

Supporting Information

Rhodium(II)-Catalyzed C–H Functionalization of Electron-Deficient Methyl Groups

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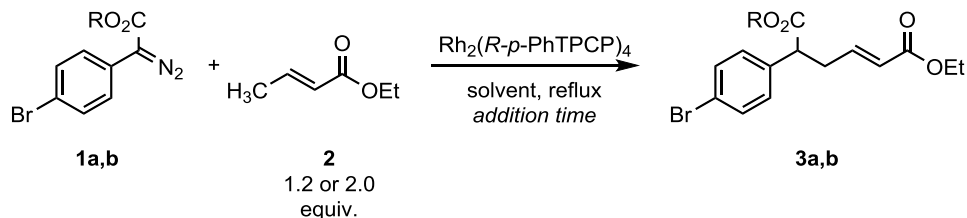
General Methods:

^1H Nuclear Magnetic Resonance ($^1\text{H-NMR}$) and ^{13}C Nuclear Magnetic Resonance ($^{13}\text{C-NMR}$) spectra were recorded on Varian INOVA 400, VNMR 400, INOVA 600 and UNITY 600 MHz. NMR spectra were recorded in deuterated chloroform (CDCl_3) at rt unless otherwise stated. The NMR data were presented as follows: chemical shift in ppm with tetramethylsilane (TMS, $\delta = 0.00$ ppm) for $^1\text{H-NMR}$ and the residual of chloroform ($\delta = 77.0$ ppm) for $^{13}\text{C-NMR}$ as internal standards, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br. = broad), coupling constant (J/Hz), integration. IR spectra were collected on a Nicolet iS10 from Thermo Scientific and reported in unit of cm^{-1} . Mass spectra were recorded on a Finnigan LTQ FTMS mass spectrometer. Optical rotations were measured on a PerkinElmer 341 polarimeter (concentration in g/100 mL). Melting points were measured on a MEL-TEMP of Electrothermal (uncorrected). All reactions were performed under argon atmosphere in oven or flame dried glassware. Acetonitrile, dichloromethane and *n*-pentane were dried by a solvent purification system (passed through activated alumina columns). Analytical TLC was performed on silica gel plates using UV light or KMnO_4 stain. Flash column chromatography was performed on silica gel 60Å (230-400 mesh) from Sorbent Technologies. Unless otherwise noted, all other chemical reagents were obtained from commercial sources and used as received.

Detailed optimization studies of relative concentration and addition time of the diazo compound

The following study was conducted to find the optimal conditions for functionalization of ethyl crotonate (**2**). The efficiency of the reaction improved significantly by employing a concentrated reaction medium, and by lengthening the slow addition of the diazo compound:

Table SI-1



entry	R	solvent	relative conc. ^b	catalyst loading (mol %)	time (h) ^c	yield (%) ^d	ee (%) ^e
1	Me	DCM	1.0	0.5	1.5	5	-
2	Me	DCM	1.0	0.5	3.0	11	-
3	Me	DCM	1.0	0.5	6.0	16	-
4	TCE	DCM	1.0	0.5	1.5	35	-
5	TCE	DCM	1.0	0.5	3.0	51	-
6	TCE	DCM	1.0	0.5	6.0	48	-
7	TCE	DCM	1.0	1.0	4.0	62	-
8	TCE	DCM	2.0	0.5	4.0	63	-
9	TCE	DCM	2.0	1.0	3.0	64	-
10	TCE	DCM	4.0	0.5	3.0	71	95
11^f	TCE	DCM	4.0	0.5	3.0	86	95
12	TCE	1,2-DCE	1.0	0.5	3.0	45	-
13	TCE	1,2-DCE	1.0	1.0	3.0	52	-

^aReaction conditions for entry 11: The diazo (0.8 mmol) in 1.2 mL DCM was added over 3 hours to a solution of the substrate (2.0 equiv.) and catalyst in 0.5 mL DCM at reflux. ^bRelative concentration (see experimental section for details). ^cAddition time of diazo. ^dDetermined by ¹H NMR using trichloroethylene as an internal standard. ^eDetermined by chiral HPLC of the isolated product. ^fReaction conducted with 2.0 equiv. of substrate. (DCM = dichloromethane; 1,2-DCE = 1,2-dichloroethane)

Relative concentrations of 1.0, 2.0 and 4.0 in Table SI-1 refer to the following amounts of diazo and solvents:

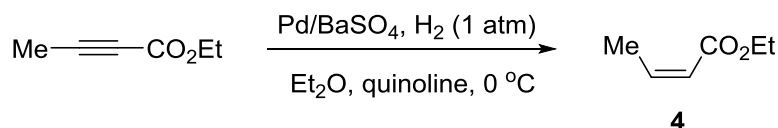
Relative concentration = 1.0: 0.4 mmol diazo in 2.5 mL of DCM, and catalyst/substrate in 1.0 mL DCM

Relative concentration = 2.0: 0.4 mmol diazo in 1.2 mL of DCM, and catalyst/substrate in 0.5 mL DCM

Relative concentration = 4.0: 0.8 mmol diazo in 1.2 mL of DCM, and catalyst/substrate in 0.5 mL DCM

Preparation of substrates:

Ethyl (*E*)-but-2-enoate (**2**), ethyl 3-methylbut-2-enoate (**7**), methyl (*E*)-2-methylbut-2-enoate (**9**), ethyl (*2E,4E*)-hexa-2,4-dienoate (**11d**), ethyl 4-methylbenzoate (**13a**), 1-bromo-4-methylbenzene (**13b**), 1-methyl-3-nitrobenzene, and 1-methyl-4-nitrobenzene were obtained from commercial sources and used as received. Diazo compounds methyl 2-(4-bromophenyl)-2-diazoacetate (**1a**), 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**), 2,2,2-trichloroethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (**15a**), 2,2,2-trichloroethyl 2-(4-(*tert*-butyl)phenyl)-2-diazoacetate (**15b**), methyl 4-(1-diazo-2-oxo-2-(2,2,2-trichloroethoxy)ethyl)benzoate (**15c**), 2,2,2-trichloroethyl 2-(3-bromophenyl)-2-diazoacetate (**15d**), and 2,2,2-trichloroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate (**15e**) were prepared according to a previously reported procedure¹. Ethyl (*Z*)-but-2-enoate (**4**), methyl (*Z*)-2-methoxybut-2-enoate (**11a**), methyl (*Z*)-2-bromobut-2-enoate (**11c**), ethyl (*2E,4E,6E*)-octa-2,4,6-trienoate (**11e**), (*2E,4E*)-*N*-methoxy-*N*-methylhexa-2,4-dienamide (**11g**), 3-((*2E,4E*)-hexa-2,4-dienoyl)oxazolidin-2-one (**11h**), methyl (*E*)-3-(*p*-tolyl)acrylate (**13c**), ethyl 3-(*p*-tolyl)propionate (**13d**) are known compounds and were prepared according to literature procedures.

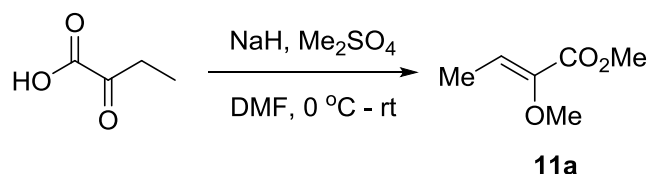


Ethyl (*Z*)-but-2-enoate (**4**):

CAS registry number: 6776-19-8.

This compound was prepared according to a literature procedure²: A solution of ethyl but-2-ynoate (3.36 g, 30.0 mmol, 1.0 equiv) in 30 mL of anhydrous diethyl ether was stirred with 5% palladium on barium sulfate (60 mg, 0.54 mmol, 1.8 mmol %), 60 mg of quinoline under an atmosphere of hydrogen (balloon) at 0 °C for 36 h. The progress of the reaction was monitored by removing aliquots that are concentrated and analyzed by ¹H NMR, monitoring the disappearance of the methyl singlet at δ 1.95. After hydrogenation is

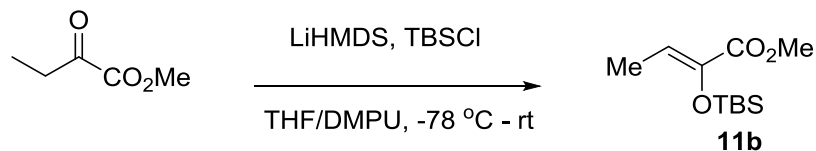
complete, the catalyst is removed by filtration through a Celite pad. The diethyl ether is removed with a rotary evaporator, and the product was purified by distillation at atmospheric pressure at 143–145°C (bath temperature) to give a clear liquid (3.01 g, 88%). ¹H NMR (400 MHz, CDCl₃): δ 6.30 (dq, *J* = 11.6, 7.2 Hz, 1H), 5.76 (dq, *J* = 11.6, 2.0 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.11 (dd, *J* = 7.3, 2.0 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H).



Methyl (Z)-2-methoxybut-2-enoate (11a):

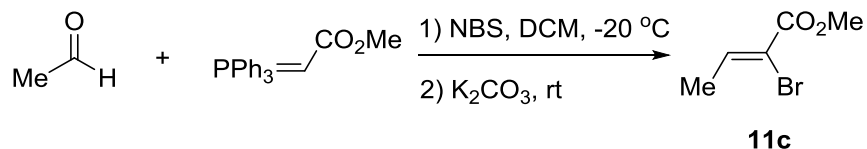
CAS registry number: 56009-30-4.

This compound was prepared according to a literature procedure³: To NaH (5.14 g, 128.5 mmol, 5.0 equiv) in *N,N*-dimethylformamide (30 mL) was added a solution of 2-oxobutanoic acid (2.65 g, 25.7 mmol, 1.0 equiv) in 10 mL of *N,N*-dimethylformamide dropwise. The resulting foam was stirred for 90 min at rt. Then the solution was cooled to 0 °C and dimethyl sulfate (12.2 mL, 128.5 mmol, 5.0 equiv) was added over 60 min by syringe pump. The reaction was stirred at rt for 3 h before it was quenched with H₂O (30 mL), and the aqueous layer was extracted with diethyl ether (2x 50 mL). The combined organic layers were washed with H₂O (50 mL) and brine (50 mL), dried over MgSO₄, and concentrated at rt. The residue was purified by flash chromatography (hexanes : diethyl ether = 10 : 1) to afford the product as a colorless oil (900 mg, 27%); *R_f* = 0.25 (hexanes : diethyl ether = 8 : 1); ¹H NMR (400 MHz; CDCl₃) δ 6.30 (q, *J* = 7.2 Hz, 1H), 3.74 (s, 3H), 3.63 (s, 3H), 1.75 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.2, 146.8, 124.1, 59.8, 51.8, 11.0; IR (neat): 2957, 2927, 2857, 1727, 1600, 1464, 1325, 1276, 1148, 1069, 811, 721 cm⁻¹; HRMS (NSI) *m/z*: [M+H]⁺ calcd for C₆H₁₁O₃ 131.0703; found 131.0703.



Methyl (Z)-2-((tert-butyldimethylsilyl)oxy)but-2-enoate (11b):

To a solution of LiHMDS (1 M in THF, 24.0 mL, 24.0 mmol, 1.2 equiv) at -78 °C was added a solution of methyl 2-oxobutanoate (2.32 g, 20.0 mmol, 1.0 equiv) in 10 mL of THF. After stirring at -78 °C for 30 min, DMPU (6 mL, 2.5 equiv) was added. The reaction was then stirred for 5 min before a solution of TBSCl (4.52 g, 30.0 mmol, 1.5 equiv) in 5 mL of THF was added dropwise. The reaction was then stirred for 5 h at rt before it was quenched with saturated aqueous NH_4Cl (20 mL), extracted with diethyl ether (30 mL \times 2). The combined organics were washed with brine (30 mL), dried over MgSO_4 , concentrated, and purified by column chromatography on silica gel eluting with hexanes : diethyl ether (60 : 1 to 30 : 1) to give methyl (Z)-2-((tert-butyldimethylsilyl)oxy)but-2-enoate (**11b**) as a yellow oil (1.74 g, 38%); $R_f = 0.63$ (hexanes : ethyl acetate = 10 : 1); $^1\text{H NMR}$ (400 MHz; CDCl_3) δ 6.09 (q, $J = 7.2$ Hz, 1H), 3.72 (s, 3H), 1.71 (d, $J = 7.2$ Hz, 3H), 0.95 (s, 9H), 0.13 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.2, 141.4, 117.9, 51.7, 25.8, 18.5, 11.4, -4.4; IR (neat): 2957, 2931, 2858, 1729, 1651, 1260, 1142, 1090, 1036, 839, 808, 784 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{23}\text{O}_3\text{Si}$ 231.1411; found 231.1411.

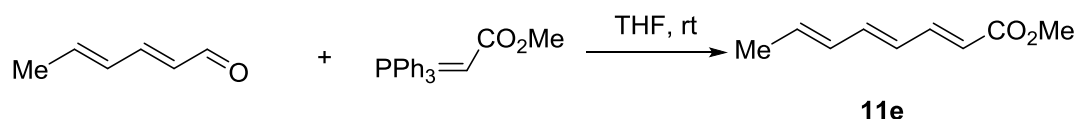


Methyl (Z)-2-bromobut-2-enoate (11c):

CAS registry number: 22966-48-9.

This compound was prepared according to a literature procedure⁴: NBS (1.96 g, 11.0 mmol, 1.1 equiv) was added portionwise under nitrogen atmosphere to a solution of methyl (triphenylphosphoranylidene)-

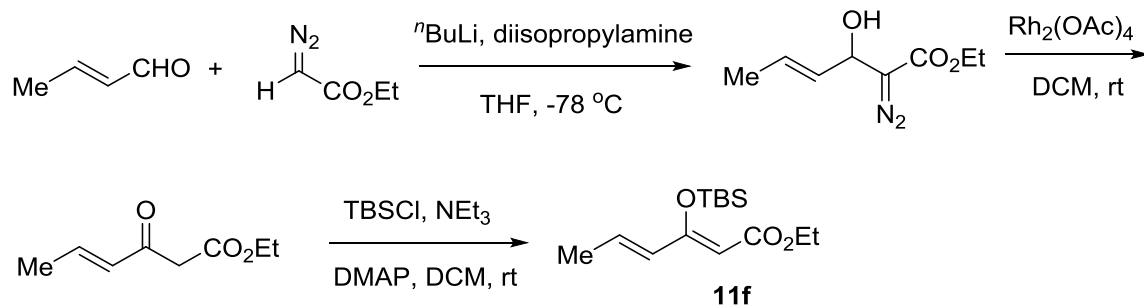
acetate (3.34 g, 10.0 mmol, 1.0 equiv) in dichloromethane (30 mL) at -20 °C . The mixture was stirred at -20 °C for 1 h and then allowed to warm to rt. Acetaldehyde (0.44 g, 10.0 mmol, 1.0 equiv) and K₂CO₃ (3.45 g, 25.0 mmol, 2.5 equiv) were added to the mixture which was stirred for 16 h. The reaction mixture was poured into 30 mL of H₂O. The organic phase was washed with brine (30 mL), dried over MgSO₄, concentrated under reduced pressure, and purified by column chromatography on silica gel eluting with hexanes : diethyl ether (20 : 1) to give the product as a colorless oil (1.14 g, 64%); ¹H NMR (400 MHz; CDCl₃) δ 7.37 (q, *J* = 6.8 Hz, 1H), 3.80 (s, 3H), 1.93 (d, *J* = 6.8 Hz, 3H).



Methyl (2E,4E,6E)-octa-2,4,6-trienoate (11e):

CAS registry number: 82388-11-2.

This compound was prepared according to a literature procedure⁵: To a solution of methyl (triphenylphosphoranylidene)acetate (2.52 g, 7.5 mmol, 1.0 equiv) in dry THF (20 mL) at rt was added (2E,4E)-hexa-2,4-dienal (0.56 g, 5.8 mmol). The mixture was stirred at rt under nitrogen, for 48 h, after which the solvent was evaporated and the residue was dissolved in a minimal amount of dichloromethane. Hexanes was added to the stirred solution to precipitate triphenylphosphine oxide. The precipitate was separated by filtration and the filtrate was concentrated. The residue was purified by column chromatography on silica gel eluting with hexanes : diethyl ether (40 : 1) to give the product as a white solid (0.66 g, 75%); ¹H NMR (400 MHz; CDCl₃) δ 7.27 (dd, *J* = 15.6, 11.6 Hz, 1H), 6.49 (dd, *J* = 14.8, 10.8 Hz, 1H), 6.25–6.06 (m, 2H), 5.91 (dq, *J* = 14.8, 6.8 Hz, 1H), 5.81 (d, *J* = 15.2 Hz, 1H), 3.71 (s, 3H), 1.80 (dd, *J* = 6.8, 1.2 Hz, 3H).



Ethyl (2Z,4E)-3-((tert-butyldimethylsilyl)oxy)hexa-2,4-dienoate (11f): Prepared following literature procedures for the preparation of similar compounds:⁶

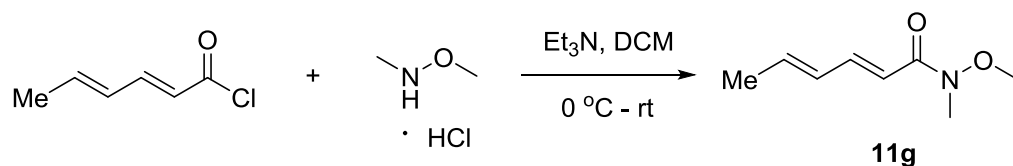
$n\text{BuLi}$ (2.5 M in hexanes, 15.0 mL, 37.5 mmol, 1.43 equiv) was added to a solution of diisopropylamine (3.60 g, 35.6 mmol, 1.36 equiv) at $-78\text{ }^\circ\text{C}$ dropwise under argon. The solution was then stirred at $-78\text{ }^\circ\text{C}$ for 30 min to give a light yellow lithium diisopropylamide (LDA) solution that was used directly.

The LDA solution prepared above was then added dropwise to a solution of (E)-but-2-enal (4.2 g, 4.9 mL, 59.4 mmol, 2.26 equiv) was added ethyl 2-diazoacetate (3.0 g, 26.3 mmol, 1.00 equiv) at $-78\text{ }^\circ\text{C}$.. After stirring at $-78\text{ }^\circ\text{C}$ for 2 h, the reaction was quenched with saturated aqueous NH_4Cl (40 mL), and was extracted with diethyl ether (100 mL \times 2). The combined organics were washed with saturated aqueous NaHCO_3 (50 mL), brine (50 mL), dried over MgSO_4 , concentrated, and purified by column chromatography on silica gel eluting with hexanes : diethyl ether (4 : 1) to give ethyl (E)-2-diazo-3-hydroxyhex-4-enoate as a yellow oil (4.6 g, *c.a.* 95% purity) that was used in the next step without further purification.

To a solution of $\text{Rh}_2(\text{OAc})_4$ (56 mg, 0.5 mol %) in dry dichloromethane (10 mL) was added the diazo compound (E)-2-diazo-3-hydroxyhex-4-enoate (4.6 g , *c.a.* 25 mmol) dropwise. The reaction mixture was stirred at rt for 2 h. Then the solvent was removed under reduced pressure to give crude ethyl (E)-3-oxohex-4-enoate, which was used directly in the next step.

To a solution of crude ethyl (E)-3-oxohex-4-enoate in dry dichloromethane (75 mL) was added TBSCl (4.1 g, 27.5 mmol, 1.0 equiv), NEt_3 (4.3 mL, 30.0 mmol, 1.1 equiv), and DMAP (154 mg, 1.25 mmol, 5 mol %) sequentially at rt. The reaction mixture was stirred at rt for 24 h before it was concentrated. The residue was

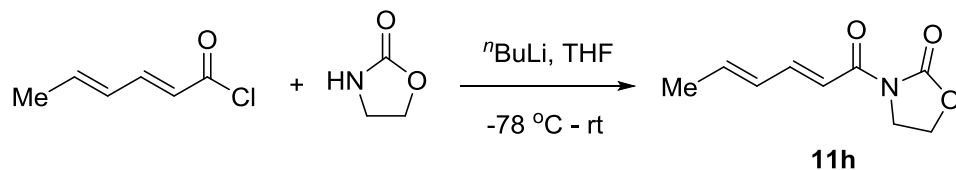
extracted with diethyl ether (100 mL × 2). The combined organics were washed with saturated aqueous NH₄Cl (50 mL), brine (50 mL), dried over MgSO₄, concentrated, and purified by column chromatography on silica gel eluting with hexanes : diethyl ether (50 : 1 to 25 : 1) to give ethyl (2*Z*,4*E*)-3-((*tert*-butyldimethylsilyl)oxy)hexa-2,4-dienoate (**11f**) as a colorless oil (3.5 g, 49% for three steps); *R_f* = 0.40 (hexanes : diethyl ether = 10 : 1); ¹H NMR (400 MHz; CDCl₃) δ 7.34 (dq, *J* = 15.2, 1.6 Hz, 1H), 6.44 (dq, *J* = 15.2, 7.2 Hz, 1H), 5.03 (s, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 1.83 (dd, *J* = 7.2, 1.6 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.93 (s, 9H), 0.19 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 167.3, 163.8, 134.9, 125.6, 98.7, 59.4, 25.6, 18.3, 18.3, 14.4, -4.6; IR (neat): 2957, 2931, 2859, 1707, 1648, 1582, 1293, 1257, 1131, 1051, 911, 823, 808, 781 cm⁻¹; HRMS (NSI) *m/z*: [M+H]⁺ calcd for C₁₄H₂₇O₃Si 271.1724; found 271.1721.



(2*E*,4*E*)-*N*-methoxy-*N*-methylhexa-2,4-dienamide (11g**):**

CAS registry number: 121712-54-7.

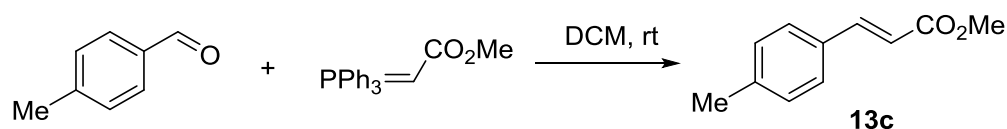
To a mixture of *N,O*-dimethylhydroxylamine hydrochloride (1.67 g, 17.14 mmol, 1.05 equiv) and triethylamine (4.95 mL, 35.90 mmol, 2.2 equiv) in dry dichloromethane (50 mL) was added (2*E*,4*E*)-hexa-2,4-dienoyl chloride (2.13 g, 16.32 mmol, 1.0 equiv) at 0 °C. The resulting mixture was stirred overnight at rt, then was diluted with diethyl ether (100 mL), washed sequentially with HCl (1 M, 50 mL) and brine (50 mL), dried over MgSO₄, concentrated, and purified by column chromatography on silica gel eluting with hexanes : ethyl acetate (4 : 1 to 2 : 1) to give the product as a light yellow oil (1.70 g, 67%). ¹H NMR (400 MHz; CDCl₃) δ 7.28 (dd, *J* = 15.2, 10.8 Hz, 1H), 6.35 (d, *J* = 15.2 Hz, 1H), 6.23 (ddq, *J* = 15.2, 10.8, 0.8 Hz, 1H), 6.12 (dq, *J* = 15.2, 6.8 Hz, 1H), 3.68 (s, 3H), 3.23 (s, 3H), 1.84 (dd, *J* = 6.8, 0.8 Hz, 3H). Data matched that of literature.⁷



3-((2E,4E)-hexa-2,4-dienoyl)oxazolidin-2-one (11h):

CAS registry number: 109299-95-8.

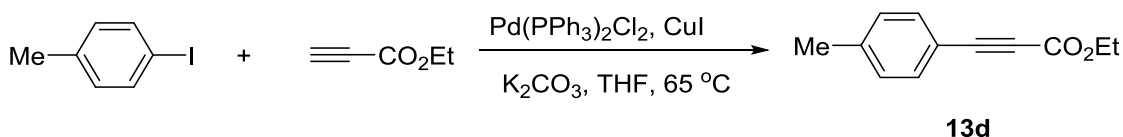
n BuLi (1.6 M in hexanes, 1.40 mL, 22.0 mmol, 1.1 equiv) was added to a stirred solution of oxazolidin-2-one (1.74 g, 20.0 mmol, 1.0 equiv) in 30 mL of THF at -78 °C over 10 min. Then (2E,4E)-hexa-2,4-dienoyl chloride (2.87 g, 22.0 mmol, 1.1 equiv) was added and the resultant mixture was stirred for a further 30 min at -78 °C, after which time the reaction mixture was allowed to warm to rt and sat. aq. NH_4Cl solution (50 mL) was added. The organic material was extracted twice with ethyl acetate (50 mL), and the combined organic extracts were washed sequentially with sat. aq. NaHCO_3 solution (50 mL) and brine (50 mL). The organics were then dried over MgSO_4 , filtered, and concentrated. The residue was purified by column chromatography on silica gel eluting with hexanes : ethyl acetate (2 : 1) to give the product as a white solid (1.30 g, 36%); ^1H NMR (400 MHz, CDCl_3): δ 7.41 (dd, $J = 15.2, 10.8$ Hz, 1H), 7.16 (d, $J = 15.2$ Hz, 1H), 6.35–6.25 (m, 1H), 6.20 (dq, $J = 15.2, 6.4$ Hz, 1H), 4.39 (t, $J = 8.0$ Hz, 2H), 4.05 (t, $J = 8.0$ Hz, 2H), 1.85 (d, $J = 6.4$ Hz, 3H). Data matched that of literature.⁸



Methyl (E)-3-(p-tolyl)acrylate (13c):

CAS registry number: 20754-20-5.

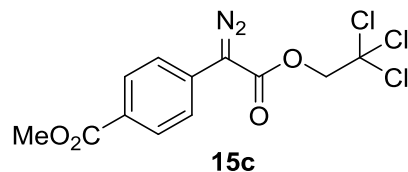
This compound was prepared according to a literature procedure⁹: To a solution of 4-methylbenzaldehyde (2.0 g, 16.6 mmol, 1.0 equiv) in dichloromethane (65 mL) was added methyl(triphenylphosphoranylidene)acetate (6.66 g, 19.9 mmol, 1.2 equiv) in one portion. The mixture was stirred at rt for 3 days and then concentrated *in vacuo*. The residue was purified by column chromatography on silica gel eluting with hexanes : diethyl ether (40 : 1 to 20 : 1) to the product as a white solid (2.80 g, 89%); ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.78 (s, 3H), 2.35 (s, 3H).



Ethyl 3-(*p*-tolyl)propiolate (13d):

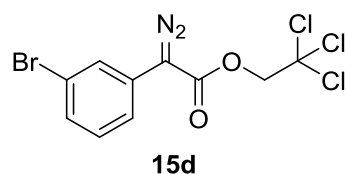
CAS registry number: 52188-06-4.

This compound was prepared according to a literature procedure¹⁰: To a solution of 1-iodo-4-methylbenzene (1.64 g, 7.5 mmol, 1.5 equiv), ethyl propiolate (490 mg, 5.0 mmol, 1.0 equiv) and K₂CO₃ (2.07 g, 15.0 mmol, 3.0 equiv) in THF (40 mL) was added Pd(PPh₃)₂Cl₂ (70 mg, 0.1 mmol, 2 mol %) and CuI (38 mg, 0.2 mmol, 4 mol %). The resulting mixture was then heated under an argon atmosphere at 65 °C for 12 h. The reaction was monitored by TLC to establish the consumption of starting material. After the mixture was cooled to rt, the solids were removed by filtration. Then the filtrate was treated with H₂O (50 mL) and extracted with ethyl acetate (2 × 50 mL), and the combined organic layer was washed with brine (50 mL) and dried over MgSO₄. The organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel eluting with hexanes : diethyl ether (30 : 1) to give the product as a colorless oil (395 mg, 42%); ¹H NMR (400 MHz, CDCl₃): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).



Methyl 4-(1-diazo-2-oxo-2-(2,2,2-trichloroethoxy)ethyl)benzoate (15c):

A yellow solid. m.p. 94-95 °C $R_f = 0.23$ (hexanes : diethyl ether = 10 : 1); ^1H NMR (400 MHz; CDCl_3) δ 8.12 (d, $J = 8.4$ Hz, 2H), 7.64 (d, $J = 8.4$ Hz, 2H), 4.99 (s, 2H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 162.5, 130.2, 130.0, 127.5, 123.0, 94.8, 73.8, 52.1 (the resonance resulting from the diazo carbon was not detected); IR (neat): 2956, 2094, 1705, 1609, 1318, 1236, 1114, 1050, 950 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{10}\text{O}_4\text{N}_2\text{Cl}_3$ 350.9701; found 350.9703.



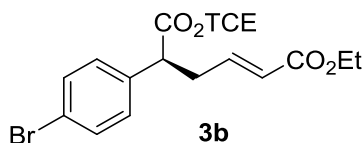
2,2,2-trichloroethyl 2-(3-bromophenyl)-2-diazoacetate (15d):

An orange crystalline solid; m.p.: 43 °C; $R_f = 0.75$ (pentane : diethyl ether, 9:1); ^1H NMR (400 MHz, CDCl_3): δ 7.71 (t, $J = 1.9$ Hz, 1H), 7.43-7.38 (m, 1H), 7.36-7.33 (m, 1H), 7.30-7.26 (m, 1H) and 4.92 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 162.75, 130.44, 129.20, 127.07, 126.64, 123.28, 122.16, 94.94, 73.92 (the resonance resulting from the diazo carbon was not detected); IR (neat): 2094, 1710, 1479, 1237, 1139 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_7\text{BrO}_2\text{Cl}_3\text{N}_2^+$ 375.0316, observed 375.0320.

General Procedure for the C-H functionalization reaction:

To an oven-dried, 10 mL round-bottomed flask, equipped with a reflux condenser and magnetic stir bar, was cooled to rt under argon before it was added with rhodium (II) catalyst (0.5 mol %) and substrate (2.0 equiv), followed by dry dichloromethane (0.5 mL). The solution was heated to reflux under argon. Then a solution of the diazo compound was dissolved in 1.2 mL dichloromethane under argon and added dropwise to the reaction mixture over 3 h by a syringe pump. The flask used to dissolve the diazo and the needle/syringe were rinsed with 0.5 mL of dichloromethane, which was added to the reaction over 30 min. The solution was stirred at reflux for 1 h and then was cooled to rt. The solvent was removed *in vacuo* and the crude residue was purified by column chromatography.

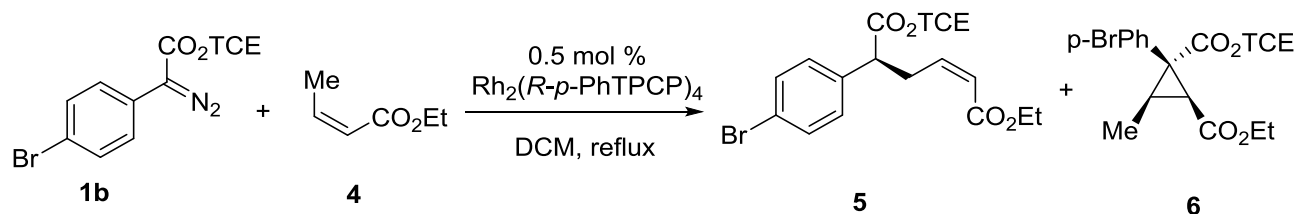
Characterization data for C-H functionalization products:



1-ethyl 6-(2,2,2-trichloroethyl) (S,E)-5-(4-bromophenyl)hex-2-enedioate (**3b**):

Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), ethyl (*E*)-but-2-enoate (**2**) (182 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (12 : 1 to 6 : 1) to afford the product as a colorless oil (270 mg, 74% isolated yield); R_f = 0.25 (hexanes : diethyl ether = 5 : 1); ^1H NMR (600 MHz; CDCl_3) δ 7.51-7.45 (m, 2H), 7.25-7.19 (m, 2H), 6.83 (app dt, J = 15.6, 7.1 Hz, 1H), 5.88 (app dt, J = 15.6, 1.5 Hz, 1H), 4.75 (d, J = 12.0 Hz, 1H), 4.70 (d, J = 12.0 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.83 (dd, J = 8.2, 7.1 Hz, 1H), 3.03 (dddd, J = 15.5, 8.5, 7.1, 1.5 Hz, 1H), 2.71 (app dtd, J = 15.3, 7.1, 1.5 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.9, 166.1, 143.9, 135.9, 132.2, 129.9, 124.4, 122.3, 94.7, 74.4, 60.6, 49.9, 35.4, 14.4; IR (neat): 2981, 1750, 1716, 1139 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4\text{Cl}_3\text{BrNa}$ 478.9190; found 478.9199; The ee was determined by chiral

HPLC: OD-H column, 1 mL/min, 1 % *i*PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 23.02 min, Minor: 20.38 min, 95% ee; $[\alpha]_D^{20}$: +43° (c 1.7, CHCl₃).

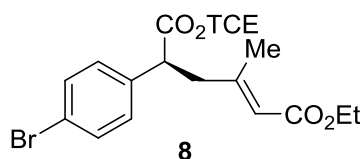


The reaction was performed according to general procedure using $\text{Rh}_2(\text{R-p-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), ethyl (Z)-but-2-enoate (**4**) (182 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (8 : 1 to 6 : 1) to afford the C–H insertion product (**5**) and cyclopropanation product (**6**).

1-ethyl 6-(2,2,2-trichloroethyl) (5,Z)-5-(4-bromophenyl)hex-2-enedioate (5): a colorless oil (180 mg, 49%); $R_f = 0.17$ (hexanes : diethyl ether = 10 : 1); $^1\text{H NMR}$ (600 MHz; CDCl₃) δ 7.43 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 6.08 (dt, $J = 11.4, 7.8$ Hz, 1H), 5.79 (dt, $J = 11.4, 1.8$ Hz, 1H), 4.71 (d, $J = 12.0$ Hz, 1H), 4.68 (d, $J = 12.0$ Hz, 1H), 4.14 (q, $J = 7.2$ Hz, 2H), 3.83 (t, $J = 7.8$ Hz, 1H), 3.34 (dtd, $J = 15.0, 7.8, 1.8$ Hz, 1H), 3.26 (dtd, $J = 15.2, 7.8, 1.8$ Hz, 1H), 1.25 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl₃) δ 171.0, 165.8, 144.7, 136.0, 131.8, 129.9, 122.3, 121.8, 94.6, 74.1, 60.1, 50.3, 31.7, 14.2; IR (neat): 2981, 1750, 1714, 1645, 1488, 1371, 1192, 1139, 1011, 820, 761, 717 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{Cl}]^-$ calcd for C₁₆H₁₆O₄BrCl₄ 490.8992; found 490.8997; The ee was determined by chiral HPLC: SS-WHELK column, 1 mL/min, 1 % *i*PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 13.08 min, Minor: 11.84 min, 97% ee. $[\alpha]_D^{20}$: +13° (c 2.6, CHCl₃).

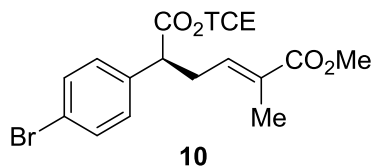
Compound **6** (stereochemistry is tentatively assigned by analogy to previous work¹¹): a colorless oil (62 mg, 17%); $R_f = 0.20$ (hexanes : diethyl ether = 10 : 1); $^1\text{H NMR}$ (600 MHz; CDCl₃) δ 7.43 (d, $J = 8.4$ Hz, 2H),

7.02 (d, $J = 8.4$ Hz, 2H), 4.61 (s, 2H), 4.35 – 3.88 (m, 2H), 2.79 (d, $J = 9.6$ Hz, 1H), 2.31 (dq, $J = 9.6, 6.6$ Hz, 1H), 1.33 (d, $J = 6.6$ Hz, 3H), 1.19 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.0, 168.3, 133.4, 131.2, 130.3, 122.1, 94.5, 74.6, 60.8, 38.7, 31.6, 27.8, 14.1, 10.2; IR (neat): 2959, 1732, 1490, 1224, 1176, 1035, 1012, 830, 809, 787, 766, 717 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{O}_4\text{BrCl}_3$ 456.9370; found 456.9378; The ee was determined by chiral HPLC: OD-H column, 1 mL/min, 1 % i -PrOH in hexanes, $\lambda = 230$ nm. t_{R} : Major: 6.14 min, Minor: 7.57 min, 93% ee. $[\alpha]_{\text{D}}^{20}$: +29° (c 2.3, CHCl_3).



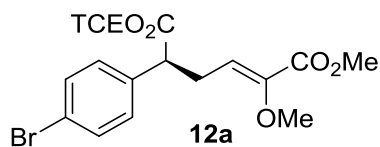
1-ethyl 6-(2,2,2-trichloroethyl) (S,E)-5-(4-bromophenyl)-3-methylhex-2-enedioate (8):

Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), ethyl 3-methylbut-2-enoate (**7**) (205 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (20 : 1 to 10 : 1) to afford the product as a colorless oil (144 mg, 38%); $R_f = 0.33$ (hexanes : diethyl ether = 8 : 1); ^1H NMR (600 MHz; CDCl_3) δ 7.45 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $J = 8.4$ Hz, 2H), 5.65 (q, $J = 1.2$ Hz, 1H), 4.73 (d, $J = 12.0$ Hz, 1H), 4.63 (d, $J = 12.0$ Hz, 1H), 4.09 (q, $J = 7.2$ Hz, 2H), 3.93 (dd, $J = 9.0, 6.6$ Hz, 1H), 2.97 (dd, $J = 14.4, 9.0$ Hz, 1H), 2.57 (dd, $J = 14.4, 6.6$ Hz, 1H), 2.14 (d, $J = 1.2$ Hz, 3H), 1.23 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.8, 166.1, 154.4, 135.9, 132.0, 129.6, 122.0, 118.2, 94.5, 74.2, 59.7, 48.8, 43.6, 18.7, 14.2; IR (neat): 2980, 1752, 1714, 1651, 1488, 1369, 1222, 1147, 1012, 836, 800, 755, 720 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{19}\text{O}_4\text{BrCl}_3$ 470.9527; found 470.9533; The ee was determined by chiral HPLC: OD-H column, 1 mL/min, 1 % i -PrOH in hexanes, $\lambda = 230$ nm. t_{R} : Major: 9.11 min, Minor: 10.12 min, 97% ee; $[\alpha]_{\text{D}}^{20}$: +27° (c 1.0, CHCl_3).



1-methyl 6-(2,2,2-trichloroethyl) (S,E)-5-(4-bromophenyl)-2-methylhex-2-enedioate (10):

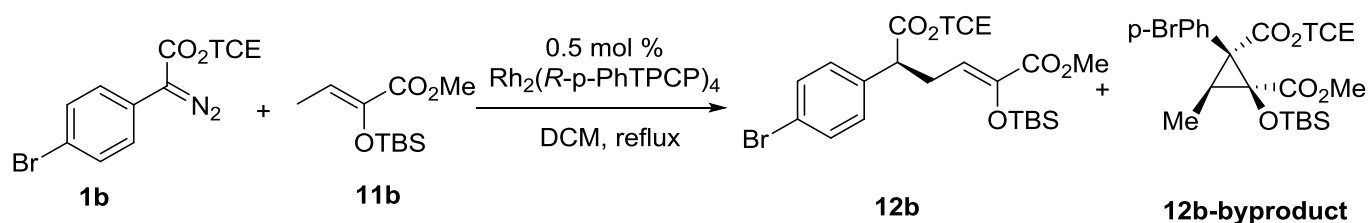
Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), methyl (*E*)-2-methylbut-2-enoate (**9**) (182 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (8 : 1) to afford the product as a colorless oil (286 mg, 78%); $R_f = 0.25$ (hexanes : diethyl ether = 6 : 1); $^1\text{H NMR}$ (400 MHz; CDCl_3) δ 7.45 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $J = 8.4$ Hz, 2H), 6.61 (tq, $J = 7.6, 1.6$ Hz, 1H), 4.73 (d, $J = 12.0$ Hz, 1H), 4.67 (d, $J = 12.0$ Hz, 1H), 3.77 (t, $J = 7.6$ Hz, 1H), 3.68 (s, 3H), 2.97 (dt, $J = 15.2, 7.6$ Hz, 1H), 2.67 (dt, $J = 14.8, 7.2$ Hz, 1H), 1.80 (d, $J = 1.6$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.0, 168.0, 137.0, 135.9, 132.0, 130.2, 129.7, 122.0, 94.6, 74.1, 51.9, 49.9, 32.0, 12.6; IR (neat): 2951, 1750, 1712, 1652, 1488, 1435, 1372, 1265, 1191, 1124, 1074, 1011, 902, 826, 755, 717 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{O}_4\text{BrCl}_3$ 456.9370; found 456.9374; The ee was determined by chiral HPLC: OJ-H column, 1 mL/min, 2 % *i*PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 15.44 min, Minor: 21.99 min, 98% ee; $[\alpha]_D^{20}$: +42° (c 2.1, CHCl_3).



1-methyl 6-(2,2,2-trichloroethyl) (S,Z)-5-(4-bromophenyl)-2-methoxyhex-2-enedioate (12a):

Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), methyl (*Z*)-2-methoxybut-2-enoate (**11a**) (208 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on

silica gel eluting with hexanes : diethyl ether (30 : 1 to 15 : 1) to afford the product as a colorless oil (334 mg, 88%); $R_f = 0.64$ (hexanes : diethyl ether = 6 : 1); $^1\text{H NMR}$ (400 MHz; CDCl_3) δ 7.45 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 6.07 (t, $J = 7.6$ Hz, 1H), 4.73 (d, $J = 12.0$ Hz, 1H), 4.68 (d, $J = 12.0$ Hz, 1H), 3.75 (t, $J = 7.6$ Hz, 1H), 3.72 (s, 3H), 3.59 (s, 3H), 2.97 (dt, $J = 15.2, 7.6$ Hz, 1H), 2.77 (dt, $J = 15.2, 7.6$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.0, 163.6, 147.6, 136.0, 131.9, 129.8, 123.3, 121.9, 94.6, 74.1, 59.9, 52.0, 49.9, 28.8; IR (neat): 2951, 2844, 1750, 1724, 1652, 1488, 1435, 1372, 1252, 1201, 1141, 1115, 1072, 1011, 943, 827, 799, 769, 716 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{O}_5\text{BrCl}_3$ 472.9320; found 472.9324; The ee was determined by chiral HPLC: OD-H column, 1 mL/min, 1 % i PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 11.88 min, Minor: 13.34 min, 98% ee; $[\alpha]_D^{20}$: +43° (c 2.5, CHCl_3).

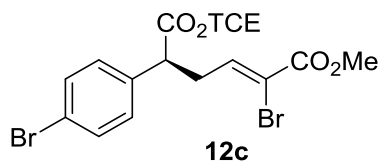


Performed according to general procedure using $\text{Rh}_2(\text{R-p-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), methyl (Z)-2-((*tert*-butyldimethylsilyloxy)but-2-enoate (**11b**) (368 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (30 : 1 to 15 : 1) to afford the products.

1-methyl 6-(2,2,2-trichloroethyl) (S,Z)-5-(4-bromophenyl)-2-((*tert*-butyldimethylsilyloxy)hex-2-enedioate (12b**):** a colorless oil (228 mg, 50%); $R_f = 0.64$ (hexanes : diethyl ether = 6 : 1); $^1\text{H NMR}$ (400 MHz; CDCl_3) δ 7.45 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $J = 8.4$ Hz, 2H), 5.83 (t, $J = 7.2$ Hz, 1H), 4.74 (d, $J = 12.0$ Hz, 1H), 4.68 (d, $J = 12.0$ Hz, 1H), 3.75 (t, $J = 7.6$ Hz, 1H), 3.68 (s, 3H), 2.96 (dt, $J = 15.2, 7.6$ Hz, 1H), 2.75 (dt, $J = 15.2, 7.6$ Hz, 1H), 0.93 (s, 9H), 0.14 (s, 3H), 0.14 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.1, 164.7, 142.2, 136.0, 131.9, 129.8, 121.9, 117.4, 94.6, 74.1, 52.0, 49.9, 28.9, 25.8, 18.6, -4.2, -4.3; IR (neat): 2953, 2930, 2857, 1754, 1728,

1647, 1489, 1371, 1252, 1136, 1012, 840, 785, 720 cm^{-1} ; HRMS (NSI) m/z : $[M+H]^+$ calcd for $\text{C}_{21}\text{H}_{29}\text{O}_5\text{BrCl}_3\text{Si}$ 573.0028; found 573.0039; The ee was determined by chiral HPLC: SS-WHELK column, 1 mL/min, 0.5 % i PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 9.62 min, Minor: 7.55 min, 93% ee. $[\alpha]_D^{20}$: $+29^\circ$ (c 2.0, CHCl_3).

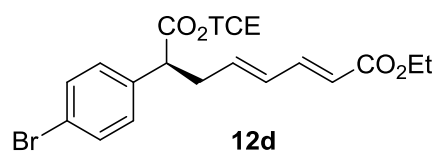
12b-byproduct (stereochemistry is tentatively assigned by analogy to previous work¹¹): obtained as a white solid (138 mg, 30%); m.p. 81-82 $^\circ\text{C}$. $R_f = 0.48$ (hexanes : diethyl ether = 6 : 1); ^1H NMR (400 MHz; CDCl_3) δ 7.43 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 4.58 (d, $J = 12.0$ Hz, 1H), 4.50 (d, $J = 12.0$ Hz, 1H), 3.73 (s, 3H), 2.61 (q, $J = 6.4$ Hz, 1H), 1.08 (d, $J = 6.4$ Hz, 3H), 0.68 (s, 9H), 0.16 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.3, 169.0, 134.2, 131.0, 129.8, 122.0, 94.5, 74.7, 66.4, 52.4, 42.8, 29.9, 25.8, 18.6, 10.1, -3.6, -3.7; IR (neat): 2953, 2930, 2857, 1747, 1489, 1252, 1207, 1153, 1050, 1013, 875, 839, 781, 768, 719 cm^{-1} ; HRMS (NSI) m/z : $[M+H]^+$ calcd for $\text{C}_{21}\text{H}_{29}\text{O}_5\text{BrCl}_3\text{Si}$ 573.0028; found 573.0034; The ee was determined by chiral HPLC: SS-WHELK column, 1 mL/min, 0.5 % i PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 5.01 min, Minor: 5.44 min, 9% ee. $[\alpha]_D^{20}$: -5° (c 1.5, CHCl_3).



1-methyl 6-(2,2,2-trichloroethyl) (S,Z)-2-bromo-5-(4-bromophenyl)hex-2-enedioate (12c):

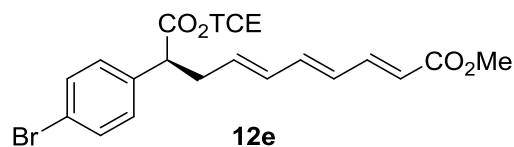
Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), methyl (Z)-2-bromobut-2-enoate (**11c**) (285 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (20 : 1 to 10 : 1) to afford the product as a colorless oil (117 mg, 28%); $R_f = 0.20$ (hexanes : diethyl ether = 10 : 1); ^1H NMR (600 MHz; CDCl_3) δ 7.46 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $J = 8.4$ Hz, 2H), 7.17 (t, $J = 7.2$ Hz, 1H), 4.73 (d, $J = 12.0$ Hz, 1H), 4.70 (d, $J = 12.0$ Hz, 1H), 3.87 (t, $J = 7.8$ Hz, 1H), 3.77 (s, 3H), 3.07 (ddd, $J = 15.0, 7.8, 6.6$ Hz, 1H), 2.88 (dt, $J = 15.0, 7.2$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ

170.6, 162.4, 141.4, 135.4, 132.1, 129.7, 122.2, 118.4, 94.5, 74.2, 53.4, 48.9, 35.0; IR (neat): 2953, 1750, 1731, 1627, 1488, 1408, 1372, 1261, 1144, 1174, 1035, 1011, 827, 799, 762, 718 cm^{-1} ; HRMS (NSI) m/z : $[M+H]^+$ calcd for $\text{C}_{15}\text{H}_{14}\text{O}_4\text{Br}_2\text{Cl}_3$ 520.8319; found 520.8328; The ee was determined by chiral HPLC: OD-H column, 1 mL/min, 1 % i PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 13.68 min, Minor: 15.02 min, 99% ee; $[\alpha]_D^{20}$: $+31^\circ$ (c 0.3, CHCl_3).



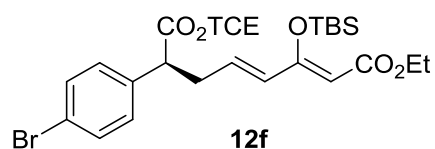
1-ethyl 8-(2,2,2-trichloroethyl) (S,2E,4E)-7-(4-bromophenyl)octa-2,4-dienedioate (12d):

Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), ethyl (2E,4E)-hexa-2,4-dienoate (**11d**) (224 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (9 : 1) to afford the product as a colorless oil (310 mg, 80%); $R_f = 0.27$ (hexanes : diethyl ether = 8 : 1); ^1H NMR (400 MHz; CDCl_3) δ 7.45 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 7.13 (dd, $J = 15.6, 10.8$ Hz, 1H), 6.20 (dd, $J = 15.2, 10.8$ Hz, 1H), 5.95 (dt, $J = 15.2, 7.2$ Hz, 1H), 5.77 (d, $J = 15.2$ Hz, 1H), 4.72 (d, $J = 12.0$ Hz, 1H), 4.66 (d, $J = 12.0$ Hz, 1H), 4.16 (q, $J = 7.2$ Hz, 2H), 3.76 (t, $J = 7.6$ Hz, 1H), 2.95 (dt, $J = 15.2, 8.0$ Hz, 1H), 2.66 (dt, $J = 14.8, 7.2$ Hz, 1H), 1.25 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 166.9, 143.7, 138.4, 135.9, 131.9, 131.1, 129.7, 121.9, 121.0, 94.6, 74.1, 60.3, 50.4, 36.1, 14.3; IR (neat): 2980, 1749, 1709, 1644, 1488, 1368, 1302, 1251, 1131, 1011, 823, 796, 756, 718 cm^{-1} ; HRMS (NSI) m/z : $[M+H]^+$ calcd for $\text{C}_{18}\text{H}_{19}\text{O}_4\text{BrCl}_3$ 482.9527; found 482.9535; The ee was determined by chiral HPLC: OD-H column, 1 mL/min, 1 % i PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 23.48 min, Minor: 18.58 min, 95% ee; $[\alpha]_D^{20}$: $+43^\circ$ (c 1.9, CHCl_3).



1-methyl 10-(2,2,2-trichloroethyl) (S,2E,4E,6E)-9-(4-bromophenyl)deca-2,4,6-trienedioate (12e):

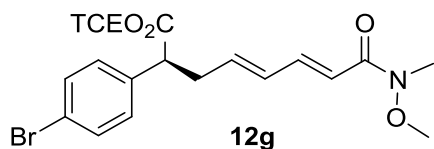
Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), ethyl (2E,4E,6E)-octa-2,4,6-trienoate (**11e**) (243 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (20 : 1 to 10 : 1) to afford the product as a colorless oil (318 mg, 80%); $R_f = 0.26$ (hexanes : diethyl ether = 10 : 1); $^1\text{H NMR}$ (400 MHz; CDCl_3) δ 7.45 (d, $J = 8.4$ Hz, 2H), 7.26 – 7.18 (m, 3H), 6.42 (dd, $J = 15.2, 10.8$ Hz, 1H), 6.19 (dt, $J = 15.2, 10.8$ Hz, 2H), 5.84 (d, $J = 15.2$ Hz, 1H), 5.77 (dt, $J = 15.2, 7.2$ Hz, 1H), 4.72 (d, $J = 12.0$ Hz, 1H), 4.66 (d, $J = 12.0$ Hz, 1H), 3.75 (dd, $J = 8.4, 7.2$ Hz, 1H), 3.72 (s, 3H), 3.03 – 2.85 (m, 1H), 2.75 – 2.58 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.0, 167.4, 144.5, 140.0, 136.0, 134.4, 132.6, 131.9, 129.7, 129.3, 121.9, 120.6, 94.6, 74.1, 51.5, 50.6, 36.2; IR (neat): 2950, 1750, 1713, 1618, 1488, 1434, 1266, 1135, 1037, 1005, 825, 755, 718 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{O}_4\text{BrCl}_3$ 494.9527; found 494.9531; The ee was determined by chiral HPLC: AD-H column, 1 mL/min, 2 % $i\text{PrOH}$ in hexanes, $\lambda = 230$ nm. t_R : Major: 23.35 min, Minor: 21.54 min, 92% ee; $[\alpha]_D^{20}$: +64° (c 1.6, CHCl_3).



1-ethyl 8-(2,2,2-trichloroethyl) (S,2Z,4E)-7-(4-bromophenyl)-3-((tert-butyldimethylsilyl)oxy)octa-2,4-dienedioate (12f):

Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), ethyl (2Z,4E)-3-((tert-butyldimethylsilyl)oxy)hexa-2,4-dienoate (**11f**) (432 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column

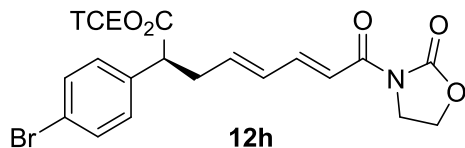
chromatography on silica gel eluting with hexanes : diethyl ether (20 : 1 to 10 : 1) to afford the product as a colorless oil (413 mg, 84%); $R_f = 0.25$ (hexanes : diethyl ether = 10 : 1); $^1\text{H NMR}$ (400 MHz; CDCl_3) δ 7.51 – 7.40 (m, 3H), 7.21 (d, $J = 8.4$ Hz, 2H), 6.24 (dt, $J = 15.2, 7.2$ Hz, 1H), 5.05 (s, 1H), 4.71 (d, $J = 12.0$ Hz, 1H), 4.67 (d, $J = 12.0$ Hz, 1H), 4.10 (q, $J = 7.2$ Hz, 2H), 3.77 (dd, $J = 8.0, 7.6$ Hz, 1H), 2.99 (dddd, $J = 14.4, 8.0, 6.8, 1.2$ Hz, 1H), 2.75 (dddd, $J = 14.8, 8.0, 6.8, 1.2$ Hz, 1H), 1.24 (t, $J = 7.2$ Hz, 3H), 0.85 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.9, 167.1, 162.9, 135.9, 134.4, 131.9, 129.9, 126.9, 121.8, 100.0, 94.6, 74.1, 59.6, 50.5, 35.5, 25.5, 18.2, 14.4, -4.7, -4.7; IR (neat): 2955, 2930, 2858, 1753, 1703, 1647, 1582, 1488, 1373, 1298, 1257, 1132, 1049, 1011, 824, 809, 783, 719 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{33}\text{O}_5\text{BrCl}_3\text{Si}$ 613.0341; found 613.0344; The ee was determined by chiral HPLC: AD-H column, 1 mL/min, 0.5 % i PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 9.21 min, Minor: 11.44 min, 58% ee; $[\alpha]_D^{20}$: +25° (c 1.9, CHCl_3).



