Supporting Information

Copper-catalyzed allylic substitution of nitroally derivatives with Grignard reagents

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I. Materials and methods

All reagent-grade chemicals and other solvents were obtained from commercial suppliers and were used as received. Anhydrous solvents were either obtained from commercial sources or distilled appropriately. Petroleum ether refers to the 40-60 °C boiling fraction. Commercially available chemicals were used as purchased, or where specified, purified by standard techniques. **NMR spectra** were recorded at 298 K using a Bruker AVANCE 400 MHz or 300 MHz spectrometer. ^{1}H NMR spectra were recorded at 400 MHz and residual solvent peaks were used as an internal reference ($CDCl_3$ δ 7.26). Data are reported as follows: chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p= quintet, hept = heptuplet, m = multiplet or overlap of non-equivalent resonances), coupling constants, integration. ^{13}C NMR spectra were recorded at 101 MHz and residual solvent peaks were used as an internal reference ($CDCl_3$ δ 77.16). ^{19}F NMR were recorded at 282 MHz. Data are reported as follows: chemical shift in ppm, coupling constants (J) in hertz (Hz), multiplicity deduced from DEPT experiments (CH_3, CH_2, CH and C_q). The assignment of ^{1}H and ^{13}C signals was assisted by COSY, HSQC and HMBC experiments where necessary. **High-resolution Mass Spectra (HRMS)** were obtained on a Bruker tims-TOF mass spectrometer, and reported as *m/z* (relative intensity). Electrospray ionization has been used in positive mode (ESI+). **IR spectra** were performed on a Perkin-Elmer FT 1600 spectrometer with wavelengths in cm^{-1} and only peaks of interest are reported. Relative intensities were reported as follows: w = weak, m = medium or s = strong. **Melting points** were determined on a Stuart SMP3 apparatus and were left uncorrected. **Analytical TLC** was performed with Merck silica gel plates, pre-coated with silica gel 60 F254 (0.2 mm). Visualisation was effected by quenching of UV fluorescence (λ_{max} = 254 nm) and by staining with potassium permanganate or vanillin TLC stain solutions, followed by heating. **Flash column chromatography** employed VWR (230-400 mesh) silica gel. Reactions were conducted under a positive pressure of dry nitrogen or argon in oven-dried or flame-dried glassware, and at ambient room temperature, unless specified otherwise.

Preparation of the Grignard reagents: The preparation of non-commercially available Grignard reagents was adapted from the procedure of Piller *et al*. (*Angew. Chem. Int. Ed.* 2008, **47**, 6802-6806). Titration of the Grignard reagents solutions was made following the method of Krasovskiy *et al*. (*Synthesis* 2006, **5**, 0890-0891). Magnesium turnings (182 mg, 7.5 mmol, 1.5 equiv.) and oven dried LiCl (318 mg, 7.5 mmol, 1.5 equiv.) were placed in a dry round bottom flask equipped with a magnetic stirrer and a septum under argon. Freshly distilled THF (5 mL, 1 M) was added. Then, the magnesium was activated with 1,2-dibromoethane (0.1 mL, 0.001 mmol). The resulting mixture was stirred for 5 min. The bromobenzene derivative was then added dropwise and the reaction mixture was stirred for 2 h. The resulting Grignard reagent was finally titrated and used immediately.

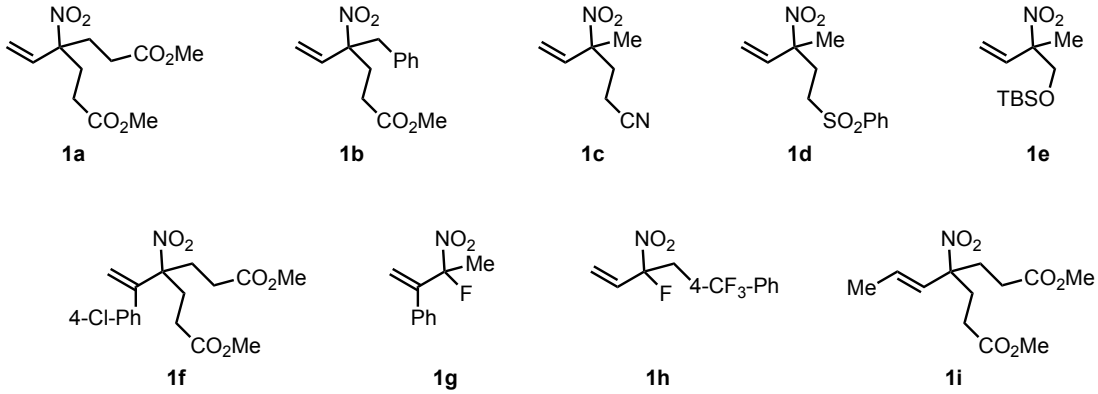
Preparation of CuCN•2LiCl solution:

In a dry tube equipped with a magnetic stirrer were added CuCN (448 mg, 5.0 mmol, 1.0 equiv.), and oven dried LiCl (424 mg, 10.0 mmol, 2.0 equiv.). The tube was then sealed and put under vacuum for 1 h. The tube was then put under argon and freshly distilled THF (10 mL, 0.5 M) was added. Stirring was continued until all salts were dissolved.

II. Experimental and spectral data

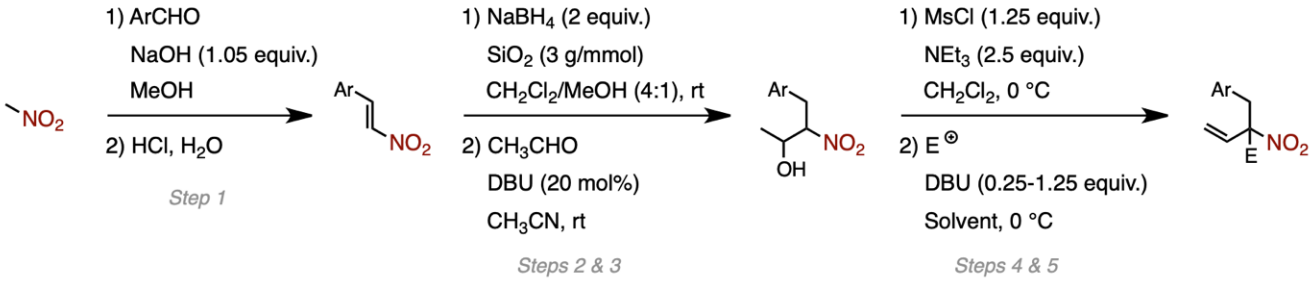
II.1. Synthesis of nitro allyl derivatives

Nitroallylic compounds prepared for the study:



Except for **1b**, all other nitro allyl derivatives were previously prepared. Spectral data and procedures for their preparation may be found in the related publication (N. Fincias, L. Clavier, C. Escande de Messières, M. Guillard, M. Dole Kerim, N. Casaretto, J. Garrec, S. Arseniyadis, L. El Kaïm. *J. Am. Chem. Soc. Au,* 2025*,* **5**, 99-110).

Methyl 4-benzyl-4-nitrohex-5-enoate (1b):



Step 1: In a 250 mL round bottom flask was added nitromethane (10.8 mL, 200 mmol, 1.0 equiv.), aldehyde (200 mmol, 1.0 equiv.) and 40 mL of MeOH. The reaction mixture was cooled down to –10 °C before a solution of sodium hydroxide, prepared by dissolving NaOH (8.4 g, 210 mmol, 1.05 equiv.) in 20 mL of ice-cold water, was added dropwise for a period of 30 min [*note: if a precipitate forms during the addition of NaOH and the mixture starts to thicken, it may be advisable to add some additional MeOH*]. After 15 min, the pasty mass was converted to a clear solution by the addition of 100-150 mL of water containing crushed ice. The resulting clear solution was then slowly added onto an aqueous solution of HCl made by diluting 40 mL of conc. HCl with 60 mL of H_2O. The addition was made at such a rate that the stream just fails to break into drops. A pale-yellow crystalline mass separated almost immediately as the alkaline solution came in contact with the acid. The resulting solution was then filtered, and the pale-yellow solid was dried *in vacuo*. The resulting nitrostyrene were used in the next step without further purification.

Step 2: To a vigorously stirred mixture of nitrostyrene (50 mmol, 1.0 equiv.) in CH_2Cl_2 and MeOH (4:1, 50 mL) was added silica gel (3g/mmol) at rt followed by $NaBH_4$ (3.78 g, 100 mmol, 2.0 equiv.) portion wise. The reaction mixture was stirred at rt until completion (approx. 2 h, reaction monitored by TLC). The reaction

mixture was then quenched with a 1M aqueous solution of HCl and filtered. The silica was washed with CH_2Cl_2 (4 x 50 mL). The organic layer was extracted with 3 x 15 mL CH_2Cl_2. The combined organic layers were washed with a saturated aqueous solution of brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting yellow oil was used in the next step without further purification.

Step 3: To a solution of nitroalkane (10 mmol, 1.0 equiv.) and acetaldehyde (20 mmol, 2.0 equiv.) in MeCN (10 mL, 1.0 M) was added DBU (0.30 mL, 2.0 mmol) at 0 °C and the solution was stirred at 0 °C for 16 h until completion. The solution was diluted with 50 mL of H_2O and quenched with 1 mL of 1.0 M aqueous solution of HCl and transferred to a separatory funnel. The organic layer was extracted with 5 x 20 mL of Et_2O, the combined organic layers were washed with a saturated aqueous solution of brine, dried over anhydrous $MgSO_4$ and the solvent was removed under vacuo. The resulting orange oil was used in next step without further purification.

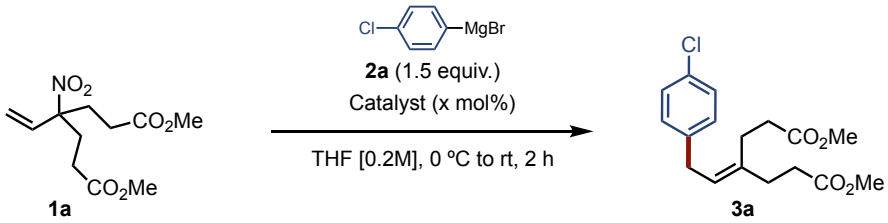
Step 4: To a solution of nitroalkanol (10 mmol, 1.0 equiv.) in CH_2Cl_2 (20 mL, 0.5 M) at 0 °C was added MsCl (0.85 mL, 11 mmol, 1.1 equiv.). The resulting solution was stirred for 15 min at the same temperature before NEt_3 (3.50 mL, 25 mmol, 2.5 equiv.) was added dropwise over a period of 20 min. The reaction mixture was further stirred 2 h until completion (reaction monitored by TLC). The reaction mixture was then diluted with 50 mL of H_2O and 15 mL of a 1.0 M aqueous solution of HCl to quench the remaining amine. The resulting biphasic mixture was transferred in a separatory funnel. The organic layer was collected, extracted with 3 x 10 mL of CH_2Cl_2, washed with a saturated aqueous solution of brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting dark orange oil was diluted in Petroleum Ether/ Et_2O solution (70:30), passed through a short plug of silica to remove any polymeric side products, and used in the next step without further purification.

Step 5: To a solution of nitroalkene (3.0 mmol, 1.0 equiv.) and methylacrylate (7.5 mmol, 2.5 equiv.) in MeCN (6 mL, 0.5 M) at 0 °C was added DBU (0.20 to 1.25 equiv.). The reaction mixture was then stirred for 4 h at the same temperature. The solution was quenched by a slow addition of 1 mL of a 1.0 M aqueous solution of HCl. The mixture was transferred in a separatory funnel with 20 mL of H_2O. The organic layer was collected, extracted with 3 x 15 mL of Et_2O, washed with a saturated aqueous solution of brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by flash column chromatography over silica gel using PE/EtOAc (90:10 to 80:20) to afford methyl 4-benzyl-4-nitrohex-5-enoate (**1b**) as a colorless oil in 44 % overall yield (352 mg, 1.34 mmol).

Rf (PE/Et_2O = 8:2) = 0.46.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 5.1, 1.8 Hz, 3H), 7.11-7.06 (m, 2H), 6.16 (ddd, *J* = 17.8, 11.3, 0.8 Hz, 1H), 5.45 (d, *J* = 11.3 Hz, 1H), 5.26 (d, *J* = 17.8 Hz, 1H), 3.68 (s, 3H), 3.38-3.26 (m, 2H), 2.55-2.27 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 134.7, 133.7, 130.3, 128.5, 127.7, 118.0, 94.7, 51.9, 45.6, 30.7, 28.9.
IR (neat) cm^{-1}: 3031, 2952, 1734, 1604, 1538, 1496, 1454, 1436, 1418, 1379, 1351, 1303, 1198, 1174, 1082, 1030, 991, 937, 896, 841, 727, 701, 673.
HRMS *m/z* (ESI+) calculated for $[C_{14}H_{17}NNaO_4]^+$ = 286.1050, found: 286.1045.

II.2. Grignard addition to nitro allyl derivatives

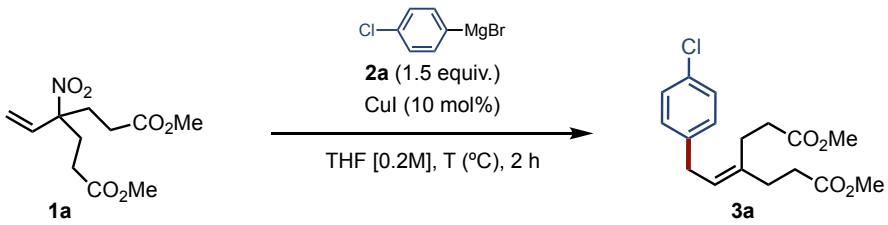
Table S1. Catalyst screen with aryl Grignard



Entry	Catalyst	Catalyst loading (mol%)	Yield[a] (%)
1	-	-	0
2	$CoBr_2$	5	0
3	$Fe(acac)_3$	5	0
4	$NiCl_2$	5	degradation
5	CuCl	5	72
6	CuI	5	64
7	$Cu(MeCN)_4PF_6$	5	70
8	CuCN	5	72
9	CuCN·2LiCl	5	83 (82[b])
10	CuClXantPhos	5	47

All reactions were carried out on a 0.5 mmol scale. [a] NMR yield determined using an internal standard. [b] Isolated yield.

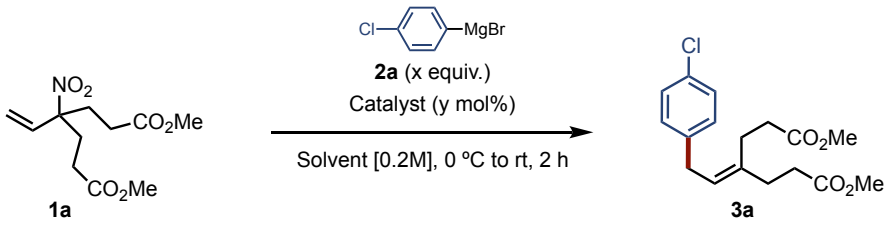
Table S2. Temperature and stoichiometry screen with aryl Grignard



Entry	Temperature (°C)	2a (x equiv.)	Yield[a] (%)
1	–78	2.0	0
2	–20	2.0	0
3	0[b]	2.0	71
4	0[b]	1.5	72

All reactions were carried out on a 0.5 mmol scale. [a] NMR yield determined using an internal standard. [b] The reaction is progressively warmed to rt in a 2 h period.

Table S3. Condition screen with alkyl Grignard



Entry	MeMgBr (x equiv.)	CuCN·2LiCl (y equiv.)	Solvent	Conversion (%)	Yield[a] (%)
1	1.5	-	THF	88	traces
2[b]	1.5	0.05	THF	<5	traces
3[c]	1.5	0.05	THF	79	3
4	1.5	0.05	THF	>99	22
5	1.5	0.5	THF	65	35
6[d]	1.5	0.5	THF	90	43
7[e]	1.1	0.5	THF	>99	16
8	1.1	0.5	Et_2O	92	0
9	1.1	0.5	DCM	70	20
10	1.1	0.5	Toluene	71	15
11	1.0	1	THF	65	42
12[f]	1.5	0.75	THF	72	70

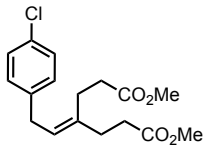
All reactions were carried out on a 0.5 mmol scale. MeMgBr is added at –0 °C and the reaction is progressively warmed to rt in a 2 h period. [a] NMR yield determined using an internal standard. [b] MeMgBr is added at –78 °C and the reaction is progressively warmed to –20 °C in a 2 h period. [c] MeMgBr is added at –20 °C and the reaction is progressively warmed to 0 °C in a 2 h period. [d] Reaction is stirred 24 h. [e] CuClXantPhos is used instead of CuCN·2LiCl. [f] Reaction run under Ono's conditions; a solution of the nitro allyl derivative in THF is added dropewise onto the organocuprate and the reaction is stirred for 12 h.

General procedure for the synthesis of substituted alkenes (A):

In a dry round bottom flask equipped with a magnetic stirrer and a septum under argon was added the allylic nitroalkane derivative (0.5 mmol, 1.0 equiv.) in THF (2.5 mL, 0.2 M). CuCN•2LiCl was then added in one portion (0.05 mL, 0.025 mmol, 0.05 equiv.).[1] The resulting mixture was cooled down to 0 °C. The Grignard reagent was then added dropwise, and the reaction was stirred for 2 h while slowly warming up to room temperature. After completion, water (5.0 mL) was added together with 1 mL of 0.3 M aqueous solution of HCl. The biphasic mixture was transferred to a separatory funnel, the organic layer was collected, and the organic layer was extracted with 3 x 10 mL of Et_2O. The combined organic layers were washed twice with a saturated aqueous solution of K_3PO_4, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude residue was purified by flash column chromatography over silica gel using PE/Et_2O as eluent.

[1] For aliphatic Grignard, CuCN•2LiCl was added in one portion (0.50 mL, 0.25 mmol, 0.5 equiv.).

Dimethyl 4-(2-(4-chlorophenyl)ethylidene)heptanedioate (3a)



MW (g.mol^{-1}): 354.40 **Molecular formula:** $C_{17}H_{21}ClO_4$

Prepared following general procedure A from **1a** (116 mg, 0.446 mmol) and 4-chlorophenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 80:20) afforded **3a** as a pale-yellow oil in 82% yield (119 mg, 0.366 mmol).

Rf (PE/Et_2O = 8:2) = 0.31

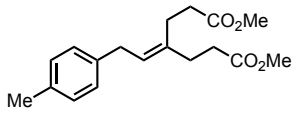
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H, 5.34 (t, *J* = 7.3 Hz, 1H), 3.65 (s, 3H), 3.61 (s, 3H), 3.33 (d, *J* = 7.3 Hz, 2H), 2.47-2.33 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 173.4, 139.4, 137.3, 131.7, 129.6, 128.5, 125.0, 51.7, 51.6, 33.2, 32.83, 32.79, 31.3, 25.6.

IR (neat) cm^{-1}: 2951, 1732, 1490, 1435, 1357, 1296, 1253, 1194, 1161, 1090, 1014, 984, 870, 816, 701, 656.

HRMS *m/z* (ESI+) calculated for $[C_{17}H_{22}ClO_4]^+$= 325.1201, found: 325.1197.

Dimethyl 4-(2-(*p*-tolyl)ethylidene)heptanedioate (3b)



MW (g.mol^{-1}): 304.39 **Molecular formula:** $C_{18}H_{24}O_4$

Prepared following general procedure A from **1a** (119 mg, 0.457 mmol) and 4-methylphenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 100:00 to 90:10) afforded **3b** as a pale-yellow oil in 82% yield (114 mg, 0.375 mmol).

Rf (PE/Et_2O = 8:2) = 0.45

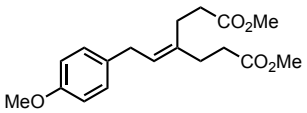
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 5.39 (t, *J* = 7.3 Hz, 1H), 3.67 (s, 3H), 3.64 (s, 3H), 3.34 (d, *J* = 7.3 Hz, 2H), 2.50-2.34 (m, 8H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 173.6, 137.9, 136.5, 135.5, 129.2, 128.2, 1 26.0, 51.8, 51.7, 33.5, 33.03, 33.01, 31.5, 25.7, 21.1.

IR (neat) cm^{-1}: 2951, 1732, 1514, 1436, 1369, 1294, 1258, 1196, 1167, 1125, 1098, 1021, 975, 895, 840, 802.

HRMS *m/z* (ESI+) calculated for $[C_{18}H_{24}NaO_4]^+$ = 327.1567, found: 327.1559.

Dimethyl 4-(2-(4-methoxyphenyl)ethylidene)heptanedioate (3c)



MW (g.mol^{-1}): 320.39 **Molecular formula:** $C_{18}H_{24}O_5$

Prepared following general procedure A from **1a** (118 mg, 0.455 mmol) and 4-methoxyphenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 80:20) afforded **3c** as a pale-yellow oil in 89% yield (124 mg, 0.405 mmol).

Rf (PE/Et_2O = 8:2) = 0.21

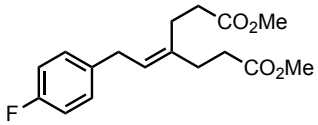
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 5.36 (t, *J* = 7.4 Hz, 1H), 3.75 (s, 3H), 3.64 (s, 3H), 3.61 (s, 3H), 3.30 (d, *J* = 7.4 Hz, 2H), 2.48-2.32 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 173.4, 157.8, 136.3, 132.9, 129.1, 126.0, 113.8, 55.2, 51.6, 51.5, 32.8, 31.3, 25.5.

IR (neat) cm^{-1}: 2950, 2837, 1732, 1599, 1586, 1490, 1435, 1356, 1249, 1194, 1160, 1077, 1031, 984, 872, 747.

HRMS *m/z* (ESI+) calculated for $[C_{18}H_{24}NaO_5]^+$ = 343.1516, found: 343.1507.

Dimethyl 4-(2-(4-fluorophenyl)ethylidene)heptanedioate (3d)



MW (g.mol^{-1}): 308.35 **Molecular formula:** $C_{17}H_{21}FO_4$

Prepared following general procedure A from **1a** (56 mg, 0.216 mmol) and 4-fluorophenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 95:05 to 90:10) afforded **3d** as a pale-yellow oil in 87% yield (58 mg, 0.188 mmol).

Rf (PE/Et_2O = 8:2) = 0.27

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 8.7, 5.5 Hz, 2H), 6.95 (t, *J* = 8.7 Hz, 2H), 5.36 (t, *J* = 7.4 Hz, 1H), 3.67 (s, 3H), 3.63 (s, 3H), 3.35 (d, *J* = 7.4 Hz, 2H), 2.49-2.34 (m, 8H).

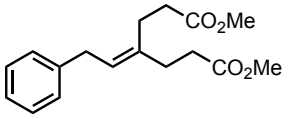
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 173.5, 161.4 (d, *J* = 243.6 Hz), 137.0, 136.63 (d, *J* = 3.2 Hz), 129.7, 129.6, 125.5, 115.4, 115.2, 51.8, 51.7, 33.1, 33.0, 31.4, 25.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ 113.93 (s, 1F).

IR (neat) cm^{-1}: 2952, 1733, 1602, 1508, 1436, 1358, 1296, 1219, 1196, 1158, 1094, 1076, 1016, 985, 827, 748.

HRMS *m/z* (ESI+) calculated for $[C_{17}H_{22}FO_4]^+$ = 309.1497, found: 309.15.

Dimethyl 4-(2-phenylethylidene)heptanedioate (3e)



MW (g.mol^{-1}): 290.36 **Molecular formula:** $C_{17}H_{22}O_4$

Prepared following general procedure A from **1a** (120 mg, 0.463 mmol) and phenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 100:00 to 90:10) afforded **3e** as a pale-yellow oil in 85% yield (114 mg, 0.393 mmol).

Rf (PE/Et_2O = 9:1) = 0.09

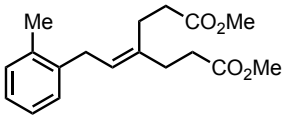
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.21-7.11 (m, 3H), 5.41 (t, *J* = 7.4 Hz, 1H), 3.67 (s, 3H), 3.63 (s, 3H), 3.39 (d, *J* = 7.4 Hz, 2H), 2.52-2.35 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 173.6, 141.0, 136.8, 128.5, 128.4, 126.0, 125.7, 51.8, 51.7, 33.9, 33.0, 31.5, 25.7.

IR (neat) cm^{-1}: 2952, 1731, 1600, 1495, 1437, 1369, 1197, 1170, 1025, 974, 749, 695.

HRMS *m/z* (ESI+) calculated for $[C_{17}H_{22}NaO_4]^+$ = 313.1410, found: 313.1403.

Dimethyl 4-(2-(*o*-tolyl)ethylidene)heptanedioate (3f)



MW (g.mol^{-1}): 304.39 **Molecular formula:** $C_{18}H_{24}O_4$

Prepared following general procedure A from **1a** (119 mg, 0.459 mmol) and 2-methylphenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 90:10) afforded **3f** as a pale-yellow oil in 83% yield (116 mg, 0.381 mmol).

Rf (PE/Et_2O = 9:1) = 0.26

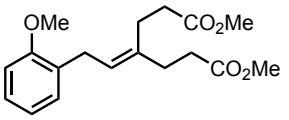
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.08 (m, 4H), 5.34 (t, *J* = 7.1 Hz, 1H), 3.68 (s, 3H), 3.63 (s, 3H), 3.34 (d, *J* = 7.1 Hz, 2H), 2.52-2.36 (m, 8H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.62, 173.57, 139.2, 136.8, 136.2, 130.2, 128.5, 126.2, 126.1, 125.1, 51.8, 51.6, 33.0, 32.8, 31.6, 31.5, 25.7, 19.6.

IR (neat) cm^{-1}: 2950, 1732, 1604, 1491, 1435, 1356, 1251, 1194, 1161, 1106, 1075, 1029, 985, 872, 838, 742.

HRMS *m/z* (ESI+) calculated for $[C_{18}H_{24}NaO_4]^+$ = 327.1567, found: 327.1557.

