

Supporting Information

Kinetic Resolution of Propargylic Ethers via [2,3]-Wittig Rearrangement to Synthesize Chiral α -Hydroxyallenes

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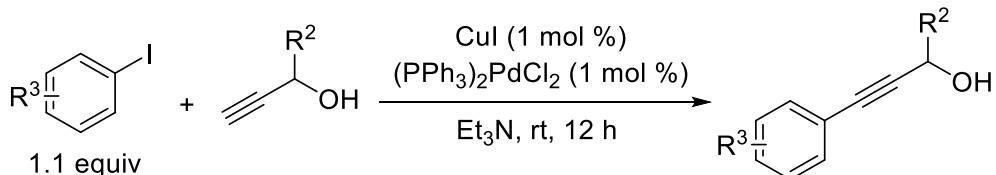
1. General remarks

¹H NMR spectra were recorded on bruker ASCEND™ 400M (400 MHz). ¹³C{¹H} NMR data were collected on bruker ASCEND™ 400M (101 MHz) with complete proton decoupling. Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard (CDCl₃, δ = 7.26) for ¹H NMR and (CDCl₃, δ = 77.0) for ¹³C{¹H} NMR. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ¹⁹F{¹H} NMR spectra were collected on bruker ASCEND™ 400M (376 MHz) with complete proton decoupling. Enantiomeric excesses were determined by chiral HPLC analysis on Daicel Chiralcel ID or chiral UPC² analysis on Phenomenex Chiralcel Lux 5u Cellulose at 35 °C with UV detector at 254 nm in comparison with the authentic racemates. Optical rotations were determined after flash column chromatography purification and reported as follows: [α]_D^T (c: g/100 mL, in CH₂Cl₂). HRMS were recorded on Thermo Q-Exactive Focus (FTMS+c ESI). All the solvents were purified by usual methods before use. Chromatography: Qingdao Haiyang silica gel, HG/T2354-92, HCP. The chiral *N,N*'-dioxides were prepared according to methods reported in the literature.¹ Unless otherwise specified, the reactions were heated by water bath.

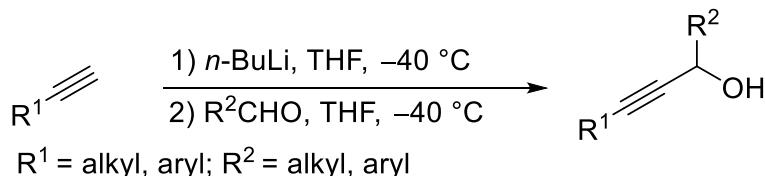
2. Substrate synthesis

2.1 General procedure for the synthesis of propargyl alcohols

a) **Method A:** Aryl propargyl alcohols were prepared by sonogashira coupling according to the literature procedure.²



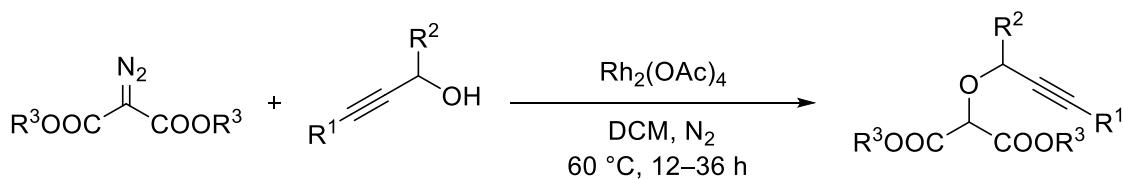
b) **Method B:** Other propargyl alcohols were prepared according to the literature procedure.³



2.2 General procedure for the synthesis of Diazomalonate⁴



2.3 General procedure for the synthesis of 2-(proparaglyoxy)malonate substrates



Rhodium acetate (0.5 mol %) and propargyl alcohol (11.0 mmol) were added into a 100 mL round-bottom flask, and the mixture was charged with N_2 three times. Subsequently, 40.0 mL DCM was added and diazomalonate (10.0 mmol) was added at once to the mixture at 60 °C in oil bath under N_2 . The reaction mixture was stirred for 24–72 hours. The solvent was removed in vacuo and the residue was subjected to column chromatography on silica gel and eluted with petroleum ether/DCM/EtOAc (18:1:1 and 16:1:1, v/v/v) to provide the corresponding substrates **1** (10–40% yield).

3. General procedure for the preparation of the racemic products

$\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (3.6 mg, 0.01 mmol), *rac-L-PiPr₂* (6.5 mg, 0.01 mmol), 2-(proparaglyoxy)malonate **1** (0.10 mmol) and ethyl acetate (0.30 mL) were added to an oven-dried reaction tube. The resulting mixture was stirred at 35 °C for 30 min, then DBU or Et₃N (1.2 equiv) was added. The reaction mixture was stirred at 50 °C for 24–48 h and directly subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (6:1 and 3:1, v/v) to afford the corresponding products (**3a**, **3d–3o**) and petroleum ether/ethyl acetate (20:1, v/v) to afford **3b** and **3c**.

4. General procedure for the catalytic asymmetric reactions

$\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (3.6 mg, 0.01 mmol), **L-PiPr₃** (7.3 mg, 0.01 mmol), 2-(proparaglyoxy)malonate **1**/ethyl acetate (0.10 mmol/0.30 mL) or (0.20 mmol/0.60 mL) were added to an oven-dried reaction tube. The resulting mixture was stirred at 35 °C for 30 min, then Et₃N (1.2 equiv) was added. The reaction mixture was stirred at 50 °C for the indicated time and directly subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (8:1–6:1, v/v) to afford the recovered material (**1a**, **1d–1o**) and petroleum ether/ethyl acetate (20:1, v/v) to afford **1b** and **1c**. The desired products (**3a**, **3d–3o**) were purified with petroleum ether/ethyl acetate/dichloromethane (3:1:0.5, v/v/v) as the eluted solvent. The desired products (**3b** and **3c**) were purified with petroleum ether/ethyl acetate (20:1, v/v/v) as the eluted solvent.

5. Optimization of the reaction conditions

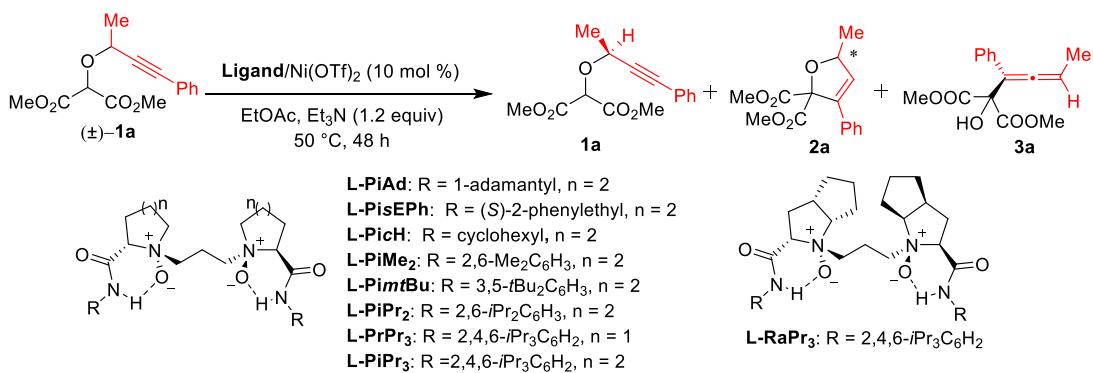
(a) Screen of metal salts

Reaction scheme showing the conversion of **(±)-1a** to **1a**, **2a**, and **3a** under various metal salt conditions. The reaction conditions are L-PiCHPh₂/metal salts (10 mol %), EtOAc, Et₃N (1.2 equiv), 50 °C, 48 h.

entry ^a	metal salts	1a+2a		3a	
		yield (%) ^b	ee (%) ^c	yield (%) ^b	ee (%) ^c
1	Sc(OTf) ₃	-	-	N.R.	-
2	Ni(OTf) ₂	52 (26/74)	29/56	29	92
3	Cu(OTf) ₂	-	-	N.R.	-
4	Zn(OTf) ₂	90	0	N.R.	-
5	La(OTf) ₃	84	0	N.R.	-
6	Mg(OTf) ₂	-	-	N.R.	-
7	Yb(OTf) ₃	-	-	N.R.	-
8	Ca(OTf) ₂	-	-	N.R.	-
9	Co(ClO ₄) ₂ •6H ₂ O	75 (79/21)	6/33	trace	86
10	Ni(ClO ₄) ₂ •6H ₂ O	70 (27/73)	29/48	25	93
11	Ni(BF ₄) ₂ •6H ₂ O	61 (26/74)	21/51	30	91
12	Ni(acac) ₂	-	-	N.R.	-
13	NiCl ₂	-	-	N.R.	-
14	Ni(NTf ₂) ₂	98 (0/100)	0	N.R.	-
15	Ni(OAc) ₂ •4H ₂ O	-	-	N.R.	-

^aAll the reactions were performed with 10 mol % metal salts, 10 mol % **L-PiCHPh₂**, **1a** (0.1 mmol) and Et₃N (1.2 equiv) in EtOAc (1.0 mL) at 50 °C for 48 h. ^bIsolated yield, the ratio in the bracket represents the ratio of **1a** to **2a** according to HPLC analysis. ^cDetermined by HPLC analysis on a chiral stationary phase.

(b) Screen of the ligands

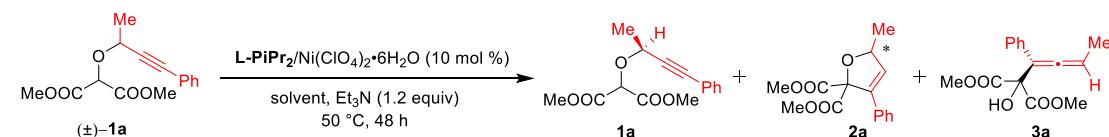


entry ^a	ligand	1a+2a		3a	
		yield (%) ^b	ee (%) ^c	yield (%) ^b	ee (%) ^c
1	L-PiAd	-	-	N.R.	-
2	L-PisEPH	-	-	trace	-
3	L-PicH	65 (70/30)	8/55	17	96
4	L-PiMe₂	86 (97/3)	2	5	95
5	L-PiPr₂	84 (99/1)	3	11	98
6	L-PiPr₃	89 (99/1)	8	14	98
7 ^d	L-PiPr₃	75 (98/2)	26	24	99

8	L-PintBu	69 (5/95)	11	32	38
9 ^e	L-RaPr₃	70 (96/4)	17	16	84
10 ^e	L-PrPr₃	67 (99/1)	20	20	96

^aAll the reactions were performed with 10 mol % Ni(OTf)₂, 10 mol % ligand, **1a** (0.1 mmol) and Et₃N (1.2 equiv) in EtOAc (1.0 mL) at 50 °C for 48 h. ^bIsolated yield, the ratio in the bracket represents the ratio of **1a** to **2a** according to HPLC analysis. ^cDetermined by HPLC analysis on a chiral stationary phase. ^d10 mol % Ni(ClO₄)₂•6H₂O/**L-PiPr₃**. ^e10 mol % Ni(ClO₄)₂•6H₂O/ligand, **1a** (0.1 mmol) and Et₃N (1.2 equiv) in EtOAc (0.3 mL) at 50 °C for 48 h.

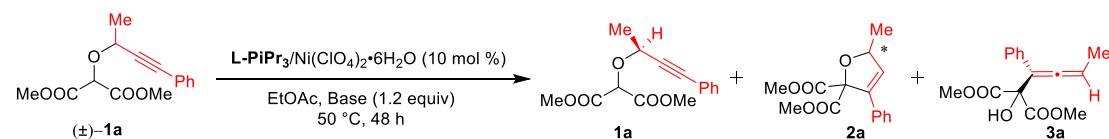
(c) Screen of the solvents



entry ^a	solvent	yield (%) ^b	ee (%) ^c	yield (%) ^b	ee (%) ^c
1 ^d	EtOAc	75 (98/2)	26	24	99
2 ^e	EtOAc	47 (95/5)	84	30	99
3 ^f	EtOAc	50 (93/7)	93	46	98
4 ^g	EtOAc	39 (90/10)	94/59	32	98
5	EtOAc	59 (93/7)	89	37	98
6	toluene	99 (99/1)	0	N.R.	-
7	MeOH	99 (99/1)	0	N.R.	-
8	n-hexane	99 (97/3)	0	-	-
9	MeCN	52 (92/8)	89	37	94
10	THF	92 (99/1)	3	7	98
11	DCE	98 (98/2)	-4	trace	-

^aAll the reactions were performed with 10 mol % **L-PiPr₂**/Ni(ClO₄)₂•6H₂O, **1a** (0.1 mmol) and Et₃N (1.2 equiv) in solvent (0.3 mL) at 50 °C for 48 h. ^bIsolated yield, the ratio in the bracket represents the ratio of **1a** to **2a** according to HPLC analysis. ^cDetermined by HPLC analysis on a chiral stationary phase. ^d10 mol % **L-PiPr₃**/Ni(ClO₄)₂•6H₂O in 1.0 mL EtOAc. ^e10 mol % **L-PiPr₃**/Ni(ClO₄)₂•6H₂O in 0.5 mL EtOAc. ^f10 mol % **L-PiPr₃**/Ni(ClO₄)₂•6H₂O in 0.3 mL EtOAc. ^g10 mol % **L-PiPr₃**/Ni(ClO₄)₂•6H₂O in 0.1 mL EtOAc.

(d) Screen of bases



entry ^a	base	yield (%) ^b	ee (%) ^c	yield (%) ^b	ee (%) ^c
1	Cs ₂ CO ₃	29 (2/98)	4	10	17
2	K ₂ CO ₃	32 (1/99)	5	42	11

3	$K_3PO_4 \cdot 7H_2O$	34 (2/98)	3	23	4
4	$NaHCO_3$	47 (95/5)	73	40	99
5	DMAP	92 (99/1)	-2	-	-
6	DIPEA	41 (93/7)	79	44	99
7	nBu_3N	68 (98/2)	37	37	99
8	Et_3N	50 (93/7)	93	46	98
9	Et_2NH	20 (96/4)	0	n.d.	-
10	TMEDA	82 (98/2)	4	n.d.	-

^aAll the reactions were performed with 10 mol % $Ni(ClO_4)_2 \cdot 6H_2O$, 10 mol % **L-PiPr₃, 1a** (0.1 mmol) and base (1.2 equiv) in EtOAc (0.3 mL) at 50 °C for 48 h. ^bIsolated yield, the ratio in the bracket represents the ratio of **1a** to **2a** according to chiral HPLC analysis. ^cDetermined by HPLC analysis on a chiral stationary phase.

(e) Screen of additives

entry ^a	additive	yield (%) ^b	ee (%) ^c	yield (%) ^b	ee (%) ^c
1 ^d	3 Å MS	49 (94/6)	76	39	98
2 ^d	4 Å MS	45 (79/21)	98/62	48	96
3 ^d	5 Å MS	46 (74/26)	97/60	44	98
4 ^e	$NaBArF_4$	42 (89/11)	85/50	46	88
5 ^e	$LiNTf_2$	32 (62/38)	97/53	47	60
6 ^f	H_2O	47 (94/6)	90	44	99

^aAll the reactions were performed with 10 mol % $Ni(ClO_4)_2 \cdot 6H_2O$, 10 mol % **L-PiPr₃, 1a** (0.1 mmol) and Et_3N (1.2 equiv) in EtOAc (0.3 mL) at 50 °C for 48 h. ^bIsolated yield, the ratio in the bracket represents the ratio of **1a** to **2a** according to HPLC analysis. ^cDetermined by HPLC analysis on a chiral stationary phase. ^d20.0 mg x Å MS. ^e10 mol %. ^f3.0 uL.

(f) Screen of other catalysts

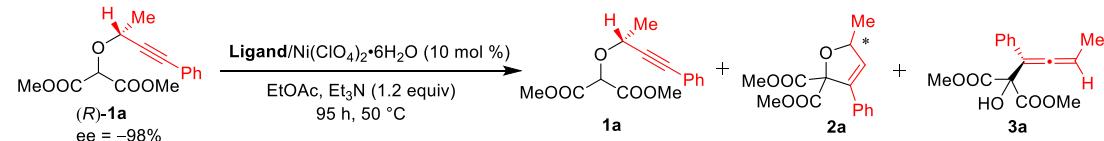
entry ^a	catalyst	base	yield (%) ^b	ee (%) ^c	yield (%) ^b	ee (%) ^c
1	G1	-	94 (99:1)	0	N.R.	-

2	G2	-	74 (99:1)	0	N.R.	-
3	G3	Et₃N	90 (99:1)	0	N.R.	-
4	G4	Et₃N	90 (99:1)	0	N.R.	-
5	G5	Et₃N	84 (99:1)	0	N.R.	-

^aAll the reactions were performed with 10 mol % catalyst, **1a** (0.1 mmol) and base (1.2 equiv) in EtOAc (0.3 mL)

at 50 °C for 48 h. ^bIsolated yield, the ratio in the bracket represents the ratio of **1a** to **2a** according to HPLC analysis. ^cDetermined by HPLC analysis on a chiral stationary phase.

(g) Reaction of (*R*)-4-phenylbut-3-yn-2-ol derived **1a**

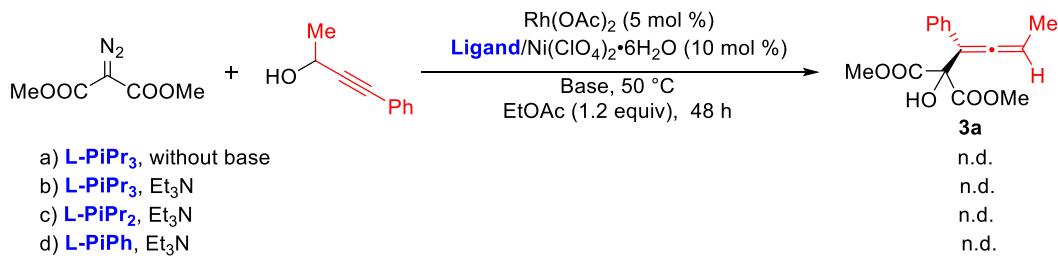


entry ^a	ligand	1a yield (%) ^b	1a ee (%) ^c	3a yield (%) ^b	3a ee (%) ^c
1	(<i>S</i>)- L-PiPr₃	38 (84/16)	-98	61	99
2	<i>ent</i> - L-PiPr₃	82 (92/8)	-98	7	82
3	<i>rac</i> - L-PiPr₃	42 (97/3)	-96	45	99

^aAll the reactions were performed with 10 mol % Ni(ClO₄)₂•6H₂O, 10 mol % ligand, (*R*)-**1a** (0.1 mmol) and Et₃N

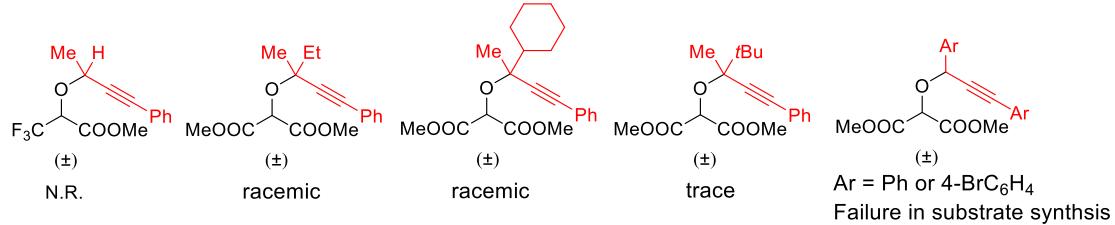
(1.2 equiv) in EtOAc (0.3 mL) at 50 °C for 95 h. ^bIsolated yield. ^cDetermined by HPLC analysis on a chiral stationary phase.

(h) The attempt of bimetallic rhodium(II)/nickel(III) relay catalysis^a

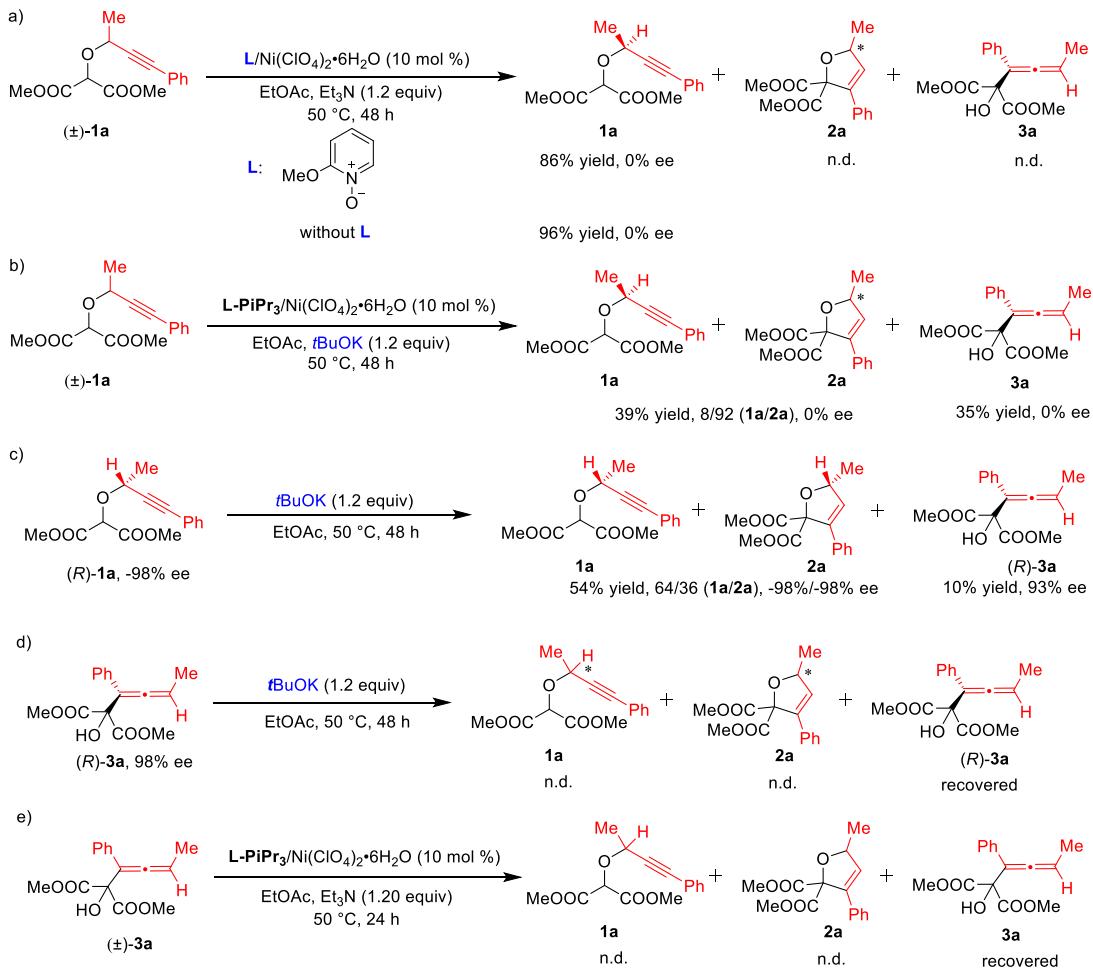


^aAll the reactions were performed with 10 mol % Ni(ClO₄)₂•6H₂O, 10 mol % ligand, and propargyl alcohol (0.11 mmol) in EtOAc (0.3 mL). Then, diazomalonate (0.1 mmol) and base (1.2 equiv) were added. The mixture was stirred at 50 °C for 48 h.

(i) Unsuccessful substrate scope



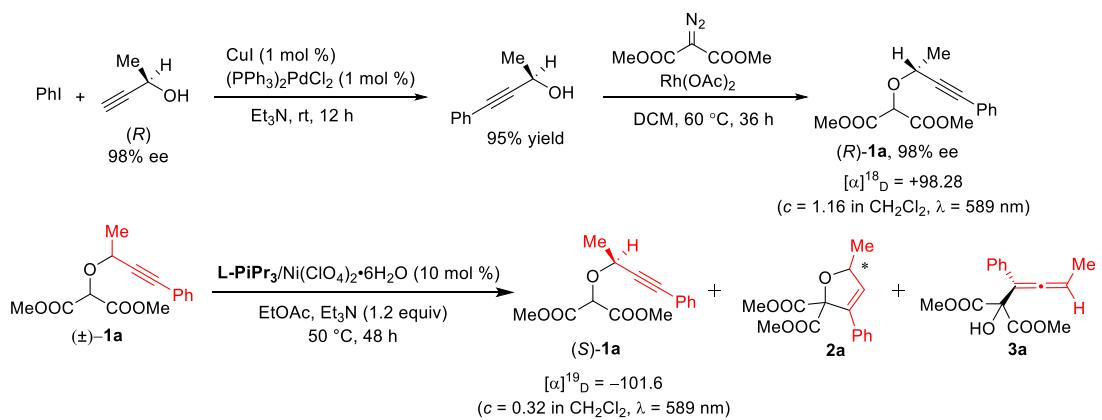
6. Control experiments



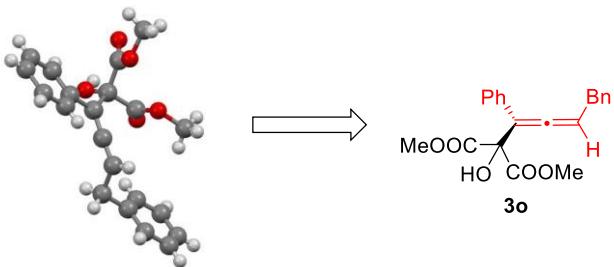
These results indicate that there is a strong ligand-accelerated catalysis (LAC) in current system. Preliminary studies indicated that **2a** was formed from starting material **1a** rather than rearrangement product **3a**. The yield of side product **2a** increased when strong bases are used, for example, *t*BuOK. Moreover, with **L-PiCHPh₂** as the ligand, (*S*)-**1a** preferably transformed into **2a**, in contrast, (*R*)-**1a** preferably rearranged into (*aR*)-**3a** (See SI Page S17 for details). At current stage, the exact pathway for the formation of **2a** was not sure, two possible routes were proposed, including conia-ene and carbanion nucleophilic attack to alkyne.

7. Determination of the absolute configuration of **1a** and **3a**

(a) The absolute configuration of recovered **1a** was (*S*) determined by comparison of the optical rotations with (+)-3-Butyn-2-ol (98% ee) derived **1a**.

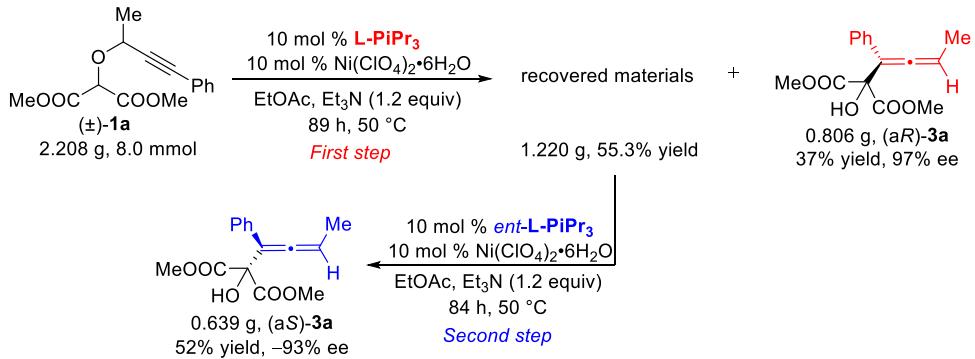


(b) The absolute configuration of **3o** was determined by X-ray chromatography analysis.



Single crystal of the rearrangement product **3o** [$C_{21}H_{20}O_5$] was obtained from the mixed solvents of *n*-hexane and dichloromethane. The absolute configuration of **3o** is (*aR*). CCDC 1951577 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

8. Experimental procedure for the scale-up reaction

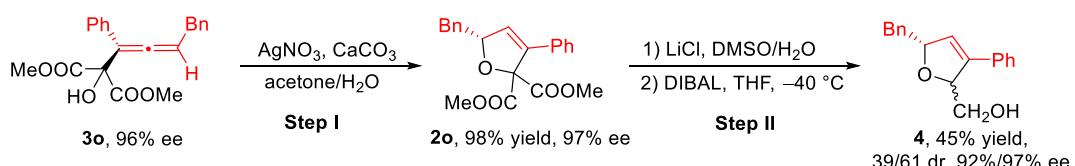


First Step: $Ni(ClO_4)_2 \cdot 6H_2O$ (288.0 mg, 0.80 mmol), **L-PiPr₃** (584.0 mg, 0.80 mmol), dimethyl 2-[(4-phenylbut-3-yn-2-yl)oxy]malonate **1a** (8.0 mmol) and ethyl acetate (20.0 mL) were added to a dry round-bottom flask. The resulting mixture was stirred for 30 min at 35 °C, Et_3N (1.2 equiv, 1.3 mL) was added. The reaction mixture was stirred at 50 °C for 89 hours. The solvent was removed in vacuo. The residue was directly purified by flash column chromatography (petroleum ether/ethyl acetate, 6:1, v/v) to afford the recovered material and (petroleum ether/ethyl acetate/dichloromethane, 3:1:0.5, v/v/v) to afford the desired product (*aR*)-**3a** (0.806 g, 37% yield, 97% ee).

97% ee).

Second Step: $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (159.0 mg, 4.42 mmol), *ent*-**L-PiPr₃** (322.0 mg, 4.42 mmol), the recovered material (1.220 g) and ethyl acetate (12.0 mL) were added to a dry round-bottom flask. The resulting mixture was stirred for 30 min at 35 °C, Et_3N (1.2 equiv, 729 μL) was added. The reaction mixture was stirred at 50 °C for 84 hours. The solvent was removed in vacuo. The residue was directly subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate/dichloromethane (6:1:0 and 3:1:0.5, v/v/v) to afford the desired product (*aS*)-**3a** (0.639 g, 52% yield, -93% ee).

9. Experimental procedure for synthesis of 4



Step I: A dry reaction tube was charged with the product **3o** (0.20 mmol, 70.4 mg, 96% ee), AgNO_3 (0.22 mmol, 37.4 mg) and CaCO_3 (0.40 mmol, 40.0 mg), then, acetone/ H_2O (4:1, v/v, 4.0 mL) was added at room temperature. The reaction mixture continued stirring at 25 °C for 24 h in the dark. Subsequently, the reaction was quenched with water and the mixture was diluted with dichloromethane. The layers were separated and the aqueous layer was extracted with dichloromethane, dried over Na_2SO_4 and concentrated. The residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (6:1, v/v) to afford the desired product **2o** (69.0 mg, 98% yield, 97% ee).

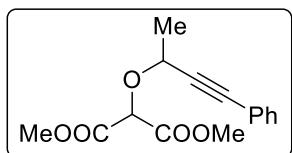
Step II: A dry reaction tube was charged with the product **2o** (69.0 mg, 97% ee), LiCl (0.42 mmol, 17.8 mg, 2.1 equiv), then, DMSO (0.6 mL) and H_2O (4 μL) were added at room temperature. The reaction mixture continued stirring in oil bath at 130 °C for 9 h. Subsequently, the reaction was cooled to room temperature, quenched with water and the mixture was diluted with dichloromethane. The layers were separated and the aqueous layer was extracted with dichloromethane, dried over Na_2SO_4 and concentrated. The residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20:1, v/v) to afford the de-esterification product (31.8 mg, 55% yield). The diastereomers could be isolated by flash chromatography.

To a solution of de-esterification product (31.8 mg, 0.11 mmol) in THF (2.0 mL) was added DIBAL (0.27 mmol, 2.5 equiv) at -40 °C. After stirring for 90 minutes at -40 °C, the reaction mixture was allowed warm to room temperature for an additional 30 minutes. Then, the reaction mixture was quenched with sat Rochelle's salts very slowly and extracted with diethyl ether. The combined organic layers were washed with brine, dried over Na_2SO_4 , evaporated in vacuo, and was purified by column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate = 6/1) to give **4** (23.6 mg, 82% yield, 39/61 d.r., 92%/97% ee). The diastereomers could be isolated by

flash chromatography and the total yield of the product **4** was 45% in two steps.

10. Characterization of typical substrates

Dimethyl 2-[(4-phenylbut-3-yn-2-yl)oxy]malonate (**1a**)

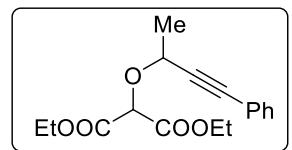


White solid, m.p. 62–64 °C; 1.10 g (40% yield); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 16/1/1); **1H NMR** (400 MHz, CDCl₃) δ = 7.49 – 7.39 (m, 2H), 7.36 – 7.27 (m, 3H), 5.00 (s, 1H), 4.69 (q, J = 6.8 Hz, 1H), 3.81 (d, J = 12.0 Hz, 6H), 1.64 (d, J = 6.4 Hz, 3H); **13C{1H} NMR** (101 MHz, CDCl₃) δ = 167.2, 166.7, 131.8, 128.7, 128.3, 122.0, 86.9, 86.7, 66.6, 53.0, 52.9, 22.0.

HRMS (ESI-TOF) calcd for C₁₅H₁₆NaO₅⁺ ([M+Na⁺]) = 299.0890, Found 299.0886.

IR (neat): (cm⁻¹) 2955, 1743, 1599, 1490, 1107, 1020, 917, 605, 550, 526, 488.

Diethyl 2-[(4-phenylbut-3-yn-2-yl)oxy]malonate (**1b**)

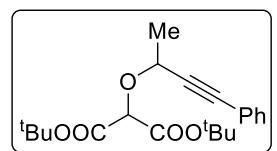


Pale yellow oil; 769 mg (25% yield); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 18/1/1); **1H NMR** (400 MHz, CDCl₃) δ = 7.47 – 7.40 (m, 2H), 7.35 – 7.28 (m, 3H), 4.95 (s, 1H), 4.70 (q, J = 6.8 Hz, 1H), 4.34 – 4.20 (m, 4H), 1.63 (d, J = 6.6 Hz, 3H), 1.29 (dt, J = 10.2, 7.2 Hz, 6H); **13C{1H} NMR** (101 MHz, CDCl₃) δ = 166.8, 166.3, 131.7, 128.6, 128.2, 122.0, 86.8, 86.7, 66.4, 61.9, 61.9, 21.9, 14.0, 13.9.

HRMS (ESI-TOF) calcd for C₁₇H₂₀KO₅ ([M+K⁺]) = 343.0942, Found 343.0933.

IR (neat): (cm⁻¹) 2936, 1740, 1446, 1109, 1024, 926, 854, 603, 551, 488.

Di-*tert*-butyl 2-[(4-phenylbut-3-yn-2-yl)oxy]malonate (**1c**)

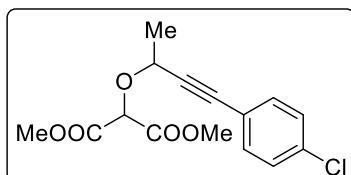


Colorless oil; 360 mg (10% yield); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 18/1/1); **1H NMR** (400 MHz, CDCl₃) δ = 7.47 – 7.41 (m, 2H), 7.34 – 7.27 (m, 3H), 4.74 (s, 1H), 4.66 (q, J = 6.8 Hz, 1H), 1.62 (d, J = 6.8 Hz, 3H), 1.49 (d, J = 10.0 Hz, 18H); **13C{1H} NMR** (101 MHz, CDCl₃) δ = 166.0, 165.3, 131.7, 128.4, 128.1, 122.3, 87.3, 86.2, 82.5, 82.4, 77.5, 65.8, 27.8, 27.8, 22.0.

