

Supplementary Information

Ester directed orthogonal dual C-H activation and *ortho* aryl C-H alkenylation *via* distal weak coordination

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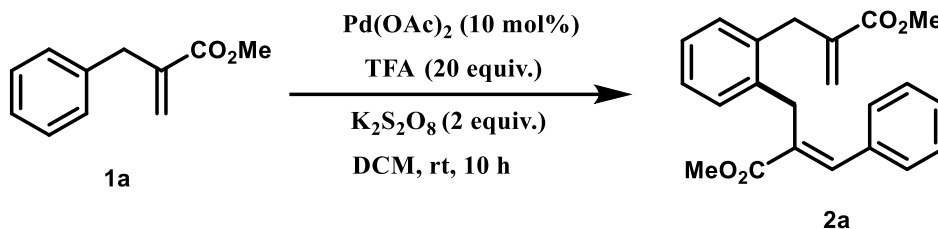
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1. General Information:

Commercial reagents were used without further purification. IR spectra were recorded on a Perkin Elmer-FTIR spectrometer using solid samples as KBr plates. IR spectra peaks are reported in wave numbers (cm^{-1}) as strong (s), medium (m), weak (w), and broad (br). For compounds ^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra were recorded in deuteriochloroform- d_3 (CDCl_3) or dimethyl sulfoxide- d_6 ($\text{DMSO}-\text{d}_6$) on a Bruker 400 MHz spectrometer using tetramethylsilane (TMS, $\delta = 0$) as an internal standard. Spin multiplicities are reported as singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m). Mass spectra were recorded on Agilent 1200 LC/MS-6110 mass spectrometry. Spectral data and copy of ^1H and ^{13}C NMR of all compounds **2a-z**, and **4a-p**, **6a-g**, **8a-k** are listed below.

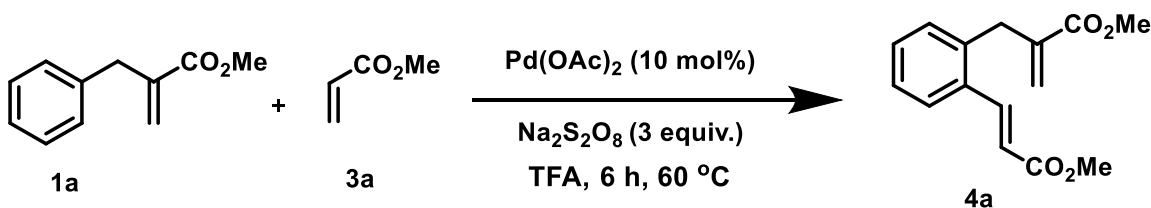
2. General Experimental Procedures

General procedure for the inter molecular aryl sp^2 and aliphatic sp^2 C-H bond activation (**2a**)



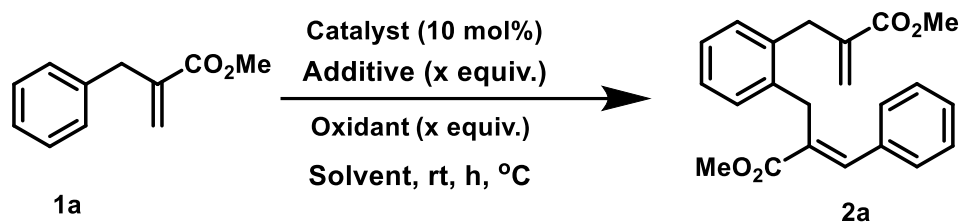
A round bottom flask containing methyl 2-benzylacrylate **1a** (0.3 mmol %), was evacuated and filled with oxygen gas using an oxygen balloon. Then dichloromethane (3.0 ml), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) (2 equiv.) and trifluoroacetic acid (TFA) (20 equiv.), palladium acetate $\text{Pd}(\text{OAc})_2$ were sequentially added to the system under an oxygen atmosphere. The reaction mixture was stirred at room temperature for 10 hr. After completion of reaction, the reaction mixture was diluted with dichloromethane (10 mL). The mixture was then filtered through a Celite pad and the Celite pad was washed with dichloromethane (30 mL). The combined filtrate was concentrated and the residue was purified by column chromatography (Silica gel, hexane-EtOAc) to give the corresponding pure coupling product **2a**.

General procedure for the intermolecular aryl sp^2 with unactivated alkene activation (**4a**)



A round bottom flask containing methyl 2-benzylacrylate **1a** (0.3 mmol %), and sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) (3 equiv.), trifluoroacetic acid (TFA) (1 mL), palladium acetate $\text{Pd}(\text{OAc})_2$ were sequentially added to the system under an oxygen atmosphere. Finally, acrylate (3 equiv.) **3a** was added and the reaction mixture was stirred at 60 °C for 6 h. After completion of reaction monitored by TLC, the reaction mixture was diluted with dichloromethane (10 mL). The mixture was then filtered through a Celite pad the combined filtrate was quenched with aqueous sodium bicarbonate solution and organic layer was concentrated and the residue was purified by column chromatography (Silica gel 100-200 mesh in, hexane-EtOAc) to give the corresponding pure oxidative coupling product **4a**.

3. Optimization studies for metal catalyzed site-selective intermolecular C-H alkylation^{a,b}

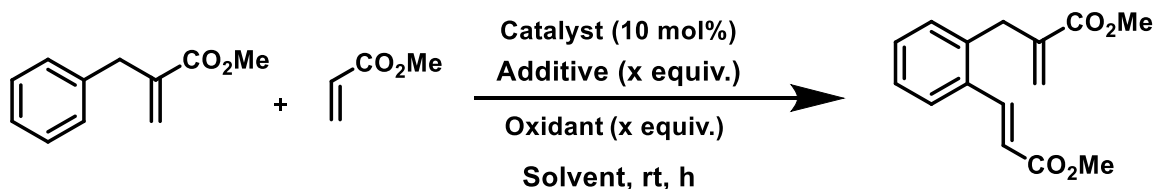


Entry	Catalyst	Oxidant/equiv	Additive/equiv.	Solvent	Temp °C/time h	Yield ^b
1	Pd(OAc) ₂	O ₂	TFA/8	DCM	RT/36	10
2	Pd(OAc) ₂	Cu(OAc) ₂ /1	TFA/8	DCM	RT/36	22
3	Pd(OAc) ₂	Cu(OAc) ₂ /1	TFA/8	DCM	RT/36	25
4	Pd(OAc) ₂	Cu(OAc) ₂ /1	TFA/TFAA (1:1)	DCM	RT/36	14
5	Pd(OAc) ₂	Cu(OAc) ₂ /1	PivOH/10	DCM	RT/24	-
6	Pd(OAc) ₂	Cu(OAc) ₂ /1	MsOH/10	DCM	RT/24	20
7	Pd(OAc) ₂	Cu(OAc) ₂ /1	TfOH/10	DCM	RT/24	32
8	Pd(OAc) ₂	Cu(OAc) ₂ /1	TFA/8	DCM	RT/24	40
9	Pd(OAc) ₂	Cu(OAc) ₂ /1	TFA/15	DCM	RT/24	45
10	Pd(OAc) ₂	Cu(OAc) ₂ /1	TFA/20	DCM	RT/24	50
11	Pd(OAc) ₂	Cu(OAc) ₂ /1	TFA/20	DCE	80/24	45
12	Pd(OAc) ₂	Cu(OAc) ₂ /1	TFA/20	CCl ₄	60/24	30
13	Pd(OAc) ₂	Ag ₂ O/1	TFA/20	DCM	RT/24	20
14	Pd(OAc) ₂	Ag ₂ CO ₃ /1	TFA/20	DCM	RT/24	26
15	Pd(OAc) ₂	Cu(OAc) ₂ /1		DCM	RT/24	-
16	Pd(OAc) ₂	BQ/1	TFA/20	DCM	RT/24	Trace
17	Pd(OAc) ₂	K ₂ S ₂ O ₈ /1	TFA/20	DCM	RT/24	55
18	Pd(OAc) ₂	K ₂ S ₂ O ₈ /2	TFA/20	DCM	RT/24	62
19	Pd(OAc)₂	K₂S₂O₈/2	TFA/20	DCM	RT/10	75
20	Pd(OAc) ₂	K ₂ S ₂ O ₈ /2	PivOH/20	DCM	RT/10	-
21	Pd(OAc) ₂	K ₂ S ₂ O ₈ /2	MsOH/20	DCM	RT/10	14
22	Pd(OAc) ₂	K ₂ S ₂ O ₈ /2	TfOH/20	DCM	RT/10	25
23	Pd(OAc) ₂	K ₂ S ₂ O ₈ /2	TFA/20	TFE	RT/10	10
24	Pd(OAc) ₂	K ₂ S ₂ O ₈ /2	TFA/20	HFIP	RT/10	42
25	Pd(OAc) ₂	K ₂ S ₂ O ₈ /2	TFA/20	THF	RT/10	-
26	Pd(OAc) ₂	K ₂ S ₂ O ₈ /2	TFA/20	-	RT/10	59
27	Pd(OAc) ₂	Na ₂ S ₂ O ₈ /2	TFA/20	DCM	RT/10	53
28	Pd(OAc) ₂	Cu(OTf) ₂ /1	TFA/20	DCM	RT/10	30
29	Pd(OAc) ₂	(NH ₄) ₂ S ₂ O ₈ /1	TFA/20	DCM	RT/10	45
30	Pd(OAc) ₂	CuBr ₂ /1	TFA/20	DCM	RT/24	10
31	Pd(PPh ₃) ₄	K ₂ S ₂ O ₈ /2	TFA/20	DCM	RT/10	-
32	(Ru(<i>p</i> -cymene)Cl ₂) ₂	Cu(OAc) ₂ . H ₂ O/1	AgSbF ₆	DCE	100/16	-
33	PdCl ₂	K ₂ S ₂ O ₈ /2	TFA/20	DCM	RT/10	10
34	Pd(OAc) ₂	K ₂ S ₂ O ₈ /2	TFA/20	THF	80/10	-

35	Pd(OAc) ₂	K ₂ S ₂ O ₈ /2	TFA/20	-	80/10	37
36	Pd(OAc) ₂	K ₂ S ₂ O ₈ /2	TFA/20	CH ₃ CN	80/10	-
37	Pd(OAc) ₂	K ₂ S ₂ O ₈ /2	TFA/20	HFIP	80/10	33
38	Pd(OAc) ₂	K ₂ S ₂ O ₈ /2	TFA/20	TFE	80/10	24
39	Pd(OAc) ₂	K ₂ S ₂ O ₈ /2	TFA/20	DMF	120/10	trace

Reaction Condition: ^a**1** (0.3 mmol), Pd(OAc)₂ (10 mol%), TFA (20 equiv.), K₂S₂O₈ (2equiv.), DCM (3 mL) at rt for 10 h under O₂ atmosphere, ^bIsolated yield of the pure product.

3.1 Optimization studies for metal catalyzed site-selective intermolecular C-H alkenylation^{a,b}

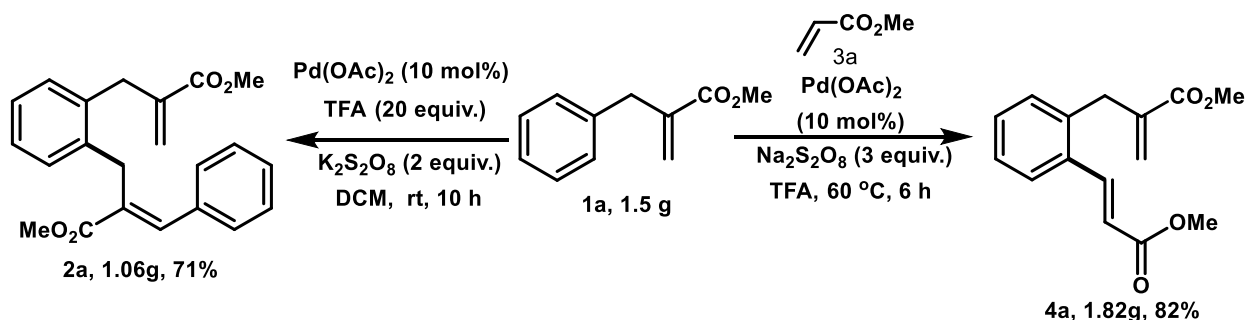


Entry	Catalyst	Oxidant/equiv	Additive/equiv	Solvent	Temp °C/time h	Yield ^b
1	Pd(OAc) ₂	Na ₂ S ₂ O ₈ /2	TFA/20	DCM	RT/10	34
2	Pd(OAc) ₂	Na ₂ S ₂ O ₈ /2	-	TFA	60/24	52
3	Pd(OAc) ₂	Na ₂ S ₂ O ₈ /2	-	TFA	60/12	76
4	Pd(OAc) ₂	Na ₂ S ₂ O ₈ /3	-	TFA	60/12	84
5	Pd(OAc)₂	Na₂S₂O₈/3	-	TFA	60/6	89
6	Pd(OAc) ₂	Na ₂ S ₂ O ₈ /3	-	TFA	80/3	72

Reaction Condition: **1a** (0.3 mmol) and acrylate **3a** (3 equiv.), Pd (OAc)₂ (10 mol%), Na₂S₂O₈ (3 equiv.), TFA as solvent. ^bIsolated yield of the pure products.

4. Gram scale synthesis and Control experiments

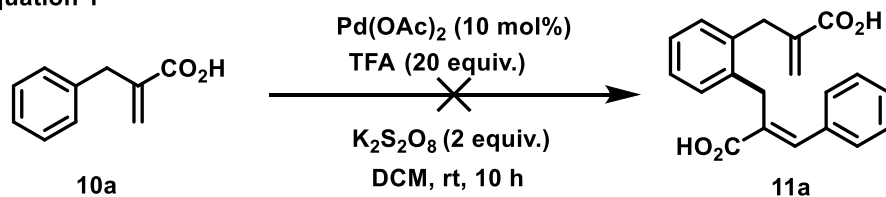
Scheme 1. Gram scale synthesis of **1a** and **4a**



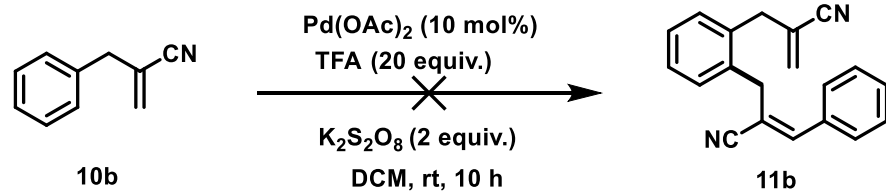
To check the importance of ester moiety we have done some control experiments. Accordingly, we prepared compound **10a**, **10b** and subjected for the orthogonal CDC reaction under the standard reaction condition. However, the expected CDC products **11a** and **11b** (Scheme 2, Equation 1 & 2) were not formed. Further, we prepared the compound **10c** where we additionally installed 2-picoline directing group to check the competitiveness of the ester and pyridine moiety as directing group for the 1, 3 diaryl derivative formation. In this case, we did not observe the desired product **11c** (Scheme 2, Equation 3). Next, we examined compound **5a** where an additional aryl group is present at the β -position of α - β unsaturated ester compared to the compound **1a** and was subjected under the standard reaction condition. We did not observe the anticipated product **12a** which may be due to the probable π - π stacking of two aryl rings that makes the ester moiety to situate away from the *ortho* C-H bond reaction site (Scheme 2, Equation 4). Furthermore, compound **13** was prepared where methyl moiety is present in the place of ester moiety and subjected for the C-H olefination reaction under the standard reaction condition used in Table 2 which did not provide the anticipated *ortho* olefinated product **14** (Scheme 2, Equation 5). Hence, all these experiments clearly indicate that the ester moiety is crucial for orthogonal dual C-H activation and intermolecular C-H activation alkenylation reaction.

Scheme 2. Control experiments for the directing group and substrates.

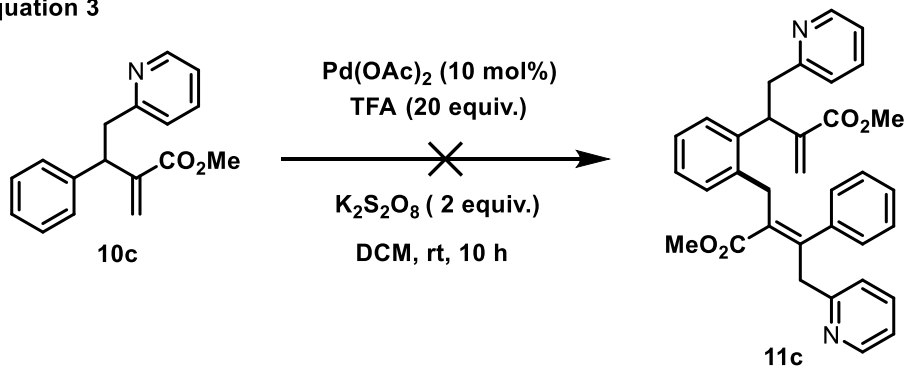
Equation 1



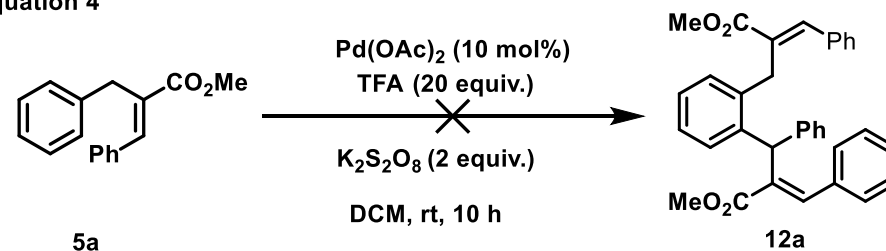
Equation 2



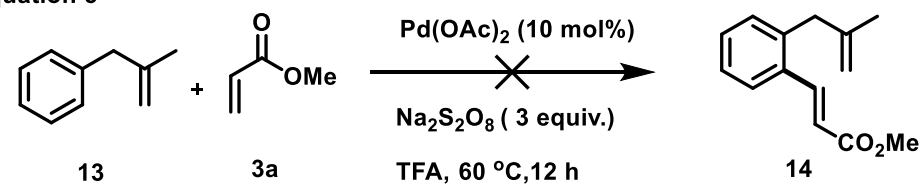
Equation 3



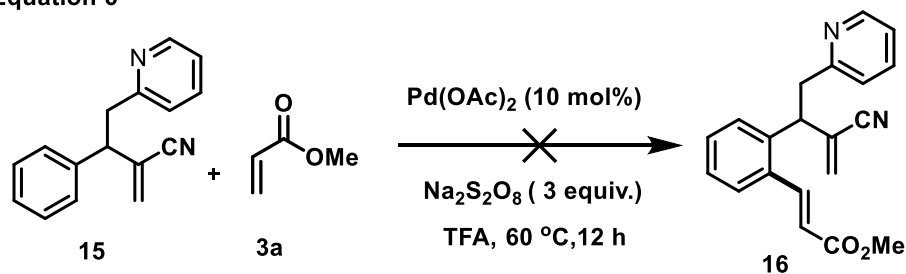
Equation 4



Equation 5



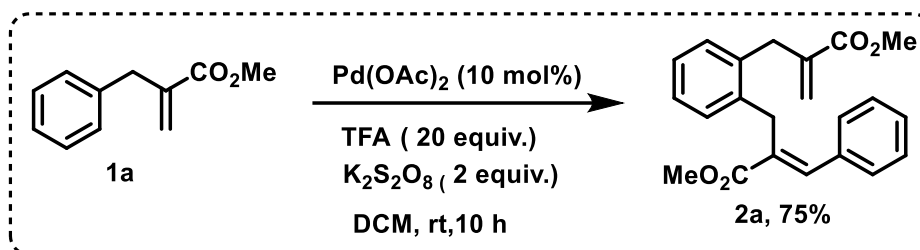
Equation 6



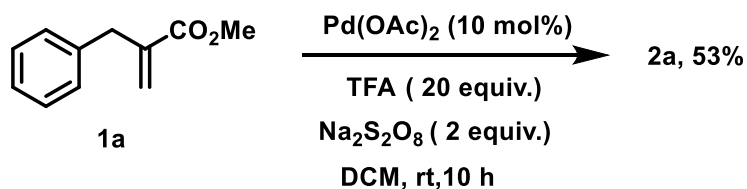
To explore the role of oxidants in the C-H activation reaction, some control experiments were performed to compare the selectivity of product formation as shown in Scheme 3. For the orthogonal dual C-H activation reaction, we changed the oxidant from $\text{K}_2\text{S}_2\text{O}_8$ to $\text{Na}_2\text{S}_2\text{O}_8$ which produced 53% yield of compound **2a** (Scheme 3, Equation 7). The same reaction was carried out for intermolecular C-H alkenylation reaction with methyl acrylate (**3a**) which provided both **2a** and **4a** in 23% and 42% yields respectively (Scheme 3, Equation 8). However, upon changing the oxidant from $\text{K}_2\text{S}_2\text{O}_8$ to $\text{Na}_2\text{S}_2\text{O}_8$, the reaction produces the desired product **4a** in 34% yield only (Scheme 3, Equation 9). Further, we carried out the same reaction by using both $\text{K}_2\text{S}_2\text{O}_8$ and $\text{Na}_2\text{S}_2\text{O}_8$ in equal amount (1.5 equiv.) which provided both the product **4a** and **2a** in 31% and 26% yields respectively (Scheme 3, Equation 10). These experiments indicate that the $\text{K}_2\text{S}_2\text{O}_8$ is more suitable for the formation of orthogonal dual C-H activation reaction product **2**. Similarly, for intermolecular C-H alkenylation reaction $\text{Na}_2\text{S}_2\text{O}_8$ is more suitable.

Scheme 3: Screening of oxidants.

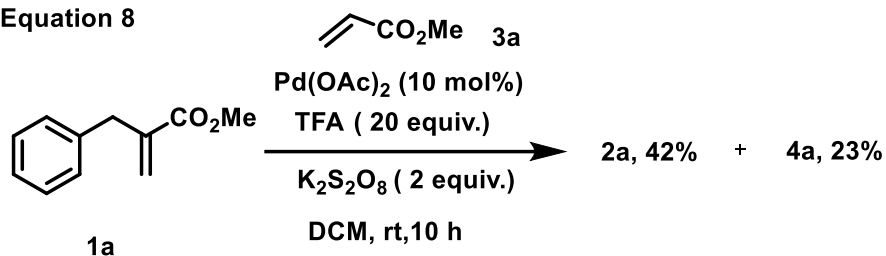
Standard condition



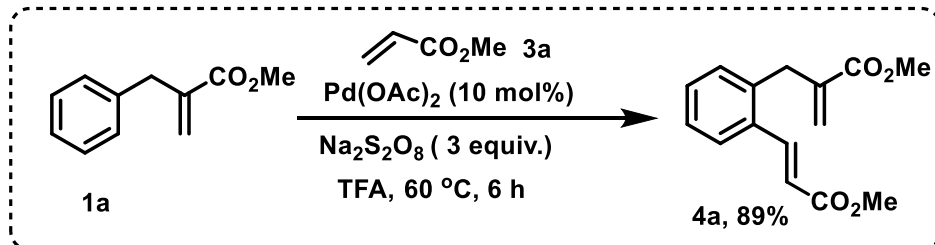
Equation 7



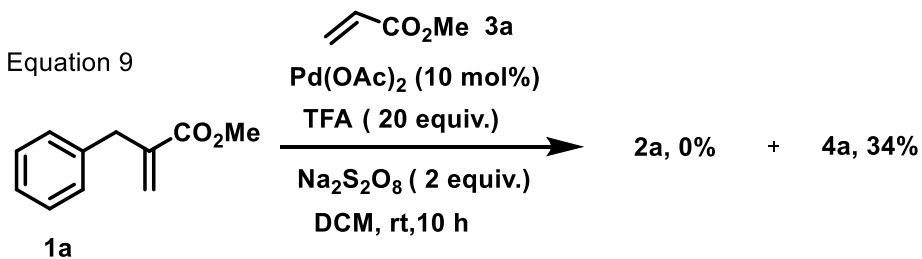
Equation 8



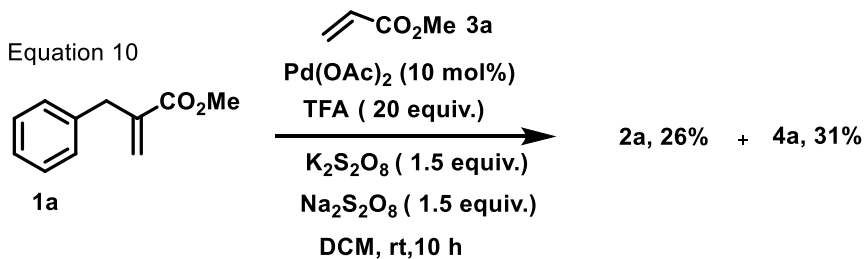
Standard condition



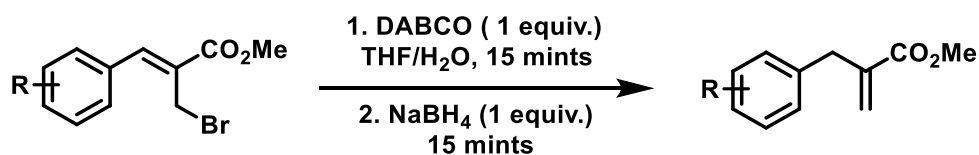
Equation 9



Equation 10



5. Preparation of starting materials^a

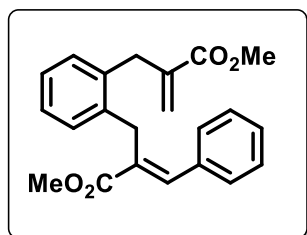


In round bottom flask, Baylis-Hillman bromo adduct was taken in the mixture of solvents (THF/H₂O (1:1)) followed by addition DABCO salt. The reaction mixture was stirred for 15 mints, followed by portion wise addition of NaBH₄ (aware of releasing hydrogen gas). The reaction mixture was allowed to continue for 15 min. After completion of reaction as evidence by TLC, the product was further purified by column chromatography.

^a D. Basavaiah, N. Kumaragurubaran, *Tetrahedron Lett*, 2001, **42**, 477–479.

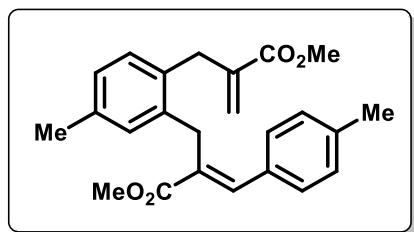
6. CHARACTERIZATION DATA FOR THE PRODUCTS

Methyl (*E*)-2-(2-(2-(methoxycarbonyl) allyl) benzyl)-3-phenylacrylate (2a):



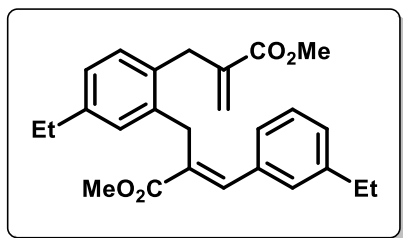
Colorless liquid, Yield (75%, 39mg) IR (Pellet, cm⁻¹) 3446.09, 2972.68, 1745.62, 1468.48, 1378.21; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (s, 1H), 7.39-7.29 (m, 5H), 7.28-7.16 (m, 4H), 6.29 (d, *J* = 1.3 Hz, 1H), 5.28 (d, *J* = 1.4 Hz, 1H), 3.89 (s, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 3.73 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 168.73, 167.57, 141.77, 139.05, 137.80, 136.55, 135.27, 130.68, 130.16, 129.32, 128.97, 128.67, 127.27, 127.13, 126.63, 126.04, 52.23, 52.06, 35.09, 30.54; HRMS (ESI): calc. for [(C₂₄H₂₆O₄)] (M+H) 351.1597, measured 351.1596

Methyl (*E*)-2-(2-(2-(methoxycarbonyl) allyl)-5-methyl benzyl)-3-(*p*-tolyl) acrylate (2b):



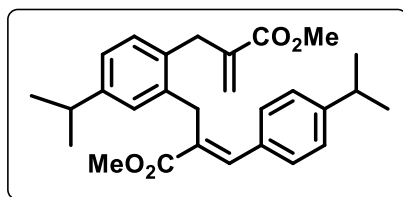
Colorless liquid, Yield (72%, 41mg); IR (Pellet, cm⁻¹) : 2973.54, 2722.08, 1744.92, 1468.04, 1378.20; ¹H NMR (400 MHz, CDCl₃) δ 7.97 (s, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.03 (dd, *J* = 21.4, 7.7 Hz, 2H), 6.91 (s, 1H), 6.23 (d, *J* = 1.3 Hz, 1H), 5.24 (d, *J* = 1.5 Hz, 1H), 3.80 (s, 2H), 3.76 (s, 3H), 3.74 (s, 3H), 3.64 (s, 2H), 2.33 (s, 3H), 2.26 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.00, 167.71, 141.87, 139.25, 137.60, 136.76, 133.41, 132.45, 130.60, 129.51, 129.44, 129.16, 127.75, 127.28, 125.96, 52.25, 52.08, 34.74, 30.51, 21.48, 21.40; HRMS (ESI): calc. for [(C₂₄H₂₆O₄)] (M+H) 379.1913, measured 379.1909.

Methyl (*E*)-2-(5-ethyl-2-(2-(methoxycarbonyl) allyl) benzyl)-3-(4-ethylphenyl) acrylate (2c):



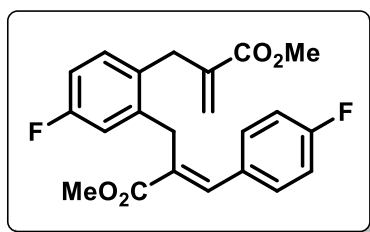
Colorless liquid, Yield (73%, 45mg); IR (Pellet, cm^{-1}): 3446.09, 2972.43, 1744.62, 1469.40, 1378.61; ^1H NMR (400 MHz, CDCl_3): δ 7.98 (s, 1H), 7.21 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 7.10-7.02 (m, 2H), 6.94 (s, 1H), 6.23 (d, $J = 1.4$ Hz, 1H), 5.25 (d, $J = 1.5$ Hz, 1H), 3.81 (s, 2H), 3.76 (s, 3H), 3.73 (s, 3H), 3.65 (s, 2H), 2.63 (q, $J = 7.6$ Hz, 2H), 2.56 (q, $J = 7.6$ Hz, 2H), 1.21 (t, $J = 16$, 3H), 1.15 (t, $J = 16$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.03, 167.73, 145.49, 143.15, 141.86, 139.26, 137.66, 133.67, 132.75, 130.65, 129.57, 129.30, 128.24, 126.74, 126.01, 125.91, 52.22, 52.07, 34.77, 30.59, 28.82, 28.69, 15.75, 15.46; HRMS (ESI): calc. for $[(\text{C}_{26}\text{H}_{30}\text{O}_4)]$ (M+H) 407.2201, measured 407.2222.

Methyl (*E*)-2-(5-isopropyl-2-(2-(methoxycarbonyl) allyl) benzyl)-3-(4-isopropylphenyl) acrylate (2d):



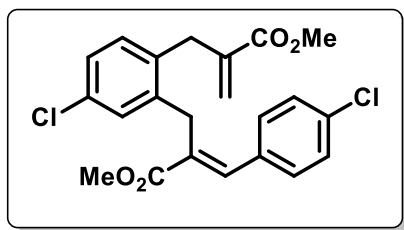
Colorless liquid, Yield (70%, 46mg); IR (Pellet, cm^{-1}): 2972.86, 2723.26, 1745.78, 1468.52, 1378.09; ^1H NMR (400 MHz, CDCl_3): δ 7.98 (s, 1H), 7.22 (d, $J = 8.2$ Hz, 2H), 7.16 (d, $J = 8$ Hz, 2H), 7.08 (dd, $J = 10.4$, 4.7 Hz, 2H), 6.96 (s, 1H), 6.23 (d, $J = 1.3$ Hz, 1H), 5.25 (d, $J = 1.5$ Hz, 1H), 3.81 (s, 2H), 3.76 (s, 3H), 3.72 (s, 3H), 3.64 (s, 2H), 2.85 (dtd, $J = 20.7$, 13.8, 6.9 Hz, 2H), 1.22 (d, $J = 8$, 6H), 1.16 (d, $J = 8$, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.73, 164.54, 147.96, 143.52, 141.05, 137.81, 137.24, 133.43, 132.06, 129.42, 128.84, 126.22, 125.69, 124.68, 52.20, 52.08, 34.09, 33.85, 30.6, 29.86, 24.12, 23.94; HRMS (ESI): calc. for $[(\text{C}_{28}\text{H}_{34}\text{O}_4)]$ (M+H) 435.2565, measured 435.2535

Methyl (*E*)-2-(5-fluoro-2-(2-(methoxycarbonyl)allyl)benzyl)-3-(4-fluorophenyl) acrylate (2e):



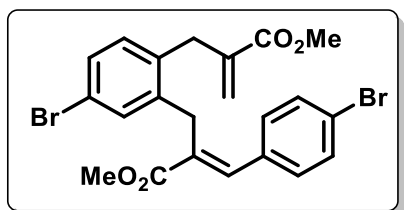
Colourless solid, Yield (73%, 42mg); IR (Pellet, cm^{-1}): 3446.09, 2972.43, 1744.62, 1469.40, 1378.61; ^1H NMR (CDCl_3 , 400 MHz): δ 7.97 (s, 1H), 7.25-6.8 (m, 7H), 6.24 (d, 1H), 5.25 (d, 1H), 3.79 (s, 2H), 3.76 (s, 6H), 3.64 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 168.34, 167.41, 141.18, 140.04, 138.95, 132.20, 132.17, 132.11, 132.03, 131.34, 131.26, 131.14, 131.11, 129.15, 126.05, 116.02, 115.80, 114.27, 114.05, 113.48, 113.27, 52.41, 52.15, 34.46, 30.58; HRMS (ESI): calc. for $[(\text{C}_{22}\text{H}_{20}\text{F}_2\text{O}_4)]$ (M+H) 419.0739, measured 419.0835.

Methyl (*E*)-2-(5-chloro-2-(2-(methoxycarbonyl) allyl) benzyl)-3-(4-chlorophenyl) acrylate (2f):



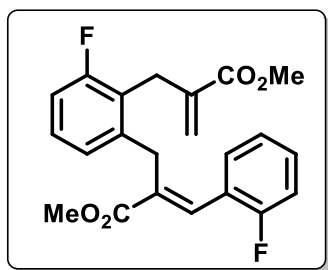
Colorless liquid, Yield (69%, 43mg); IR (Pellet, cm^{-1}): 3445.96, 2973.03, 2723.14, 1745.90, 1468.17, 1378.22; ^1H NMR (400 MHz, CDCl_3) δ 7.96 (s, 1H), 7.30 (d, J = 8.5 Hz, 2H), 7.20-7.17 (m, 3H), 7.11 (d, J = 8.1 Hz, 1H), 7.04 (d, J = 1.9 Hz, 1H), 6.25 (d, J = 1.1 Hz, 1H), 5.26 (d, J = 1.2 Hz, 1H), 3.78 (s, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.64 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 168.15, 167.30, 141.04, 139.57, 138.69, 135.16, 133.45, 133.15, 131.95, 130.60, 129.91, 129.08, 127.16, 126.91, 126.24, 52.46, 52.18, 34.62, 30.50; HRMS (ESI): calc. for $[(\text{C}_{22}\text{H}_{20}\text{Cl}_2\text{O}_4)]$ (M+H) 419.0837, measured 419.0817.

Methyl (*E*)-2-(5-bromo-2-(2-(methoxycarbonyl)allyl)benzyl)-3-(4-bromophenyl) acrylate (2g):



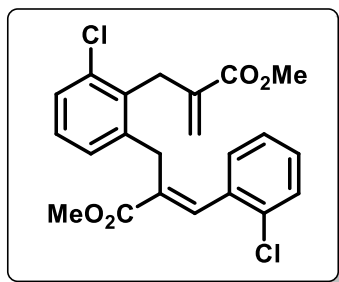
Colourless liquid, Yield (64%, 49 mg) ; IR (Pellet, cm^{-1}): 3445.02, 2973.46, 2723.65, 1745.02, 1467.32, 1377.20; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (s, 1H), 7.45 (d, J = 8 Hz 2H), 7.33 (dd, J = 8.1, 2.1 Hz, 1H)), 7.17 (d, 1H), 7.11 (dd, J = 7.5, 3.2 Hz, 1H), 7.05 (d, J = 8.1 Hz, 1H), 6.25 (d, J = 1.2 Hz, 1H), 5.25 (d, J = 1.2 Hz, 1H), 3.77 (s, 2H), 3.76 (s, 3H), 3.76 (s, 3H), 3.61 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.12, 167.27, 141.14, 139.87, 138.53, 135.66, 133.84, 130.80, 129.98, 129.90, 129.42, 128.03, 126.30, 123.53, 121.30, 52.49, 52.20, 34.67, 30.43; HRMS (ESI): calc. for $[(\text{C}_{22}\text{H}_{20}\text{Br}_2\text{O}_4)]$ (M+H) 508.9753, measured 508.9786.

Methyl (*E*)-2-(3-fluoro-2-(2-(methoxycarbonyl) allyl) benzyl)-3-(2-fluorophenyl) acrylate (2j):



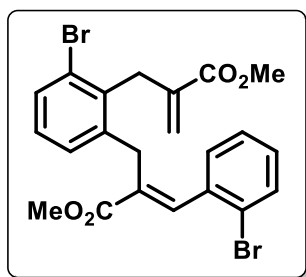
Colorless white solid, Yield (69%, 40mg); IR (Pellet, cm^{-1}): 3445.02, 2972.83, 2723.65, 1746.45, 1468.23, 1379.09; ^1H NMR (400 MHz, CDCl_3): δ 8.02 (s, 1H), 7.32 (dd, J = 5.4, 1.9 Hz, 1H), 7.21-7.16 (m, 1H), 7.13-7.06 (m, 2H), 7.03-6.94 (m, 2H), 6.90 (d, J = 7.7 Hz, 1H), 6.17 (d, J = 1.0 Hz, 1H), 5.11 (s, 1H), 3.77 (s, 3H), 3.74 (s, 5H), 3.69 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.98, 167.42, 140.49, 137.43, 134.63, 131.98, 131.00, 129.58, 128.41, 125.06, 124.22, 122.84, 115.99, 115.78, 113.76, 113.53, 52.38, 52.17, 30.62, 27.03; HRMS (ESI): calc. for $[(\text{C}_{22}\text{H}_{20}\text{F}_2\text{O}_4)]$ (M+H) 387.1402, measured 387.1408.

Methyl (*E*)-2-(3-chloro-2-(2-(methoxycarbonyl)allyl) benzyl)-3-(2-chlorophenyl) acrylate (2k):



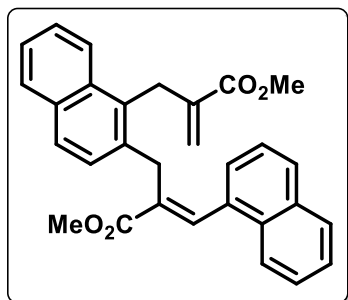
Colorless liquid, Yield (65% 41mg); IR (Pellet, cm^{-1}): 3445, 2973.03, 2723.14, 1745.90, 1468.17, 1378, 2296, ^1H NMR (400 MHz, CDCl_3): δ 8.06 (s, 1H), 7.41 (dd, $J = 8.0, 0.9$ Hz, 1H), 7.30 (d, $J = 7.7$ Hz, 1H), 7.18-7.02, (m, 6H), 6.13 (d, $J = 1.0$ Hz, 1H), 4.98 (d, $J = 1.0$ Hz, 1H), 3.80 (s, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 3.69 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.41, 161.18, 140.44, 139.14, 136.67, 135.83, 134.50, 133.73, 131.76, 130.16, 129.91, 129.44, 128.18, 127.91, 126.81, 125.79, 124.77, 52.39, 52.17, 31.64, 31.20; HRMS (ESI): calc. for $[(\text{C}_{22}\text{H}_{20}\text{Cl}_2\text{O}_4)]$ (M+H) 419.0820 measured 419.0817.

Methyl (*E*)-2-(3-bromo-2-(2-(methoxy carbonyl)allyl) benzyl)-3-(2-bromophenyl) acrylate (2l):



Colorless liquid, Yield (65%, 50mg); IR (Pellet, cm^{-1}): 3445.76, 2973.25, 2723.24, 1745.65, 1467.42, 1378.22; ^1H NMR (400 MHz, CDCl_3): δ 8.00 (s, 1H), 7.60 (dd, $J = 5.7, 3.6$ Hz, 1H), 7.49 (dd, $J = 6.3, 2.9$ Hz, 1H), 7.17 (dd, $J = 5.9, 3.4$ Hz, 2H), 7.09-7.067 (m, 2H), 6.13 (d, $J = 1.0$ Hz, 1H), 4.97 (d, $J = 0.9$ Hz, 1H), 3.82 (s, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 3.68 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.86, 167.37, 141.36, 140.52, 136.49, 136.10, 135.52, 133.09, 131.45, 131.29, 130.30, 129.48, 128.55, 127.42, 126.85, 126.44, 124.92, 124.48, 52.43, 52.21, 34.54, 31.44, 29.85; HRMS (ESI): calc. for $[(\text{C}_{22}\text{H}_{20}\text{Br}_2\text{O}_4)]$ (M+H) 508.9779, measured 508.9786.

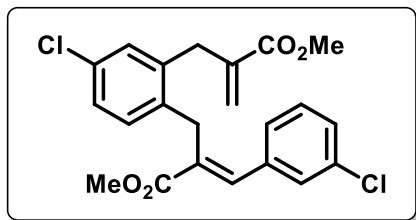
Methyl (*E*)-2-((1-(2-(methoxycarbonyl) allyl) naphthalen-2-yl) methyl)-3-(naphthalen-1-yl) acrylate (2m):



Colorless liquid, Yield (60% 81mg); IR (Pellet, cm^{-1}): 3446.08, 2973.91, 2723.15, 1745.69, 1468.34; ^1H NMR (400 MHz, CDCl_3) δ 8.54 (s, 1H), 8.05-8.02 (m, 1H), 7.87 (d, $J = 4$, Hz, 1H), 7.83-7.80 (m, 3H), 7.75 (d, $J = 8.5$ Hz, 1H), 7.57-7.53 (m, 2H), 7.46-7.42 (m, 2H), 7.38 (d, $J = 8.5$ Hz, 1H), 7.31 – 7.30 (m, 2H), 6.07 (d, $J = 4$ Hz, 1H), 4.84 (d, $J = 1.2$ Hz, 1H), 4.02 (s, 2H), 3.93 (s, 2H), 3.78 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.43, 167.69, 140.05, 137.77, 136.09, 133.58, 132.75, 132.67, 132.61, 132.46, 131.73, 131.57,

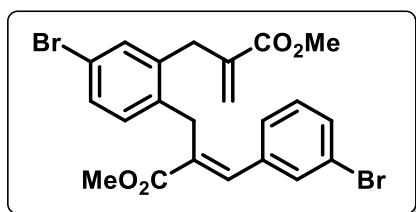
129.28, 128.73, 128.58, 127.61, 126.74, 126.42, 126.39, 126.07, 125.97, 125.89, 125.29, 125.18, 124.60, 124.10, 52.29, 52.14, 31.60, 29.90; HRMS (ESI): calc. for $[(C_{30}H_{26}O_4)]$ (M+H) 451.1901, measured 451.1909.

Methyl (*E*)-2-(4-chloro-2-(2-(methoxy carbonyl) allyl) benzyl)-3-(3-chlorophenyl) acrylate (2n):



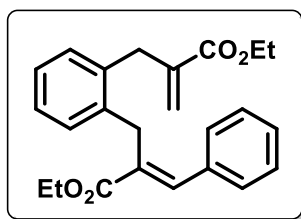
Colorless liquid Yield (60%, 38mg); IR (Pellet, cm^{-1}): 3445.79, 2971.98, 2723.09, 1745.59, 1468.01, 1378.11; 1H NMR ($CDCl_3$, 400 MHz): δ 7.90 (s, 1H), 7.30-7.00 (m, 7H), 6.13 (d, $J=1.2$ 1H), 5.25 (d, $J=1.2$ 1H), 3.76 (s, 3H), 3.75 (s, 5H), 3.63 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 168.15, 167.26, 140.47, 138.56, 138.29, 136.85, 135.97, 134.69, 132.42, 131.13, 130.57, 130.03, 129.16, 129.12, 128.49, 127.35, 127.13, 126.58, 52.48, 52.22, 34.89, 30.06; HRMS (ESI): calc. for $[(C_{22}H_{20}Cl_2O_4)]$ (M+H) 419.0820, measured 419.0817.

Methyl (*E*)-2-(4-bromo-2-(2-(methoxycarbonyl) allyl) benzyl)-3-(3-bromophenyl) acrylate (2o):



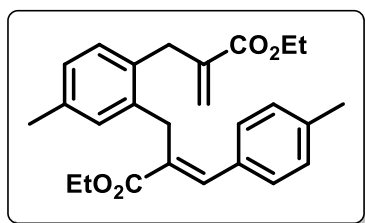
Colorless liquid, Yield (67%, 51mg); IR (Pellet, cm^{-1}): 3445.74, 2973.25, 2723.10, 1745.59, 1467.72, 1378.18; 1H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.45-7.43 (m, 1H), 7.38 (s, 1H), 7.31 (dd, $J = 4.3, 2.2$ Hz, 2H), 7.19-7.12 (m, 2H), 6.95 (d, $J = 8.8$ Hz, 1H), 6.26 (d, $J = 1.1$ Hz, 1H), 5.26 (d, $J = 1.0$ Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.73 (s, 2H), 3.63 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.06, 167.19, 140.36, 138.90, 138.27, 137.11, 136.52, 133.41, 132.09, 132.01, 131.10, 130.30, 130.26, 128.85, 127.46, 126.60, 122.81, 120.52, 52.45, 52.20, 34.82, 30.10; HRMS (ESI): calc. for $[(C_{22}H_{20}Br_2O_4)]$ (M+H) 508.9795, measured 508.9786.

Ethyl (*E*)-2-(2-(2-(ethoxycarbonyl)allyl)benzyl)-3-phenyl acrylate (2p):



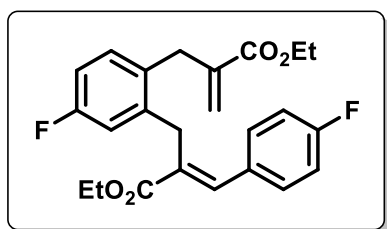
Colorless Liquid; Yield (73%, 41mg); IR (Pellet, cm^{-1}): 1743, 1565, 1472, 1445, 1166; 1H NMR ($CDCl_3$, 400 MHz): δ 7.98 (s, 1H), 7.31-7.17 (m, 9H) 6.22 (d, $J = 16$ Hz, 1H), 5.19 (d, $J = 16$ Hz, 1H), 4.23-4.16 (m, 4H) 3.82 (s, 2H) 3.67 (s, 2H), 1.30-1.21 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.16, 167.05, 141.31, 139.20, 137.80, 136.44, 135.25, 130.57, 130.32, 129.17, 128.76, 128.53, 127.07, 126.43, 125.62, 123.95, 60.91, 60.81, 34.99, 32.40, 22.92, 14.18; HRMS (ESI): calc. for $[(C_{24}H_{26}O_4)]$ (M+H) 379.1831, measured 379.1899.

Ethyl (*E*)-2-(2-(2-(ethoxycarbonyl)allyl)-5-methylbenzyl)-3-(*p*-tolyl) acrylate (2q):



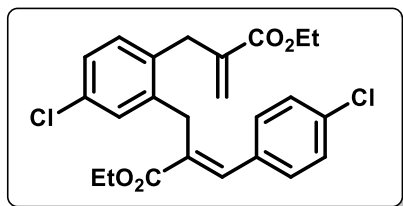
Colorless liquid, Yield (75%, 46mg); IR (Pellet, cm^{-1}): 3445.62, 2973.20, 2723.09, 1744.92, 1468.04, 1378.20; ^1H NMR (400 MHz, CDCl_3): δ 7.95 (s, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 7.7 Hz, 2H), 7.00 (t, J = 7.6 Hz, 1H), 6.91 (s, 1H), 6.22 (d, J = 0.9 Hz, 1H), 5.21 (d, J = 1.5 Hz, 1H), 4.20 (qd, J = 7.0, 4.8 Hz, 4H), 3.79 (s, 2H), 3.64 (s, 2H), 2.33 (s, 2H), 2.26 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 168.52, 167.27, 141.45, 139.56, 139.10, 137.77, 136.63, 133.49, 132.57, 130.61, 129.67, 129.47, 129.42, 127.85, 127.19, 125.63, 60.96, 60.91, 34.77, 30.49, 21.48, 21.38, 14.34; HRMS (ESI): calc. for $[(\text{C}_{26}\text{H}_{30}\text{O}_4)]$ (M+H) 407.2217, measured 407.2222.

Ethyl (*E*)-2-(2-(2-(ethoxycarbonyl) allyl)-5-fluorobenzyl)-3-(4-fluorophenyl) acrylate (2r):



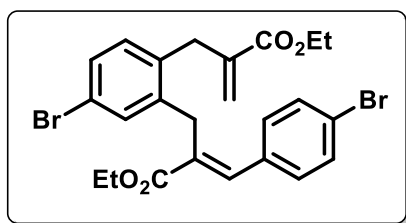
Colorless liquid, Yield (72%, 45mg); IR (Pellet, cm^{-1}): 3192.60, 2838.85, 1744.86, 1467.58, 1377.68; ^1H NMR (400 MHz, CDCl_3): δ 7.96 (s, 1H), 7.25 -7.22 (m, 2H), 7.14 (dd, J = 8.4, 5.9 Hz, 1H), 7.00 (t, J = 8.7 Hz, 2H), 6.88 (dd, J = 8.3, 2.7 Hz, 1H), 6.82 (dd, J = 10.2, 2.6 Hz, 1H), 6.23 (d, J = 1.3 Hz, 1H), 5.21 (d, J = 1.4 Hz, 1H), 4.21 (qd, J = 7.1, 2.9 Hz, 4H), 3.78 (s, 2H), 3.63 (s, 2H), 1.32 -1.23 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.86, 166.97, 164.27, 163.44, 161.79, 161.01, 140.81, 140.19, 140.13, 139.25, 132.28, 132.25, 132.09, 132.01, 131.30, 131.25, 131.21, 129.58, 125.73, 115.98, 115.76, 114.30, 114.08, 113.38, 113.17, 61.24, 61.02, 34.47, 30.54, 14.30; HRMS (ESI): calc. for $[(\text{C}_{24}\text{H}_{24}\text{F}_2\text{O}_4)]$ (M+H) 415.1698, measured 415.1721.