Dimethyl 4-(2-(2-methoxyphenyl)ethylidene)heptanedioate (3g)



MW (g.mol^{-1}): 320.39 **Molecular formula:** $C_{18}H_{24}O_5$

Prepared following general procedure A from **1a** (120 mg, 0.461 mmol) and 2-methoxyphenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 90:10) afforded **3g** as a pale-yellow oil in 75% yield (111 mg, 0.346 mmol).

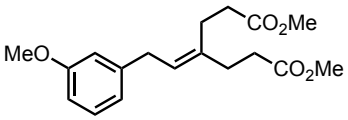
Rf (PE/Et_2O = 8:2) = 0.25

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (td, *J* = 8.1, 1.7 Hz, 1H), 7.08 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.87 (td, *J* = 7.4, 1.1 Hz, 1H), 6.83 (dd, *J* = 8.1, 1.1 Hz, 1H), 5.38 (t, *J* = 7.4 Hz, 1H), 3.82 (s, 3H), 3.67 (s, 3H), 3.62 (s, 3H), 3.35 (d, *J* = 7.4 Hz, 2H), 2.51-2.33 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 157.3, 136.4, 129.3, 127.2, 125.2, 120.5, 110.2, 55.3, 51.6, 51.5, 33.0, 31.6, 28.1, 25.6. **IR** (neat) cm^{-1}: 2950, 2838, 1732, 1599, 1587, 1492, 1456, 1436, 1356, 1290, 1240, 1194, 1160, 1108, 1076, 1050, 1028, 984, 874, 837, 753.

HRMS *m/z* (ESI+) calculated for $[C_{18}H_{24}NaO_5]^+$ = 343.1516, found: 343.1504.

Dimethyl 4-(2-(3-methoxyphenyl)ethylidene)heptanedioate (3h)



MW (g.mol^{-1}): 320.39 **Molecular formula:** $C_{18}H_{24}O_5$

Prepared following general procedure A from **1a** (119 mg, 0.460 mmol) and 3-methoxyphenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 90:10 to 80:20) afforded **3h** as a pale-yellow oil in 63% yield (93 mg, 0.290 mmol).

Rf (PE/Et_2O = 8:2) = 0.23

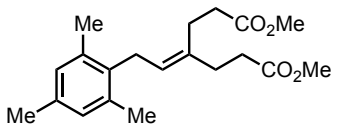
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.8 Hz, 1H), 6.72 (m, 3H), 5.39 (t, *J* = 7.4 Hz, 1H), 3.78 (s, 3H), 3.66 (s, 3H), 3.63 (s, 3H), 3.36 (d, *J* = 7.4 Hz, 2H), 2.49-2.34 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 173.5, 159.8, 142.6, 136.9, 129.4, 125.4, 120.7, 114.1, 111.3, 55.2, 51.74, 51.65, 33.9, 32.9, 31.4, 25.7.

IR (neat) cm^{-1}: 2951, 2837, 1732, 1599, 1584, 1488, 1435, 1356, 1256, 1194, 1159, 1078, 1041, 984, 863, 778, 734, 694.

HRMS *m/z* (ESI+) calculated for $[C_{18}H_{24}NaO_5]^+$ = 343.1516, found: 343.1504.

Dimethyl 4-(2-mesitylethylidene)heptanedioate (3i)



MW (g.mol^{-1}): 332.44 **Molecular formula:** $C_{20}H_{28}O_4$

Prepared following general procedure A from **1a** (129 mg, 0.499 mmol) and 2,4,6-trimethylphenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 90:10 to 80:20) afforded **2h** as a pale-yellow oil in 85% yield (141 mg, 0.424 mmol).

Rf (PE/Et_2O = 8:2) = 0.34

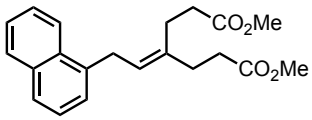
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 2H), 5.05 (t, *J* = 6.4 Hz, 1H), 3.72 (s, 3H), 3.60 (s, 3H), 3.32 (d, *J* = 6.4 Hz, 2H), 2.58-2.30 (m, 8H), 2.26 (s, 3H), 2.24 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 173.6, 136.2, 136.1, 135.4, 134.8, 128.9, 125.1, 51.8, 51.6, 33.0, 32.7, 31.5, 28.0, 25.8, 20.9, 20.1.

IR (neat) cm^{-1}: 2950, 1735, 1613, 1484, 1436, 1355, 1297, 1250, 1195, 1163, 1075, 1029, 985, 889, 851.

HRMS *m/z* (ESI+) calculated for $[C_{20}H_{28}NaO_4]^+$ = 355.1880, found: 355.1863.

Dimethyl 4-(2-(naphthalen-1-yl)ethylidene)heptanedioate (3j)



MW (g.mol^{-1}): 340.42 **Molecular formula:** $C_{21}H_{24}O_4$

Prepared following general procedure A from **1a** (119 mg, 0.459 mmol) and 1-naphthylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 90:10) afforded **3j** as a pale-yellow oil in 66% yield (103 mg, 0.303 mmol).

Rf (PE/Et_2O = 8:2) = 0.29

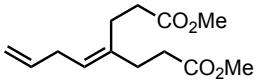
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 1H), 7.86 (dd, *J* = 7.4, 2.3 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.50 (dtd, *J* = 14.1, 6.9, 1.6 Hz, 2H), 7.39 (dd, *J* = 8.2, 6.9 Hz, 1H), 7.29 (d, *J* = 6.4 Hz, 1H), 5.50 (t, *J* = 7.1 Hz, 1H), 3.82 (d, *J* = 7.1 Hz, 2H), 3.68 (s, 3H), 3.59 (s, 3H), 2.60-2.54 (m, 2H), 2.50-2.38 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 173.6, 137.1, 137.1, 134.0, 132.0, 128.8, 126.9, 126.0, 125.7, 125.7, 125.7, 125.4, 123.9, 51.8, 51.7, 33.0, 32.9, 31.5, 31.3, 25.9.

IR (neat) cm^{-1}: 2949, 1731, 1434, 1355, 1253, 1194, 1162, 1016, 984, 876, 791, 775, 498.

HRMS *m/z* (ESI+) calculated for $[C_{21}H_{25}O_4]^+$ = 341.1747, found: 341.1740.

Dimethyl 4-(but-3-en-1-ylidene)heptanedioate (3k)



MW (g.mol^{-1}): 240.30 **Molecular formula:** $C_{13}H_{20}O_4$

Prepared following general procedure A from **1a** (122 mg, 0.470 mmol) and vinylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 90:10) afforded **3k** as a pale-yellow oil in 54% yield (61 mg, 0.254 mmol).

Rf (PE/Et_2O = 8:2) = 0.33

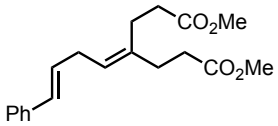
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (ddt, *J* = 17.1, 10.1, 6.1 Hz, 1H), 5.21 (t, *J* = 7.4 Hz, 1H), 5.01-4.90 (m, 2H), 3.65 (s, 3H), 3.64 (s, 3H), 2.75 (t, *J* = 6.7 Hz, 2H), 2.45-2.28 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 173.6, 137.02, 136.95, 124.1, 114.8, 51.74, 51.67, 33.0, 32.0, 31.5, 25.6.

IR (neat) cm^{-1}: 2954, 1732, 1438, 1174, 1062, 984.

HRMS *m/z* (ESI+) calculated for $[C_{13}H_{20}NaO_4]^+$ = 263.1254, found: 263.1251.

Dimethyl 4-(4-phenylbut-3-en-1-ylidene)heptanedioate (3l)



MW (g.mol^{-1}): 316.40 **Molecular formula:** $C_{19}H_{24}O_4$

Prepared following general procedure A from **1a** (93 mg, 0.358 mmol) and styrylmagnesium bromide (*E*/*Z* = 60:40). Purification by flash column chromatography over silica gel (PE/Et_2O 90:10) afforded **3l** as a mixture of *E* and *Z* diastereoisomers in 31% yield (35 mg, 0.111 mmol, *E*/*Z* = 60:40).

Major Isomer E[2]*:*

Rf (PE/Et_2O = 8:2) = 0.33

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.10 (m, 5H), 6.29 (d, *J* = 15.9 Hz, 1H), 6.08 (dt, *J* = 15.9, 6.4 Hz, 1H), 5.23 (t, *J* = 7.4 Hz, 1H), 3.59 (s, 6H), 2.86 (t, *J* = 6.9 Hz, 2H), 2.41-2.21 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 173.6, 137.7, 137.3, 130.2, 128.8, 128.6, 128.3, 127.1, 126.1, 124.2, 51.8, 51.74, 33.0, 31.5, 31.2, 25.7.

Minor Isomer Z[2]*:*

Rf (PE/Et_2O = 8:2) = 0.33

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.10 (m, 5H), 6.37 (d, *J* = 11.5 Hz, 1H), 5.51 (dt, *J* = 11.5, 7.3 Hz, 1H), 5.18 (t, *J* = 7.3 Hz, 1H), 3.58 (s, 3H), 3.57 (s, 3H), 2.96 (t, *J* = 6.9 Hz, 2H), 2.41-2.21 (m, 8H).

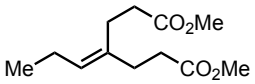
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 173.5, 137.4, 136.9, 130.8, 129.4, 128.6, 128.9, 126.1, 126.8, 125.2, 51.74, 51.71, 32.8, 31.5, 27.3, 25.7

IR[2] (neat) cm^{-1}: 2951, 1736, 1494, 1436, 1168, 994, 748, 699.

HRMS *m/z* (ESI+) calculated for $[C_{19}H_{25}O_4]^+$ = 317.1747, found: 317.1730.

[2] Sample contained 60% of the *E* isomer and 40% of the *Z* isomer.

Dimethyl 4-propylideneheptanedioate (3m)



MW (g.mol^{-1}): 228.29 **Molecular formula:** $C_{12}H_{20}O_4$

Prepared following general procedure A from **1a** (130 mg, 0.500 mmol) and methylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 90:10) afforded **3m** as a pale-yellow oil in 43% yield (49 mg, 0.215 mmol).

Rf (PE/Et_2O = 8:2) = 0.39

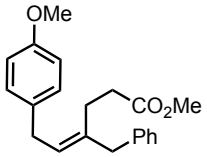
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (t, *J* = 7.5 Hz, 1H), 3.65 (s, 3H), 3.64 (s, 3H), 2.42-2.25 (m, 8H), 1.99 (p, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 173.7, 135.0, 129.1, 51.7, 51.6, 33.1, 31.5, 25.5, 21.1, 14.5.

IR (neat) cm^{-1}: 2954, 1733, 1436, 1358, 1254, 1195, 1165, 1056, 1023, 984, 893, 859.

HRMS *m/z* (ESI+) calculated for $[C_{12}H_{20}NaO_4]^+$ = 251.1254, found: 251.1244.

Methyl 4-benzyl-6-(4-methoxyphenyl)hex-4-enoate (3n)



MW (g.mol^{-1}): 324.42 **Molecular formula:** $C_{21}H_{24}O_3$

Prepared following general procedure A from **1b** (132 mg, 0.500 mmol) and 4-methoxyphenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 100:00 to 95:05) afforded **3n** as a mixture of *E* and *Z* diastereoisomers in 71% yield (115 mg, 0.355 mmol, *E*/*Z* = 53:47).

Major Isomer E[3]*:*

Rf (PE/Et_2O = 8:2) = 0.60

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.2 Hz, 2H), 7.23-7.17 (m, 3H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.48 (t, *J* = 7.5 Hz, 1H), 3.80 (s, 3H), 3.65 (s, 3H), 3.38 (d, *J* = 7.5 Hz, 2H), 3.37 (s, 2H) 2.44-2.32 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 158.0, 139.9, 137.5, 133.2, 129.3, 129.0, 128.5, 127.8, 126.3, 114.0, 55.4, 51.7, 43.6, 33.2, 33.0, 25.2.

Minor Isomer Z[4]*:*

Rf (PE/Et_2O = 8:2) = 0.60

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.24-7.18 (m, 3H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.49 (t, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 3.61 (s, 3H), 3.53 (s, 1H), 3.46 (d, *J* = 7.2 Hz, 1H), 2.45-2.30 (m, 4H).

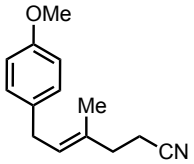
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 158.0, 139.6, 136.8, 133.2, 129.4, 128.63, 128.59, 126.23, 126.19, 114.0, 55.4, 51.6, 36.2, 33.5, 33.0, 31.8.

[3] Sample contained 95% of the *E* isomer and 5% of the *Z* isomer.
[4] Sample contained 71% of the *E* isomer and 29% of the *Z* isomer.

IR[4] (neat) cm^{-1}: 2950, 1736, 1610, 1510, 1435, 1300, 1243, 1172, 1033, 819, 731, 699.

HRMS *m/z* (ESI+) calculated for $[C_{21}H_{24}NaO_3]^+$ = 347.1618, found: 347.1612.

6-(4-Methoxyphenyl)-4-methylhex-4-enenitrile (3o)



MW (g.mol^{-1}): 215.30 **Molecular formula:** $C_{14}H_{17}NO$

Prepared following general procedure A from **1c** (100 mg, 0.650 mmol) and 4-methoxyphenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 90:10) afforded **3o** as a mixture of *E* and *Z* diastereoisomers in 40% yield (56 mg, 0.260 mmol, *E*/*Z* = 85:15).

Major Isomer E[5]*:*

Rf (PE/Et_2O = 8:2) = 0.38

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.47 (tq, *J* = 7.2, 1.3 Hz, 1H), 3.79 (s, 3H), 3.34 (d, *J* = 7.2 Hz, 2H), 2.50-2.35 (m, 4H), 1.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 132.8, 132.0, 129.2, 126.6, 119.5, 113.9, 55.3, 35.0, 33.3, 16.3, 15.8.

Minor Isomer Z[5]*:*

Rf (PE/Et_2O = 8:2) = 0.38

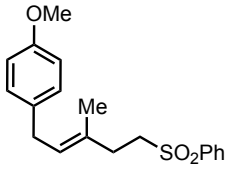
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.52 (t, *J* = 7.3, 1H), 3.79 (s, 3H), 3.34 (d, *J* = 7.3 Hz, 2H), 2.50-2.35 (m, 4H), 1.79 (q, *J* = 1.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 132.8, 131.8, 129.2, 127.8, 119.5, 114.0, 55.3, 33.2, 27.6, 22.8, 16.0.

IR[5] (neat) cm^{-1}: 2990, 1610, 1510, 1442, 1243, 1176, 1033, 818, 750.

HRMS *m/z* (ESI+) calculated for $[C_{14}H_{18}NO]^+$ = 216.1383, found: 216.1384.

1-Methoxy-4-(3-methyl-5-(phenylsulfonyl)pent-2-en-1-yl)benzene (3p)



MW (g.mol^{-1}): 330.44 **Molecular formula:** $C_{19}H_{22}O_3S$

Prepared following general procedure A from **1d** (91 mg, 0.339 mmol) and 4-methoxyphenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 90:10) afforded **3p** as a mixture of *E* and *Z* diastereoisomers in 66% yield (74 mg, 0.224 mmol, *E*/*Z* = 67:33).

Major Isomer E[6]*:*

Rf (PE/Et_2O = 8:2) = 0.18

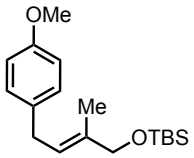
[5] Sample contained 85% of the *E* isomer and 15% of the *Z* isomer.
[6] Sample contained 67% of the *E* isomer and 33% of the *Z* isomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.89 (m, 2H), 7.69-7.63 (m, 1H), 7.57 (dt, *J* = 8.6, 6.8 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.81 (dd, *J* = 8.6, 2.2 Hz, 2H), 5.31 (tdd, *J* = 7.3, 2.7, 1.3 Hz, 1H), 3.77 (s, 3H), 3.24 (d, *J* = 7.3 Hz, 2H), 3.22-3.15 (m, 4H, 2H), 2.46-2.40 (m, 2H), 1.68 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 139.1, 133.8, 132.9, 131.4, 129.3, 129.2, 128.1, 126.2, 113.9, 55.3, 55.0, 33.3, 32.2, 16.1.

Minor Isomer Z[6]*:*
Rf (PE/Et_2O 8:2) = 0.18
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.89 (m, 2H), 7.69-7.63 (m, 1H), 7.57 (dt, *J* = 8.6, 6.8 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.81 (dd, *J* = 8.6, 2.2 Hz, 2H), 5.41 (t, *J* = 7.4 Hz, 1H), 3.78 (s, 3H), 3.22-3.15 (m, 2H), 3.14-3.08 (m, 2H), 2.56-2.50 (m, 2H), 1.67 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 139.0, 133.9, 132.8, 131.3, 129.4, 129.1, 128.1, 127.1, 113.95, 55.3, 54.5, 33.0, 25.0, 23.0.

IR[6] (neat) cm^{-1}: 2913, 1610, 1510, 1446, 1305, 1245, 1177, 1148, 1086, 1034, 825, 744, 689, 586, 537.
HRMS *m/z* (ESI+) calculated for $[C_{19}H_{22}NaO_3S]^+$ = 353.1182, found: 353.1175.

***tert*-Butyl((4-(4-methoxyphenyl)-2-methylbut-2-en-1-yl)oxy)dimethylsilane (3q)**



MW (g.mol^{-1}): 306.52 **Molecular formula:** $C_{18}H_{30}O_5Si$

Prepared following general procedure A from **1e** (118 mg, 0.479 mmol) and 4-methoxyphenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 97:03) afforded **3q** as a mixture of *E* and *Z* diastereoisomers in 75% yield (110 mg, 0.359 mmol, *E*/*Z* = 90:10).

Major Isomer E[7]*:*
Rf (PE/Et_2O 95:05) = 0.23
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.60 (tq, *J* = 7.4, 1.4 Hz, 1H), 4.08 (s, 2H), 3.80 (s, 3H), 3.36 (d, *J* = 7.4 Hz, 2H), 1.73 (s, 3H), 0.93 (s, 9H), 0.08 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 135.4, 133.5, 129.3, 123.7, 113.9, 68.7, 55.4, 33.0, 26.1, 18.6, 13.7, –5.1.

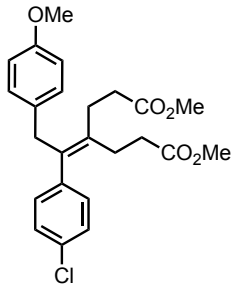
Minor Isomer Z[8]*:*
Rf (PE/Et_2O 95:05) = 0.23
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.40 (tq, *J* = 7.6, 1.3 Hz, 1H), 4.27 (s, 2H), 3.80 (s, 3H), 3.36 (d, *J* = 7.4 Hz, 2H), 1.81 (q, *J* = 1.3 Hz, 3H), 0.94 (s, 9H), 0.11 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 135.7, 133.4, 129.4, 125.5, 113.9, 61.9, 55.4, 33.1, 26.1, 21.4, 18.5, –5.1.

IR[8] (neat) cm^{-1}: 2953, 2928, 2855, 1611, 1511, 1463, 1300, 1245, 1175, 1106, 1065, 1039, 836, 775, 667.

[7] Sample contained 93% of the *E* isomer and 7% of the *Z* isomer.
[8] Sample contained 87% of the *E* isomer and 13% of the *Z* isomer.

HRMS *m/z* (ESI+) calculated for $[C_{18}H_{30}NaO_2Si]^+$ = 329.1907, found: 329.1911.

Dimethyl 4-(1-(4-methoxyphenyl)-2-(4-chlorophenyl)ethylidene)heptanedioate (3r)



MW (g.mol^{-1}): 430.93 **Molecular formula:** $C_{24}H_{27}ClO_5$

Prepared following general procedure A from **1f** (130 mg, 0.351 mmol) and 4-methoxyphenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 90:10 to 80:20) afforded **3r** as a pale-yellow oil in 59% yield (89 mg, 0.207 mmol).

Rf (PE/Et_2O = 8:2) = 0.17

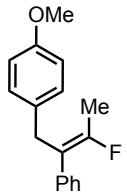
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H), 3.71 (s, 3H), 3.60 (s, 3H), 3.59 (d, *J* = 2.6 Hz, 2H), 2.68-2.61 (m, 2H), 2.54-2.48 (m, 2H), 2.33-2.27 (m, 2H), 2.25-2.18 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 173.4, 158.1, 141.0, 137.5, 133.9, 132.4, 130.9, 130.1, 129.7, 128.4, 113.8, 55.3, 51.9, 51.8, 39.5, 33.4, 33.3, 27.7, 26.5.

IR (neat) cm^{-1}: 2951, 2837, 1732, 1610, 1583, 1545, 1510, 1487, 1435, 1394, 1365, 1300, 1243, 1194, 1171, 1090, 1034, 1012, 984, 892, 834, 765, 706.

HRMS *m/z* (ESI+) calculated for $[C_{24}H_{27}ClNaO_5]^+$ = 453.1439, found: 453.1442.

1-(3-Fluoro-2-phenylbut-2-en-1-yl)-4-methoxybenzene (3s)



MW (g.mol^{-1}): 256.32 **Molecular formula:** $C_{17}H_{17}FO$

Prepared following general procedure A from **1g** (98 mg, 0.500 mmol) and 4-methoxyphenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/DCM 100:00 to 80:20) afforded **(*E*)-3s** (53 mg, 42% yield) and **(*Z*)-3s** (69 mg, 53% yield) respectively (*E*/*Z* = 44:56).

Minor isomer – (*E*)-3s:

Rf (PE/DCM = 9:1) = 0.24

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.20 (m, 3H, 7.08-7.05 (m, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 3.70 (d, J_F = 2.7 Hz, 2H), 1.93 (d, J_F = 17.9 Hz, 3H).

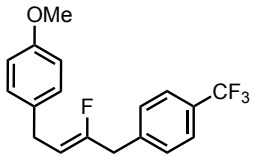
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 154.4 (d, *J* = 250.1 Hz), 139.0 (d, *J* = 8.8 Hz), 131.8 (d, *J* = 2.2 Hz), 129.8), 129.2 (d, *J* = 2.9 Hz), 128.3, 126.9, 118.8 (d, *J* = 18.7 Hz), 113.7, 55.3, 35.5 (d, *J* = 6.6 Hz), 22.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ -100.37 (q, *J* = 17.0 Hz, 1F).

IR (neat) cm^{-1}: 3002, 2923, 2835, 1693, 1611, 1584, 1510, 1493, 1463, 1442, 1382, 1301, 1244, 1175, 1108, 1071, 1035, 1010, 948, 818, 776, 751, 725, 700, 646, 617.
HRMS *m/z* (ESI+) calculated for $[C_{17}H_{18}FO]^+$ = 257.1336, found: 257.1328.

Major isomer – (*Z*)-3s*:*
Rf (PE/DCM = 9:1) = 0.20.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.12 (m, 4H), 7.09-7.04 (m, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 3.64 (s, 3H), 3.51 (s, 2H), 2.03 (d, J_F = 17.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 154.2, (d, *J* = 251.4 Hz), 137.5 (d, *J* = 1.7 Hz), 131.3 (d, *J* = 3.2 Hz), 129.2, 128.7 (d, *J* = 3.6Hz). 128.1, 126.8, 116.1 (d, *J* = 12.9 Hz), 113.9, 55.3, 36.8 (d, *J* = 5.1 Hz), 15.9 (d, *J* = 31.6 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ –97.72 (q, *J* = 17.5 Hz, 1F).
IR (neat) cm^{-1}: 3002, 2923, 2835, 1693, 1611, 1584, 1510, 1493, 1463, 1442, 1382, 1301, 1244, 1175, 1108, 1071, 1035, 1010, 948, 818, 776, 751, 725, 700, 646, 617.
HRMS *m/z* (ESI+) calculated for $[C_{17}H_{18}FO]^+$ = 257.1336, found: 257.1328.

1-(3-Fluoro-4-(4-(trifluoromethyl)phenyl)but-2-en-1-yl)-4-methoxybenzene (3t)



MW (g.mol^{-1}): 324.32 **Molecular formula:** $C_{18}H_{16}F_4O$

Prepared following general procedure A from **1h** (47 mg, 0.178 mmol) and 4-methoxyphenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 95:05) afforded **3t** as a mixture of *E* and *Z* diastereoisomers in 83% yield (48 mg, 0.148 mmol, *E*/*Z* = 18:82).

Minor Isomer E[9]*:*
Rf (PE/Et_2O = 8:2) = 0.85.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.43 (dt, *J* = 8.1 Hz, J_F = 20.7, 1H), 3.80 (s, 3H), 3.57 (d, J_F = 17.4 Hz, 2H), 3.37 (d, *J* = 7.4 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 157.4 (d, *J* = 255.0 Hz), 140.8, 132.4 (d, *J* = 1.8 Hz), 129.7 (q, *J* = 46.2 Hz), 129.3, 129.3, 125.6 (q, *J* = 3.7 Hz), 124.4 (q, J = 272.0 Hz), 114.1, 107.1 (d, *J* = 14.7 Hz), 55.4, 34.3 (d, *J* = 28.7 Hz), 30.9 (d, *J* = 9.5 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ –62.42 (s, 3F), -101.92 (q, *J* = 22.6 Hz, 1F).

Major Isomer Z[9]*:*
Rf (PE/Et_2O = 8:2) = 0.85.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.82 (dt, *J* = 7.4 Hz, J_F = 35.6 Hz, 1H), 3.80 (s, 3H), 3.57 (d, J_F = 17.4 Hz, 2H), 3.38 (d, *J* = 7.4 Hz, 2H).

[9] Sample contained 18% of the *E* isomer and 82% of the *Z* isomer.

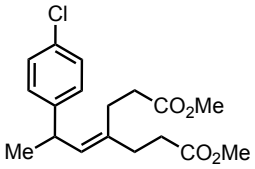
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 157.5 (d, *J* = 255.0 Hz), 140.8, 132.4 (d, *J* = 1.8 Hz), 129.7 (q, *J* = 46.2 Hz), 129.3, 129.30, 125.6 (q, *J* = 3.7 Hz), 124.4 (q, J = 272.0 Hz), 114.1, 107.2 (d, *J* = 14.7 Hz), 55.4, 38.6 (d, *J* = 29.1 Hz), 29.2 (d, *J* = 5.5 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.42 (s, 3F), -109.41 (dt, *J* = 35.6, 17.4 Hz, 1F).

