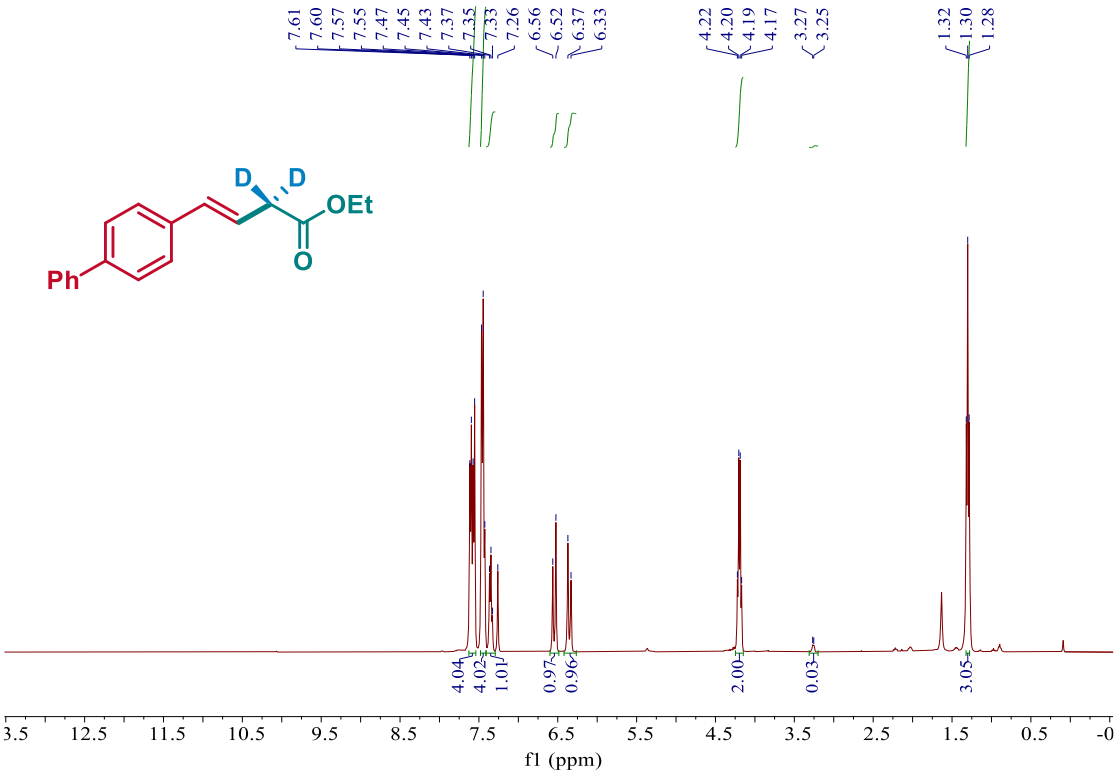
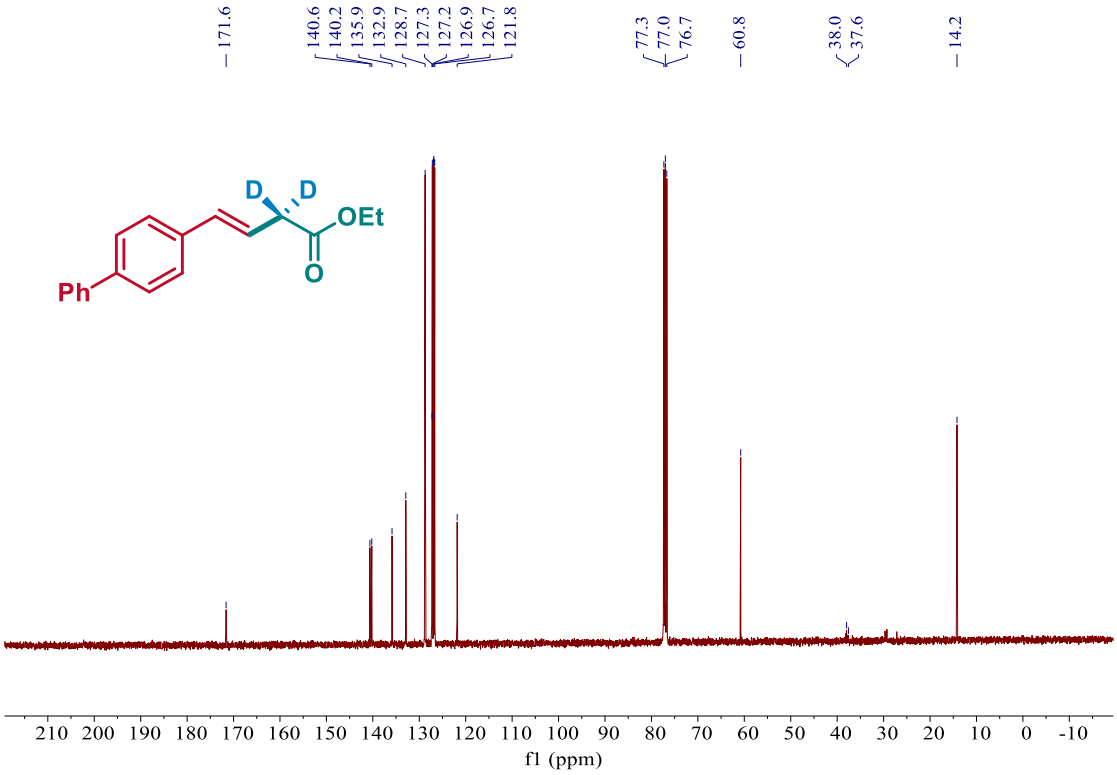