Ethyl (*E*)-2-(5-chloro-2-(2-(ethoxycarbonyl) allyl) benzyl)-3-(4-chlorophenyl) acrylate (2s):



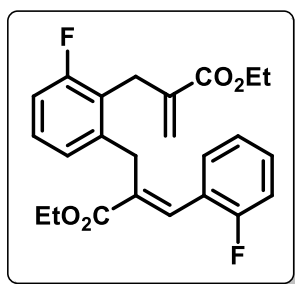
Colorless liquid, Yield (70%, 49mg); IR (Pellet, cm^{-1}): 3445.71, 2972.83, 2723.32, 1745.74, 1468.70, 1378.22; ^1H NMR (400 MHz, CDCl_3): δ 7.94 (s, 1H), 7.30 (d, J = 1.8 Hz, 1H), 7.28 (s, 1H), 7.18 (dd, J = 10.9, 2.5 Hz, 3H), 7.11 (d, J = 8.1 Hz, 1H), 7.05 (d, J = 2.0 Hz, 1H), 6.23 (d, J = 1.2 Hz, 1H), 5.22 (d, J = 1.3 Hz, 1H), 4.23-4.18 (m, 4H), 3.76 (d, J = 4 Hz, 2H), 3.62 (s, 2H), 1.31-1.24 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.70, 166.88, 140.69, 139.72, 138.96, 135.23, 135.11, 133.55, 133.04, 131.97, 130.58, 130.31, 129.05, 127.25, 126.83, 125.94, 61.34, 61.09, 34.63, 30.48, 14.32; HRMS (ESI): calc. for $[(\text{C}_{24}\text{H}_{24}\text{Cl}_2\text{O}_4)]$ (M+H) 447.1125, measured 447.1130.

Ethyl (E)-2-(5-bromo-2-(2-(ethoxycarbonyl)allyl) benzyl)-3-(4-bromophenyl) acrylate (2t):



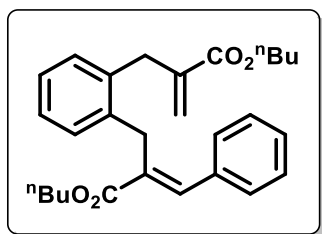
Colorless liquid, Yield (61%, 46mg); IR (Pellet, cm^{-1}): 2972.86, 2723.26, 1745.78, 1468.52, 1378.09; ^1H NMR (400 MHz, CDCl_3): δ 8.00 (s, 1H), 7.33-7.28 (m, 1H), 7.21-7.15 (m, 1H), 7.13-7.06 (m, 2H), 7.02 (dd, J = 7.5, 0.9 Hz, 1H), 6.98 (dd, J = 8.6, 4.7 Hz, 1H), 6.92 (t, J = 7.4 Hz, 1H), 6.16 (d, J = 1.1 Hz, 1H), 5.09 (d, J = 0.9 Hz, 1H), 4.21 (dq, J = 11.1, 7.1 Hz, 4H), 3.73 (s, 2H), 3.69 (d, J = 1.7 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.49, 166.96, 140.65, 137.73, 137.70, 134.33, 132.38, 130.89, 129.62, 128.31, 124.75, 124.21, 123.35, 122.87, 115.97, 115.75, 113.67, 113.44, 61.24, 61.05, 30.60, 27.01, 14.34, 14.29 43; HRMS (ESI): calc. for $[(\text{C}_{24}\text{H}_{24}\text{Br}_2\text{O}_4)]$ (M+H) 537.0080, measured 537.0099.

Ethyl (E)-2-(2-(2-(ethoxycarbonyl) allyl)-3-fluorobenzyl)-3-(2-fluorophenyl) acrylate (2u):



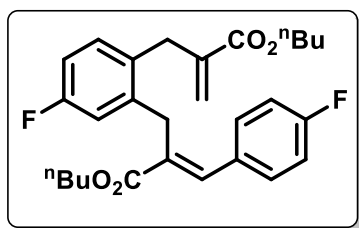
Colorless liquid, Yield (68%, 42mg); IR (Pellet, cm^{-1}): 3445.71, 2972.83, 2723.32, 1745.74, 1468.70, 1378.22; ^1H NMR (400 MHz, CDCl_3): δ 7.91 (s, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.32 (dd, J = 8.1, 2.1 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H), 7.11 (d, J = 8.3 Hz, 2H), 7.04 (d, J = 8.1 Hz, 1H), 6.23 (d, J = 1.2 Hz, 1H), 5.22 (d, J = 1.3 Hz, 1H), 4.24- 4.18 (m, 4H), 3.76 (s, 2H), 3.60 (s, 2H), 1.27 (dt, J = 13.3, 7.1 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 167.65, 166.83, 140.73, 140.04, 138.83, 135.75, 133.97, 132.29, 132.00, 130.78, 130.40, 130.12, 129.81, 129.39, 128.05, 125.98, 123.40, 121.19, 61.34, 61.09, 34.69, 30.44, 14.32; HRMS (ESI): calc. for $[(\text{C}_{24}\text{H}_{24}\text{F}_2\text{O}_4)]$ (M+H) 415.1722, measured 415.1721.

Butyl (E)-2-(2-(2-(butoxycarbonyl)allyl)benzyl)-3-phenyl acrylate (2v):



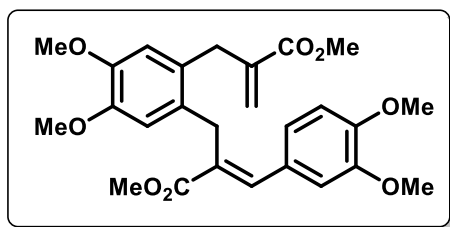
Colorless liquid, Yield (73%, 47mg); IR (Pellet, cm^{-1}): 2958.12, 2723.34, 1745.75, 1468.20; ^1H NMR (400 MHz, CDCl_3): δ 7.99 (s, 1H), 7.30-7.28 (m, 5H), 7.20-7.18 (m, 4H), 6.22 (d, J = 1.4 Hz, 1H), 5.20 (d, J = 1.5 Hz, 1H), 4.14 (dd, J = 12.4, 6.6 Hz, 4H), 3.82 (s, 1H), 3.67 (s, 1H), 1.63 (dd, J = 14.8, 6.9 Hz, 2H), 1.59 – 1.55 (m, 2H), 1.38-1.35 (m, 2H), 1.28-1.23 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 168.38, 167.24, 141.50, 139.36, 137.97, 136.62, 135.41, 130.68, 130.55, 129.31, 128.90, 128.68, 127.21, 127.14, 126.56, 125.74, 64.95, 64.87, 35.15, 30.77, 19.34, 19.21, 13.88, 13.81; HRMS (ESI): calc. for $[(\text{C}_{28}\text{H}_{34}\text{O}_4)]$ (M+H) 435.2584, measured 435.2535.

Butyl (E)-2-(2-(2-(butoxycarbonyl) allyl)-5-fluorobenzyl)-3-(4-fluorophenyl) acrylate (2w):



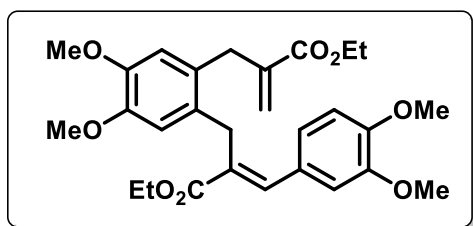
Colorless liquid, Yield (71%, 50mg); IR (Pellet, cm^{-1}): 3446.48, 2973.62, 1745.70, 1468.75, 1378.29; ^1H NMR (400 MHz, CDCl_3): δ 7.96 (s, 1H), 7.25-7.21 (m, 2H), 7.13 (d, $J = 5.9$ Hz, 1H), 7.02-6.98 (m, 2H), 6.92-6.80 (m, 2H), 6.22 (d, $J = 1.2$ Hz, 1H), 5.21 (d, $J = 1.4$ Hz, 1H), 4.15 (td, $J = 6.6, 3.0$ Hz, 4H), 3.77 (s, 2H), 3.63 (s, 2H), 1.66-1.57 (m, 4H), 1.40-1.25 (m, 4H), 0.91 (dt, $J = 14.8, 7.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.95, 167.04, 140.87, 140.20, 139.27, 132.29, 132.08, 132.00, 131.29, 131.21, 129.58, 125.71, 115.98, 115.77, 114.28, 114.06, 113.37, 113.16, 65.13, 64.94, 34.49, 30.76, 19.32, 19.23, 13.85, 13.78; HRMS (ESI): calc. for $[(\text{C}_{28}\text{H}_{32}\text{F}_2\text{O}_4)]$ (M+H) 471.2332, measured 471.2347.

Methyl (E)-2-(4,5-dimethoxy-2-(2-(methoxycarbonyl)allyl)benzyl)-3-(3,4-dimethoxyphenyl)acrylate (2x):



White solid; Yield: (84%, 59mg); IR (Pellet, cm^{-1}): 3445.79, 2973.76, 1745.63, 1468.70, 1377.92; ^1H NMR (CDCl_3 , 400 MHz): δ 7.93 (s, 1H), 6.94-6.91 (dd, $J=4\text{Hz}, 4\text{Hz}$ 1H), 6.85 (d, $J=1\text{Hz}$ 1H), 6.80 (d, $J=4\text{Hz}$ 1H), 6.70 (s, 1H), 6.67 (s, 1H), 6.23 (d, $J=4\text{Hz}$ 1H), 5.27 (d, $J=4\text{Hz}$ 1H), 3.87 (s, 3H), 3.80 (s, 3H), 3.75 (s, 2H), 3.74 (s, 3H), 3.73 (s, 3H), 3.63 (s, 3H), 3.62 (s, 3H), 3.62 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): 169.0, 167.6, 149.9, 148.9, 147.9, 147.4, 141.8, 139.2, 129.8, 128.5, 128.2, 128.0, 125.9, 123.0, 114.2, 112.5, 111.1, 110.9, 56.1, 56.0, 55.7, 55.7, 52.3, 52.1, 34.8, 30.3; HRMS (ESI): calc. for $[(\text{C}_{26}\text{H}_{30}\text{O}_8)]$ (M+H) 471.2001, measured 471.2019.

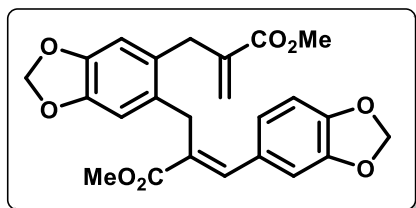
Ethyl (E)-3-(3, 4-dimethoxyphenyl)-2-(2-(2-(ethoxycarbonyl) allyl)-4, 5-dimethoxybenzyl) acrylate (2y):



Colorless liquid, Yield (87%, 65mg); IR (Pellet, cm^{-1}): 3446.42, 2973.52, 1744.77, 1468.61, 1377.91; ^1H NMR (400 MHz, CDCl_3): δ 7.92 (s, 1H), 6.93-6.91 (m, 1H), 6.85 (d, $J = 1.9$ Hz, 1H), 6.80 (d, $J = 8.4$ Hz, 1H), 6.70 (s, 1H), 6.67 (s, 1H), 6.21 (d, $J = 1.4$ Hz, 1H), 5.23 (d, $J = 1.5$ Hz, 1H), 4.20 (qd, $J = 7.1, 1.0$ Hz, 4H), 3.87 (s, 3H), 3.84 (s, 3H), 3.80 (s, 2H), 3.73 (s, 3H), 3.63 (s, 3H), 3.62 (s, 2H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.25 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 168.54, 167.19, 149.81, 148.86, 147.84, 147.33, 141.41, 139.47, 129.97, 128.66, 128.57, 128.12, 125.56, 122.94, 114.13, 112.47, 111.12, 110.87, 61.00, 60.95, 56.09, 56.07,

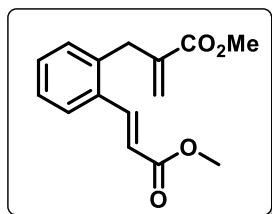
56.01, 55.70, 34.82, 30.32, 14.43, 14.34; HRMS (ESI): calc. for [(C₂₈H₃₄O₈)] (M+H) 499.2321, measured 499.2332.

Methyl (E)-3-(benzo[d][1,3]dioxol-5-yl)-2-((6-(2-(methoxycarbonyl)allyl)benzo[d][1,3]dioxol-5-yl)methyl) acrylate (2z):



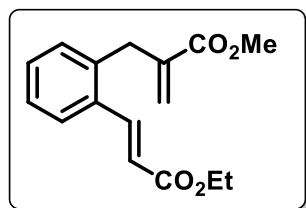
Colorless liquid, Yield (80%, 53mg); IR (Pellet, cm⁻¹): 3445.80, 2973.22, 2723.15, 1745.76, 1468.15, 1378.39; ¹H NMR (400 MHz, CDCl₃): δ 7.88 (s, 1H), 6.81 (d, *J* = 1.2 Hz, 1H), 6.76 (d, *j* = 8 Hz, 1H), 6.74 (d, *J* = 1.6 Hz, 1H), 6.68 (s, 1H), 6.61 (s, 1H), 6.25 (d, *J* = 1.3 Hz, 1H), 5.96 (s, 2H), 5.91 (s, 2H), 5.29 (d, *J* = 1.3 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.72 (s, 2H), 3.59 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 168.81, 167.59, 148.45, 148.02, 146.82, 146.17, 141.69, 139.03, 130.82, 129.61, 129.20, 128.32, 126.03, 124.81, 110.99, 109.28, 108.64, 107.69, 101.49, 101.05, 52.29, 52.11, 34.98, 30.40; HRMS (ESI): calc. for [(C₂₄H₂₂O₈)] (M+H) 439.1382 measured 439.1393.

Methyl (E)-2-(2-(3-methoxy-3-oxoprop-1-en-1-yl) benzyl) acrylate 4a:



Colorless liquid, Yield (89%, 69mg) IR (Pellet, cm⁻¹) 3446.09, 2972.68, 1745.62, 1468.48, 1378.21; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 15.8 Hz, 1H), 7.58 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.35 – 7.25 (m, 1H), 7.20 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 6.25 (d, *J* = 1.1 Hz, 1H), 5.21 (d, *J* = 1.1 Hz, 1H), 3.79 (s, 1H), 3.76 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 167.37, 167.24, 142.26, 139.28, 137.90, 133.83, 131.02, 130.32, 127.36, 127.02, 126.83, 119.66, 52.14, 51.82, 35.12. HRMS (ESI): calc. for [(C₁₅H₁₆O₄)] (M+H) 261.1127, measured 261.1097

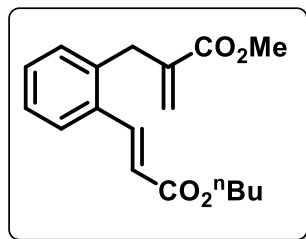
Ethyl (E)-3-(2-(2-(methoxycarbonyl)allyl)phenyl) acrylate (4b):



Colorless liquid, Yield (87%, 72mg) IR (Pellet, cm⁻¹) 3064.6, 2983.4, 2952.9, 1716.4, 1633.4, 1661.0, 1484.4; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 15.8 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.33-7.18 (m, 3H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.24 (s, 1H), 5.21 (s, 1H), 4.25 (q, 2H), 3.76 (s, 5H), 1.31 (t, *J* = 6.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.13, 166.85, 141.93, 139.25, 137.82, 133.83, 130.95, 130.17, 127.27, 126.93,

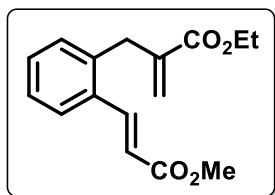
126.75, 120.02, 60.53, 52.03, 35.08, 14.34. HRMS (ESI): calc. for $[(C_{16}H_{18}O_4)]$ (M+H) 275.1283, measured 275.1277

Butyl (E)-3-(2-(2-(methoxycarbonyl)allyl)phenyl) acrylate (4c):



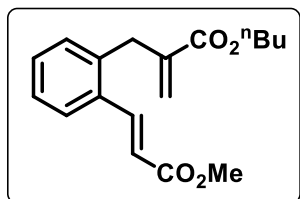
Colorless liquid, Yield (92%, 83mg) IR (Pellet, cm^{-1}) 3446.09, 2972.68, 1745.62, 1468.48, 1378.21; 1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 15.8 Hz, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.34 - 7.19 (m J = 30.3, 18.4, 7.3 Hz, 3H), 6.35 (d, J = 15.8 Hz, 1H), 6.24 (s, 1H), 5.21 (s, 1H), 4.19 (t, J = 6.4 Hz, 2H), 3.76 (s, 5H), 1.70 - 1.64 (m, 2H), 1.44 - 1.39 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.17, 167.00, 141.96, 139.23, 137.80, 133.83, 131.00, 130.20, 127.31, 126.99, 126.75, 120.03, 64.49, 52.12, 35.13, 30.79, 19.26, 13.75. HRMS (ESI): calc. for $[(C_{18}H_{22}O_4)]$ (M+H) 303.1596, measured 303.1591

Ethyl (E)-2-(2-(3-methoxy-3-oxoprop-1-en-1-yl)benzyl) acrylate (4d):



Colorless liquid, Yield (86%, 71mg) IR (Pellet, cm^{-1}) 3065.5, 2983.4, 2952.2, 2853.6, 1718.9, 1633.5, 1601.0, 1571.7, 1483.2; 1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 15.8 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.29 (d, J = 7.3 Hz, 1H), 7.24 (s, 1H), 7.18 (d, J = 7.3 Hz, 1H), 6.33 (d, J = 15.7 Hz, 1H), 6.22 (s, 1H), 5.18 (s, 1H), 4.19 (q, J = 6.6 Hz, 2H), 3.76 (s, 3H), 3.73 (s, 2H), 1.26 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.40, 166.81, 142.35, 139.61, 138.07, 133.86, 131.04, 130.31, 127.33, 126.84, 126.77, 119.67, 61.07, 51.84, 35.13, 14.28. HRMS (ESI): calc. for $[(C_{16}H_{18}O_4)]$ (M+H) 275.1283, measured 275.1275

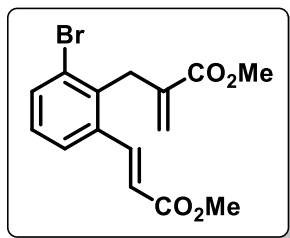
Butyl (E)-2-(2-(3-methoxy-3-oxoprop-1-en-1-yl)benzyl) acrylate (4e):



Colorless liquid, Yield (76%, 69mg) IR (Pellet, cm^{-1}) 3064.5, 2958.6, 2873.3, 1718.9, 1633.7, 1601.2, 1572.2, 1436.0; 1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 15.8 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.24 - 7.19 (m, 2H), 7.13 (d, J = 7.3 Hz, 1H), 6.28 (d, J = 15.8 Hz, 1H), 6.18 (s, 1H), 5.14 (s, 1H), 4.09 (t, J = 6.3 Hz, 2H), 3.72 (s, 3H), 3.69 (s, 2H), 1.60 - 1.53 (m, 2H), 1.30-1.26 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.38, 166.88, 142.33, 139.59, 138.06, 133.85, 130.96, 130.30, 127.31, 126.84, 126.78, 119.68,

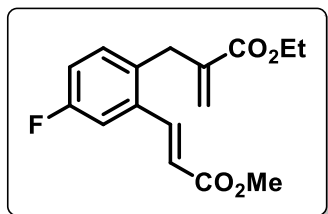
64.96, 51.83, 35.15, 30.73, 19.29, 13.84. HRMS (ESI): calc. for $[(C_{18}H_{22}O_4)]$ (M+H) 303.1596, measured 303.1887

Methyl (E)-3-(3-bromo-2-(2-(methoxycarbonyl)allyl)phenyl) acrylate (4f):



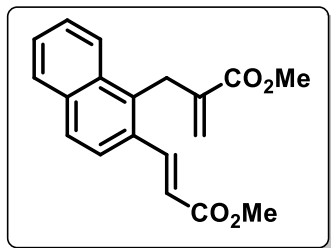
Colorless liquid, Yield (76%, 74mg) IR (Pellet, cm^{-1}) 3064.6, 3023.6, 2997.3, 2952.2, 2849.7, 1719.19, 1633.4, 1601.1; 1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, $J = 15.8$ Hz, 1H), 7.58 (d, $J = 7.6$ Hz, 1H), 7.33 – 7.29 (m, 1H), 7.20 (d, $J = 7.5$ Hz, 1H), 6.35 (d, $J = 15.7$ Hz, 1H), 6.25 (s, 1H), 5.21 (s, 1H), 3.79 (s, 3H), 3.77 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.37, 167.24, 142.27, 139.29, 137.91, 133.85, 131.03, 130.32, 127.37, 127.02, 126.84, 119.67, 52.15, 51.83, 35.14. HRMS (ESI): calc. for $[(C_{15}H_{15}BrO_4)]$ (M+H) 339.0232, measured 339.0199

Ethyl (E)-2-(4-fluoro-2-(3-methoxy-3-oxoprop-1-en-1-yl)benzyl) acrylate (4g):



Colorless liquid, Yield (83%, 73mg) IR (Pellet, cm^{-1}) 2922.6, 2852.7, 1719.7, 1635.1, 1491.8; 1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, $J = 15.8$ Hz, 1H), 7.27 – 7.17 (m, 2H), 7.07 (t, $J = 8.2$ Hz, 1H), 6.37 (d, $J = 15.8$ Hz, 1H), 6.29 (s, 1H), 5.27 (s, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 3.84 (s, 3H), 3.76 (s, 2H), 1.33 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.05, 166.68, 163.09, 160.64, 141.26, 139.53, 135.69, 135.61, 133.82, 132.69, 132.61, 126.78, 120.82, 117.30, 117.09, 113.35, 113.13, 61.13, 51.95, 34.52, 14.28. HRMS (ESI): calc. for $[(C_{16}H_{17}FO_4)]$ (M+H) 293.1189, measured 293.1181

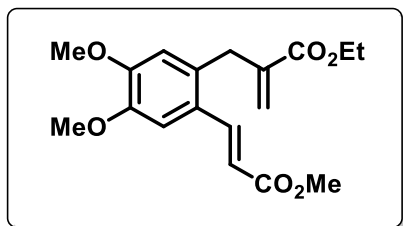
Methyl (E)-2-((2-(3-methoxy-3-oxoprop-1-en-1-yl)naphthalen-1-yl)methyl) acrylate (4h):



Colorless liquid, Yield (79%, 74mg) IR (Pellet, cm^{-1}) 3446.09, 2972.68, 1745.62, 1468.48, 1378.21; 1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, $J = 15.8$ Hz, 1H), 7.89 – 7.76 (m, 3H), 7.68 (d, $J = 8.6$ Hz, 1H), 7.50 – 7.48 (m, 2H), 6.49 (d, $J = 15.7$ Hz, 1H), 6.19 (s, 1H), 4.87 (s, 1H), 4.23 (s, 2H), 3.88 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.43, 142.45, 138.52, 134.72, 134.50, 132.44, 131.49, 128.72, 128.11, 127.09, 126.95,

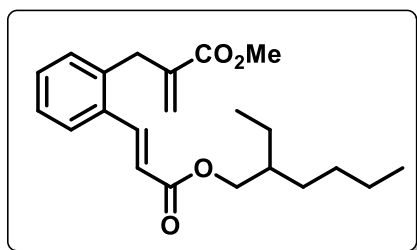
125.08, 123.70, 120.59, 52.33, 51.91, 30.00. HRMS (ESI): calc. for $[(C_{19}H_{18}O_4)]$ (M+H) 311.1283, measured 311.1277

Ethyl (E)-2-(4,5-dimethoxy-2-(3-methoxy-3-oxoprop-1-en-1-yl)benzyl) acrylate (4i):



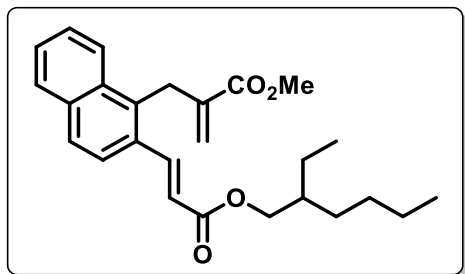
Colorless liquid, Yield (71%, 71mg) IR (Pellet, cm^{-1}) 3446.09, 2972.68, 1745.62, 1468.48, 1378.21; 1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 15.8 Hz, 1H), 7.09 (s, 1H), 6.69 (s, 1H), 6.27 (d, J = 15.7 Hz, 1H), 6.25 (d, J = 1.2 Hz, 1H), 5.21 (d, J = 1.2 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.91 (s, 3H), 3.88 (s, 3H), 3.79 (s, 3H), 3.74 (d, J = 2.8 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.71, 166.90, 151.03, 148.08, 141.88, 139.88, 131.93, 129.17, 128.56, 126.59, 126.48, 125.87, 116.98, 113.45, 108.72, 61.10, 56.05, 52.07, 51.81, 38.17, 14.33. HRMS (ESI): calc. for $[(C_{18}H_{22}O_6)]$ (M+H) 335.1494, measured 335.1511

2-Ethyl hexyl (E)-3-(2-(2-(methoxycarbonyl)allyl) phenyl) acrylate (4j):



Colorless liquid, Yield (91%, 98mg) IR (Pellet, cm^{-1}) 3446.09, 2972.68, 1745.62, 1468.48, 1378.21; 1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 15.8 Hz, 1H), 7.61 (dd, J = 7.7, 1.4 Hz, 1H), 7.33 – 7.19 (m, 3H), 6.36 (d, J = 15.8 Hz, 1H), 6.25 (d, J = 1.1 Hz, 1H), 5.21 (d, J = 1.1 Hz, 1H), 4.11 (dd, J = 5.8, 4.8 Hz, 2H), 3.77 (s, 5H), 1.64 – 1.61 (m, 3H), 1.40 – 1.25 (m, 11H), 0.92 (t, J = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.23, 167.18, 141.89, 139.26, 137.83, 133.90, 131.10, 130.29, 129.17, 128.56, 127.38, 127.02, 126.81, 120.11, 67.08, 52.16, 38.94, 35.22, 30.60, 29.08, 24.00, 23.11, 14.21, 11.18. HRMS (ESI): calc. for $[(C_{22}H_{30}O_4)]$ (M+H) 359.2222, measured 359.2208

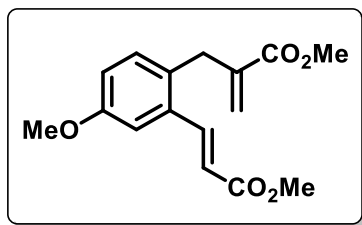
2-Ethylhexyl (E)-3-(1-(2-(methoxycarbonyl)allyl)naphthalen-2-yl) acrylate (4k):



Colorless liquid, Yield (84%, 103mg) IR (Pellet, cm^{-1}) 3063.4, 2957.9, 2930.1, 2860.7, 1716.4, 1630.0, 1459.9; 1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 15.8 Hz, 1H), 7.92 – 7.70 (m, 4H), 7.50 – 7.49 (m, 2H), 6.50

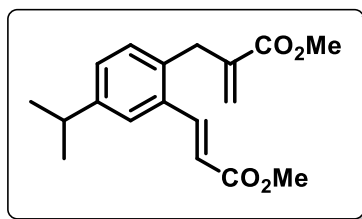
(d, $J = 15.7$ Hz, 1H), 6.20 (s, 1H), 4.89 (s, 1H), 4.24 (s, 2H), 4.14 (t, $J = 5.4$ Hz, 2H), 3.88 (s, 3H), 1.66 (d, $J = 5.6$ Hz, 1H), 1.40 (dd, $J = 24.9, 17.7$ Hz, 8H), 0.99 – 0.86 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.37, 167.20, 142.12, 138.48, 134.65, 134.48, 132.48, 131.53, 128.72, 128.06, 127.07, 126.93, 125.06, 123.70, 120.98, 67.17, 52.30, 38.99, 30.64, 30.01, 29.10, 24.05, 23.10, 14.19, 11.19. HRMS (ESI): calc. for $[(\text{C}_{26}\text{H}_{32}\text{O}_4)]$ (M+H) 409.2379, measured 409.2372

Methyl (*E*)-3-(5-methoxy-2-(2-(methoxycarbonyl)allyl)phenyl) acrylate (4l):



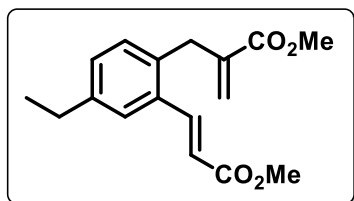
Colorless liquid, Yield (88%, 77mg) IR (Pellet, cm^{-1}) 2998.1, 2951.7, 2840.1, 1720.5, 1634.3, 1607.1, 1571.2, 1497.0; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 15.8$ Hz, 1H), 7.12– 7.08(m, 2H), 6.89 (d, $J = 8.3$ Hz, 1H), 6.33 (d, $J = 15.7$ Hz, 1H), 6.22 (s, 1H), 5.19 (s, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H), 3.69 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.34, 167.33, 158.66, 142.32, 139.72, 134.78, 132.20, 130.23, 126.75, 119.77, 116.40, 111.54, 55.46, 52.11, 51.86, 34.40. HRMS (ESI): calc. for $[(\text{C}_{16}\text{H}_{18}\text{O}_5)]$ (M+H) 291.1232, measured 291.1223.

Methyl (*E*)-3-(5-isopropyl-2-(2-(methoxycarbonyl)allyl)phenyl) acrylate (4m):



Colorless liquid, Yield (68%, 62mg) IR (Pellet, cm^{-1}) 3446.09, 2972.68, 1745.62, 1468.48, 1378.21; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 15.8$ Hz, 1H), 7.43 (d, $J = 1.1$ Hz, 1H), 6.36 (d, $J = 15.8$ Hz, 1H), 6.24 (s, 1H), 5.22 (s, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.73 (s, 2H), 2.90 (dt, $J = 13.8, 6.9$ Hz, 1H), 1.26 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.49, 167.36, 147.88, 142.65, 139.46, 135.36, 133.60, 131.04, 128.68, 126.97, 124.81, 119.27, 52.14, 51.83, 34.77, 33.88, 24.02. HRMS (ESI): calc. for $[(\text{C}_{18}\text{H}_{28}\text{O}_4)]$ (M+H) 303.1596, measured 303.1593

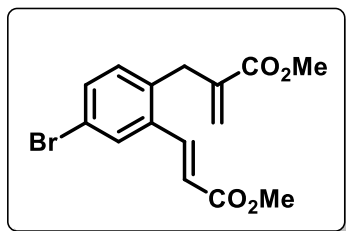
Methyl (*E*)-3-(5-ethyl-2-(2-(methoxycarbonyl)allyl)phenyl) acrylate (4n):



Colorless liquid, Yield (79%, 68mg) IR (Pellet, cm^{-1}) 3446.09, 2972.68, 1745.62, 1468.48, 1378.21; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 15.8$ Hz, 1H), 7.45 (s, 1H), 7.18 (dd, $J = 23.5, 7.6$ Hz, 2H), 6.40 (d, $J = 15.8$

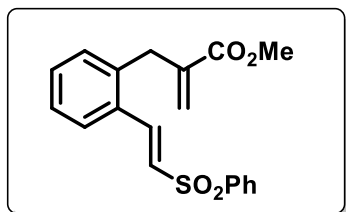
Hz, 1H), 6.28 (s, 1H), 5.26 (s, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.77 (s, 2H), 2.68 (dd, $J = 14.9, 7.3$ Hz, 2H), 1.28 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.51, 163.74, 143.28, 142.58, 139.54, 135.26, 133.69, 131.07, 130.10, 126.93, 126.22, 119.35, 52.15, 51.83, 34.80, 28.57, 15.55. HRMS (ESI): calc. for $[(\text{C}_{17}\text{H}_{20}\text{O}_4)]$ (M+H) 289.144 measured 289.1431

Methyl (*E*)-3-(5-bromo-2-(2-(methoxycarbonyl)allyl)phenyl)acrylate (4o):



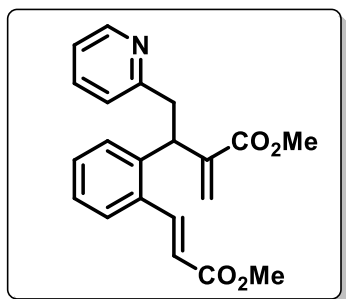
Colorless liquid, Yield (83%, 84mg) IR (Pellet, cm^{-1}) 3446.09, 2972.68, 1745.62, 1468.48, 1378.21; ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 15.8$ Hz, 1H), 7.69 (s, 1H), 7.43 (d, $J = 7.1$ Hz, 1H), 7.08 (d, $J = 8.0$ Hz, 1H), 6.33 (d, $J = 16.0$ Hz, 1H), 6.25 (s, 1H), 5.25 (s, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.70 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.02, 166.98, 140.84, 138.73, 136.77, 135.88, 133.05, 132.69, 132.01, 129.66, 127.24, 121.16, 52.27, 51.97, 34.76. HRMS (ESI): calc. for $[(\text{C}_{15}\text{H}_{15}\text{BrO}_4)]$ (M+H) 339.0232, measured 339.0227.

Methyl (*E*)-2-(2-(2-(phenylsulfonyl)vinyl)benzyl)acrylate (4p):



Colorless liquid, Yield (62%, 84mg) ^1H NMR (400 MHz, CDCl_3) δ 7.83 (t, $J = 9.6$ Hz, 3H), 7.58 – 7.35 (m, 4H), 7.26 (t, $J = 7.3$ Hz, 1H), 7.16 (t, $J = 9.1$ Hz, 2H), 6.70 (d, $J = 15.2$ Hz, 1H), 6.16 (s, 1H), 5.17 (s, 1H), 3.69 (s, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.93, 140.54, 140.03, 139.08, 138.41, 133.46, 131.64, 131.23, 131.11, 129.37, 128.88, 127.72, 127.45, 127.18, 127.15, 52.16, 35.19. HRMS (ESI): calc. for $[(\text{C}_{19}\text{H}_{18}\text{O}_4\text{S})]$ (M+H) 343.1004, measured 343.0975.

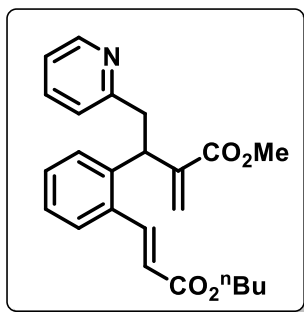
Methyl (*E*)-3-(2-(3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-2-methylene-4-(pyridin-2-yl)butanoate (4q):



Colourless liquid, Yield (55%, 58mg); ^1H NMR (400 MHz, CDCl_3) δ 8.43 (d, $J = 4.8$ Hz, 1H), 7.97 (d, $J = 15.8$ Hz, 1H), 7.42 – 7.29 (m, 5H), 7.19 – 7.15 (m, 1H), 7.04 – 7.01 (m, 1H), 6.75 (d, $J = 7.8$ Hz, 1H), 6.43 (s, 1H), 5.99 (d, $J = 15.7$ Hz, 1H), 5.83 (s, 1H), 4.81 (dd, $J = 9.0, 6.1$ Hz, 1H), 3.79 (s, 3H), 3.60 (s, 3H), 3.39 (dd, $J =$

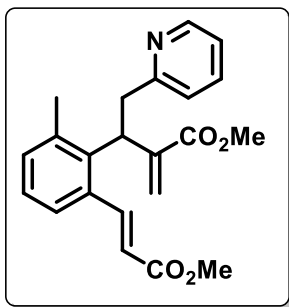
13.2, 6.0 Hz, 1H), 3.08 (dd, $J = 13.2, 9.3$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.20, 166.96, 158.98, 149.27, 142.84, 142.65, 141.19, 136.22, 134.30, 130.03, 127.46, 127.00, 126.89, 125.52, 123.62, 121.56, 119.78, 52.06, 51.77, 43.58, 42.11. HRMS (ESI): calc. for $[(\text{C}_{24}\text{H}_{21}\text{NO}_4)]$ (M+H) 352.1549, measured 352.1543

Methyl (*E*)-3-(2-(3-butoxy-3-oxoprop-1-en-1-yl)phenyl)-2-methylene-4-(pyridin-2-yl)butanoate (4r):



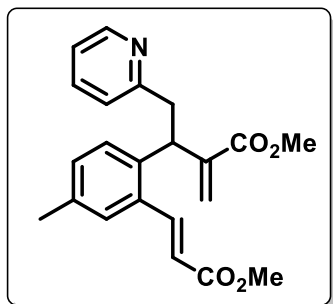
Colourless liquid, Yield (60%, 71mg); ^1H NMR (400 MHz, CDCl_3) δ 8.43 (d, $J = 4.6$ Hz, 1H), 7.97 (d, $J = 15.7$ Hz, 1H), 7.43 – 7.28 (m, 4H), 7.17 (dd, $J = 5.6, 2.2$ Hz, 1H), 7.09 – 7.00 (m, 1H), 6.78 (d, $J = 7.7$ Hz, 1H), 6.42 (s, 1H), 6.01 (d, $J = 15.7$ Hz, 1H), 5.82 (s, 1H), 4.82 (d, $J = 6.4$ Hz, 1H), 4.19 (t, $J = 6.7$ Hz, 2H), 3.60 (s, 3H), 3.39 (dd, $J = 13.2, 6.2$ Hz, 1H), 3.10 (dd, $J = 13.2, 9.1$ Hz, 1H), 1.74 – 1.66 (m, 2H), 1.44 (dd, $J = 15.0, 7.4$ Hz, 2H), 0.97 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.97, 166.86, 160.20, 159.03, 149.27, 144.86, 142.76, 142.33, 141.13, 137.48, 136.20, 134.36, 129.95, 127.50, 126.97, 126.93, 125.59, 123.56, 121.51, 120.29, 117.52, 64.43, 52.03, 43.51, 42.16, 30.92, 19.32, 13.92. HRMS (ESI): calc. for $[(\text{C}_{24}\text{H}_{27}\text{NO}_4)]$ (M+H) 394.2018, measured 394.2014

Methyl (*E*)-3-(2-(3-methoxy-3-oxoprop-1-en-1-yl)-6-methylphenyl)-2-methylene-4-(pyridin-2-yl)butanoate (4s):



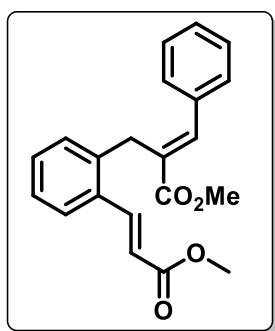
Colourless liquid, Yield (51%, 56mg); ^1H NMR (400 MHz, CDCl_3) δ 8.43 (dd, $J = 4.9, 0.9$ Hz, 1H), 7.94 (d, $J = 15.8$ Hz, 1H), 7.41 (td, $J = 7.7, 1.8$ Hz, 1H), 7.22 – 7.10 (m, 3H), 7.02 (ddd, $J = 7.5, 4.9, 1.0$ Hz, 1H), 6.78 (d, $J = 7.8$ Hz, 1H), 6.39 (s, 1H), 6.00 (d, $J = 15.7$ Hz, 1H), 5.80 (d, $J = 0.7$ Hz, 1H), 5.29 (s, 1H), 4.77 (dd, $J = 9.0, 6.3$ Hz, 1H), 3.78 (s, 3H), 3.60 (s, 3H), 3.43 – 3.32 (m, 1H), 3.16 – 3.02 (m, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.27, 167.02, 159.10, 149.20, 142.98, 142.76, 138.22, 136.45, 136.25, 133.99, 130.97, 127.43, 125.35, 123.64, 121.51, 119.42, 52.03, 51.72, 41.78, 31.71, 21.10. HRMS (ESI): calc. for $[(\text{C}_{22}\text{H}_{23}\text{NO}_4)]$ (M+H) 366.1705, measured 366.1707

Methyl (*E*)-3-(2-(3-methoxy-3-oxoprop-1-en-1-yl)-4-methylphenyl)-2-methylene-4-(pyridin-2-yl) butanoate (4t):



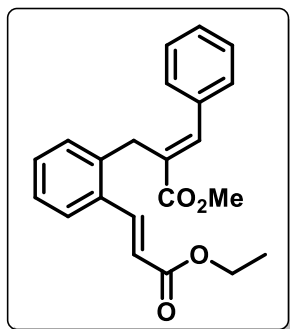
Colourless liquid, Yield (52%, 57 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.50 – 8.42 (m, 1H), 7.96 (d, J = 15.8 Hz, 1H), 7.43 (td, J = 7.7, 1.8 Hz, 1H), 7.24 – 7.12 (m, 3H), 7.08 – 7.01 (m, 1H), 6.80 (d, J = 7.8 Hz, 1H), 6.42 (s, 1H), 6.02 (d, J = 15.7 Hz, 1H), 5.82 (d, J = 0.6 Hz, 1H), 4.79 (dd, J = 8.9, 6.3 Hz, 1H), 3.80 (s, 3H), 3.62 (s, 3H), 3.39 (dd, J = 13.2, 6.1 Hz, 1H), 3.09 (dd, J = 13.2, 9.3 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.25, 166.99, 159.09, 149.21, 142.97, 142.75, 138.21, 136.42, 136.20, 133.96, 130.95, 127.42, 125.32, 123.61, 121.47, 119.40, 52.01, 51.71, 43.55, 41.76, 21.09. HRMS (ESI): calc. for $[(\text{C}_{22}\text{H}_{23}\text{NO}_4)]$ (M+H) 366.1705, measured 366.1704

Methyl (*E*)-2-(2-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl) benzyl)-3-phenyl acrylate (6a):



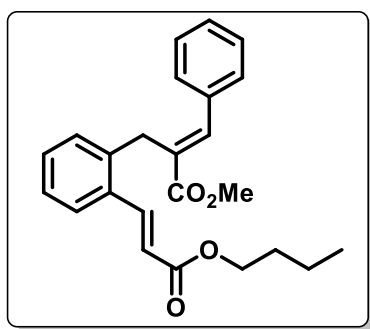
Colorless liquid, Yield (78%, 79mg) IR (Pellet, cm^{-1}) 3446.09, 2972.68, 1745.62, 1468.48, 1378.21; ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 15.8 Hz, 1H), 8.03 (s, 1H), 7.60 (dd, J = 7.6, 1.4 Hz, 1H), 7.33 – 7.25 (m, 7H), 7.17 – 7.15 (m, 1H), 6.39 (d, J = 15.8 Hz, 1H), 4.05 (s, 2H), 3.79 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.53, 167.39, 142.21, 142.10, 138.65, 135.11, 133.49, 130.44, 129.81, 129.28, 129.10, 128.78, 127.60, 127.08, 126.83, 119.82, 52.36, 51.84, 30.89. HRMS (ESI): calc. for $[(\text{C}_{21}\text{H}_{20}\text{O}_4)]$ (M+H) 337.1444, measured 337.1441

Methyl (*E*)-2-(2-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)benzyl)-3-phenyl acrylate (6b):



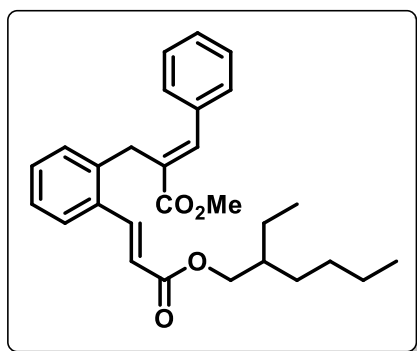
Colorless liquid, Yield (71%, 75mg) ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, J = 17.8 Hz, 2H), 7.63 – 7.55 (m, 1H), 7.34 – 7.27 (m, 6H), 7.14 (s, 1H), 6.39 (d, J = 15.8 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 4.06 (s, 2H), 3.75 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.37, 167.42, 142.41, 141.22, 139.23, 137.15, 134.50, 133.41, 130.91, 130.36, 130.27, 128.88, 127.96, 127.93, 126.94, 126.68, 126.01, 119.68, 52.29, 51.82, 30.55. HRMS (ESI): calc. for $[(\text{C}_{22}\text{H}_{22}\text{O}_4)]$ (M+H) 351.1596, measured 351.1591

Methyl (*E*)-2-(2-((*E*)-3-butoxy-3-oxoprop-1-en-1-yl)benzyl)-3-phenyl acrylate (6c):



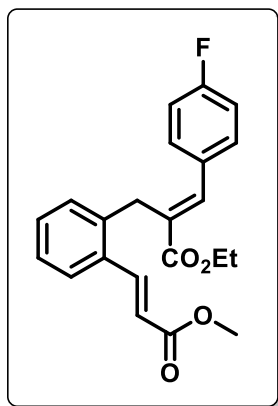
Colorless liquid, Yield (72%, 82mg) ^1H NMR (400 MHz, CDCl_3) δ 8.09 – 8.01 (m, 2H), 7.64 – 7.57 (m, 1H), 7.34 – 7.27 (m, 6H), 7.15 (d, J = 7.4 Hz, 1H), 6.39 (d, J = 15.8 Hz, 1H), 4.20 (t, J = 6.7 Hz, 2H), 4.05 (s, 2H), 3.75 (s, 3H), 1.68 (tt, J = 12.8, 6.4 Hz, 2H), 1.49 – 1.36 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.54, 167.08, 142.09, 141.95, 138.61, 135.15, 133.63, 130.34, 129.88, 129.28, 129.08, 128.78, 127.55, 127.12, 126.79, 120.36, 64.59, 52.33, 30.89, 19.31, 13.86. HRMS (ESI): calc. for $[(\text{C}_{24}\text{H}_{26}\text{O}_4)]$ (M+H) 379.1909 measured 379.1904

Methyl (*E*)-2-(2-((*E*)-3-((2-ethylhexyl)oxy)-3-oxoprop-1-en-1-yl)benzyl)-3-phenyl acrylate (6d):



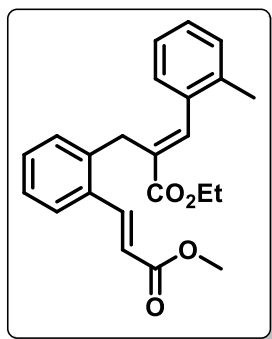
Colorless liquid, Yield (80%, 104mg) ; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, J = 15.8 Hz, 1H), 7.61 (dd, J = 7.7, 1.4 Hz, 1H), 7.33 – 7.19 (m, 3H), 6.36 (d, J = 15.8 Hz, 1H), 6.25 (d, J = 1.1 Hz, 1H), 5.21 (d, J = 1.1 Hz, 1H), 4.11 (dd, J = 5.8, 4.8 Hz, 2H), 3.77 (s, 5H), 1.64 – 1.61 (m, 3H), 1.40 – 1.25 (m, 5H), 0.92 (t, J = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.23, 167.18, 141.89, 139.26, 137.83, 133.90, 131.10, 130.29, 129.17, 128.56, 127.38, 127.02, 126.81, 120.11, 67.08, 52.16, 38.94, 35.22, 30.60, 29.08, 24.00, 23.11, 14.21, 11.18. HRMS (ESI): calc. for $[(\text{C}_{28}\text{H}_{34}\text{O}_4)]$ (M+H) 435.2475, measured 435.2465

Ethyl (*E*)-3-(4-fluorophenyl)-2-(2-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)benzyl) acrylate (6e):



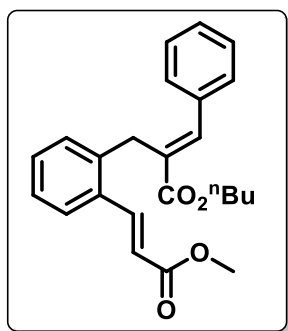
Colorless liquid, Yield (67%, 74mg) ; ^1H NMR (400 MHz, CDCl_3) δ 8.11 – 7.99 (m, 2H), 7.60 (d, J = 6.9 Hz, 1H), 7.34 – 7.25 (m, 6H), 7.15 (d, J = 7.5 Hz, 1H), 6.39 (d, J = 15.8 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 4.06 (s, 2H), 3.75 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.54, 166.97, 142.09, 141.95, 138.61, 135.14, 133.61, 130.35, 129.85, 129.28, 129.08, 128.78, 127.54, 127.11, 126.80, 120.35, 60.65, 52.33, 30.89, 14.44. HRMS (ESI): calc. for $[(\text{C}_{21}\text{H}_{21}\text{FO}_4)]$ (M+H) 369.1502, measured 369.1492

Ethyl (*E*)-2-(2-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)benzyl)-3-(*o*-tolyl) acrylate (6f):



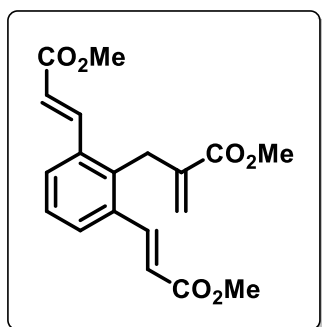
Colorless liquid, Yield (75%, 82mg) ; ^1H NMR (400 MHz, CDCl_3) δ 8.04 (s, 1H), 7.99 (d, J = 15.8 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.33 – 7.17 (m, 2H), 7.14 – 7.03 (m, 3H), 6.33 (d, J = 15.8 Hz, 1H), 3.91 (s, 2H), 3.78 (s, 3H), 3.74 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.37, 167.42, 142.41, 141.22, 139.23, 137.15, 134.50, 133.41, 130.91, 130.36, 130.27, 128.88, 127.96, 127.93, 126.94, 126.68, 126.01, 119.68, 52.29, 51.82, 30.55, 20.13. HRMS (ESI): calc. for $[(\text{C}_{23}\text{H}_{24}\text{O}_4)]$ (M+H) 365.1753, measured 365.1773

