Electronic Supplementary Information

Ti/Pd-Promoted Catalyzed intramolecular Michael-type addition of allylic carboxylates to activated alkenes

Alba Millán, Ana Martín-Lasanta, Delia Miguel, Luis Álvarez de Cienfuegos, Juan M. Cuerva

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Granada, Avda. Severo Ochoa s/n, 18071-Granada, Spain

jmcuerva@ugr.es, *lac@ugr.es*, *dmalvarez@ugr.es*

Index

General Information

All intramolecular cyclization reactions were assembled under argon atmosphere in oven-dried glassware with magnetic stirring. For the reactions employing titanocene all solvents and additives were rigorously deoxygenated prior to use. THF was previously distilled and dried over sodium. All commercially available reagents and solvents used in extraction and purification, ether, hexane and ethyl acetate, were obtained from standard chemical suppliers and used without further purification. TLC was performed on aluminium-backed plates coated with silica gel 60 (230-240 mesh) with F_{254} indicator. The spots were visualized with UV light (254 nm) and/or staining with Ce/Mo reagent or phosphomolybdic acid solution and subsequent heating.

NMR Spectra were measured at room temperature. ^{1}H NMR spectra were recorded at 300, 400 or 500 MHz. The ratio of isomers was determined by integration of the allylic proton in ^{1}H-NMR spectra in C_6D_6 or $CDCl_3$. In case of mixture of isomers, the protons and carbons are assigned to the major or minor isomer when it is possible. When nothing is said the two isomers appear together and therefore the number of protons/carbons specified corresponds to both of them. Chemical shifts are reported in ppm using residual solvent peak as reference ($CHCl_3$: δ 7.26). Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, quint: quintuplet; m: multiplet, dd: doublet of doublets, dt: doublet of triplets, dq: doublet of quartets, td: triplet of doublets, bs: broad singlet), coupling constant (*J* in Hz) and integration. ^{13}C-NMR spectra were recorded at 75, 100 or 126 MHz using broadband proton decoupling and chemical shifts are reported in ppm using residual solvent peaks as reference ($CDCl_3$: δ 77.16). Carbon multiplicities were assigned by DEPT techniques. The stereochemistry of the cyclization products was assigned using the Beckwith-Houk rules for radical cyclizations and the described ^{13}C NMR for the *trans* isomer of a very closely related derivative of **2**[1]

High resolution mass spectra (HRMS) were recorded on a Micromass AutoSpec using EI at 70eV.

The following known compounds were isolated as pure samples and showed NMR spectra identical to reported data: **(Z)-I**[2], **(E)-I**[3], **II**[4], (*Z*)-$BrCH_2CH{=}CHCH_2CO_2Et$[5], **VII**[3], **IX**[6], *trans*-4-acetoxy-1-bromo-2-methyl-2-butene[7], **XV**[8], carbonate **XIX**[9].

---

[1] M. Terakado, K. Murai, M. Miyazawa, K. Yamamoto, *Tetrahedron*, 1994, **19**, 5705-5718

[2] A. G. Campaña, N. Fuentes, E. Gómez-Bengoa, C. Mateo, J. E. Oltra, A. M. Echavarren, J. M. Cuerva, *J. Org. Chem.*, 2007, **72**, 8127-8130.

[3] A. G. Campaña, B. Bazdi, N. Fuentes, R. Robles, J. M. Cuerva, J. E. Oltra, S. Porcel, A. M. Echavarren, *Angew. Chem. Int. Ed.*, 2008, **47**, 7515-7519.

[4] C. Fernández-Rivas, M. Méndez, C. Nieto-Oberhuber, A. M. Echavarren, *J. Org. Chem.*, 2002, **67**, 5197-5201.

[5] W. Oppolzer, A. Fürstner., *Helv. Chim. Acta.*, 1993, **69**, 2369-2337.

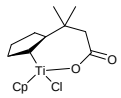
[6] R. E. Estévez, J. Justicia, B. Bazdi, N. Fuentes, M. Paradas, D. Choquesillo-Lazarte, J. M. García-Ruiz, R. Robles, A. Gansaüer, J. M. Cuerva, J. E. Oltra, *Chem. Eur. J.*, 2009, **15**, 2774-2791.

[7] K. Sato, S. Inoue, S. Ota, Y. Fujita, *J. Org. Chem.*, 1972, **37**, 462-466.

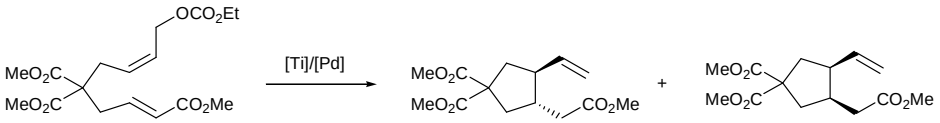
[8] C. Fernández-Rivas, M. Méndez, C. Nieto-Oberhuber, A. M. Echavarren, *J. Org. Chem.* 2002, **67**, 5197-5201.

[9] B. M. Trost, J. I. Luengo, *J. Am. Chem. Soc* 1988**, 110,** 8239-8241.

Optimization of the reaction conditions for the Pd^0-Ti^{III}-promoted Michael-type addition of allylic carboxylates to activated alkenes

Entry	Ti catalyst (mol%)	Ligand (mol%)	Pd catalyst (mol%)	Mn (mol%)	TMSCl (mol%)	2,4,6-Collidine (mol%)	Yield (*cis*:*trans*)
1	(tBuCp)$_2$TiCl$_2$ (150)	PPh_3 (40)	$PdCl_2$ (20)	800	-	-	54 (4:1)
2	 (150)	PPh_3 (40)	$PdCl_2$ (20)	800	-	-	62 (4:1)
3	-	PPh_3 (40)	$PdCl_2$ (20)	800	400	-	62 (4:1)
4	Cp_2TiCl_2 (40)	-	$PdCl_2$ (20)	800	400	700	0
5	Cp_2TiCl_2 (40)	PPh_3 (40)	-	800	400	700	0
6	Cp_2TiCl_2 (40)	PPh_3 40)	$PdCl_2$ (20)	-	400	700	0
7	-	PPh_3 (40)	$PdCl_2$ (20)	800	-	-	0
8	Cp_2TiCl_2 (40)	PPh_3 (40)	$PdCl_2$ (20)	800	400	-	71 (4:1)
9	-	-	$Pd(PPh_3)_4$ (20)	-	-	-	0

Influence of the phosphorous ligand and the palladium complex in the Pd^0-Ti^{III}-promoted Michael-type addition of allylic carboxylates to activated alkenes.



(*z*)-1 **2-*trans*** **2-*cis***

Entry	Ligand (mol %)	Pd catalyst (mol %)	Yield, (2_{cis}:2_{trans})
1	PCy_3 (40)	$PdCl_2$ (20)	--
2	$P(C_6F_5)_3$ (40)	$PdCl_2$ (20)	--
3	_	$[Pd_2(dba)_3]dba$ (20)	<5%
4	dppm (40)	$PdCl_2$ (20)	--
5	*o*-Tolylphosphine (40)	$PdCl_2$ (20)	<5%
6	$(2\text{-}MeOC_6H_4)_3PPh_3$ (40)	$PdCl_2$ (20)	--
7	dppe (40)	$PdCl_2$ (20)	--
8	$P(OPh)_3$ (40)	$PdCl_2$ (20)	<5%
9	-	$Pd(PPh_3)_4$ (20)	51, (4:1)

Synthesis of compound **(Z)-1:**

(*Z*)-I **(*Z*)-1**

Methyl 4-bromocrotonate (230mg, 1.1 mmol) was added to a mixture of NaH (44 mg, 1.1 mmol) and dimethylmalonate derivative **(Z)-I**[2] (274 mg, 1 mmol) in DMF (10 mL) at 0ºC. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na_2SO_4. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give a 6:1 mixture (253 mg, 68 %) of the *Z*- and *E*- isomers of the carbonate as a colourless oil. Data of the major isomer **(*Z*)-1**:

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.76 (dt, *J* = 15.4, 7.6 Hz, 1H), 5.91 – 5.81 (m, 1H), 5.74 – 5.60 (m, 1H), 5.50 (ddd, *J* = 11.1, 8.5, 4.5 Hz, 1H), 4.63 (d, *J* = 6.8 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.72 (s, *J* = 3.3 Hz, 6H), 3.70 (s, *J* = 3.3 Hz, 3H), 2.76 (d, *J* = 7.7 Hz, 2H), 2.70 (d, *J* = 7.7 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 170.5 (2xC), 166.2 (C), 155.1 (C), 142.4 (CH), 127.8 (CH), 127.6 (CH), 125.1 (CH), 64.2 (CH_2), 63.1 (CH_2), 57.3 (C), 52.9 (2xCH_3), 51.7 (CH_3), 35.8 (CH_2), 31.3 (CH_2), 14.4 (CH_3.)

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{17}H_{24}O_9$ $[M]^+$: 372.1420; found: 372.1403.

Synthesis of compound **(*E*)-1:**

(*E*)-I **(*E*)-1**

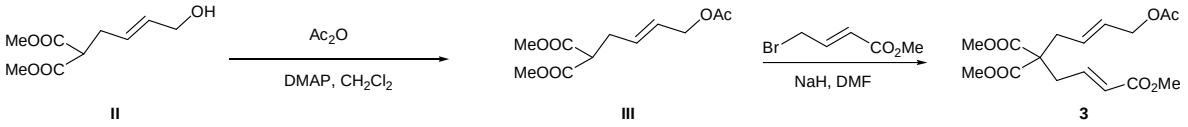
Methyl 4-bromocrotonate (979mg, 5.5 mmol) was added to a mixture of NaH (219 mg, 5.5 mmol) and dimethylmalonate derivative **(*E*)-I**[2] (1 g, 3.7 mmol) in DMF (25 mL) at 0ºC. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na_2SO_4. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give a 6:1 mixture (936 mg, 68%) of the *E*- and *Z*- isomers of the carbonate as a colourless oil. Data of the major isomer **(*E*)-1**:

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.75 (dt, *J* = 15.3, 7.6 Hz, 1H), 5.85 (d, *J* = 15.6 Hz, 1H), 5.72 - 5.52 (m, 2H), 4.53 (d, *J* = 4.9 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 6H), 3.70 (s, 3H), 2.79 - 2.67 (m, 2H), 2.64 (d, *J* = 5.9 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 170.4 (2xC), 166.2 (C), 154.9 (C), 142.4 (CH), 129.2 (CH), 128.7 (CH), 124.9 (CH), 67.5 (CH_2), 64.0 (CH_2), 57.3 (C), 52.7 (2xCH_3), 51.6 (CH_3), 36.0 (CH_2), 35.6 (CH_2), 14.3 (CH_3).

HRMS (EI, 70 eV) *m/z* calcd. for $C_{17}H_{24}O_9$ $[M]^+$: 372.1420; found: 372.1418.

Synthesis of compound **3**:



II **III** **3**

Compound III: Ac_2O (102 mg, 1 mmol) was added to a solution of compound **II**[4] (202 mg, 1 mmol) and DMAP (121 mg, 1mmol) in CH_2Cl_2 (15mL). The mixture was stirred for 1h and then solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give **III** (232 mg, 95%) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.72 - 5.64 (m, 2H), 4.48 (d, *J* = 4.9 Hz, 2H), 3.73 (s, 6H), 3.44 (t, *J* = 7.5 Hz, 1H), 2.69 - 2.60 (m, 2H), 2.04 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 169.2 (3xC), 130.8 (CH), 127.4 (CH), 64.6 (CH_2), 52.7 (2xCH_3), 51.4 (CH), 31.6 (CH_2), 21.1 (CH_3).

HRMS (EI, 70eV) *m/z* calcd. for $C_{11}H_{17}O_6$ $[M+1]^+$: 245.1025; found: 245.1017

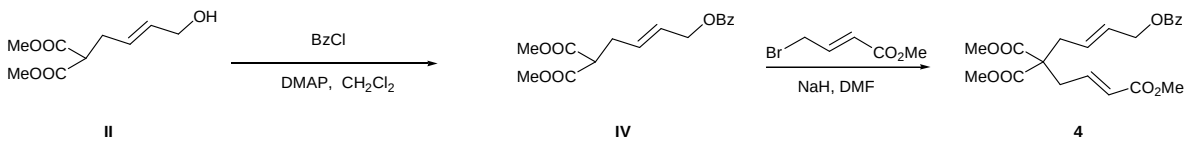
Compound 3: Methyl 4-bromocrotonate (220 mg, 1.23 mmol) was added to a mixture of NaH (49 mg, 1.23 mmol) and **III** (200 mg, 0.82 mmol) in DMF (15 mL) at 0ºC. The resulting solution was stirred at room temperature for 16 h.Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na_2SO_4. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give a 7:1 mixture (221 mg, 79%) of the *E*- and *Z*- isomers of the carbonate as a colourless oil. Data of the major isomer **3**:

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.73 (dt, *J* = 15.3, 7.6 Hz, 1H), 5.84 (d, *J* = 15.5 Hz, 1H), 5.68 - 5.49 (m, 2H), 4.46 (d, *J* = 4.2 Hz, 2H), 3.70 (bs, 9H), 2.72 (d, *J* = 7.2 Hz, 2H), 2.61 (d, *J* = 5.6 Hz, 2H), 2.02 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 170.5 (3xC), 166.2 (C), 142.5 (CH), 129.3 (CH), 128.6 (CH), 125.0 (CH), 64.4 (CH_2), 57.3 (C), 52.7 (2xCH_3), 51.6 (CH_3), 36.0 (CH_2), 35.6 (CH_2), 20.9 (CH_3).

HRMS (EI, 70eV) *m/z* calcd. for $C_{16}H_{22}O_8$ $[M]^+$: 342.1315; found: 342.1304

Synthesis of compound **4**:



II **IV** **4**

Compound IV: Benzoyl chloride (140 mg, 1mmol) was added to a solution of compound **II** (202 mg, 1 mmol) and DMAP (122 mg, 1 mmol) in CH_2Cl_2 (15mL). The mixture was stirred for 1h and then

solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give **IV** (281 mg, 92%) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.02 (d, *J* = 8.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 5.80 (m, 2H), 4.74 (d, *J* = 4.0 Hz, 2H), 3.72 (s, 6H), 3.47 (t, *J* = 7.5 Hz, 1H), 2.70-2.62 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 169.2 (2xC), 166.3 (C), 133.1 (CH), 130.9 (CH), 130.3 (C), 129.7 (2xCH), 128.5 (2xCH), 127.5 (CH), 65.0 (CH_2), 52.6 (2xCH_3), 51.4 (CH), 31.6 (CH_2).

HRMS (EI, 70eV) *m*/*z* calcd. for $C_{16}H_{18}O_6$ $[M]^+$: 306.1103; found: 306.1103.

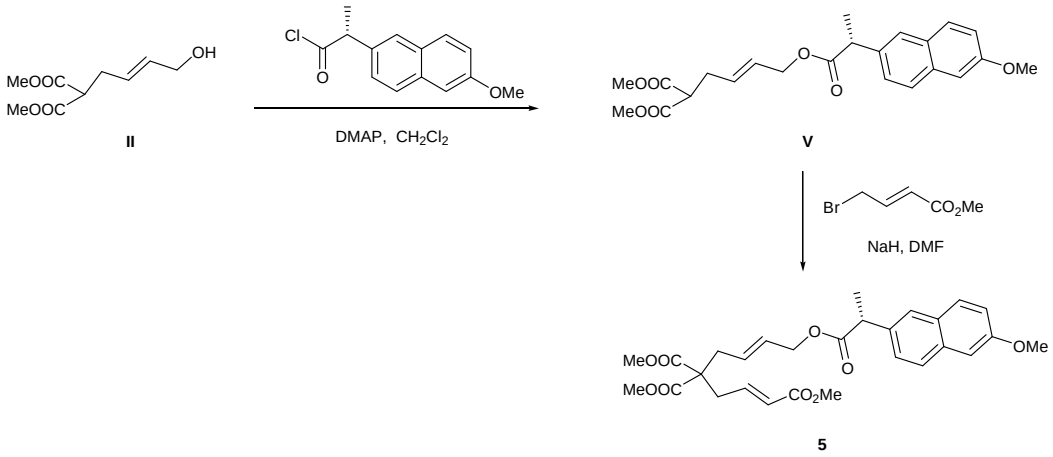
Compound 4: Methyl 4-bromocrotonate (220 mg, 1.23 mmol) was added to a mixture of NaH (49 mg, 1.23 mmol) and **IV** (250 mg, 0.82 mmol) in DMF (15 mL) at 0ºC. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na_2SO_4. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give a 12:1 mixture (248 mg, 75%) of the *E*- and *Z*- isomers in the carbonate as a colourless oil. Data of the major isomer **4**:

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.96 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 6.72 (dt, *J* = 15.3, 7.6 Hz, 1H), 5.82 (d, *J*= 15.5 Hz, 1H), 5.76 - 5.56 (m, 2H), 4.68 (d, *J* = 4.2 Hz, 2H), 3.65 (bs, 9H), 2.72 (d, *J* = 7.2 Hz, 2H), 2.62 (d, *J* = 5.6 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 170.3 (3xC), 165.9 (C), 142.3 (CH), 132.8 (CH), 130.1 (C), 129.4 (2xCH), 129.1 (CH), 128.6 (CH), 128.3 (2xCH), 124.8 (CH), 64.7 (CH_2), 57.1 (C), 52.5 (2xCH_3), 51.3 (CH_3), 35.9 (CH_2), 35.5 (CH_2).

HRMS (EI, 70eV) *m*/*z* calcd.for $C_{21}H_{24}O_8$ $[M]^+$: 404.1471; found: 404.1455.

Synthesis of compound **5**:



Compound V: (*R*)-2-(6-Methoxynaphthalen-2-yl)propanoyl chloride (248 mg, 1mmol) was added to a solution of compound **II** (202 mg, 1 mmol) and DMAP (122 mg, 1 mmol) in CH_2Cl_2 (15mL). The

mixture was stirred for 3h and then solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give **V** (364 mg, 88%) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.68 (m, 2H), 7.41 (d, *J* = 1.7 Hz, 1H), 7.38 (d, *J* = 1.7 Hz, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.12 (d, *J* = 3.8 Hz, 1H), 5.59 (m, 2H), 4.55 - 4.40 (m, 2H), 3.90 (s, 3H), 3.84 (q, *J* = 7.1 Hz, 1H), 3.68 (s, 6H), 3.36 (t, *J* = 7.6 Hz, 1H), 2.63 - 2.54 (m, 2H), 1.57 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 174.3 (C), 169.1 (2xC), 157.7 (C), 135.7 (C), 133.8 (C), 130.5 (CH), 129.3 (CH), 129.0 (C), 127.3 (CH), 127.2 (CH), 126.3 (CH), 126.0 (CH), 119.1 (CH), 105.7 (CH), 64.8 (CH_2), 55.4 (CH_3), 52.5 (2xCH_3), 51.3 (CH), 45.8 (CH), 31.5 (CH_2), 18.6 (CH_3).

HRMS (EI, 70eV) *m*/*z* calcd. for $C_{23}H_{26}O_7$ $[M]^+$: 414.1679; found: 414.1681.

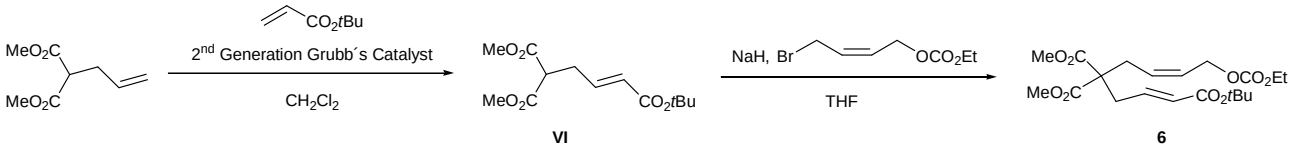
Compound 5: Methyl 4-bromocrotonate (193 mg, 1.08 mmol) was added to a mixture of NaH (43 mg, 1.08 mmol) and **V** (300 mg, 0.72 mmol) in DMF (15 mL) at 0ºC. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na_2SO_4. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give **5** (225 mg, 61%) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.66 (m, 2H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.38 (d, *J* = 1.8 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 7.11 (d, *J* = 2.2 Hz, 1H), 6.71 (m, 1H), 5.78 (d, *J* = 15.5 Hz, 1H), 5.66 - 5.41 (m, 2H), 4.50 (d, *J* = 5.7 Hz, 2H), 3.90 (s, 3H), 3.85 (q, *J* = 7.1 Hz, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.65 (s, 3H), 2.63 (d, *J* = 6.9 Hz, 2H), 2.58 (d, *J* = 6.8 Hz, 2H), 1.57 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 174.2 (C), 170.4 (2xC), 166.2 (C), 157.7 (C), 142.4 (CH), 135.6 (C), 133.7 (C), 129.3 (CH), 129.1 (CH), 128.9 (C) , 128.3 (CH), 127.2 (CH), 126.2 (CH), 126.0 (CH), 124.8 (CH), 119.0 (CH), 105.6 (CH), 64.6 (CH_2), 57.3 (C), 55.3 (CH_3), 52.6 (2xCH_3), 51.6 (CH), 45.5 (CH_3), 35.9 (CH_2), 35.4 (CH_2), 18.5 (CH_3).

HRMS (EI, 70eV) *m*/*z* calcd. for $C_{28}H_{32}O_9$ $[M]^+$: 512.2046; found: 512.2042.

Synthesis of compound **6**:



VI **6**

Compound VI: *Tert*-butylacrylate (0.192 g, 1.5 mmol) was added to a solution of Grubb´s 2nd generation catalyst (21 mg, 0.025 mmol) and allyldimethylmalonate (86 mg, 0.5 mmol) in CH_2Cl_2 (5 ml) and the mixture was stirred under reflux for 24h. The solvent was removed and the residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give **VI** (106 mg, 78 %) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.71 (dt, *J* = 15.2, 7.1 Hz, 1H), 5.77 (d, *J* = 15.6 Hz, 1H), 3.71 (s, 6H), 3.47 (t, *J* = 7.4 Hz, 1H), 2.73 (dd, *J* = 10.4, 4.0 Hz, 2H), 1.43 (d, *J* = 6.3 Hz, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 168.8 (2xC), 165.4 (C), 142.3 (CH), 125.7 (CH), 80.5 (C), 52.8 (2xCH_3), 50.5 (CH), 31.0 (CH_2), 28.1 (3xCH_3)

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{13}H_{21}O_6$ $[M+1]^+$: 273.1338; found: 273.1344.

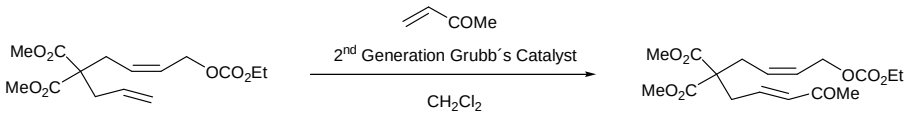
Compound 6: A sample of (*Z*)-$BrCH_2CH{=}CHCH_2CO_2Et$[5] (120 mg, 0.54 mmol) was added to a mixture of NaH (22 mg, 0.54 mmol) and **VI** (98 mg, 0.36 mmol) in DMF (5 mL) at 0ºC. The resulting solution was stirred at room temperature for 16h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na_2SO_4. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give **6** (132 mg, 89 %) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.63 (dtd, *J* = 12.1, 7.7, 4.4 Hz, 1H), 5.79 (d, *J* = 15.5 Hz, 1H), 5.73 – 5.64 (m, 1H), 5.56 – 5.47 (m, 1H), 4.64 (d, *J* = 6.8 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.73 (s, *J* = 3.7 Hz, 6H), 2.75 (d, *J* = 7.7 Hz, 2H), 2.70 (d, *J* = 7.8 Hz, 2H), 1.46 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 170.6 (2xC), 165.2 (C), 155.2 (C), 140.7 (CH), 128.0 (CH), 127.5 (CH), 127.3 (CH), 80.6 (C), 64.2 (CH_2), 63.2 (CH_2), 57.3 (C), 52.9 (CH_3), 52.8 (CH_3), 35.7 (CH_2), 31.3 (CH_2), 28.2 (3x CH_3), 14.4 (CH_3)

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{20}H_{31}O_9$ $[M+1]^+$: 415.1958; found: 415.1960.

*Synthesis of compound **7**:*



VII **7**

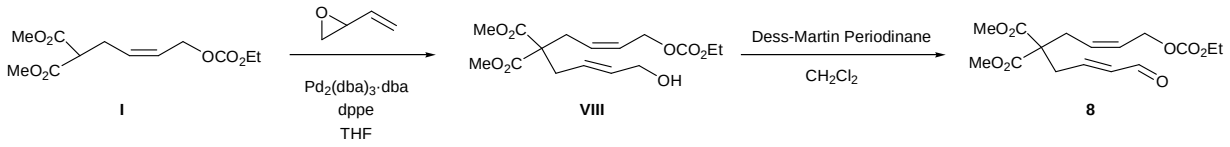
Compound 7: Methyl vinyl ketone (0.43 g, 5.2 mmol) was added to a solution of the Grubb´s 2nd generation catalyst ((210 mg, 0.25 mmol)) and the allyldimethylmalonate derivative **VII**[3] (300 mg, 1.74 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred under reflux for 24h. The solvent was removed and the residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give **7** (353 mg, 95 %) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.68 – 6.58 (m, 1H), 6.09 (d, *J* = 15.9 Hz, 1H), 5.73 – 5.59 (m, 2H), 4.55 (d, *J* = 5.6 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 6H), 2.75 (dd, *J* = 7.6, 0.9 Hz, 2H), 2.66 (d, *J* = 6.6 Hz, 2H), 2.23 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 198.1 (C), 170.6 (2xC), 155.1 (C), 141.4 (CH), 134.7 (CH), 129.3 (CH), 128.9 (CH), 67.6 (CH_2), 64.2 (CH_2), 57.5 (C), 52.9 (2xCH_3), 36.4 (CH_2), 36.2 (CH_2), 27.2 (CH_3), 14.4 (CH_3)

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{14}H_{18}O_5$ $[M-C_3H_6O_3]^+$: 266.1154; found: 266.1150.

*Synthesis of compound **8**:*



Compound VIII: Butadiene monoxide (0.02 mL, 0.38 mmol) was added to a solution of the dimethylmalonate derivative **I** (100 mg, 0.38 mmol), $Pd_2(dba)_3$·dba (3 mg, 0.019 mmol) and dppe (8 mg, 0.019 mmol) in THF (10 mL). The resulting mixture was stirred at room temperature for 16 h and then solvent was removed. The residue was filtered through a short silica pad to give **VIII** (71 mg, 54 %) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.77 – 5.49 (m, 4H), 4.54 (d, *J* = 4.2 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.08 (d, *J* = 5.6 Hz, 2H), 3.71 (s, 6H), 2.64 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 171.2 (2xC), 155.2 (C), 134.6 (CH), 130.1 (CH), 128.4 (CH), 125.2 (CH), 67.8 (CH_2), 64.2 (CH_2), 63.1 (CH_2), 58.0 (C), 52.8 (CH_3), 52.7 (CH_3), 35.8 (CH_2), 35.7 (CH_2), 14.5 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{14}H_{21}O_6$ $[M\text{-}CO_2Me]^+$: 285.1338; found: 285.1341.

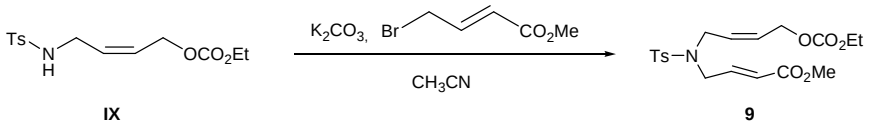
Compound 8: Dess-Martin periodinane (DMP) (148 mg, 0.35 mmol) was added to a solution of **VIII** (100 mg, 0.29 mmol) in CH_2Cl_2 (20 mL). The resulting mixture was stirred for 3 h at room temperature and then washed with saturated aqueous solution of $Na_2S_2O_3$ and $NaHCO_3$ in 1:1 proportion, dried over anhydrous Na_2SO_4 and the solvent removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give a 8:1 mixture (84 mg, 85 %) of the *Z*- and *E*-isomers in the carbonate as a colourless oil. Data of the major isomer **8**:

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.49 (d, *J* = 7.8 Hz, 1H), 6.77 – 6.65 (m, 1H), 6.13 (d, *J* = 7.8 Hz, 1H), 5.66 (dd, *J* = 10.5, 6.1 Hz, 2H), 4.54 (d, *J* = 5.6 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 6H), 2.85 (d, *J* = 7.4 Hz, 2H), 2.67 (d, *J* = 6.8 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 193.4 (C), 170.4 (2xC), 155.9 (C), 151.4 (CH), 136.1 (CH), 129.1 (CH), 129.0 (CH), 67.5 (CH_2), 64.2 (CH_2), 57.4 (C), 53.0 (CH_3), 52.9 (CH_3), 36.6 (CH_2), 36.3 (CH_2), 14.4 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{13}H_{17}O_5$ $[M\text{-}OCO_2Et]^+$: 253.1076; found: 253.1071.

Synthesis of compound **9:**



In a round-bottom flask methyl 4-bromocrotonate (230mg, 1.1 mmol), the tosyl amide derivative **IX**[6] (341 mg, 1 mmol), K_2CO_3 (152 mg, 1.1 mmol) and CH_3CN (10 mL) were placed. The resulting

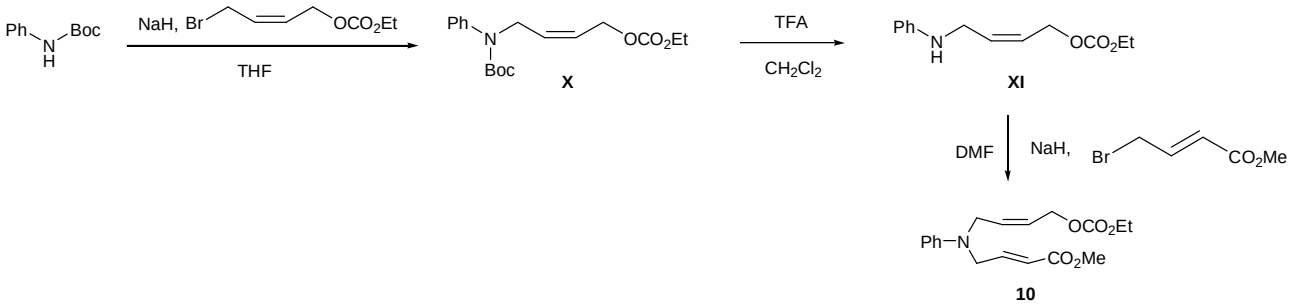
mixture was stirred under reflux for 3 h. Then K_2CO_3 was filtered and the solvent was removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give **9** (298 mg, 68 %) as a colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.69 (dt, *J* = 8.3, 2.1 Hz, 2H), 7.30 (dd, *J* = 8.5, 2.5 Hz, 2H), 6.73 (dt, *J* = 15.6, 5.8 Hz, 1H), 5.93 (dt, *J* = 15.6, 1.7 Hz, 1H), 5.75 – 5.45 (m, 2H), 4.56 (dd, *J* = 7.0, 1.4 Hz, 2H), 4.23 – 4.12 (m, 2H), 3.91 (dd, *J* = 5.7, 1.7 Hz, 2H), 3.87 (d, *J* = 1.4 Hz, 2H), 3.71 (s, 3H), 2.42 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 166.1(C), 143.9 (C), 142.8 (C), 136.7 (C), 130.0 (2xCH), 129.9 (CH), 127.6 (CH), 127.4 (2xCH), 127.3 (CH), 123.7 (CH), 64.3 (CH_2), 62.5 (CH_2), 51.8 (CH_3), 48.2 (CH_2), 44.8 (CH_2), 21.6 (CH_3), 14.3 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{19}H_{26}NO_7S$ $[M+1]^+$: 412.1430; found: 412.1430.

Synthesis of compound **10:**



Compound X: A sample of (*Z*)-$BrCH_2CH{=}CHCH_2CO_2Et$ (1 g, 4.5 mmol) was added to a mixture of NaH (270 mg, 6.8 mmol) and *N*-Boc aniline (878 mg, 4.5 mmol) in DMF (20 mL) at 0ºC. The resulting solution was stirred at 60ºC for 15 h. Then the mixture was diluted with EtOAc, washed with HCl (10%), dried over anhydrous Na_2SO_4, and the solvent removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 1:9) to give **X** (1 g, 70 %) as a colorless oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.34 – 7.28 (m, 2H), 7.24 – 7.16 (m, 3H), 5.99 – 5.85 (m, 1H), 5.80 – 5.64 (m, 1H), 4.62 (dd, *J* = 6.0, 1.0 Hz, 2H), 4.28 – 4.15 (m, 4H), 1.46 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 155.2 (C), 154.6 (C), 142.9 (C), 131.7 (CH), 128.9 (3xCH), 126.7 (CH), 126.1 (CH), 125.9 (CH), 80.7 (C), 67.6 (CH_2), 64.2 (CH_2), 51.9 (CH_2), 28.5 (3xCH_3), 14.5 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{18}H_{25}NO_5$ $[M]^+$: 335.1733; found: 335.1733.

Compound XI: An excess of trifluoroacetic acid (TFA) was added to a solution of **X** (502 mg, 1.5mmol) in CH_2Cl_2 (15 mL). The resulting mixture was stirred at room temperature for 2h and then the solvent was removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give **XI** (318 mg, 90%) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.21 – 7.15 (m, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 2H), 5.98 – 5.90 (m, 1H), 5.89 – 5.80 (m, 1H), 4.62 (d, *J* = 5.9 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.79 (d, *J* = 5.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 155.1 (C), 132.8 (CH), 129.3 (2xCH), 128.8 (C), 125.3 (CH), 117.8 (CH), 113.1 (2xCH), 67.6 (CH_2), 64.1 (CH_2), 45.3 (CH_2), 14.4 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{13}H_{17}NO_3$ $[M]^+$: 235.1208; found: 235.1210

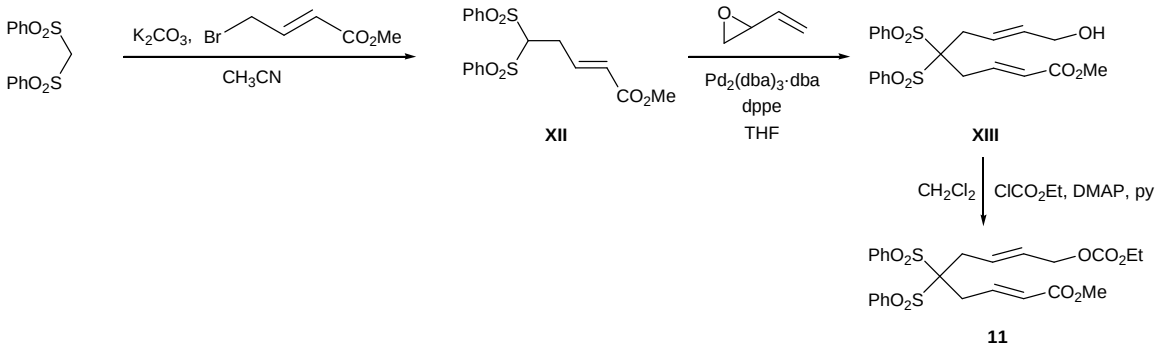
Compound 10: Methyl 4-bromocrotonate (314mg, 1.5 mmol) was added to a mixture of NaH (60 mg, 1.5 mmol) and **XI** (235 mg, 1 mmol) in DMF (10 mL) at 0ºC. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na_2SO_4. The residue was submitted to flash chromatography (EtOAc: Hexane, 4:6) to give **10** (111 mg, 33 %) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.21 (t, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 14.4 Hz, 1H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 2H), 5.96 (d, *J* = 16.2 Hz, 1H), 5.80 – 5.68 (m, 2H), 4.72 (d, *J* = 3.7 Hz, 2H), 4.26 – 4.18 (m, 2H), 4.08 – 4.01 (m, 4H), 3.72 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 166.7 (C), 155.2 (C), 144.9 (C), 132.1 (CH), 129.5 (3xCH), 125.8 (CH), 121.9 (CH), 117.6 (CH), 112.9 (2xCH), 64.3 (CH_2), 63.0 (CH_2), 51.9 (CH_2), 51.7 (CH_3), 48.0 (CH_2), 14.4 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{18}H_{23}NO_5$ $[M]^+$: 333.1576; found: 335.1575.

Synthesis of compound **11:**



Compound XII: In a round-bottom flask methyl 4-bromocrotonate (230mg, 1.1 mmol), bis(phenylsulfonyl)methane (296 mg, 1 mmol), K_2CO_3 (152 mg, 1.1 mmol) and CH_3CN (10 mL) were placed. The resulting mixture was stirred under reflux for 3 h. Then K_2CO_3 was filtered and the solvent was removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 3:7) to give **XII** (276mg, 70 %) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.85 (d, *J* = 7.4 Hz, 4H), 7.61 (t, *J* = 7.3 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 4H), 6.71 (dt, *J* = 14.3, 7.0 Hz, 1H), 5.69 (d, *J* = 15.5 Hz, 1H), 4.53 (t, *J* = 5.9 Hz, 1H), 3.61 (s, 3H), 3.00 (t, *J* = 6.4 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 165.9 (C), 141.7 (CH), 137.6 (2xC), 134.9 (2xCH), 129.7 (4xCH), 129.3 (4xCH), 124.4 (CH), 82.3 (CH), 51.7 (CH_3), 28.3 (CH_2).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{18}H_{18}O_6S_2$ [M^+]: 394.0545; found: 394.0537.