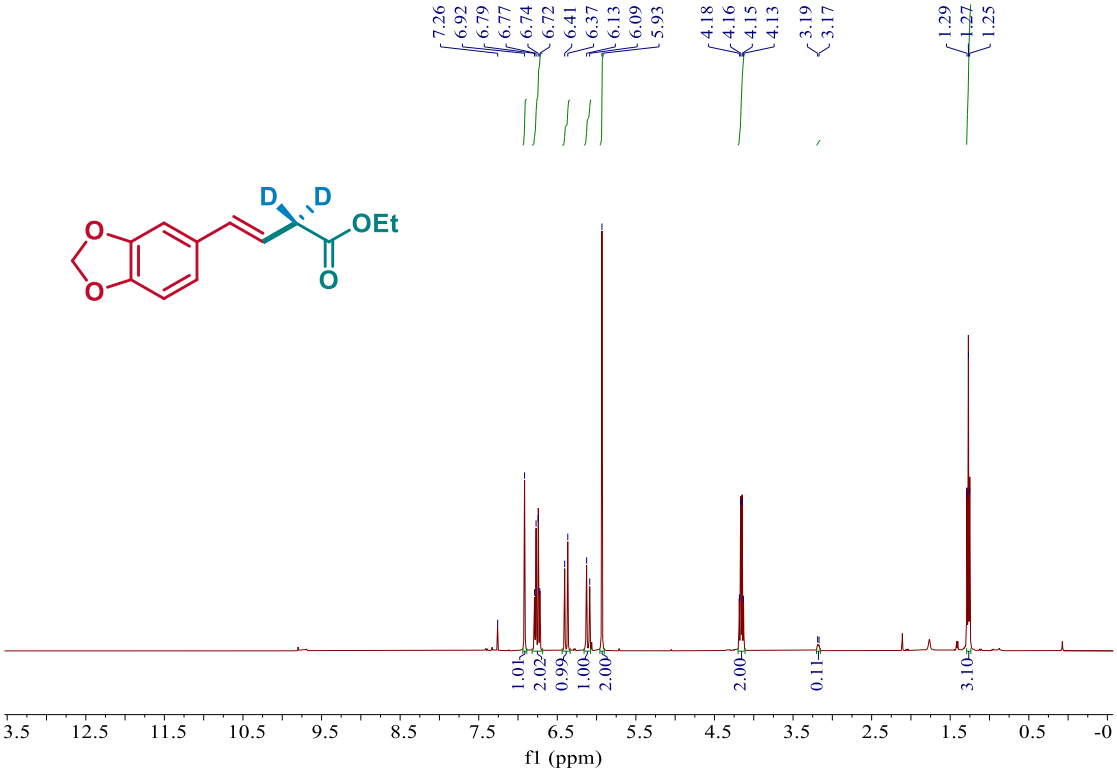
^{1}H NMR Spectrum of ethyl (*E*)-4-([1,1'-biphenyl]-4-yl)but-3-enoate-2,2-D_2 3e'



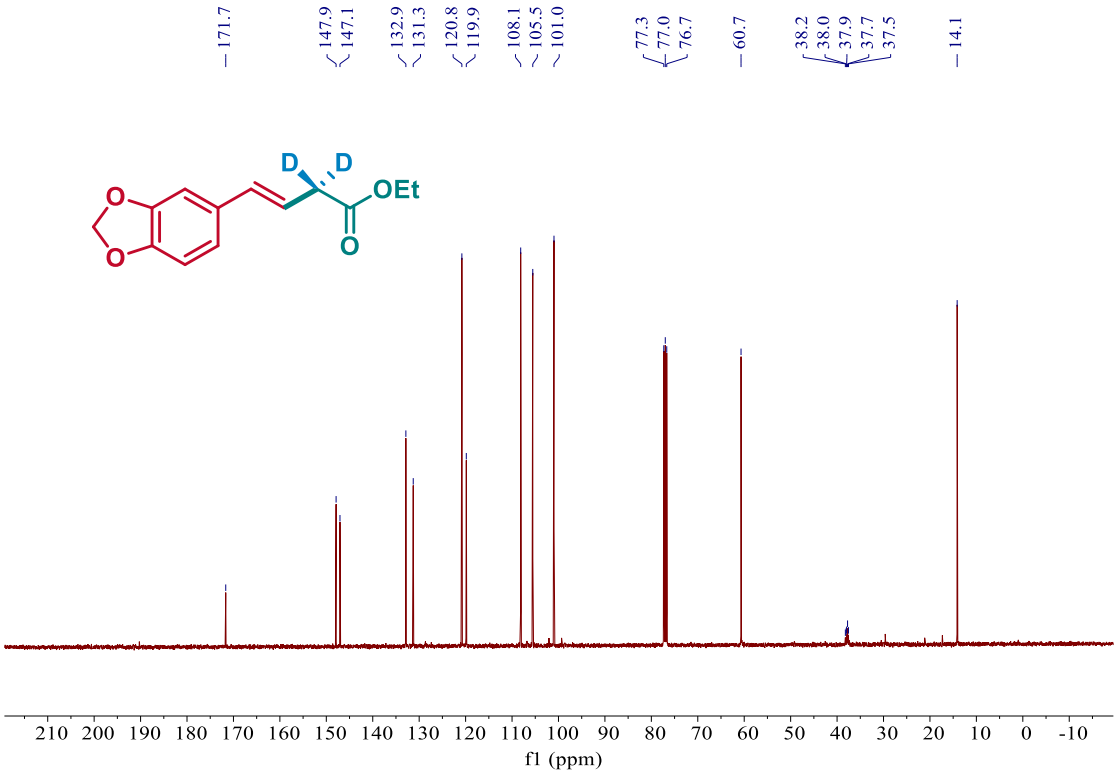
^{13}C NMR Spectrum of ethyl (*E*)-4-([1,1'-biphenyl]-4-yl)but-3-enoate-2,2-D_2 3e'



