Supporting Information

Bromine Radical Catalysis by Energy Transfer Photosensitization

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1. General Considerations

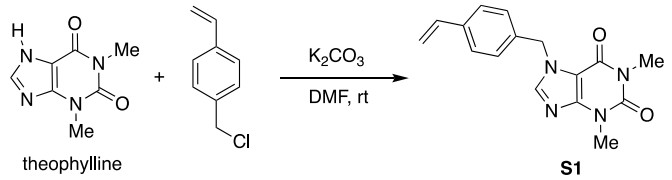
Commercial reagents and anhydrous solvents were purchased from *Millipore-Sigma*, *Alfa* and *TCI*, and were used as received unless otherwise indicated. All catalytic reactions were carried out under N_2 with oven-dried vials. Thin layer chromatography was performed on SiliCycle® 250 um, 60A plates. Column chromatography was performed on *SiliCycle®SilicaFlash®* P60, 40-63 um, 60A. Visualization was accomplished with I_2-silica.

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker 400 Hz (101 Hz, 162 Hz and 376 Hz for ^{13}C, ^{31}P and ^{19}F, respectively) spectrometer at ambient temperature. All NMR spectra are referenced to the residual solvent ($CHCl_3$) signal. Data for ^{1}H, ^{19}F and ^{31}P NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported as follows: chemical shift (δ ppm).

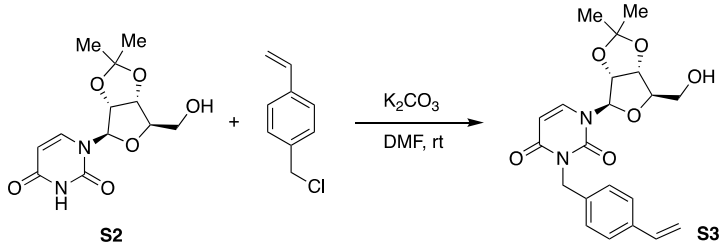
Mass spectra (MS) were obtained from Colorado State University Central Instrument Facility on an Agilent 6224 Time of flight (TOF) LC-MS spectrometer using ESI+/DART+ ionization model.

2. Substrate Synthesis and Characterization

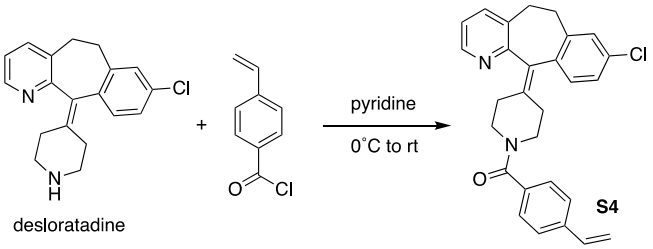
2.1 Alkene Synthesis



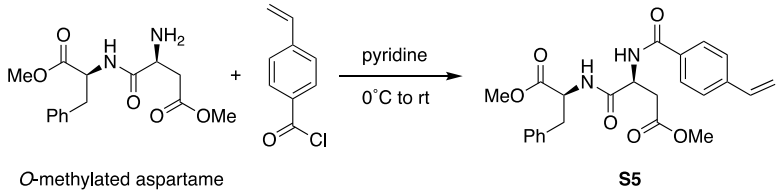
To a solution of theophylline (0.90 g, 5.0 mmol, 1.0 equiv) in 15.0 mL of anhydrous DMF, 4-vinylbenzyl chloride (1.15 g, 7.5 mmol, 1.5 equiv) and K_2CO_3 (1.38g, 10.0 mmol, 2.0 equiv) were added sequentially. The slurry was vigorously stirred at room temperature for 12h. The white solid was filtered off, and the filtrate was diluted with EtOAc (100 mL), washed with H_2O (50 mL × 3), brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was subjected to silica gel chromatography using hexane/acetone (10:1 to 5:1) as the eluent, giving **S1** as a white solid (1.31g, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.46 – 7.35 (m, 2H), 7.30 – 7.26 (m, 2H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.74 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.48 (s, 2H), 5.27 (dd, *J* = 10.9, 0.8 Hz, 1H), 3.58 (s, 3H), 3.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.3, 151.7, 148.9, 140.8, 138.0, 136.0, 134.7, 128.2, 126.9, 114.8, 107.0, 50.1, 29.8, 28.0. **DART-TOF-LC/MS** m/z calcd. for $C_{16}H_{17}N_4O_2$ [M+H$^+$] 297.1352, found 297.1351.



To a solution of protected uridine **S2**[1] (1.42 g, 5.0 mmol, 1.0 equiv) in 15.0 mL of anhydrous DMF, 4-vinylbenzyl chloride (1.15g, 7.5 mmol, 1.5 equiv) and K_2CO_3 (1.38g, 10.0 mmol, 2.0 equiv) were added sequentially. The slurry was vigorously stirred at room temperature. After 12 h, the solid was filtered off. The filtrate was diluted with EtOAc (100 mL), washed with H_2O (50 mL × 3), brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was subjected to silica gel chromatography using hexane/acetone (10:1 to 5:1) as the eluent, giving **S3** as a colorless oil (1.41g, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 13.3 Hz, 1H), 6.63 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.73 (d, *J* = 8.0 Hz, 1H), 5.66 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.48 (d, *J* = 2.9 Hz, 1H), 5.17 (dd, *J* = 10.9, 0.9 Hz, 1H), 5.08 – 4.88 (m, 4H), 4.23 (q, *J* = 3.1 Hz, 1H), 3.89 – 3.81 (m, 1H), 3.74 (ddd, *J* = 12.0, 7.5, 3.3 Hz, 1H), 2.70 (dd, *J* = 7.5, 3.3 Hz, 1H), 1.52 (s, 3H), 1.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 151.0, 140.7, 137.1, 136.4, 135.9, 129.5, 126.2, 114.3, 114.0, 102.2, 97.0, 86.9, 83.8, 80.3, 62.7, 43.9, 27.3, 25.3. **ESI-TOF-LC/MS** m/z calcd. for $C_{21}H_{25}N_2O_6$ [M+H$^+$] 401.1713, found 401.1710.

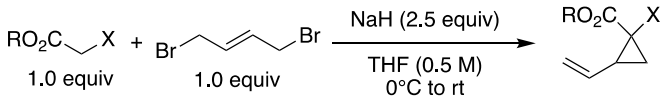


To a solution of desloratadine (1.0 g, 3.2 mmol, 1.0 equiv) in 5.0 mL of anhydrous pyridine at 0 °C, 4-vinylbenzoyl chloride (0.54g, 3.2 mmol, 1.0 equiv) was added dropwise. The mixture was stirred at 0 °C for 30 min, then was warmed up to room temperature and stirred for 12h. The reaction was quenched by addition of sat. NH_4Cl (20 mL), then diluted with CH_2Cl_2 (100 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic phase was washed with H_2O (50 mL × 3), brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was subjected to silica gel chromatography using hexane/acetone (5:1 to 3:1) as the eluent, giving the final product as a while solid (1.12g, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (brs, 1H), 7.48 – 7.33 (m, 5H), 7.22 – 7.01 (m, 4H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.77 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.29 (*J* = 10.9, 0.8 Hz, 1H), 4.18 (brs, 1H), 3.64 (brs, 1H), 3.45 – 3.13 (m, 4H), 2.92 – 2.73 (m, 4H), 2.70 – 2.15 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 156.8, 146.7, 139.6, 138.9, 137.6, 136.9, 136.1, 135.2, 134.7, 133.4, 133.0, 130.5, 129.0, 127.3, 126.2, 122.4, 115.2, 31.7, 31.5. **ESI-TOF-LC/MS** m/z calcd. for $C_{28}H_{26}ClN_2O$ [M+H$^+$] 441.1734, found 441.1735.



To a solution of O-methylated aspartame[2] (0.72 g, 2.0 mmol, 1.0 equiv) in 4.0 mL of anhydrous pyridine at 0 °C, 4-vinylbenzoyl chloride (0.33g, 2.0 mmol, 1.0 equiv) was added dropwise. The mixture was stirred at 0 °C for 30 min, then was warmed up to room temperature and stirred for 12h. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic phase was washed with H_2O (50 mL×3), brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was subjected to silica gel chromatography using CH_2Cl_2/MeOH (20:1 to 1:1) as the eluent, giving the final product as a colorless oil (0.73g, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.18 – 7.02 (m, 6H), 6.76 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.87 (d, *J* = 17.5 Hz, 1H), 5.39 (d, *J* = 10.9 Hz, 1H), 5.00 (ddd, *J* = 7.9, 6.4, 3.8 Hz, 1H), 4.80 (td, *J* = 7.3, 5.3 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.22 – 2.98 (m, 3H), 2.67 (dd, *J* = 17.0, 6.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1, 171.4, 170.1, 166.7, 141.2, 135.9, 135.6, 132.2, 129.2, 128.5, 127.5, 127.1, 126.4, 116.3, 53.5, 52.4, 52.2, 49.3, 37.7, 34.9. **DART-TOF-LC/MS** m/z calcd. for $C_{24}H_{30}N_3O_6$ [M+NH_4^+] 456.2135, found 456.2133.

2.2 Vinylcyclopropane Synthesis



Procedure A: To a suspension of 60% NaH (1.0 g, 25.0 mmol, 2.5 equiv) in 25.0 mL of anhydrous THF at 0 °C, *trans*-1,4-dibromo-2-butene (2.1 g, 10.0 mmol, 1.0 equiv) was added in one portion. Appropriate activated methylene compounds (10.0 mmol, 1.0 equiv) was added dropwise over 10 min. The reaction was then vigorously stirred at room temperature. Conversion was assessed by TLC (10% EtOAc in hexanes). Upon completion, the reaction was cooled to 0 °C with an ice bath and carefully quenched by slow addition of sat. NH_4Cl (10 mL). The mixture was then diluted with H_2O (30 mL) and ether (100 mL). The layers were separated, and the aqueous phase was extracted with ether (30 mL × 3). The combined organic phasewas washed with H_2O (50 mL × 2), brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel chromatography using hexane/EtOAc as the eluent.

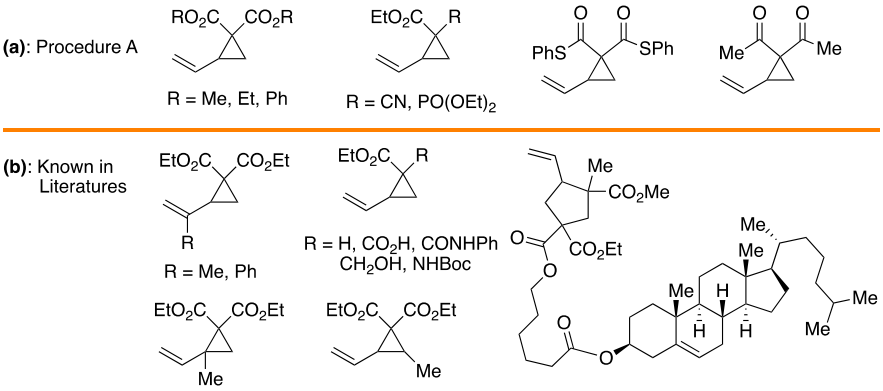
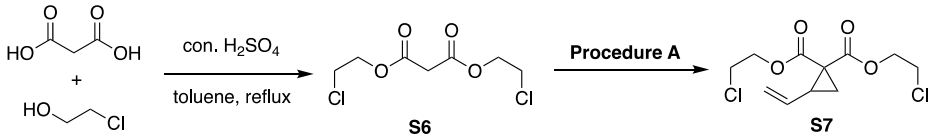
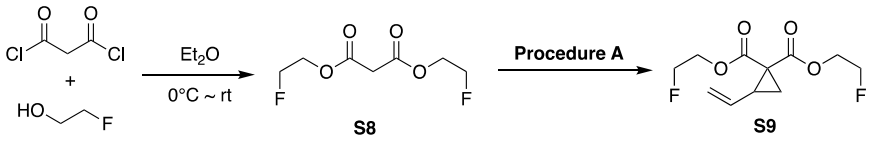


Figure S1. Known vinylcyclopropanes synthesized according to **Procedure A** or methods in literature.[3]

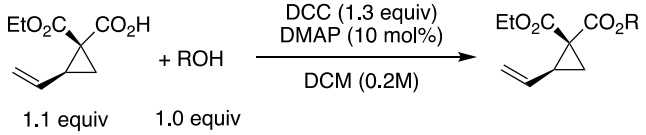


A solution of malonic acid (4.0 g, 38.5 mmol), 2-chloroethanol (13.0 mL, 206 mmol) and concentrated H_2SO_4 (0.5 mL) in anhydrous toluene (20.0 mL) was heated to reflux for 3 h. After cooling to room temperature, the reaction was carefully quenched by slow addition of 10% $NaHCO_3$. The layers were separated, and the aqueous phase was extracted with ether (50 mL × 3). The combined organic phase was washed with 5% $NaHCO_3$ (50 mL × 2), H_2O (50 mL × 2) and brine (50 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo* to give crude **S6** as a colorless oil (5.2 g), which was used without further purification. **S7** was then synthesized according to **Procedure A**. Colorless oil, 4.34 g, 40% yield for two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.48 (ddd, *J* = 17.0, 10.2, 8.1 Hz, 1H), 5.32 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.17 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.50 – 4.28 (m, 4H), 3.90 – 3.40 (m, 4H), 2.65 (dd, *J* = 9.0, 7.7 Hz, 1H), 1.79 (dd, *J* = 7.7, 5.0 Hz, 1H), 1.64 (dd, *J*

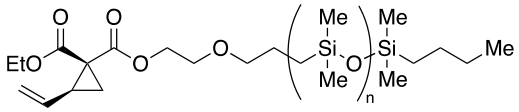
= 9.0, 5.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.0, 166.7, 132.4, 119.2, 65.1, 65.0, 41.3, 41.2, 35.6, 31.8, 20.8. **DART-TOF-LC/MS** m/z calcd. for $C_{11}H_{18}Cl_2NO_4$ [M+NH_4^+] 298.0613, found 298.0611.



To a solution of 2-fluoroethanol (1.41 mL, 24.0 mmol) in anhydrous Et_2O (100 mL) at 0 °C, malonyl chloride (2.82 g, 38.5 mmol) was added dropwise. The reaction was vigorously stirred at room temperature. After 12h, the reaction was carefully quenched by slow addition of 10% $NaHCO_3$. The layers were separated, and the aqueous phase was extracted with ether (50 mL × 2). The combined organic layer was washed with 5% $NaHCO_3$ (100 mL), H_2O (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo* to give crude **S8** as a colorless oil, which was used without further purification. **S9** was then synthesized according to **Procedure A**. Colorless oil, 2.89 g, 57% yield for two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.47 (ddd, *J* = 17.0, 10.1, 8.1 Hz, 1H), 5.36 – 5.28 (m, 1H), 5.19 – 5.15 (m, 1H), 4.68 – 4.62 (m, 2H), 4.56 – 4.52 (m, 2H), 4.51 – 4.26 (m, 4H), 2.65 (dd, *J* = 9.0, 7.9 Hz, 1H), 1.79 (dd, *J* = 7.7, 5.0 Hz, 1H), 1.64 (dd, *J* = 9.0, 5.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.2, 166.9, 132.4, 119.2, 81.9 (d, *J* = 12.2 Hz), 80.2 (d, *J* = 12.2 Hz), 64.5 (d, *J* = 14.7 Hz), 64.2 (d, *J* = 14.7 Hz), 35.6, 31.8, 20.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -224.7, -224.9. **DART-TOF-LC/MS** m/z calcd. for $C_{11}H_{18}F_2NO_4$ [M+NH_4^+] 266.1204, found 266.1207.

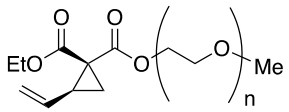


Procedure B: To a solution of 1-(ethoxycarbonyl)-2-vinylcyclopropane-1-carboxylic acid[3b] (1.1 equiv.) in anhydrous DCM (0.2 M) at 0 °C, appropriate alcohol (1.0 equiv), DMAP (0.10 equiv.), and DCC (1.3 equiv.) was sequentially added. The mixture was then vigorously stirred at room temperature for 12h. The white precipitate was filtered off and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel chromatography using hexane/EtOAc as the eluent.

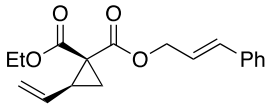


Synthesized from 1-(ethoxycarbonyl)-2-vinylcyclopropane-1-carboxylic acid and 1 kDa monocarbinol terminated polydimethylsiloxane (5.0 mmol scale). Colorless oil, 5.23g, 88% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.44 (ddd, *J* = 17.0, 10.2, 8.3 Hz, 1H), 5.29 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.13 (dd, *J* = 10.1, 1.7 Hz, 1H), 4.35 – 4.07 (m, 4H), 3.62 (t, *J* = 5.0 Hz, 2H), 3.41 (t, *J* = 7.0 Hz, 2H), 2.60 (q, *J* = 8.3 Hz, 1H), 1.71 (dd, *J* = 7.6, 4.9 Hz, 1H), 1.64 – 1.50 (m, 3H), 1.36 – 1.16 (m, 7H), 0.92 – 0.78 (m, 3H), 0.59 – 0.46 (m, 4H), 0.09 – 0.03 (m, 89H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.6, 166.2, 132.0, 117.5,

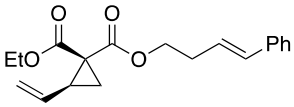
73.1, 67.2, 63.7, 60.4, 34.8, 30.3, 25.3, 24.4, 22.4, 19.5, 16.9, 13.1, 13.0, 12.8, 0.4, 0.1, 0.0, -0.4, -0.9, -1.0. M_n (NMR) = 1.4 kDa.



Synthesized from 1-(ethoxycarbonyl)-2-vinylcyclopropane-1-carboxylic acid and PEG 550 (5.0 mmol scale). Colorless oil, 5.23g, 88% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.43 (ddd, *J* = 17.0, 10.1, 8.2 Hz, 1H), 5.28 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.13 (dd, *J* = 10.0, 1.7 Hz, 1H), 4.33 – 4.13 (m, 4H), 3.68 (t, *J* = 4.9 Hz, 2H), 3.65 – 3.61 (m, 34H), 3.55 – 3.52 (m, 2H), 3.37 (s, 3H), 2.58 (q, *J* = 8.3 Hz, 1H), 1.70 (dd, *J* = 7.6, 4.9 Hz, 1H), 1.56 (dd, *J* = 9.0, 4.9 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 1169.6, 167.2, 133.0, 118.6, 71.9, 70.63, 70.60, 70.57, 70.51, 68.8, 64.6, 61.5, 59.0, 35.8, 31.3, 20.5, 14.2. M_n (NMR) = 625.



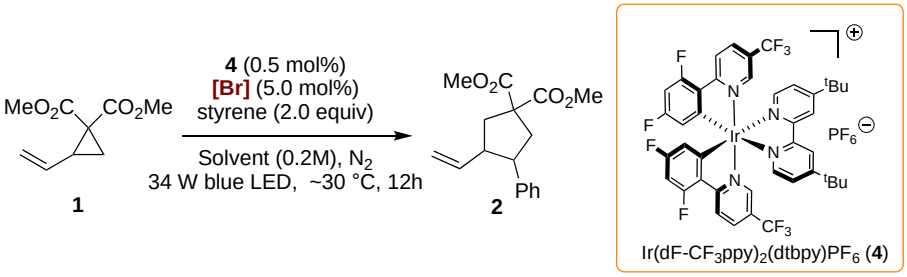
Synthesized from 1-(ethoxycarbonyl)-2-vinylcyclopropane-1-carboxylic acid and cinnamyl alcohol (2.0 mmol scale). Colorless oil, 0.49 g, 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.14 (m, 5H), 6.59 (d, *J* = 15.8 Hz, 1H), 6.24 – 6.13 (m, 1H), 5.36 (dd, *J* = 10.0, 8.1 Hz, 1H), 5.23 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.07 (dd, *J* = 10.0, 1.6 Hz, 1H), 4.80 – 4.65 (m, 2H), 4.24 – 4.05 (m, 2H), 2.54 (dd, *J* = 9.0, 7.6 Hz, 1H), 1.66 (dd, *J* = 7.6, 4.9 Hz, 1H), 1.52 (dd, *J* = 9.0, 4.9 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 167.3, 136.1, 134.3, 133.0, 128.6, 128.1, 126.6, 122.7, 118.6, 66.1, 61.5, 35.9, 31.3, 20.5, 14.2. **DART-TOF-LC/MS** m/z calcd. for $C_{18}H_{24}NO_4$ [M+NH_4^+] 318.1705, found 318.1705.



Synthesized from 1-(ethoxycarbonyl)-2-vinylcyclopropane-1-carboxylic acid and *trans*-4-phenylbut-3-en-1-ol (2.0 mmol scale). Colorless oil, 0.44 g, 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.09 (m, 5H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.07 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.35 (ddd, *J* = 16.6, 10.1, 8.3 Hz, 1H), 5.19 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.04 (dd, *J* = 10.0, 1.6 Hz, 1H), 4.31 – 4.02 (m, 4H), 2.56 – 2.40 (m, 3H), 1.61 (dd, J = 7.5, 4.9 Hz, 1H), 1.47 (dd, J = 9.0, 4.9 Hz, 1H), 1.14 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.6, 167.3, 137.2, 133.1, 132.6, 128.5, 127.3, 126.1, 125.3, 118.5, 64.7, 61.5, 35.9, 32.3, 31.2, 20.5, 14.2. **DART-TOF-LC/MS** m/z calcd. for $C_{19}H_{26}NO_4$ [M+NH_4^+] 332.1862, found 332.1860.

3. Complementary Optimization of Conditions

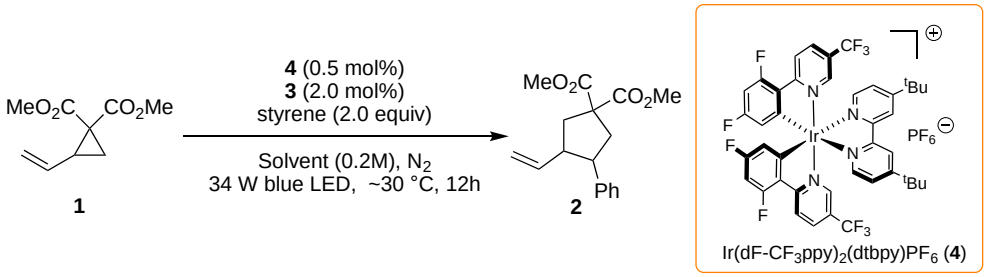
Table S1. Single-electron oxidation of bromide salts to generate bromine radicals for the [3+2] cycloaddition of **1** and styrene. [a]



Entry	[Br]	Solvent	NMR Yield (%)[b]
1	NaBr	MeCN	0
2	KBr	MeCN	0
3	LiBr	MeCN	0
4	TBAB	MeCN	0
5	NaBr	DMSO	0
6	KBr	DMSO	0
7	LiBr	DMSO	0
8	TBAB	DMSO	0
9	NaBr	DMF	0
10	KBr	DMF	0
11	LiBr	DMF	0
12	TBAB	DMF	0
13	LiBr	acetone	0
14	TBAB	acetone	0
15	LiBr	THF	0
16	TBAB	THF	0
17	LiBr	MeOH	0
18	TBAB	MeOH	0

[a]General reaction conditions: **1** (0.2 mmol), styrene (0.4 mmol), **4** (0.5%), bromide salt (5.0 %), anhydrous solvent (1.0 mL), 34 W Kessil blue LED. [b]Trimethoxybenzene was used as an internal standard. TBAB = tetrabutylammonium bromide

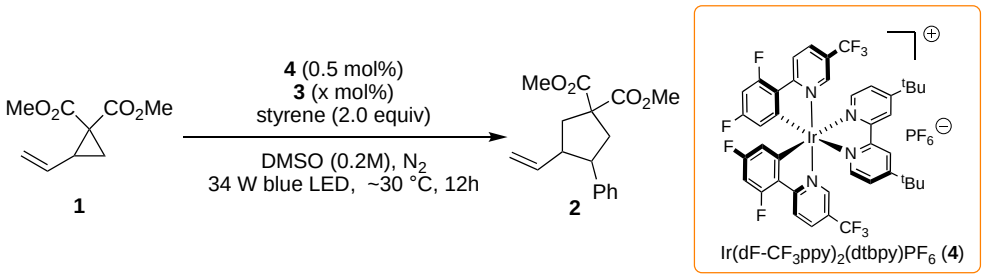
Table S2. Solvent effect in the [3+2] cycloaddition of **1** and styrene using cinnamyl bromide as the precatalyst.[a]



Entry	Solvent	NMR Yield (%)[b]
1	MeCN	< 5
2	acetone	< 5
3	DMF	11
4	THF	0
5	MeOH	0
6	benzene	0
7	DMSO	95
8	NMP	22
9	DCM	0
10	DCE	0
11	PhCl	< 5

[a]Reaction conditions: **1** (0.2 mmol), styrene (0.4 mmol), **4** (0.5%), cinnamyl bromide **3** (2.0 %), anhydrous solvent (1.0 mL), 34 W Kessil blue LED. [b]Trimethoxylbenzene was used as an internal standard.

Table S3. Examination of precatalyst (**3**) loading in the [3+2] cycloaddition of **1** and styrene.[a]



Entry	x	NMR Yield %[b]
1	2.0	95
2	5.0	95
3	1.0	94
4	0.5	77
5	0.1	41
11	0.01	< 5

[a]Reaction conditions: **1** (0.2 mmol), styrene (0.4 mmol), **4** (0.5%), **3** (x mol%), anhydrous DMSO (1.0 mL), 34 W Kessil blue LED. [b]Trimethoxylbenzene was used as an internal standard.

4. General Reaction Setup and Experimental Procedures

Procedure C*:* In a N_2-filled glovebox, an oven-dried vial (0.5 dram) equipped with a magnet stir bar was charged with vinyl- or ethynylcycloproane (0.2 mmol, 1.0 equiv.), appropriate alkene (2.0 equiv.), 50 uL stock solution of cinnamyl bromide **3** in DMSO (40 mM for 1.0 mol%; 80 mM for 2.0 mol%), anhydrous DMSO (1.90 mL for 0.1 M; 0.90 mL for 0.2 M; 0.40 mL for 0.4 M), and 50 uL stock solution of 4CzIPN **7** in DMSO (0.2 mM for 50 ppm; 2.0 mM for 500 ppm). The vial was then tightly capped and removed out of glovebox. The reaction was placed into a photoreactor (HeptatoChem HCK 1006-01-004) equipped with a blue LED (Kessil, 34 W). The reactor was cooling by air flow that the temperature was ~30 °C). After 12 h, the reaction mixture was diluted with water (10 mL) and extracted with ether (20 mL × 3). The combined organic phase was washed with H_2O (20 mL × 3), brine (30 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo*. The residue was then subjected to silica gel chromatography for purification.

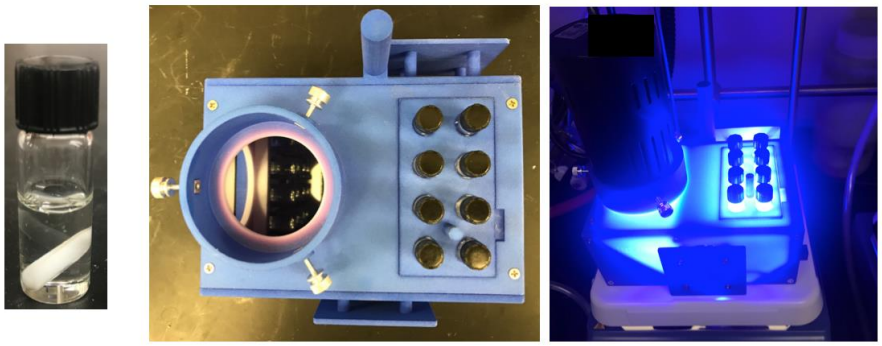


Figure S2. Reaction setup (HeptatoChem HCK 1006-01-004 with Kessil 34 W H-150 blue LED).

5. Mechanistic Study

5.1 TEMPO-trapping experiment

In a N_2-filled glovebox, an oven-dried vial (0.5 dram) equipped with a magnet stir bar was charged with cinnamyl bromide **3** (39.4 mg, 0.2 mmol), TEMPO (93.8 mg, 0.6 mmol), anhydrous DMSO (1.0 mL) and 4CzIPN **7** (1.6 mg, 0.002 mmol). The vial was then tightly capped and removed out of glovebox. The reaction was placed into a photoreactor (HeptatoChem HCK 1006-01-004) equipped with a blue LED (Kessil, 34 W). The reactor was cooling by air flow that the temperature was ~30 °C). After 2 h, an aliquot of 10 uL was taken for ESI-TOF LC/MS analysis. The reaction mixture was diluted with water (10 mL) and extracted with ether (20 mL × 3). The combined organic phase was washed with H_2O (20.0 mL × 2), brine (30 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo*. 32.0 mg (81% yield) cinnamyl bromide was recovered through silica gel chromatography.

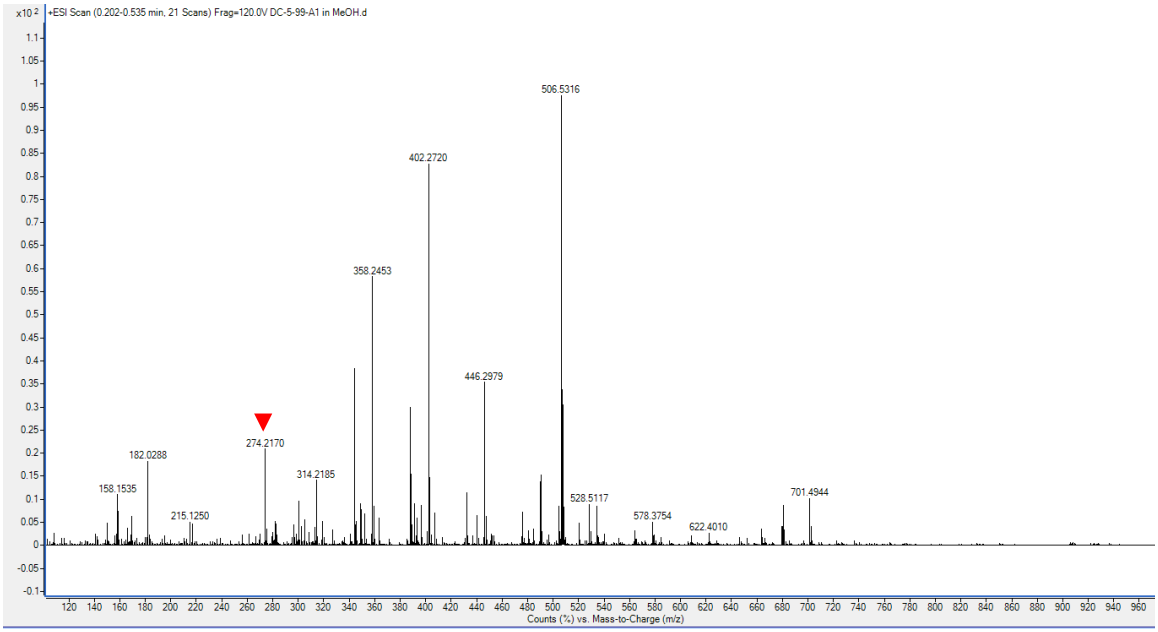


Figure S3. ESI-TOF LC/MS spectrum of aliquot taken from TEMPO-trapping experiment

5.2 Investigation of alternative precatalysts

n a N_2-filled glovebox, an oven-dried vial (0.5 dram) equipped with a magnet stir bar was charged with vinylcycloproane **1** (0.2 mmol, 1.0 equiv.), styrene (46.0 uL, 0.4 mmol), 50 uL stock solution of **7** in DMSO (0.2 mM), anhydrous DMSO (0.90 mL), and 50 uL stock solution of precatalyst in DMSO (40 mM). The vial was then tightly capped and removed out of glovebox. The reaction was placed into a photoreactor (HeptatoChem HCK 1006-01-004) equipped with a blue LED (Kessil, 34 W). The reactor was cooling by air flow that the temperature was ~30 °C). After 12 h, the vial was opened to the air and 1,3,5-trimethoxylbenzene (16.8 mg, 0.1 mmol) was added as an internal standard. An aliquot of 0.10 mL was taken for direct ^{1}H NMR analysis to determine the yield.

Table S4. Results of [3+2] cycloaddition of **1** and styrene using alternative precatalyst.[a]

Entry	precatalyst	**7**	light	NMR Yield (%)[b]
1	allyl bromide	√	√	0
2	cinnamyl chloride	√	√	0
3	NBS	√	√	41
4	NBS	√	×	0
5	NBS	×	√	0
6	NBS	×	×	0
7	Br_2	√	√	26
8	Br_2	√	×	0
9	Br_2	×	√	16
10	Br_2	×	×	0

[a]Reaction conditions: **1** (0.2 mmol), styrene (0.4 mmol), **7** (50 ppm), precatalyst (1.0 %), anhydrous DMSO (1.0 mL), 34 W Kessil blue LED, 12h. [b]Trimethoxylbenzene was used as an internal standard.

5.3 Radical epimerization experiment

In a N_2-filled glovebox, an oven-dried vial (0.5 dram) equipped with a magnet stir bar was charged with *cis*-1-(ethoxycarbonyl)-2-vinylcyclopropane-1-carboxylic acid (36.8 mg, 0.2 mmol), 50 uL stock solution of cinnamyl bromide **3** in DMSO (40 mM), anhydrous DMSO (0.90 mL), and 50 uL stock solution of 4CzIPN **7** in DMSO (0.2 mM). The vial was then tightly capped and removed out of glovebox. The reaction was placed into a photoreactor (HeptatoChem HCK 1006-01-004) equipped with a blue LED (Kessil, 34W). The reactor was cooling by air flow that the temperature was ~30 °C). After 12 h, the reaction mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined organic phase was washed with brine (30.0 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. Crude ^{1}H NMR was taken to determine the cis/trans ratio.

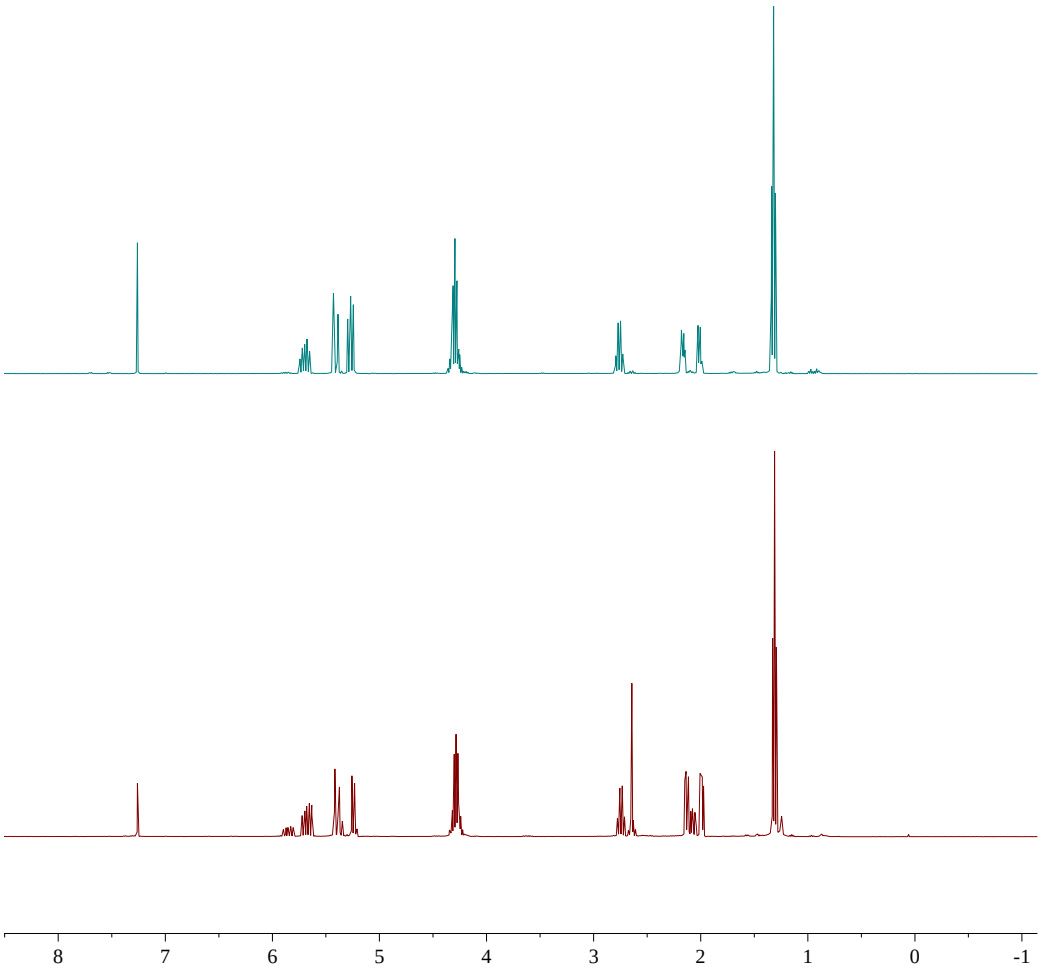


Figure S4. Comparison of ^{1}H NMR spectra before (teal, top) and after (bottom) radical epimerization

5.4 Cyclic voltammetry

Cyclic voltammetry (CV) was performed on an Interface 1010B Potentiostat (*Gamry Instruments*) with a scan rate of 0.10 V/s. A solution of $Ag/AgNO_3$ (0.01M) and 0.1 M Bu_4NPF_6 in MeCN was used as the reference electrode (*Gamry Instruments*, part no. 930-00059). A 0.1 M Bu_4NPF_6 in MeCN was used as the electrolyte for cinnamyl bromide solution (0.05M). A platinum disk was used for the working electrode (*Gamry Instruments*, part no. 932-00024) and a platinum wire was used as the counter electrode (*Gamry Instruments*, part no. 990-00193).

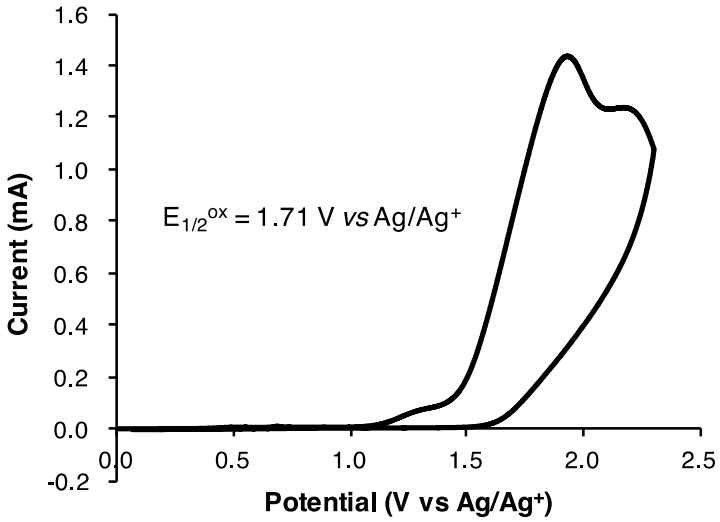


Figure S5. CV spectrum of cinnamyl bromide ($E_{1/2}^{ox}$ = 1.71 vs Ag/Ag^+ = 2.01 V vs SCE)

5.5 Stern-Volmer quenching experiment

Stern-Volmer experiments were operated on pectrofluorometer FS5 (*Edinburgh Instruments*) and with different solutions containing 10.0 uM 4CzIPN **7** in DMSO and x mM **3** ((x = 1. 5, 10, 20, 40)), or vinylcyclopropane **1** (x = 10, 20, 30, 50), or styrene (x = 10, 20, 30, 50) in DMSO under irradiation at 380 nm. The luminescence was measured at 560 nm. Averaged data from three different runs were used for graphical representation.

Table S5. Luminescence quenching of 4CzIPN **7** at variable concentration of **3**

3a (mM)	0	1	5	10	20	40
I_0/I	1.0000	1.0344	1.1250	1.2273	1.4040	1.6488

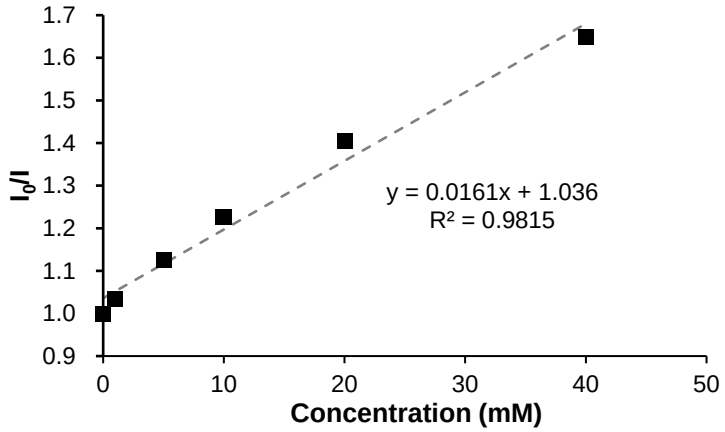


Figure S6. Stern-Volmer plots of 4CzIPN **7** at variable concentration of **3**.

Table S6. Luminescence quenching of 4CzIPN **7** at variable concentration of vinylcyclopropane **1**

1 (mM)	0	10	20	30	50
I_0/I	1.0000	1.0076	1.0013	1.0036	0.9949

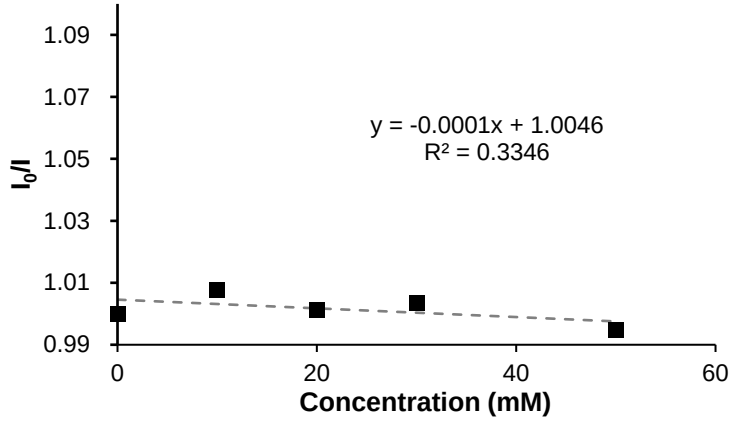


Figure S7. Stern-Volmer plots of 4CzIPN **7** at variable concentration of vinylcyclopropane **1**.

Table S7. Luminescence quenching of 4CzIPN **7** at variable concentration of styrene

styrene (mM)	0	10	20	30	50
I_0/I	1.0000	1.0076	1.0013	1.0036	0.9949

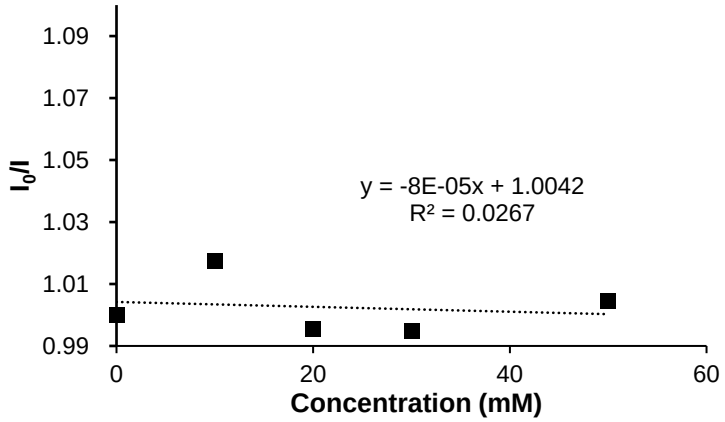


Figure S8. Stern-Volmer plots of 4CzIPN **7** at variable concentration of styrene.

5.6 “On/off” experiment

The reaction was set up in a N_2-filled glovebox according to the **Procedure C**. The reaction mixture was irradiated for an hour. An aliquot of 0.10 mL was taken from the reaction mixture and injected into a vial containing 0.50 mL of $CDCl_3$ containing trimethoxylbenzene (4.2 mg) as the internal standard. The yield of product was determined by crude ^1H NMR analysis. The reaction mixture was then wrapped by aluminum foil and re-subject to 34 W Kessil Blue LED. The yields later on were determined in the same way after some time light on or off.

Table S8. Results of “on/off” experiment

Entry	Time (h)	NMR Yield (%)[a]
1	0	0
2	1	15
3	2 (off)	15
4	3	27
5	4 (off)	27
6	6	46
7	7 (off)	46
8	9	60

[a]Trimethoxybenzene was used as an internal standard.

5.7 Determination of quantum yield (Φ)

In a N_2-filled glovebox, an oven-dried J-Young NMR tube equipped with a micro stir bar was charged with vinylcyclopropane **1** (18.4 mg, 0.10 mmol), styrene (23.0 uL, 0.20 mmol), 25 uL stock solution of cinnamyl bromide **3** in DMSO (40 mM), anhydrous DMSO (0.45 mL), and 25 uL stock solution of 4CzIPN **7** in DMSO (0.2 mM). The sealed NMR tube was removed out of the glovebox and irradiated at 419 nm. After 8 h (t = 28800 s), 8.0 mg trimethoxylbenzene was added to the NMR tube. An aliquot (0.050 mL) was then taken and injected into a HPLC vial containing 0.55 mL of $CDCl_3$ for direct ^{1}H-NMR analysis. The NMR yield was determined to be 5.2% (Fig. S8).

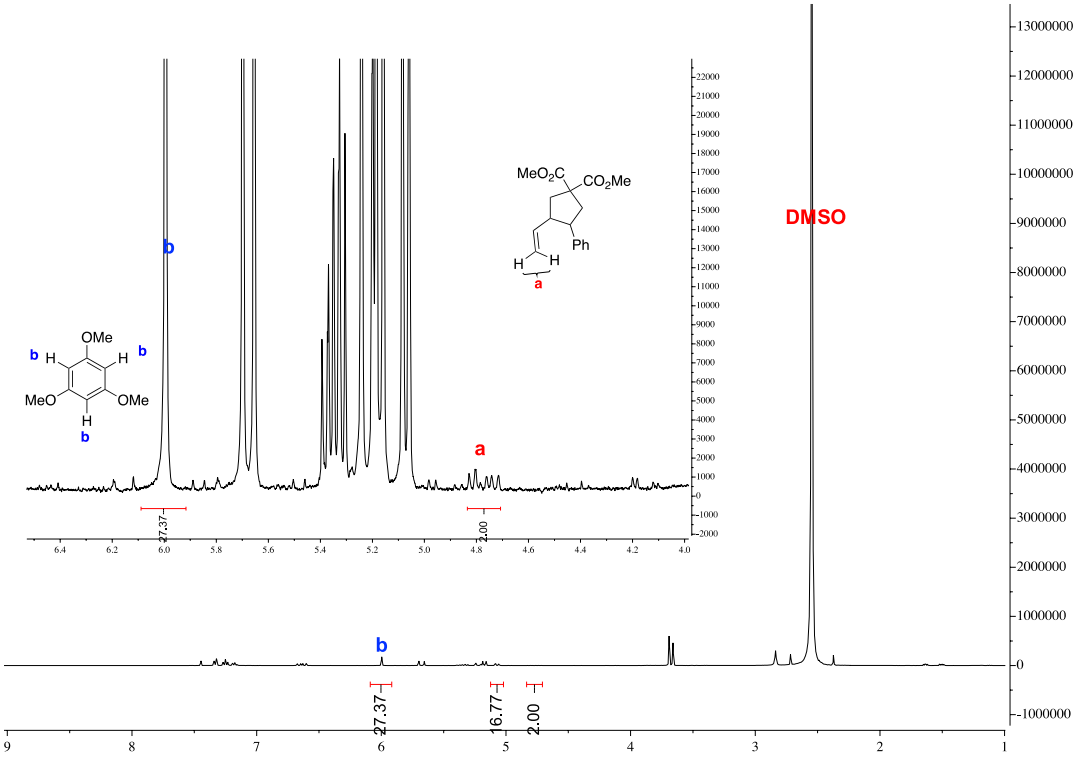


Figure S9. Crude ^{1}H NMR analysis.

The quantum yield (Φ) can be calculated by using the equation as shown below:

$$\Phi = \frac{\text{mol product}}{\text{photon flux} \cdot f \cdot t}$$

The photon flux at 419 nm for the aforementioned setup was previously determined to be 5.2×10^{-9} einstein/s.

Fraction of light absorbed (f) was calculated by $f = 1 - 10^{-A}$. A is the absorbance of PC in a specific solvent and concentration. In this experiment, the concentration of 4CzIPN was 10 uM. A was determined to be 0.09146 at 419 nm for a 10 uM solution of 4CzIPN in DMSO (Fig. S10), therefore, f = 0.1899.

The quantum yield was calculated by:

$$\Phi = \frac{\text{mol product}}{\text{photon flux} \cdot f \cdot t}$$

$$= \frac{5.2\% \text{ x } 0.1/1000}{5.2 \text{ x } 10^{-9} \text{ x } 0.1899 \text{ x } 28800} = 18.3\%$$

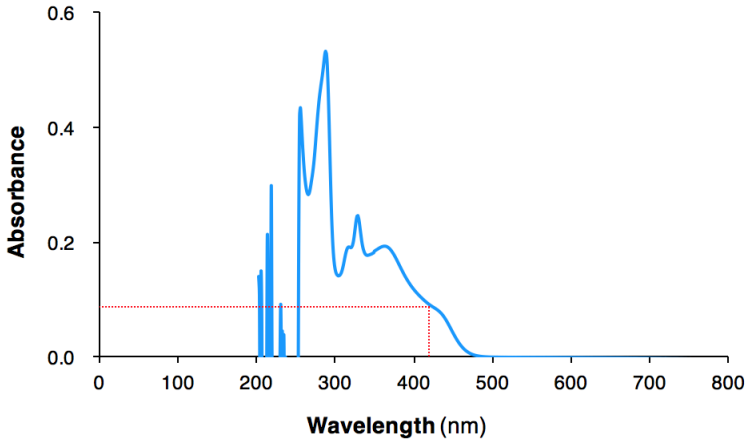
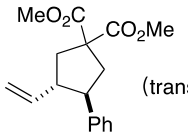


Figure S10. UV-Vis Spectrum of 4CZIPN in DMSO (10 uM)

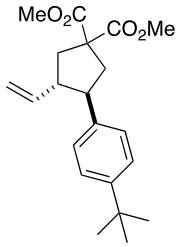
6. Characterization of Products



2
(trans: cis = 70:30)

Prepared according to ***Procedure C***. Colorless oil (50.4 mg, 88% yield) as a mixture of diastereomers (trans : cis = 70:30). R_f = 0.35 (10% EtOAc in hexane).

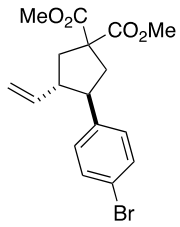
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 6.95 (m, 5H), 5.57 (ddd, *J* = 16.8, 10.8, 7.0 Hz, 0.30H), 5.29 (ddd, *J* = 17.1, 10.3, 8.0 Hz, 0.70H), 4.90 – 4.58 (m, 2.0H), 3.80 – 3.55 (m, 6.0H), 3.37 (dt, *J* = 10.7, 7.5 Hz, 0.70H), 2.94 (p, *J* = 7.3 Hz, 0.70H), 2.84 – 2.43 (m, 3.30H), 2.38 – 2.21 (m, 1.0H), 2.15 – 2.03 (m, 0.30H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 173.0, 172.9, 172.7, 141.5, 140.8, 138.7, 138.2, 128.4, 128.3, 128.1, 127.6, 126.6, 126.3, 115.6, 115.4, 59.0, 58.1, 52.9, 52.8, 51.5, 50.9, 48.0, 47.3, 42.5, 40.3, 39.0, 38.1.
DART-TOF LC/MS m/z calcd. for $C_{17}H_{21}O_4$ [M+H$^+$] 289.1440, found 289.1442.



8
(trans: cis = 70:30)

Prepared according to ***Procedure C***. Colorless oil (60.1 mg, 87% yield) as a mixture of diastereomers (trans : cis = 70:30). R_f = 0.45 (10% EtOAc in hexane).

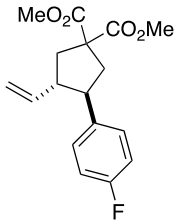
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2.0H), 7.15 (d, *J* = 8.3 Hz, 0.60H), 7.08 (d, *J* = 8.3 Hz, 1.40H), 5.73 – 5.60 (m, 0.30H), 5.39 (ddd, *J* = 17.1, 10.3, 7.9 Hz, 0.70H), 4.99 – 4.80 (m, 2.0H), 3.82 – 3.70 (m, 6.0H), 3.41 (dt, *J* = 10.5, 7.4 Hz, 0.70H), 3.05 – 2.96 (m, 0.70H), 2.92 – 2.52 (m, 3.30H), 2.46 – 2.27 (m, 1.0H), 2.21 – 2.11 (m, 0.30H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 173.0, 173.0, 172.7, 149.3, 149.0, 139.0, 138.4, 138.3, 137.6, 128.0, 127.2, 125.3, 124.9, 115.5, 115.3, 59.0, 58.1, 52.9, 52.8, 50.8, 50.4, 47.6, 47.2, 42.6, 40.3, 38.9, 38.2, 34.4, 34.4, 31.4.
DART-TOF LC/MS m/z calcd. for $C_{21}H_{29}O_4$ [M+H$^+$] 345.2066, found 345.2067.



9
(trans: cis = 70:30)

Prepared according to ***Procedure C***. Colorless oil (67.3 mg, 92% yield) as a mixture of diastereomers (trans : cis = 70:30). R_f = 0.40 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 8.4, 6.5 Hz, 2.0H), 7.09 (d, *J* = 8.5 Hz, 0.60H), 7.04 – 6.98 (m, 1.40H), 5.60 (ddd, *J* = 17.3, 10.3, 7.1 Hz, 0.30H), 5.33 (ddd, *J* = 17.1, 10.3, 8.1 Hz, 0.70H), 4.94 – 4.79 (m, 2.0H), 3.90 – 3.70 (m, 6.0H), 3.39 (dt, *J* = 10.7, 7.5 Hz, 0.70H), 3.04 – 2.93 (m, 0.70H), 2.87 – 2.47 (m, 3.30H), 2.40 – 2.26 (m, 1.0H), 2.22 – 2.09 (m, 0.30H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 172.9, 172.8, 172.6, 140.6, 139.8, 138.3, 137.8, 131.5, 131.1, 130.1, 129.4, 120.3, 120.1, 116.0, 115.8, 58.9, 58.1, 53.0, 52.9, 52.9, 52.8, 51.0, 50.9, 47.5, 47.3, 42.2, 40.3, 39.0, 38.1.
DART-TOF LC/MS m/z calcd. for $C_{17}H_{19}BrO_4$ [M+H$^+$] 367.0545, found 367.0541.



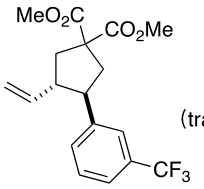
10
(trans: cis = 72:28)

Prepared according to ***Procedure C***. Colorless oil (52.7 mg, 86% yield) as a mixture of diastereomers (trans : cis = 72:28). R_f = 0.35 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 6.90 (m, 4.0H), 5.59 (d, *J* = 17.3 Hz, 0.28H), 5.34 (ddd, *J* = 17.1, 10.3, 8.1 Hz, 0.72H), 4.94 – 4.77 (m, 2.0H), 3.90 – 3.65 (m, 6.0H), 3.41 (dt, *J* = 10.8, 7.5 Hz, 0.72H), 3.05 – 2.93 (m, 0.72H), 2.89 – 2.47 (m, 2.28H), 2.40 – 2.26 (m, 1.0H), 2.22 – 2.10 (m, 0.28H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 172.9, 172.8, 172.6, 162.8, 162.6, 160.4, 160.2, 138.5, 138.0, 137.2, 137.1, 136.4, 136.4, 129.7, 129.6, 129.0, 128.9, 115.8, 115.6, 115.3, 115.1, 114.9, 114.7, 58.9, 58.0, 52.9, 52.8, 52.8, 51.1, 50.7, 47.4, 47.3, 42.4, 40.2, 38.9, 38.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.6, -117.0.

DART-TOF LC/MS m/z calcd. for $C_{17}H_{19}FO_4$ [M+H$^+$] 307.1346, found 307.1349.



11
(trans: cis = 72:28)

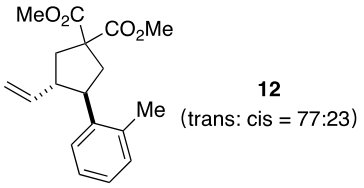
Prepared according to ***Procedure C***. Colorless oil (49.6 mg, 70% yield) as a mixture of diastereomers (trans : cis = 72:28). R_f = 0.40 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.30 (m, 4H), 5.62 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 0.28H), 5.32 (ddd, *J* = 17.1, 10.3, 8.2 Hz, 0.72H), 4.96 – 4.76 (m, 2.0H), 3.90 – 3.65 (m, 6.0H), 3.55 – 3.42 (m, 0.72H), 3.17 – 3.00 (m, 0.72H), 2.98 – 2.86 (m, 0.28H), 2.85 – 2.52 (m, 3.0H), 2.45 – 2.30 (m, 1.0H), 2.25 – 2.12 (m, 0.28H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 172.8, 172.7, 172.5, 142.6, 141.7, 138.2, 137.5, 131.7, 131.7, 131.7, 131.0, 130.9, 130.8, 130.5, 130.5, 130.2, 129.9, 128.8, 128.5, 125.6, 125.1, 125.1, 125.0, 125.0, 124.4, 124.4, 124.3, 123.5, 123.4, 123.4, 123.2, 123.2, 123.1,

123.1, 122.9, 116.2, 116.1, 58.9, 58.1, 53.0, 52.9, 52.8, 51.1, 51.0, 47.9, 47.3, 42.2, 40.3, 38.9, 37.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.60, -62.61.

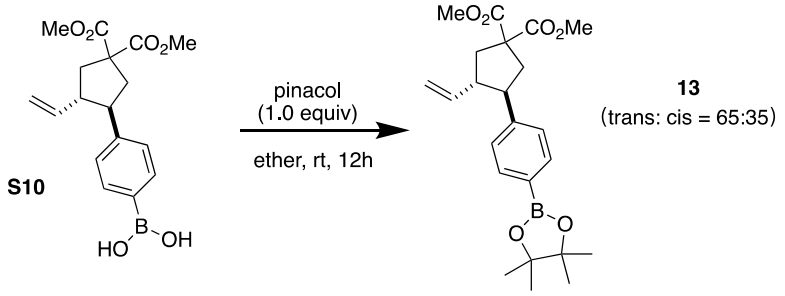
DART-TOF LC/MS m/z calcd. for $C_{18}H_{19}F_3O_4$ [M+H$^+$] 357.1314, found 357.1314.



12
(trans: cis = 77:23)

Prepared according to ***Procedure C***. Colorless oil (53.9 mg, 89% yield) as a mixture of diastereomers (trans : cis = 72:28). R_f = 0.40 (10% EtOAc in hexane).

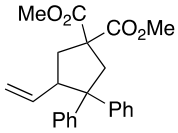
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.06 (m, 4.0H), 5.63 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 0.23H), 5.31 (ddd, *J* = 17.0, 10.3, 8.3 Hz, 0.77H), 4.97 – 4.70 (m, 2.0H), 3.83 – 3.72 (m, 6.0H), 3.58 (ddd, *J* = 11.0, 8.3, 7.1 Hz, 0.77H), 3.23 – 3.03 (m, 1.0H), 2.95 – 2.55 (m, 3.0H), 2.39 – 2.27 (m, 3.77H), 2.13 (ddd, *J* = 13.8, 11.3, 2.4 Hz, 0.46H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 173.0, 173.0, 172.7, 139.6, 138.6, 138.5, 138.3, 136.5, 136.4, 130.2, 130.1, 126.7, 126.3, 126.2, 126.1, 125.7, 125.6, 115.6, 114.9, 58.8, 58.0, 52.9, 52.8, 50.0, 46.6, 45.0, 43.9, 42.1, 40.0, 39.1, 38.1, 20.1, 19.8.
DART-TOF LC/MS m/z calcd. for $C_{18}H_{23}O_4$ [M+H$^+$] 303.1596, found 303.1595.



13
(trans: cis = 65:35)

The boric acid product **S10** was prepared according to ***Procedure C***. To a solution of crude **S10** in anhydrous ether (10.0 mL), pinacol (23.6 mg, 0.2 mmol, 1.0 equiv) was added. The reaction was stirred at room temperature for 12h. The solvent was then removed under vacuum, and the residue was purified by silica gel chromatography to give **13** as a colorless oil (69.7 mg, 84% yield, trans : cis = 65:35). R_f = 0.45 (10% EtOAc in hexane).

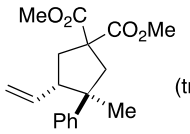
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.66 (m, 2.0H), 7.24 – 7.20 (m, 0.70H), 7.17 – 7.12 (m, 1.30H), 5.62 (ddd, *J* = 16.7, 10.7, 7.1 Hz, 0.35H), 5.34 (ddd, *J* = 17.1, 10.3, 8.0 Hz, 0.65H), 4.92 – 4.74 (m, 2.0H), 3.95 – 3.65 (m, 6.0H), 3.50 – 3.40 (m, 0.65H), 3.10 – 2.98 (m, 0.65H), 2.88 (td, *J* = 11.1, 7.6 Hz, 0.35H), 2.81 – 2.53 (m, 3.0H), 2.44 – 2.30 (m, 1.0H), 2.22 – 2.12 (m, 0.35H), 1.32 (s, 12.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 172.9, 172.8, 172.6, 144.8, 144.0, 138.6, 138.0, 134.9, 134.6, 127.8, 127.1, 115.7, 115.5, 83.7, 59.0, 58.1, 52.9, 52.8, 52.8, 51.7, 50.9, 48.2, 47.3, 42.3, 40.3, 39.0, 37.9, 24.9, 24.9, 24.8.
DART-TOF LC/MS m/z calcd. for $C_{23}H_{32}BO_6$ [M+H$^+$] 415.2292, found 415.2292.



14

Prepared according to ***Procedure C***. Colorless oil (70.1 mg, 96% yield). R_f = 0.40 (10% EtOAc in hexane).

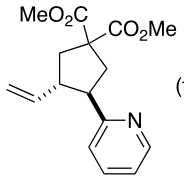
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 6.75 (m, 10H), 5.37 (ddd, *J* = 17.1, 10.3, 8.1 Hz, 1H), 5.03 (dd, *J* = 17.2, 1.4 Hz, 1H), 4.92 – 4.81 (m, 1H), 3.69 (s, 3H), 3.56 (dd, *J* = 8.6, 6.4 Hz, 1H), 3.47 (s, 3H), 3.44 (d, *J* = 14.7 Hz, 1H), 2.89 (d, *J* = 14.7 Hz, 1H), 2.59 (dd, *J* = 13.8, 6.4 Hz, 1H), 2.14 (dd, *J* = 13.8, 9.2 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 172.6, 148.2, 144.9, 138.5, 129.0, 128.1, 127.6, 127.4, 126.1, 126.0, 116.1, 58.1, 57.8, 53.0, 52.8, 50.2, 46.5, 38.7.
DART-TOF LC/MS m/z calcd. for $C_{23}H_{25}O_4$ $[M+H]^+$ 365.1753, found 365.1758.



15
(trans: cis = 60:40)

Prepared according to ***Procedure C***. Colorless oil (50.0 mg, 83% yield) as a mixture of diastereomers (trans : cis = 60:40). R_f = 0.40 (10% EtOAc in hexane).

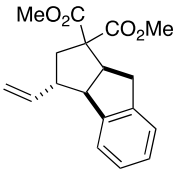
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.01 (m, 5.0H), 5.64 (ddd, *J* = 17.4, 10.5, 7.0 Hz, 0.60H), 5.11 (ddd, *J* = 17.1, 10.1, 8.5 Hz, 0.40H), 4.99 – 4.72 (m, 2.0H), 3.75 – 3.61 (m, 6.0H), 3.04 – 2.89 (m, 1.0H), 2.72 – 2.58 (m, 1.0H), 2.58 – 2.33 (m, 2.60H), 2.22 (dd, *J* = 13.8, 8.6 Hz, 0.40H), 1.33 (s, 1.20H), 1.14 (d, *J* = 0.8 Hz, 1.80H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 173.4, 173.0, 172.8, 147.7, 146.0, 138.6, 136.6, 128.2, 127.8, 127.3, 126.1, 126.0, 125.8, 116.5, 115.6, 58.7, 57.5, 55.0, 53.0, 53.0, 52.9, 52.9, 52.8, 49.9, 49.5, 48.8, 45.8, 39.2, 38.3, 29.4, 21.8.
DART-TOF LC/MS m/z calcd. for $C_{18}H_{23}O_4$ $[M+H^+]$ 303.1596, found 303.1602.



16
(trans: cis = 67:33)

Prepared according to ***Procedure C***. Colorless oil (30.2 mg, 52% yield) as a mixture of diastereomers (trans : cis = 67:33). R_f = 0.25 (30% EtOAc in hexane).

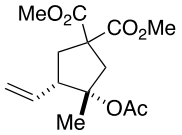
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.44 (m, 1.0H), 7.63 – 7.48 (m, 1.0H), 7.17 – 7.01 (m, 2.0H), 5.67 (ddd, *J* = 17.1, 10.4, 7.5 Hz, 0.33H), 5.33 (ddd, *J* = 17.1, 10.2, 8.3 Hz, 0.67H), 4.94 – 4.69 (m, 2.0H), 3.85 – 3.69 (m, 6.0H), 3.56 (dd, *J* = 8.0, 7.9 Hz, 0.67H), 3.18 – 2.68 (m, 3.33H), 2.62 – 2.43 (m, 1.67H), 2.13 (dd, *J* = 13.7, 10.7 Hz, 0.33H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 173.1, 172.6, 172.6, 160.8, 160.8, 149.4, 148.9, 138.9, 138.1, 136.2, 135.7, 123.3, 123.0, 121.7, 121.3, 115.5, 115.4, 59.6, 58.4, 53.3, 52.9, 52.8, 52.8, 52.7, 50.3, 50.2, 47.7, 40.9, 40.1, 39.1, 37.8.
DART-TOF LC/MS m/z calcd. for $C_{16}H_{20}NO_4$ $[M+H^+]$ 290.1392, found 290.1393.



17
(trans: cis = 66:34)

Prepared according to ***Procedure C***. Colorless oil (54.8 mg, 91% yield) as a mixture of diastereomers (trans : cis = 66:34). R_f = 0.40 (10% EtOAc in hexane).

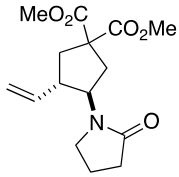
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.05 (m, 4.0H), 5.95 – 5.79 (m, 0.34H), 5.35 (ddd, *J* = 17.1, 10.1, 8.6 Hz, 0.66H), 5.12 – 4.88 (m, 2.0H), 4.01 – 3.71 (m, 6.68H), 3.66 (s, 1.0H), 3.49 (dd, *J* = 8.5, 7.1 Hz, 0.34H), 3.08 (ddd, *J* = 16.7, 9.7, 7.9 Hz, 1.0H), 2.91 – 2.72 (m, 1.66H), 2.67 – 2.55 (m, 0.66H), 2.28 – 1.94 (m, 1.66H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 172.3, 171.2, 170.8, 145.2, 142.7, 142.0, 141.7, 140.6, 138.9, 126.9, 126.9, 126.8, 126.7, 125.9, 124.4, 124.1, 123.8, 115.2, 114.7, 64.1, 62.9, 56.5, 52.9, 52.9, 52.7, 52.5, 52.3, 50.2, 50.0, 47.8, 45.5, 41.8, 37.9, 35.9, 34.9.
DART-TOF LC/MS m/z calcd. for $C_{18}H_{21}O_4$ [M+H$^+$] 301.1440, found 301.1442.