HRMS (ESI-TOF) calcd for $C_{21}H_{28}NaO_5^+$ ($[M+Na^+]$) = 383.1829, Found 383.1828.

IR (neat): (cm^{-1}) 2940, 1742, 1456, 1108, 1025, 927, 850, 607, 553, 490.

Dimethyl 2-{{[4-(4-chlorophenyl)but-3-yn-2-yl]oxy}malonate (1d)}

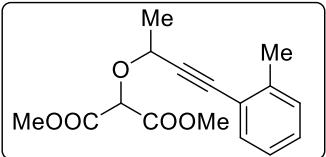


Colorless oil; 465 mg (15% yield); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 16/1/1); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ = 7.40 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 4.96 (s, 1H), 4.67 (q, J = 6.6 Hz, 1H), 3.81 (d, J = 12.4 Hz, 6H), 1.63 (d, J = 6.6 Hz, 3H); **$^{13}\text{C}\{^1\text{H}\} \text{NMR}$** (101 MHz, CDCl_3) δ = 167.0, 166.5, 134.7, 132.9, 128.5, 120.4, 87.7, 85.6, 76.3, 66.4, 52.9, 52.8, 21.8.

HRMS (ESI-TOF) calcd for $C_{15}H_{15}\text{ClNaO}_5^+$ ($[M+Na^+]$) = 333.0500 and 335.0471, Found 333.0495 and 335.0463.

IR (neat): (cm^{-1}) 2956, 2361, 1745, 1488, 1437, 1090, 829, 524.

Dimethyl 2-{{[4-(*o*-tolyl)but-3-yn-2-yl]oxy}malonate (1e)}

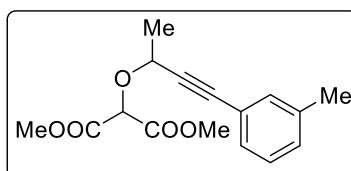


Colorless oil; 435 mg (15% yield); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 18/1/1); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ = 7.43 – 7.35 (m, 1H), 7.25 – 7.16 (m, 2H), 7.16 – 7.08 (m, 1H), 5.03 (s, 1H), 4.73 (q, J = 6.4 Hz, 1H), 3.79 (d, J = 14.8 Hz, 6H), 2.41 (s, 3H), 1.65 (d, J = 6.4 Hz, 3H); **$^{13}\text{C}\{^1\text{H}\} \text{NMR}$** (101 MHz, CDCl_3) δ = 167.3, 166.7, 140.3, 132.1, 129.5, 128.7, 125.5, 121.8, 90.6, 85.9, 66.7, 53.0, 52.9, 22.2, 20.6.

HRMS (ESI-TOF) calcd for $C_{16}H_{18}\text{NaO}_5^+$ ($[M+Na^+]$) = 313.1046, Found 313.1043.

IR (neat): (cm^{-1}) 2954, 2361, 1744, 1437, 1110, 1022, 605, 452.

Dimethyl 2-{{[4-(*m*-tolyl)but-3-yn-2-yl]oxy}malonate (1f)}



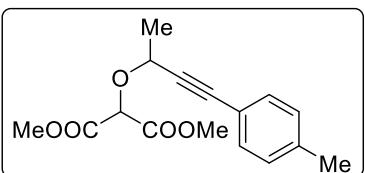
Colorless oil; 551 mg (19% yield); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 16/1/1); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ = 7.25 – 7.11

(m, 4H), 5.00 (s, 1H), 4.67 (q, $J = 6.4$ Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.32 (s, 3H), 1.62 (d, $J = 6.4$ Hz, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) $\delta = 167.3, 166.7, 138.0, 132.3, 129.6, 128.8, 128.2, 121.8, 87.1, 86.2, 66.6, 53.0, 52.9, 22.0, 21.2$.

HRMS (ESI-TOF) calcd for $\text{C}_{16}\text{H}_{18}\text{NaO}_5^+$ ($[\text{M}+\text{Na}^+]$) = 313.1046, Found 313.1047.

IR (neat): (cm^{-1}) 2955, 2362, 1745, 1602, 1438, 606.

Dimethyl 2-{{[4-(*p*-tolyl)but-3-yn-2-yl]oxy}malonate (1g)}

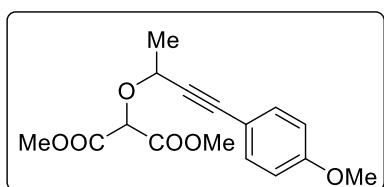


Pale yellow oil; 609 mg (21% yield); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 18/1/1); ^1H NMR (400 MHz, CDCl_3) $\delta = 7.32$ (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 5.00 (s, 1H), 4.67 (q, $J = 6.4$ Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.35 (s, 3H), 1.63 (d, $J = 6.4$ Hz, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) $\delta = 167.3, 166.8, 138.9, 131.7, 129.0, 118.9, 87.1, 86.0, 66.7, 53.0, 53.0, 52.9, 52.9, 22.0, 21.5$.

HRMS (ESI-TOF) calcd for $\text{C}_{16}\text{H}_{18}\text{NaO}_5^+$ ($[\text{M}+\text{Na}^+]$) = 313.1046, Found 313.1044.

IR (neat): (cm^{-1}) 2956, 2361, 1745, 1509, 1438, 1265, 1110, 604, 526.

Dimethyl 2-{{[4-(4-methoxyphenyl)but-3-yn-2-yl]oxy}malonate (1h)}

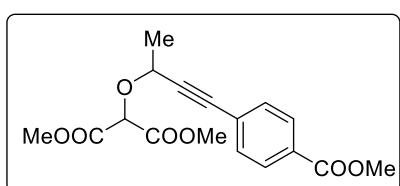


White solid, m.p. 57-59 °C; 1.0 g (33% yield); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 16/1/1); ^1H NMR (400 MHz, CDCl_3) $\delta = 7.37$ (d, $J = 8.4$ Hz, 2H), 6.84 (d, $J = 8.4$ Hz, 2H), 5.00 (s, 1H), 4.67 (q, $J = 6.4$ Hz, 1H), 3.86 – 3.75 (m, 9H), 1.62 (d, $J = 6.0$ Hz, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) $\delta = 167.3, 166.8, 159.9, 133.3, 114.1, 113.9, 87.0, 85.3, 66.7, 55.3, 52.9, 22.1$.

HRMS (ESI-TOF) calcd for $\text{C}_{16}\text{H}_{18}\text{NaO}_6^+$ ($[\text{M}+\text{Na}^+]$) = 329.0996, Found 329.0989.

IR (neat): (cm^{-1}) 2956, 2362, 1745, 1606, 1509, 1438, 1264, 1104, 1024, 605, 539.

Dimethyl 2-{{[4-(methoxycarbonyl)phenyl]but-3-yn-2-yl}oxy}malonate (1i)



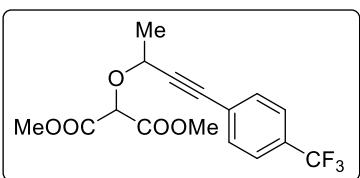
White solid, m.p. 56-58 °C; 501 mg (15% yield);

eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 16/1/1); **¹H NMR** (400 MHz, CDCl₃) δ = 7.98 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 1.6 Hz, 1H), 5.39 – 5.22 (m, 1H), 3.91 (s, 3H), 3.78 (d, *J* = 2.0 Hz, 6H), 1.46 (d, *J* = 6.8 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 168.6, 168.6, 166.6, 136.9, 136.2, 134.9, 129.7, 129.4, 127.7, 93.1, 83.7, 53.1, 53.0, 52.1, 21.1.

HRMS (ESI-TOF) calcd for C₁₇H₁₈NaO₇⁺ ([M+Na⁺]) = 357.0945, Found 357.0941.

IR (neat): (cm⁻¹) 2955, 2362, 1722, 1606, 1437, 1107, 1019, 919, 861, 612.

Dimethyl 2-(4-[4-(trifluoromethyl)phenyl]but-3-yn-2-yl)oxy)malonate (**1j**)

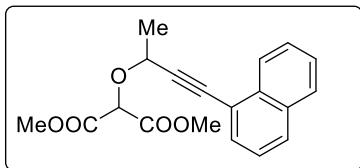


Colorless oil; 584 mg (17% yield); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 18/1/1); **¹H NMR** (400 MHz, CDCl₃) δ = 7.63 – 7.48 (m, 4H), 4.97 (s, 1H), 4.70 (q, *J* = 6.4 Hz, 1H), 3.82 (d, *J* = 11.6 Hz, 6H), 1.65 (d, *J* = 6.4 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 167.0, 166.5, 132.0, 130.4 (*J*_{C-F} = 65.0, 32.5 Hz), 127.8, 125.8 (*J*_{C-F} = 1.7), 125.2 (*J*_{C-F} = 7.5, 3.7 Hz), 122.4, 89.2, 85.4, 76.5, 66.5, 53.0, 52.9, 21.8. **¹⁹F{¹H} NMR** (376 MHz, CDCl₃) δ = -62.9 (s, 3F).

HRMS (ESI-TOF) calcd for C₁₆H₁₅F₃NaO₅⁺ ([M+Na⁺]) = 367.0764, Found 367.0760.

IR (neat): (cm⁻¹) 2959, 2362, 1746, 1616, 1440, 1325, 1125, 843, 602.

Dimethyl 2-{[4-(naphthalen-1-yl)but-3-yn-2-yl]oxy}malonate (**1k**)

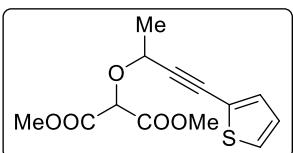


Pale yellow oil (the mixture of **1k** and 4-(naphthalen-1-yl)but-3-yn-2-ol, their ratio is 32/68 determined by **¹H NMR**, the mixture could not be separated); 456 mg (14% yield); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 18/1/1); **¹H NMR** (400 MHz, CDCl₃) δ = 8.35 – 7.33 (m, 7H), 5.11 (s, 1H), 4.84 (q, *J* = 6.6 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 1.74 (d, *J* = 6.4 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 167.2, 166.7, 133.1, 133.0, 130.8, 129.2, 128.2, 126.9, 126.4, 125.8, 95.9, 91.5, 66.9, 58.9, 52.9.

HRMS (ESI-TOF) calcd for C₁₉H₁₈NaO₅⁺ ([M+Na⁺]) = 349.1046, Found 349.1037.

IR (neat): (cm^{-1}) 2984, 2362, 1744, 1584, 1115, 1016, 595, 565, 527, 433.

Dimethyl 2-{{[4-(thiophen-2-yl)but-3-yn-2-yl]oxy}malonate (1l)}

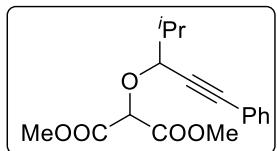


Brown solid, m.p. 49-51 °C; 366 mg (13% yield); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 18/1/1); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ = 7.28 (dd, J = 5.2, 1.2 Hz, 1H), 7.23 - 7.22 (m, 1H), 6.98 (dd, J = 5.2, 3.6 Hz, 1H), 4.96 (s, 1H), 4.69 (q, J = 6.8 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 1.63 (d, J = 6.8 Hz, 3H); **$^{13}\text{C}\{^1\text{H}\} \text{NMR}$** (101 MHz, CDCl_3) δ = 167.1, 166.6, 132.8, 127.7, 127.0, 121.8, 90.5, 80.2, 66.7, 53.0, 53.0, 53.0, 52.9, 21.8.

HRMS (ESI-TOF) calcd for $\text{C}_{13}\text{H}_{14}\text{NaO}_5\text{S}^+$ ($[\text{M}+\text{Na}^+]$) = 305.0454, Found 305.0441.

IR (neat): (cm^{-1}) 2955, 2361, 1745, 1437, 1109, 1021, 902, 605.

Dimethyl 2-[(4-methyl-1-phenylpent-1-yn-3-yl)oxy]malonate (1m)

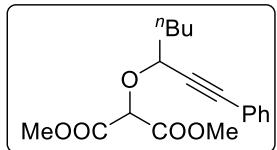


Pale yellow oil; 912 mg (30% yield); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 16/1/1); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ = 7.49 – 7.38 (m, 2H), 7.36 – 7.28 (m, 3H), 5.00 (s, 1H), 4.33 (d, J = 5.6 Hz, 1H), 3.80 (d, J = 14.0 Hz, 6H), 2.16 (dq, J = 13.4, 6.6 Hz, 1H), 1.14 – 1.05 (m, 6H); **$^{13}\text{C}\{^1\text{H}\} \text{NMR}$** (101 MHz, CDCl_3) δ = 167.4, 166.8, 131.8, 128.6, 128.3, 122.2, 88.3, 84.9, 76.6, 76.2, 52.9, 52.8, 33.2, 18.6, 17.7.

HRMS (ESI-TOF) calcd for $\text{C}_{17}\text{H}_{20}\text{NaO}_5^+$ ($[\text{M}+\text{Na}^+]$) = 327.1203, Found 327.1201.

IR (neat): (cm^{-1}) 2928, 2361, 1742, 1438, 1264, 1116.

Dimethyl 2-[(1-phenylhept-1-yn-3-yl)oxy]malonate (1n)



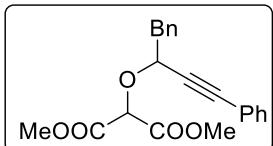
Colorless oil; 890 mg (28% yield); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 16/1/1); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ = 7.47 - 7.39 (m, 2H), 7.36 - 7.28 (m, 3H), 5.00 (s, 1H), 4.53 (t, J = 6.4 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.04 - 1.80 (m, 2H), 1.60 - 1.48 (m, 2H), 1.44 - 1.33 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); **$^{13}\text{C}\{^1\text{H}\} \text{NMR}$** (101

MHz, CDCl₃) δ = 167.3, 166.8, 131.8, 128.7, 128.3, 122.1, 87.6, 86.1, 70.9, 53.0, 52.9, 52.9, 35.3, 27.3, 22.3, 14.0.

HRMS (ESI-TOF) calcd for C₁₈H₂₂NaO₅⁺ ([M+Na⁺]) = 341.1359, Found 341.1340.

IR (neat): (cm⁻¹) 2957, 2362, 1746, 1438, 1114, 1021, 607.

Dimethyl 2-[(1,4-diphenylbut-3-yn-2-yl)oxy]malonate (**1o**)



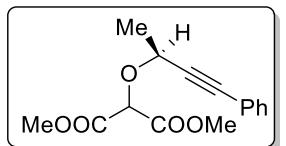
Pale yellow oil; 1.26 g (36% yield); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 16/1/1); **¹H NMR** (400 MHz, CDCl₃) δ = 7.41 – 7.33 (m, 4H), 7.33 – 7.21 (m, 6H), 4.99 (s, 1H), 4.74 (dd, *J* = 7.6, 6.0 Hz, 1H), 3.78 (d, *J* = 6.0 Hz, 6H), 3.30 (dd, *J* = 13.2, 5.6 Hz, 1H), 3.16 (dd, *J* = 13.6, 7.6 Hz, 1H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 167.0, 166.6, 136.3, 131.7, 129.8, 128.7, 128.2, 128.1, 126.8, 121.9, 88.8, 85.3, 76.5, 76.5, 71.8, 52.9, 52.9, 52.8, 52.8, 41.9.

HRMS (ESI-TOF) calcd for C₂₁H₂₀NaO₅⁺ ([M+Na⁺]) = 375.1203, Found 375.1202.

IR (neat): (cm⁻¹) 2954, 2361, 1744, 1600, 1492, 1437, 1119, 1022, 609, 568.

11. The analytical and spectral characterization data of recovered **1a** and the rearrangement products

Dimethyl (S)-2-[(4-phenylbut-3-yn-2-yl)oxy]malonate (recovered **1a**)

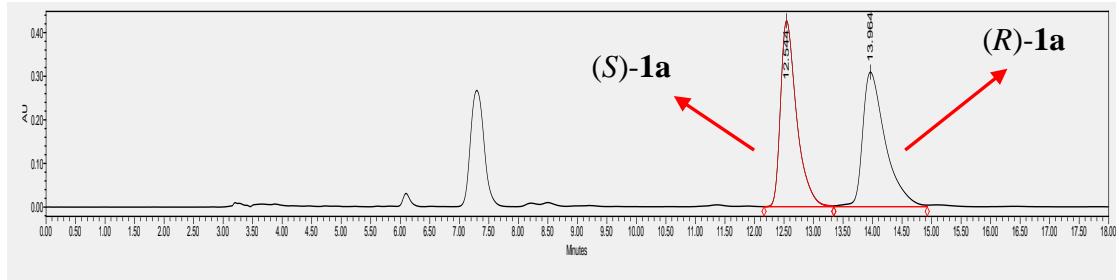


Colorless oil; at 50 °C for 48 h on 0.1 mmol scale; 50% yield (13.8 mg); eluted solvent (petroleum ether/ethyl acetate = 6/1); **HPLC** (Chiralcel **ID**, hexane/i-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm) *t_r* (major) = 12.68 min, *t_r* (minor) = 14.27 min, ee = 93%, [α]¹⁹D = -101.6 (*c* = 0.32 in CH₂Cl₂, λ = 589 nm).

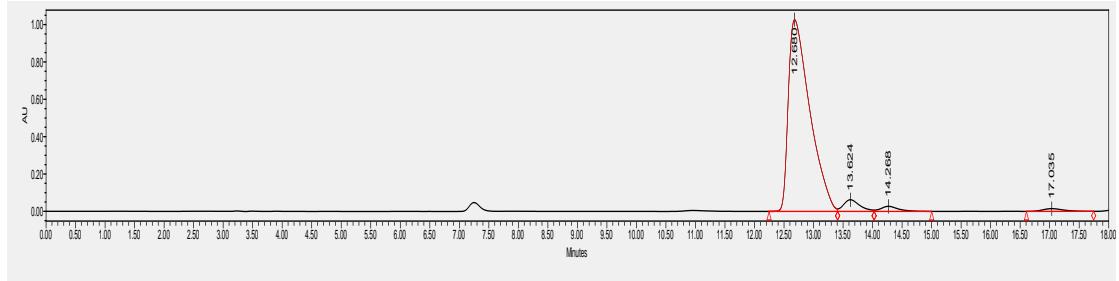
¹H NMR (400 MHz, CDCl₃) δ = 7.47 – 7.40 (m, 2H), 7.37 – 7.28 (m, 3H), 5.00 (s, 1H), 4.69 (q, *J* = 6.6 Hz, 1H), 3.81 (d, *J* = 12.1 Hz, 6H), 1.64 (d, *J* = 6.6 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 167.2, 166.7, 131.8, 128.7, 128.3, 122.0, 86.9, 86.7, 66.6, 53.0, 52.9, 22.0.

HRMS (ESI-TOF) calcd for C₁₅H₁₆NaO₅⁺ ([M+Na⁺]) = 299.0890, Found 299.0894.

IR (neat): (cm⁻¹) 2955, 2230, 1743, 1597, 1436, 1107, 1020, 917, 606, 551.

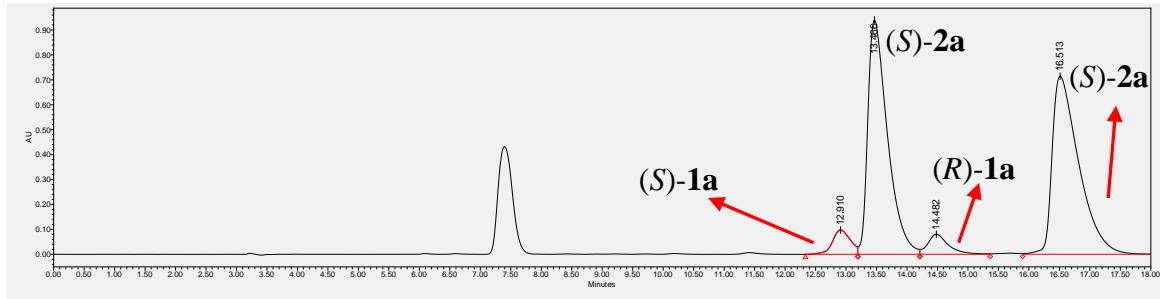


	Retention Time	Area	% Area
1	12.544	8064086	49.48
2	13.964	8233128	50.52

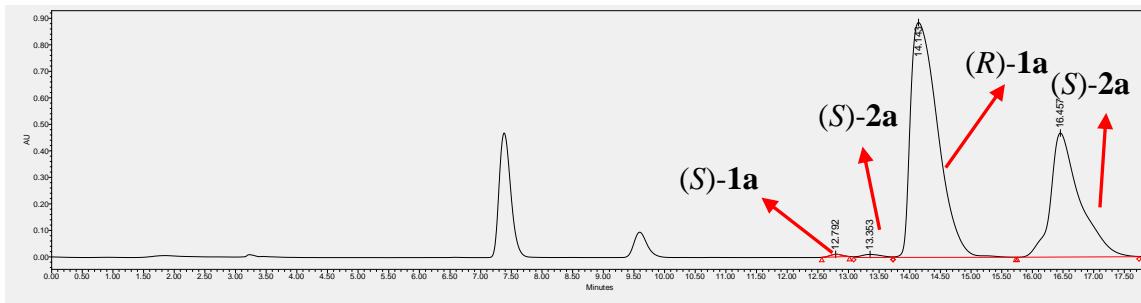


	Retention Time	Area	% Area
1	12.680	25911401	92.44
2	13.624	1199758	4.28
3	14.268	563549	2.01
4	17.035	354332	1.26

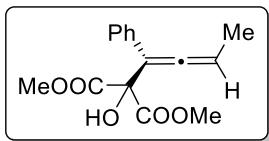
Recovered **1a** in control experiment b



Recovered **1a** in control experiment c



Dimethyl 2-hydroxy-2-(1-phenylbuta-1,2-dien-1-yl)malonate (3a)

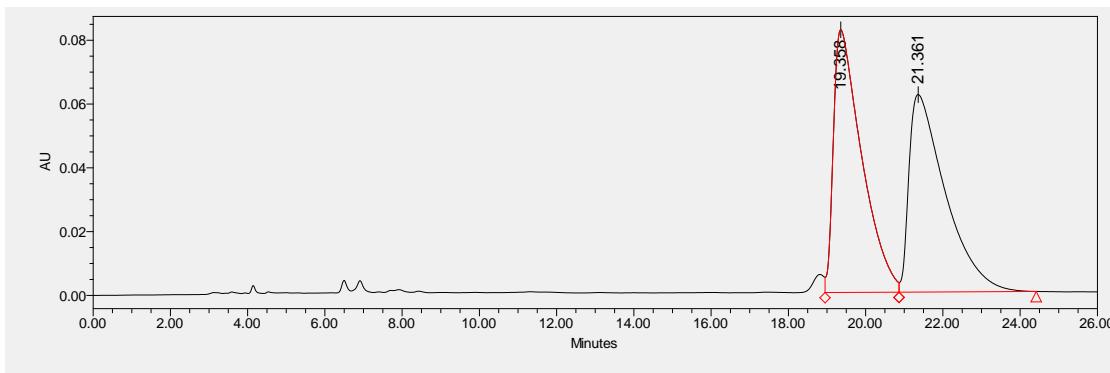


Colorless oil; at 50 °C for 48 h on 0.1 mmol scale; 46% yield (12.7 mg); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 3/1/0.5); **HPLC** (Chiralcel ID, hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 18.90 min, t_r (minor) = 21.98 min, ee = 97%, $[\alpha]^{18}_D$ = +8.66 (c = 2.06 in CH₂Cl₂, λ = 589 nm).

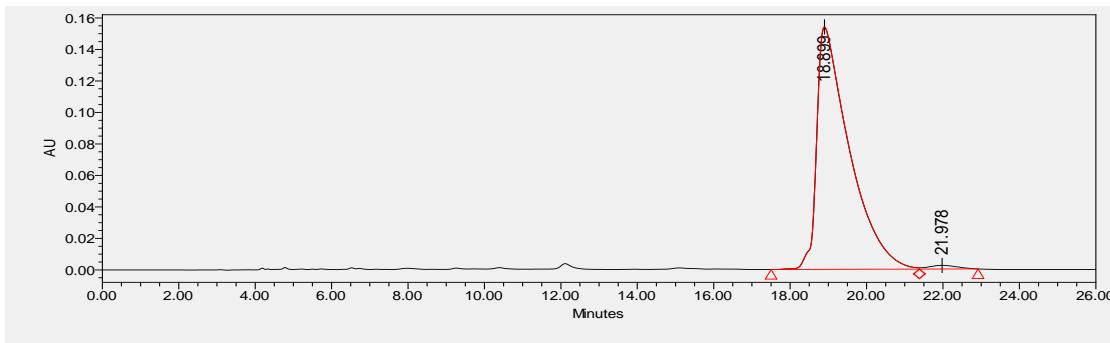
¹H NMR (400 MHz, CDCl₃) δ = 7.44 – 7.37 (m, 2H), 7.32 – 7.25 (m, 2H), 7.24 – 7.17 (m, 1H), 5.65 (q, J = 7.2 Hz, 1H), 4.11 (s, 1H), 3.79 (s, 6H), 1.79 (d, J = 7.2 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 205.4, 170.1, 169.9, 133.8, 128.3, 127.2, 127.1, 105.5, 91.8, 91.7, 81.9, 53.6, 53.6, 13.6.

HRMS (ESI-TOF) calcd for C₁₅H₁₆NaO₅⁺ ([M+Na⁺]) = 299.0890, Found 299.0880.

IR (neat): (cm⁻¹) 3479, 3057, 2361, 1742, 1438, 1114, 942, 623.

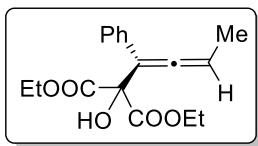


	Retention Time	Area	% Area
1	19.358	4179146	50.79
2	21.361	4049688	49.21



	Retention Time	Area	% Area
1	18.899	9122353	98.69
2	21.978	120857	1.31

Diethyl 2-hydroxy-2-(1-phenylbuta-1,2-dien-1-yl)malonate (3b)

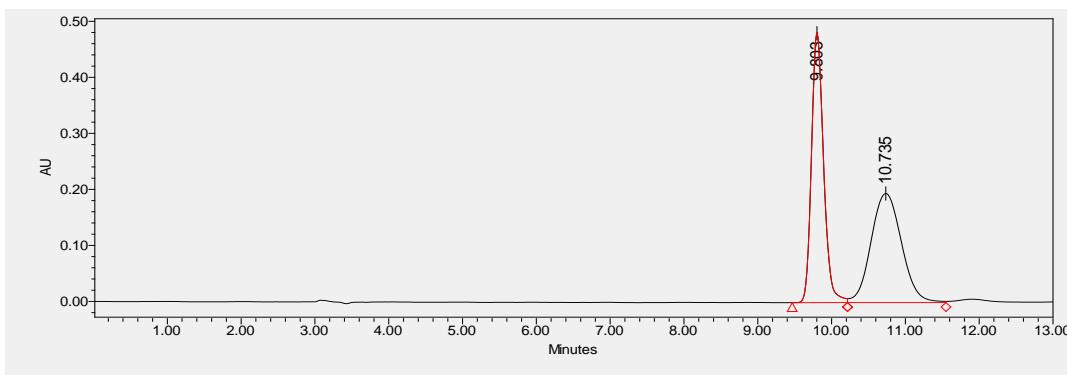


Colorless oil; at 50 °C for 30 h on 0.1 mmol scale; 39% yield (11.8 mg); eluted solvent (petroleum ether/ethyl acetate = 20/1); **HPLC** (Chiralcel IH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 9.83 min, t_r (minor) = 10.91 min, ee = 99%, $[\alpha]^{20}_D$ = +62.17 (c = 0.23 in CH₂Cl₂, λ = 589 nm).

¹H NMR (400 MHz, CDCl₃) δ = 7.48 – 7.38 (m, 2H), 7.33 – 7.26 (m, 2H), 7.23 – 7.16 (m, 1H), 5.63 (q, J = 7.2 Hz, 1H), 4.30 – 4.17 (m, 4H), 4.12 (s, 1H), 1.79 (d, J = 7.2 Hz, 3H), 1.21 (td, J = 7.2, 5.4 Hz, 6H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 205.5, 169.6, 169.5, 134.2, 128.2, 127.3, 127.1, 105.5, 91.6, 81.6, 62.8, 62.8, 13.9, 13.8, 13.7.

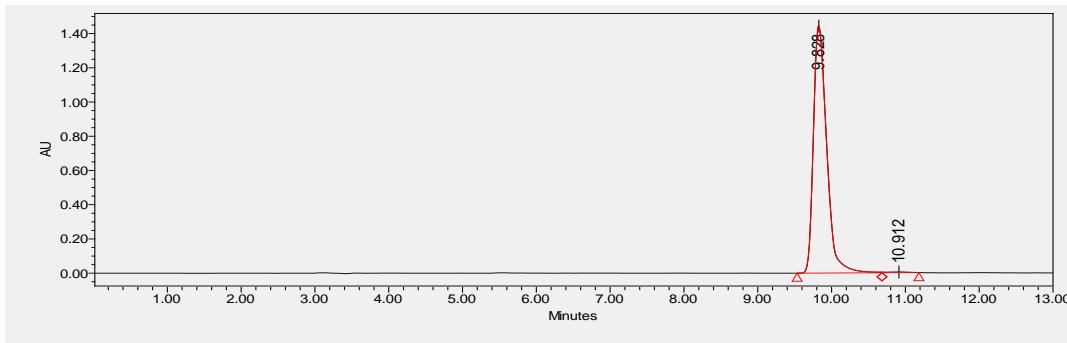
HRMS (ESI-TOF) calcd for C₁₇H₂₀NaO₅ ([M+Na⁺]) = 327.1203, Found 327.1200.

IR (neat): (cm⁻¹) 3465, 2955, 1800, 1719, 1437, 1112, 1022, 963, 863, 503.



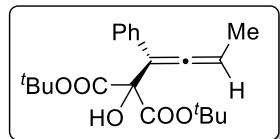
	Retention Time	Area	% Area
1	9.803	5493052	49.57

2	10.735	5587872	50.43
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	Retention Time	Area	% Area
1	9.828	18053126	99.48
2	10.912	93523	0.52

Di-*tert*-butyl 2-hydroxy-2-(1-phenylbuta-1,2-dien-1-yl)malonate (3c)

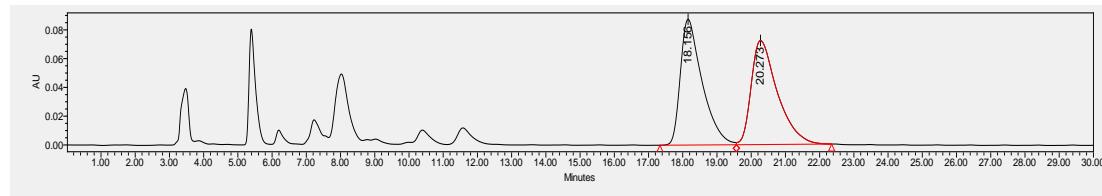


Colorless oil; at 50 °C for 96 h on 0.1 mmol scale; 22% yield (7.9 mg); eluted solvent (petroleum ether/ethyl acetate = 20/1); **HPLC** (Chiralcel **ID**, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 18.00 min, t_r (minor) = 20.27 min, ee = 99%, $[\alpha]^{16}_D$ = 43.20 (c = 0.22 in CH₂Cl₂, λ = 589 nm).

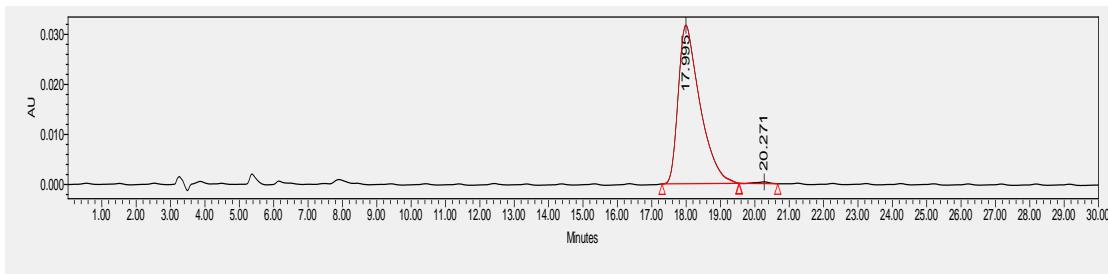
¹H NMR (400 MHz, CDCl₃) δ = 7.51 – 7.41 (m, 2H), 7.30 – 7.25 (m, 2H), 7.22 – 7.14 (m, 1H), 5.57 (q, J = 7.2 Hz, 1H), 4.15 (s, 1H), 1.80 (d, J = 7.2 Hz, 3H), 1.40 (d, J = 4.2 Hz, 18H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 205.5, 168.6, 168.6, 135.2, 128.0, 127.5, 126.8, 106.0, 91.0, 83.3, 83.1, 81.3, 27.6, 14.0.

HRMS (ESI-TOF) calcd for C₂₁H₂₈NaO₅⁺ ([M+Na⁺]) = 383.1829, Found 383.1838.

IR (neat): (cm⁻¹) 3315, 2927, 2362, 1742, 1600, 1443, 1102, 568, 509.

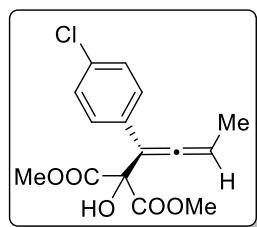


	Retention Time	Area	% Area
1	18.156	3856295	50.07
2	20.273	3844918	49.93



	Retention Time	Area	% Area
1	17.995	1386130	99.35
2	20.271	9055	0.65

Dimethyl 2-[1-(4-chlorophenyl)buta-1,2-dien-1-yl]-2-hydroxymalonate (3d)

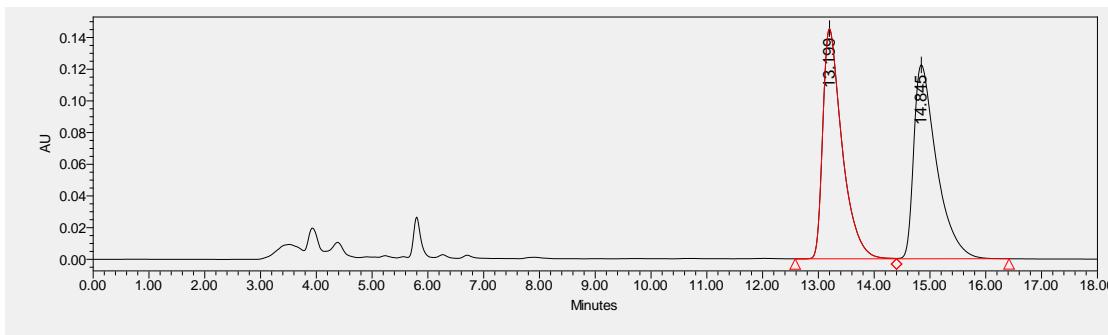


White solid, m.p. 90–92 °C; at 50 °C for 72 h on 0.2 mmol scale; 47% yield (29.1 mg); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 3/1/0.5); **HPLC** (Chiralcel **ID**, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 13.06 min, t_r (minor) = 15.18 min, ee = 95%, $[\alpha]^{17}_D = -7.59$ ($c = 0.22$ in CH_2Cl_2 , $\lambda = 589$ nm).

