Supporting Information

Iron-catalysed Highly Selective Hydroalkoxycarbonylation of Alkynes Using CO as C1 Source

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1. General methods and materials:

All air and moisture sensitive manipulations were carried out using standard vacuum line and Schlenk techniques, or in a M-Braun glove box containing a purified argon atmosphere. Tetrahydrofuran and toluene were distilled from sodium/benzophenone under argon atmosphere. [$Fe_2(CO)_9$] (99%) was purchased from Alfa Aesar, DABCO and phenyl acetylene derivatives were purchased from Sigma-Aldrich. Ligands L1-L4 were purchased from Sigma Aldrich, and Spectrochem. Ligand L5[1], L6[2], L7[3], L8[4] were prepared according to literature procedure. Different alcohols were purchased from Sigma Aldrich and Spectrochem.

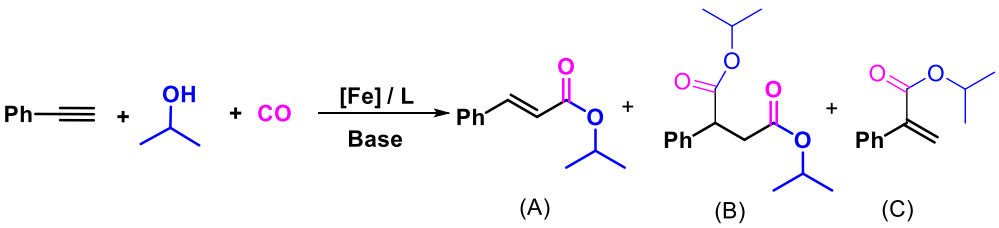
^1H and ^{13}C NMR spectra were recorded on a Bruker Avance/Varian NMR 400 and 500 MHz spectrometers at 298 K unless mentioned otherwise. All spectra were obtained at ambient temperature unless mentioned otherwise. The chemical shifts (δ) were recorded in parts per million (ppm) and the coupling constants (J) in Hertz (Hz). ^1H and ^{13}C NMR multiplicity and coupling constants are reported wherever applicable. ^1H and ^{13}C spectra were referenced to the residual deuterated solvent peak ($CHCl_3$ 7.27 ppm, 77.00 ppm). Mass spectrometry (HRMS) were recorded on a Thermo Scientific Q-Exactive spectrometer. EPR spectra were recorded on Bruker EMX microX A300 ESR spectrometer.

Gas Chromatography (GC) analysis for P1-P40 were performed on an Agilent 7890B GC system using HP-05 column (30 m × 320 μm × 0.25 μm), split ratio 30:1, column pressure 10 psi, injector temperature of 260 °C, detector temperature of 330 °C, argon carrier gas. Temperature program: Initial temperature 70 °C, hold for 1 min.; ramp 1: 4 °C/min. to 120 °C; ramp 2: 10 °C/min. to 250 °C; ramp 3: 20 °C/min. to 320 °C, hold for 2 min. The instrument was set to an injection volume of 1 μL, an inlet split ratio of 10:1, and inlet and detector temperatures of 250 and 320 °C, respectively. UHP-grade argon was used as carrier gas with a flow rate of 30 mL/min. Response factors for all the necessary compounds with respect to standard n-dodecane were calculated from the average of three independent GC runs.

2. General procedure for iron-catalysed, hydroalkoxycarbonylation of alkynes

In a glove box, an oven-dried vial (4 mL) containing a stirring bar was charged with [$Fe_2(CO)_9$] (0.005 mmol, 1.8 mg), L1-L8 (0.01 mmol), DABCO (0.89 mmol, 100 mg), aryl alkyne (0.2 mmol), and alcohol (4 mmol). The vial was then sealed with a PTFE/white rubber septum and was taken out from the glove box. Subsequently, toluene (0.38 mL), and THF (0.3 mL) were added by syringe under argon. The vial was placed in a beaker, which was transferred into a stainless steel autoclave (450 mL) and pierced with a needle. After flushing the autoclave three times with CO, a pressure of 10 bar of CO was adjusted at ambient temperature. Then, the mixture was stirred for 36 hrs at 110 °C. After that, the autoclave was cooled down to room temperature and the pressure was released carefully. The conversion was determined by the GC and product was purified by column chromatography.

Table S1. Hydroalkoxycarbonylation of phenyl acetylene using different iron precursors.[a]



Entry	[M]/L	base	time	Temp./Press.	%Conv.[b] (A/B/C). %
1.	$FeCl_2$ / L7	DABCO	36	110/10	11/0/0
2.	$FeCl_3$ / L7	DABCO	36	110/10	0
3.	$Fe_3(CO)_{12}$ / L7	DABCO	36	110/10	5/0/0
4.	$BDAFe(CO)_3$/L7	DABCO	36	110/10	72/0/0
5.	$HFe(CO)_4SiPh_3$/L7	DABCO	36	110/10	58/0/0
6.	$[HFe(CO)_4]$PPN/L7	DABCO	36	110/10	2/0/0

7.	$Fe_2(CO)_9$/L7	DABCO	36	110/10	97/0/0
8.	$Fe_2(CO)_9$/ L1	DABCO	36	110/10	80/0/0
9.	$Fe_2(CO)_9$/ L2	DABCO	36	110/10	12/0/0
10.	$Fe_2(CO)_9$/ L3	DABCO	36	110/10	79/0/0
11.	$Fe_2(CO)_9$/L4	DABCO	36	110/10	82/0/0
12.	$Fe_2(CO)_9$/ L5	DABCO	36	110/10	92/0/0
13.	$Fe_2(CO)_9$/ L6	DABCO	36	110/10	90/0/0
14.	$Fe_2(CO)_9$/ L8	DABCO	36	110/10	70/0/0
15.	$Fe_2(CO)_9$/L7	Cs_2CO_3	36	110/10	0
16.	$Fe_2(CO)_9$/L7	K_2CO_3	36	110/10	7/0/0
17.	$Fe_2(CO)_9$/L7	$NaOSiMe_3$	36	110/10	25/0/0
18.	$Fe_2(CO)_9$/L7	NaO^tBu	36	110/10	72/0/0
19.	$Fe_2(CO)_9$/L7	DBU	36	110/10	24/0/0
20.	$Fe_2(CO)_9$/L7	Et_3N	36	110/10	59/0/0
21.	----/L7	DABCO	36	110/10	0
22.	$Fe_2(CO)_9$/--	DABCO	36	110/10	76/0/0
23.	$Fe_2(CO)_9$/L7	DABCO	16	110/10	36/0/0
24.	$Fe_2(CO)_9$/L7	DABCO	24	110/10	78/0/0
25. [c]	$Fe_2(CO)_9$/L7	DABCO	36	110/10	62/0/0

26.	$Fe_2(CO)_9$/L7	DABCO	36	110/5	80/0/0
27.	$Fe_2(CO)_9$/L7	DABCO	36	110/20	92/0/0
28.	$Fe_2(CO)_9$/L7	DABCO	36	80/10	45/0/0
29.	$Fe_2(CO)_9$/L7	DABCO	36	120/10	97/0/0
30.	$Fe_2(CO)_9$/--	DABCO	48	110/10	84/0/0
31.	$Fe_2(CO)_9$/--	DABCO	36	120/10	86/0/0

Conditions: a) [Fe] = 0.0018 g (0.005 mmol) (5 mol%), L = 0.01 mmol, DABCO = 4.5 equiv, Phenyl acetylene = 0.02 mL (0.2 mmol), Solvent = Tol.:THF, IPA = 0.3 ml (3.9 mmol); b) conversion determined by GC; c) 2.2 equiv DABCO. IPA: Isopropyl alcohol; Tol: Toluene; THF: Tetrahydrofuran.

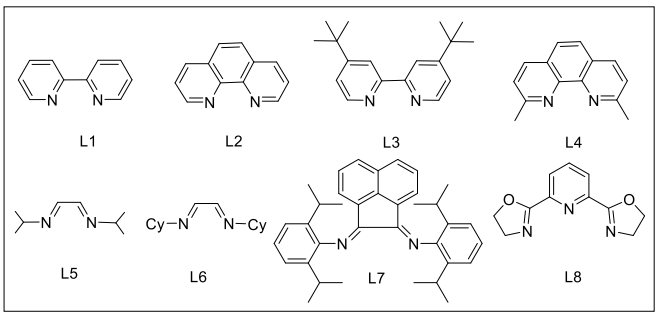


Figure S1: Various ligands for hydroalkoxycarbonylation of alkyne

3. Substrate Scope

3a. Alkyne Scope:

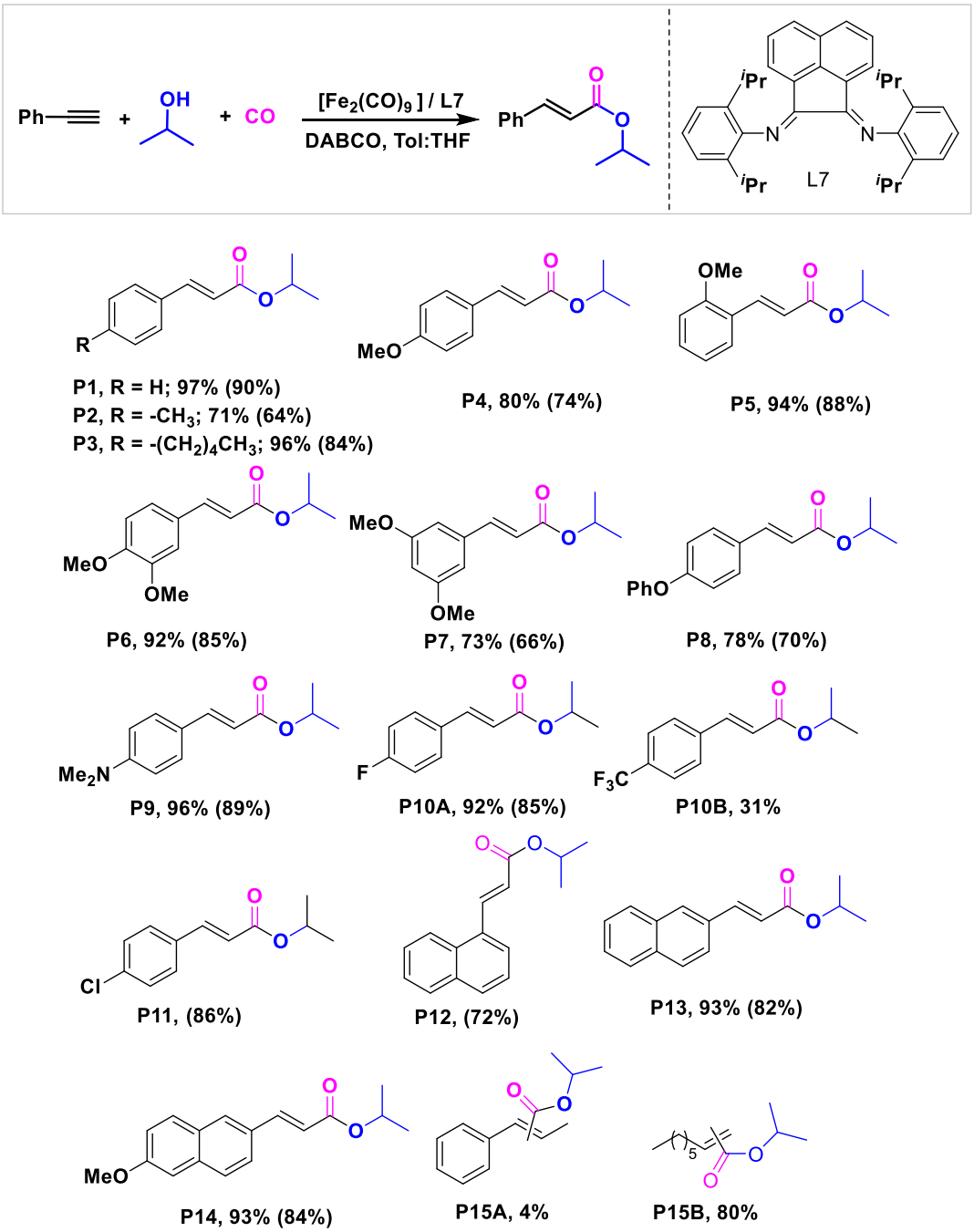
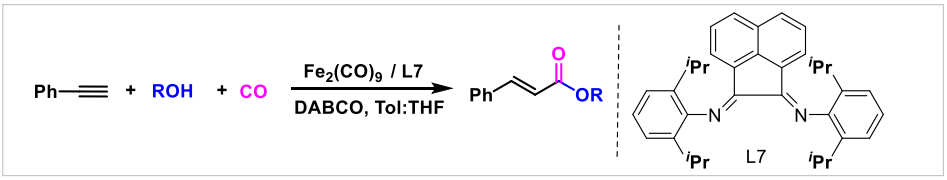


Figure S2A: A set of hydroalkoxycarbonylated products from various alkyne demonstrating the scope of the reaction. **Conditions:** a) $[Fe_2(CO)_9]$ = 0.0018 g (0.005 mmol) (5 mol%), L = 0.005 g (0.01 mmol), DABCO = 4.5 equivalent, Phenyl acetylene = 0.02 mL (0.2 mmol), Solvent = Tol.:THF, IPA = 0.3 ml (3.9 mmol); b) Conversion is determined by GC and isolated yield given in parenthesis.

3b. Alcohol scope:



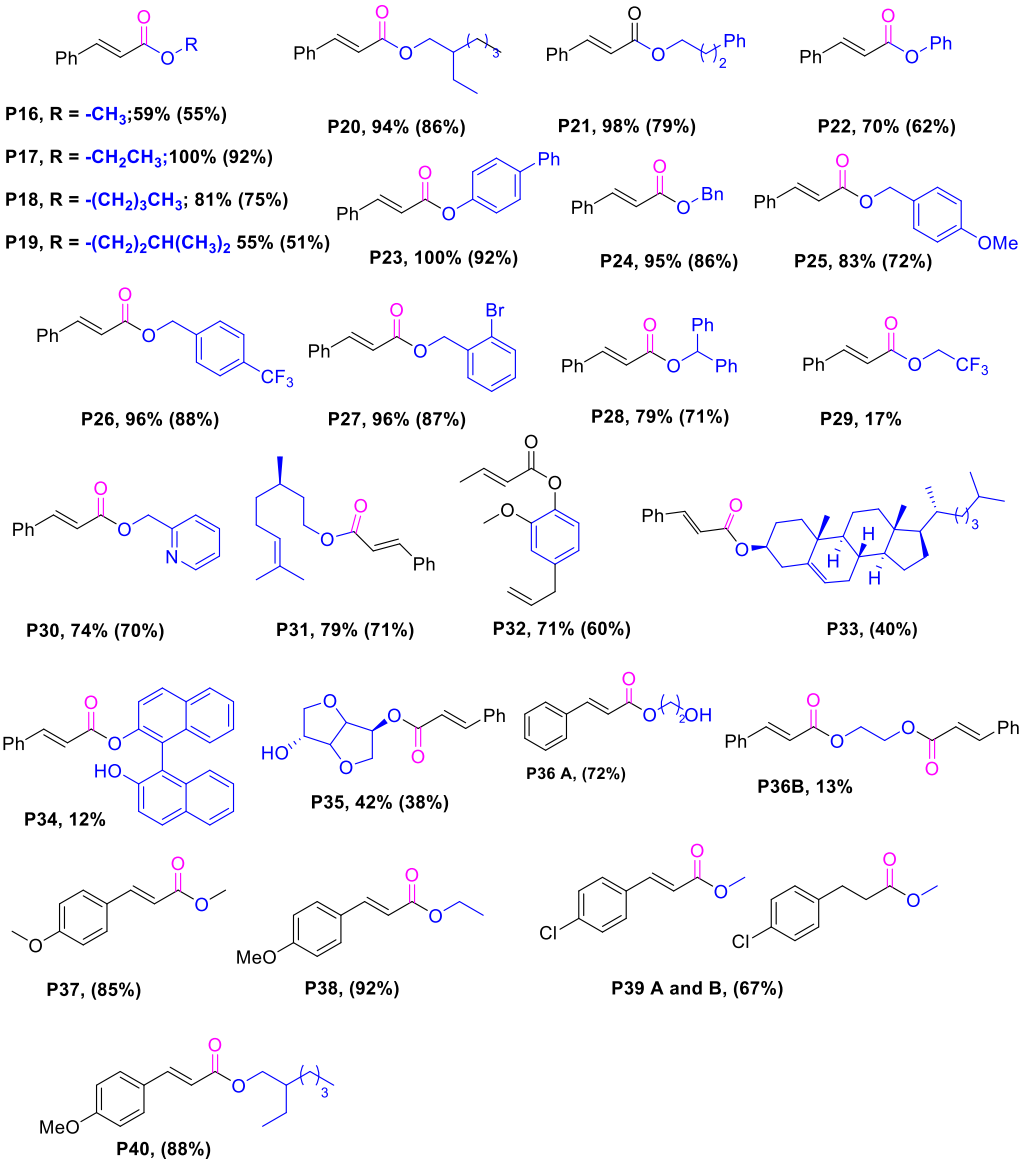
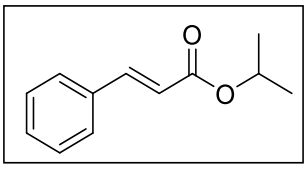


Figure S2B: A set of hydroalkoxycarbonylated products with various alcohol demonstrating the scope of the reaction. **Conditions:** a) [$Fe_2(CO)_9$] = 0.0018 g (0.005 mmol) (5 mol%), L7 = 0.005 g (0.01 mmol), DABCO = 4.5 equiv, Phenyl acetylene = 0.02 mL (0.2 mmol); b) conversion determined by GC and isolated yield given in parenthesis.

4. Characterization of P1-P40 by NMR spectroscopy:

Isopropyl cinnamate P1:



Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 90% yield (34.2 mg). GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P1 = 15.5 min.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 16.01 Hz, 1H), 7.46-7.43 (m, 2H), 7.30-7.29 (m, 3H), 6.37 (d, *J* = 16.01 Hz, 1H), 5.14-5.05 (m, 1H), 1.26 (d, *J* = 6.32 Hz, 6H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 166.4, 144.3, 134.5, 130.1, 128.8, 120.0, 118.8, 67.7, 21.9. The above data is in accordance with previous reports for compound P1.[5]

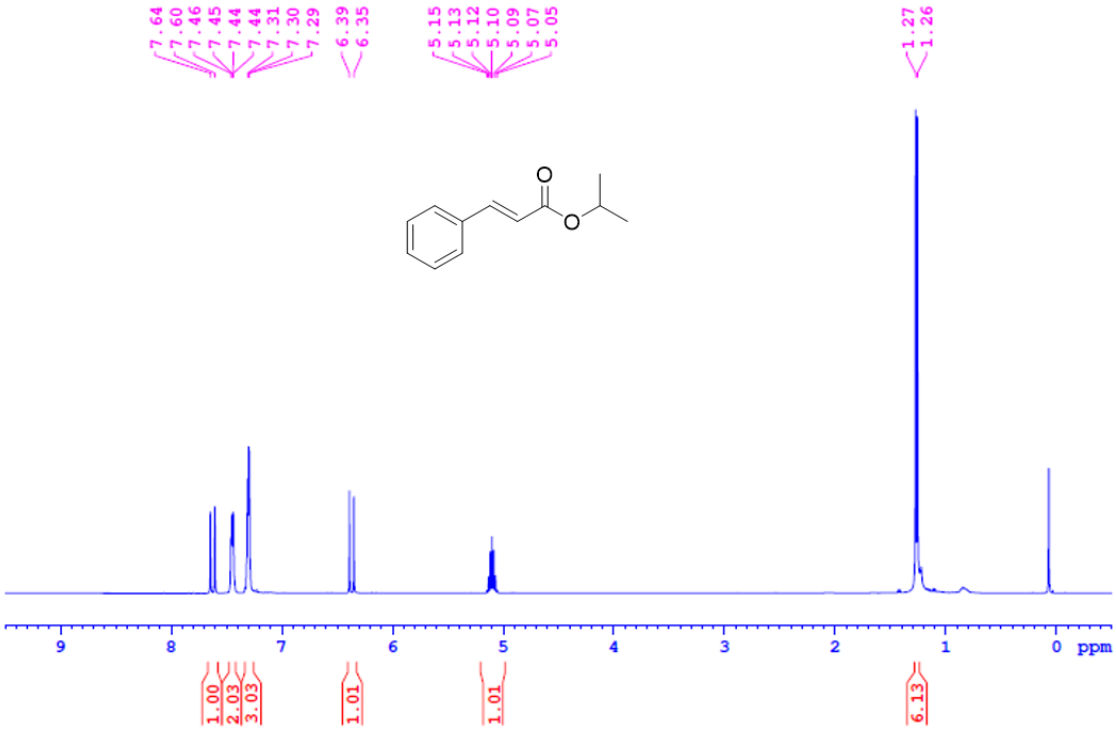


Figure S3: ^{1}H NMR spectrum of P1 in $CDCl_3$.

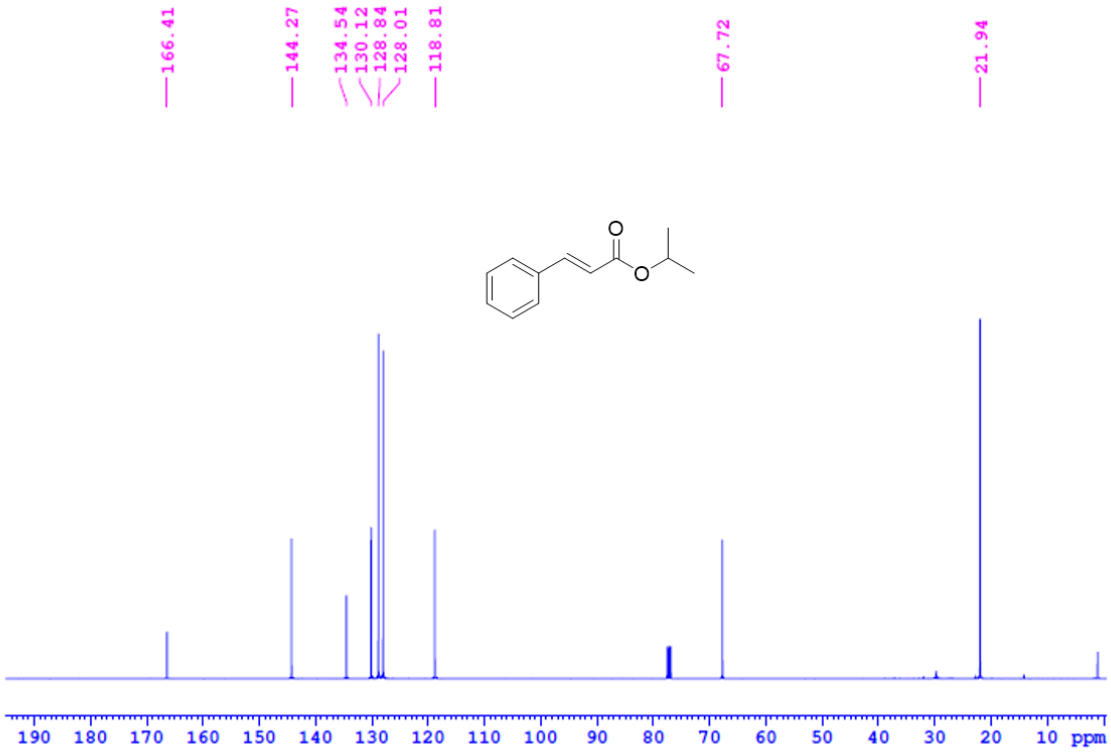
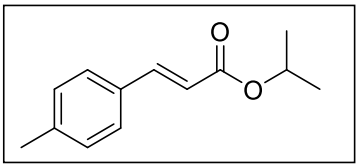


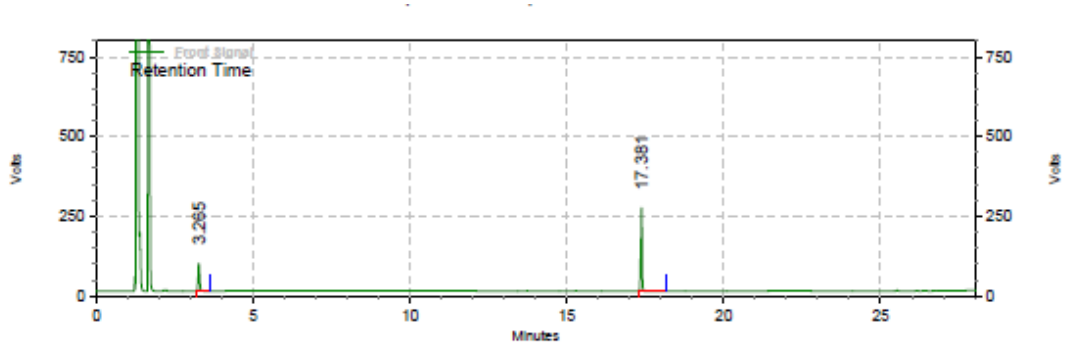
Figure S4: ^{13}C NMR spectrum of P1 in $CDCl_3$.

Isopropyl (E)-3-(p-tolyl)acrylate P2:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 64% yield (26.15 mg). GC retention time for Ethynyl toluene = 3.26 min.; hydroalkoxycarbonylated product P2 =17.38 min.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 15.99 Hz, 1H), 7.40 (d, *J* = 8.15 Hz, 2H), 7.16 (d, *J* = 7.98 Hz, 2H), 6.35 (d, *J* = 15.98 Hz, 1H), 5.12 (sep., *J* = 6.25 Hz, 1H), 2.35 (s, 3H), 1.29 (d, *J* = 6.27 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 166.8 (C_q), 144.4, 140.6, 131.9, 129.7, 128.1, 117.9, 67.8, 22.1, 21.6 (CH_3). The above data is in accordance with previous reports for compound P2.[6]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
3.265	2387941	28.64	675206	25.16
17.381	5949638	71.36	2008518	74.84
Totals	8337579	100.00	2683724	100.00

Figure S5: GC trace of P2.

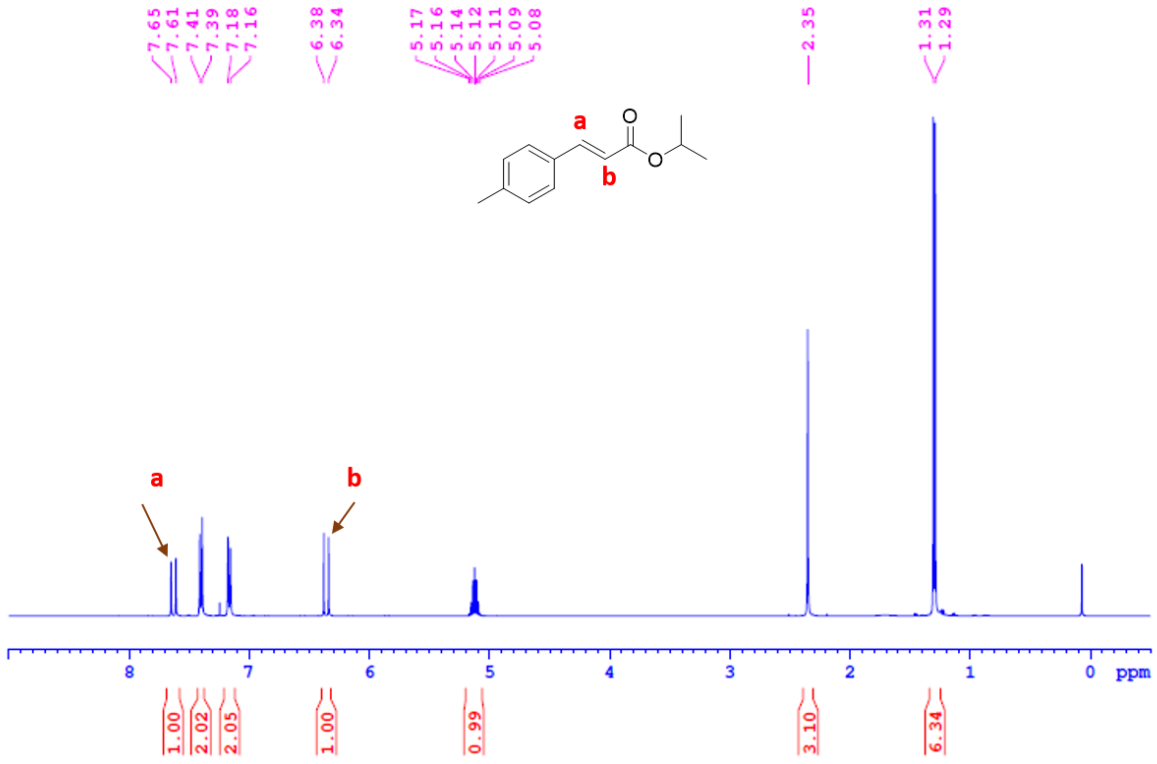


Figure S6: ^{1}H NMR spectrum of P2 in $CDCl_3$.

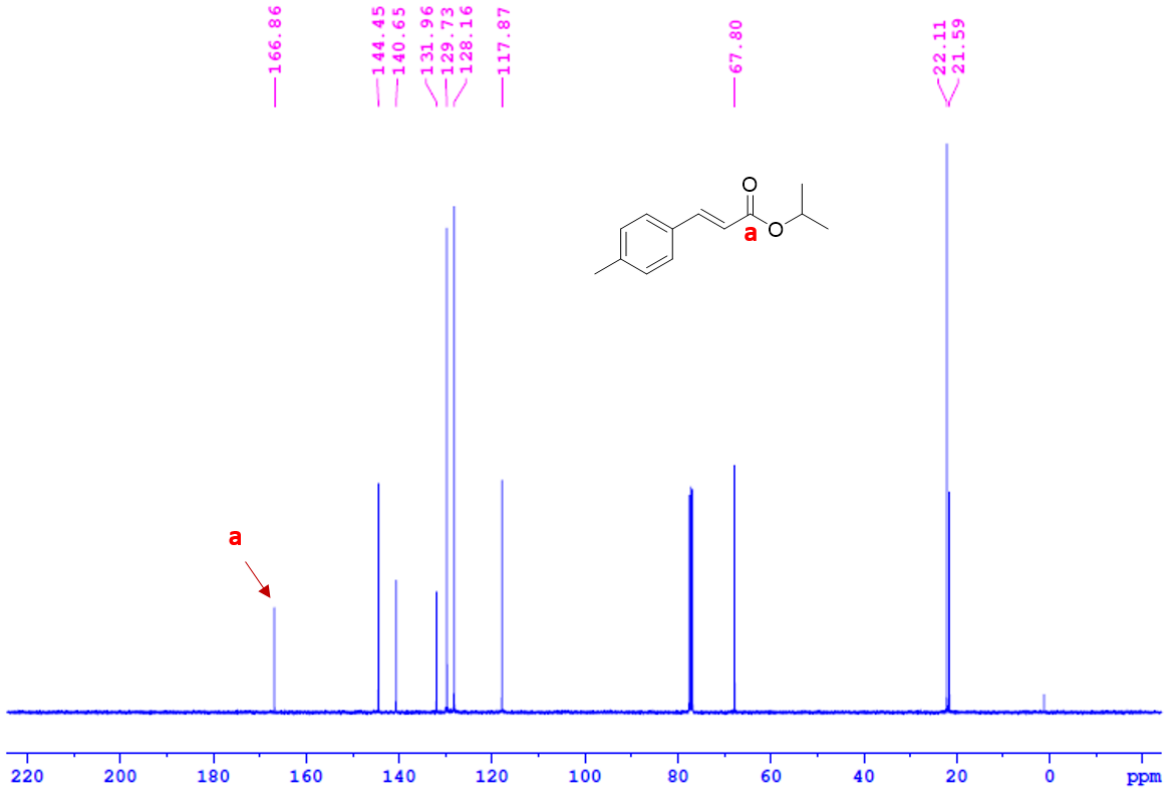
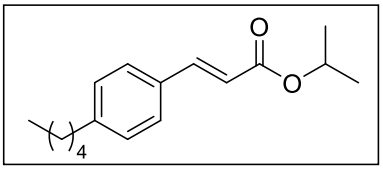


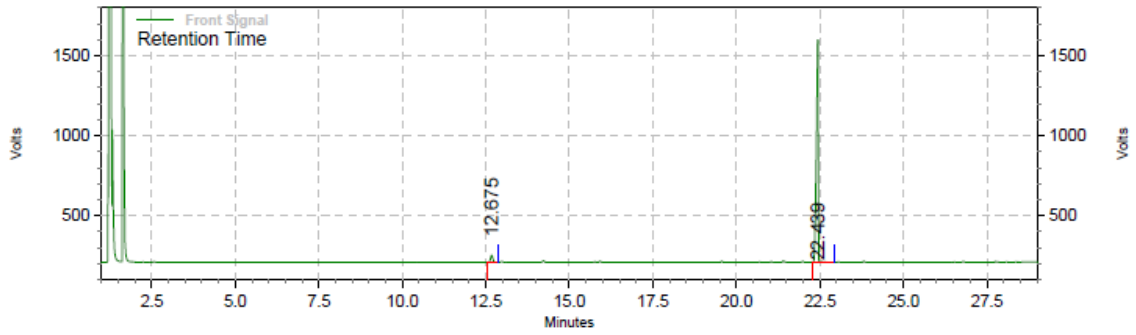
Figure S7: ^{13}C NMR spectrum of P2 in $CDCl_3$.

Isopropyl (E)-3-(4-pentylphenyl)acrylate P3:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 84% yield (43.7 mg). GC retention time for 4-pentyl phenyl acetylene = 12.67 min.; hydroalkoxycarbonylated product P3 = 22.43 minutes.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 15.99 Hz, 1H), 7.43 (d, *J* = 8.12 Hz, 2H), 7.18 (d, *J* = 8.09 Hz, 2H), 6.37 (d, *J* = 15.98 Hz, 1H), 5.14 (sep, *J* = 12.51 Hz, 1H), 2.61 (t, *J* = 15.48 Hz, 2H), 1.65-1.58 (m, 2H), 1.33-1.30 (m, 10H), 0.89 (t, *J* = 6.90 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 166.9 (C_q), 145.7, 144.5, 132.2, 129.1, 128.2, 117.8, 67.8, 35.9, 31.6, 31.1, 22.7, 22.1, 14.1 (CH_3).



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
12.675	1636526	3.94	346619	3.15
22.439	39923149	96.06	10669549	96.85
Totals	41559675	100.00	11016168	100.00

Figure S8: GC trace of P3.

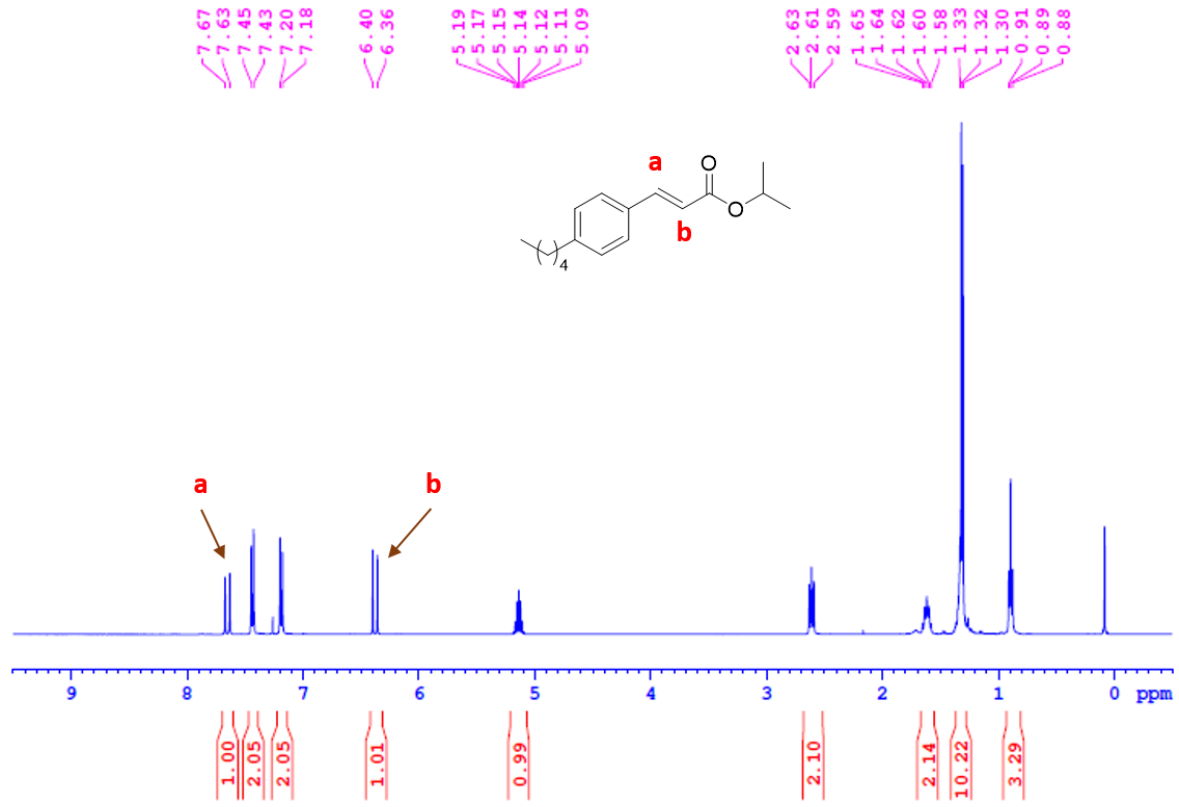


Figure S9: ^{1}H NMR of P3 in $CDCl_3$.

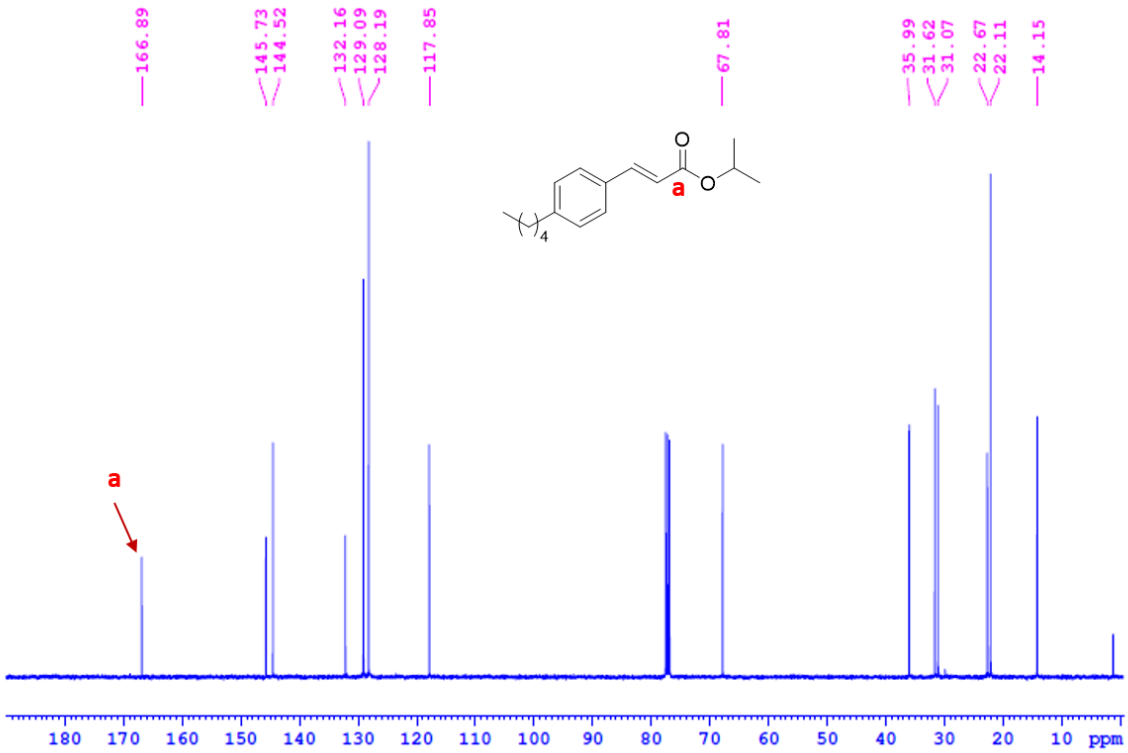
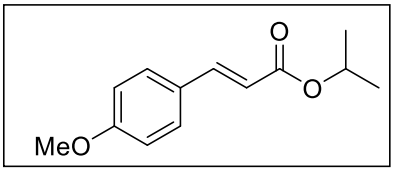


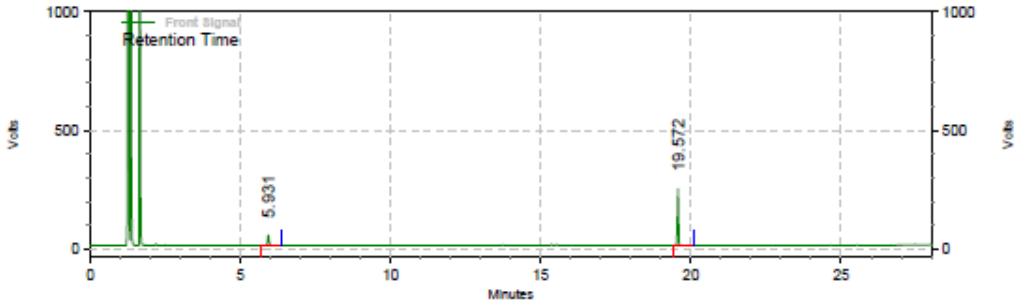
Figure S10: ^{13}C NMR of P3 in $CDCl_3$.

Isopropyl (E)-3-(4-methoxyphenyl)acrylate P4:



Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 74% yield (32.5 mg). GC retention time for 4-methoxy phenylacetylene = 5.93 min.; hydroalkoxycarbonylated product P4 = 19.57 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 15.94 Hz, 1H), 7.46 (d, *J* = 8.41 Hz, 2H), 6.88 (d, *J* = 8.47 Hz, 2H), 6.27 (d, *J* = 15.94 Hz, 2H), 5.15-5.09 (m, 1H), 3.82 (s, 3H), 1.29 (d, *J* = 6.17 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 167.0 (C_q), 161.4, 144.1, 129.8, 127.4, 116.5, 114.4, 67.7, 55.5, 22.1 (CH_3). The above data is in accordance with previous reports for compound P4.[7]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
5.931	1194193	19.18	336330	15.49
19.572	5032066	80.82	1835025	84.51
Totals	6226259	100.00	2171355	100.00

Figure S11: GC trace of P4.

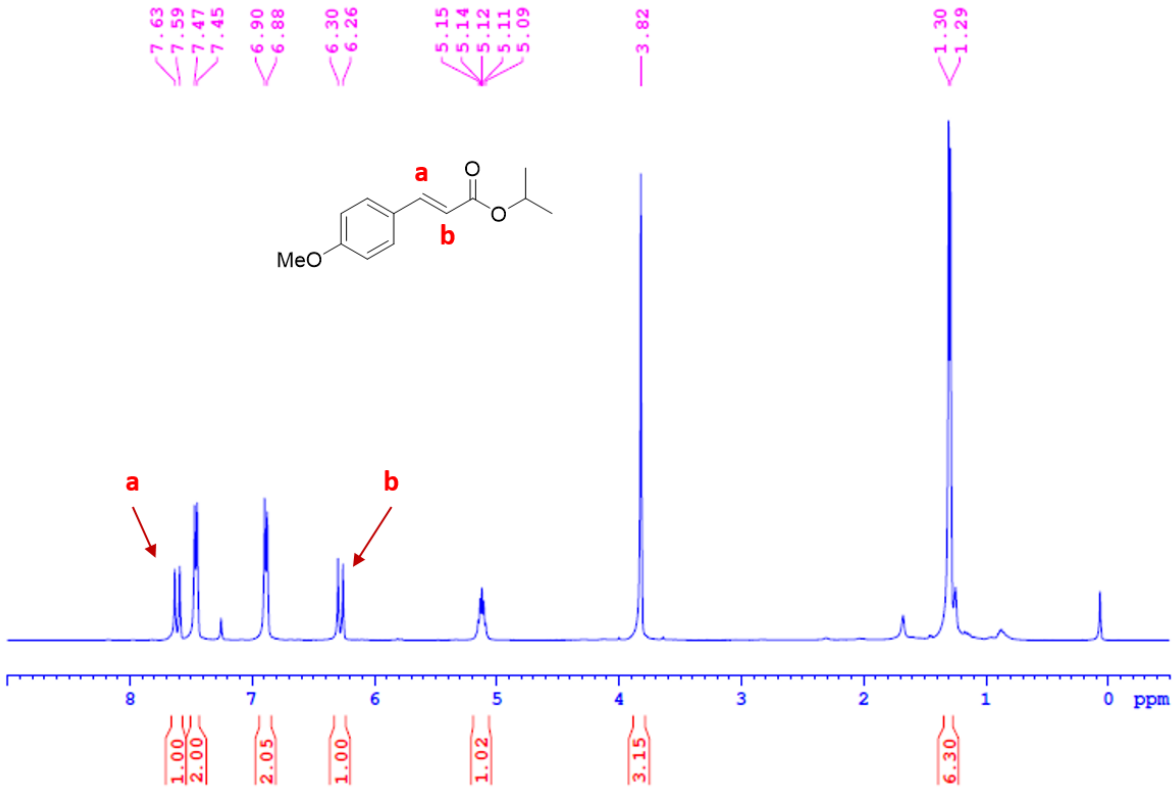


Figure S12: ^{1}H NMR spectrum of P4 in $CDCl_3$.

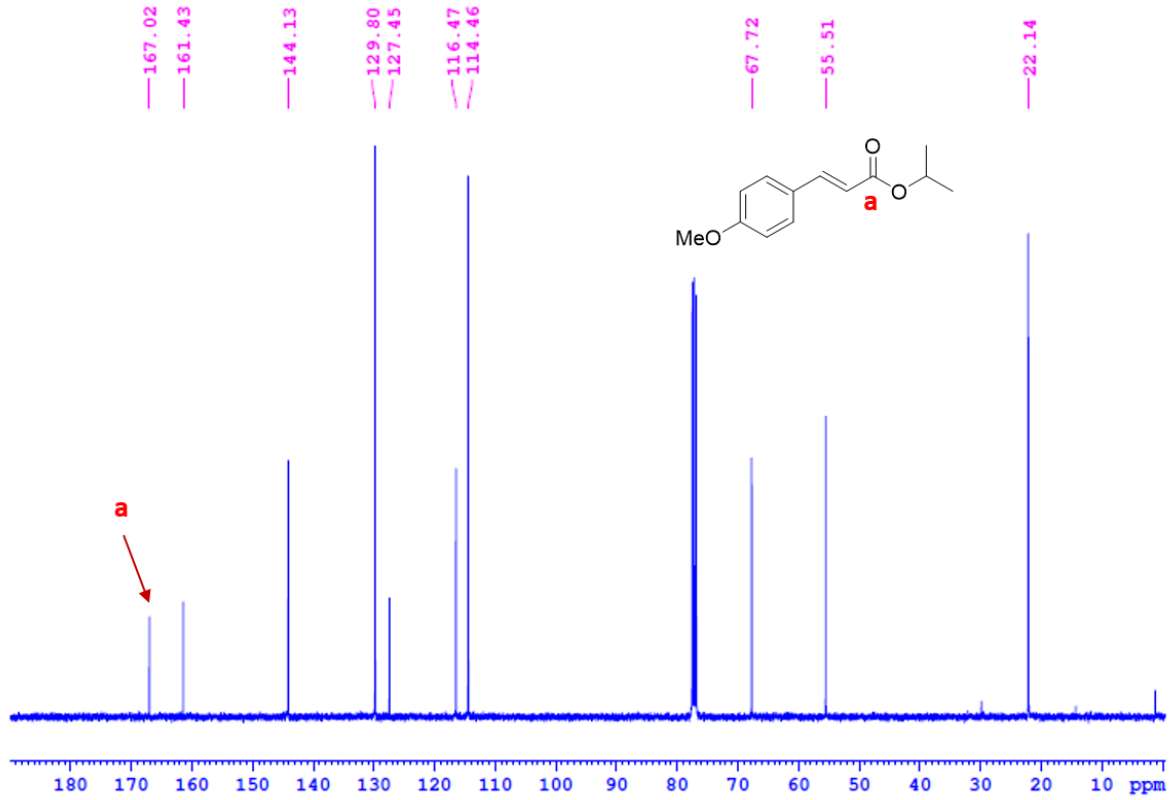
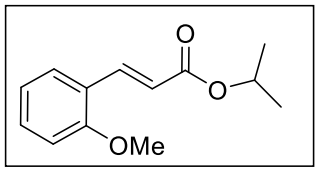


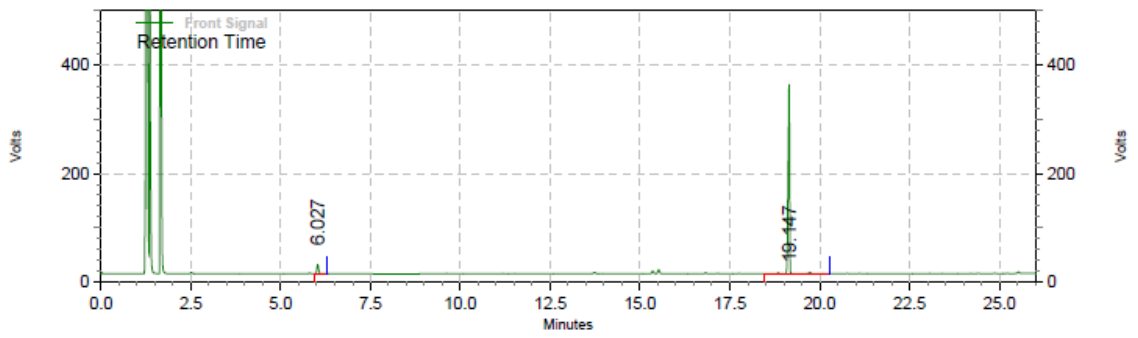
Figure S13: ^{13}C NMR spectrum of P4 in $CDCl_3$.