18
(cis: trans = 80:20)

Prepared according to ***Procedure C***. Colorless oil (19.0 mg, 32% yield) as a mixture of diastereomers (cis : trans = 80:20). R_f = 0.35 (30% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 – 5.60 (m, 1.0H), 5.17 – 5.05 (m, 2.0H), 3.93 – 3.52 (m, 6.0H), 3.40 (d, *J* = 15.4 Hz, 0.20H), 2.99 – 2.87 (m, 0.80H), 2.83 – 2.57 (m, 2.40H), 2.52 – 2.18 (m, 0.80H), 2.04 (dd, *J* = 14.0, 9.4 Hz, 0.80H), 1.95 (s, 2.40H), 1.92 (s, 0.60H), 1.52 (s, 0.60H), 1.37 (s, 2.40H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 172.4, 172.4, 172.3, 170.5, 170.3, 136.0, 134.9, 118.1, 117.1, 89.2, 88.6, 57.3, 57.1, 55.5, 52.9, 52.8, 52.7, 51.9, 45.1, 43.5, 38.2, 36.0, 22.0, 22.0, 21.2, 20.0.
DART-TOF LC/MS m/z calcd. for $C_{14}H_{24}NO_6$ [M+NH_4^+] 302.1604, found 302.1604.

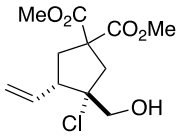


19
(trans: cis = 95:5)

Prepared according to ***Procedure C***. Colorless oil (45.4 mg, 77% yield) as a mixture of diastereomers (trans : cis = 95:5). R_f = 0.30 (50% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 – 5.62 (m, 1H), 5.07 – 4.91 (m, 2H), 4.59 (q, *J* = 8.0 Hz, 1H), 3.68 (d, *J* = 6.3 Hz, 6H), 3.32 (dt, *J* = 9.3, 7.0 Hz, 1H), 3.24 (dt, *J* = 9.3, 6.8 Hz, 1H), 2.90 (dddd, *J* = 9.7, 6.9, 2.8, 1.5 Hz, 1H), 2.60 (ddd, *J* = 14.4, 8.1, 1.0 Hz, 1H), 2.49 (ddd, *J* = 13.8, 7.1, 0.9 Hz, 1H), 2.36 – 2.23 (m, 3H), 2.16 (dd, *J* = 13.7, 9.6 Hz, 1H), 1.93 – 1.78 (m, 2H).

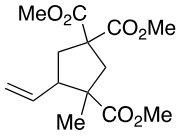
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 172.1, 172.0, 136.0, 116.5, 58.2, 53.7, 53.0, 52.9, 45.7, 45.3, 37.7, 35.5, 31.1, 18.3.
DART-TOF LC/MS m/z calcd. for $C_{15}H_{23}NO_5$ $[M+H]^+$ 296.1498, found 296.1495.



20
(cis: trans = 57:43)

Prepared according to ***Procedure C***. Colorless oil (28.3 mg, 51% yield) as a mixture of diastereomers (cis : trans = 57:43). R_f = 0.35 (50% EtOAc in hexane).

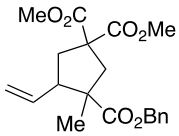
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 – 5.66 (m, 1.0H), 5.23 – 5.00 (m, 2.0H), 3.79 – 3.48 (m, 8.0H), 3.14 – 2.53 (m, 4.0H), 2.38 (dd, *J* = 13.5, 7.0 Hz, 0.43H), 2.22 – 2.06 (m, 1.57H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 172.5, 171.9, 171.6, 135.4, 134.2, 118.6, 118.2, 77.4, 77.0, 76.7, 67.8, 67.0, 57.4, 57.0, 54.9, 53.2, 53.2, 53.1, 53.0, 50.6, 46.5, 44.9, 38.2, 37.6.
DART-TOF LC/MS m/z calcd. for $C_{12}H_{18}ClO_5$ $[M+H^+]$ 277.0843, found 277.0846.



21
(cis: trans = 50:50)

Prepared according to ***Procedure C***. Colorless oil (48.6 mg, 85% yield) as a mixture of diastereomers (cis : trans = 50:50). R_f = 0.40 (20% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 – 5.66 (m, 0.50H), 5.66 – 5.55 (m, 0.50H), 5.12 – 4.94 (m, 2H), 3.82 – 3.48 (m, 9.0H), 3.12 – 2.98 (m, 0.50H), 2.91 (d, *J* = 14.4 Hz, 0.50H), 2.82 (d, *J* = 14.3 Hz, 0.50H), 2.57 – 2.44 (m, 1.50H), 2.40 – 2.29 (m, 1.0H), 2.28 – 2.11 (m, 1.0H), 1.26 (s, 1.50H), 1.07 (s, 1.50H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 175.6, 173.5, 172.5, 172.1, 136.0, 135.7, 117.1, 116.8, 58.7, 57.8, 54.6, 53.0, 53.0, 52.9, 52.9, 52.7, 52.1, 51.9, 51.5, 49.7, 44.8, 44.7, 38.9, 37.5, 22.7, 18.9.
DART-TOF LC/MS m/z calcd. for $C_{14}H_{21}O_6$ $[M+H^+]$ 285.1338, found 285.1334.

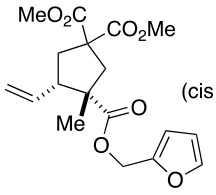


22
(cis: trans = 54:46)

Prepared according to ***Procedure C***. Colorless oil (64.7 mg, 90% yield) as a mixture of diastereomers (cis : trans = 54:46). R_f = 0.40 (50% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 5.74 (ddd, *J* = 17.4, 10.5, 7.2 Hz, 0.46H), 5.65 – 5.53 (m, 0.54H), 5.16 – 4.94 (m, 4.0H), 3.81 – 3.55 (m, 6.0H), 3.15 – 3.04 (m, 0.46H), 2.94 (dd, *J* = 32.8, 14.4 Hz, 1.0H), 2.62 – 2.48 (m, 1.54H), 2.44 – 2.14 (m, 2.0H), 1.32 (s, 1.62H), 1.13 (s, 1.38H).

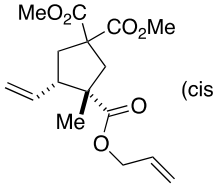
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 175.1, 173.5, 172.5, 172.4, 171.9, 135.9, 135.8, 135.6, 128.5, 128.5, 128.4, 128.2, 128.1, 127.9, 117.2, 117.0, 66.6, 66.4, 58.7, 57.9, 54.7, 53.0, 53.0, 52.9, 52.9, 52.7, 51.9, 49.8, 44.8, 44.7, 38.9, 37.6, 22.9, 19.1.
DART-TOF LC/MS m/z calcd. for $C_{20}H_{25}O_6$ [M+H$^+$] 361.1651, found 361.1652.



23
(cis: trans = 66:34)

Prepared according to ***Procedure C***. Colorless oil (59.6 mg, 85% yield) as a mixture of diastereomers (cis : trans = 66:34). R_f = 0.40 (20% EtOAc in hexane).

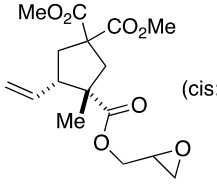
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 1.9, 0.8 Hz, 1.0H), 6.39 – 6.29 (m, 2.0H), 5.70 (ddd, *J* = 17.4, 10.5, 7.2 Hz, 0.34H), 5.60 – 5.48 (m, 0.66H), 5.10 – 4.91 (m, 4.0H), 3.70 (dd, *J* = 8.2, 1.9 Hz, 6.0H), 3.10 – 3.00 (m, 0.34H), 2.95 (d, *J* = 14.4 Hz, 0.66H), 2.84 (d, *J* = 14.3 Hz, 0.34H), 2.60 – 2.44 (m, 1.66H), 2.39 – 2.30 (m, 1.0H), 2.27 – 2.12 (m, 1.0H), 1.27 (s, 1.98H), 1.08 (s, 1.02H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 174.8, 173.5, 172.4, 172.4, 171.9, 149.5, 149.4, 143.1, 143.0, 135.8, 135.5, 117.1, 117.0, 110.6, 110.5, 110.4, 58.7, 58.4, 58.0, 57.9, 54.7, 53.0, 53.0, 52.9, 52.7, 52.0, 49.8, 44.7, 44.6, 38.9, 37.5, 22.8, 18.9.
DART-TOF LC/MS m/z calcd. for $C_{18}H_{23}O_7$ [M+H$^+$] 351.1444, found 351.1449.



24
(cis: trans = 55:45)

Prepared according to ***Procedure C***. Colorless oil (50.7 mg, 82% yield) as a mixture of diastereomers (cis : trans = 55:45). R_f = 0.45 (20% EtOAc in hexane).

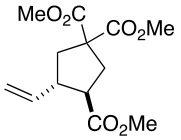
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 – 5.48 (m, 1.0H), 5.40 – 4.94 (m, 4.0H), 4.59 – 4.45 (m, 2.0H), 3.78 – 3.63 (m, 6.0H), 3.14 – 3.02 (m, 0.45H), 2.94 (d, *J* = 14.4 Hz, 0.55H), 2.86 (d, *J* = 14.3 Hz, 0.45H), 2.61 – 2.46 (m, 1.55H), 2.42 – 2.30 (m, 1.0H), 2.29 – 2.11 (m, 1.0H), 1.29 (s, 1.65H), 1.10 (s, 1.35H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 174.8, 173.5, 172.4, 172.4, 172.0, 136.0, 135.7, 132.1, 118.2, 118.0, 117.2, 116.9, 65.4, 65.2, 58.7, 57.9, 54.6, 53.0, 52.9, 52.9, 52.7, 51.9, 49.7, 44.8, 44.7, 39.0, 37.5, 22.8, 19.0.
DART-TOF LC/MS m/z calcd. for $C_{16}H_{23}O_6$ [M+H$^+$] 311.1495, found 311.1491.



25
(cis: trans = 58:42)

Prepared according to ***Procedure C***. Colorless oil (58.6 mg, 90% yield) as a mixture of diastereomers (cis : trans = 58:42). R_f = 0.30 (20% EtOAc in hexane).

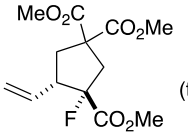
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 – 5.55 (m, 1.0H), 5.13 – 4.99 (m, 2.0H), 4.39 (ddd, *J* = 12.3, 4.6, 3.0 Hz, 0.42H), 4.31 (dd, *J* = 12.2, 3.1 Hz, 0.58H), 3.90 (ddd, *J* = 12.3, 6.1, 1.5 Hz, 0.42H), 3.81 (ddd, *J* = 12.3, 6.4, 0.9 Hz, 0.58H), 3.74 – 3.67 (m, 6.0H), 3.21 – 2.73 (m, 3.40H), 2.67 – 2.46 (m, 2.60H), 2.42 – 2.13 (m, 2.0H), 1.28 (s, 1.74H), 1.09 (s, 1.26H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 175.7, 174.9, 174.8, 173.4, 172.4, 172.0, 171.9, 135.8, 135.6, 117.3, 117.1, 117.0, 65.3, 65.2, 65.1, 65.1, 58.6, 57.9, 54.5, 54.5, 53.1, 53.0, 52.9, 52.9, 52.8, 52.7, 52.0, 52.0, 49.7, 49.2, 49.1, 49.1, 44.8, 44.7, 44.6, 44.6, 44.4, 44.4, 38.8, 38.8, 37.5, 22.8, 22.8, 19.1, 19.0.
DART-TOF LC/MS m/z calcd. for $C_{16}H_{26}NO_7$ [M+NH_4^+] 344.1709, found 344.1705.



26
(trans: cis = 76:24)

Prepared according to ***Procedure C***. Colorless oil (39.8 mg, 74% yield) as a mixture of diastereomers (trans : cis = 76:24). R_f = 0.30 (30% EtOAc in hexane).

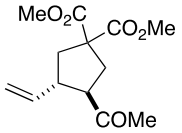
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 – 5.56 (m, 1.0H), 5.16 – 4.90 (m, 2.0H), 3.89 – 3.52 (m, 9.0H), 3.17 – 2.79 (m, 1.76H), 2.74 – 2.31 (m, 4.0H), 1.97 (dd, *J* = 13.6, 10.8 Hz, 0.24H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 173.6, 172.9, 172.3, 172.0, 171.8, 138.3, 136.6, 116.5, 115.9, 59.3, 58.7, 52.9, 52.9, 52.8, 51.8, 51.5, 49.5, 48.0, 47.5, 45.8, 39.9, 38.6, 37.4, 35.9.
DART-TOF LC/MS m/z calcd. for $C_{13}H_{19}O_6$ [M+H^+] 271.1182, found 271.1180.



27
(trans: cis = 70:30)

Prepared according to ***Procedure C***. Colorless oil (33.3 mg, 58% yield) as a mixture of diastereomers (trans : cis = 70:30). R_f = 0.35 (30% EtOAc in hexane).

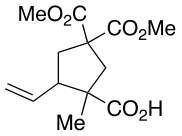
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 – 5.49 (m, 1.0H), 5.24 – 4.96 (m, 2.0H), 4.01 – 3.55 (m, 9.0H), 3.28 – 2.69 (m, 3.70H), 2.57 (dd, *J* = 13.6, 7.7 Hz, 0.30H), 2.51 – 2.42 (m, 0.30H), 2.24 (dd, *J* = 13.7, 10.0 Hz, 0.70H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 171.5, 171.1, 171.0, 169.9, 169.8, 169.6, 169.6, 133.8, 133.7, 132.2, 132.1, 119.1, 118.6, 103.7, 103.1, 101.8, 101.1, 57.9, 57.9, 57.8, 53.2, 53.2, 53.1, 53.0, 52.8, 52.7, 52.4, 52.2, 52.0, 44.1, 43.9, 42.8, 42.6, 37.6, 37.6, 37.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ -149.0, -170.0.
DART-TOF LC/MS m/z calcd. for $C_{13}H_{18}FO_6$ [M+H^+] 289.1087, found 289.1086.



28
(trans: cis = 65:35)

Prepared according to ***Procedure C***. Colorless oil (37.0 mg, 73% yield) as a mixture of diastereomers (trans : cis = 65:35). R_f = 0.30 (30% EtOAc in hexane).

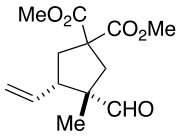
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (ddd, *J* = 17.0, 10.2, 7.6 Hz, 0.35H), 5.59 (ddd, *J* = 17.0, 10.1, 9.2 Hz, 0.65H), 5.15 – 4.96 (m, 2.0H), 3.94 – 3.50 (m, 6.0H), 3.22 (td, *J* = 8.6, 7.1 Hz, 0.65H), 3.08 – 2.96 (m, 0.65H), 2.86 – 2.72 (m, 0.65H), 2.67 – 2.50 (m, 1.35H), 2.48 – 2.22 (m, 2.35H), 2.12 (s, 1.05H), 2.08 (s, 1.95H), 2.02 – 1.89 (m, 0.35H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 208.3, 208.2, 172.9, 172.4, 172.0, 171.9, 139.1, 137.0, 116.6, 116.1, 59.0, 58.7, 57.2, 55.4, 52.9, 52.9, 52.8, 47.0, 45.8, 40.3, 39.4, 36.4, 34.8, 31.0, 30.0.
DART-TOF LC/MS m/z calcd. for $C_{34}H_{19}O_5$ [M+H$^+$] 255.1232, found 255.1233.



29
(trans: cis = 50:50)

Prepared according to ***Procedure C***. Colorless oil (48.7 mg, 90% yield) as a mixture of diastereomers (trans : cis = 50:50). R_f = 0.40 (10% MeOH in DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.63 (brs, 1.0H), 5.93 – 5.54 (m, 1.0H), 5.19 – 4.98 (m, 2.0H), 3.88 – 3.60 (m, 6.0H), 3.13 – 3.03 (m, 0.50H), 2.95 (d, *J* = 14.4 Hz, 0.50H), 2.88 (d, *J* = 14.4 Hz, 0.50H), 2.55 (ddd, *J* = 12.4, 9.2, 4.8 Hz, 1.50H), 2.44 – 2.33 (m, 1.0H), 2.31 – 2.13 (m, 1.0H), 1.28 (s, 1.50H), 1.10 (s, 1.50H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 182.7, 181.9, 173.4, 172.4, 172.4, 171.9, 135.6, 135.4, 117.7, 117.2, 58.8, 57.9, 54.7, 53.0, 53.0, 53.0, 52.8, 52.8, 51.7, 49.6, 44.8, 44.6, 39.0, 37.6, 22.6, 18.8.
DART-TOF LC/MS m/z calcd. for $C_{13}H_{20}O_6$ [M+H$^+$] 271.1182, found 271.1185.

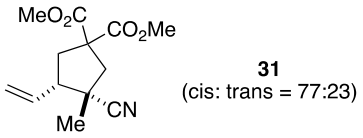


30
(cis: trans = 60:40)

Prepared according to ***Procedure C***. Colorless oil (43.8 mg, 86% yield) as a mixture of diastereomers (cis : trans = 60:40). R_f = 0.40 (20% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 0.40H), 9.43 (s, 0.60H), 5.76 (ddd, *J* = 17.1, 10.3, 8.0 Hz, 0.40H), 5.60 (ddd, *J* = 17.1, 10.5, 7.5 Hz, 0.60H), 5.22 – 4.97 (m, 2.0H), 3.93 – 3.55 (m, 6.0H), 2.89 (dd, *J* = 11.7, 0.9 Hz, 0.60H), 2.78 (dd, *J* = 25.8, 14.5 Hz, 1.0H), 2.52 (dd, *J* = 13.6, 6.9 Hz, 1.0H), 2.45 – 2.37 (m, 0.40H), 2.36 – 2.10 (m, 2.0H), 1.24 (s, 1.20H), 1.00 (s, 1.80H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.7, 203.1, 172.9, 172.4, 172.1, 171.9, 135.0, 134.4, 118.0, 117.6, 58.4, 58.1, 56.2, 56.1, 53.8, 53.1, 53.0, 53.0, 52.9, 47.5, 41.8, 40.5, 38.9, 38.0, 19.8, 15.8.

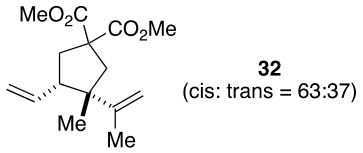
DART-TOF LC/MS m/z calcd. for $C_{13}H_{19}O_5$ [M+H$^+$] 255.1232, found 255.1231.



31
(cis: trans = 77:23)

Prepared according to ***Procedure C***. Colorless oil (37.8 mg, 75% yield) as a mixture of diastereomers (trans : cis = 77:23). R_f = 0.30 (30% EtOAc in hexane).

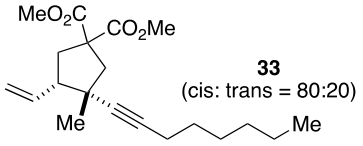
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 – 5.62 (m, 1.0H), 5.31 – 5.14 (m, 2.0H), 3.96 – 3.53 (m, 6.0H), 3.05 – 2.90 (m, 1.0H), 2.83 (d, *J* = 14.4 Hz, 0.77H), 2.62 – 2.48 (m, 1.77H), 2.48 – 2.31 (m, 0.46H), 2.30 – 2.14 (m, 1.0H), 1.38 (s, 0.69H), 1.20 (s, 2.31H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 171.7, 171.6, 171.0, 134.4, 133.3, 123.8, 122.0, 119.7, 119.2, 57.7, 57.5, 53.9, 53.3, 53.2, 53.2, 53.2, 51.5, 45.7, 45.2, 43.4, 40.3, 39.2, 36.6, 22.8, 19.7.
DART-TOF LC/MS m/z calcd. for $C_{13}H_{18}NO_4$ [M+H$^+$] 252.1236, found 252.1232.



32
(cis: trans = 63:37)

Prepared according to ***Procedure C***. Colorless oil (27.1 mg, 51% yield) as a mixture of diastereomers (cis : trans = 63:37). R_f = 0.40 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 – 5.57 (m, 1.0H), 5.08 – 4.89 (m, 2.0H), 4.85 – 4.69 (m, 2.0H), 4.02 – 3.52 (m, 6.0H), 2.88 – 2.76 (m, 1.0H), 2.71 (dd, *J* = 14.1, 6.8 Hz, 0.37H), 2.51 – 2.20 (m, 3.63H), 1.77 (d, *J* = 1.0 Hz, 1.89H), 1.69 (d, *J* = 1.4 Hz, 1.11H), 1.11 (s, 1.11H), 0.96 (s, 1.89H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 173.4, 173.1, 173.0, 149.7, 149.6, 139.0, 137.0, 116.0, 114.7, 111.0, 110.5, 58.5, 57.4, 53.3, 52.9, 52.9, 52.8, 51.3, 49.9, 49.0, 46.2, 44.0, 38.9, 38.0, 26.2, 21.0, 20.1, 20.0.
DART-TOF LC/MS m/z calcd. for $C_{15}H_{26}NO_4$ [M+NH$_4^+$] 284.1862, found 284.1868.

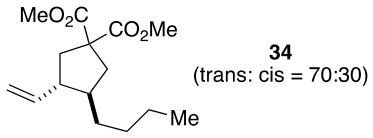


33
(cis: trans = 80:20)

Prepared according to ***Procedure C***. Colorless oil (33.6 mg, 50% yield) as a mixture of diastereomers (cis : trans = 80:20). R_f = 0.45 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 – 2.42 (m, 1.0H), 5.24 – 4.88 (m, 2.0H), 3.93 – 3.43 (m, 6.0H), 2.81 – 2.63 (m, 1.0H), 2.60 – 2.42 (m, 2.60H), 2.33 – 2.02 (m, 3.40H), 1.50 – 1.21 (m, 8.0H), 1.19 (s, 0.60H), 0.99 (s, 2.40H), 0.90 – 0.84 (m, 3.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 172.8, 172.8, 172.2, 137.6, 136.2, 116.8, 116.4, 85.8, 83.9, 82.5, 80.9, 57.8, 57.7, 55.0, 53.4, 52.9, 52.8, 52.8, 52.6, 48.9, 48.0, 42.5, 40.8, 39.4, 36.8, 31.3, 31.3, 29.0, 28.9, 28.4, 28.4, 25.3, 22.5, 22.0, 18.6, 14.0, 14.0.

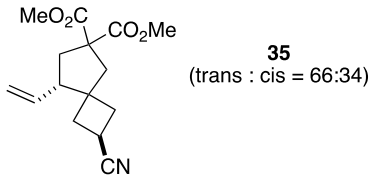
DART-TOF LC/MS m/z calcd. for $C_{20}H_{31}O_4$ [M+H$^+$] 335.2222, found 335.2226.



34
(trans: cis = 70:30)

Prepared according to ***Procedure C***. Colorless oil (31.2 mg, 58% yield) as a mixture of diastereomers (trans : cis = 70:30). R_f = 0.45 (10% EtOAc in hexane).

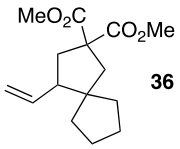
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 – 5.50 (m, 1H), 5.06 – 4.91 (m, 2.0H), 3.76 – 3.66 (m, 6.0H), 2.76 – 2.62 (m, 0.70H), 2.59 – 2.51 (m, 0.30H), 2.47 (dd, *J* = 13.9, 7.1 Hz, 1.0H), 2.40 – 2.31 (m, 0.70H), 2.23 – 1.89 (m, 3.0H), 1.78 (dd, *J* = 13.4, 10.8 Hz, 0.30H), 1.67 – 1.05 (m, 6.0H), 0.90 – 0.82 (m, 3.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 168.5, 168.4, 168.4, 135.6, 133.6, 110.5, 110.4, 72.6, 72.3, 72.0, 54.2, 53.6, 48.0, 48.0, 45.7, 41.6, 40.5, 38.3, 35.9, 35.6, 34.5, 28.1, 25.6, 25.6, 25.3, 18.1, 18.1, 9.3, 9.2.
DART-TOF LC/MS m/z calcd. for $C_{15}H_{25}O_4$ [M+H$^+$] 269.1753, found 269.1757.



35
(trans : cis = 66:34)

Prepared according to ***Procedure C***. Colorless oil (39.8 mg, 72% yield) as a mixture of diastereomers (trans : cis = 66:34). R_f = 0.30 (20% EtOAc in hexane).

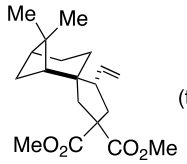
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 – 5.64 (m, 1.0H), 5.31 – 4.96 (m, 2.0H), 3.90 – 3.45 (m, 6.0H), 3.07 – 2.92 (m, 0.34H), 2.88 – 2.73 (m, 0.66H), 2.61 (dd, *J* = 27.5, 14.0 Hz, 1.0H), 2.52 – 1.88 (m, 8.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 172.5, 172.5, 136.0, 135.7, 122.4, 122.0, 118.4, 118.3, 57.4, 57.3, 52.3, 52.9, 51.5, 51.4, 47.5, 47.3, 47.2, 45.3, 37.9, 37.7, 34.4, 34.4, 33.3, 32.4, 16.9, 16.4.
DART-TOF LC/MS m/z calcd. for $C_{15}H_{23}N_2O_4$ [M+NH$_4^+$] 295.1658, found 295.1656.



36

Prepared according to ***Procedure C*** (0.4 mmol). Colorless oil (67.2 mg, 63% yield). R_f = 0.45 (10% EtOAc in hexane).

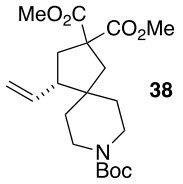
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 – 5.60 (m, 1H), 5.08 – 4.91 (m, 2H), 3.70 (s, 3H), 3.69 (s, 3H), 2.57 – 2.31 (m, 3H), 2.19 – 2.01 (m, 2H), 1.65 – 1.13 (m, 8H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 173.2, 137.6, 116.2, 57.8, 53.7, 52.7, 52.7, 51.8, 47.4, 39.2, 37.2, 32.1, 24.7, 24.4.
DART-TOF LC/MS m/z calcd. for $C_{15}H_{23}O_4$ [M+H$^+$] 267.1596, found 267.1600.



37
(trans : cis = 68:32)

Prepared according to ***Procedure C***. Colorless oil (43.5 mg, 68% yield) as a mixture of diastereomers (trans : cis = 68:32). R_f = 0.40 (10% EtOAc in hexane).

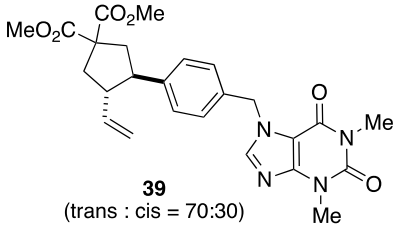
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 – 5.82 (m, 0.68H), 5.72 – 5.52 (m, 0.32H), 5.09 – 4.81 (m, 2.0H), 3.75 – 3.65 (m, 6.0H), 2.60 (d, *J* = 14.1 Hz, 0.68H), 2.50 – 2.24 (m, 2.64H), 2.18 (d, *J* = 14.1 Hz, 0.68H), 2.12 – 1.97 (m, 2.0H), 1.94 – 1.59 (m, 5.32H), 1.45 – 1.22 (m, 1.68H), 1.17 (s, 3.0H), 0.99 (s, 2.04H), 0.97 (s, 0.96H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 173.4, 173.3, 173.3, 139.1, 138.9, 115.9, 114.8, 59.4, 57.8, 55.9, 53.5, 52.8, 52.7, 52.7, 50.6, 50.2, 49.3, 48.4, 47.2, 40.2, 39.8, 39.2, 38.9, 38.3, 37.8, 29.6, 28.1, 27.8, 27.8, 27.6, 25.6, 25.4, 23.9, 23.8, 22.6.
DART-TOF LC/MS m/z calcd. for $C_{19}H_{32}NO_4$ [M+NH_4^+] 338.2331, found 338.2326.



38

Prepared according to ***Procedure C***. Colorless oil (50.3 mg, 66% yield). R_f = 0.30 (30% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (ddd, *J* = 17.0, 10.3, 7.7 Hz, 1H), 5.11 – 4.92 (m, 2H), 3.89 (brs, 2H), 3.70 (s, 3H), 3.70 (s, 3H), 2.93 – 2.67 (m, 2H), 2.57 (d, *J* = 14.2 Hz, 1H), 2.48 (dd, *J* = 12.9, 6.0 Hz, 1H), 2.35 – 2.11 (m, 2H), 2.01 (dd, *J* = 14.1, 1.5 Hz, 1H), 1.64 – 1.50 (m, 1H), 1.41 (s, 9H), 1.34 – 1.13 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 173.0, 154.8, 136.3, 117.1, 79.3, 57.8, 53.6, 52.9, 52.8, 44.3, 41.7, 37.5, 36.1, 29.7, 28.4.
DART-TOF LC/MS m/z calcd. for $C_{20}H_{32}NO_6$ [M+H^+] 382.2230, found 382.2232.

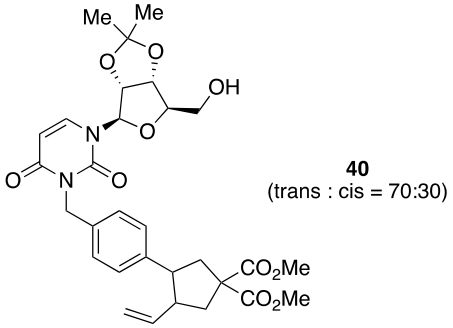


39
(trans : cis = 70:30)

Prepared according to ***Procedure C***. Colorless oil (82.5 mg, 86% yield) as a mixture of diastereomers (trans : cis = 70:30). R_f = 0.30 (30% acetone in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 0.30H), 7.51 (s, 0.70H), 7.23 – 7.04 (m, 4.0H), 5.54 (ddd, *J* = 17.2, 10.5, 7.0 Hz, 0.30H), 5.40 (s, 2.0H), 5.25 (ddd, *J* = 17.1, 10.3, 8.0 Hz, 0.70H), 4.86 – 4.68 (m, 2.0H), 3.90 – 3.58 (m, 6.0H), 3.49 (s, 3H), 3.42 – 3.26 (m,

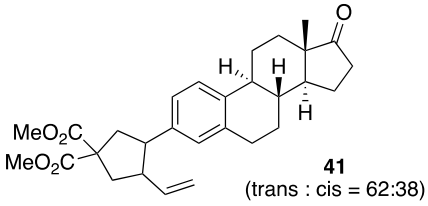
3.70H), 3.00 – 2.88 (m, 0.70H), 2.86 – 2.74 (m, 0.30H), 2.72 – 2.41 (m, 3.0H), 2.33 – 2.16 (m, 1.0H), 2.14 – 2.03 (m, 0.30H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 172.8, 172.7, 172.5, 155.2, 151.6, 148.8, 142.1, 141.4, 140.9, 138.5, 137.8, 133.7, 133.3, 129.0, 128.3, 128.1, 127.8, 115.8, 115.6, 106.9, 106.9, 58.8, 58.0, 52.9, 52.8, 52.8, 50.9, 50.7, 49.9, 49.9, 47.7, 47.3, 42.2, 40.2, 38.9, 38.0, 29.7, 27.9.
DART-TOF LC/MS m/z calcd. for $C_{25}H_{29}N_4O_6$ [M+H$^+$] 481.2087, found 481.2089.



40
(trans : cis = 70:30)

Prepared according to ***Procedure C***. Colorless oil (85.2 mg, 73% yield) as a mixture of diastereomers (trans : cis = 70:30). R_f = 0.30 (30% acetone in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 3.0H), 7.17 – 7.00 (m, 2.0H), 5.73 (dd, *J* = 8.0, 1.1 Hz, 1.0H), 5.66 – 5.54 (m, 1.30H), 5.33 (ddd, *J* = 17.1, 10.3, 7.9 Hz, 0.70H), 5.12 – 4.76 (m, 6.0H), 4.28 (q, *J* = 2.9 Hz, 1.0H), 3.94 – 3.82 (m, 1.0H), 3.81 – 3.69 (m, 7.0H), 3.43 – 3.30 (m, 0.70H), 3.10 – 2.92 (m, 1.70H), 2.88 – 2.77 (m, 0.30H), 2.76 – 2.46 (m, 3.0H), 2.36 (dd, *J* = 14.0, 6.0 Hz, 0.70H), 2.32 – 2.22 (m, 0.30H), 2.19 – 2.07 (m, 0.30H), 1.55 (s, 3.0H), 1.34 (s, 3.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 172.9, 172.9, 172.6, 162.6, 151.0, 141.1, 140.5, 140.3, 138.6, 138.1, 134.6, 134.3, 129.3, 128.9, 128.4, 127.6, 115.7, 115.5, 114.2, 102.0, 96.4, 96.4, 86.9, 84.0, 80.4, 62.6, 58.9, 58.1, 52.9, 52.9, 52.8, 51.0, 50.6, 50.5, 47.7, 47.2, 43.9, 42.5, 40.2, 38.9, 38.1, 27.3, 25.3.
ESI-TOF LC/MS m/z calcd. for $C_{30}H_{37}N_2O_{10}$ [M+H$^+$] 585.2448, found 585.2453.

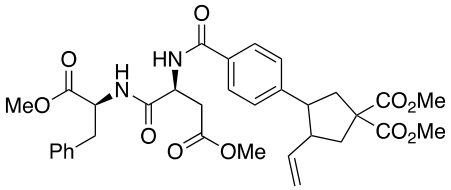


41
(trans : cis = 62:38)

Prepared according to ***Procedure C***. Colorless oil (50.8 mg, 55% yield) as a mixture of diastereomers (trans : cis = 62:38). R_f = 0.35 (20% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 1.0H), 7.05 – 6.82 (m, 2.0H), 5.73 – 5.58 (m, 0.38H), 5.49 – 5.32 (m, 0.62H), 5.01 – 4.76 (m, 2.0H), 4.00 – 3.55 (m, 6.0H), 3.44 – 3.27 (m, 0.62H), 3.06 – 2.95 (m, 0.62H), 2.92 – 1.91 (m, 13.76H), 1.74 – 1.37 (m, 6.0H), 0.90 (s, 3.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 173.0, 173.0, 172.9, 172.7, 138.9, 138.9, 138.4, 138.1, 138.1, 138.0, 138.0, 137.6, 136.4, 136.4, 136.0, 129.2, 128.8, 128.4, 128.0, 126.0,

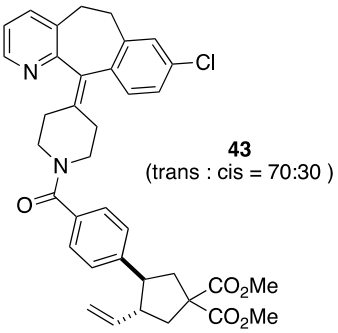
125.7, 125.4, 125.4, 125.1, 125.0, 124.8, 115.5, 115.3, 58.9, 58.0, 52.9, 52.8, 50.9, 50.9, 50.5, 50.3, 50.3, 48.0, 47.5, 47.5, 47.1, 47.1, 44.3, 44.3, 42.7, 42.6, 40.2, 39.0, 38.3, 38.2, 38.2, 38.1, 35.9, 31.6, 29.7, 29.5, 29.4, 26.6, 25.7, 21.6, 13.9.
DART-TOF LC/MS m/z calcd. for $C_{29}H_{37}O_5$ $[M+H^+]$ 465.2641, found 465.2642.



42
(trans : cis = 65:35)

Prepared according to ***Procedure C***. Colorless oil (100.4 mg, 81% yield) as a mixture of diastereomers (trans : cis = 65:35). R_f = 0.30 (30% acetone in hexane).

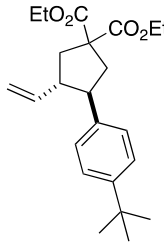
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.54 (m, 3.0H), 7.35 – 6.98 (m, 8.0H), 5.69 – 5.56 (m, 0.35H), 5.34 (ddd, *J* = 17.1, 10.3, 8.2 Hz, 0.65H), 5.07 – 4.70 (m, 4.0H), 3.83 – 3.76 (m, 6.0H), 3.71 (s, 6.0H), 3.55 – 3.44 (m, 0.65H), 3.19 – 2.53 (m, 8.0H), 2.44 – 2.32 (m, 1.0H), 2.26 – 2.13 (m, 0.35H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 173.1, 173.0, 172.9, 172.8, 172.5, 171.4, 170.2, 167.0, 146.2, 145.4, 138.3, 137.7, 135.6, 135.6, 131.5, 131.1, 129.1, 128.6, 128.5, 128.5, 127.9, 127.4, 127.0, 127.0, 116.1, 115.9, 59.0, 58.2, 53.5, 53.0, 53.0, 52.9, 52.9, 52.4, 52.2, 51.3, 49.3, 47.9, 47.5, 42.1, 40.4, 39.0, 38.0, 37.9, 37.7, 34.8.
ESI-TOF LC/MS m/z calcd. for $C_{33}H_{42}N_3O_{10}$ $[M+NH_4^+]$ 640.2870, found 640.2872.



43
(trans : cis = 70:30)

Prepared according to ***Procedure C***. Colorless oil (92.7 mg, 74% yield) as a mixture of diastereomers (trans : cis = 70:30). R_f = 0.35 (30% acetone in hexane).

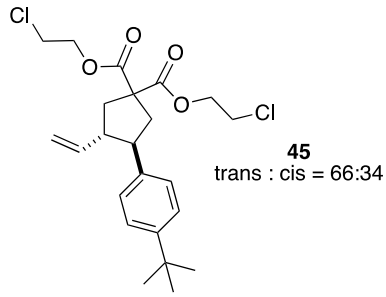
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (brs, 1.0H), 7.50 – 6.95 (m, 9.0H), 5.59 (ddd, *J* = 17.2, 10.5, 6.9 Hz, 0.30H), 5.29 (ddd, *J* = 17.0, 10.3, 8.0 Hz, 0.70H), 4.89 – 4.74 (m, 2.0H), 4.17 (brs, 1.0H), 3.86 – 3.70 (m, 6.0H), 3.68 – 3.54 (m, 1H), 3.50 – 3.13 (m, 4.30H), 3.05 – 2.94 (m, 0.70H), 2.91 – 2.08 (m, 11.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 172.9, 172.8, 172.5, 170.4, 170.4, 146.7, 143.4, 142.7, 139.6, 138.3, 137.8, 137.6, 136.9, 134.7, 134.3, 133.9, 133.4, 133.0, 130.5, 129.0, 128.4, 127.7, 127.1, 126.8, 126.2, 122.3, 115.9, 115.8, 58.9, 58.1, 53.0, 52.9, 52.9, 52.9, 51.2, 50.9, 47.9, 47.3, 42.3, 40.3, 38.9, 38.1, 31.7, 31.6, 31.5.
ESI-TOF LC/MS m/z calcd. for $C_{37}H_{38}ClN_2O_5$ $[M+H]^+$ 625.2469, found 625.2473.



44
trans : cis = 65:35

Prepared according to ***Procedure C***. Colorless oil (69.1 mg, 93% yield) as a mixture of diastereomers (trans : cis = 65:35). R_f = 0.45 (10% EtOAc in hexane).

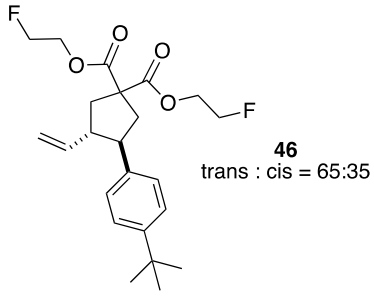
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2.0H), 7.20 – 7.02 (m, 2.0H), 5.68 (ddd, *J* = 17.3, 10.5, 6.9 Hz, 0.35H), 5.40 (ddd, *J* = 17.0, 10.3, 7.8 Hz, 0.65H), 4.98 – 4.78 (m, 2.0H), 4.44 – 4.00 (m, 4.0H), 3.45 – 3.33 (m, 0.65H), 3.07 – 2.95 (m, 0.65H), 2.91 – 2.51 (m, 3.35H), 2.44 – 2.25 (m, 1.0H), 2.15 (dd, *J* = 13.2, 10.5 Hz, 0.35H), 1.39 – 1.16 (m, 15.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 172.6, 172.6, 172.3, 149.2, 148.9, 139.1, 138.5, 138.5, 137.8, 128.0, 127.2, 125.2, 124.9, 115.4, 115.2, 61.6, 61.5, 61.5, 59.1, 58.2, 50.9, 50.4, 47.6, 47.3, 42.5, 40.1, 38.8, 38.1, 34.4, 34.4, 31.4, 14.1, 14.0.
DART-TOF LC/MS m/z calcd. for $C_{23}H_{33}O_4$ [M+H$^+$] 373.2379, found 373.2381.



45
trans : cis = 66:34

Prepared according to ***Procedure C***. Colorless oil (72.5 mg, 82% yield) as a mixture of diastereomers (trans : cis = 66:34). R_f = 0.45 (10% EtOAc in hexane).

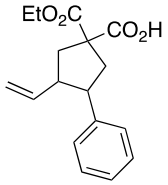
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2.0H), 7.19 – 7.05 (m, 2.0H), 5.68 (ddd, *J* = 16.6, 11.0, 6.9 Hz, 0.34H), 5.41 (ddd, *J* = 17.1, 10.3, 7.8 Hz, 0.66H), 5.01 – 4.78 (m, 2.0H), 4.68 – 4.20 (m, 4.0H), 3.78 – 3.66 (m, 4.0H), 3.45 (dt, *J* = 10.5, 7.4 Hz, 0.66H), 3.11 – 2.98 (m, 0.66H), 2.94 – 2.58 (m, 3.34H), 2.51 – 2.32 (m, 1.0H), 2.26 – 2.17 (m, 0.34H), 1.31 (s, 9.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 171.9, 171.9, 171.7, 149.4, 149.2, 138.8, 138.2, 138.1, 137.4, 128.0, 127.2, 125.3, 125.0, 115.6, 115.5, 65.1, 65.1, 65.0, 59.0, 58.1, 50.9, 50.4, 47.6, 47.3, 42.5, 41.4, 41.4, 40.1, 38.9, 38.2, 34.4, 34.4, 31.4.
DART-TOF LC/MS m/z calcd. for $C_{23}H_{31}Cl_2O_4$ [M+H$^+$] 441.1599, found 441.1602.



46
trans : cis = 65:35

Prepared according to ***Procedure C***. Colorless oil (74.5 mg, 91% yield) as a mixture of diastereomers (trans : cis = 65:35). R_f = 0.33 (30% EtOAc in hexane).

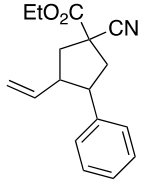
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2.0H), 7.20 – 7.04 (m, 2.0H), 5.78 – 5.61 (m, 0.35H), 5.41 (ddd, *J* = 17.1, 10.3, 7.8 Hz, 0.65H), 4.99 – 4.81 (m, 2.0H), 4.70 – 4.62 (m, 2.0H), 4.58 – 4.52 (m, 2.0H), 4.46 – 4.43 (m, 2.0H), 4.42 – 4.34 (m, 2.0H), 3.45 (dt, *J* = 10.6, 7.4 Hz, 0.65H), 3.11 – 2.98 (m, 0.65H), 2.95 – 2.57 (m, 3.35H), 2.51 – 2.32 (m, 1.0H), 2.27 – 2.15 (m, 0.35H), 1.31 (s, 9.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 172.2, 172.1, 171.9, 149.4, 149.1, 138.8, 138.2, 138.1, 137.4, 128.0, 127.2, 125.3, 125.0, 115.6, 115.4, 81.8, 80.2, 80.1, 64.6, 64.5, 64.5, 64.4, 64.3, 64.3, 58.9, 58.1, 50.8, 50.4, 47.6, 47.3, 42.5, 40.1, 38.8, 38.1, 34.4, 34.4, 31.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -225.09, -225.10, -225.12, -225.12, -225.16, -225.16.
DART-TOF LC/MS m/z calcd. for $C_{23}H_{34}F_2NO_4$ $[M+NH_4^+]$ 426.2456, found 426.2452.



47
d.r. = 62:30:4:4

Prepared according to ***Procedure C***. Colorless oil (53.0 mg, 92% yield) as a mixture of diastereomers (d.r. = 62:30:4:4). R_f = 0.35 (10% MeOH in DCM).

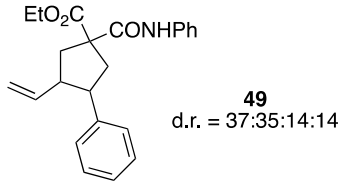
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.14 (brs, 1.0H), 7.43 – 6.79 (m, 5.0H), 5.73 – 5.57 (m, 0.30H), 5.46 – 5.32 (m, 0.66H), 5.28 – 5.22 (m, 0.04H), 4.97 – 4.76 (m, 2.0H), 4.37 – 4.12 (m, 2.0H), 3.58 – 3.40 (m, 0.66H), 3.14 – 2.98 (m, 0.66H), 2.97 – 1.93 (m, 4.68H), 1.45 – 1.20 (m, 3.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 178.3, 178.1, 172.1, 171.8, 141.3, 140.7, 140.6, 138.6, 138.1, 138.0, 128.4, 128.3, 128.1, 127.6, 126.7, 126.3, 115.8, 115.8, 115.5, 115.5, 62.1, 62.0, 59.1, 59.1, 58.1, 51.6, 50.9, 50.9, 48.1, 48.0, 47.4, 42.6, 42.5, 40.4, 40.3, 39.0, 39.0, 38.1, 38.1, 14.0.
DART-TOF LC/MS m/z calcd. for $C_{17}H_{21}O_4$ $[M+H^+]$ 289.1440, found 289.1441.



48
d.r. = 50:30:20

Prepared according to ***Procedure C***. Colorless oil (45.1 mg, 84% yield) as a mixture of diastereomers (d.r. = 50:30:20). R_f = 0.35 (30% EtOAc in hexane).

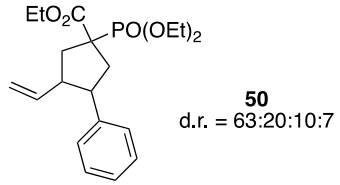
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 6.99 (m, 5.0H), 5.67 – 5.50 (m, 0.30H), 5.42 – 5.31 (m, 0.20H), 5.25 (ddd, *J* = 17.1, 10.2, 8.1 Hz, 0.50H), 4.99 – 4.68 (m, 2.0H), 4.40 – 4.10 (m, 2.0H), 3.68 – 3.56 (m, 0.50H), 3.52 – 3.41 (m, 0.20H), 3.20 – 3.12 (m, 0.50H), 3.09 – 2.31 (m, 4.50H), 2.27 – 2.15 (m, 0.30H), 1.36 – 1.21 (m, 3.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 169.7, 169.6, 169.1, 140.5, 139.9, 139.7, 139.1, 137.7, 137.2, 137.1, 136.5, 128.7, 128.6, 128.4, 128.3, 128.3, 128.2, 127.6, 127.5, 127.1, 127.0, 126.7, 121.3, 121.2, 121.1, 116.7, 116.7, 116.6, 116.1, 63.1, 51.7, 51.6, 51.2, 50.5, 48.5, 47.8, 47.8, 47.3, 47.0, 45.2, 45.1, 43.3, 43.1, 42.0, 41.6, 41.6, 40.8, 14.0, 14.0.
DART-TOF LC/MS m/z calcd. for $C_{17}H_{23}N_2O_2$ $[M+NH_4^+]$ 287.1760, found 287.1758.



49
d.r. = 37:35:14:14

Prepared according to ***Procedure C***. Colorless oil (67.6 mg, 93% yield) as a mixture of diastereomers (d.r. = 37:35:14:14). R_f = 0.45 (30% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (brs, 0.28H), 8.07 (brs, 0.37H), 7.99 (brs, 0.35H), 7.52 – 7.39 (m, 2.0H), 7.32 – 6.96 (m, 8.0H), 5.70 – 5.49 (m, 0.30H), 5.32 (dddd, *J* = 17.1, 10.4, 7.9, 1.7 Hz, 0.70H), 4.92 – 4.66 (m, 2.0H), 4.37 – 4.08 (m, 2.0H), 3.46 (dt, *J* = 10.8, 7.4 Hz, 0.37H), 3.36 (dt, *J* = 10.6, 7.7 Hz, 0.35H), 3.09 – 2.40 (m, 4.86H), 2.39 – 2.29 (m, 0.28H), 2.22 – 2.12 (m, 0.14H), 1.36 – 1.19 (m, 3.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 174.8, 174.7, 169.1, 168.7, 168.1, 141.6, 141.0, 140.9, 138.9, 138.8, 138.5, 138.2, 137.9, 137.8, 129.1, 129.0, 128.5, 128.4, 128.3, 128.1, 128.0, 127.7, 127.6, 126.6, 126.6, 126.3, 126.2, 124.5, 124.5, 120.0, 120.0, 119.9, 119.9, 115.6, 115.6, 115.4, 115.3, 62.5, 62.4, 62.3, 61.1, 60.5, 59.3, 52.0, 51.5, 51.3, 51.0, 48.1, 48.0, 47.4, 47.3, 43.1, 42.9, 41.1, 39.5, 39.4, 38.2, 37.7, 14.1, 14.0.
DART-TOF LC/MS m/z calcd. for $C_{23}H_{29}N_2O_3$ $[M+NH_4^+]$ 381.2178, found 381.2173.



50
d.r. = 63:20:10:7

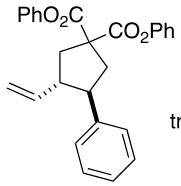
Prepared according to ***Procedure C***. Colorless oil (65.7 mg, 86% yield) as a mixture of diastereomers (d.r. = 37:35:14:14). R_f = 0.35 (30% acetone in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.05 (m, 5.0H), 5.56 (ddd, *J* = 17.2, 9.9, 7.2 Hz, 0.32H), 5.28 (ddd, *J* = 17.1, 10.2, 8.4 Hz, 0.68H), 4.91 – 4.57 (m, 2.0H), 4.35 – 3.92 (m, 6.0H), 3.52 – 3.15 (m, 0.73H), 3.04 – 2.03 (m, 5.27H), 1.54 – 1.02 (m, 9.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 171.8, 171.7, 141.9, 141.4, 141.3, 139.2, 138.9, 138.5, 137.4, 128.6, 128.4, 128.2, 128.0, 128.0, 127.7, 127.6, 126.6, 126.5, 126.2, 126.1,

115.8, 115.7, 115.4, 114.9, 63.1, 63.0, 62.9, 62.9, 62.9, 62.8, 62.8, 62.7, 61.8, 61.8, 55.0, 53.6, 51.6, 51.6, 51.5, 51.1, 51.0, 50.8, 50.8, 47.8, 47.7, 47.6, 47.4, 47.2, 41.1, 41.1, 40.2, 38.0, 38.0, 37.6, 37.6, 37.3, 37.3, 16.5, 16.5, 16.4, 16.4, 14.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.3, 26.6, 26.1.

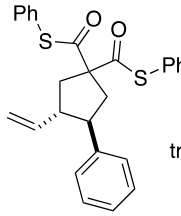
DART-TOF LC/MS m/z calcd. for $C_{20}H_{33}NPO_5$ $[M+NH_4^+]$ 398.2096, found 398.2100.



51
trans : cis = 70:30

Prepared according to ***Procedure C***. Colorless oil (75.9 mg, 92% yield) as a mixture of diastereomers (trans : cis = 70:30). R_f = 0.35 (10% EtOAc in hexane).

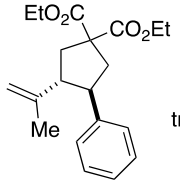
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 6.94 (m, 15.0H), 5.64 (ddd, *J* = 17.3, 9.9, 7.0 Hz, 0.30H), 5.39 (ddd, *J* = 17.1, 10.3, 7.9 Hz, 0.70H), 4.95 – 4.76 (m, 2.0H), 3.54 (dt, *J* = 10.6, 7.4 Hz, 0.70H), 3.17 – 3.04 (m, 0.70H), 3.02 – 2.74 (m, 3.30H), 2.65 – 2.50 (m, 1.0H), 2.45 – 2.31 (m, 0.30H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 170.6, 150.7, 150.7, 141.2, 140.4, 138.4, 137.8, 129.6, 128.6, 128.4, 128.2, 127.7, 126.8, 126.5, 126.3, 121.2, 121.2, 116.0, 115.9, 59.3, 58.4, 51.6, 50.9, 48.2, 47.6, 42.6, 40.4, 39.1, 38.2.
DART-TOF LC/MS m/z calcd. for $C_{27}H_{28}NO_4$ $[M+NH_4^+]$ 430.2018, found 430.2015.



52
trans : cis = 75:25

Prepared according to ***Procedure C***. Colorless oil (69.4 mg, 78% yield) as a mixture of diastereomers (trans : cis = 75:25). R_f = 0.40 (30% EtOAc in hexane).

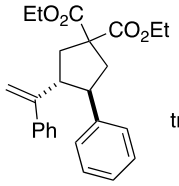
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 6.96 (m, 15.0H), 5.68 – 5.48 (m, 0.25H), 5.27 (ddd, *J* = 17.6, 10.3, 7.8 Hz, 0.75H), 4.94 – 4.65 (m, 2.0H), 3.46 – 3.31 (m, 0.75H), 3.07 – 2.41 (m, 5.0H), 2.30 (dd, *J* = 13.8, 10.8 Hz, 0.25H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 196.6, 196.5, 196.0, 141.1, 140.4, 138.4, 137.8, 134.8, 134.8, 134.7, 129.8, 129.4, 129.4, 128.5, 128.4, 128.2, 127.6, 127.0, 127.0, 126.8, 126.5, 116.1, 115.8, 74.8, 73.8, 51.3, 50.6, 47.6, 46.9, 42.3, 40.1, 38.8, 38.0.
DART-TOF LC/MS m/z calcd. for $C_{27}H_{28}NO_2S_2$ $[M+NH_4^+]$ 462.1561, found 462.1560.



53
trans : cis = 68:32

Prepared according to ***Procedure C***. Colorless oil (52.0 mg, 79% yield) as a mixture of diastereomers (trans : cis = 68:32). R_f = 0.35 (4:1 hex:EtOAc).

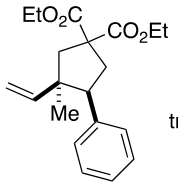
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 6.99 (m, 5.0H), 4.64 – 4.50 (m, 2.0H), 4.26 – 4.09 (m, 4.0H), 3.49 – 3.36 (m, 0.68H), 3.06 – 2.64 (m, 2.32H), 2.56 (dd, *J* = 13.6, 7.4 Hz, 0.32H), 2.49 – 2.34 (m, 2.0H), 2.18 (ddd, *J* = 25.3, 13.7, 11.6 Hz, 0.68H), 1.56 (s, 0.96H), 1.24 – 1.10 (m, 8.04H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 172.6, 172.6, 172.1, 145.0, 144.1, 142.4, 142.1, 128.4, 127.8, 127.4, 126.5, 126.1, 112.1, 111.7, 61.6, 61.5, 59.3, 57.9, 53.5, 49.9, 49.1, 46.8, 42.8, 40.1, 39.5, 37.8, 22.7, 19.8, 14.1.
DART-TOF LC/MS m/z calcd. for $C_{20}H_{30}NO_4$ [M+NH_4^+] 348.2175, found 348.2171.



54
trans : cis = 70:30

Prepared according to ***Procedure C***. Colorless oil (63.2 mg, 81% yield) as a mixture of diastereomers (trans : cis = 70:30). R_f = 0.35 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 6.58 (m, 10.0H), 5.10 (d, *J* = 0.9 Hz, 0.30H), 5.02 (d, *J* = 0.8 Hz, 0.30H), 4.95 (d, *J* = 0.9 Hz, 0.70H), 4.75 (d, *J* = 0.8 Hz, 0.70H), 4.31 – 4.04 (m, 4.0H), 3.64 – 3.51 (m, 0.70H), 3.42 (td, *J* = 8.7, 5.9 Hz, 0.70H), 3.32 – 3.11 (m, 0.60H), 2.95 (ddd, *J* = 14.5, 8.6, 1.2 Hz, 0.70H), 2.84 (dd, *J* = 13.8, 7.5 Hz, 0.30H), 2.75 (dd, *J* = 13.6, 6.9 Hz, 0.30H), 2.64 (dd, *J* = 13.2, 12.1 Hz, 0.70H), 2.52 (ddd, *J* = 13.2, 6.1, 1.2 Hz, 0.70H), 2.38 (dd, *J* = 14.5, 5.9 Hz, 0.70H), 2.21 (dd, *J* = 13.8, 10.9 Hz, 0.30H), 2.01 (dd, *J* = 13.6, 11.2 Hz, 0.30H), 1.34 – 1.08 (m, 6.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 172.6, 172.3, 172.1, 148.9, 148.0, 142.7, 142.0, 142.0, 141.9, 128.7, 128.4, 128.1, 127.9, 127.5, 127.4, 127.2, 127.1, 126.5, 126.5, 126.3, 125.9, 113.2, 113.2, 61.7, 61.6, 61.6, 61.5, 59.2, 57.7, 50.3, 49.7, 47.0, 46.3, 42.8, 41.7, 40.8, 38.1, 14.1, 14.1, 14.0.
DART-TOF LC/MS m/z calcd. for $C_{25}H_{32}NO_4$ [M+NH_4^+] 410.2331, found 410.2330.

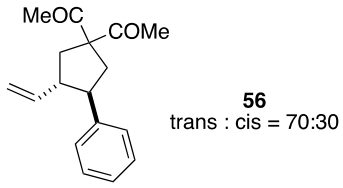


55
trans : cis = 46:54

Prepared according to ***Procedure C***. Colorless oil (38.8 mg, 59% yield) as a mixture of diastereomers (trans : cis = 46:54). R_f = 0.40 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.05 (m, 5.0H), 5.83 (dd, *J* = 17.4, 10.7 Hz, 0.46H), 5.46 (dd, *J* = 17.4, 10.9 Hz, 0.54H), 4.97 – 4.64 (m, 2.0H), 4.26 – 4.05 (m, 4.0H), 3.02 (dd, *J* = 13.4, 6.6 Hz, 0.46H), 2.92 (dd, *J* = 13.7, 6.0 Hz, 0.54H), 2.82 (t, *J* = 13.5 Hz, 0.46H), 2.74 – 2.58 (m, 1.08H), 2.55 – 2.46 (m, 0.92H), 2.41 – 2.28 (m, 1.08H), 2.22 (d, *J* = 14.1 Hz, 0.46H), 1.24 – 1.14 (m, 6.0H), 1.07 (s, 1.62H), 0.70 (s, 1.38H).

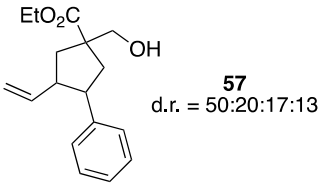
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 172.9, 172.6, 172.4, 146.4, 141.9, 138.4, 138.3, 128.9, 128.5, 127.7, 127.7, 126.7, 126.6, 113.1, 112.4, 61.6, 61.6, 61.5, 57.4, 57.1, 55.4, 53.8, 48.4, 48.3, 47.0, 44.4, 38.0, 37.1, 25.7, 19.0, 14.1, 14.0.
DART-TOF LC/MS m/z calcd. for $C_{20}H_{30}NO_4$ $[M+NH_4^+]$ 348.2175, found 348.2172.



56
trans : cis = 70:30

Prepared according to ***Procedure C***. Colorless oil (44.1 mg, 86% yield) as a mixture of diastereomers (trans : cis = 70:30). R_f = 0.35 (20% EtOAc in hexane).

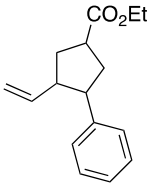
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 6.97 (m, 5.0H), 5.61 – 5.44 (m, 0.30H), 5.22 (ddd, *J* = 17.1, 10.3, 7.9 Hz, 0.70H), 4.90 – 4.66 (m, 2.0H), 3.18 (dt, *J* = 10.6, 7.2 Hz, 0.70H), 2.90 – 2.80 (m, 0.70H), 2.75 (dd, *J* = 13.2, 7.4 Hz, 0.30H), 2.68 – 2.57 (m, 1.40H), 2.56 – 2.47 (m, 0.30H), 2.45 – 2.22 (m, 2.0H), 2.13 – 2.01 (m, 6.0H), 2.00 (dd, *J* = 13.3, 11.2 Hz, 0.30H), 1.84 (dd, *J* = 13.3, 10.8 Hz, 0.30H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.9, 204.6, 204.5, 204.5, 141.4, 140.6, 138.7, 138.0, 128.5, 128.2, 128.1, 127.5, 126.7, 126.3, 115.7, 115.6, 74.4, 73.2, 51.2, 50.3, 47.8, 47.3, 39.3, 36.9, 35.5, 34.3, 27.0, 26.4, 26.3, 26.0.
DART-TOF LC/MS m/z calcd. for $C_{14}H_{24}NO_2$ $[M+NH_4^+]$ 274.1807, found 274.1804.



57
d.r. = 50:20:17:13

Prepared according to ***Procedure C***. Colorless oil (44.3 mg, 81% yield) as a mixture of diastereomers (d.r. = 50:20:17:13). R_f = 0.30 (30% EtOAc in hexane).

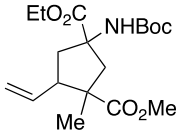
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 6.96 (m, 5.0H), 5.71 – 5.27 (m, 1.0H), 4.87 – 4.68 (m, 2.0H), 4.24 – 4.09 (m, 2.0H), 3.79 – 3.60 (m, 2.0H), 3.52 (dt, *J* = 11.8, 7.2 Hz, 0.50H), 3.31 (dt, *J* = 10.5, 7.4 Hz, 0.17H), 3.12 – 1.45 (m, 6.0H), 1.32 – 1.11 (m, 3.0H), 0.95 – 0.80 (m, 0.33H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 177.6, 177.6, 177.4, 142.0, 142.0, 141.3, 141.3, 139.4, 139.3, 139.0, 138.8, 128.4, 128.4, 128.3, 128.1, 128.0, 127.6, 127.5, 126.4, 126.1, 126.1, 115.3, 115.2, 115.2, 115.0, 69.2, 68.1, 68.0, 67.5, 61.2, 61.1, 61.1, 61.1, 54.3, 53.8, 52.8, 52.8, 51.8, 51.3, 51.1, 50.4, 48.2, 48.0, 47.4, 42.5, 41.6, 40.2, 39.1, 38.5, 38.2, 37.6, 36.2, 14.2, 14.2, 14.1.
DART-TOF LC/MS m/z calcd. for $C_{17}H_{26}NO_3$ $[M+NH_4^+]$ 292.1907, found 292.1905.



58
d.r. = 35:30:20:15

Prepared according to ***Procedure C*** (0.4 mmol). Colorless oil (60.9 mg, 62% yield) as a mixture of diastereomers (trans : cis = 35:30:20:15). R_f = 0.45 (10% EtOAc in hexane).

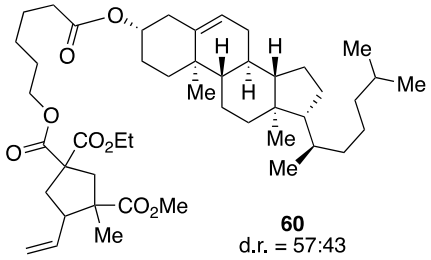
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.01 (m, 5.0H), 5.72 – 5.50 (m, 0.55H), 5.42 – 5.22 (m, 0.45H), 4.91 – 4.57 (m, 2.0H), 4.24 – 3.91 (m, 2.0H), 3.45 – 1.74 (m, 7.0H), 1.32 – 1.04 (m, 3.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 176.4, 176.3, 175.9, 143.2, 142.6, 141.8, 141.5, 140.0, 139.8, 139.3, 138.6, 128.5, 128.4, 128.3, 128.3, 128.0, 128.0, 127.6, 127.5, 126.4, 126.3, 126.1, 114.9, 114.8, 114.6, 60.5, 60.5, 52.6, 52.3, 51.2, 50.8, 49.0, 48.8, 48.1, 48.1, 42.9, 42.0, 41.8, 41.5, 38.7, 38.1, 36.6, 35.7, 34.9, 34.7, 34.2, 33.4, 14.3, 14.3.
DART-TOF LC/MS m/z calcd. for $C_{14}H_{24}NO_2$ [M+NH_4^+] 262.1807, found 262.1805.



59
d.r. = 50:25:15:10

Prepared according to ***Procedure C***. Colorless oil (63.7 mg, 90% yield) as a mixture of diastereomers (trans : cis = 50:25:15:10). R_f = 0.35 (20% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 – 5.57 (m, 1.0H), 5.44 – 4.80 (m, 3.0H), 4.28 – 4.04 (m, 2.0H), 3.75 – 3.40 (m, 3.0H), 3.36 – 1.72 (m, 5.0H), 1.58 – 0.92 (m, 15.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 176.6, 175.9, 174.4, 173.4, 173.2, 155.2, 136.3, 136.2, 136.0, 135.9, 116.9, 116.7, 116.6, 65.2, 61.5, 61.4, 61.4, 61.4, 54.2, 54.0, 53.1, 52.5, 52.3, 52.0, 51.8, 51.7, 51.6, 51.0, 49.2, 48.8, 48.0, 42.1, 28.3, 24.9, 22.9, 20.7, 14.1, 14.1, 14.1.
ESI-TOF LC/MS m/z calcd. for $C_{18}H_{30}NO_6$ [M+H^+] 356.2073, found 356.2075.

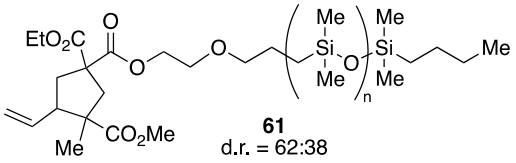


60
d.r. = 57:43

Prepared according to ***Procedure C***. Colorless oil (89.2 mg, 58% yield) as a mixture of diastereomers (d.r. = 57:43). R_f = 0.50 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 – 5.55 (m, 1.0H), 5.36 (brs, 1.0H), 5.16 – 4.98 (m, 2.0H), 4.72 – 4.51 (m, 1.0H), 4.29 – 3.97 (m, 4.0H), 3.67 (s, 1.29H), 3.60 (s, 1.71H), 3.12 – 3.01 (m, 0.43H), 2.91 (dd, *J* = 14.4, 4.7 Hz, 0.57H), 2.83 (dd, *J* = 14.3, 3.2 Hz, 0.43H), 2.58 – 2.44 (m, 1.57H), 2.41 – 2.14 (m, 6.0H), 2.05 – 0.59 (m, 53.0H).

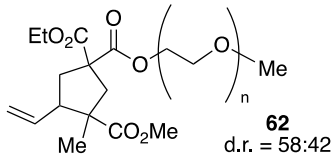
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 175.7, 173.1, 173.0, 172.8, 172.8, 172.8, 172.1, 172.0, 171.6, 171.5, 139.6, 136.1, 135.9, 122.6, 117.0, 116.8, 73.8, 73.8, 65.5, 65.5, 65.3, 61.7, 61.7, 61.7, 61.4, 58.9, 58.0, 56.7, 56.1, 54.6, 54.6, 53.0, 52.1, 52.0, 51.5, 51.5, 50.0, 49.8, 49.7, 44.8, 44.7, 44.6, 42.3, 39.7, 39.5, 38.9, 38.8, 38.1, 37.4, 37.0, 36.6, 36.2, 35.8, 34.5, 34.4, 31.9, 31.8, 28.2, 28.2, 28.0, 27.8, 25.4, 25.3, 24.6, 24.6, 24.5, 24.3, 23.8, 22.9, 22.9, 22.8, 22.6, 21.0, 19.3, 19.0, 18.9, 18.7, 14.1, 14.0, 11.8.
ESI-TOF LC/MS m/z calcd. for $C_{47}H_{75}O_8$ $[M+H^+]$ 767.5462, found 767.5466.



61
d.r. = 62:38

Prepared according to ***Procedure C***. Colorless oil (229.7 mg, 77% yield) as a mixture of diastereomers (d.r. = 62:38). R_f = 0.50 (10% EtOAc in hexane).