2,2,2-trichloroethyl (*S,4E,6E*)-2-(4-bromophenyl)-8-(methoxy(methyl)amino)-8-oxoocta-4,6-dienoate (12g**):**

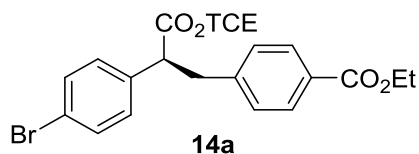
Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), (*2E,4E*)-*N*-methoxy-*N*-methylhexa-2,4-dienamide (**11g**) (248 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : ethyl acetate (4 : 1 to 2 : 1) to afford the product as a colorless oil (140 mg, 35%); $R_f = 0.23$ (hexanes : ethyl acetate = 2 : 1); $^1\text{H NMR}$ (400 MHz; CDCl_3) δ 7.45 (d, $J = 8.4$ Hz, 2H), 7.23 – 7.13 (m, 3H), 6.37 (d, $J = 15.2$ Hz, 1H), 6.26 (dd, $J = 15.2, 11.0$ Hz, 1H), 5.95 (dt, $J = 14.8, 7.1$ Hz, 1H), 4.73 (d, $J = 12.0$ Hz, 1H), 4.66 (d, $J = 12.0$ Hz, 1H), 3.77 (dd, $J = 8.3, 7.0$ Hz, 1H), 3.67 (s, 3H), 3.22 (s, 3H), 3.02 – 2.89 (m, 1H), 2.65 (dtd, $J = 14.3, 6.9, 1.4$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.0, 167.0, 142.6, 137.7, 136.0, 131.9, 131.6, 129.7, 121.9, 118.6, 94.6, 74.1, 61.8, 50.4, 36.2, 32.4; IR (neat): 2923, 2853, 1750, 1657, 1630, 1607, 1488, 1377, 1135, 1001, 818, 794, 756, 719 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for

$C_{18}H_{20}O_4NBrCl_3$ 497.9636; found 497.9643; The ee was determined by chiral HPLC: AD-H column, 1 mL/min, 10 % *i*PrOH in hexanes, $\lambda = 254$ nm. t_R : Major: 15.83 min, Minor: 14.89 min, 97% ee; $[\alpha]_D^{20}$: +38° (c 1.3, $CHCl_3$).



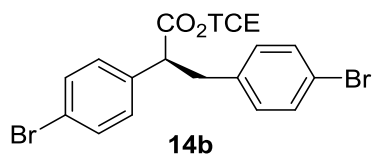
2,2,2-trichloroethyl (*S*,4*E*,6*E*)-2-(4-bromophenyl)-8-oxo-8-(2-oxooxazolidin-3-yl)octa-4,6-dienoate (12h**):**

Prepared according to general procedure using $Rh_2(R-p\text{-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), 3-((2*E*,4*E*)-hexa-2,4-dienoyl)oxazolidin-2-one (**11h**) (290 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether : dichloromethane (1 : 1 : 0 to 1 : 1 : 0.01) to afford the product as a colorless solid (340 mg, 81%); m.p. 76-78 °C $R_f = 0.22$ (hexanes : diethyl ether = 1 : 1); 1H NMR (400 MHz; $CDCl_3$) δ 7.45 (d, $J = 8.0$ Hz, 2H), 7.32 (dd, $J = 15.2, 10.8$ Hz, 1H), 7.25 – 7.12 (m, 3H), 6.33 (dd, $J = 15.2, 10.8$ Hz, 1H), 6.04 (dt, $J = 14.8, 7.2$ Hz, 1H), 4.72 (d, $J = 12.0$ Hz, 1H), 4.66 (d, $J = 12.0$ Hz, 1H), 4.39 (t, $J = 8.0$ Hz, 2H), 4.04 (t, $J = 8.0$ Hz, 2H), 3.78 (dd, $J = 7.6$ Hz, 1H), 2.98 (ddd, $J = 14.8, 14.8, 7.6$ Hz, 1H), 2.68 (ddd, $J = 14.8, 14.8, 7.2$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 165.3, 153.5, 145.5, 140.1, 135.8, 132.0, 131.6, 129.7, 121.9, 119.4, 94.6, 74.1, 62.0, 50.3, 42.7, 36.2; IR (neat): 2921, 1770, 1749, 1675, 1632, 1603, 1488, 1385, 1361, 1270, 1136, 1031, 1009, 908, 825, 794, 756, 708 cm^{-1} ; HRMS (NSI) m/z : $[M+H]^+$ calcd for $C_{19}H_{18}O_5NBrCl_3$ 523.9428; found 523.9435; The ee was determined by chiral HPLC: AD-H column, 1 mL/min, 20 % *i*PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 31.35 min, Minor: 35.56 min, 97% ee; $[\alpha]_D^{20}$: +62° (c 2.8, $CHCl_3$).



Ethyl (S)-4-(2-(4-bromophenyl)-3-oxo-3-(2,2,2-trichloroethoxy)propyl)benzoate (14a):

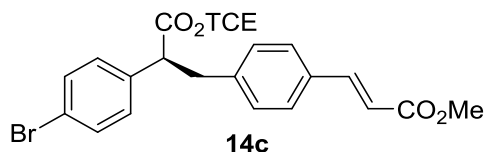
Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), ethyl 4-methylbenzoate (**13a**) (262 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (12 : 1 to 6 : 1) to afford the product as a colorless oil (311 mg, 77%); $R_f = 0.23$ (hexanes : diethyl ether = 6 : 1); $^1\text{H NMR}$ (600 MHz; CDCl_3) δ 7.95 (d, $J = 8.4$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 7.8$ Hz, 2H), 7.22 (d, $J = 7.8$ Hz, 2H), 4.71 (d, $J = 12.0$ Hz, 1H), 4.68 (d, $J = 12.0$ Hz, 1H), 4.38 (q, $J = 7.2$ Hz, 2H), 4.01 (t, $J = 7.8$ Hz, 1H), 3.52 (dd, $J = 13.8, 8.4$ Hz, 1H), 3.16 (dd, $J = 13.8, 7.2$ Hz, 1H), 1.40 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 170.9, 166.3, 143.1, 136.0, 131.9, 129.8, 129.7, 129.0, 128.9, 121.9, 94.5, 74.1, 60.9, 52.4, 39.1, 14.3; IR (neat): 2980, 1750, 1712, 1611, 1488, 1367, 1274, 1137, 1100, 1073, 1021, 1011, 908, 832, 798, 753, 718 cm^{-1} ; HRMS (APCI) m/z : $[\text{M}-\text{H}]^-$ calcd for $\text{C}_{20}\text{H}_{19}\text{O}_4\text{BrCl}_3$ 506.9527; found 506.9532; The ee was determined by chiral HPLC: OJ-H column, 1 mL/min, 1 % i PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 28.98 min, Minor: 34.51 min, 97% ee; $[\alpha]_D^{20}$: +61° (c 2.3, CHCl_3).



2,2,2-trichloroethyl (S)-2,3-bis(4-bromophenyl)propanoate (14b):

Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), 1-bromo-4-methylbenzene (**13b**) (274 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with

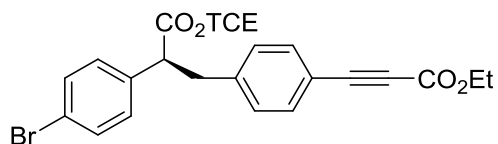
hexanes : diethyl ether (30 : 1) to afford the product as a colorless solid (366 mg, 89%); m.p. 74-75 °C, R_f = 0.70 (hexanes : diethyl ether = 5 : 1); $^1\text{H NMR}$ (400 MHz; CDCl_3) δ 7.43 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.2 Hz, 2H), 4.67 (d, J = 12.0 Hz, 1H), 4.63 (d, J = 12.0 Hz, 1H), 3.91 (dd, J = 8.0, 6.8 Hz, 1H), 3.38 (dd, J = 14.0, 8.0 Hz, 1H), 3.02 (dd, J = 14.0, 6.8 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.0, 136.9, 136.0, 131.9, 131.6, 130.7, 129.8, 121.9, 120.7, 94.5, 74.1, 52.6, 38.6; IR (neat): 2954, 1748, 1487, 1371, 1202, 1135, 1072, 1011, 812, 753, 716 cm^{-1} ; HRMS (APCI) m/z : $[\text{M}-\text{H}]^-$ calcd for $\text{C}_{17}\text{H}_{12}\text{O}_2\text{Br}_2\text{Cl}_3$ 510.8275; found 510.8266; The ee was determined by chiral HPLC: AS-H column, 0.5 mL/min, 0.5 % i PrOH in hexanes, λ = 230 nm. t_R : Major: 14.75 min, Minor: 18.39 min, 98% ee; $[\alpha]_D^{20}$: +70° (c 2.0, CHCl_3).



Methyl (*S,E*)-3-(4-(2-(4-bromophenyl)-3-oxo-3-(2,2,2-trichloroethoxy)propyl)phenyl)acrylate (14c**):**

Prepared according to general procedure using $\text{Rh}_2(\text{R-}p\text{-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), methyl (*E*)-3-(*p*-tolyl)acrylate (**13c**) (282 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (15 : 1 to 15 : 2) to afford the product as a colorless oil (368 mg, 86%); R_f = 0.21 (hexanes : diethyl ether = 8 : 1); $^1\text{H NMR}$ (400 MHz; CDCl_3) δ 7.61 (d, J = 16.0 Hz, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 6.37 (d, J = 16.0 Hz, 1H), 4.67 (d, J = 12.0 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 3.95 (dd, J = 8.8, 7.2 Hz, 1H), 3.78 (s, 3H), 3.43 (dd, J = 14.0, 8.8 Hz, 1H), 3.08 (dd, J = 14.0, 7.2 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.0, 167.4, 144.4, 140.5, 136.1, 132.9, 131.9, 129.8, 129.5, 128.2, 121.9, 117.5, 94.5, 74.1, 52.5, 51.7, 39.1; IR (neat): 2950, 1749, 1715, 1635, 1488, 1435, 1314, 1273, 1167, 1136, 1011, 982, 818, 797, 754, 717 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for

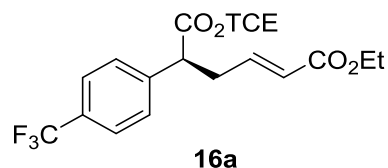
$C_{22}H_{19}O_4BrCl_3$ 518.9527; found 518.9533; The ee was determined by chiral HPLC: AD-H column, 1 mL/min, 2 % i PrOH in hexanes, $\lambda = 254$ nm. t_R : Major: 32.01 min, Minor: 34.73 min, 97% ee; $[\alpha]_D^{20}$: +100° (c 1.6, $CHCl_3$).



14d

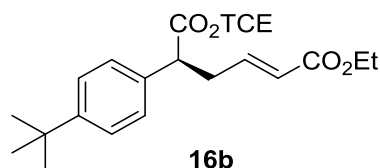
Ethyl (S)-3-(4-(2-(4-bromophenyl)-3-oxo-3-(2,2,2-trichloroethoxy)propyl)phenyl)propionate (14d):

Prepared according to general procedure using $Rh_2(R-p\text{-PhTPCP})_4$ (7.0 mg, 0.004 mmol, 0.5 mol %), ethyl 3-(*p*-tolyl)propionate (**13d**) (301 mg, 1.6 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1b**) (298 mg, 0.8 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (20 : 1 to 10 : 1) to afford the product as a colorless oil (345 mg, 81%); $R_f = 0.20$ (hexanes : diethyl ether = 12 : 1); 1H NMR (400 MHz; $CDCl_3$) δ 7.56 – 7.36 (m, 4H), 7.18 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.2$ Hz, 2H), 4.67 (d, $J = 12.0$ Hz, 1H), 4.61 (d, $J = 12.0$ Hz, 1H), 4.26 (q, $J = 7.2$ Hz, 2H), 3.93 (dd, $J = 8.8, 7.2$ Hz, 1H), 3.43 (dd, $J = 14.0, 8.8$ Hz, 1H), 3.07 (dd, $J = 14.0, 7.2$ Hz, 1H), 1.32 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 154.0, 141.0, 135.9, 133.1, 131.9, 129.8, 129.3, 122.0, 118.0, 94.5, 85.8, 80.8, 74.1, 62.1, 52.4, 39.2, 14.1; IR (neat): 2928, 2235, 2209, 1751, 1704, 1488, 1368, 1290, 1194, 1176, 1140, 1011, 824, 720 cm^{-1} ; HRMS (NSI) m/z : $[M+H]^+$ calcd for $C_{22}H_{19}O_4BrCl_3$ 530.9527; found 530.9532; The ee was determined by chiral HPLC: OD-H column, 1 mL/min, 1 % i PrOH in hexanes, $\lambda = 254$ nm. t_R : Major: 22.54 min, Minor: 20.12 min, 96% ee; $[\alpha]_D^{20}$: +92° (c 2.2, $CHCl_3$).



1-ethyl 6-(2,2,2-trichloroethyl) (S,E)-5-(4-(trifluoromethyl)phenyl)hex-2-enedioate (16a):

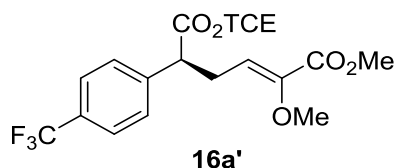
Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (3.5 mg, 0.002 mmol, 0.5 mol %), ethyl (*E*)-but-2-enoate (**2**) (91 mg, 0.8 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (**15a**) (145 mg, 0.4 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexane: diethyl ether (12 : 1 to 6 : 1) to afford the product as a colorless oil (120 mg, 67%); $R_f = 0.20$ (hexane : diethyl ether = 5 : 1); $^1\text{H NMR}$ (400 MHz; CDCl_3) δ 7.59 (d, $J = 8.0$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, 2H), 6.82 (dt, $J = 15.6, 7.2$ Hz, 1H), 5.87 (d, $J = 15.6$ Hz, 1H), 4.74 (d, $J = 12.0$ Hz, 1H), 4.68 (d, $J = 12.0$ Hz, 1H), 4.13 (q, $J = 7.2$ Hz, 2H), 3.92 (t, $J = 7.6$ Hz, 1H), 3.06 (dt, $J = 15.2, 8.0$ Hz, 1H), 2.72 (dt, $J = 15.2, 7.2$ Hz, 1H), 1.23 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.4, 165.8, 143.4, 140.6, 130.3 (q, $J = 32$ Hz), 128.4, 125.8 (q, $J = 4$ Hz), 123.9 (q, $J = 271$ Hz), 124.3, 94.4, 74.2, 60.4, 50.0, 35.1, 14.2.; IR (neat): 2984, 1753, 1717, 1324, 1267, 1162, 1125, 1068, 975, 842, 716 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{17}\text{O}_4\text{Cl}_3\text{F}_3$ 447.0139; found 447.0145; The ee was determined by chiral HPLC: OJ-H column, 1 mL/min, 1 % *i*PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 17.65 min, Minor: 24.57 min, 98% ee; $[\alpha]_D^{20}$: +38° (c 2.0, CHCl_3).



1-ethyl 6-(2,2,2-trichloroethyl) (S,E)-5-(4-(tert-butyl)phenyl)hex-2-enedioate (16b):

Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (3.5 mg, 0.002 mmol, 0.5 mol %), ethyl (*E*)-but-2-enoate (**2**) (92 mg, 0.8 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-(*tert*-butyl)phenyl)-2-diazoacetate (**15b**) (140 mg, 0.4 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting

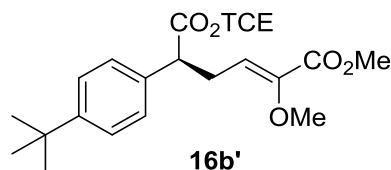
with hexane: diethyl ether (20 : 1 to 10 : 1) to afford the product as a colorless oil (122 mg, 70%); $R_f = 0.31$ (hexane : diethyl ether = 10 : 1); $^1\text{H NMR}$ (400 MHz; CDCl_3) δ 7.34 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 6.87 (dt, $J = 16.0, 7.6$ Hz, 1H), 5.89 (d, $J = 16.0$ Hz, 1H), 4.77 (d, $J = 12.0$ Hz, 1H), 4.63 (d, $J = 12.0$ Hz, 1H), 4.14 (q, $J = 7.2$ Hz, 2H), 3.82 (dd, $J = 8.4, 6.8$ Hz, 1H), 3.04 (dt, $J = 15.6, 8.4$ Hz, 1H), 2.70 (dt, $J = 15.2, 6.4$ Hz, 1H), 1.29 (s, 9H), 1.24 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.3, 166.1, 150.9, 144.5, 133.7, 127.5, 125.8, 123.7, 94.7, 74.1, 60.3, 49.8, 35.4, 34.5, 31.3, 14.2; IR (neat): 2961, 2870, 1751, 1718, 1656, 1367, 1266, 1136, 1038, 974, 833, 720 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{26}\text{O}_4\text{Cl}_3$ 435.0891; found 435.0893; The ee was determined by chiral HPLC: OD-H column, 1 mL/min, 0.5 % i PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 14.26 min, Minor: 23.45 min, 99% ee; $[\alpha]_D^{20}$: +49° (c 1.9, CHCl_3).



1-methyl 6-(2,2,2-trichloroethyl) (S,Z)-2-methoxy-5-(4-(trifluoromethyl)phenyl)hex-2-enedioate (16a'):

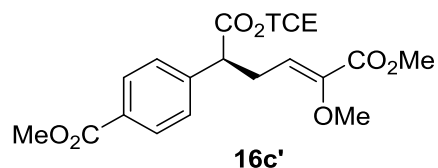
Prepared according to general procedure using $\text{Rh}_2(\text{R-}p\text{-PhTPCP})_4$ (3.5 mg, 0.002 mmol, 0.5 mol %), methyl (Z)-2-methoxybut-2-enoate (**11a**) (104 mg, 0.8 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (**15a**) (145 mg, 0.4 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (12 : 1 to 6 : 1) to afford the product as a colorless oil (152 mg, 82%); $R_f = 0.30$ (hexanes : diethyl ether = 6 : 1); $^1\text{H NMR}$ (400 MHz; CDCl_3) δ 7.59 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 6.09 (t, $J = 7.6$ Hz, 1H), 4.75 (d, $J = 12.0$ Hz, 1H), 4.69 (d, $J = 12.0$ Hz, 1H), 3.87 (t, $J = 7.6$ Hz, 1H), 3.73 (s, 3H), 3.59 (s, 3H), 3.02 (dt, $J = 14.8, 7.6$ Hz, 1H), 2.82 (dt, $J = 14.8, 7.6$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.8, 163.5, 147.7, 140.9, 130.2 (q, $J = 32$ Hz), 128.5, 125.7 (q, $J = 4$ Hz), 123.9 (q, $J = 271$ Hz), 122.9, 94.5, 74.2, 59.9, 52.0, 50.2, 28.8; IR (neat): 2954, 1752, 1726, 1323, 1269, 1163, 1116, 1068, 1018, 843, 779, 716 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{17}\text{O}_5\text{Cl}_3\text{F}_3$ 463.0088; found 463.0093; The ee was determined

by chiral HPLC: OD-H column, 1 mL/min, 0.5 % *i*PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 7.84 min, Minor: 9.00 min, 99% ee; $[\alpha]_D^{20}$: +34° (c 1.5, CHCl₃).



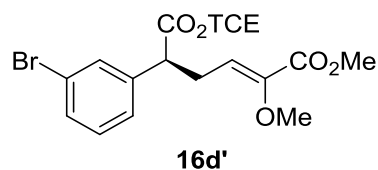
1-methyl 6-(2,2,2-trichloroethyl) (*S,Z*)-5-(4-(*tert*-butyl)phenyl)-2-methoxyhex-2-enedioate (16b'**):**

Prepared according to general procedure using Rh₂(*R-p*-PhTPCP)₄ (3.5 mg, 0.002 mmol, 0.5 mol %), methyl (*Z*)-2-methoxybut-2-enoate (**11a**) (104 mg, 0.8 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(4-(*tert*-butyl)phenyl)-2-diazoacetate (**15b**) (140 mg, 0.4 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (12 : 1 to 8 : 1) to afford the product as a colorless oil (141 mg, 78%); $R_f = 0.26$ (hexanes : diethyl ether = 8 : 1); ¹H NMR (400 MHz; CDCl₃) δ 7.33 (d, $J = 8.4$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 6.17 (t, $J = 7.6$ Hz, 1H), 4.78 (d, $J = 12.0$ Hz, 1H), 4.63 (d, $J = 12.0$ Hz, 1H), 3.77 (dd, $J = 8.0, 7.6$ Hz, 1H), 3.73 (s, 3H), 3.58 (s, 3H), 3.01 (ddd, $J = 14.8, 8.0, 7.6$ Hz, 1H), 2.79 (dt, $J = 14.8, 7.6$ Hz, 1H), 1.28 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 171.7, 163.8, 150.8, 147.3, 134.0, 127.6, 125.7, 124.3, 94.7, 74.0, 59.9, 52.0, 50.0, 34.5, 31.3, 29.1; IR (neat): 2957, 1751, 1727, 1435, 1365, 1269, 1202, 1138, 1109, 1034, 835, 800, 778, 720 cm⁻¹; HRMS (NSI) m/z : [M+H]⁺ calcd for C₂₀H₂₆O₅Cl₃ 451.0840; found 451.0844; The ee was determined by chiral HPLC: OD-H column, 1 mL/min, 0.5 % *i*PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 11.47 min, Minor: 14.88 min, >99% ee; $[\alpha]_D^{20}$: +44° (c 2.2, CHCl₃).



1-methyl 6-(2,2,2-trichloroethyl) (S,Z)-2-methoxy-5-(4-(methoxycarbonyl)phenyl)hex-2-enedioate (16c'):

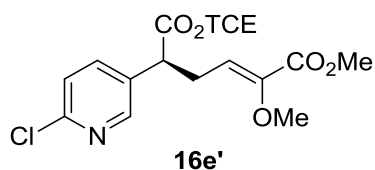
Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (3.5 mg, 0.002 mmol, 0.5 mol %), methyl (Z)-2-methoxybut-2-enoate (**11a**) (104 mg, 0.8 mmol, 2.0 equiv), and methyl 4-(1-diazo-2-oxo-2-(2,2,2-trichloroethoxy)ethyl)benzoate (**15c**) (141 mg, 0.4 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (5 : 1) to afford the product as a colorless oil (110 mg, 60%); $R_f = 0.25$ (hexanes : diethyl ether = 5 : 1); $^1\text{H NMR}$ (500 MHz; CDCl_3) δ 8.02 (d, $J = 8.5$ Hz, 2H), 7.44 (d, $J = 8.5$ Hz, 2H), 6.12 (t, $J = 7.5$ Hz, 1H), 4.75 (s, 2H), 3.92 (s, 3H), 3.89 (t, $J = 8.0$ Hz, 1H), 3.75 (s, 3H), 3.61 (s, 3H), 3.05 (dt, $J = 15.0, 7.5$ Hz, 1H), 2.85 (dt, $J = 15.0, 7.5$ Hz, 1H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 170.8, 166.6, 163.6, 147.6, 142.0, 130.1, 129.8, 128.2, 123.1, 94.6, 74.2, 59.9, 52.2, 52.0, 50.5, 28.8; IR (neat): 2954, 1751, 1720, 1611, 1436, 1278, 1184, 1149, 1110, 1020, 965, 858, 747, 719 cm^{-1} ; HRMS (NSI) m/z : $[\text{M-H}]^-$ calcd for $\text{C}_{18}\text{H}_{18}\text{O}_7\text{Cl}_3$ 451.0124; found 451.0127; The ee was determined by chiral HPLC: AS-H column, 1 mL/min, 1 % i PrOH in hexanes, $\lambda = 210$ nm, 230 nm. t_R : Major: 18.33 min, Minor: 21.94 min, 89% ee; $[\alpha]_D^{20}$: $+40^\circ$ (c 0.9, CHCl_3).



1-methyl 6-(2,2,2-trichloroethyl) (S,Z)-5-(3-bromophenyl)-2-methoxyhex-2-enedioate (16d'):

Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (3.5 mg, 0.002 mmol, 0.5 mol %), methyl (Z)-2-methoxybut-2-enoate (**11a**) (104 mg, 0.8 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2,2,2-

trichloroethyl 2-(3-bromophenyl)-2-diazoacetate (**15d**) (149 mg, 0.4 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (15 : 1 to 15 : 2) to afford the product as a colorless oil (165 mg, 87%); $R_f = 0.21$ (hexanes : diethyl ether = 8 : 1); $^1\text{H NMR}$ (400 MHz; CDCl_3) δ 7.50 (t, $J = 1.6$ Hz, 1H), 7.42 – 7.40 (m, 1H), 7.27 (d, $J = 7.6$ Hz, 1H), 7.20 (t, $J = 8.0$ Hz, 1H), 6.09 (t, $J = 7.6$ Hz, 1H), 4.74 (d, $J = 12.0$ Hz, 1H), 4.70 (d, $J = 12.0$ Hz, 1H), 3.77 – 3.73 (m, 4H), 3.60 (s, 3H), 2.99 (dt, $J = 15.2, 7.6$ Hz, 1H), 2.79 (dt, $J = 14.8, 7.6$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.8, 163.6, 147.6, 139.1, 131.1, 131.0, 130.3, 126.8, 123.2, 122.7, 94.6, 74.1, 59.9, 52.0, 50.1, 28.8; IR (neat): 2951, 2846, 1750, 1724, 1651, 1434, 1315, 1265, 1200, 1141, 1114, 1033, 998, 804, 777, 717, 693 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{16}\text{O}_5\text{BrCl}_3\text{Na}$ 494.9139; found 494.9140; The ee was determined by chiral HPLC: AS-H column, 0.5 mL/min, 1 % i PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 16.19 min, Minor: 15.28 min, 88% ee. $[\alpha]_D^{20}$: $+30^\circ$ (c 1.4, CHCl_3).

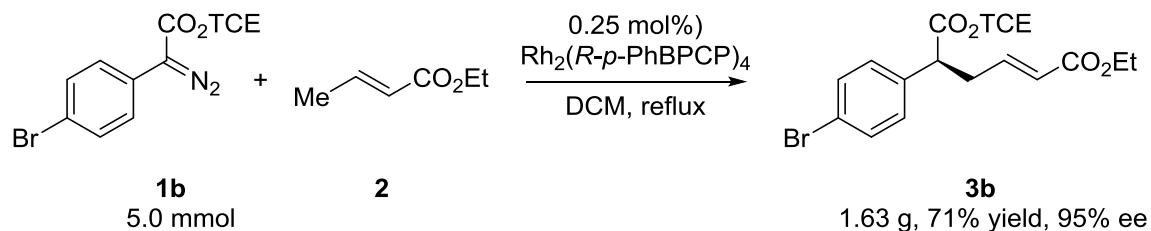


1-methyl 6-(2,2,2-trichloroethyl) (S,Z)-5-(6-chloropyridin-3-yl)-2-methoxyhex-2-enedioate (16e'):

Prepared according to general procedure using $\text{Rh}_2(R\text{-}p\text{-PhTPCP})_4$ (3.5 mg, 0.002 mmol, 0.5 mol %), methyl (Z)-2-methoxybut-2-enoate (**11a**) (104 mg, 0.8 mmol, 2.0 equiv), and 2,2,2-trichloroethyl 2-(6-chloropyridin-3-yl)-2-diazoacetate (**15e**) (132 mg, 0.4 mmol, 1.0 equiv). Purified by column chromatography on silica gel eluting with hexanes : diethyl ether (4 : 1 to 2 : 1) to afford the product as a yellow oil (83 mg, 48%); $R_f = 0.23$ (hexanes : diethyl ether = 2 : 1); $^1\text{H NMR}$ (400 MHz; CDCl_3) δ 8.34 (d, $J = 2.8$ Hz, 1H), 7.67 (dd, $J = 8.4, 2.8$ Hz, 1H), 7.31 (d, $J = 8.4$ Hz, 1H), 6.04 (t, $J = 7.6$ Hz, 1H), 4.72 (s, 2H), 3.83 (t, $J = 7.6$ Hz, 1H), 3.72 (s, 3H), 3.60 (s, 3H), 2.99 (dt, $J = 14.8, 7.6$ Hz, 1H), 2.80 (dt, $J = 14.8, 7.6$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.4, 163.3, 151.1, 149.5, 147.9, 138.2, 131.7, 124.4, 122.0, 94.4, 74.2, 59.9, 52.1, 47.2, 28.6; IR (neat): 2922, 1612, 1497,

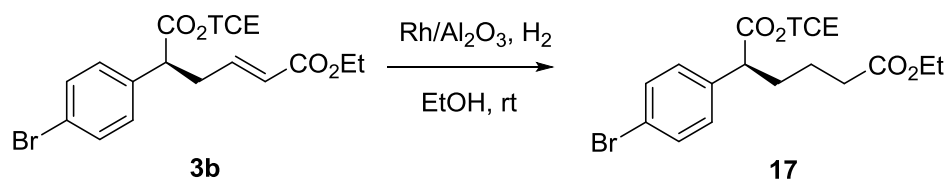
1342, 1156, 1095, 999, 956, 914, 800, 751, 734, 666 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{O}_5\text{NCl}_4$ 429.9777; found 429.9780; The ee was determined by chiral HPLC: OD-H column, 1 mL/min, 5 % i PrOH in hexanes, $\lambda = 254 \text{ nm}$. t_{R} : Major: 13.63 min, Minor: 16.49 min, 92% ee; $[\alpha]_{\text{D}}^{20}$: $+34^\circ$ (c 1.5, CHCl_3).

Procedure for gram-scale preparation of **3b**



An oven-dried round-bottomed flask, equipped with a reflux condenser and magnetic stir bar was charged with $\text{Rh}_2(\text{R-}p\text{-PhTCP})_4$ (22.0 mg, 0.0125 mmol, 0.25 mol %), ethyl (*E*)-but-2-enoate (**2**) (1.14 g, 10.0 mmol), and dichloromethane (5 mL). The solution was heated to reflux. The diazo ester (**1b**) (1.86 g, 5.0 mmol, 1.0 equiv) in 6 mL dichloromethane, was added dropwise over 3 h by a syringe pump. After the addition was complete, the needle and syringe were rinsed with 2 mL dichloromethane, and was added to the reaction over 30 min. The solution was stirred for further refluxed for 3 h and then was cooled to rt. The solvent was removed *in vacuo* and the crude residue purified by column chromatography on silica gel eluting hexanes : diethyl ether = 6 : 1 to give the product as a colorless oil (1.63 g, 71% yield, 95% ee).

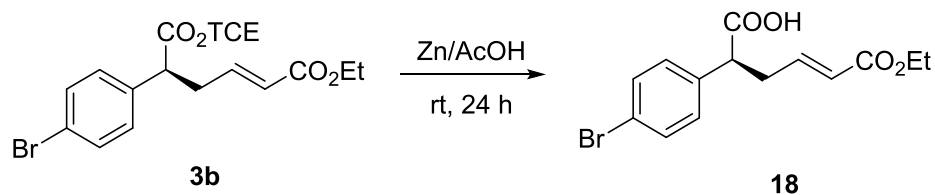
Selective hydrogenation



6-ethyl 1-(2,2,2-trichloroethyl) (S)-2-(4-bromophenyl)hexanedioate (17):

A solution of the ester (**3b**) (92 mg, 0.20 mmol, 1.0 equiv) in 2 mL of ethanol was stirred with 10 mg of 5% rhodium on alumina under 1 atm of hydrogen (balloon) at rt for 3 h. Upon complete conversion of the starting material as indicated by TLC analysis, the solution was filtered through celite. The filtrate was concentrated and the residue was purified by column chromatography on silica gel eluting with hexanes : diethyl ether = 12 : 1 to 6 : 1 to give the product as a colorless oil (85 mg, 92% yield). $R_f = 0.24$ (hexanes : diethyl ether = 5 : 1); $^1\text{H NMR}$ (500 MHz; CDCl_3) δ 7.47 (d, $J = 8.5$ Hz, 2H), 7.23 (d, $J = 8.5$ Hz, 2H), 4.75 (d, $J = 12.0$ Hz, 1H), 4.70 (d, $J = 12.0$ Hz, 1H), 4.12 (q, $J = 7.2$ Hz, 2H), 3.68 (t, $J = 7.5$ Hz, 1H), 2.33 (td, $J = 7.5, 3.0$ Hz, 2H), 2.23 – 2.04 (m, 1H), 1.92 – 1.85 (m, 1H), 1.78 – 1.48 (m, 2H), 1.25 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 172.9, 171.6, 136.6, 131.9, 129.8, 121.7, 94.7, 74.1, 60.4, 50.7, 33.8, 32.3, 22.7, 14.2; IR (neat): 2955, 1731, 1488, 1372, 1133, 1073, 1011, 916, 824, 761, 717 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{19}\text{O}_4\text{BrCl}_3$ 458.9527; found 458.9535; The ee was determined by chiral HPLC: OD-H column, 1 mL/min, 1 % i PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 13.44 min, Minor: 11.28 min, 95% ee; $[\alpha]_D^{20}$: +17° (c 2.4, CHCl_3).

Deprotection of trichloroethyl ester

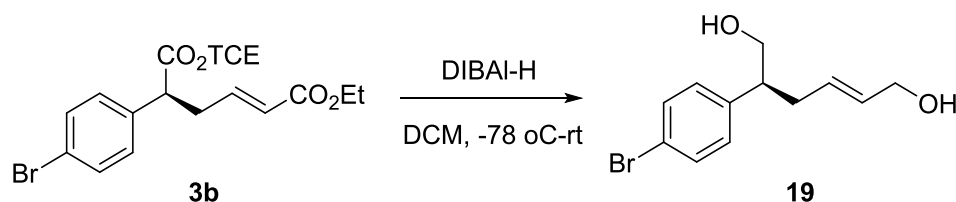


(*S,E*)-2-(4-bromophenyl)-6-ethoxy-6-oxohex-4-enoic acid (**18**):

The ester (**3b**) (160 mg, 0.35 mmol, 1.0 equiv) was dissolved in 2 mL of glacial acetic acid, and zinc powder (137 mg, 2.1 mmol, 6.0 equiv) was added. The solution was allowed to stir at rt for 24 h. Upon complete conversion of the starting material as indicated by TLC analysis, the solution was diluted with H₂O (10 mL) and extracted with ethyl acetate (3 x 15 mL). The organic extracts were washed with H₂O (20 mL) and brine (20 mL), dried over MgSO₄ and concentrated to give the product as a colorless oil (109 mg, 95% yield). $^1\text{H NMR}$ (500 MHz; CDCl_3) δ 7.47 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.1$ Hz, 2H), 6.81 (dt, $J = 15.5, 7.0$ Hz,

1H), 5.85 (d, $J = 16.0$ Hz, 1H), 4.17 (q, $J = 7.0$ Hz, 2H), 3.69 (t, $J = 7.5$ Hz, 1H), 2.95 (dt, $J = 15.0, 7.5$ Hz, 1H), 2.64 (dt, $J = 15.0, 7.5$ Hz, 1H), 1.27 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 177.9, 166.2, 144.3, 136.1, 132.1, 129.7, 123.9, 122.0, 60.5, 49.8, 35.1, 14.2; IR (neat): 2982, 1712, 1655, 1489, 1370, 1273, 1201, 11589, 1074, 1012, 824 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{O}_4\text{Br}$ 327.0227; found 327.0229; The ee was determined by chiral HPLC: OJ-H column, 1 mL/min, 10 % i PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 11.25 min, Minor: 10.15 min, 96% ee; $[\alpha]_D^{20}$: $+70^\circ$ (c 0.6, CHCl_3).

Reduction of **3b** to diol

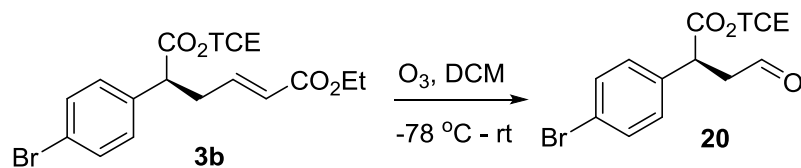


(*S,E*)-5-(4-bromophenyl)hex-2-ene-1,6-diol (**19**):

A solution of the ester (**3b**) (46 mg, 0.10 mmol, 1.0 equiv) in 1 mL of dichloromethane was added dropwise to 0.42 mL of 1.0 M DIBAL-H in dichloromethane (0.42 mmol, 4.2 equiv) under argon at -78°C . The solution was stirred overnight while warmed up to rt before it was quenched carefully with 0.5 mL of 2 M HCl and extracted with ethyl acetate (3 x 3 mL). The organic extracts were washed with brine (3 mL), dried over Na_2SO_4 and concentrated to give the product as colorless oil (28 mg, quantitative yield). $R_f = 0.15$ (hexane : ethyl acetate = 1 : 2); ^1H NMR (500 MHz; CDCl_3) δ 7.46 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 5.65 (dt, $J = 15.0, 5.5$ Hz, 1H), 5.57 (dt, $J = 15.0, 6.5$ Hz, 1H), 4.03 (d, $J = 5.5$ Hz, 2H), 3.78 (dd, $J = 11.0, 5.5$ Hz, 1H), 3.72 (dd, $J = 11.0, 7.0$ Hz, 1H), 2.85 (p, $J = 7.0$ Hz, 1H), 2.49 (dt, $J = 14.0, 7.0$ Hz, 1H), 2.35 (dt, $J = 14.5, 7.0$ Hz, 1H), 1.73 (br s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 140.9, 131.7, 131.2, 129.8, 129.8, 120.6, 66.6, 63.4, 47.7, 34.8; IR (neat): 2955, 1754, 1727, 1652, 1619, 1437, 1325, 1271, 1165, 1119, 1069, 844, 718 cm^{-1} ; HRMS (NSI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2\text{Br}$ 271.0328; found 271.0332; The ee was determined by chiral HPLC: OJ-H column,

1 mL/min, 10 % *i*PrOH in hexanes, $\lambda = 230$ nm. t_R : Major: 13.79 min, Minor: 12.57 min, 95% ee; $[\alpha]_D^{20}$: +26° (c 0.6, CHCl₃).

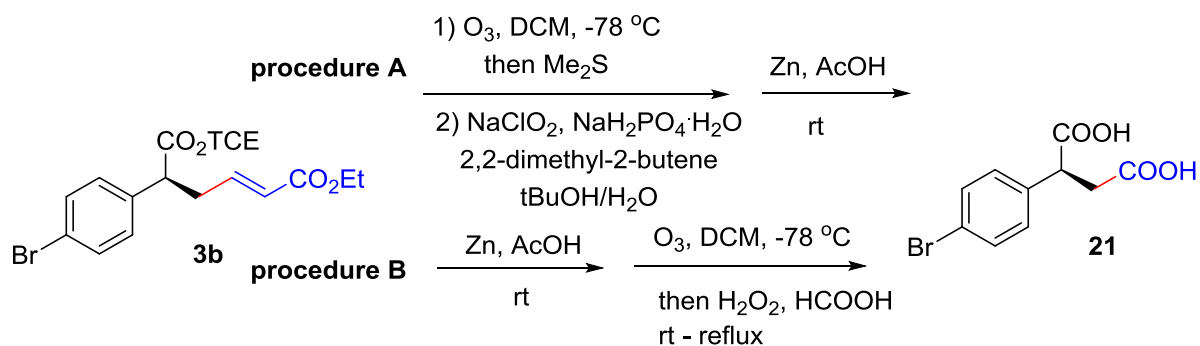
Ozonolysis of **3b** with reductive work-up



2,2,2-trichloroethyl (*S*)-2-(4-bromophenyl)-4-oxobutanoate (**20**):

A solution of the ester (**3b**) (46 mg, 0.10 mmol) in dichloromethane (1.2 mL) was cooled to -78 °C. Then ozone was passed through the solution until a blue color persisted. Excess ozone was purged from the system by bubbling oxygen through the reaction mixture for 15 min, followed by addition of dimethyl sulfide (0.10 mL). The reaction was warmed to rt, concentrated and the residue purified by column chromatography on silica gel eluting hexanes : diethyl ether = 6 : 1 to 3 : 1 to give the product as a colorless oil (33.5 mg, 86% yield). $R_f = 0.25$ (hexanes : diethyl ether = 3 : 1); ¹H NMR (400 MHz; CDCl₃) δ 9.77 (s, 1H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 4.74 (d, $J = 12.0$ Hz, 1H), 4.66 (d, $J = 12.0$ Hz, 1H), 4.21 (dd, $J = 9.6, 4.8$ Hz, 1H), 3.43 (dd, $J = 18.8, 10.0$ Hz, 1H), 2.88 (dd, $J = 18.8, 4.8$ Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 198.5, 170.7, 135.5, 132.1, 129.7, 122.0, 94.5, 74.3, 46.5, 44.1; IR (neat): 2924, 2849, 1751, 1723, 1489, 1376, 1220, 1150, 1074, 1011, 916, 828, 769, 718 cm⁻¹; HRMS (NSI) m/z : [M+H]⁺ calcd for C₁₂H₁₀O₃BrCl₃Na 408.8771; found 408.8775; The ee was determined by chiral HPLC: AS-H column, 1 mL/min, 1 % *i*PrOH in hexanes, $\lambda = 210$ nm, 230 nm. t_R : Major: 15.11 min, Minor: 16.65 min, 95% ee; $[\alpha]_D^{20}$: +52° (c 1.5, CHCl₃).

Conversion of **3b** to diacid and assignment of absolute configuration



Procedure A: A solution of the ester (**3b**) (160 mg, 0.35 mmol) in dichloromethane (2 mL) was cooled to $-78\text{ }^\circ\text{C}$. Ozone was then passed through the solution until a light blue color persisted. Excess ozone was purged from the system by bubbling oxygen through the reaction mixture for 15 min, followed by addition of methyl sulfide (0.10 mL). The reaction was warmed to rt and concentrated. The residue was suspended in $\text{tBuOH}/\text{H}_2\text{O}$ (2 mL/2 mL), then NaClO_2 (317 mg, 3.50 mmol, 10.0 equiv), $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ (483 mg, 3.50 mmol, 10.0 equiv), 2,2-dimethyl-2-butene (0.62 mL, 5.35 mmol, 15.0 equiv) were added. The reaction was stirred at rt over night before it was quenched with 10 mL of H_2O , and acidified with 1 M HCl to pH 3. The aqueous layer was extracted with ethyl acetate (3 x 20 mL), washed with brine (30 mL), dried over Na_2SO_4 , and concentrated. The residue was dissolved in 2 mL of glacial acetic acid, and zinc powder (137 mg, 2.1 mmol, 6.0 equiv) was added. The solution was allowed to stir at rt for 24 h. Upon complete conversion of the starting material as indicated by TLC analysis, the solution was diluted with H_2O (10 mL) and extracted with ethyl acetate (3 x 15 mL). The organic extracts were washed with H_2O (20 mL) and brine (20 mL), dried over Na_2SO_4 and concentrated. The solids obtained were triturated with dichloromethane/hexanes (3/1 v/v, 4 mL) to give the product as a white solid (72 mg, 75%).

Procedure B: The ester (**3b**) (160 mg, 0.35 mmol, 1.0 equiv) was dissolved in 2 mL of glacial acetic acid, and zinc powder (137 mg, 2.1 mmol, 6.0 equiv) was added. The solution was allowed to stir at rt for 24 h. Upon complete conversion of the starting material as indicated by TLC analysis, the solution was diluted with H_2O

(10 mL) and extracted with ethyl acetate (3 x 15 mL). The organic extracts were washed with H₂O (20 mL) and brine (20 mL), dried over MgSO₄ and concentrated.

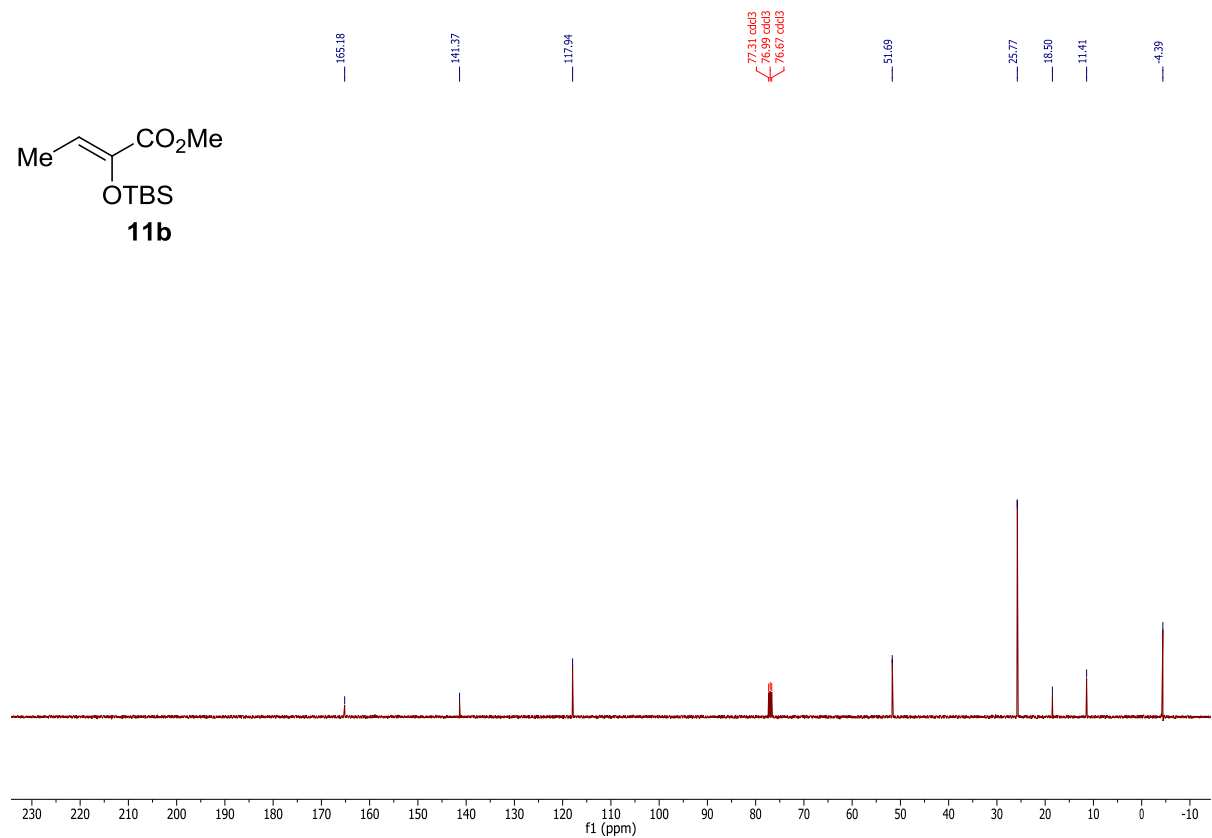
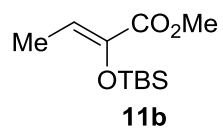
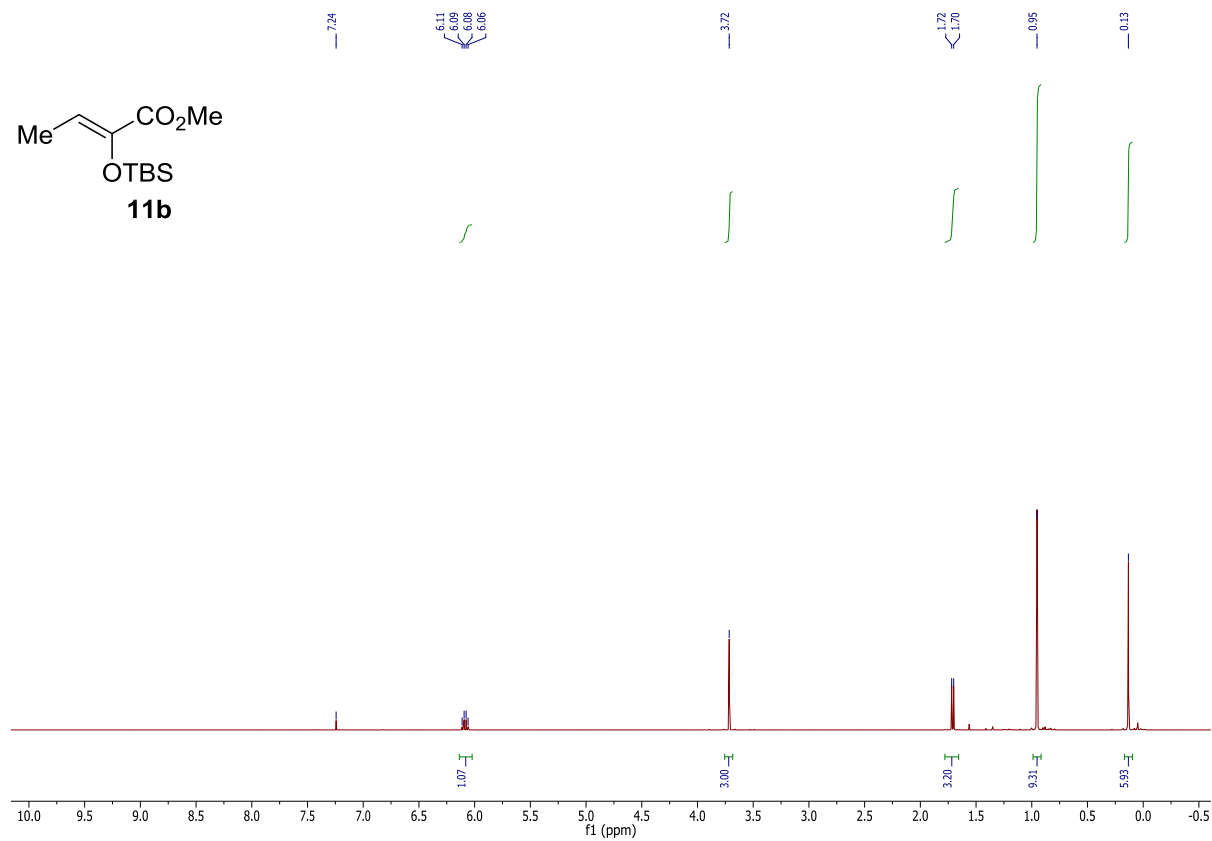
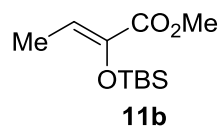
The residue in dichloromethane (4 mL) was cooled to -78 °C. Then ozone was passed through the solution until a blue color persisted. Excess ozone was purged from the system by bubbling oxygen through the reaction mixture for 15 min, followed by addition of methyl sulfide. The reaction was warmed to rt and concentrated. The residue was dissolved in 1 mL of formic acid, followed by addition of H₂O₂ (30% solution in H₂O, 0.3 mL). The mixture was stirred at rt for 2 h before it was refluxed for 1 h. Additional 1 mL of formic acid was added and the reaction was heated to reflux for 2 h. The reaction was cooled to rt, and 10 mL of H₂O was added. The organics were extracted with ethyl acetate (15 mL x 3), dried over Na₂SO₄, concentrated, and dried in vacuo. The solids were triturated with dichloromethane/hexanes (3/1 v/v, 4 mL) to give the product as a white solid (44 mg, 46%).

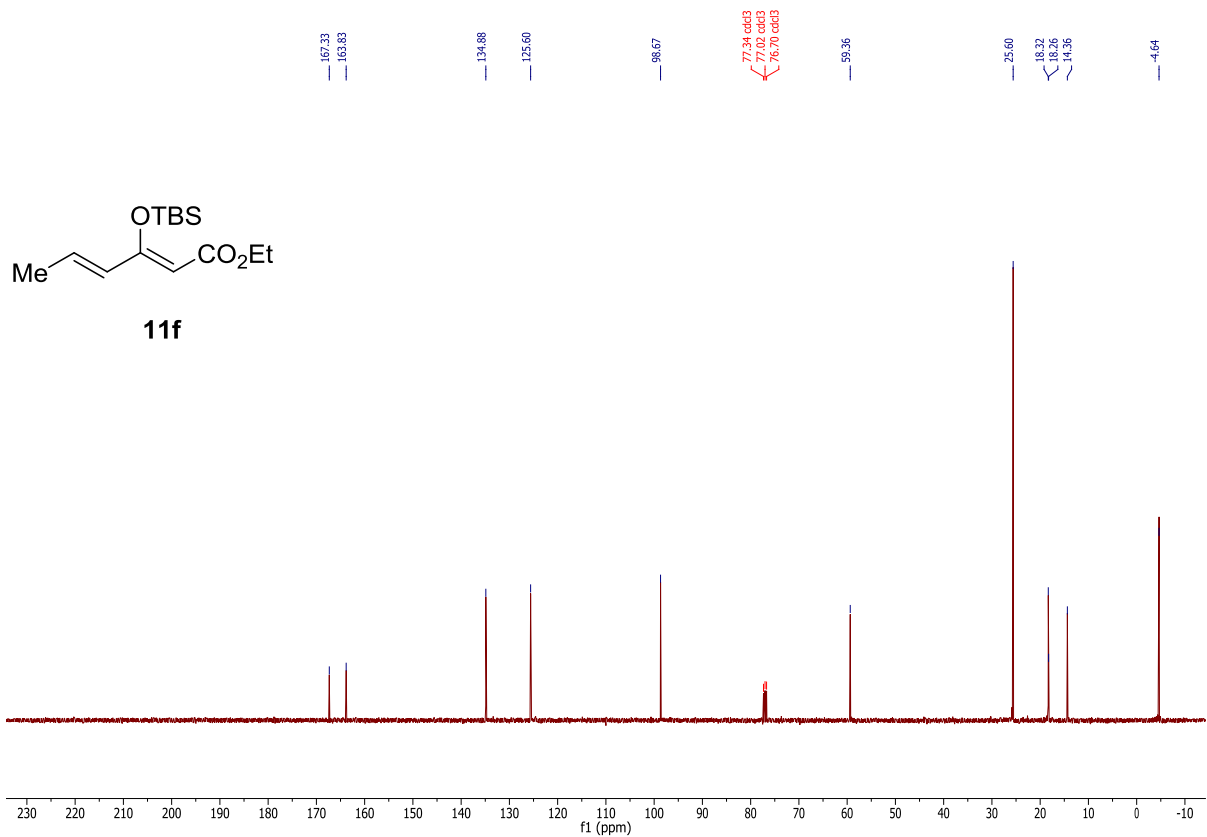
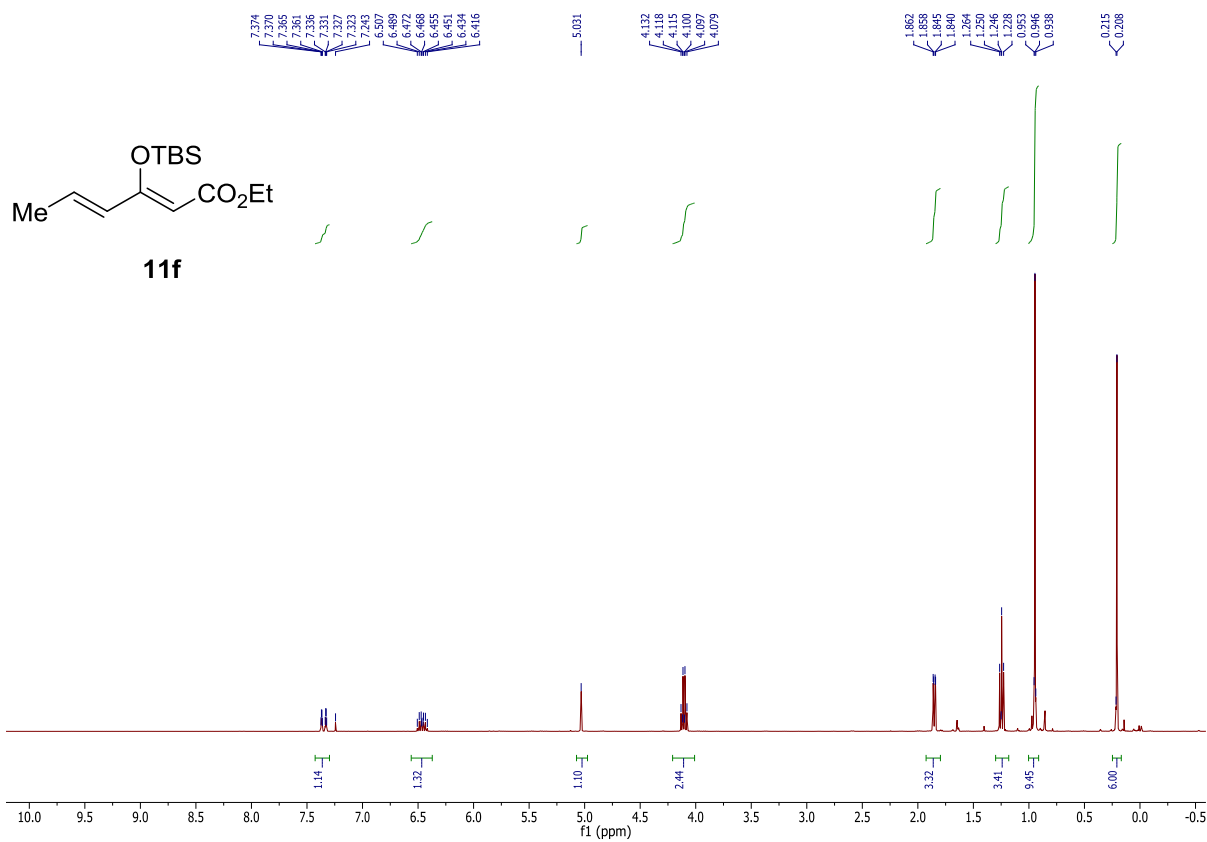
(S)-2-(4-bromophenyl)succinic acid (21): obtained as a white solid, m.p. 197-198 °C (lit.,¹² m.p. 198-199 °C); ¹H NMR (500 MHz; acetone-*d*₆) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.09 (dd, *J* = 10.0, 5.5 Hz, 1H), 3.15 (dd, *J* = 17.0, 10.0 Hz, 1H), 2.70 (dd, *J* = 17.0, 5.5 Hz, 1H); ¹³C NMR (125 MHz, acetone-*d*₆) δ 173.1, 171.8, 138.2, 131.7, 130.0, 120.8, 46.4, 36.9; IR (neat): 2921, 1690, 1488, 1414, 1306, 1289, 1201, 1175, 1073, 1012, 927, 799, 748 cm⁻¹; HRMS (NSI) *m/z*: [M-H]⁻ calcd for C₁₀H₈O₄Br 270.9611; found 270.9615; [α]_D²⁰: +105 (c 1.3, EtOH) (lit.,¹² [α]_D²⁰: +114 (c 0.7, EtOH)).