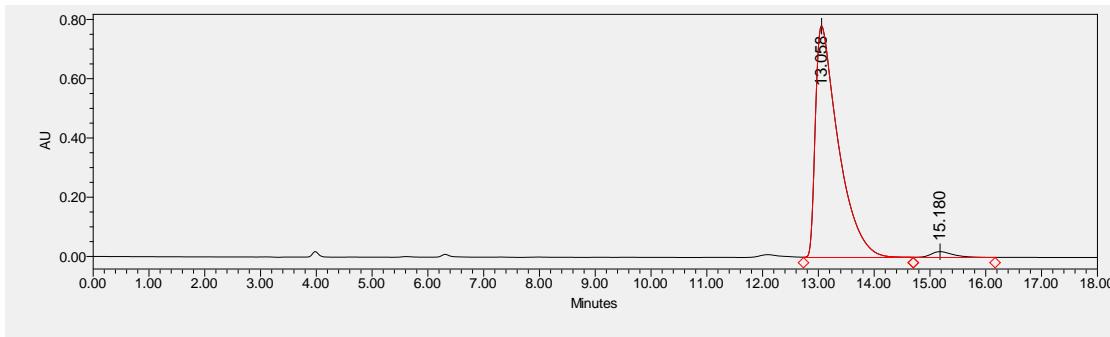
¹H NMR (400 MHz, CDCl_3) δ = 7.35 (d, J = 8.8 Hz, 2H), 7.29 – 7.21 (m, 2H), 5.66 (q, J = 7.2 Hz, 1H), 4.12 (s, 1H), 3.79 (s, 6H), 1.79 (d, J = 7.2 Hz, 3H); **¹³C{¹H}** NMR (101 MHz, CDCl_3) δ = 205.4, 169.8, 169.7, 133.0, 132.4, 128.5, 128.4, 104.7, 92.2, 81.8, 53.6, 13.5.

HRMS (ESI-TOF) calcd for $\text{C}_{15}\text{H}_{15}\text{ClNaO}_5^+$ ($[\text{M}+\text{Na}^+]$) = 333.0500 and 335.0471, Found 333.0506 and 335.0472.

IR (neat): (cm^{-1}) 3470, 3060, 23619, 1745, 1430, 1110, 950, 620, 488.

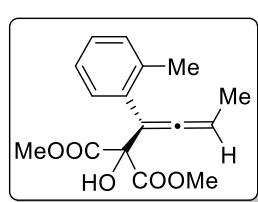


	Retention Time	Area	% Area
1	13.199	3478193	50.04
2	14.845	3471988	49.96



	Retention Time	Area	% Area
1	13.058	22240869	97.55
2	15.180	559127	2.45

Dimethyl 2-hydroxy-2-[1-(*o*-tolyl)buta-1,2-dien-1-yl]malonate (3e)

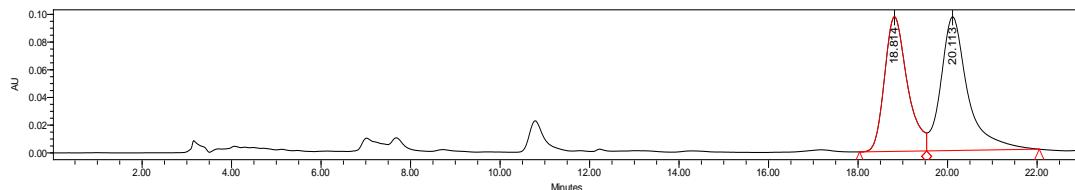


Colorless oil; at 50 °C for 166 h on 0.1 mmol scale; 44% yield (12.7 mg); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 3/1/0.5); **HPLC** (Chiralcel **ADH**, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 18.76 min, t_r (minor) = 21.40 min, ee = 99%, $[\alpha]^{20}_D$ = +24.88 (c = 0.40 in CH₂Cl₂, λ = 589 nm).

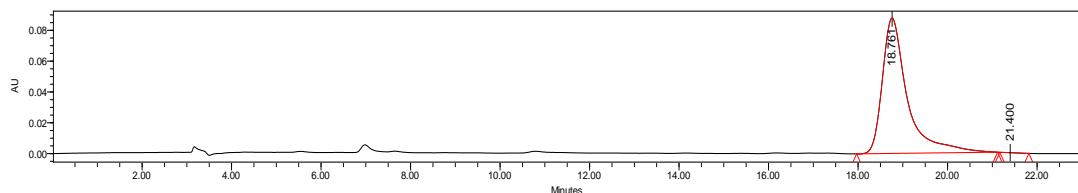
¹H NMR (400 MHz, CDCl₃) δ = 7.42 – 7.37 (m, 1H), 7.22 – 7.09 (m, 3H), 5.40 (q, J = 7.2 Hz, 1H), 4.02 (s, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 2.37 (s, 3H), 1.74 (d, J = 7.2 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 204.9, 169.9, 169.6, 137.5, 133.2, 130.3, 128.8, 127.7, 125.5, 102.0, 89.5, 82.2, 53.5, 53.4, 20.4, 13.0.

HRMS (ESI-TOF) calcd for C₁₆H₁₈NaO₅⁺ ([M+Na⁺]) = 313.1046, Found 313.1044.

IR (neat): (cm⁻¹) 3477, 2954, 2362, 1737, 1436, 1114, 1025, 941, 623, 450.

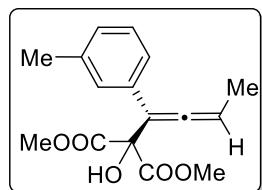


	Retention Time	Area	% Area
1	18.814	3436267	48.13
2	20.113	4012795	51.87



	Retention Time	Area	% Area
1	18.761	3402478	99.98
2	21.400	671	0.02

Dimethyl 2-hydroxy-2-[1-(*m*-tolyl)buta-1,2-dien-1-yl]malonate (3f)

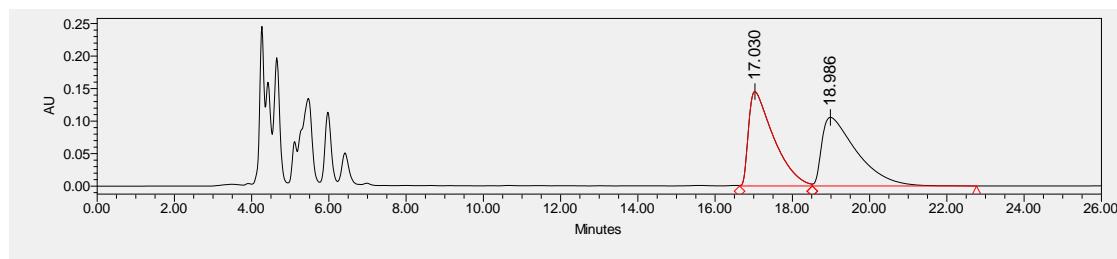


Colorless oil; at 50 °C for 166 h on 0.2 mmol scale; 43% yield (24.9 mg); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 3/1/0.5); **HPLC** (Chiralcel ID, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 16.60 min, t_r (minor) = 19.75 min, ee = 98%, $[\alpha]^{17}_D = -10.04$ ($c = 0.48$ in CH₂Cl₂, $\lambda = 589$ nm).

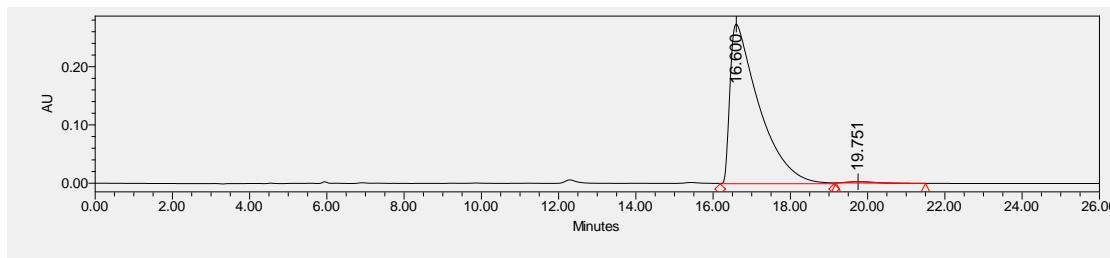
¹H NMR (400 MHz, CDCl₃) δ = 7.24 – 7.12 (m, 3H), 7.06 – 6.97 (m, 1H), 5.64 (q, J = 7.2 Hz, 1H), 4.10 (s, 1H), 3.83 – 3.73 (m, 6H), 2.34 – 2.28 (m, 3H), 1.79 (d, J = 7.2 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 205.4, 170.1, 169.9, 137.8, 133.6, 128.2, 128.0, 127.9, 124.2, 105.5, 91.6, 82.0, 53.6, 53.5, 21.5, 13.6.

HRMS (ESI-TOF) calcd for C₁₆H₁₈NaO₅⁺ ([M+Na⁺]) = 313.1046, Found 313.1036.

IR (neat): (cm⁻¹) 3475, 2987, 1743, 1607, 1438, 1117.

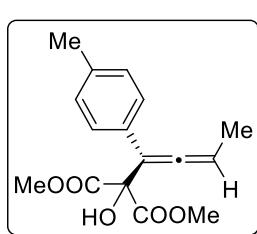


	Retention Time	Area	% Area
1	17.030	6567886	49.81
2	18.986	6618443	50.19



	Retention Time	Area	% Area
1	16.600	14307792	99.27
2	19.751	105302	0.73

Dimethyl 2-hydroxy-2-[1-(*p*-tolyl)buta-1,2-dien-1-yl]malonate (3g)

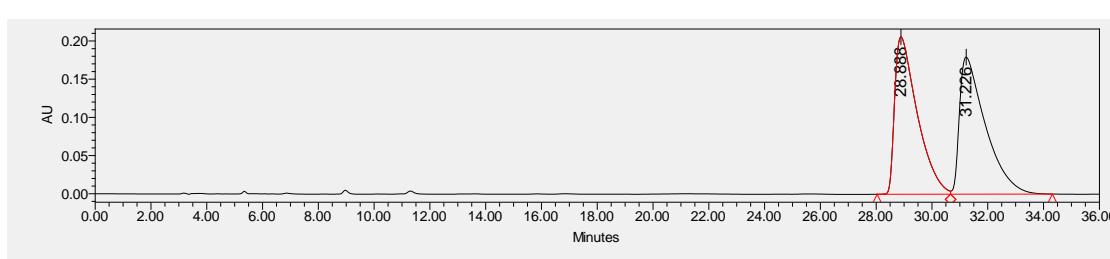


Colorless oil; at 50 °C for 166 h on 0.1 mmol scale; 45% yield (13.1 mg); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 3/1/0.5); **HPLC** (Chiralcel ID, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 28.41 min, t_r (minor) = 32.09 min, ee = 97%, $[\alpha]^{18}\text{D}$ = +12.07 (c = 0.46 in CH_2Cl_2 , λ = 589 nm).

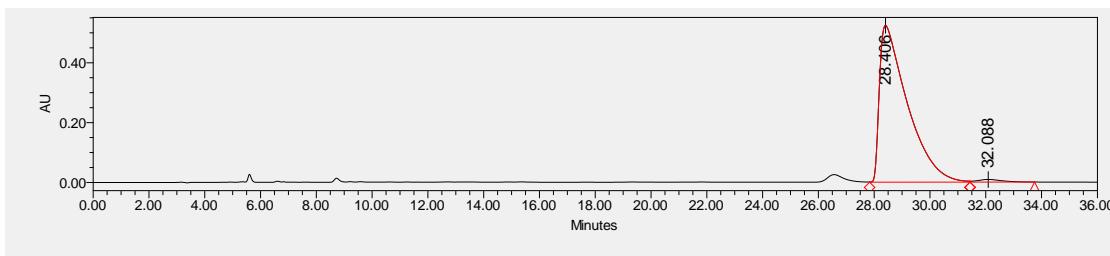
¹H NMR (400 MHz, CDCl_3) δ = 7.32 – 7.27 (m, 2H), 7.12 – 7.05 (m, 2H), 5.63 (q, J = 7.2 Hz, 1H), 4.09 (s, 1H), 3.83 – 3.73 (m, 6H), 2.31 (s, 3H), 1.78 (d, J = 6.8 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl_3) δ = 205.2, 170.1, 169.9, 136.9, 130.7, 129.0, 127.1, 105.4, 91.6, 91.6, 82.0, 53.6, 53.5, 21.1, 13.7.

HRMS (ESI-TOF) calcd for $\text{C}_{16}\text{H}_{18}\text{NaO}_5^+$ ([M+Na⁺]) = 313.1046, Found 313.1043.

IR (neat): (cm^{-1}) 3466, 2954, 2361, 1740, 1609, 1437, 1112, 821, 594, 513.

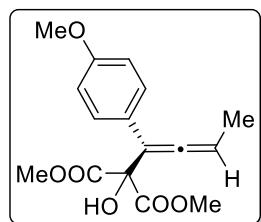


	Retention Time	Area	% Area
1	28.888	11541580	49.90
2	31.226	11587305	50.10



	Retention Time	Area	% Area
1	28.406	36336616	98.58
2	32.088	522240	1.42

Dimethyl 2-hydroxy-2-[1-(4-methoxyphenyl)buta-1,2-dien-1-yl]malonate (3h)

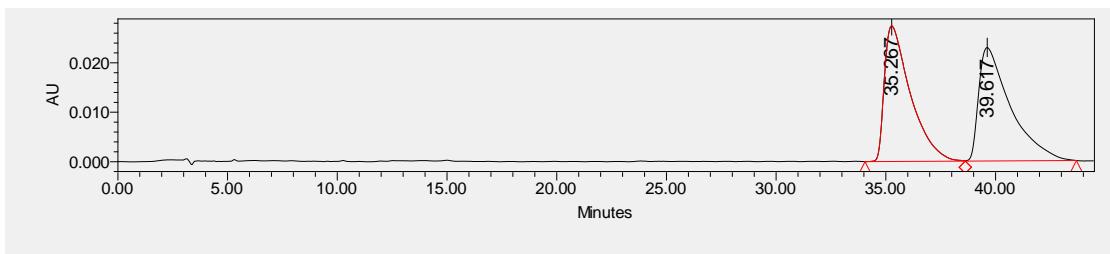


Colorless oil; at 50 °C for 30 h on 0.1 mmol scale; 42% yield (12.8 mg); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 3/1/0.5); **HPLC** (Chiralcel ID, hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 34.07 min, t_r (minor) = 40.96 min, ee = 98%, $[\alpha]^{20}_D$ = +57.36 (c = 0.26 in CH₂Cl₂, λ = 589 nm).

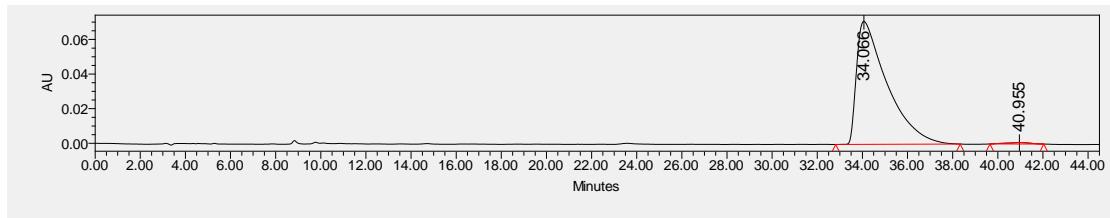
¹H NMR (400 MHz, CDCl₃) δ = 7.33 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 5.62 (q, J = 7.2 Hz, 1H), 4.08 (s, 1H), 3.79 (s, 9H), 1.77 (d, J = 7.2 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 204.9, 170.1, 169.9, 158.7, 128.5, 125.9, 113.8, 105.1, 91.5, 82.0, 55.2, 53.6, 13.8.

HRMS (ESI-TOF) calcd for C₁₆H₁₈NaO₆⁺ ([M+Na⁺]) = 329.0996, Found 329.0995.

IR (neat): (cm⁻¹) 3466, 2954, 2361, 1738, 1606, 1510, 1438, 1180, 1027, 964, 939, 598, 528.

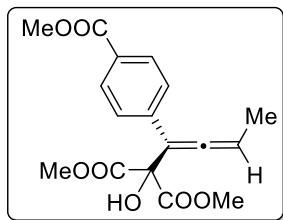


	Retention Time	Area	% Area
1	35.267	2260136	49.48
2	39.617	2307384	50.52



	Retention Time	Area	% Area
1	34.066	6676651	99.08
2	40.955	62115	0.92

Dimethyl 2-hydroxy-2-{1-[4-(methoxycarbonyl)phenyl]buta-1,2-dien-1-yl} malonate (3i)

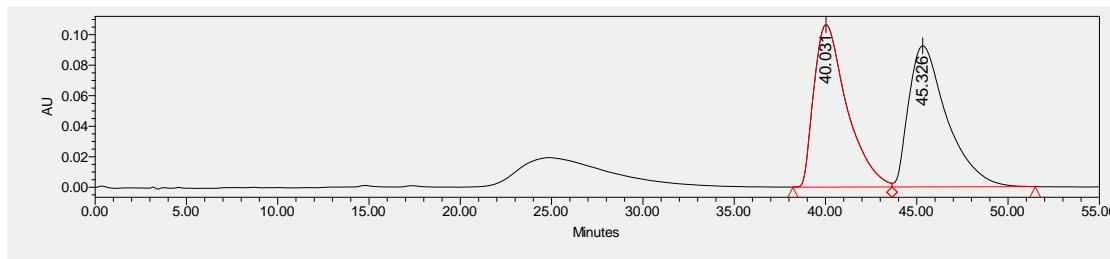


White solid, m.p. 94–96 °C; at 50 °C for 96 h on 0.2 mmol scale; 42% yield (14.0 mg); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 3/1/0.5); **HPLC** (Chiralcel **ID**, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, $\lambda = 254$ nm) t_r (major) = 39.24 min, t_r (minor) = 45.59 min, ee = 94%, $[\alpha]^{18}_D = +34.73$ ($c = 0.62$ in CH_2Cl_2 , $\lambda = 589$ nm).

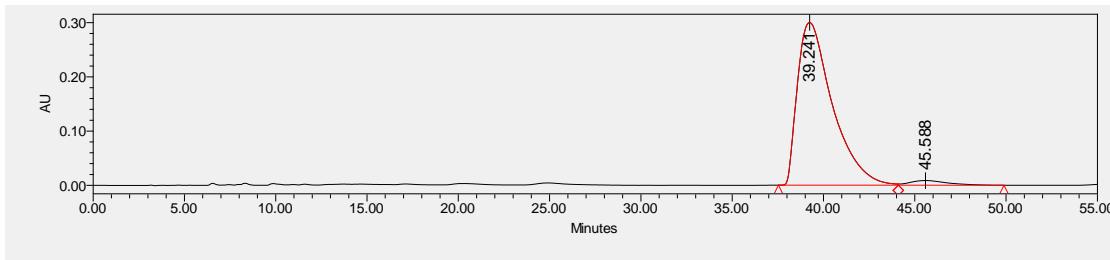
¹H NMR (400 MHz, CDCl_3) δ = 8.01 – 7.87 (m, 2H), 7.53 – 7.43 (m, 2H), 5.72 (q, J = 7.2 Hz, 1H), 4.22 (s, 1H), 3.90 (s, 3H), 3.79 (s, 6H), 1.81 (d, J = 7.2 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl_3) δ = 206.1, 169.8, 169.7, 166.8, 138.8, 129.5, 128.6, 126.9, 105.2, 92.5, 92.4, 81.7, 53.7, 53.6, 52.1, 52.0, 13.4.

HRMS (ESI-TOF) calcd for $\text{C}_{17}\text{H}_{18}\text{NaO}_7^+$ ([M+Na⁺]) = 357.0945, Found 357.0943.

IR (neat): (cm^{-1}) 3459, 2955, 1951, 1716, 1606, 1436, 1109, 1020, 862, 774, 636, 504.

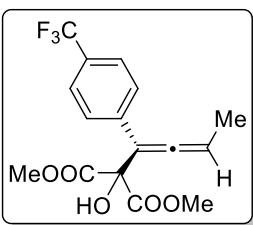


	Retention Time	Area	% Area
1	40.031	13306242	49.72
2	45.326	13458698	50.28



	Retention Time	Area	% Area
1	39.241	39918557	97.04
2	45.588	1217776	2.96

Dimethyl 2-hydroxy-2-{1-[4-(trifluoromethyl)phenyl]buta-1,2-dien-1-yl}malonate (3j)

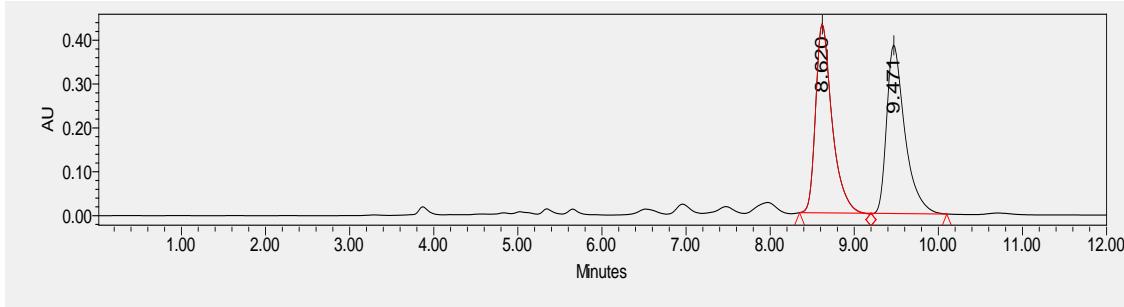


Colorless oil; at 50 °C for 136 h on 0.1 mmol scale; 44% yield (15.1 mg); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 3/1/0.5); **HPLC** (Chiralcel ID, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 8.60 min, t_r (minor) = 9.47 min, ee = 91%, $[\alpha]^{22}_{\text{D}} = +38.73$ ($c = 0.20$ in CH_2Cl_2 , $\lambda = 589$ nm).

¹H NMR (400 MHz, CDCl_3) δ = 7.53 (s, 4H), 5.72 (q, J = 7.2 Hz, 1H), 4.17 (s, 1H), 3.80 (s, 6H), 1.81 (d, J = 7.2 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl_3) δ = 206.0, 169.8, 169.6, 137.8, 129.0 ($J_{\text{C}-\text{F}} = 32.0$ Hz), 127.4, 125.5, 125.2 ($J_{\text{C}-\text{F}} = 8.0, 4.0$ Hz), 122.8, 104.8, 92.5, 81.7, 53.7, 13.4. **¹⁹F{¹H} NMR** (376 MHz, CDCl_3) δ = -62.9 (s, 3F).

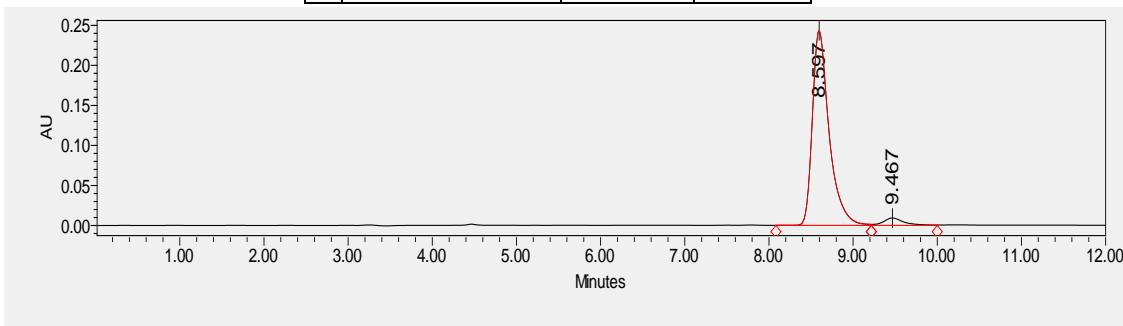
HRMS (ESI-TOF) calcd for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{NaO}_5^+$ ($[\text{M}+\text{Na}^+]$) = 367.0764. Found 367.0766.

IR (neat): (cm^{-1}) 3468, 2957, 1740, 1616, 1437, 1323, 1110, 1064, 1018, 963, 846, 632, 489.



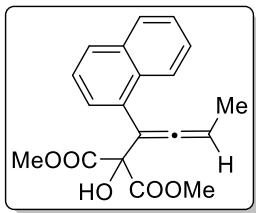
	Retention Time	Area	% Area
1	8.620	5846285	50.36

2	9.471	5762226	49.64
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	Retention Time	Area	% Area
1	8.597	3353786	95.42
2	9.467	161113	4.58

Dimethyl 2-hydroxy-2-[1-(naphthalen-1-yl)buta-1,2-dien-1-yl]malonate (3k)

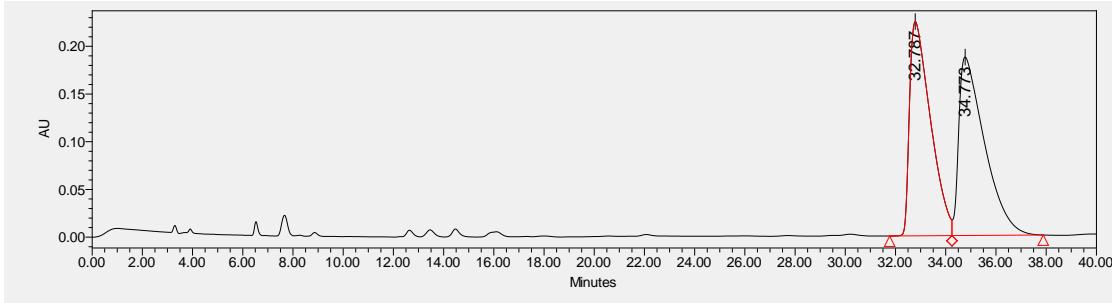


Colorless oil; at 50 °C for 136 h on 0.2 mmol scale; 38% yield (24.7 mg, yield based on the amount of 1-Nap substrate); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 3/1/0.5); **HPLC** (Chiralcel ID, hexane/i-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 32.93 min, t_r (minor) = 35.65 min, ee = 90%, $[\alpha]^{20}_D = -8.80$ ($c = 0.25$ in CH₂Cl₂, $\lambda = 589$ nm).

¹H NMR (400 MHz, CDCl₃) δ = 8.23 (d, J = 8.4 Hz, 1H), 7.87 – 7.73 (m, 2H), 7.63 (dd, J = 7.2, 1.2 Hz, 1H), 7.55 – 7.37 (m, 3H), 5.48 (q, J = 6.8 Hz, 1H), 4.06 (s, 1H), 3.73 (d, J = 21.2 Hz, 6H), 1.78 (d, J = 7.2 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 205.7, 169.8, 169.6, 133.8, 132.4, 131.4, 128.3, 128.1, 127.0, 126.0, 125.9, 125.6, 125.1, 101.0, 89.7, 82.3, 53.5, 13.2.

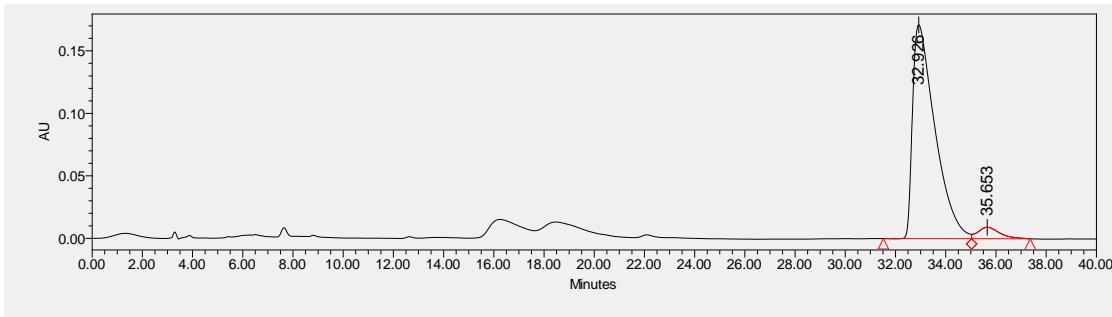
HRMS (ESI-TOF) calcd for C₁₉H₁₈NaO₅⁺ ([M+Na⁺]) = 349.1046, Found 349.1035.

IR (neat): (cm⁻¹) 3471, 2952, 2362, 1962, 1735, 1591, 1436, 1115, 1029, 653, 609, 540, 429.



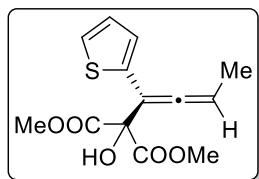
	Retention Time	Area	% Area
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1	32.787	12976939	49.33
2	34.773	13331955	50.67



	Retention Time	Area	% Area
1	32.926	10620604	95.02
2	35.653	557019	4.98

Dimethyl 2-hydroxy-2-[1-(thiophen-2-yl)buta-1,2-dien-1-yl]malonate (3l)

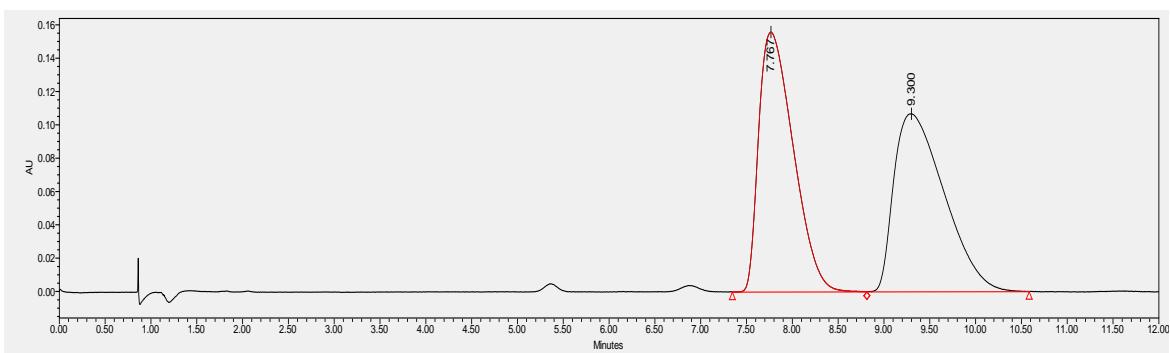


Pale brown oil; at 50 °C for 64 h on 0.2 mmol scale; 49% yield (27.6 mg); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 3/1/0.5); SFC (UPC² Daicel CHIRALPAK AD, CO₂/CH₃OH = 96/4, flow rate = 1.5 mL/min, λ = 254 nm) t_R (major) = 7.54 min, t_R (minor) = 9.20 min, ee = 95%, $[\alpha]^{20}_D$ = +7.80 (c = 0.28 in CH₂Cl₂, λ = 589 nm).

¹H NMR (400 MHz, CDCl₃) δ = 7.18 (dd, J = 5.2, 1.2 Hz, 1H), 7.06 – 6.99 (m, 1H), 6.97 – 6.88 (m, 1H), 5.67 (q, J = 7.2 Hz, 1H), 4.10 (s, 1H), 3.81 (d, J = 1.6 Hz, 6H), 1.79 (d, J = 7.2 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 204.5, 169.6, 169.5, 136.5, 127.3, 125.3, 125.0, 101.0, 92.4, 81.8, 53.6, 13.7.

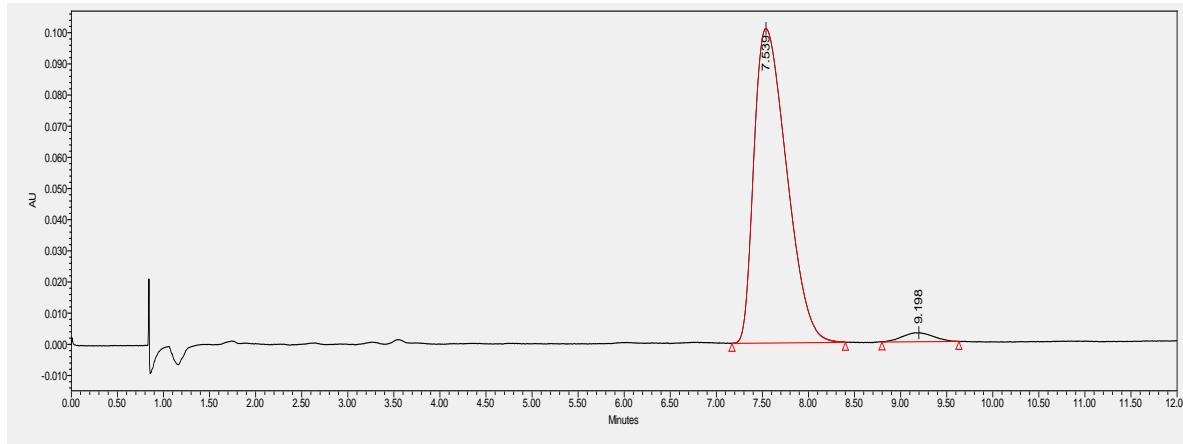
HRMS (ESI-TOF) calcd for C₁₃H₁₄NaO₅S⁺ ([M+Na⁺]) = 305.0454, Found 305.0452.

IR (neat): (cm⁻¹) 3467, 2361, 1741, 1432, 1100, 829.



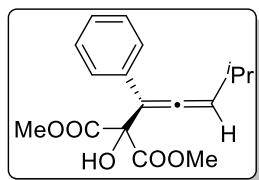
	Retention Time	Area	% Area
1	7.767	4101407	50.10

2	9.300	4085531	49.90
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	Retention Time	Area	% Area
1	7.539	2481626	97.33
2	9.198	68009	2.67

Dimethyl 2-hydroxy-2-(4-methyl-1-phenylpenta-1,2-dien-3-yl)malonate (3m)

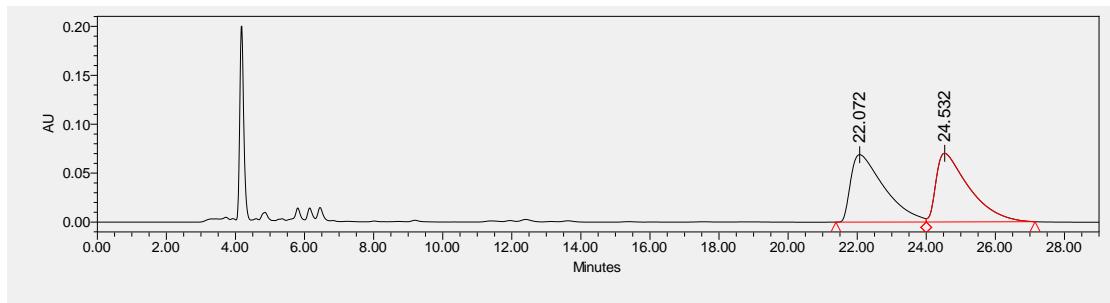


Colorless oil; at 50 °C for 184 h on 0.2 mmol scale; 35% yield (21.3 mg); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 3/1/0.5); **HPLC** (Chiralcel ID, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 22.45 min, t_r (major) = 23.30 min, ee = 97%, $[\alpha]^{19}_D$ = +53.4 (c = 0.15 in CH₂Cl₂, λ = 589 nm).