Butyl (E)-2-(2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)benzyl)-3-phenyl acrylate (6g):



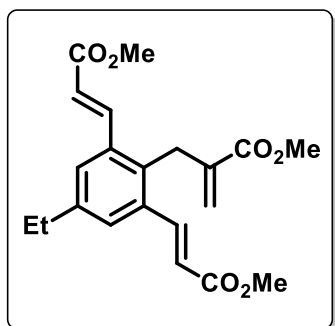
Colorless liquid, Yield (71%, 87mg); ^1H NMR (400 MHz, CDCl_3) δ 8.12 – 8.08 (d, $J=15.8$, 1H), 8.06 (s, 1H), 7.63 (d, $J = 7.4$ Hz, 6H), 7.21 (d, $J = 7.5$ Hz, 1H), 6.42 (d, $J = 15.8$ Hz, 1H), 4.17 (t, $J = 6.5$ Hz, 2H), 4.08 (s, 2H), 3.83 (s, 3H), 1.61 – 1.54 (m, 2H), 1.30 – 1.23 (m, 3H), 0.88 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.10, 167.39, 142.32, 141.77, 138.86, 135.26, 133.51, 130.39, 130.32, 129.23, 129.01, 128.77, 127.65, 127.04, 126.77, 119.81, 65.00, 51.84, 30.71, 19.16, 13.76. HRMS (ESI): calc. for $[(\text{C}_{24}\text{H}_{26}\text{O}_4)]$ (M+H) 379.1909, measured 379.1901

Dimethyl 3,3'-(2-(2-(methoxycarbonyl)allyl)-1,3-phenylene)(2E,2'E)-diacrylate (8a):



Colorless liquid, Yield (64%, 44mg), ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 15.8$ Hz, 2H), 7.59 (d, $J = 7.8$ Hz, 2H), 7.36 – 7.31 (m, 1H), 6.32 (d, $J = 15.8$ Hz, 2H), 6.24 (s, 1H), 4.94 (s, 1H), 3.83 (s, 3H), 3.79 (s, 8H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.05, 166.94, 142.14, 138.22, 136.42, 135.53, 128.74, 127.78, 127.10, 121.37, 52.36, 51.96, 30.92. HRMS (ESI): calc. for $[(\text{C}_{19}\text{H}_{20}\text{O}_6)]$ (M+H) 345.1338, measured 345.1396

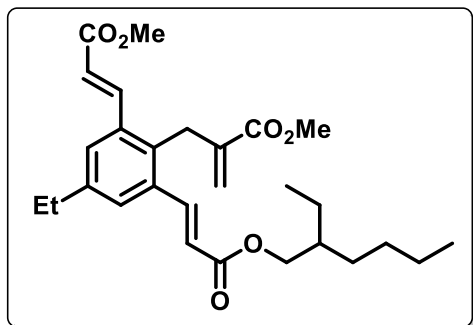
Dimethyl 3,3'-(5-ethyl-2-(2-(methoxycarbonyl)allyl)-1,3-phenylene)(2E,2'E)-diacrylate (8b):



Colorless liquid, Yield (74%, 55mg); ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 15.8$ Hz, 2H), 7.45 (s, 2H), 6.35 (d, $J = 15.8$ Hz, 2H), 6.26 (d, $J = 0.8$ Hz, 1H), 4.97 (d, $J = 0.7$ Hz, 1H), 3.85 (s, 3H), 3.84 (s, 2H), 3.81 (s,

6H), 2.70 (q, $J = 7.6$ Hz, 2H), 0.91 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.13, 167.02, 143.57, 142.41, 138.42, 135.40, 133.82, 128.34, 127.05, 121.02, 52.31, 51.92, 38.81, 36.85, 28.56, 15.42. HRMS (ESI): calc. for $[(\text{C}_{21}\text{H}_{24}\text{O}_6)]$ (M+H) 373.1618, measured 373.1638

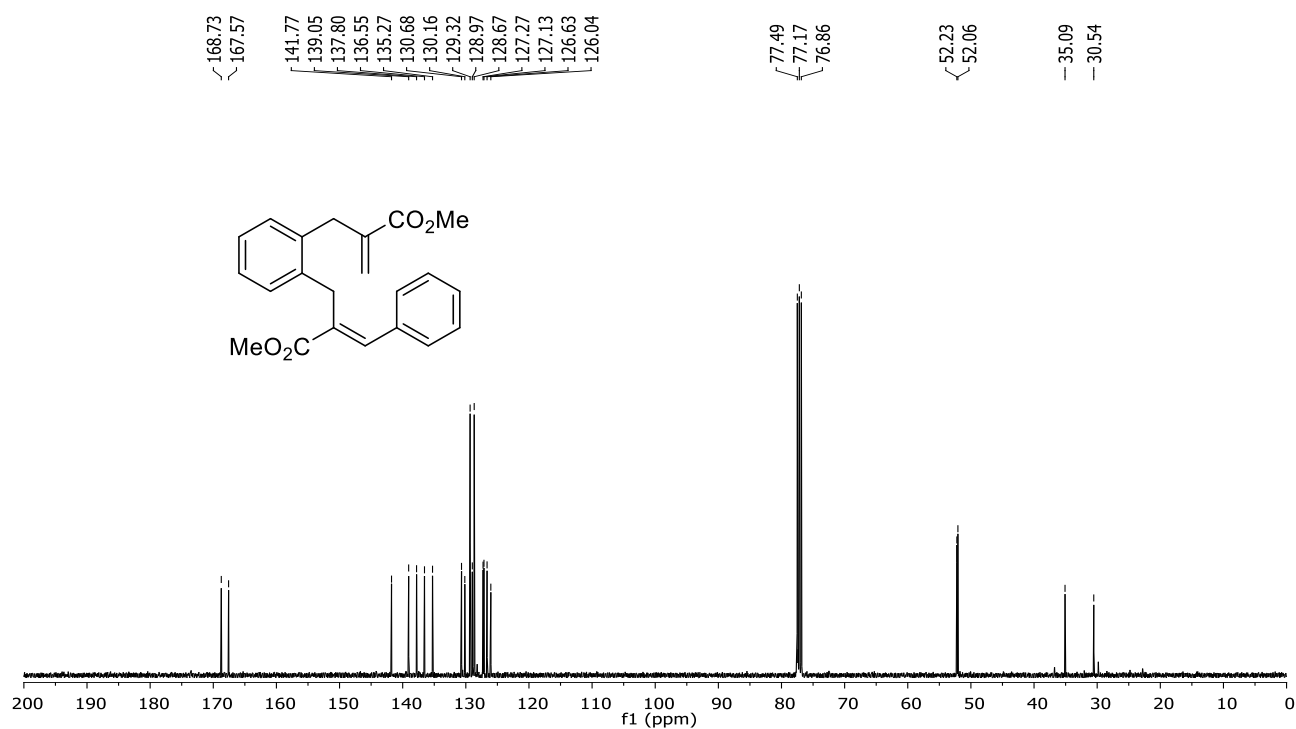
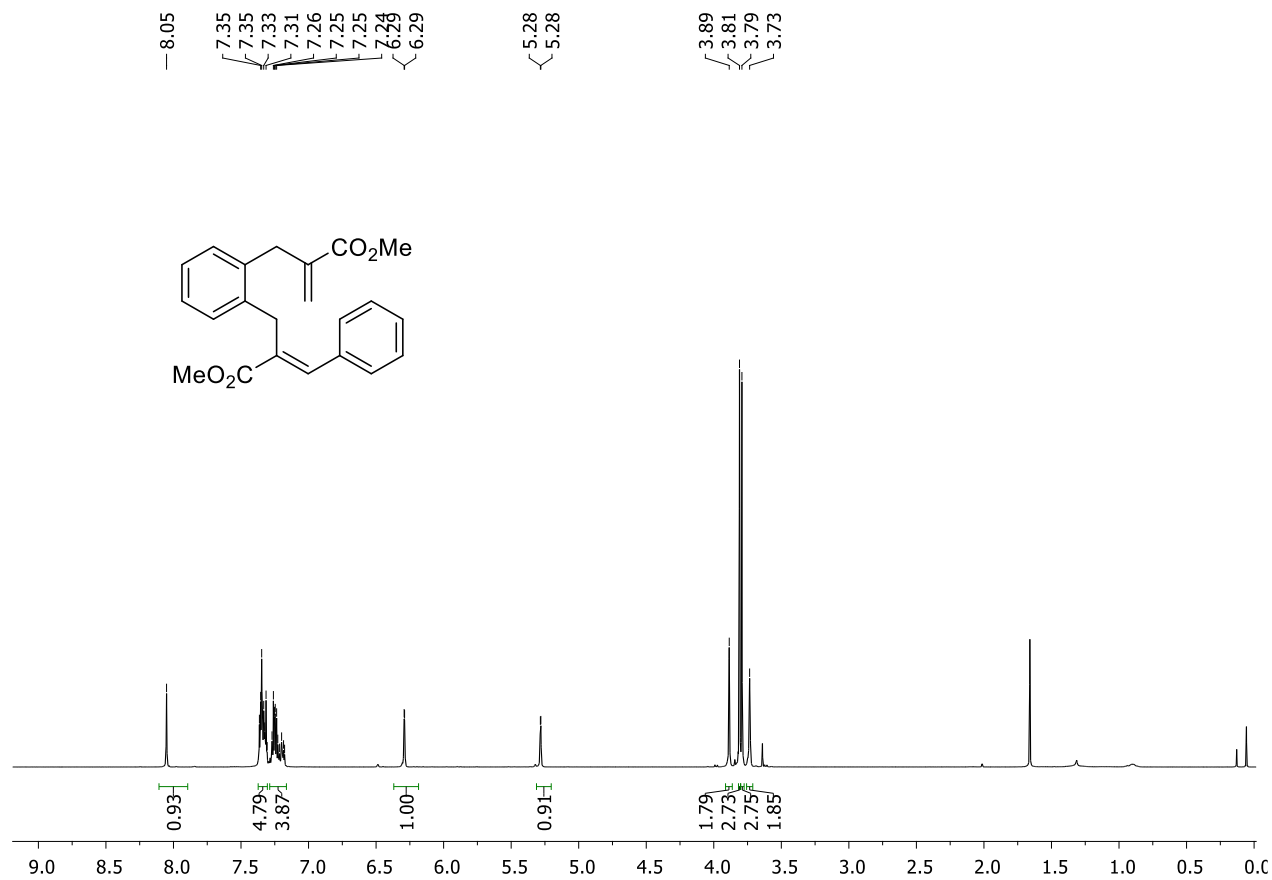
2-Ethylhexyl (*E*)-3-(5-ethyl-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-2-(2-(methoxycarbonyl) allyl)phenyl) acrylate (8c):



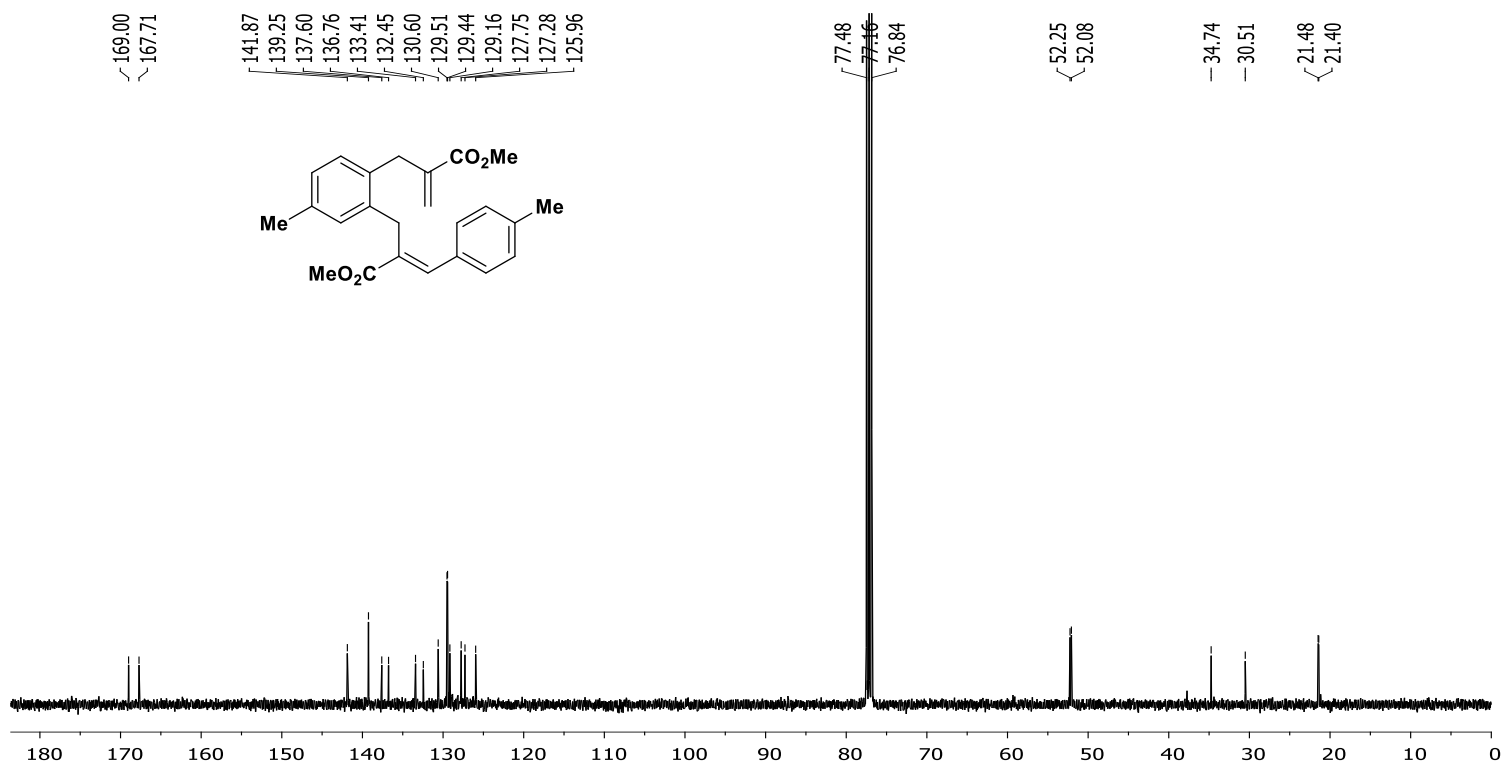
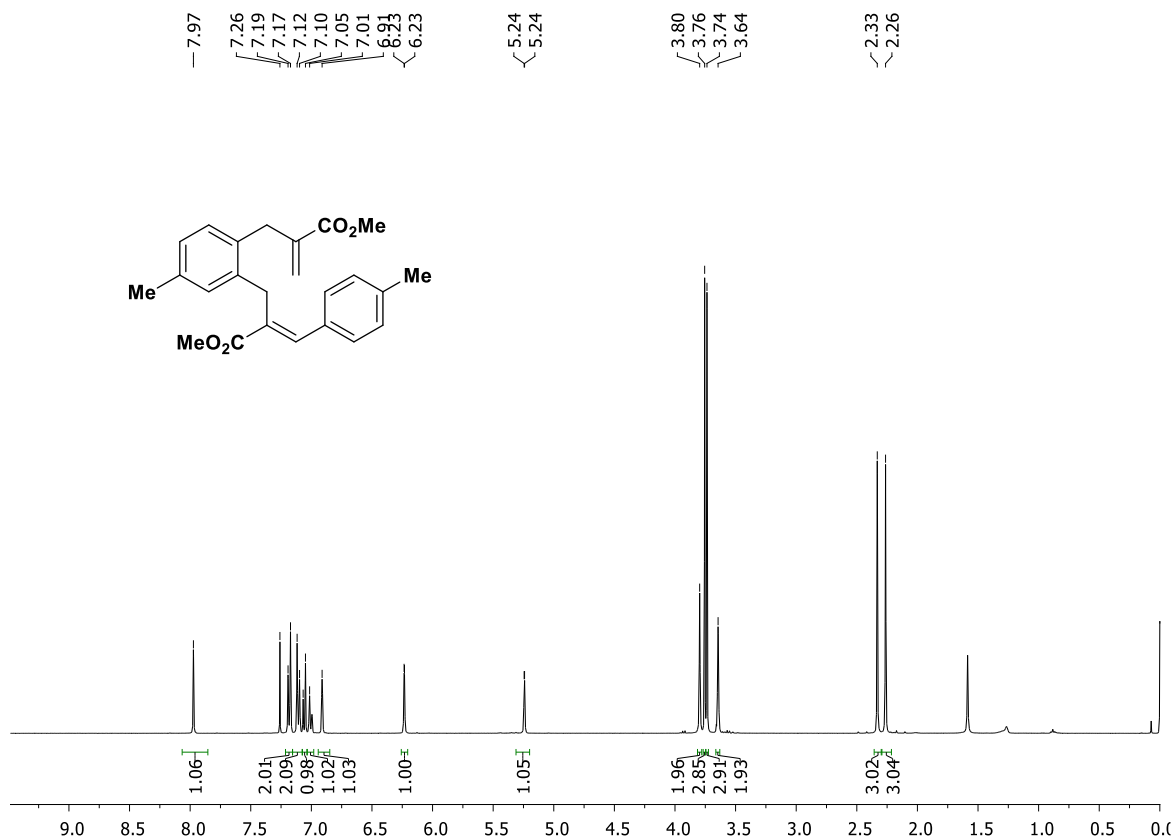
Colorless liquid, Yield (68%, 64mg); ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 5.8$ Hz, 1H), 7.81 (d, $J = 5.8$ Hz, 1H), 7.49 – 7.44 (m, 2H), 6.37 (d, $J = 2.3$ Hz, 1H), 6.33 (d, $J = 2.3$ Hz, 1H), 6.25 (d, $J = 0.7$ Hz, 1H), 4.98 (d, $J = 0.7$ Hz, 1H), 4.12 (dd, $J = 6.3, 5.6$ Hz, 2H), 3.84 (s, 5H,), 3.81(s, 3H), 2.70 (q, $J = 7.6$ Hz, 2H), 1.44 – 1.37 (m, 3H), 1.37 – 1.23 (m, 13H), 0.93 (dd, $J = 10.5, 4.5$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.13, 166.94, 166.89, 143.54, 142.44, 142.03, 138.40, 135.40, 133.79, 128.28, 127.00, 121.37, 120.99, 114.28, 67.14, 52.26, 51.91, 38.95, 30.58, 29.08, 28.57, 24.00, 23.09, 15.46, 14.19, 11.17. HRMS (ESI): calc. for $[(\text{C}_{28}\text{H}_{38}\text{O}_6)]$ (M+H) 471.2718, measured 471.2727.

7. Copies of ^1H and ^{13}C NMR Spectra of the Products

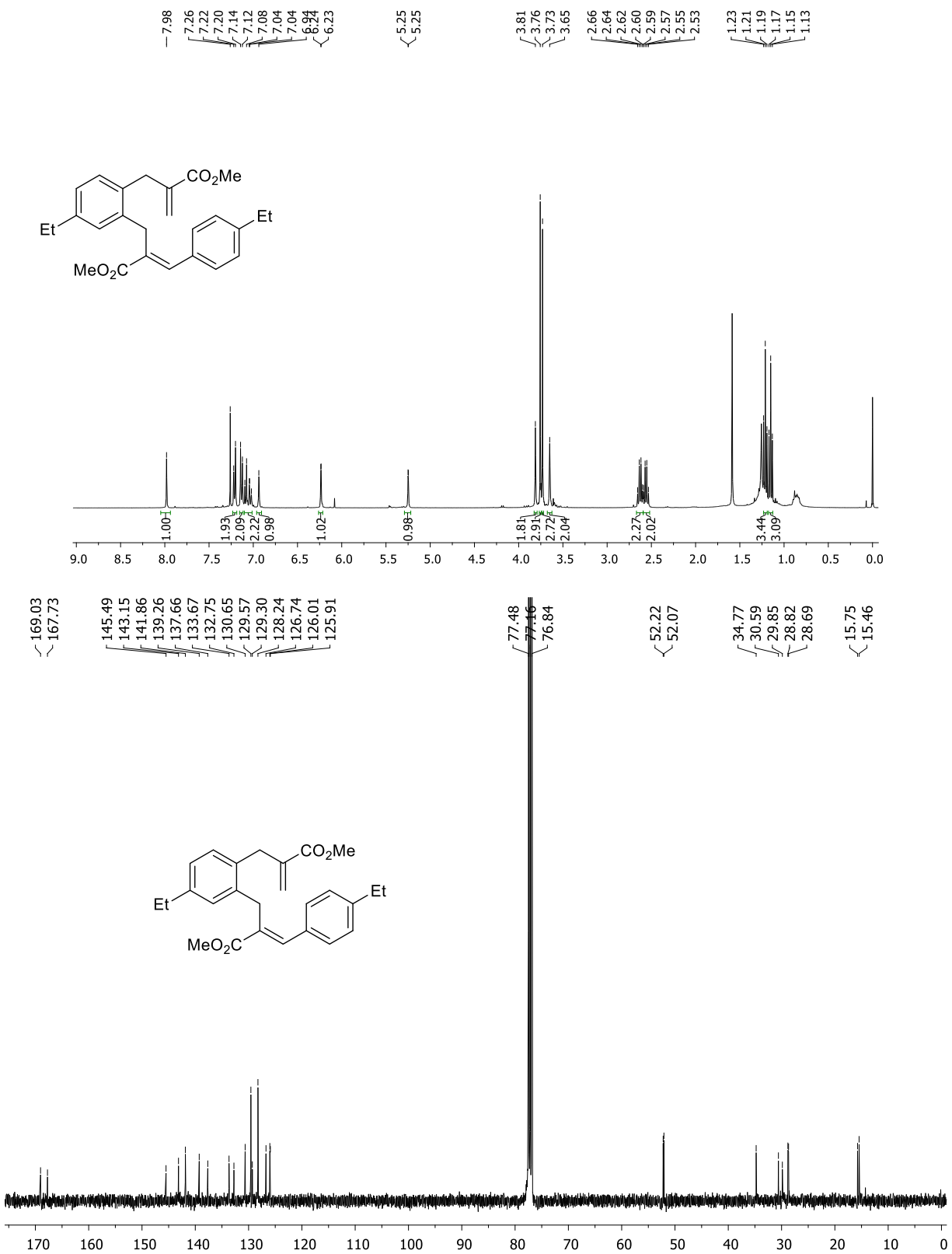
Methyl (*E*)-2-(2-(2-(methoxycarbonyl) allyl) benzyl)-3-phenylacrylate (2a)



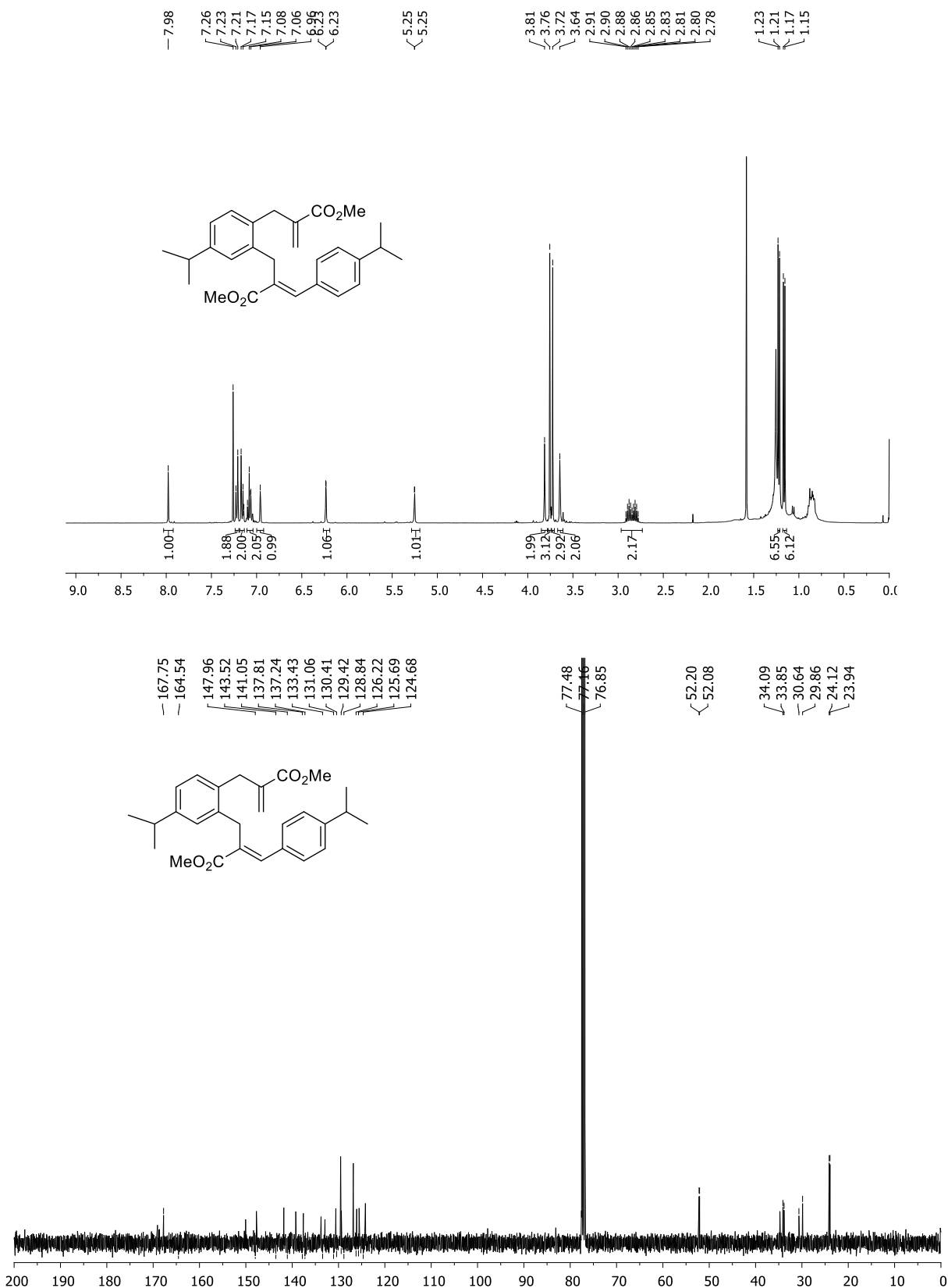
Methyl (*E*)-2-(2-(2-(methoxycarbonyl)allyl)-5-methylbenzyl)-3-(*p*-tolyl)acrylate (2b):



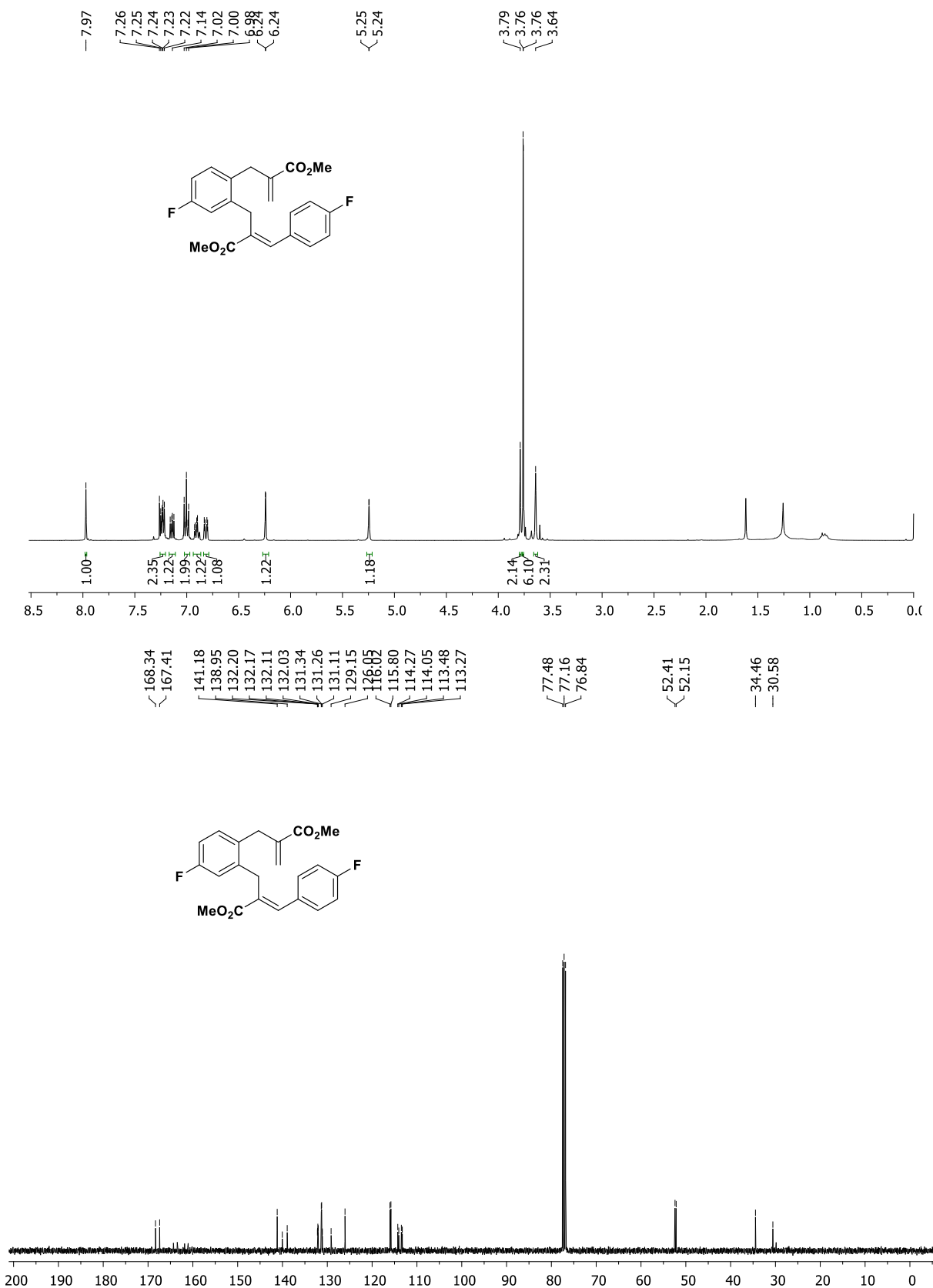
Methyl (*E*)-2-(5-ethyl-2-(2-(methoxycarbonyl) allyl) benzyl)-3-(4-ethylphenyl) acrylate (2c):



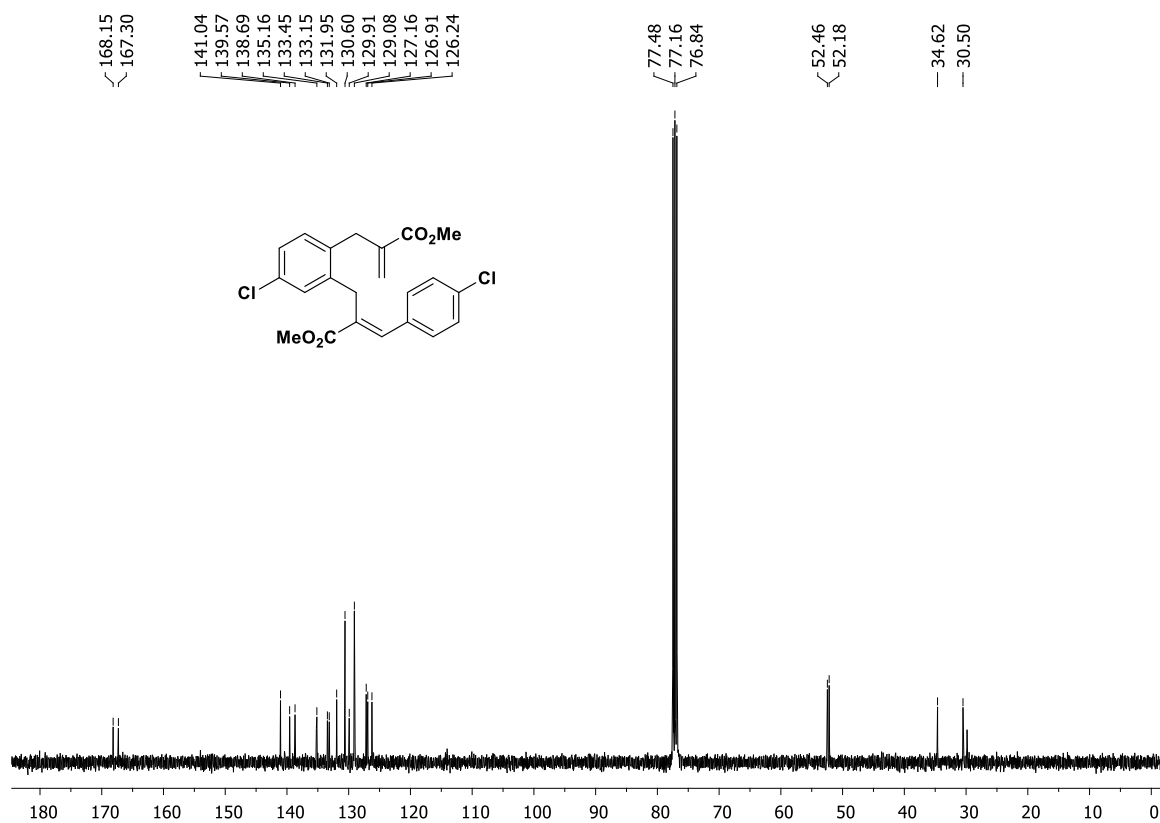
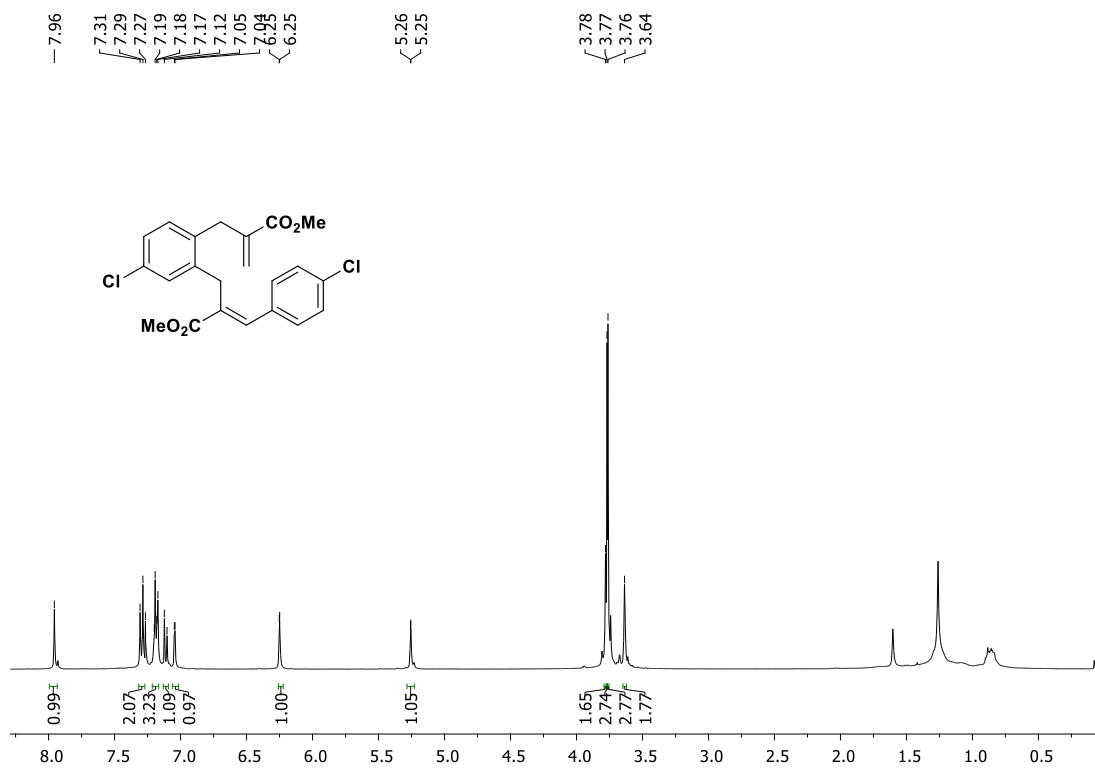
Methyl (*E*)-2-(5-isopropyl-2-(2-(methoxycarbonyl) allyl) benzyl)-3-(4-isopropylphenyl) acrylate (2d):



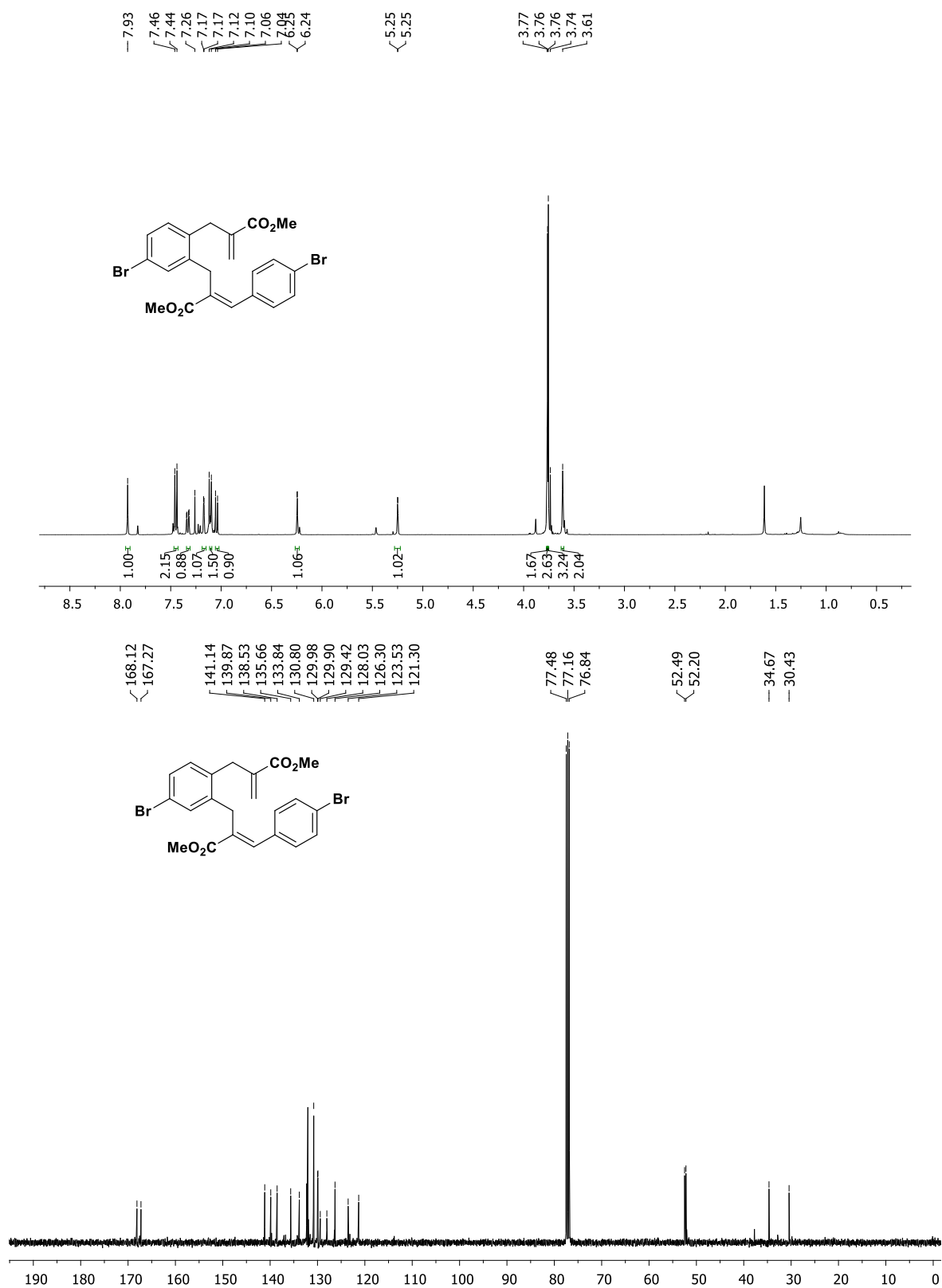
Methyl (*E*)-2-(5-fluoro-2-(2-(methoxycarbonyl)allyl)benzyl)-3-(4-fluorophenyl) acrylate (2f):



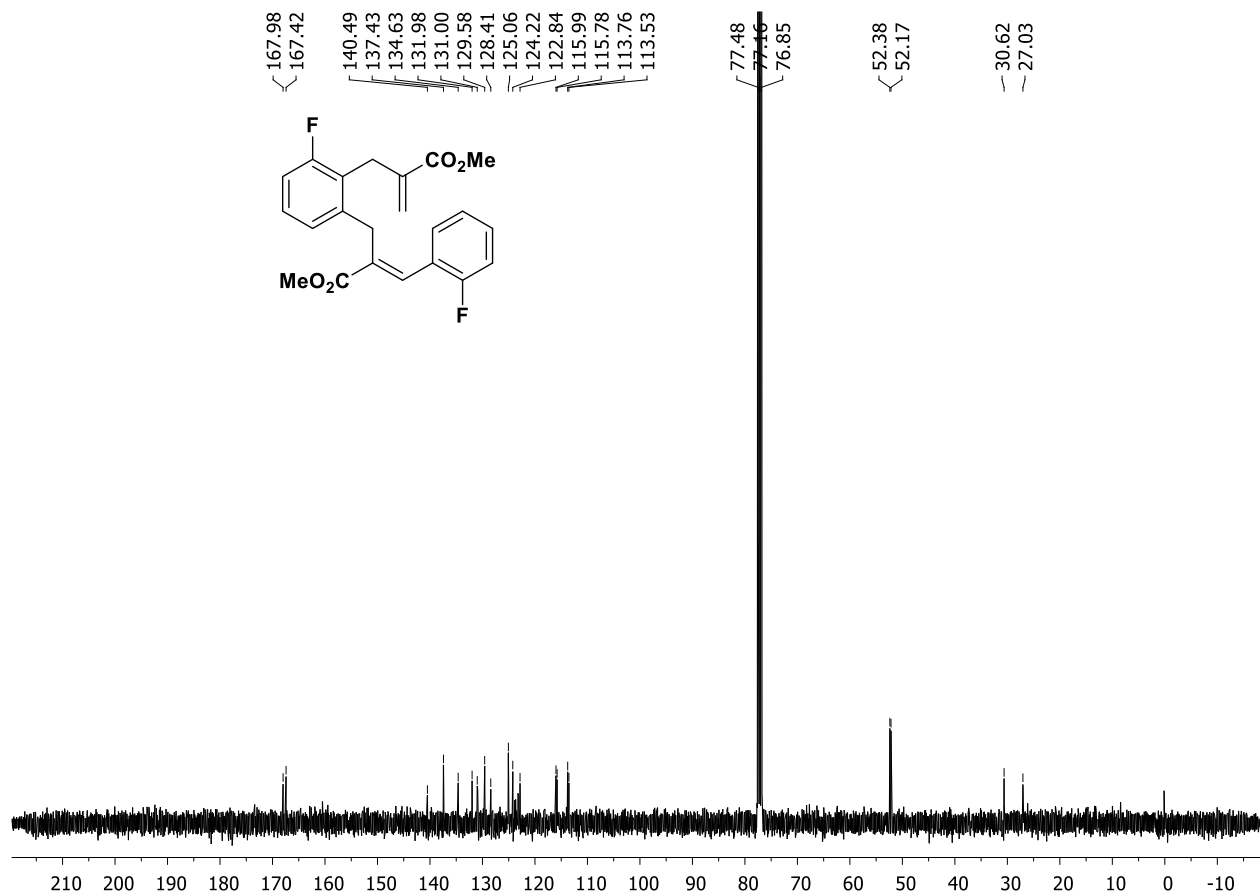
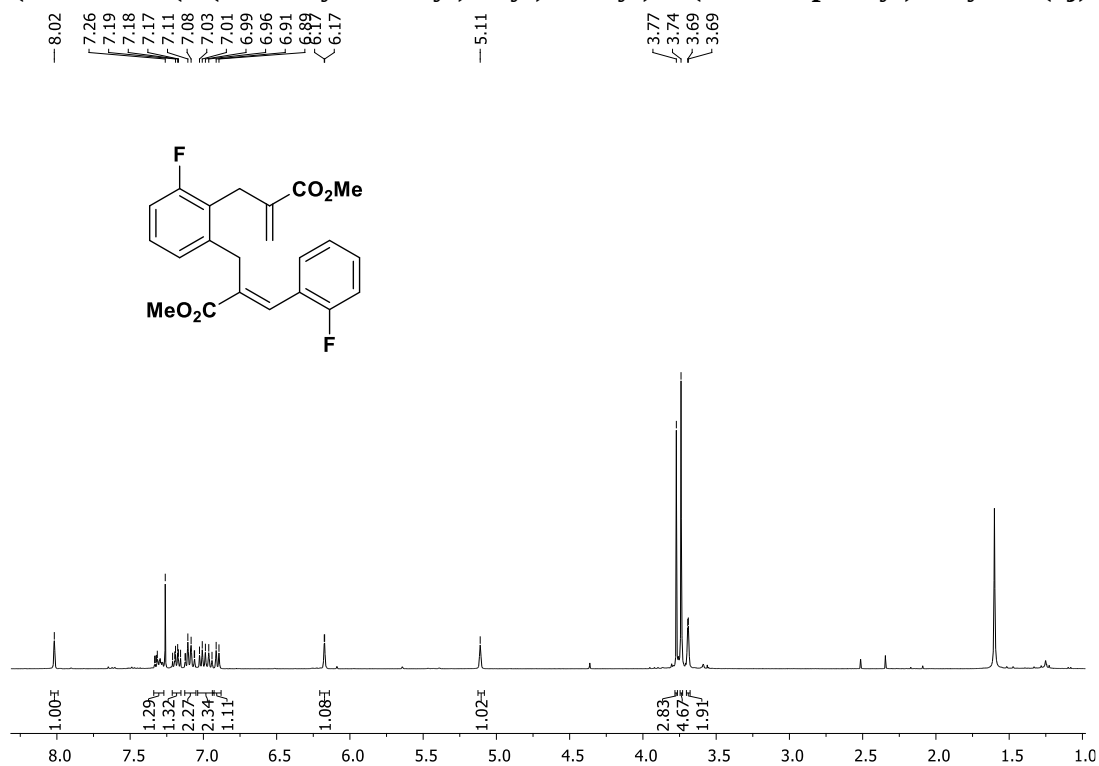
Methyl (*E*)-2-(5-chloro-2-(2-(methoxycarbonyl) allyl) benzyl)-3-(4-chlorophenyl) acrylate (2g):



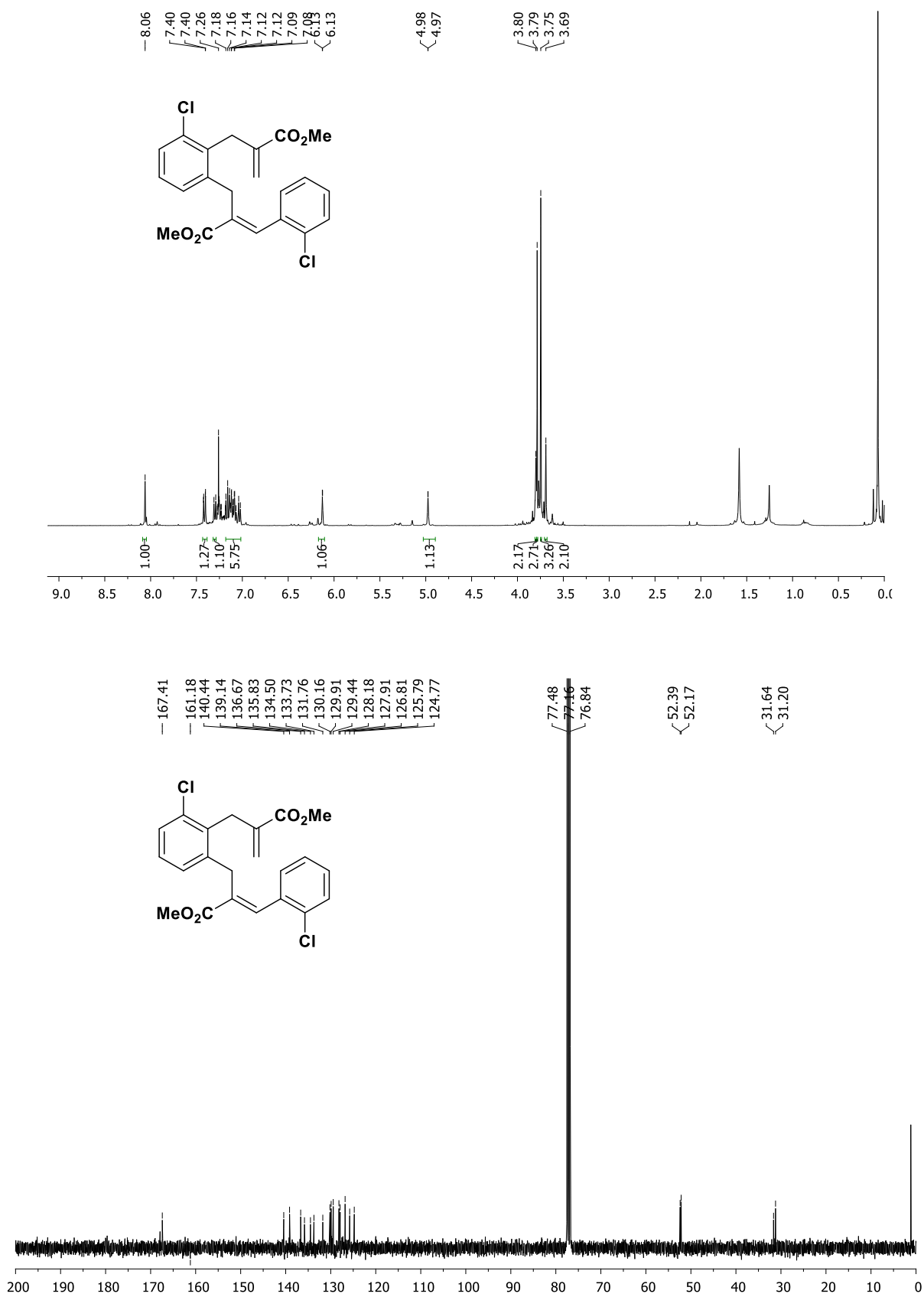
Methyl (*E*)-2-(5-bromo-2-(2-(methoxycarbonyl)allyl)benzyl)-3-(4-bromophenyl) acrylate (2g):