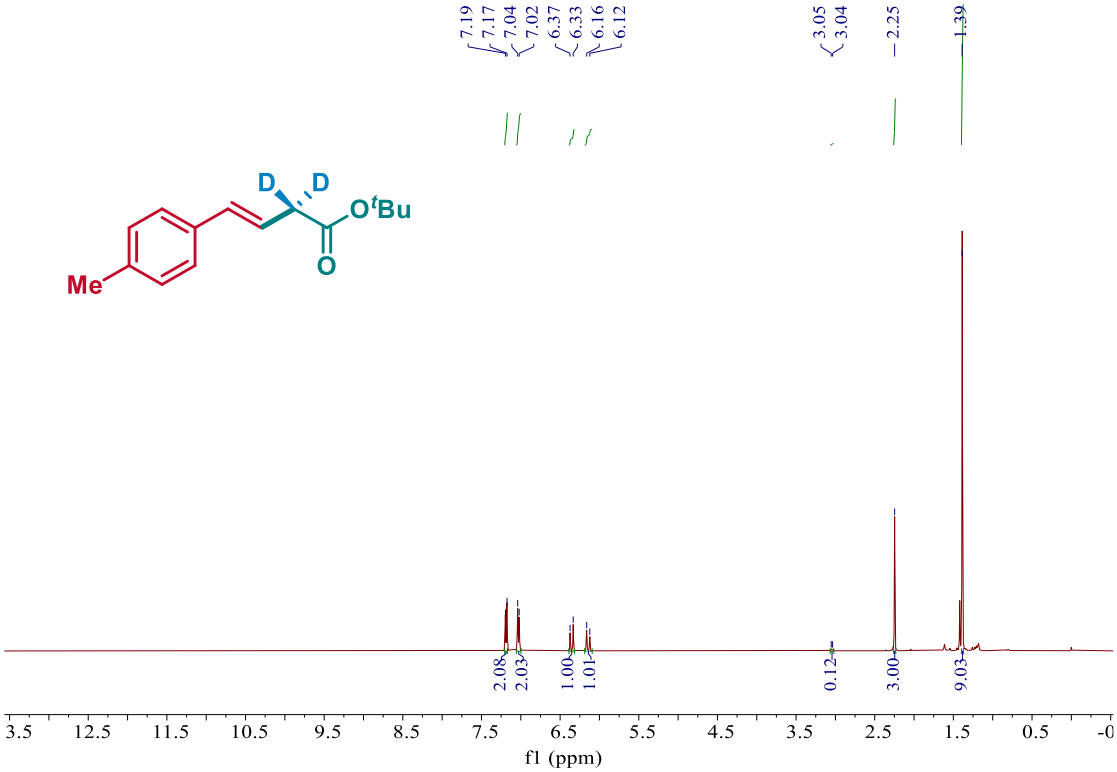
^{1}H NMR Spectrum of ethyl (*E*)-4-(benzo[*d*][1,3]dioxol-5-yl)but-3-enoate-2,2-D_2 3s'



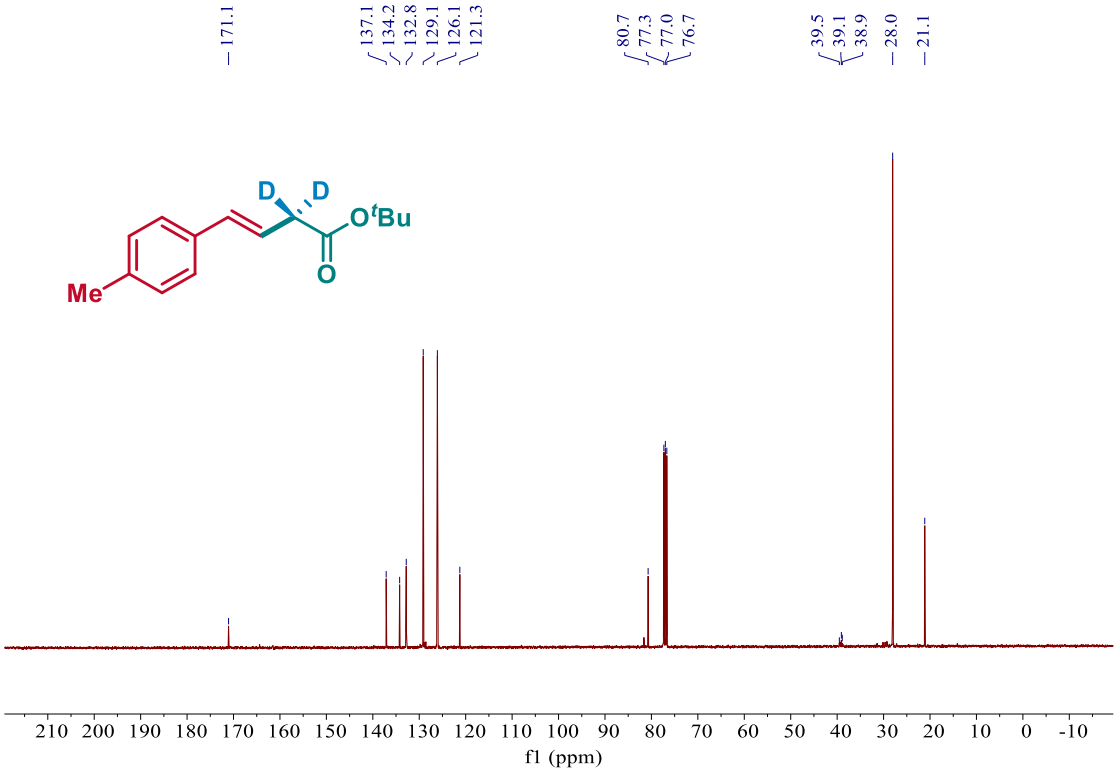
^{13}C NMR Spectrum of ethyl (*E*)-4-(benzo[*d*][1,3]dioxol-5-yl)but-3-enoate-2,2-D_2 3s'