IR[9] (neat) cm^{-1}: 2936, 2838, 1705, 1602, 1512, 1420, 1324, 1247, 1164, 1123, 1066, 1034, 1020, 815, 410.

HRMS *m/z* (ESI+) calculated for $[C_{18}H_{17}F_4O]^+$ = 325.1210, found: 325.1215.

Dimethyl 4-(2-(4-chlorophenyl)propylidene)heptanedioate (3u)



MW (g.mol^{-1}): 338.83 **Molecular formula:** $C_{18}H_{23}ClO_4$

Prepared following general procedure A from **1i** (291 mg, 1.063 mmol) and 4-chlorophenylmagnesium bromide. Purification by flash column chromatography over silica gel (PE/Et_2O 90:10 to 87:13) afforded **3u** as a transparent oil in 30% yield (108 mg, 0.319 mmol).

Rf (PE/Et_2O = 8:2) = 0.17.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 5.30 (d, *J* = 9.6 Hz, 1H), 3.71-3.66 (m, 1H), 3.65 (s, 3H), 3.61 (s, 3H), 2.45-2.39 (m, 4H), 2.36-2.30 (m, 4H), 1.26 (d, *J* = 6.9 Hz, 3H).

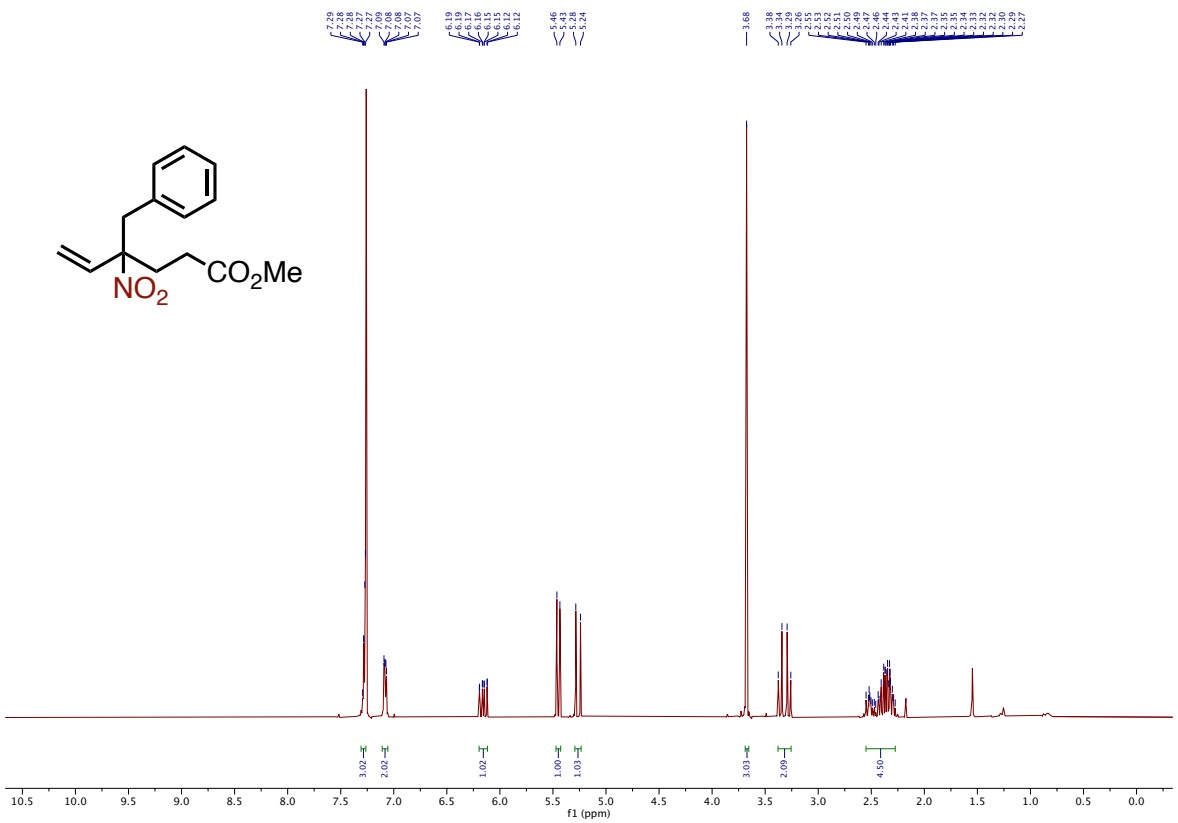
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 173.5, 145.1, 135.2, 132.0, 131.7, 128.6, 128.3, 51.8, 51.7, 37.2, 33.0, 32.9, 31.4, 25.8, 22.8.

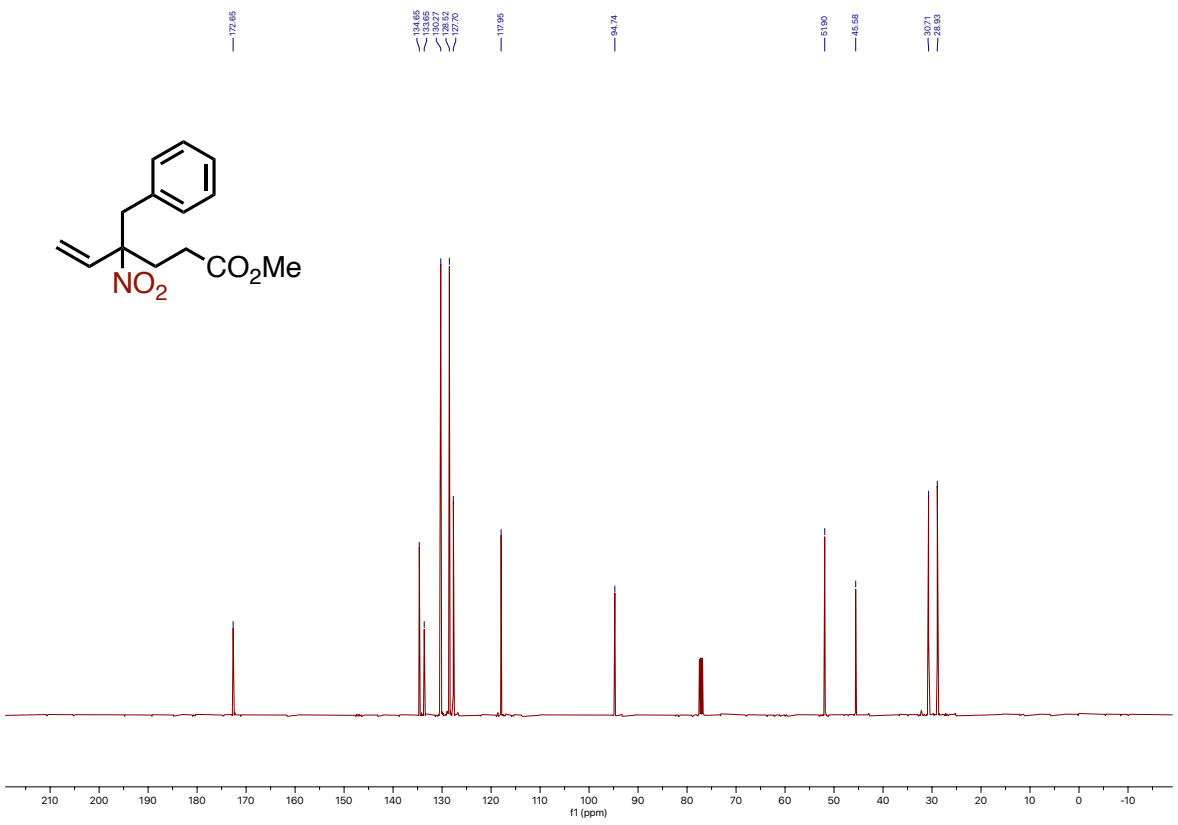
IR (neat) cm^{-1}: 2939, 1737, 1491, 1436, 1344, 1251, 1188, 1169, 1094, 1012, 906, 815, 747.

HRMS *m/z* (ESI+) calculated for $[C_{18}H_{24}ClO_4]^+$ = 339.1358, found: 339.1362.

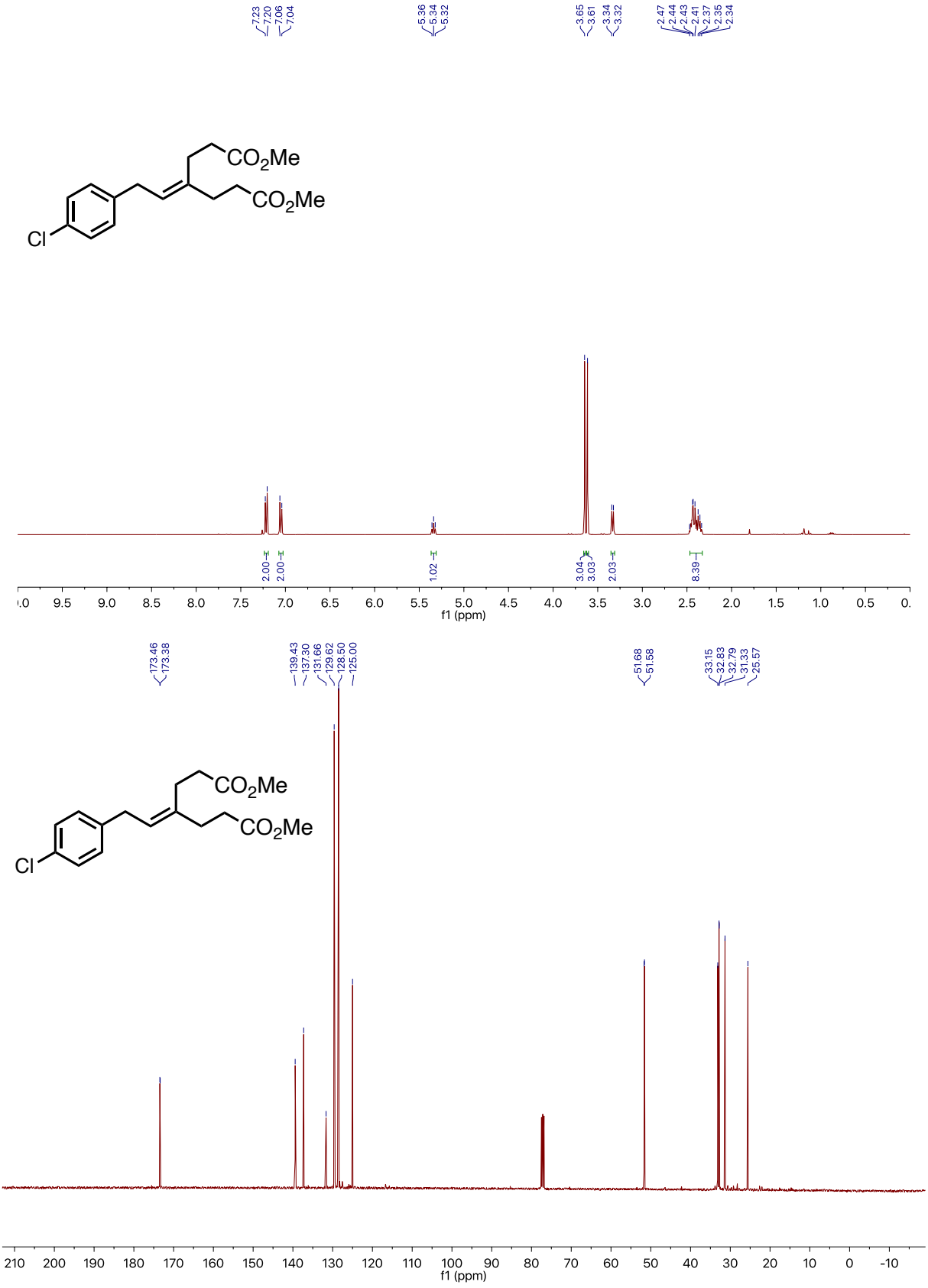
III. ^{1}H, ^{13}C and ^{19}F NMR spectra copies

Methyl 4-benzyl-4-nitrohex-5-enoate (1n)

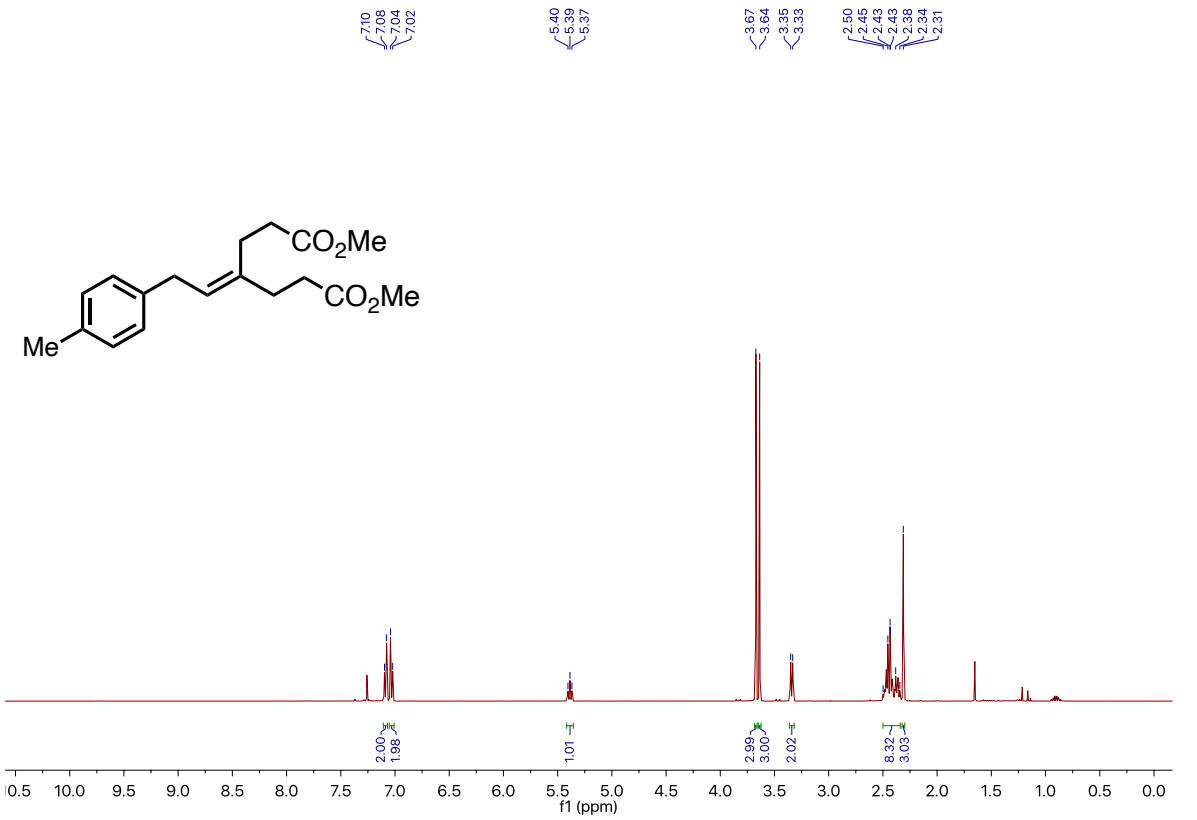


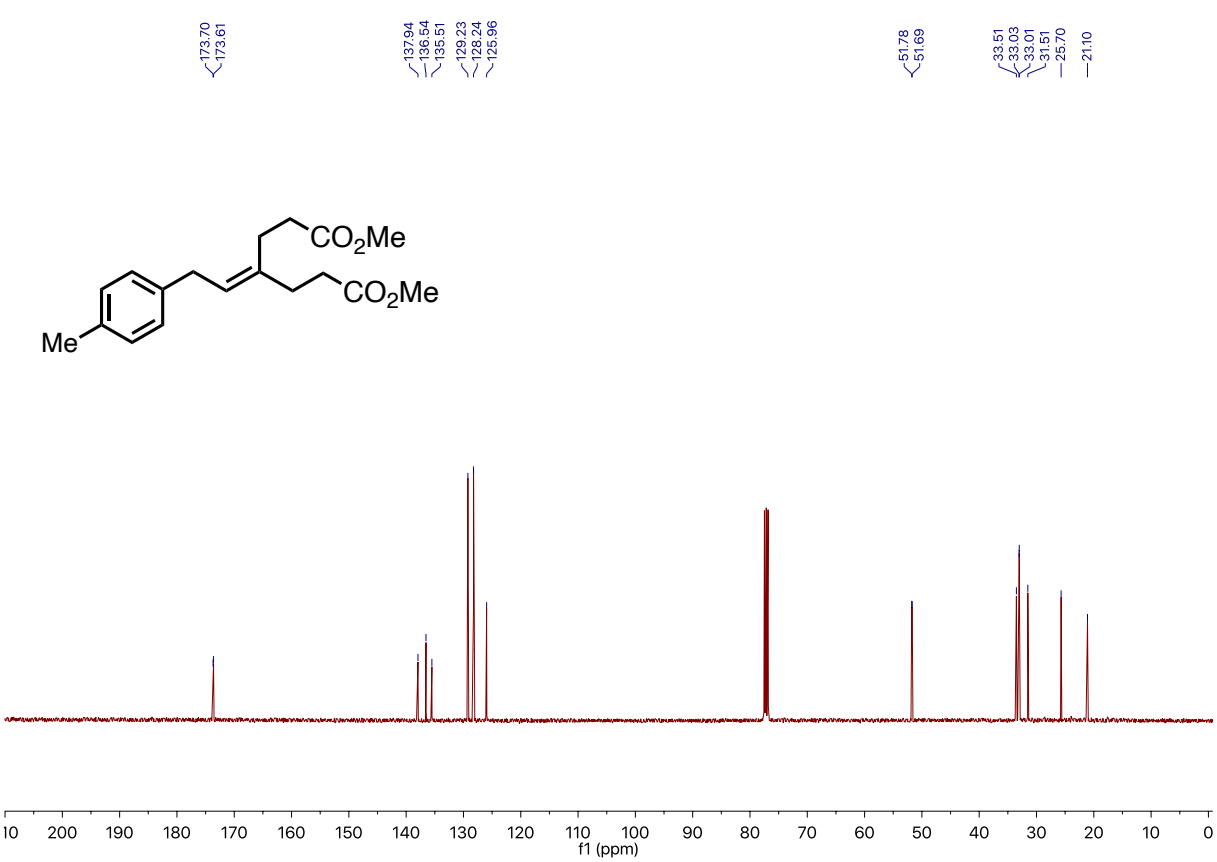


Dimethyl 4-(2-(4-chlorophenyl)ethylidene)heptanedioate (3a)

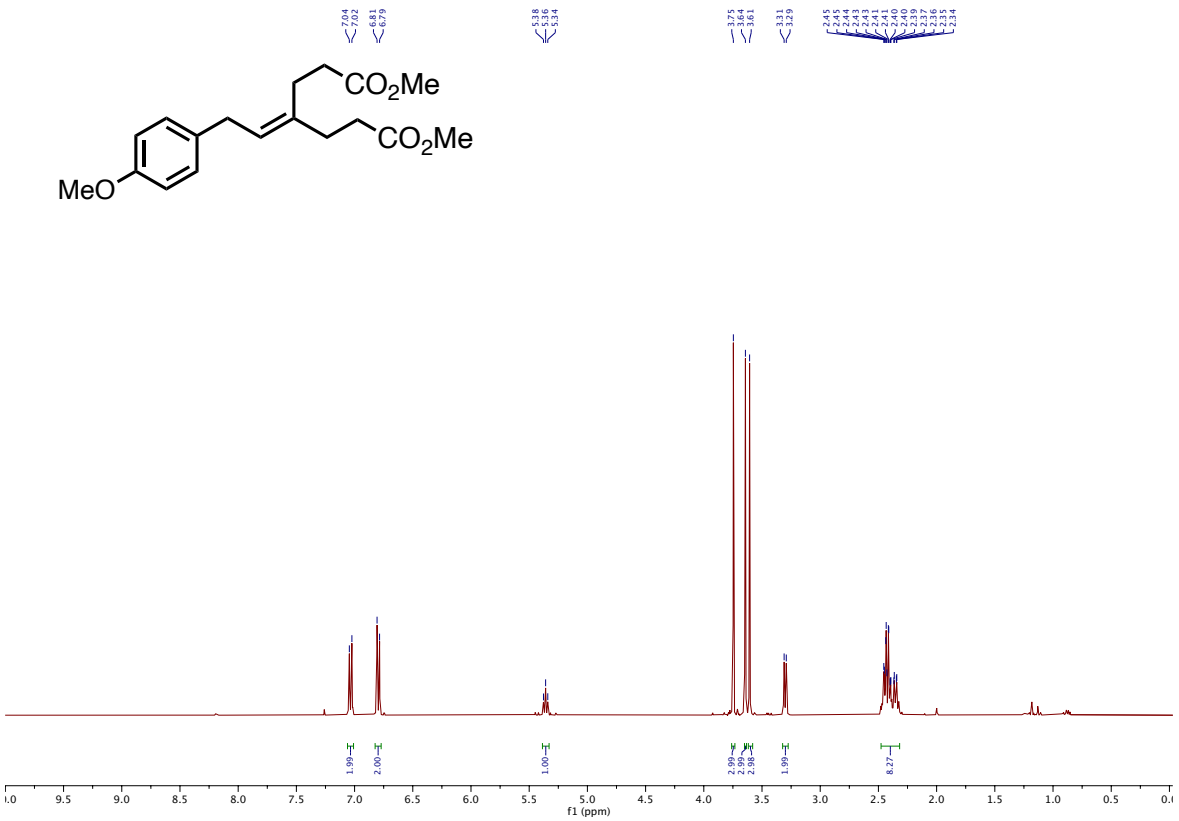


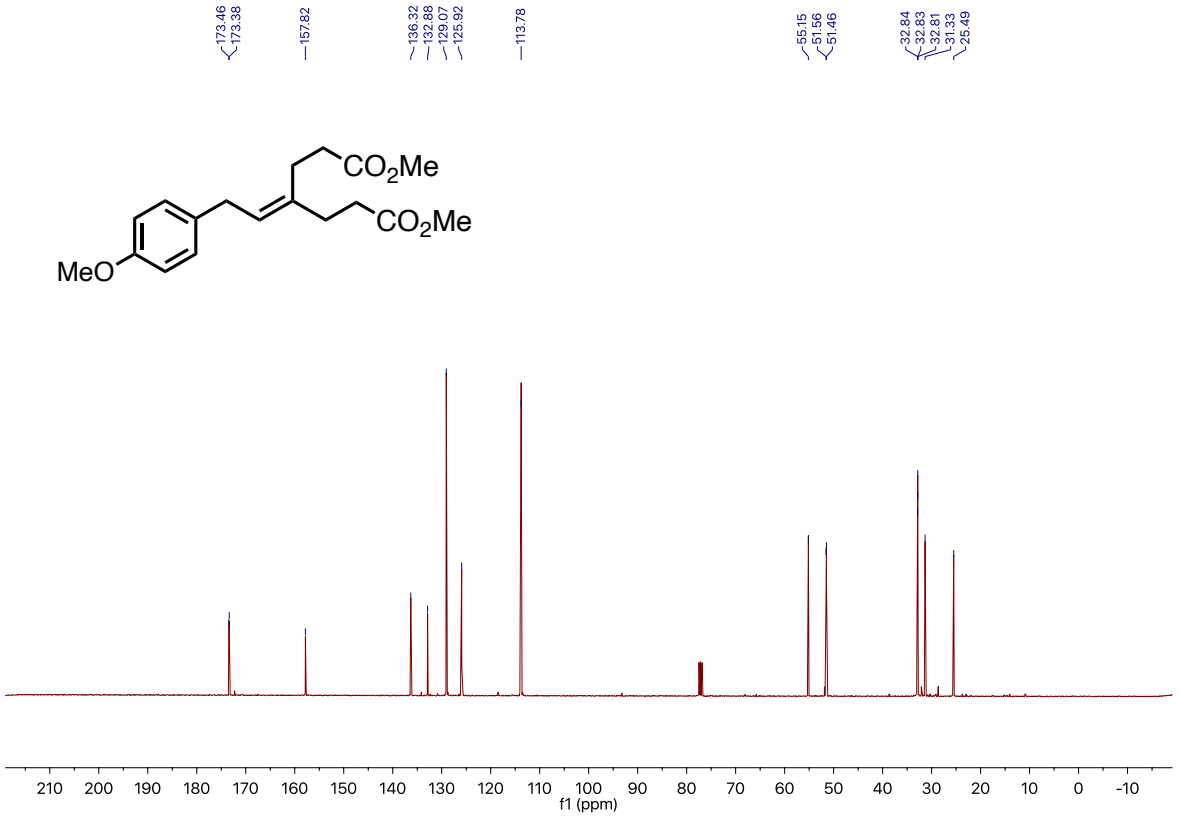
Dimethyl 4-(2-(*p*-tolyl)ethylidene)heptanedioate (3b)