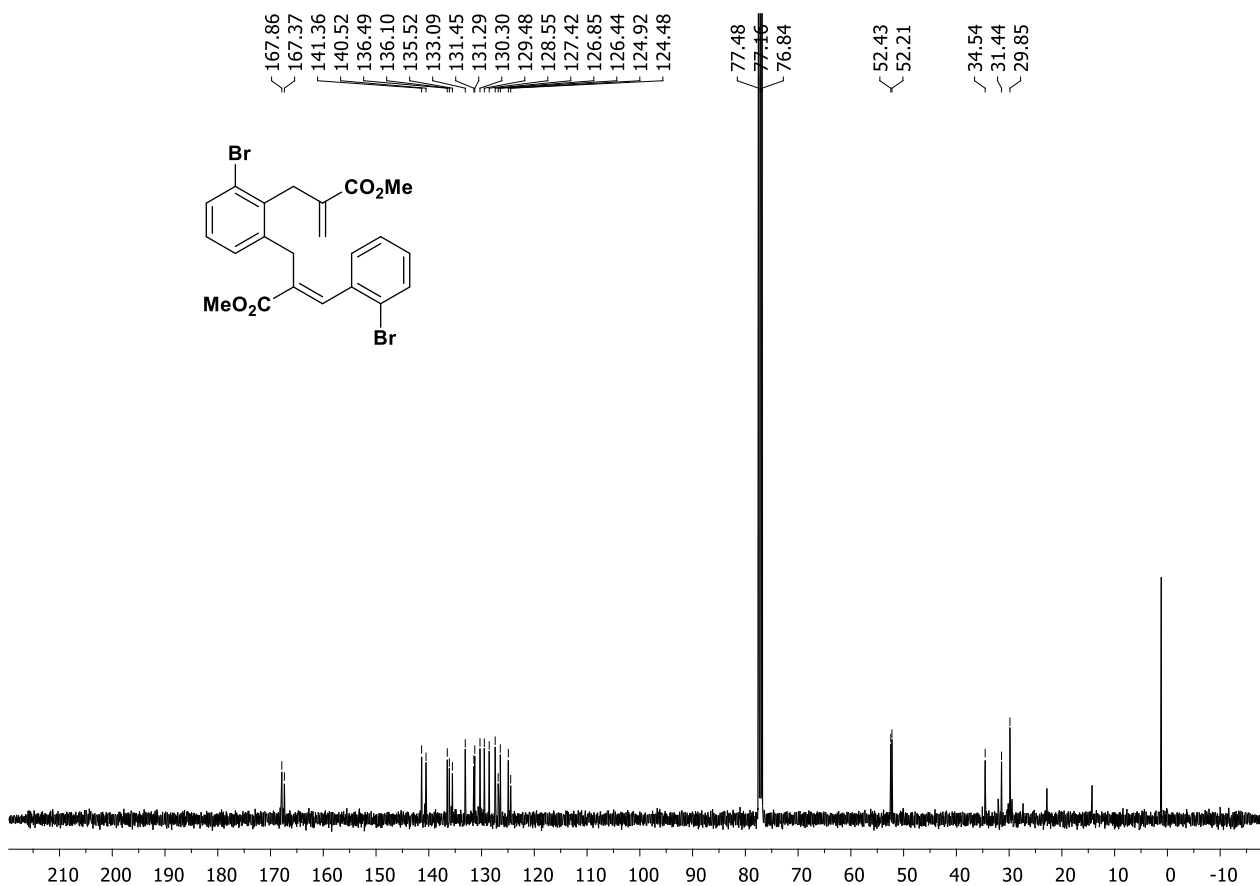
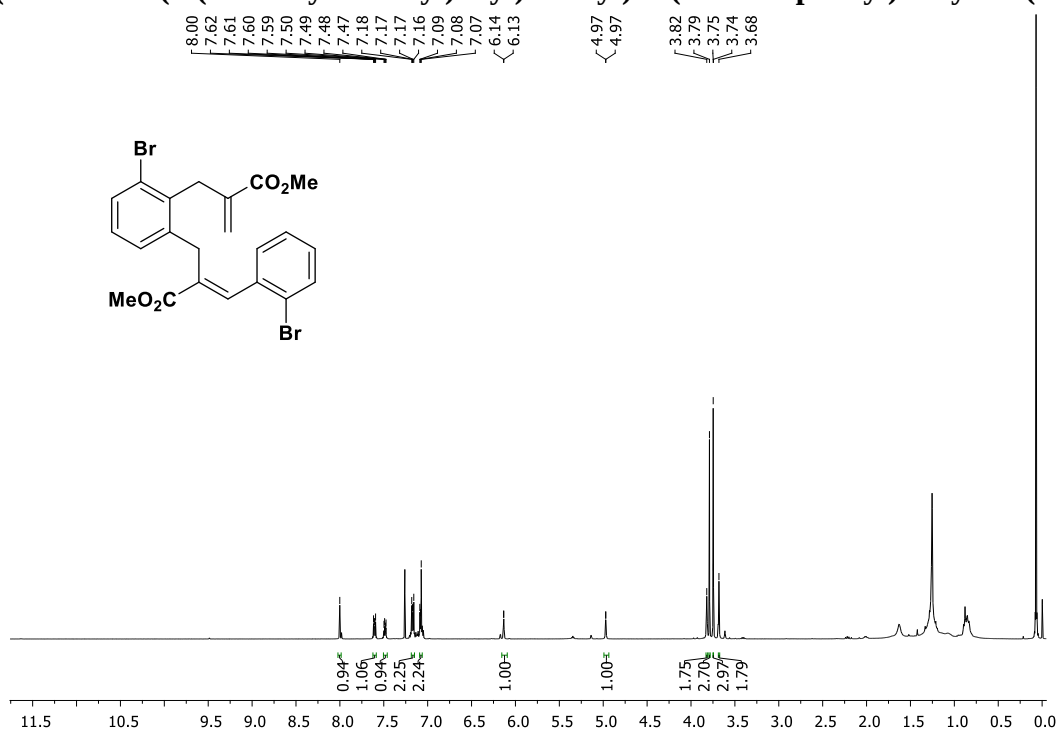
Methyl (*E*)-2-(3-fluoro-2-(2-(methoxycarbonyl) allyl) benzyl)-3-(2-fluorophenyl) acrylate (2j):



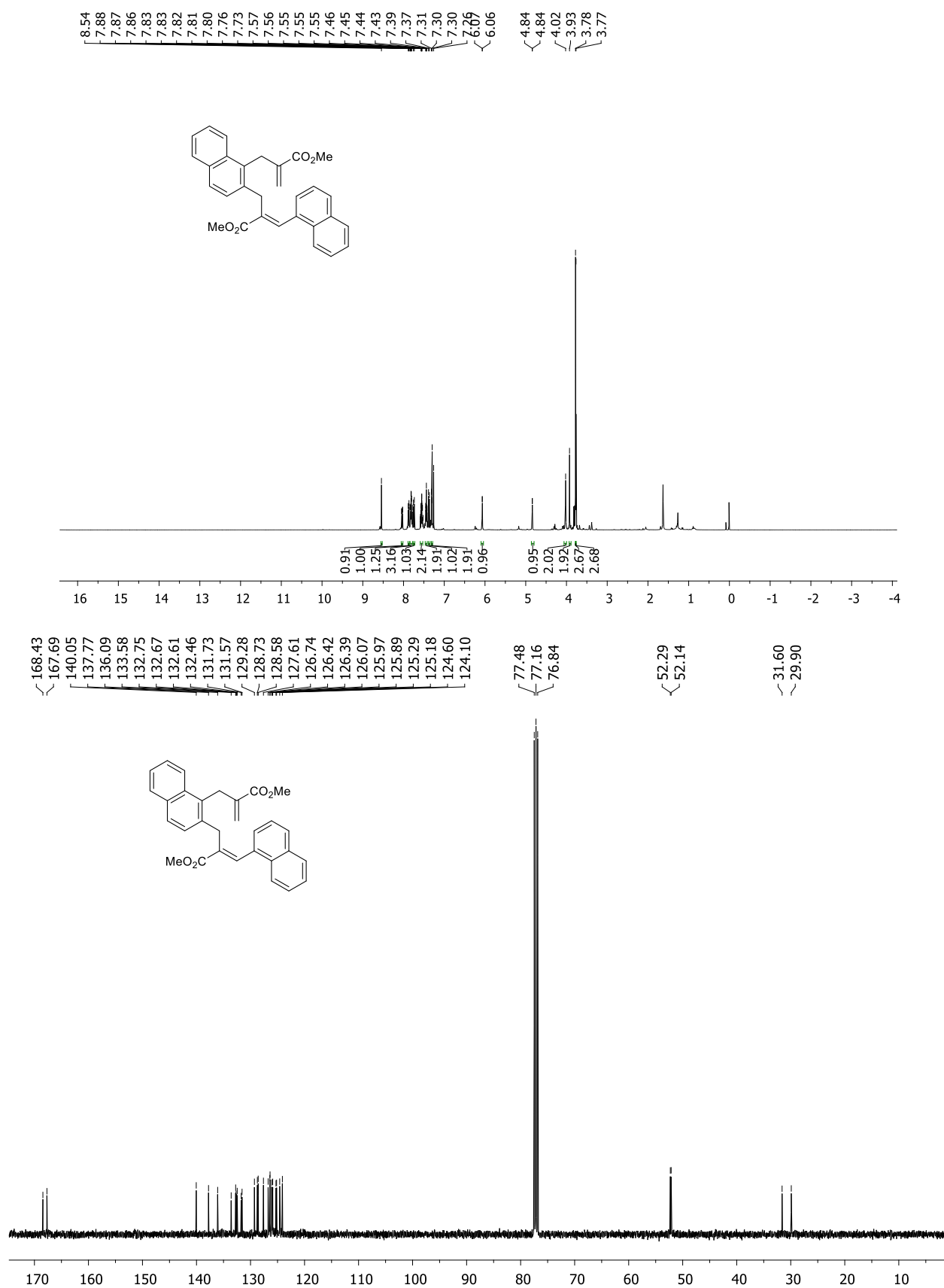
Methyl (*E*)-2-(3-chloro-2-(2-(methoxycarbonyl)allyl) benzyl)-3-(2-chlorophenyl) acrylate (2k):



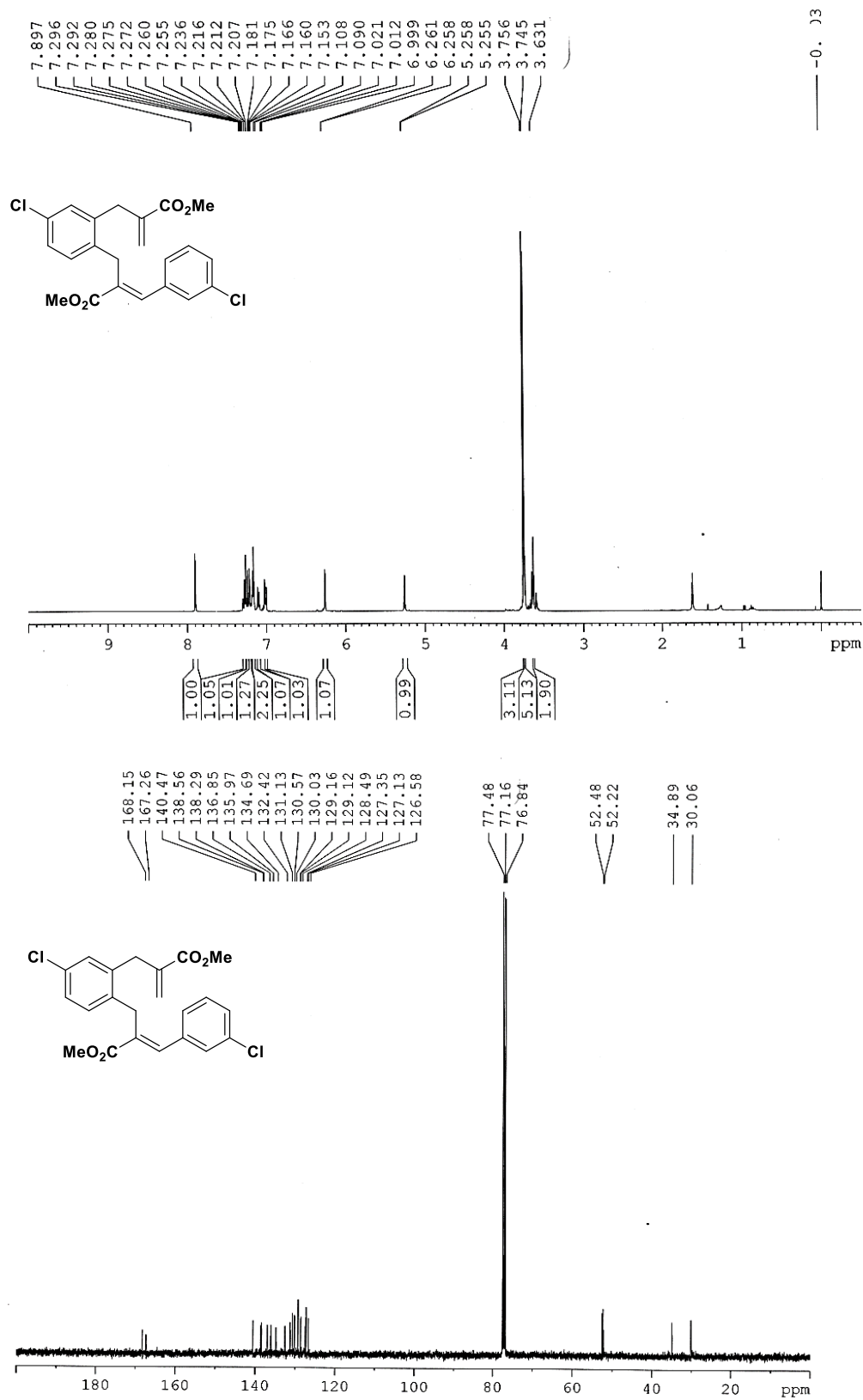
Methyl (*E*)-2-(3-bromo-2-(2-(methoxycarbonyl)allyl) benzyl)-3-(2 bromophenyl) acrylate (2l):



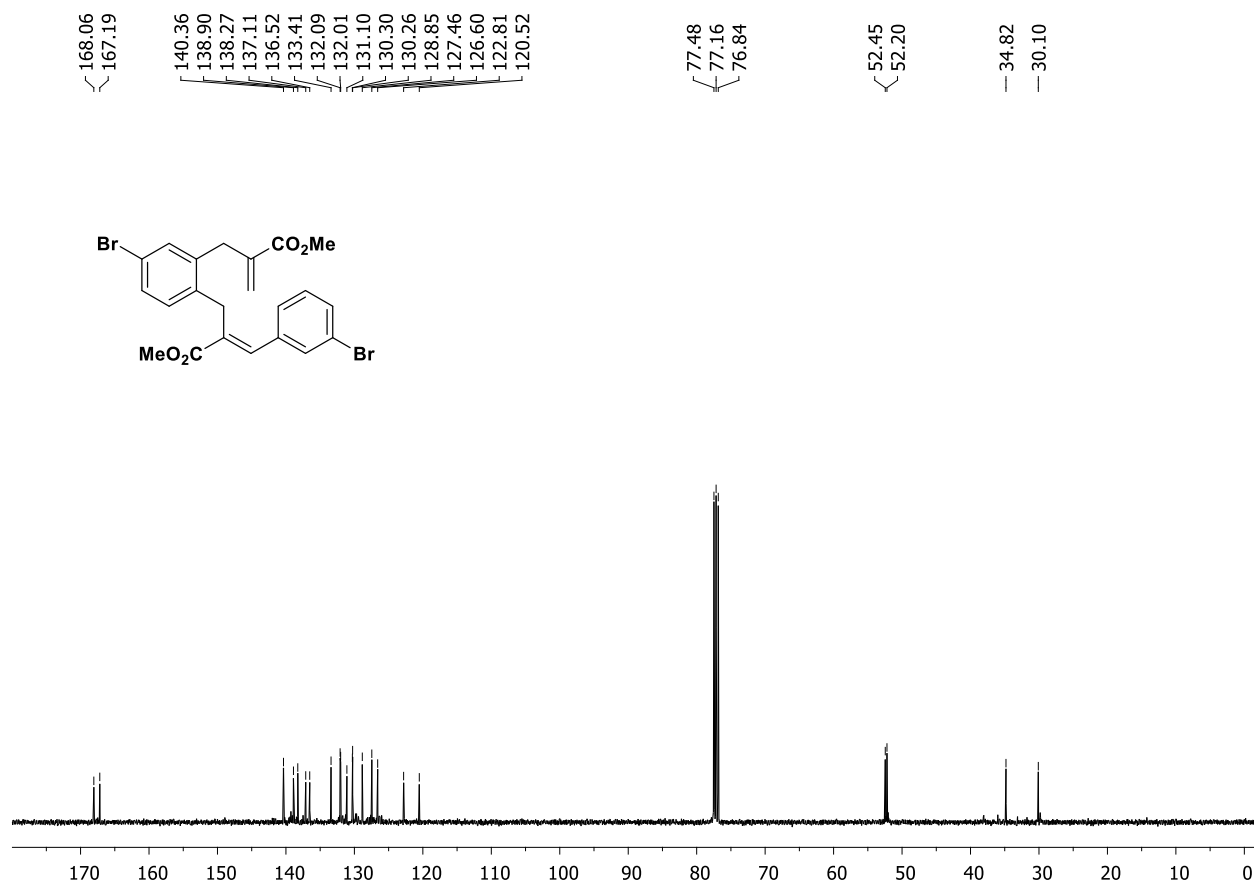
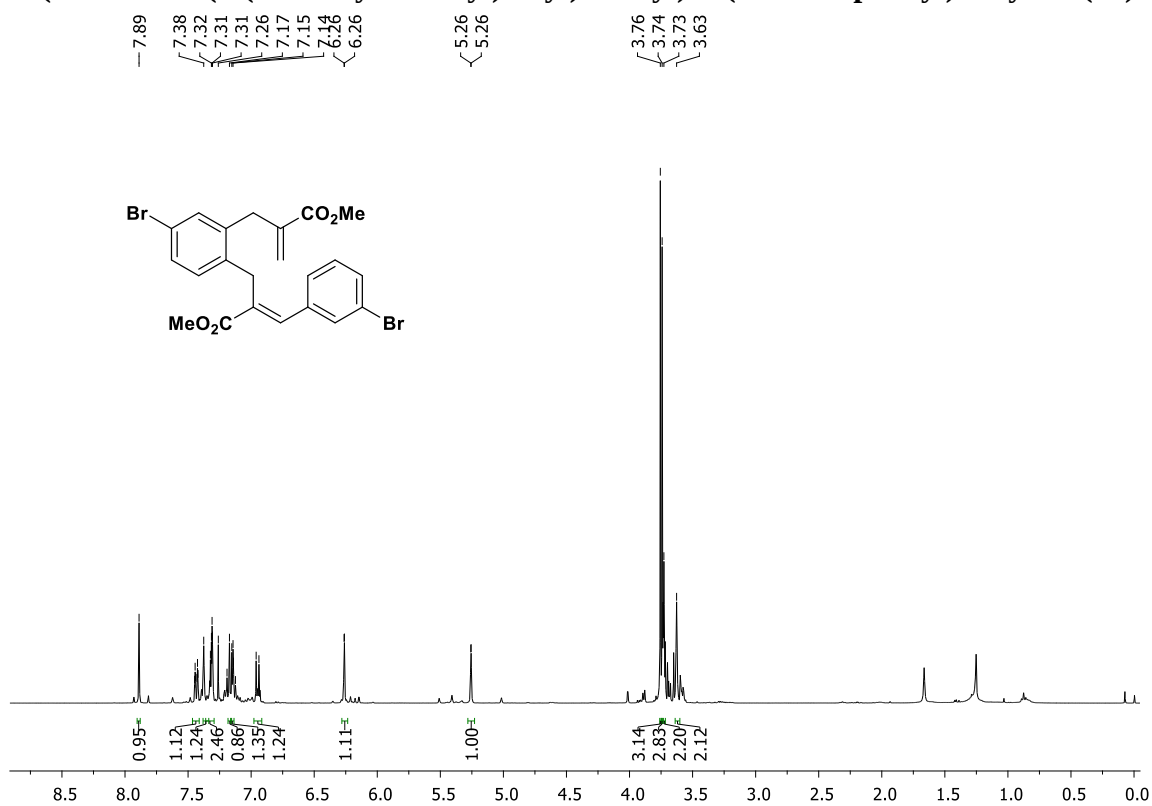
Methyl (*E*)-2-((1-(2-(methoxycarbonyl) allyl) naphthalen-2-yl) methyl)-3-(naphthalen-1-yl) acrylate (2m):



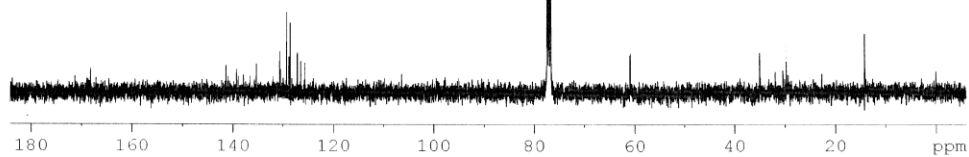
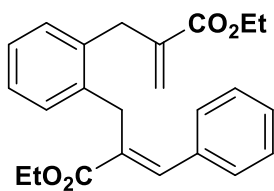
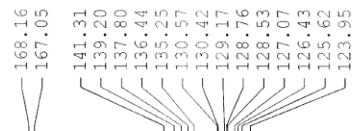
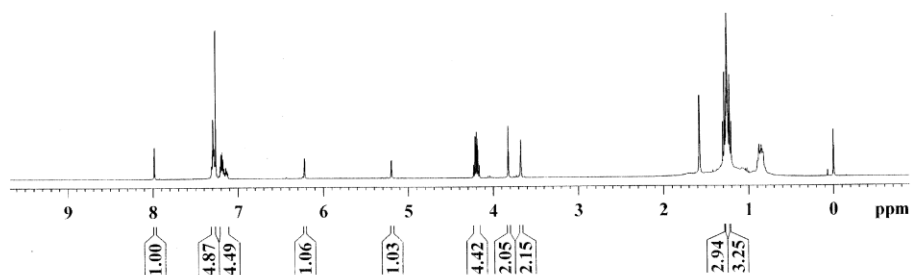
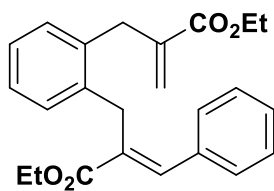
Methyl (*E*)-2-(4-chloro-2-(2-(methoxycarbonyl)allyl)benzyl)-3-(3-chlorophenyl) acrylate (2n):



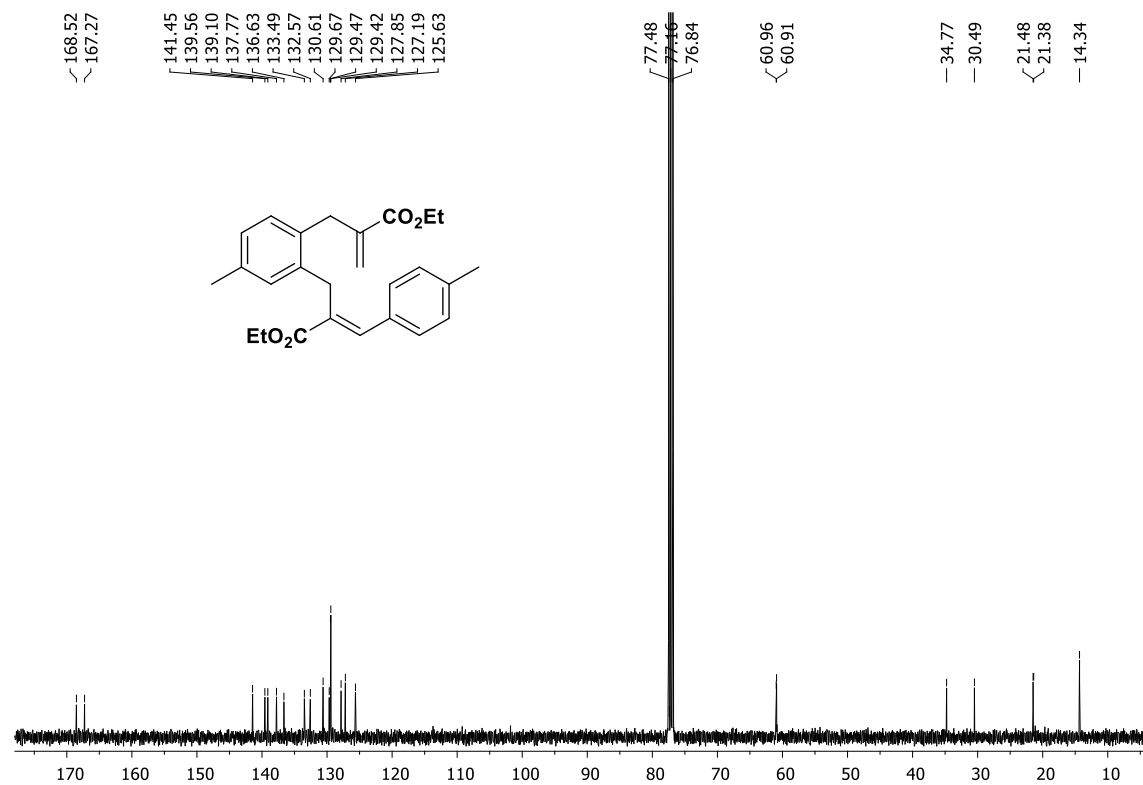
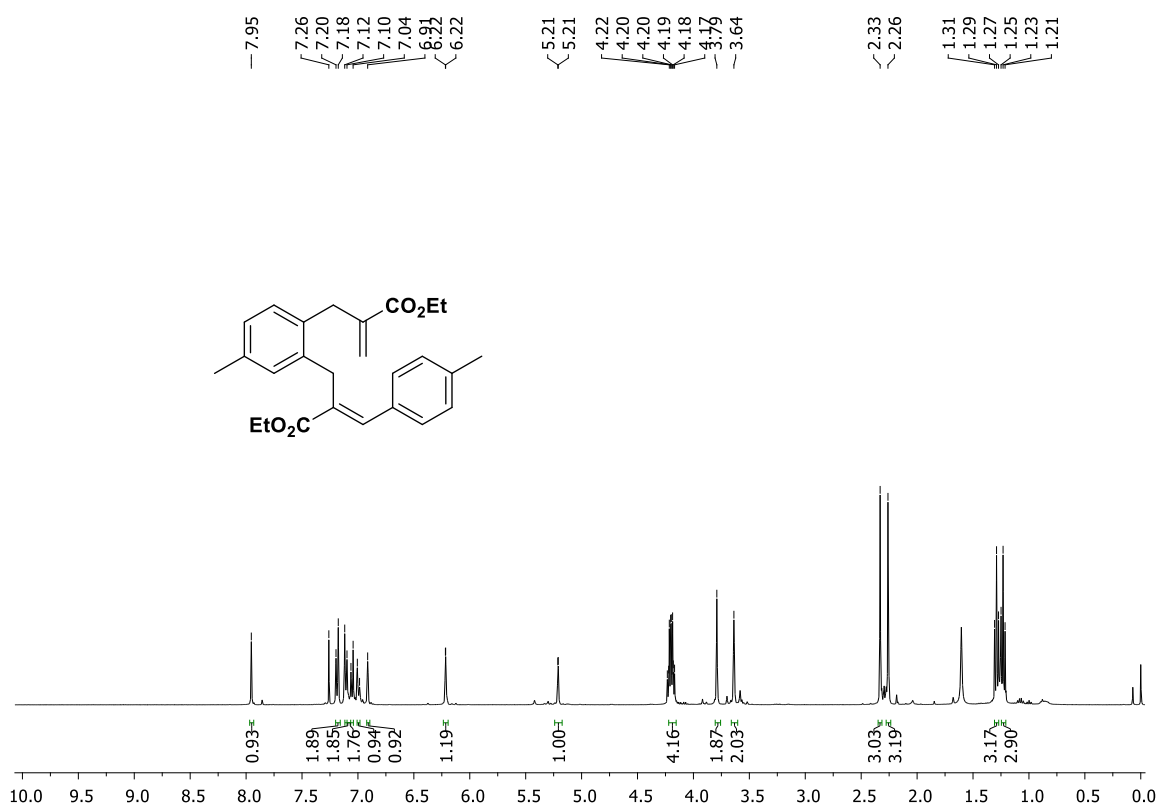
Methyl (*E*)-2-(4-bromo-2-(2-(methoxycarbonyl) allyl) benzyl)-3-(3-bromophenyl) acrylate (2o):



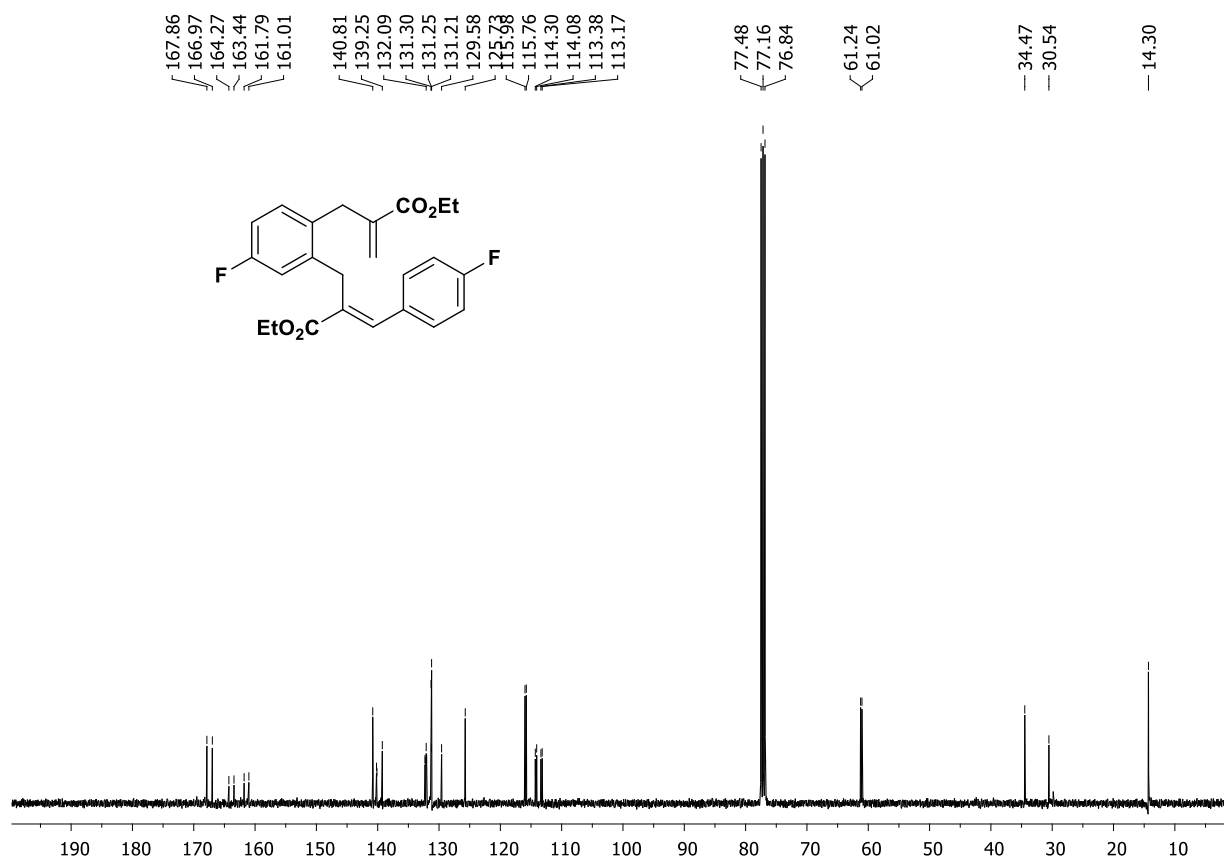
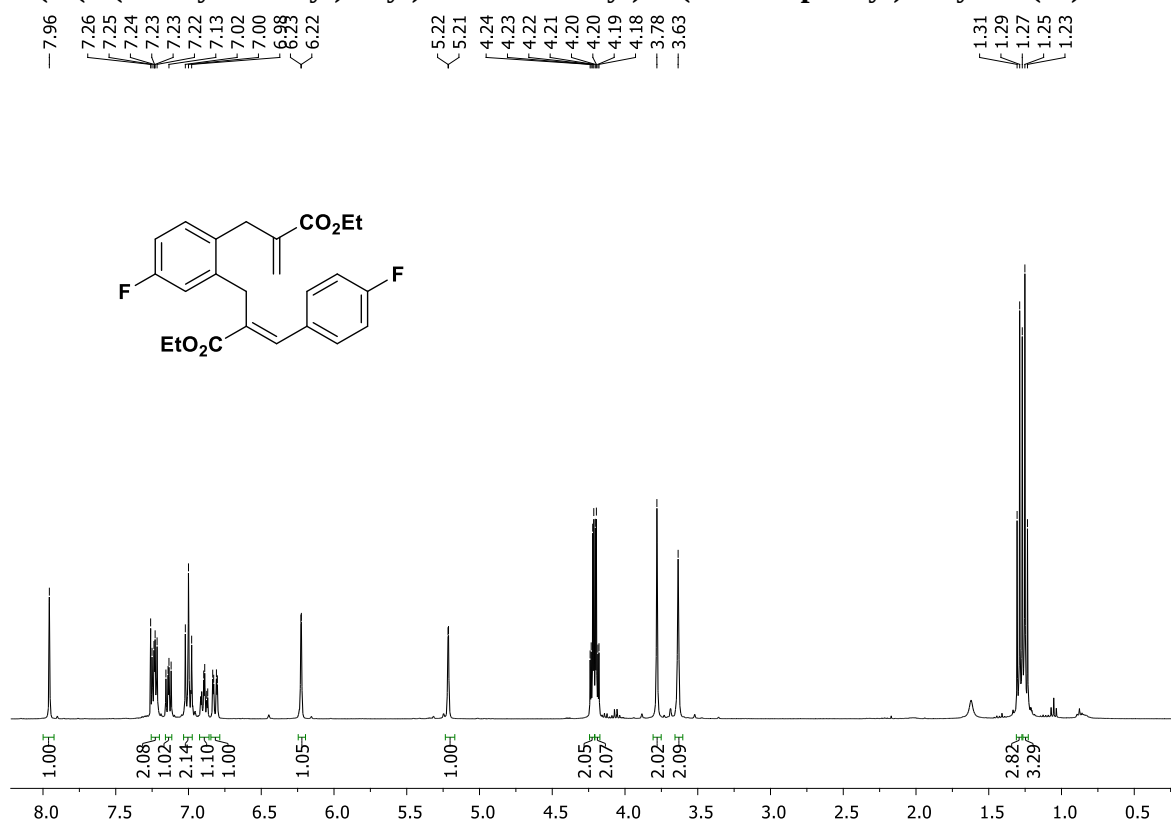
Methyl (*E*)-2-(2-(2-(ethoxycarbonyl)allyl)benzyl)-3-phenylacrylate (2p):



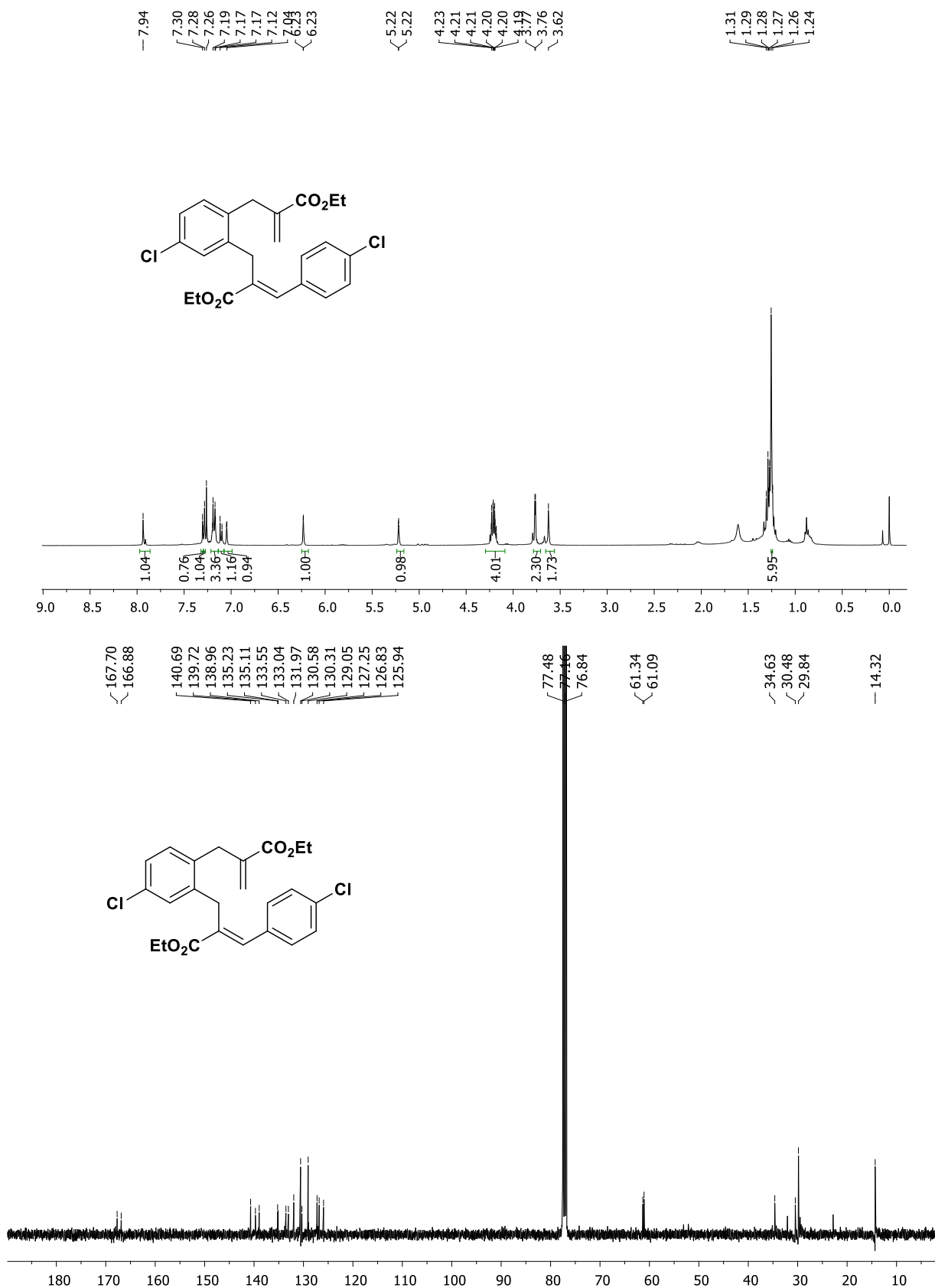
Ethyl (*E*)-2-(2-(2-(ethoxycarbonyl)allyl)-5-methylbenzyl)-3-(*p*-tolyl) acrylate (2q):



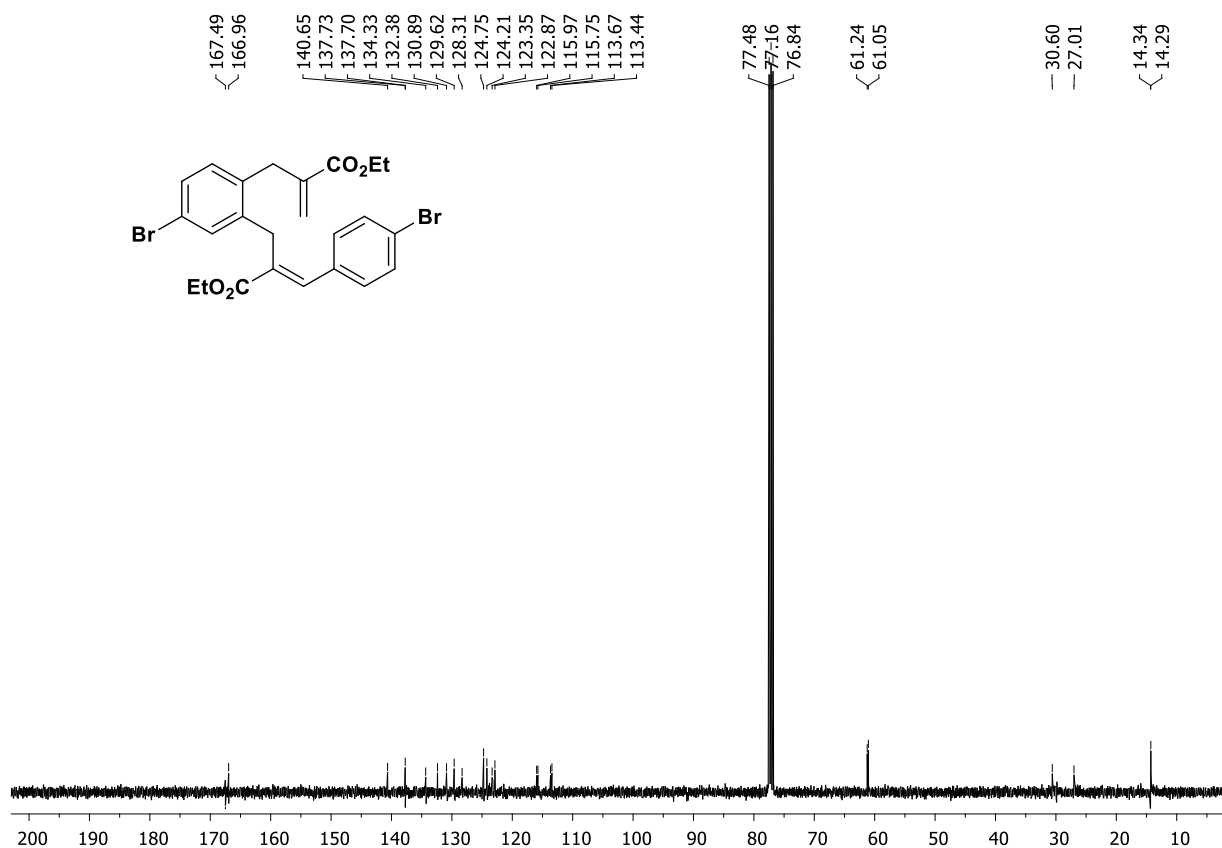
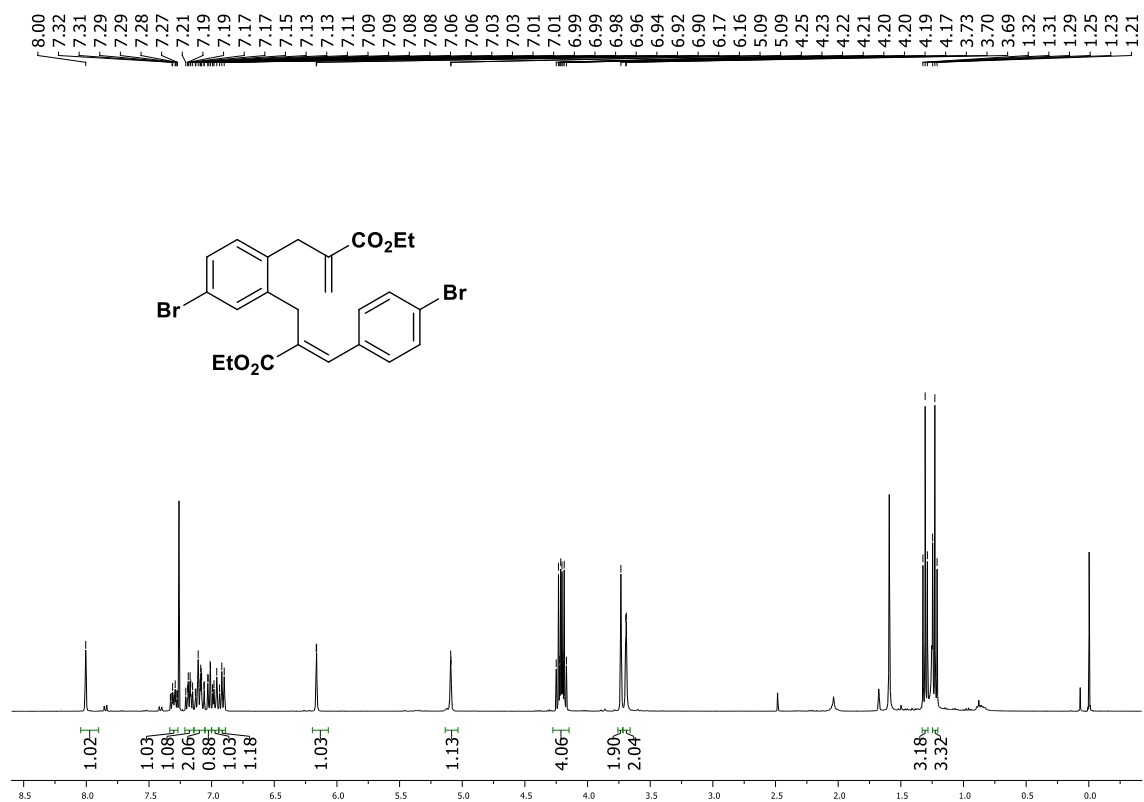
Ethyl (E)-2-(2-(2-(ethoxycarbonyl) allyl)-5-fluorobenzyl)-3-(4-fluorophenyl) acrylate (2r):



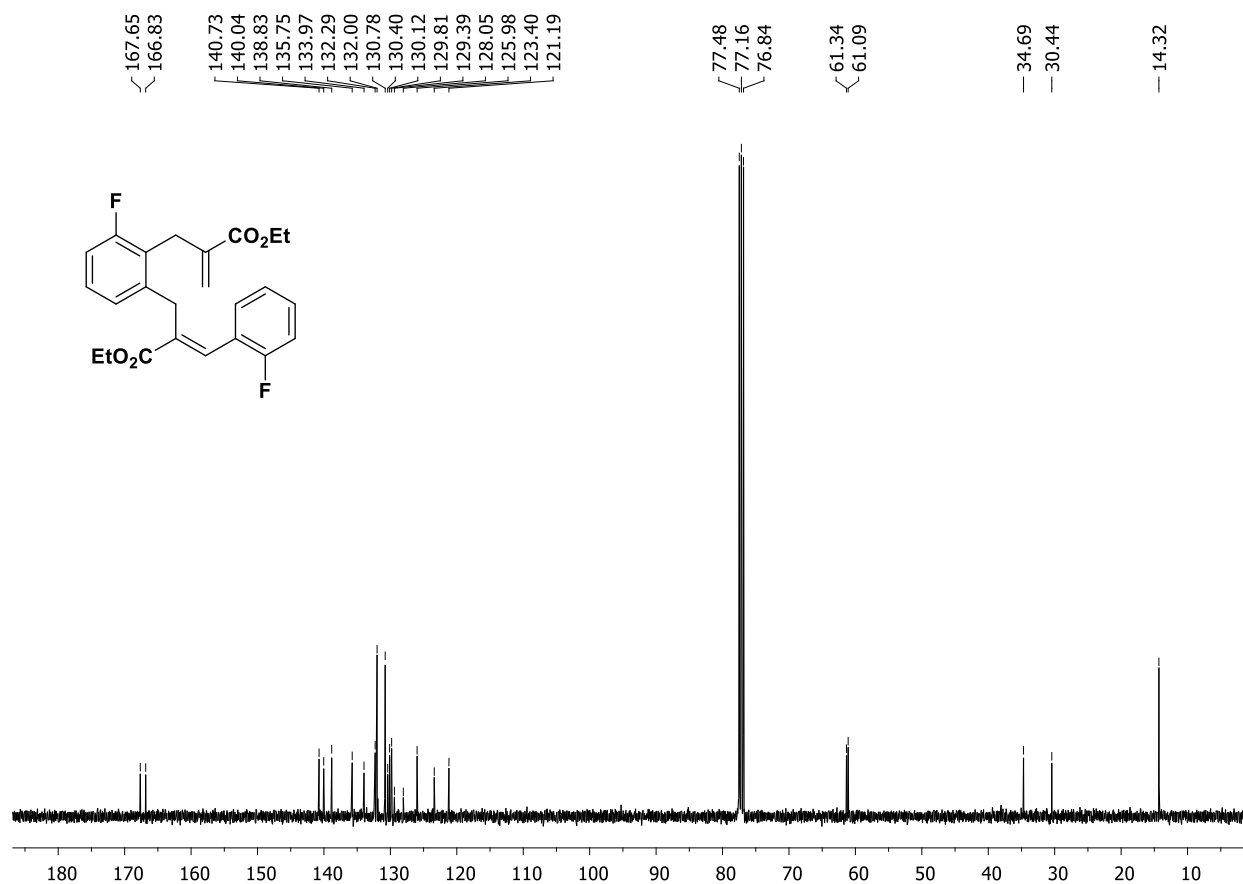
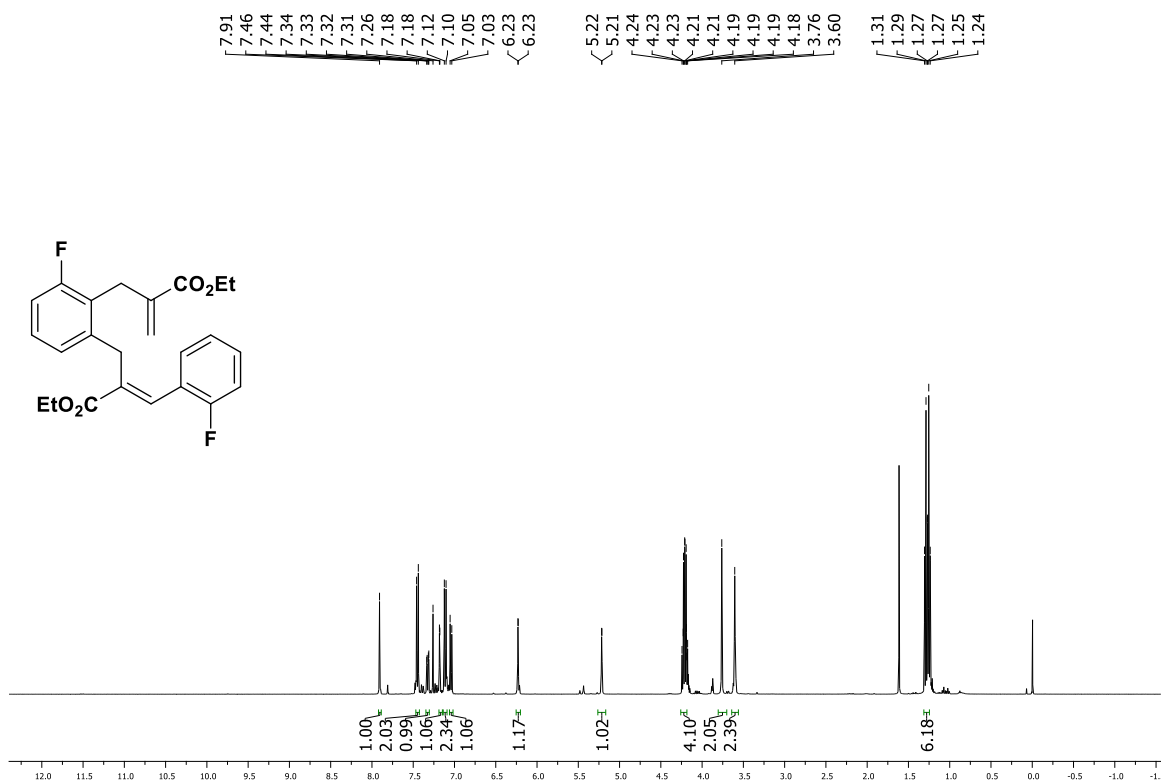
Ethyl (*E*)-2-(5-chloro-2-(2-(ethoxycarbonyl)allyl)benzyl)-3-(4-chlorophenyl) acrylate (2s):



