Rapid Access to *t*-Butylalkylated Olefins Enabled by Ni-Catalyzed Intermolecular Regio- and *trans*-Selective Cross-Electrophile *t*-Butylalkylation of Alkynes

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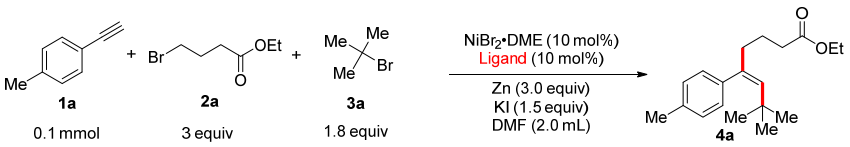
1. General Information

General Remarks: NMR spectra were recorded on 400 MHz or 600 MHz Bruker spectrometers. Chemical shifts are given in ppm. The spectra are calibrated to the residual 1H and 13C signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (br). High-resolution electrospray ionization and electronic impact mass spectrometry was performed on a Thermo Scientific Q Exactive mass spectrometer (mass analyzer type: Orbitrap). A mass accuracy ≤ 2 ppm was obtained in the peak matching acquisition mode by using a solution containing 2 <l PEG200, 2 <l PPG450, and 1.5 mg NaOAc (all obtained from Sigma-Aldrich, CH-Buchs) dissolved in 100 mL MeOH (HPLC Supra grade, Scharlau, E-Barcelona) as internal standard.

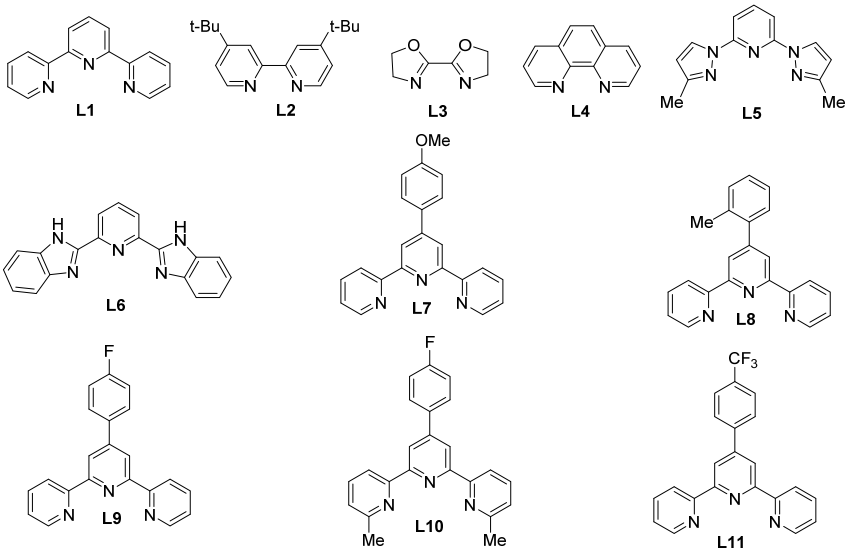
Materials and Methods: All reactions were carried out under an inert atmosphere of nitrogen in oven dried or flame dried glassware with magnetic stirring. Unless otherwise stated, starting materials were purchased from Aladdin (KI), Macklin Reagent (DMA), Bide Pharm ($NiBr_2$·DME), Solvents were purchased in HPLC quality, degassed by purging with nitrogen and dried over activated molecular sieves of appropriate size. DMA was handled by vacuum distillation after dried over CaH_2. Conversion was monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 F254. Compounds were visualized by UV light at 254 nm and by dipping the plates in an ethanolic phosphomolybdic acid solution or an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (300-400 mesh).

2. Optimization of Reaction Conditions

Table S1. Optimization of ligand

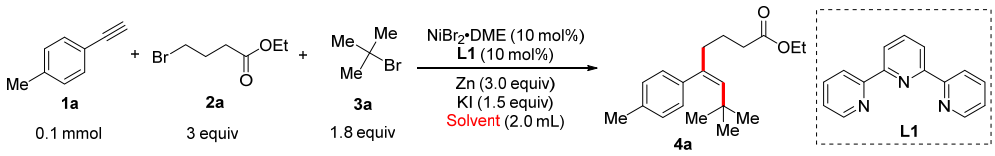


Entry	Ligand	Yield of **4a**[a]
1	**L1**	58%
2	**L2**	trace
3	**L3**	trace
4	**L4**	trace
5	**L5**	21%
6	**L6**	trace
7	**L7**	26%
8	**L8**	39%
9	**L9**	37%
10	**L10**	13%
11	**L11**	38%



[a] Reaction was run using 0.1 mmol of **1a**, 0.3 mmol of **2a**, and 0.18 mmol of **3a** under indicated conditions for 24 h. Yield was determined by GC analysis using *n*-dodecane as internal standard.

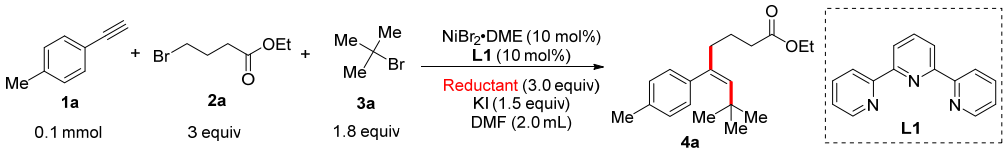
Table S2. Optimization of solvent



Entry	Solvent	Yield of **4a**[a]
1	DMF	58%
2	DMA	42%
3	DMSO	53%
4	DMPU	24%
5	DMI	39%
6	NMP	48%
7	CH_3CN	trace
8	1,4-dioxane	ND
9	THF	ND
10	Et_2O	trace
11	Toluene	ND
12	PhCl	ND
13	DCM	ND

[a] Reaction was run using 0.1 mmol of **1a**, 0.3 mmol of **2a**, and 0.18 mmol of **3a** under indicated conditions for 24 h. Yield was determined by GC analysis using *n*-dodecane as internal standard.

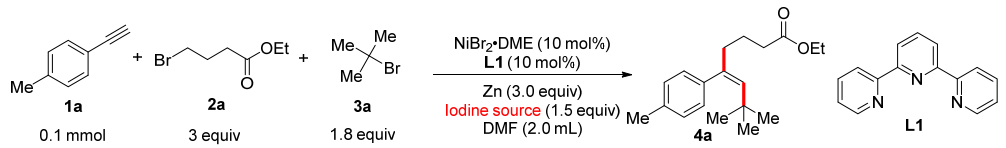
Table S3. Optimization of reductant



Entry	Reductant	Yield of **4a**[a]
1	Zn	58%
2	Mn	53%
3	TDAE	19%

[a] Reaction was run using 0.1 mmol of **1a**, 0.3 mmol of **2a**, and 0.18 mmol of **3a** under indicated conditions for 24 h. Yield was determined by GC analysis using *n*-dodecane as internal standard.

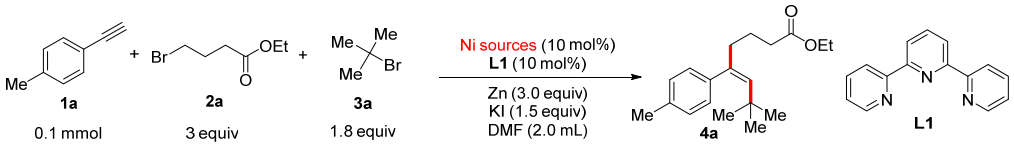
Table S4. Optimization of iodine sources



Entry	Iodine source	Yield of **4a**[a]
1	LiI	55%
2	NaI	54%
3	KI	58%
4	CsI	55%

[a] Reaction was run using 0.1 mmol of **1a**, 0.3 mmol of **2a**, and 0.18 mmol of **3a** under indicated conditions for 24 h. Yield was determined by GC analysis using *n*-dodecane as internal standard.

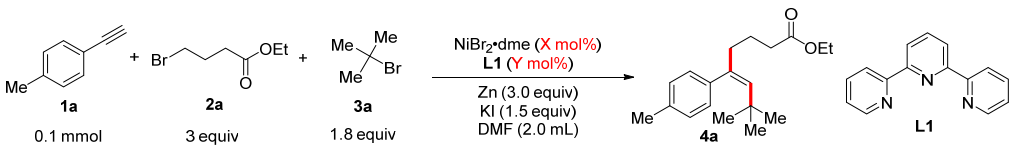
Table S5. Optimization of Ni sources



Entry	Ni sources	Yield of **4a**[a]
1	$NiBr_2$·DME	58%
2	$NiCl_2$·DME	48%
3	$NiBr_2$	57%
4	NiI_2	53%
5	$Ni(ClO_4)_2·6H_2O$	49%
6	$Ni(acac)_2$	57%
7	$NiCl_2$	35%
8	$Ni(OTf)_2$	trace
9	$Ni(OAc)_2·4H_2O$	50%
10	$Ni(PPh_3)_2Cl_2$	21%

[a] Reaction was run using 0.1 mmol of **1a**, 0.3 mmol of **2a**, and 0.18 mmol of **3a** under indicated conditions for 24 h. Yield was determined by GC analysis using *n*-dodecane as internal standard.

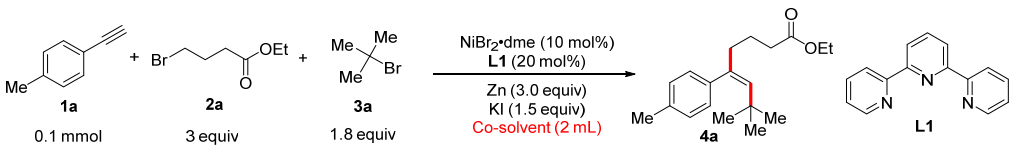
Table S6. Optimization of Ni and ligand



Entry	Amount of Ni and **L1**	Yield of **4a**[a]
1	X = 10, Y = 5	42%
2	X = 10, Y = 10	55%
3	X = 10, Y = 15	61%
4	X = 10, Y = 20	63%
5	X = 5, Y = 10	48%
6	X = 8, Y = 16	54%
7	X = 12, Y = 24	51%

[a] Reaction was run using 0.1 mmol of **1a**, 0.3 mmol of **2a**, and 0.18 mmol of **3a** under indicated conditions for 24 h. Yield was determined by GC analysis using *n*-dodecane as internal standard.

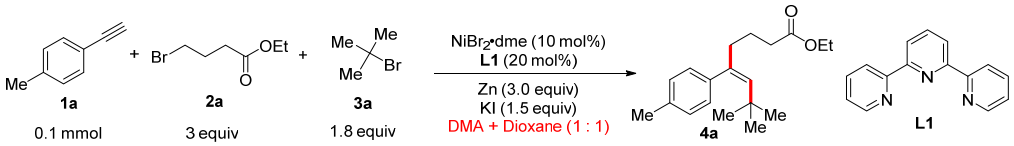
Table S7. Optimization of Co-solvent



Entry	Co-solvent	Yield of **4a**[a]
1	DMF (1 mL) + Toluene (1 mL)	65%
2	DMF (1 mL) + Dioxane (1 mL)	67%
3	DMF (1 mL) + DCM (1 mL)	3%
4	DMF (1 mL) + THF (1 mL)	64%
5	DMF (1 mL) + DMA (1 mL)	66%
6	DMF (1 mL) + DMSO (1 mL)	58%
7	DMA (1 mL) + Dioxane (1 mL)	69%
8	DMA (1 mL) + DCM (1 mL)	13%
9	DMA (1 mL) + THF (1 mL)	64%
10	DMA (1 mL) + DMSO (1 mL)	66%

[a] Reaction was run using 0.1 mmol of **1a**, 0.3 mmol of **2a**, and 0.18 mmol of **3a** under indicated conditions for 24 h. Yield was determined by GC analysis using *n*-dodecane as internal standard.

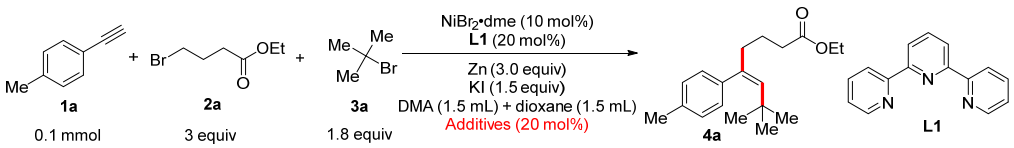
Table S8. Optimization of concentration



Entry	Concentration	Yield of **4a**[a]
1	DMA (0.5 mL) + dioxane (0.5 mL)	61%
2	DMA (0.8 mL) + dioxane (0.8 mL)	66%
3	DMA (1 mL) + dioxane (1 mL)	69%
4	DMA (1.2 mL) + dioxane (1.2 mL)	70%
5	DMA (1.5 mL) + dioxane (1.5 mL)	72%
6	DMA (1.8 mL) + dioxane (1.8 mL)	71%
7	DMA (2 mL) + dioxane (2 mL)	66%

[a] Reaction was run using 0.1 mmol of **1a**, 0.3 mmol of **2a**, and 0.18 mmol of **3a** under indicated conditions for 24 h. Yield was determined by GC analysis using *n*-dodecane as internal standard.

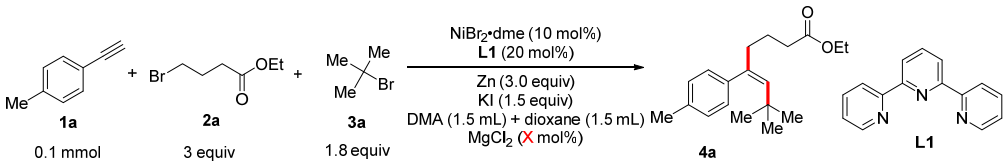
Table S9. Optimization of additives



Entry	Additives	Yield of **4a**[a]
1	$MgCl_2$	75%
2	$CeCl_3$	62%
3	KCl	73%
4	KBr	73%
5	$ZnBr_2$	68%
6	$MgBr_2 \cdot Et_2O$	72%
7	DMAP	60%

[a] Reaction was run using 0.1 mmol of **1a**, 0.3 mmol of **2a**, and 0.18 mmol of **3a** under indicated conditions for 24 h. Yield was determined by GC analysis using *n*-dodecane as internal standard.

Table S10. Optimization the amount of $MgCl_2$

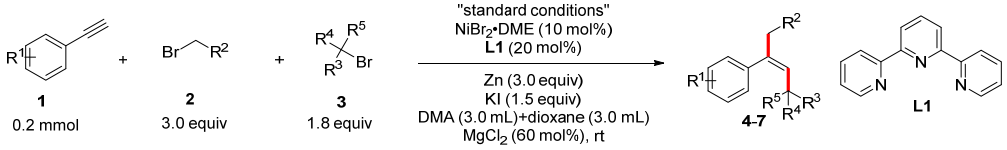


Entry	Amount of $MgCl_2$ (X mol%)	Yield of **4a**[a]
1	10	72%
2	20	75%
3	40	75%
4	60	77% (75%)[b]
5	80	72%
6	100	67%

[a] Reaction was run using 0.1 mmol of **1a**, 0.3 mmol of **2a**, and 0.18 mmol of **3a** under indicated conditions for 24 h. Yield was determined by GC analysis using *n*-dodecane as internal standard. [b] Isolated yield.

3. General Procedures

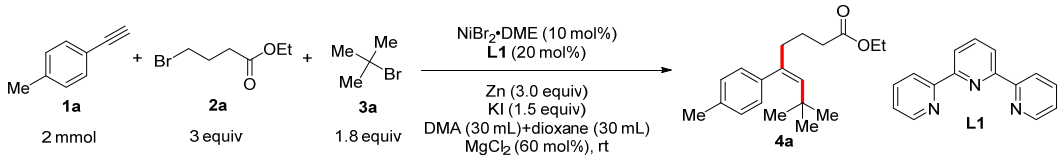
3.1. General procedure of the reaction



The reaction was operated in a nitrogen-filled glove box. Zinc (39.2 mg, 0.6 mmol, 3.0 equiv), $MgCl_2$ (0.12 mmol, 0.6 equiv), KI (0.3 mmol, 1.5 equiv), **L1** (9.33 mg, 0.04 mmol, 20 mol%), $NiBr_2$·DME (6.17 mg, 0.02 mmol, 10 mol%), and alkyne (if solid, 0.2 mmol, 1.0 equiv) were added to an oven-dried 10 mL Schlenk tube containing a magnetic stir bar. Anhydrous DMA (0.1 mmol/1.5 mL) and anhydrous 1,4-dioxane (0.1

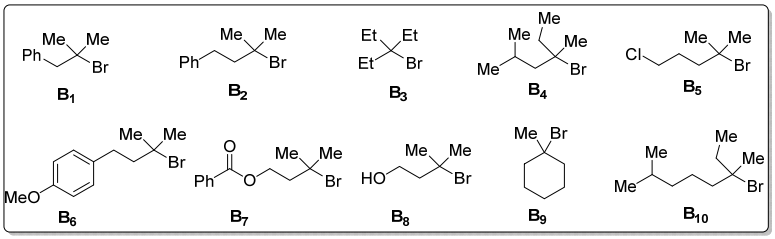
mmol/1.5 mL) were added and rapid stirring was commenced. Then, alkyne (if liquid, 0.2 mmol, 1.0 equiv), alkyl bromide **3** (0.36 mmol, 1.8 equiv) and alkyl bromide **2** (0.6 mmol, 3.0 equiv) were added in turn via syringe. The resulting mixture was sealed with a screw-cap. The reaction was stirred vigorously at room temperature for 24 h. The reaction was diluted with ethyl acetate (50 mL) and washed with brine (50 mL, three times). The aqueous layer was extracted with ethyl acetate (20 mL). The combined organic layer was dried over magnesium sulfate, evaporated and purified by silica gel chromatography with hexane : ethyl acetate mixtures as eluent to give the corresponding products (**4**-**7**) in pure form.

3.2. Scaled up procedure



The reaction was operated in a nitrogen-filled glove box. Zinc (0.39 g, 6.0 mmol, 3.0 equiv), $MgCl_2$ (0.11 g, 1.2 mmol, 0.6 equiv), KI (0.49 g, 3.0 mmol, 1.5 equiv), **L1** (93.2 mg, 0.4 mmol, 20 mol%) and $NiBr_2$·DME (61.7 mg, 0.2 mmol, 10 mol%) were added to an oven-dried 100 mL Schlenk tube containing a magnetic stir bar. Anhydrous DMA (30 mL) and anhydrous 1,4-dioxane (30 mL) were added and rapid stirring was commenced. Then, 4-ethynyltoluene (0.23 g, 2.0 mmol, 0.26 mL), 2-bromo-2-methylpropane (0.49 g, 3.6 mmol, 0.4 mL, 1.8 equiv) and ethyl 4-bromobutyrate (1.17 g, 6.0 mmol, 0.86 mL, 3.0 equiv) were added in turn via syringe and sealed with a screw-cap. The reaction was stirred vigorously at room temperature for 24 h. The reaction was diluted with ethyl acetate (300 mL) and washed with brine (100 mL, three times). The aqueous layer was extracted with ethyl acetate (100 mL). The combined organic layer was dried over magnesium sulfate, evaporated and purified by silica gel chromatography with hexane and ethyl acetate mixtures as eluent (100% hexane ~ 1% ethyl acetate : hexane) to give the product **4a** (0.41 g, 72% yield) as a yellow oil.

3.3. General procedure for the synthesis of tertiary bromides



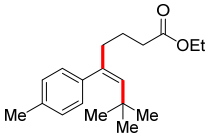
General procedure A: The tertiary alkyl bromides were prepared according to a literature procedure[1] from the corresponding tertiary alcohols. A mixture of alcohol (5.0 mmol) in the case of solids, which had been powdered for 1-2 min and TMSBr (0.84 g, 5.5 mmol, 0.73 mL, 1.1 equiv) was transferred to a 10 mL screw-capped vial, and stirred at rt for overnight. The progress of the reaction mixture was monitored by TLC. Upon completion of the reaction, the crude reaction mixture was cooled down to the room temperature and volatile product $(TMS)_2O$ was removed by evaporation at 30-35°C under reduced pressure and the residue was purified by column chromatography on dried aluminum oxide to afford the product.

General procedure B: The tertiary alkyl bromides were prepared according to a literature procedure[2] from the corresponding tertiary alcohols. To a solution of alcohol (10.0 mmol) in CH_2Cl_2 (neat or a solution in a minimal amount of CH_2Cl_2) was added LiBr (1.80 g, 20.0 mmol, 2.0 equiv) in 48 wt% aqueous HBr at 0 °C. The reaction mixture was allowed to warm to rt and stirred for overnight. Then the mixture was diluted with Et_2O, washed with water, saturated $NaHCO_3$, and brine. The organic phase was dried over $MgCl_2$, filtrated and concentrated. The residue was purified by column chromatograph to afford the product.

NOTE: **B_1-B_5**, **B_8-B_{10}** were synthesized following General procedure A. **B_6** and **B_7** were synthesized following General procedure B.

4. Characterization of New Compounds

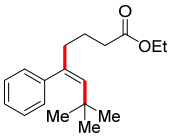
Ethyl (*Z*)-7,7-dimethyl-5-(*p*-tolyl)oct-5-enoate (4a)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate :

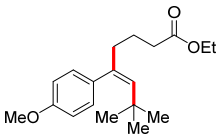
hexanes = 1 : 200) to give the product **4a** (43.2 mg, 75% yield) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.10 – 7.07 (m, 2H), 6.99 – 6.95 (m, 2H), 5.41 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 2.27 (t, *J* = 7.6 Hz, 2H), 2.22 – 2.18 (m, 2H), 1.65 – 1.59 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.85 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.85, 139.00, 138.07, 137.55, 135.81, 128.91, 128.35, 60.23, 41.86, 33.67, 33.39, 31.53, 23.28, 21.23, 14.33; **HR-MS** (ESI) m/z calcd for $C_{19}H_{29}O_2$[M+H$^+$]: 289.2162, found: 289.2154.

Ethyl (*Z*)-7,7-dimethyl-5-phenyloct-5-enoate (4b)



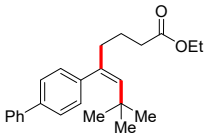
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4b** (35.6 mg, 65% yield) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22 – 7.18 (m, 2H), 7.16 – 7.12 (m, 1H), 7.02 – 6.99 (m, 2H), 5.35 (t, *J* = 1.2 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 2.20 (t, *J* = 7.6 Hz, 2H), 2.17 – 2.12 (m, 2H), 1.58 – 1.52 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.77 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.80, 142.07, 138.11, 137.54, 129.05, 127.65, 126.34, 60.23, 41.76, 33.66, 33.41, 31.49, 23.25, 14.32; **HR-MS** (ESI) m/z calcd for $C_{18}H_{27}O_2$[M+H$^+$]: 275.2006, found: 275.2008.

Ethyl (*Z*)-5-(4-methoxyphenyl)-7,7-dimethyloct-5-enoate (4c)



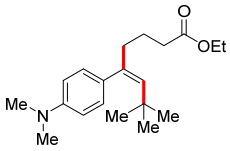
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **4c** (37.1 mg, 61% yield) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 – 6.95 (m, 2H), 6.86 – 6.78 (m, 2H), 5.41 (t, *J* = 1.2 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.26 (t, *J* = 7.6 Hz, 2H), 2.23 – 2.15 (m, 2H), 1.65 – 1.56 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.85 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.85, 158.19, 138.37, 137.19, 134.18, 130.00, 113.09, 60.23, 55.22, 41.90, 33.66, 33.38, 31.52, 23.28, 14.32; **HR-MS** (ESI) m/z calcd for $C_{19}H_{29}O_3$[M+H$^+$]: 305.2111, found: 305.2113.

Ethyl (*Z*)-5-([1,1'-biphenyl]-4-yl)-7,7-dimethyloct-5-enoate (4d)



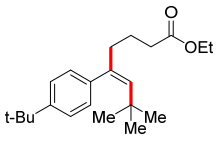
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4d** (43.7 mg, 62% yield) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.55 – 7.51 (m, 2H), 7.46 – 7.41 (m, 2H), 7.36 – 7.30 (m, 1H), 7.18 – 7.14 (m, 2H), 5.47 (t, *J* = 1.2 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 2.28 – 2.23 (m, 2H), 1.71 – 1.63 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.89 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.82, 141.16, 140.99, 139.13, 138.42, 137.21, 129.48, 128.80, 127.19, 127.03, 126.33, 60.27, 41.75, 33.68, 33.48, 31.57, 23.33, 14.33; **HR-MS** (ESI) m/z calcd for $C_{24}H_{30}NaO_2$[M+Na$^+$]: 373.2138, found: 373.2143.

Ethyl (*Z*)-5-(4-(dimethylamino)phenyl)-7,7-dimethyloct-5-enoate (4e)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **4e** (37.1 mg, 62% yield) as a yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 6.96 – 6.92 (m, 2H), 6.68 – 6.67 (m, 2H), 5.39 (t, *J* = 1.2 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.94 (s, 6H), 2.27 (t, *J* = 7.6 Hz, 2H), 2.21 – 2.17 (m, 2H), 1.64 – 1.59 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.86 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.95, 149.07, 138.06, 137.71, 129.69, 112.00, 60.19, 42.00, 40.80, 33.69, 33.35, 31.58, 23.37, 14.34; **HR-MS** (ESI) m/z calcd for $C_{20}H_{32}NO_2$[M+H$^+$]: 318.2428, found: 318.2420.

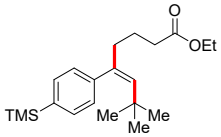
Ethyl (*Z*)-5-(4-(*tert*-butyl)phenyl)-7,7-dimethyloct-5-enoate (4f)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4f** (43.2 mg, 65% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.22 – 7.17 (m, 2H), 6.94 – 6.90 (m, 2H), 5.33 (t, *J* = 1.1 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.20 (t, *J* =7.6 Hz, 2H), 2.16 – 2.10 (m, 2H), 1.59 – 1.52 (m, 2H), 1.24 (s, 9H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.77 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.92, 149.15, 138.88, 138.04, 137.65, 128.60, 124.43,

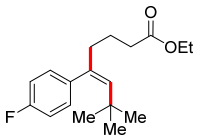
60.23, 41.81, 34.49, 33.68, 33.37, 31.52, 23.33, 14.33; **HR-MS** (ESI) m/z calcd for $C_{22}H_{35}O_2$[M+H$^+$]: 331.2632, found: 331.2635.

Ethyl (*Z*)-7,7-dimethyl-5-(4-(trimethylsilyl)phenyl)oct-5-enoate (4g)



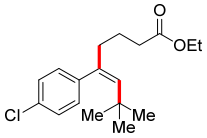
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4g** (46.5 mg, 67% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.38 (m, 2H), 7.09 – 7.03 (m, 2H), 5.41 (t, *J* = 1.2 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.28 (t, *J* = 7.6 Hz, 2H), 2.23 – 2.18 (m, 2H), 1.67 – 1.58 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.84 (s, 9H), 0.26 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.86, 142.51, 138.06, 137.98, 137.62, 132.62, 128.36, 60.25, 41.75, 33.67, 33.40, 31.54, 23.31, 14.33, -0.94; **HR-MS** (ESI) m/z calcd for $C_{21}H_{35}O_2Si$[M+H$^+$]: 347.2401, found: 347.2405.

Ethyl (*Z*)-5-(4-fluorophenyl)-7,7-dimethyloct-5-enoate (4h)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4h** (35.2 mg, 60% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.06 – 7.01 (m, 2H), 7.00 – 6.94 (m, 2H), 5.43 (t, *J* = 1.2 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.27 (t, *J* = 7.6 Hz, 2H), 2.22 – 2.16 (m, 2H), 1.64 – 1.56 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.84 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.74, 161.69 (d, *J* = 245.4 Hz), 138.81, 137.77 (d, *J* = 3.0 Hz), 136.50, 130.46 (d, *J* = 8.0 Hz), 114.58 (d, *J* = 21.2 Hz), 60.30, 41.75, 33.62, 33.45, 31.49, 23.21, 14.32; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -116.67 – -116.76 (m, 1F); **HR-MS** (ESI) m/z calcd for $C_{18}H_{26}FO_2$[M+H$^+$]: 293.1911, found: 293.1907.

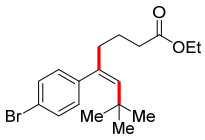
Ethyl (*Z*)-5-(4-chlorophenyl)-7,7-dimethyloct-5-enoate (4i)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 300) to give the product **4i** (35.4 mg, 57% yield) as a yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.20 – 7.17 (m, 2H), 6.97 – 6.93 (m, 2H), 5.37 (t, *J* = 1.2 Hz, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 2.19 (t, *J* = 7.6 Hz, 2H), 2.14 – 2.10 (m, 2H), 1.56

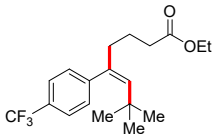
– 1.50 (m, 2H), 1.17 (t, J = 7.2 Hz, 3H), 0.77 (s, 9H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 173.68, 140.50, 138.86, 136.30, 132.29, 130.40, 127.92, 60.31, 41.60, 33.61, 33.48, 31.50, 23.21, 14.32; **HR-MS** (ESI) m/z calcd for $C_{18}H_{26}ClO_2$[M+H$^+$]: 309.1616, found: 309.1608.

Ethyl (*Z*)-5-(4-bromophenyl)-7,7-dimethyloct-5-enoate (4j)



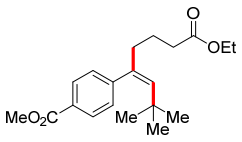
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4j** (40.0 mg, 57% yield) as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.43 – 7.37 (m, 2H), 6.98 – 6.94 (m, 2H), 5.44 (t, J = 1.2 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.26 (t, J = 7.5 Hz, 2H), 2.21 – 2.16 (m, 2H), 1.64 – 1.55 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H), 0.84 (s, 9H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 173.66, 141.00, 138.85, 136.27, 130.87, 130.77, 120.38, 60.31, 41.55, 33.60, 33.48, 31.51, 23.20, 14.32; **HR-MS** (ESI) m/z calcd for $C_{18}H_{26}BrO_2$[M+H$^+$]: 353.1111, found: 353.1115.

Ethyl (*Z*)-7,7-dimethyl-5-(4-(trifluoromethyl)phenyl)oct-5-enoate (4k)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4k** (36.4 mg, 53% yield) as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.56 – 7.51 (m, 2H), 7.24 – 7.18 (m, 2H), 5.49 – 5.46 (m, 1H), 4.11 (q, J = 7.2 Hz, 2H), 2.28 (t, J = 7.5 Hz, 2H), 2.24 – 2.19 (m, 2H), 1.64 – 1.56 (m, 2H), 1.23 (t, J = 7.2 Hz, 3H), 0.84 (s, 9H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 173.60, 146.14 (d, J = 1.0 Hz), 139.08, 136.21, 129.39, 128.77 (q, J = 32.3 Hz), 124.69 (q, J = 4.0 Hz), 124.39 (q, J = 272.7 Hz), 60.34, 41.46, 33.58, 33.53, 31.48, 23.20, 14.30; **^{19}F NMR (376 MHz, CDCl$_3$)** δ -62.36 (s, 3F); **HR-MS** (ESI) m/z calcd for $C_{19}H_{25}F_3NaO_2$[M+Na$^+$]: 365.1699, found: 365.1704.

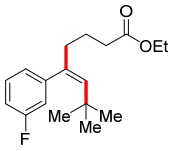
Methyl (*Z*)-4-(8-ethoxy-2,2-dimethyl-8-oxooct-3-en-4-yl)benzoate (4l)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **4l** (24.5 mg, 37% yield) as

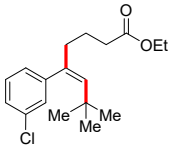
a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 – 7.93 (m, 2H), 7.20 – 7.14 (m, 2H), 5.45 (m, *J* = 1.2 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 3H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.24 – 2.19 (m, 2H), 1.63 – 1.56 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.83 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.62, 167.16, 147.46, 138.76, 136.57, 129.15, 129.06, 128.34, 60.30, 52.10, 41.37, 33.58, 33.52, 31.45, 23.21, 14.30; **HR-MS** (ESI) m/z calcd for $C_{20}H_{28}NaO_4$[M+Na$^+$]: 355.1880, found: 355.1868.

Ethyl (*Z*)-5-(3-fluorophenyl)-7,7-dimethyloct-5-enoate (4m)



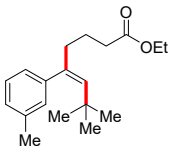
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4m** (35.7 mg, 61% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33 – 7.27 (m, 1H), 7.01 – 6.95 (m, 1H), 6.94 – 6.90 (m, 1H), 6.88 – 6.83 (m, 1H), 5.48 (t, *J* = 1.2 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 2.29 – 2.23 (m, 2H), 1.72 – 1.61 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.91 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.68, 162.42 (d, *J* = 252.5 Hz), 144.37 (d, *J* = 7.1 Hz), 138.69, 136.26 (d, *J* = 2.0 Hz), 129.13 (d, *J* = 8.1 Hz), 124.90 (d, *J* = 3.0 Hz), 115.96 (d, *J* = 20.2 Hz), 113.28 (d, *J* = 20.2 Hz), 60.30, 41.47, 33.60, 33.48, 31.40, 23.24, 14.31; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -114.07 – -114.16 (m, 1F); **HR-MS** (ESI) m/z calcd for $C_{18}H_{25}FNaO_2$[M+Na$^+$]: 315.1731, found: 315.1734.

Ethyl (*Z*)-5-(3-chlorophenyl)-7,7-dimethyloct-5-enoate (4n)



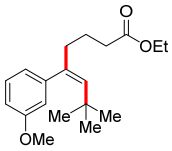
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4n** (37.0 mg, 60% yield) as a yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.23 – 7.19 (m, 2H), 7.09 – 7.08 (m, 1H), 6.99 – 6.95 (m, 1H), 5.43 (t, *J* = 1.2 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.22 – 2.18 (m, 2H), 1.64 – 1.59 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.85 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.67, 144.00, 138.89, 136.11, 133.58, 128.99, 128.97, 127.38, 126.60, 60.32, 41.47, 33.62, 33.53, 31.48, 23.23, 14.32; **HR-MS** (ESI) m/z calcd for $C_{18}H_{26}ClO_2$[M+H$^+$]: 309.1616, found: 309.1619.

Ethyl (*Z*)-7,7-dimethyl-5-(*m*-tolyl)oct-5-enoate (4o)



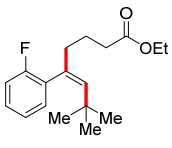
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4o** (39.4 mg, 68% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.18 – 7.12 (m, 1H), 7.05 – 7.01 (m, 1H), 6.90 – 6.85 (m, 2H), 5.39 (t, *J* = 1.2 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.23 – 2.17 (m, 2H), 1.66 – 1.58 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.85 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.86, 142.01, 137.85, 137.65, 137.08, 129.68, 127.47, 127.03, 126.17, 60.23, 41.76, 33.69, 33.42, 31.51, 23.31, 21.54, 14.33; **HR-MS** (ESI) m/z calcd for $C_{19}H_{28}NaO_2[M+Na^+]$: 311.1982, found: 311.1975.

Ethyl (*Z*)-5-(3-methoxyphenyl)-7,7-dimethyloct-5-enoate (4p)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **4p** (37.3 mg, 61% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.21 – 7.15 (m, 1H), 6.79 – 6.74 (m, 1H), 6.70 – 6.66 (m, 1H), 6.65 – 6.62 (m, 1H), 5.39 (t, *J* = 1.1 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 2.27 (t, *J* = 7.6 Hz, 2H), 2.23 – 2.18 (m, 2H), 1.67 – 1.58 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.86 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.81, 159.01, 143.52, 138.01, 137.33, 128.61, 121.72, 114.91, 111.56, 60.24, 55.22, 41.62, 33.66, 33.44, 31.43, 23.33, 14.32; **HR-MS** (ESI) m/z calcd for $C_{19}H_{28}NaO_3[M+Na^+]$: 327.1931, found: 327.1933.

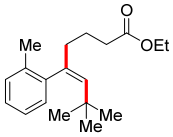
Ethyl (*Z*)-5-(2-fluorophenyl)-7,7-dimethyloct-5-enoate (4q)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4q** (39.7 mg, 67% yield) as a yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.24 – 7.19 (m, 1H), 7.08 – 7.04 (m, 2H), 7.02 – 6.98 (m, 1H), 5.54 (t, *J* = 1.2 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.30 (t, *J* = 7.6 Hz, 2H), 2.26 – 2.20 (m, 2H), 1.67 – 1.60 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.86 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.81, 159.66 (d, *J* = 243.9 Hz), 140.25, 131.54 (d, *J* = 3.0 Hz), 130.79, 129.22 (d, *J* = 18.2 Hz), 128.48 (d, *J* = 7.5 Hz), 123.40 (d, *J* = 3.0 Hz), 115.29 (d, *J* = 22.8 Hz), 60.25, 40.63, 33.62, 33.48, 30.77, 23.21, 14.32; **^{19}F NMR (565 MHz,**

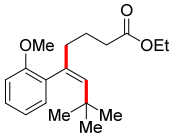
$CDCl_3$) δ -114.26 – -114.34 (m, 1F); **HR-MS** (ESI) m/z calcd for $C_{18}H_{26}FO_2[M+H^+]$: 293.1911, found: 293.1904.

Ethyl (*Z*)-7,7-dimethyl-5-(*o*-tolyl)oct-5-enoate (4r)



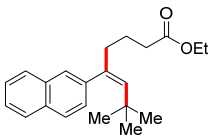
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4r** (34.7 mg, 60% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.16 – 7.12 (m, 2H), 7.11 – 7.06 (m, 1H), 6.98 – 6.94 (m, 1H), 5.42 (t, *J* = 1.3 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.34 – 2.26 (m, 2H), 2.24 (s, 3H), 2.18 – 2.10 (m, 2H), 1.75 – 1.60 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.82 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.80, 141.33, 137.69, 136.20, 135.16, 129.82, 129.78, 126.60, 124.81, 60.25, 40.15, 33.91, 33.54, 30.80, 23.44, 19.71, 14.32; **HR-MS** (ESI) m/z calcd for $C_{19}H_{29}O_2[M+H^+]$: 289.2162, found: 289.2154.

Ethyl (*Z*)-5-(2-methoxyphenyl)-7,7-dimethyloct-5-enoate (4s)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **4s** (42.9 mg, 68% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 – 7.18 (m, 1H), 7.00 – 6.95 (m, 1H), 6.90 – 6.81 (m, 2H), 5.46 (t, *J* = 1.2 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 2.26 – 2.13 (m, 2H), 1.68 – 1.56 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.84 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.03, 156.60, 138.53, 133.97, 130.94, 130.62, 127.90, 119.75, 110.23, 60.14, 55.10, 40.14, 33.76, 33.35, 30.81, 23.37, 14.33; **HR-MS** (ESI) m/z calcd for $C_{19}H_{29}O_3[M+H^+]$: 305.2111, found: 305.2112.

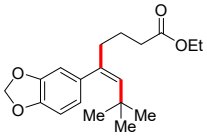
Eethyl (*Z*)-7,7-dimethyl-5-(naphthalen-2-yl)oct-5-enoate (4t)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **4t** (43.5 mg, 67% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 – 7.67 (m, 3H), 7.47 – 7.45 (m, 1H), 7.42 – 7.34 (m, 2H), 7.19 – 7.15 (m, 1H), 5.44 (t, *J* = 1.2 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.25 – 2.19 (m, 4H), 1.62 – 1.53 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.79 (s, 9H);

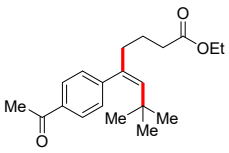
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.78, 139.66, 138.62, 137.46, 133.03, 132.19, 127.88, 127.85, 127.71, 127.34, 127.19, 125.99, 125.54, 60.26, 41.76, 33.70, 33.52, 31.58, 23.37, 14.32; **HR-MS** (ESI) m/z calcd for $C_{22}H_{29}O_2[M+H^+]$: 325.2162, found: 325.2166.

Ethyl (*Z*)-5-(benzo[d][1,3]dioxol-5-yl)-7,7-dimethyloct-5-enoate (4u)



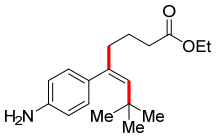
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **4u** (42.9 mg, 67% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.74 – 6.70 (m, 1H), 6.58 – 6.56 (m, 1H), 6.54 – 6.50 (m, 1H), 5.94 (s, 2H), 5.39 – 5.37 (m, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.26 (t, *J* = 7.6 Hz, 2H), 2.20 – 2.14 (m, 2H), 1.64 – 1.57 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.87 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.79, 147.02, 146.05, 138.47, 137.03, 135.61, 122.15, 109.59, 107.67, 100.84, 60.26, 41.80, 33.65, 33.45, 31.46, 23.30, 14.32; **HR-MS** (ESI) m/z calcd for $C_{19}H_{27}O_4[M+H^+]$: 319.1904, found: 319.1908.

Ethyl (*Z*)-5-(4-acetylphenyl)-7,7-dimethyloct-5-enoate (4v)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 50) to give the product **4v** (30.6 mg, 48% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 – 7.86 (m, 2H), 7.22 – 7.17 (m, 2H), 5.47 – 5.45 (t, *J* = 1.2 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 3H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.24 – 2.19 (m, 2H), 1.64 – 1.55 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.84 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.88, 173.55, 147.68, 138.77, 136.43, 135.37, 129.27, 127.81, 60.26, 41.32, 33.51, 33.47, 31.40, 26.57, 23.16, 14.25; **HR-MS** (ESI) m/z calcd for $C_{20}H_{29}O_3[M+H^+]$: 317.2111, found: 317.2115.

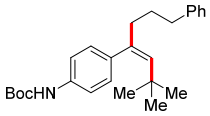
Ethyl (*Z*)-5-(4-aminophenyl)-7,7-dimethyloct-5-enoate (4w)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 10) to give the product **4w** (31.4 mg, 54% yield) as a yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 6.87 (d, *J* = 8.1 Hz, 2H), 6.66 (d, *J* = 8.0 Hz,

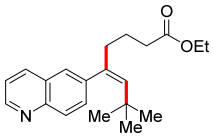
2H), 5.38 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.70 (br s, 2H), 2.26 (t, *J* = 7.6 Hz, 2H), 2.17 (t, *J* = 7.5 Hz, 2H), 1.63 – 1.58 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.85 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.92, 143.91, 138.19, 137.49, 132.71, 129.89, 114.92, 60.22, 41.91, 33.68, 33.36, 31.55, 23.30, 14.33; **HR-MS** (ESI) m/z calcd for $C_{18}H_{28}NO_2[M+H^+]$: 290.2115, found: 290.2116.

***tert*-Butyl (*Z*)-(4-(2,2-dimethyl-7-phenylhept-3-en-4-yl)phenyl)carbamate (4x)**



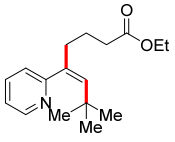
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 20) to give the product **4x** (44.6 mg, 54% yield) as a white solid. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.23 – 7.15 (m, 4H), 7.11 – 7.08 (m, 1H), 7.07 – 7.04 (m, 2H), 6.96 – 6.91 (m, 2H), 6.39 (s, 1H), 5.34 (s, 1H), 2.52 – 2.47 (m, 2H), 2.13 (t, *J* = 7.5 Hz, 2H), 1.55 – 1.48 (m, 2H), 1.44 (s, 9H), 0.77 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.83, 142.66, 137.86, 137.72, 137.05, 136.56, 129.54, 128.47, 128.23, 125.60, 117.72, 80.44, 42.10, 35.38, 33.33, 31.54, 29.73, 28.38; **HR-MS** (ESI) m/z calcd for $C_{26}H_{35}NNaO_2[M+Na^+]$: 416.2560, found: 416.2566.

Ethyl (*Z*)-7,7-dimethyl-5-(quinolin-6-yl)oct-5-enoate (4y)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 50) to give the product **4y** (25.5 mg, 39% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.90 – 8.86 (m, 1H), 8.15 – 8.10 (m, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.40 (dd, *J* = 8.3, 4.3 Hz, 1H), 5.54 (t, *J* = 1.3 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.33 – 2.27 (m, 4H), 1.68 – 1.60 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.85 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.67, 149.99, 147.07, 140.66, 139.16, 136.66, 136.15, 131.61, 128.59, 127.81, 127.11, 121.27, 60.30, 41.61, 33.64, 33.56, 31.54, 23.32, 14.30; **HR-MS** (ESI) m/z calcd for $C_{21}H_{28}NO_2[M+H^+]$: 326.2115, found: 326.2122.

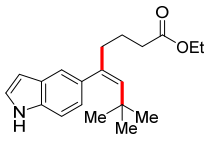
Ethyl (*Z*)-7,7-dimethyl-5-(pyridin-2-yl)oct-5-enoate (4z)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 :

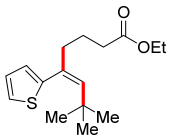
50) to give the product **4z** (16.5 mg, 30% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.60 – 8.56 (m, 1H), 7.64 – 7.58 (m, 1H), 7.18 – 7.12 (m, 2H), 5.51 (t, *J* = 1.3 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.35 – 2.28 (m, 4H), 1.68 – 1.60 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.84 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.79, 160.62, 148.81, 139.47, 136.40, 135.72, 124.63, 121.63, 60.28, 39.88, 33.69, 33.62, 31.13, 23.32, 14.31; **HR-MS** (ESI) m/z calcd for $C_{17}H_{26}NO_2[M+H^+]$: 276.1958, found: 276.1957.

Ethyl (*Z*)-5-(1*H*-indol-5-yl)-7,7-dimethyloct-5-enoate (4aa)



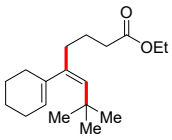
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 50) to give the product **4aa** (33.5 mg, 53% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 (s, 1H), 7.35 – 7.33 (m, 1H), 7.32 – 7.29 (m, 1H), 7.20 – 7.17 (m, 1H), 6.93 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.53 – 6.50 (m, 1H), 5.46 (t, *J* = 1.2 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.33 – 2.25 (m, 4H), 1.70 – 1.62 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.86 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.06, 138.50, 137.92, 134.64, 133.38, 127.38, 124.28, 123.70, 120.71, 110.12, 102.55, 60.22, 42.37, 33.75, 33.42, 31.57, 23.40, 14.31; **HR-MS** (ESI) m/z calcd for $C_{20}H_{28}NO_2[M+H^+]$: 314.2115, found: 314.2117.

Ethyl (*Z*)-7,7-dimethyl-5-(thiophen-2-yl)oct-5-enoate (4ab)



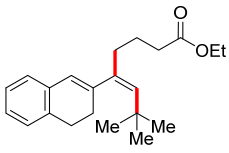
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4ab** (26.1 mg, 46% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.24 – 7.20 (m, 1H), 6.95 – 6.91 (m, 1H), 6.76 – 6.72 (m, 1H), 5.58 (t, *J* = 1.1 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.30 – 2.26 (m, 2H), 2.26 – 2.22 (m, 2H), 1.70 – 1.62 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.93 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.74, 142.68, 142.20, 130.12, 126.37, 126.33, 124.51, 60.27, 42.15, 33.61, 33.41, 31.04, 23.54, 14.33; **HR-MS** (ESI) m/z calcd for $C_{15}H_{25}O_2S[M+H^+]$: 281.1570, found: 281.1574.

Ethyl (*Z*)-5-(cyclohex-1-en-1-yl)-7,7-dimethyloct-5-enoate (4ac)



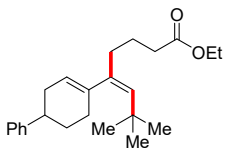
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4ac** (32.6 mg, 58% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.33 – 5.29 (m, 1H), 5.06 (t, *J* = 1.2 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.25 (t, *J* = 7.6 Hz, 2H), 2.07 – 2.00 (m, 2H), 2.00 – 1.94 (m, 4H), 1.67 – 1.61 (m, 4H), 1.60 – 1.53 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.03 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.08, 140.20, 137.11, 136.30, 124.55, 60.20, 37.61, 33.61, 33.35, 31.35, 28.94, 25.19, 23.67, 22.96, 22.20, 14.35; **HR-MS** (ESI) m/z calcd for $C_{18}H_{31}O_2$[M+H$^+$]: 279.2319, found: 279.2319.

Ethyl (*Z*)-5-(3,4-dihydronaphthalen-2-yl)-7,7-dimethyloct-5-enoate (4ad)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 150) to give the product **4ad** (31.6 mg, 48% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.16 – 7.12 (m, 1H), 7.12 – 7.09 (m, 2H), 7.03 – 6.99 (m, 1H), 6.16 (s, 1H), 5.24 (t, *J* = 1.1 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.86 (t, *J* = 8.1 Hz, 2H), 2.38 – 2.32 (m, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.13 – 2.06 (m, 2H), 1.74 – 1.66 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.09 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.83, 140.32, 138.56, 137.53, 134.54, 134.48, 127.35, 126.64, 126.57, 125.97, 125.64, 60.27, 37.81, 33.59, 33.37, 31.54, 28.06, 27.96, 23.71, 14.35.

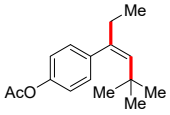
Ethyl (*Z*)-7,7-dimethyl-5-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oct-5-enoate (4ae)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **4ae** (31.6 mg, 51% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 5.47 – 5.37 (m, 1H), 5.12 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.90 – 2.65 (m, 1H), 2.41 – 2.31 (m, 1H), 2.31 – 2.25 (m, 2H), 2.24 – 2.18 (m, 2H), 2.16 – 2.07 (m, 1H), 2.06 – 1.98 (m, 2H), 1.98 – 1.94 (m, 1H), 1.85 – 1.74 (m, 1H), 1.69 (p, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.08 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.08, 147.27, 139.71,

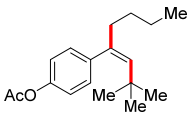
137.12, 136.75, 128.49, 127.01, 126.12, 124.26, 60.29, 39.89, 37.74, 33.66, 33.47, 31.45, 30.18, 29.77, 23.77, 14.42.

(*Z*)-4-(5,5-Dimethylhex-3-en-3-yl)phenyl acetate (5a)



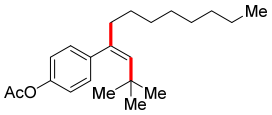
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **5a** (29.7 mg, 60% yield) as a yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.10 – 7.06 (m, 2H), 7.03 – 6.99 (m, 2H), 5.41 (s, 1H), 2.29 (s, 3H), 2.18 (q, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.84 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.48, 149.17, 140.18, 139.56, 136.45, 130.00, 120.56, 35.26, 33.26, 31.59, 21.26, 13.19; **HR-MS** (ESI) m/z calcd for $C_{16}H_{23}O_2$[M+H$^+$]: 247.1693, found: 247.1695.

(*Z*)-4-(2,2-Dimethyloct-3-en-4-yl)phenyl acetate (5b)



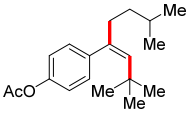
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **5b** (35.6 mg, 65% yield) as a yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.09 – 7.06 (m, 2H), 7.02 – 6.99 (m, 2H), 5.41 (s, 1H), 2.29 (s, 3H), 2.16 (t, *J* = 7.1 Hz, 2H), 1.30 – 1.24 (m, 4H), 0.86 (t, *J* = 6.7 Hz, 3H), 0.84 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.48, 149.14, 140.20, 137.94, 137.59, 129.96, 120.54, 42.19, 33.36, 31.59, 30.24, 22.28, 21.27, 14.04; **HR-MS** (ESI) m/z calcd for $C_{18}H_{26}NaO_2$[M+Na$^+$]: 297.1825, found: 297.1829.

(*Z*)-4-(2,2-Dimethyldodec-3-en-4-yl)phenyl acetate (5c)



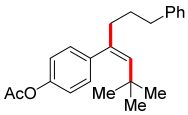
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **5c** (46.3 mg, 68% yield) as a yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.10 – 7.05 (m, 2H), 7.02 – 6.98 (m, 2H), 5.41 (s, 1H), 2.29 (s, 3H), 2.15 (t, *J* = 6.9 Hz, 2H), 1.30 – 1.22 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.84 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.46, 149.14, 140.21, 137.96, 137.60, 129.95, 120.53, 42.44, 33.36, 31.95, 31.59, 29.53, 29.40, 29.17, 28.02, 22.73, 21.26, 14.18; **HR-MS** (ESI) m/z calcd for $C_{22}H_{34}NaO_2$[M+Na$^+$]: 353.2451, found: 353.2454.

(*Z*)-4-(2,2,7-Trimethyloct-3-en-4-yl)phenyl acetate (5d)



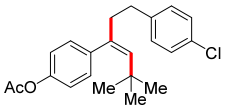
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **5d** (34.0 mg, 59% yield) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.10 – 7.06 (m, 2H), 7.03 – 6.99 (m, 2H), 5.41 (t, *J* = 1.3 Hz, 1H), 2.29 (s, 3H), 2.19 – 2.13 (m, 2H), 1.55 – 1.46 (m, 1H), 1.21 – 1.15 (m, 2H), 0.85 (s, 3H), 0.84 (s, 12H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.48, 149.13, 140.25, 138.23, 137.35, 129.96, 120.53, 40.33, 37.33, 33.34, 31.59, 27.67, 22.63, 21.28; **HR-MS** (ESI) m/z calcd for $C_{19}H_{29}O_2$[M+H$^+$]: 289.2162, found: 289.2163.

(*Z*)-4-(2,2-Dimethyl-7-phenylhept-3-en-4-yl)phenyl acetate (5e)



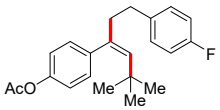
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **5e** (45.7 mg, 68% yield) as a yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.20 – 7.16 (m, 2H), 7.10 – 7.05 (m, 3H), 7.03 – 7.00 (m, 2H), 6.95 – 6.92 (m, 2H), 5.36 (t, *J* = 1.2 Hz, 1H), 2.52 – 2.49 (m, 2H), 2.21 (s, 3H), 2.17 – 2.12 (m, 2H), 1.57 – 1.52 (m, 2H), 0.77 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.45, 149.21, 142.59, 139.93, 138.16, 137.36, 129.94, 128.52, 128.32, 125.71, 120.64, 41.99, 35.43, 33.43, 31.56, 29.78, 21.26; **HR-MS** (ESI) m/z calcd for $C_{23}H_{28}NaO_2$[M+Na$^+$]: 359.1982, found: 359.1980.

(*Z*)-4-(1-(4-Chlorophenyl)-5,5-dimethylhex-3-en-3-yl)phenyl acetate (5f)



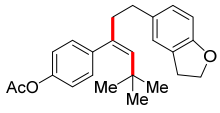
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **5f** (42.8 mg, 60% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.24 – 7.19 (m, 2H), 7.13 – 7.08 (m, 2H), 7.08 – 7.02 (m, 4H), 5.40 (t, *J* = 1.2 Hz, 1H), 2.61 – 2.55 (m, 2H), 2.49 – 2.43 (m, 2H), 2.30 (s, 3H), 0.82 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.45, 149.36, 140.47, 139.58, 138.82, 136.59, 131.43, 130.03, 129.91, 128.33, 120.78, 43.89, 34.00, 33.43, 31.45, 21.28; **HR-MS** (ESI) m/z calcd for $C_{22}H_{25}ClNaO_2$[M+Na$^+$]: 379.1435, found: 379.1427.

(*Z*)-4-(1-(4-Fluorophenyl)-5,5-dimethylhex-3-en-3-yl)phenyl acetate (5g)



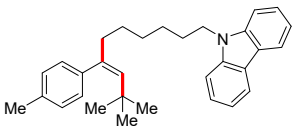
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **5g** (42.1 mg, 62% yield) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.13 – 7.10 (m, 2H), 7.10 – 7.06 (m, 2H), 7.06 – 7.03 (m, 2H), 6.96 – 6.91 (m, 2H), 5.40 (t, *J* = 1.2 Hz, 1H), 2.61 – 2.57 (m, 2H), 2.48 – 2.44 (m, 2H), 2.30 (s, 3H), 0.82 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.46, 162.25 (d, *J* = 243.1 Hz), 149.33, 139.67, 138.73, 137.60 (d, *J* = 3.0 Hz), 136.66, 129.95 (d, *J* = 21.1 Hz), 129.83, 120.75, 114.94 (d, *J* = 21.1 Hz), 44.11, 33.80, 33.41, 31.45, 21.27; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -118.04 - -117.99 (m, 1F); **HR-MS** (ESI) m/z calcd for $C_{22}H_{26}FO_2[M+H^+]$: 341.1911, found: 341.1910.

(*Z*)-4-(1-(2,3-Dihydrobenzofuran-5-yl)-5,5-dimethylhex-3-en-3-yl)phenyl acetate (5h)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 70) to give the product **5h** (45.9 mg, 63% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15 – 7.08 (m, 2H), 7.07 – 6.99 (m, 2H), 6.97 (m, 1H), 6.90 – 6.83 (m, 1H), 6.67 (m, 1H), 5.42 (t, *J* = 1.2 Hz, 1H), 4.53 (t, *J* = 8.7 Hz, 2H), 3.15 (t, *J* = 8.7 Hz, 2H), 2.59 – 2.50 (m, 2H), 2.47 – 2.38 (m, 2H), 2.30 (s, 3H), 0.84 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.62, 158.33, 149.42, 140.07, 138.50, 137.32, 134.28, 130.19, 128.03, 126.98, 125.17, 120.83, 109.02, 71.33, 44.88, 34.36, 33.56, 31.66, 30.04, 21.44; **HR-MS** (ESI) m/z calcd for $C_{24}H_{28}NaO_3[M+Na^+]$: 387.1931, found: 387.1930.

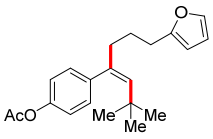
(*Z*)-9-(9,9-Dimethyl-7-(*p*-tolyl)dec-7-en-1-yl)-9*H*-carbazole (5i)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **5i** (45.7 mg, 54% yield) as a yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.07 (t, *J* = 7.3 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 2H), 6.79 (d, *J* = 7.6 Hz, 2H), 5.20 (s, 1H), 4.11 (t, *J* = 7.3 Hz, 2H), 2.18 (s, 3H),

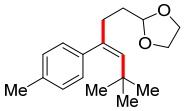
1.98 (t, *J* = 7.3 Hz, 2H), 1.72 – 1.65 (m, 2H), 1.23 – 1.11 (m, 6H), 0.69 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.48, 139.44, 138.55, 137.14, 135.62, 128.90, 128.25, 125.62, 122.88, 120.40, 118.75, 108.71, 43.11, 42.56, 33.30, 31.58, 28.98, 28.95, 27.86, 27.18, 21.24; **HR-MS** (ESI) m/z calcd for $C_{31}H_{38}N[M+H^+]$: 424.2999, found: 424.2999.

(*Z*)-4-(7-(Furan-2-yl)-2,2-dimethylhept-3-en-4-yl)phenyl acetate (5j)



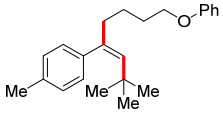
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **5j** (33.5 mg, 51% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 – 7.27 (m, 1H), 7.13 – 7.06 (m, 2H), 7.05 – 6.99 (m, 2H), 6.29 – 6.24 (m, 1H), 5.96 – 5.91 (m, 1H), 5.44 (s, 1H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 2.26 – 2.19 (m, 2H), 1.69 – 1.60 (m, 2H), 0.85 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.45, 156.25, 149.24, 140.77, 139.78, 138.43, 137.02, 129.95, 120.67, 110.10, 104.82, 41.77, 33.44, 31.54, 27.32, 26.26, 21.26; **HR-MS** (ESI) m/z calcd for $C_{21}H_{26}NaO_3[M+Na^+]$: 349.1774, found: 349.1779.

(*Z*)-2-(5,5-Dimethyl-3-(*p*-tolyl)hex-3-en-1-yl)-1,3-dioxolane (5k)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **5k** (40.6 mg, 72% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.14 – 7.04 (m, 2H), 7.02 – 6.93 (m, 2H), 5.45 (s, 1H), 4.83 (t, *J* = 1.2 Hz, 1H), 3.99 – 3.86 (m, 2H), 3.88 – 3.77 (m, 2H), 2.33 (s, 3H), 2.32 – 2.22 (m, 2H), 1.71 – 1.61 (m, 2H), 0.84 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.96, 137.71, 137.32, 135.69, 128.94, 128.27, 104.32, 64.84, 36.89, 33.27, 32.66, 31.44, 21.16; **HR-MS** (ESI) m/z calcd for $C_{18}H_{27}O_2[M+H^+]$: 257.2006, found: 257.2008.

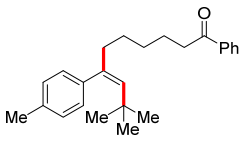
(*Z*)-1-(2,2-Dimethyl-8-phenoxyoct-3-en-4-yl)-4-methylbenzene (5l)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **5l** (42.5 mg, 66% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.22 – 7.16 (m, 2H), 7.04 – 6.99 (m, 2H), 6.93 – 6.88 (m, 2H), 6.87 – 6.78 (m, 3H), 5.35 (t, *J* = 1.2 Hz, 1H), 3.84 (t, *J* = 6.6 Hz, 2H), 2.27 (s, 3H), 2.19

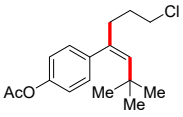
– 2.14 (m, 2H), 1.73 – 1.65 (m, 2H), 1.41 – 1.32 (m, 2H), 0.78 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.15, 139.29, 138.26, 137.55, 135.72, 129.46, 128.96, 128.30, 120.51, 114.57, 67.86, 42.29, 33.35, 31.59, 28.77, 24.42, 21.25; **HR-MS** (ESI) m/z calcd for $C_{23}H_{30}NaO[M+Na^+]$: 345.2189, found: 345.2180.

(*Z*)-9,9-Dimethyl-1-phenyl-7-(*p*-tolyl)dec-7-en-1-one (5m)



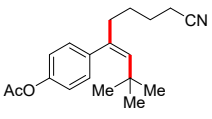
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 80) to give the product **5m** (33.4 mg, 48% yield) as a yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.98 – 7.91 (m, 2H), 7.59 – 7.52 (m, 1H), 7.49 – 7.42 (m, 2H), 7.10 – 7.04 (m, 2H), 6.98 – 6.93 (m, 2H), 5.39 (s, 1H), 2.96 – 2.88 (m, 2H), 2.33 (s, 3H), 2.22 – 2.14 (m, 2H), 1.75 – 1.66 (m, 2H), 1.41 – 1.28 (m, 4H), 0.84 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.65, 139.44, 138.55, 137.21, 137.17, 135.63, 132.92, 128.94, 128.61, 128.25, 128.14, 42.42, 38.67, 33.31, 31.59, 28.82, 27.82, 24.31, 21.24; **HR-MS** (ESI) m/z calcd for $C_{25}H_{33}O[M+H^+]$: 349.2526, found: 349.2526.

(*Z*)-4-(7-Chloro-2,2-dimethylhept-3-en-4-yl)phenyl acetate (5n)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **5n** (34.2 mg, 58% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.10 – 7.06 (m, 2H), 7.04 – 7.00 (m, 2H), 5.49 (t, *J* = 1.2 Hz, 1H), 3.51 (t, *J* = 6.6 Hz, 2H), 2.35 – 2.30 (m, 2H), 2.29 (s, 3H), 1.79 – 1.71 (m, 2H), 0.85 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.42, 149.37, 139.34, 139.12, 135.91, 129.93, 120.83, 44.46, 39.41, 33.50, 31.47, 30.79, 21.25; **HR-MS** (ESI) m/z calcd for $C_{17}H_{23}ClNaO_2[M+Na^+]$: 317.1279, found: 317.1278.

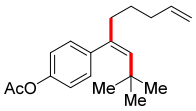
(*Z*)-4-(8-Cyano-2,2-dimethyloct-3-en-4-yl)phenyl acetate (5o)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 30) to give the product **5o** (31.1 mg, 52% yield) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.09 – 7.05 (m, 2H), 7.04 – 7.00 (m, 2H), 5.44 (t, *J* = 1.2

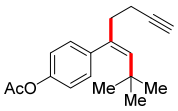
Hz, 1H), 2.32 – 2.28 (m, 5H), 2.23 – 2.18 (m, 2H), 1.68 – 1.59 (m, 2H), 1.48 – 1.39 (m, 2H), 0.84 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.44, 149.34, 139.38, 138.69, 136.58, 129.88, 120.81, 119.82, 41.47, 33.45, 31.49, 27.01, 24.92, 21.24, 17.09; **HR-MS** (ESI) m/z calcd for $C_{19}H_{26}NO_2$[M+H$^+$]: 300.1958, found: 300.1951.

(*Z*)-4-(2,2-Dimethylnona-3,8-dien-4-yl)phenyl acetate (5p)



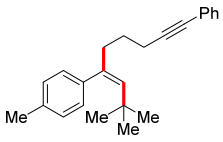
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **5p** (33.5 mg, 62% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.10 – 7.05 (m, 2H), 7.03 – 6.99 (m, 2H), 5.83 – 5.72 (m, 1H), 5.43 (t, *J* = 1.2 Hz, 1H), 5.01 – 4.90 (m, 2H), 2.29 (s, 3H), 2.21 – 2.15 (m, 2H), 2.06 – 2.00 (m, 2H), 1.43 – 1.34 (m, 2H), 0.84 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.46, 149.19, 139.99, 138.89, 138.04, 137.47, 129.95, 120.61, 114.56, 41.80, 33.40, 33.25, 31.56, 27.23, 21.26; **HR-MS** (ESI) m/z calcd for $C_{19}H_{26}NaO_2$[M+Na$^+$]: 309.1825, found: 309.1818.