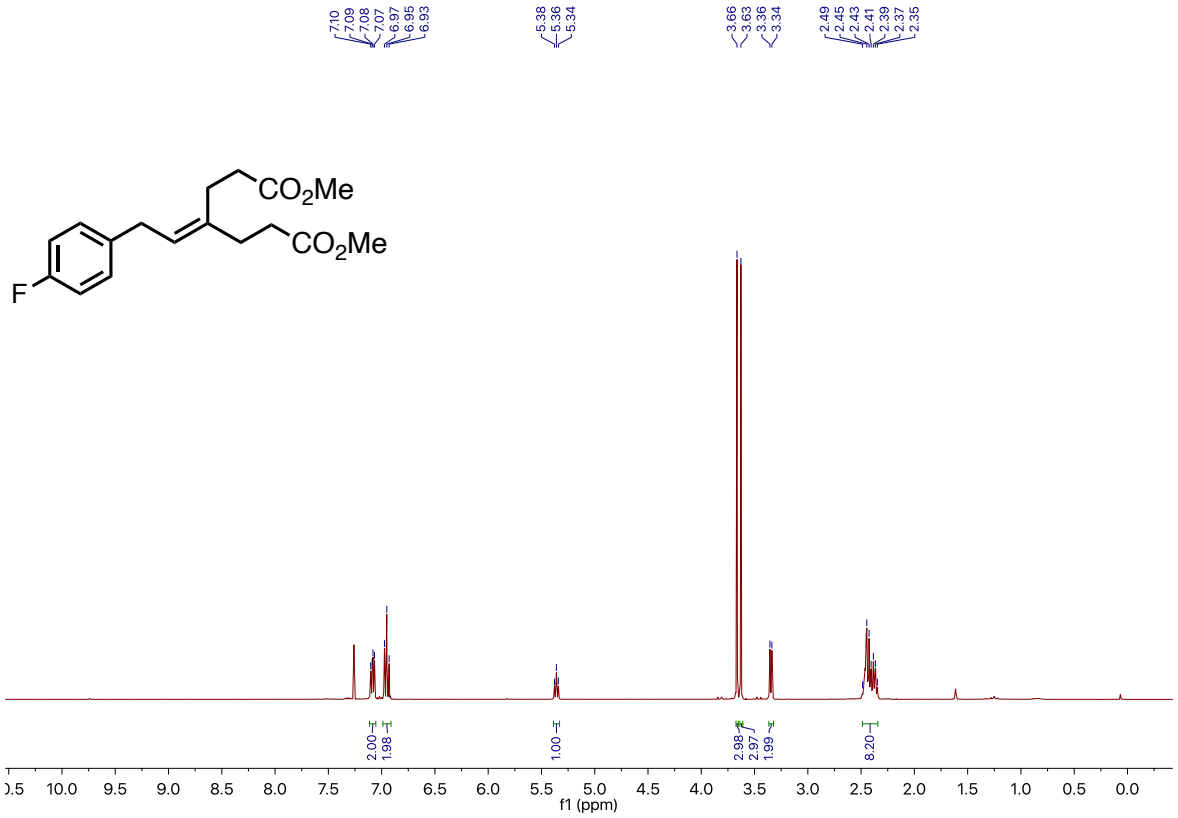


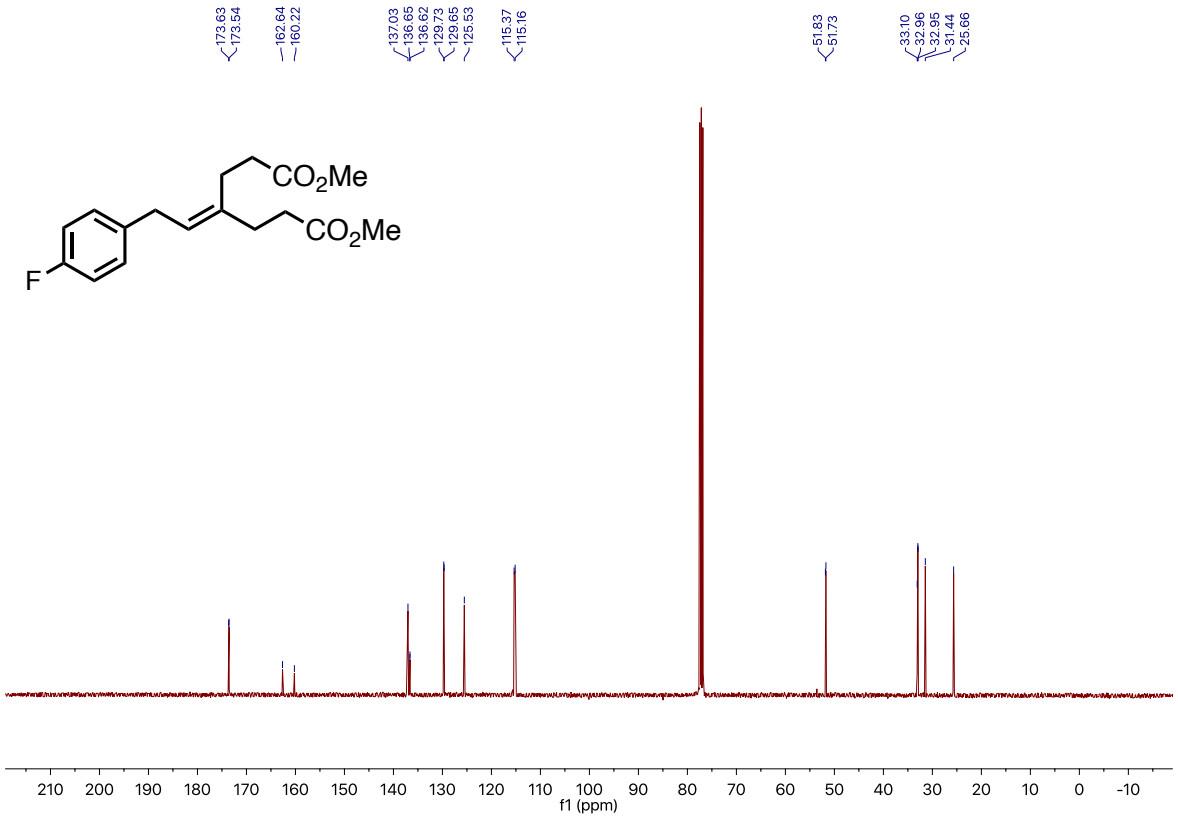
Dimethyl 4-(2-(4-methoxyphenyl)ethylidene)heptanedioate (3c)

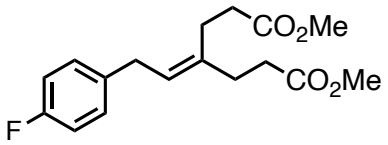




Dimethyl 4-(2-(4-fluorophenyl)ethylidene)heptanedioate (3d)






CO2Me
CO2Me
F

111.93
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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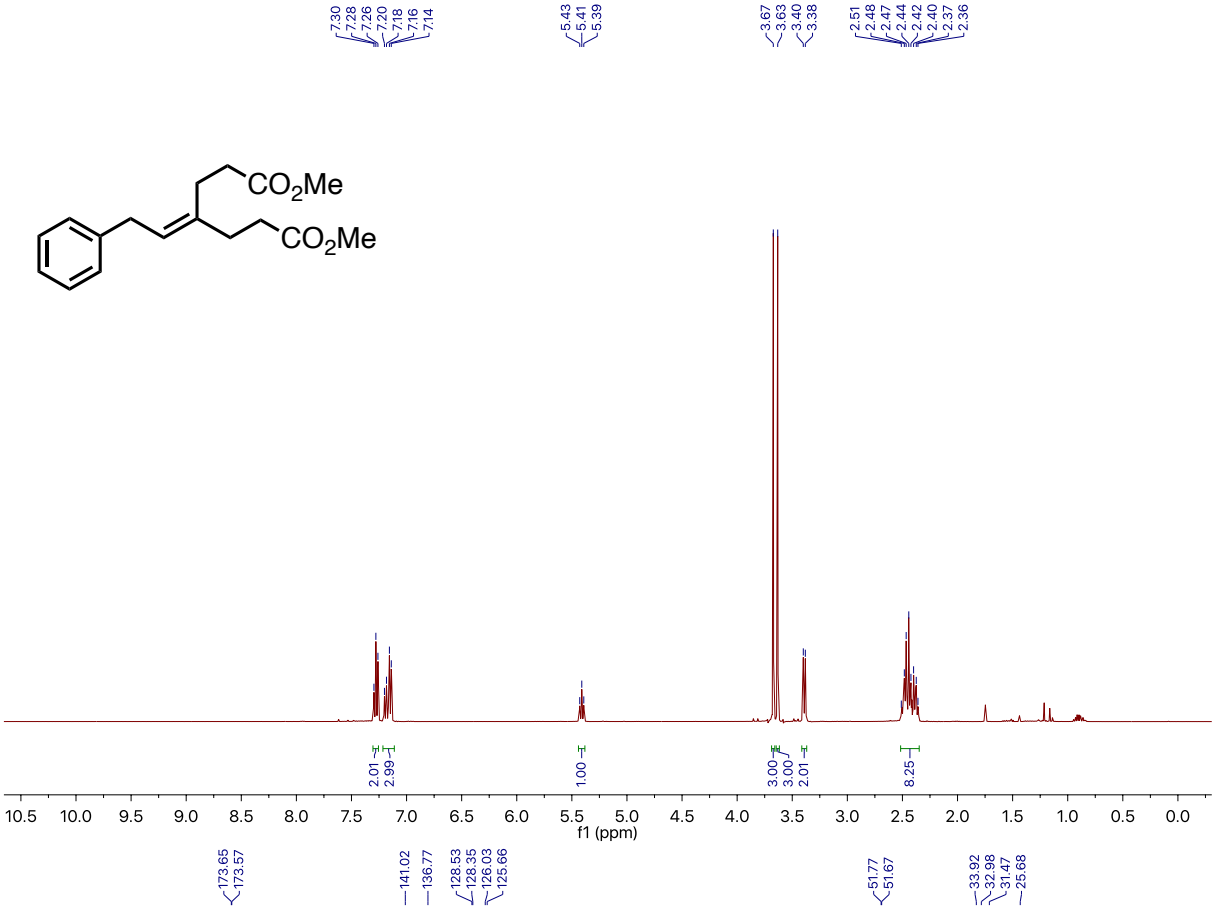
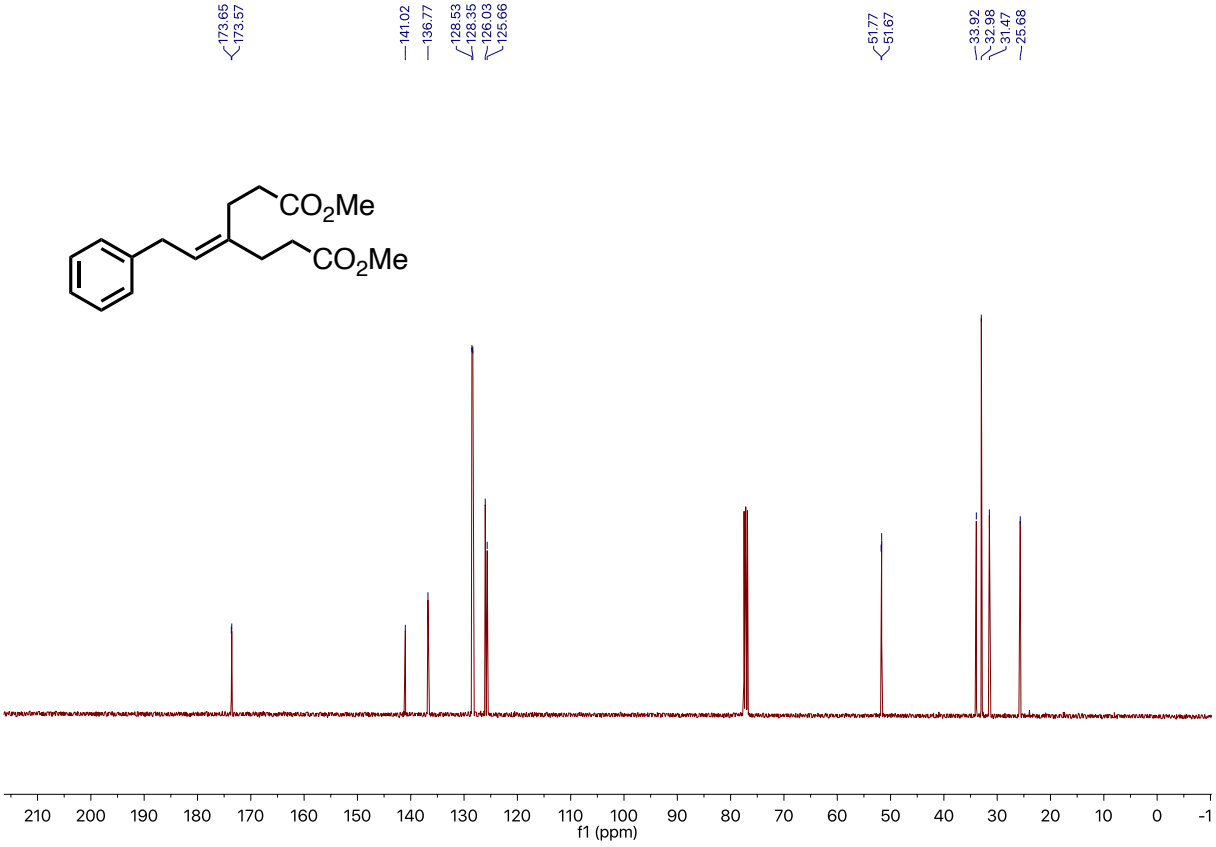
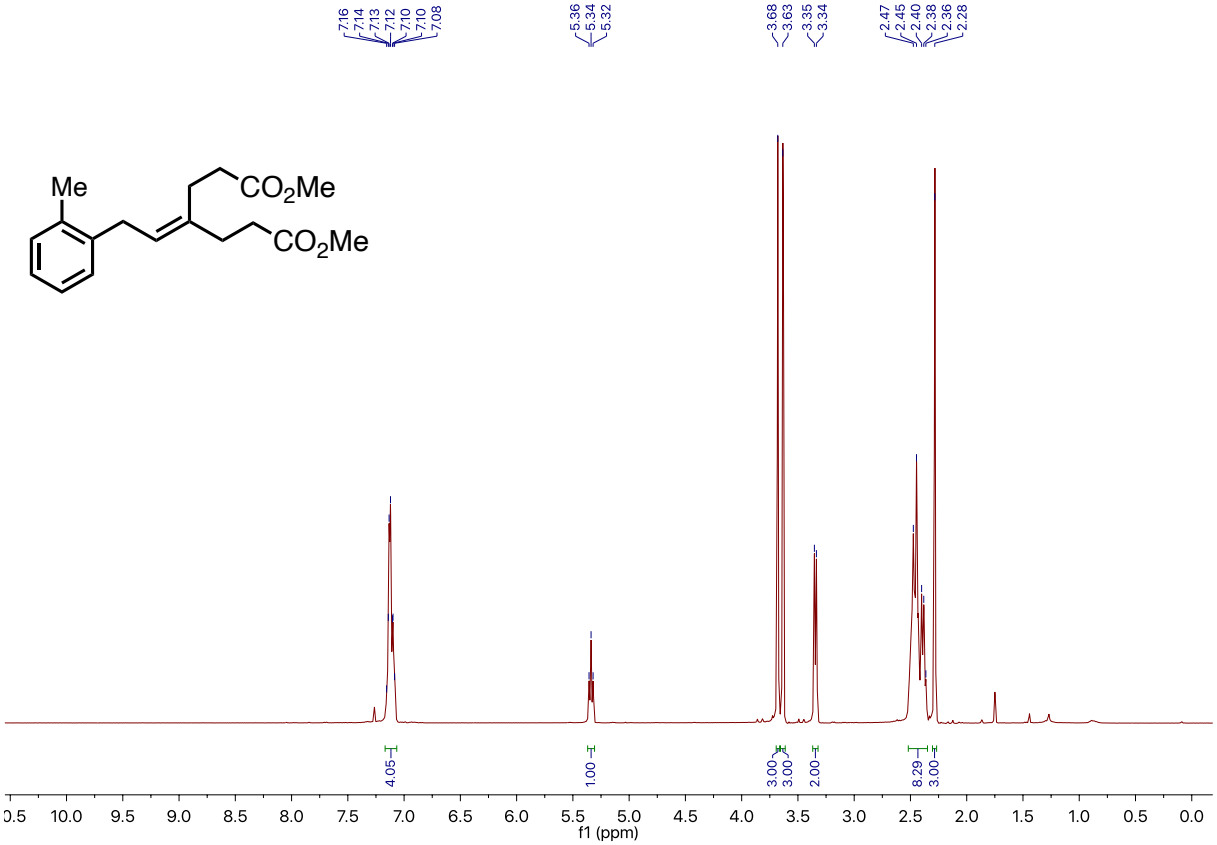
-180
-190
-200
-210
f1 (ppm)

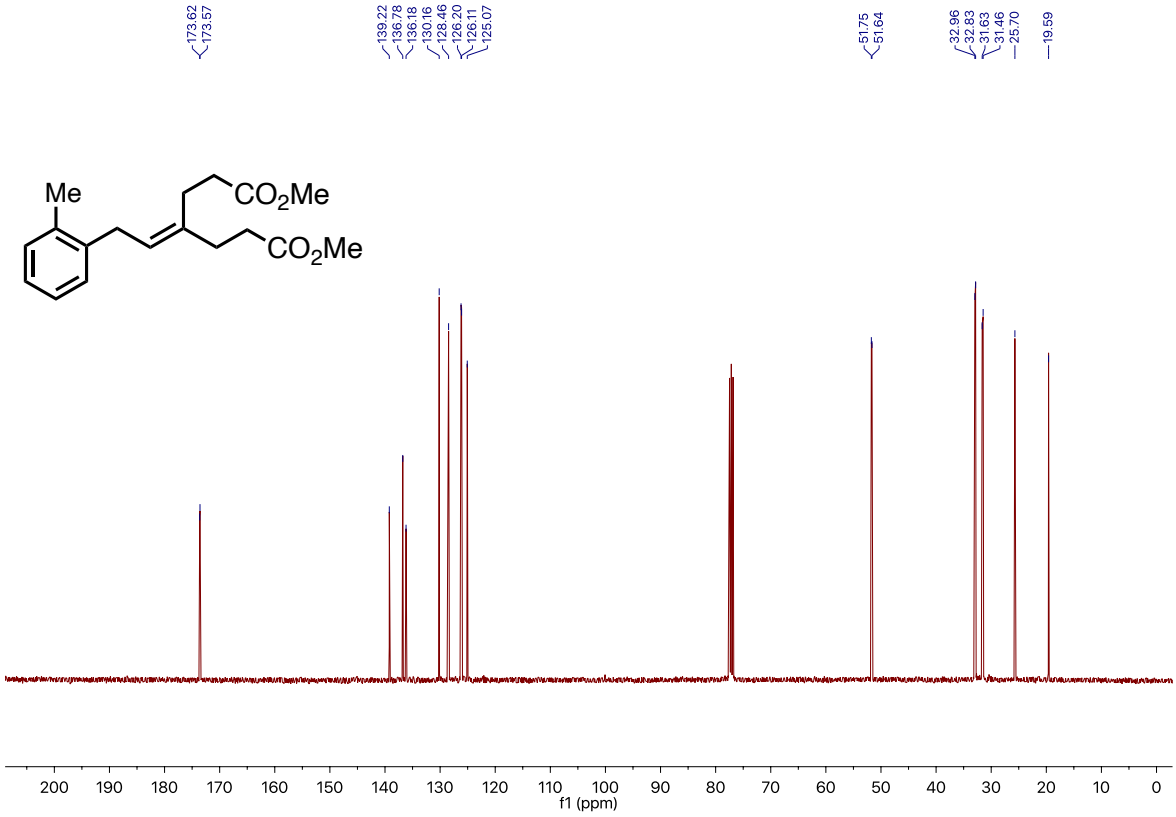
Dimethyl 4-(2-phenylethylidene)heptanedioate (3e)



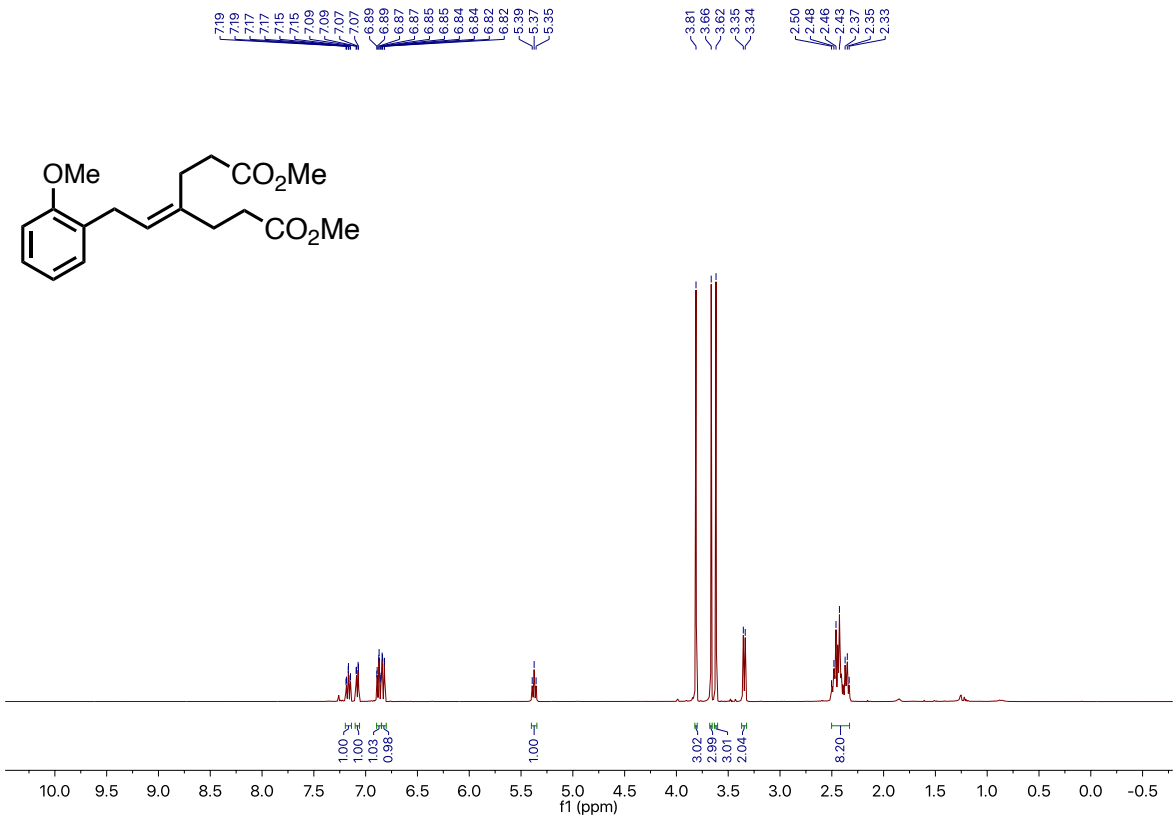


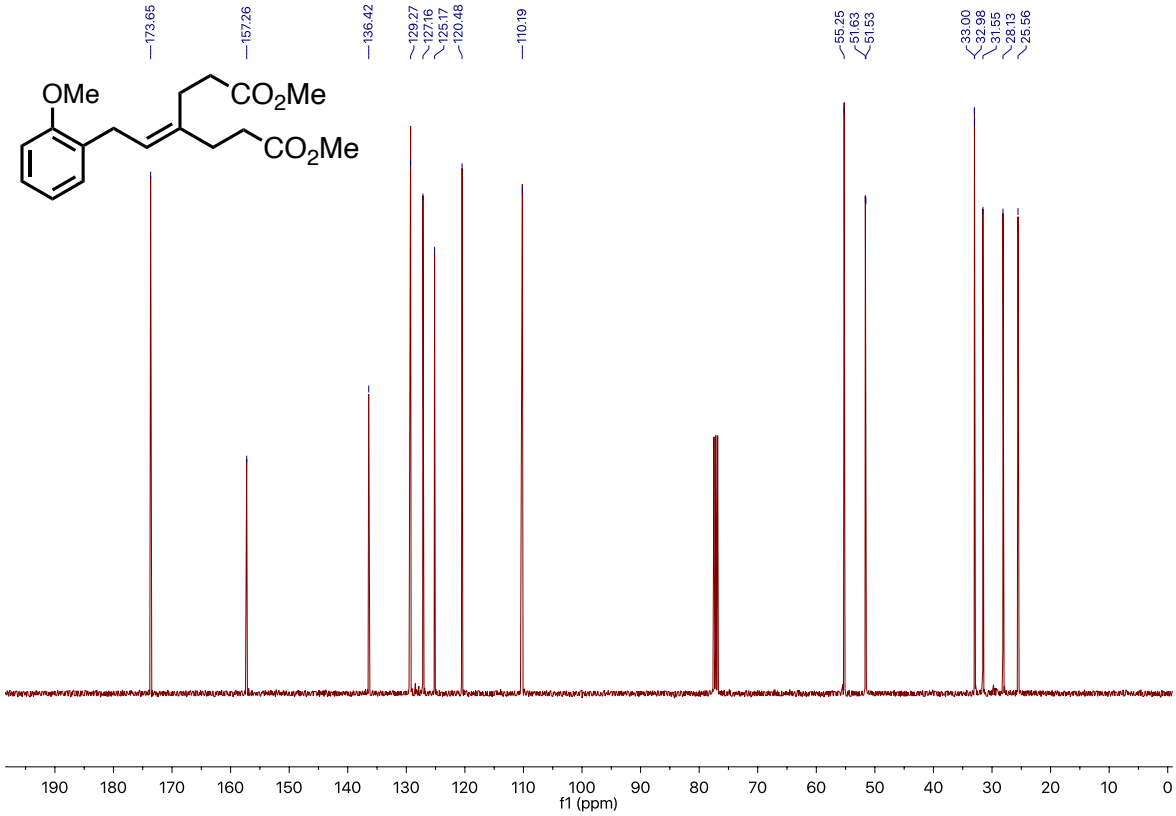
Dimethyl 4-(2-(*o*-tolyl)ethylidene)heptanedioate (3f)