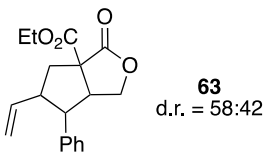
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 – 5.50 (m, 1.0H), 5.15 – 4.91 (m, 2.0H), 4.37 – 4.05 (m, 4.0H), 3.77 – 3.54 (m, 5.0H), 3.46 – 3.32 (m, 2.0H), 3.16 – 3.02 (m, 0.38H), 2.94 (d, *J* = 14.4 Hz, 0.62H), 2.86 (dd, *J* = 14.3, 10.6 Hz, 0.38H), 2.61 – 2.47 (m, 1.62H), 2.44 – 2.16 (m, 2.0H), 1.66 – 1.50 (m, 2.0H), 1.38 – 1.19 (m, 9.0H), 1.10 (d, *J* = 1.4 Hz, 1.0H), 0.92 – 0.82 (m, 3.0H), 0.61 – 0.45 (m, 4.0H), 0.28 – -0.17 (m, 74.0H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 174.7, 174.6, 172.0, 171.9, 171.1, 170.8, 170.6, 170.3, 135.1, 134.9, 134.8, 116.0, 116.0, 115.8, 73.1, 73.0, 67.2, 67.2, 63.8, 63.7, 63.6, 60.7, 60.7, 60.6, 60.4, 57.9, 57.8, 57.0, 53.6, 53.5, 52.0, 52.0, 51.0, 50.9, 50.4, 48.7, 48.7, 43.7, 43.6, 43.6, 37.8, 36.4, 25.3, 24.4, 22.4, 21.9, 21.8, 17.9, 17.8, 16.9, 13.1, 13.1, 13.0, 12.9, 12.8, 0.4, 0.1, 0.00, -0.4, -0.9, -1.0.



62
d.r. = 58:42

Prepared according to ***Procedure C***. Colorless oil (108.3 mg, 75% yield) as a mixture of diastereomers (d.r. = 58:42). R_f = 0.30 (30% acetone in hexane).

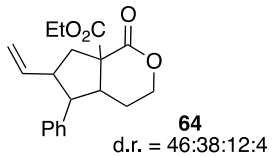
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 – 5.54 (m, 1.0H), 5.15 – 4.90 (m, 2.0H), 4.36 – 4.09 (m, 4.0H), 3.81 – 3.48 (m, 44.0H), 3.35 (s, 3.0H), 3.11 – 2.99 (m, 0.42H), 2.90 (d, *J* = 14.4 Hz, 0.58H), 2.83 (dd, *J* = 14.3, 5.6 Hz, 0.42H), 2.60 – 2.43 (m, 1.58H), 2.41 – 2.14 (m, 2.0H), 1.35 – 1.17 (m, 4.74H), 1.08 (d, *J* = 1.8 Hz, 1.26H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 175.6, 175.6, 172.9, 172.8, 172.0, 171.8, 171.8, 171.5, 171.3, 136.0, 135.9, 135.8, 117.0, 117.0, 116.8, 71.9, 70.6, 70.6, 70.5, 70.5, 68.8, 68.8, 68.8, 64.7, 64.7, 64.6, 64.5, 61.7, 61.7, 61.7, 61.4, 59.0, 58.8, 58.8, 57.9, 57.9, 54.6, 53.0, 53.0, 52.0, 52.0, 51.9, 51.5, 49.7, 49.7, 44.7, 44.6, 44.6, 38.8, 37.3, 37.3, 22.9, 22.77, 18.9, 18.8, 14.0, 14.0.



63
d.r. = 58:42

Prepared according to ***Procedure C***. Colorless oil (25.7 mg, 43% yield) as a mixture of diastereomers (d.r. = 58:42). R_f = 0.30 (10% EtOAc in hexane).

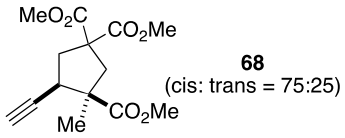
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 6.91 (m, 5.0H), 5.56 – 5.43 (m, 0.42H), 5.32 – 5.15 (m, 0.58H), 4.93 – 4.63 (m, 2.0H), 4.58 – 4.07 (m, 4.0H), 3.77 – 1.69 (m, 5.0H), 1.35 – 1.05 (m, 3.0H).
^{13}C NMR (101 MHz, CDCl3) δ 176.5, 176.4, 171.3, 169.7, 169.4, 169.0, 138.9, 138.9, 138.6, 137.7, 137.1, 136.5, 128.9, 128.5, 128.4, 128.1, 127.8, 127.5, 127.0, 126.8, 116.5, 116.4, 115.1, 72.0, 69.8, 69.4, 62.5, 62.5, 62.4, 61.6, 60.7, 59.3, 57.7, 56.6, 55.9, 55.1, 52.5, 51.8, 50.4, 48.7, 43.4, 38.1, 37.5, 33.6, 14.2, 14.1.
DART-TOF LC/MS m/z calcd. for $C_{18}H_{24}NO_4$ [M+NH_4^+] 318.1705, found 318.1703.



64
d.r. = 46:38:12:4

Prepared according to ***Procedure C***. Colorless oil (45.1 mg, 72% yield) as a mixture of diastereomers (d.r. = 46:38:12:4). R_f = 0.30 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 6.96 (m, 5.0H), 5.82 (ddd, *J* = 17.5, 10.2, 7.8 Hz, 0.04H), 5.51 (ddd, *J* = 17.4, 10.5, 7.1 Hz, 0.46H), 5.40 (ddd, *J* = 17.0, 10.4, 8.0 Hz, 0.38H), 5.23 (ddd, *J* = 17.2, 10.2, 8.1 Hz, 0.12H), 4.490 – 4.23 (m, 2.0H), 4.48 – 4.07 (m, 4.0H), 3.77 – 2.71 (m, 3.0H), 2.69 – 1.70 (m, 3.0H), 1.63 – 1.42 (m, 1.0H), 1.32 – 1.20 (m, 3.0H).
^{13}C NMR (101 MHz, CDCl3) δ 172.1, 171.7, 171.5, 171.4, 171.2, 170.1, 139.9, 139.5, 138.9, 138.9, 137.8, 137.6, 128.7, 128.7, 128.6, 128.3, 128.3, 127.7, 127.5, 127.2, 126.8, 126.6, 116.0, 115.9, 114.6, 67.9, 67.2, 67.0, 62.6, 62.4, 62.1, 59.5, 59.1, 59.0, 57.6, 56.9, 50.0, 50.0, 49.5, 47.9, 46.5, 45.2, 44.2, 40.7, 39.7, 37.0, 28.0, 27.9, 22.8, 14.1, 14.0, 14.0.
DART-TOF LC/MS m/z calcd. for $C_{19}H_{26}NO_4$ [M+NH_4^+] 332.1862, found 332.1858.

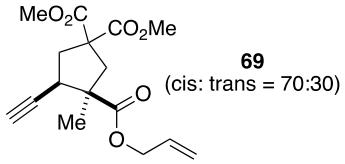


68
(cis: trans = 75:25)

Prepared according to ***Procedure C***. Colorless oil (37.3 mg, 66% yield) as a mixture of inseparable diastereomers (cis : trans = 75:25). R_f = 0.30 (20% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 2.25H), 3.72 (s, 3.00H), 3.71 (s, 0.75H), 3.70 (s, 0.75H), 3.67 (s, 2.25H), 3.34 (ddd, *J* = 10.0, 7.2, 2.5 Hz, 0.25 H), 2.99 (d, *J* = 14.5 Hz, 0.75H), 2.81 – 2.66 (m, 2H), 2.60 (dd, *J* = 13.0, 6.9 Hz, 0.75H), 2.45 (d, *J* = 14.3 Hz, 0.25H), 2.33 (dd, *J* = 13.8, 10.2 Hz, 0.25H), 2.20 – 2.10 (m, 1.75H), 1.36 (s, 2.25H), 1.33 (s, 0.75H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 175.0, 173.0, 172.0, 171.7, 171.4, 82.1, 81.7, 72.1, 71.5, 58.9, 58.1, 53.7, 53.1, 53.0, 53.0, 52.9, 52.4, 51.8, 43.8, 43.7, 41.4, 39.7, 39.2, 37.9, 29.7, 23.0, 20.5.
DART-TOF LC/MS m/z calcd. for $C_{14}H_{22}NO_6$ $[M+NH_4^+]$ 300.1447, found 300.1446.



69
(cis: trans = 70:30)

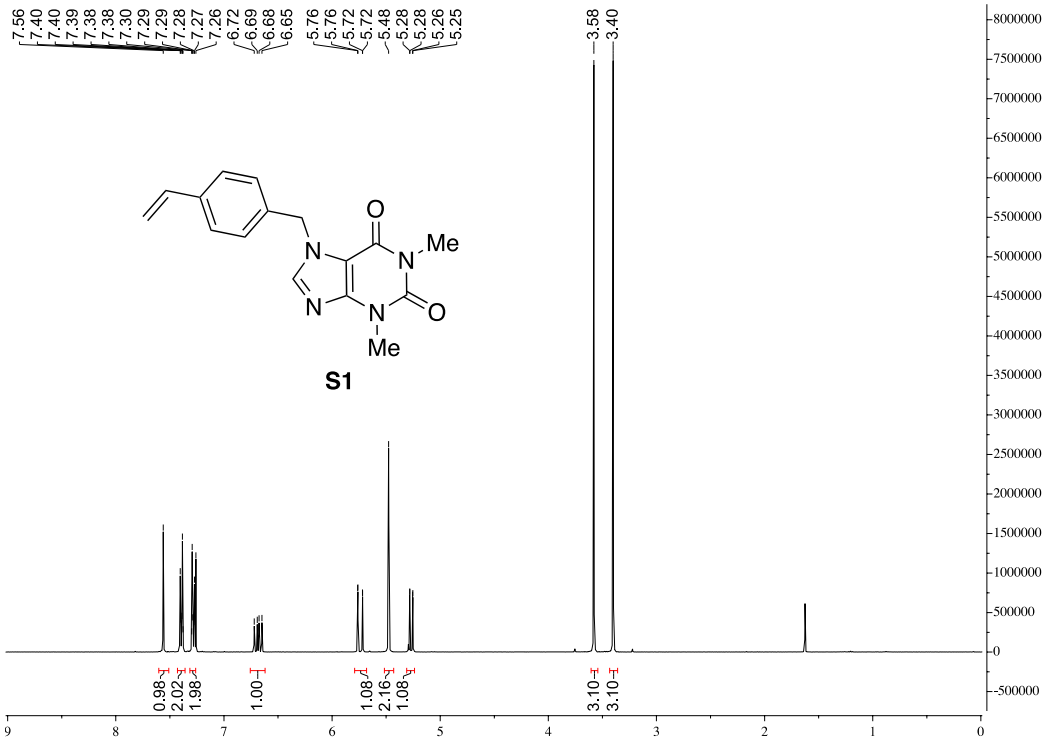
Prepared according to ***Procedure C***. Colorless oil (29.8 mg, 48% yield) as a mixture of inseparable diastereomers (cis : trans = 70:30). R_f = 0.35 (20% EtOAc in hexane).

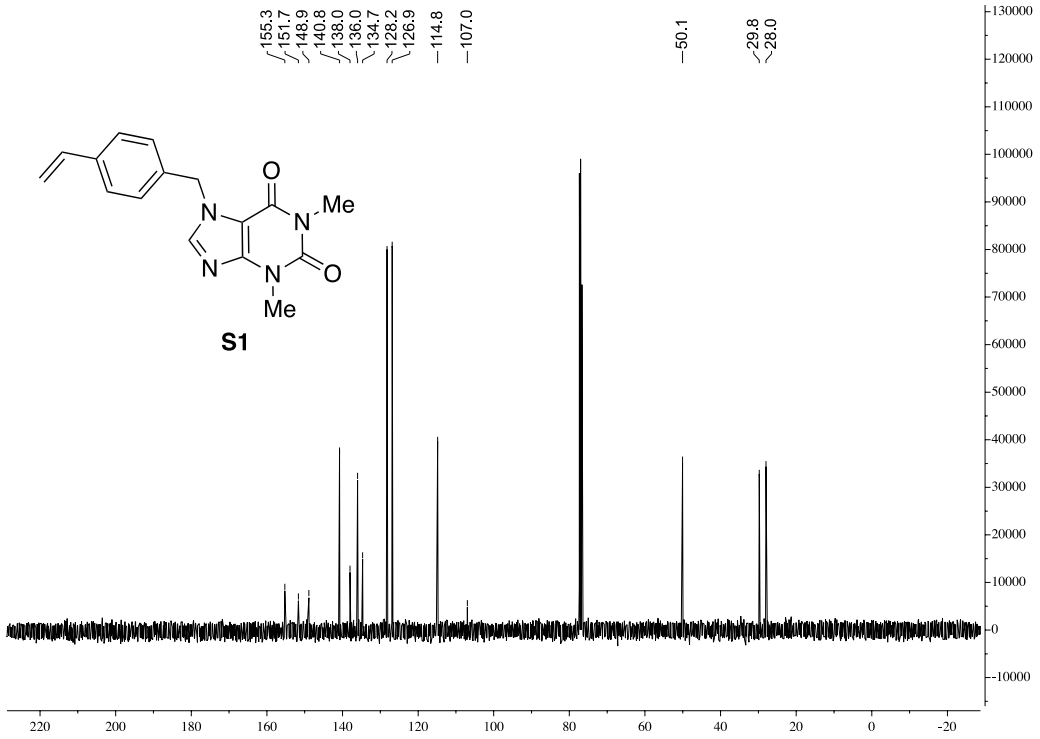
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 – 5.76 (m, 1.0H), 5.26 (d, *J* = 17.2, 1.0H), 5.20 – 5.10 (m, 1.0H), 4.59 – 4.44 (m, 2.0H), 3.75 – 3.58 (m, 6.0H), 3.30 (ddd, *J* = 10.0, 7.2, 2.5 Hz, 0.30H), 2.96 (d, *J* = 14.5 Hz, 0.70H), 2.77 – 2.62 (m, 2.0H), 2.55 (dd, *J* = 13.0, 6.8 Hz, 0.70H), 2.41 (d, *J* = 14.4 Hz, 0.30H), 2.28 (dd, *J* = 13.7, 10.3 Hz, 0.30H), 2.18 – 2.02 (m, 1.70H), 1.33 (s, 2.10H), 1.30 (s, 0.90H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 174.2, 173.1, 171.9, 171.7, 171.4, 132.1, 131.9, 118.2, 118.0, 82.1, 81.7, 72.1, 71.7, 65.7, 65.6, 58.9, 58.1, 53.7, 53.1, 53.1, 53.0, 52.9, 51.9, 43.8, 43.7, 41.4, 39.8, 39.3, 37.9, 29.7, 23.1, 20.5.
DART-TOF LC/MS m/z calcd. for $C_{16}H_{24}NO_6$ $[M+NH_4^+]$ 326.1604, found 326.1602.

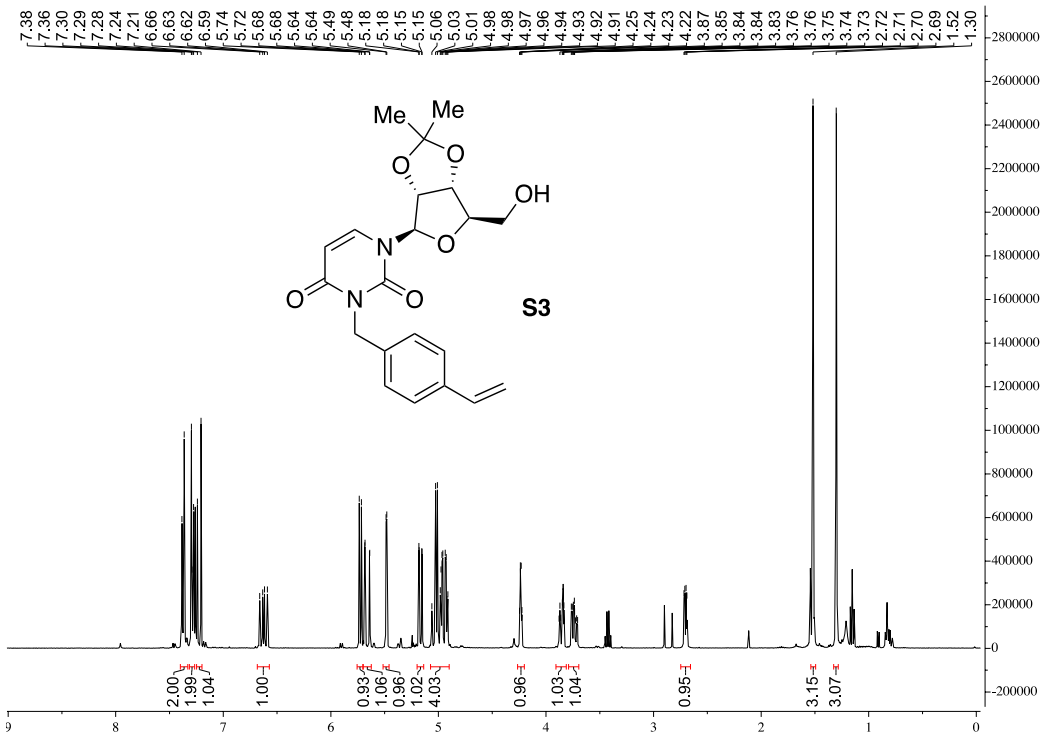
7. Reference

1. Fujihashi, M.; Ishida, T.; Kuroda, S.; Kotra, L. P.; Pai, E. F.; Miki, K. Substrate Distortion Contributes to the Catalysis of Orotidine 5′-Monophosphate Decarboxylase. *J. Am. Chem. Soc.* **2013**, *135*, 17432-17443.
2. Ding, S.; Cao, S.; Zhu, A.; Shi, G. Wettability Switching of Electrode for Signal Amplification: Conversion of Conformational Change of Stimuli-Responsive Polymer into Enhanced Electrochemical Chiral Analysis. *Anal. Chem.* **2016**, *88*, 12219 -12226.
3. (a) Hashimoto, T.; Kawamata, Y.; Maruoka, K. An organic thiyl radical catalyst for enantioselective cyclization. *Nat. Chem.* **2014**, *6*, 702-705. (b) Emmett, M. R.; Kerr, M. A. Nucleophilic ring opening of cyclopropane hemimalonates using internal Brønsted acid activation. *Org. Lett.* **2011**, *13*, 4180-4183. (c) Seiji, Y.; Akiko, A.; Naoko, K.; Keiko, H.; Hajime, Y.; Yoshiro, H. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 215-2219. (d) Pierre L. Beaulieu, P. L.; Gillard, J.; Bailey, M. D.; Boucher, C.; Duceppe, J.-C.; Simoneau, B.; Wang, X.-J.; Zhang, L.; Grozinger, K.; Houpis, I.; Farina, V.; Heimroth, H.; Krueger, T.; Schnaubelt, J. Synthesis of (1R,2S)-1-amino-2-vinylcyclopropanecarboxylic acid vinyl-ACCA derivatives: key intermediates for the preparation of inhibitors of the hepatitis C virus NS3 protease. *J. Org. Chem.* **2005**, *70*, 5869-5879. (e) Umeyama, T.; Naka, K.; Chujo, Y. Radical copolymerization of cyclic diarsine with vinyl monomers. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3023−3028.

8. NMR Spectra



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5.68
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5.18
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5.15
5.15
5.06
5.03
5.01
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4.98
4.97
4.96
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3.76
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2.72
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1.30
Me
Me
O
O
OH
N
O
O
N
O
S3
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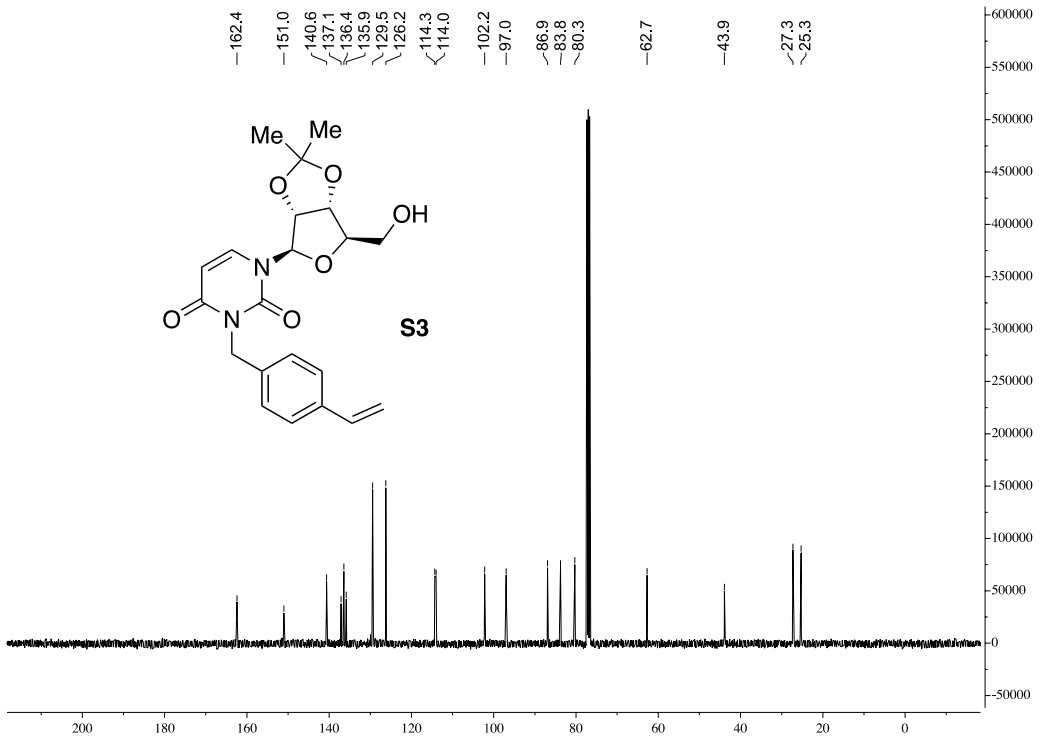
4.03
0.96
1.03
1.04
0.95
3.15
3.07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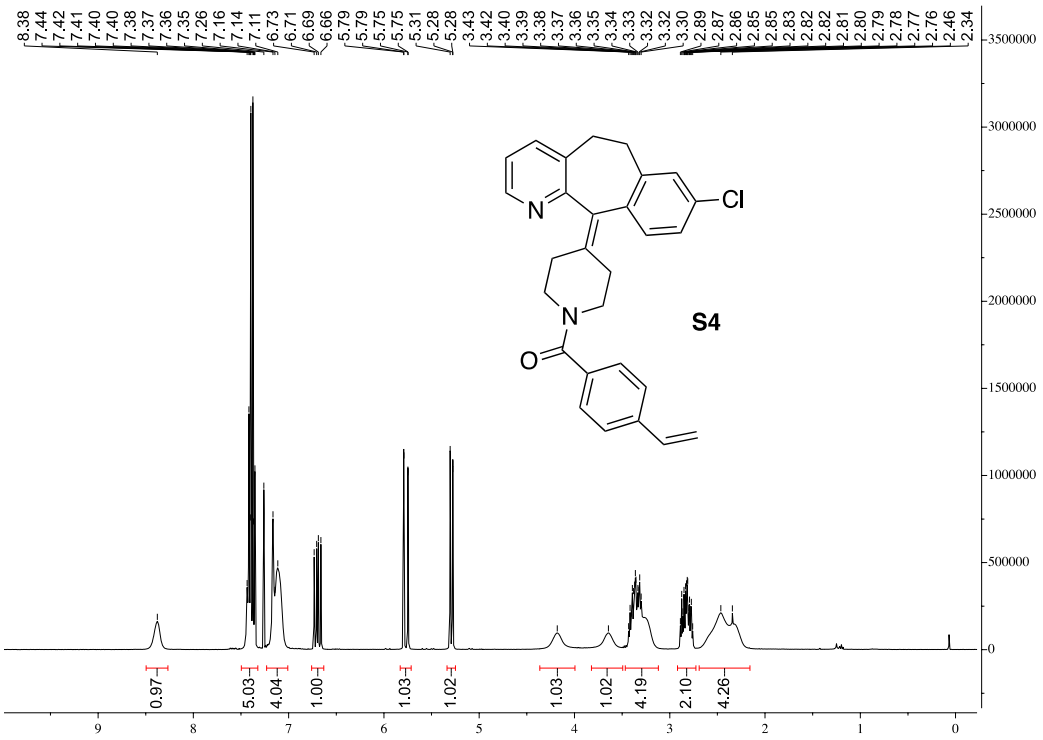
O
N
O
S3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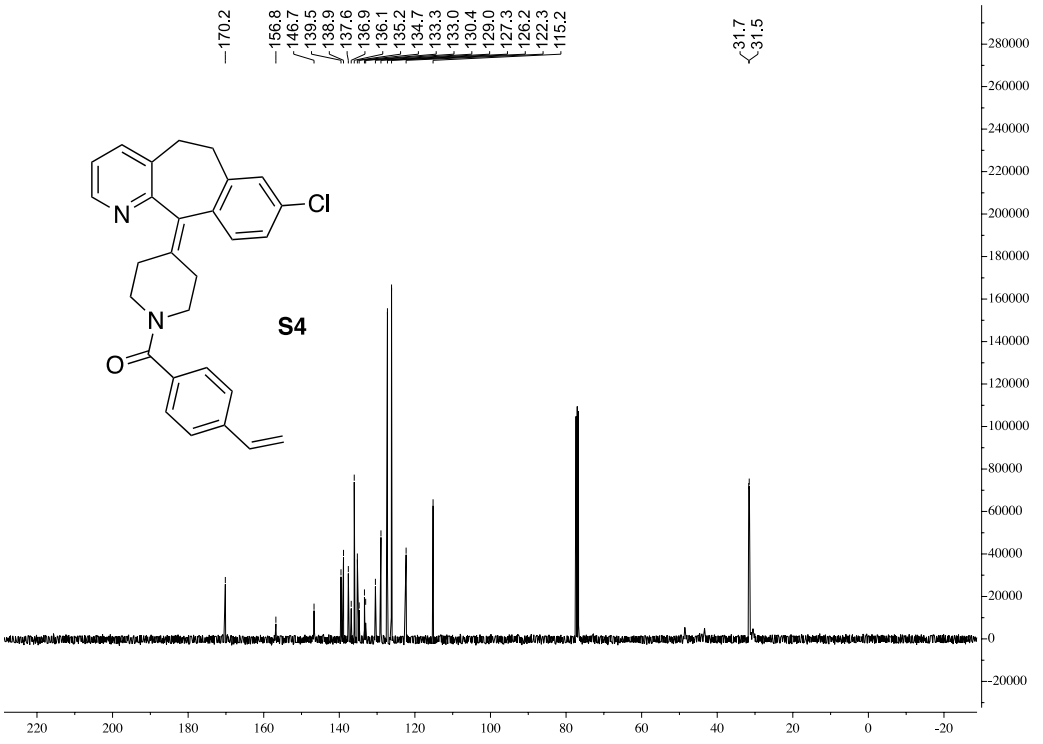
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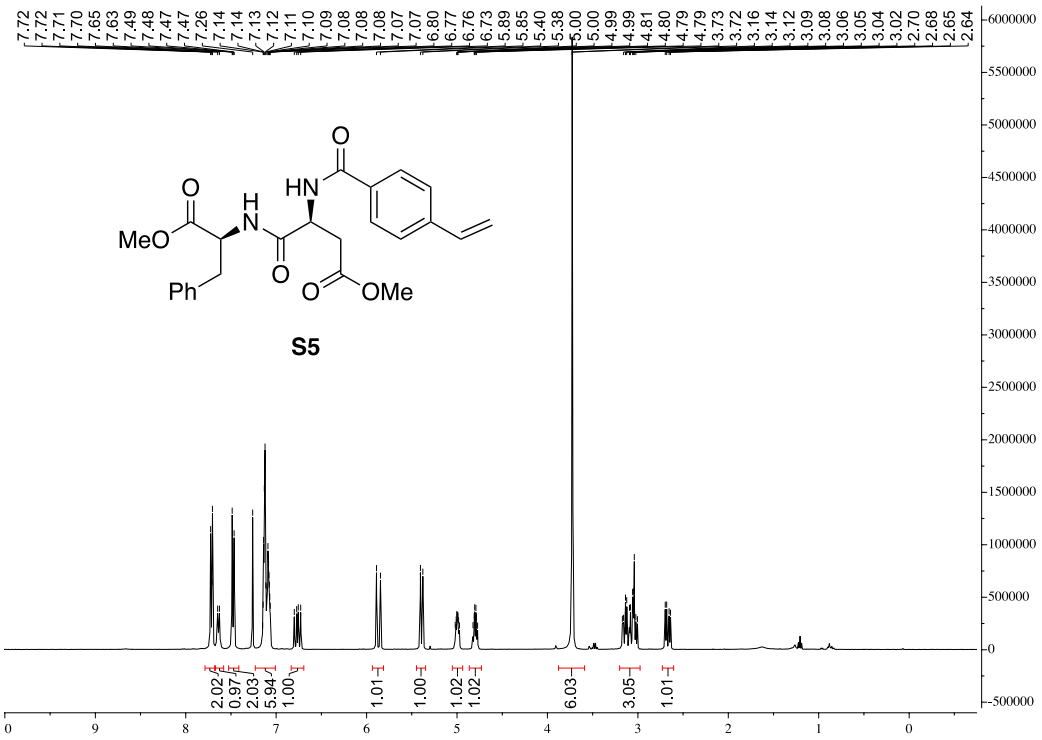
S4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Ph
OMe
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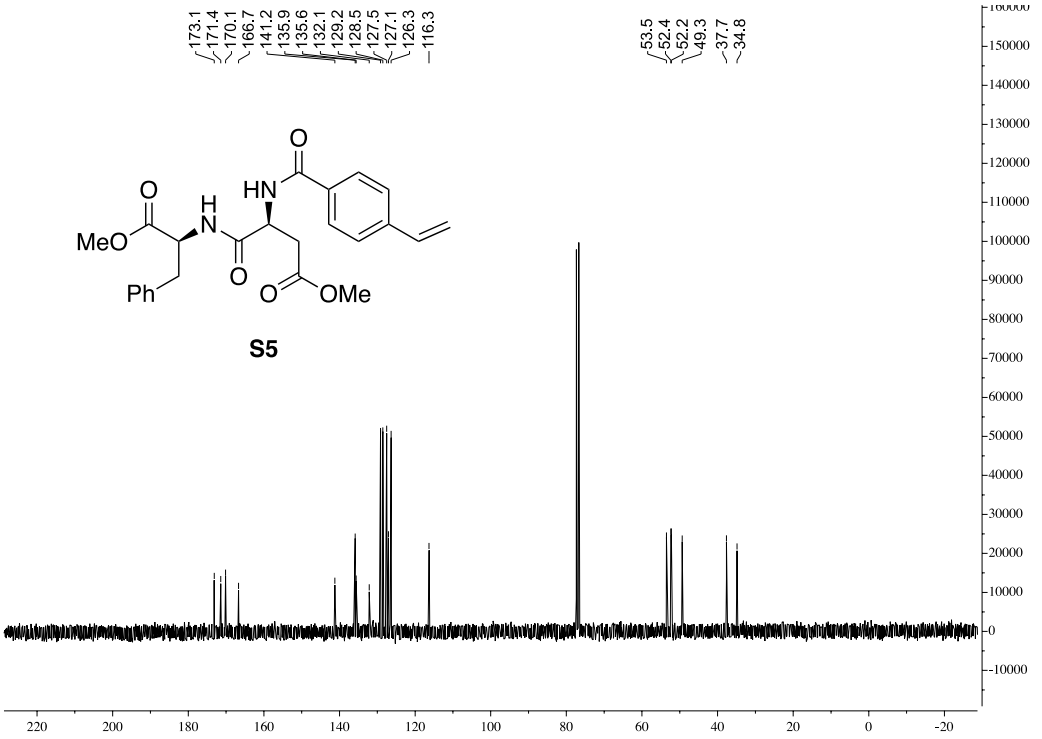
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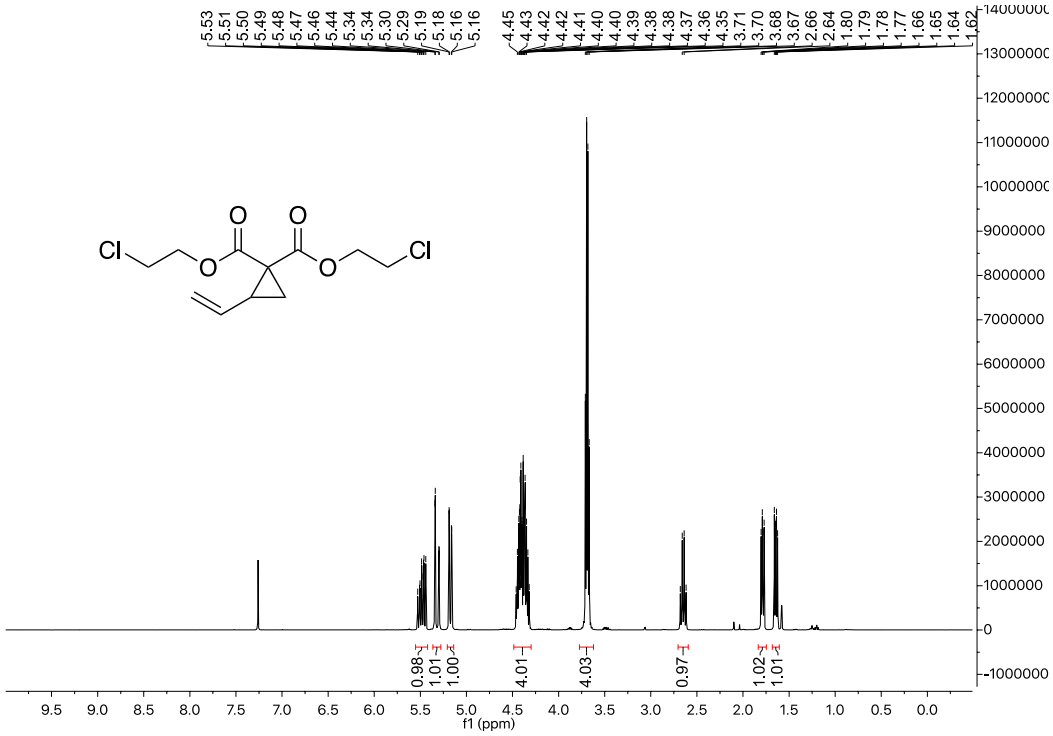
MeO
Ph
OMe
S5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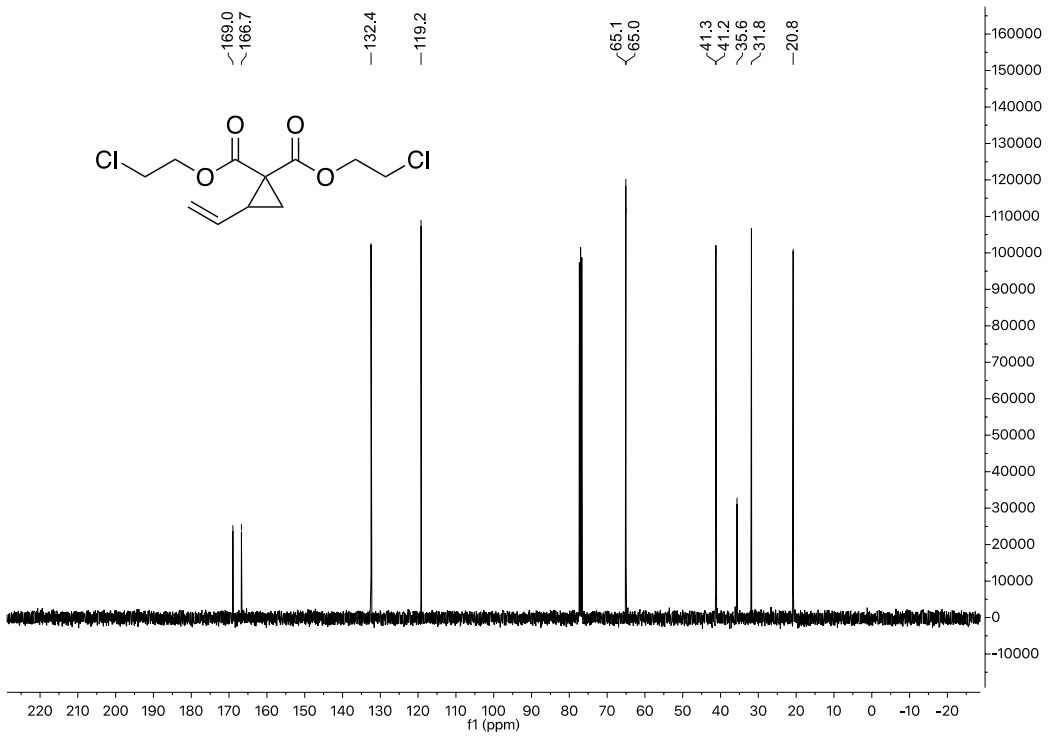
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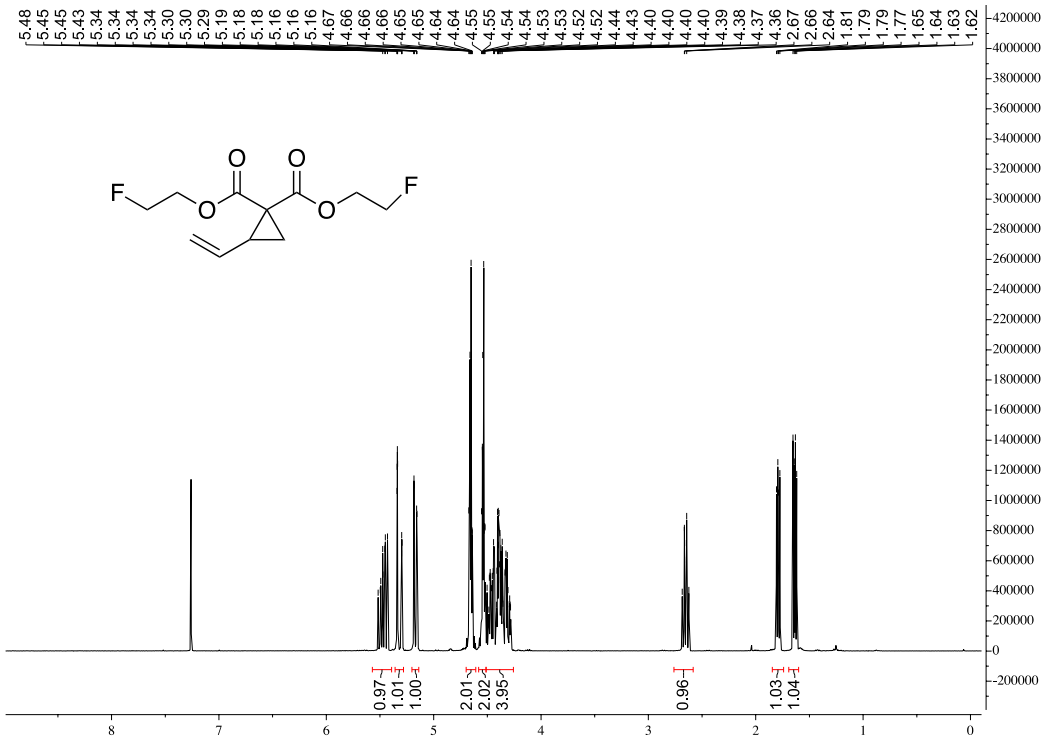
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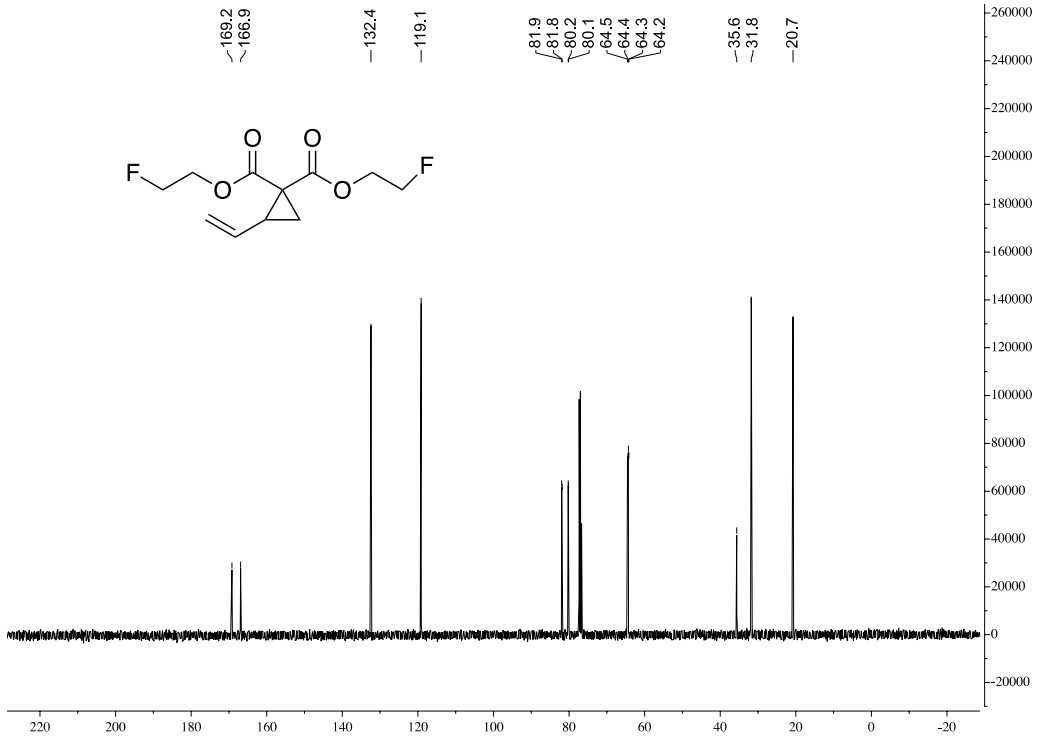
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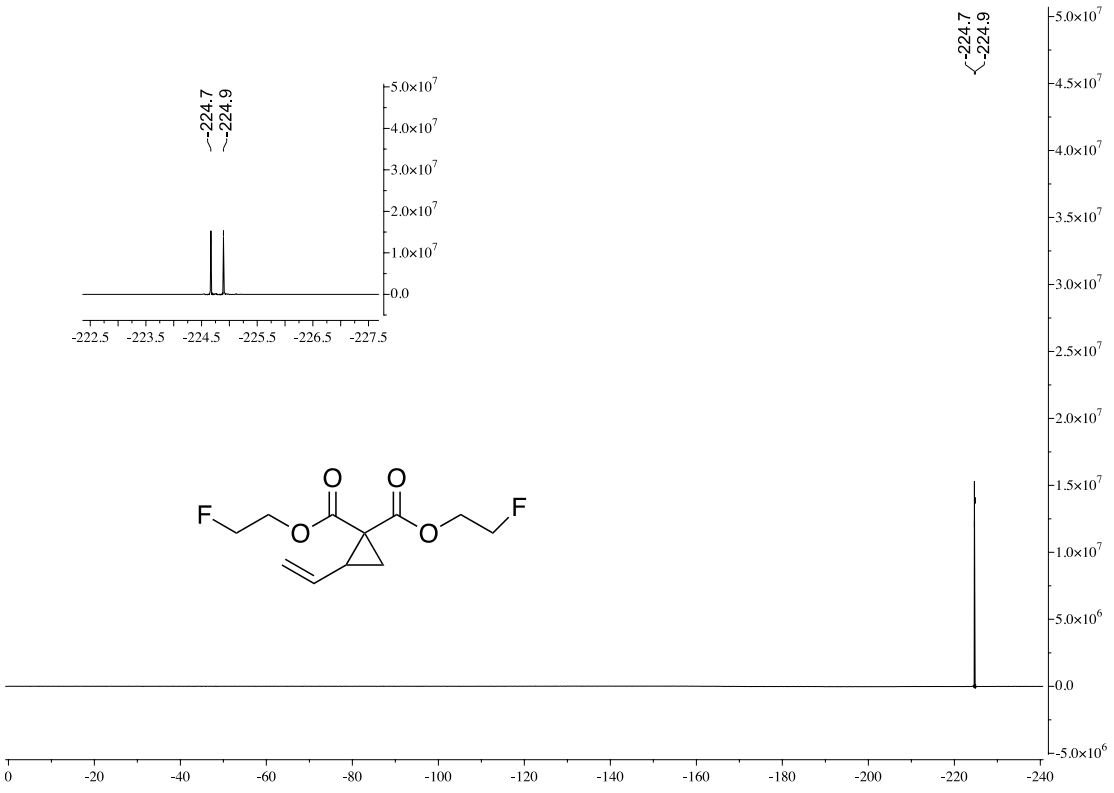
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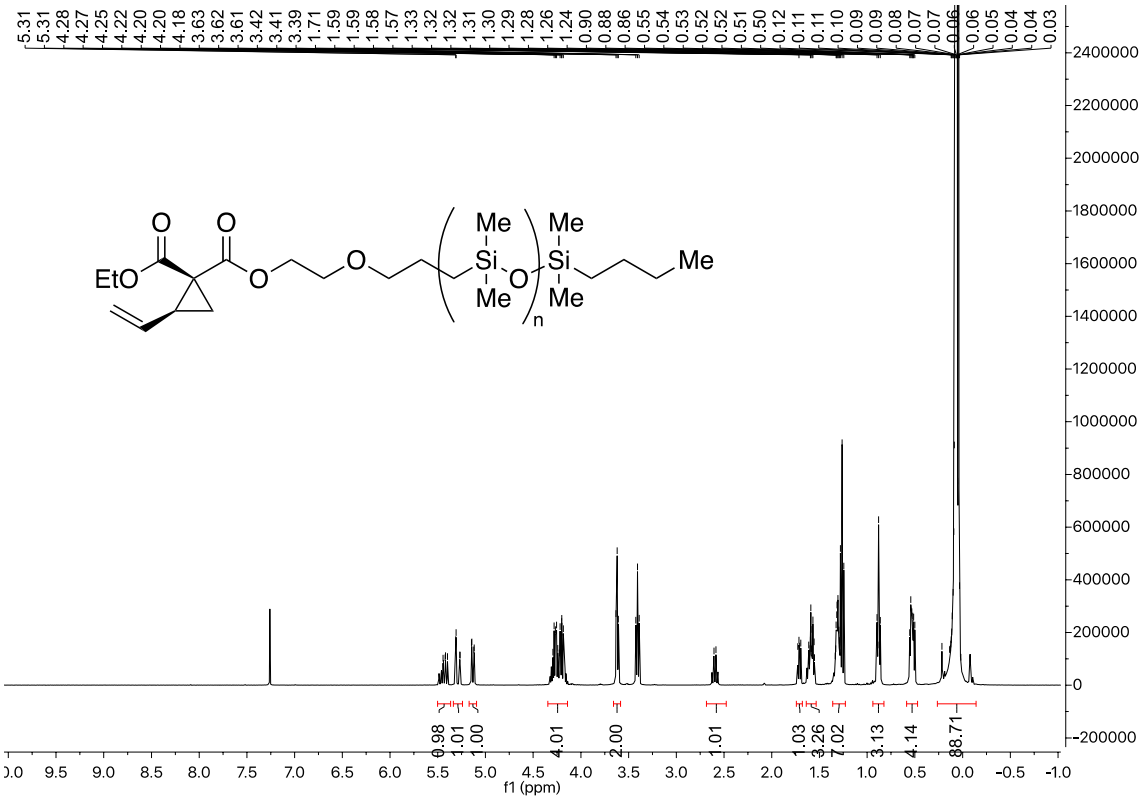
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O O EtO O O Me Si O Si Me Me Me Me Me n
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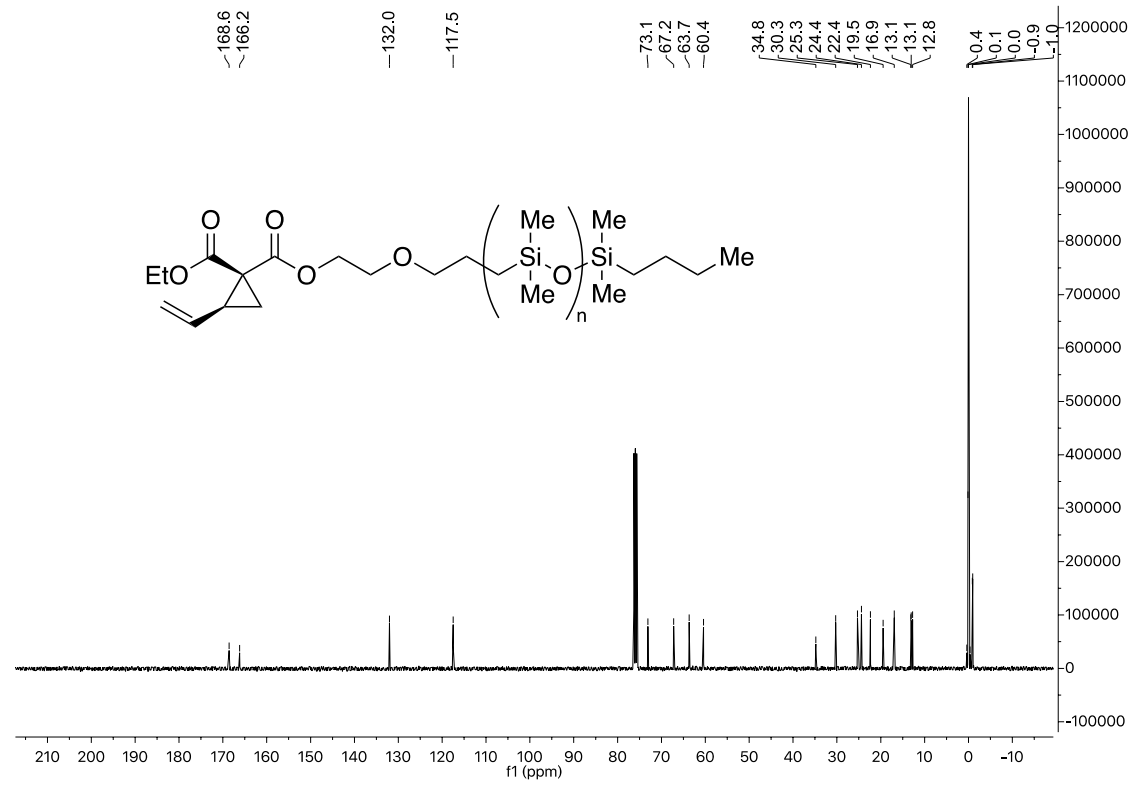
f1 (ppm)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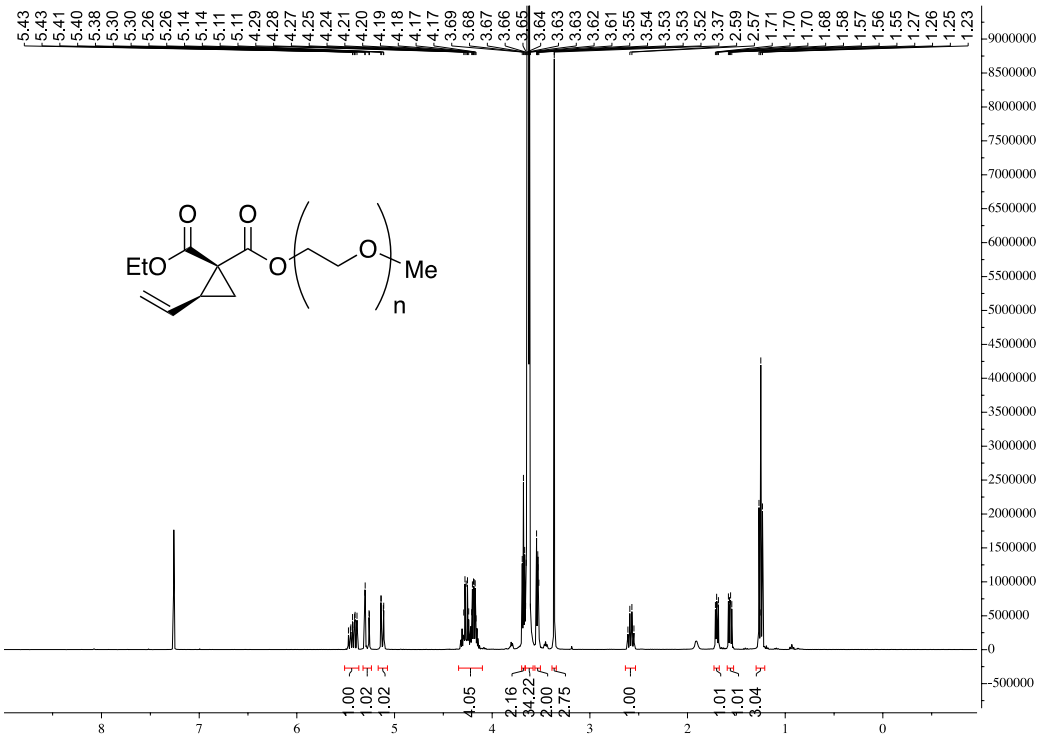
f1 (ppm)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n
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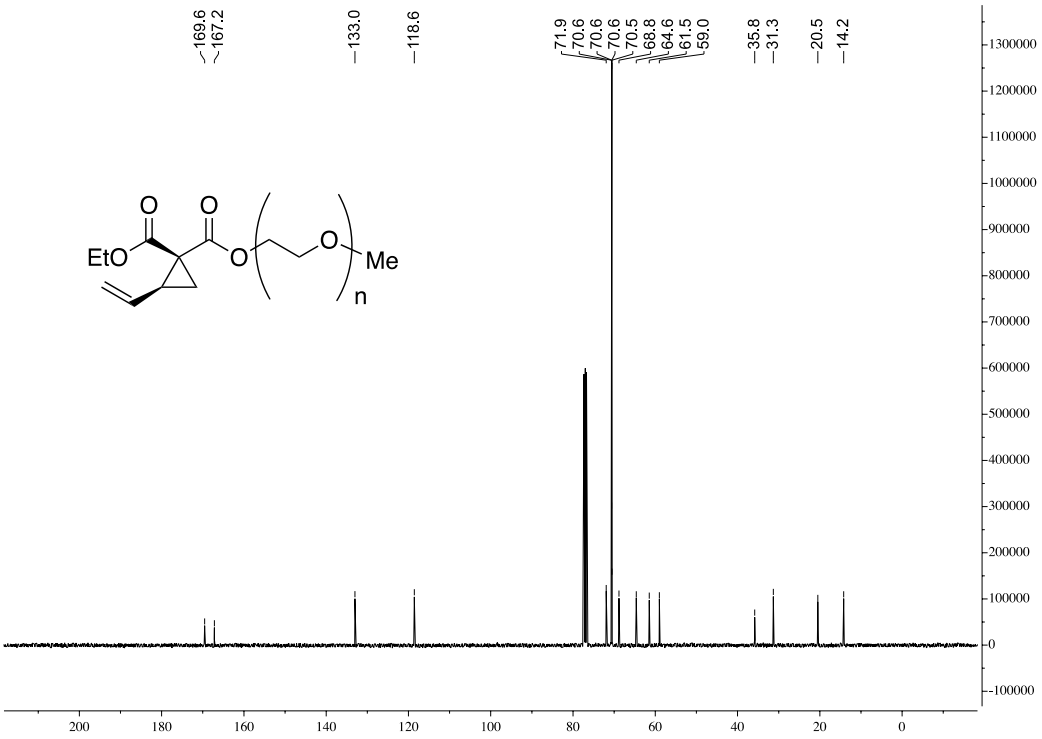
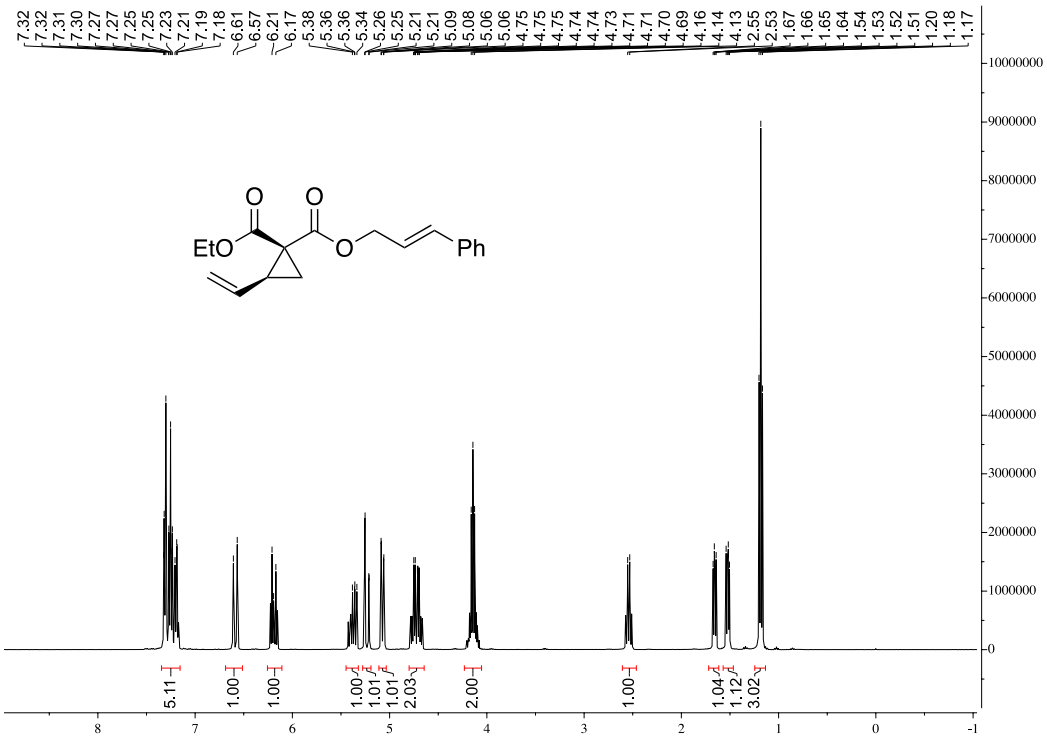
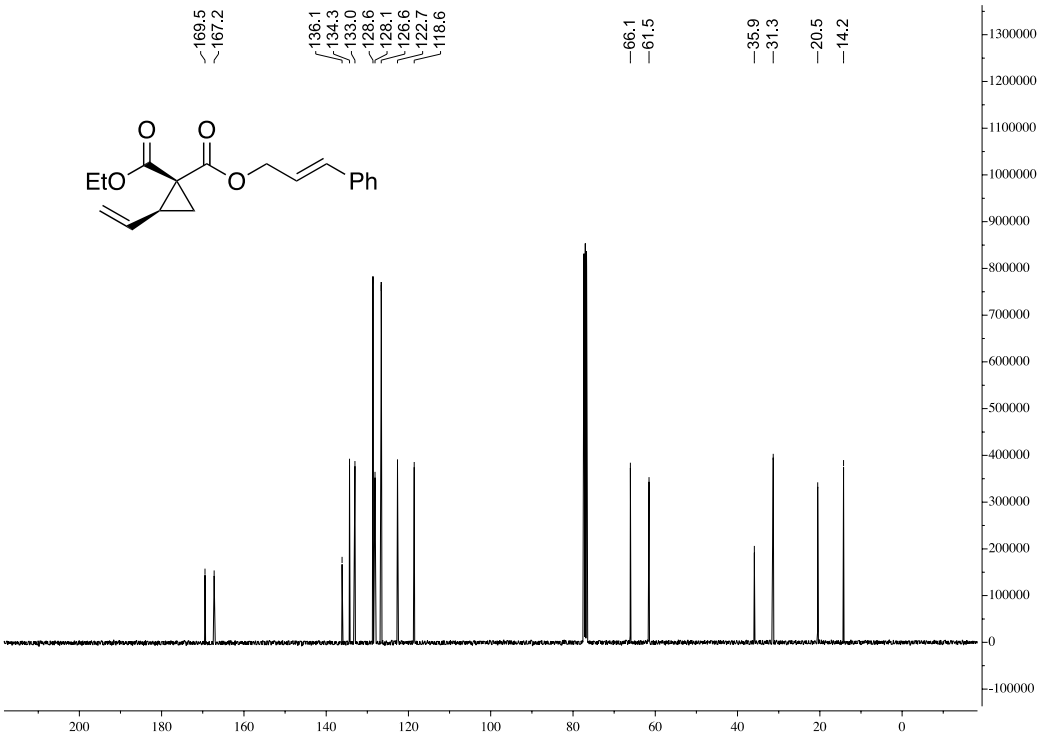
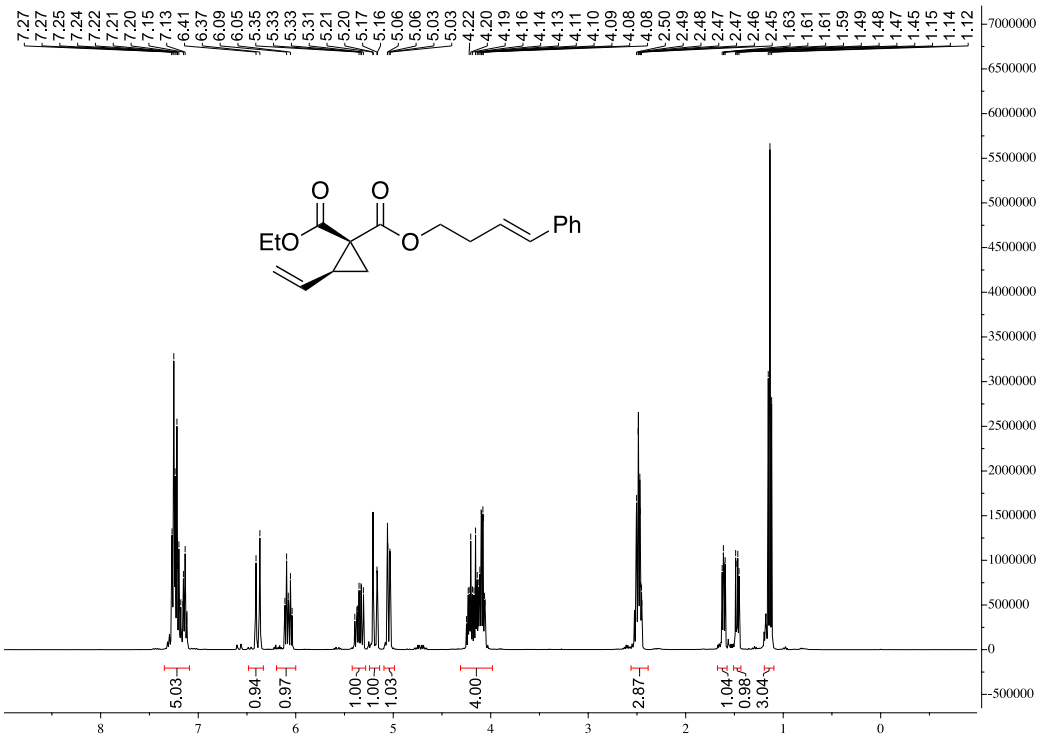
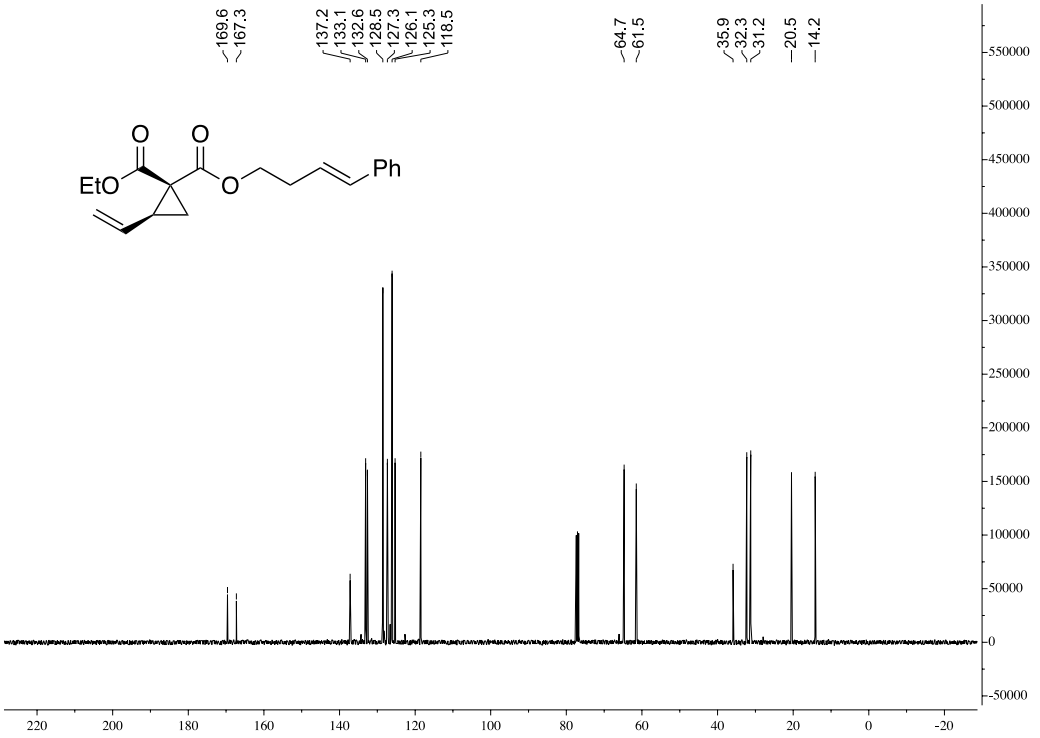
1.01
3.04

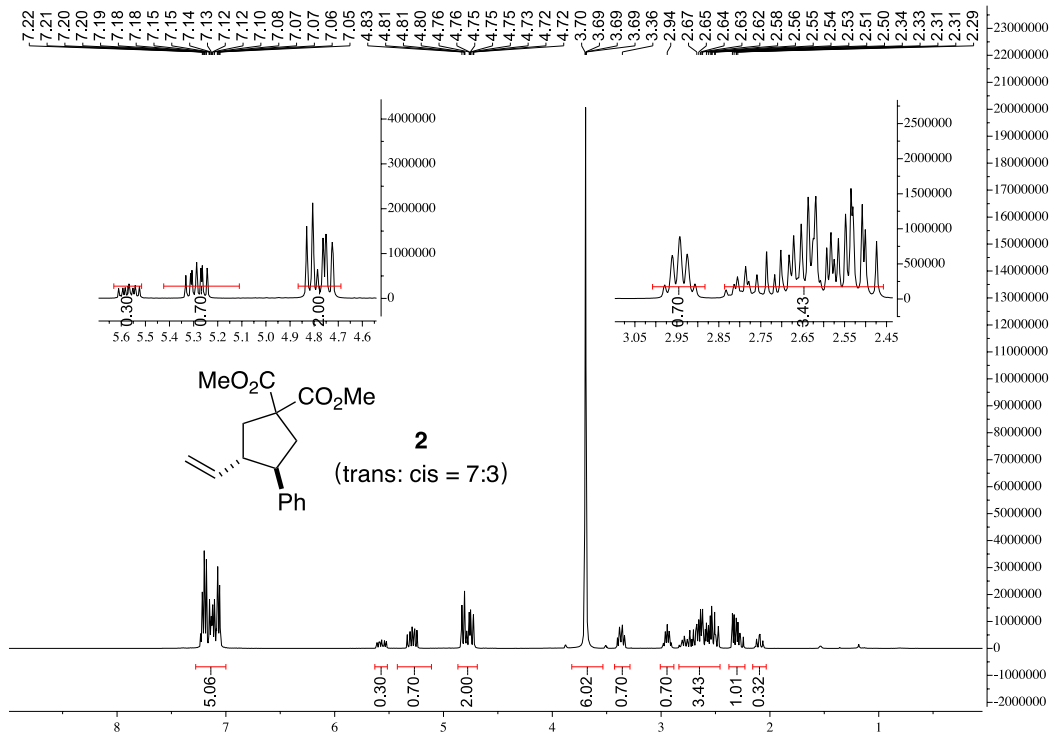

169.6
167.2
133.0
118.6
71.9
70.6
70.6
70.6
70.5
68.8
64.6
61.5
59.0
35.8
31.3
20.5
14.2
EtO
O
O
O
O
Me
n