(*Z*)-4-(2,2-Ddimethyloct-3-en-7-yn-4-yl)phenyl acetate (5q)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **5q** (30.0 mg, 55% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.14 – 7.09 (m, 2H), 7.04 – 6.99 (m, 2H), 5.52 (t, *J* = 1.2 Hz, 1H), 2.41 – 2.36 (m, 2H), 2.29 (s, 3H), 2.17 – 2.12 (m, 2H), 1.95 (t, *J* = 2.6 Hz, 1H), 0.85 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.42, 149.44, 139.66, 138.83, 135.38, 130.07, 120.81, 83.93, 68.87, 40.98, 33.53, 31.44, 21.25, 17.56; **HR-MS** (ESI) m/z calcd for $C_{18}H_{22}NaO_2$[M+Na$^+$]: 293.1512, found: 293.1515.

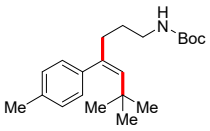
(*Z*)-1-(2,2-Dimethyl-9-phenylnon-3-en-8-yn-4-yl)-4-methylbenzene (5r)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **5r** (31.6 mg, 50% yield) as a yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.39 – 7.34 (m, 2H), 7.28 – 7.23 (m, 3H), 7.08 (d, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 5.45 (s, 1H), 2.36 (t, *J* = 7.2 Hz, 2H),

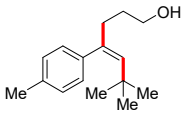
2.33 (s, 3H), 2.32 – 2.29 (m, 2H), 1.61 – 1.55 (m, 2H), 0.84 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.16, 138.00, 137.64, 135.80, 131.62, 128.96, 128.35, 128.25, 127.53, 124.18, 90.35, 80.79, 41.75, 33.41, 31.57, 27.08, 21.25, 18.83; **HR-MS** (ESI) m/z calcd for $C_{24}H_{29}[M+H^+]$: 317.2264, found: 317.2260.

***tert*-Butyl (*Z*)-(6,6-dimethyl-4-(*p*-tolyl)hept-4-en-1-yl)carbamate (5s)**



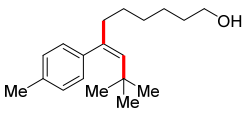
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 60) to give the product **5s** (44.4 mg, 67% yield) as a yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.10 – 7.06 (m, 2H), 6.98 – 6.94 (m, 2H), 5.42 (t, *J* = 1.2 Hz, 1H), 4.46 (br s, 1H), 3.08 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 2.19 (t, *J* = 7.5 Hz, 2H), 1.48 – 1.44 (m, 2H), 1.43 (s, 9H), 0.84 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 155.95, 147.15, 138.96, 137.77, 135.84, 128.93, 128.35, 79.05, 40.35, 39.95, 33.35, 31.51, 28.50, 28.33, 21.22; **HR-MS** (ESI) m/z calcd for $C_{21}H_{33}NNaO_2[M+Na^+]$: 354.2404, found: 354.2393.

(*Z*)-6,6-Dimethyl-4-(*p*-tolyl)hept-4-en-1-ol (5t)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 30) to give the product **5t** (28.3 mg, 61% yield) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.11 – 7.07 (m, 2H), 7.00 – 6.95 (m, 2H), 5.45 (s, 1H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.34 (s, 3H), 2.25 (t, *J* = 7.6 Hz, 2H), 1.59 – 1.53 (m, 2H), 0.85 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.05, 138.10, 137.64, 135.83, 128.97, 128.35, 62.79, 38.88, 33.36, 31.52, 31.08, 21.23; **HR-MS** (ESI) m/z calcd for $C_{16}H_{25}O[M+H^+]$: 233.1900, found: 233.1899.

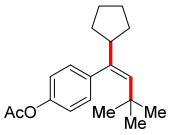
(*Z*)-9,9-Dimethyl-7-(*p*-tolyl)dec-7-en-1-ol (5u)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 30) to give the product **5u** (36.7 mg, 67% yield) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.08 (d, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 7.5 Hz, 2H), 5.38 (t, *J* = 1.6 Hz, 1H), 3.61 (t, *J* = 6.7 Hz, 2H), 2.34 (s, 3H), 2.18 – 2.12 (m, 2H), 1.56 – 1.50

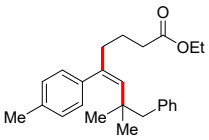
(m, 2H), 1.34 – 1.27 (m, 6H), 0.84 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.53, 138.69, 137.07, 135.60, 128.93, 128.23, 63.14, 42.54, 33.30, 32.84, 31.59, 28.93, 28.00, 25.64, 21.24; **HR-MS** (ESI) m/z calcd for $C_{19}H_{31}O[M+H^+]$: 275.2369, found: 275.2370.

(*Z*)-4-(1-Cyclopentyl-3,3-dimethylbut-1-en-1-yl)phenyl acetate (5v)



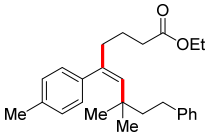
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **5v** (29.7 mg, 52% yield) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.07 – 7.03 (m, 2H), 7.02 – 6.98 (m, 2H), 5.45 (d, *J* = 1.2 Hz, 1H), 2.51 – 2.41 (m, 1H), 2.29 (s, 3H), 1.69 – 1.61 (m, 2H), 1.58 – 1.48 (m, 4H), 1.32 – 1.26 (m, 2H), 0.82 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.46, 149.13, 140.56, 139.18, 136.23, 130.71, 120.23, 50.93, 33.26, 31.65, 31.50, 24.44, 21.29; **HR-MS** (ESI) m/z calcd for $C_{19}H_{27}O_2[M+H^+]$: 287.2006, found: 287.2005.

Ethyl (*Z*)-7,7-dimethyl-8-phenyl-5-(*p*-tolyl)oct-5-enoate (6a)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **6a** (36.4 mg, 50% yield) as a yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.22 – 7.17 (m, 2H), 7.16 – 7.12 (m, 1H), 7.06 – 7.01 (m, 2H), 6.91 – 6.87 (m, 2H), 6.57 – 6.53 (m, 2H), 5.28 (s, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 2H), 2.22 (s, 3H), 2.18 (t, *J* = 7.5 Hz, 2H), 2.15 – 2.11 (m, 2H), 1.54 – 1.49 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.69 (s, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.82, 139.39, 138.72, 138.28, 136.16, 135.68, 130.78, 128.65, 128.15, 127.62, 125.91, 60.23, 50.59, 42.16, 38.16, 33.75, 28.98, 23.20, 21.19, 14.34; **HR-MS** (ESI) m/z calcd for $C_{25}H_{33}O_2[M+H^+]$: 365.2475, found: 365.2465.

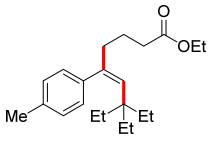
Ethyl (*Z*)-7,7-dimethyl-9-phenyl-5-(*p*-tolyl)non-5-enoate (6b)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **6b** (39.4 mg, 52% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.21 – 7.15 (m, 2H), 7.11 – 7.07 (m, 1H), 7.07 – 7.02 (m, 3H), 7.01 – 6.99 (m, 1H), 6.94 – 6.90 (m, 2H), 5.31 (t, *J* = 1.2 Hz, 1H),

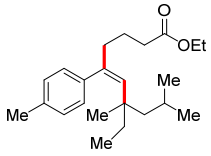
4.04 (q, *J* = 7.1 Hz, 2H), 2.51 – 2.45 (m, 2H), 2.27 (s, 3H), 2.22 (t, *J* = 7.6 Hz, 2H), 2.20 – 2.15 (m, 2H), 1.61 – 1.52 (m, 2H), 1.45 – 1.39 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.78 (s, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.80, 143.46, 138.85, 138.71, 136.48, 135.93, 128.81, 128.41, 128.38, 128.31, 125.55, 60.25, 46.83, 42.09, 36.69, 33.66, 31.64, 29.30, 23.32, 21.23, 14.33; **HR-MS** (ESI) m/z calcd for $C_{26}H_{34}NaO_2$[M+Na^+]: 401.2451, found: 401.2444.

Ethyl (*Z*)-7,7-diethyl-5-(*p*-tolyl)non-5-enoate (6c)



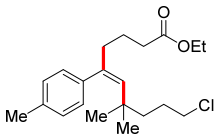
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 300) to give the product **6c** (39.7 mg, 60% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.09 – 7.04 (m, 2H), 6.99 – 6.94 (m, 2H), 5.09 (t, *J* = 1.2 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 2.31 – 2.21 (m, 4H), 1.66 – 1.57 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.13 (q, *J* = 7.5 Hz, 6H), 0.70 (t, *J* = 7.5 Hz, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.86, 139.27, 139.24, 135.79, 135.68, 128.30, 128.25, 60.21, 42.80, 42.69, 33.71, 28.96, 23.51, 21.23, 14.30, 8.29; **HR-MS** (ESI) m/z calcd for $C_{22}H_{34}NaO_2$[M+Na^+]: 353.2451, found: 353.2443.

Ethyl (*Z*)-7-ethyl-7,9-dimethyl-5-(*p*-tolyl)dec-5-enoate (6d)



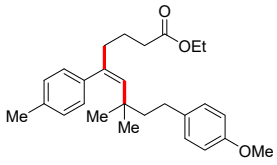
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **6d** (34.4 mg, 50% yield) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.09 – 7.05 (m, 2H), 6.99 – 6.94 (m, 2H), 5.23 (t, *J* = 1.2 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 2.27 (t, *J* = 7.6 Hz, 2H), 2.25 – 2.20 (m, 2H), 1.73 – 1.59 (m, 3H), 1.23 (m, 4H), 1.20 – 1.17 (m, 1H), 1.16 – 1.07 (m, 2H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H), 0.78 (t, *J* = 7.4 Hz, 3H), 0.55 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.85, 139.20, 138.12, 136.46, 135.67, 128.76, 128.24, 60.22, 52.66, 42.44, 40.62, 36.31, 33.78, 25.49, 25.09, 24.75, 24.18, 23.36, 21.23, 14.32, 8.99; **HR-MS** (ESI) m/z calcd for $C_{23}H_{37}O_2$[M+H^+]: 345.2788, found: 345.2787.

Eethyl (*Z*)-10-chloro-7,7-dimethyl-5-(*p*-tolyl)dec-5-enoate (6e)



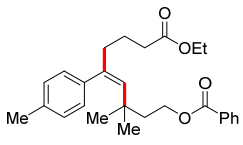
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **6e** (39.7 mg, 56% yield) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.09 (d, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 7.7 Hz, 2H), 5.29 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.21 (t, *J* = 7.5 Hz, 2H), 1.75 – 1.69 (m, 2H), 1.65 – 1.59 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.91 – 0.84 (m, 2H), 0.81 (s, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.75, 138.89, 138.70, 136.09, 136.01, 128.67, 128.43, 60.25, 45.90, 42.02, 41.51, 36.22, 33.65, 29.43, 28.64, 23.32, 21.22, 14.33; **HR-MS** (ESI) m/z calcd for $C_{21}H_{31}ClNaO_2$[M+Na^+]: 373.1905, found: 373.1897.

Ethyl (*Z*)-9-(4-methoxyphenyl)-7,7-dimethyl-5-(*p*-tolyl)non-5-enoate (6f)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **6f** (43.3 mg, 53% yield) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.12 – 7.07 (m, 2H), 7.06 – 7.03 (m, 2H), 7.02 – 6.99 (m, 2H), 6.84 – 6.79 (m, 2H), 5.38 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 2.53 – 2.48 (m, 2H), 2.35 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 2.25 (t, *J* = 7.5 Hz, 2H), 1.67 – 1.62 (m, 2H), 1.50 – 1.45 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.85 (s, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.81, 157.61, 138.87, 138.61, 136.53, 135.91, 135.52, 129.20, 128.81, 128.40, 113.76, 60.25, 55.33, 47.08, 42.08, 36.65, 33.65, 30.66, 29.30, 23.31, 21.22, 14.33; **HR-MS** (ESI) m/z calcd for $C_{27}H_{37}O_3$[M+H^+]: 409.2737, found: 409.2738.

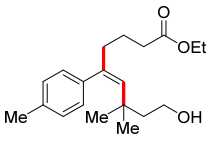
(*Z*)-9-Ethoxy-3,3-dimethyl-9-oxo-5-(*p*-tolyl)non-4-en-1-yl benzoate (6g)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 100) to give the product **6g** (43.1 mg, 51% yield) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 – 7.98 (m, 2H), 7.57 – 7.52 (m, 1H), 7.46 – 7.40 (m, 2H), 7.09 – 7.04 (m, 2H), 6.99 – 6.95 (m, 2H), 5.39 (t, *J* = 1.2 Hz, 1H), 4.31 (t, *J* = 7.3 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 2.26 (t, *J* = 7.6 Hz, 2H),

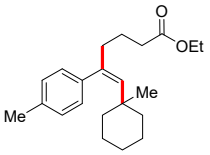
2.23 – 2.18 (m, 2H), 1.69 – 1.64 (m, 2H), 1.63 – 1.57 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 6H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 173.75, 166.74, 139.34, 138.51, 136.06, 135.56, 132.84, 130.58, 129.59, 128.64, 128.50, 128.36, 62.98, 60.27, 42.09, 42.03, 35.65, 33.69, 29.76, 23.29, 21.21, 14.31; **HR-MS** (ESI) m/z calcd for $C_{27}H_{35}O_4$[M+H$^+$]: 423.2530, found: 423.2528.

Ethyl (*Z*)-9-hydroxy-7,7-dimethyl-5-(*p*-tolyl)non-5-enoate (6h)



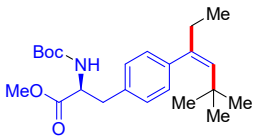
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 30) to give the product **6h** (29.9 mg, 47% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.11 – 7.06 (m, 2H), 6.99 – 6.94 (m, 2H), 5.35 (t, *J* = 1.3 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.64 (t, *J* = 7.4 Hz, 2H), 2.33 (s, 3H), 2.26 (t, *J* = 7.6 Hz, 2H), 2.23 – 2.18 (m, 2H), 1.65 – 1.57 (m, 2H), 1.51 – 1.46 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.82 (s, 6H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 173.76, 138.86, 138.57, 136.18, 136.11, 128.65, 128.47, 60.49, 60.29, 46.73, 41.98, 35.59, 33.65, 29.74, 23.27, 21.22, 14.31; **HR-MS** (ESI) m/z calcd for $C_{20}H_{31}O_3$[M+H$^+$]: 319.2268, found: 319.2267.

Ethyl (*Z*)-6-(1-methylcyclohexyl)-5-(*p*-tolyl)hex-5-enoate (6i)



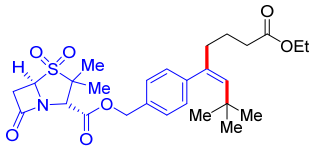
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **6i** (35.5 mg, 54% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.11 – 7.05 (m, 2H), 7.00 – 6.95 (m, 2H), 5.33 (m, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 2.29 (m, 2H), 2.26 – 2.21 (m, 2H), 1.67 – 1.59 (m, 2H), 1.47 – 1.29 (m, 8H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.01 – 0.91 (m, 2H), 0.87 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 173.88, 139.17, 138.70, 136.81, 135.83, 128.52, 128.41, 60.24, 42.11, 39.53, 36.55, 33.64, 26.26, 23.39, 22.89, 21.24, 14.33; **HR-MS** (ESI) m/z calcd for $C_{22}H_{32}NaO_2$[M+Na$^+$]: 351.2295, found: 351.2298.

Methyl (*S*,*Z*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-(5,5-dimethylhex-3-en-3-yl)phenyl)propanoate (7a)



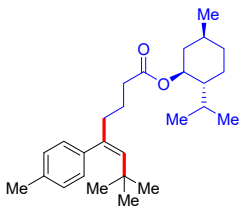
According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 30) to give the product **7a** (43.8 mg, 56% yield) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.09 – 6.96 (m, 4H), 5.38 (t, *J* = 1.4 Hz, 1H), 5.10 – 4.87 (m, 1H), 4.65 – 4.50 (m, 1H), 3.66 (s, 3H), 3.12 – 2.98 (m, 2H), 2.22 – 2.12 (m, 2H), 1.42 (s, 9H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.82 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.58, 155.11, 141.38, 140.06, 135.98, 133.84, 129.28, 128.40, 79.94, 54.62, 52.14, 38.46, 35.23, 33.21, 31.56, 28.37, 13.19; **HR-MS** (ESI) m/z calcd for $C_{23}H_{35}NNaO_4$[M+Na^+]: 412.2458, found: 412.2462.

4-((*Z*)-8-Ethoxy-2,2-dimethyl-8-oxooct-3-en-4-yl)benzyl (*2S*,*5R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (7b)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 5) to give the product **7b** (50.0 mg, 48% yield) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 – 7.28 (m, 2H), 7.13 – 7.09 (m, 2H), 5.44 (t, *J* = 1.2 Hz, 1H), 5.32 (d, *J* = 11.8 Hz, 1H), 5.13 (d, *J* = 11.9 Hz, 1H), 4.60 – 4.57 (m, 1H), 4.40 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.53 – 3.39 (m, 2H), 2.27 (t, *J* = 7.6 Hz, 2H), 2.23 – 2.18 (m, 2H), 1.63 – 1.57 (m, 2H), 1.54 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.20 (s, 3H), 0.82 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.69, 170.79, 166.88, 143.17, 138.63, 136.68, 132.52, 129.55, 128.53, 68.08, 63.17, 62.86, 61.12, 60.31, 41.57, 38.36, 33.59, 33.48, 31.47, 23.20, 20.12, 18.61, 14.32; **HR-MS** (ESI) m/z calcd for $C_{27}H_{37}NNaO_7S$[M+Na^+]: 542.2183, found: 542.2193.

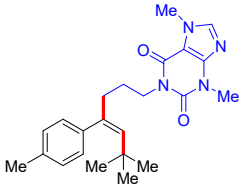
(*1S*,*2R*,*5S*)-2-Isopropyl-5-methylcyclohexyl (*Z*)-7,7-dimethyl-5-(*p*-tolyl)oct-5-enoate (7c)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 50) to give the product **7c** (51.0 mg, 64% yield) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.08 (d, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 5.41 (s, 1H), 4.70 – 4.63 (m, 1H), 2.34 (s, 3H), 2.29 –

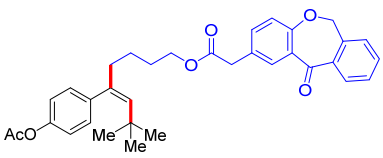
2.23 (m, 2H), 2.20 (t, J = 7.5 Hz, 2H), 2.00 – 1.93 (m, 1H), 1.89 – 1.81 (m, 1H), 1.71 – 1.63 (m, 2H), 1.65 – 1.57 (m, 2H), 1.53 – 1.44 (m, 1H), 1.39 – 1.31 (m, 1H), 1.10 – 1.00 (m, 1H), 0.97 – 0.91 (m, 2H), 0.91 – 0.87 (m, 6H), 0.85 (s, 9H), 0.75 (d, J = 7.0 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 173.36, 138.97, 138.09, 137.60, 135.76, 128.90, 128.34, 73.94, 47.09, 41.78, 41.04, 34.37, 33.89, 33.37, 31.53, 31.44, 26.31, 23.48, 23.41, 22.11, 21.23, 20.84, 16.36; **HR-MS** (ESI) m/z calcd for $C_{27}H_{43}O_2$[M+H$^+$]: 399.3258, found: 399.3250.

(*Z*)-1-(6,6-Dimethyl-4-(*p*-tolyl)hept-4-en-1-yl)-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione (7d)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 1) to give the product **7d** (45.8 mg, 58% yield) as a white solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.48 (s, 1H), 7.09 – 7.04 (m, 2H), 7.03 – 6.98 (m, 2H), 5.41 (t, J = 1.4 Hz, 1H), 4.01 – 3.95 (m, 5H), 3.55 (s, 3H), 2.31 (s, 3H), 2.28 – 2.22 (m, 2H), 1.70 – 1.61 (m, 2H), 0.82 (s, 9H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 155.32, 151.49, 148.71, 141.32, 139.14, 137.68, 137.45, 135.64, 129.00, 128.26, 107.73, 41.37, 40.01, 33.62, 33.32, 31.49, 29.74, 26.35, 21.21; **HR-MS** (ESI) m/z calcd for $C_{23}H_{31}N_4O_2$[M+H$^+$]: 395.2442, found: 395.2435.

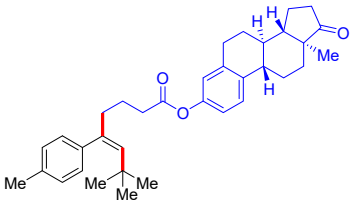
(*Z*)-5-(4-Acetoxyphenyl)-7,7-dimethyloct-5-en-1-yl-2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (7e)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 10) to give the product **7e** (61.1 mg, 58% yield) as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.11 (d, J = 2.4 Hz, 1H), 7.91 – 7.86 (m, 1H), 7.60 – 7.53 (m, 1H), 7.50 – 7.44 (m, 1H), 7.43 – 7.39 (m, 1H), 7.38 – 7.34 (m, 1H), 7.09 – 7.04 (m, 2H), 7.03 – 6.99 (m, 3H), 5.41 (t, J = 1.3 Hz, 1H), 5.18 (s, 2H), 4.07 (t, J = 6.7 Hz, 2H), 3.62 (s, 2H), 2.29 (s, 3H), 2.21 – 2.15 (m, 2H), 1.65 – 1.58 (m, 2H), 1.37 – 1.29 (m, 2H), 0.83 (s, 9H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 190.92, 171.57, 169.46, 160.51, 149.25, 140.56, 139.70, 138.31, 137.14,

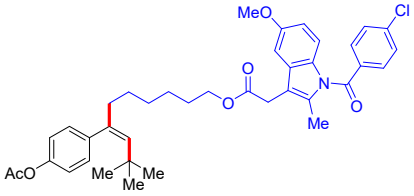
136.43, 135.65, 132.82, 132.52, 129.93, 129.57, 129.33, 128.04, 127.87, 125.19, 121.09, 120.68, 73.71, 65.05, 41.87, 40.29, 33.41, 31.54, 28.01, 24.19, 21.27; **HR-MS** (ESI) m/z calcd for $C_{34}H_{36}NaO_6$[M+Na^+]: 563.2404, found: 563.2413.

(*8R,9S,13S,14S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl (*Z*)-7,7-dimethyl-5-(*p*-tolyl)oct-5-enoate (7f)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 40) to give the product **7f** (59.4 mg, 58% yield) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.29 – 7.26 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.84 – 6.80 (m, 1H), 6.80 – 6.76 (m, 1H), 5.46 (s, 1H), 2.93 – 2.88 (m, 2H), 2.54 – 2.48 (m, 3H), 2.43 – 2.38 (m, 1H), 2.34 (s, 3H), 2.31 – 2.27 (m, 3H), 2.19 – 2.11 (m, 1H), 2.09 – 1.99 (m, 2H), 1.99 – 1.94 (m, 1H), 1.77 – 1.71 (m, 2H), 1.67 – 1.57 (m, 3H), 1.55 – 1.45 (m, 3H), 0.91 (s, 3H), 0.87 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 220.88, 172.54, 148.68, 138.86, 138.33, 137.99, 137.37, 137.29, 135.88, 128.90, 128.40, 126.40, 121.65, 118.83, 50.49, 48.01, 44.21, 41.76, 38.07, 35.92, 33.63, 33.41, 31.61, 31.52, 29.45, 26.41, 25.81, 23.28, 21.65, 21.23, 13.89; **HR-MS** (ESI) m/z calcd for $C_{35}H_{44}NaO_3$[M+Na^+]: 535.3183, found: 535.3194.

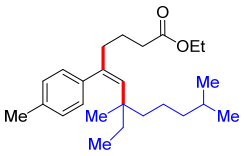
(*Z*)-7-(4-Methoxyphenyl)-9,9-dimethyldec-7-en-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (7g)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 20) to give the product **7g** (69.7 mg, 53% yield) as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 – 7.63 (m, 2H), 7.50 – 7.44 (m, 2H), 7.09 – 7.04 (m, 2H), 7.03 – 6.98 (m, 2H), 6.97 – 6.95 (m, 1H), 6.89 – 6.85 (m, 1H), 6.69 – 6.64 (m, 1H), 5.40 (t, *J* = 1.2 Hz, 1H), 4.07 (t, *J* = 6.7 Hz, 2H), 3.82 (s, 3H), 3.65 (s, 2H), 2.38 (s, 3H), 2.29 (s, 3H), 2.16 – 2.09 (m, 2H), 1.61 – 1.55 (m, 2H), 1.29 – 1.21 (m, 6H), 0.84 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 171.00, 169.46, 168.33, 156.09, 149.16,

139.99, 139.28, 137.76, 137.69, 135.92, 134.02, 131.23, 130.86, 130.74, 129.90, 129.17, 120.59, 114.99, 112.82, 111.73, 101.37, 65.21, 55.73, 42.31, 33.35, 31.55, 30.48, 28.79, 28.68, 27.89, 25.81, 21.25, 13.43; **HR-MS** (ESI) m/z calcd for $C_{39}H_{45}ClNO_6$[M+H$^+$]: 658.2930, found: 658.2929.

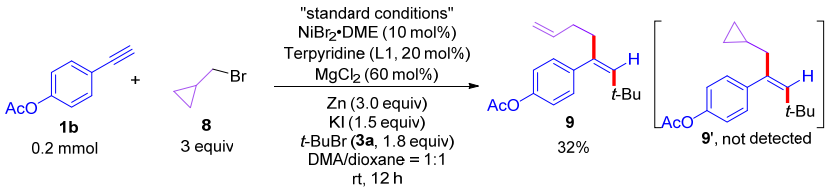
Eethyl (*Z*)-7-ethyl-7,11-dimethyl-5-(*p*-tolyl)dodec-5-enoate (7h)



According to general procedure, the crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 300) to give the product **7h** (41.9 mg, 56% yield) as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.10 – 7.05 (m, 2H), 6.98 – 6.93 (m, 2H), 5.19 (t, *J* = 1.2 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 2.28 (t, *J* = 7.6 Hz, 2H), 2.25 – 2.20 (m, 2H), 1.67 – 1.57 (m, 2H), 1.55 – 1.46 (m, 1H), 1.29 – 1.20 (m, 5H), 1.19 – 1.00 (m, 6H), 0.86 (d, *J* = 6.6 Hz, 6H), 0.78 (t, *J* = 7.4 Hz, 3H), 0.59 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 173.87, 139.09, 138.69, 136.07, 135.69, 128.68, 128.25, 60.21, 42.77, 42.30, 39.90, 39.86, 35.36, 33.65, 28.03, 24.43, 23.35, 22.81, 22.76, 22.24, 21.23, 14.31, 8.93; **HR-MS** (ESI) m/z calcd for $C_{25}H_{40}NaO_2$[M+Na$^+$]: 395.2921, found: 359.2911.

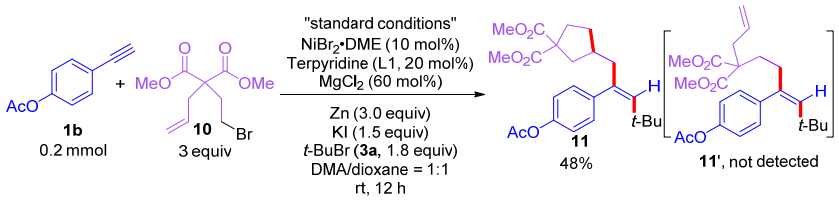
5. Mechanistic Investigations and Control Experiments

5.1 Radical clock reaction



The reaction was setup in a nitrogen-filled glove box. Zinc (39.2 mg, 0.6 mmol, 3.0 equiv), $MgCl_2$ (11.4 mg, 0.12 mmol, 0.6 equiv), KI (49.8 mg, 0.3 mmol, 1.5 equiv), terpyridine (9.33 mg, 0.04 mmol, 20 mol%), **1b** (32.0 mg, 0.2 mmol) and $NiBr_2$·DME (6.17 mg, 0.02 mmol, 10 mol%) were added to an oven-dried 10 mL Schlenk tube containing a magnetic stir bar. Anhydrous DMA (3.0 mL) and anhydrous 1,4-dioxane (3.0 mL) were added and rapid stirring was commenced. Then, **8** (81.0 mg, 0.6 mmol,

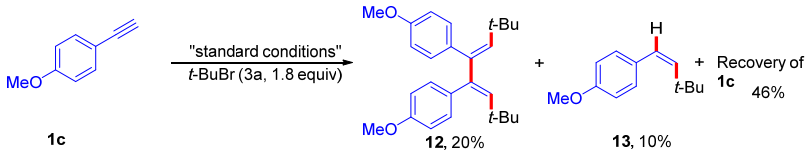
58.3 μL, 3.0 equiv) and **3a** (49.3 mg, 0.36 mmol, 40.4 μL, 1.8 equiv) were added in turn via syringe and sealed with a screw-cap. The reactions were removed from the glove box and placed in a magnetic stir bar to stir vigorously for 24 h. The reaction was diluted with ethyl acetate (50 mL) and washed with brine (50 mL, three times), aqueous layer was extracted with ethyl acetate (20 mL). The combined organic layers were dried over magnesium sulfate and evaporated. The crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 200) to give the product **9** (17.4 mg, 32% yield) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.09 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 5.82 – 5.74 (m, 1H), 5.44 (s, 1H), 5.01 – 4.91 (m, 2H), 2.29 (s, 3H), 2.26 (t, *J* = 7.8 Hz, 2H), 2.08 – 2.02 (m, 2H), 0.84 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 169.48, 149.24, 139.78, 138.44, 138.30, 136.97, 130.03, 120.65, 114.64, 41.68, 33.42, 32.29, 31.55, 21.28; **HR-MS** (ESI) m/z calcd for $C_{18}H_{24}NaO_2$[M+Na^+]: 295.1669, found: 295.1675.



The reaction was setup in a nitrogen-filled glove box. Zinc (39.2 mg, 0.6 mmol, 3.0 equiv), $MgCl_2$ (11.4 mg, 0.12 mmol, 0.6 equiv), KI (49.8 mg, 0.3 mmol, 1.5 equiv), terpyridine (9.33 mg, 0.04 mmol, 20 mol%), **1b** (32.0 mg, 0.2 mmol) and $NiBr_2$·DME (6.17 mg, 0.02 mmol, 10 mol%) were added to an oven-dried 10 mL Schlenk tube containing a magnetic stir bar. Anhydrous DMA (3.0 mL) and anhydrous 1,4-dioxane (3.0 mL) were added and rapid stirring was commenced. Then, **10** (0.17 g, 0.6 mmol, 3.0 equiv) and **3a** (49.3 mg, 0.36 mmol, 40.4 μL, 1.8 equiv) were added in turn via syringe and sealed with a screw-cap. The reactions were removed from the glove box and placed in a magnetic stir bar to stir vigorously for 24 h. The reaction was diluted with ethyl acetate (50 mL) and washed with brine (50 mL, three times), aqueous layer was extracted with ethyl acetate (20 mL). The combined organic layers were dried over magnesium sulfate and evaporated. The crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 30) to give the

product **11** (40.0 mg, 48% yield) as a colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.07 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 5.42 (s, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 2.42 – 2.37 (m, 1H), 2.32 – 2.26 (m, 4H), 2.23 – 2.15 (m, 2H), 2.13 – 2.07 (m, 1H), 1.97 – 1.88 (m, 1H), 1.79 – 1.72 (m, 2H), 1.34 – 1.27 (m, 1H), 0.83 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.46, 173.25, 169.59, 149.41, 139.77, 139.19, 136.69, 130.02, 120.84, 60.20, 52.86, 52.83, 48.34, 40.30, 37.23, 34.11, 33.62, 31.78, 31.65, 21.41; **HR-MS** (ESI) m/z calcd for $C_{24}H_{32}NaO_6$[M+Na^+]: 439.2091, found: 439.2100.

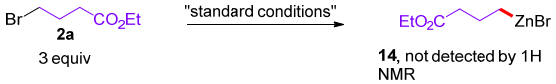
5.2 Control experiments



1c **12**, 20% **13**, 10%

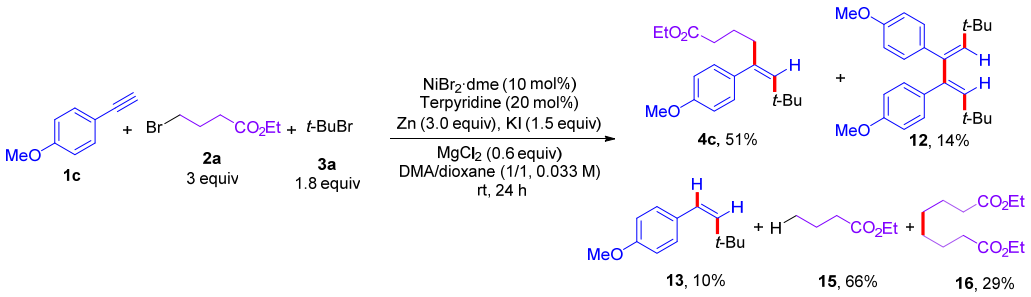
The reaction was setup in a nitrogen-filled glove box. Zinc (39.2 mg, 0.6 mmol, 3.0 equiv), $MgCl_2$ (11.4 mg, 0.12 mmol, 0.6 equiv), KI (49.8 mg, 0.3 mmol, 1.5 equiv), terpyridine (9.33 mg, 0.04 mmol, 20 mol%) and $NiBr_2$·DME (6.17 mg, 0.02 mmol, 10 mol%) were added to an oven-dried 10 mL Schlenk tube containing a magnetic stir bar. Anhydrous DMA (3.0 mL) and anhydrous 1,4-dioxane (3.0 mL) were added and rapid stirring was commenced. Then, **1c** (26.4 mg, 0.2 mmol, 26.1 μL) and **3a** (49.3 mg, 0.36 mmol, 40.4 μL, 1.8 equiv) were added in turn via syringe and sealed with a screw-cap. The reactions were removed from the glove box and placed in a magnetic stir bar to stir vigorously for 24 h. The reaction was diluted with ethyl acetate (50 mL) and washed with brine (50 mL, three times), aqueous layer was extracted with ethyl acetate (20 mL). The combined organic layers were dried over magnesium sulfate and evaporated. The crude mixture was purified by flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 30) to give **12** as a colorless oil (15.1 mg, 20% yield) and **13** a colorless oil (4.1 mg, 10% yield).

5.3 Detection of zinc reagent



The reaction was setup in a nitrogen-filled glove box. Zinc (39.2 mg, 0.6 mmol), $MgCl_2$ (11.4 mg, 0.12 mmol), KI (49.8 mg, 0.3 mmol), terpyridine (9.33 mg, 0.04 mmol) and $NiBr_2$·DME (6.17 mg, 0.02 mmol) were added to an oven-dried 10 mL Schlenk tube containing a magnetic stir bar. Anhydrous DMA (3.0 mL) and anhydrous 1,4-dioxane (3.0 mL) were added and rapid stirring was commenced. Then **2a** (0.12 g, 0.6 mmol, 86.1 μL) was added in turn via syringe and sealed with a screw-cap. The reactions were run in the glove box and placed in a magnetic stir bar to stir vigorously. After 24 h, 60 μL of the reaction mixture was taken out and filtered through a syringe filter using $CDCl_3$ as solvent in glove box, the sample was then analyzed by ^1H NMR of the crude mixture and the organic zinc species **14** was not detected.[3]

5.4 Identification of byproducts of the reaction



The reaction was setup in a nitrogen-filled glove box. Zinc (0.19 g, 3.0 mmol, 3.0 equiv), $MgCl_2$ (57.0 mg, 0.6 mmol, 0.6 equiv), KI (0.25 g, 1.5 mmol, 1.5 equiv), terpyridine (46.6 mg, 0.2 mmol, 20 mol%) and $NiBr_2$·DME (30.8 mg, 0.1 mmol, 10 mol%) were added to an oven-dried 100 mL Schlenk tube containing a magnetic stir bar. Anhydrous DMA (15.0 mL) and anhydrous 1,4-dioxane (15.0 mL) were added and rapid stirring was commenced. Then, **2a** (0.58 g, 3.0 mmol, 0.43 mL, 3.0 equiv), **1c** (0.13 g, 1.0 mmol, 130.5 μL) and **3a** (0.25 g, 1.8 mmol, 0.2 mL, 1.8 equiv) were added in turn via syringe and sealed with a screw-cap. The reaction was removed from the glove box and stirred vigorously at room temperature for 24 h. The reaction was diluted with ethyl acetate (100 mL) and washed with brine (100 mL, three times). Aqueous layer was extracted with ethyl acetate (100 mL, three times). The combined organic layer was dried over magnesium sulfate and evaporated. The residue was purified by

flash chromatography on silica gel (eluted with ethyl acetate : hexanes = 1 : 30) to give the desired product **4c** as a yellow oil (155.2 mg, 51% yield).

12 was isolated as a colorless oil (53.0 mg, 14% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.98 (d, *J* = 8.6 Hz, 4H), 6.82 (d, *J* = 8.6 Hz, 4H), 5.12 (s, 2H), 3.83 (s, 6H), 0.73 (s, 18H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.14, 143.32, 141.20, 133.02, 131.58, 112.74, 55.21, 33.46, 31.42, 29.80; **HR-MS** (ESI) m/z calcd for $C_{26}H_{35}O_2[M+H^+]$: 379.2632, found: 379.2625.

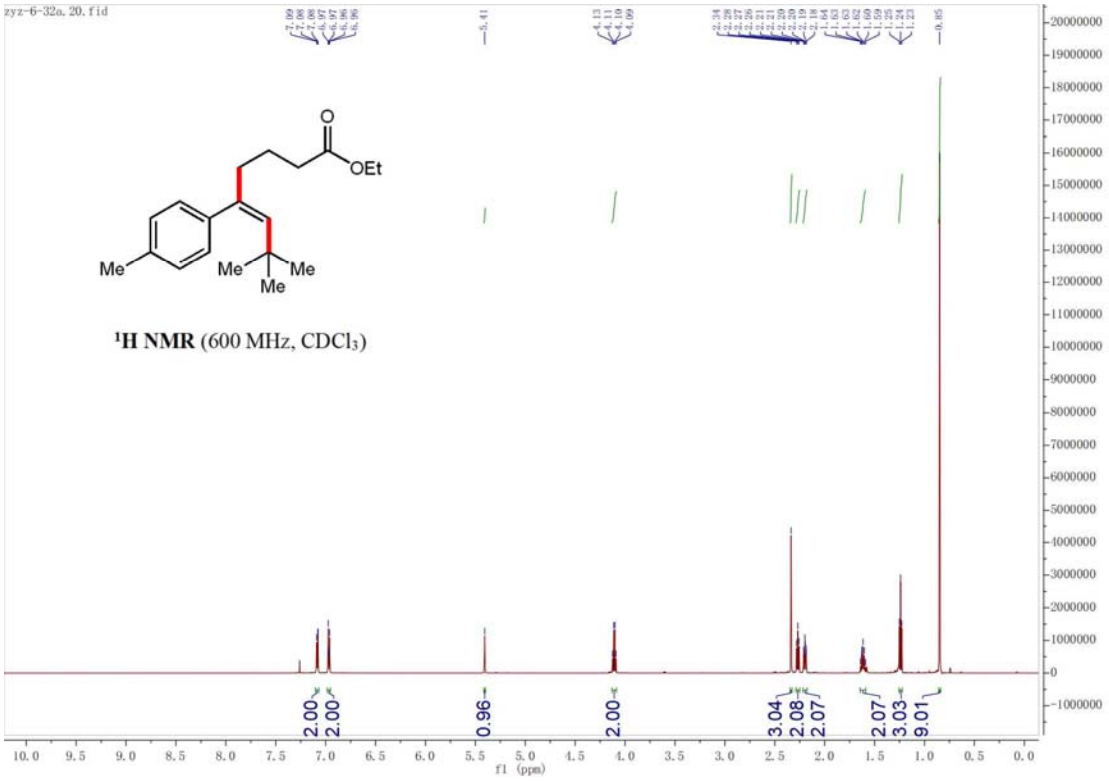
13 was isolated as a colorless oil (20.5 mg, 10% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.11 – 7.08 (m, 2H), 6.84 – 6.79 (m, 2H), 6.35 (d, *J* = 12.5 Hz, 1H), 5.56 (d, *J* = 12.5 Hz, 1H), 3.80 (s, 3H), 0.99 (m, 9H). The data was in accordance with the literature.[4]

15 was determined to be 66% yield by GC analysis using *n*-dodecane as internal standard and compared with commercially available ethyl butyrate.

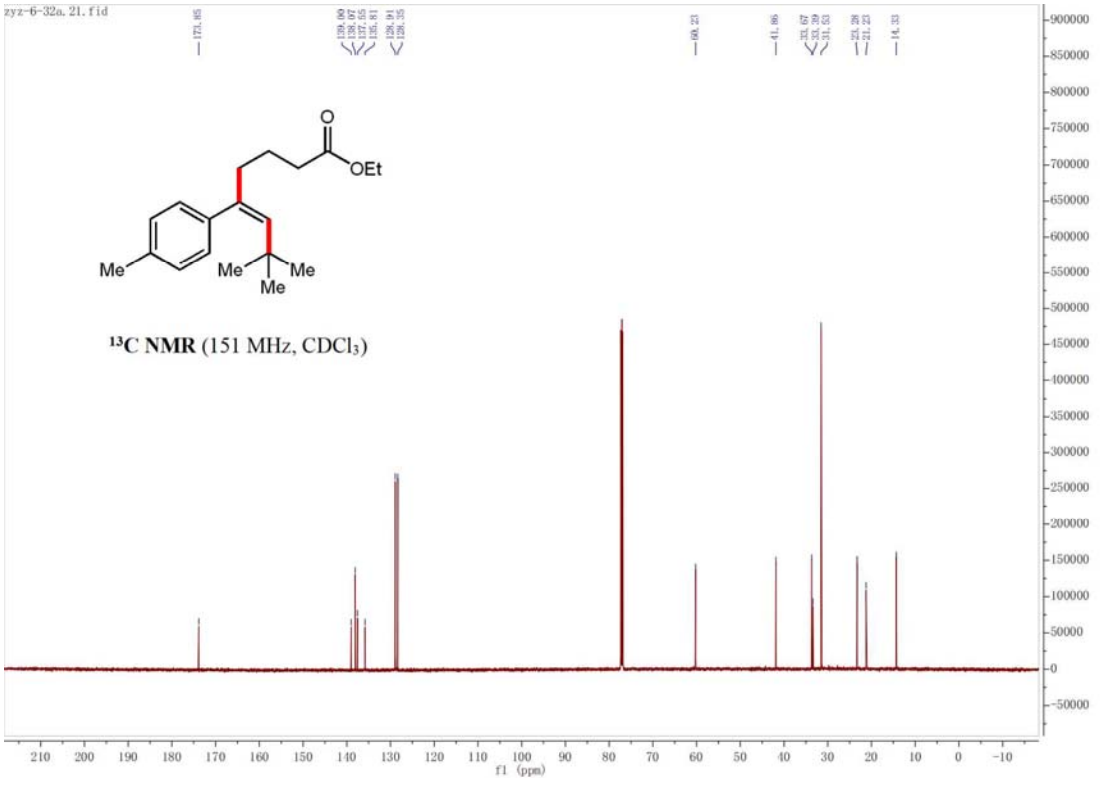
16 was determined to be 29% yield by GC analysis using *n*-dodecane as internal standard. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.11 (q, *J* = 7.1 Hz, 4H), 2.27 (t, *J* = 7.5 Hz, 4H), 1.66 – 1.58 (m, 4H), 1.37 – 1.30 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 6H). The data was in accordance with the literature.[5]

6. ^{1}H, ^{13}C, and ^{19}F Spectra of New Compounds

Ethyl (*Z*)-7,7-dimethyl-5-(*p*-tolyl)oct-5-enoate (4a)

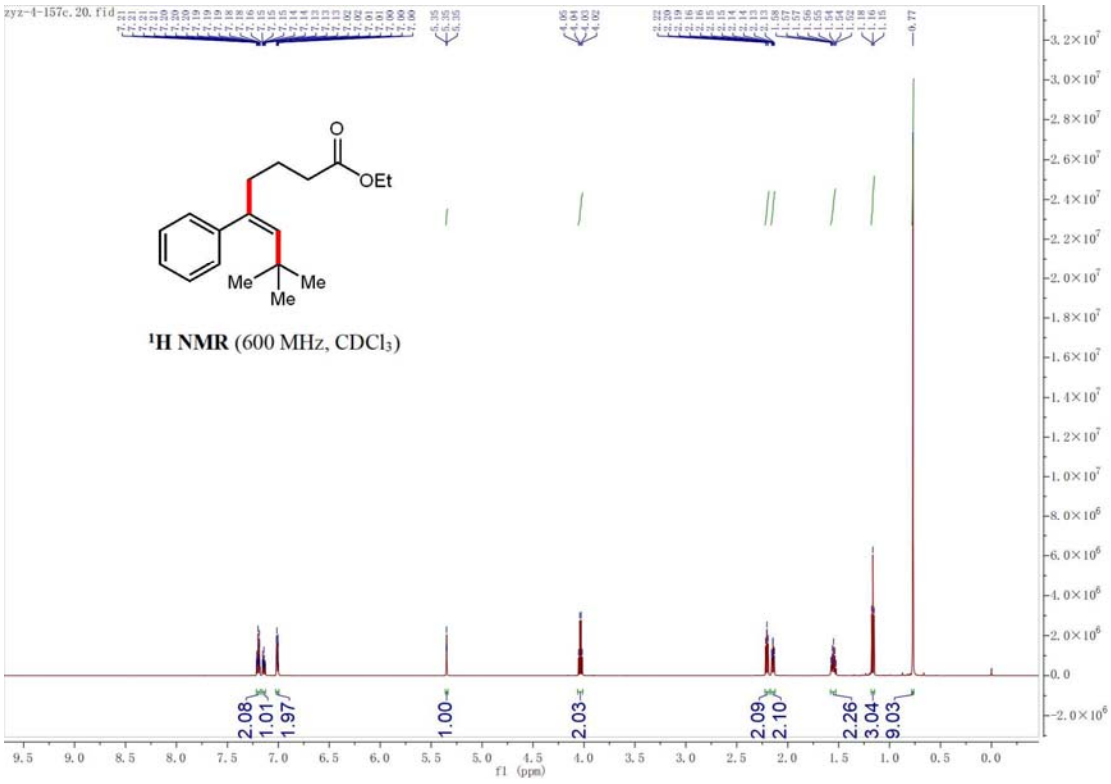


^{1}H NMR (600 MHz, $CDCl_3$)

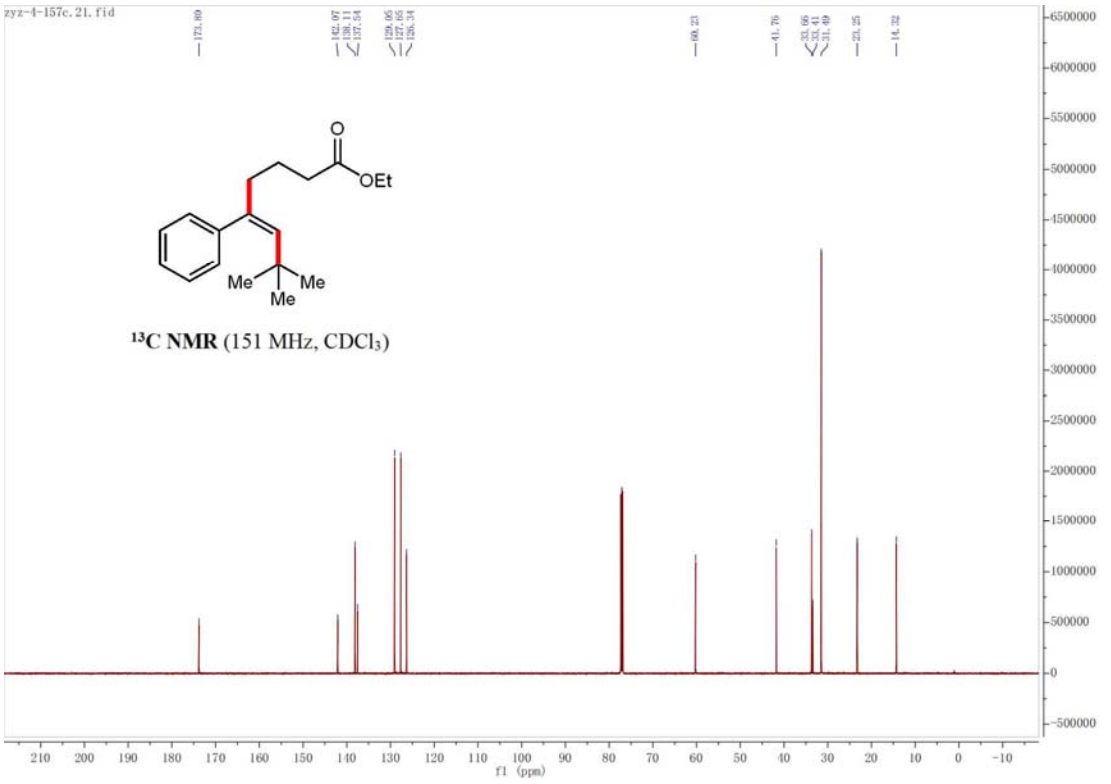


^{13}C NMR (151 MHz, $CDCl_3$)

Ethyl (Z)-7,7-dimethyl-5-phenyloct-5-enoate (4b)

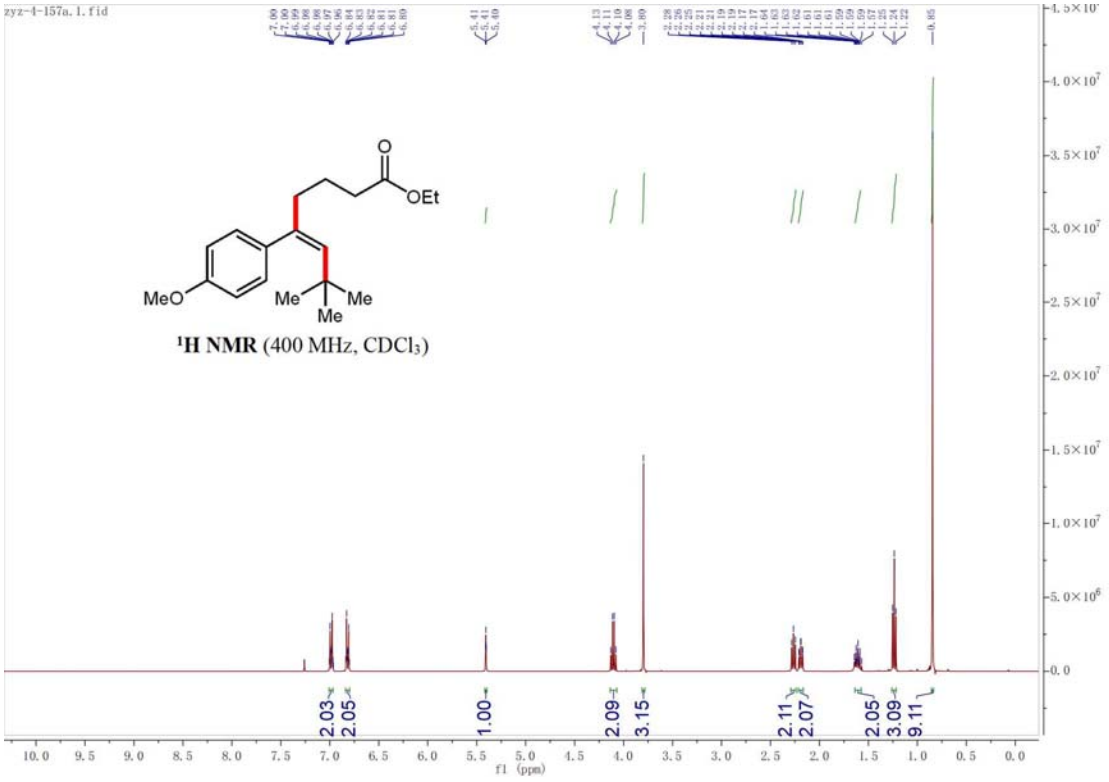


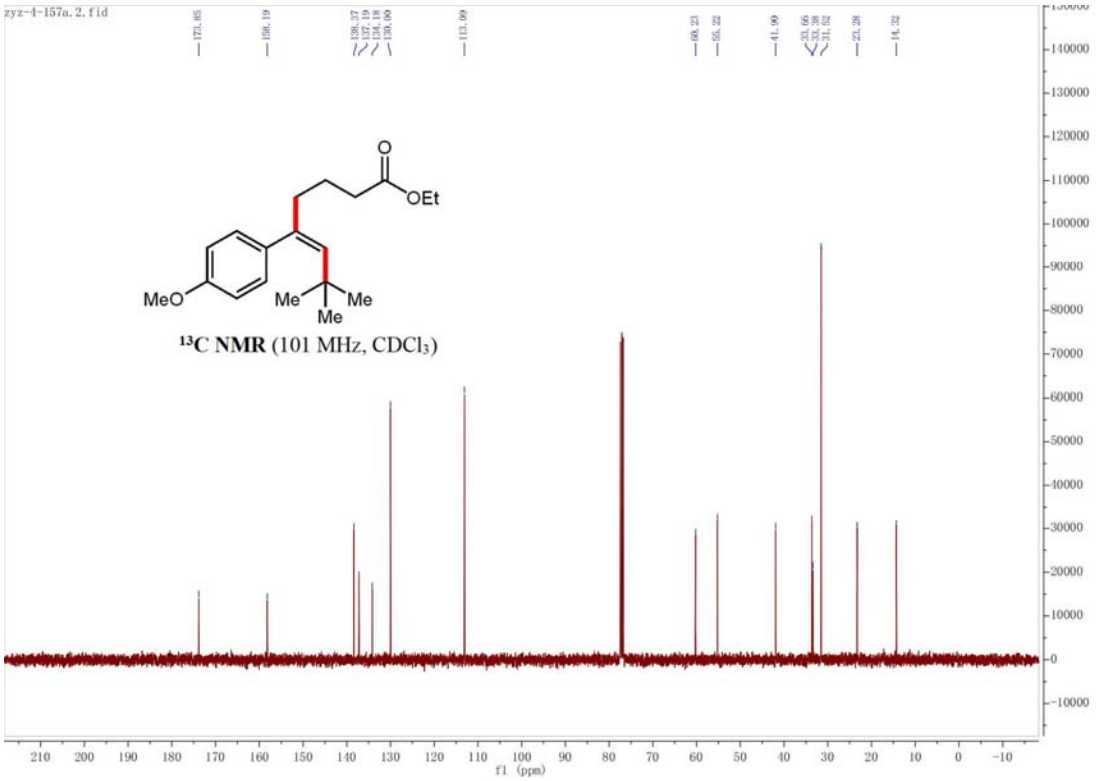
^{1}H NMR (600 MHz, $CDCl_3$)



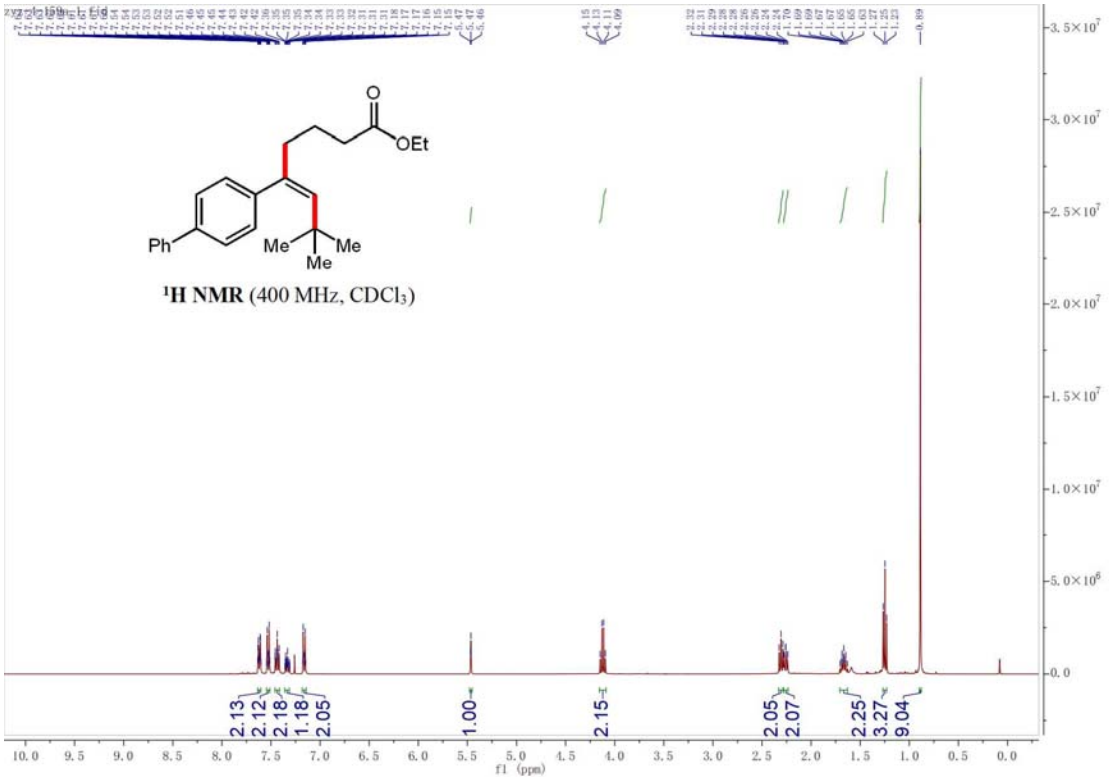
^{13}C NMR (151 MHz, $CDCl_3$)

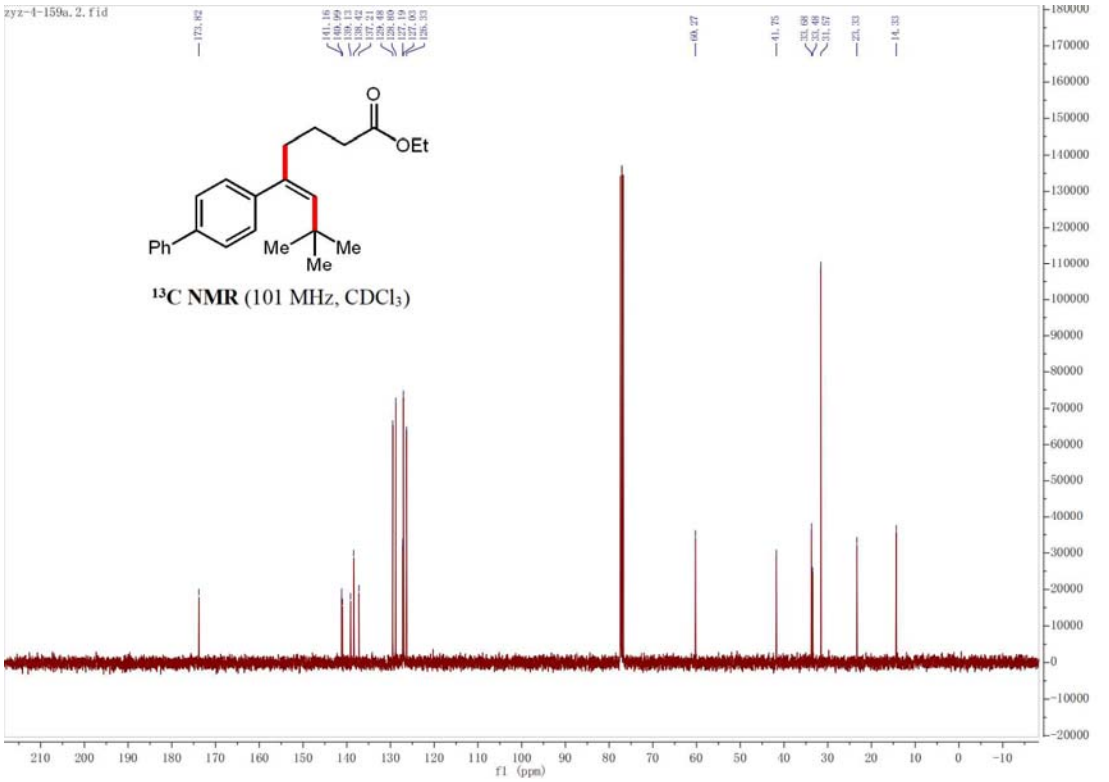
Ethyl (*Z*)-5-(4-methoxyphenyl)-7,7-dimethyloct-5-enoate (4c)



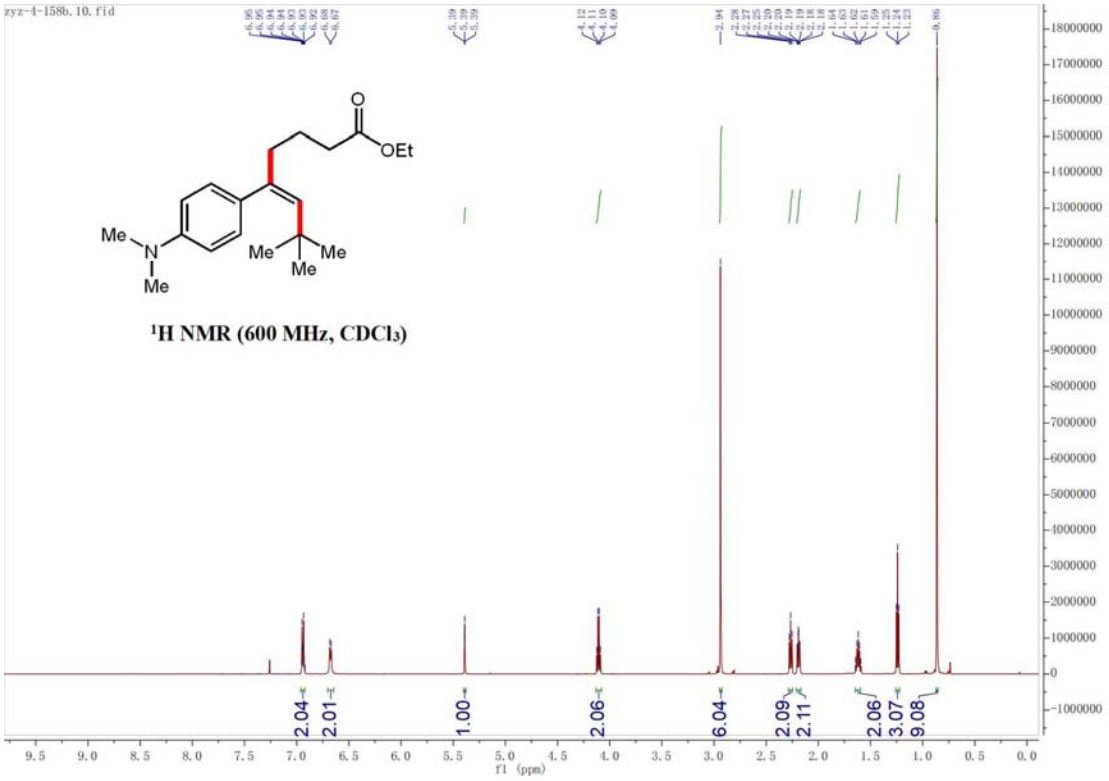


Ethyl (*Z*)-5-([1,1'-biphenyl]-4-yl)-7,7-dimethyloct-5-enoate (4d)

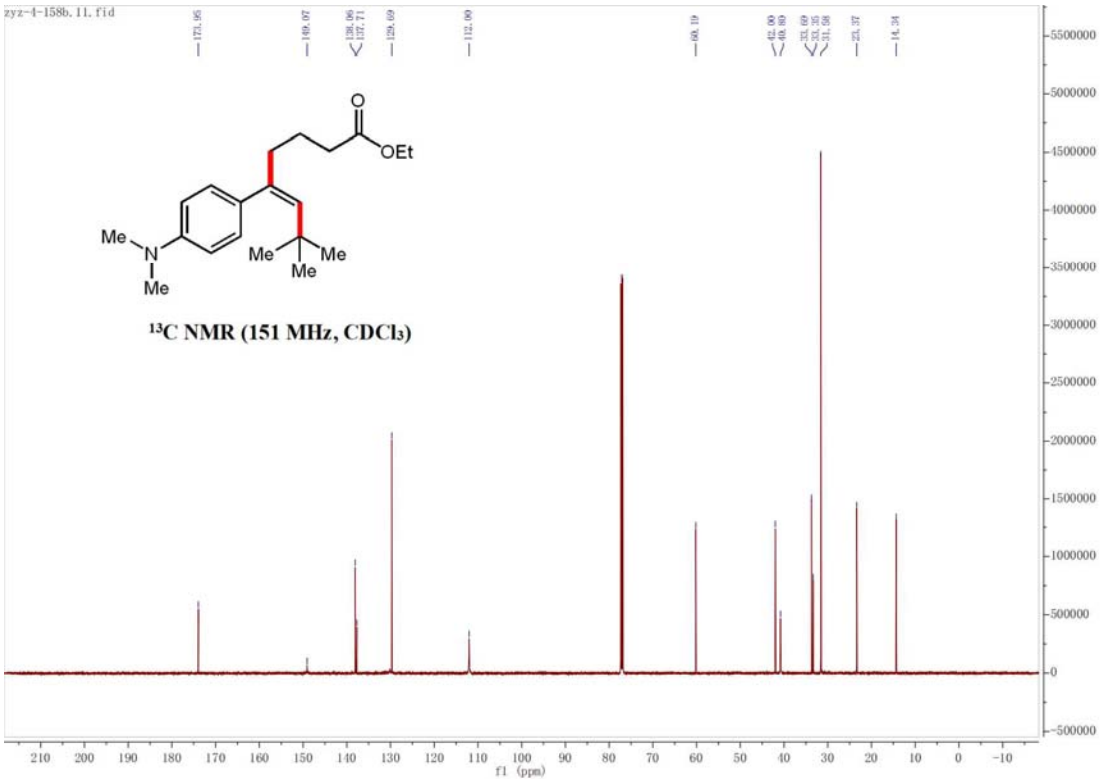




Ethyl (Z)-5-(4-(dimethylamino)phenyl)-7,7-dimethyloct-5-enoate (4e)