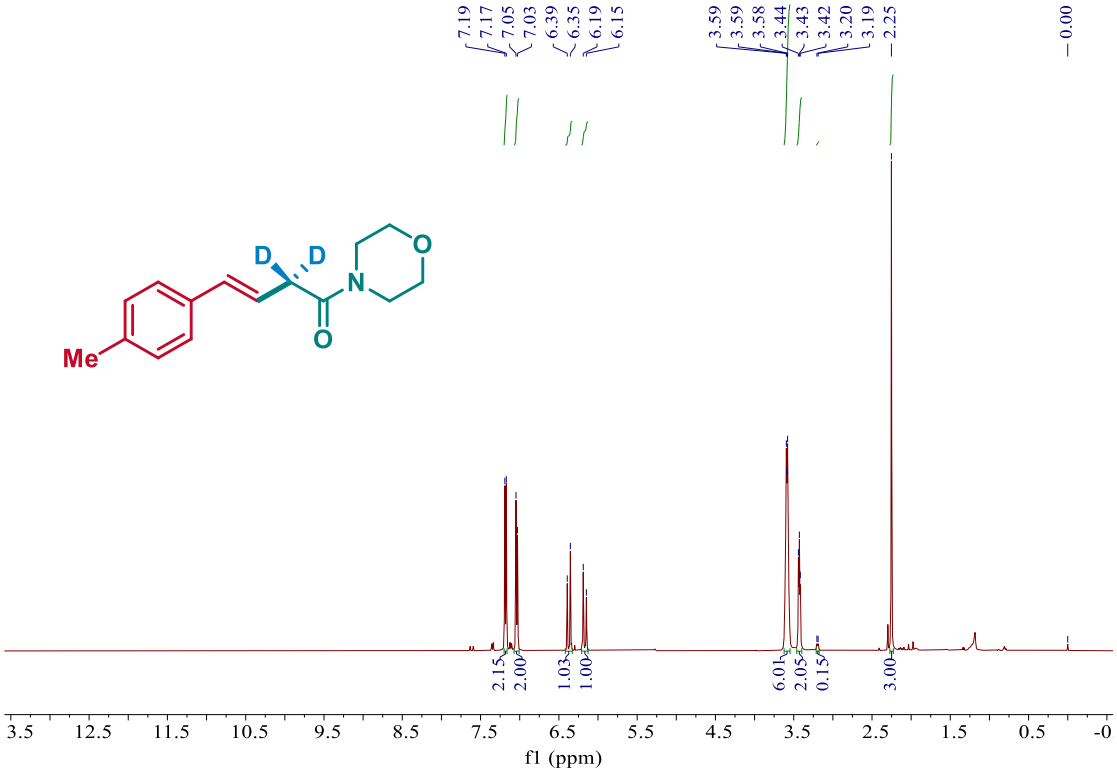
^{1}H NMR Spectrum of *tert*-butyl (*E*)-4-(*p*-tolyl)but-3-enoate-2,2-D$_2$ 3ab'



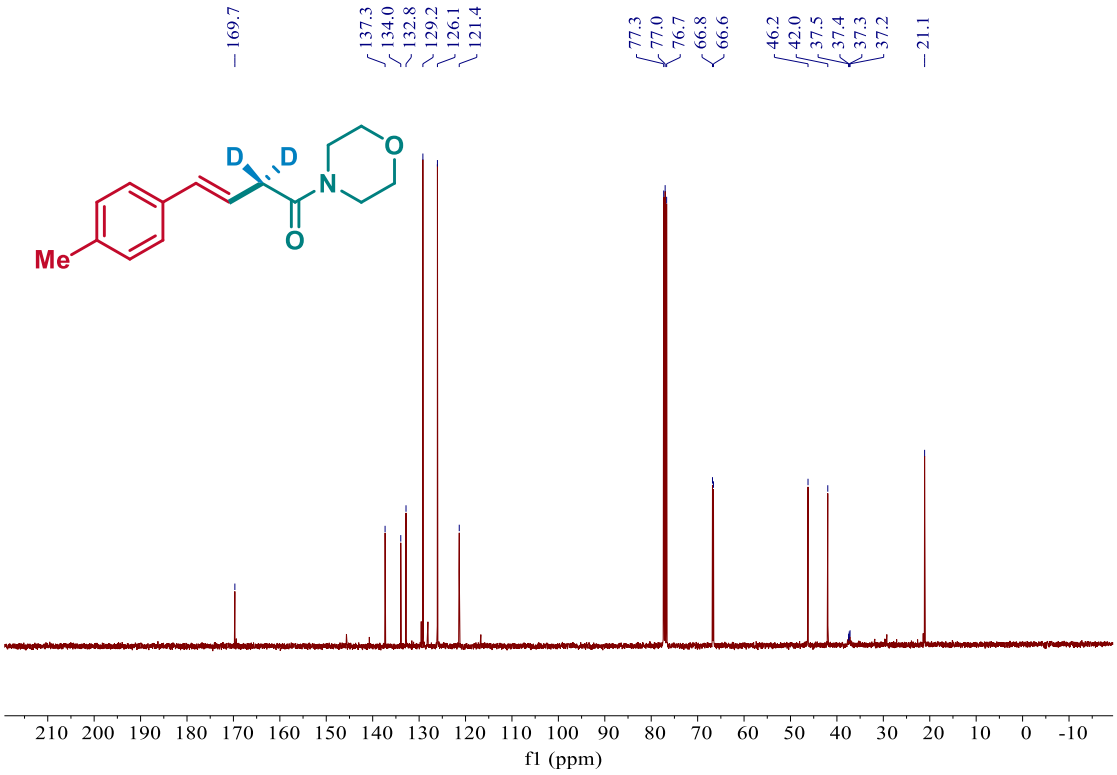
^{13}C NMR Spectrum of *t*ert-butyl (*E*)-4-(*p*-tolyl)but-3-enoate-2,2-D$_2$ 3ab'