Compound XIII: Butadiene monoxide (35mg, 0.5mmol) was added to a solution of **XII** (197mg, 0.5mmol), $Pd_2(dba)_3$·dba (4mg, 0.025mmol) and dppe (10mg, 0.025mmol) in THF (10mL). The resulting mixture was stirred at room temperature for 16 h and then solvent was removed. The residue was filtered through a short silica pad to give **XIII** (47mg, 63%) as a white foam.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.95 (d, *J* = 7.8 Hz, 4H), 7.64 (t, *J* = 7.4 Hz,2H), 7.51 (t, *J* = 7.5 Hz, 4H), 7.00 – 6.89 (m, 1H), 5.80 (d, *J* = 15.7 Hz, 1H), 5.74 (t, *J* = 6.5 Hz, 1H), 5.68 (dd, *J* = 9.5, 4.7 Hz, 1H), 4.00 (d, *J* = 4.6 Hz, 2H), 3.64 (s, 3H), 3.04 (d, *J* = 6.9 Hz, 2H), 2.94 (d, *J* = 6.2 Hz, 2H), 2.18 (s, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 166.0 (C), 140.3 (CH), 136.4 (2xC), 136.2 (CH), 135.0 (2xCH), 131.5 (4xCH), 128.8 (4xCH), 125.5 (CH), 122.3 (CH), 89.6 (C), 62.8 (CH_2), 51.8 (CH_3), 32.9 (CH_2), 32.4 (CH_2).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{22}H_{25}O_7S_2$ [M+1]$^+$: 465.1042; found: 465.1044.

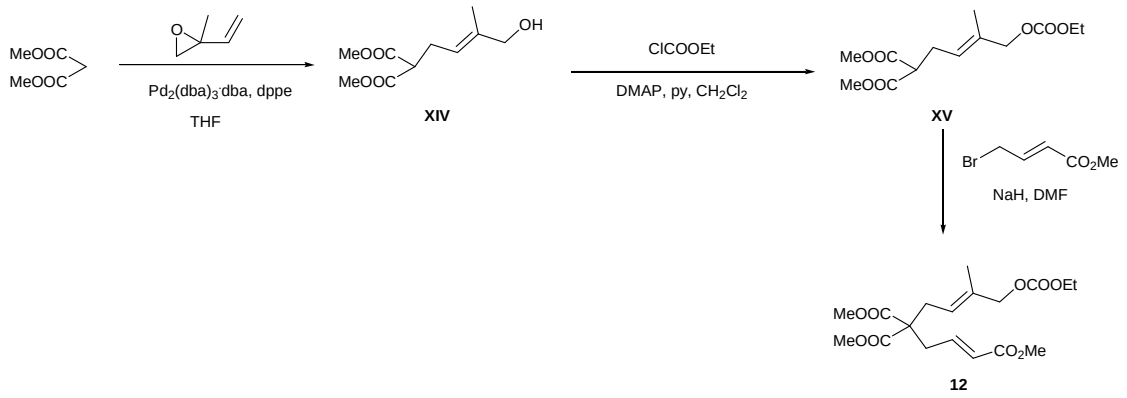
Compound 11: Ethyl chloroformiate (31 mg, 0.29 mmol) was added to a solution of **XIII** (122 mg, 0.26 mmol), dimethylaminopyridine (DMAP) (10 mg, 0.08 mmol), pyridine (62 mg, 0.8 mmol) in CH_2Cl_2 (5 mL), and it was stirred at room temperature for 16 h. Then the mixture was diluted with CH_2Cl_2, washed with HCl (10%), NaOH (10%) and brine and dried over anhydrous Na_2SO_4. The residue was submitted to flash chromatography (EtOAc: Hexane, 4:6) to give **11** (85 mg, 55%) as a colorless foam.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.03 (d, *J* = 8.3 Hz, 4H), 7.72 (t, *J* = 7.1 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 4H), 7.05 – 6.95 (m, 1H), 5.98 – 5.90 (m, 1H), 5.88 (d, *J* = 15.5 Hz, 1H), 5.75 – 5.67 (m, 1H), 4.55 (d, *J* = 6.1 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.11 (d, *J* = 6.9 Hz, 2H), 3.02 (d, *J* = 6.7 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 165.8 (C), 155.0 (C), 139.9 (CH), 136.5 (2xC), 135.1 (2xCH), 131.7 (4xCH), 130.4 (CH), 128.9 (4xCH), 126.7 (CH), 125.9 (CH), 89.6 (C), 67.3 (CH_2), 64.3 (CH_2), 51.8 (CH_3), 33.1 (CH_2), 32.6 (CH_2), 14.4 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{25}H_{28}O_9S_2$ [M]$^+$: 536.1175; found: 536.1176.

Synthesis of compound **12:**



Compound XIV: Isoprene monoxide (191 mg, 2.27 mmol) was added to a solution dimethylmalonate (300 mg, 2.27 mmol), $Pd_2(dba)_3$·dba (20 mg, 0.11 mmol) and dppe (44 mg, 0.11 mmol) in THF (10 mL). The resulting mixture was stirred at room temperature for 3 h and then solvent was removed. The residue was filtered through a short silica pad to give **XIV** (476 mg, 97%) as colourless oil. Its spectroscopic data were identical to the reported compound.[8]

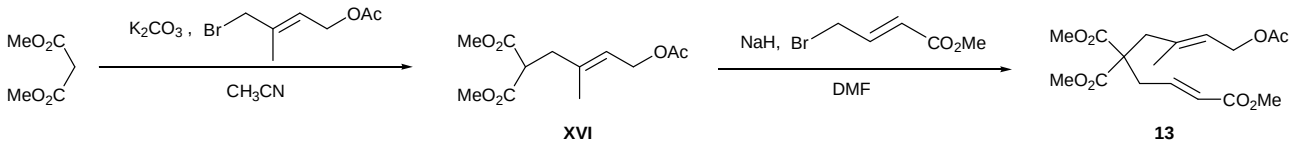
Compound XV: Ethyl chloroformiate (285 mg, 2.64 mmol) was added to a solution of **II** (476 mg, 2.20 mmol), dimethylaminopyridine (DMAP) (81 mg, 0.66 mmol), pyridine (521 mg, 6.6 mmol) in CH_2Cl_2, and it was stirred at room temperature for 16 h. Then the mixture was diluted with CH_2Cl_2, washed with HCl (10%), NaOH (10%) and brine and dried over anhydrous Na_2SO_4. The residue was submitted to flash chromatography (EtOAc:Hexane, 4:6) to give **XV** (628 mg, 99%) as a colourless oil. Its spectroscopic data were identical to the reported compound.[8]

Compound 12: Methyl 4-bromocrotonate (585 mg, 3.27 mmol) was added to a mixture of NaH (131 mg, 3.27 mmol) and **XV** (628 mg, 2.18 mmol) in DMF (15 mL) at 0ºC. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with HCl (10%) and dried over anhydrous Na_2SO_4. The residue was submitted to flash chromatography (EtOAc:Hexane, 4:6) to give **12** (513 mg, 61%, 3:2 mixture of isomers) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.81 - 6.73 (m, 2H), 5.87 (dd, *J* = 3.9, 2.5 Hz, 1H, major isomer), 5.84 (dd, *J* = 3.9, 2.5 Hz, 1H, minor isomer), 5.33 (dd, *J* = 8.1, 6.8 Hz, 1H, minor isomer), 5.25 (dd, *J* = 8.1, 6.8 Hz, 1H, major isomer), 4.59 (s, 2H, major isomer), 4.48 (s, 2H, minor isomer), 4.20 (q, *J* = 7.1 Hz, 4H), 3.73 (s, 12H), 3.71 (s, 6H), 2.76 (d, *J* = 7.7 Hz, 4H), 2.70 (d, *J* = 7.8 Hz, 2H, major isomer), 2.66 (d, *J* = 7.1 Hz, 2H, minor isomer), 1.78 (s, 3H, major isomer), 1.67 (s, 3H, minor isomer), 1.31 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 170.8 (2xC), 166.3 (C), 155.3 (C), 142.7 (CH), 134.4 (C), 125.0 (CH), 123.6 (CH, major isomer), 122.5 (CH, minor isomer), 72.9 (CH_2), 65.9 (CH_2, major isomer), 64.2 (CH_2, minor isomer), 57.5 (C), 52.9 (2xCH_3), 51.7 (CH_3), 35.7(CH_2), 31.6 (CH_2), 21.7 (CH_3), 14.4 (CH_3). **HRMS** (EI, 70eV) *m*/*z* calcd. for $C_{18}H_{26}O_9$ $[M]^+$: 386.1577; found: 386.1581.

Synthesis of compound **13:**



Compound XVI: In a round-bottom flask dimethylmalonate (660 mg, 5 mmol), K_2CO_3 (760 mg, 5.5 mmol), *trans*-4-acetoxy-1-bromo-2-methyl-2-butene[7] (1.13 g, 5.5 mmol), and CH_3CN (15 mL) were placed. The resulting mixture was stirred under reflux for 16 h. Then K_2CO_3 was filtered and the solvent was removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give **XVI** (894mg, 69 %) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.34 (t, *J* = 6.3 Hz, 1H), 4.50 (d, *J* = 6.9 Hz, 2H), 3.69 (s, 6H), 3.55 (t, *J* = 7.9 Hz, 1H), 2.60 (d, *J* = 7.7 Hz, 2H), 1.99 (s, 3H), 1.68 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 170.9 (C), 169.3 (2xC), 137.6 (C), 121.4 (CH), 60.9 (CH_2), 52.6 (2xCH_3), 50.3 (CH), 38.3 (CH_2), 21.0 (CH_3), 16.3 (CH_3).

A good quality mass spectra could not be obtained.

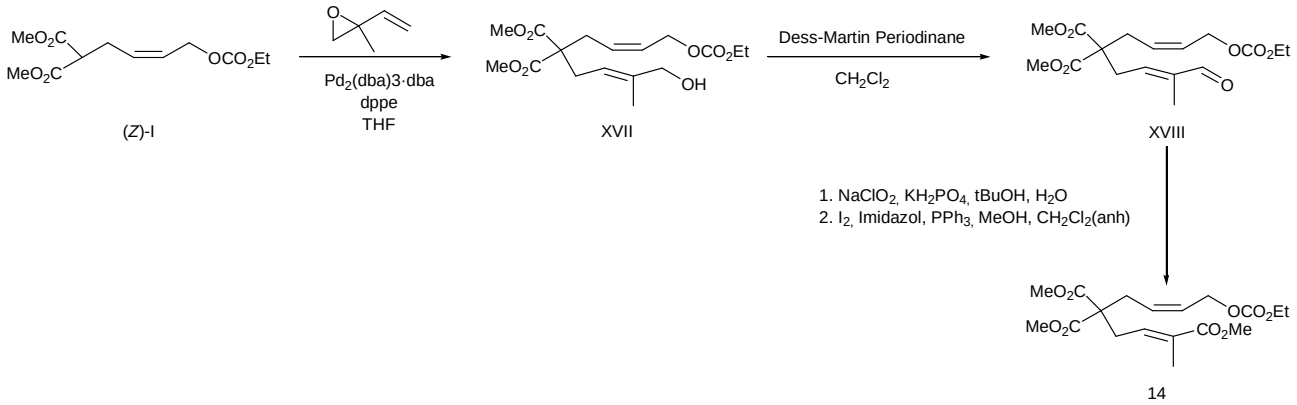
Compound 13: Methyl 4-bromocrotonate (107mg, 0.6 mmol) was added to a mixture of NaH (30 mg, 0.75 mmol) and **XVI** (125 mg, 0.5 mmol) in DMF (5 mL) at 0ºC. The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with EtOAc, washed with aqueous NH_4Cl, dried over anhydrous Na_2SO_4, and the solvent removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give **13** (90 mg, 50%) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.78 (tt, *J* = 15.4, 7.6 Hz, 1H), 5.87 (t, *J* = 15.9 Hz, 1H), 5.43 – 5.33 (m, 1H), 4.55 (d, *J* = 6.8 Hz, 2H), 3.72 (s, 6H), 3.72 (s, 3H), 2.75 (dd, *J* = 7.6, 1.2 Hz, 2H), 2.72 (d, *J* = 6.0 Hz, 2H), 2.04 (s, 3H), 1.62 (s, 3H)

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 171.0 (2xC), 166.3 (C), 142.9 (CH), 136.0 (C), 125.0 (CH), 124.9 (CH), 124.2 (C), 61.0 (CH_2), 57.3 (C), 52.8 (2xCH_3), 51.7 (CH_3), 42.8 (CH_2), 35.7 (CH_2), 21.0 (CH_3), 17.2 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{17}H_{24}O_8$ $[M]^+$: 356.1471; found: 356.1462.

Synthesis of compound **14:**



Compound XVII: Isoprene monoxide (0.04 mL, 0.38 mmol) was added to a solution of the dimethylmalonate derivative **(Z)-I** (100 mg, 0.038 mmol), $Pd_2(dba)_3$·dba (6 mg, 0.1 mmol) and dppe (16 mg, 0.038 mmol) in THF (10 mL) and the mixture was stirred at room temperature for 16 h. The solvent was removed and the residue was submitted to flash chromatography (EtOAc: Hexane,) to give **XVII** (105 mg, 79 %) as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.74 – 5.58 (m, 2H), 5.11 (t, *J* = 8.3 Hz, 1H), 4.53 (d, *J* = 4.8 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.07 (d, *J* = 2.3 Hz, 2H), 3.71 (s, 6H), 2.68 – 2.56 (m, 4H), 1.79 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) = 171.3 (C), 154.9 (C), 139 (C), 129.9 (CH), 128.1 (CH), 120.5 (CH), 120.4 (CH), 67.6 (CH_2), 64.0 (CH_2), 61.2 (CH_2), 57.8 (C), 52.6 (CH_3), 52.6 (CH_3), 35.8 (CH_2), 31.0 (CH_2), 21.7 (CH_3), 14.2 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{14}H_{21}O_5$ $[M\text{-}OCO_2Et]^+$: 269.1389; found: 269.1361.

Compound XVIII: Dess-Martin periodinane (DMP) (77 mg, 0.17 mmol) was added to a solution of **XVII** (29 mg, 0.08 mmol) in CH_2Cl_2 (5 mL). The resulting mixture was stirred for 3 h at room temperature and then washed with saturated aqueous solution of $Na_2S_2O_3$ and $NaHCO_3$ in 1:1 proportion, dried over anhydrous Na_2SO_4 and the solvent removed. The residue was submitted to flash chromatography (EtOAc: Hexane,) to give **XVIII** (20 mg, 69 %) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.39 (s, 1H), 6.35 (t, *J* = 7.3 Hz, 1H), 5.66 (m, 2H), 4.54 (d, *J* = 4.7 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 6H), 2.90 (d, *J* = 7.3 Hz, 2H), 2.69 (d, *J* = 5.8 Hz, 2H), 1.74 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 193.4 (CH), 170.4 (2xC), 155.0 (C), 151.4 (CH), 136.1 (CH), 129.1 (CH), 129.0 (CH), 67.5 (CH_2), 64.2 (CH_2), 57.4 (C), 52.9 (2xCH_3), 36.6 (CH_2), 36.3 (CH_2), 29.8 (CH_3), 14.4 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{15}H_{21}O_6$ $[M\text{-}CO_2Me]^+$: 297.1338; found: 297.1347.

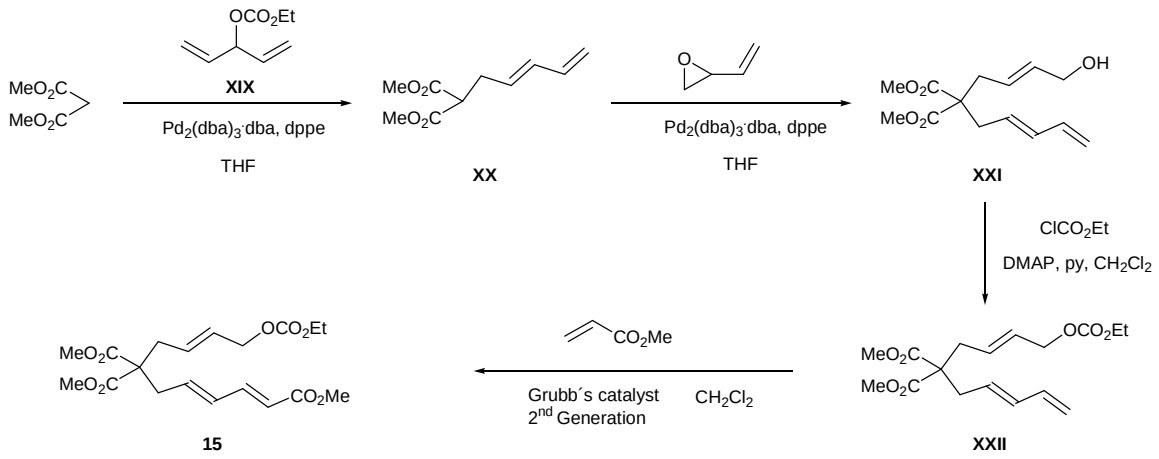
Compound 14: Sodium chlorite (660 mg, 7.25 mmol) and potassium dihydrogen phosphate (720 mg, 5.28 mmol) were added to a solution of **XVIII** (190 mg, 0.55 mmol) in water (4 mL) and *t*-butanol (10 mL). The resulting solution was stirred at room temperature for 16 h. Then the mixture was diluted with diethyl ether, washed with water, dried over anhydrous Na_2SO_4, and the solvent removed. In a separated flask equipped with a magnetic stir bar, a solution of iodine (183 mg, 1.05 mmol) in dry CH_2Cl_2 (10 mL) and triphenylphosphine (275 mg, 1.5 mmol) was prepared. Then, imidazole (160 mg, 3.3 mmol) was added and a white solid appeared. Subsequently, the carboxylic acid without further purification (160 mg, 0.7 mmol) and dissolved in dry CH_2Cl_2 (5 mL) was added and then dry MeOH (1 mL). The resulting mixture was stirred at room temperature for 16 h. Then the mixture was diluted with CH_2Cl_2, washed with 2 N HCl, dried over anhydrous Na_2SO_4, and the solvent removed. The residue was submitted to flash chromatography (EtOAc: Hexane,) to give **14** (148 mg, 70%) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.53 (t, *J* = 7.4 Hz, 1H), 5.70 – 5.62 (m, 1H), 5.51 – 5.43 (m, 1H), 4.58 (d, *J* = 6.8 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 6H), 3.67 (s, 3H), 2.73 (d, *J* = 7.5 Hz, 2H), 2.68 (d, *J* = 7.7 Hz, 2H), 1.78 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 170.7 (2xC), 167.9 (C), 155.0 (C), 134.8 (CH), 131.1 (C), 128.0 (CH), 127.4 (CH), 64.0 (CH_2), 63.0 (CH_2), 57.1 (C), 52.8 (2xCH_3), 51.9 (CH_3), 32.0 (CH_2), 31.2 (CH_2), 14.3 (CH_3), 12.6 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{18}H_{26}O_9$ $[M]^+$: 386.1577; found: 386.1575.

Synthesis of compound **15:**



Compound XX: Carbonate **XIX** (590 mg, 3.79 mmol) was added to a solution of dimethylmalonate (500 mg, 2.27 mmol), $Pd_2(dba)_3$·dba (33 mg, 0.19 mmol) and dppe (75 mg, 0.19 mmol) in THF (10 mL). The resulting mixture was stirred at room temperature for 3 h and then solvent was removed. The

residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give **XX** (549 mg, 73%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.34 – 6.20 (m, 1H), 6.17 - 6.01 (m, 1H), 5.62 (dt, *J* = 14.9, 7.3 Hz, 1H), 5.13 (dd, *J* = 16.7, 1.6 Hz, 1H), 5.02 (dd, *J* = 10.1, 1.6 Hz, 1H), 3.73 (s, 6H), 3.44 (t, *J* = 7.6 Hz, 1H), 2.66 (dd, *J* = 13.8, 7.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 169.7 (2xC), 137.0 (CH), 134.3 (CH), 129.8 (CH), 117.1 (CH_2), 53.0 (2xCH_3), 52.1 (CH), 32.3 (CH_2).

LRMS (EI, 70 eV) *m*/*z* calcd. for $C_6H_9O_4$ $[M\text{-}C_4H_5]^+$: 145.05; found: 145.03. A good HRMS could not be obtained.

Compound XXI: Butadiene monoxide (176 mg, 2.52 mmol) was added to a solution of compound **XX** (500 mg, 2.52 mmol), $Pd_2(dba)_3$·dba (22 mg, 0.13 mmol) and dppe (50 mg, 0.13 mmol) in THF (10 mL). The resulting mixture was stirred at room temperature for 16 h and then solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 4:6) to give **XXI** (506 mg, 75%) as colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.26 (dt, *J* = 17.0, 10.3 Hz, 1H), 6.12 - 6.03 (m, 1H), 5.75 - 5.64 (m, 1H), 5.51 (ddt, *J* = 18.1, 15.2, 7.5 Hz, 2H), 5.12 (dd, *J* = 16.6, 4.5 Hz, 1H), 5.02 (dd, *J* = 9.9, 5.3 Hz, 1H), 4.07 (d, *J* = 5.4 Hz, 2H), 3.70 (s, 6H), 2.64 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 171.1 (2xC), 136.5 (CH), 135.2 (CH), 134.0 (CH), 127.6 (CH), 125.8 (CH), 116.6 (CH_2), 63.2 (CH_2), 58.0 (C), 52.4 (2xCH_3), 35.9 (CH_2), 35.6 (CH_2).

LRMS (EI, 70 eV) *m*/*z* calcd. for $C_6H_9O_4$ $[M\text{-}C_8H_{11}O]^+$: 145.05; found: 145.04. A good HRMS could not be obtained.

Compound XXII: Ethyl chloroformiate (245 mg, 2.27 mmol) was added to a solution of **XXI** (506 mg, 1.89 mmol), dimethylaminopyridine (DMAP) (70 mg, 0.57 mmol) and pyridine (448 mg, 5.67 mmol) in CH_2Cl_2, and it was stirred at room temperature for 16 h. Then the mixture was diluted with CH_2Cl_2, washed with HCl (10%), NaOH (10%) and brine and dried over anhydrous Na_2SO_4. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give **XXII** (513 mg, 80%) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.23 (dt, *J* = 16.9, 10.2 Hz, 1H), 6.03 (dd, *J* = 14.6, 10.7 Hz, 1H), 5.65 - 5.58 (m, 2H), 5.44 (dt, *J* = 15.1, 7.6 Hz, 1H), 5.09 (d, *J* = 16.8 Hz, 1H), 4.98 (d, *J* = 10.1 Hz, 1H), 4.55 - 4.42 (m, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.67 (s, 6H), 2.63 - 2.55 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 171.5 (2xC), 155.5 (C), 137.1 (CH), 135.9 (CH), 130.5 (CH), 128.8 (CH), 128.1 (CH), 117.2 (CH_2), 68.2 (CH_2), 64.6 (CH_2), 58.4 (C), 53.0 (2xCH_3), 36.6 (CH_2), 36.3 (CH_2), 14.9 (CH_3).

HRMS (EI, 70eV) *m*/*z* calcd. for $C_{17}H_{24}O_7$ $[M]^+$: 340.1522; found: 340.1527

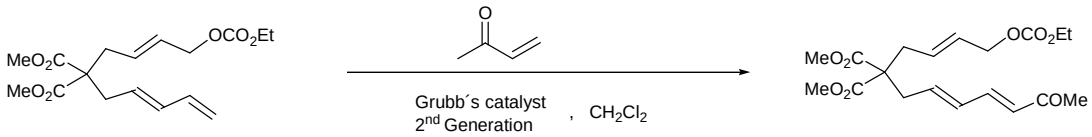
Compound 15: Methylacrilate (163 mg, 1.90 mmol) was added to a deoxygenated solution of Grubb´s 2nd generation catalyst (11 mg, 0.03 mmol) and compound **XXII** (215 mg, 0.63 mmol) in dry CH_2Cl_2 (2 mL). The resulting mixture was refluxed for 16 hours and the solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give a 10: 1 mixture (120 mg, 48%) of the *E*- and *Z*- isomers in the carbonate as a colourless oil. Data of the major isomer **15**:

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.20 (dd, *J* = 15.4, 11.0 Hz, 1H), 6.24 - 6.10 (m, 1H), 5.98 - 5.86 (m, 1H), 5.81 (d, *J* = 15.4 Hz, 1H), 5.70 - 5.57 (m, 2H), 4.53 (d, *J* = 4.9 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 3.70 (s, 6H), 2.72 - 2.68 (m, 2H), 2.67 - 2.54 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 170.8 (2xC), 167.5 (C), 155.1 (C), 144.1 (CH), 137.0 (CH), 132.4 (CH), 129.7 (CH), 128.7 (CH), 120.8 (CH), 67.7 (CH_2), 64.2 (CH_2), 57.8 (C), 52.8 (2xCH_3), 51.7 (CH_3), 36.7 (CH_2), 36.2 (CH_2), 14.5 (CH_3).

HRMS (EI, 70eV) *m*/*z* calcd. for $C_{19}H_{26}O_9$ $[M]^+$: 398.1577; found: 398.1566.

Synthesis of compound **16:**



XXII **16**

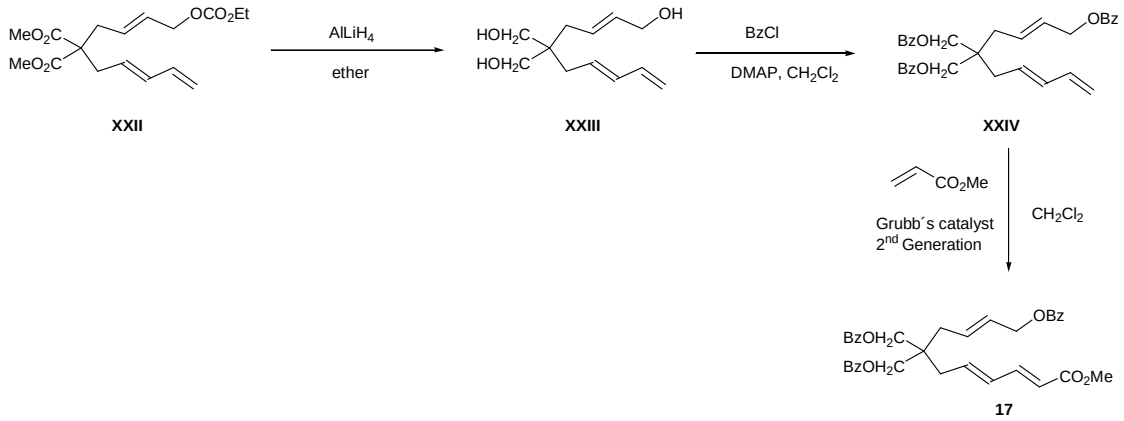
Compound 16: Methylvinylketone (185 mg, 2.65 mmol) was added to a deoxygenated solution of Grubb´s 2nd generation catalyst (15 mg, 0.05 mmol) and compound **XXII** (300 mg, 0.88 mmol) in dry CH_2Cl_2 (2 mL). The resulting mixture was refluxed for 16 hours and the solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give a 5:1 mixture (100 mg, 30%) of the *E*- and *Z*- isomers in the carbonate as a colourless oil. Data of the major isomer **16**:

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.02 (dd, *J* = 15.7, 10.7 Hz, 1H), 6.25 - 6.12 (m, 1H), 6.03 (d, *J* = 15.7 Hz, 1H), 6.03 - 5.91 (m, 1H), 5.65 - 5.59 (m, 2H), 4.52 (d, *J* = 4.9 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 6H), 2.74 - 2.65 (m, 2H), 2.65 - 2.57 (m, 2H), 2.23 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 198.9 (C), 171.0 (2xC), 155.3 (C), 143.0 (CH), 138.0 (CH), 133.1 (CH), 130.6 (CH), 129.8 (CH), 128.9 (CH), 67.9 (CH_2), 64.4 (CH_2), 58.0 (C), 53.0 (2xCH_3), 37.0 (CH_2), 36.4 (CH_2), 27.5 (CH_3), 14.7 (CH_3).

HRMS (EI, 70eV) *m*/*z* calcd. for $C_{19}H_{26}O_8$ $[M]^+$: 382.1628; found: 382.1624.

Synthesis of compound **17:**



Compound XXIII and XXIV: $AlLiH_4$ (489 mg, 13.23 mmol) was added to a solution of compound **XXII** (300 mg, 0.88 mmol) in THF (20 mL). The mixture was stirred at room temperature for 24 h. Then the mixture was diluted with EtOAc, washed with H_2O, dried over anhydrous Na_2SO_4, and the solvent removed. The mixture was filtered through a short silica pad. The crude was diluted in CH_2Cl_2 (15 mL) and DMAP (313 mg, 2.56 mmol) and benzoyl chloride (360 mg, 2.56 mmol) was added. The mixture was stirred at room temperature for 16h and then the solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give **XXIV** (113 mg, 25%) as a viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.04 - 7.98 (m, 6H), 7.57 - 7.49 (m, 3H), 7.46 - 7.37 (m, 6H), 6.30 (dt, *J* = 17.0, 10.2 Hz, 1H), 6.14 (ddd, *J* = 15.2, 12.3, 7.3 Hz, 1H), 6.02 - 5.88 (m, 1H), 5.88 - 5.68 (m, 2H), 5.08 (d, *J* = 16.9 Hz, 1H), 5.00 (d, *J* = 10.1 Hz, 1H), 4.76 (d, *J* = 6.1 Hz, 2H), 4.33 (s, 4H), 2.37 (d, *J* = 7.6 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 166.3 (3xC), 136.6 (CH), 135.5 (CH), 133.3 (3xCH), 133.0 (CH), 130.7 (CH), 130.0 (3xC), 129.7 (6xCH), 128.6 (6xCH), 128.0 (CH), 116.6 (CH_2), 66.9 (2xCH_2), 65.2 (CH_2), 41.6 (C), 36.0 (CH_2), 35.8 (CH_2).

HRMS (EI, 70eV) *m*/*z* calcd. for $C_{33}H_{32}O_6$ $[M]^+$: 524.2199; found: 524.2188.

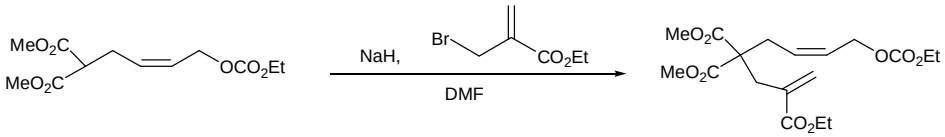
Compound 17: Methyacrylate (46 mg, 0.53 mmol) was added to a deoxygenated solution of Grubb´s 2º generation catalyst (4 mg, 0.05 mmol) and compound **XXIV** (93 mg, 0.18 mmol) in dry CH_2Cl_2 (2 mL). The resulting mixture was refluxed for 24 hours and the solvent was removed. The residue was submitted to flash chromatography (EtOAc:Hexane, 2:8) to give a 5:1 mixture (43 mg, 42%) of the *E*- and *Z*- isomers in the benzoate as a colourless oil. Data of the major compound **17**:

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.01 (d, *J* = 7.1 Hz, 6H), 7.60 - 7.51 (m, 3H), 7.43 (t, *J* = 7.5 Hz, 6H), 7.28 - 7.18 (m, 1H), 6.25 - 6.17 (m, 2H), 5.95 - 5.87 (m, 1H), 5.86 - 5.79 (m, 1H), 5.76 (d, *J* = 15.5 Hz, 1H), 4.77 (d, *J* = 5.7 Hz, 2H), 4.35 (s, 4H), 3.73 (s, 3H), 2.45 (d, *J* = 6.6 Hz, 2H), 2.38 (d, *J* = 7.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) =167.4 (C), 166.2 (3xC), 144.1 (CH), 137.4 (CH), 133.4 (3xCH), 132.5 (CH), 130.2 (3xC), 129.7 (6xCH), 129.2 (CH), 129.1 (CH), 128.6 (6xCH), 120.5 (CH), 66.6 (2xCH_2), 65.1 (CH_2), 51.6 (CH_3), 41.8 (C), 36.4 (CH_2), 35.8 (CH_2).

A good quality mass spectra could not be obtained.

Synthesis of compound **18:**



(*Z*)-I **18**

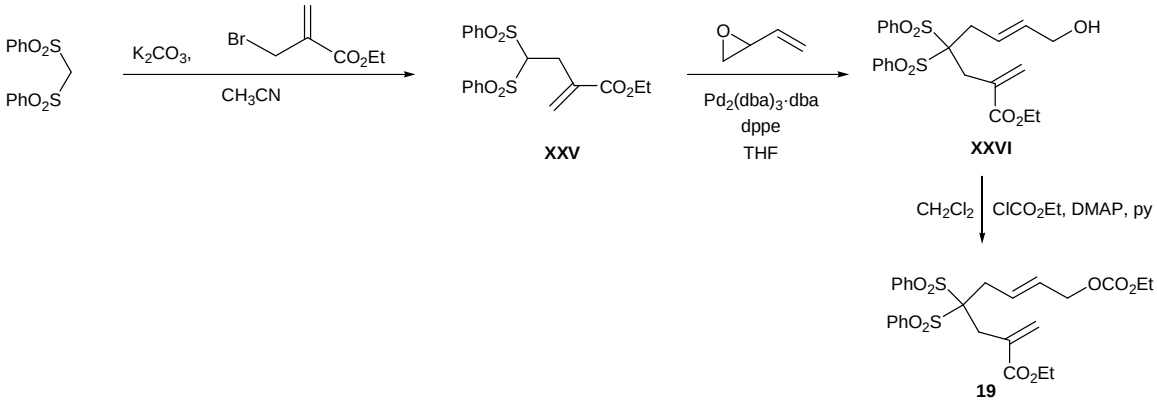
Ethyl (2-bromomethyl)acrylate (212 mg, 1.1 mmol) was added to a mixture of NaH (44 mg, 1.1 mmol) and **(Z)-I** (274 mg, 1 mmol) in DMF (10 mL) at 0ºC. The resulting solution was stirred at room temperature for 24 h. Then the mixture was diluted with EtOAc, washed with aqueous NH_4Cl, dried over anhydrous Na_2SO_4, and the solvent removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 2:8) to give **18** (211 mg, 52%) as a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.26 (d, *J* = 1.2 Hz, 1H), 5.68 (dt, *J* = 13.4, 6.7 Hz, 1H), 5.61 (s, 1H), 5.63 – 5.56 (m, 1H), 4.64 (d, *J* = 6.6 Hz, 2H), 4.171 (q, *J* = 7.1 Hz, 2H), 4.166 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 6H), 2.97 (d, *J* = 11.9 Hz, 2H), 2.64 (d, *J* = 7.3 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 170.9 (2xC), 166.9 (C), 155.2 (C), 136.1 (C), 129.1 (CH_2), 128.5 (CH), 127.0 (CH), 64.1 (CH_2), 63.3 (CH_2), 61.1 (CH_2), 57.8 (C), 52.6 (2xCH_3), 34.2 (CH_2), 31.1 (CH_2), 14.4 (CH_3), 14.3 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{18}H_{26}O_9$ $[M]^+$: 386.1577; found: 386.1577

Synthesis of compound **19:**



Compound XXV: In a round-bottom flask ethyl (2-bromomethyl)acrylate (213mg, 1.1 mmol), bis(phenylsulfonyl)methane (296 mg, 1 mmol), K_2CO_3 (152 mg, 1.1 mmol) and CH_3CN (10 mL) were

placed. The resulting mixture was stirred under reflux for 5 h. Then K_2CO_3 was filtered and the solvent was removed. The residue was submitted to flash chromatography (EtOAc: Hexane, 3:7) to give **XXV** (320 mg, 79 %) as a colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.97 – 7.85 (m, 4H), 7.68 (t, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 4H), 6.24 (s, 1H), 5.73 (s, 1H), 5.32 (t, *J* = 7.0 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.18 (d, *J* = 7.0 Hz, 2H), 1.25 (t, *J* = 7.1 Hz,3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 138.4 (C), 134.6 (2xCH), 134.1 (C), 132.0 (C), 129.70 (CH_2), 129.67 (4xCH), 129.2 (4xCH), 128.7 (C), 81.2 (CH), 61.2 (CH_2), 29.6 (CH_2), 14.2 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{19}H_{20}O_6S_2$ $[M]^+$: 408.0701; found: 408.0703.

Compound XXVI: Butadiene monoxide (53mg, 0.75mmol) was added to a solution of **XXV** (306 mg, 0.75mmol), $Pd_2(dba)_3$·dba (6 mg, 0.0375mmol) and dppe (15 mg, 0.0375mmol) in THF (10mL) and the mixture was stirred at room temperature for 16h. The solvent was removed and the residue was submitted to flash chromatography (EtOAc: Hexane, 4:6) to give **XXVI** (230mg, 64%) as a colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.26 (d, *J* = 1.2 Hz, 1H), 5.68 (dt, *J* = 13.4, 6.7 Hz, 1H), 5.61 (s, 1H), 5.63 – 5.56 (m, 1H), 4.64 (d, *J* = 6.6 Hz, 2H), 4.171 (q, *J* = 7.1 Hz, 2H), 4.166 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 6H), 2.97 (d, *J* = 11.9 Hz, 2H), 2.64 (d, *J* = 7.3 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.4 (C), 137.3 (2xC), 134.8 (2xCH), 134.5 (CH), 133.7 (C), 132.7 (CH_2), 131.8 (4xCH), 128.8 (4xCH), 124.5 (CH), 90.8 (C), 63.2 (CH_2), 61.5 (CH_2), 33.7 (CH_2), 31.6 (CH_2), 14.1 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{23}H_{26}O_7S_2$ $[M]^+$: 478.1120; found: 478.1119.