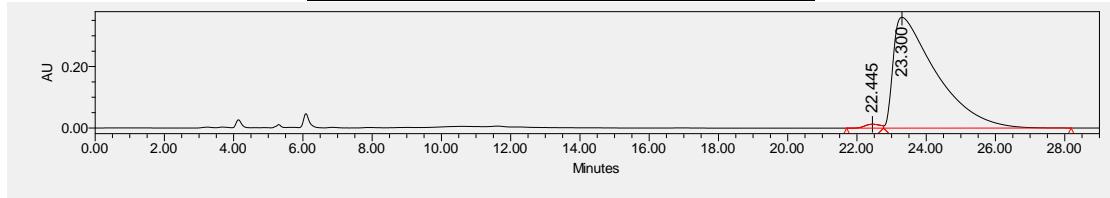
¹H NMR (400 MHz, CDCl₃) δ = 7.46 – 7.38 (m, 2H), 7.31 – 7.28 (m, 1H), 7.24 – 7.18 (m, 1H), 5.70 (d, J = 5.6 Hz, 1H), 4.08 (s, 1H), 3.79 (d, J = 6.8 Hz, 6H), 2.45 (pd, J = 6.8, 5.6 Hz, 1H), 1.08 (dd, J = 6.8, 3.2 Hz, 6H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 203.0, 170.1, 169.9, 133.8, 128.3, 127.1, 127.0, 107.1, 104.5, 82.0, 53.6, 53.5, 28.5, 22.2, 22.0.

HRMS (ESI-TOF) calcd for C₁₇H₂₀NaO₅⁺ ([M+Na⁺]) = 327.1203, Found 327.1201.

IR (neat): (cm⁻¹) 3478, 2960, 1741, 1439, 1115, 1021.

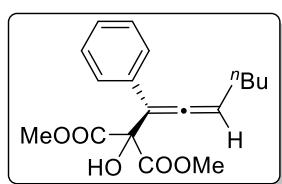


	Retention Time	Area	% Area
1	22.072	4637915	49.94
2	24.532	4649368	50.06



	Retention Time	Area	% Area
1	22.445	392109	1.25
2	23.300	31085421	98.75

Dimethyl 2-hydroxy-2-(1-phenylhepta-1,2-dien-3-yl)malonate (3n)

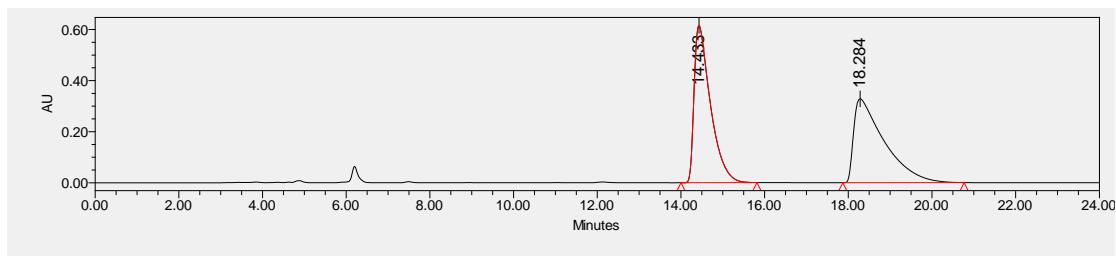


Colorless oil; at 50 °C for 96 h on 0.2 mmol scale; 48% yield (30.5 mg); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 3/1/0.5); **HPLC** (Chiralcel ID, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 14.74 min, t_r (major) = 17.88 min, ee = 98%, $[\alpha]^{19}_D$ = +45.18 (c = 0.23 in CH₂Cl₂, λ = 589 nm).

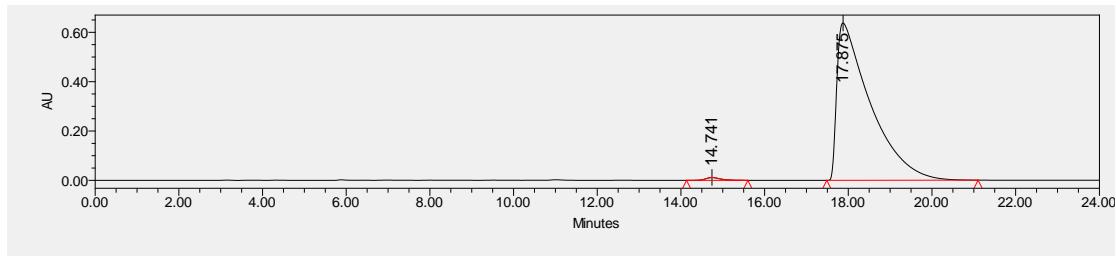
¹H NMR (400 MHz, CDCl₃) δ = 7.46 – 7.37 (m, 2H), 7.33 – 7.24 (m, 2H), 7.24 – 7.16 (m, 1H), 5.69 (t, J = 8.0 Hz, 1H), 4.09 (s, 1H), 3.78 (d, J = 8.0 Hz, 6H), 2.13 (q, J = 8.0 Hz, 2H), 1.51 – 1.29 (m, 4H), 0.91 (t, J = 4.0 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 204.4, 170.0, 170.0, 133.8, 128.3, 127.1, 127.1, 106.0, 97.3, 81.9, 53.6, 53.5, 30.9, 28.2, 22.3, 13.8.

HRMS (ESI-TOF) calcd for C₁₈H₂₂NaO₅⁺ ([M+Na⁺]) = 341.1359, Found 341.1341.

IR (neat): (cm⁻¹) 3471, 2955, 2362, 1737, 1437, 1180, 964, 622, 519.

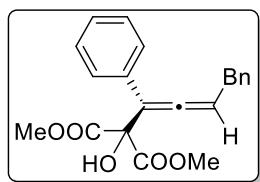


	Retention Time	Area	% Area
1	14.433	16609879	49.99
2	18.284	16615954	50.01



	Retention Time	Area	% Area
1	14.741	270084	0.76
2	17.875	35379738	99.24

Dimethyl 2-(1,4-diphenylbuta-2,3-dien-2-yl)-2-hydroxymalonate (3o)

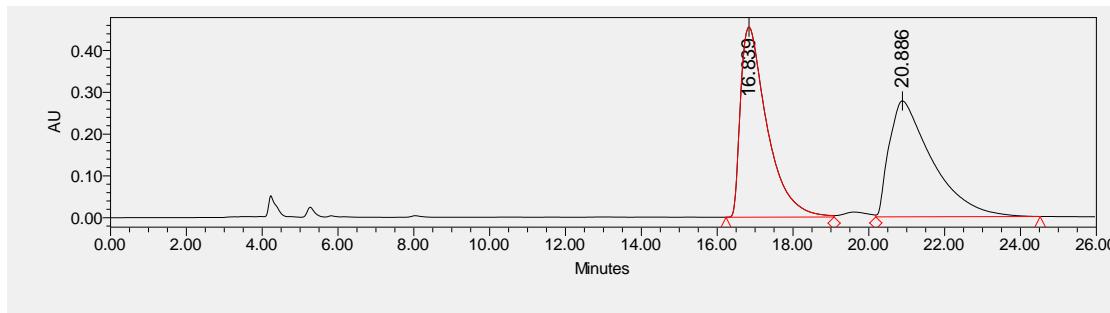


White solid, m.p. 93-96 °C; at 50 °C for 138 h on 0.2 mmol scale; 47% yield (33.0 mg); eluted solvent (petroleum ether/ethyl acetate/dichloromethane = 3/1/0.5); **HPLC** (Chiralcel **ID**, hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 17.10 min, t_r (major) = 21.14 min, ee = 96%, $[\alpha]^{17}_D$ = +45.48 (c = 0.33 in CH₂Cl₂, λ = 589 nm).

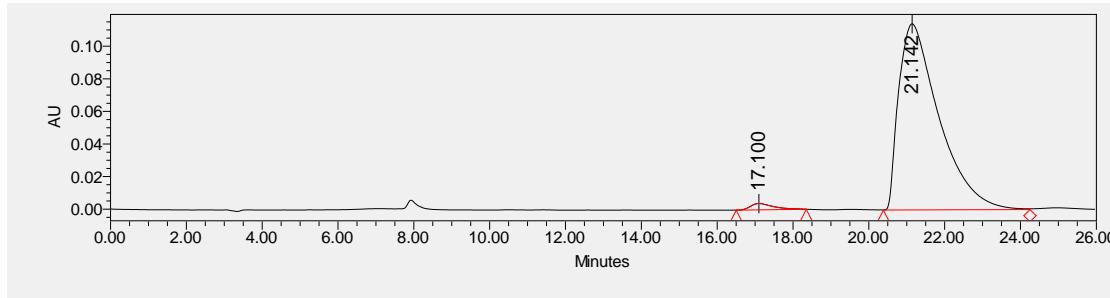
¹H NMR (400 MHz, CDCl₃) δ = 7.41 – 7.35 (m, 2H), 7.33 – 7.18 (m, 8H), 5.84 (t, J = 7.2 Hz, 1H), 4.06 (s, 1H), 3.76 – 3.63 (m, 6H), 3.46 (qd, J = 15.2, 7.4 Hz, 2H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 204.8, 169.8, 139.1, 133.5, 128.5, 128.5, 128.3, 127.3, 126.5, 106.5, 96.5, 96.5, 81.7, 53.5, 35.1.

HRMS (ESI-TOF) calcd for C₂₁H₂₀NaO₅⁺ ([M+Na⁺]) = 375.1203, Found 375.1192.

IR (neat): (cm⁻¹) 3471, 2953, 2361, 1738, 1600, 1437, 1114, 624, 534.

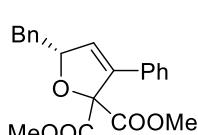


	Retention Time	Area	% Area
1	16.839	22073375	50.32
2	20.886	21791512	49.68



	Retention Time	Area	% Area
1	17.100	163311	1.90
2	21.142	8418484	98.10

Dimethyl (*R*)-5-benzyl-3-phenylfuran-2,2(5*H*)-dicarboxylate (2o)

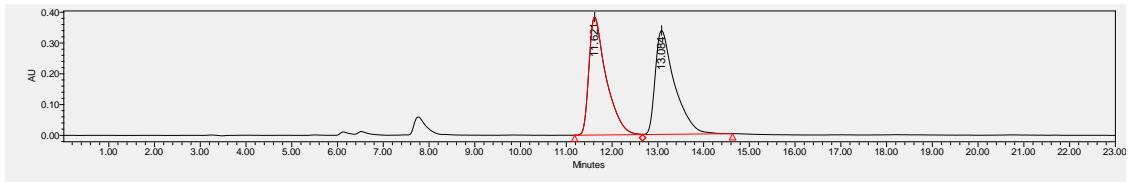


Colorless oil; 98% yield (69.0 mg), HPLC (Chiralcel ID, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 11.44 min, t_r (major) = 12.68 min, ee = 97%, $[\alpha]^{18}_D$ = -12.0 (c = 1.6 in CH₂Cl₂, λ = 589 nm).

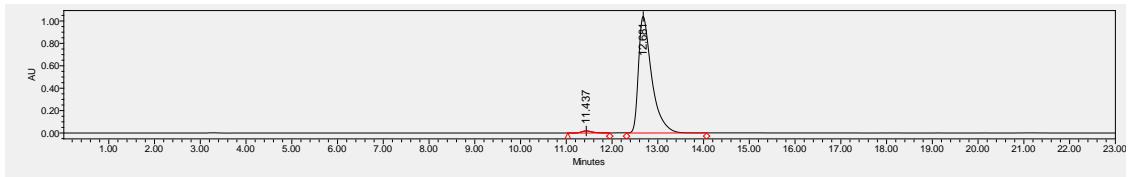
¹H NMR (400 MHz, CDCl₃) δ = 7.42 – 7.35 (m, 2H), 7.35 – 7.27 (m, 5H), 7.26 – 7.18 (m, 3H), 6.32 (d, J = 1.6 Hz, 1H), 5.41 – 5.31 (m, 1H), 3.75 (d, J = 12.4 Hz, 6H), 3.21 (dd, J = 13.2, 6.0 Hz, 1H), 2.93 (dd, J = 13.6, 8.0 Hz, 1H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 168.6, 168.5, 138.3, 136.9, 131.6, 130.9, 129.4, 128.4, 128.3, 128.1, 127.6, 126.5, 93.3, 88.3, 52.9, 52.8, 42.2.

HRMS (ESI-TOF) calcd for C₂₁H₂₀NaO₅⁺ ([M+Na⁺]) = 375.1203, Found 375.1211.

IR (neat): (cm⁻¹) 2953, 2361, 1739, 1590, 1487, 1107, 1048, 968, 821, 520.



	Retention Time	Area	% Area
1	11.621	9985736	50.15
2	13.084	9925742	49.85



	Retention Time	Area	% Area
1	11.437	311835	1.47
2	12.681	20918978	98.53

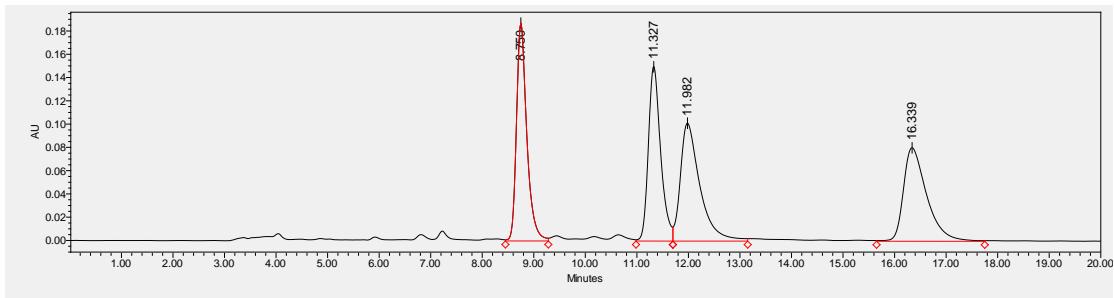
(5-Benzyl-3-phenyl-2,5-dihydrofuran-2-yl)methanol (4)

Colorless oil; 45% yield (23.6 mg), **HPLC** (Chiralcel ID, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) $t_{\text{minor isomer}}$ (minor) = 7.78 min, $t_{\text{minor isomer}}$ (major) = 12.09; $t_{\text{major isomer}}$ (minor) = 11.35 min, $t_{\text{minor isomer}}$ (major) = 16.52 min, dr = 39/61, ee = 92%/97%.

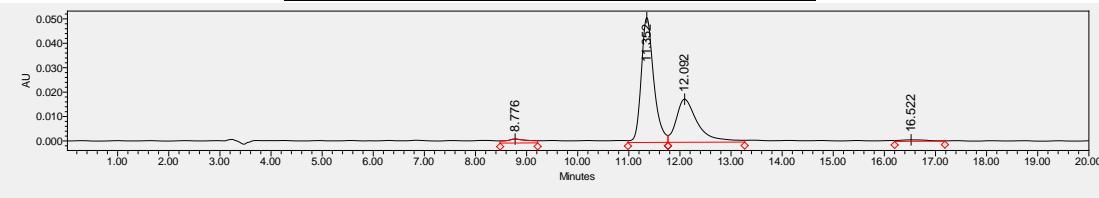
¹H NMR (400 MHz, CDCl₃) δ = 7.42 – 7.27(m, 7H), 7.27 – 7.19 (m, 3H), 6.15 – 6.04 (m, 1H), 5.44 – 5.12 (m, 2H), 3.96 – 3.70(m , 1H), 3.66 – 3.32 (m, 1H), 3.13 – 3.01 (m, 1H), 3.00 – 2.83 (m, 1H), 1.99 – 1.63 (m, 1H); **¹³C{¹H} NMR** (101 MHz, CDCl₃) δ = 139.7, 137.7, 137.4, 132.8, 129.6, 129.5, 128.7, 128.4, 128.4, 128.2, 126.6, 126.4, 126.3, 87.0, 86.7, 86.3, 64.5, 64.2, 43.2.

HRMS (ESI-TOF) calcd for C₁₈H₁₈NaO₂⁺ ([M+Na⁺]) = 289.1199, Found 289.1202.

IR (neat): (cm⁻¹) 3729, 3401, 2924, 2855, 2362, 2336, 1455, 1074, 697.



	Retention Time	Area	% Area
1	8.750	2595931	25.32
2	11.327	2480823	24.20
3	11.982	2660653	25.95
4	16.339	2515682	24.54



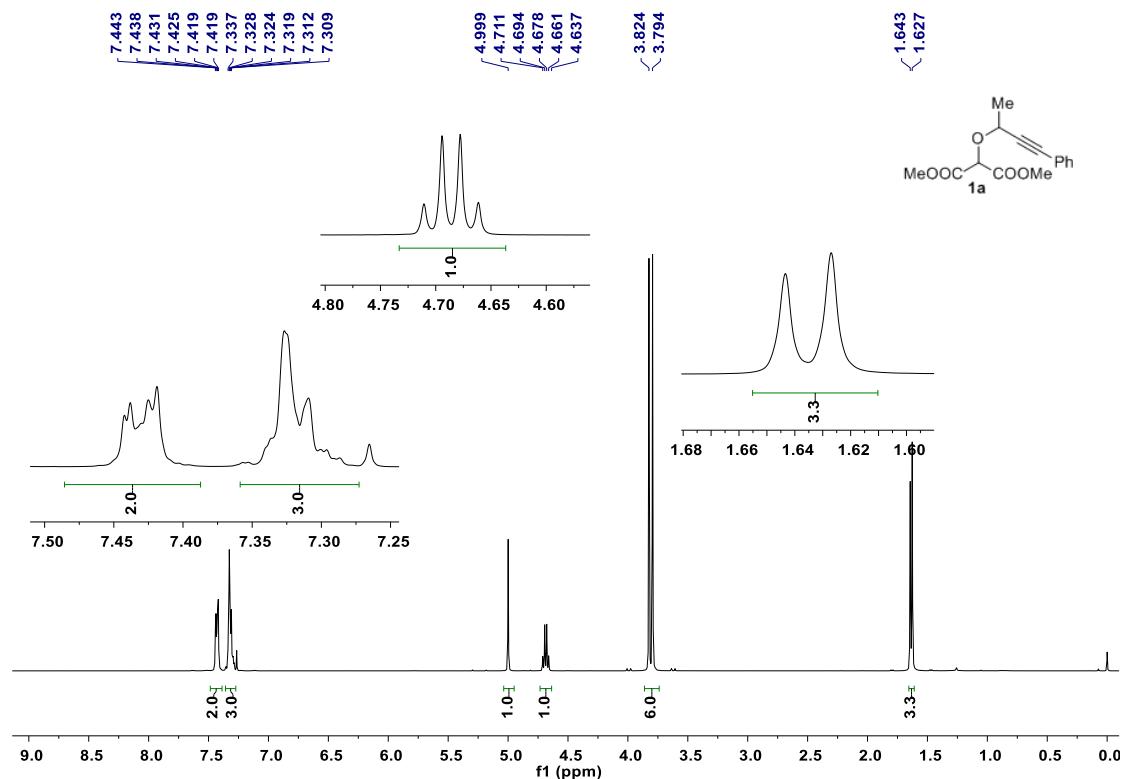
	Retention Time	Area	% Area
1	8.776	51111	3.49
2	11.352	871878	59.62
3	12.092	515684	35.26
4	16.522	23754	1.62

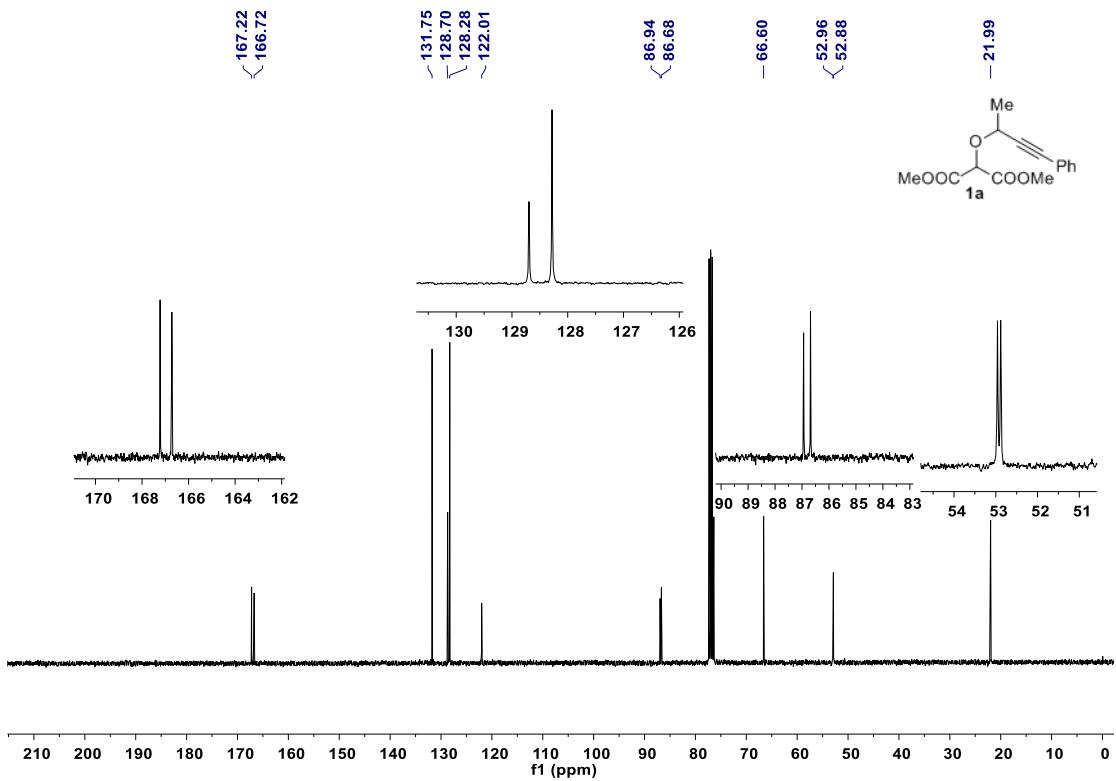
12. References

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- (a) Panteleev, J.; Huang, R. Y.; Lui, E. K. J.; Lautens, M. Addition of Arylboronic Acids to Arylpropargyl Alcohols en Route to Indenes and Quinolines. *Org. Lett.* **2011**, 13, 19, 5314-5317. (b) Yamabe, H.; Mizuno, A.; Kusama, H.; Iwasawa, N. Rh(I)-Catalyzed Cyclization of 1-Arylprop-2-yn-1-ol Derivatives Utilizing Rhodium 1,4-Migration. *J. Am. Chem. Soc.* **2005**, 127, 10, 3248-3249.
- Zhang, X. B.; Lu, Z.; Fu, C. L.; Ma, S. M. Synthesis of highly substituted allylic alcohols by a regio- and stereo-defined CuCl-mediated carbometallation reaction of 3-aryl-substituted secondary propargylic alcohols with Grignard reagents. *Org. Biomol. Chem.*, **2009**, 7, 3258–3263.
- Kennedy, C. R.; Guidera, J. A.; Jacobsen, E. N. Synergistic Ion-Binding Catalysis Demonstrated via an Enantioselective, Catalytic [2,3]-Wittig Rearrangement. *ACS*

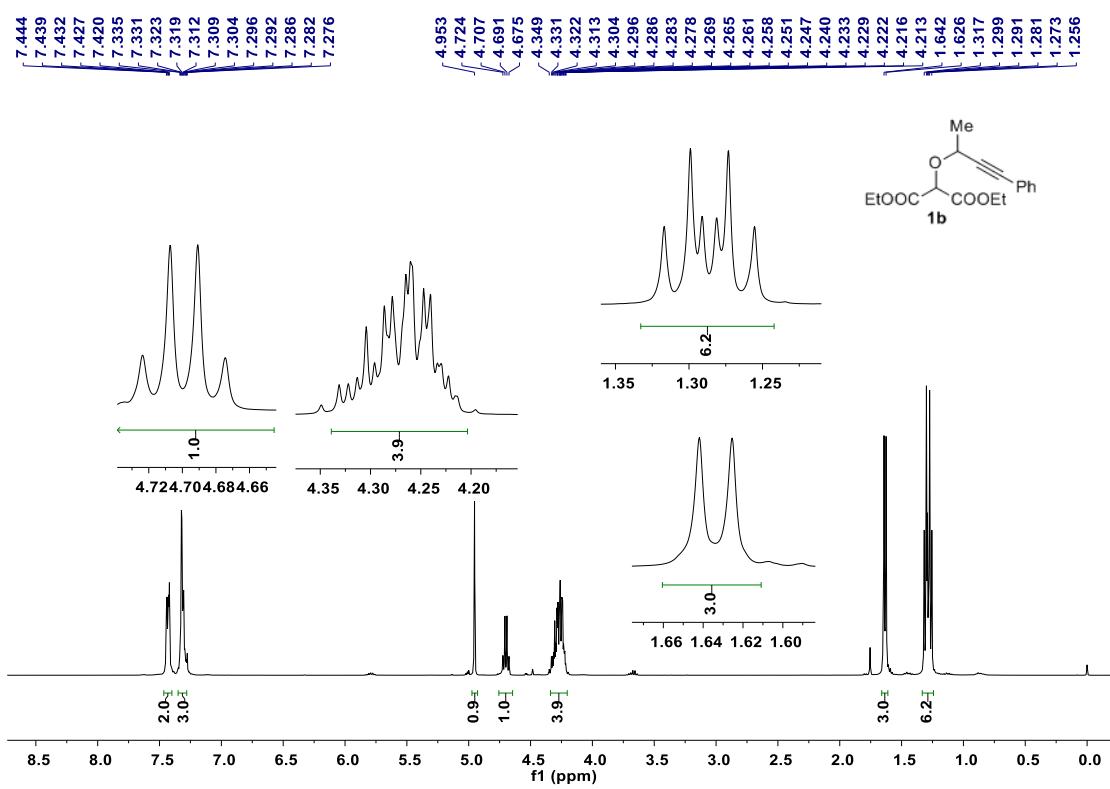
13. Copies of NMR spectra

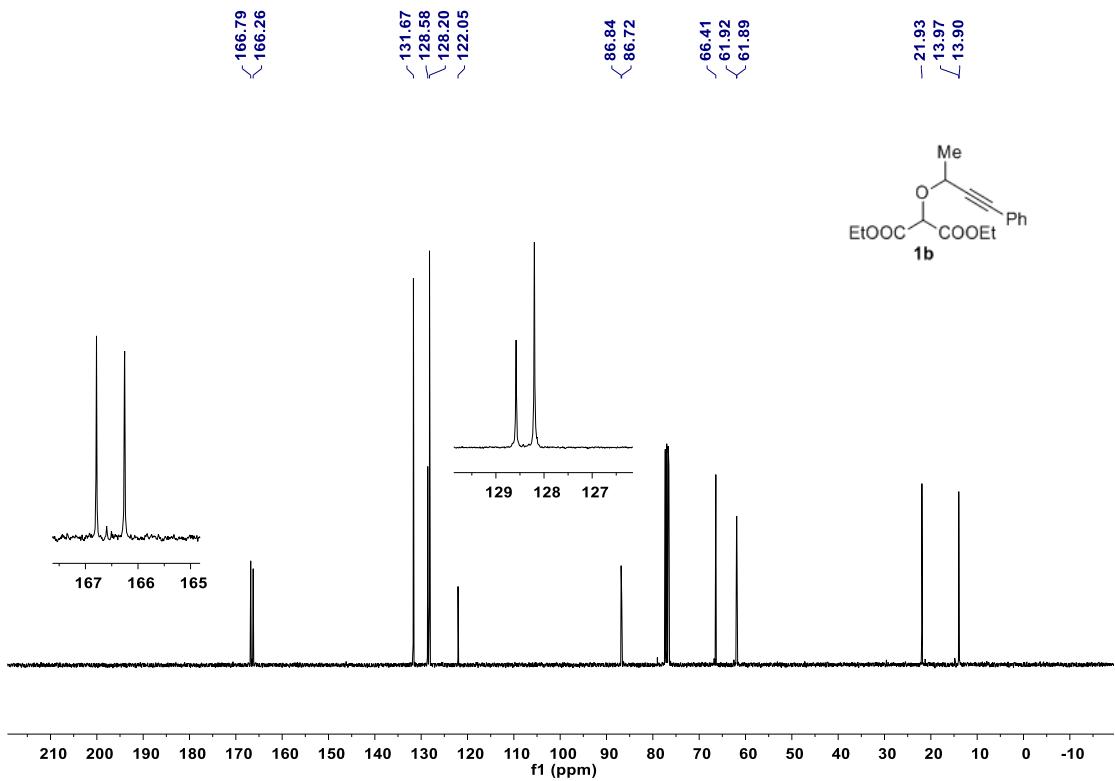
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **1a**



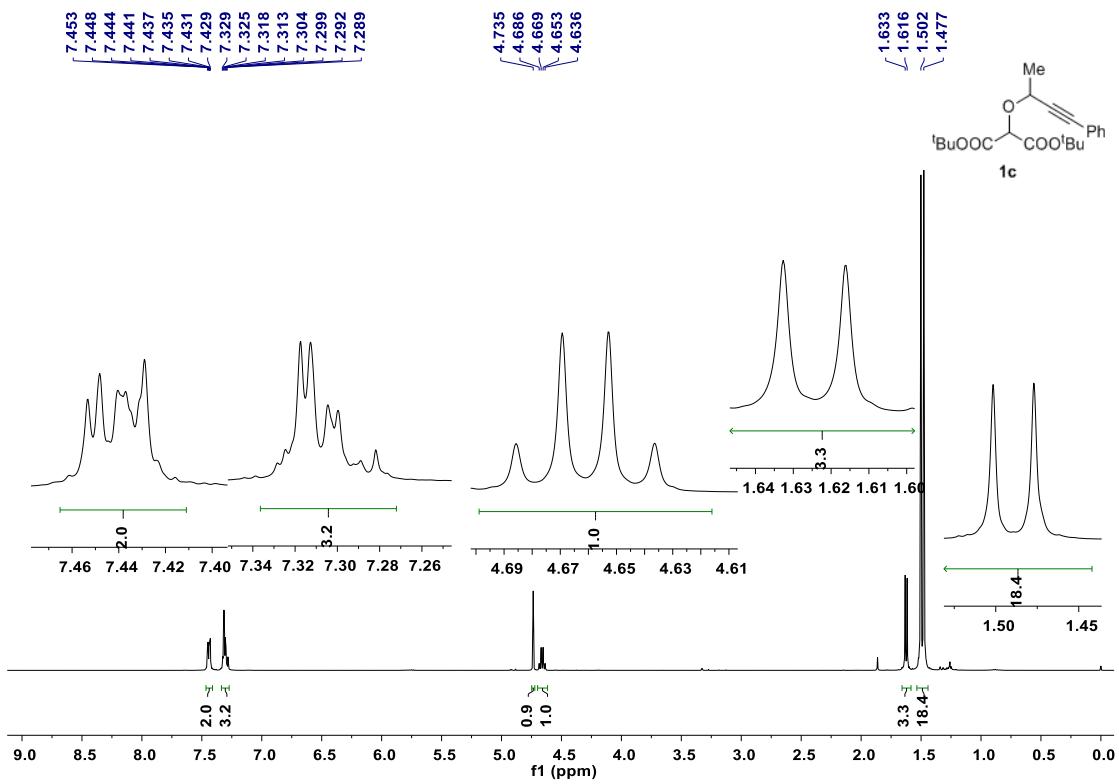


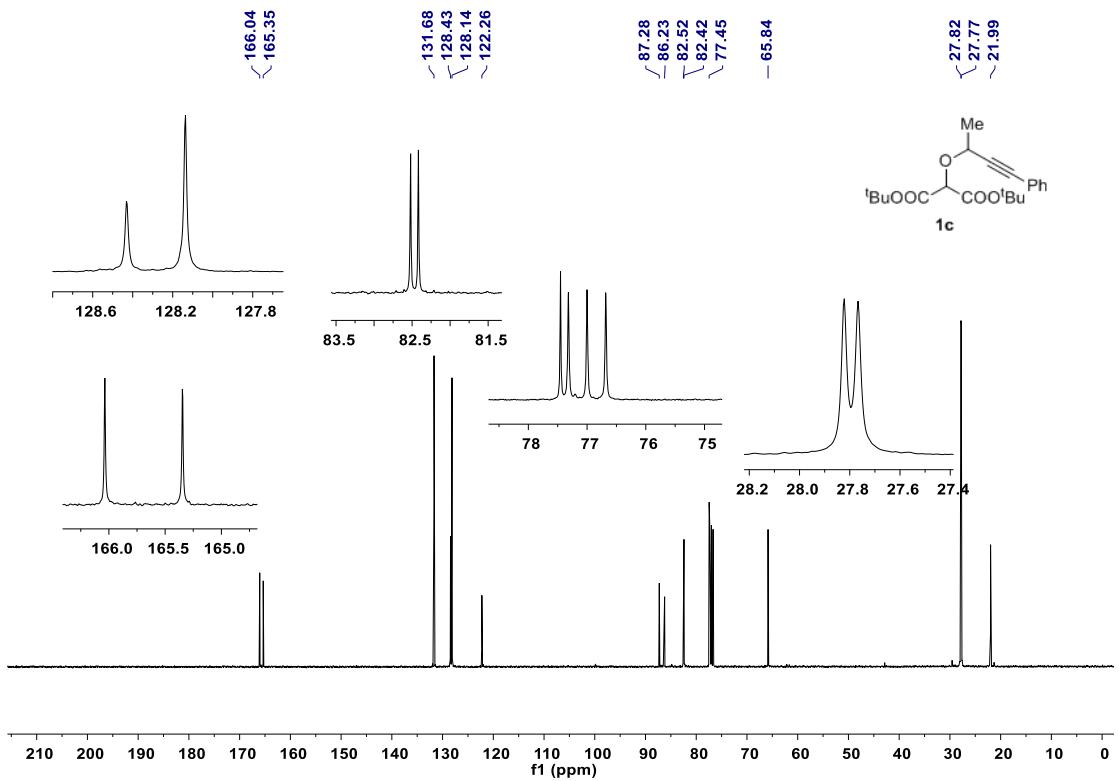
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **1b**