Isopropyl (E)-3-(2-methoxyphenyl)acrylate P5:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 88% yield (38.7 mg). GC retention time for 2-methoxyphenylacetylene = 6.02 min.; hydroalkoxycarbonylated product P5 = 19.14 min.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 16.03 Hz, 1H), 7.47 (d, *J* = 7.33 Hz, 1H), 7.31 (t, *J* = 7.79 Hz, 1H), 6.94-6.87 (m, 2H), 6.49 (d, *J* = 15.57 Hz, 1H), 5.14-5.09 (m, 1H), 3.85 (s, 3H), 1.29 (d, *J* = 5.04 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 167.1 (C_q), 158.4, 139.8, 131.4, 129.0, 123.6, 120.8, 119.4, 111.2, 67.6, 55.5, 22.1 (CH_3).



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
6.027	443441	5.47	130386	4.64
19.147	7664471	94.53	2677311	95.36
Totals	8107912	100.00	2807697	100.00

Figure S14: GC trace of P5.

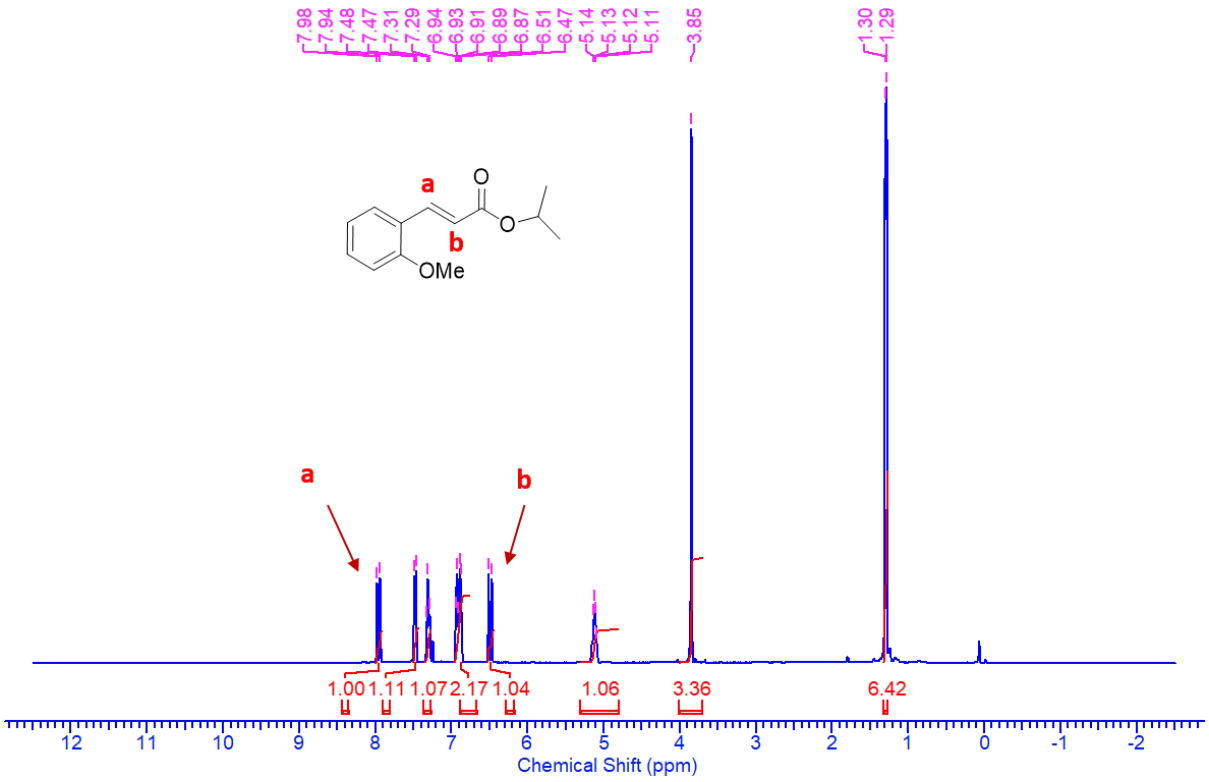


Figure S15: ^{1}H NMR spectrum of P5 in $CDCl_3$.

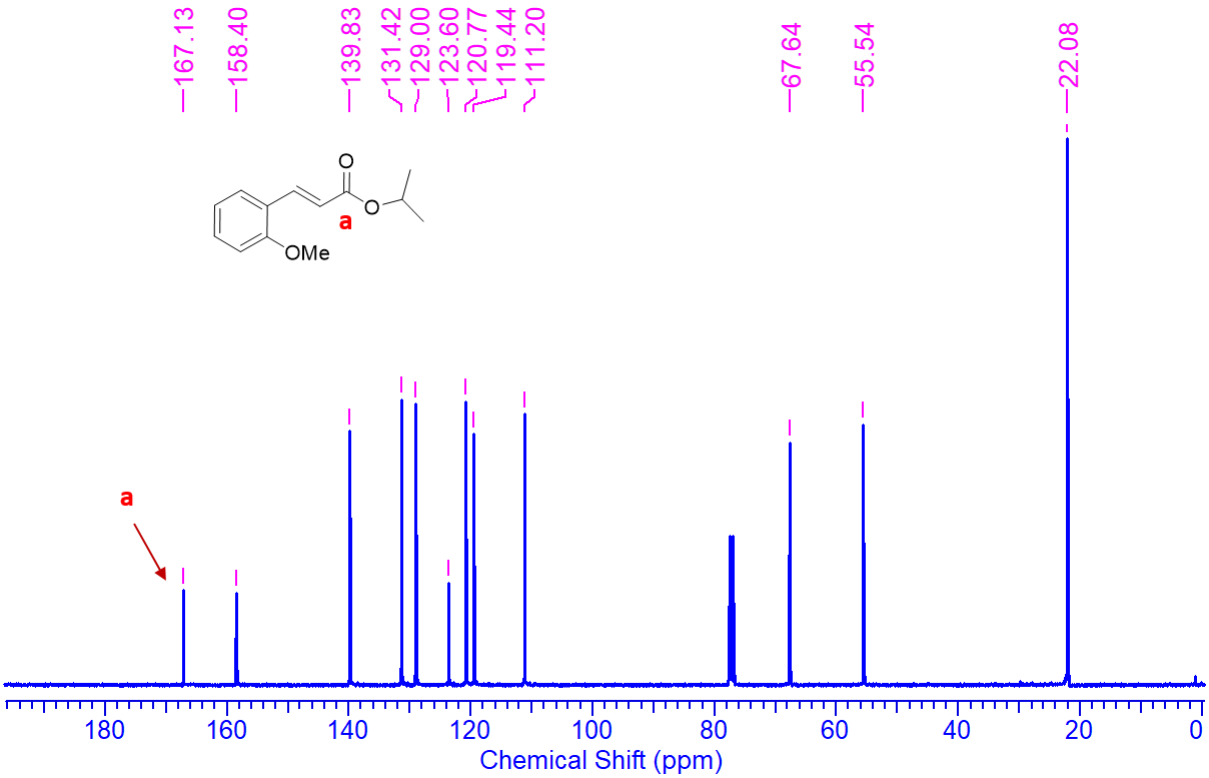
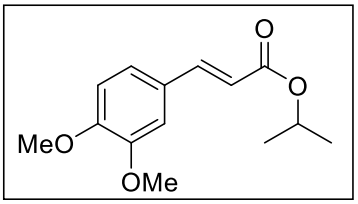


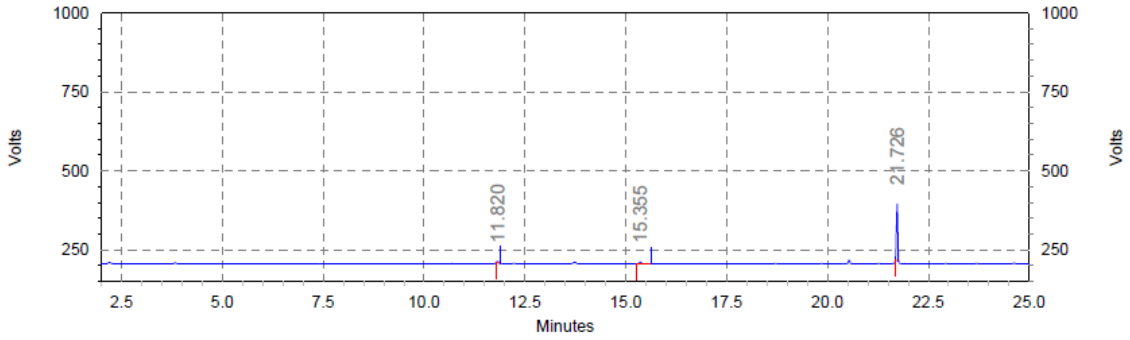
Figure S16: ^{13}C NMR spectrum of P5 in $CDCl_3$.

Isopropyl (E)-3-(3,4-dimethoxyphenyl)acrylate P6:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (96:4). After column, a pale yellow liquid was isolated in 85% yield (42.5 mg). GC retention time for 3,4-dimethoxyphenylacetylene = 11.82 min.; hydroalkoxycarbonylated product P6 = 21.72 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 15.91 Hz, 1H), 7.08 (d, *J* = 10.17 Hz,1H), 7.04 (s, 1H), 6.85 (d, *J* = 8.27 Hz, 1H), 6.28 (d, *J* = 15.90 Hz, 1H), 5.13 (sep., *J* = 12.50 Hz, 1H), 3.90 (s, 6H), 1.30 (d, *J* = 6.26 Hz, 6H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 166.8 (C_q), 151.1, 149.2, 144.3, 127.6, 122.6, 116.5, 111.1, 109.6, 67.6, 56.0, 55.9, 22.0. The above data is in accordance with previous reports for compound P6.[8]



Front Signal Results

Retention Time	Area	Area %	Height	Height %
11.820	106177	2.99	34303	2.36
15.355	157974	4.45	40134	2.76
21.726	3289710	92.57	1379158	94.88
Totals	3553861	100.00	1453595	100.00

Figure S17: GC trace of P6.

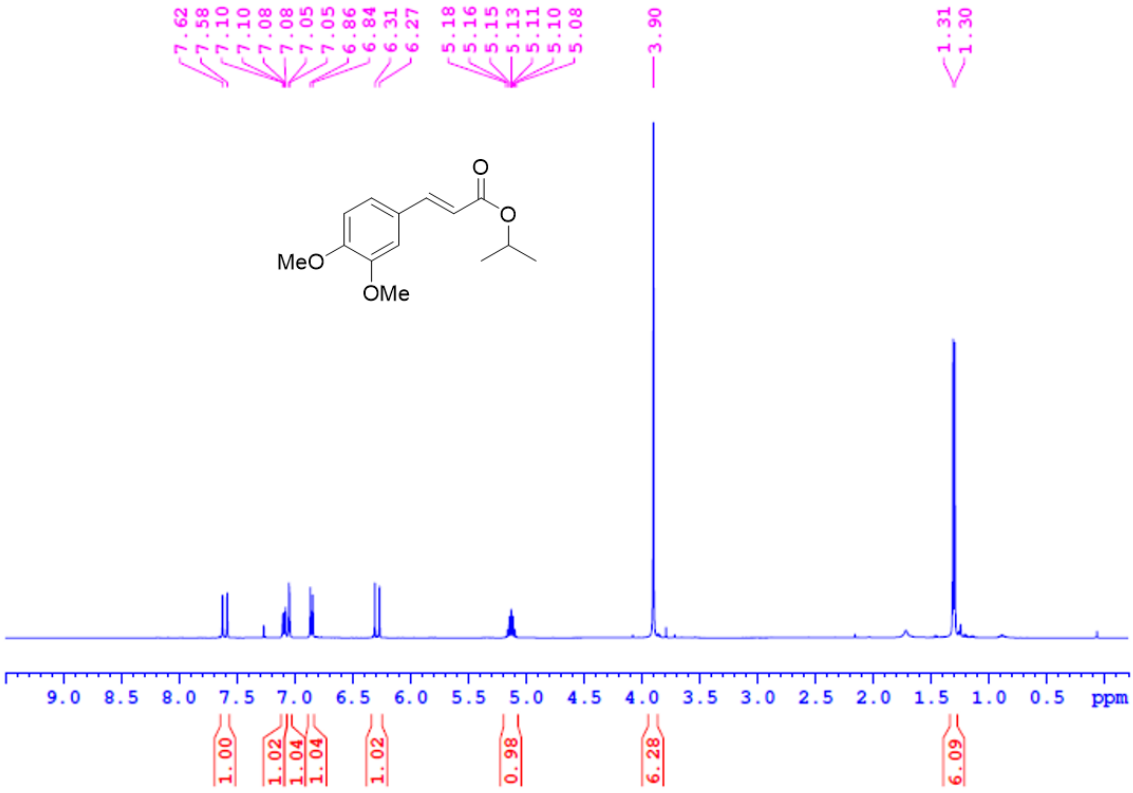


Figure S18A: ^{1}H NMR spectrum of P6 in $CDCl_3$.

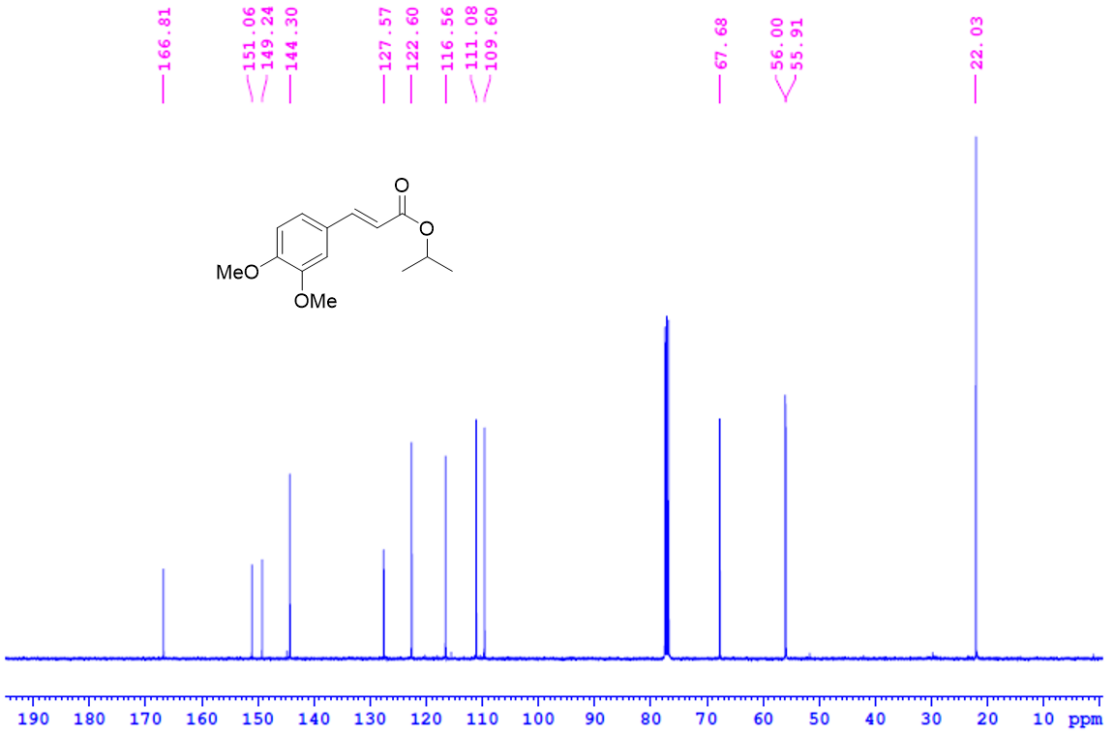
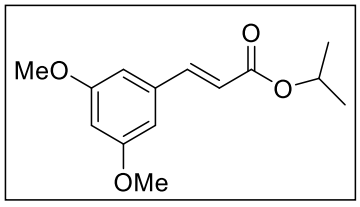


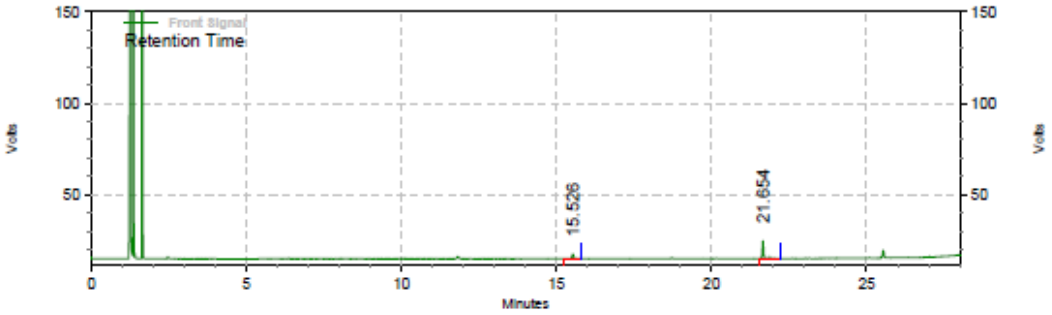
Figure S18B: ^{13}C NMR spectrum of P6 in $CDCl_3$.

Isopropyl (E)-3-(3,5-dimethoxyphenyl)acrylate P7:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (96:4). After column, a pale yellow liquid was isolated in 66% yield (33.3 mg). GC retention time for 3,5 di-methoxy phenylacetylene = 15.5 min.; hydroalkoxycarbonylated product P7 = 21.65 min.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 15.94 Hz, 1H), 6.65 (br s, 2H), 6.47 (s, 1H), 6.37 (d, *J* = 15.94 Hz, 1H), 5.13 (sep, *J* = 12.47 Hz, 1H), 3.79 (s, 6H), 1.30 (d, *J* = 6.25 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 166.5 (C_q), 161.1, 144.4, 136.5, 119.4, 106.0, 102.6, 67.9, 55.5, 22.1(CH_3).



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
15.526	79671	27.10	19963	21.17
21.654	214272	72.90	74348	78.83
Totals	293943	100.00	94311	100.00

Figure S19: GC trace of P7.

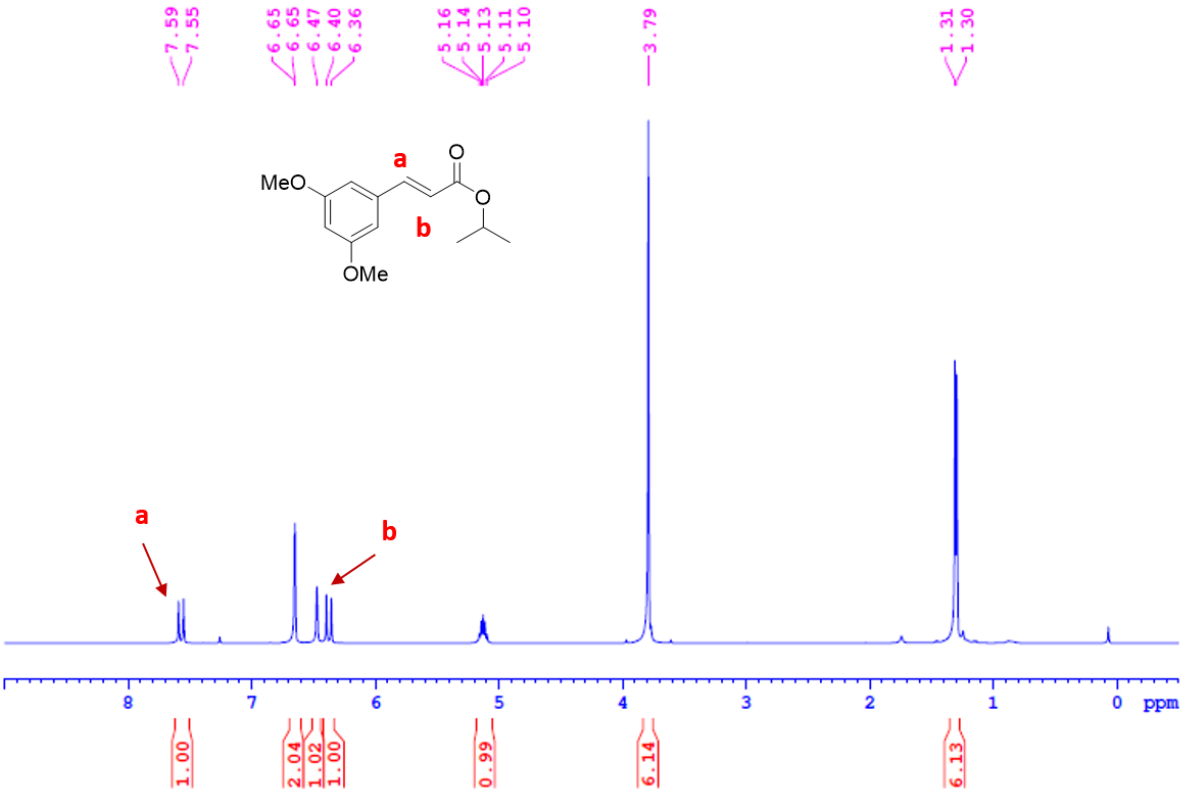


Figure S20: ^{1}H NMR spectrum of P7 in $CDCl_3$.

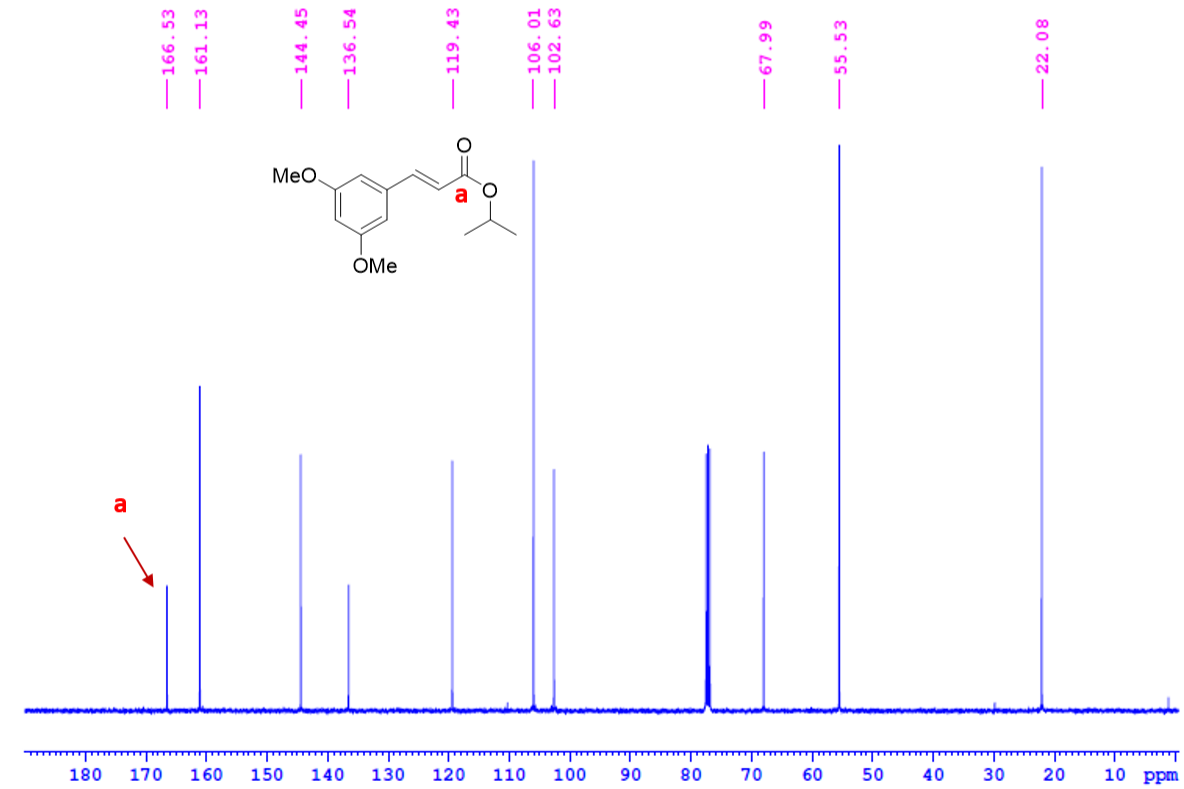
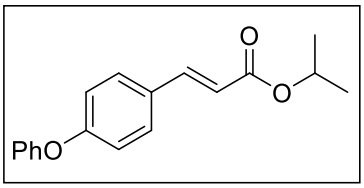


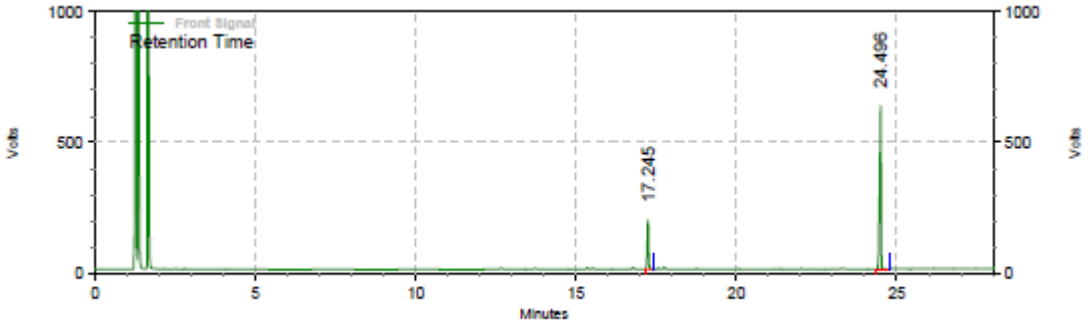
Figure S21: ^{13}C NMR spectrum of P7 in $CDCl_3$.

Isopropyl (E)-3-(4-phenoxyphenyl)acrylate P8:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 70% yield (39.5 mg). GC retention time for 4-phenoxy phenyl acetylene = 17.24 min.; hydroalkoxycarbonylated product P8 = 24.49 min.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 15.97 Hz, 1H), 7.46 (d, *J* = 8.50 Hz, 2H), 7.34 (t, J = 7.77 Hz, 2H), 7.13 (m, 1H), 7.02 (d, *J* = 7.85 Hz, 2H), 6.95 (d, *J* = 8.48 Hz, 2H), 6.30 (d, *J* = 15.96 Hz, 1H), 5.12 (sep, *J* = 6.20 Hz, 1H), 1.29 (d, *J* = 6.21 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 166.77 (C_q), 159.5, 156.3, 143.7, 130.1, 129.8, 129.4, 124.2, 119.8, 118.5, 117.6, 67.8, 22.1 (CH_3).



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
17.245	4115498	21.97	1436604	23.05
24.496	14612970	78.03	4794910	76.95
Totals	18728468	100.00	6231514	100.00

Figure S22: GC trace of P8.

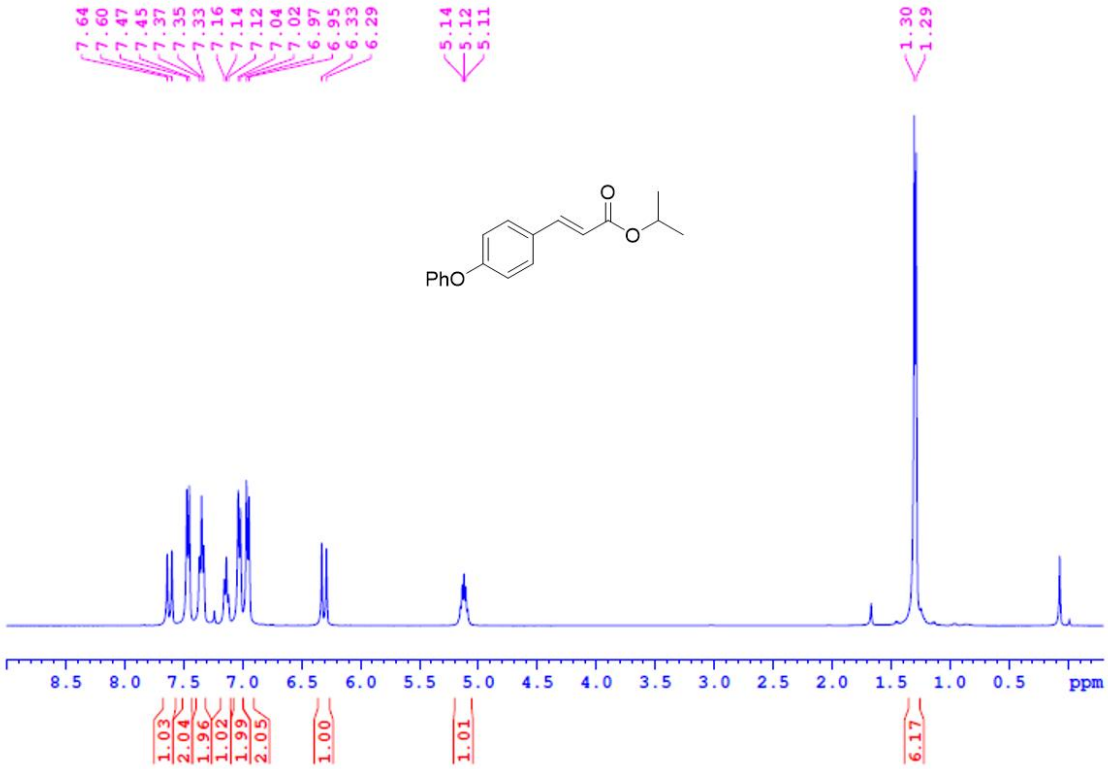


Figure S23: ^{1}H NMR spectrum of P8 in $CDCl_3$.

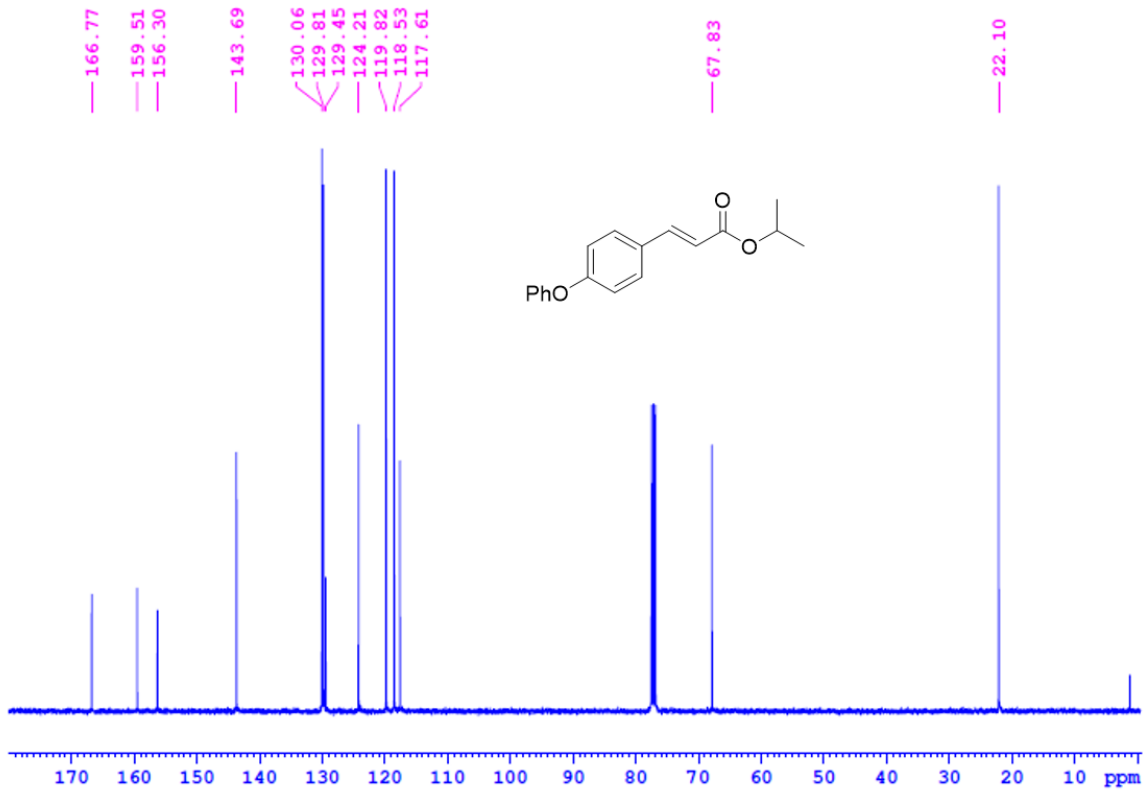
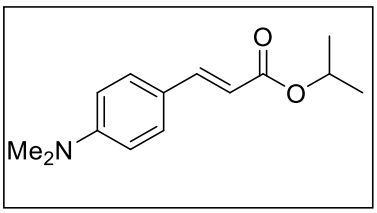


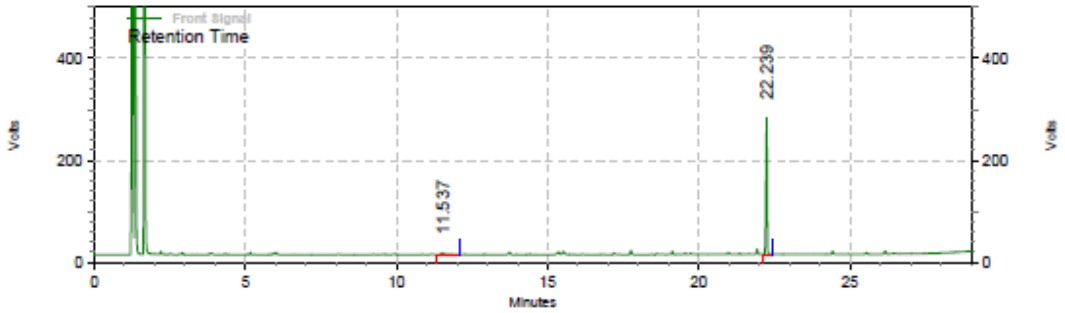
Figure S24: ^{13}C NMR spectrum of P8 in $CDCl_3$.

Isopropyl (E)-3-(4-(dimethylamino)phenyl)acrylate P9:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 89% yield (41.5 mg). GC retention time for 4-Dimethylaminophenylacetylene = 11.53 min.; hydroalkoxycarbonylated product P9 = 22.23 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 15.84 Hz, 1H), 7.41 (d, *J* = 8.85 Hz, 2H), 6.66 (d, *J* = 8.87 Hz, 2H), 6.20 (d, *J* = 15.83 Hz, 1H), 5.12 (sep, *J* = 12.51 Hz, 1H), 3.01 (s, 6H), 1.29 (d, *J* = 6.26 Hz, 6H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 167.6 (C_q), 151.8, 145.0, 129.8, 122., 113.3, 111.9, 67.4, 40.3, 22.2 (CH_3).



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
11.537	180943	3.21	23093	1.11
22.239	5456394	96.79	2059399	98.89
Totals	5637337	100.00	2082492	100.00

Figure S25: GC trace of P9.

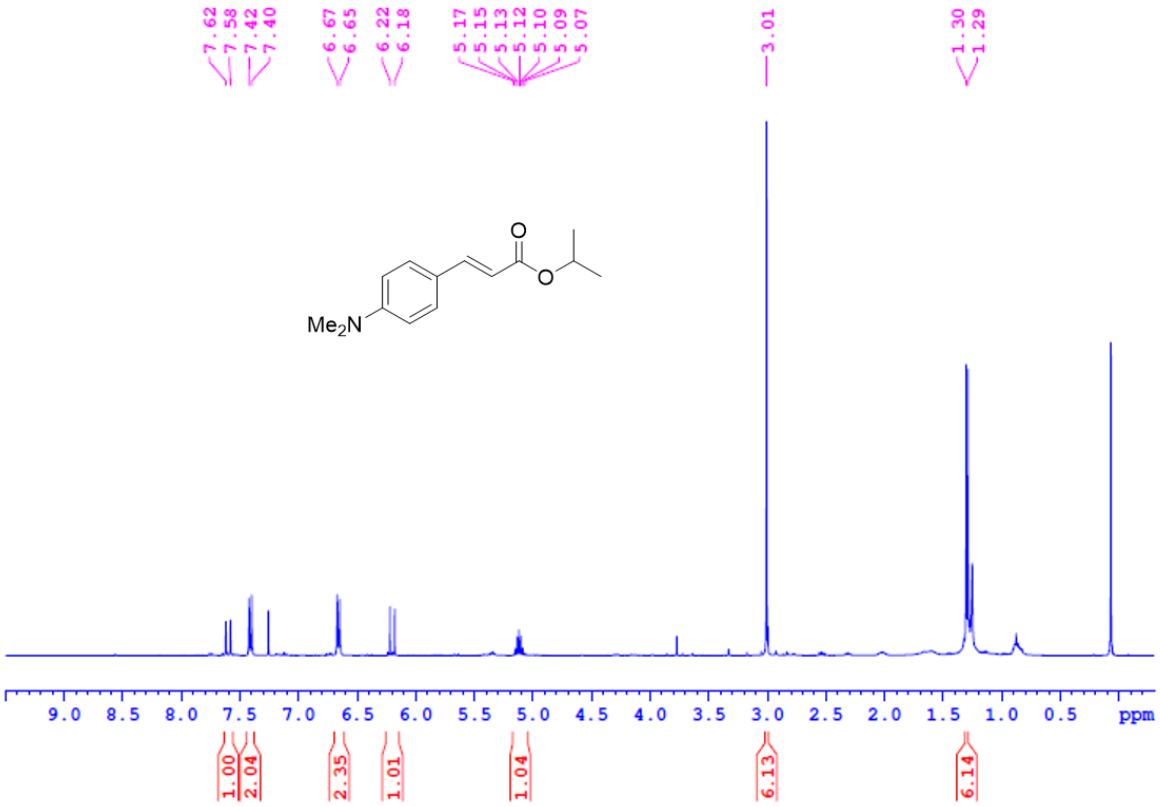


Figure S26: ^{1}H NMR spectrum of P9 in $CDCl_3$.

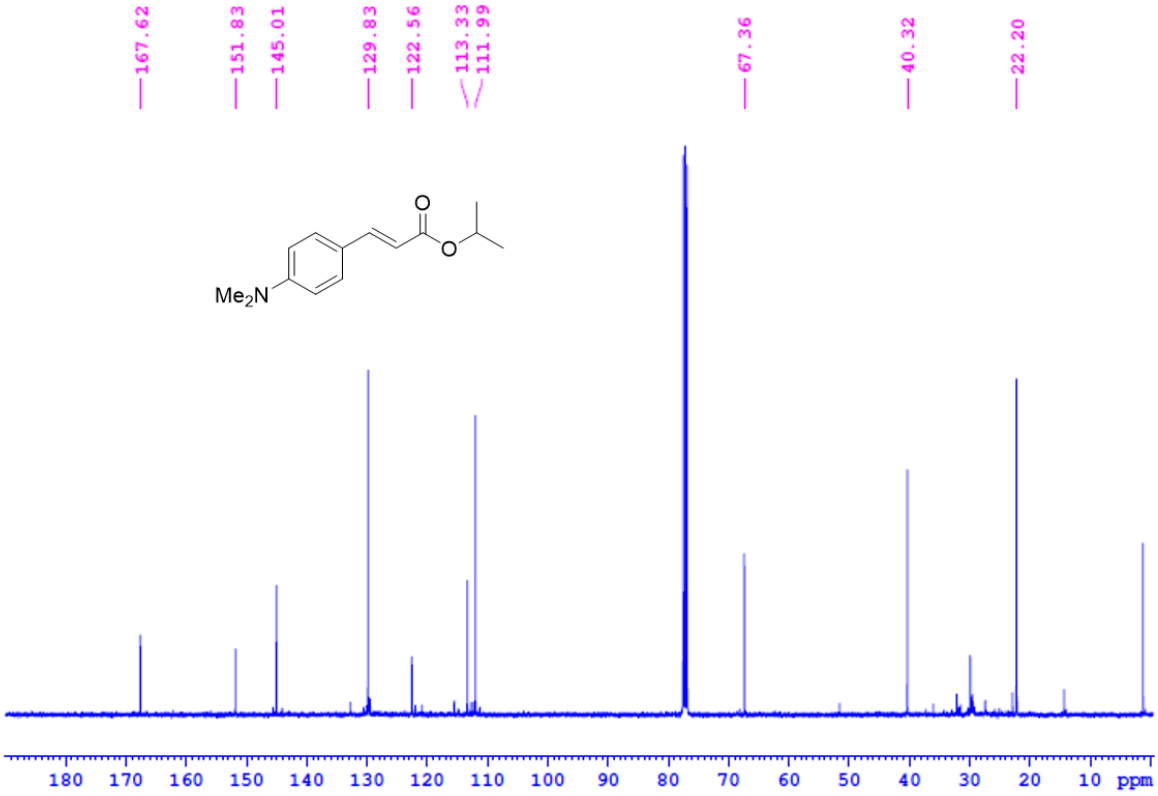
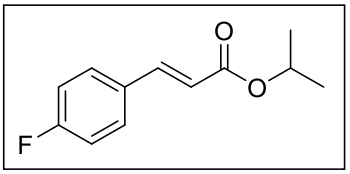


Figure S27: ^{13}C NMR spectrum of P9 in $CDCl_3$.

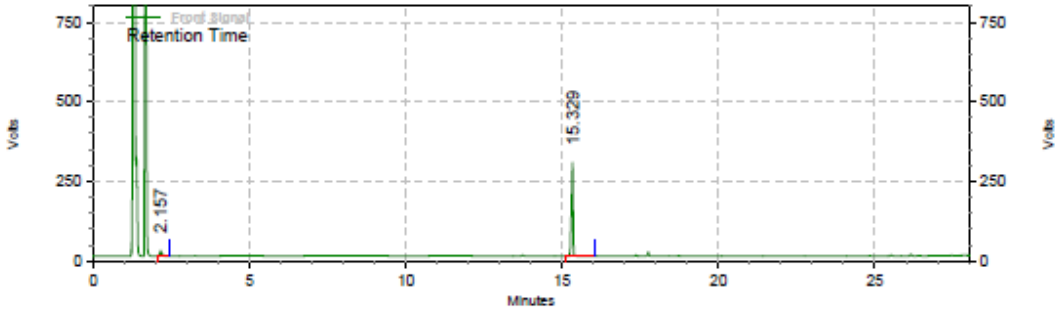
Isopropyl (E)-3-(4-fluorophenyl)acrylate P10A:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 85% yield (35.4 mg). GC retention time for 4-fluoro phenyl acetylene = 2.15 min.; hydroalkoxycarbonylated product P10 = 15.32 min.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 16.00 Hz, 1H), 7.51-7.47 (m, 2H), 7.05(t, J = 8.63 Hz, 2H), 6.32 (d, J = 15.98 Hz, 1H), 5.12 (sep, J = 12.52 Hz, 1H), 1.30 (d, J = 6.27 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 166.5 (C_q), 163.9 (Cq, d, $^{1}J_{C\text{-}F}$ = 251.04 Hz), 143.1,

130.9, 130.0 (d, $^{3}J_{C\text{-}F}$ = 8.45 Hz), 118.7, 116.1 (d, $^{2}J_{C\text{-}F}$ = 22.07 Hz), 68.0, 22.1 (CH_3). The above data is in accordance with previous reports for compound P10.[9]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.157	603256	6.59	134068	5.61
15.329	8556295	93.41	2257539	94.39
Totals	9159551	100.00	2391607	100.00

Figure S28: GC trace of P10A.

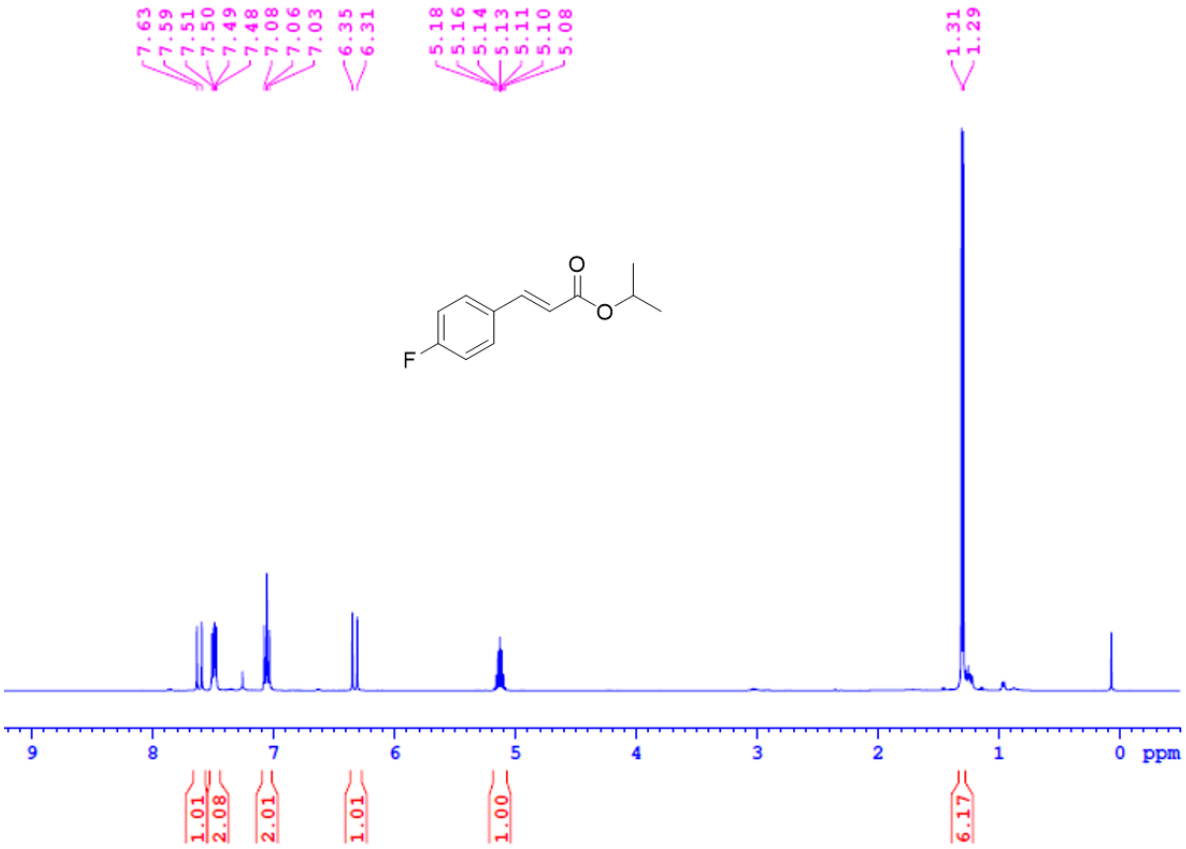


Figure S29A: ^{1}H NMR spectrum of P10A in $CDCl_3$.