Compound 19: Ethyl chloroformiate (52 mg, 0.48 mmol) was added to a solution of **XXVI** (208 mg, 0.44 mmol), dimethylaminopyridine (DMAP) (16 mg, 0.13 mmol), pyridine (103 mg, 1.3 mmol) in CH_2Cl_2 (10 mL), and it was stirred at room temperature for 16 h. Then the mixture was diluted with CH_2Cl_2, washed with saturated NH_4Cl and dried over anhydrous Na_2SO_4. The residue was submitted to flash chromatography (EtOAc: Hexane, 3:7) to give **32** (110 mg, 49%) as a colourless oil.

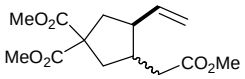
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.04 (d, *J* = 7.9 Hz, 4H), 7.71 (t, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 4H), 6.46 (s, 1H), 6.12 (s, 1H), 6.02 – 5.94 (m, 1H), 5.68 – 5.60 (m, 1H), 4.49 (d, *J* = 6.3 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.38 (s, 2H), 3.00 (d, *J* = 6.4 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 167.1 (C), 155.1 (C), 137.4 (2xC), 134.8 (2xCH), 133.5 (C), 132.6 (CH_2), 131.9 (4xCH), 128.8 (4xCH), 128.7 (CH), 128.6 (CH), 90.7 (C), 67.7 (CH_2), 64.2 (CH_2), 61.4 (CH_2), 33.9 (CH_2), 31.9 (CH_2), 14.4 (CH_3), 14.2 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{26}H_{30}O_9S_2$ $[M]^+$: 550.1331; found: 550.1331.

General procedure for Pd^0-Ti^{III} catalyzed intramolecular Michael-type addition of allylic carboxylates to activated alkenes:

Rigorously deoxygenated THF (10 mL) was added to a mixture of Cp_2TiCl_2 (0.1 mmol), $PdCl_2$ (0.05 mmol), PPh_3 (0.1 mmol) and Mn dust (2 mmol) under Ar atmosphere, and the suspension was stirred at room temperature until it turned dark green (about 15 min). A solution of the activated alkene (0.25 mmol) and 2,4,6-collidine (1.75 mmol) in THF (2 mL) and Me_3SiCl (1 mmol) was then added. The mixture was stirred at room temperature for 21 h and then diluted with AcOEt, washed with HCl (10%), dried over anhydrous Na_2SO_4 and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane mixtures) to give the corresponding products **2**, **20**-**33**.



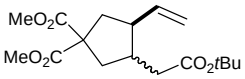
2

Colourless oil. Yield: 73%. Mixture of isomers ≈ 4:1 (*cis-*:*trans-*).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.58 (ddt, *J* = 13.3, 8.3, 6.7 Hz, 1H, major isomer), 5.53-5.47 (m, 1H, minor isomer), 5.00 – 4.88 (m, 2H), 3.65 (s, 3H), 3.64 (s, 3H), 3.56 (s, 3H), 2.79 – 2.68 (m, 1H), 2.51 – 2.37 (m, 1H), 2.25 (dd, *J* = 16.0, 7.0 Hz, 2H), 2.17 – 2.09 (m, 2H), 1.99 – 1.91 (m, 2H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 173.2 (2xC), 172.9 (C), 139.2 (CH, minor isomer), 137.4 (CH, major isomer), 116.5 (CH_2, major isomer), 116.4 (CH_2, minor isomer), 59.0 (C, major isomer), 58.5 (C, minor isomer), 52.94 (CH_3), 52. 90 (CH_3), 51.6 (CH_3, major isomer), 50.2 (CH_3, minor isomer), 45.9 (CH, major isomer), 41.5 (CH, minor isomer), 40. 5 (CH_2, minor isomer), 40.0 (CH_2, minor isomer), 39.2 (CH_2, major isomer), 39.1 (CH), 38.8 (CH_2, major isomer), 37.6 (CH_2, minor isomer), 35.3 (CH_2, major isomer)

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{14}H_{20}O_6$ $[M]^+$: 284.1260; found: 284.1265.



20

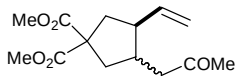
Colourless oil. Yield: 73%. Mixture of isomers ≈ 5:1 (*cis-*:*trans-*).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.66 (ddd, *J* = 16.7, 10.6, 8.7 Hz, 1H, major isomer), 5.62 – 5.56 (m, 1H, minor isomer), 5.06 – 4.97 (m, 2H), 3.71 (s, 3H), 3.71 (s, 3H), 2.83 – 2.75 (m, 1H, major isomer), 2.66 – 2.60 (m, 1H, minor isomer), 2.52 (d, *J* = 7.4 Hz, 1H, minor isomer), 2.50 – 2.47 (m, 2H, major isomer), 2.45 (t, *J* = 6.5 Hz, 1H), 2.23 (dd, *J* = 15.9, 6.9 Hz, 1H), 2.17 (dd, *J* = 14.1, 6.3 Hz, 1H), 2.09 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.06 – 1.97 (m, 1H), 1.42 (s, 9H, minor isomer), 1.41 (s, 9H, major isomer).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 173.1 (C, minor isomer) 173.01 (C, major isomer), 172.97 (C, major isomer), 172.9 (C, minor isomer), 172.1 (C, major isomer), 172.0 (C, minor isomer), 139.4 (CH, minor isomer), 137.6 (CH, major isomer), 116.4 (CH_2), 80.5 (C, minor isomer), 80.4 (C, major isomer),

59.0 (C, major isomer), 58.5 (C, minor isomer), 52.92 (CH_3, major isomer), 52.87 (CH_3, major isomer), 52.85 (2xCH_3, minor isomer), 50.1 (CH, minor isomer), 45.9 (CH, major isomer), 41.7 (CH, minor isomer), 40.5 (CH_2, minor isomer), 39.9 (CH_2, minor isomer), 39.3 (CH, major isomer), 39.2 (CH_2, major isomer), 39.1 (CH_2, minor isomer), 38.9 (CH_2, major isomer), 36.8 (CH_2, major isomer), 28.23 (3xCH_3, minor isomer), 28.21 (3xCH_3, major isomer).

HRMS calcd for $C_{17}H_{27}O_6$ [M^++1]: 327.1808; found:327.1806.



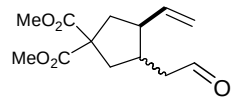
21

Colourless oil. Yield: 63%. Mixture of isomers ≈ 6:1 (*cis-:trans-*).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.69 – 5.58 (m, 1H), 5.07 – 4.94 (m, 2H), 3.721 (s, 3H), 3.716 (s, 3H), 2.85 – 2.76 (m, 1H), 2.62 (ddd, *J* = 19.5, 10.2, 6.1 Hz, 1H), 2.55 (dd, *J* = 13.9, 7.2 Hz, 1H), 2.50 – 2.41 (m, 2H), 2.33 (dd, *J* = 17.4, 7.4 Hz, 1H), 2.13 (dd, *J* = 12.5, 4.9 Hz, 1H), 2.09 (s, 3H), 1.97 (dd, *J* = 13.7, 9.2 Hz, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 207.7 (C), 173.2 (C), 173.0 (C), 137.9 (CH), 116.3 (CH_2), 58.9 (C), 53.0 (CH_3), 52.9 (CH_3), 45.7 (CH_2), 44.5 (CH_2), 39.3 (CH_2), 38.89 (CH_2), 38.0 (CH_2), 30.6 (CH_3).

A good high resolution mass spectra could not be obtained.



22

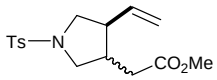
Pale yellow oil. Yield: 26%. Mixture of isomers ≈ 3:2 (*cis-:trans-*).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.75 (t, *J* = 2.0 Hz, 1H, minor isomer), 9.74 (t, *J* = 1.4 Hz, 1H, major isomer), 5.63 (dddd, *J* = 18.2, 17.2, 10.2, 8.4 Hz, 1H, major isomer), 5.59–5.56 (m, 1H, minor isomer), 5.10 – 4.98 (m, 2H), 3.74 (s, 3H, major isomer), 3.73 (s, 3H, minor isomer), 3.73 (s, 3H), 2.88 – 2.80 (m, 1H, minor isomer), 2.70 – 2.60 (m, 2H), 2.56 (dd, *J* = 14.2, 7.4 Hz, 1H), 2.53 – 2.46 (m, 2H), 2.38 – 2.29 (m, 1H), 2.21 – 2.14 (m, 1H), 2.04 (ddd, *J* = 19.4, 13.6, 10.0 Hz, 1H, major isomer), 1.92–1.86 (m, 1H, minor isomer).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 201.5 (C, minor isomer), 201.4 (C, major isomer), 173.0 (2xC, major isomer), 172.9 (C, minor isomer), 172.8 (C, minor isomer), 139.1 (CH, minor isomer), 137.6 (CH, major isomer), 116.9 (CH_2, minor isomer), 116.8 (CH_2, major isomer), 59.0 (C, major isomer), 58.7 (C, minor isomer), 53.03 (2xCH_3, minor isomer), 52.98 (2xCH_3, major isomer), 50.4 (CH, minor isomer), 47.5 (CH_2, minor isomer), 45.9 (CH, major isomer), 45.1 (CH_2, major isomer), 40.4 (CH_2, minor isomer),

40.0 (CH_2, major isomer), 39.5 (CH, minor isomer), 39.3 (CH_2, minor isomer), 38.9 (CH_2, major isomer), 37.1 (CH, major isomer).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{13}H_{18}O_5$ $[M]^+$: 254.1154; found: 254.1155.



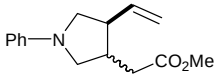
23

Colourless oil. Yield: 67%. Mixture of isomers ≈ 3:2 (*cis*-:*trans*-).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.71 (d, *J* = 8.1 Hz, 4H), 7.32 (d, *J* = 7.7 Hz, 4H), 5.45 (dt, *J* = 18.7, 9.6 Hz, 2H), 5.10 – 4.94 (m, 4H), 3.62 (s, 6H), 3.50 (ddd, *J* = 22.4, 10.0, 7.5 Hz, 1H), 3.38 (dd, *J* = 10.0, 6.6 Hz, 1H), 3.23 (dd, *J* = 10.0, 4.4 Hz, 1H), 3.03 (dd, *J* = 10.0, 7.8 Hz, 1H), 2.94 (dd, *J* = 18.6, 9.0 Hz, 2H), 2.80 (dt, *J* = 13.0, 6.5 Hz, 1H), 2.51 (tt, *J* = 14.3, 7.2 Hz, 1H), 2.43 (s, 6H), 2.31 – 2.22 (m, 2H), 2.15 – 2.03 (m, 2H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 172.4 (C, major isomer), 172.2 (C, minor isomer), 143.64 (C, minor isomer), 143.62 (C, major isomer), 136.0 (CH, minor isomer), 134.5 (CH, major isomer), 134.0 (C, minor isomer), 134.1 (C, major isomer), 129.83 (2xCH, minor isomer), 129.82 (2xCH, major isomer), 127.63 (2xCH, minor isomer), 127.57 (2xCH, major isomer), 118.2 (CH_2, minor isomer), 118.1 (CH_2, major isomer), 53.0 (CH_2, minor isomer), 52.5 (CH_2, major isomer), 51.9 (CH_2, minor isomer), 51.81 (CH_3, minor isomer), 51.79 (CH_3, major isomer), 51.7 (CH_2, major isomer), 48.9 (CH, minor isomer), 45.1 (CH, major isomer), 40.5 (CH, minor isomer), 38.4 (CH, major isomer), 35.9 (CH_2, minor isomer), 33.2 (CH_2, major isomer), 21.64 (CH_3, minor isomer), 21.63 (CH_3, major isomer).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{16}H_{22}NO_4S$ $[M+1]^+$: 324.1270; found: 324.1271.



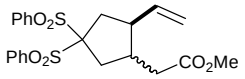
24

Pale orange oil. Yield: 47%. Mixture of isomers ≈ 1:1 (*cis*-:*trans*-).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.25 – 7.20 (m, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.3 Hz, 2H), 5.83 – 5.70 (m, 1H), 5.22 – 5.07 (m, 2H), 3.70 (s, 3H, one isomer), 3.69 (s, 3H, other isomer), 3.51 (ddd, *J* = 12.1, 9.6, 4.5 Hz, 2H), 3.28 (dd, *J* = 9.4, 4.0 Hz, 1H, one isomer), 3.18 – 3.08 (m, 1H), 3.05 (t, *J* = 9.0 Hz, 1H), 2.83 (dt, *J* = 13.8, 6.9 Hz, 1H, one isomer), 2.63 (dt, *J* = 10.6, 5.3 Hz, 1H, other isomer), 2.56 (dt, *J* = 16.7, 8.4 Hz, 1H, one isomer), 2.53 – 2.44 (m, 1H), 2.41 – 2.28 (m, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 173.2 (C), 172.9 (C), 147.7 (C), 147.5 (C), 137.9 (CH), 136.3 (CH), 129.3 (4xCH), 117.5 (CH_2), 117.2 (CH_2), 116.0 (CH), 115.9 (CH), 111.6 (4xCH), 53.4 (CH_2), 53.0 (CH_2), 52.2 (CH_2), 52.0 (CH_2), 51.8 (2xCH_3), 49.2 (CH), 45.3 (CH), 40.7 (CH), 38.4 (CH), 36.6 (CH_2), 34.1 (CH_2).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{15}H_{19}NO_2$ [M]$^+$: 245.1416; found: 254.1410



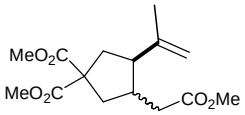
25

Pale yellow solid. Yield: 50%. Mixture of isomers ≈3:2.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.06 (dd, *J* = 13.3, 4.9 Hz, 4H), 7.75 – 7.68 (m, 2H), 7.60 (tdd, *J* = 10.7, 6.1, 4.5 Hz, 4H), 5.81 – 5.71 (m, 1H, minor isomer), 5.48 (ddd, *J* = 17.0, 10.2, 8.5 Hz, 1H, major isomer), 5.09 – 4.98 (m, 2H), 3.65 (s, 3H, minor isomer), 3.64 (s, 3H, major isomer), 3.06–2.96 (m, 1H, minor isomer), 2.86 (dt, *J* = 21.8, 9.1 Hz, 1H, major isomer), 2.74 – 2.66 (m, 2H), 2.53 (ddd, *J* = 14.3, 6.8, 4.2 Hz, 1H), 2.47 (dd, *J* = 15.8, 4.0 Hz, 1H), 2.40 (d, *J* = 11.4 Hz, 1H), 2.36 – 2.32 (m, 2H), 2.32 – 2.24 (m, 1H), 2.17 – 2.08 (m, 1H), 2.02 – 1.95 (m, 1H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 172.9 (C), 172.3 (C), 137.6 (CH), 136.6 (CH), 136.3 (C), 136.1 (C), 134.8 (2xCH), 134.7 (CH), 134.6 (CH), 131.6 (2xCH), 131.5 (2xCH), 131.46 (2xCH), 131.45 (2xCH), 129.8 (C), 129.2 (C), 128.94 (2xCH), 128.89 (2xCH), 128.87 (2xCH), 128.8 (2xCH), 118.1 (CH_2), 117.3 (CH_2), 93.8 (C), 91.8 (C), 51.73 (CH_3), 51.71 (CH_3), 49.9 (CH), 46.5 (CH), 41.5 (CH), 39.1 (CH), 38.2 (CH_2), 37.9 (CH_2), 36.9 (CH_2), 36.8 (CH_2), 36.5 (CH_2), 35.0 (CH_2).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{22}H_{24}O_6S_2$ [M]$^+$: 448.1014; found:448.1011.



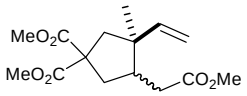
26

Colourless oil. Yield: 68%. Mixture of isomers ≈5:2.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm)= 4.86 (s, 1H, major isomer), 4.79 (s, 1H, minor isomer), 4.76 (s, 1H, minor isomer), 4.69 (s, 1H, major isomer), 3.73 (s, 6H, minor isomer), 3.72 (s, 6H, major isomer), 3.64 (s, 3H, major isomer), 3.63 (s, 3H, minor isomer), 2.72 – 2.58 (m, 2H), 2.54 (dd, *J* = 14.4, 7.0 Hz, 1H), 2.45 (dd, *J* = 15.4, 4.3 Hz, 1H, minor isomer), 2.39 (dd, *J* = 13.4, 6.1 Hz, 1H, major isomer), 2.25 – 2.18 (m, 1H), 2.17 (d, *J* = 4.4 Hz, 1H), 2.14 (d, *J* = 4.1 Hz, 1H), 2.04 (dd, *J* = 16.1, 10.4 Hz, 1H, major isomer) 1.97 – 1.89 (m, 1H, minor isomer), 1.71 (s, 3H, major isomer), 1.67 (s, 3H, minor isomer).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm)= 173.7 (C), 173.1 (2xC), 144.0 (C, minor isomer), 143.6 (C, major isomer), 112.9 (CH_2, minor isomer), 111.8 (CH_2, major isomer), 58.3 (C), 53.1 (CH_3, minor isomer), 53.0 (CH_3, major isomer), 51.6 (CH), 48.9 (2xCH_3), 39.9 (CH_2, minor isomer), 39.4 (CH_2, major isomer), 39.1 (CH_2, minor isomer), 38.9 (CH, minor isomer), 37.9 (CH_2, minor isomer), 37.1 (CH major isomer), 36.1 (CH_2, major isomer), 34.4 (CH_2, major isomer), 23.2 (CH_3).

HRMS (EI, 70eV) (EI, 70 eV) *m*/*z* calcd. for $C_{15}H_{22}O_6$ [M]$^+$: 298.1416; found: 298.1412.



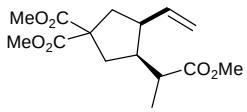
27

Colourless oil. Yield: 35%. Mixture of isomers ≈3:2.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.73 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.06 – 4.94 (m, 2H), 3.72 (s, 6H, minor isomer), 3.72 (s, 6H, major isomer), 3.65 (s, 3H, minor isomer), 3.63 (s, 3H, major isomer), 2.60 – 2.49 (m, 1H), 2.46 (d, *J* = 14.3 Hz, 1H, minor isomer), 2.35 (d, *J* = 14.0 Hz, 1H, major isomer), 2.28 (dt, *J* = 9.0, 3.8 Hz, 1H), 2.25 – 2.03 (m, 4H), 1.13 (s, 3H, minor isomer), 0.88 (s, 3H, major isomer).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 173.5 (C), 173.3 (2xC), 173.2 (C), 173.04 (C), 172.97 (C), 145.7 (CH), 141.5 (CH), 113.8 (CH_2), 113.09 (CH_2), 57.9 (C), 57.8 (C), 53.1 (CH_3), 52.9 (CH_3), 51.69 (CH_3), 51.66 (CH_3), 47.6 (2xCH_2), 47.4 (C), 47.3 (C), 46.2 (CH_2), 46.11 (CH), 44.7 (2xCH), 39.4 (CH_2), 38.7 (CH_2), 34.8 (CH_2), 34.1 (CH_2), 24.1 (CH_3), 17.6 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{15}H_{22}O_6$ $[M]^+$: 298.1416; found:298.1420.



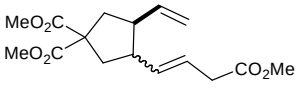
28

Colourless oil. Yield: 64%. Mixture of isomers >15:1. Only one isomer could be characterized and a C-3, C-7-*cis* stereochemistry was tentatively assigned. The stereochemistry at C-8 could not be determined.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.66 (dd, *J* = 16.6, 10.1 Hz, 1H), 5.04 (d, *J* = 10.1 Hz, 1H), 5.00 (s, 1H), 3.70 (s, 6H), 3.65 (s, 3H), 2.77 (m, 1H), 2.58 (dd, *J* = 14.3, 7.3 Hz, 1H), 2.36 – 2.09 (m, 5H), 1.12 (d, *J* = 6.7 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 176.6 (C), 173.0 (C), 172.98 (C), 137.0 (CH), 116.5 (CH_2), 58.8 (C), 53.0 (CH_3), 52.9 (CH_3), 51.6 (CH_3), 46.6 (CH), 45.2 (CH), 40.9 (CH), 39.9 (CH_2), 37.3 (CH_2), 16.0 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{15}H_{22}O_6$ $[M]^+$: 298.1416; found: 298.1415.



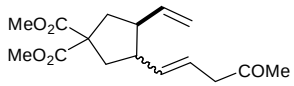
29

Colourless oil. Yield: 80%. Mixture of isomers ≈2:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.73 - 5.60 (m, 1H), 5.59 - 5.48 (m, 1H), 5.48 - 5.38 (m, 1H), 4.99 (m, 2H), 3.73 (s, 6H), 3.67 (s, 3H), 3.03 (d, *J* = 6.4 Hz, 2H), 2.82 - 2.71 (m, 1H), 2.59 - 2.52 (m, 1H), 2.48 (dd, *J* = 13.8, 6.8 Hz, 1H), 2.34 - 2.27 (m, 1H), 2.23 - 2.15 (m, 1H), 2.08 - 1.98 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 173.2 (2xC), 173.0 (C), 139.2 (CH, minor isomer), 138.3 (CH, major isomer), 135.0 (CH, minor isomer), 134.3 (CH, major isomer), 123.1 (CH, minor isomer), 122.9 (CH, major isomer) 115.6 (CH_2), 59.2 (C), 53.0 (2xCH_3), 51.9 (CH_3), 49.8 (CH, minor isomer), 48.6 (CH, minor isomer), 47.3 (CH, major isomer), 46.1 (CH, major isomer), 40.4 (CH_2, minor isomer), 40.2 (CH_2, major isomer), 39.2 (CH_2, minor isomer) 39.1 (CH_2, major isomer), 38.0 (CH_2).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{16}H_{22}O_6$ $[M]^+$: 310.1416; found: 310.1420.



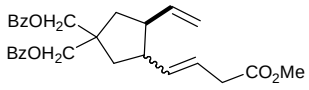
30

Colourless oil. Yield: 47%. Mixture of isomers ≈2:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.74 - 5.57 (m, 1H), 5.60 - 5.47 (m, 1H), 5.48 – 5.35 (m, 1H), 4.99 (dd, *J* = 15.6, 5.5 Hz, 2H), 3.73 (s, 6H), 3.10 (d, *J* = 6.7 Hz, 2H), 2.78 (dt, *J* = 14.1, 7.0 Hz, 1H), 2.57 – 2.43 (m, 2H), 2.39 – 2.23 (m, 1H), 2.25 – 2.14 (m, 1H), 2.13 (s, 3H), 2.07 – 1.97 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 207.3 (C), 172.9 (2xC), 139.2 (CH, minor isomer), 138.3 (CH, major isomer), 135.6 (CH, minor isomer), 134.7 (CH, major isomer), 123.4 (CH, minor isomer), 123.2 (CH, major isomer), 115.8 (CH_2, minor isomer), 115.6 (CH_2, major isomer), 59.1 (C, major isomer), 58.4 (C, minor isomer), 53.0 (2xCH_3), 49.9 (CH, minor isomer), 48.7 (CH, major isomer), 47.7(CH_2), 47.3 (CH, major isomer), 46.1 (CH, minor isomer), 40.4 (CH_2, minor isomer), 40.2 (CH_2, major isomer), 39.3 (CH_2, major isomer) , 38.9, (CH_2, minor isomer) 29.8 (CH_3, major isomer), 29.4 (CH_3, minor isomer).

HRMS (EI, 70eV) calcd. for $C_{16}H_{21}O_5$ $[M-1]^+$: 293.1389; found: 293.1390.



31

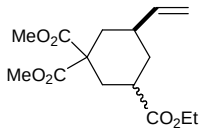
Colourless oil. Yield: 53%. Mixture of isomers ≈1:1.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm)= 8.02 (d, *J* = 7.6 Hz, 4H), 7.56 (t, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 4H), 5.84 – 5.75 (m, 1H), 5.75 – 5.63 (m, 1H), 5.60 – 5.52 (m, 1H), 5.07 – 4.96 (m, 2H), 4.41 (s, 4H, minor isomer), 4.34 (s, 4H, major isomer), 3.67 (s, 3H), 3.02 (d, *J* = 18.0 Hz, 2H), 2.93 - 2.83 (m, 1H), 2.47 – 2.31 (m, 1H), 2.05 (m, 1H), 2.00 – 1.90 (m, 1H), 1.79 – 1.69 (m, 1H), 1.64 – 1.47 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 172.4 (C), 166.7 (2xC), 139.8 (CH, one isomer), 139.1 (CH, other isomer), 135.7 (CH, one isomer), 134.9 (CH, other isomer), 133.2 (2xCH), 130.1 (2xC), 129.7 (4xCH), 128.6 (4xCH), 122.8 (CH, one isomer), 122.7 (CH, other isomer), 115.4 (CH_2), 69.3 (CH_2, one isomer), 68.8 (CH_2, other isomer), 68.7 (CH_2, one isomer), 68.1 (CH_2, other isomer), 51.9 (CH_3), 49.6 (CH, one isomer), 48.3 (CH, other isomer), 47.2 (CH, one isomer), 45.9 (CH, other isomer), 44.6 (C), 39.2

(CH_2, one isomer), 39.0 (CH_2, other isomer), 38.0 (CH_2), 37.9 (CH_2, one isomer), 37.7 (CH_2, other isomer).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{28}H_{30}O_6$ $[M]^+$: 462.2042; found: 462.2030.



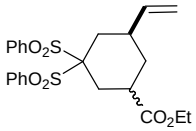
32

Colourless oil. Yield: 61%. Mixture of isomers ≈ 6:1. Data of the major isomer:

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 5.72 (ddd, *J* = 23.4, 10.9, 5.7 Hz, 1H), 5.07 – 4.96 (m, 2H), 4.19 – 4.03 (m, 2H), 3.69 (s, 3H), 3.68 (s, *J* = 2.6 Hz, 3H), 2.89 (dq, *J* = 11.8, 6.0 Hz, 1H), 2.68 (dd, *J* = 4.1, 1.7 Hz, 1H), 2.34 – 2.24 (m, 3H), 1.95 – 1.87 (m, 1H), 1.74 (dt, *J* = 19.0, 9.6 Hz, 1H), 1.58 (ddd, *J* = 13.3, 8.3, 4.7 Hz, 1H), 1.25 (td, *J* = 7.1, 2.5 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) = 174.8 (C), 172.3 (C), 171.8 (C), 141.4 (CH), 114.0 (CH_2), 60.6 (CH_2), 52.8 (CH_3), 54.9 (C), 52.70 (CH_3), 52.66 (CH_3), 36.4 (CH), 35.7 (CH_2), 34.0 (CH), 31.7 (CH_2), 31.2 (CH_2), 14.3 (CH_3).

HRMS (EI, 70 eV) *m*/*z* calcd. for $C_{15}H_{22}O_6$ $[M\text{-}CH_2]^+$: 298.1416; found: 298.1408.



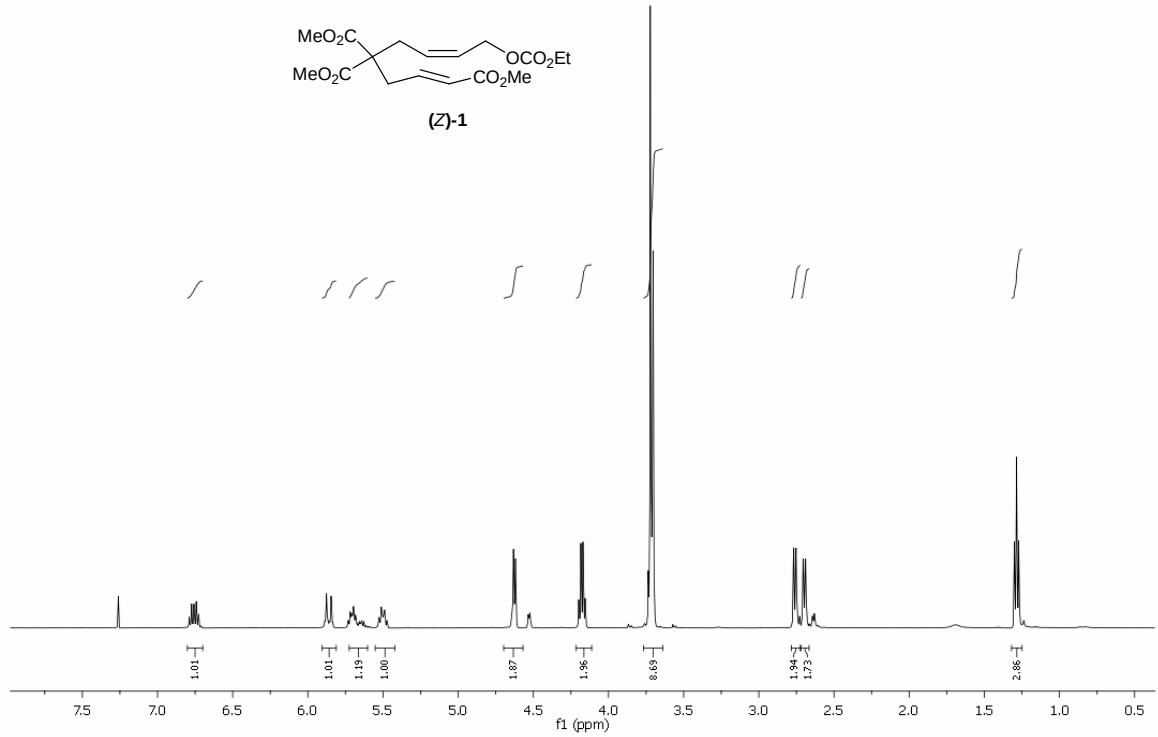
33

Colourless oil. Yield: 60%. Mixture of isomers ≈ 9:1. Data of the major isomer:

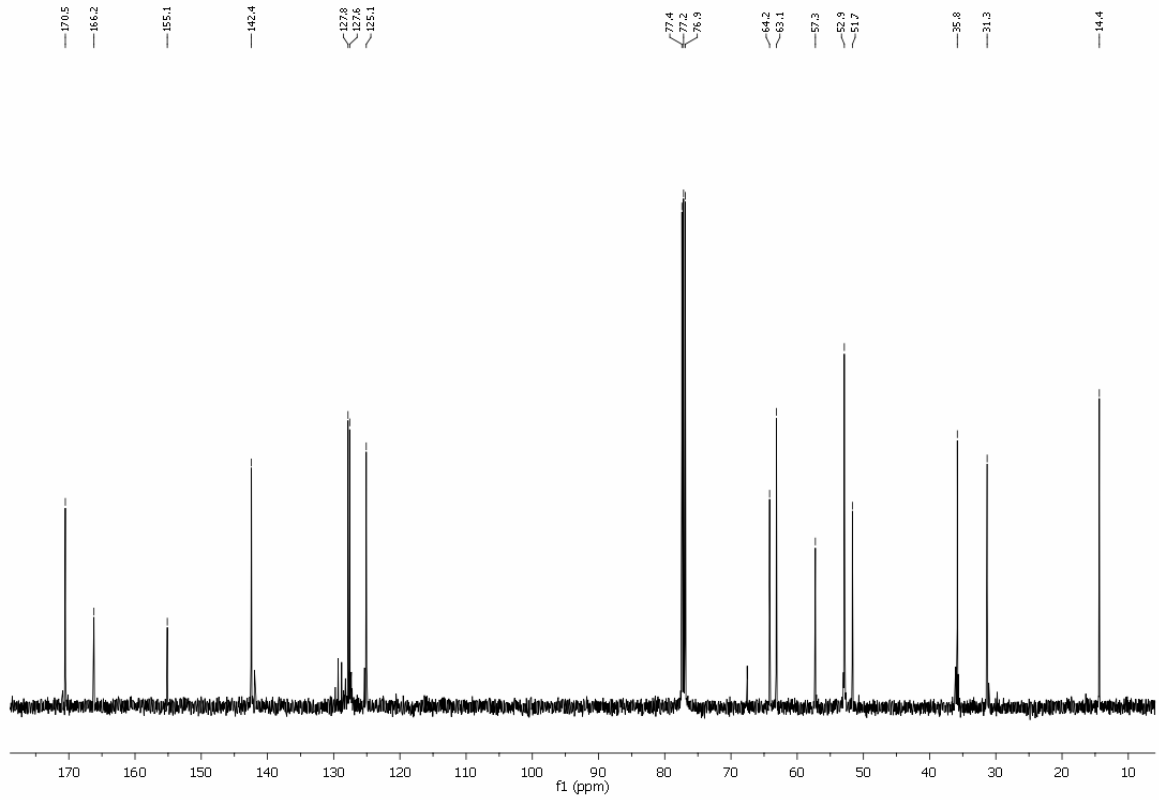
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.05 (m, 4H), 7.77 – 7.67 (m, 2H), 7.65 – 7.52 (m, 4H), 5.70 (ddd, *J* = 16.7, 10.8, 7.0 Hz, 1H), 5.04 – 4.91 (m, 2H), 4.18 (qd, *J* = 7.1, 1.9 Hz, 2H), 3.15 – 3.02 (m, 2H), 2.71-2.47 (ddd, *J* = 20.9, 15.6, 7.4 Hz, 2H), 2.39-1.99 (m, 2H), 1.60-1.49 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

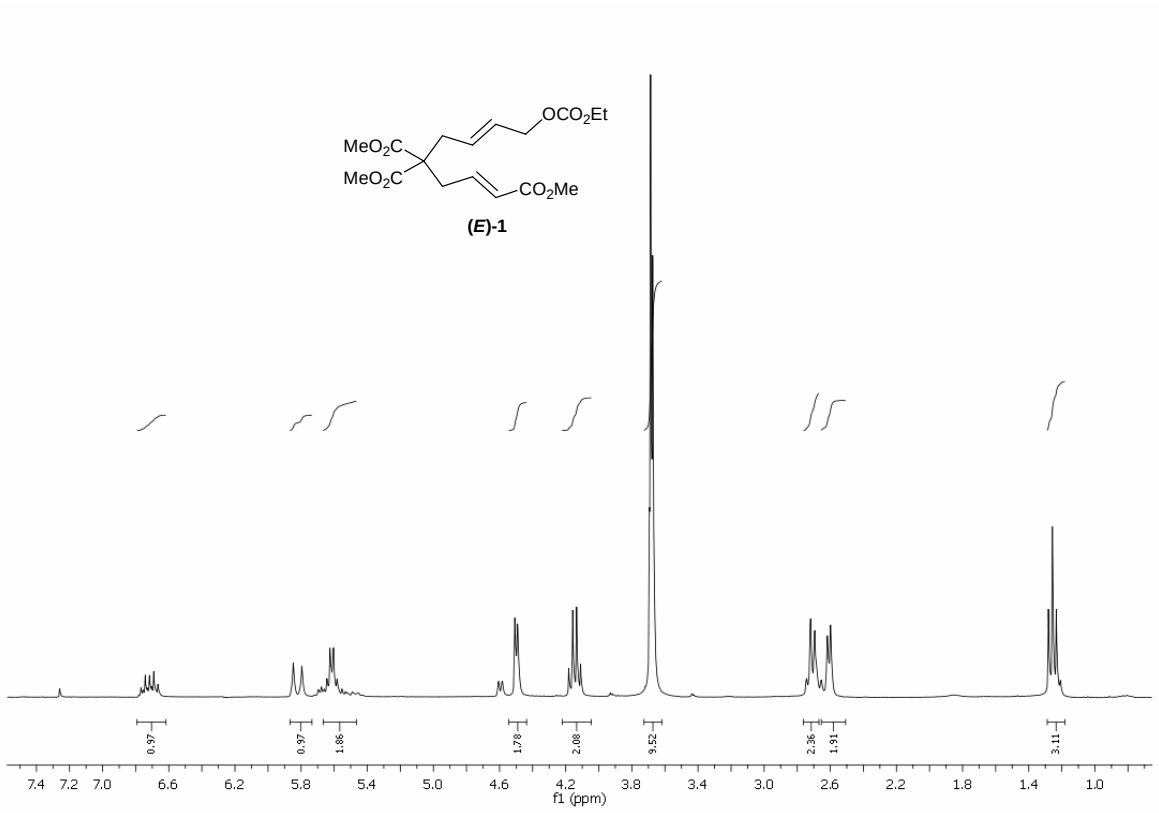
^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 174.0 (C), 140.8 (CH), 136.2 (2xC), 134.8 (2xCH), 131.7 (2xCH), 131.5 (2xCH), 128.9 (2xCH), 128.8 (2xCH), 114.9 (CH_2), 87.1 (C), 61.1 (CH_2), 35.6 (CH), 33.2 (CH), 30.1 (CH_2), 29.6 (CH_2), 26.4 (CH_2), 14.3 (CH_3).

