Supplementary Information

Calcium-Catalyzed Dehydrative Allylation of P-ylides and Sequential Wittig Reaction for Streamlined Access to Versatile 1,4-Dienes

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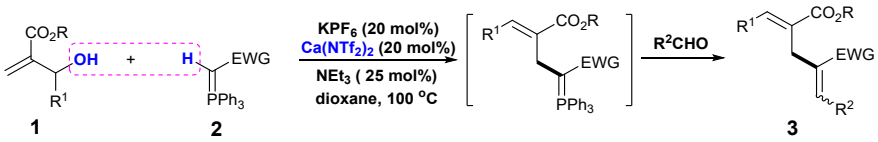
Contents

1. General Information

Unless otherwise noted, all commercially available compounds were used as received. All solvents were purified according to standard procedures. NMR spectra were recorded on a JEOL ECS-400S. The ^{1}H NMR and spectra was recorded at 400MHz, ^{13}C NMR was recorded at 101MHz, ^{19}F NMR and spectra were recorded at 376 MHz. ^{1}H and ^{13}C NMR Chemical shifts were calibrated to tetramethylsilane as an external reference. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet); coupling constants (*J*) are in Hertz (Hz). IR spectra were recorded on a Thermo Scientific Nicolet iS-5 FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. (analyzer type: TOF). Melting points were measured on a RY-I apparatus and are reported uncorrected. The starting materials **1**[1] and **2**[2] were readily prepared according to the related literatures. The KPF_6, Triethylamine, dioxane and methyl aldehyde were purchased from *Energy Chemical* (Shanghai). The catalyst $Ca(NTf_2)_2$ was purchased from TCI (Shanghai).

2. General Procedure

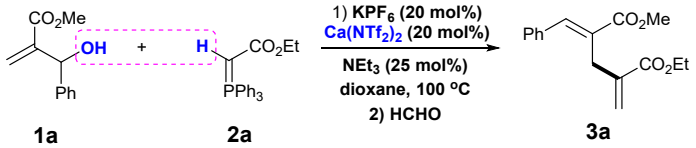
2.1 General procedure for preparation of 3



1 **2** **3**

1 (0.20 mmol), **2** (0.50 mmol, 2.5 equiv.), $Ca(NTf_2)_2$ (20 mol%), and KPF_6 (20 mol%) was add in a dried Schlenk tube (10 mL), dissolved in dioxane (2 mL) and NEt_3 (25 mol%) subsequently under nitrogen atmosphere. The reaction was stirred at 100 °C for 12h, R^2CHO (4.0 equiv.) was then added and stirred for 10h. After complete conversion, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography or PTLC (for the details, see each compound) to afford the corresponding products **3a-3ai.**

2.2 Procedure for gram scale (5.0 mmol) reaction



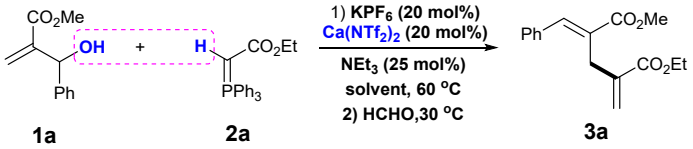
1a **2a** **3a**

Methyl 2-(hydroxy(phenyl)methyl)acrylate **1a** (5.0 mmol), ethyl 2-(triphenyl-λ^5-phosphaneylidene) acetate **2a** (12.5 mmol), $Ca(NTf_2)_2$ (20 mol%), and KPF_6 (20 mol%) was add in a dried Schle

nk tube (100 mL), dissolved in dioxane (50 mL) and NEt_3 (25 mol%) subsequently under nitr ogen atmosphere. The reaction was stirred at 100 °C for 12h, HCHO (4.0 equiv.) was then ad ded and stirred for 10h. After complete conversion, the solvent was removed under reduced pr essure. The residue was purified via column chromatography (Petroleum ether (bp: 60-90 °C)/et hyl acetate = 10:1) to afford the corresponding products **3a** in 72% yield (0.99g).

2.3 Optimization of the Reaction Conditions

Table S1. The effect of solvent on this reaction [a].

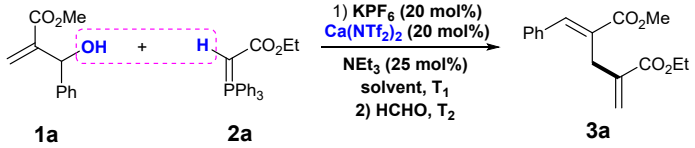


1a **2a** **3a**

Entry	Solvent	Yield of **3a** (%)[b]
1	DMSO	NR
2	DMF	NR
3	DCE	21
4	CHCl3	27
5	Toluene	39
6	Tert-amyl alcohol	Trace
7	**tBuOH**	**52**
8	iPrOH	48
9	Acetone	17
10	**dioxane**	**43**
11	anisole	NR
12	Isopropyl ether	24

[a] Experimental condition: **1a** (0.20 mmol), **2a** (0.24 mmol), $Ca(NTf_2)_2$ (20 mol%), and KPF_6 (20 mol%) dissolved in solvent (2 mL) and NEt_3 (25 mol%) subsequently under nitrogen atmosphere. The reaction was stirred at 100 °C for 12h, HCHO (2.0 equiv.) was then added and stirred for 10h. [b] The yield of **3a** was determined by ^1H NMR of the crude product with Mesitylene as internal standard.

Table S2. The effect of temperature on this reaction [a].

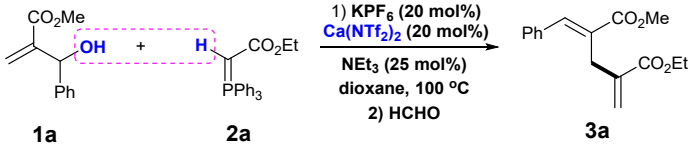


1a **2a** **3a**

Entry	Solvent	T_1 (°C)	T_1 (°C)	Yield of **3a** (%)[b]
1	^{t}BuOH	60	80	45
2	^{t}BuOH	60	70	44
3	^{t}BuOH	60	60	49
4	^{t}BuOH	60	50	35
5	^{t}BuOH	60	40	37
6	dioxane	120	120	45
7	dioxane	110	110	53
8	**dioxane**	**100**	**100**	**54**
9	dioxane	90	90	50
10	dioxane	80	80	45
11	dioxane	70	70	43
12	dioxane	60	60	34
13	dioxane	60	50	35
14	dioxane	60	40	41

[a] Experimental condition: **1a** (0.20 mmol), **2a** (0.24 mmol), $Ca(NTf_2)_2$ (20 mol%), and KPF_6 (20 mol%) dissolved in solvent (2 mL) and NEt_3 (25 mol%) subsequently under nitrogen atmosphere for 12h, HCHO (6.0 equiv.) was then added and stirred for 10h. [b] The yield of **3a** was determined by ^{1}H NMR of the crude product with Mesitylene as internal standard.

Table S3. Screening the equivalent of **2a** [a].

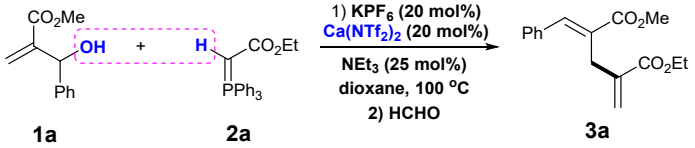


1a **2a** **3a**

Entry	**2a** (equiv.)	Yield of **3a** (%)[b]
1	1.2	54
2	1.5	67
3	2.0	76
4	**2.5**	**82**
5	3.0	83
6	4.0	81
7	5.0	85

[a] Experimental condition: **1a** (0.20 mmol), **2a**, $Ca(NTf_2)_2$ (20 mol%), and KPF_6 (20 mol%) dissolved in dioxane (2 mL) and NEt_3 (25 mol%) subsequently under nitrogen atmosphere. The reaction was stirred at 100 °C for 12h, HCHO (6.0 equiv.) was then added and stirred for 10h. [b] The yield of **3a** was determined by ^{1}H NMR of the crude product with Mesitylene as internal standard.

Table S4. Screening the equivalent of HCHO [a].

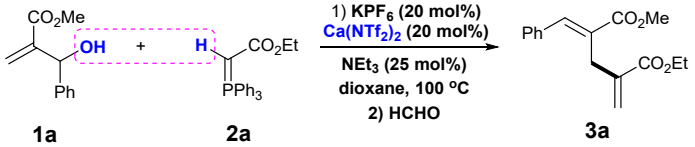


1a **2a** **3a**

Entry	HCHO (equiv.)	Yield of **3a** (%)[b]
1	2.5	82
2	3.0	81
3	**4.0**	**85**
4	5.0	82
5	6.0	82
6	7.0	83

[a] Experimental condition: **1a** (0.20 mmol), 2**a** (0.50 mmol), $Ca(NTf_2)_2$ (20 mol%), and KPF_6 (20 mol%) dissolved in dioxane (2 mL) and NEt_3 (25 mol%) subsequently under nitrogen atmosphere. The reaction was stirred at 100 °C for 12h, HCHO was then added and stirred for 10h. [b] The yield of **3a** was determined by ^1H NMR of the crude product with Mesitylene as internal standard.

Table S5. The effect of catalyst and additives on this reaction [a].

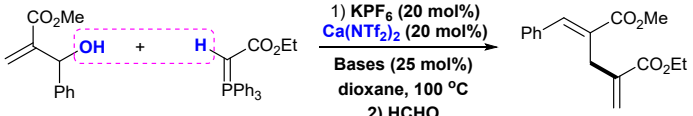


1a **2a** **3a**

Entry	Catalyst	Add.	Yield of **3a** (%)[b]
1	$Ca(NTf_2)_2$	None	75
2	**$Ca(NTf_2)_2$**	**KPF_6**	**85**
3	$Ca(NTf_2)_2$	$^tBu_4NBF_4$	59
4	$Ca(NTf_2)_2$	$AgSbF_6$	Trace
5	$Ca(NTf_2)_2$	$NaSbF_6$	Trace
6	$Mg(OTf)_2$	KPF_6	Trace
7	$Mg(NTf_2)_2$	KPF_6	25
8	$Ba(NTf_2)_2$	KPF_6	35
9	$Ca(OTf)_2$	KPF_6	40
10	$Cu(OTf)_2$	KPF_6	NR
11	$Al(OTf)_3$	KPF_6	36
12	None	KPF_6	NR
13	$CaCl_2$	KPF_6	NR
14	$HNTf_2$	KPF_6	NR

[a] Experimental condition: **1a** (0.20 mmol), **2a** (0.50 mmol), catalyst (20 mol%), and additive (20 mol%) dissolved in dioxane (2 mL) and NEt_3 (25 mol%) subsequently under nitrogen atmosphere. The reaction was stirred at 100 °C for 12h, HCHO (4.0 equiv.) was then added and stirred for 10h. [b] The yield of **3a** was determined by ^1H NMR of the crude product with Mesitylene as internal standard.

Table S6. The effect of bases on this reaction [a].



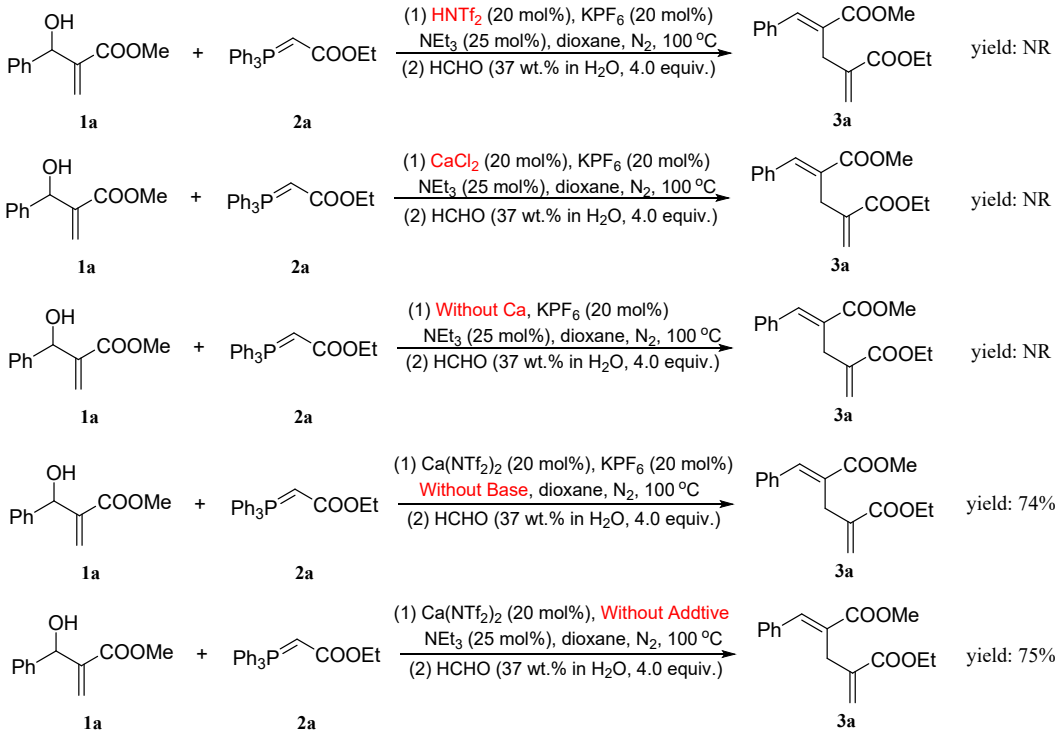
1a **2a** **3a**

Entry	Bases	Yield of **3a** (%)[b]
1	DABCO	54
2	DBU	41
3	DBN	55
4	NaOH	50
5	K_2CO_3	69
6	KOH	68
7	None	74
8	**Et_3N**	**90(88)[c]**

[a] Experimental condition: **1a** (0.20 mmol), **2a** (0.50 mmol), $Ca(NTf_2)_2$ (20 mol%), and KPF_6 (20 mol%) dissolved in dioxane (2 mL) and bases (25 mol%) subsequently under nitrogen atmosphere. The reaction was stirred at 100 °C for 12h, HCHO (4.0 equiv.) was then added and stirred for 10h. [b] The yield of **3a** was determined by ^1H NMR of the crude product with Mesitylene as internal standard. [c] Isolated yield.

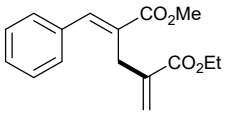
3. Mechanistic Study

3.1 Control experiment.



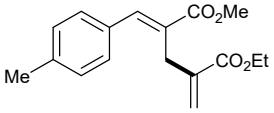
4. Analytical Data for All New Compounds

5-ethyl 1-methyl (*E*)-2-benzylidene-4-methylenepentanedioate (3a)



Following the general procedure, the reaction was conducted in 0.2 mmol scale, **3a** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (48.0 mg, 88% yield, E/Z = 96/4 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.37 – 7.32 (m, 5H), 6.29 (s, 1H), 5.49 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.57 (s, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 166.9, 142.0, 138.4, 135.0, 129.2, 129.1, 128.9, 128.7, 124.6, 61.0, 52.3, 29.9, 14.3. IR (KBr): 2984, 2952, 1715, 1633, 1447, 1221, 1138, 768, 698 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{16}H_{19}O_4$ 275.1283; found 275.1278.

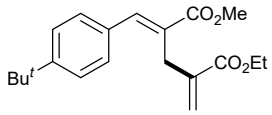
1-ethyl 5-methyl (*E*)-4-(4-methylbenzylidene)-2-methylenepentanedioate (3b)



Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale, **3b** was isolated

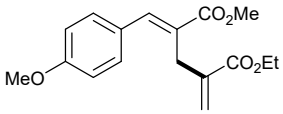
by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (48.0 mg, 83% yield, E/Z = 97/3 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.28 (s, 1H), 5.48 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.57 (s, 2H), 2.35 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 167.0, 142.1, 139.4, 138.3, 132.1, 129.5, 129.3, 127.8, 124.6, 61.0, 52.3, 29.9, 21.5, 14.3. IR (KBr): 2989, 1715, 1275, 1260, 1137, 1092, 750 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{17}H_{20}O_4K$ 327.0999; found 327.0992.

5-ethyl 1-methyl (*E*)-2-(4-(tert-butyl)benzylidene)-4-methylenepentanedioate (3c)



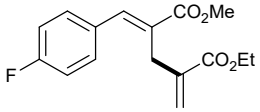
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale, **3c** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (53.9 mg, 82% yield, E/Z = 96/4 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.28 (s, 1H), 5.49 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.59 (s, 2H), 1.35 – 1.31 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 167.0, 152.5, 142.0, 138.3, 132.1, 129.3, 127.8, 125.7, 124.6, 61.1, 52.3, 34.9, 31.3, 30.0, 14.3. IR (KBr): 2960, 2870, 1716, 1274, 1206, 1111, 1092, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{20}H_{27}O_4$ 331.1909; found 331.1900.

1-ethyl 5-methyl (*E*)-4-(4-methoxybenzylidene)-2-methylenepentanedioate (3d)



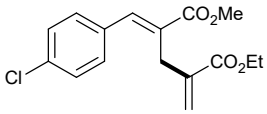
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale, **3d** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as white solid (46 mg, 76% yield, E/Z > 99/1 as determined by ^{1}H NMR). Mp: 45.4-46.7 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.28 (s, 1H), 5.49 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 3.79 (s, 3H), 3.58 (s, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 167.0, 160.4, 141.8, 138.1, 131.2, 127.5, 126.3, 124.6, 114.2, 61.1, 55.4, 52.2, 29.9, 14.3. IR (KBr): 2952, 2839, 1713, 1605, 1512, 1258, 1177, 1136, 1029, 750 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{17}H_{20}O_4K$ 343.0948; found 343.0942.

1-ethyl 5-methyl (*E*)-4-(4-fluorobenzylidene)-2-methylenepentanedioate (3e)



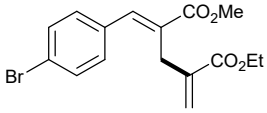
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale, **3e** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (46.2 mg, 80% yield, E/Z = 97/3 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.34 – 7.31 (m, 2H), 7.08 – 7.04 (m, 2H), 6.29 (s, 1H), 5.48 (s, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.54 (s, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.3, 166.8, 163.0 (d, *J* = 250.2 Hz), 140.8, 138.1, 131.2 (d, *J* = 8.4 Hz), 131.1, 128.6, 124.6, 115.8 (d, *J* = 21.6 Hz), 61.1, 52.3, 29.8, 14.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.15. IR (KBr): 2986, 2953, 1716, 1509, 1275, 1227, 1161, 1138, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{16}H_{18}O_4F$ 293.1189; found 293.1193.

5-ethyl 1-methyl (*E*)-2-(4-chlorobenzylidene)-4-methylenepentanedioate (3f)



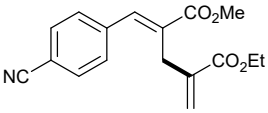
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale, **3f** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as white solid (54.3 mg, 88% yield, E/Z > 99/1 as determined by ^{1}H NMR). Mp: 27.8-29.3 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.29 (s, 1H), 5.47 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.53 (s, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 166.7, 140.6, 138.1, 135.1, 133.4, 130.5, 129.5, 129.0, 124.7, 61.1, 52.4, 29.8, 14.3. IR (KBr): 2985, 2953, 1715, 1633, 1492, 1435, 1275, 1260, 1090, 765, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{16}H_{18}O_4Cl$ 309.0894; found 309.0885.

5-ethyl 1-methyl (*E*)-2-(4-bromobenzylidene)-4-methylenepentanedioate (3g)



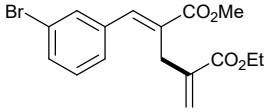
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale, **3g** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as light yellow solid. (58.8 mg, 84% yield, E/Z = 97/3 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.28 (s, 1H), 5.46 (s, 1H), 4.25 (q, *J* = 7.6, 7.2 Hz, 2H), 3.79 (s, 3H), 3.52 (s, 2H), 1.32 (t, *J* = 7.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 166.7, 140.7, 138.1, 133.9, 132.0, 130.7, 129.6, 124.7, 123.4, 61.1, 52.4, 29.9, 14.3. IR (KBr): 2984, 2952, 1716, 1307, 1275, 1138, 1092, 1026, 764, 750 cm^{-1}. HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for: $C_{16}H_{17}O_4BrNa$ 375.0208; found 375.0202.

5-ethyl 1-methyl (*E*)-2-(4-cyanobenzylidene)-4-methylenepentanedioate (3h)



Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale**, 3h** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as white solid (26.0 mg, 48% yield, E/Z = 94/6 as determined by ^{1}H NMR). Mp: 63.2-64.5 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.68 – 7.65 (m, 2H), 7.44 – 7. (m, 2H), 6.30 (s, 1H), 5.47 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 3.52 (s, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 166.5, 139.6, 138.0, 132.5, 132.1, 129.6, 128.8, 124.9, 118.5, 112.4, 61.2, 52.6, 29.9, 14.3. IR (KBr): 2984, 2229, 1715, 1435, 1261, 1207, 1139, 1092, 764, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{17}H_{18}O_4N$ 300.1236; found 300.1232.

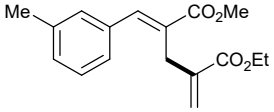
5-ethyl 1-methyl (*E*)-2-(3-bromobenzylidene)-4-methylenepentanedioate (3i)



Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale, **3i** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (56.6 mg, 81% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.47 – 7.45 (m, 2H), 7.2 – 7.23 (m, 2H), 6.29 (s, 1H), 5.47 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.53 (s, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 166.7, 140.2, 138.1, 137.1, 132.1,

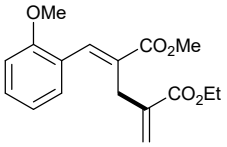
131.9, 130.4, 130.2, 127.4, 124.8, 122.7, 61.1, 52.4, 29.7, 14.3. IR (KBr): 2984, 2952, 1716, 1435, 1275, 1201, 1138, 1094, 765, 750 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{16}H_{17}O_4BrK$ 390.9947; found 390.9938.

1-ethyl 5-methyl (*E*)-4-(3-methylbenzylidene)-2-methylenepentanedioate (3j)



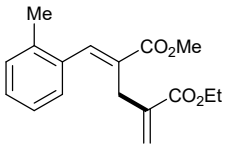
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale. **3j** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (50.0 mg, 87% yield, E/Z = 97/3 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.27 – 7.23 (m, 1H), 7.16 – 7.13 (m, 3H), 6.28 (s, 1H), 5.49 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.56 (s, 2H), 2.34 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 166.9, 142.2, 138.4, 138.3, 135.0, 130.1, 129.9, 128.7, 128.6, 126.1, 124.6, 61.0, 52.3, 29.8, 21.5, 14.3. IR (KBr): 2984, 2952, 1716, 1436, 1275, 1207, 1137, 1093, 764, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{17}H_{21}O_4$ 289.1440; found 289.1448.

1-ethyl 5-methyl (*E*)-4-(2-methoxybenzylidene)-2-methylenepentanedioate (3k)



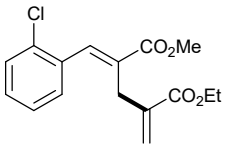
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3k** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as white solid (54.5 mg, 90% yield, E/Z > 99/1 as determined by ^{1}H NMR). Mp: 57.6-59.7 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.35 – 7.30 (m, 1H), 7.21 – 7.19 (m, 1H), 6.93 – 6.89 (m, 2H), 6.28 (s, 1H), 5.49 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 3.79 (s, 3H), 3.50 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 166.9, 157.7, 138.9, 137.9, 130.6, 128.9, 128.7, 124.5, 124.1, 120.5, 110.6, 61.0, 55.6, 52.2, 30.0, 14.3. IR (KBr): 2983, 2951, 1715, 1488, 1274, 1138, 1027, 788, 752 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{17}H_{20}O_5K$ 343.0948; found 343.0939.

1-ethyl 5-methyl (*E*)-4-(2-methylbenzylidene)-2-methylenepentanedioate (3l)



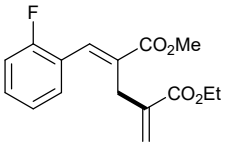
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3l** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (54.2 mg, 94% yield, E/Z = 97/3 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.24 – 7.14 (m, 4H), 6.25 (s, 1H), 5.45 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.43 (s, 2H), 2.31 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 166.8, 141.2, 139.0, 137.0, 134.4, 130.2, 129.8, 128.9, 127.7, 125.9, 124.4, 61.0, 52.3, 29.6, 20.1, 14.3. IR (KBr): 2985, 2952, 1717, 1633, 1435, 1275, 1260, 1137, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{17}H_{21}O_4$ 289.1440; found 289.1436.

5-ethyl 1-methyl (*E*)-2-(2-chlorobenzylidene)-4-methylenepentanedioate (3m)



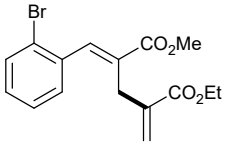
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3m** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (56.5 mg, 92% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.43 – 7.41 (m, 1H), 7.31 – 7.23 (m, 3H), 6.27 (s, 1H), 5.48 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 3.45 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 166.7, 139.0, 138.5, 134.3, 133.7, 131.0, 130.1, 129.8, 129.4, 126.9, 124.8, 61.1, 52.4, 29.7, 14.3. IR (KBr): 2983, 2951, 1715, 1488, 1274, 1138, 1027, 788, 752 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{16}H_{17}O_4ClK$ 347.0452; found 347.0446.

1-ethyl 5-methyl (*E*)-4-(2-fluorobenzylidene)-2-methylenepentanedioate (3n)



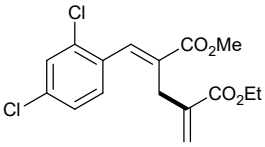
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3n** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (46.0 mg, 78% yield, E/Z = 97/3 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.36 – 7.25 (m, 2H), 7.14 – 7.07 (m, 2H), 6.28 (s, 1H), 5.48 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 3.51 (s, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 166.8, 160.6 (d, *J* = 250.1 Hz), 138.3, 134.5 (d, *J* = 4.4 Hz), 131.1, 130.9 (d, *J* = 8.3 Hz), 129.4 (d, *J* = 2.5 Hz), 124.7, 124.2 (d, *J* = 3.8 Hz), 123.1 (d, *J* = 13.4 Hz), 115.8 (d, *J* = 21.6 Hz), 61.1, 52.4, 30.0, 14.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.20. IR (KBr): 2986, 2954, 1716, 1275, 1213, 1138, 1102, 764 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{16}H_{17}O_4FK$ 331.0748; found 331.0757.

5-ethyl 1-methyl (*E*)-2-(2-bromobenzylidene)-4-methylenepentanedioate (3o)



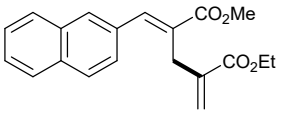
Following the general procedure, The reaction was conducted at 100 °C in 0.2 mmol scale with **3o** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (54.9 mg, 78% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.62 – 7.60 (m, 1H), 7.31 – 7.17 (m, 3H), 6.26 (s, 1H), 5.48 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 3.43 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 166.7, 141.1, 138.5, 135.6, 132.9, 130.9, 130.2, 129.4, 127.4, 124.7, 124.3, 61.0, 52.4, 29.5, 14.2. IR (KBr): 3057, 2983, 2906, 2844, 1717, 1633, 1435, 1259, 1206, 1139, 1027, 765, 733 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{16}H_{18}O_4Br$ 353.0388; found 353.0382.

5-ethyl 1-methyl (*E*)-2-(2,4-dichlorobenzylidene)-4-methylenepentanedioate (3p)



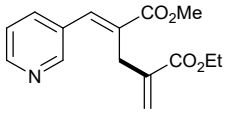
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3p** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (61.0 mg, 89% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.45 – 7.44 (m, 1H), 7.25 – 7.18 (m, 2H), 6.26 (s, 1H), 5.46 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 3.43 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 166.5, 138.4, 137.7, 135.3, 135.0, 132.3, 131.6, 130.1, 129.7, 127.3, 124.8, 61.1, 52.5, 29.7, 14.3. IR (KBr): 2984, 2953, 1720, 1585, 1436, 1274, 1207, 1161, 1092, 755 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{16}H_{17}O_4Cl_2$ 343.0504; found 343.0501.

1-ethyl 5-methyl (*E*)-2-methylene-4-(naphthalen-2-ylmethylene)pentanedioate (3q)



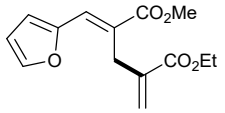
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3q** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (50.5 mg, 79% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.96 – 7.93 (m, 1H), 7.87 – 7.82 (m, 2H), 7.57 – 7.51 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.36 – 7.34 (m, 1H), 6.25 (s, 1H), 5.50 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 3.48 (s, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 166.8, 140.3, 139.1, 133.5, 132.4, 131.6, 131.4, 129.3, 128.7, 126.7, 126.3, 125.6, 125.4, 124.6, 124.5, 61.0, 52.4, 30.0, 14.2. IR (KBr): 2984, 2951, 1717, 1435, 1276, 1256, 1137, 1096, 765, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{20}H_{21}O_4$ 325.1440; found 325.1437.

1-ethyl 5-methyl (*E*)-2-methylene-4-(pyridin-3-ylmethylene)pentanedioate (3r)



Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3r** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (19.3 mg, 35% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 – 8.55 (m, 2H), 7.87 (s, 1H), 7.66 – 7.63 (m, 1H), 7.33 – 7.30 (m, 1H), 6.30 (s, 1H), 5.48 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 3.55 (s, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 166.6, 150.3, 149.9, 138.2, 138.0, 136.0, 131.3, 130.9, 124.9, 123.6, 61.2, 52.5, 29.9, 14.3. IR (KBr): 2954, 1715, 1275, 1207, 1138, 1091, 764, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{15}H_{18}O_4N$ 276.1236; found 276.1231.

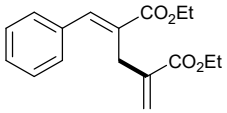
1-ethyl 5-methyl (*E*)-4-(furan-2-ylmethylene)-2-methylenepentanedioate (3s)



Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3s** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (50.2 mg, 95% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (s, 1H), 7.50 (d, *J* = 1.8 Hz, 1H), 6.61 (d, *J* = 3.4 Hz, 1H), 6.48 – 6.46 (m, 1H), 6.16 (s, 1H), 5.38 (s, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 3.75 (s, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 167.2, 151.0, 144.8, 137.7, 128.2, 125.1, 124.0, 115.9, 112.2, 61.0, 52.3, 29.8, 14.3. IR (KBr): 2984, 2952, 1713, 1634, 1435, 1275, 1211, 1137, 1091, 750 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd.

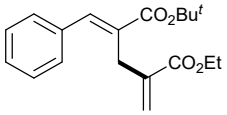
for: $C_{14}H_{16}O_5K$ 303.0635; found 303.0638.

Diethyl (E)-2-benzylidene-4-methylenepentanedioate (3t)



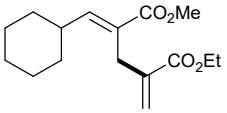
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3t** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (35.4 mg, 76% yield, E/Z = 97/3 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.37 – 7.33 (m, 5H), 6.29 (s, 1H), 5.50 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 4H), 3.56 (s, 2H), 1.34 – 1.29 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 166.9, 141.7, 138.5, 135.1, 129.3, 129.2, 129.0, 128.7, 124.6, 61.1, 61.0, 29.8, 14.3, 14.3. IR (KBr): 2987, 1715, 1436, 1275, 1260, 1137, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{17}H_{21}O_4$ 289.1440; found 289.1431.

1-(tert-butyl) 5-ethyl (*E*)-2-benzylidene-4-methylenepentanedioate (3u)



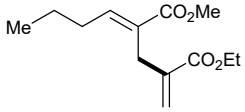
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3u** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (31.1 mg, 49% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.36 – 7.30 (m, 5H), 6.29 (s, 1H), 5.50 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.51 (s, 2H), 1.50 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 167.0, 140.7, 138.9, 135.4, 130.8, 129.0, 128.8, 128.7, 124.4, 81.0, 61.0, 29.8, 28.1, 14.3. IR (KBr): 2979, 1710, 1274, 1260, 1161, 1095, 764, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{19}H_{25}O_4$ 317.1753; found 317.1750.

5-ethyl 1-methyl (*E*)-2-(cyclohexylmethylene)-4-methylenepentanedioate (3v)



Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3v** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (32.0 mg, 57% yield, E/Z > 99/1 as determined by ^{1}H NMR) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.79 (d, *J* = 10.2 Hz, 1H), 6.17 (q, *J* = 1.5 Hz, 1H), 5.39 (q, *J* = 1.9 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 3H), 3.33 (s, 2H), 2.31 – 2.21 (m, 1H), 1.76 – 1.64 (m, 3H), 1.63 – 1.55 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.30 – 1.10 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.3, 167.1, 150.6, 138.6, 126.6, 124.3, 60.9, 51.9, 37.9, 32.1, 28.5, 25.8, 25.5, 14.3. IR (KBr): 2927, 2851, 1717, 1436, 1274, 1261, 1138, 1073, 767, 749 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{16}H_{25}O_4$ 281.1753; found 281.1745.