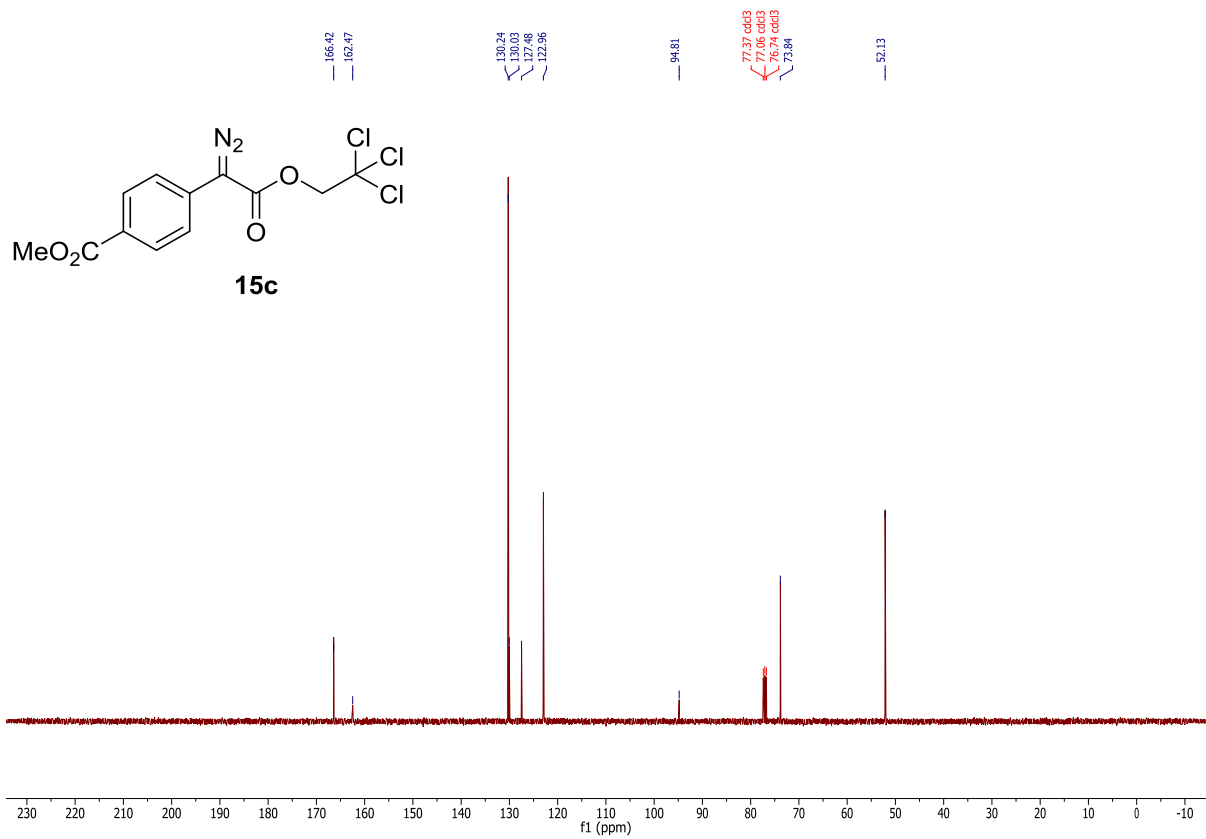
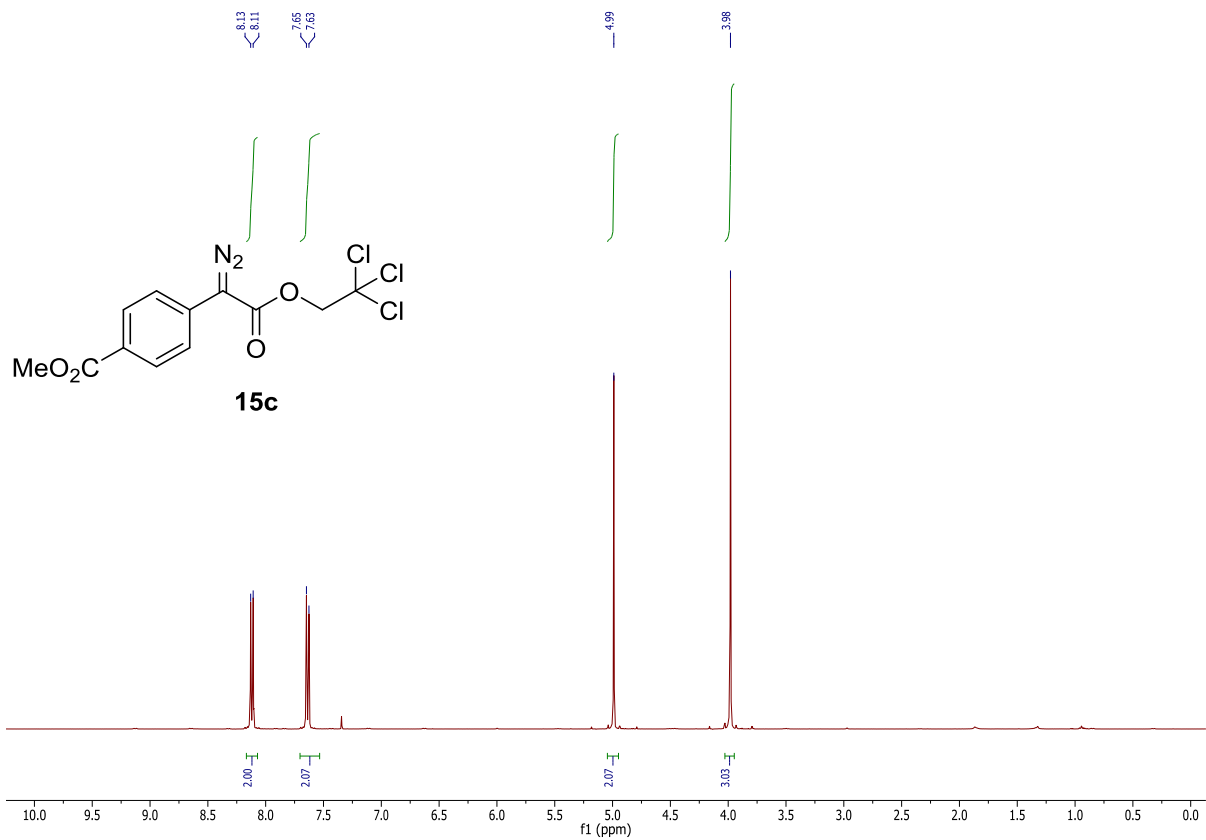
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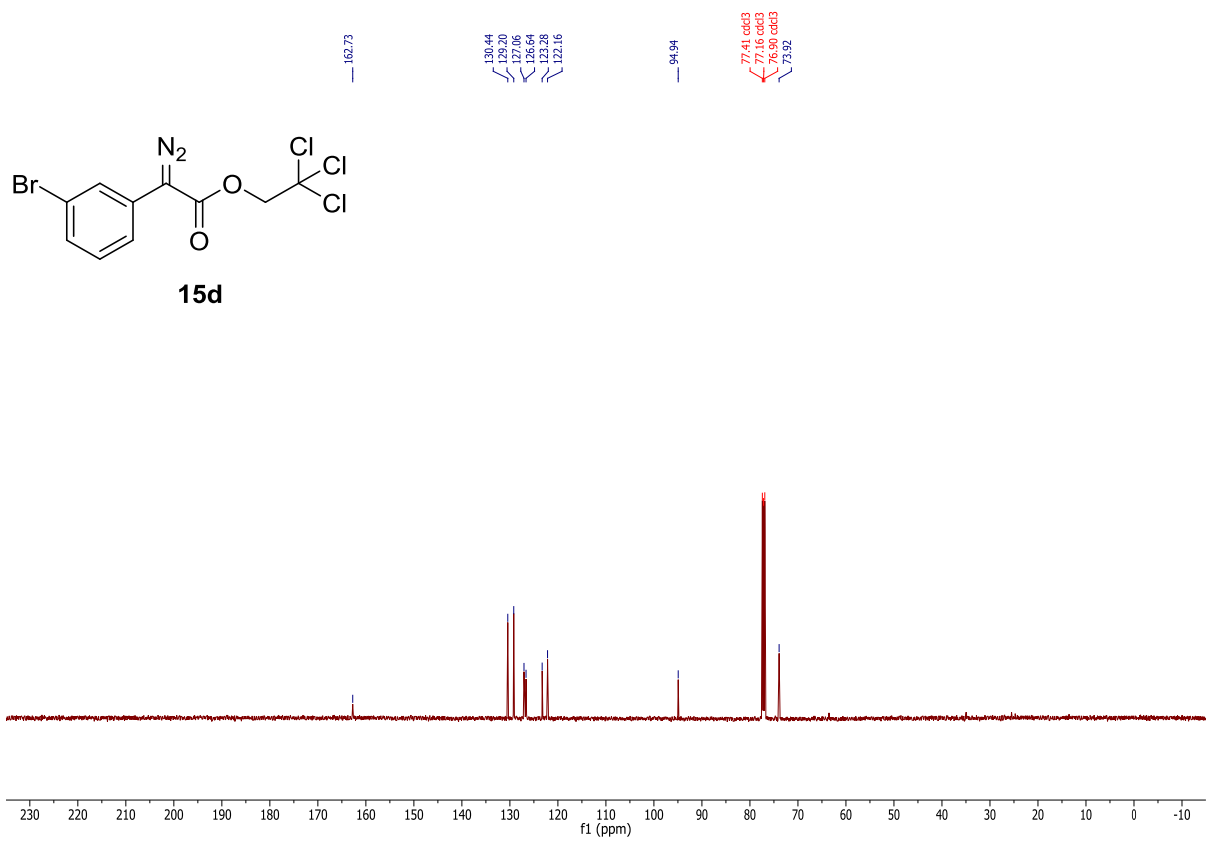
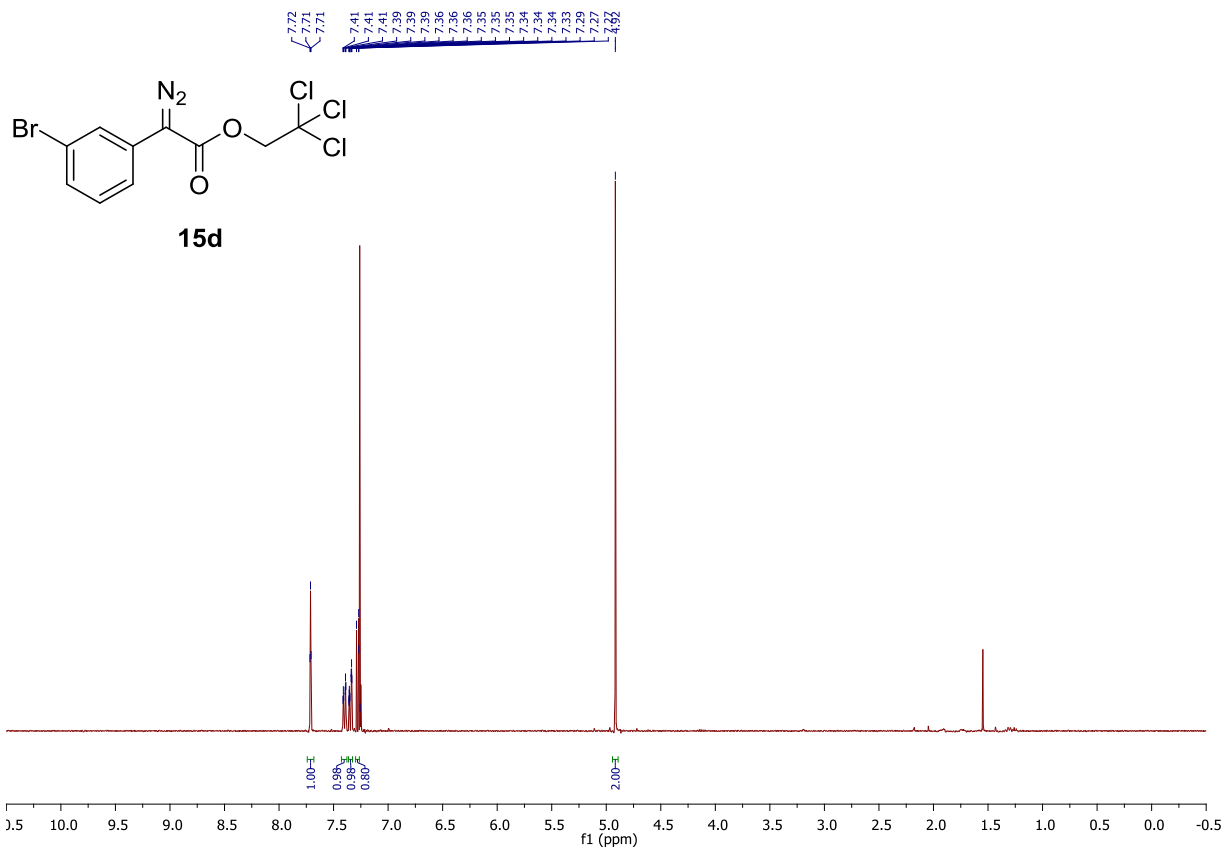
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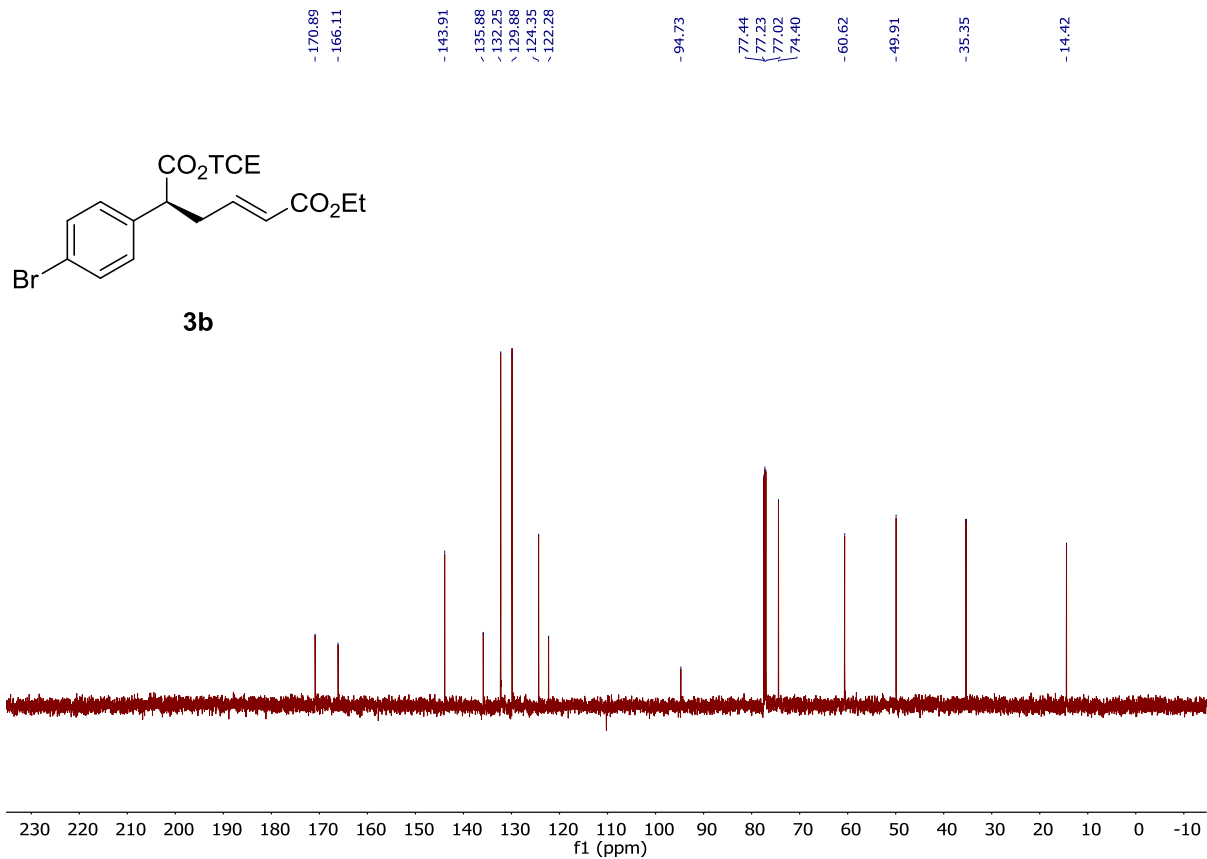
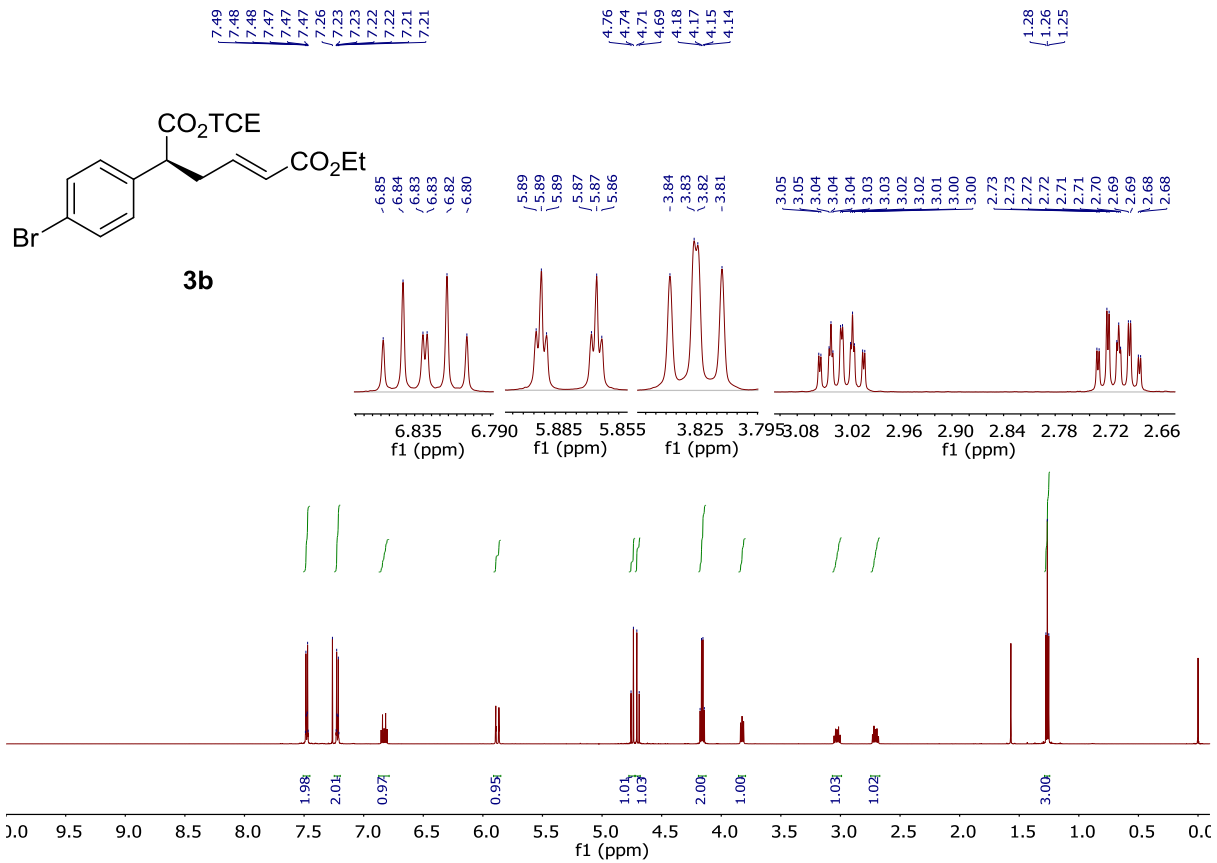
¹H and ¹³C NMR Spectra of new compounds

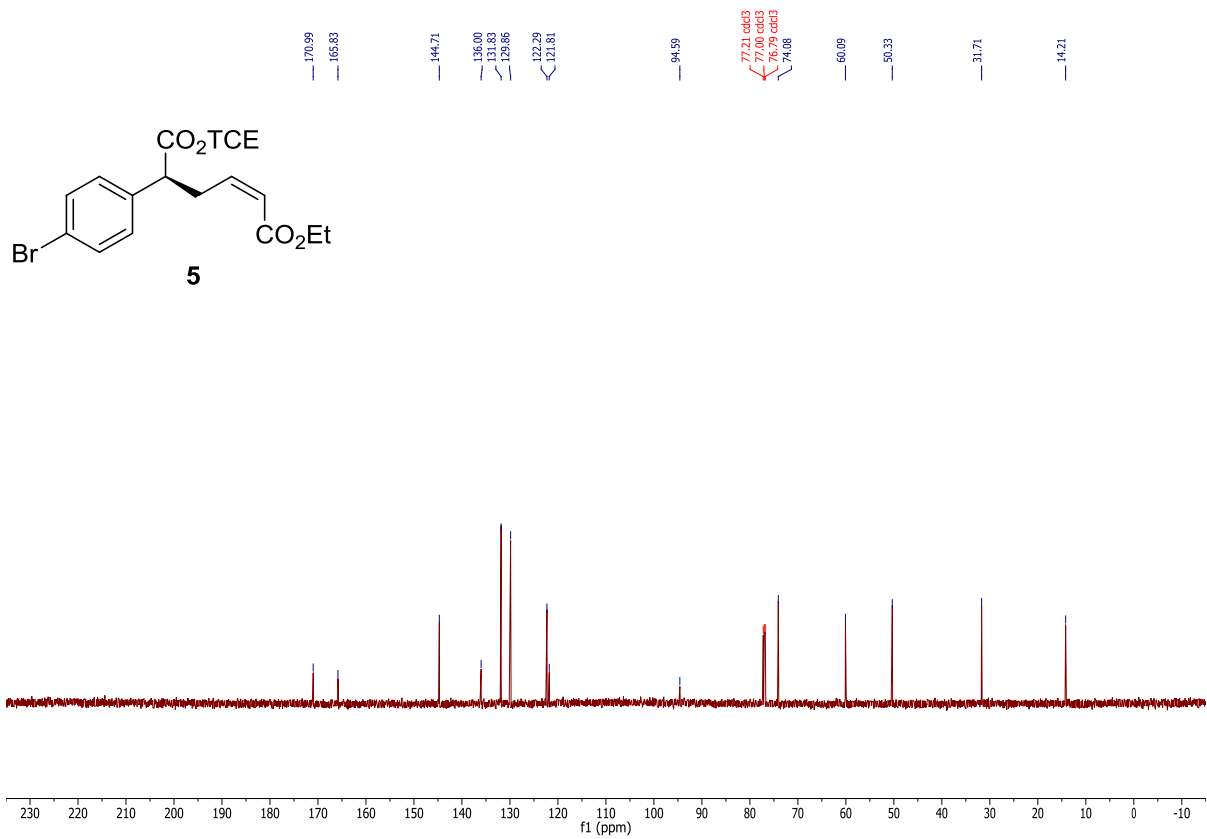
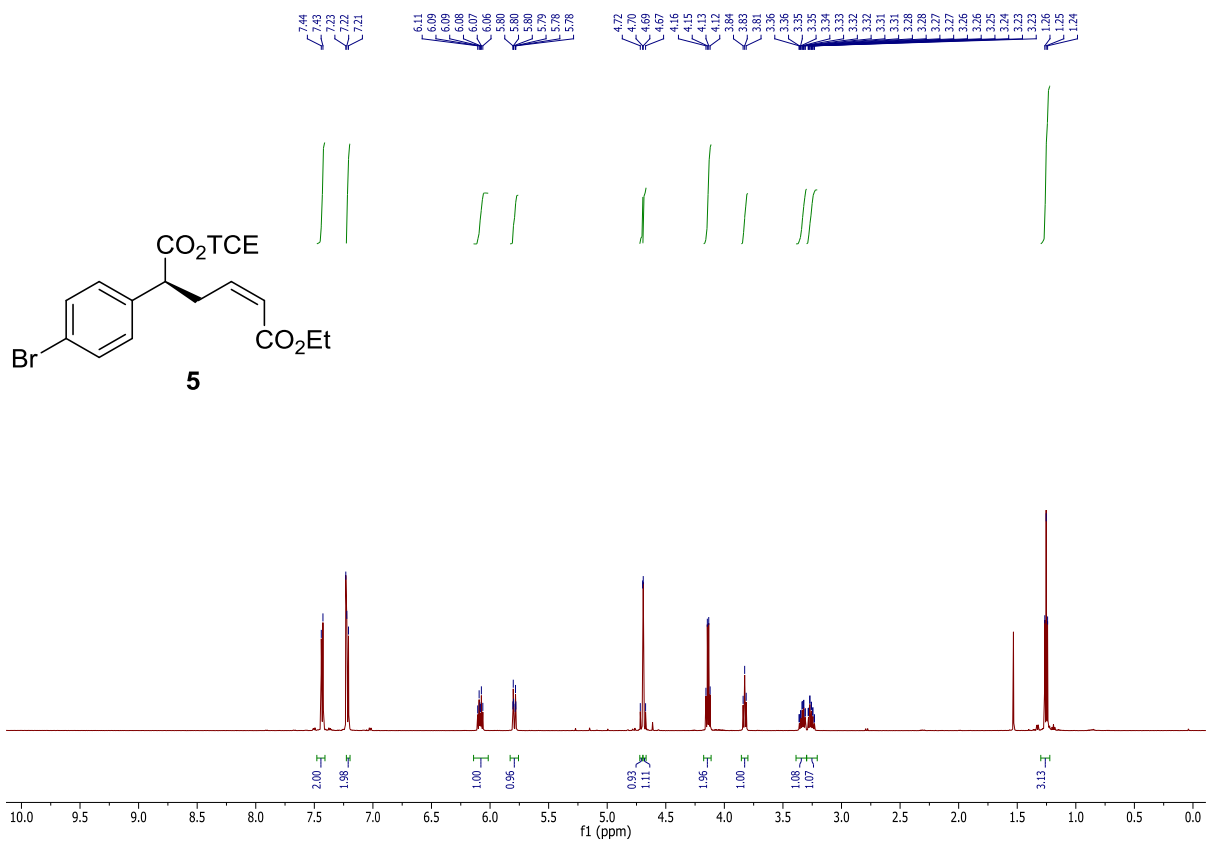


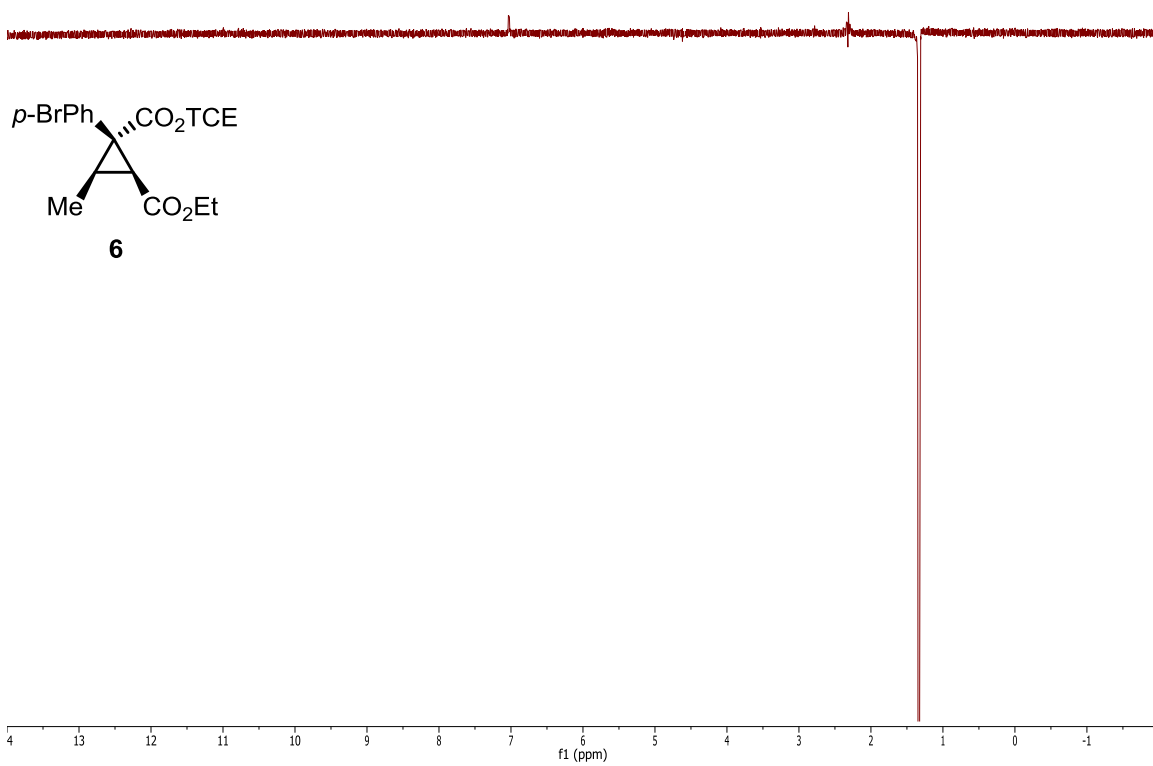
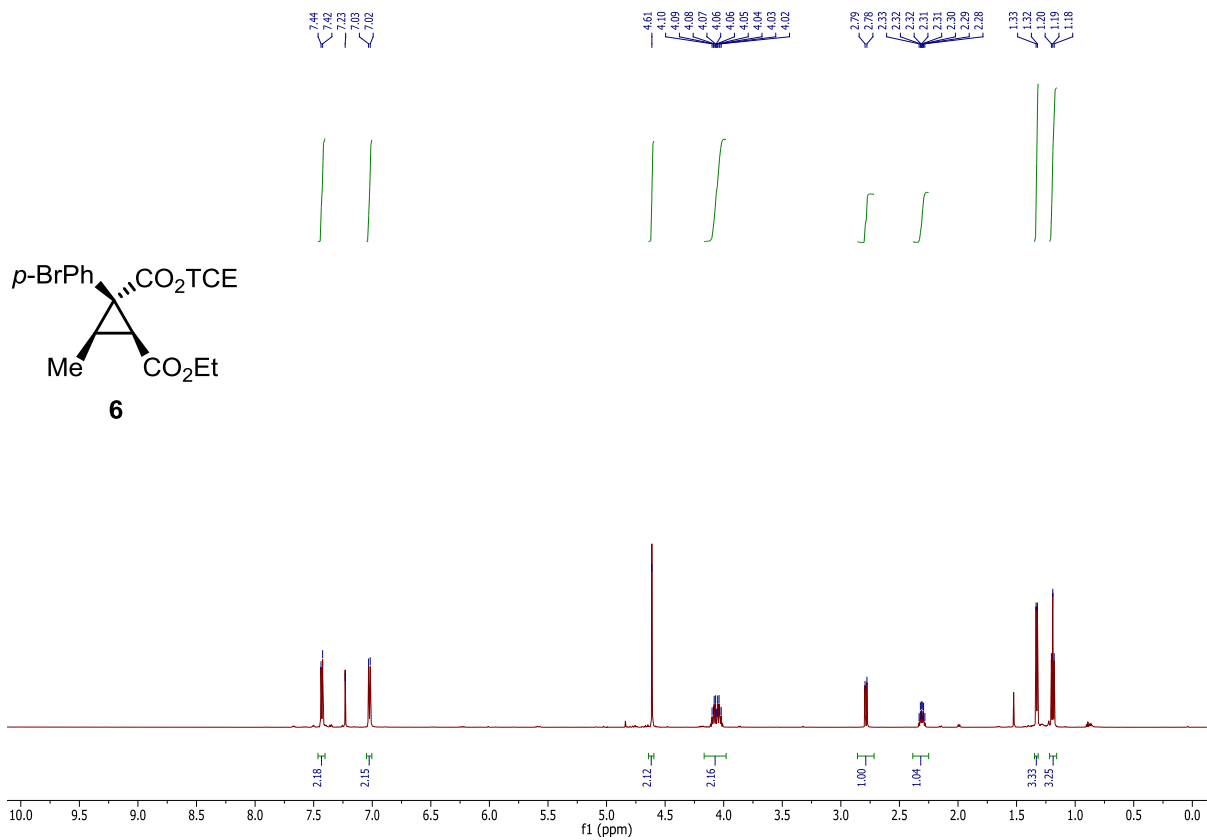


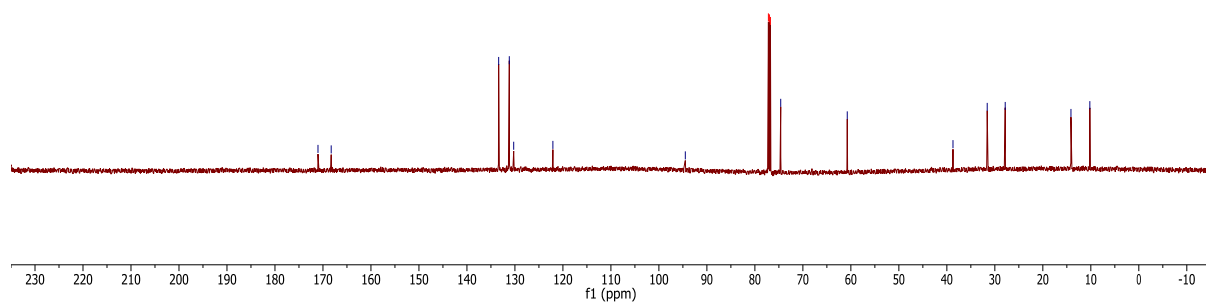
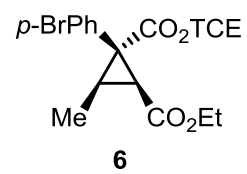
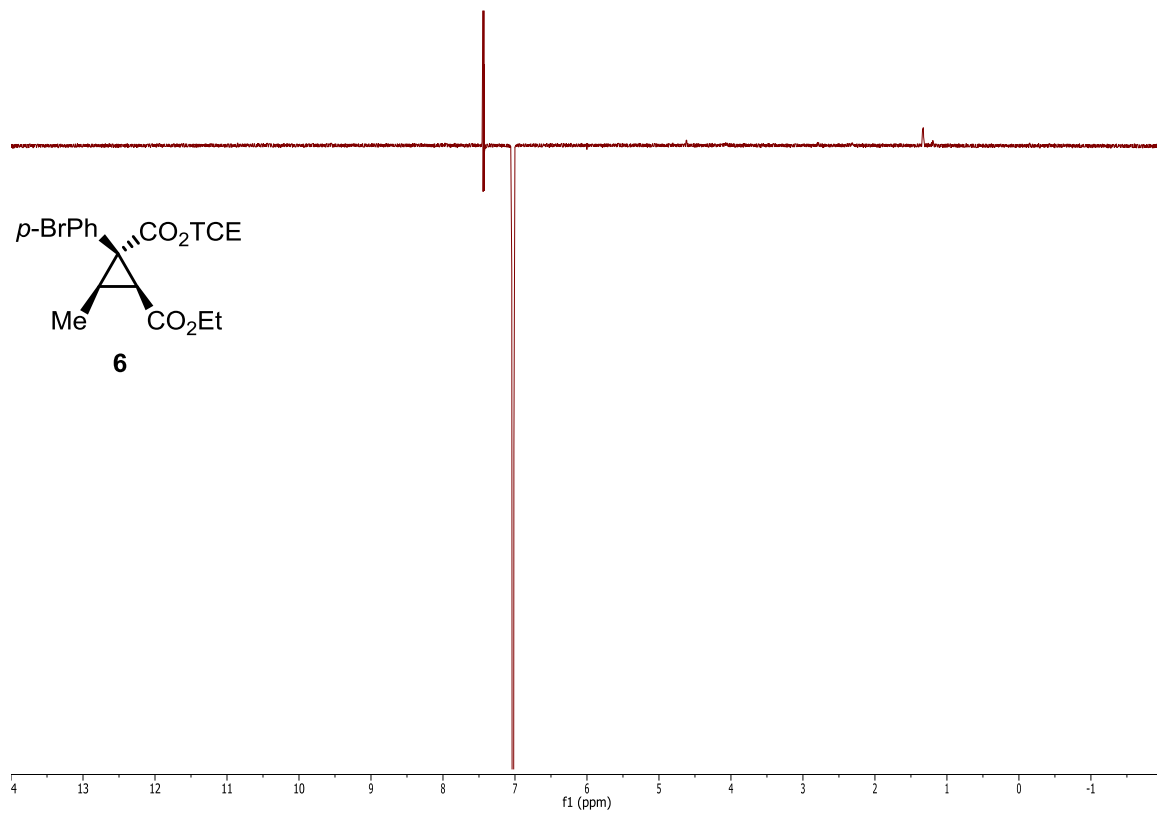


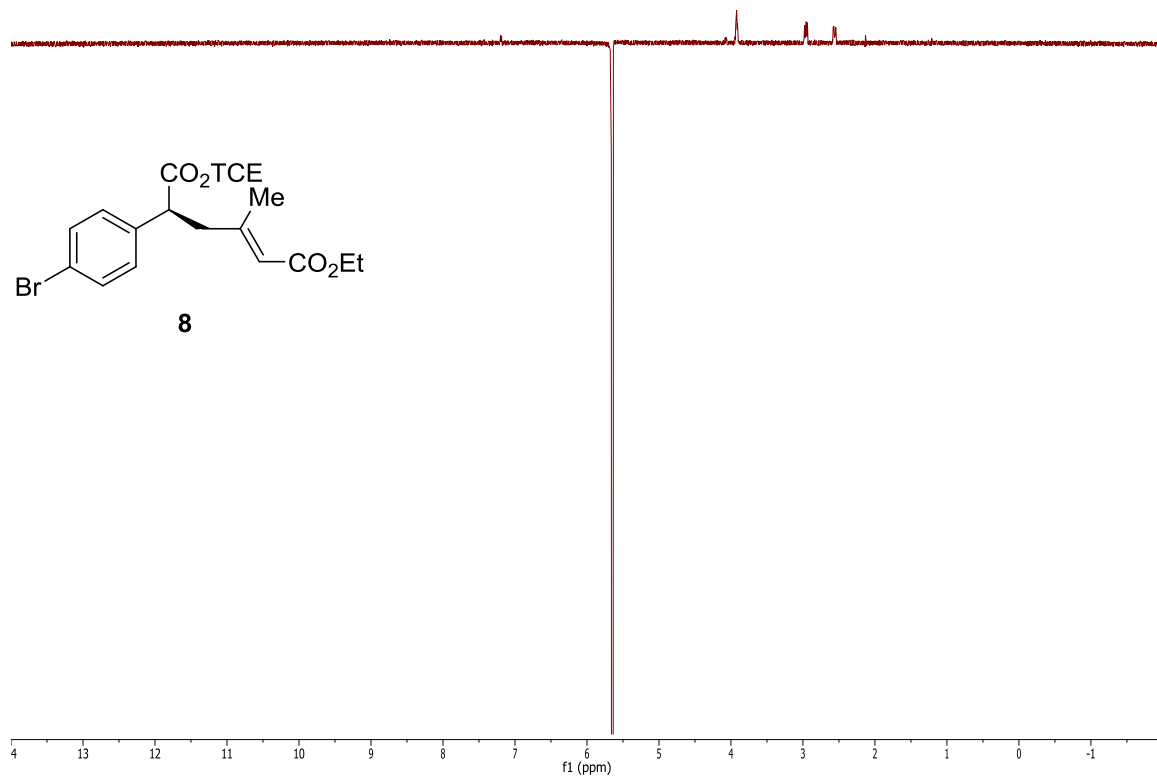
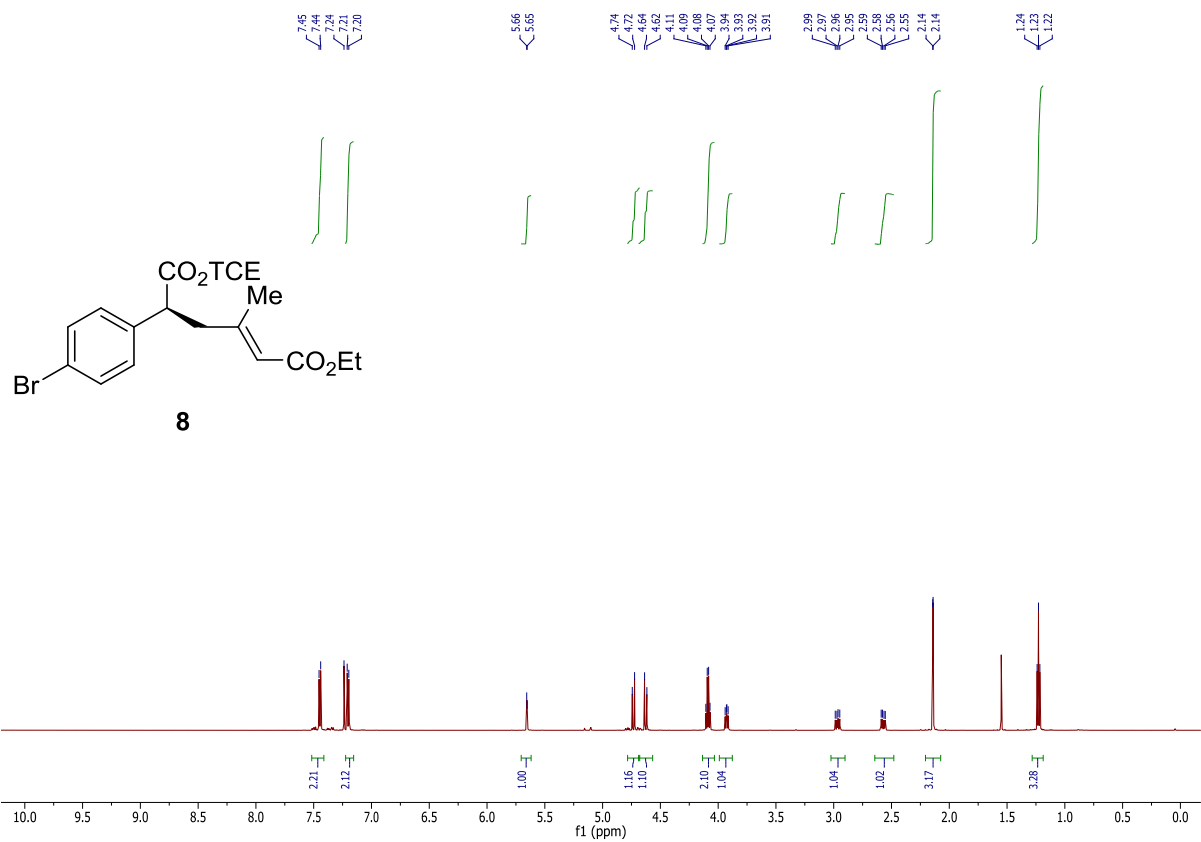


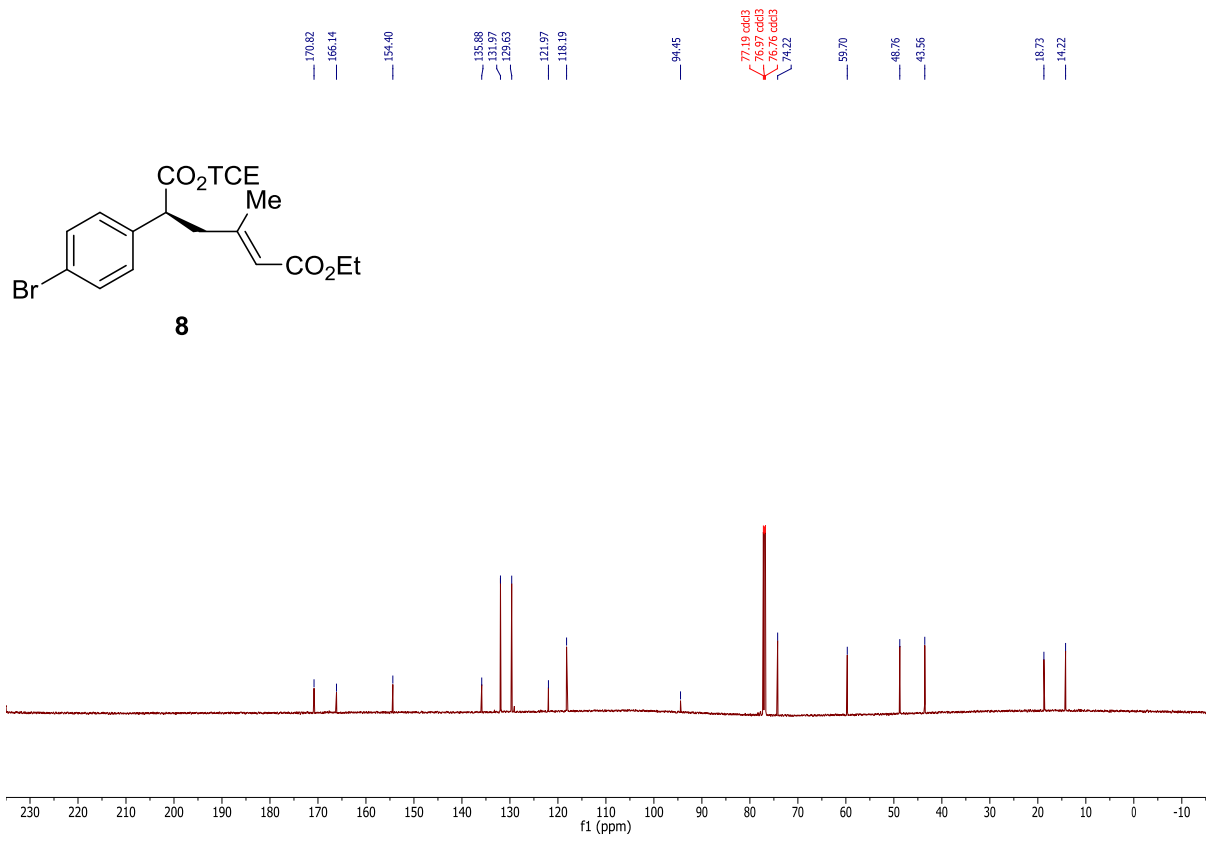


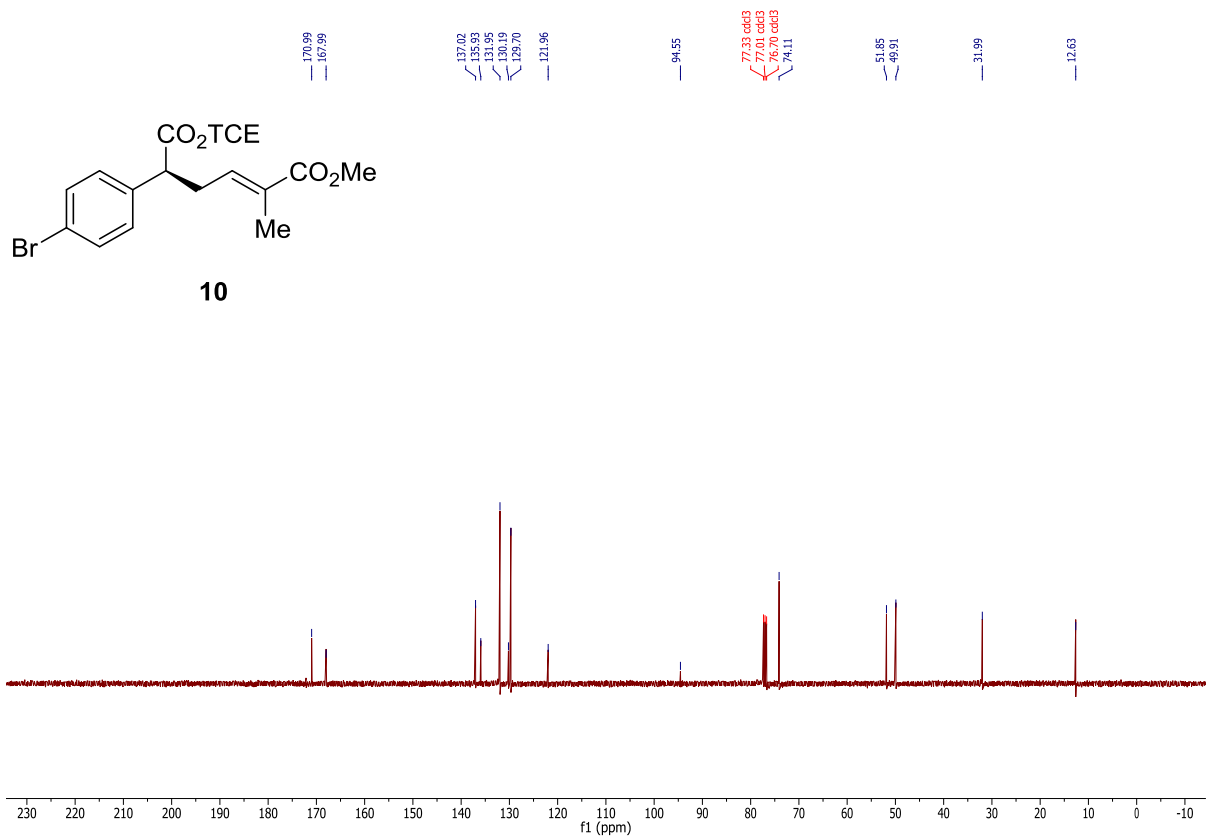
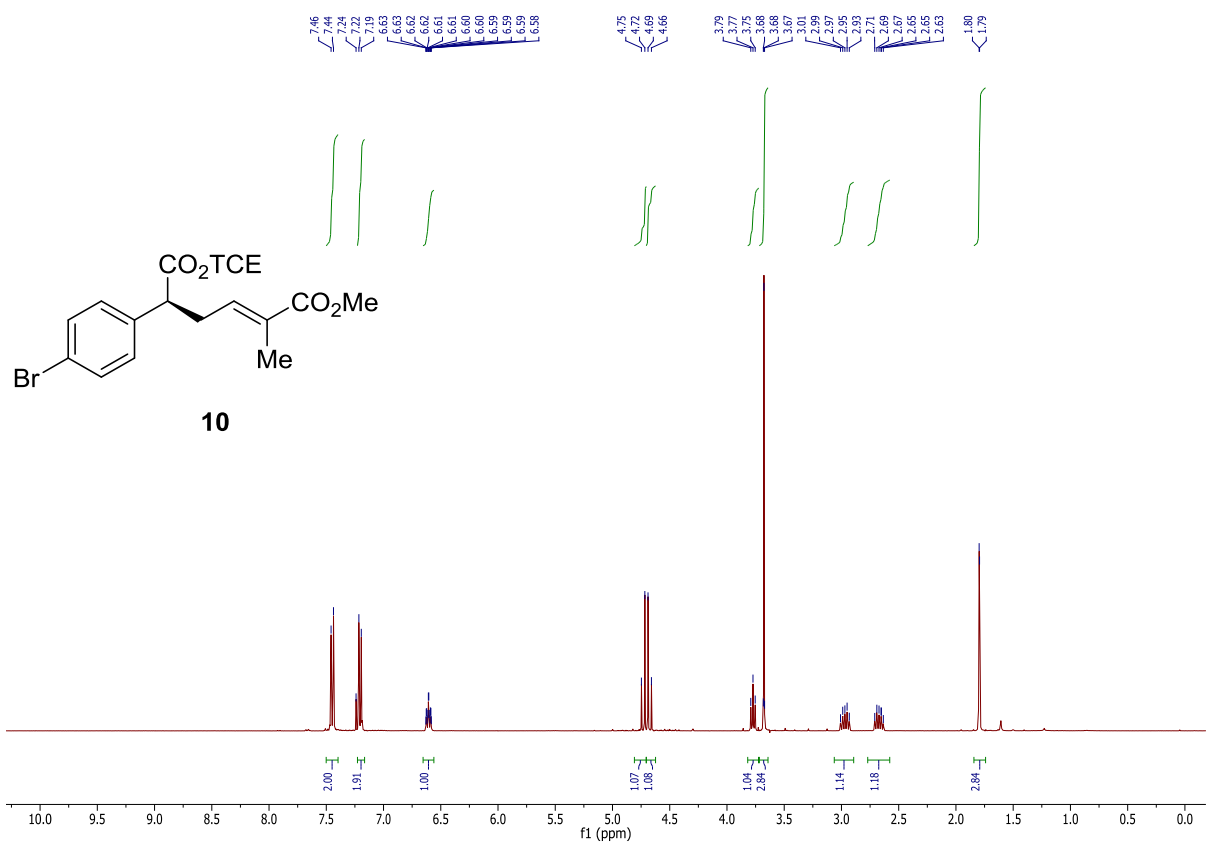