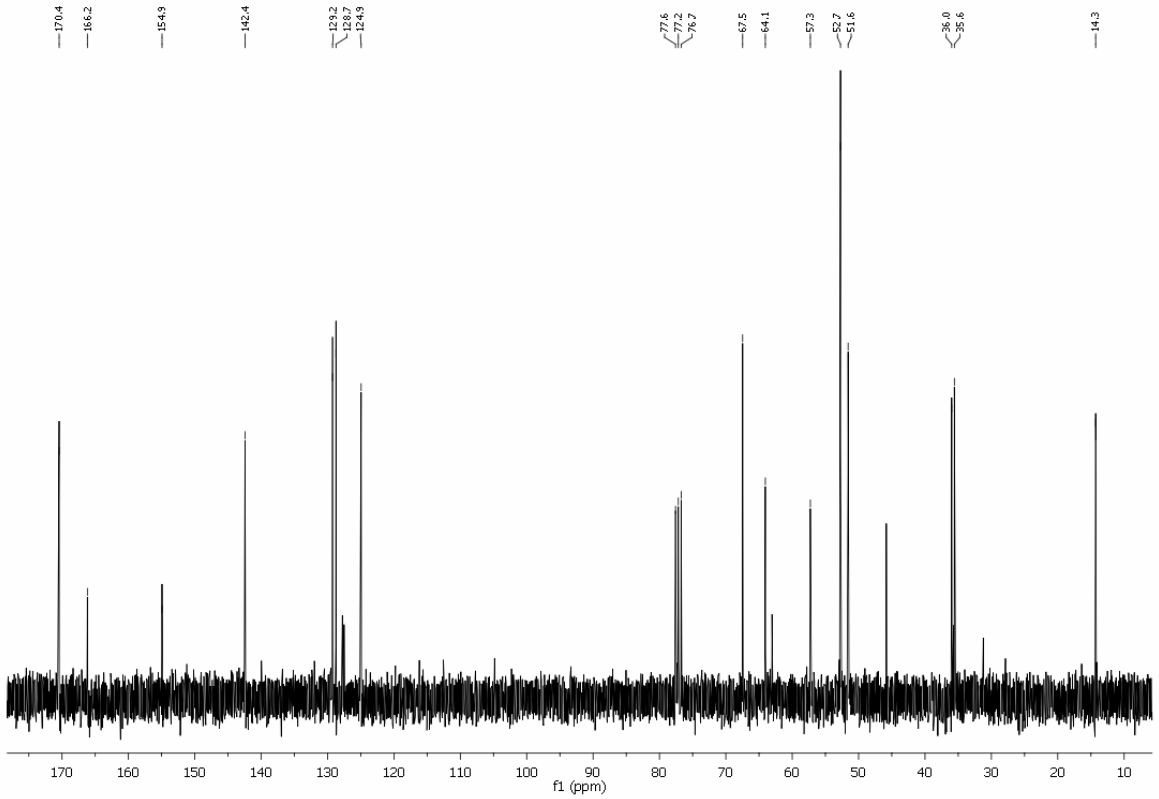
(EI, 70 eV) *m*/*z* calcd. for $C_{23}H_{27}O_6S_2$ $[M+1]^+$: 463.1249; found: 463.1241.

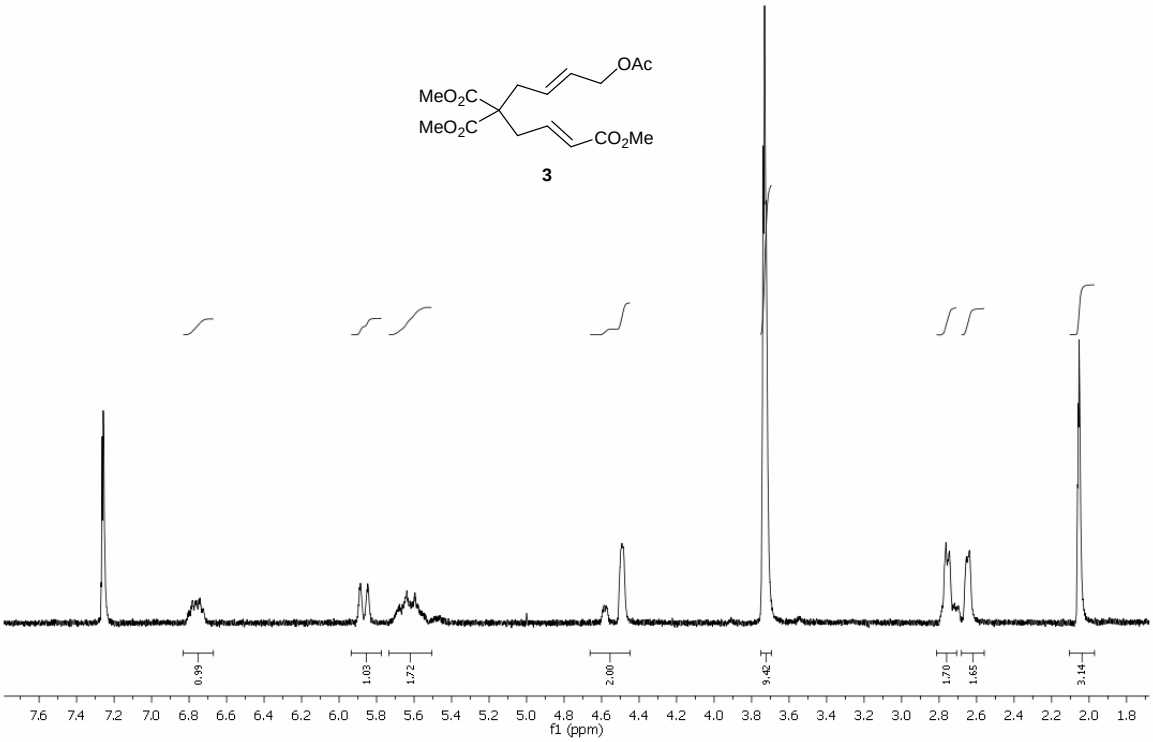

MeO2C
MeO2C
OCO2Et
CO2Me
1.01
1.01
1.19
1.00
1.87
1.96
8.69
1.94
1.73
2.86
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

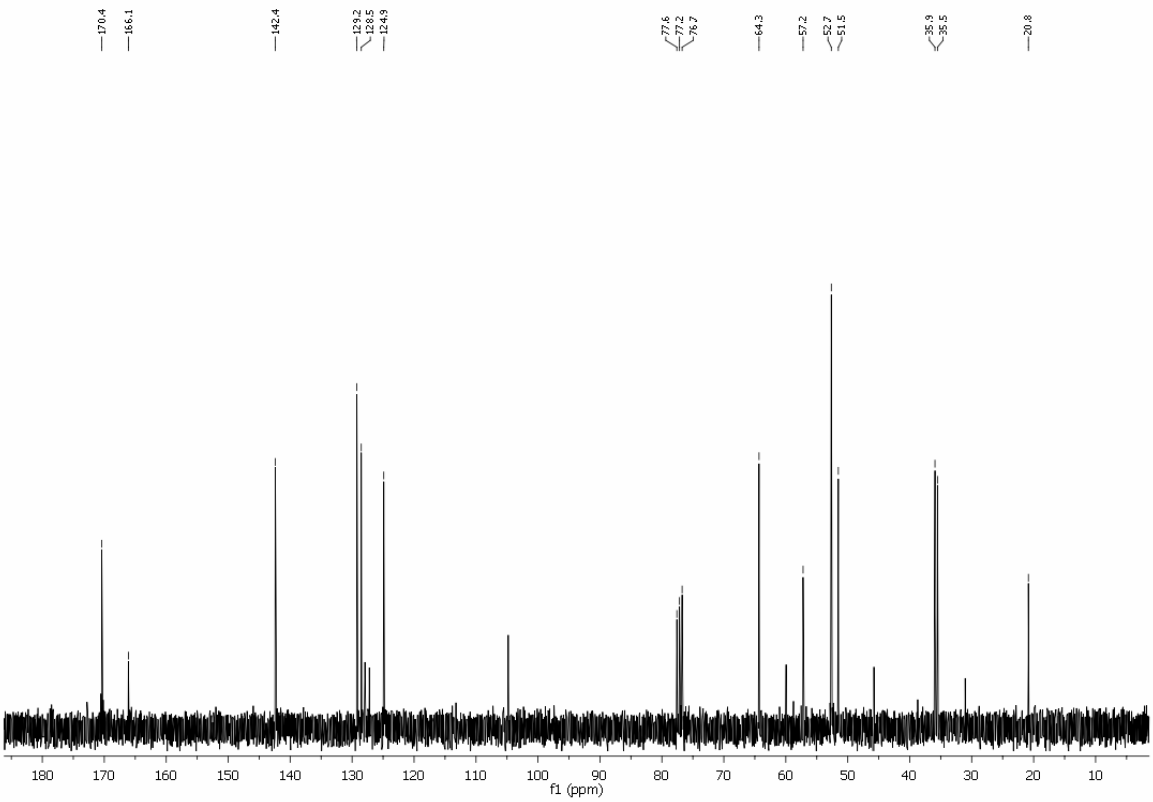
(*Z*)-1

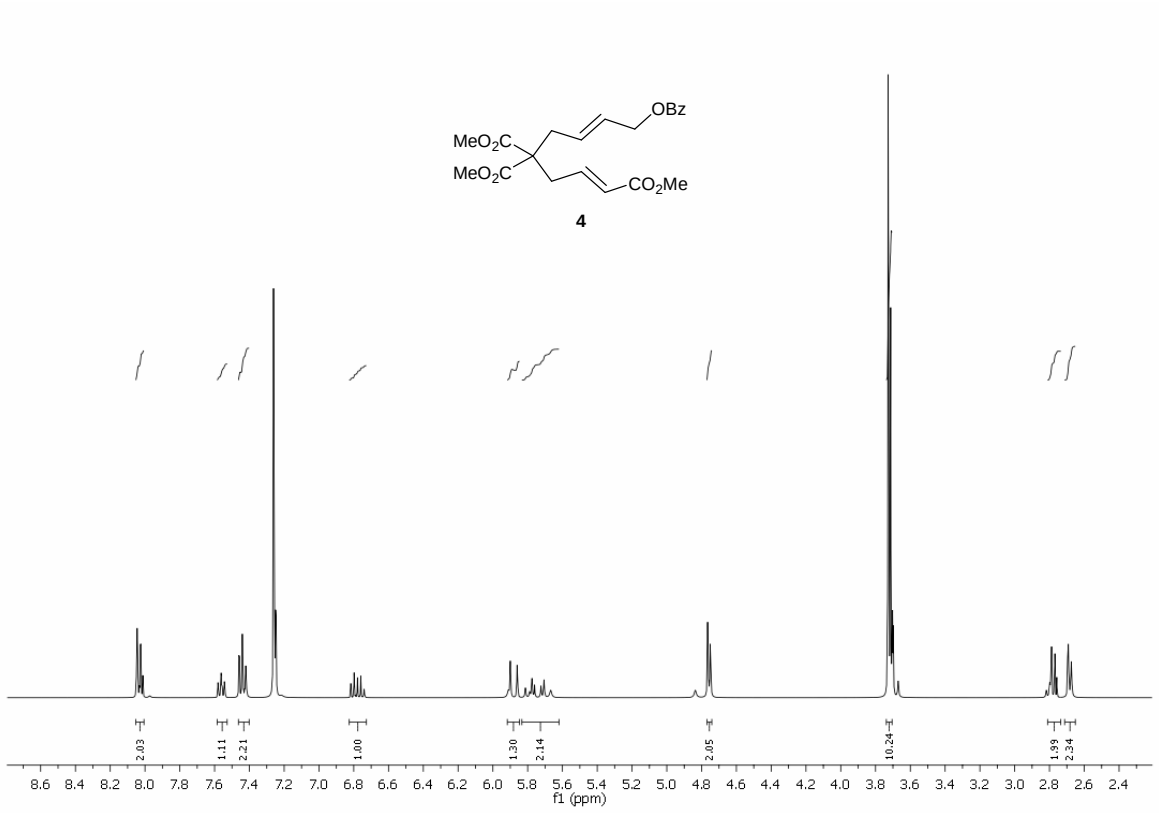

170.5
166.2
155.1
142.4
127.8
127.6
125.1
77.4
77.2
76.9
64.2
63.1
57.3
52.9
51.7
35.8
31.3
14.4
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

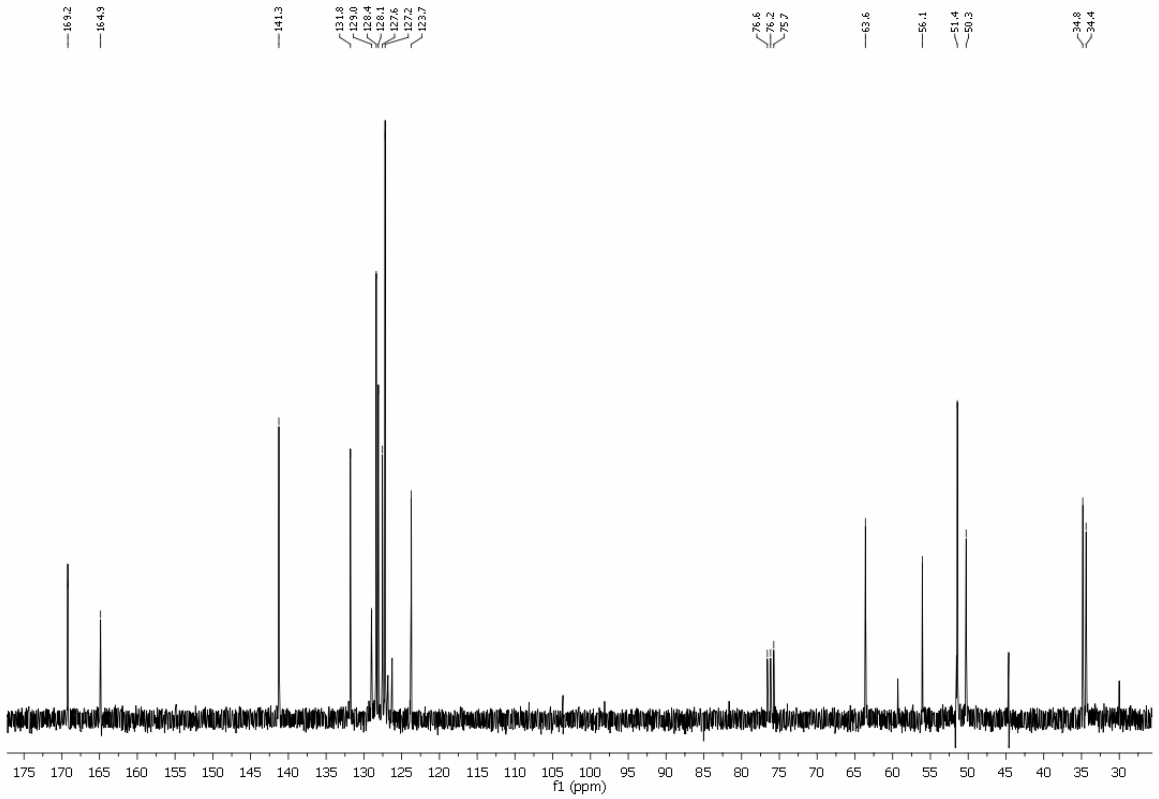

OCO2Et
MeO2C
MeO2C
CO2Me
(E)-1
0.97
0.97
1.86
1.78
2.08
3.52
2.36
1.91
3.11
7.4 7.2 7.0 6.6 6.2 5.8 5.4 5.0 4.6 4.2 3.8 3.4 3.0 2.6 2.2 1.8 1.4 1.0
f1 (ppm)

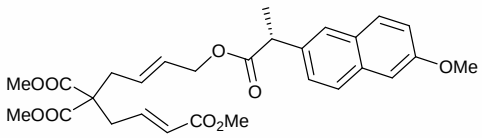

170.4
166.2
154.9
142.4
129.2
128.7
124.9
77.6
77.2
76.7
67.5
64.1
57.3
52.7
51.6
36.0
35.6
14.3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


OAc
MeO2C
MeO2C
CO2Me
3
0.99
1.03
1.72
2.00
9.42
1.70
1.65
3.14
f1 (ppm)


170.4
166.1
142.4
129.2
128.5
124.9
77.6
77.2
76.7
64.3
57.2
52.7
51.5
35.9
35.5
20.8
f1 (ppm)

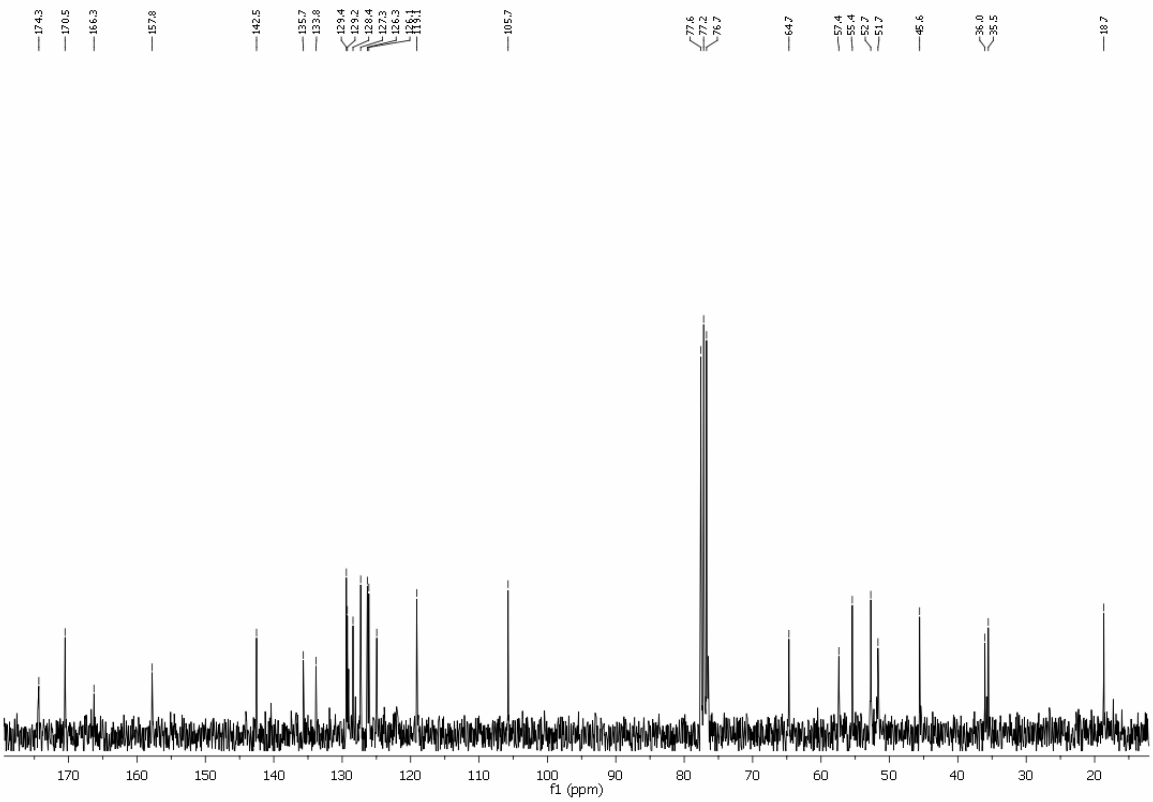

OBz
MeO2C
MeO2C
CO2Me
4
2.03
1.11
2.21
1.00
1.30
2.14
2.05
10.24
1.99
2.34
f1 (ppm)

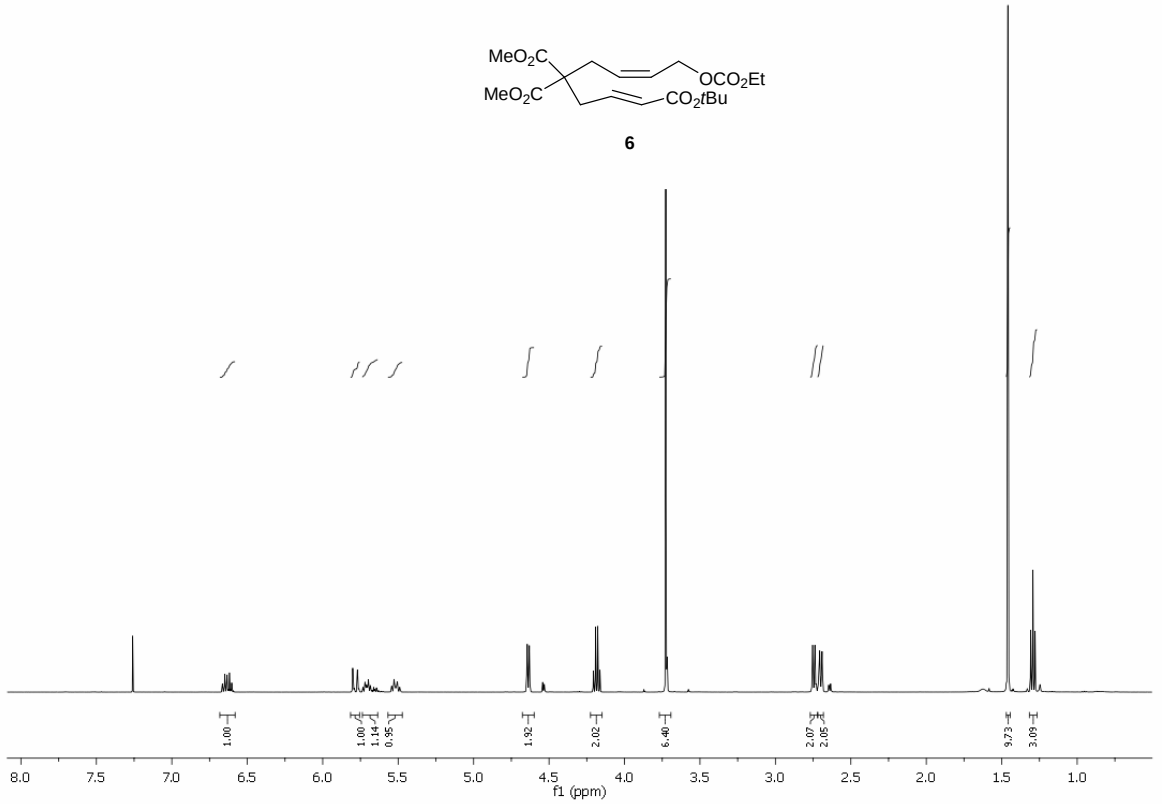

169.2
164.9
141.3
131.8
129.0
128.4
128.1
127.6
127.2
123.7
76.6
76.2
75.7
63.6
56.1
51.4
50.3
34.8
34.4
f1 (ppm)

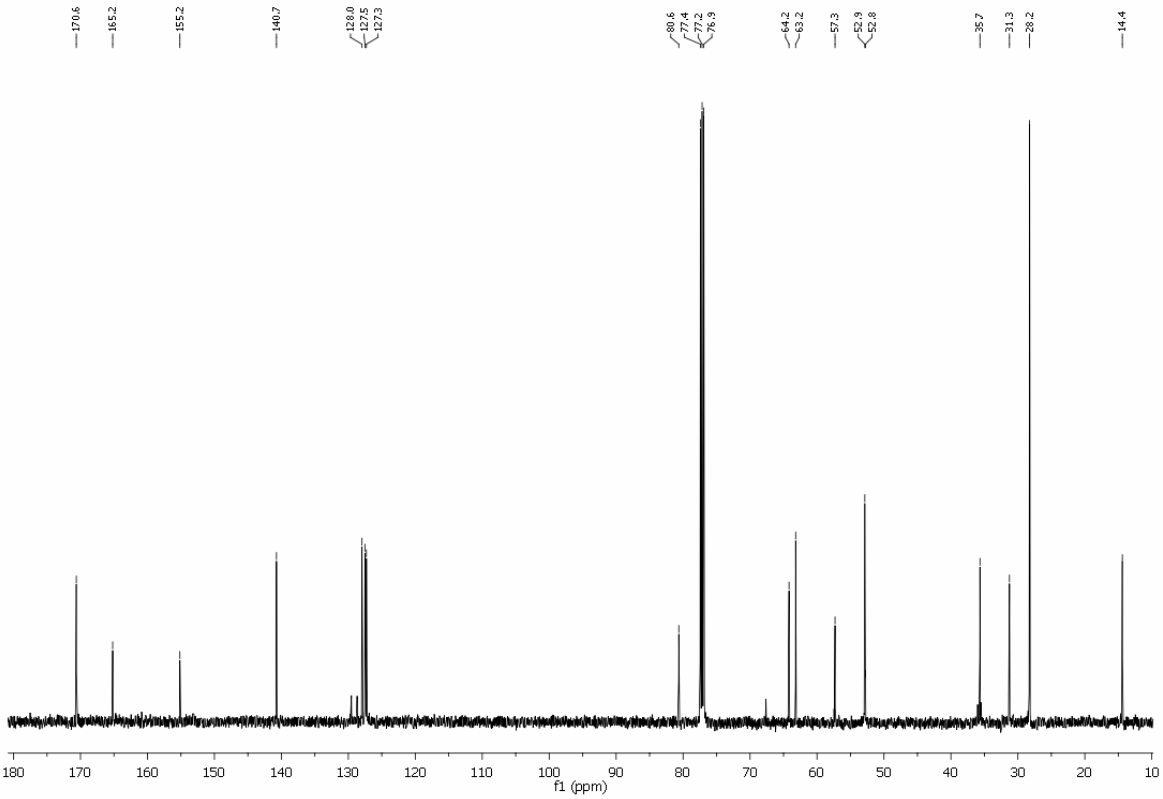

MeOOC
MeOOC
CO2Me
O
O
OMe

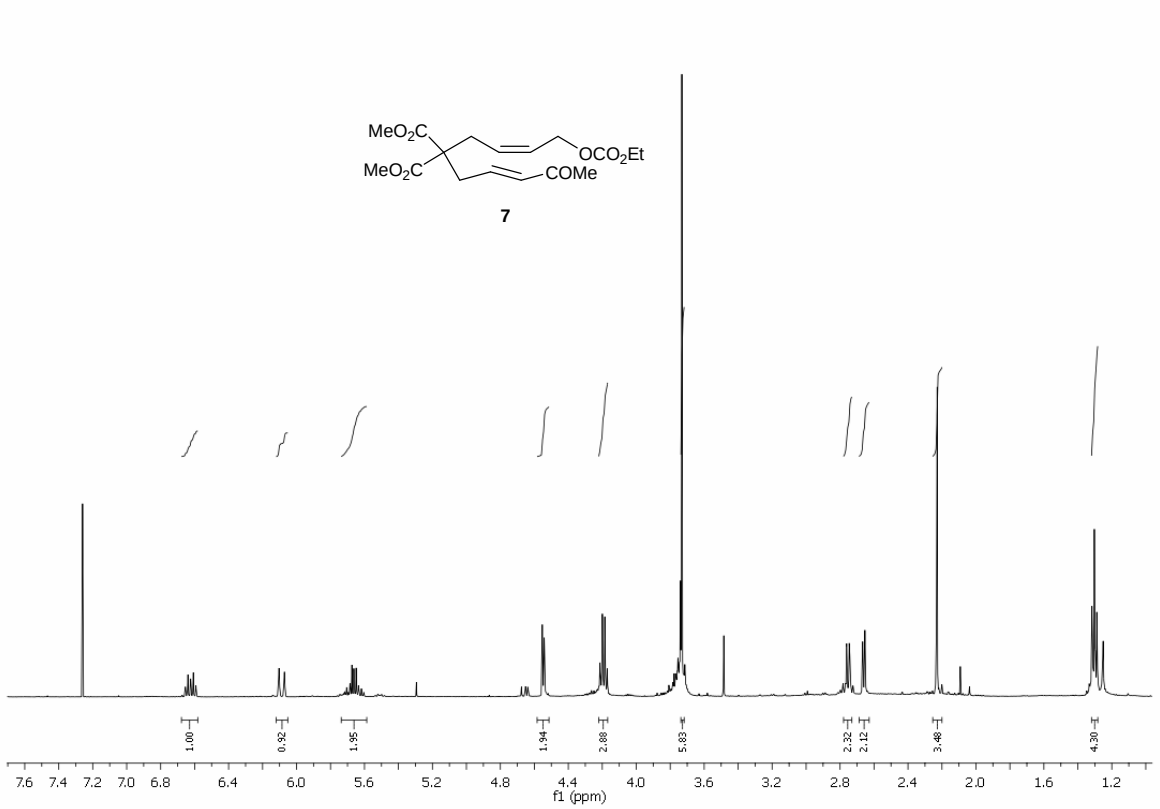
5

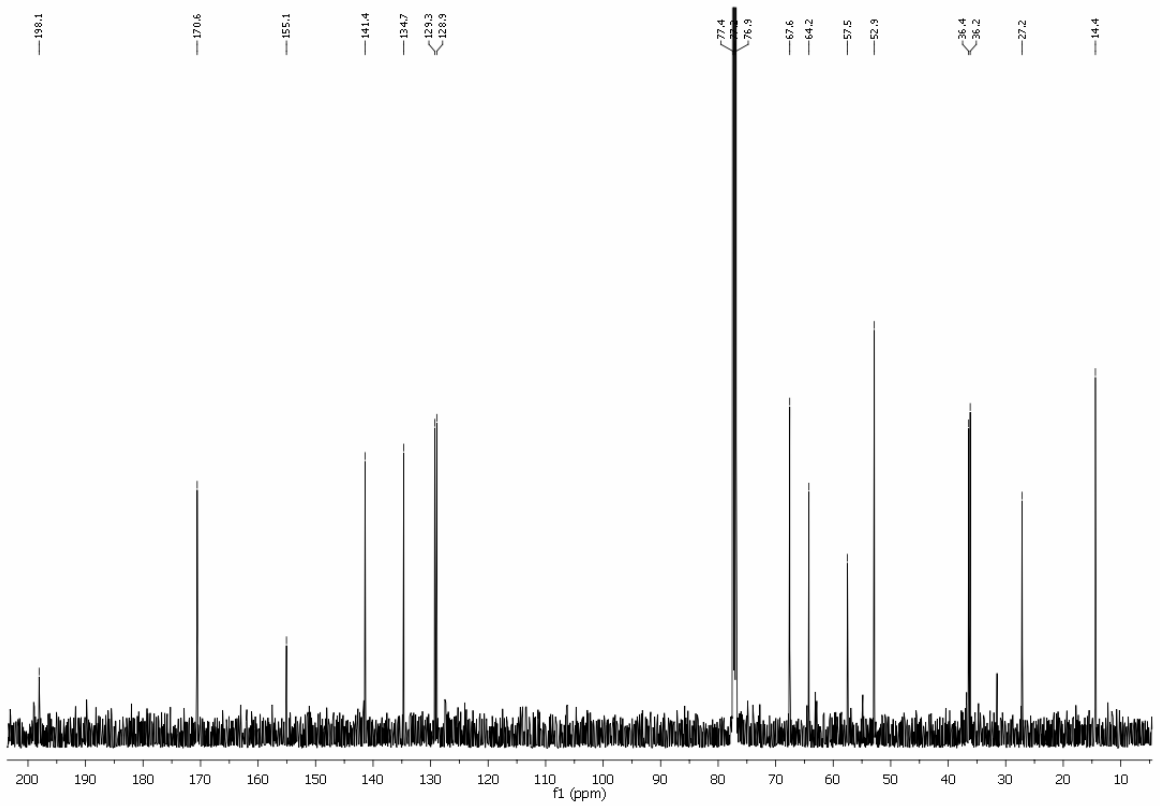
2.41
0.69
0.62
0.42
0.97
1.00
0.85
1.22
2.09
3.82
1.37
3.36
3.28
2.91
2.14
2.22
4.15
f1 (ppm)

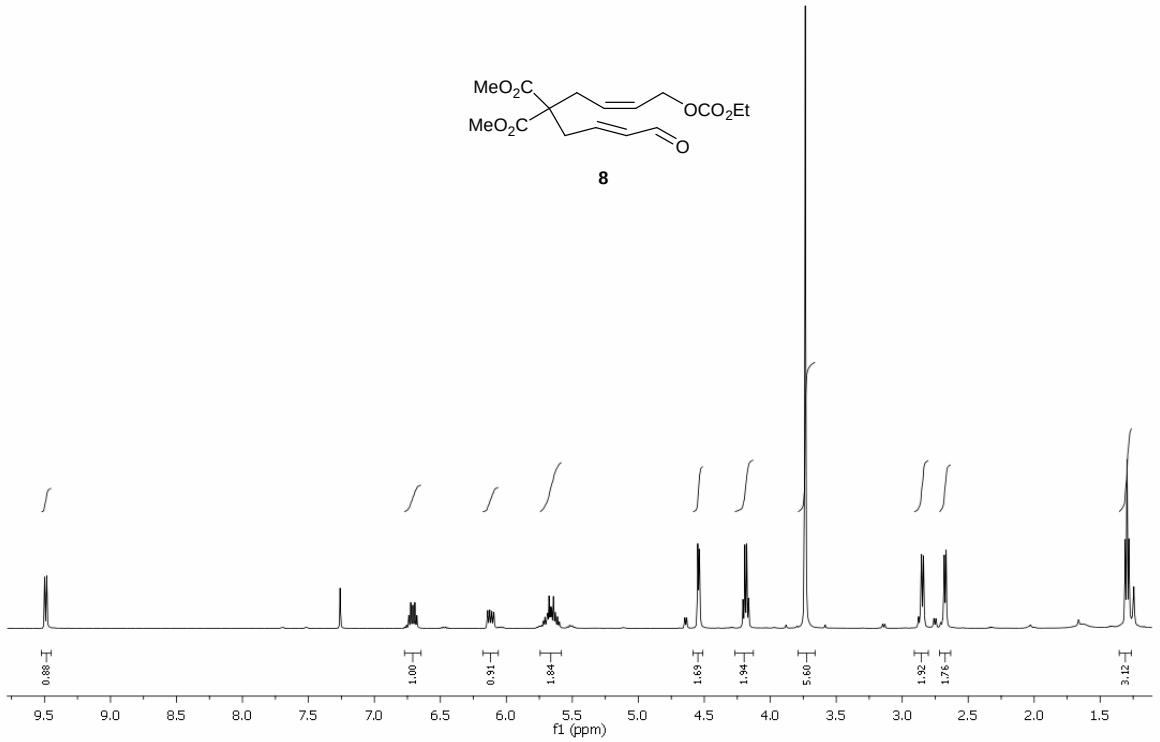

174.3
170.5
166.3
157.8
142.5
135.7
133.8
129.4
129.2
128.4
127.3
126.3
126.1
119.1
105.7
77.6
77.2
76.7
64.7
57.4
55.4
52.7
51.7
45.6
36.0
35.5
18.7
f1 (ppm)

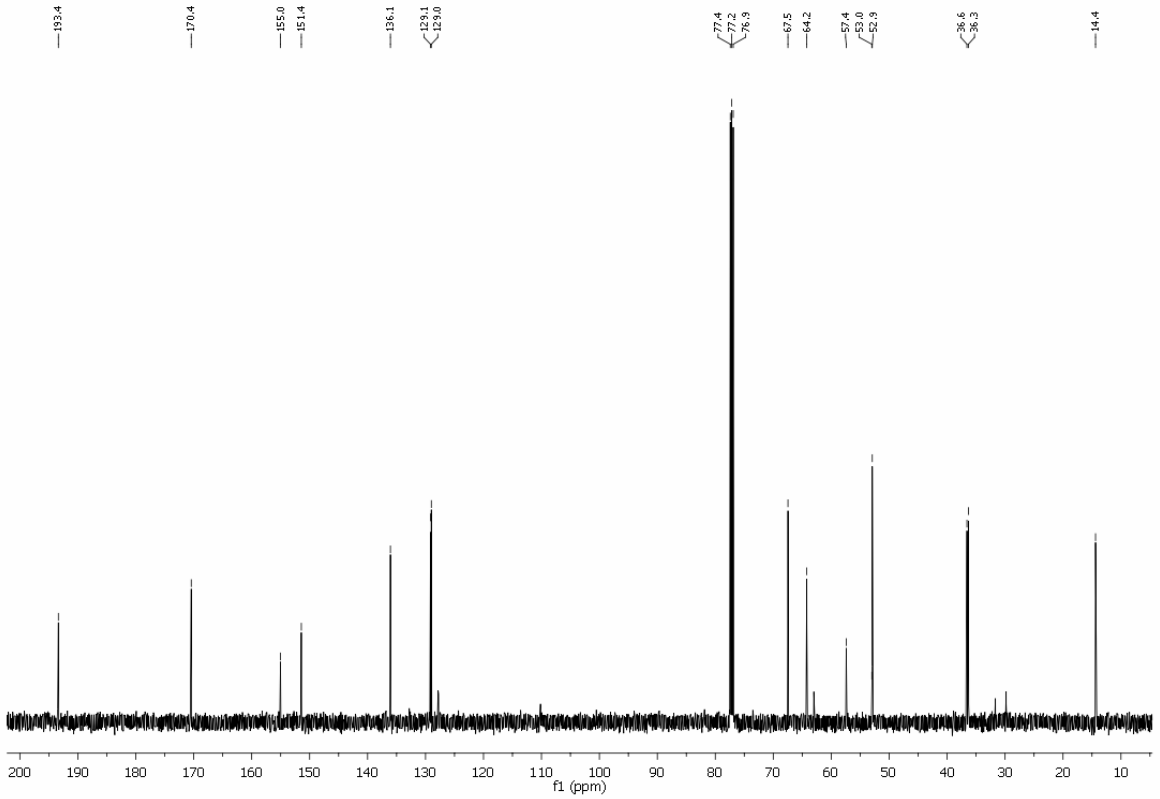

MeO2C
MeO2C
OCO2Et
CO2tBu
6
1.00
1.00
1.14
0.95
1.92
2.02
6.40
2.07
2.05
9.73
3.09
f1 (ppm)