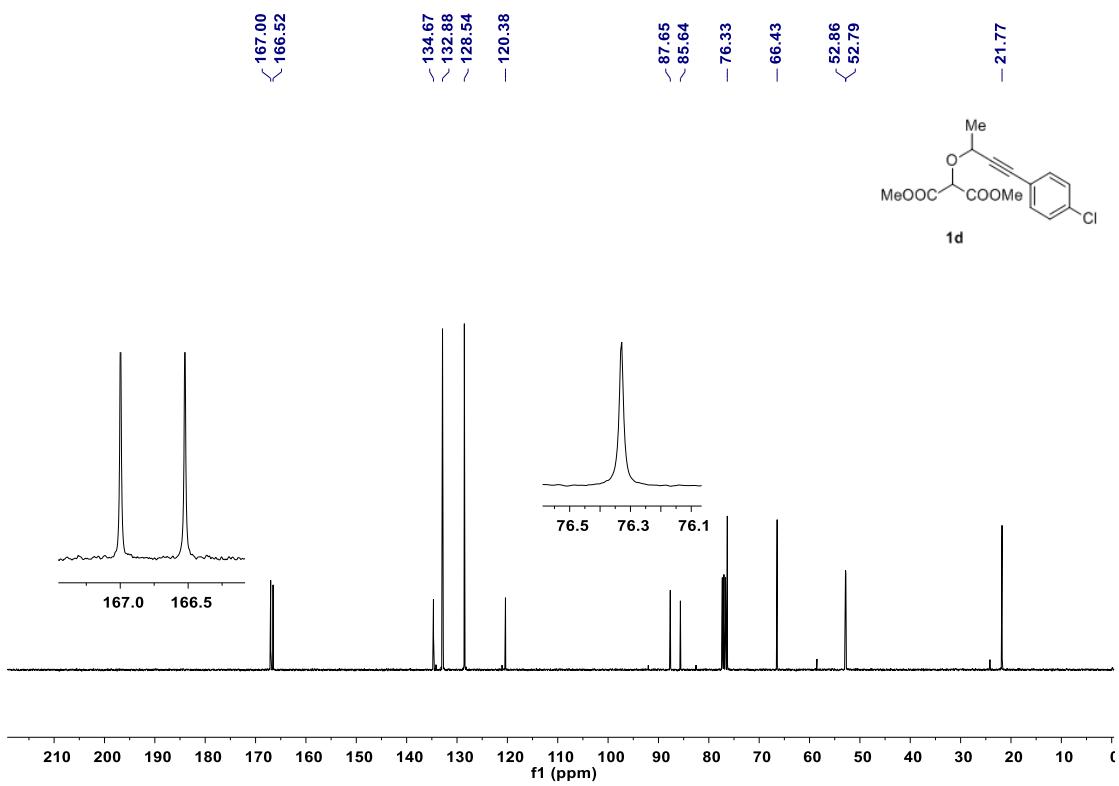


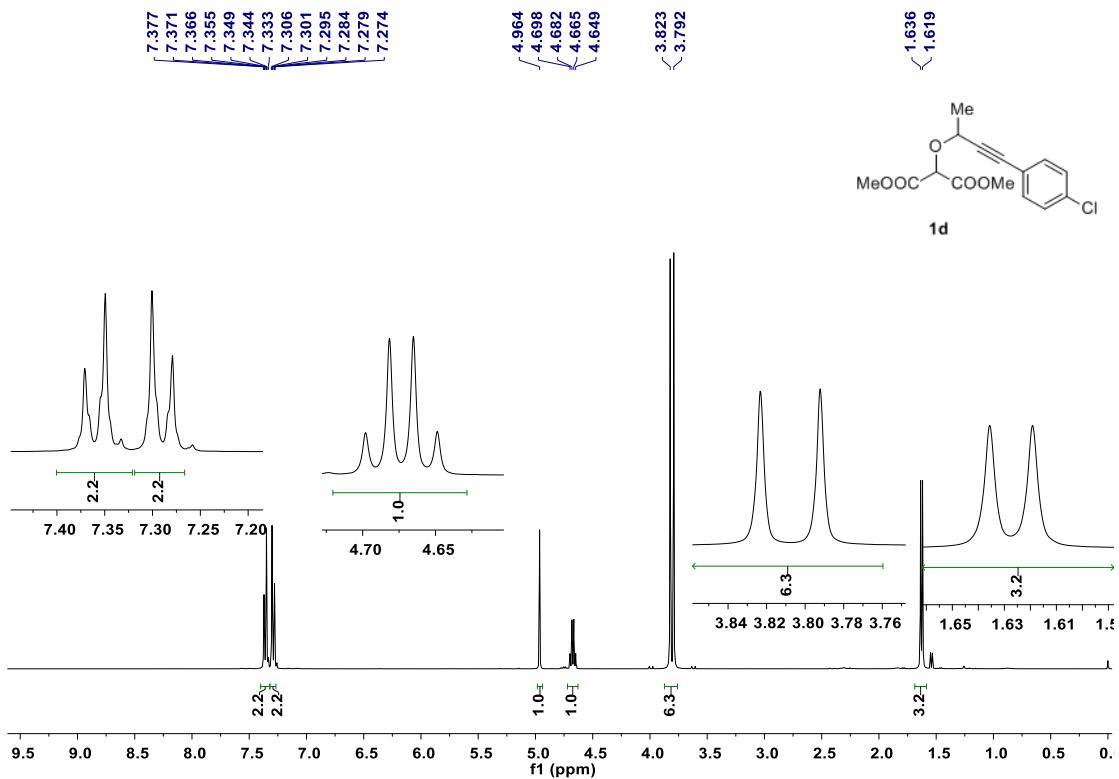
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **1c**



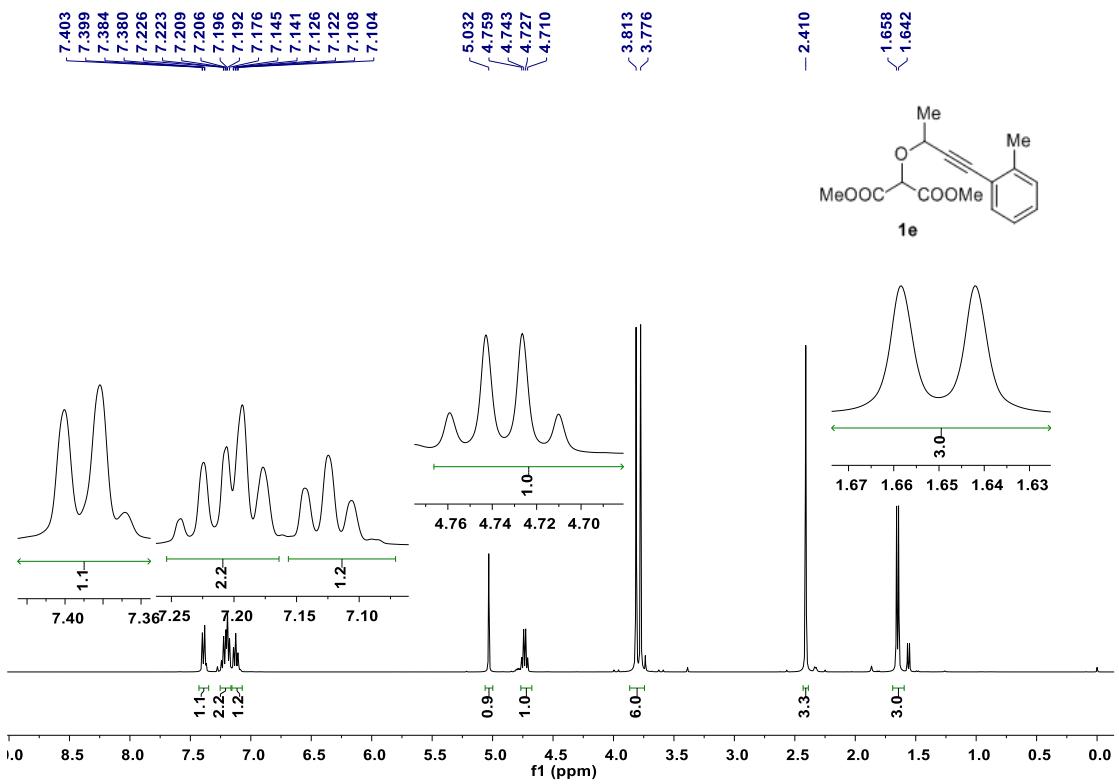


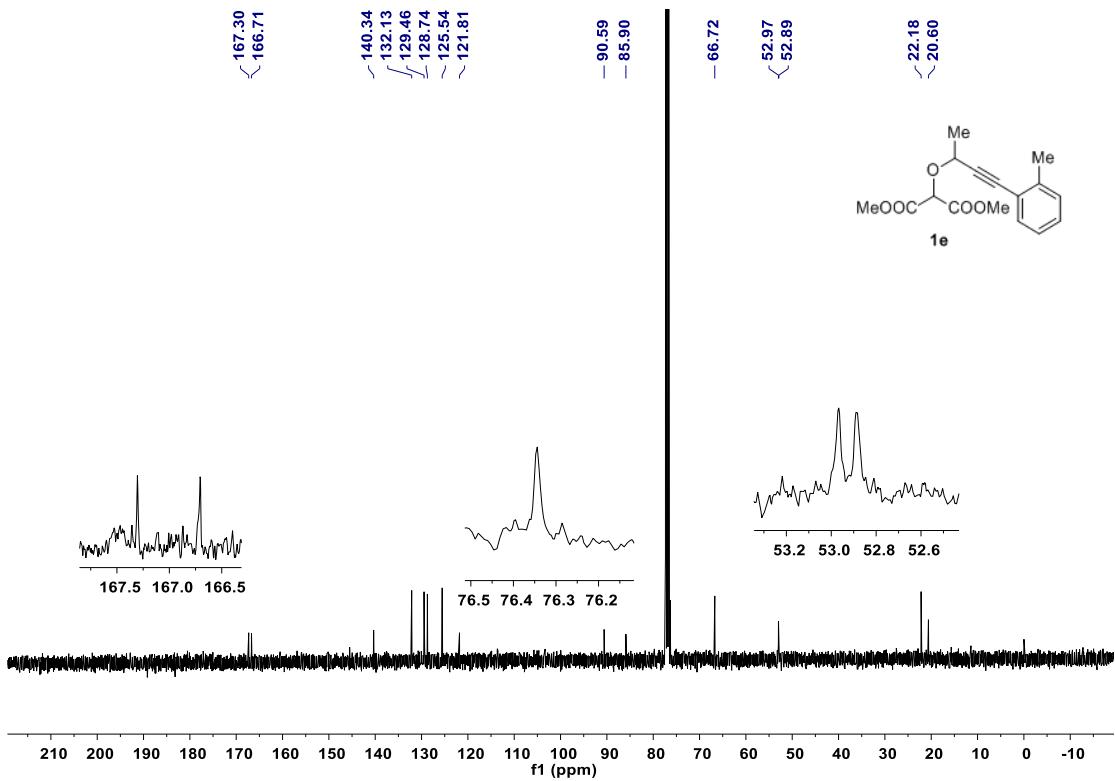
¹H NMR spectrum (400 MHz, CDCl₃) and ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **1d**



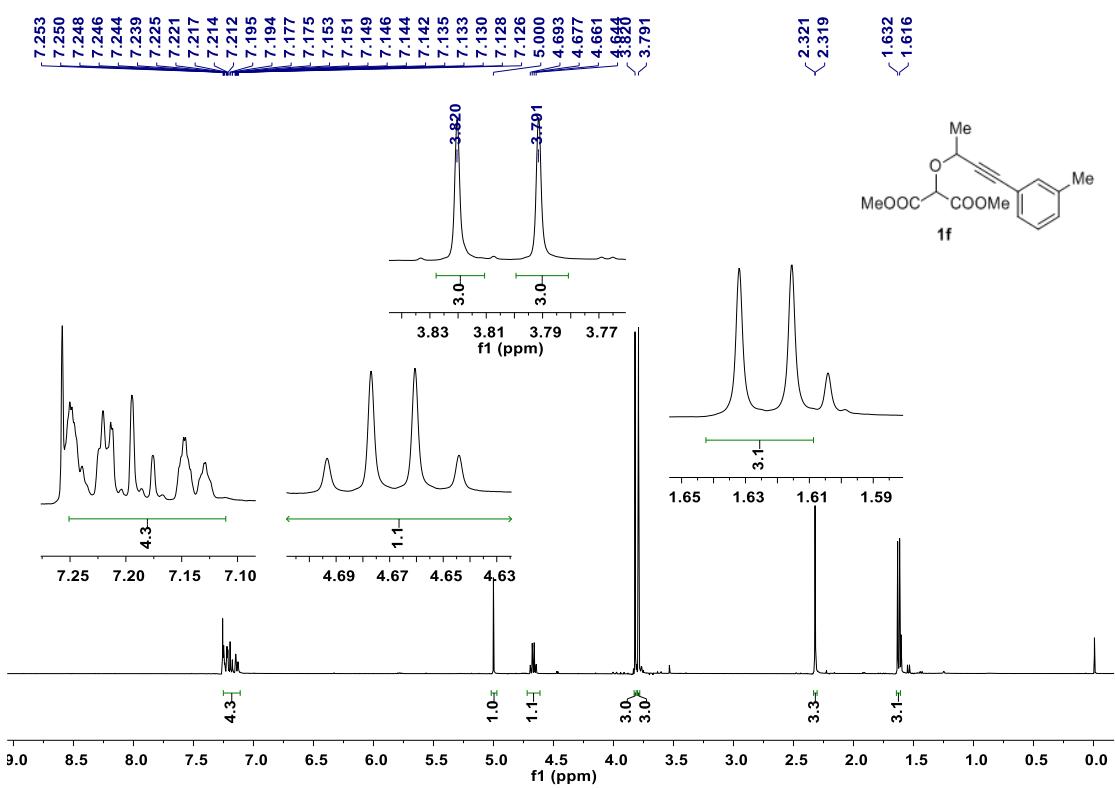


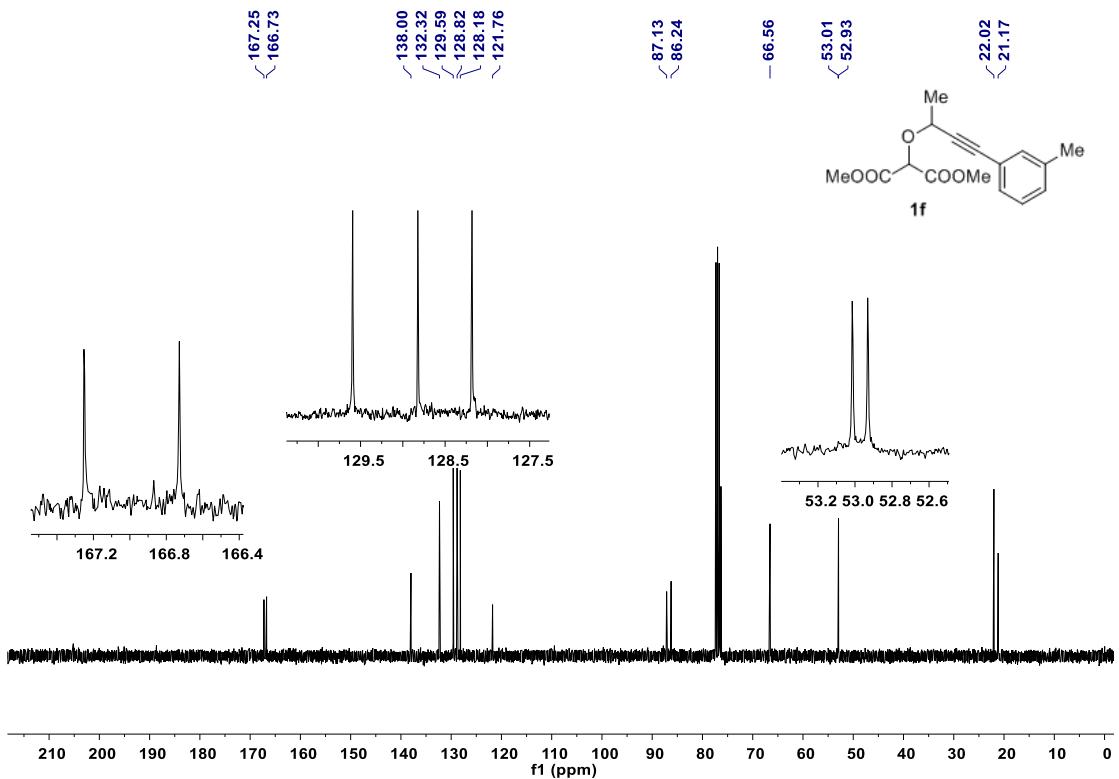
¹H NMR spectrum (400 MHz, CDCl₃) and ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **1e**



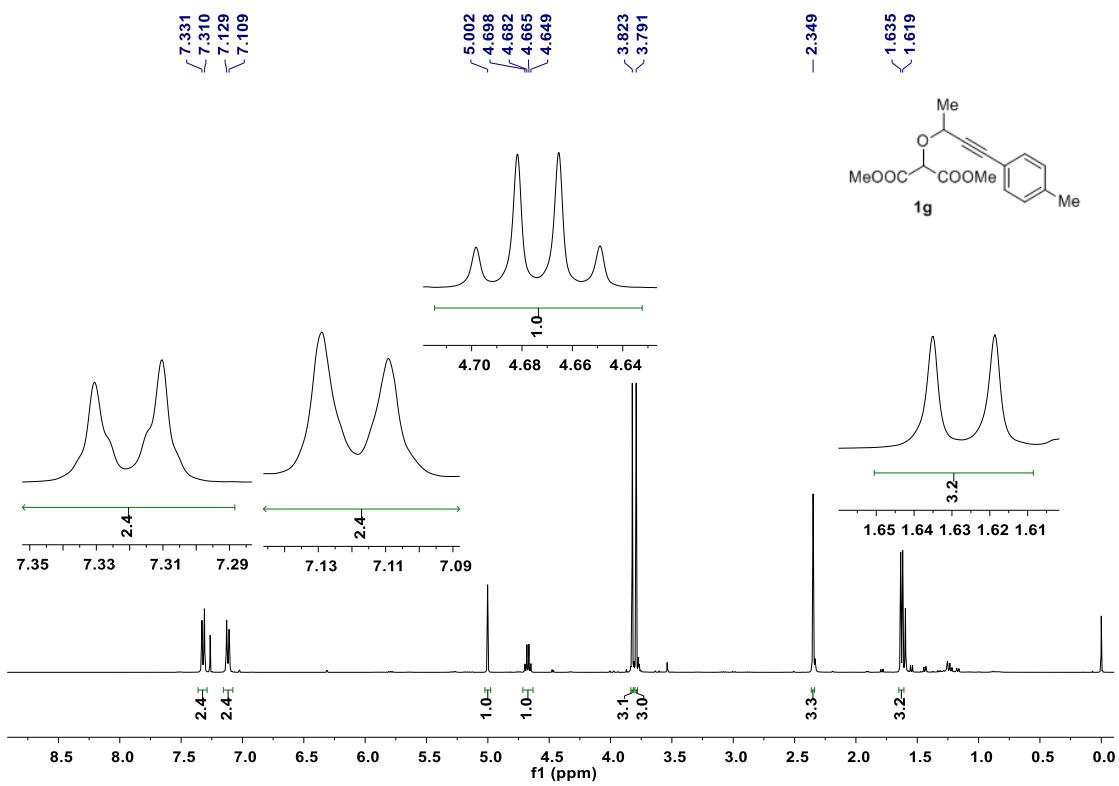


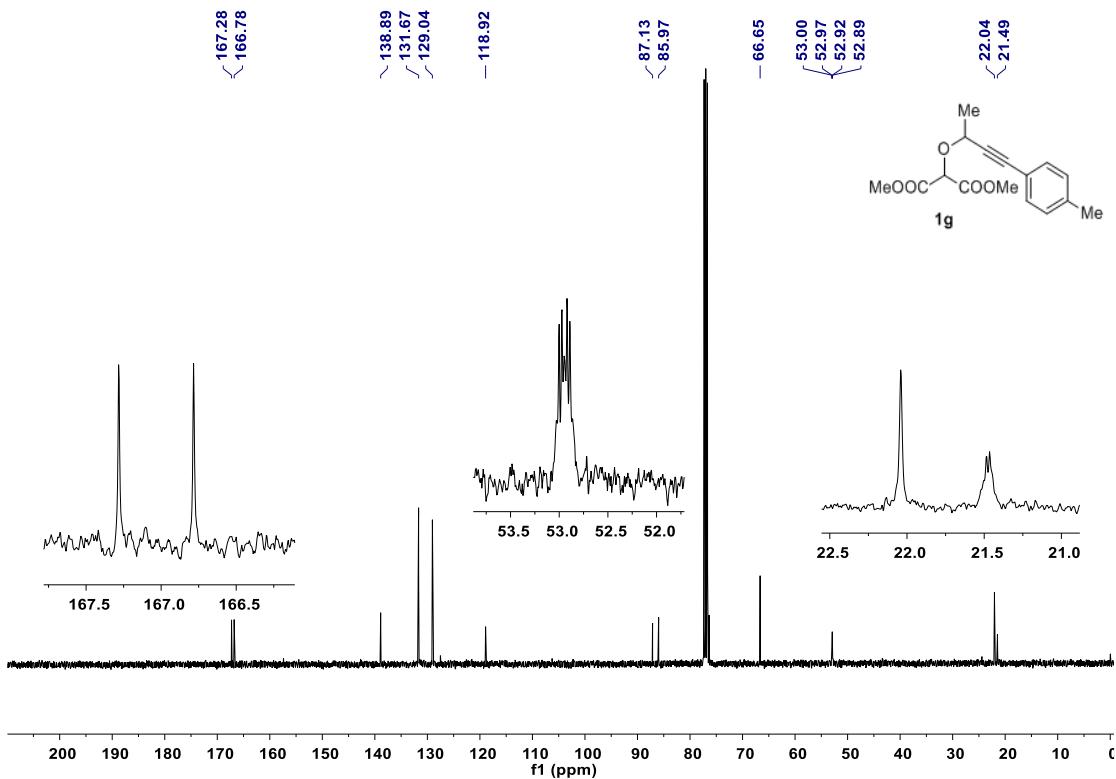
¹H NMR spectrum (400 MHz, CDCl₃) and ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **1f**



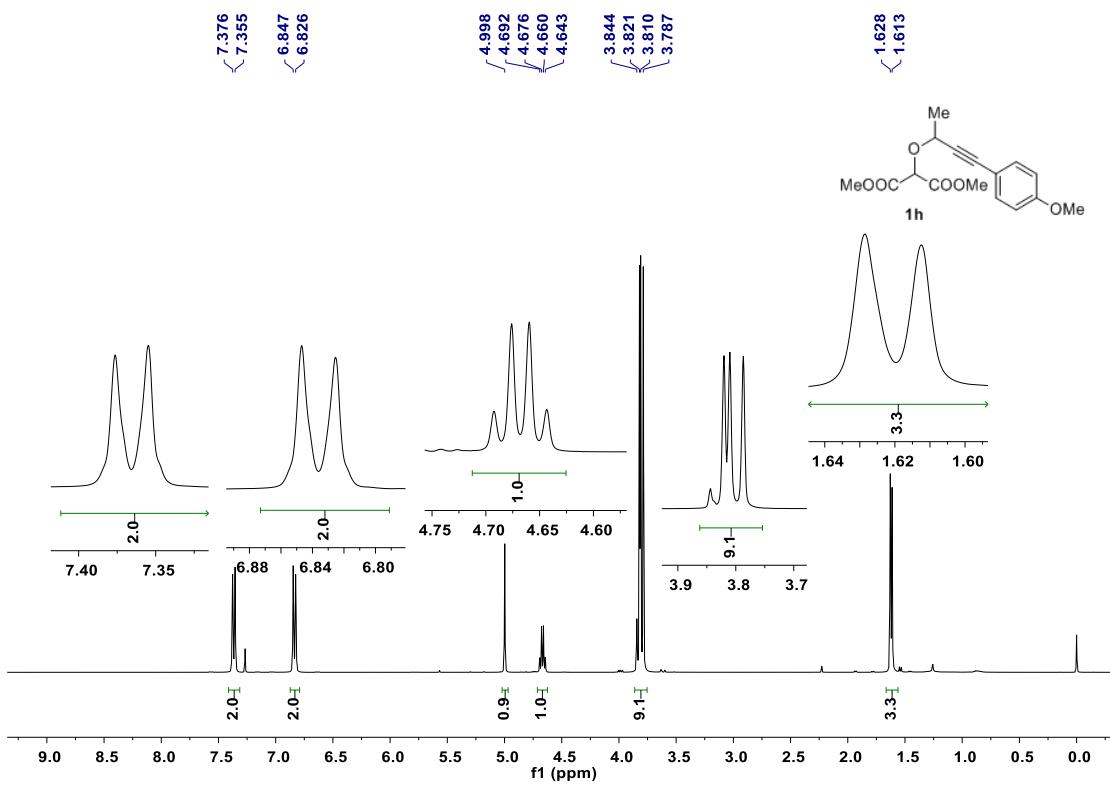


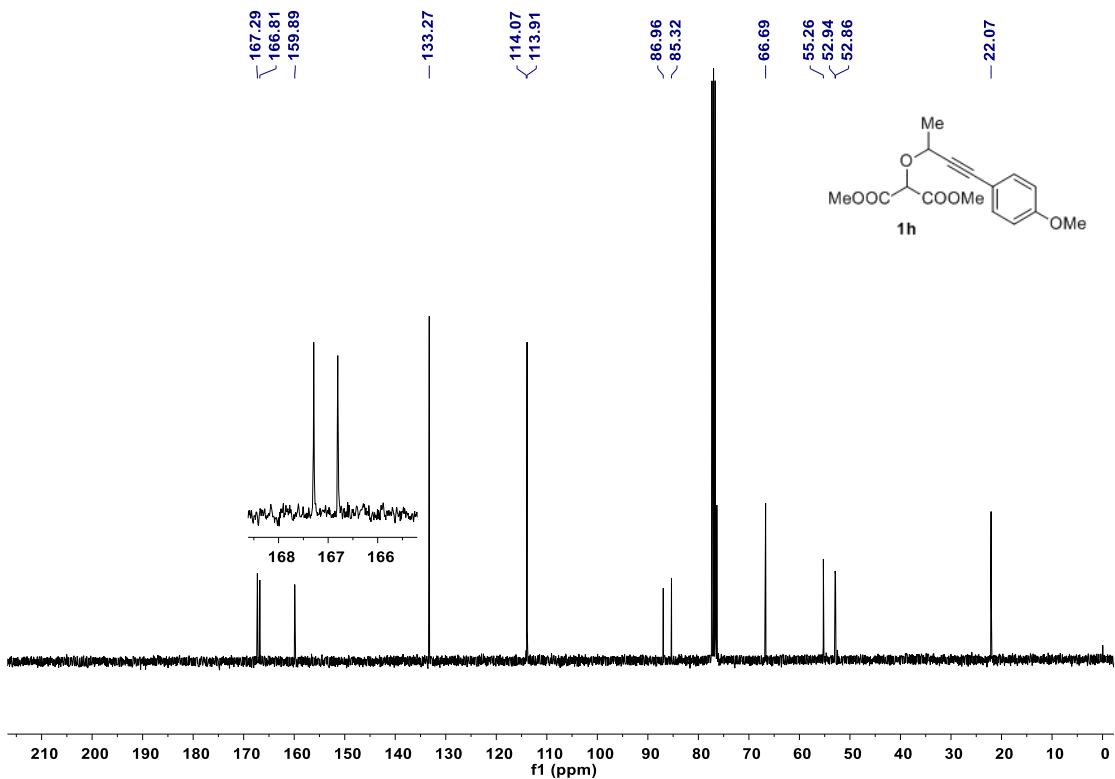
¹H NMR spectrum (400 MHz, CDCl₃) and ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **1g**



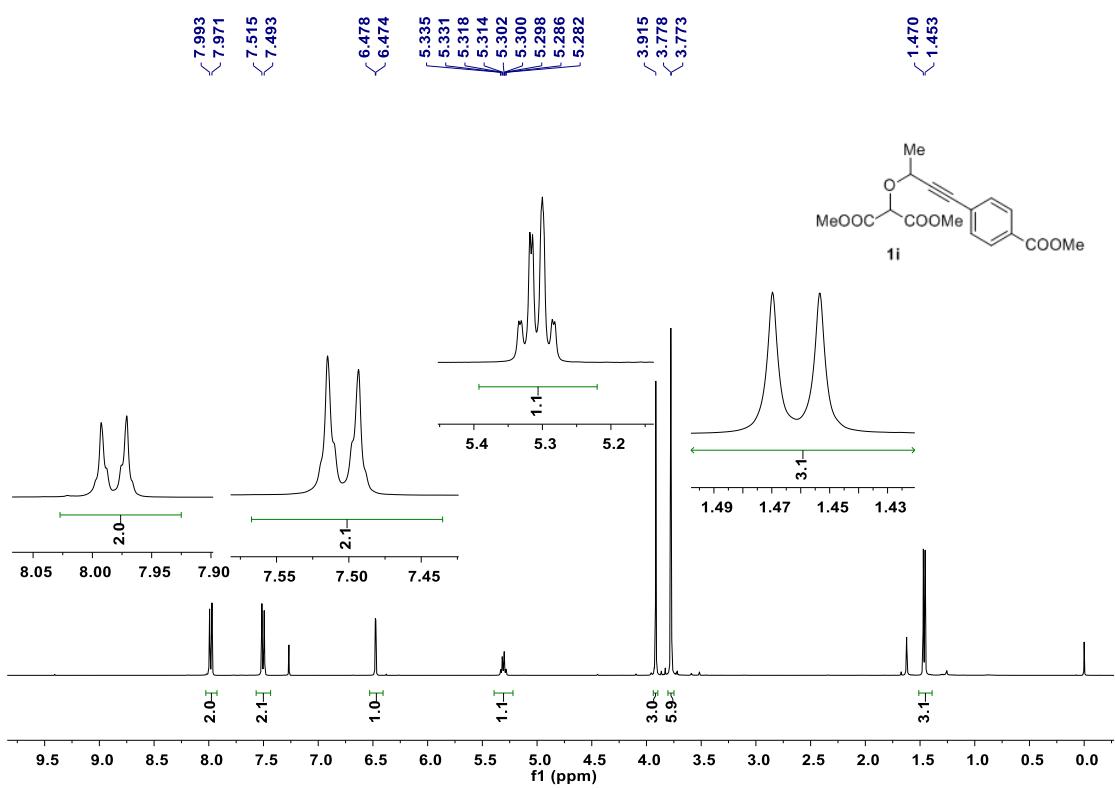


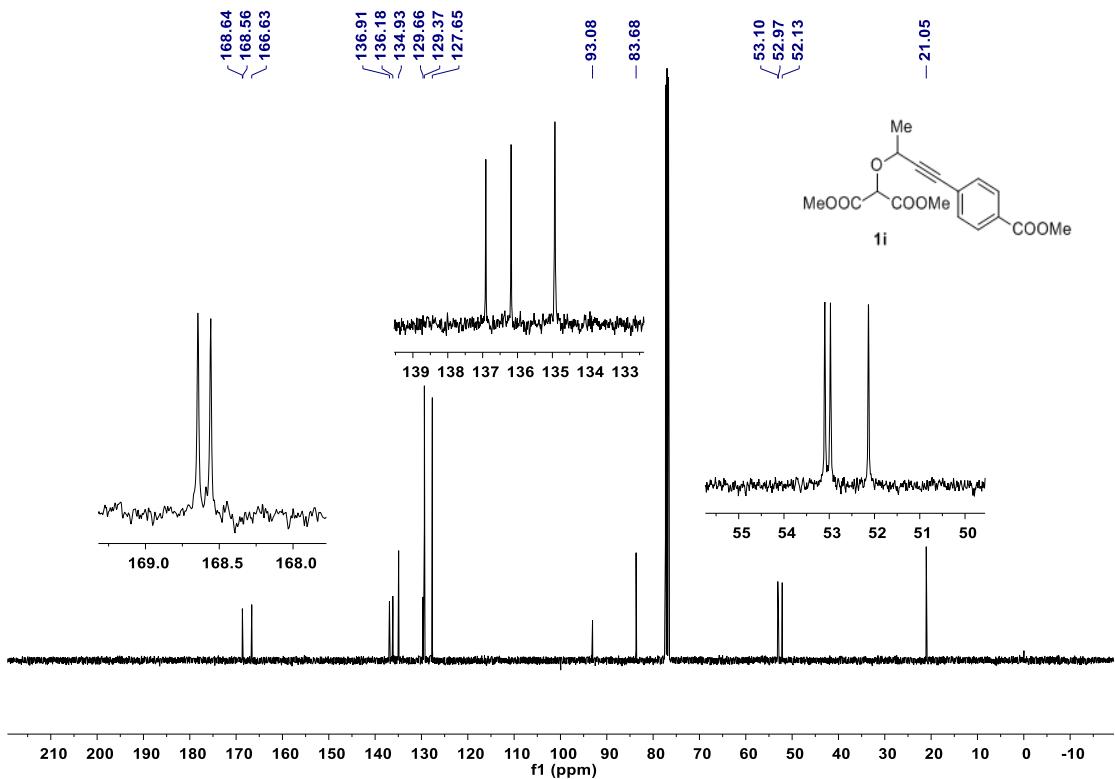
¹H NMR spectrum (400 MHz, CDCl₃) and ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **1h**



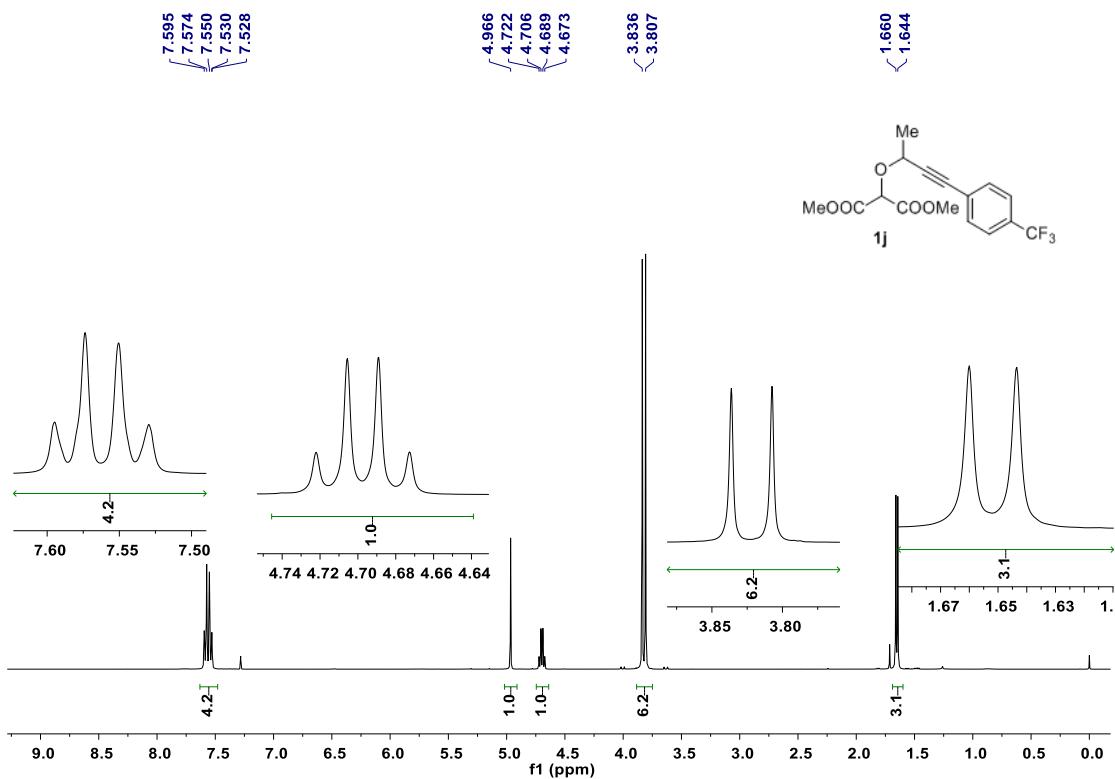


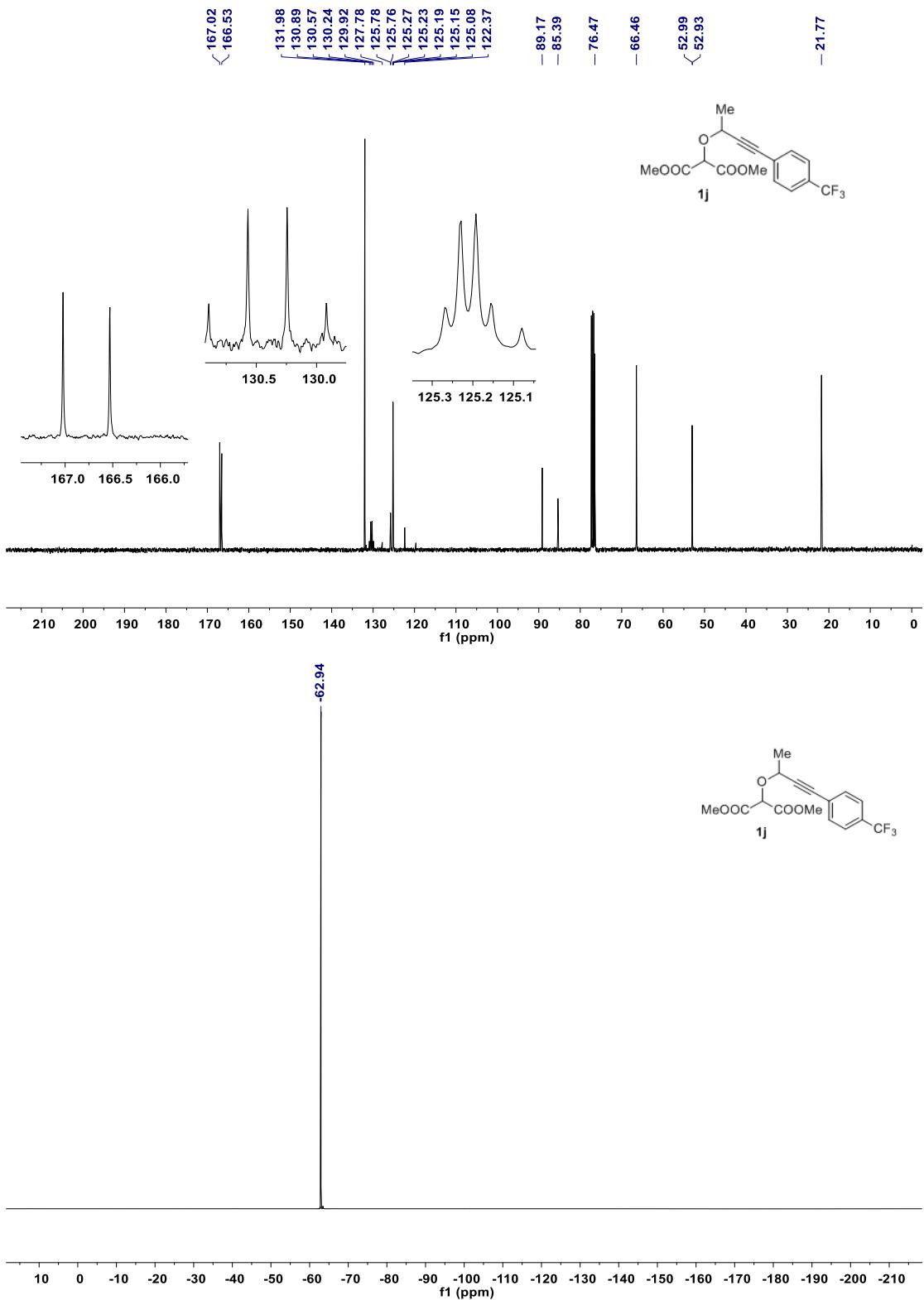
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **1i**