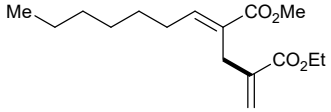
5-ethyl 1-methyl (*E*)-2-butylidene-4-methylenepentanedioate (3w)



Following the general procedure, the reaction was conducted at 100 °C in 0.3 mmol scale with **3w** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (33.0 mg, 70% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.97 (t, *J* = 7.5 Hz, 1H), 6.17 (q, *J* = 1.5 Hz, 1H), 5.40 (q, *J* = 1.9 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 3.34 (s, 2H), 2.14 (q, *J* = 7.4 Hz, 2H), 1.52 – 1.42 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C

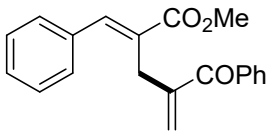
NMR (101 MHz, Chloroform-*d*) δ 168.0, 167.1, 145.8, 138.0, 128.7, 124.5, 60.9, 51.9, 30.8, 28.4, 22.0, 14.3, 14.0. IR (KBr): 2960, 2874, 1717, 1274, 1209, 1134, 1095, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{13}H_{21}O_4$ 241.1440; found 241.1443.

1-ethyl 5-methyl (*E*)-4-heptylidene-2-methylenepentanedioate (3x)



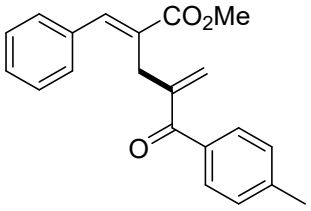
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3x** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (42.0 mg, 74% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (401 MHz, Chloroform-*d*) δ 6.97 (t, *J* = 7.5 Hz, 1H), 6.17 (s, 1H), 5.39 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.72 (s, 3H), 3.33 (s, 2H), 2.15 (q, *J* = 7.5 Hz, 2H), 1.47 – 1.37 (m, 2H), 1.35 – 1.26 (m, 9H), 0.91 – 0.85 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 167.0, 146.0, 138.0, 128.6, 124.4, 60.9, 51.9, 31.7, 29.1, 28.8, 28.7, 28.4, 22.6, 14.3, 14.1. IR (KBr): 2929, 2857, 1718, 1436, 1274, 1208, 1137, 764, 750 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{16}H_{26}O_4K$ 321.1468; found 321.1465.

Methyl (*E*)-4-benzoyl-2-benzylidenepent-4-enoate (3y)



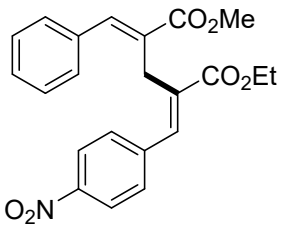
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3y** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (20.2 mg, 33% yield, E/Z = 90/10 as determined by ^{1}H NMR) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.0 (s, 1H), 7.8 – 7.8 (m, 2H), 7.6 – 7.5 (m, 1H), 7.5 (t, *J* = 7.5 Hz, 3H), 7.4 – 7.4 (m, 3H), 7.4 – 7.3 (m, 1H), 5.8 (t, *J* = 1.9 Hz, 1H), 5.7 (t, *J* = 1.5 Hz, 1H), 3.8 (s, 3H), 3.7 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.9, 168.5, 145.6, 142.1, 137.6, 135.1, 133.2, 132.5, 129.7, 129.3, 129.1, 128.8, 128.4, 125.6, 52.3, 30.1. HRMS (ESI/$[M+H]^+$) Calcd. For: $C_{20}H_{19}O_3$ 307.1334; found 307.1331.

Methyl (*E*)-2-benzylidene-4-(4-methylbenzoyl)pent-4-enoate (3z)



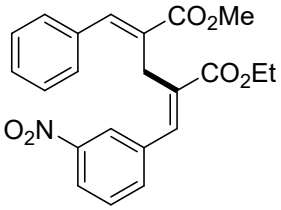
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3z** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (24.4 mg, 38% yield, E/Z = 90/10 as determined by ^{1}H NMR) ^{1}H NMR (401 MHz, Chloroform-*d*) δ 8.0 (s, 1H), 7.7 (d, *J* = 8.2 Hz, 2H), 7.4 – 7.3 (m, 5H), 7.3 – 7.2 (m, 2H), 5.7 (s, 1H), 5.7 (s, 1H), 3.8 (s, 3H), 3.7 (s, 2H), 2.4 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.7, 168.5, 145.7, 143.3, 142.1, 135.1, 134.8, 130.0, 129.3, 129.1, 128.8, 128.3, 124.7, 52.3, 30.3, 21.7. HRMS (ESI/$[M+H]^+$) Calcd. For: $C_{21}H_{21}O_3$ 321.1491; found 321.1482.

5-ethyl 1-methyl 2-((*E*)-benzylidene)-4-((*E*)-4-nitrobenzylidene)pentanedioate (**3aa**)



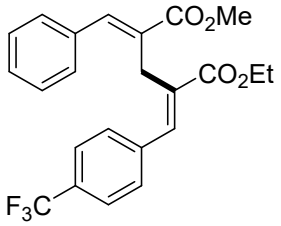
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3aa** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (50.0 mg, 63% yield, E/Z = 61/39 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.1 (d, *J* = 8.7 Hz, 2H), 7.6 (d, *J* = 10.4 Hz, 2H), 7.4 – 7.3 (m, 5H), 7.2 – 7.2 (m, 2H), 4.3 (q, *J* = 7.1 Hz, 2H), 3.9 (s, 2H), 3.7 (s, 3H), 1.3 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 167.5, 147.1, 142.2, 140.1, 136.5, 135.1, 134.8, 129.8, 129.2, 128.8, 128.5, 123.5, 61.4, 52.1, 32.5, 26.1, 14.3. IR (KBr): 2952, 1713, 1596, 1519, 1345, 1250, 1203, 1099, 764, 695 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{22}O_6N$ 396.1447; found 396.1440.

5-ethyl 1-methyl 2-((*E*)-benzylidene)-4-((*E*)-3-nitrobenzylidene)pentanedioate (3ab)



Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3ab** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (55.4 mg, 70% yield, E/Z = 52/48 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.1 – 8.0 (m, 2H), 7.6 (d, *J* = 7.4 Hz, 2H), 7.5 – 7.5 (m, 1H), 7.5 – 7.3 (m, 2H), 7.3 – 7.3 (m, 2H), 7.2 – 7.2 (m, 2H), 4.2 (q, *J* = 7.1 Hz, 2H), 3.9 (s, 2H), 3.7 (s, 3H), 1.3 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 167.5, 148.1, 140.2, 137.3, 136.4, 135.1, 134.8, 134.2, 130.1, 129.3, 129.2, 128.7, 128.5, 123.8, 122.9, 61.4, 52.2, 26.0, 14.3. IR (KBr): 2988, 1713, 1530, 1530, 1436, 1351, 1275, 1259, 1205, 1098, 764, 750, 701 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{22}H_{22}O_6N$ 396.1447; found 396.1441.

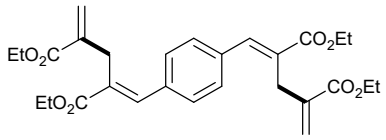
5-ethyl 1-methyl 2-((*E*)-benzylidene)-4-((*E*)-4-(trifluoromethyl)benzylidene)pentanedioate (3ac)



Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3ac** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (36.9 mg, 44% yield, E/Z = 56/44 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.6 (d, *J* = 6.6 Hz, 2H), 7.5 (d, *J* = 8.0 Hz, 2H), 7.3 – 7.3 (m, 5H), 7.2 – 7.2 (m, 2H), 4.2 (q, *J* = 7.1 Hz, 2H), 3.9 (s, 2H), 3.7 (s, 3H), 1.3 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.3, 167.8, 139.9, 139.2, 137.5, 135.3, 133.4, 130.4, 129.3, 129.2, 128.6, 128.5, 125.2 (q, *J* = 3.9 Hz), 61.2, 52.1, 26.1, 14.3. ^{19}F NMR

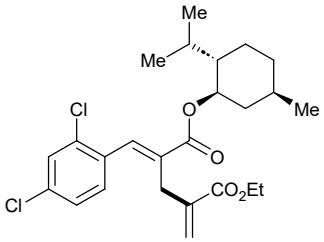
(376 MHz, Chloroform-*d*) δ -62.56. IR (KBr): 2952, 1713, 1615, 1435, 1368, 1324, 1249, 1165, 1098, 1067, 1016, 860, 765, 607cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{23}H_{22}O_4F_3$ 419.1470; found 419.1462.

Tetraethyl 4,4'-(1,4-phenylenebis(methaneylylidene))(4*E*,4'*E*)-bis(2-methylenepentanedioate) (3ad)



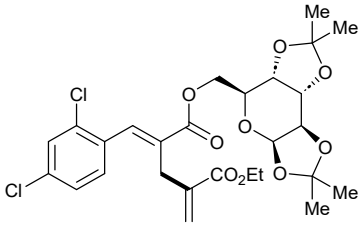
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3ad** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as white solid (64.2 mg, 68% yield, E,E/E,Z = 95/5 as determined by ^{1}H NMR) Mp: 65.3-68.9 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 2H), 7.34 (s, 4H), 6.30 (s, 2H), 5.49 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 8H), 3.57 (s, 4H), 1.35 – 1.30 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 166.8, 140.7, 138.3, 135.6, 130.1, 129.5, 124.7, 61.2, 61.1, 29.8, 14.3, 14.3. IR (KBr): 2923, 1713, 1275, 1261, 1139, 1026, 764, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{28}H_{35}O_8$ 499.2332; found 499.2336.

5-ethyl 1-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl) 2-((*E*)-2,4-dichlorobenzylidene)-4-methylenepentanedioate (3ae)



Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3ae** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (47.5mg, 51% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.44 (s, 1H), 7.25 – 7.16 (m, 2H), 6.26 (s, 1H), 5.46 (s, 1H), 4.82 – 4.73 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.44 (q, 2H), 2.10 – 2.01 (m, 1H), 1.93 – 1.82 (m, 1H), 1.74 – 1.65 (m, 2H), 1.56 – 1.40 (m, 2H), 1.33 – 1.28 (m, 3H), 1.13 – 0.99 (m, 2H), 0.93 – 0.87 (m, 7H), 0.78 – 0.74 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 166.6, 138.6, 137.1, 135.2, 135.1, 132.4, 132.4, 130.1, 129.7, 127.2, 124.6, 75.4, 61.1, 47.2, 40.8, 34.3, 31.5, 29.7, 26.4, 23.5, 22.1, 20.8, 16.4, 14.3. IR (KBr): 2956, 2929, 2870, 1714, 1469, 1370, 1275, 1204, 1140, 1093, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{25}H_{33}O_4Cl_2$ 467.1756; found 467.1750.

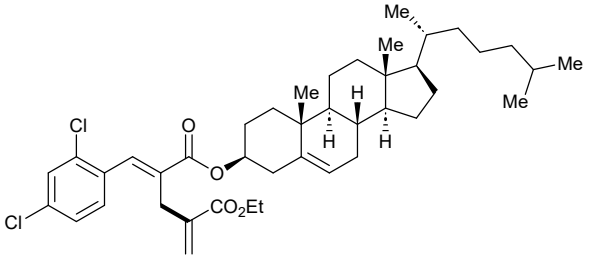
5-ethyl 1-(((3a*R*,5*S*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl) 2-((*E*)-2,4-dichlorobenzylidene)-4-methylenepentanedioate (3af)



Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3af** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (103.0mg, 88%

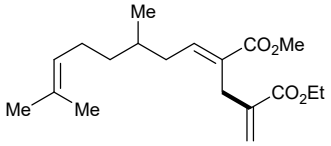
yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.25 – 7.16 (m, 2H), 6.27 (s, 1H), 5.54 (d, *J* = 5.0 Hz, 1H), 5.50 (s, 1H), 4.63 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.42 (dd, *J* = 11.5, 4.7 Hz, 1H), 4.38 – 4.30 (m, 2H), 4.26 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 4.13 – 4.04 (m, 1H), 3.42 (s, 2H), 1.50 (s, 3H), 1.47 (s, 3H), 1.34 (d, *J* = 5.9 Hz, 6H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 166.5, 138.1, 138.0, 135.3, 135.1, 132.2, 131.4, 130.1, 129.7, 127.3, 125.2, 109.7, 108.8, 96.3, 71.1, 70.7, 70.5, 66.1, 64.3, 61.1, 29.8, 26.1, 26.0, 25.1, 24.5, 14.3. IR (KBr): 2988, 2953, 1717, 1275, 1258, 1071, 1008, 751 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{27}H_{33}O_9Cl_2$ 571.1502; found 571.1505.

1-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl) 5-ethyl 2-((*E*)-2,4-dichlorobenzylidene)-4-methylenepentanedioate (3ag)



Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3ag** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow solid (123.0 mg, 88% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.44 (d, *J* = 1.9 Hz, 1H), 7.24 – 7.17 (m, 2H), 6.25 (s, 1H), 5.46 (s, 1H), 5.41 – 5.37 (m, 1H), 4.77 – 4.68 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.41 (s, 2H), 2.37 (d, *J* = 6.7 Hz, 2H), 2.03 – 1.79 (m, 5H), 1.68 – 1.41 (m, 8H), 1.36 – 1.24 (m, 8H), 1.21 – 1.07 (m, 7H), 1.03 (s, 3H), 0.97 (d, *J* = 5.2 Hz, 1H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 1.9 Hz, 3H), 0.86 (d, *J* = 1.8 Hz, 3H), 0.68 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 166.5, 139.6, 138.6, 137.2, 135.1, 135.0, 132.5, 130.2, 129.6, 127.2, 124.8, 122.9, 75.0, 61.1, 56.8, 56.2, 50.1, 42.4, 39.8, 39.6, 38.1, 37.0, 36.7, 36.3, 35.9, 32.0, 31.9, 29.6, 28.3, 28.1, 27.8, 24.4, 23.9, 22.9, 22.7, 21.1, 19.5, 18.8, 14.3, 11.9. IR (KBr): 2936, 2867, 1716, 1585, 1469, 1275, 1260, 1138, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{42}H_{59}O_4Cl_2$ 697.3790; found 697.3787.

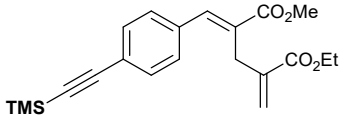
5-ethyl 1-methyl (*E*)-2-(3,7-dimethyloct-6-en-1-ylidene)-4-methylenepentanedioate (3ah)



Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3ah** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (42.6 mg, 66% yield, E/Z > 99/1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.00 (t, *J* = 7.5 Hz, 1H), 6.17 (s, 1H), 5.38 (s, 1H), 5.20 – 4.94 (m, 1H), 4.26 – 4.18 (m, 2H), 3.72 (s, 3H), 3.33 (s, 2H), 2.23 – 2.11 (m, 1H), 2.10 – 1.88 (m, 3H), 1.68 (s, 3H), 1.64 (d, *J* = 5.8 Hz, 1H), 1.59 (s, 3H), 1.40 – 1.34 (m, 1H), 1.33 – 1.29 (m, 3H), 1.19 (q, *J* = 9.6, 8.8 Hz, 1H), 0.90 (dd, *J* = 6.7, 3.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 167.1, 145.0, 137.9, 131.6, 129.3, 124.5, 60.9, 51.9, 36.9, 36.0, 32.6, 28.5, 25.8, 25.6, 19.7, 17.8, 14.3. IR (KBr): 2988, 2955, 1718, 1275, 1251, 1137, 1029, 764, 750 cm^{-1} HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{19}H_{30}O_4K$ 361.1781; found 361.1784.

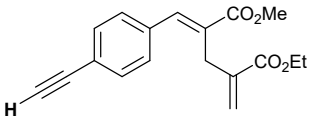
1-ethyl 5-methyl (*E*)-2-methylene-4-(4-((trimethylsilyl)ethynyl)benzylidene)pentanedioate (

3ai)



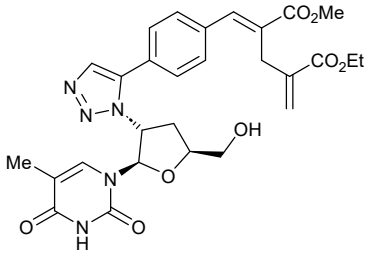
Following the general procedure, the reaction was conducted at 100 °C in 0.2 mmol scale with **3ai** was isolated by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 10:1) as yellow oil (57.0mg, 77% yield, E/Z = 97/3 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.28 (s, 1H), 5.47 (s, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 3.80 (s, 3H), 3.54 (s, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 0.25 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 166.8, 141.2, 138.1, 135.0, 132.2, 129.5, 129.1, 124.7, 123.8, 104.6, 96.2, 61.1, 52.4, 29.9, 14.3, 0.0. IR (KBr): 2956, 2157, 1716, 1436, 1275, 1206, 1137, 750 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{21}H_{27}O_4Si$ 371.1679; found 371.1674.

1-ethyl 5-methyl (*E*)-4-(4-ethynylbenzylidene)-2-methylenepentanedioate (4)



The 3**ai** (0.3 mmol) was dissolved in anhydrous THF (3 mL) in a 10 mL Schlenk flask. Then, H_2O (10.0 mmol, 40 equiv.) and TBAF (0.6 mmol, 1 M in THF) were added into the solution slowly at 0 ºC (low temperature magnetic stirrer, with ethylene glycol bath), and the mixture was stirred for 5 h. The reaction mixture was poured into water (5 mL) and extracted with EtOAc (10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product. The product 4 was isolated from the crude mixture by PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 15:1) as white solid (78.1 mg, 87% yield). Mp: 36.7-39.5 °C ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.29 (s, 1H), 5.48 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.55 (s, 2H), 3.18 (s, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 166.7, 141.0, 138.1, 135.4, 132.4, 129.7, 129.1, 124.7, 122.8, 83.2, 78.9, 61.1, 52.4, 29.9, 14.3. IR (KBr): 3291, 2985, 2952, 1715, 1585, 1275, 1206, 1138, 764, 750 cm^{-1}. HRMS (ESI) m/z: $[M + K]^+$ Calcd. for: $C_{18}H_{18}O_4K$ 337.0842; found 337.0836.

1-ethyl 5-methyl 4-((*E*)-4-(1-((2*R*,3*R*,5*S*)-5-(hydroxymethyl)-2-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)tetrahydrofuran-3-yl)-1H-1,2,3-triazol-5-yl)benzylidene)-2-methylenepentanedioate (5)



Under argon atmosphere, a flame-dried 10 mL schlenk tube was charged with compound 4 (0.16 mmol, 1.0 equiv.), zidovudine (0.18 mmol, 1.1 equiv.), ^{t}BuOH (1.5 mL) and a stir bar was added a freshly prepared solution of $CuSO_4 \cdot 5H_2O$ (0.1 equiv.) and sodium ascorbate (0.2 equiv.) in H_2O (1 mL). the resulting solution was stirred at room temperature for 20 h. The reaction mixture was concentrated and subjected to PTLC (ethanol/ dichloromethane = 1:20) to give 5 as a white solid (147 mg, 85% yield).

Mp: 66.1-67.5 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.15 (s, 1H), 8.13 (s, 1H), 7.89 (s, 1H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.58 (s, 1H), 7.36 (d, *J* = 7.7 Hz, 2H), 6.33 (s, 1H), 6.28 (s, 1H), 5.56 (s, 1H), 5.49 (s, 1H), 4.48 (s, 1H), 4.35 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.04 (d, *J* = 11.3 Hz, 1H), 3.93 – 3.84 (m, 1H), 3.80 (s, 3H), 3.56 (s, 2H), 3.09 – 2.87 (m, 2H), 1.82 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.3, 167.0, 164.6, 150.9, 147.2, 141.3, 138.1, 137.6, 134.9, 130.7, 129.9, 129.0, 125.9, 124.8, 120.7, 111.1, 87.2, 85.2, 61.4, 61.2, 59.6, 52.4, 37.9, 29.9, 14.3, 12.5. IR (KBr): 2929, 1706, 1436, 1371, 1275, 1223, 1095, 766 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for: $C_{28}H_{32}O_8N_5$ 566.2251; found 566.2247.

5. References

(1) B. Li, W. Zeng, L. Wang, Z. Geng, T.-P. Loh, P. Xie, Visible-Light-Induced Trifluoromethylation of Allylic Alcohols, *Org. Lett.* **2021**, 23, 13, 5235–5240.
(2) P. Xie, W. Fu, X. Cai, Z. Sun, Y. Wu, S. Li, C. Gao, X. Yang, T-P. Loh, A Ba/Pd Catalytic System Enables Dehydrative Cross-Coupling andExcellentE-Selective Wittig Reactions, *Org. Lett*. **2019**, 21, 17, 7055–7059.