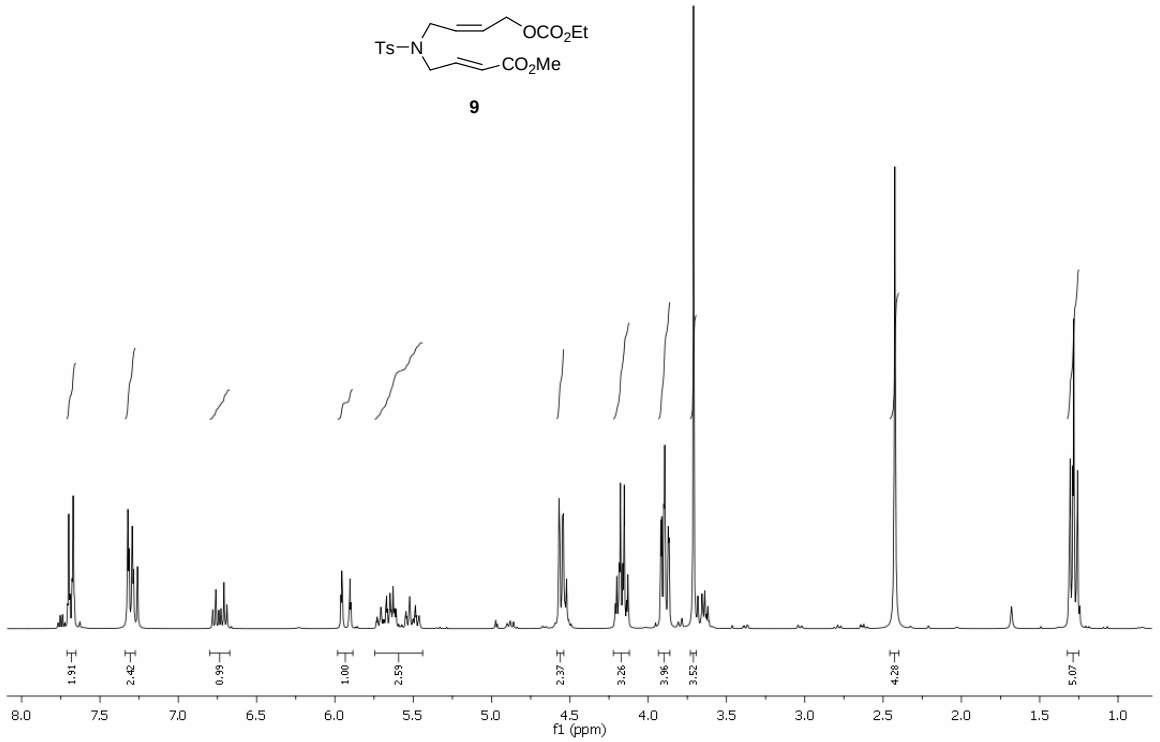

170.6
165.2
155.2
140.7
128.0
127.5
127.3
80.6
77.4
77.2
76.9
64.2
63.2
57.3
52.9
52.8
35.7
31.3
28.2
14.4
f1 (ppm)

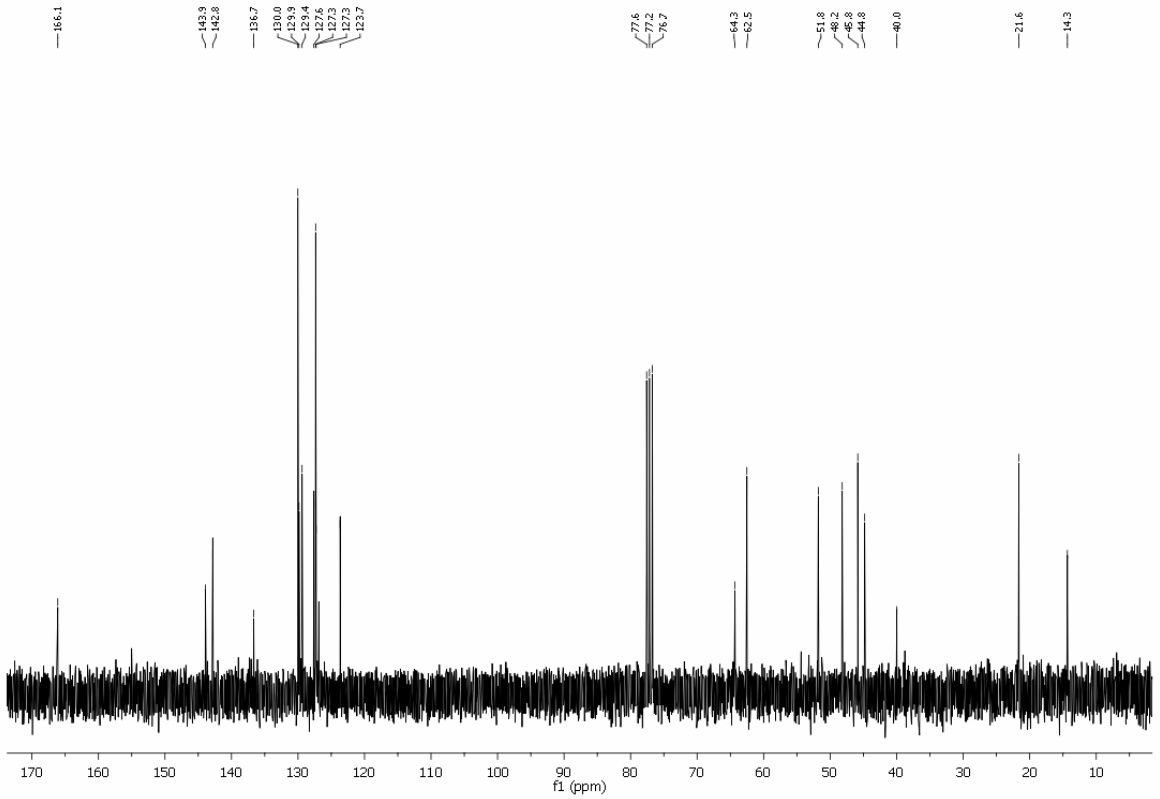

MeO2C
MeO2C
OCO2Et
COMe
7
1.00
0.92
1.95
1.94
2.88
5.83
2.32
2.12
3.48
4.30
7.6 7.4 7.2 7.0 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2
f1 (ppm)

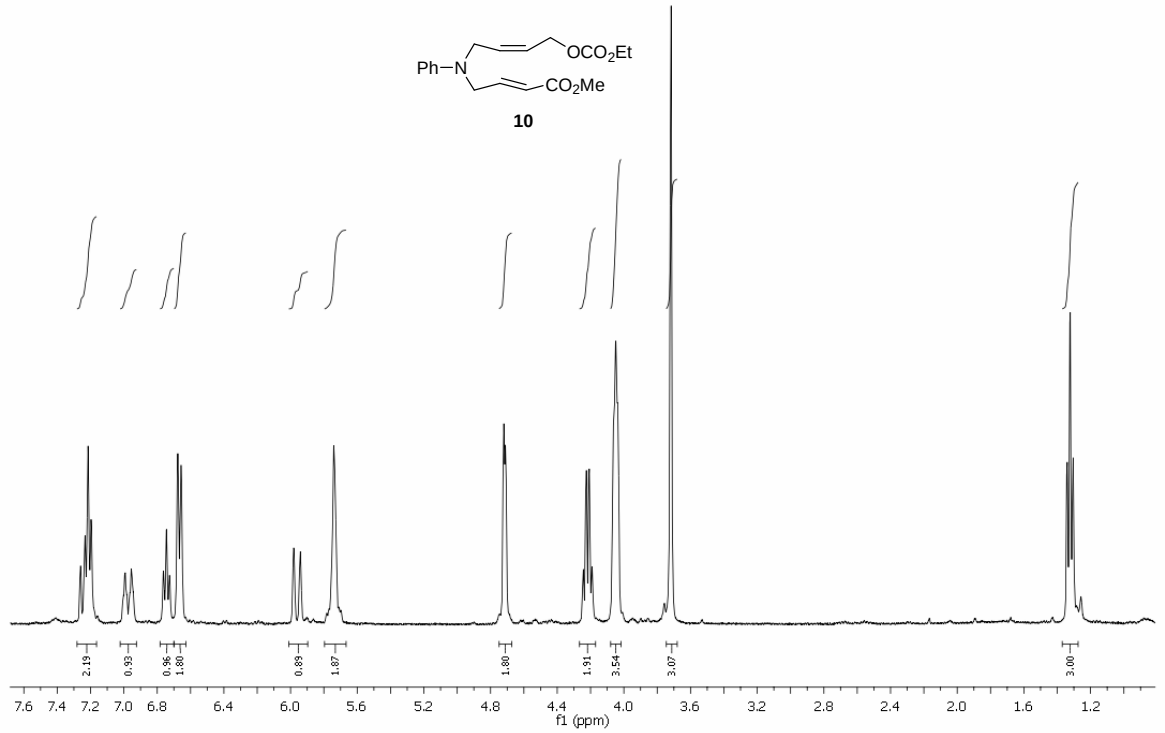

198.1
170.6
155.1
141.4
134.7
129.3
128.9
77.4
76.9
67.6
64.2
57.5
52.9
36.4
36.2
27.2
14.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

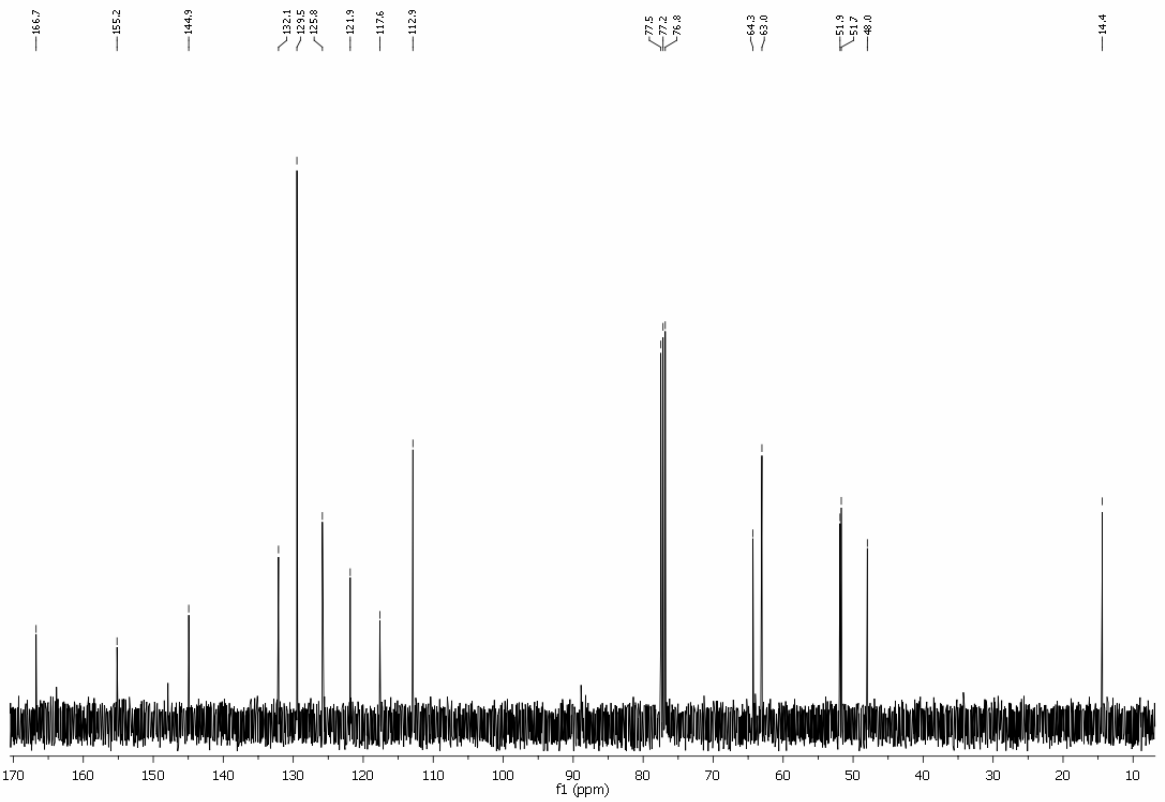

MeO2C
MeO2C
OCO2Et
O
8
0.88
1.00
0.91
1.84
1.69
1.94
5.60
1.92
1.76
3.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)

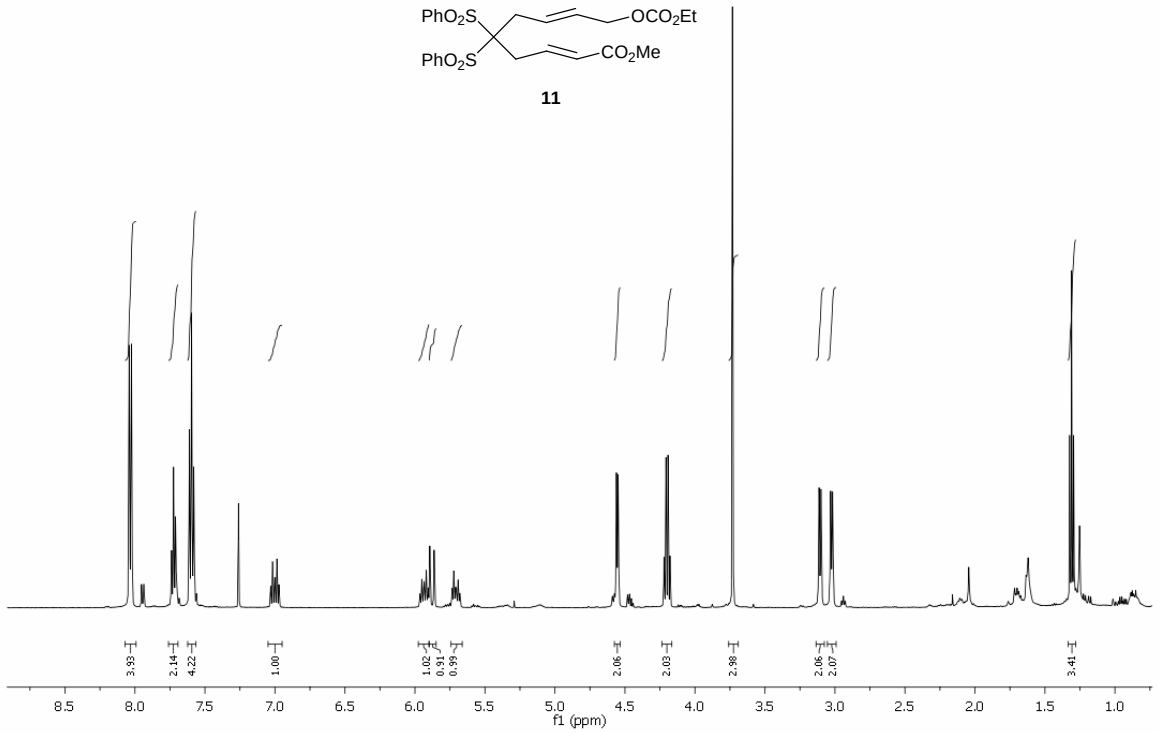

193.4
170.4
155.0
151.4
136.1
129.1
129.0
77.4
77.2
76.9
67.5
64.2
57.4
53.0
52.9
36.6
36.3
14.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

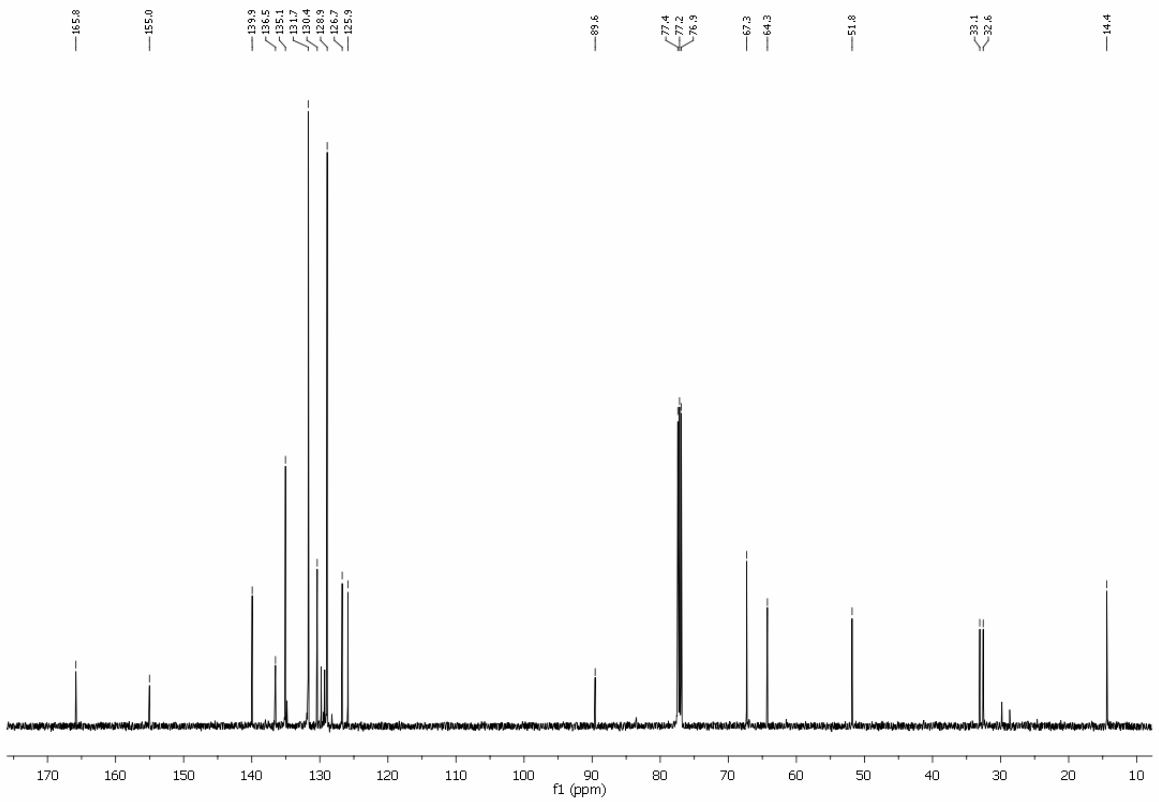

Ts–N
OCO2Et
CO2Me
9
1.91
2.42
0.99
1.00
2.59
2.37
3.26
3.96
3.52
4.28
5.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

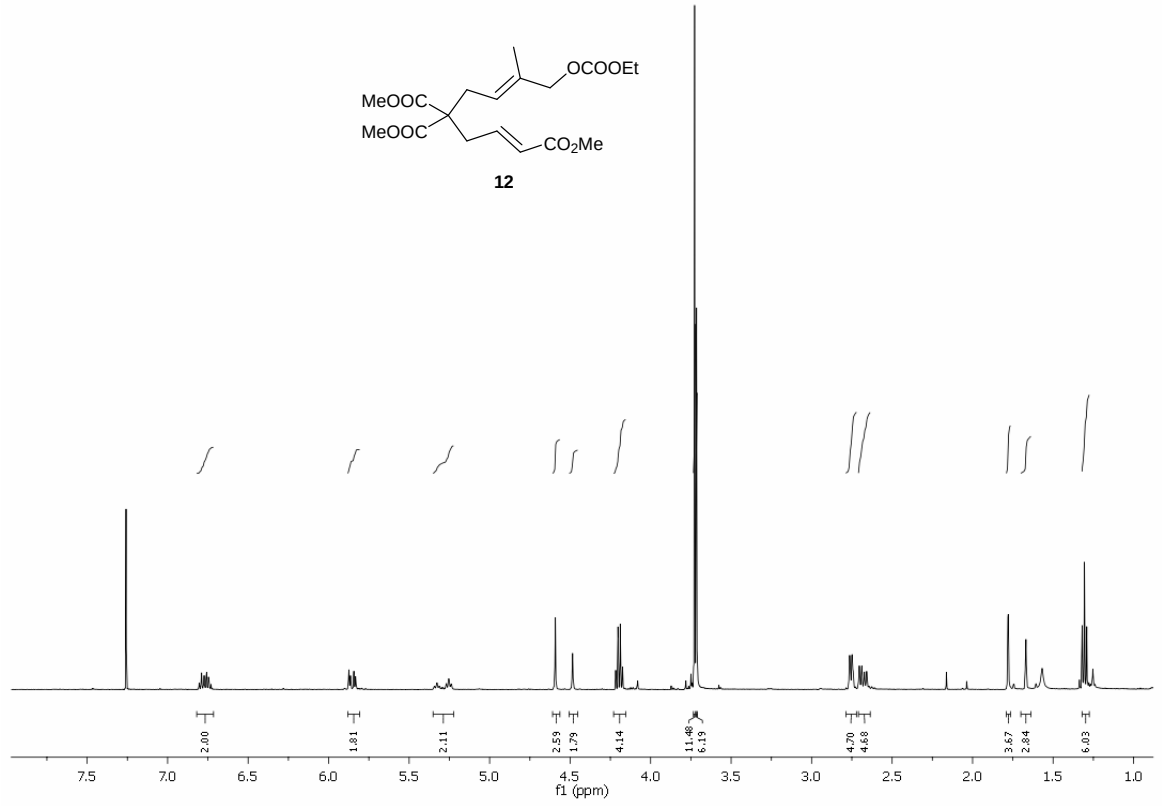

166.1
143.9
142.8
136.7
130.0
129.9
129.4
127.6
127.3
127.3
123.7
77.6
77.2
76.7
64.3
62.5
51.8
48.2
45.8
44.8
40.0
21.6
14.3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

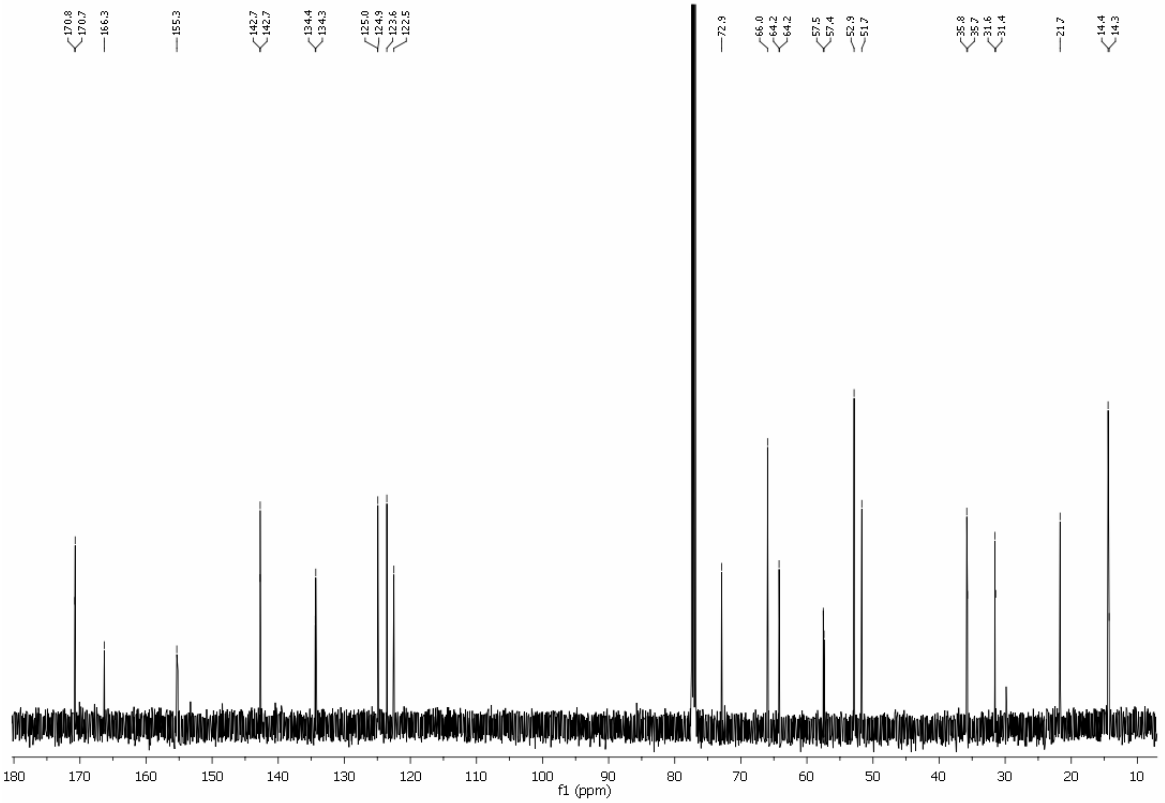

Ph—N
OCO2Et
CO2Me
10
2.19
0.93
0.96
1.80
0.89
1.87
1.80
1.91
3.54
3.07
3.00
7.6 7.4 7.2 7.0 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2
f1 (ppm)

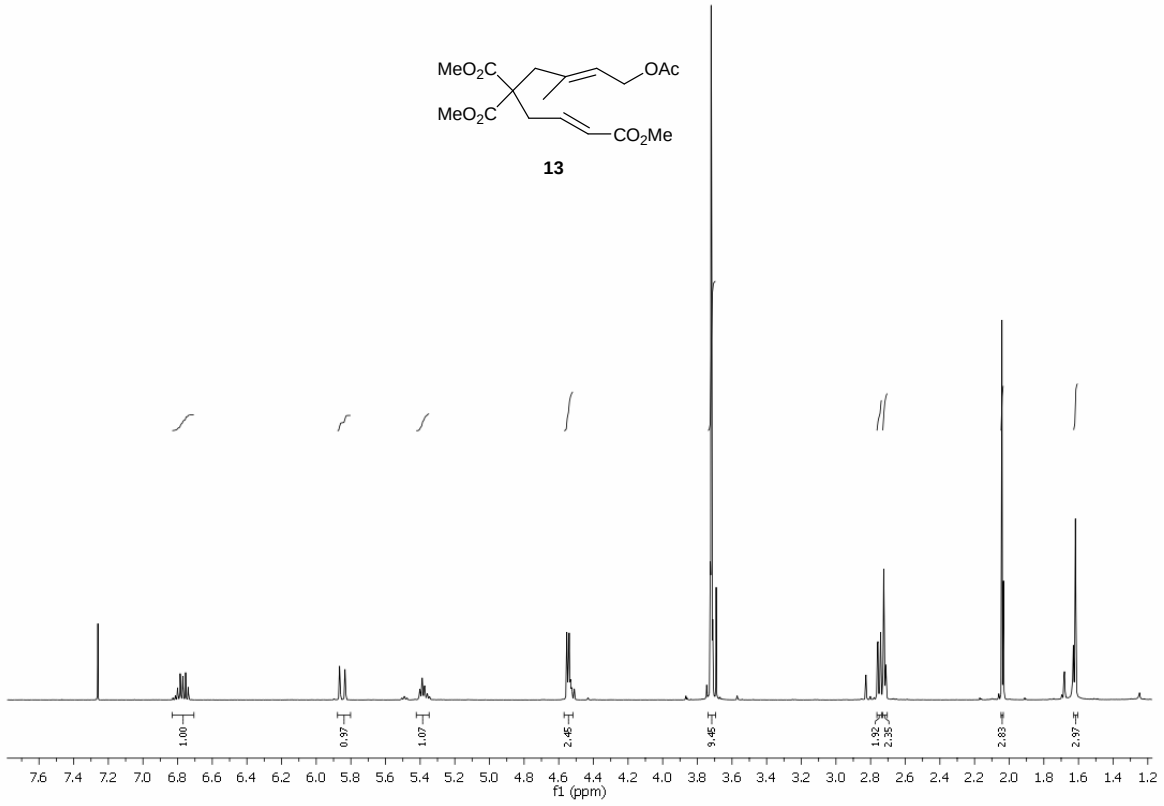

166.7
155.2
144.9
132.1
129.5
125.8
121.9
117.6
112.9
77.5
77.2
76.8
64.3
63.0
51.9
51.7
48.0
14.4
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


PhO2S
PhO2S
OCO2Et
CO2Me
11
3.93
2.14
4.22
1.00
1.02
0.91
0.99
2.06
2.03
2.98
2.06
2.07
3.41
f1 (ppm)

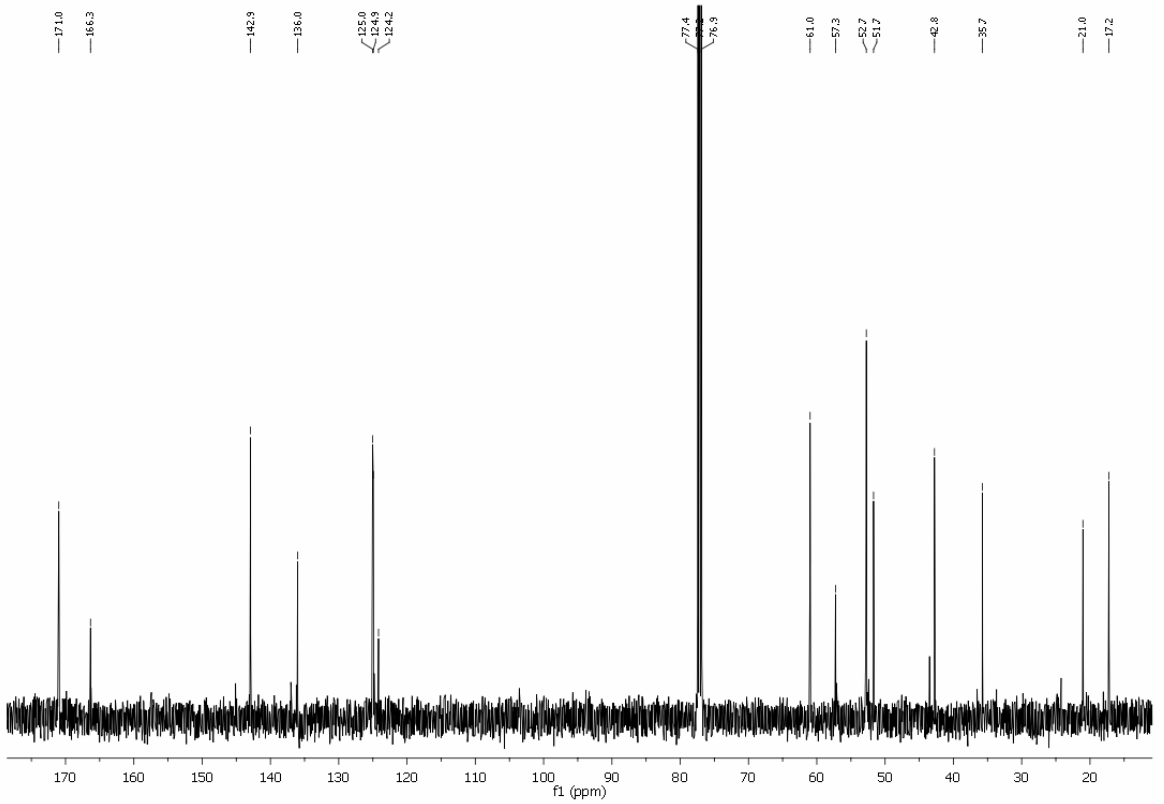

165.8
155.0
139.9
136.5
135.1
131.7
130.4
128.9
126.7
125.9
89.6
77.4
77.2
76.9
67.3
64.3
51.8
33.1
32.6
14.4
f1 (ppm)

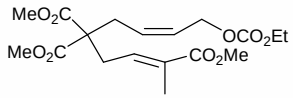

OCOOEt
MeOOC
MeOOC
CO2Me
12
2.00
1.81
2.11
2.59
1.79
4.14
11.48
6.19
4.70
4.68
3.67
2.84
6.03
f1 (ppm)


170.8
170.7
166.3
155.3
142.7
142.7
134.4
134.3
125.0
124.9
123.6
122.5
72.9
66.0
64.2
64.2
57.5
57.4
52.9
51.7
35.8
35.7
31.6
31.4
21.7
14.4
14.3
f1 (ppm)


MeO2C
MeO2C
OAc
CO2Me
1.00
0.97
1.07
2.45
9.46
1.92
2.35
2.83
2.97
f1 (ppm)

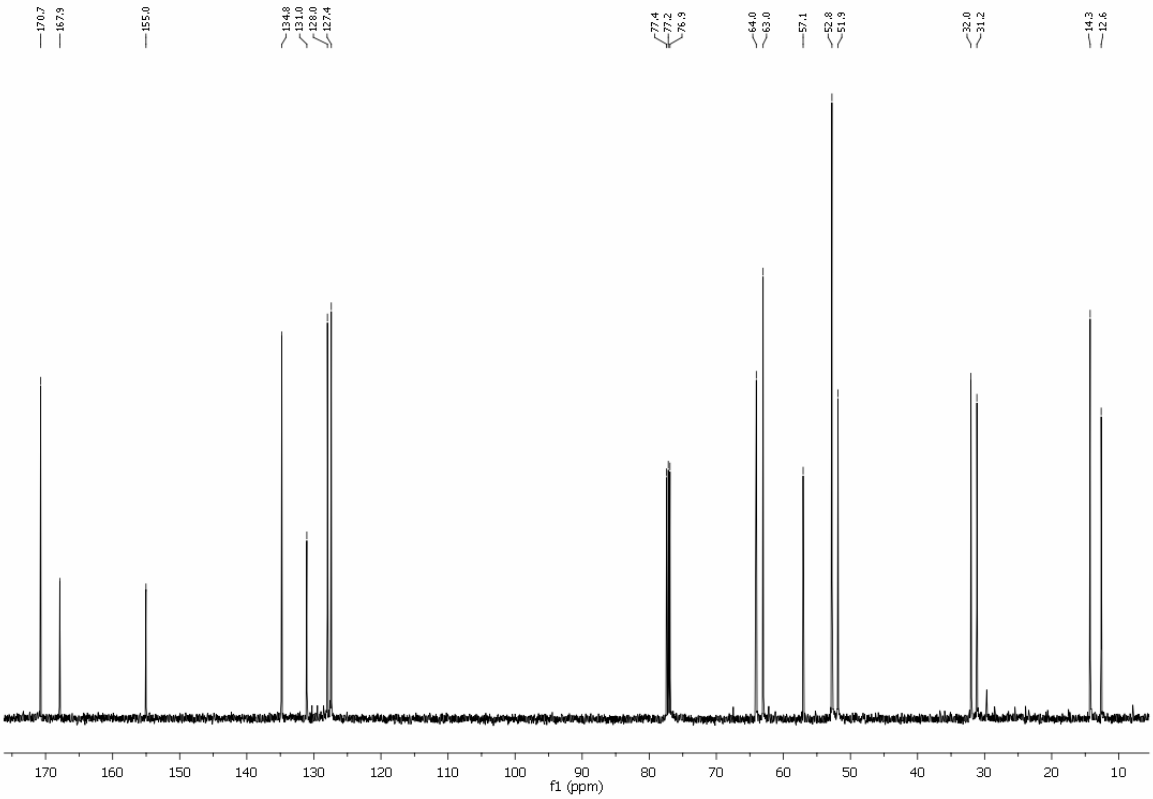
13

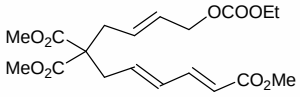

171.0
166.3
142.9
136.0
125.0
124.9
124.2
77.4
76.9
61.0
57.3
52.7
51.7
42.8
35.7
21.0
17.2
f1 (ppm)


MeO2C
MeO2C
OCO2Et
CO2Me

14

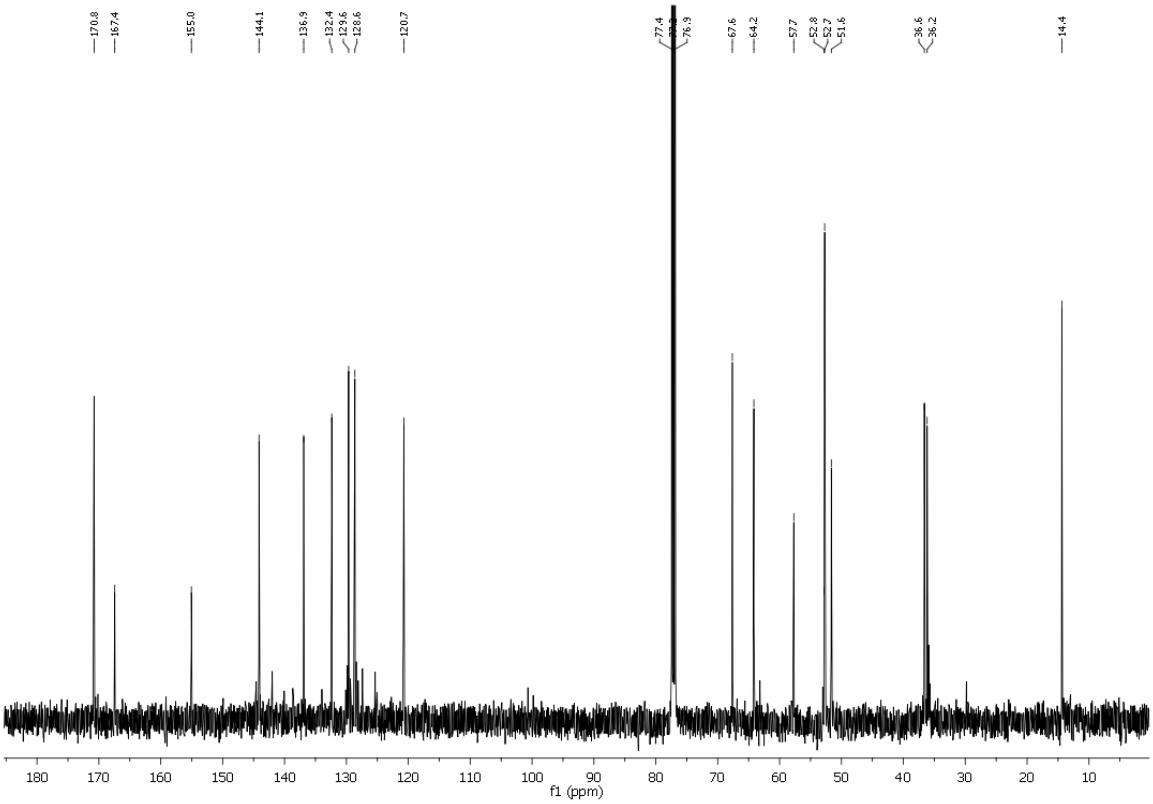
0.99
1.09
1.07
2.01
2.07
5.31
3.05
1.95
1.98
2.80
2.98
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

