Versatile Stereoselective Oxidative Alkoxycarbonylation of Styrenes at Room-Temperature

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1. General Methods

General Experimental Methods

All reactions were prepared under nitrogen atmosphere with dry solvents under anhydrous conditions, by using Schlenk technique. Reactions were monitored by ^{1}H NMR taking a direct sample of the crude mixture. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 101 MHz), using $CDCl_3$ as solvent. Chemical shifts are reported in the δ scale relative to residual $CHCl_3$ (s, 7.26 ppm), MeOH (p, 3.31 ppm), DMSO (p, 2.50 ppm) and to the central line of $CDCl_3$ (77.16 ppm), CD_3OD (49.00 ppm), DMSO-d_6 (39.52 ppm) for ^{13}C NMR. ^{13}C NMR were recorded with ^{1}H broadband decoupling. The following abbreviations were used to explain the multiplicities: s = singlet, br = broad, d = doublet, app d = apparent as doublet, t = triplet, q = quartet, hept = heptet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublets of doublets, td = triplet of doublets, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). ESI-MS spectra were recorded on Waters Micromass ZQ 4000, using electrospray ionisation techniques, with samples dissolved in MeOH or CH_3CN. Carbon monoxide (Cp grade 99.99%) was supplied by Air Liquide (carbon monoxide is a toxic gas with potentially lethal action, therefore adequate precautions must be observed). The *p*-benzoquinone was purchased by Alfa Aesar and was filtered off a plug of silica gel washing with CH_2Cl_2, obtaining a yellow solid after drying the solution under vacuum. Pure compounds **4** were isolated through flash column chromatography on silica gel 60 (40-60 μm, 230-400 mesh). Olefins **2a-2h**, **2l**, **2n-v** were purchased from Merck Sigma-Aldrich or BLD Pharma. Liquid purchased olefins were filtered off a plug of neutral Al_2O_3 and used without further purification. Olefins **2i**[1] and **2m**[2] have been synthesized as already described in the literature, while the synthesis of **2j** and **2k** is reported in the Supporting Information. Anhydrous THF was distilled from sodium-benzophenone and methanol was distilled from $Mg(OMe)_2$. Benzyl alcohol **3a** was dried over molecular sieves (Alfa Aesar, 4 Å, 1–2 mm, beads). The *N*-benzyloxycarbonyl-D-glucosamine **3l**[3] and the disaccharide LTA **3m**[4] were prepared according to literature methods. All the other alcohols and sugars **3** were purchased from Merck Sigma-Aldrich or BLD Pharma and used without purification. $Pd(TFA)_2$ was purchased by Flurochem. The ligands **1a-1f** were synthesized according to literature procedures.[5] All other chemicals were purchased from Merck Sigma-Aldrich and used without further purification. All solid reagents were weighed in an analytical balance without excluding moisture and air.

CCDC.2302341 (compound **4ba**), CCDC.2302342 (compound **4ca**), CCDC.2302343 (compound **4ga**) and CCDC.2302344 (complex **A**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details

All DFT calculations have been performed using the ORCA 4.2.1 suite of quantum chemistry programs.[6] For a limited set of computations (thermochemical properties) version 5.0.2 of the same code was used. Geometries were optimized in vacuum using the M06L functional[7] and the def2-TZVP basis.[8] Dispersion corrections were also accounted for, following the DFT-D3 procedure (with zero damping functions) as suggested by Grimme et al.[9] Vibrational frequencies were calculated at the optimized geometries to check the stability of the stationary points. Transition states were located my means of a series constrained optimizations along the expected reaction coordinate or, in the most complex cases, by means of the Nudged Elastic Band (NEB) method.[10] Once a transition state was located and optimized, the Intrinsic Reaction Coordinate (IRC)[11] method was applied to determine if it connects the expected couple of reactants and products. Zero point energies (ZPE) and thermal contributions, needed to calculate the free energies at 298K, were evaluated by applying a scale factor of 0.9824 to the vibrational frequencies, adequate for the present combination of DFT functional and basis set[12] and a fictitious pressure of 302 atm for the THF solvent,[13] in order

to correct the overestimation of entropic contributions. Final single point energy calculations at the previously optimized geometries were performed with the large def2-QZVPP basis[8] and the M06 functional,[14] with the inclusion of solvation effects through the SMD model[15] and of dispersion interactions.[9] The final energy of each structure, used to evaluate the relative free energies of the various products and intermediates, was built by summing the difference between the def2-TZVP electronic and free energies to the def2-QZVPP single point electronic energy.