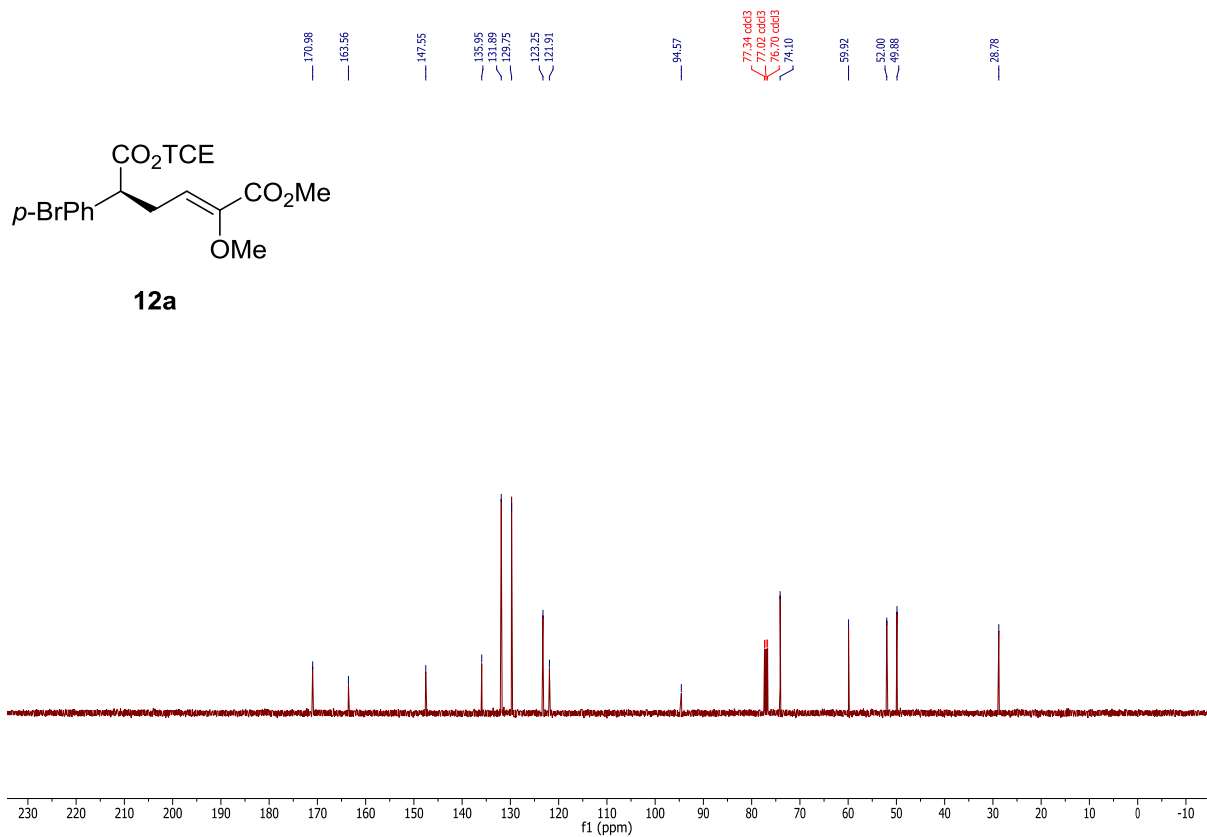
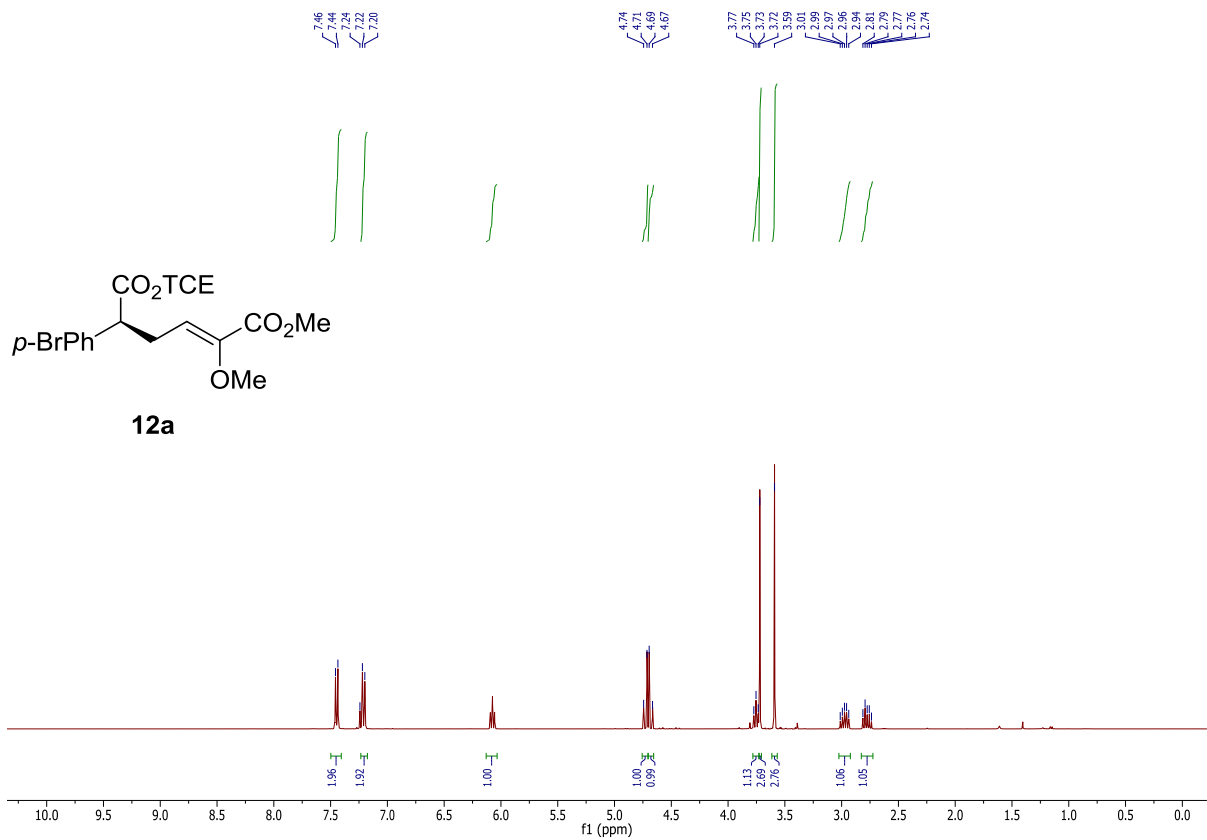


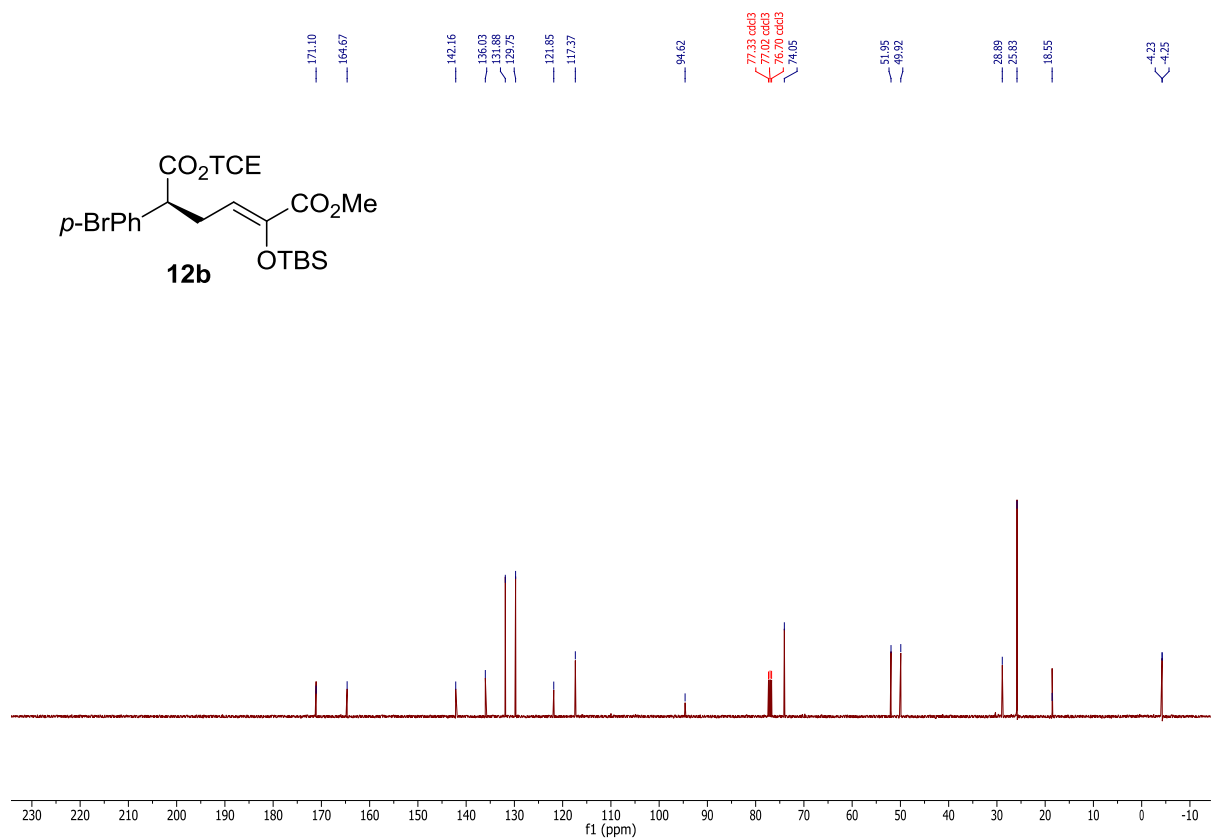
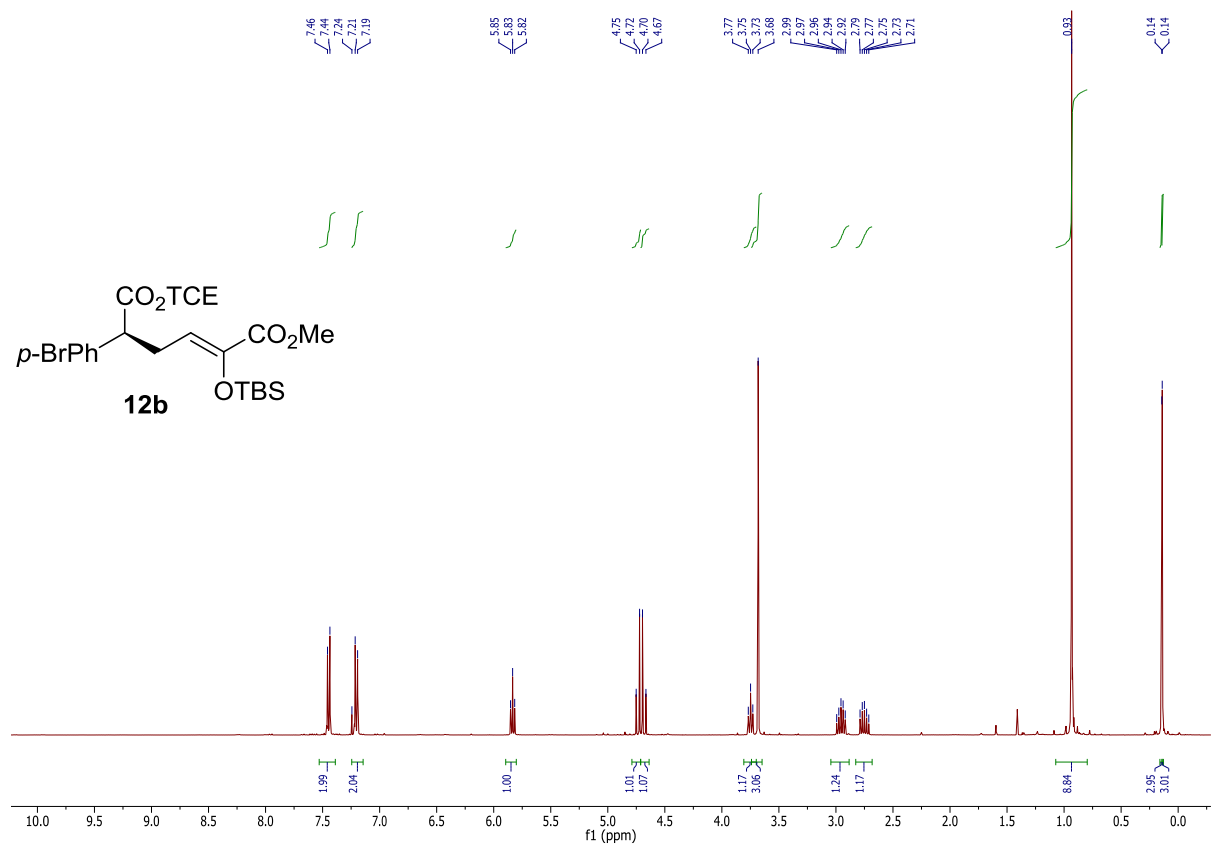


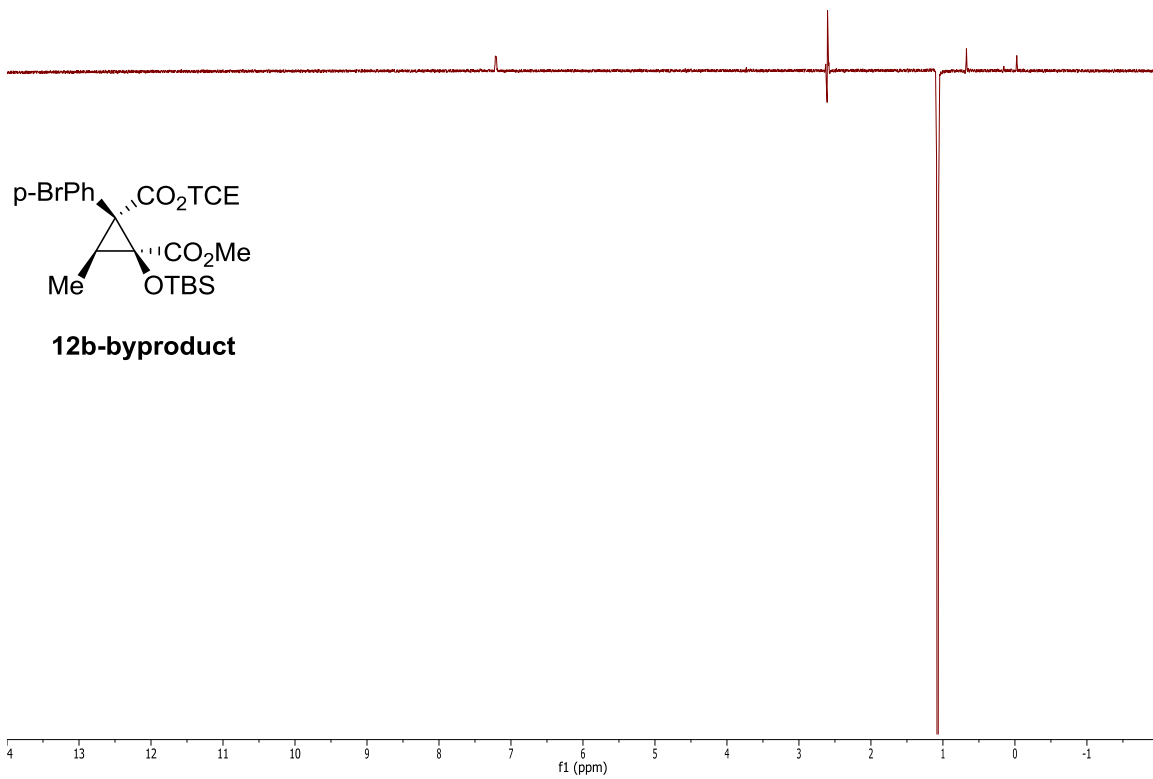
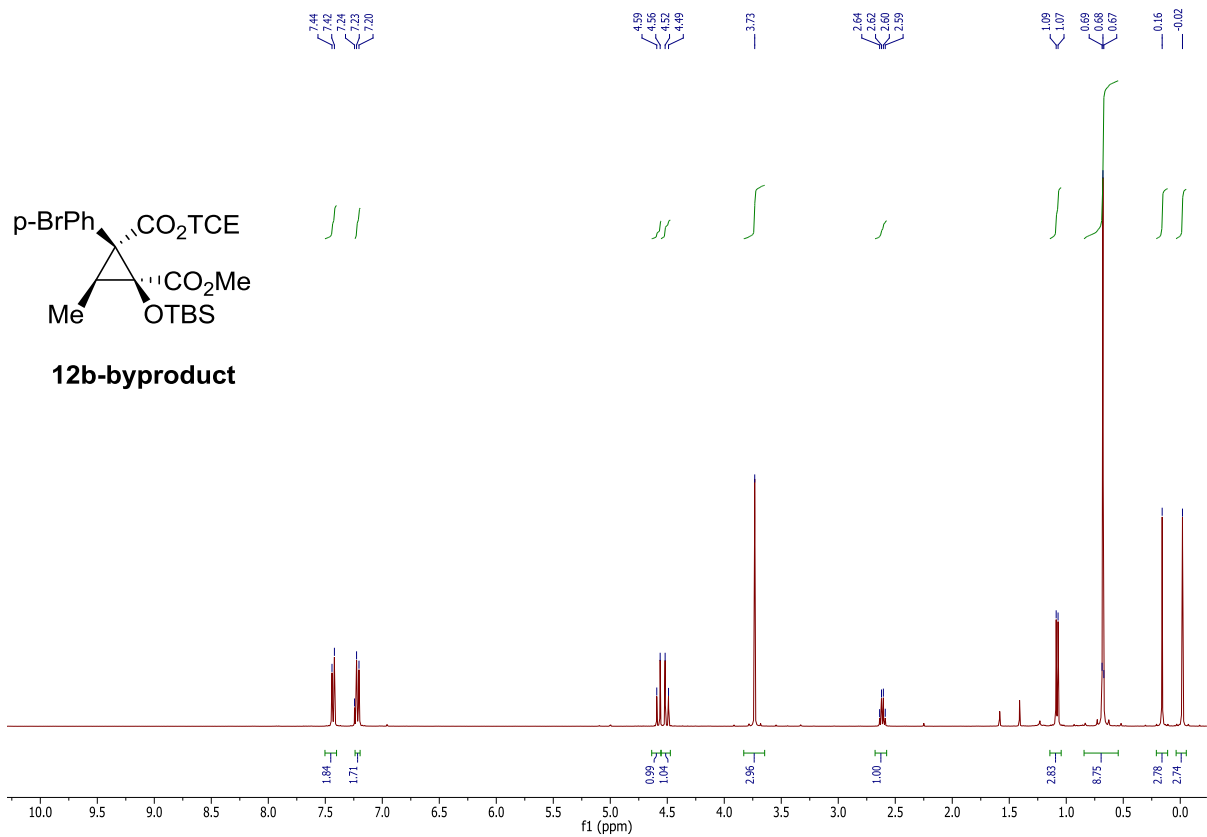


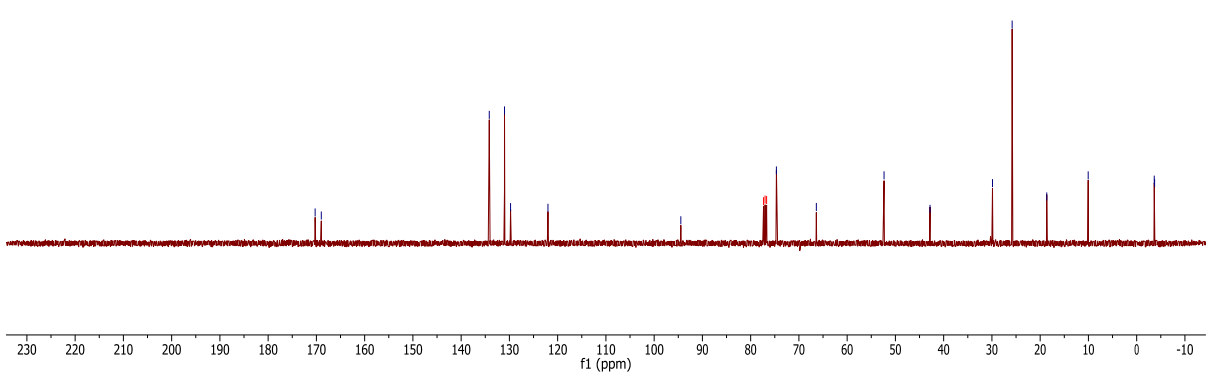
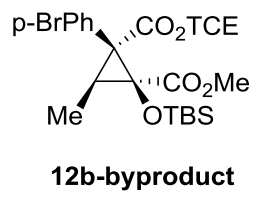
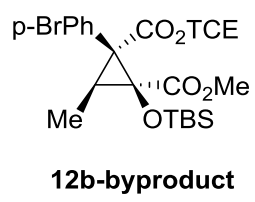
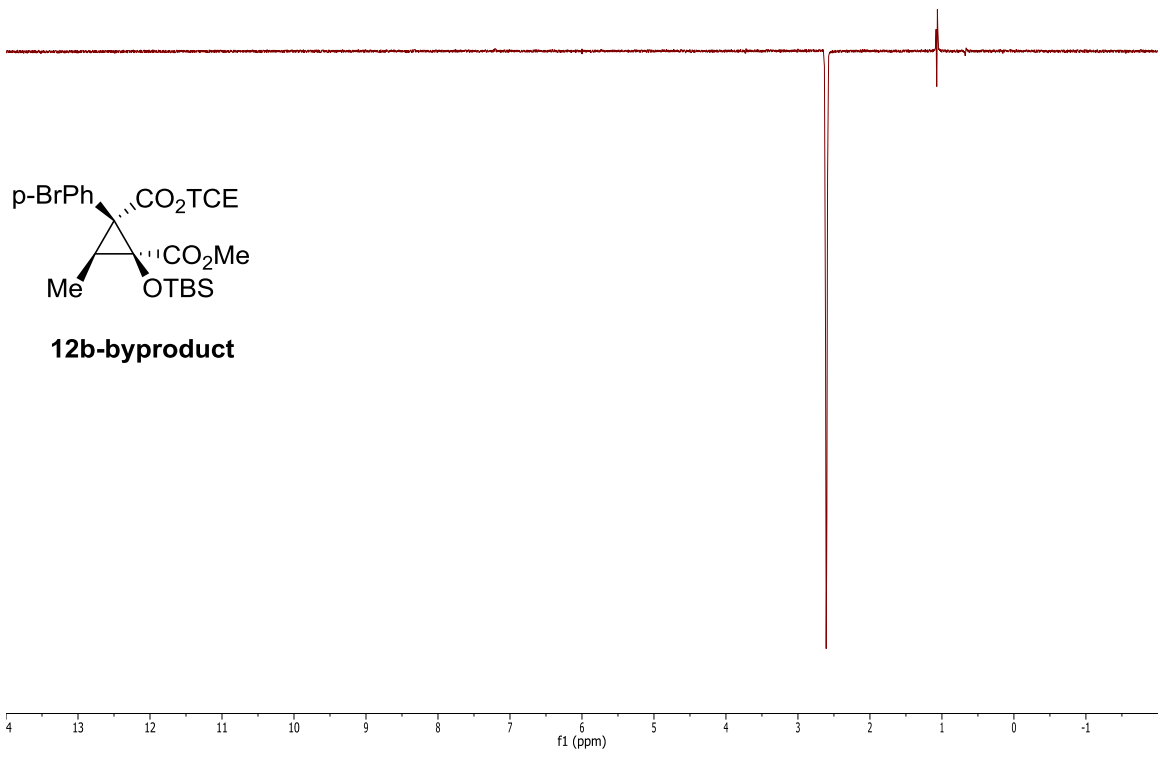


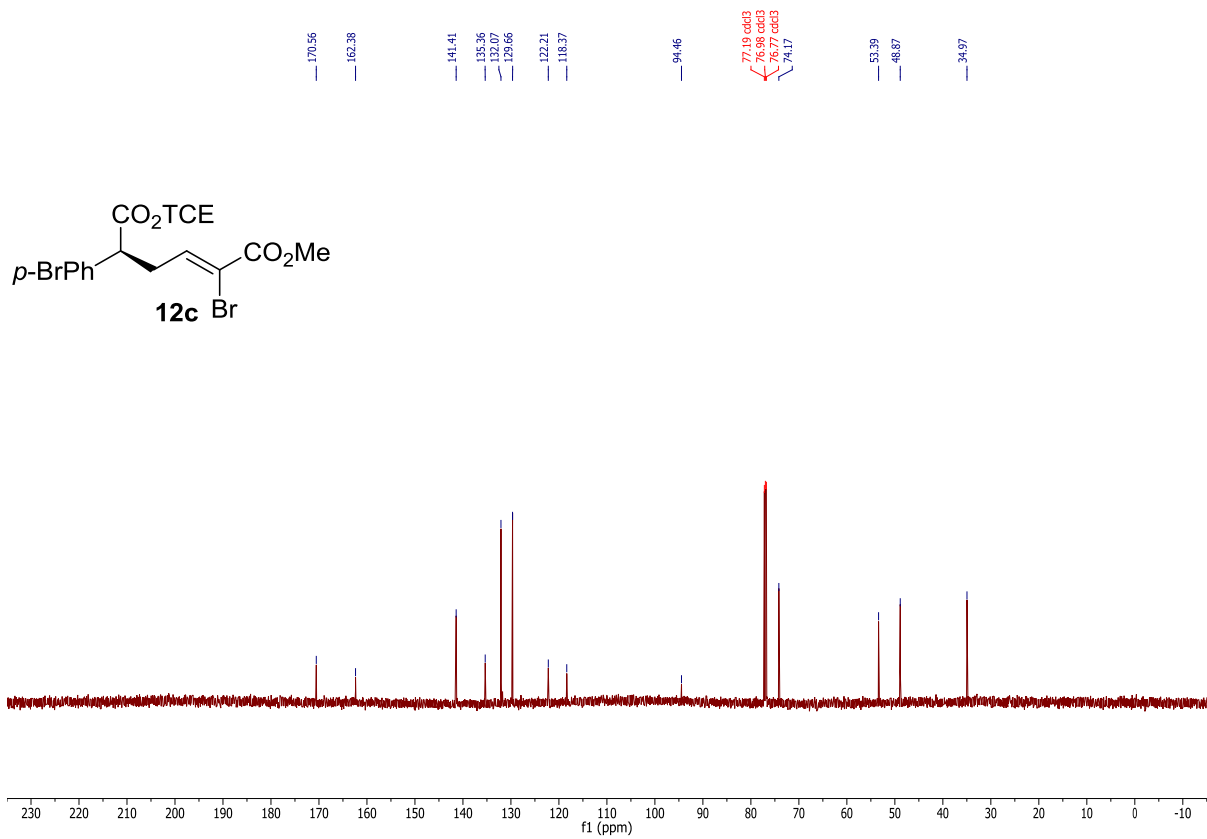
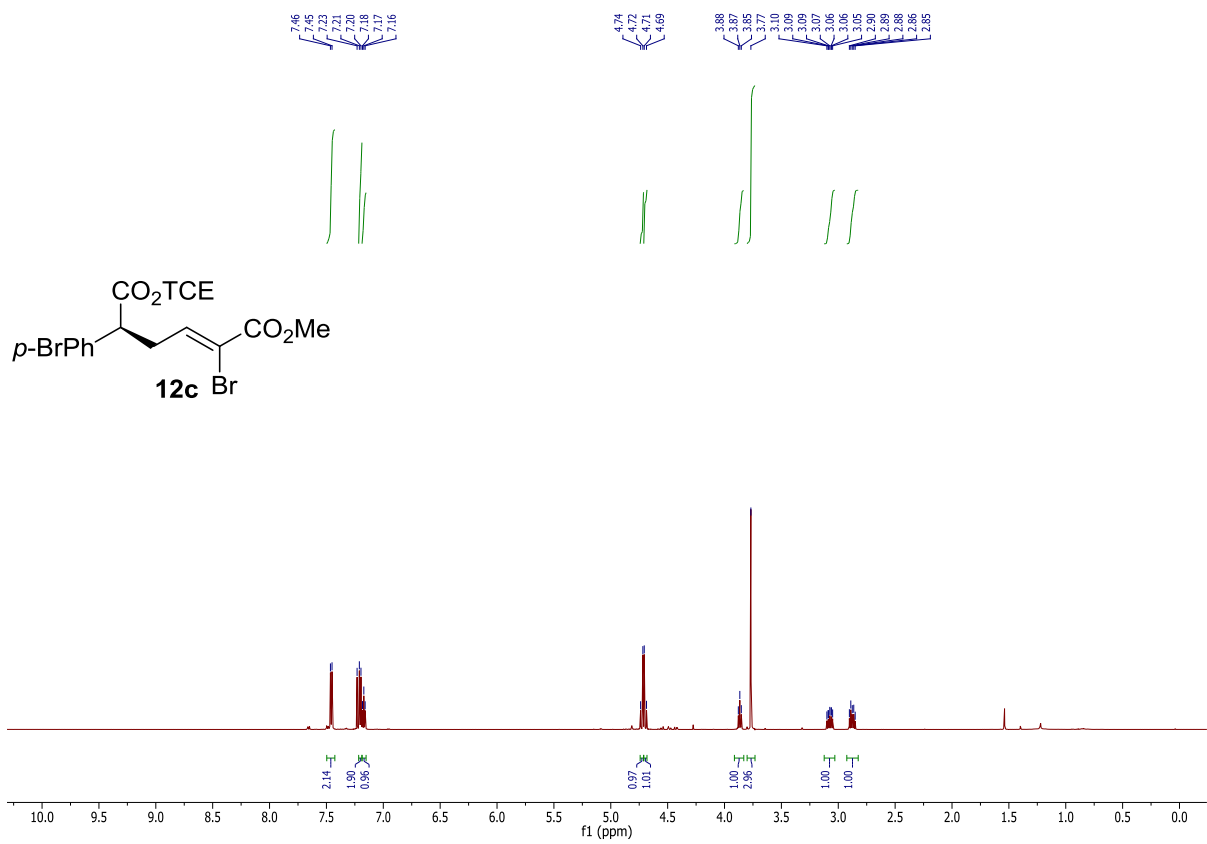


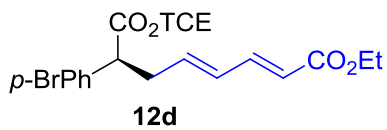
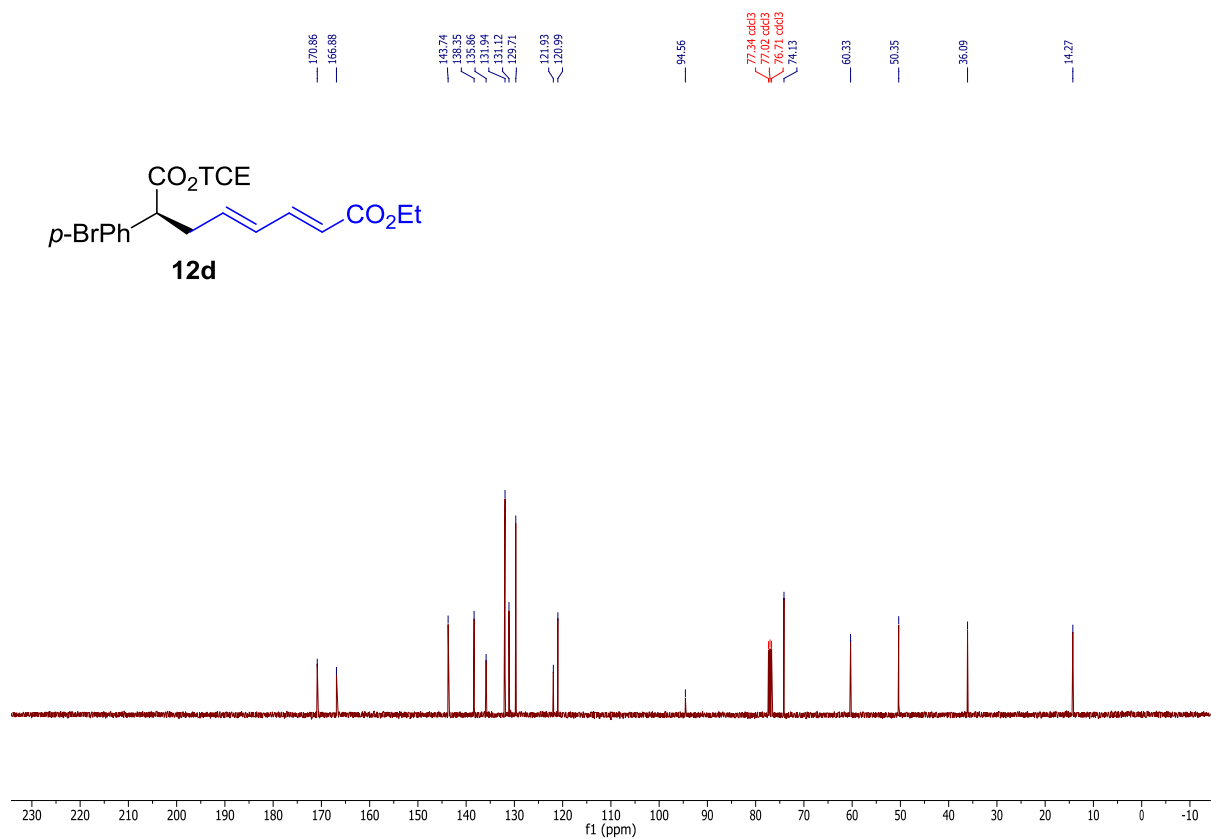
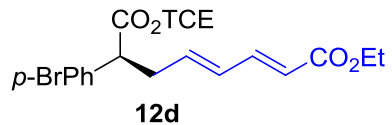
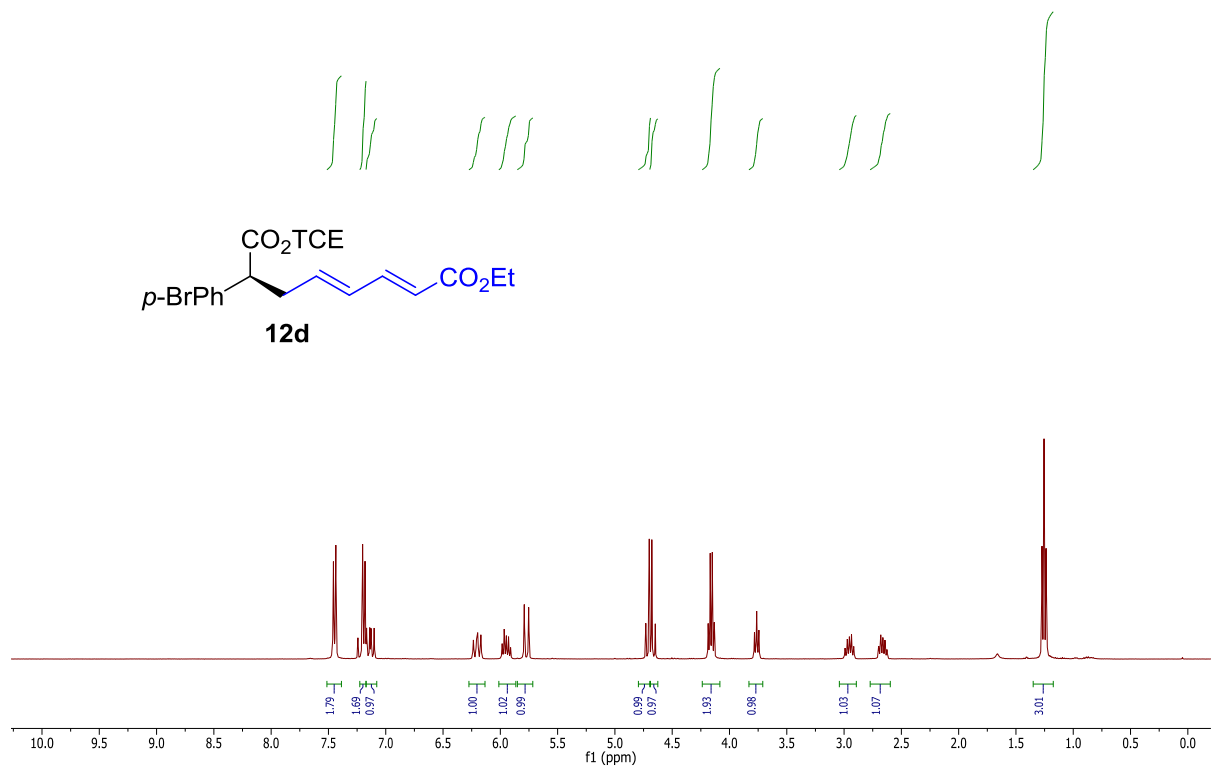


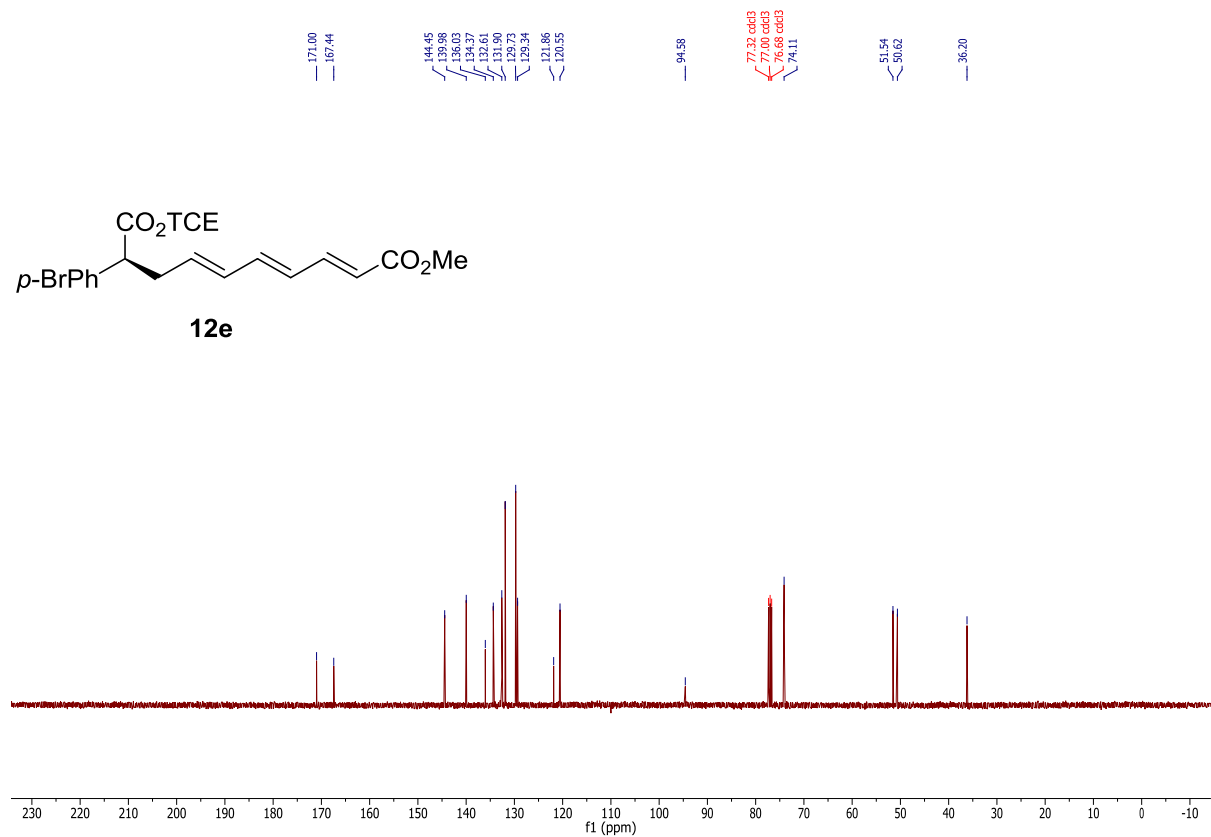
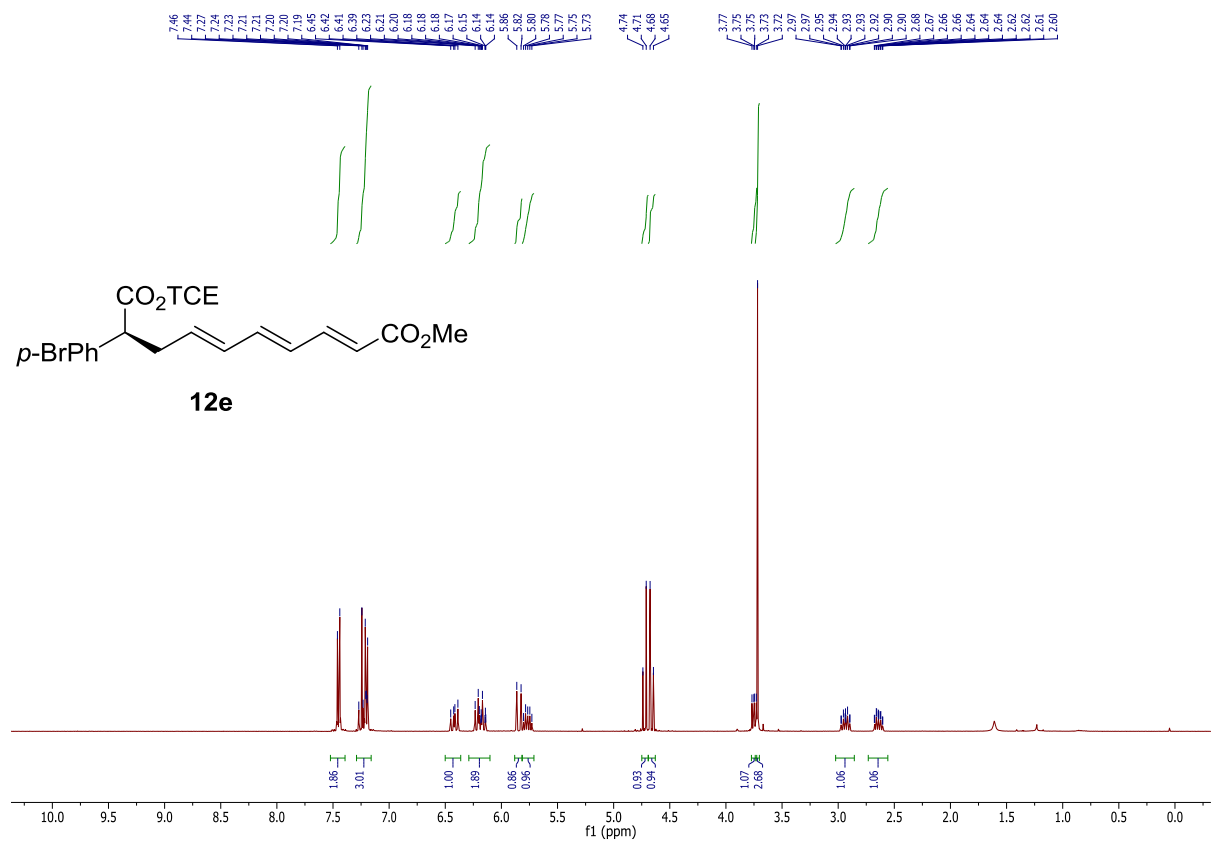


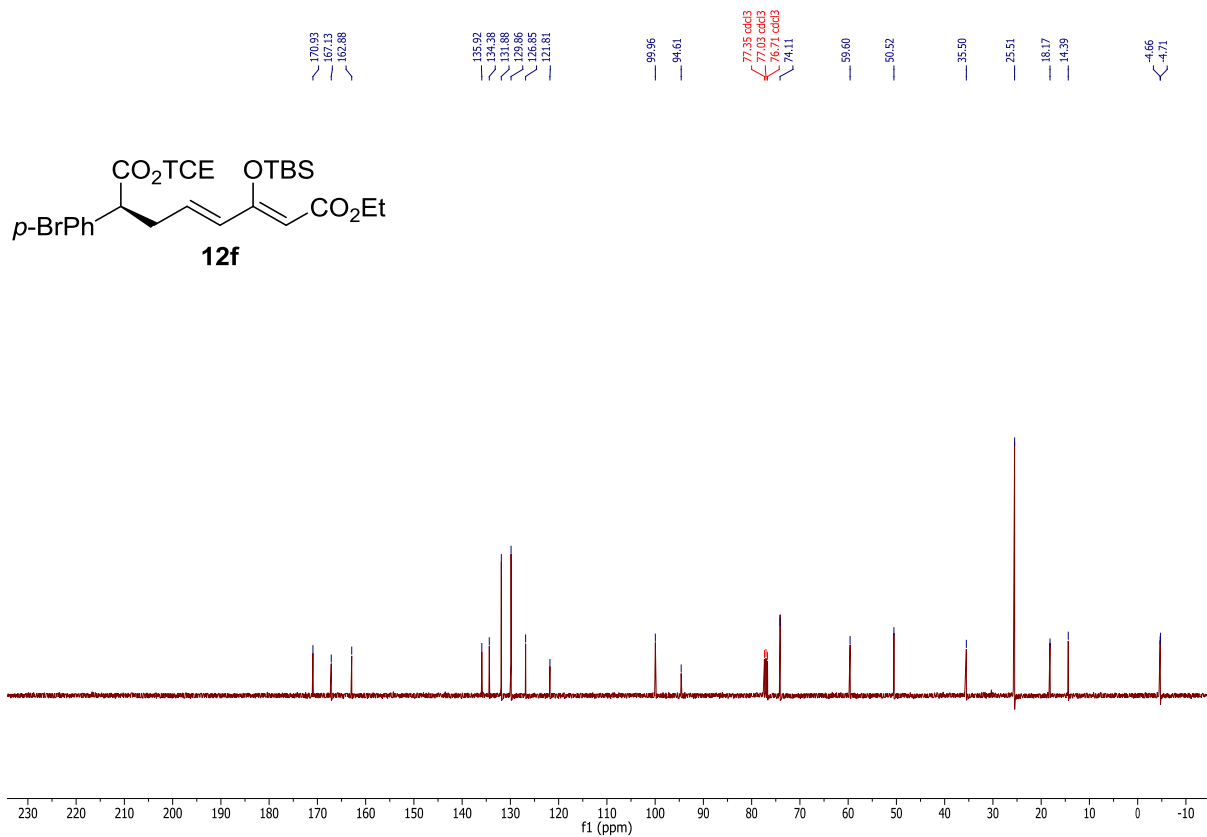
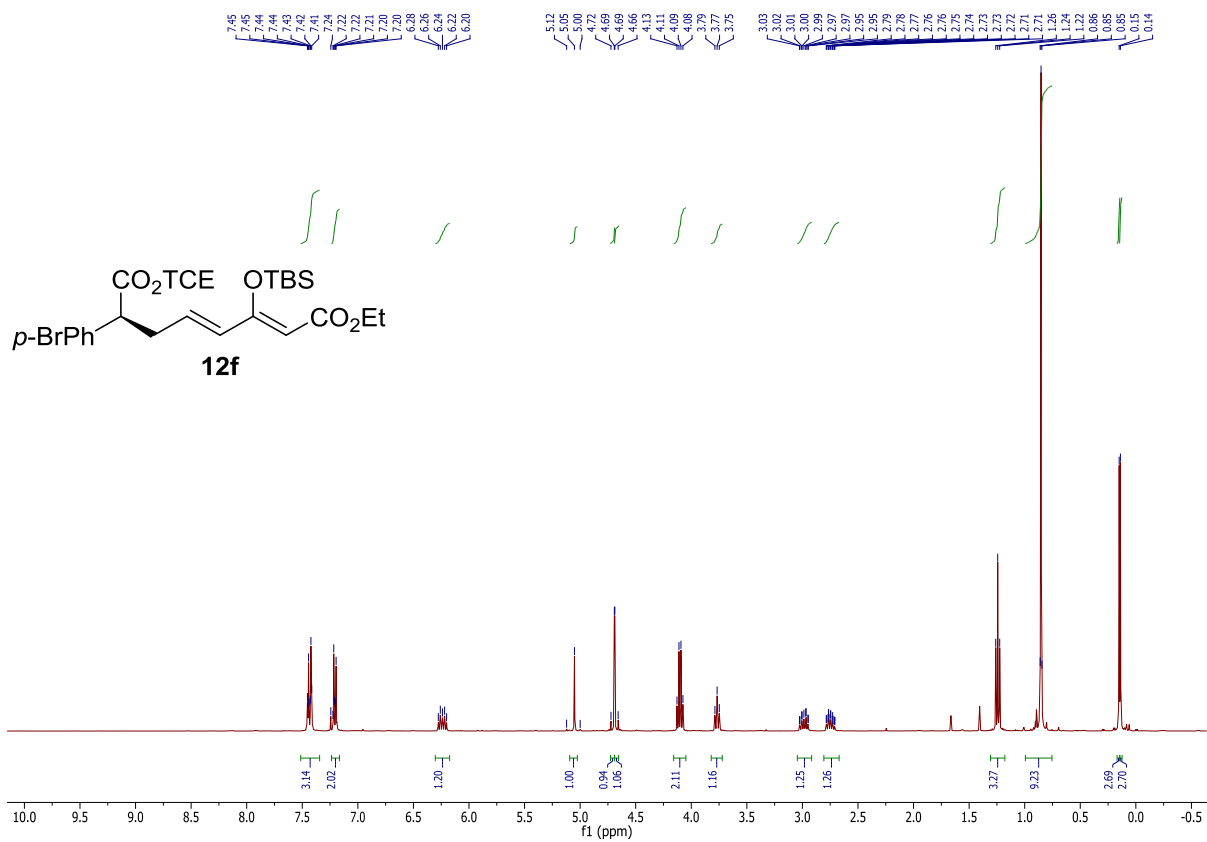


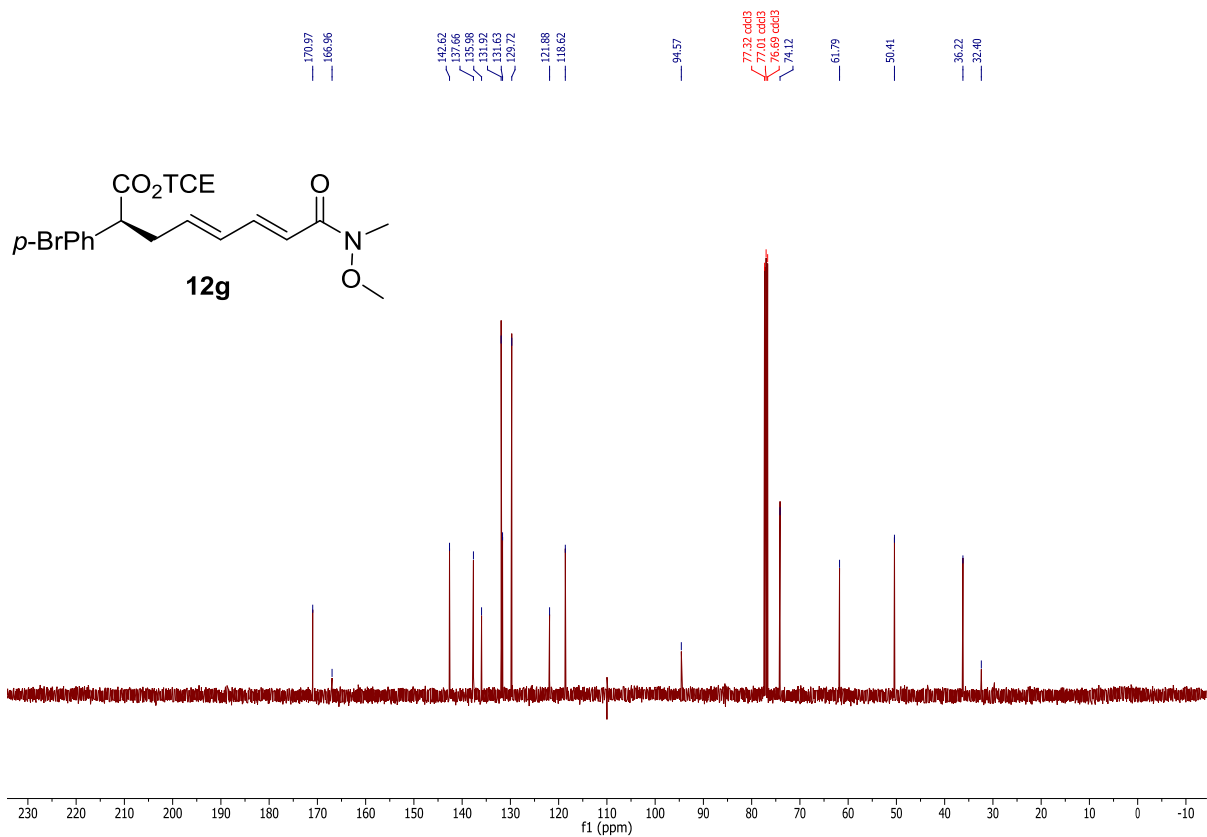
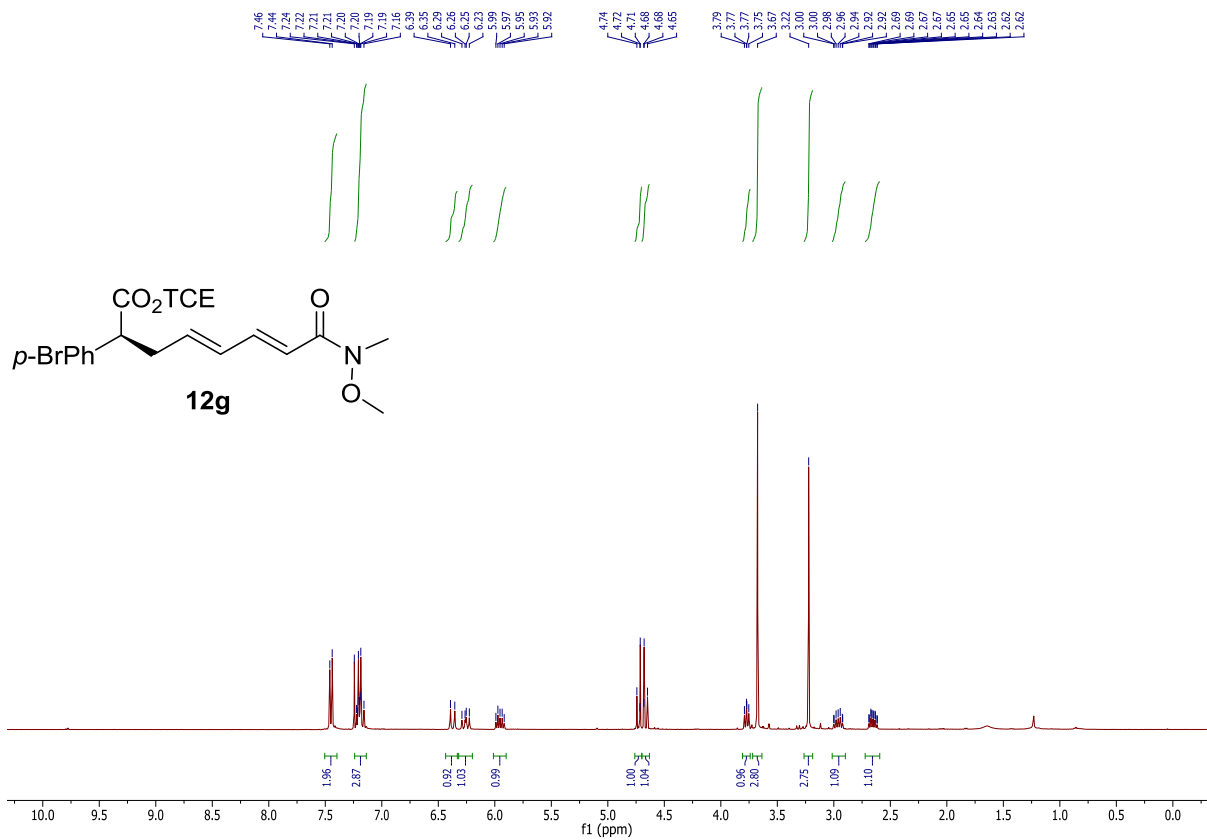