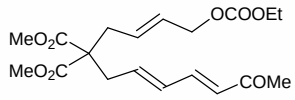

170.7
167.9
155.0
134.8
131.0
128.0
127.4
77.4
77.2
76.9
64.0
63.0
57.1
52.8
51.9
32.0
31.2
14.3
12.6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


OCOOEt
MeO2C
MeO2C
CO2Me

15

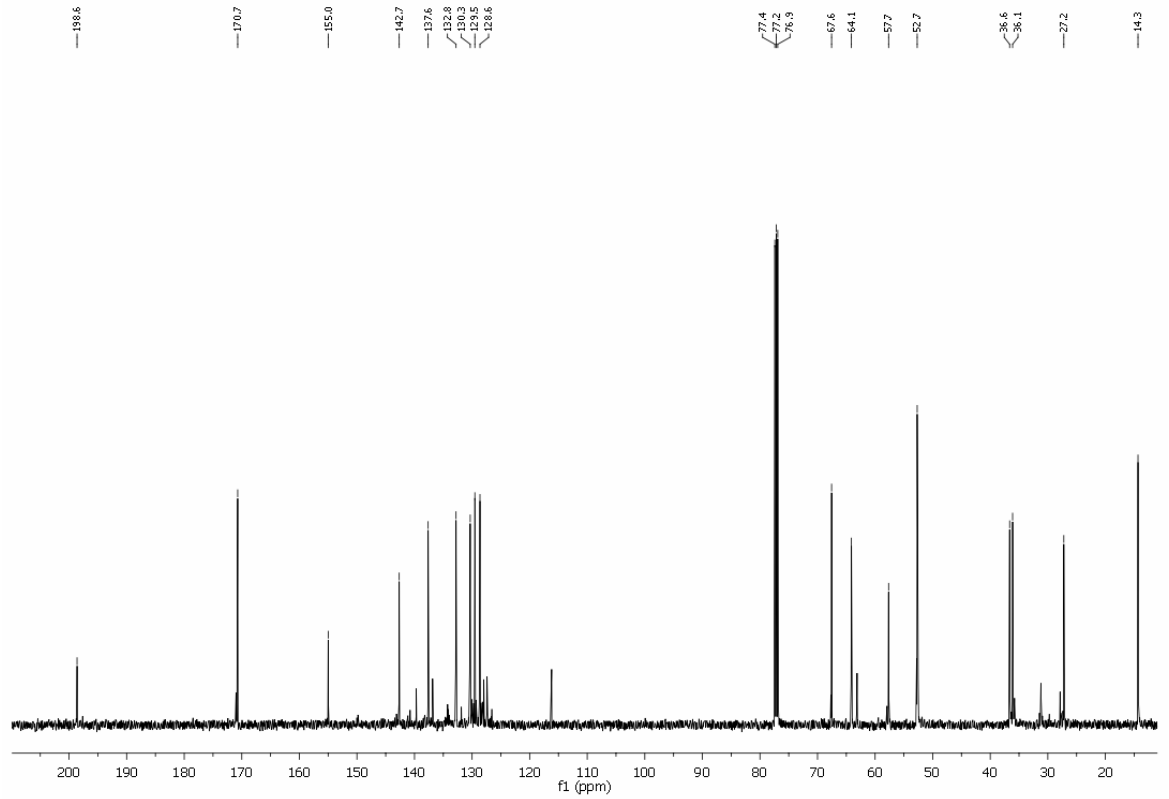
1.00
1.27
1.26
1.15
2.06
2.39
2.31
2.91
6.19
2.20
2.26
3.34
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f1 (ppm)

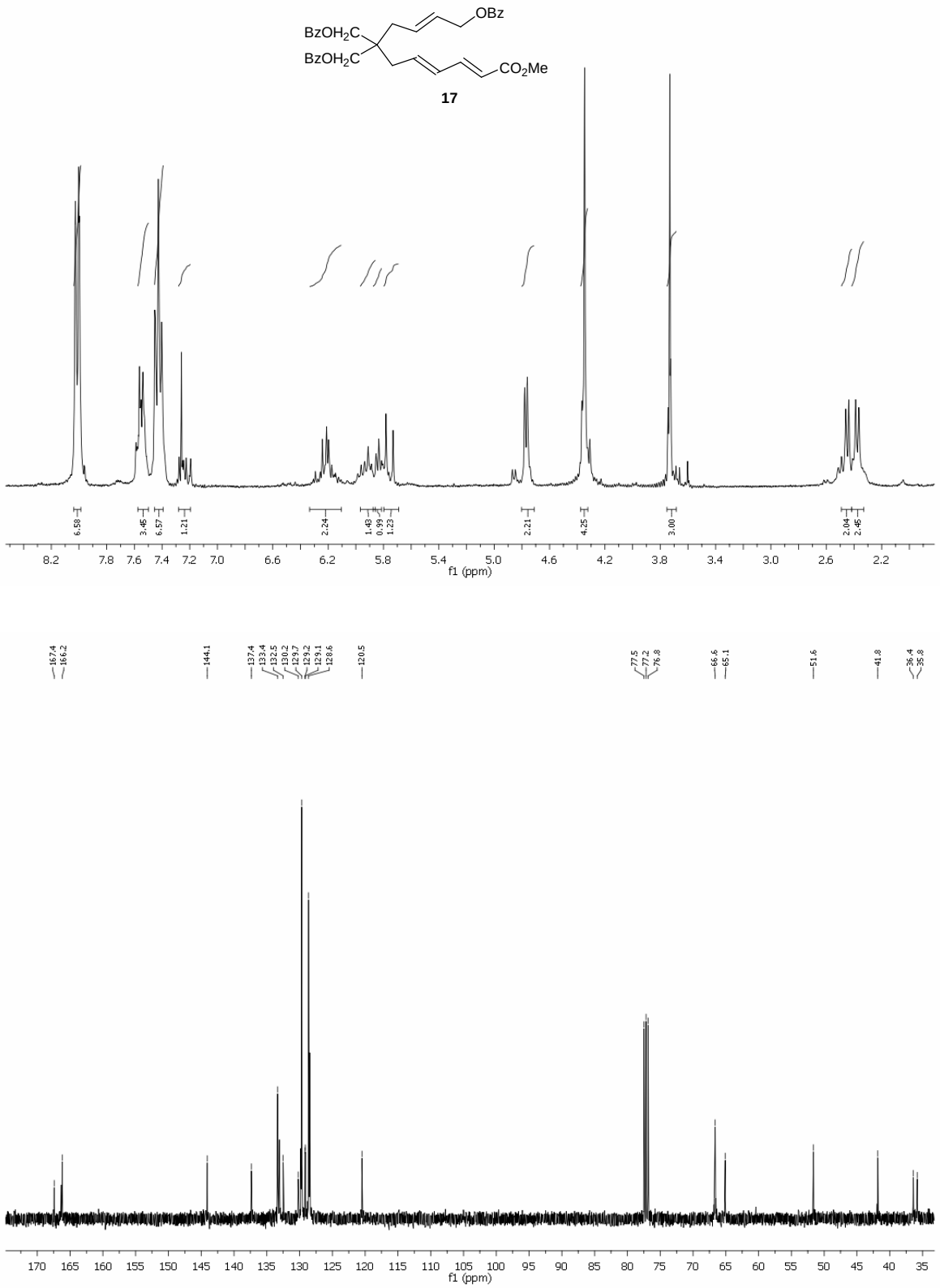

170.8
167.4
155.0
144.1
136.9
132.4
129.6
128.6
120.7
77.4
76.9
67.6
64.2
57.7
52.8
52.7
51.6
36.6
36.2
14.4
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

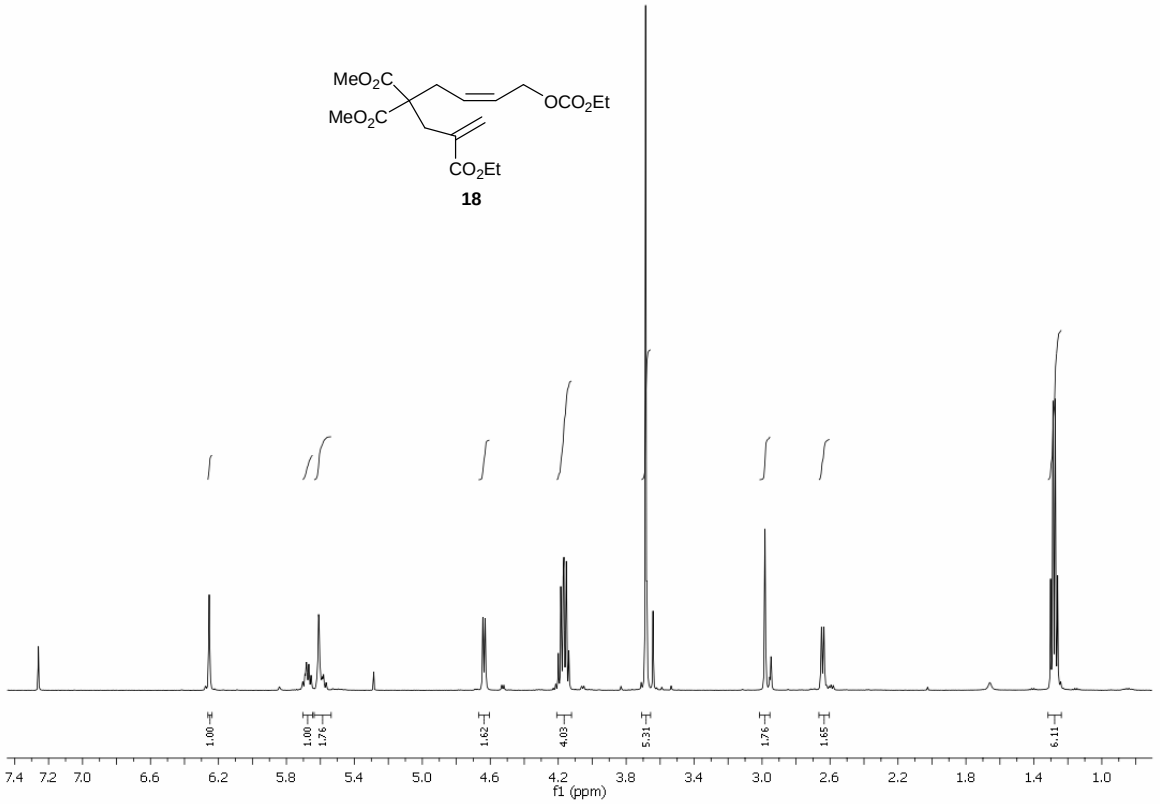

OCOOEt
MeO2C
MeO2C
COMe

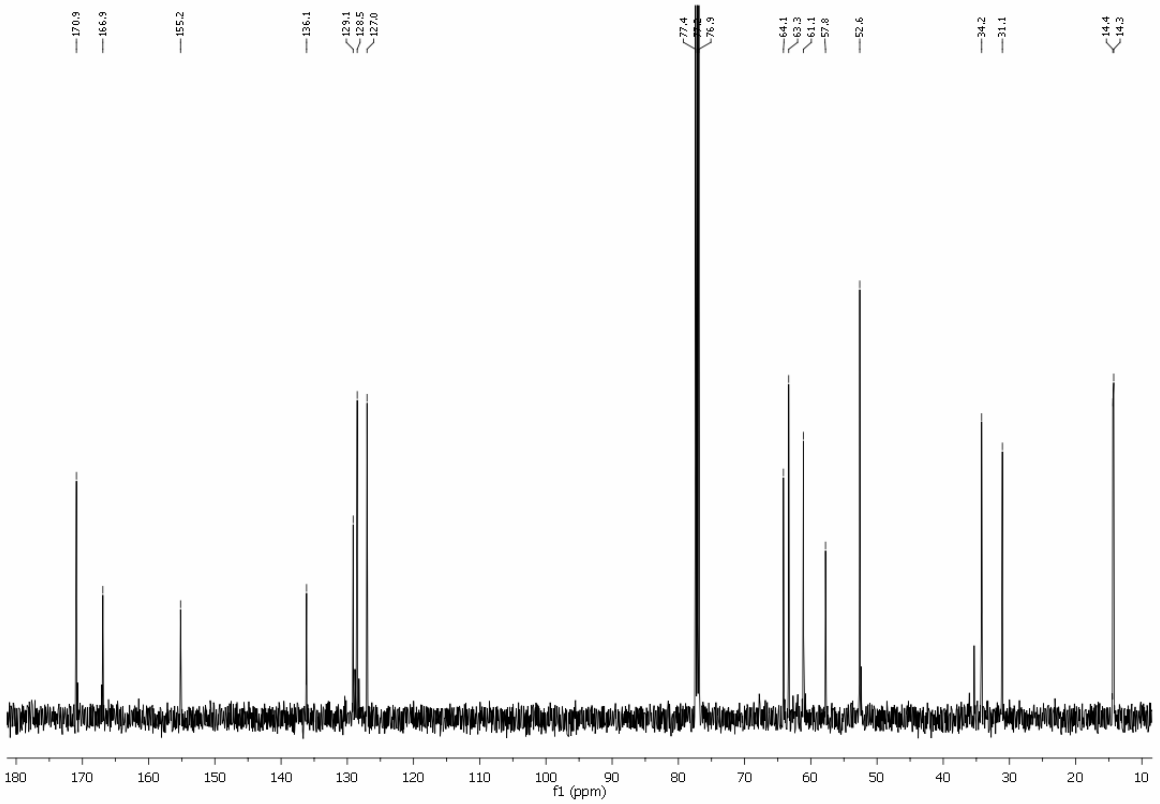
16

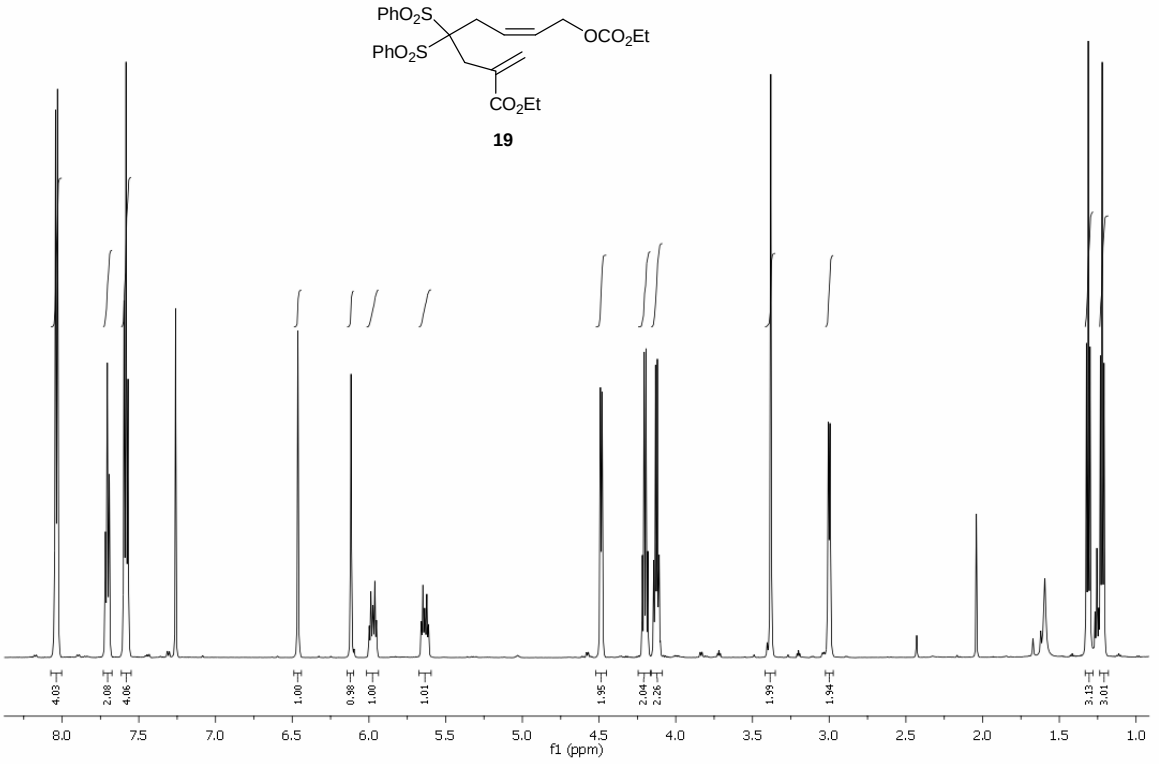
1.00
1.00
1.26
1.07
1.96
2.01
2.37
6.12
2.37
1.97
3.11
3.19
7.6 7.4 7.2 7.0 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2
f1 (ppm)


198.6
170.7
155.0
142.7
137.6
132.8
130.3
129.5
128.6
77.4
77.2
76.9
67.6
64.1
57.7
52.7
36.6
36.1
27.2
14.3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

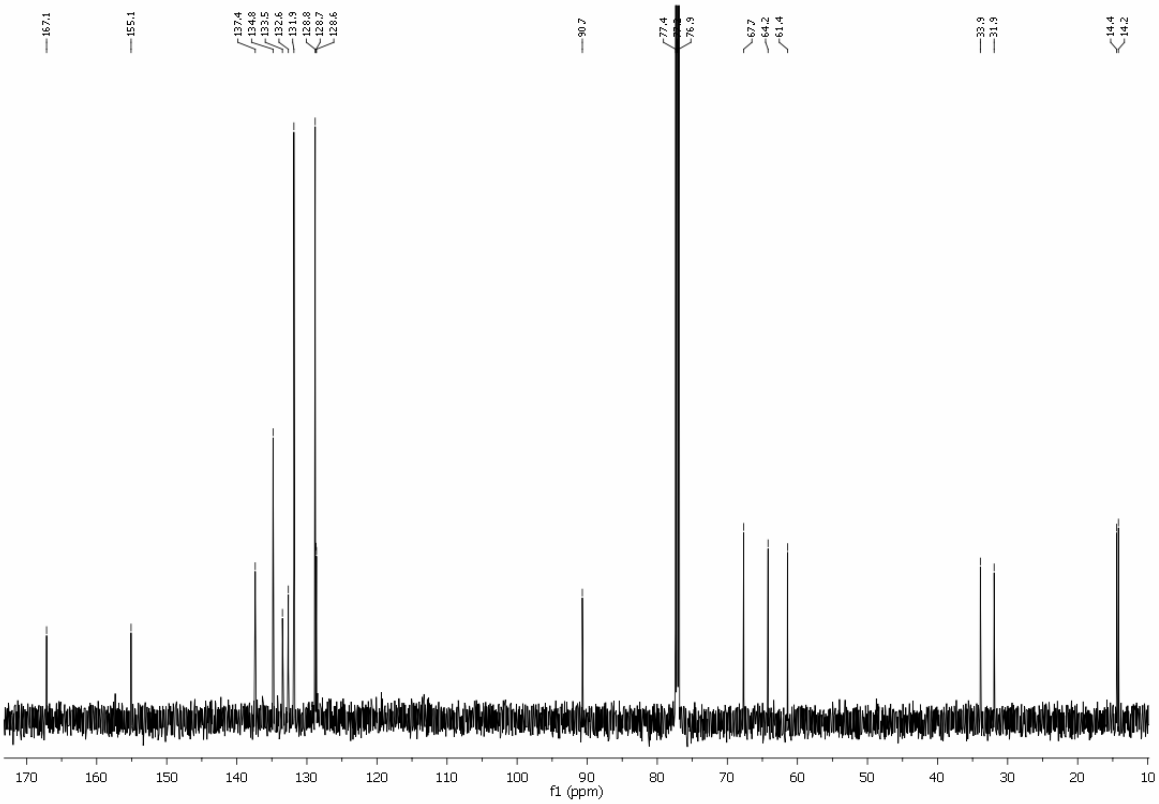

OBz
BzOH2C
BzOH2C
CO2Me
17
6.58
3.46
6.57
1.21
2.24
1.43
0.99
1.23
2.21
4.25
3.00
2.04
2.45
f1 (ppm)
167.4
166.2
144.1
137.4
133.4
132.5
130.2
129.7
129.2
129.1
128.6
120.5
77.5
77.2
76.8
66.6
65.1
51.6
41.8
36.4
35.8
f1 (ppm)

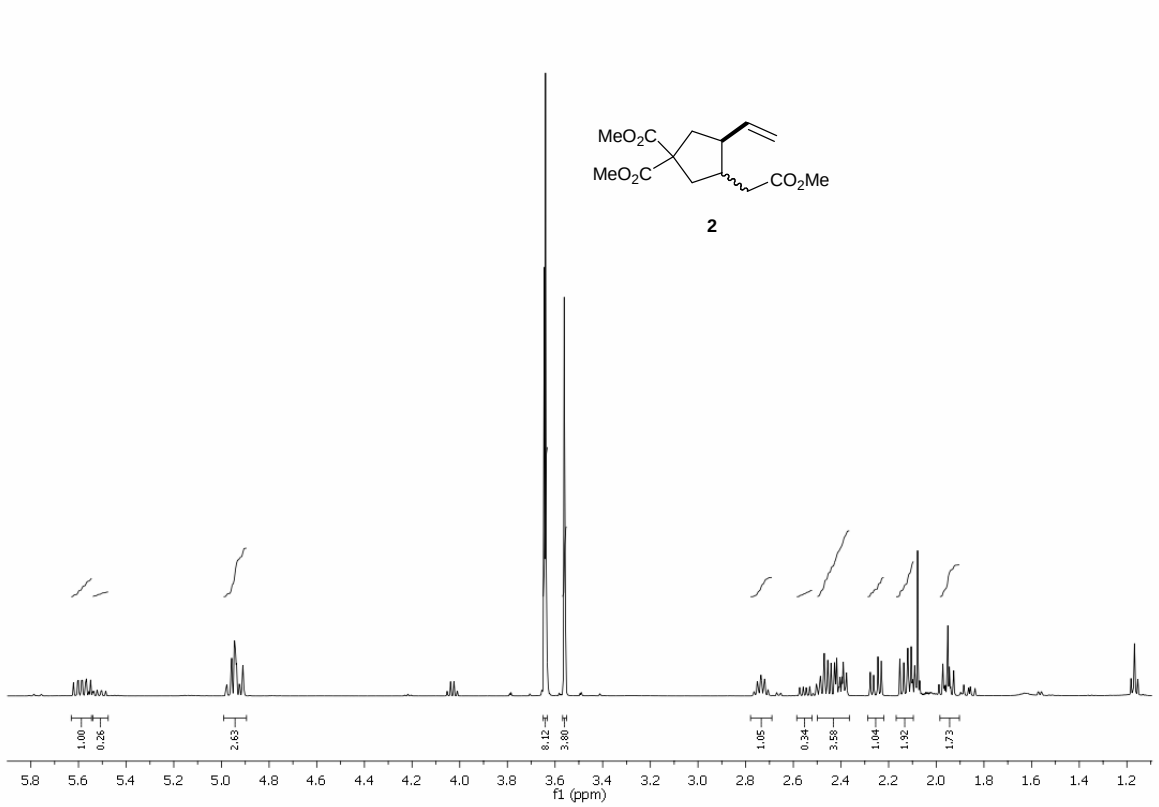

MeO2C
MeO2C
OCO2Et
CO2Et
18
1.00
1.00
1.76
1.62
4.03
5.31
1.76
1.65
6.11
7.4 7.2 7.0 6.6 6.2 5.8 5.4 5.0 4.6 4.2 3.8 3.4 3.0 2.6 2.2 1.8 1.4 1.0
f1 (ppm)

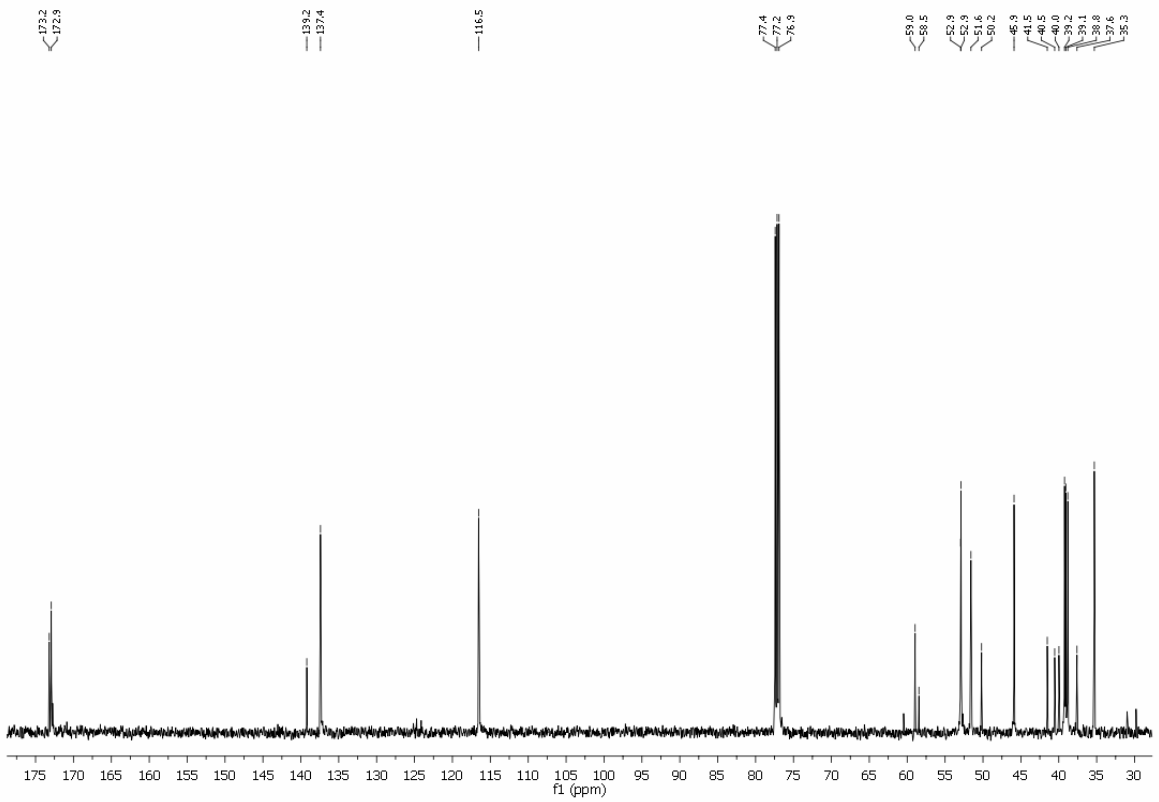

170.9
166.9
155.2
136.1
129.1
128.5
127.0
77.4
76.8
76.9
64.1
63.3
61.1
57.8
52.6
34.2
31.1
14.4
14.3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

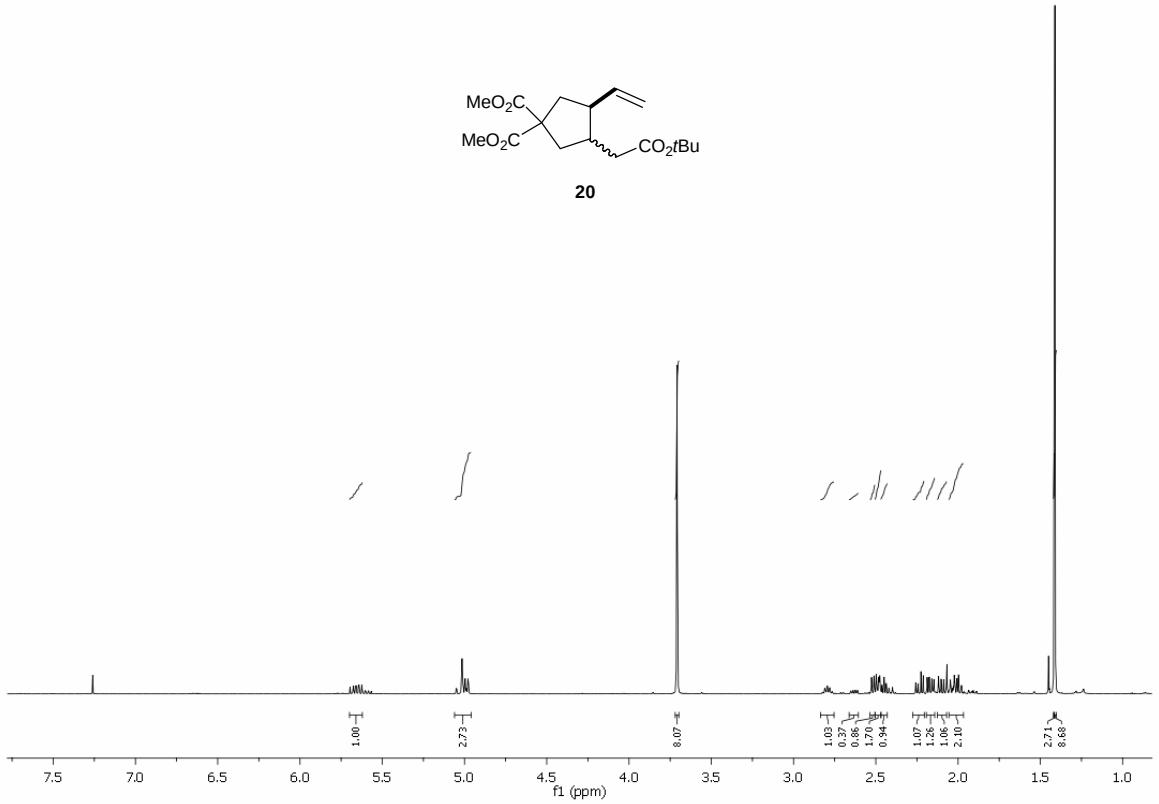

PhO2S
PhO2S
OCO2Et
CO2Et
4.03
2.08
4.06
1.00
0.98
1.00
1.01
1.95
2.04
2.26
1.99
1.94
3.13
3.01
f1 (ppm)

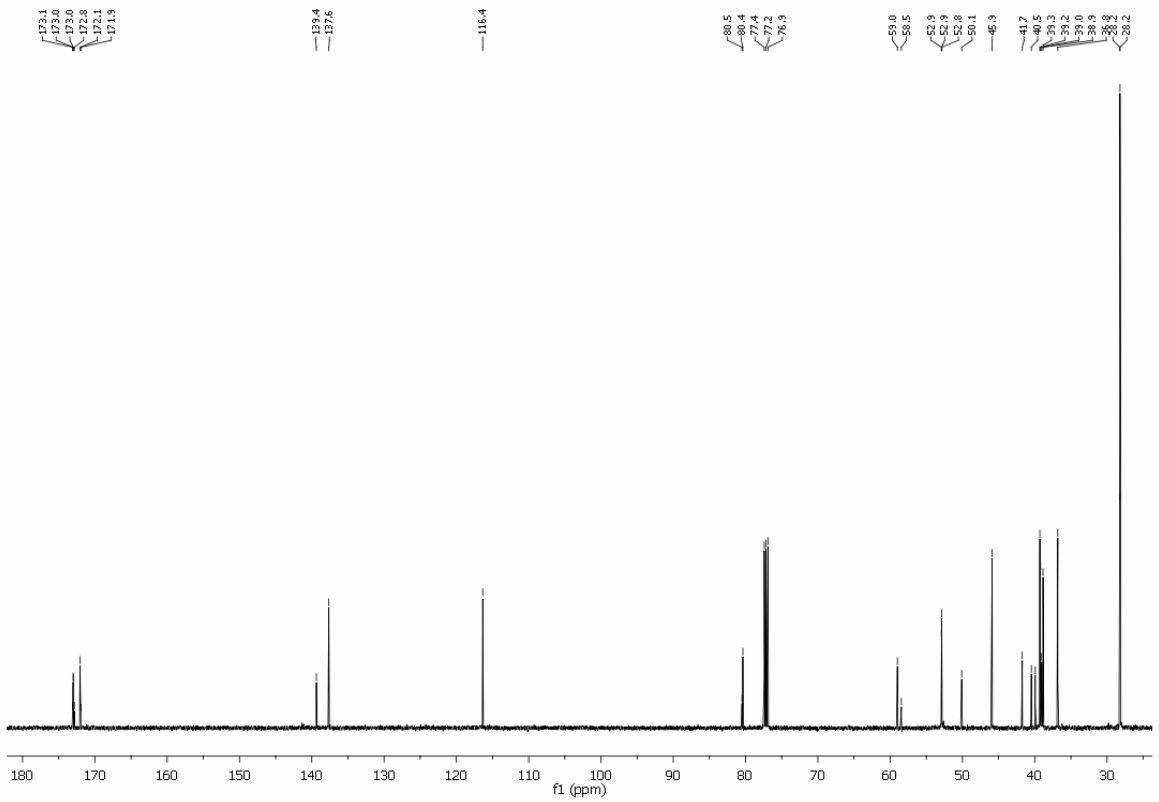
19

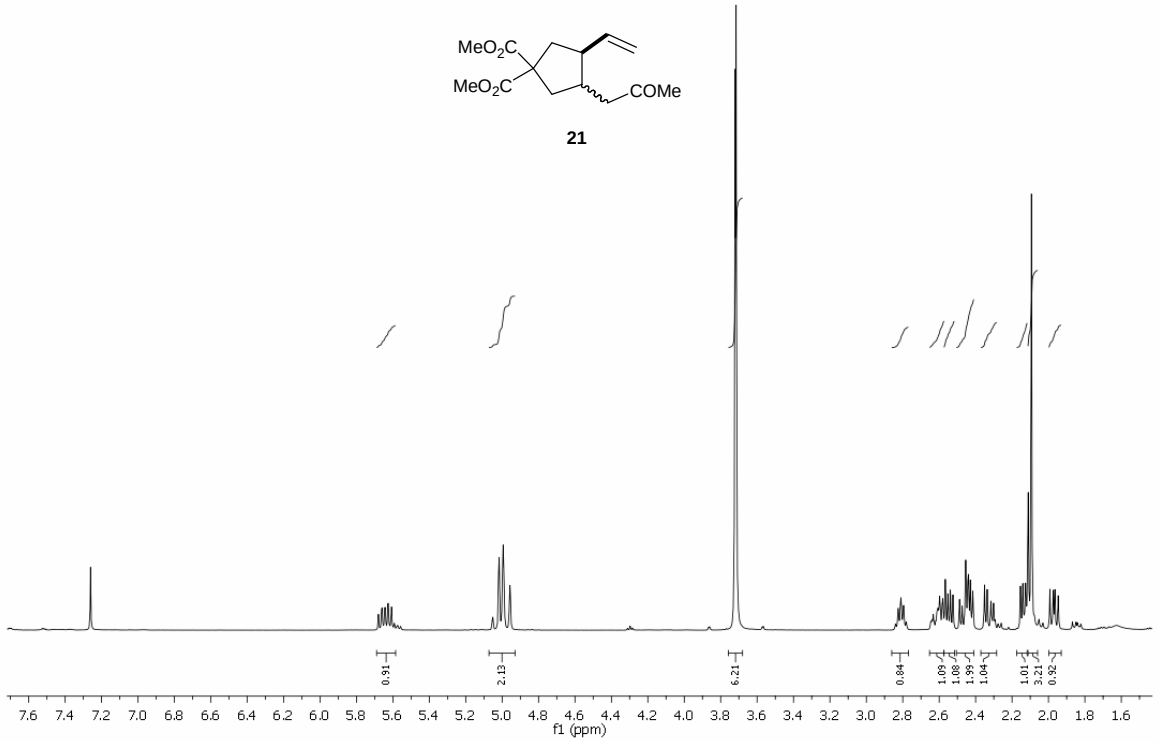

167.1
155.1
137.4
134.8
133.5
132.6
131.9
128.8
128.7
128.6
90.7
77.4
76.9
67.7
64.2
61.4
33.9
31.9
14.4
14.2
f1 (ppm)