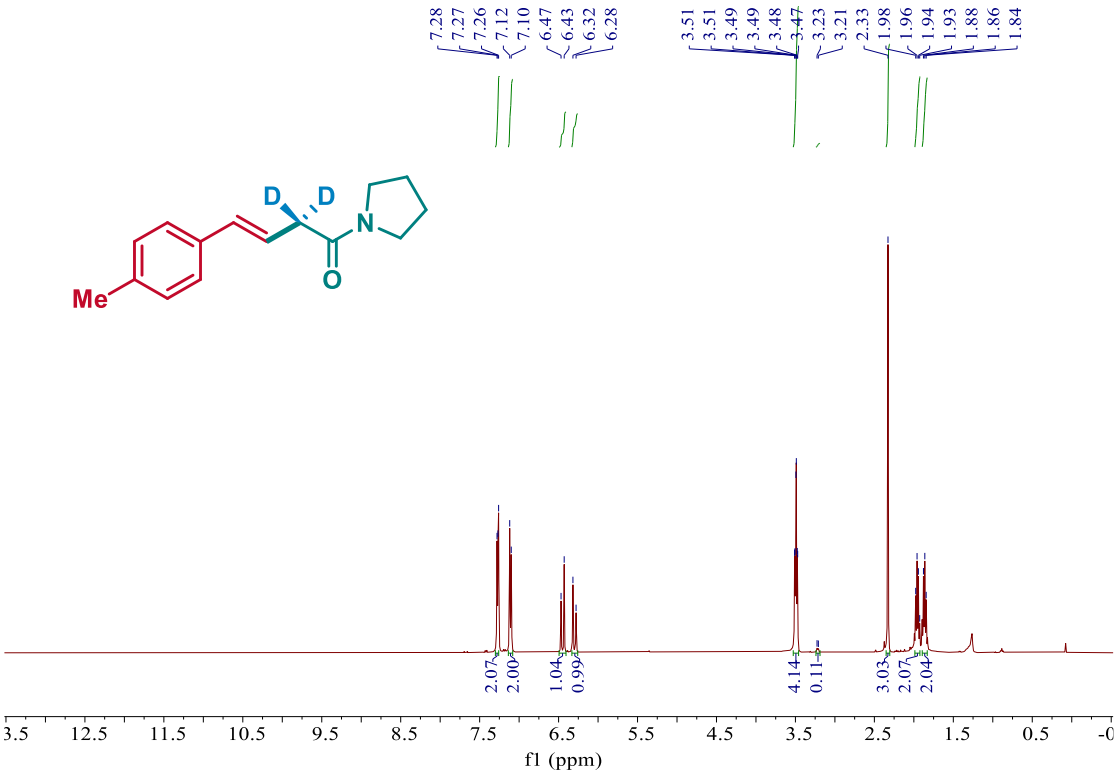
^{1}H NMR Spectrum of (*E*)-1-morpholino-4-(*p*-tolyl)but-3-en-1-one-2,2-D$_2$ 3ak'



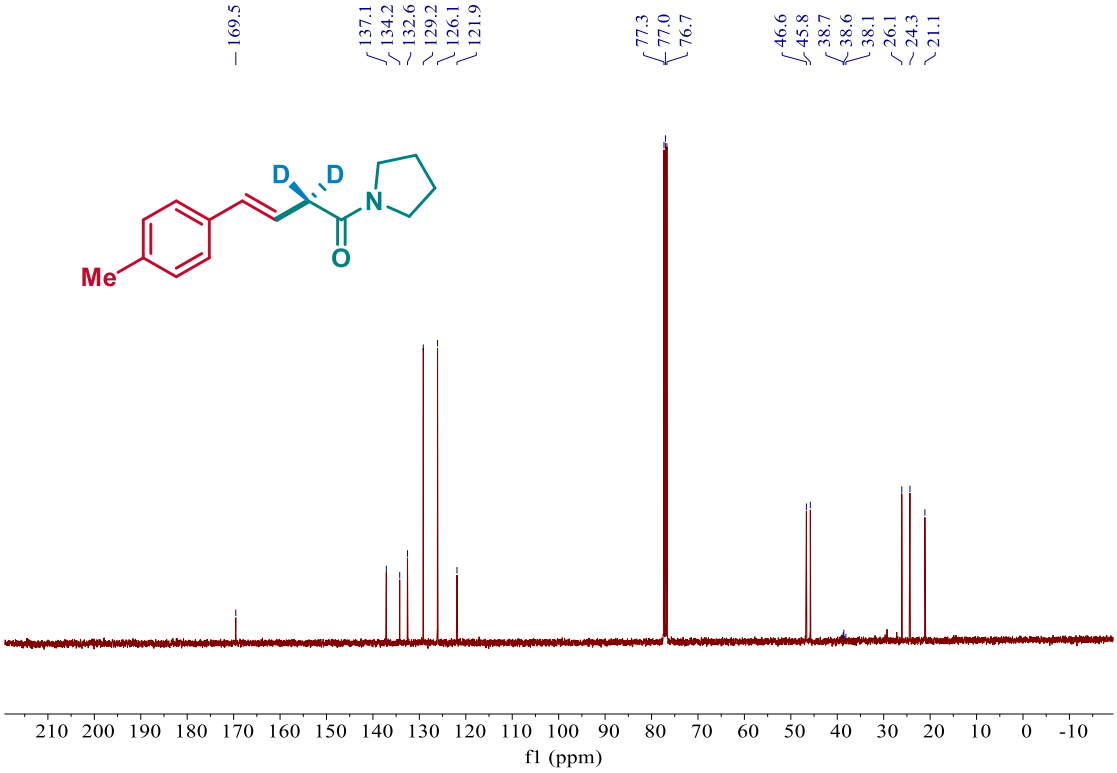
^{13}C NMR Spectrum of (*E*)-1-morpholino-4-(*p*-tolyl)but-3-en-1-one-2,2-D$_2$ 3ak'