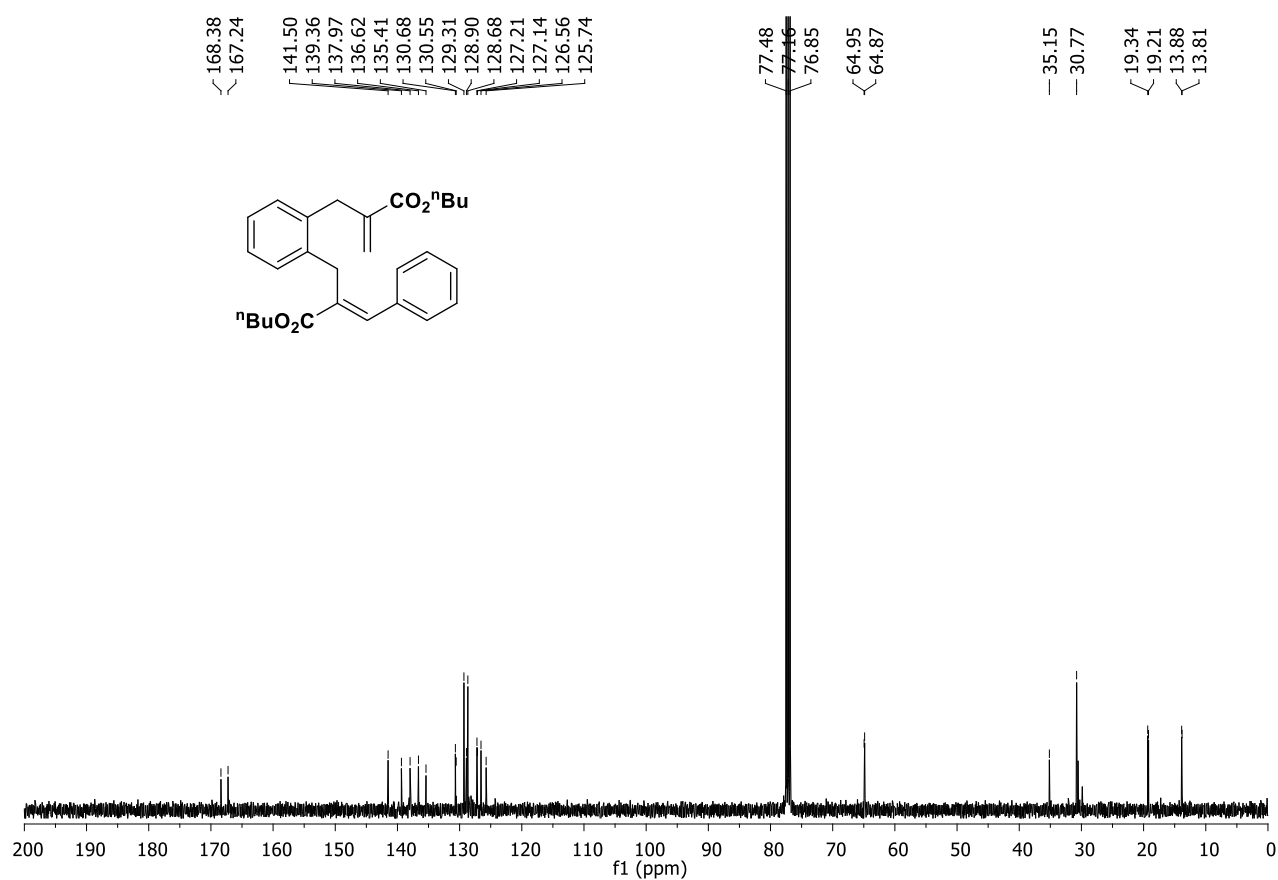
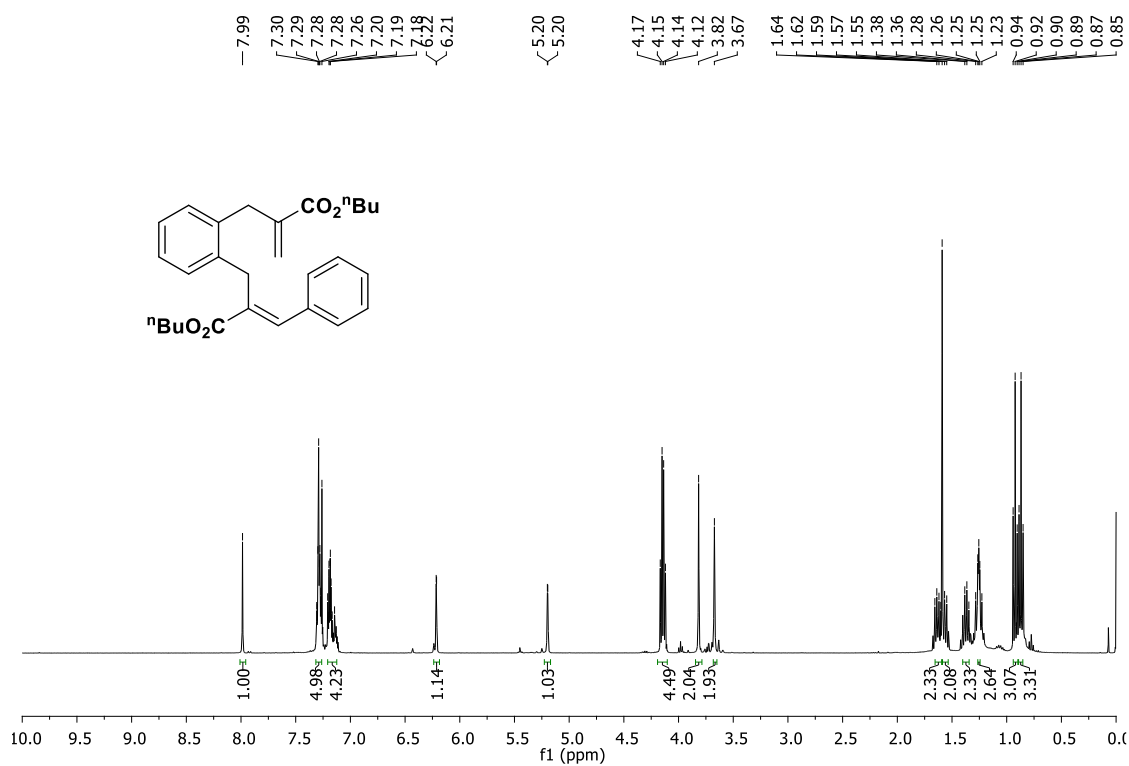
Ethyl (E)-2-(5-bromo-2-(2-(ethoxycarbonyl)allyl)benzyl)-3-(4-bromophenyl) acrylate (2t):



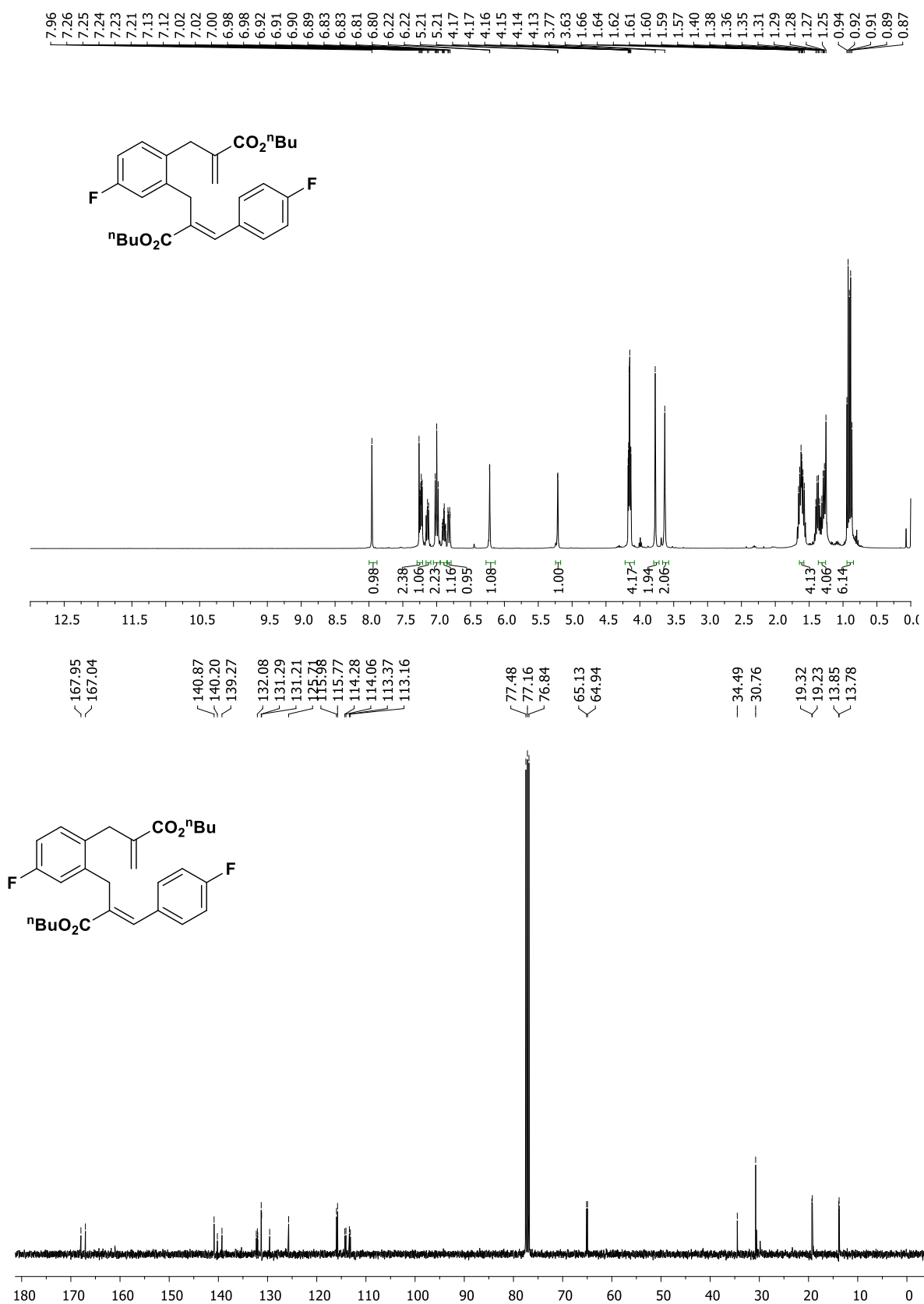
Ethyl (*E*)-2-(2-(2-(ethoxycarbonyl)allyl)-3-fluorobenzyl)-3-(2-fluorophenyl) acrylate (2u):



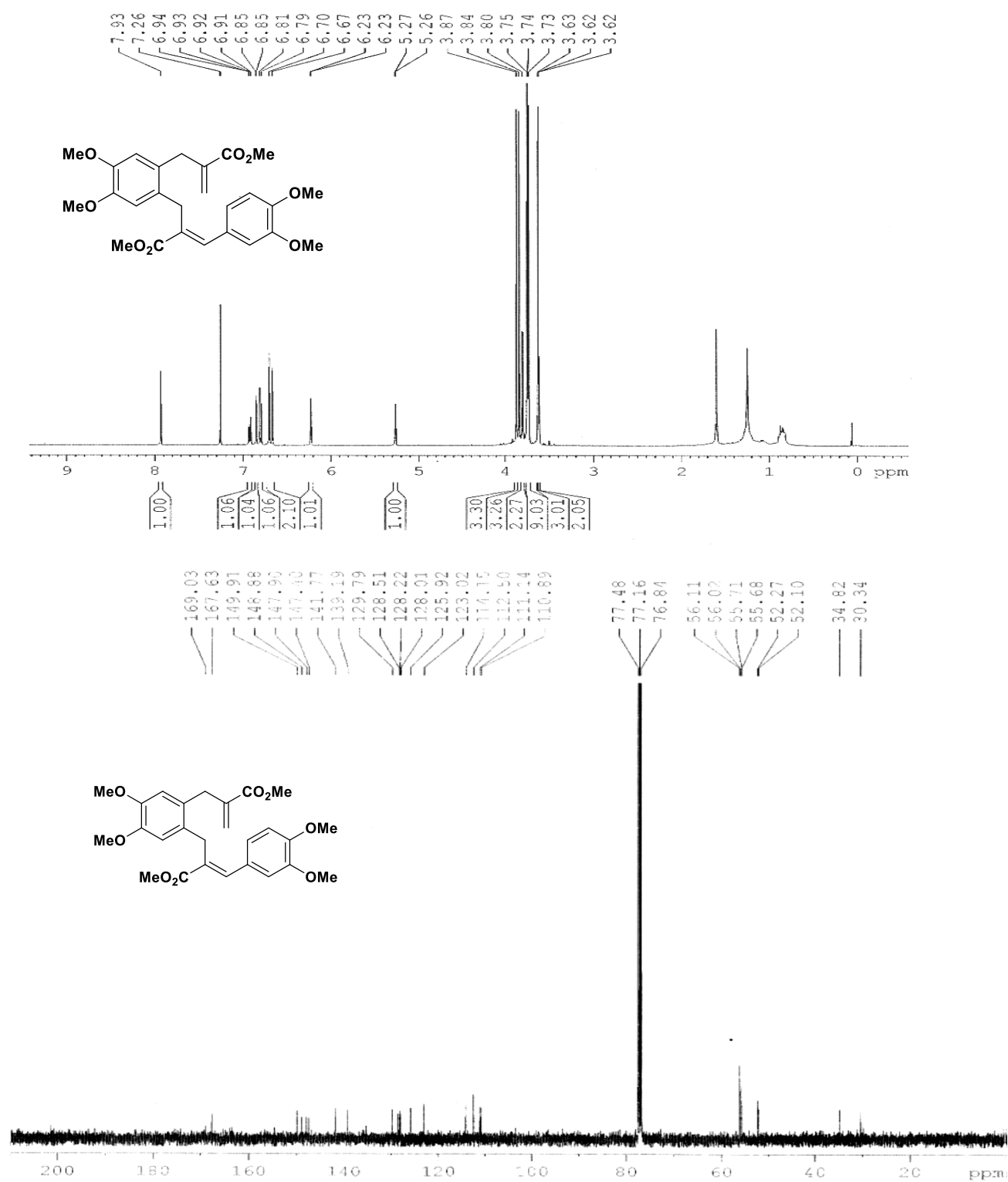
Butyl (E)-2-(2-(2-(butoxycarbonyl)allyl)benzyl)-3-phenylacrylate (2v):



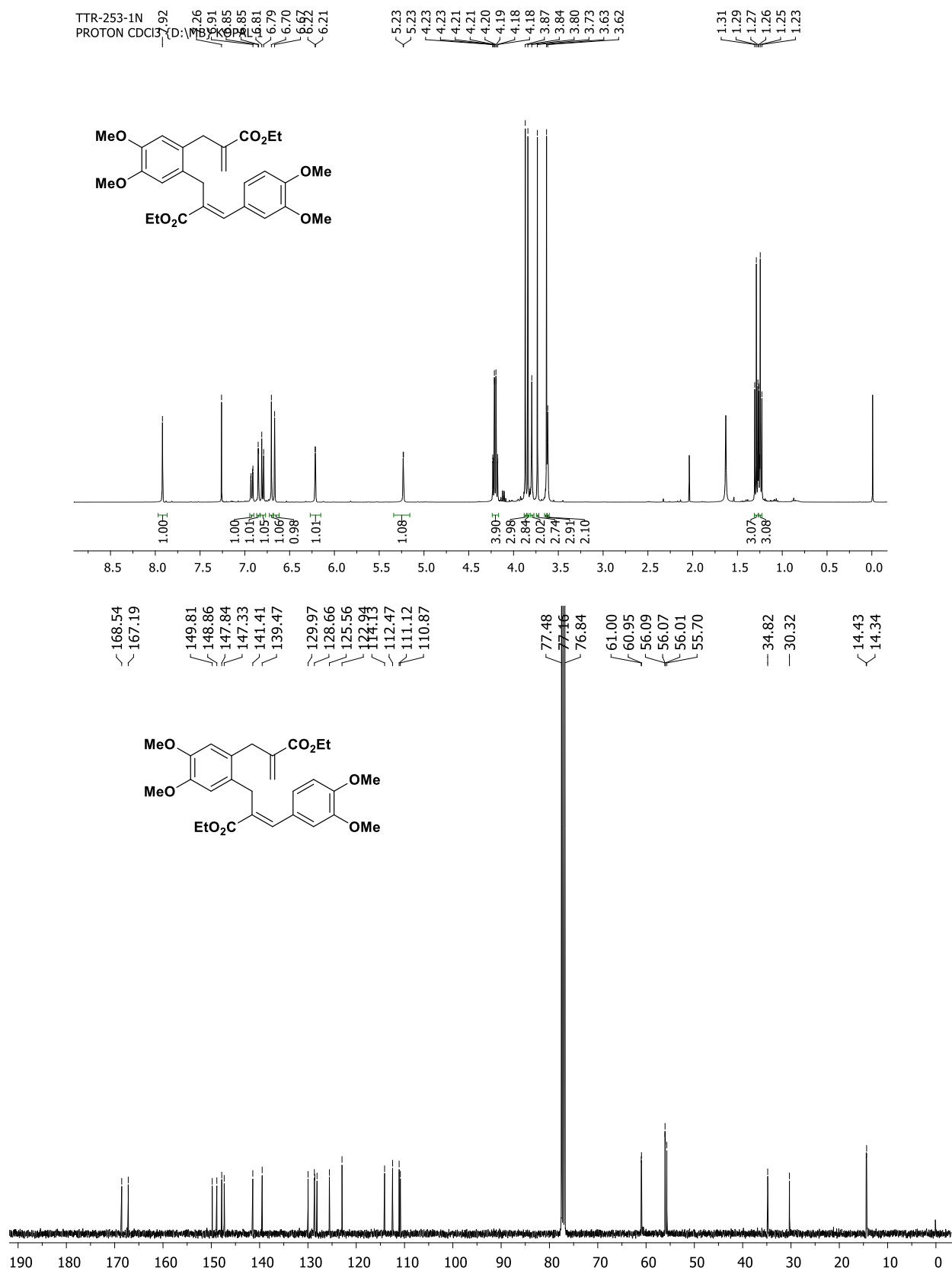
Butyl (E)-2-(2-(2-(butoxycarbonyl)allyl)-5-fluorobenzyl)-3-(4-fluorophenyl) acrylate (2w):



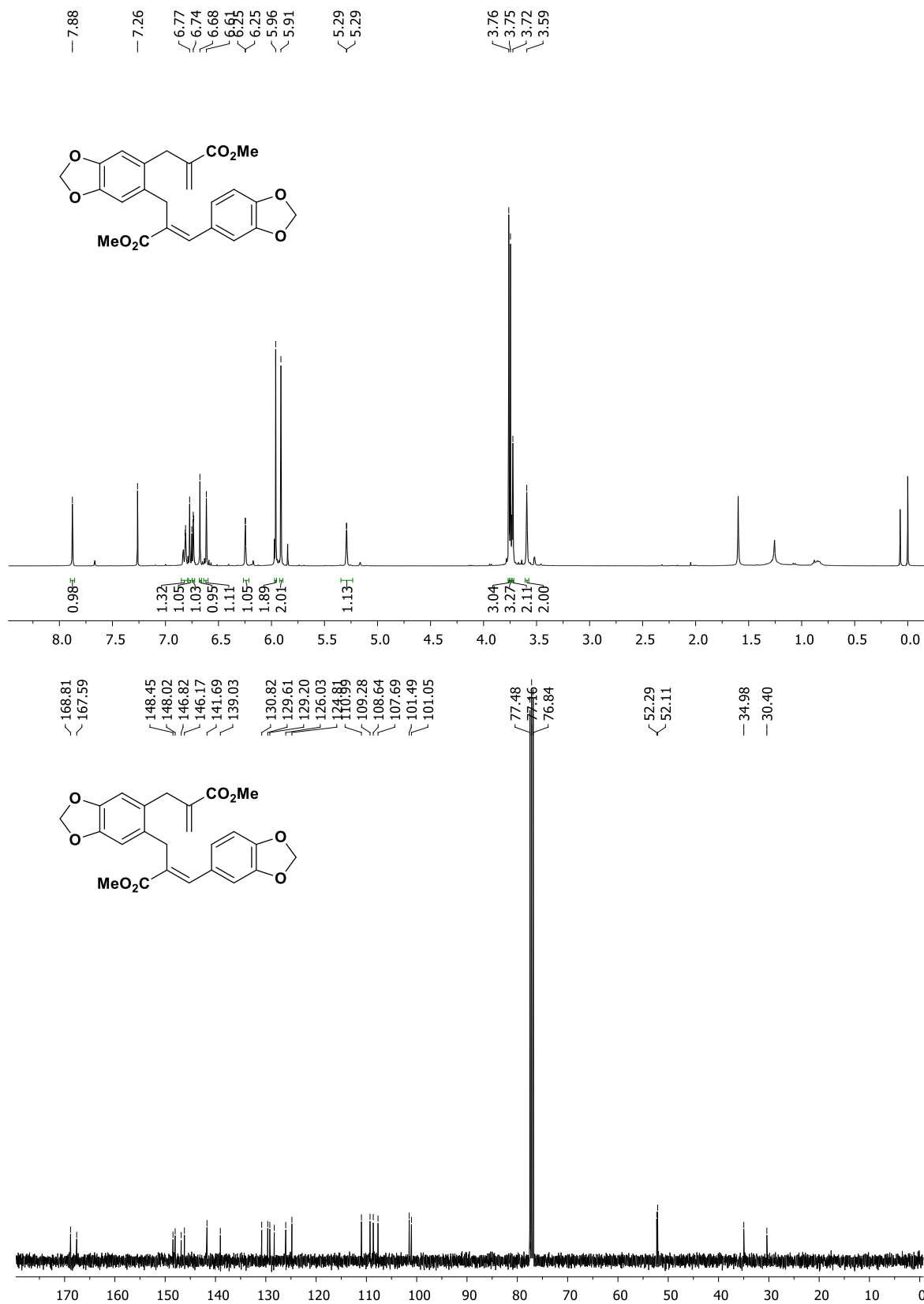
Methyl (*E*)-2-(4,5-dimethoxy-2-(2-(methoxycarbonyl)allyl)benzyl)-3-(3,4-dimethoxyphenyl)acrylate (2x):



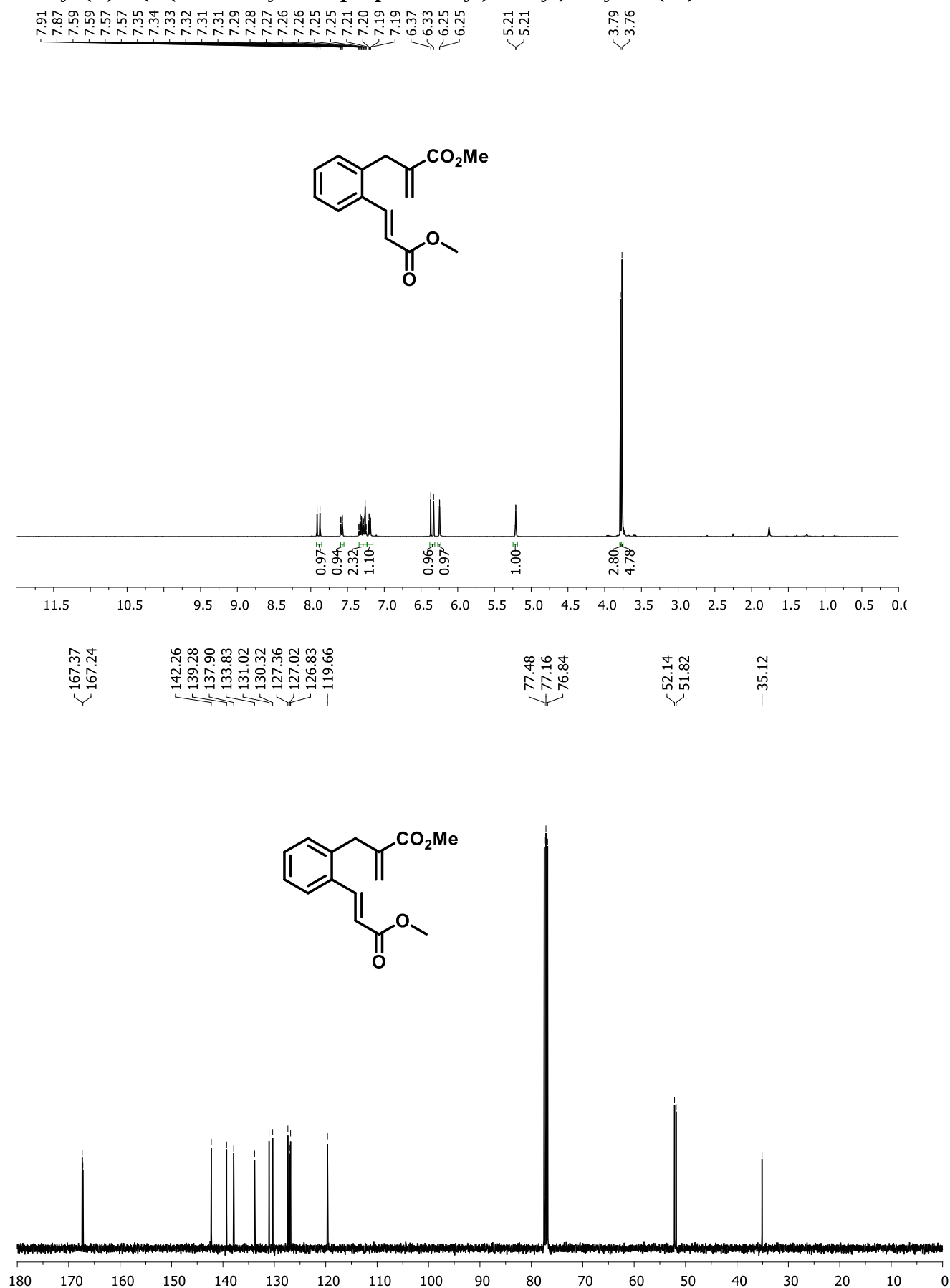
Ethyl (*E*)-3-(3,4-dimethoxyphenyl)-2-(2-(2-(ethoxycarbonyl)allyl)-4,5-dimethoxybenzyl)acrylate (2y):



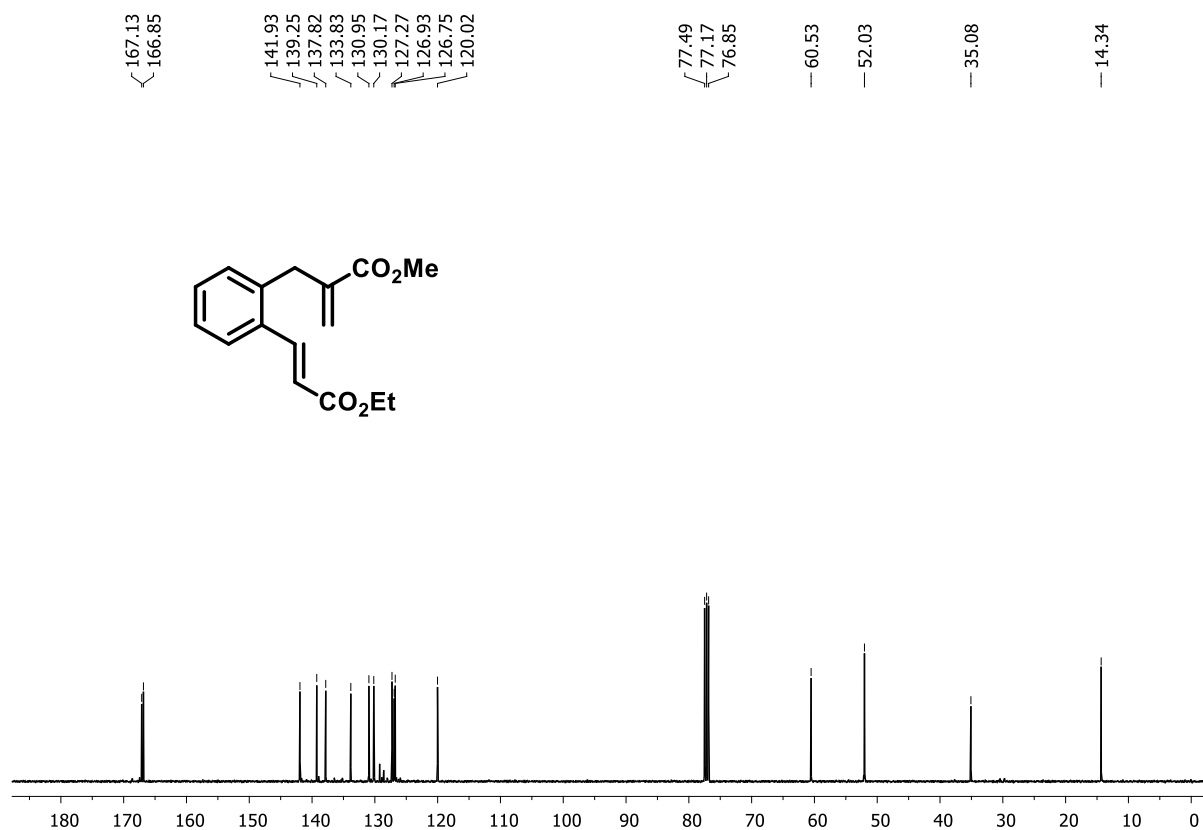
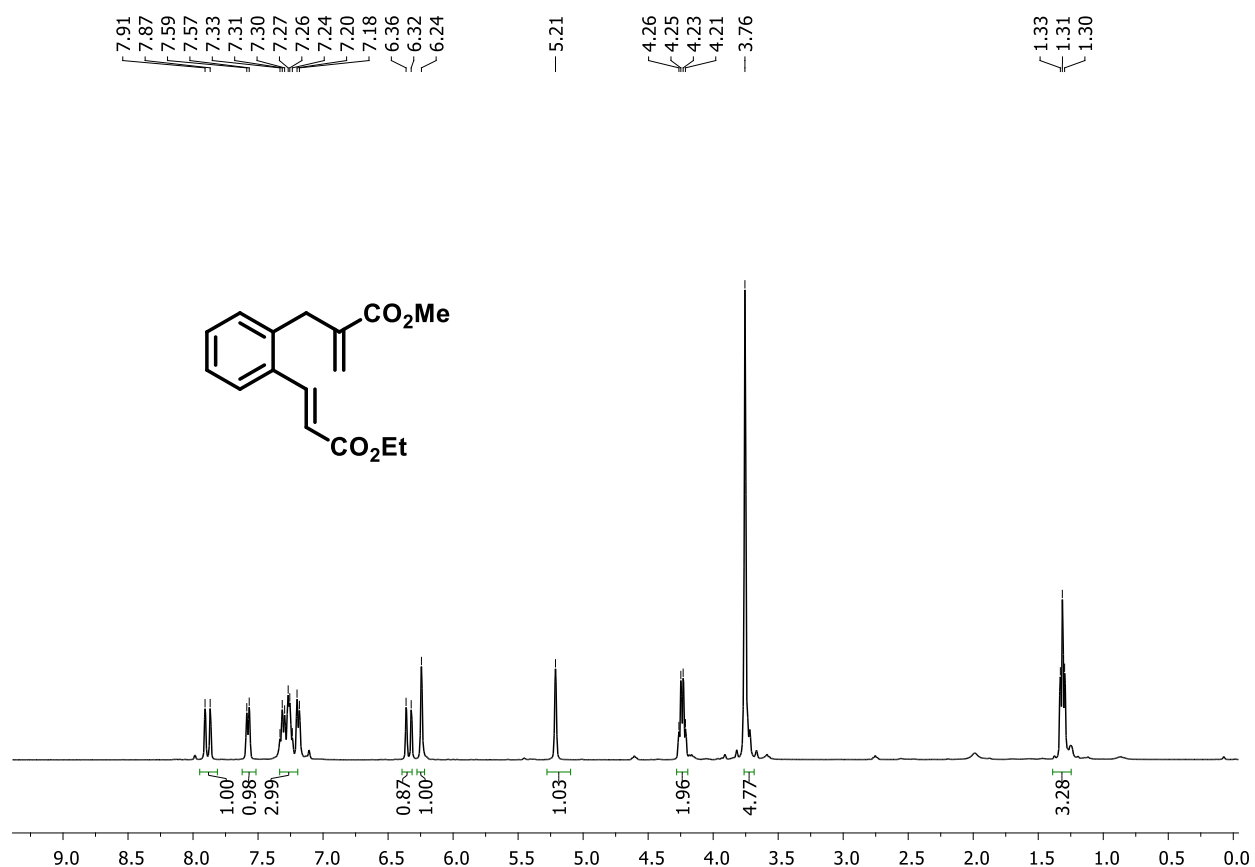
Methyl (*E*)-3-(benzo[d][1,3]dioxol-5-yl)-2-((6-(2-(methoxycarbonyl) allyl)benzo[d][1,3]dioxol-5-yl)methyl) acrylate (2z):



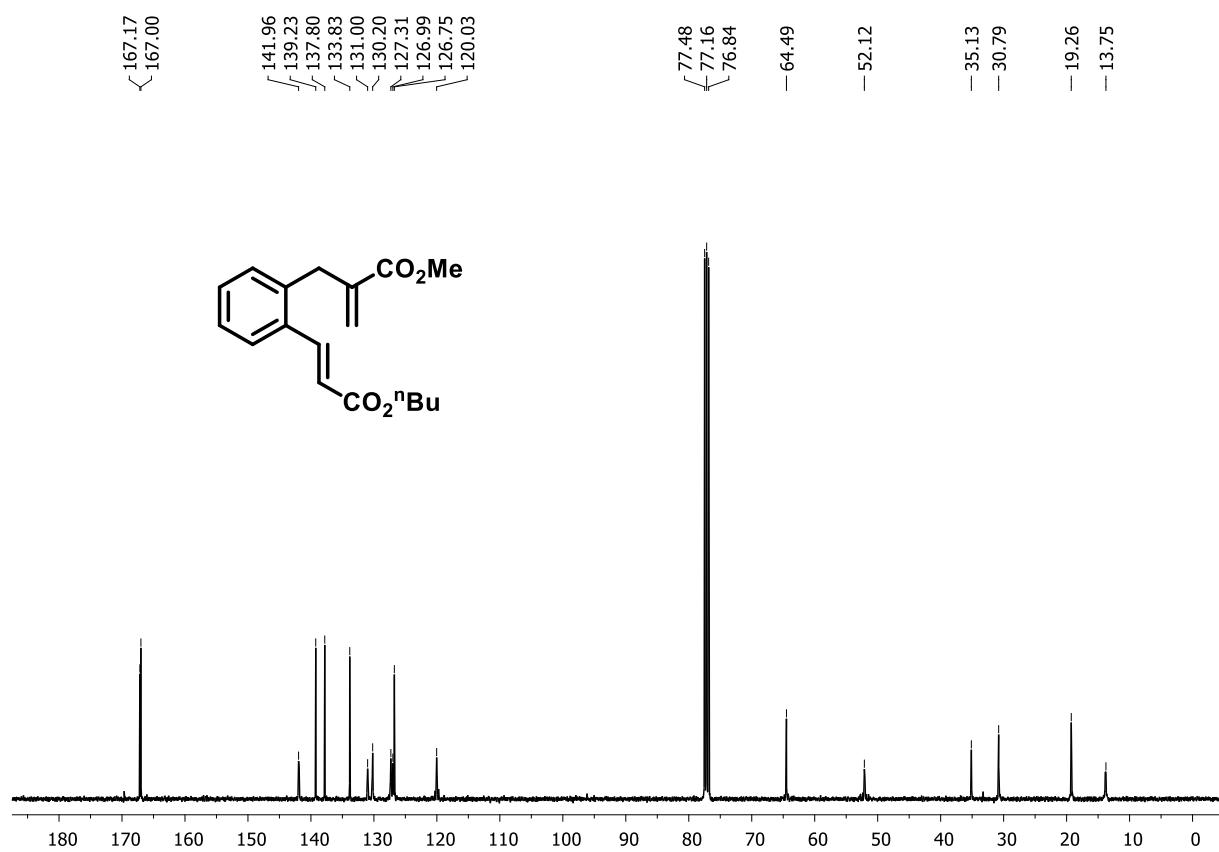
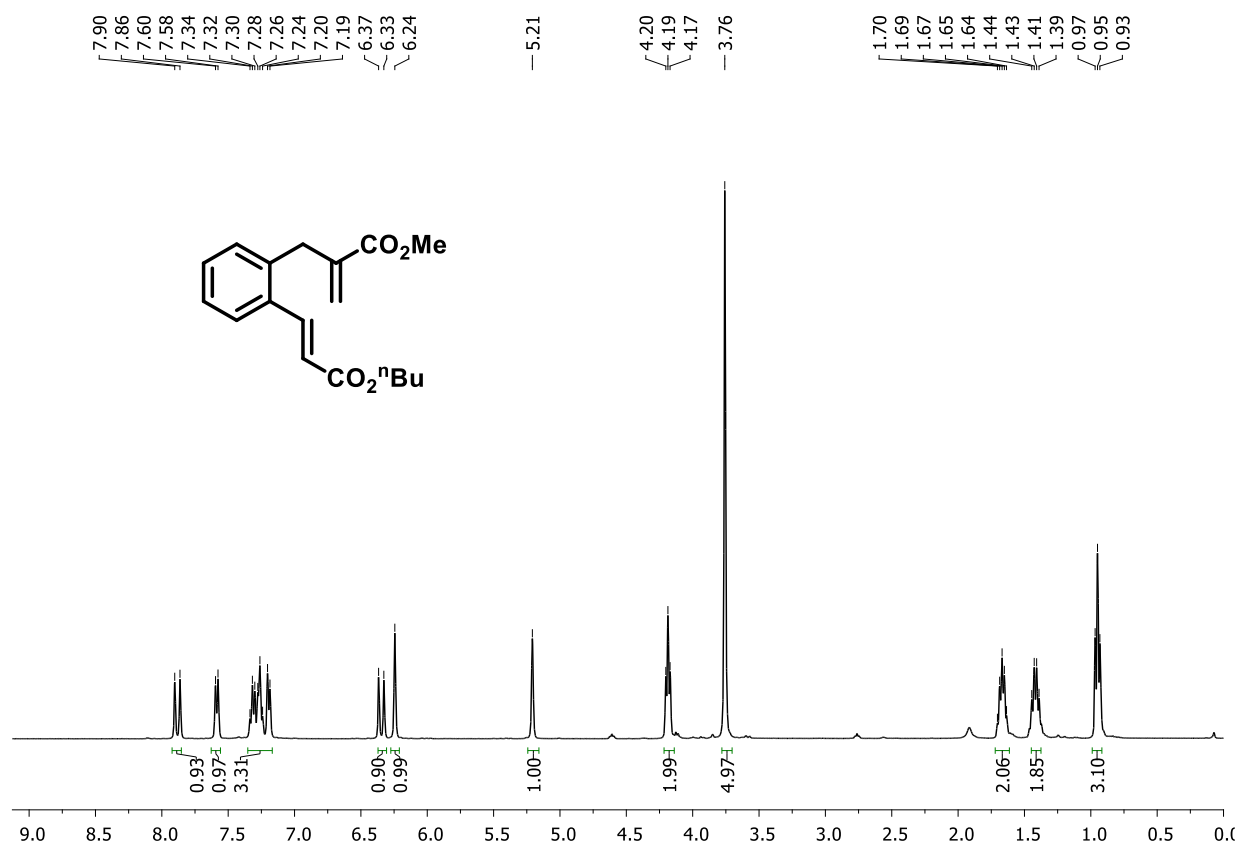
Methyl (*E*)-2-(2-(3-methoxy-3-oxoprop-1-en-1-yl) benzyl) acrylate (4a):



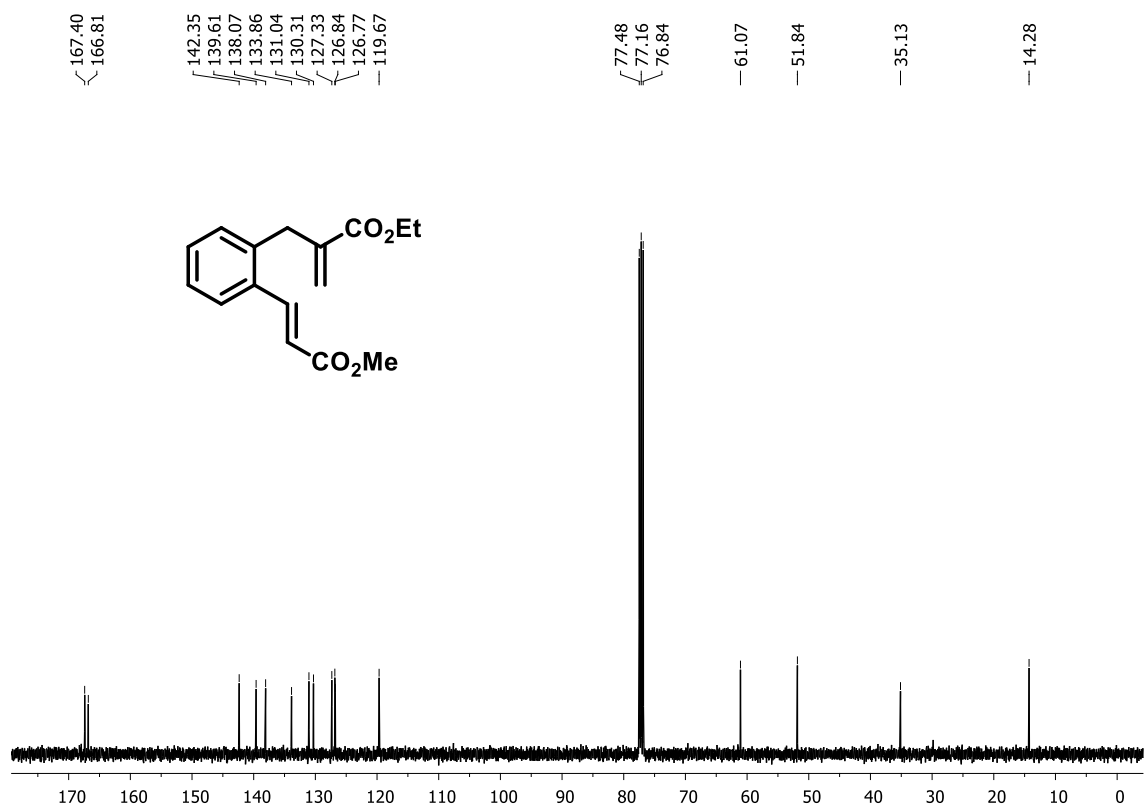
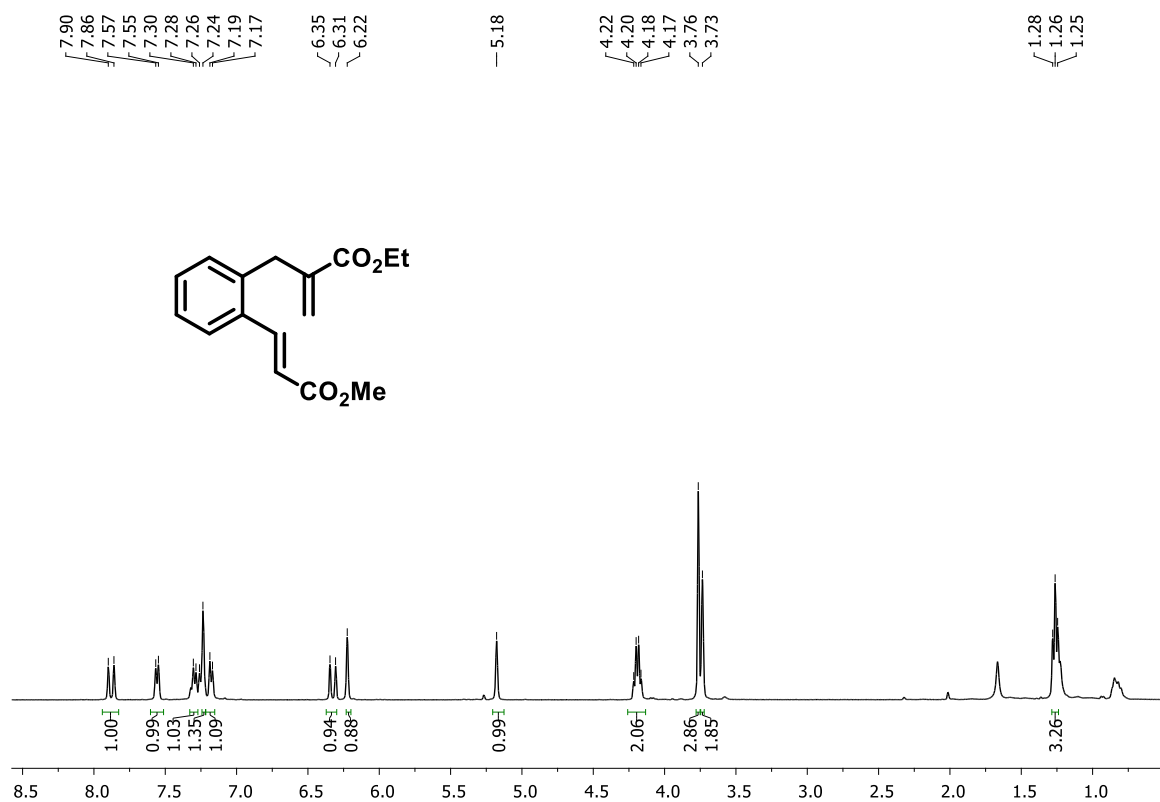
Ethyl (*E*)-3-(2-(2-(methoxycarbonyl)allyl)phenyl) acrylate (4b):