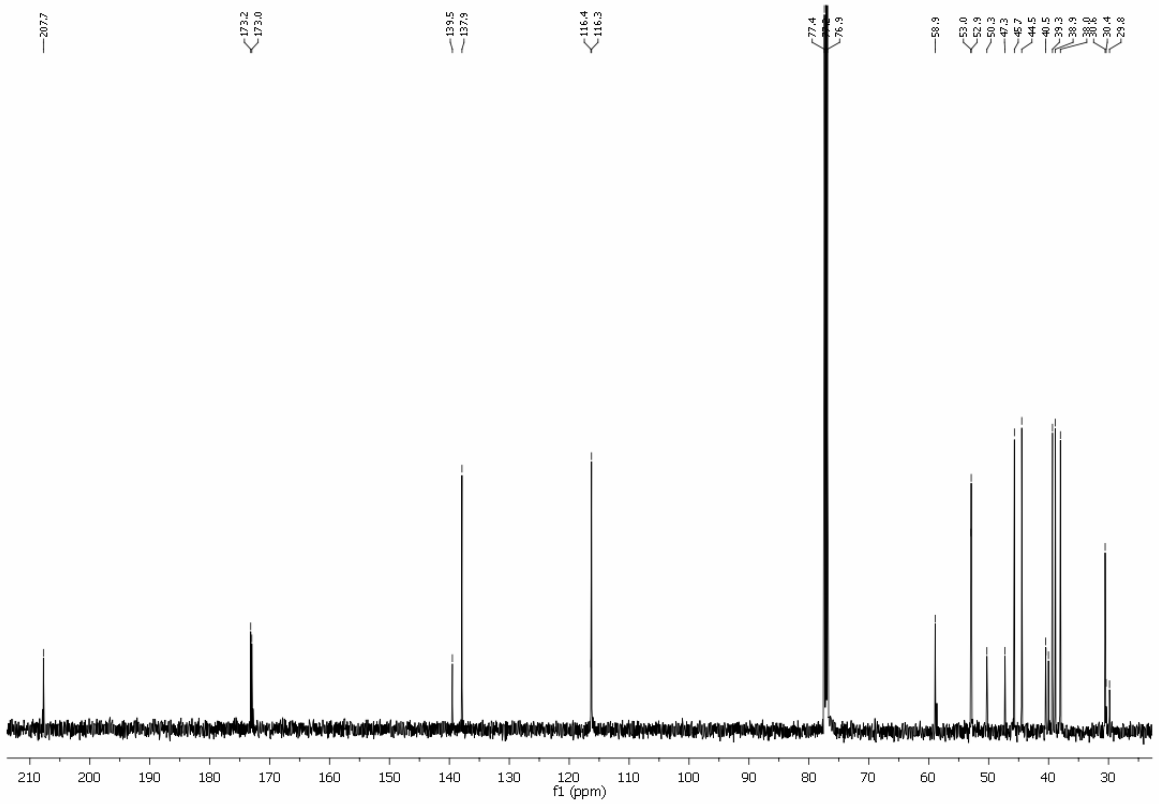

MeO2C
MeO2C
CO2Me
2
1.00
0.26
2.63
8.12
3.80
1.05
0.34
3.58
1.04
1.92
1.73
f1 (ppm)

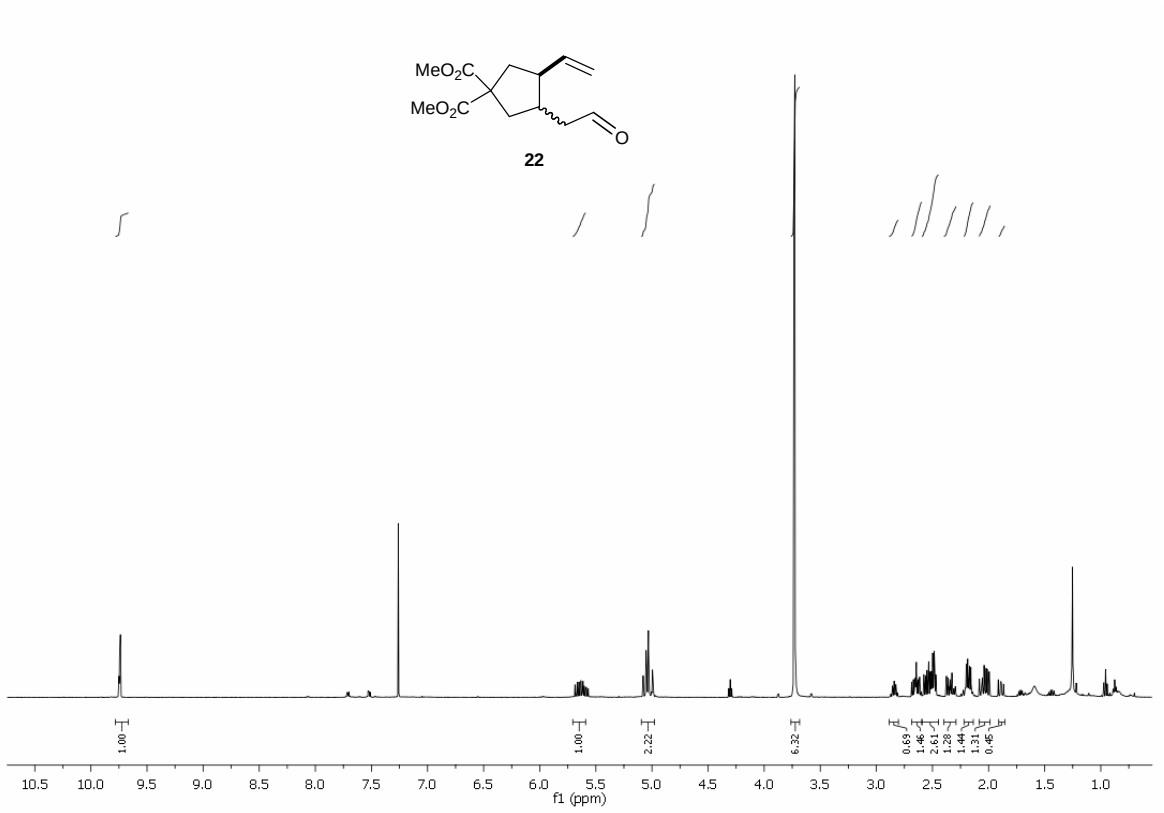

173.2
172.9
139.2
137.4
116.5
77.4
77.2
76.9
59.0
58.5
52.9
52.9
51.6
50.2
45.9
41.5
40.5
40.0
39.2
39.1
38.8
37.6
35.3
f1 (ppm)

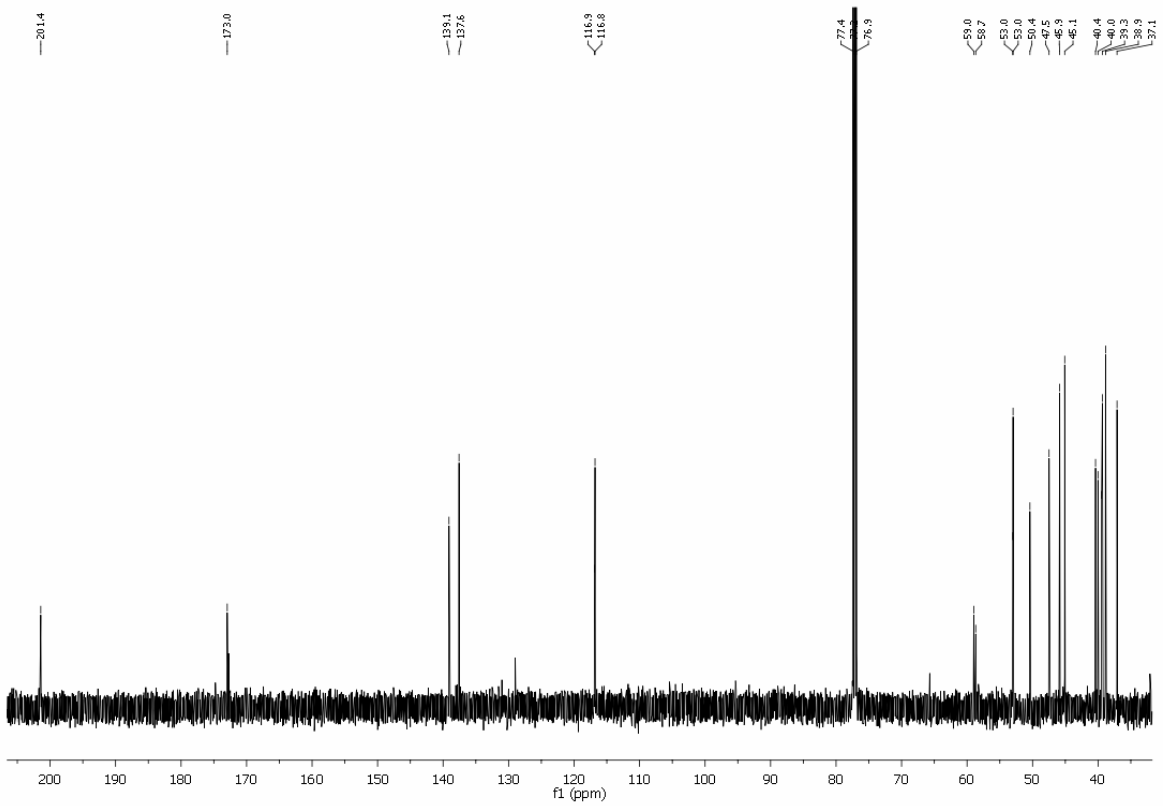

MeO2C
MeO2C
CO2tBu
20
1.00
2.73
8.07
1.03
0.37
0.86
1.70
0.94
1.07
1.26
1.06
2.10
2.71
8.68
f1 (ppm)

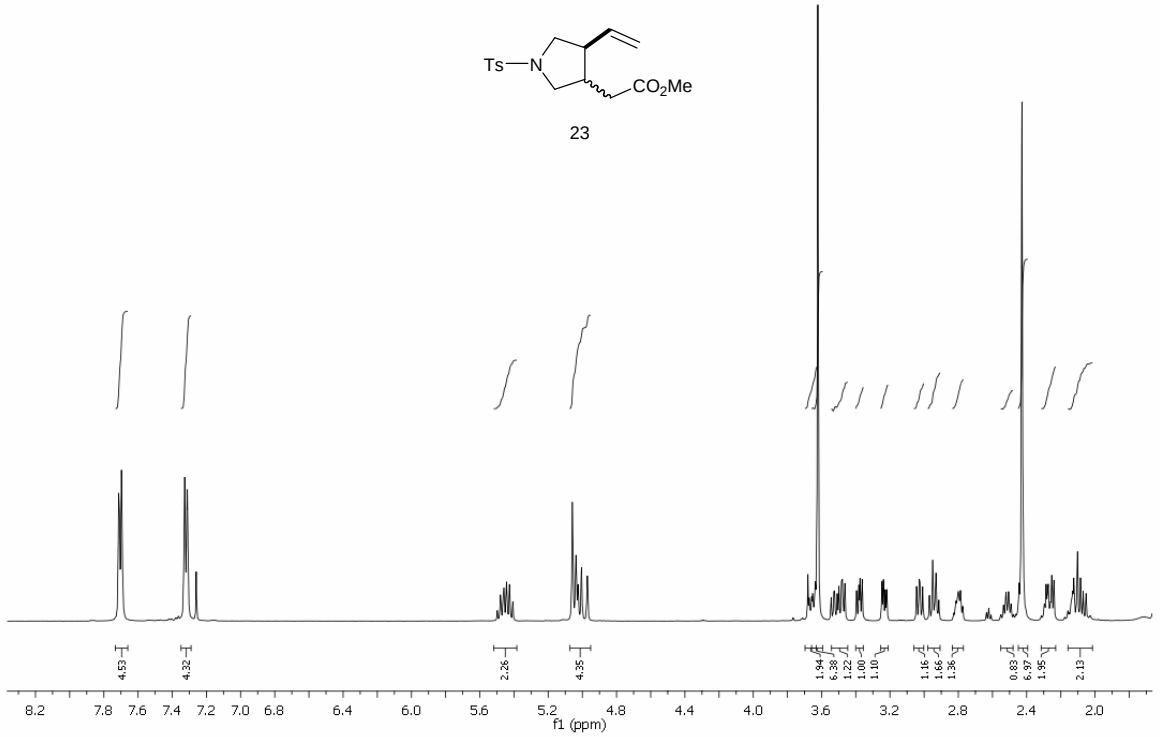

173.1
173.0
173.0
172.8
172.1
171.9
139.4
137.6
116.4
80.5
80.4
77.4
77.2
76.9
59.0
58.5
52.9
52.9
52.8
50.1
45.9
41.7
40.5
39.3
39.2
39.0
38.9
28.2
28.2
f1 (ppm)

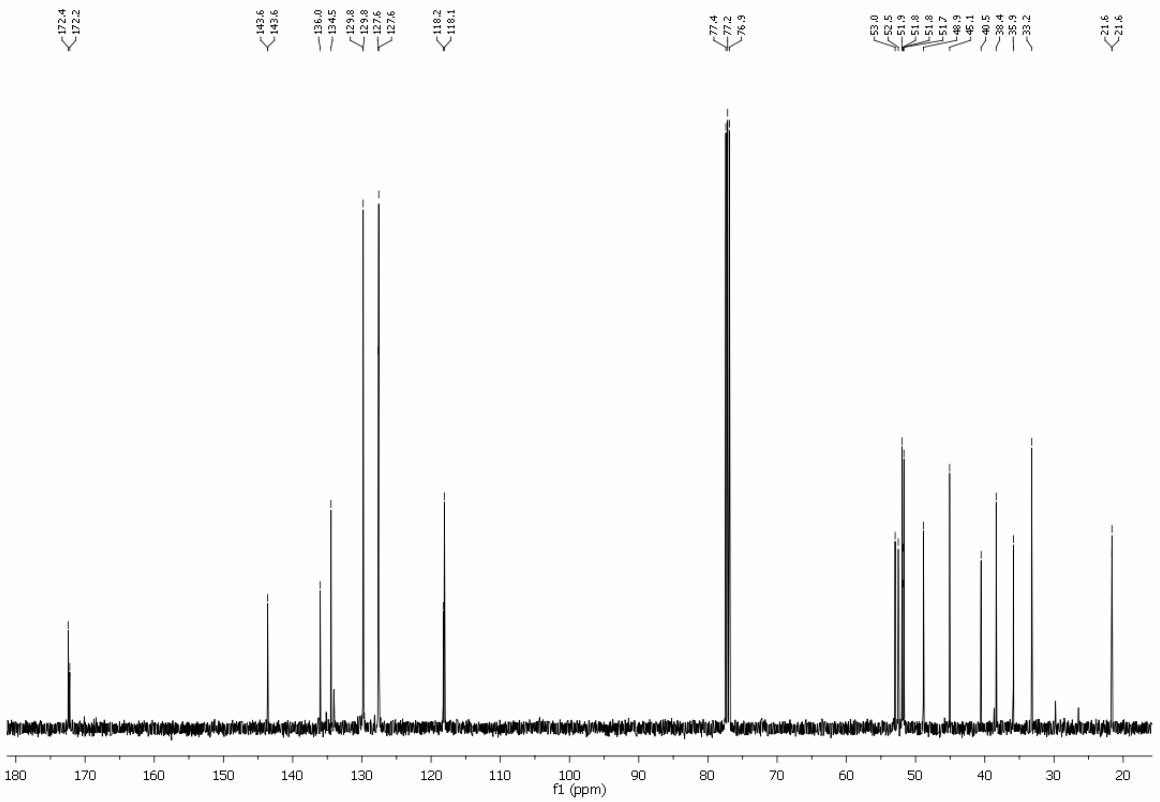

MeO2C
MeO2C
COMe
21
0.91
2.13
6.21
0.84
1.09
1.08
1.99
1.04
1.01
3.21
0.92
f1 (ppm)

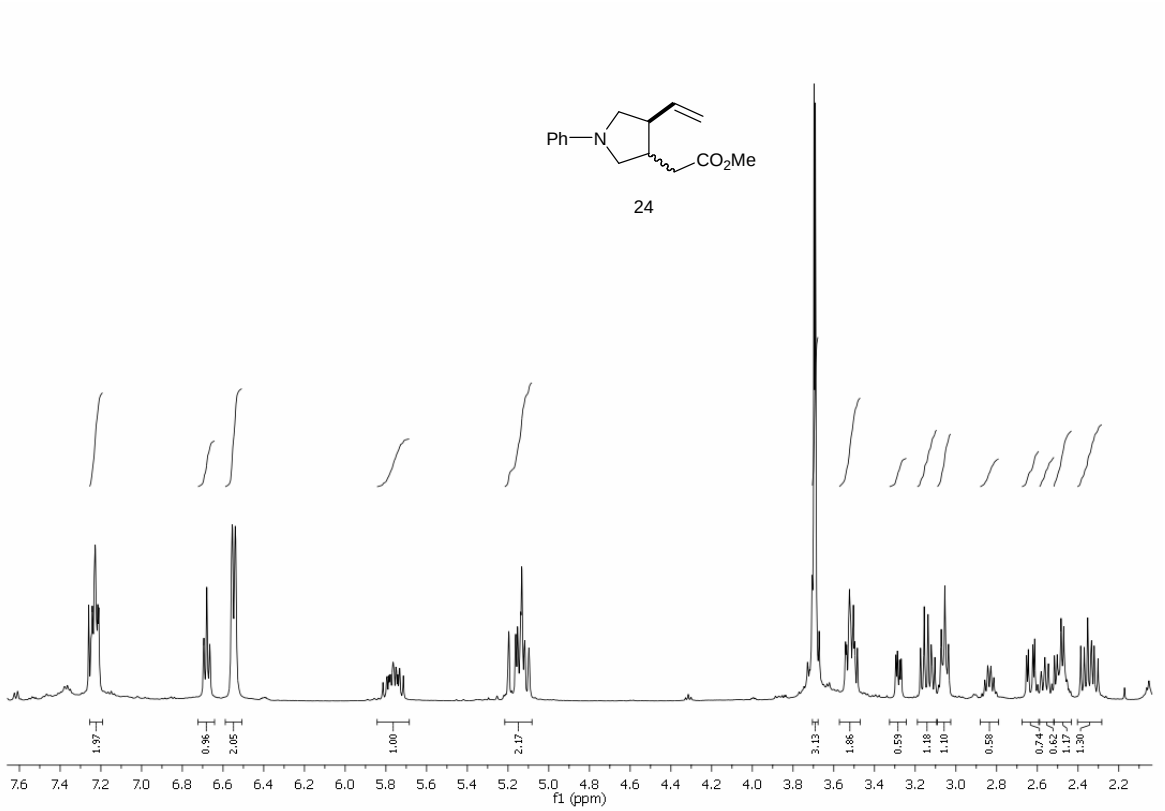

207.7
173.2
173.0
139.5
137.9
116.4
116.3
77.4
76.9
58.9
53.0
52.9
50.3
47.3
45.7
44.5
40.5
39.3
38.9
38.0
30.4
29.8
f1 (ppm)

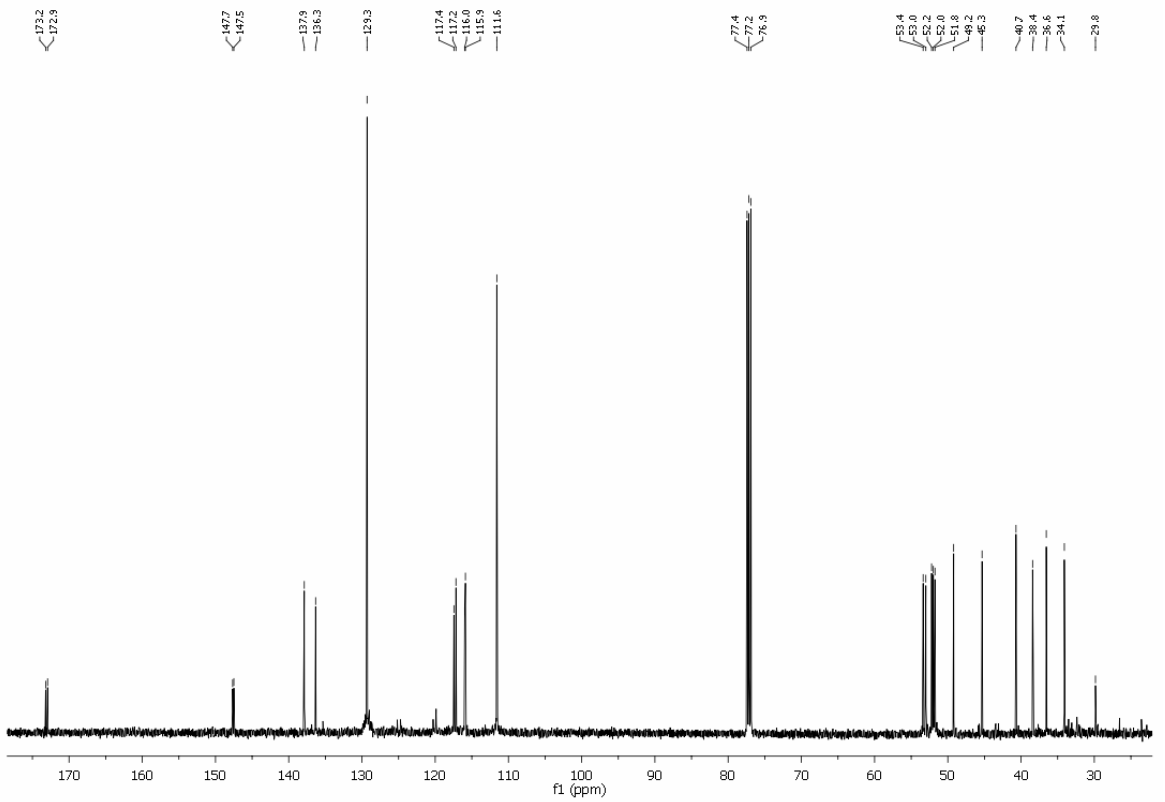

MeO2C
MeO2C
O
22
1.00
1.00
2.22
6.32
0.69
1.46
2.61
2.08
1.44
1.31
0.45
f1 (ppm)

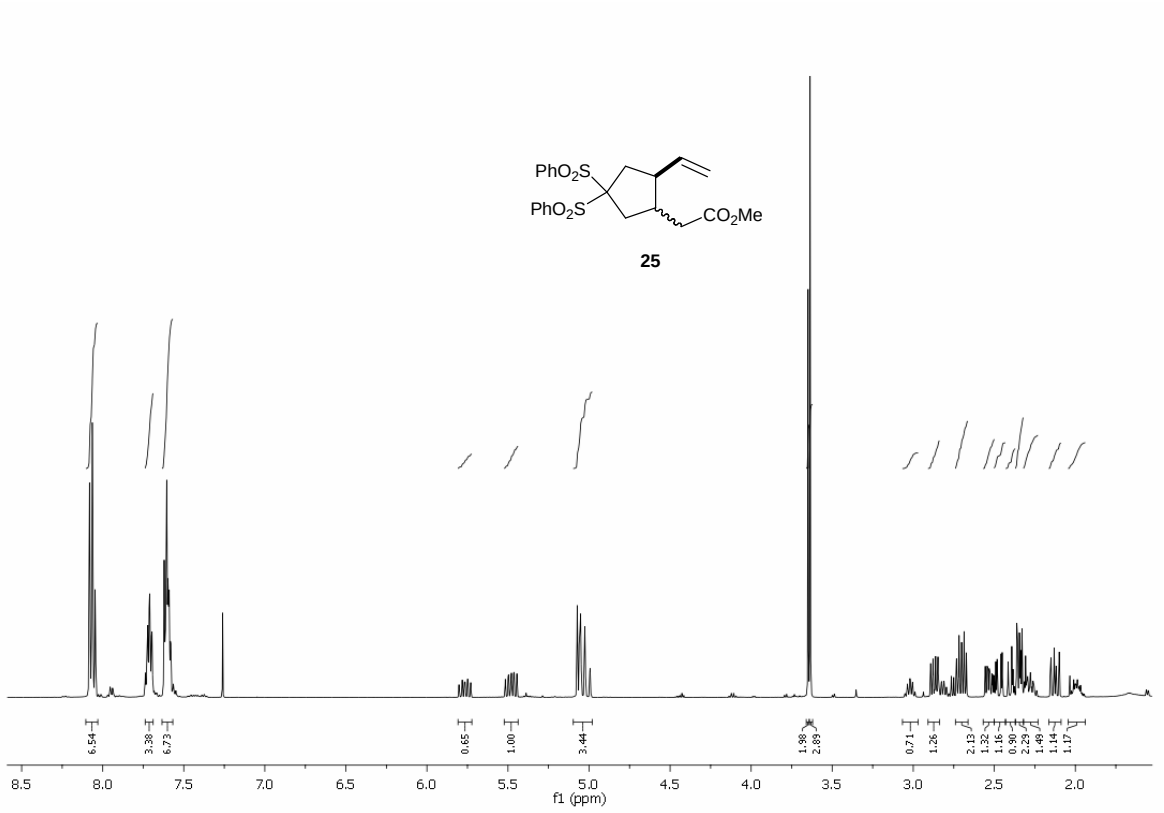

201.4
173.0
139.1
137.6
116.9
116.8
77.4
76.9
59.0
58.7
53.0
53.0
50.4
47.5
45.9
45.1
40.4
40.0
39.3
38.9
37.1
f1 (ppm)

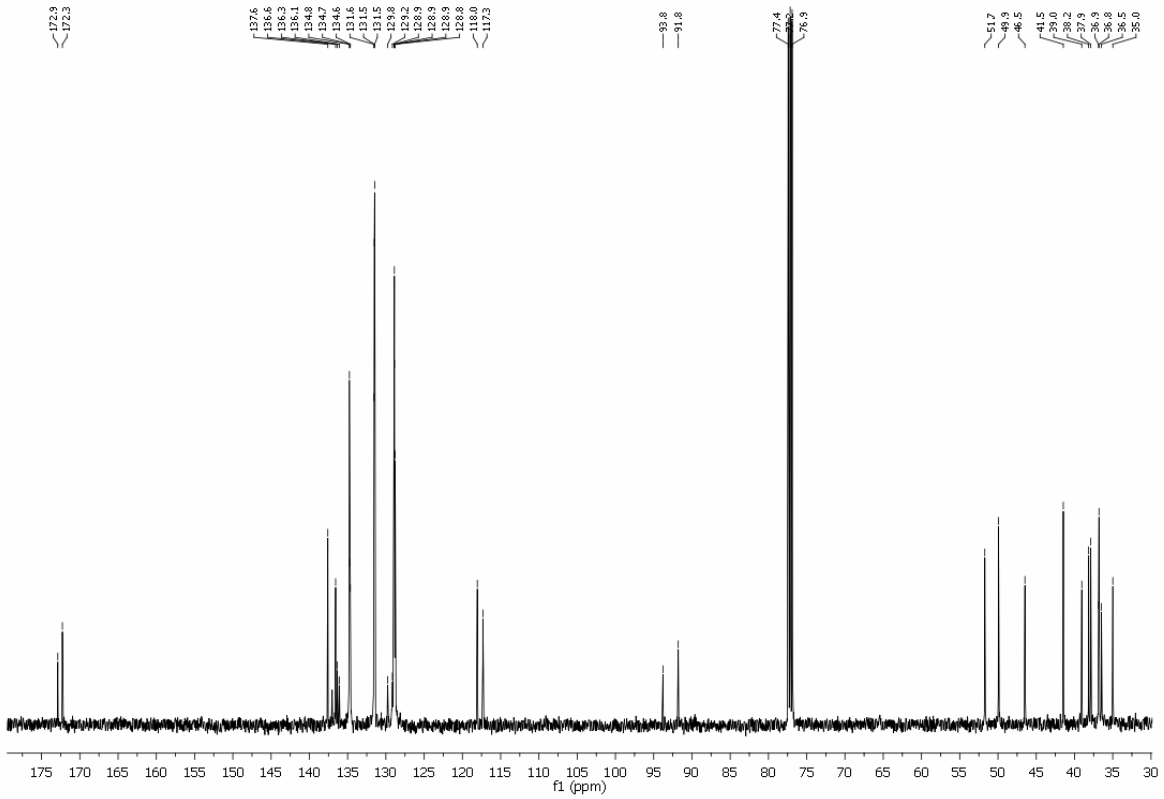

Ts—N
CO2Me
23
f1 (ppm)

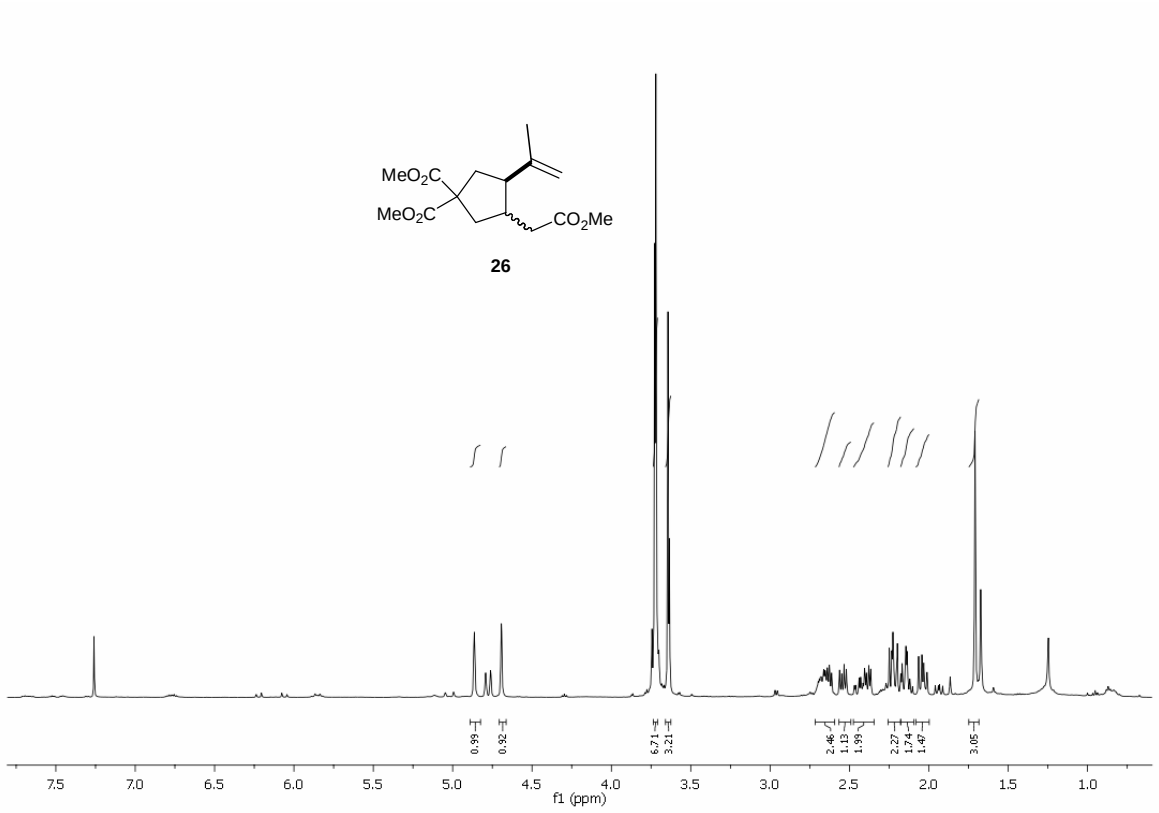

f1 (ppm)

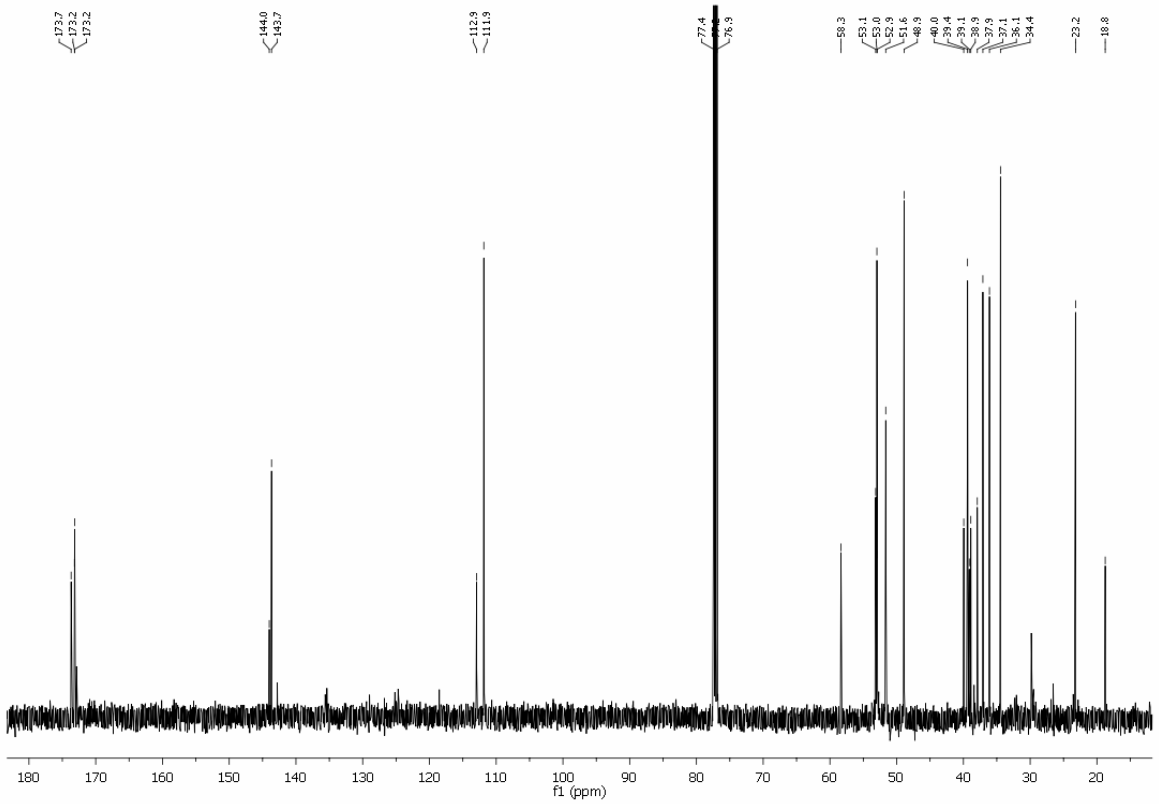

Ph—N
CO2Me
24
1.97
0.96
2.05
1.00
2.17
3.13
1.86
0.59
1.18
1.10
0.58
0.74
0.62
1.17
1.30
f1 (ppm)

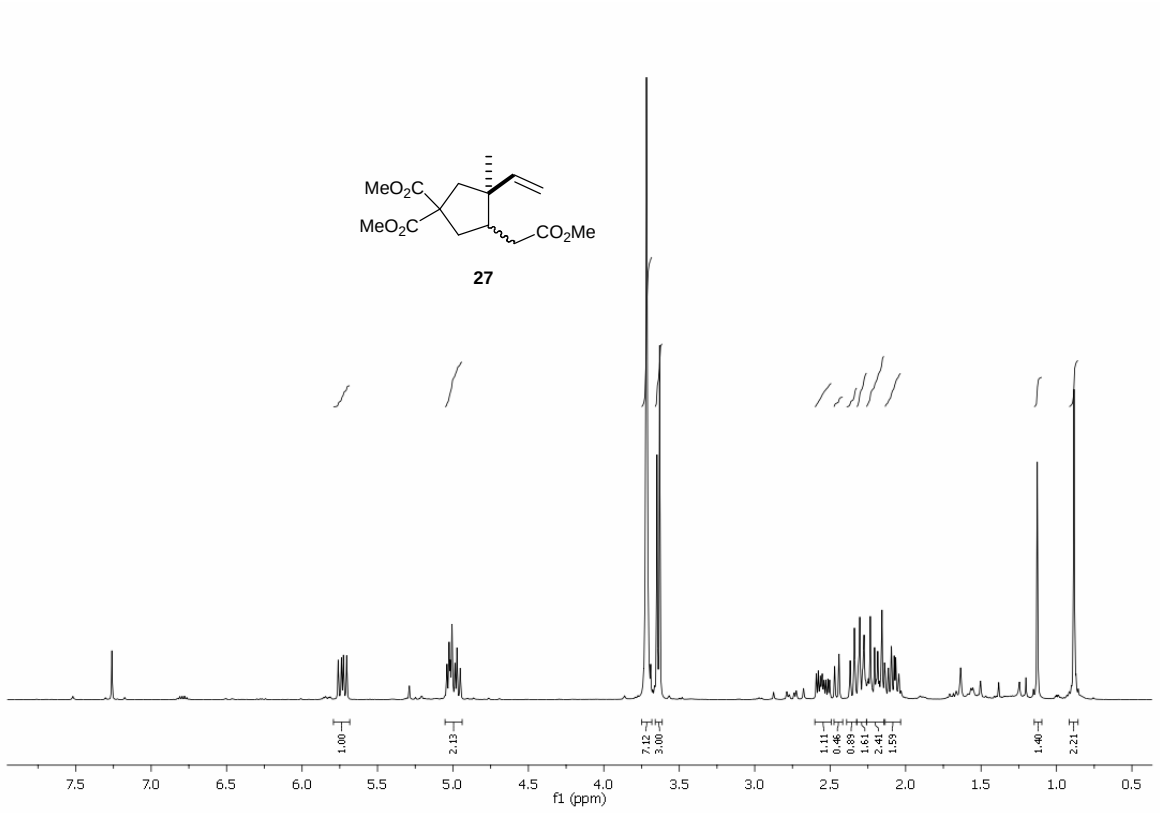

173.2
172.9
147.7
147.5
137.9
136.3
129.3
117.4
117.2
116.0
115.9
111.6
77.4
77.2
76.9
53.4
53.0
52.2
52.0
51.8
49.2
46.3
40.7
38.4
36.6
34.1
29.8
f1 (ppm)