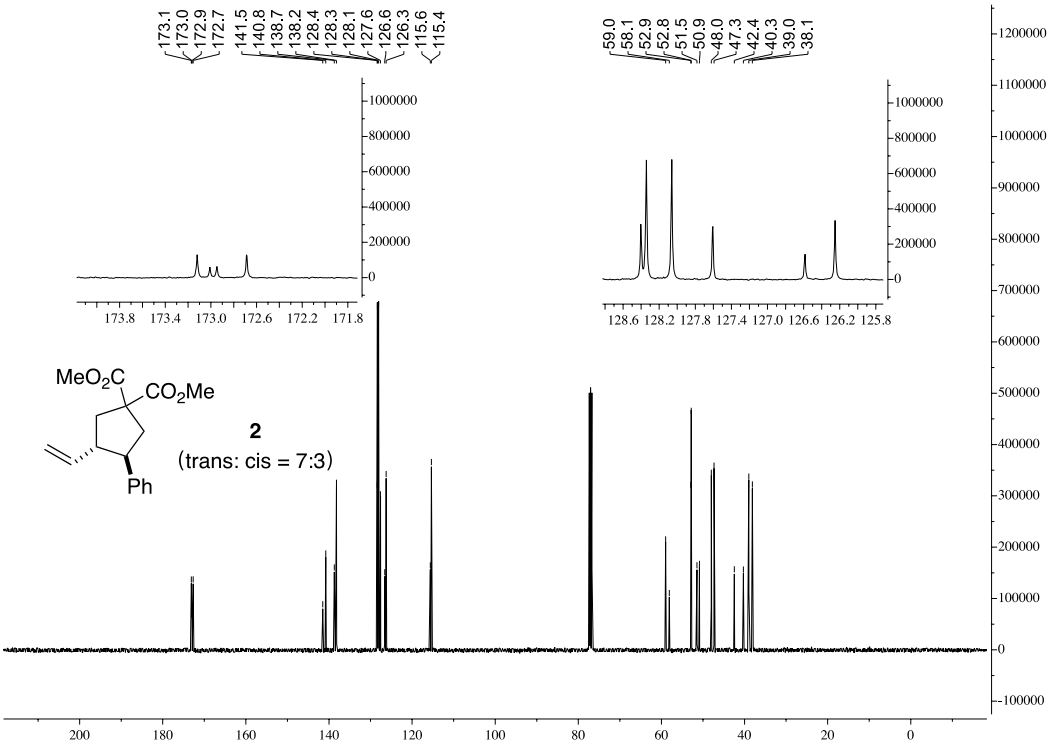

7.32
7.32
7.31
7.30
7.27
7.27
7.25
7.25
7.23
7.21
7.19
7.18
6.61
6.57
6.21
6.17
5.38
5.36
5.36
5.34
5.26
5.25
5.21
5.21
5.09
5.08
5.06
5.06
4.75
4.75
4.74
4.74
4.73
4.71
4.71
4.70
4.69
4.16
4.14
4.13
2.55
2.53
1.67
1.66
1.65
1.64
1.54
1.53
1.52
1.51
1.20
1.18
1.17
O
O
EtO
O
Ph
5.11
1.00
1.00
1.00
1.01
1.01
2.03
2.00
1.00
1.04
1.12
3.02

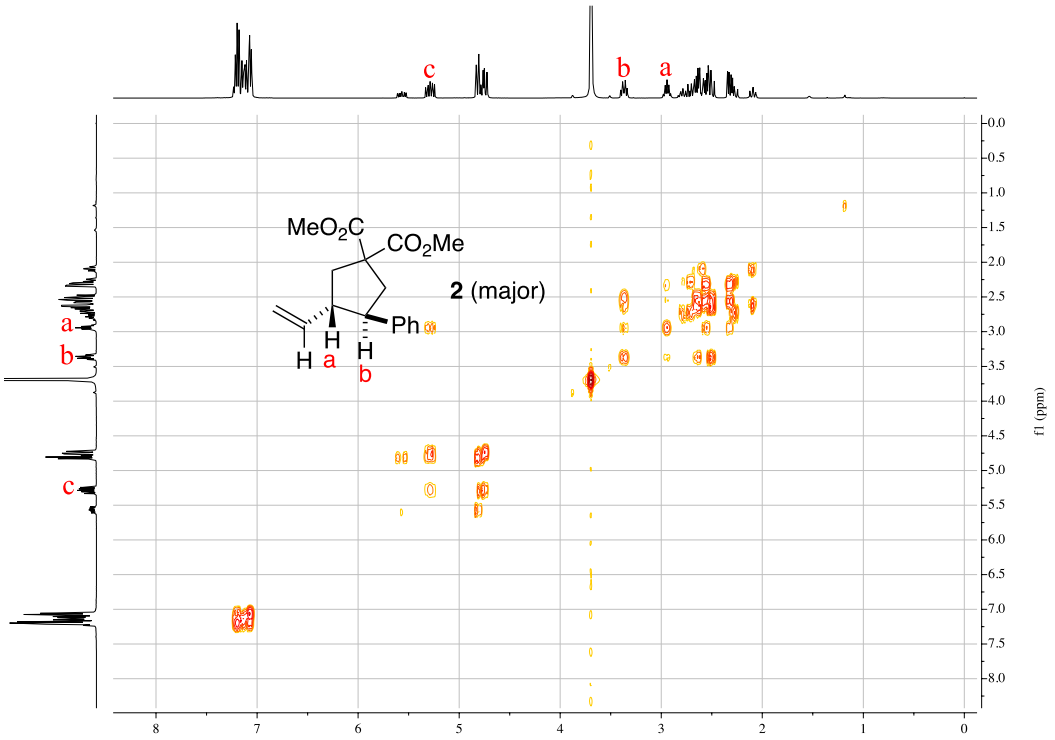

169.5
167.2
136.1
134.3
133.0
128.6
128.1
126.6
122.7
118.6
66.1
61.5
35.9
31.3
20.5
14.2
O
O
EtO
O
Ph

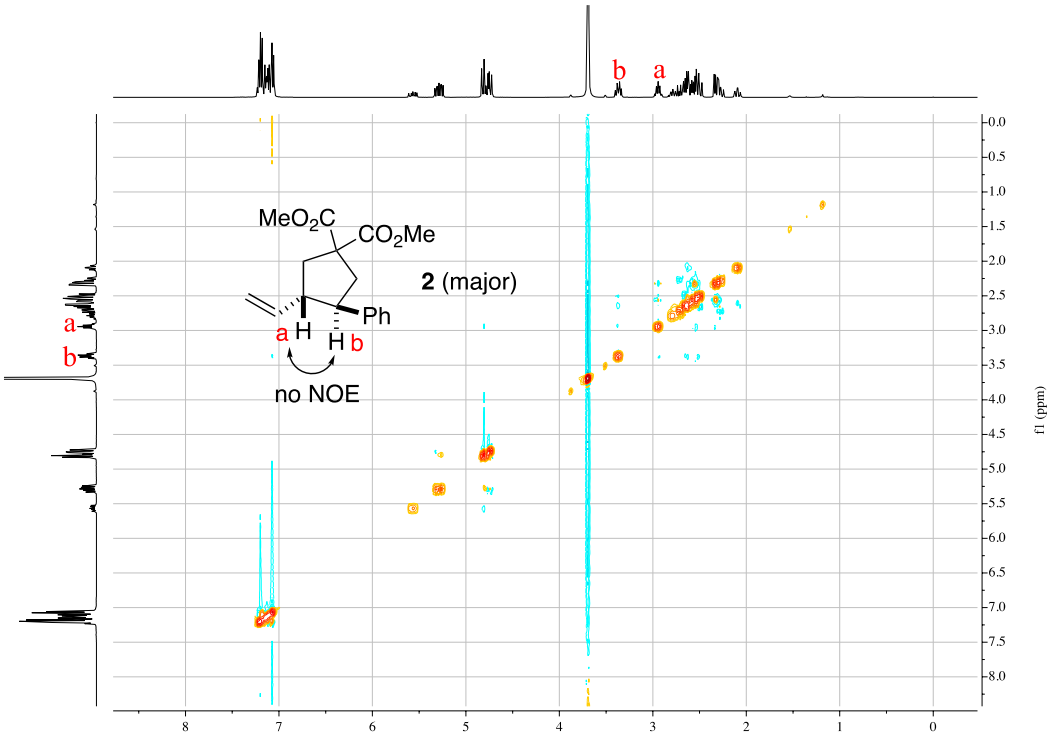

7.27
7.27
7.25
7.24
7.22
7.21
7.20
7.15
7.13
6.41
6.37
6.09
6.05
5.35
5.33
5.33
5.31
5.21
5.20
5.17
5.16
5.06
5.06
5.03
5.03
4.22
4.20
4.19
4.16
4.14
4.13
4.11
4.10
4.09
4.08
4.08
2.50
2.49
2.48
2.47
2.47
2.46
2.45
1.63
1.61
1.61
1.59
1.49
1.48
1.47
1.45
1.15
1.14
1.12
EtO
O
O
O
Ph
5.03
0.94
0.97
1.00
1.00
1.03
4.00
2.87
1.04
0.98
3.04

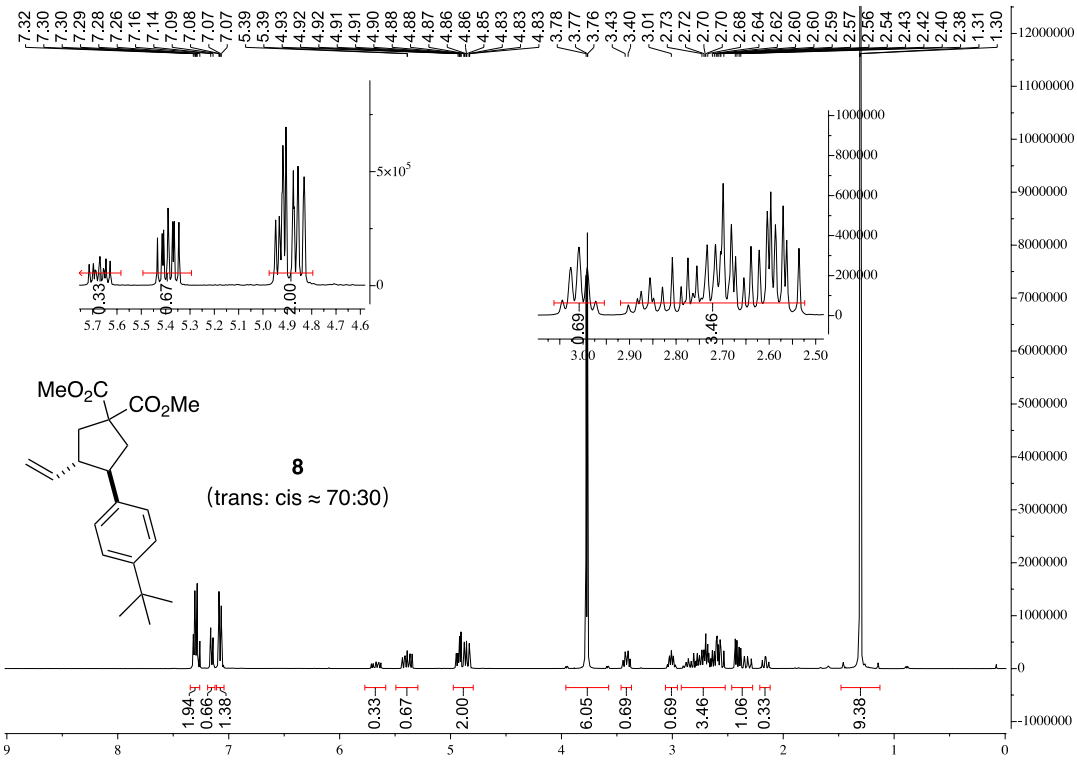

169.6
167.3
137.2
133.1
132.6
128.5
127.3
126.1
125.3
118.5
64.7
61.5
35.9
32.3
31.2
20.5
14.2
EtO
O
O
O
Ph

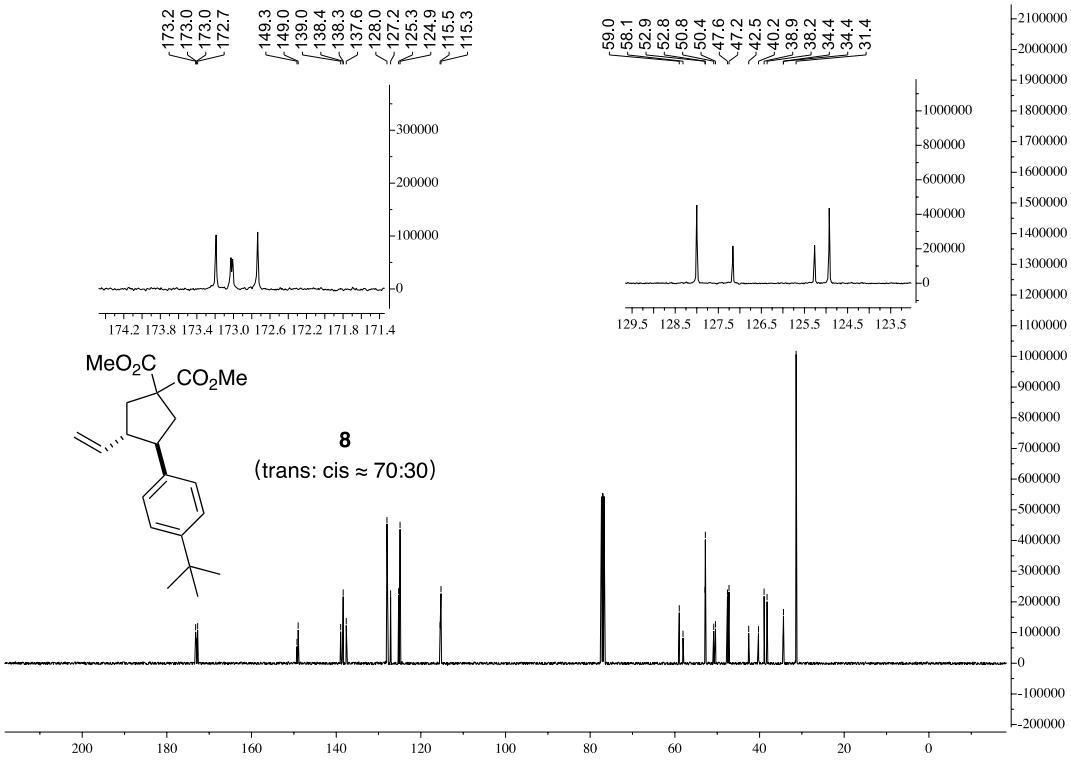

MeO2C
CO2Me
Ph
2
(trans: cis = 7:3)

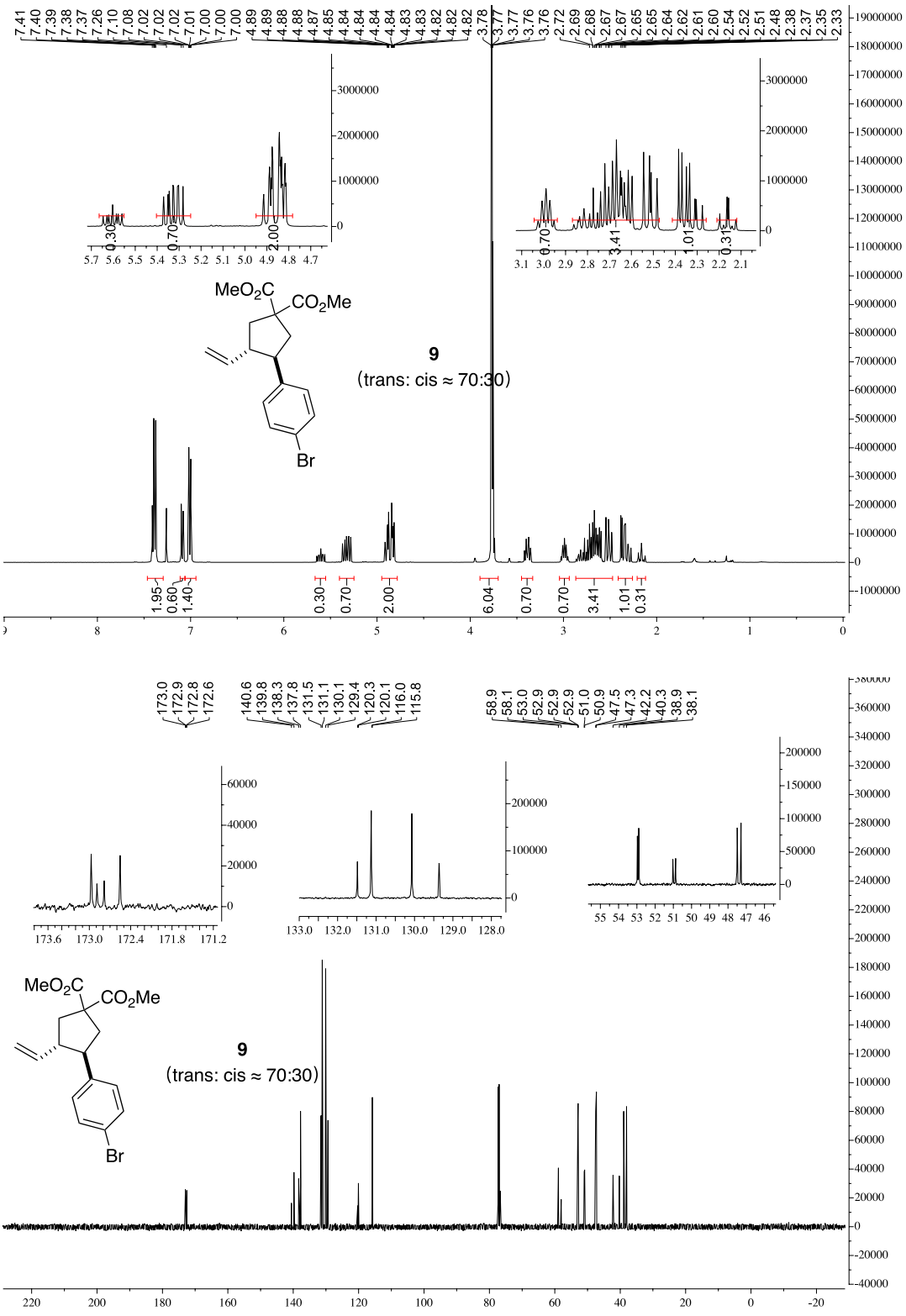

MeO2C
CO2Me
Ph
2
(trans: cis = 7:3)

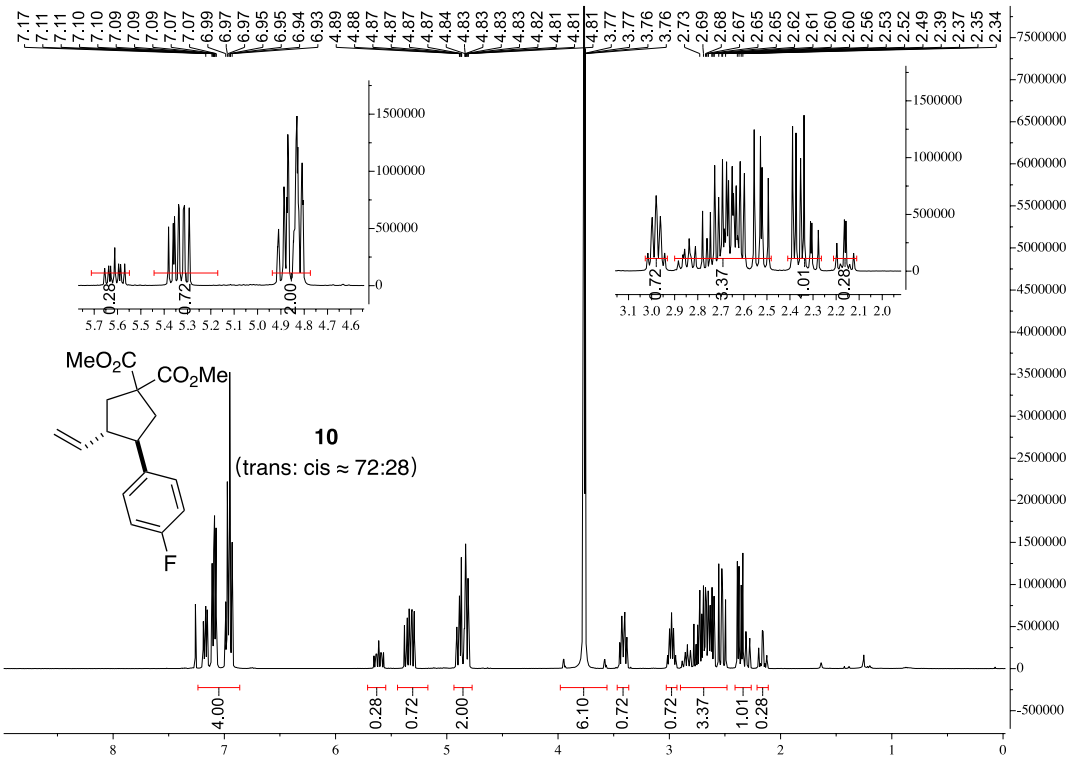

c
b
a
MeO2C
CO2Me
2 (major)
Ph
H
H
H
a
b
a
b
c
f1 (ppm)

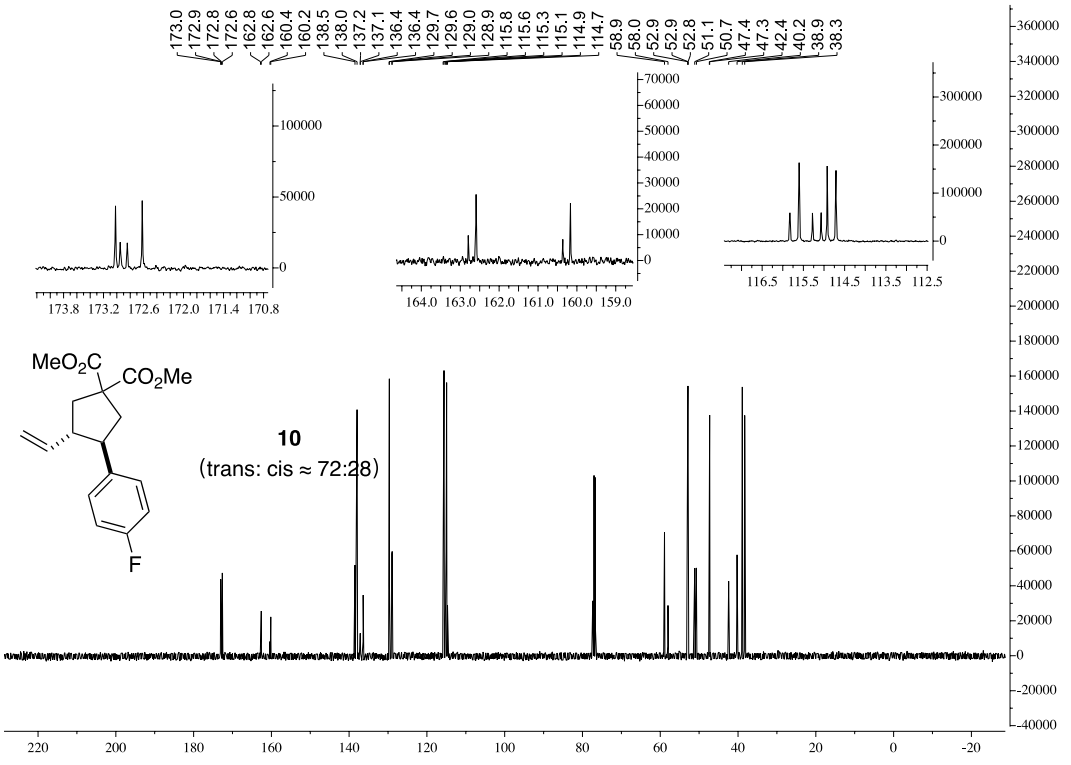

b
a
MeO2C
CO2Me
2 (major)
Ph
a H
H b
no NOE
a
b
f1 (ppm)

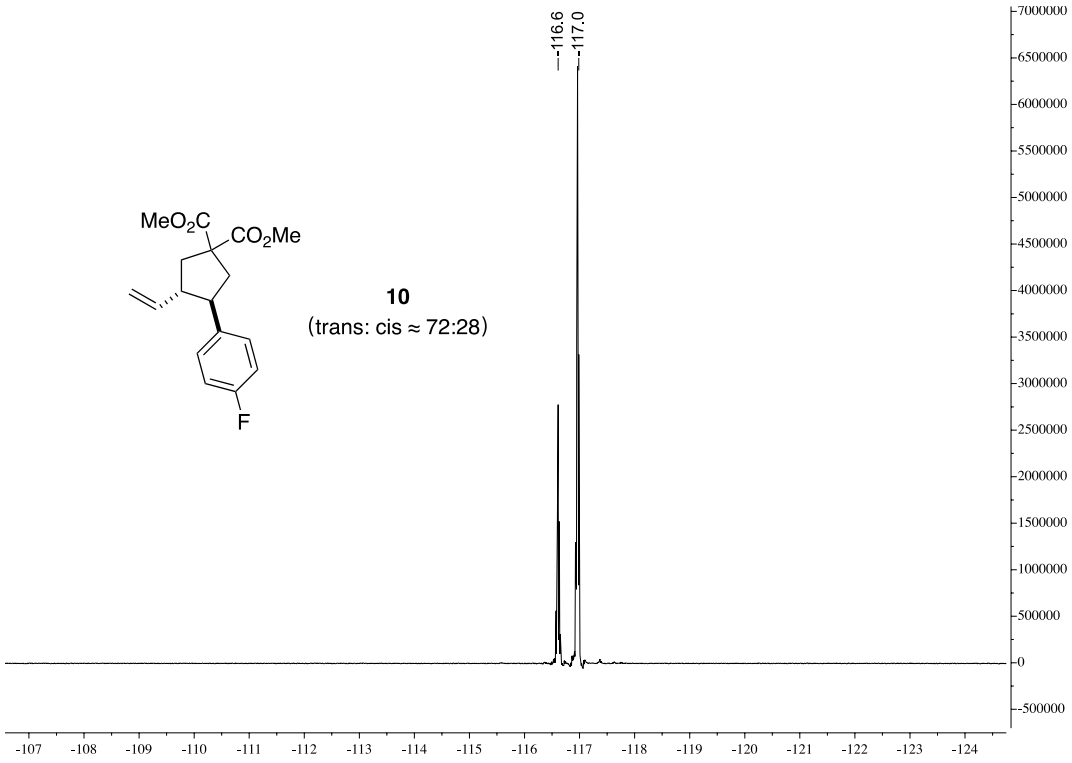

MeO2C
CO2Me
8
(trans: cis ≈ 70:30)

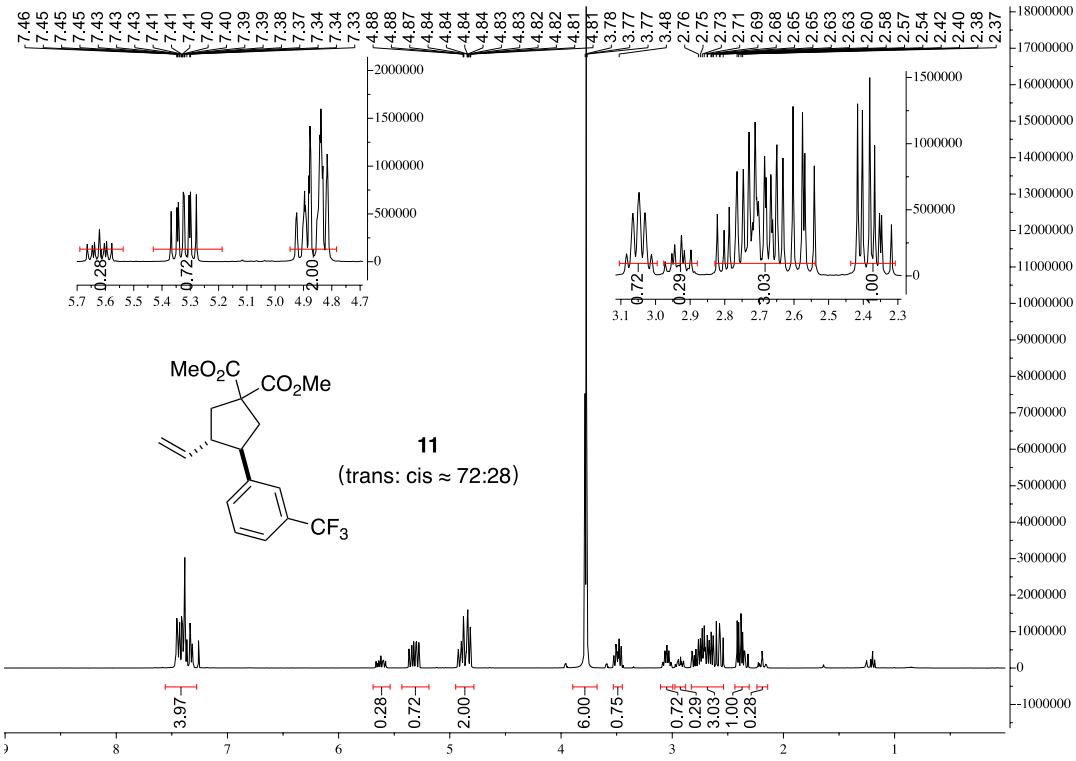

MeO2C
CO2Me
8
(trans: cis ≈ 70:30)

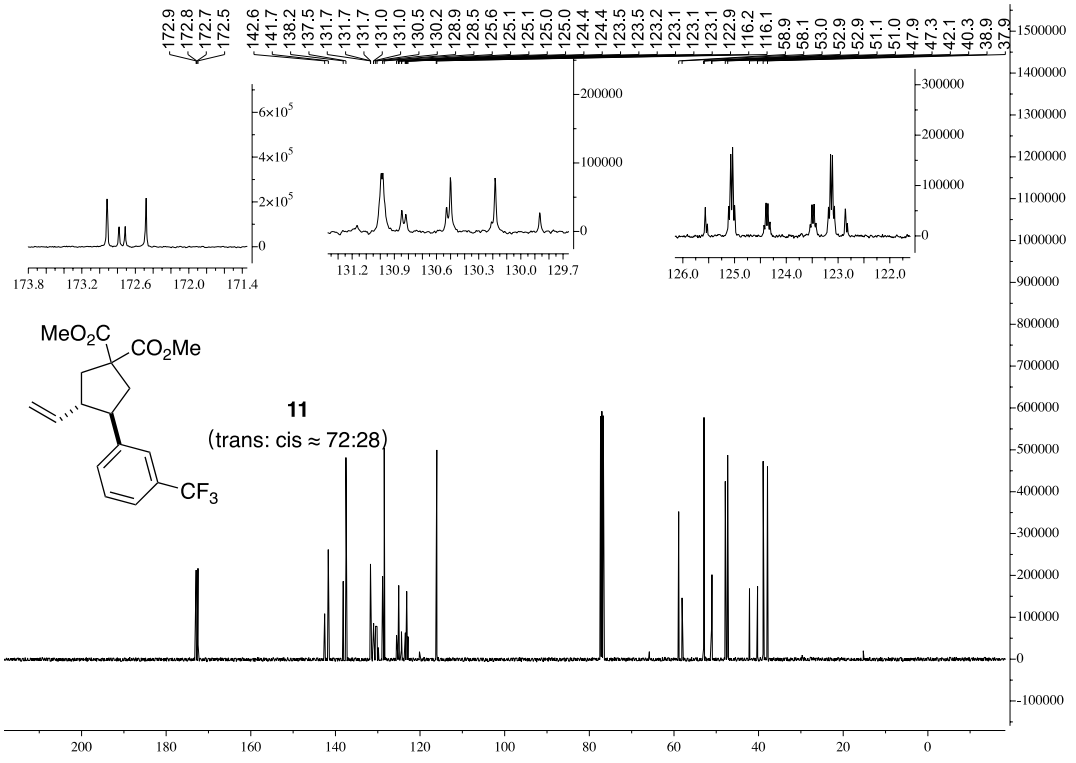

MeO2C
CO2Me
Br
9
(trans: cis ≈ 70:30)
MeO2C
CO2Me
Br
9
(trans: cis ≈ 70:30)

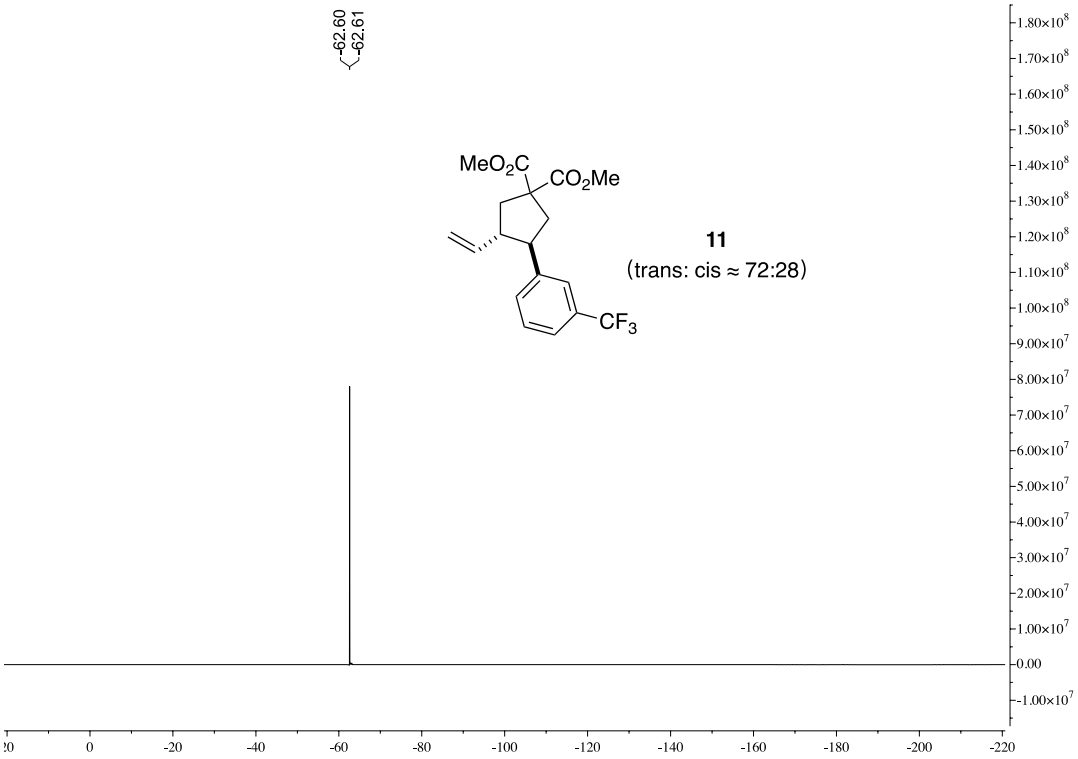

MeO2C
CO2Me
F
10
(trans: cis ≈ 72:28)

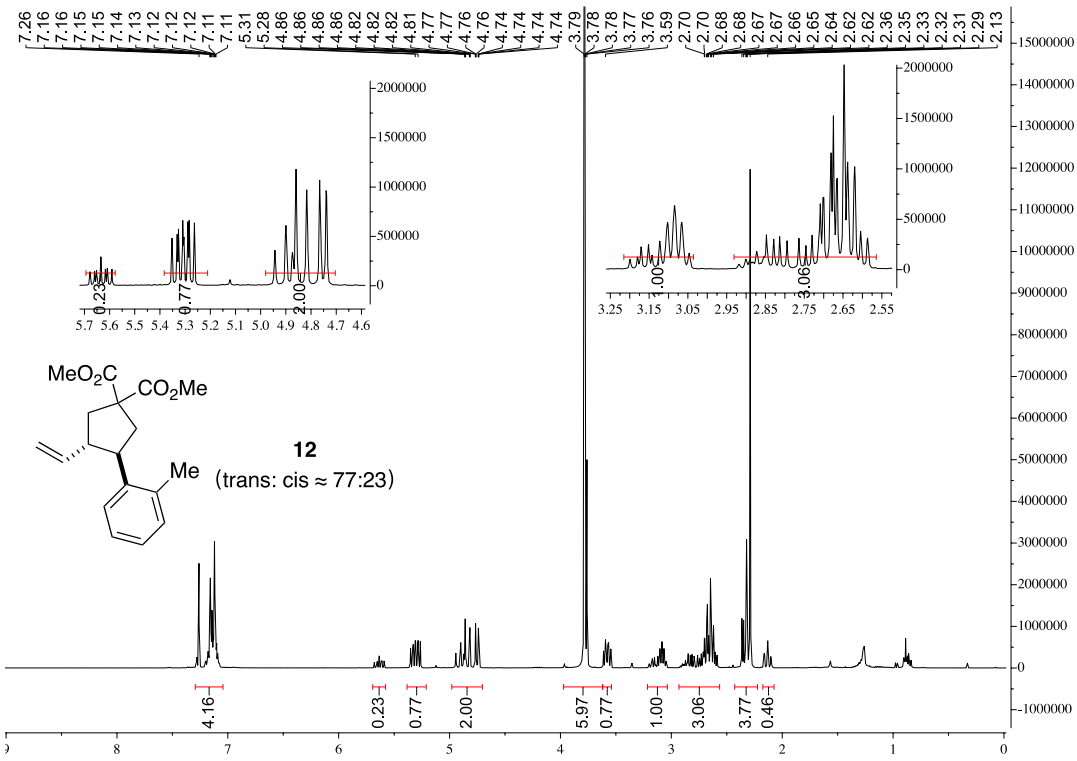

MeO2C
CO2Me
F
10
(trans: cis ≈ 72:28)

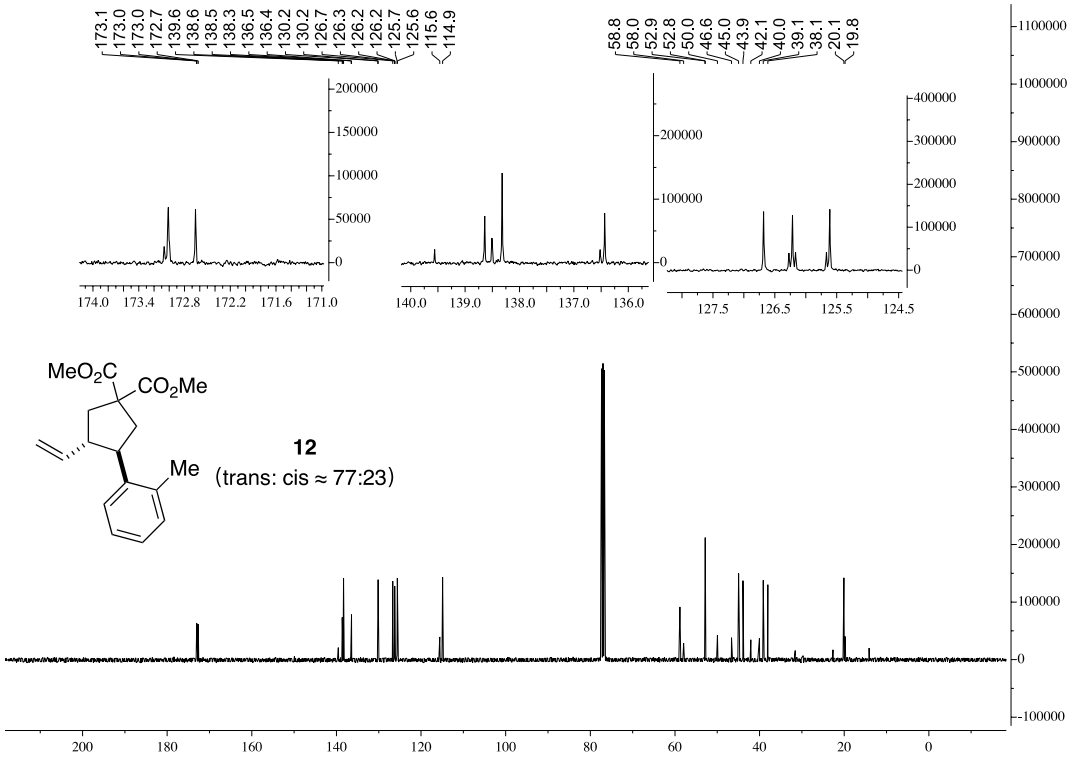

MeO2C
CO2Me
F
10
(trans: cis ≈ 72:28)
-116.6
-117.0
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
-119
-120
-121
-122
-123
-124

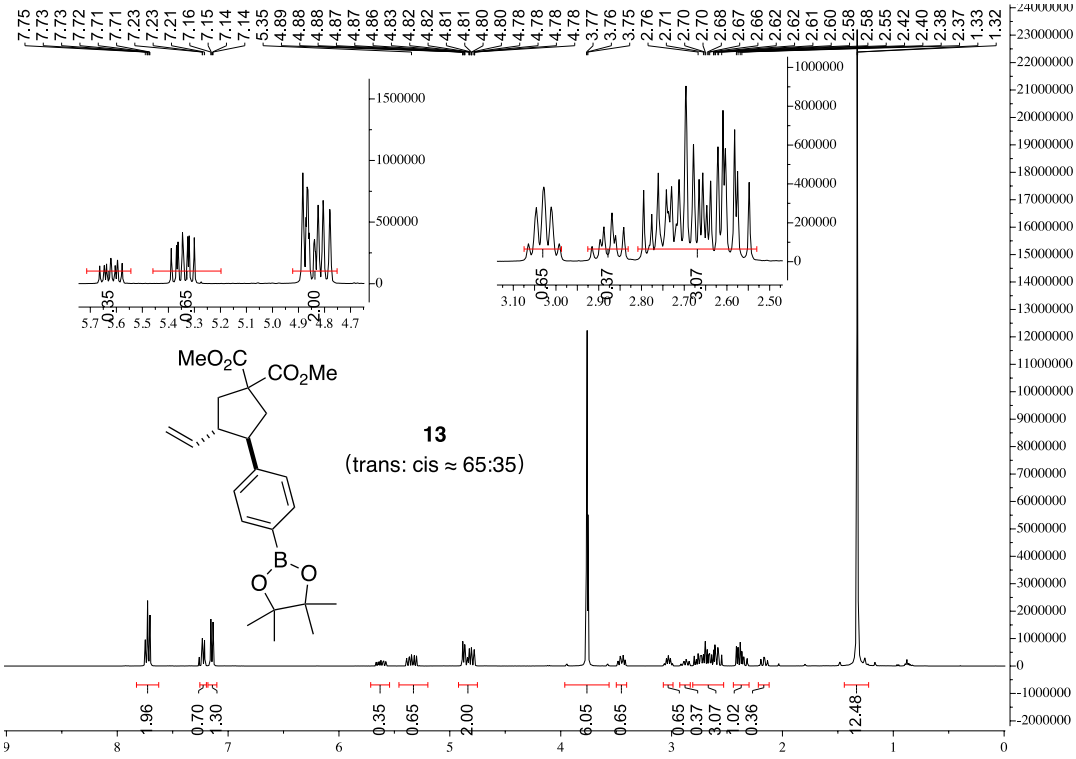

MeO2C
CO2Me
CF3
11
(trans: cis ≈ 72:28)

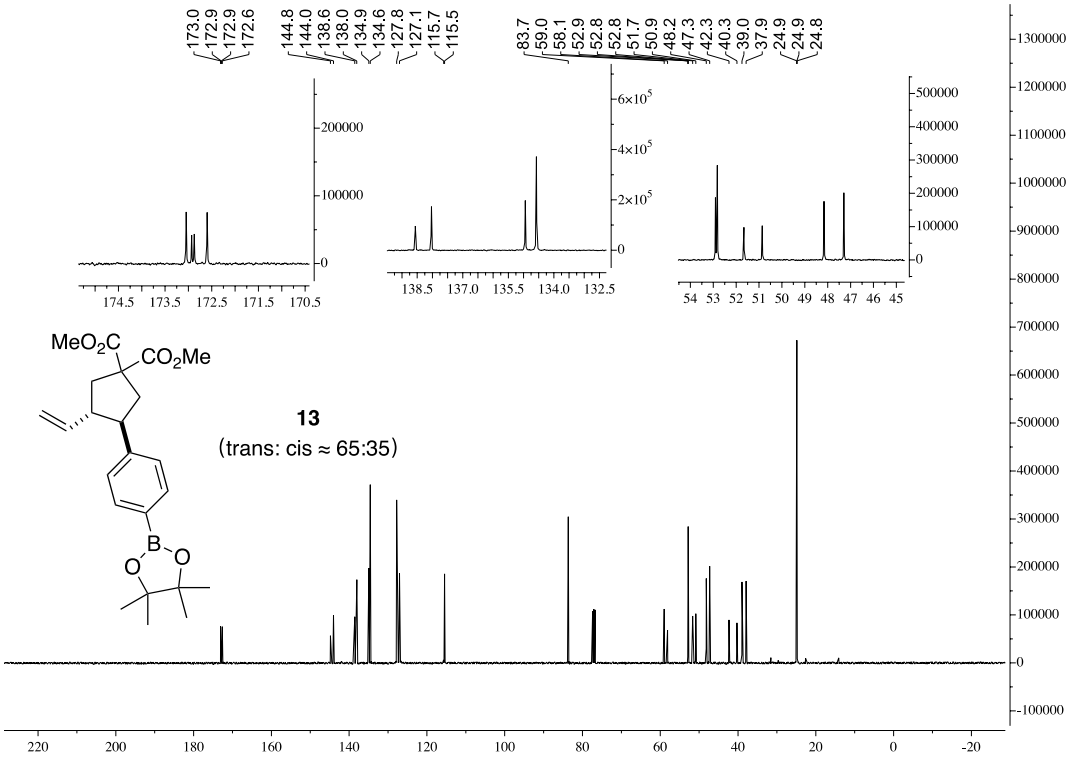

MeO2C
CO2Me
CF3
11
(trans: cis ≈ 72:28)

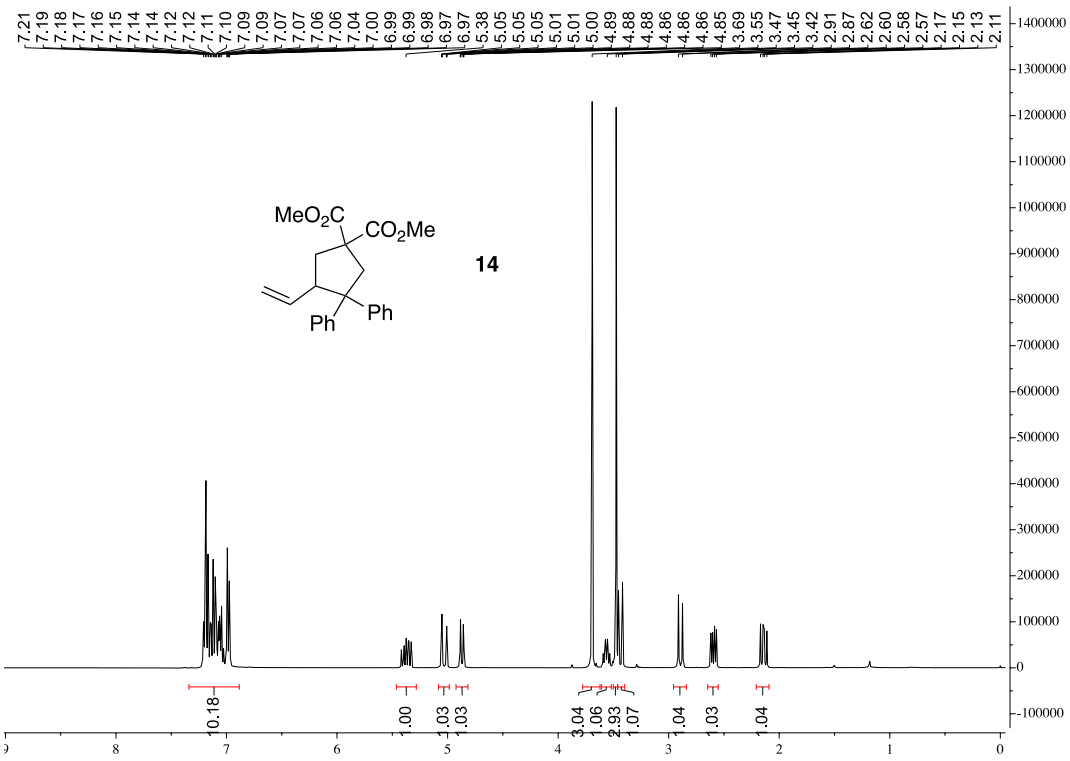

-62.60
-62.61
MeO2C
CO2Me
CF3
11
(trans: cis ≈ 72:28)
1.80×10^8
1.70×10^8
1.60×10^8
1.50×10^8
1.40×10^8
1.30×10^8
1.20×10^8
1.10×10^8
1.00×10^8
9.00×10^7
8.00×10^7
7.00×10^7
6.00×10^7
5.00×10^7
4.00×10^7
3.00×10^7
2.00×10^7
1.00×10^7
0.00
-1.00×10^7
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220

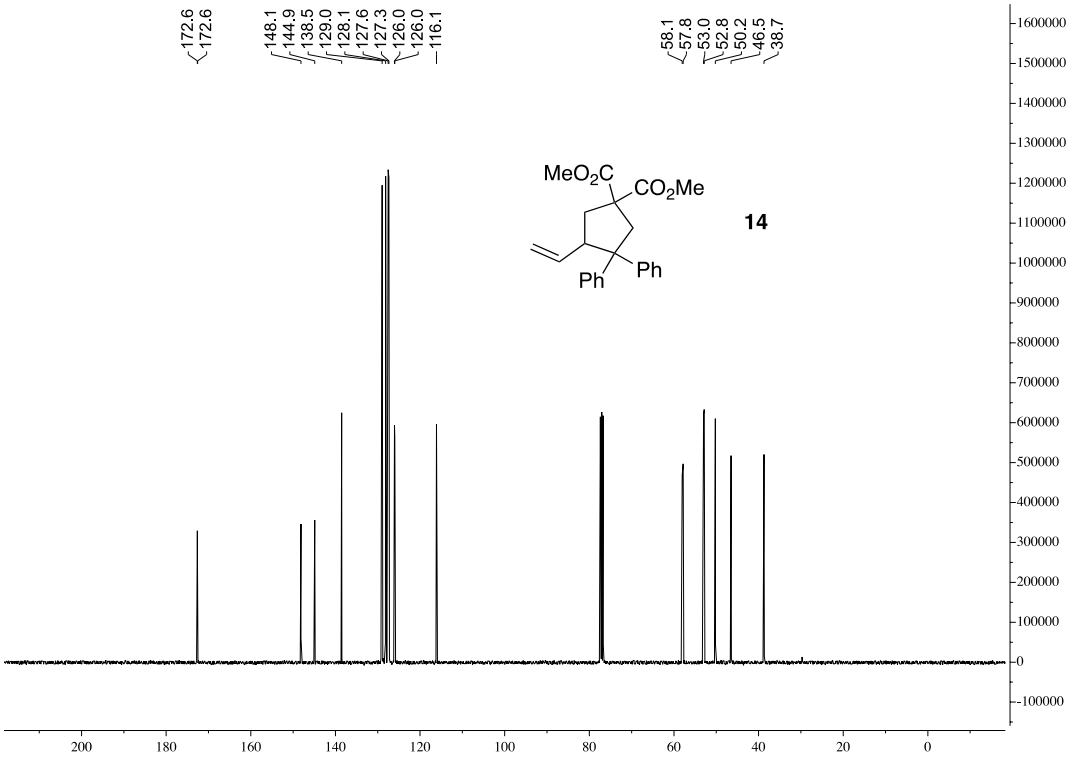

MeO2C
CO2Me
Me
12
(trans: cis ≈ 77:23)

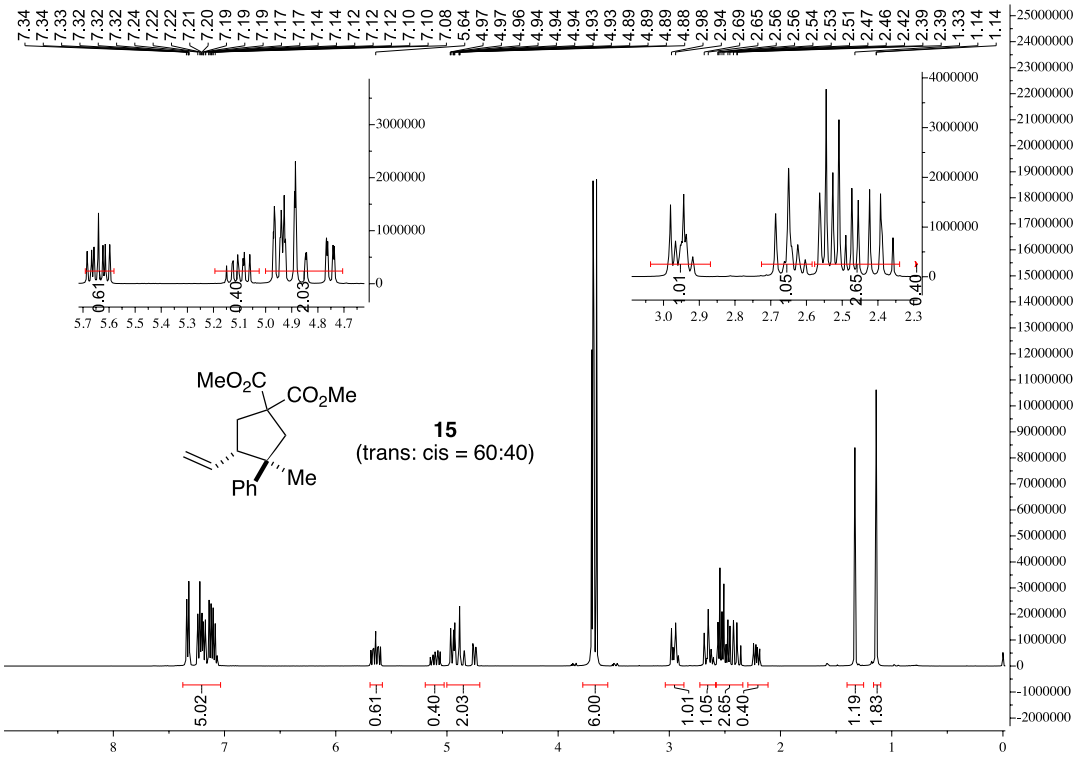

MeO2C
CO2Me
Me
12
(trans: cis ≈ 77:23)

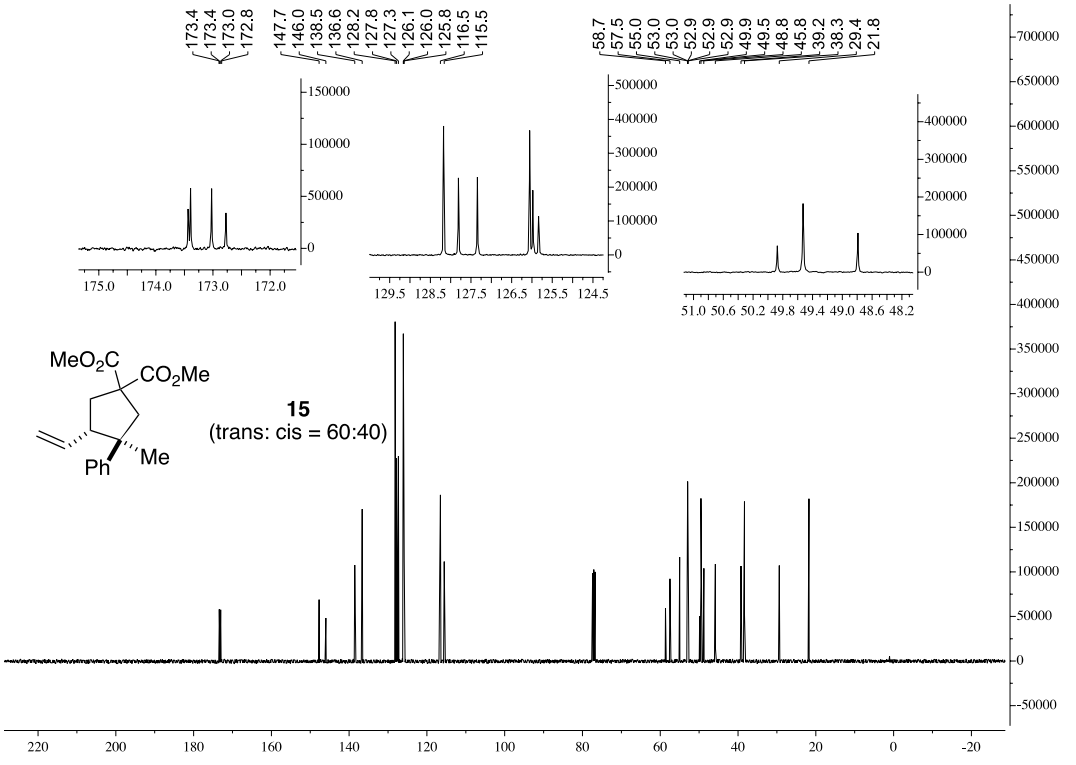

MeO2C
CO2Me
B
O
O
13
(trans: cis ≈ 65:35)

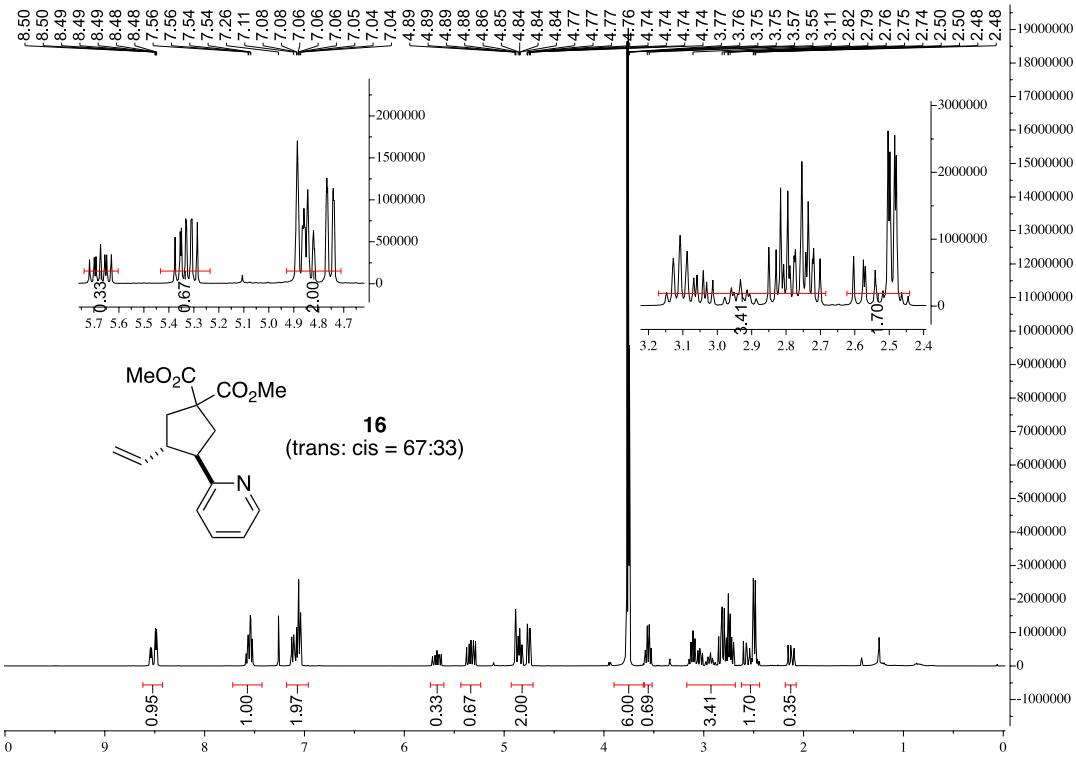

MeO2C
CO2Me
B
O
O
13
(trans: cis ≈ 65:35)

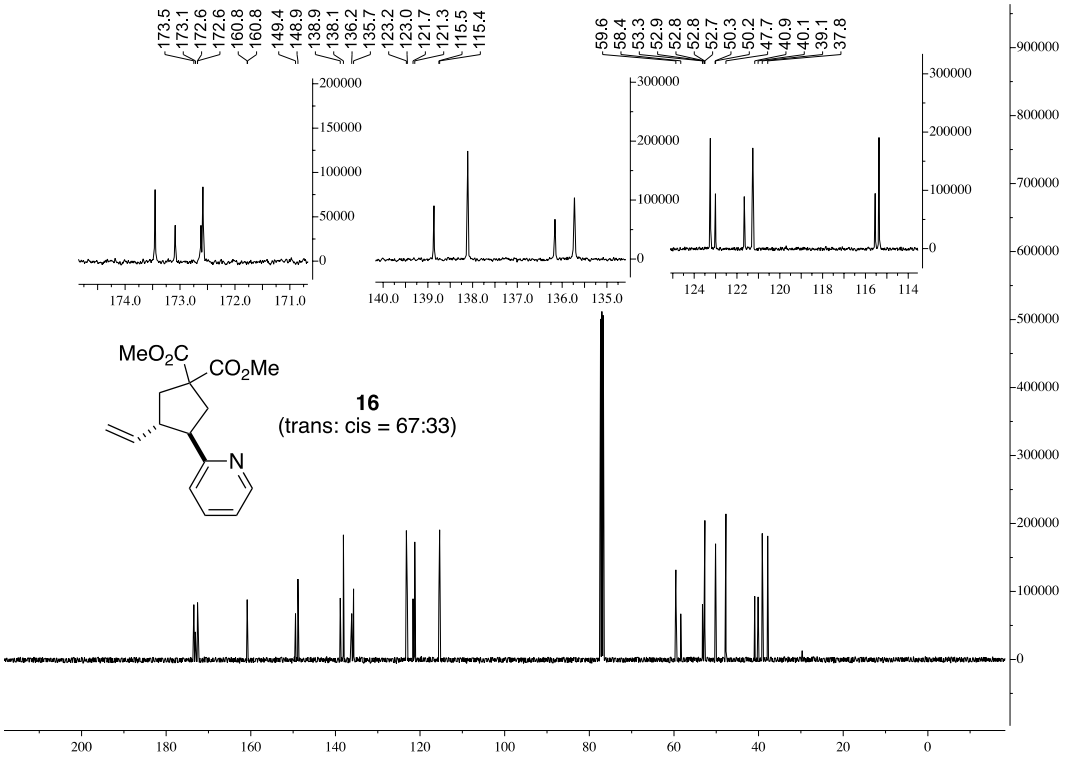

MeO2C
CO2Me
Ph
Ph
14

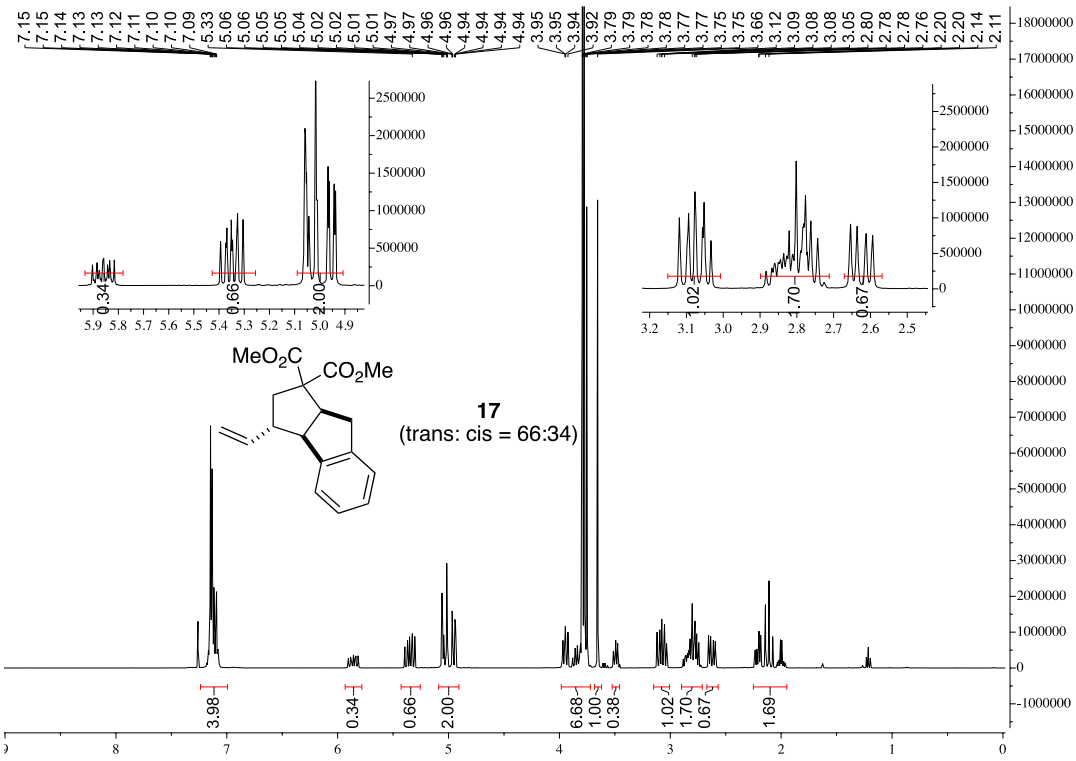

MeO2C
CO2Me
Ph
Ph
14

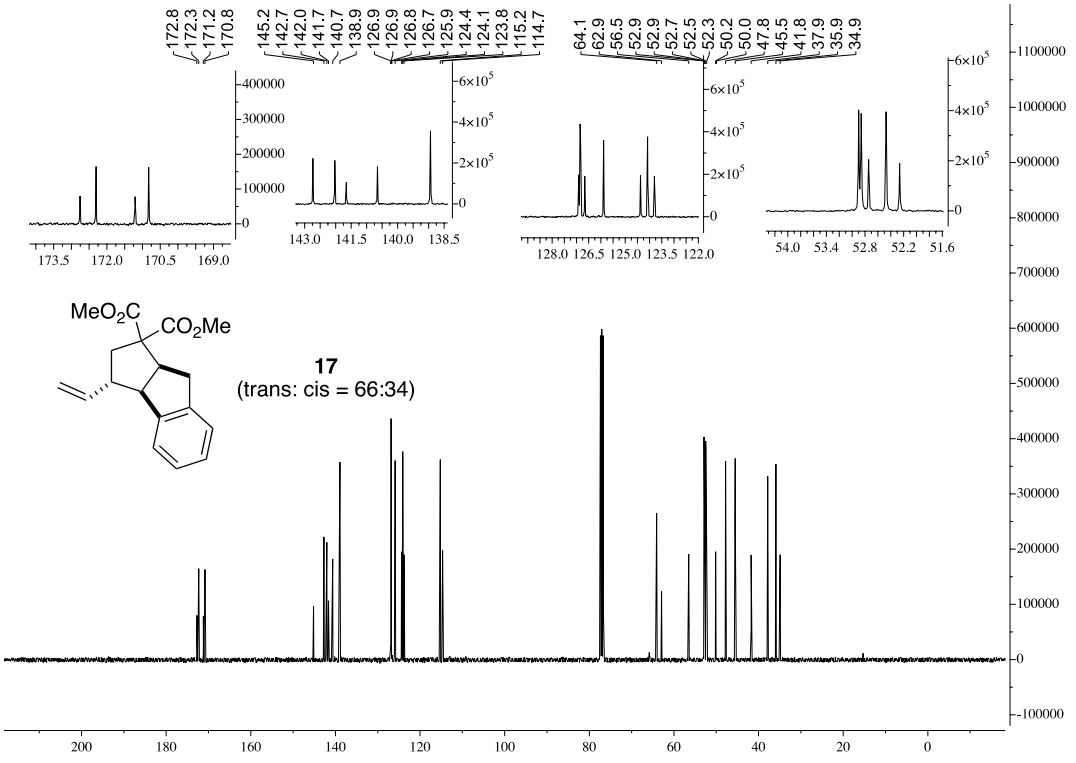

MeO2C
CO2Me
Ph
Me
15
(trans: cis = 60:40)