Typical Procedure for the Room Temperature Oxidative Alkoxycarbonylation of Styrenes
In a nitrogen flushed dried Schlenk tube, equipped with a magnetic stirring bar, the $Pd(TFA)_2$ (3.3 mg, 0.01 mmol) and THF (1.0 mL) were added in sequence. After the mixture turned in a red/brown color (10 min), the ligand **1e** (5.5 mg, 0.011 mmol) was added. The mixture was left under stirring for 10 min, turning in a dark orange color. Then, *p*-benzoquinone (81.2 mg, 0.75 mmol), *p*-TSA·H_2O (1.9 mg, 0.01 mmol), the selected alcohol **3a-3i** (0.55 mmol) or sugar **3j-3m** (0.5 mmol), and the olefin **2** (0.5 mmol) were added in sequence. The reaction was vigorously stirred at room temperature (20°C) under balloon pressure of CO, for 17 h, having the Schlenk tube covered with an aluminum foil. The CO was removed, and the reaction mixture was analyzed by ^{1}H NMR to determine the conversion of the olefin. The crude was dried under reduced pressure and the product **4** was eventually obtained after column chromatography on silica gel.

For the synthesis of compound **3ai**$_2$, 1.0 mmol of styrene **2a** and 0.5 mmol of glycerol **3i** were utilized. For the synthesis of compound **3ai**$_3$, 1.55 mmol of styrene **2a** and 0.5 mmol of glycerol **3i** were utilized in the presence of 5 mol% of catalyst loading for 60 h.

Typical Procedure for the Room Temperature Oxidative Alkoxycarbonylation of substituted olefins 2t, 2u, 2v
In a nitrogen flushed dried Schlenk tube, equipped with a magnetic stirring bar, the $Pd(TFA)_2$ (8.3 mg, 0.025 mmol) and THF (1.0 mL) were added in sequence. After the mixture turned in a red/brown color (10 min), the ligand **1f** (10.7 mg, 0.0275 mmol) was added. The mixture was left under stirring for 10 min. Then, *p*-benzoquinone (81.2 mg, 0.75 mmol), *p*-TSA·H_2O (1.9 mg, 0.01 mmol), the selected benzyl alcohol **3a** (58μL, 0.55 mmol) and the olefin **2t-2v** (0.5 mmol) were added in sequence. The reaction was vigorously stirred at 60°C in an oil bath under balloon pressure of CO, for 17 h. The CO was removed, and the reaction mixture was analyzed by ^{1}H NMR to determine the conversion of the olefin. The crude was dried under reduced pressure and the products were eventually obtained after column chromatography on silica gel.