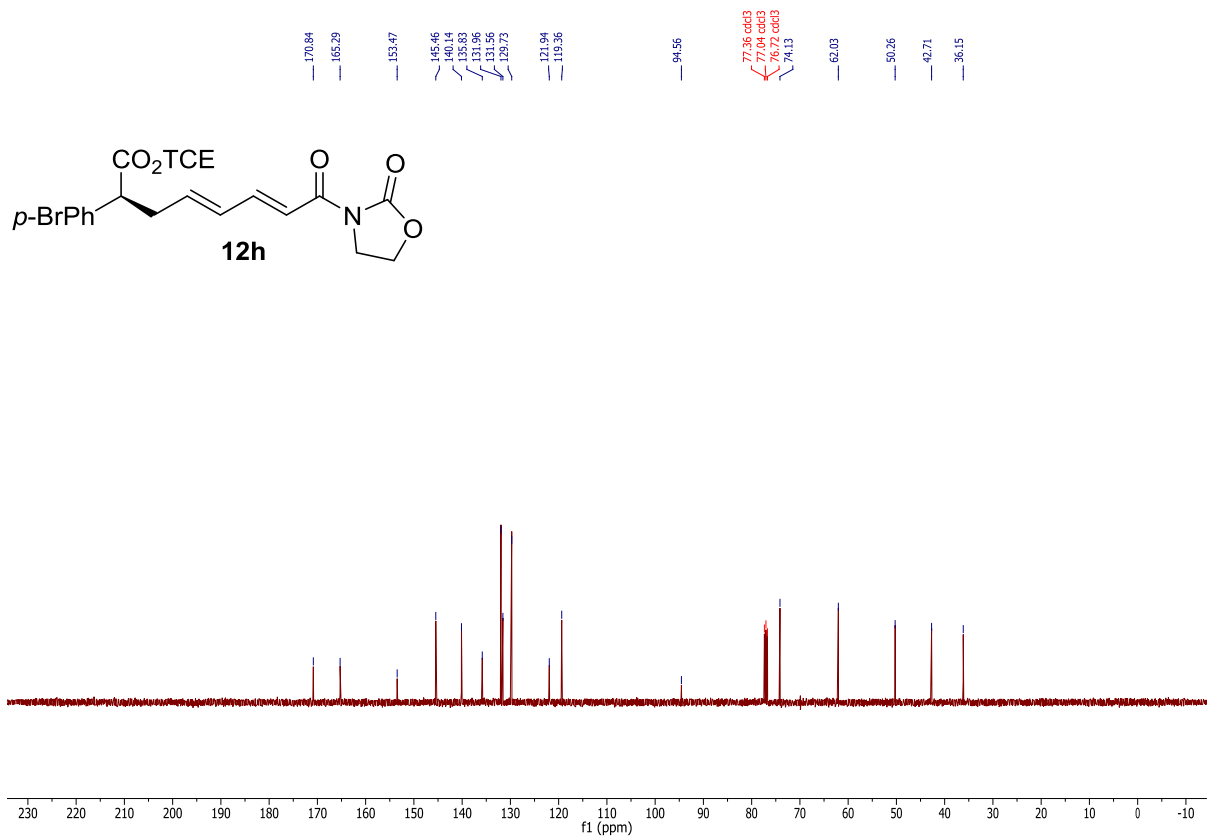
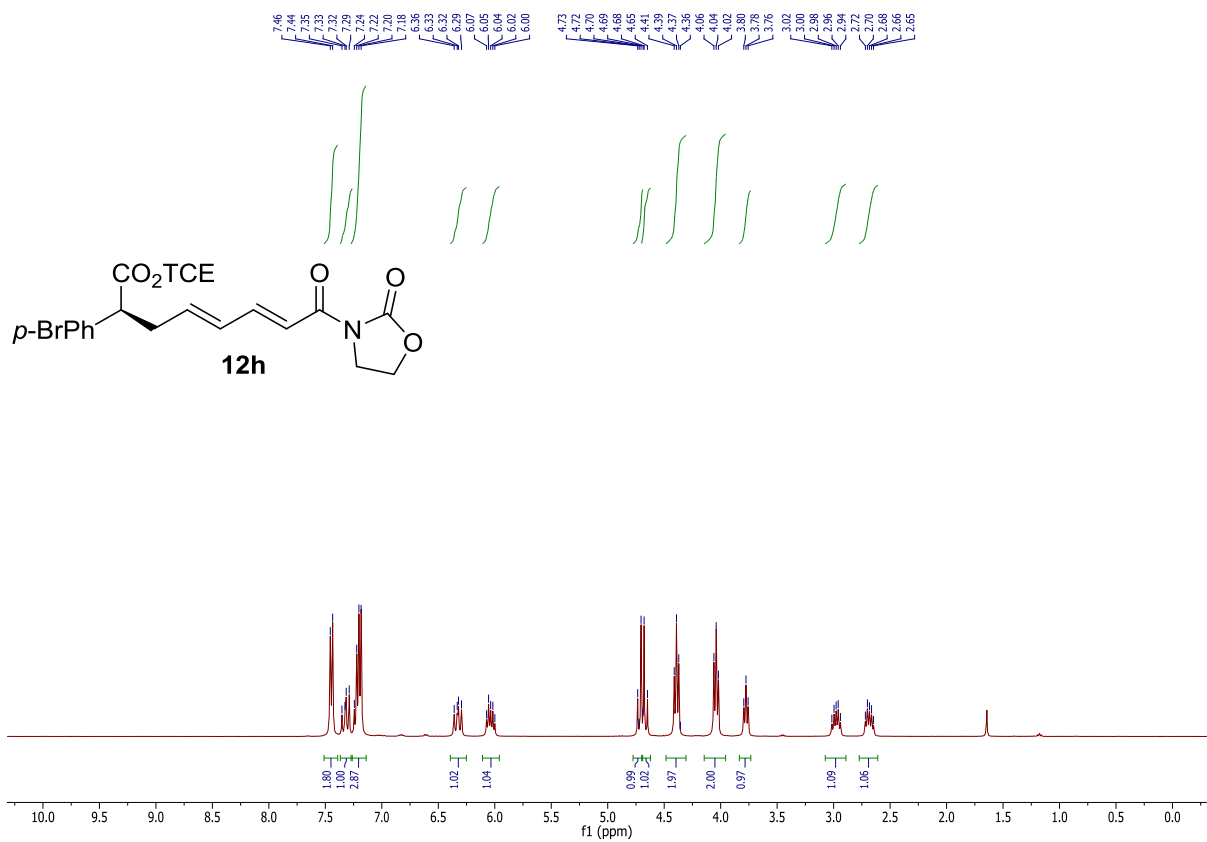


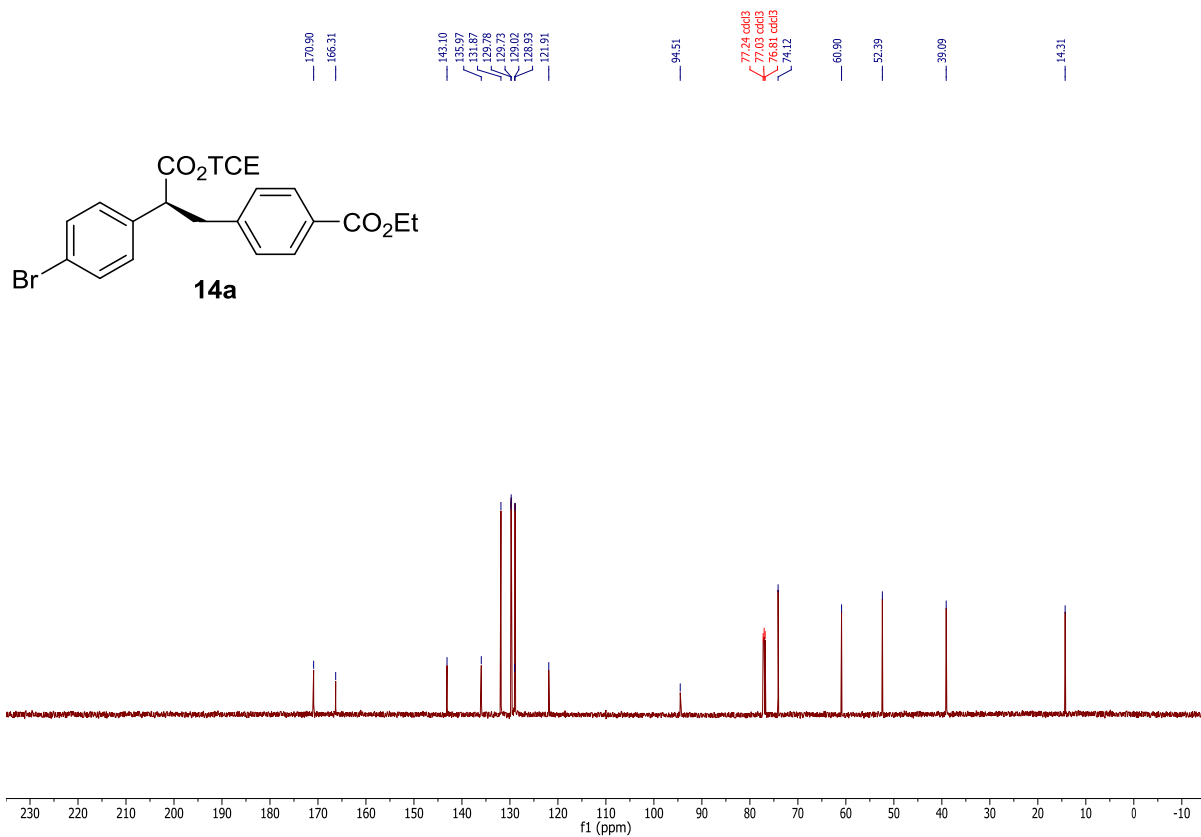
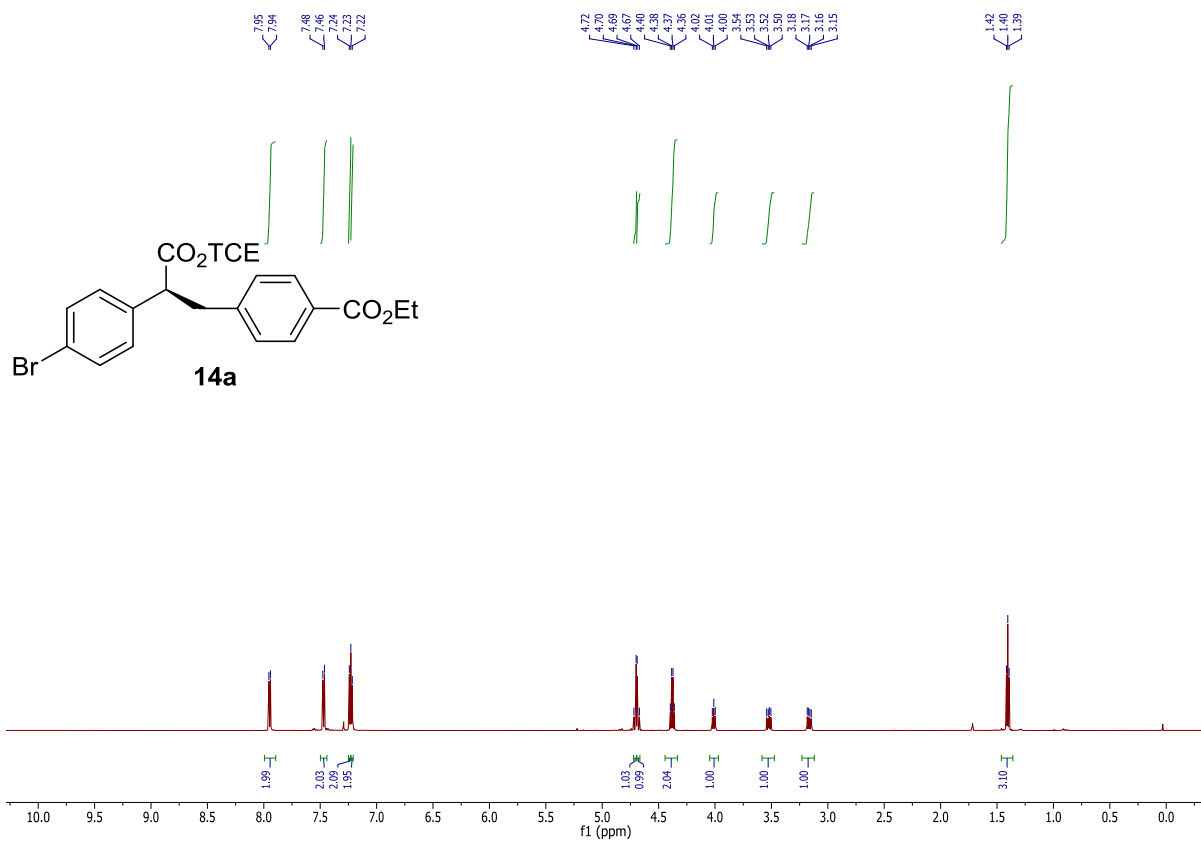


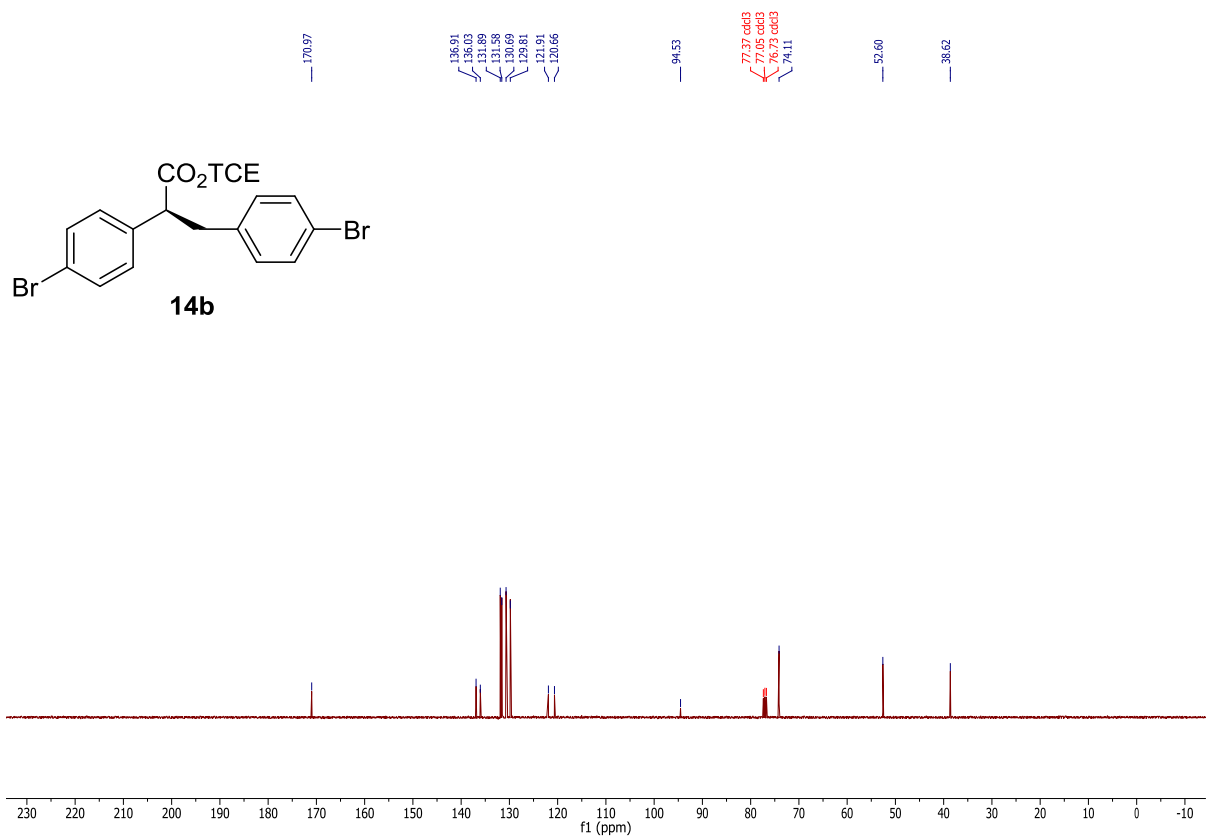
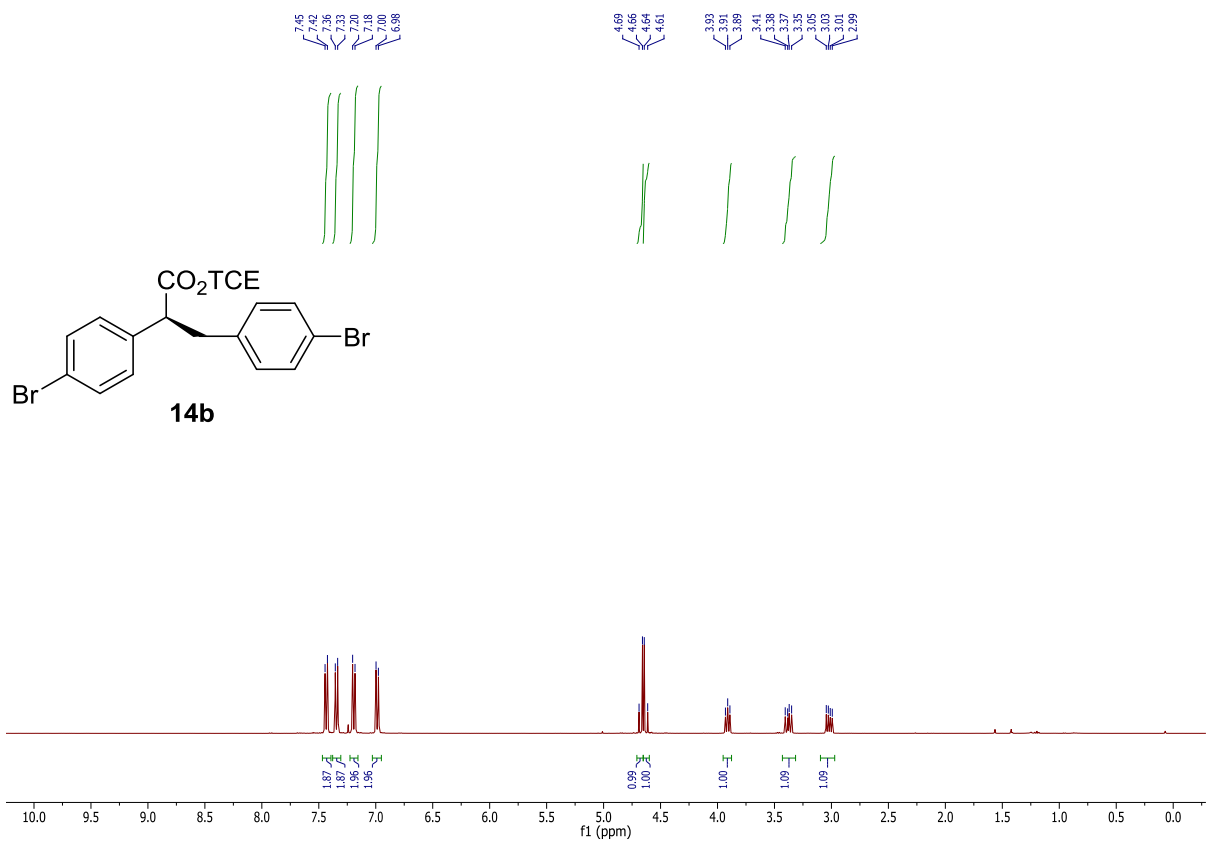


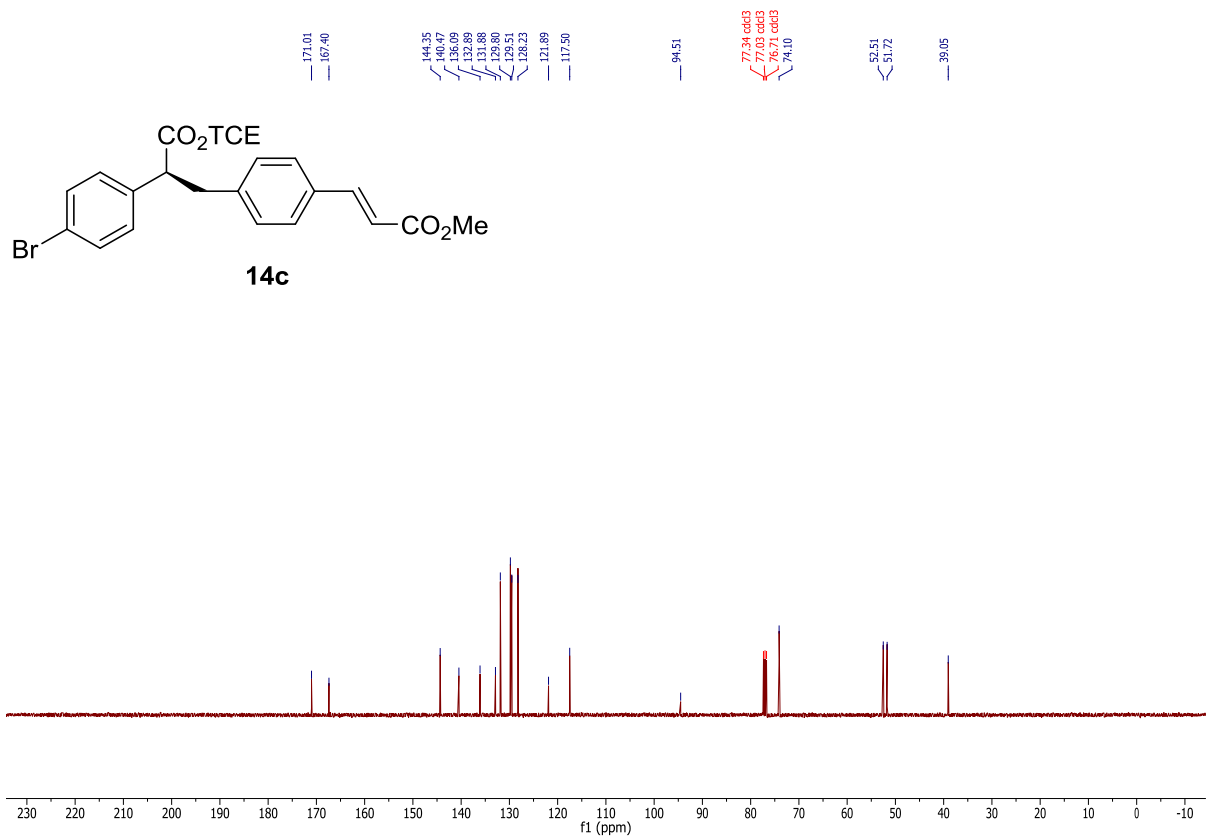
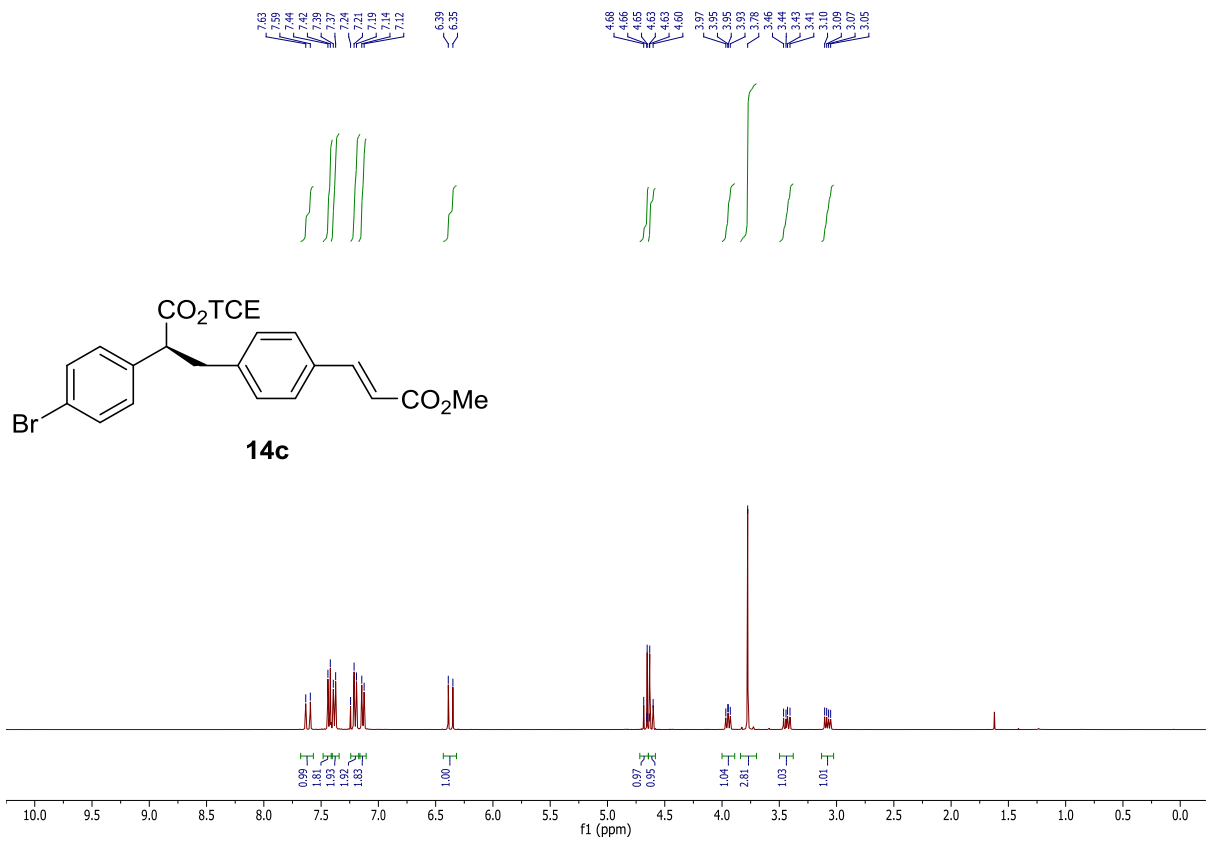


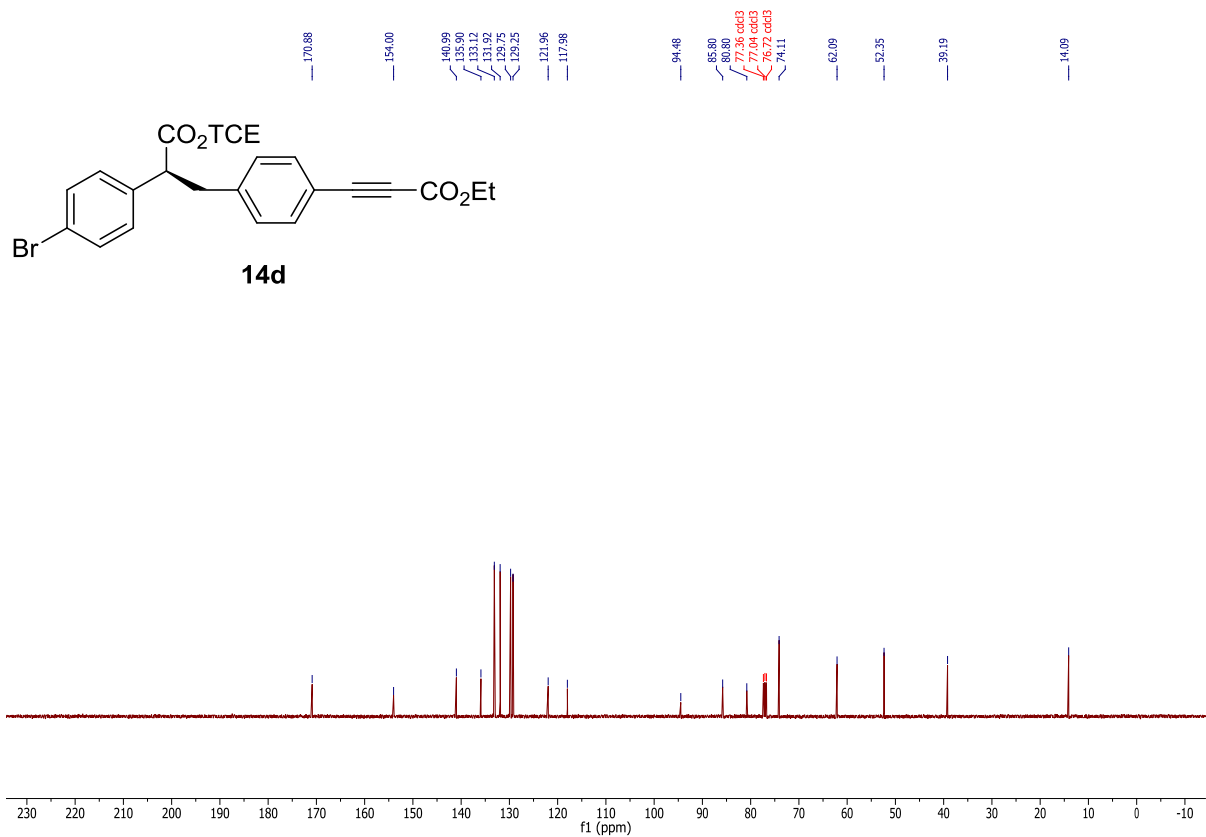
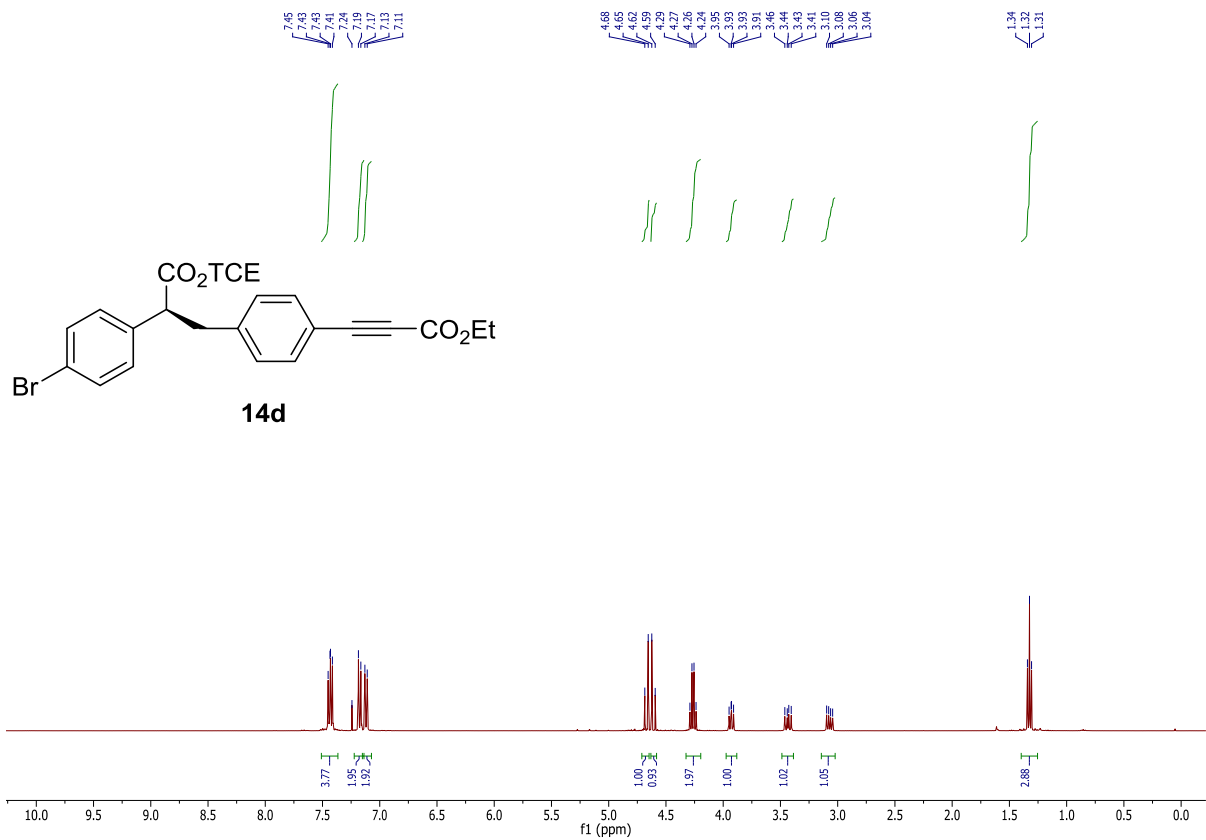


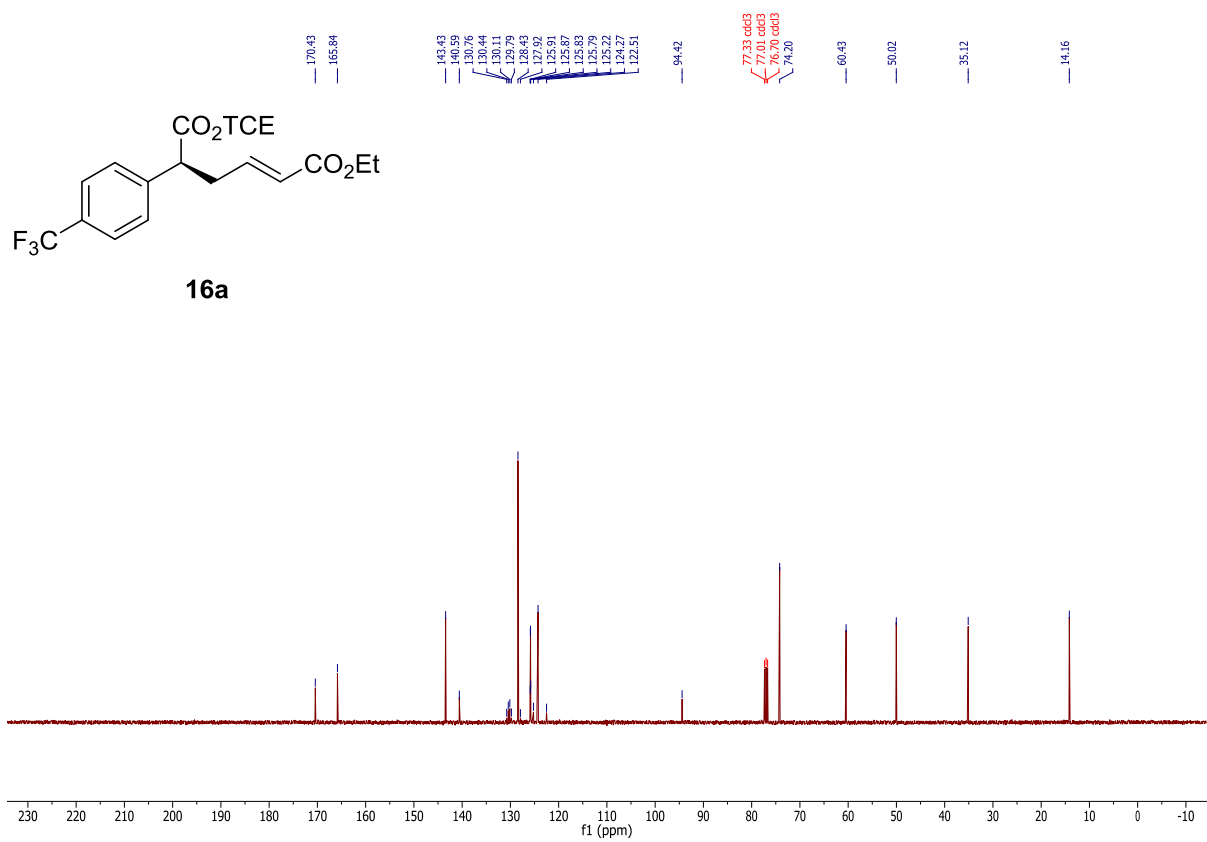
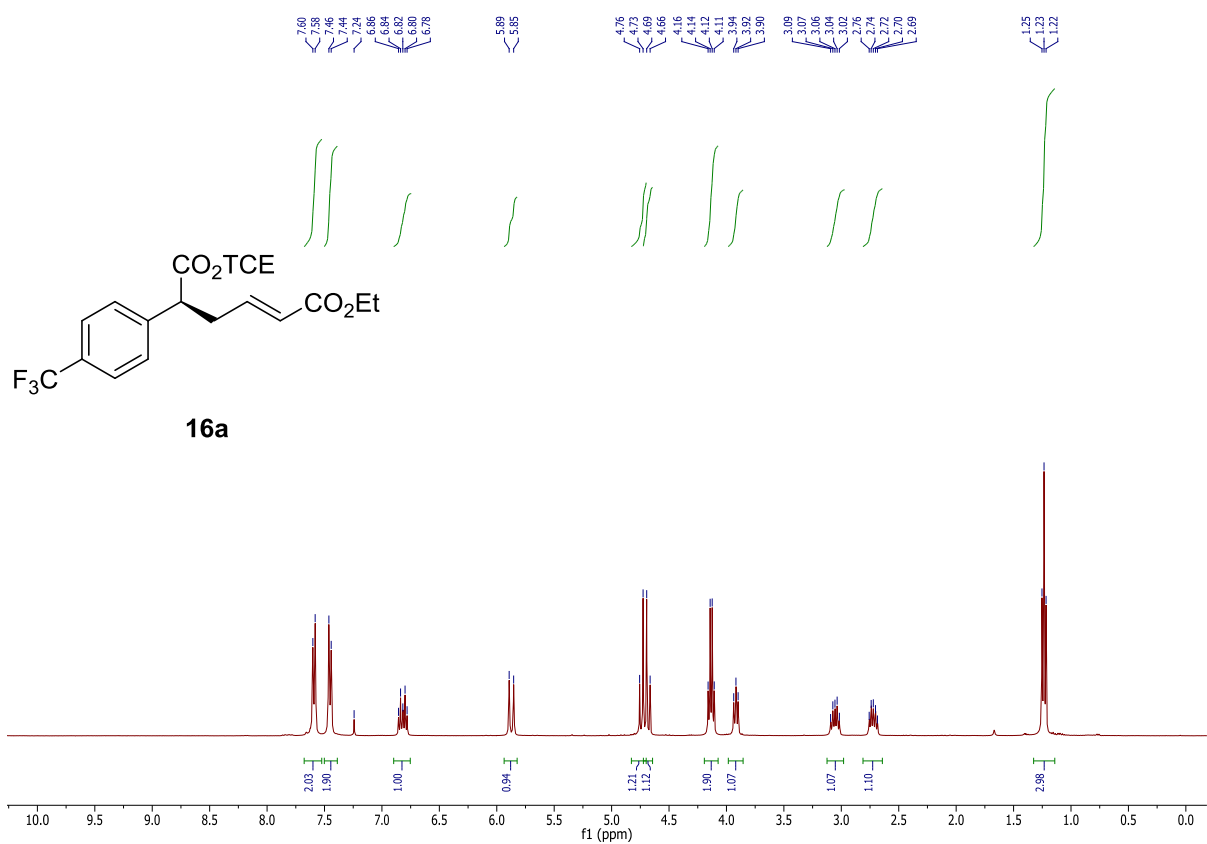


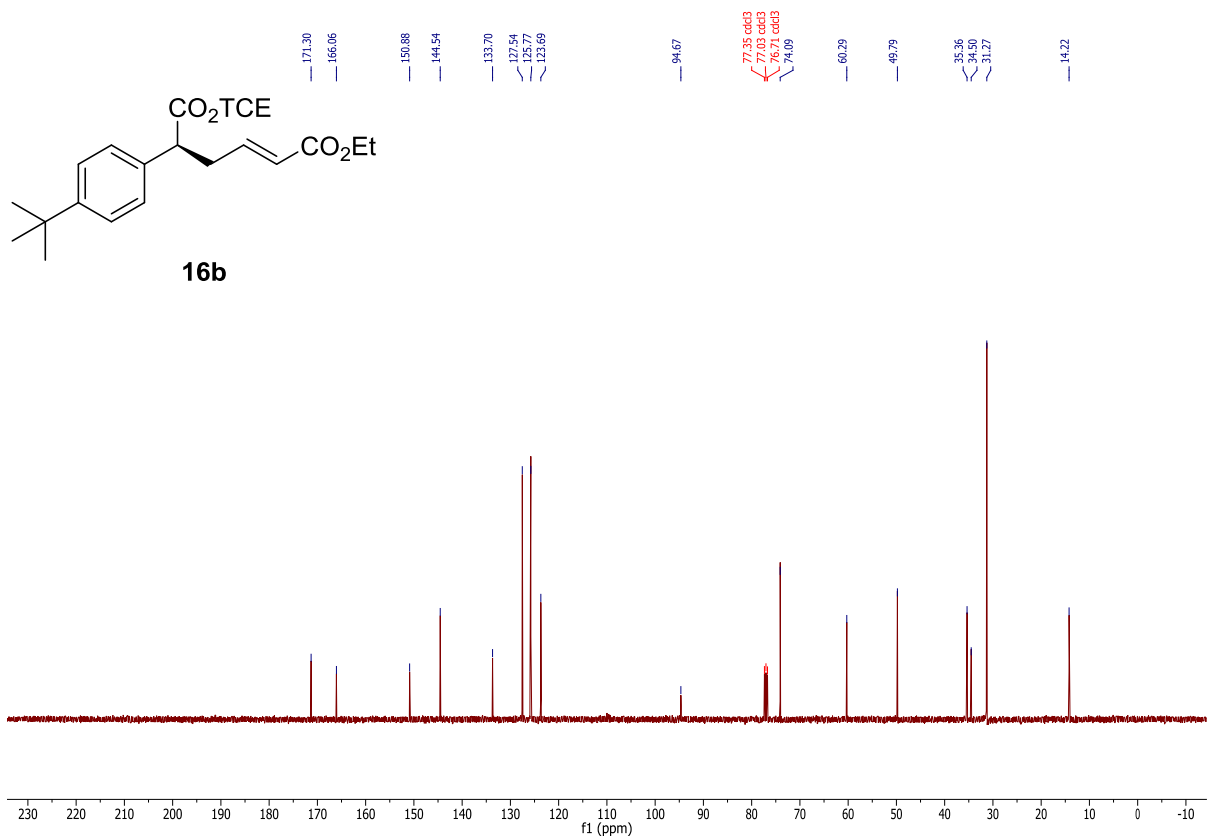
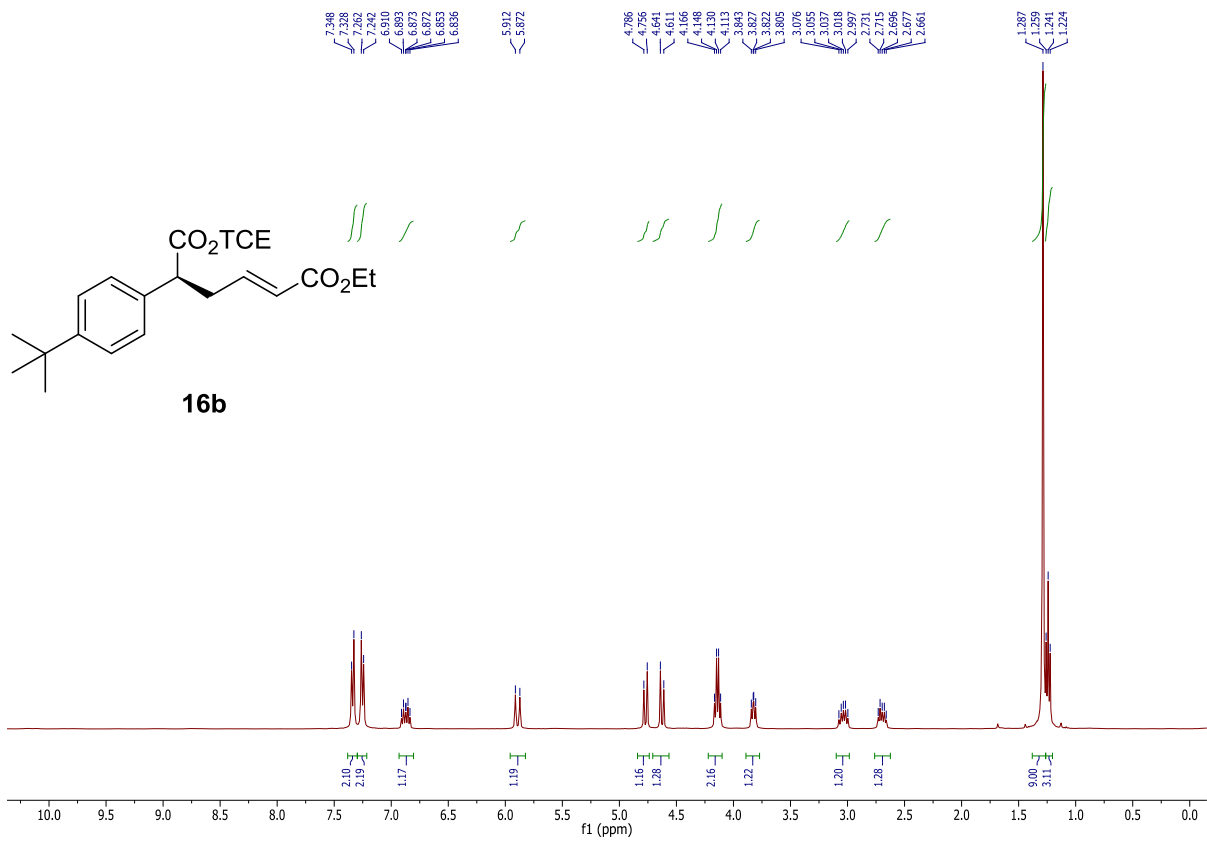


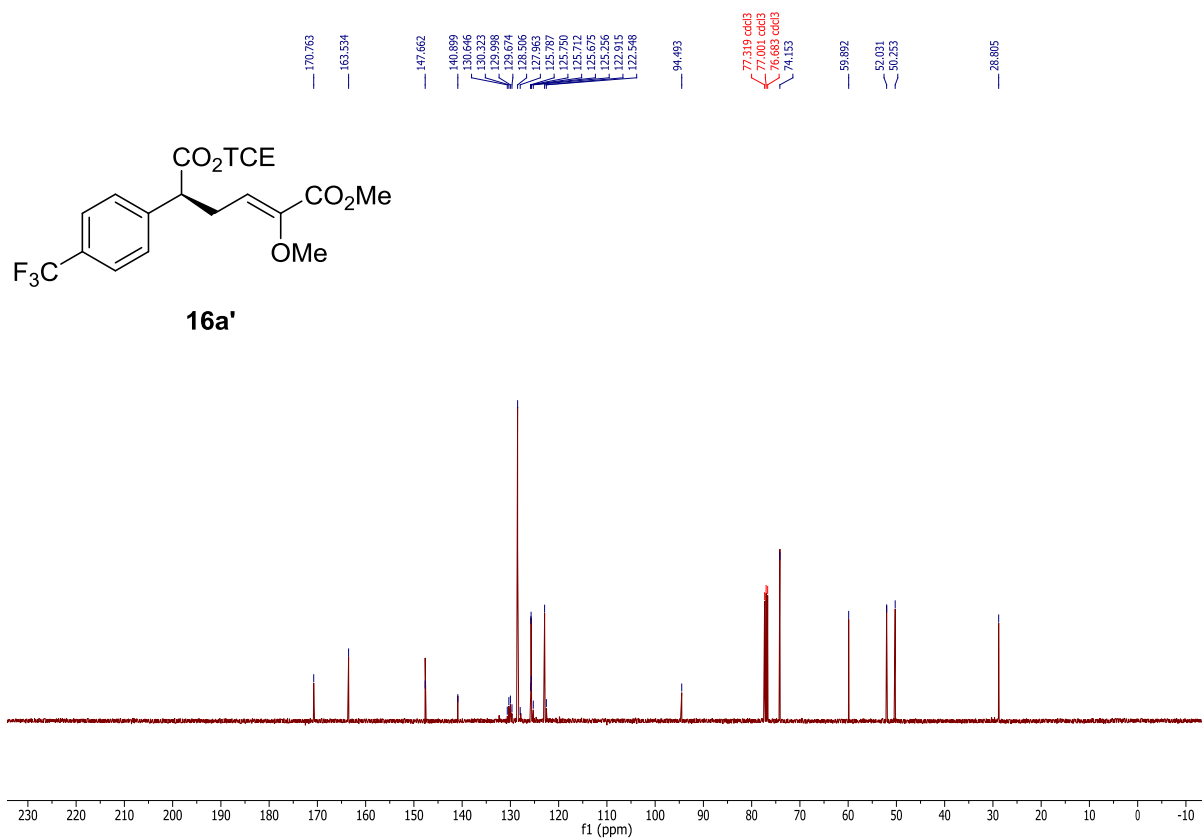
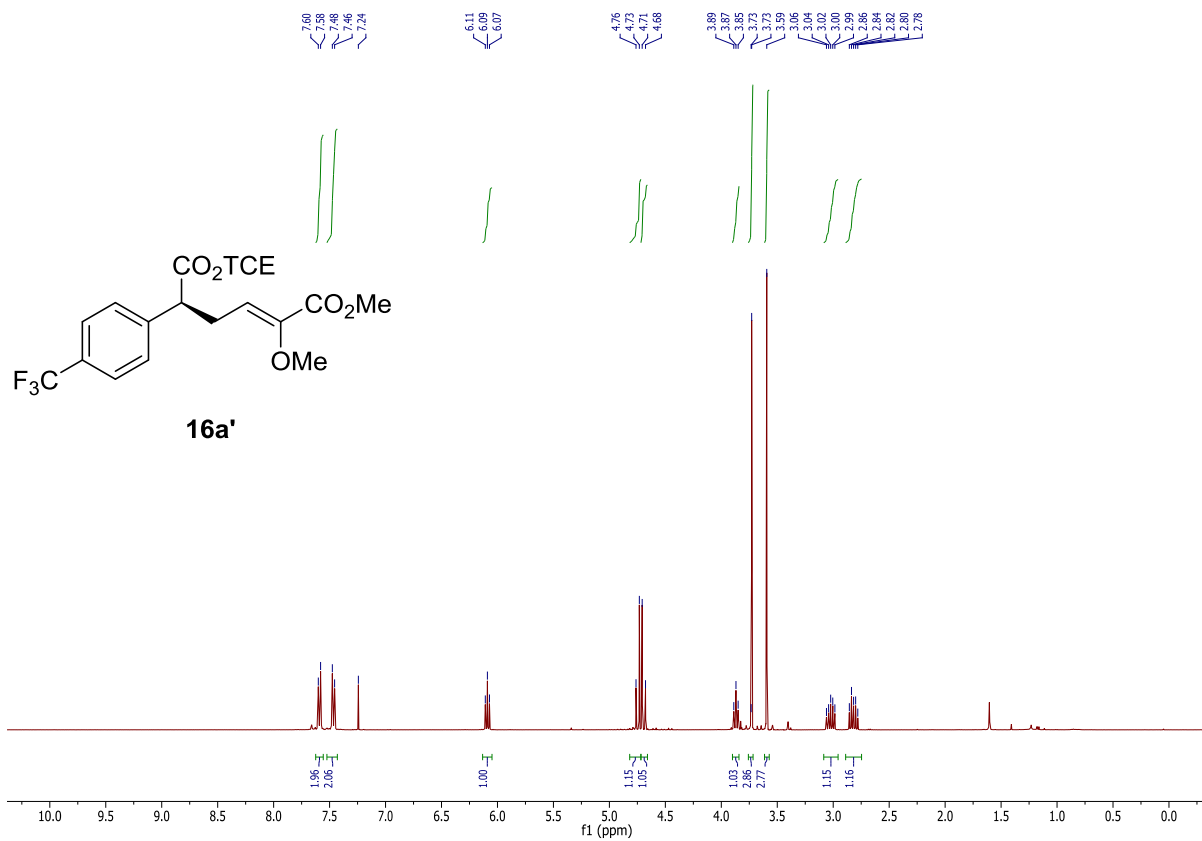