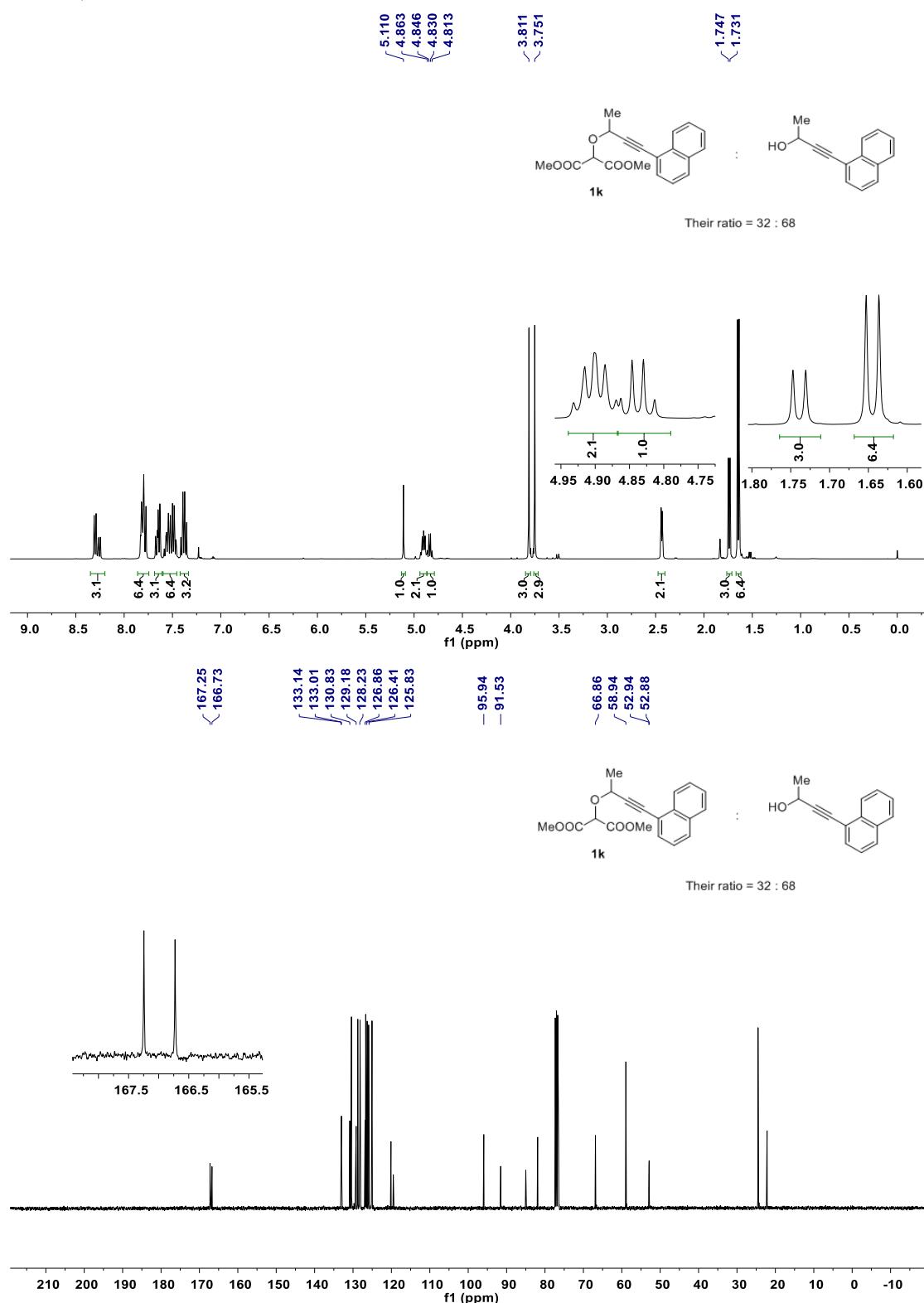


¹H NMR spectrum (400 MHz, CDCl₃), ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃), and ¹⁹F{¹H} NMR spectrum (376 MHz, CDCl₃) of **1j**

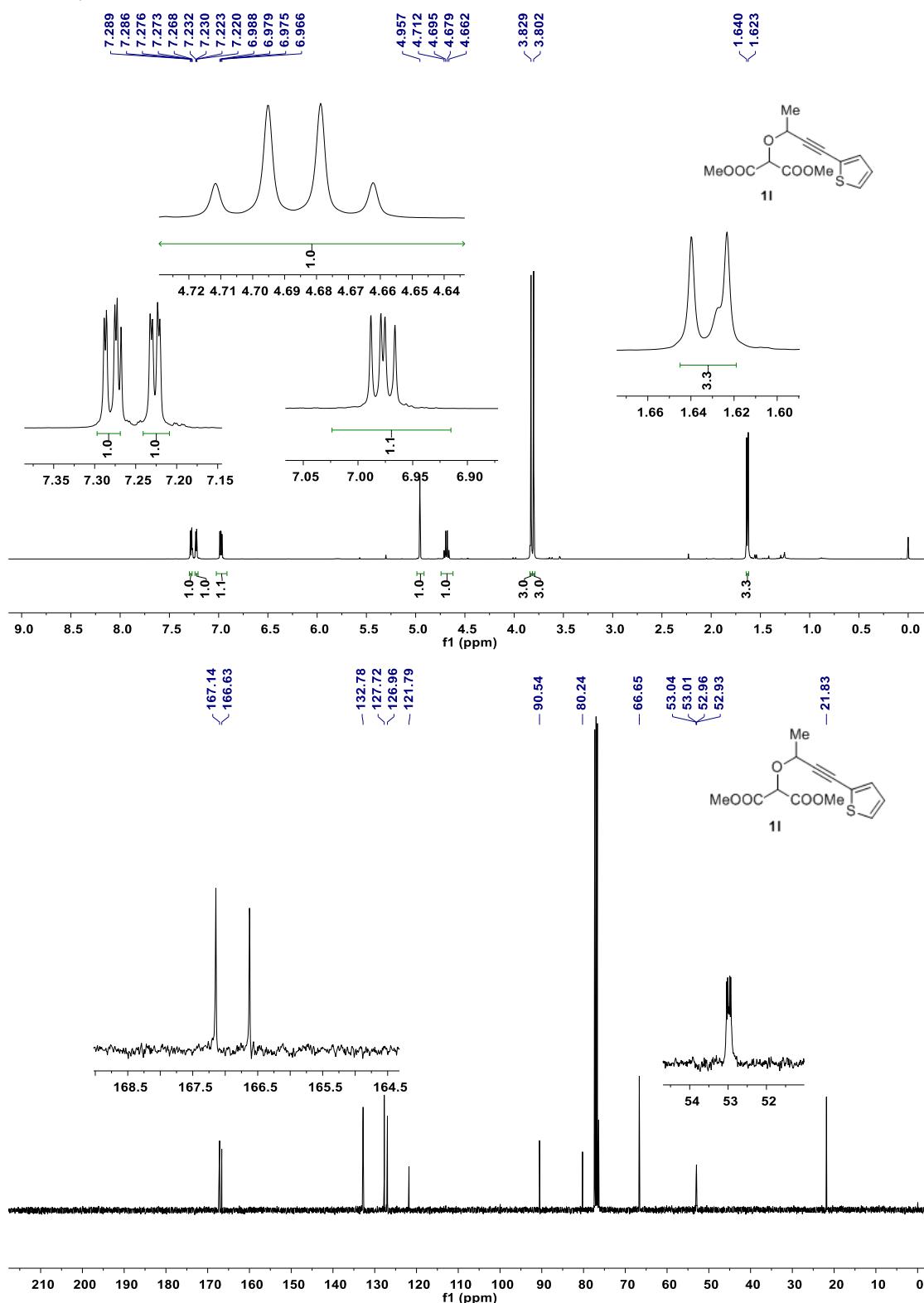




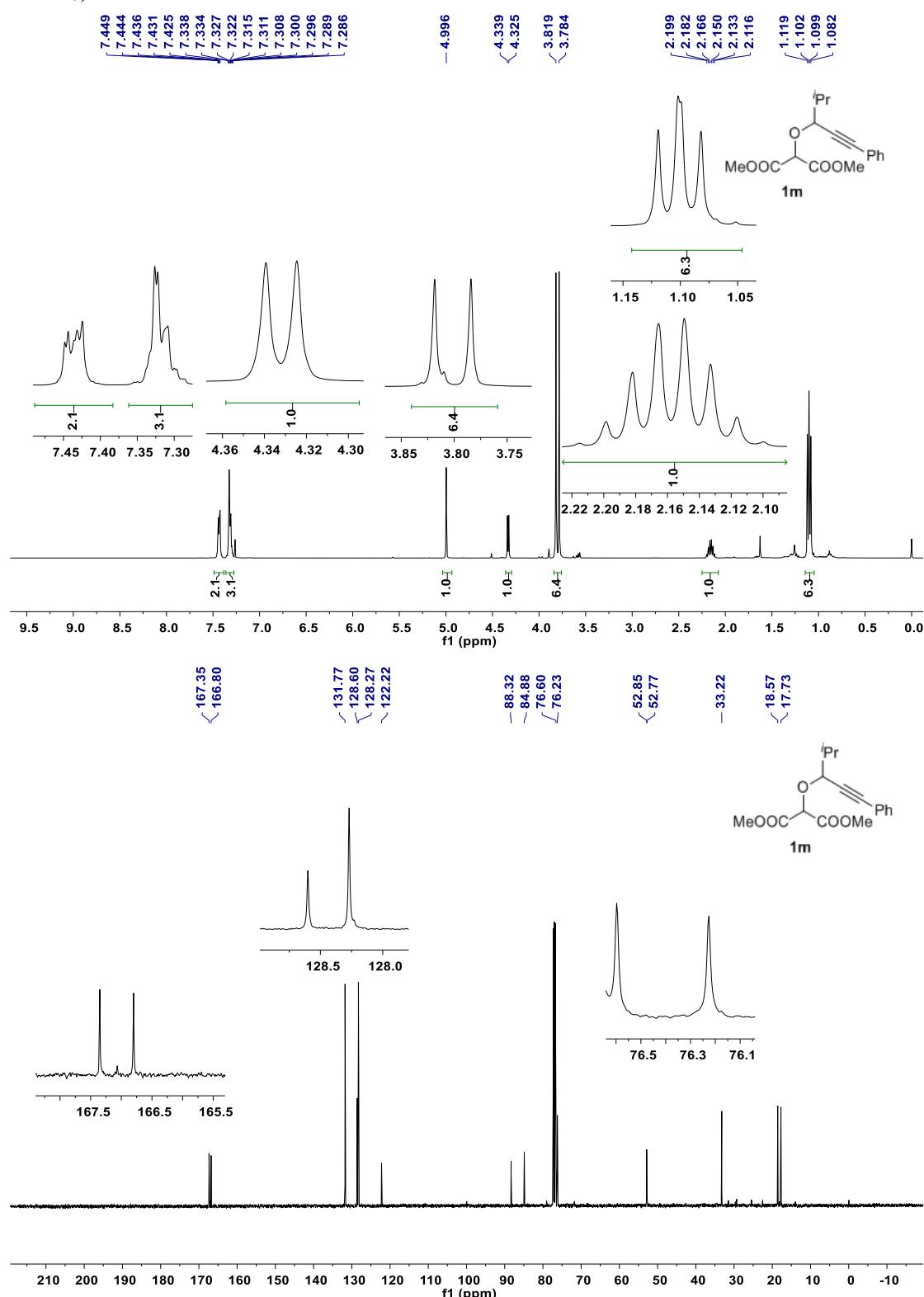
¹H NMR spectrum (400 MHz, CDCl₃) and ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **1k**



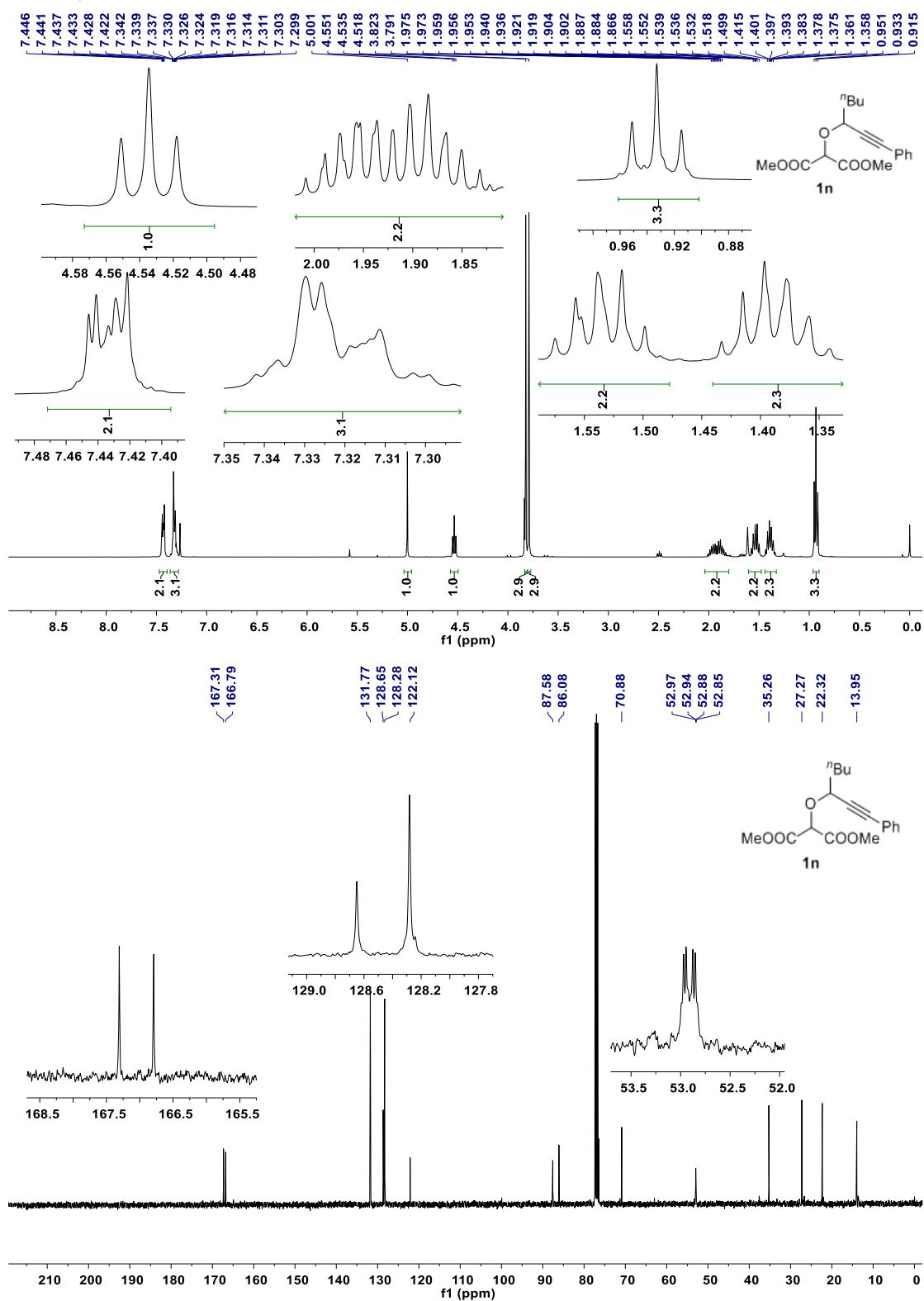
¹H NMR spectrum (400 MHz, CDCl₃) and ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **1l**



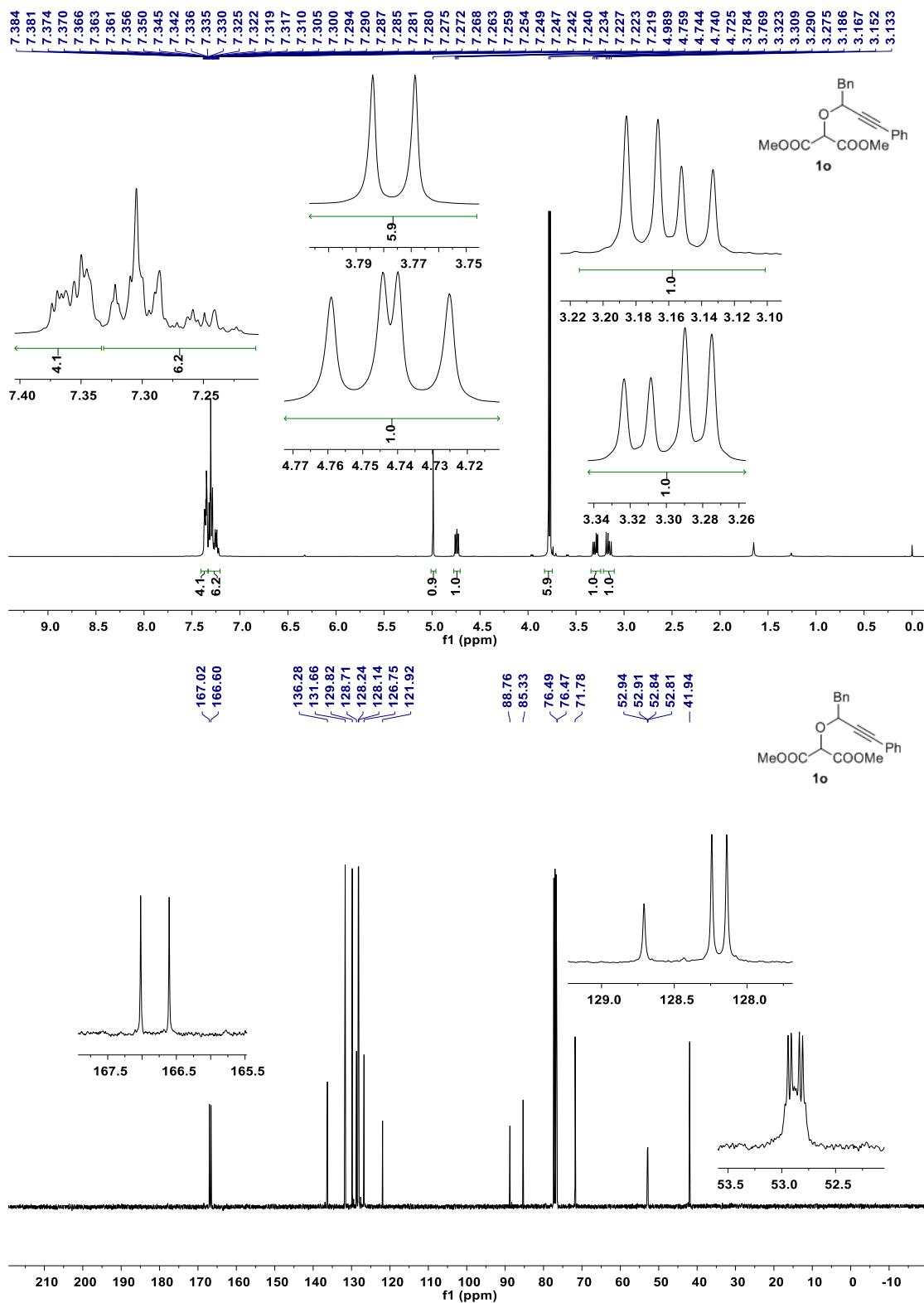
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **1m**



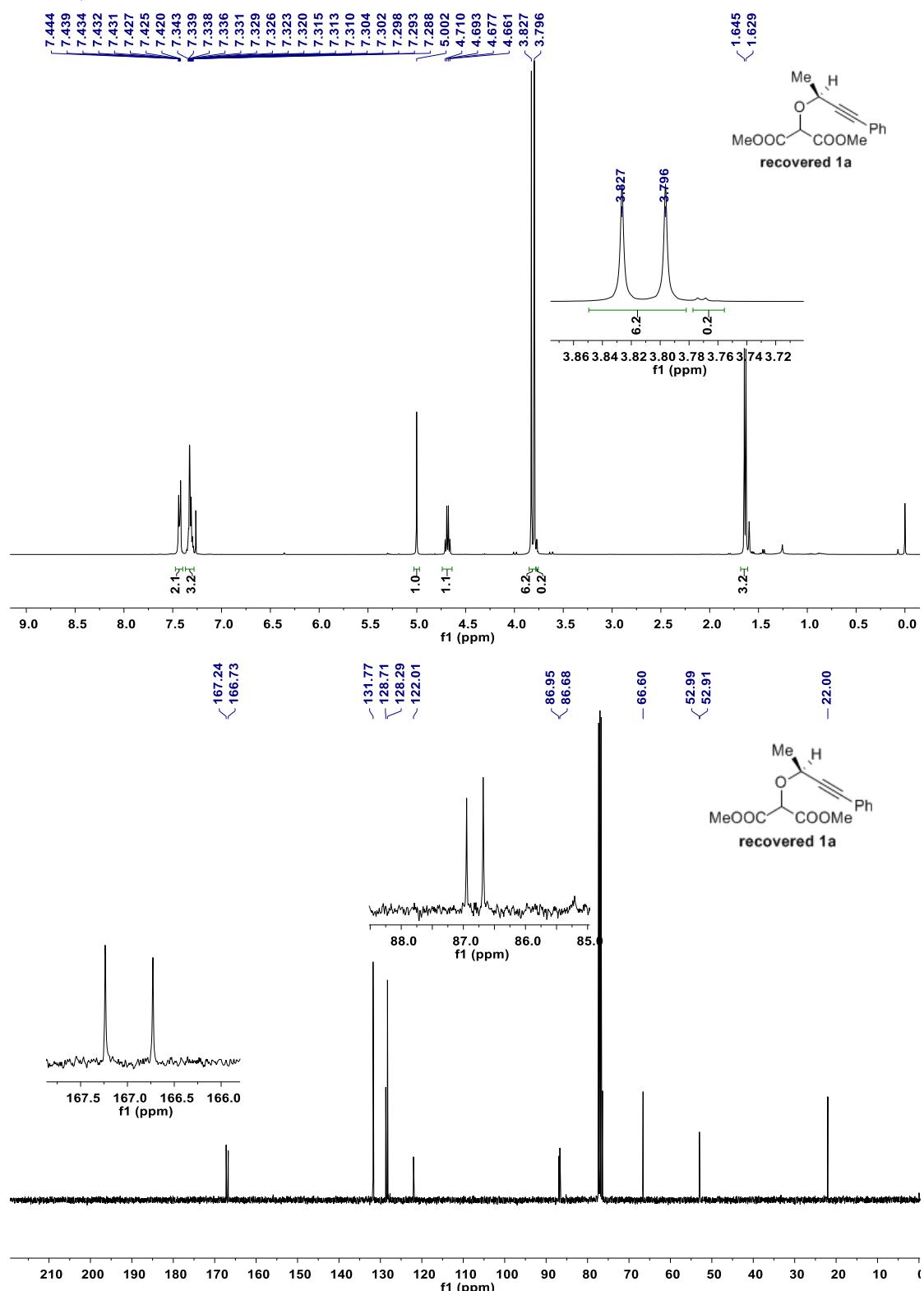
¹H NMR spectrum (400 MHz, CDCl₃) and ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **1n**



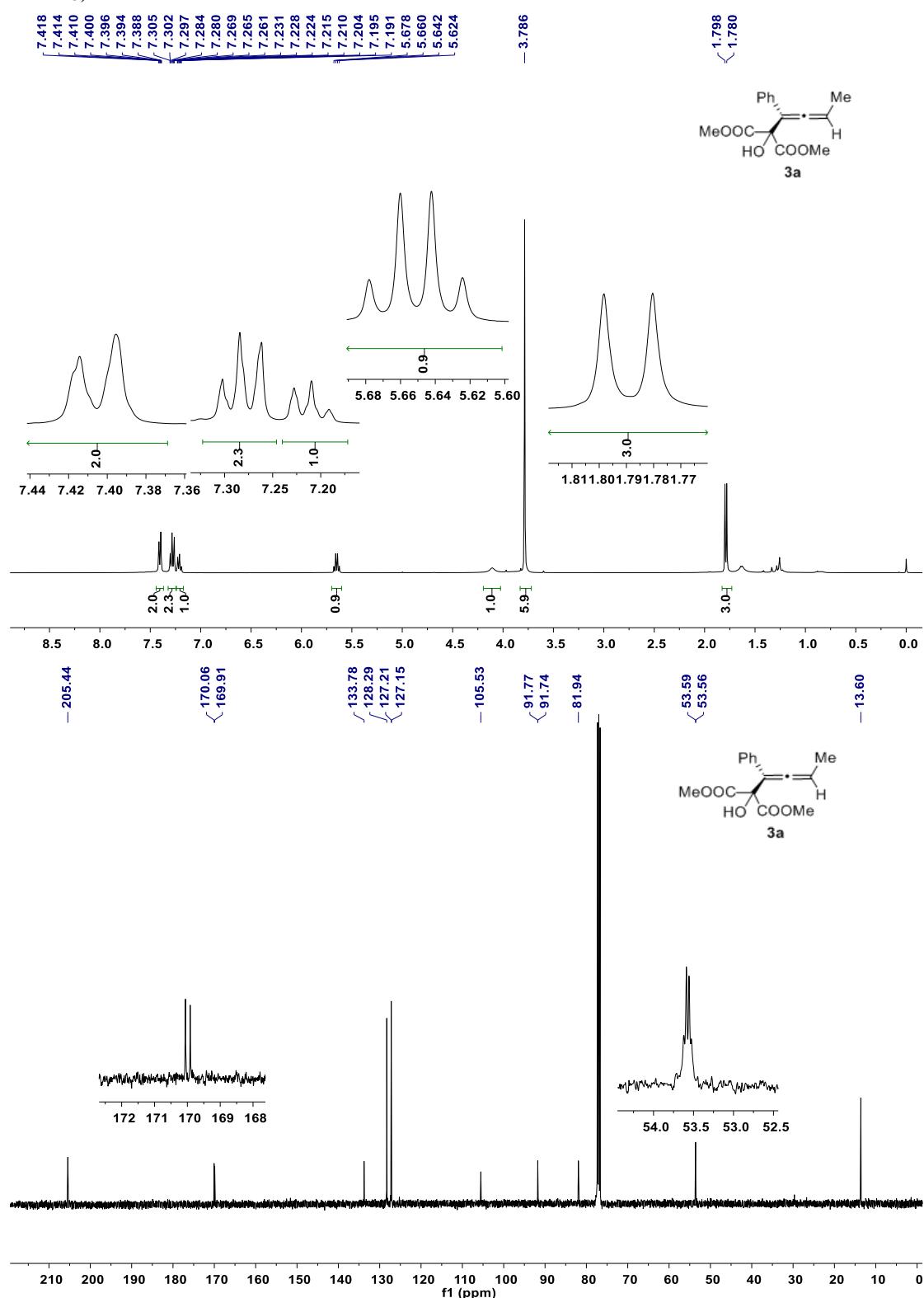
¹H NMR spectrum (400 MHz, CDCl₃) and ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **1o**



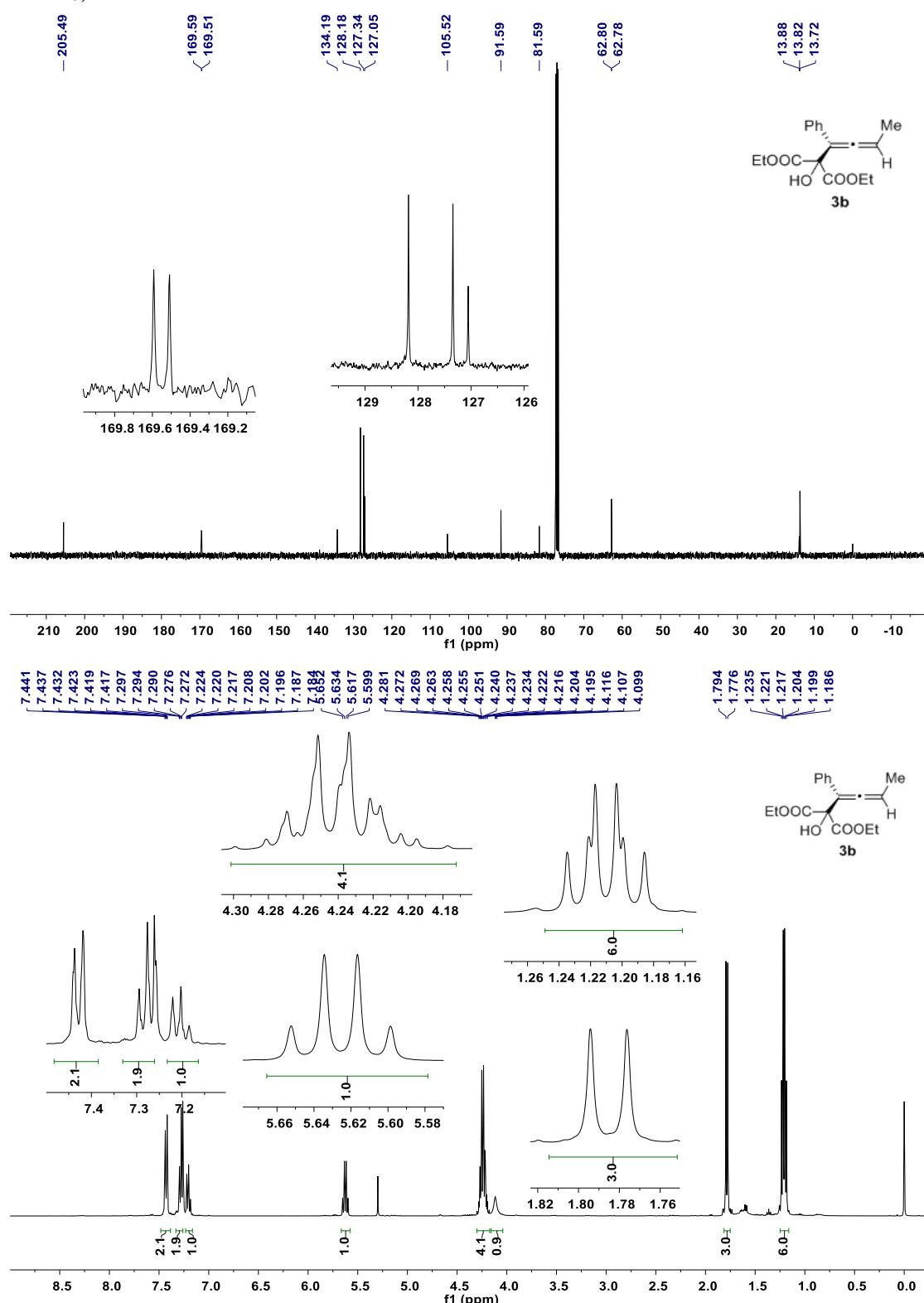
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of recovered **1a**