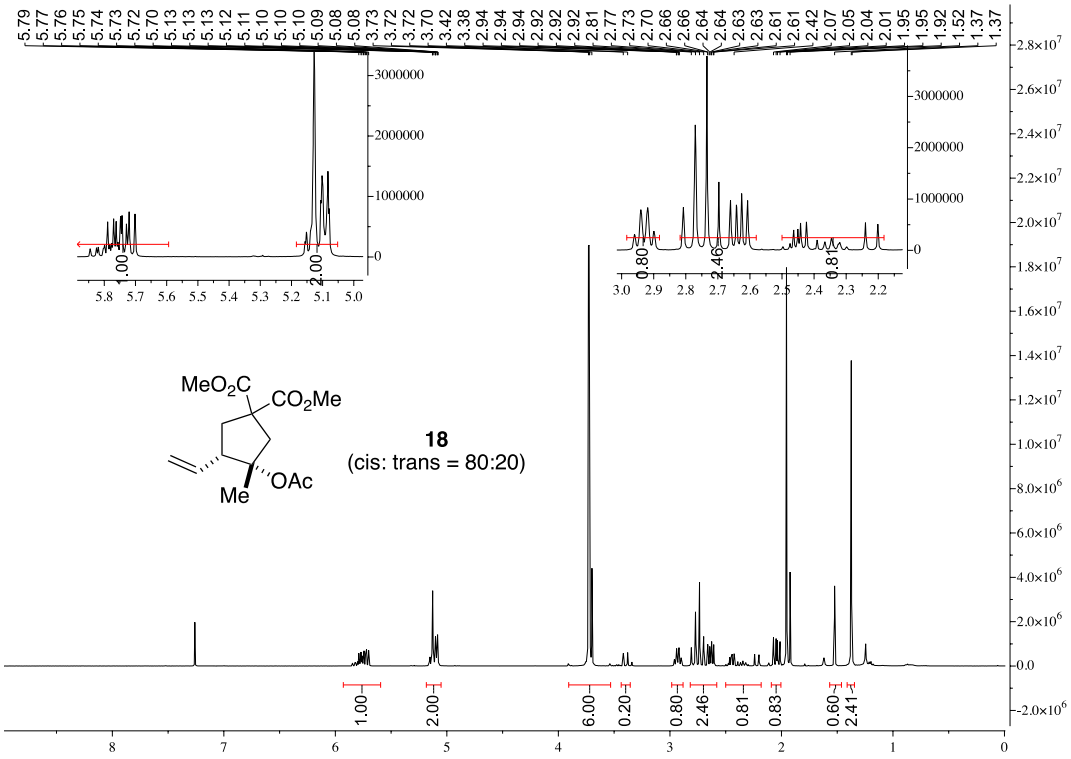

MeO2C
CO2Me
Ph
Me
15
(trans: cis = 60:40)

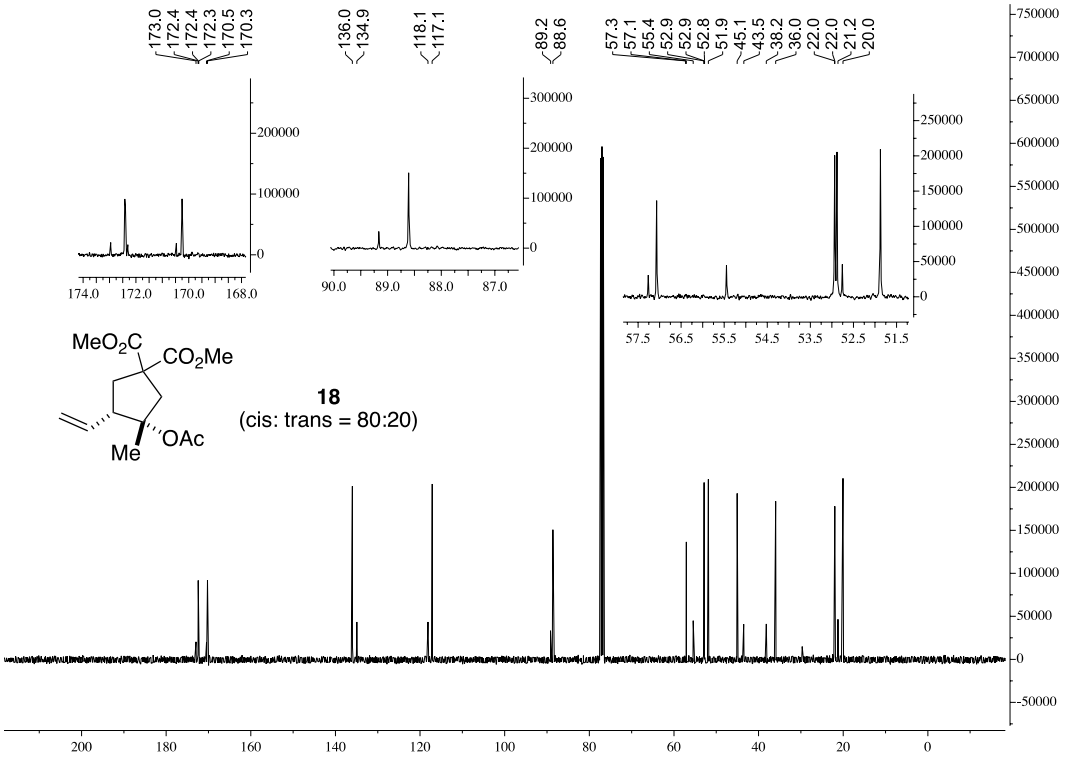

MeO2C
CO2Me
N
16
(trans: cis = 67:33)

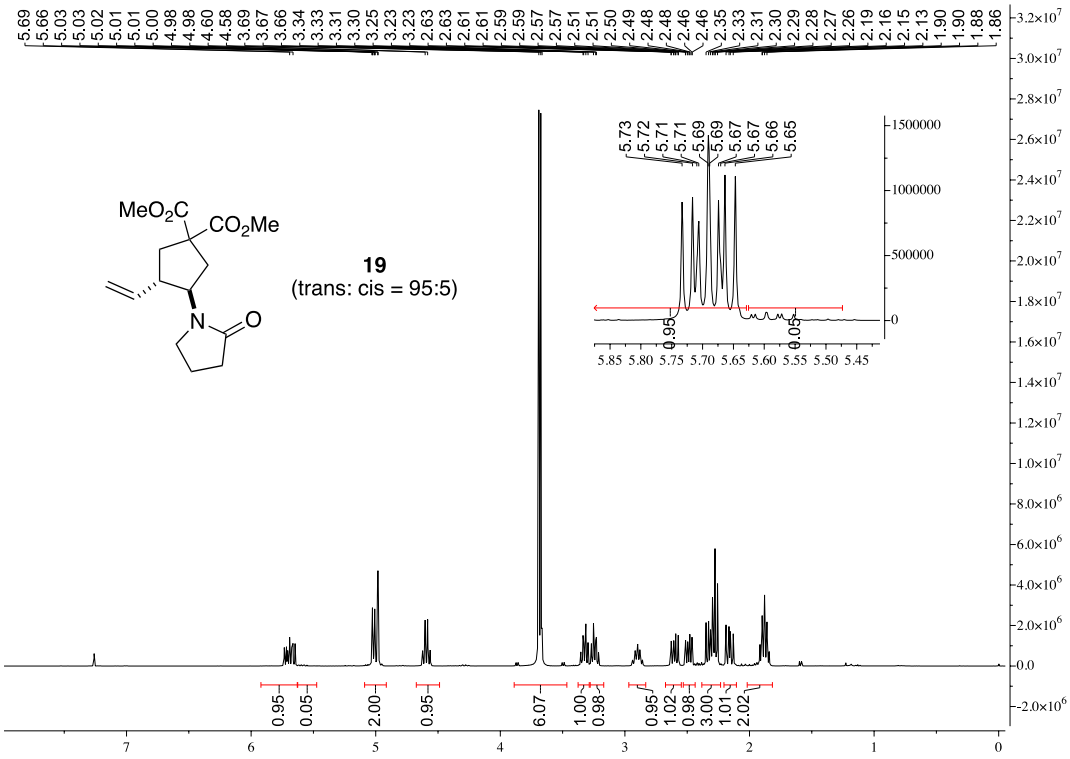

MeO2C
CO2Me
N
16
(trans: cis = 67:33)

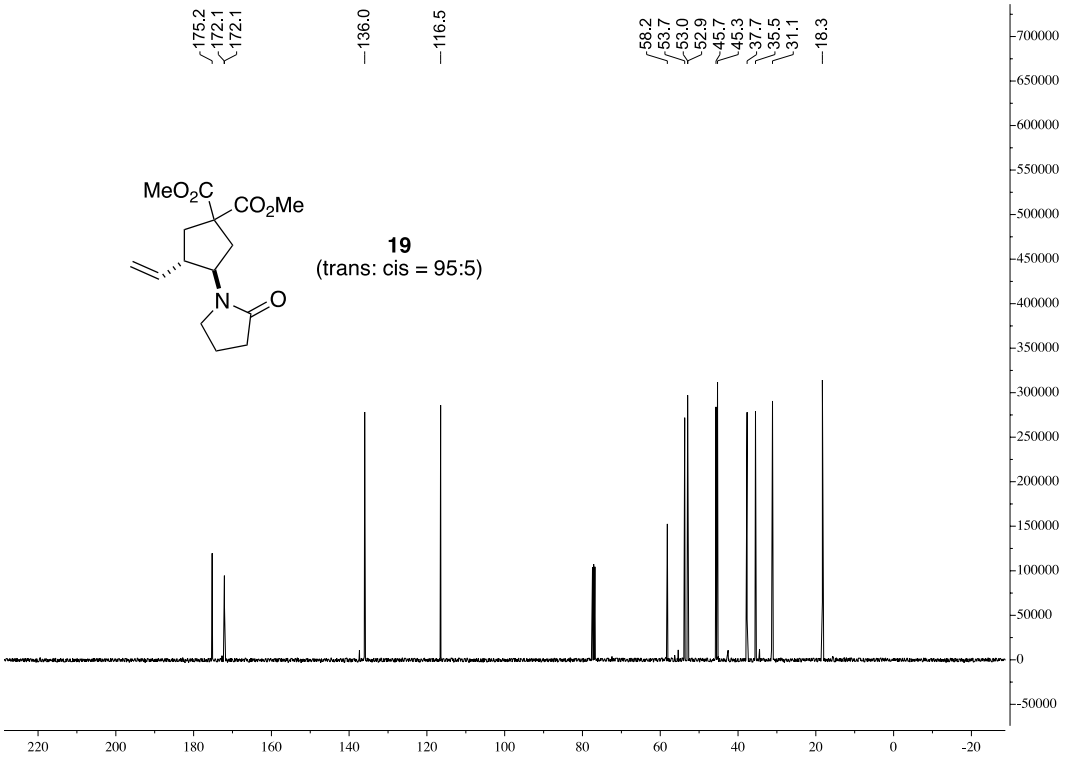

MeO2C
CO2Me
17
(trans: cis = 66:34)

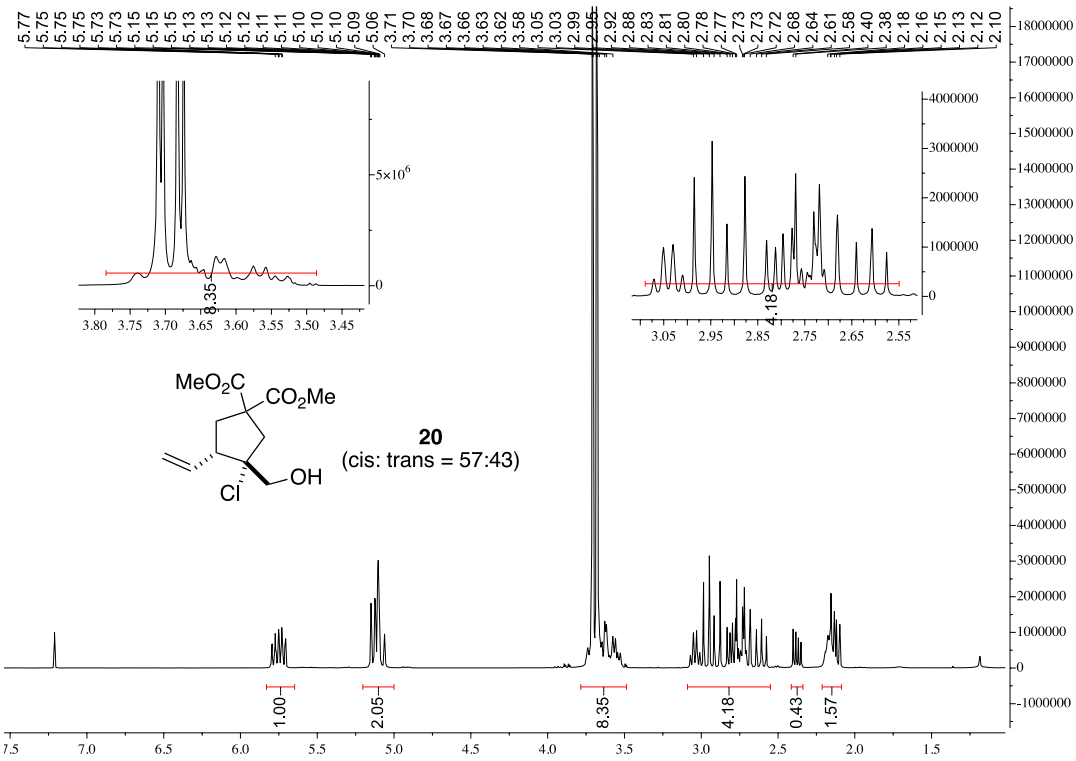

MeO2C
CO2Me
17
(trans: cis = 66:34)

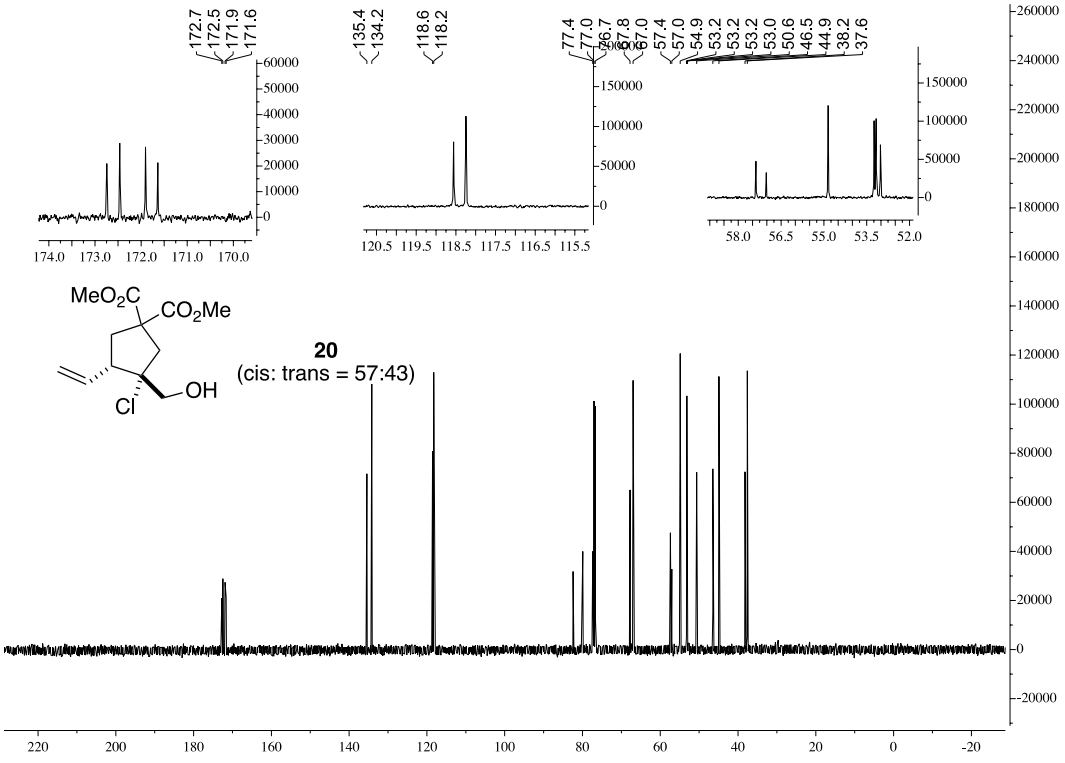

MeO2C
CO2Me
Me
OAc
18
(cis: trans = 80:20)

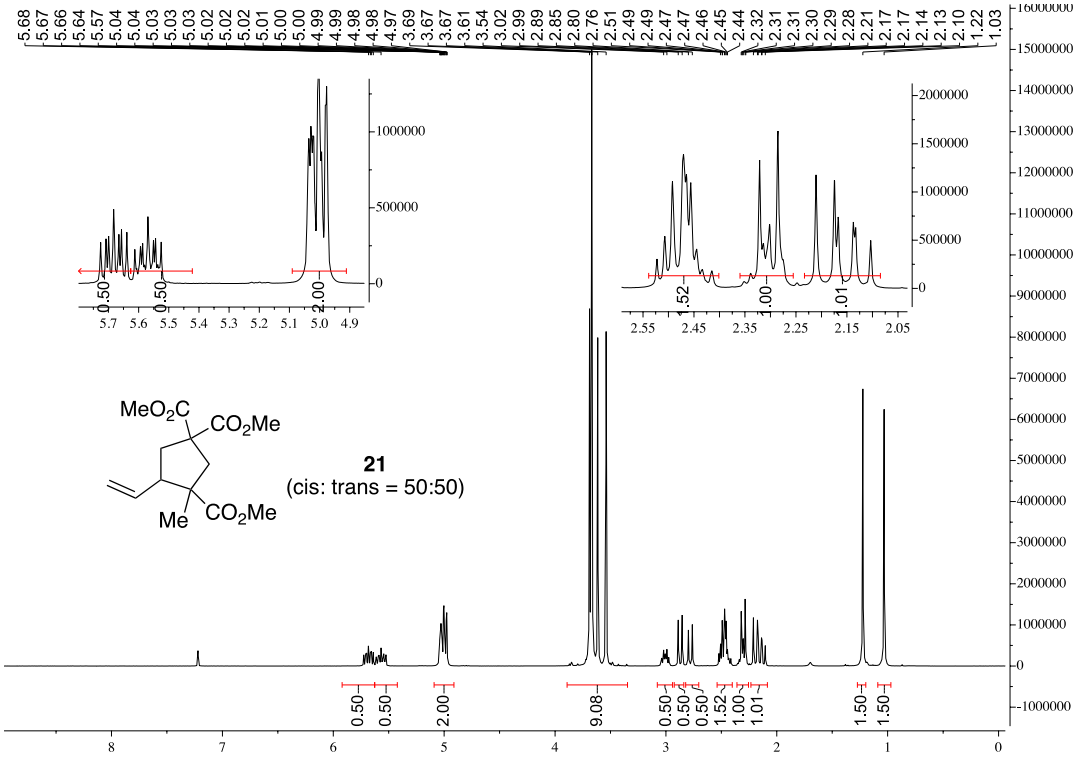

MeO2C
CO2Me
Me
OAc
18
(cis: trans = 80:20)

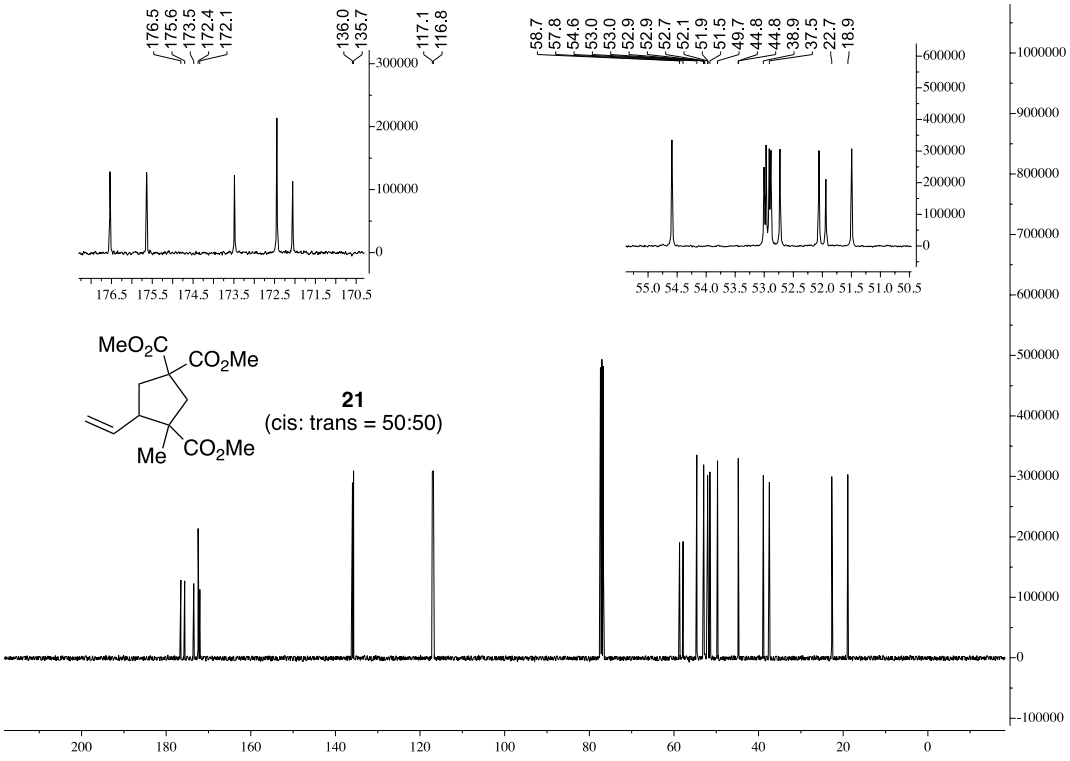

MeO2C
CO2Me
N
O
19
(trans: cis = 95:5)

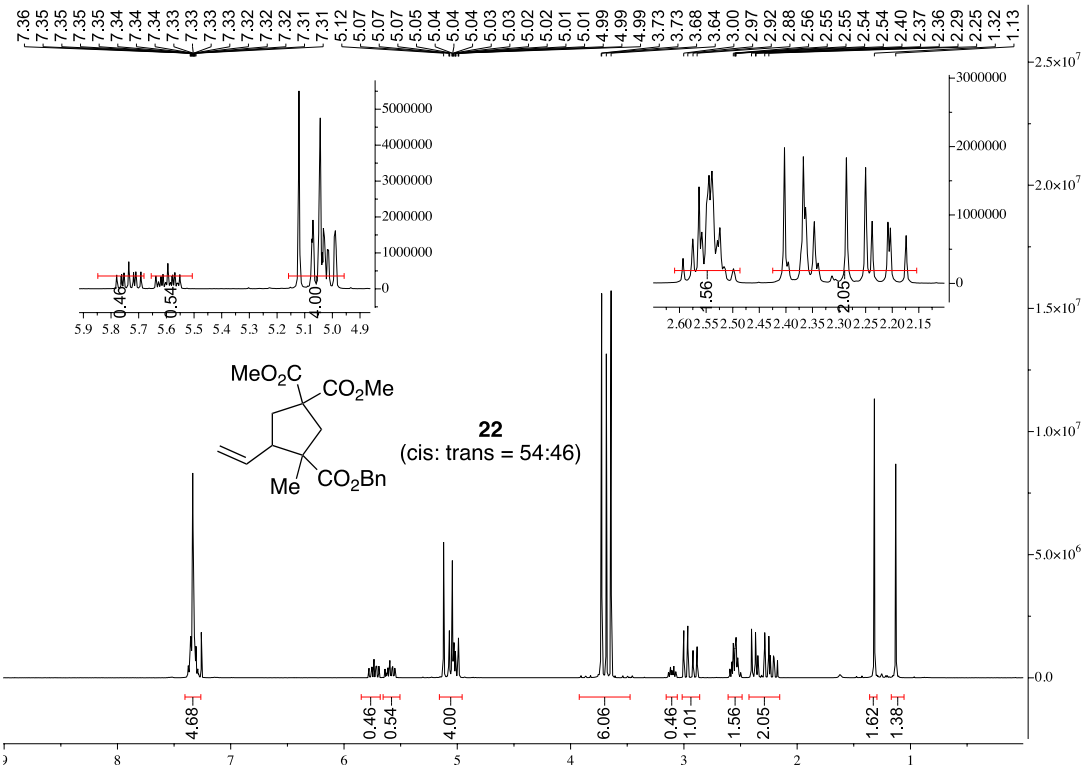

MeO2C
CO2Me
N
O
19
(trans: cis = 95:5)

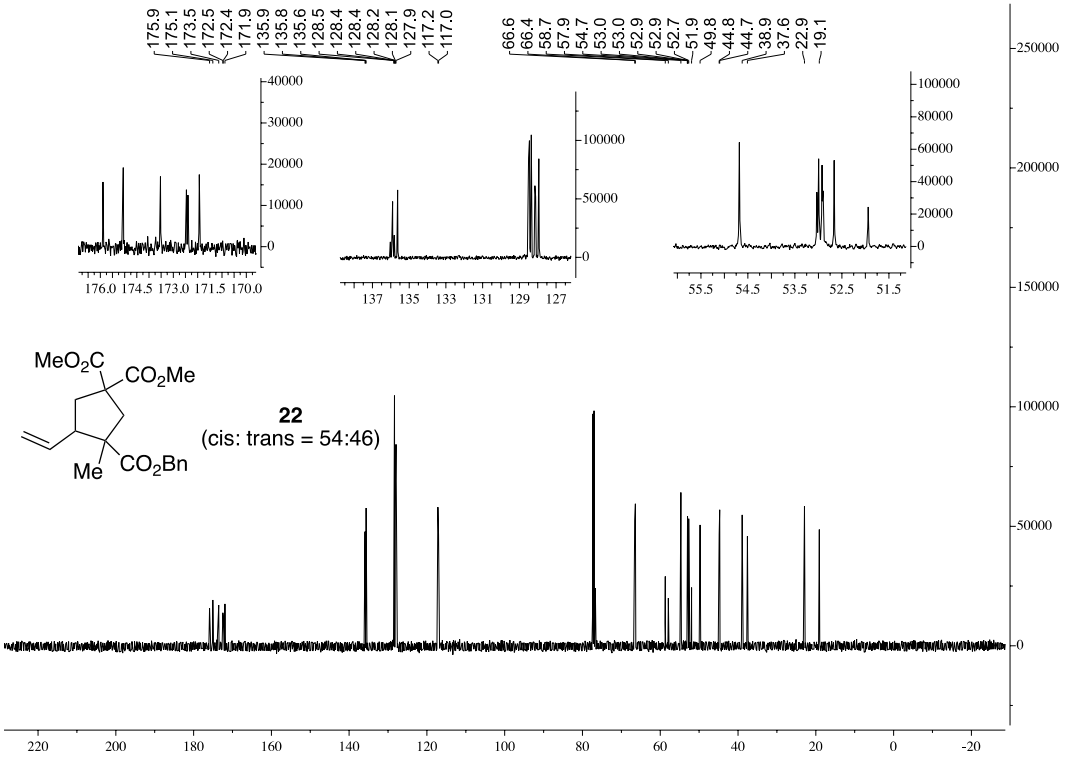

MeO2C
CO2Me
OH
Cl
20
(cis: trans = 57:43)

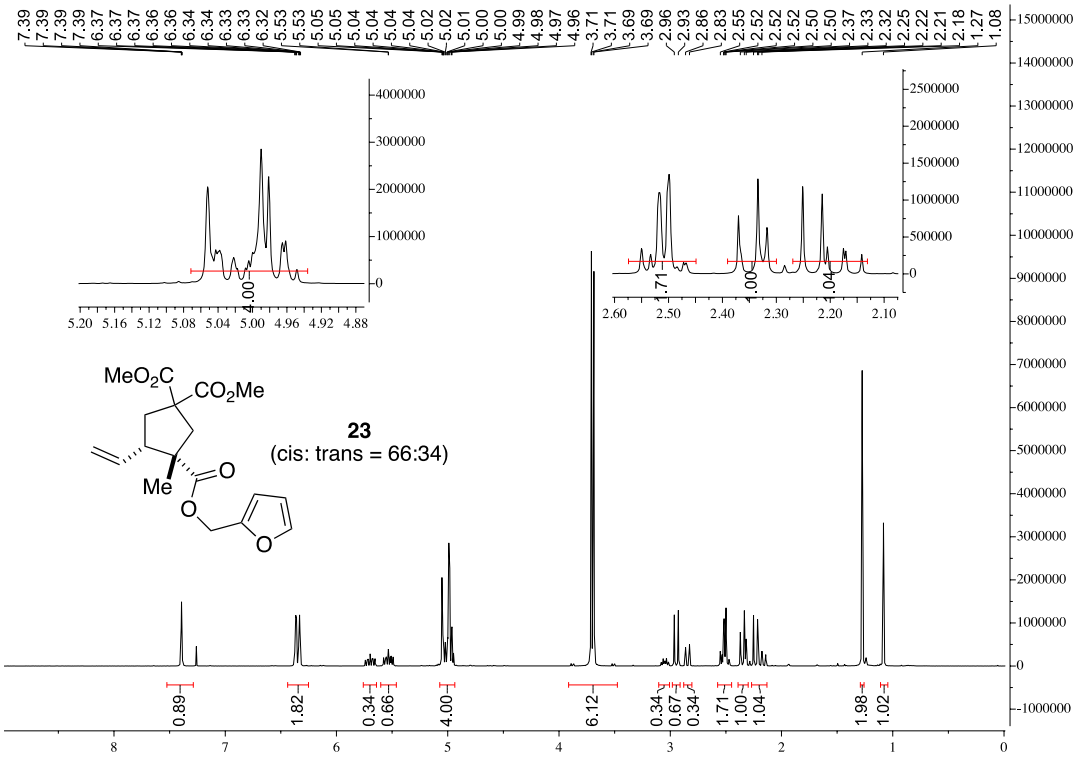

MeO2C
CO2Me
OH
Cl
20
(cis: trans = 57:43)

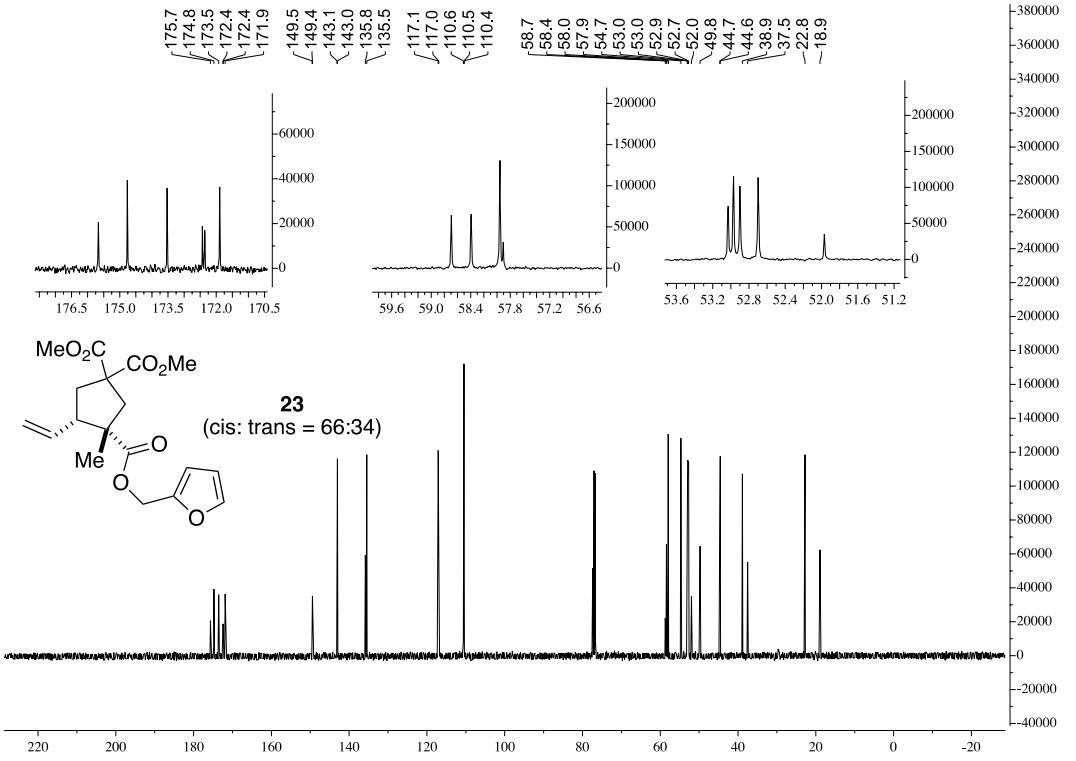

MeO2C
CO2Me
Me
CO2Me
21
(cis: trans = 50:50)

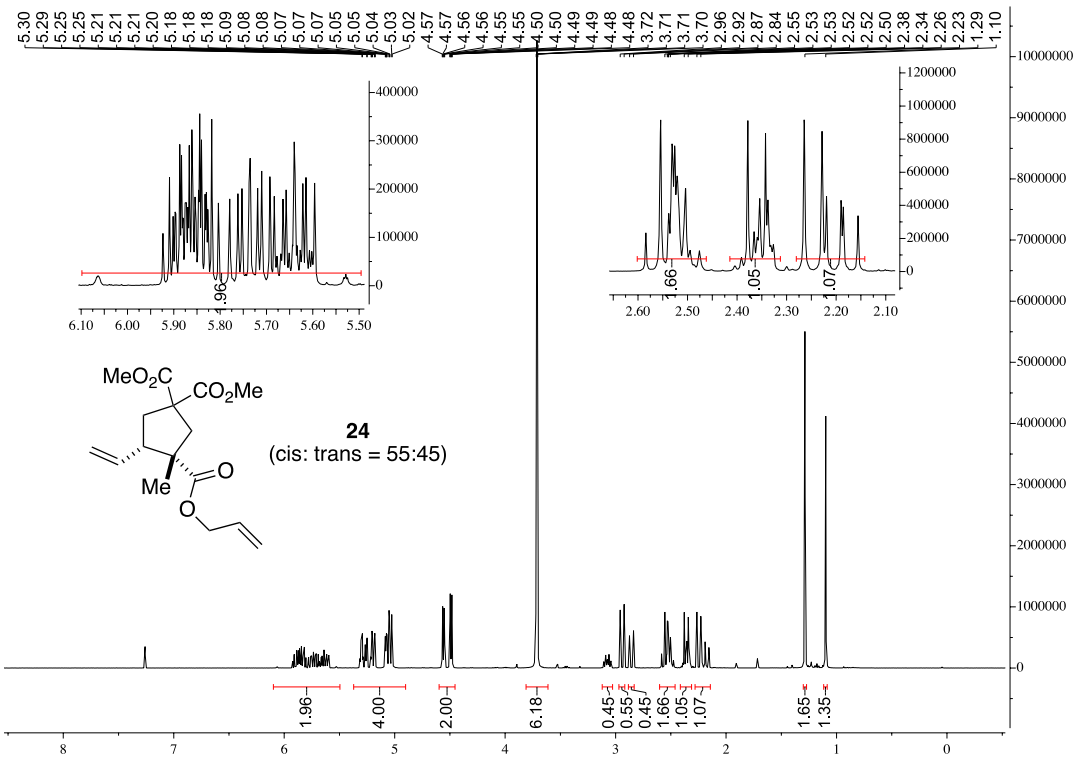

MeO2C
CO2Me
Me
CO2Me
21
(cis: trans = 50:50)

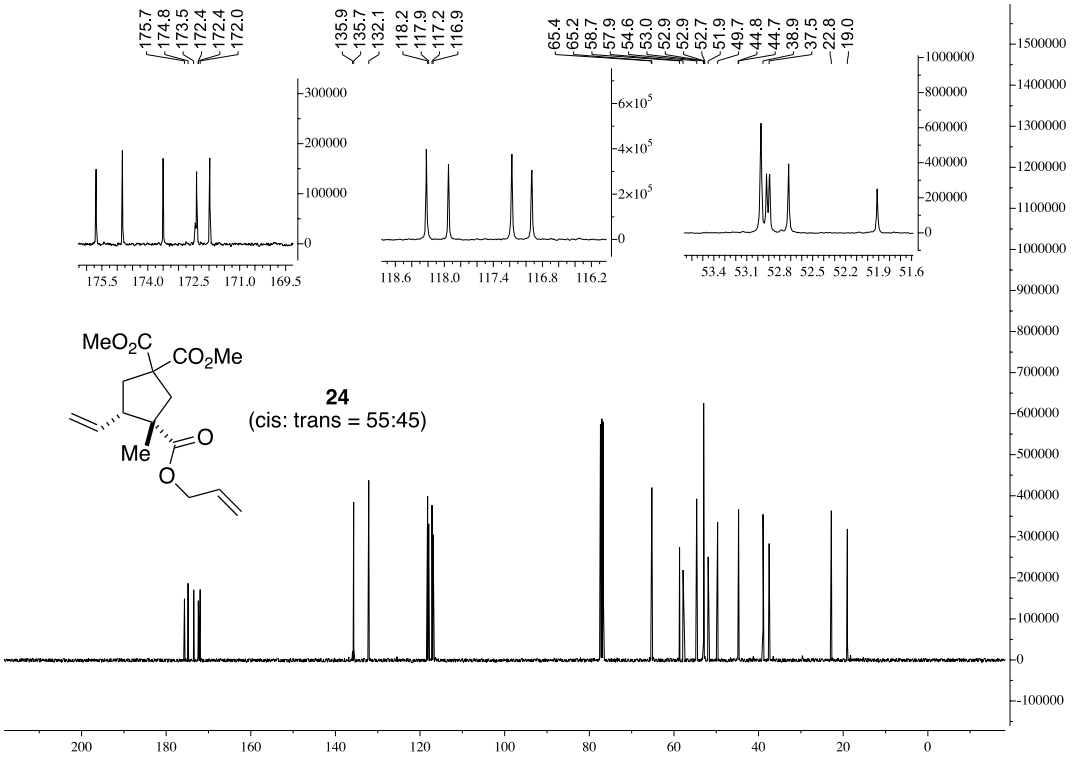

MeO2C
CO2Me
Me
CO2Bn
22
(cis: trans = 54:46)

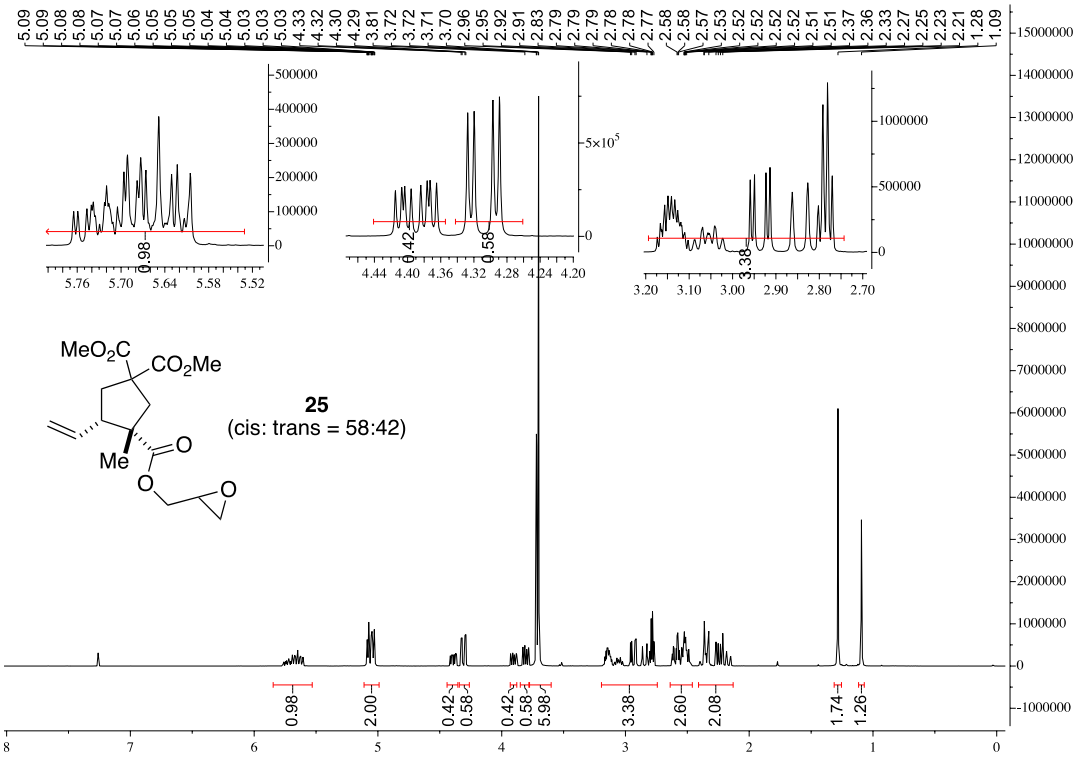

MeO2C
CO2Me
Me
CO2Bn
22
(cis: trans = 54:46)

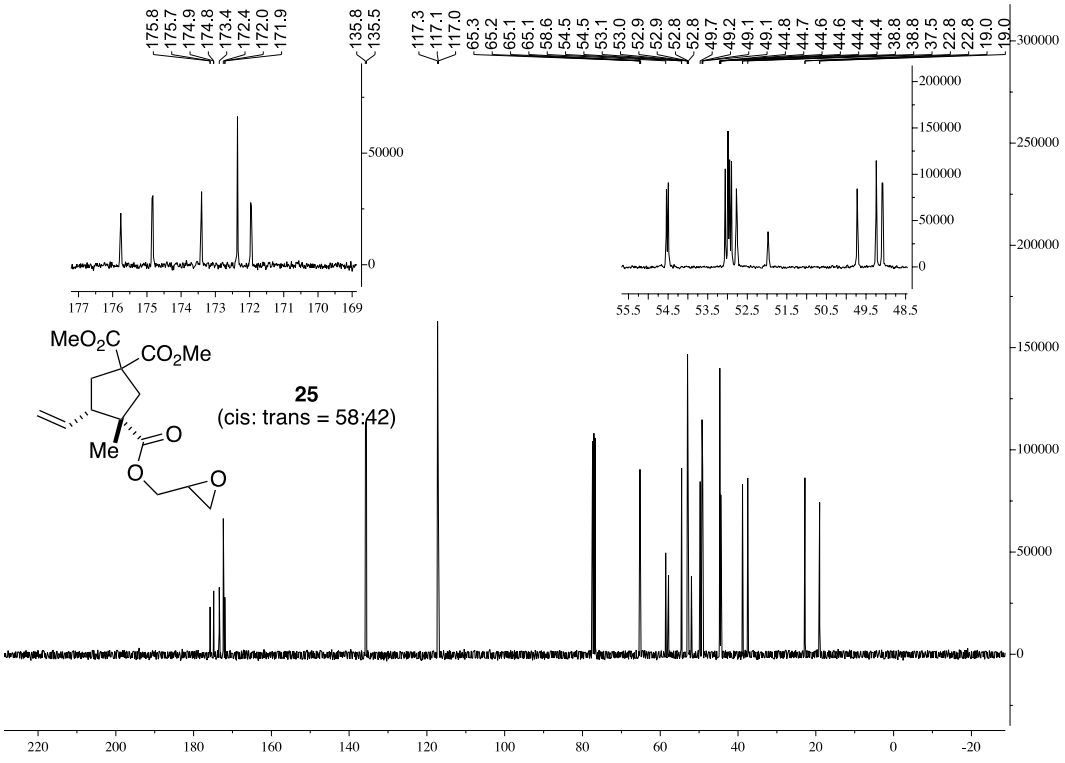

MeO2C
CO2Me
Me
O
O
O
23
(cis: trans = 66:34)

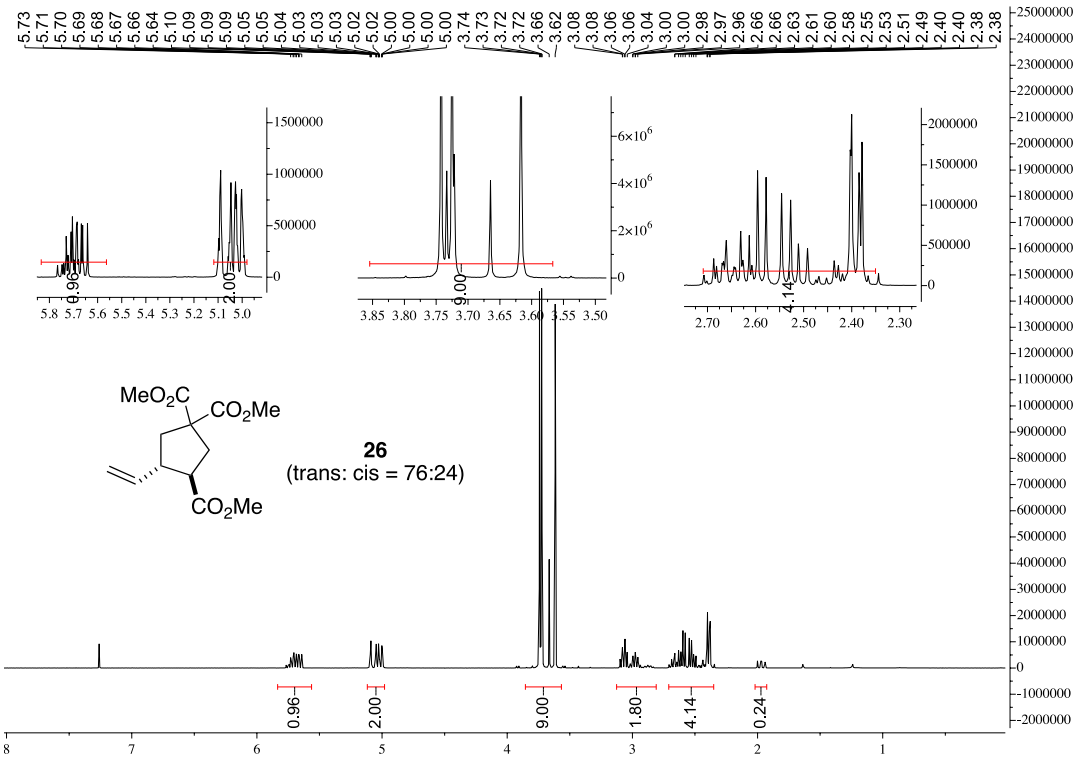

MeO2C
CO2Me
Me
O
O
O
23
(cis: trans = 66:34)

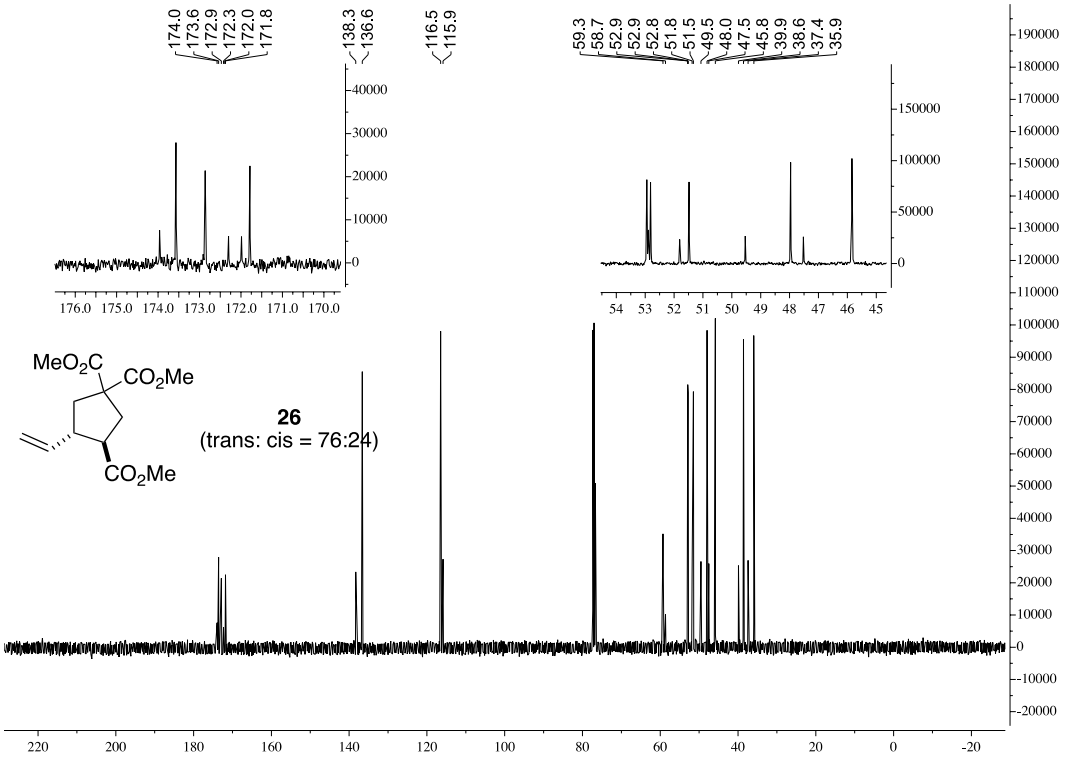

MeO2C
CO2Me
Me
O
O
24
(cis: trans = 55:45)

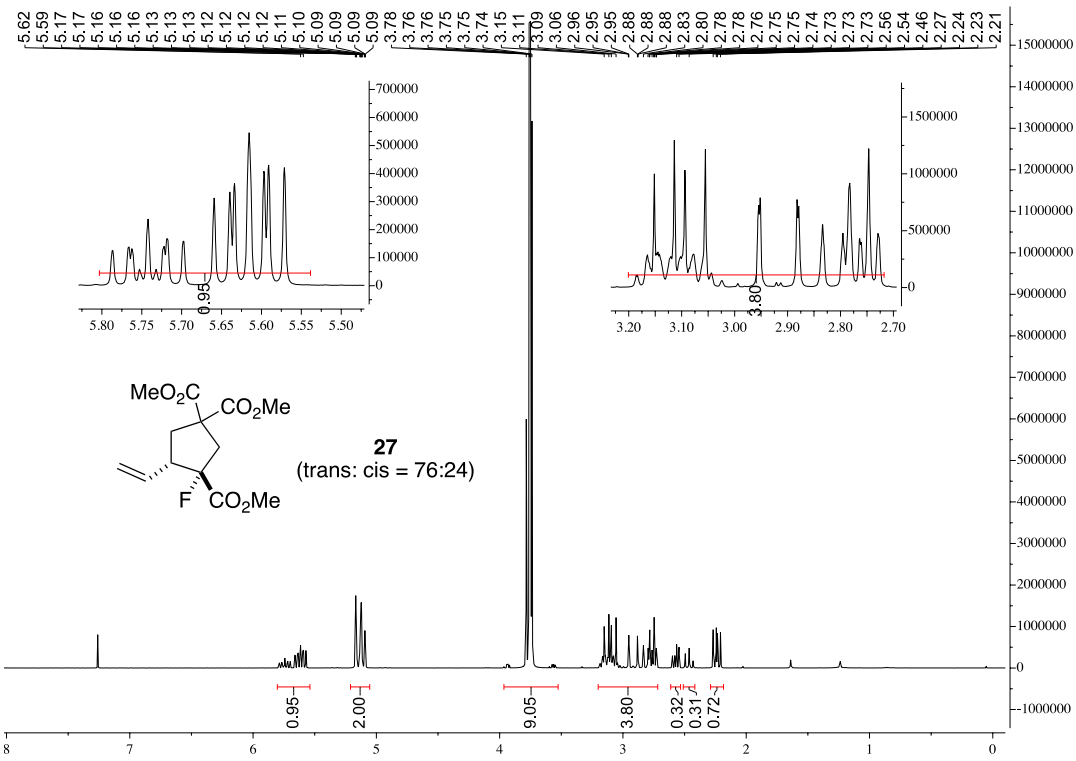

MeO2C
CO2Me
Me
O
O
24
(cis: trans = 55:45)

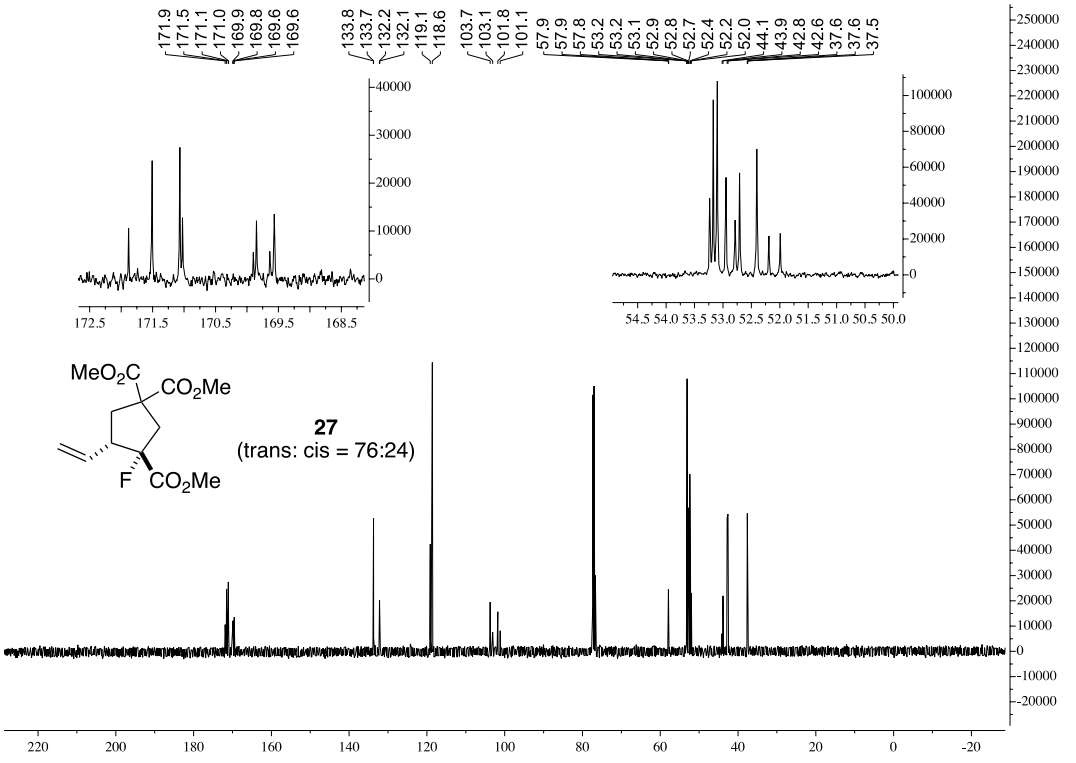

MeO2C
CO2Me
Me
O
O
O
25
(cis: trans = 58:42)

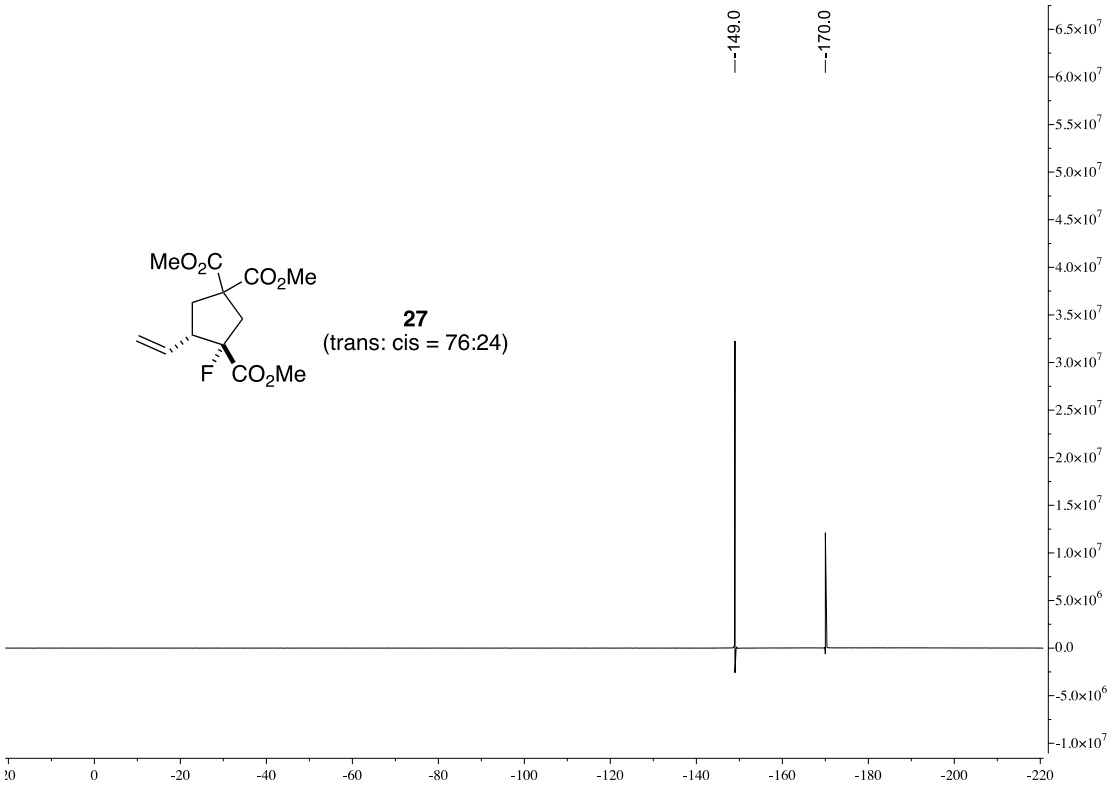

MeO2C
CO2Me
Me
O
O
O
25
(cis: trans = 58:42)

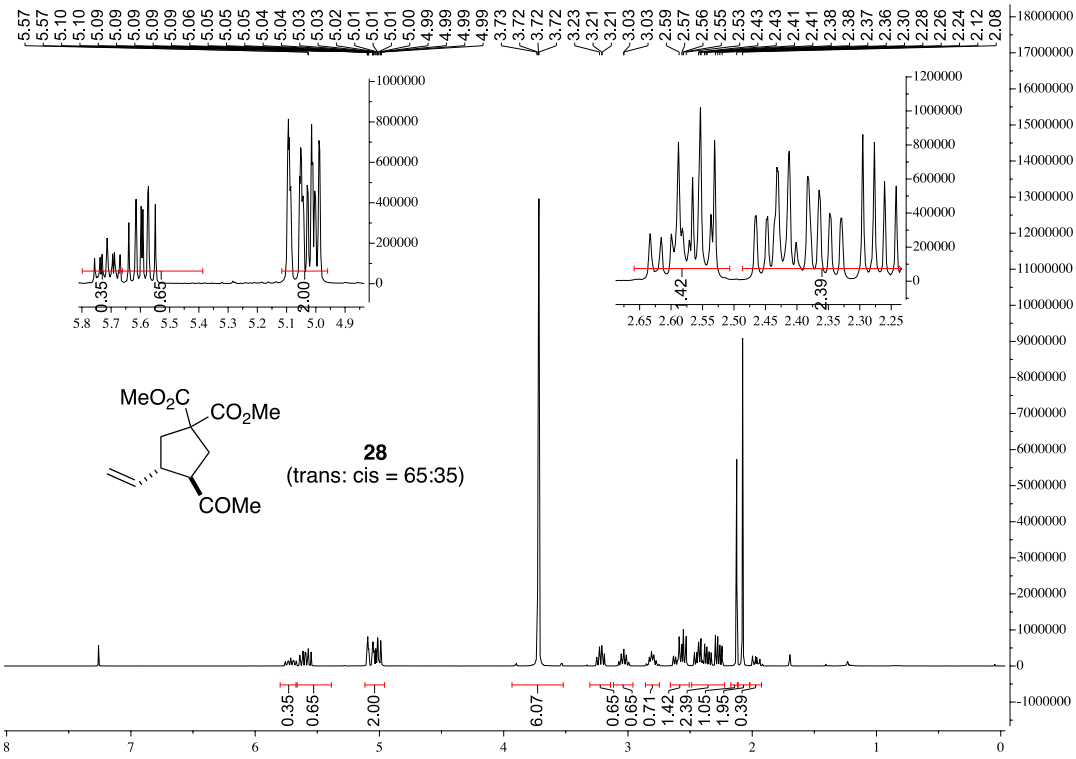

MeO2C
CO2Me
CO2Me
26
(trans: cis = 76:24)
0.96
2.00
9.00
1.80
4.14
0.24

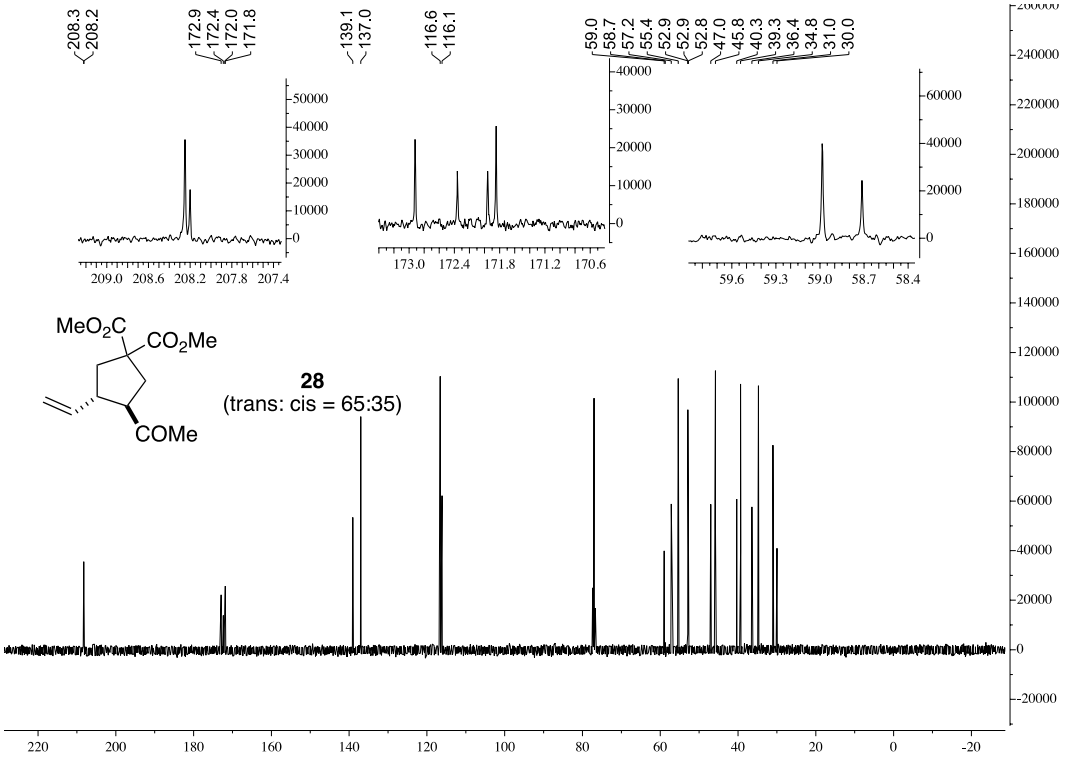

MeO2C
CO2Me
CO2Me
26
(trans: cis = 76:24)

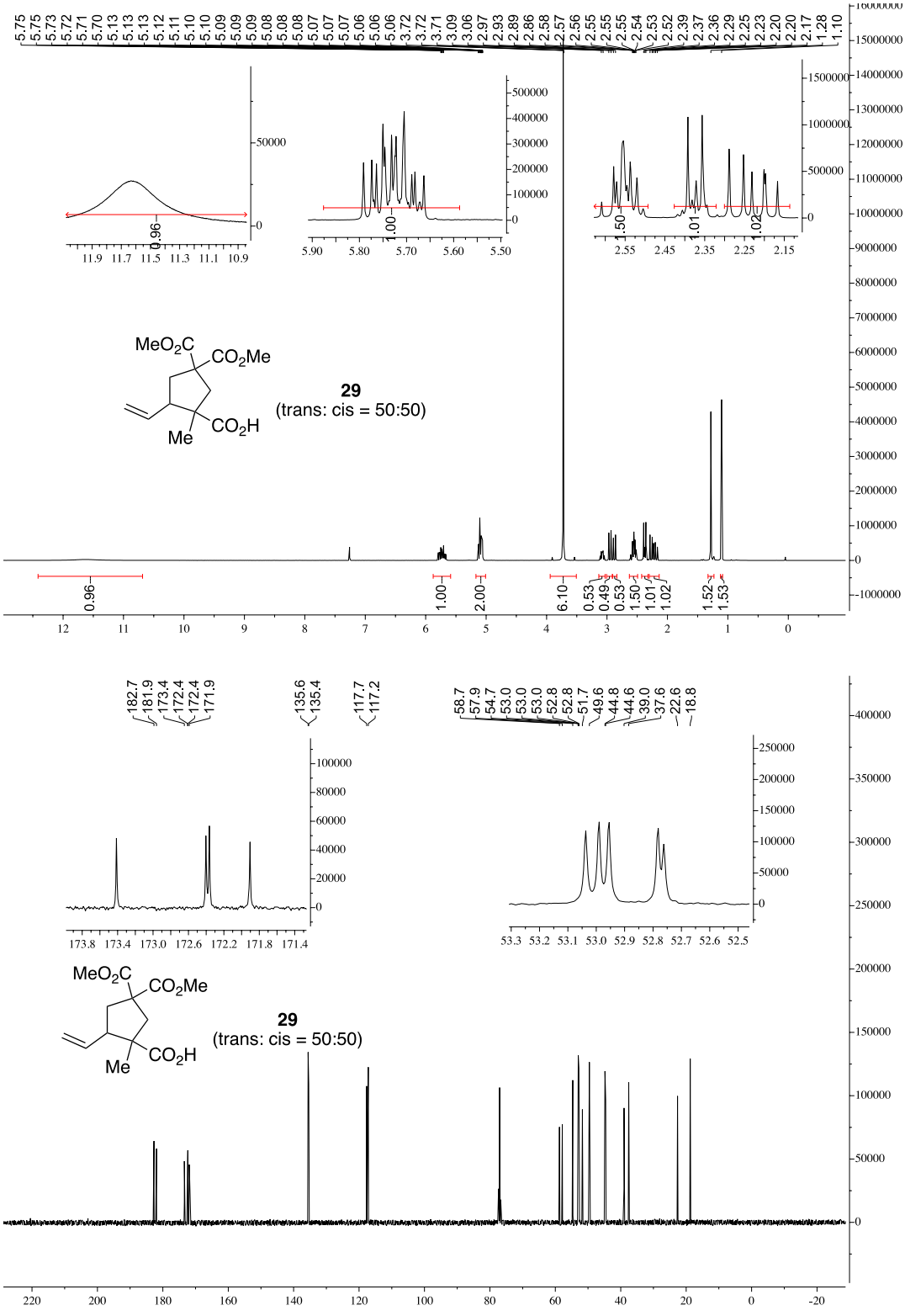

MeO2C
CO2Me
F
CO2Me
27
(trans: cis = 76:24)

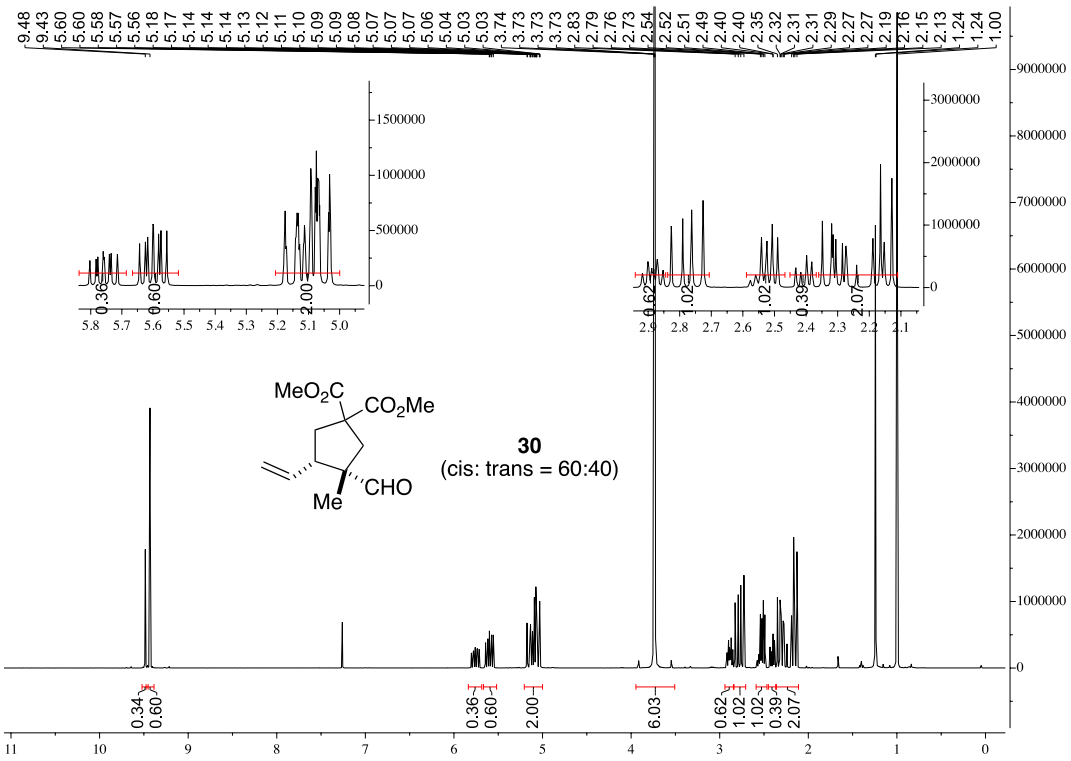

MeO2C
CO2Me
F
CO2Me
27
(trans: cis = 76:24)