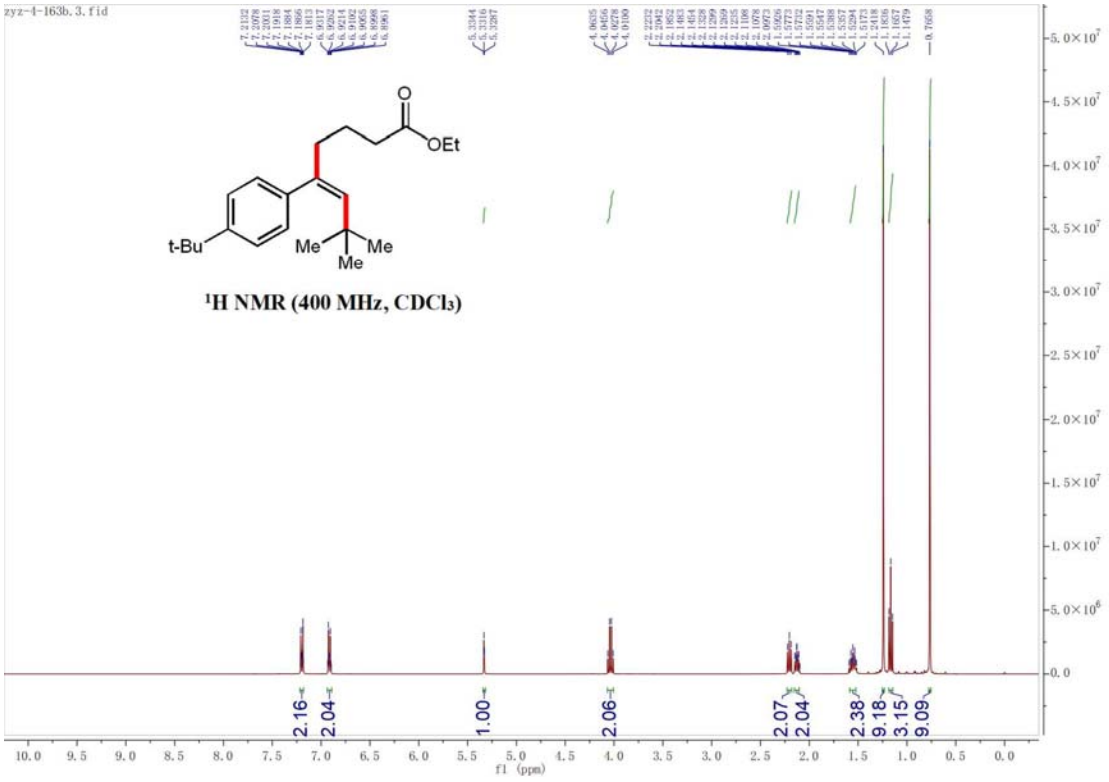


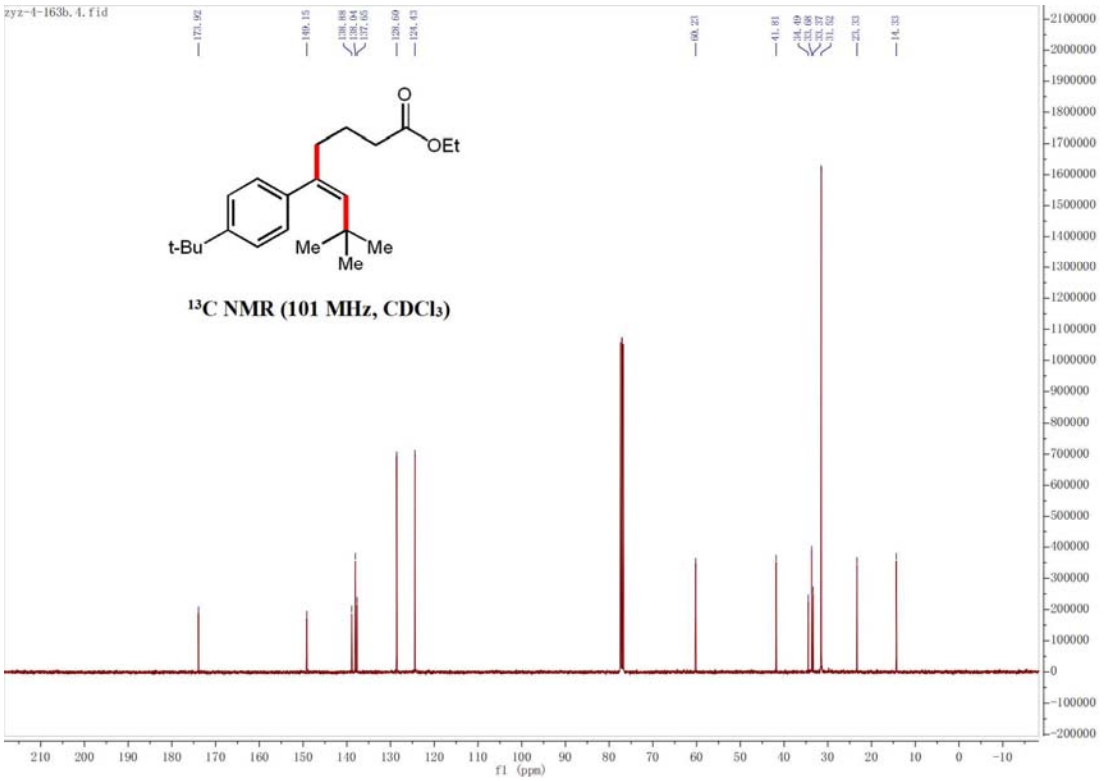
^{1}H NMR (600 MHz, $CDCl_3$)



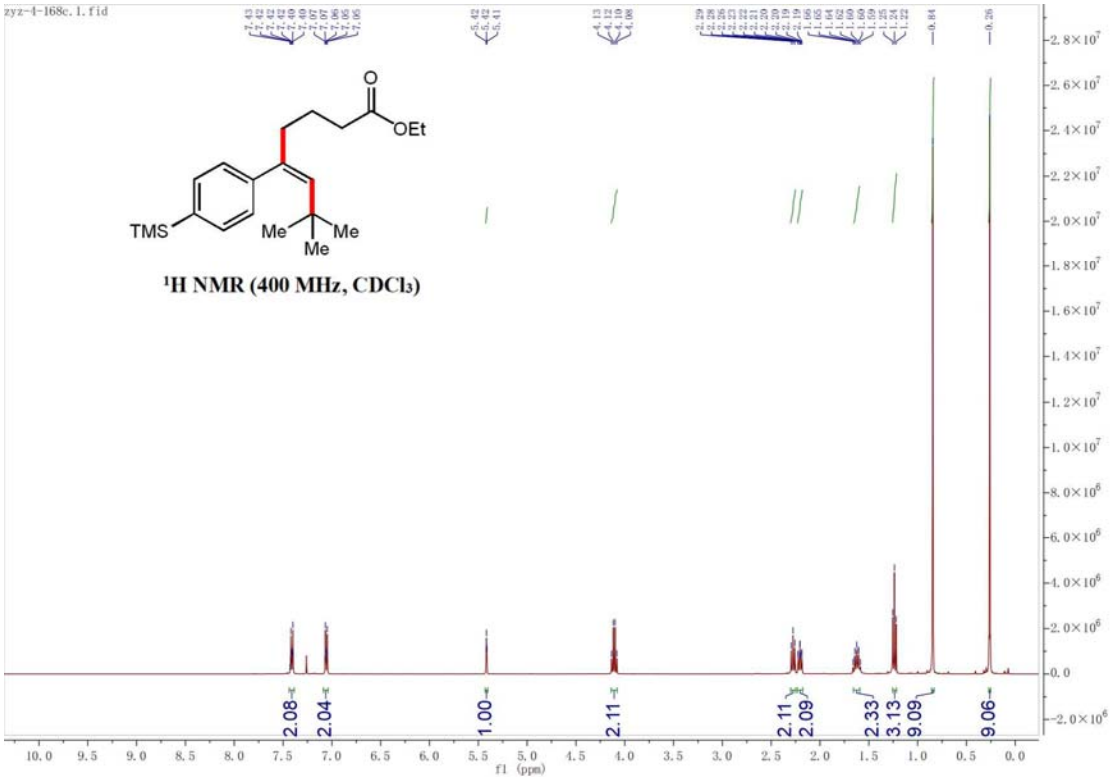
^{13}C NMR (151 MHz, $CDCl_3$)

Ethyl (*Z*)-5-(4-(*tert*-butyl)phenyl)-7,7-dimethyloct-5-enoate (4f)

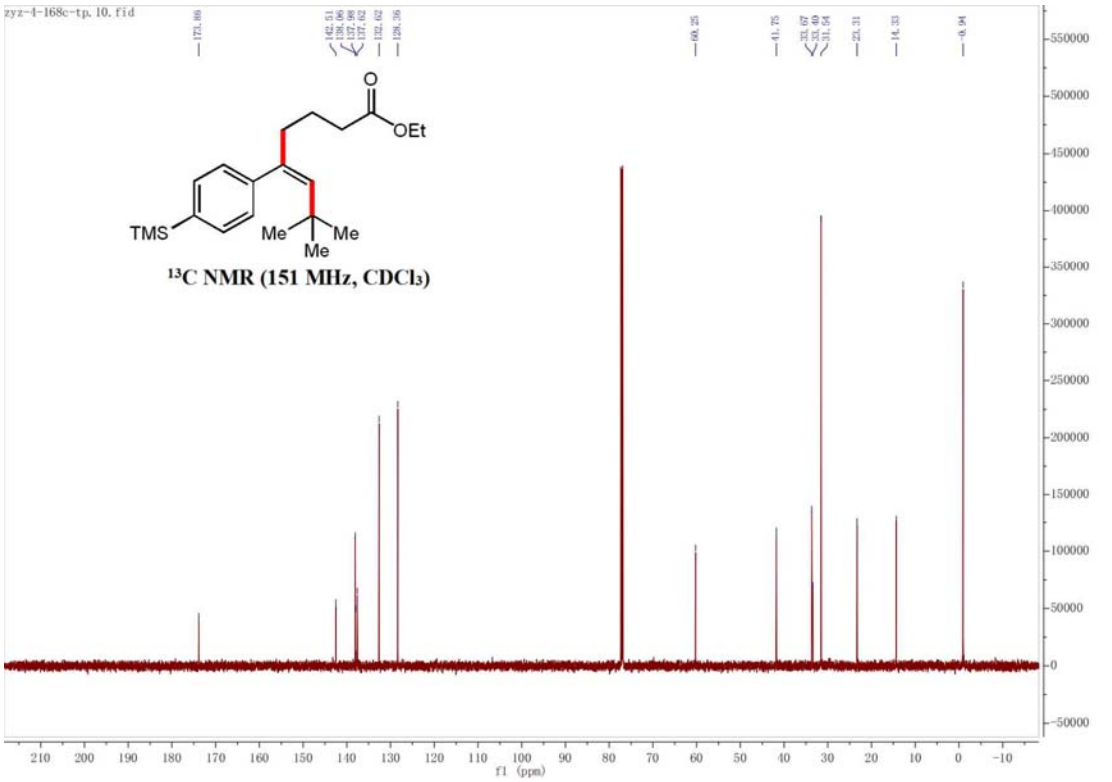




Ethyl (Z)-7,7-dimethyl-5-(4-(trimethylsilyl)phenyl)oct-5-enoate (4g)

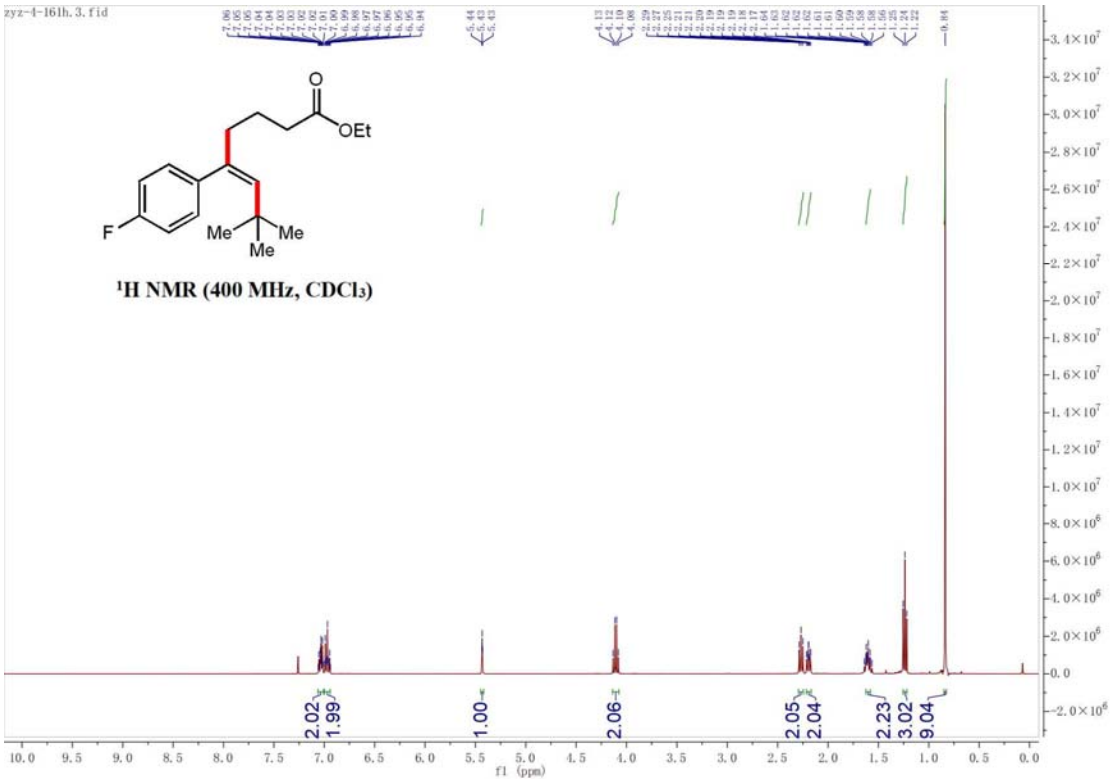


^{1}H NMR (400 MHz, $CDCl_3$)

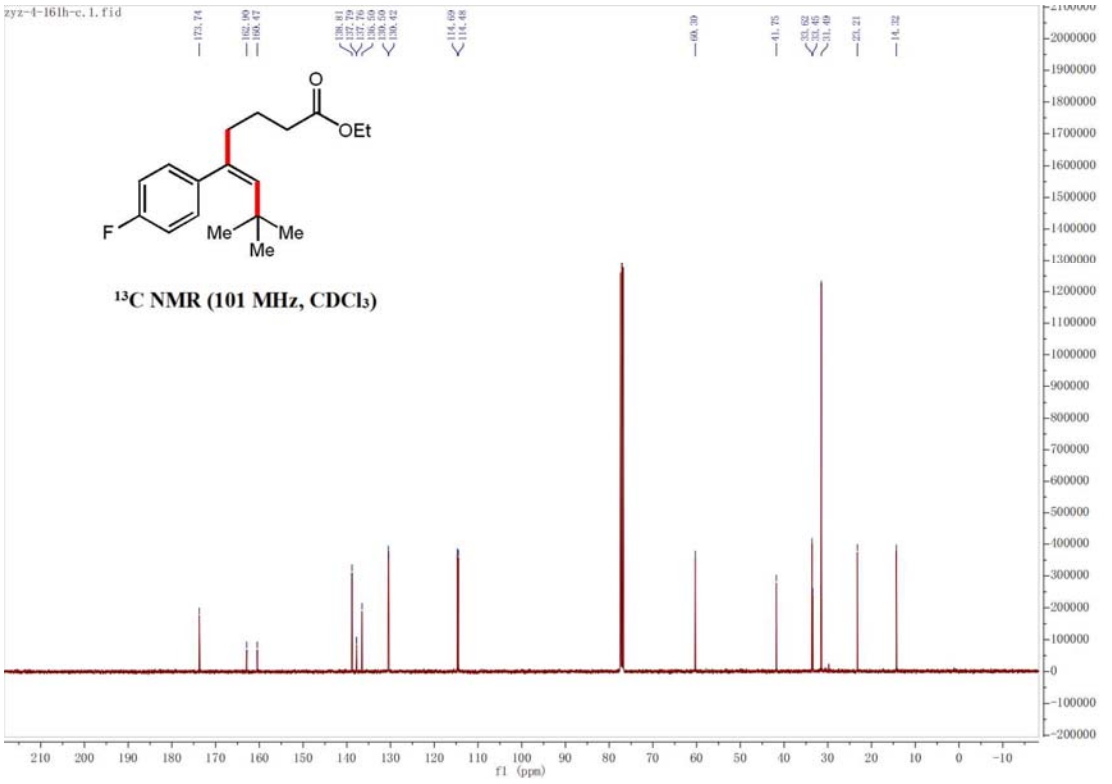


^{13}C NMR (151 MHz, $CDCl_3$)

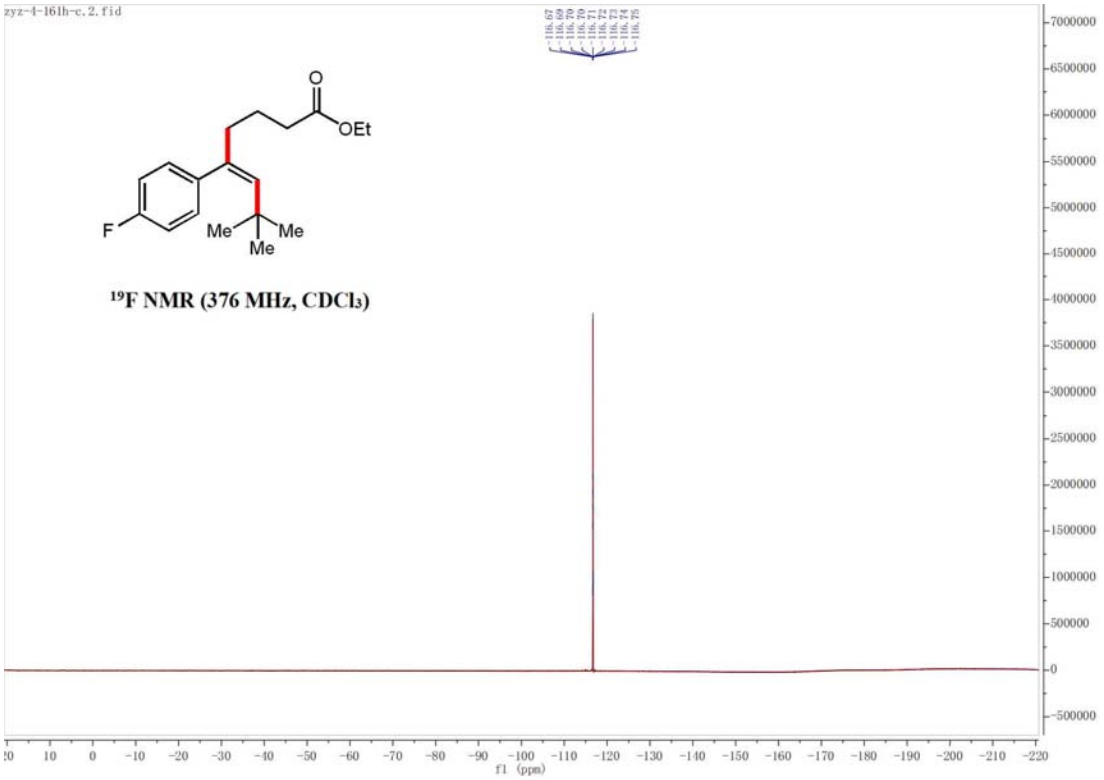
Ethyl (*Z*)-5-(4-fluorophenyl)-7,7-dimethyloct-5-enoate (4h)



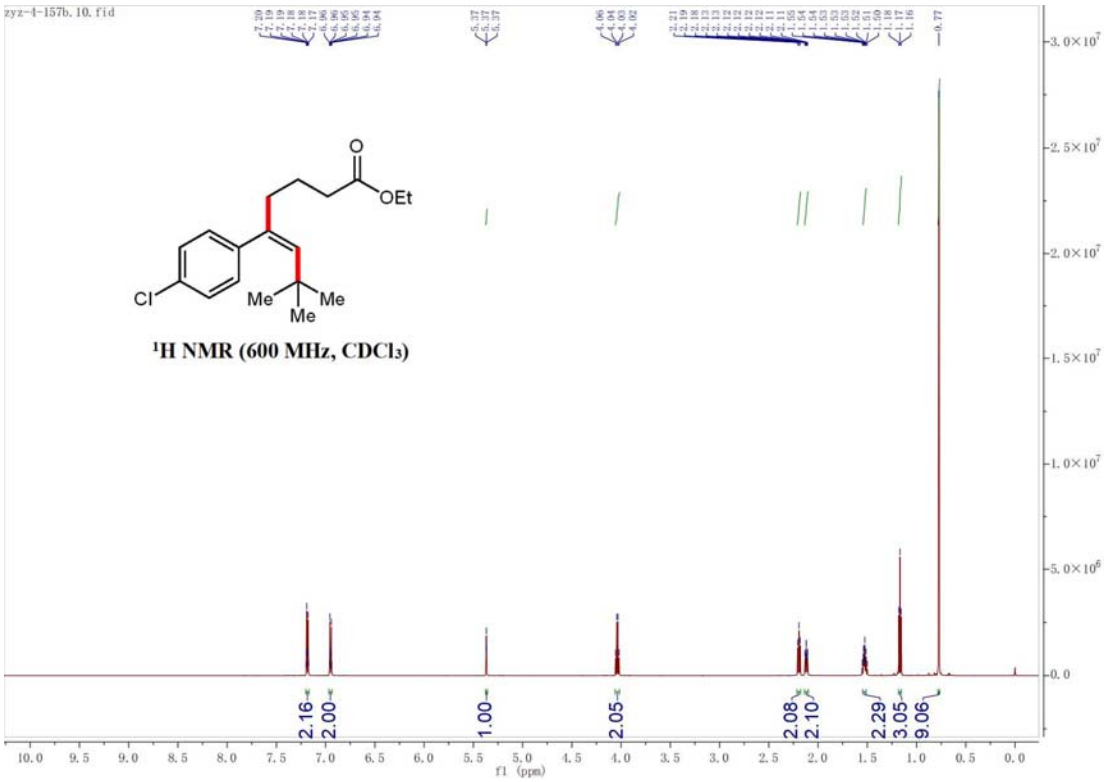
^{1}H NMR (400 MHz, $CDCl_3$)

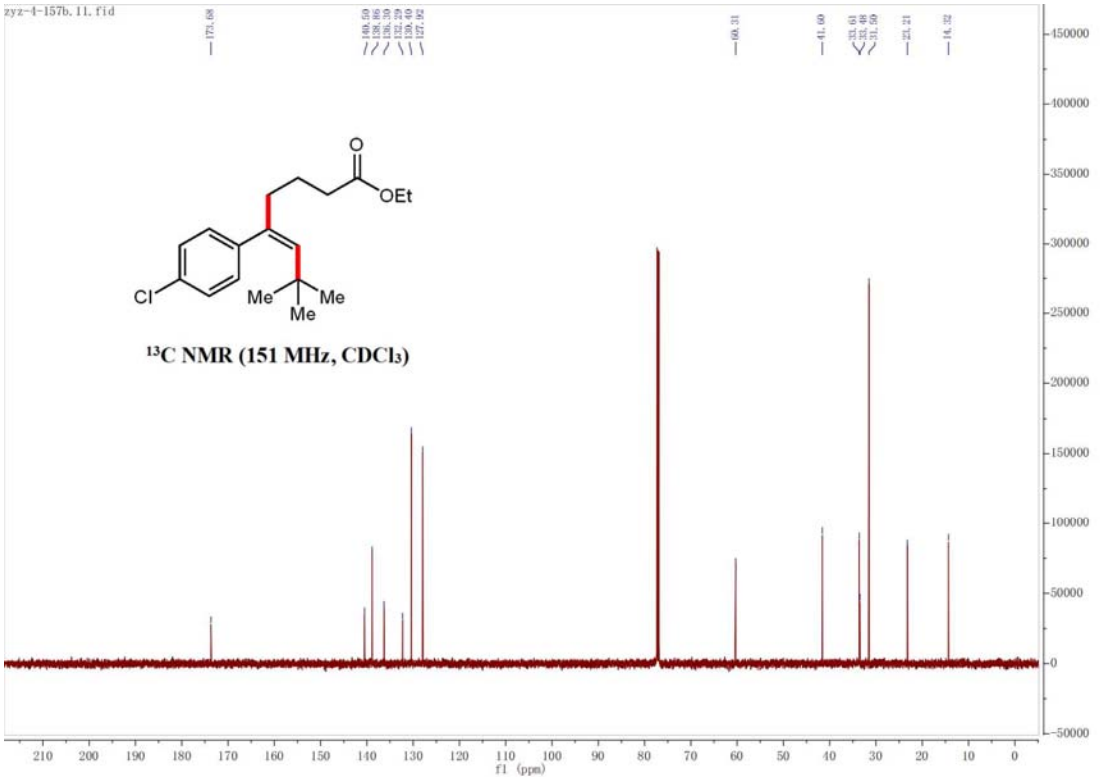


^{13}C NMR (101 MHz, $CDCl_3$)

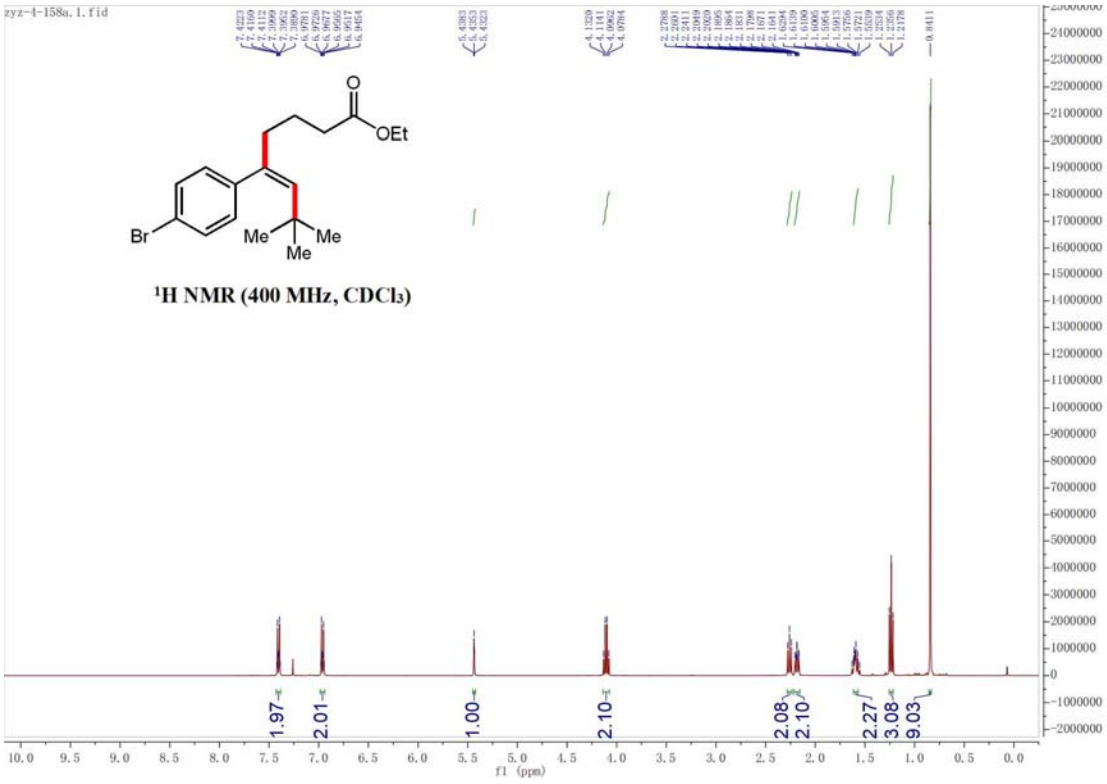


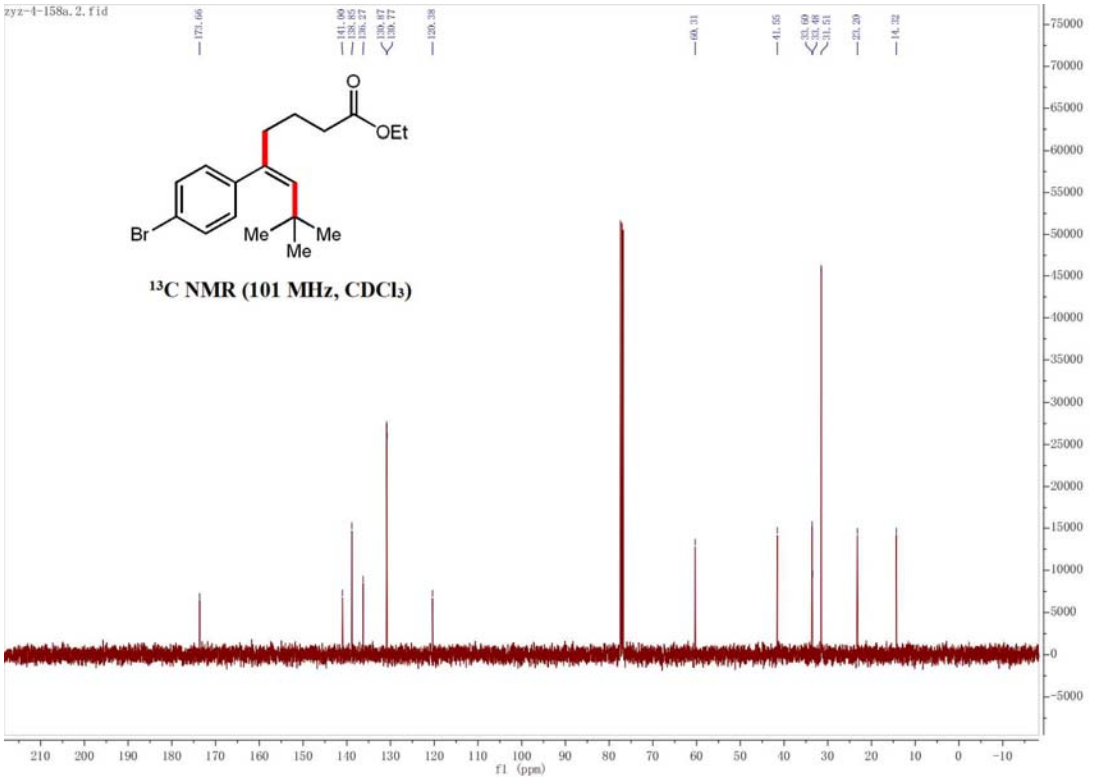
Ethyl (*Z*)-5-(4-chlorophenyl)-7,7-dimethyloct-5-enoate (4i)



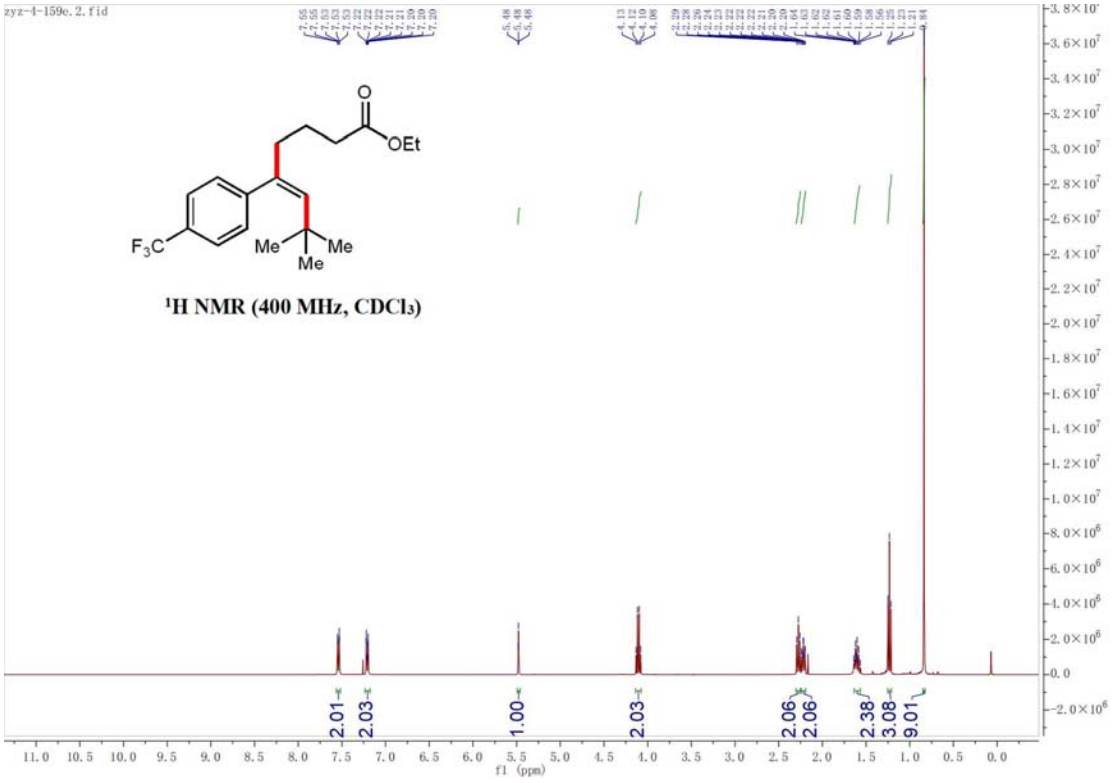


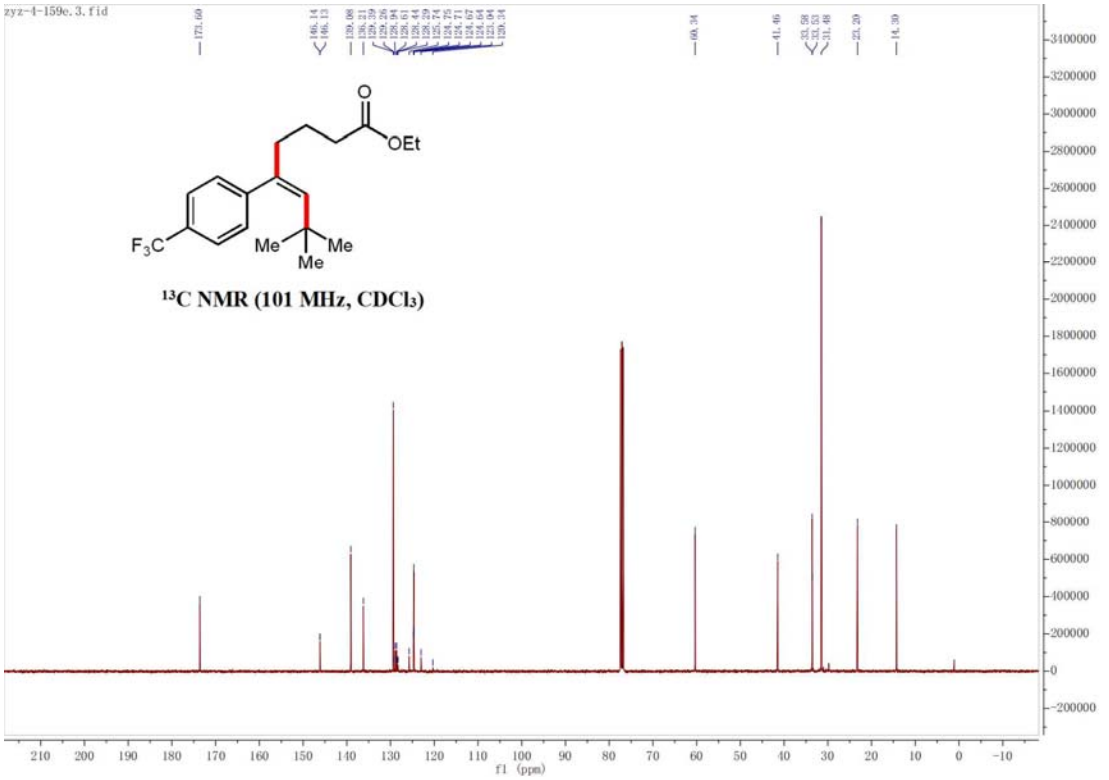
Ethyl (*Z*)-5-(4-bromophenyl)-7,7-dimethyloct-5-enoate (4j)



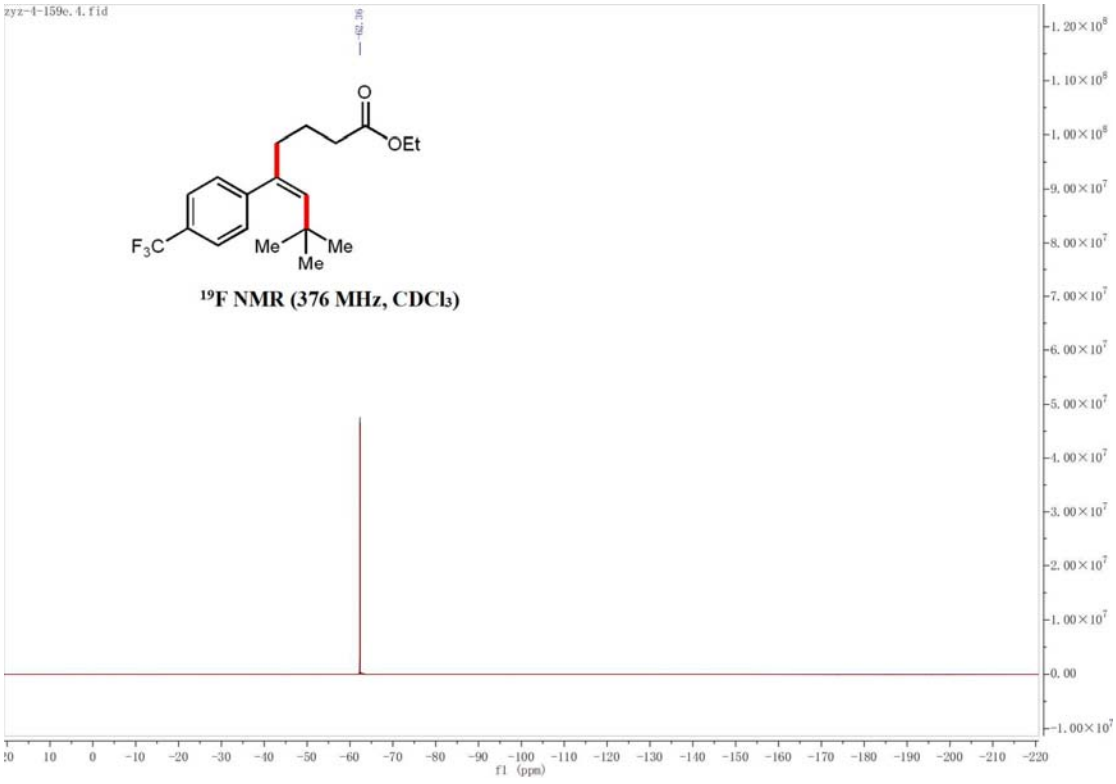


Ethyl (*Z*)-7,7-dimethyl-5-(4-(trifluoromethyl)phenyl)oct-5-enoate (4k)



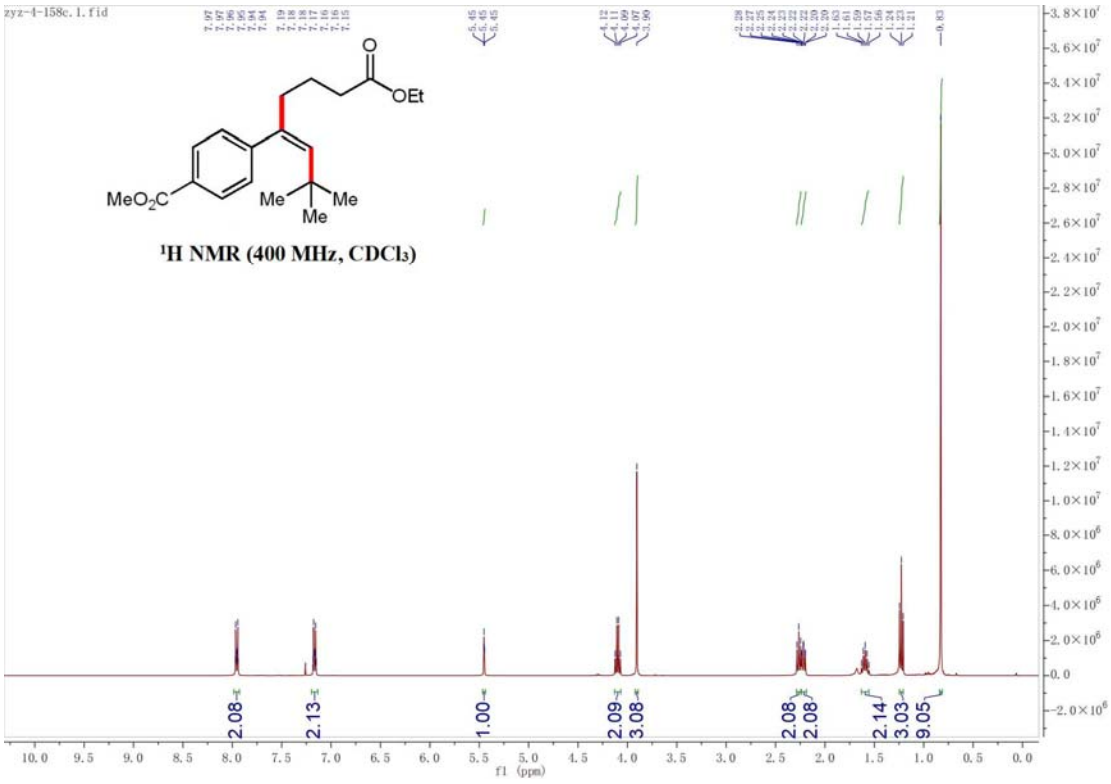


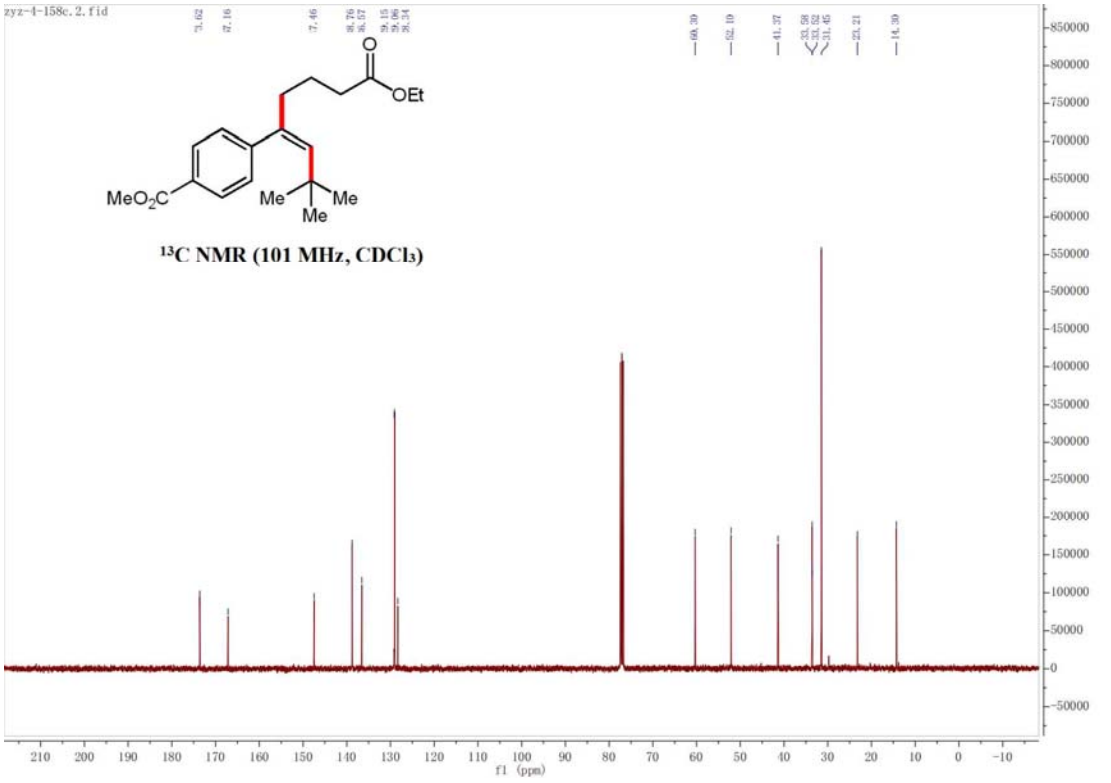
^{13}C NMR (101 MHz, $CDCl_3$)



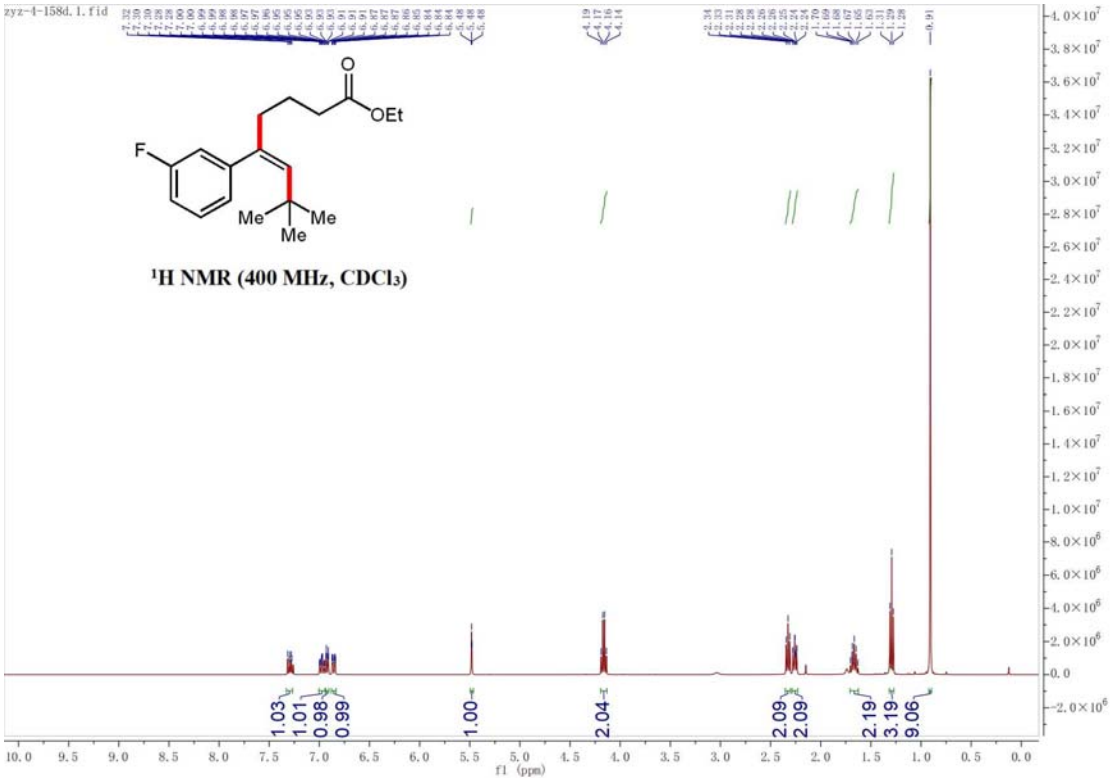
^{19}F NMR (376 MHz, $CDCl_3$)

Methyl (*Z*)-4-(8-ethoxy-2,2-dimethyl-8-oxooct-3-en-4-yl)benzoate (4l)

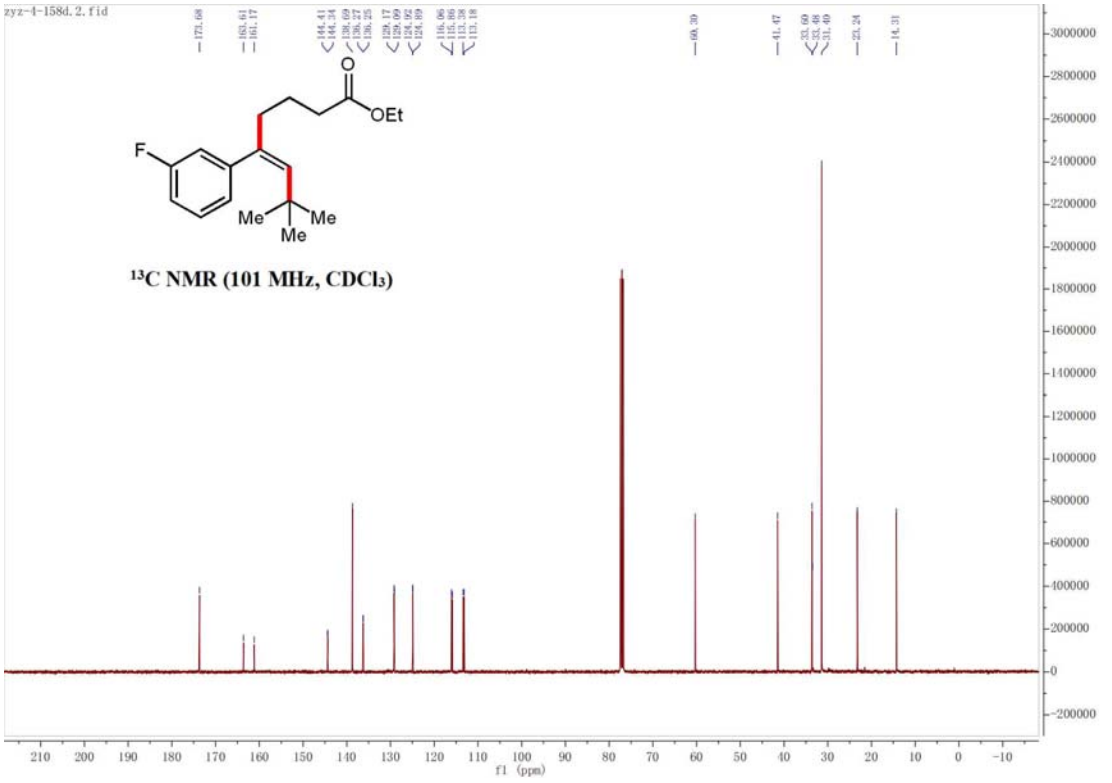




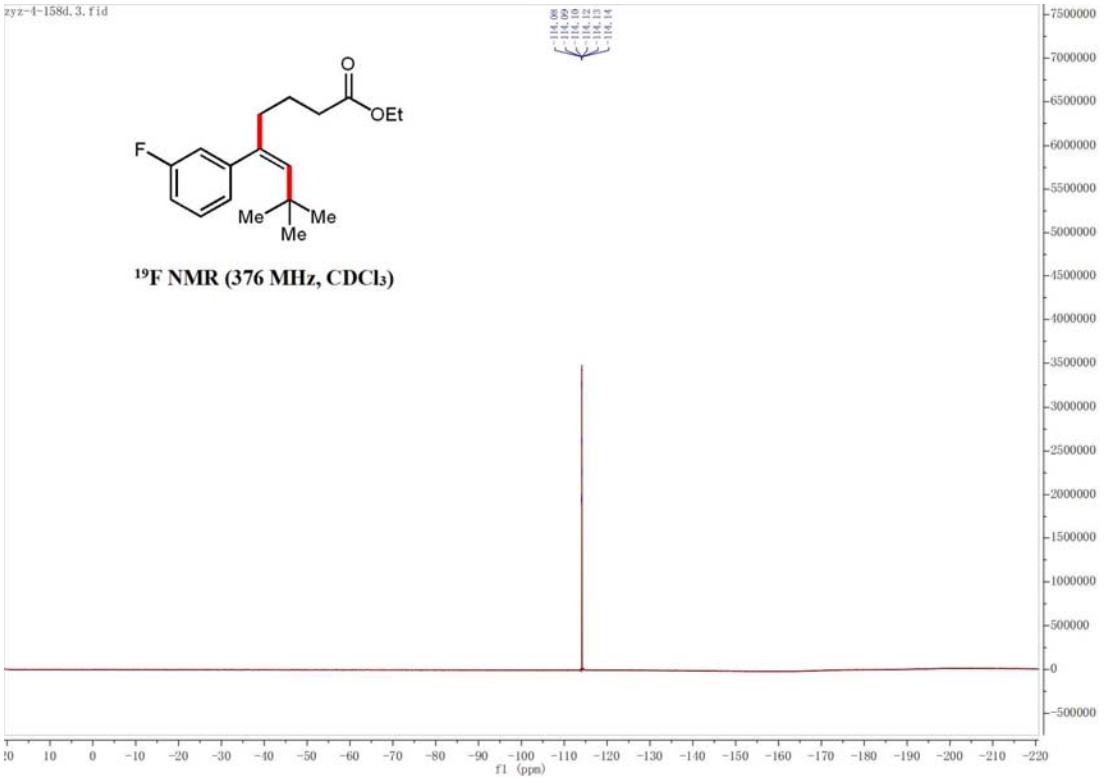
Ethyl (*Z*)-5-(3-fluorophenyl)-7,7-dimethyloct-5-enoate (4m)



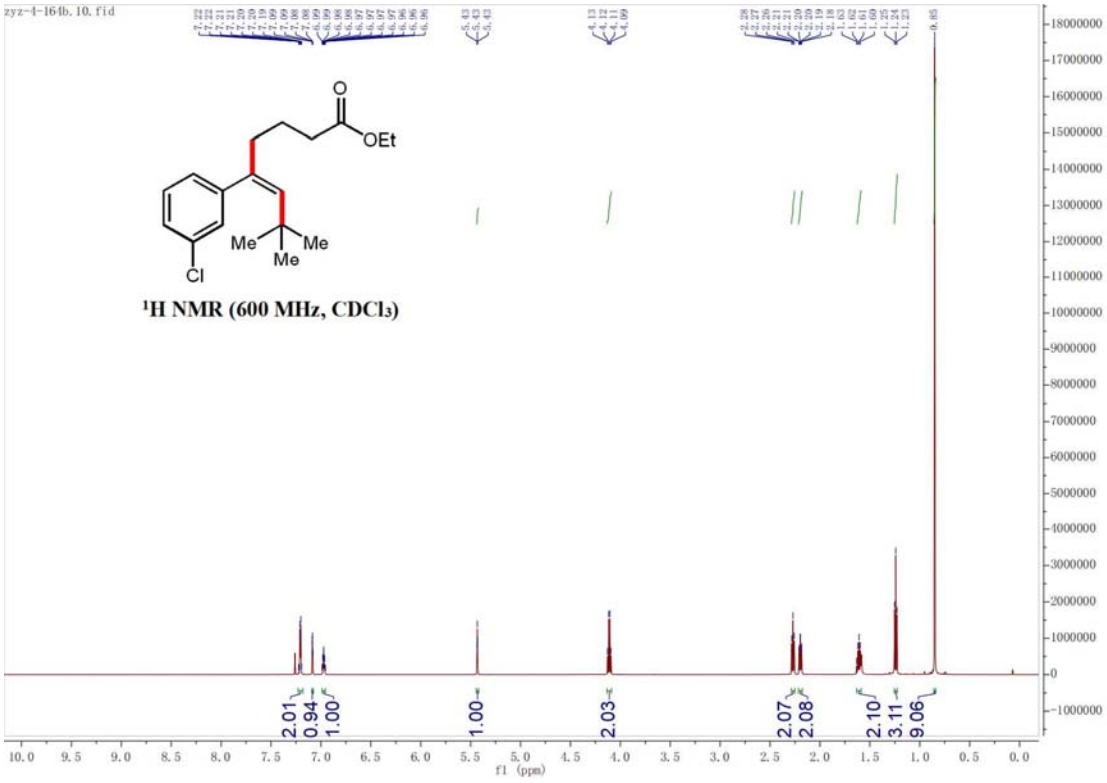
^{1}H NMR (400 MHz, $CDCl_3$)

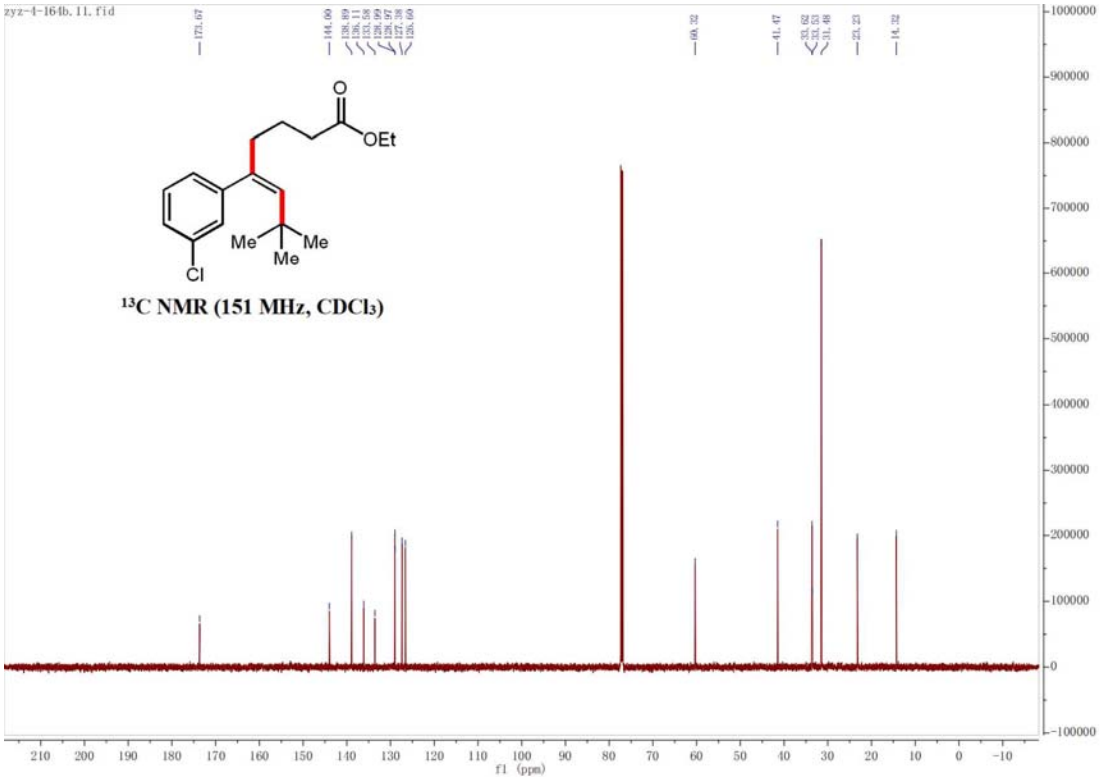


^{13}C NMR (101 MHz, $CDCl_3$)



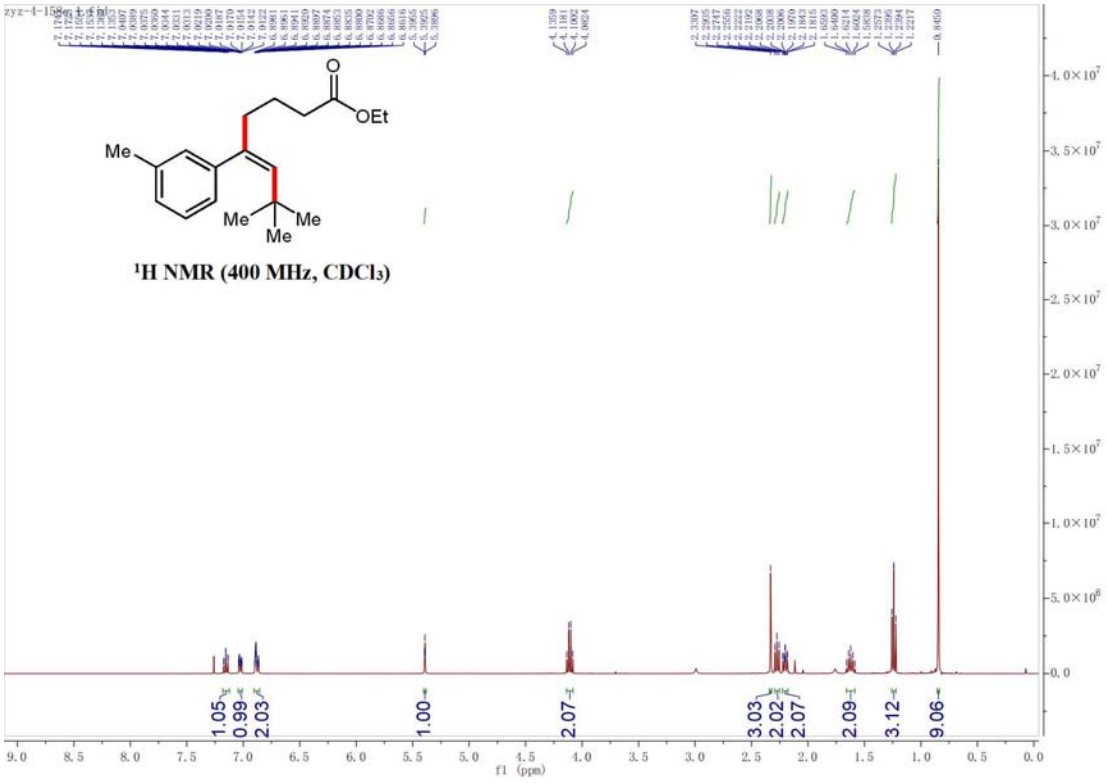
Ethyl (*Z*)-5-(3-chlorophenyl)-7,7-dimethyloct-5-enoate (4n)



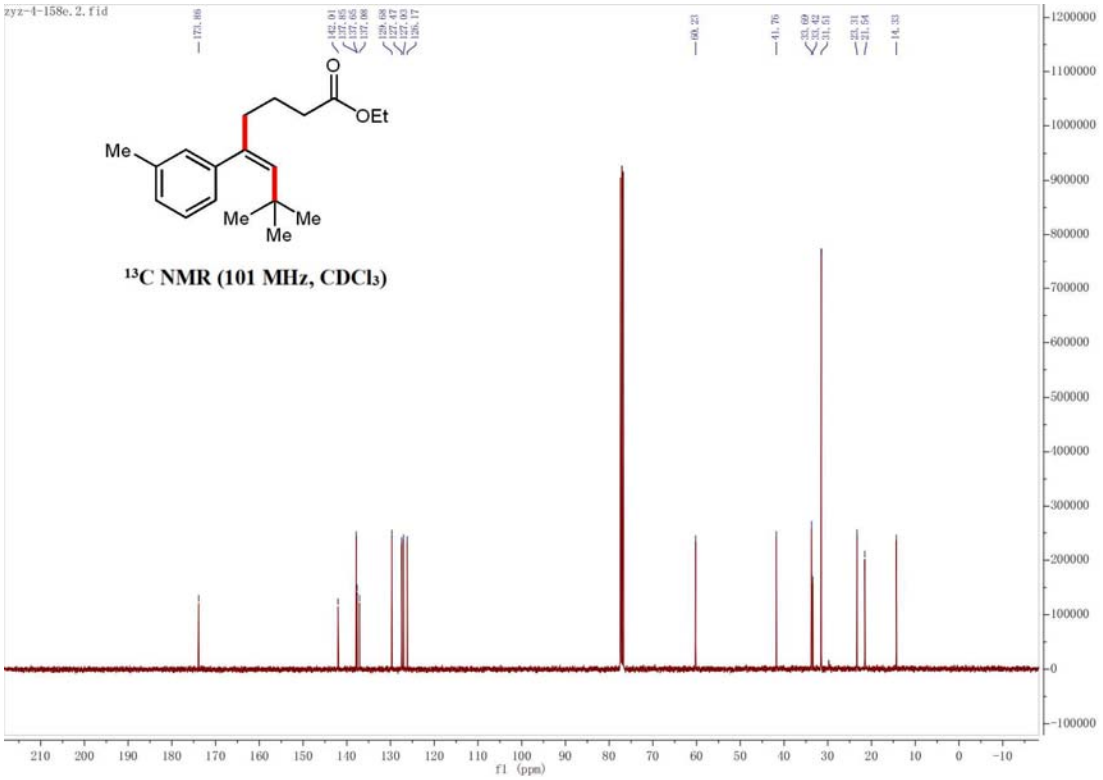


^{13}C NMR (151 MHz, $CDCl_3$)

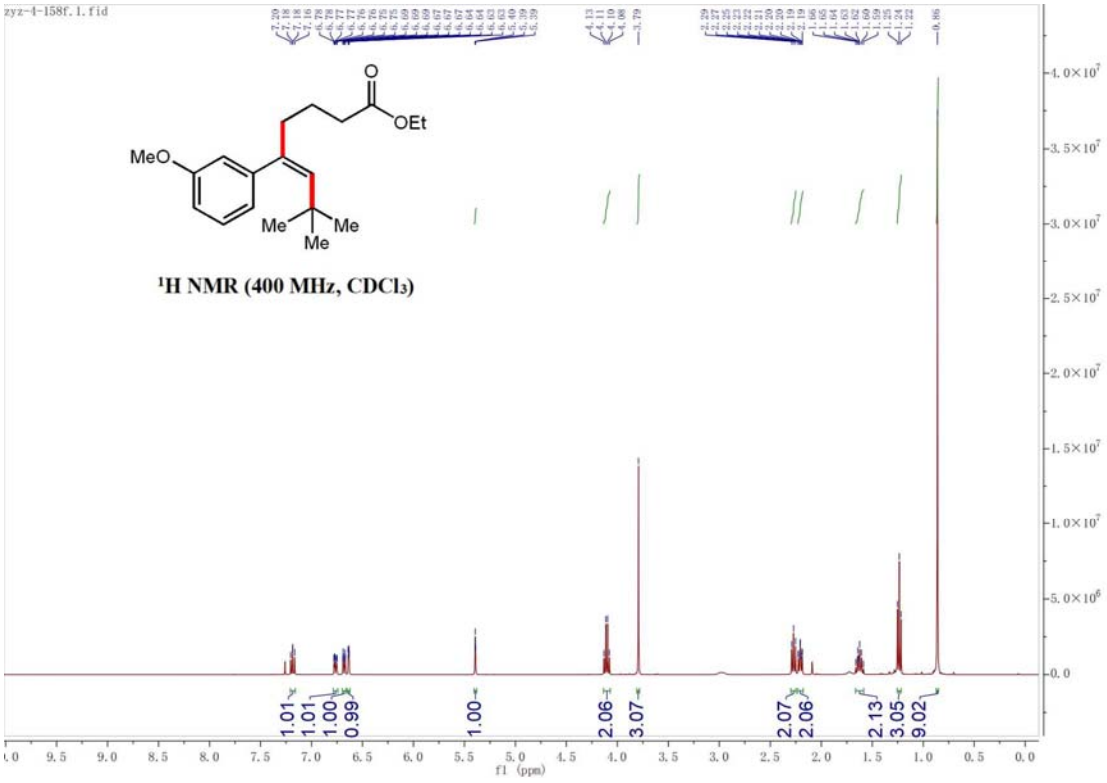
Ethyl (*Z*)-7,7-dimethyl-5-(*m*-tolyl)oct-5-enoate (4o)