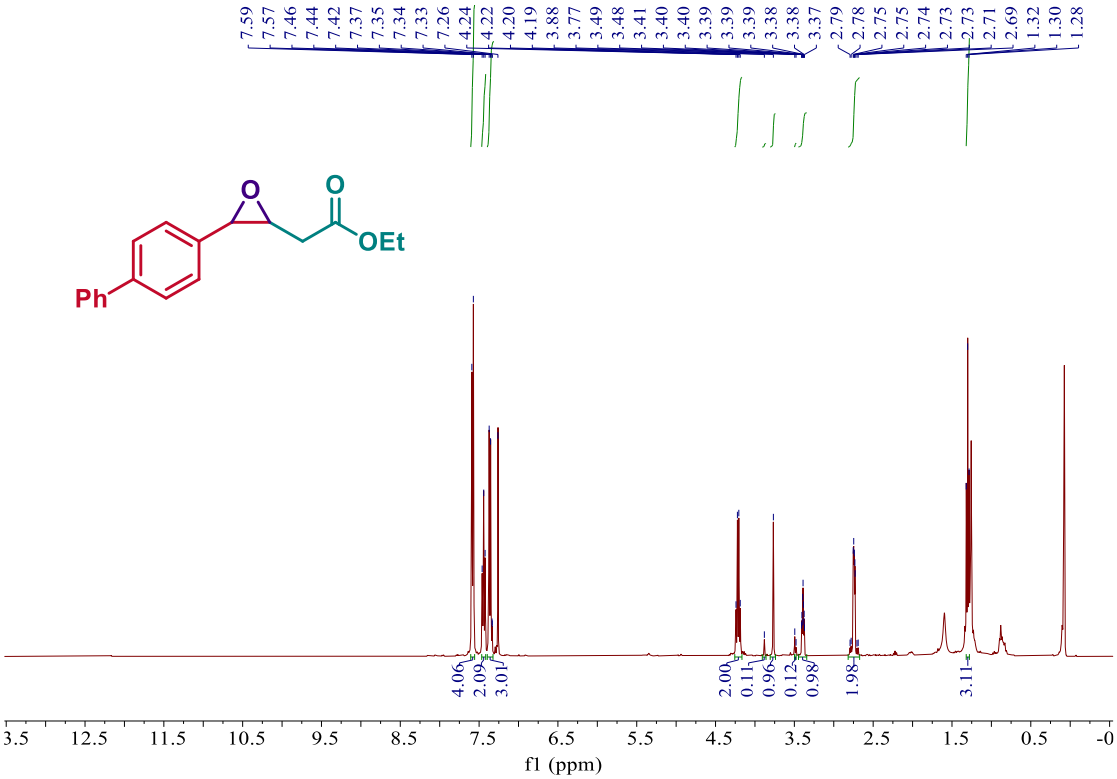
^{1}H NMR Spectrum of (*E*)-1-(pyrrolidin-1-yl)-4-(*p*-tolyl)but-3-one-2,2-D$_2$ 3al'



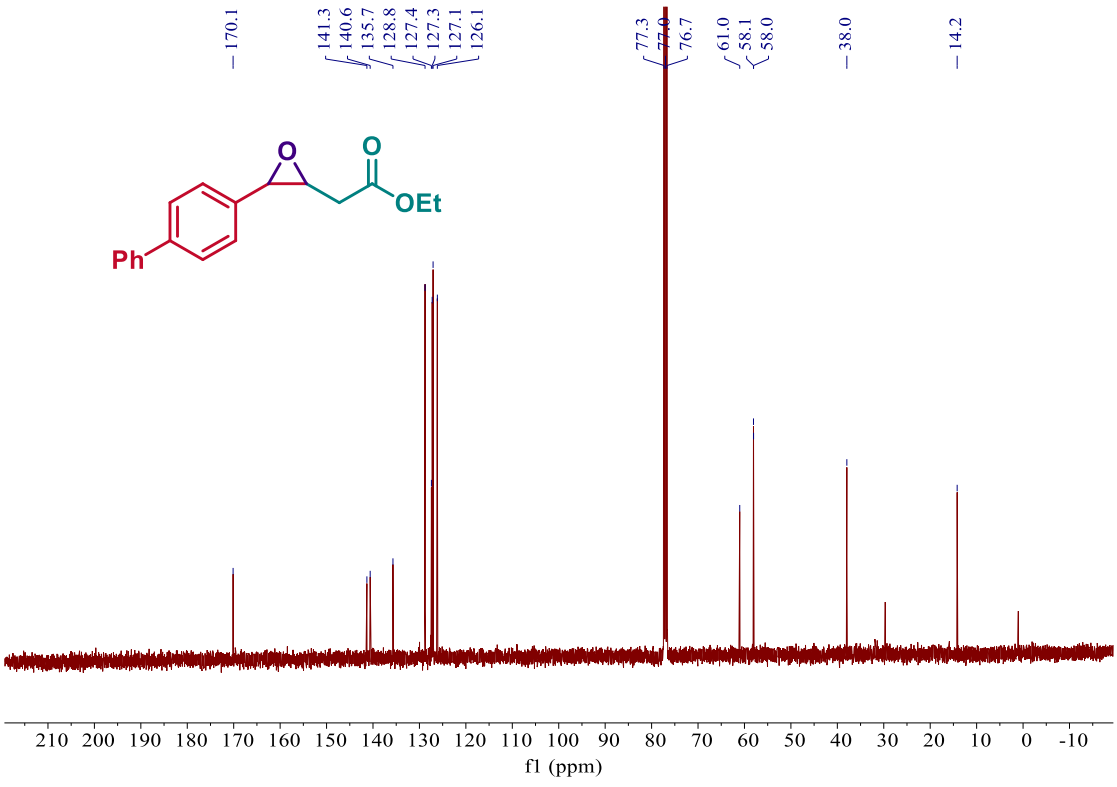
^{13}C NMR Spectrum of (*E*)-1-(pyrrolidin-1-yl)-4-(*p*-tolyl)but-3-one-2,2-D$_2$ 3al'