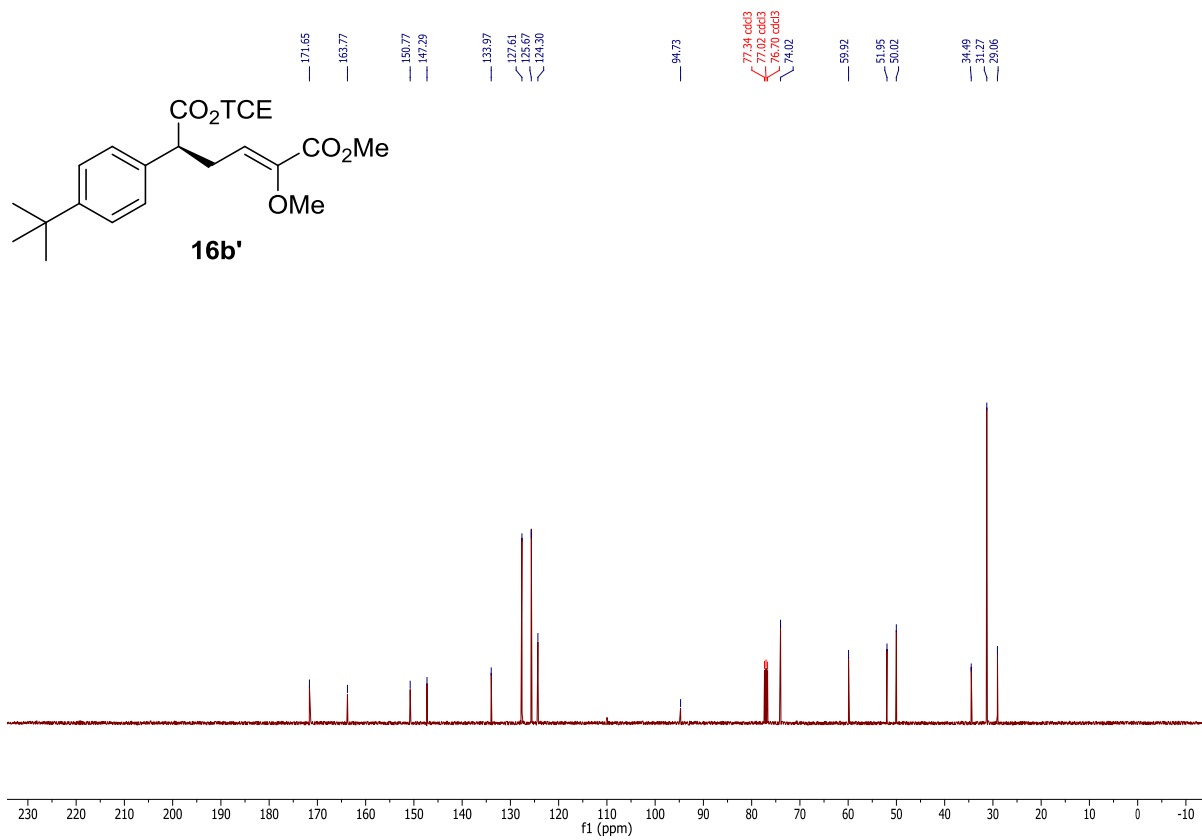
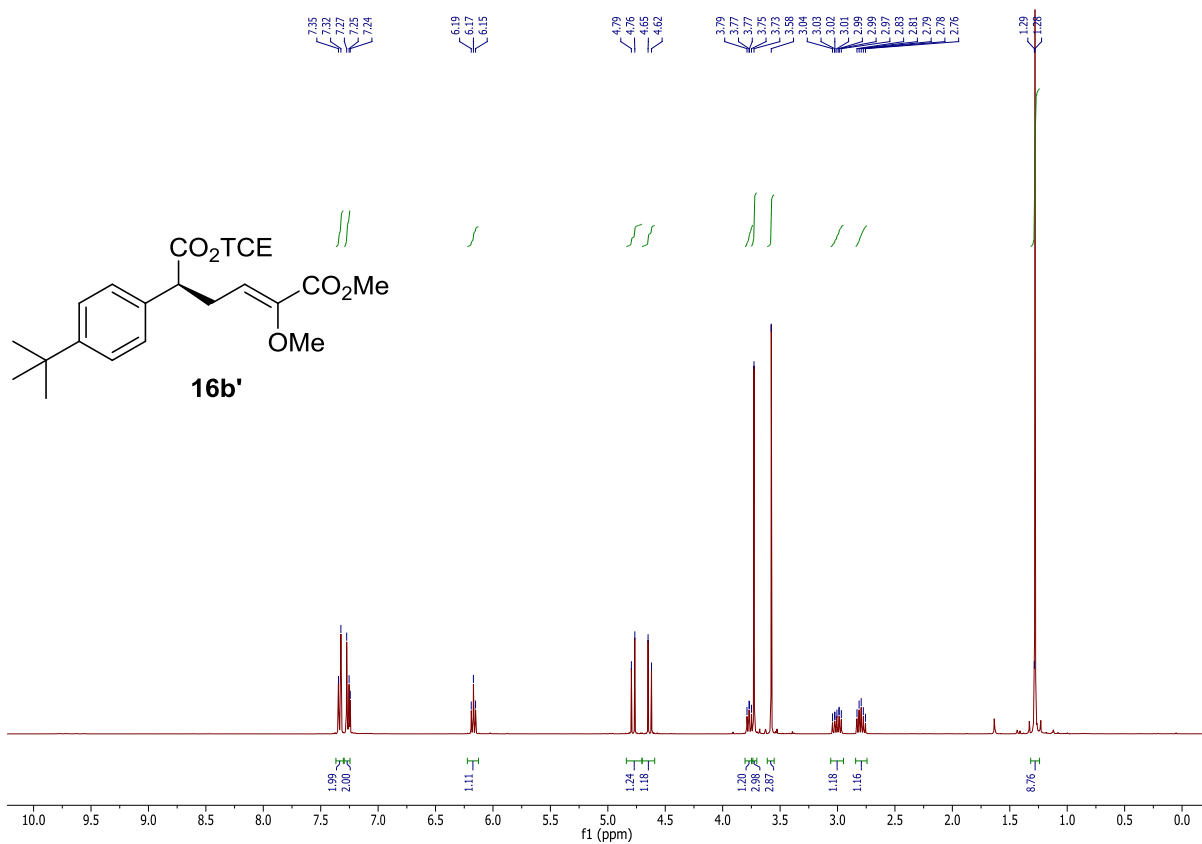


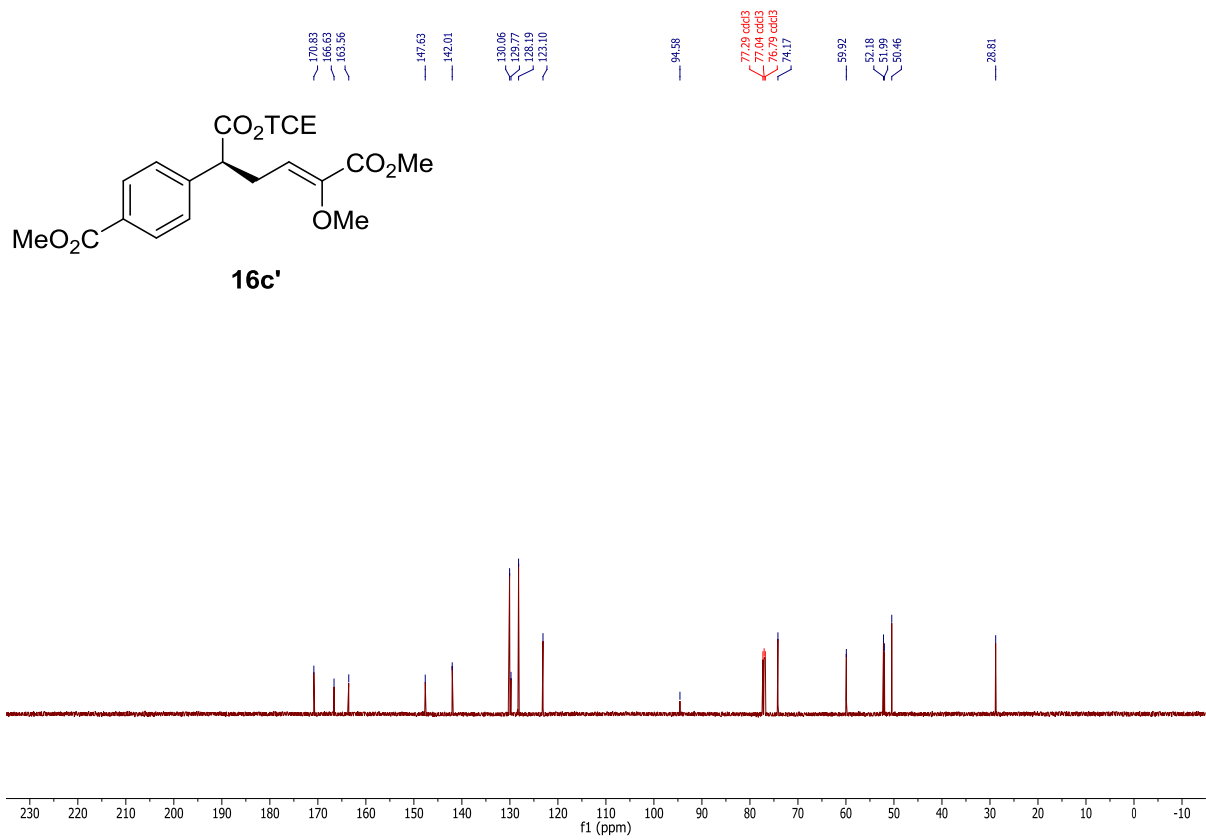
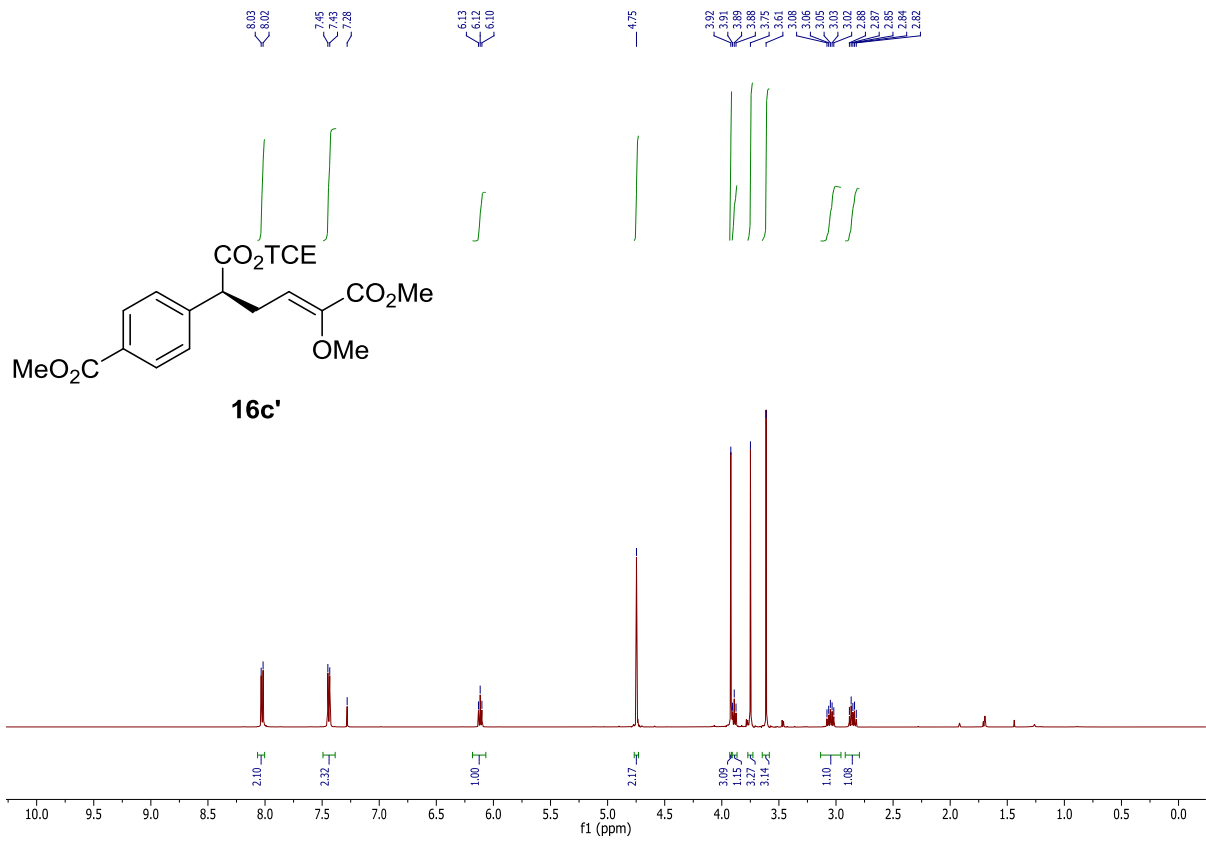


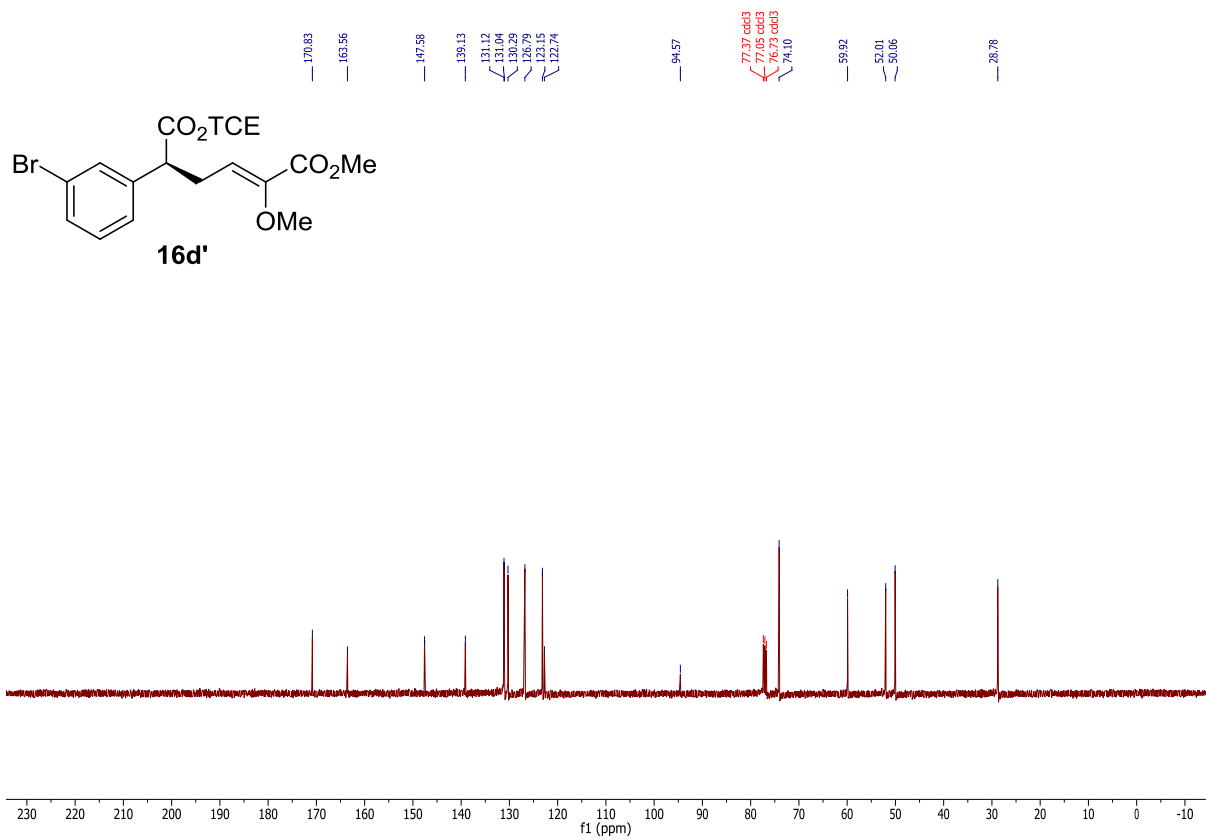
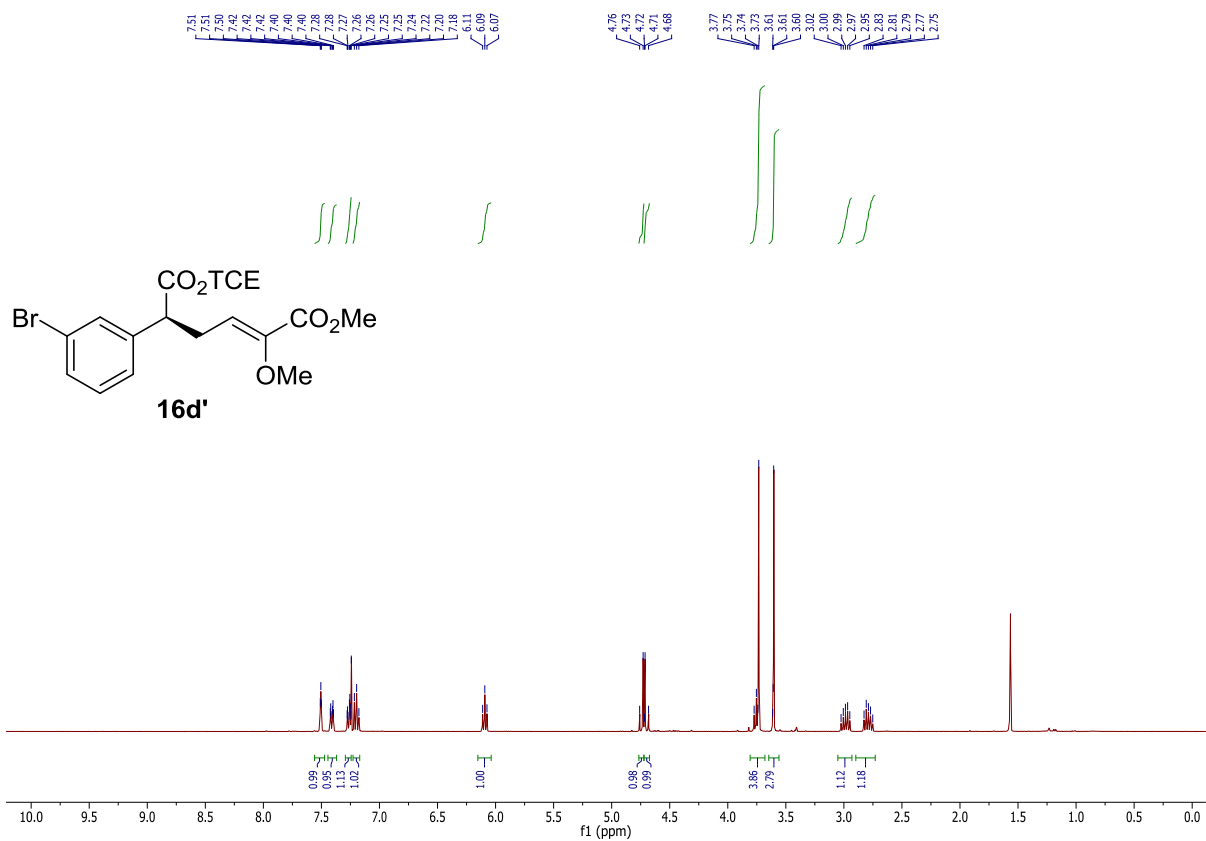


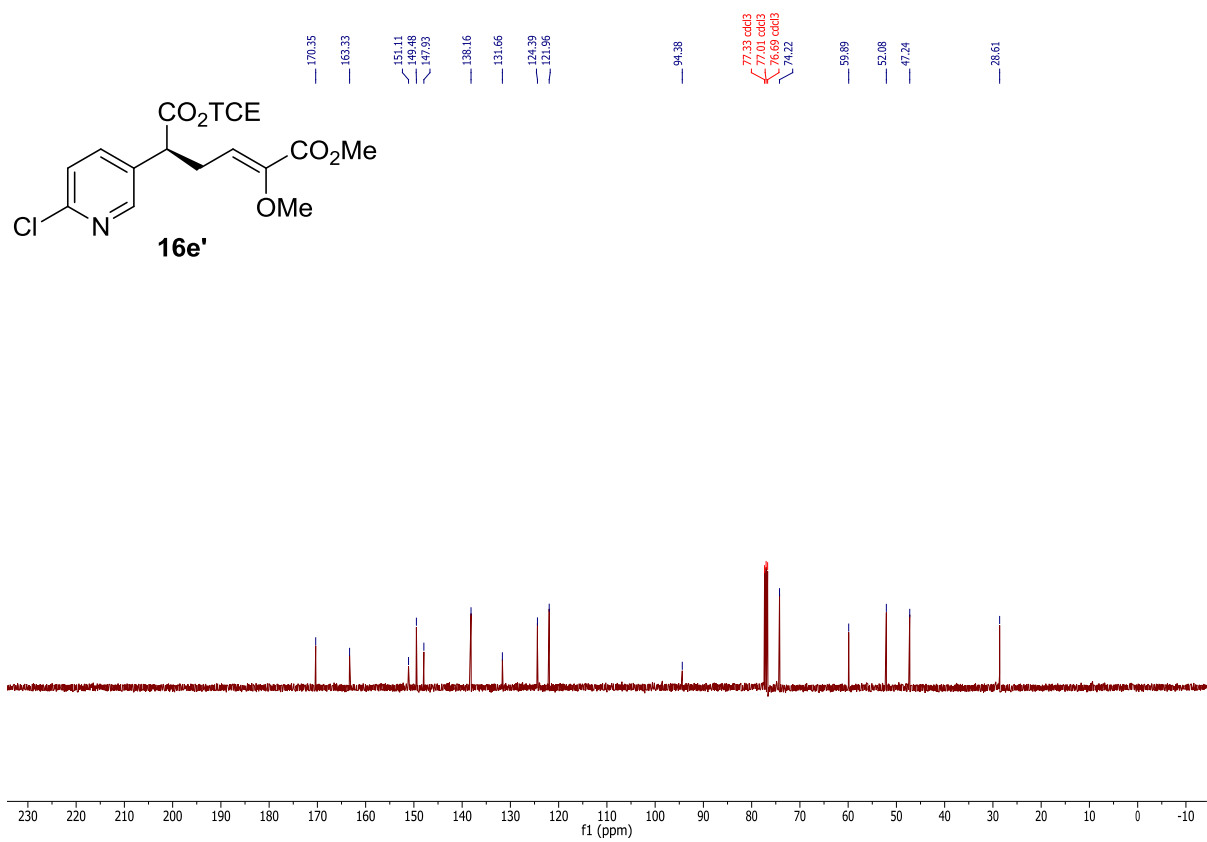
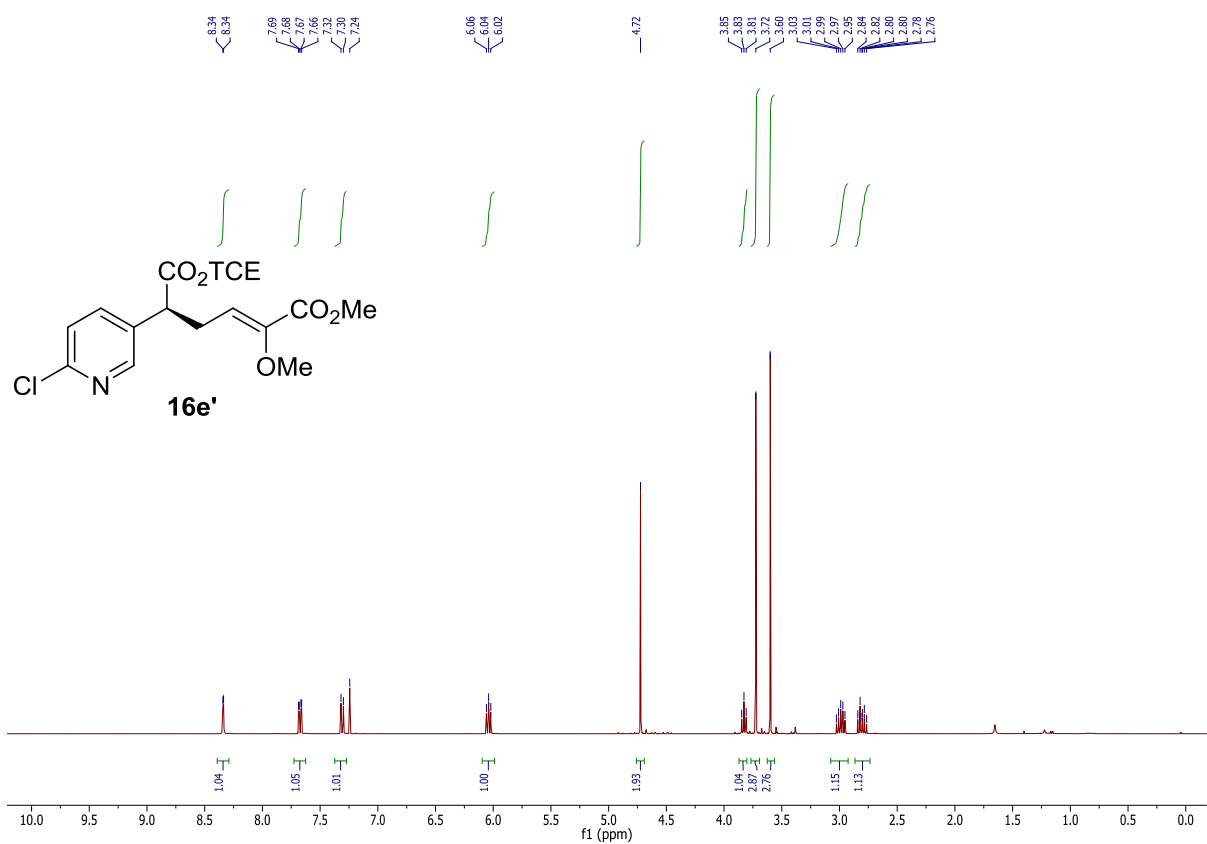


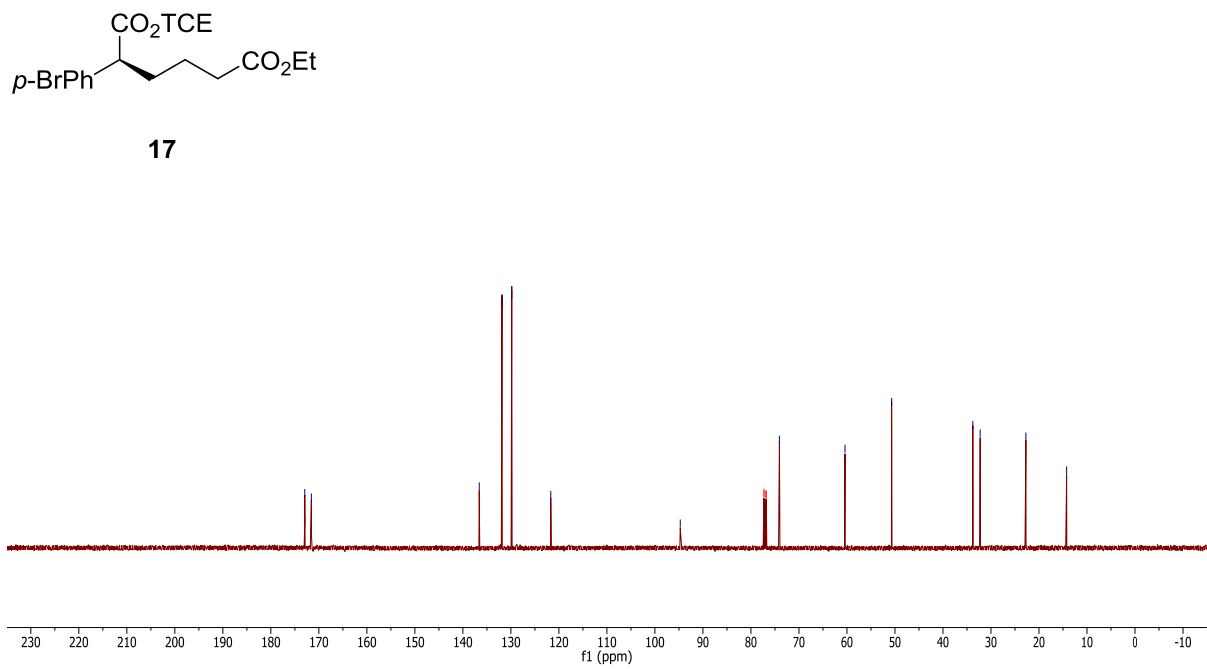
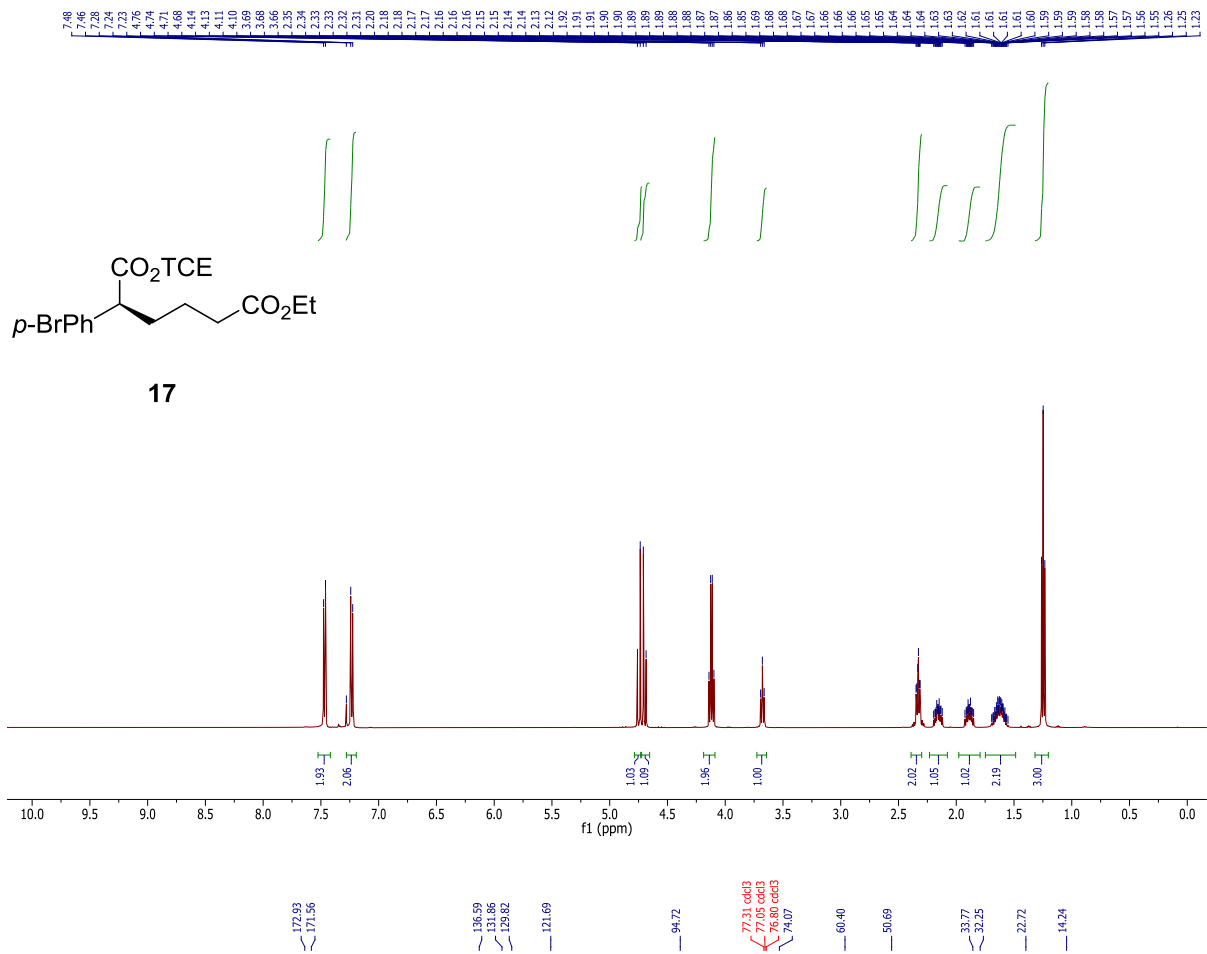


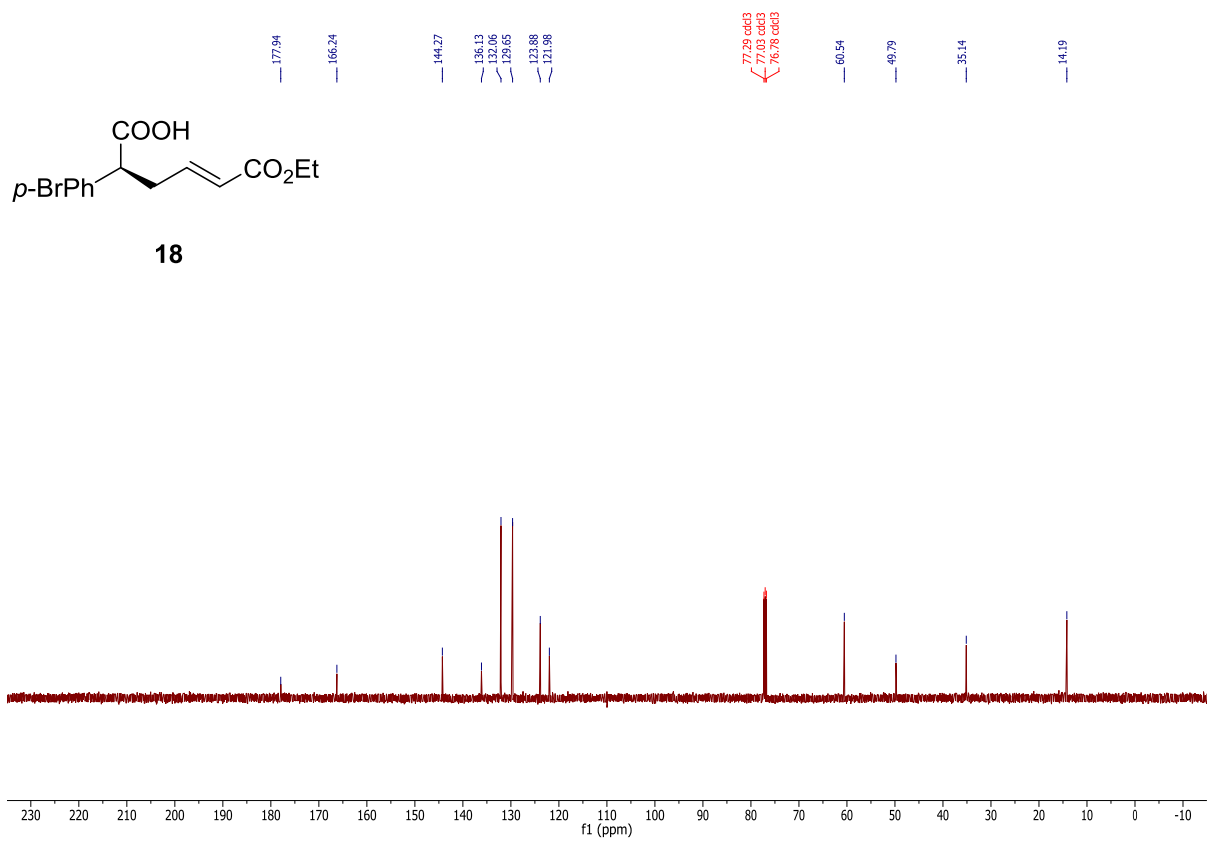
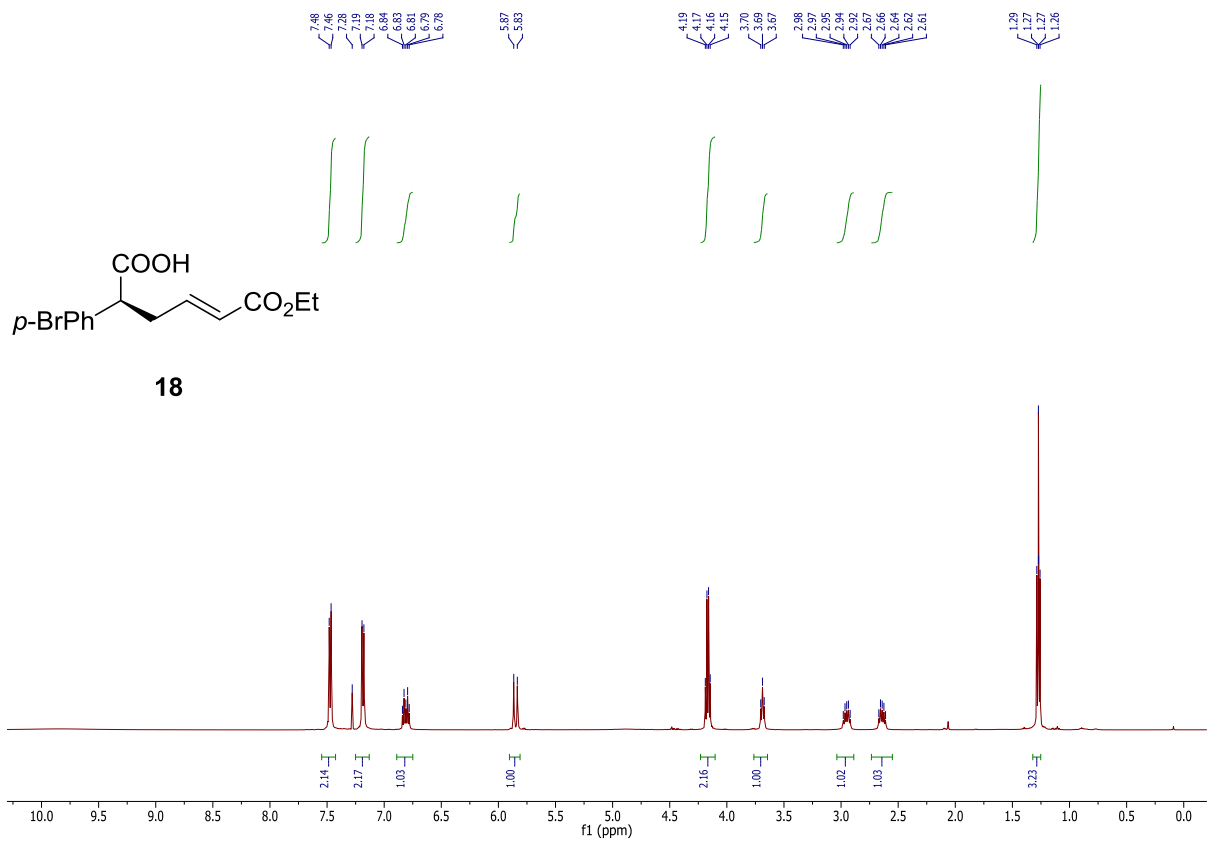


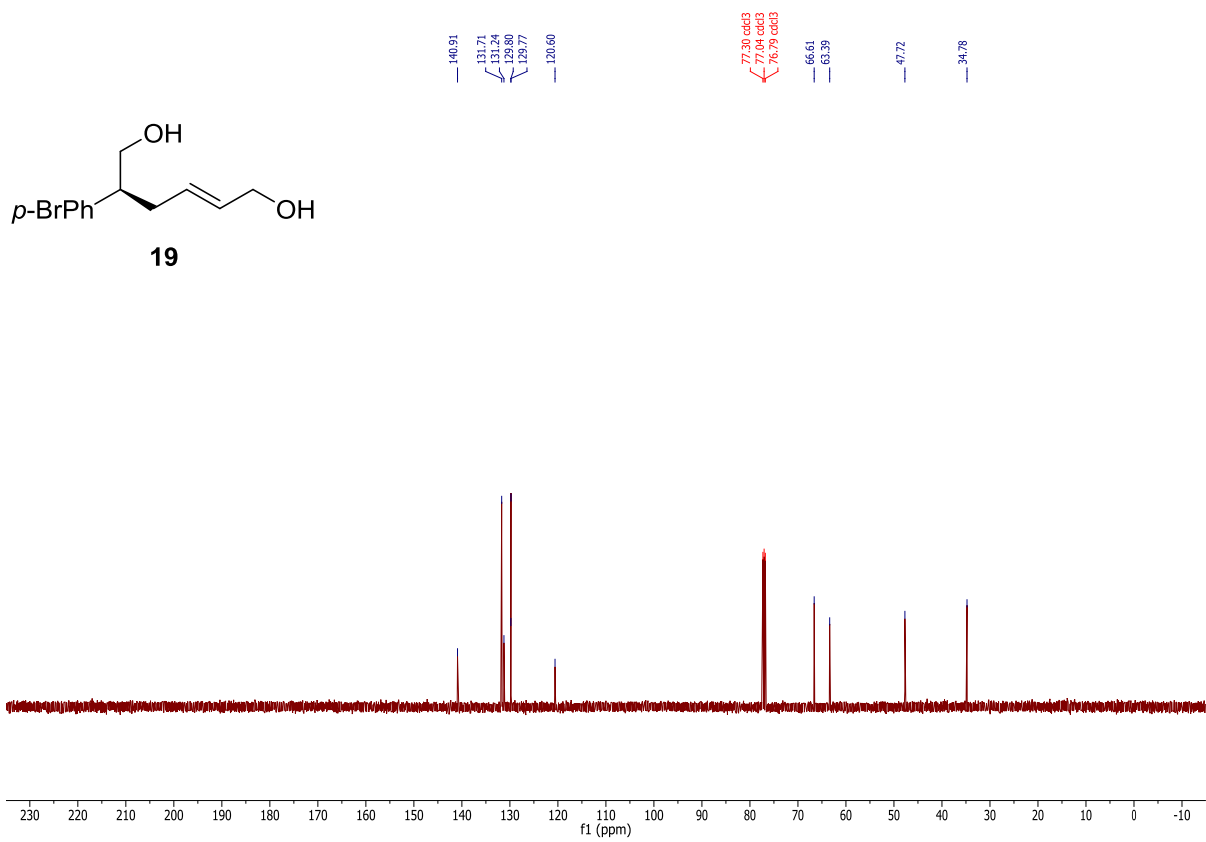
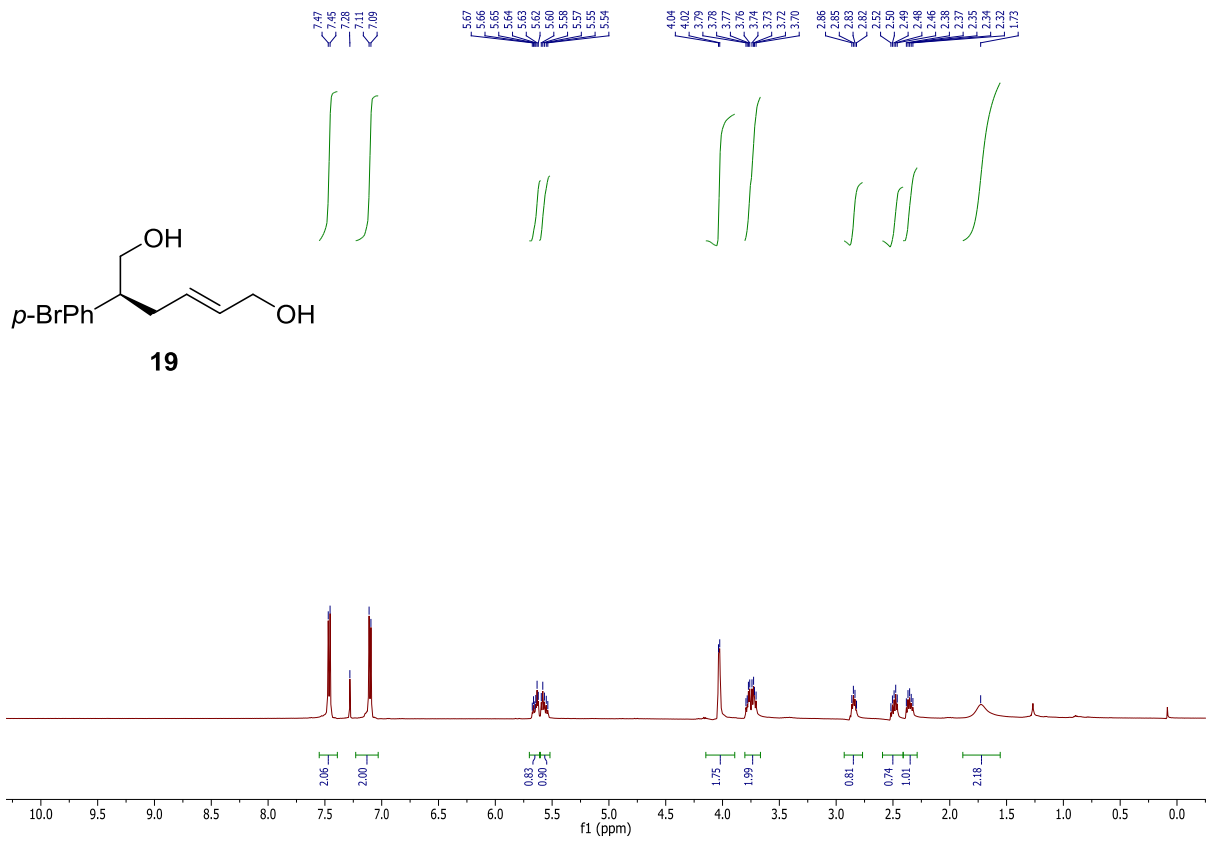


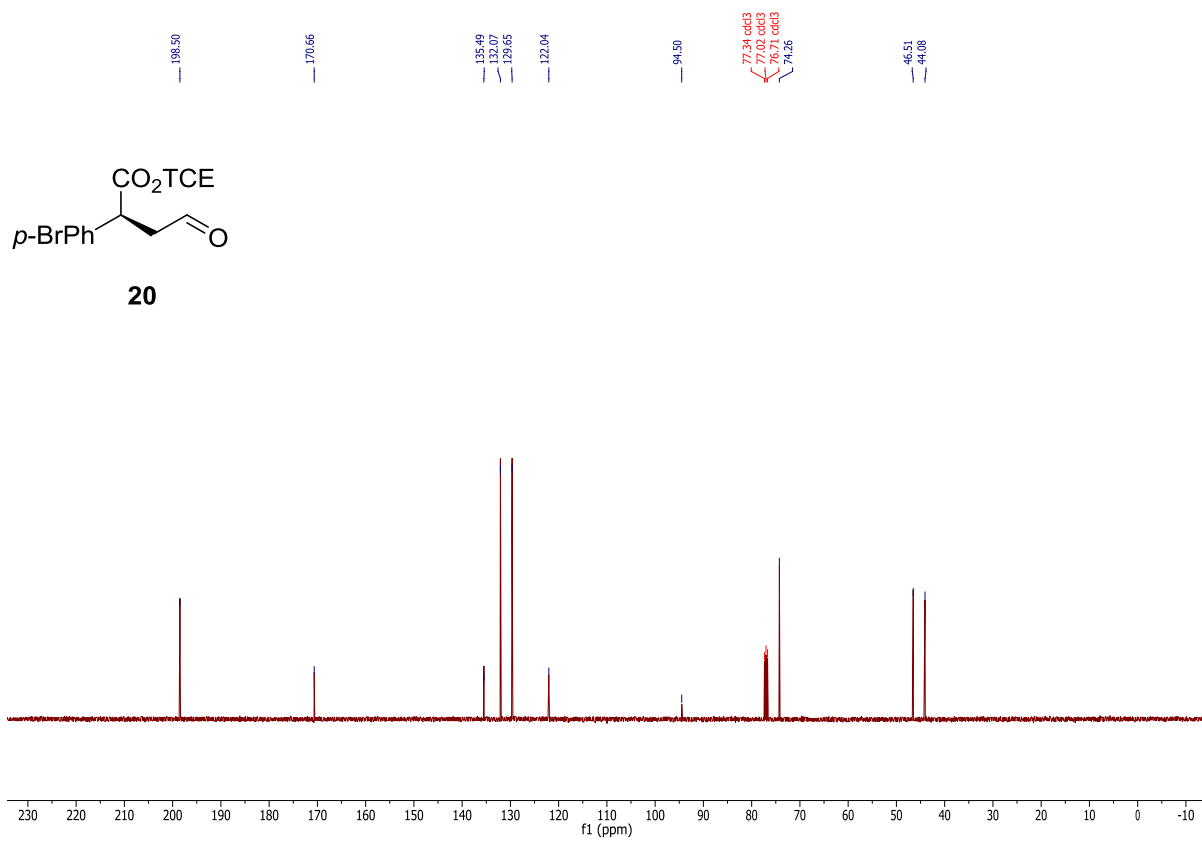
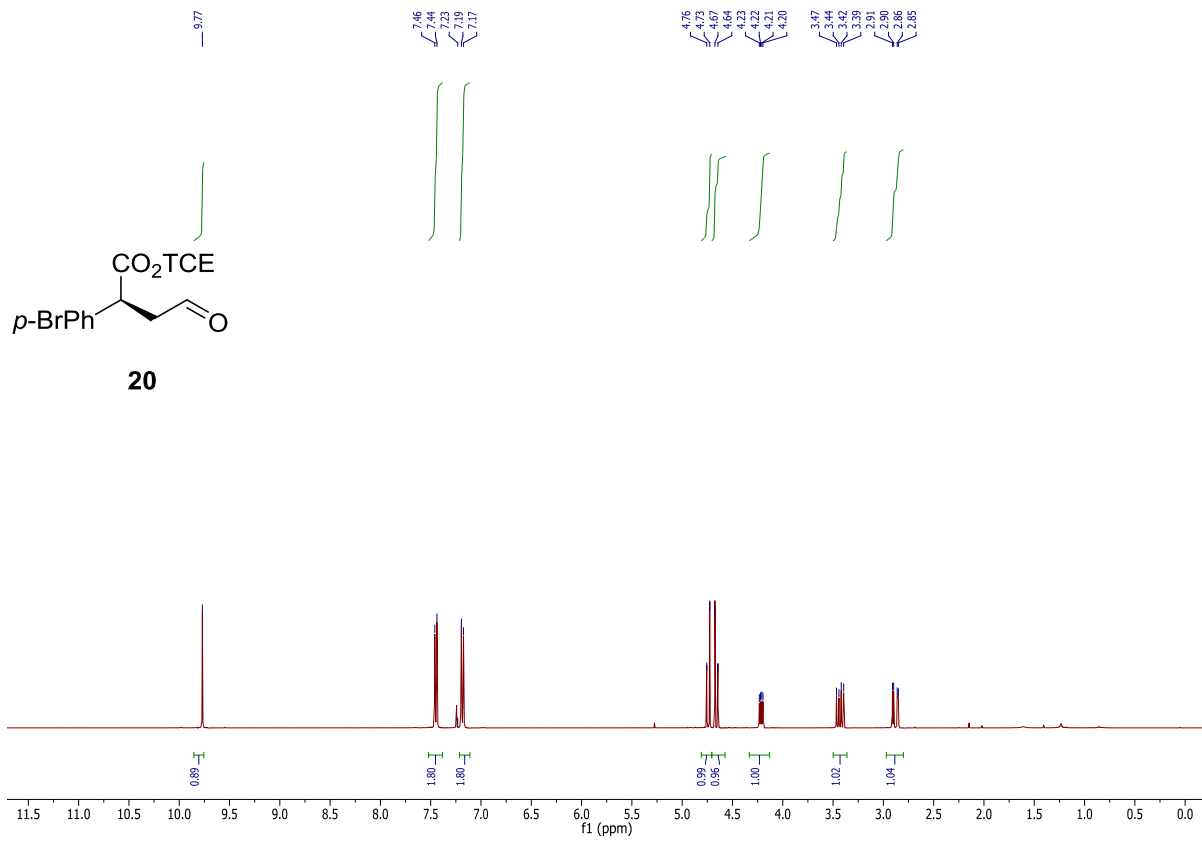


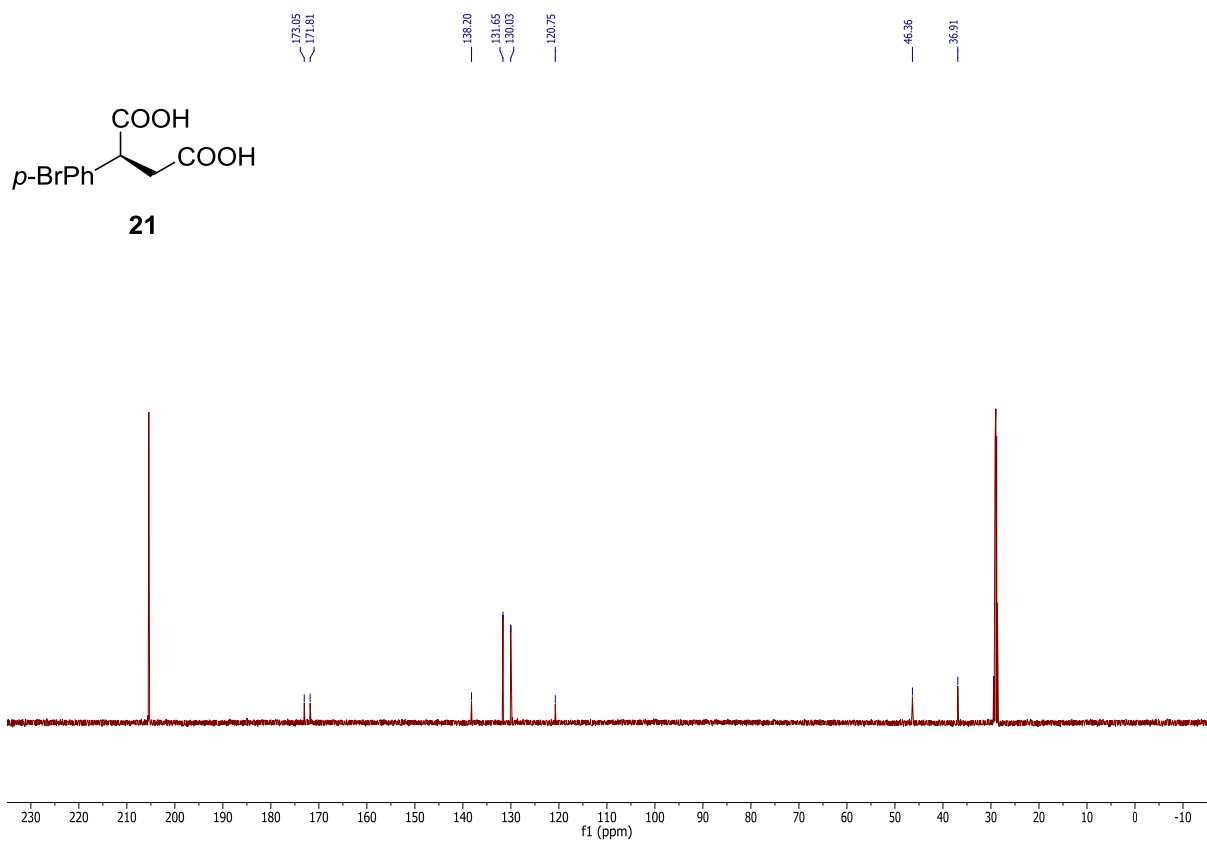
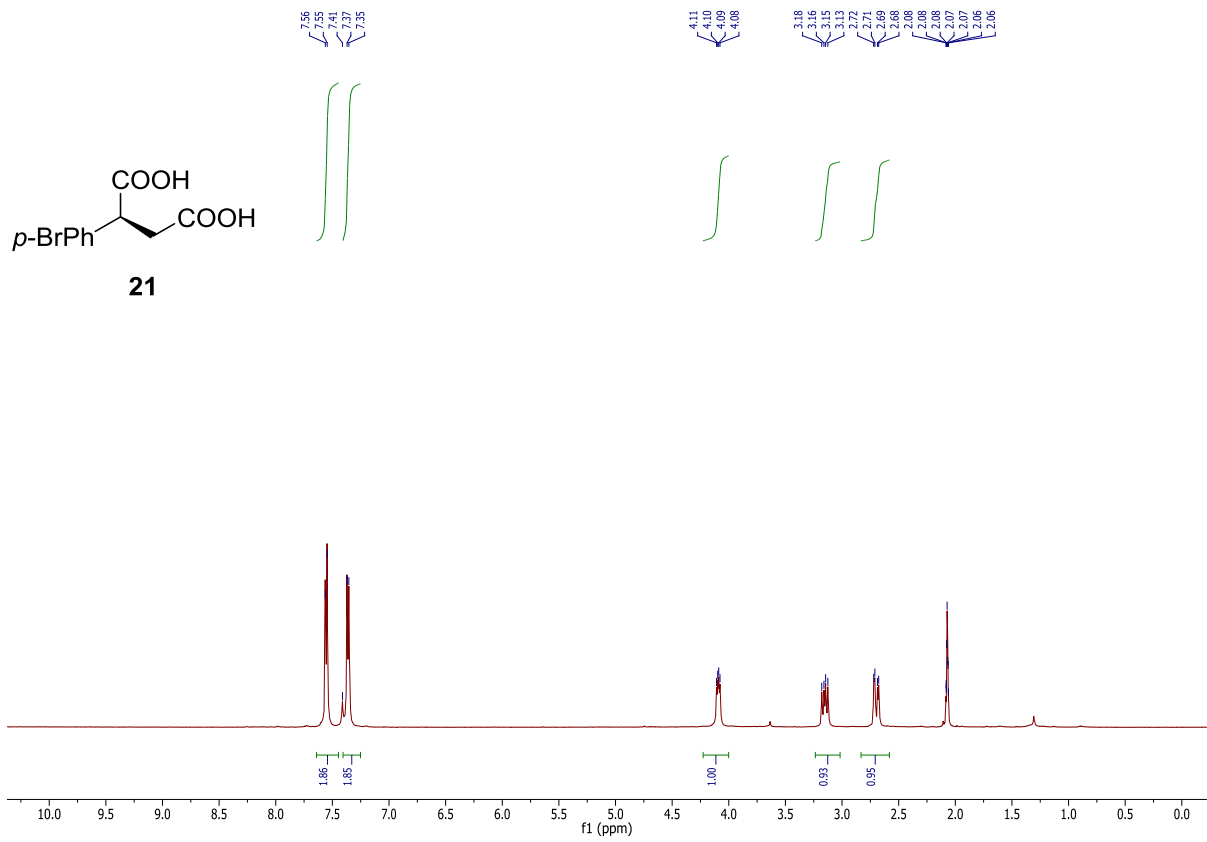