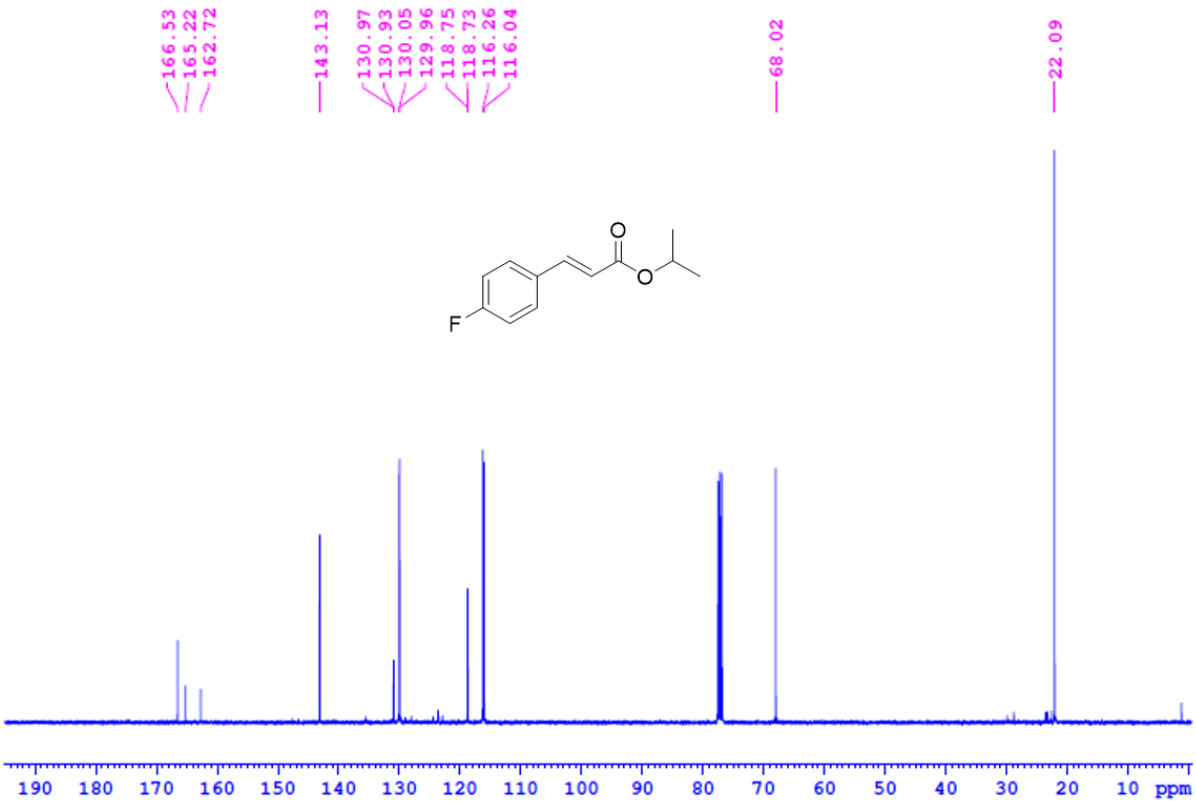
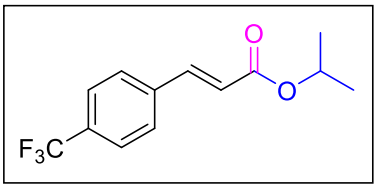


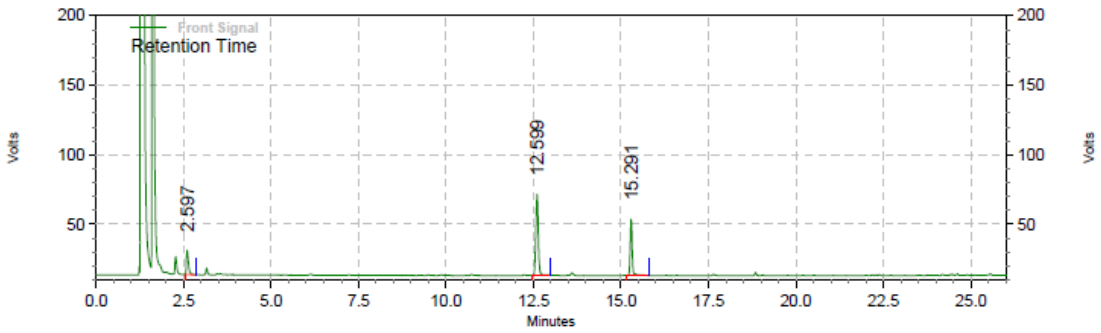
Figure S29B: ^{13}C NMR spectrum of P10A in $CDCl_3$.

Isopropyl (E)-3-(4-(trifluoromethyl)phenyl)acrylate P10B:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a yellow liquid was isolated in 26% yield (13.4 mg). GC retention time for 4-trifluoromethyl phenyl acetylene = 2.5 min.; hydroalkoxycarbonylated product P10b = 15.32 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68-7.60 (m, 3H), 7.52-7.37 (m, 2H), 6.48 (d, J = 16.01 Hz, 1H), 5.18-5.13 (m, 1H), 1.32 (d, J = 6.17 Hz, 6H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 166.1, 144.5, 142.6, 129.0, 128.3, 126.0 (J_{C-F} = 3.69 Hz), 121.6, 119.0, 68.4, 22.1.



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.597	561296	14.12	134863	15.09
12.599	2179627	54.84	447701	50.09
15.291	1233645	31.04	311250	34.82
Totals	3974568	100.00	893814	100.00

Figure S30A: GC trace of P10B.

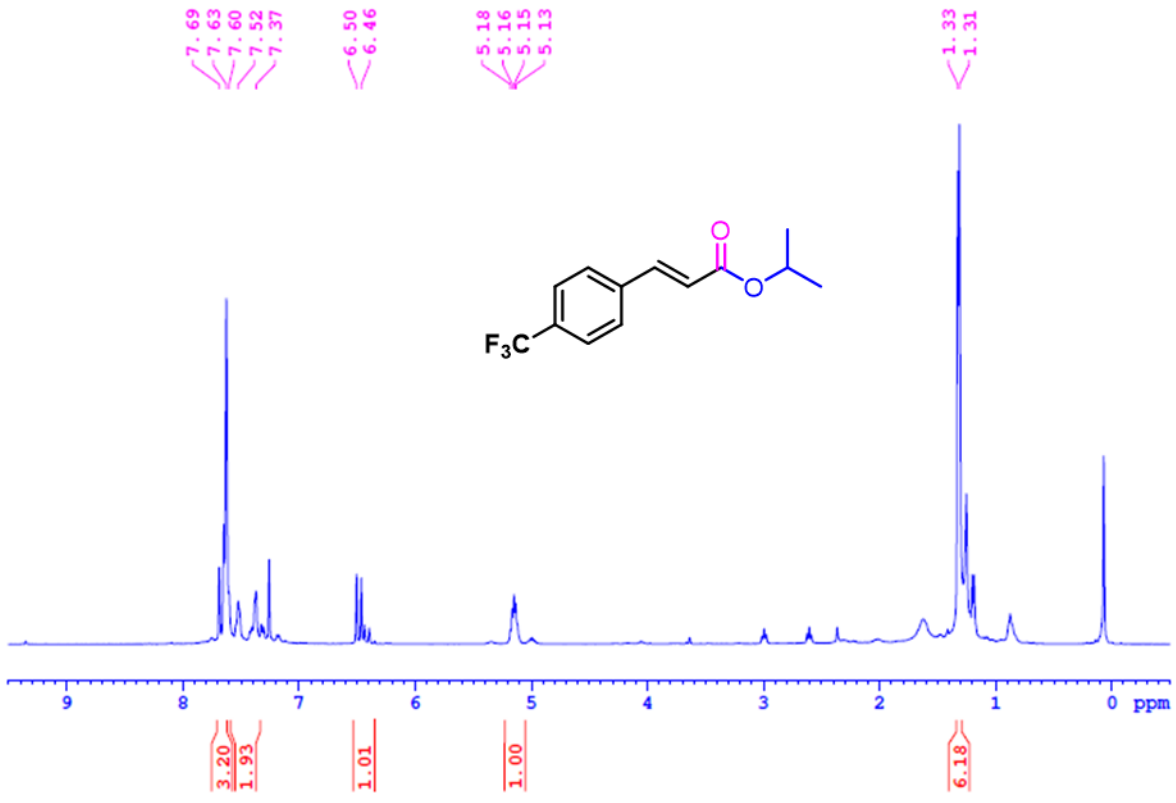


Figure S30B: ^{1}H NMR spectrum of P10B in $CDCl_3$.

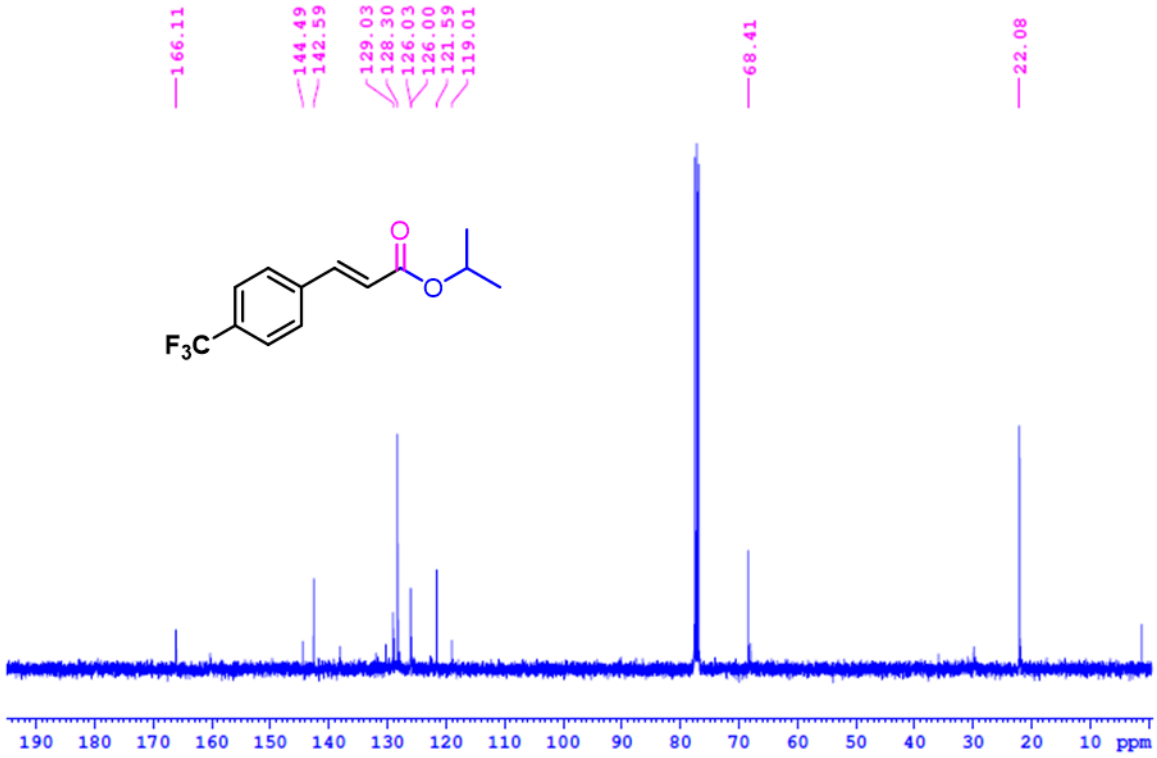
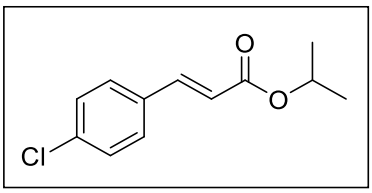


Figure S30C: ^{13}C NMR spectrum of P10B in $CDCl_3$.

Isopropyl (E)-3-(4-chlorophenyl)acrylate P11:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a yellow orange liquid was isolated in 86% yield (38.6 mg).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 16.01 Hz, 1H), 7.44 (d, *J* = 8.38 Hz, 2H), 7.34 (d, *J* = 8.51 Hz, 2H), 6.38 (d, *J* = 16.00 Hz, 1H), 5.13 (sep, *J* = 12.51 Hz, 1H), 7.30 (d, *J* = 6.26 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 166.4, 143.0, 136.2, 133.2, 129.3, 129.3, 119.6, 68.1, 22.1. The above data is in accordance with previous reports for compound P11.[10]

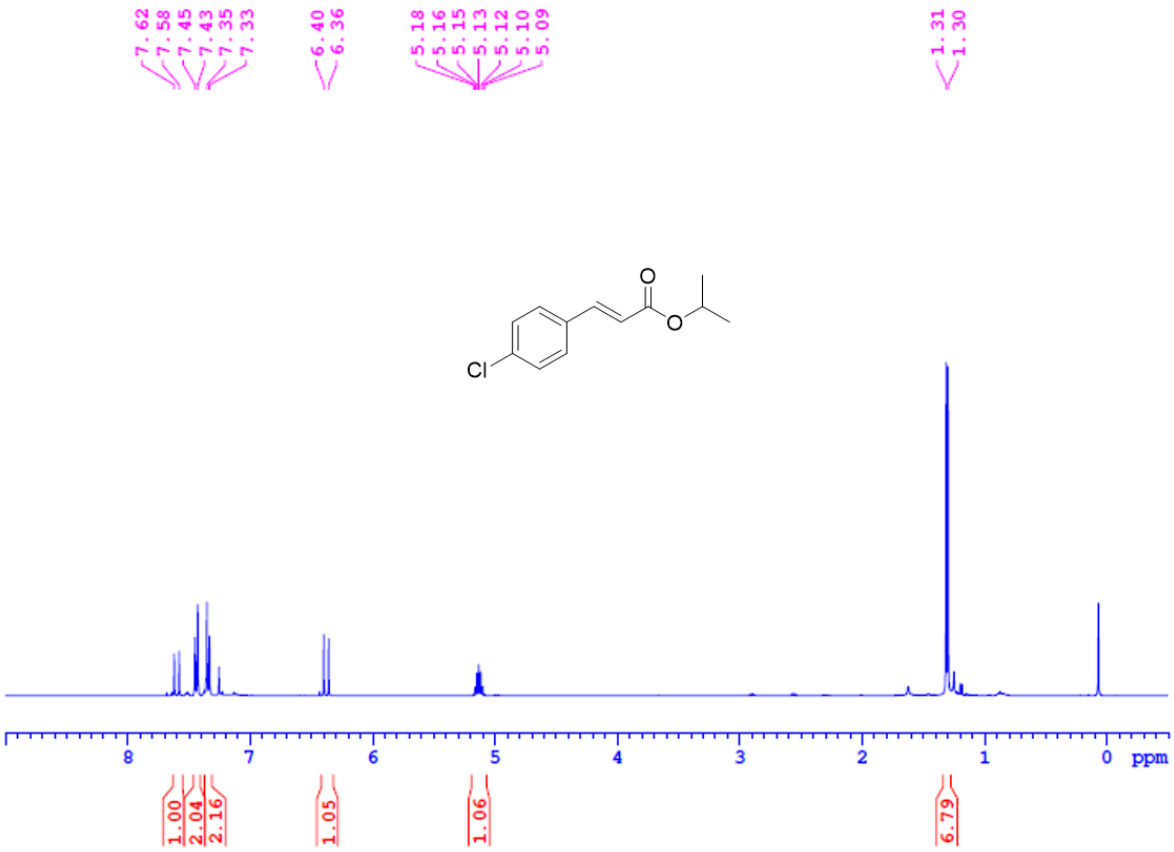


Figure S31: ^{1}H NMR spectrum of P11 in $CDCl_3$.

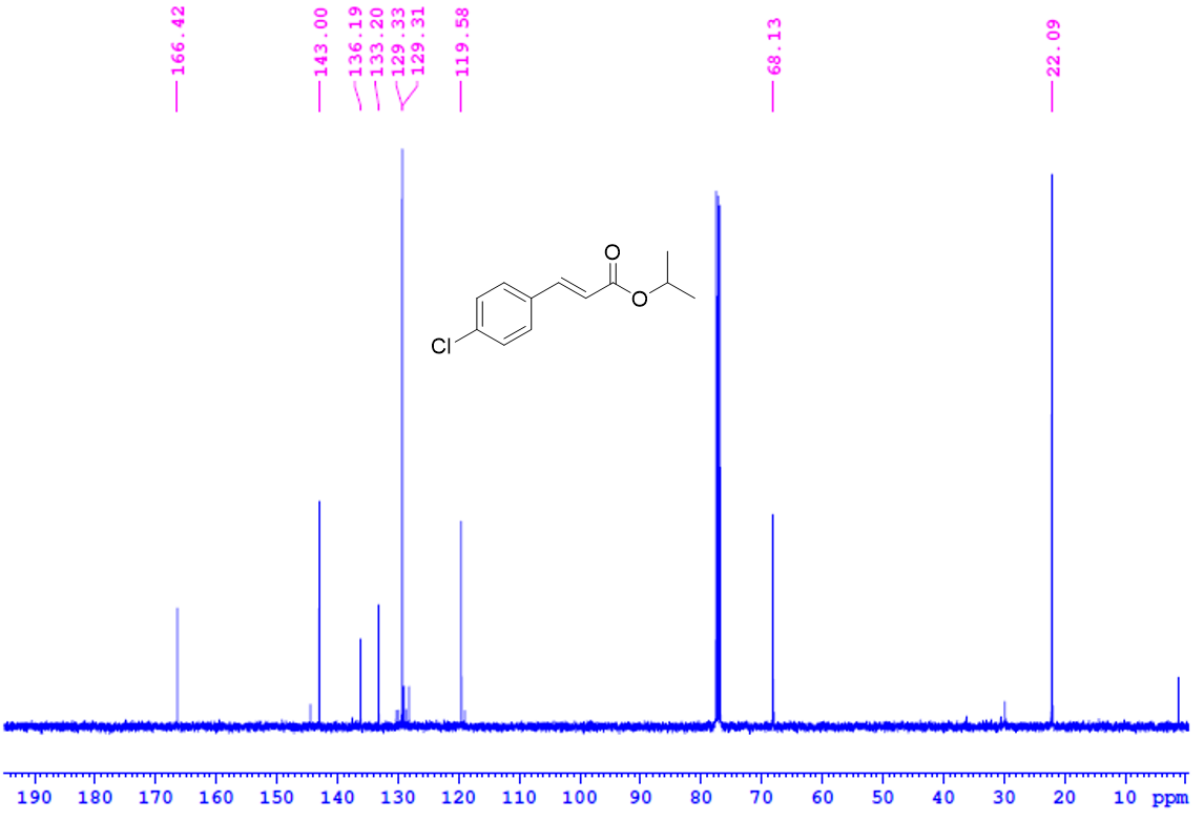
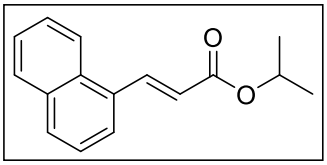


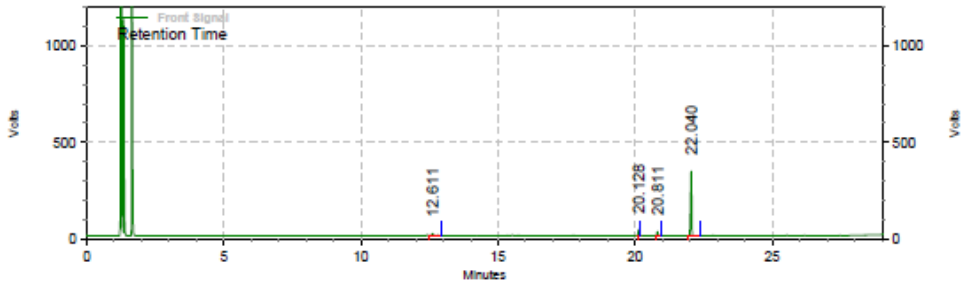
Figure S32: ^{13}C NMR spectrum of P11 in $CDCl_3$.

Isopropyl (E)-3-(naphthalen-1-yl)acrylate P12:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 72% yield (34.6 mg). GC retention time for 1-ethynyl naphthalene = 12.61 min.; hydroalkoxycarbonylated product P12 = 22.04 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 15.74 Hz, 1H), 8.19 (d, *J* = 8.35 Hz, 1H), 7.87 (t, *J* = 13.66 Hz, 2H), 7.74 (d, *J* = 7.22 Hz, 1H), 7.59-7.45 (m, 3H), 6.50 (d, *J* = 15.74 Hz, 1H), 5.19 (sep, *J* = 12.49 Hz, 1H), 1.35 (d, *J* = 6.26 Hz, 6H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 166.6, 141.5, 133.8, 132.0, 131.5, 130.5, 128.8, 126.9, 126.3, 125.6, 125.1, 123.6, 121.6, 68.1, 22.1.



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
12.611	462681	5.46	85444	2.78
20.128	619085	7.31	240826	7.84
20.811	454748	5.37	173529	5.65
22.040	6935305	81.86	2570469	83.72
Totals	8471819	100.00	3070268	100.00

Figure S33: GC trace of P12.

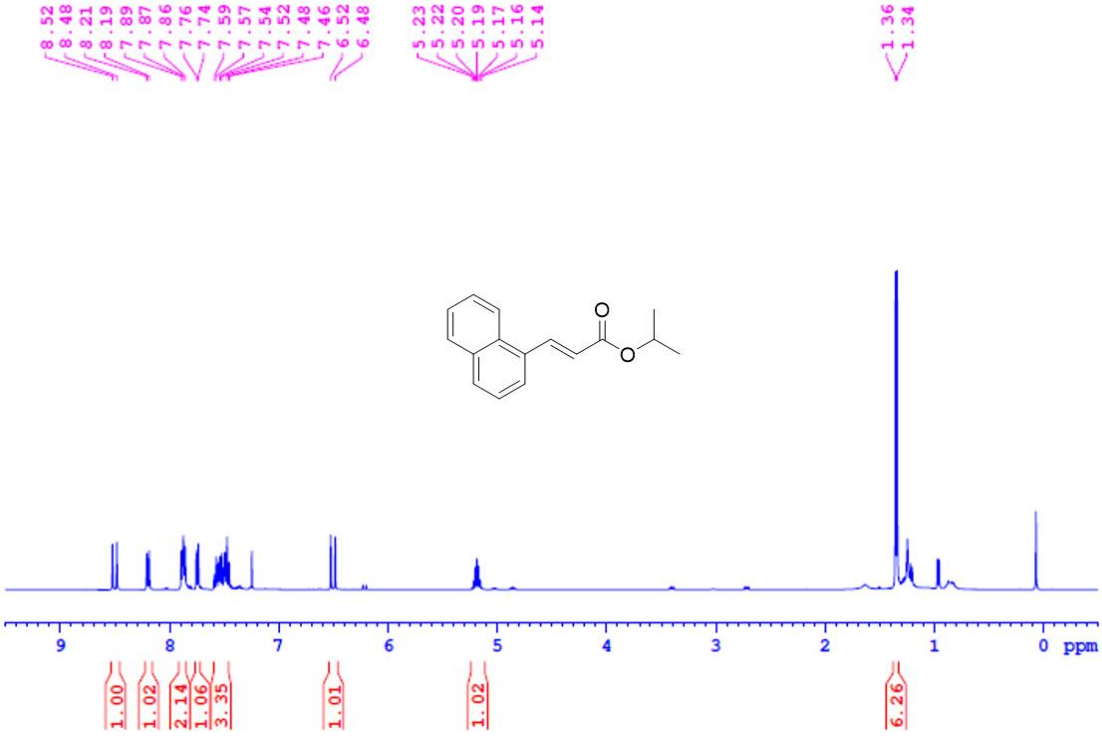


Figure S34: ^{1}H NMR spectrum of P12 in $CDCl_3$.

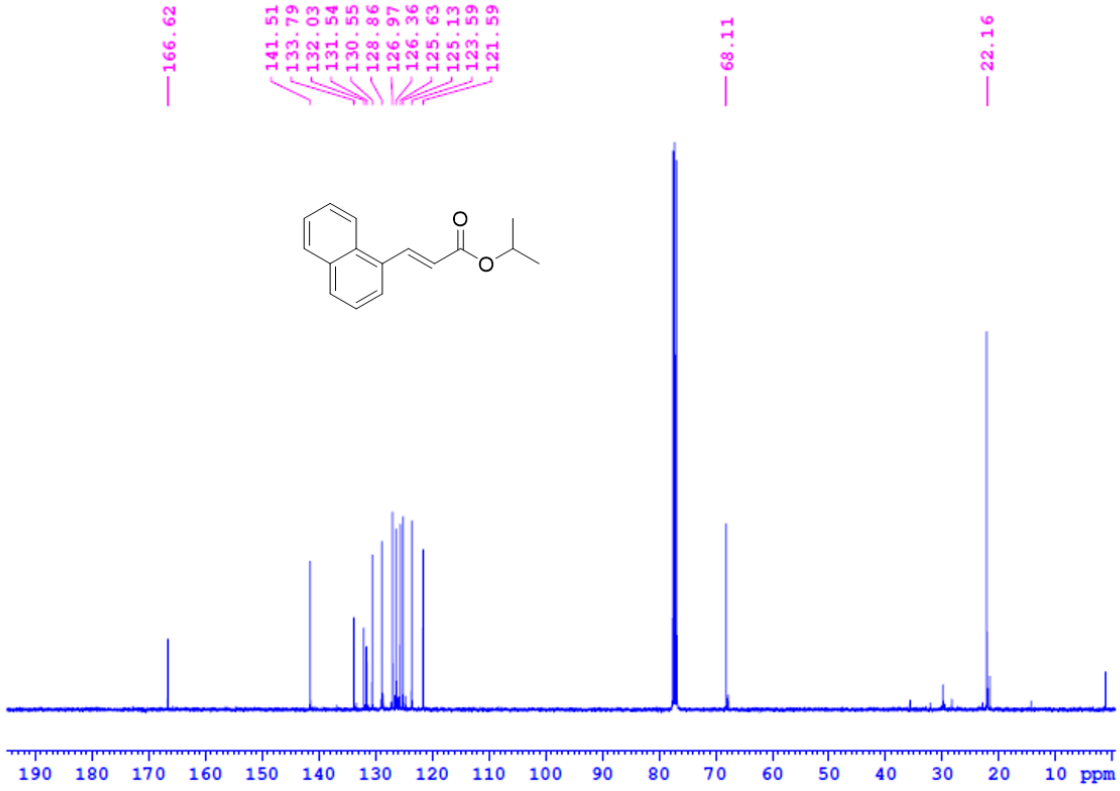
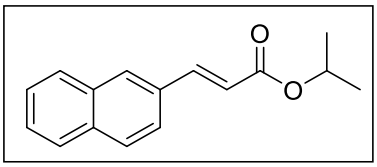


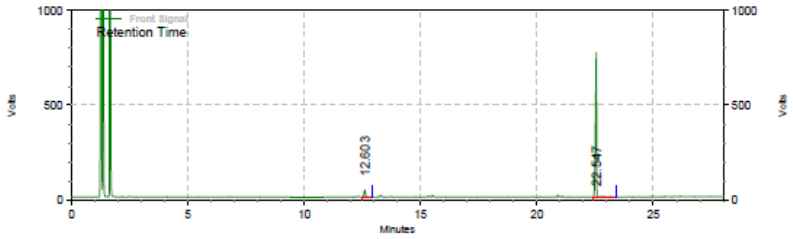
Figure S35: ^{13}C NMR spectrum of P12 in $CDCl_3$.

Isopropyl (E)-3-(naphthalen-2-yl)acrylate P13:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 82% yield (39.4 mg). GC retention time for 2-ethynylnaphthalene = 12.56 min.; hydroalkoxycarbonylated product P13 = 22.54 min.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85-7.74 (m, 5H), 7.59 (d, *J* = 8.36 Hz, 1H), 7.45-7.43 (m, 2H), 6.48 (d, *J* = 15.96 Hz, 1H), 5.17-5.10 (m, 1H), 1.29 (d, *J* = 6.23 Hz, 6H).



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
12.603	1246047	6.07	279862	4.56
22.547	19267523	93.93	5852277	95.44
Totals				
	20513570	100.00	6132139	100.00

Figure S36: GC trace of P13.

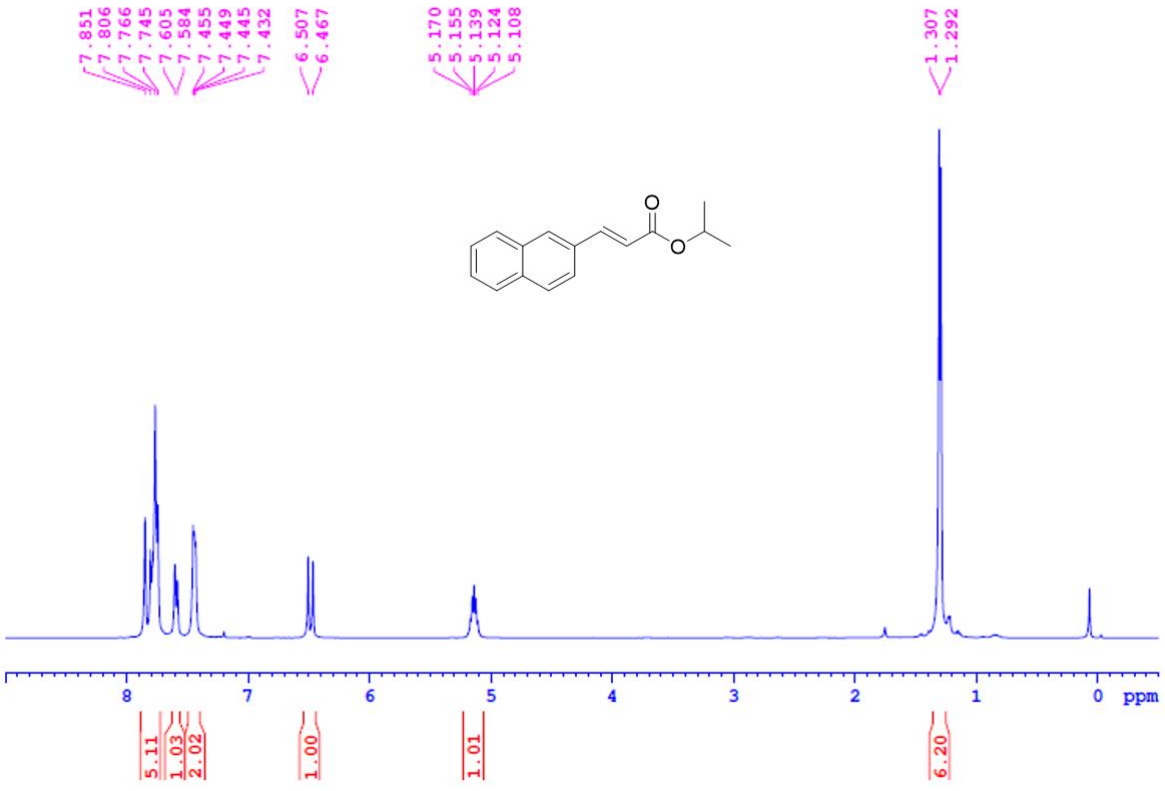
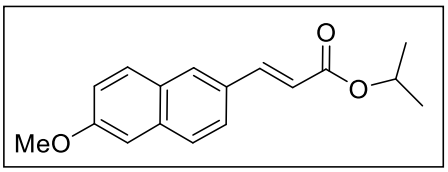


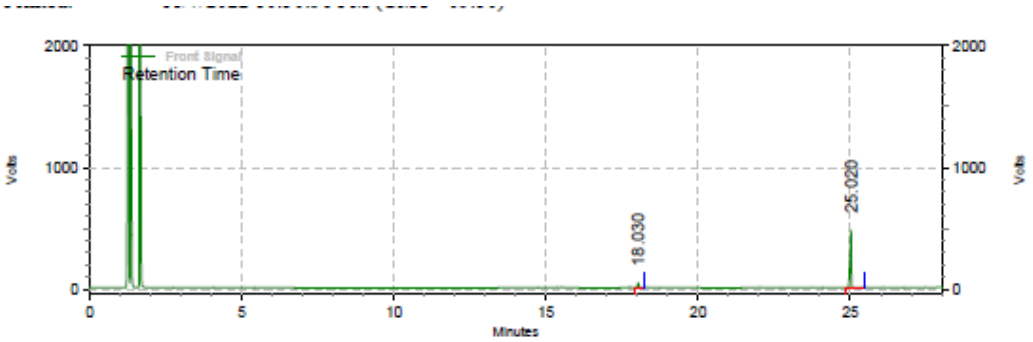
Figure S37: ^{1}H NMR spectrum of P13 in $CDCl_3$.

Isopropyl (E)-3-(6-methoxynaphthalen-2-yl)acrylate P14:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 84% yield (45.4 mg). GC retention time for 2-ethynyl-6-methoxynaphthalene = 18.03 min.; hydroalkoxycarbonylated product P14 = 25.02 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79-7.57 (m, 5H), 7.12 (d, J = 8.87 Hz, 1H), 7.07 (br s, 1H), 6.45 (d, J = 15.91 Hz, 1H), 5.14 (sep. J = 12.45 Hz, 1H), 3.87 (s, 3H), 1.30 (d, J = 6.24 Hz, 6H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 166.8 (C_q), 158.8, 144.6, 135.7, 130.2, 130.0, 129.7, 128.8, 127.6, 124.3, 119.5, 117.9, 106.1, 67.8, 55.5, 22.1 (CH_3).



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
18.030	833524	6.86	295380	7.55
25.020	11320191	93.14	3618023	92.45
Totals	12153715	100.00	3913403	100.00

Figure S38: GC trace of P14.

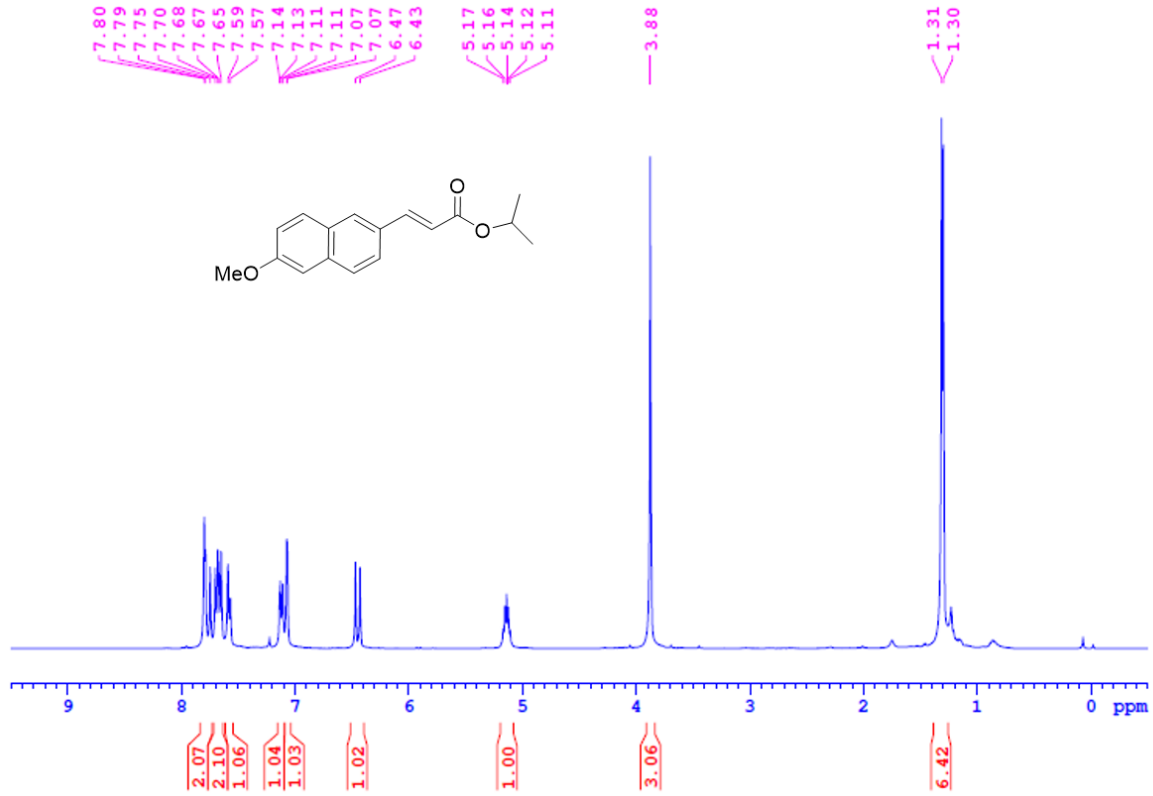


Figure S39A: ^{1}H NMR spectrum of P14 in $CDCl_3$.

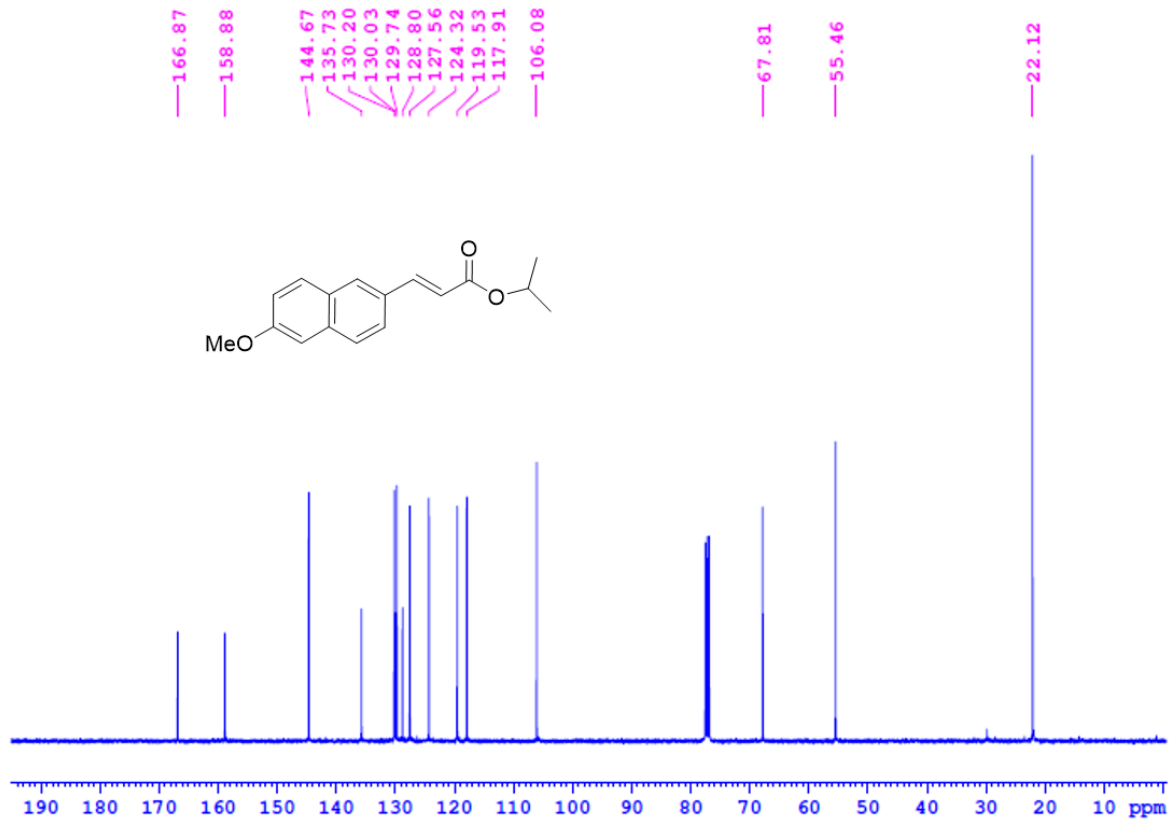
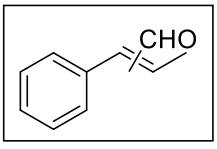
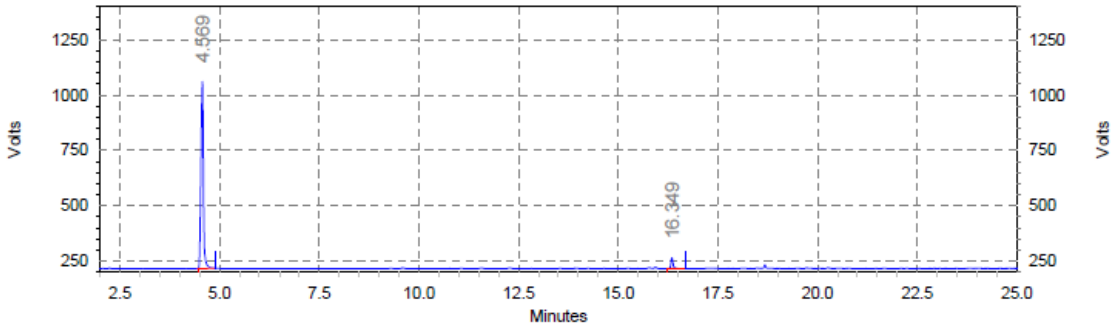


Figure S39B: ^{13}C NMR spectrum of P14 in $CDCl_3$.

2-methyl-3-phenylacrylaldehyde or 2-phenylbut-2-enal P15A:

GC retention time for methylphenylacetylene = 4.56 min.; hydroalkoxycarbonylated product P15 = 16.35 min.





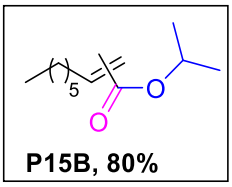
Front Signal Results

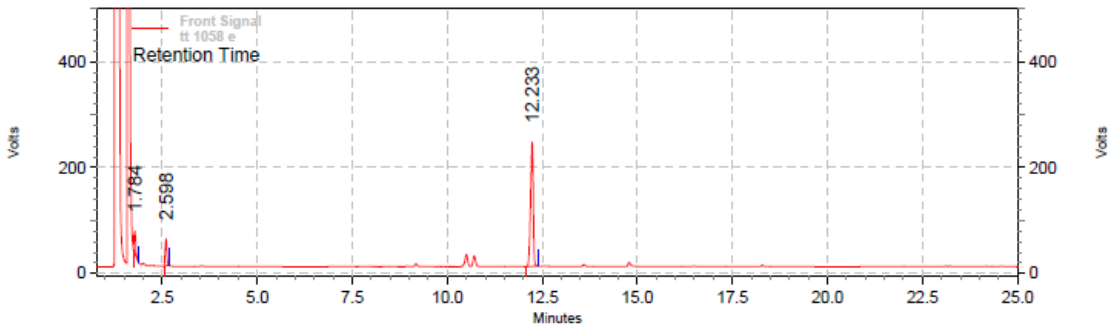
Retention Time	Area	Area %	Height	Height %
4.569	28890392	95.63	6488914	94.63
16.349	1321740	4.37	368350	5.37
Totals	30212132	100.00	6857264	100.00

Figure S40A: GC trace of P15.

isopropyl 2-methyleneoctanoate or isopropyl (E)-non-2-enoate P15B:

GC retention time for 1-octyne = 1.8 min.; hydroalkoxycarbonylated product P15B = 12.2 min.





Front Signal Results

Retention Time	Area	Area %
1.784	946402	8.74
2.598	1166483	10.77
12.233	8713289	80.48
Totals	10826174	100.00

Figure S40B: GC trace of P15B.

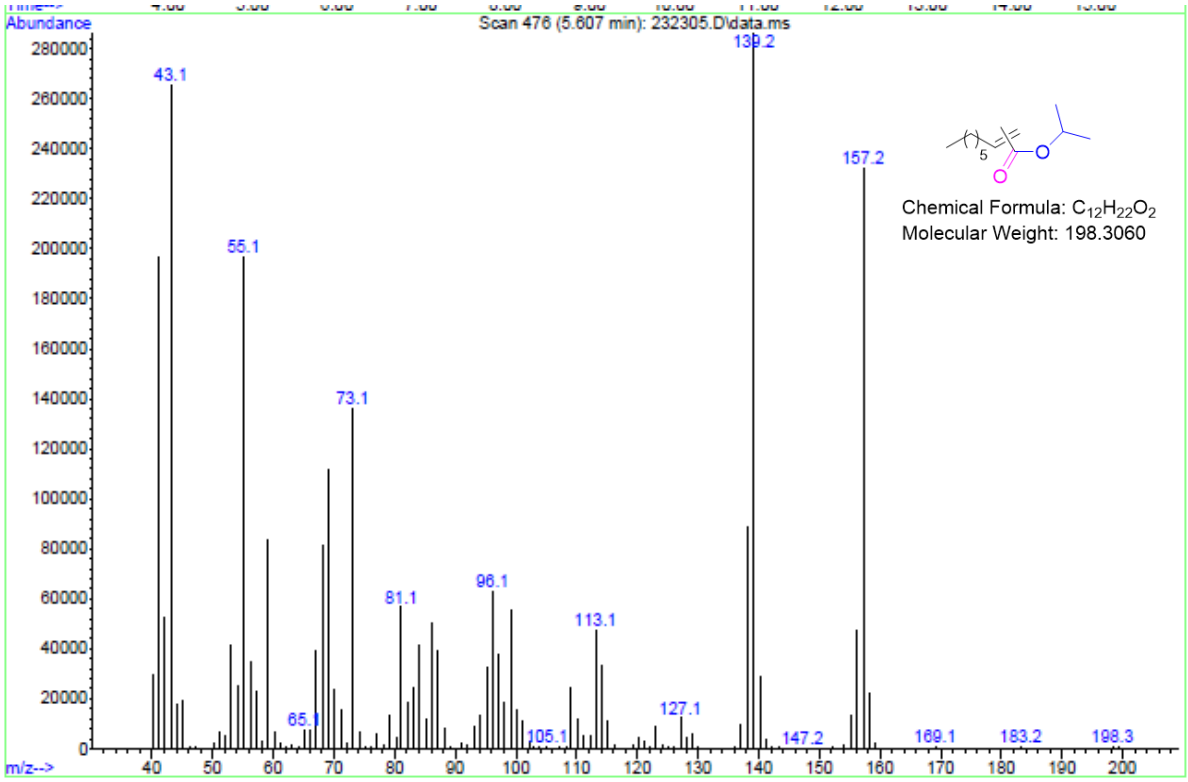
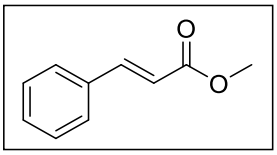


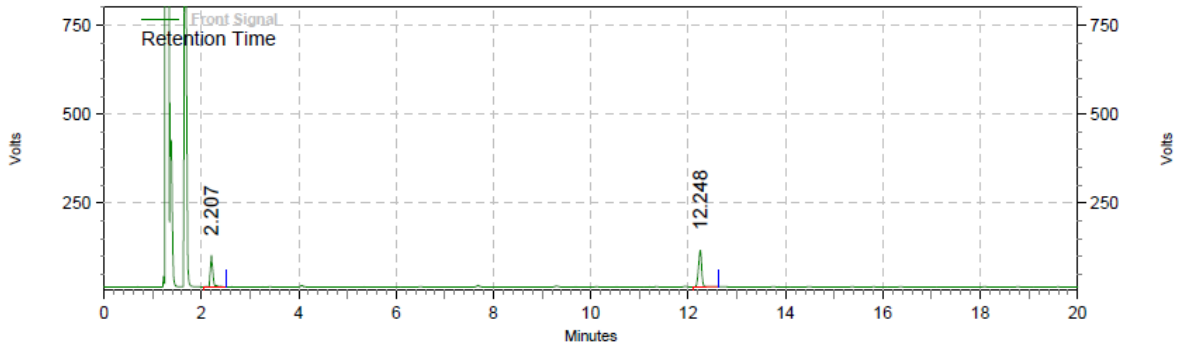
Figure S40C: GC-MS chromatogram of P15B.