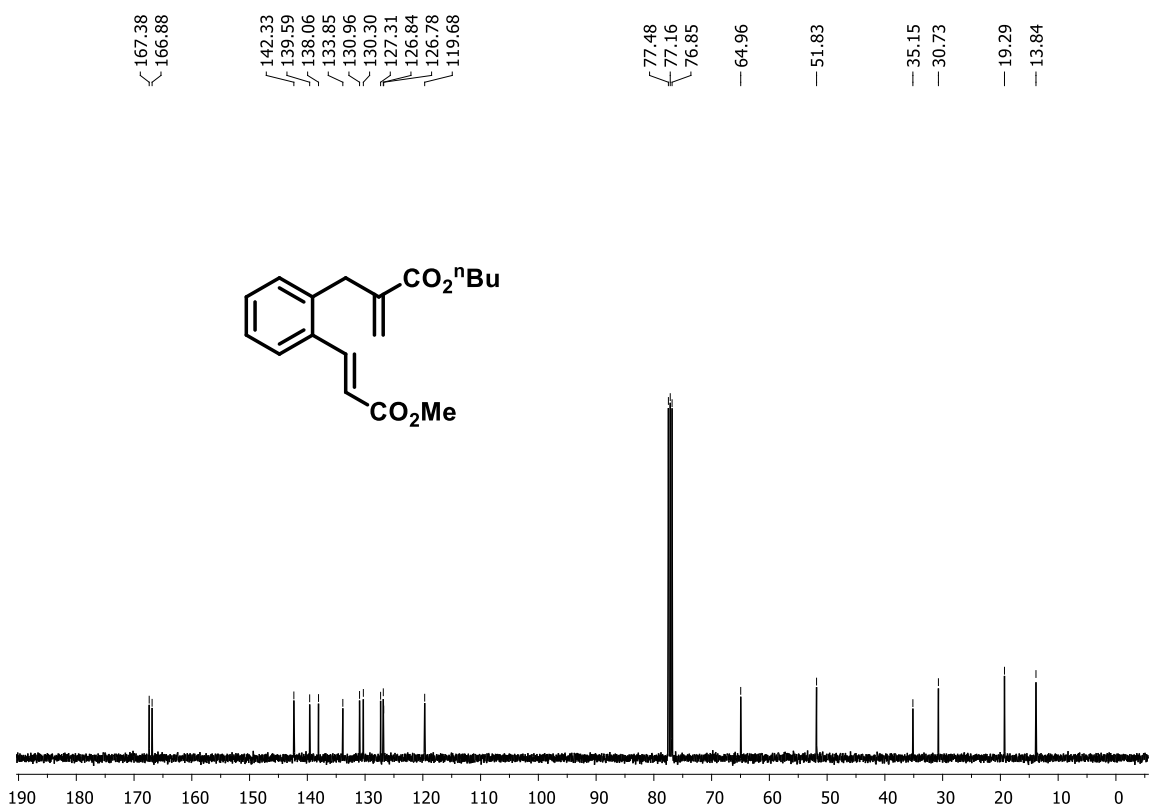
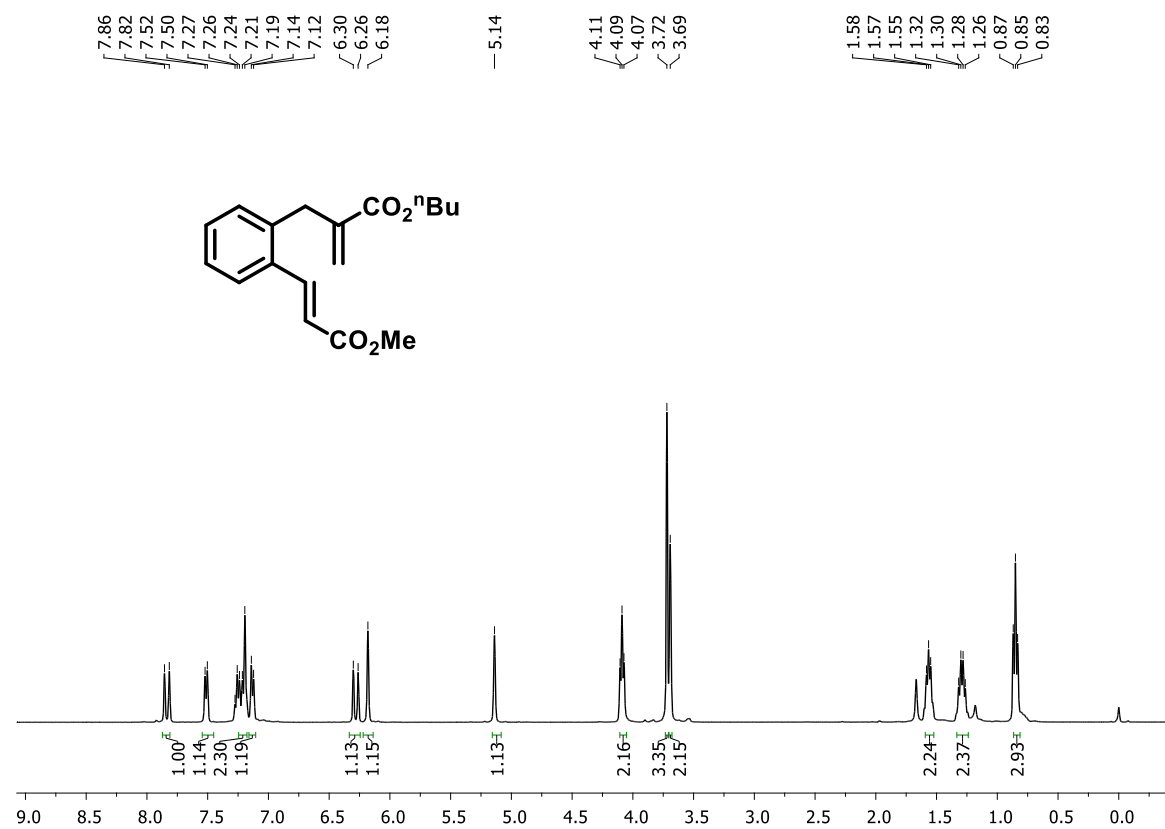
Butyl (E)-3-(2-(2-(methoxycarbonyl)allyl)phenyl) acrylate (4c):



Ethyl (*E*)-2-(2-(3-methoxy-3-oxoprop-1-en-1-yl)benzyl) acrylate (4d):



Butyl (E)-2-(2-(3-methoxy-3-oxoprop-1-en-1-yl)benzyl) acrylate (4e):



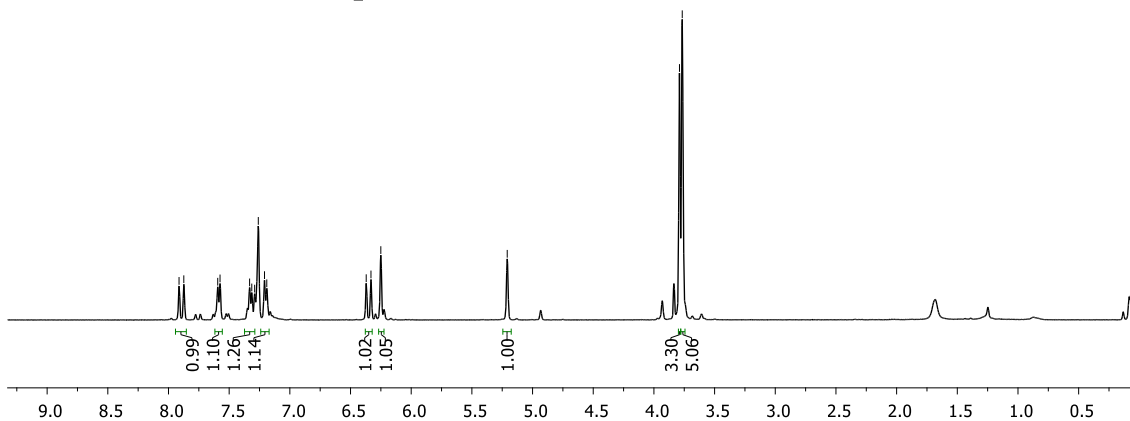
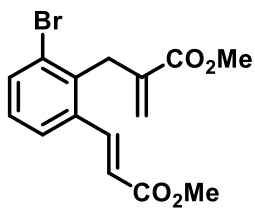
Methyl (*E*)-3-(3-bromo-2-(2-(methoxycarbonyl)allyl)phenyl) acrylate (4f):

TTR-S-233
PROTON

7.91
7.87
7.59
7.58
7.33
7.31
7.29
7.26
7.21
7.19
6.37
6.33
6.25

— 5.21

3.79
3.77



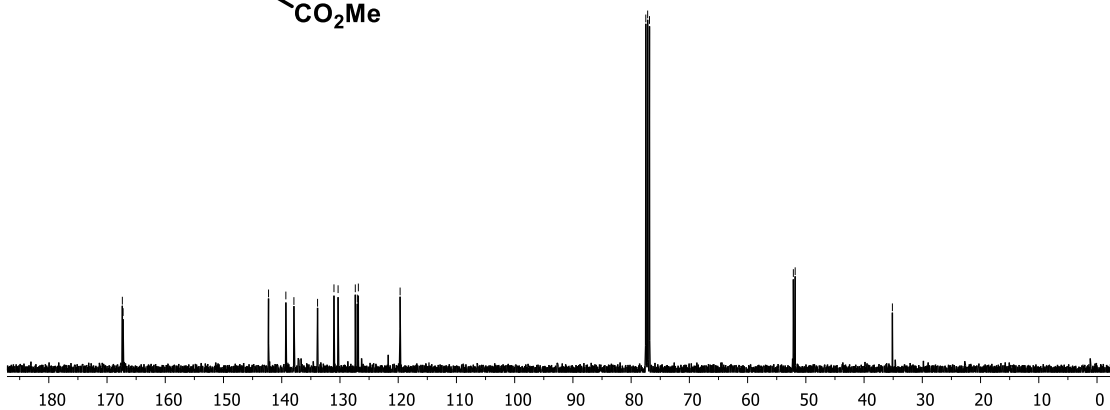
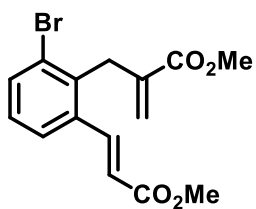
167.37
167.24

142.27
139.29
137.91
133.85
131.03
130.32
127.37
127.02
126.84
119.67

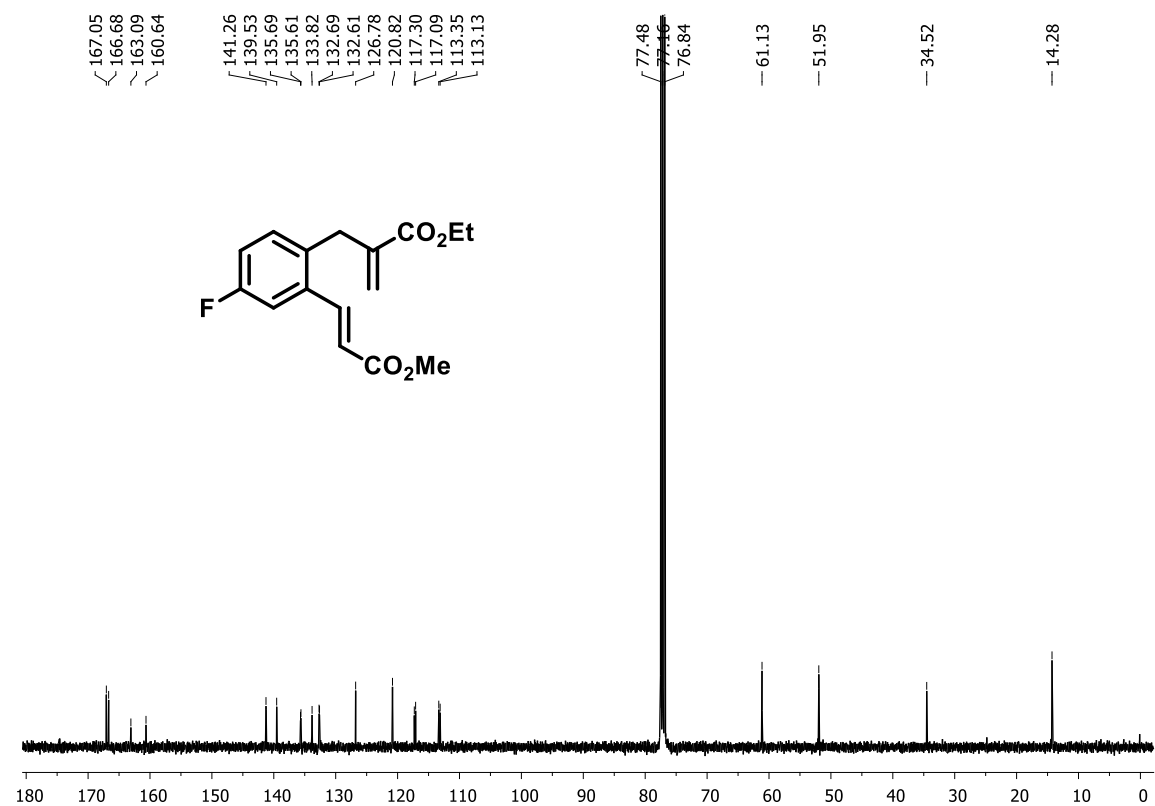
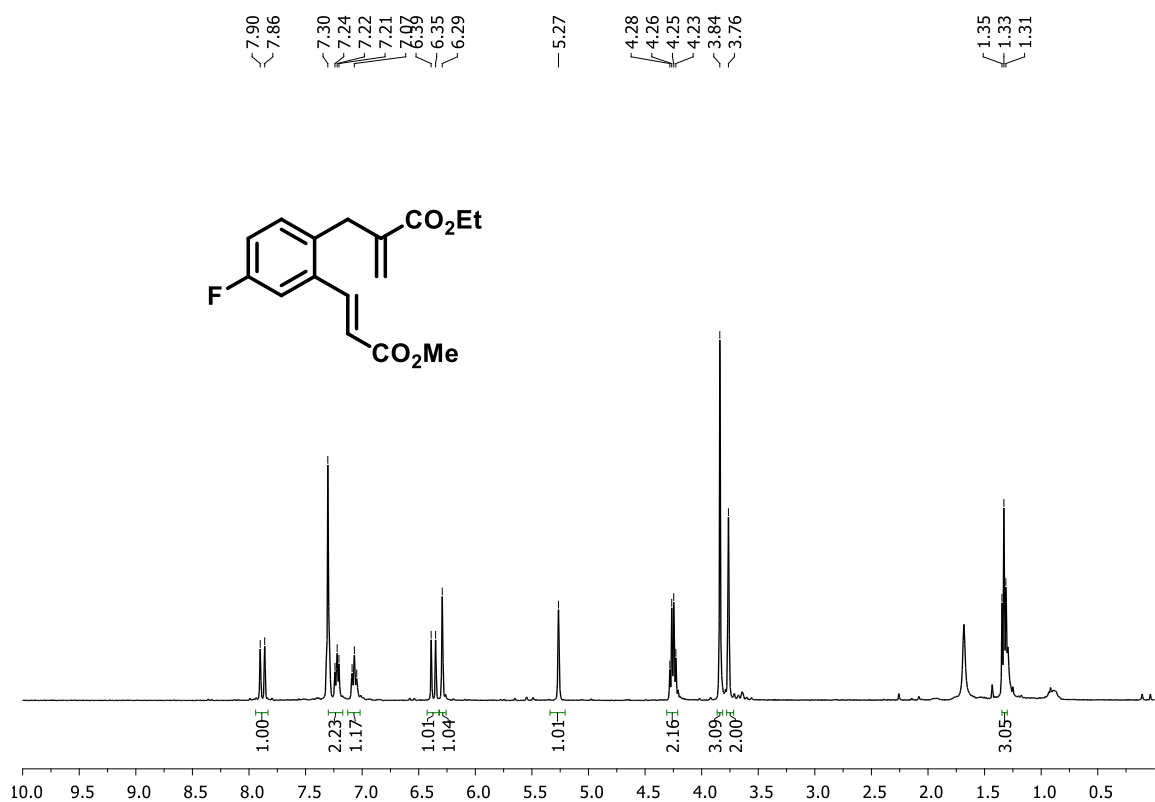
77.48
77.16
76.85

52.15
51.83

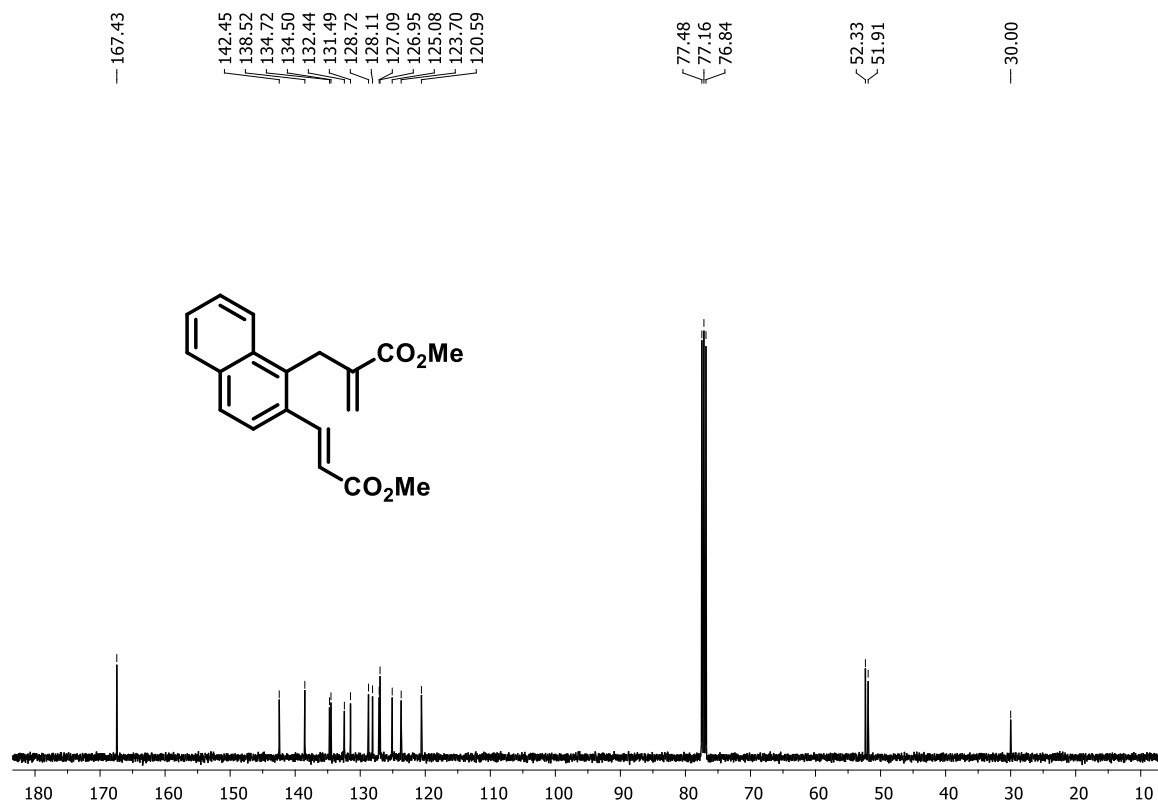
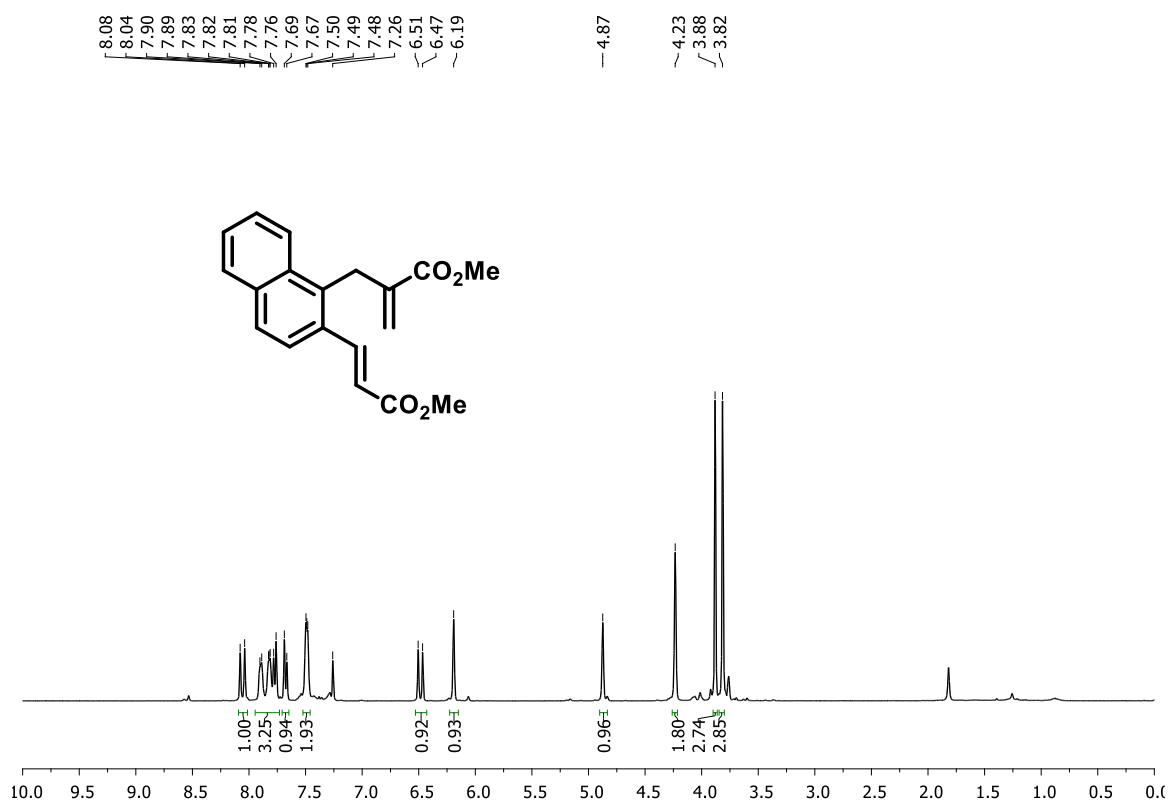
— 35.14



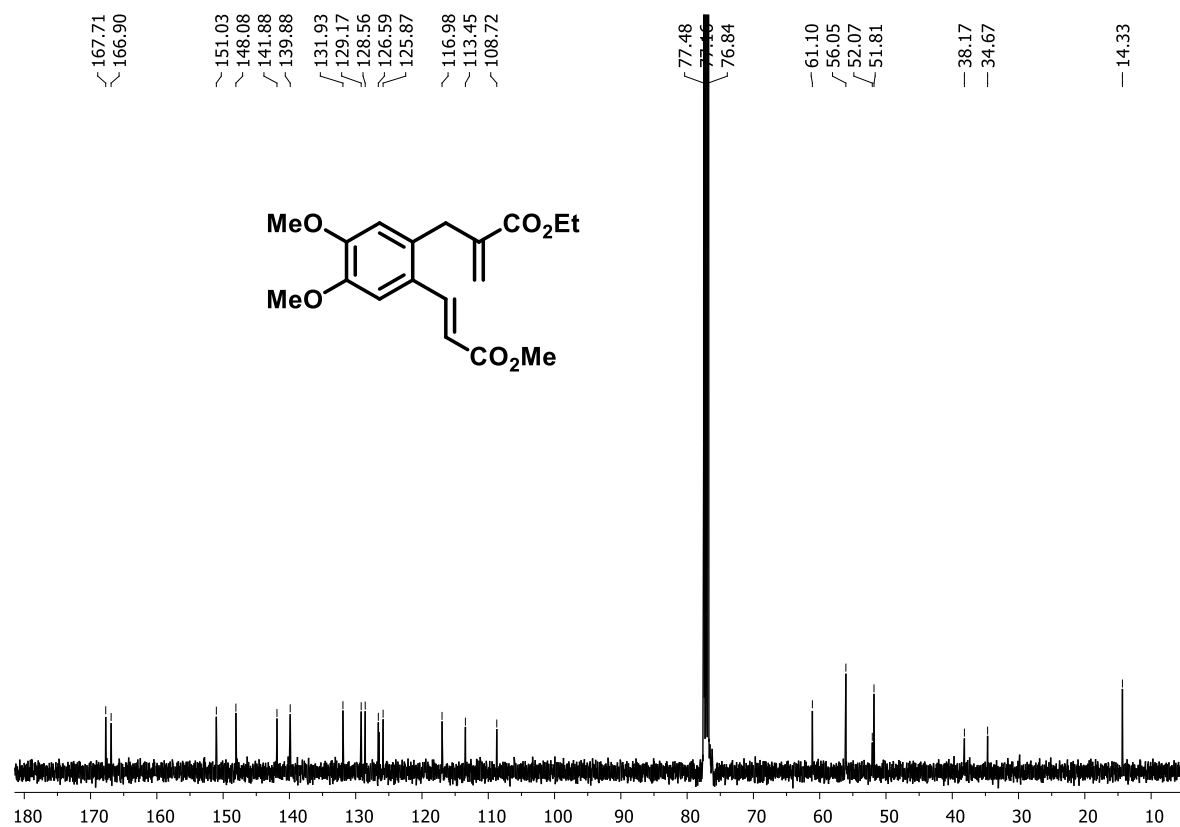
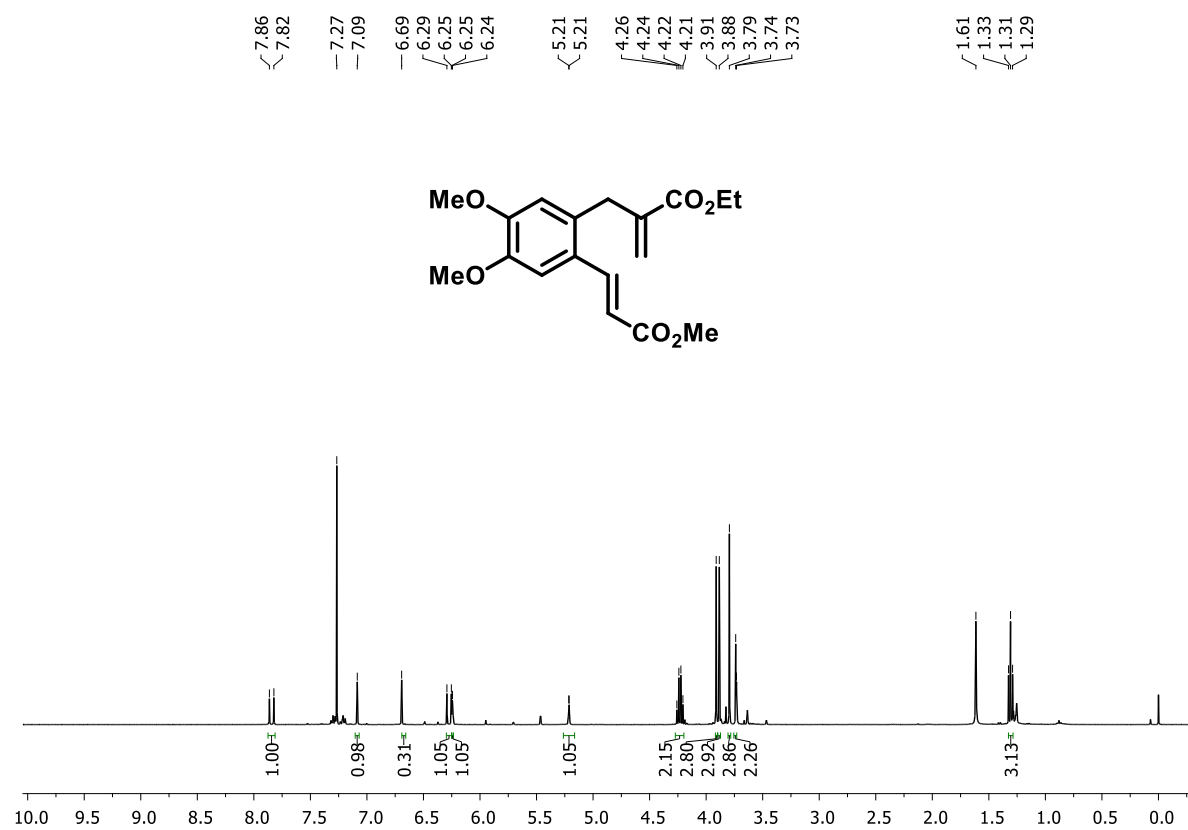
Ethyl (E)-2-(4-fluoro-2-(3-methoxy-3-oxoprop-1-en-1-yl)benzyl) acrylate (4g):



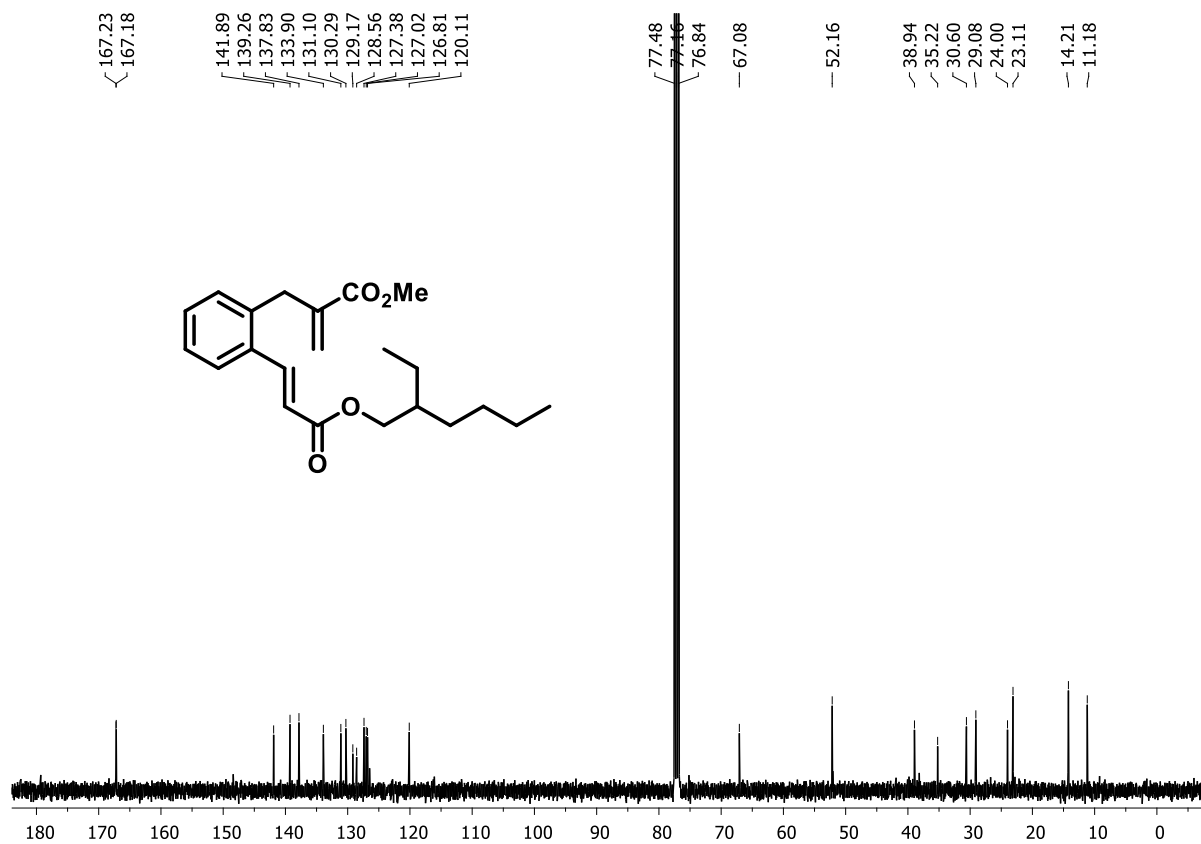
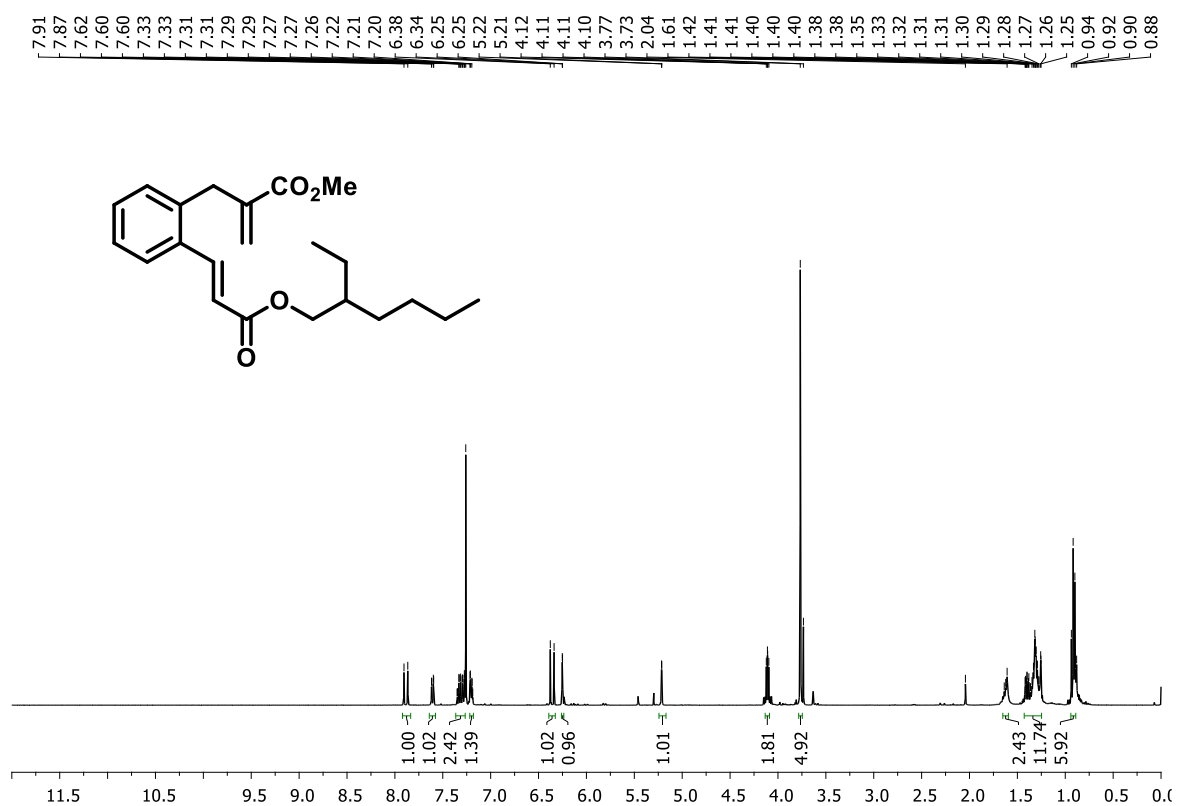
Methyl (*E*)-2-((2-(3-methoxy-3-oxoprop-1-en-1-yl)naphthalen-1-yl)methyl) acrylate (4h**):**



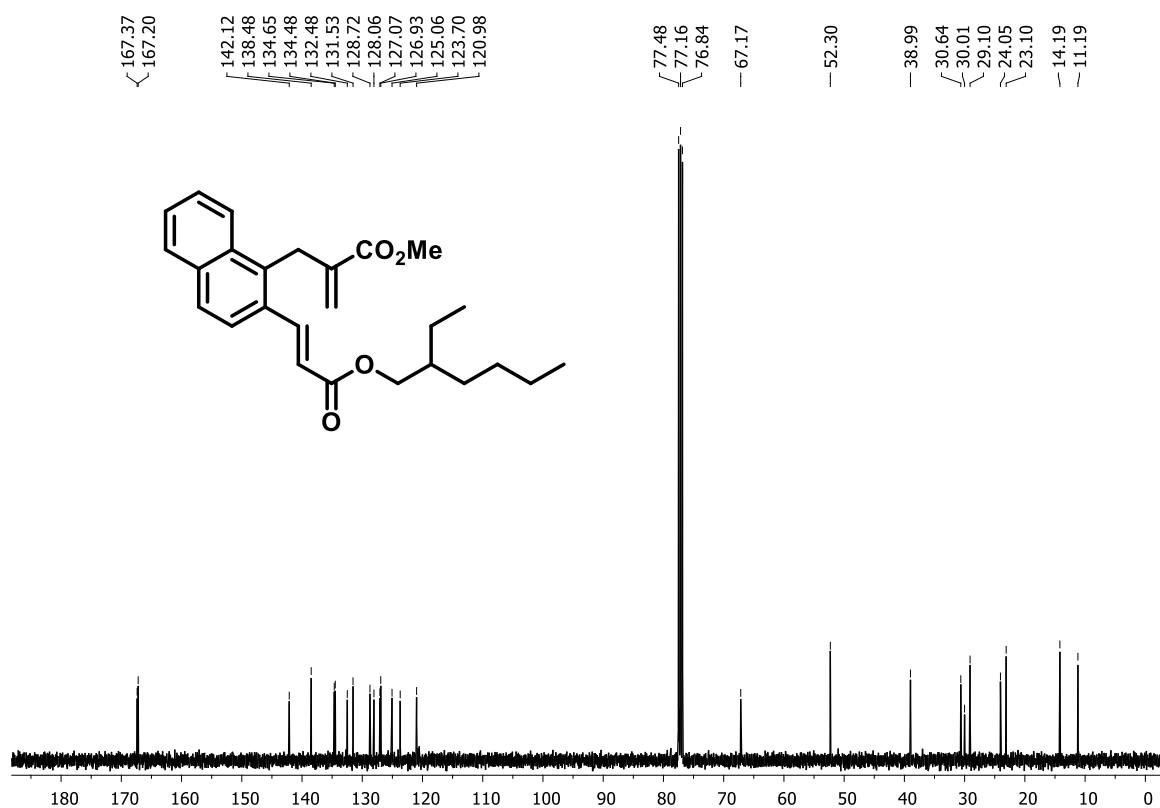
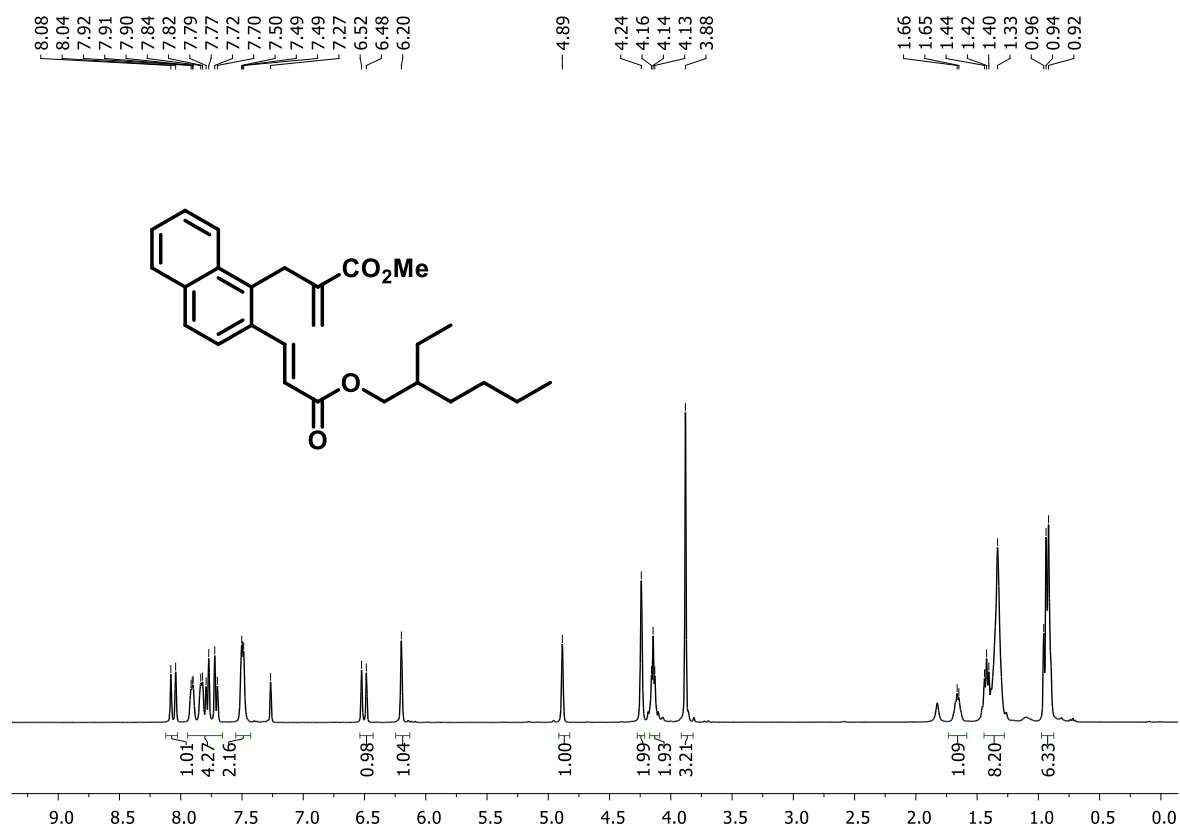
Ethyl (E)-2-(4,5-dimethoxy-2-(3-methoxy-3-oxoprop-1-en-1-yl)benzyl)acrylate (4i):



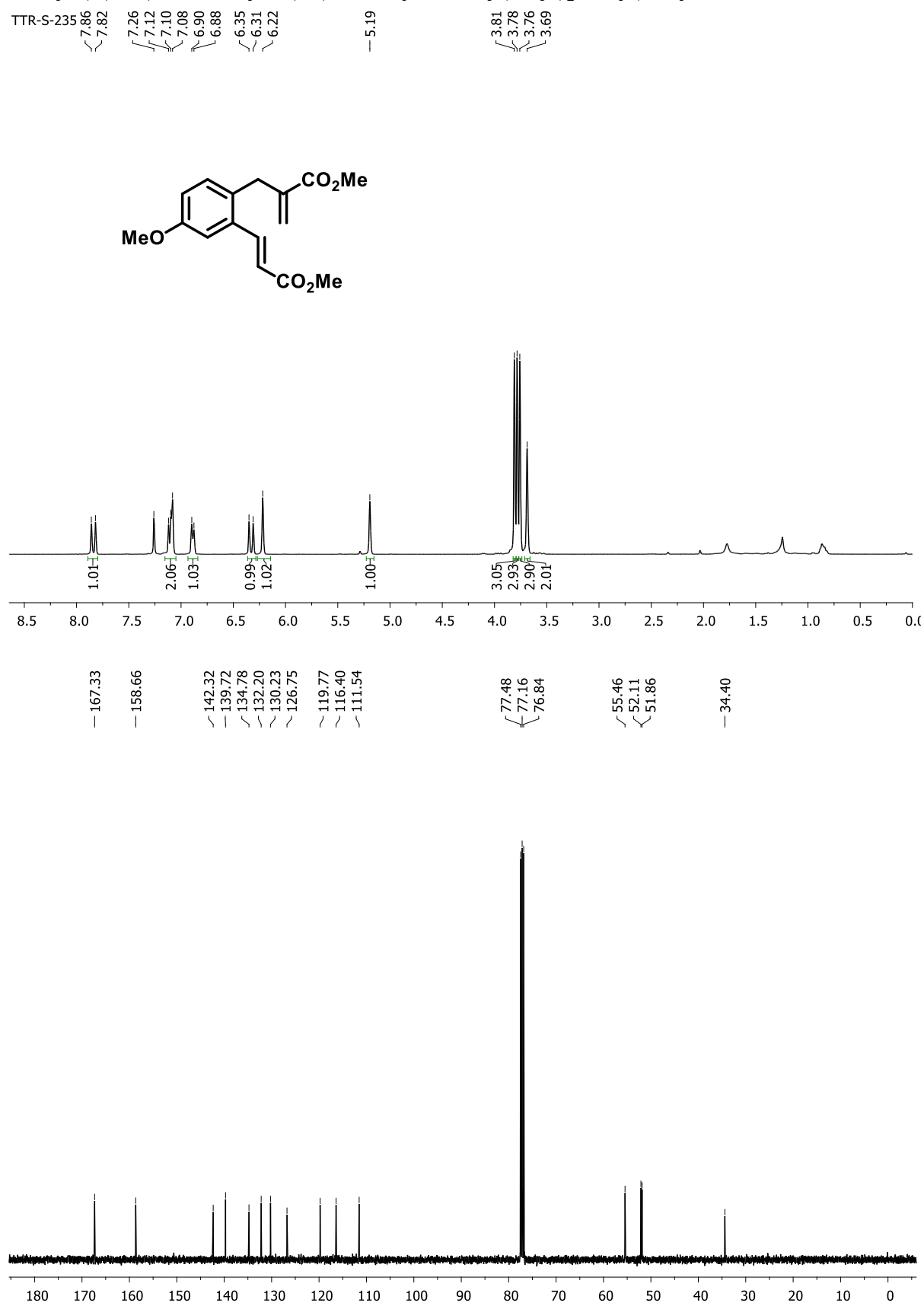
2-Ethylhexyl (*E*)-3-(2-(2-(methoxycarbonyl)allyl) phenyl) acrylate (4j):



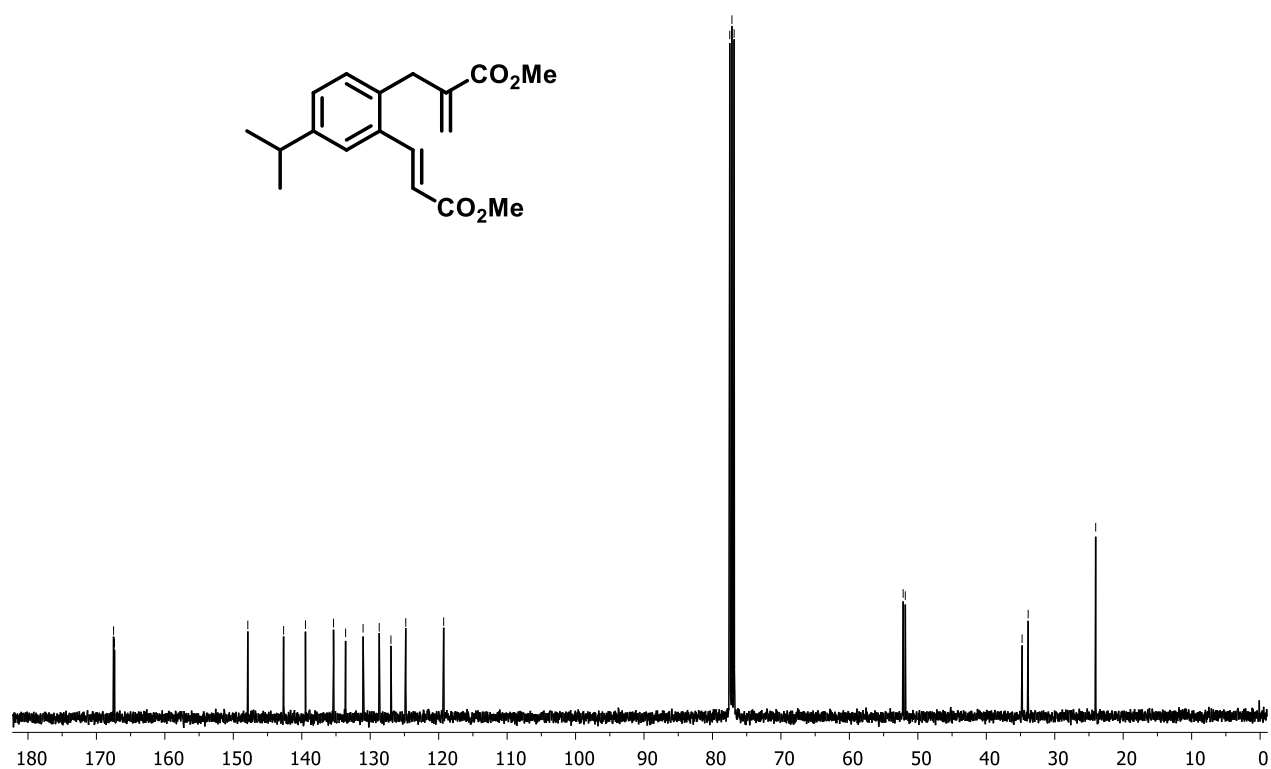
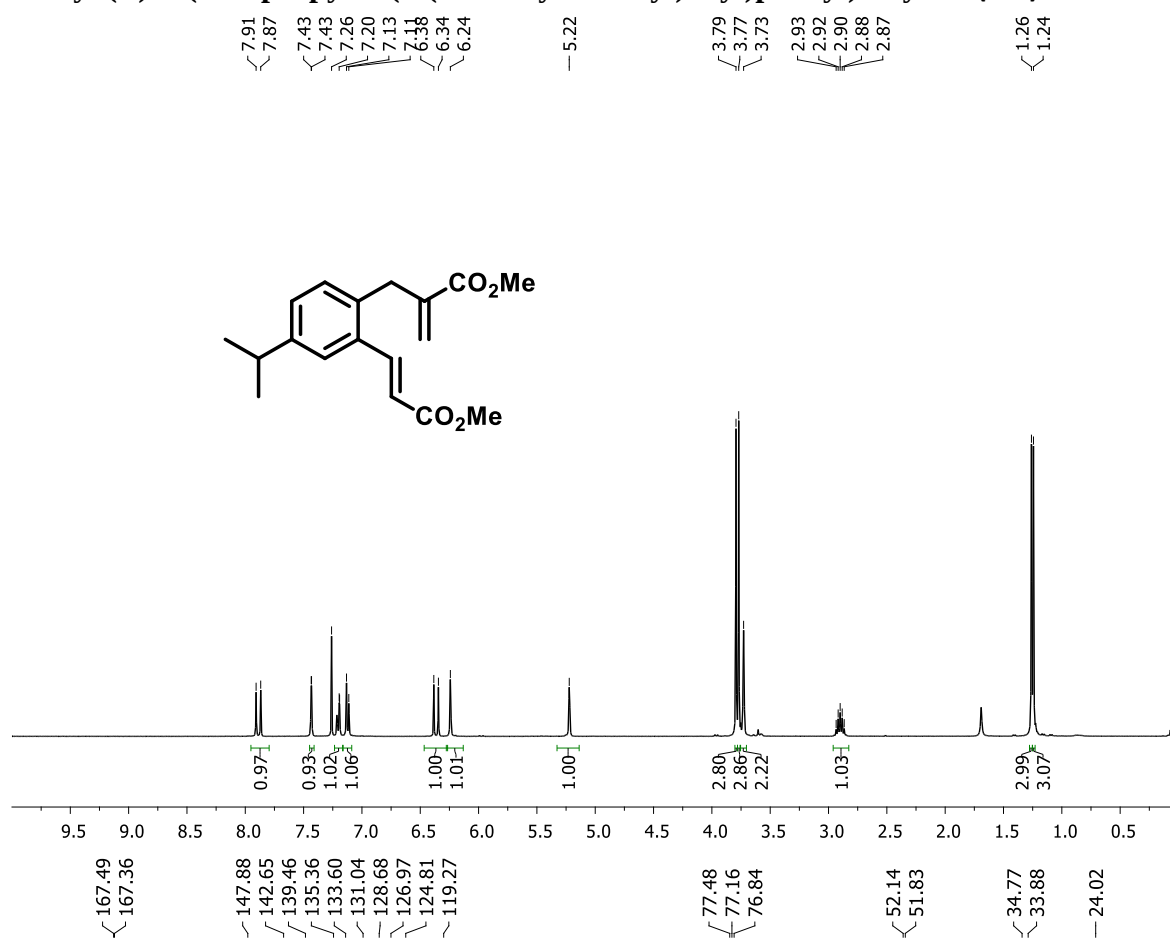
2-Ethylhexyl (*E*)-3-(1-(2-(methoxycarbonyl)allyl)naphthalen-2-yl)acrylate (4k**):**