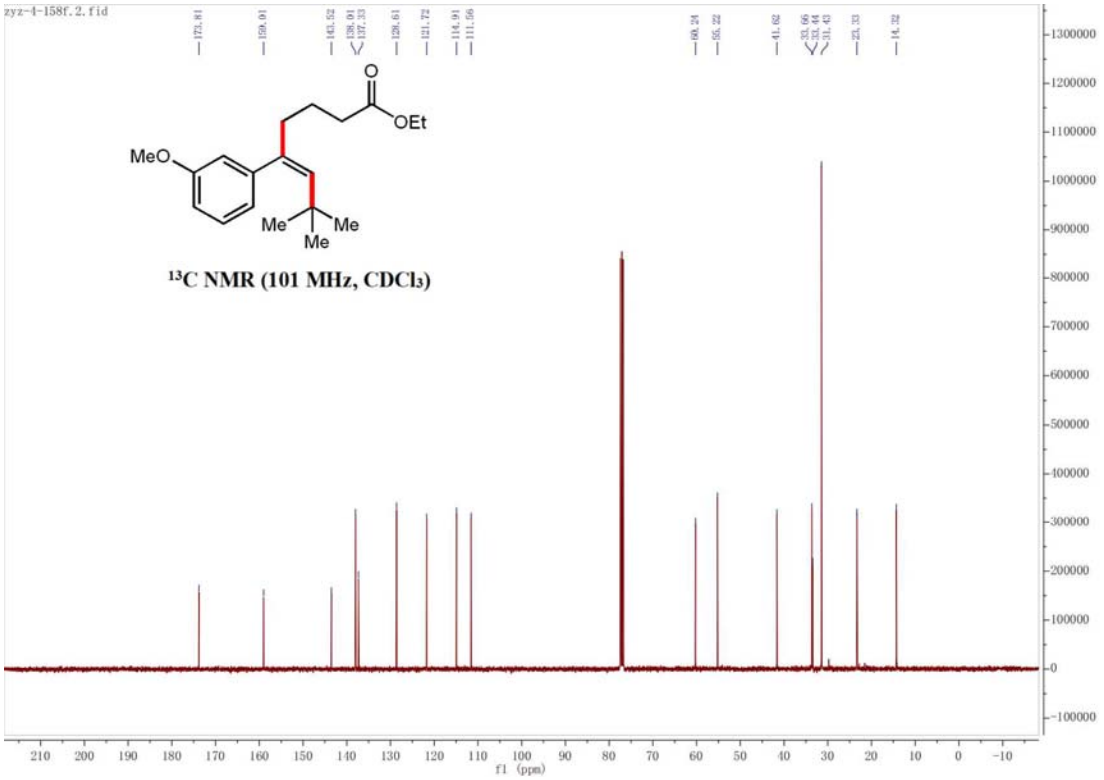


^{1}H NMR (400 MHz, $CDCl_3$)

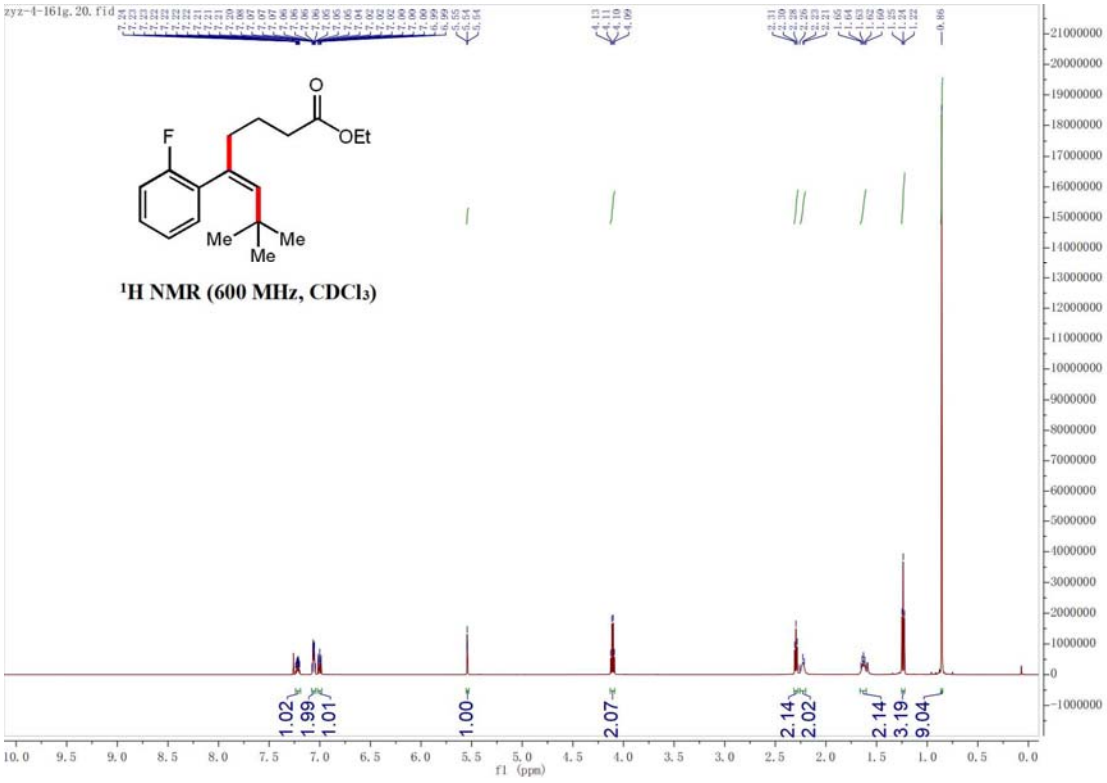


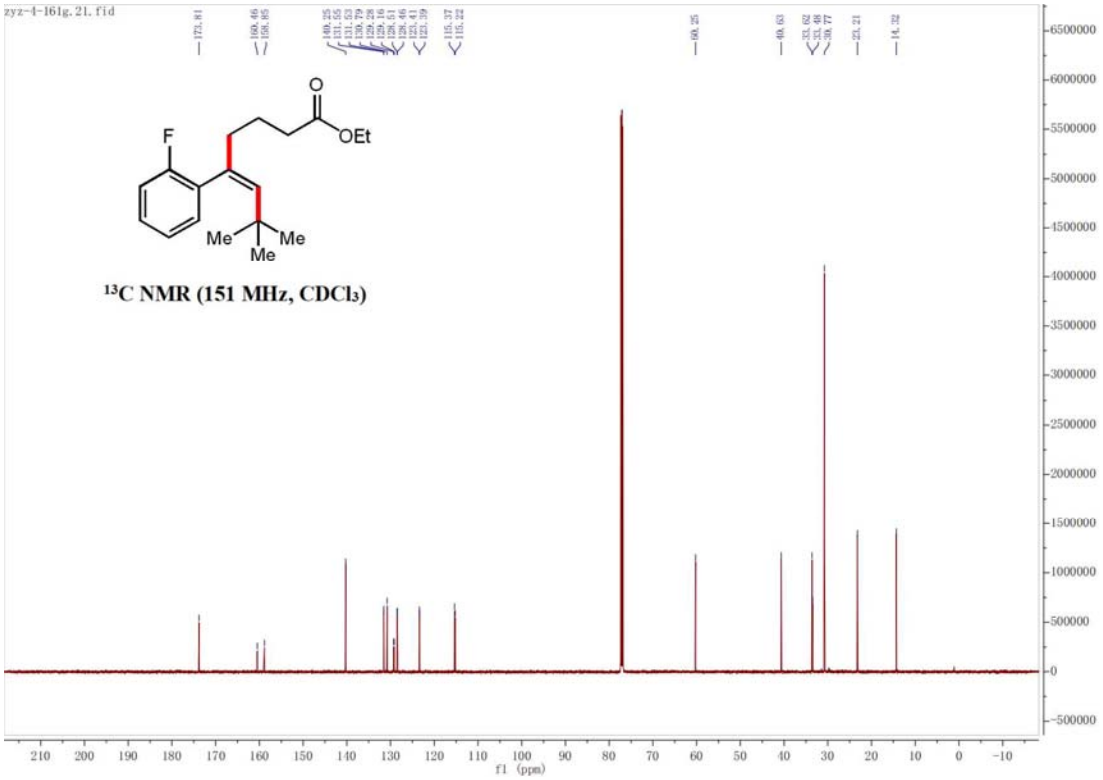
Ethyl (*Z*)-5-(3-methoxyphenyl)-7,7-dimethyloct-5-enoate (4p)



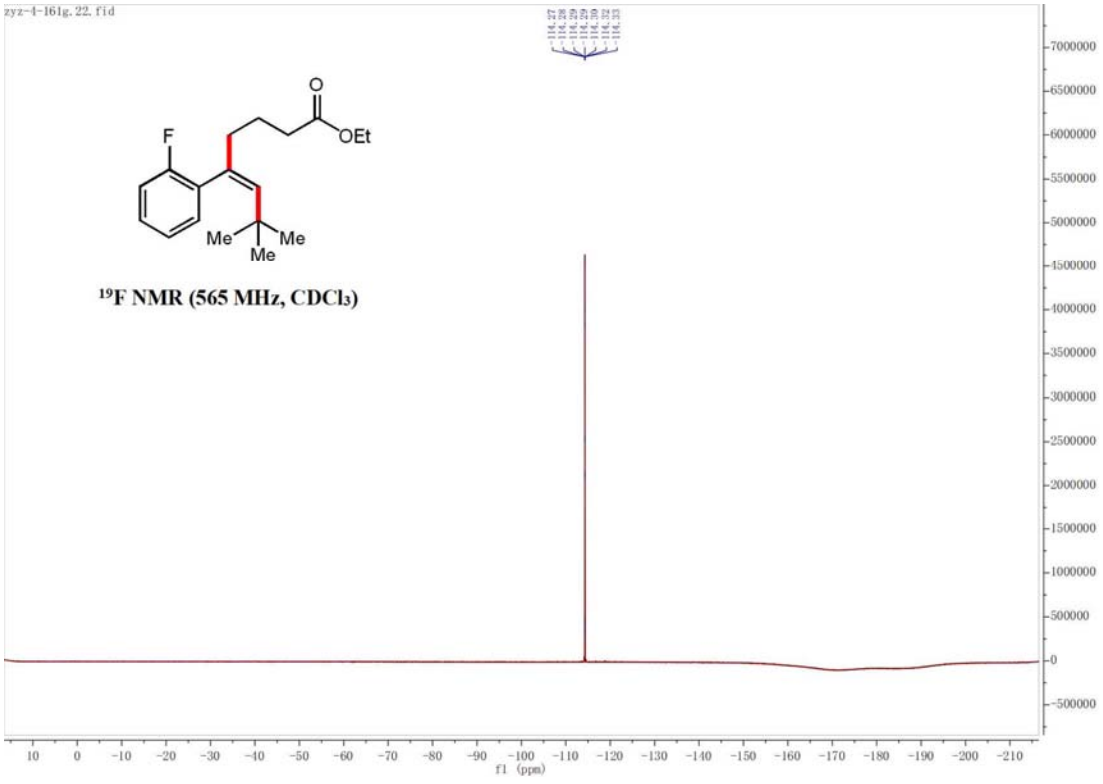


Ethyl (*Z*)-5-(2-fluorophenyl)-7,7-dimethyloct-5-enoate (4q)



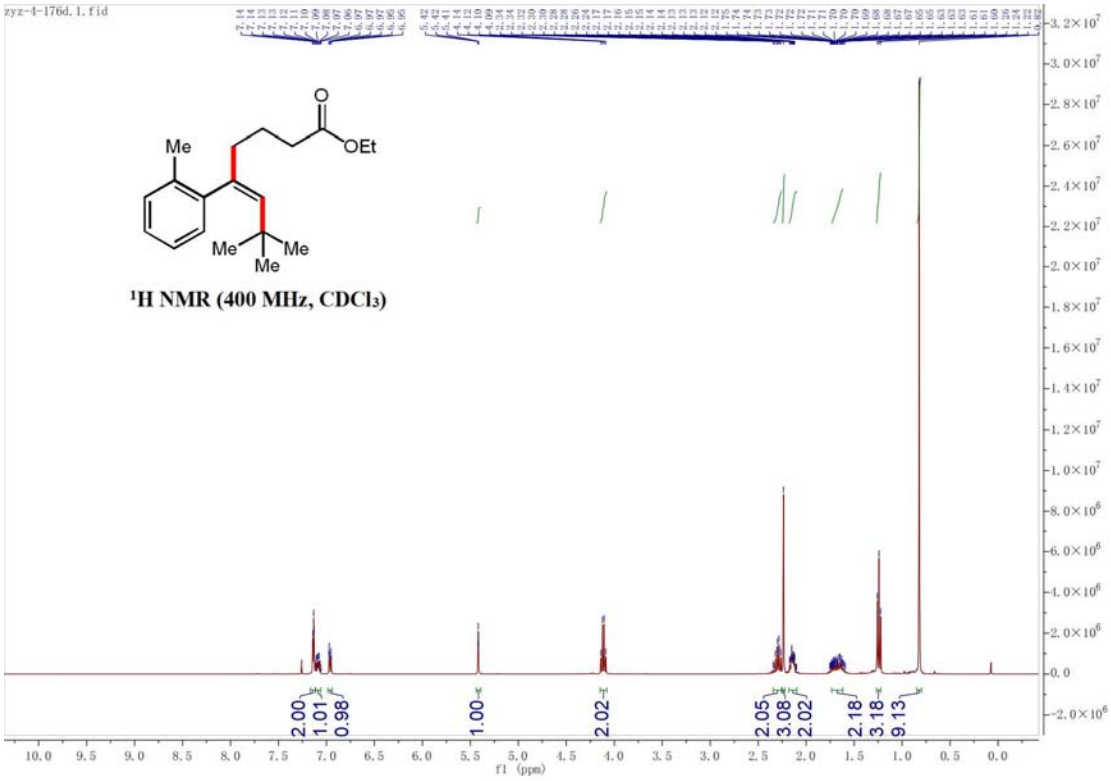


^{13}C NMR (151 MHz, $CDCl_3$)

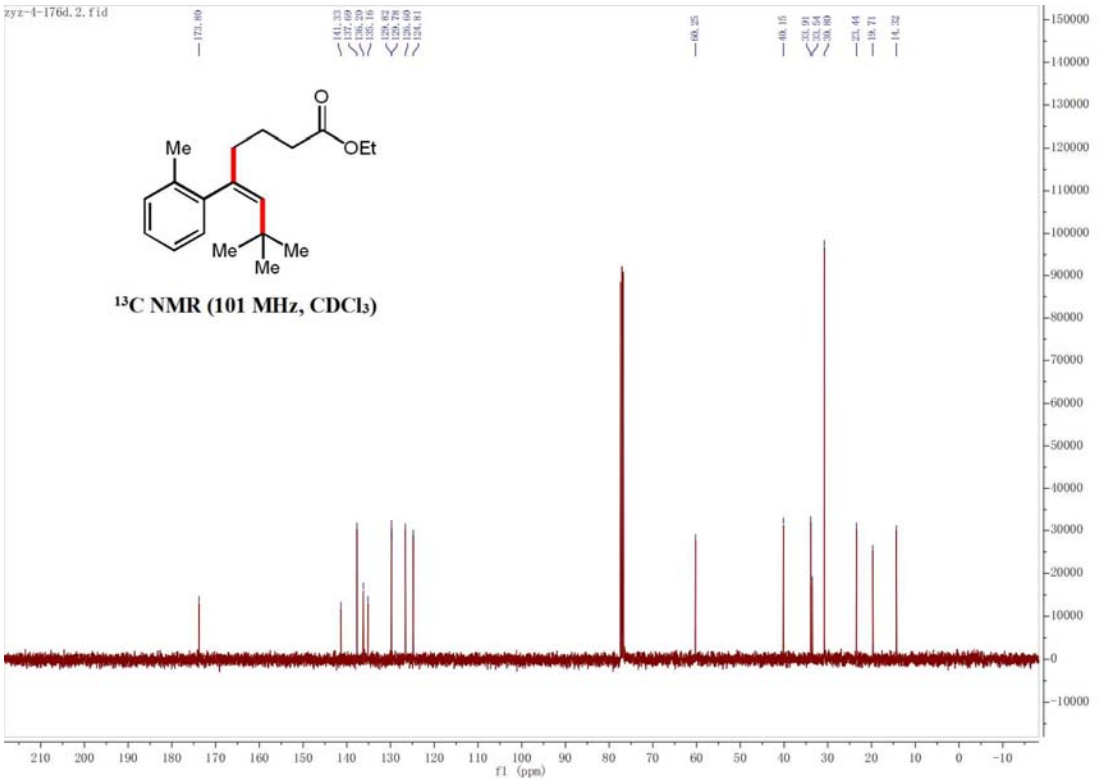


^{19}F NMR (565 MHz, $CDCl_3$)

Ethyl (*Z*)-7,7-dimethyl-5-(*o*-tolyl)oct-5-enoate (4r)

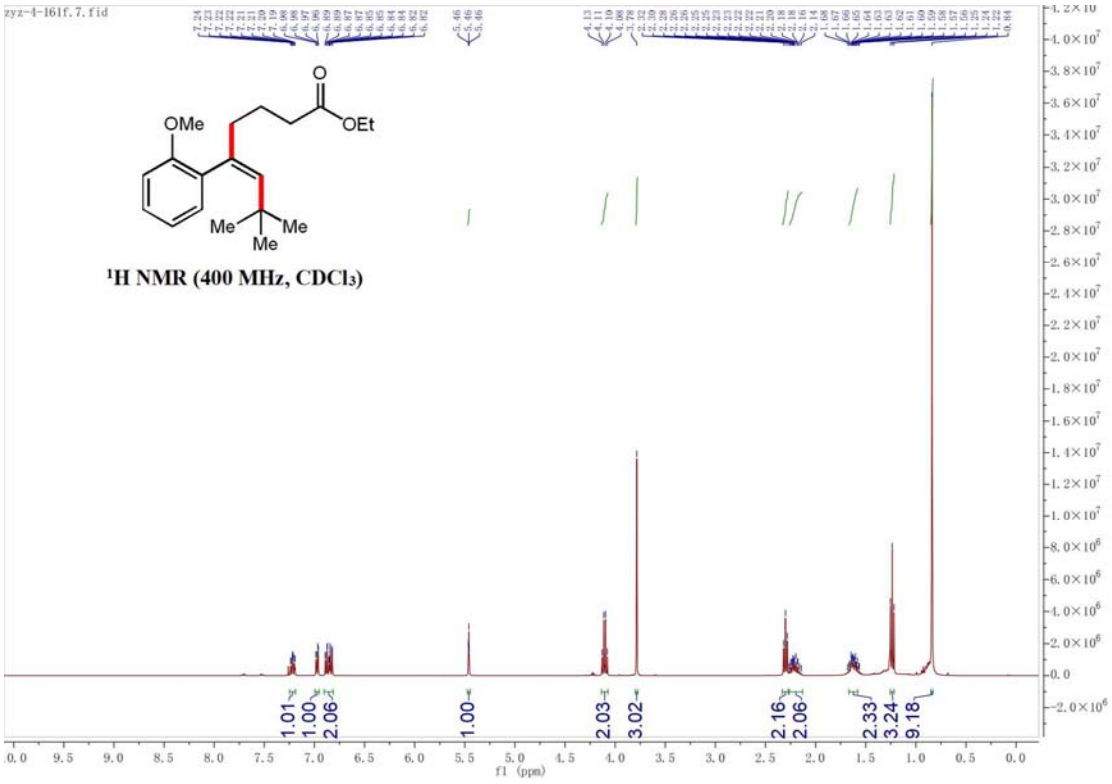


^{1}H NMR (400 MHz, $CDCl_3$)

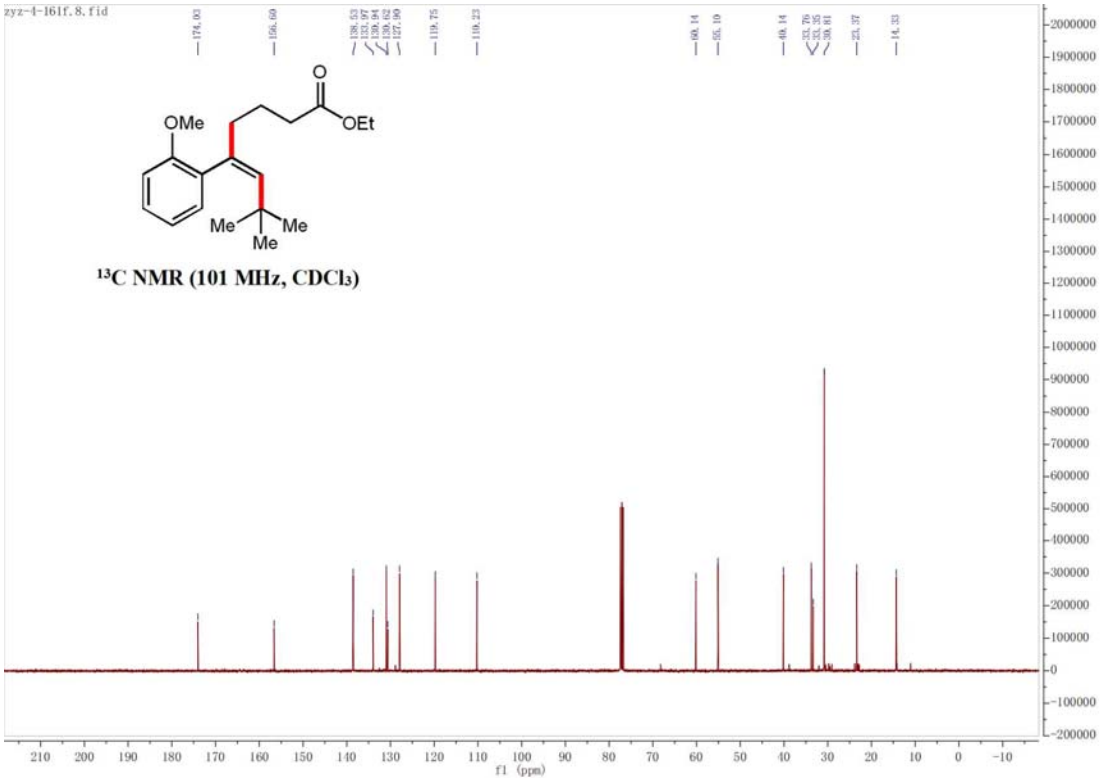


^{13}C NMR (101 MHz, $CDCl_3$)

Ethyl (*Z*)-5-(2-methoxyphenyl)-7,7-dimethyloct-5-enoate (4s)

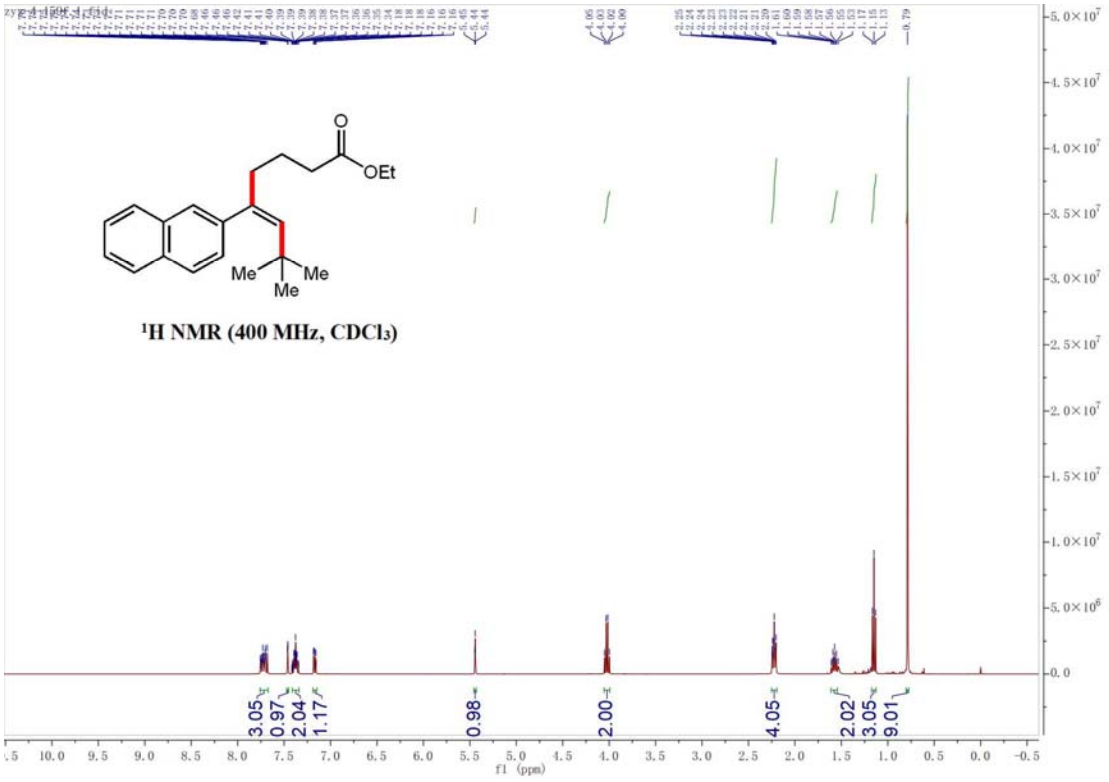


^{1}H NMR (400 MHz, $CDCl_3$)

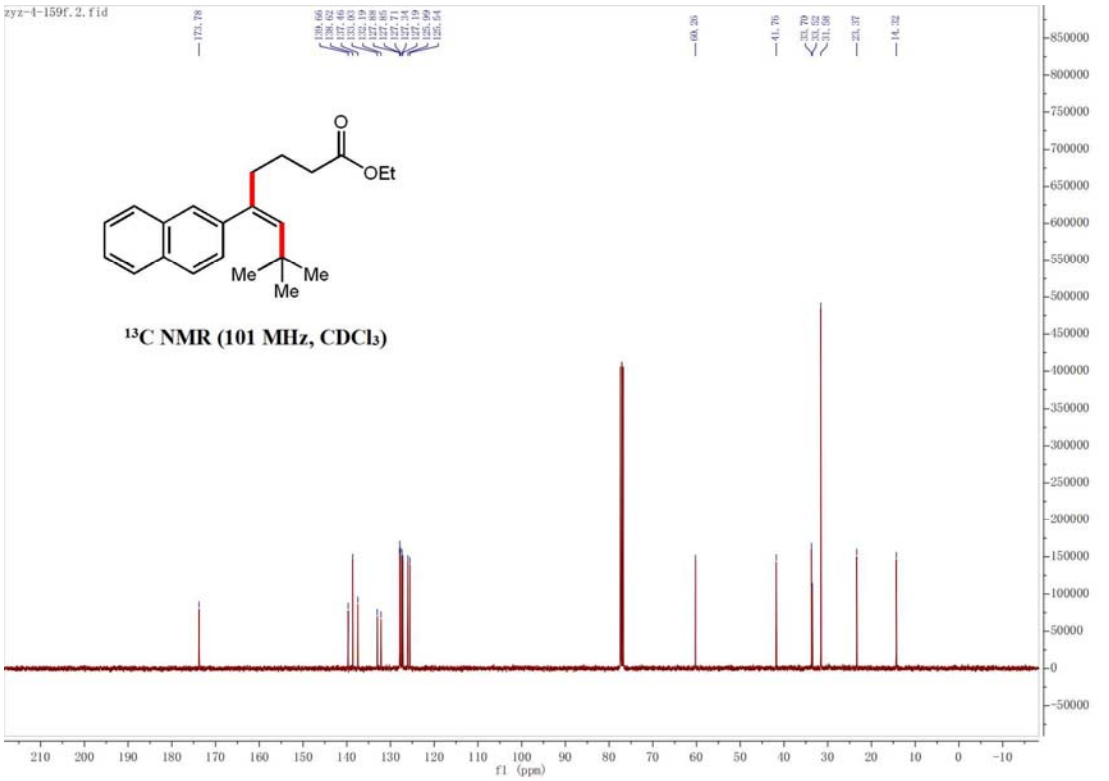


^{13}C NMR (101 MHz, $CDCl_3$)

Ethyl (*Z*)-7,7-dimethyl-5-(naphthalen-2-yl)oct-5-enoate (4t)

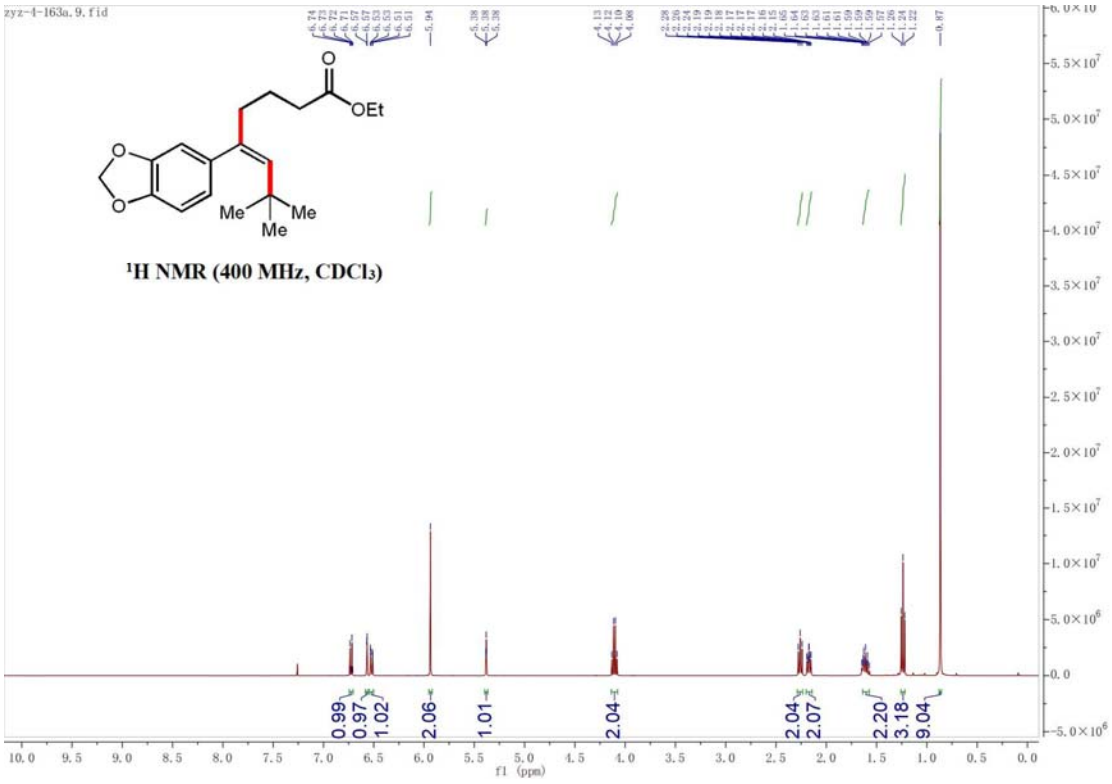


^{1}H NMR (400 MHz, $CDCl_3$)

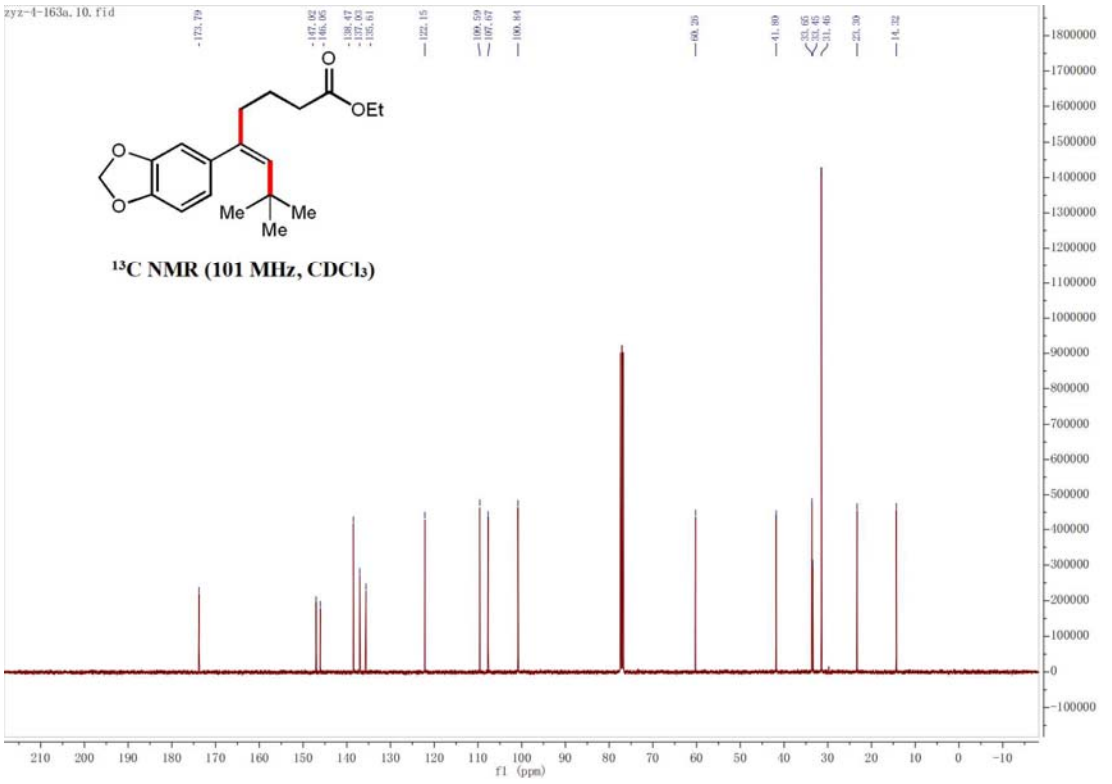


^{13}C NMR (101 MHz, $CDCl_3$)

Ethyl (*Z*)-5-(benzo[d][1,3]dioxol-5-yl)-7,7-dimethyloct-5-enoate (4u)

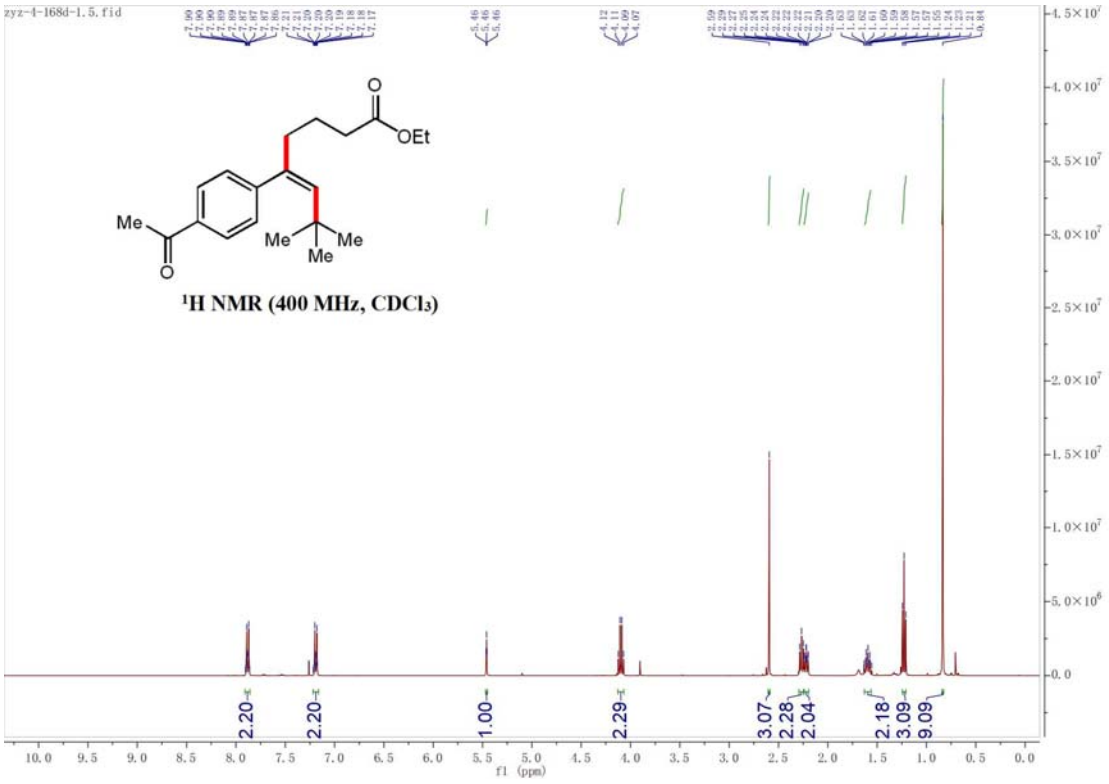


^{1}H NMR (400 MHz, $CDCl_3$)

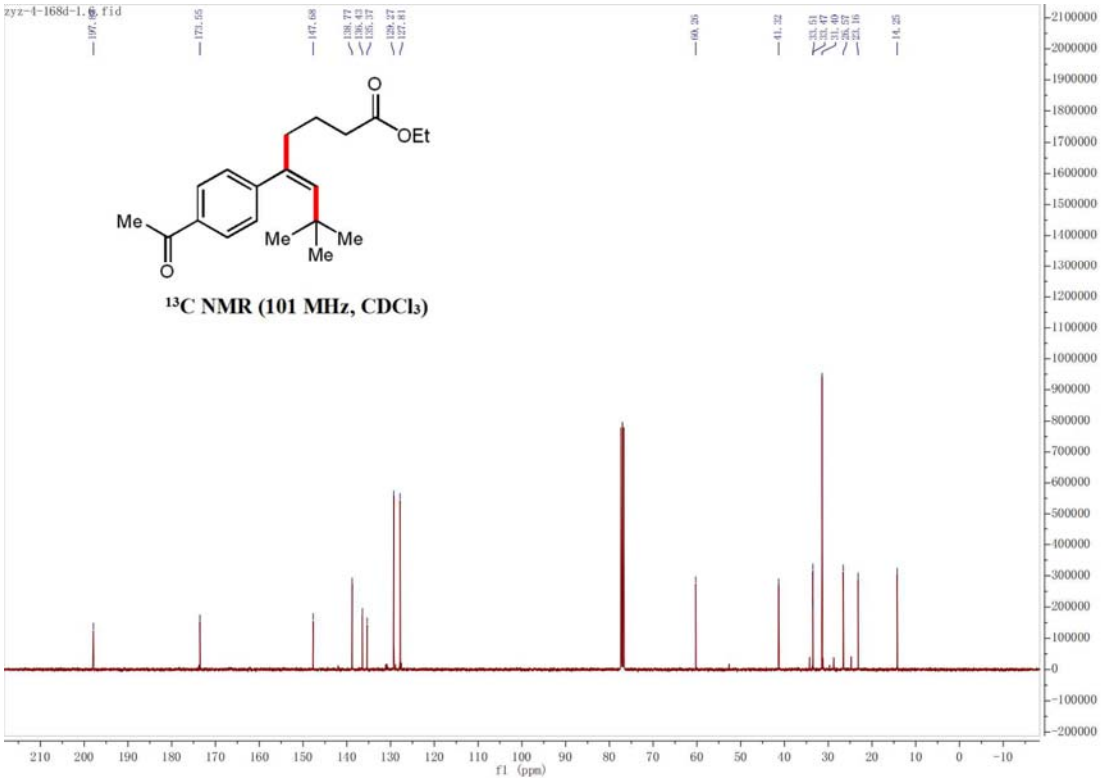


^{13}C NMR (101 MHz, $CDCl_3$)

Ethyl (Z)-5-(4-acetylphenyl)-7,7-dimethyloct-5-enoate (4v)

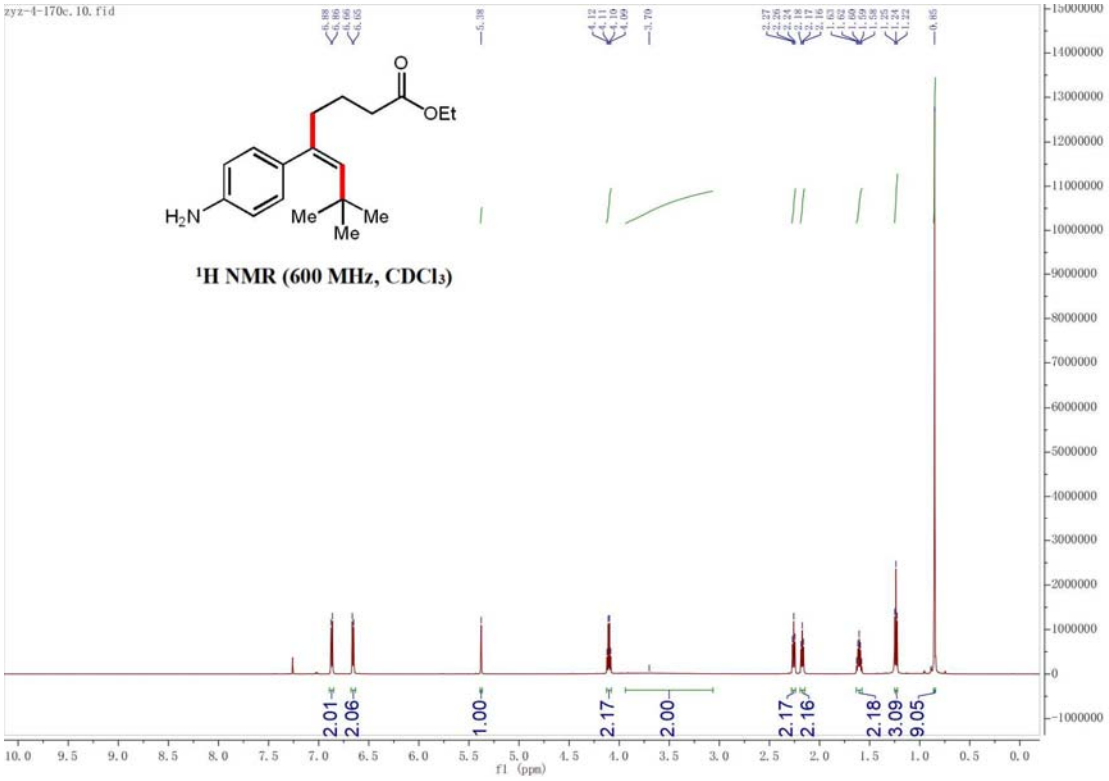


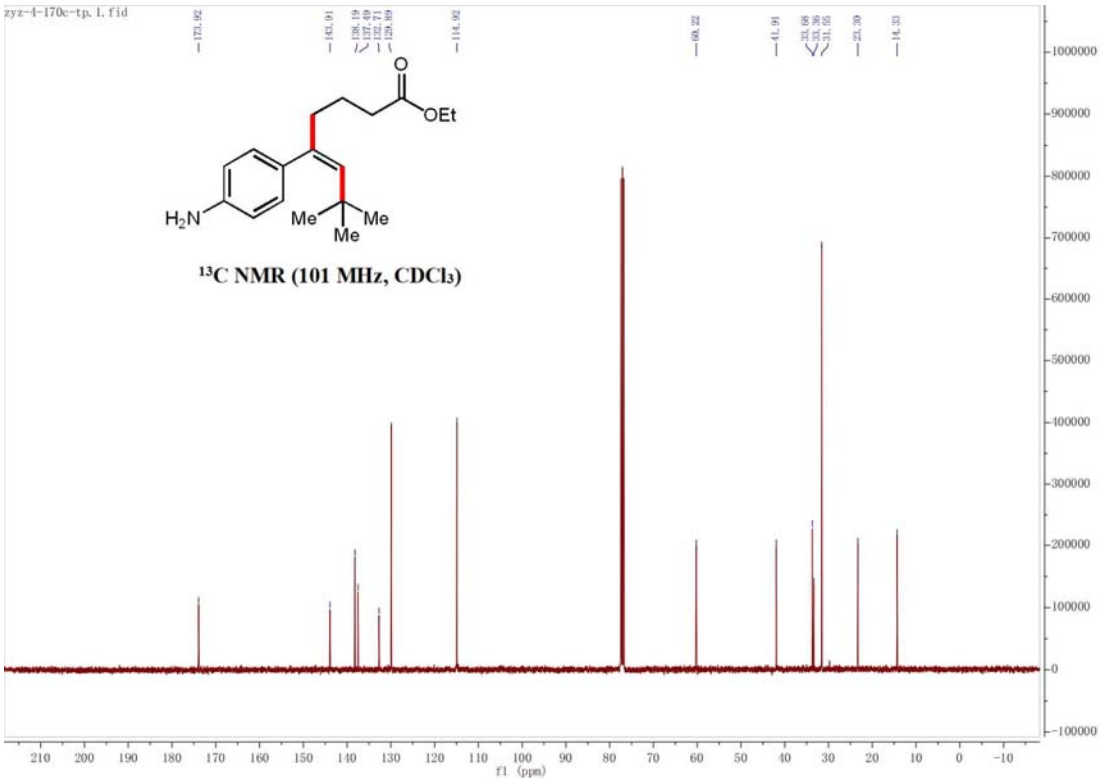
^{1}H NMR (400 MHz, $CDCl_3$)



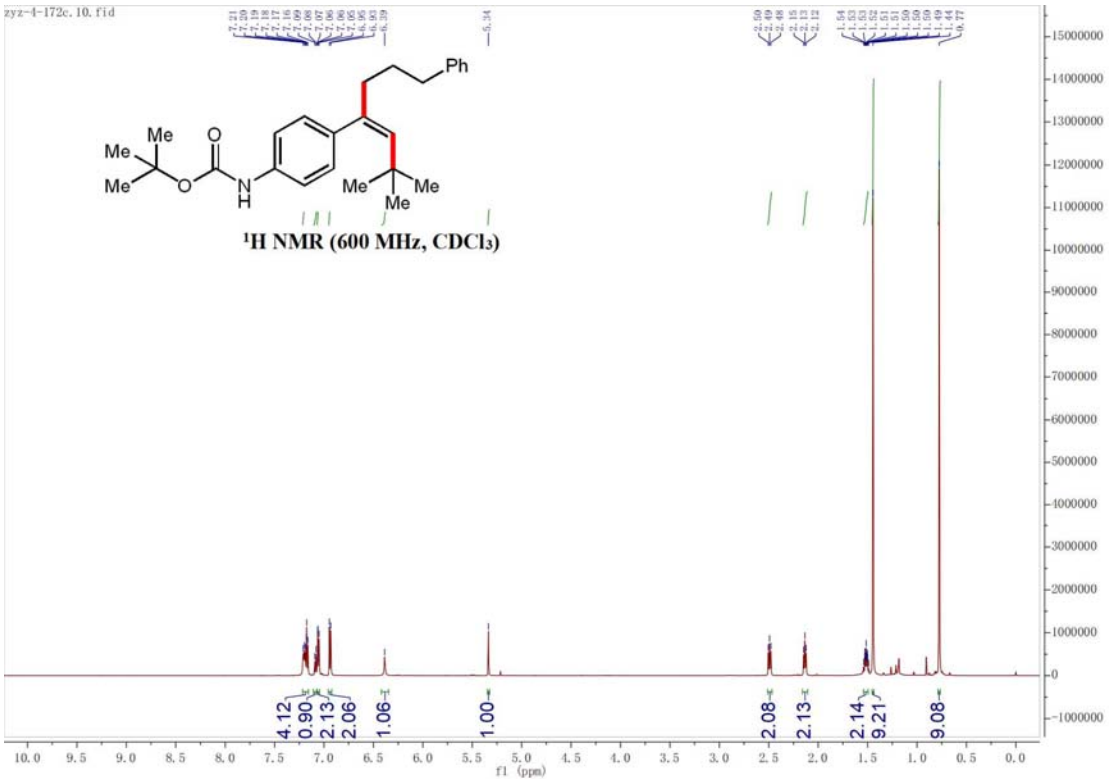
^{13}C NMR (101 MHz, $CDCl_3$)

Ethyl (*Z*)-5-(4-aminophenyl)-7,7-dimethyloct-5-enoate (4w)

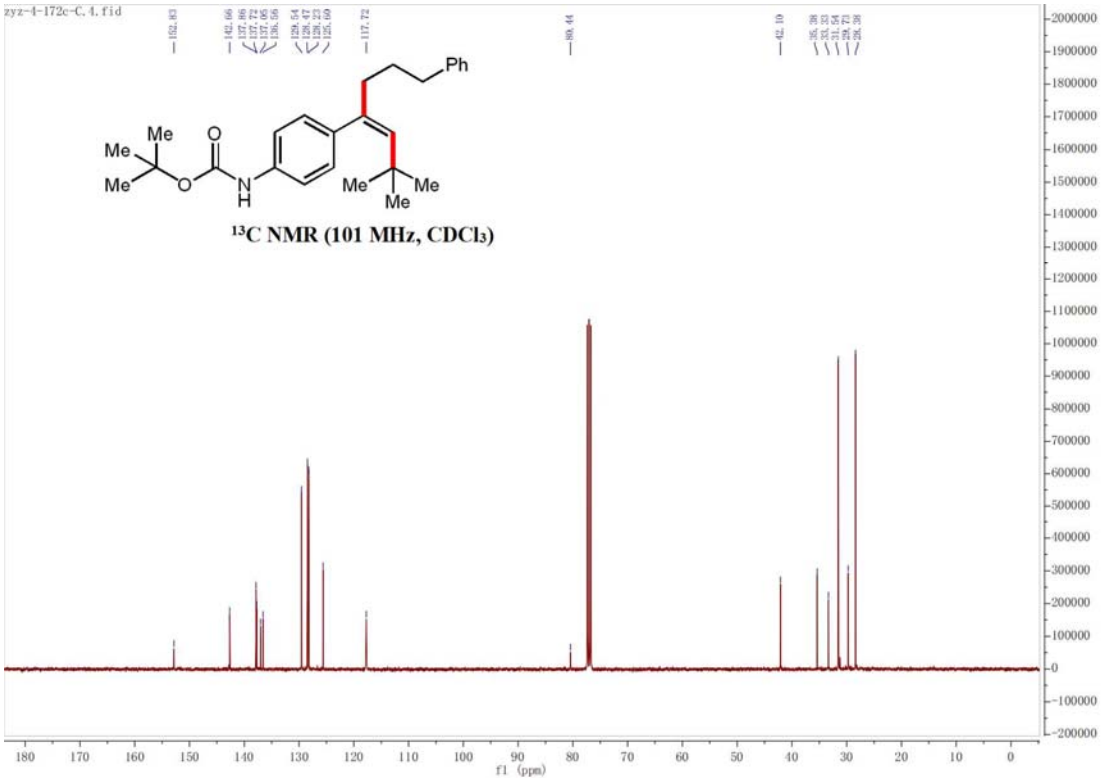




tert-Butyl (_Z_)-(4-(2,2-dimethyl-7-phenylhept-3-en-4-yl)phenyl)carbamate (4x)

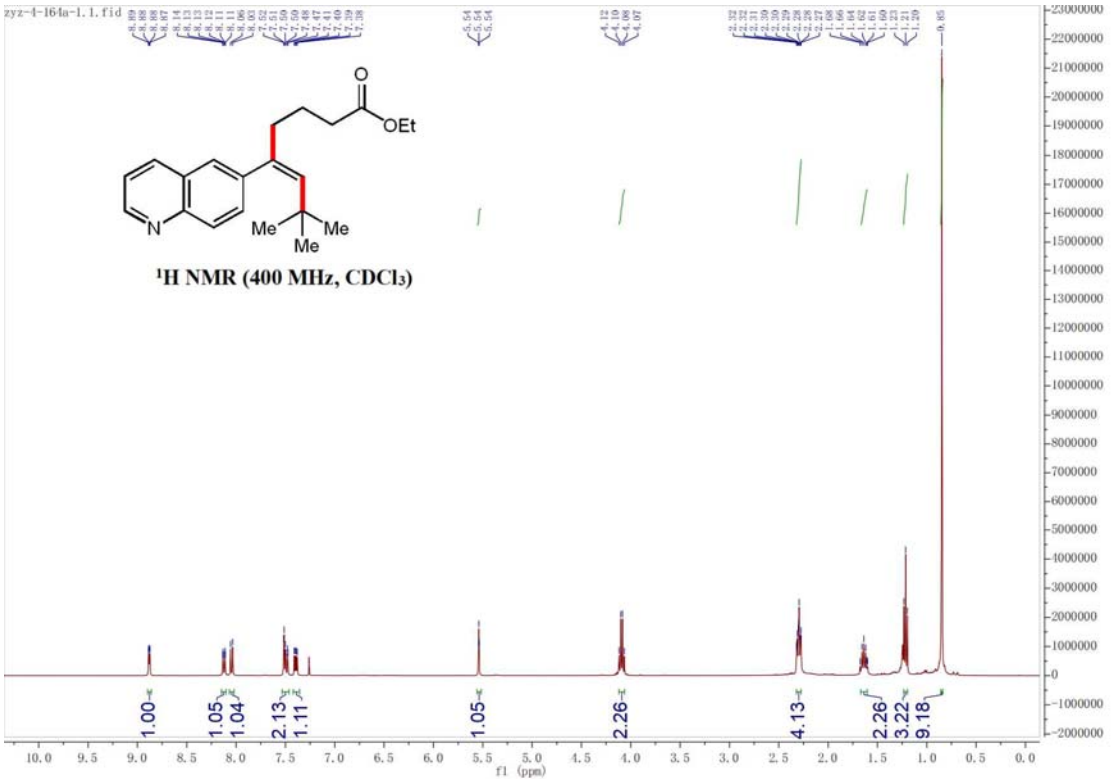


^{1}H NMR (600 MHz, $CDCl_3$)

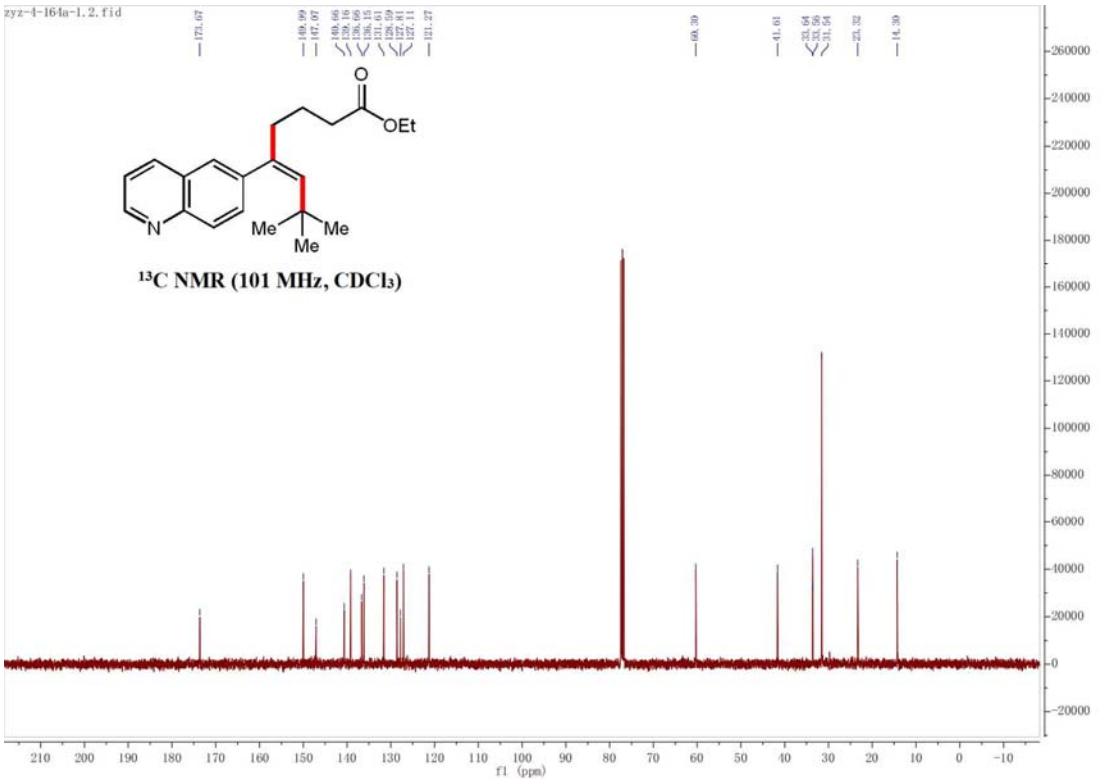


^{13}C NMR (101 MHz, $CDCl_3$)

Ethyl (Z)-7,7-dimethyl-5-(quinolin-6-yl)oct-5-enoate (4y)

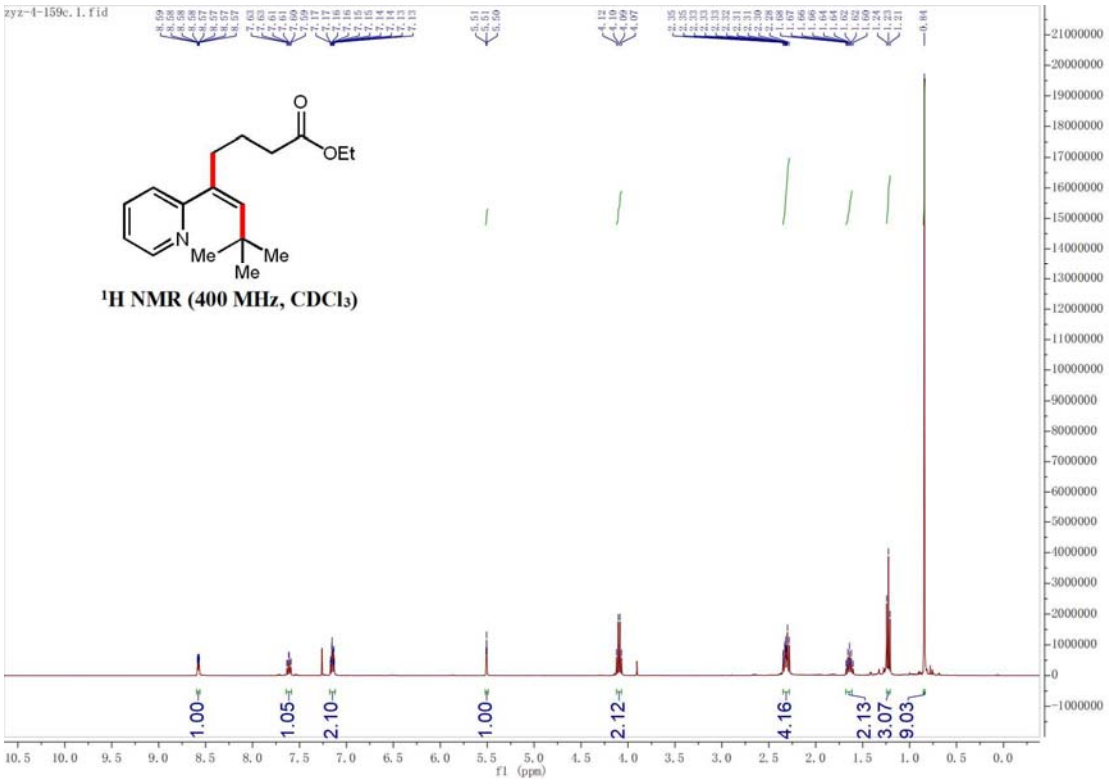


^{1}H NMR (400 MHz, $CDCl_3$)

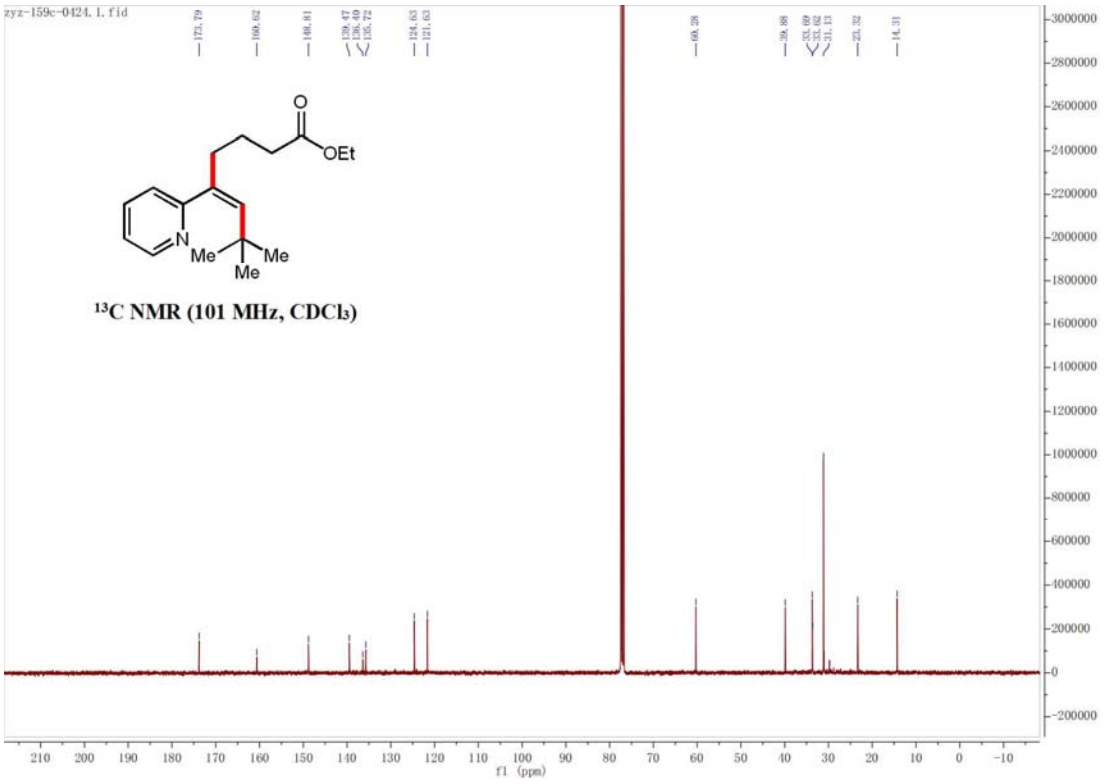


^{13}C NMR (101 MHz, $CDCl_3$)

Ethyl (Z)-7,7-dimethyl-5-(pyridin-2-yl)oct-5-enoate (4z)

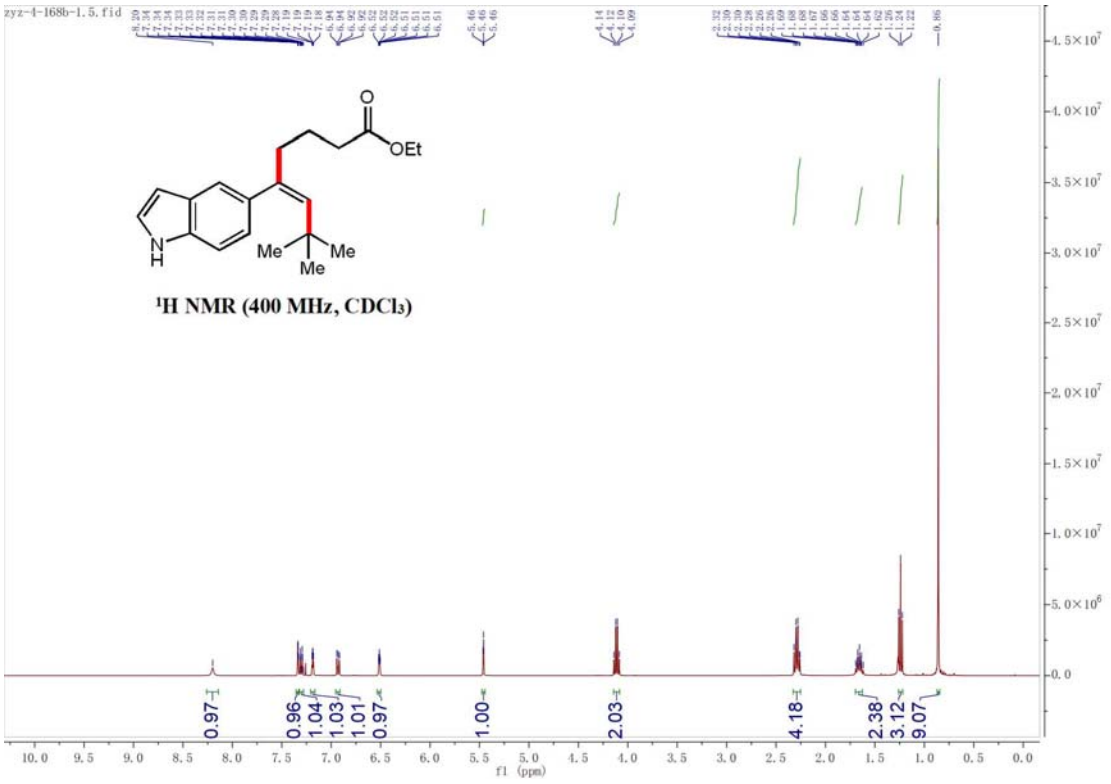


^{1}H NMR (400 MHz, $CDCl_3$)