Methyl cinnamate P16:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (96:4). After column, a pale yellow liquid was isolated in 55% yield (17.7 mg). GC retention time for phenyl acetylene = 2.2 min.; hydroalkoxycarbonylated product P16 = 12.24 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 16.03 Hz, 1H), 7.53-7.51 (m, 2H), 7.39-7.37 (m, 3H), 6.44 (d, *J* = 16.03 Hz, 1H), 3.81 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 167.6 (C_q), 145.1, 134.6, 130.5, 129.1, 128.2, 117.9, 51.9 (CH_3). The above data is in accordance with previous reports for compound P16.[5]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.207	2408023	40.23	678611	46.27
12.248	3577798	59.77	787906	53.73
Totals	5985821	100.00	1466517	100.00

Figure S41: GC trace of P16.

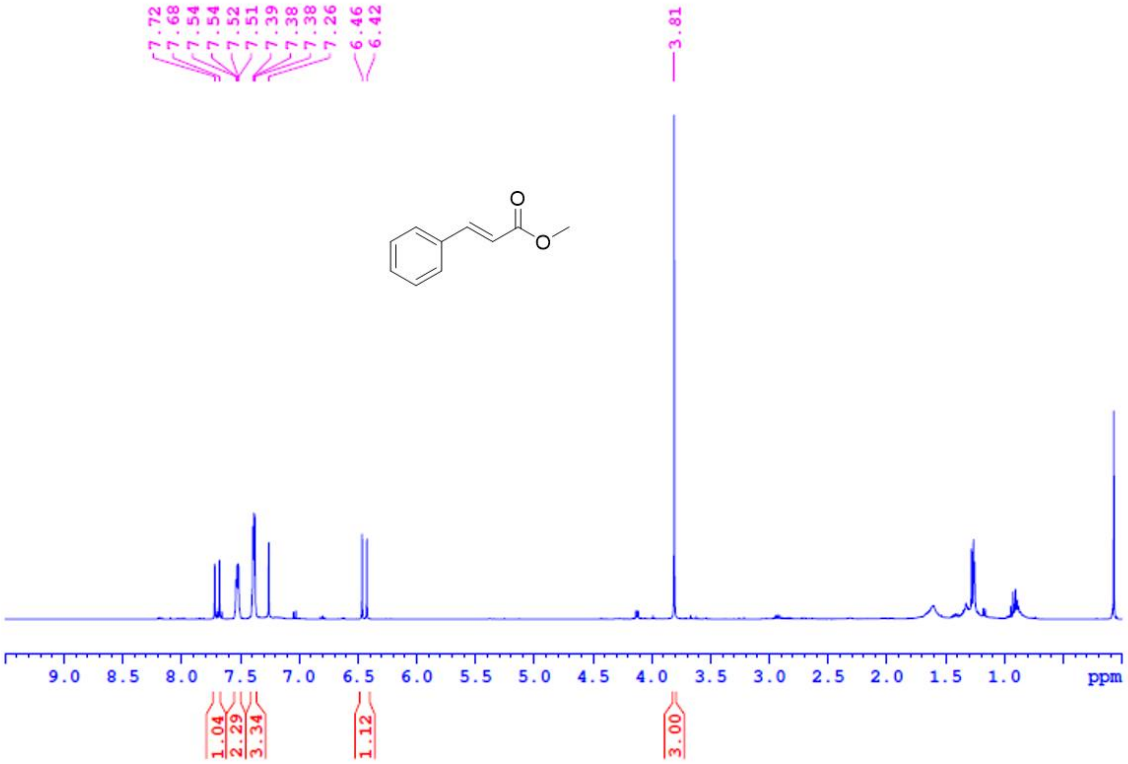


Figure S42: ^{1}H NMR spectrum of P16 in $CDCl_3$.

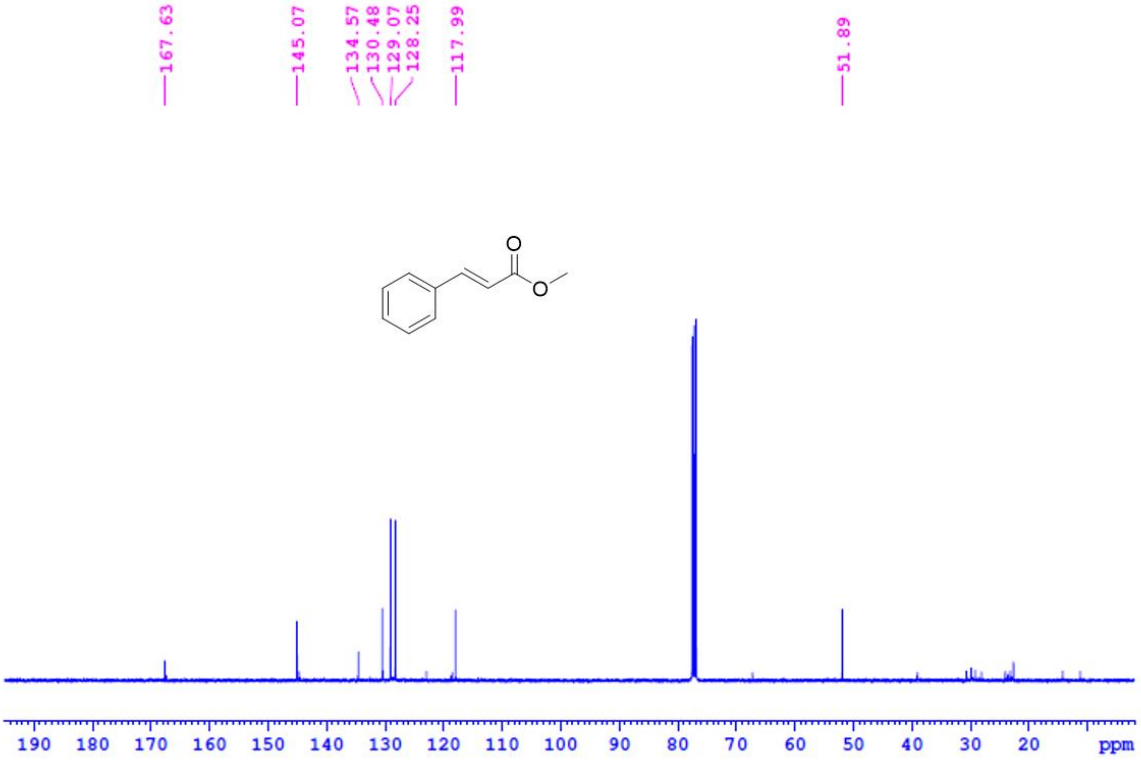
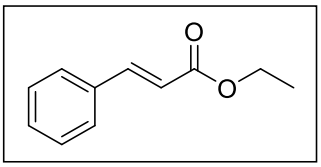


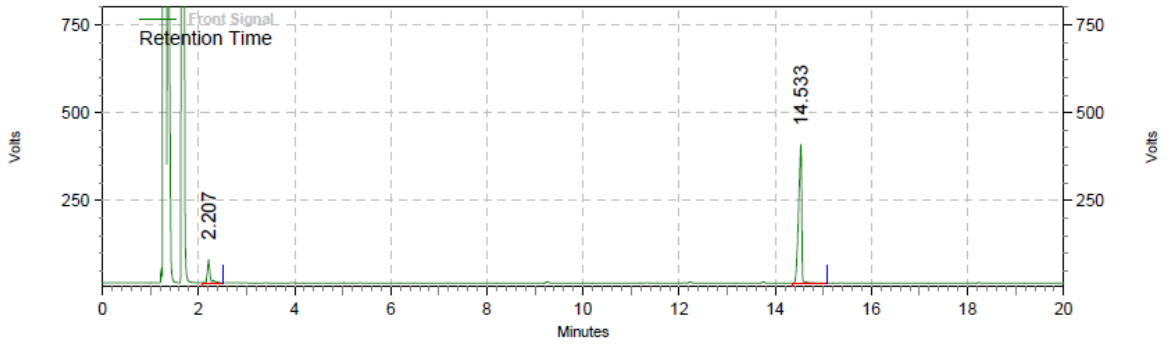
Figure S43: ^{13}C NMR spectrum of P16 in $CDCl_3$.

Ethyl cinnamate P17:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (96:4). After column, a pale yellow liquid was isolated in 78% yield (27.4 mg). GC retention time for phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P17 = 14.53 min.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 16.02 Hz. 1H), 7.52-7.49 (m, 2H), 7.37-7.35 (m, 3H), 6.42 (d, *J* = 16.02 Hz, 1H), 4.24 (q, *J* = 7.13 Hz, 2H), 1.32 (t, *J* = 7.13 Hz, 3H). The above data is in accordance with previous reports for compound P17. [5]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.207	1919756	12.31	510980	14.44
14.533	13674606	87.69	3027233	85.56
Totals	15594362	100.00	3538213	100.00

Figure S44: GC trace of P17.

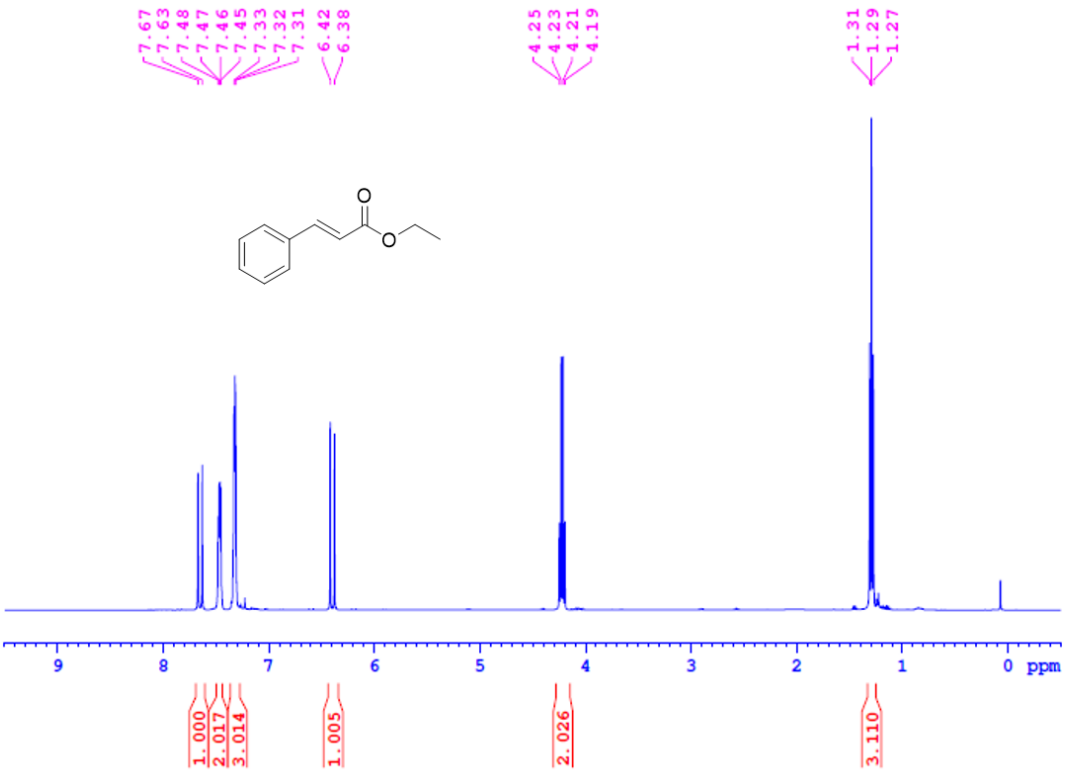


Figure S45: ^{1}H NMR spectrum of P17 in $CDCl_3$.

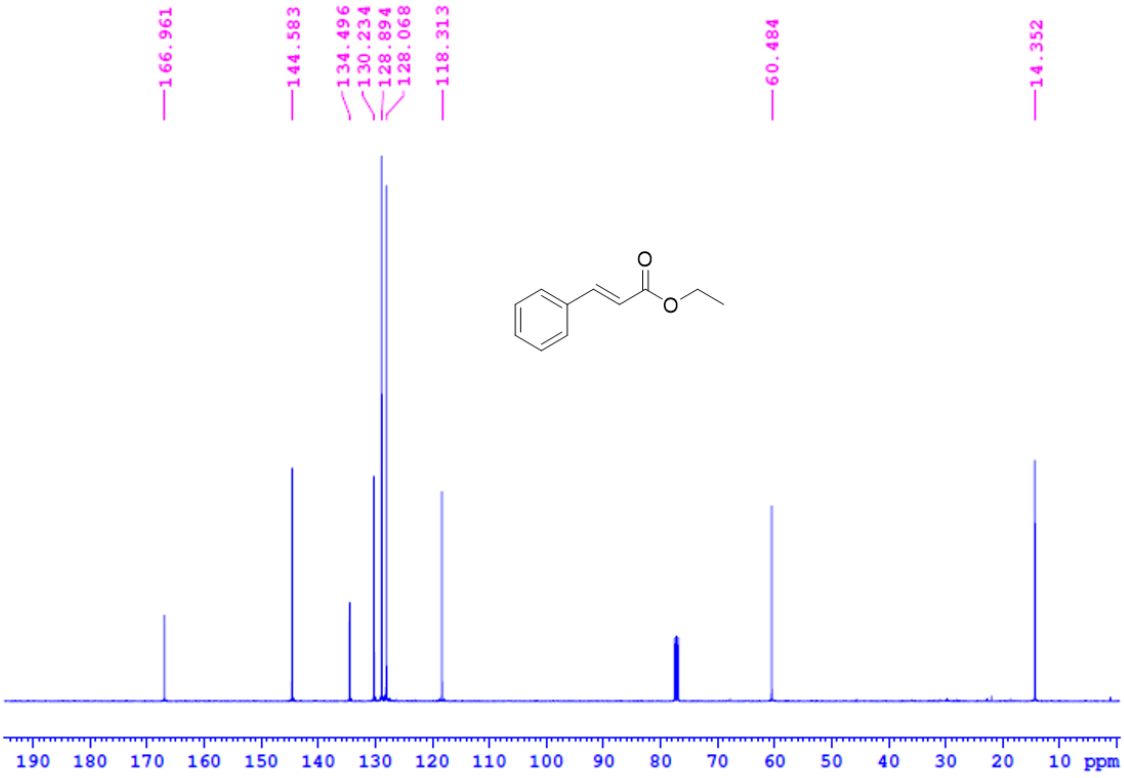
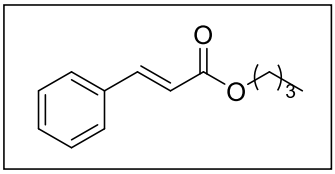


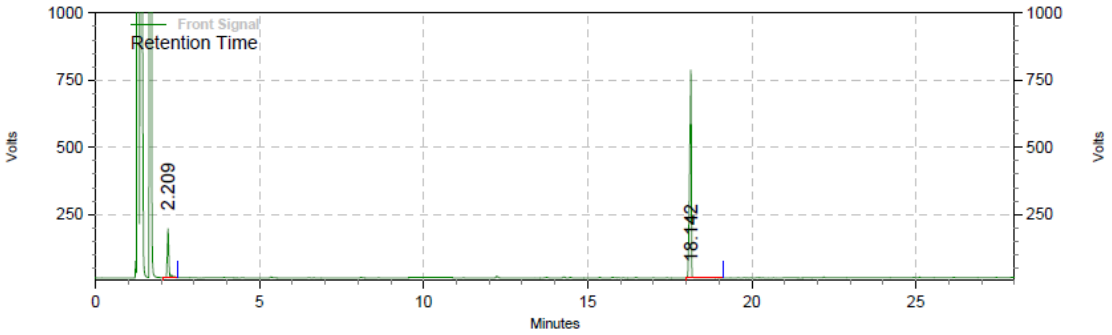
Figure S46: ^{13}C NMR spectrum of P17 in $CDCl_3$.

***n*-butyl cinnamate P18:**

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 75% yield (30.6 mg). GC retention time for phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P18 = 18.14 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 16.02 Hz, 1H), 7.53-7.51 (m, 2H), 7.38-7.37 (m, 3H), 6.44 (d, *J* = 16.01 Hz, 1H), 4.21 (t, *J* = 6.69 Hz, 2H), 1.73-1.66 (m, 2H), 1.49-1.39 (m, 2H), 0.96 (t, *J* = 7.39 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 167.2 (C_q), 144.7, 134.6, 130.3, 129.0, 128.2, 118.4, 64.6, 30.9, 19.3, 13.9 (CH_3). The above data is in accordance with previous reports for compound P18.[11]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.209	4695980	18.69	1403178	19.12
18.142	20435099	81.31	5936356	80.88
Totals	25131079	100.00	7339534	100.00

Figure S47: GC trace of P18.

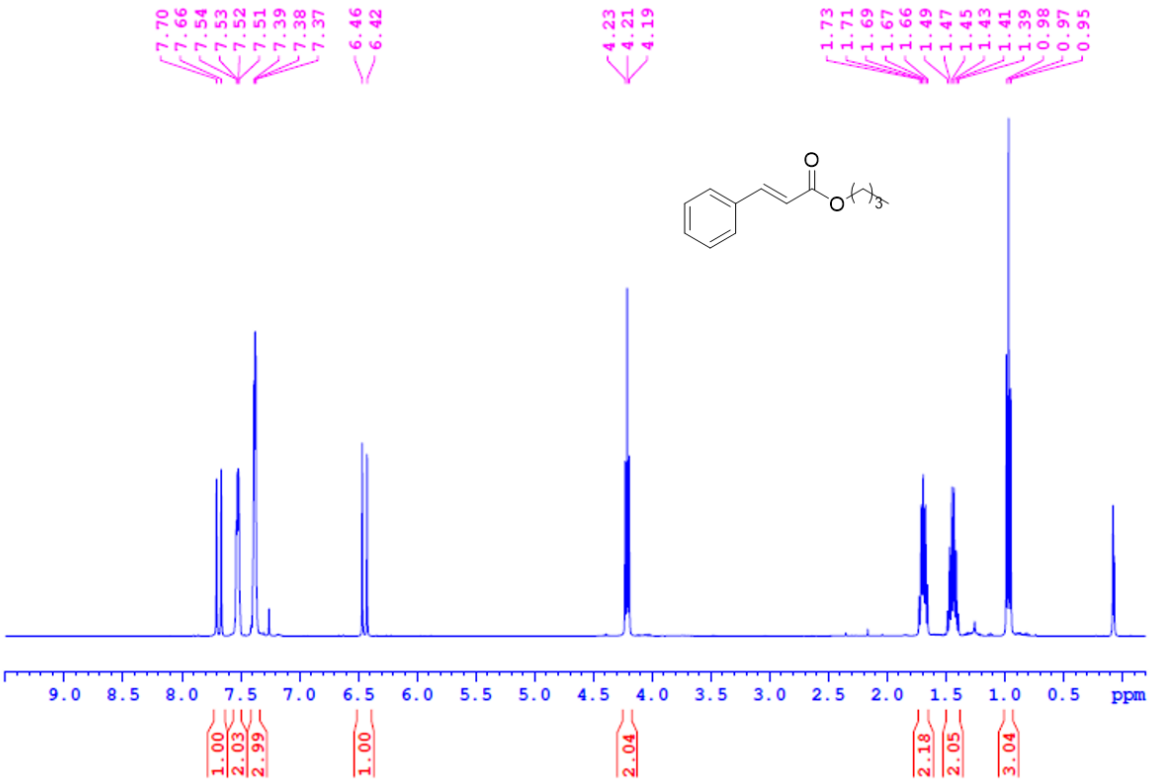


Figure S48: ^{1}H NMR spectrum of P18 in $CDCl_3$.

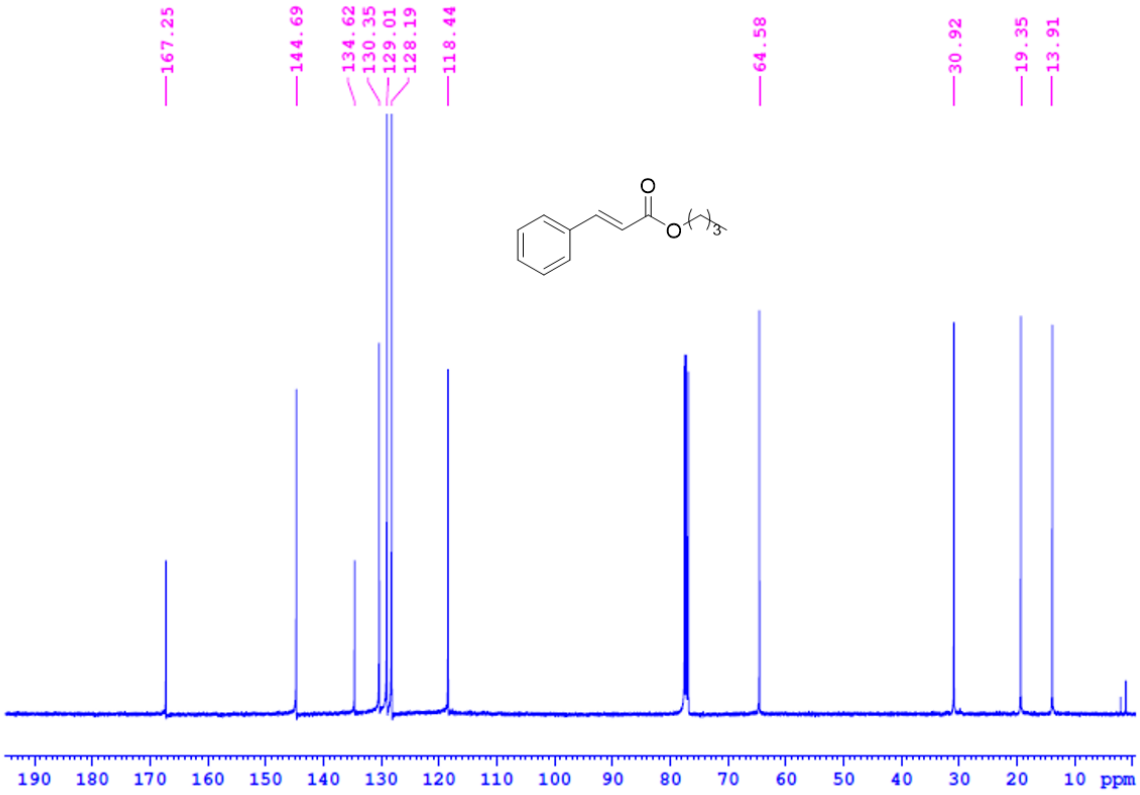
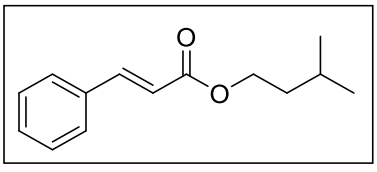


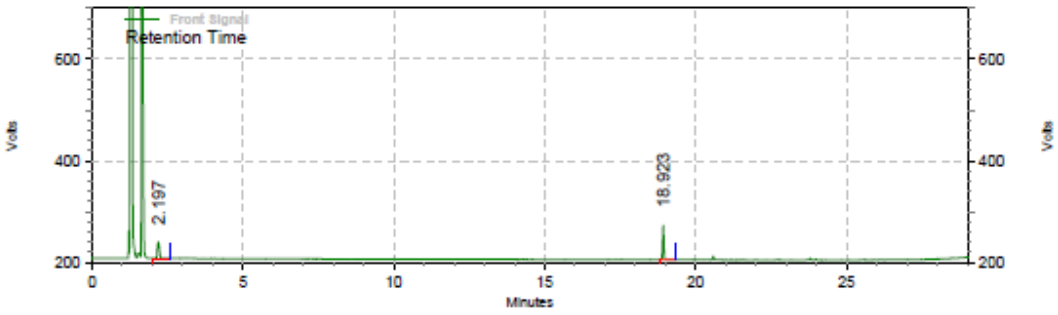
Figure S49: ^{13}C NMR spectrum of P19 in $CDCl_3$.

Isopentyl cinnamate P19:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (96:4). After column, a pale yellow liquid was isolated in 51% yield (22.26 mg). GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P19 = 18.92 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 16.00 Hz, 1H), 7.50 (s, 2H), 7.35 (s, 3H), 6.42 (d, *J* = 15.99 Hz, 1H), 4.22 (t, *J* = 6.64 Hz, 2H), 1.75-1.70 (m, 1H), 1.61-1.56 (m, 2H), 0.94 (d, *J* = 6.46 Hz, 6H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 167.2 (C_q), 144.7, 134.6, 130.3, 128.9, 128.2, 118.4, 63.3, 37.6, 25.2, 22.6. The above data is in accordance with previous reports for compound P19. [5]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.197	1215283	44.96	245667	32.06
18.923	1487849	55.04	520509	67.94
Totals	2703132	100.00	766176	100.00

Figure S50: GC trace of P19.

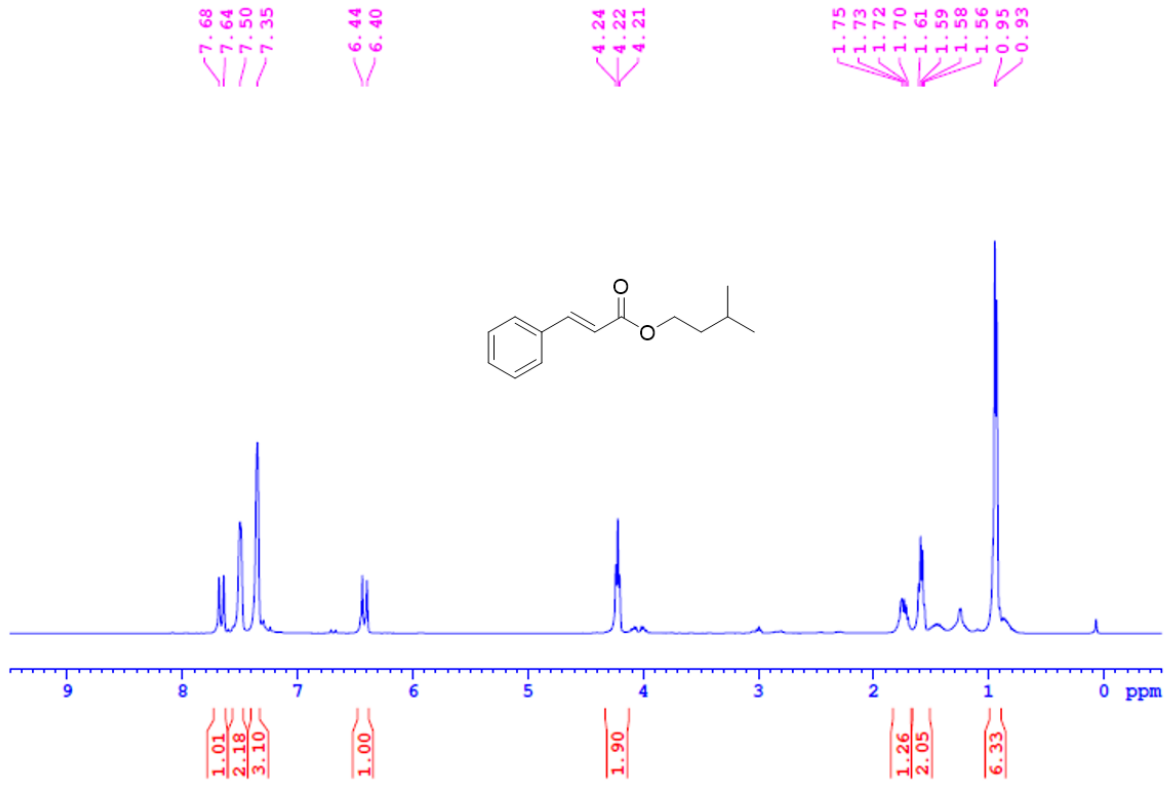


Figure S51: ^{1}H NMR spectrum of P19 in $CDCl_3$.

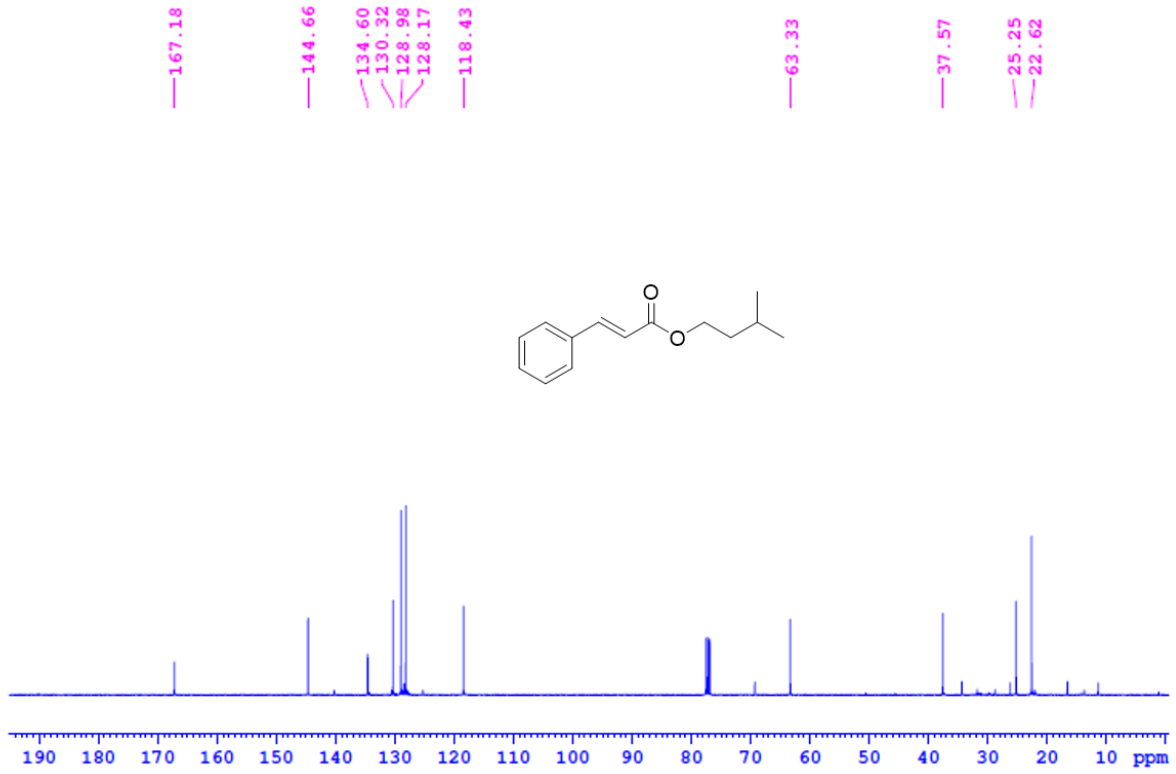
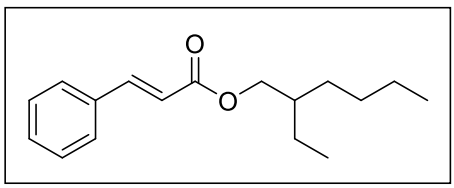


Figure S52: ^{13}C NMR spectrum of P19 in $CDCl_3$.

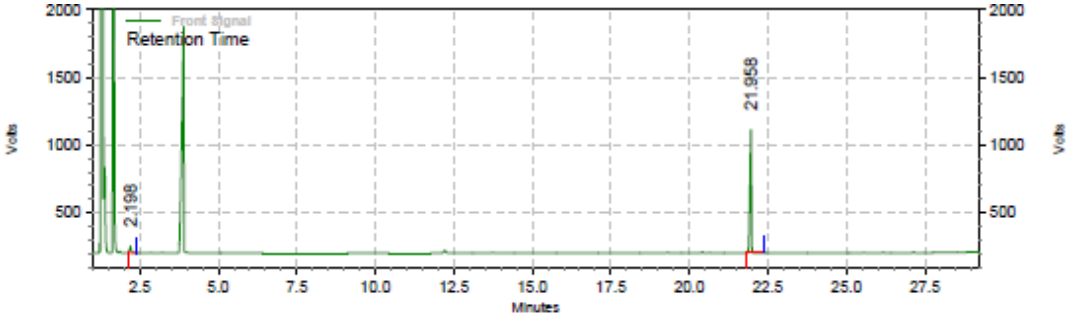
2-ethylhexyl cinnamate P20:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 86% yield (44.8 mg). GC retention time for phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P20 = 21.95 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 16.01 Hz, 1H), 7.55-7.22 (m, 2H), 7.39-7.38 (m, 3H), 6.45 (d, *J* = 16.01 Hz, 1H), 4.13 (d, J = 2.50 Hz, 1H), 4.11 (d, J = 2.75 Hz, 1H) 1.59

(br s, 4H), 1.32-1.31 (m, 6H), 0.92-0.90 (m, 5H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 167.4 (C_q), 144.7, 134.6, 130.4, 129.0, 128.2, 118.5, 67.2, 39.0, 30.6, 29.1, 24.0, 23.2, 14.3, 11.2 (CH_3). The above data is in accordance with previous reports for compound P20.[12]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.198	1346736	5.84	383664	5.21
21.958	21715040	94.16	6982032	94.79
Totals	23061776	100.00	7365696	100.00

Figure S53: GC trace of P20.

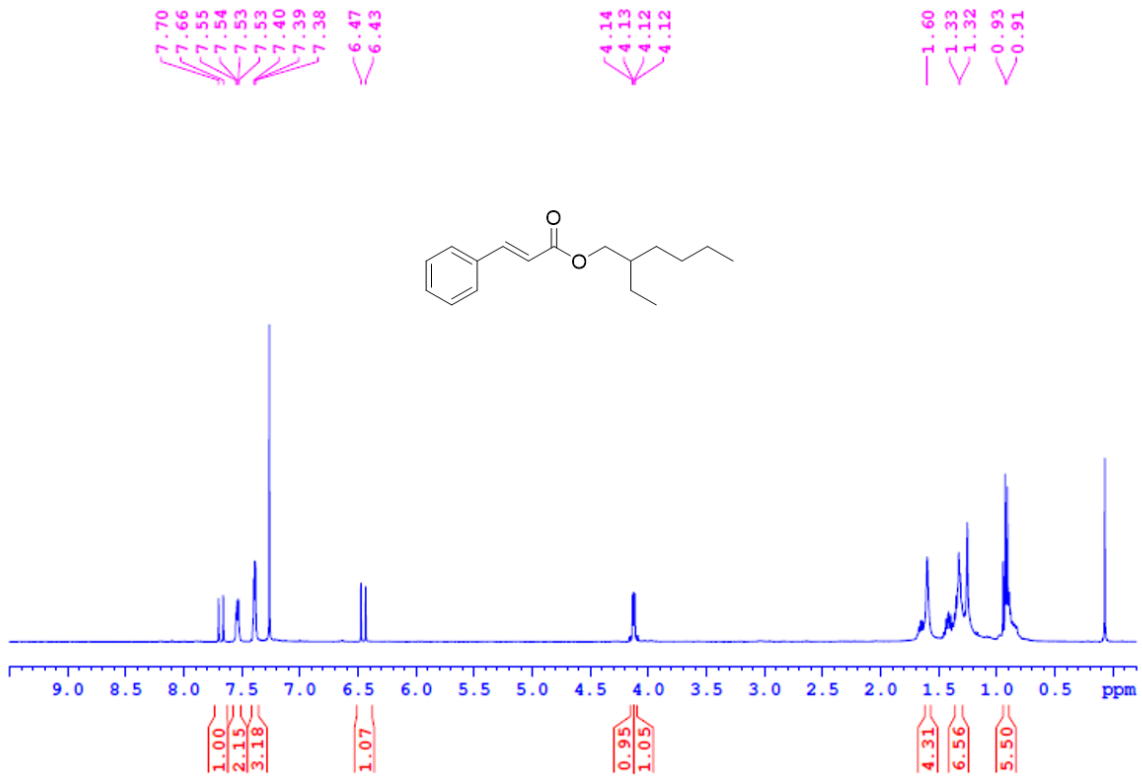


Figure S54: ^{1}H NMR spectrum of P20 in $CDCl_3$.

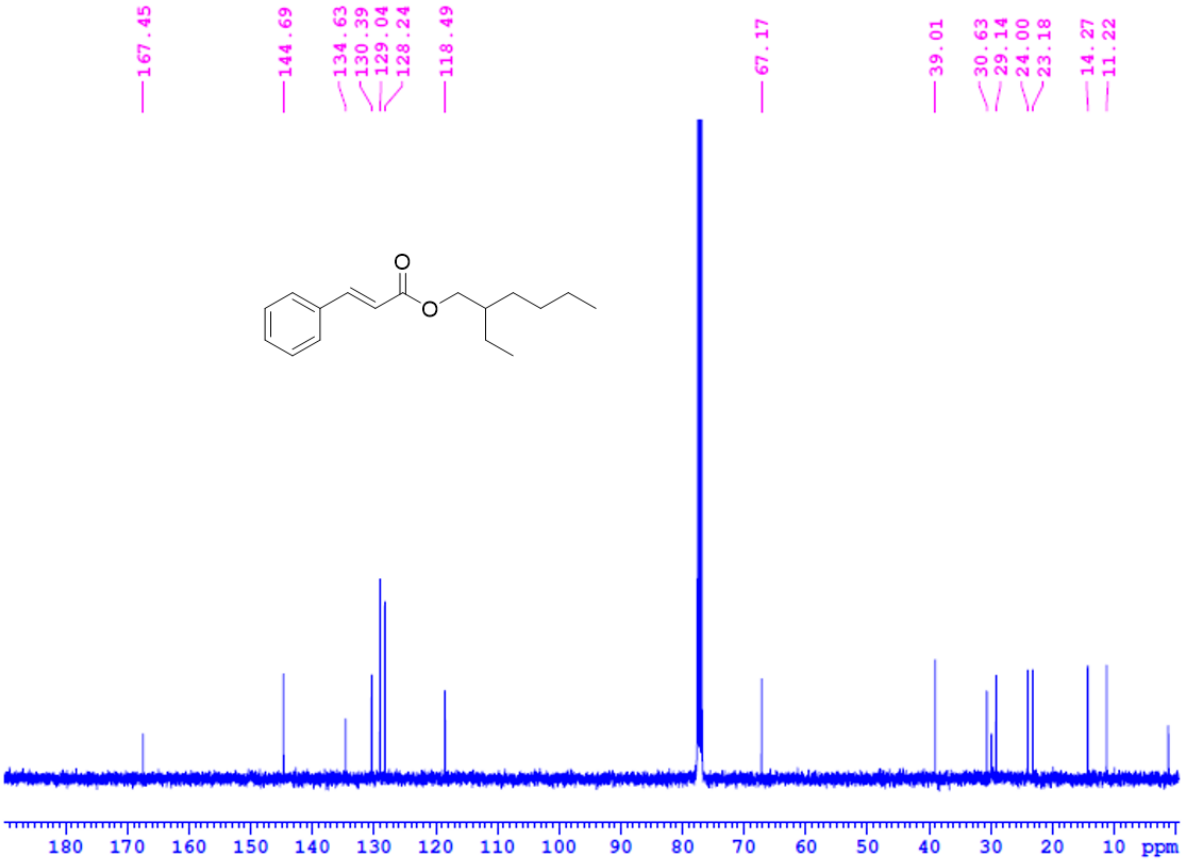
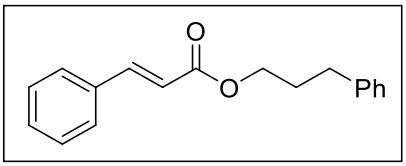


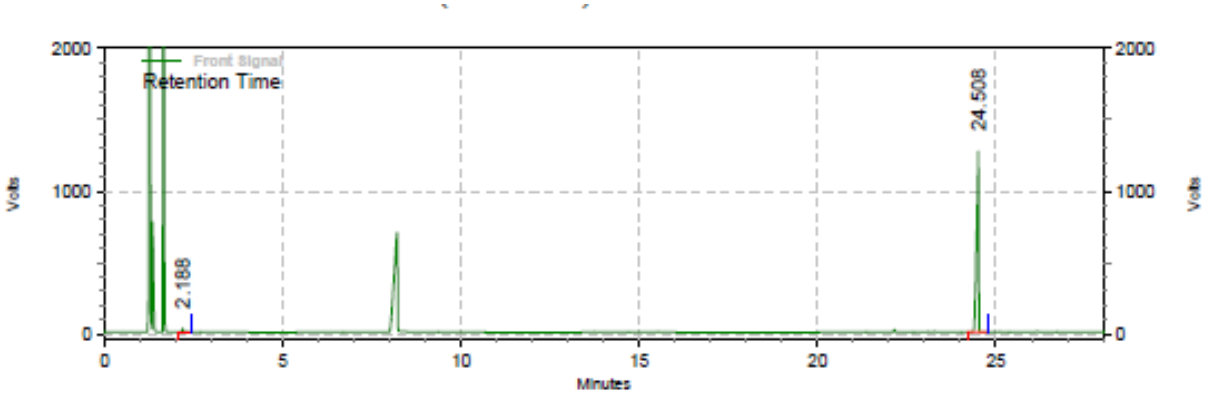
Figure S55: ^{13}C NMR spectrum of P20 in $CDCl_3$.

3-phenylpropyl cinnamate P21:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 79% yield (42.1 mg). GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P21 = 24.50 min.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 16.02 Hz, 1H), 7.46-7.44 (m, 2H), 7.30-7.29 (m, 3H), 7.25-7.21 (m, 2H), 7.15-7.11 (m, 3H), 6.39 (d, *J* = 16.01 Hz, 1H), 4.17 (t, *J* = 6.54 Hz, 2H), 2.68 (t, *J* = 15.35, Hz, 2H), 1.97 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 166.9 (C_q), 144.7, 141.3, 134.5, 130.3, 128.9, 128.5, 128.5, 128.1, 126.1, 118.2, 63.9, 32.3, 30.3. The above data is in accordance with previous reports for compound P21.[13]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.188	534176	1.35	186100	1.88
24.508	38944455	98.65	9699550	98.12
Totals	39478631	100.00	9885650	100.00

Figure S56: GC trace of P21.

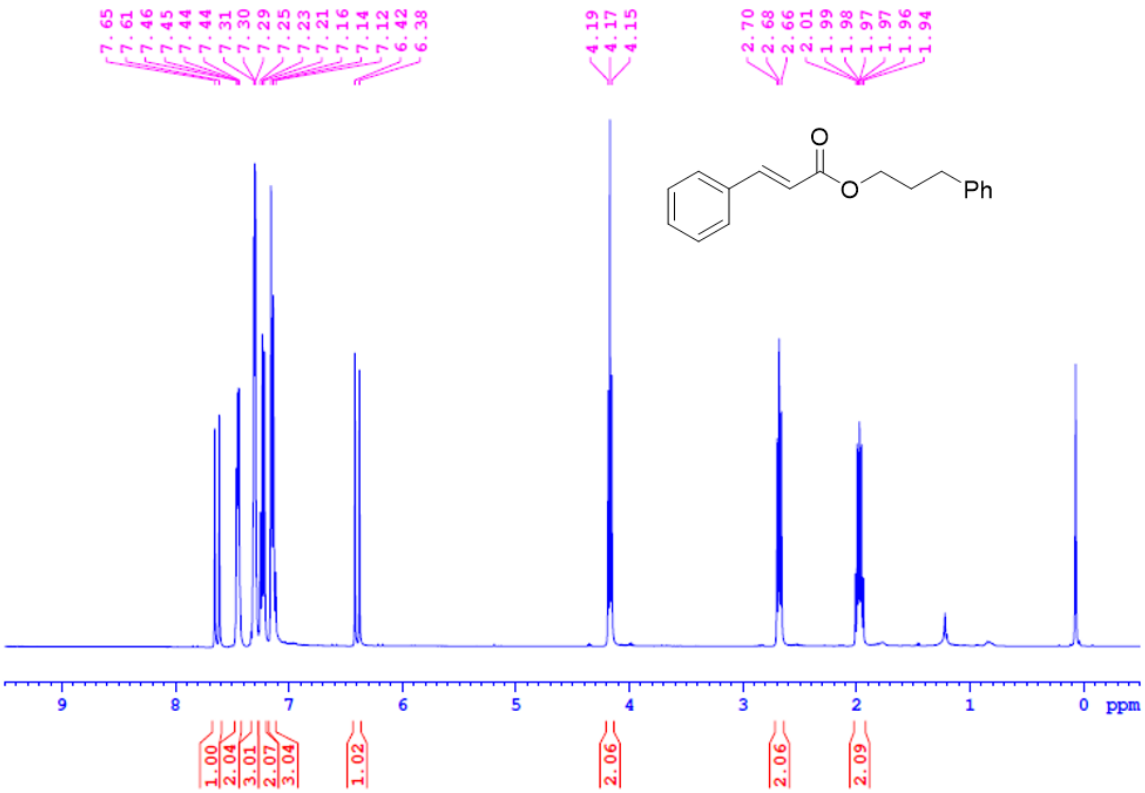


Figure S57: ^{1}H NMR spectrum of P21 in $CDCl_3$.

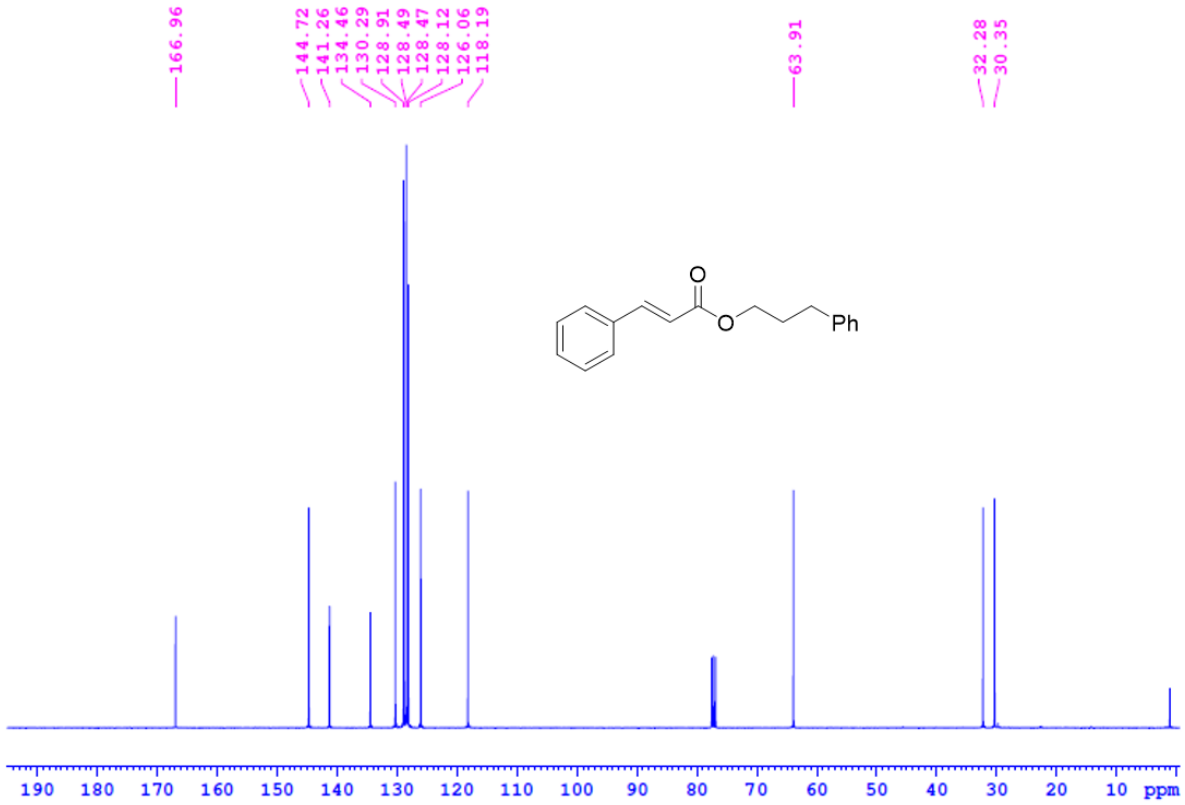
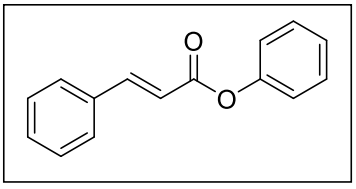


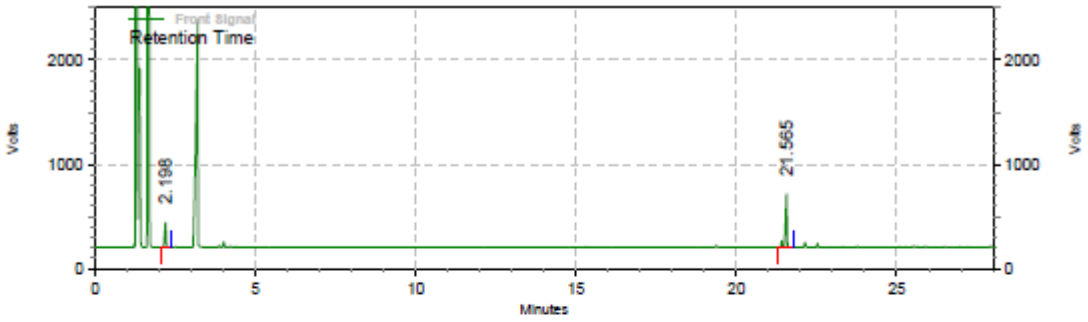
Figure S58: ^{13}C NMR spectrum of P21 in $CDCl_3$.