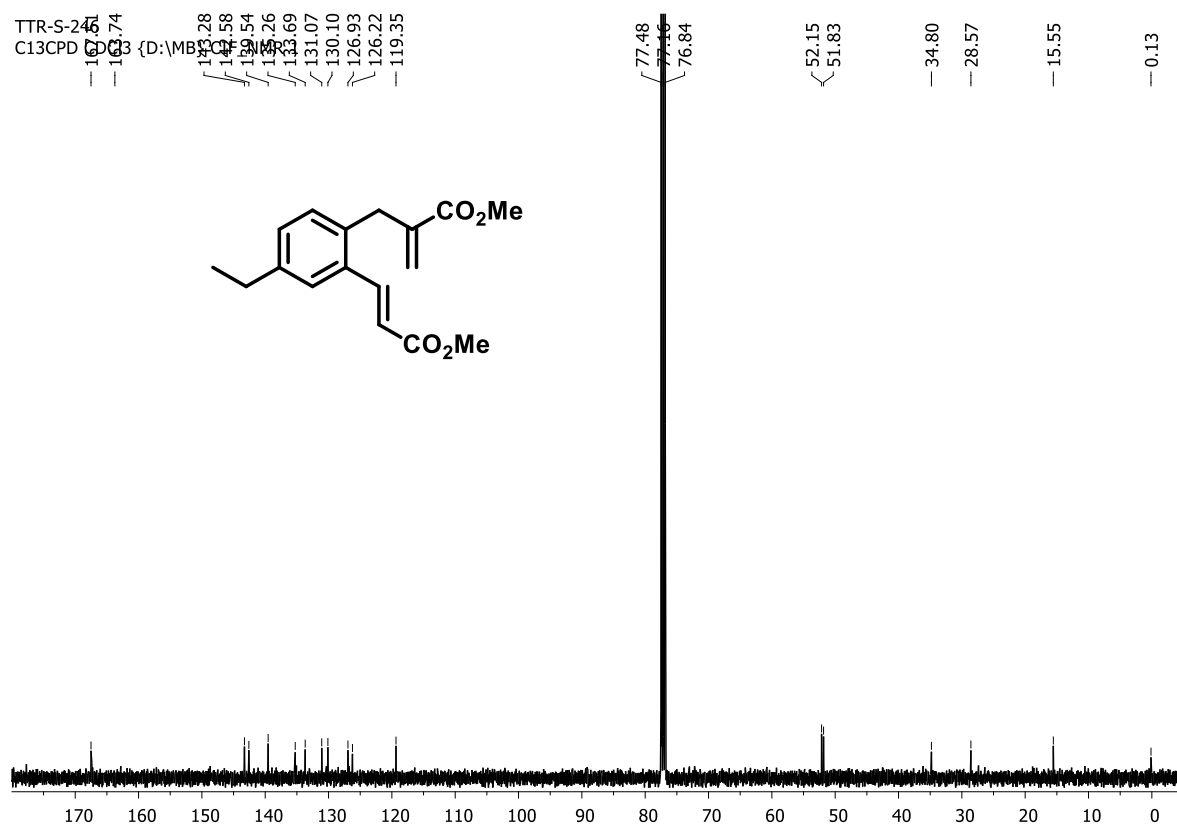
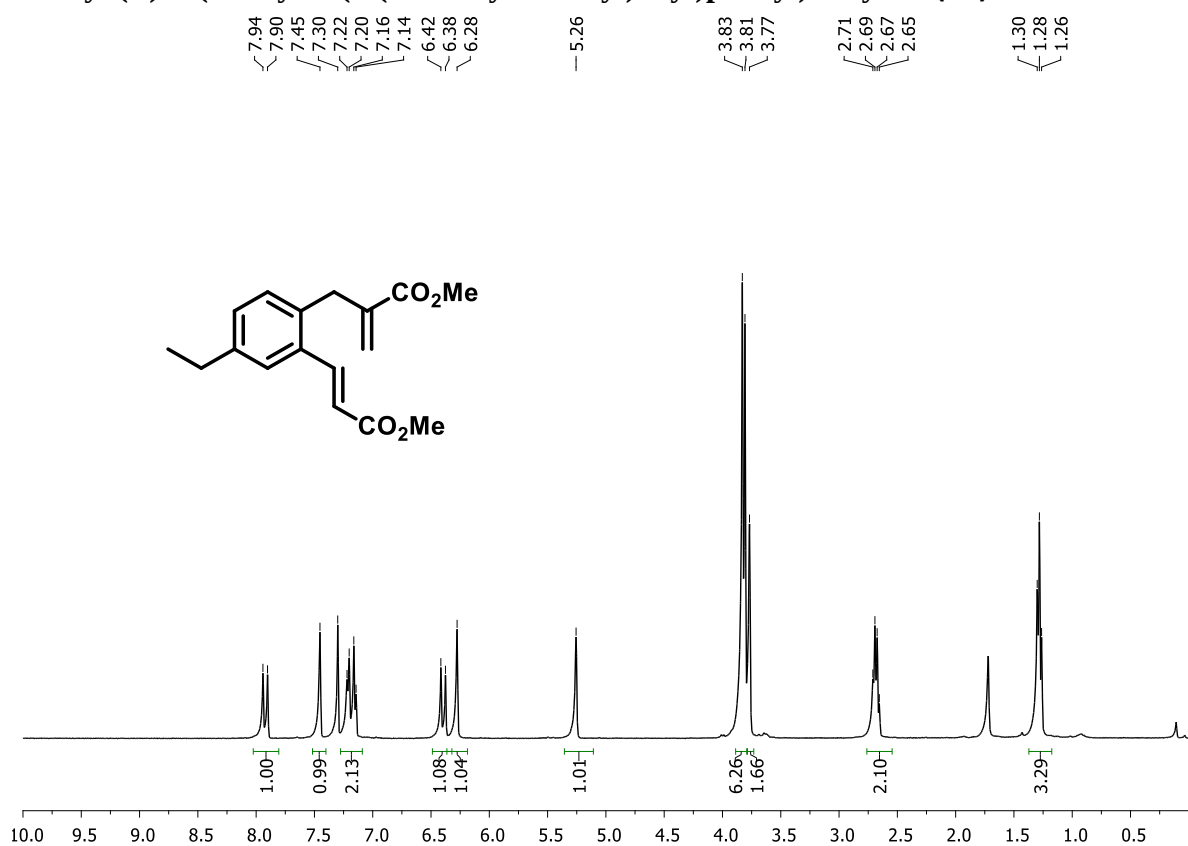
Methyl (*E*)-3-(5-methoxy-2-(2-(methoxycarbonyl)allyl)phenyl)acrylate (4l):



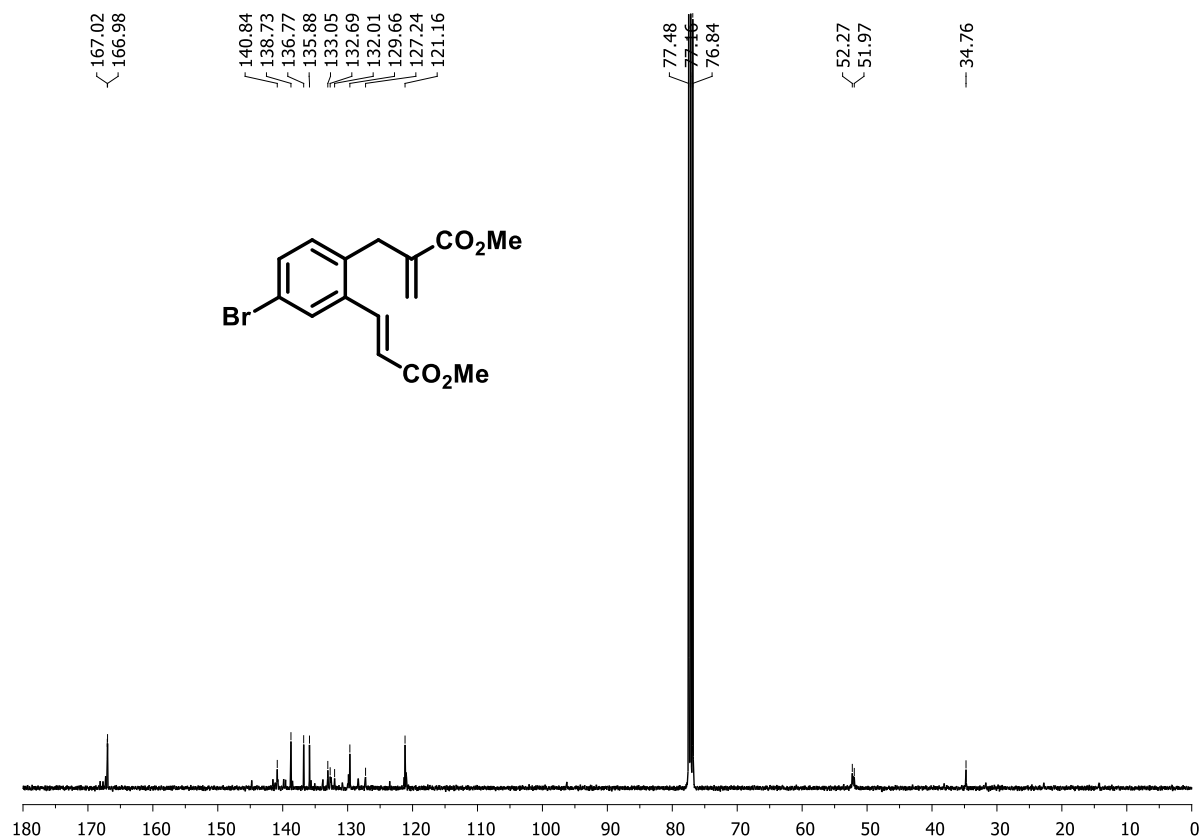
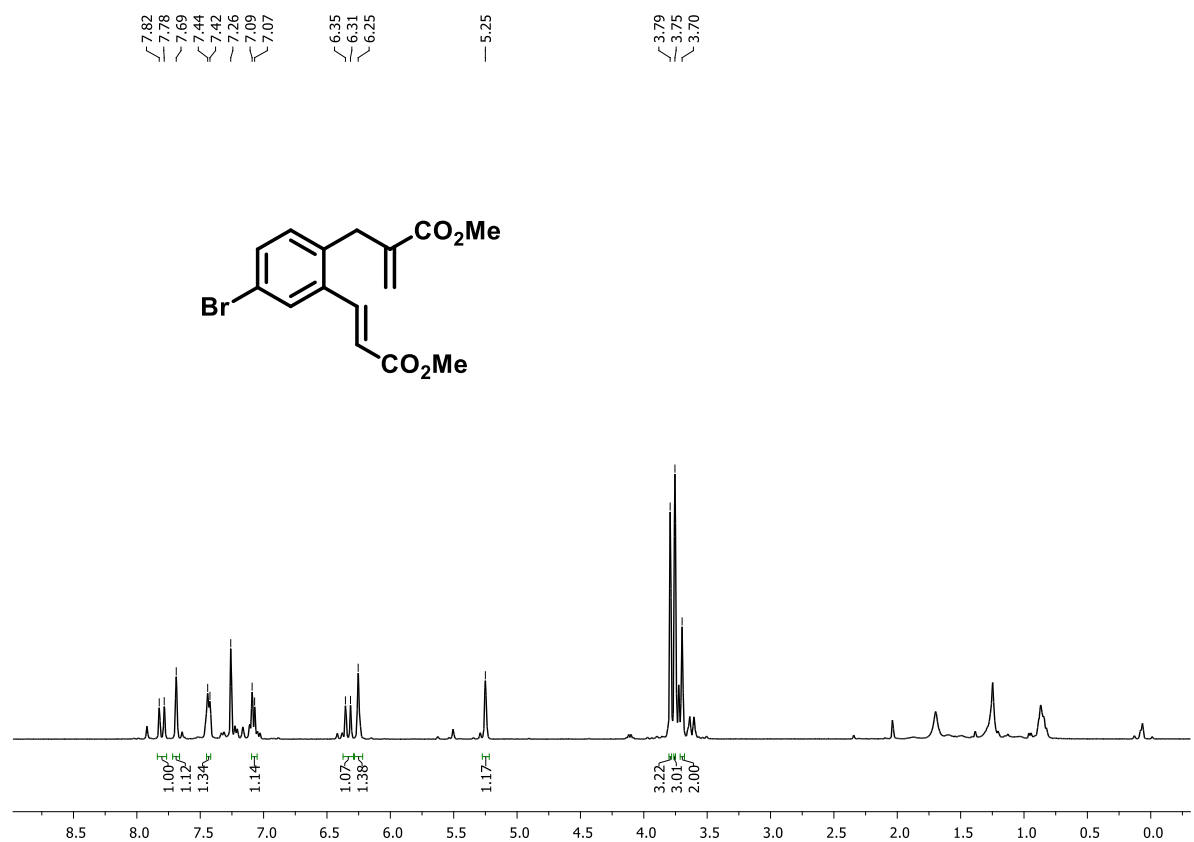
Methyl (*E*)-3-(5-isopropyl-2-(2-(methoxycarbonyl)allyl)phenyl)acrylate (4m):



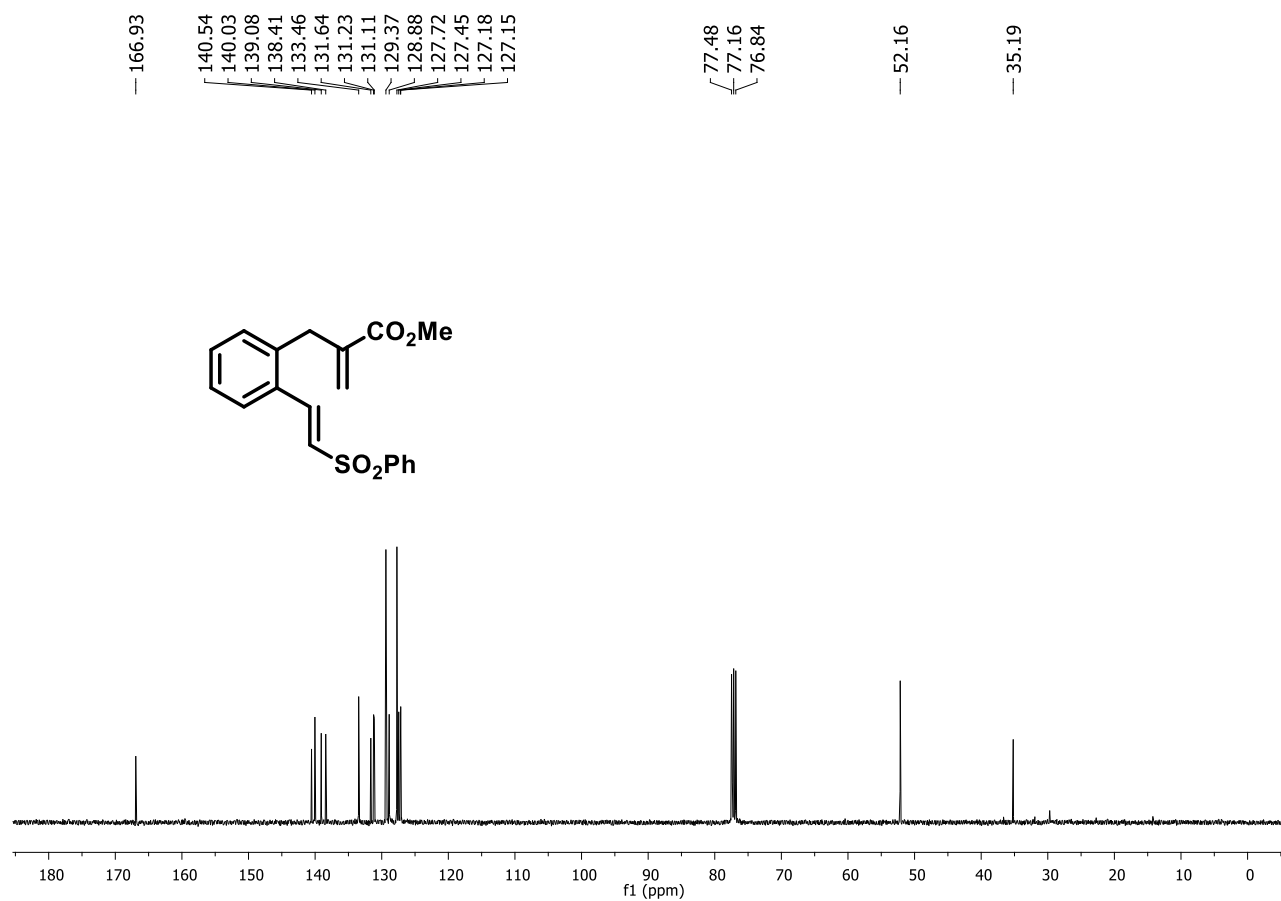
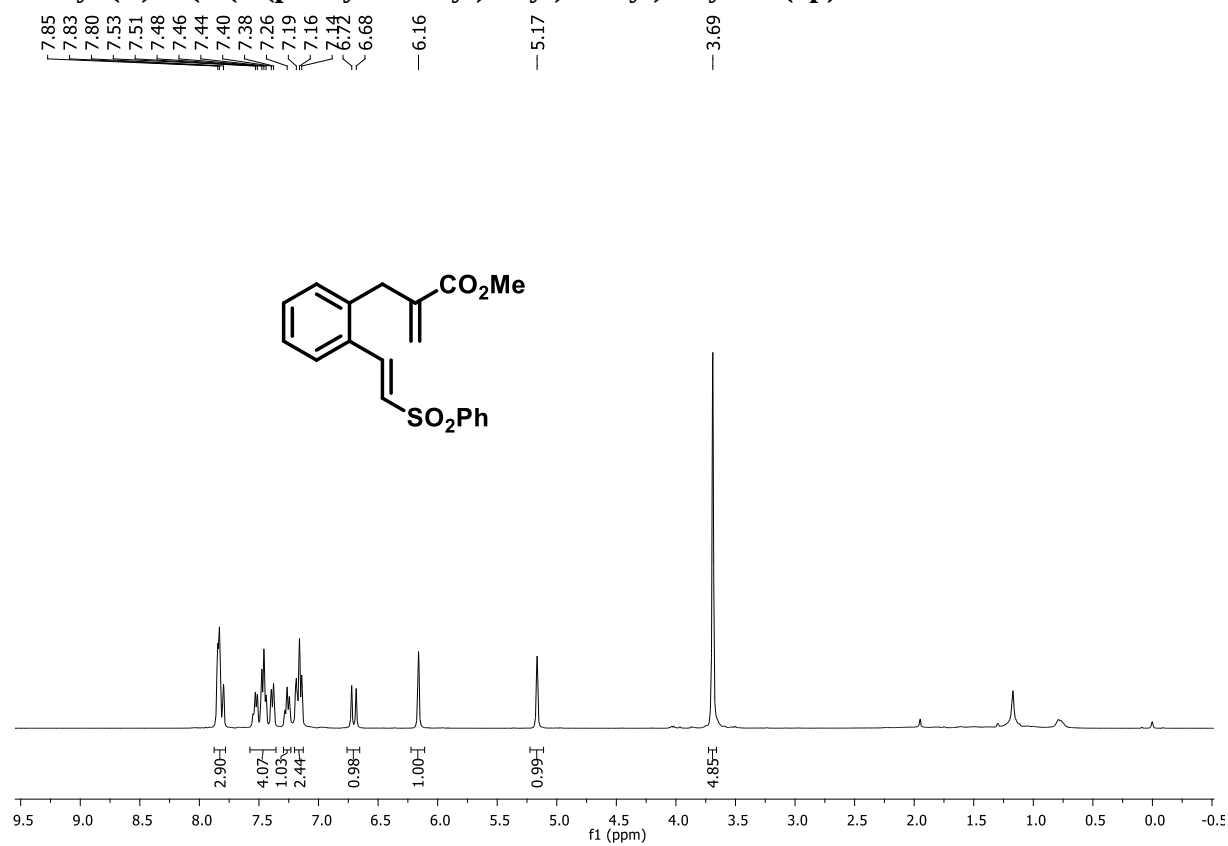
Methyl (*E*)-3-(5-ethyl-2-(2-(methoxycarbonyl)allyl)phenyl) acrylate (4n):



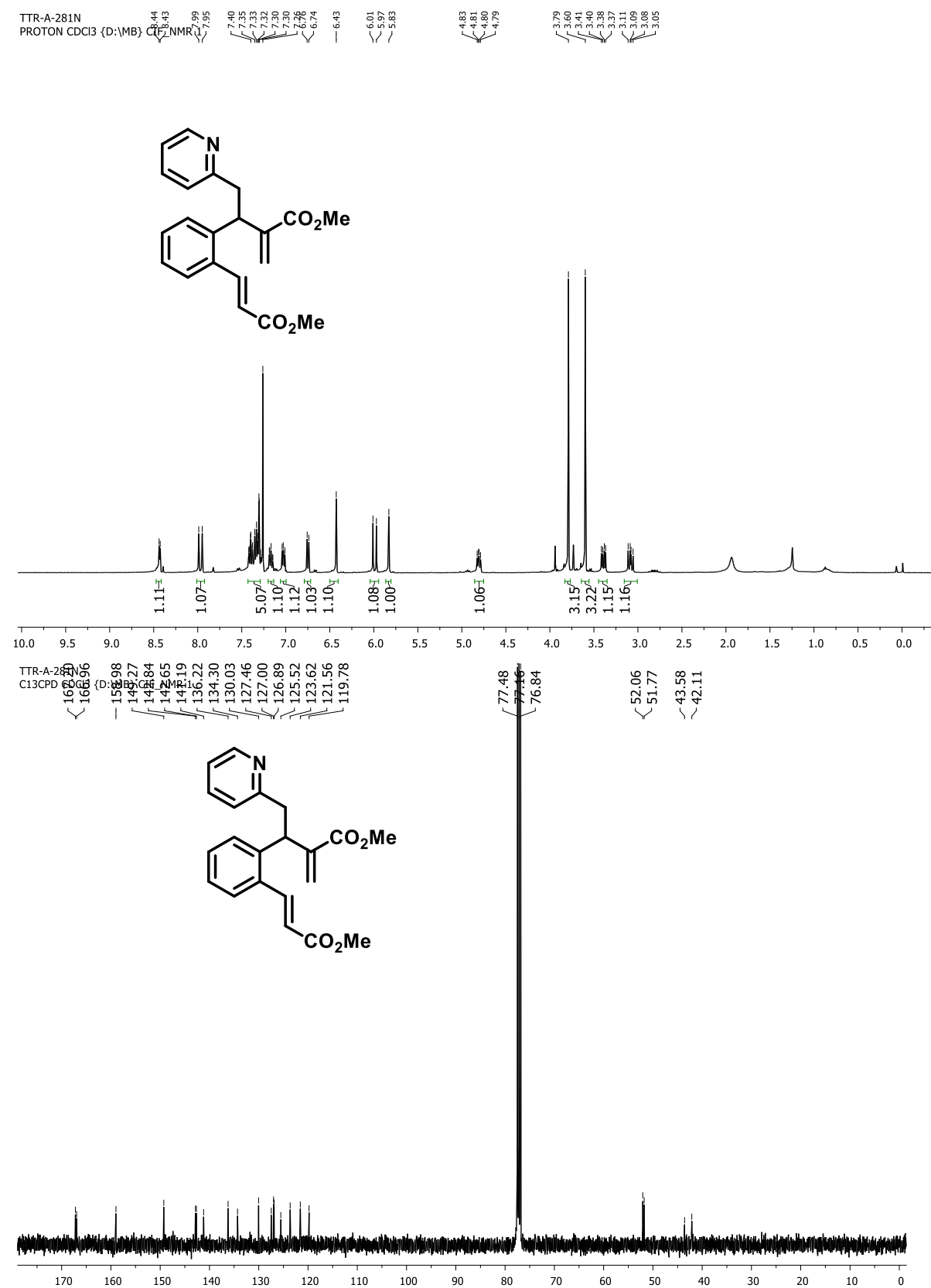
Methyl (*E*)-3-(5-bromo-2-(2-(methoxycarbonyl)allyl)phenyl) acrylate (4o):



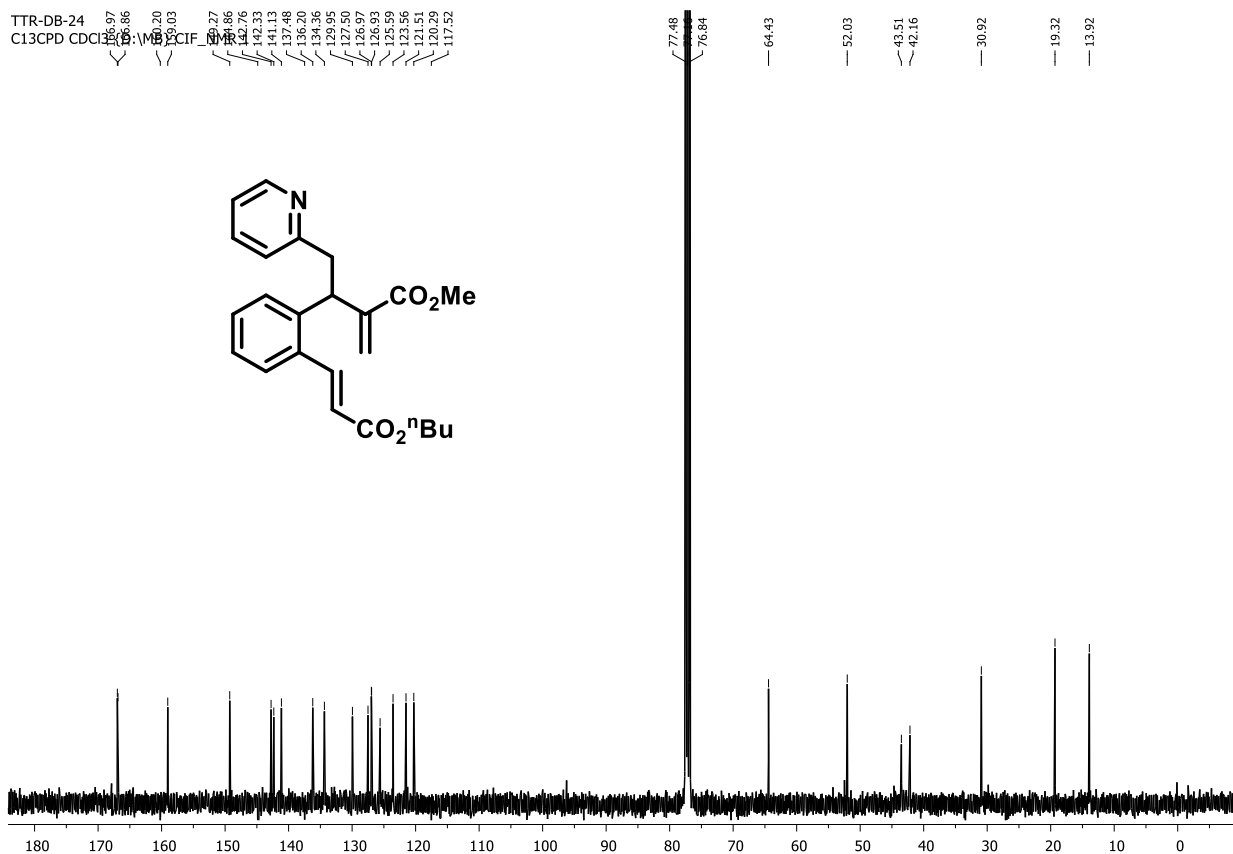
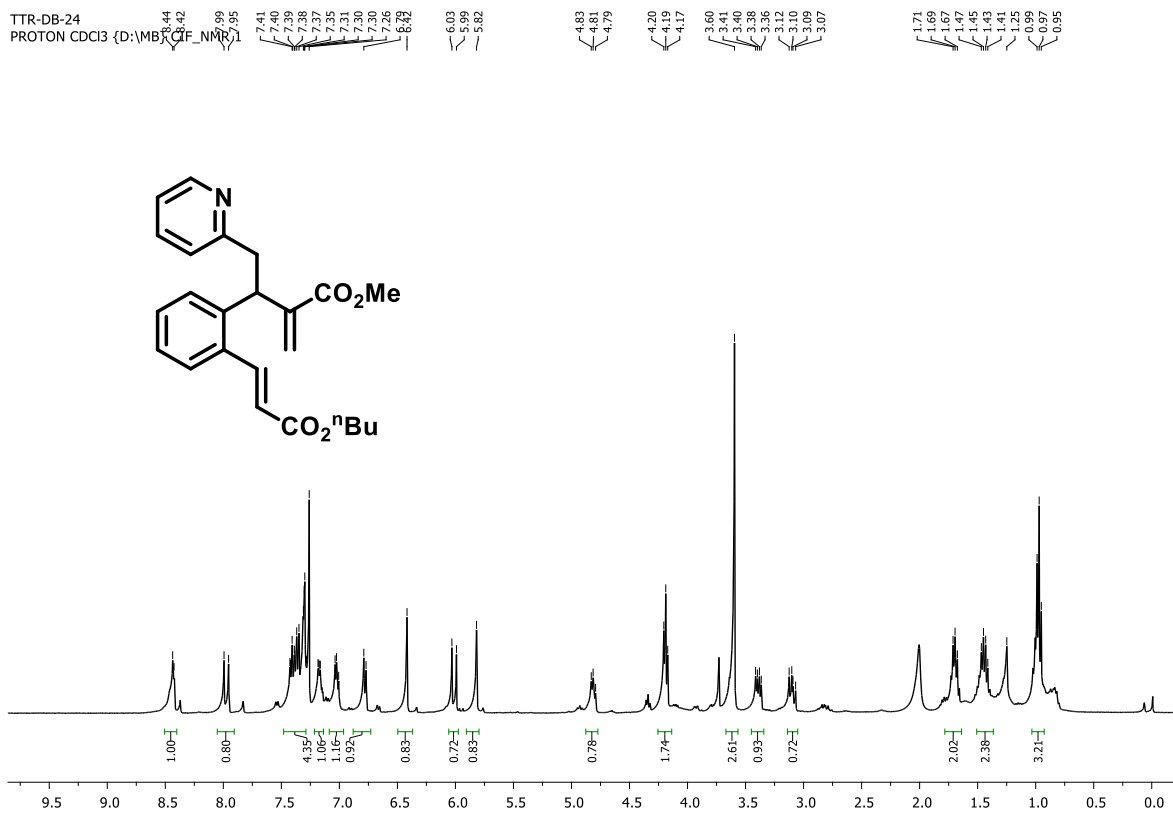
Methyl (E)-2-(2-(2-(phenylsulfonyl)vinyl)benzyl)acrylate (4p)



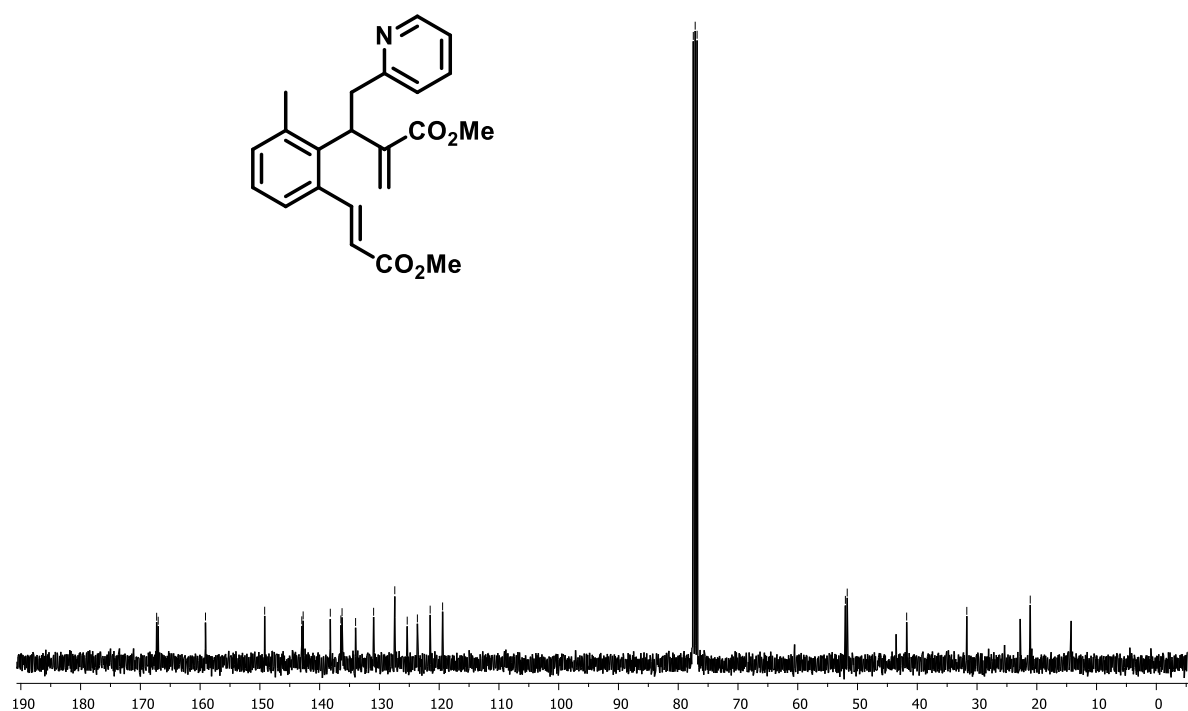
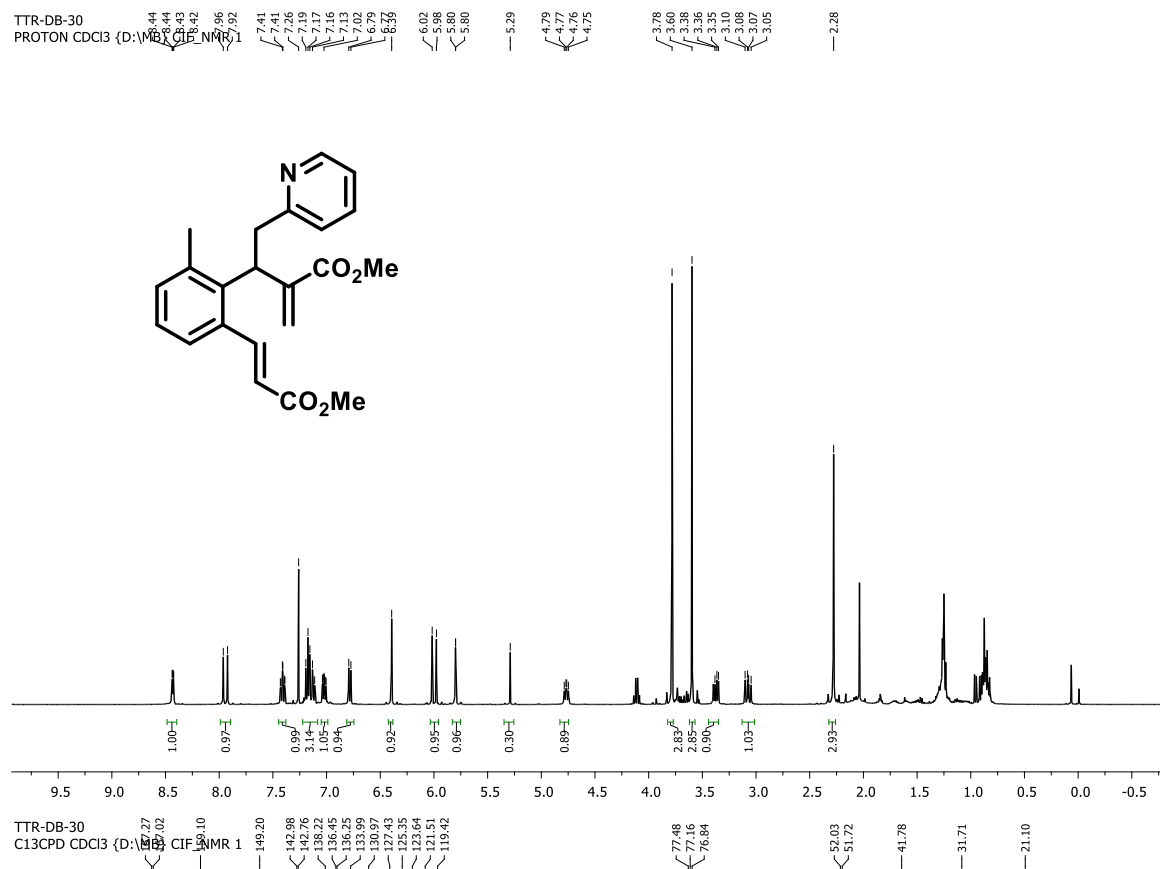
Methyl (E)-3-(2-(3-methoxy-3-oxoprop-1-en-1-yl)phenyl)-2-methylene-4-(pyridin-2-yl)butanoate(4q):



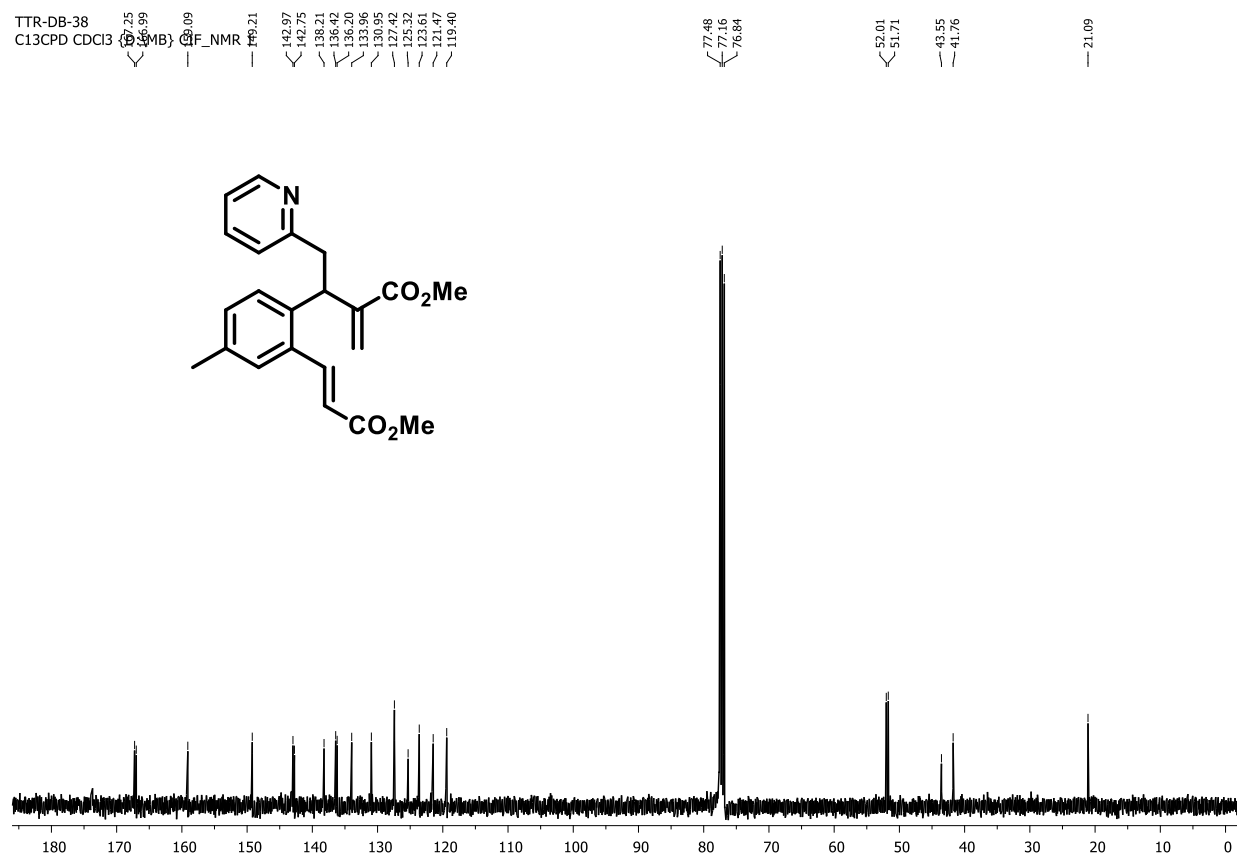
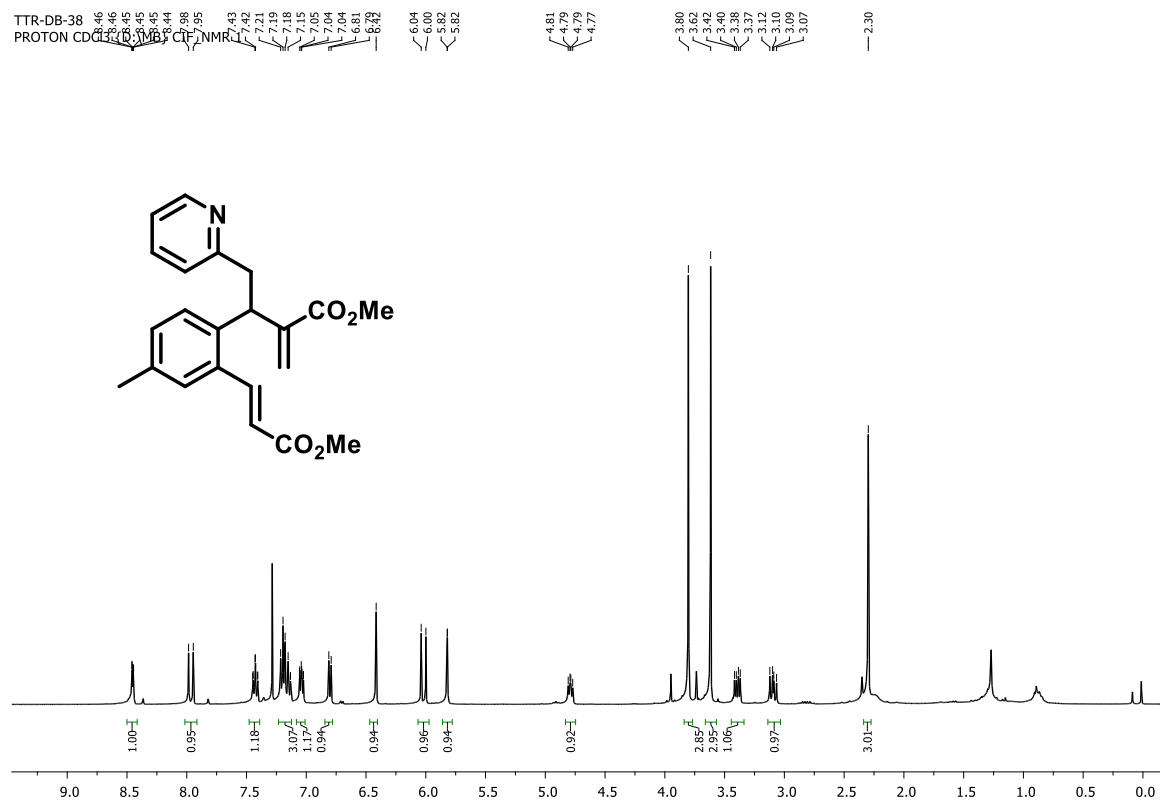
Methyl (E)-3-(2-(3-butoxy-3-oxoprop-1-en-1-yl)phenyl)-2-methylene-4-(pyridin-2-yl)butanoate(4r):



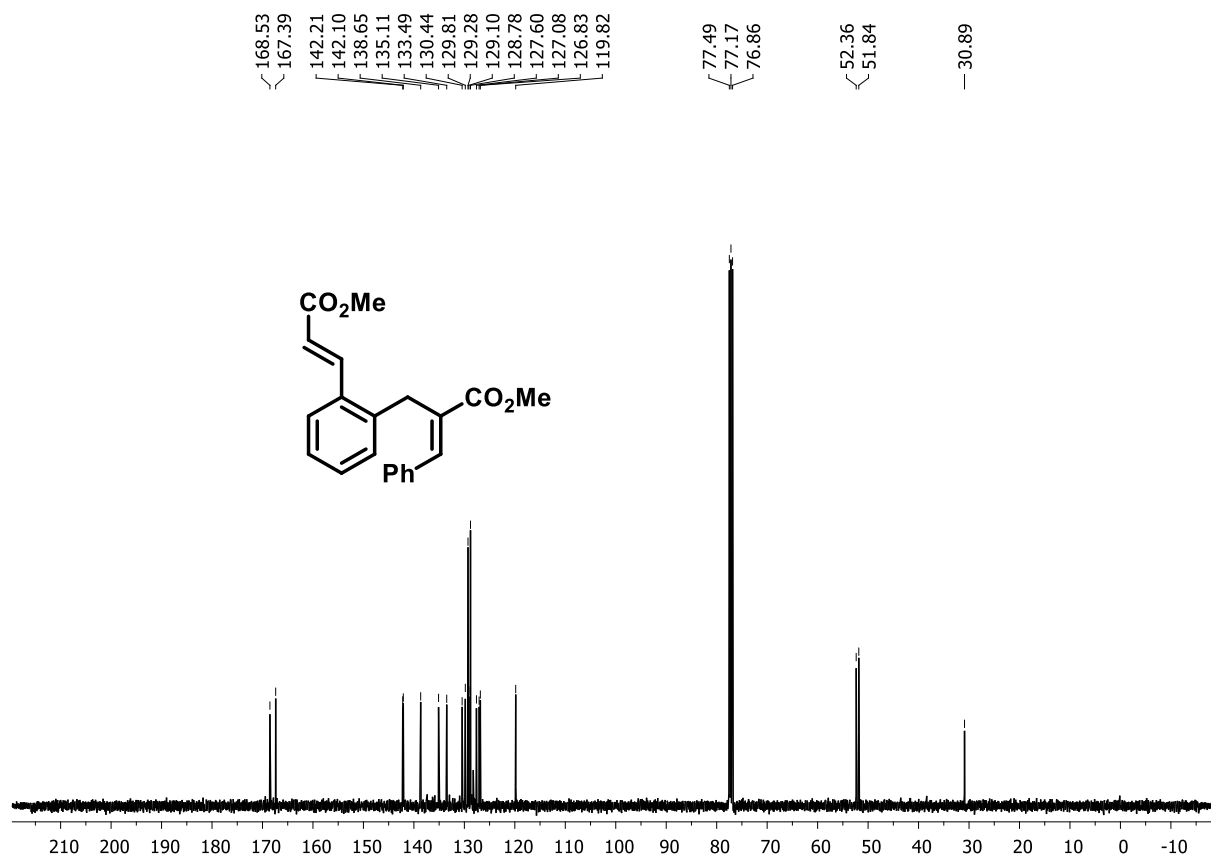
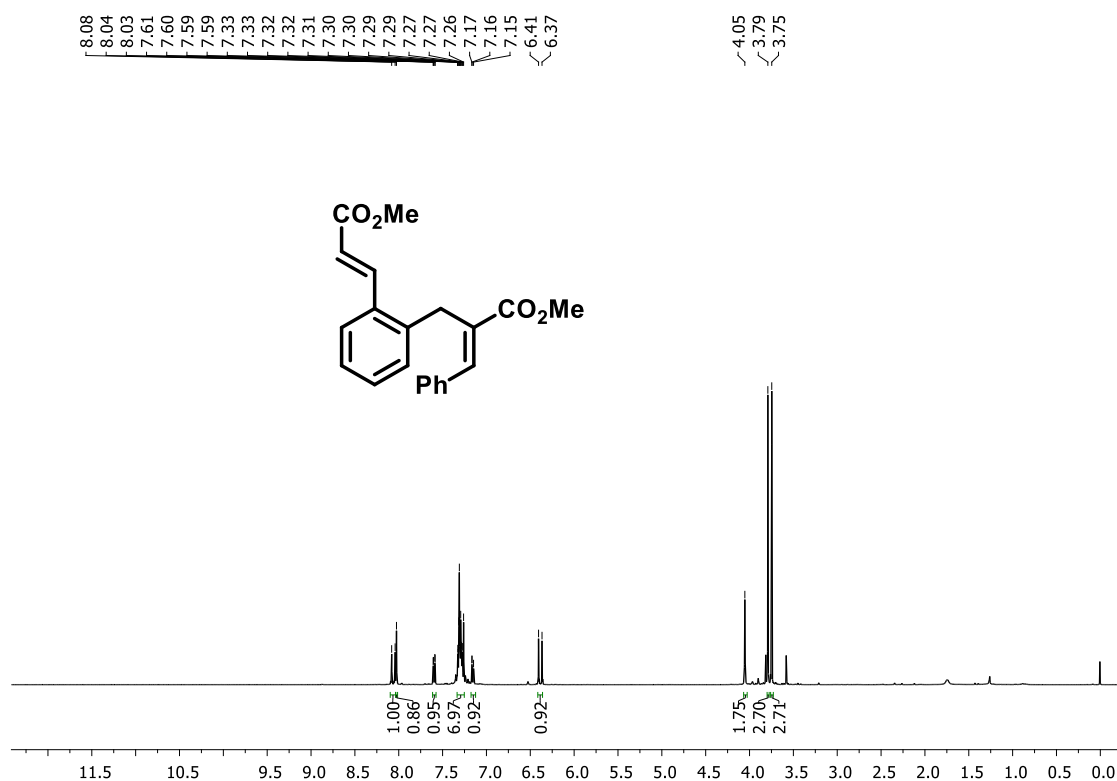
Methyl (E)-3-(2-(3-methoxy-3-oxoprop-1-en-1-yl)-6-methylphenyl)-2-methylene-4-(pyridin-2-yl)butanoate(4s):