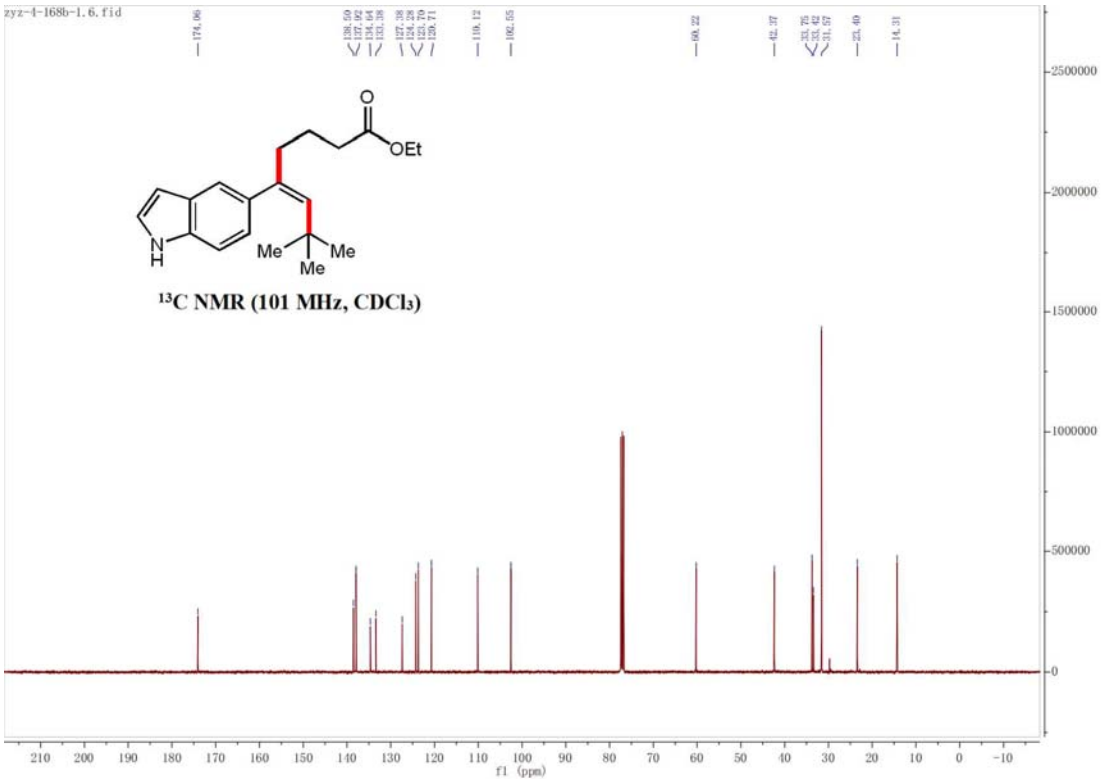


^{13}C NMR (101 MHz, $CDCl_3$)

Ethyl (Z)-5-(1H-indol-5-yl)-7,7-dimethyloct-5-enoate (4aa)

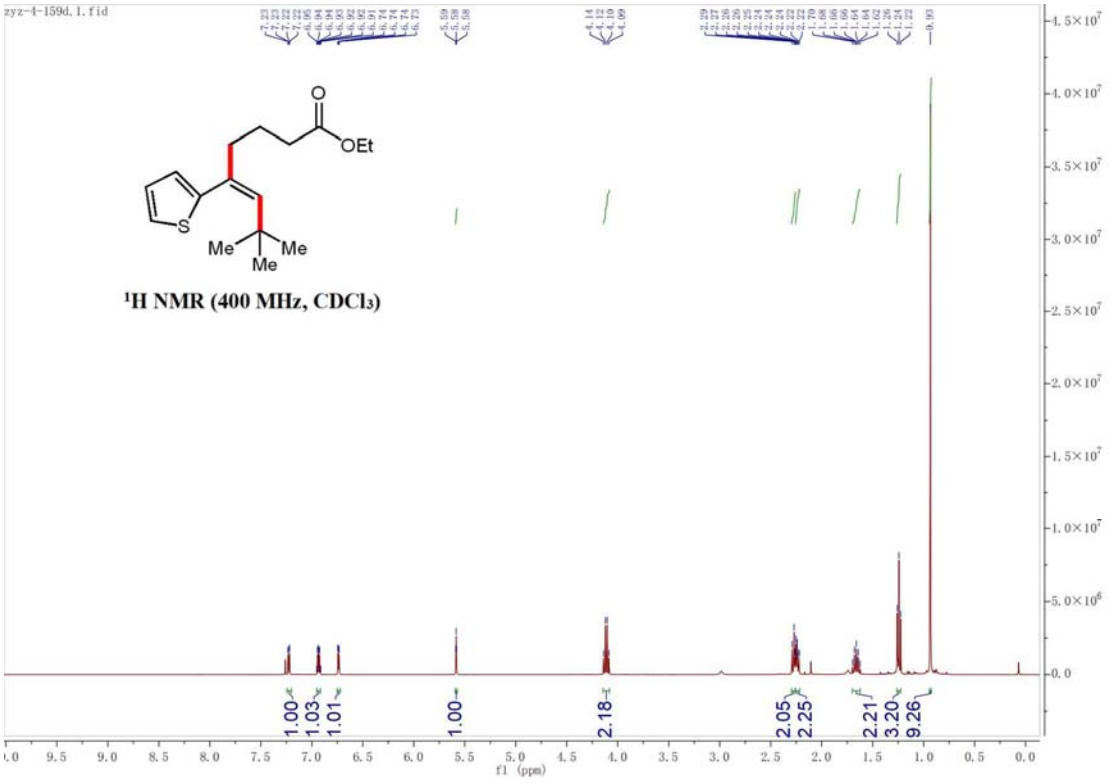


^{1}H NMR (400 MHz, $CDCl_3$)

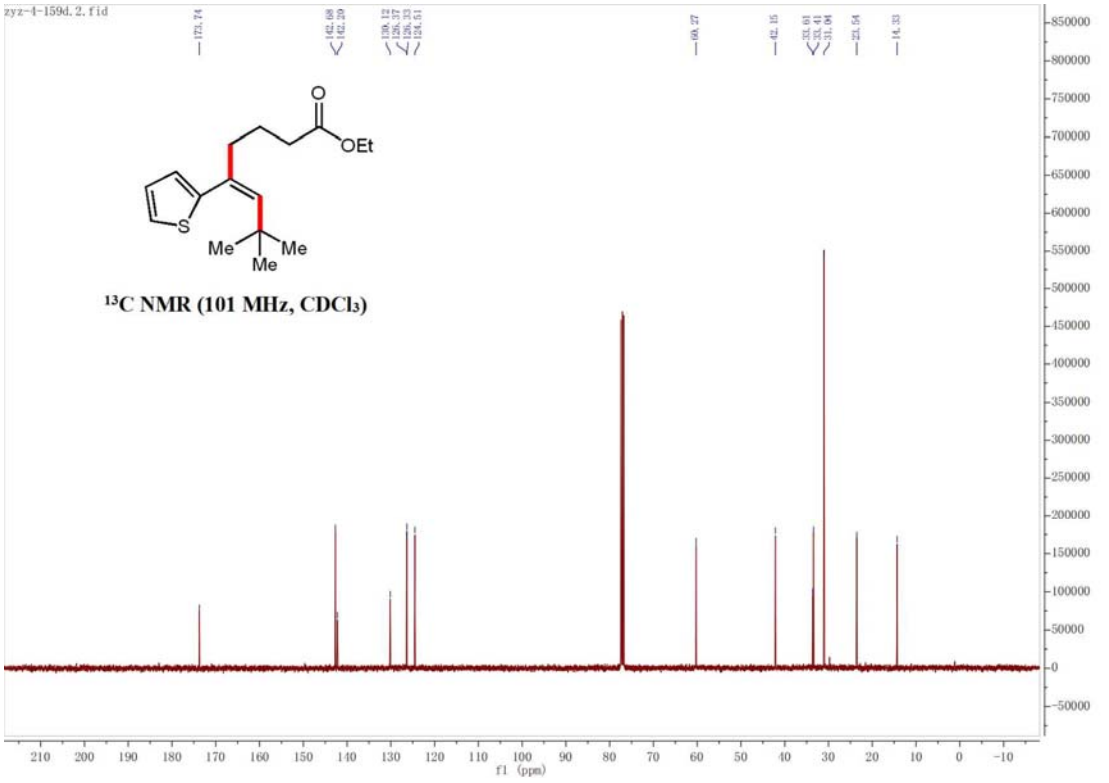


^{13}C NMR (101 MHz, $CDCl_3$)

Ethyl (Z)-7,7-dimethyl-5-(thiophen-2-yl)oct-5-enoate (4ab)

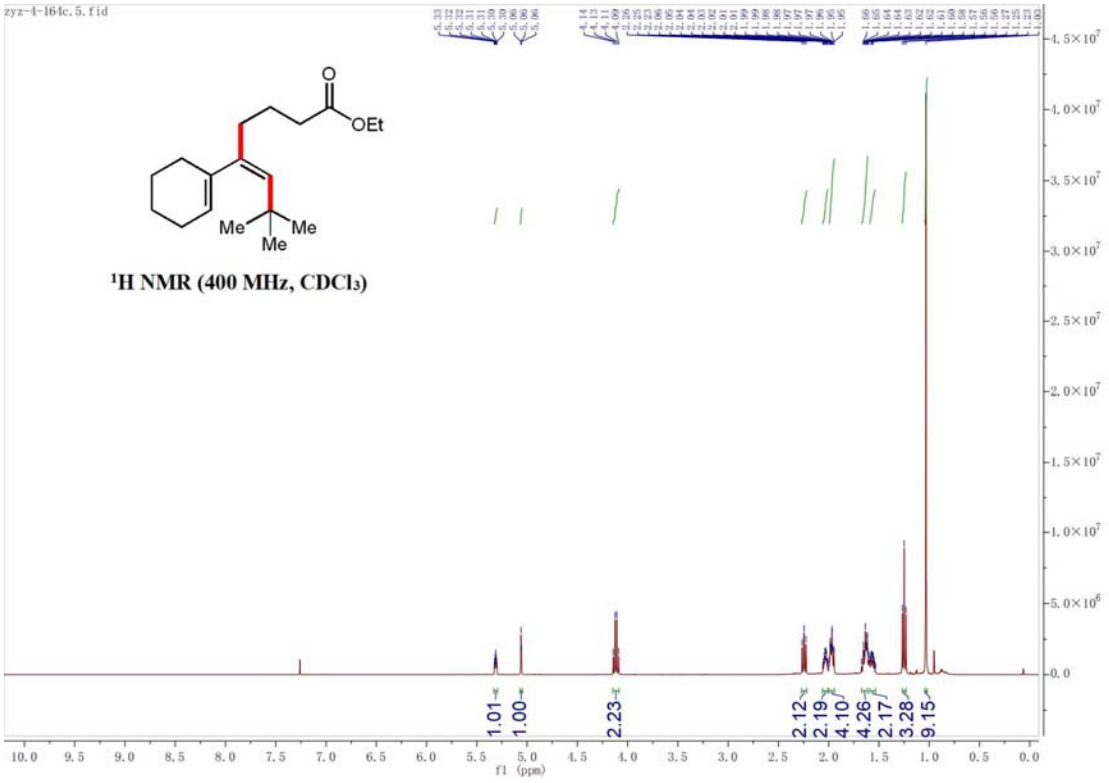


^{1}H NMR (400 MHz, $CDCl_3$)

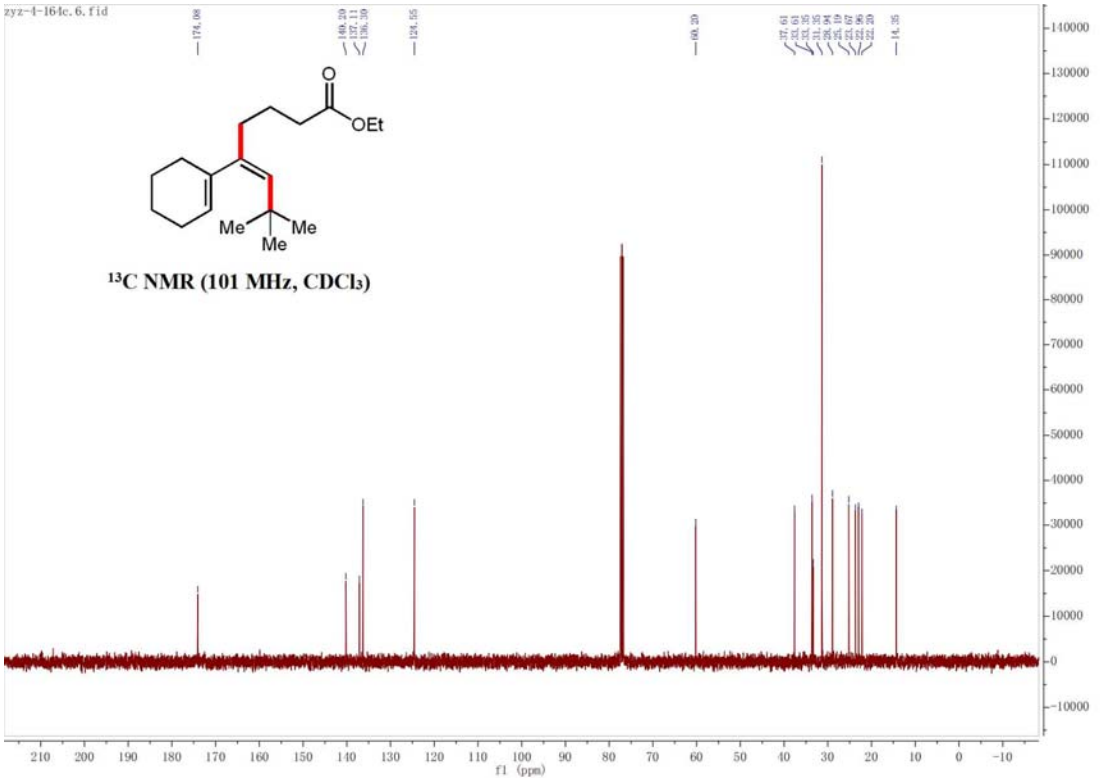


^{13}C NMR (101 MHz, $CDCl_3$)

Ethyl (Z)-5-(cyclohex-1-en-1-yl)-7,7-dimethyloct-5-enoate (4ac)

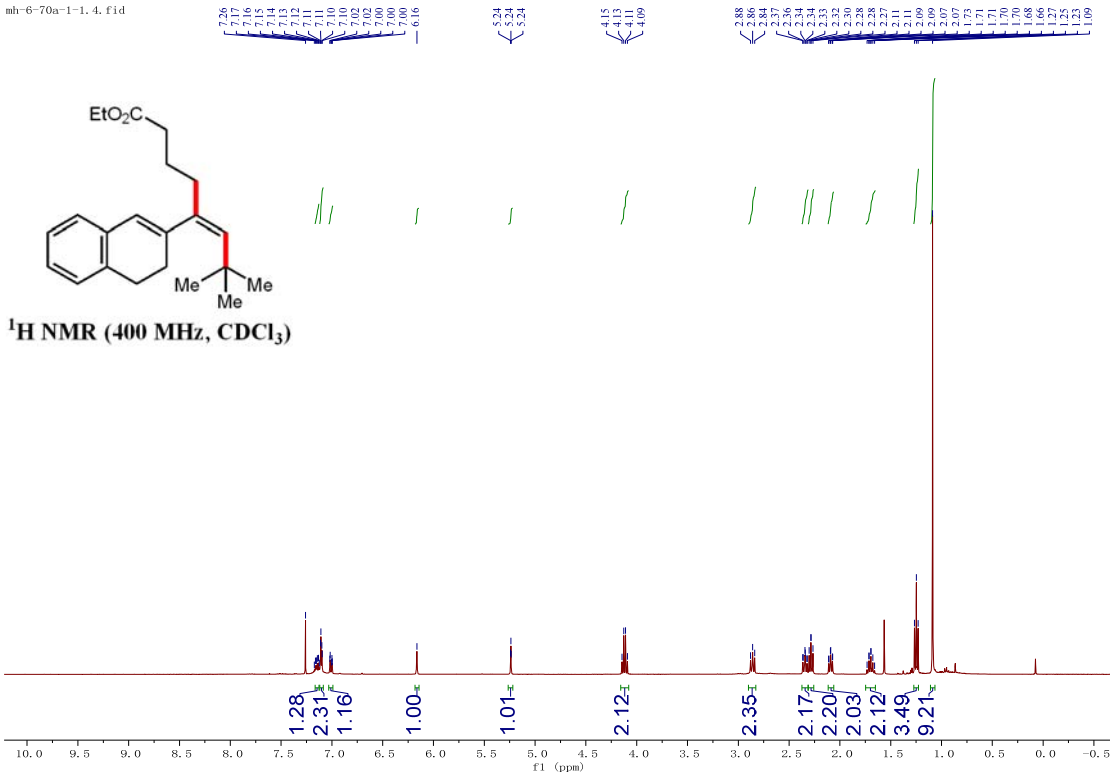


^{1}H NMR (400 MHz, $CDCl_3$)

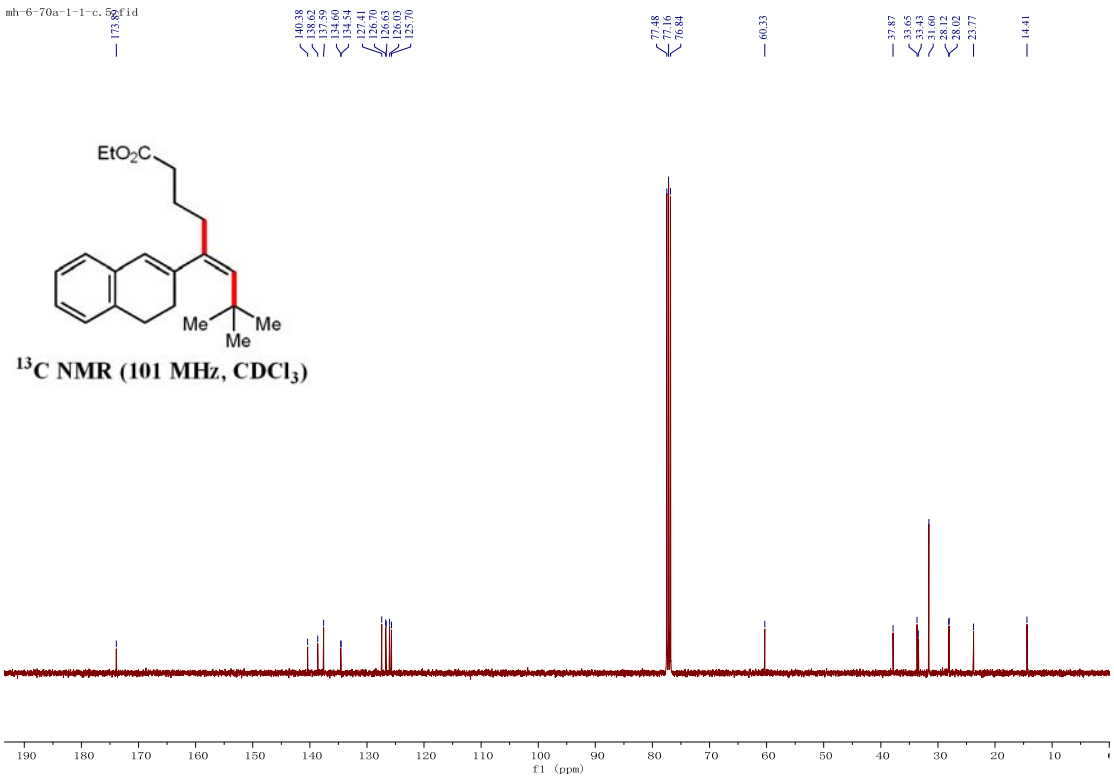


^{13}C NMR (101 MHz, $CDCl_3$)

Ethyl (*Z*)-5-(3,4-dihydronaphthalen-2-yl)-7,7-dimethyloct-5-enoate (4ad)

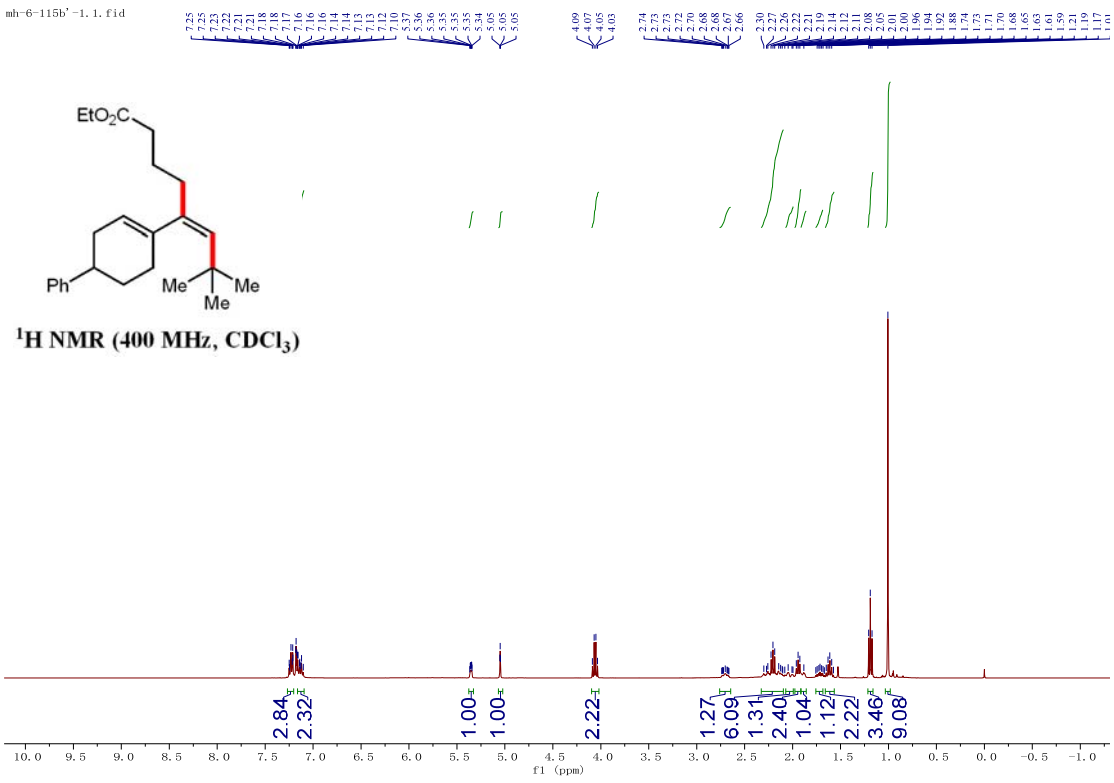


^{1}H NMR (400 MHz, $CDCl_3$)

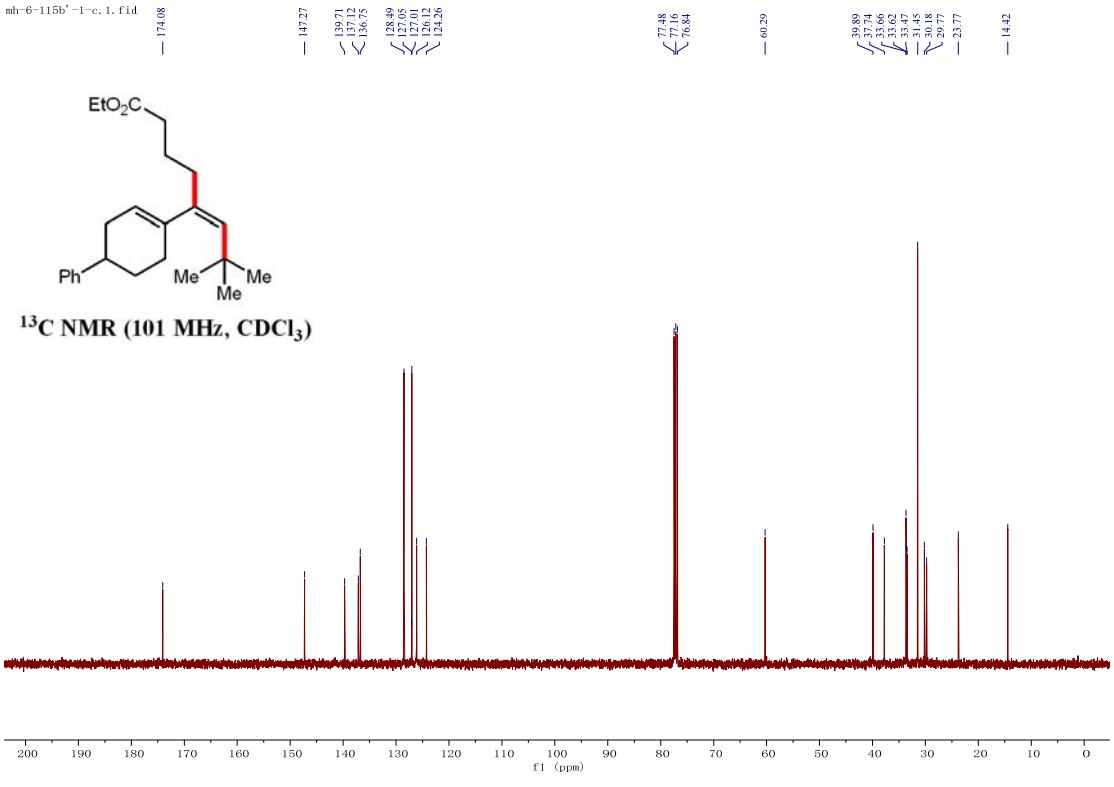


^{13}C NMR (101 MHz, $CDCl_3$)

Ethyl (*Z*)-7,7-dimethyl-5-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oct-5-enoate (4ae)

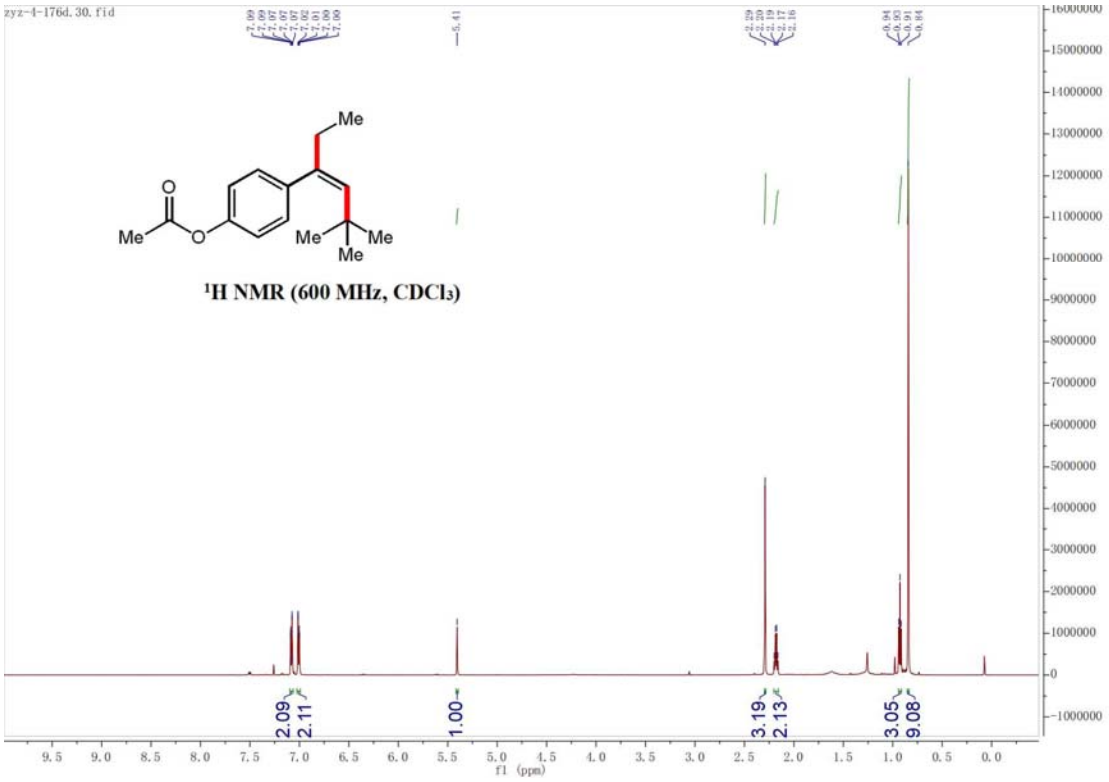


^{1}H NMR (400 MHz, $CDCl_3$)

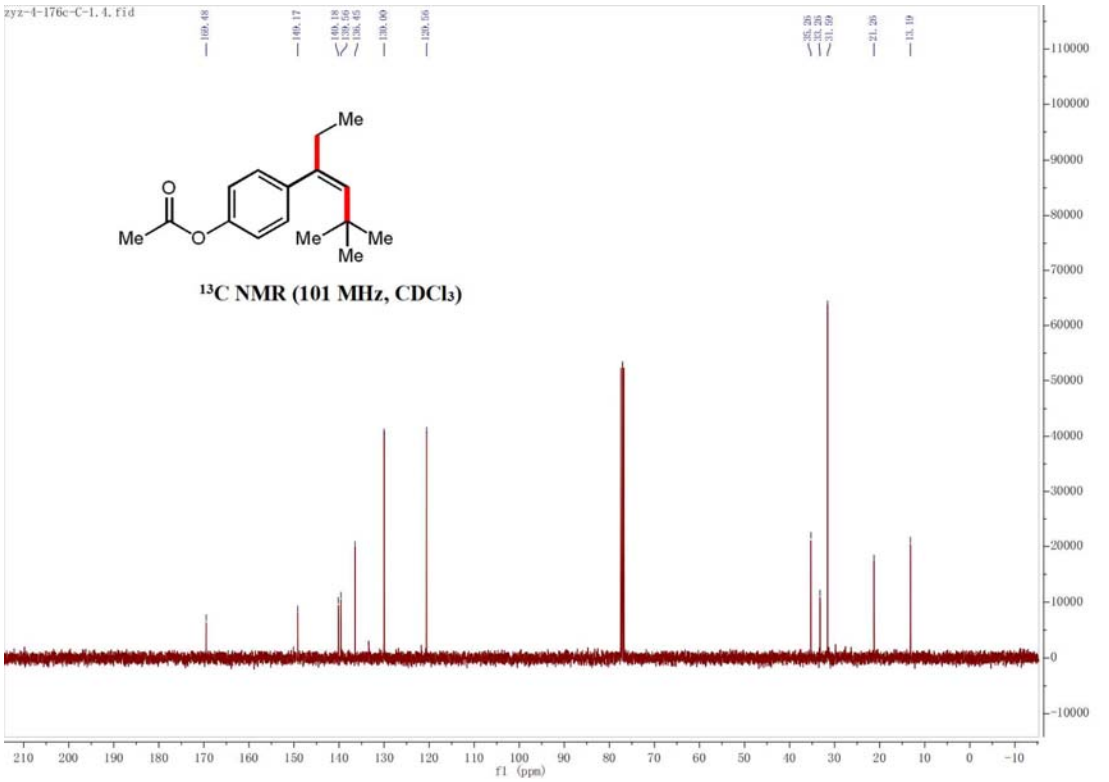


^{13}C NMR (101 MHz, $CDCl_3$)

(*Z*)-4-(5,5-Dimethylhex-3-en-3-yl)phenyl acetate (5a)

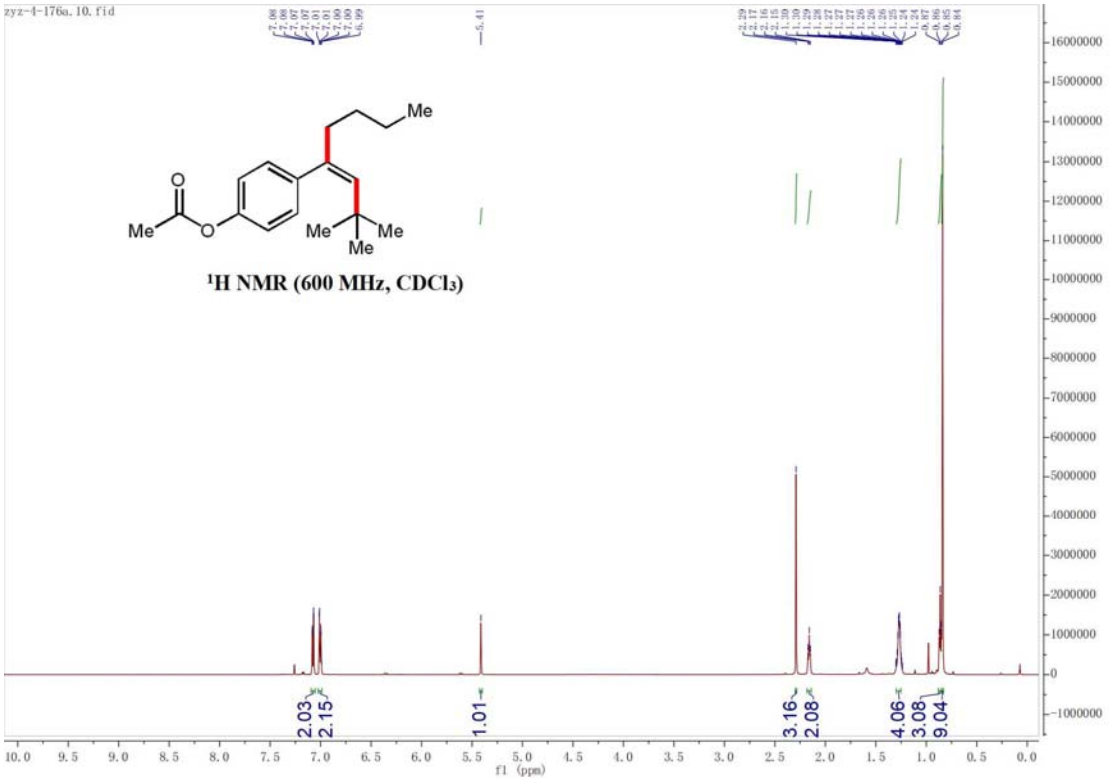


^{1}H NMR (600 MHz, $CDCl_3$)

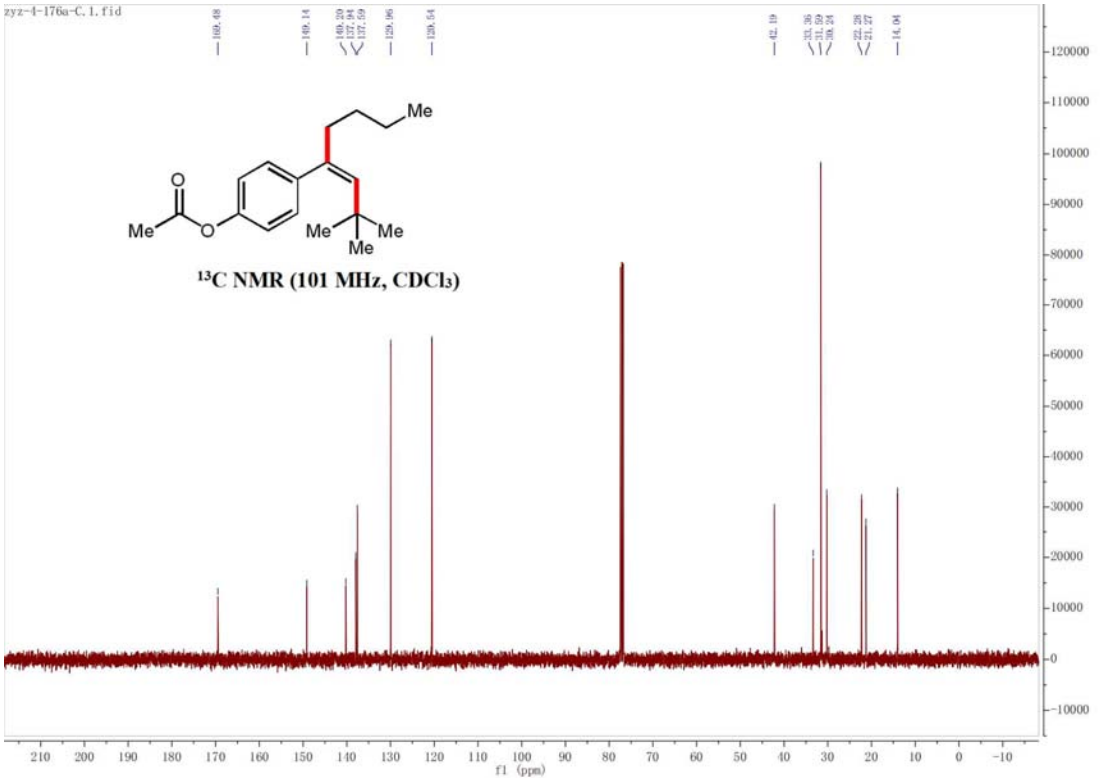


^{13}C NMR (101 MHz, $CDCl_3$)

(*Z*)-4-(2,2-Dimethyloct-3-en-4-yl)phenyl acetate (5b)

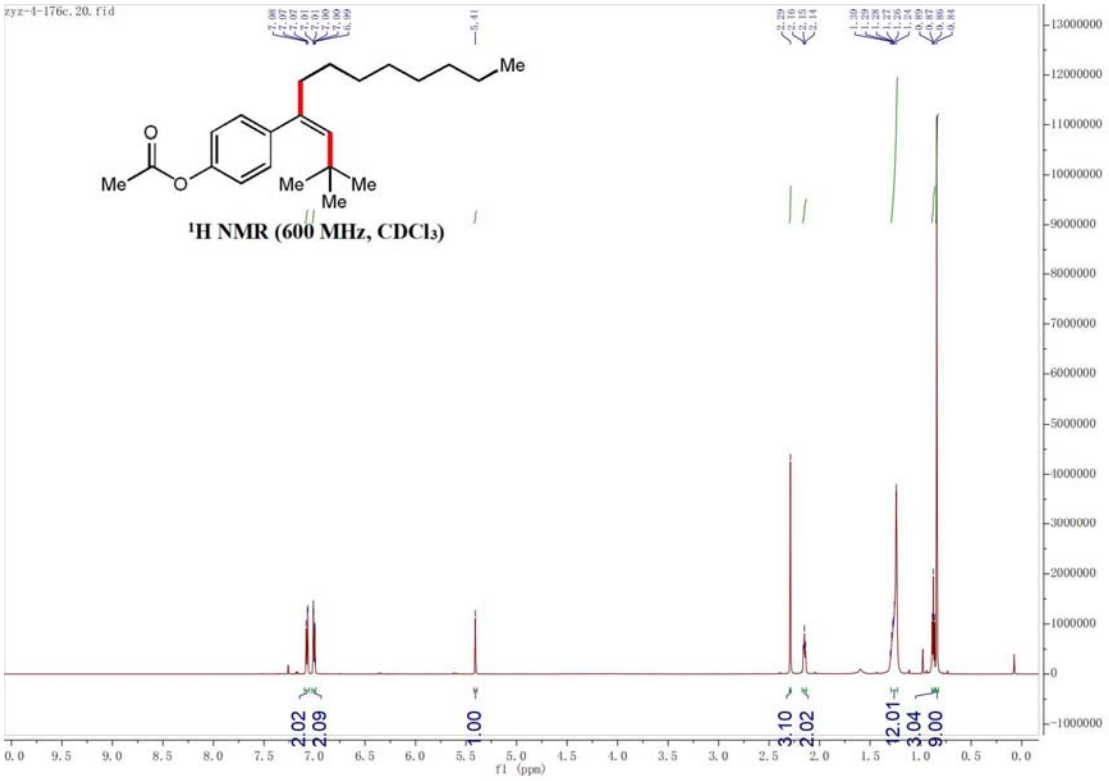


^{1}H NMR (600 MHz, $CDCl_3$)

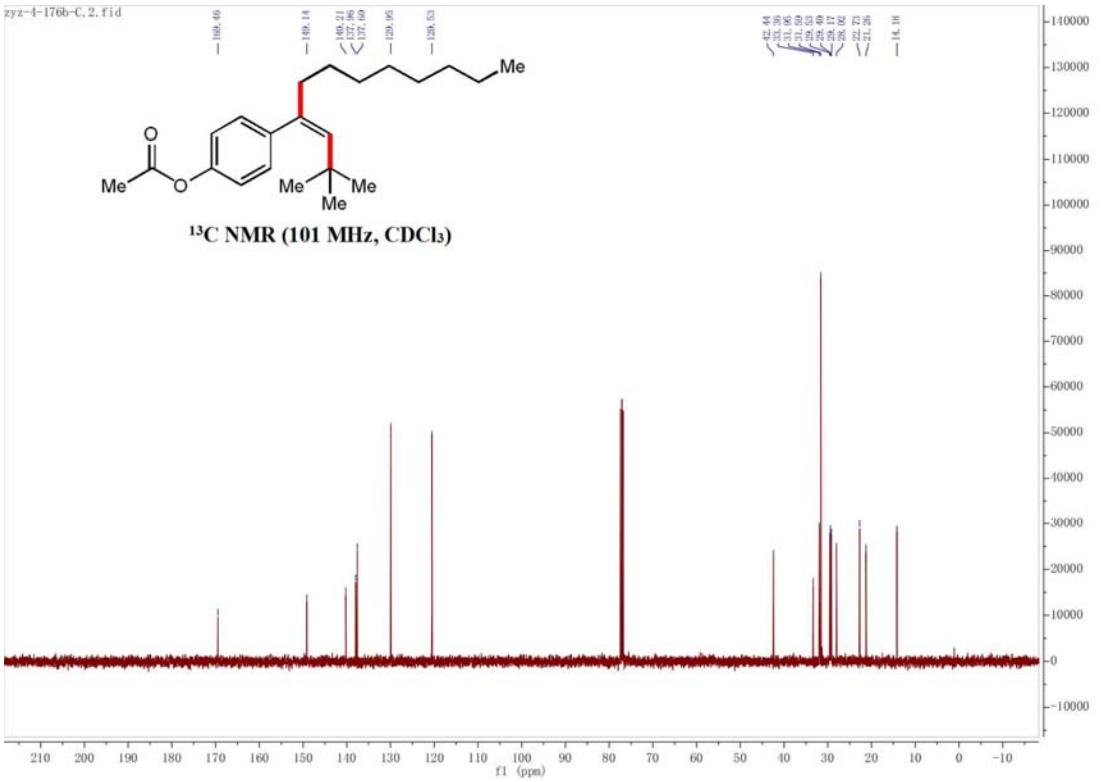


^{13}C NMR (101 MHz, $CDCl_3$)

(*Z*)-4-(2,2-Dimethyldodec-3-en-4-yl)phenyl acetate (5c)

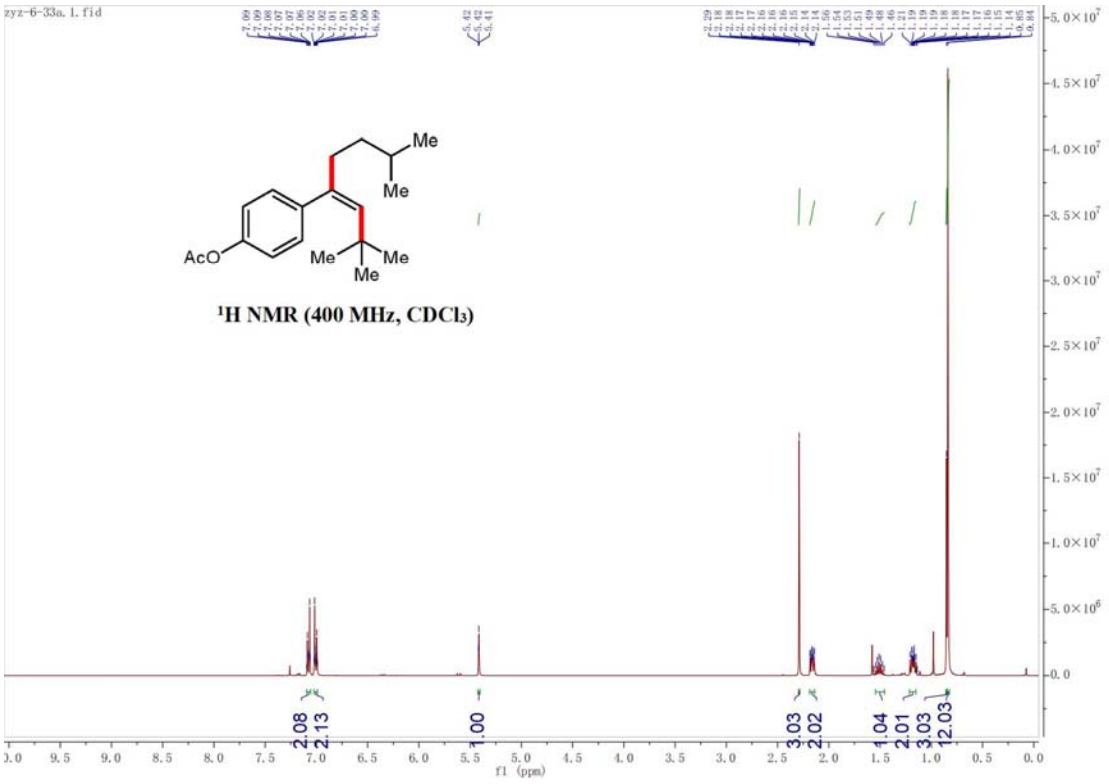


^{1}H NMR (600 MHz, $CDCl_3$)

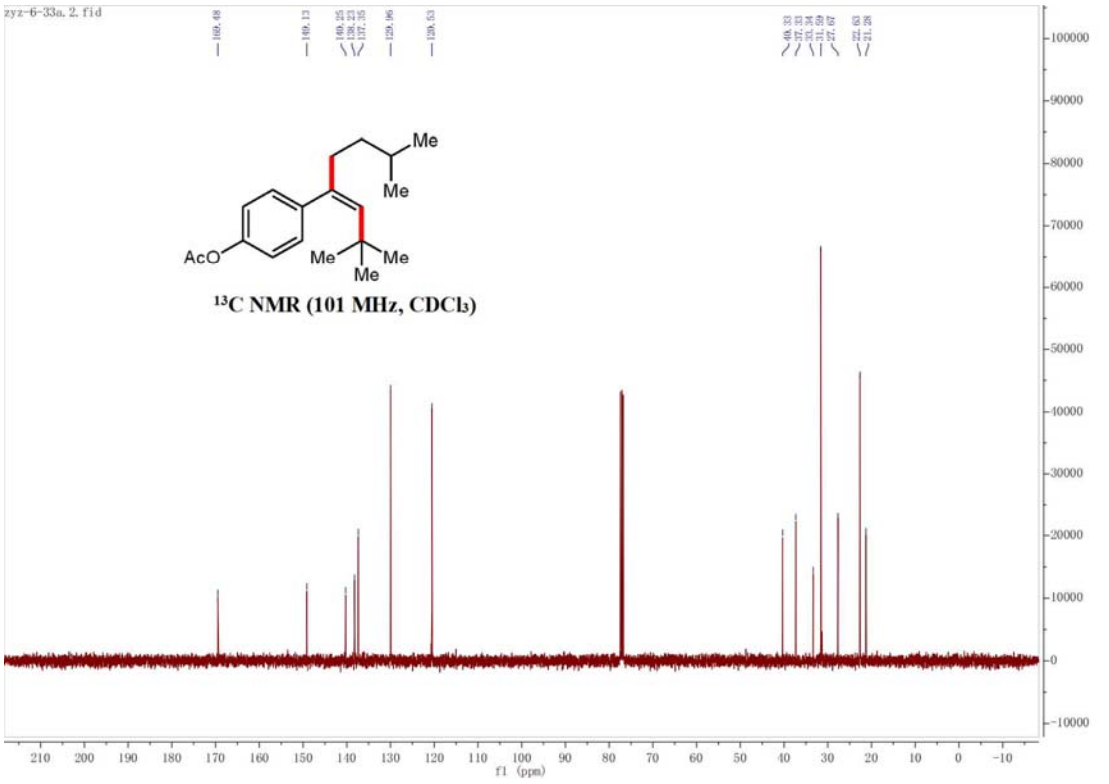


^{13}C NMR (101 MHz, $CDCl_3$)

(*Z*)-4-(2,2,7-Trimethyloct-3-en-4-yl)phenyl acetate (5d)

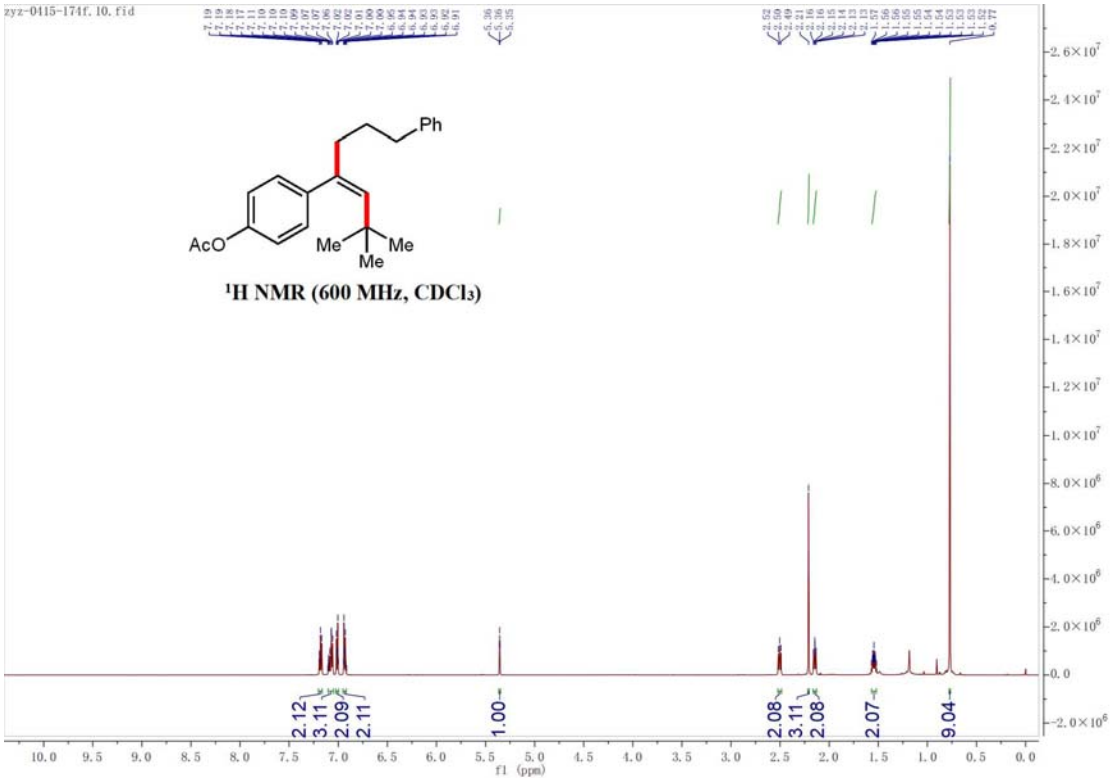


^{1}H NMR (400 MHz, $CDCl_3$)

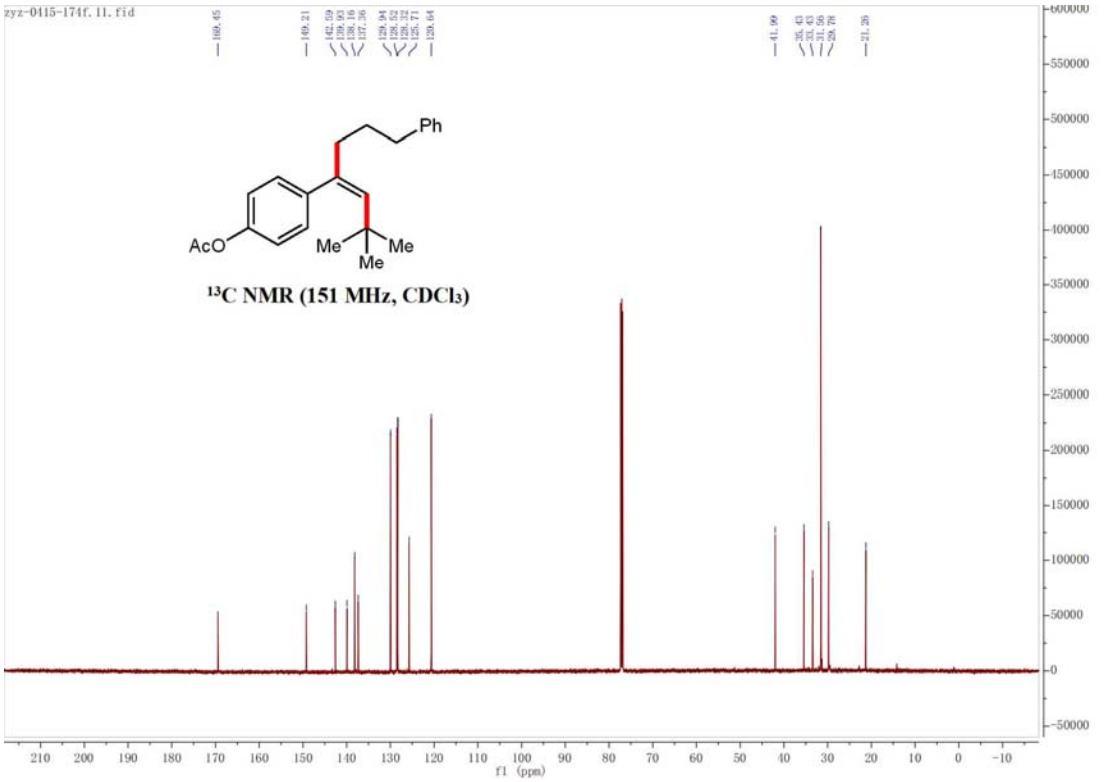


^{13}C NMR (101 MHz, $CDCl_3$)

(*Z*)-4-(2,2-Dimethyl-7-phenylhept-3-en-4-yl)phenyl acetate (5e)

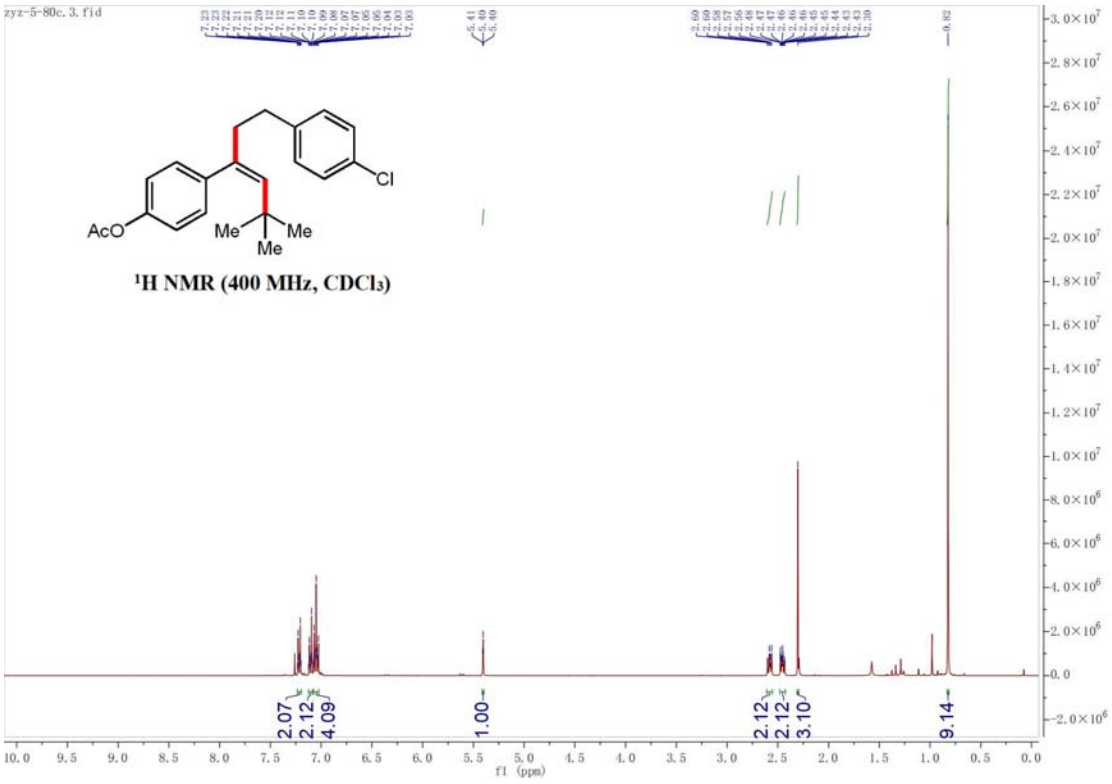


^{1}H NMR (600 MHz, $CDCl_3$)

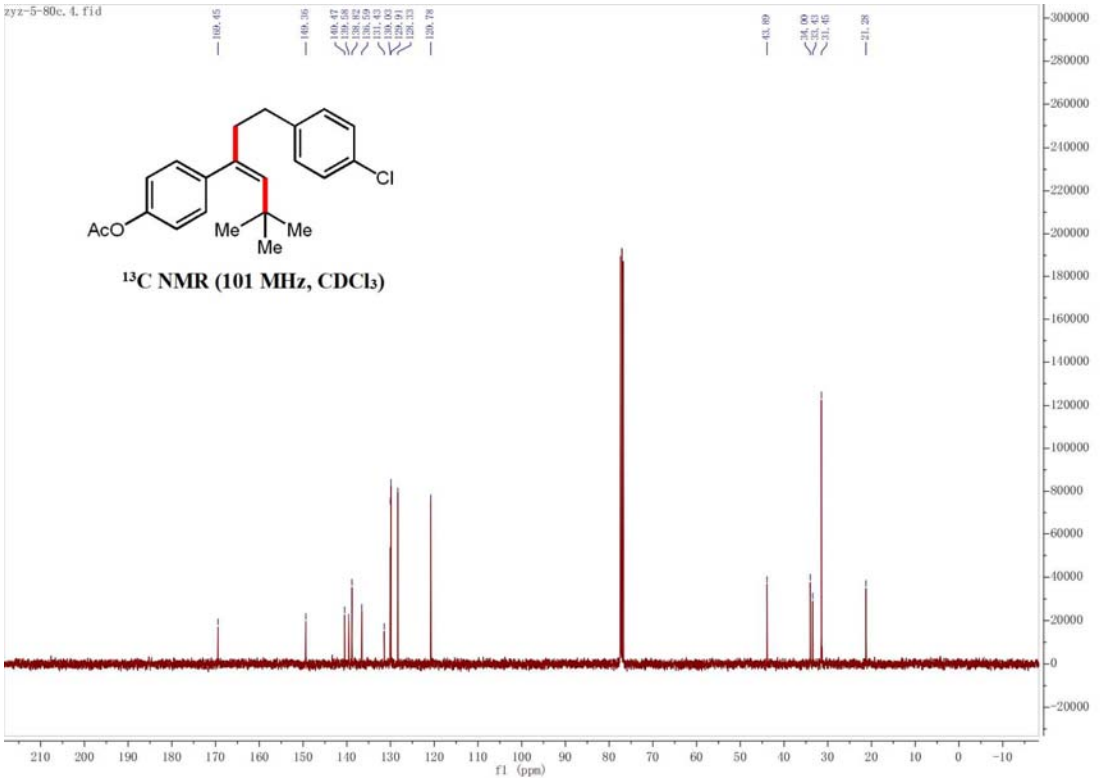


^{13}C NMR (151 MHz, $CDCl_3$)

(*Z*)-4-(1-(4-Chlorophenyl)-5,5-dimethylhex-3-en-3-yl)phenyl acetate (5f)

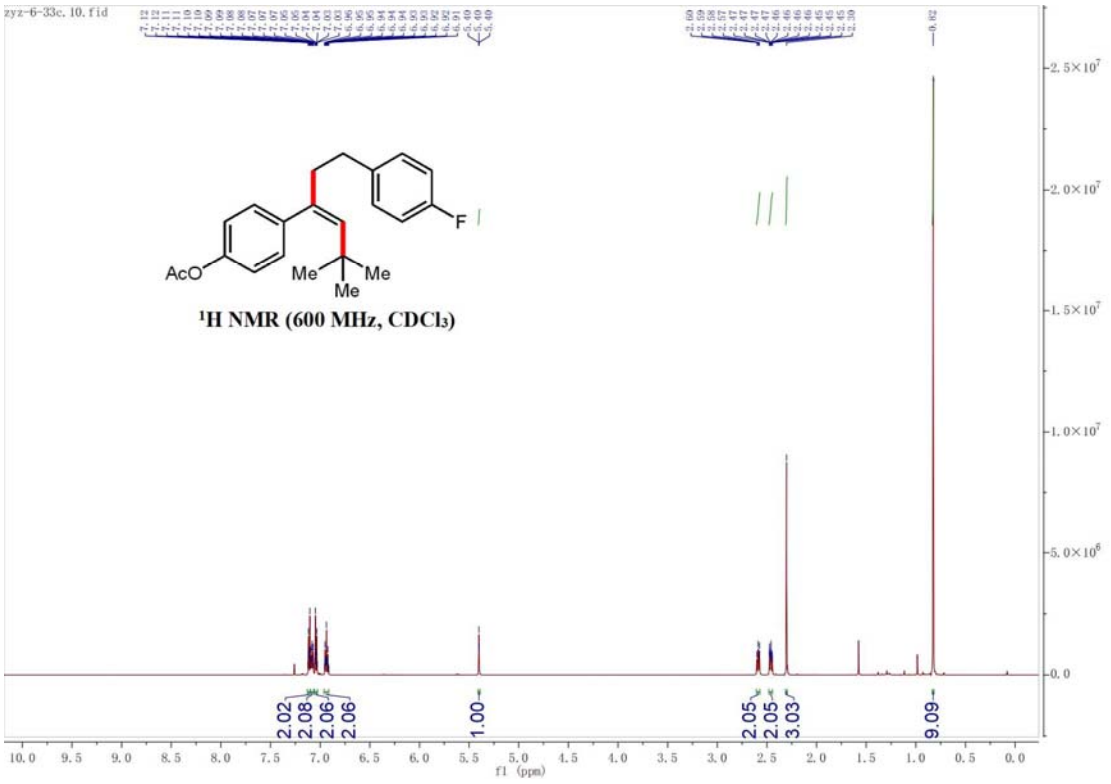


^{1}H NMR (400 MHz, $CDCl_3$)

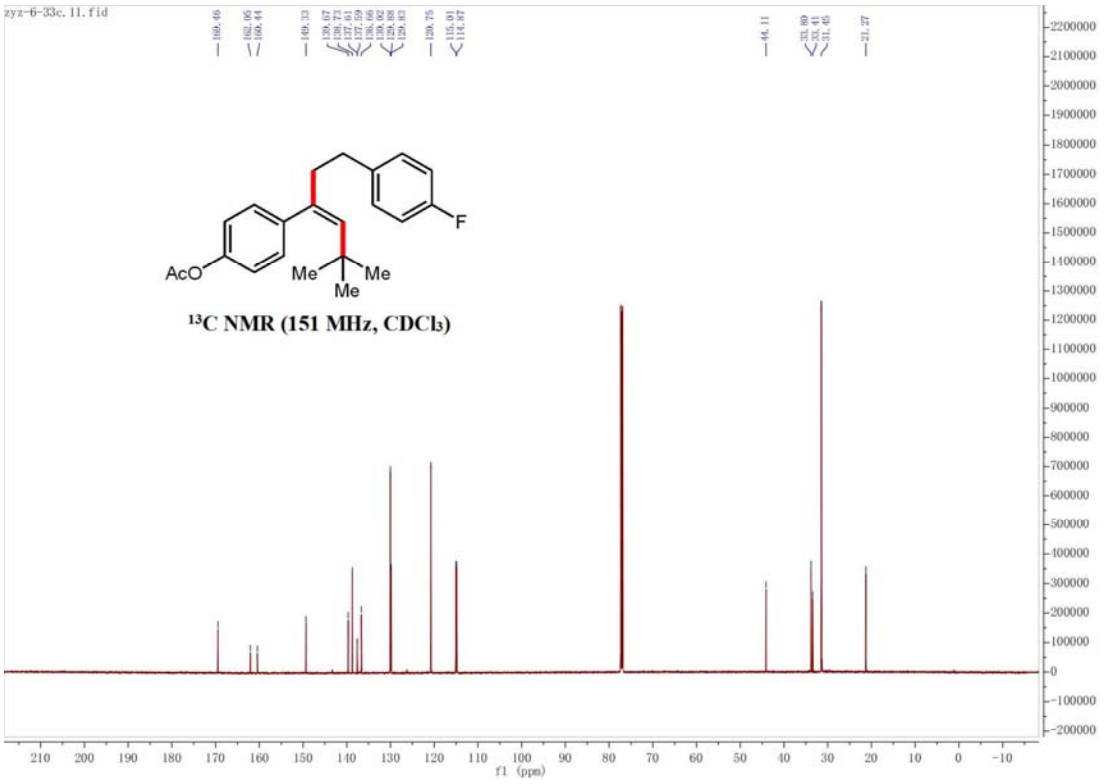


^{13}C NMR (101 MHz, $CDCl_3$)