2. List of the utilized olefins 2 and alcohols 3

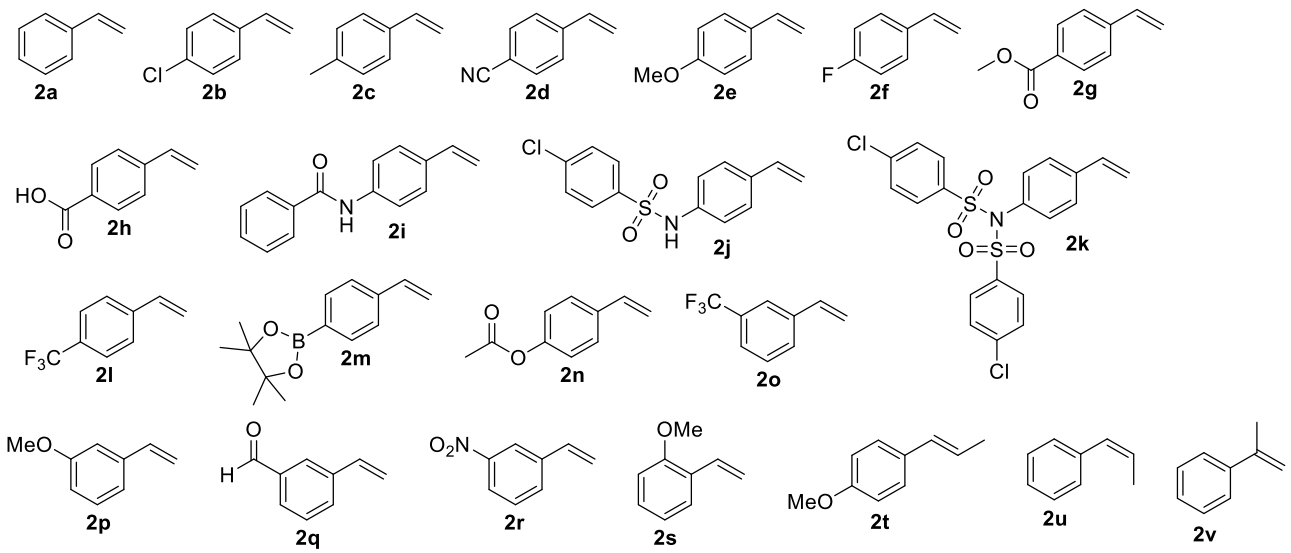


Figure S1 – Complete list of the utilized olefins **2**

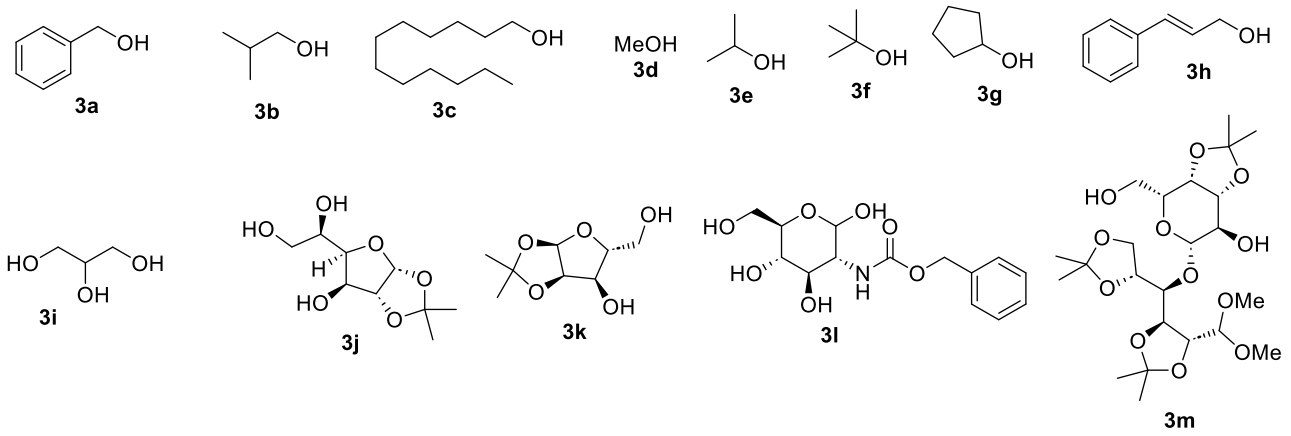
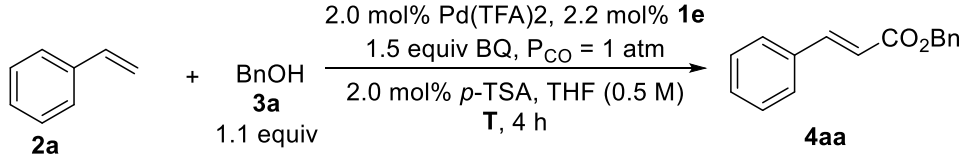


Figure S2 – Complete list of the utilized alcohols **3**

3. Effect of the temperature on the reaction

Table S1 – Effect of the temperature on the oxidative alkoxycarbonylation of styrene **2a**



Entry[a]	T (°C)	Conversion (%)[b]	Yield 4aa (%)[b]	Selectivity 4aa (%)[c]
1	20	41	40	98
2	40	90	83	91
3	60	95	87	91

[a] Reaction performed at 1 atm of CO pressure, with olefin **2a** (0.25 mmol-scale), 2.0 mol% $Pd(TFA)_2$, 2.2 mol% ligand **1e**, using 1.1 equiv of BnOH **3a**, 1.5 equiv of *p*-BQ, 2.0 mol% of *p*-TSA in THF (0.5 M), for 4 h at the indicated temperature. [b]Determined by ^1H NMR analysis of the reaction crude. [c] Calculated as: Selectivity = Yield/Conversion.