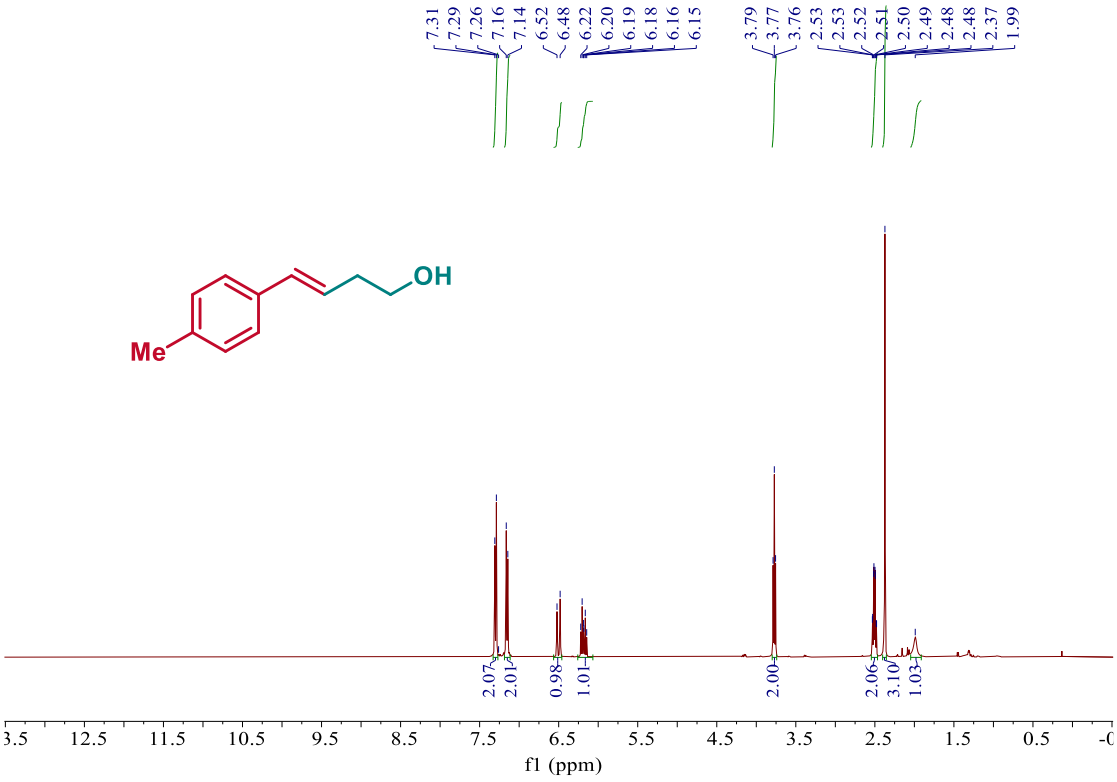
^{1}H NMR Spectrum of ethyl 2-((2*S*,3*R*)-3-([1,1'-biphenyl]-4-yl)oxiran-2-yl)acetate 4



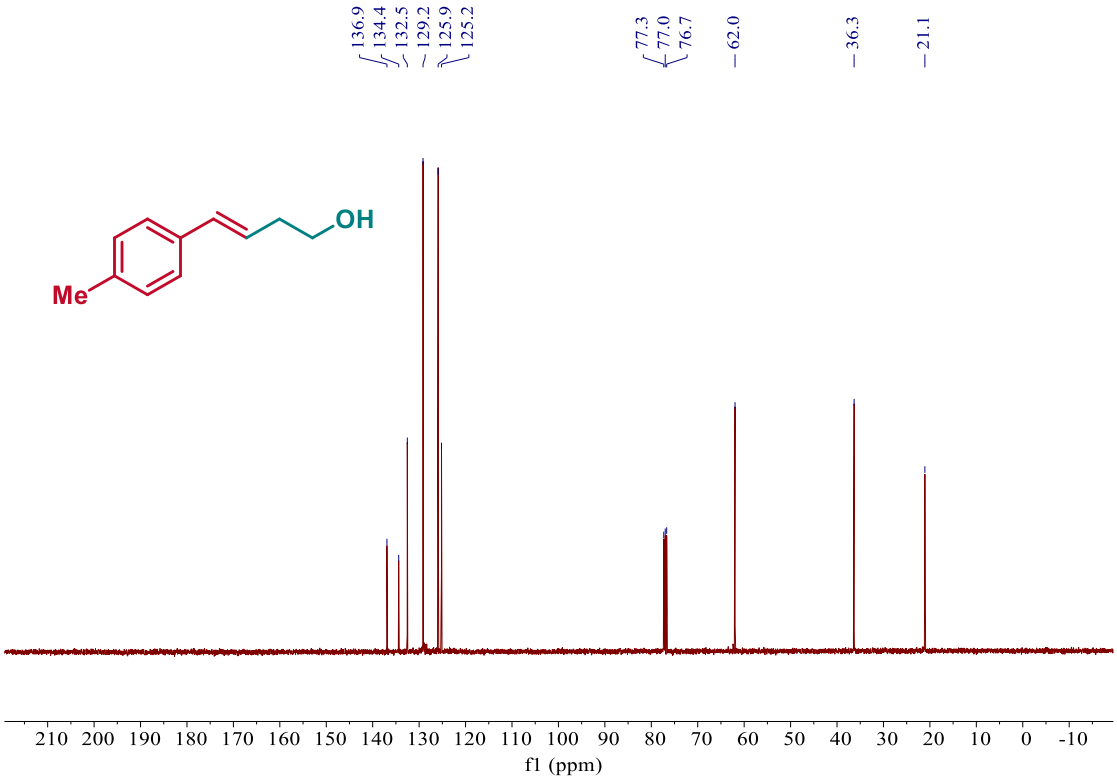
^{13}C NMR Spectrum of ethyl 2-((2*S*,3*R*)-3-([1,1'-biphenyl]-4-yl)oxiran-2-yl)acetate 4