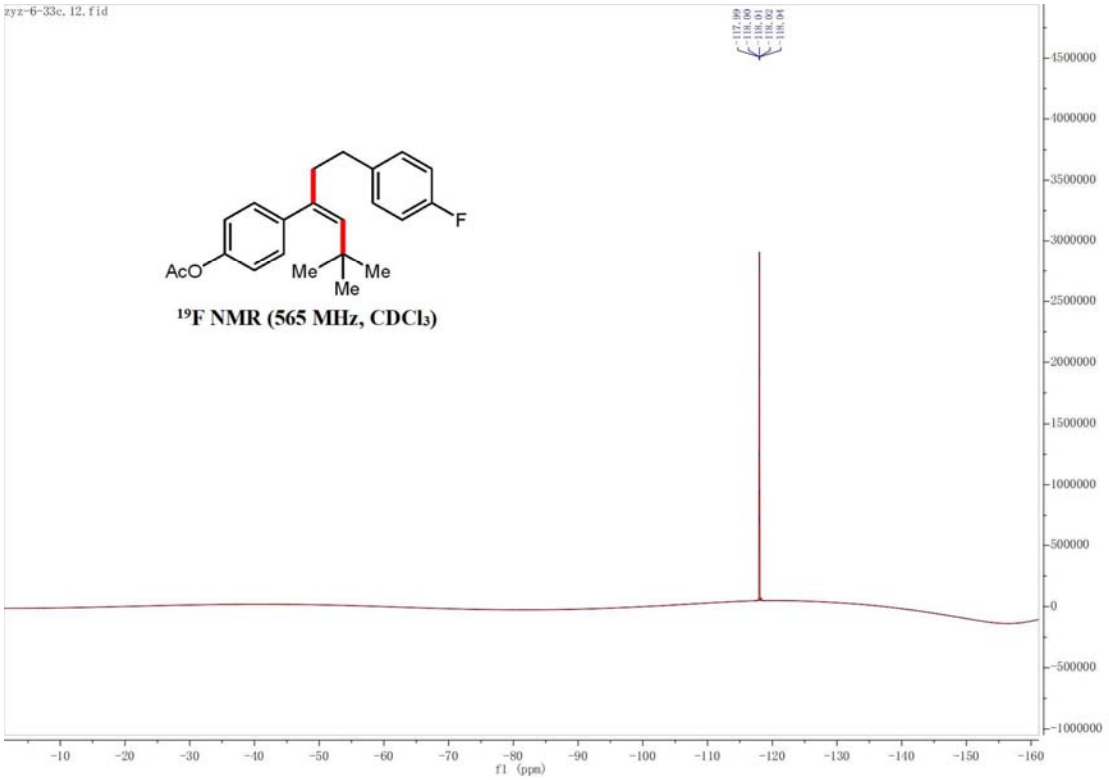
(*Z*)-4-(1-(4-Fluorophenyl)-5,5-dimethylhex-3-en-3-yl)phenyl acetate (5g)



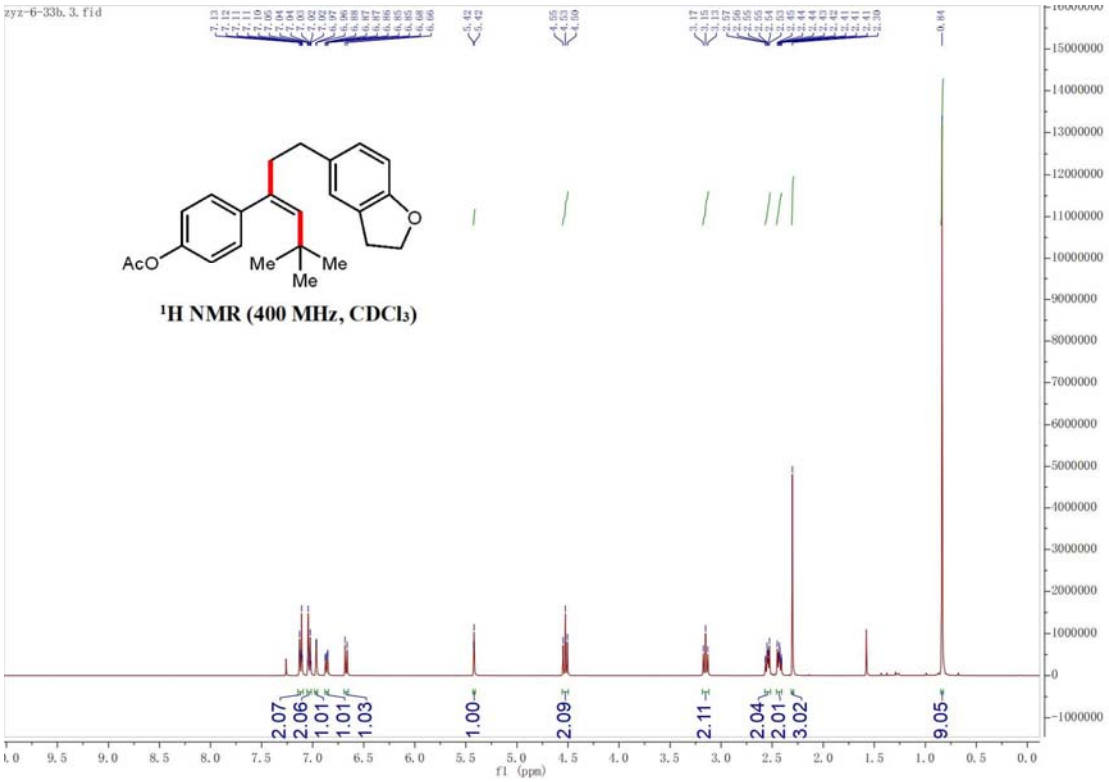
^{1}H NMR (600 MHz, $CDCl_3$)

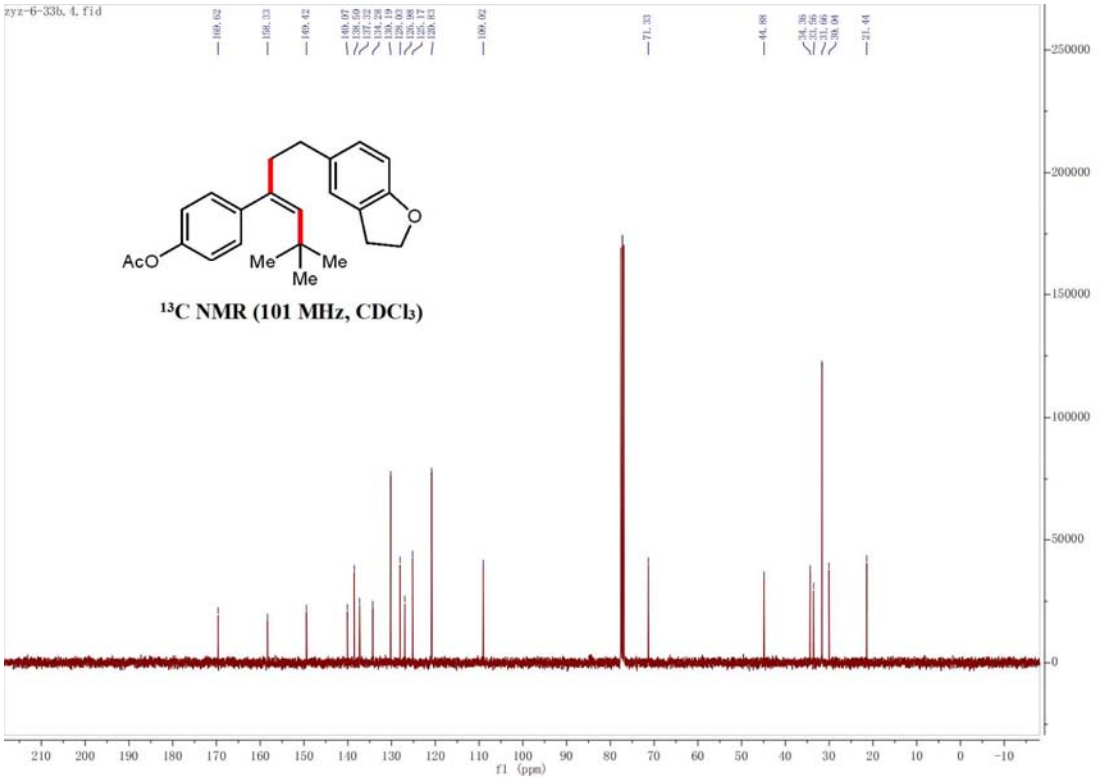


^{13}C NMR (151 MHz, $CDCl_3$)

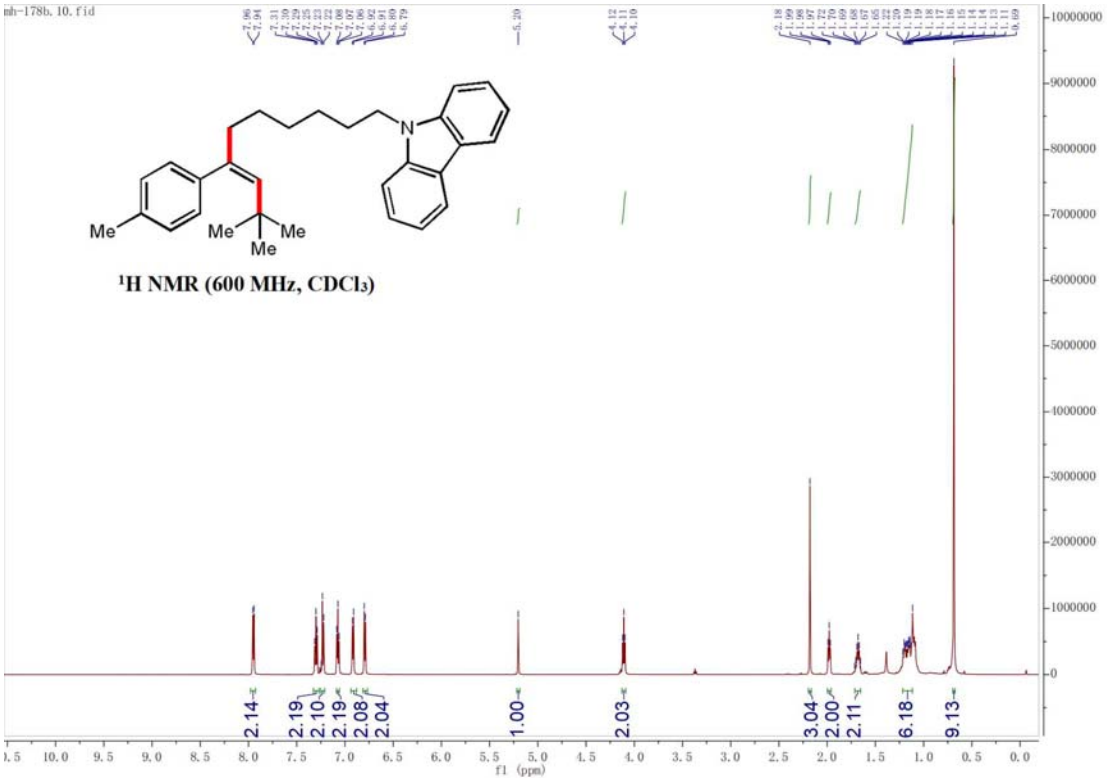


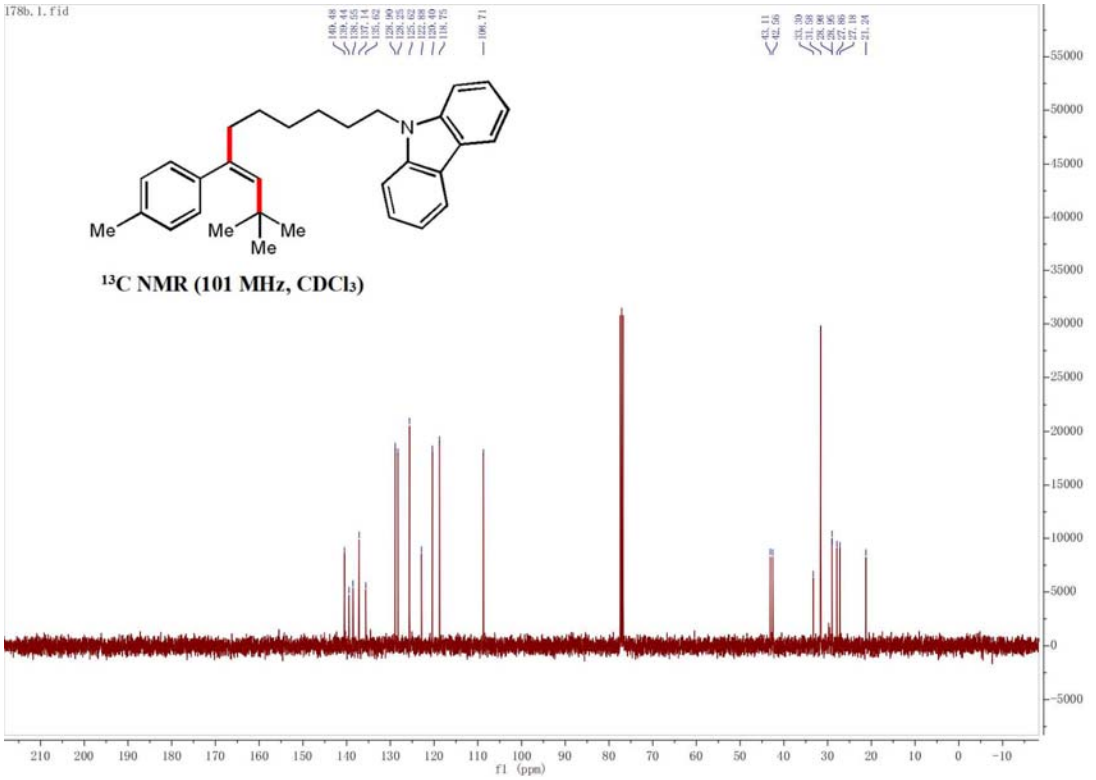
(*Z*)-4-(1-(2,3-Dihydrobenzofuran-5-yl)-5,5-dimethylhex-3-en-3-yl)phenyl acetate (5h)



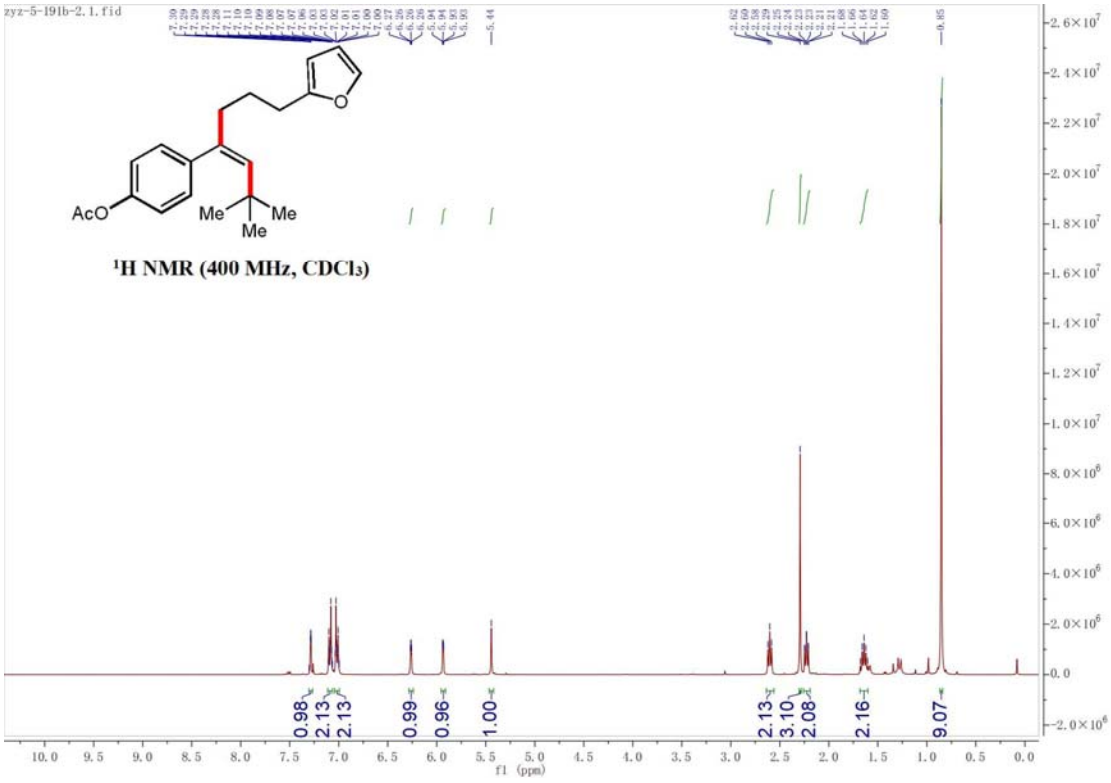


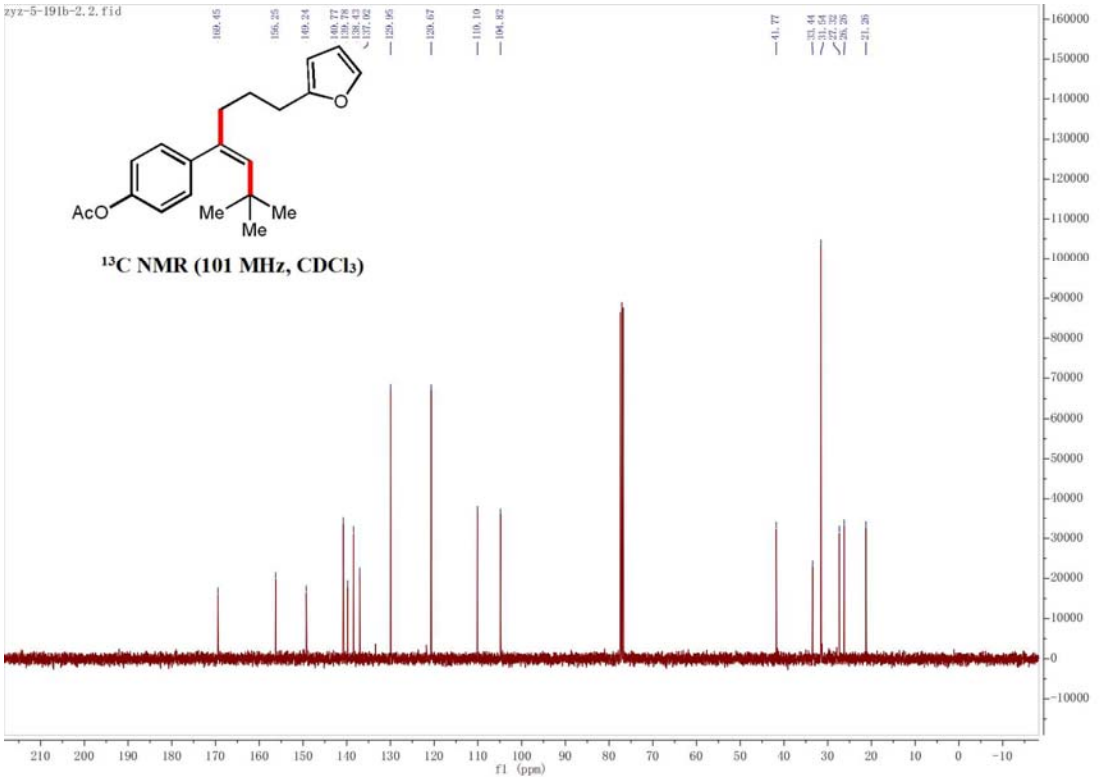
(*Z*)-9-(9,9-Dimethyl-7-(*p*-tolyl)dec-7-en-1-yl)-9H-carbazole (5i)



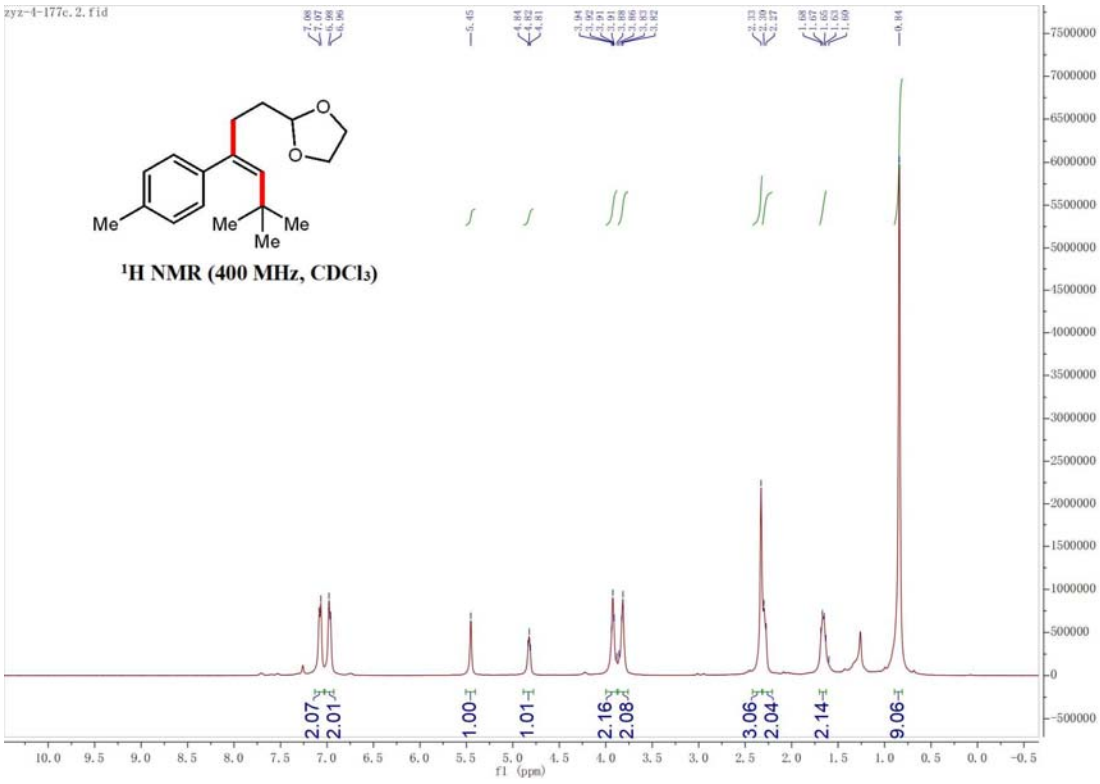


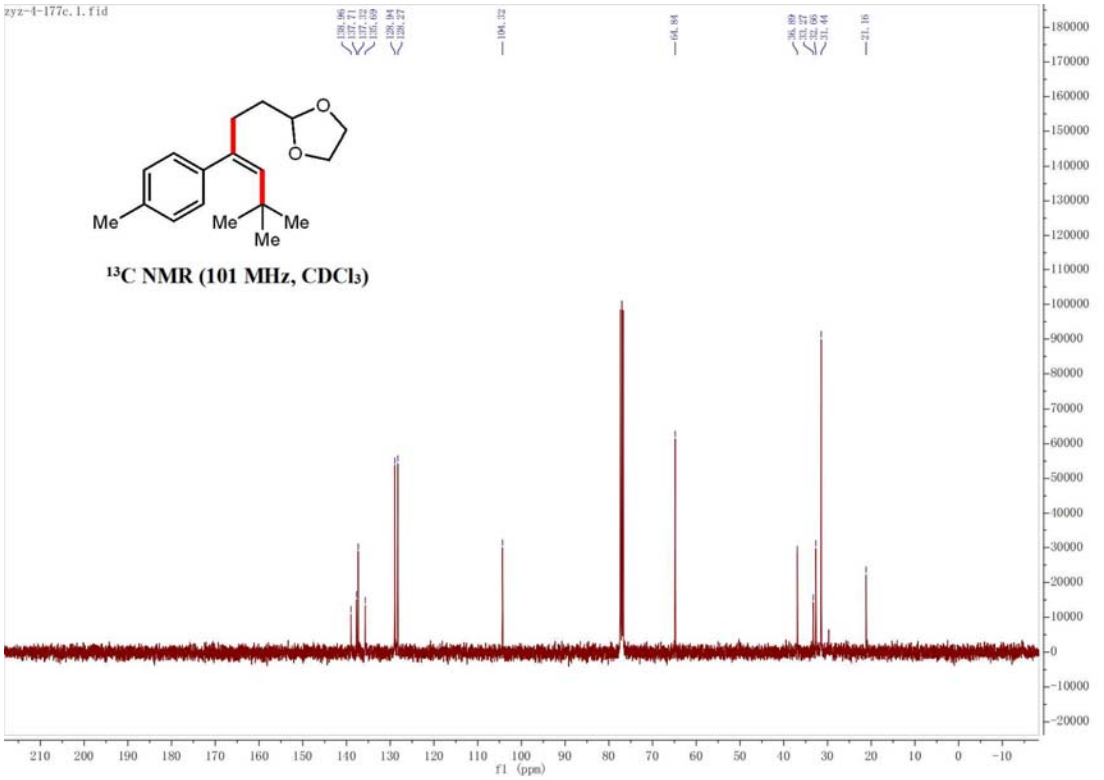
(*Z*)-4-(7-(Furan-2-yl)-2,2-dimethylhept-3-en-4-yl)phenyl acetate (5j)



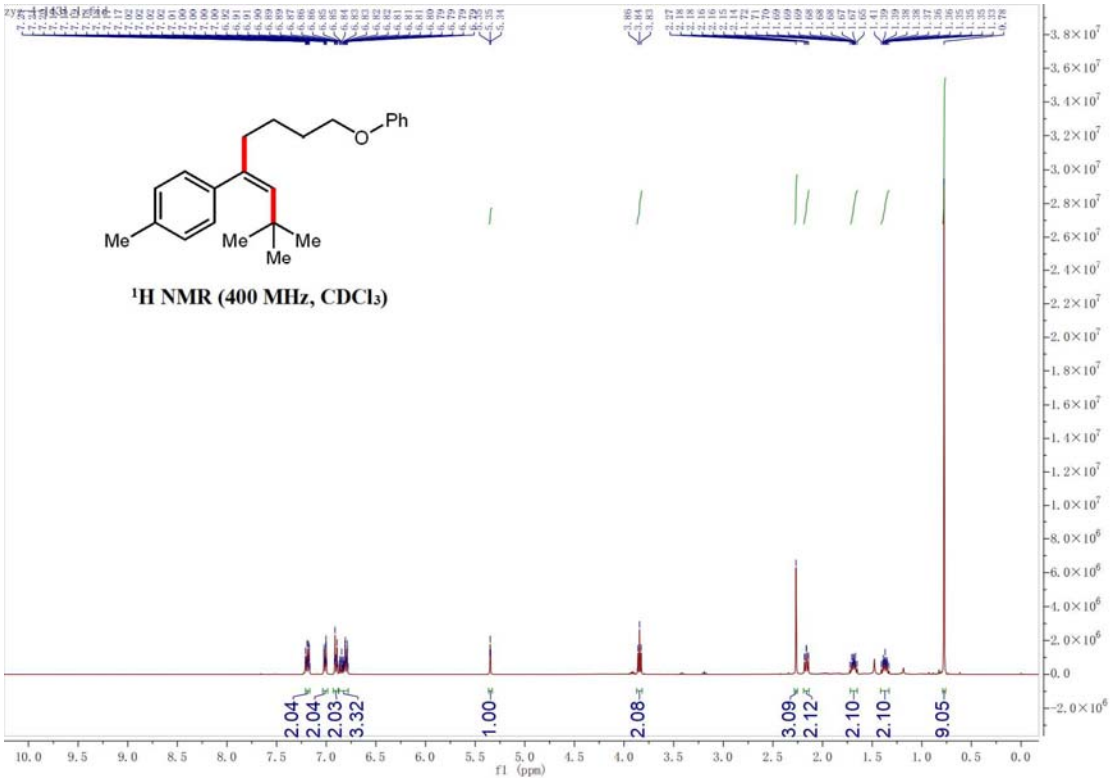


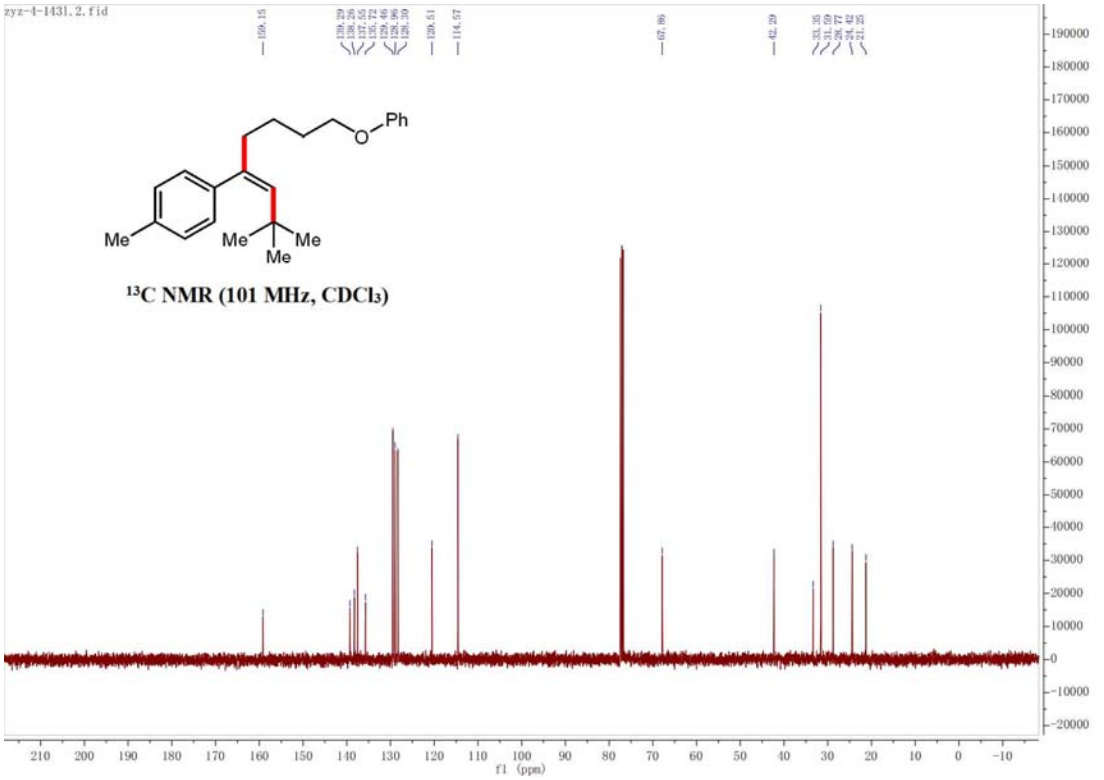
(*Z*)-2-(5,5-Dimethyl-3-(*p*-tolyl)hex-3-en-1-yl)-1,3-dioxolane (5k)



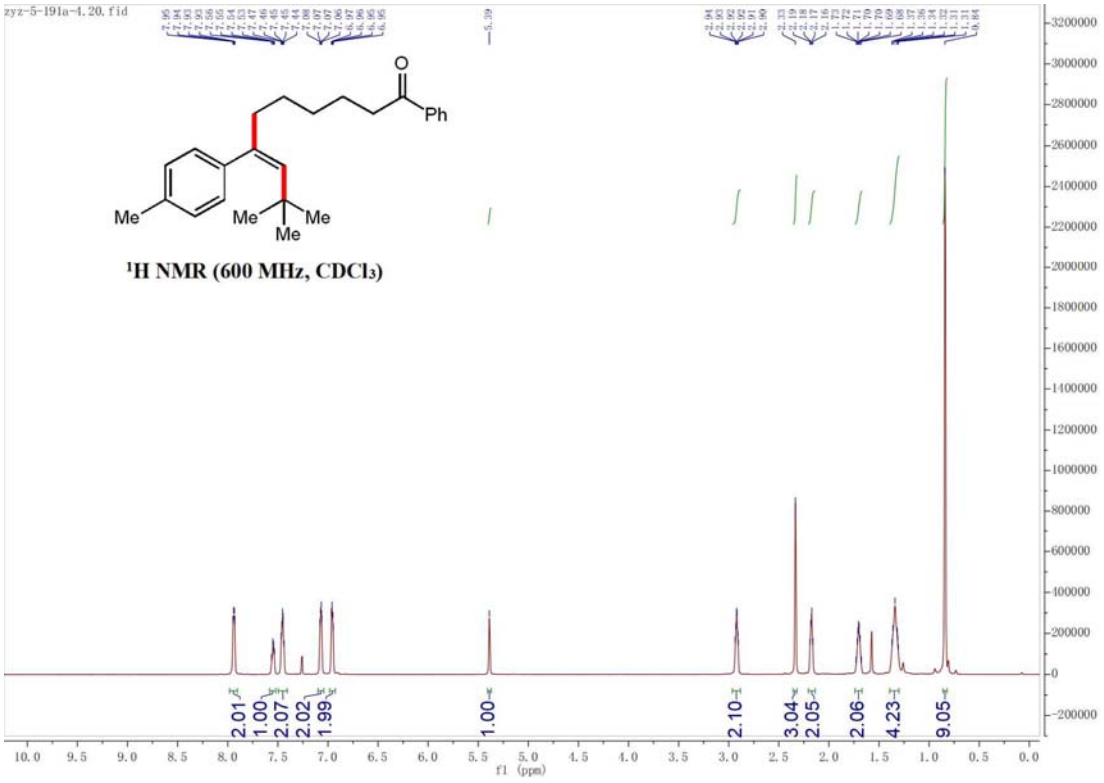


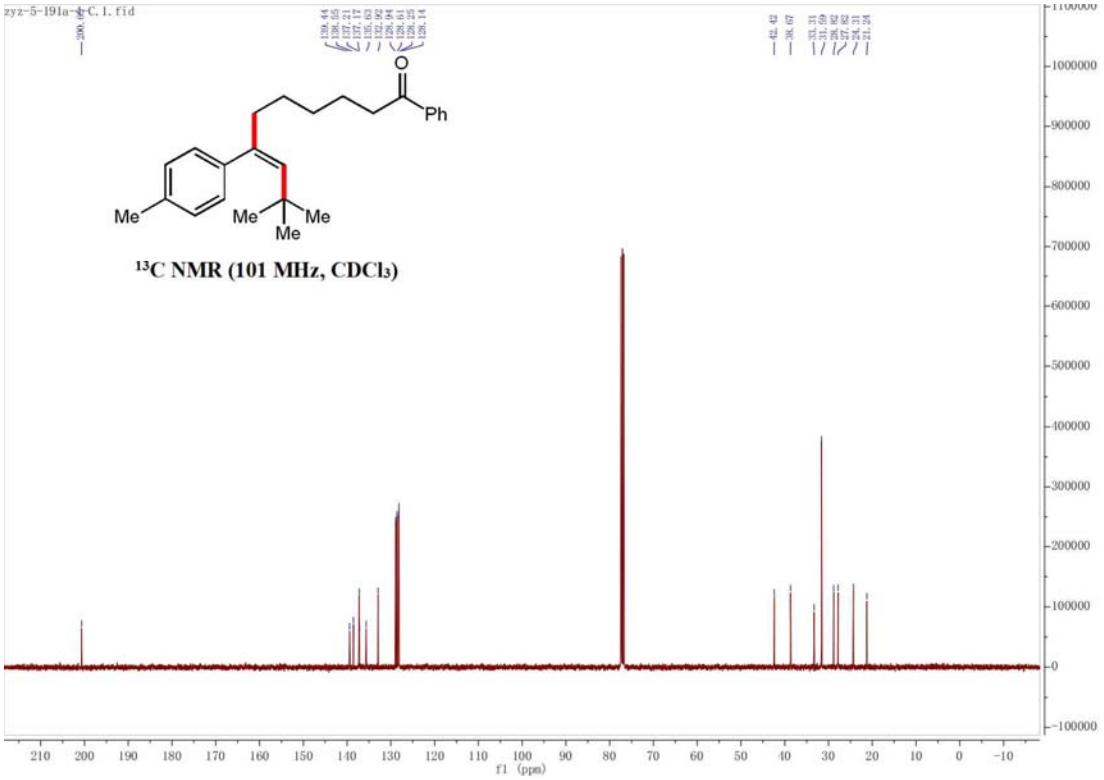
(*Z*)-1-(2,2-Dimethyl-8-phenoxyoct-3-en-4-yl)-4-methylbenzene (5l)



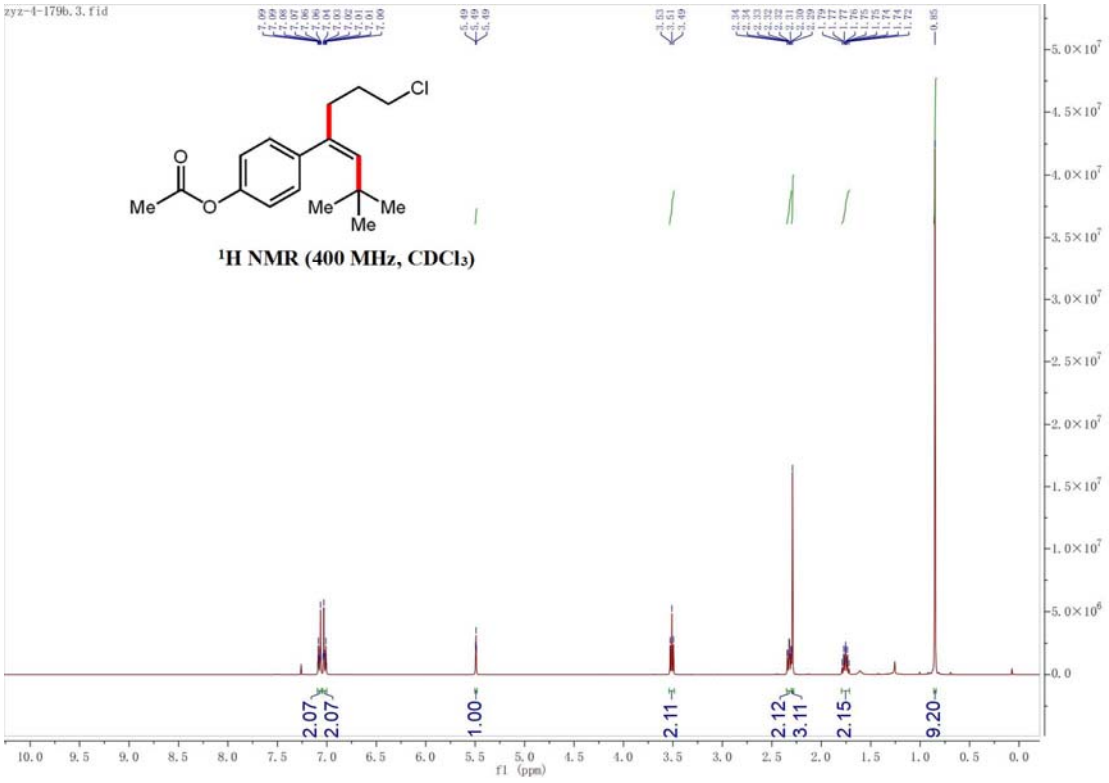


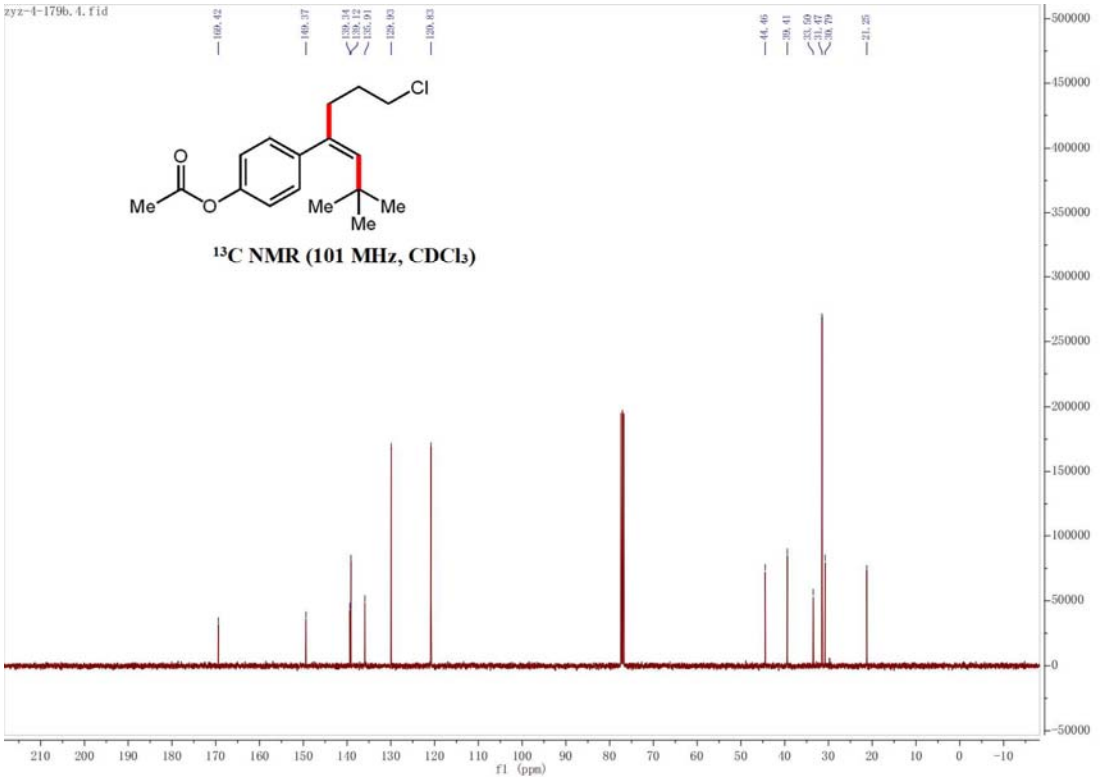
(*Z*)-9,9-Dimethyl-1-phenyl-7-(*p*-tolyl)dec-7-en-1-one (5m)



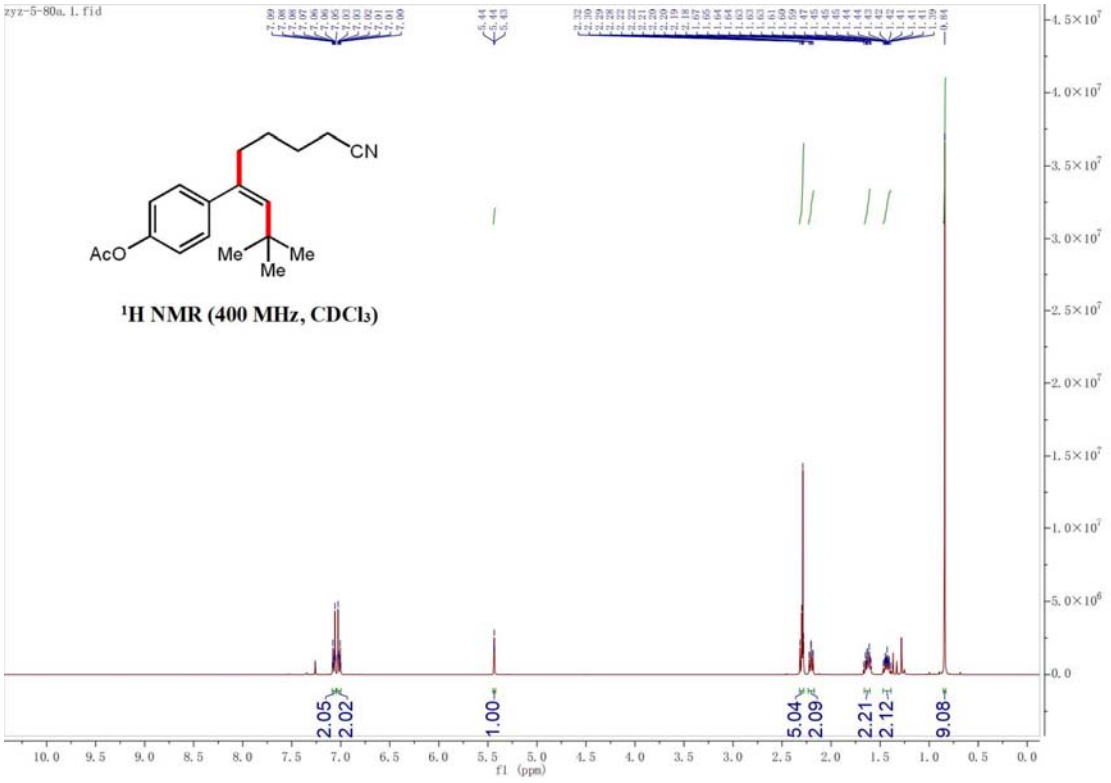


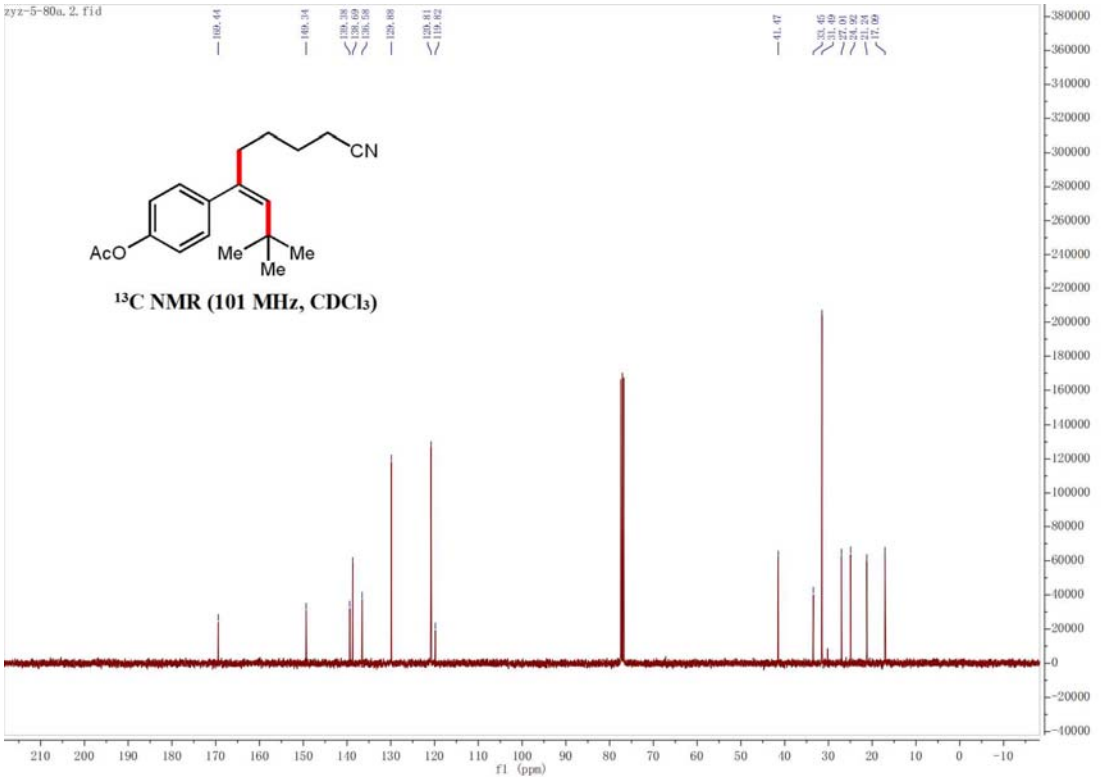
(*Z*)-4-(7-Chloro-2,2-dimethylhept-3-en-4-yl)phenyl acetate (5n)



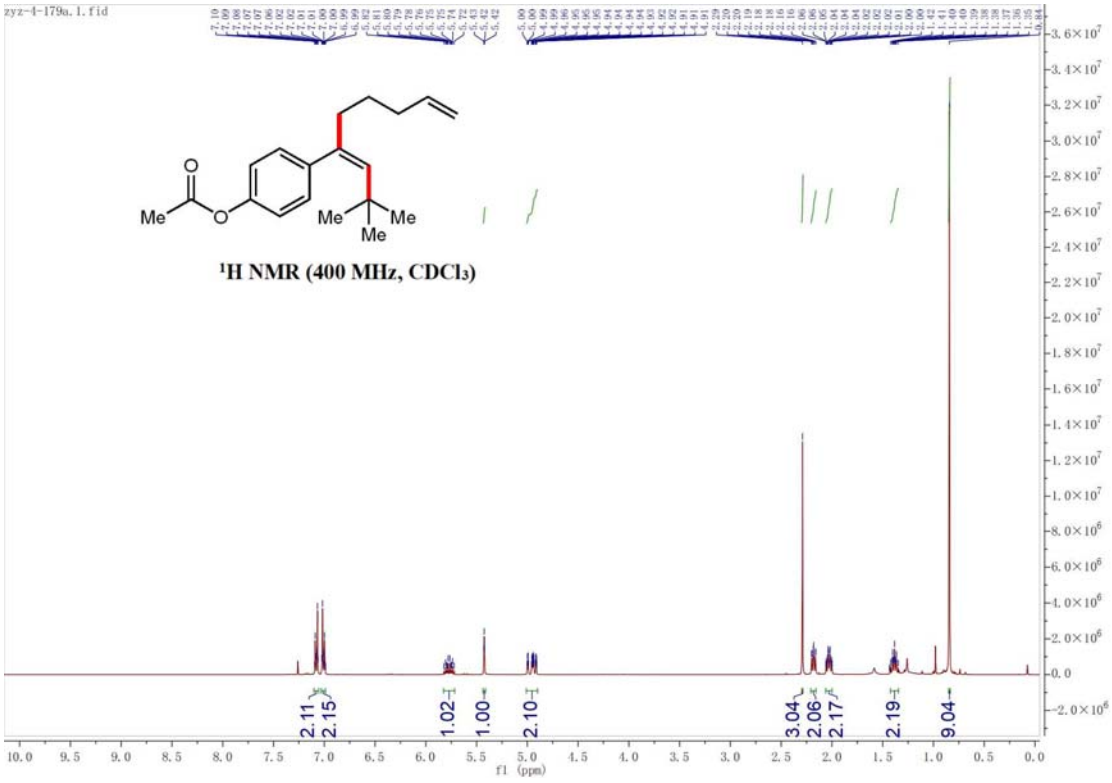


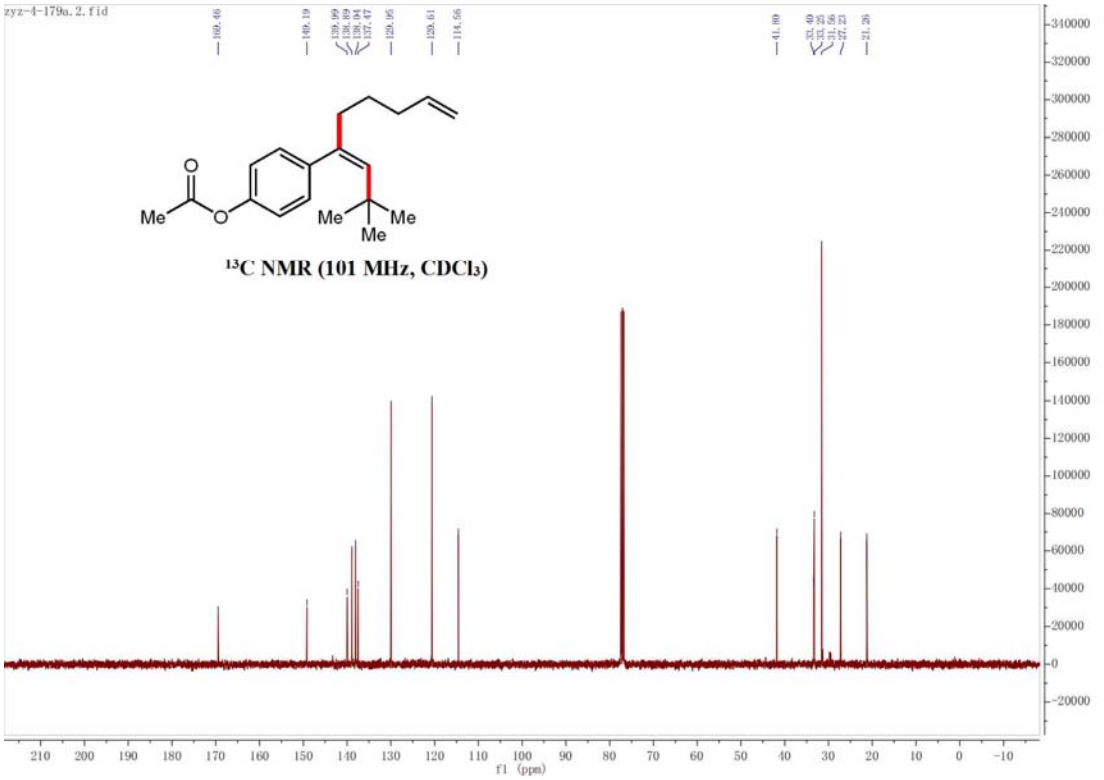
(*Z*)-4-(8-Cyano-2,2-dimethyloct-3-en-4-yl)phenyl acetate (5o)



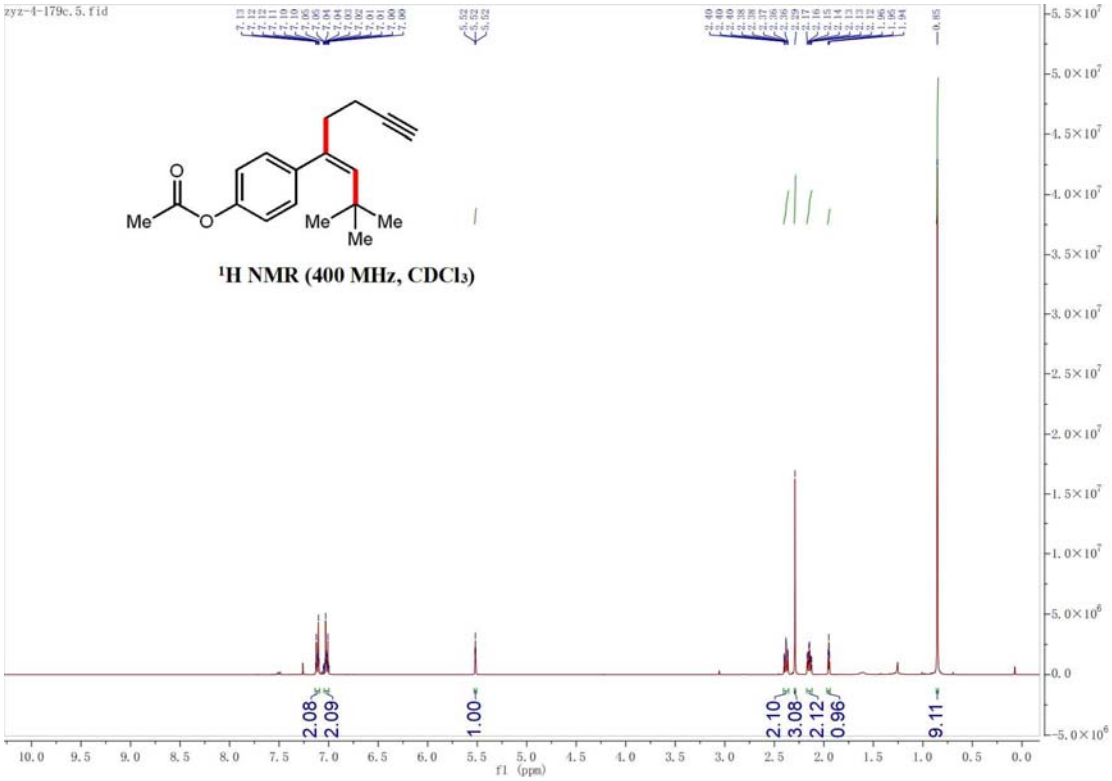


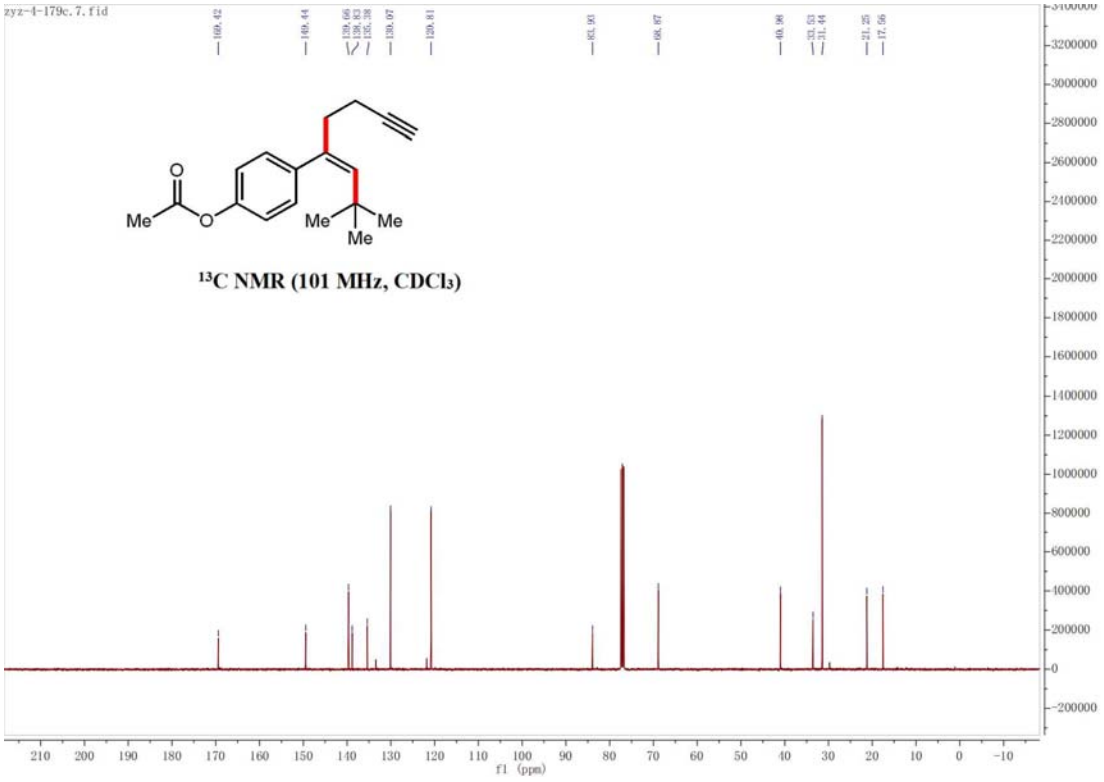
(*Z*)-4-(2,2-Dimethylnona-3,8-dien-4-yl)phenyl acetate (5p)



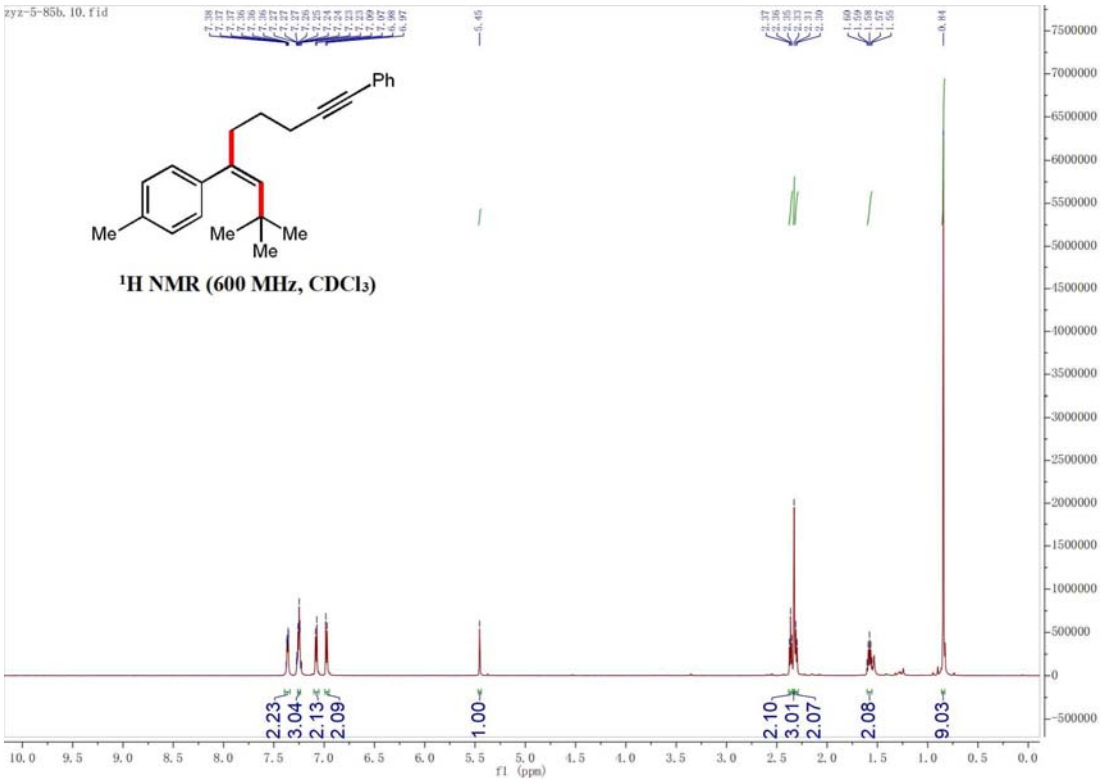


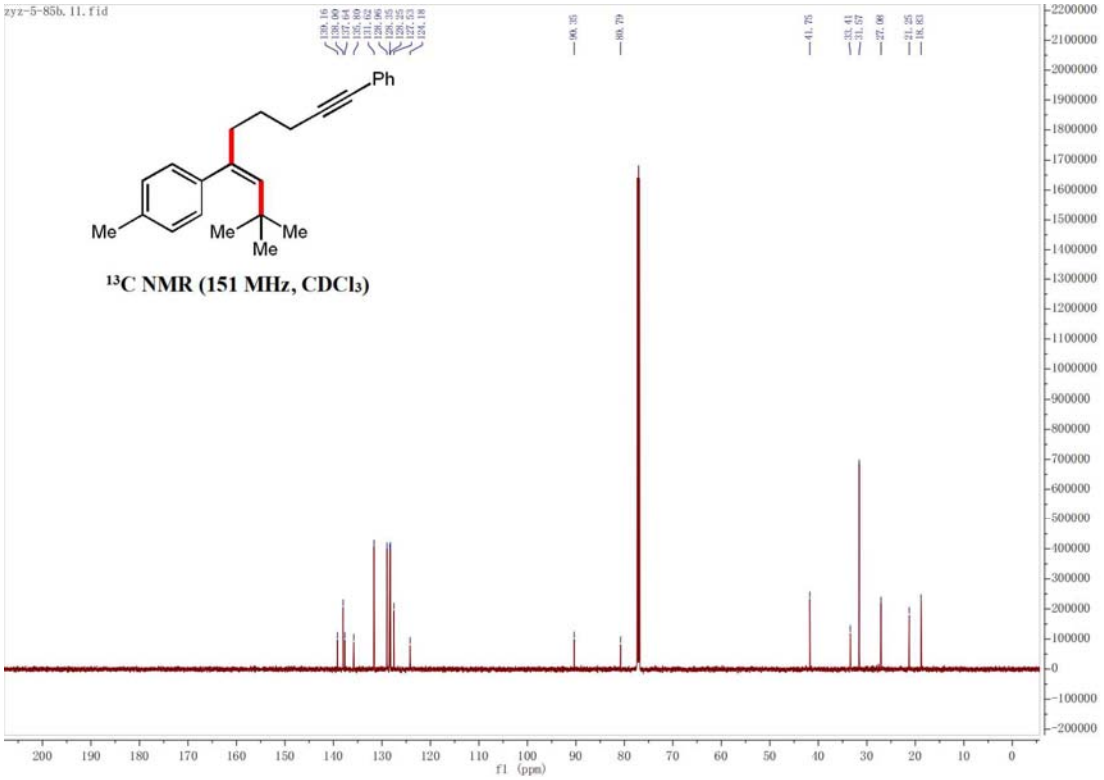
(*Z*)-4-(2,2-Dimethyloct-3-en-7-yn-4-yl)phenyl acetate (5q)



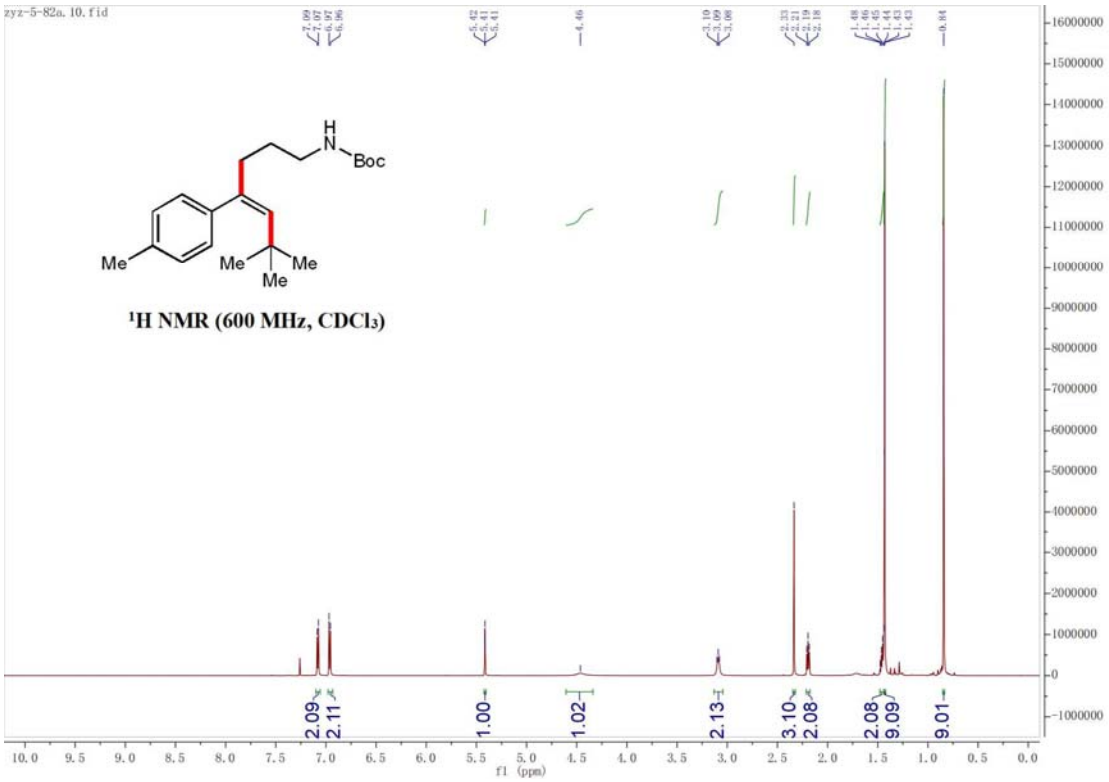


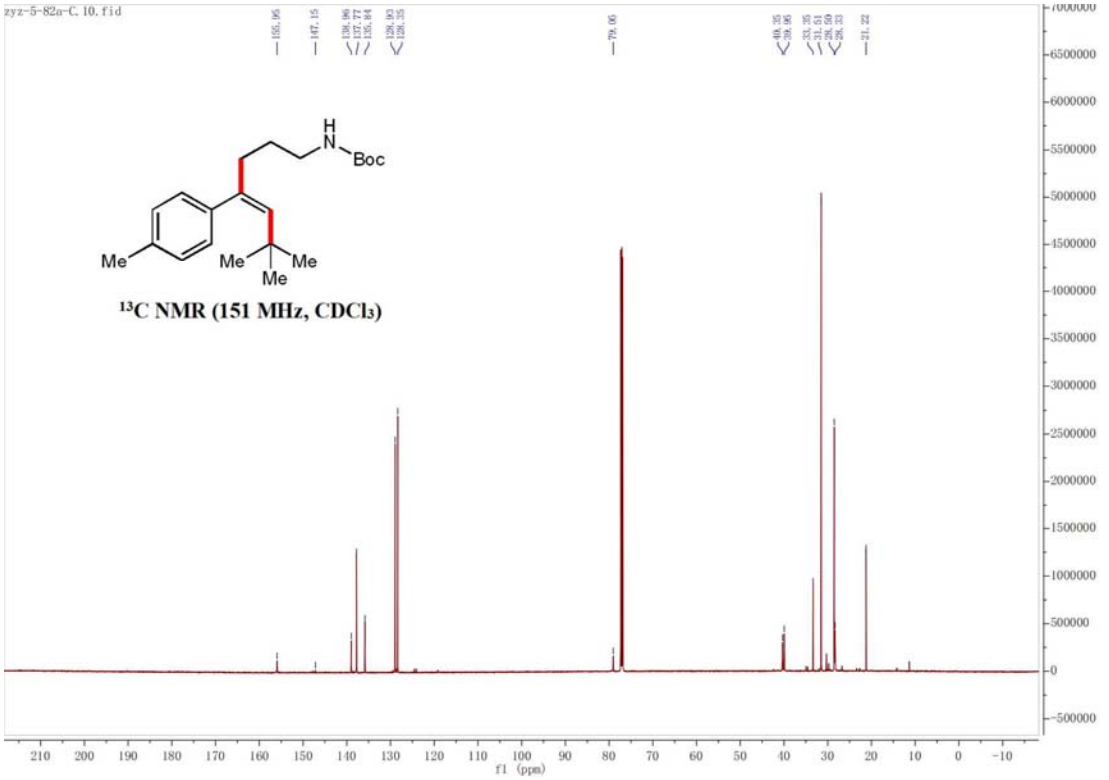
(*Z*)-1-(2,2-Dimethyl-9-phenylnon-3-en-8-yn-4-yl)-4-methylbenzene (5r)