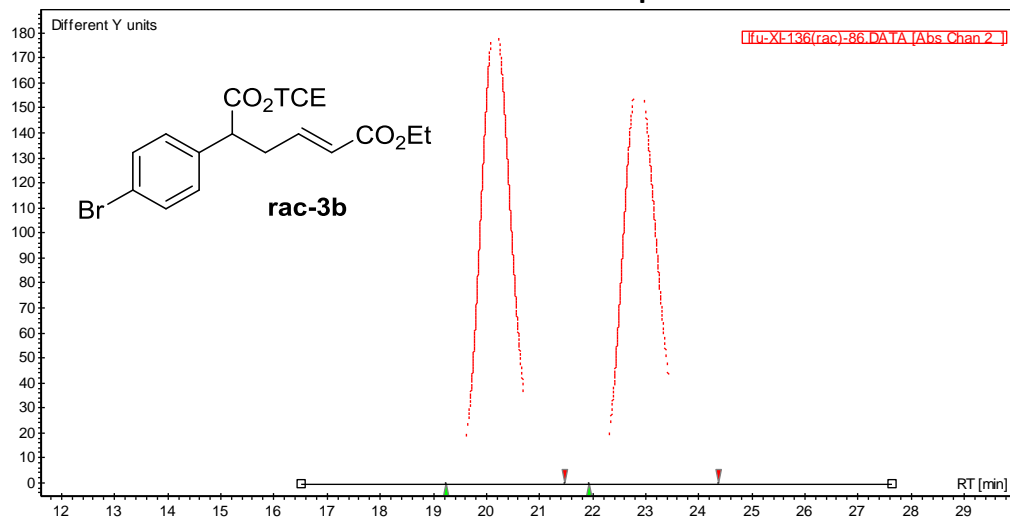




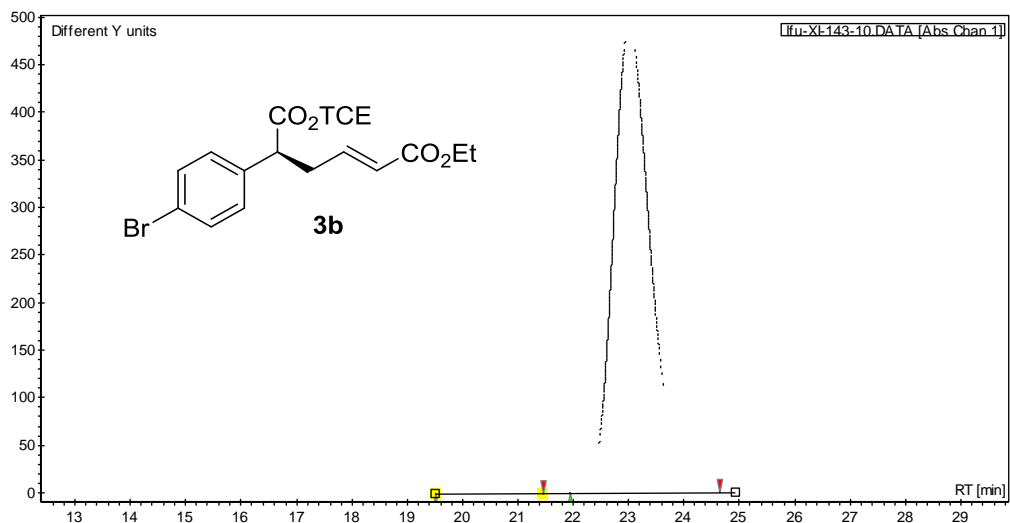




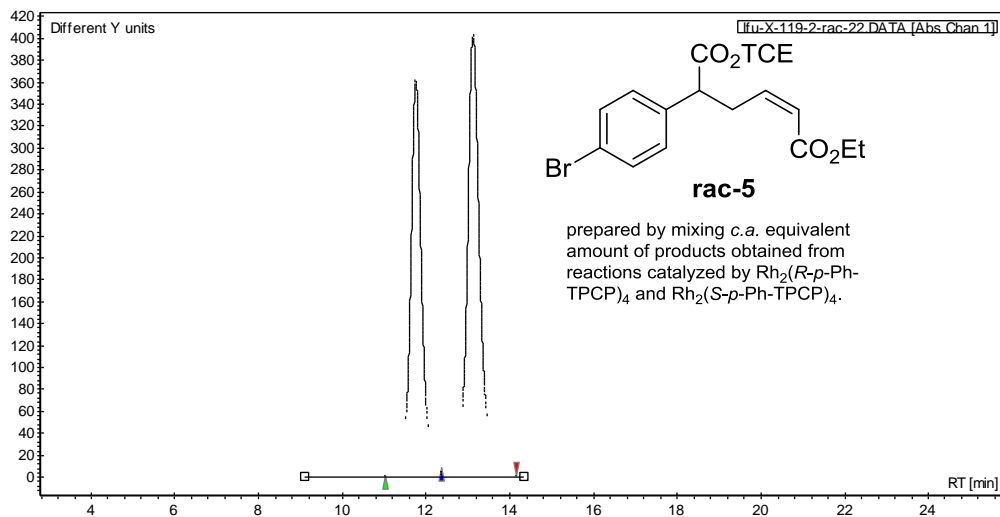
HPLC traces of products



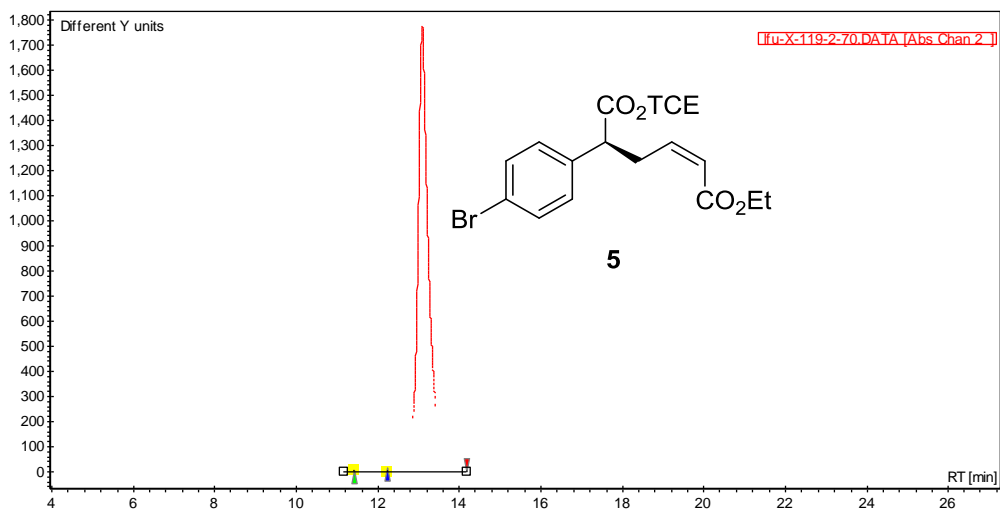
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	20.16	50.04	185.3	128.1	50.041
2	UNKNOWN	22.86	49.96	163.8	127.9	49.959
Total		100.00	349.1	255.9	100.000	



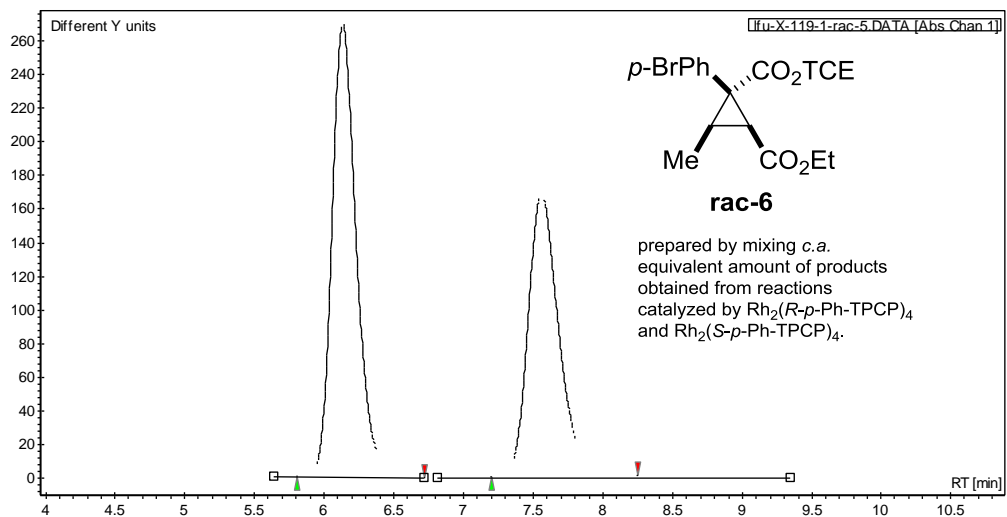
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	20.38	2.38	12.6	9.3	2.376
2	UNKNOWN	23.02	97.62	493.9	382.2	97.624
Total		100.00	506.6	391.5	100.000	



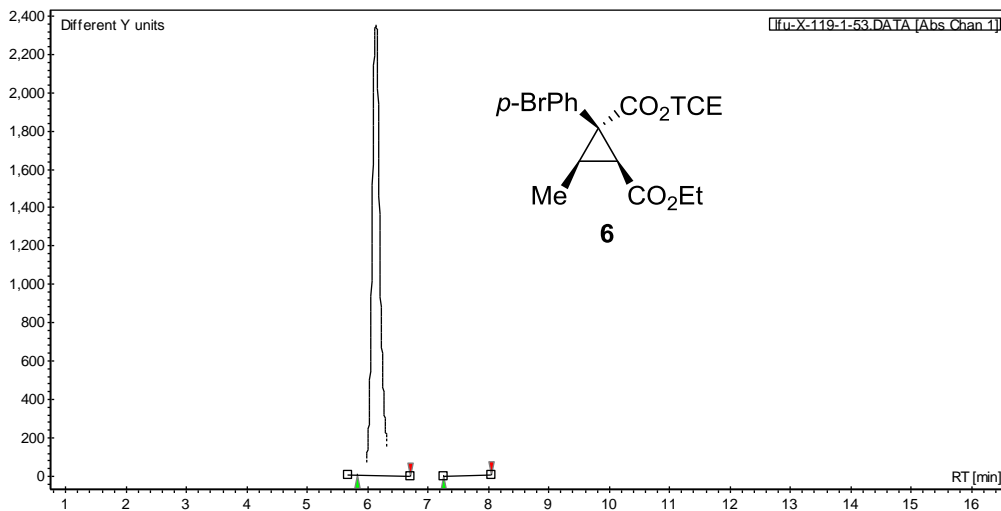
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.75	44.20	365.2	115.8	44.196
2	UNKNOWN	13.12	55.80	407.0	146.2	55.804
Total		100.00	772.2	262.0	100.000	



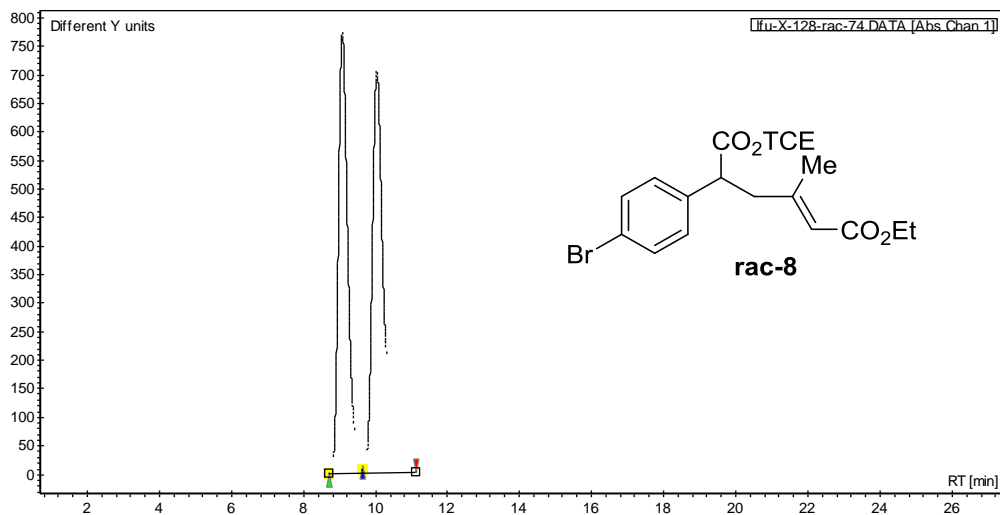
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.84	1.72	33.4	10.0	1.724
2	UNKNOWN	13.08	98.28	1781.4	570.7	98.276
Total		100.00	1814.8	580.7	100.000	



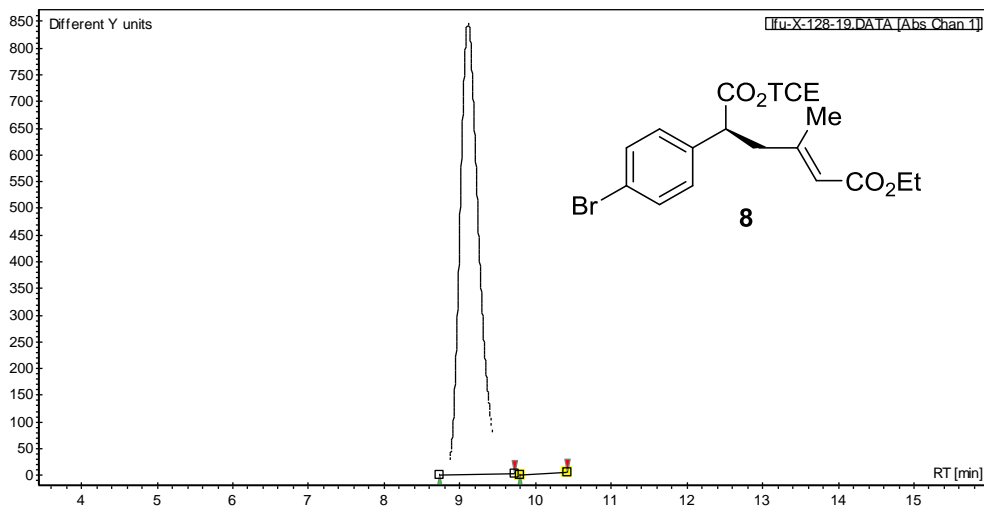
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	6.13	55.30	270.2	54.7	55.295
2	UNKNOWN	7.56	44.70	168.8	44.2	44.705
Total		100.00	439.0	98.9	100.000	



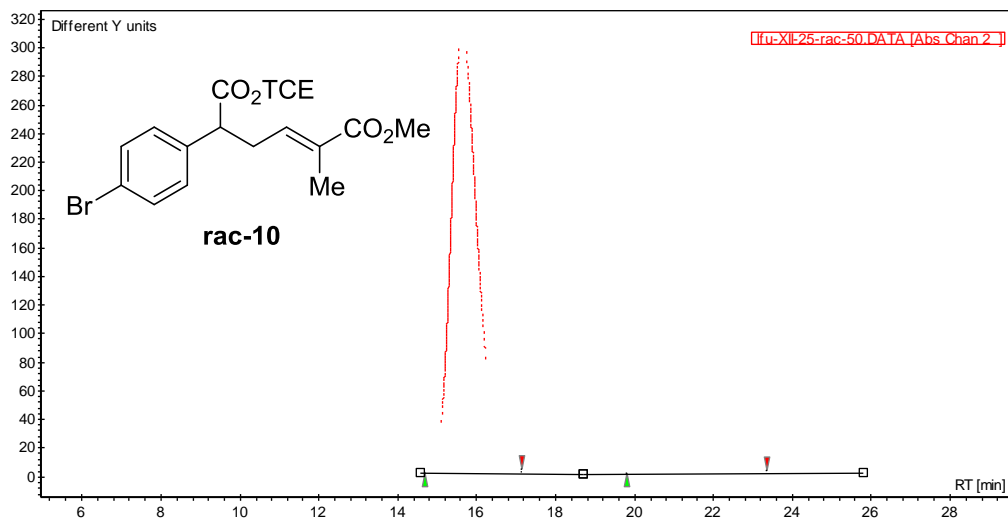
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	6.14	96.43	2354.5	368.8	96.429
2	UNKNOWN	7.57	3.57	49.3	13.7	3.571
Total		100.00	2403.8	382.5	100.000	



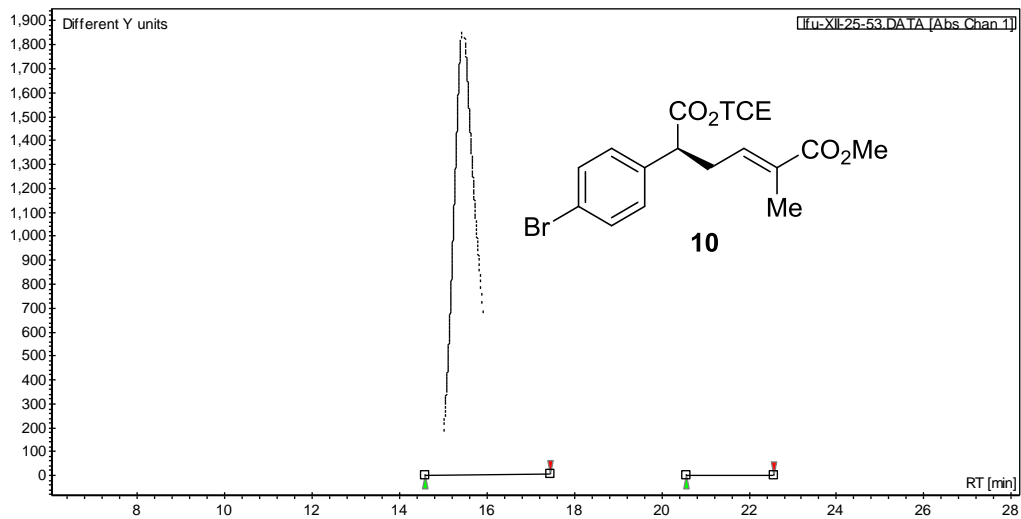
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	9.08	44.99	778.1	232.8	44.988
2	UNKNOWN	10.04	55.01	709.4	284.7	55.012
Total		100.00	1487.4	517.6	100.000	



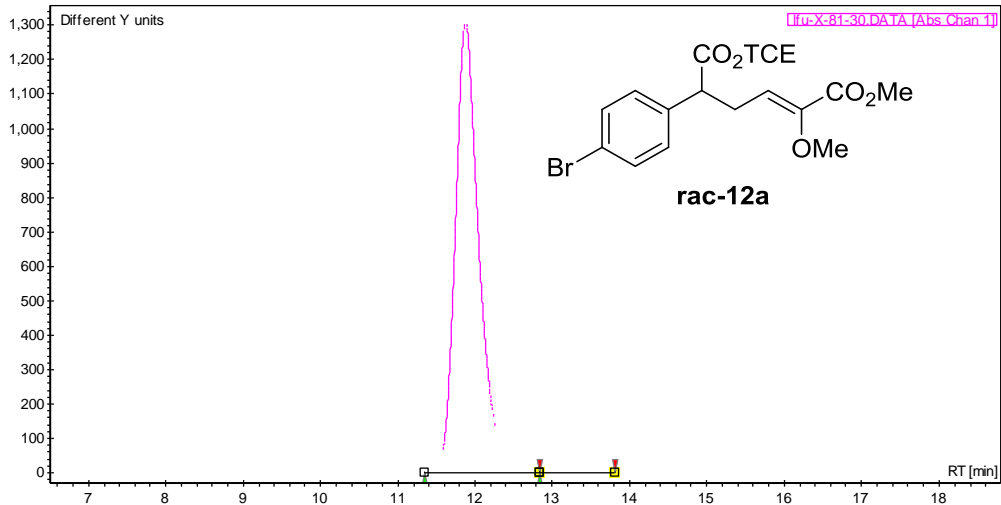
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	9.11	98.35	850.2	246.8	98.345
1	UNKNOWN	10.12	1.65	15.2	4.2	1.655
Total		100.00	865.4	251.0	100.000	



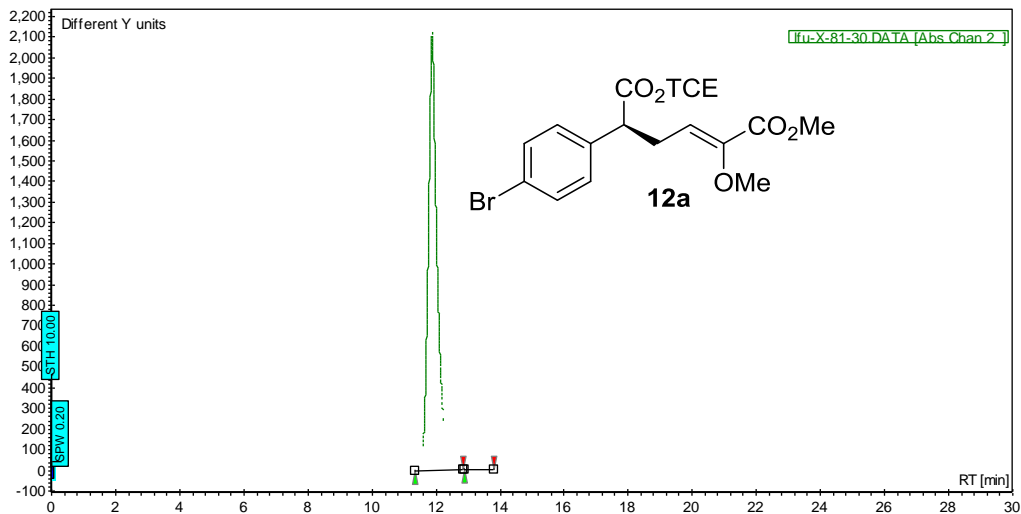
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15.64	49.84	310.4	244.1	49.836
2	UNKNOWN	21.25	50.16	196.0	245.8	50.164
Total		100.00	506.4	489.9	100.000	



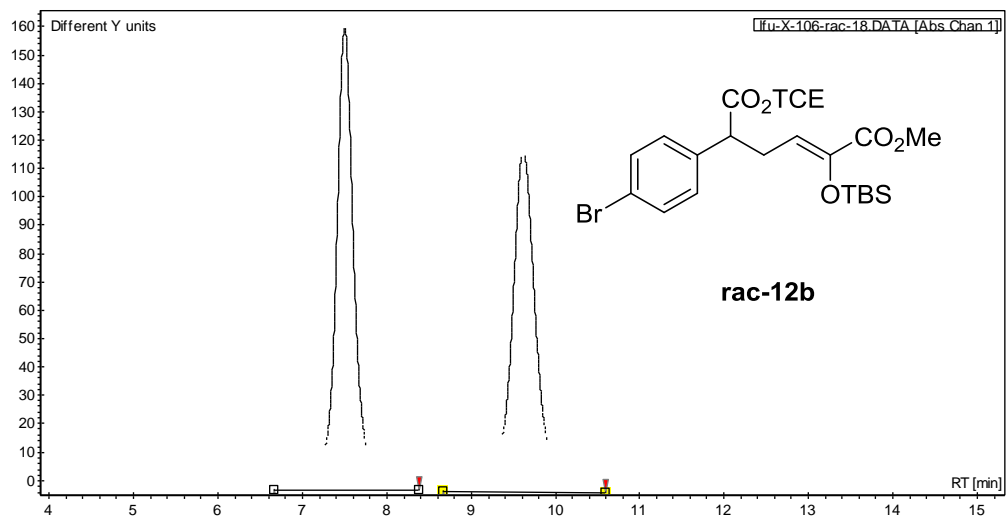
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15.44	99.09	1885.6	1263.8	99.091
2	UNKNOWN	21.49	0.91	11.0	11.6	0.909
Total		100.00	1896.6	1275.4	100.000	



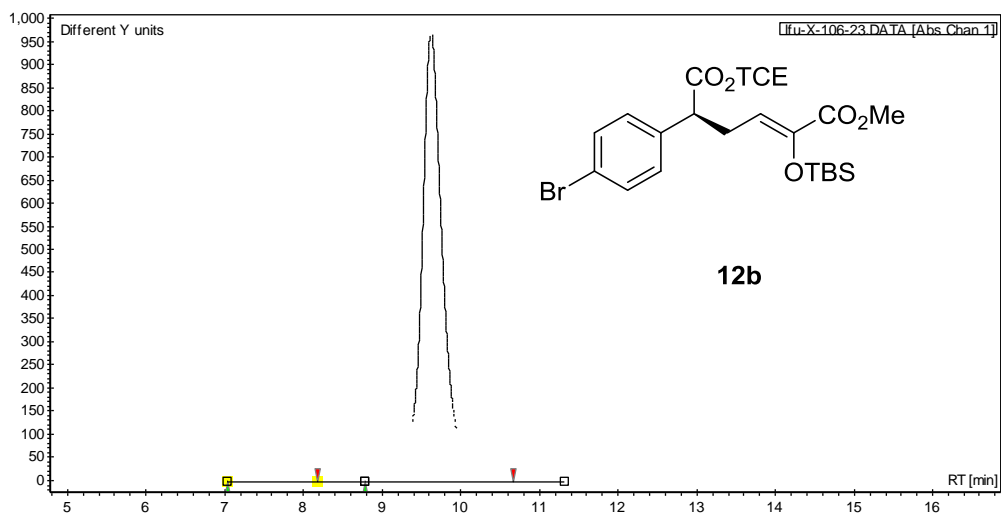
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.88	99.11	1312.3	459.4	99.107
2	UNKNOWN	13.34	0.89	10.0	4.1	0.893
Total		100.00	1322.2	463.6	100.000	



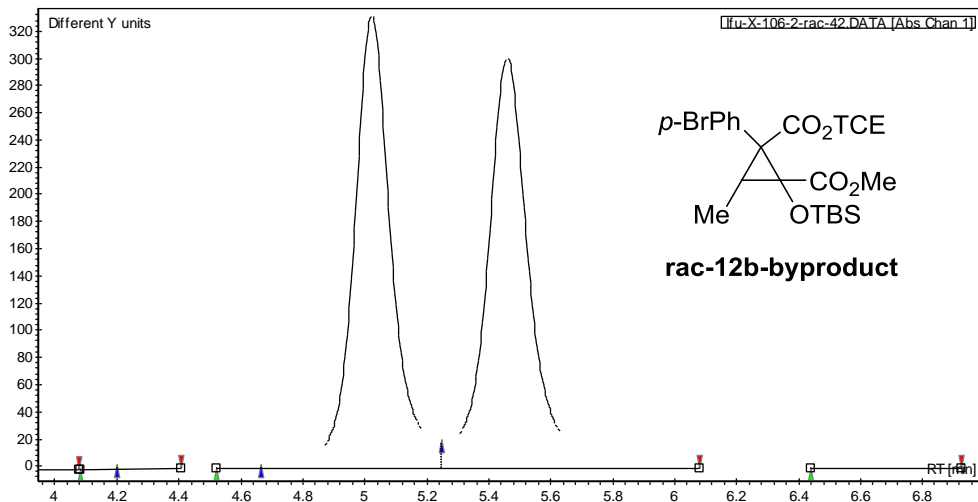
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.88	99.15	2124.9	672.4	99.154
2	UNKNOWN	13.35	0.85	14.1	5.7	0.846
Total		100.00	2139.1	678.1	100.000	



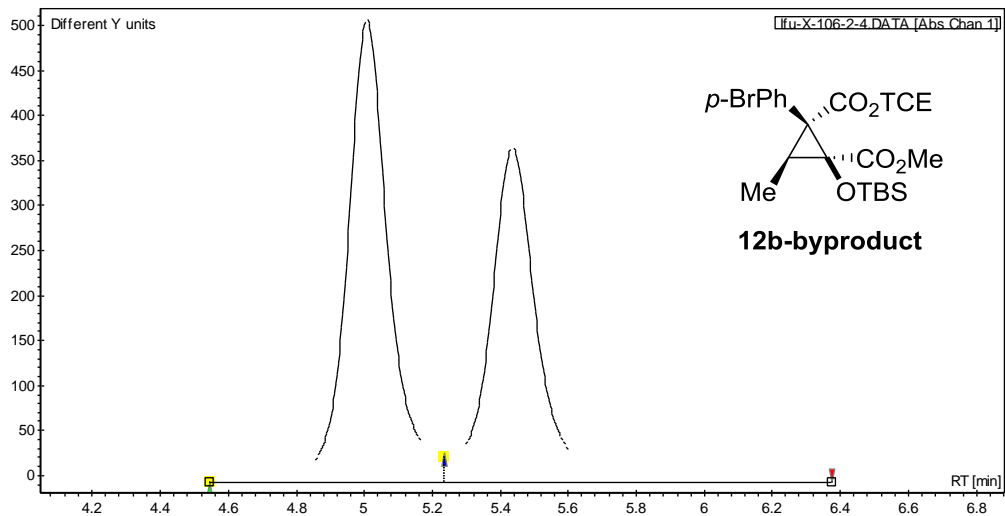
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	7.50	50.21	163.6	40.9	50.207
1	UNKNOWN	9.62	49.79	120.6	40.6	49.793
Total		100.00	284.2	81.5	100.000	



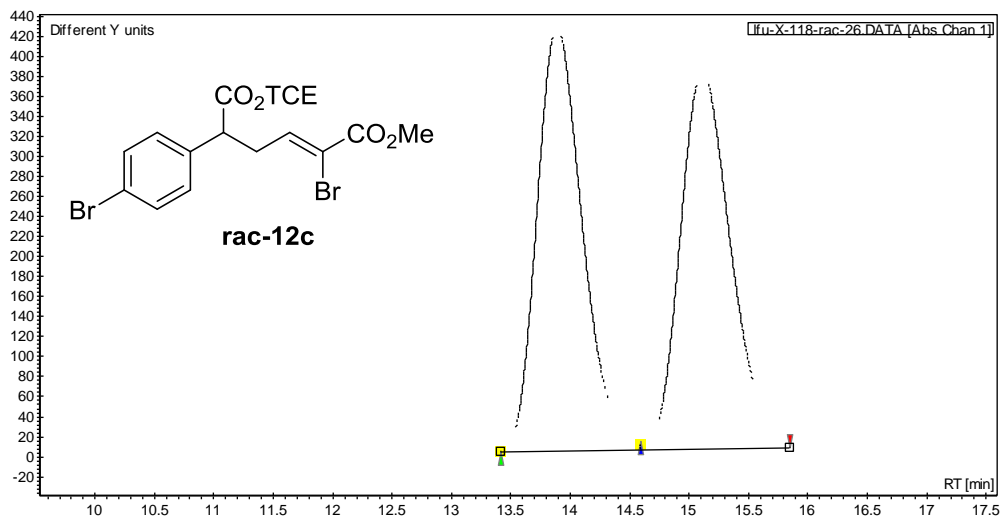
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.55	3.50	45.8	11.4	3.504
2	UNKNOWN	9.62	96.50	980.4	314.5	96.496
Total		100.00	1026.2	326.0	100.000	



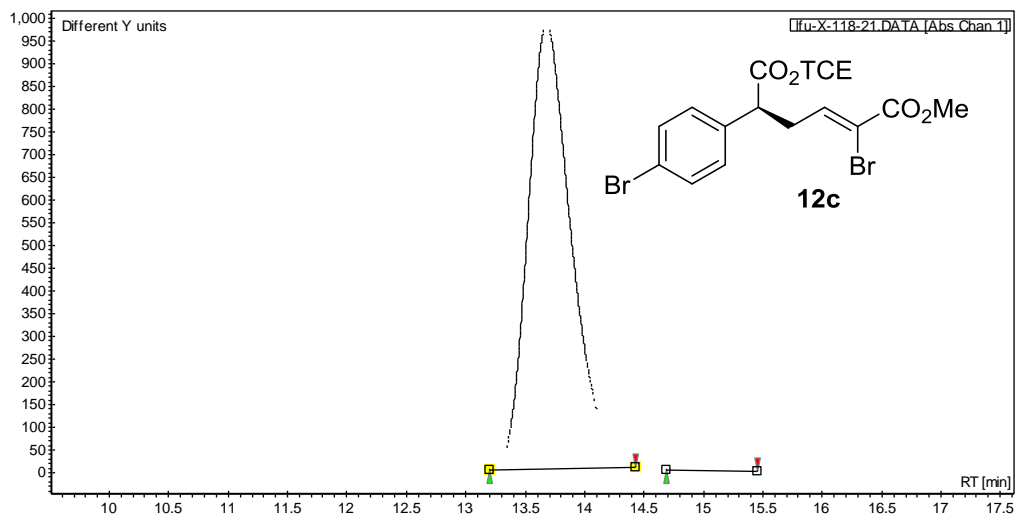
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	5.02	50.24	322.1	42.4	50.236
2	UNKNOWN	5.46	49.76	289.5	42.0	49.764
Total		100.00	611.7	84.4	100.000	



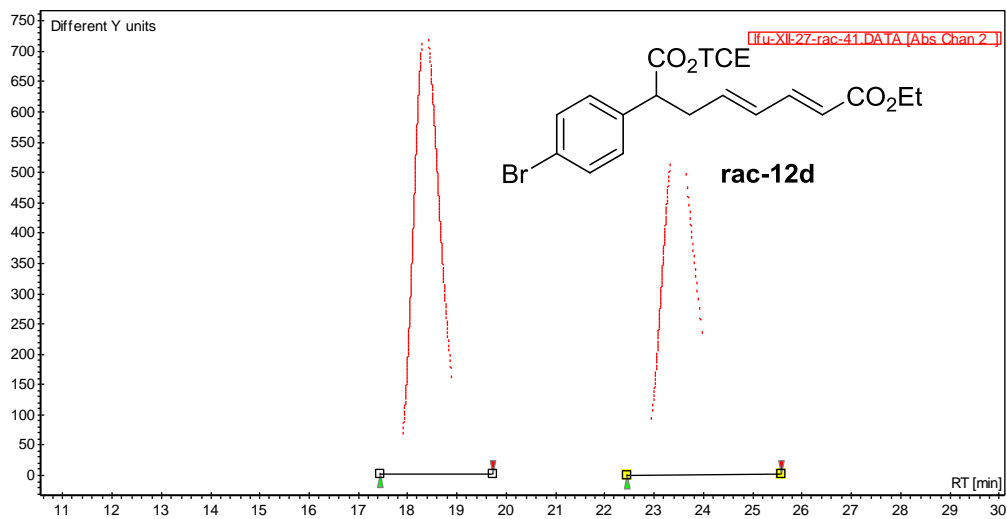
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	5.01	54.71	513.7	73.2	54.715
2	UNKNOWN	5.44	45.29	372.2	60.6	45.285
Total		100.00	885.8	133.9	100.000	



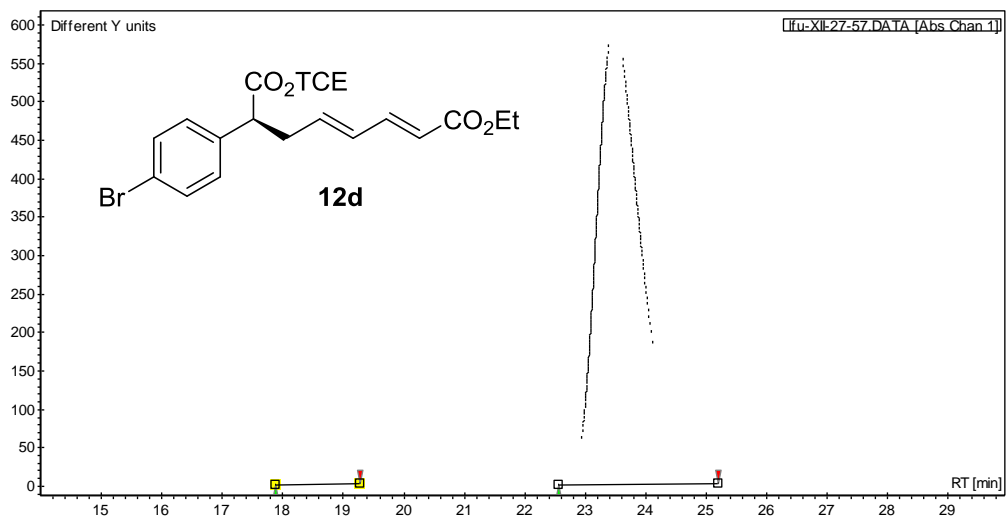
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.89	50.26	424.9	187.1	50.262
2	UNKNOWN	15.11	49.74	378.5	185.1	49.738
Total		100.00	803.5	372.2	100.000	



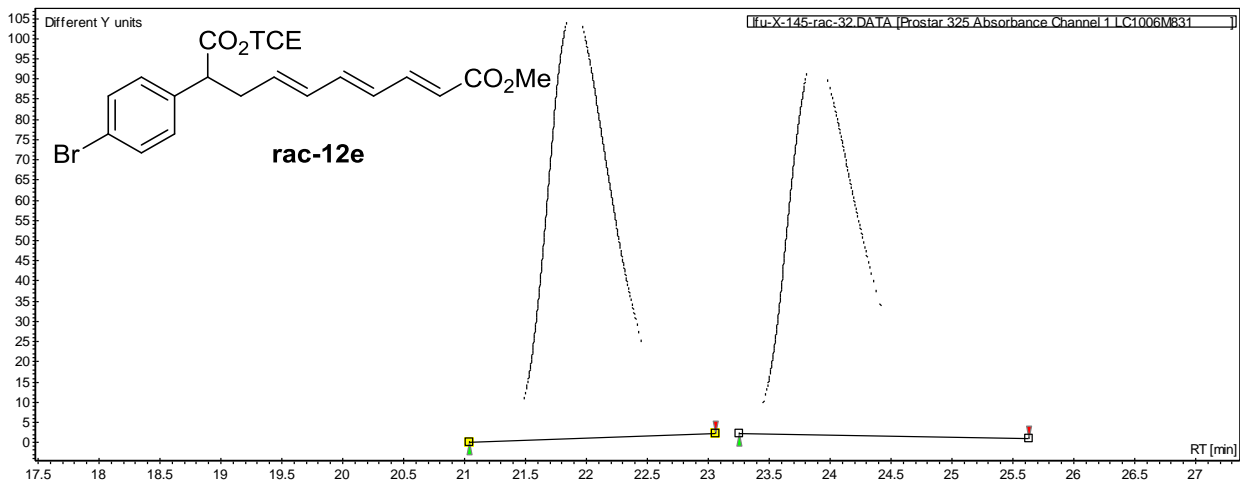
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.68	99.53	981.5	414.1	99.531
2	UNKNOWN	15.02	0.47	5.3	2.0	0.469
Total		100.00	986.8	416.0	100.000	



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	18.35	50.29	739.5	479.5	50.288
1	UNKNOWN	23.46	49.71	567.0	474.0	49.712
Total		100.00	1306.5	953.5	100.000	

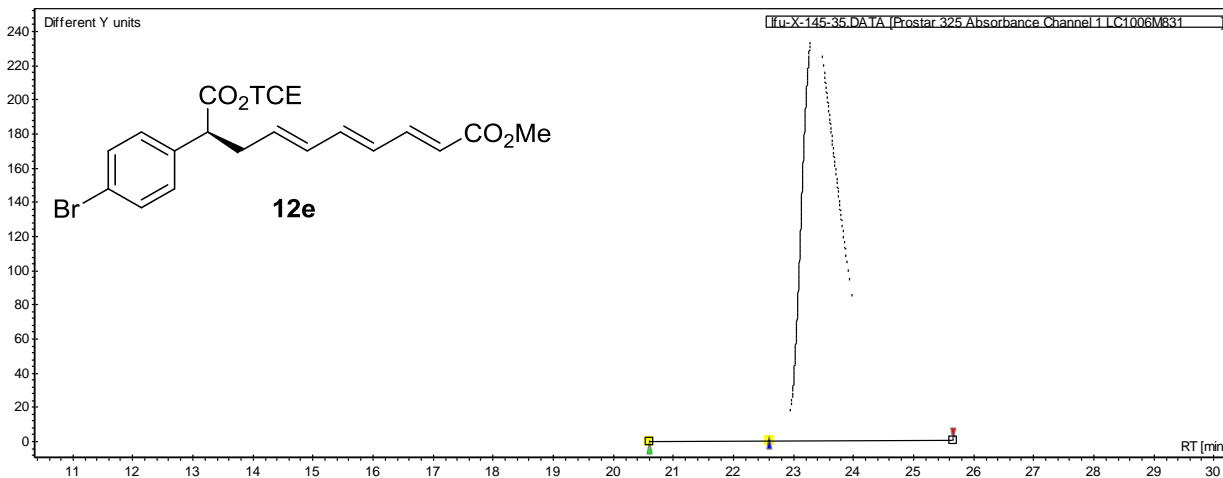


#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.58	2.35	19.5	12.1	2.348
2	UNKNOWN	23.48	97.65	599.2	504.2	97.652
Total		100.00	618.7	516.4	100.000	



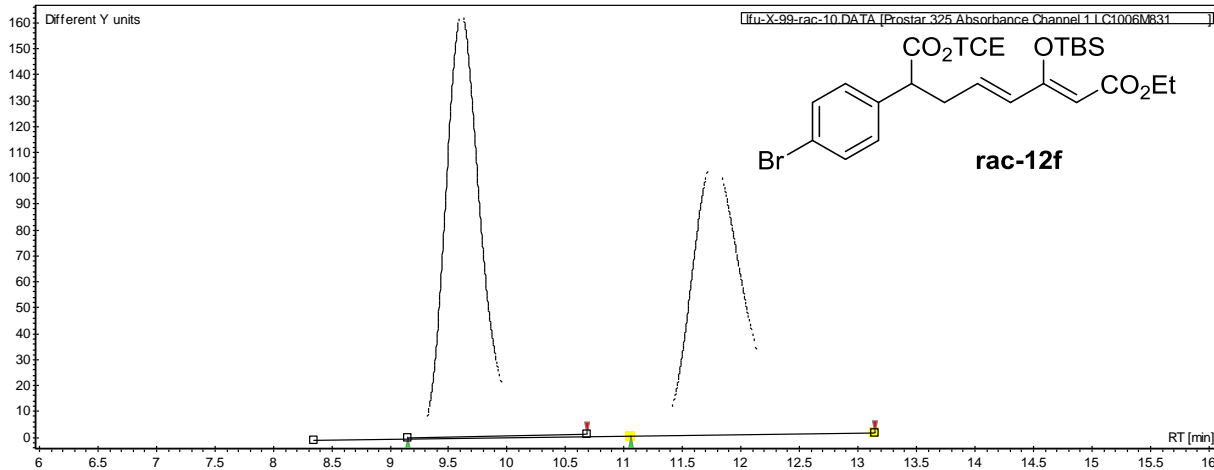
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	21.89	50.11	106.4	67.6	50.111
2	UNKNOWN	23.88	49.89	93.6	67.3	49.889

Total 100.00 200.0 134.8 100.000

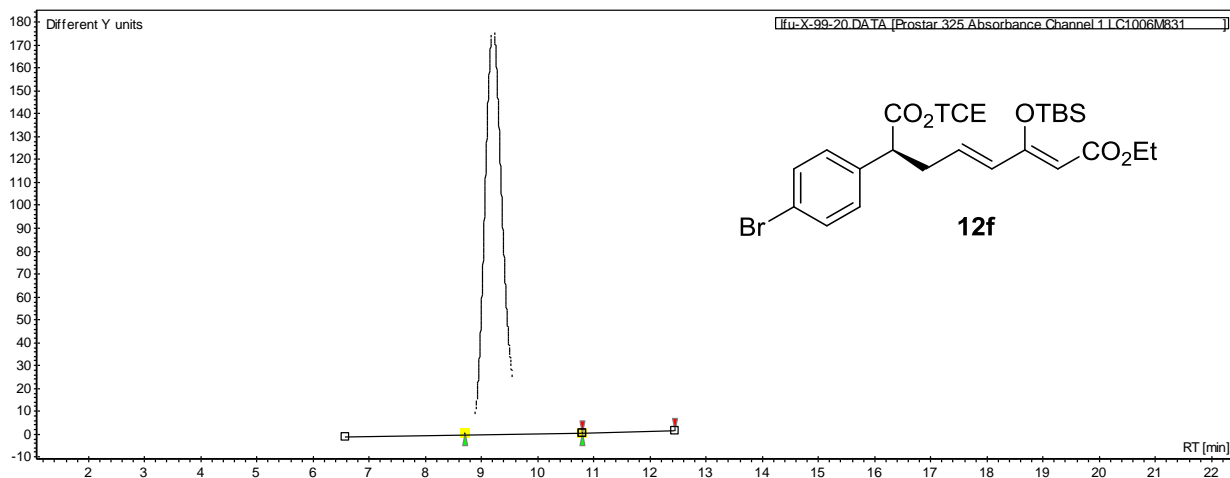


#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	21.54	4.15	12.9	8.3	4.155
2	UNKNOWN	23.35	95.85	243.0	191.2	95.845

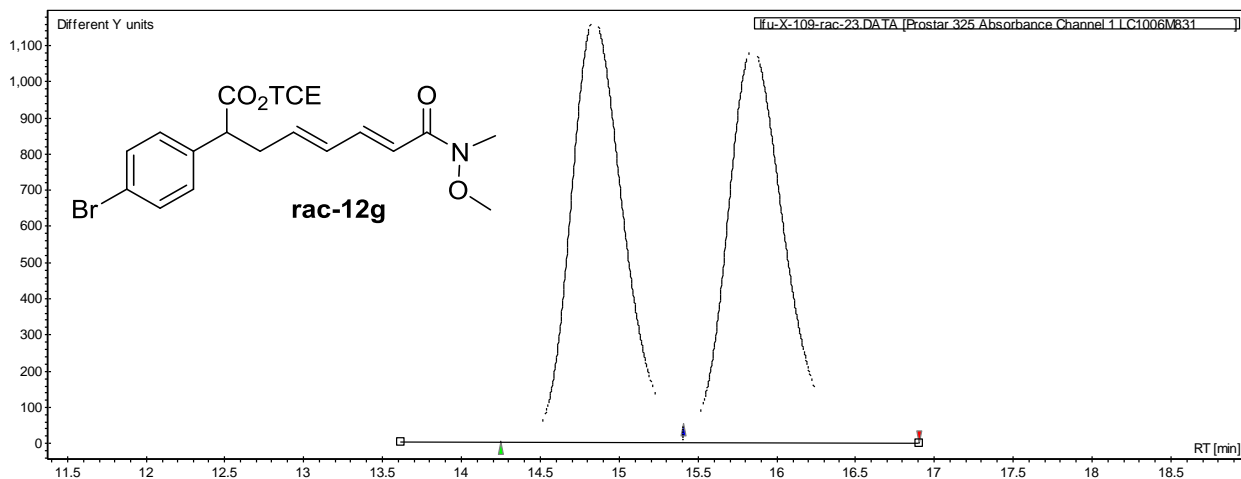
Total 100.00 255.8 199.5 100.000



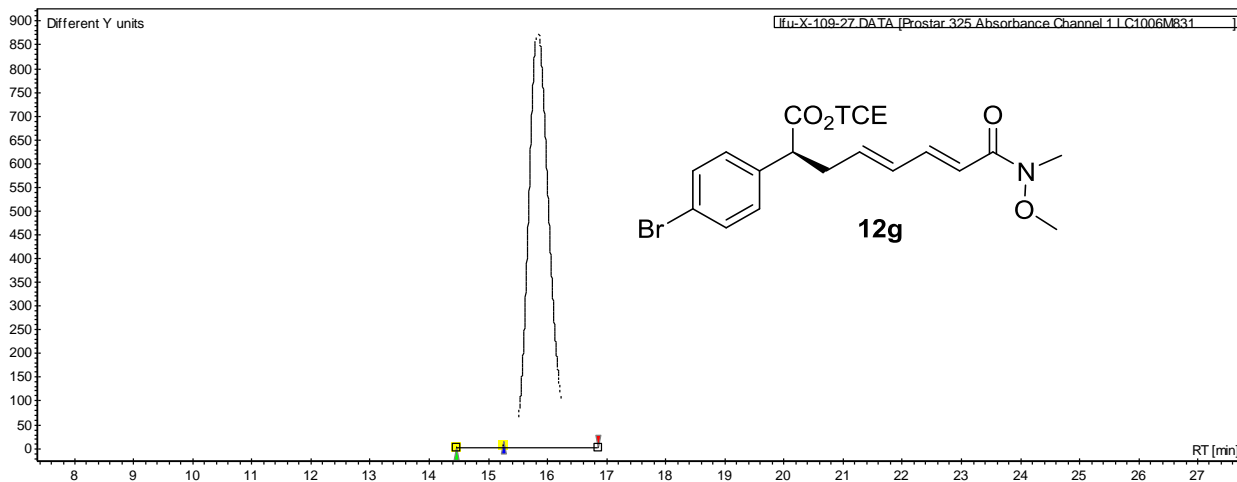
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	9.61	50.61	163.0	57.9	50.614
1	UNKNOWN	11.76	49.39	106.1	56.5	49.386
Total		100.00	269.1	114.3	100.000	



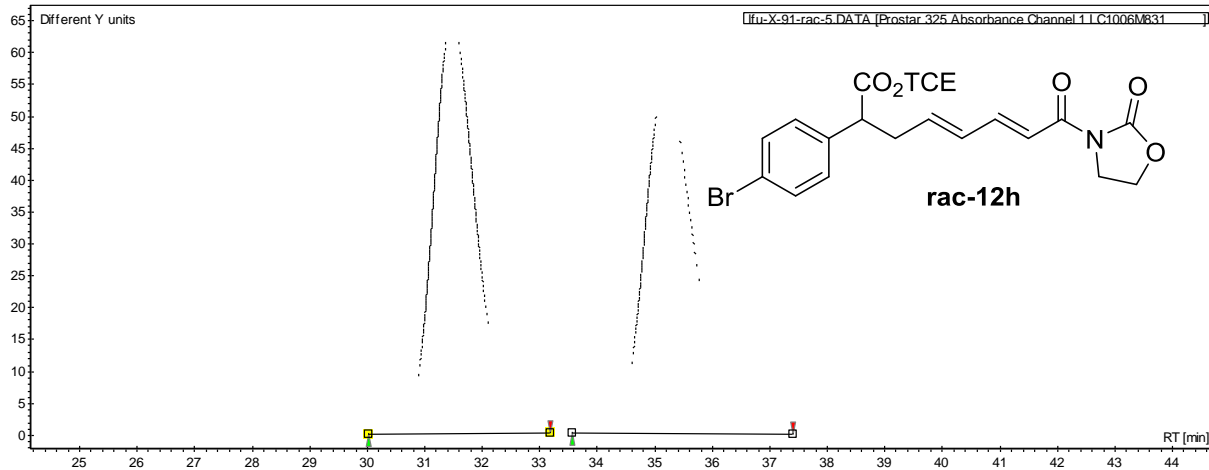
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	9.21	78.94	177.8	67.9	78.937
2	UNKNOWN	11.44	21.06	34.7	18.1	21.063
Total		100.00	212.5	86.0	100.000	



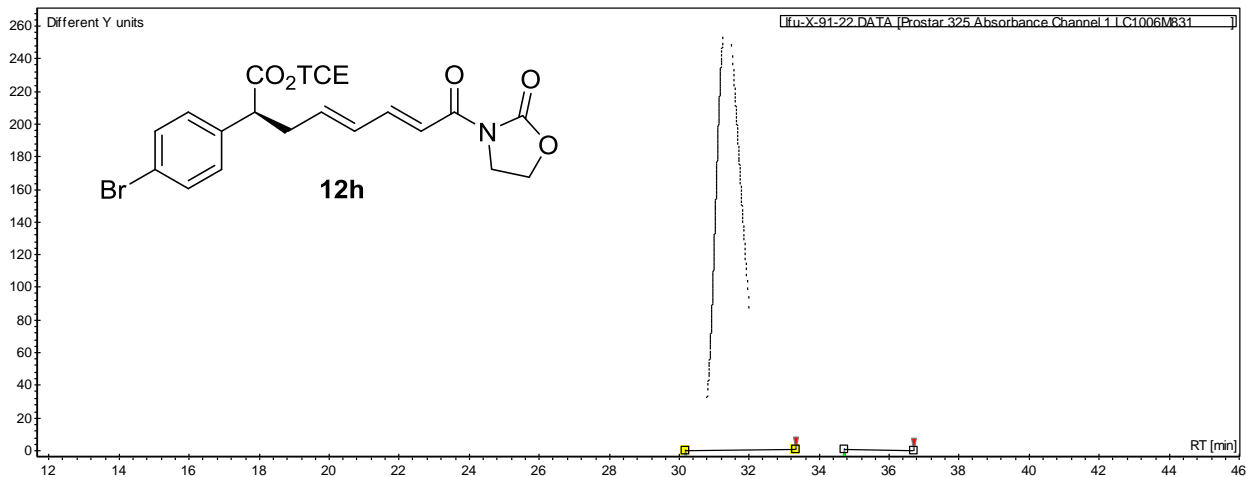
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	14.84	49.71	1170.9	456.4	49.712
2	UNKNOWN	15.85	50.29	1090.8	461.7	50.288
Total		100.00	2261.7	918.1	100.000	