4. Crystallographic Data for Compounds 4ba, 4ca, 4ga and Complex A

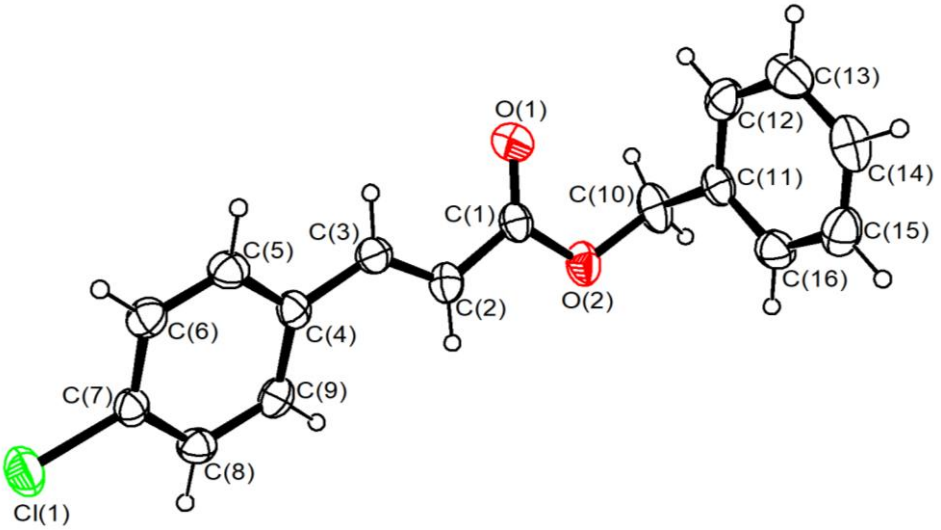


Figure S3 - Molecular structure of **4ba**. Displacement ellipsoids are at the 30 % probability level. Main bond distances (Å) and angles (°): C(1)-O(1) 1.216(3), C(1)-O(2) 1.325(3), O(2)-C(10) 1.477(3), C(1)-C(2) 1.465(3), C(2)-C(3) 1.297(3), C(3)-C(4) 1.471(3), C(7)-Cl(1) 1.738(2), C(2)-C(1)-O(1) 124.3(2), C(2)-C(1)-O(2) 112.7(2), O(2)-C(1)-O(2) 123.0(2), C(1)-O(2)-C(10) 115.0(2), C(1)-C(2)-C(3) 122.2(2), C(2)-C(3)-C(4) 128.6(2), O(2)-C(10)-C(11) 111.6(2).

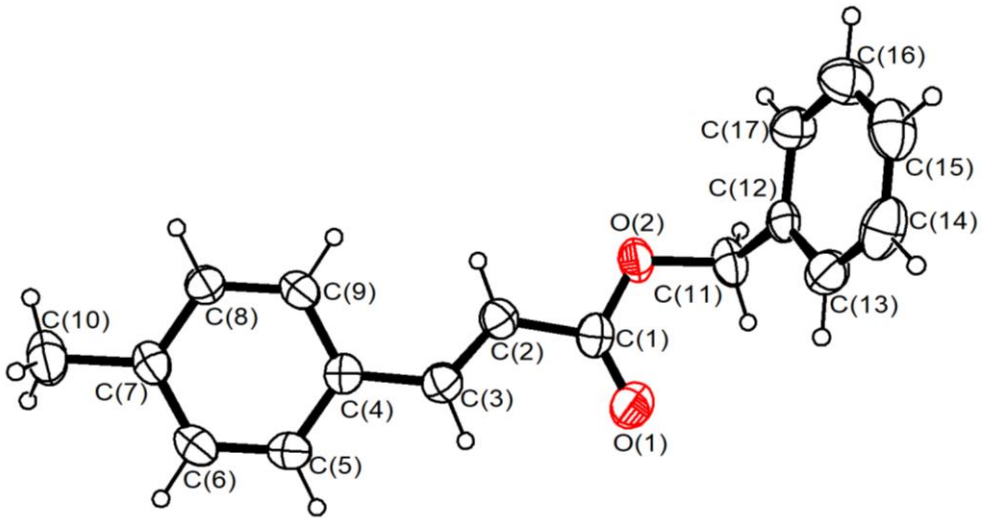


Figure S4 - Molecular structure of **4ca**. Displacement ellipsoids are at the 30 % probability level. Main bond distances (Å) and angles (°): C(1)-O(1) 1.185(3), C(1)-O(2) 1.327(3), O(2)-C(11) 1.452(2), C(1)-C(2) 1.477(3), C(2)-C(3) 1.296(3), C(3)-C(4) 1.467(3), C(2)-C(1)-O(1) 126.4(2), C(2)-C(1)-O(2) 110.2(2), O(1)-C(1)-O(2) 123.4(2), C(1)-O(2)-C(11) 118.46(19), C(1)-C(2)-C(3) 122.7(2), C(2)-C(3)-C(4) 127.0(2), O(2)-C(11)-C(12) 109.80(17).