Phenyl cinnamate P22:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 62% yield (27.8 mg). GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P22 = 21.56 min.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 15.97 Hz, 1H), 7.57 (m, 2H), 7.41-7.40 (m, 5H), 7.24 (t, *J* = 7.14 Hz, 1H), 7.16 (d, *J* = 7.89 Hz, 2H), 6.63 (d, *J* = 15.97 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 165.56 (C_q), 150.9, 146.7, 134.4, 130.9, 129.6, 129.2, 128.5, 125.9, 121.8, 117.5. The above data is in accordance with previous reports for compound P22.[14]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.198	5512448	29.68	1831645	31.81
21.565	13061583	70.32	3926064	68.19
Totals	18574031	100.00	5757709	100.00

Figure S59: GC trace of P22.

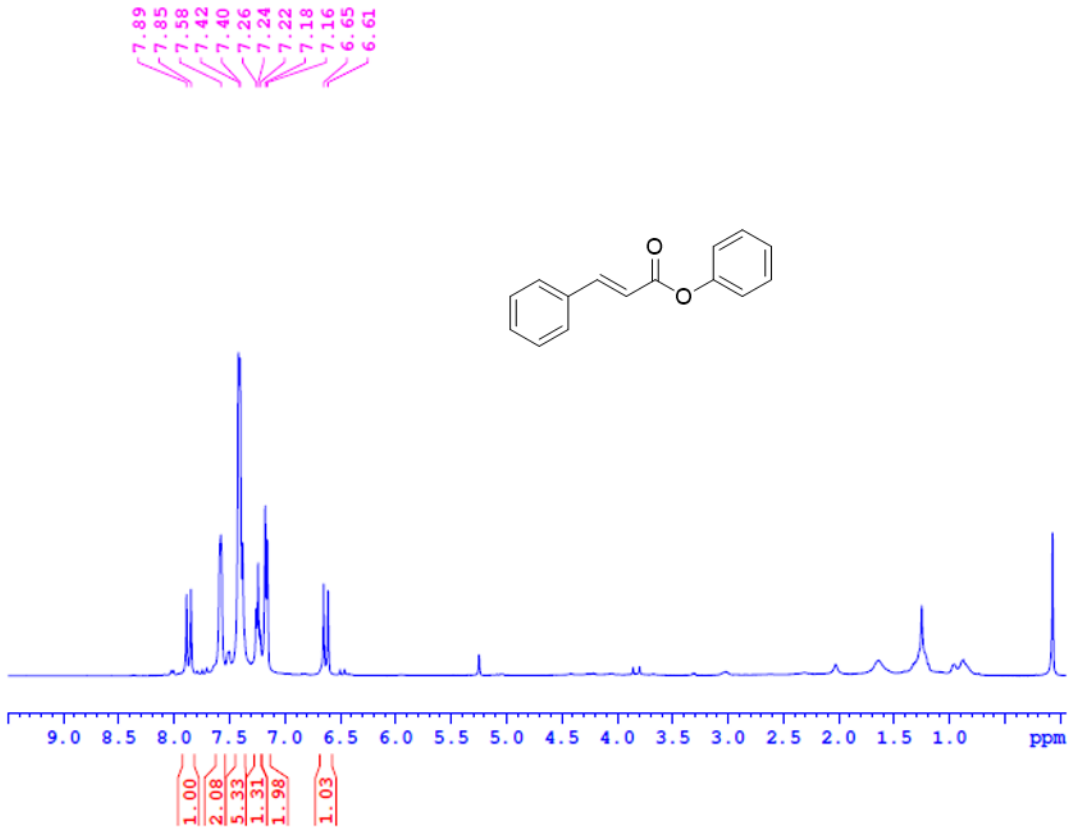


Figure S60: ^{1}H NMR spectrum of P22 in $CDCl_3$.

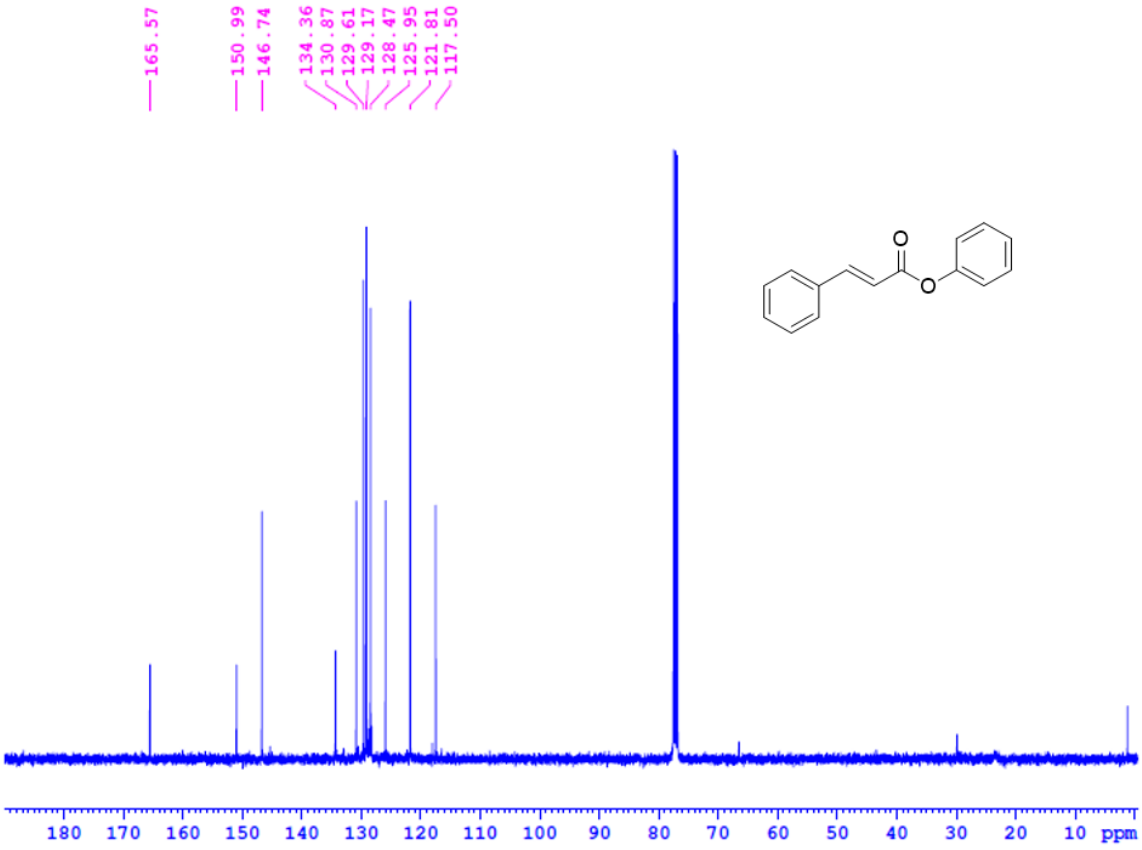
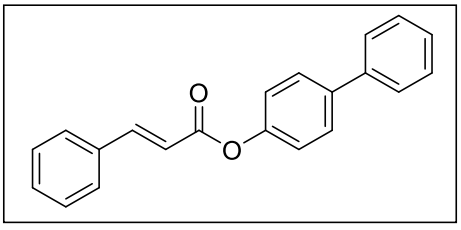


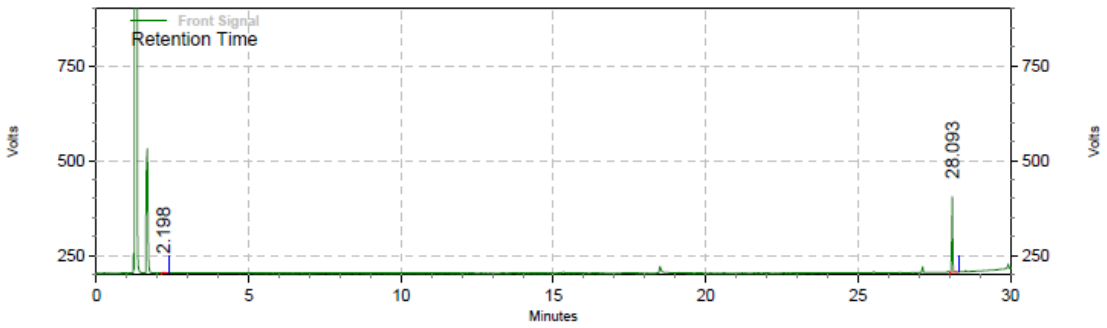
Figure S61: ^{13}C NMR spectrum of P22 in $CDCl_3$.

[1,1'-biphenyl]-4-yl cinnamate P23:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (96:4). After column, a pale yellow liquid was isolated in 92% yield (55.3 mg). GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P23 = 28.09 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 16.01 Hz, 1H), 7.62-7.56 (m, 6H), 7.45-7.41 (m, 5H), 7.36-7.32 (m, 1H), 7.25-7.23 (m, 2H), 6.65 (d, *J* = 16.00 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 165.6 (C_q), 150.4, 146.9, 140.6, 139.1, 134.3, 130.9, 129.2, 128.9, 128.5, 128.4, 127.5, 127.3, 122.1, 117.4. The above data is in accordance with previous reports for compound P23.[15]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.198	46642	1.41	7215	0.47
28.093	3269670	98.59	1524933	99.53
Totals	3316312	100.00	1532148	100.00

Figure S62: GC trace of P23.

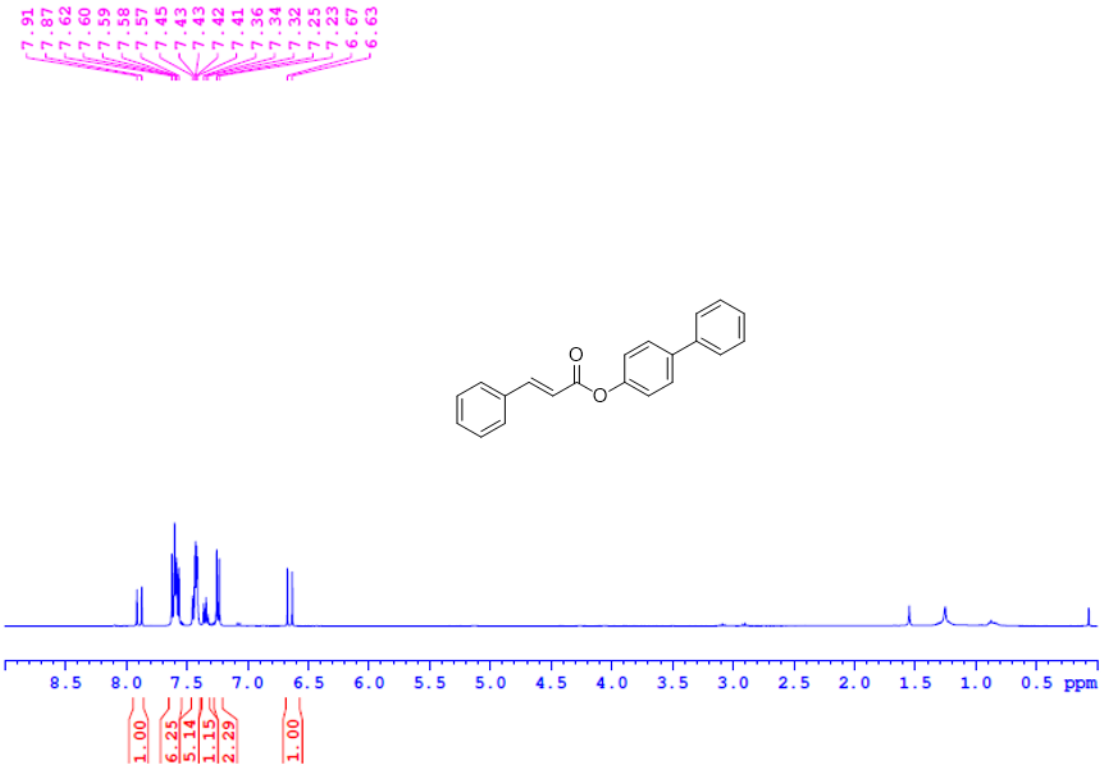


Figure S63: ^{1}H NMR spectrum of P23 in $CDCl_3$.

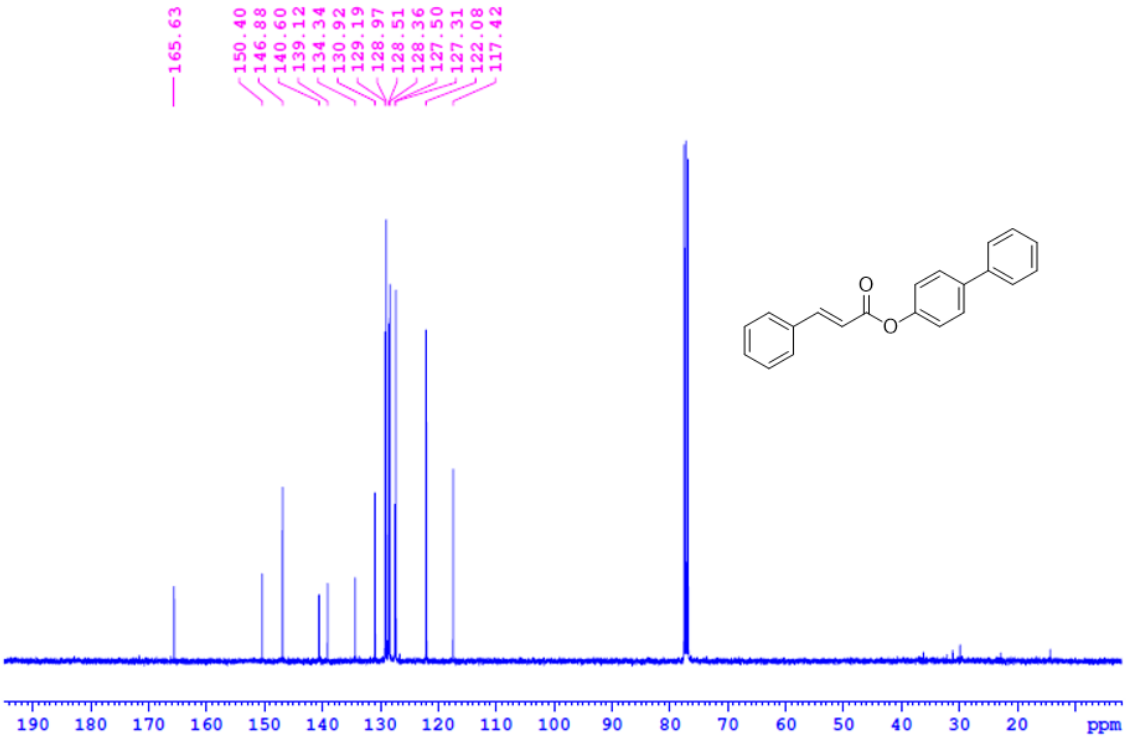
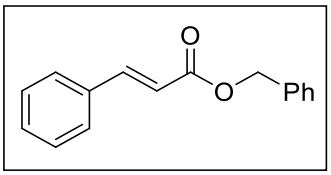


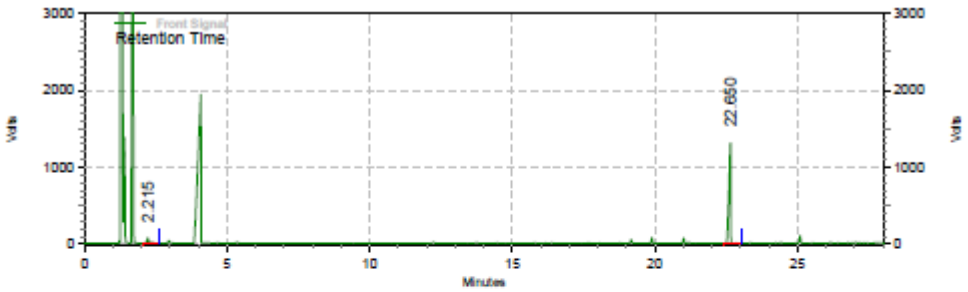
Figure S64: ^{13}C NMR spectrum of P23 in $CDCl_3$.

Benzyl cinnamate P24:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (96:4). After column, a pale yellow liquid was isolated in 86% yield (40.9 mg). GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P24 = 22.65 min.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 16.02 Hz, 1H), 7.533-7.51 (m, 2H), 7.44-7.37 (m, 8H), 6.49 (d, *J* = 16.06 Hz, 1H), 5.26 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 166.9 (C_q), 136.2, 134.6, 130.5, 129.1, 128.8, 128.6, 128.5, 128.3, 118.1, 65.5. The above data is in accordance with previous reports for compound P24.[5]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.215	2267880	5.16	520944	4.97
22.650	41661452	94.84	9967963	95.03
Totals	43929332	100.00	10488907	100.00

Figure S65: GC trace of P24.

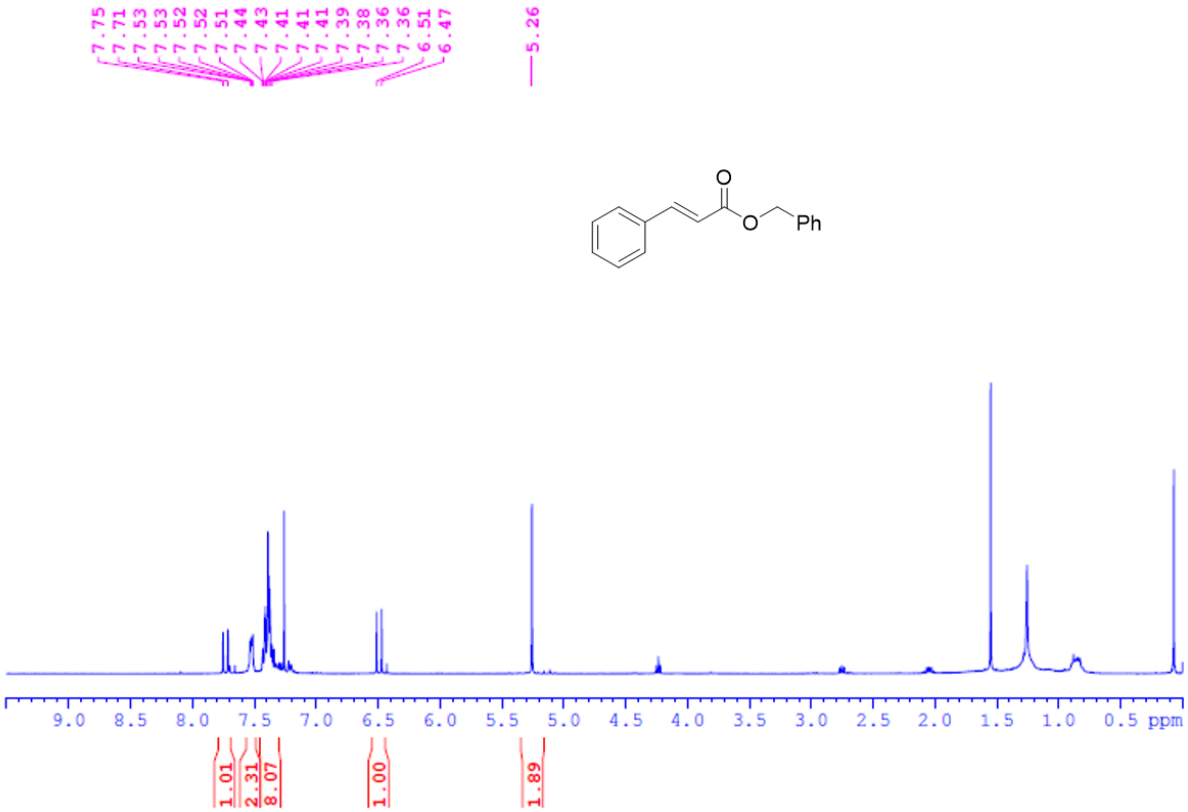


Figure S66: ^{1}H NMR spectrum of P24 in $CDCl_3$.

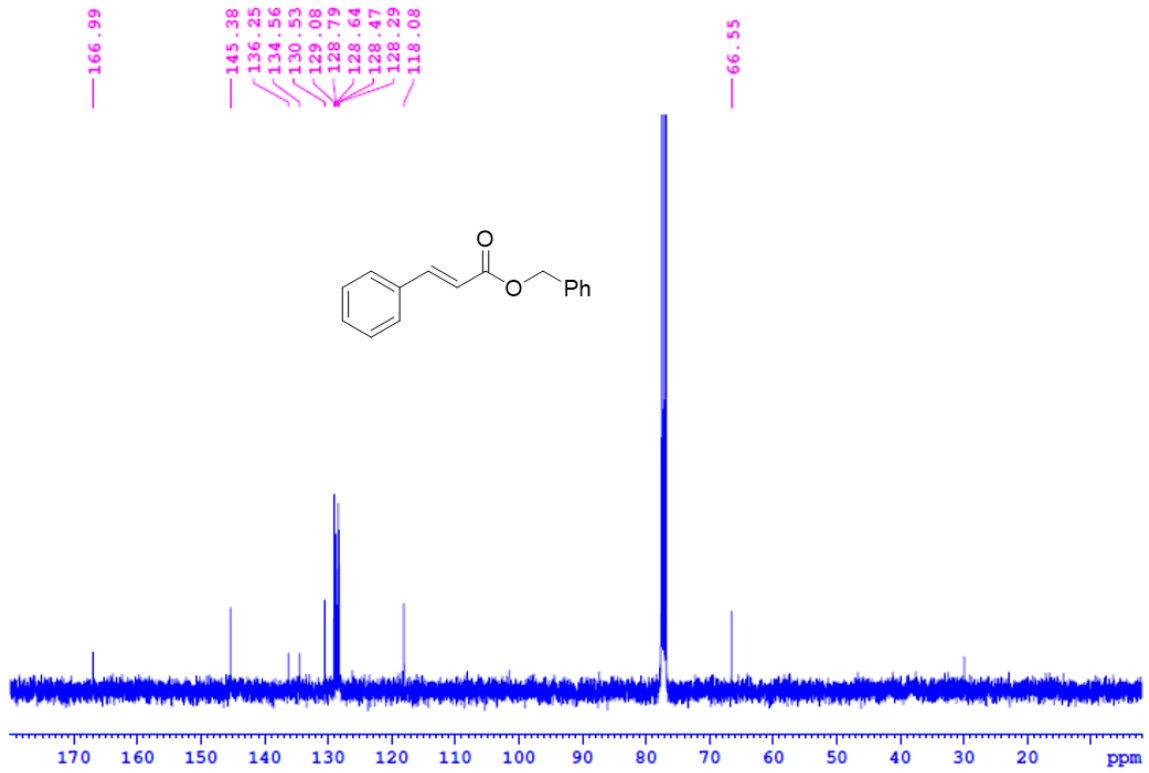
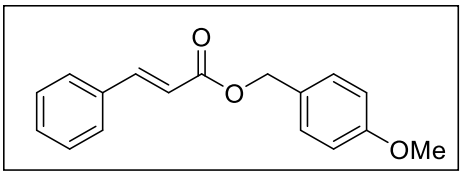


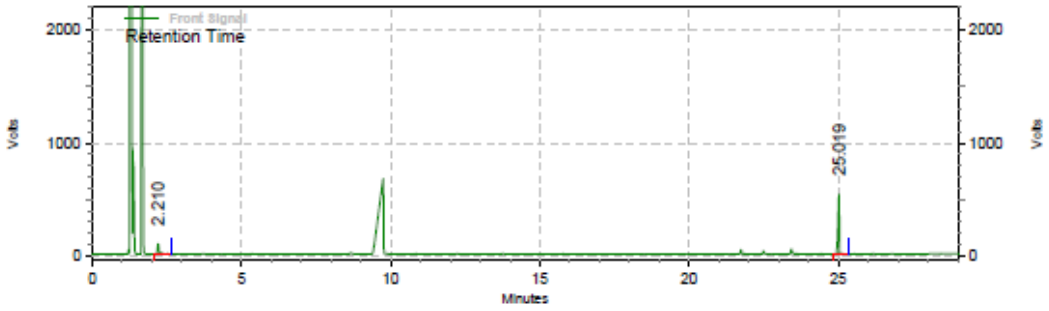
Figure S67: ^{13}C NMR spectrum of P24 in $CDCl_3$.

4-methoxybenzyl cinnamate P25:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 72% yield (38.6 mg). GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P25 = 25.01 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 16.02 Hz, 1H), 7.48-7.45 (m, 2H), 7.34-7.32 (m, 5H), 6.88 (d, *J* = 8.69 Hz, 2H), 6.43 (d, *J* = 16.01 Hz, 1H), 5.16 (s, 2H), 3.77 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 166.9 (C_q), 159.8, 145.1, 134.5, 130.4, 130.3, 128.9, 128.3, 128.2, 118.1, 114.1, 66.3, 55.4. The above data is in accordance with previous reports for compound P25.[5]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.210	2624229	16.78	711689	14.90
25.019	13014989	83.22	4065480	85.10
Totals	15639218	100.00	4777169	100.00

Figure S68: GC trace of P25.

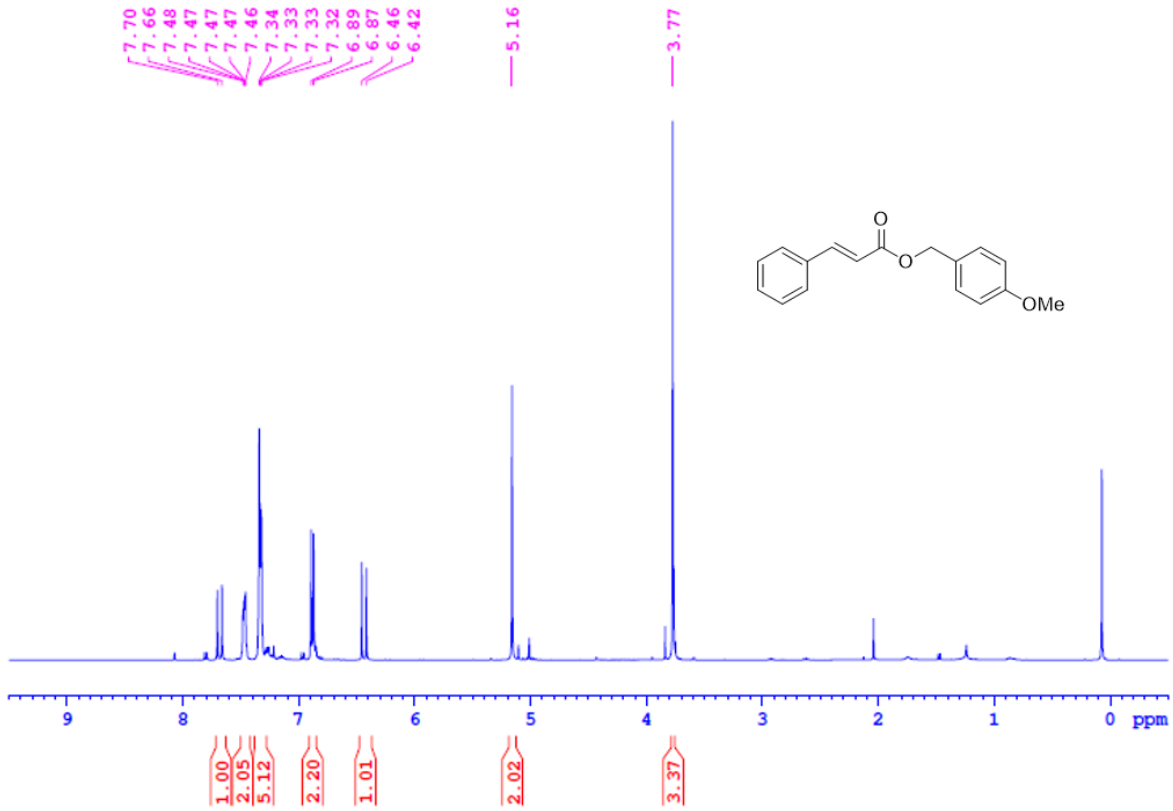


Figure S69: ^{1}H NMR spectrum of P25 in $CDCl_3$.

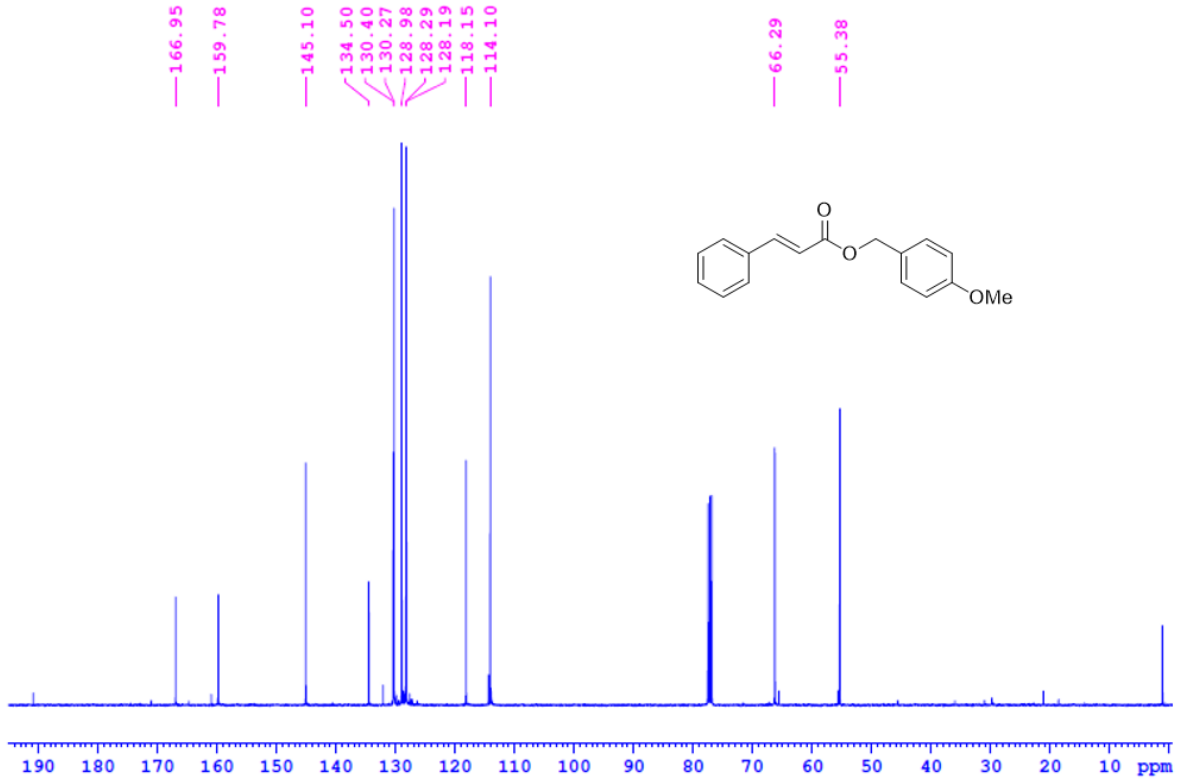
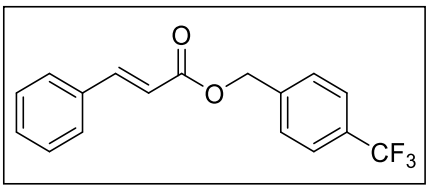


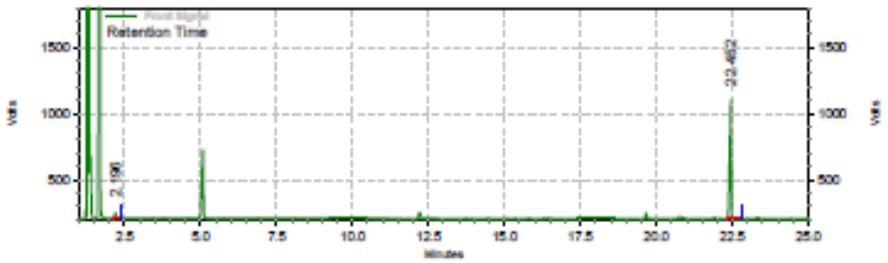
Figure S70: ^{13}C NMR spectrum of P25 in $CDCl_3$.

4-(trifluoromethyl)benzyl cinnamate P26:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (96:4). After column, a pale yellow liquid was isolated in 88% yield (54 mg). GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P26 = 22.45 min.



^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 16.03 Hz, 1H), 7.66-7.61 (m, 2H), 7.54-7.50 (m, 4H), 7.40-7.37 (m, 3H), 6.49 (d, *J* = 16.02 Hz, 1H), 5.29 (s, 2H). The above data is in accordance with previous reports for compound P26.[16]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.196	1081137	4.25	332394	4.62
22.452	24362489	95.75	6869421	95.38
Totals	25443626	100.00	7201815	100.00

Figure S71: GC trace of P26.

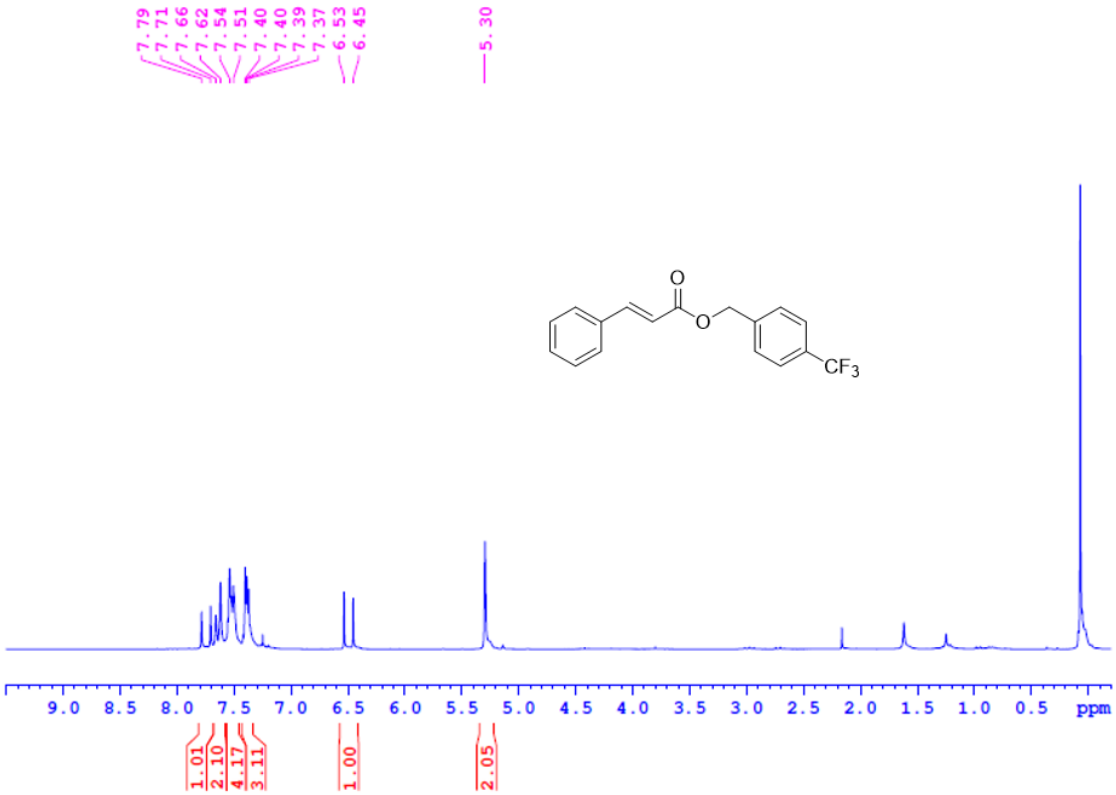
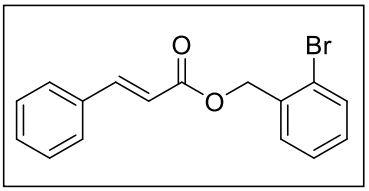


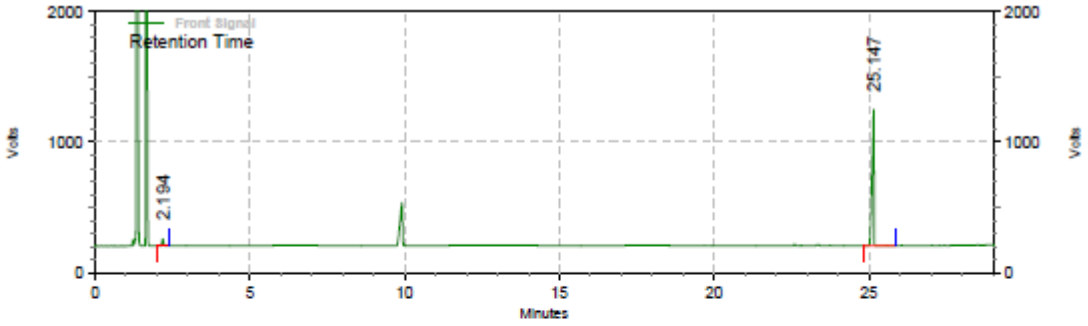
Figure S72: ^{1}H NMR spectrum of P26 in $CDCl_3$.

2-bromobenzyl cinnamate P27:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 87% yield (55.2 mg). GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P27 = 25.14 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 16.02 Hz, 1H), 7.55 (d, *J* = 7.96 Hz, 1H), 7.49-7.47 (m, 2H), 7.43 (d, *J* = 7.58 Hz, 1H), 7.35-7.33 (m, 3H), 7.29 (t, *J* = 7.51 Hz, 1H), 7.15 (t, *J* = 7.61 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 5.29 (s, 2H). **^{13}C NMR (500 MHz, $CDCl_3$):** δ = 166.6, 145.6, 135.4, 134.3, 132.9, 130.5, 129.9, 129.8, 128.9, 128.2, 127.6, 123.5, 117.6, 65.9. The above data is in accordance with previous reports for compound P27.[5]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.194	1377863	3.90	413429	4.91
25.147	33953885	96.10	8001022	95.09
Totals	35331748	100.00	8414451	100.00

Figure S73: GC trace of P27.

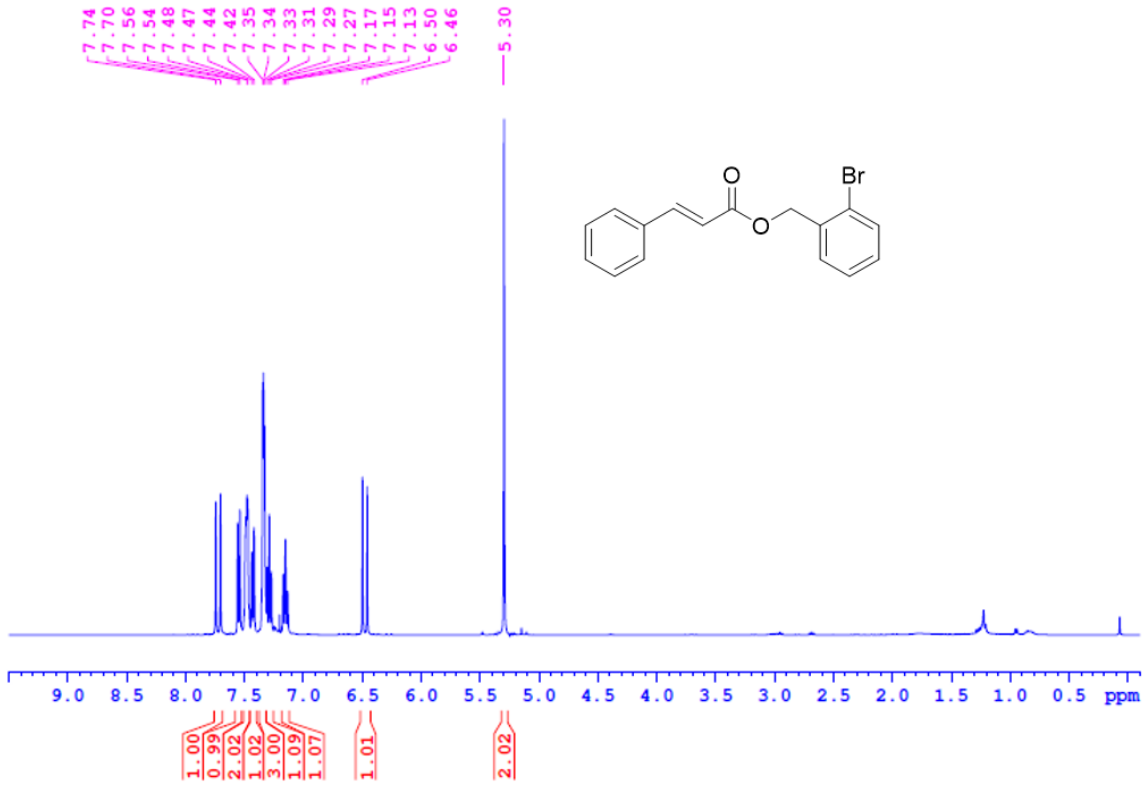


Figure S74: ^{1}H NMR spectrum of P27 in $CDCl_3$.

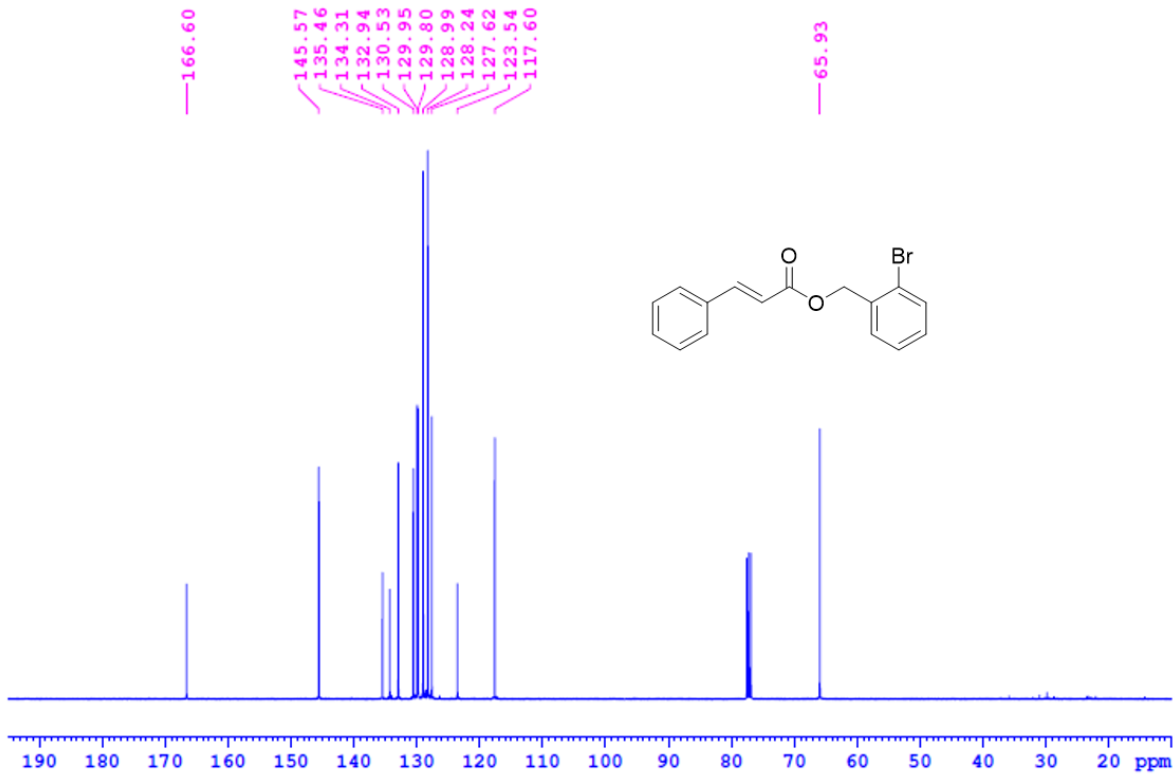
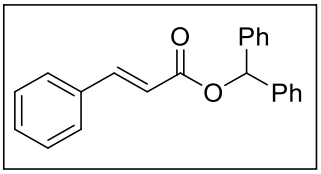


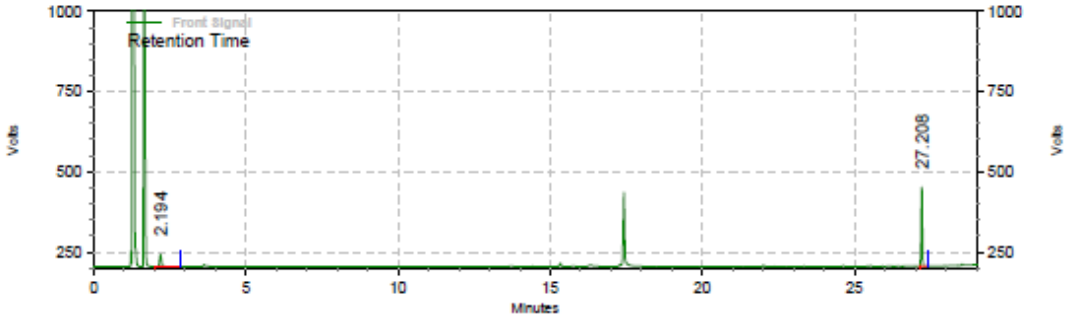
Figure S75: ^{13}C NMR spectrum of P27 in $CDCl_3$.

Benzhydryl cinnamate P28:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 71% yield (44.6 mg). GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P28 = 27.20 min.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 15.98 Hz, 1H), 7.50 (br s, 2H), 7.37-7.27 (m, 13H), 7.01 (s, 1H), 6.54 (d, *J* = 15.99 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 166.1 (C_q), 145.6, 140.4, 134.5, 130.5, 129.0, 128.7, 128.3, 128.1, 127.3, 118.2, 77.1. The above data is in accordance with previous reports for compound P28. [5]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.194	1227119	20.88	290178	13.27
27.208	4651236	79.12	1896217	86.73
Totals	5878355	100.00	2186395	100.00

Figure S76: GC trace of P28.