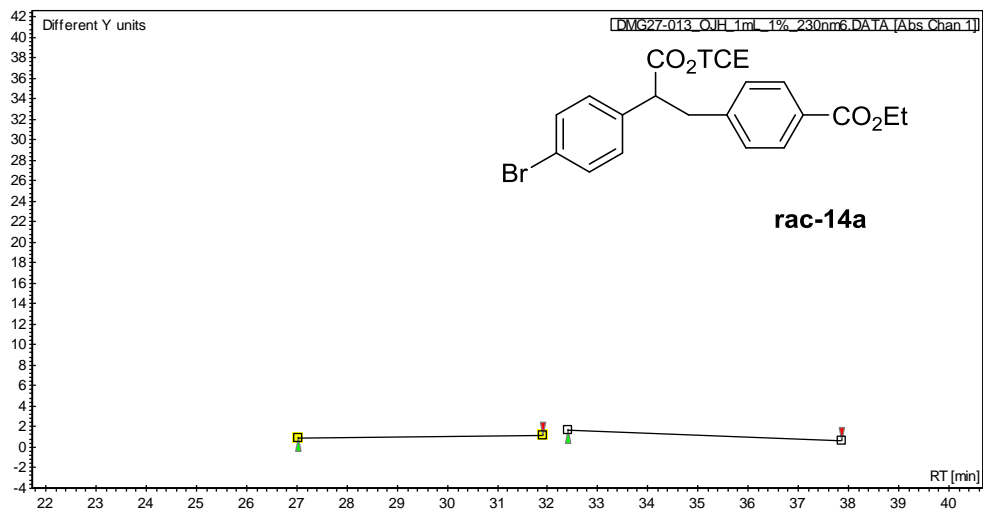
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	14.89	1.74	15.6	6.4	1.738
2	UNKNOWN	15.83	98.26	882.2	362.1	98.262
Total		100.00	897.8	368.5	100.000	



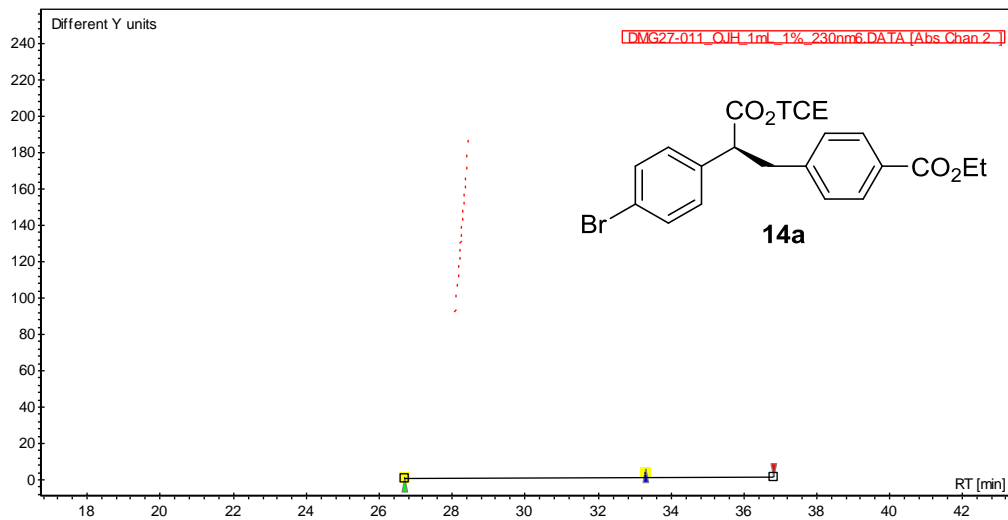
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	31.47	50.12	65.0	55.7	50.123
2	UNKNOWN	35.19	49.88	55.3	55.4	49.877
Total		100.00	120.3	111.1	100.000	



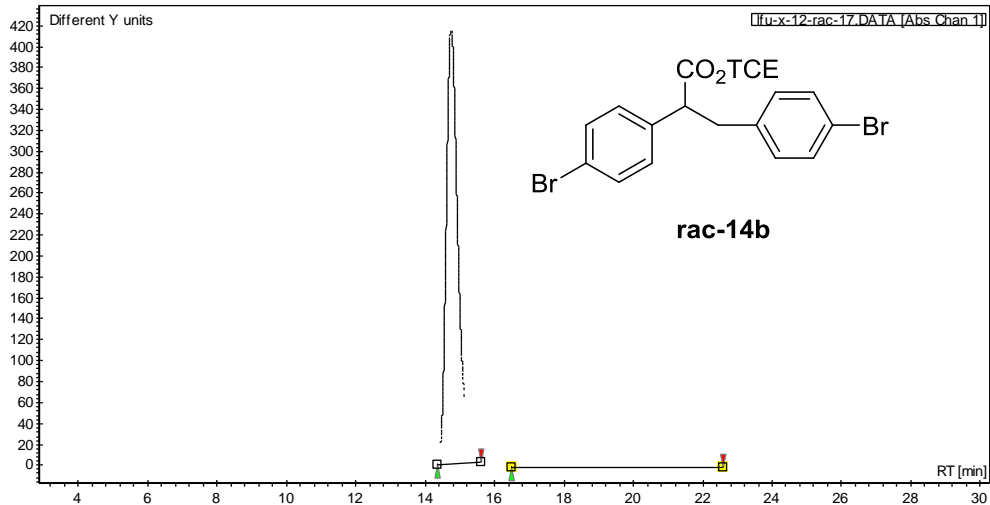
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	31.35	98.60	266.5	240.1	98.601
2	UNKNOWN	35.56	1.40	3.8	3.4	1.399
Total		100.00	270.3	243.5	100.000	



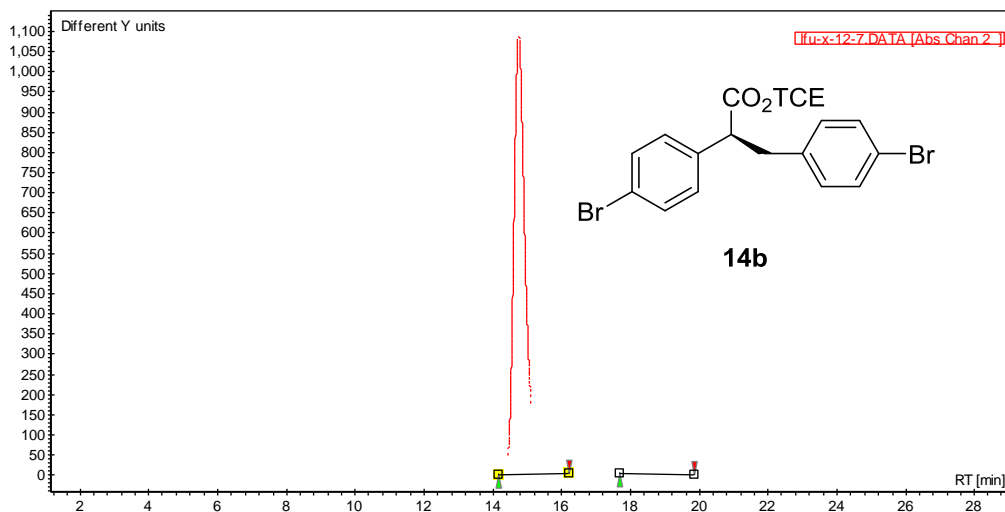
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	29.08	50.34	35.8	70.6	50.338
2	UNKNOWN	34.51	49.66	30.0	69.6	49.662
Total		100.00	65.9	140.2	100.000	



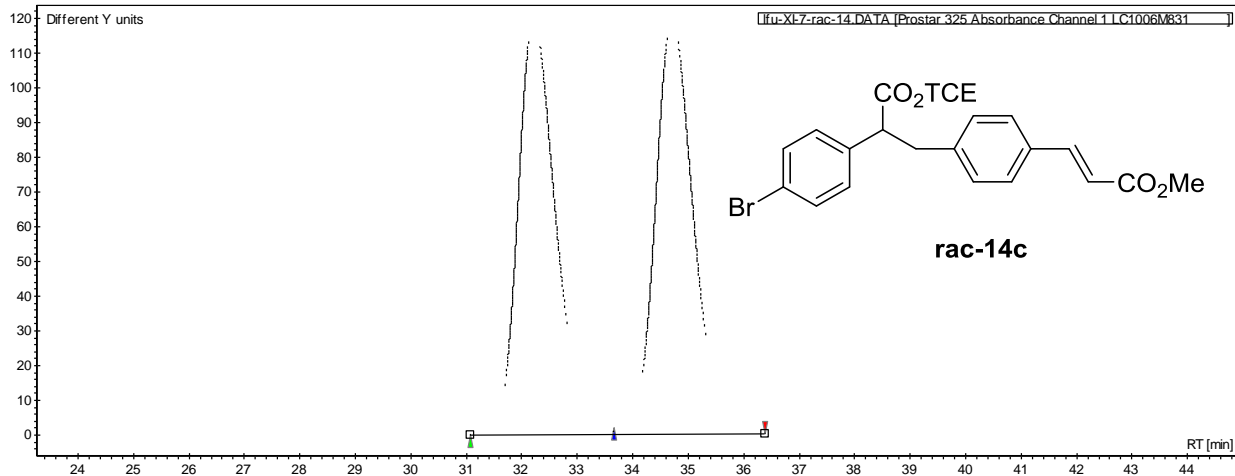
#	Time [Min]	Area % [%]
1	28.98	98.667
2	34.51	1.333
Total		100.000



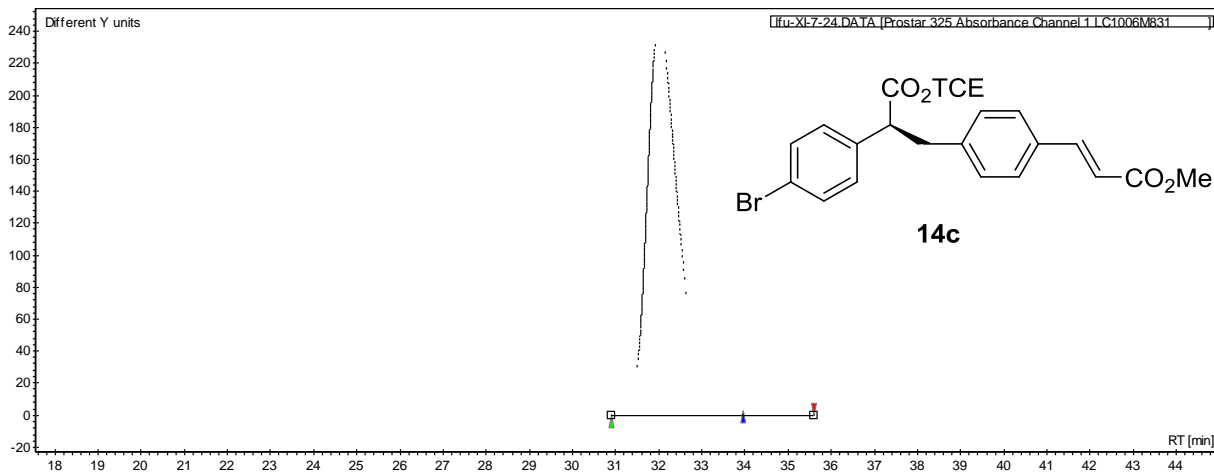
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	14.75	50.94	419.4	163.1	50.937
1	UNKNOWN	18.40	49.06	81.3	157.1	49.063
Total		100.00	500.7	320.2	100.000	



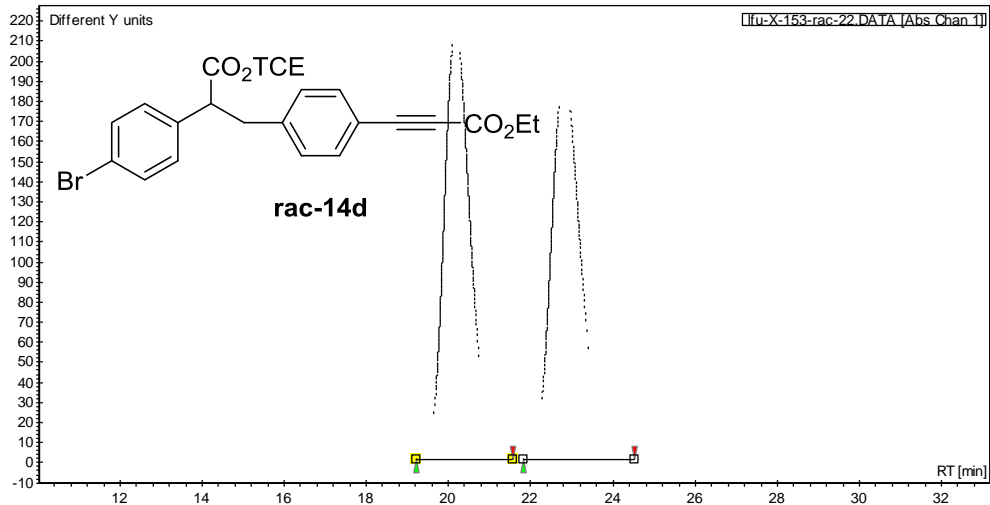
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	14.75	99.07	1095.5	425.0	99.070
2	UNKNOWN	18.39	0.93	3.2	4.0	0.930
Total		100.00	1098.7	429.0	100.000	



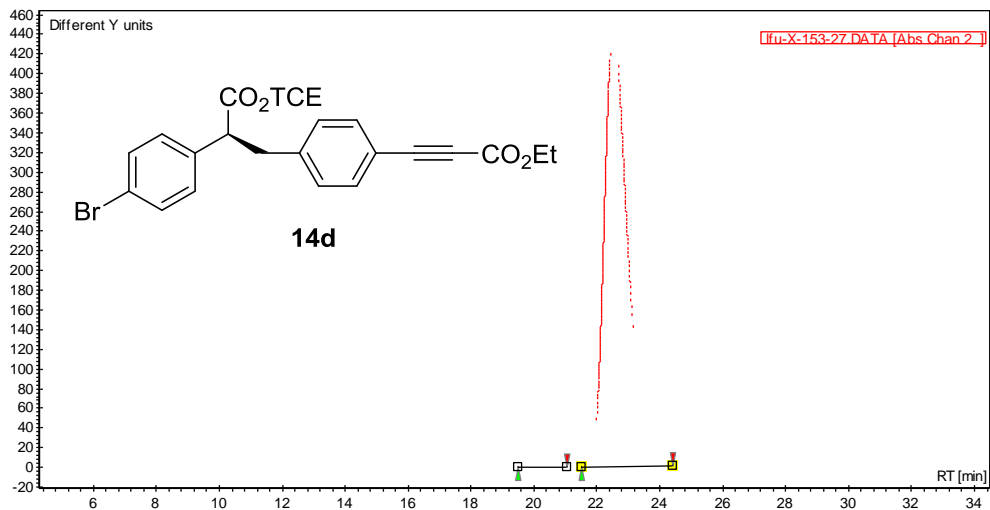
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	32.21	49.93	119.7	94.2	49.926
2	UNKNOWN	34.71	50.07	119.7	94.5	50.074
Total		100.00	239.4	188.6	100.000	



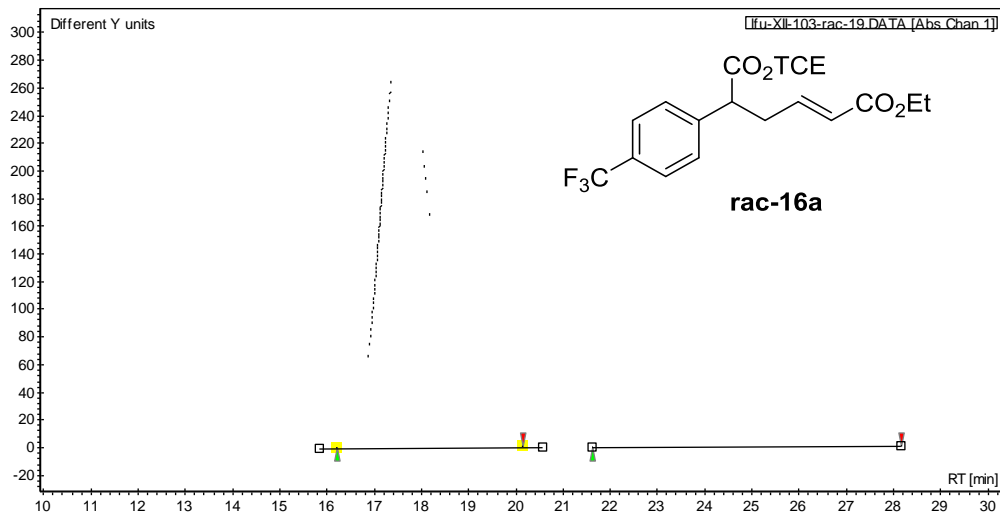
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	32.01	98.66	246.3	205.5	98.657
2	UNKNOWN	34.73	1.34	3.7	2.8	1.343
Total		100.00	250.0	208.3	100.000	



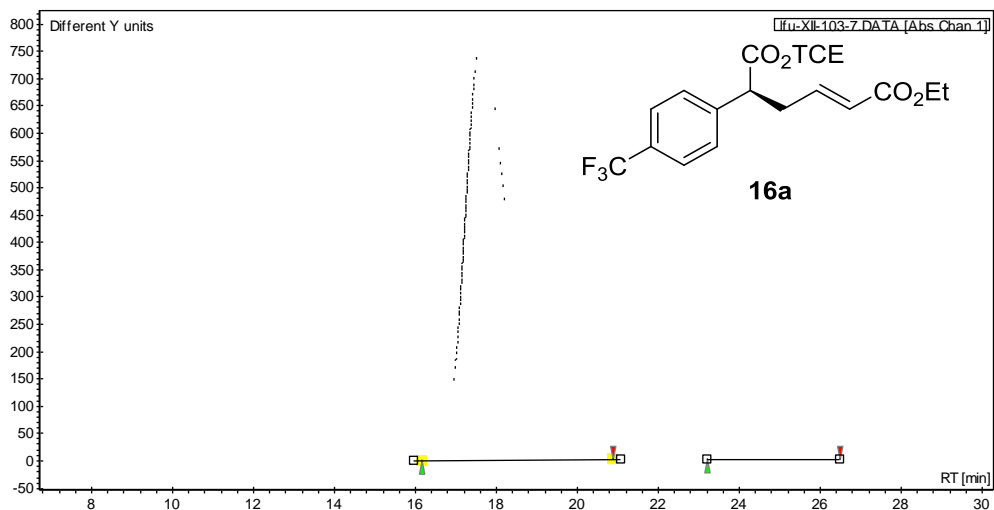
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	20.17	49.99	215.9	159.4	49.993
2	UNKNOWN	22.81	50.01	192.0	159.4	50.007
Total		100.00	407.9	318.8	100.000	



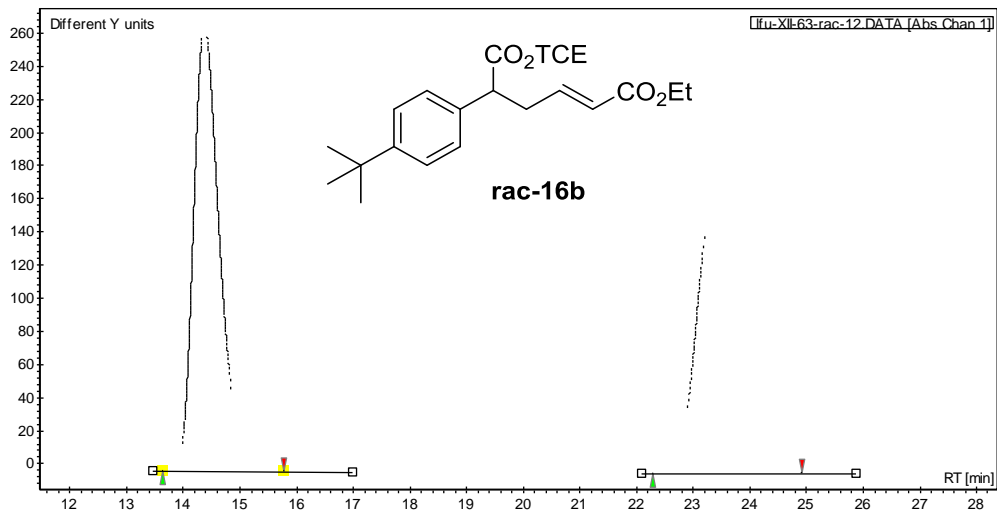
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	20.12	2.01	11.0	7.7	2.013
1	UNKNOWN	22.54	97.99	445.9	376.7	97.987
Total		100.00	456.9	384.4	100.000	



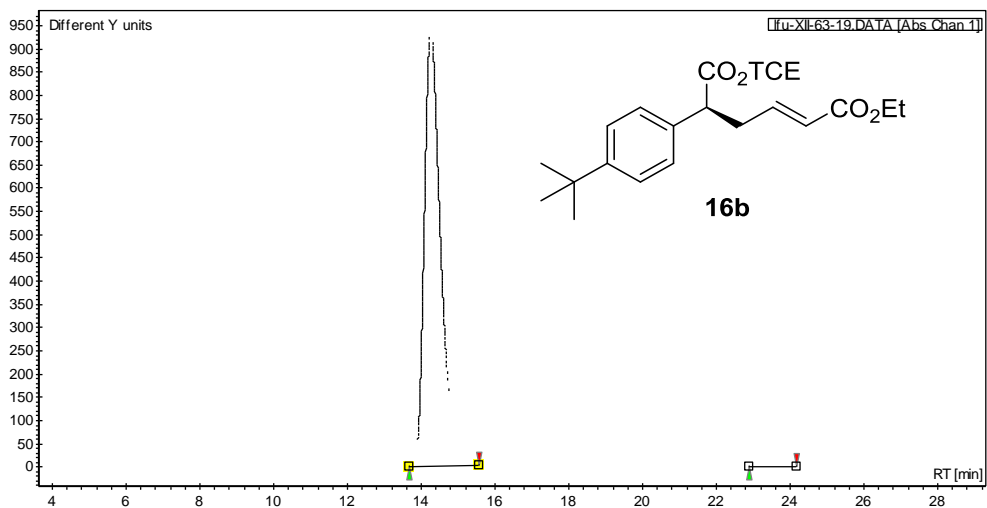
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	17.60	53.07	304.9	379.4	53.074
2	UNKNOWN	24.04	46.93	152.1	335.5	46.926
Total		100.00	457.0	714.9	100.000	



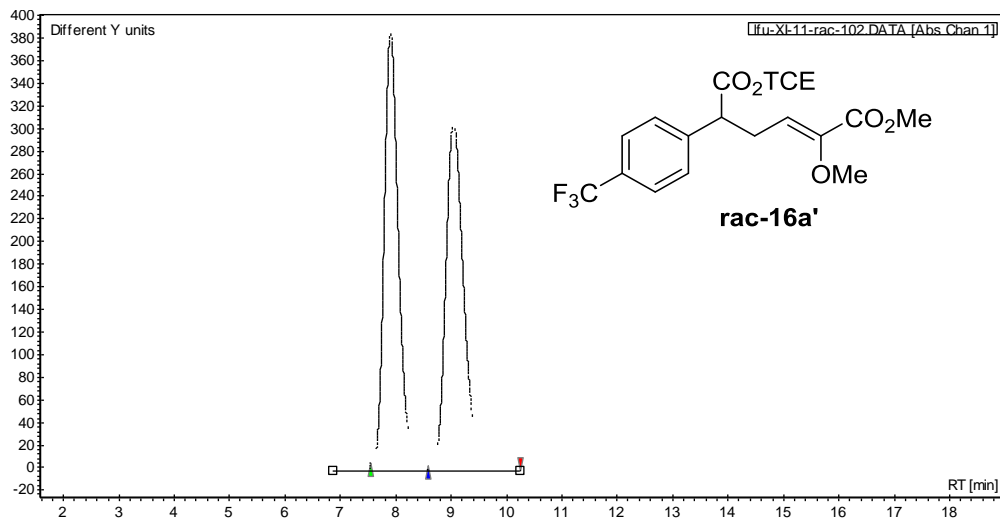
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	17.65	99.03	791.8	962.5	99.025
2	UNKNOWN	24.57	0.97	5.6	9.5	0.975
Total		100.00	797.4	971.9	100.000	



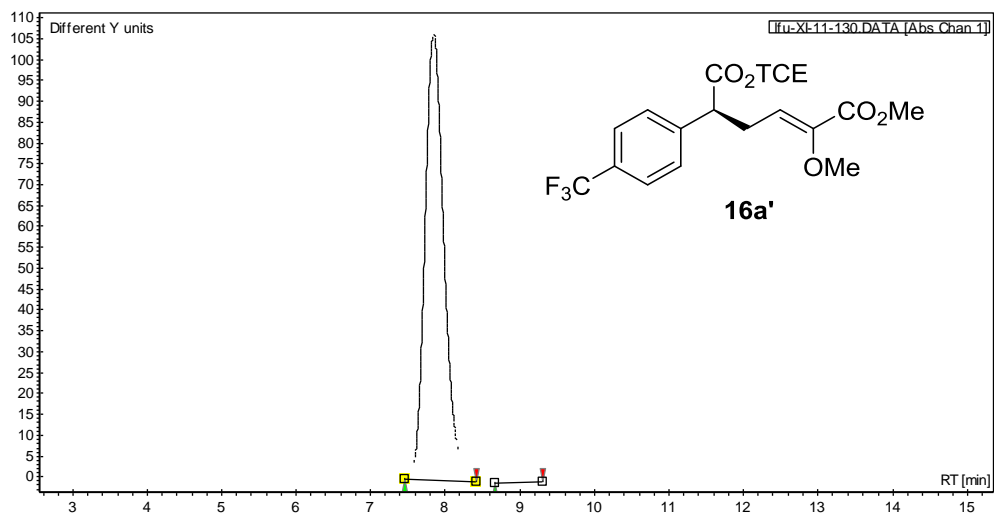
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	14.37	50.13	269.5	144.0	50.126
2	UNKNOWN	23.37	49.87	166.3	143.3	49.874
Total		100.00	435.9	287.3	100.000	



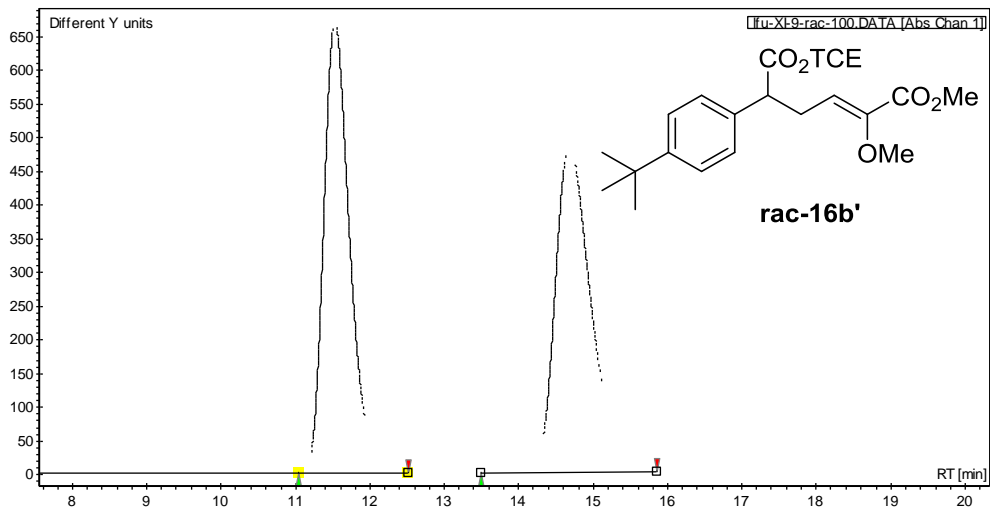
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	14.26	99.59	941.0	477.5	99.590
2	UNKNOWN	23.45	0.41	2.8	2.0	0.410
Total		100.00	943.8	479.4	100.000	



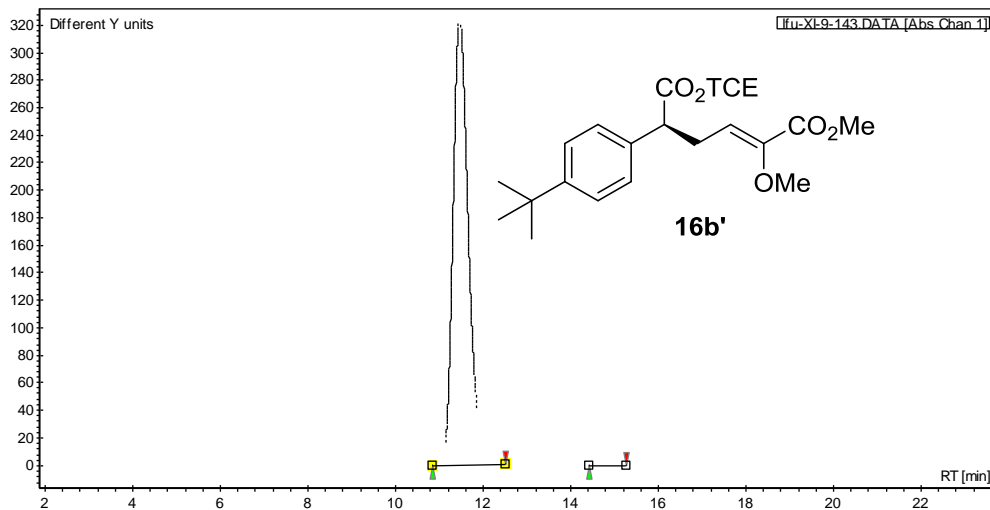
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.90	50.14	388.1	116.6	50.140
2	UNKNOWN	9.04	49.86	310.1	115.9	49.860
Total		100.00	698.2	232.5	100.000	



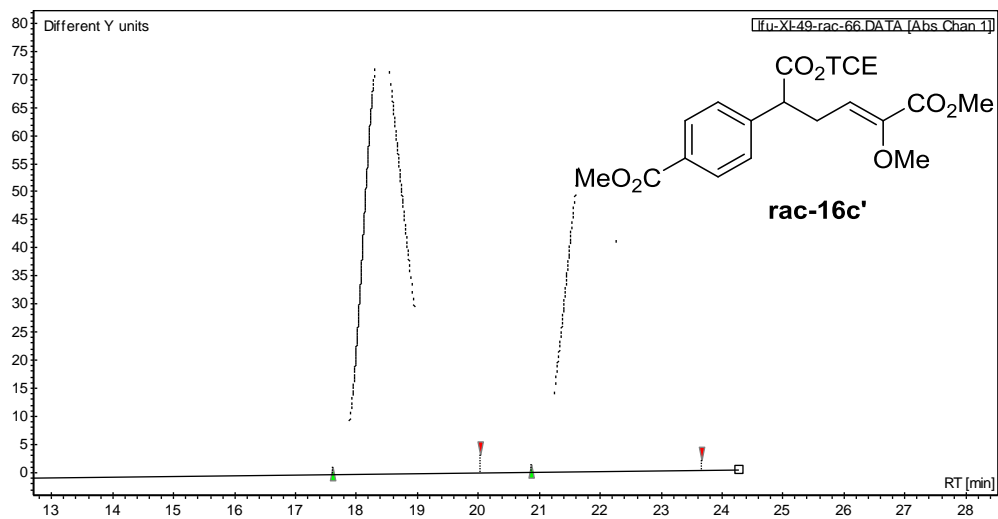
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.84	99.48	107.3	31.5	99.485
2	UNKNOWN	9.00	0.52	0.6	0.2	0.515
Total		100.00	107.9	31.7	100.000	



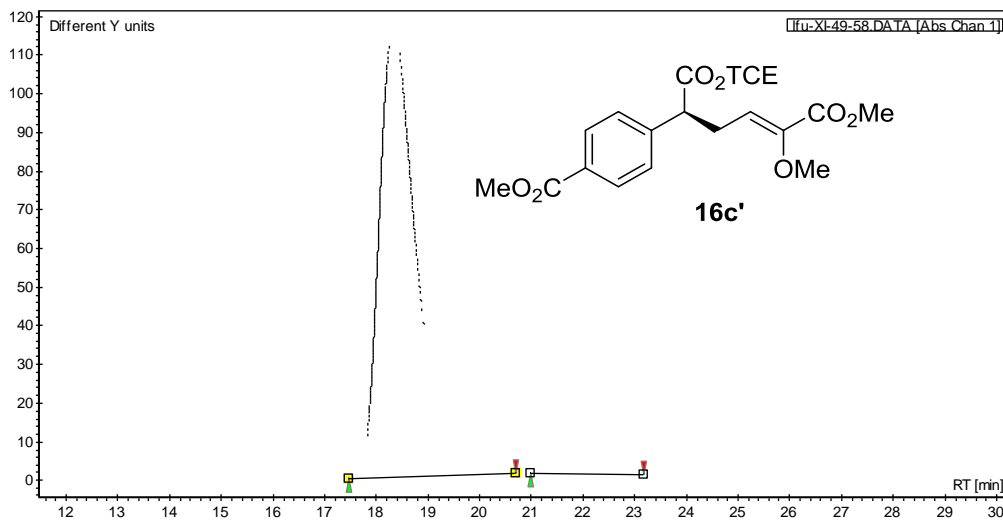
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.53	49.52	670.0	268.1	49.521
2	UNKNOWN	14.68	50.48	486.9	273.3	50.479
Total		100.00	1156.9	541.4	100.000	



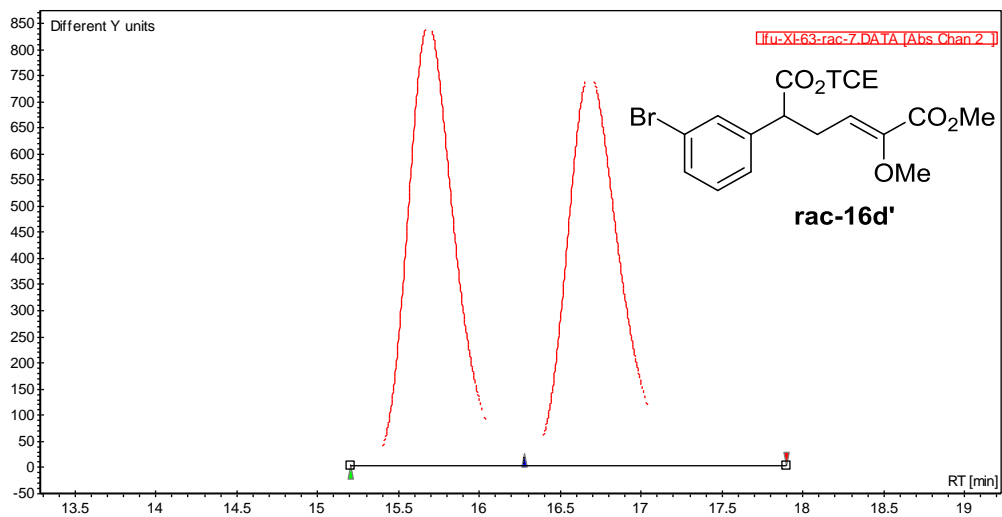
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.47	99.78	325.9	132.1	99.779
2	UNKNOWN	14.88	0.22	0.7	0.3	0.221
Total		100.00	326.6	132.4	100.000	



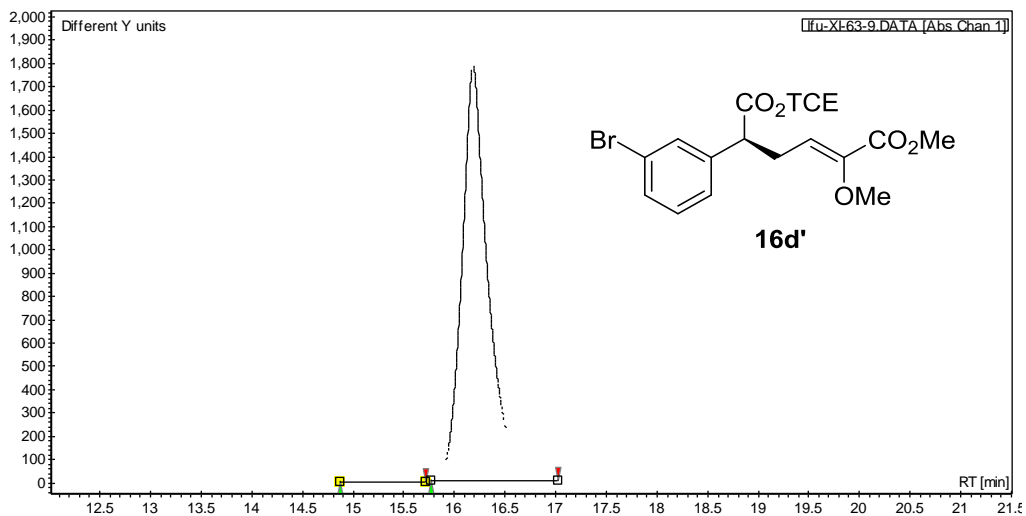
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.41	49.93	76.6	67.2	49.929
2	UNKNOWN	21.84	50.07	60.6	67.4	50.071
Total		100.00	137.2	134.5	100.000	



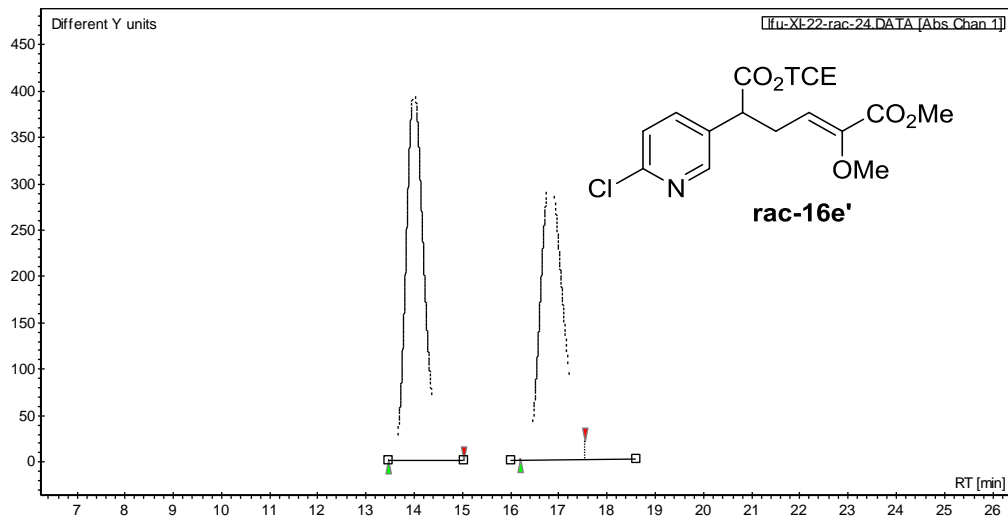
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.33	94.38	117.1	99.1	94.385
2	UNKNOWN	21.94	5.62	5.8	5.9	5.615
Total		100.00	122.9	105.0	100.000	



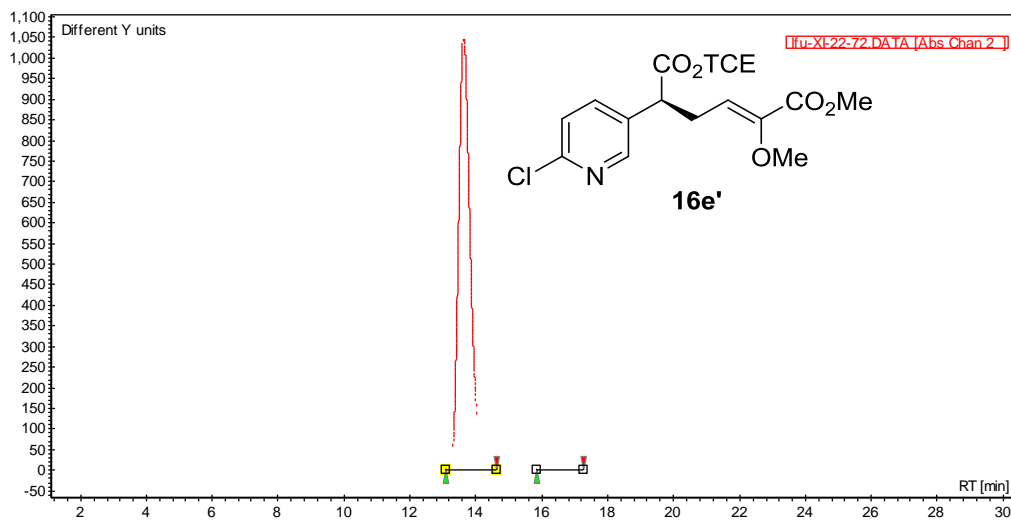
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15.68	49.82	846.9	287.8	49.824
2	UNKNOWN	16.68	50.18	750.4	289.8	50.176
Total		100.00	1597.2	577.6	100.000	



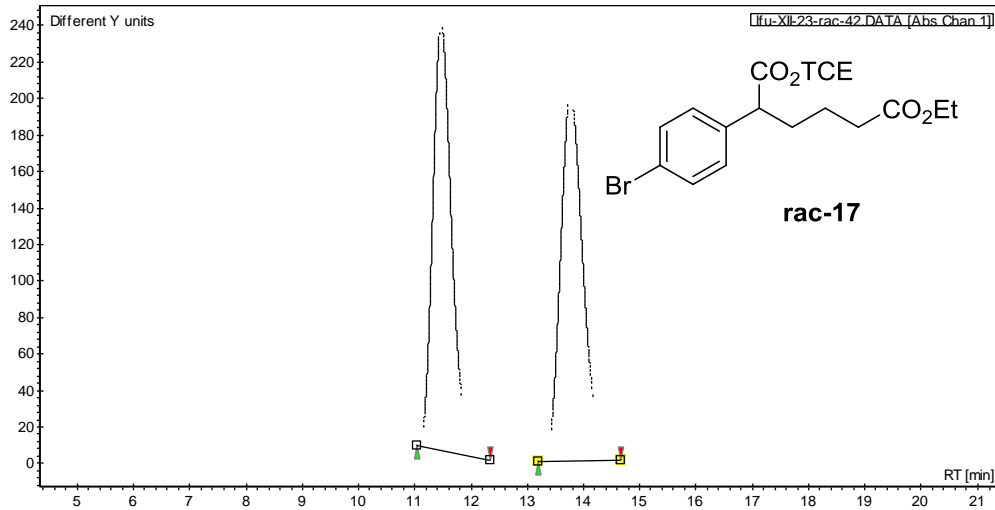
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15.28	5.99	107.2	34.2	5.986
2	UNKNOWN	16.19	94.01	1787.0	537.2	94.014
Total		100.00	1894.2	571.4	100.000	



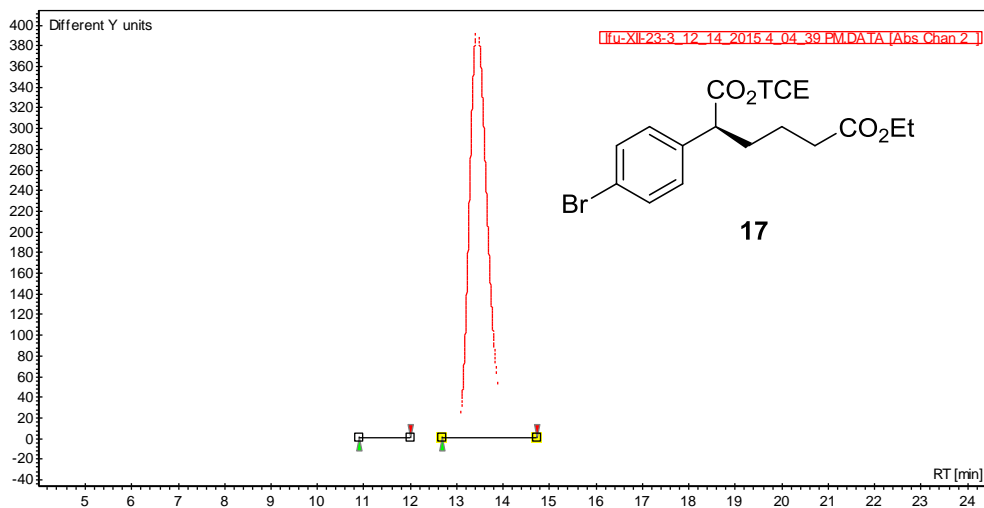
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.99	50.51	400.8	171.9	50.513
2	UNKNOWN	16.82	49.49	308.9	168.4	49.487
Total		100.00	709.8	340.2	100.000	



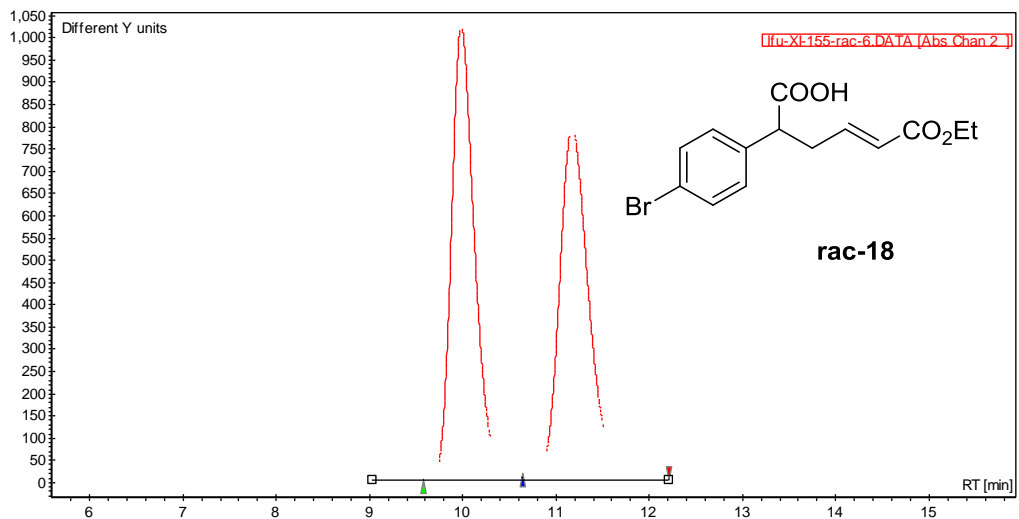
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.63	96.22	1064.7	433.0	96.225
2	UNKNOWN	16.49	3.78	32.2	17.0	3.775
Total		100.00	1096.8	450.0	100.000	



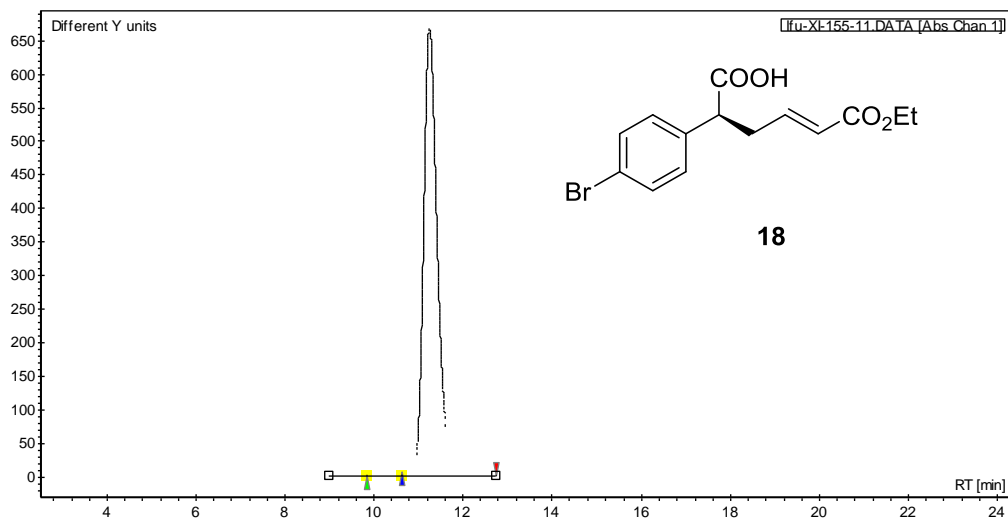
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	11.47	49.59	234.3	91.9	49.593
1	UNKNOWN	13.77	50.41	200.6	93.4	50.407
Total		100.00	434.9	185.2	100.000	



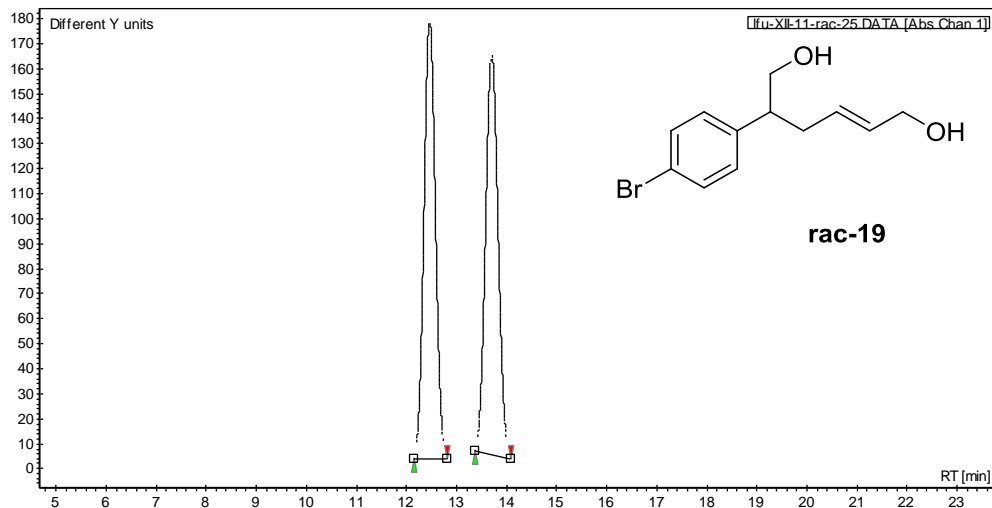
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	11.28	2.29	11.0	4.2	2.285
1	UNKNOWN	13.44	97.71	399.0	181.2	97.715
Total		100.00	410.0	185.4	100.000	



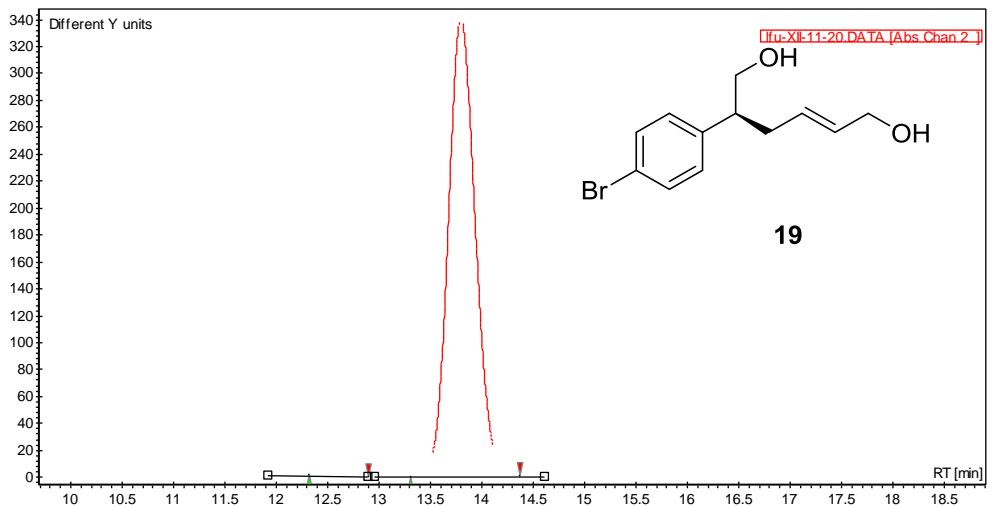
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	9.99	50.49	1022.6	294.7	50.492
2	UNKNOWN	11.18	49.51	793.1	288.9	49.508
Total		100.00	1815.6	583.6	100.000	



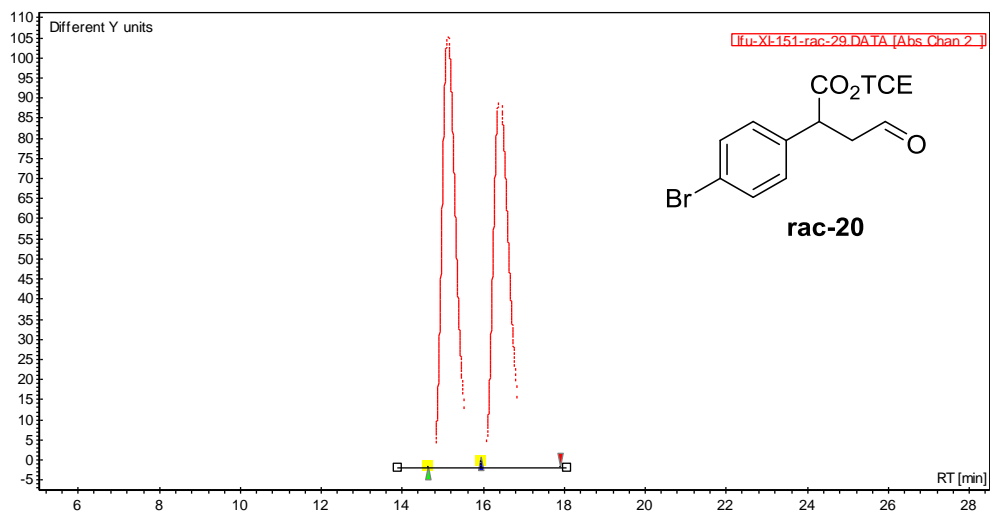
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	10.15	2.03	16.8	5.0	2.032
2	UNKNOWN	11.25	97.97	675.2	240.3	97.968
Total		100.00	692.1	245.3	100.000	



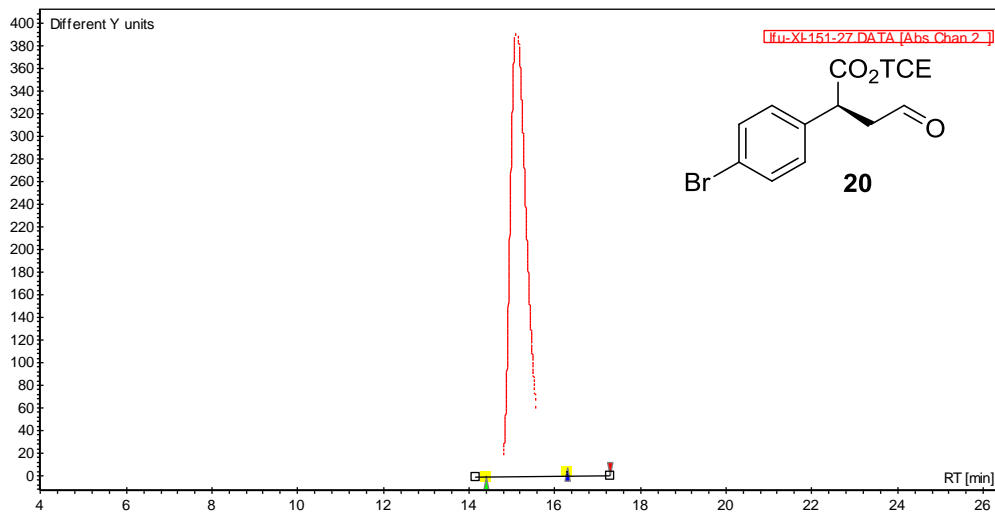
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	12.46	49.86	175.7	46.1	49.856
2	UNKNOWN	13.70	50.14	160.6	46.4	50.144
Total		100.00	336.4	92.5	100.000	



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	12.57	2.45	9.4	2.6	2.452
2	UNKNOWN	13.79	97.55	340.4	103.9	97.548
Total		100.00	349.7	106.5	100.000	



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15.12	49.79	108.0	44.5	49.787
2	UNKNOWN	16.41	50.21	93.2	44.9	50.213
Total		100.00	201.2	89.4	100.000	



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15.11	97.61	399.7	182.7	97.607
2	UNKNOWN	16.65	2.39	9.0	4.5	2.393
Total		100.00	408.8	187.2	100.000	