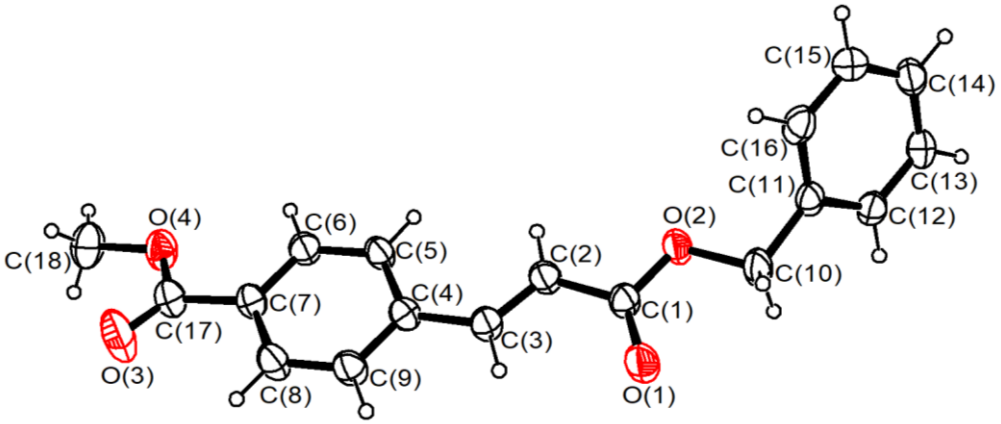


Figure S5 - Molecular structure of **4ga**. Displacement ellipsoids are at the 30 % probability level. Main bond distances (Å) and angles (°): C(1)-O(1) 1.195(5), C(1)-O(2) 1.335(5), O(2)-C(10) 1.453(5), C(1)-C(2) 1.469(6), C(2)-C(3) 1.318(6), C(3)-C(4) 1.454(6), C(17)-O(3) 1.186(6), C(17)-O(4) 1.319(6). O(4)-C(18) 1.440(6), C(2)-C(1)-O(1) 124.7(4), C(2)-C(1)-O(2) 113.0(3), O(2)-C(1)-O(2) 122.3(4), C(1)-O(2)-C(10) 113.8(3), C(1)-C(2)-C(3) 118.7(4), C(2)-C(3)-C(4) 129.2(4), O(2)-C(10)-C(11) 109.1(3). C(7)-C(17)-O(3) 124.3(4), C(7)-C(17)-O(4) 122.9(5), O(3)-C(17)-O(4) 122.9(5), C(17)-O(4)-C(18) 115.9(4).

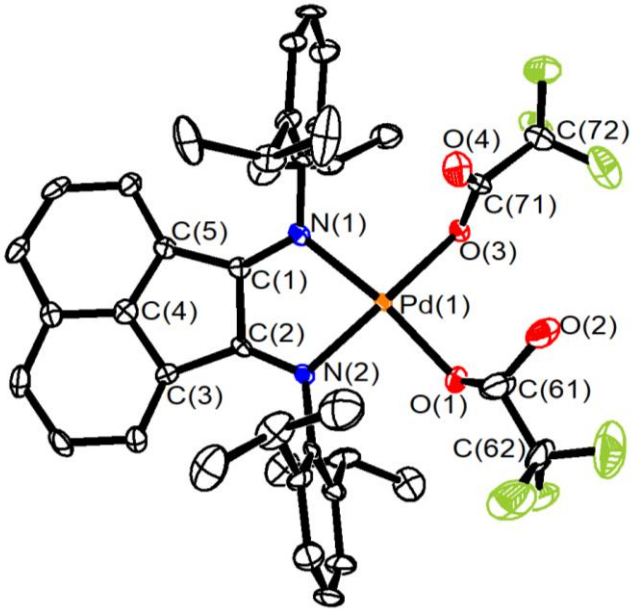


Figure S6 - Molecular structure of complex **A**. Displacement ellipsoids are at the 30 % probability level. Main bond distances (Å) and angles (°): Pd(1)-N(1) 2.019(9), Pd(1)-N(2) 1.996(9), Pd(1)-O(1) 1.982(8), Pd(1)-O(3) 2.037(8), C(1)-N(1) 1.287(14), C(2)-N(2) 1.283(13), C(1)-C(2) 1.486(15), C(1)-C(5) 1.441(15), C(2)-C(3) 1.475(14), C(3)-C(4) 1.419(15), C(4)-C(5) 1.407(17), C(61)-O(1) 1.224(18), C(61)-O(2) 1.29(2), C(61)-C(62) 1.48(2), C(71)-O(3) 1.252(15), C(71)-O(4) 1.223(15), C(71)-C(72) 1.504(18), N(1)-Pd(1)-N(2) 81.6(4), O(1)-Pd(1)-O3) 91.1(3), N(1)-Pd(1)-O(1) 172.1(4), N(2)-Pd(1)-O3) 171.7(4), Pd(1)-N(1)-C(1) 112.1(7), Pd(1)-N(2)-C(2) 113.2(7), N(1)-C(1)-C(2)-116.4(9), N(2)-C(2)-C(1) 116.1(9), Pd(1)-O(1)-C(61) 120.9(10), Pd(1)-O(3)-C(71) 116.5(8).