5. NMR Spectra for New Compounds

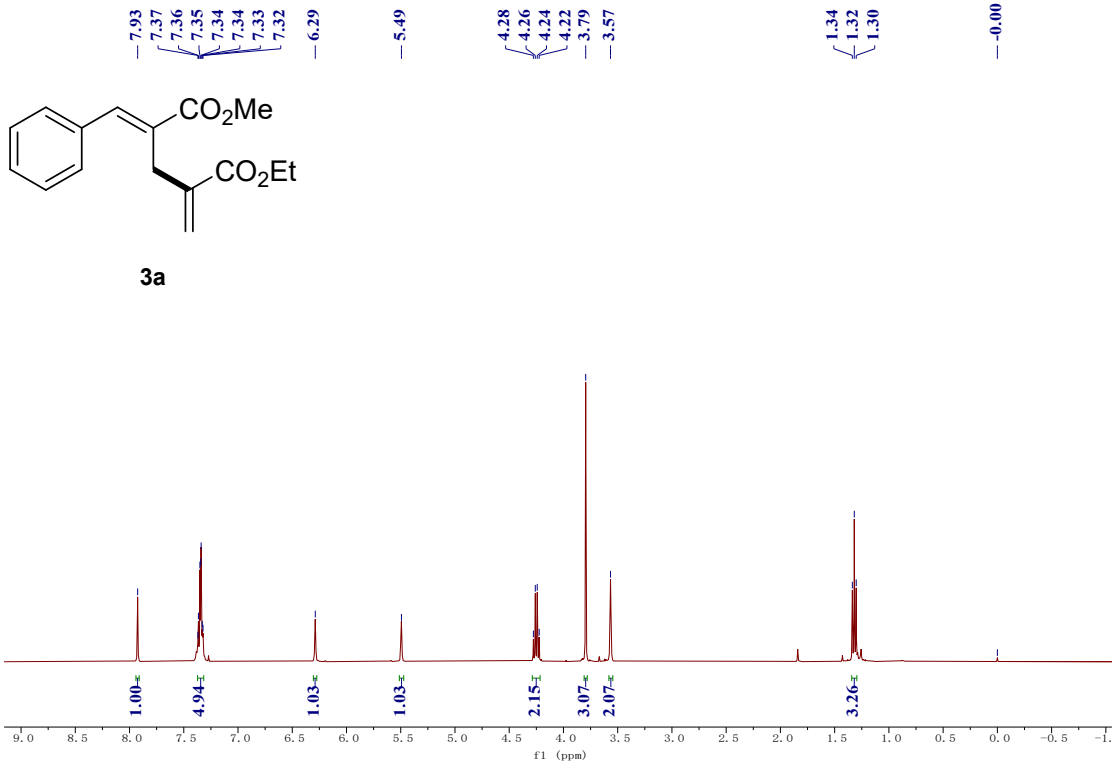


Figure S1 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3a**

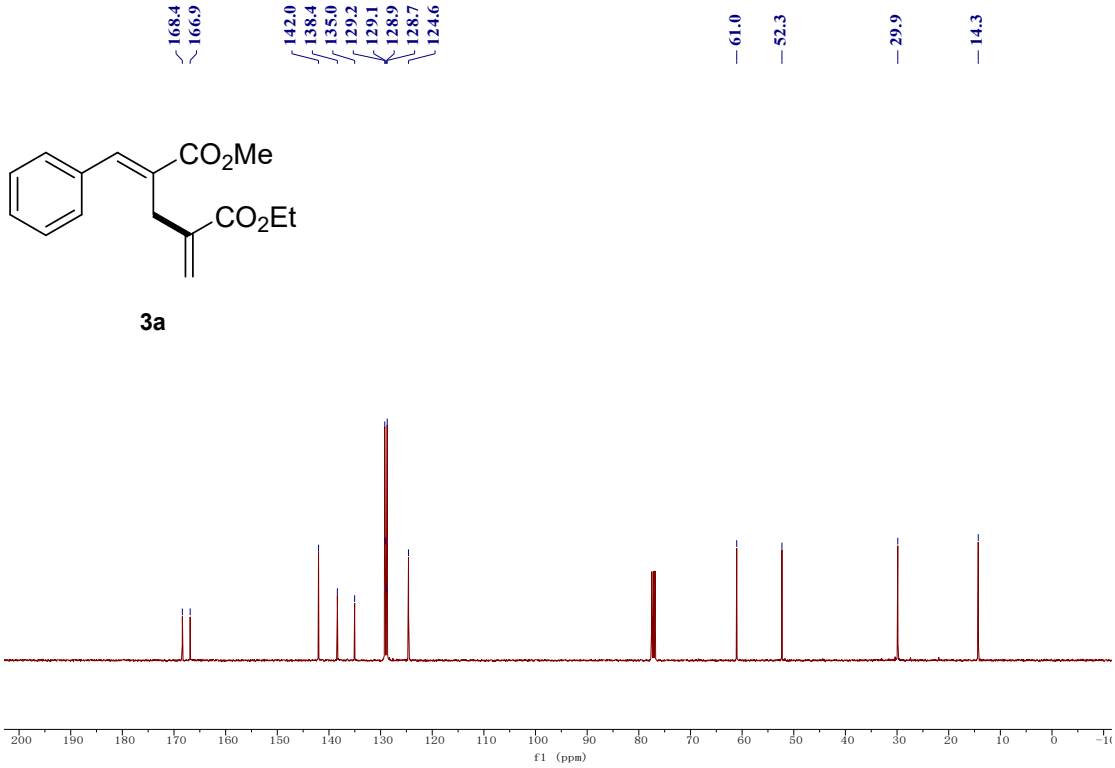


Figure S2 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3a**

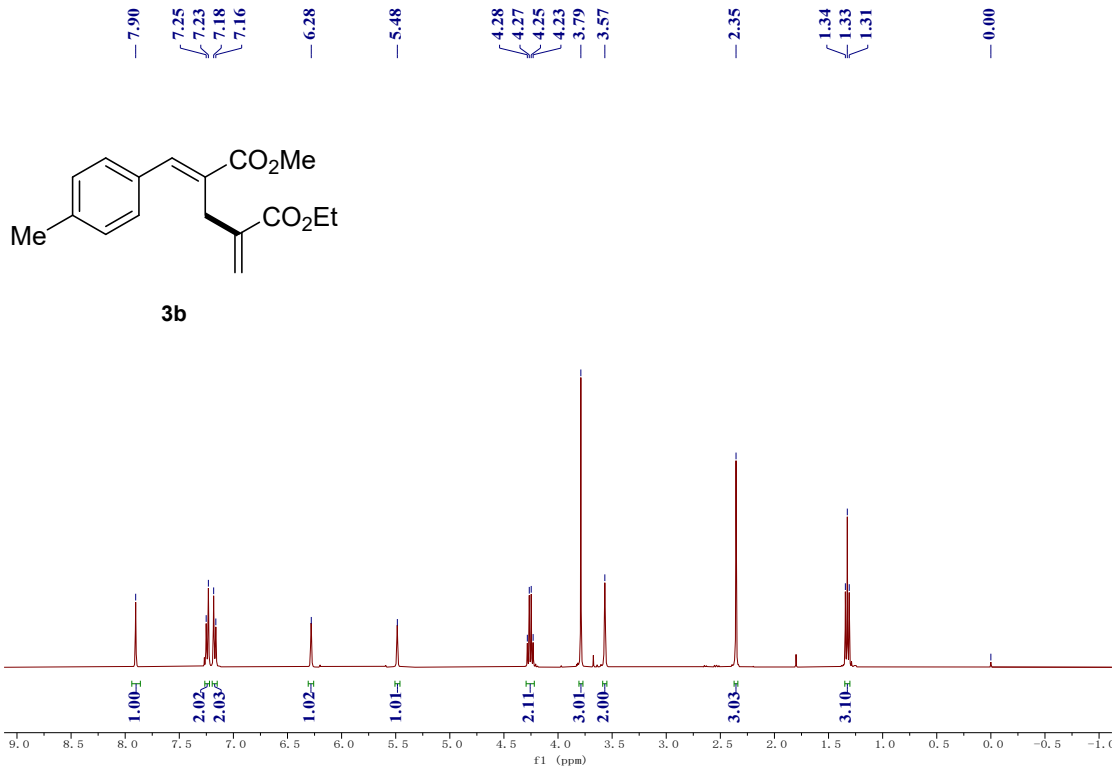


Figure S3 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3b**

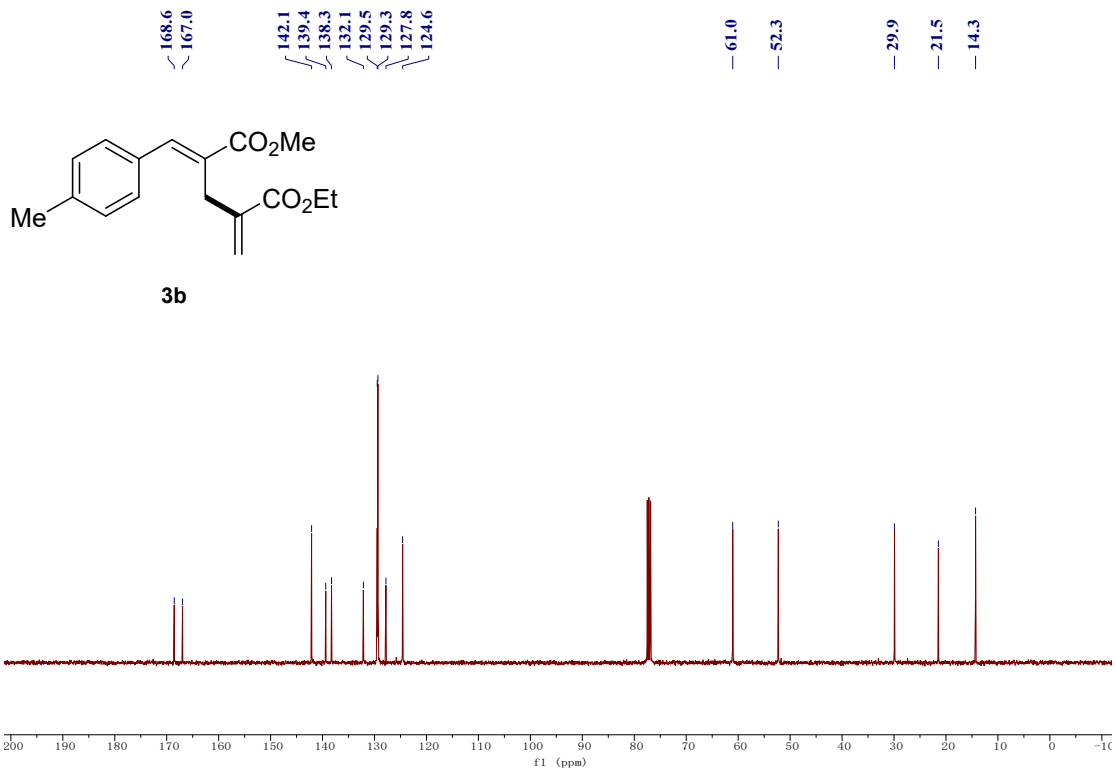


Figure S4 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3b**

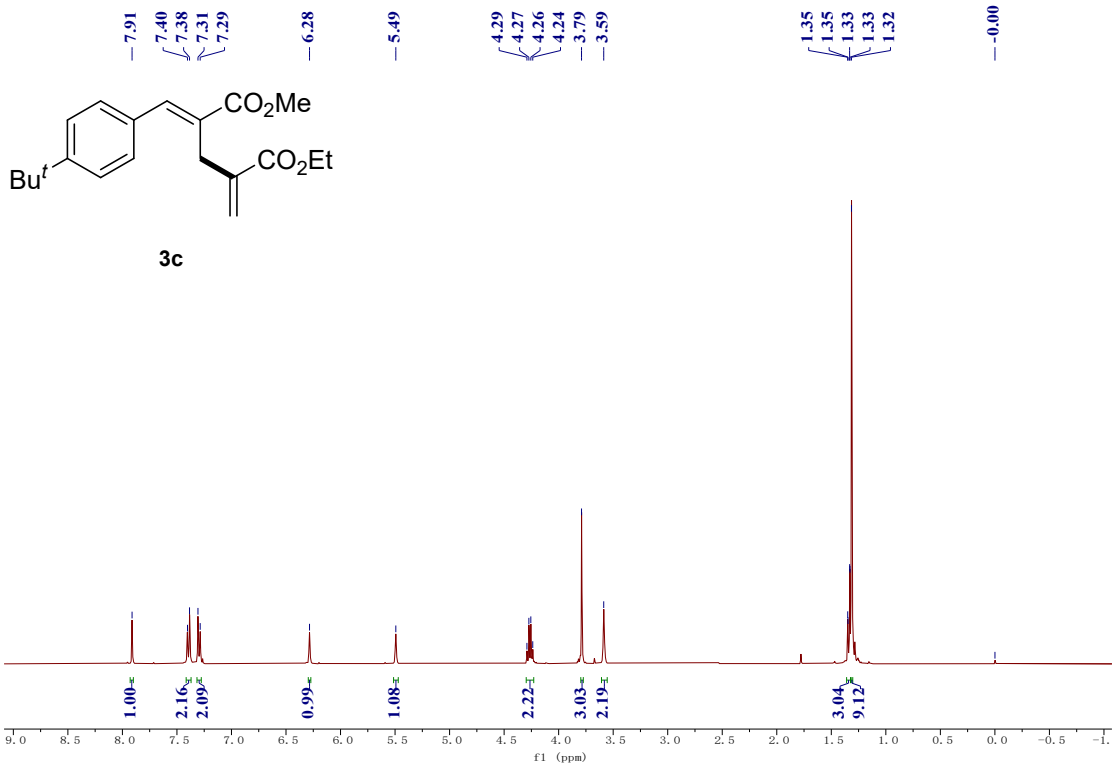


Figure S5 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3c**

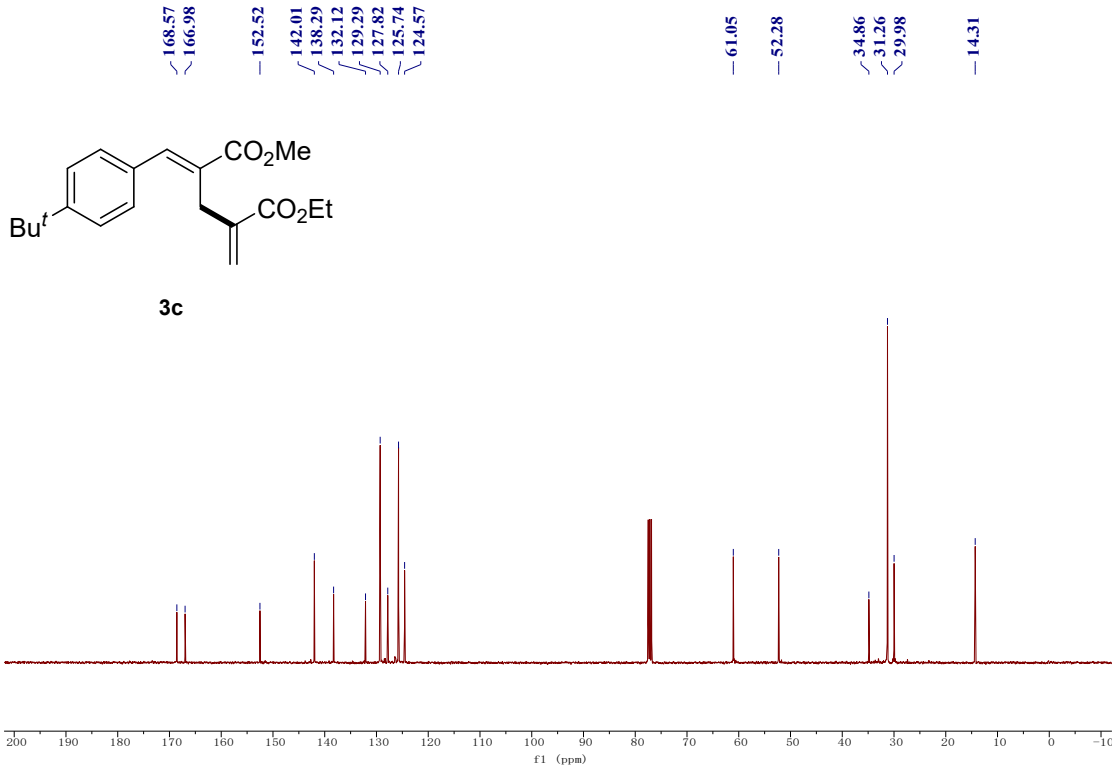


Figure S6 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3c**

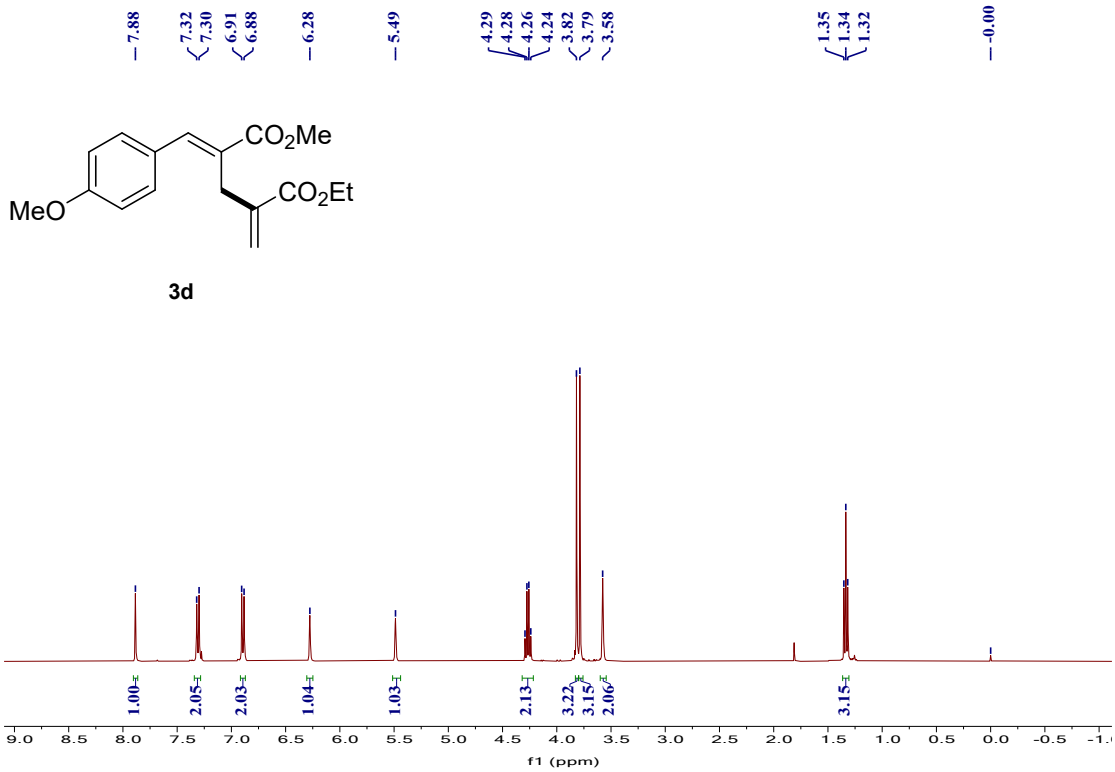


Figure S7 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3d**

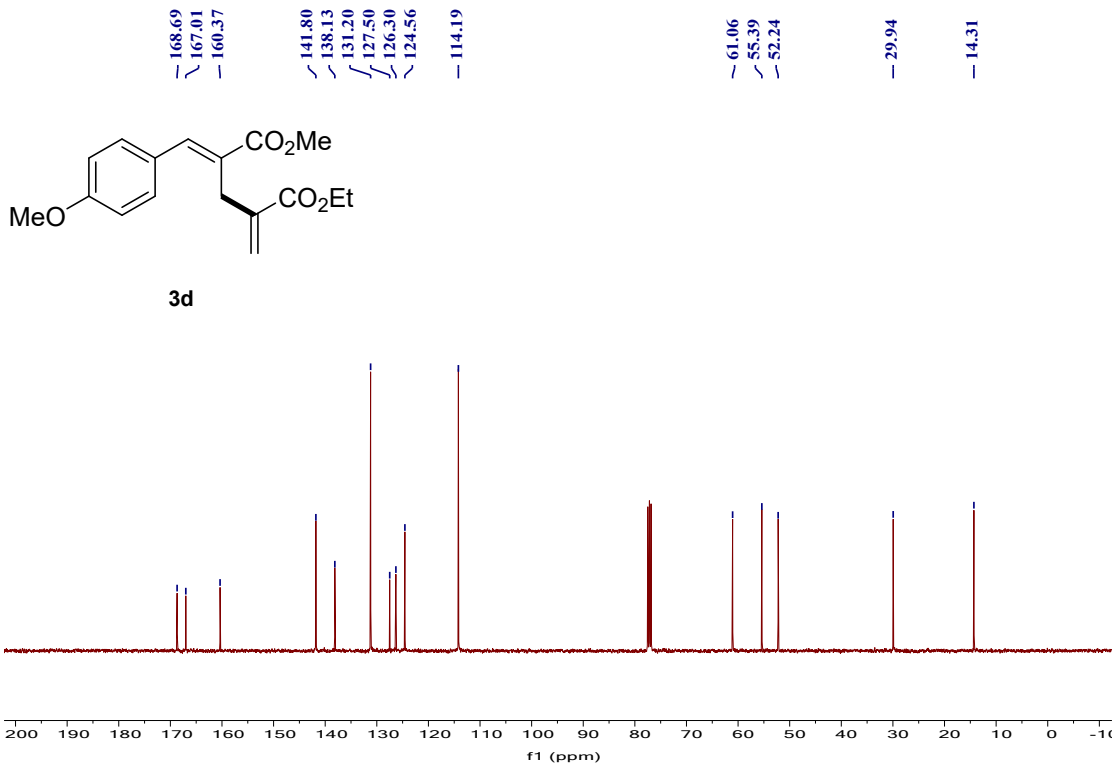


Figure S8 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3d**

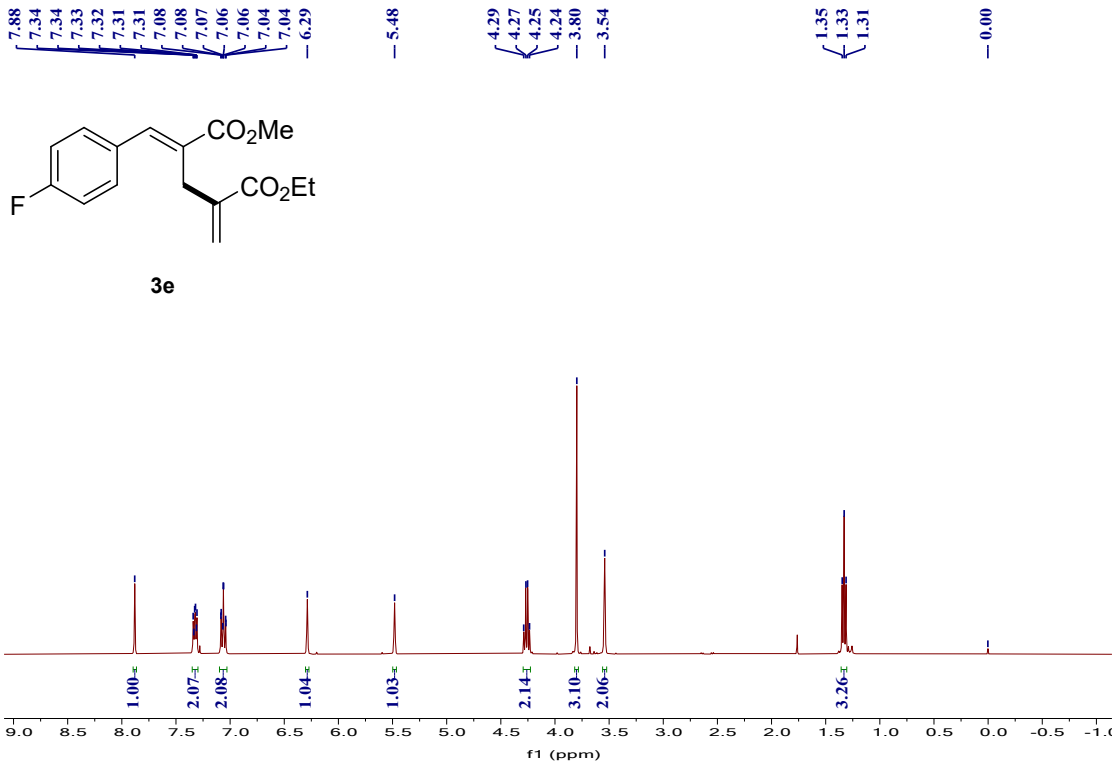


Figure S9 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3e**

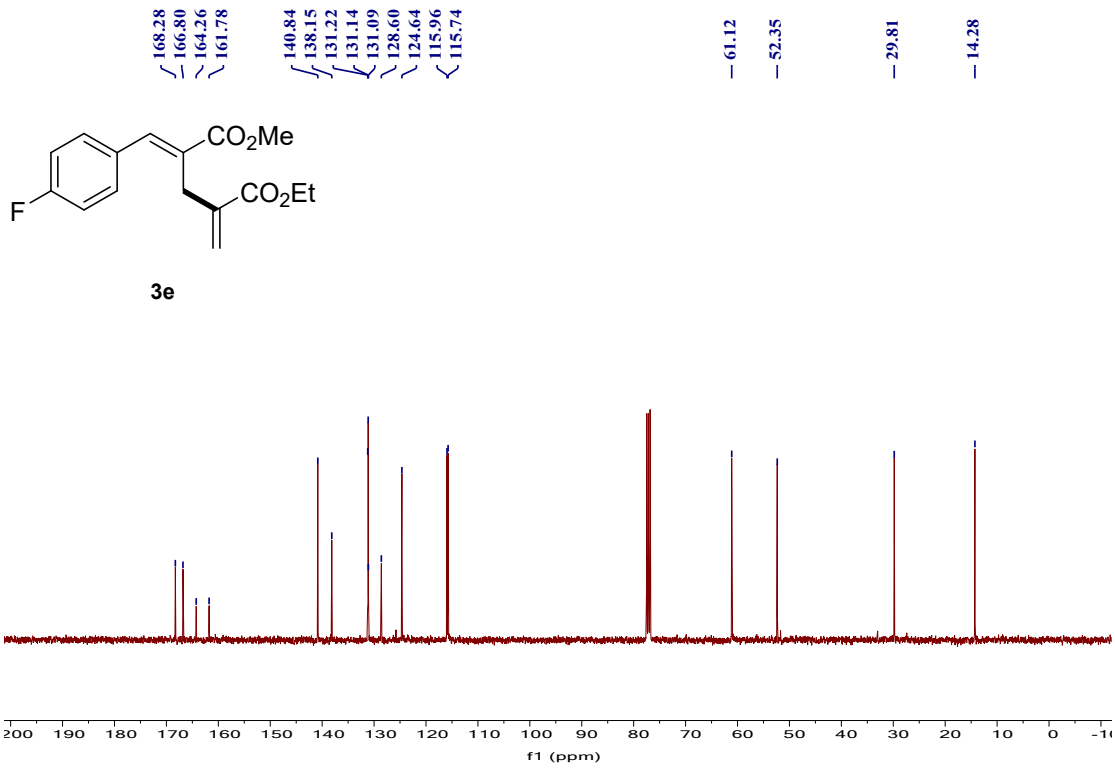


Figure S10 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3e**

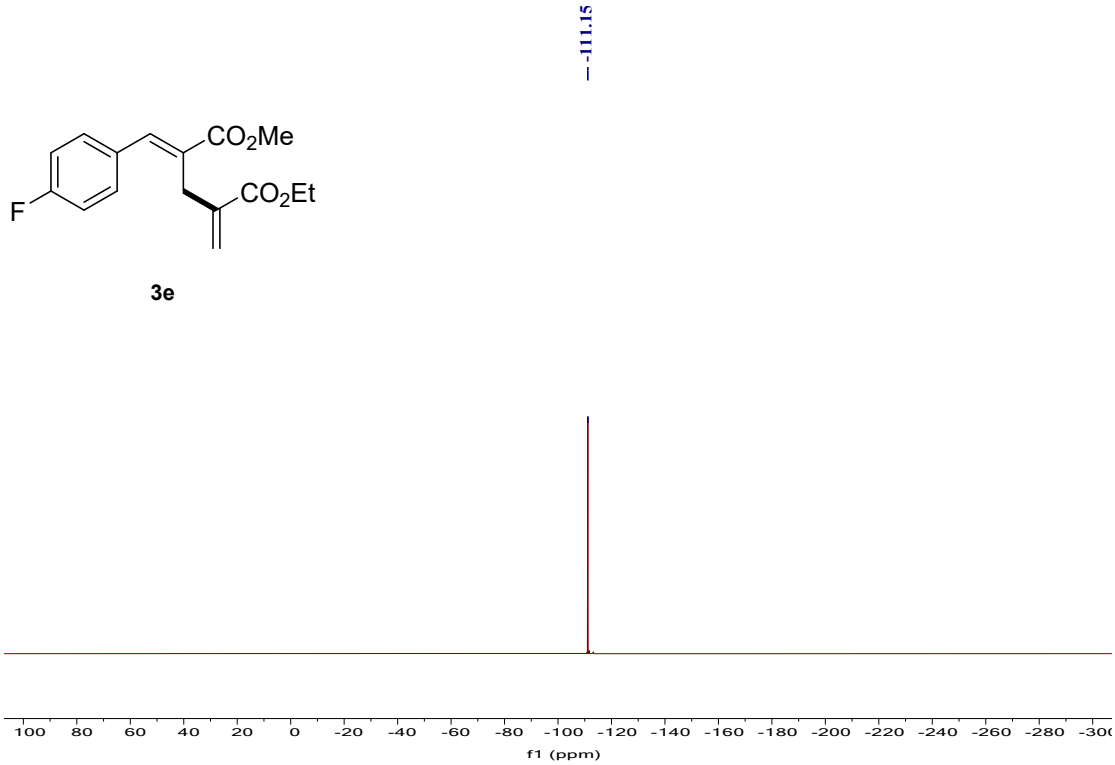


Figure S11 | ^{19}F NMR (376 MHz, Chloroform-*d*) spectra for compound **3e**

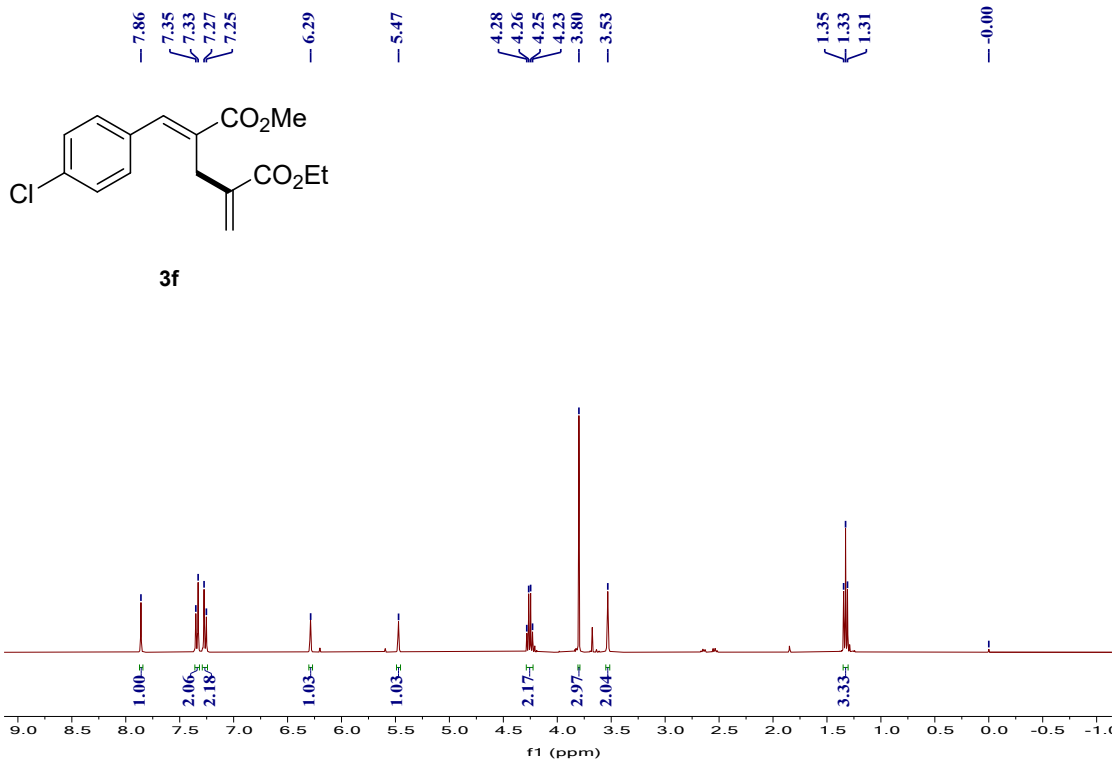


Figure S12 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3f**

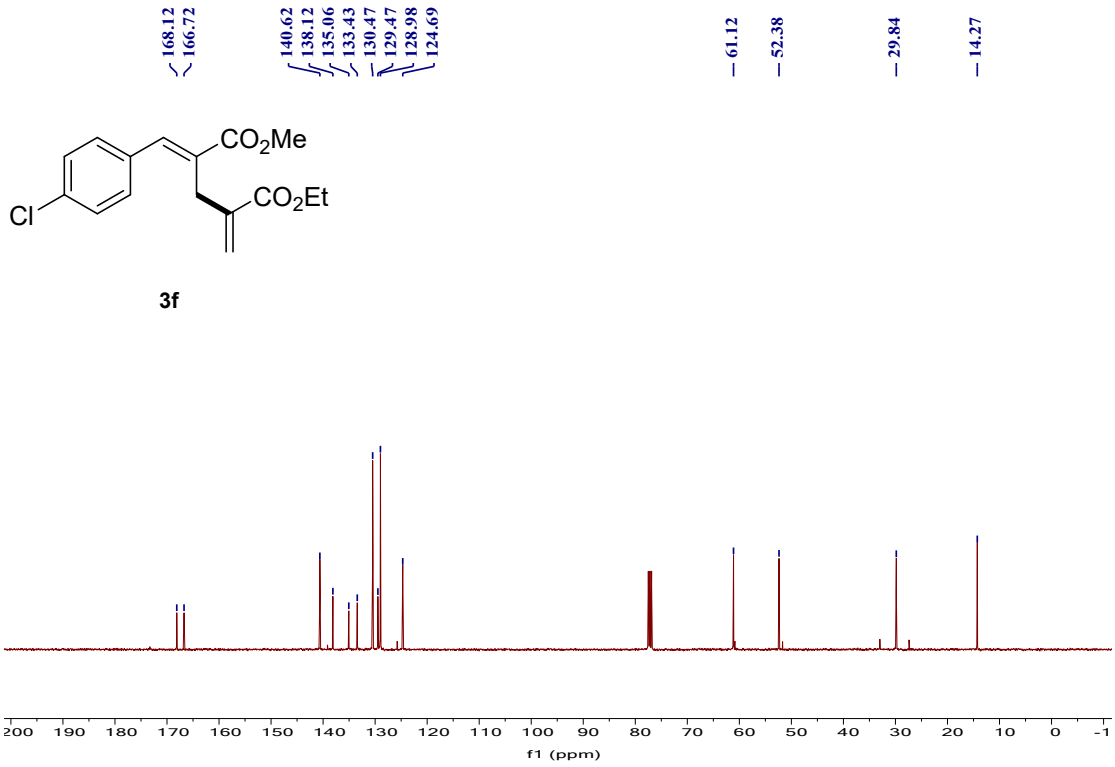


Figure S13 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3f**

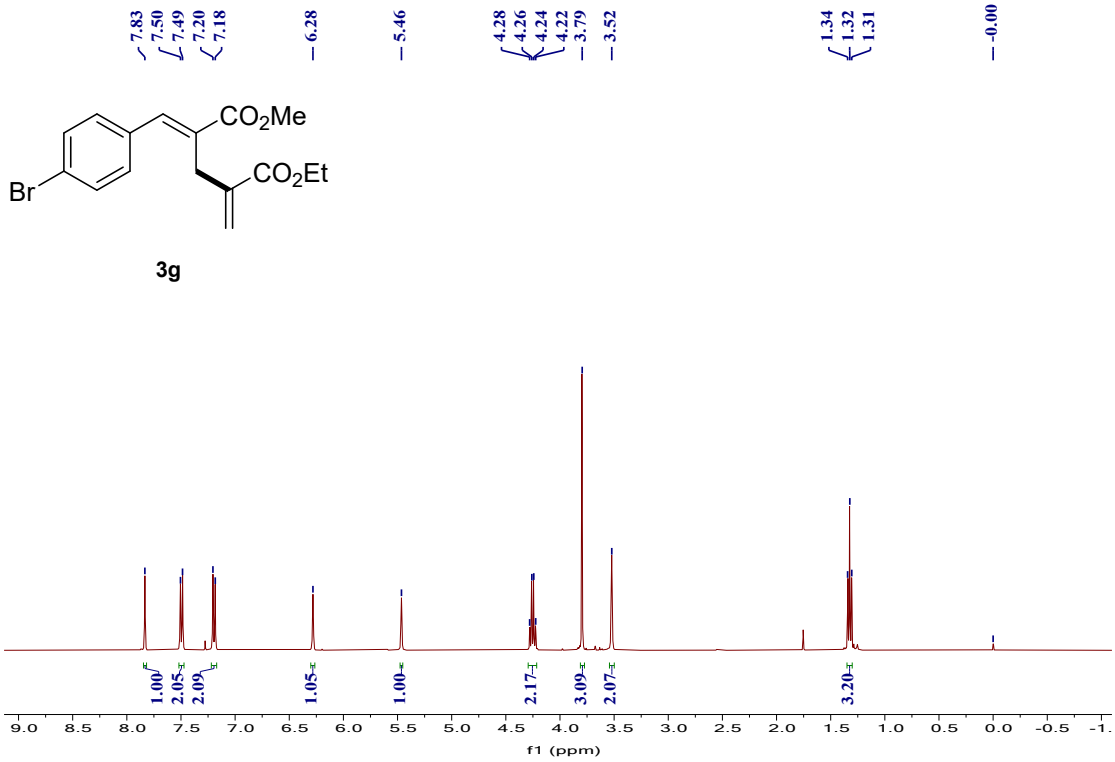


Figure S14 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3g**

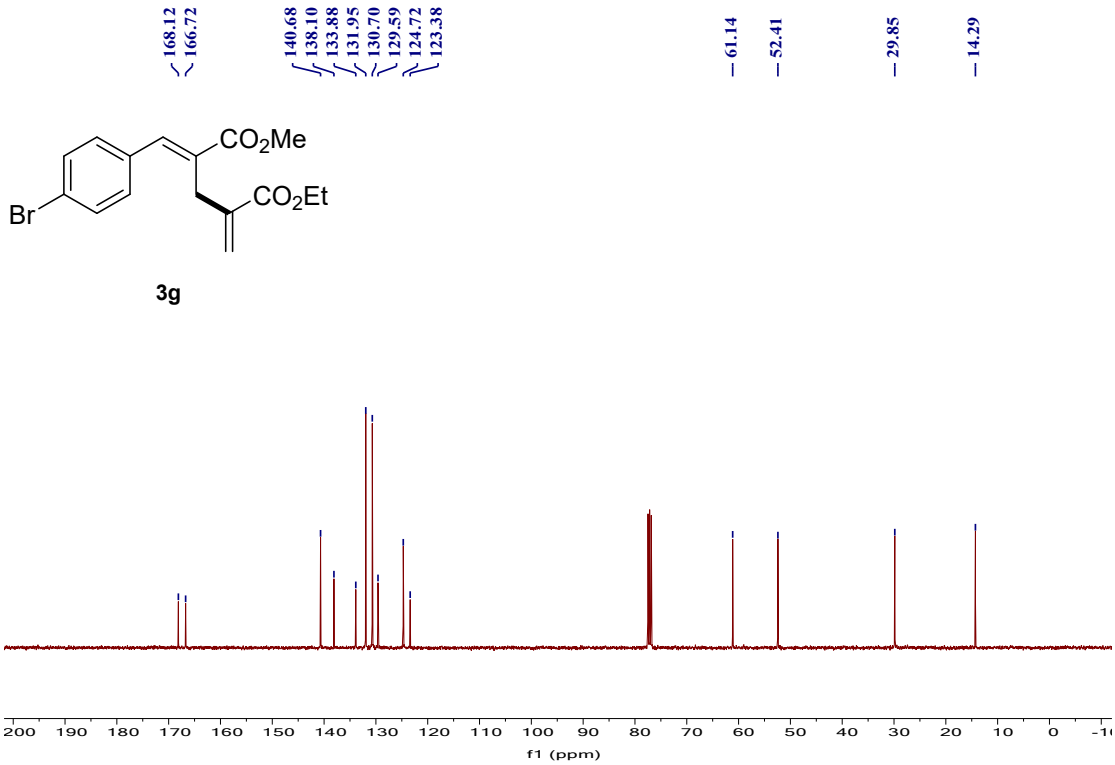


Figure S15 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3g**