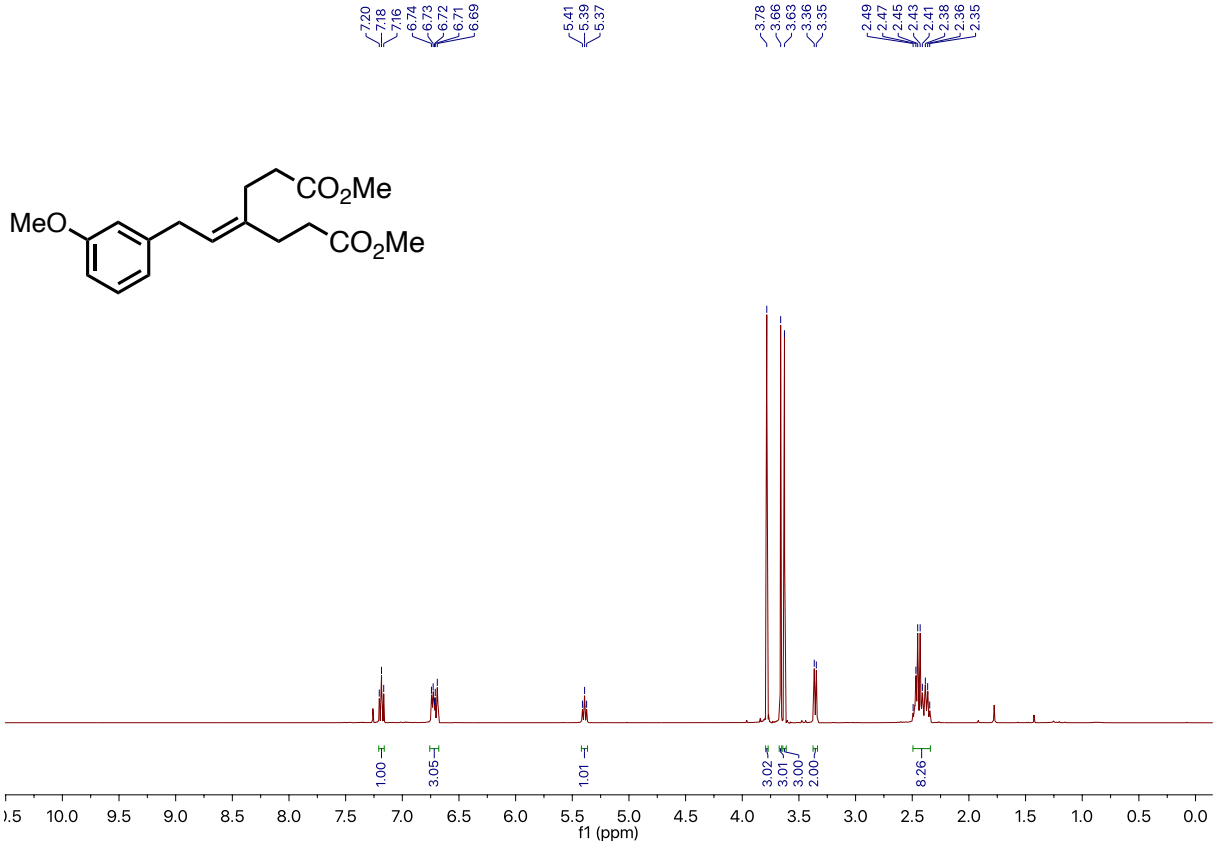


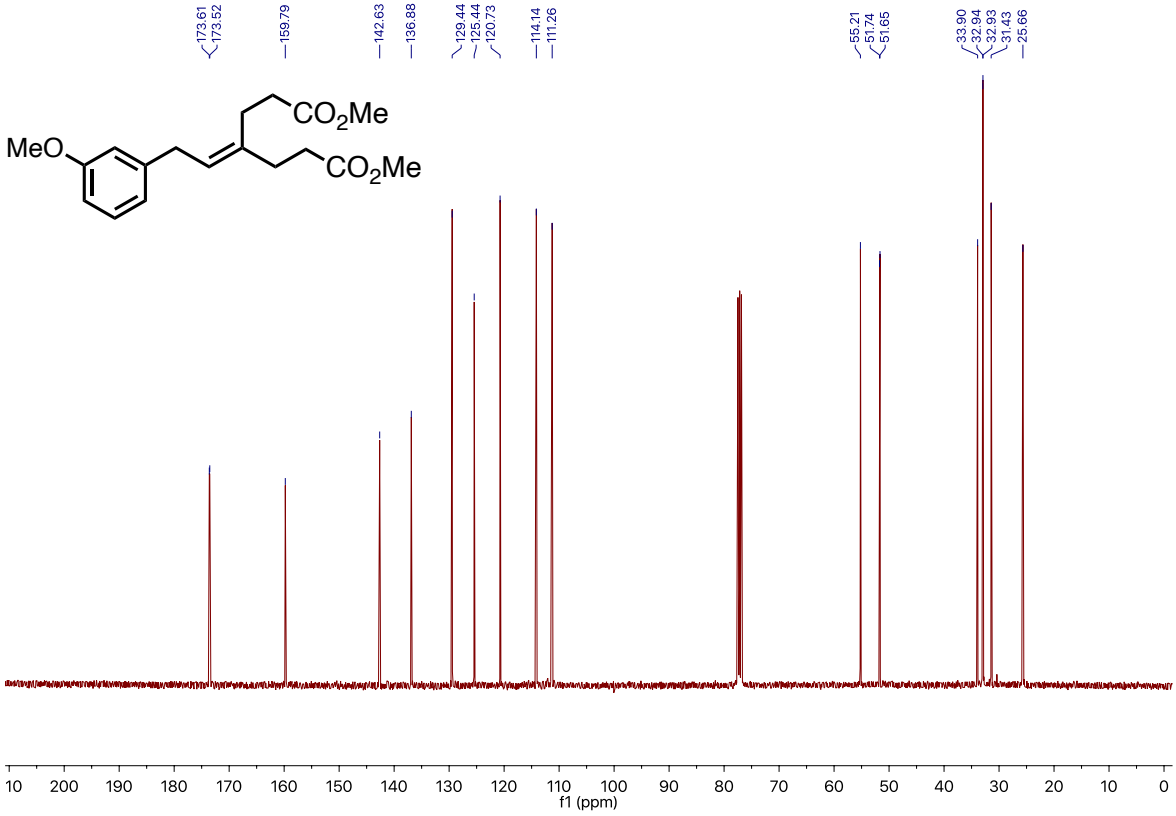
Dimethyl 4-(2-(2-methoxyphenyl)ethylidene)heptanedioate (3g)



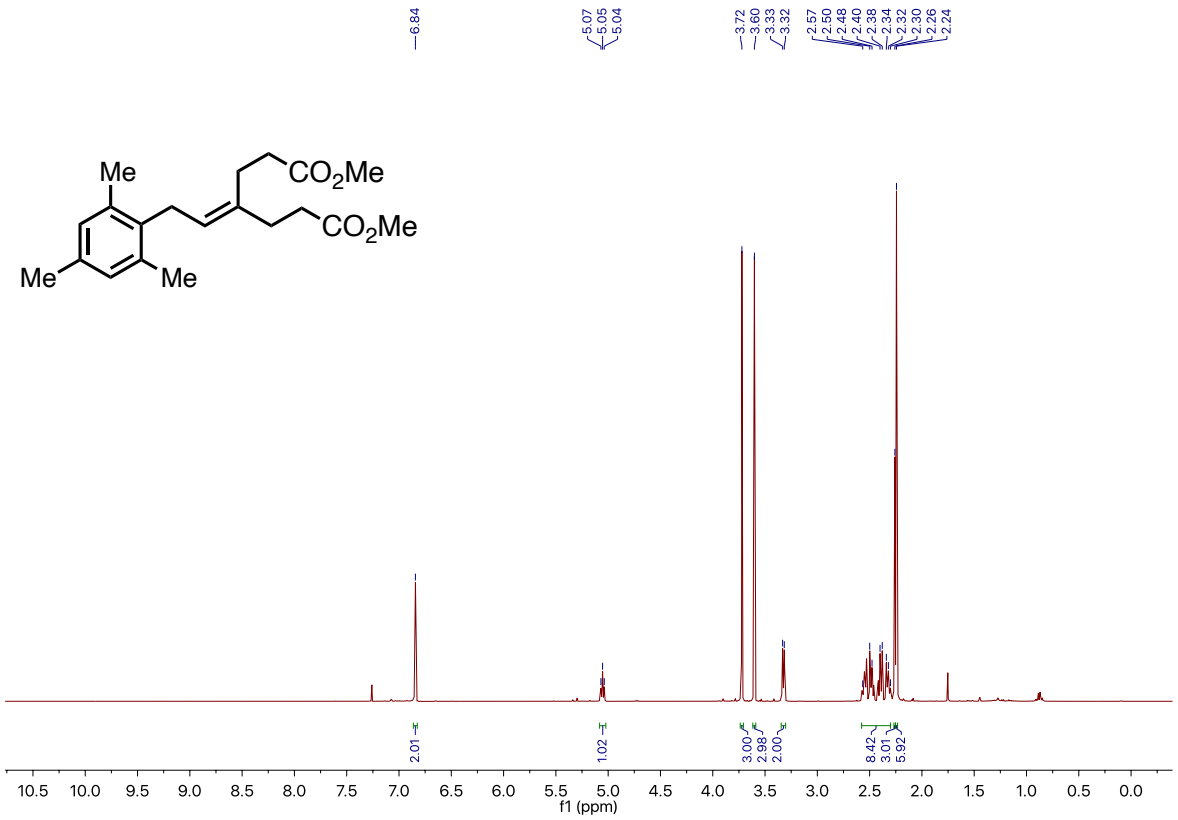


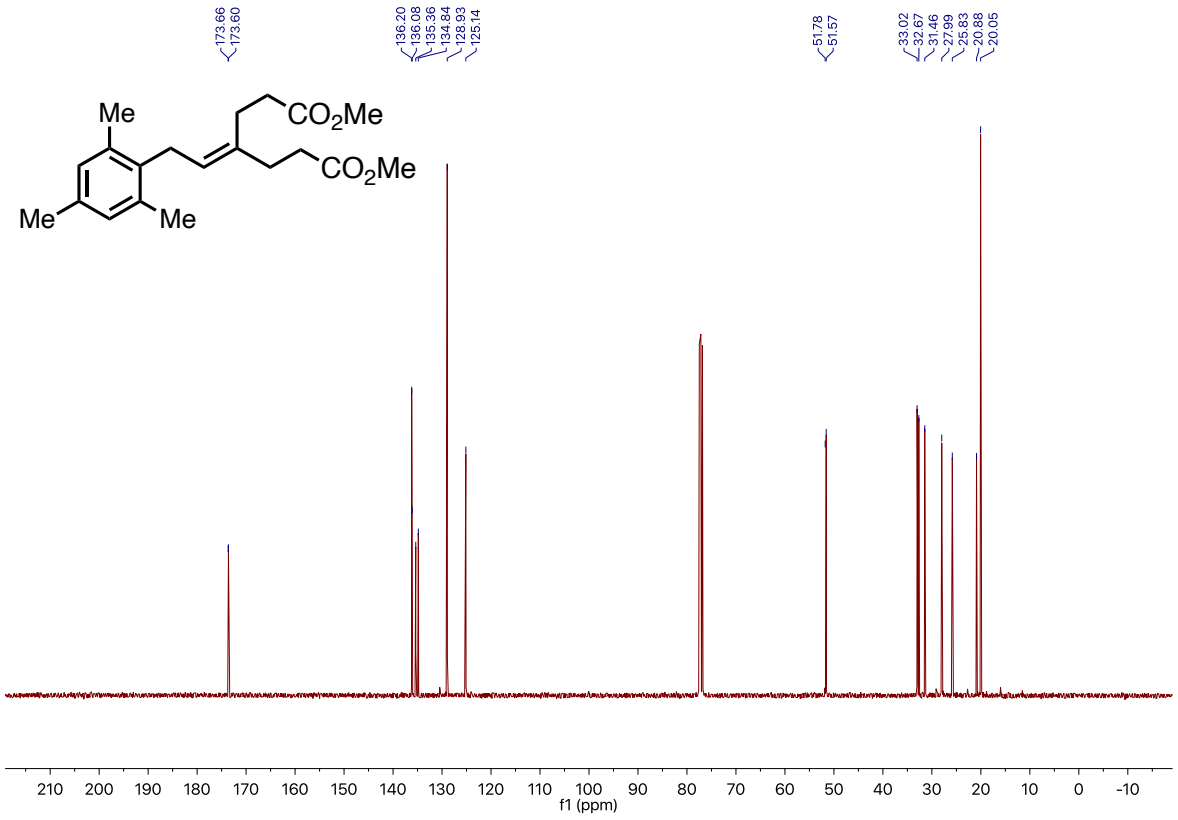
Dimethyl 4-(2-(3-methoxyphenyl)ethylidene)heptanedioate (3h)



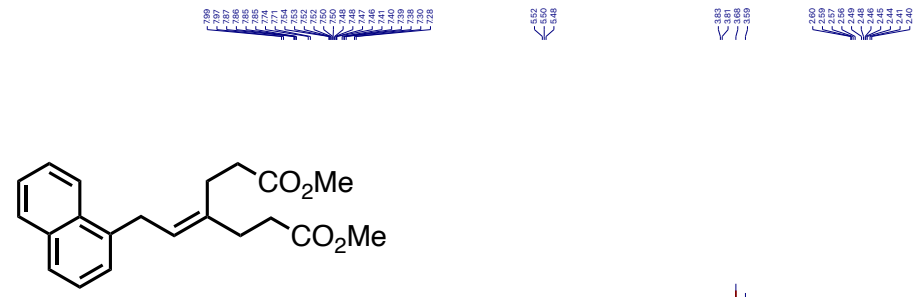


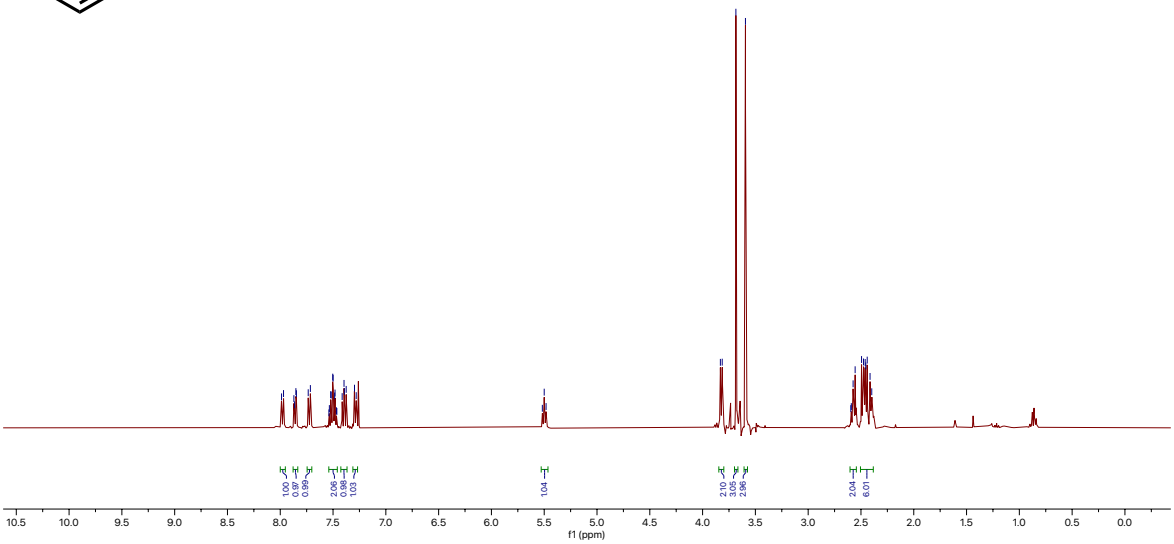
Dimethyl 4-(2-mesitylethylidene)heptanedioate (3i)

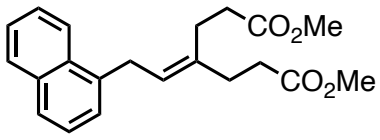


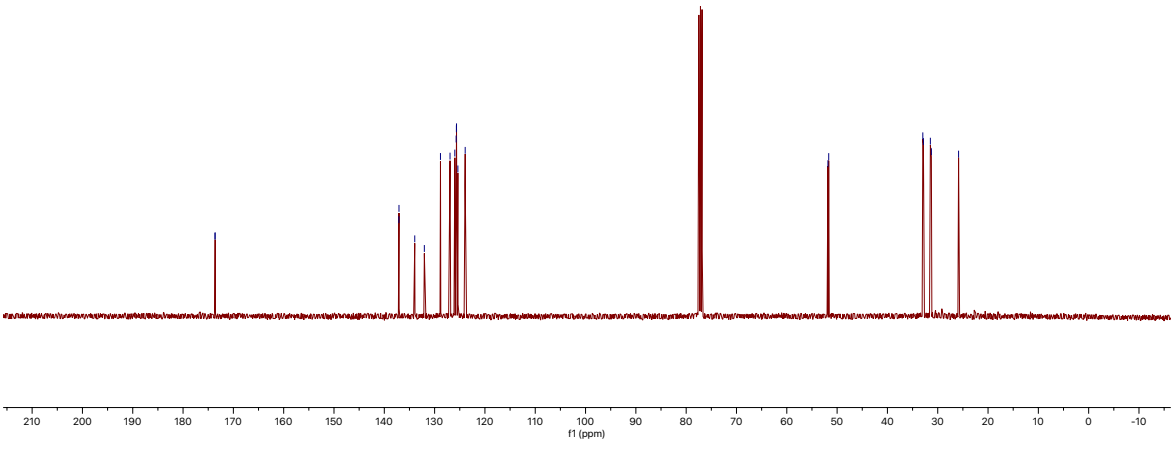


Dimethyl 4-(2-(naphthalen-1-yl)ethylidene)heptanedioate (3j)

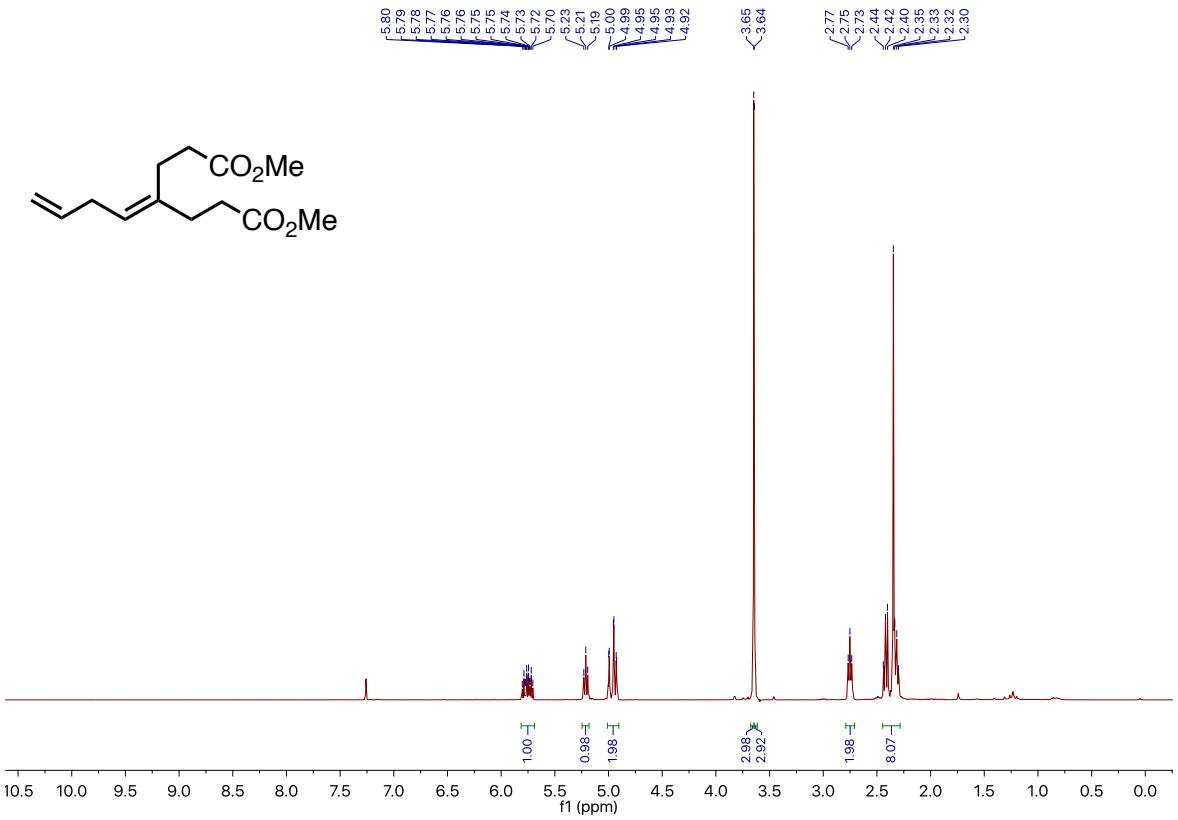


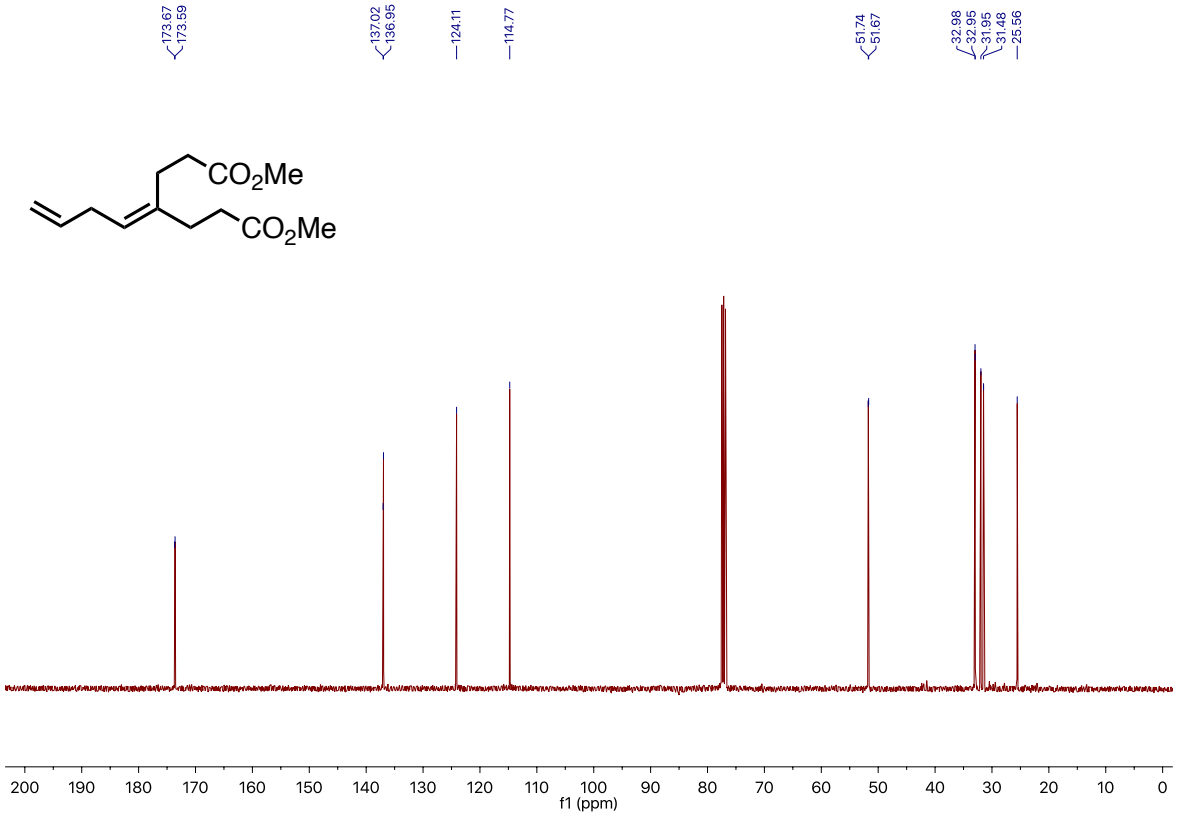




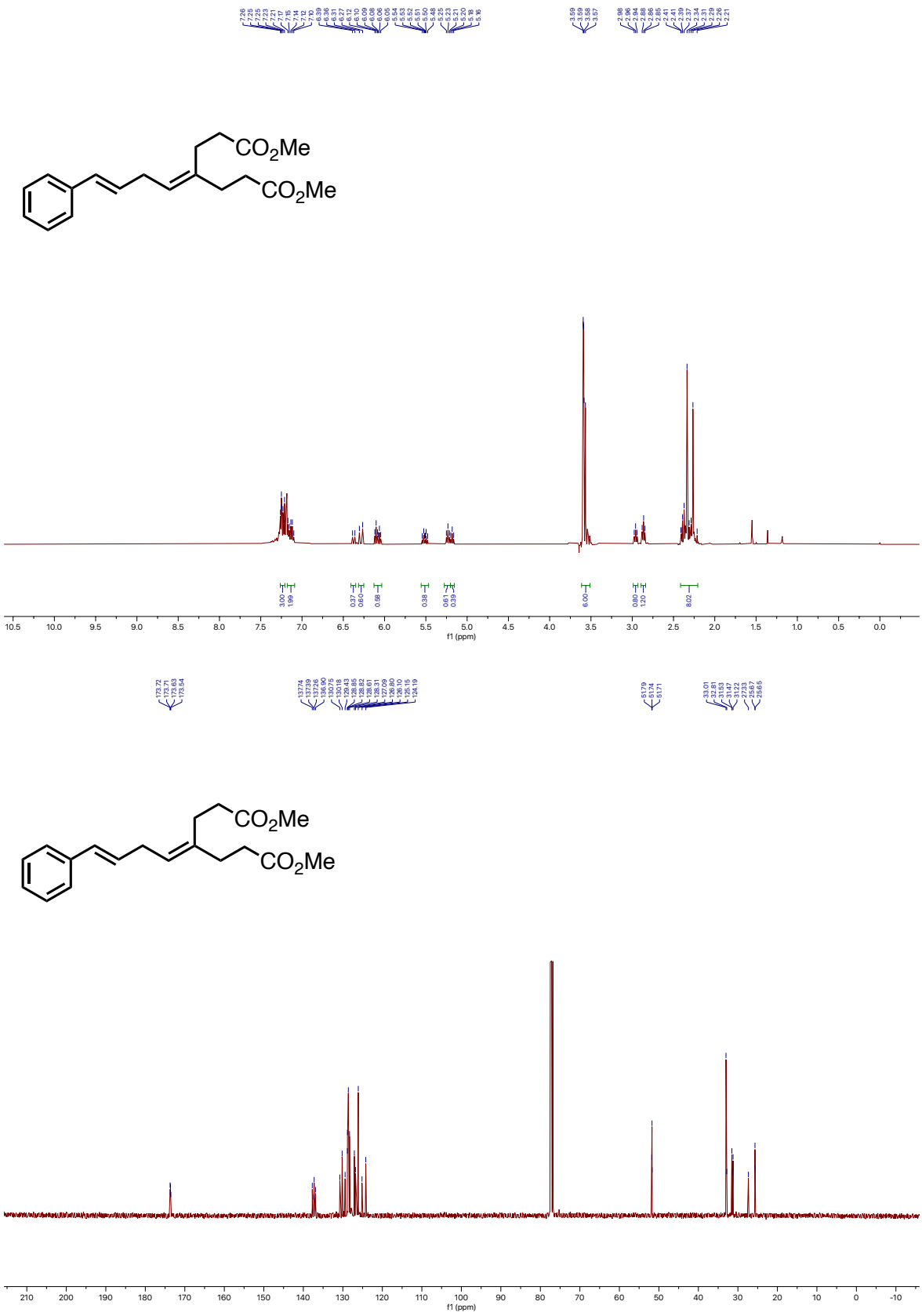


Dimethyl 4-(but-3-en-1-ylidene)heptanedioate (3k)