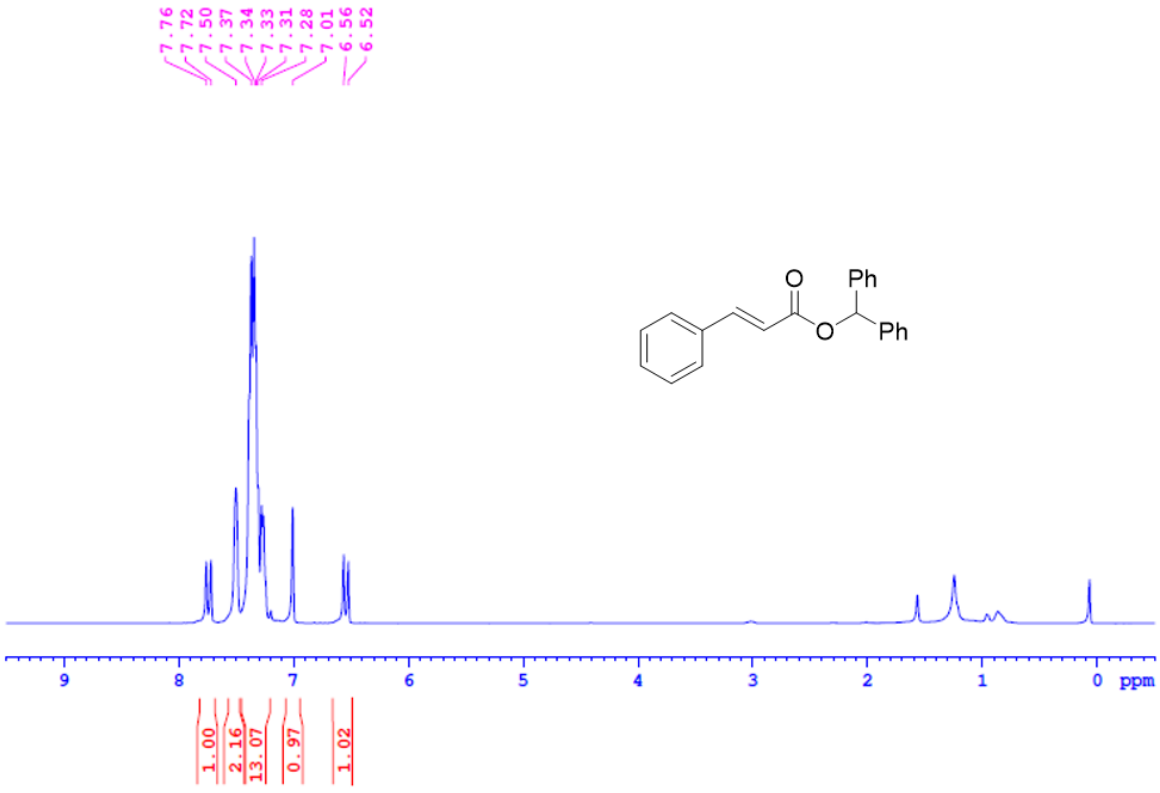


Figure S77: ^{1}H NMR spectrum of P28 in $CDCl_3$.

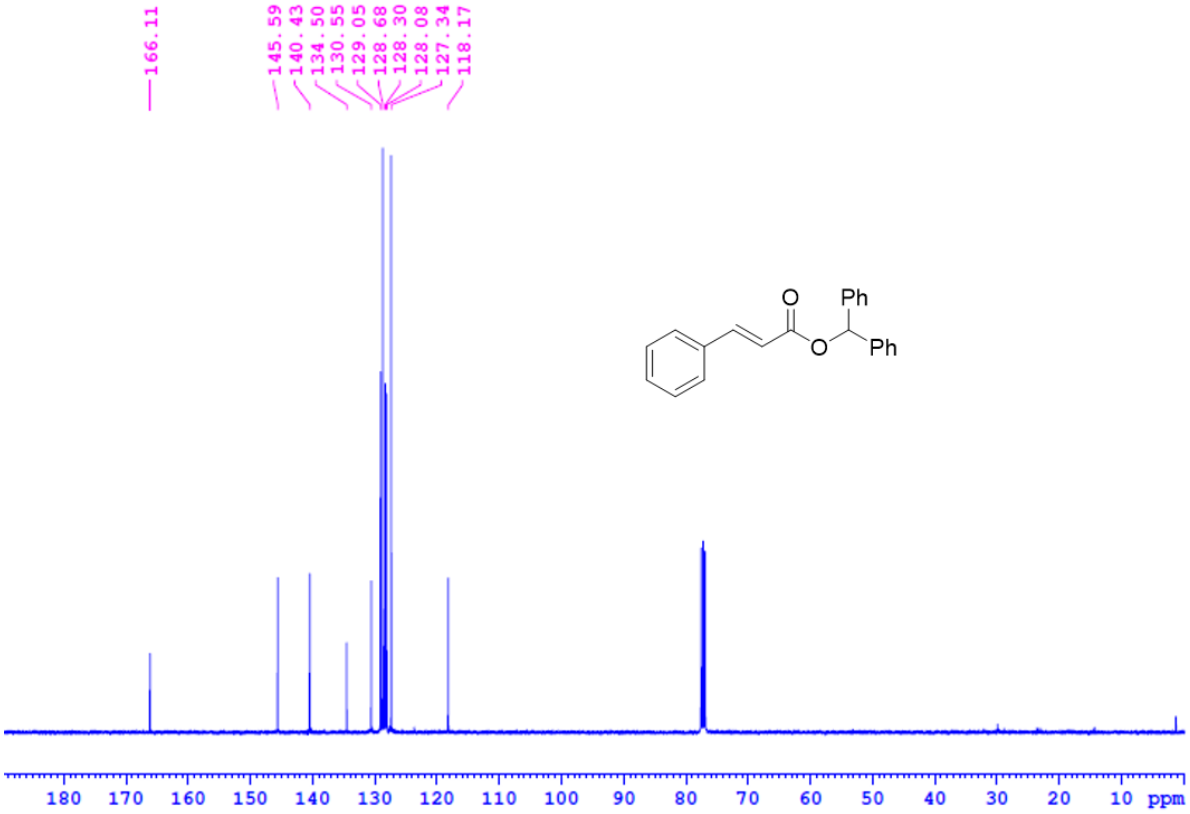
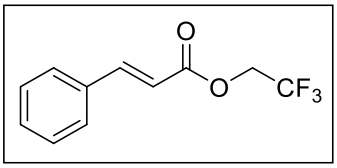
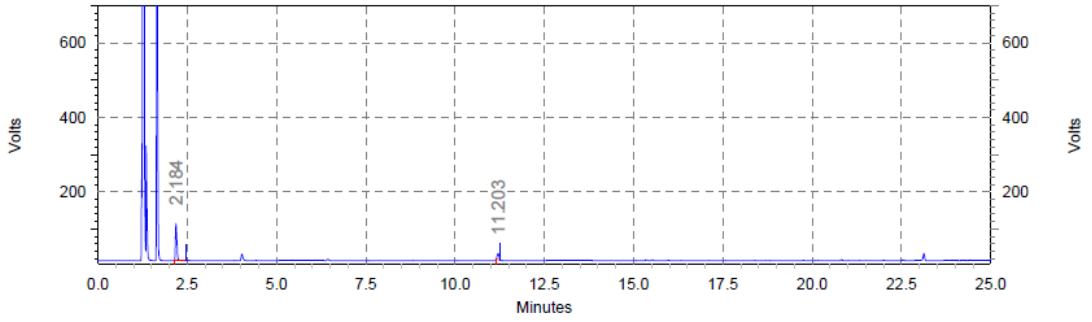


Figure S78: ^{13}C NMR spectrum of P28 in $CDCl_3$.

2,2,2-trifluoroethyl cinnamate P29:



GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P29 = 11.20 min.



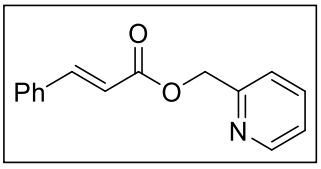
Front Signal Results

Retention Time	Area	Area %	Height	Height %
2.184	2153814	82.27	766577	86.02
11.203	464043	17.73	124576	13.98
Totals	2617857	100.00	891153	100.00

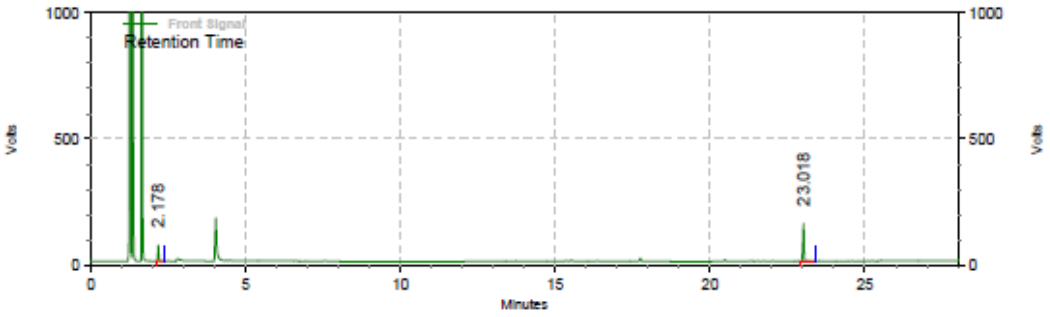
Figure S79: GC chromatogram for P29.

Pyridin-2-ylmethyl cinnamate P30:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (96:4). After column, a pale yellow liquid was isolated in 70% yield (33.5 mg). GC retention time for Phenylacetylene = 2.17 min.; hydroalkoxycarbonylated product P30 = 23.01 min.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (br s, 1H), 7.76 (d, *J* = 16.02 Hz, 1H), 7.71 (t, *J* = 7.70 Hz, 1H), 7.54-7,51 (m, 2H), 7.41-7.37 (m, 4H), 7.26-7.22 (m, 1H), 6.54 (d, *J* = 16.02 Hz, 1H), 5.37 (s, 2H). **^{13}C NMR (400 MHz, $CDCl_3$):** δ = 166.7, 156.1, 149.6, 145.7, 136.9, 134.4, 130.6, 129.1, 128.3, 123.0, 122.0, 117.7, 66.9. The above data is in accordance with previous reports for compound P30.[13b]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.178	1009985	25.03	486189	29.81
23.018	3025159	74.97	1144662	70.19
Totals	4035144	100.00	1630851	100.00

Figure S80: GC trace of P30.

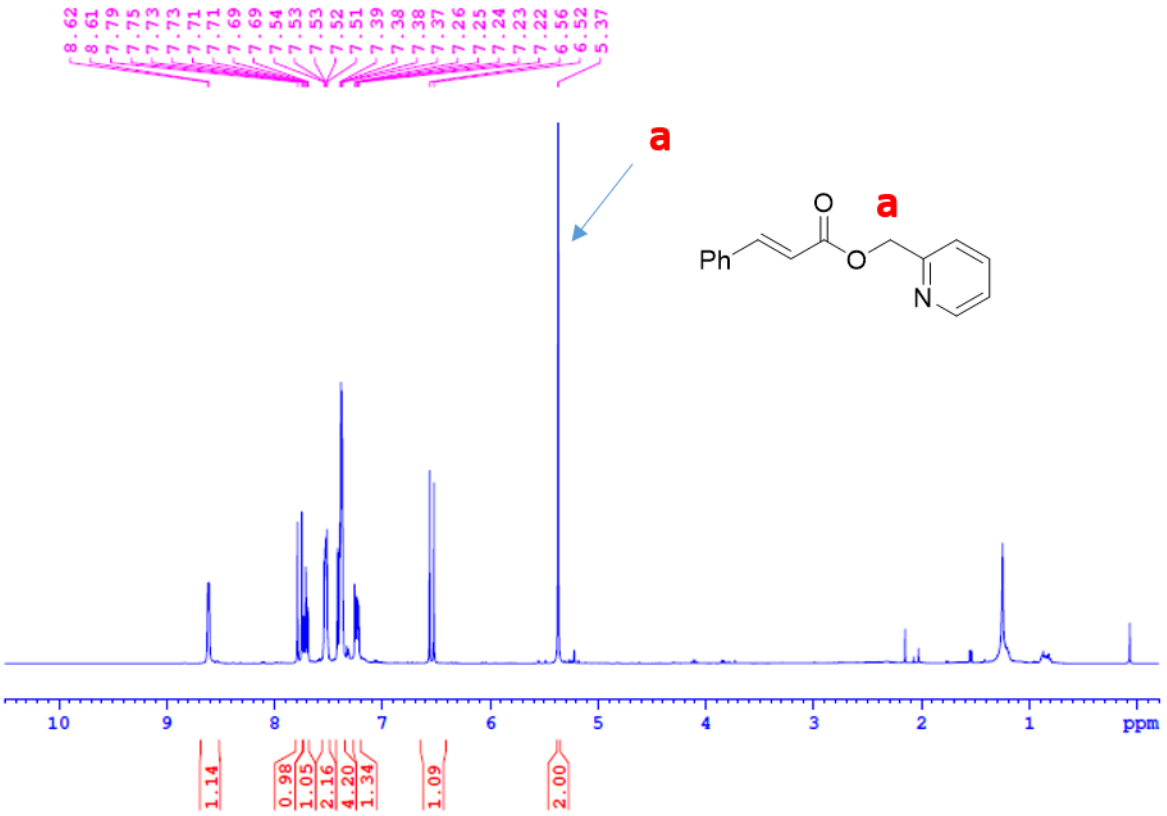


Figure S81: ^{1}H NMR spectrum of P30 in $CDCl_3$.

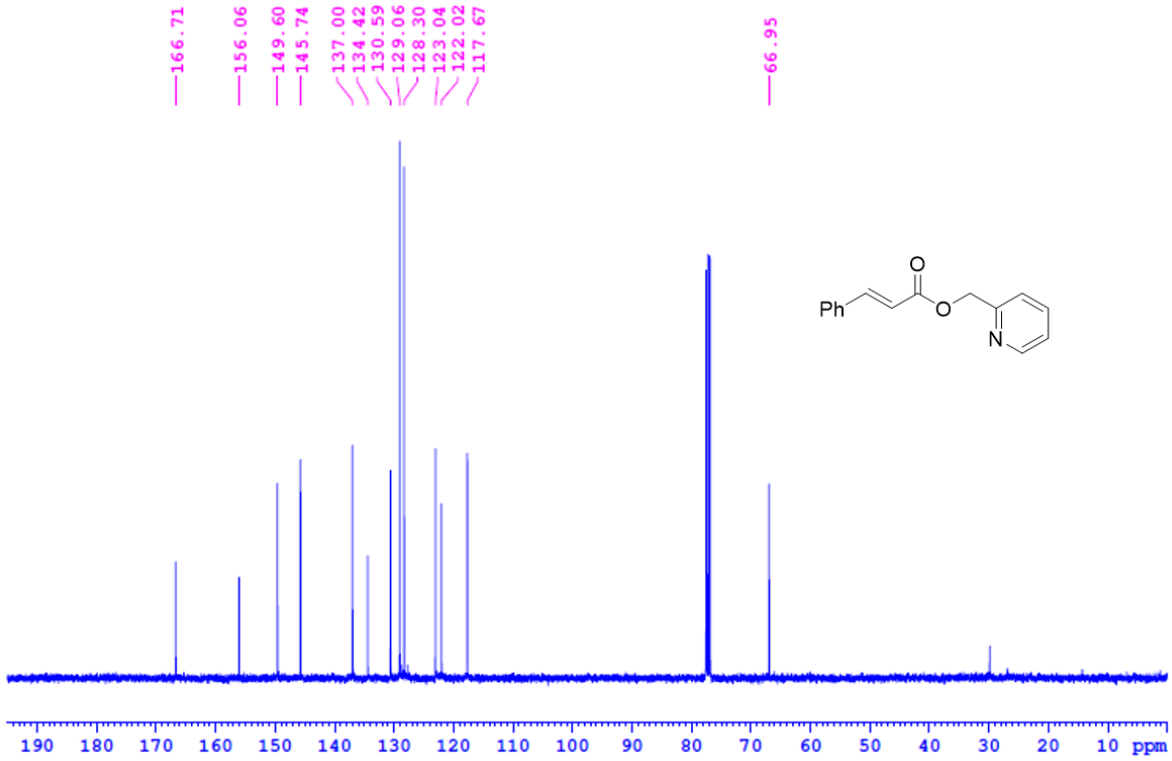
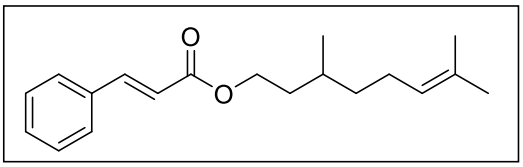


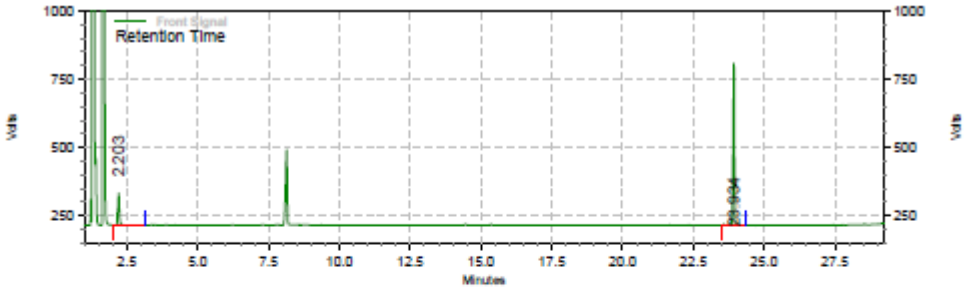
Figure S82: ^{13}C NMR spectrum of P30 in $CDCl_3$.

3,7-dimethyloct-6-en-1-yl cinnamate P31:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (96:4). After column, a pale yellow liquid was isolated in 71% yield (40.6 mg). GC retention time for Phenylacetylene =2.2 min.; hydroalkoxycarbonylated product P31 = 23.93 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 16.02 Hz, 1H), 7.54-7.51 (m, 2H), 7.39-7.37 (m, 3H), 6.44 (d, *J* = 16.02 Hz, 1H), 5.10 (t, *J* = 7.11 Hz, 1H), 4.29-4.19 (m, 2H), 2.08-1.92 (m, 2H), 1.79-1.72 (m, 1H), 1.68 (s, 3H), 1.61 (s, 3H), 1.59-1.48 (m, 2H), 1.43-1.17 (m, 3H), 0.95 (d, *J* = 6.54 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 167.3 (C_q), 144.7, 134.7, 131.5, 130.4, 129.1, 128.2, 124.8, 118.5, 63.3, 37.2, 35.7, 29.7, 25.9, 25.6, 19.6, 17.8. The above data is in accordance with previous reports for compound P31.[17]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.203	3518401	20.20	903480	16.55
23.934	13895517	79.80	4556413	83.45
Totals				
	17413918	100.00	5459893	100.00

Figure S83: GC trace of P31.

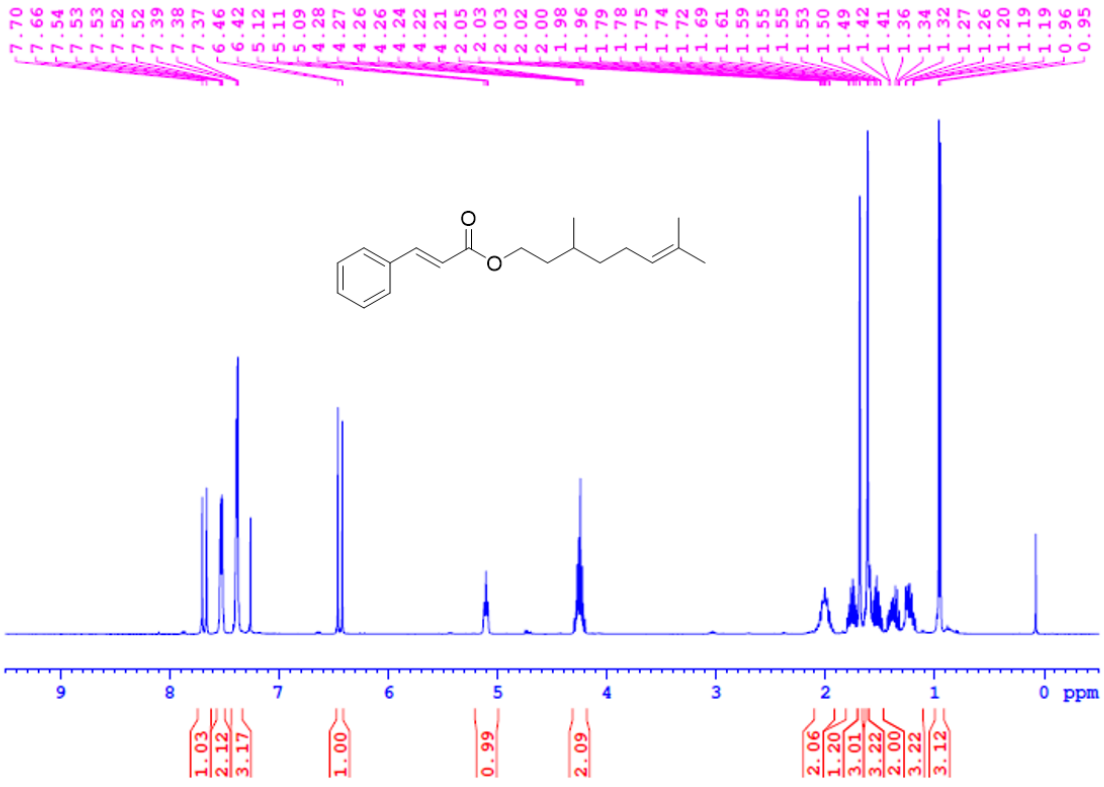


Figure S84: ^{1}H NMR spectrum of P31 in $CDCl_3$.

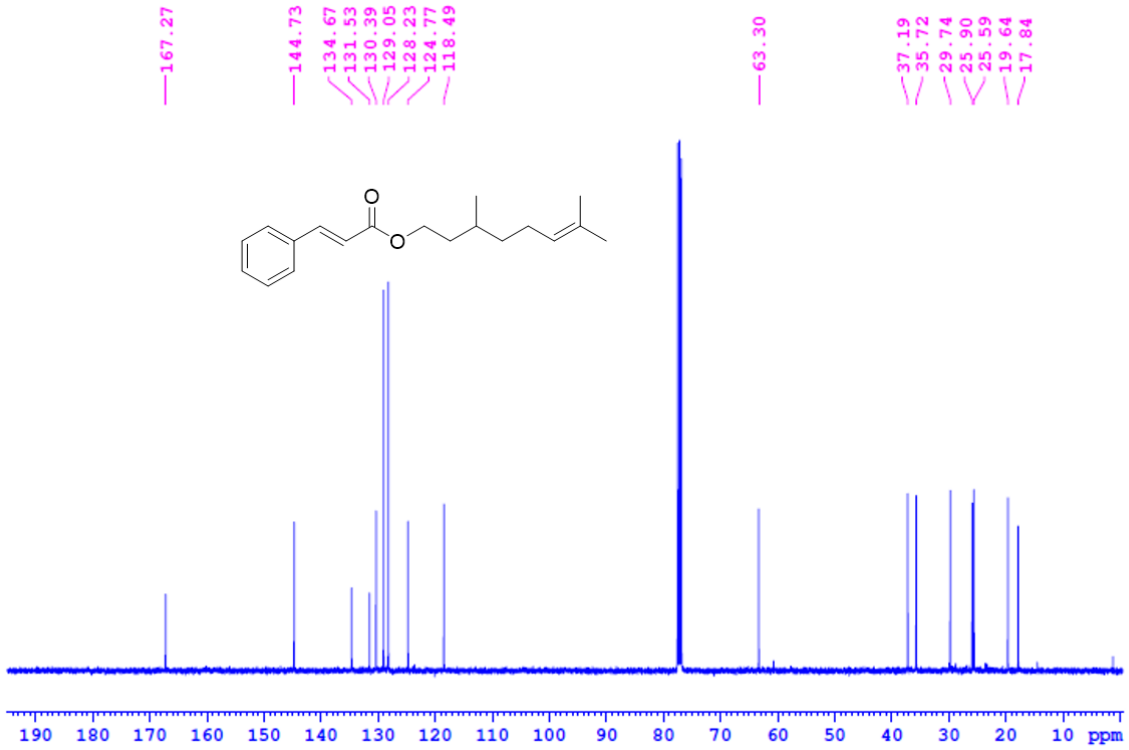
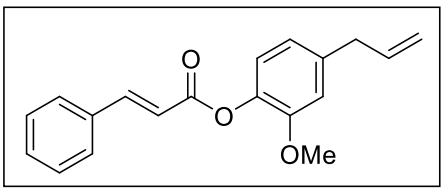


Figure S85: ^{13}C NMR spectrum of P31 in $CDCl_3$.

4-allyl-2-methoxyphenyl cinnamate P32:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (96:4). After column, a pale yellow liquid was isolated in 60% yield (35 mg).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 15.99 Hz, 1H), 7.58 (s, 2H), 7.42 (s, 3H), 7.03 (d, *J* = 7.90 Hz, 1H), 6.83-6.79 (m, 2H), 6.67 (d, *J* = 15.99 Hz, 1H), 6.04-5.94 (m, 1H), 5.13 (d, *J* = 12.95 Hz, 2H), 3.83 (s, 3H), 3.40 (d, *J* = 6.47 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 165.3 (C_q), 151.2, 146.6, 139.1, 138.2, 137.2, 134.5, 130.7, 129.1, 128.4, 122.8, 120.9,

117.3, 116.3, 112.9, 56.1, 40.3. The above data is in accordance with previous reports for compound P32.[18]

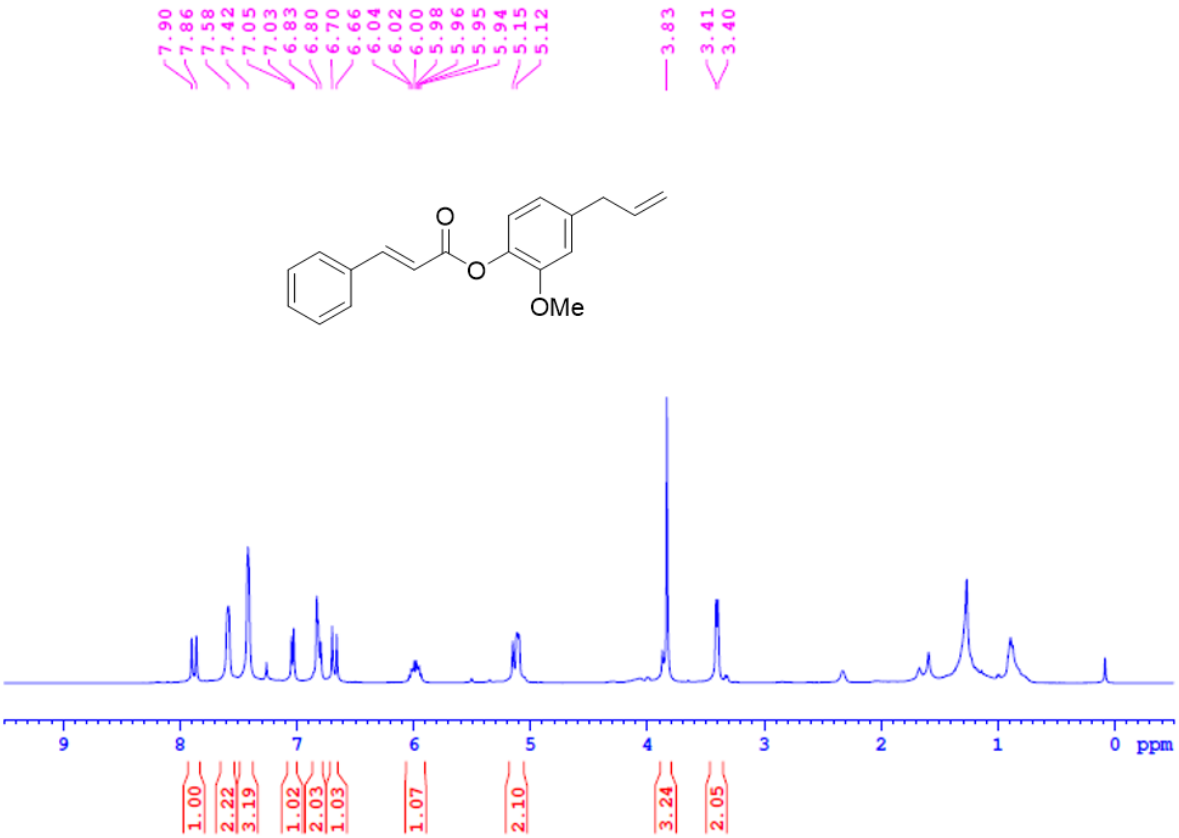


Figure S86: ^{1}H NMR spectrum of P32 in $CDCl_3$.

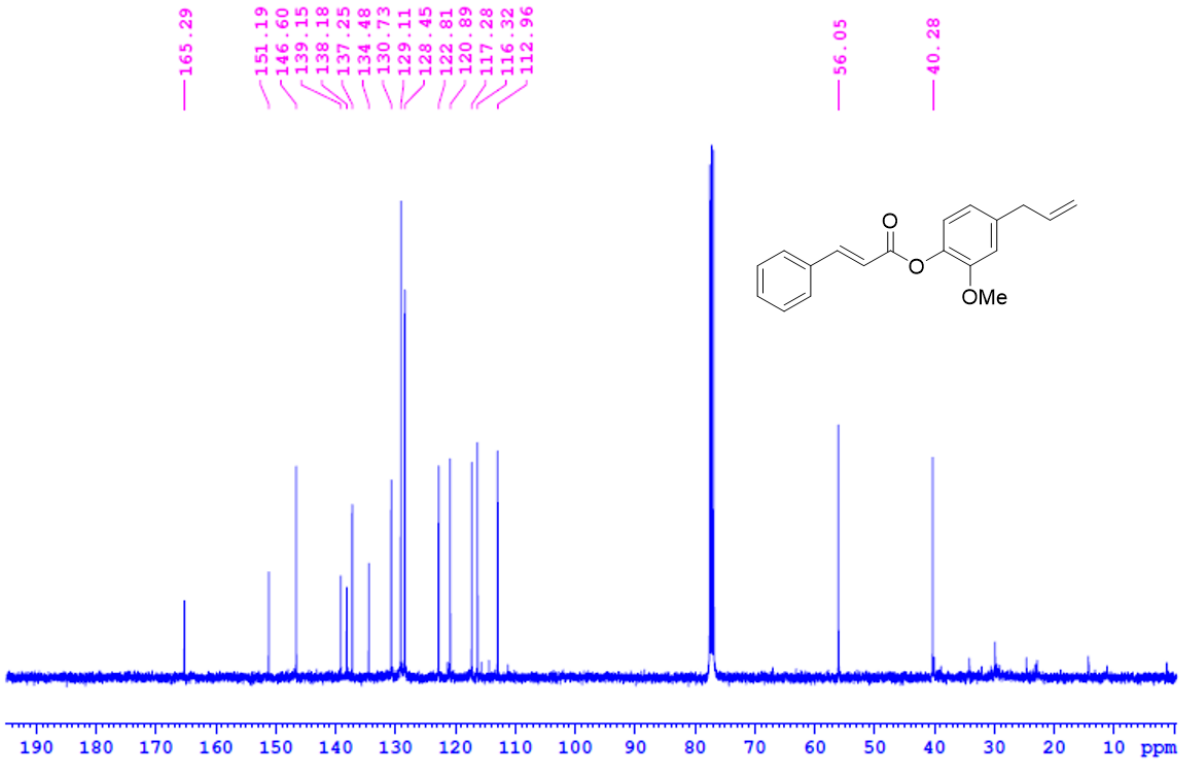
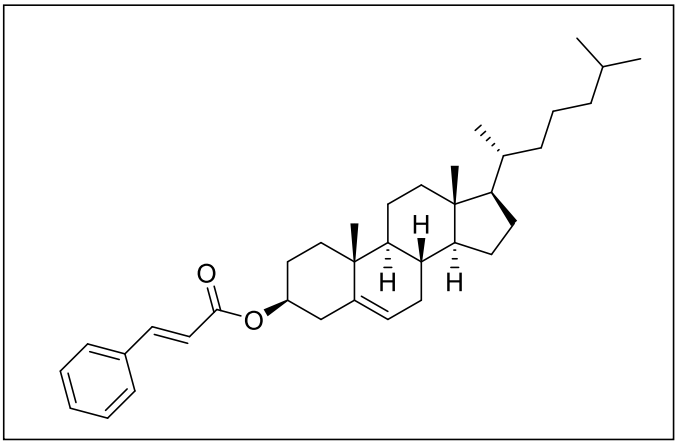


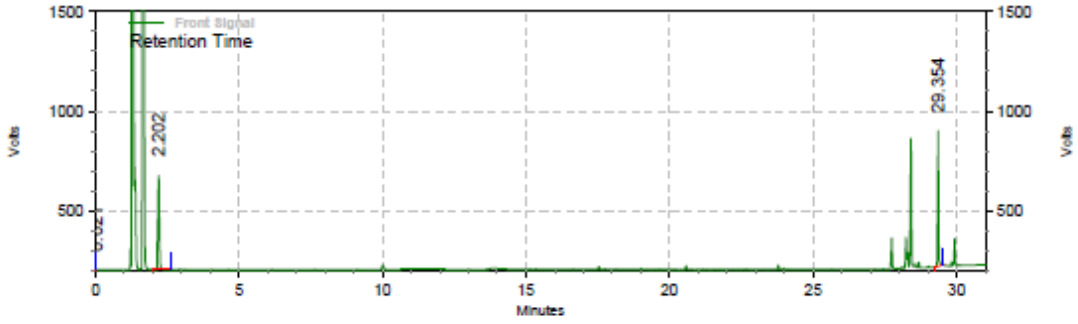
Figure S87: ^{13}C NMR spectrum of P32 in $CDCl_3$.

(3S,8S,9S,10R,13R,14S,17R)-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 cinnamate P33:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 40% yield (41.3 mg). GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P33 = 29.35 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 16.00 Hz, 1H), 7.53-7.50 (m, 2H), 7.38-7.36 (m, 3H), 6.42 (d, *J* = 16.00 Hz, 1H) 5.41-5.39 (br s, 1H), 4.78-4.70 (m, 1H), 2.40 (d, *J* = 7.68 Hz, 2H), 2.03-1.08 (m, 26H), 1.04 (s, 3H), 0.92 (d, *J* = 6.53 Hz, 3H), 0.87-0.85 (d, *J* = 6.61 Hz, *J* = 1.77 Hz 6H), 0.68 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 166.6 (C_q), 144.6, 139.9, 134.7, 130.3, 129.0, 128.2, 122.9, 118.9, 74.3, 56.9, 56.3, 50.2, 42.5, 39.9, 39.7, 38.4, 37.2, 36.8, 36.4, 35.9, 32.1, 28.4, 28.2, 28.1, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0. The above data is in accordance with previous reports for compound P33.[19]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
0.021	155	0.00	477	0.01
2.202	12872064	51.09	3627324	40.94
29.354	12322145	48.91	5232586	59.06
Totals	25194364	100.00	8860387	100.00

Figure S88: GC trace of P33.

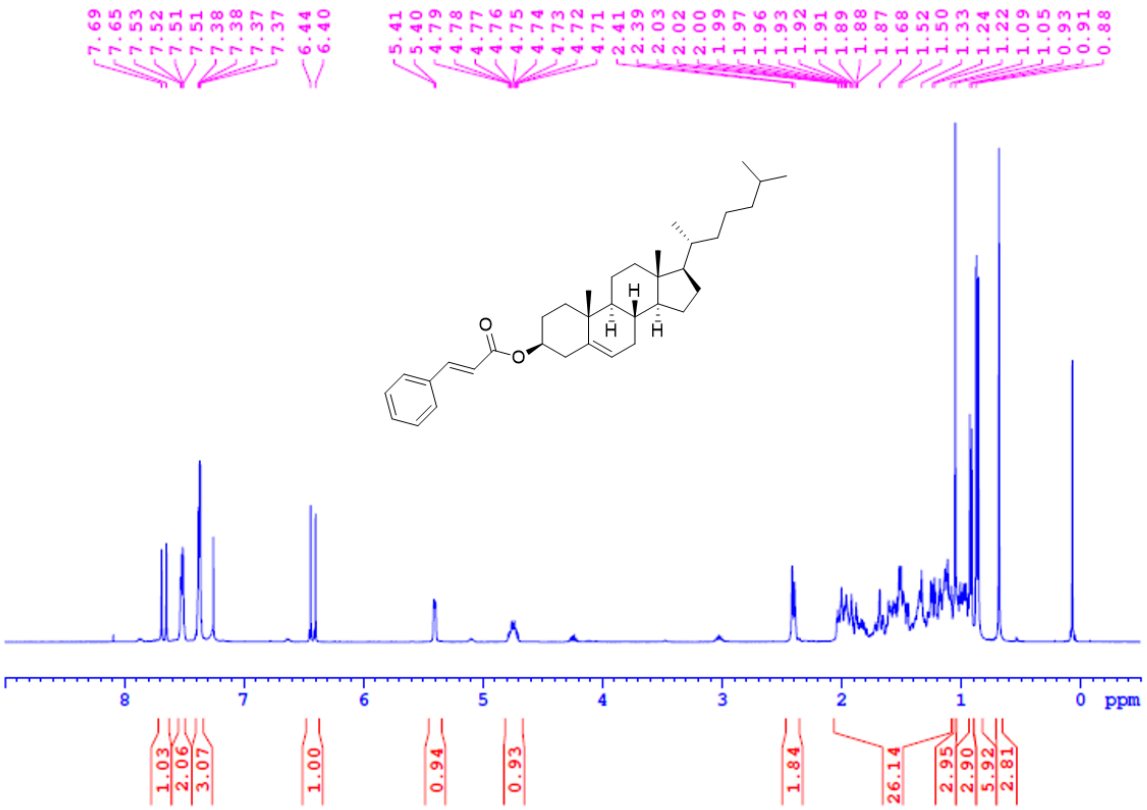


Figure S89: ^{1}H NMR spectrum of P33 in $CDCl_3$.

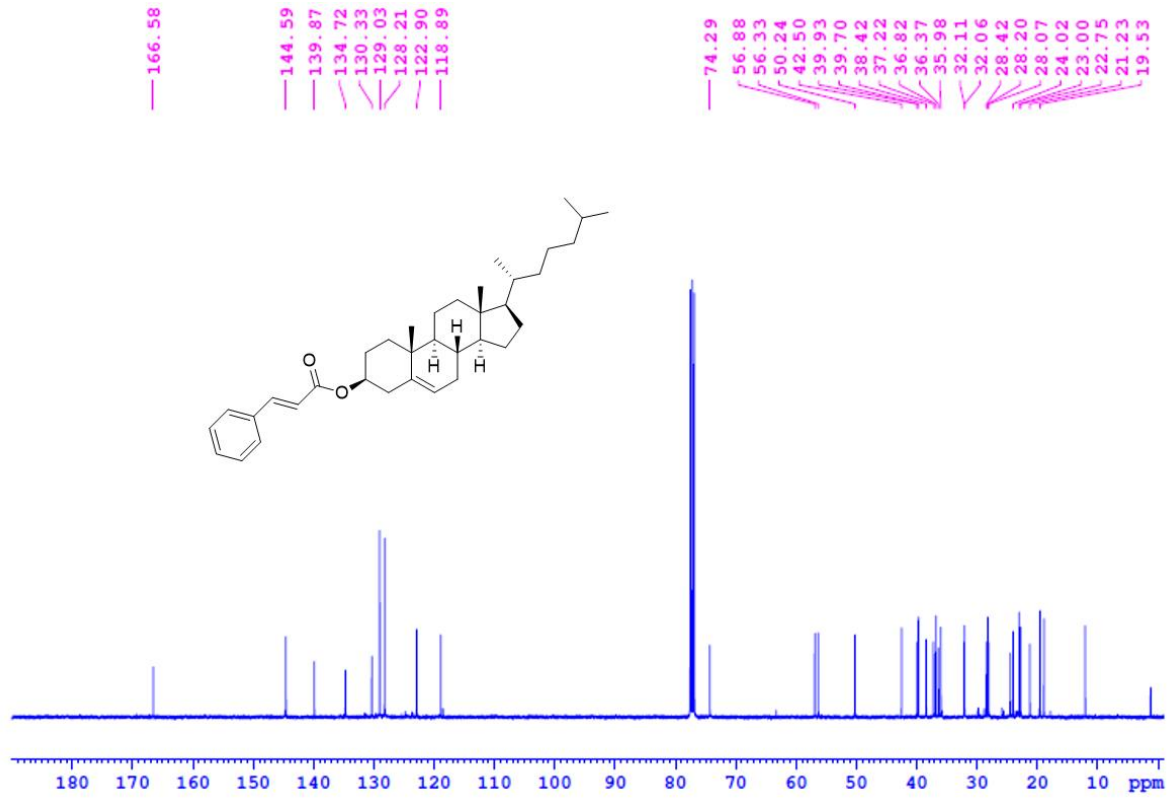
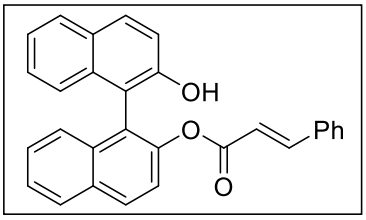


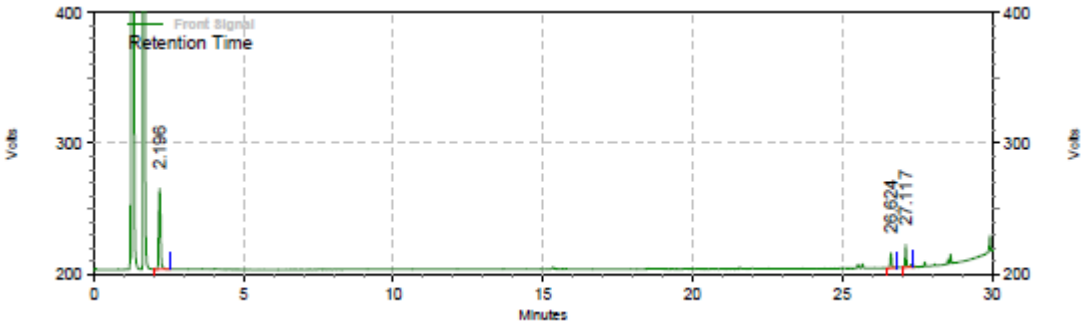
Figure S90: ^{13}C NMR spectrum of P33 in $CDCl_3$.

2'-hydroxy-[1,1'-binaphthalen]-2-yl cinnamate P34:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 12% yield (10 mg). GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxycarbonylated product P34 = 27.11 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.87 Hz, 1H), 7.97-7.92 (m, 2H), 7.86-7.83 (m, 2H), 7.81-7.78 (m, 2H), 7.50-7.44 (m, 1H), 7.35 (br s, 1H), 7.34-7.32 (m, 2H), 7.29-7.27 (m, 5H), 7.13-7.08 (m, 2H), 6.20 (d, *J* = 15.97 Hz, 1H), 5.33 (s, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 166.4, 152.9, 152.0, 148.3, 147.2, 134.0, 133.7, 133.6, 132.4, 131.5, 131.0, 130.9, 130.5, 129.6, 129.2, 129.0, 128.6, 128.4, 128.2, 127.6, 126.8, 126.4, 125.9, 124.8, 124.4, 124.2, 123.6, 123.4, 122.0, 118.5, 117.9, 116.3, 114.2, 111.1. The above data is in accordance with previous reports for compound P34.[20]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.196	2083321	75.25	475093	68.15
26.624	273025	9.86	88646	12.72
27.117	412038	14.88	133346	19.13
Totals	2768384	100.00	697085	100.00

Figure S91: GC trace of P34.

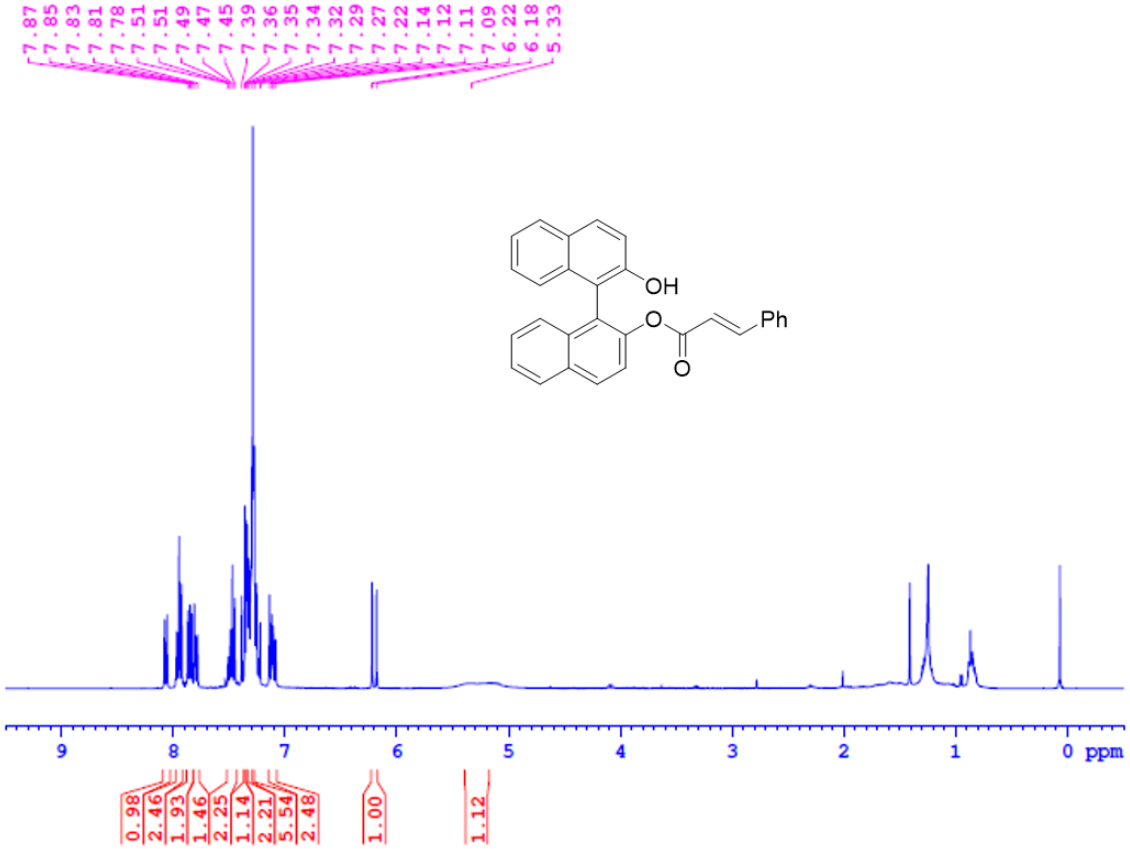


Figure S92: ^{1}H NMR spectrum of P34 in $CDCl_3$.

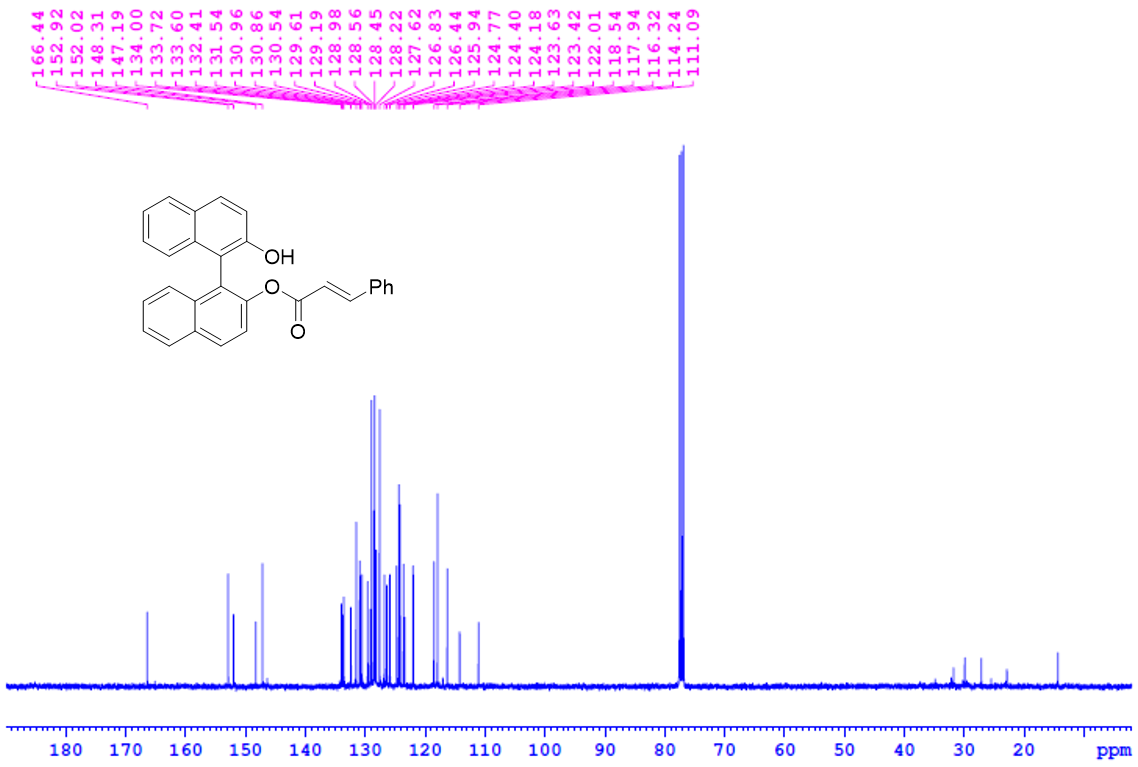
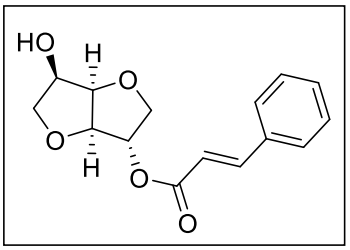


Figure S93: ^{13}C NMR spectrum of P34 in $CDCl_3$.