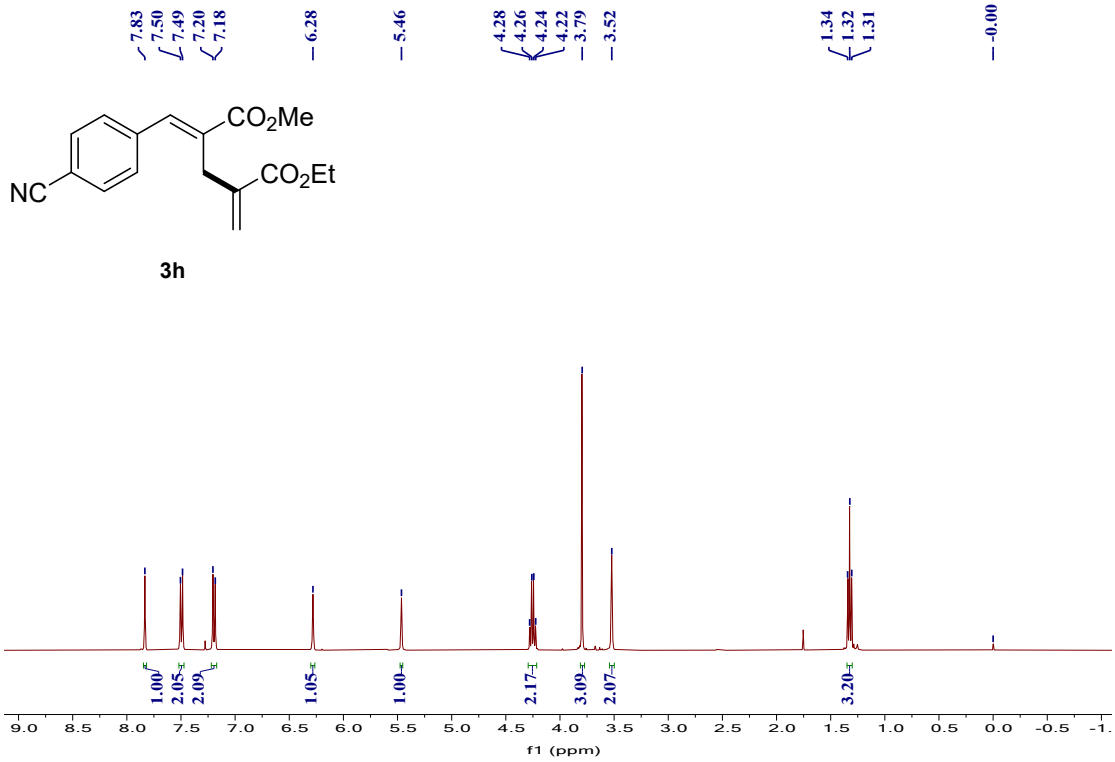


Figure S16 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3h**

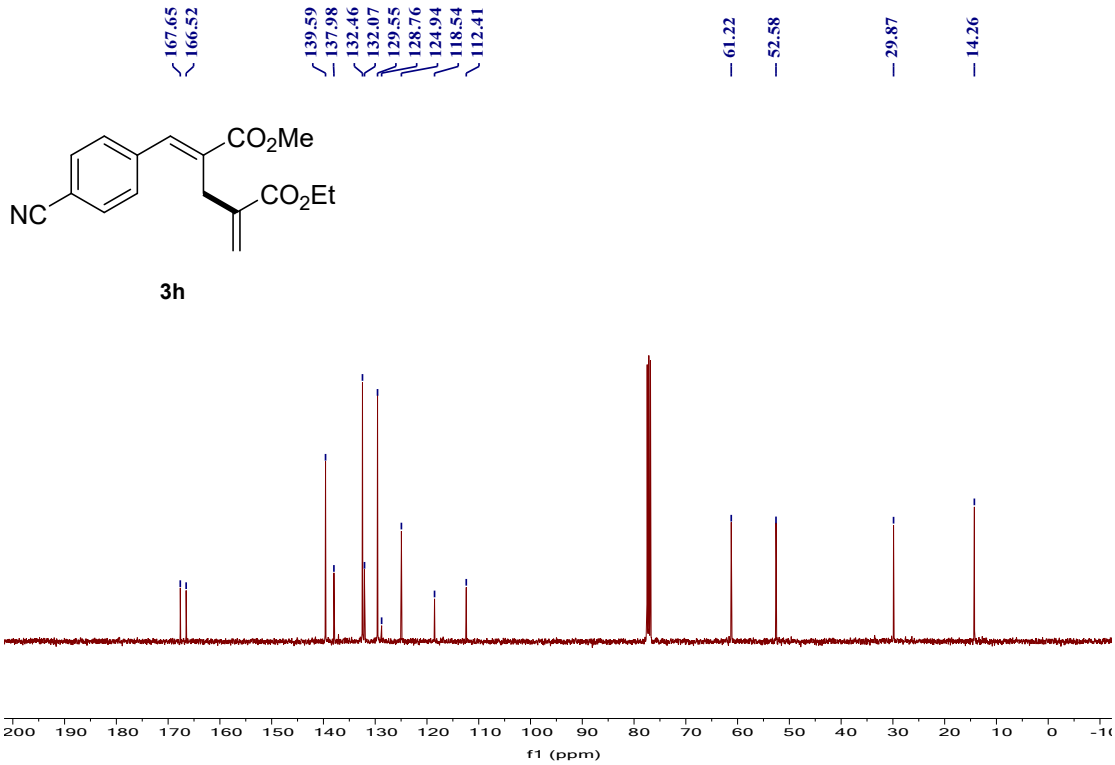


Figure S17 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3h**

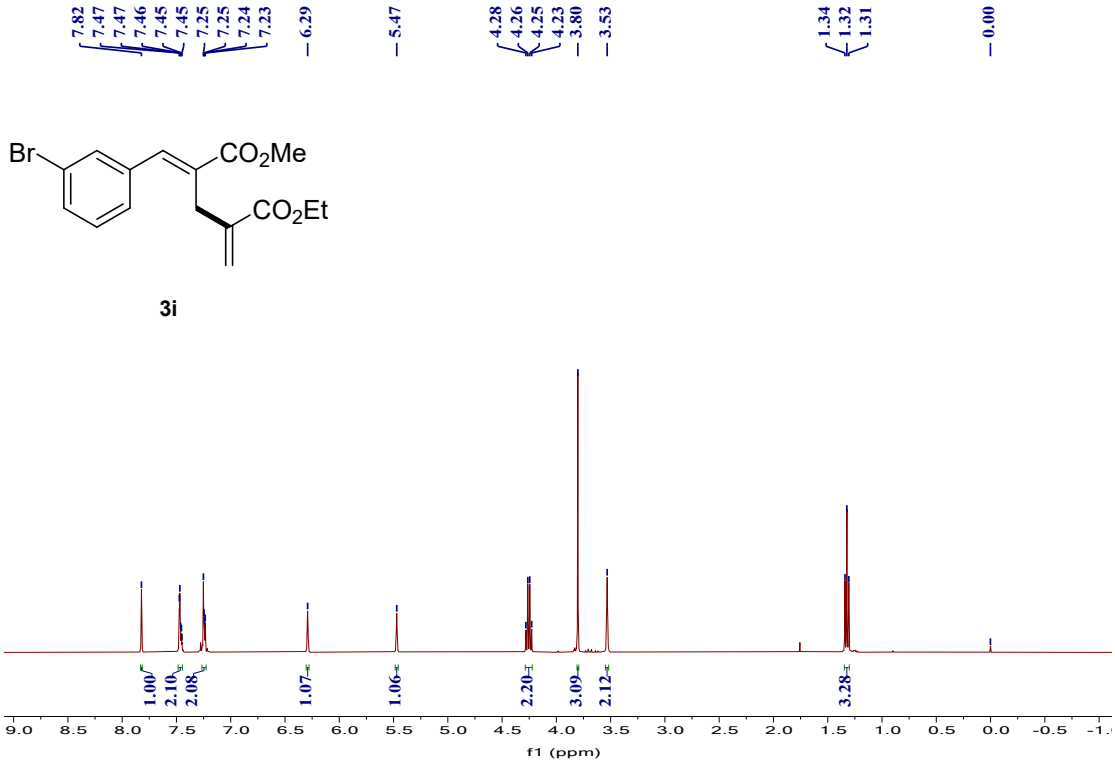


Figure S18 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3i**

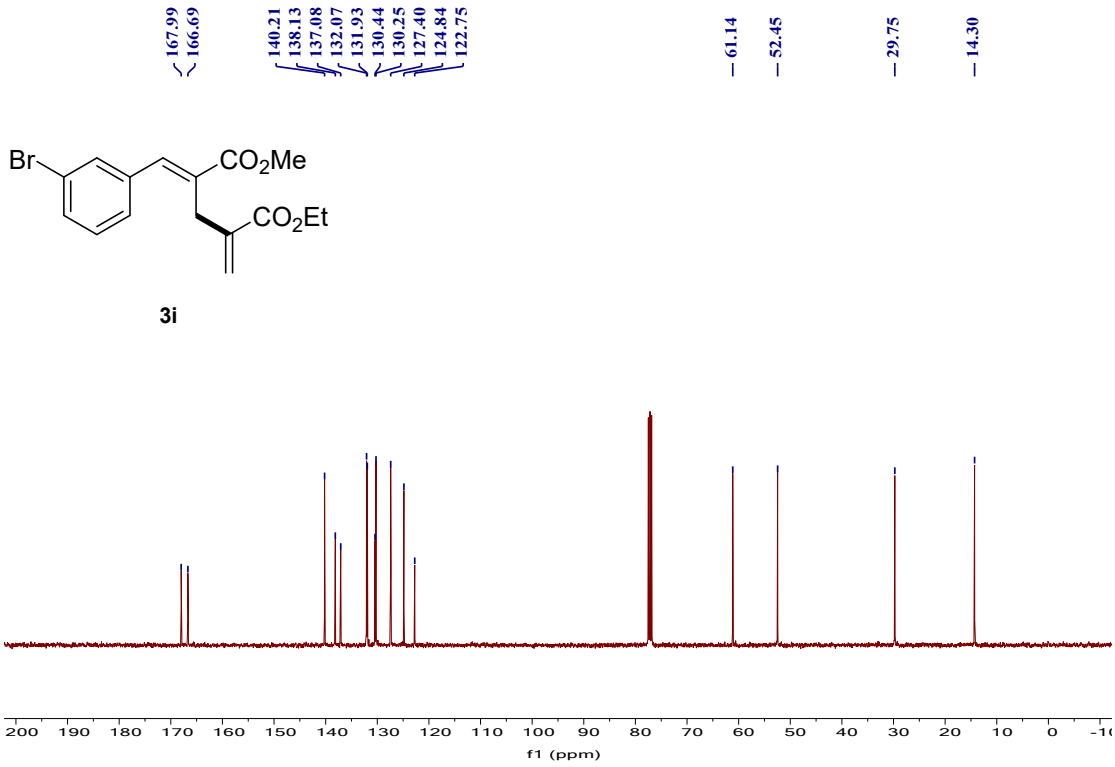


Figure S19 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3i**

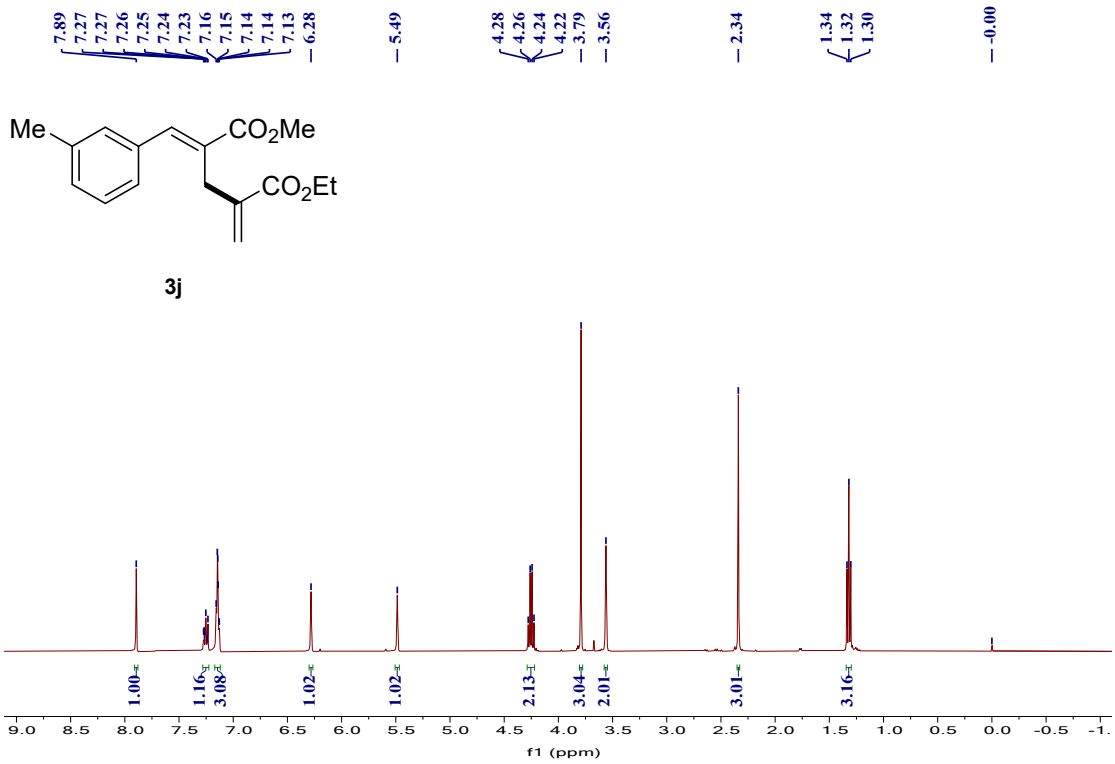


Figure S20 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3j**

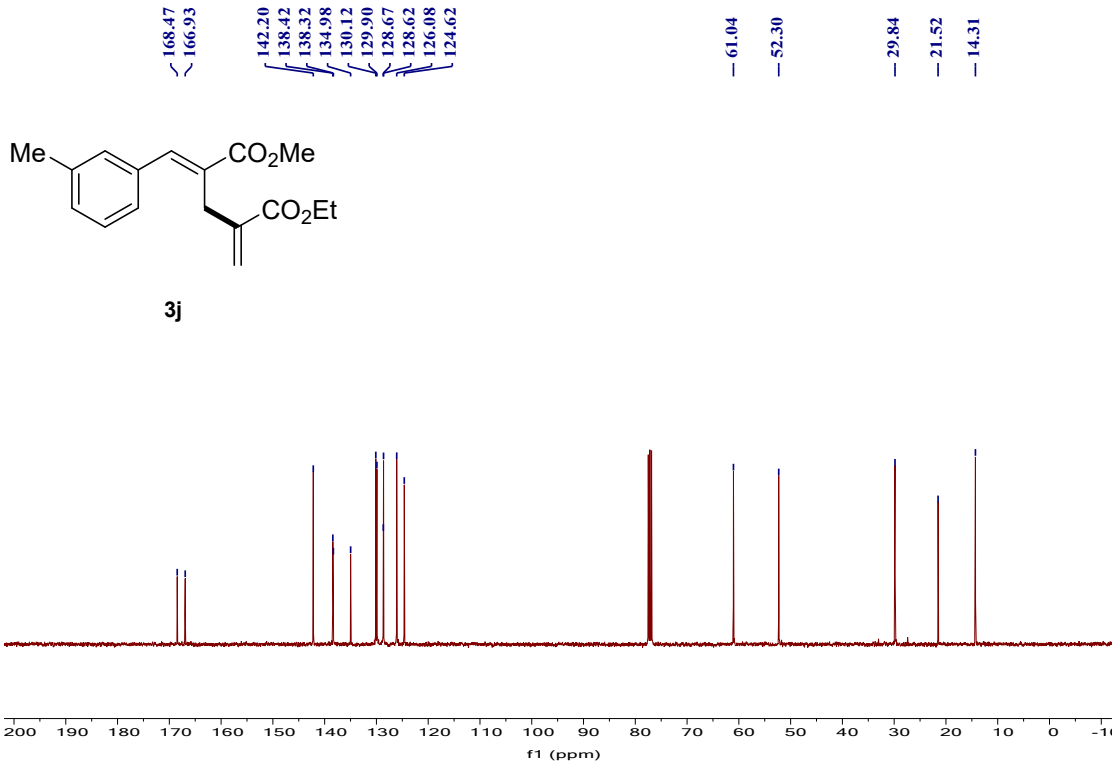


Figure S21 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3j**

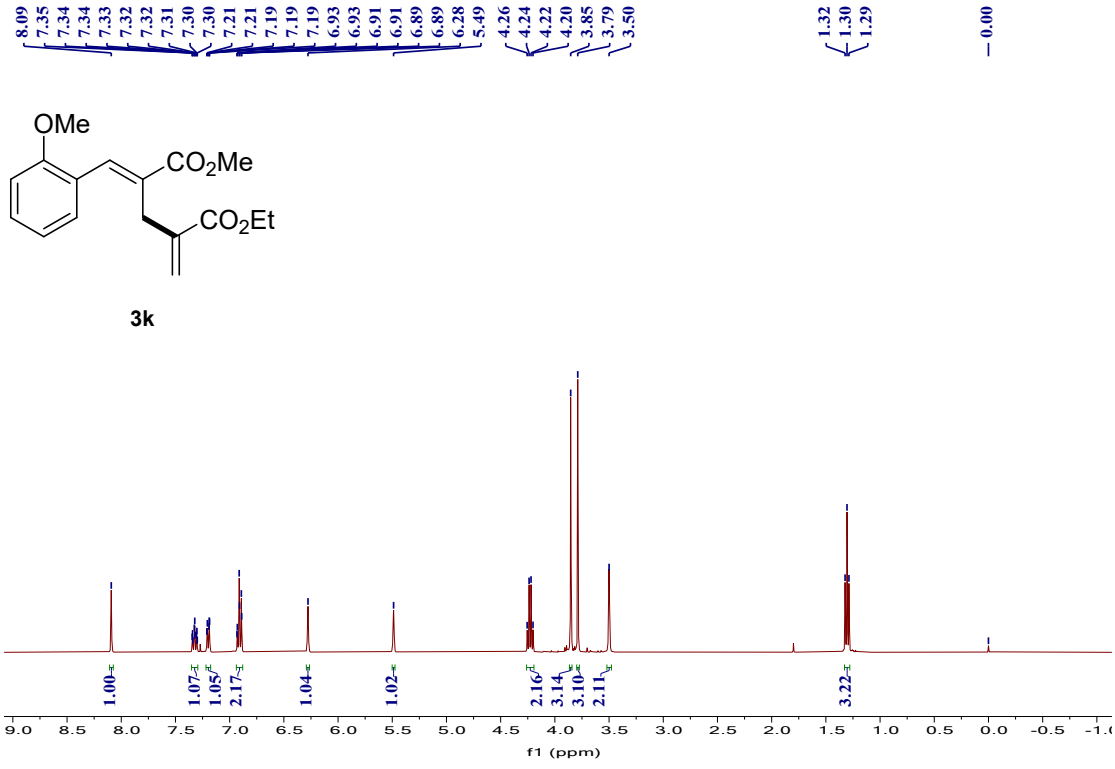


Figure S22 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3k**

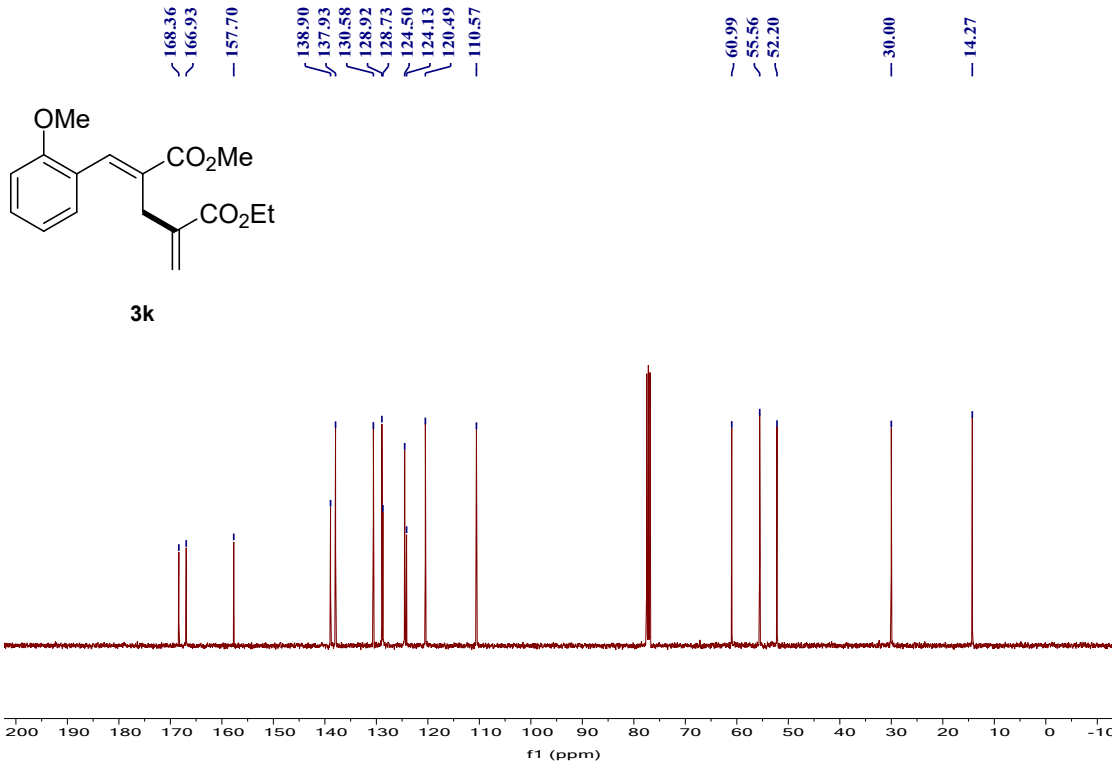


Figure S23 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3k**

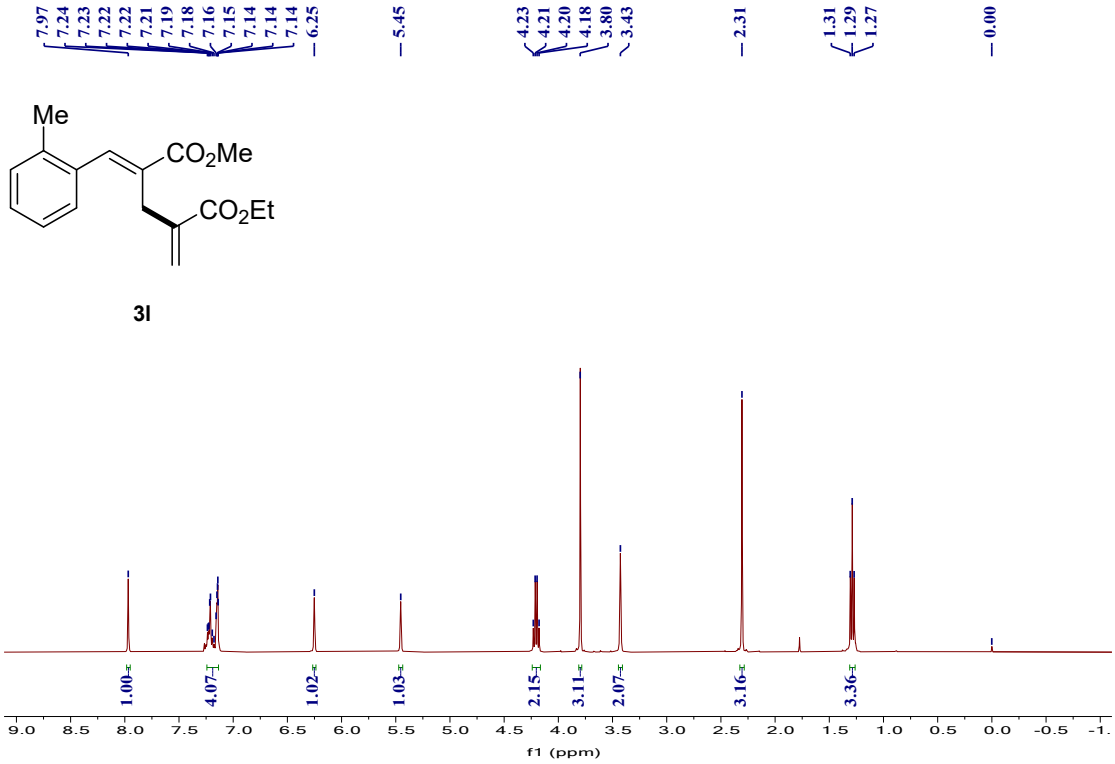


Figure S24 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3l**

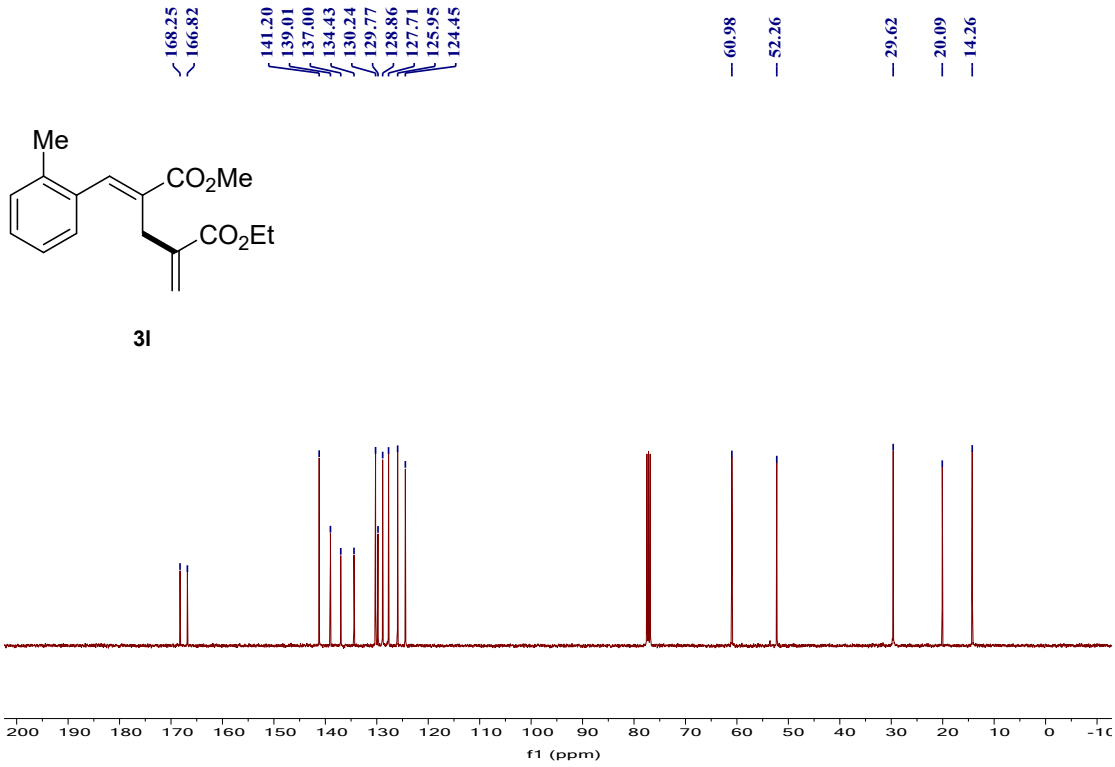


Figure S25 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3l**

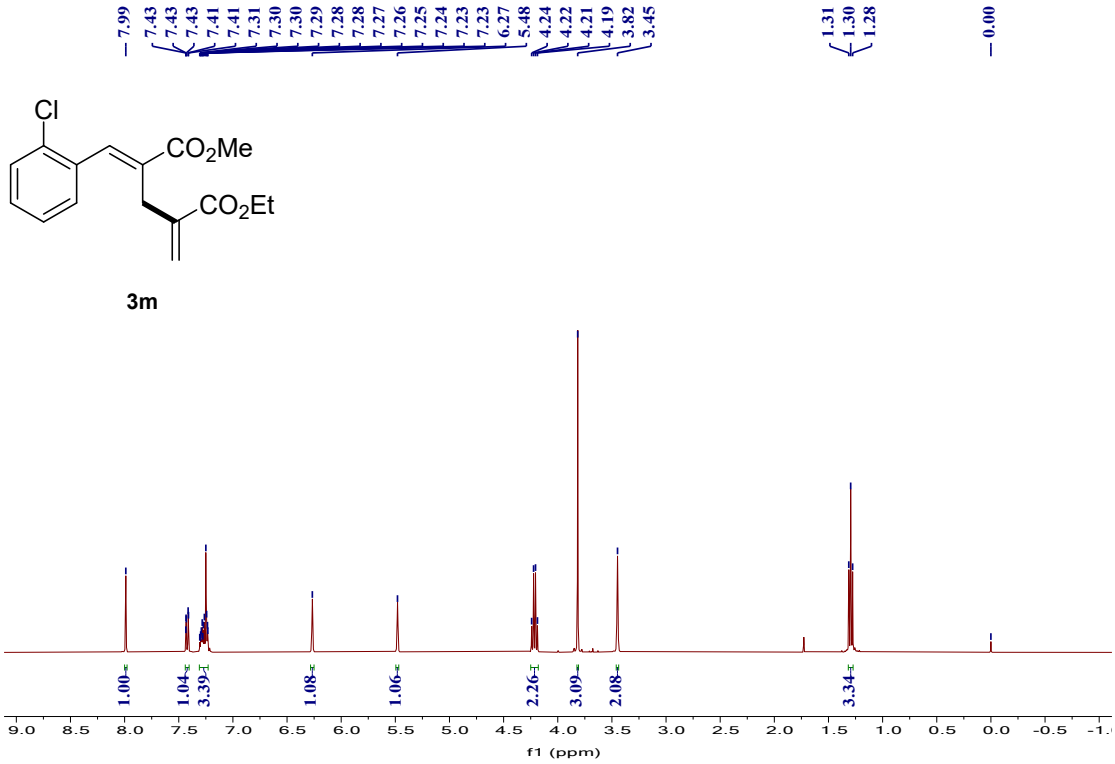


Figure S26 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3m**

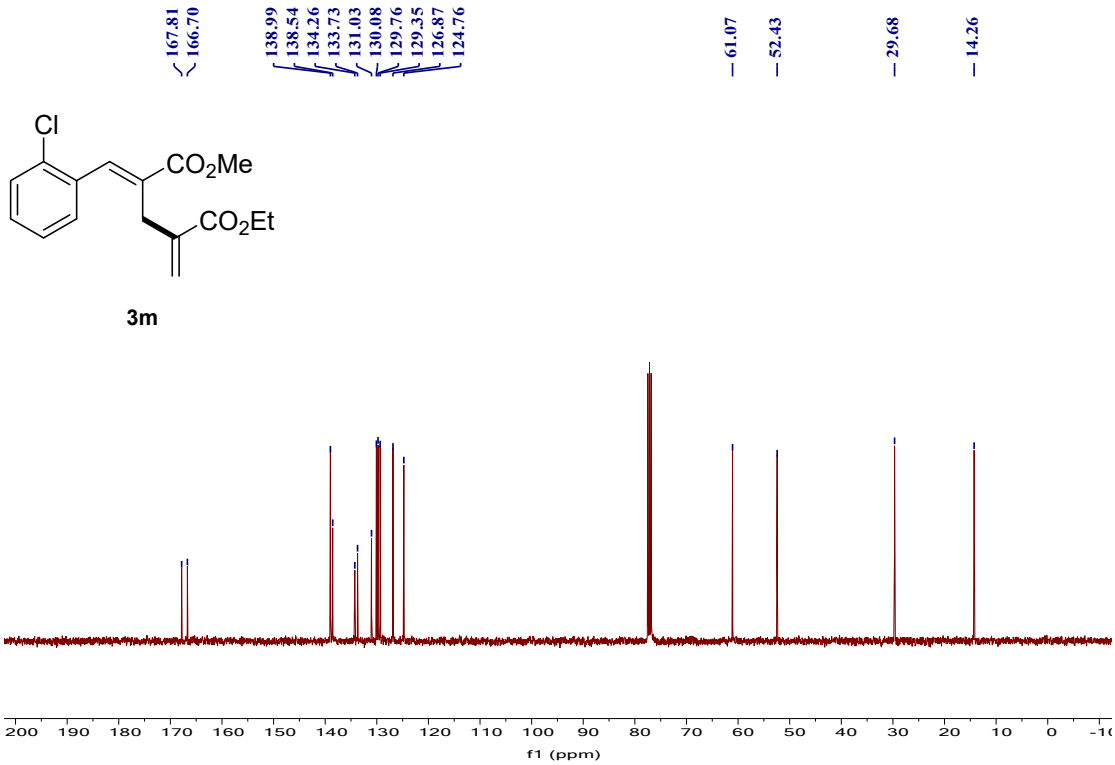


Figure S27 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3m**

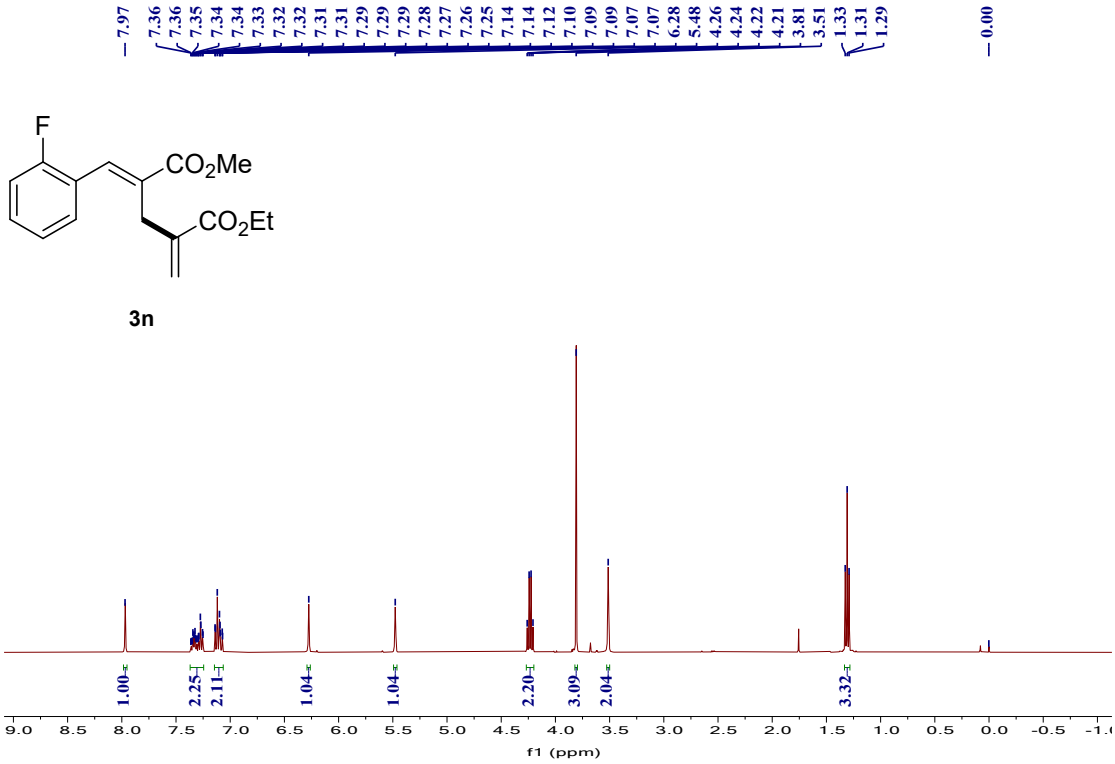


Figure S28 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3n**

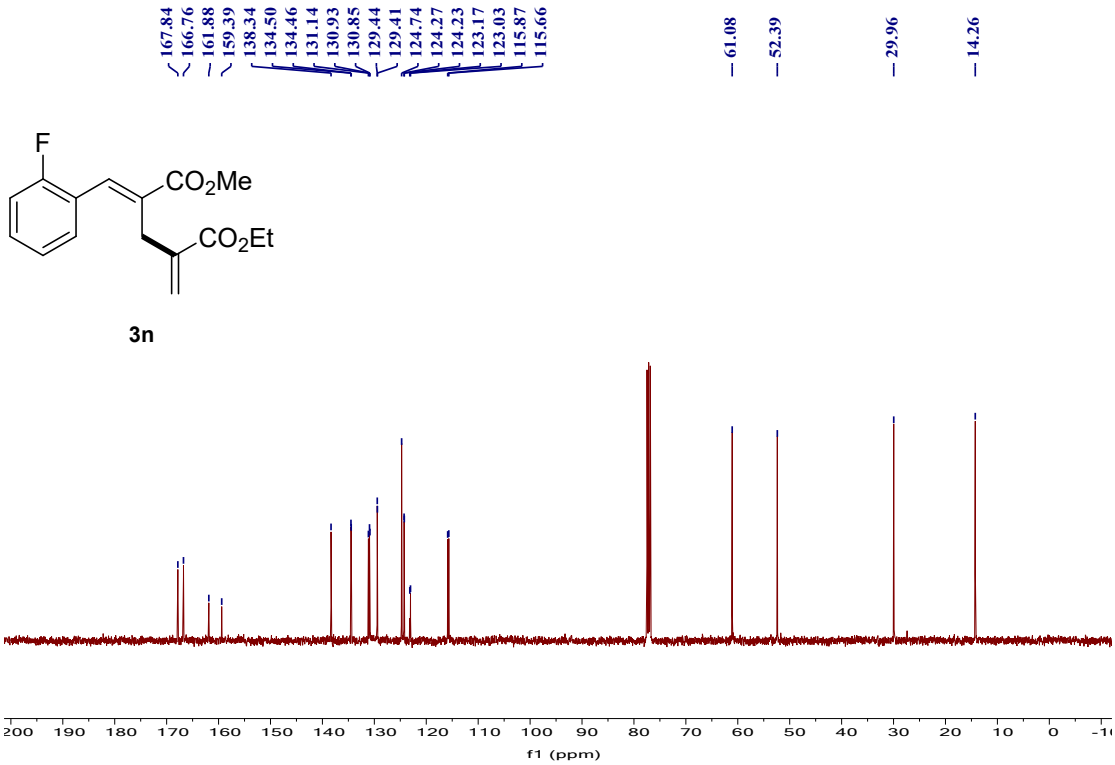


Figure S29 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3n**

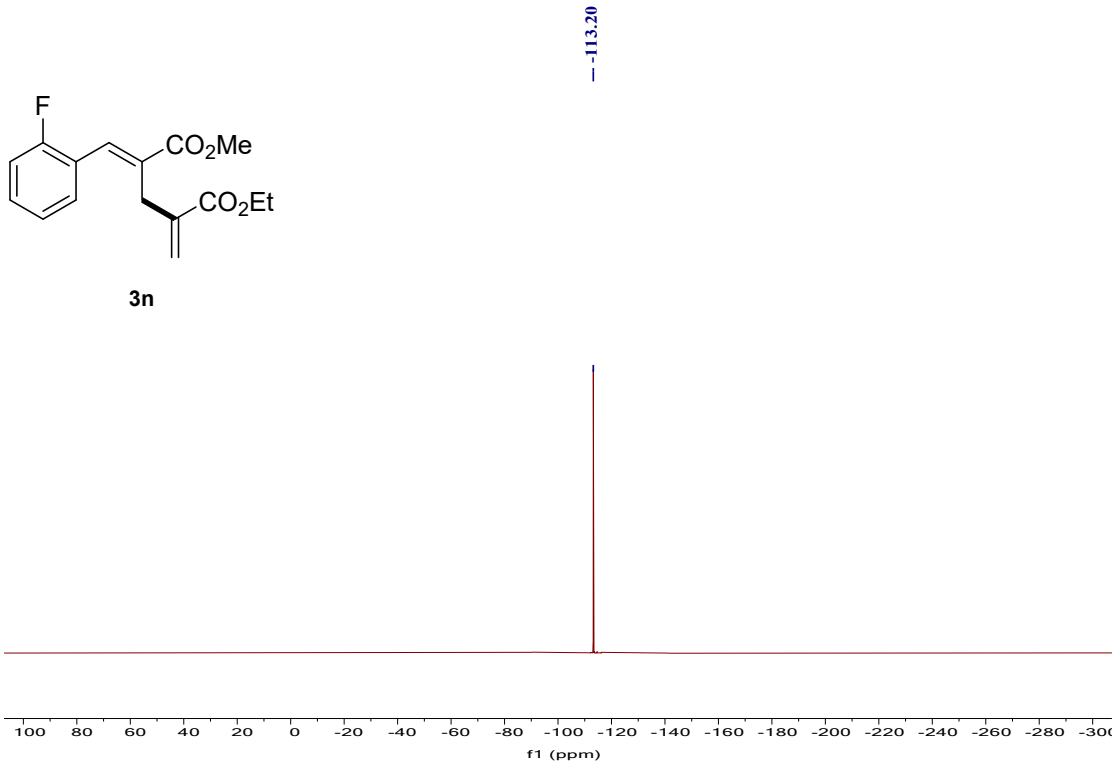


Figure S30 | ^{19}F NMR (376 MHz, Chloroform-*d*) spectra for compound **3n**

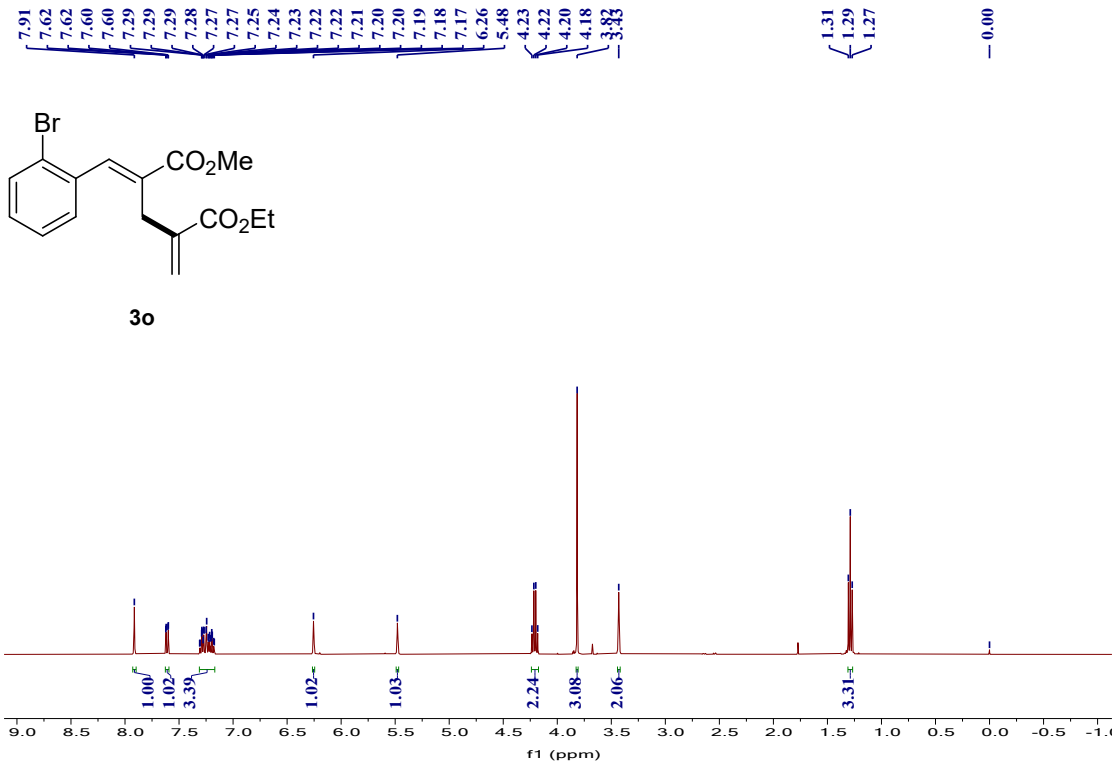