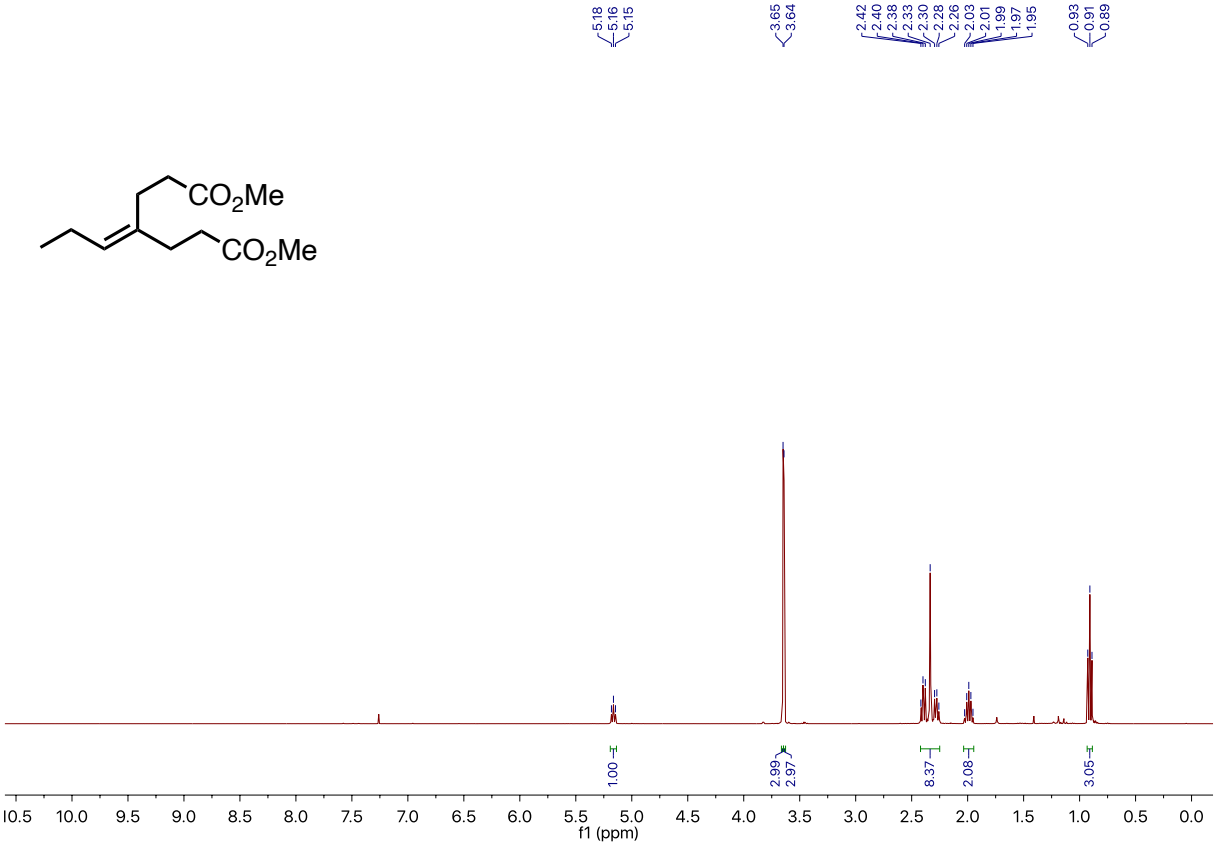


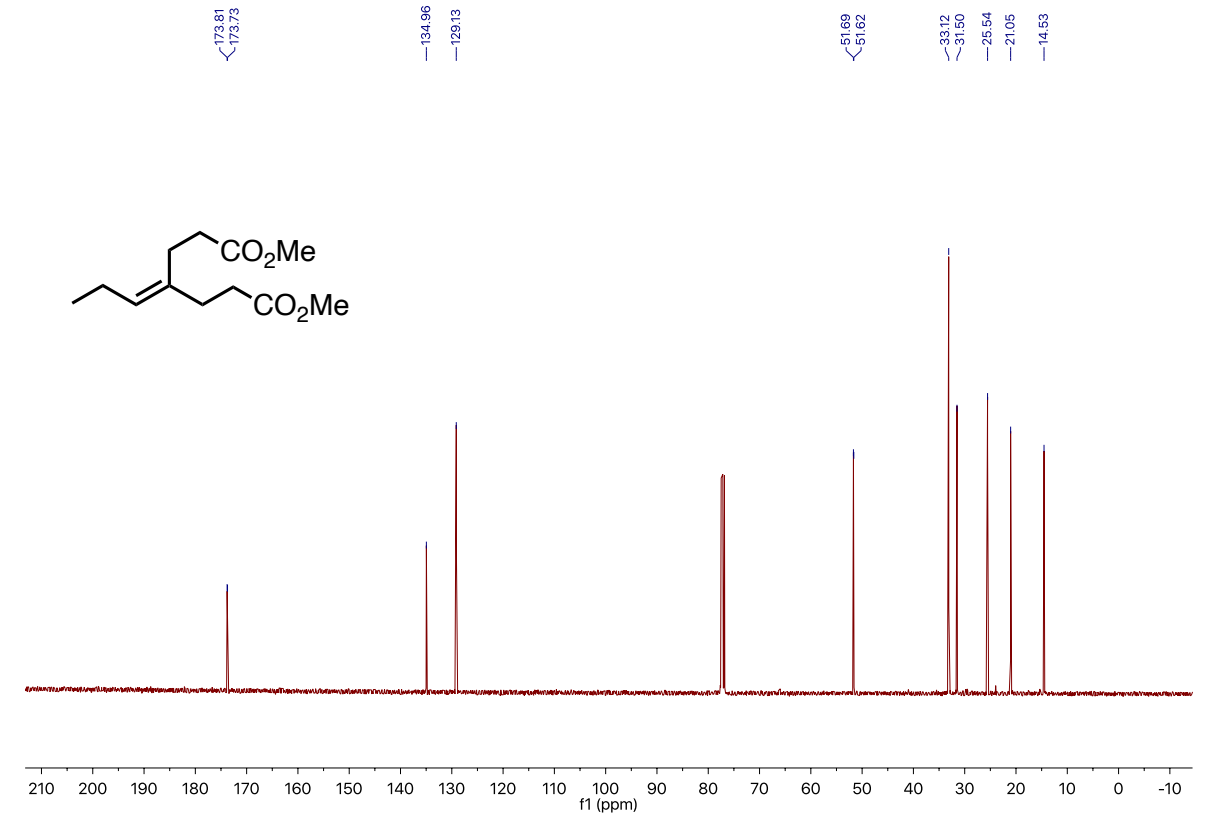
Dimethyl 4-(4-phenylbut-3-en-1-ylidene)heptanedioate (3l)



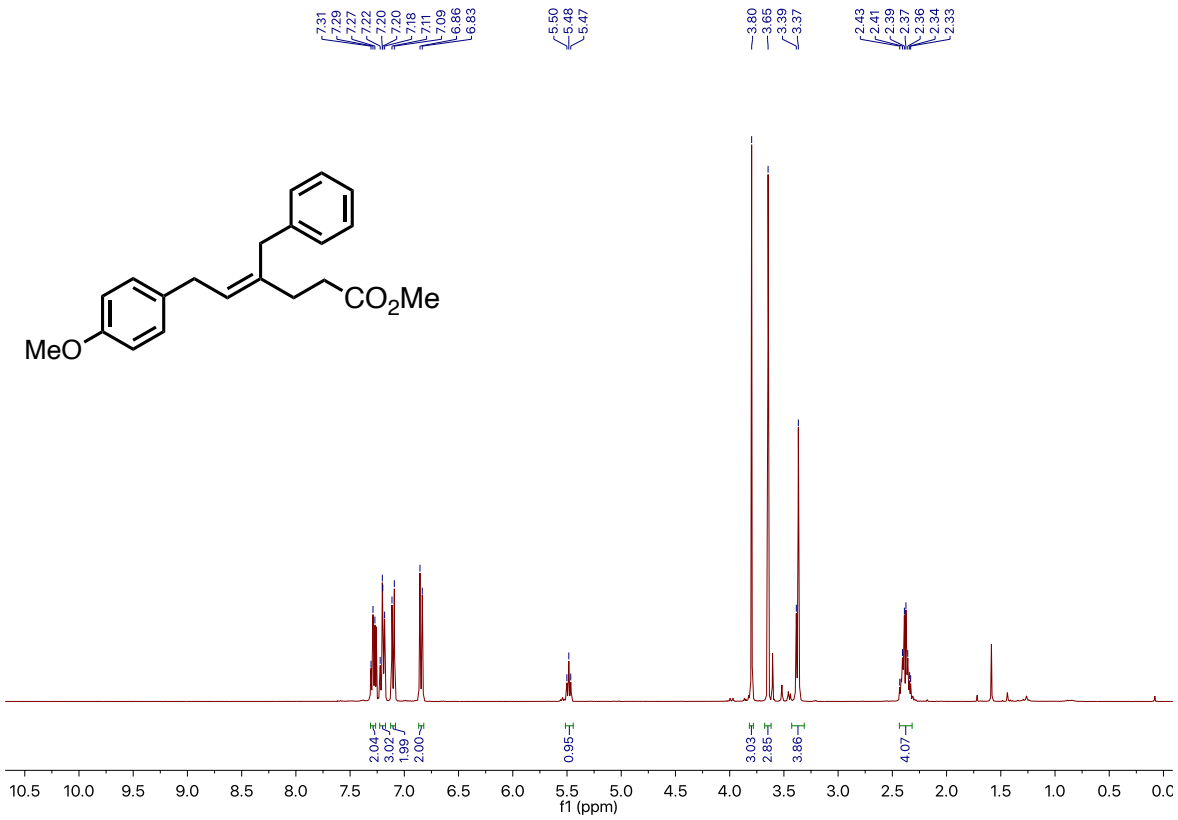
The sample used for these NMR spectra contains 60% of E isomer and 40% of Z isomer.

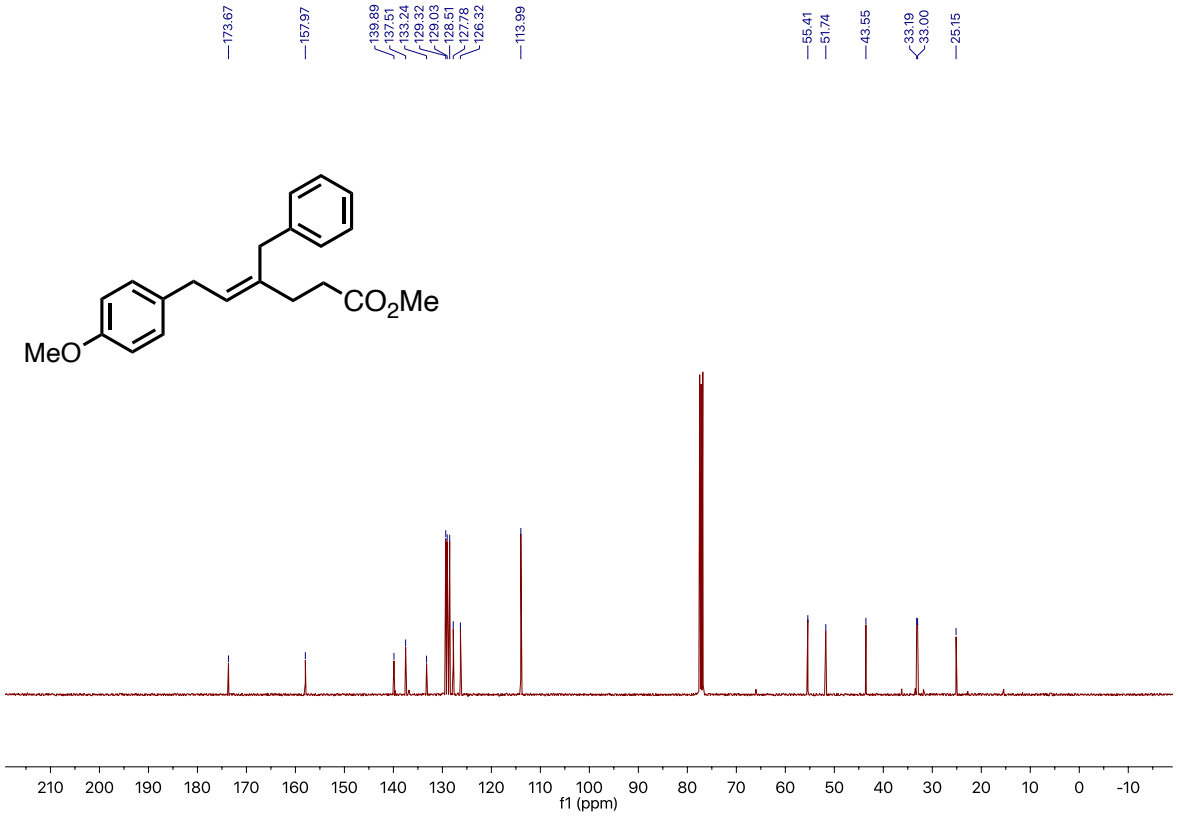
Dimethyl 4-propylideneheptanedioate (3m)





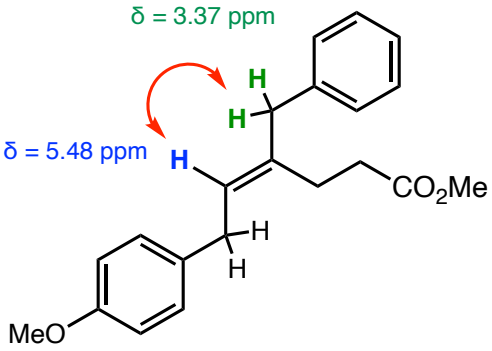
(*E*)-Methyl 4-benzyl-6-(4-methoxyphenyl)hex-4-enoate (3n *E* isomer)





The sample used for these NMR spectra contains 95% of E isomer and 5% of Z isomer.

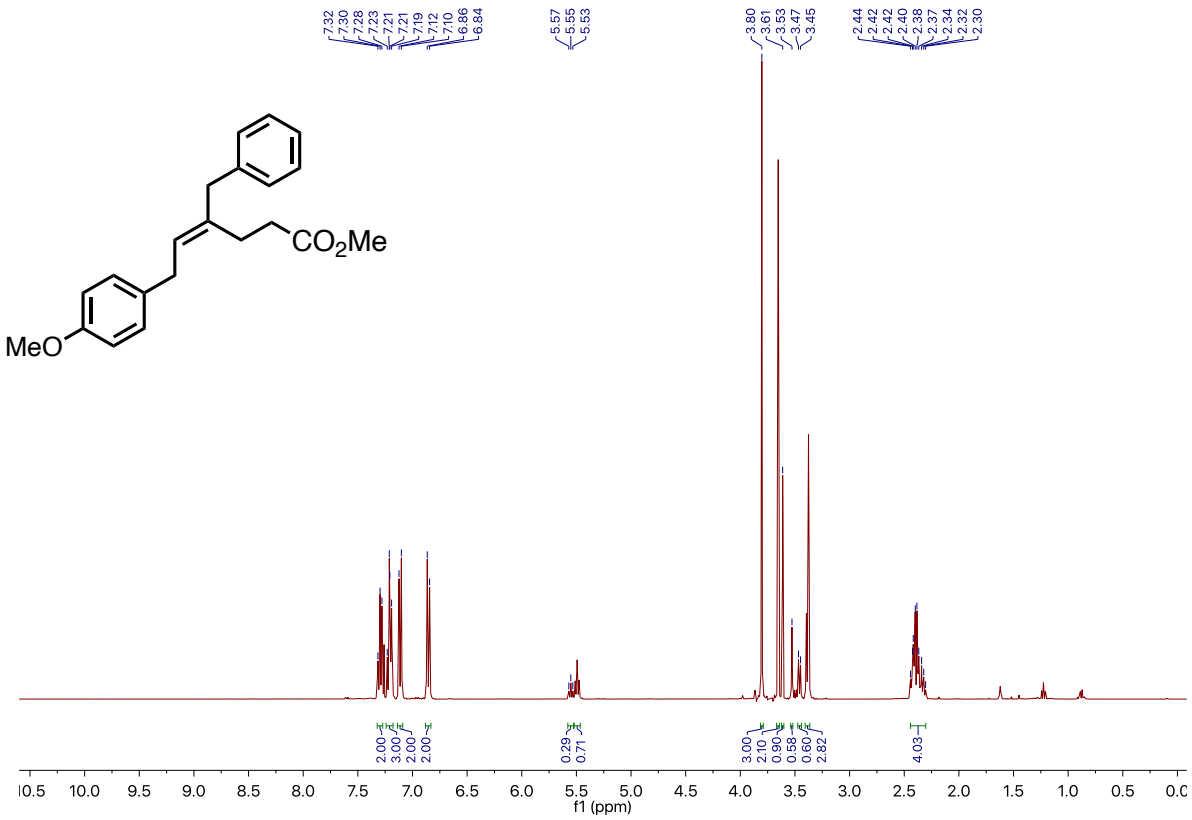
NOESY NMR of compound 3n (Major *E* isomer)

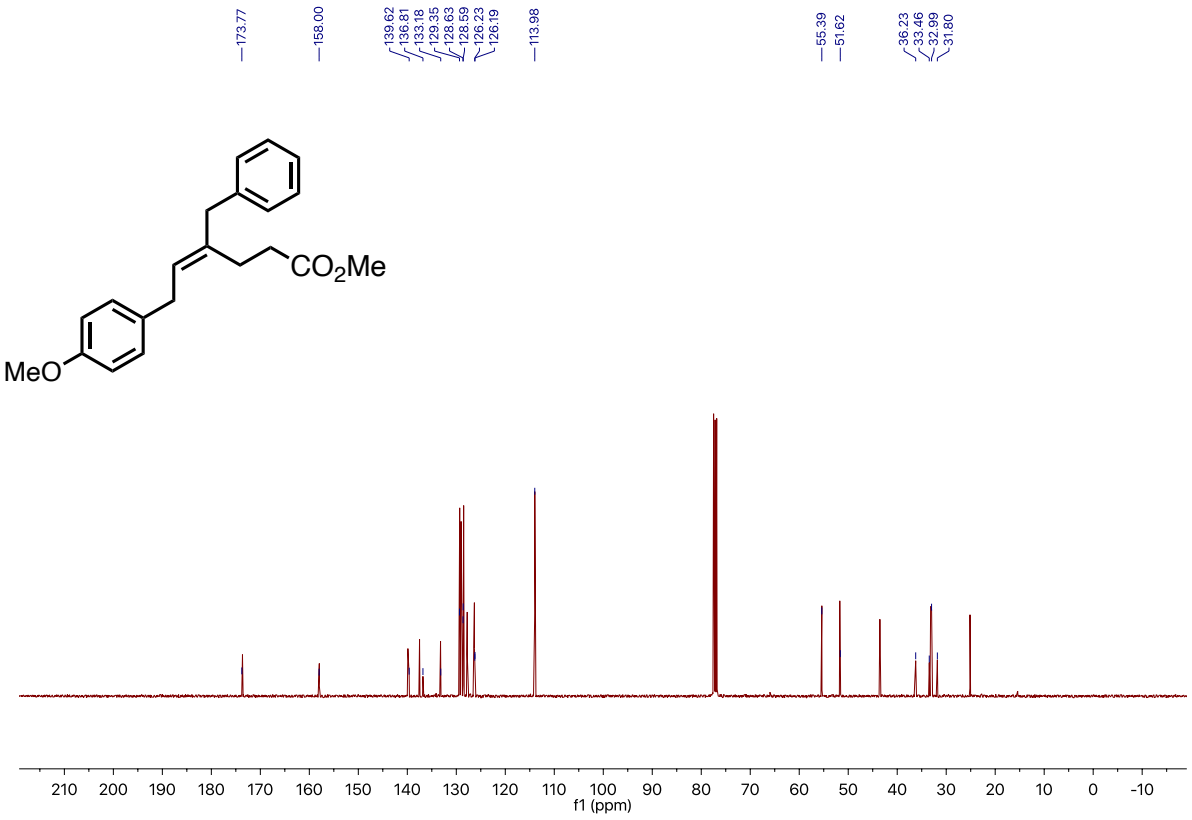


NOESY spectrum
(400 MHz, $CDCl_3$)

The sample used for this NOESY NMR spectra contains 95% of E isomer and 5% of Z isomer.

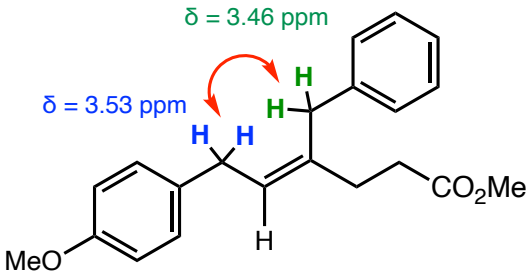
(*Z*)-Methyl 4-benzyl-6-(4-methoxyphenyl)hex-4-enoate (3n – *Z* isomer)





The sample used for these NMR spectra contains 71% of E isomer and 29% of Z isomer.