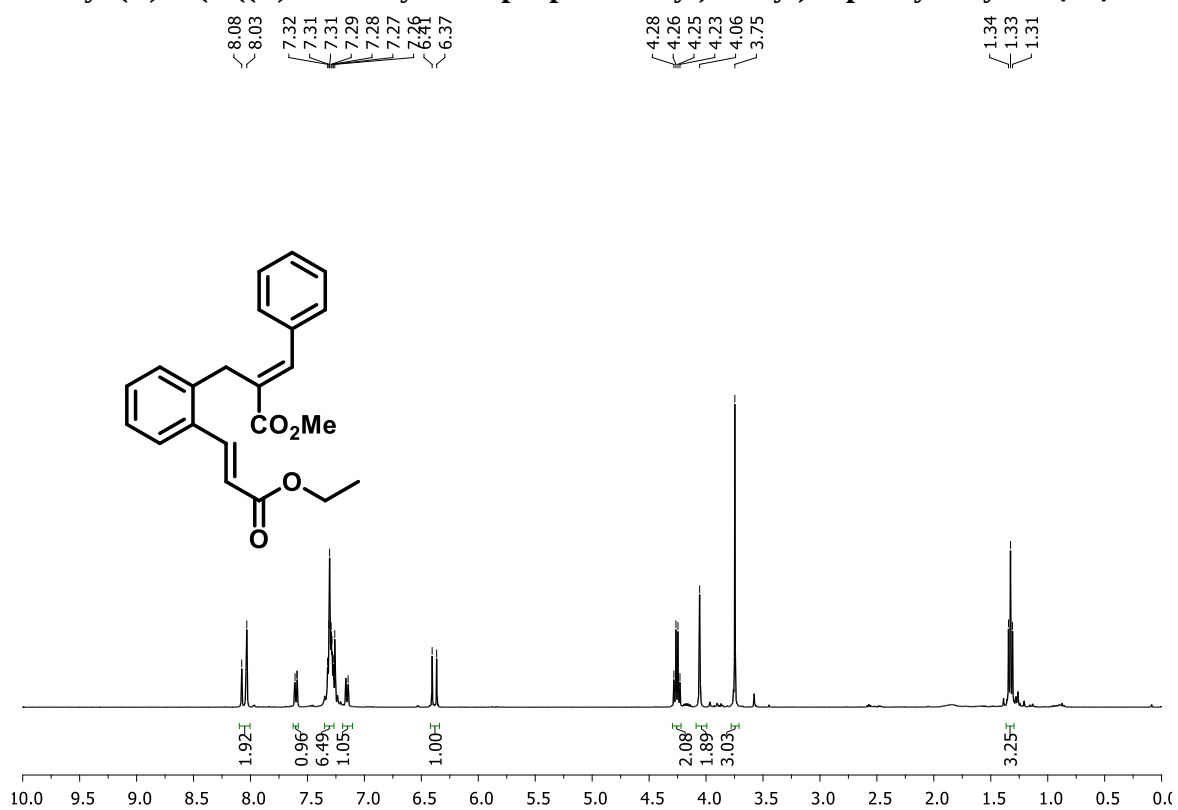
Methyl (E)-3-(2-(3-methoxy-3-oxoprop-1-en-1-yl)-4-methylphenyl)-2-methylene-4-(pyridin-2-yl)butanoate (4t):



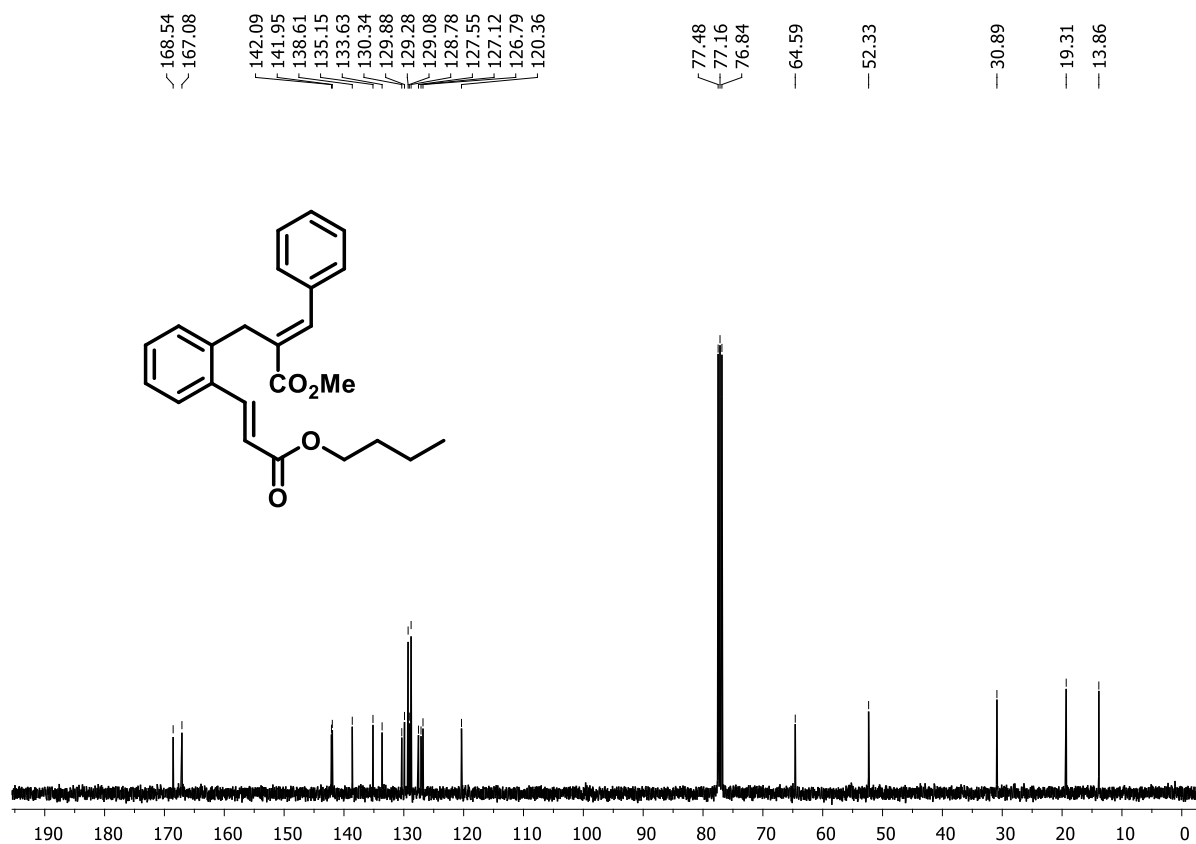
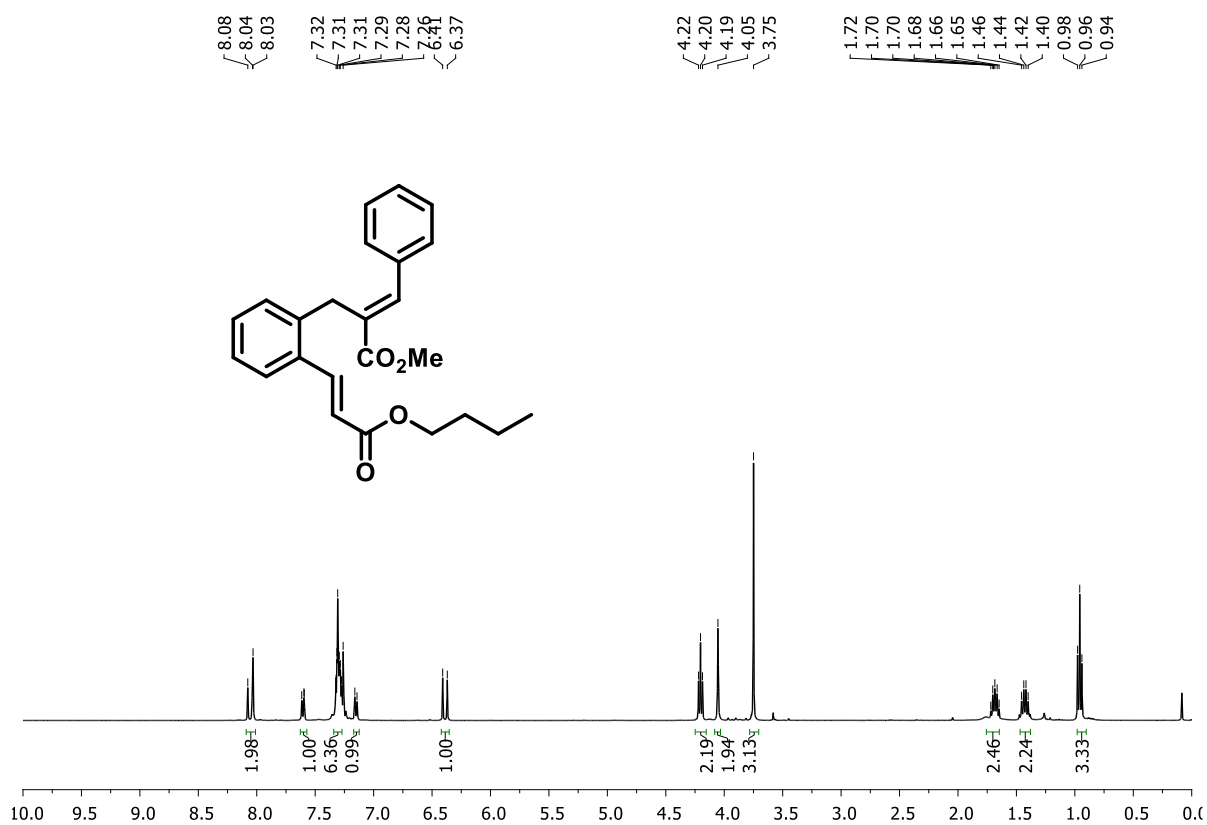
Methyl (*E*)-2-(2-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl) benzyl)-3-phenyl acrylate (6a):



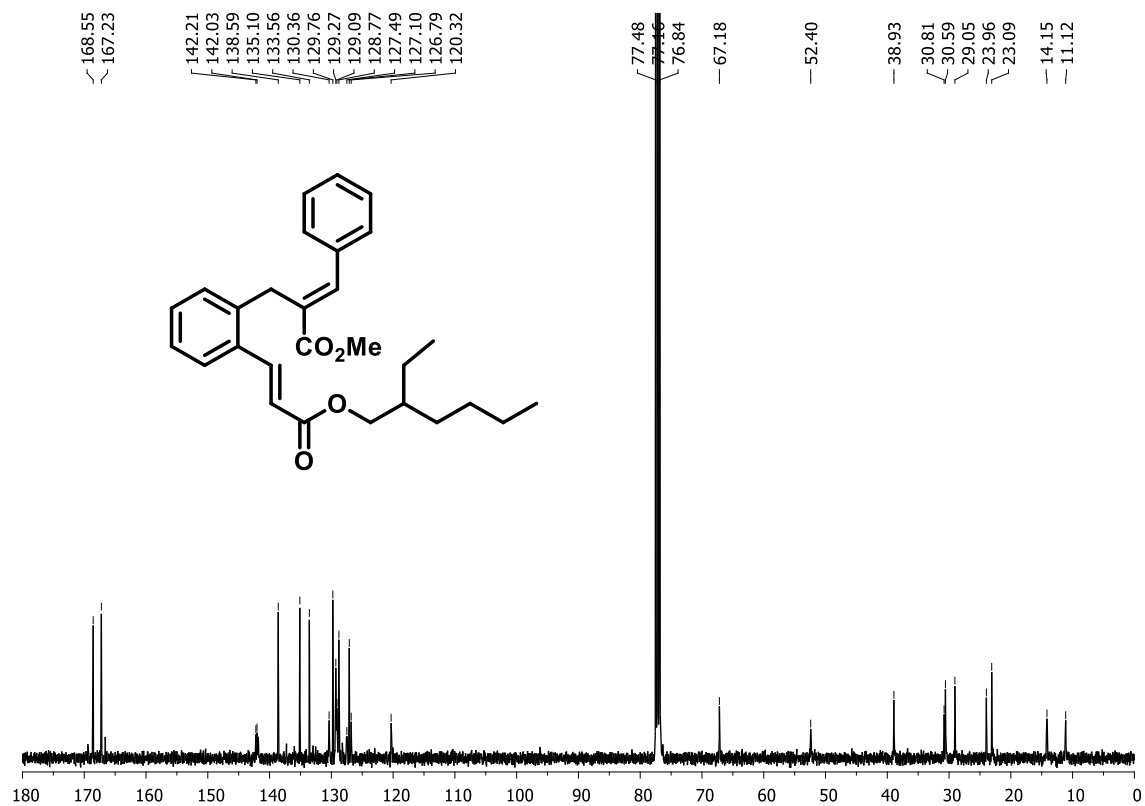
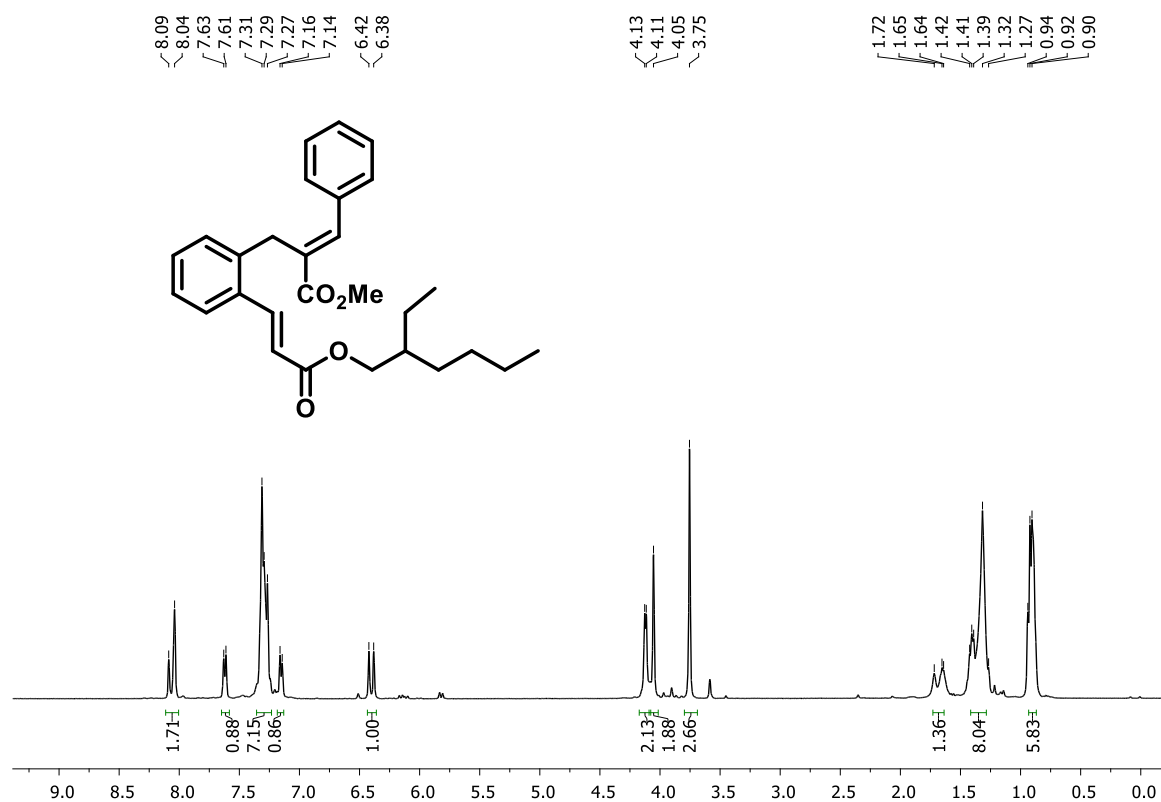
Methyl (*E*)-2-(2-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)benzyl)-3-phenylacrylate (6b):



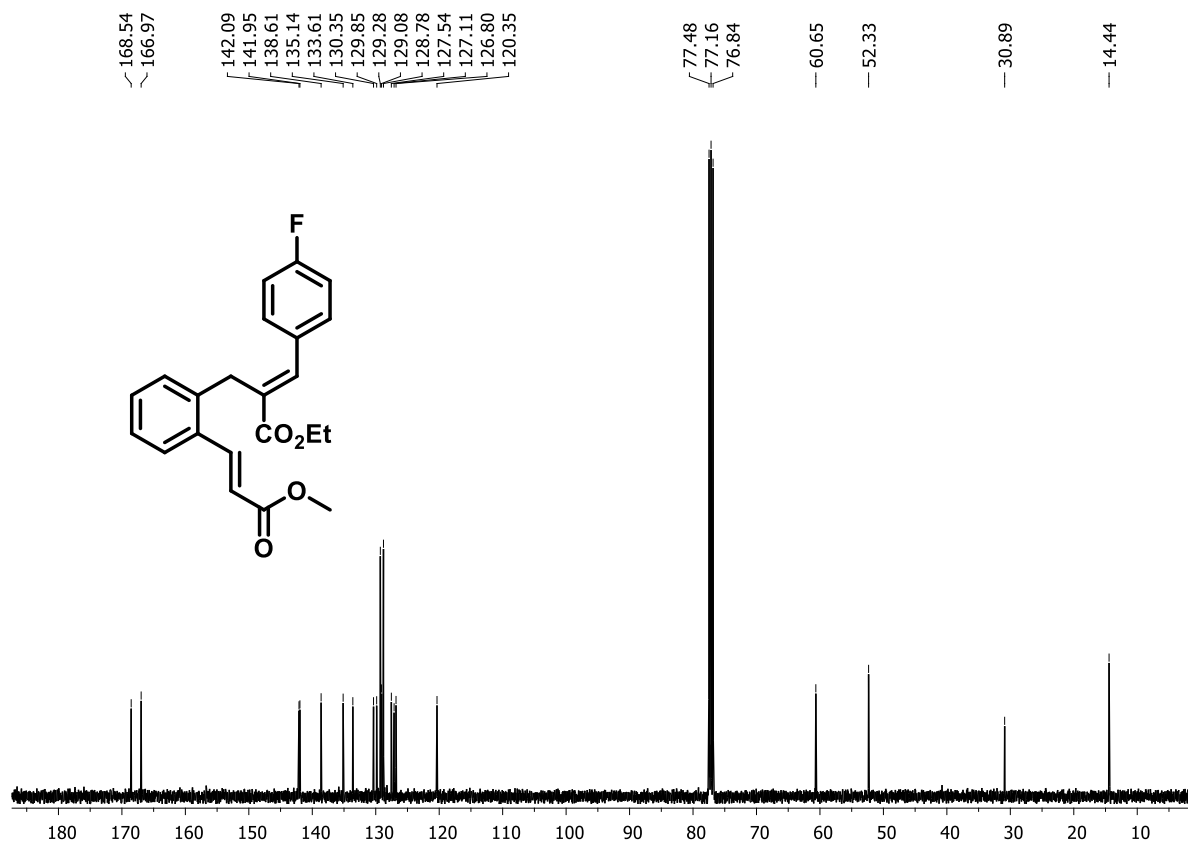
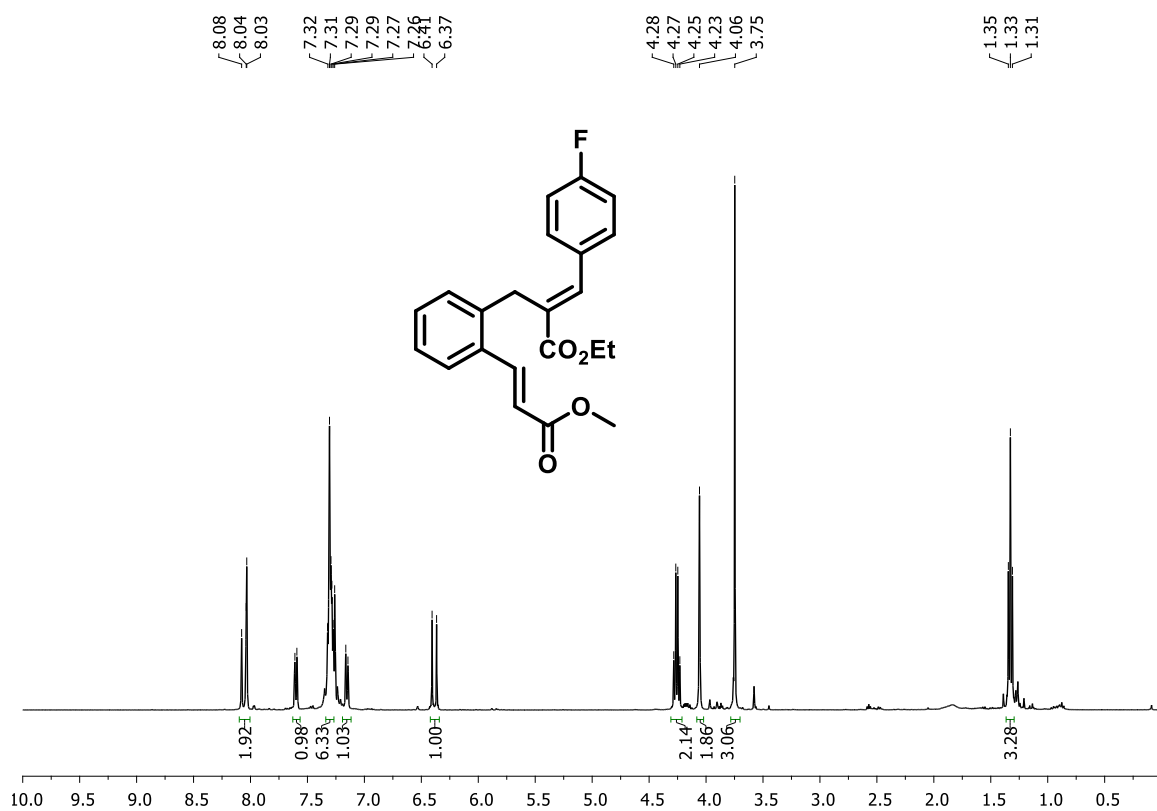
Methyl (*E*)-2-(2-((*E*)-3-butoxy-3-oxoprop-1-en-1-yl)benzyl)-3-phenylacrylate (6b):



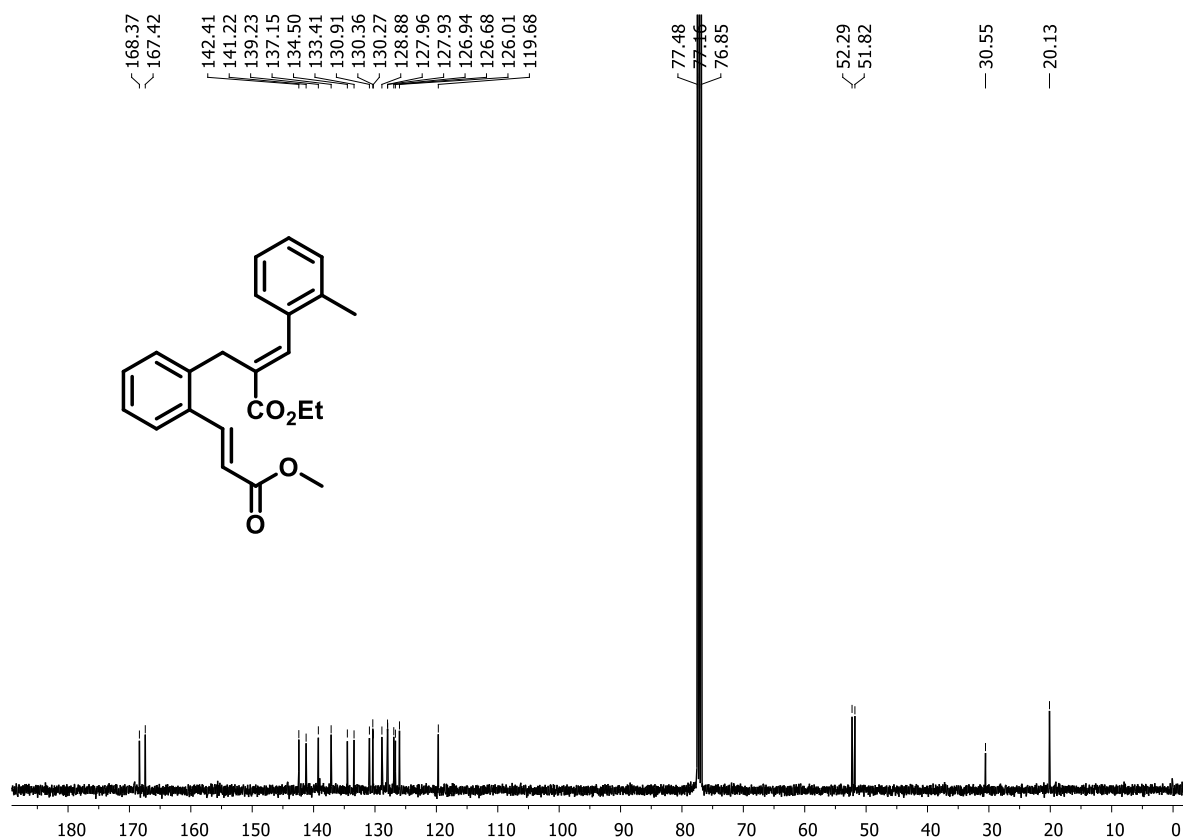
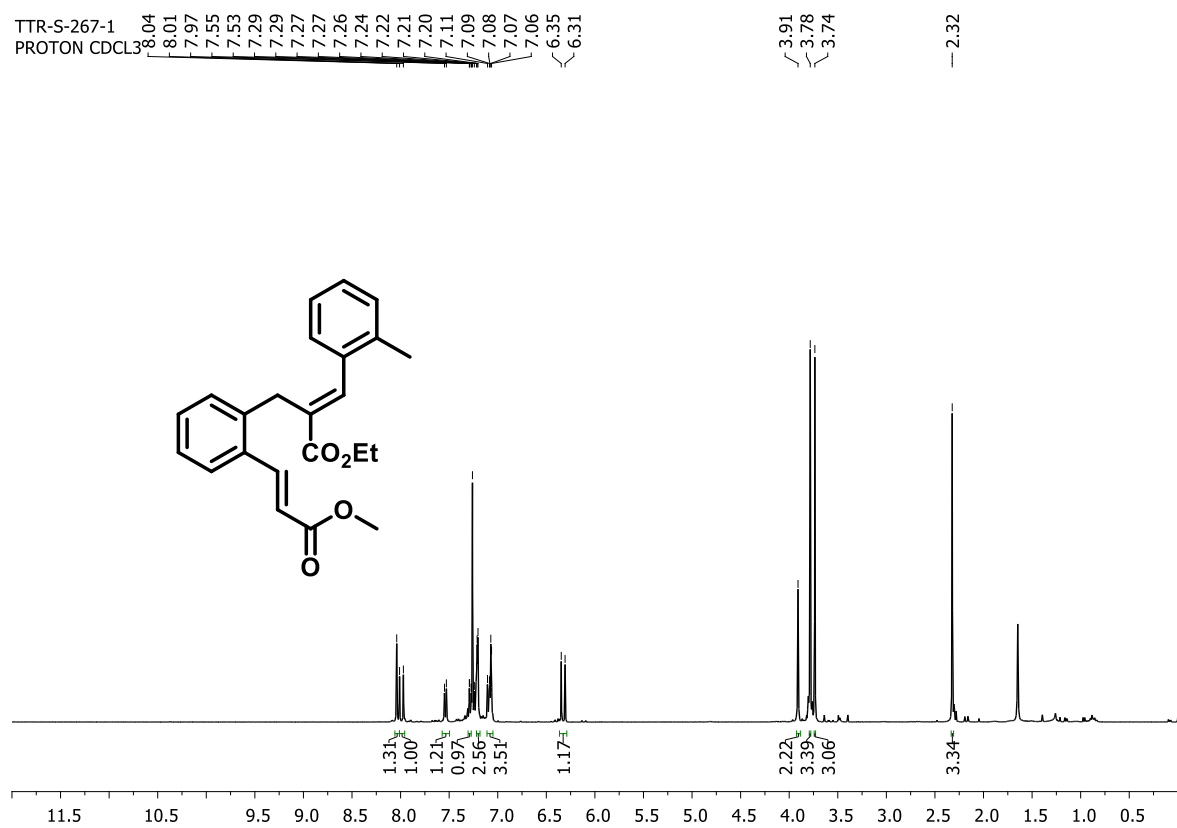
Methyl (*E*)-2-(2-((*E*)-3-((2-ethylhexyl)oxy)-3-oxoprop-1-en-1-yl)benzyl)-3-phenylacrylate (6c):



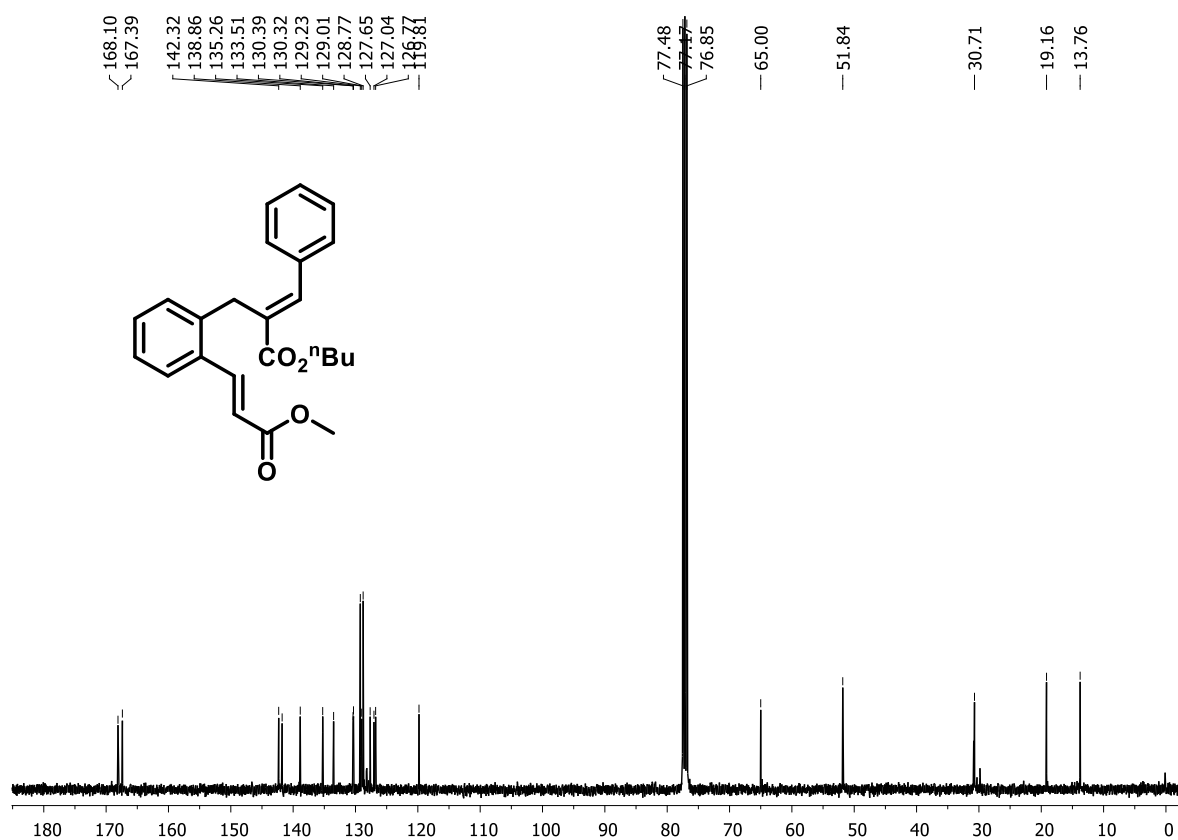
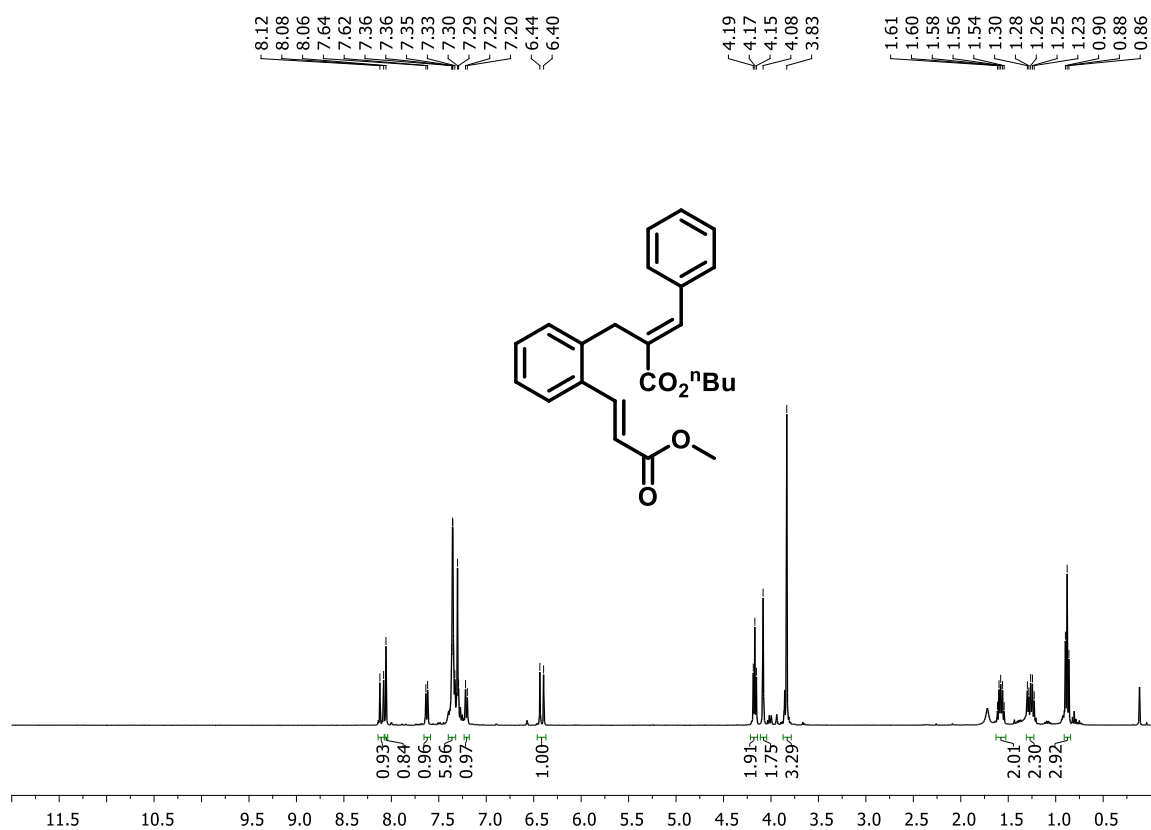
Ethyl (*E*)-3-(4-fluorophenyl)-2-(2-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)benzyl)acrylate (6d):



Ethyl (E)-2-(2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)benzyl)-3-(o-tolyl)acrylate (6e):



Butyl (E)-2-(2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)benzyl)-3-phenylacrylate (6f):

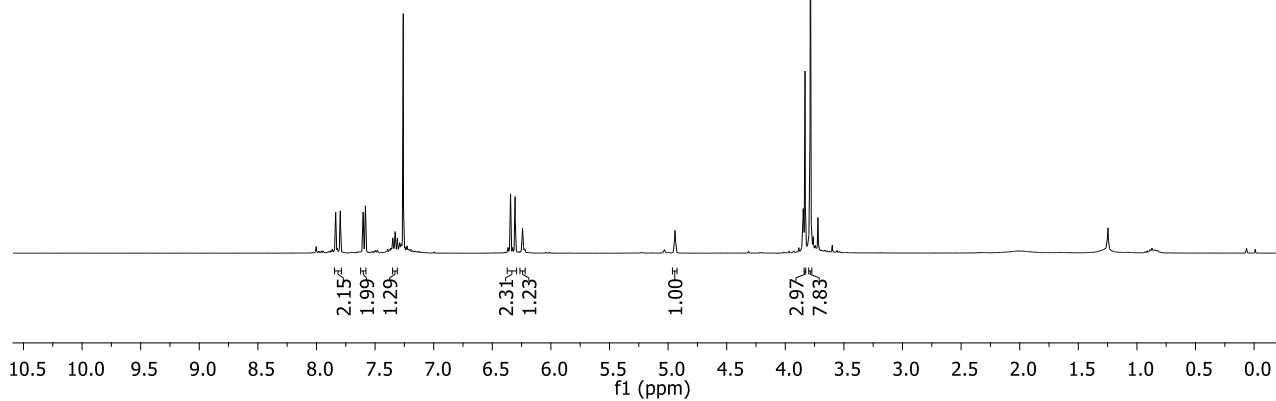
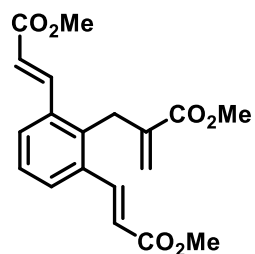


Dimethyl 3,3'-(2-(2-(methoxycarbonyl)allyl)-1,3-phenylene)(2*E*,2'*E*)-diacrylate (8a):

TTR-S-256

PROTON_PU CDCl₃ {D:\MB} CIF_NMR

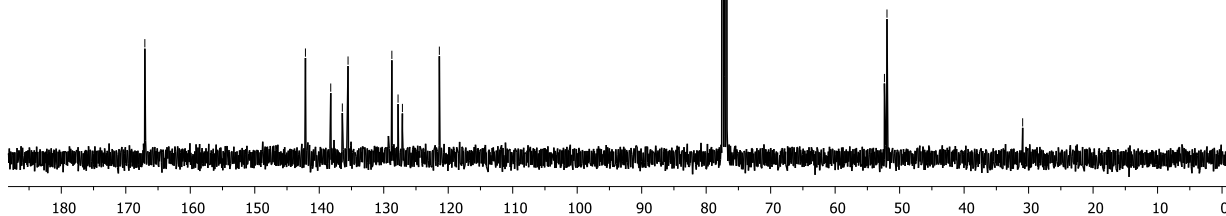
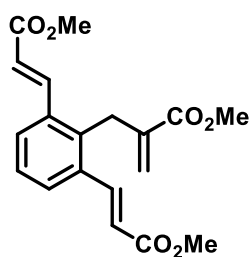
7.84 7.80 7.60 7.58 7.35 7.33 7.31 7.26 6.34 6.31 6.24 — 4.94 3.83 3.79



TTR-S-256

C13CPD CDCl₃ {D:\MB} CIF_NMR 1

162.05 161.94 161.85 142.14 138.22 136.42 135.53 128.74 127.78 127.10 121.37 77.48 77.46 77.44 76.84 52.36 51.96 — 30.92



Dimethyl 3,3'-(5-ethyl-2-(2-(methoxycarbonyl)allyl)-1,3-phenylene)(2E,2'E)-diacrylate (8b):

TTR-A-191-2
PROTON CDCl₃ {D:\MB} CIF_NMR

7.85
7.81
7.45
7.28

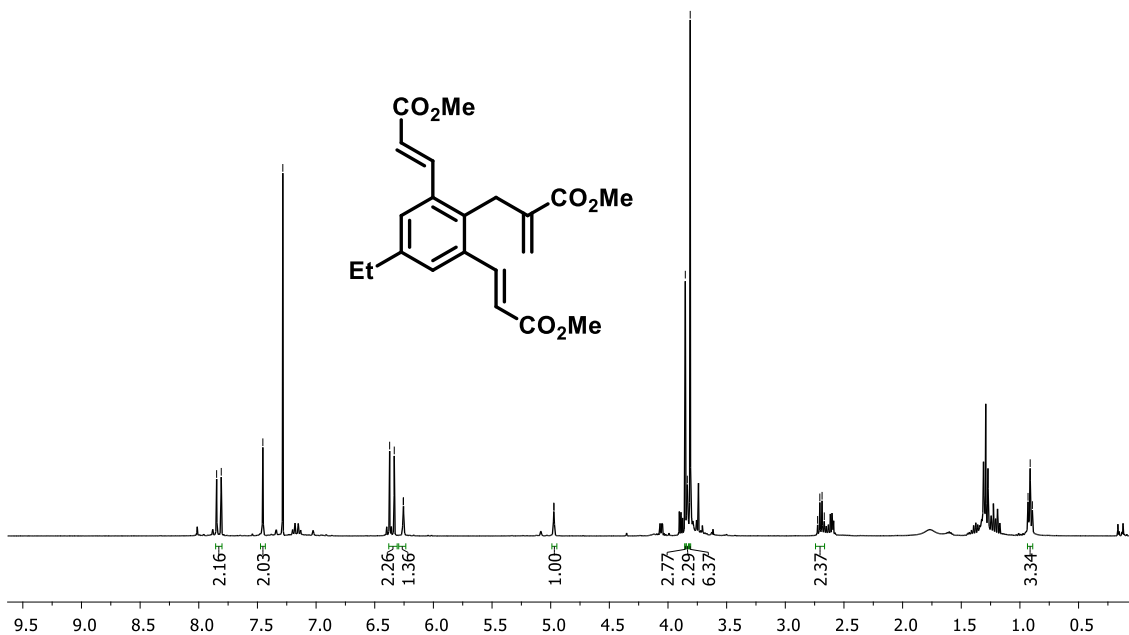
6.37
6.33
6.26
6.26

4.97
4.97

3.85
3.84
3.81

2.72
2.71
2.69
2.67

0.93
0.91
0.89



TTR-A-191-2
C13CPD CDCl₃ {D:\MB} CIF_NMR

167.13
167.02
166.01

143.57
142.41
138.42
135.40
133.82
128.34
127.05
121.02

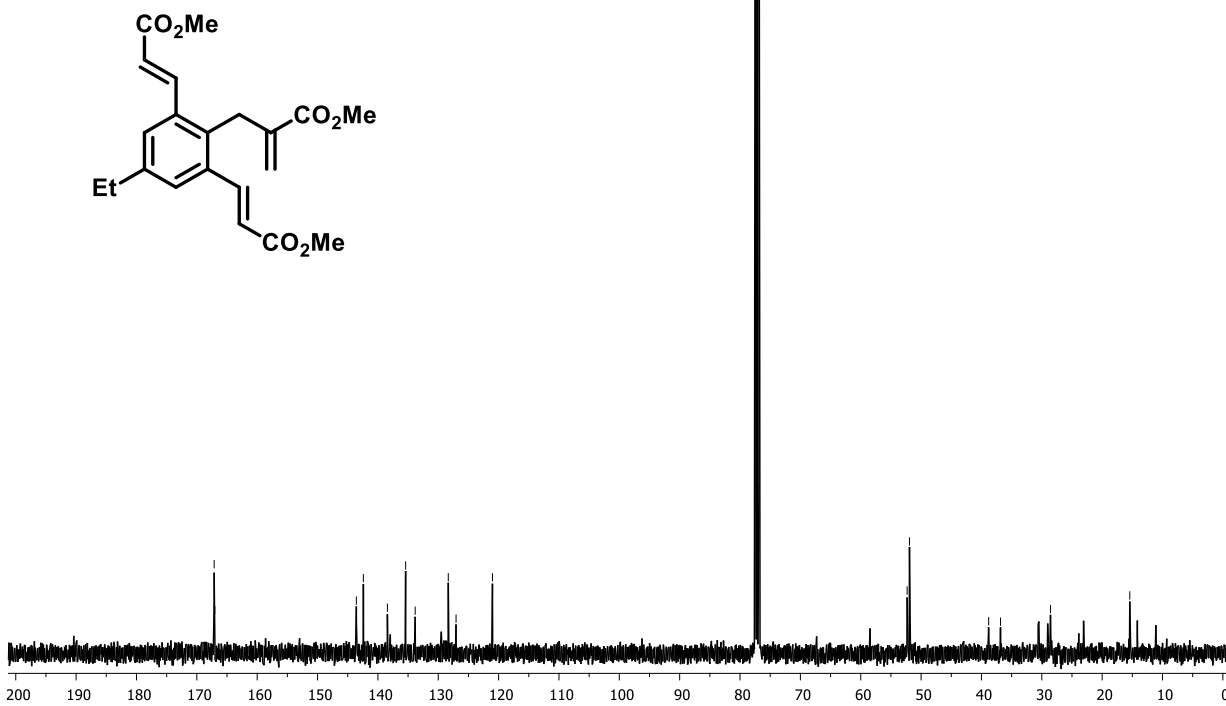
77.48
77.46
76.84

52.31
51.92

38.81
36.85

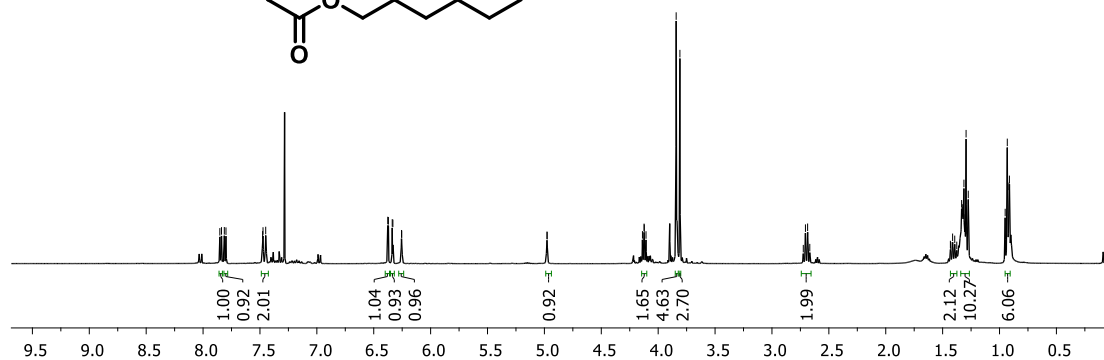
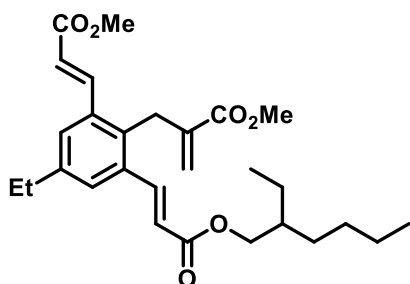
28.56

15.42

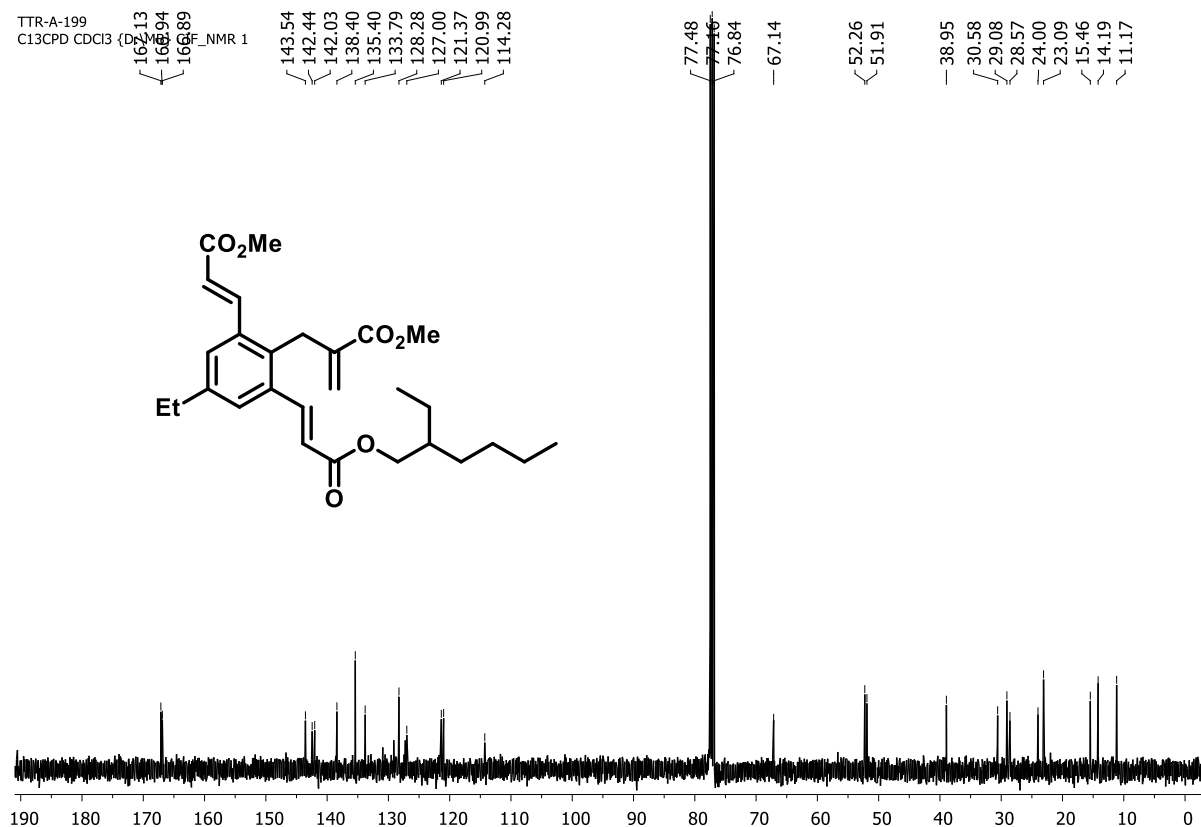
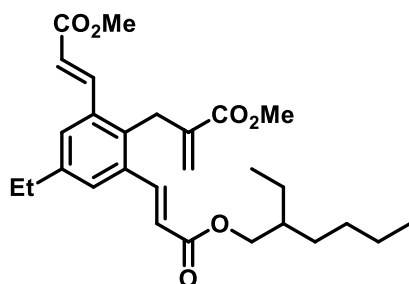


2-Ethylhexyl (*E*)-3-(5-ethyl-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-2-(2-(methoxycarbonyl) allyl)phenyl) acrylate (8c):

TTR-A-199
PROTON CDCl₃ (D₂O) MB: C13CPD NMR 1



TTR-A-199
C13CPD CDCl₃ (D₂O) MB: C13CPD NMR 1



8. X-ray Crystallographic Data of 2e.

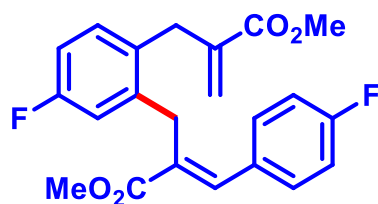


Table 1. Crystal data and structure refinement for Cif for compound 2e.

Identification code	Cif for compound 2e
Empirical formula	C ₂₂ H ₁₈ F ₂ O ₄
Formula weight	384.36
Temperature/K	295
Crystal system	monoclinic
Space group	P2 ₁ /a
a/Å	7.7331(11)
b/Å	20.6428(19)
c/Å	12.1338(15)
α /°	90.00
β /°	94.067(11)
γ /°	90.00
Volume/Å ³	1932.1(4)
Z	4
ρ_{calc} /cm ³	1.321
μ /mm ⁻¹	0.103
F(000)	800.0
Crystal size/mm ³	0.75 × 0.32 × 0.12
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	8.76 to 58.36
Index ranges	-10 ≤ h ≤ 9, -25 ≤ k ≤ 25, -11 ≤ l ≤ 15
Reflections collected	12321
Independent reflections	4469 [R _{int} = 0.0647, R _{sigma} = 0.0648]
Data/restraints/parameters	4469/0/264
Goodness-of-fit on F ²	1.041
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0940, wR ₂ = 0.2446
Final R indexes [all data]	R ₁ = 0.1453, wR ₂ = 0.2798
Largest diff. peak/hole / e Å ⁻³	0.34/-0.27