Figure S31 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3o**

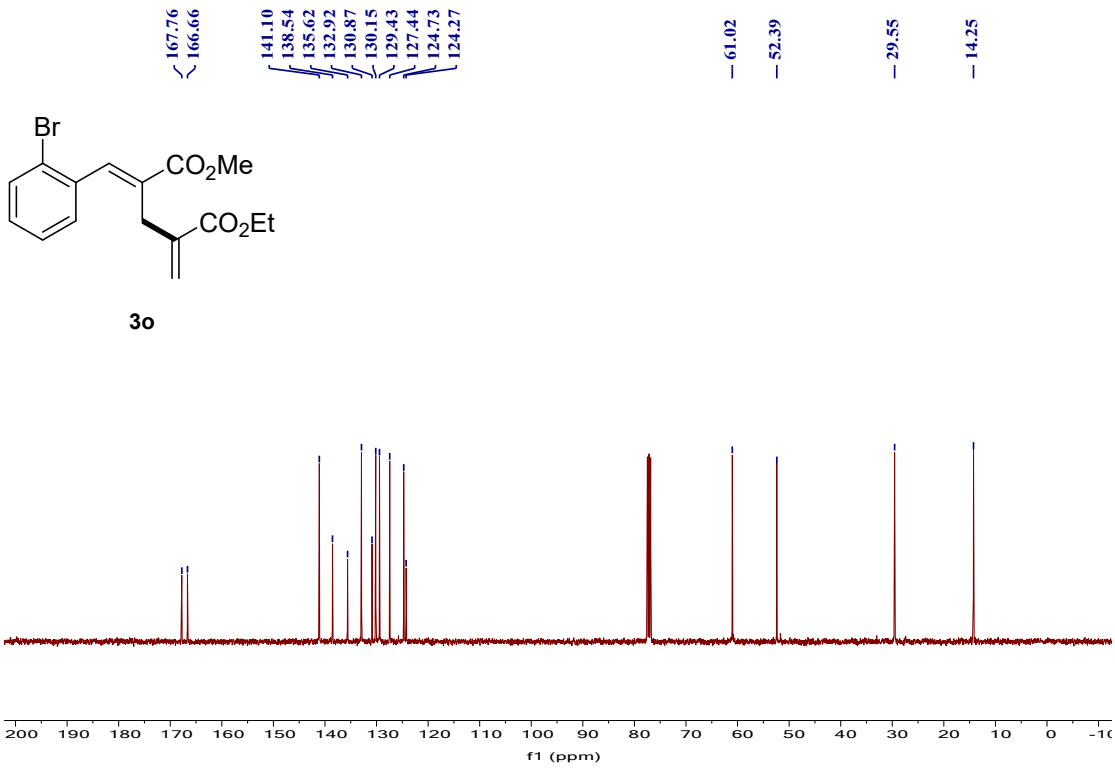


Figure S32 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3o**

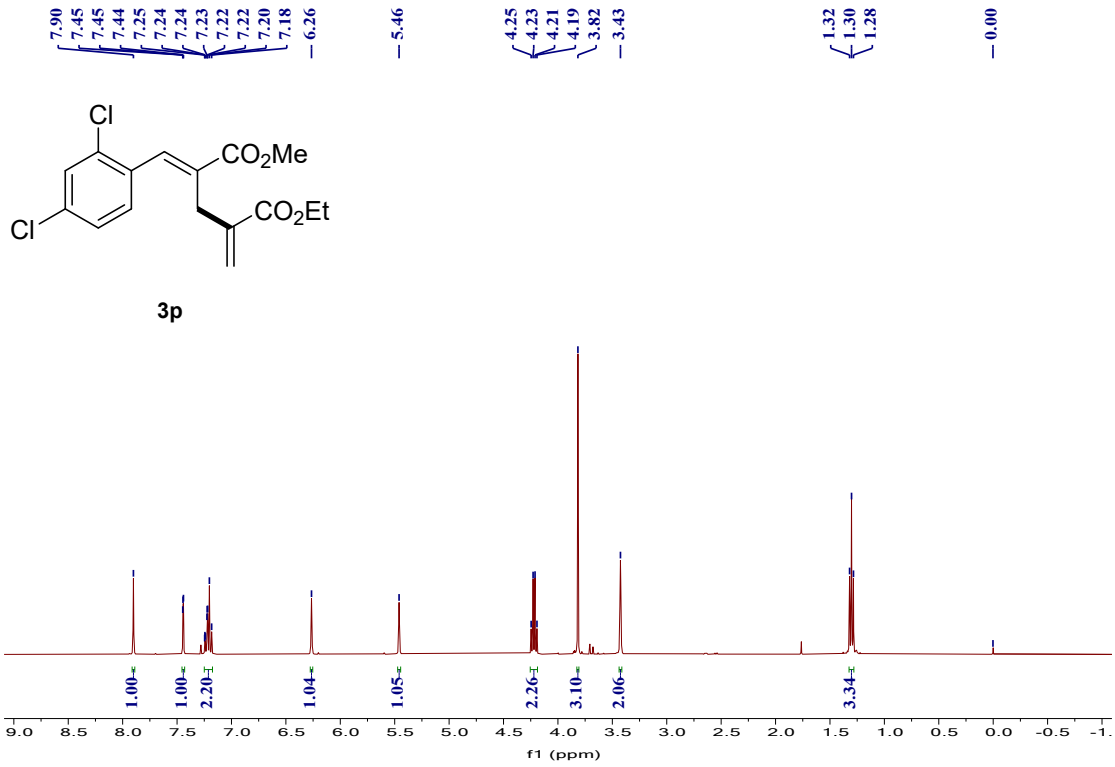


Figure S33 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3p**

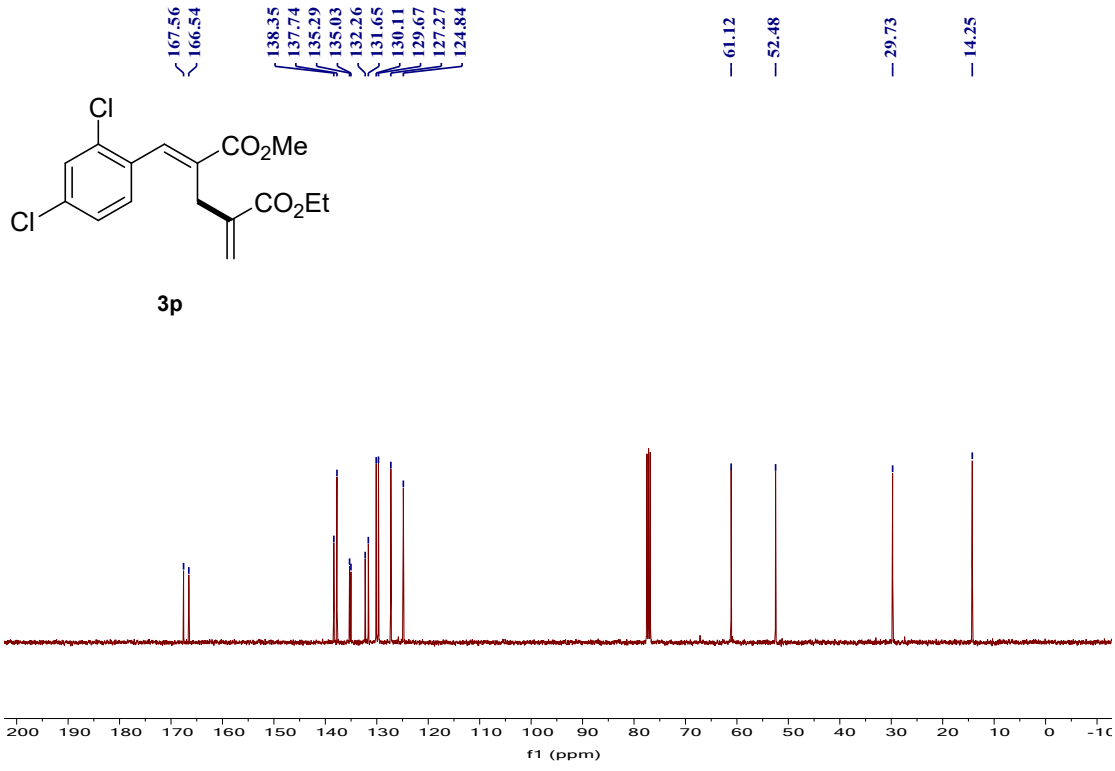


Figure S34 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3p**

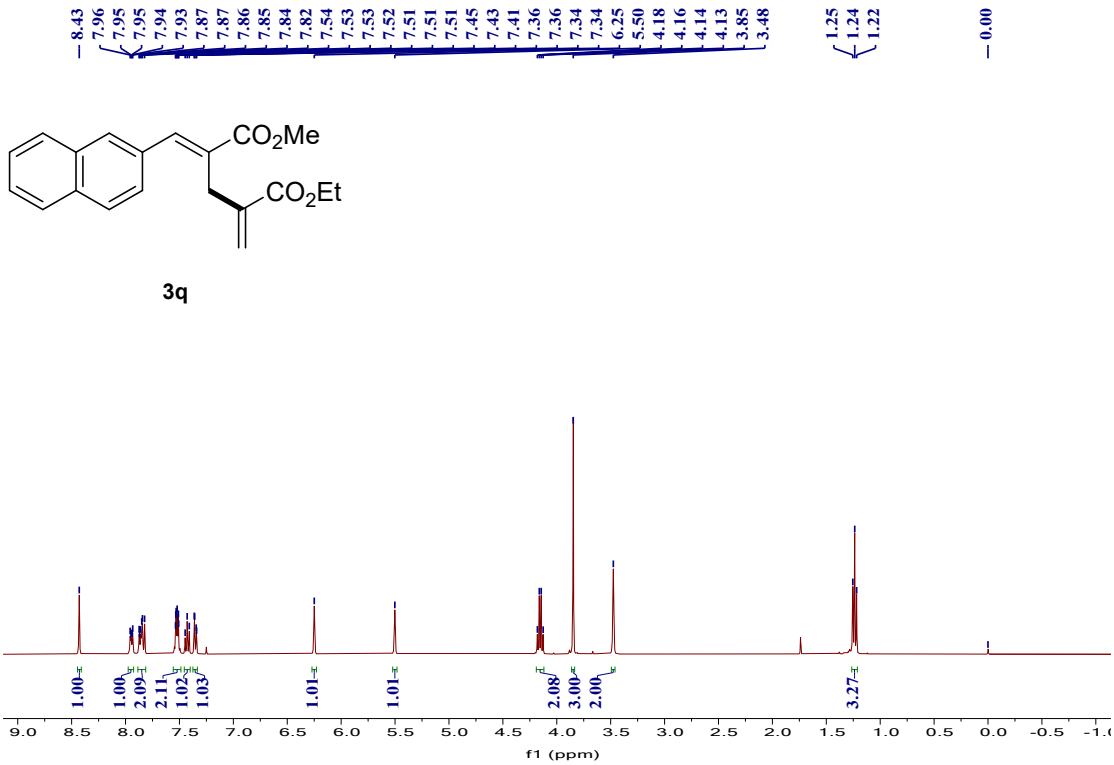


Figure S35 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3q**

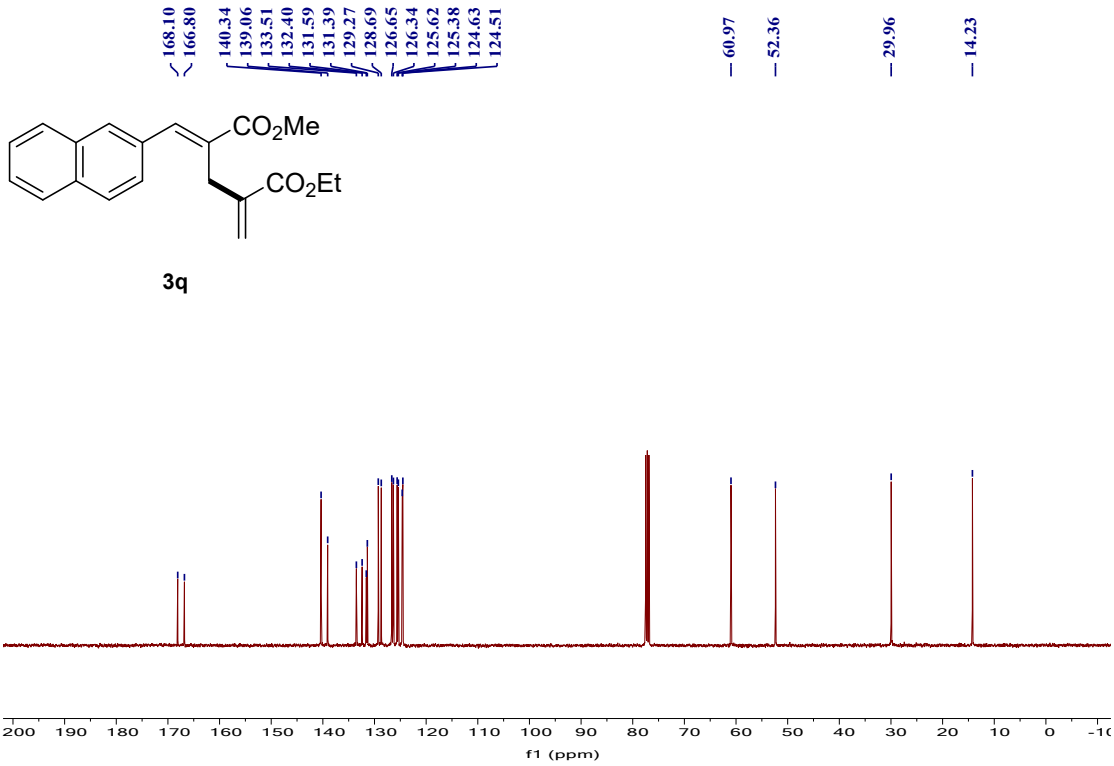


Figure S36 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3q**

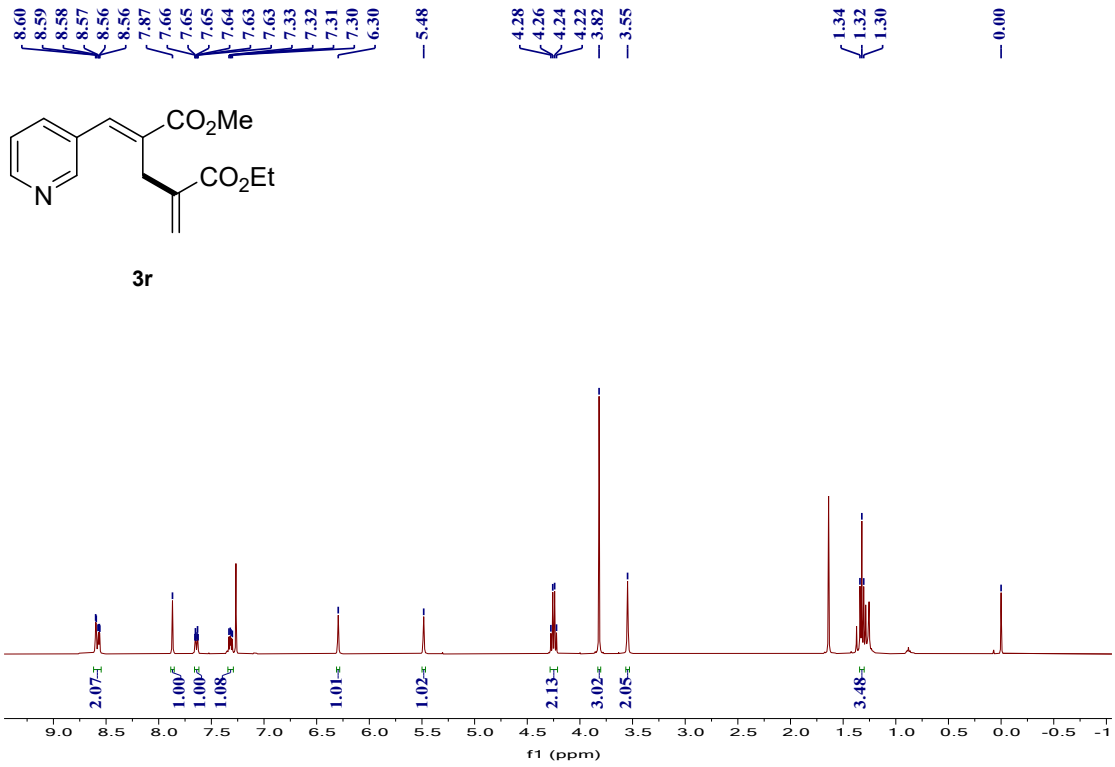


Figure S37 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3r**

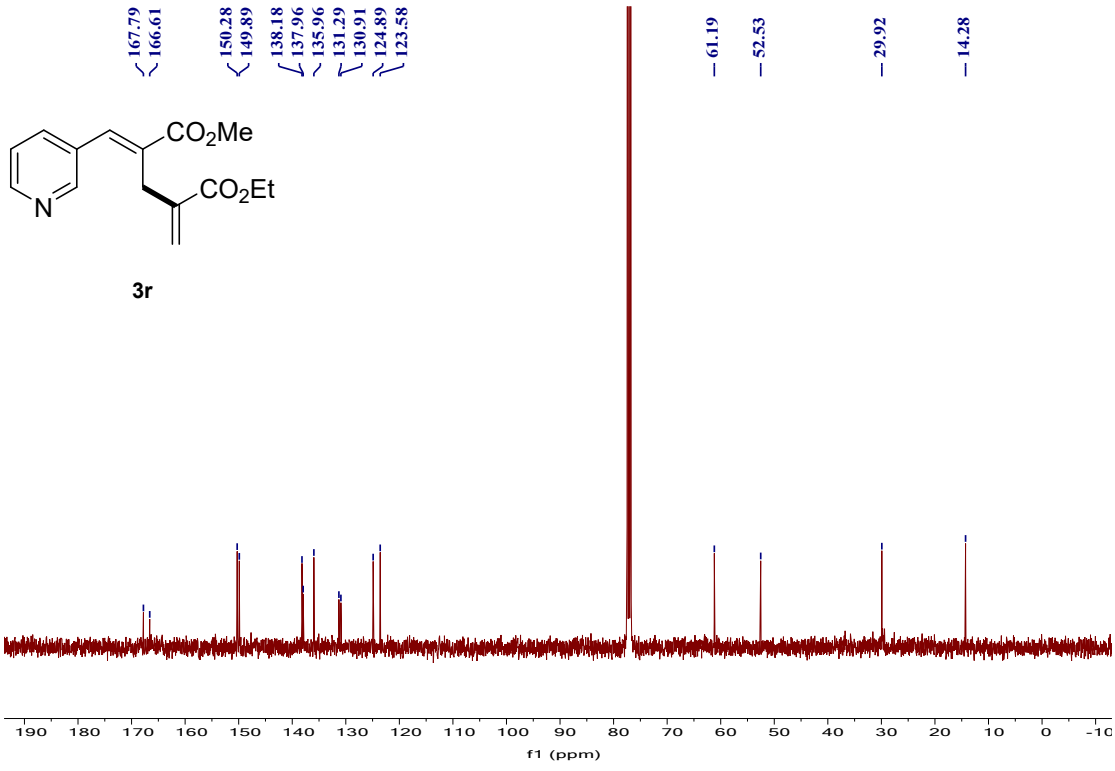


Figure S38 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3r**

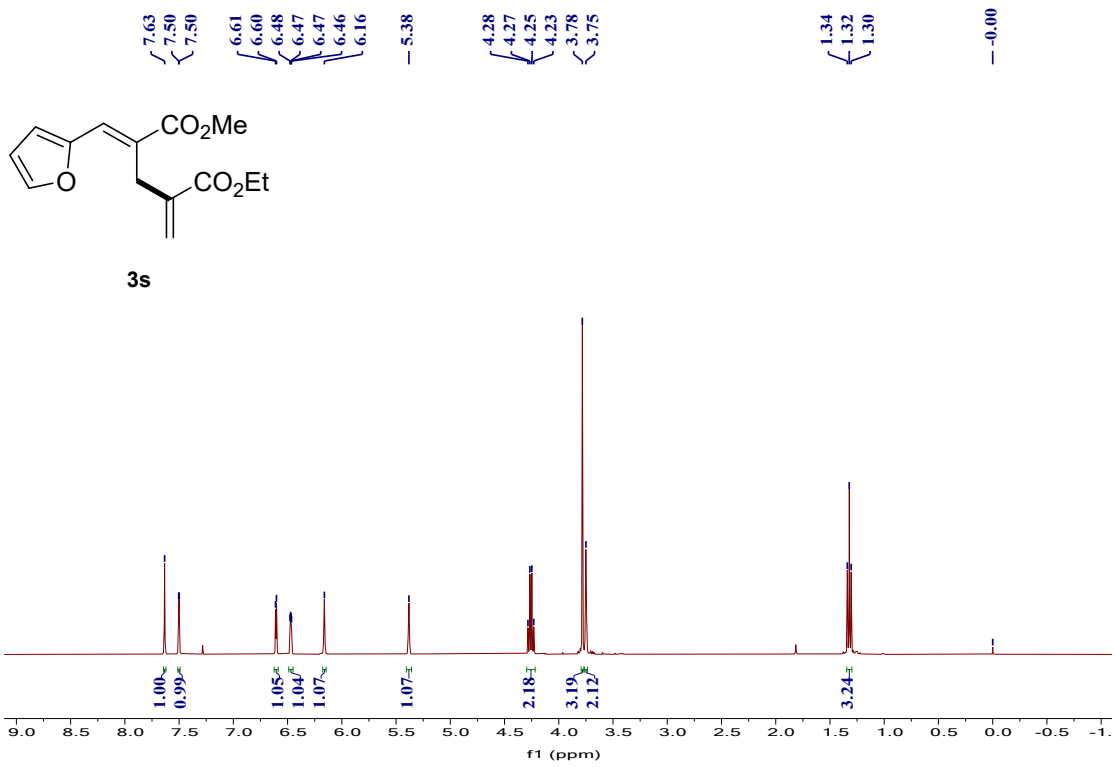


Figure S39 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3s**

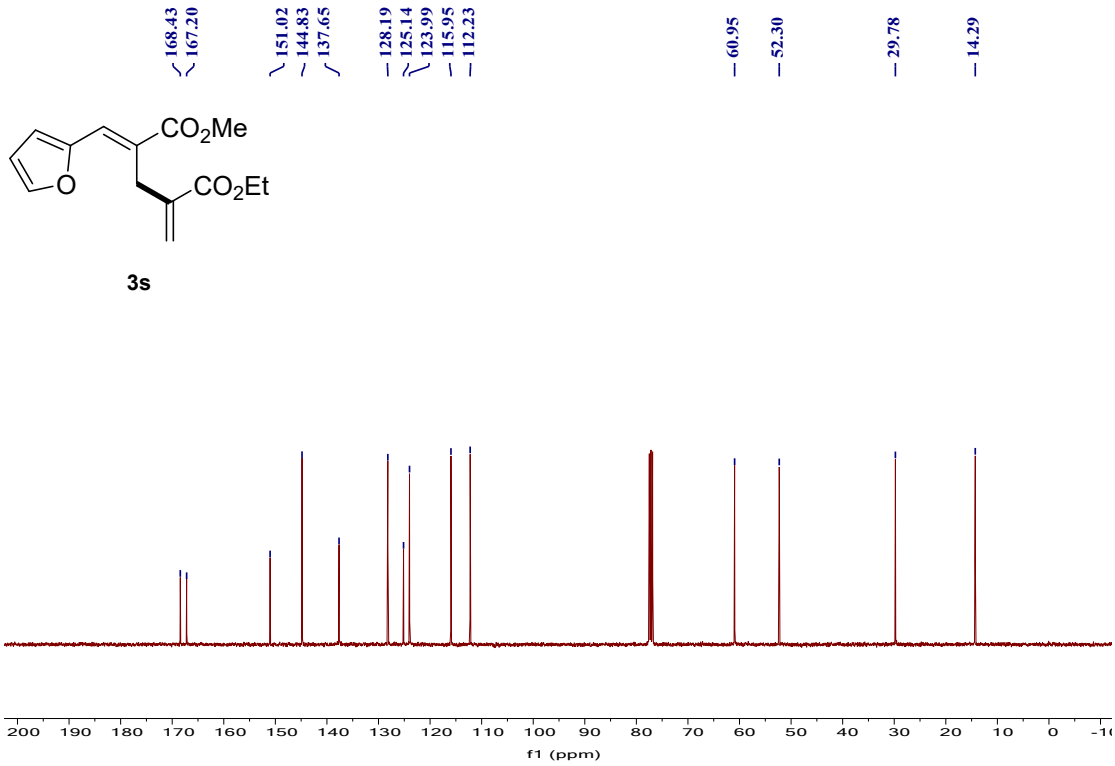


Figure S40 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3s**

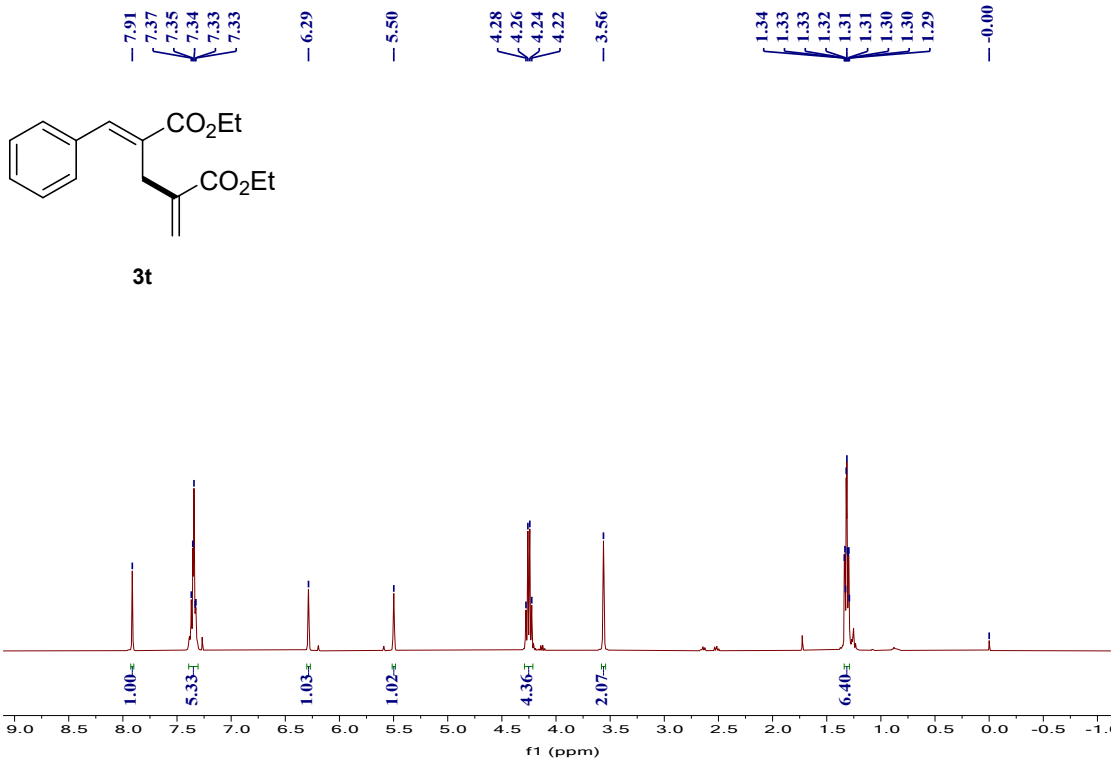


Figure S41 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3t**

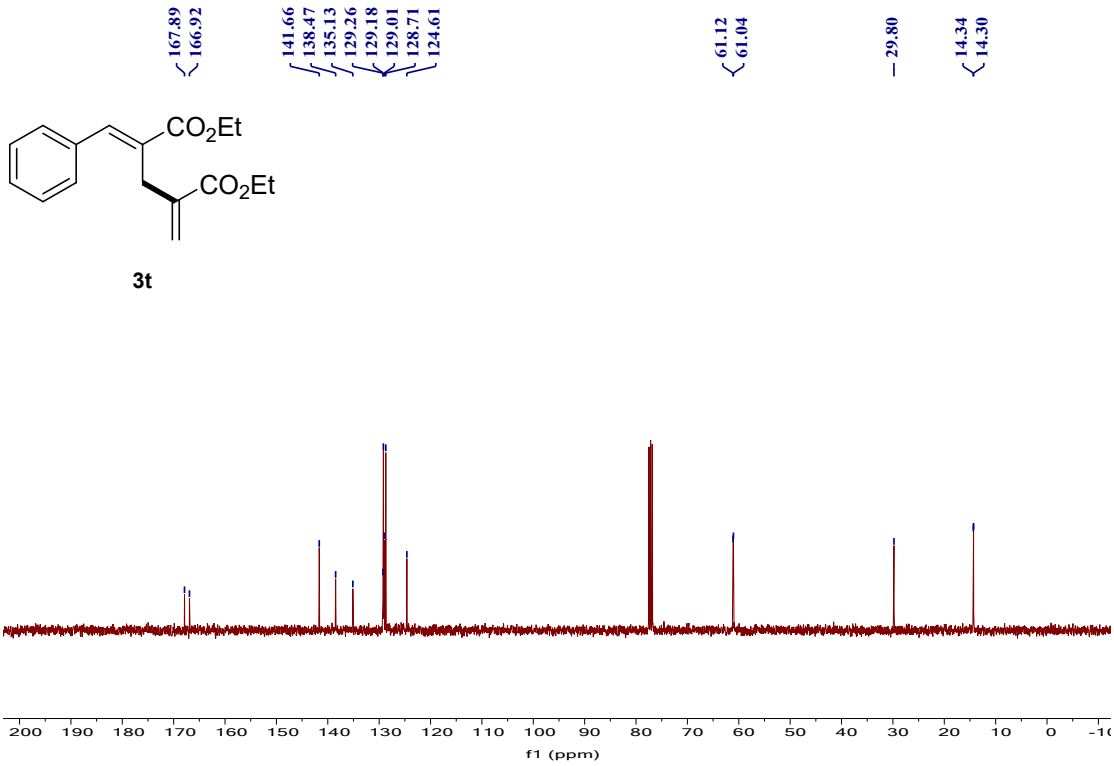


Figure S42 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3t**

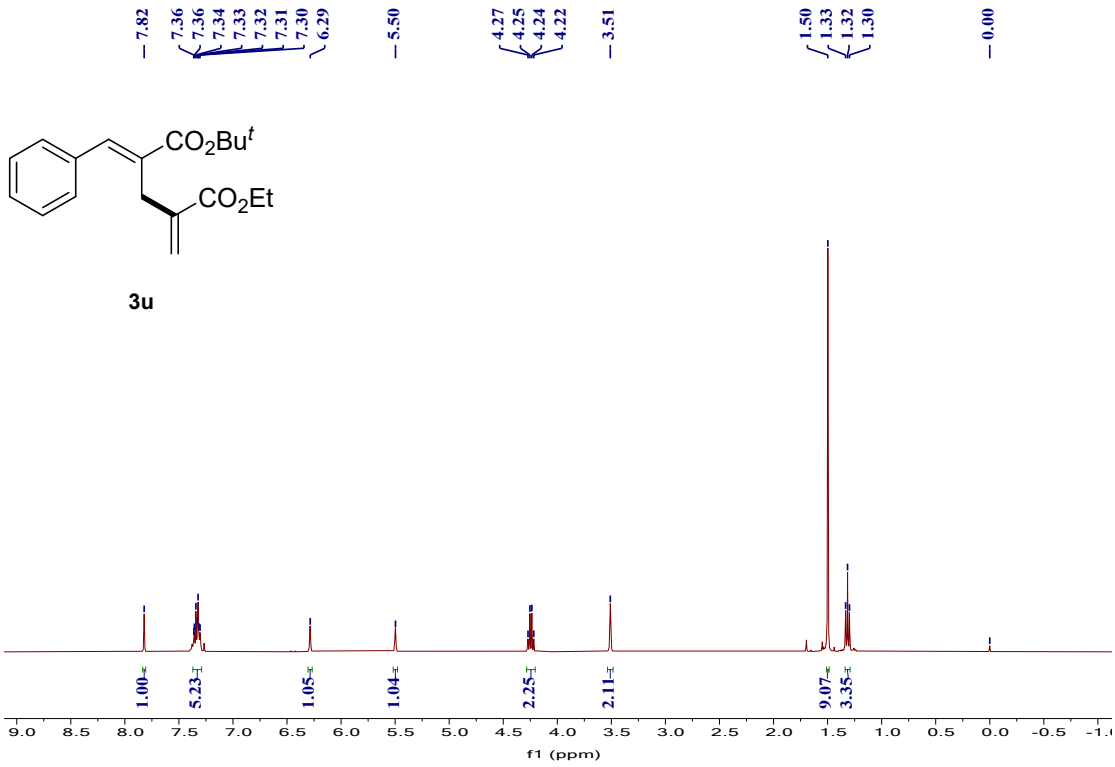


Figure S43 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3u**

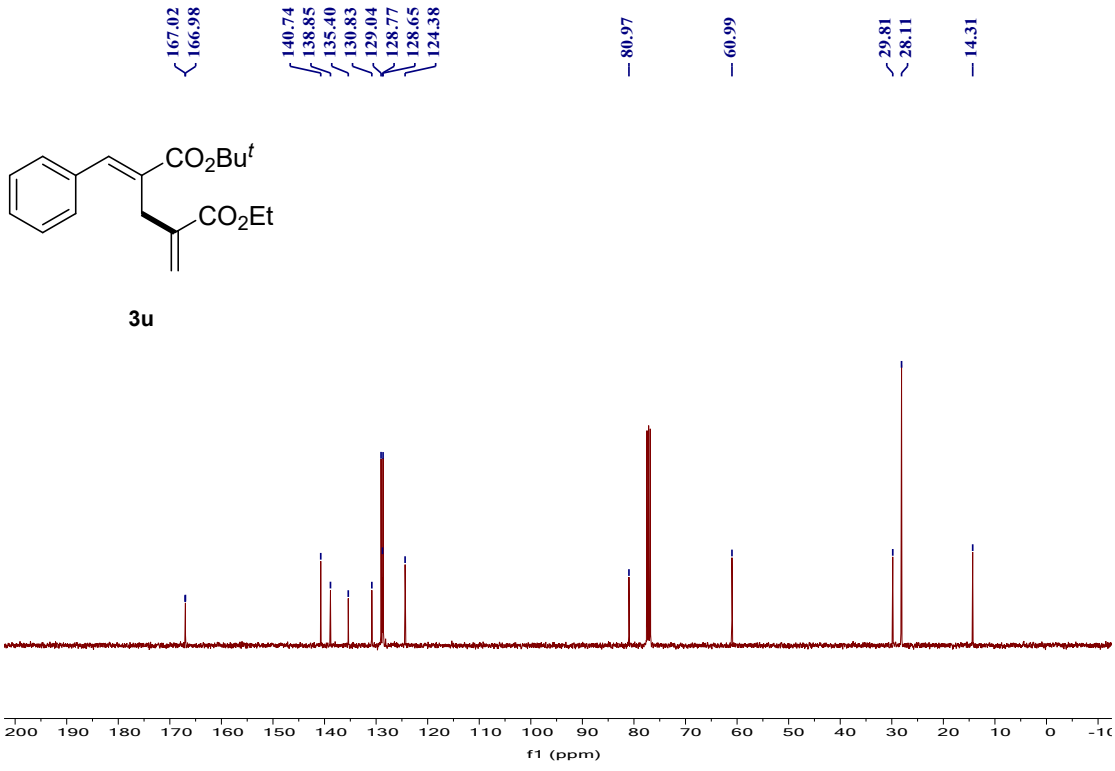


Figure S44 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3u**

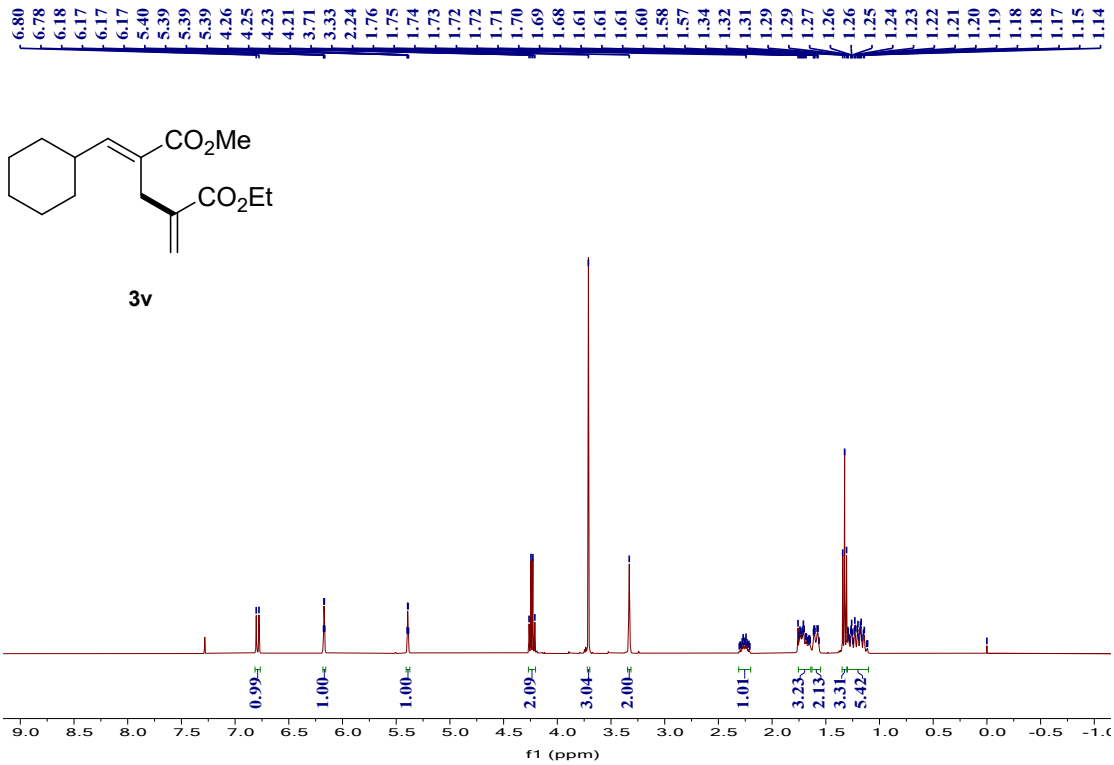


Figure S45 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3v**

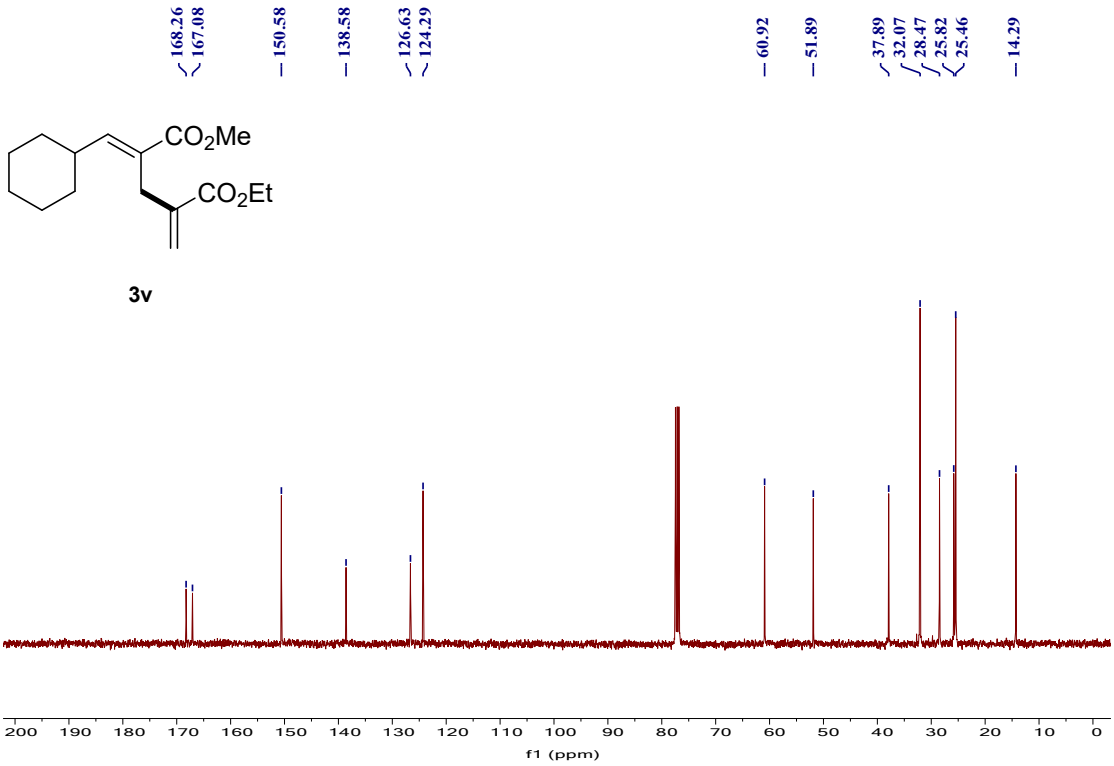


Figure S46 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3v**