NOESY NMR of compound 3n (Minor *Z* isomer)

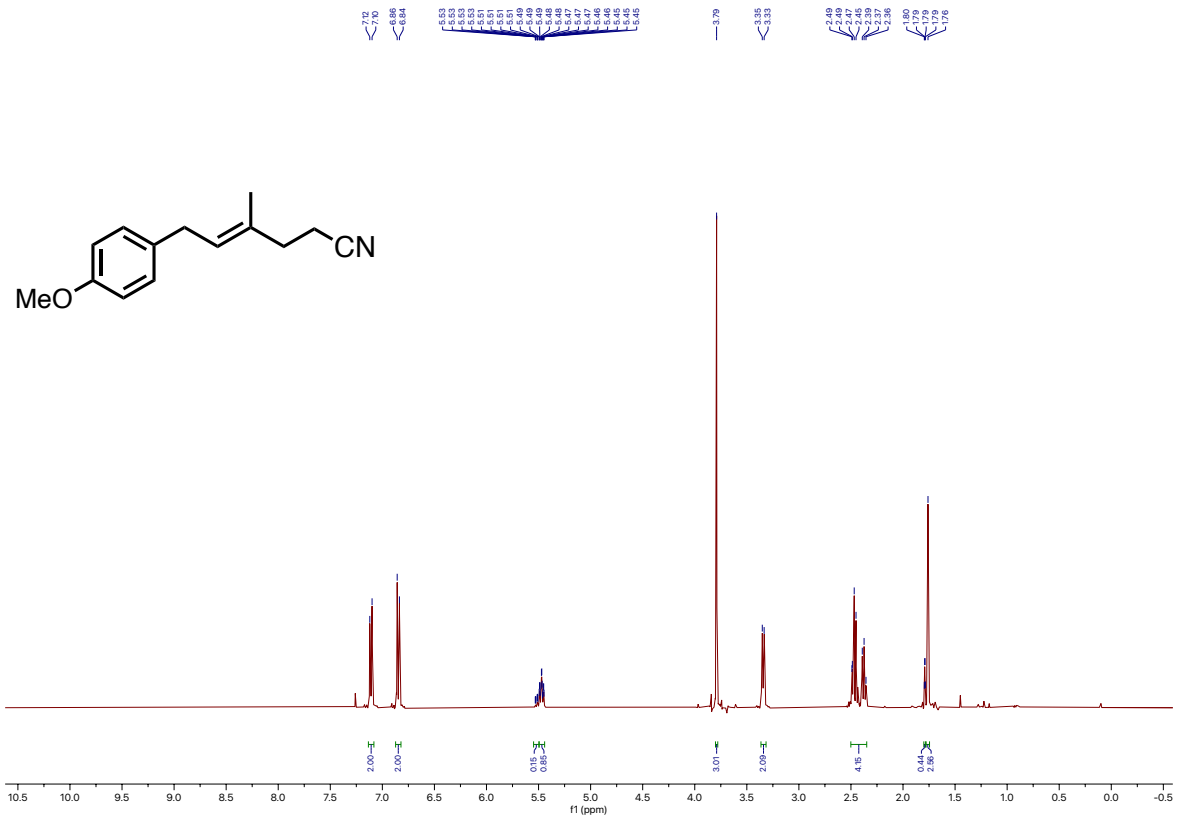


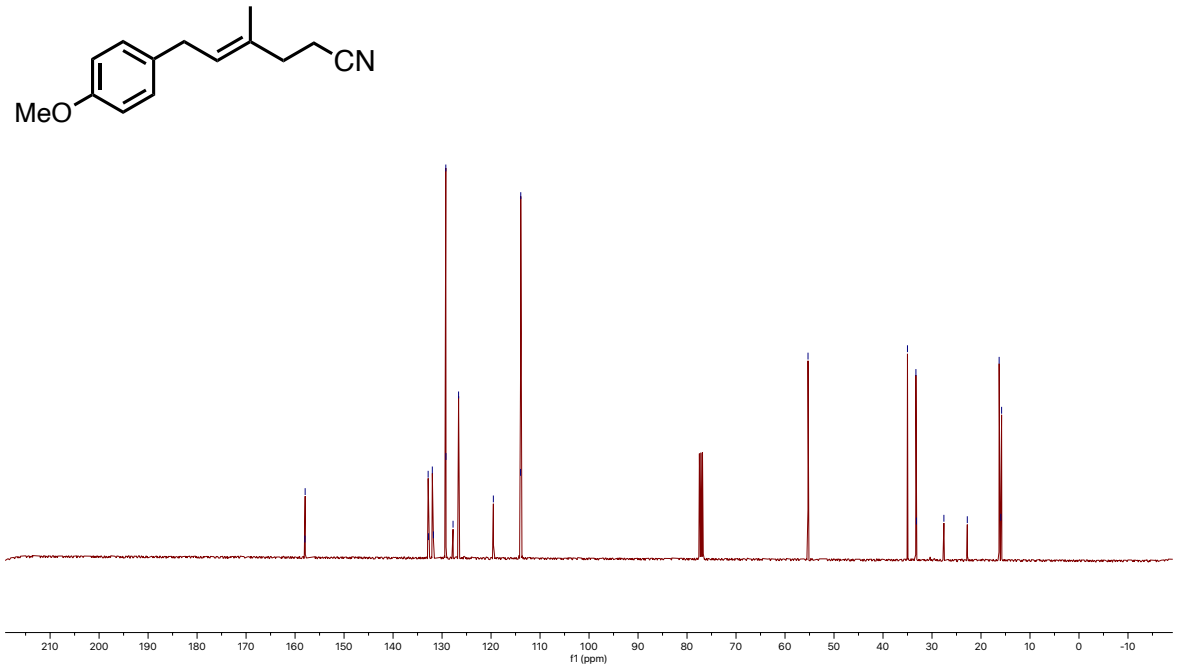
NOESY spectrum

(400 MHz, $CDCl_3$)

*The sample used for this NOESY NMR contains 16% of E isomer, 51% of Z isomer and 33% of starting material **1b**.*

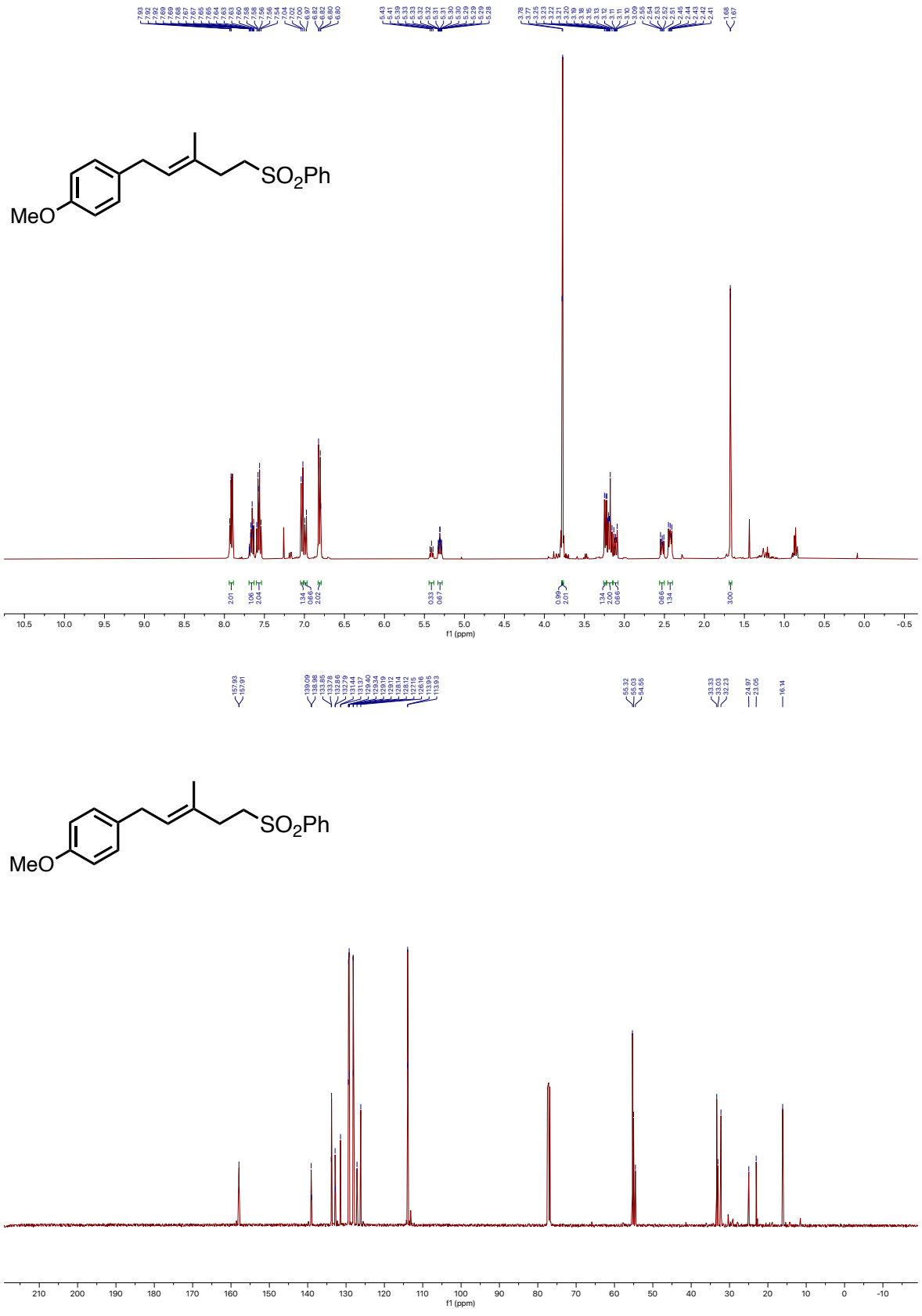
6-(4-Methoxyphenyl)-4-methylhex-4-enenitrile (3o)





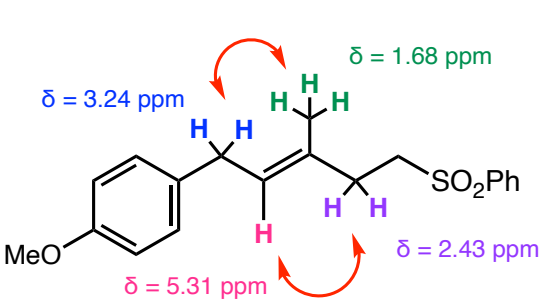
The sample used for these NMR spectra contains 85% of E isomer and 15% of Z isomer.

1-Methoxy-4-(3-methyl-5-(phenylsulfonyl)pent-2-en-1-yl)benzene (3p)

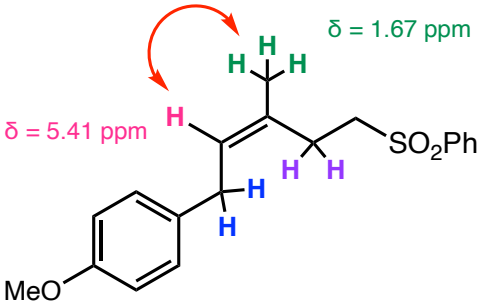


The sample used for these NMR spectra contains 67% of E isomer and 33% of Z isomer.

NOESY NMR of compound 3p

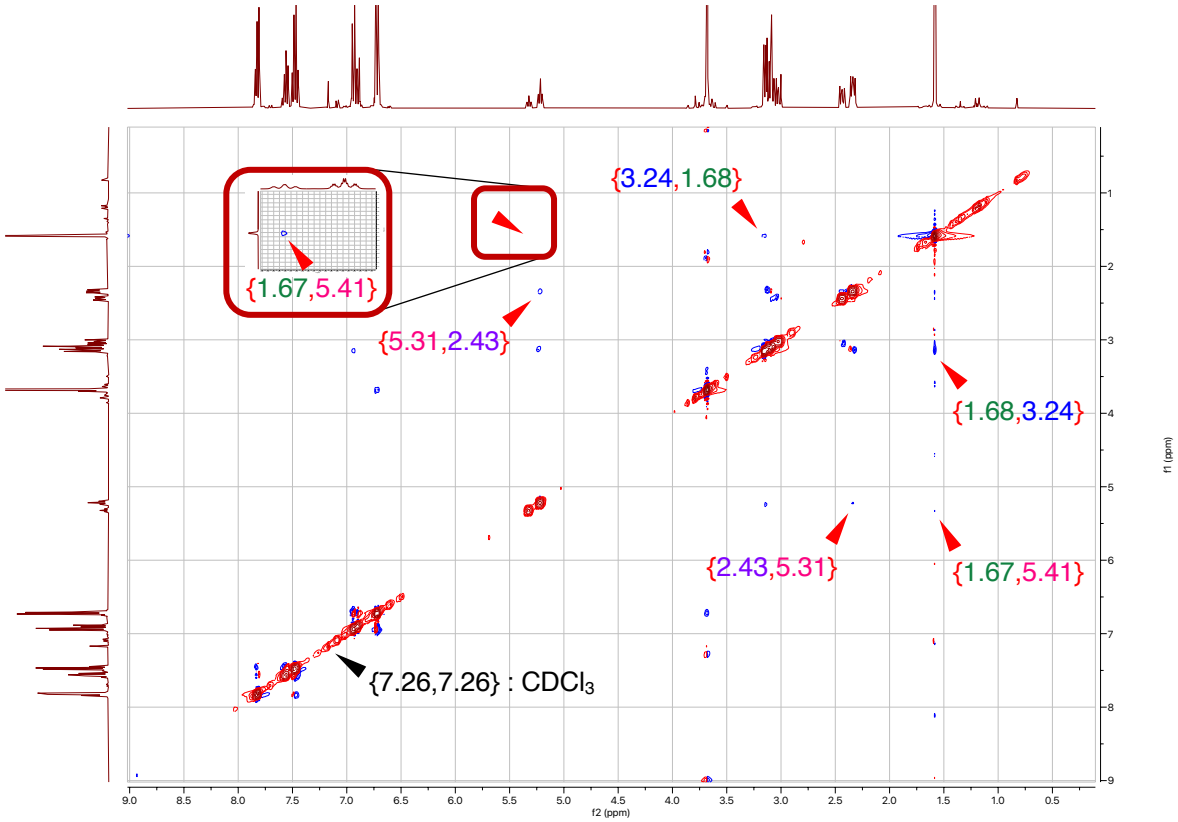


***E* Major Isomer**



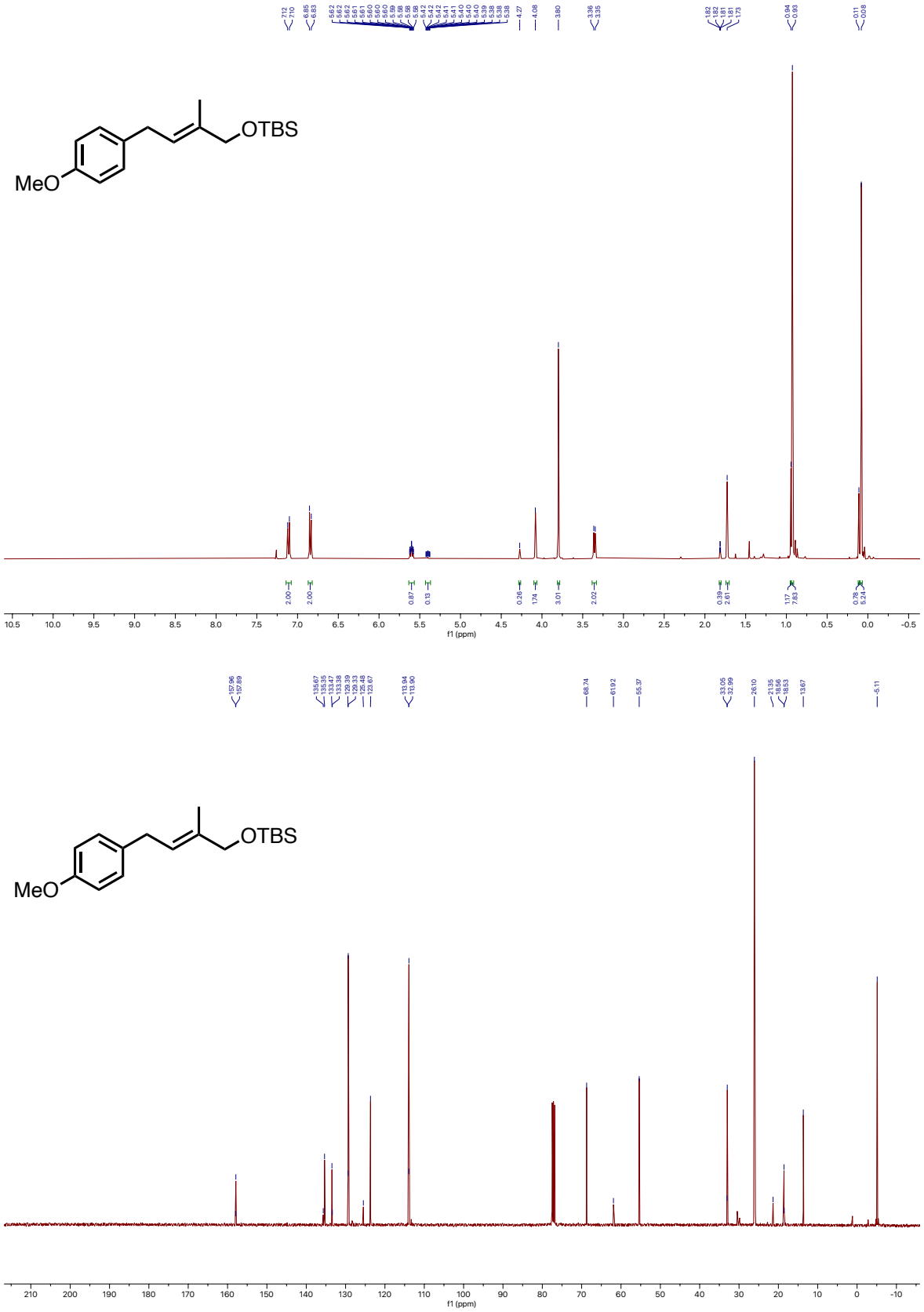
***Z* Minor Isomer**

NOESY spectrum
(400 MHz, $CDCl_3$)



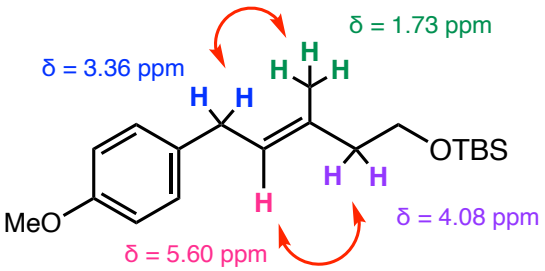
The sample used for this NOESY NMR contains 85% of E isomer and 15% of Z isomer.

tert-Butyl((4-(4-methoxyphenyl)-2-methylbut-2-en-1-yl)oxy)dimethylsilane (3q)



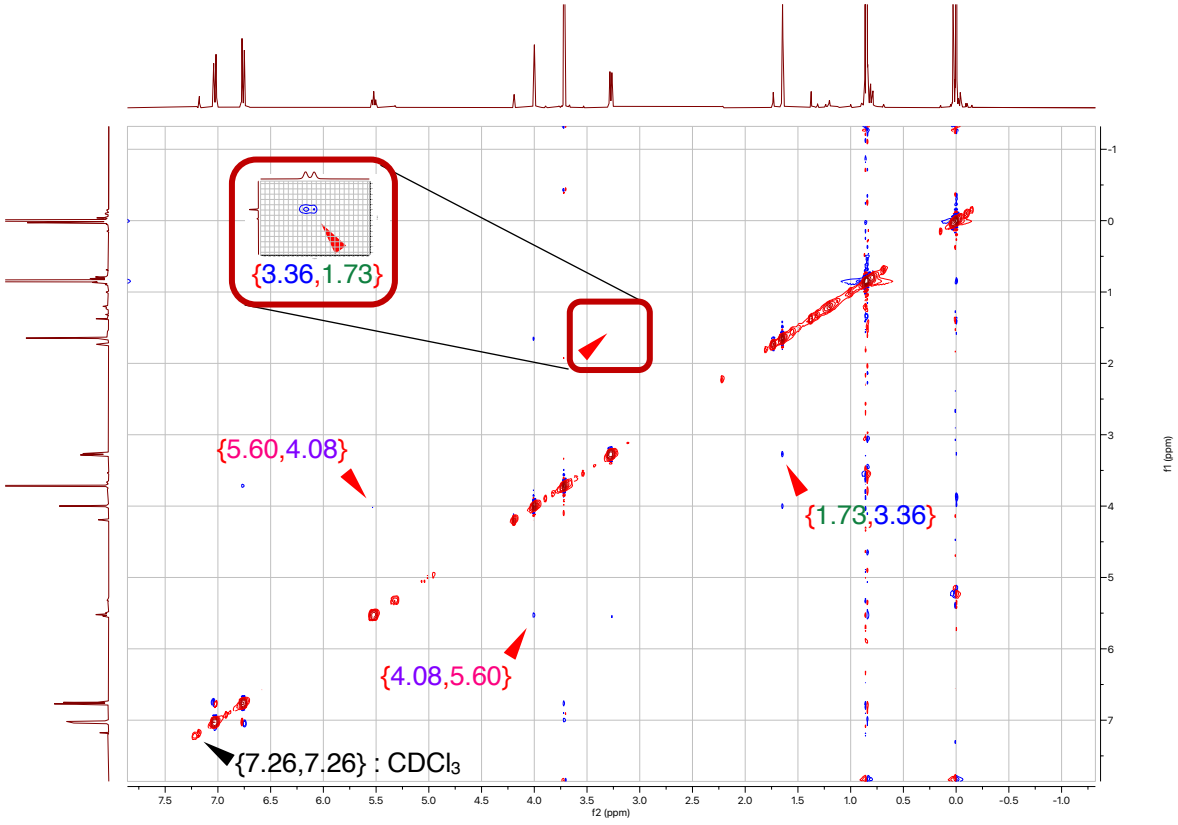
The sample used for these NMR spectra contains 87% of E isomer and 13% of Z isomer.

NOESY NMR of compound 3q (Major isomer *E*)



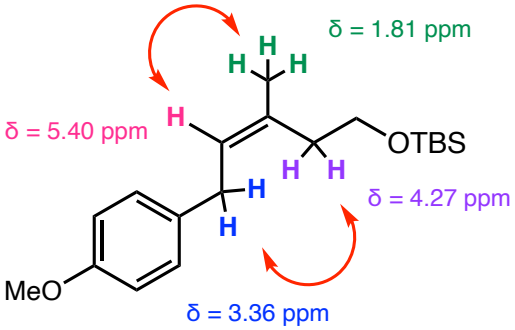
***E* Major Isomer**

NOESY spectrum
(400 MHz, $CDCl_3$)



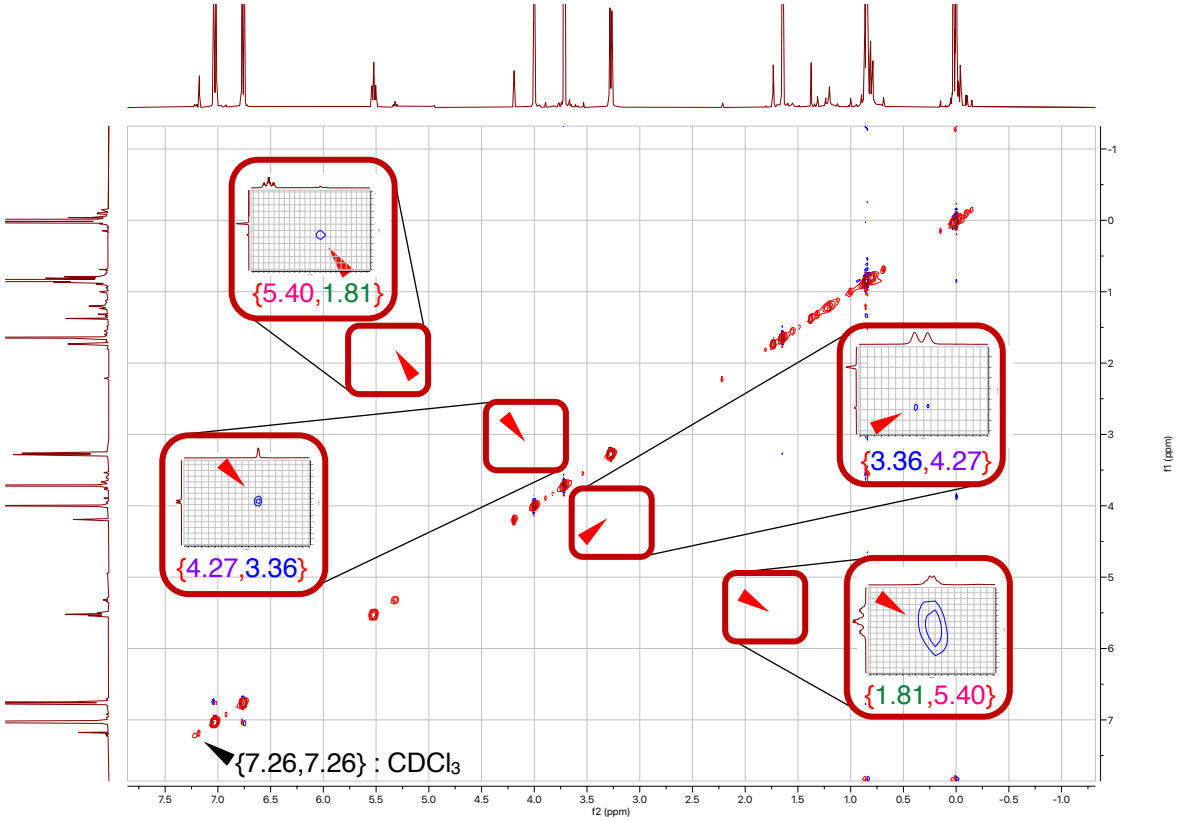
The sample used for this NOESY NMR contains 93% of *E* isomer and 7% of *Z* isomer.