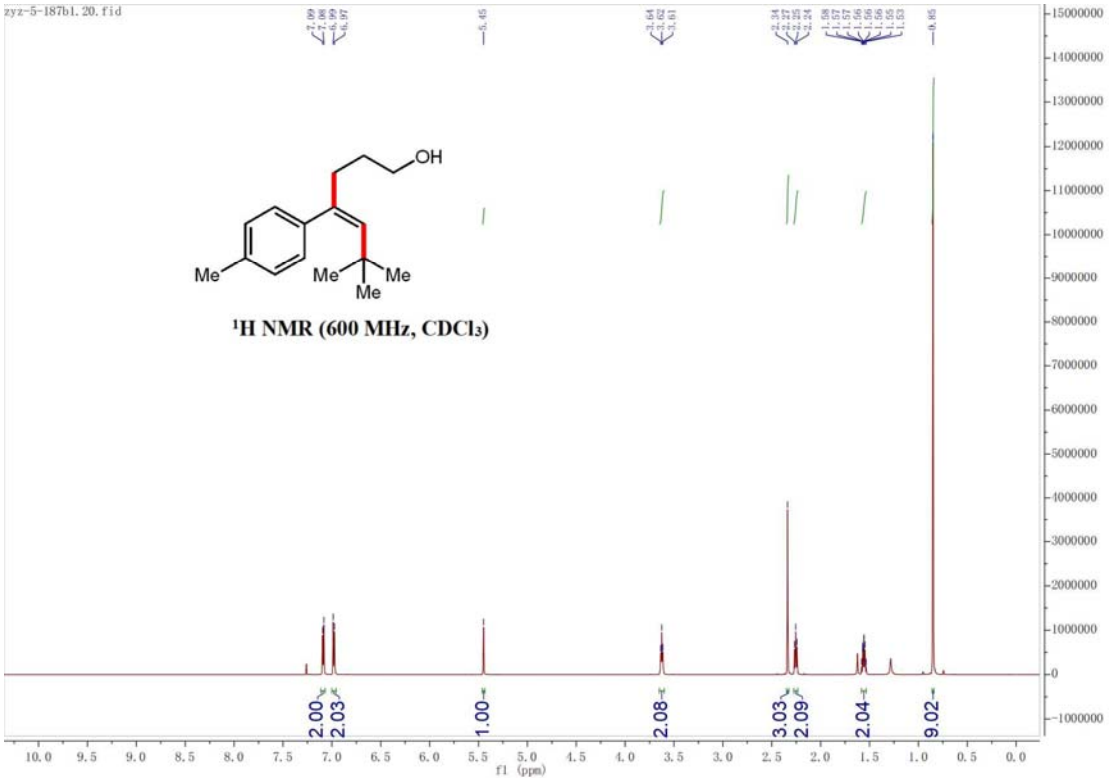


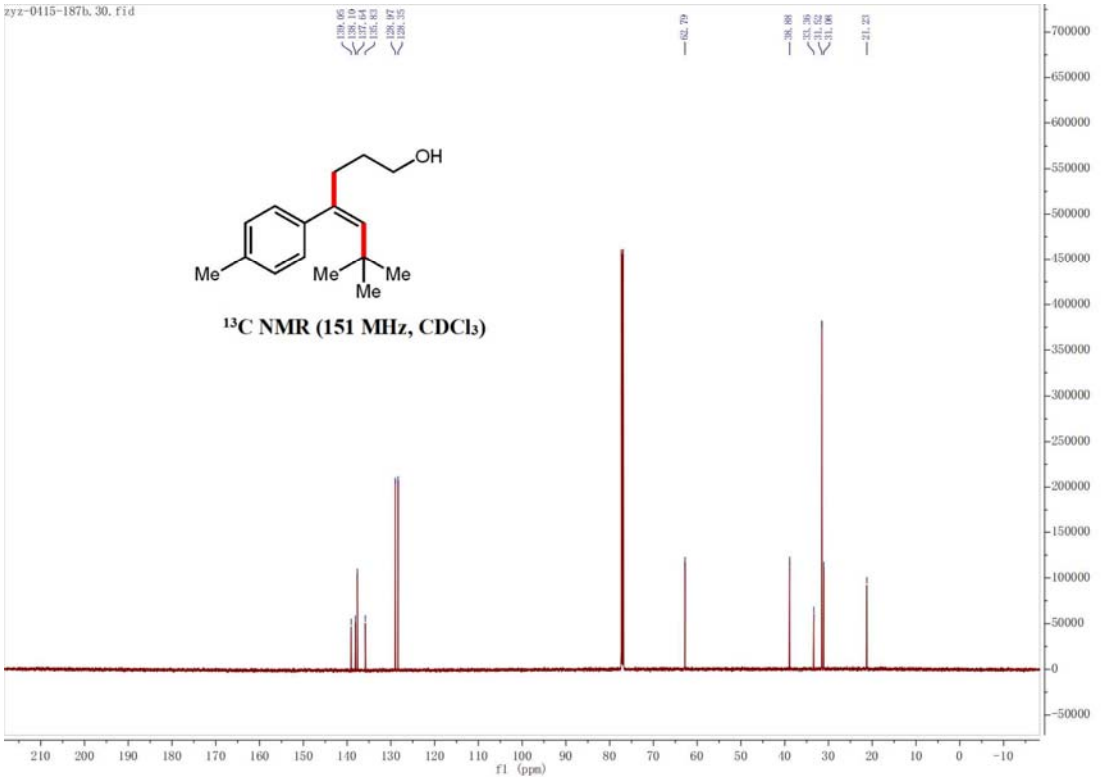
***tert*-Butyl (*Z*)-(6,6-dimethyl-4-(p-tolyl)hept-4-en-1-yl)carbamate (5s)**



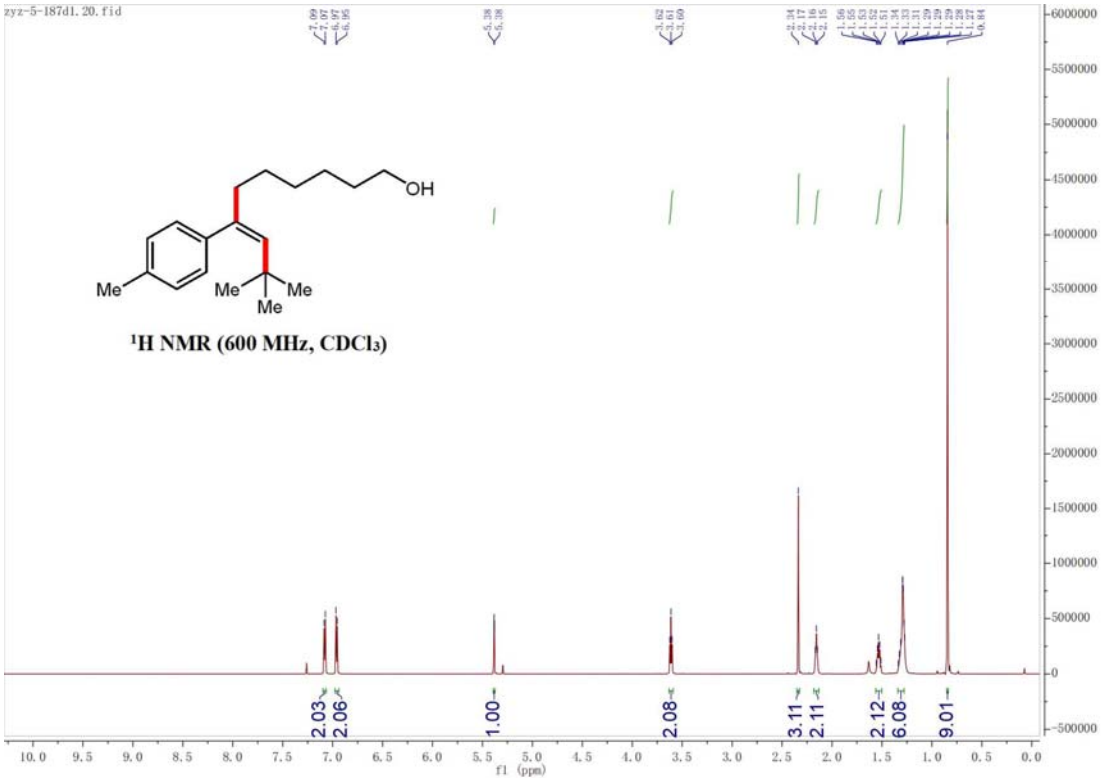


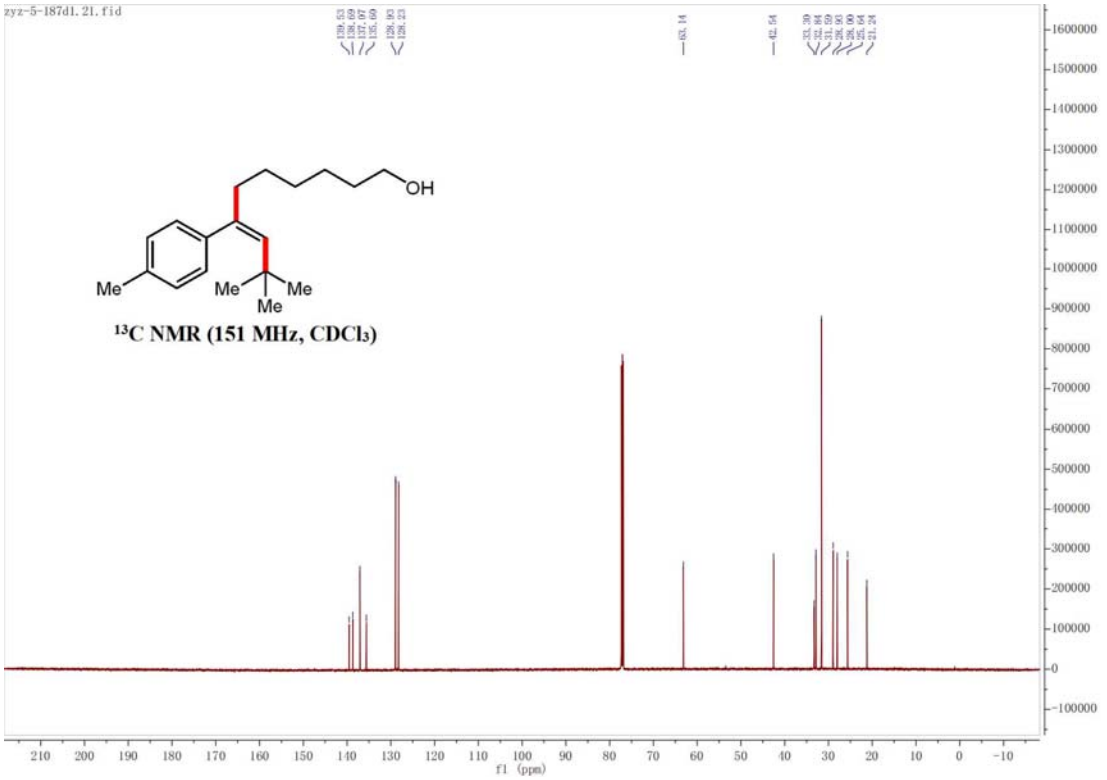
(*Z*)-6,6-Dimethyl-4-(*p*-tolyl)hept-4-en-1-ol (5t)



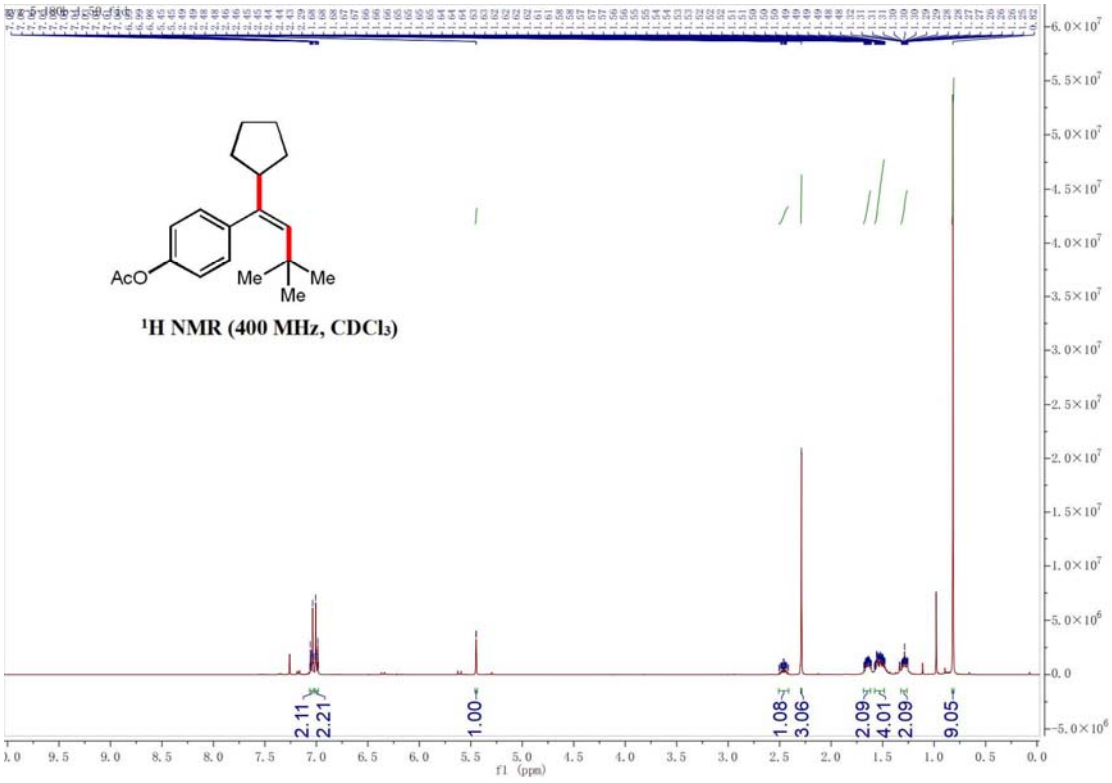


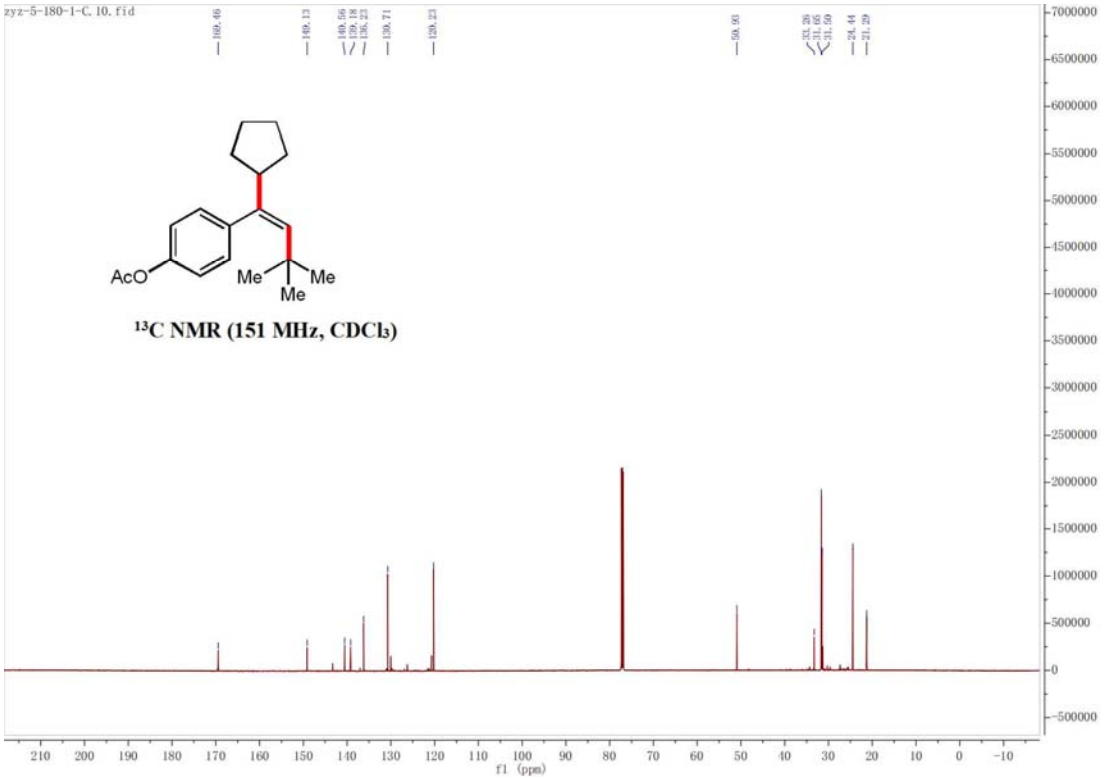
(*Z*)-9,9-Dimethyl-7-(*p*-tolyl)dec-7-en-1-ol (5u)



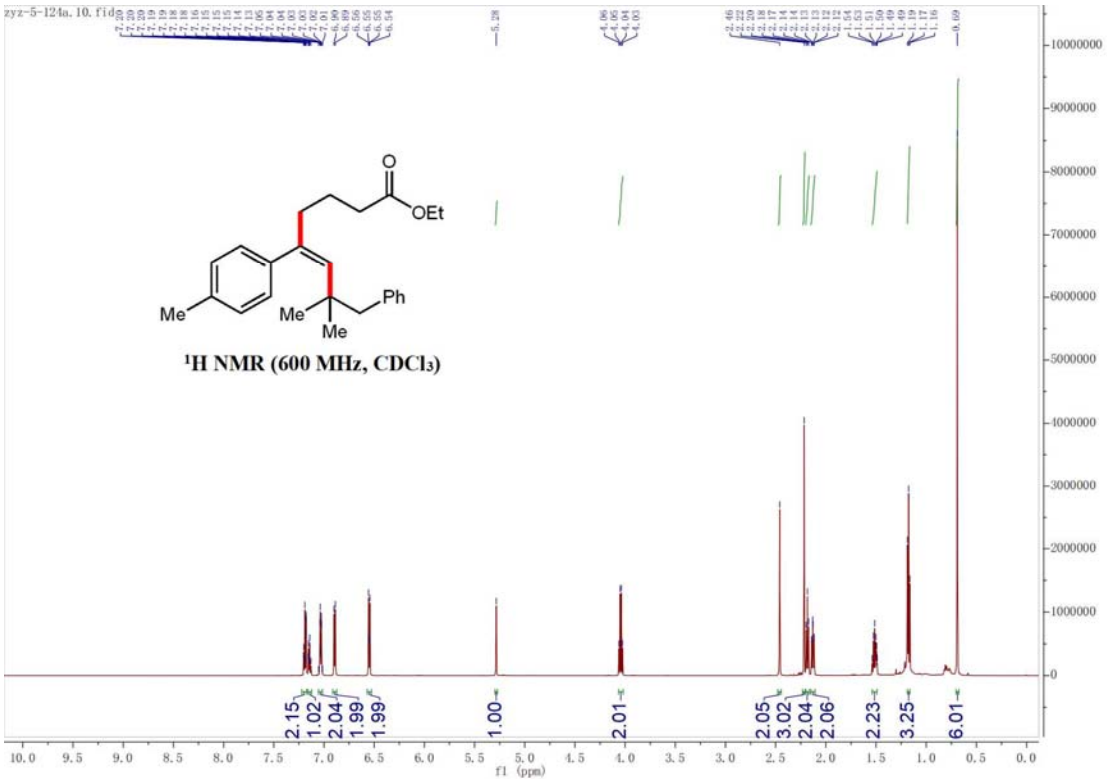


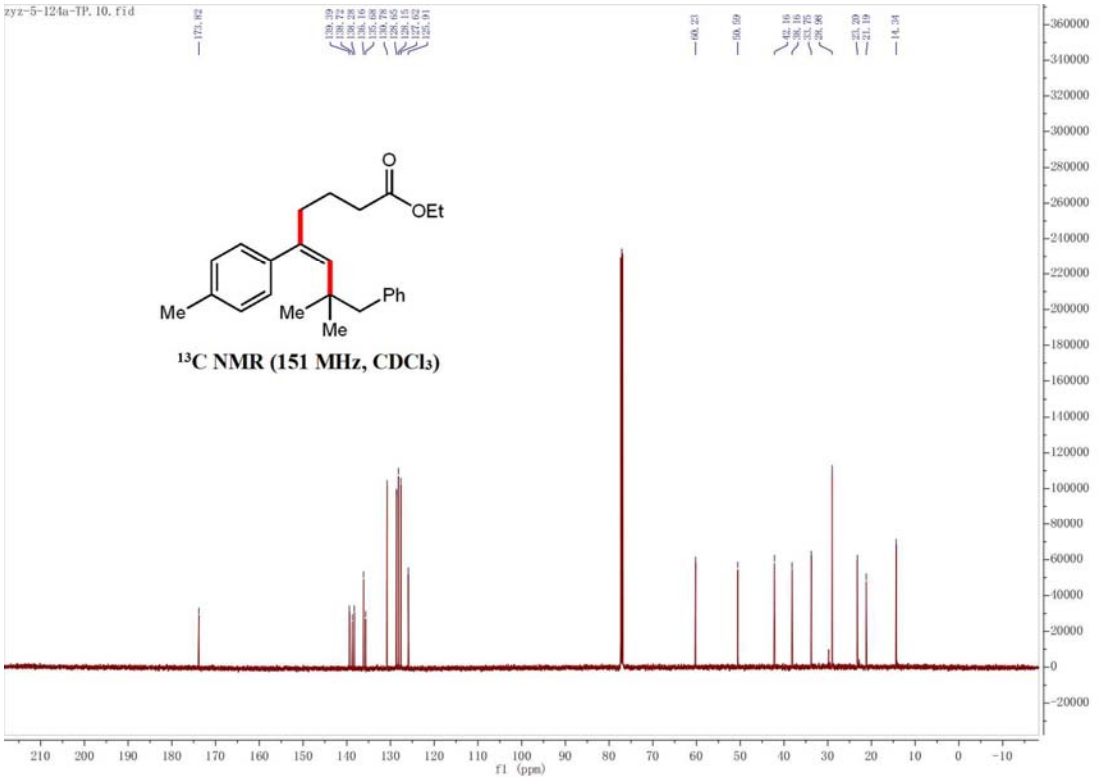
(*Z*)-4-(1-Cyclopentyl-3,3-dimethylbut-1-en-1-yl)phenyl acetate (5v)



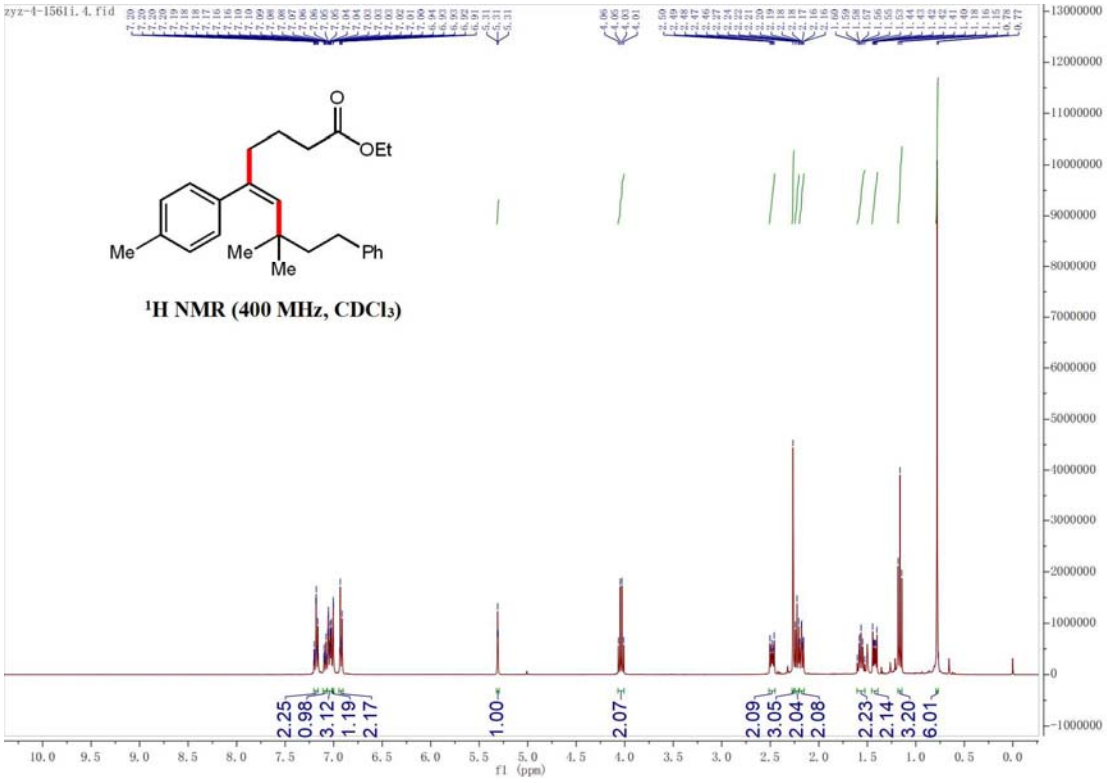


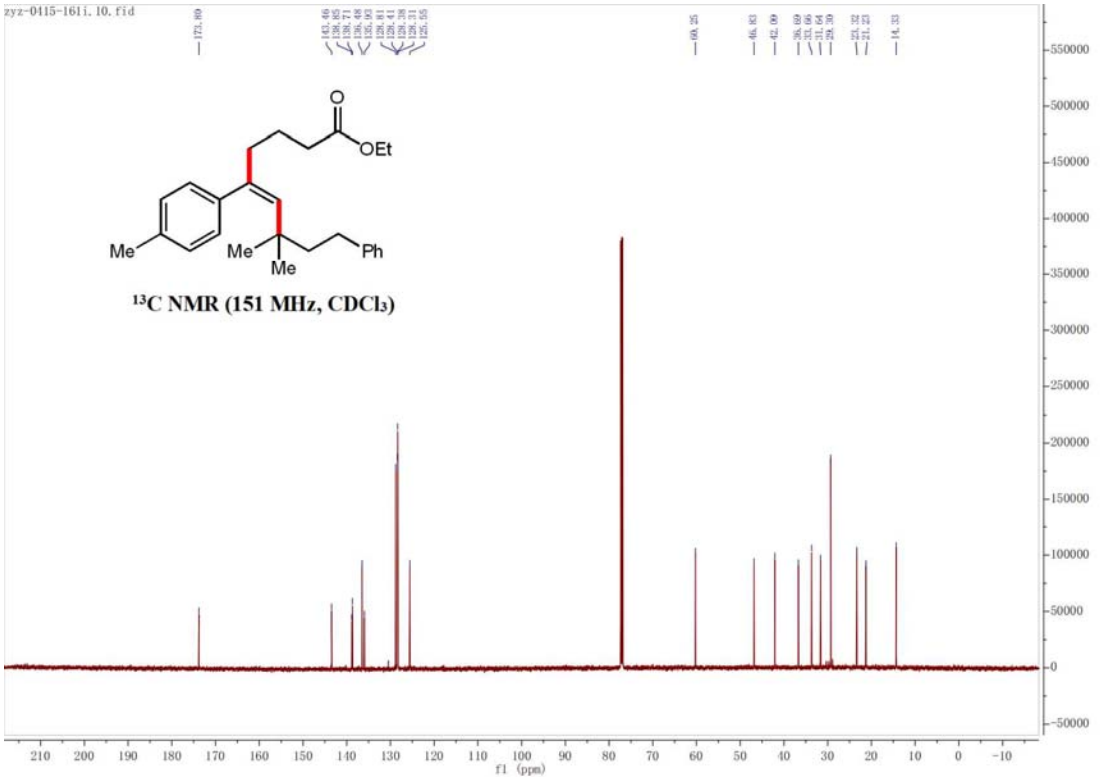
Ethyl (*Z*)-7,7-dimethyl-8-phenyl-5-(*p*-tolyl)oct-5-enoate (6a)



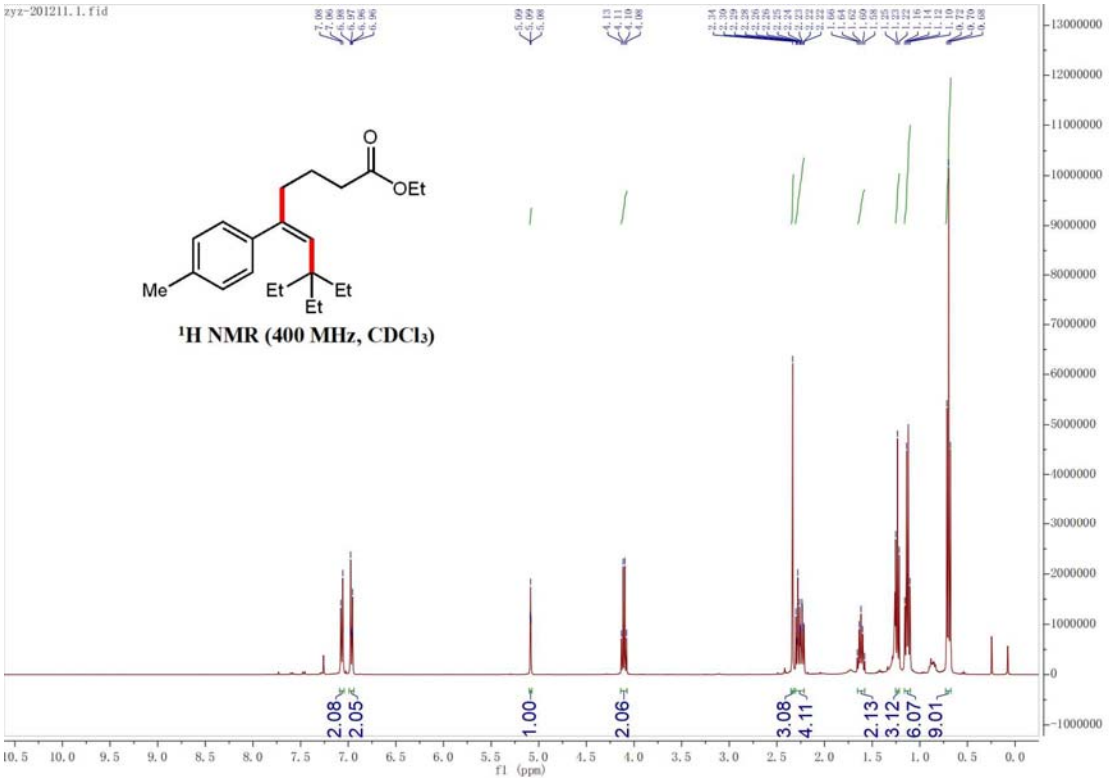


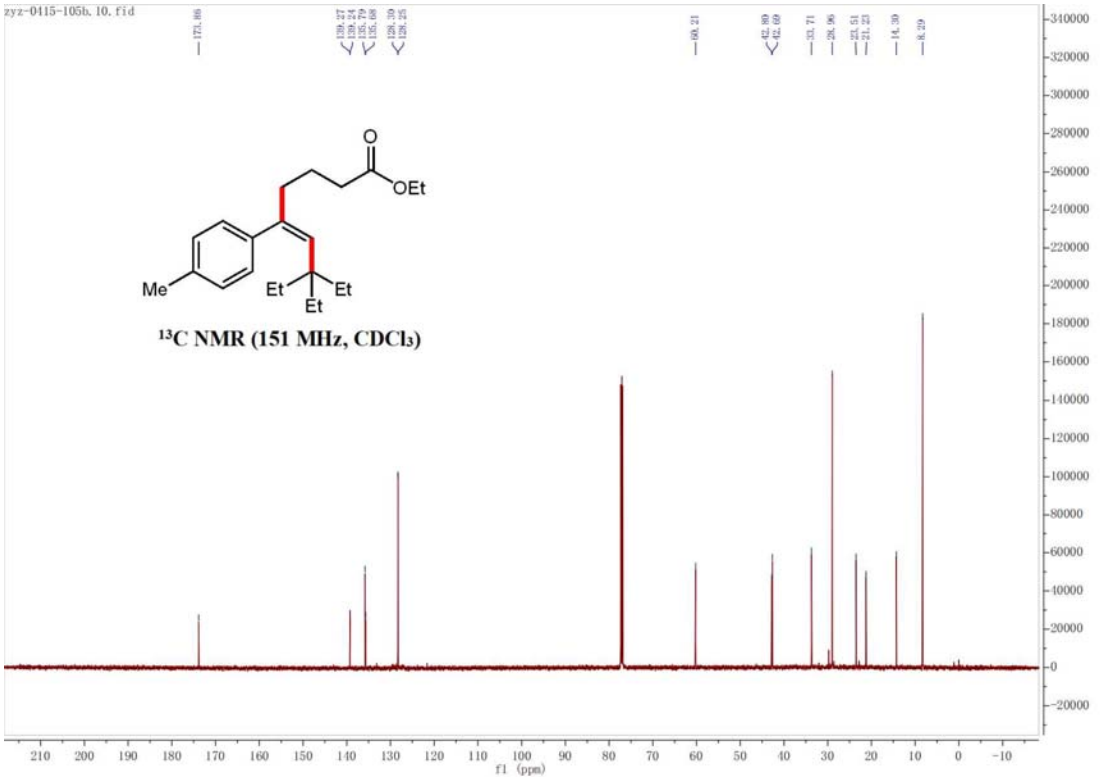
Ethyl (*Z*)-7,7-dimethyl-9-phenyl-5-(*p*-tolyl)non-5-enoate (6b)



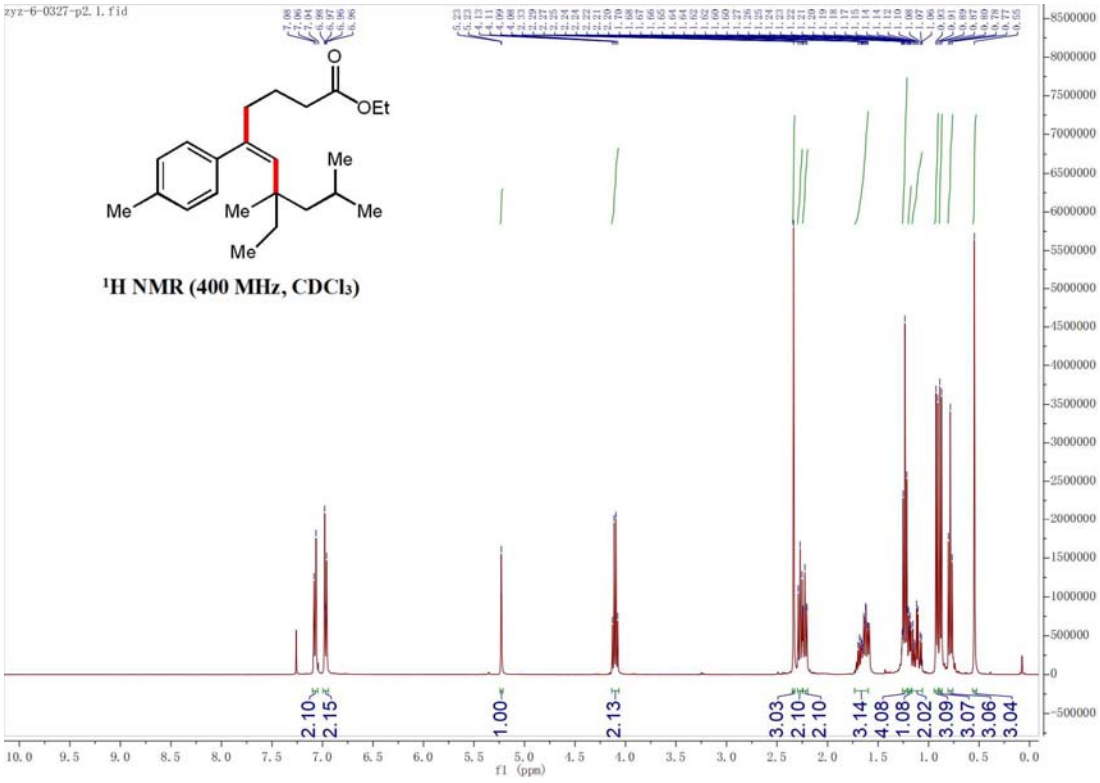


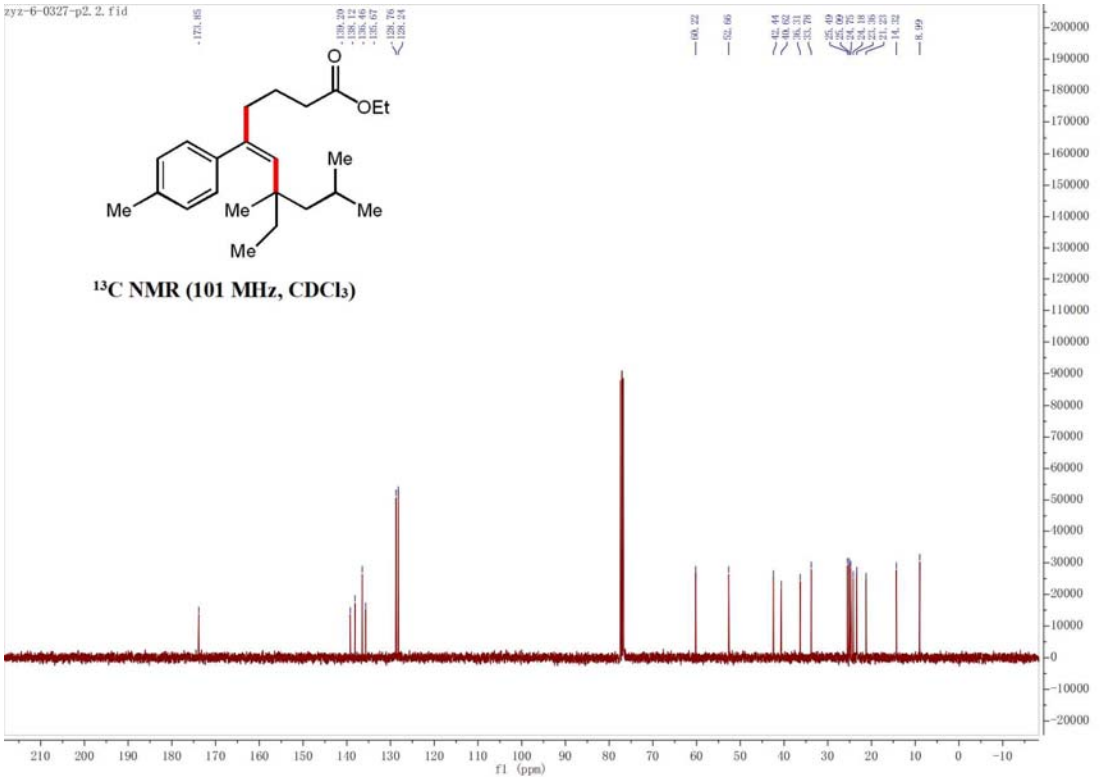
Ethyl (*Z*)-7,7-diethyl-5-(*p*-tolyl)non-5-enoate (6c)



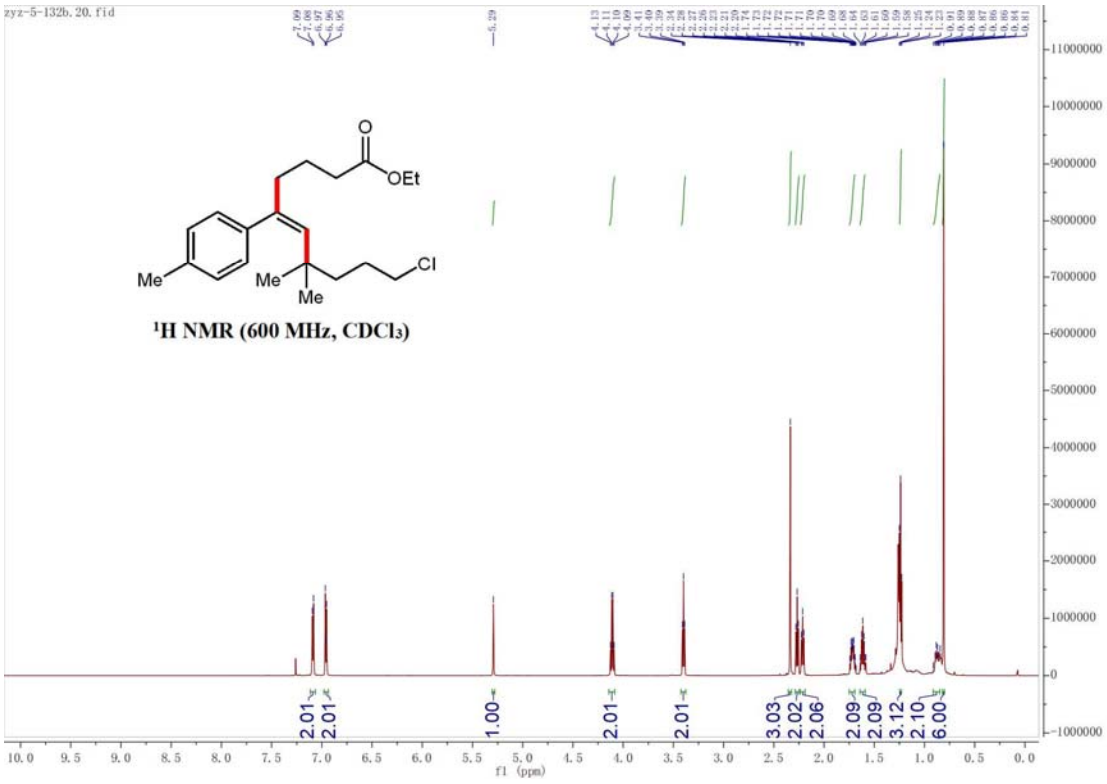


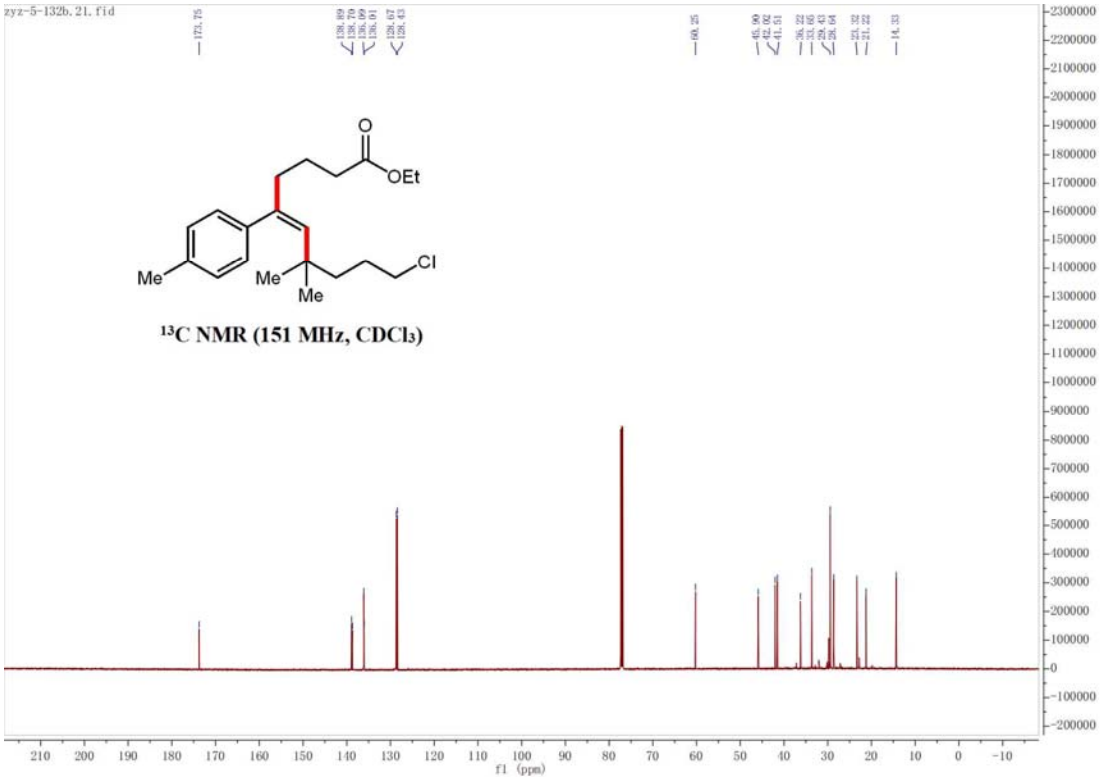
Ethyl (*Z*)-7-ethyl-7,9-dimethyl-5-(*p*-tolyl)dec-5-enoate (6d)



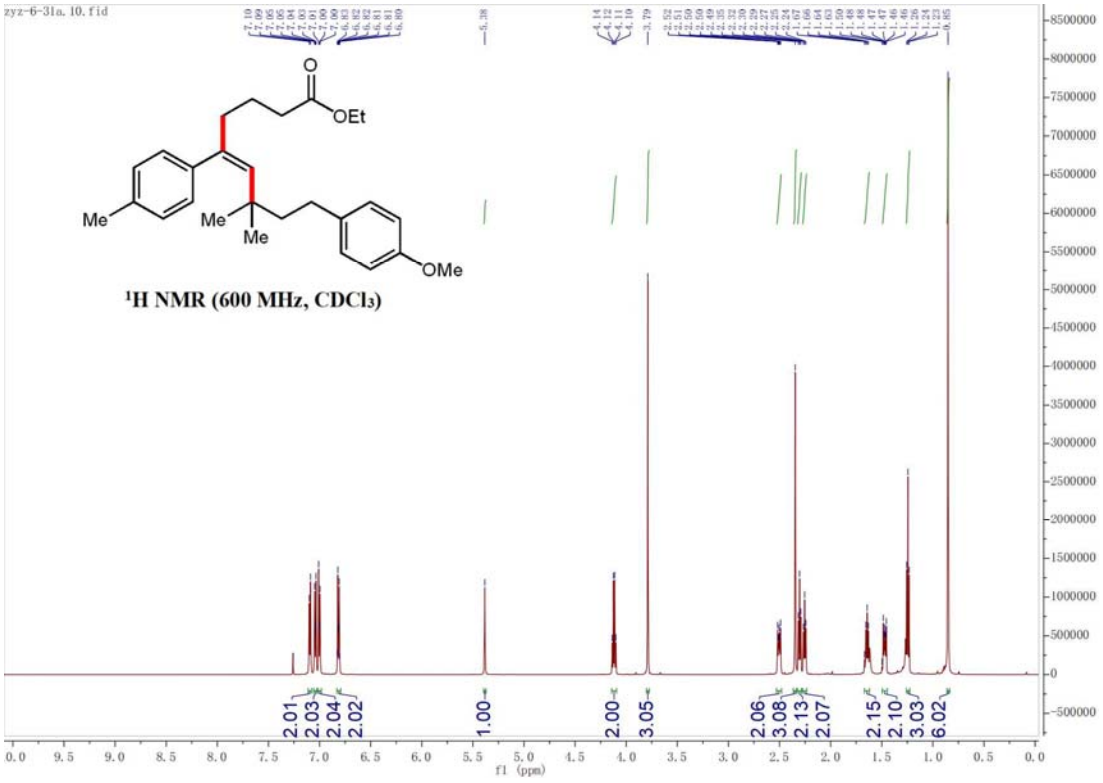


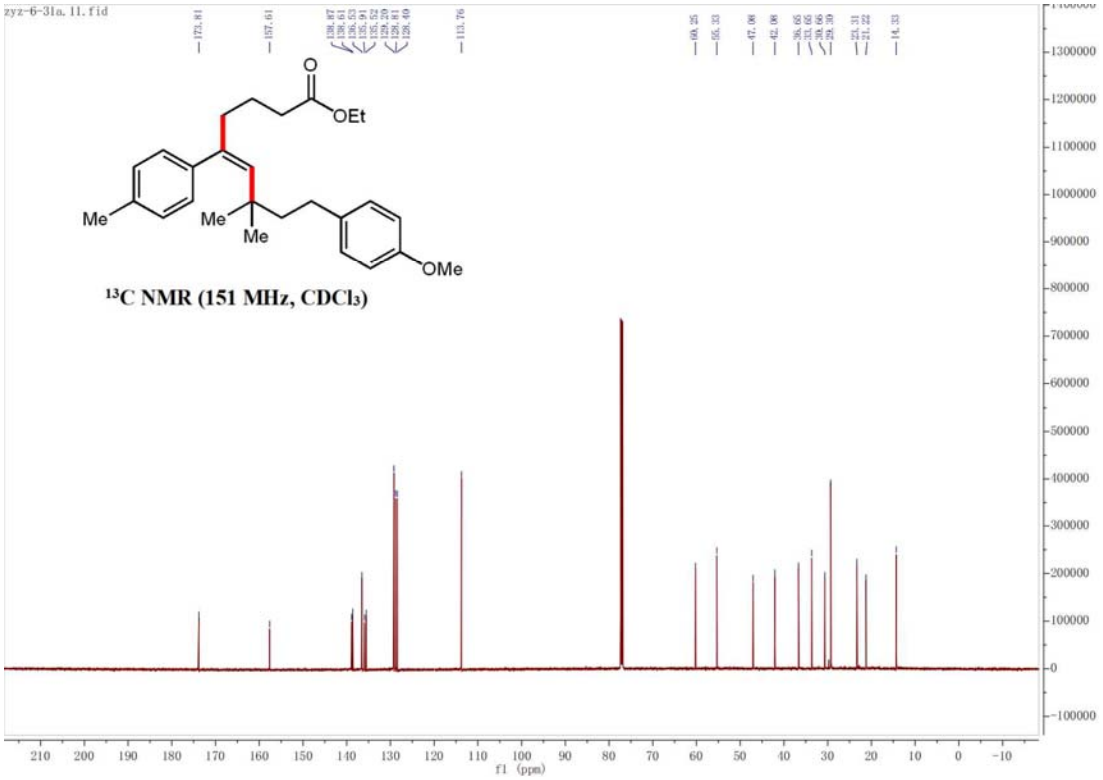
Ethyl (*Z*)-10-chloro-7,7-dimethyl-5-(*p*-tolyl)dec-5-enoate (6e)



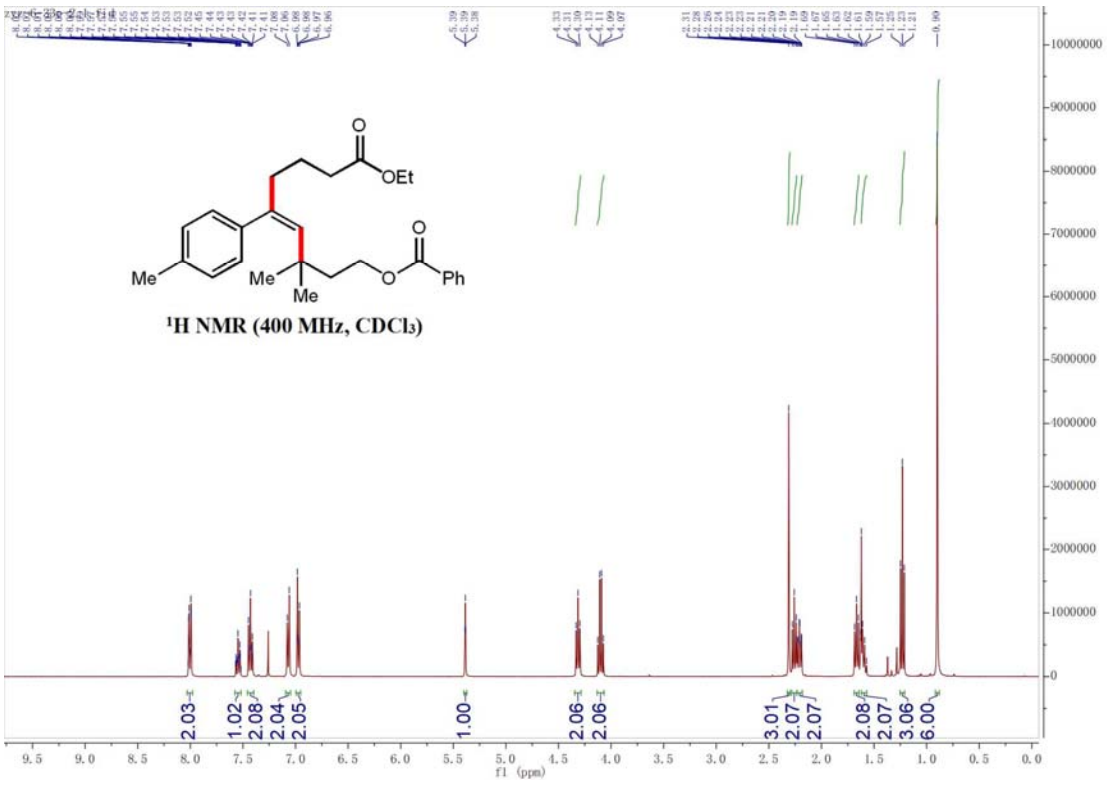


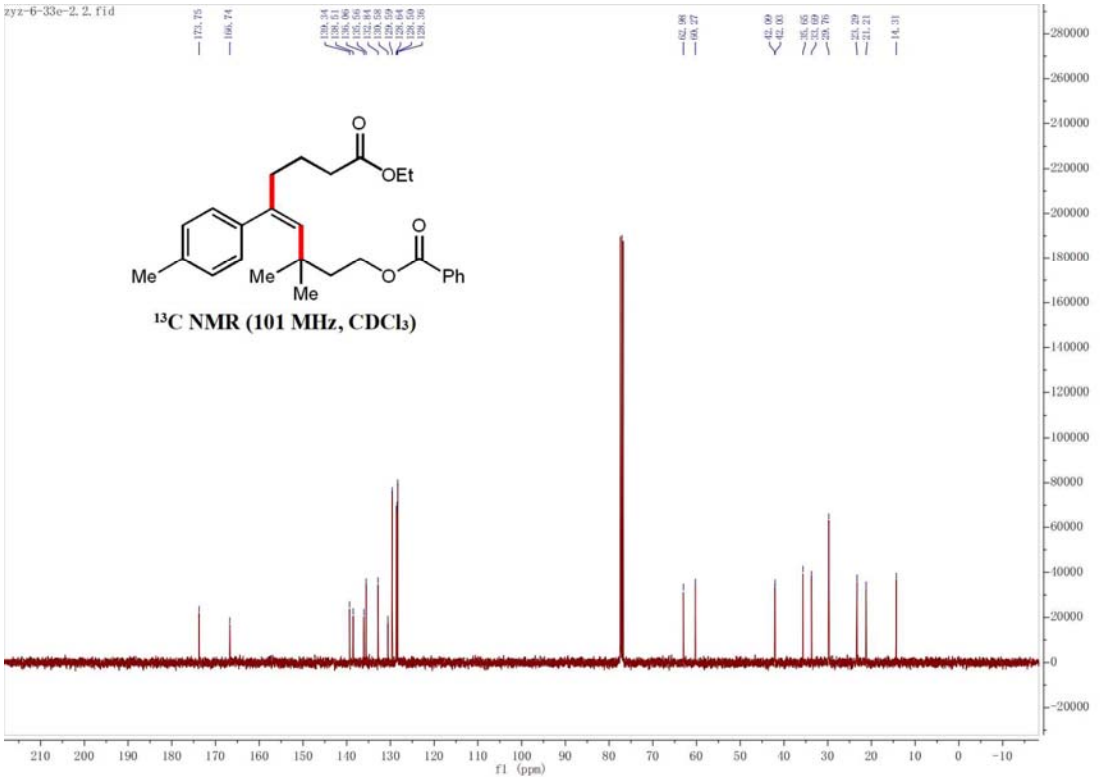
Ethyl (*Z*)-9-(4-methoxyphenyl)-7,7-dimethyl-5-(*p*-tolyl)non-5-enoate (6f)



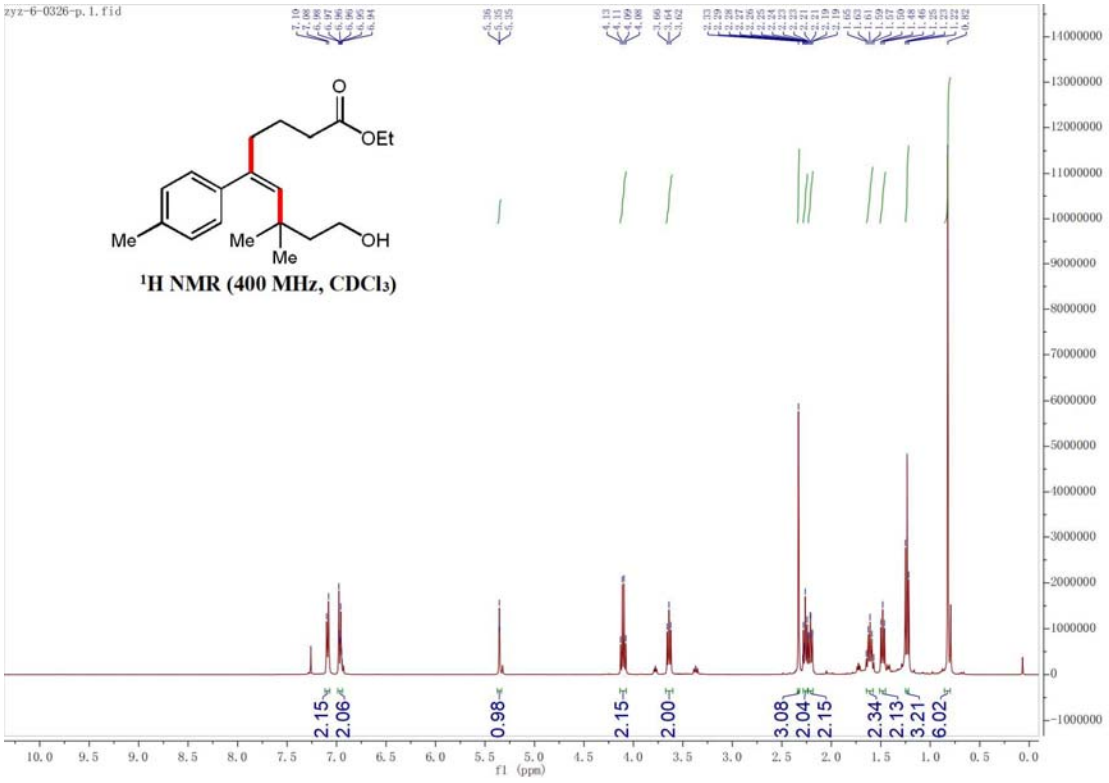


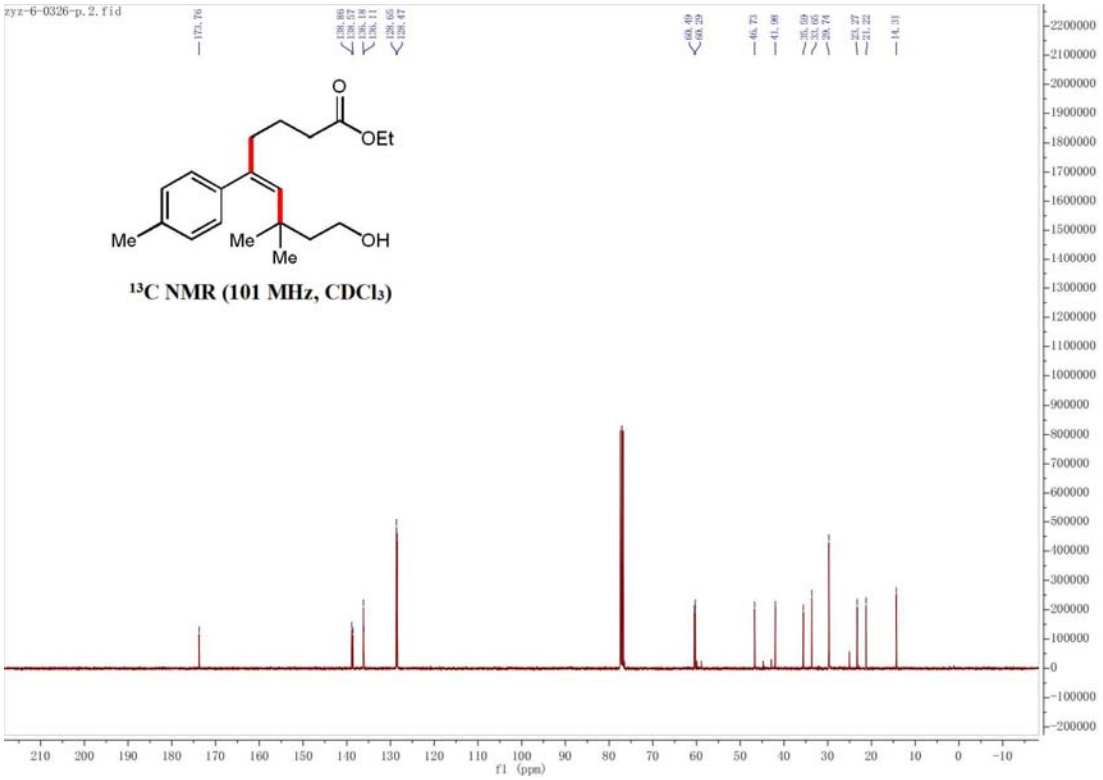
(*Z*)-9-Ethoxy-3,3-dimethyl-9-oxo-5-(*p*-tolyl)non-4-en-1-yl benzoate (6g)