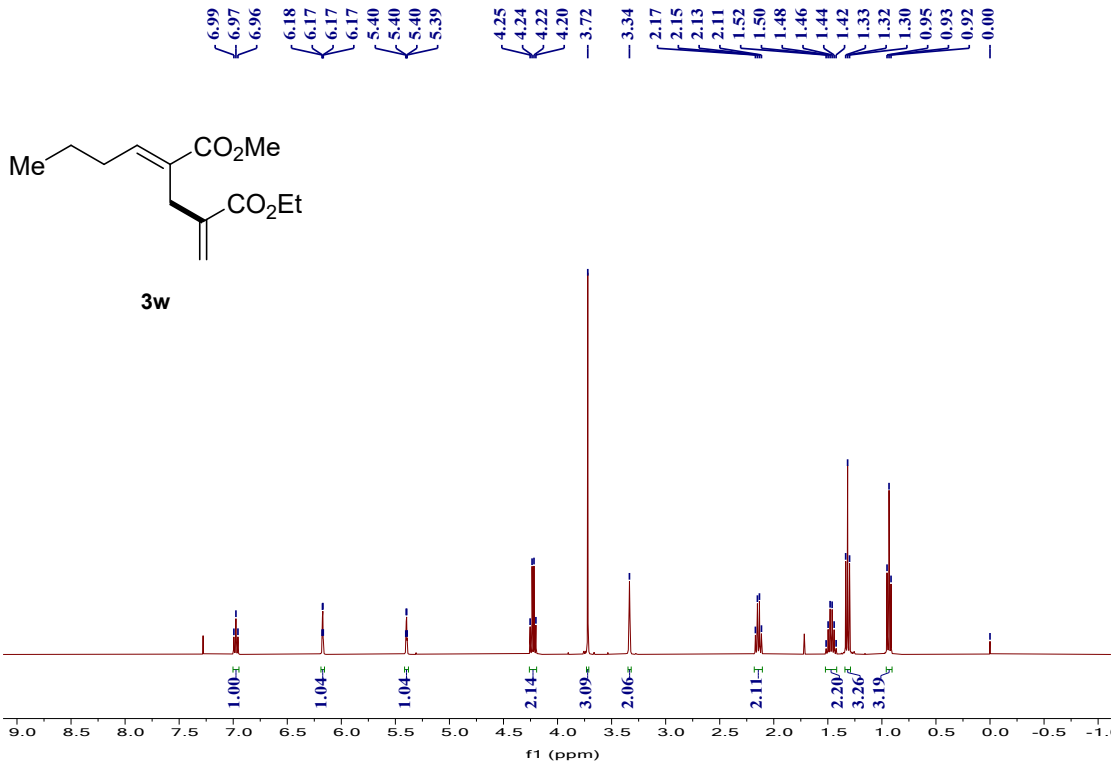


Figure S47 | [1]H NMR (400 MHz, Chloroform-d) spectra for compound **3w**

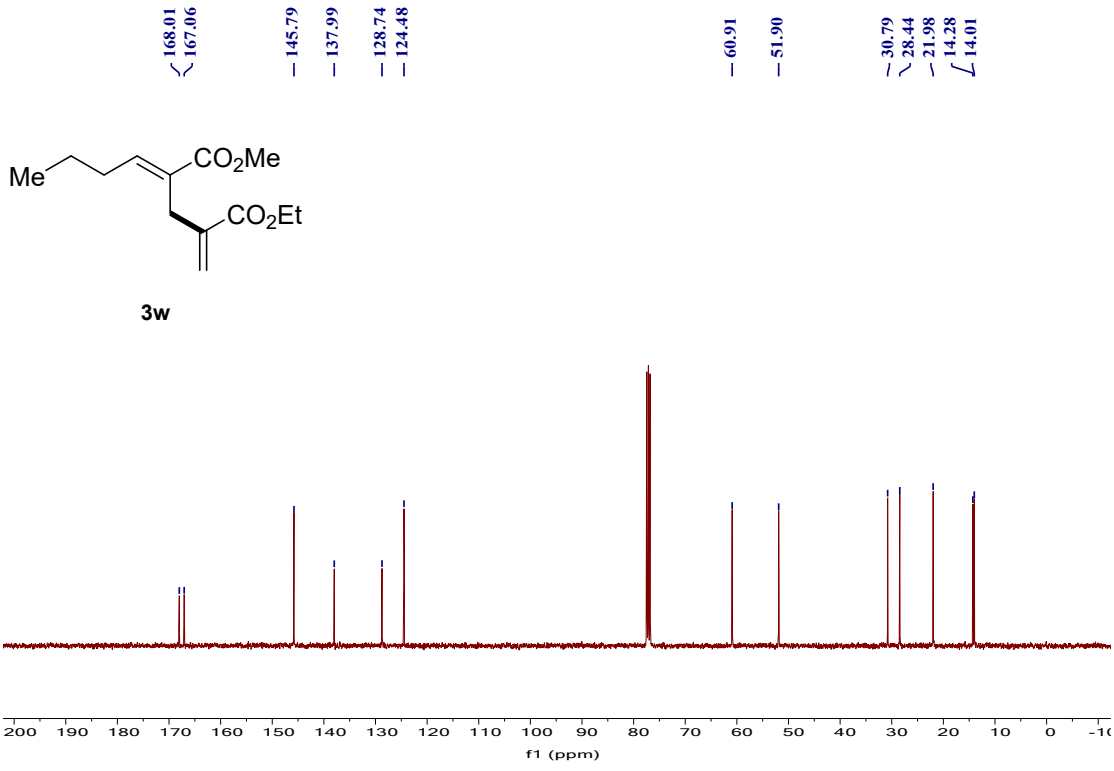


Figure S48 | [13]C NMR (101 MHz, Chloroform-*d*) spectra for compound **3w**

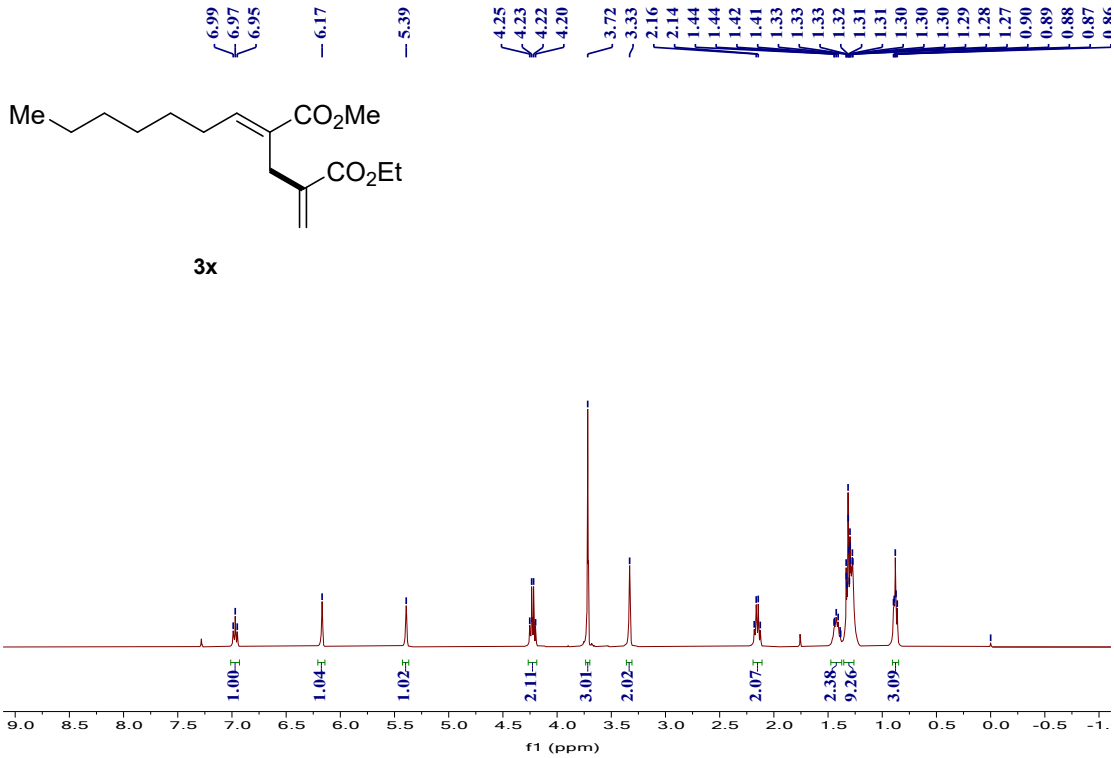


Figure S49 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3x**

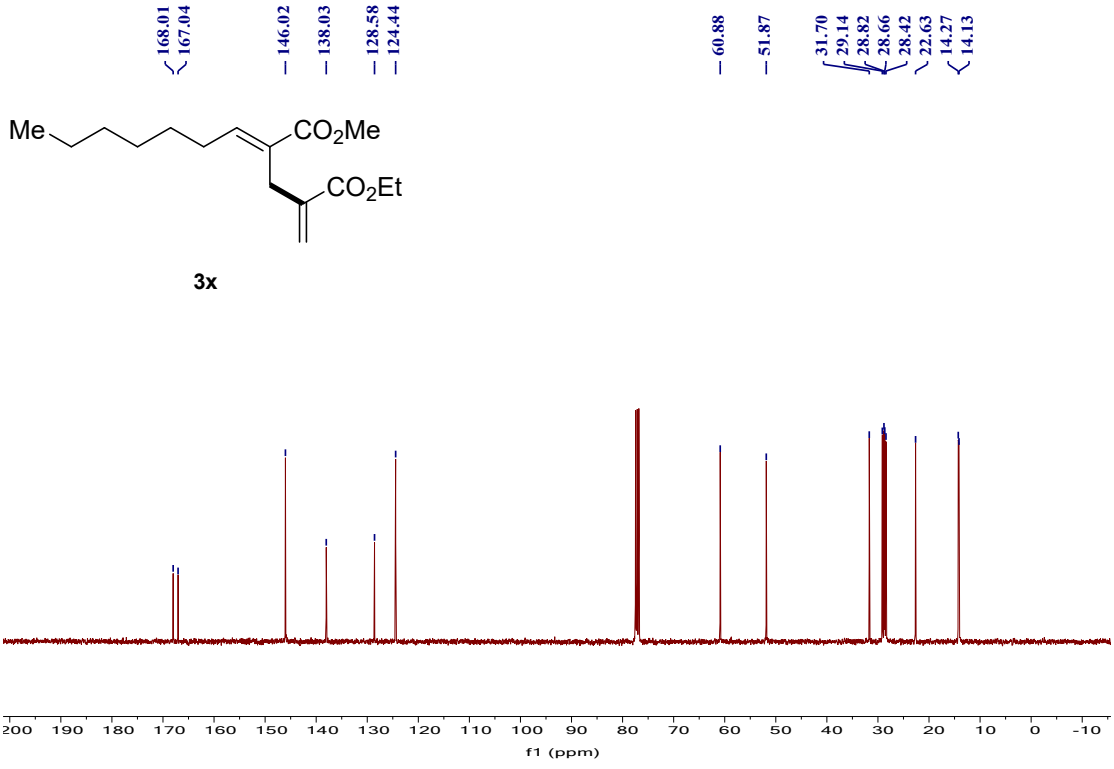


Figure S50 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3x**

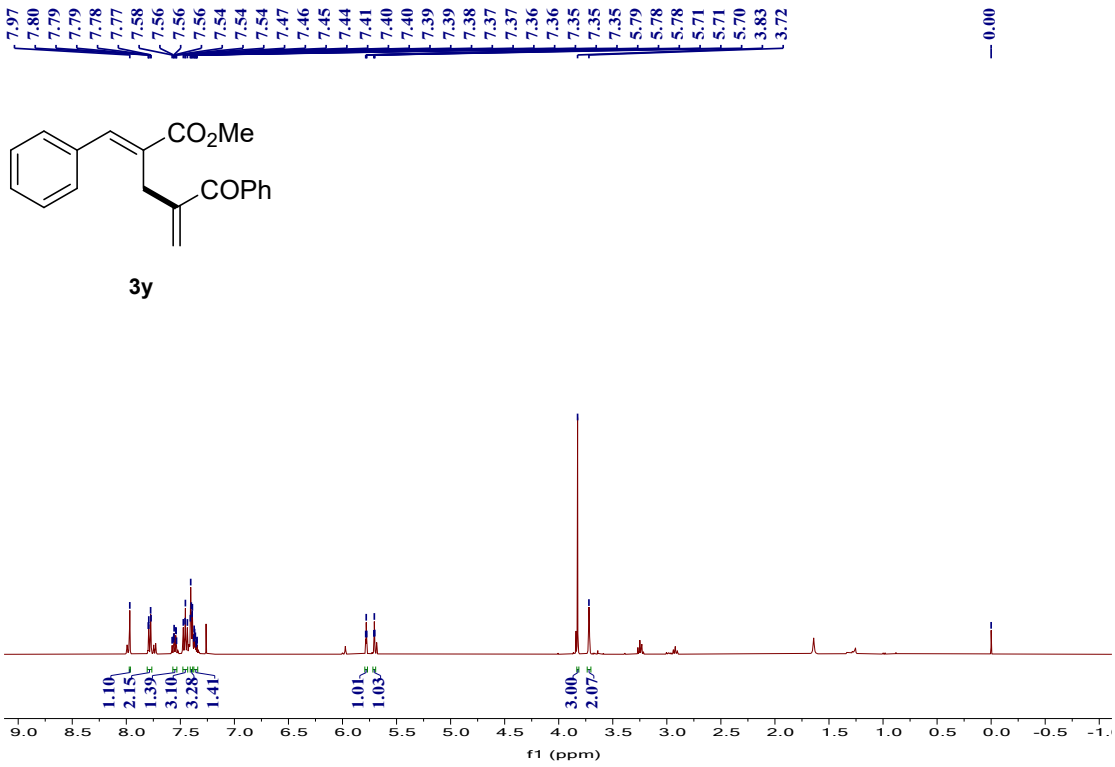


Figure S51 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3y**

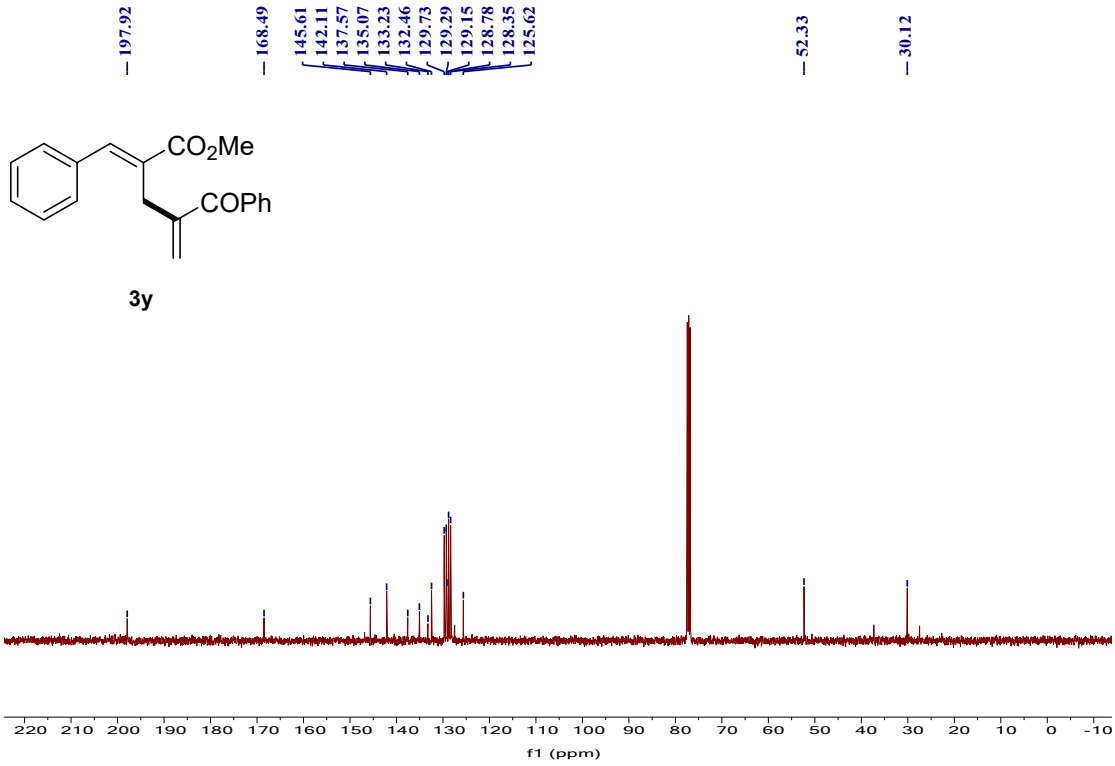


Figure S52 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3y**

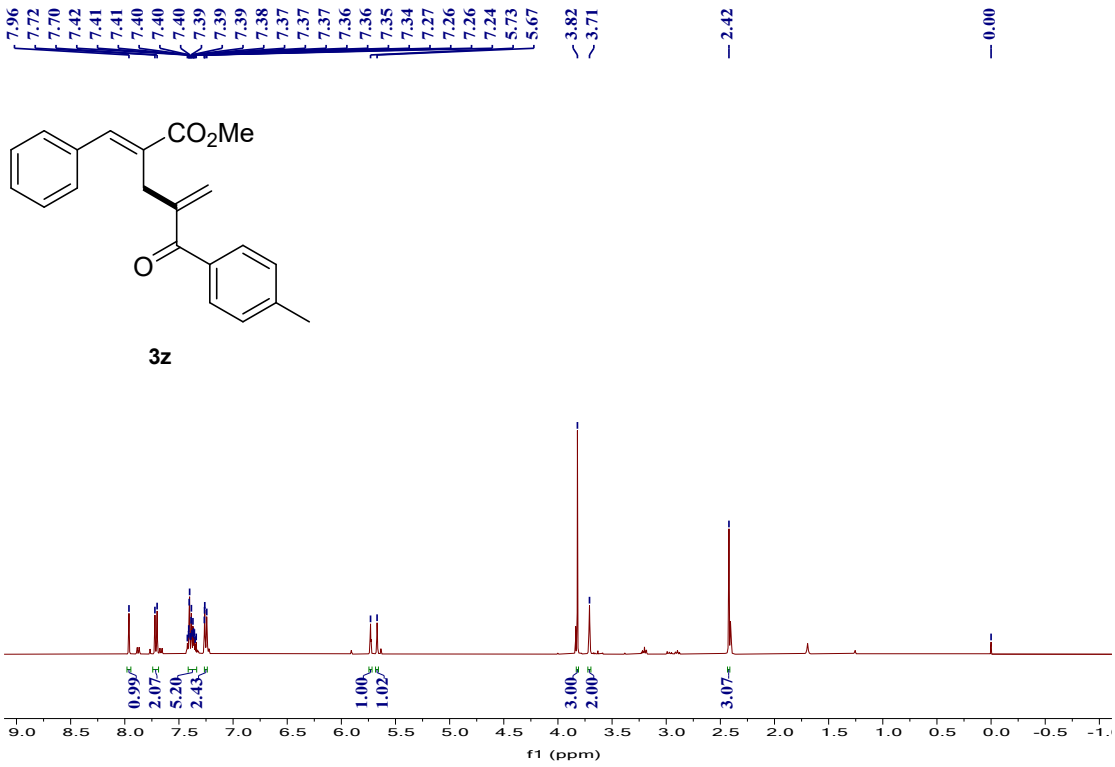


Figure S53 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3z**

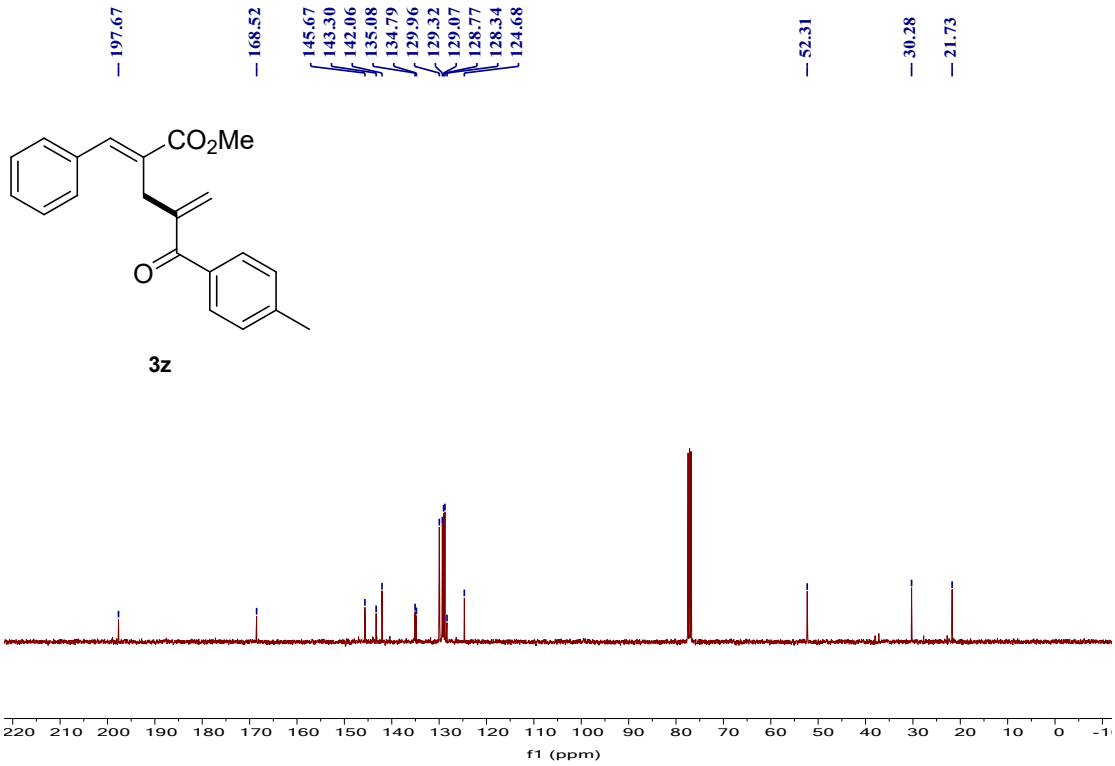


Figure S54 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3z**

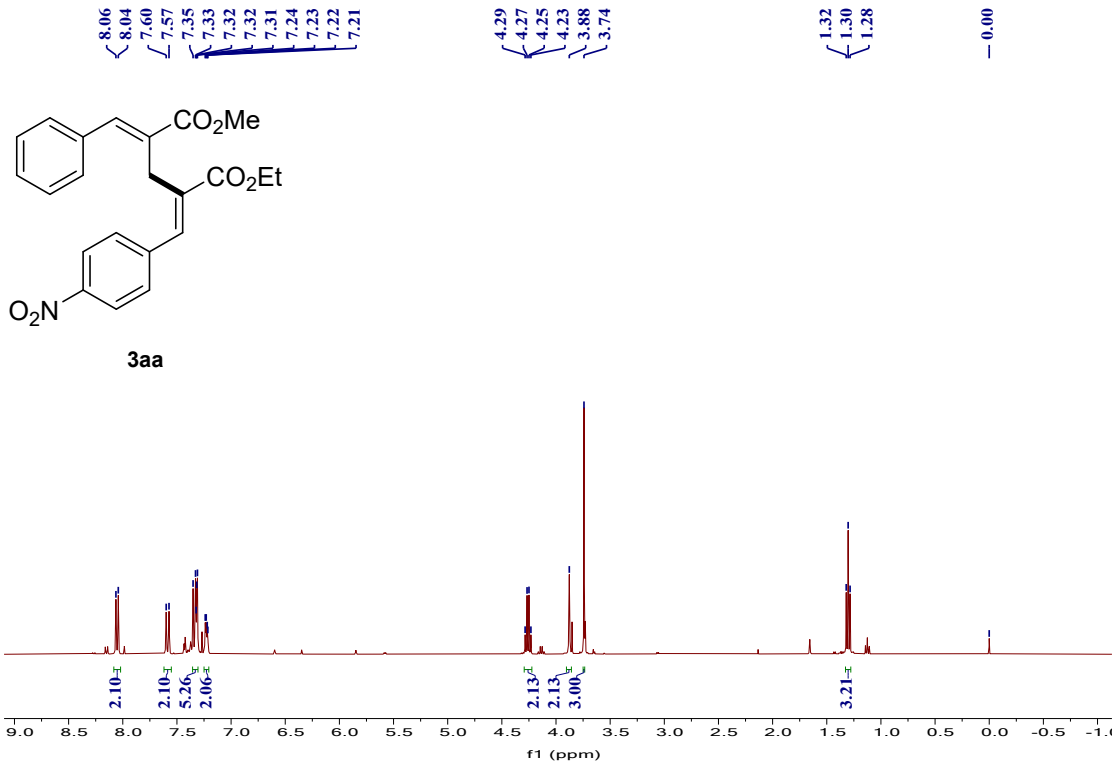


Figure S55 | [1]H NMR (400 MHz, Chloroform-d) spectra for compound **3aa**

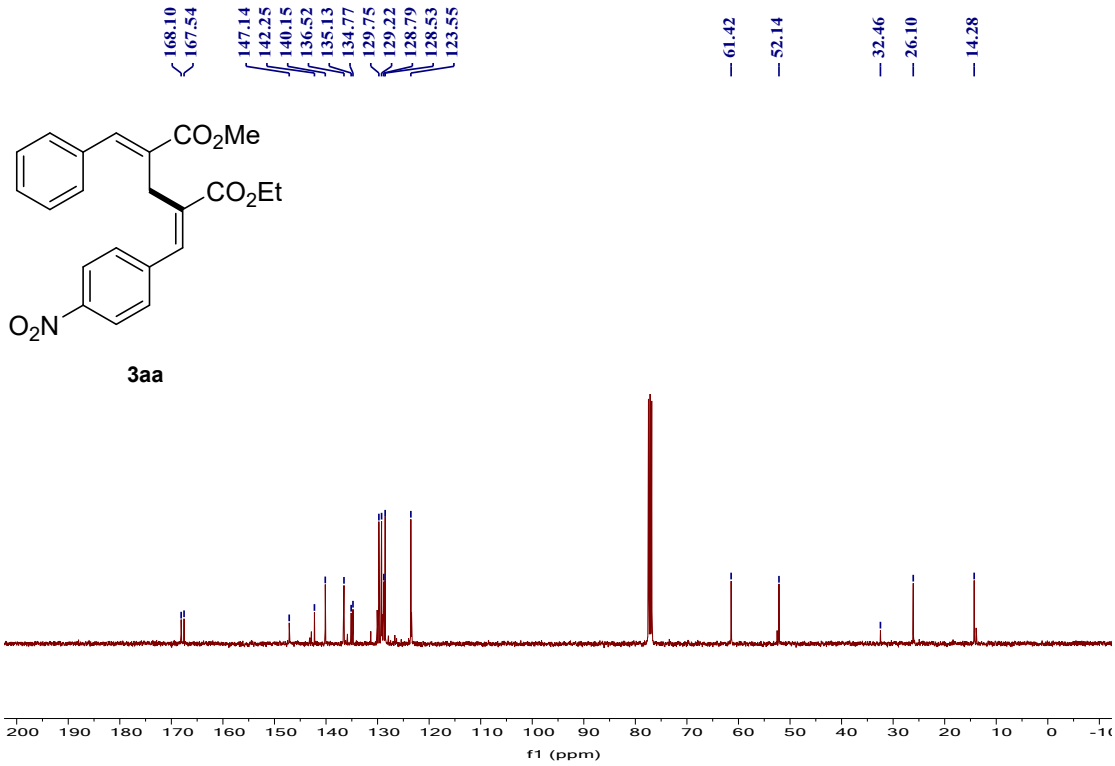


Figure S56 | [13]C NMR (101 MHz, Chloroform-*d*) spectra for compound **3aa**

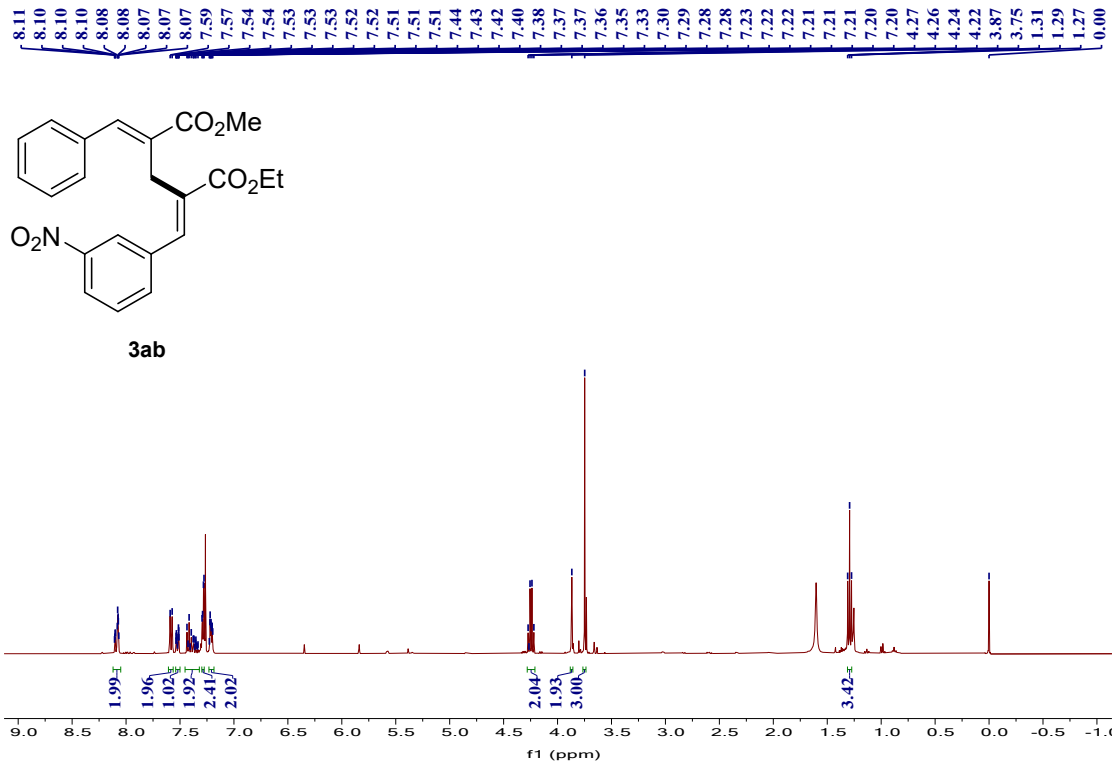


Figure S57 | [1]H NMR (400 MHz, Chloroform-d) spectra for compound **3ab**

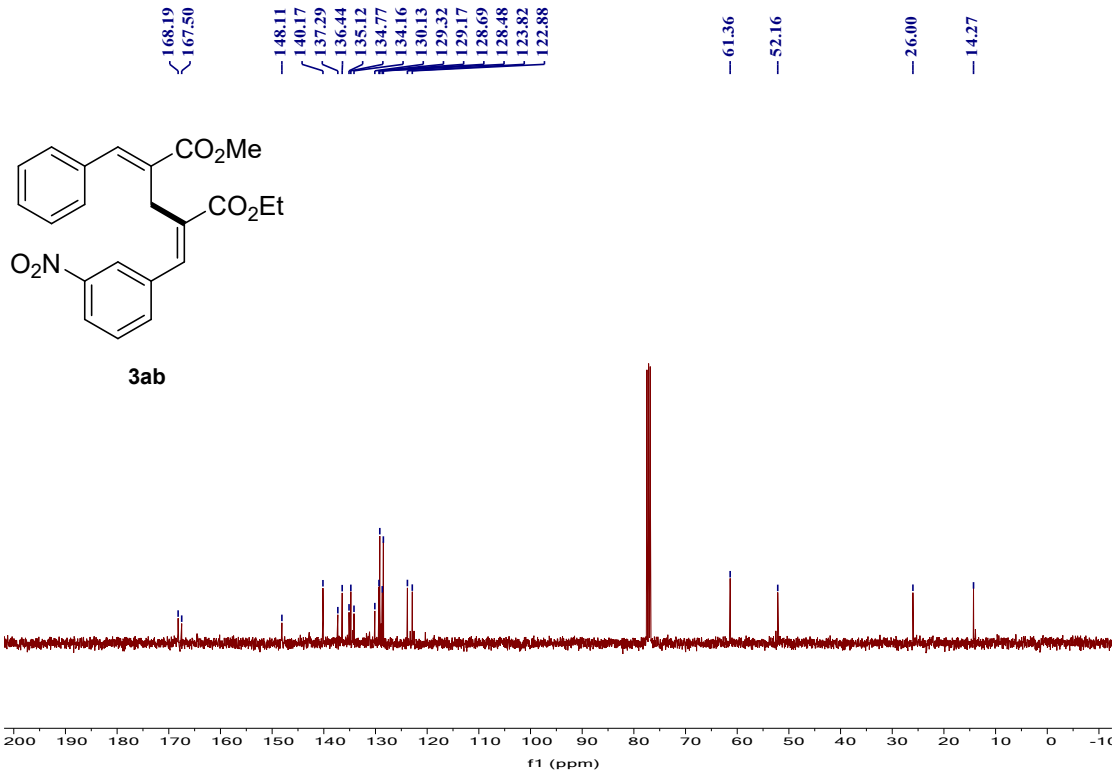


Figure S58 | [13]C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ab**

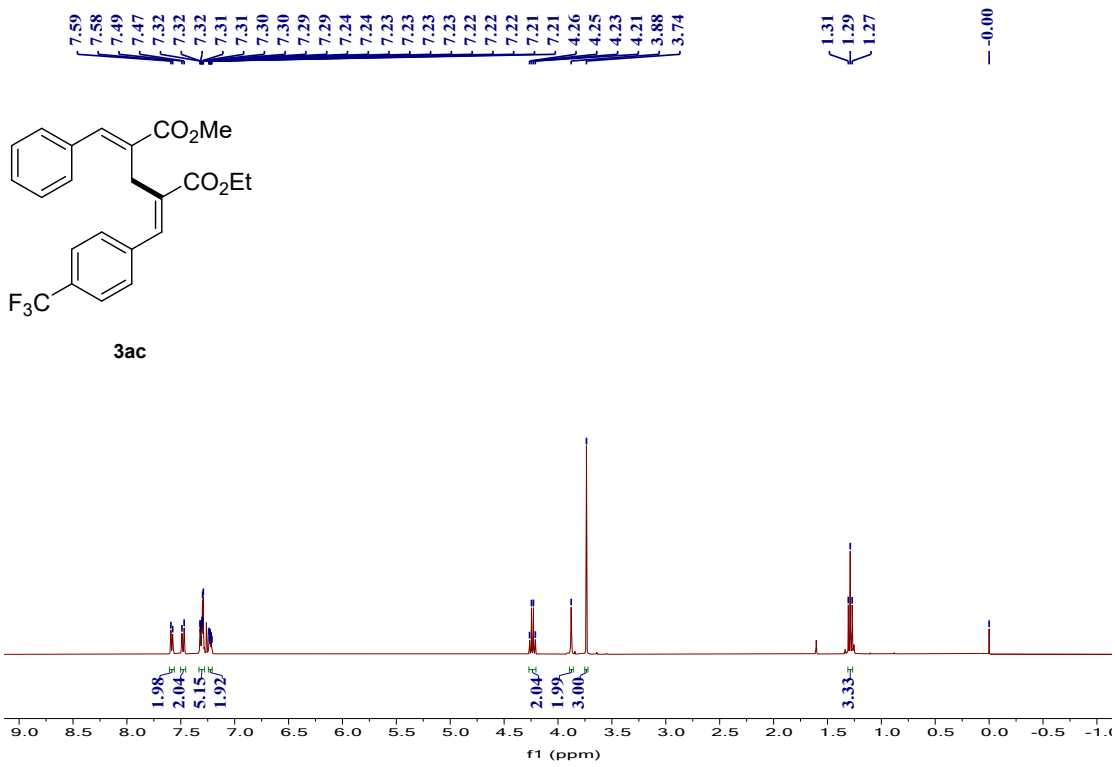


Figure S59 | [1]H NMR (400 MHz, Chloroform-d) spectra for compound **3ac**

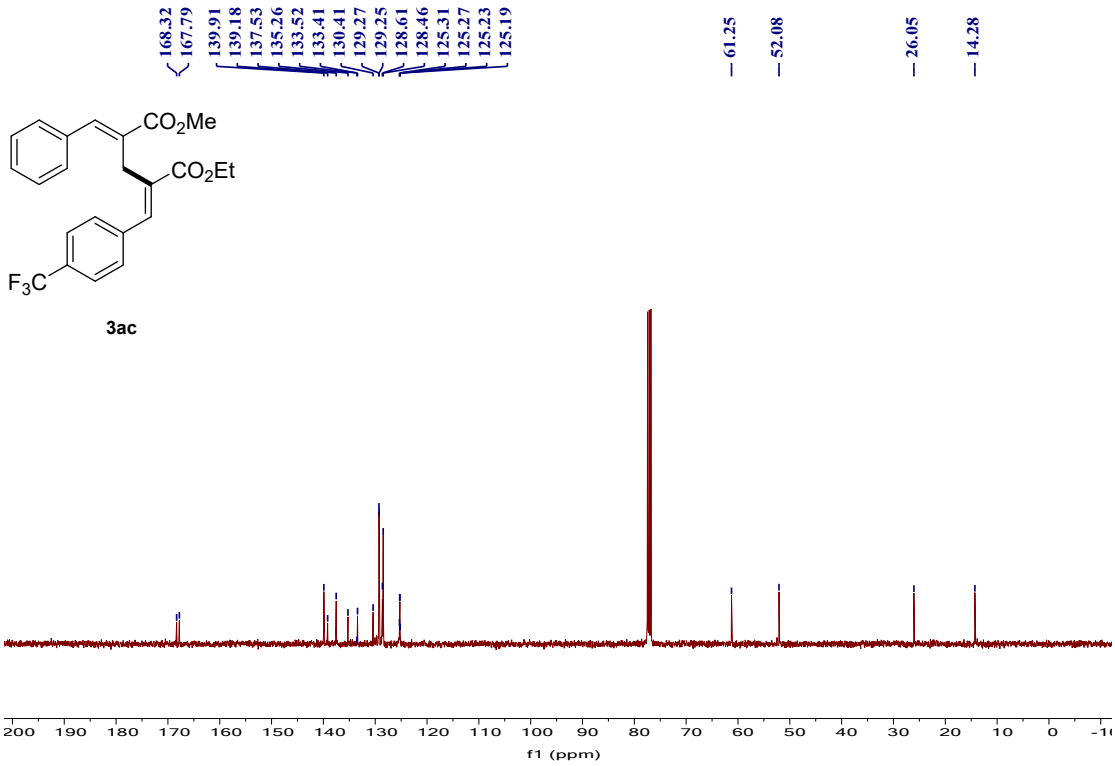


Figure S60 | [13]C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ac**

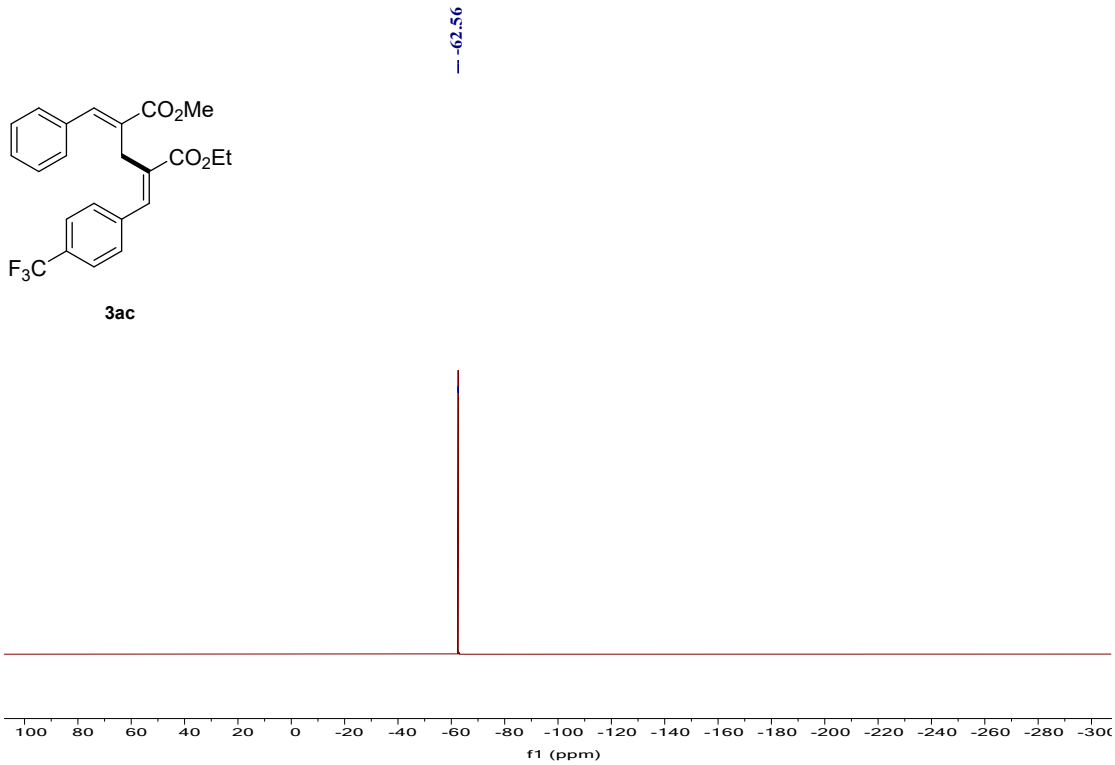


Figure S61 | ^{19}F NMR (376 MHz, Chloroform-*d*) spectra for compound **3ac**