NOESY NMR of compound 3q (Minor isomer *Z*)



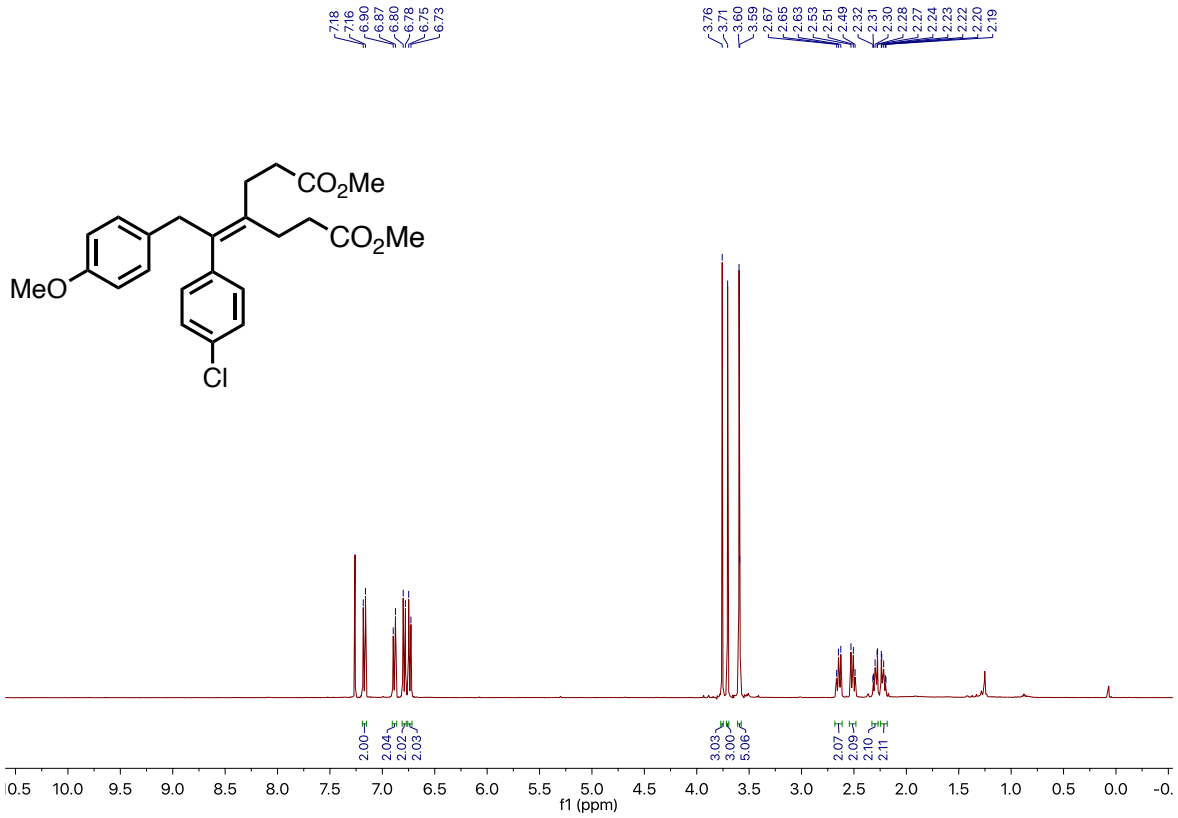
***Z* Minor Isomer**

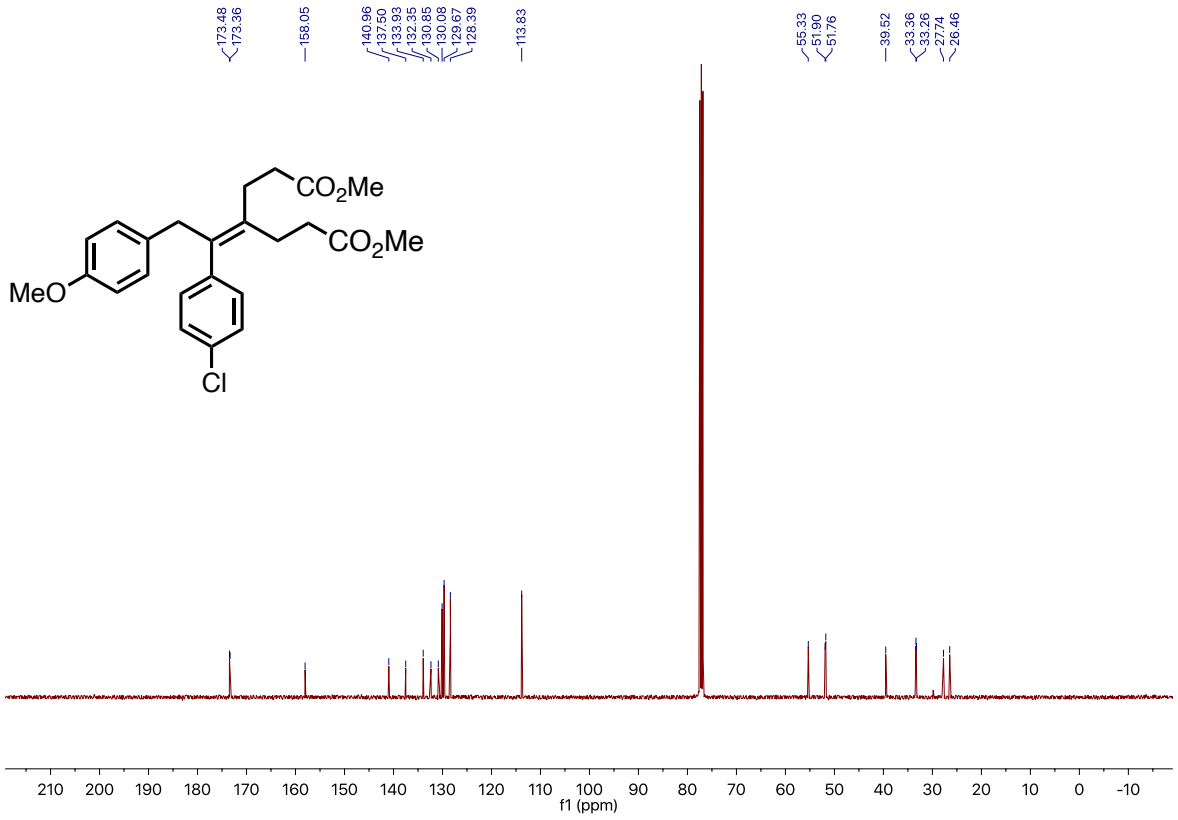
NOESY spectrum
(400 MHz, $CDCl_3$)



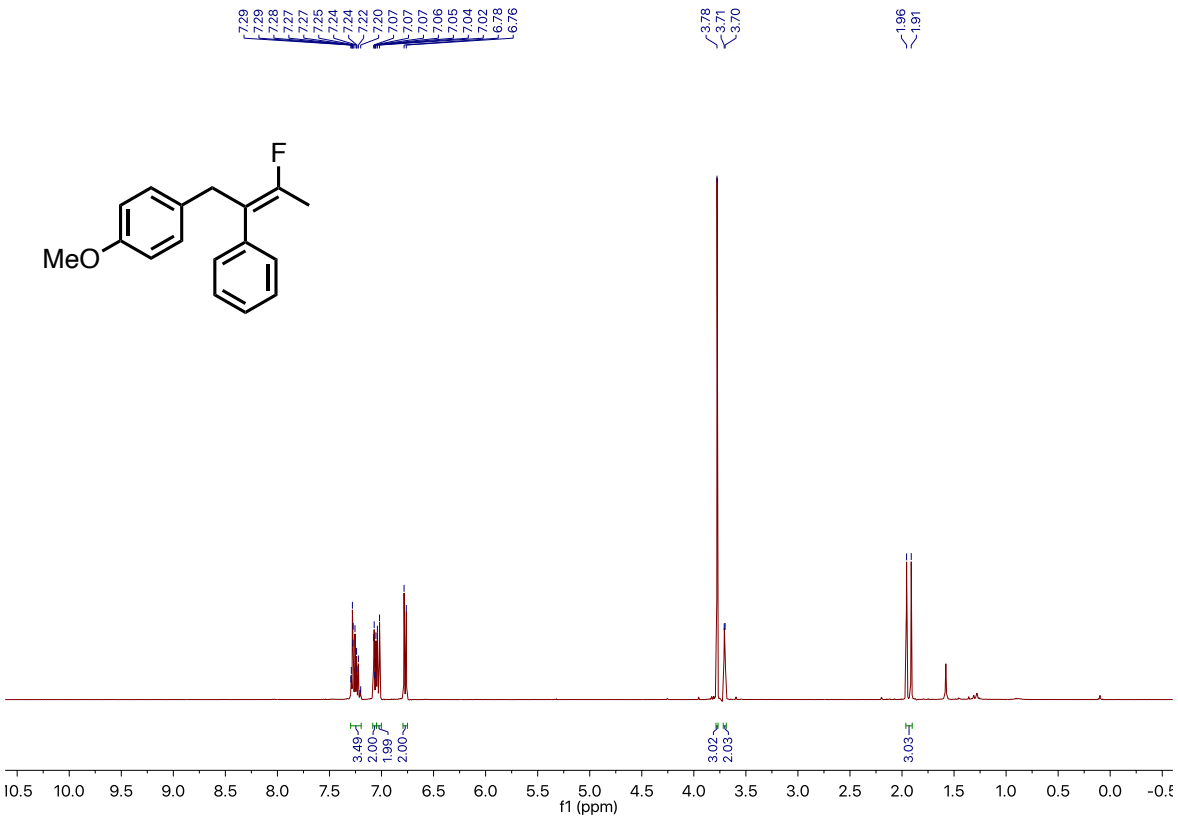
The sample used for this NOESY NMR contains 87% of *E* isomer and 13% of *Z* isomer.

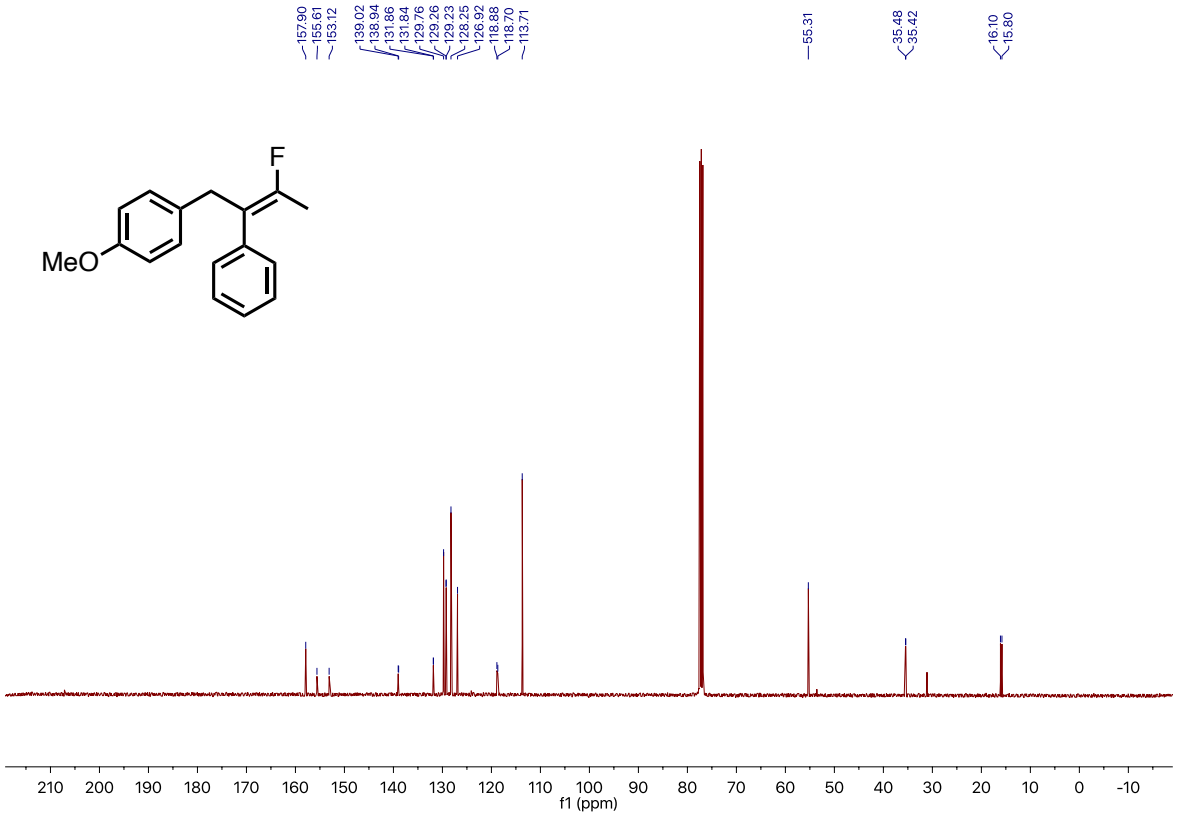
Dimethyl 4-(1-(4-chlorophenyl)-2-(4-methoxyphenyl)ethylidene)heptanedioate (3r)

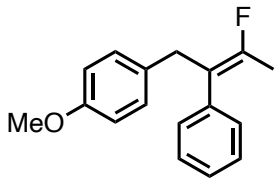




(*E*)-1-(3-Fluoro-2-phenylbut-2-en-1-yl)-4-methoxybenzene (3s – *E* isomer)

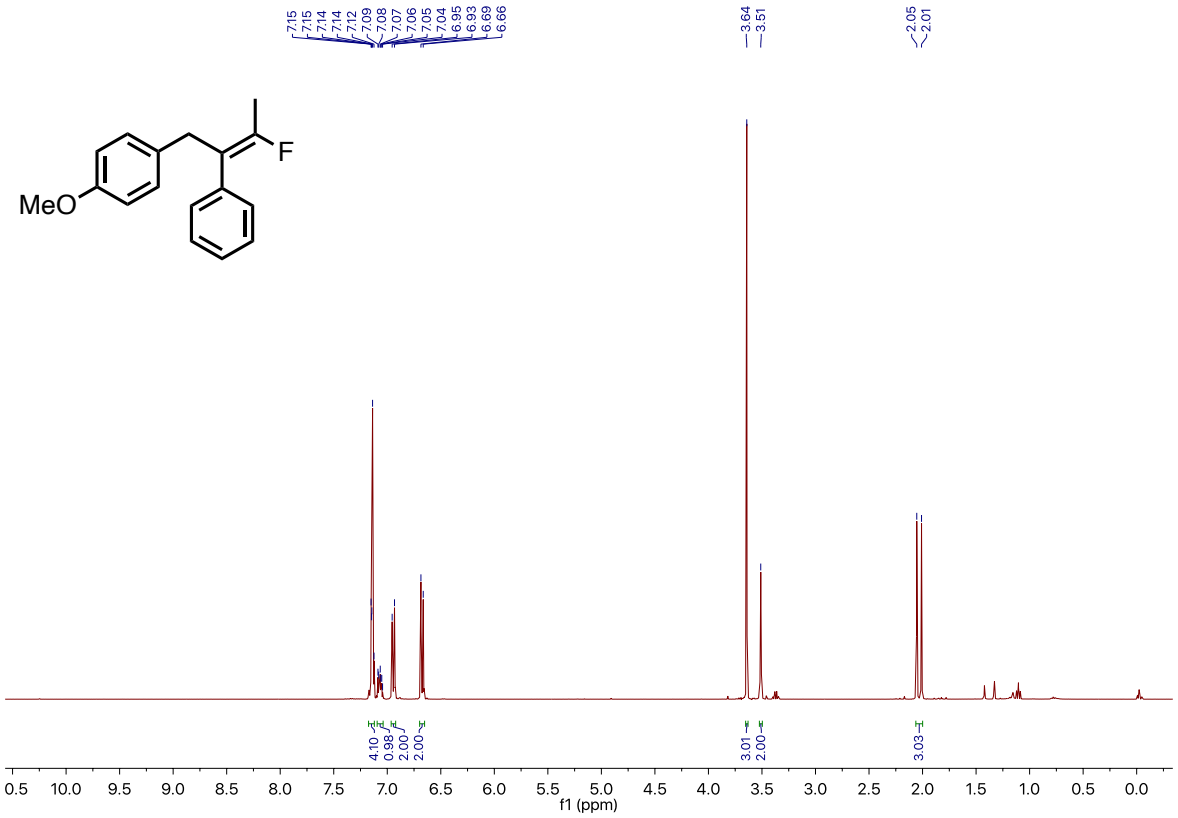


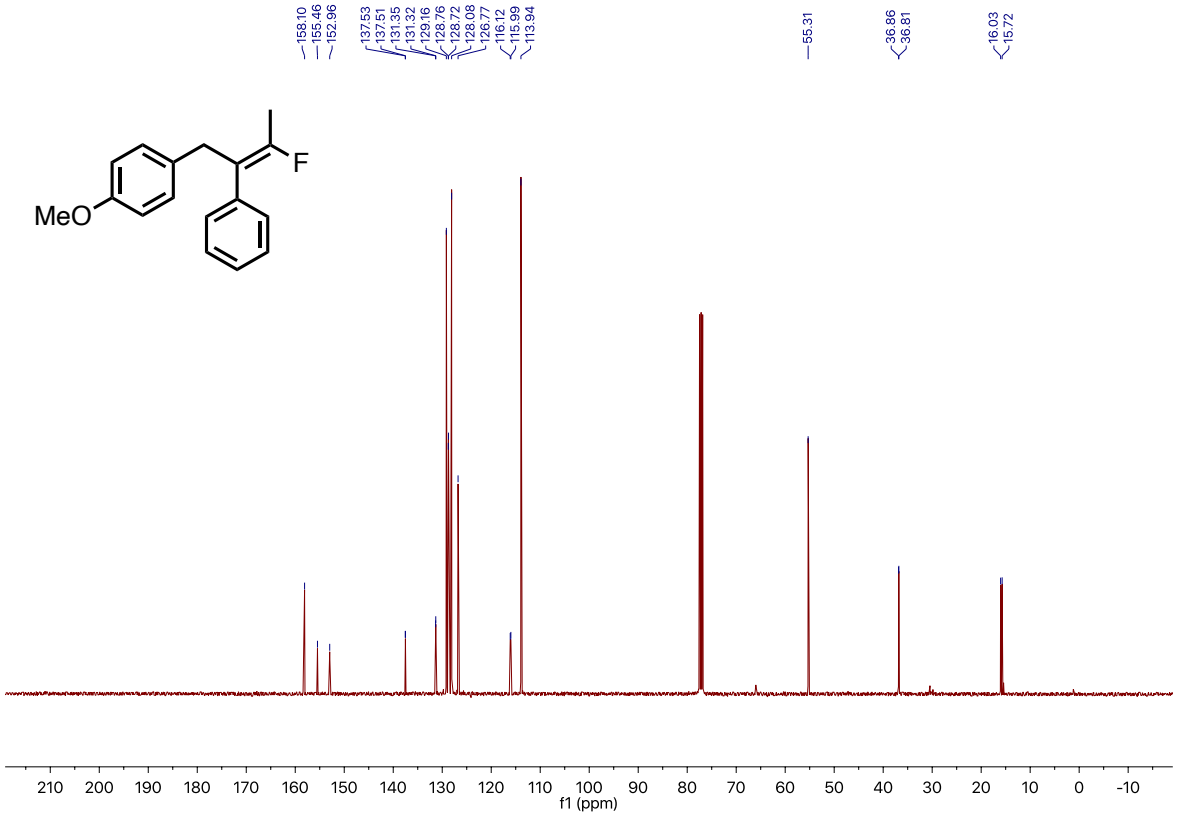


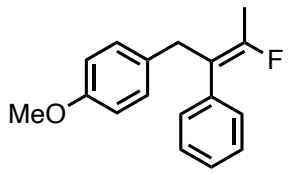

F
MeO

-100.28
-100.34
-100.40
-100.46
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

(*Z*)-1-(3-Fluoro-2-phenylbut-2-en-1-yl)-4-methoxybenzene (3s – *Z* isomer)

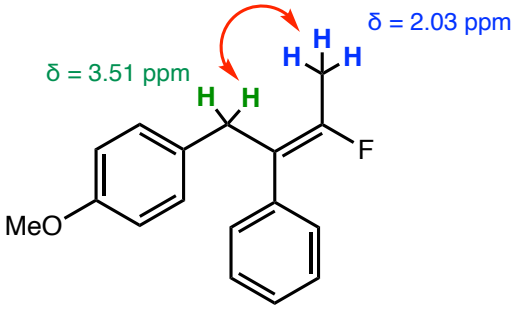





F
MeO

-97.62
-97.68
-97.75
-97.81
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

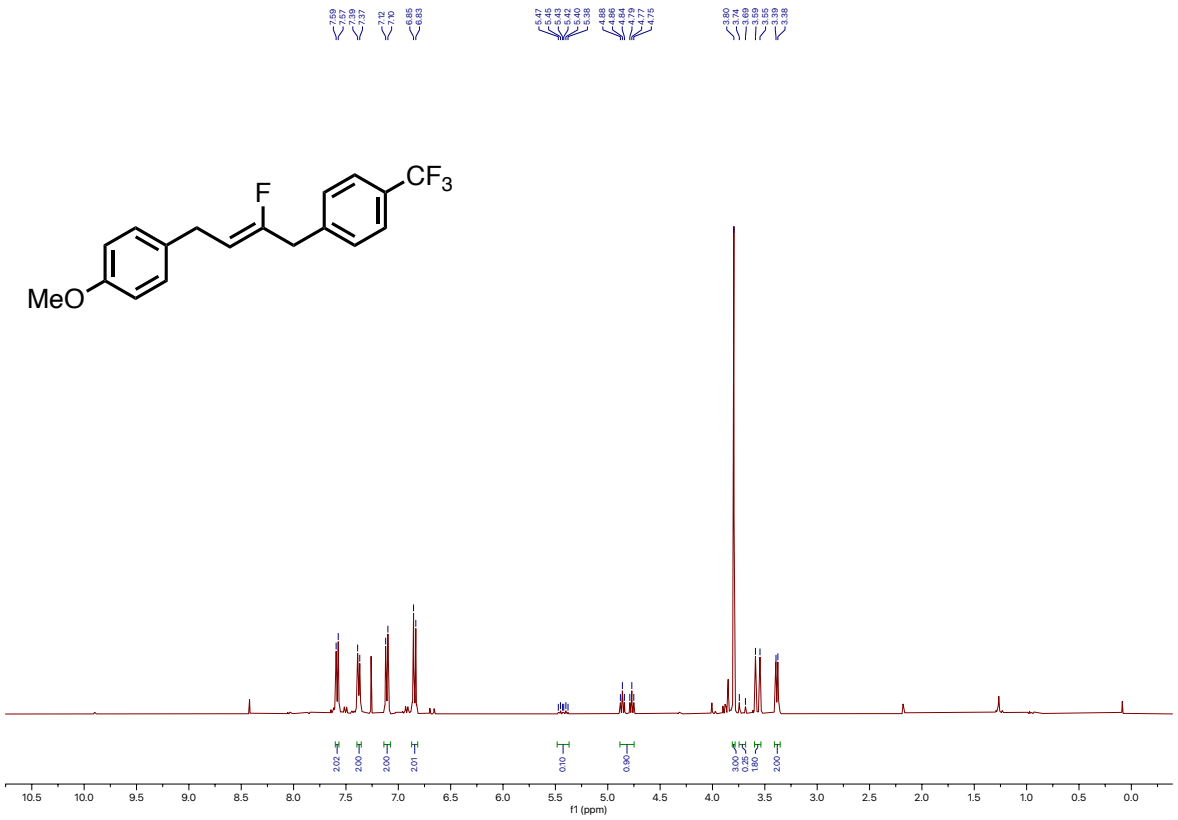
NOESY NMR of compound 3s (Major *Z* isomer)

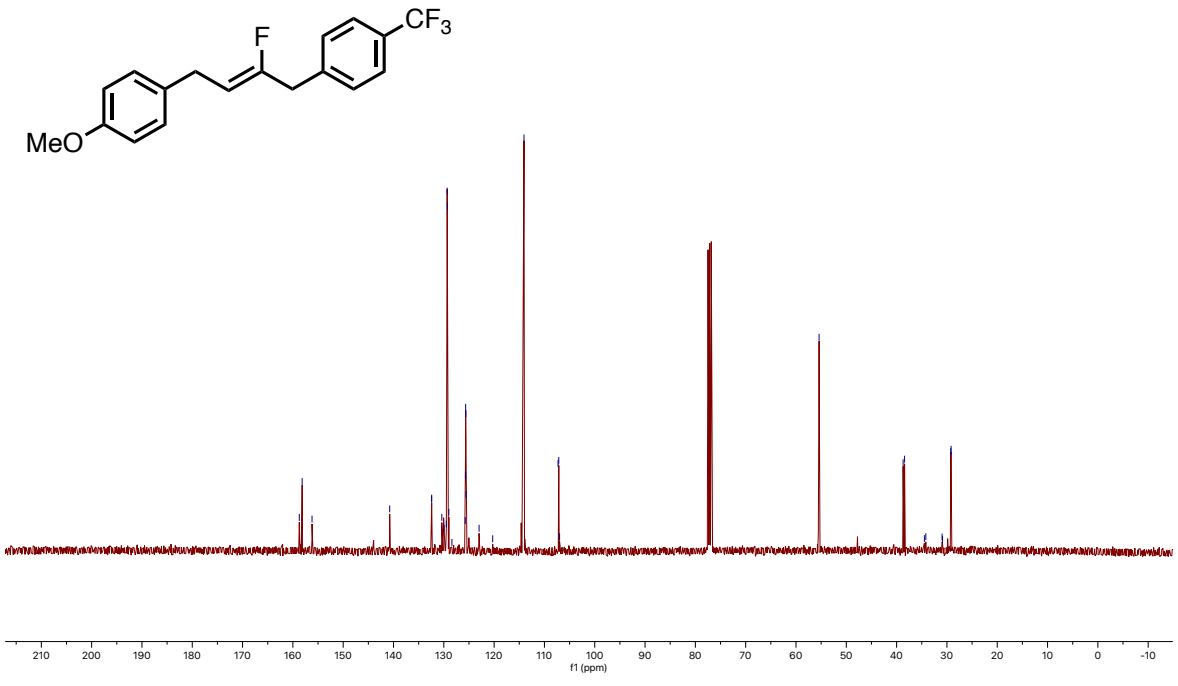


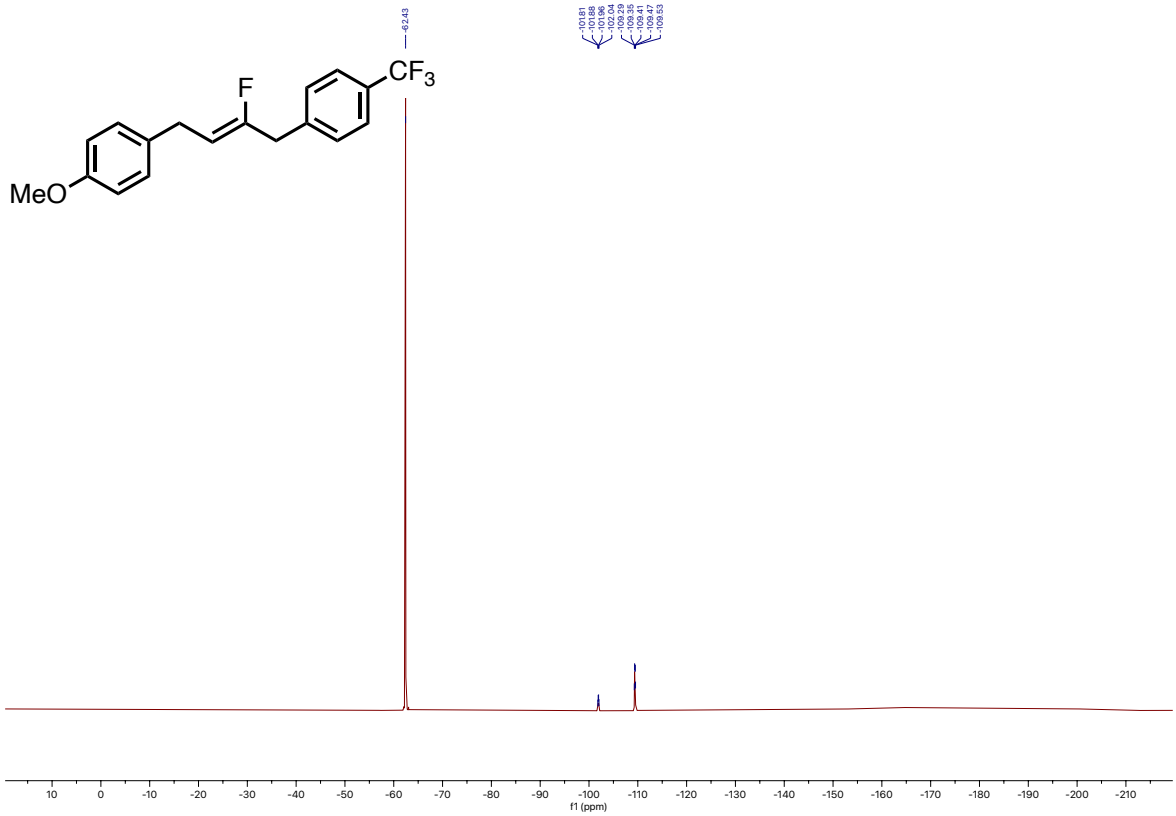
NOESY spectrum
(400 MHz, $CDCl_3$)

This interaction was not observed on minor isomer E.

1-(3-Fluoro-4-(4-(trifluoromethyl)phenyl)but-2-en-1-yl)-4-methoxybenzene (3t)







The sample used for these NMR spectra contains 90% of Z isomer and 10% of E isomer.

Dimethyl 4-(2-(4-chlorophenyl)propylidene)heptanedioate (3u)