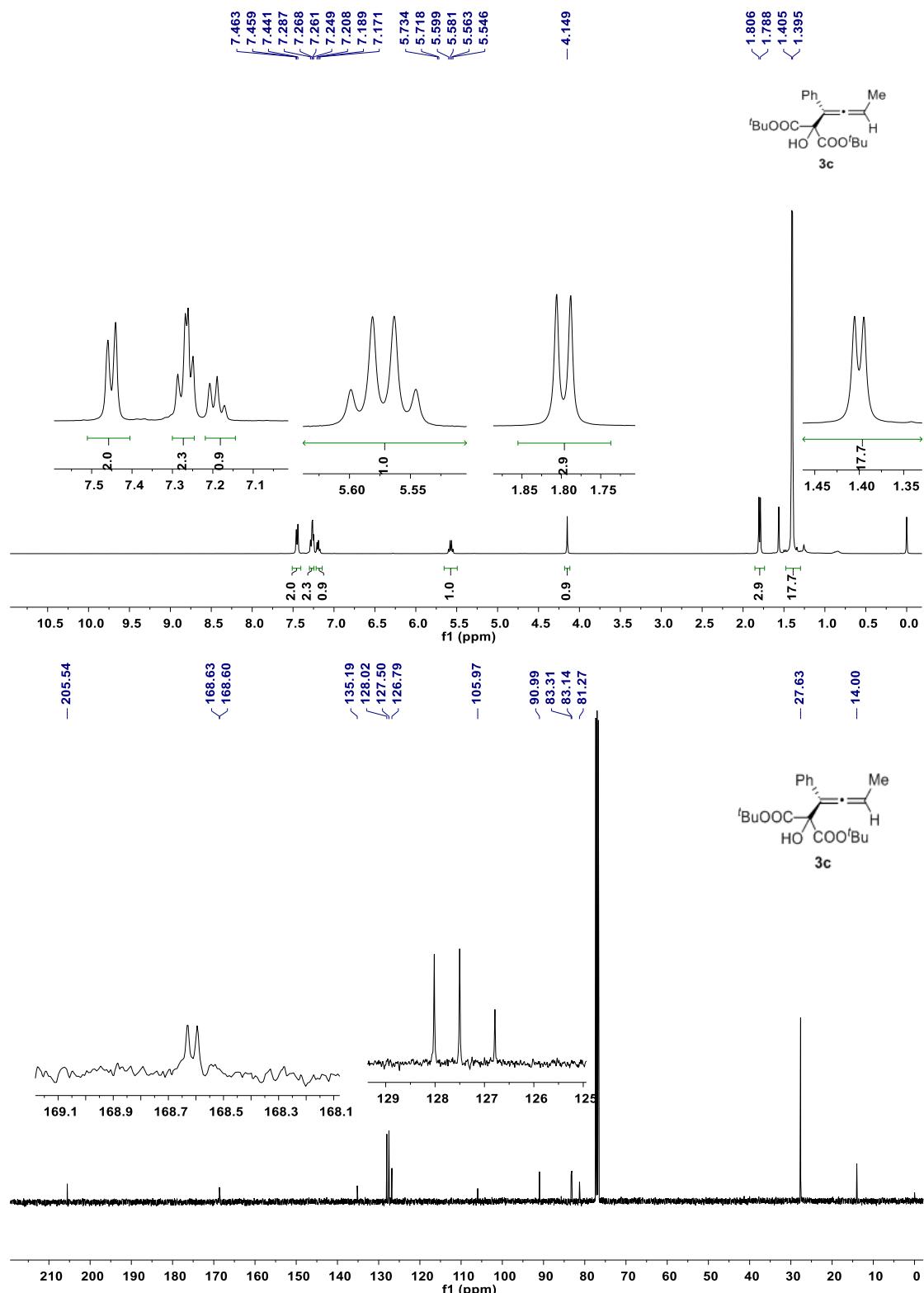
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **3a**



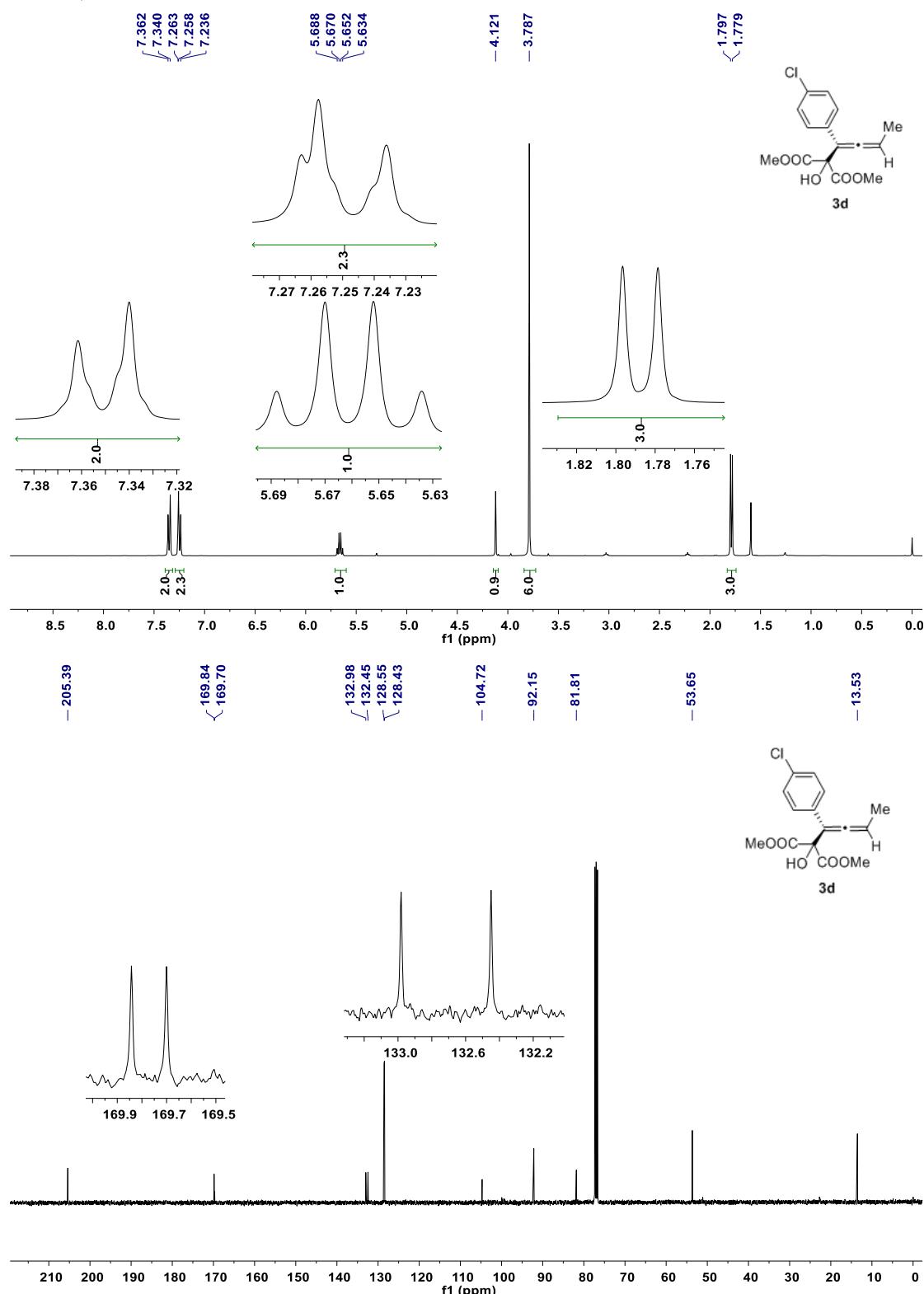
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **3b**



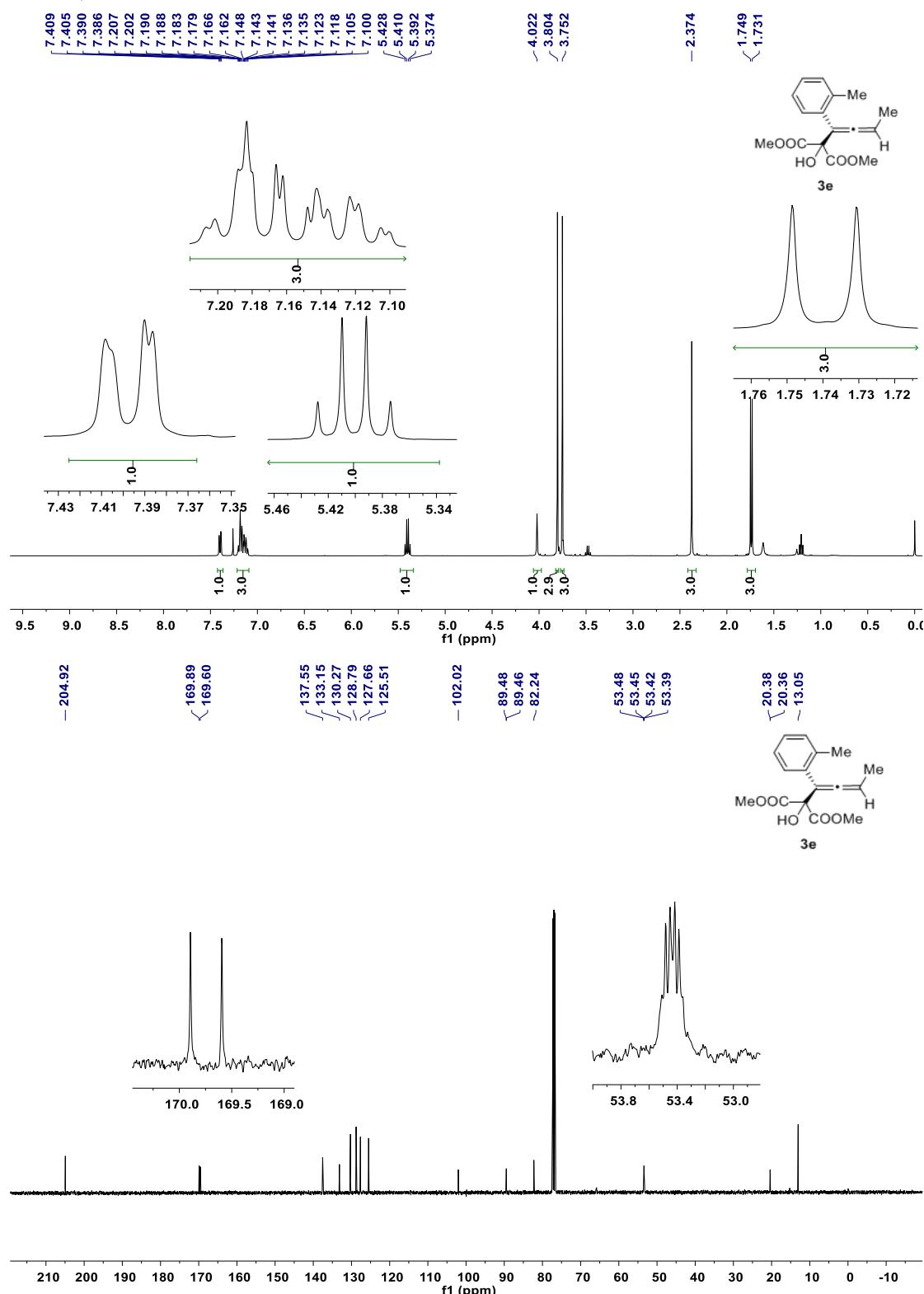
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **3c**



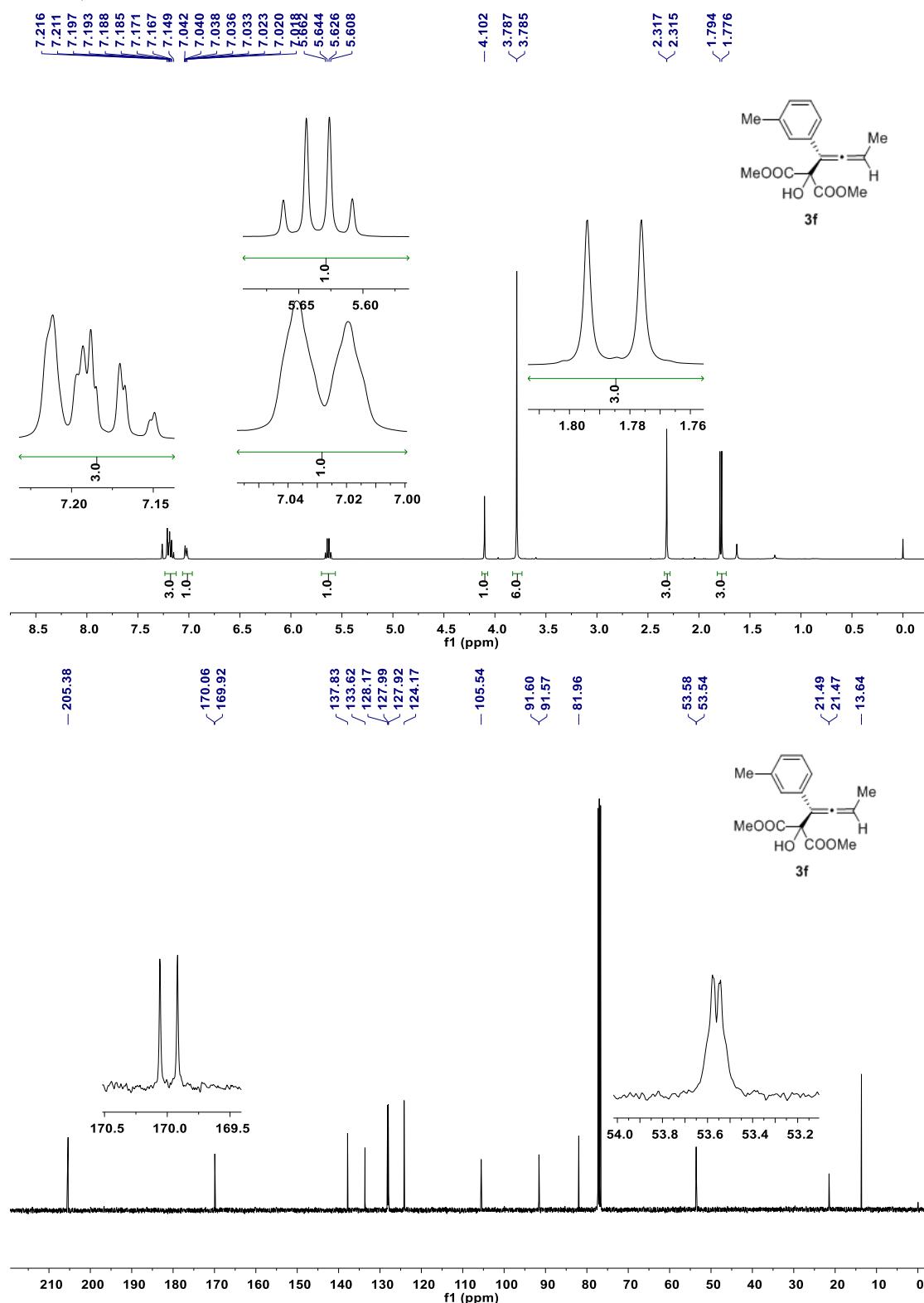
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **3d**



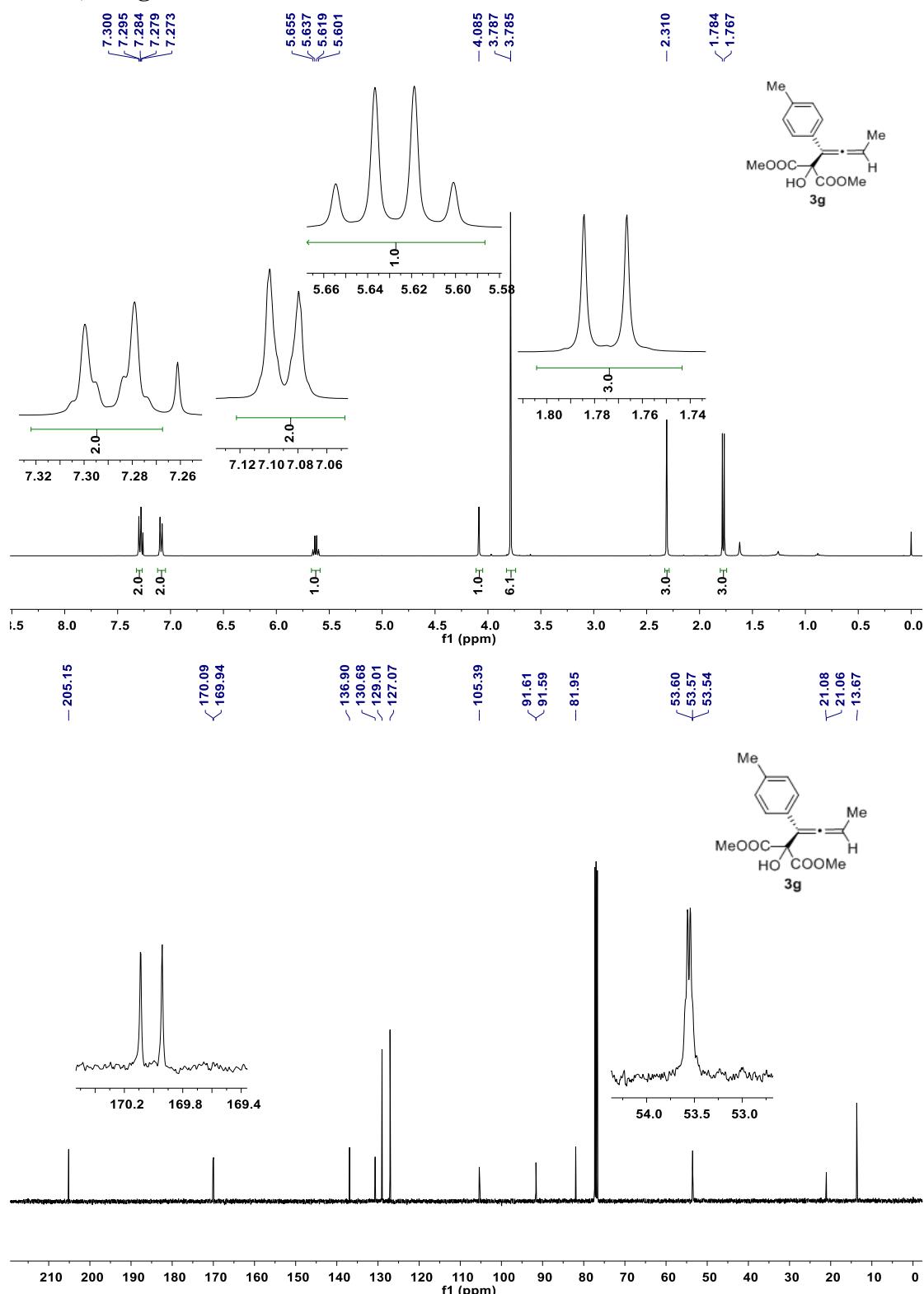
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **3e**



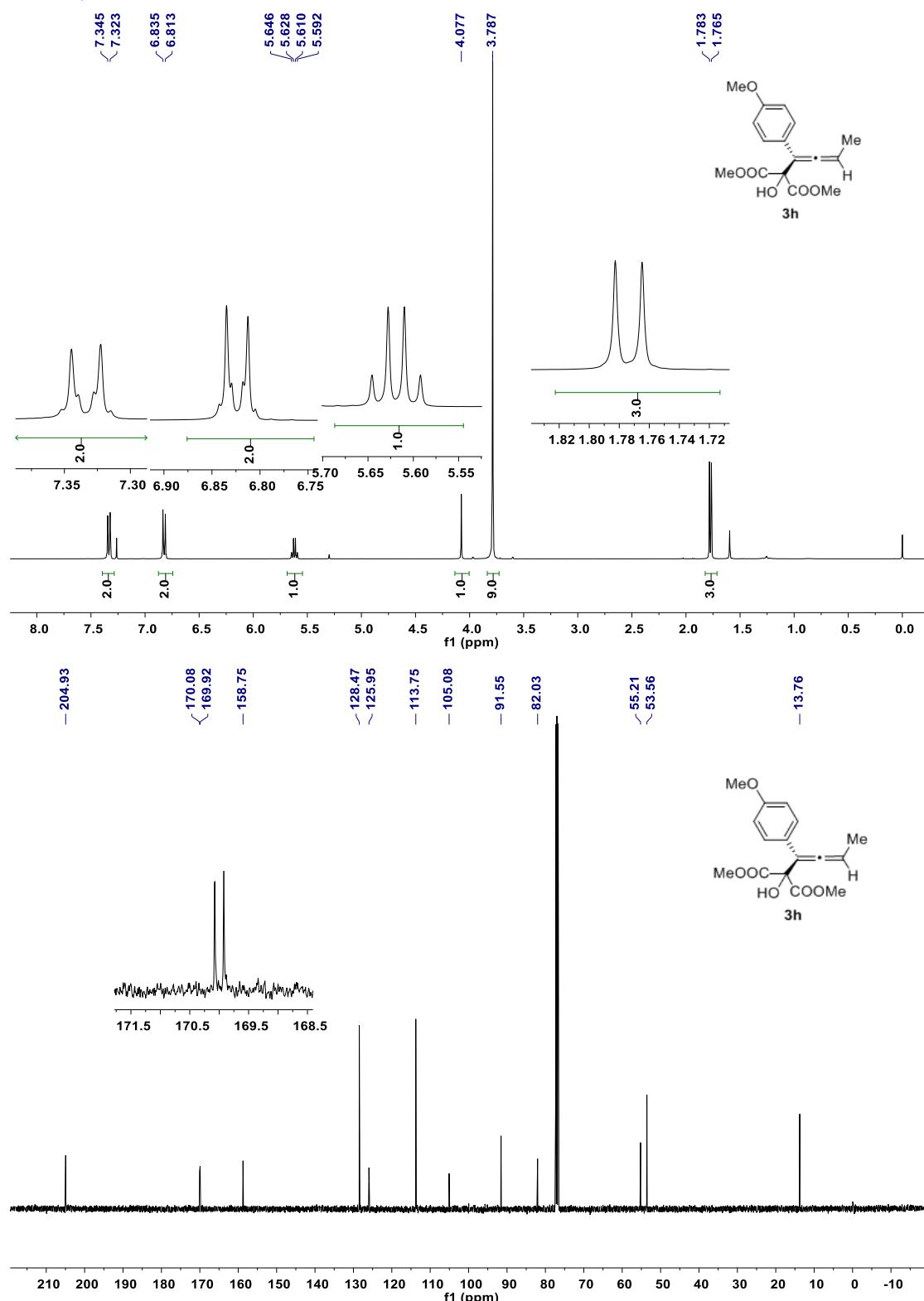
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **3f**



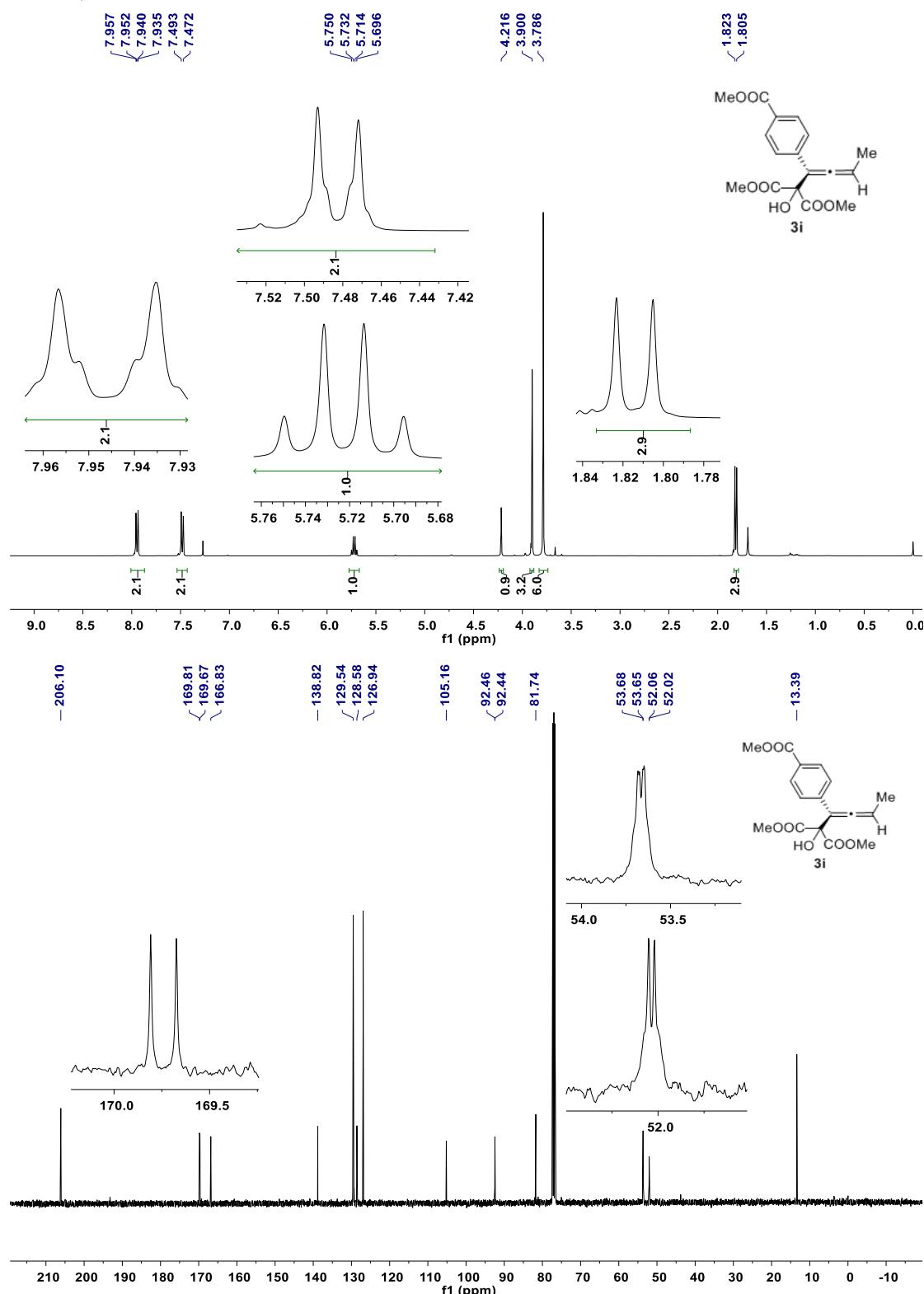
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **3g**



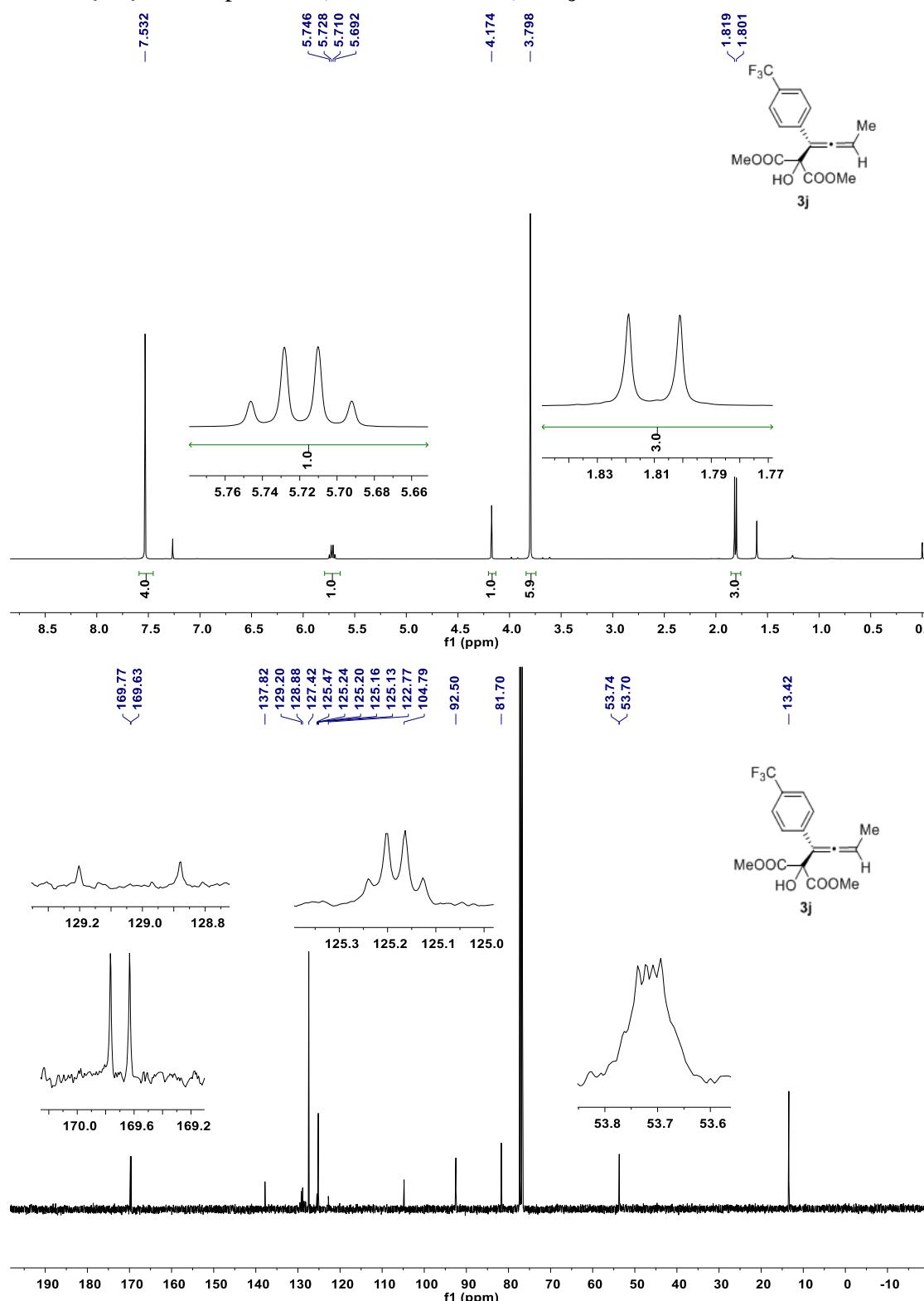
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **3h**

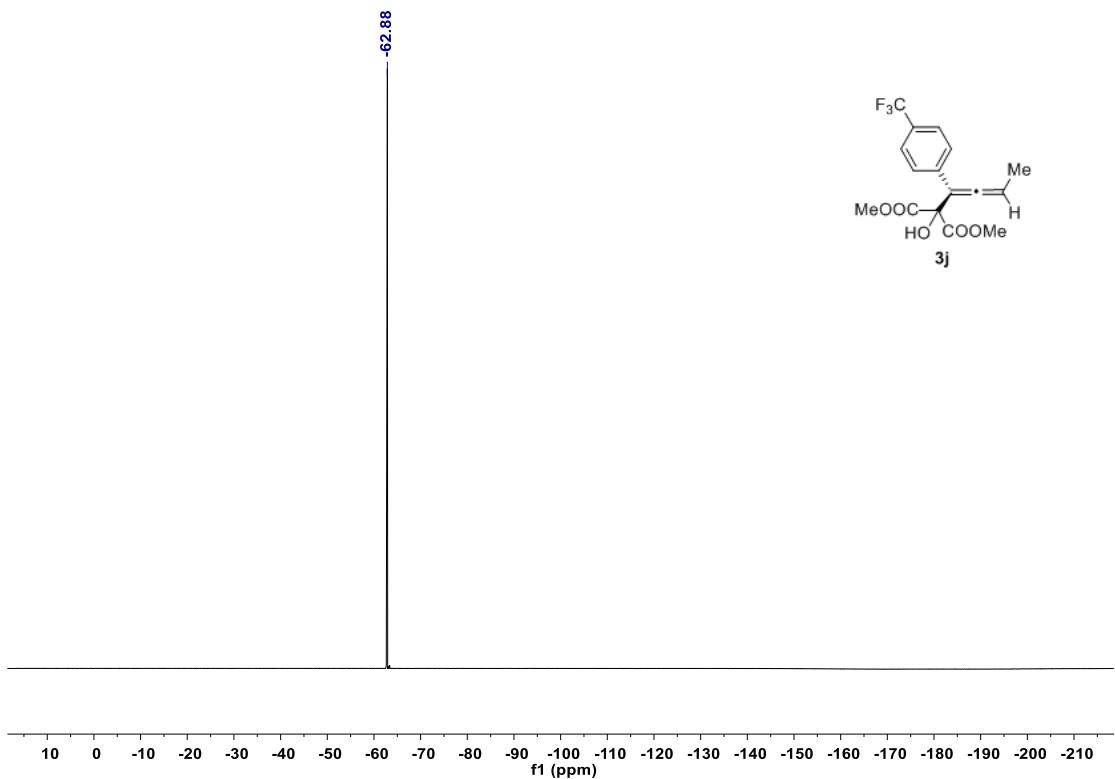


^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **3i**

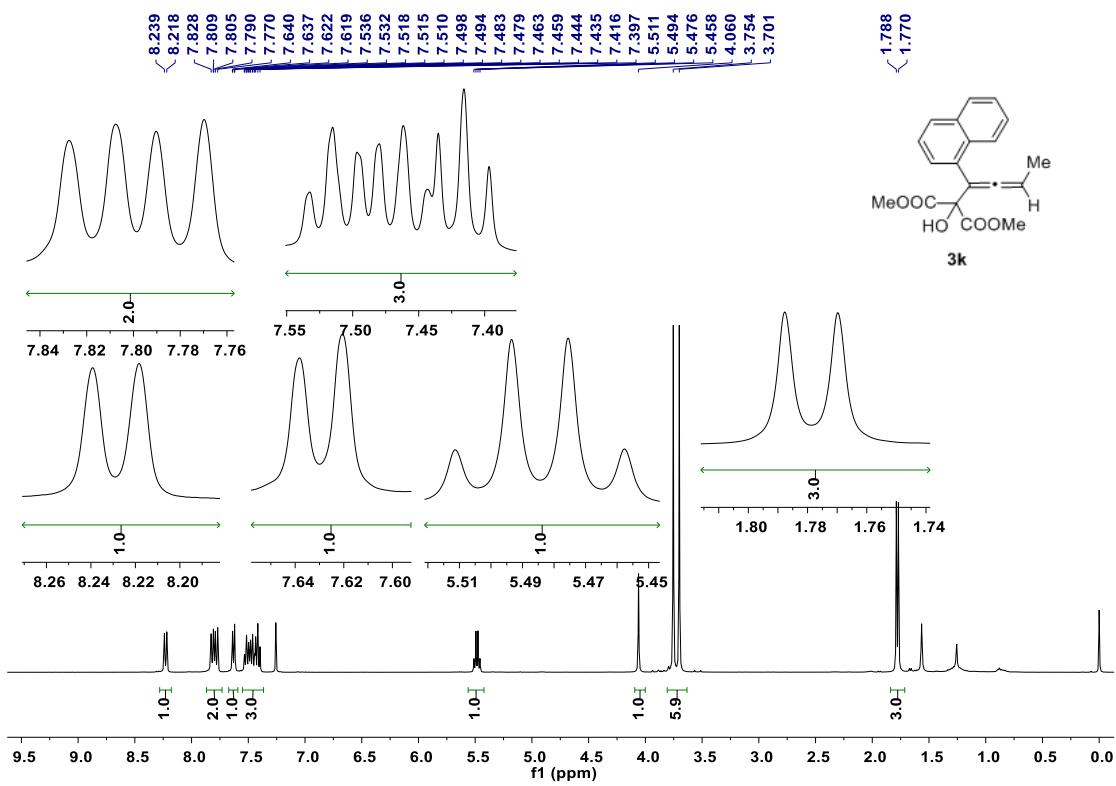


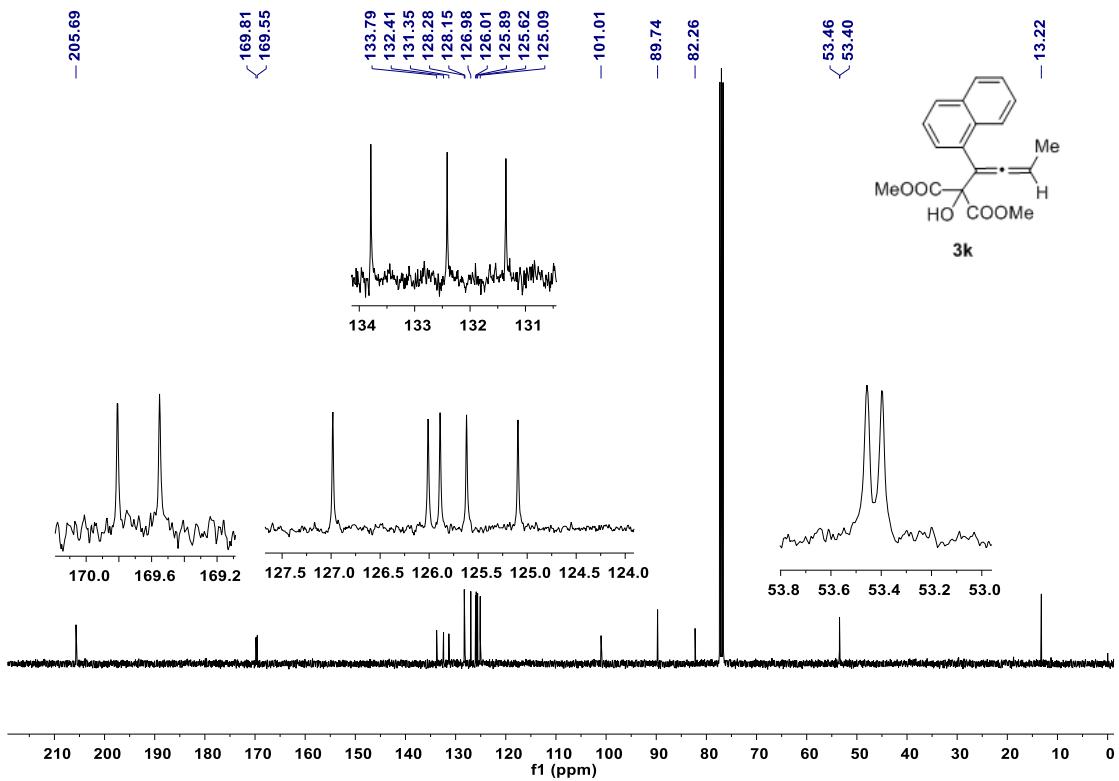
^1H NMR spectrum (400 MHz, CDCl_3), $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3), and $^{19}\text{F}\{\text{H}\}$ NMR spectrum (376 MHz, CDCl_3) of **3j**