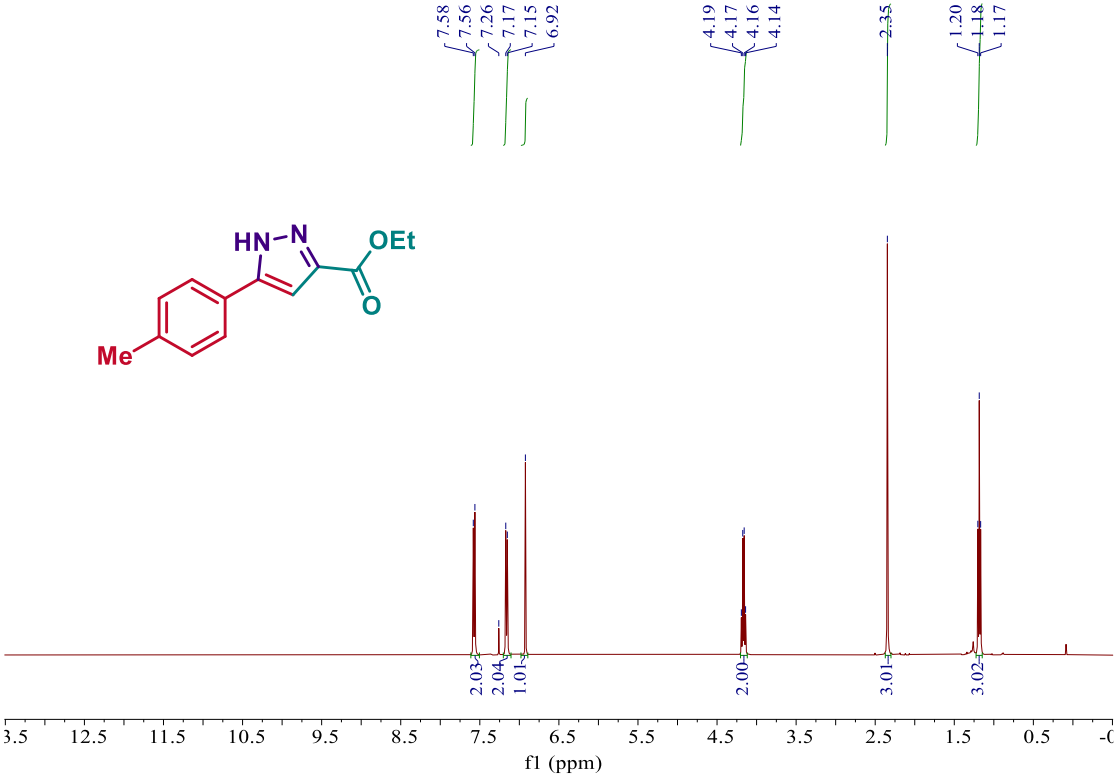
^{1}H NMR Spectrum of (*E*)-4-(*p*-tolyl)but-3-en-1-ol 5



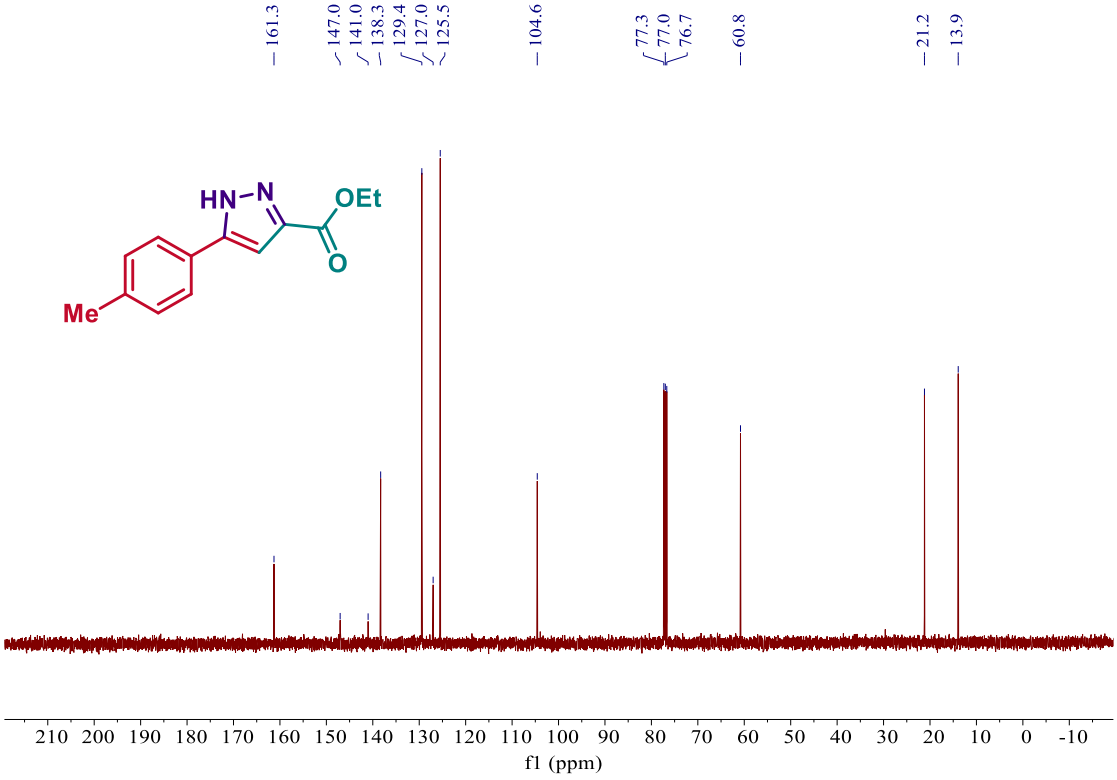
^{13}C NMR Spectrum of (*E*)-4-(*p*-tolyl)but-3-en-1-ol 5



^{1}H NMR Spectrum of ethyl 5-(*p*-tolyl)-1*H*-pyrazole-3-carboxylate 6



^{13}C NMR Spectrum of ethyl 5-(*p*-tolyl)-1*H*-pyrazole-3-carboxylate 6



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