X-ray crystallography

Crystal data and collection details for **4ba**, **4ca, 4ga** and complex **A** are reported in Table S2. Data were recorded on a Bruker APEX II diffractometer equipped with a PHOTON2 detector using Mo–Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[16] Hydrogen atoms were fixed at calculated positions and refined using a riding model.

Table S2 - Crystal data and measurement details for **4ba, 4ca**, **4ga** and **complex A.**

Compound	**4ba**	**4ca**	**4ga**	**Complex A**
Formula	$C_{16}H_{13}ClO_2$	$C_{17}H_{16}O_2$	$C_{18}H_{16}O_4$	$C_{40}H_{40}F_6N_2O_4Pd$
FW	272.71	252.30	296.31	833.14
T, K	294(2)	294(2)	294(2)	100(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P1$	$P2_12_12_1$
a, Å	5.8554(3)	8.0158(5)	5.6784(6)	16.6778(19)
b, Å	9.0008(4)	5.8699(4)	10.2315(11)	18.963(2)
c, Å	13.1475(6)	29.8521(18)	14.2380(15)	25.108(3)
α,°	93.165(2)	90	110.267(4)	90
β,°	100.887(2)	92.130(2)	99.033(4)	90
γ°	96.054(2)	90	92.221(4)	90
Cell Volume, Å^3	674.64(6)	1403.63(15)	762.49(14)	7941.0(16)
Z	2	4	2	8
D_c, g·cm^{-3}	1.342	1.194	1.291	1.394
μ, mm^{-1}	0.277	0.077	0.091	0.536
F(000)	284	536	312	3408
Crystal size, mm	0.21×0.18×0.12	0.16×0.15×0.10	0.18×0.13×0.10	0.18×0.13×0.11
θ limits,°	2.282-25.999	2.608-25.995	2.133-24.993	1.622-24.998
Reflections collected	9371	17533	8594	49885
Independent reflections	2639 [R_{int} = 0.0445]	2731 [R_{int} = 0.0491]	5054 [R_{int} = 0.0492]	13579 [R_{int} = 0.0980]
Data / restraints /parameters	2639 / 0 / 172	2731 / 3 / 173	5054 / 3 / 400	13579 / 262 / 1005
Goodness on fit on F^2 [a]	1.086	1.047	1.050	1.070
R_1 ($I > 2\sigma(I)$) [b]	0.0617	0.0631	0.0493	0.0721
wR_2 (all data) [c]	0.1724	0.1776	0.1402	0.1663
Largest diff. peak and hole, e Å^{-3}	0.487 / –0.349	0.323 / –0.214	0.163/ –0.197	1.516 / –1.201

[a] Goodness on fit on $F^2 = [\Sigma w(F_O^2 - F_C^2)^2/(N_{ref} - N_{param})]^{1/2}$, where $w = 1/[\sigma^2(F_O^2) + (aP)^2 + bP]$, where $P = (F_O^2 + 2F_C^2)/3$; N_{ref} = number of reflections used in the refinement; N_{param} = number of refined parameters. [b] $R_1 = \Sigma||F_O| - |F_C||/\Sigma|F_O|$. [c] $wR_2 = [\Sigma w(F_O^2 - F_C^2)^2/\Sigma w(F_O^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_O^2) + (aP)^2 + bP]$, where $P = (F_O^2 + 2F_C^2)/3$.