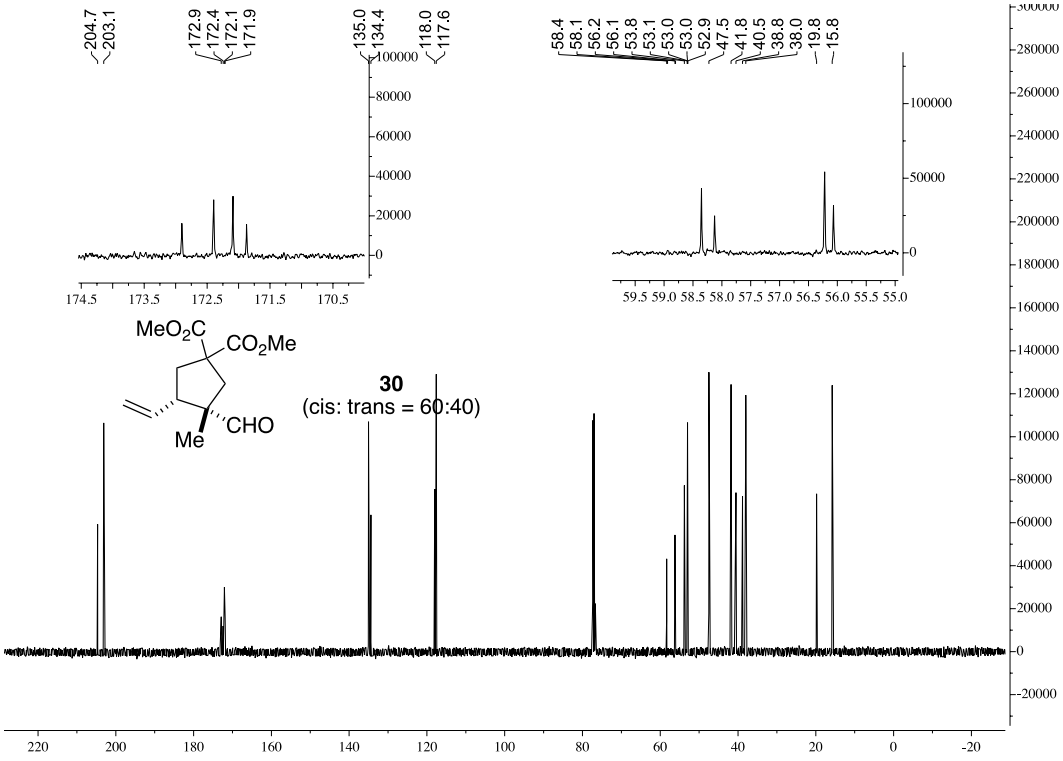

MeO2C
CO2Me
F
CO2Me
27
(trans: cis = 76:24)
-149.0
-170.0
6.5×10^7
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6
-1.0×10^7
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220

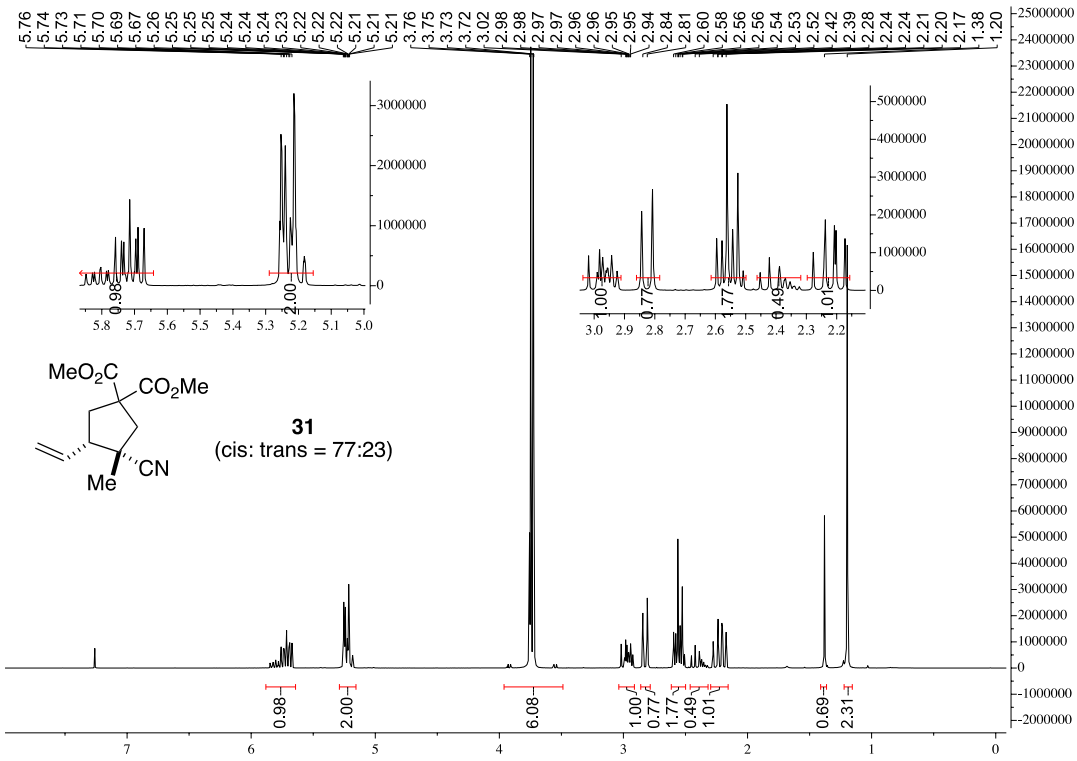

MeO2C
CO2Me
COMe
28
(trans: cis = 65:35)

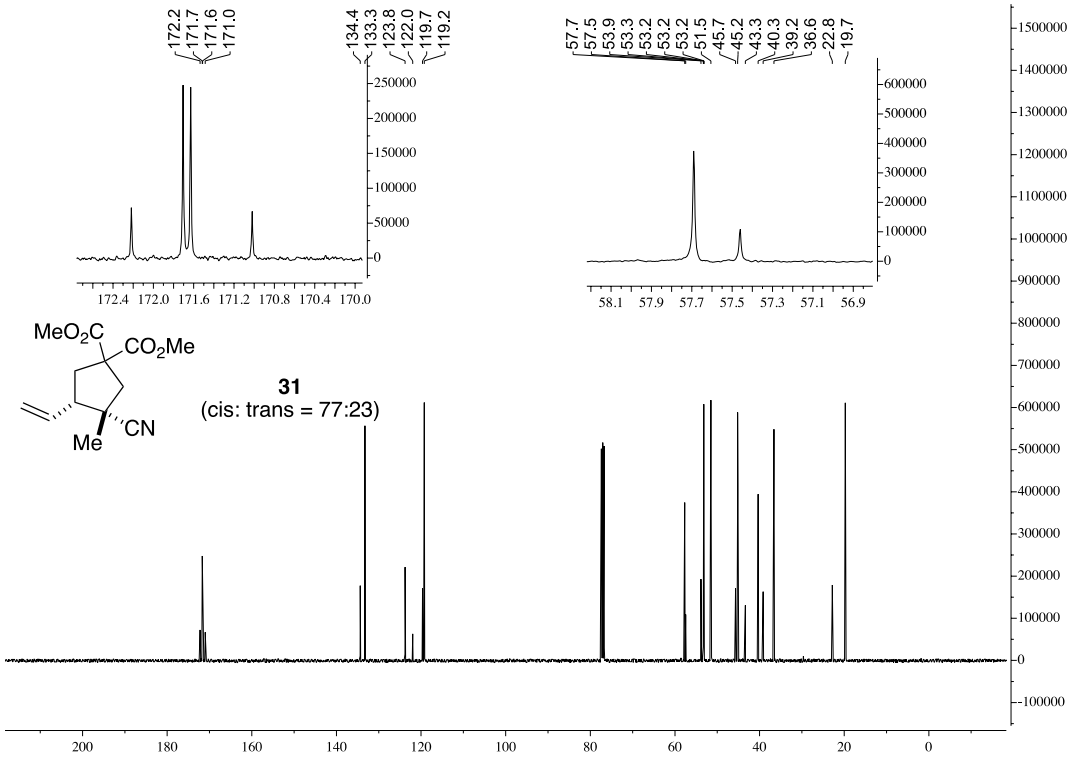

MeO2C
CO2Me
COMe
28
(trans: cis = 65:35)

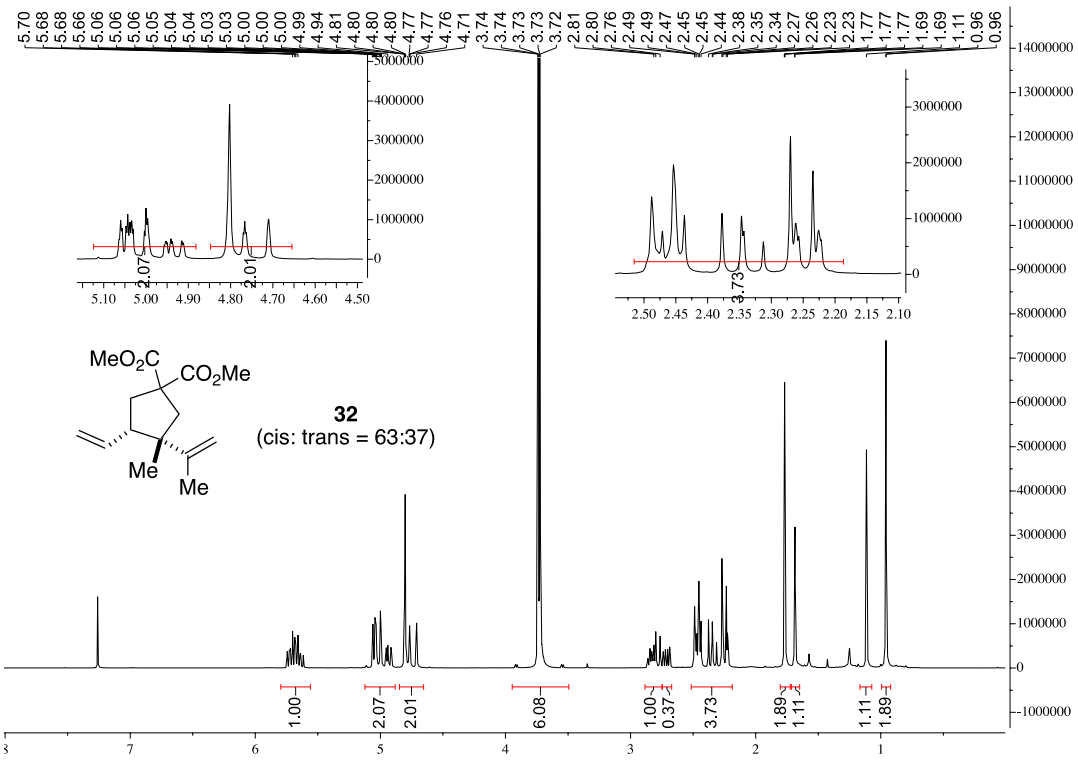

MeO2C
CO2Me
CO2H
Me
29
(trans: cis = 50:50)

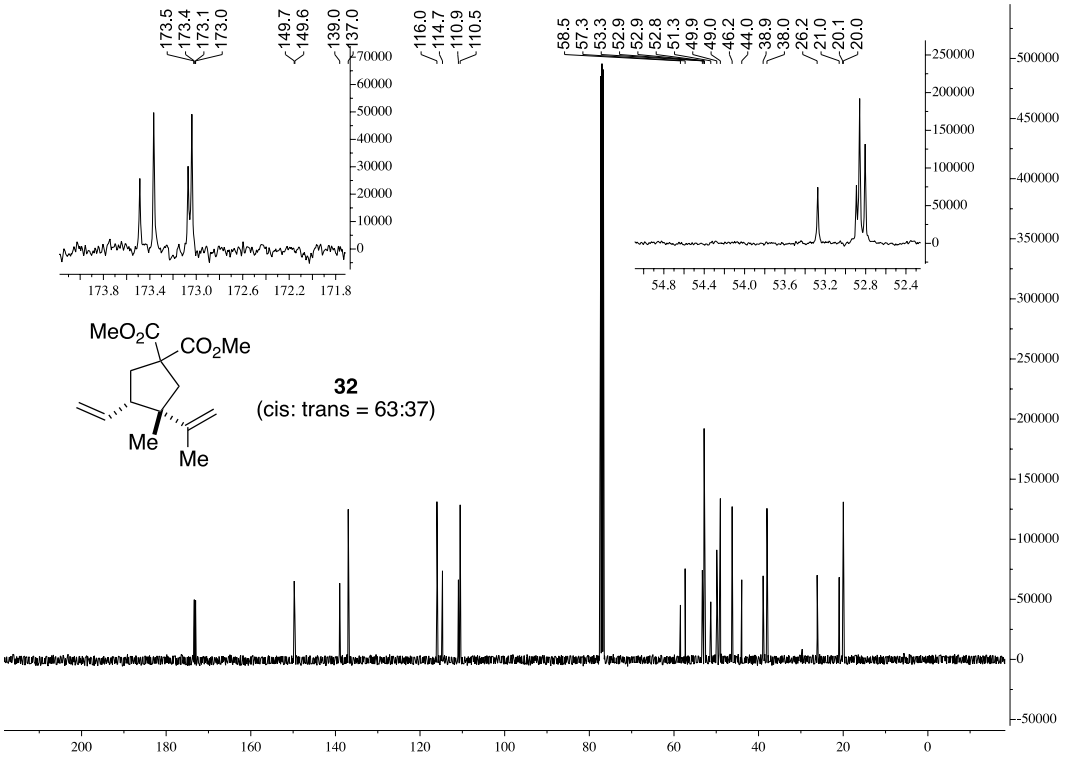

MeO2C
CO2Me
CHO
Me
30
(cis: trans = 60:40)

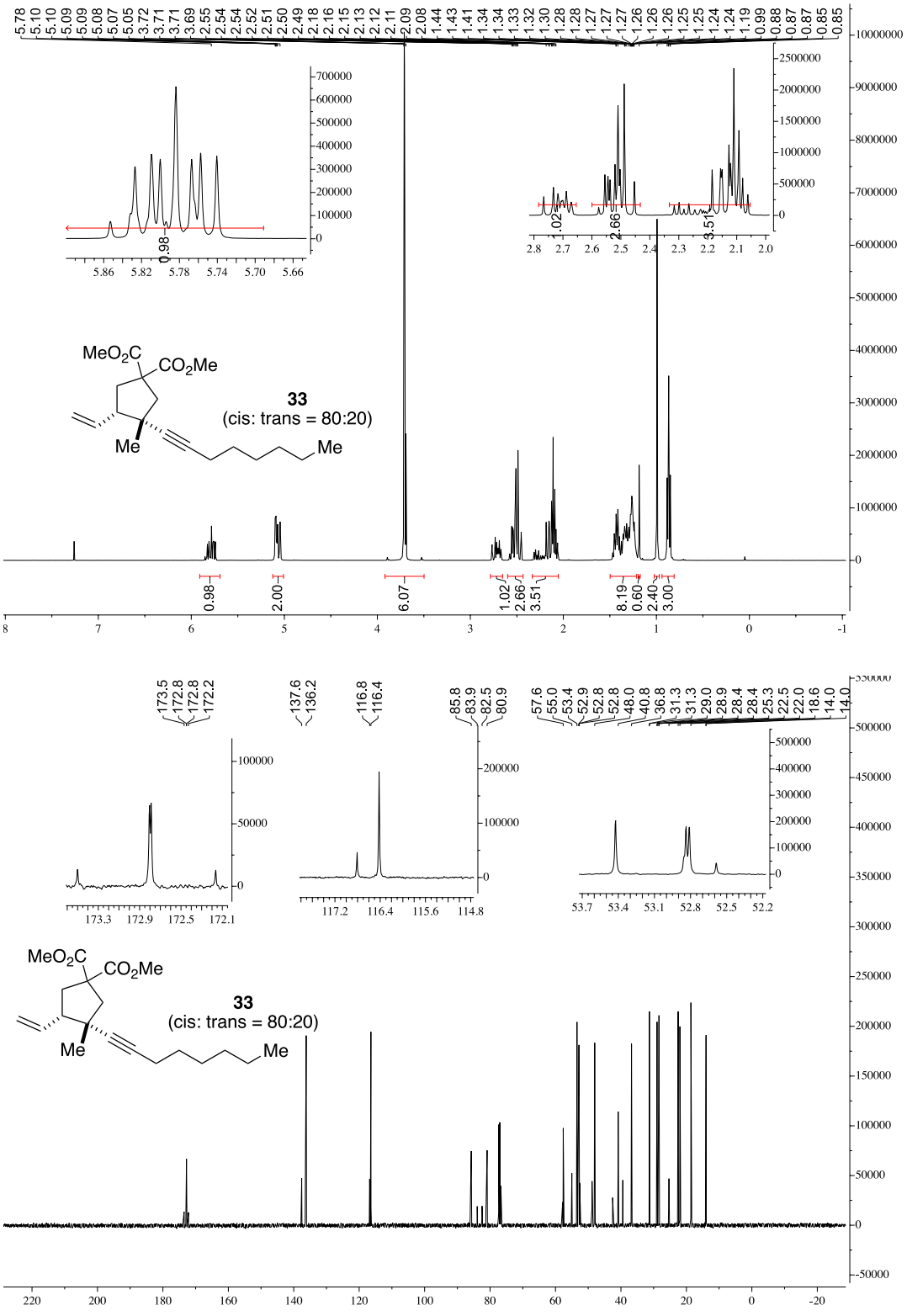

MeO2C
CO2Me
CHO
Me
30
(cis: trans = 60:40)

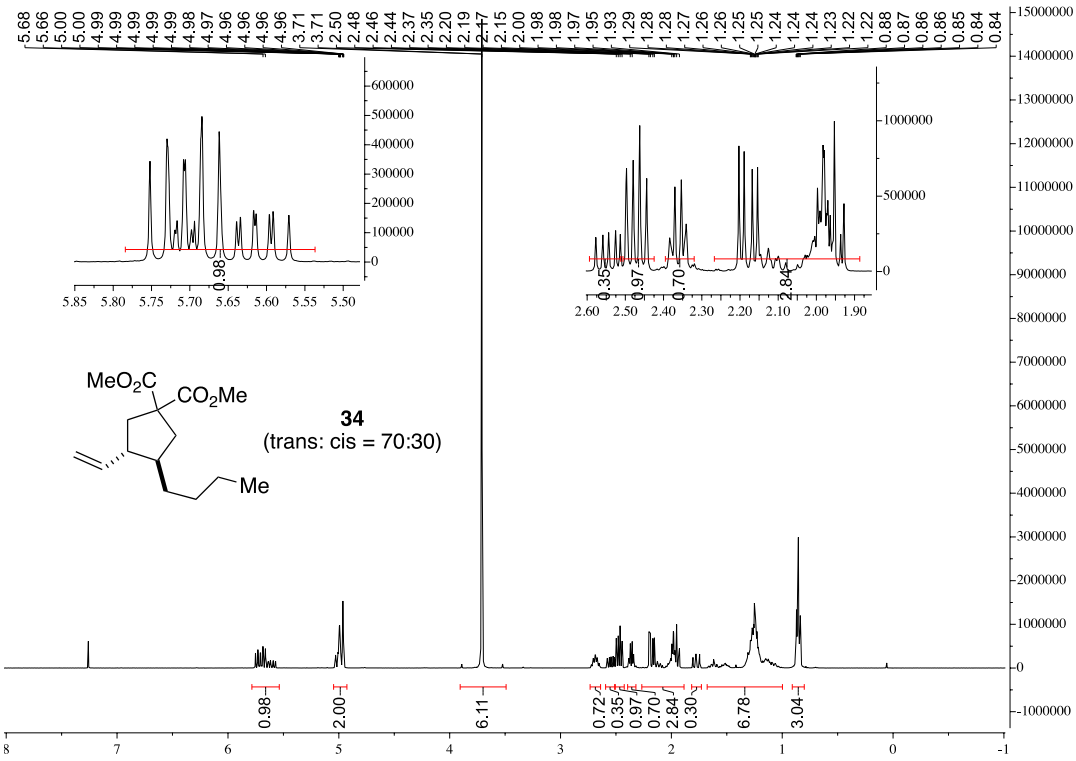

MeO2C
CO2Me
Me
CN
31
(cis: trans = 77:23)

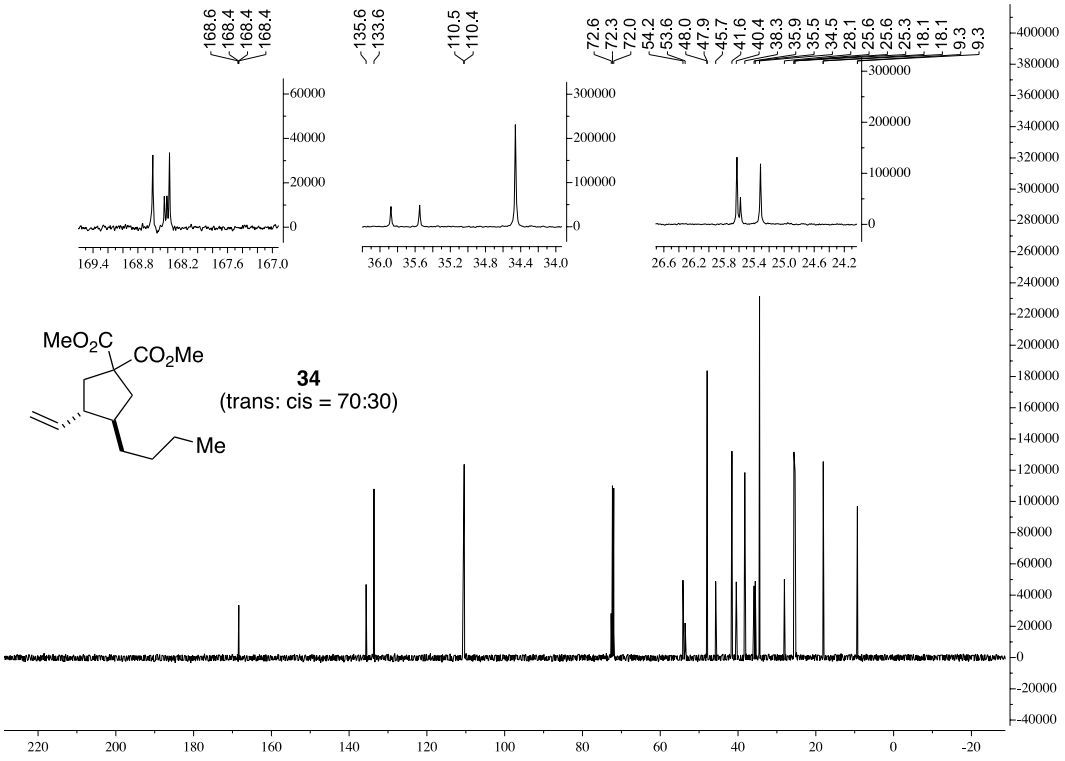

MeO2C
CO2Me
Me
CN
31
(cis: trans = 77:23)

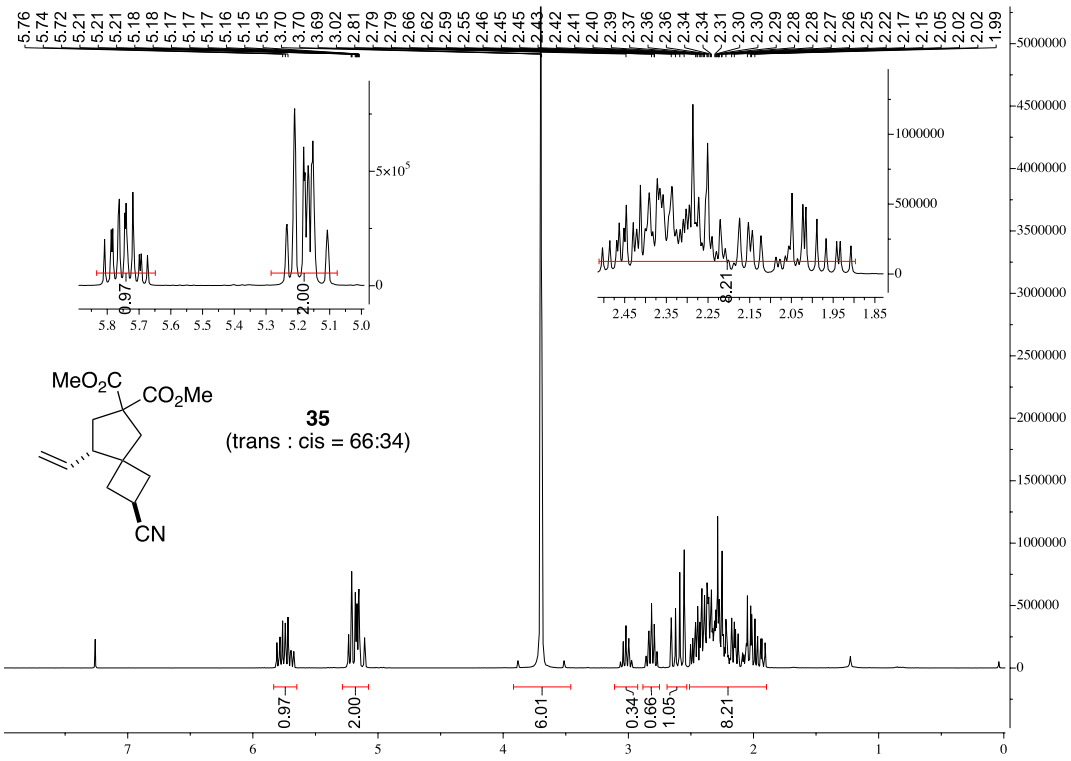

MeO2C
CO2Me
Me
Me
32
(cis: trans = 63:37)

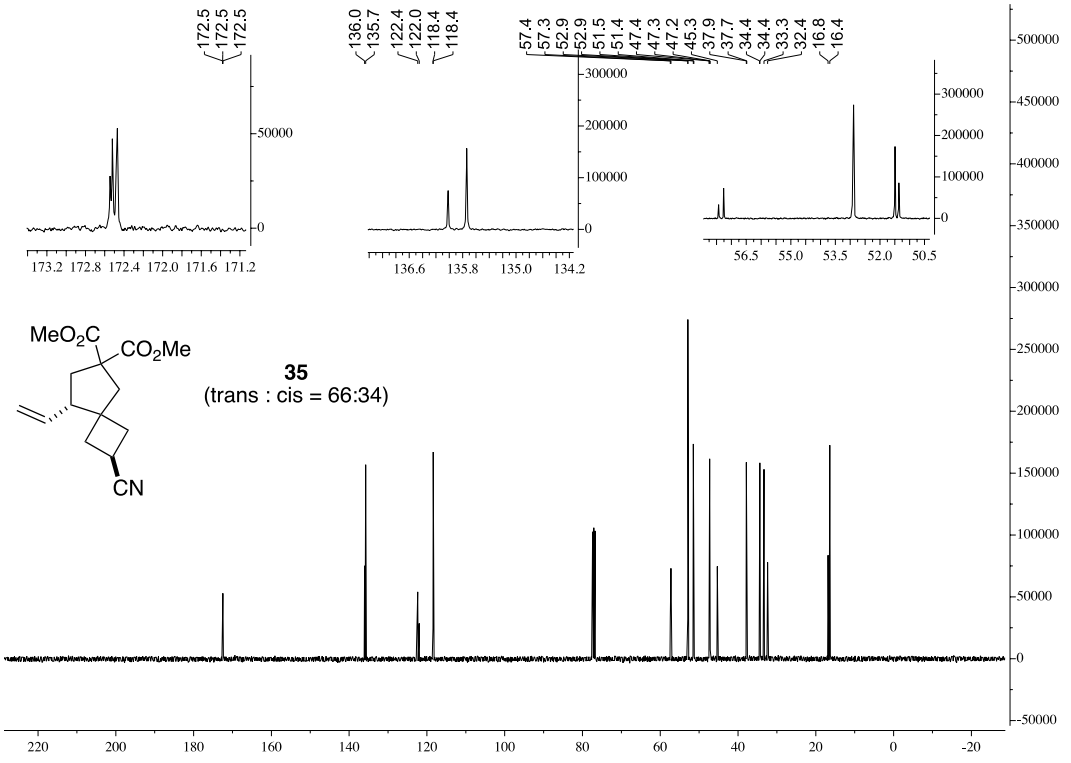

MeO2C
CO2Me
Me
Me
32
(cis: trans = 63:37)

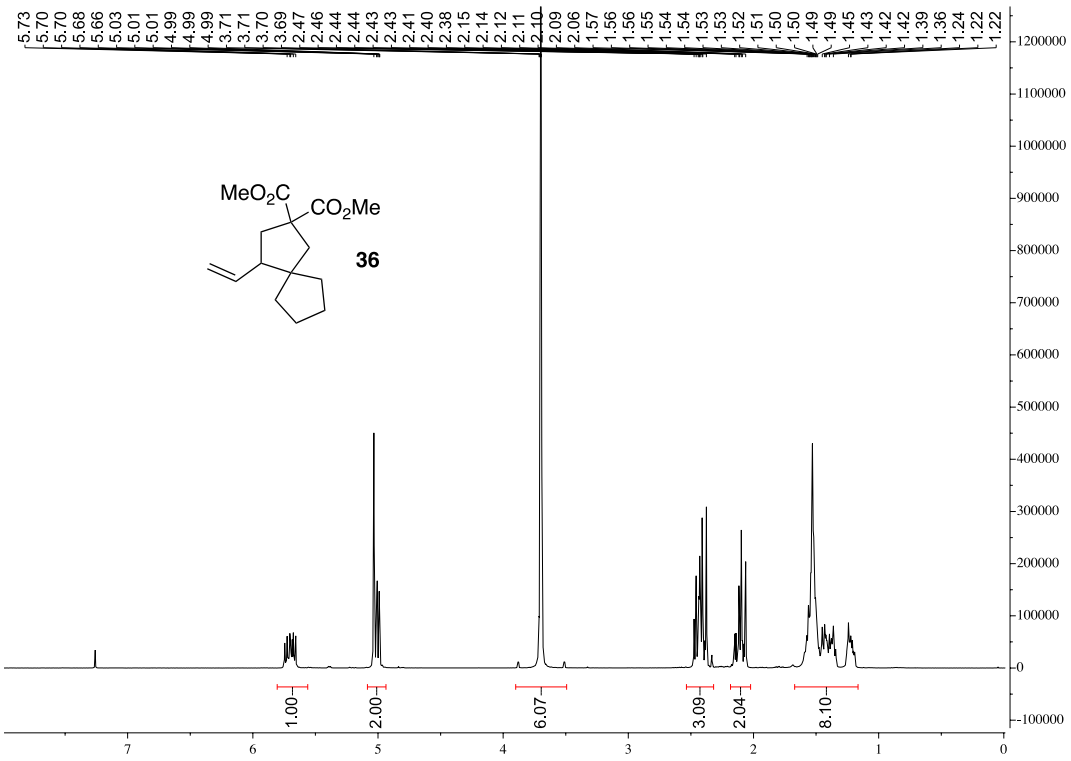

MeO2C
CO2Me
Me
Me
33
(cis: trans = 80:20)

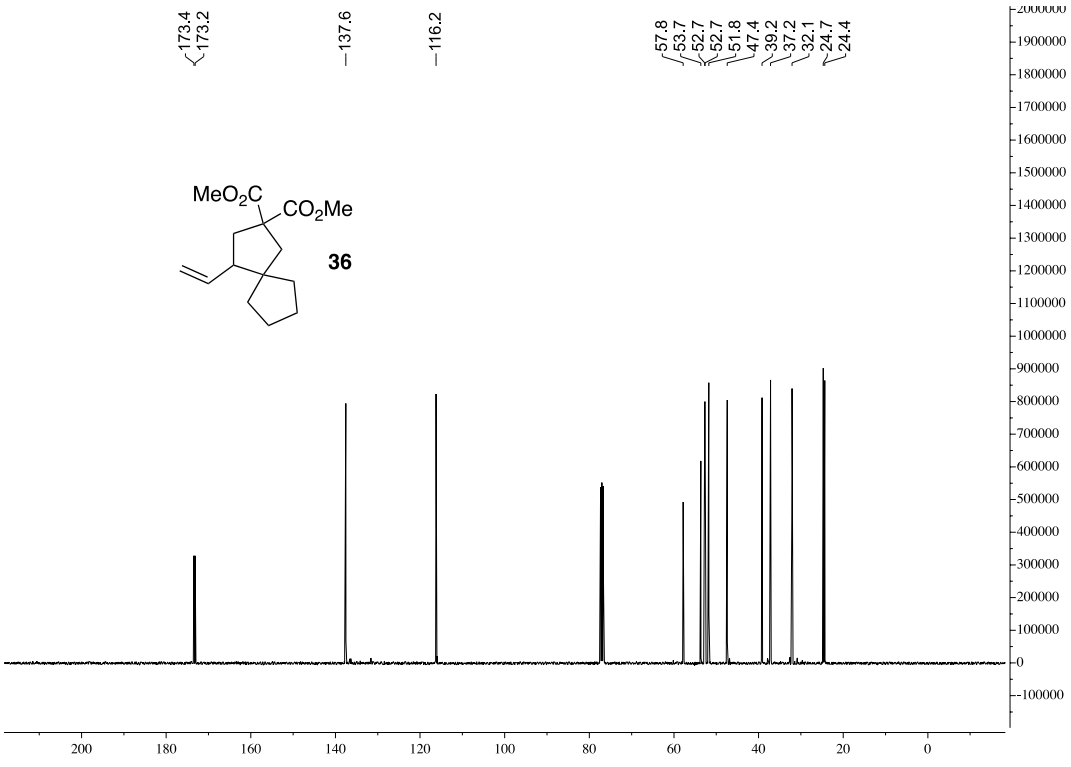

MeO2C
CO2Me
Me
34
(trans: cis = 70:30)

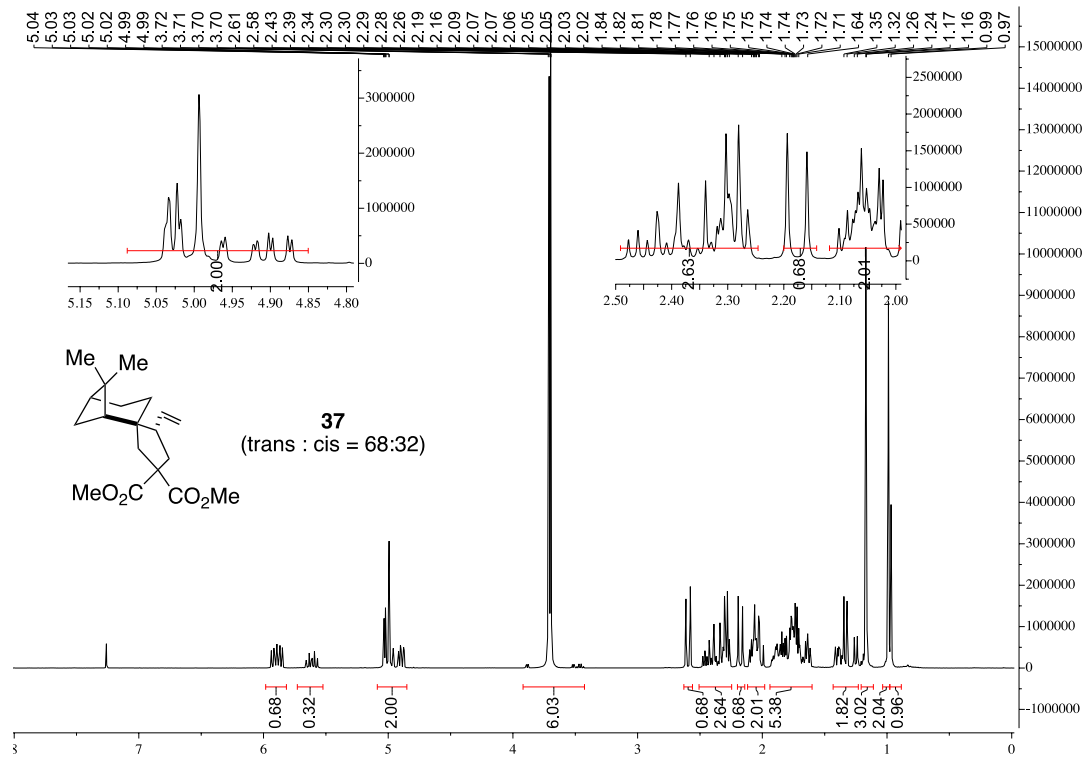

MeO2C
CO2Me
Me
34
(trans: cis = 70:30)

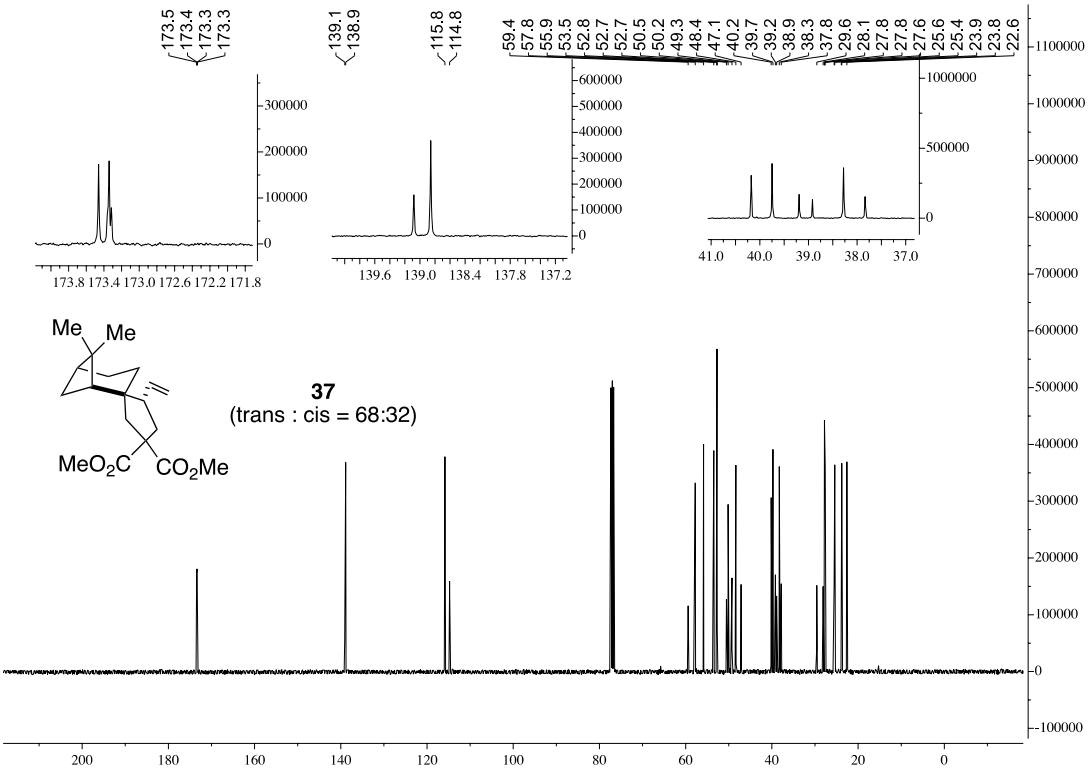

MeO2C
CO2Me
CN
35
(trans : cis = 66:34)
0.97
2.00
6.01
0.34
0.66
1.05
8.21

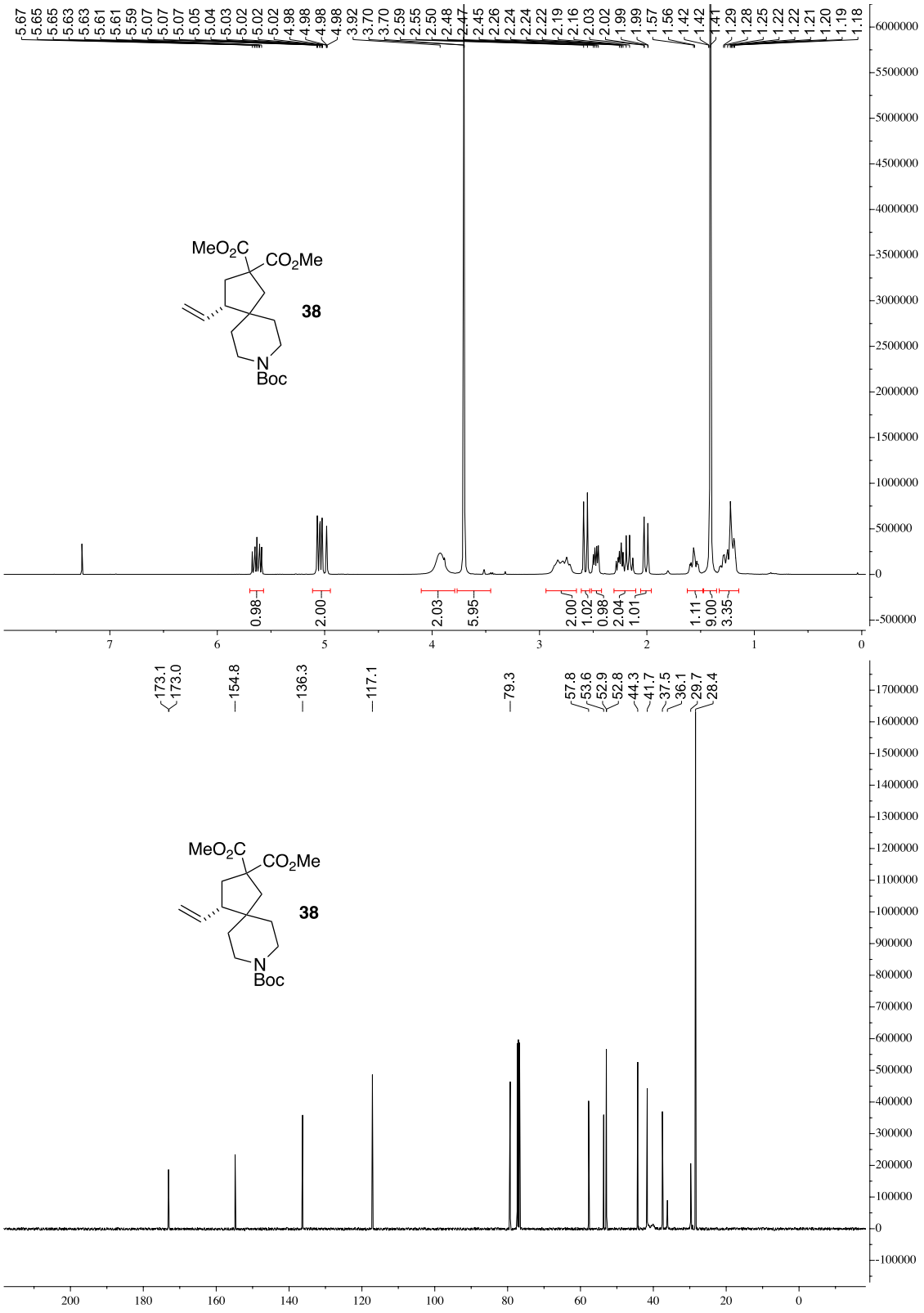

MeO2C
CO2Me
CN
35
(trans : cis = 66:34)

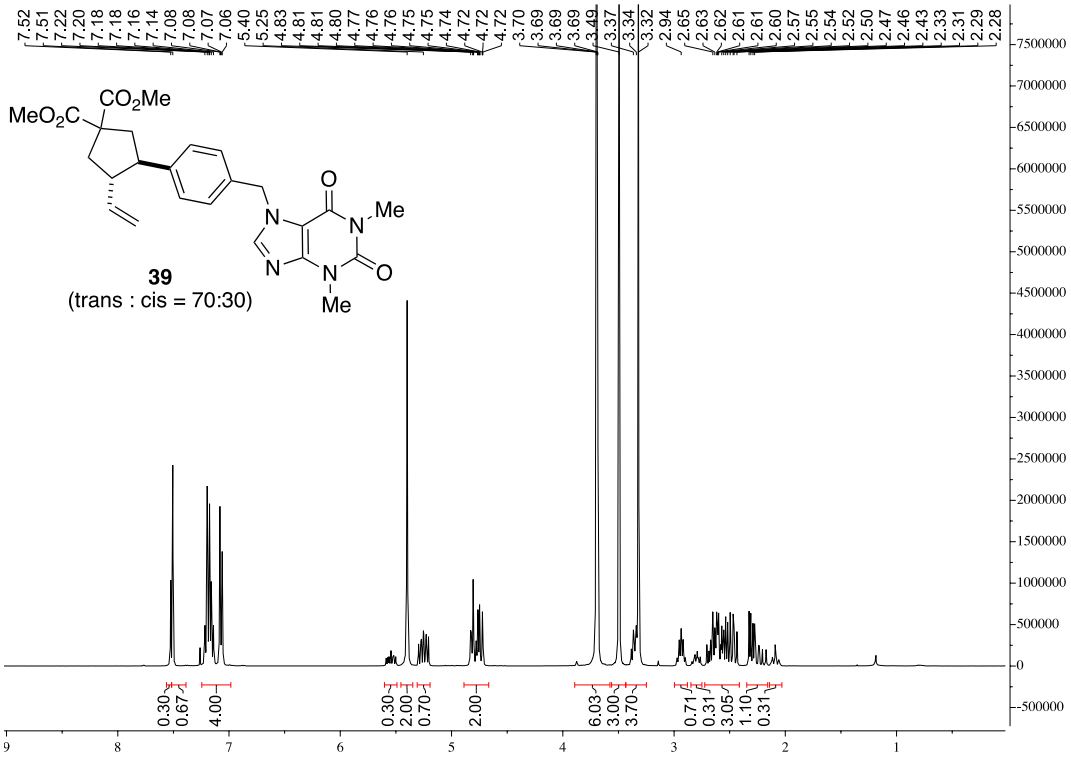

5.73
5.70
5.70
5.68
5.66
5.03
5.01
5.01
4.99
4.99
4.99
3.71
3.71
3.70
3.69
2.47
2.46
2.44
2.44
2.43
2.43
2.41
2.40
2.38
2.15
2.14
2.12
2.11
2.10
2.09
2.06
1.57
1.56
1.56
1.55
1.54
1.54
1.53
1.53
1.52
1.51
1.50
1.50
1.49
1.49
1.45
1.43
1.42
1.42
1.39
1.36
1.24
1.22
1.22
MeO2C
CO2Me
36
1.00
2.00
6.07
3.09
2.04
8.10

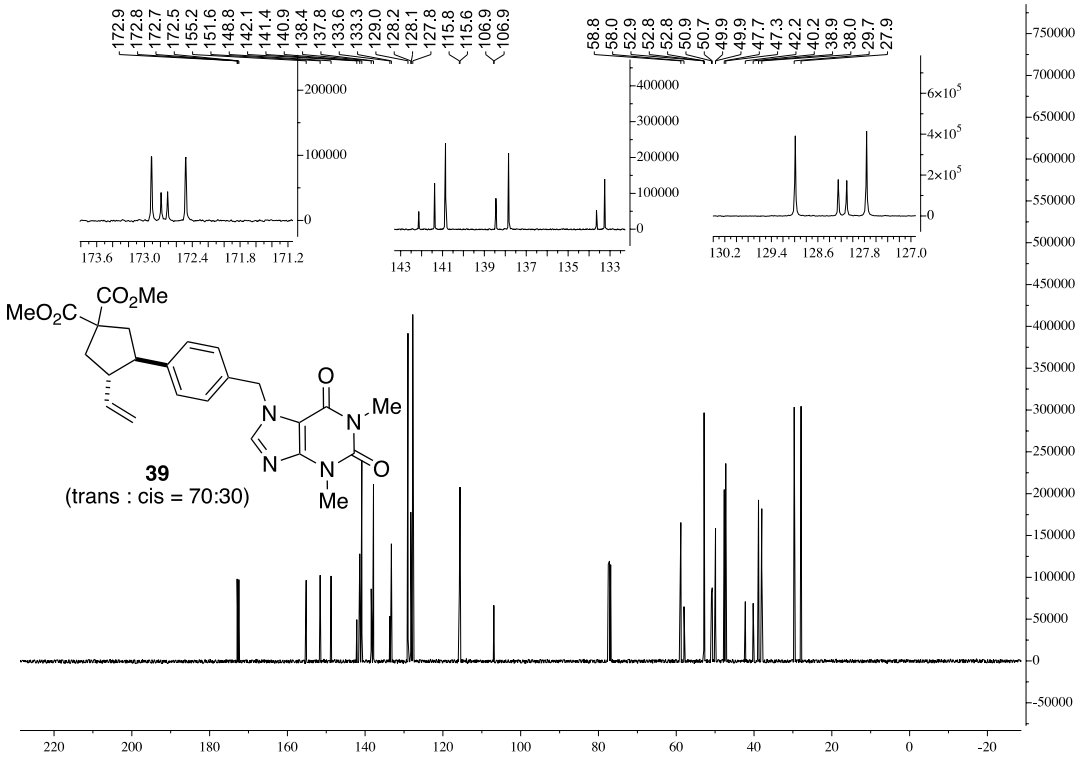

173.4
173.2
137.6
116.2
57.8
53.7
52.7
52.7
51.8
47.4
39.2
37.2
32.1
24.7
24.4
MeO2C
CO2Me
36

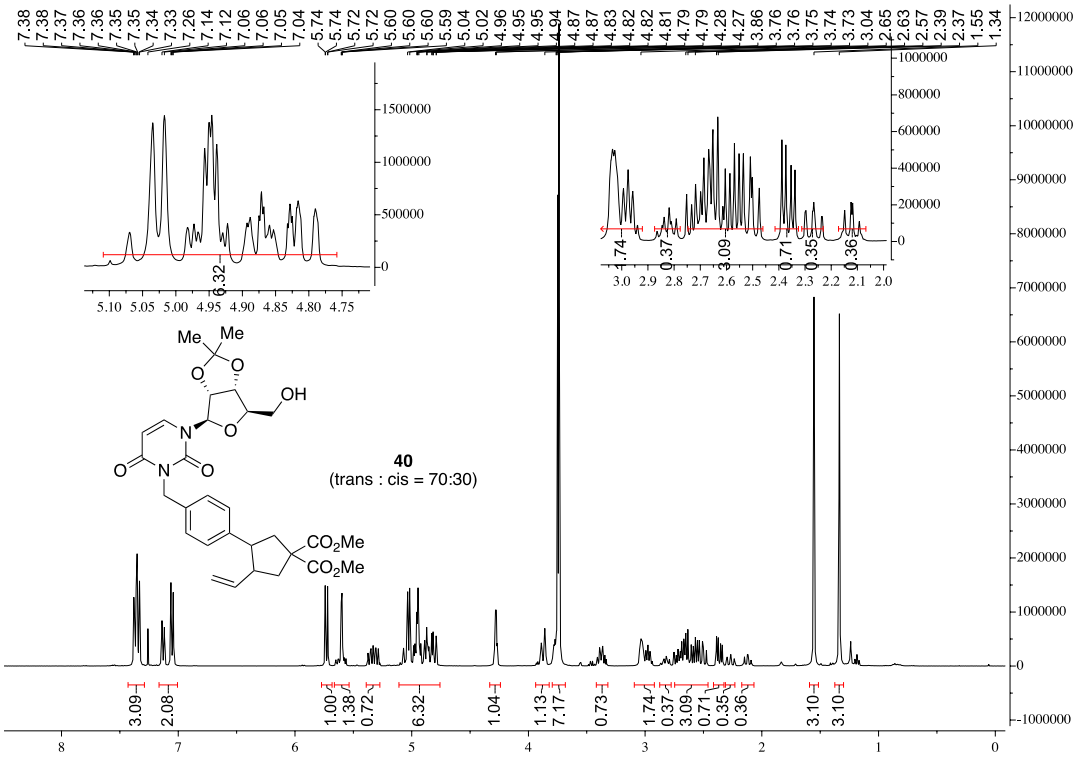

Me
Me
MeO2C
CO2Me
37
(trans : cis = 68:32)

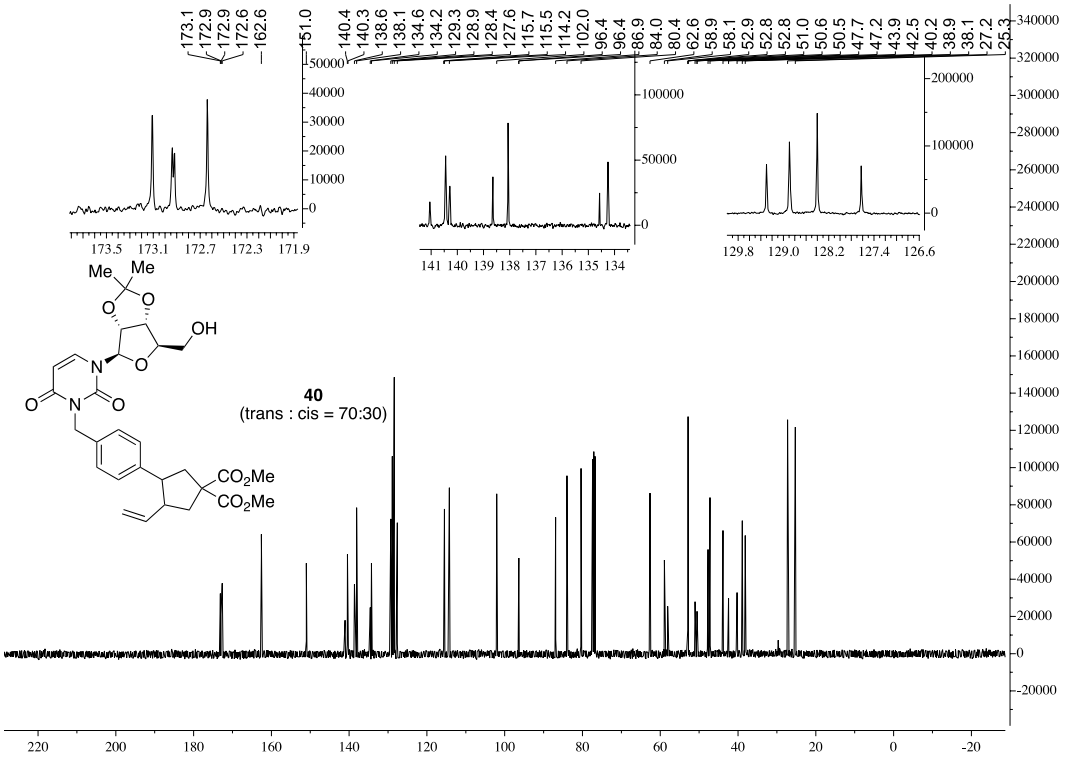

Me
Me
MeO2C
CO2Me
37
(trans : cis = 68:32)

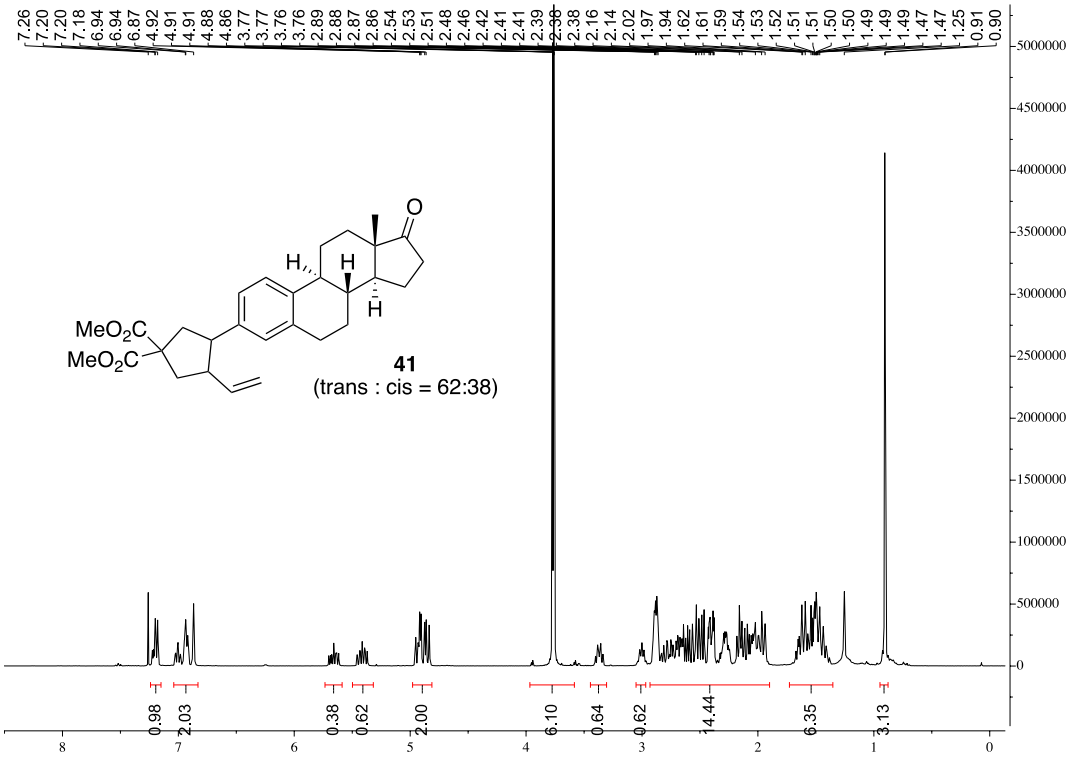

MeO2C
CO2Me
38
N
Boc
5.67 5.65 5.65 5.63 5.63 5.61 5.61 5.59 5.07 5.07 5.07 5.05 5.04 5.03 5.02 5.02 5.02 4.98 4.98 4.98 3.92 3.70 3.70 2.59 2.55 2.50 2.48 2.47 2.45 2.26 2.24 2.24 2.22 2.19 2.16 2.03 2.02 1.99 1.99 1.57 1.56 1.42 1.42 1.41 1.29 1.28 1.25 1.22 1.22 1.21 1.20 1.19 1.18
0.98 2.00 2.03 5.95 2.00 1.02 0.98 2.04 1.01 1.11 9.00 3.35
173.1 173.0 154.8 136.3 117.1 79.3 57.8 53.6 52.9 52.8 44.3 41.7 37.5 36.1 29.7 28.4

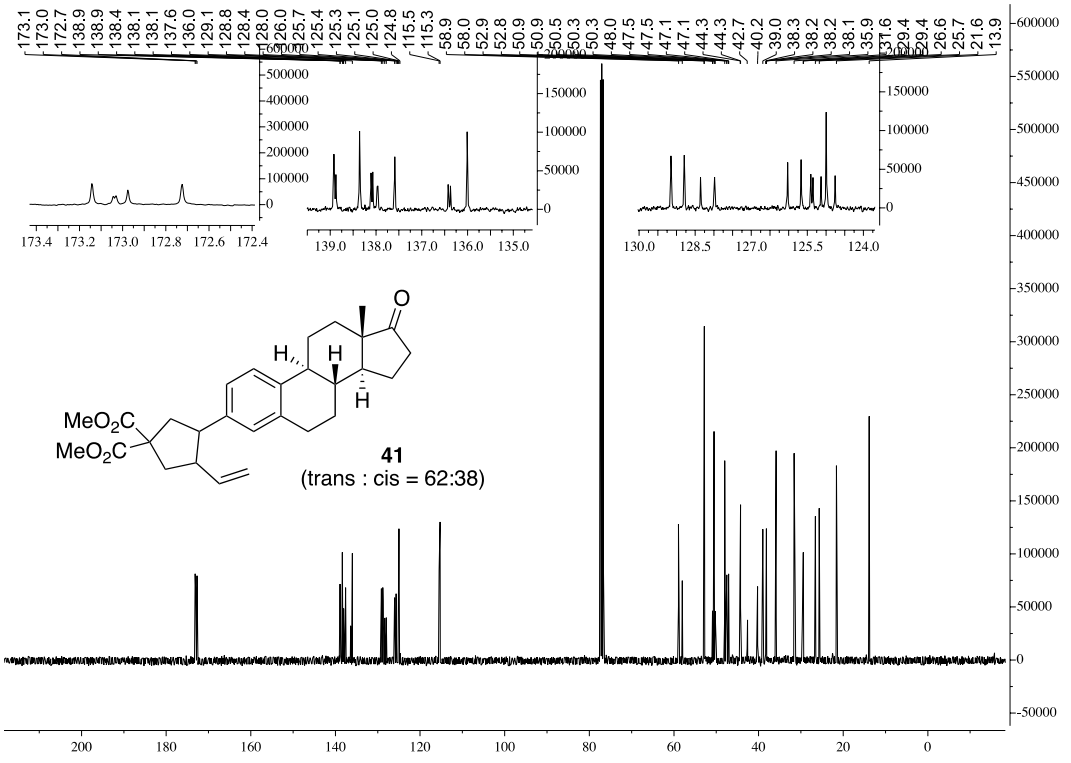

7.52 7.51 7.22 7.20 7.18 7.18 7.16 7.14 7.08 7.08 7.07 7.06 5.40 5.25 4.83 4.81 4.81 4.80 4.77 4.76 4.76 4.75 4.74 4.72 4.72 4.72 3.70 3.69 3.69 3.69 3.49 3.37 3.34 3.32 2.94 2.65 2.63 2.62 2.61 2.61 2.60 2.57 2.55 2.54 2.52 2.50 2.47 2.46 2.43 2.33 2.31 2.29 2.28
MeO2C
CO2Me
N
O
Me
N
N
N
O
Me
39
(trans : cis = 70:30)
0.30
0.67
4.00
0.30
2.00
0.70
2.00
6.03
3.00
3.70
0.71
0.31
3.05
1.10
0.31

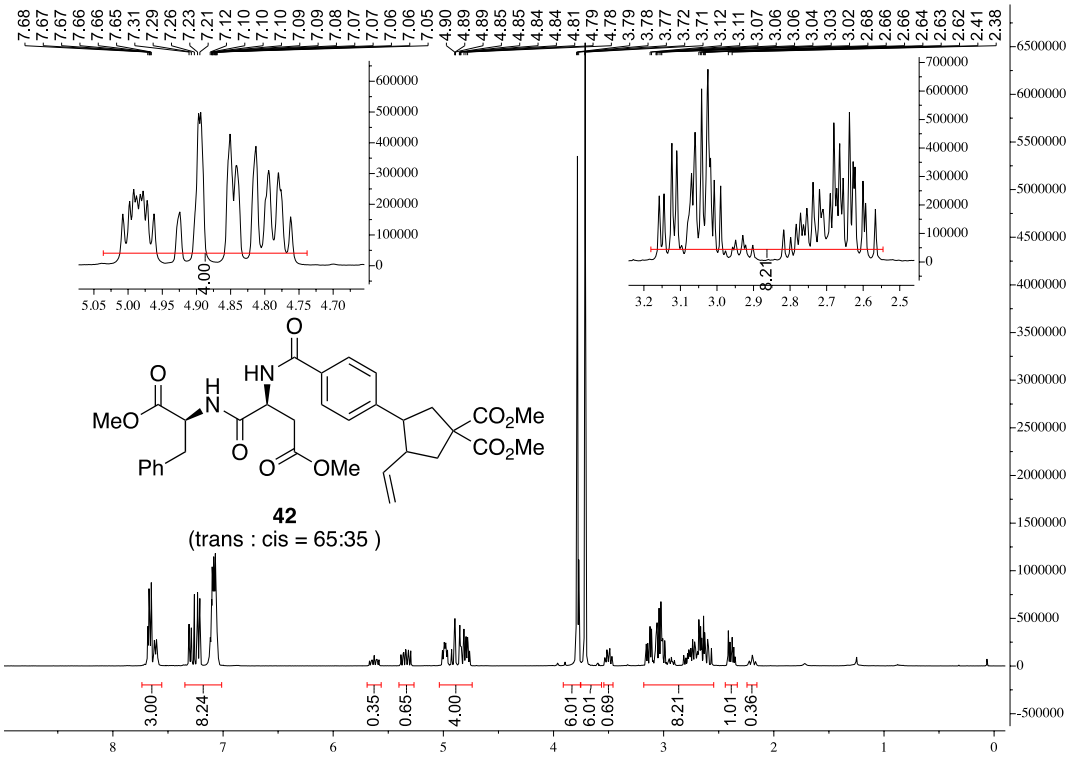

172.9 172.8 172.7 172.5 155.2 151.6 148.8 142.1 141.4 140.9 138.4 137.8 133.6 133.3 129.0 128.2 128.1 127.8 115.8 115.6 106.9 106.9
58.8 58.0 52.9 52.8 52.8 50.9 50.7 49.9 49.9 47.7 47.3 42.2 40.2 38.9 38.0 29.7 27.9
MeO2C
CO2Me
N
O
Me
N
N
N
O
Me
39
(trans : cis = 70:30)

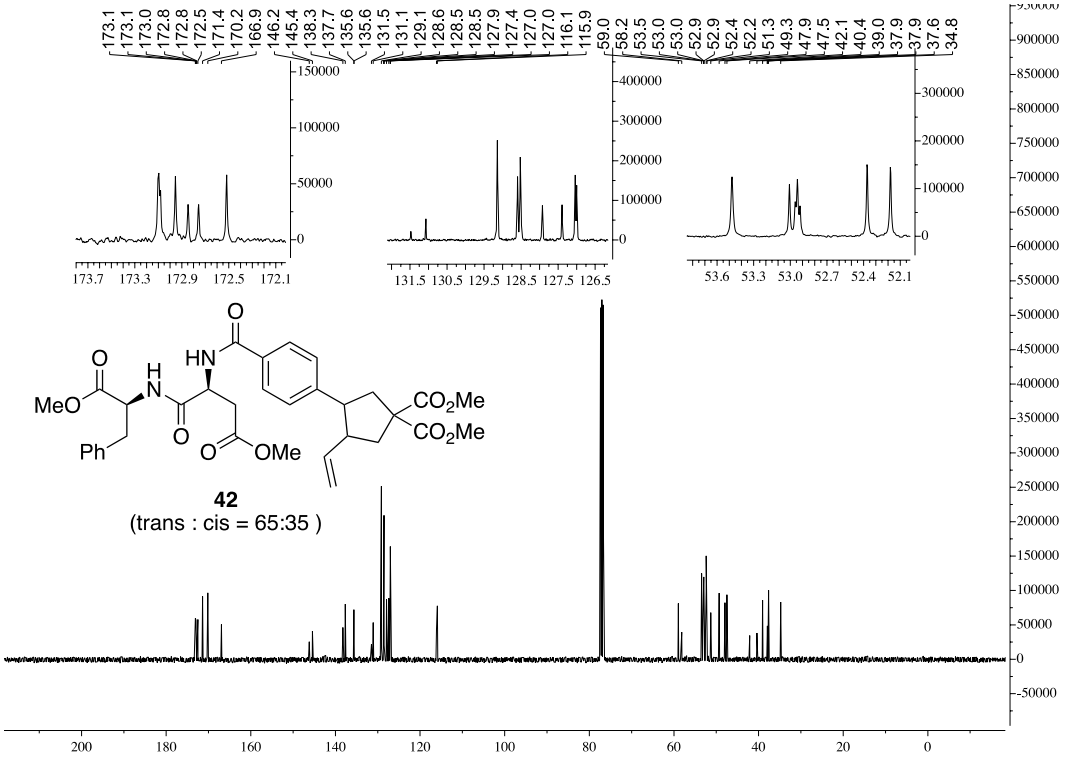

Me
Me
O
O
OH
N
O
O
N
O
CO2Me
CO2Me
40
(trans : cis = 70:30)