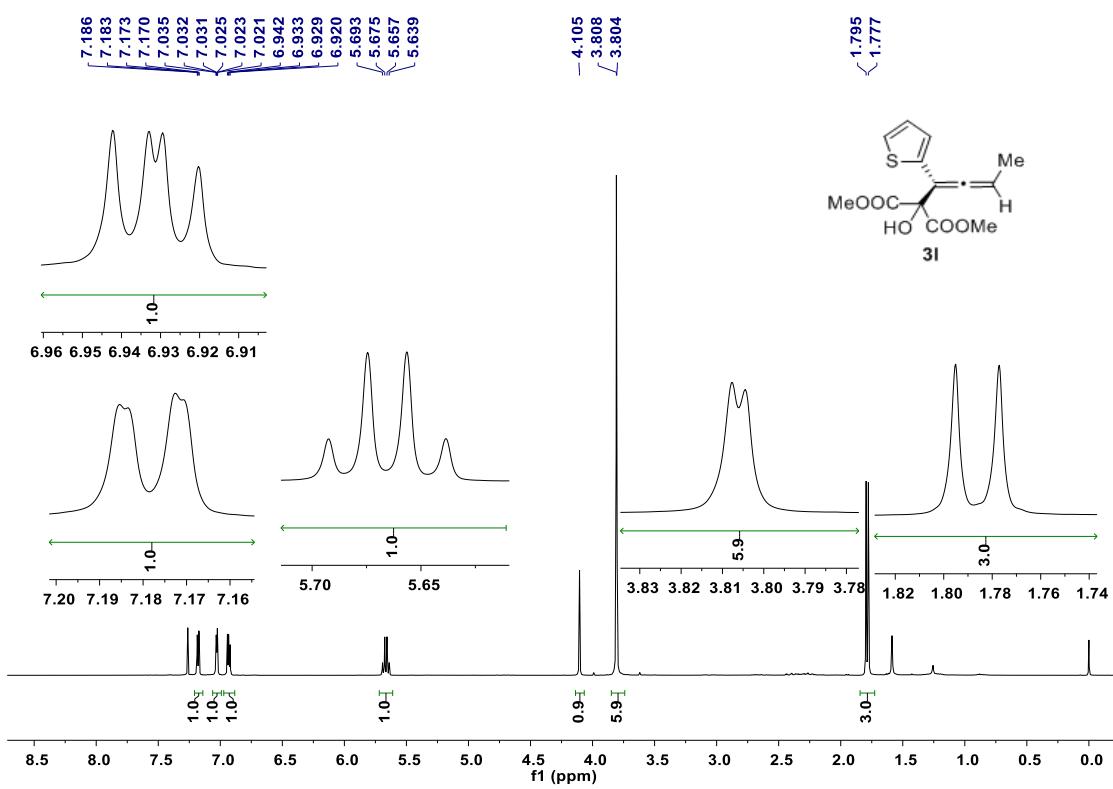


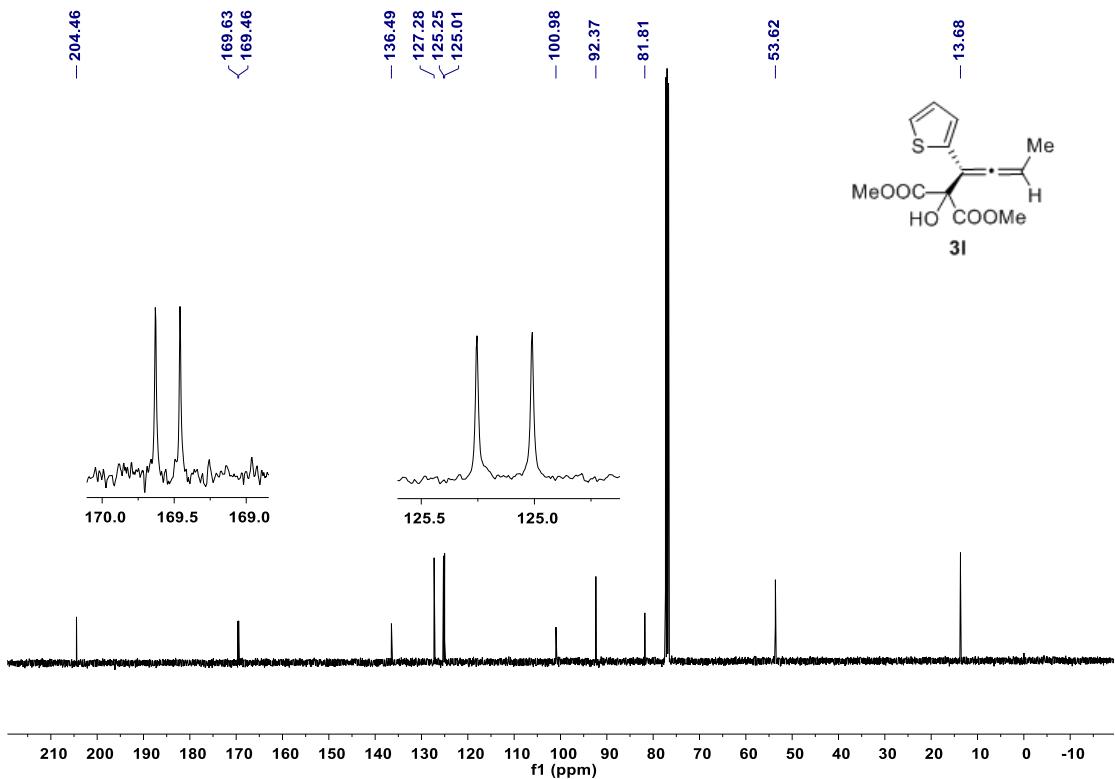
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **3k**



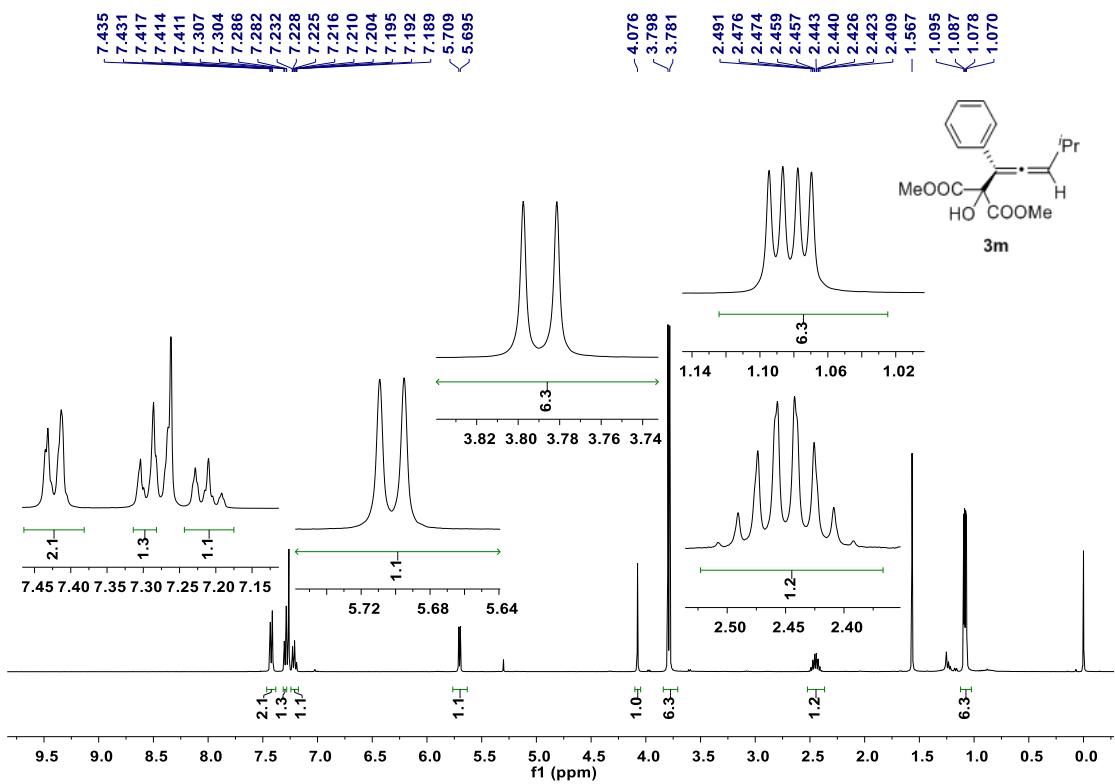


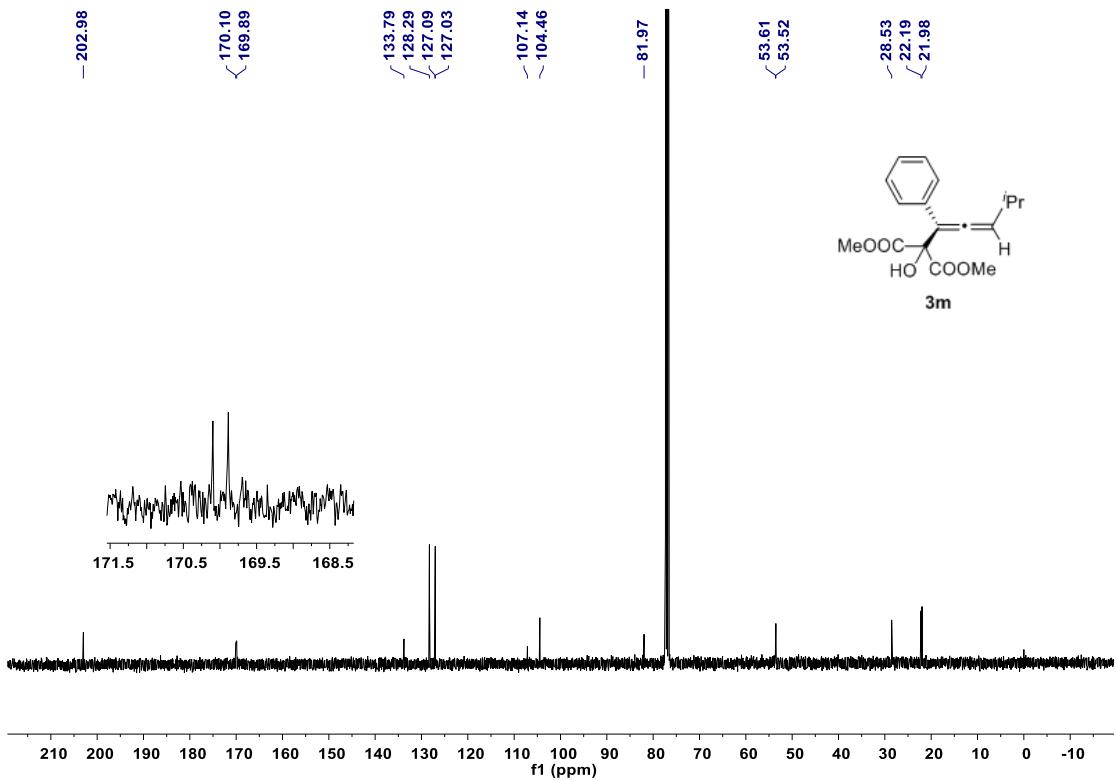
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **3l**



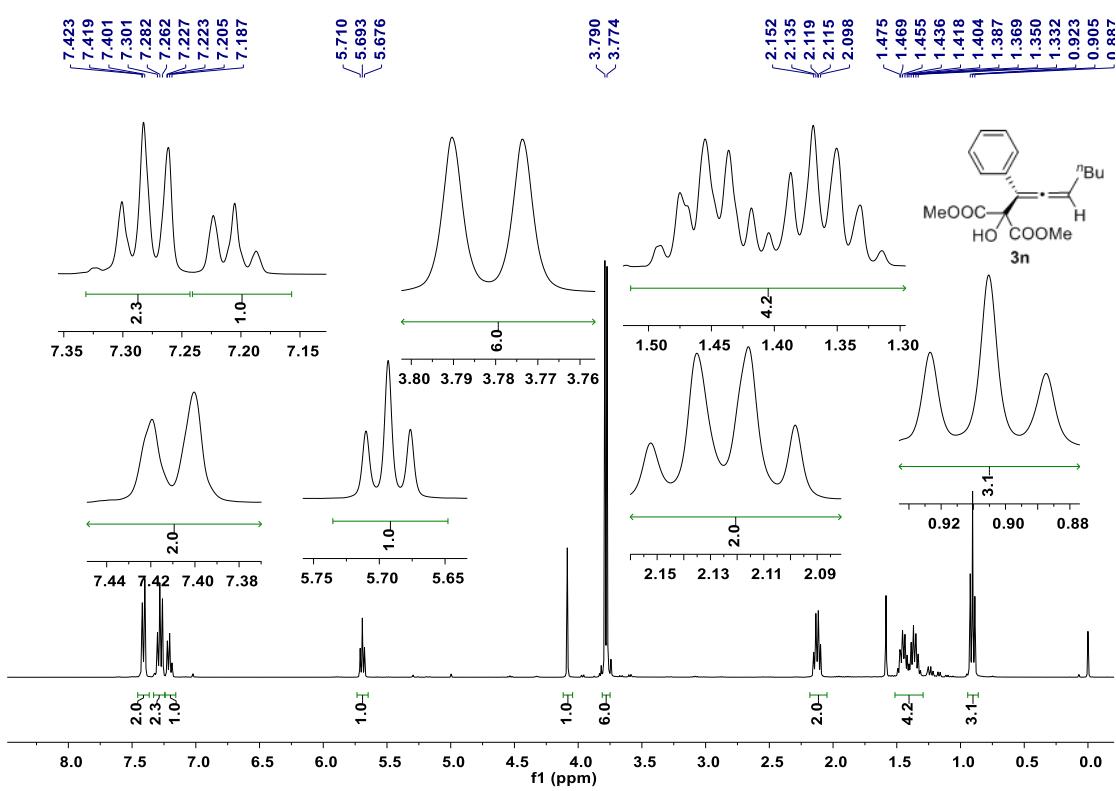


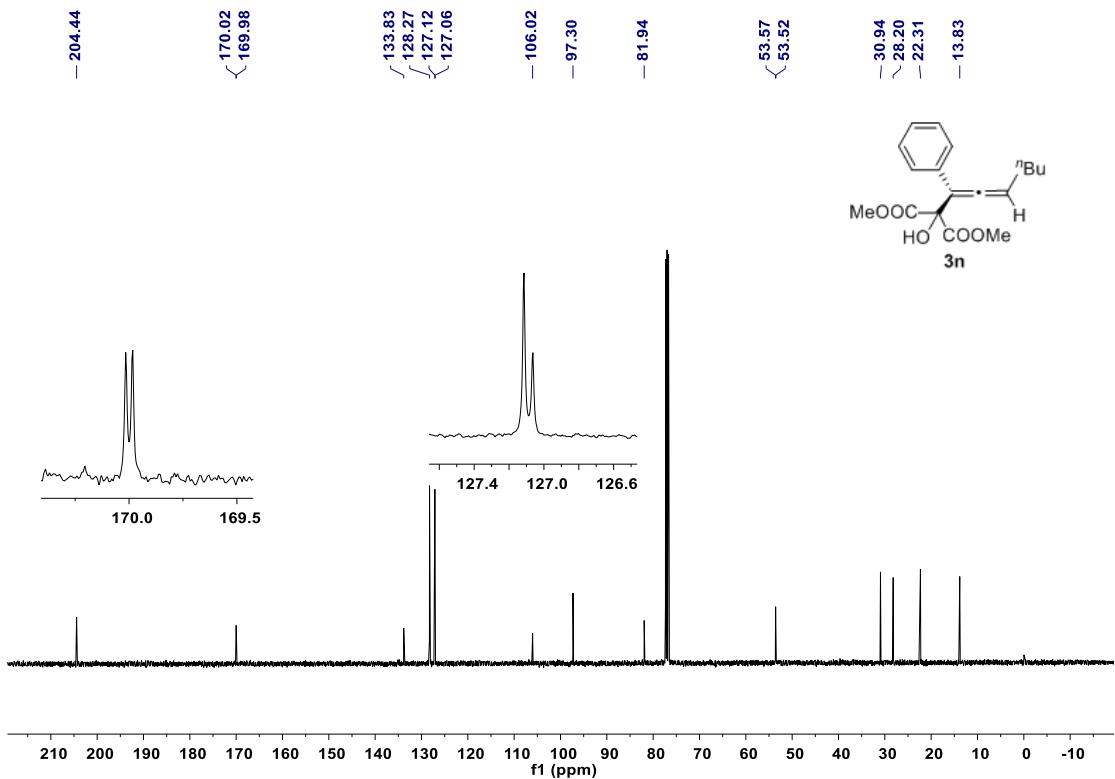
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **3m**



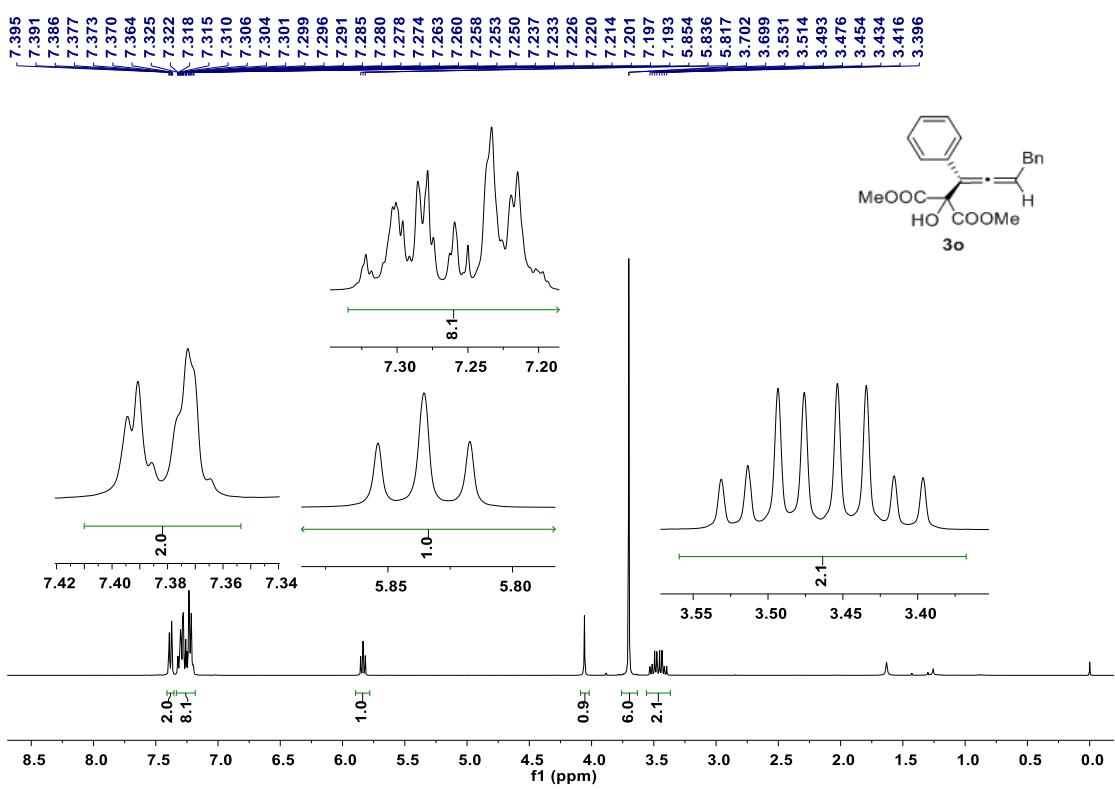


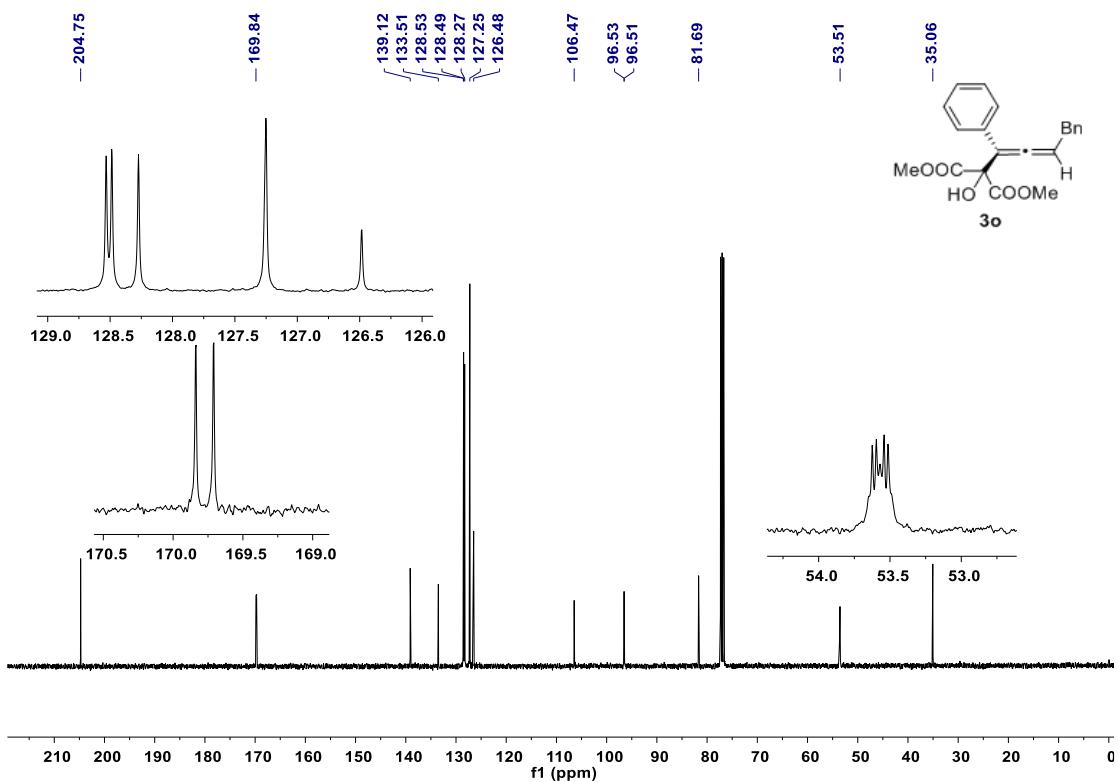
^1H NMR spectrum (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of **3n**



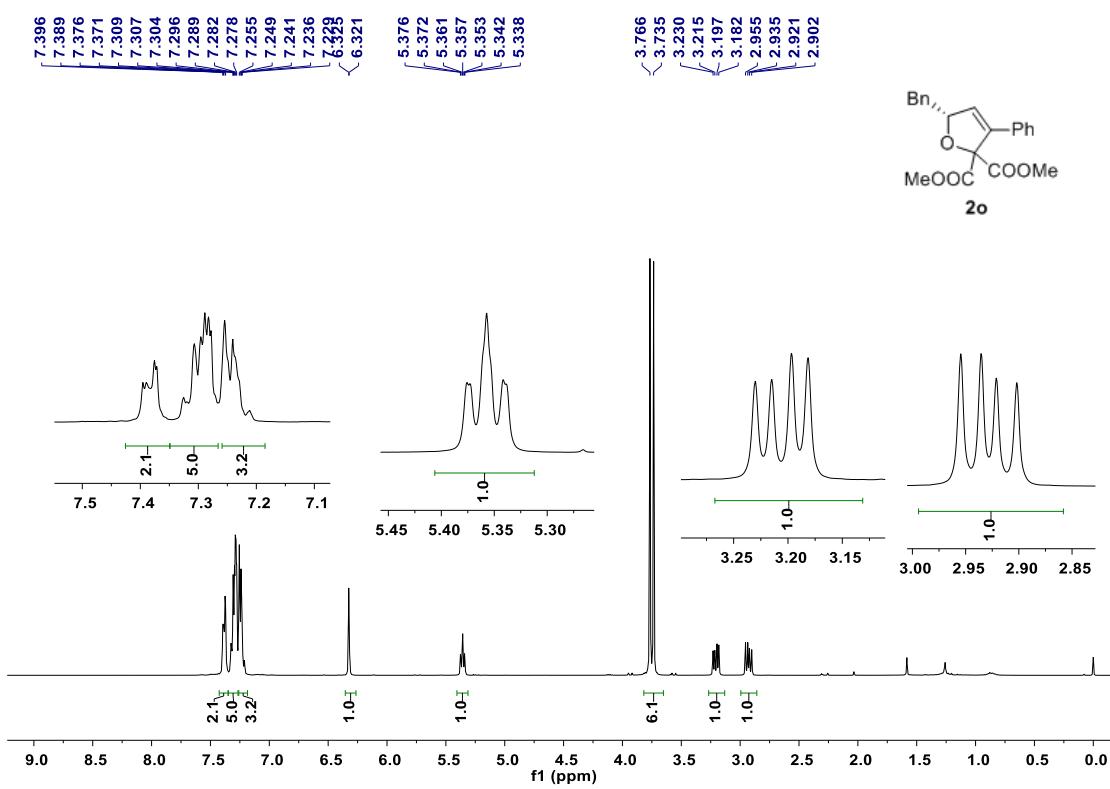


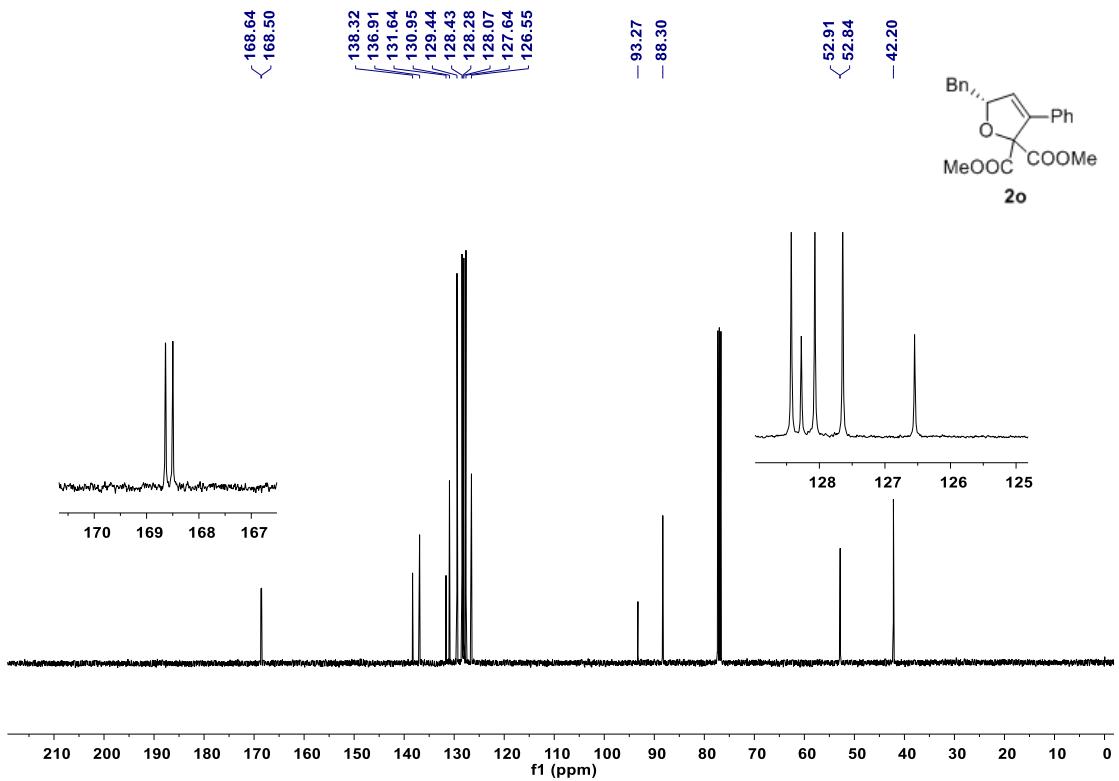
¹H NMR spectrum (400 MHz, CDCl₃) and ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **3o**



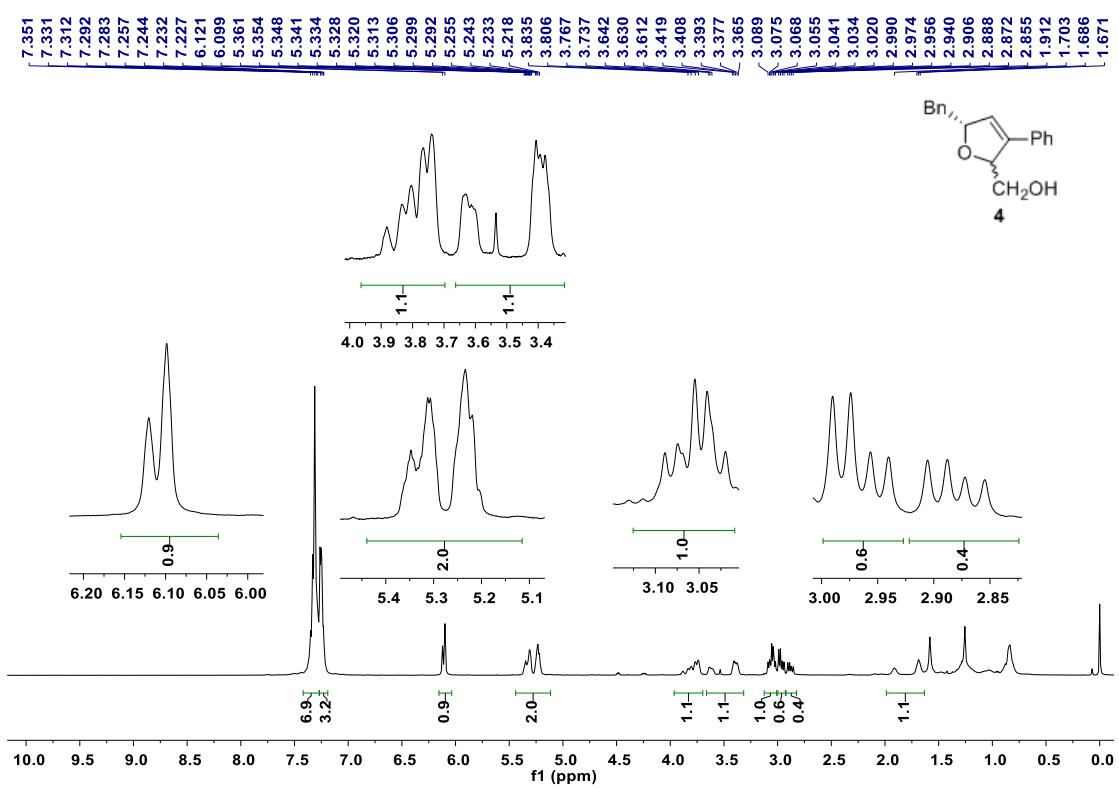


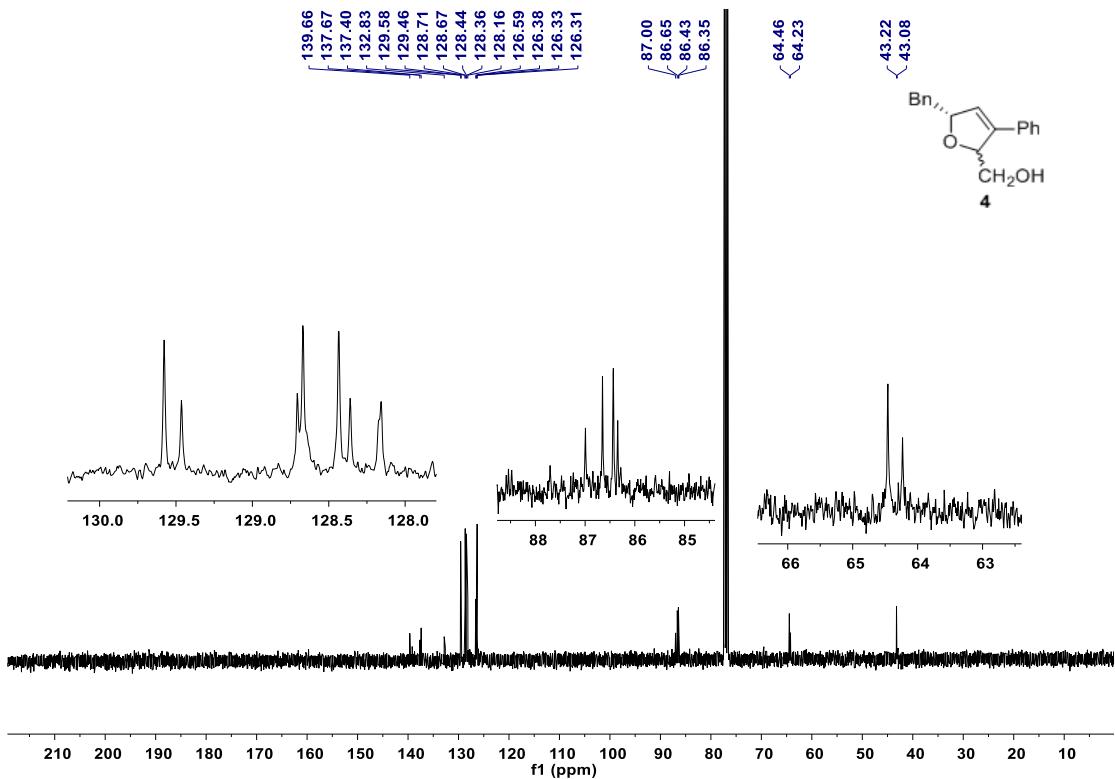
¹H NMR spectrum (400 MHz, CDCl₃) and ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **2o**





¹H NMR spectrum (400 MHz, CDCl₃) and ¹³C{¹H} NMR spectrum (101 MHz, CDCl₃) of **4**





14. Copy of CD spectra in dichloromethane