5. NMR Characterization of the Cyclic Compound 6

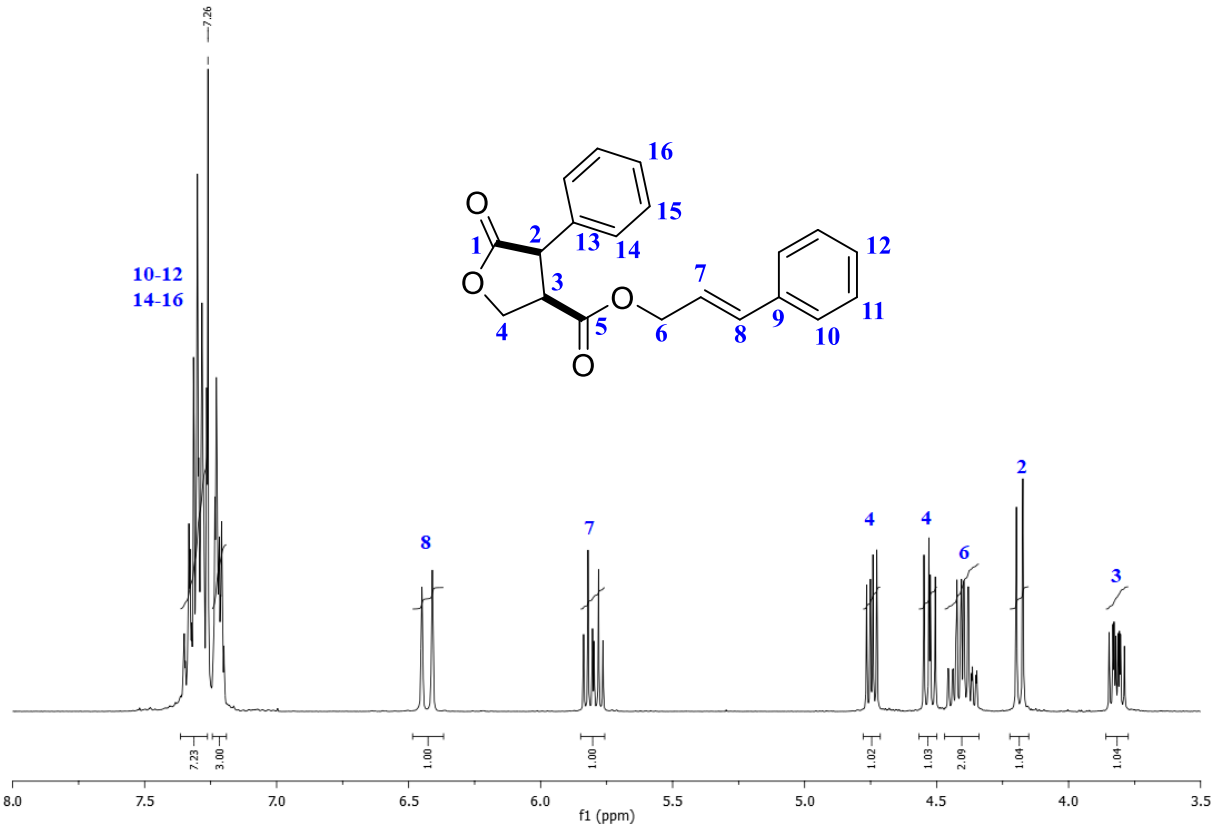


Figure S7 – ^{1}H NMR (from 8.0 ppm to 3.5 ppm) of the compound **6** (solvent: $CDCl_3$)