Isosorbide-2-O-cinnamate P35:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 38 % yield (20.7 mg).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 15.84 Hz, 1H), 7.52 (br s, 2H), 7.39 (s, 3H), 6.43 (d, *J* = 16.01 Hz, 1H), 5.36 (br s, 1H), 4.68 (s, 1H), 4.56 (s, 1H), 4.34 (s, 1H), 4.09 (m, 2H), 3.91 (t, *J* = 15.02 Hz, 1H), 3.59 (t, *J* = 14.99 Hz, 1H), 2.68 (S, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 166.0 (C_q), 146.2, 134.2, 130.8, 129.1, 128.3, 117.3, 85.9, 82.2, 78.6, 73.8, 73.7, 72.5. The above data is in accordance with previous reports for compound P35.[21]

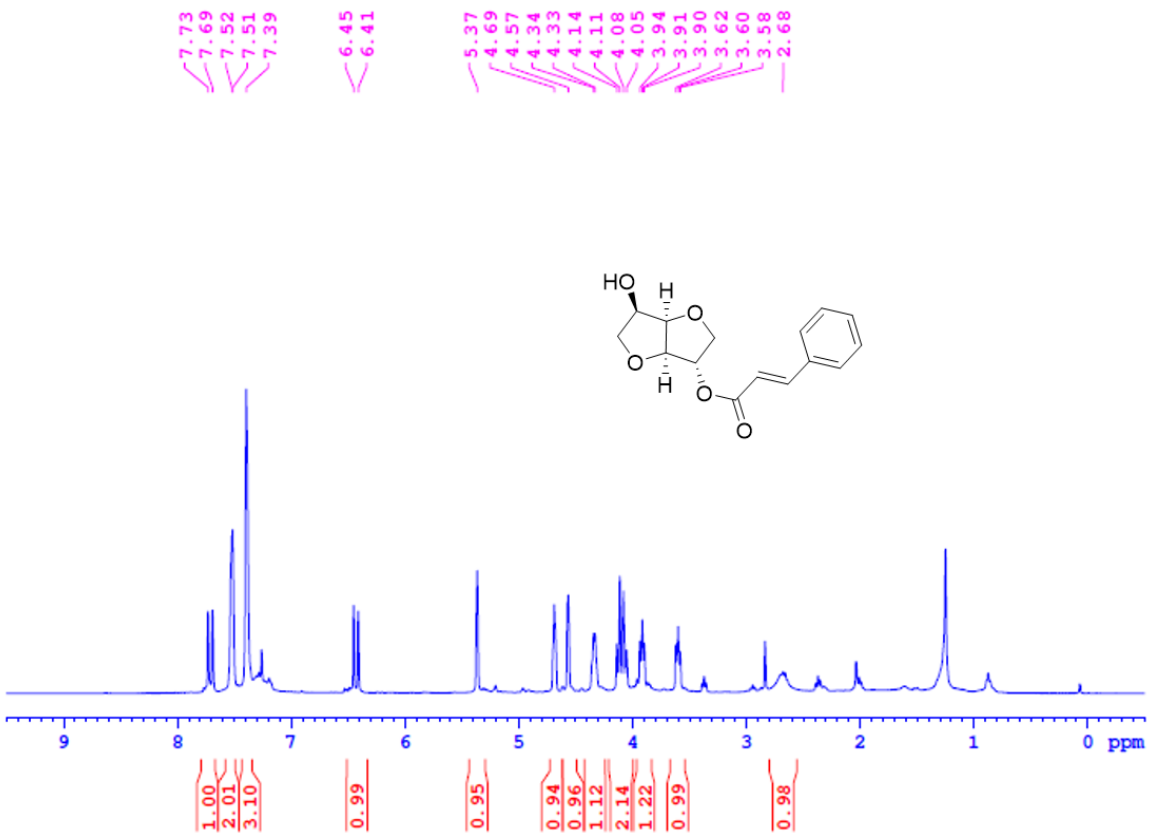


Figure S94: ^{1}H NMR spectrum of P35 in $CDCl_3$.

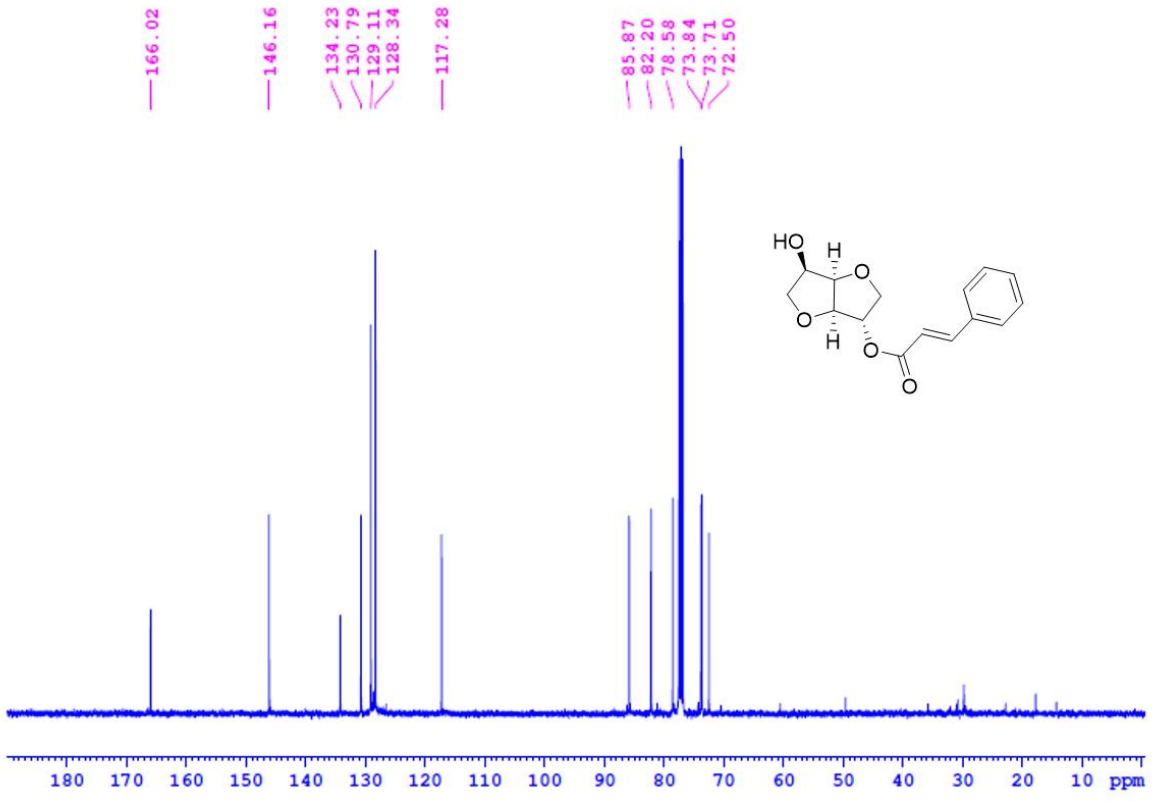
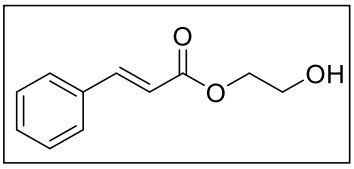


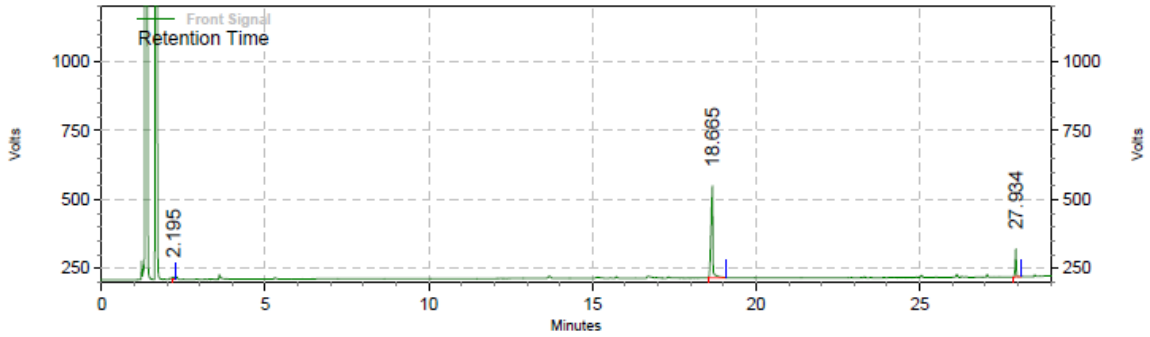
Figure S95: ^{13}C NMR spectrum of P35 in $CDCl_3$.

2-hydroxyethyl cinnamate P36A:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 72% yield (27 mg). GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxyated product P36A = 18.66 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 16.00 Hz, 1H), 7.47 (br s, 2H), 7.34 (s, 3H), 6.44 (d, *J* = 15.99 Hz, 1H), 4.32 (s, 2H), 3.87 (s, 2H), 2.84 (s, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 167.4, 145.5, 134.3, 130.5, 128.9, 128.2, 117.6, 66.2, 61.2. The above data is in accordance with previous reports for compound P36A.[22]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.195	191065	1.56	60300	1.77
18.665	10362639	84.66	2570065	75.35
27.934	1686338	13.78	780555	22.88
Totals	12240042	100.00	3410920	100.00

Figure S96: GC trace of P36A and P36B .

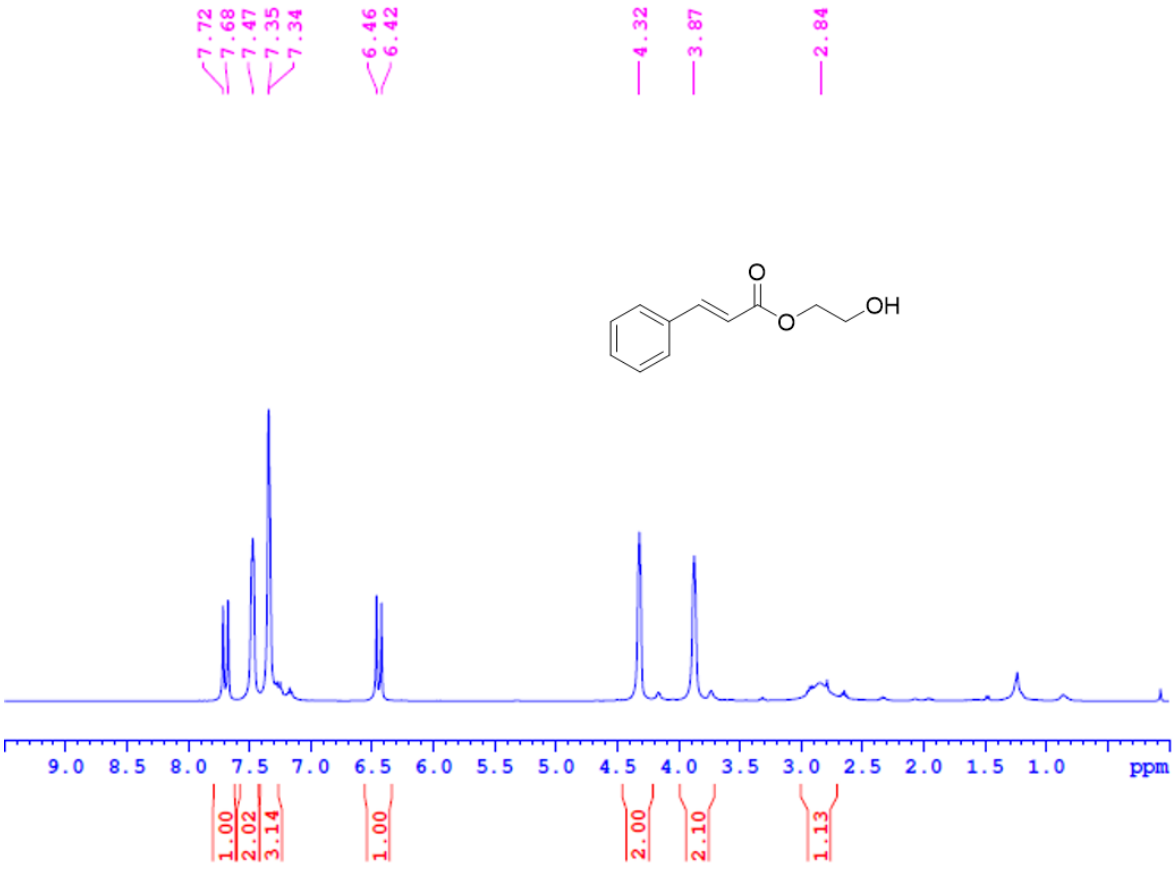


Figure S97: ^{1}H NMR spectrum of P36A in $CDCl_3$.

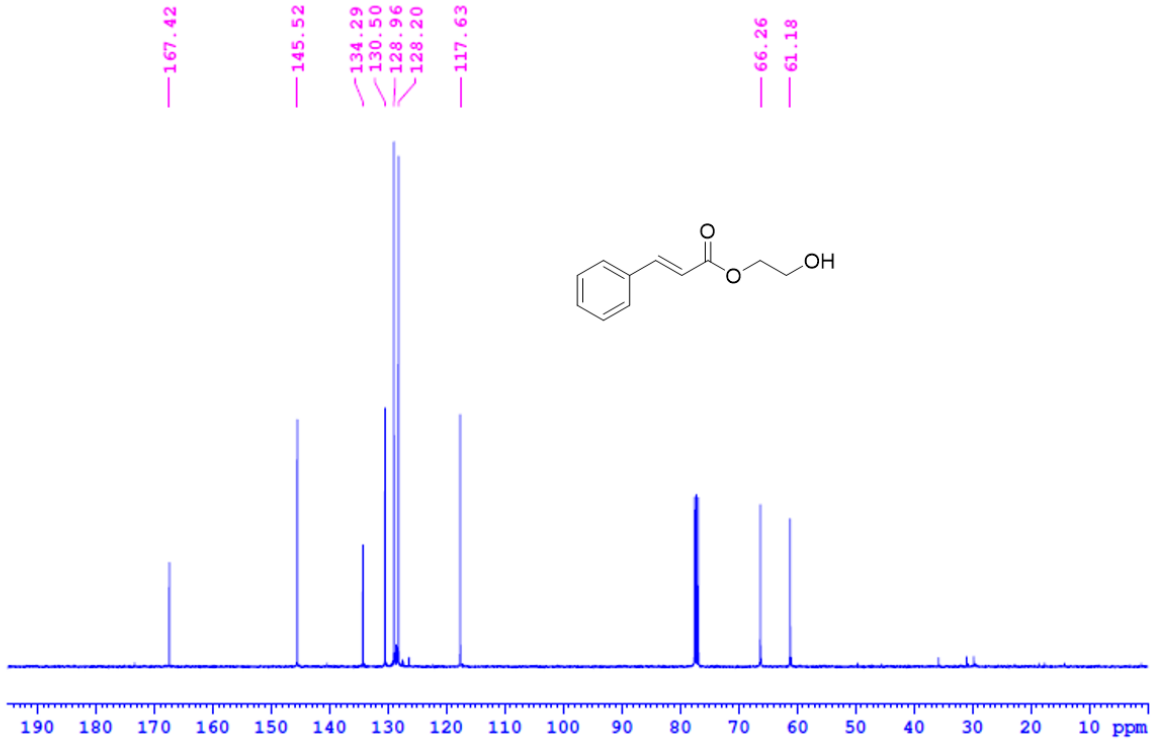
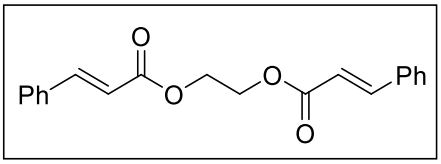


Figure S98: ^{13}C NMR spectrum of P36A in $CDCl_3$.

2-(((E)-2-oxo-4-phenylbut-3-en-1-yl)oxy)ethyl cinnamate P36B:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 10% yield (6.4 mg). GC retention time for Phenylacetylene = 2.2 min.; hydroalkoxyated product P36B = 27.93 min.



^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 15.94 Hz, 2H), 7.55 (s, 4H), 7.40 (s, 6H), 6.48 (d, *J* = 16.03 Hz, 2H), 4.49 (s, 4H). The above data is in accordance with previous reports for compound P36B.[23]

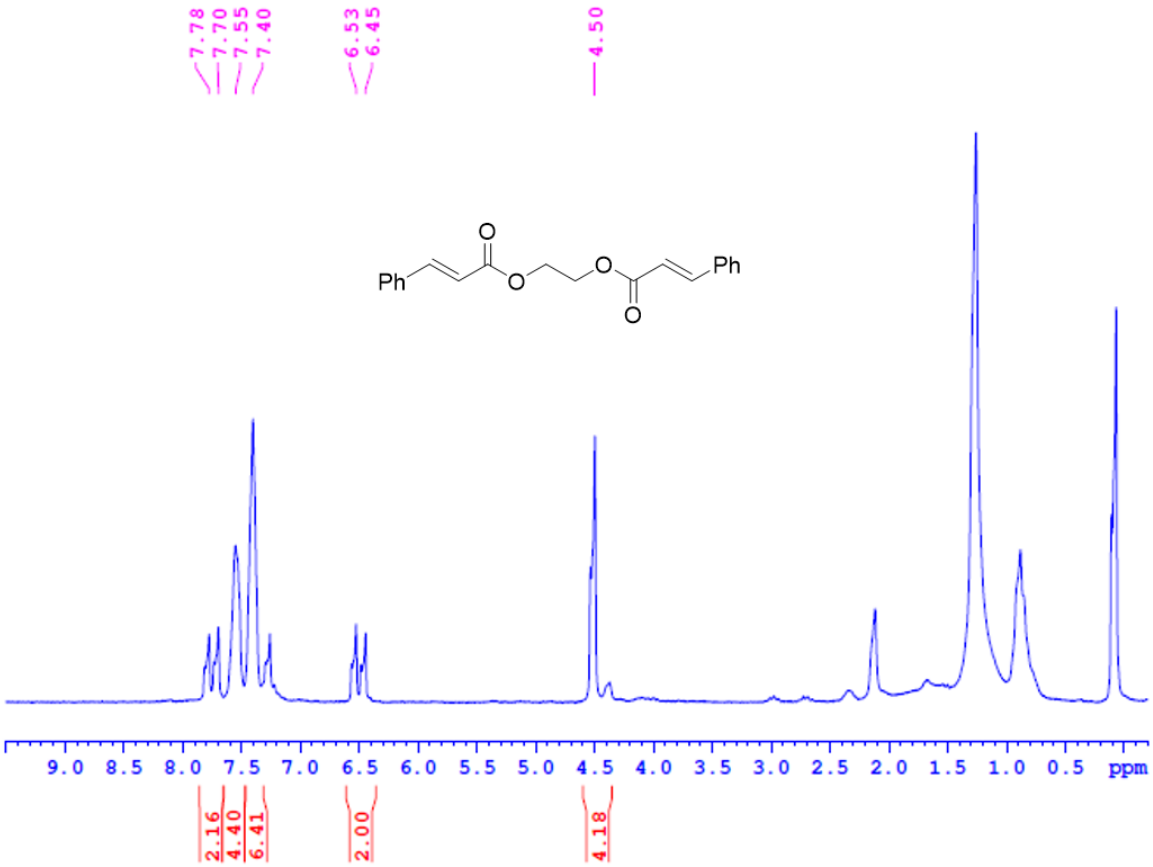
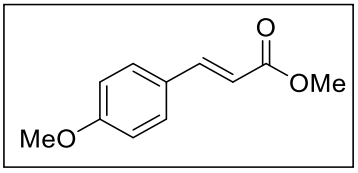


Figure S99: ^{1}H NMR spectrum of P36B in $CDCl_3$.

Methyl (E)-3-(4-methoxyphenyl)acrylate P37:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (97:3). After column, a pale yellow liquid was isolated in 85% yield (32.6 mg).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 15.97 Hz, 1H), 7.46 (d, *J* = 8.68 Hz, 2H), 6.89 (d, *J* = 8.68 Hz, 2H), 6.30 (d, *J* = 15.96 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 167.9, 161.5, 144.7, 129.9, 127.2, 115.3, 114.4, 55.5, 51.7. The above data is in accordance with previous reports for compound P37.[7]

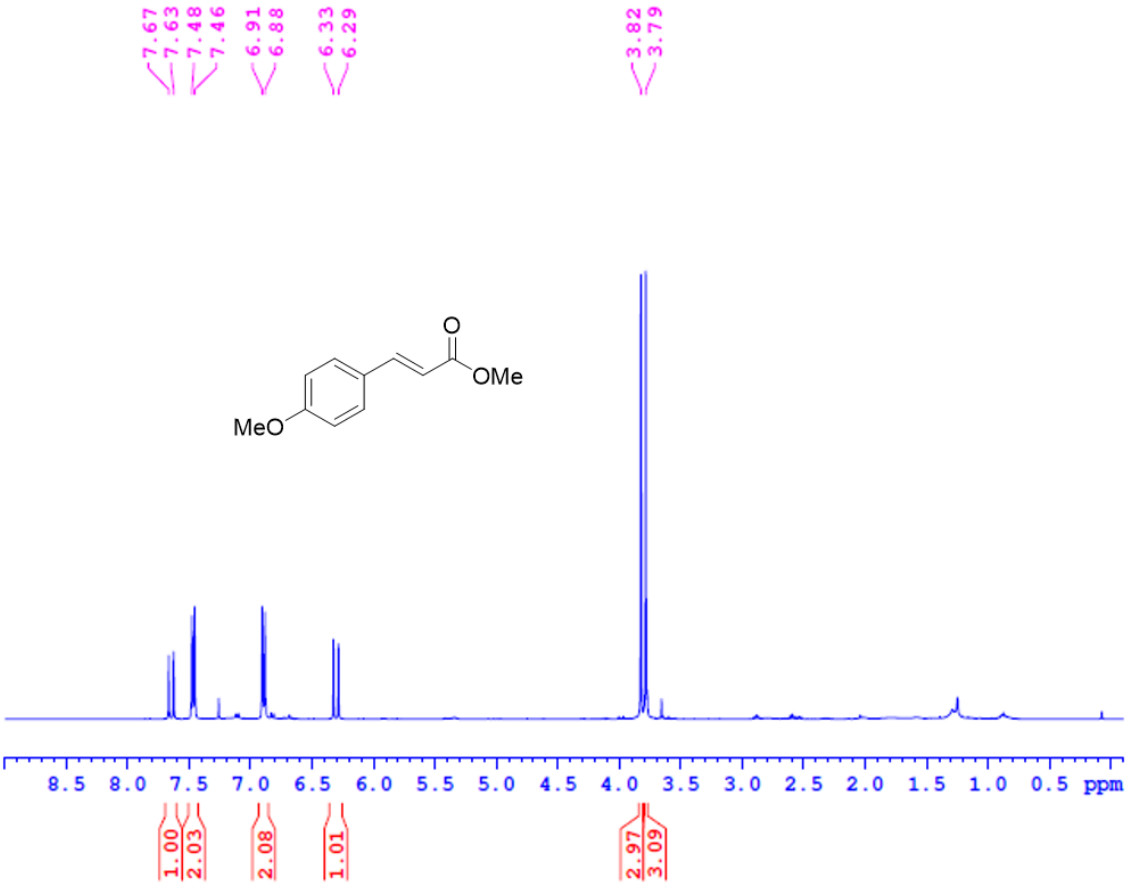


Figure S100: ^{1}H NMR spectrum of P37 in $CDCl_3$.

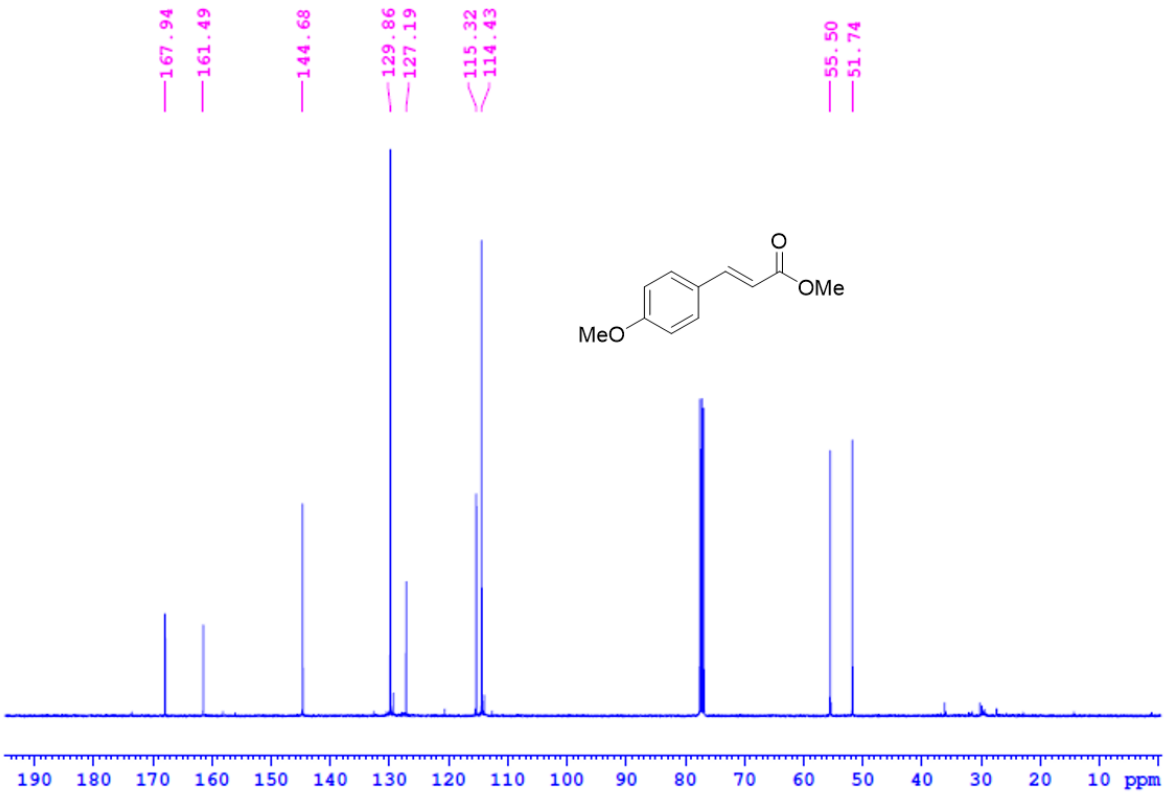
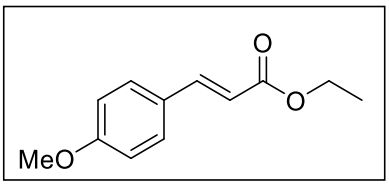


Figure S101: ^{13}C NMR spectrum of P37 in $CDCl_3$.

Ethyl (E)-3-(4-methoxyphenyl)acrylate P38:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 92% yield (37.9 mg).



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 15.95 Hz, 1H), 7.39 (d, *J* = 8.73 Hz, 2H), 6.83 (d, *J* = 8.74 Hz, 2H), 6.25 (d, *J* = 15.96 Hz, 1H), 4.19 (q, *J* = 7.13 Hz, 2H), 3.74 (s, 3H), 1.27 (t, *J* = 7.13 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 167.2 (C_q), 161.3, 144.2, 129.6, 127.1, 115.7, 114.3, 60.2, 55.2, 14.3 (CH_3). The above data is in accordance with previous reports for compound P38.[7]

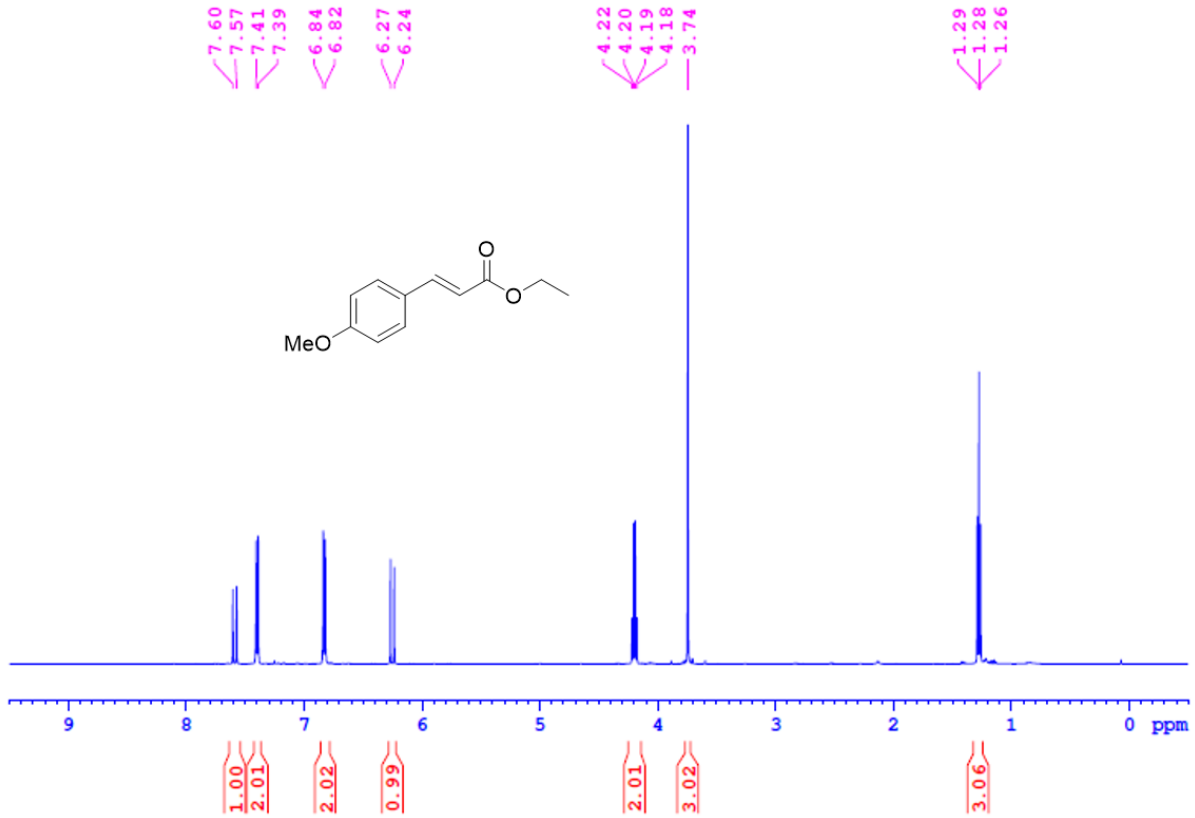


Figure S102: ^{1}H NMR spectrum of P38 in $CDCl_3$.

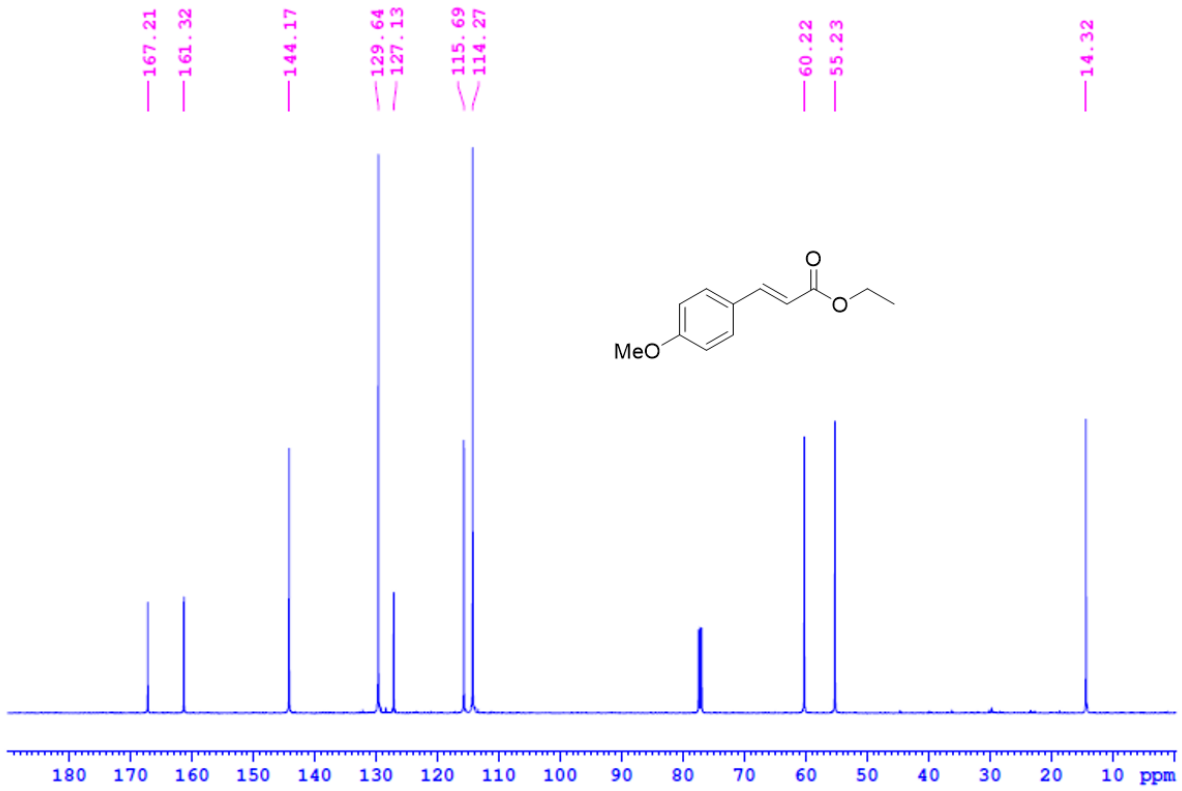
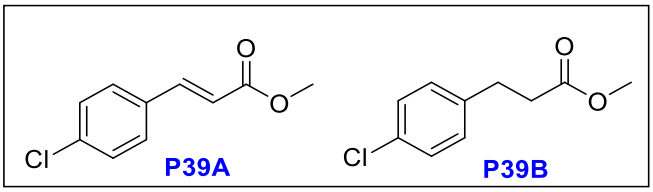


Figure S103: ^{13}C NMR spectrum of P38 in $CDCl_3$.

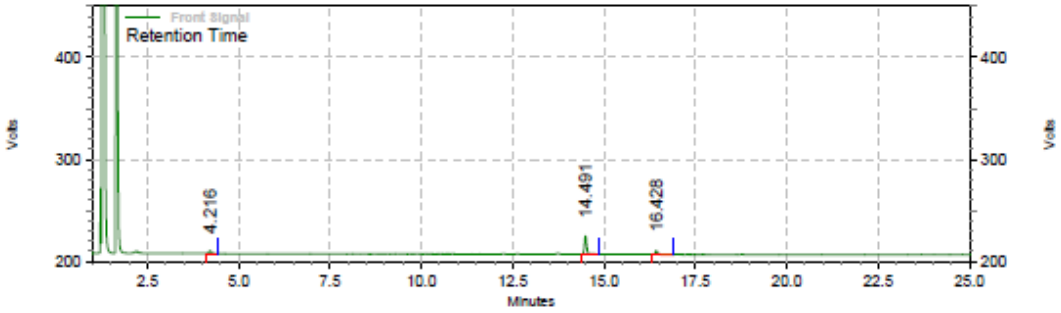
Methyl (E)-3-(4-chlorophenyl)acrylate P39A and Methyl 3-(4-chlorophenyl)propanoate P39B:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (96:4). After column, a pale yellow liquid was isolated in 67% yield (26.3 mg). GC retention time for 4 chlorophenylacetylene = 4.21 min.; hydroalkoxycarbonylated product P39 = 14.49 min. The NMR investigations suggest that both P39A and P39B exist in solution and the ratio between them is about 1:1. Iron catalyzed direct and transfer hydrogenation of different alkene has been reported. Accordingly, the 4-chloro phenyl acetylene after hydroalkoxycarbonylation, might further undergo hydrogenation (of P39A) to form P39B.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 16.03 Hz, 1H), 7.46-7.34 (m, 4H), 7.24 (d, *J* = 8.54 Hz, 2H), 7.12 (d, *J* = 8.33 Hz, 2H), 6.40 (d, *J* = 16.02 Hz, 1H), 3.80 (s, 3H), 3.65 (s, 3H), 2.91 (t, *J* = 15.37 Hz, 2H), 2.60 (t, *J* = 15.38 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 173.2

(C_q), 167.3 (C_q), 143.6, 139.1, 136.4, 133.0, 132.2, 129.8, 129.4, 129.3, 128.8, 118.6, 51.9 (CH_3), 51.8 (CH_3), 35.7 (CH_2), 30.4 (CH_2). The above data is in accordance with previous report for compound P39.[10]



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
4.216	90822	10.84	21294	11.33
14.491	610322	72.82	137407	73.13
16.428	136957	16.34	29194	15.54
Totals	838101	100.00	187895	100.00

Figure S104: GC trace of P39.

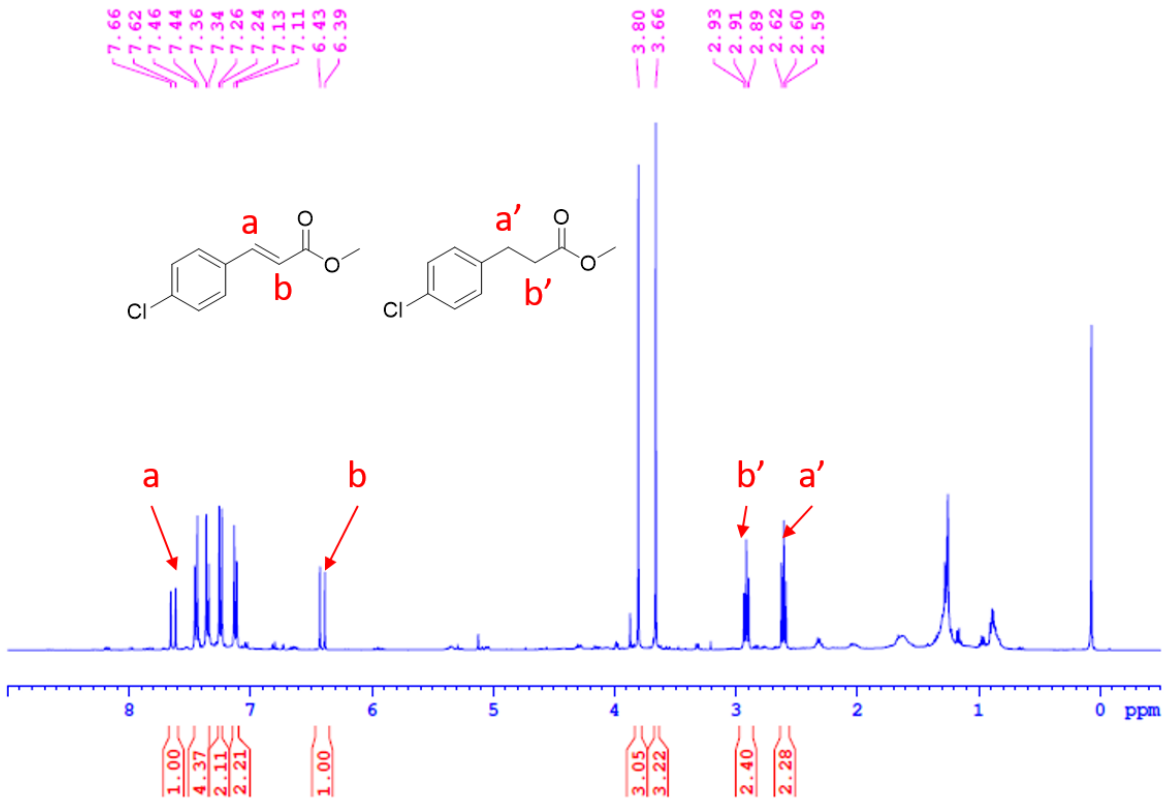


Figure S105: ^{1}H NMR spectrum of P39 in $CDCl_3$.

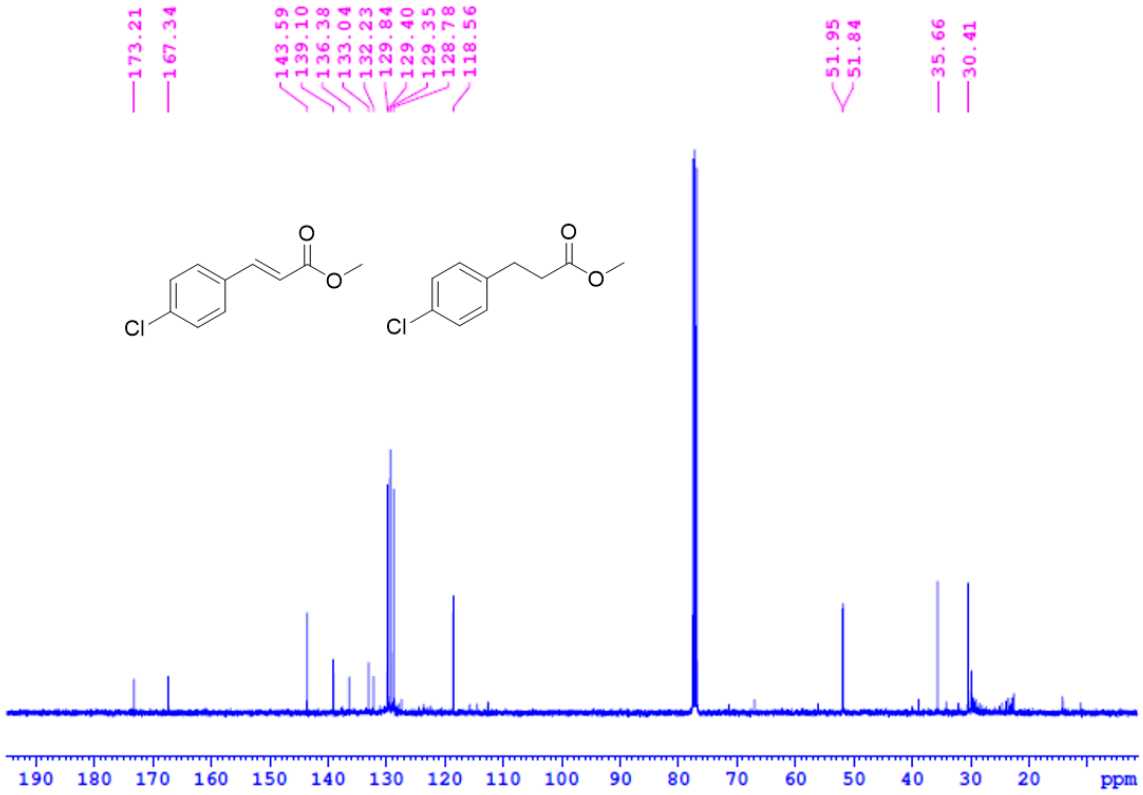
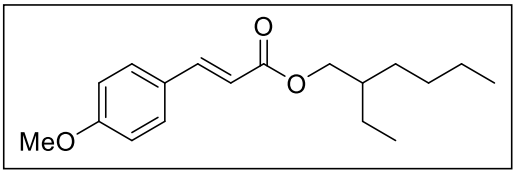


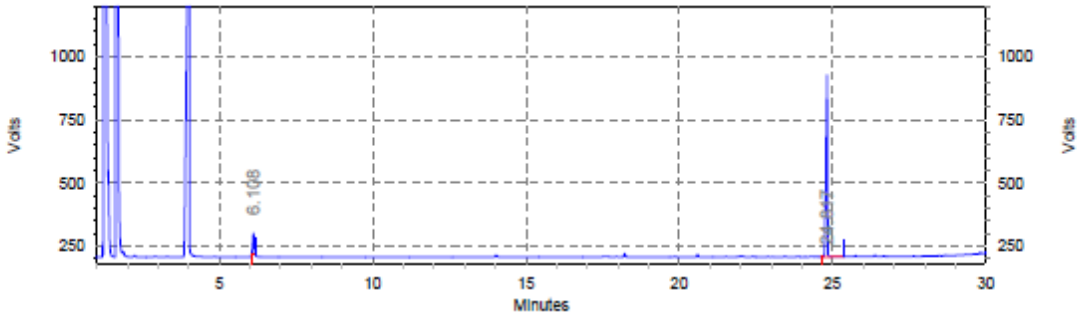
Figure S106: ^{13}C NMR spectrum of P39 in $CDCl_3$.

2-ethylhexyl (E)-3-(4-methoxyphenyl)acrylate P40:

Purified by silica gel chromatography using petroleum ether and ethyl acetate (98:2). After column, a pale yellow liquid was isolated in 88% yield (51 mg). GC retention time for 4-methoxyphenylacetylene = 6.1 min.; hydroalkoxycarbonylated product P40 = 24.8 min.



^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (d, *J* = Hz, 1H), 7.47 (d, *J* = Hz, 2H), 6.88 (d, *J* = Hz, 2H), 6.31 (d, *J* = Hz, 1H), 4.14-4.06 (m, 2H), 3.82 (s, 3H), 1.66-1.59 (m, 1H), 1.42-1.24 (m, 8H), 0.93-0.87 (m, 6H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 167.7, 161.4, 144.3, 129.8, 127.3, 115.9, 114.4, 66.9, 55.5, 38.9, 30.6, 29.1, 23.9, 23.1, 14.2, 11.2. The above data is in accordance with previous reports for compound P40.[24]



Front Signal Results

Retention Time	Area	Area %	Height	Height %
6.108	2190191	10.70	637304	10.33
24.817	18270495	89.30	5534230	89.67
Totals	20460686	100.00	6171534	100.00

Figure S107: GC trace of P40.

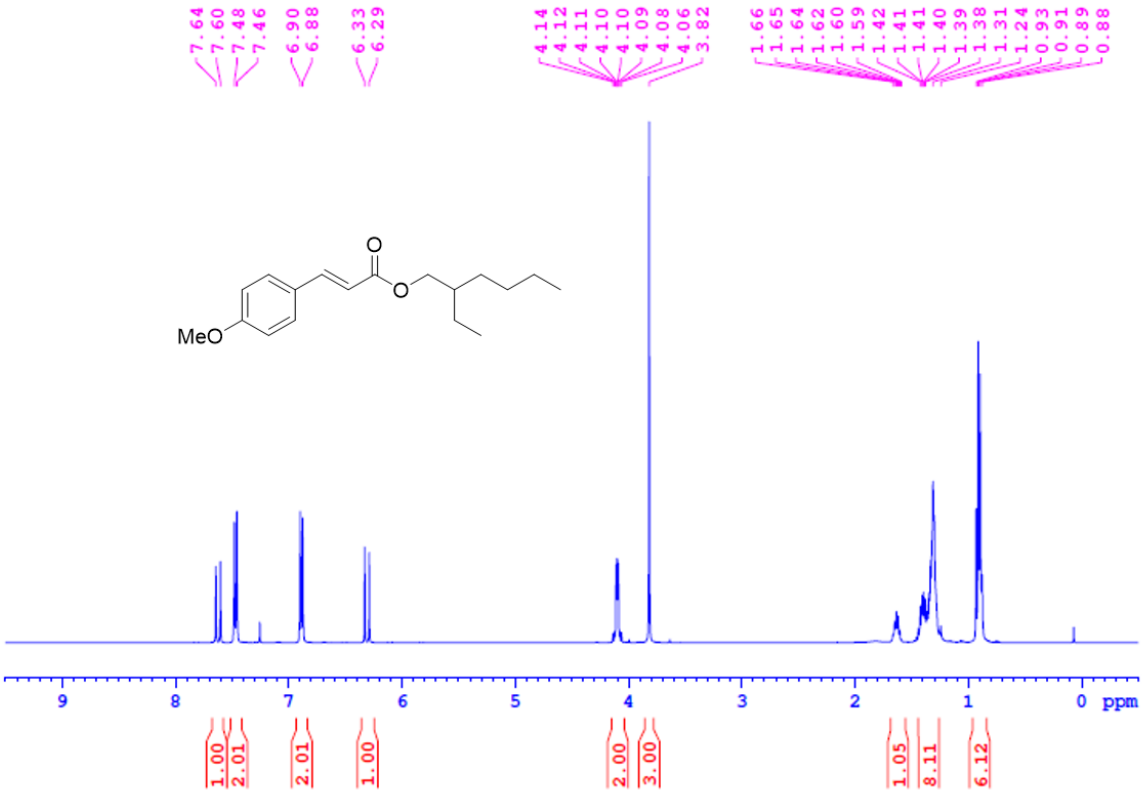


Figure S108: ^{1}H NMR spectrum of P40 in $CDCl_3$.