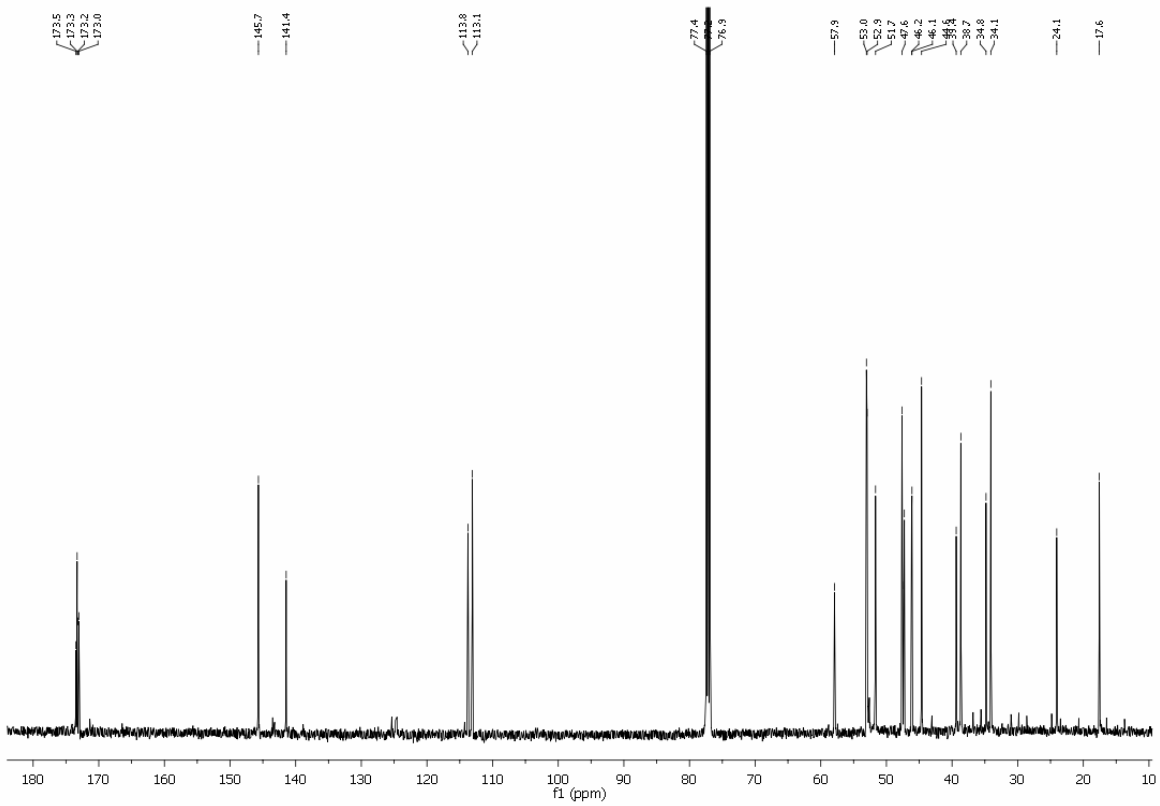

PhO2S
PhO2S
CO2Me
25
6.54
3.38
6.73
0.65
1.00
3.44
1.98
2.89
0.71
1.26
2.13
1.32
1.16
0.90
2.29
1.49
1.14
1.17
f1 (ppm)

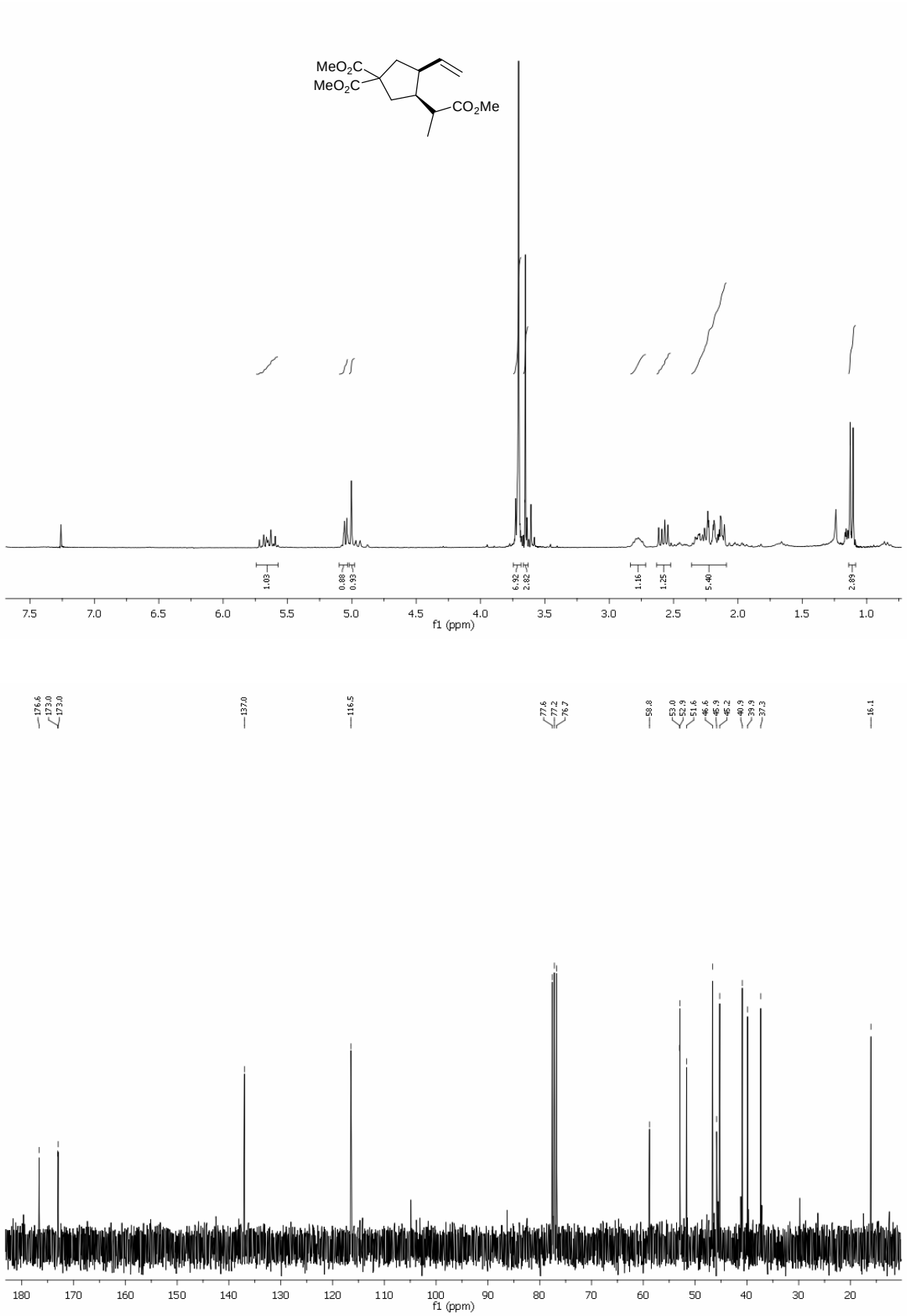

172.9
172.3
137.6
136.6
136.3
136.1
134.8
134.7
134.6
131.6
131.5
131.5
129.8
129.2
128.9
128.9
128.9
128.8
118.0
117.3
93.8
91.8
77.4
76.9
51.7
49.3
46.5
41.5
39.0
38.2
37.9
36.9
36.8
36.5
35.0
f1 (ppm)

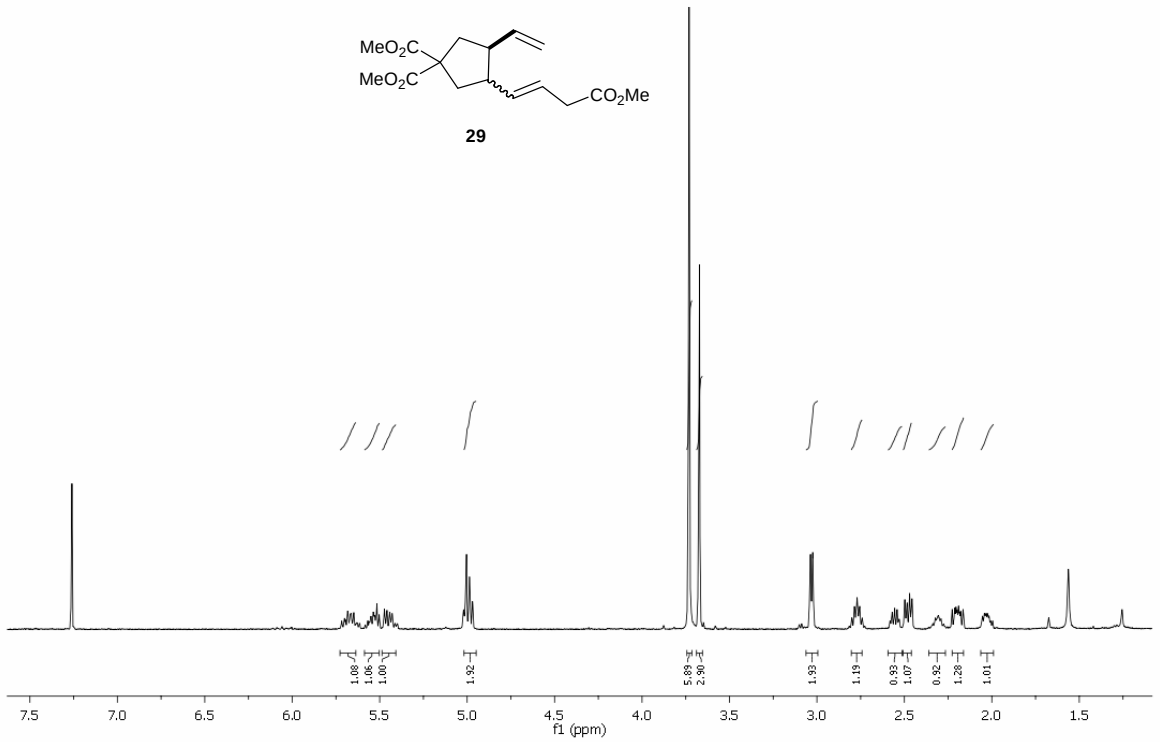

MeO2C
MeO2C
CO2Me
26
0.99
0.92
6.71
3.21
2.46
1.13
1.99
2.27
1.74
1.49
3.05
f1 (ppm)

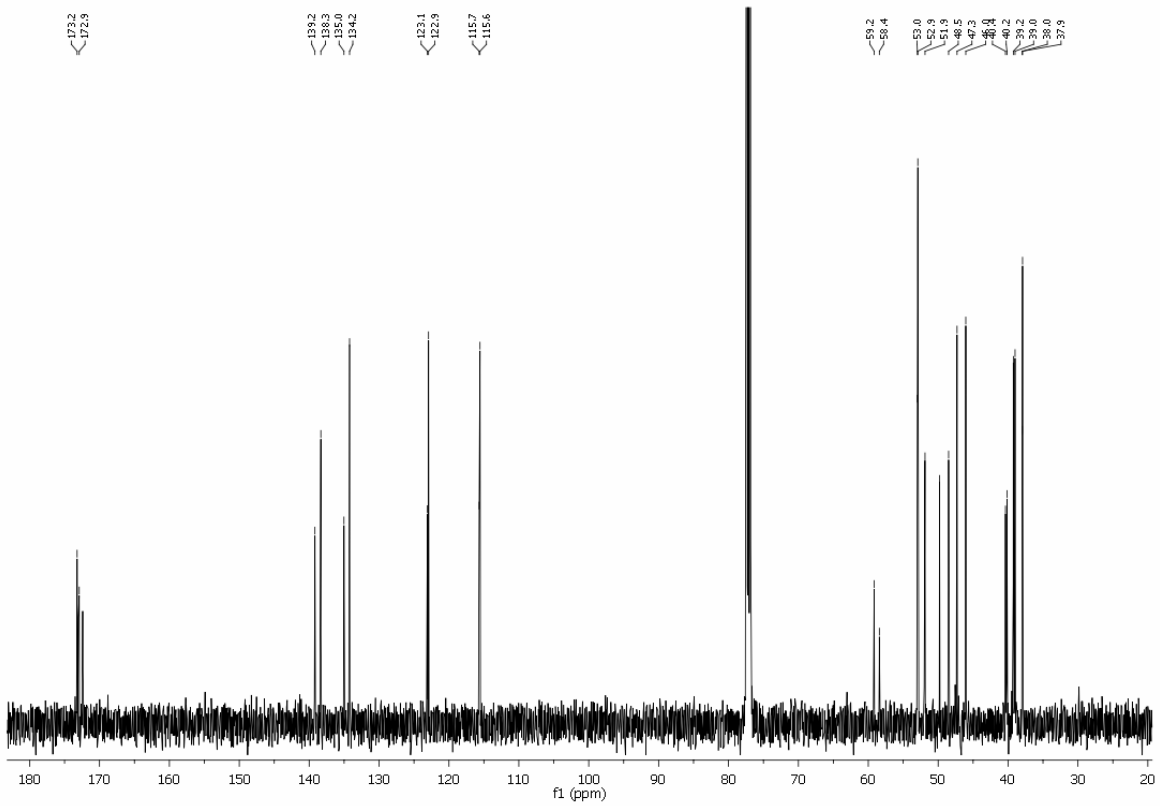

173.7
173.2
173.2
144.0
143.7
112.9
111.9
77.4
76.9
76.3
50.3
53.1
53.0
52.9
51.6
40.9
40.0
39.4
39.1
38.9
37.9
37.1
36.1
34.4
23.2
18.8
f1 (ppm)

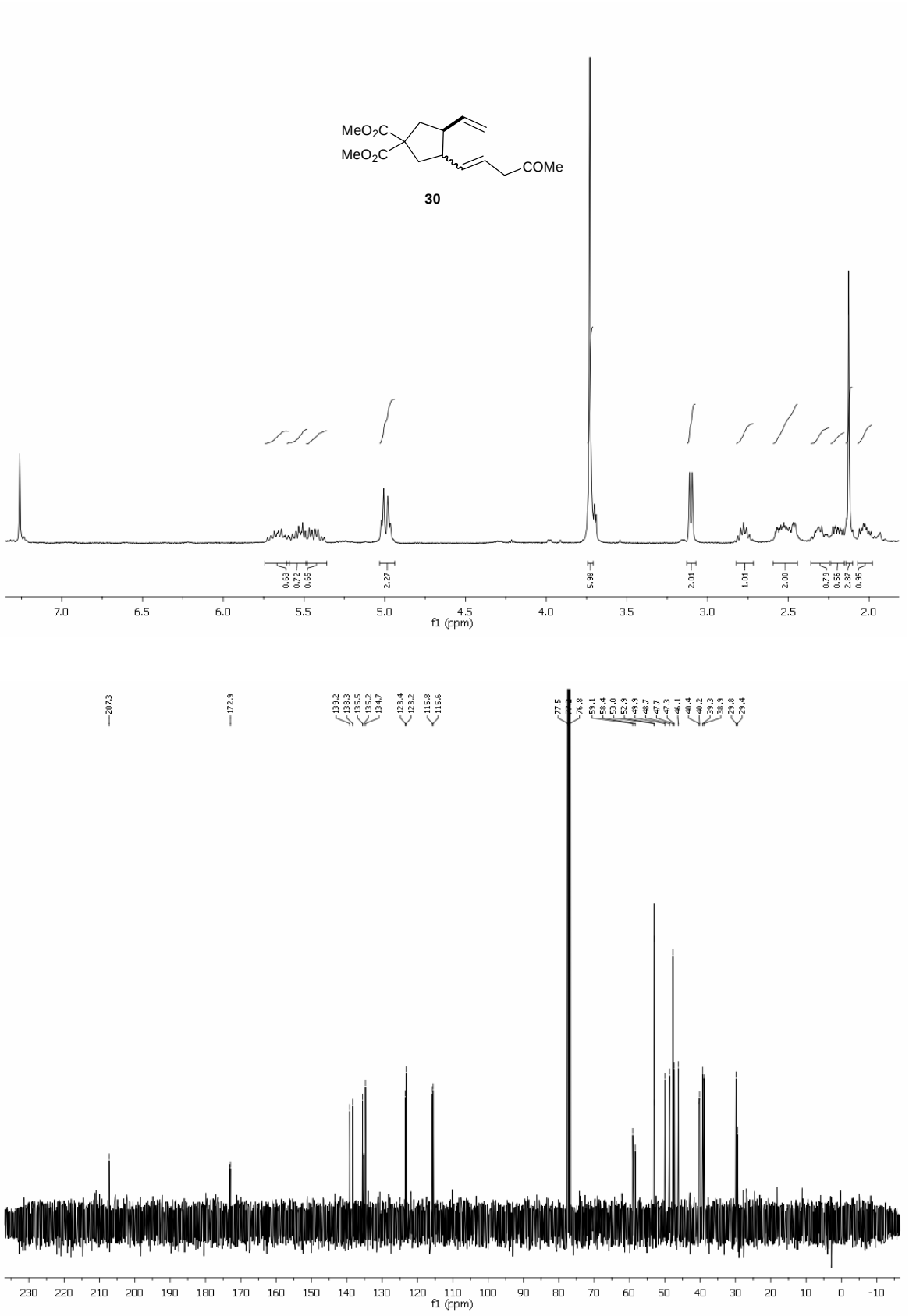

MeO2C
MeO2C
CO2Me
27
1.00
2.13
7.12
3.00
1.11
0.46
0.89
1.61
2.41
1.59
1.40
2.21
f1 (ppm)

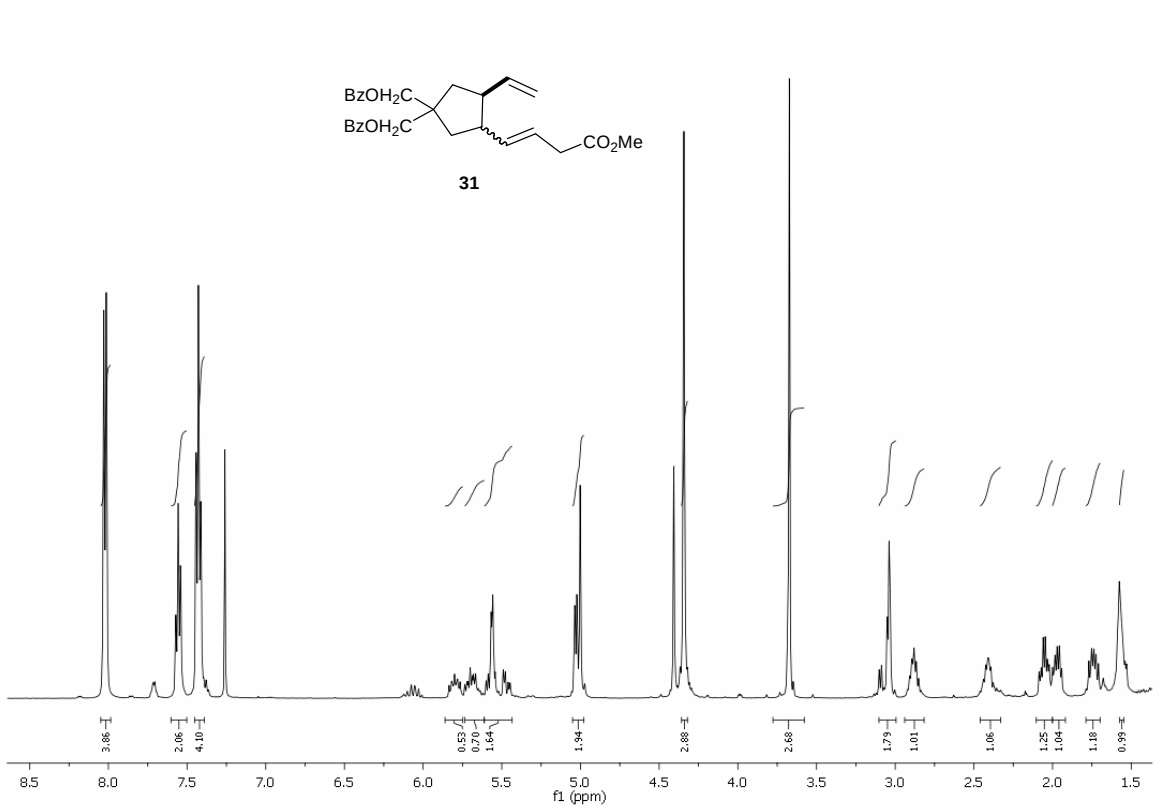

173.5
173.3
173.2
173.0
145.7
141.4
113.8
113.1
77.4
76.9
57.9
53.0
52.9
51.7
47.6
46.2
46.1
38.7
34.8
34.1
24.1
17.6
f1 (ppm)

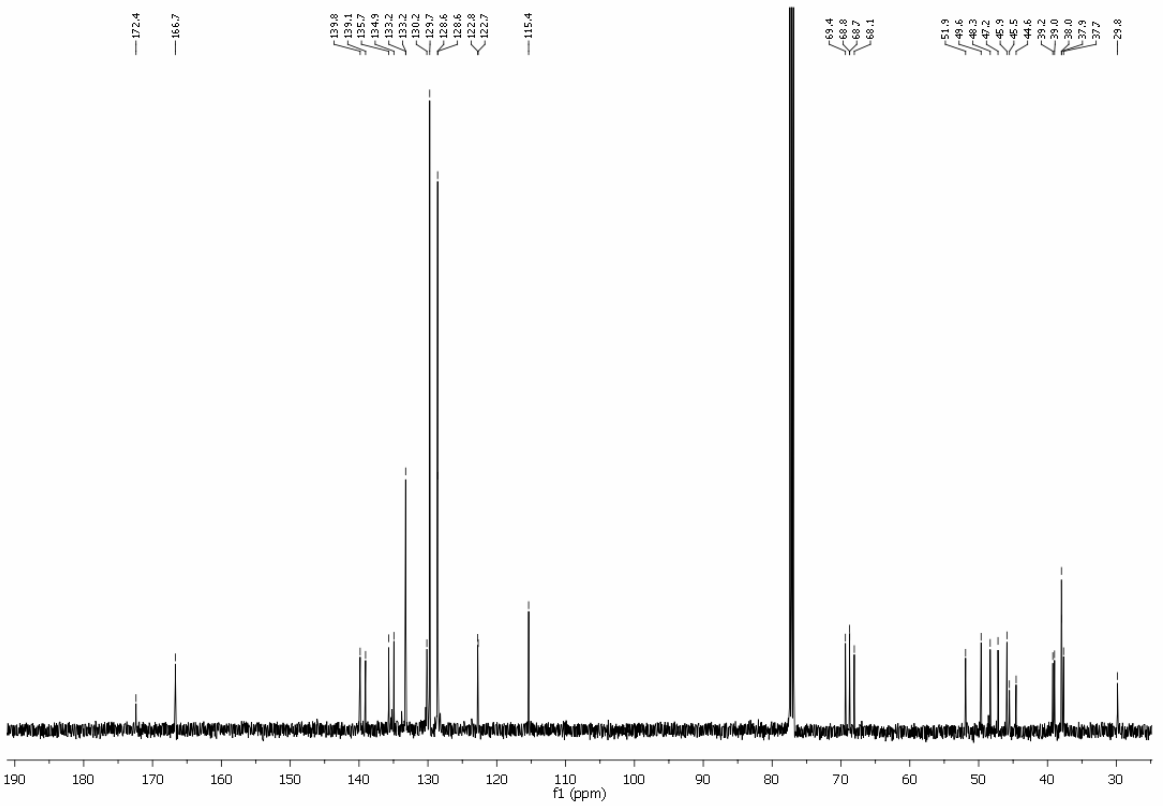

MeO2C
MeO2C
CO2Me
1.03
0.88
0.93
6.92
2.82
1.16
1.25
5.40
2.89
f1 (ppm)
176.6
173.0
173.0
137.0
116.5
77.6
77.2
76.7
58.8
53.0
52.9
51.6
46.6
45.9
45.2
40.9
39.9
37.3
16.1
f1 (ppm)

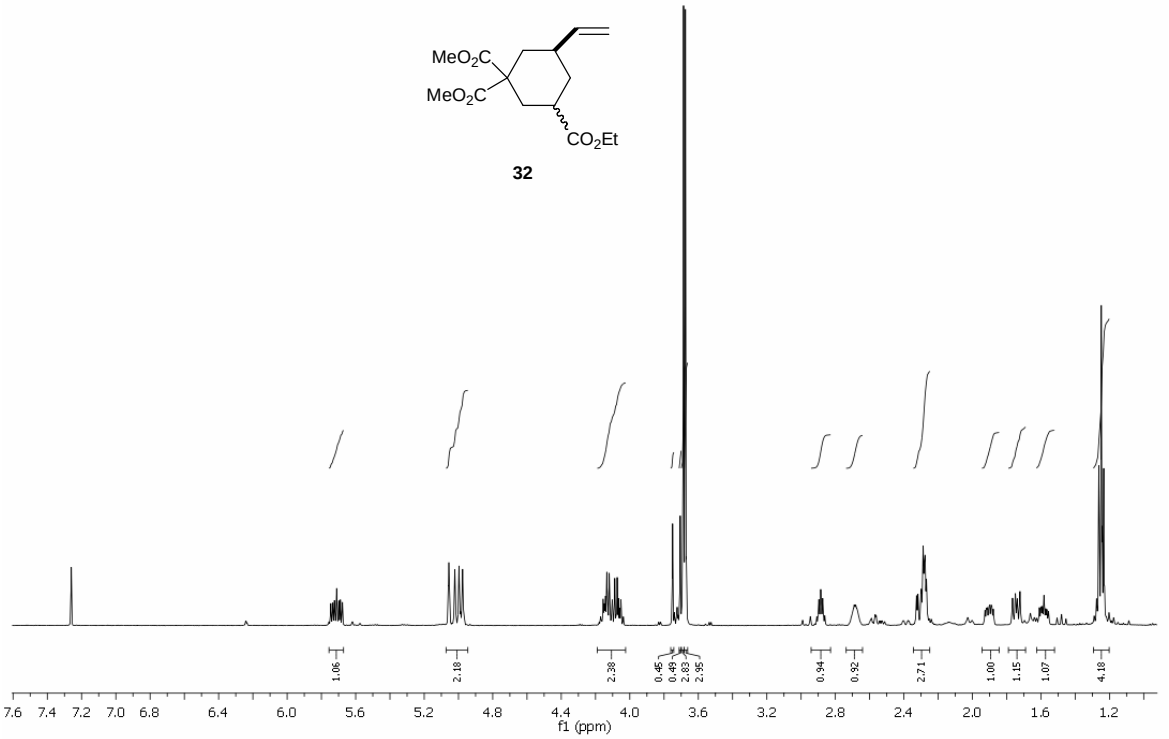

MeO2C
MeO2C
CO2Me
29
1.08
1.06
1.00
1.92
5.89
2.90
1.93
1.19
0.93
1.07
0.92
1.28
1.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


173.2
172.9
139.2
138.3
135.0
134.2
123.1
122.9
115.7
115.6
59.2
58.4
53.0
52.9
51.9
48.5
47.3
40.2
39.2
39.0
38.0
37.9
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

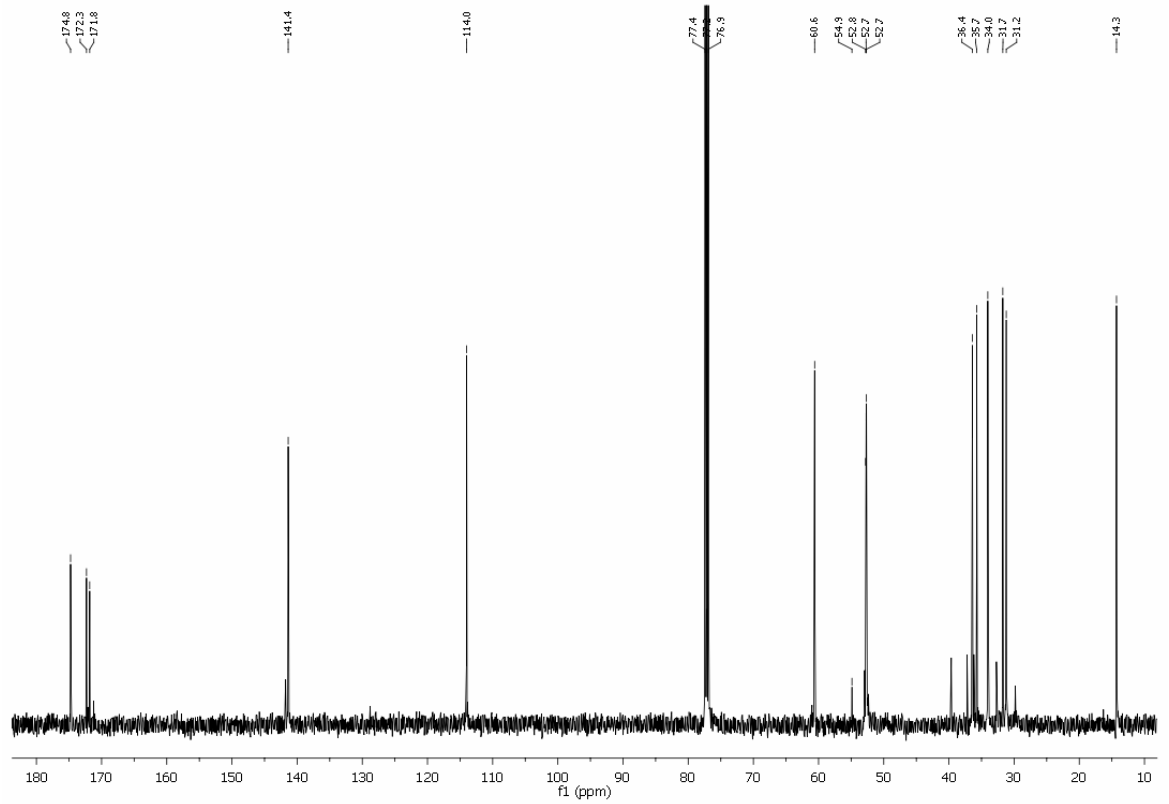

MeO2C
MeO2C
COMe
30
0.63
0.72
0.65
2.27
5.98
2.01
1.01
2.00
0.79
0.56
2.87
0.95
f1 (ppm)
207.3
172.9
139.2
138.3
135.5
135.2
134.7
123.4
123.2
115.8
115.6
77.5
76.8
59.1
58.4
53.0
52.9
49.9
48.7
47.7
47.3
46.1
40.4
40.2
39.3
38.9
29.8
29.4
f1 (ppm)

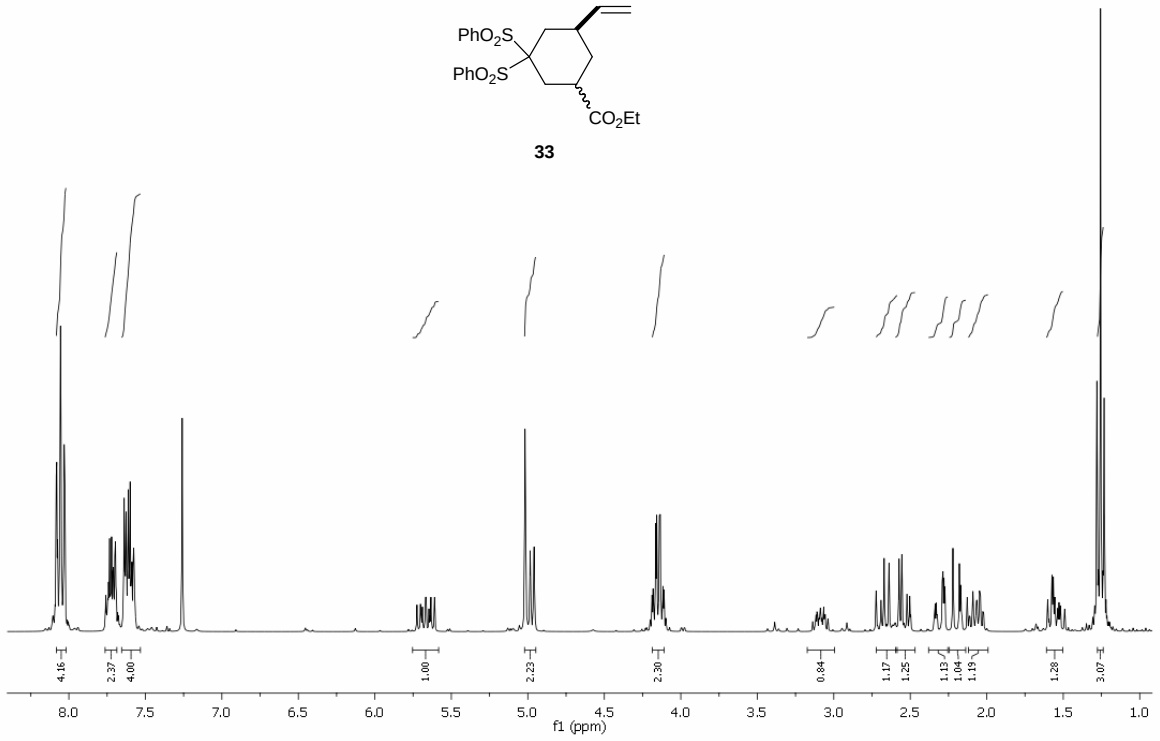

BzOH2C
BzOH2C
CO2Me
31
3.86
2.06
4.10
0.53
0.70
1.64
1.94
2.88
2.68
1.79
1.01
1.06
1.25
1.04
1.18
0.99
f1 (ppm)


172.4
166.7
139.8
139.1
135.7
134.9
133.2
133.2
130.2
129.7
128.6
128.6
122.8
122.7
115.4
69.4
68.8
68.7
68.1
51.9
49.6
48.3
47.2
45.9
45.5
44.6
39.2
39.0
38.0
37.9
37.7
29.8
f1 (ppm)

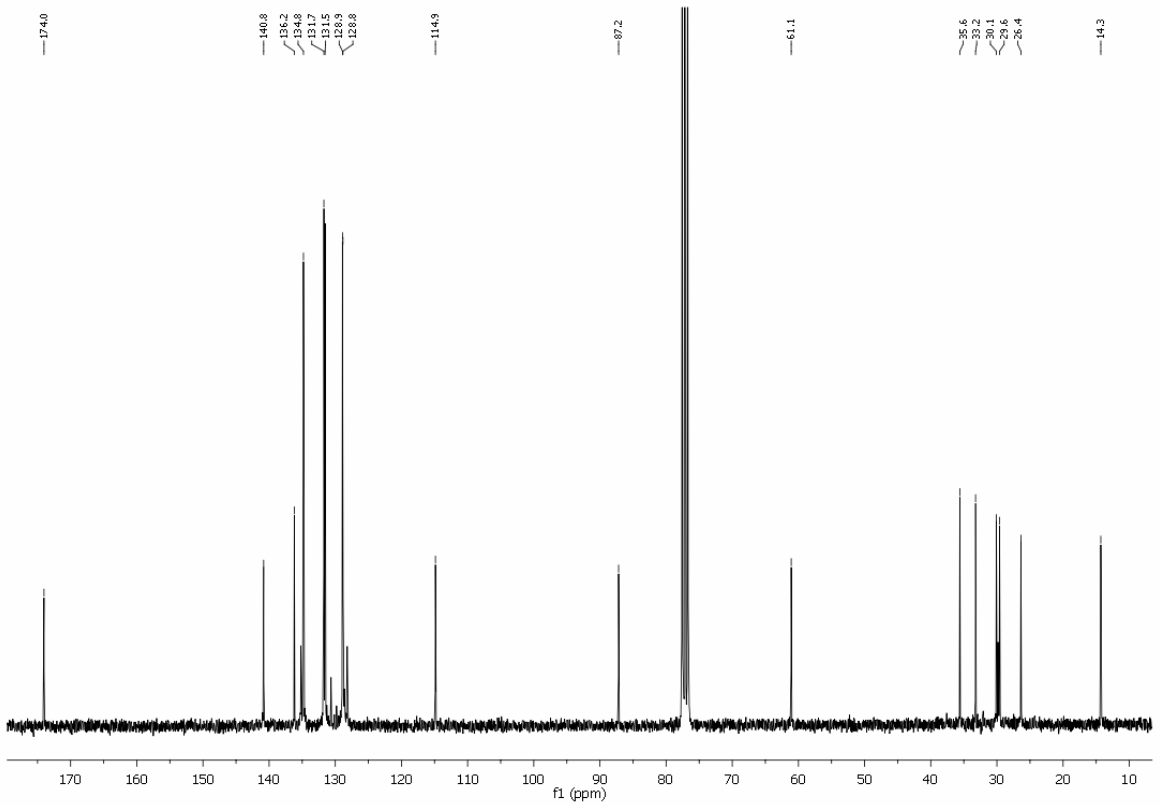


32




PhO2S
PhO2S
CO2Et
4.16
2.37
4.00
1.00
2.23
2.30
0.84
1.17
1.25
1.13
1.04
1.19
1.28
3.07
f1 (ppm)

33


174.0
140.8
136.2
134.8
131.7
131.5
128.9
128.8
114.9
87.2
61.1
35.6
33.2
30.1
25.6
20.4
14.3
f1 (ppm)