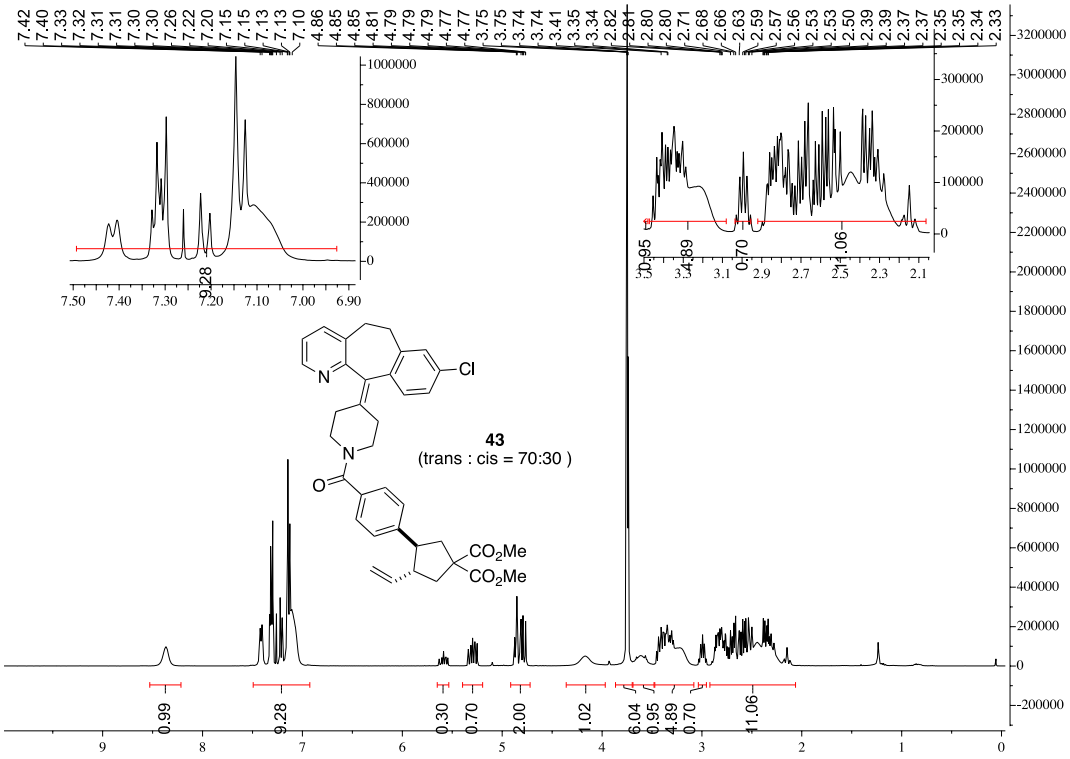

Me
Me
O
O
OH
N
O
O
N
O
CO2Me
CO2Me
40
(trans : cis = 70:30)

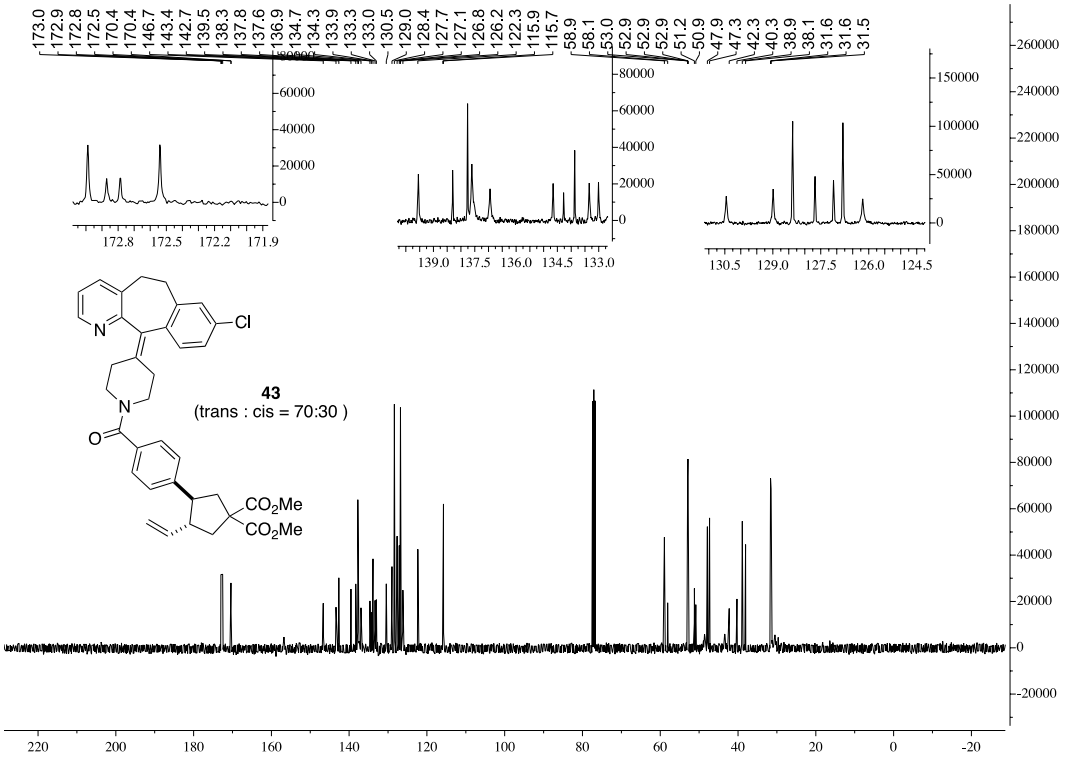

MeO2C
MeO2C
41
(trans : cis = 62:38)

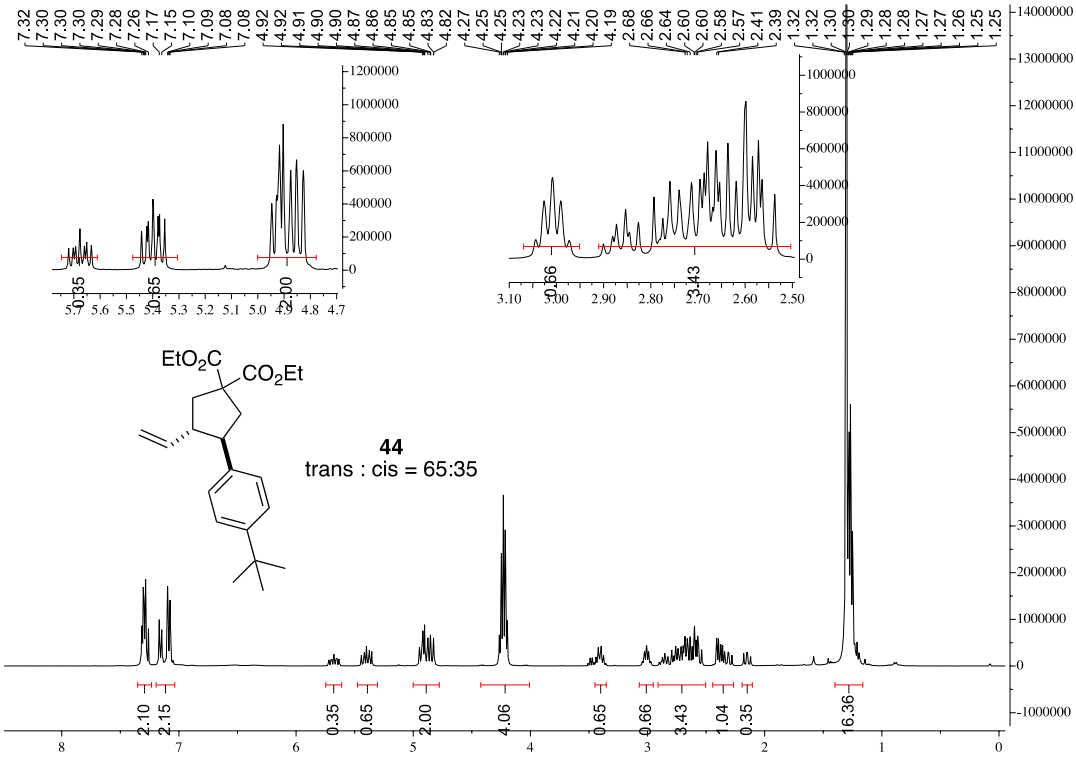

MeO2C
MeO2C
41
(trans : cis = 62:38)

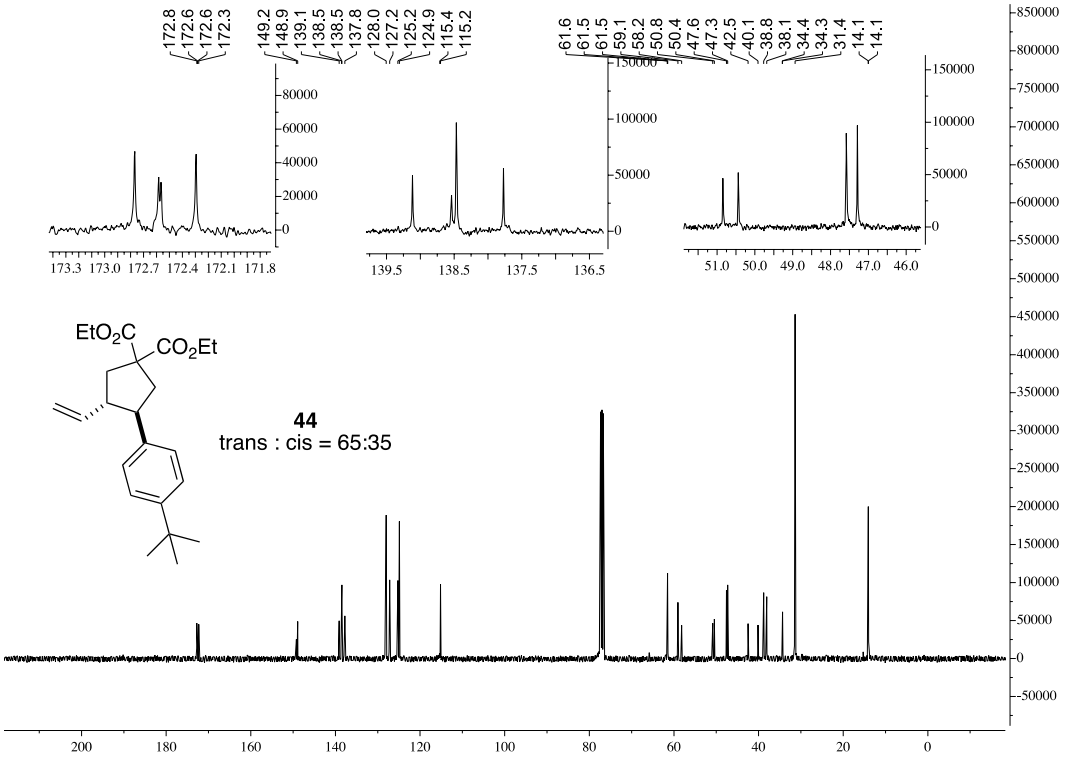

MeO
Ph
HN
CO2Me
CO2Me
OMe
42
(trans : cis = 65:35)

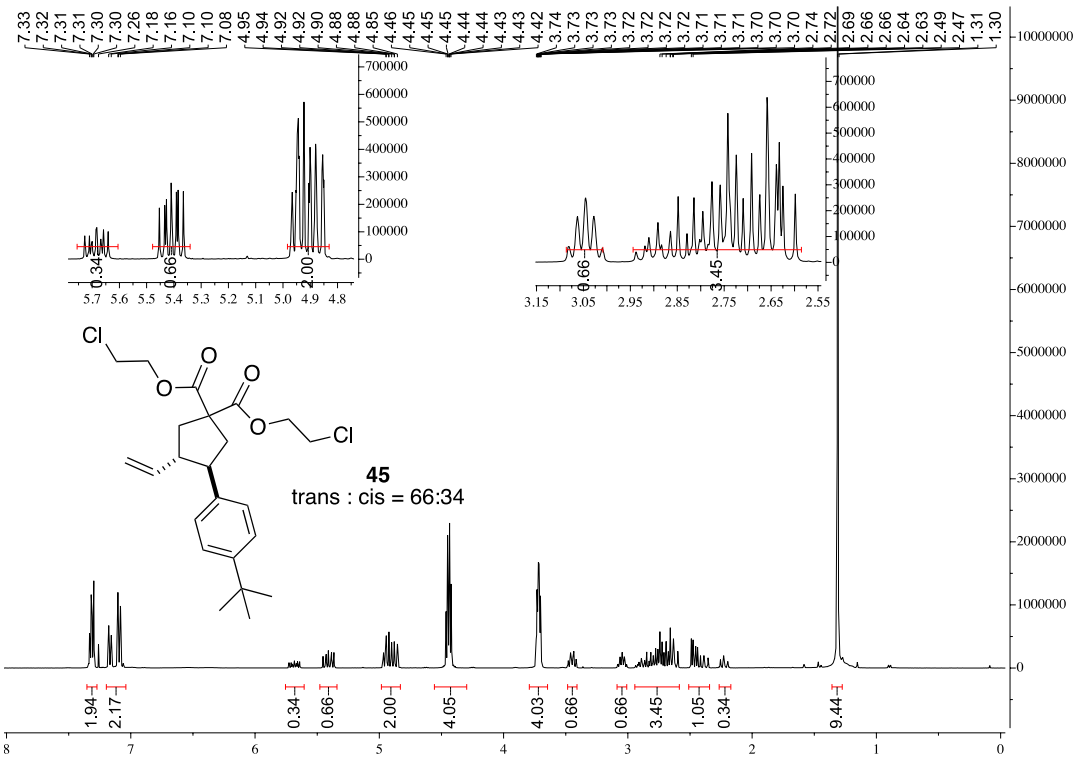

MeO
Ph
HN
CO2Me
CO2Me
OMe
42
(trans : cis = 65:35)

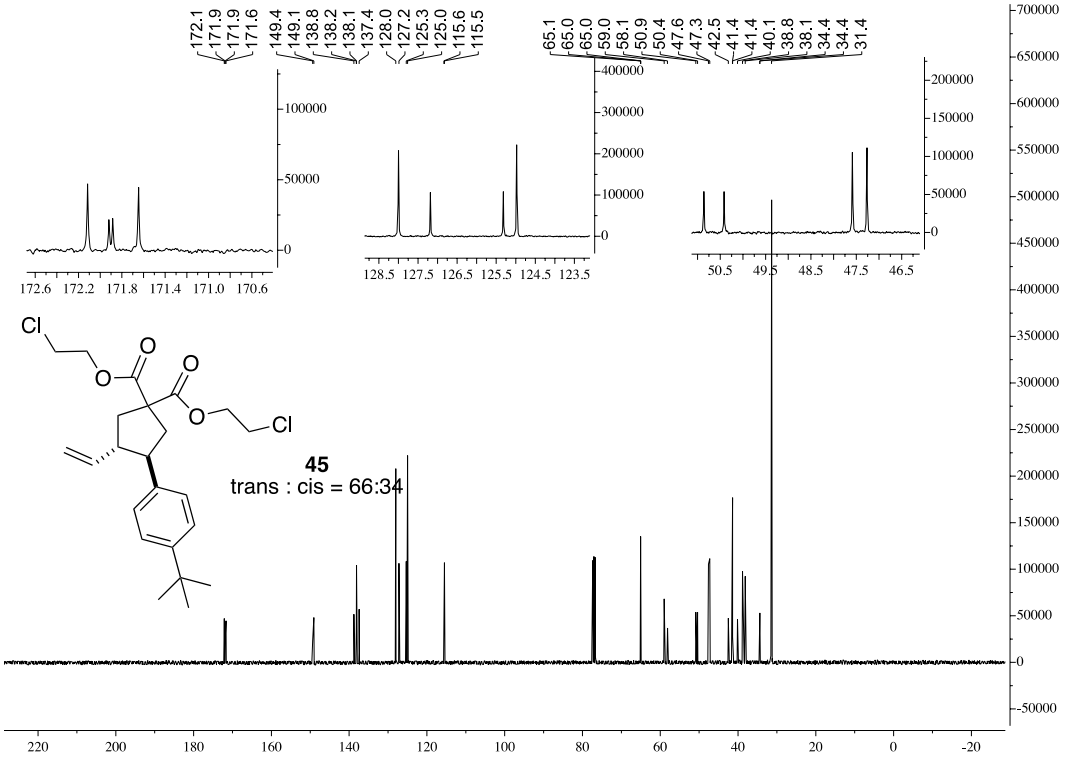

43
(trans : cis = 70:30)
Cl
N
O
CO2Me
CO2Me

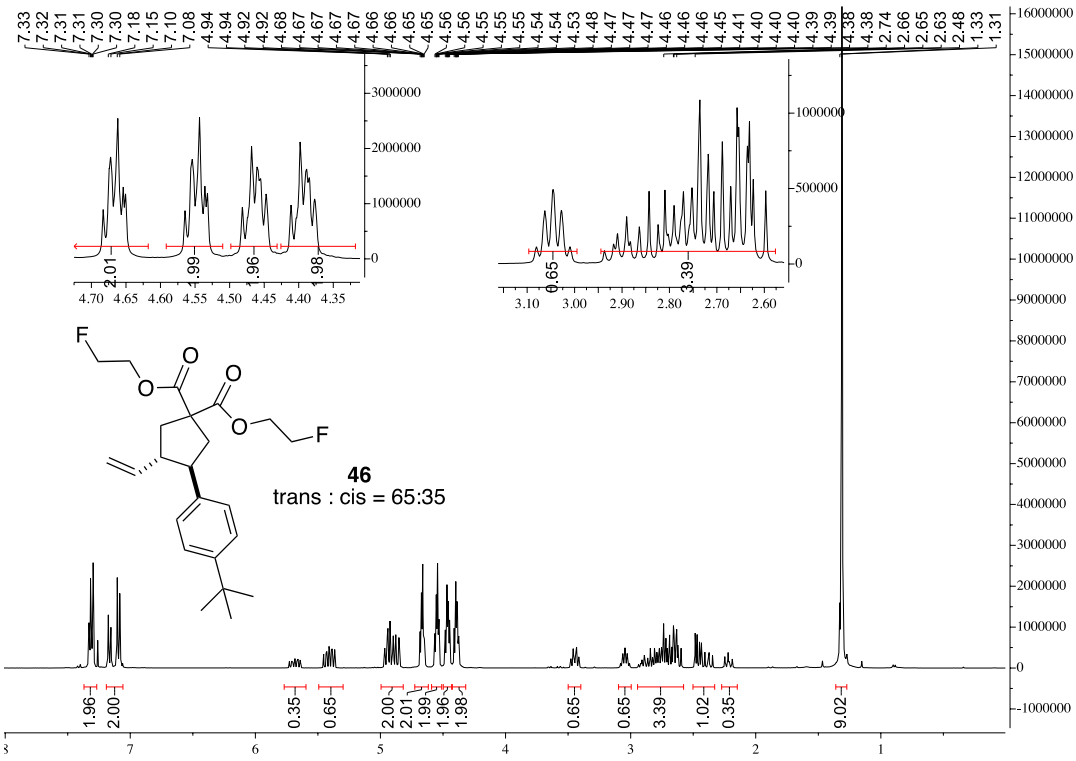

43
(trans : cis = 70:30)
Cl
N
O
CO2Me
CO2Me

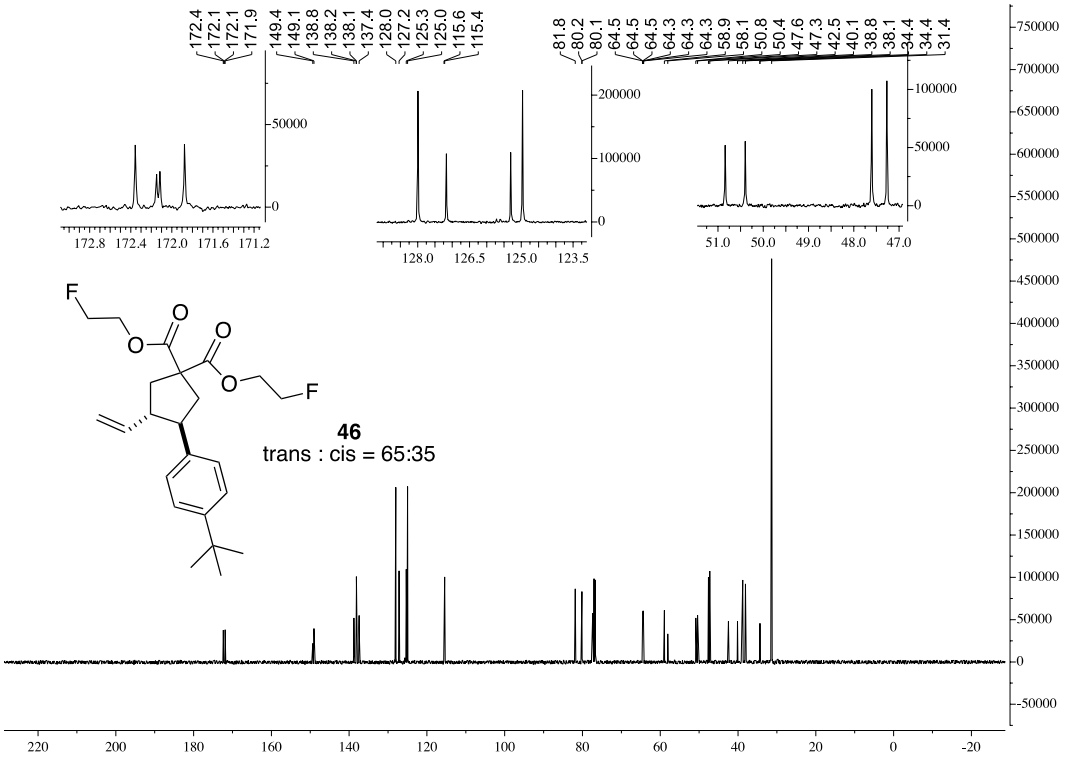

EtO2C
CO2Et
44
trans : cis = 65:35

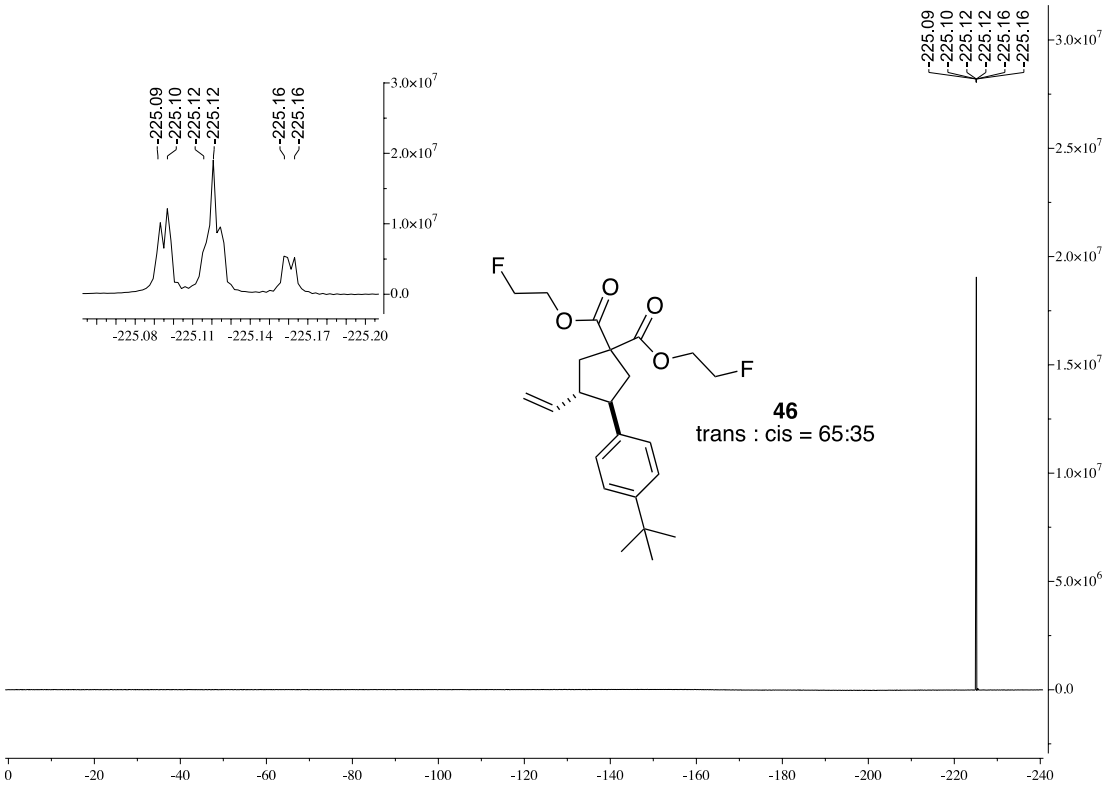

EtO2C
CO2Et
44
trans : cis = 65:35

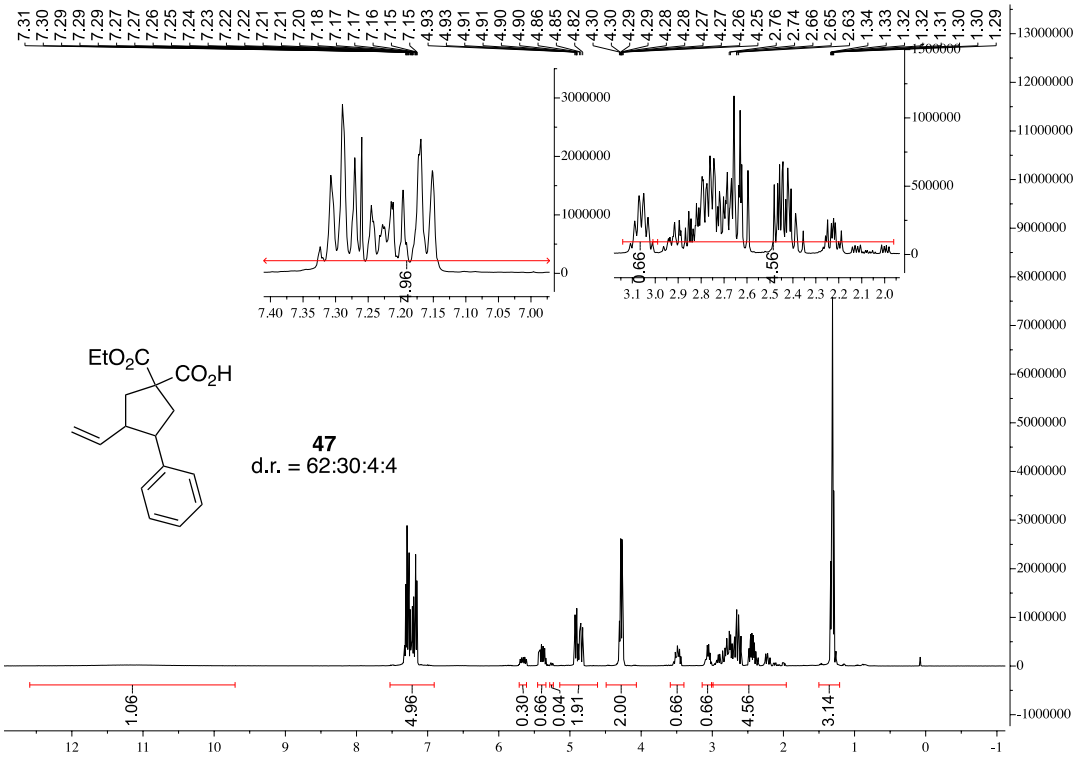

45
trans : cis = 66:34

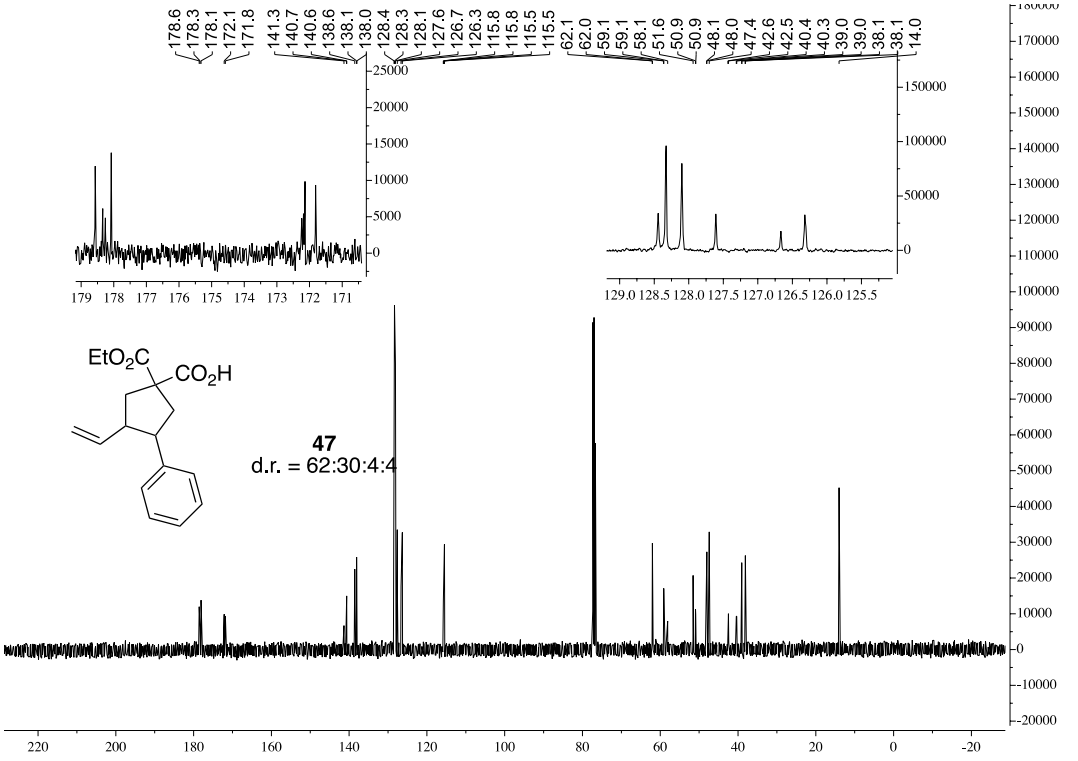

45
trans : cis = 66:34

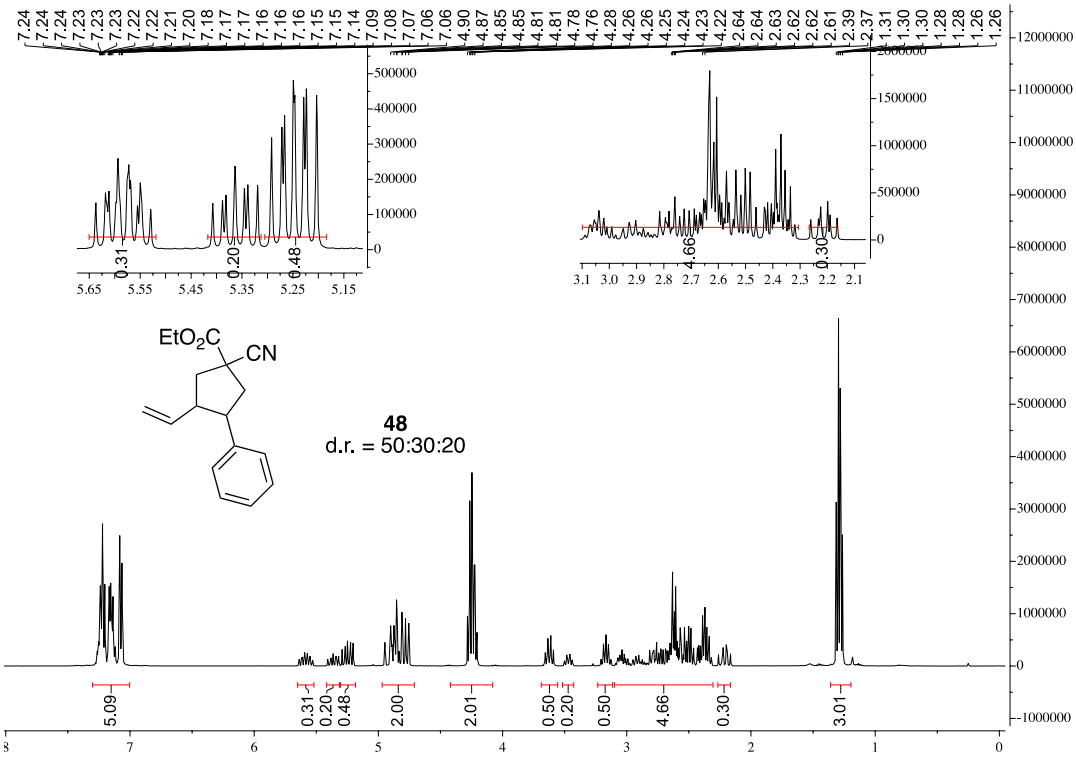

46
trans : cis = 65:35

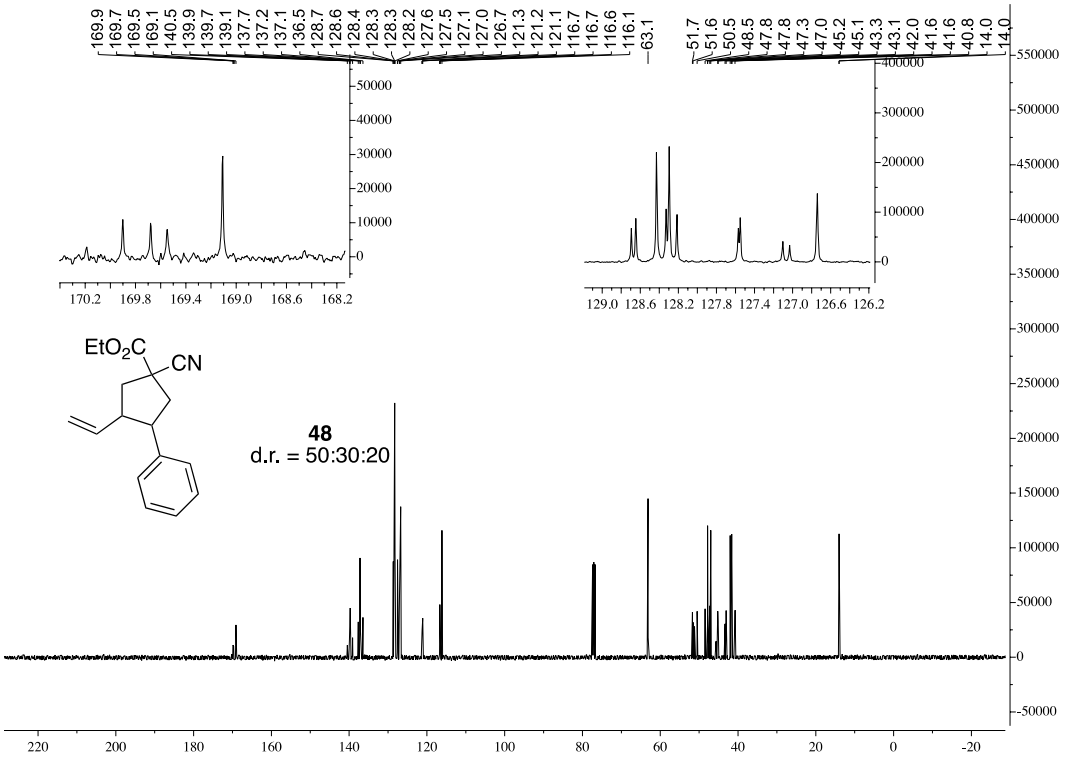

46
trans : cis = 65:35

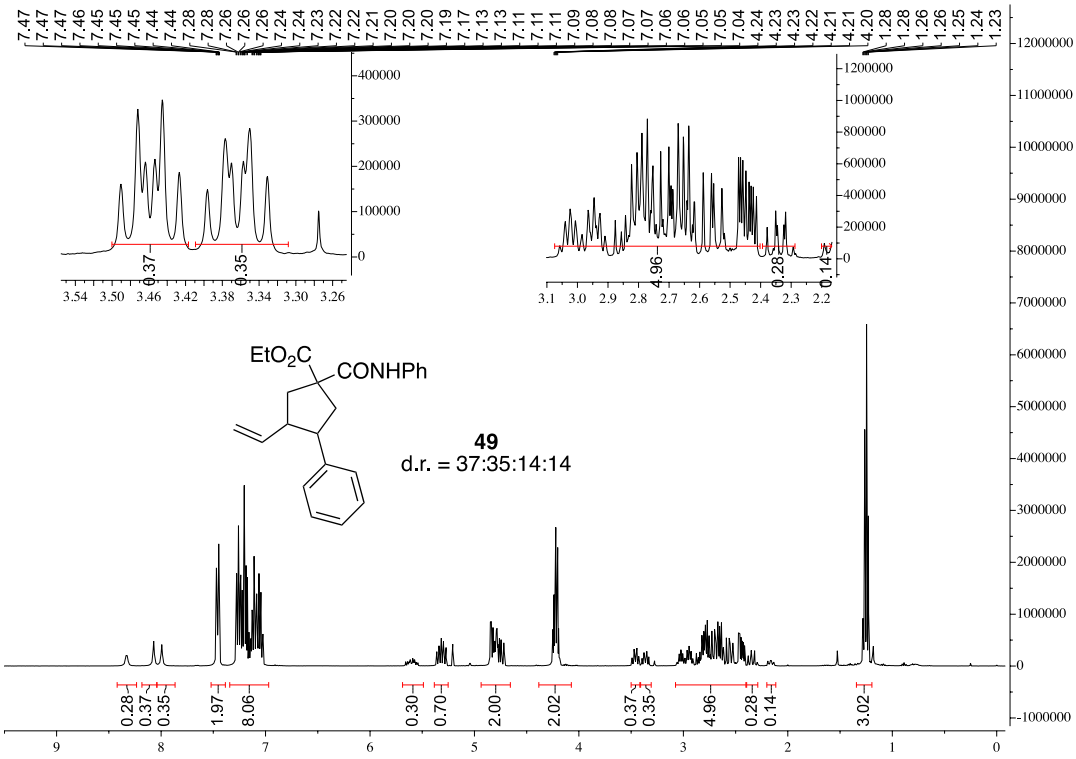

-225.09
-225.10
-225.12
-225.12
-225.16
-225.16
3.0×10^7
2.0×10^7
1.0×10^7
0.0
-225.08
-225.11
-225.14
-225.17
-225.20
F
O
O
O
O
F
46
trans : cis = 65:35
2.5×10^7
1.5×10^7
5.0×10^6
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240