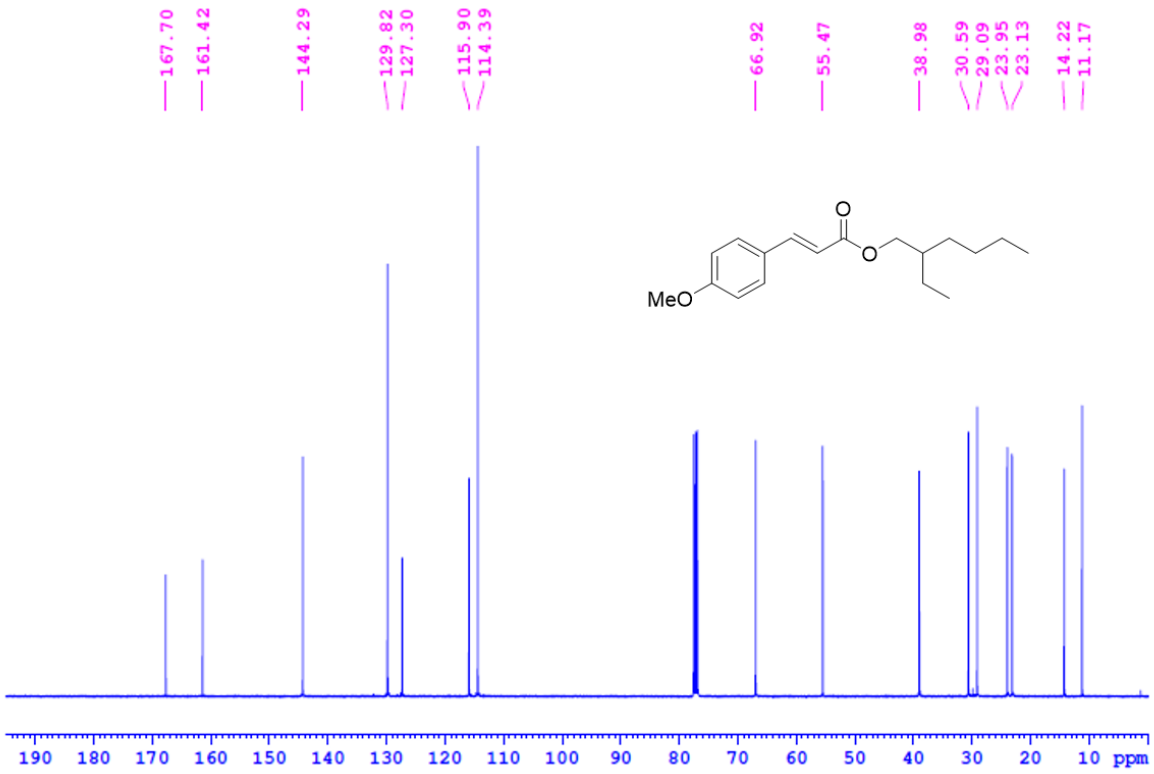


Figure S109: ^{13}C NMR spectrum of P40 in $CDCl_3$.

5. Sytnthetic application of product:

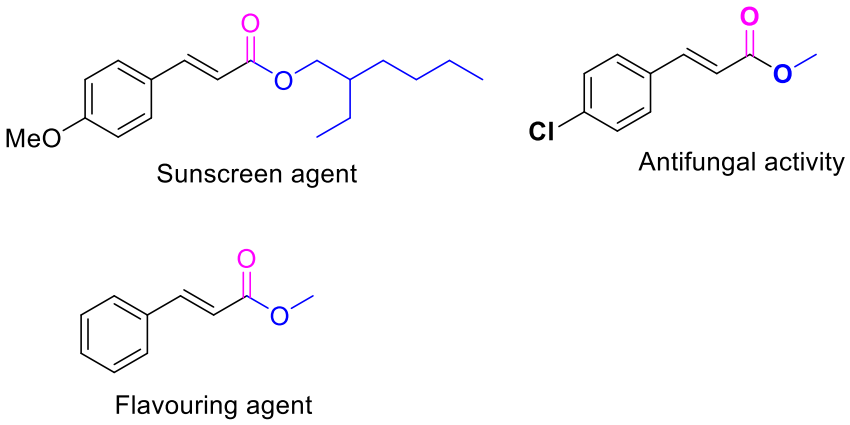
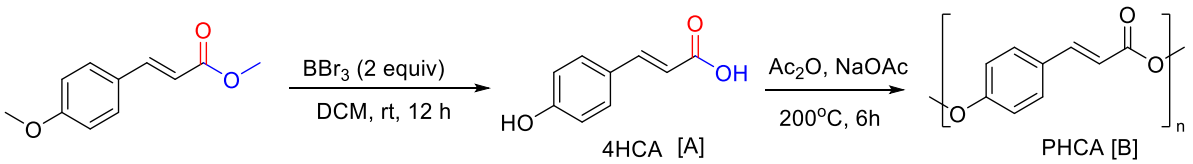


Figure S110: Practical utility of esters.

6. Further functionalization:

Product [A] and [B] were prepared by following previous literature procedure.[25]



Scheme 1: Deprotection of Methyl-4-methoxy cinnamate and polymerization of 4-HCA

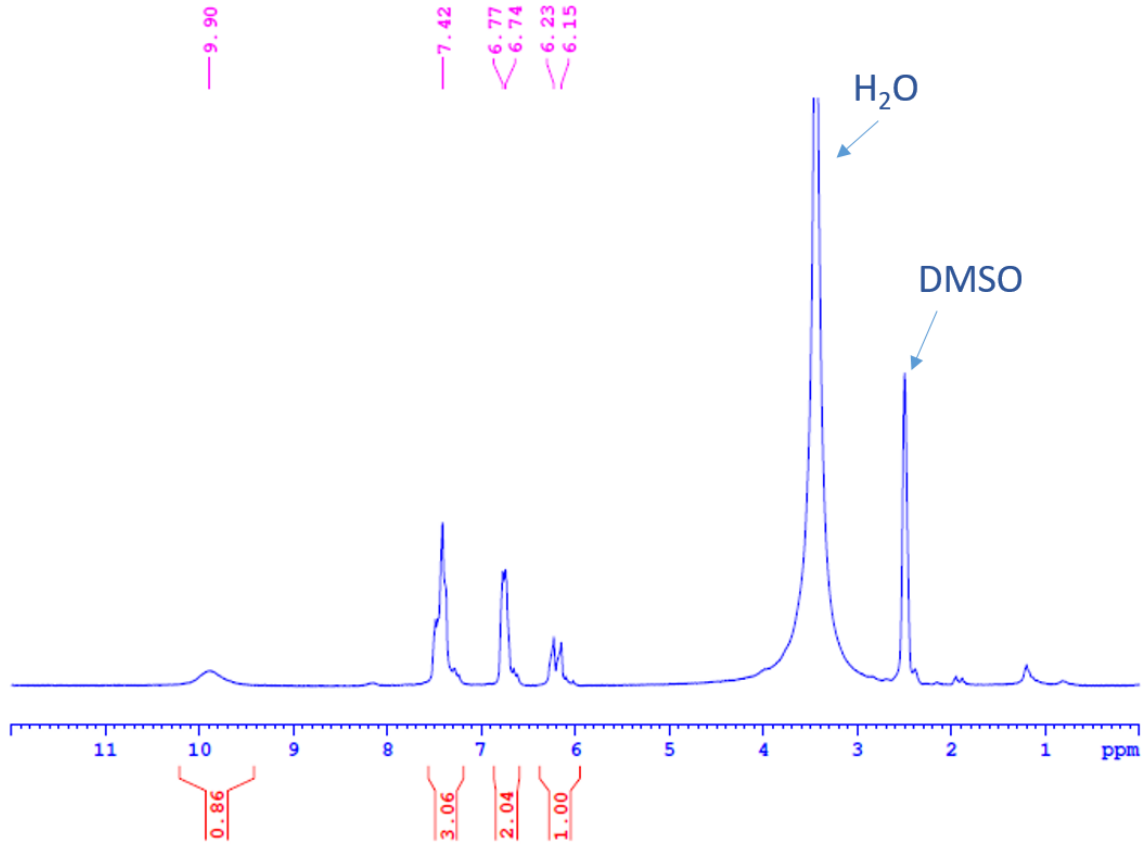
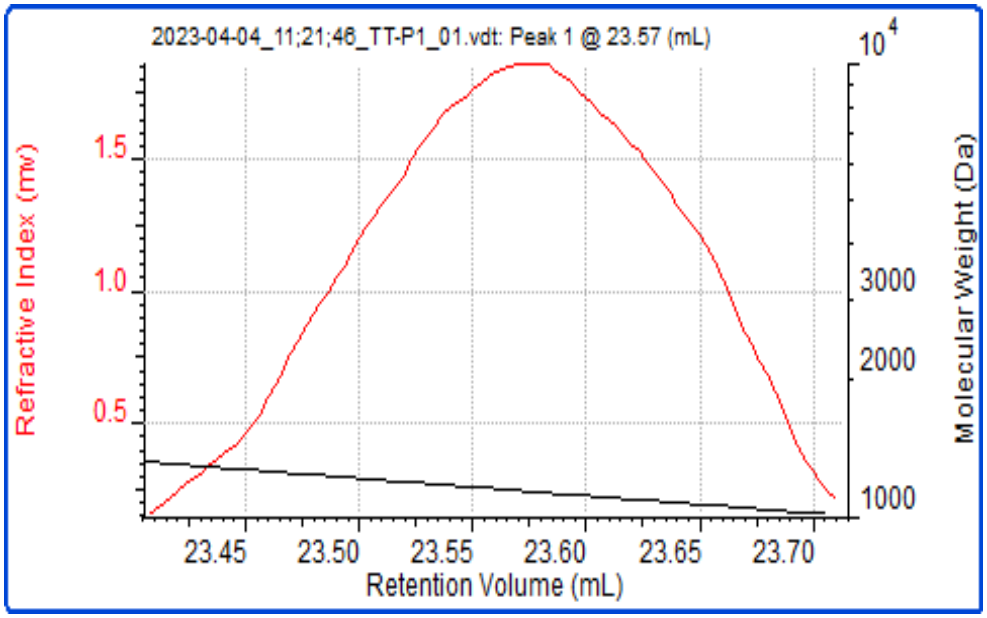


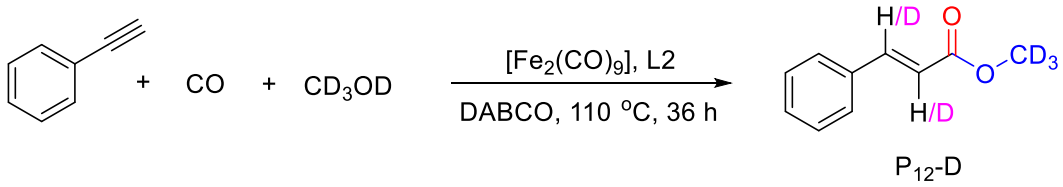
Figure S111: [1]H NMR spectrum of [A] in DMSO.



Conventional calibration. Homopolymers result	
Peak RV - (ml)	23.573
Mn - (Daltons)	1,140
Mw - (Daltons)	1,144
Mz - (Daltons)	1,148
Mp - (Daltons)	1,137
Mw / Mn	1.003

Figure S112: Molecular weight of polymer [B] by GPC in DMF

7. Deuterium labelling experiment:



P_{12}-D

In a glove box, an oven-dried vial (4 mL) containing a stirring bar was charged with $[Fe_2(CO)_9]$ (0.005 mmol, 1.8 mg), L7 (0.01 mmol, 5 mg), DABCO (0.89 mmol, 100 mg), phenyl acetylene (0.2 mmol, 0.02 mL), and CD_3OD (1 mmol, 36.06 mg). The vial was then sealed with a PTFE/white rubber septum and was taken out from the glove box. Then, PhMe (0.3 mL), and THF (0.3 mL) were added by syringe under argon. The vial was placed in a beaker, which was

transferred into a stainless steel autoclave (450 mL). After flushing the autoclave three times with CO, a pressure of 10 bar of CO was adjusted at ambient temperature. Then, the mixture was stirred for 36 h at 110 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. The conversion was determined by the GC and was purified by column chromatography on silica gel (P.E./EA) to obtain the desired product.

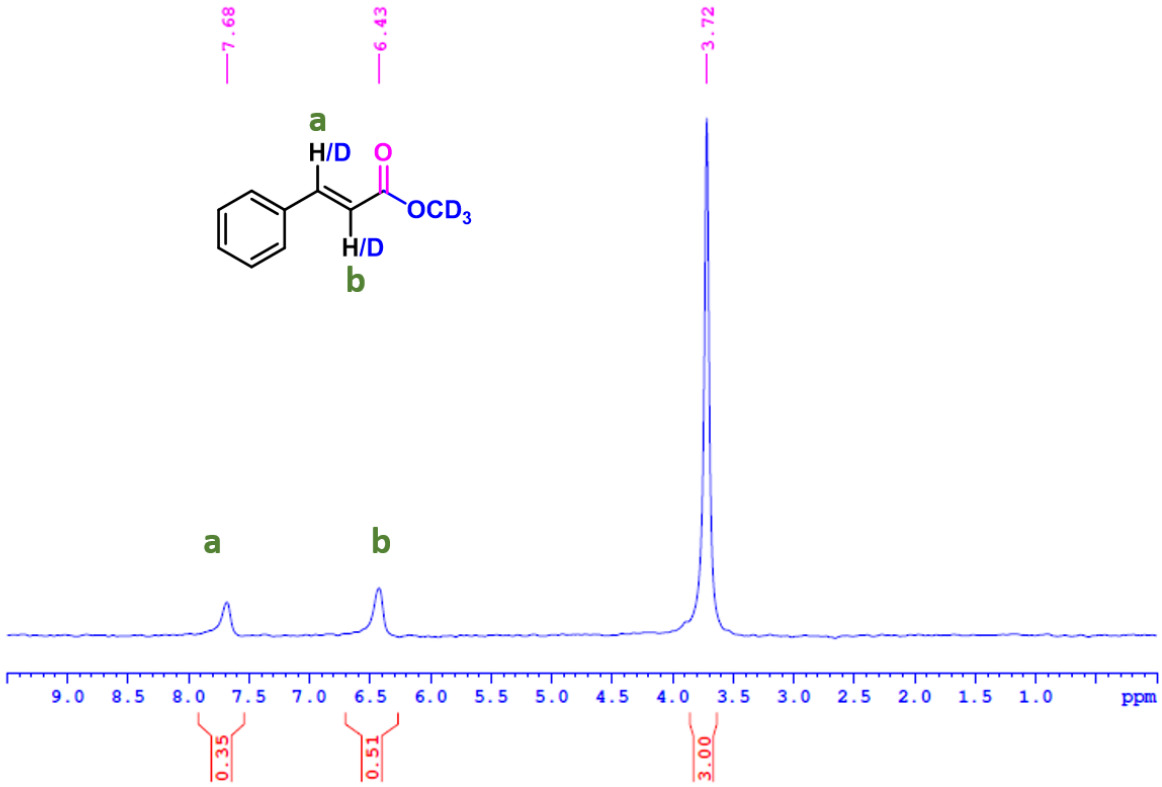


Figure S113: ^{2}H-NMR spectrum of deuterated methyl cinnamate in $CHCl_3$.

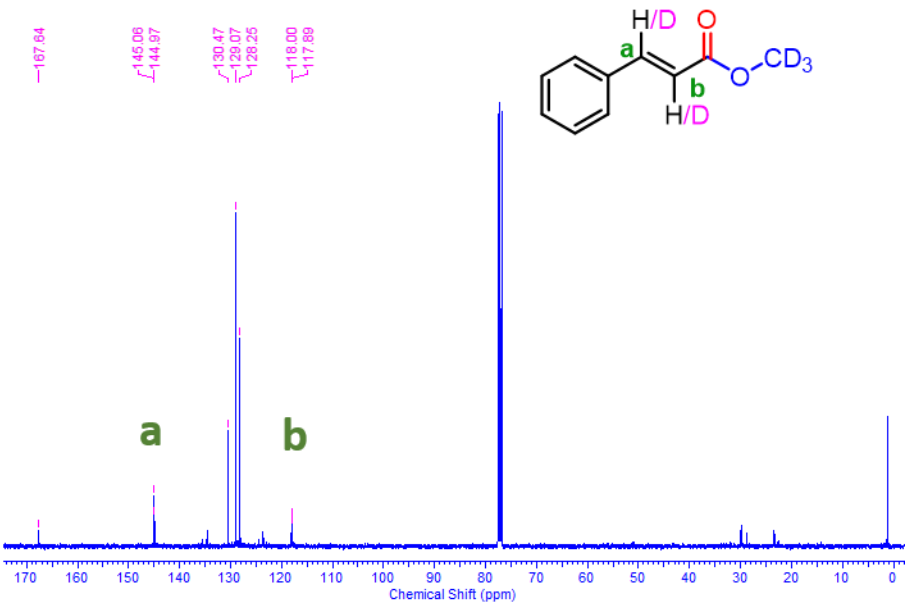
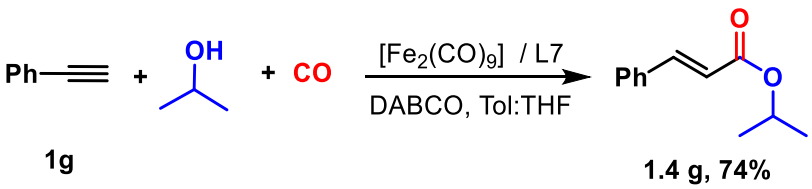
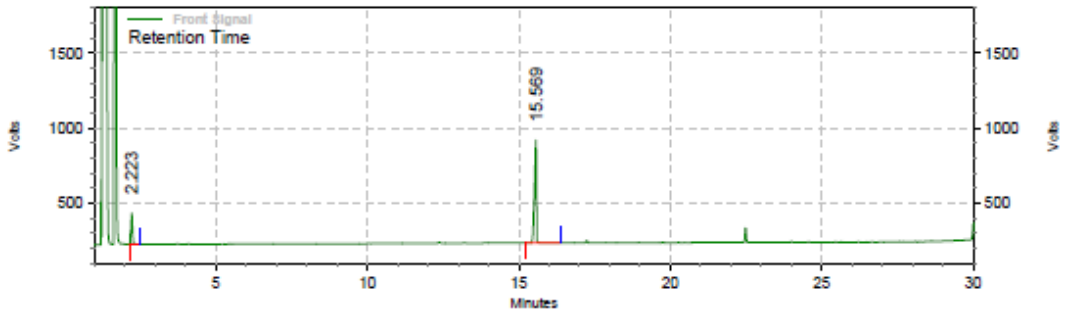


Figure S114: ^{13}C-NMR spectrum of deuterated methyl cinnamate in $CDCl_3$.

8. Scalability test:



In a glove box, an oven-dried conical flask (100 mL) containing a stirring bar was charged with $[Fe_2(CO)_9]$ (0.489 mmol, 88.9 mg), L7 (0.489 mmol, 244.5 mg), DABCO (48.9 mmol, 5.48 g), Phenyl acetylene (9.79 mmol, 1 g), and IPA (97.9 mmol, 7.48 mL). Then, Toluene (14 mL), and THF (14 mL) were added. Next, the content was transferred into a stainless steel autoclave (450 mL). After flushing the autoclave three times with CO, a pressure of 10 bar of CO was adjusted at ambient temperature. Then, the mixture was stirred for 36 h at 110 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. The conversion was determined by the GC and product was purified by column chromatography on silica gel (P.E./EA).



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
2.223	5496025	19.07	1606863	23.41
15.569	23325604	80.93	5258193	76.59
Totals	28821629	100.00	6865056	100.00

Figure S115: GC chromatogram of isopropyl cinnamate

9. Mechanistic studies:

9a. Kinetic analysis:

In a glove box, an oven-dried vial (4 mL) containing a stirring bar was charged with [$Fe_2(CO)_9$] (0.005 mmol, 1.8 mg), L7 (0.01mmol, 5 mg), DABCO (0.89 mmol, 100 mg), aryl alkyne (0.2 mmol), and alcohol (4 mmol). The vial was then sealed with a PTFE/white rubber septum and removed from the glovebox. Then, Toluene (0.38 mL), and THF (0.3 mL) were added by syringe under argon. The vial was placed in a beaker, which was transferred into a stainless steel autoclave (450 mL). After flushing the autoclave three times with CO, a pressure of 10 bar of CO was adjusted at ambient temperature. Then, the mixture was stirred for 0.5/1/1.5/2/2.5 hrs at 110 °C. After that, the autoclave was cooled down to room temperature and the pressure was released carefully. The product yield was determined in the presence of internal standard (dodecane 45.4 µL, 0.2 mmol) by GC.

Sr. No.	Time (min.)	Conc.of Product P1 ($Mmin^{-1}$)
1.	10	0.0011
2.	20	0.0047
3.	30	0.0058
4.	60	0.03
5.	90	0.046
6.	120	0.072
7.	150	0.089

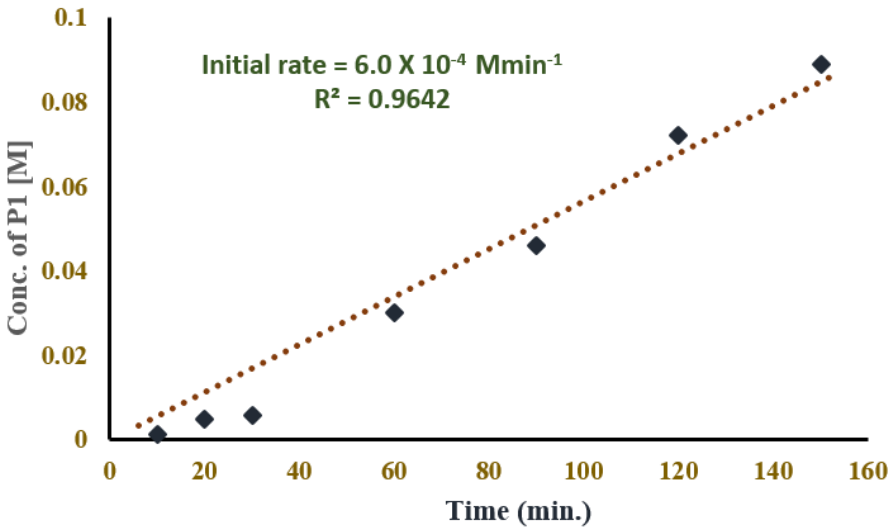


Figure S116A: Time-dependent formation of α- aryl aldehyde **P1** using iron catalyst.

Sr. No.	Time (min.)	Conc.of Product P1 [M]	
		In presence of ligand	In absence of ligand
1.	30	0.0058	0.0018
2.	60	0.03	0.013
3.	90	0.046	0.022
4.	120	0.072	0.031
5.	150	0.089	0.048

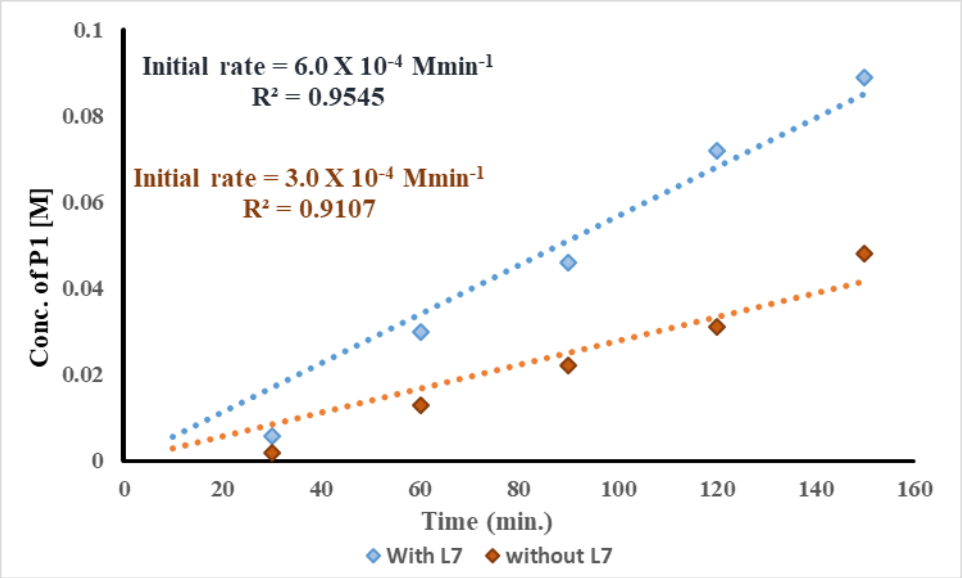
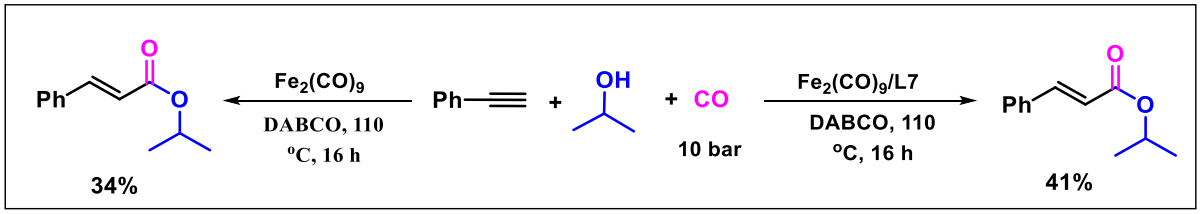
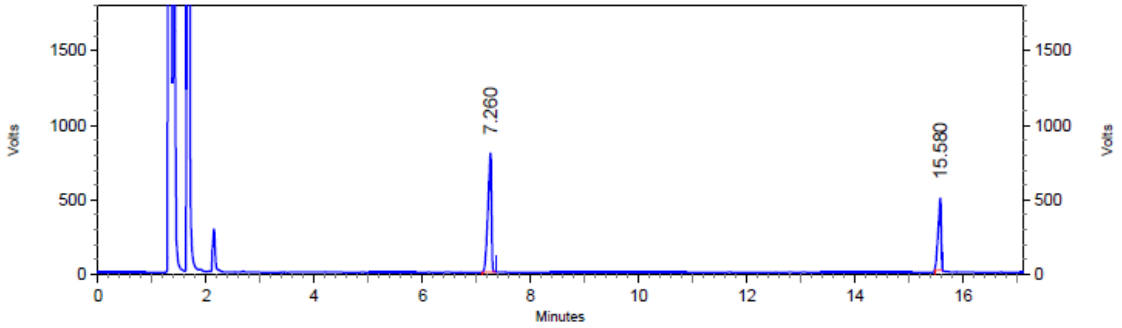


Figure S116B: Initial rate comparison for the formation of α- aryl aldehyde **P1** in presence and absence of ligand.

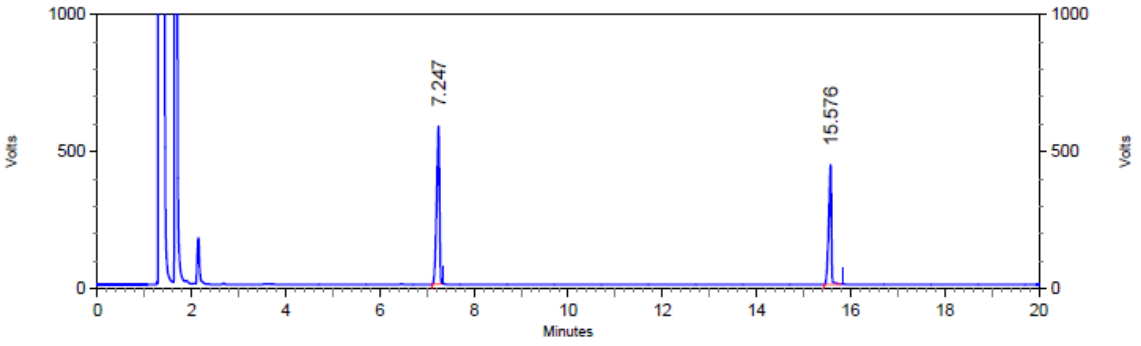




Front Signal
Results

Retention Time	Area	Area %	Height	Height %
7.260	27794955	65.82	6119065	62.32
15.580	14436803	34.18	3699352	37.68
Totals	42231758	100.00	9818417	100.00

Figure S116C: GC chromatogram for hydroalkoxycarbonylation of phenyl acetylene in absence of ligand



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
7.247	19007000	58.33	4431069	56.90
15.576	13578126	41.67	3355903	43.10
Totals	32585126	100.00	7786972	100.00

Figure S116D: GC chromatogram for hydroalkoxycarbonylation of phenyl acetylene in presence of ligand

In the presence of ligand we obtained 41% of product P1, while, in the absence of ligand, we observed 34% of product P1 with respect to internal standard and the corresponding GC yield is 71% and 51% respectively.

		Conc. of P1 [M]			
Time (h)	Catalyst mol %	1	2.5	5	7.5
	0.5	0.00557	0.00657	0.0058	0.0184
	1	0.00836	0.0225	0.03	0.0472
	1.5	0.0129	0.03012	0.046	0.088
	2	0.02896	0.0482	0.072	0.115

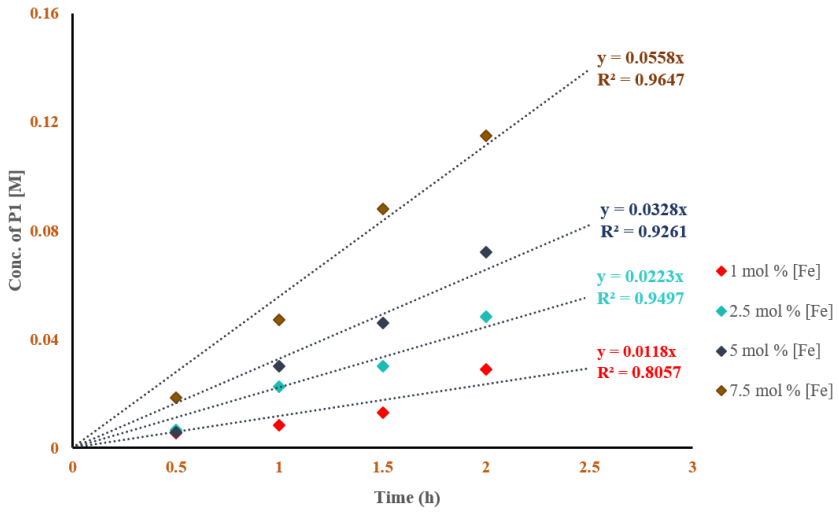


Figure S117A: Time-dependent formation of **P1** at different concentration of Iron catalyst.

log [cat.]	log rate
-3	-1.95
-2.6	-1.65
-2.3	-1.48
-2.12	-1.25

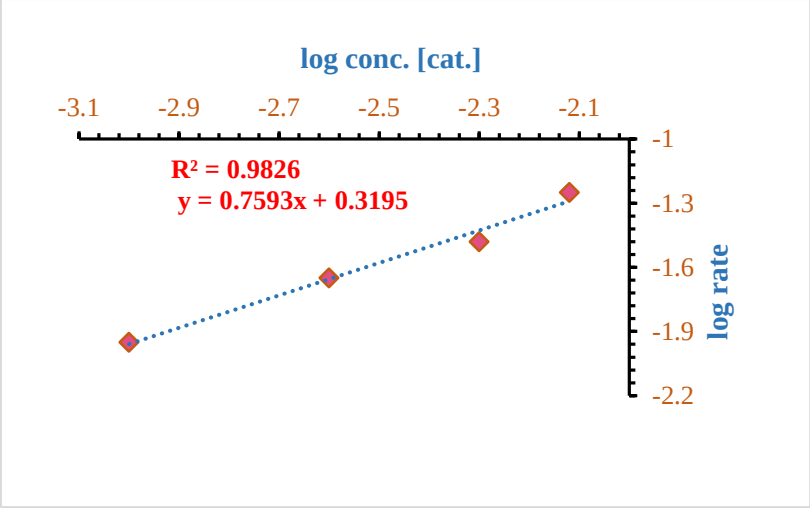


Figure S117B: Plot of log(rate) versus log(conc $Fe_2(CO)_9$.

	Conc. of P1 [M]				
Time	Substrate Conc. [S1]	0.2M	0.4M	0.6M	0.8M
	0.5	0.0058	0.0078	0.011	0.015
	1	0.03	0.03	0.043	0.049
	1.5	0.046	0.064	0.0541	0.07
	2	0.072	0.078	0.067	0.075

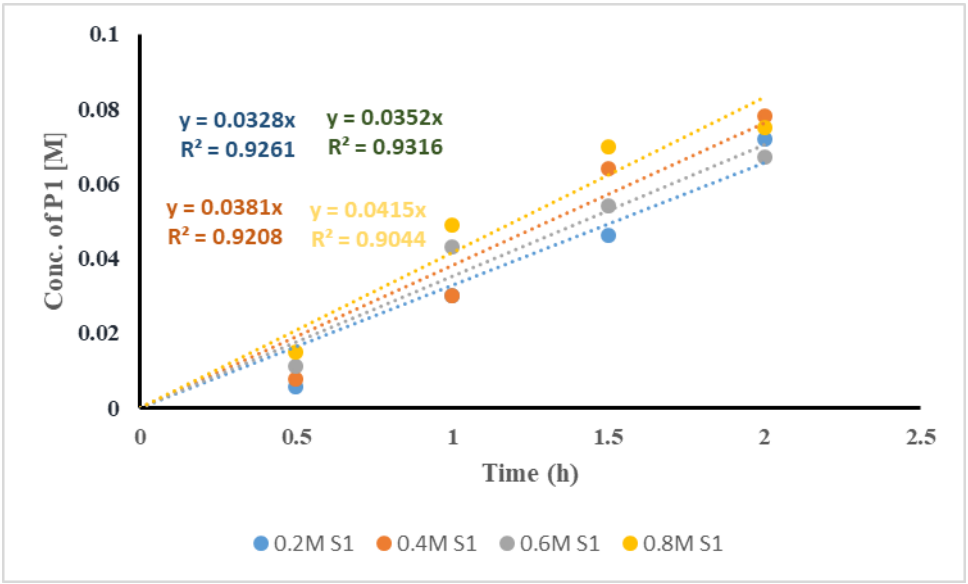


Figure S118A: Time-dependent formation of **P1** at different Substrate (S1 = Phenyl acetylene) concentration.

Conc. of S1	Initial rate
0.2	0.033
0.4	0.035
0.6	0.038
0.8	0.04

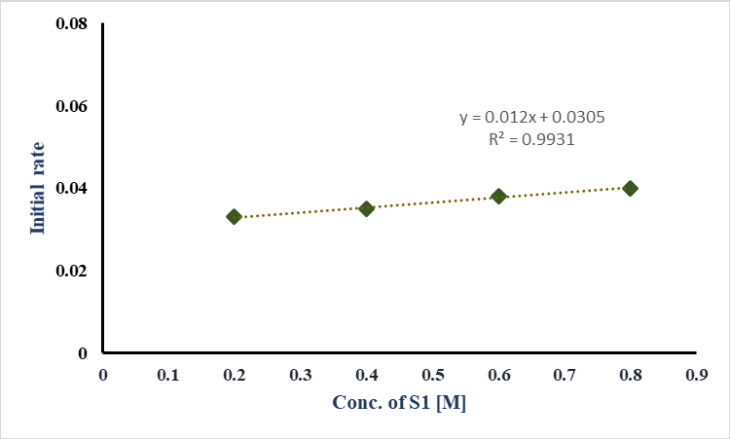


Figure S118B: Plot of initial rate versus substrate concentration.

9b. Control experiment:

Presence of Iron hydride:

An oven dried Schlenk tube was charged with $[Fe_2(CO)_9]$ (0.1 mmol, 36.3 mg, DABCO (0.1 mmol, 11.12 mg), MeOH (0.6 mmol, 24µL), further THF (0.5 mL) was added into it and the content was stirred for 1.5h/10h at room temperature. The presence of iron hydride has been determined by ^{1}H NMR spectroscopy.

$$[Fe_2(CO)_9] + DABCO + MeOH \longrightarrow [Fe\text{-}H]$$

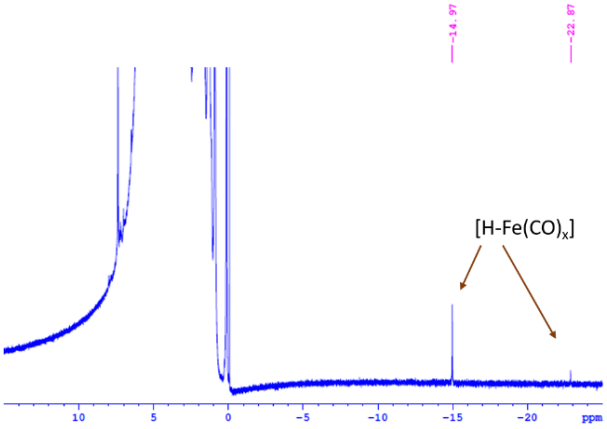


Figure S119: ^{1}H NMR of reaction mixture

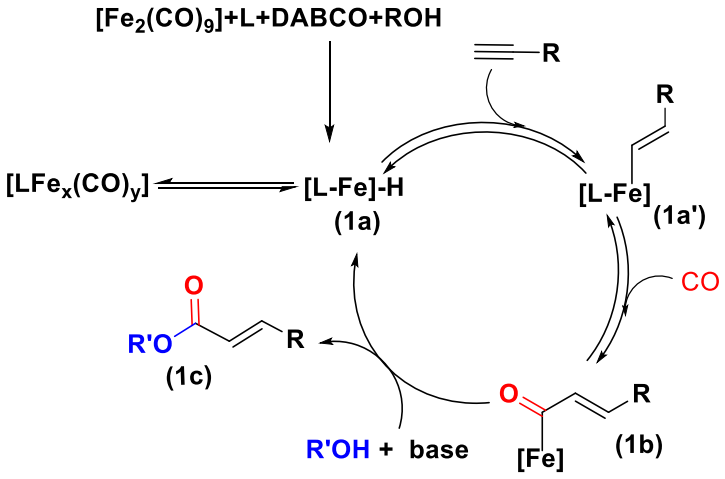
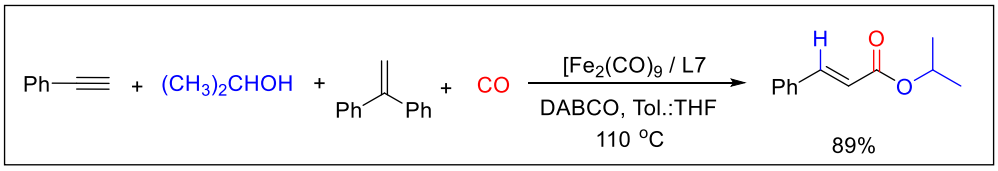


Figure S120: Proposed catalytic cycle

9c. Radical trap experiment:

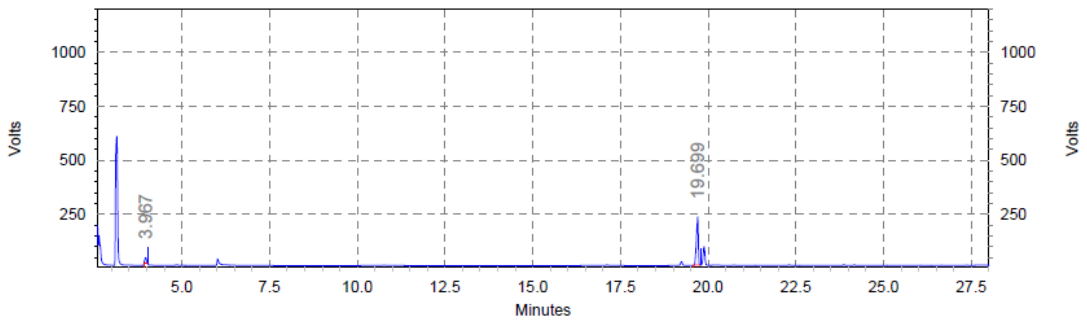
To confirm the involvement of radical species in the reaction, the reaction was performed in the presence diphenylethylene which hardly affected the reaction and gives product with slight less yield (89%).[26]



Scheme S2: Radical trap experiment for hydroalkoxycarbonylation reaction

In a glove box, an oven-dried vial (4 mL) containing a stirring bar was charged with $Fe_2(CO)_9$ (0.005 mmol, 1.8 mg), L7 (0.01 mmol, 5 mg), DABCO (0.89 mmol, 100 mg), phenyl acetylene (0.2 mmol, 0.02 mL) and DPE (0.2 mmol, 36.05 mg). The vial was then sealed and removed from the glovebox. Then IPA (4 mmol, 0.3 mL), Toluene (0.3 mL), and THF (0.3 mL) were added by syringe under argon. The vial was placed in a beaker, which was transferred into an autoclave. After flushing the autoclave three times with CO, a pressure of 10 bar of CO was adjusted at ambient temperature. Then, the mixture was stirred for 36 h at 110 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. The reaction mixture was then analyzed by GC and the result is shown below.

Gas Chromatography (GC) analysis for P1 was performed on an Agilent 7890B GC system using HP-05 column (30 m × 320 µm × 0.25 µm), split ratio 30:1, column pressure 5 psi, injector temperature of 260 °C, detector temperature of 300 °C, argon carrier gas. Temperature program: Initial temperature 70 °C, hold for 1 min.; ramp 1: 4 °C/min. to 120 °C; ramp 2: 6 °C/min. to 160 °C; ramp 3: 10 °C/min. to 250 °C ramp 4: 20 °C/min. to 320 °C, hold for 2 min. GC retention time for Phenyl acetylene = 3.9 min.; ester product P1 = 19.8 min.



Front Signal Results

Retention Time	Area	Area %	Height	Height %
3.967	728693	10.21	210432	10.89
19.699	6409368	89.79	1721425	89.11
Totals	7138061	100.00	1931857	100.00

Figure S121: GC data of P1 in the presence of DPE.

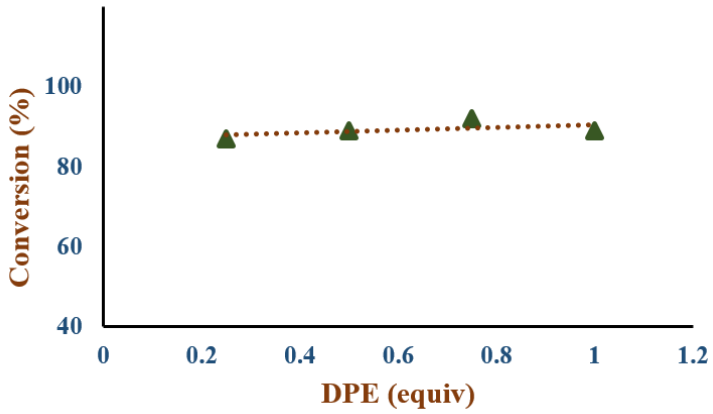


Figure S122 : Effect of DPE concentration in hydroalkoxycarbonylation of alkyne

Table S2: Effect of DPE loading on hydroakoxycarbonylation of alkyne

DPE equiv	Product conversion (%)
0.25	87
0.5	89
0.75	92
1.00	89

9d. Procedure for EPR analysis:

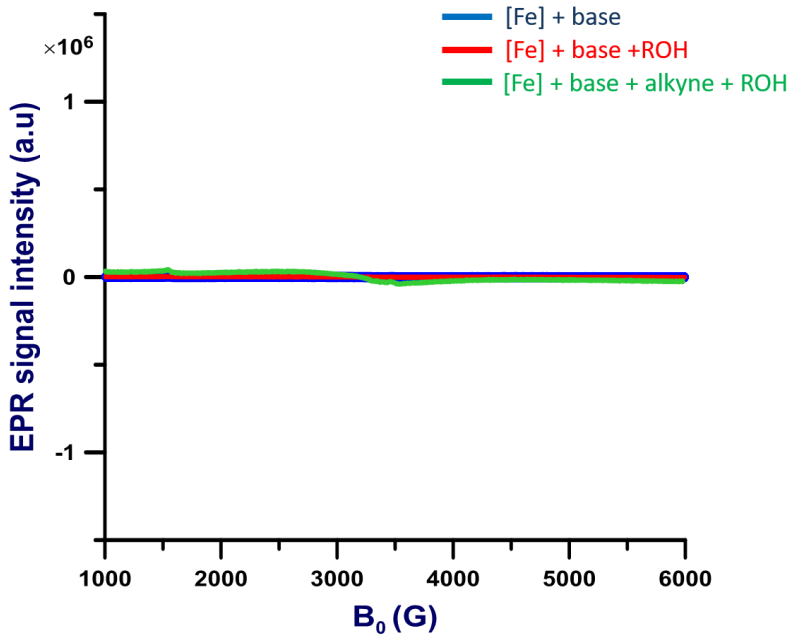
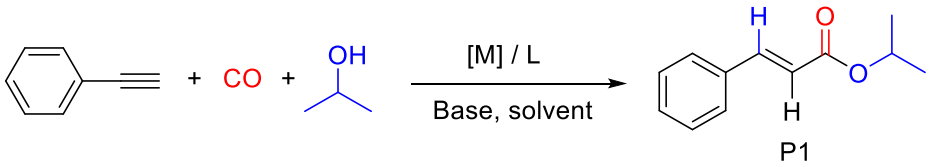


Figure S123: EPR spectra of the control experiments.

Reaction vials (4 mL) containing stirring bars were charged with [$Fe_2(CO)_9$] (0.05 mmol, 18.2 mg), L7 (0.05 mmol, 25 mg), DABCO (0.2 mmol, 22.4 mg), isopropyl alcohol (0.4 mmol, 30 µL), alkyne (0.1 mmol, 10 µL) then toluene:THF (0.3:0.1 mL) was added in the glove box. The vials were then sealed with a PTFE caps and taken out from the glove box. Then, mixtures were heated at 110 ^oC under 10 bar CO pressure in autoclave for 45 min. then content was cooled down and then reaction mixture was transferred to EPR tubes in glove box and was frozen at 77 K, which was then subjected to the EPR measurement.

As seen in figure S123, the blue line (Fe+base) and red line (Fe+base+ROH) does not show any EPR signal. The green line (Fe+base+alkyne+ROH) disclosed a broad hump. However, there is no clear signal to conclude the existence of radical species. A similar observation is made by Wu and co-workers and it was concluded that such hump can not be assigned as an EPR signal. In line with this report, figure S123 does not show any clear EPR signal and the possibility of existence of a radical species is very dim.

10. Investigation of possible metal contaminations:



P1

Table S3: Testing of other metals.

Entry	Catalyst [M]	Conversion (%)[b]
1.	$Co_2(CO)_8$	0.88
2.	$PdCl_2$	0.55
3.	CuBr	0.3
4.	CuCl	0
5.	$Ni(COD)_2$	0.6
6.	$Pd_2(DBA)_3$	0.8
7.	$Ru_3(CO)_{12}$	0.8
8.	$Cu(OAc)_2$	0.6

Conditions: a) [M] = 0.0006 mmol (0.3 mol%), L = 0.0006 mmol, DABCO = 4.5 equiv, Phenyl acetylene = 0.02 mL (0.2 mmol); b) conversion determined by GC.

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