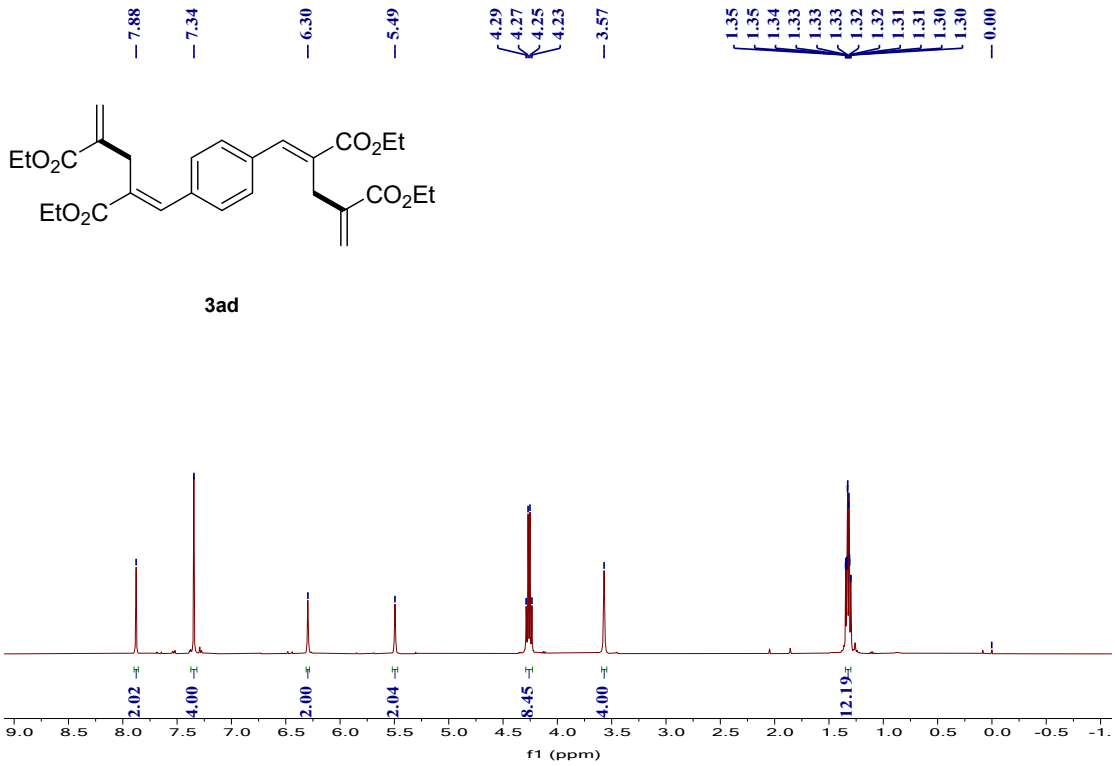


Figure S62 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3ad**

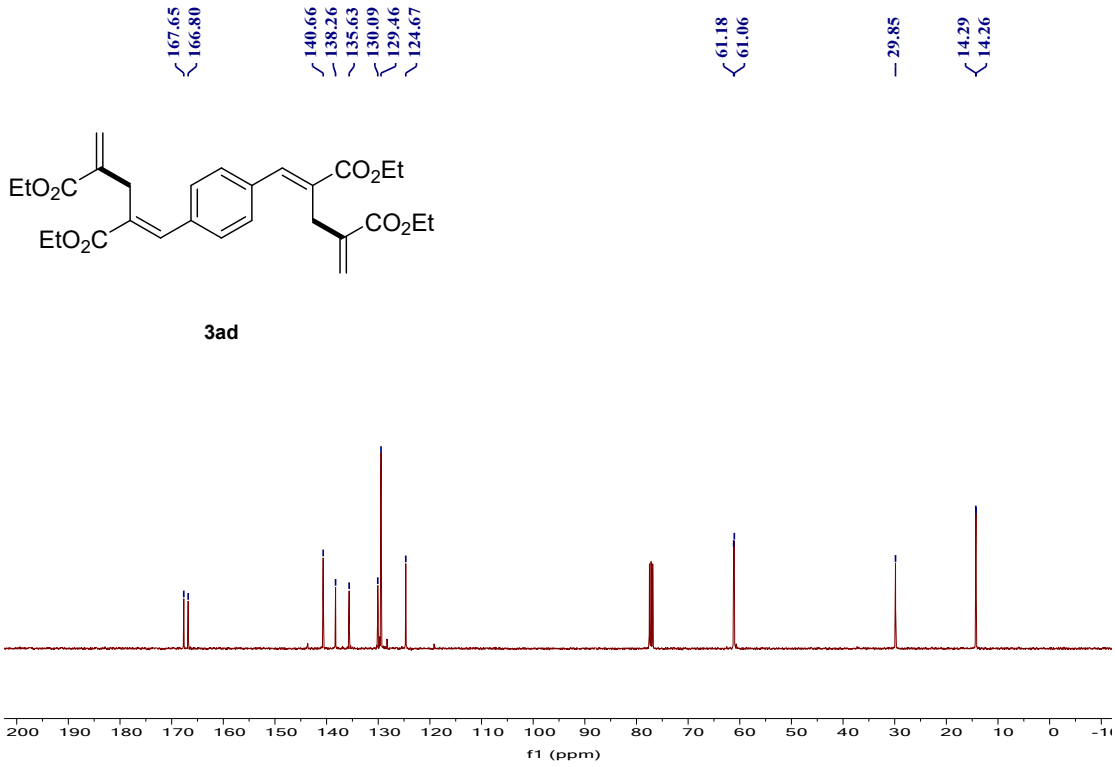


Figure S63 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ad**

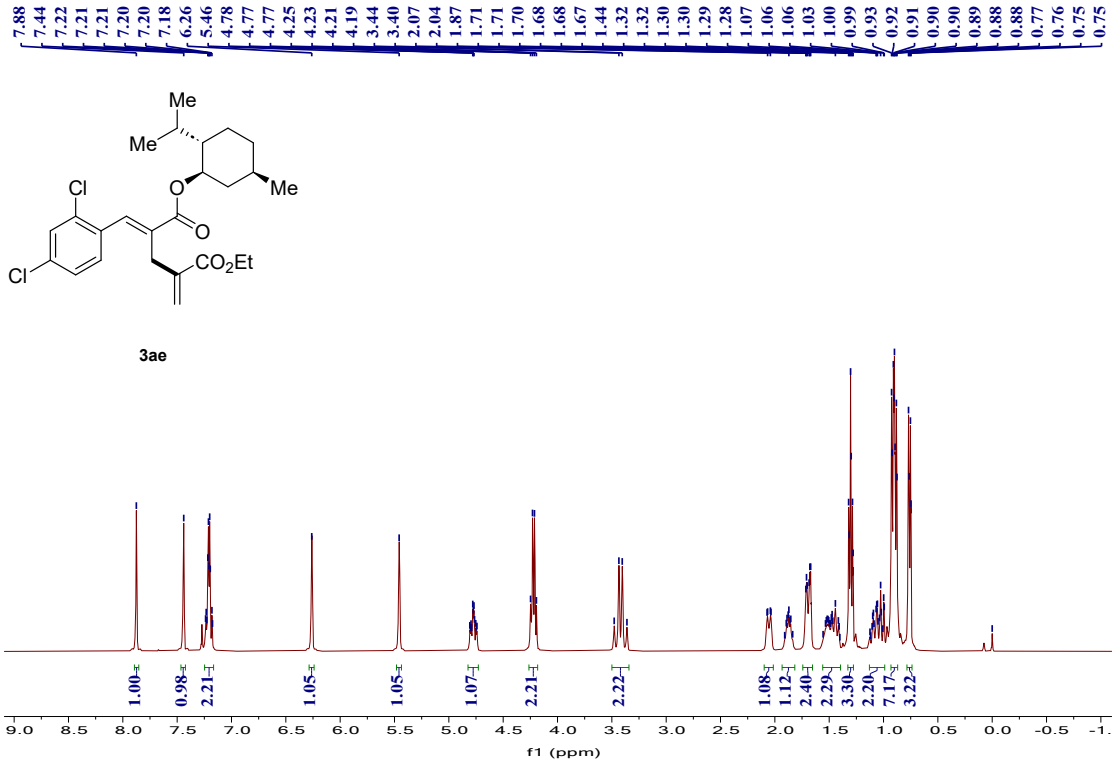


Figure S64 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3ae**

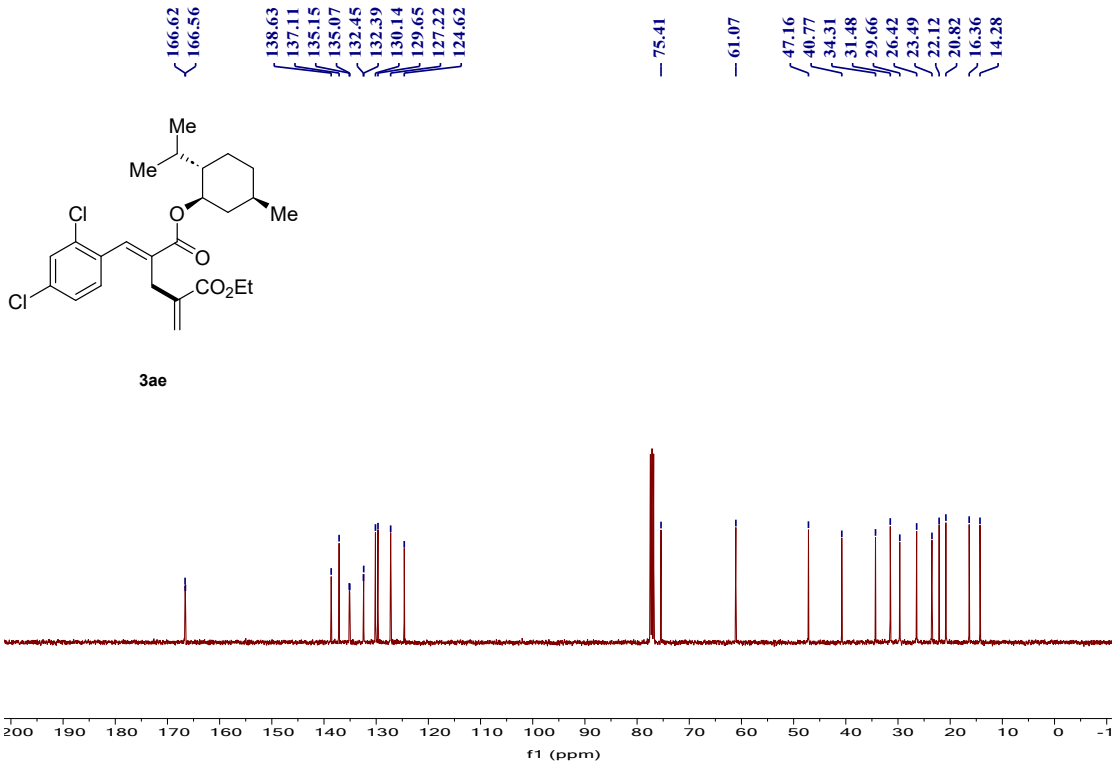


Figure S65 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ae**

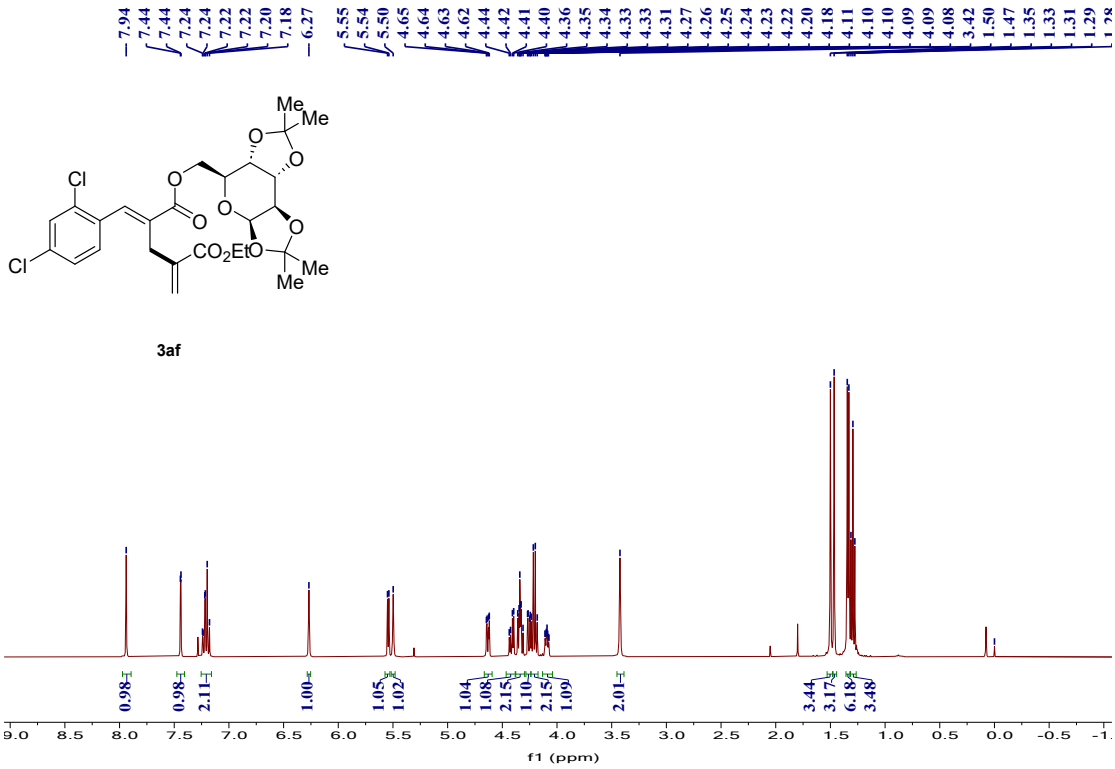


Figure S66 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3af**

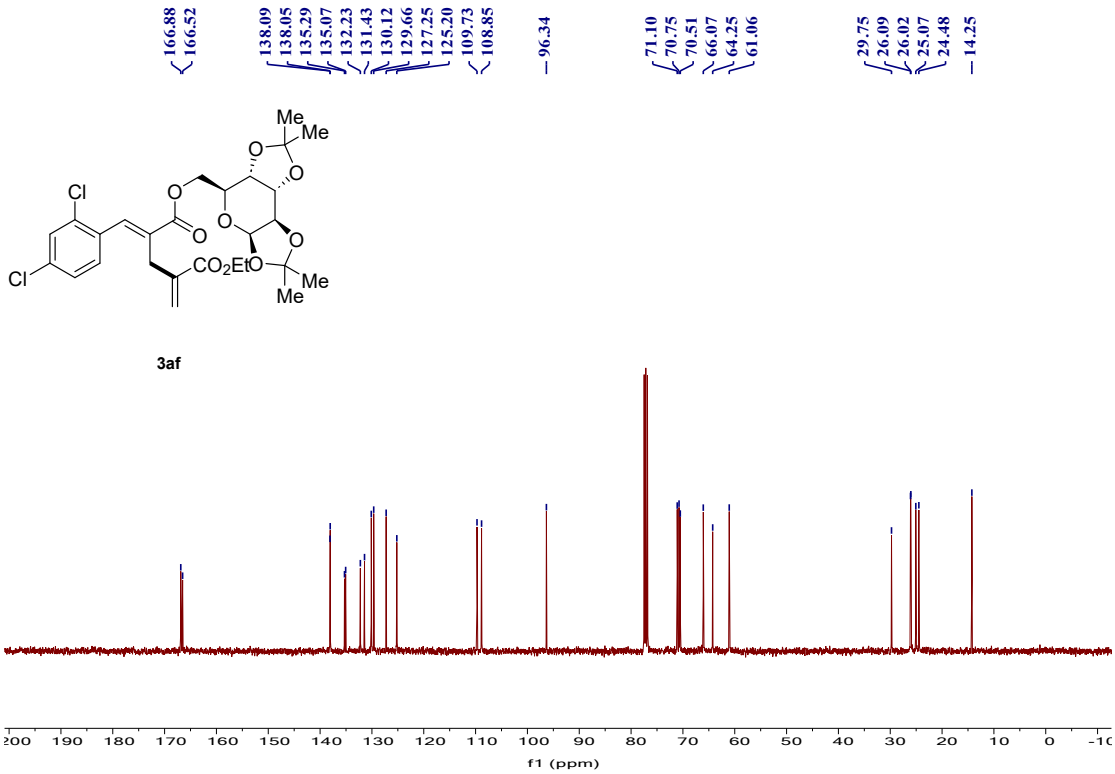


Figure S67 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3af**

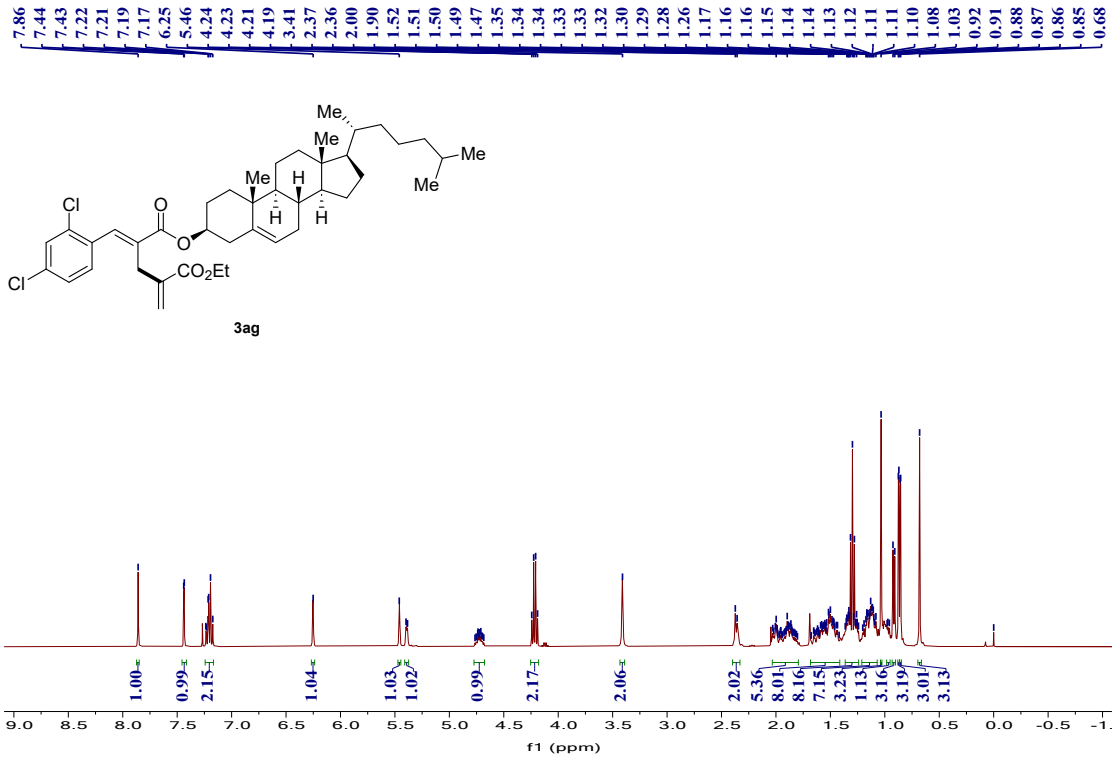


Figure S68 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3ag**

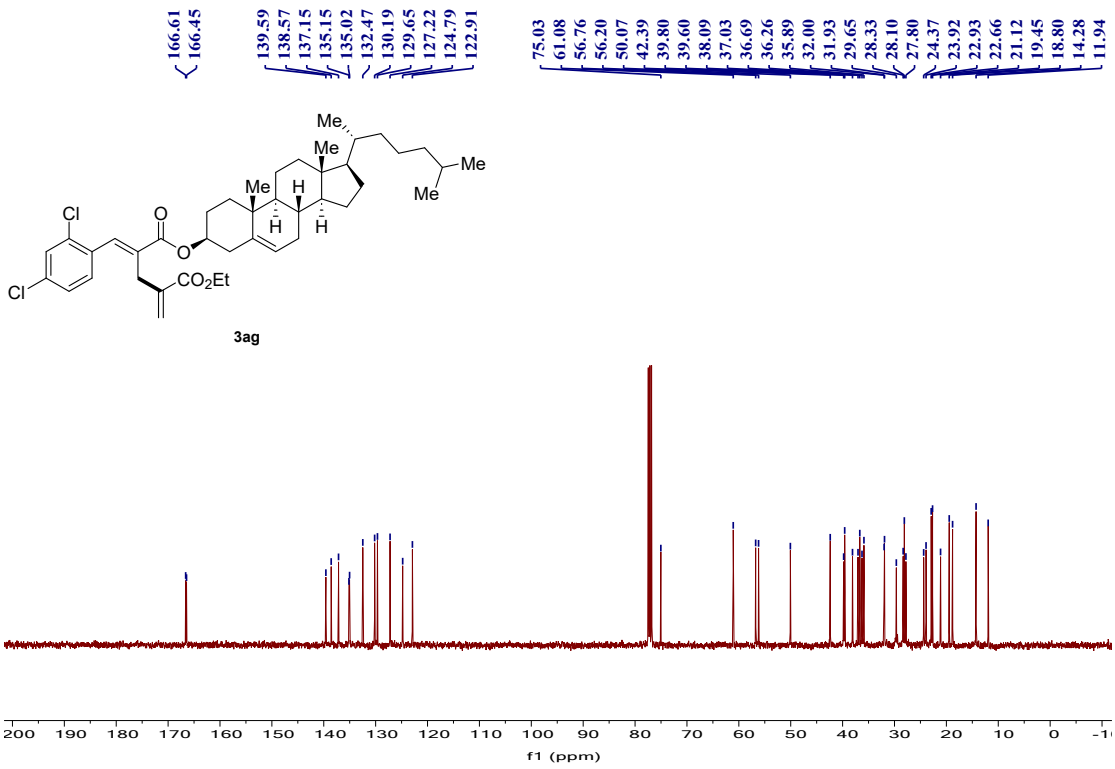


Figure S69 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ag**

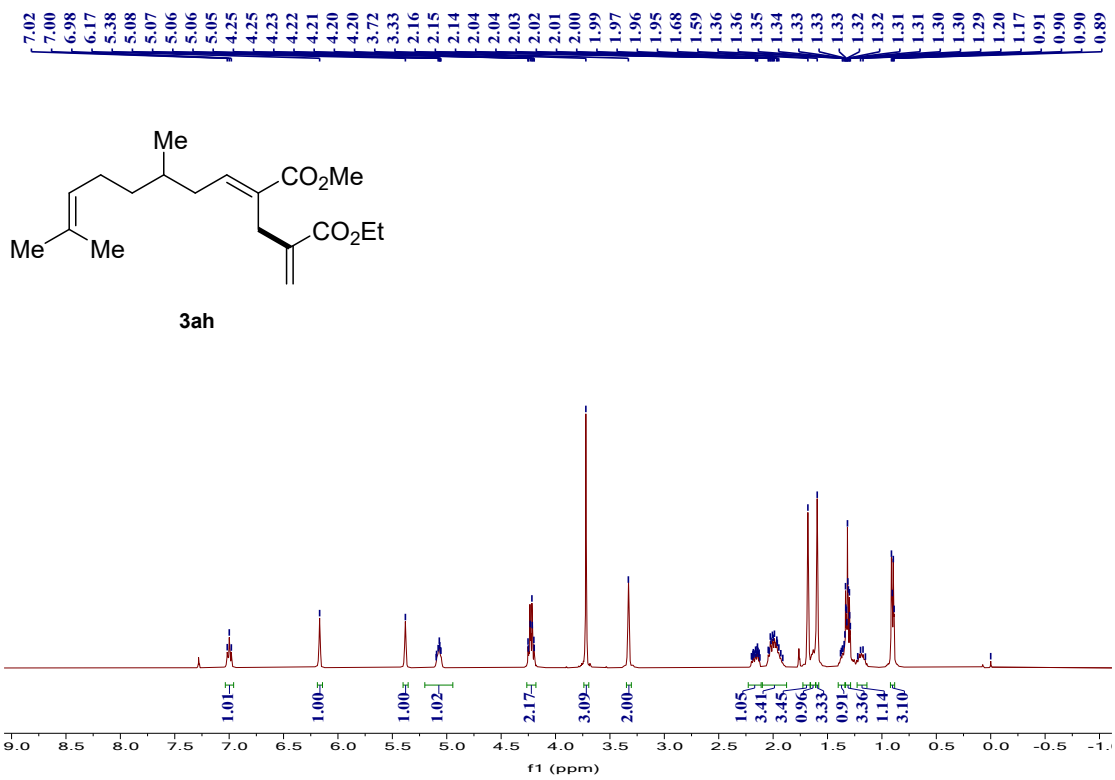


Figure S70 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3ah**

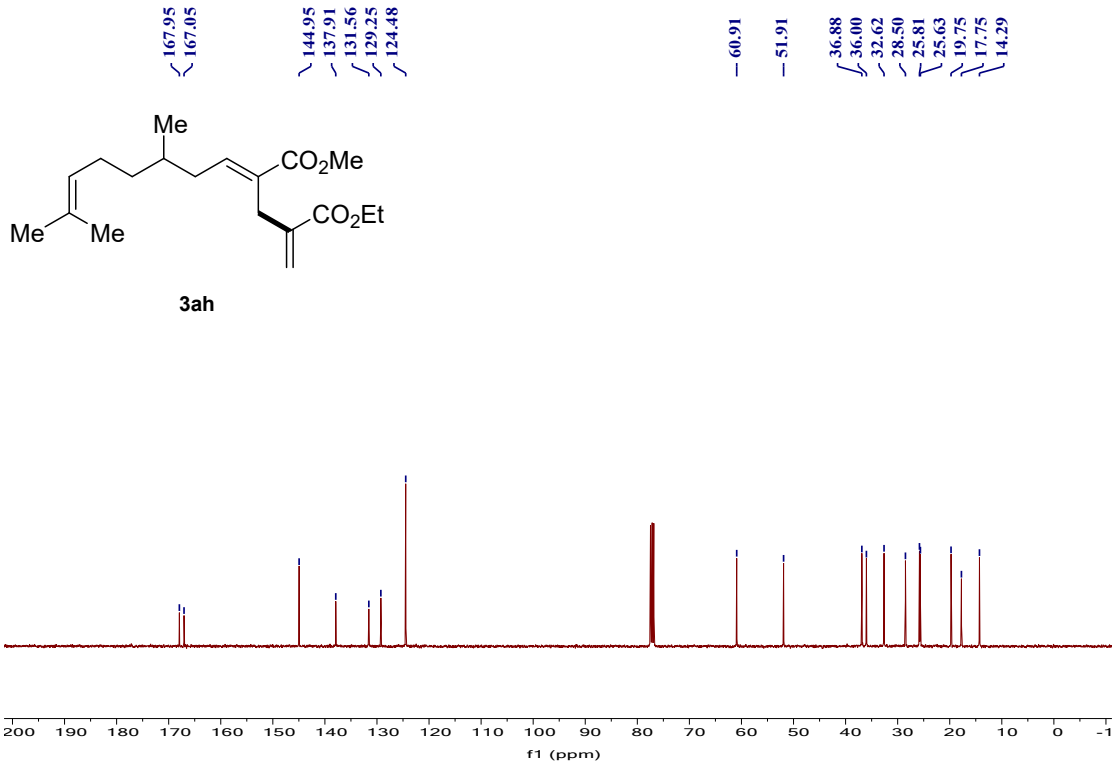


Figure S71 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ah**

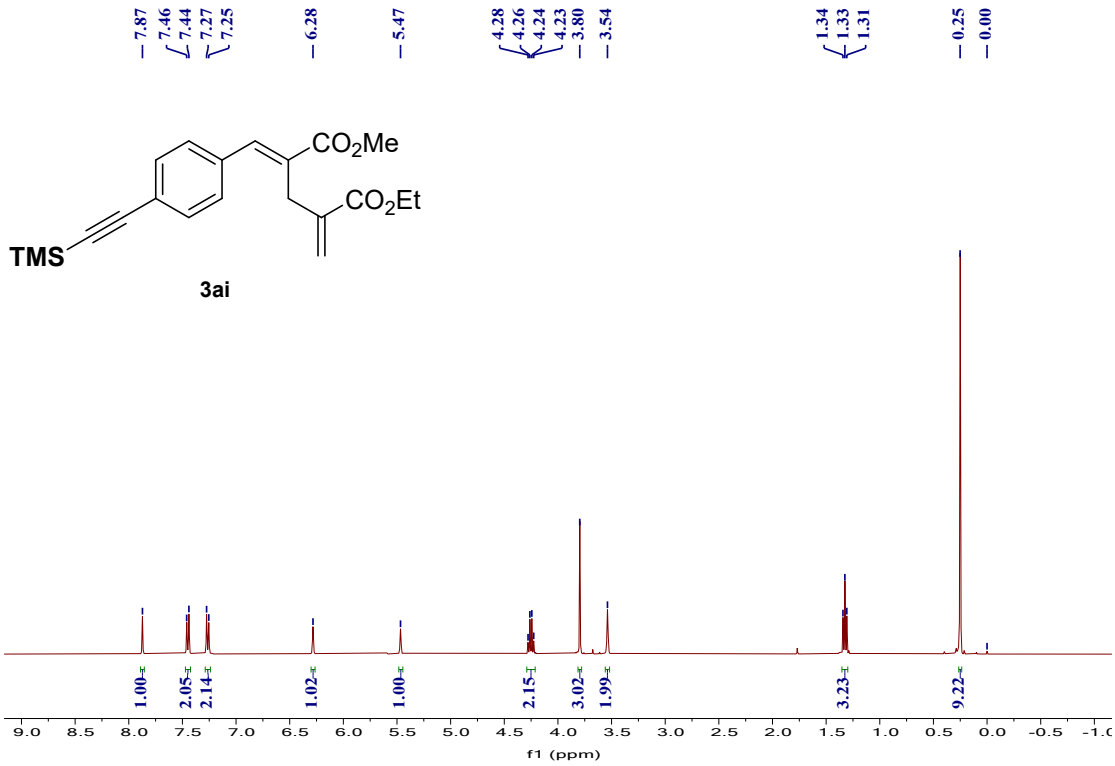


Figure S72 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **3ai**

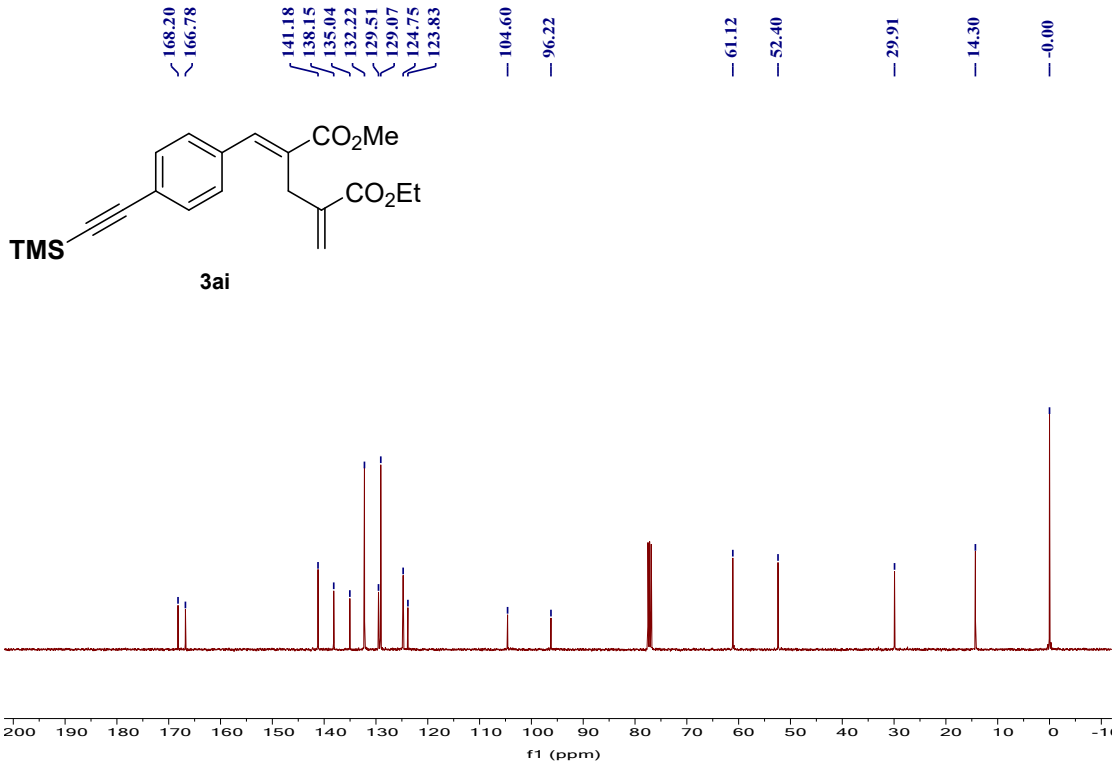


Figure S73 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **3ai**

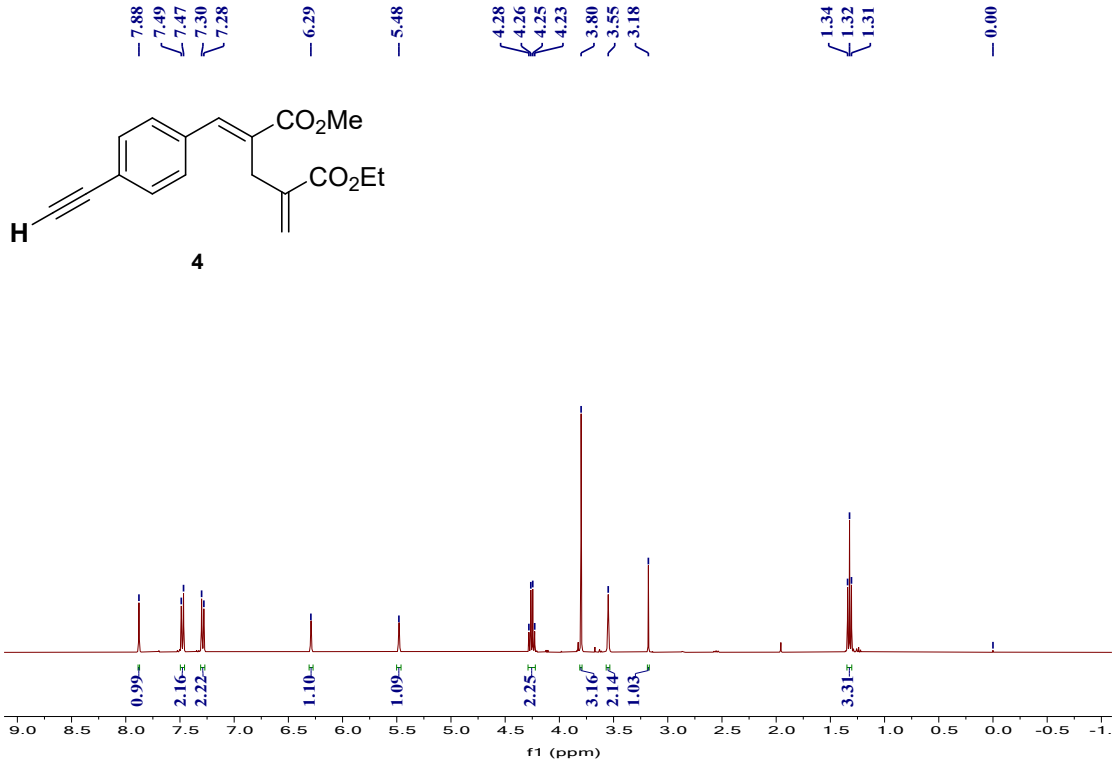


Figure S74 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **4**

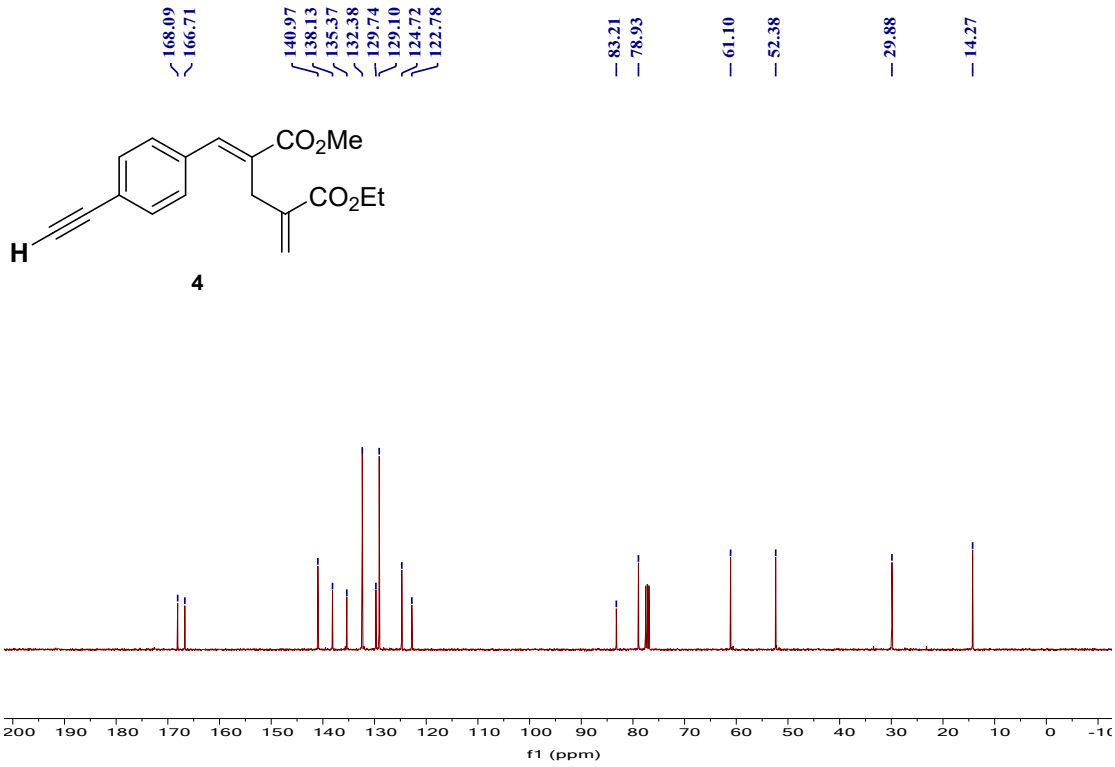


Figure S75 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **4**

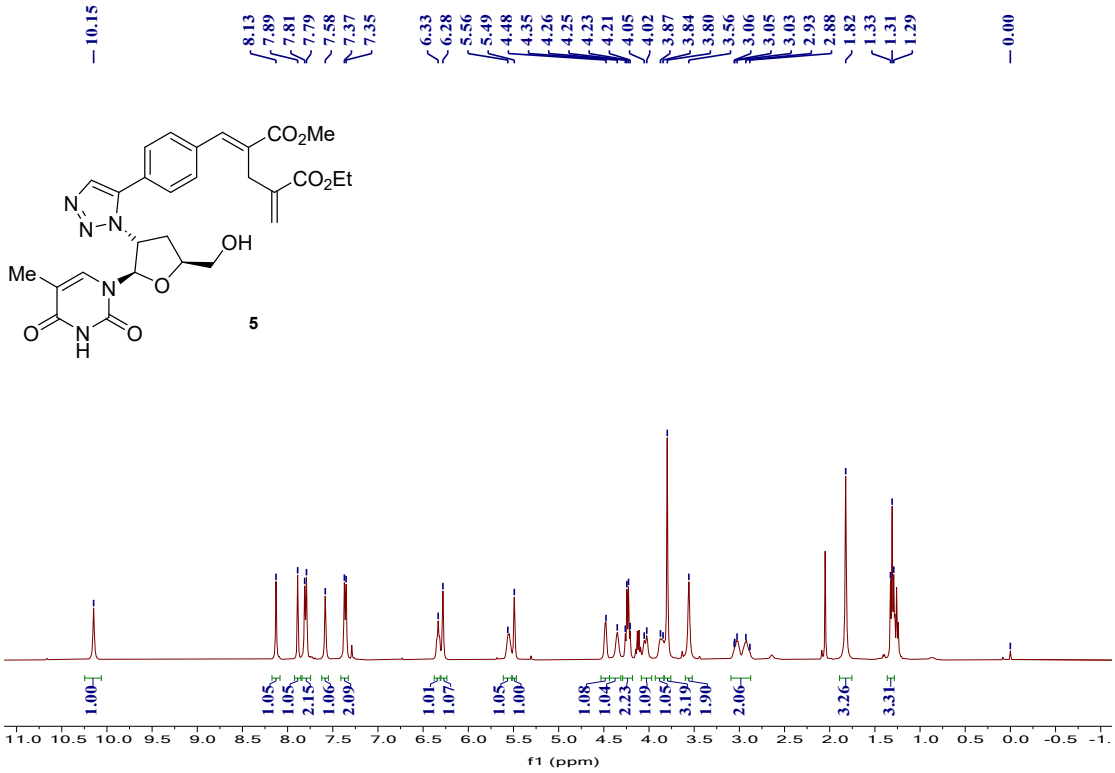


Figure S76 | ^{1}H NMR (400 MHz, Chloroform-d) spectra for compound **5**