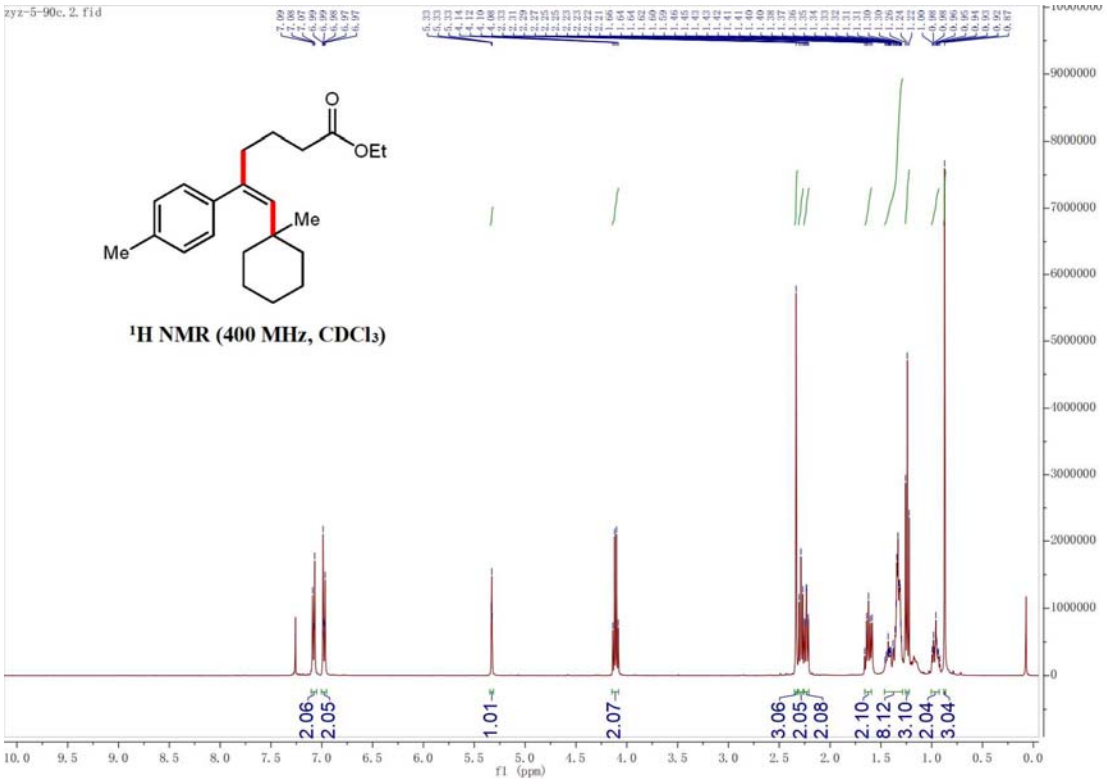


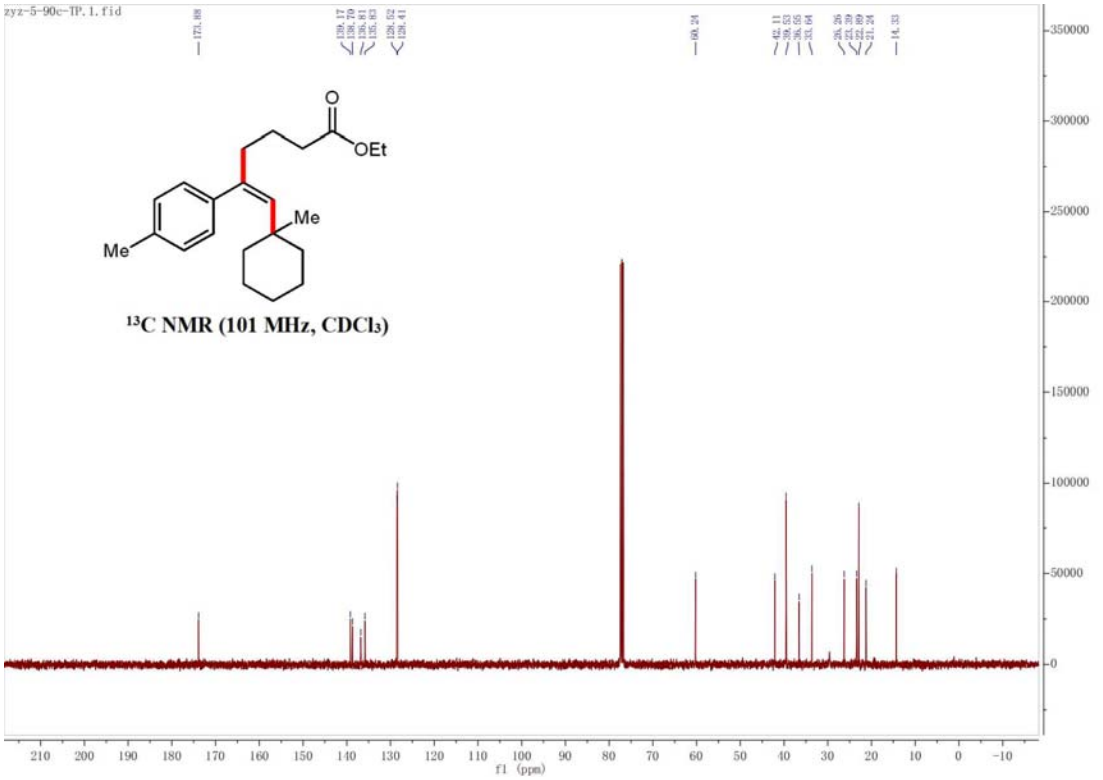
Ethyl (*Z*)-9-hydroxy-7,7-dimethyl-5-(*p*-tolyl)non-5-enoate (6h)



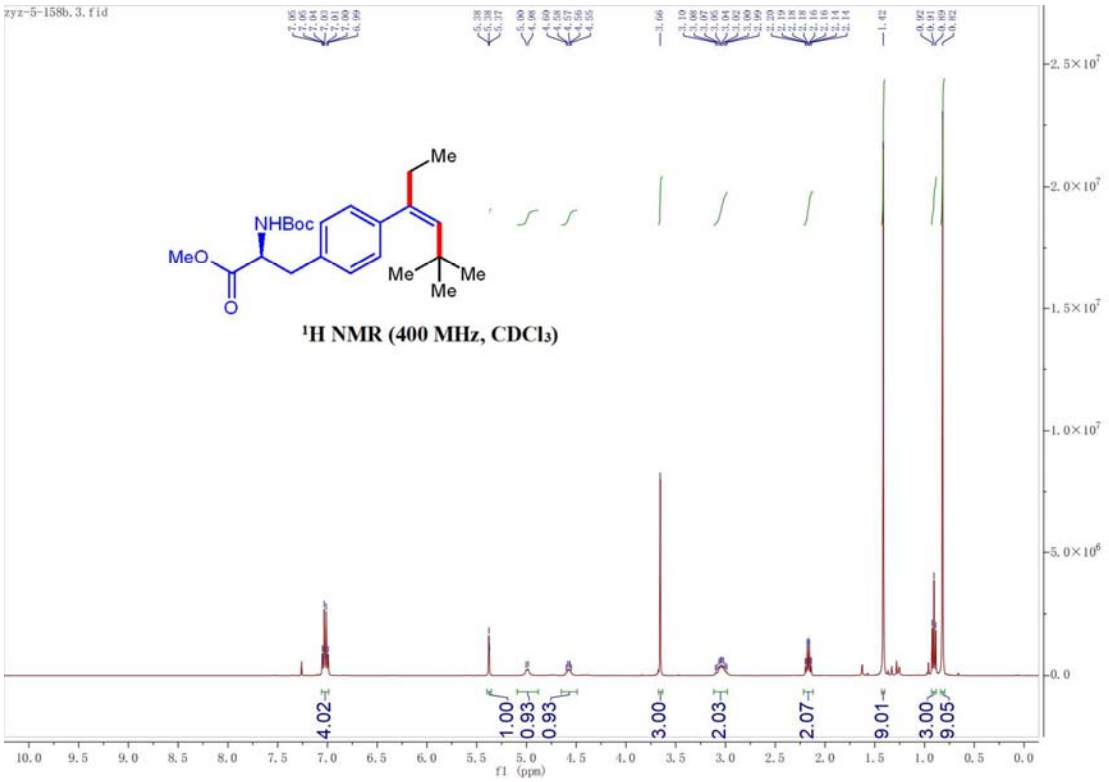


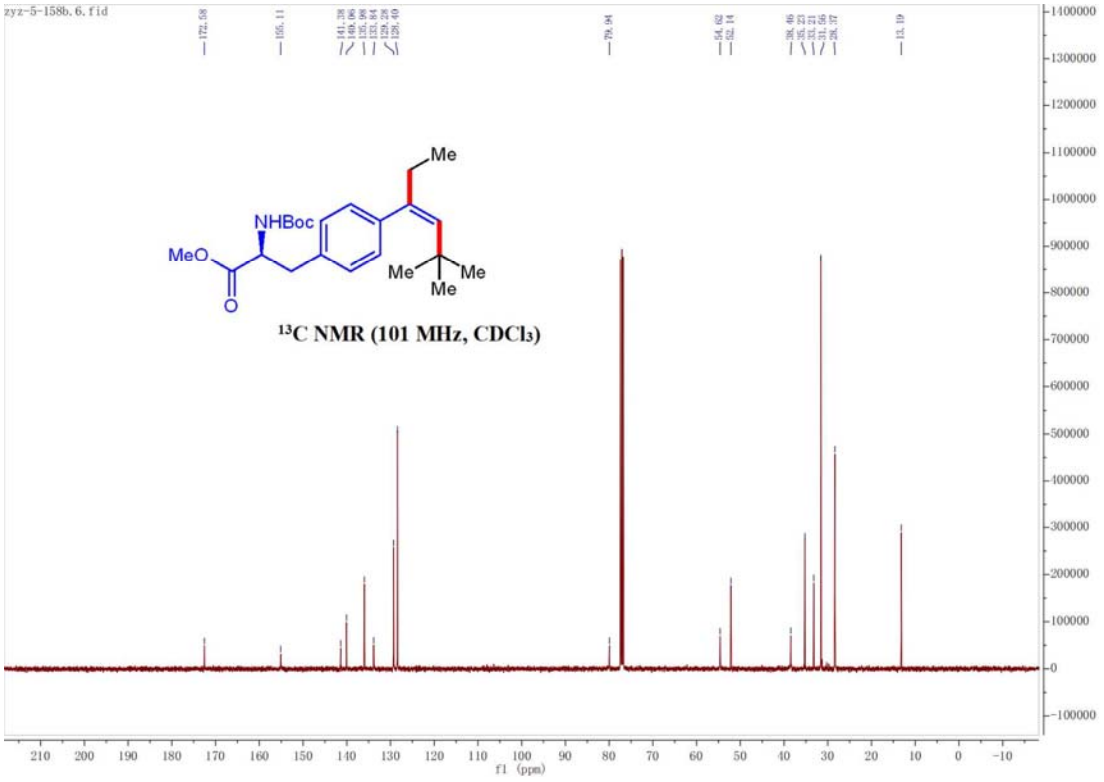
Ethyl (*Z*)-6-(1-methylcyclohexyl)-5-(*p*-tolyl)hex-5-enoate (6i)



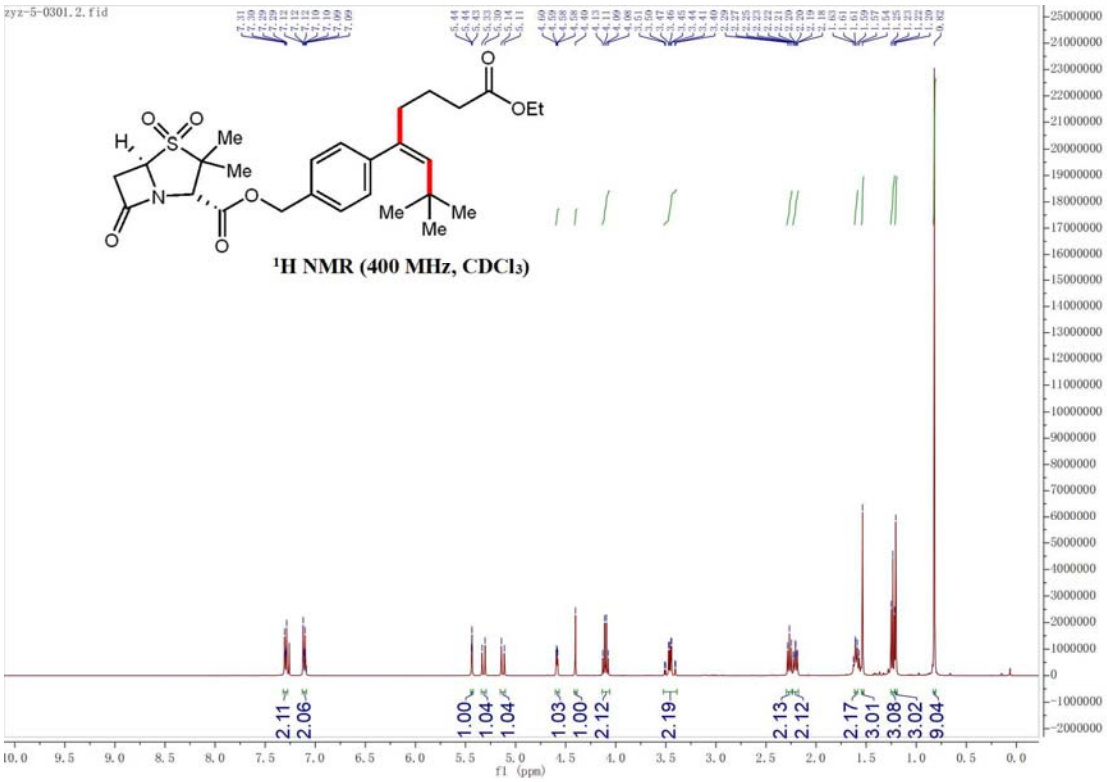


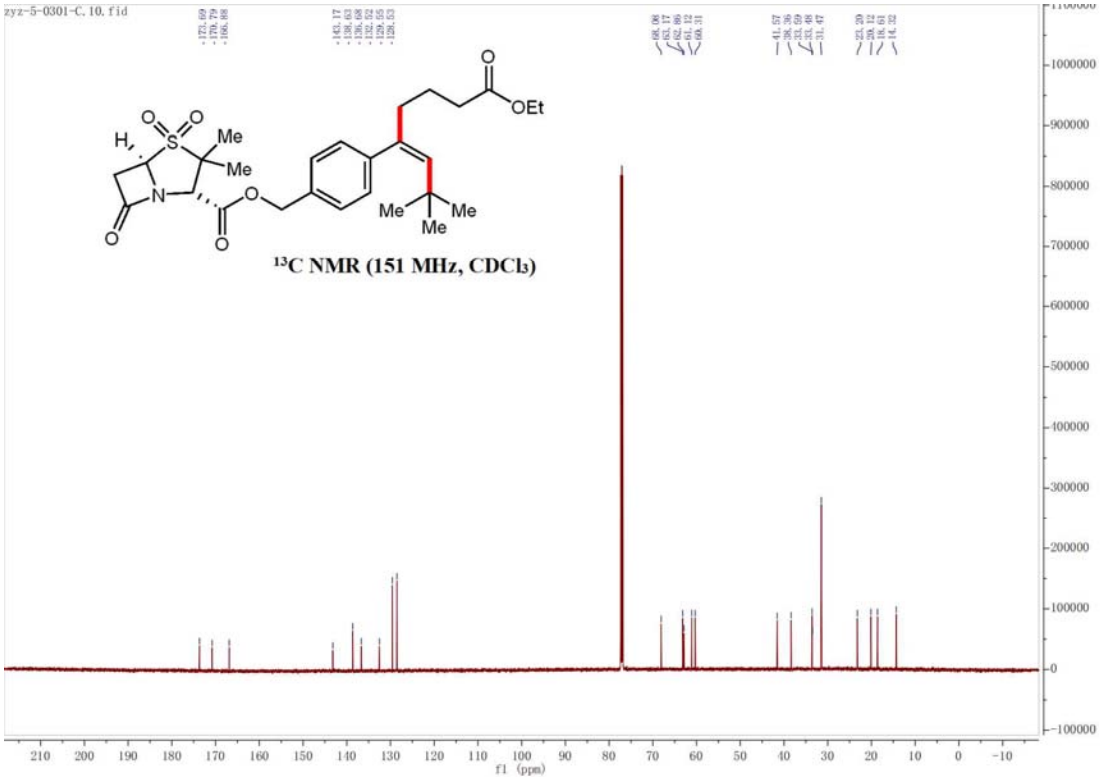
Methyl (*S,Z*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-(5,5-dimethylhex-3-en-3-yl)phenyl)propanoate (7a)



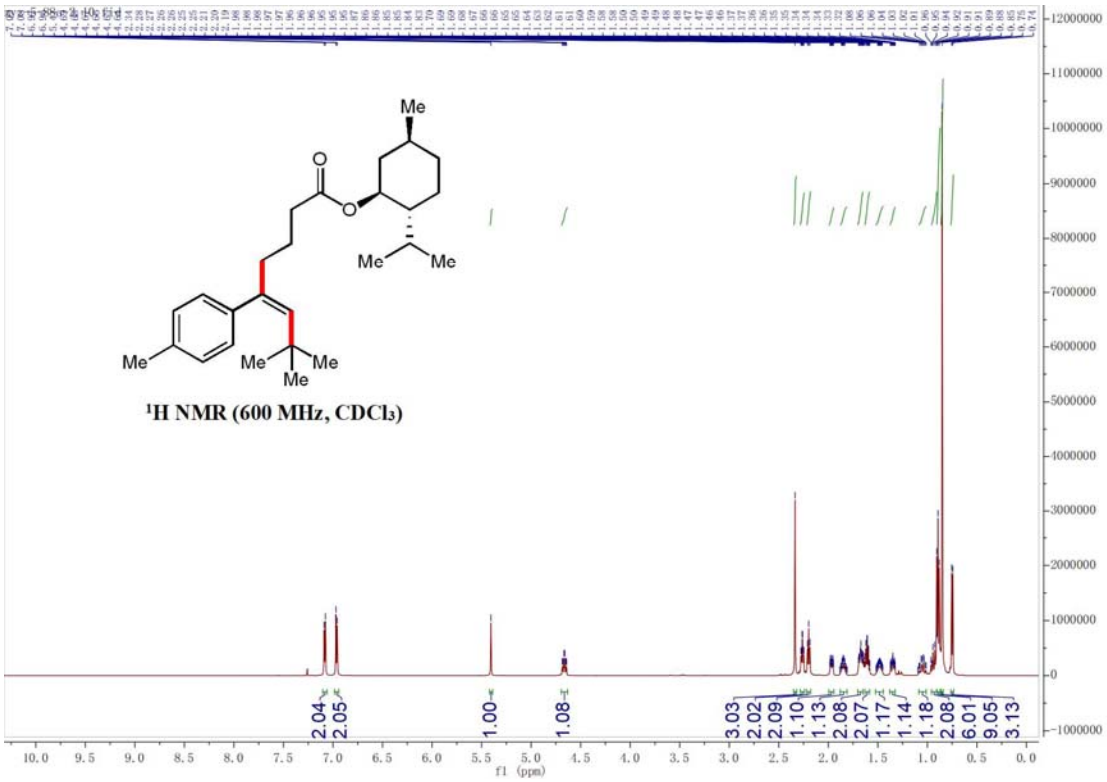


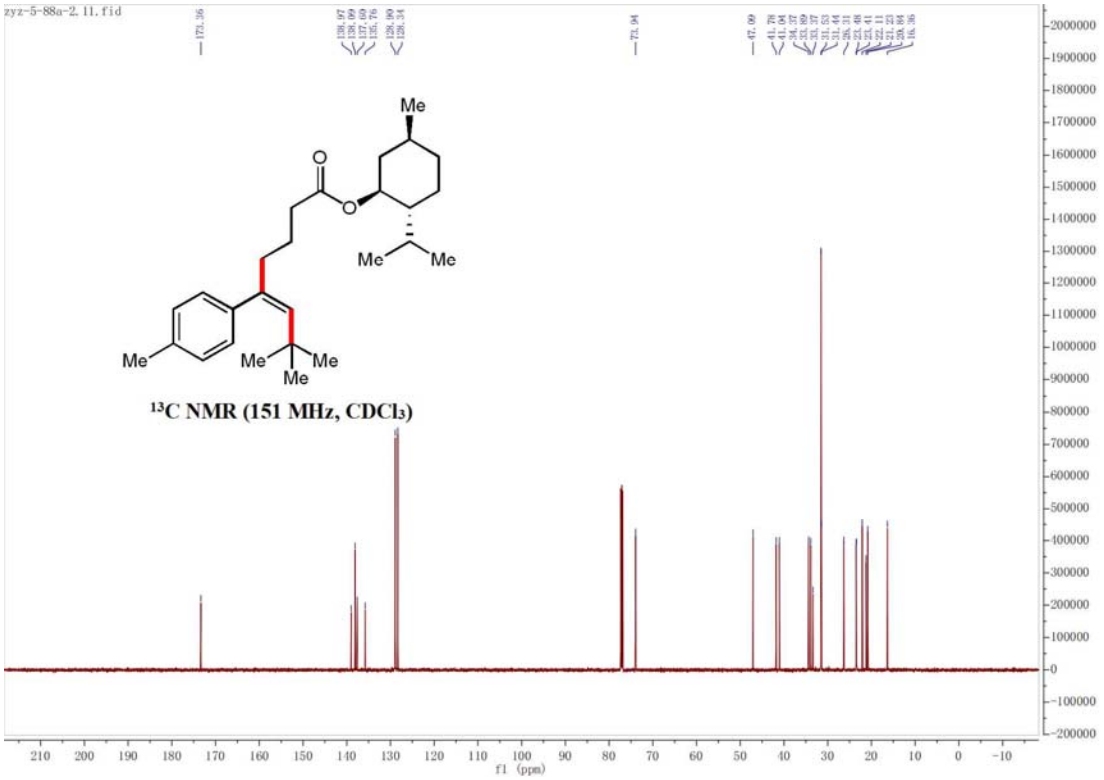
4-((*Z*)-8-Ethoxy-2,2-dimethyl-8-oxooct-3-en-4-yl)benzyl (*2S,5R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (7b)



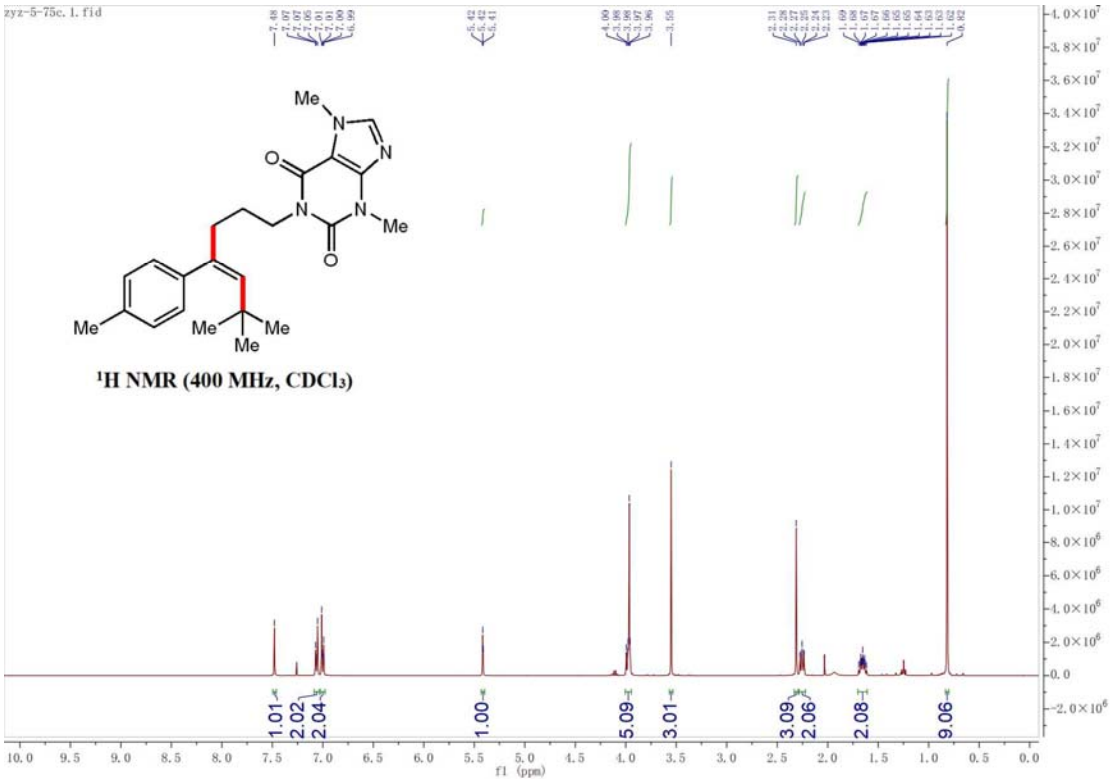


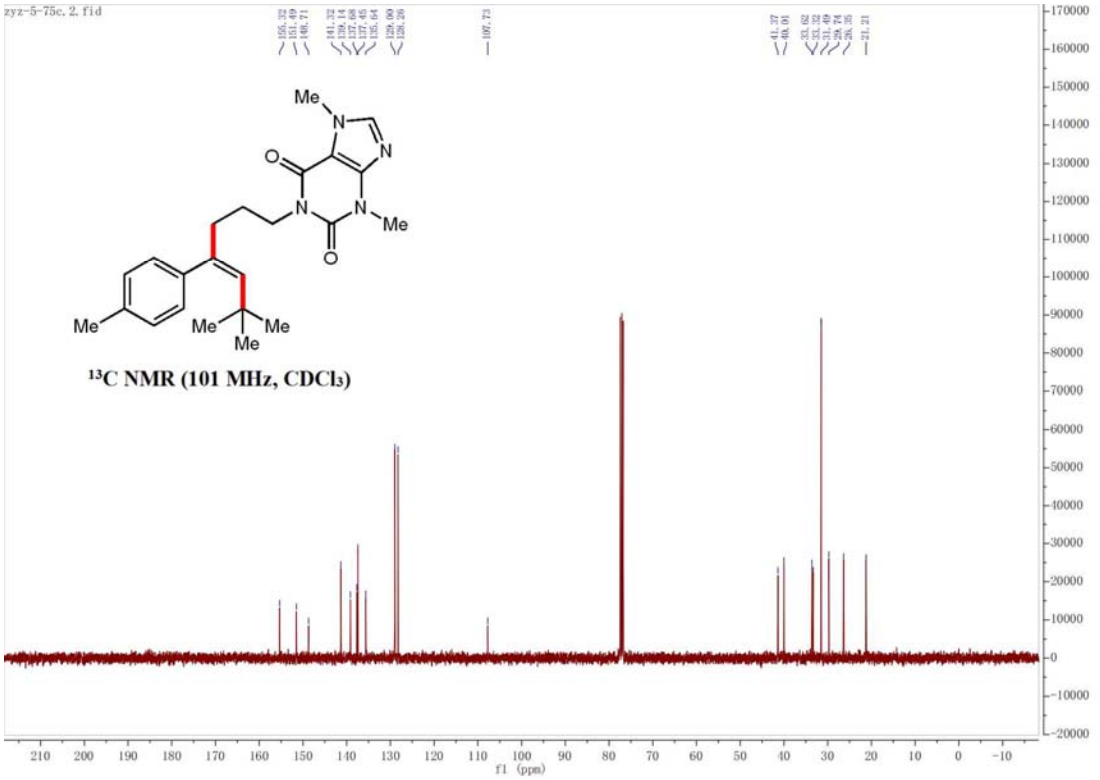
(*1S,2R,5S*)-2-Isopropyl-5-methylcyclohexyl (*Z*)-7,7-dimethyl-5-(*p*-tolyl)oct-5-enoate (7c)



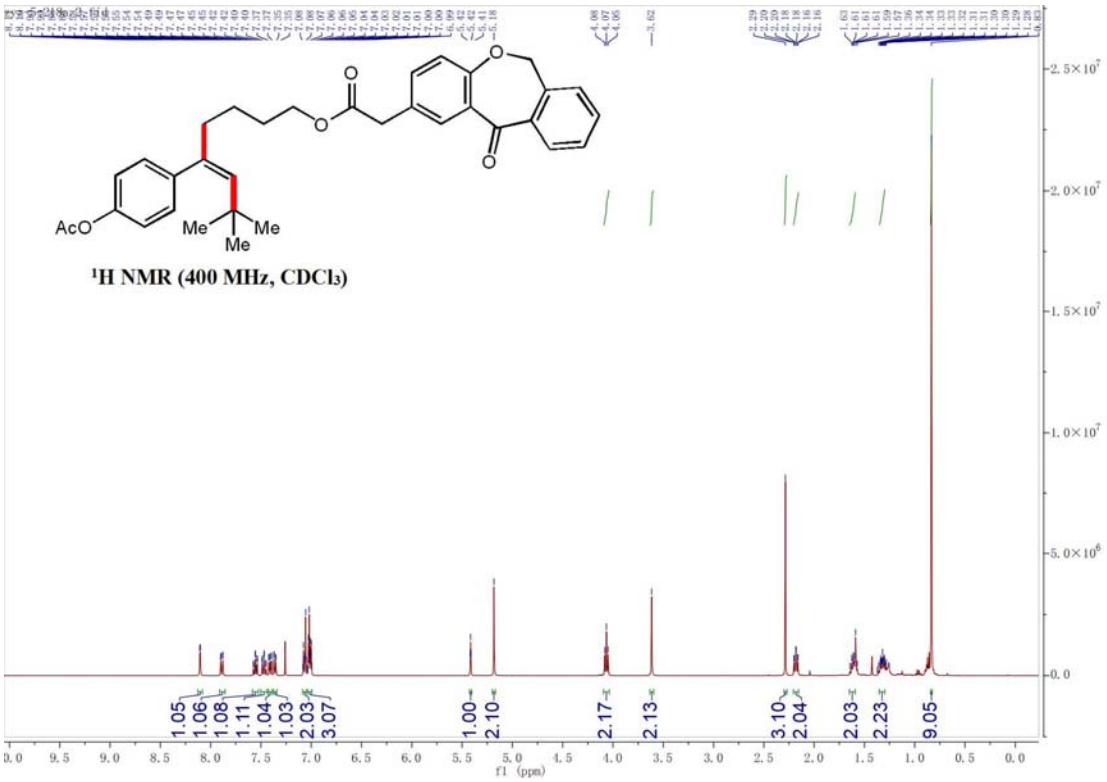


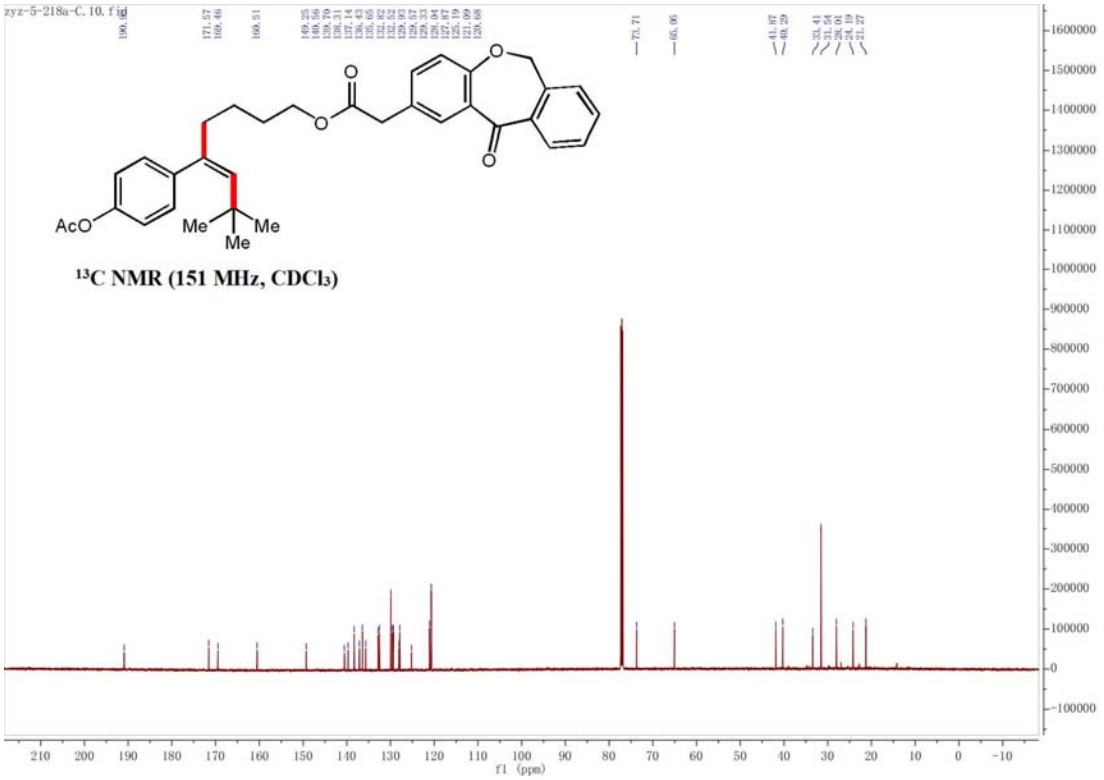
(*Z*)-1-(6,6-Dimethyl-4-(*p*-tolyl)hept-4-en-1-yl)-3,7-dimethyl-3,7-dihydro-1H-purine-2,6-dione (7d)



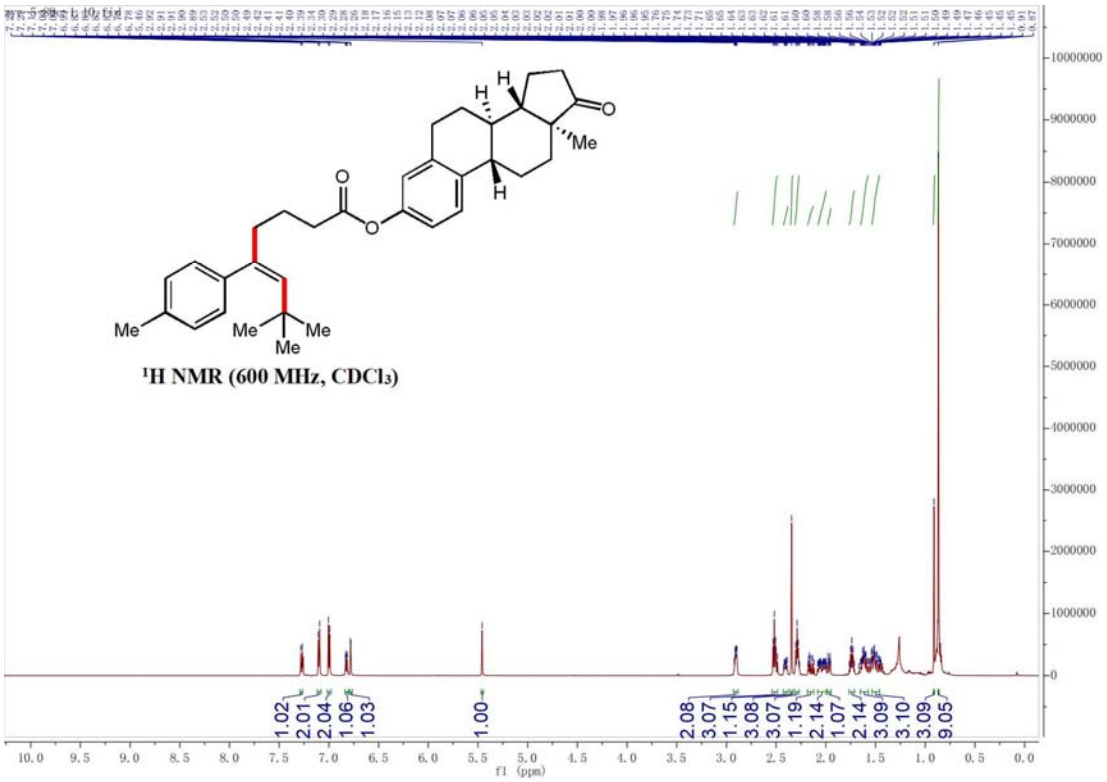


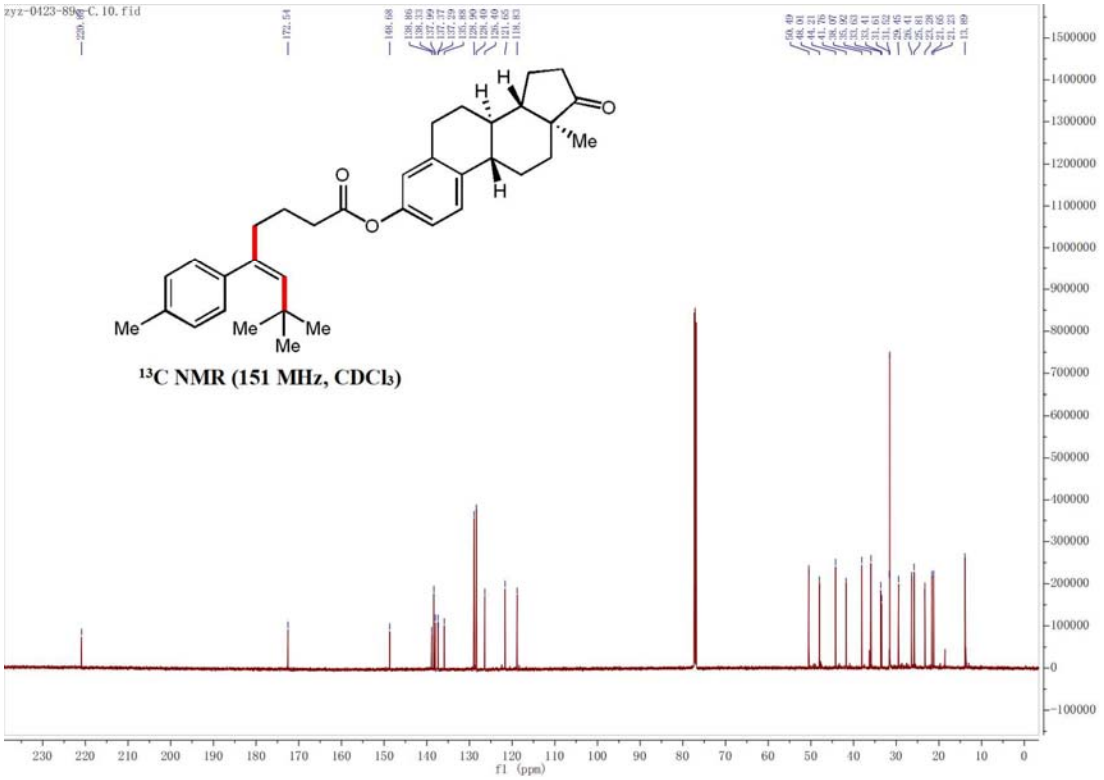
(*Z*)-5-(4-Acetoxyphenyl)-7,7-dimethyloct-5-en-1-yl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (7e)



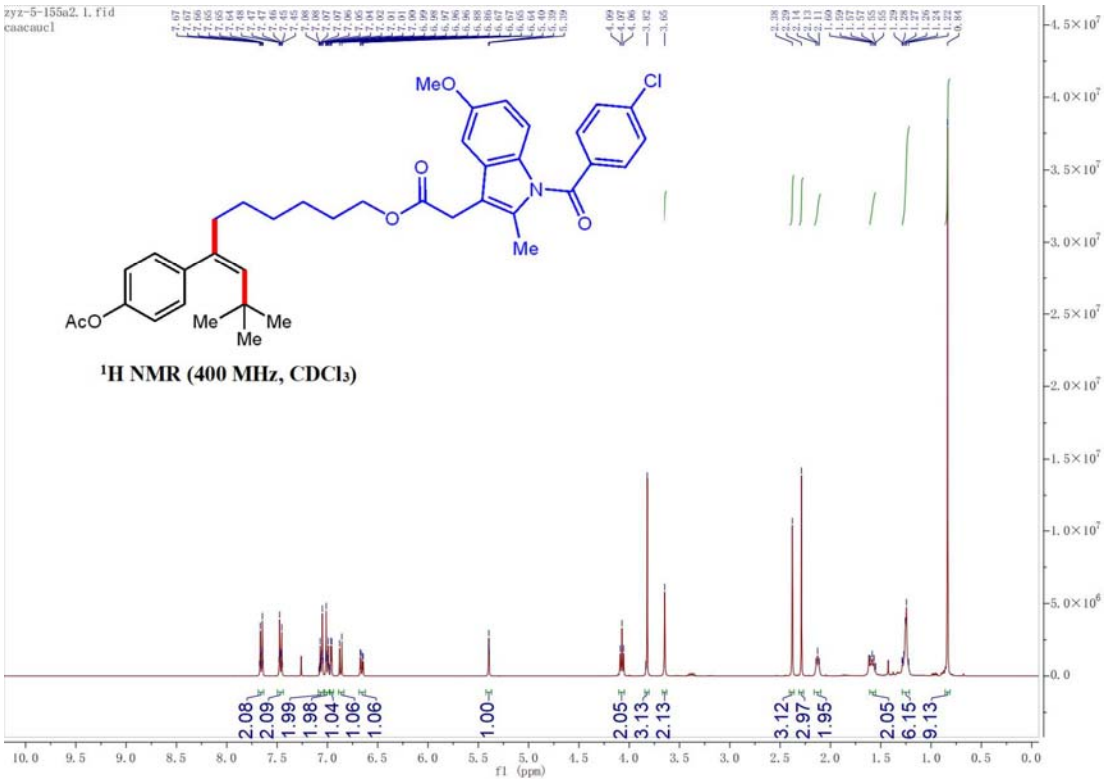


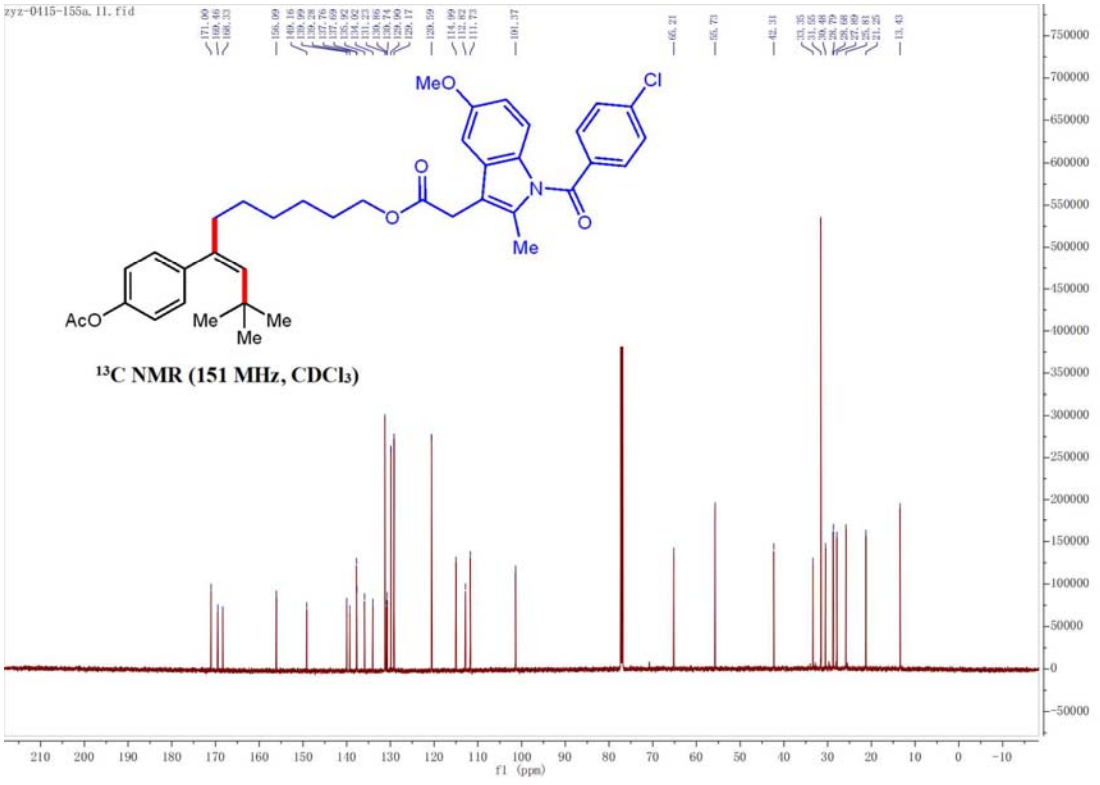
(*8R,9S,13S,14S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl (*Z*)-7,7-dimethyl-5-(*p*-tolyl)oct-5-enoate (7f)



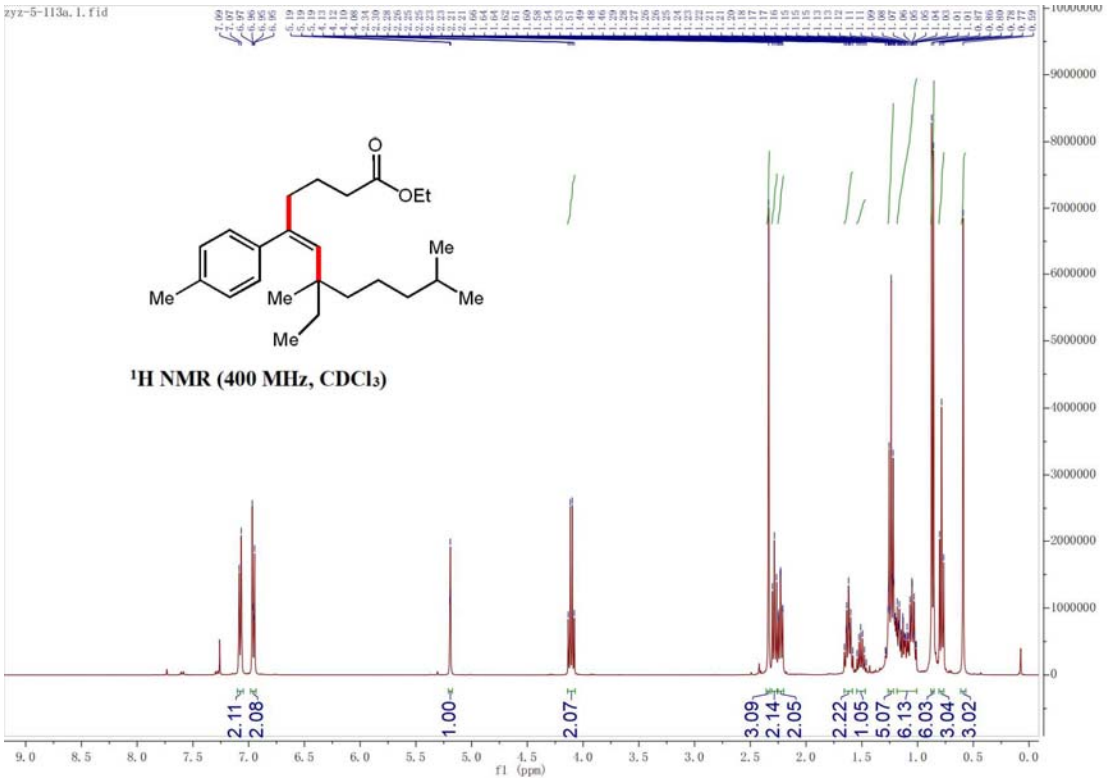


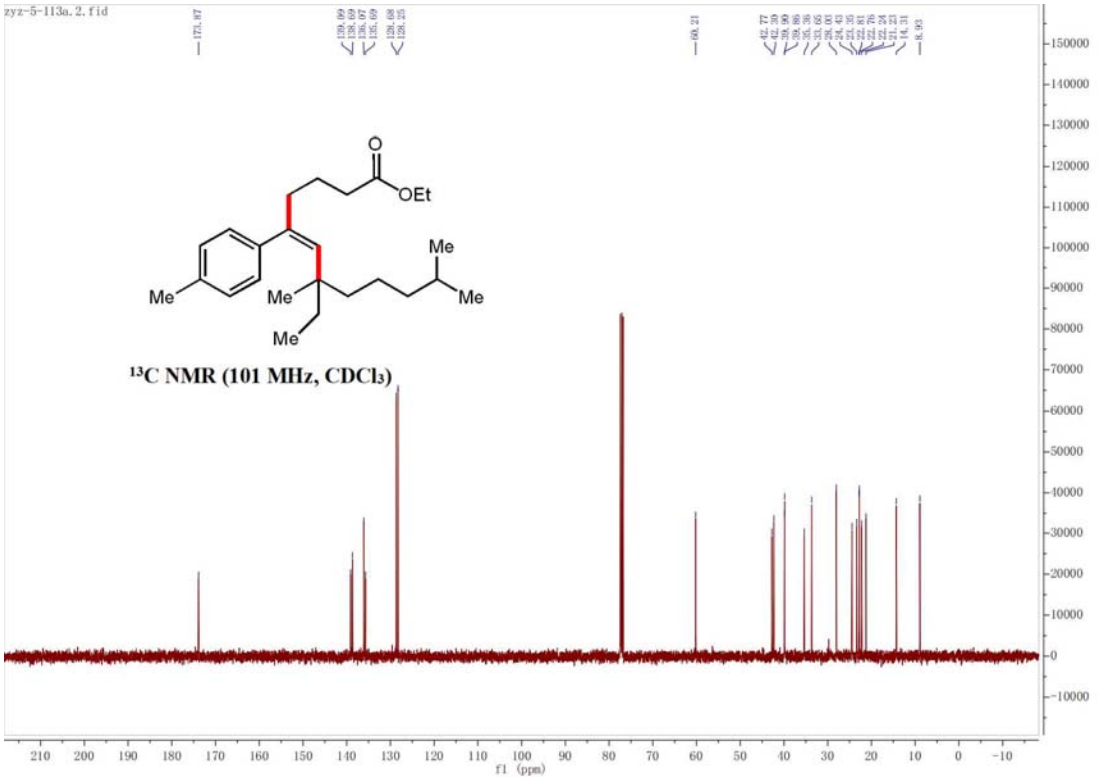
(*Z*)-7-(4-Methoxyphenyl)-9,9-dimethyldec-7-en-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (7g)



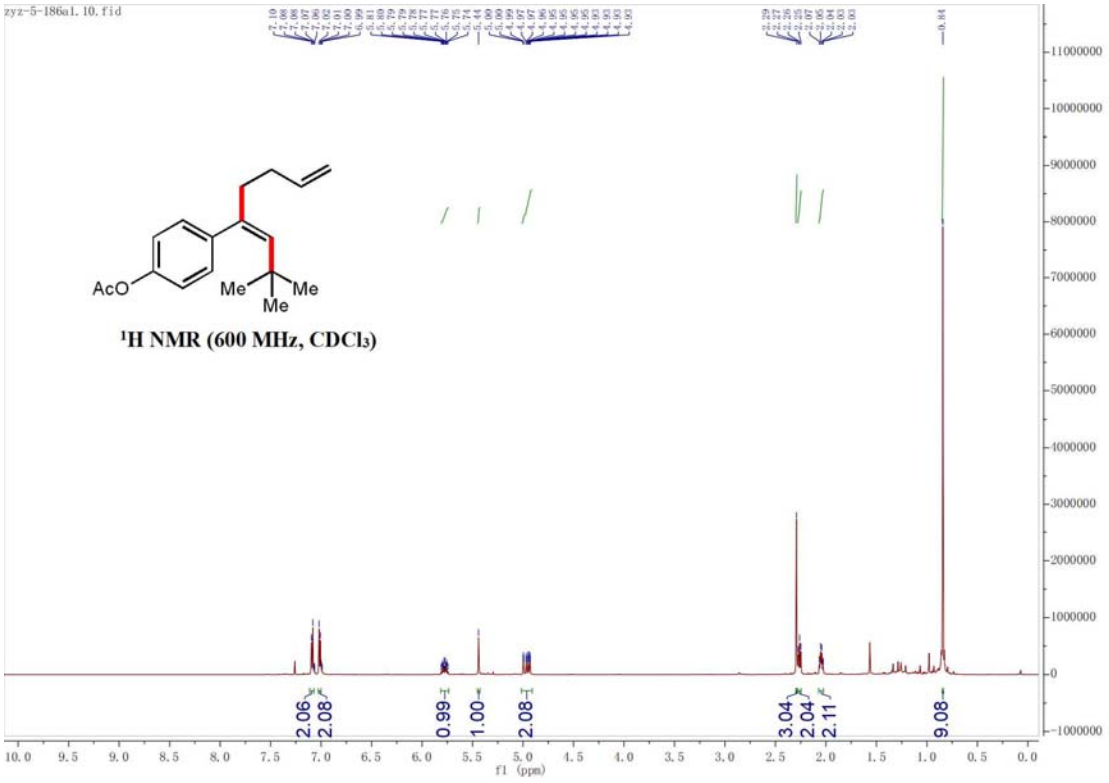


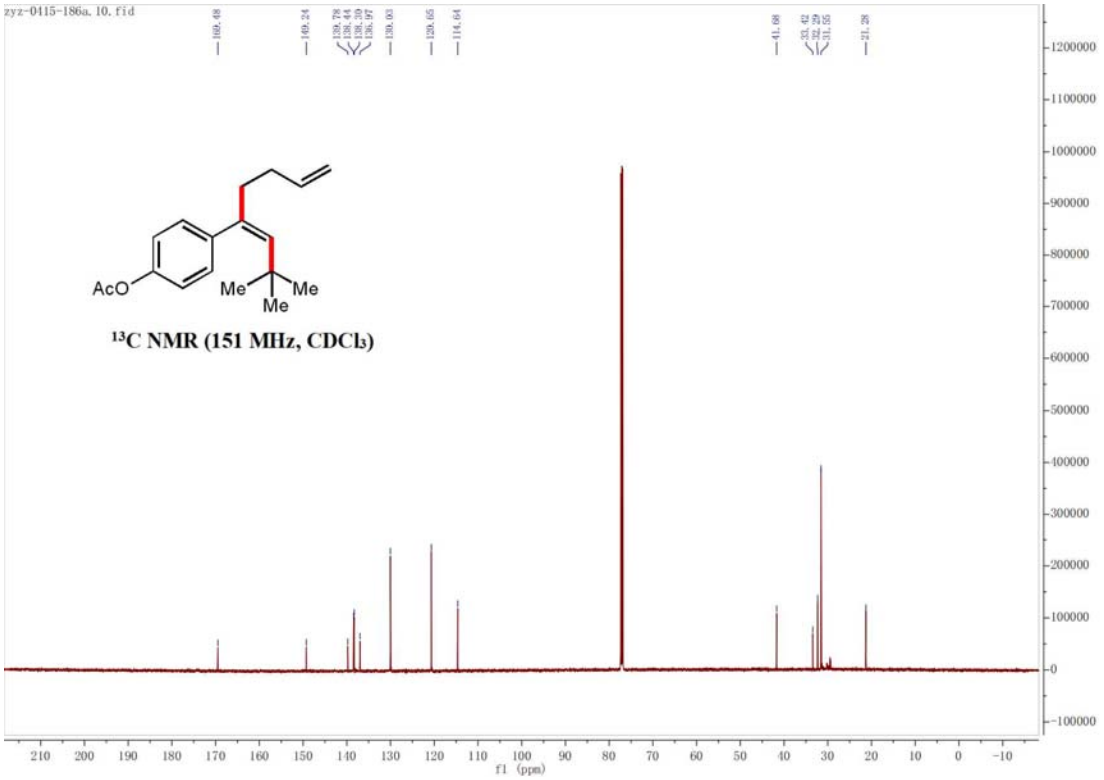
Ethyl (*Z*)-7-ethyl-7,11-dimethyl-5-(*p*-tolyl)dodec-5-enoate (7h)



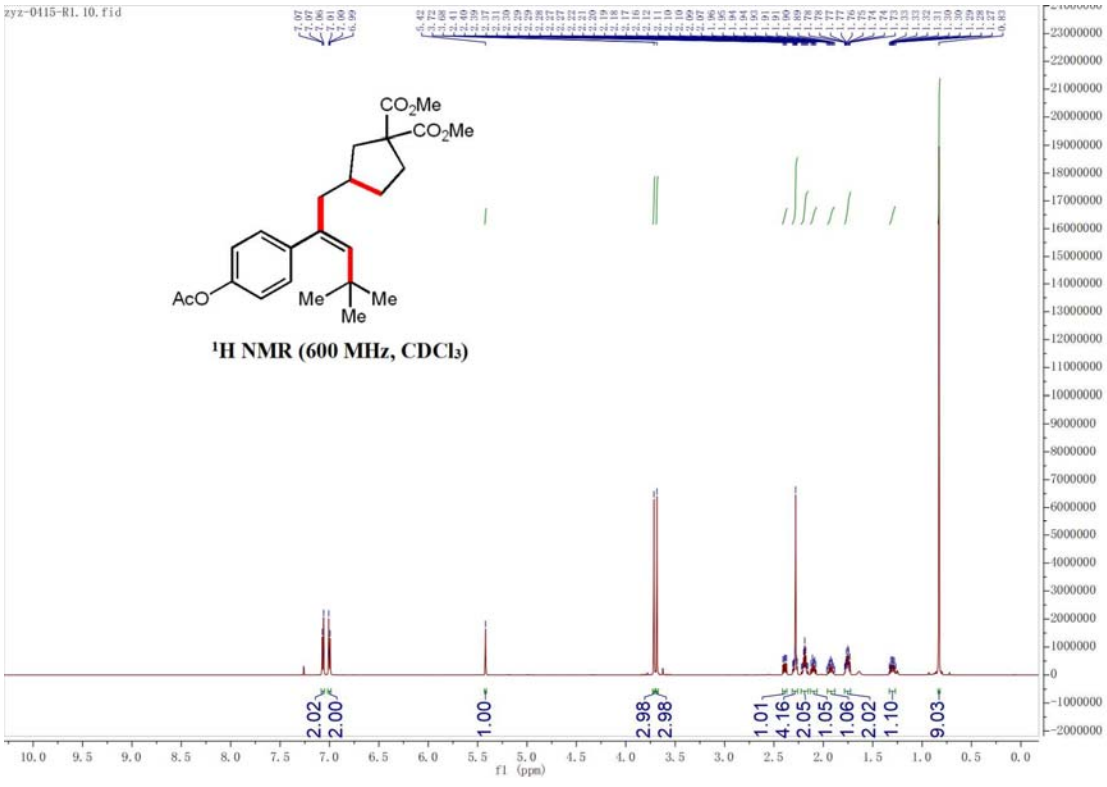


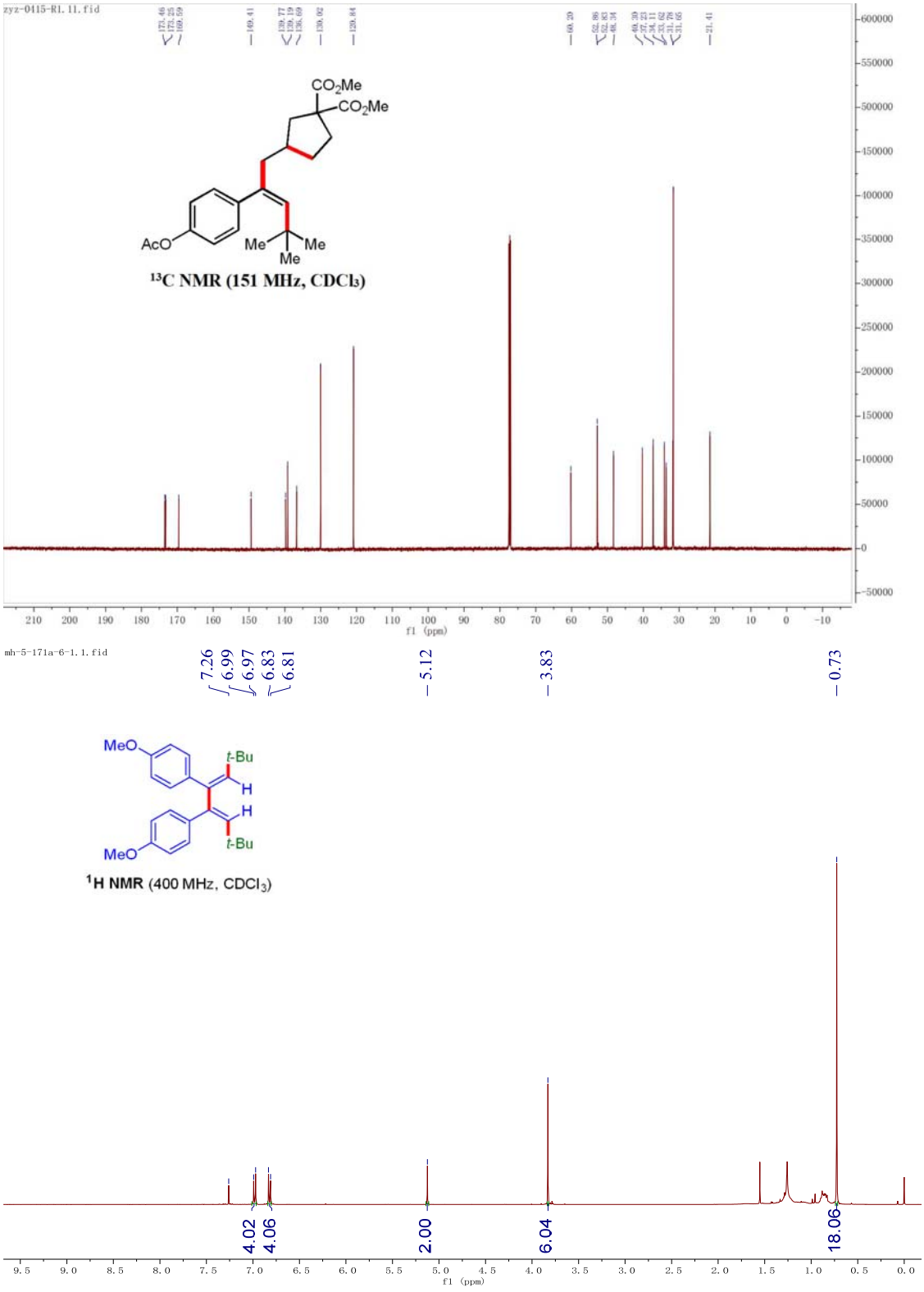
(*Z*)-4-(2,2-Dimethylocta-3,7-dien-4-yl)phenyl acetate (9)



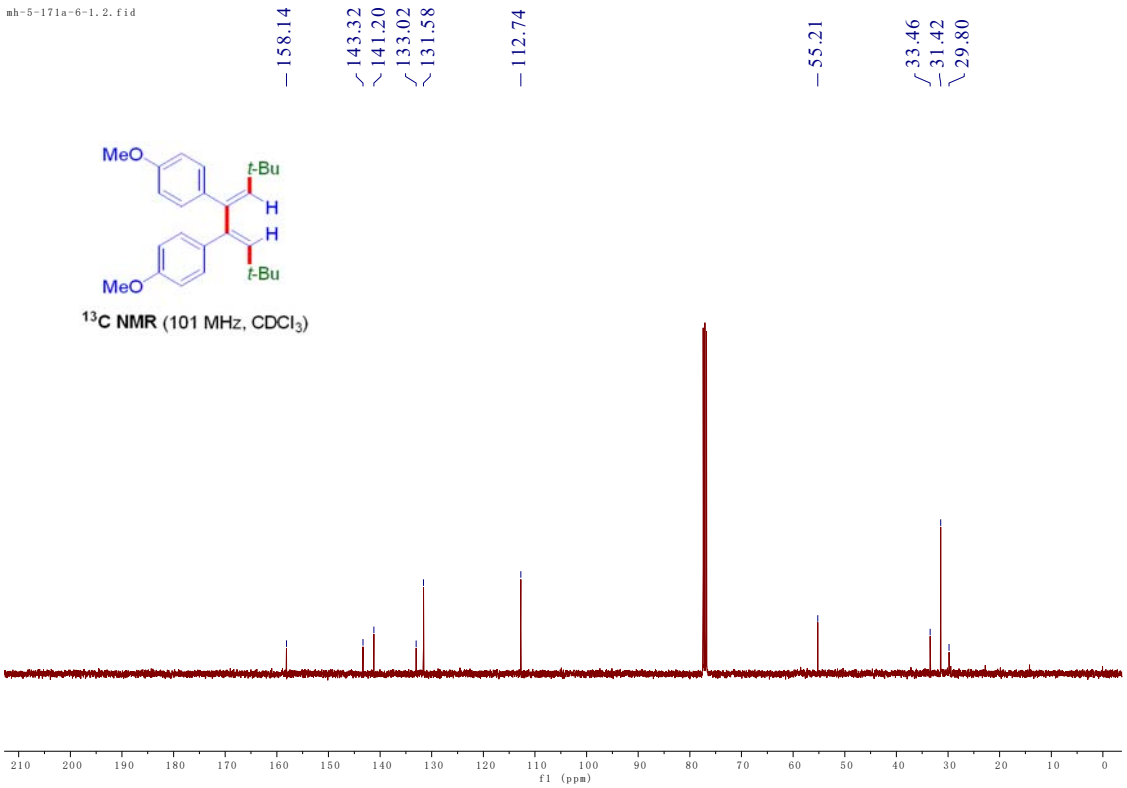


Dimethyl (*S*,*Z*)-3-(2-(4-acetoxyphenyl)-4,4-dimethylpent-2-en-1-yl)cyclopentane-1,1-dicarboxylate (11)





^{1}H NMR of **12** (400 MHz, $CDCl_3$)



^{13}C NMR of **12** (101 MHz, $CDCl_3$)

7. X-ray Diffraction Data of 7d

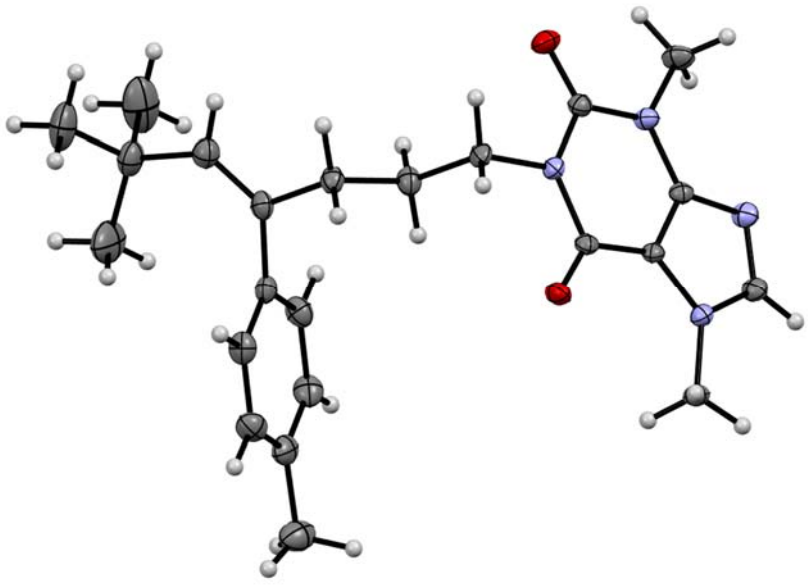


Table S11 Crystal data and structure refinement for **7d** (CCDC 2061399).

Identification code	cxy1538_0ma
Empirical formula	$C_{23}H_{30}N_4O_2$

Formula weight	394.51
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.0767(6)
b/Å	12.9097(5)
c/Å	10.9767(4)
α/°	90
β/°	99.7120(10)
γ/°	90
Volume/Å^3	2245.51(15)
Z	4
ρ_{calc}g/cm^3	1.167
μ/mm^{-1}	0.076
F(000)	848.0
Crystal size/mm^3	0.38 × 0.34 × 0.29
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.912 to 55.176
Index ranges	$-20 \leq h \leq 18$, $-16 \leq k \leq 16$, $-14 \leq l \leq 14$
Reflections collected	21610
Independent reflections	5190 [R_{int} = 0.0390, R_{sigma} = 0.0373]
Data/restraints/parameters	5190/0/269
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1064
Final R indexes [all data]	R_1 = 0.0680, wR_2 = 0.1204
Largest diff. peak/hole / e Å^{-3}	0.30/-0.22

8. References

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(2) A. S. Dudnik and G. C. Fu, *J. Am. Chem. Soc.* 2012, **134**, 10693-10697.

(3) Y.-Z. Zhan, N. Xiao and W. Shu, *Nat. Commun.* 2021, **12**, 928.

(4) C. Zheng, W.-M, Cheng, H.-L. Li, R.-S. Na and R. Shang, *Org. Lett*. 2018, **20**, 2559-2563.

(5) M. R. Prinsell, D. A. Everson and D. J. Weix, Chem. Commun. 2010, 46, 5743-5745.