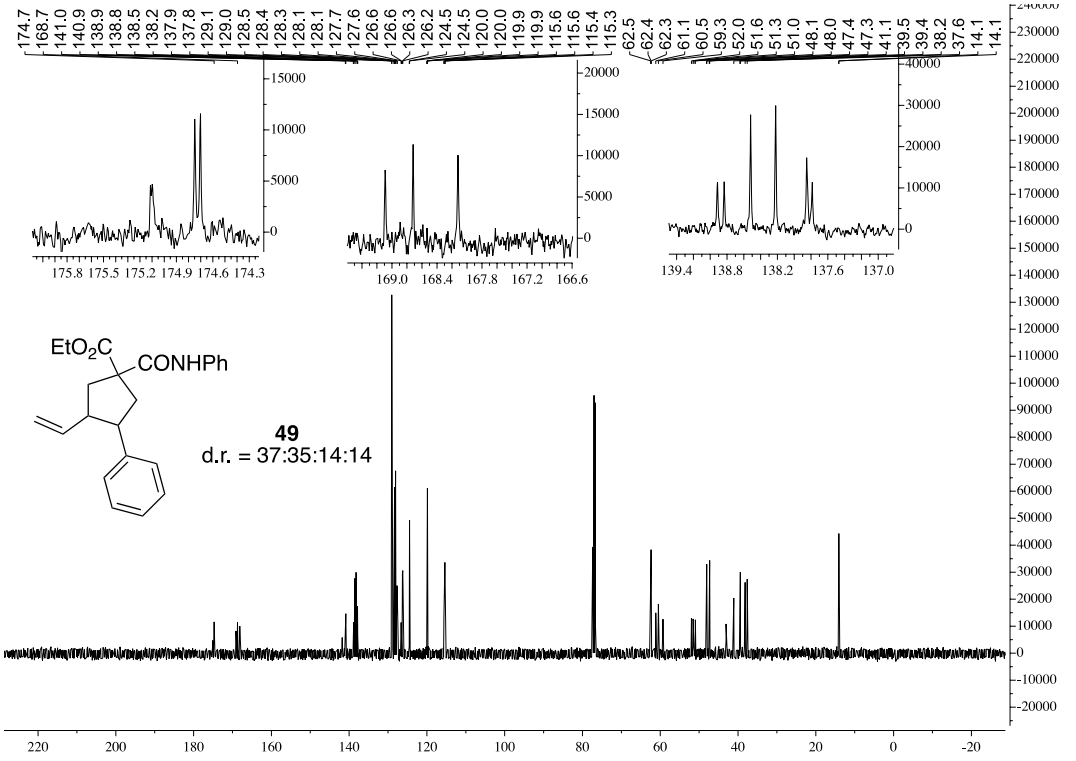

EtO2C
CO2H
47
d.r. = 62:30:4:4

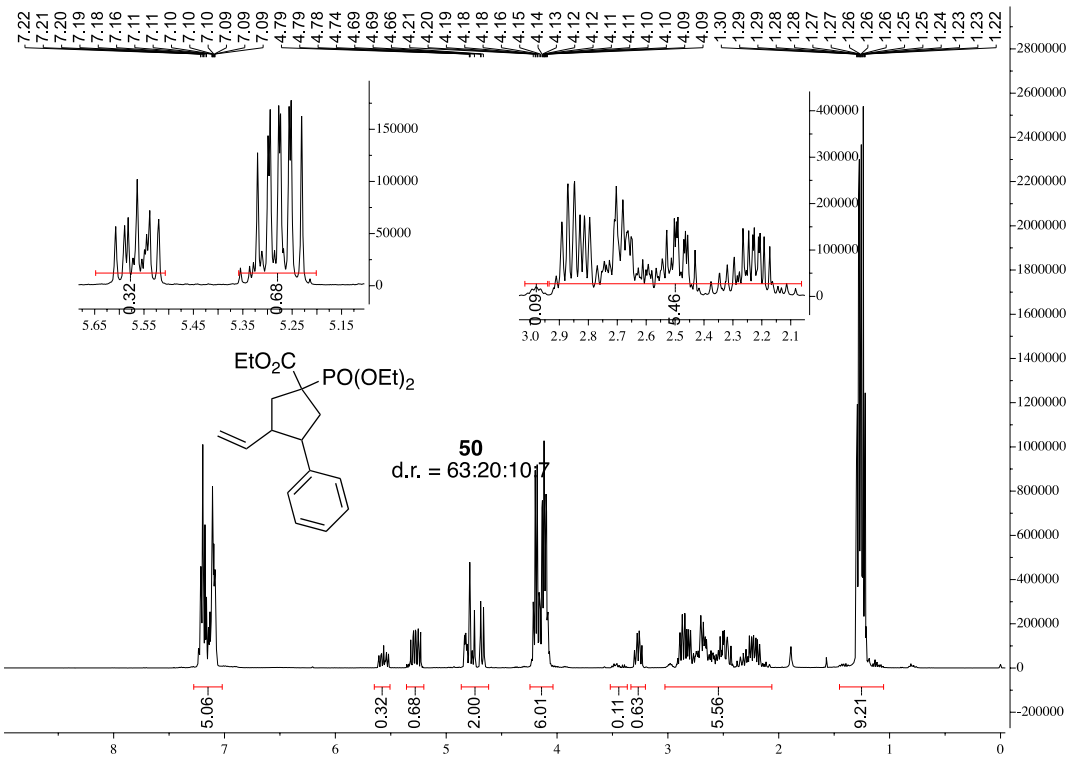

EtO2C
CO2H
47
d.r. = 62:30:4:4

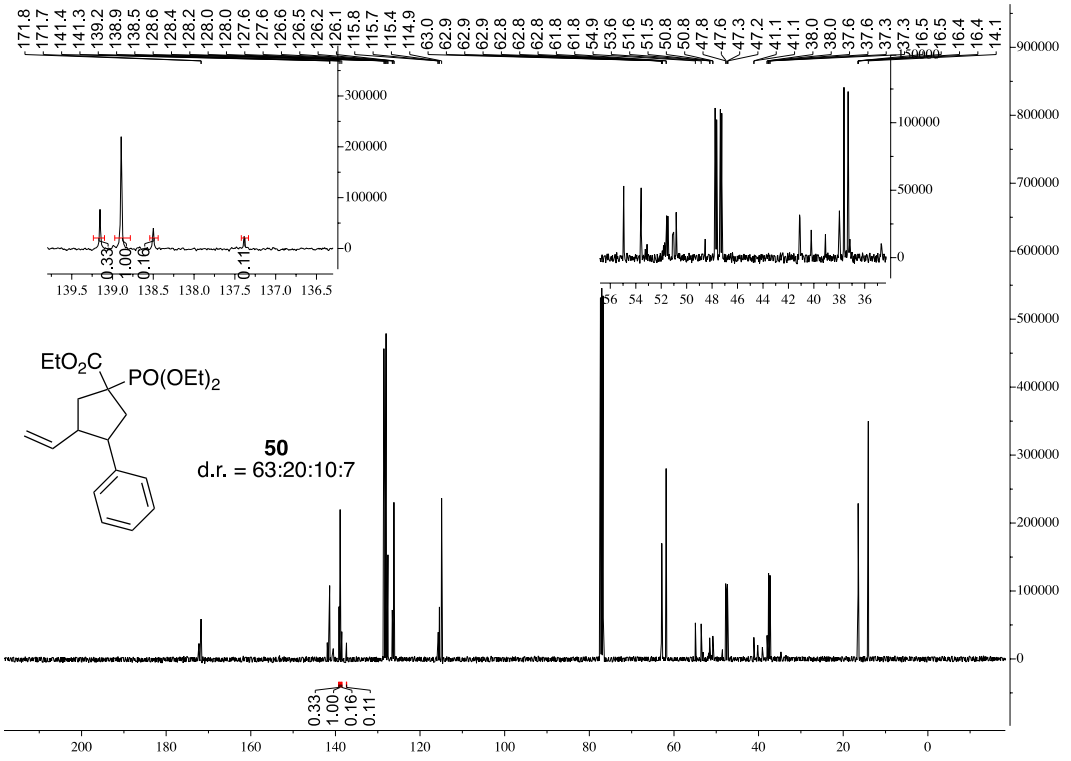

EtO2C
CN
48
d.r. = 50:30:20

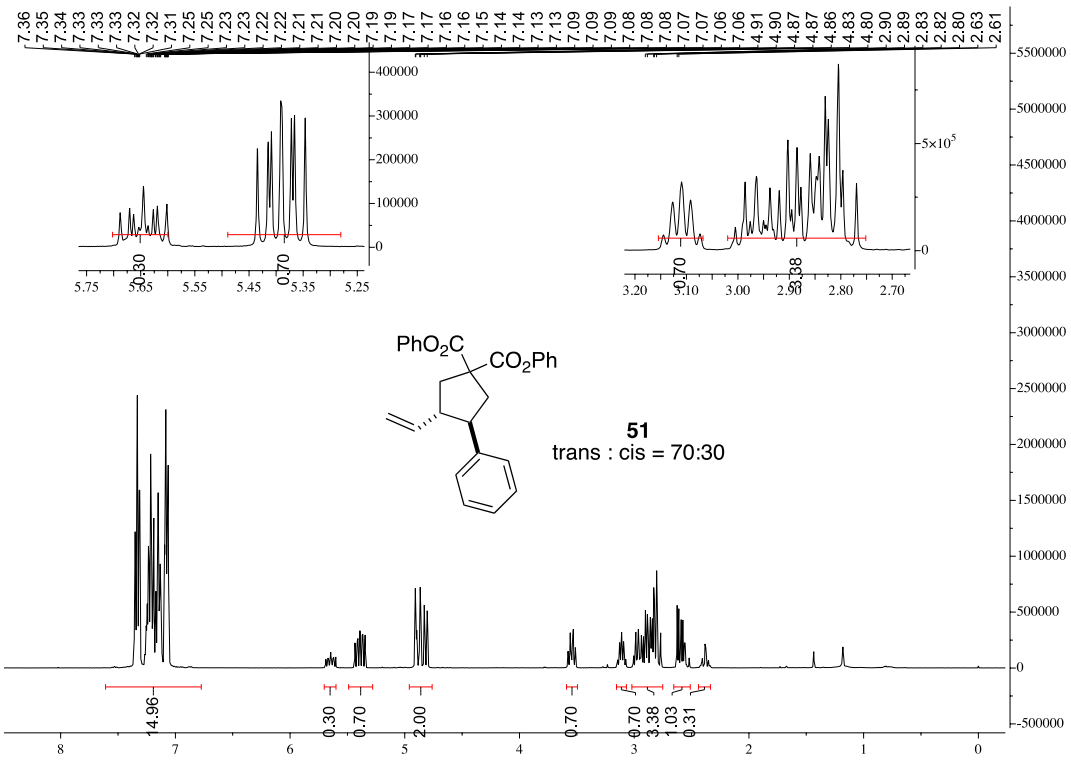

EtO2C
CN
48
d.r. = 50:30:20

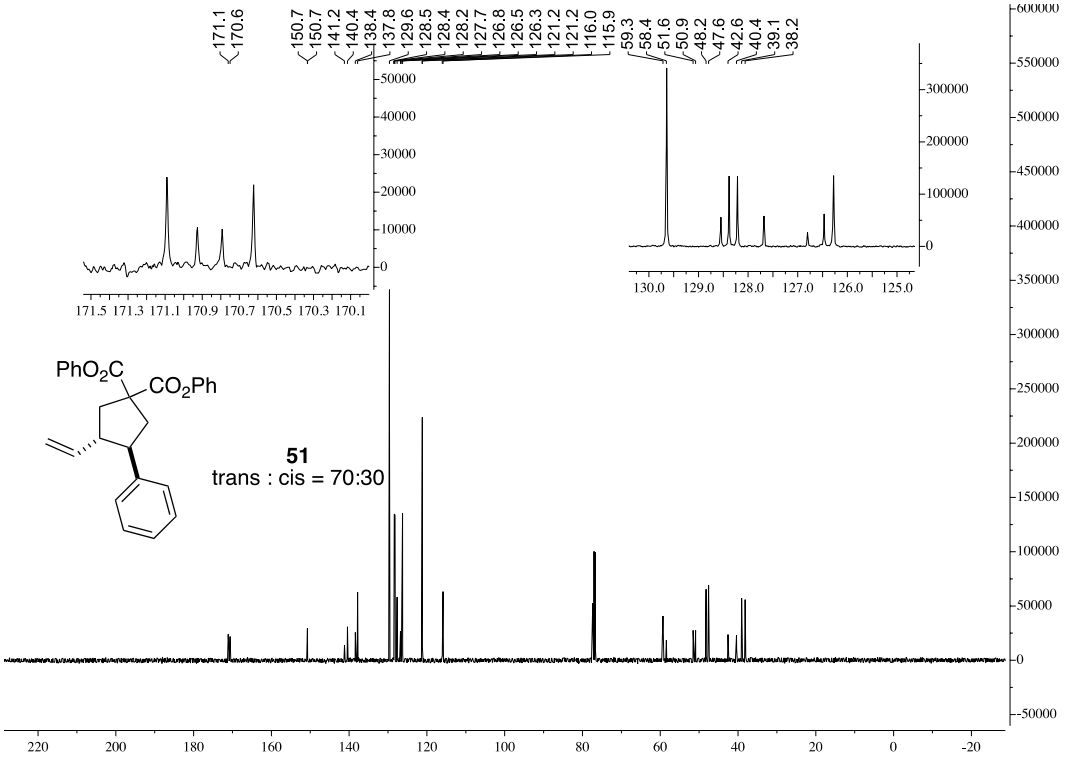

EtO2C
CONHPh
49
d.r. = 37:35:14:14

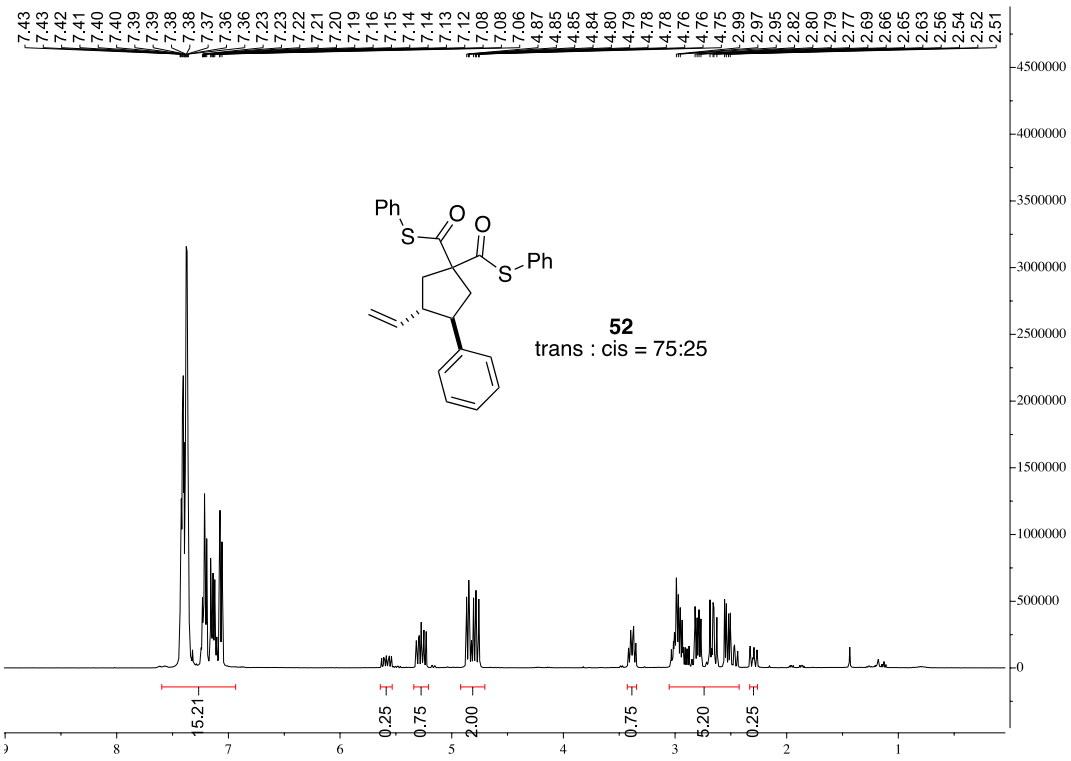

EtO2C
CONHPh
49
d.r. = 37:35:14:14

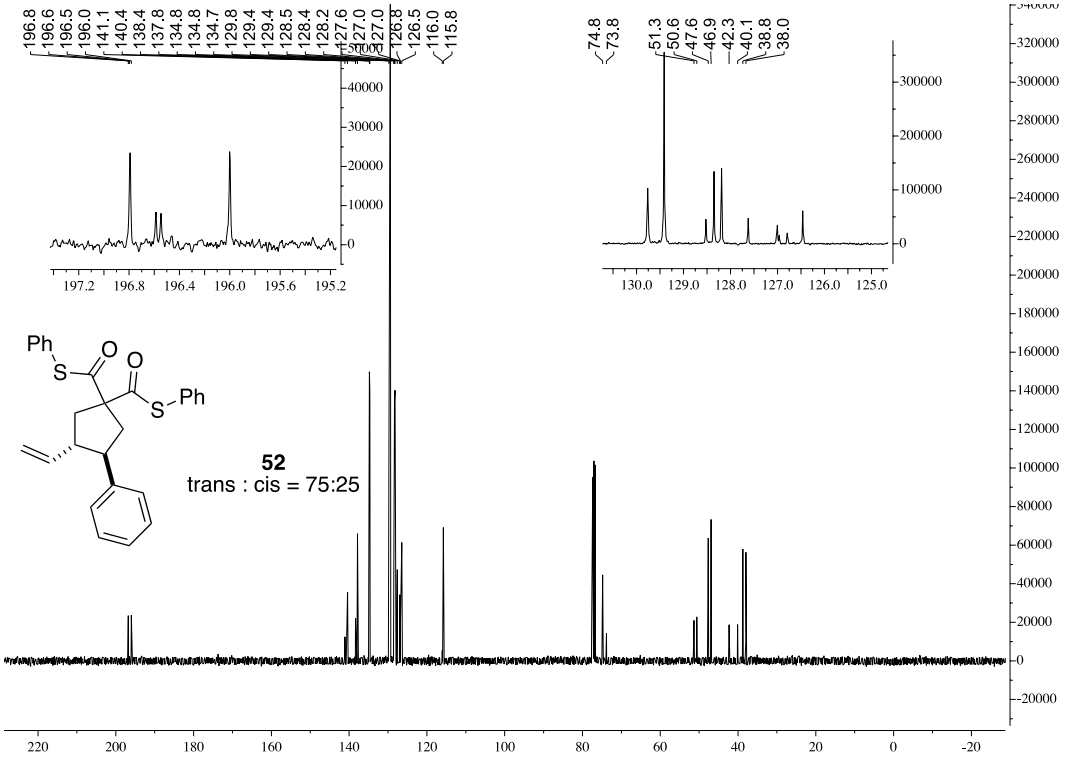

EtO2C
PO(OEt)2
50
d.r. = 63:20:10:7

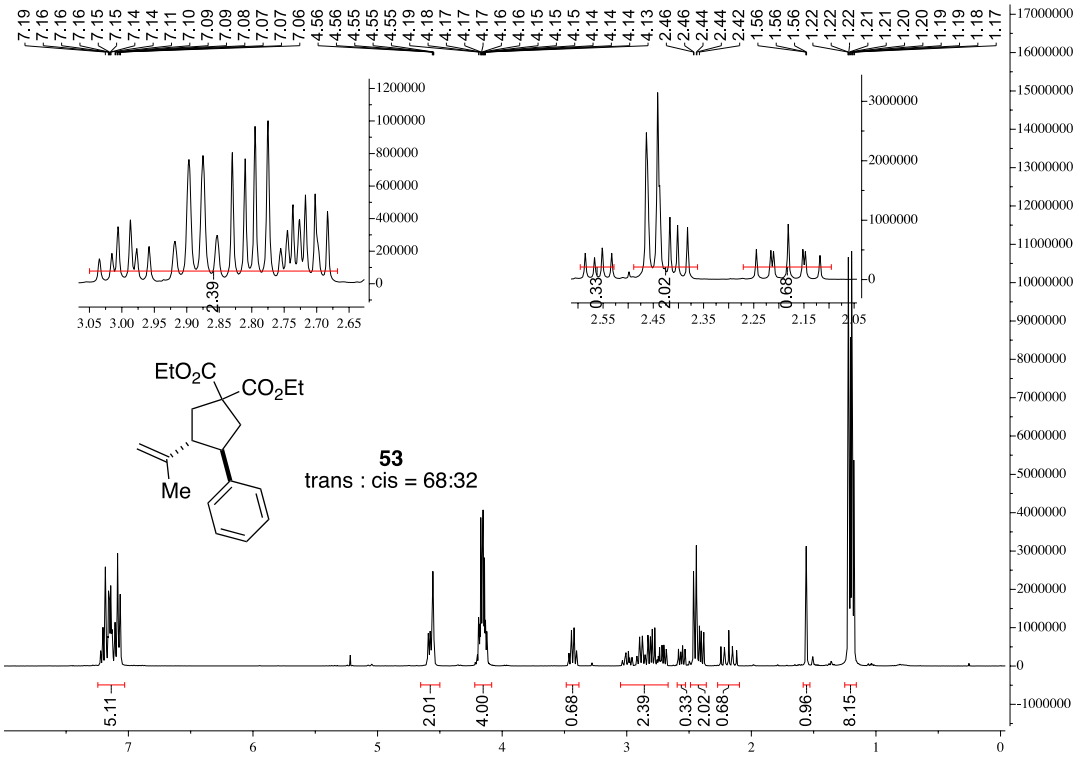

EtO2C
PO(OEt)2
50
d.r. = 63:20:10:7

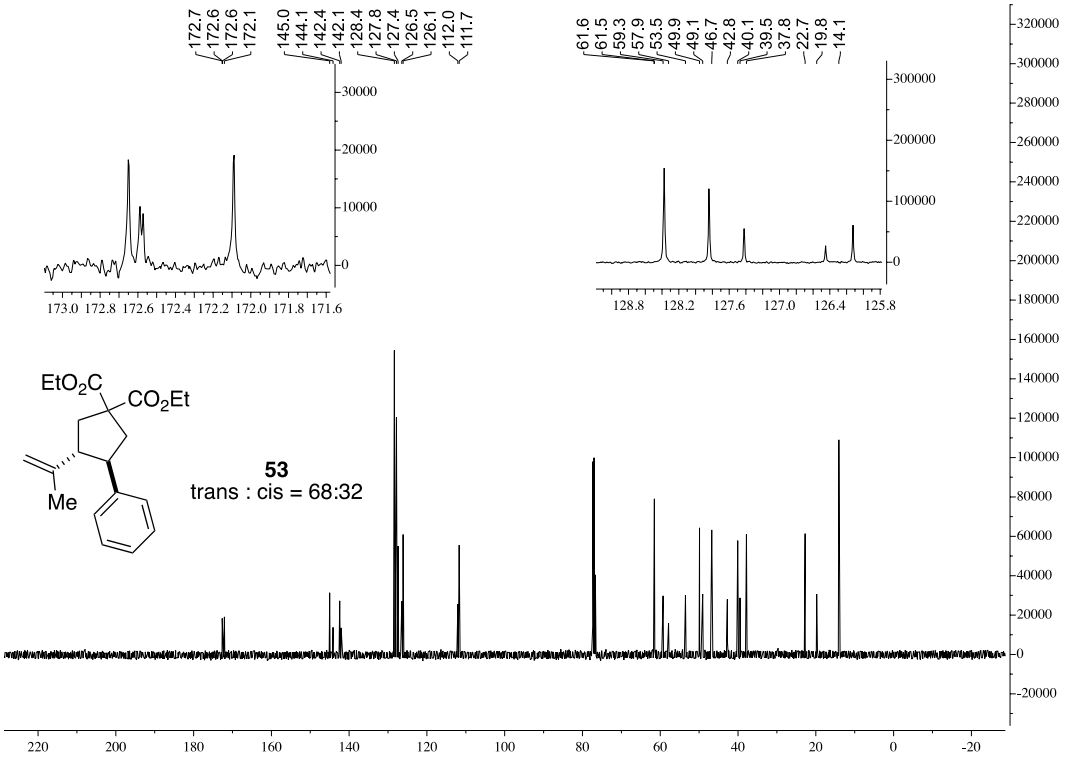

PhO2C
CO2Ph
51
trans : cis = 70:30

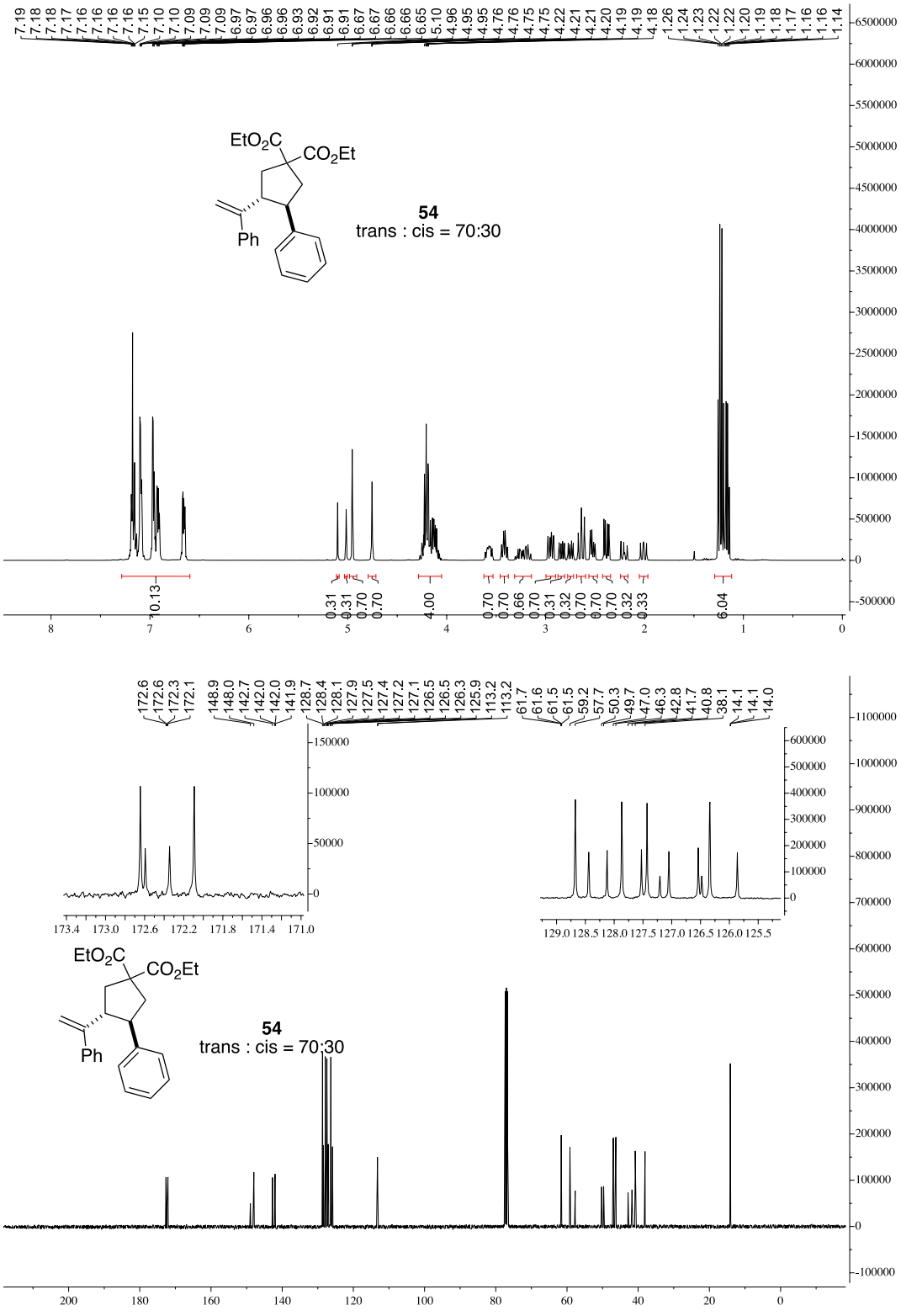

PhO2C
CO2Ph
51
trans : cis = 70:30

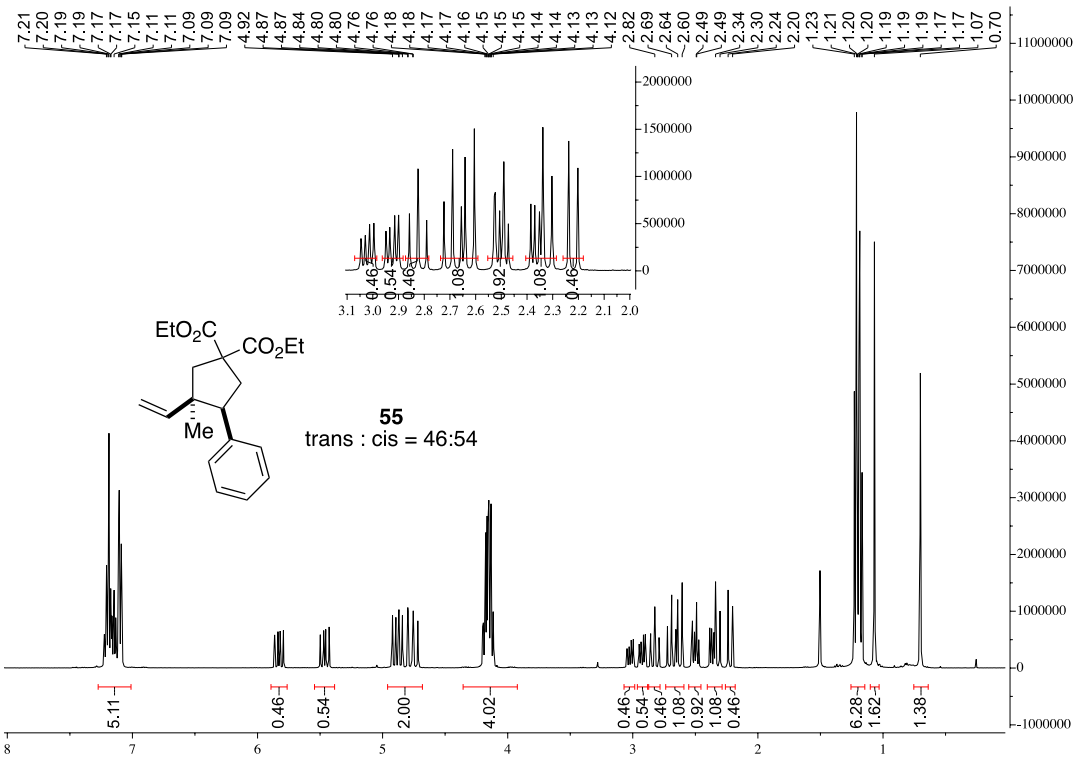

Ph
S
O
O
S
Ph
52
trans : cis = 75:25
15.21
0.25
0.75
2.00
0.75
5.20
0.25

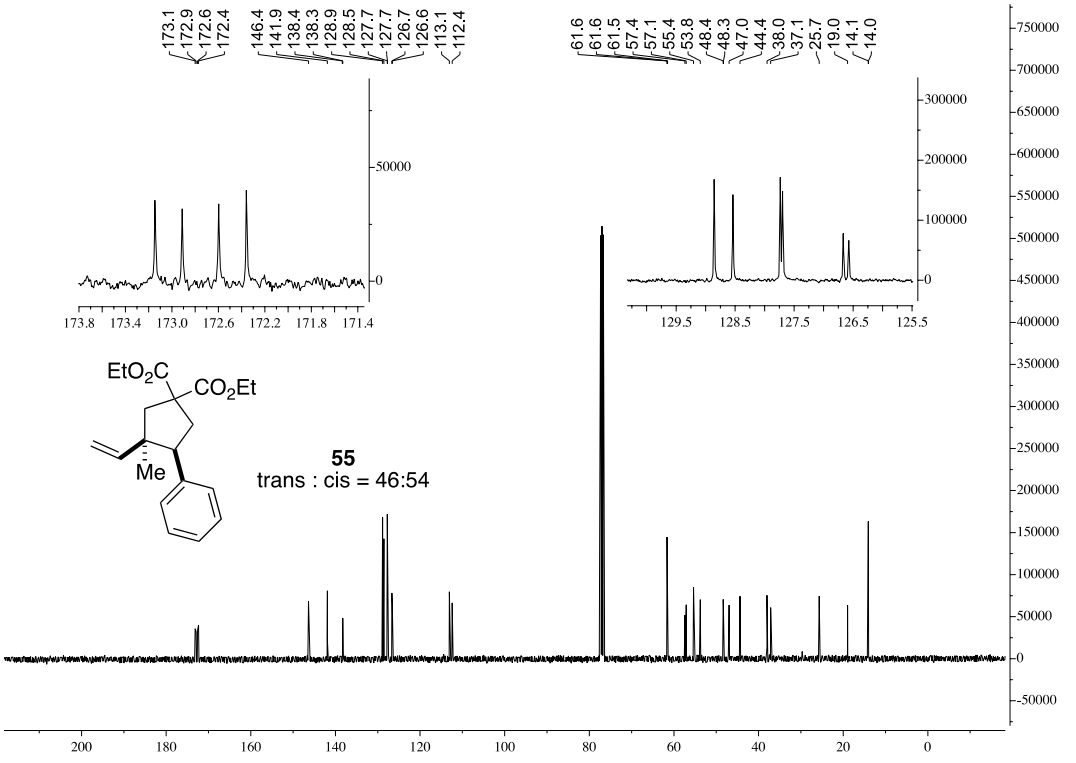

Ph
S
O
O
S
Ph
52
trans : cis = 75:25

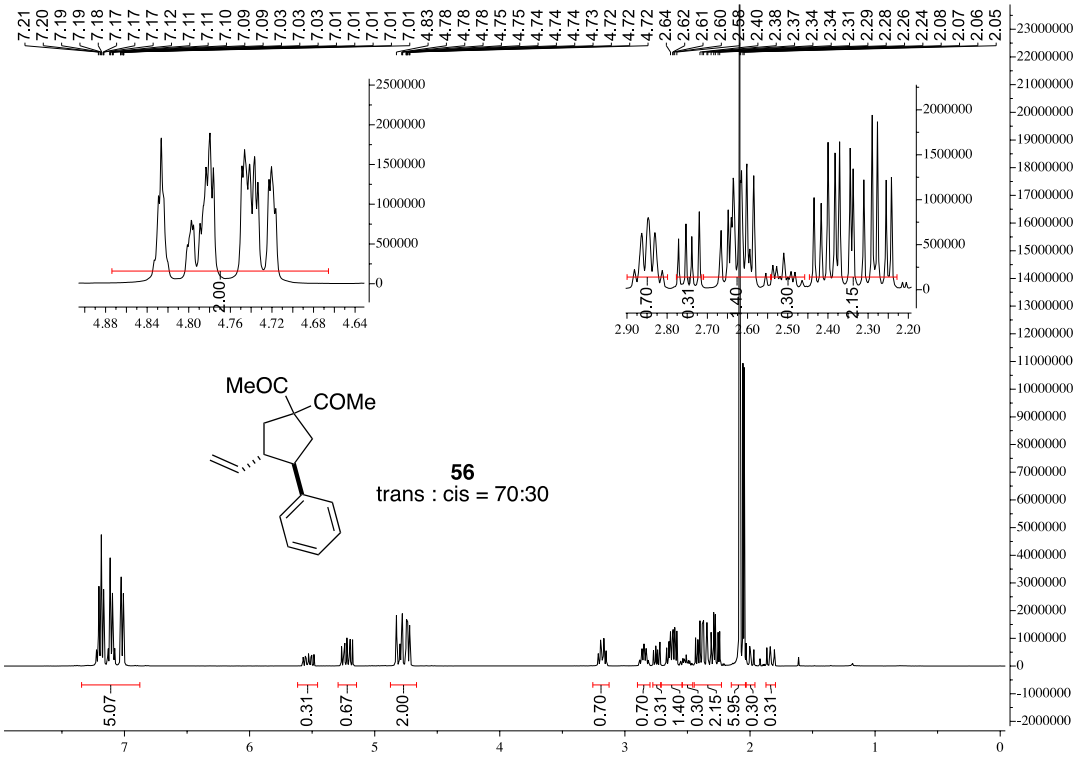

EtO2C
CO2Et
Me
53
trans : cis = 68:32

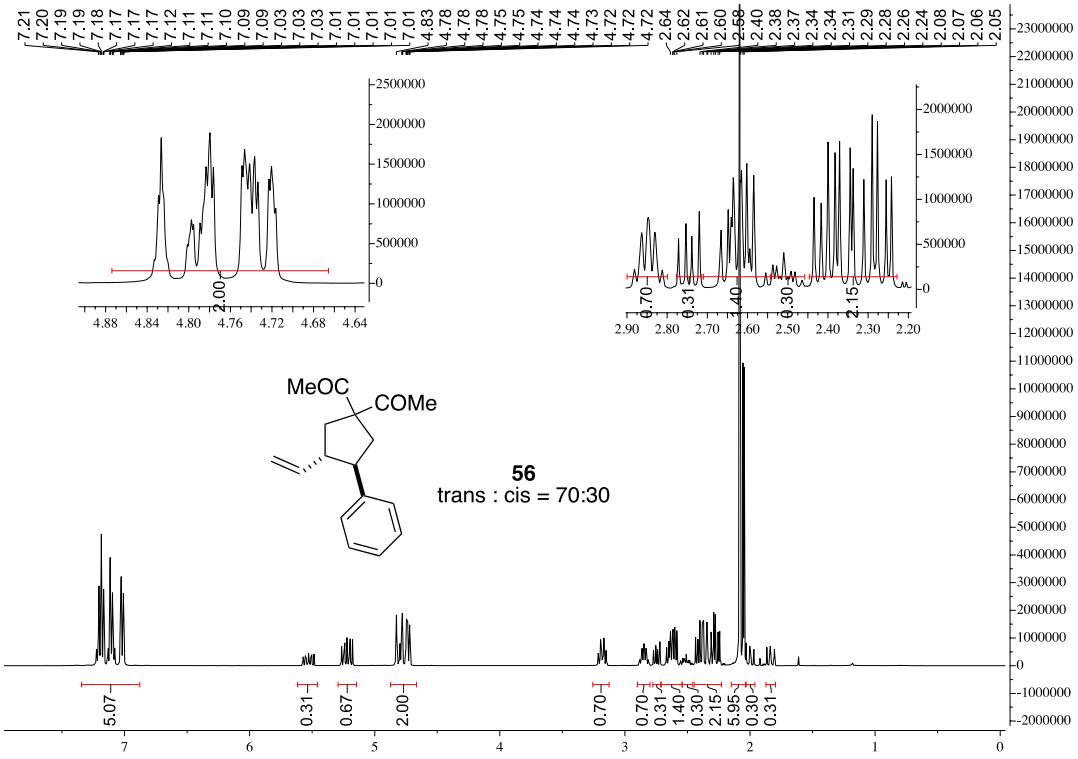

EtO2C
CO2Et
Me
53
trans : cis = 68:32

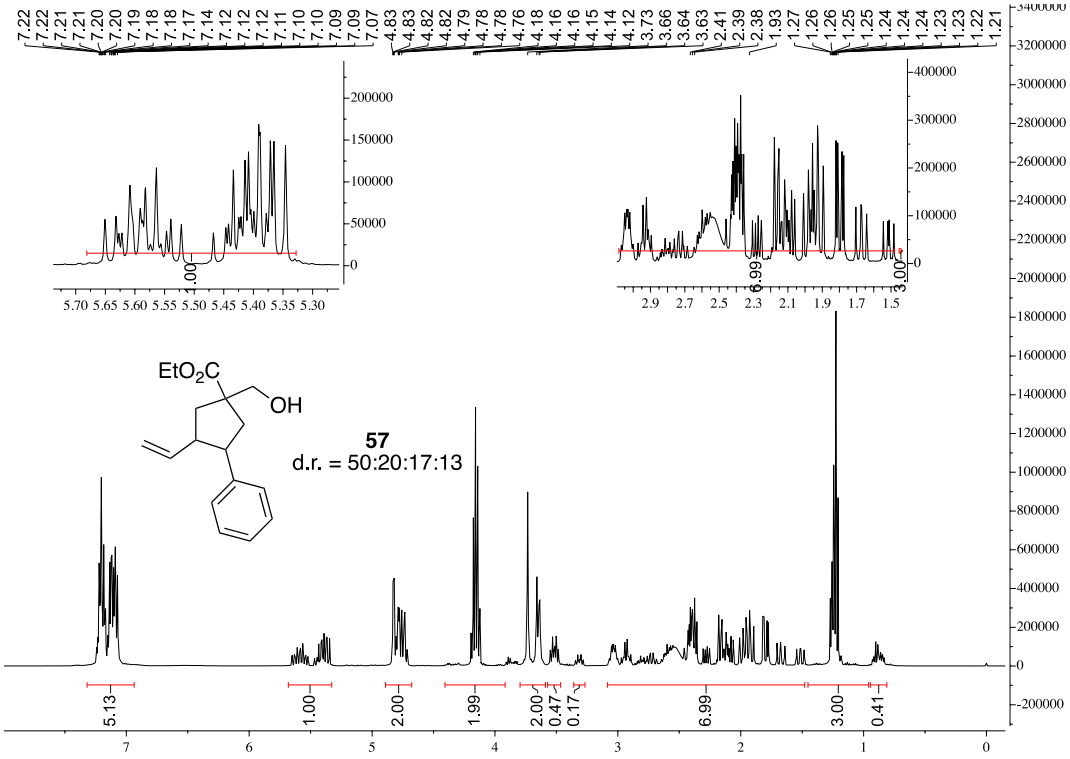

EtO2C
CO2Et
Ph
54
trans : cis = 70:30
54
trans : cis = 70:30

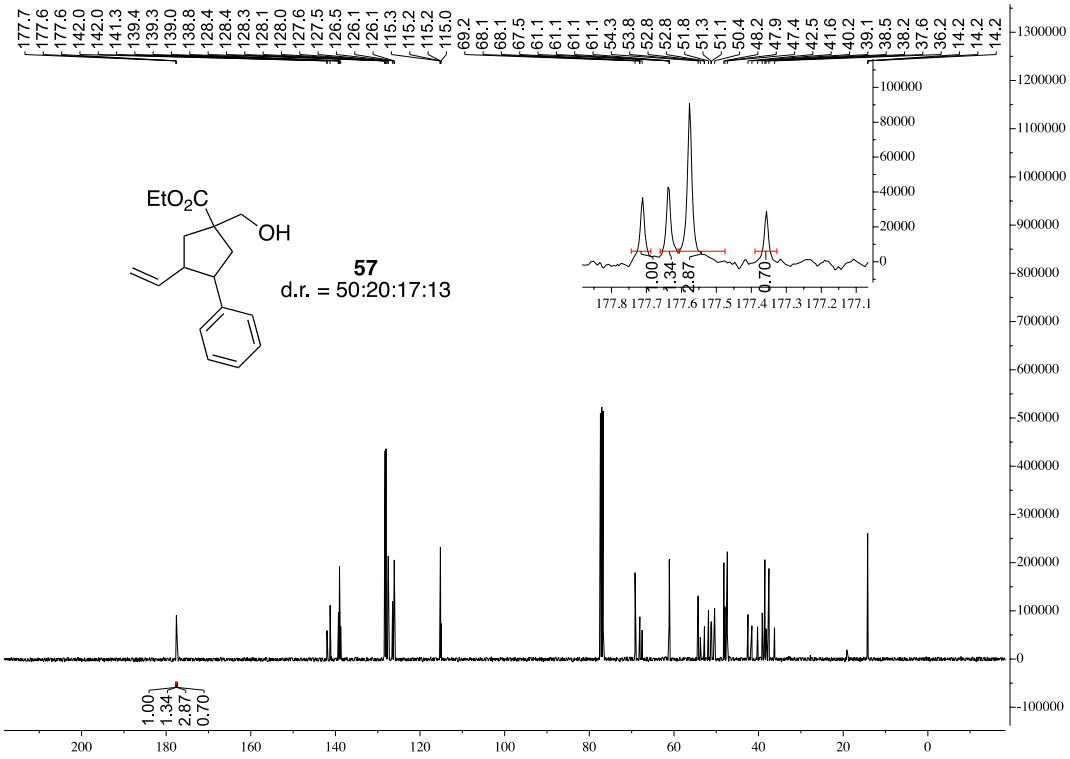

EtO2C
CO2Et
Me
55
trans : cis = 46:54

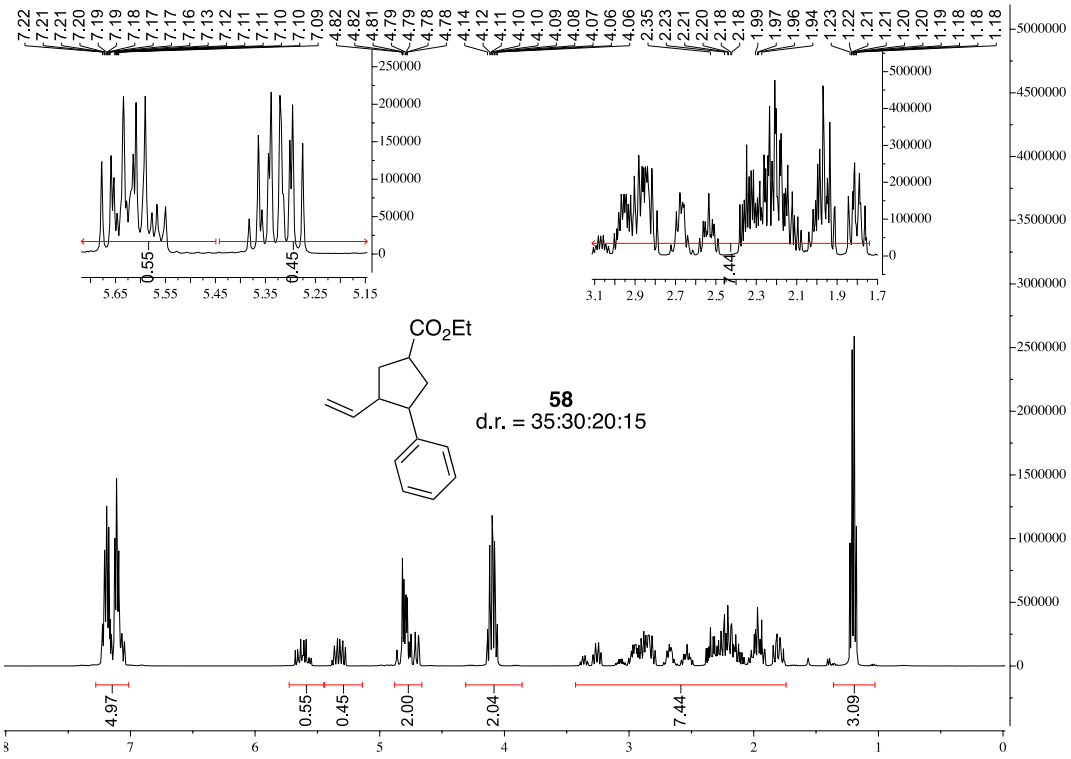

EtO2C
CO2Et
Me
55
trans : cis = 46:54

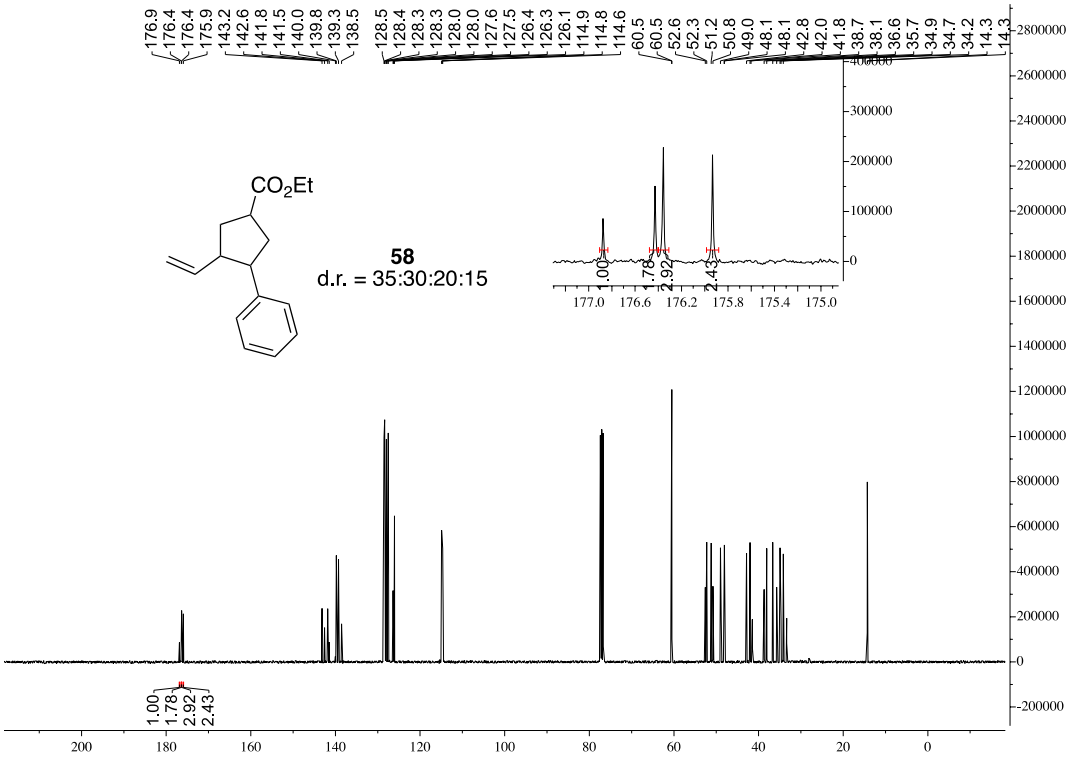

MeOC
COMe
56
trans : cis = 70:30

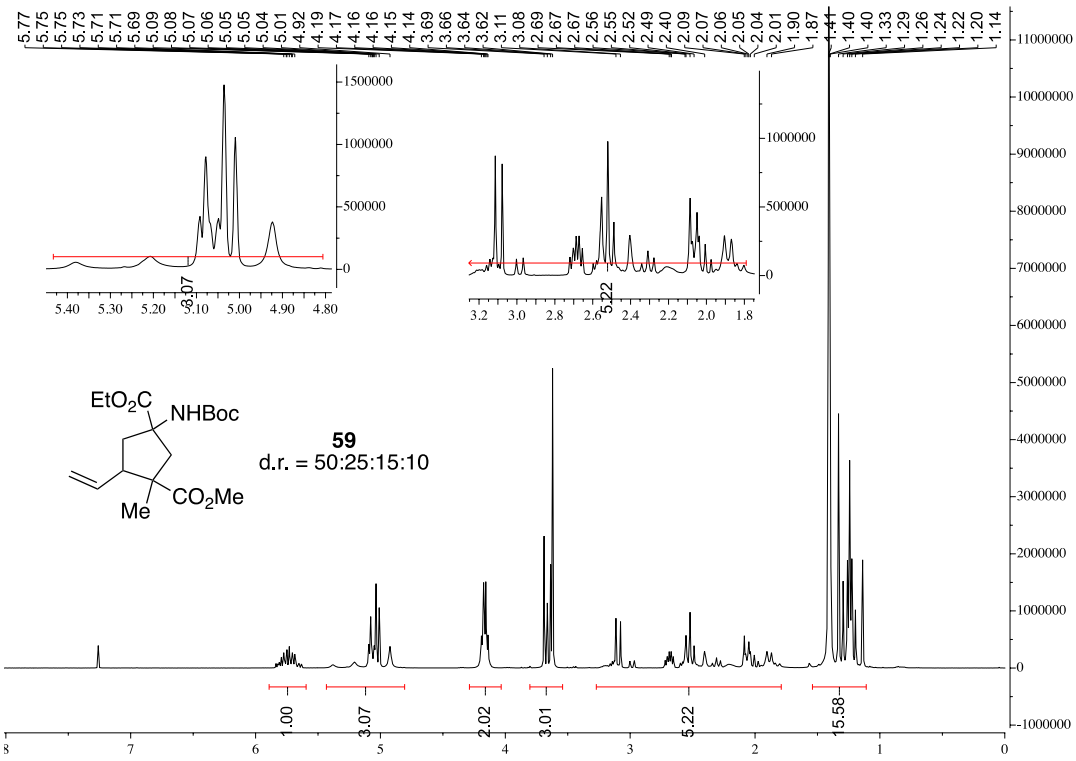

MeOC
COMe
56
trans : cis = 70:30

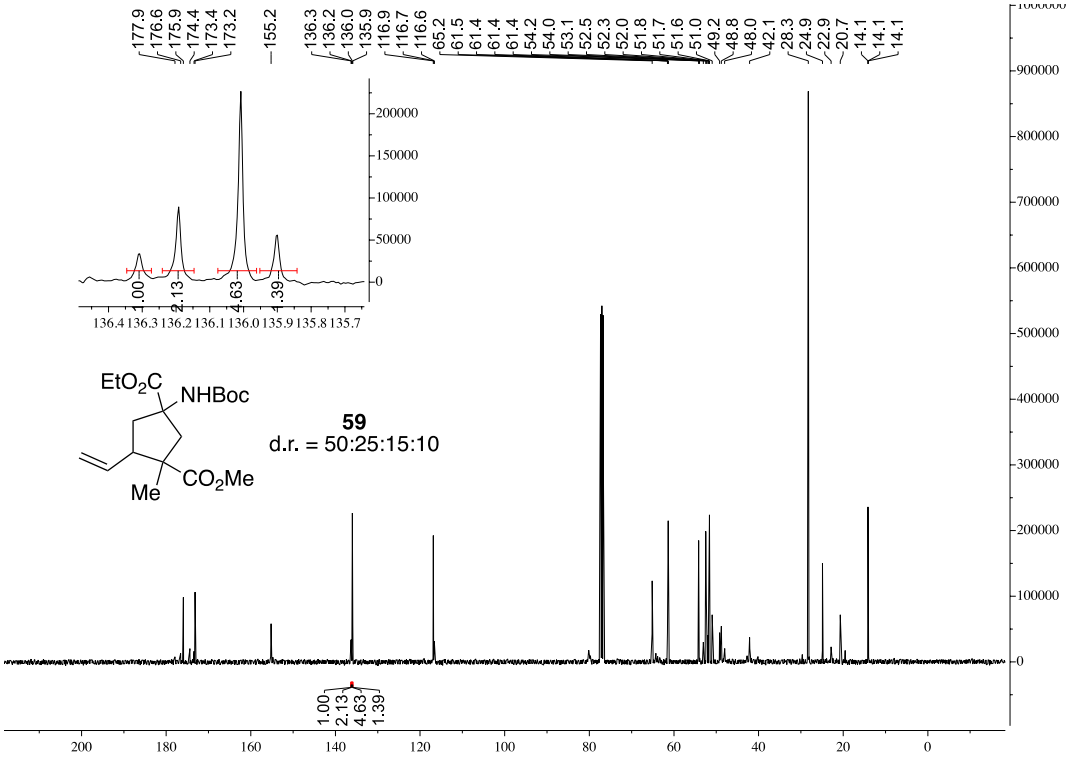

EtO2C
OH
57
d.r. = 50:20:17:13

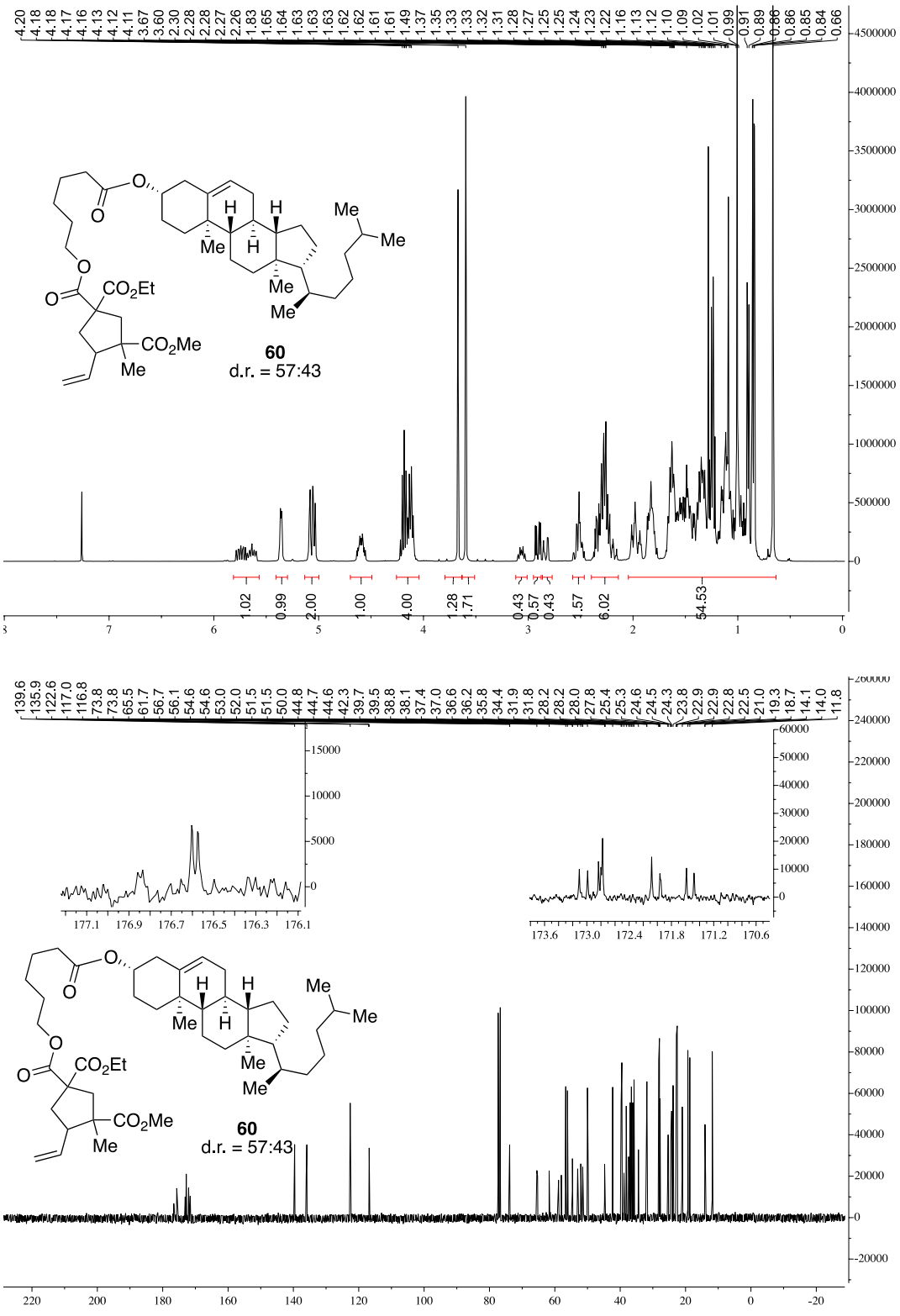

EtO2C
OH
57
d.r. = 50:20:17:13

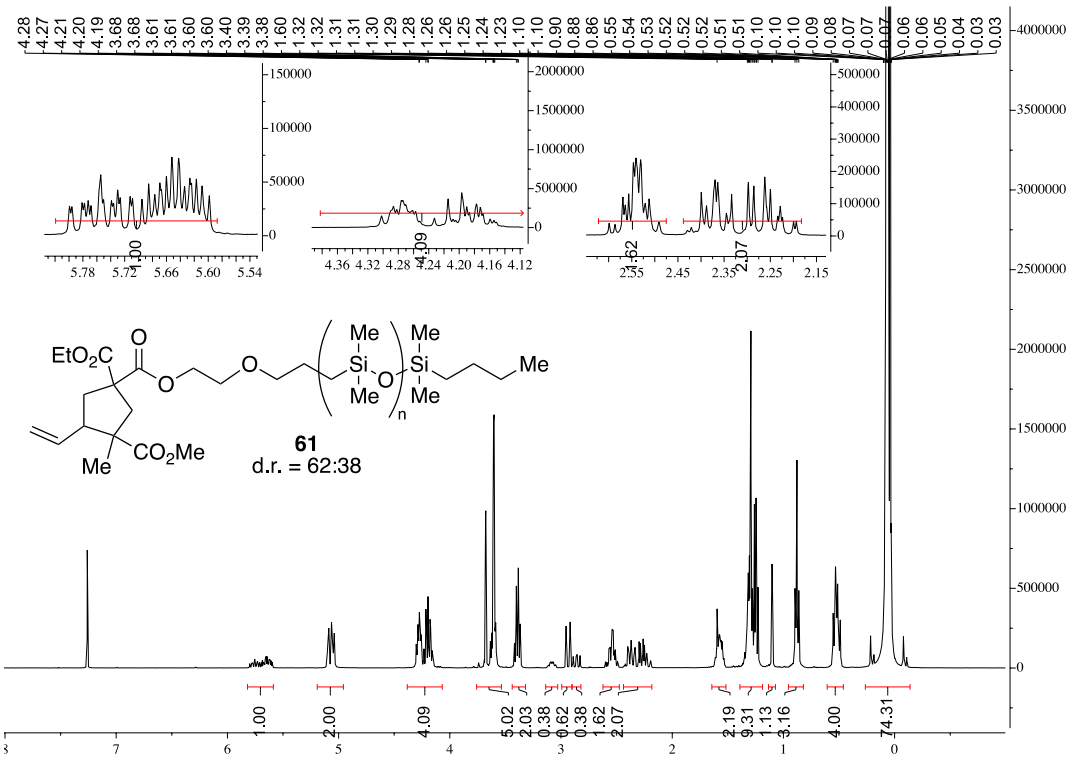

CO2Et
58
d.r. = 35:30:20:15

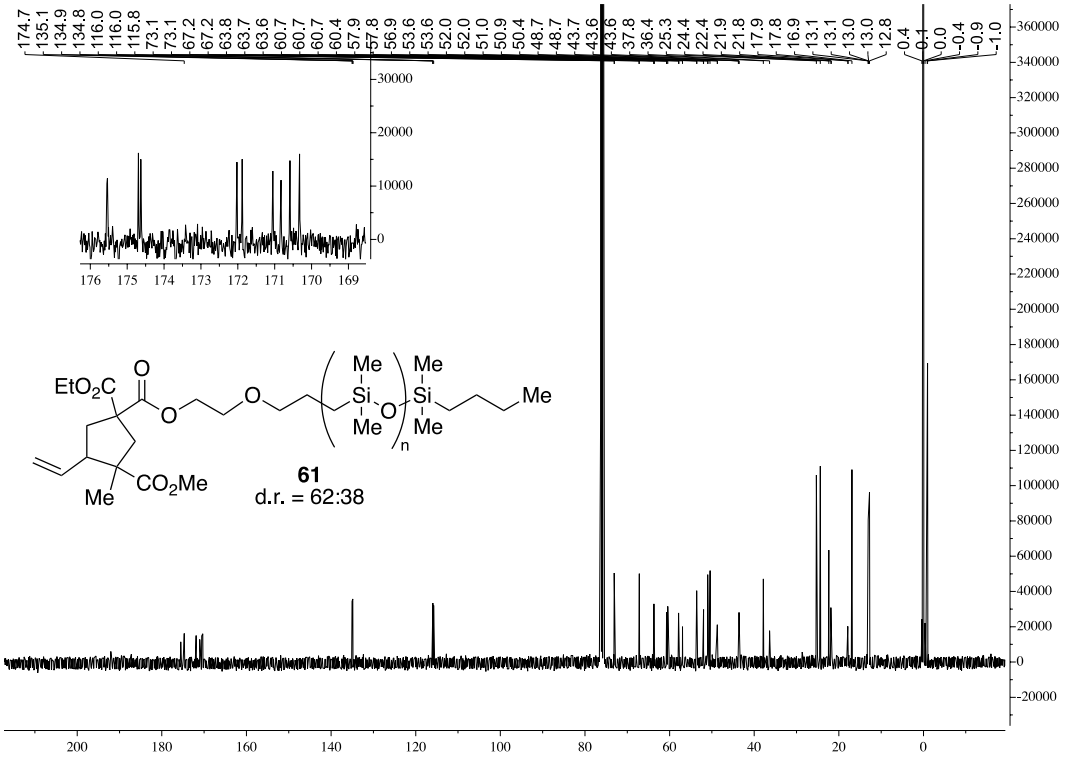

CO2Et
58
d.r. = 35:30:20:15

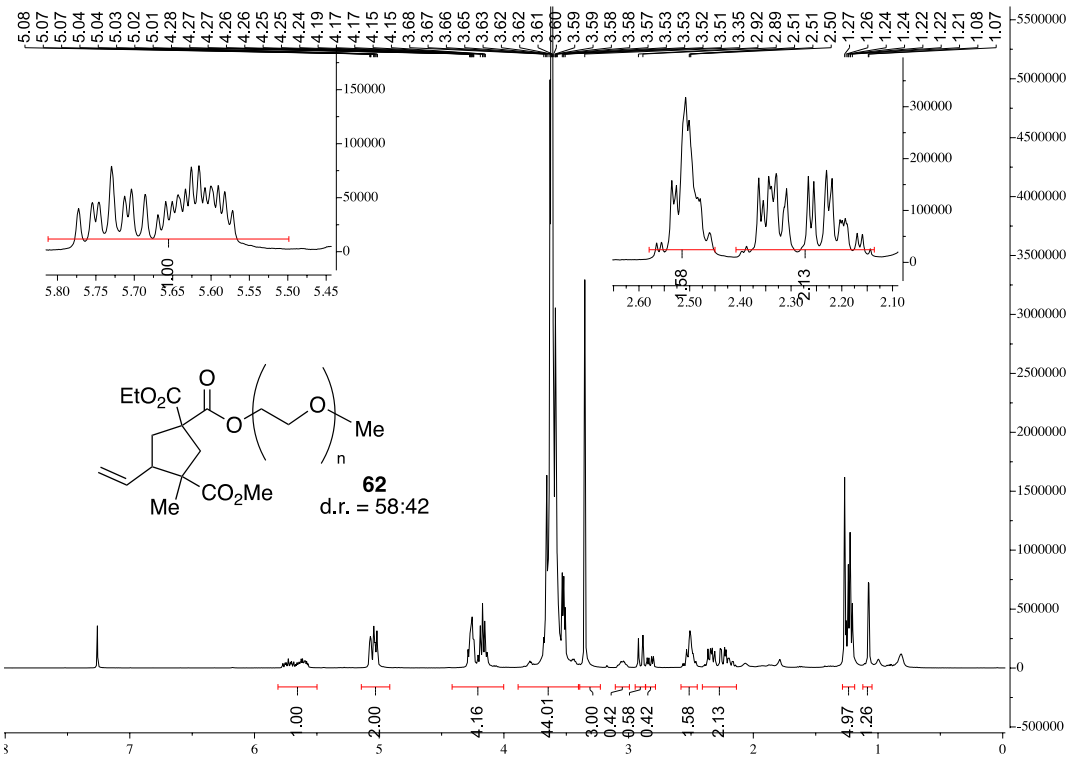

EtO2C
NHBoc
CO2Me
Me
59
d.r. = 50:25:15:10

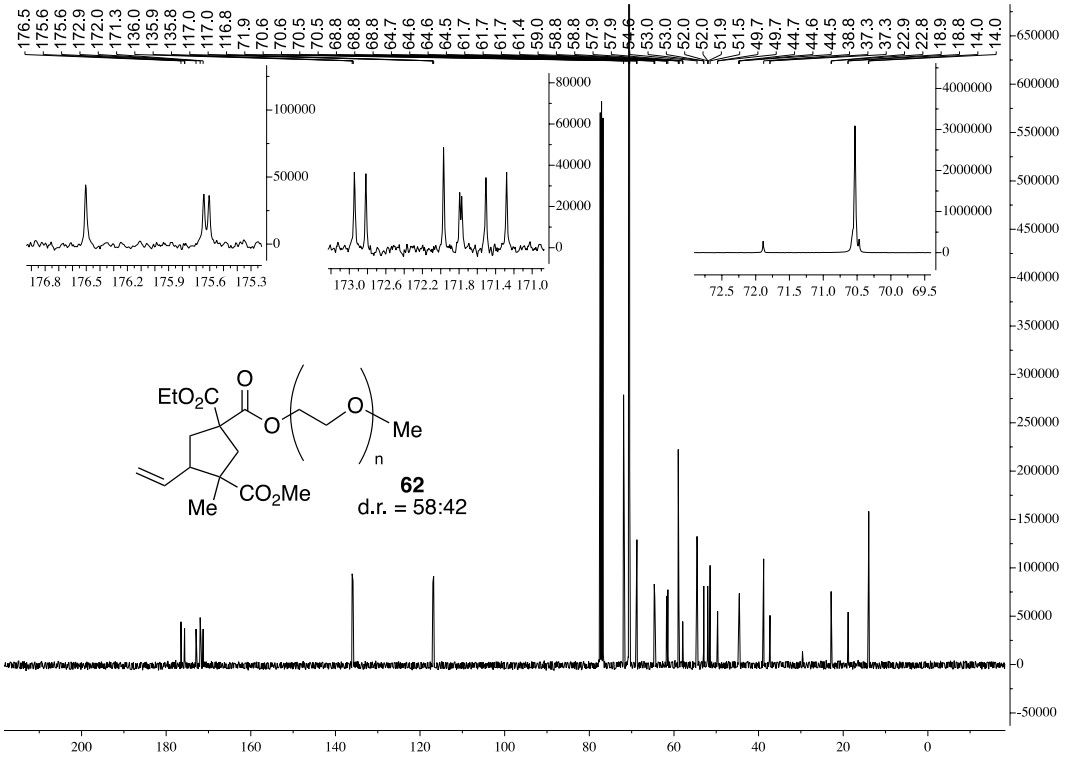

EtO2C
NHBoc
CO2Me
Me
59
d.r. = 50:25:15:10

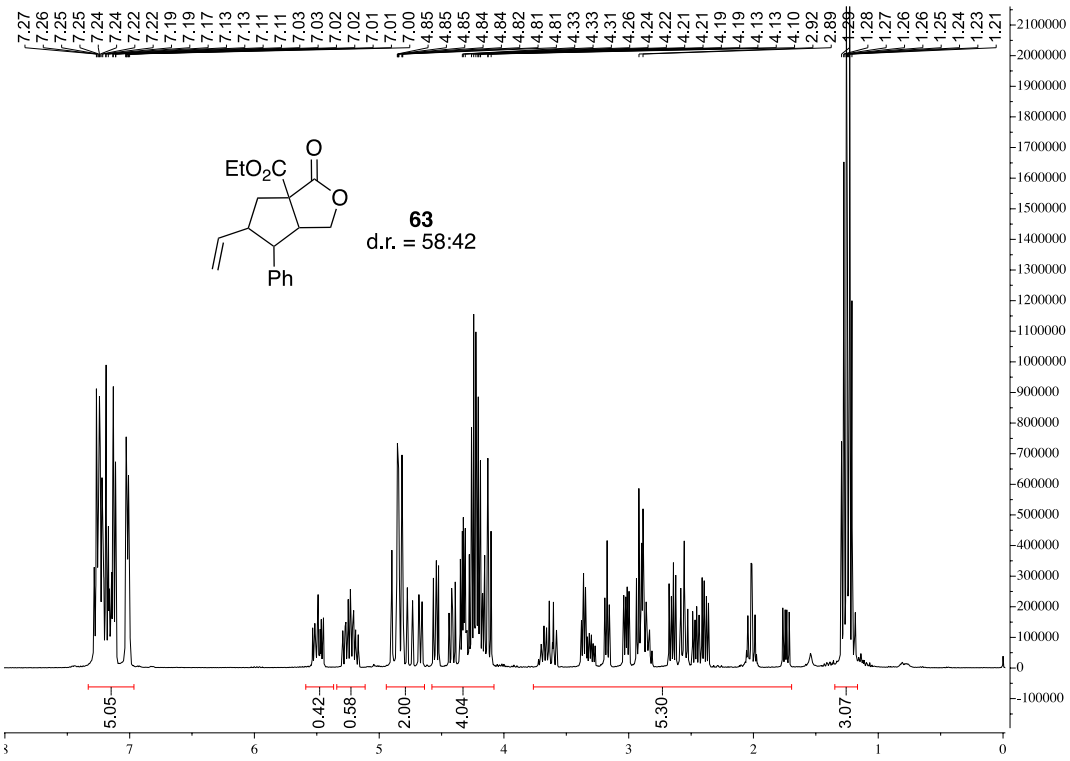

60
d.r. = 57:43
60
d.r. = 57:43

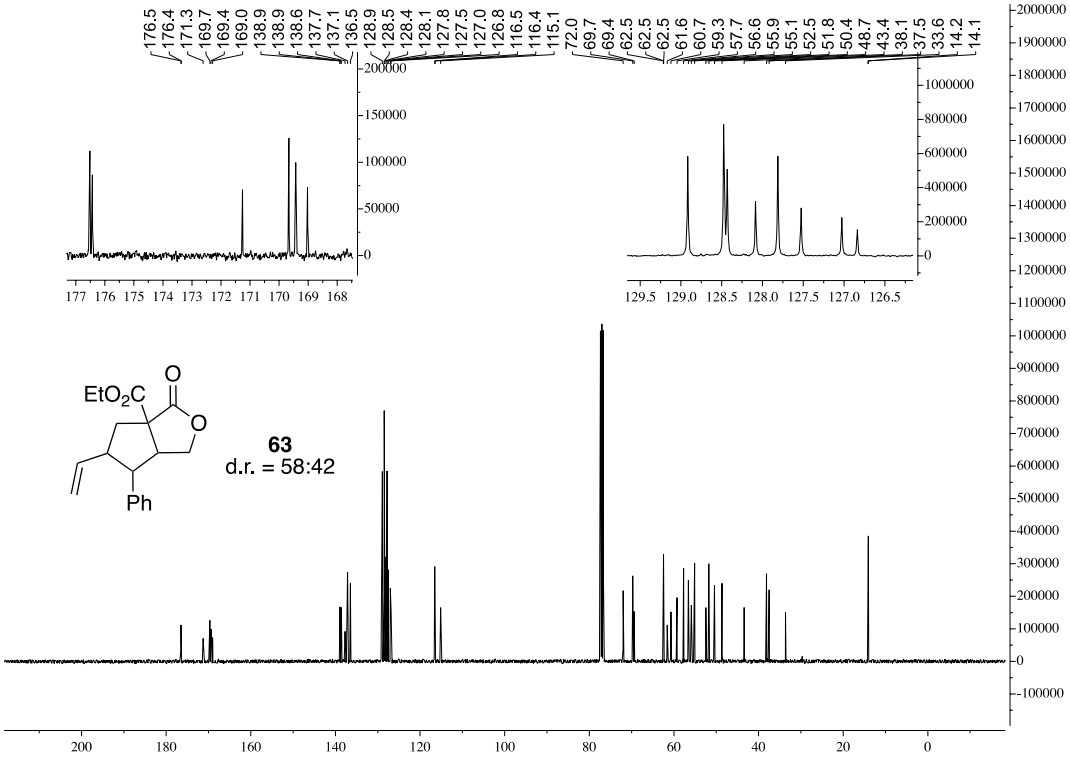

EtO2C
O
O
O
Me
Si
O
Si
Me
Me
Me
Me
Me
n
Me
CO2Me
Me
61
d.r. = 62:38

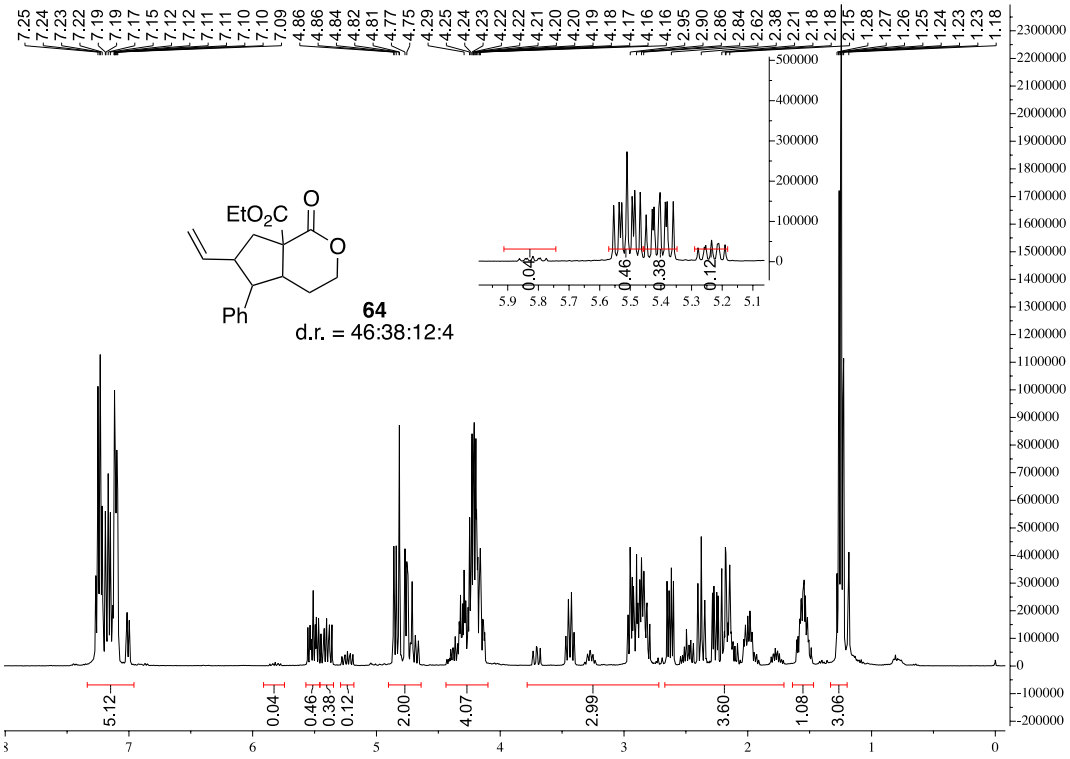

EtO2C
O
O
O
Me
Si
O
Si
Me
Me
Me
Me
Me
n
Me
CO2Me
Me
61
d.r. = 62:38

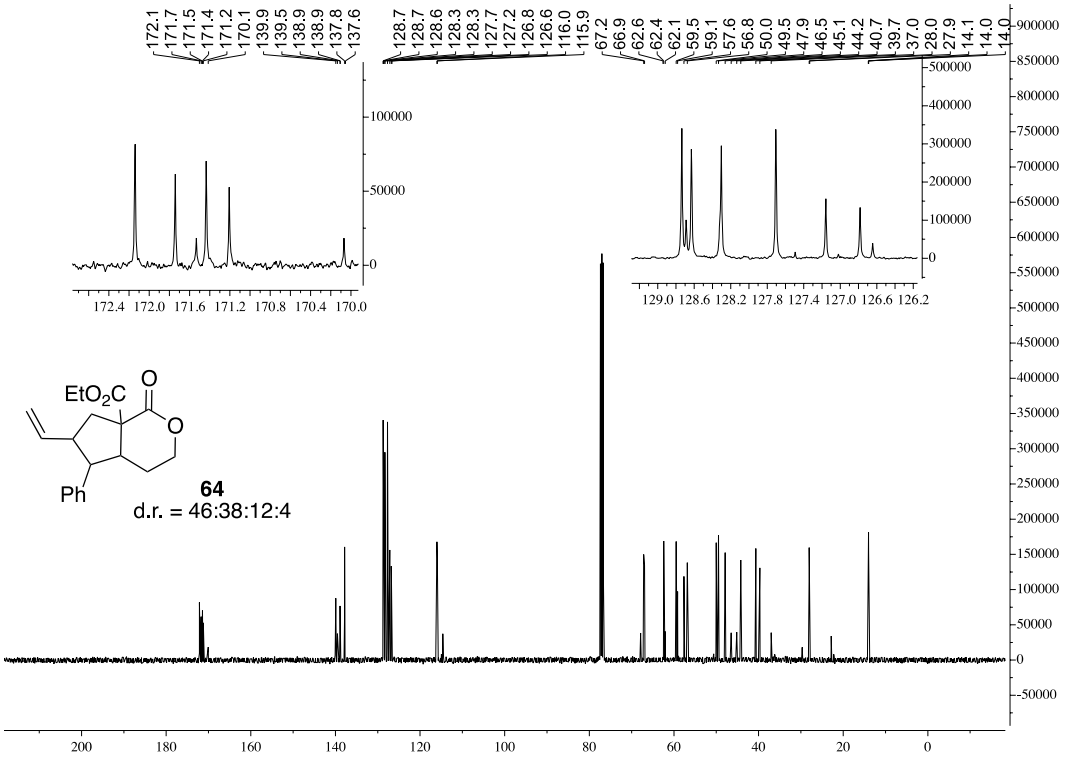

EtO2C
O
O
O
Me
n
CO2Me
Me
62
d.r. = 58:42

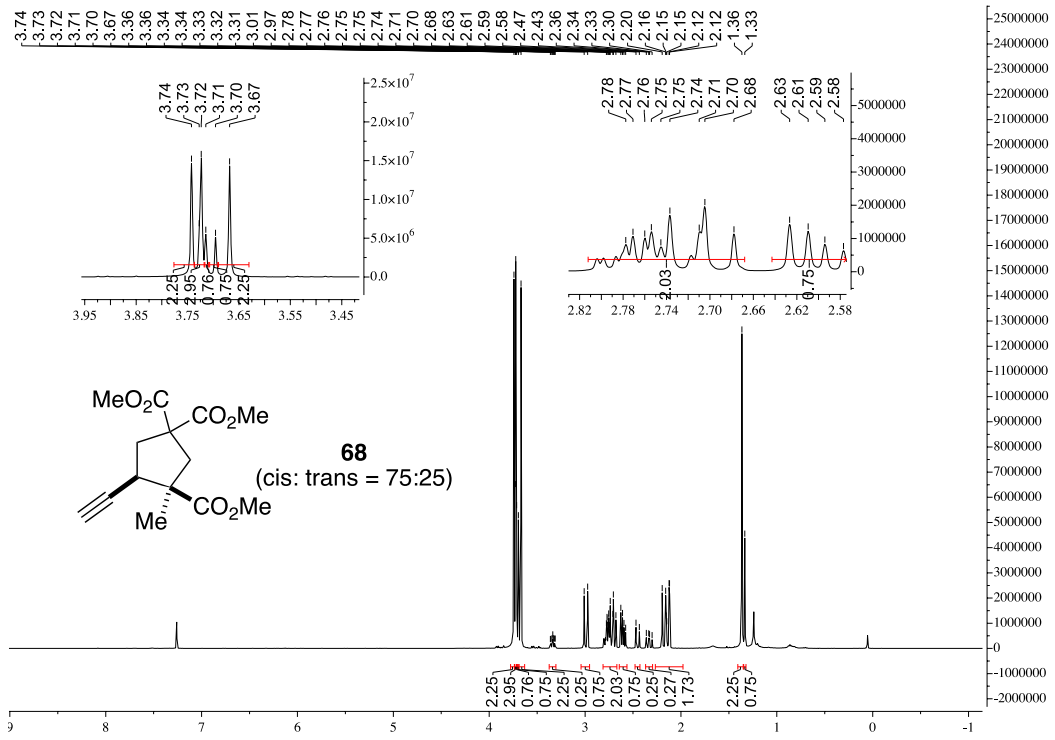

EtO2C
O
O
O
Me
n
CO2Me
Me
62
d.r. = 58:42

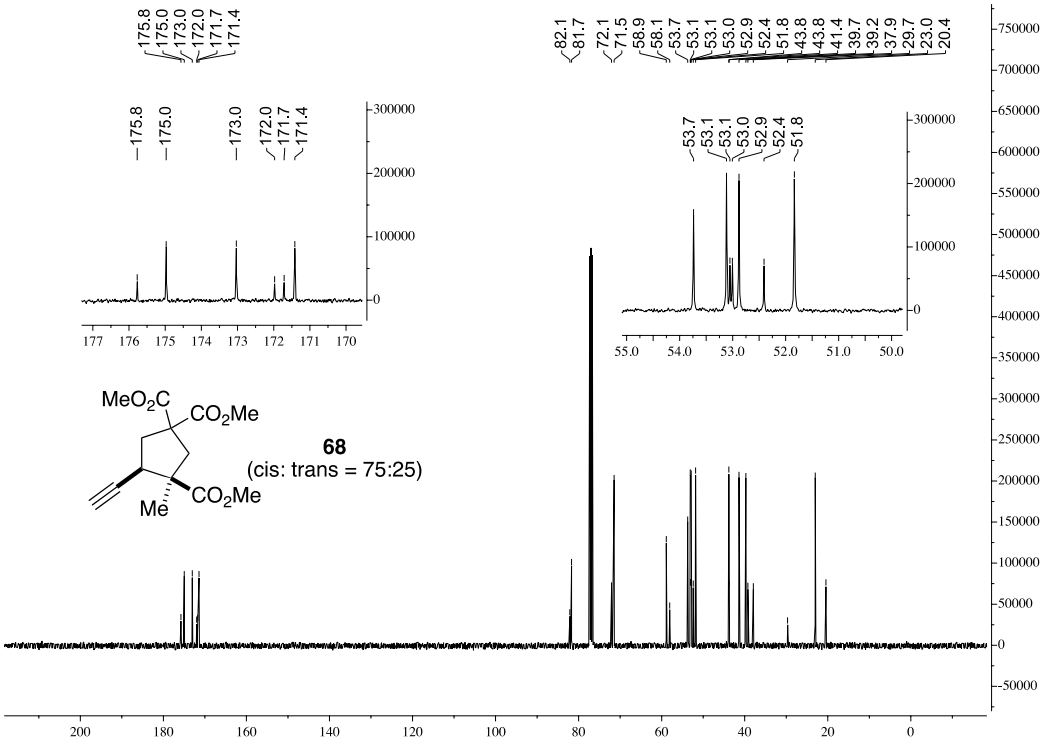

EtO2C
O
O
Ph
63
d.r. = 58:42

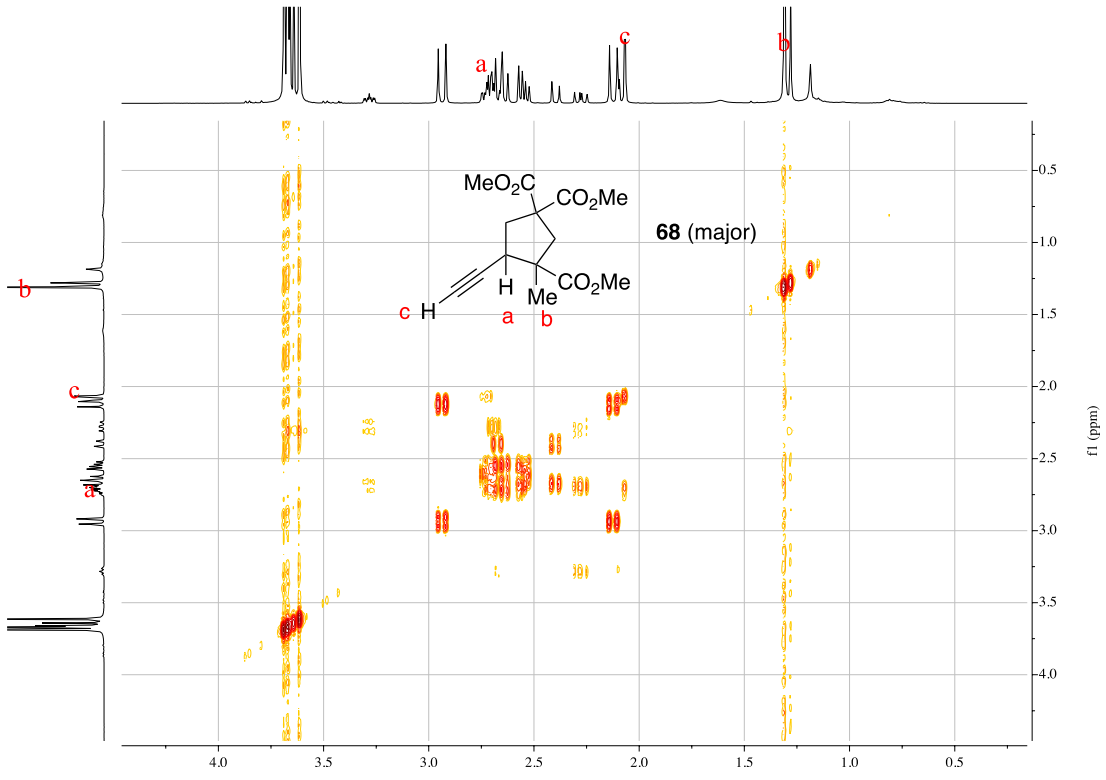

EtO2C
O
O
Ph
63
d.r. = 58:42

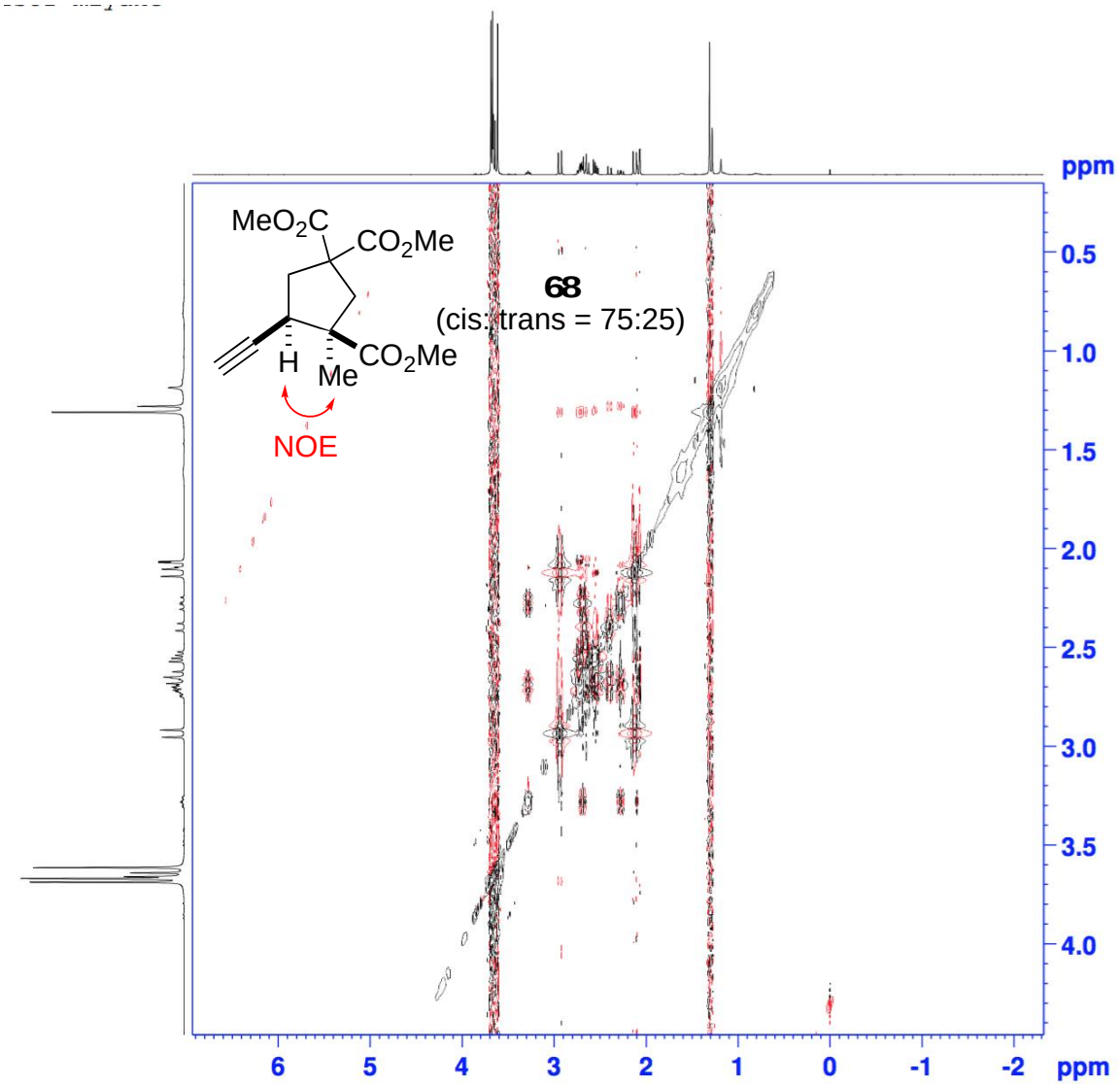

EtO2C
O
O
Ph
64
d.r. = 46:38:12:4

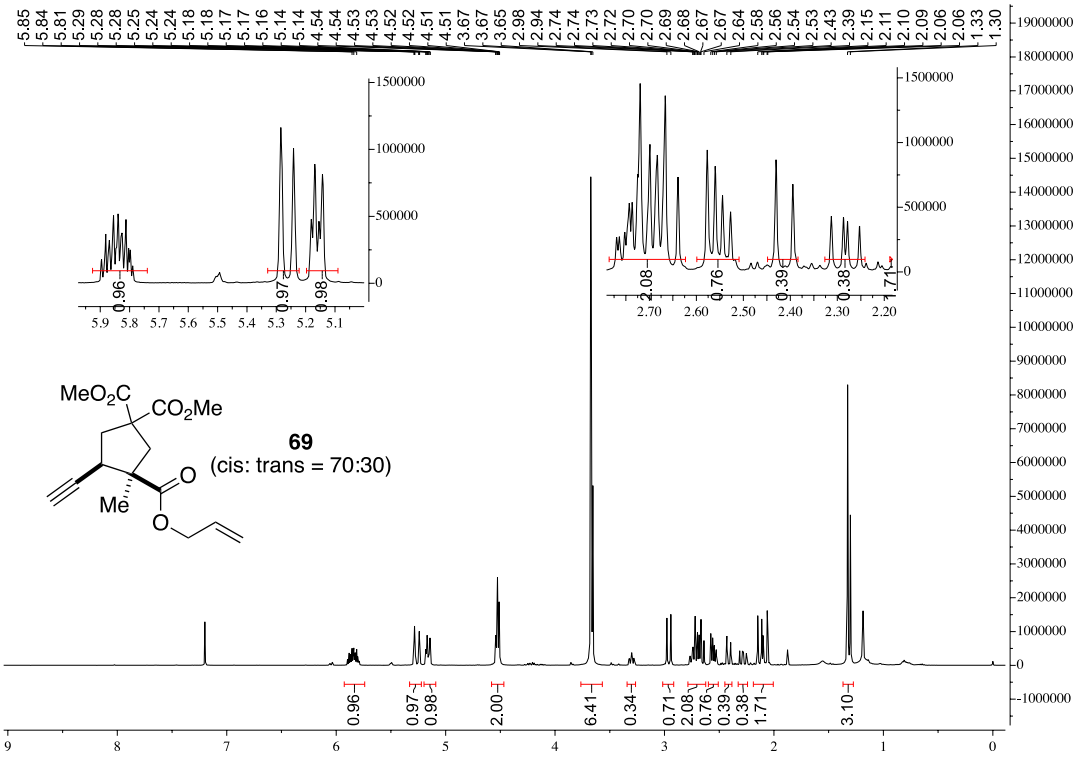

EtO2C
O
O
Ph
64
d.r. = 46:38:12:4

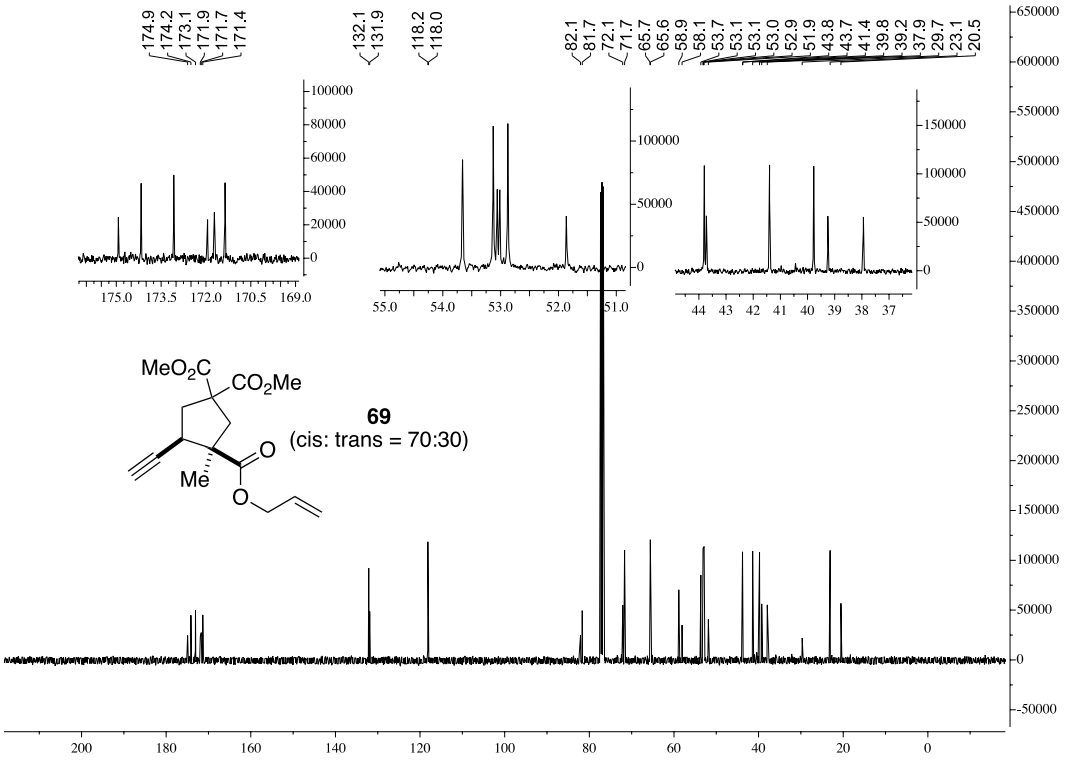

MeO2C
CO2Me
Me
CO2Me
68
(cis: trans = 75:25)


MeO2C
CO2Me
Me
CO2Me
68
(cis: trans = 75:25)


a
c
b
MeO2C
CO2Me
68 (major)
H
Me
CO2Me
c H
a
b
f1 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0


MeO2C
CO2Me
H
Me
CO2Me
NOE
68
(cis:trans = 75:25)
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
6
5
4
3
2
1
0
-1
-2
ppm


MeO2C
CO2Me
O
Me
O
69
(cis: trans = 70:30)


MeO2C
CO2Me
O
Me
O
69
(cis: trans = 70:30)