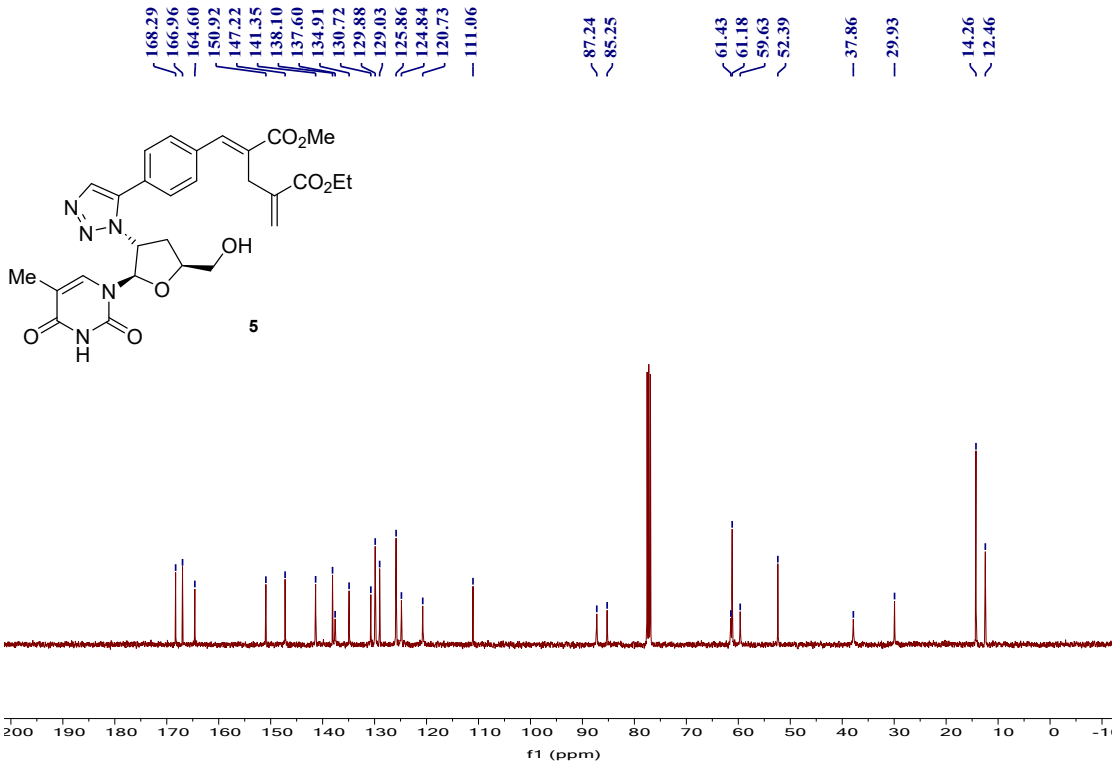


Figure S77 | ^{13}C NMR (101 MHz, Chloroform-*d*) spectra for compound **5**

6. X-ray Data Collection and Structure Determinations

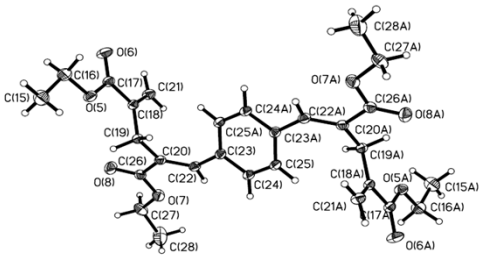
Single crystals of **3ad** were grown by slow diffusion of *n*-hexane into EtOAc solution. X-ray single-crystal diffraction data was collected on a Rigaku XtaLAB P200 diffractometer at 296(2) K with MoK α radiation (λ=0.71073 Å) in the ω scan mode. The program SAINT was used for integration of the diffraction profiles. All of the structures were solved using direct methods using the SHELXS program of the SHELXTL package and refined using full matrix least-squares methods with SHELXL (semi empirical absorption corrections were applied using the SADABS program). Other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on *F*2. The hydrogen atoms were generated theoretically onto the specific atoms and refined isotopically with fixed thermal factors. Detailed crystallographic data were summarized (**Table S4**).

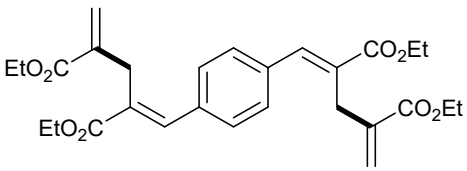
Table S4. Crystal Date and Structure Refinements for **3ad**.

	3ad
Chemical formula	$C_{28}H_{34}O_8$
Formula weight	498.55
Crystal system	monoclinic
Space group	P -1
a (Å)	5.4044(3)
b (Å)	14.2246(7)
c (Å)	17.7580(8)
V (Å^3)	1319.95(12)
α (°)	79.753(2)
β (°)	81.874(2)
γ (°)	81.718(2)
Z	2
F(000)	532.0
GOF	1.075
D/g cm^{-3}	1.254
μ (mm^{-1})	0.753
T/K	193
ΛMoK\a (Å)	1.54718
R^a/R^b	0.0400(4423)/0.1133(4815)

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(Fo^2)^2]^{1/2}$

X-ray Crystal Structures (30% thermal ellipsoid probability levels) **3ad.**





CCDC-**2255280** (**3ad**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk/structures/Search?ccdc=2255280.