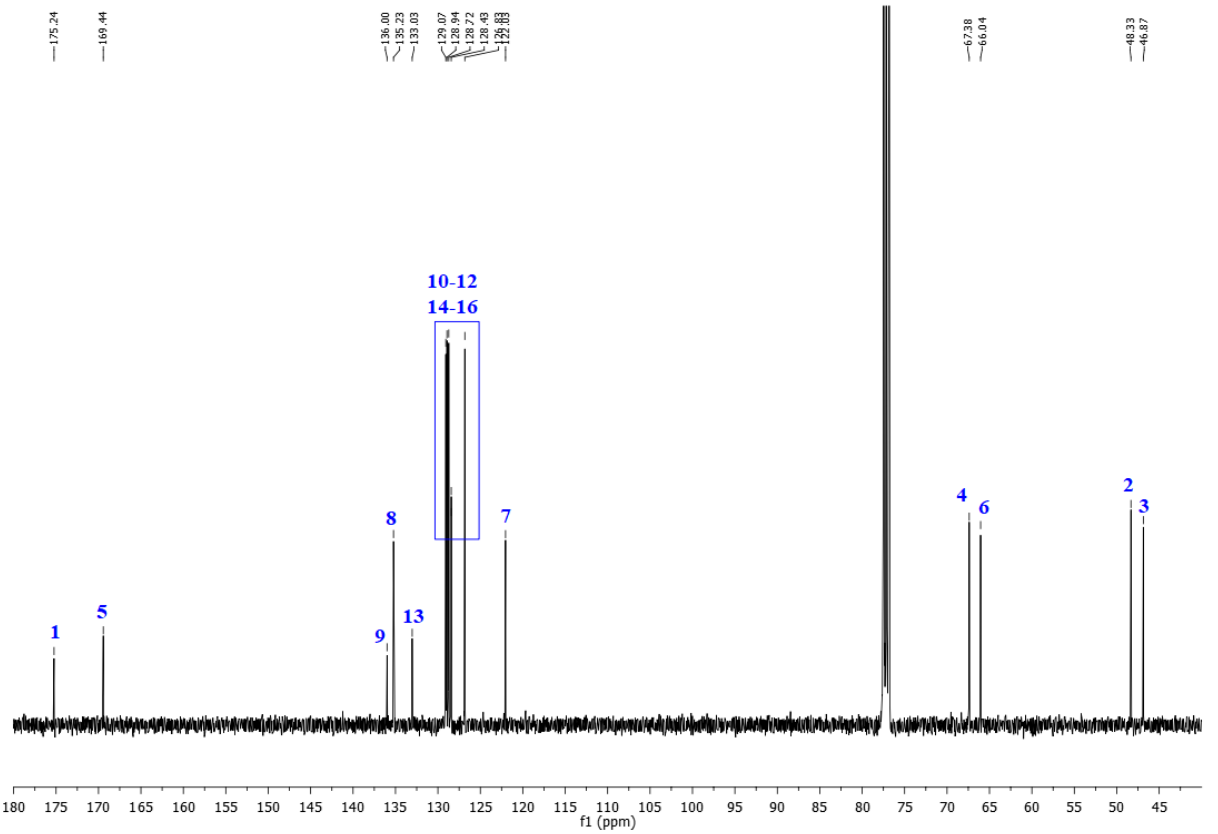


Figure S8 – ^{13}C NMR (from 180 ppm to 40 ppm) of the compound **6** (solvent: $CDCl_3$)

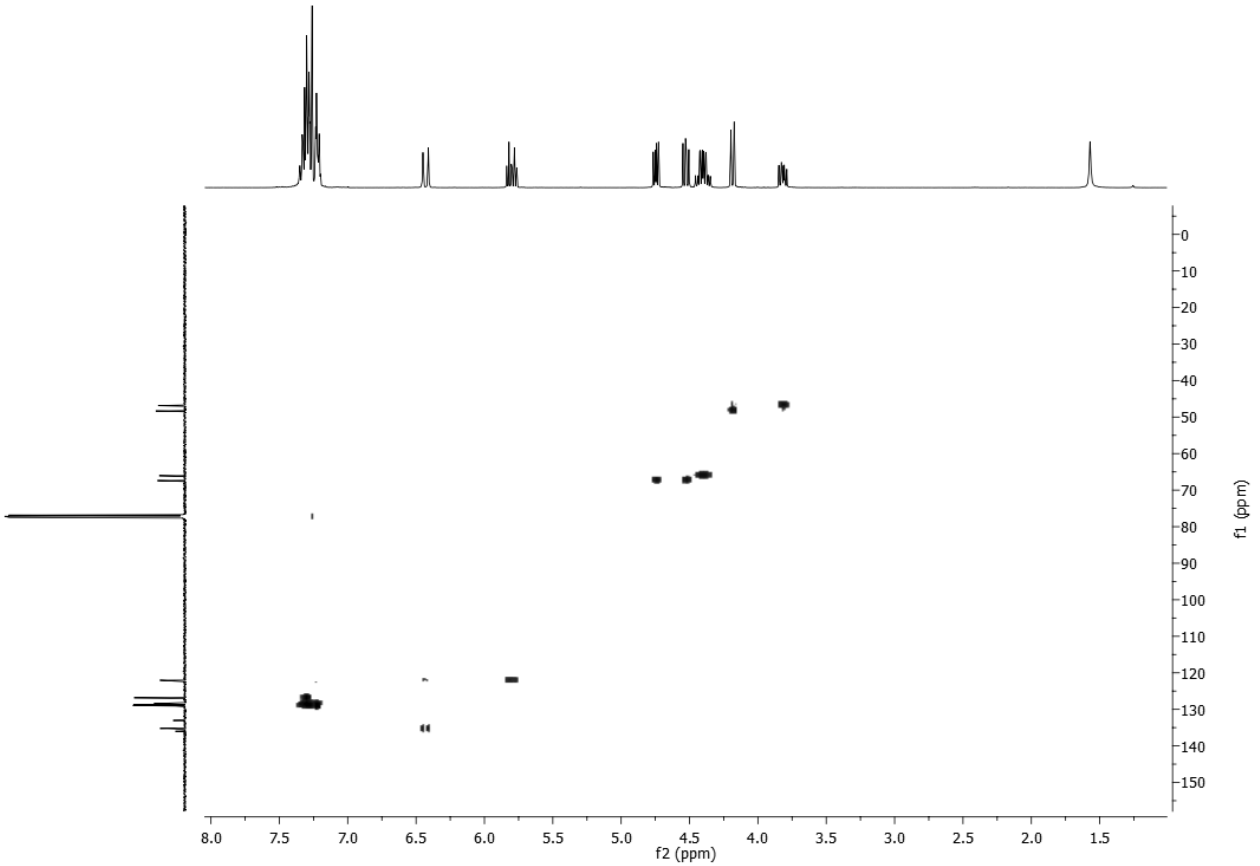


Figure S9 – HSQC NMR of the compound **6** (solvent: $CDCl_3$)

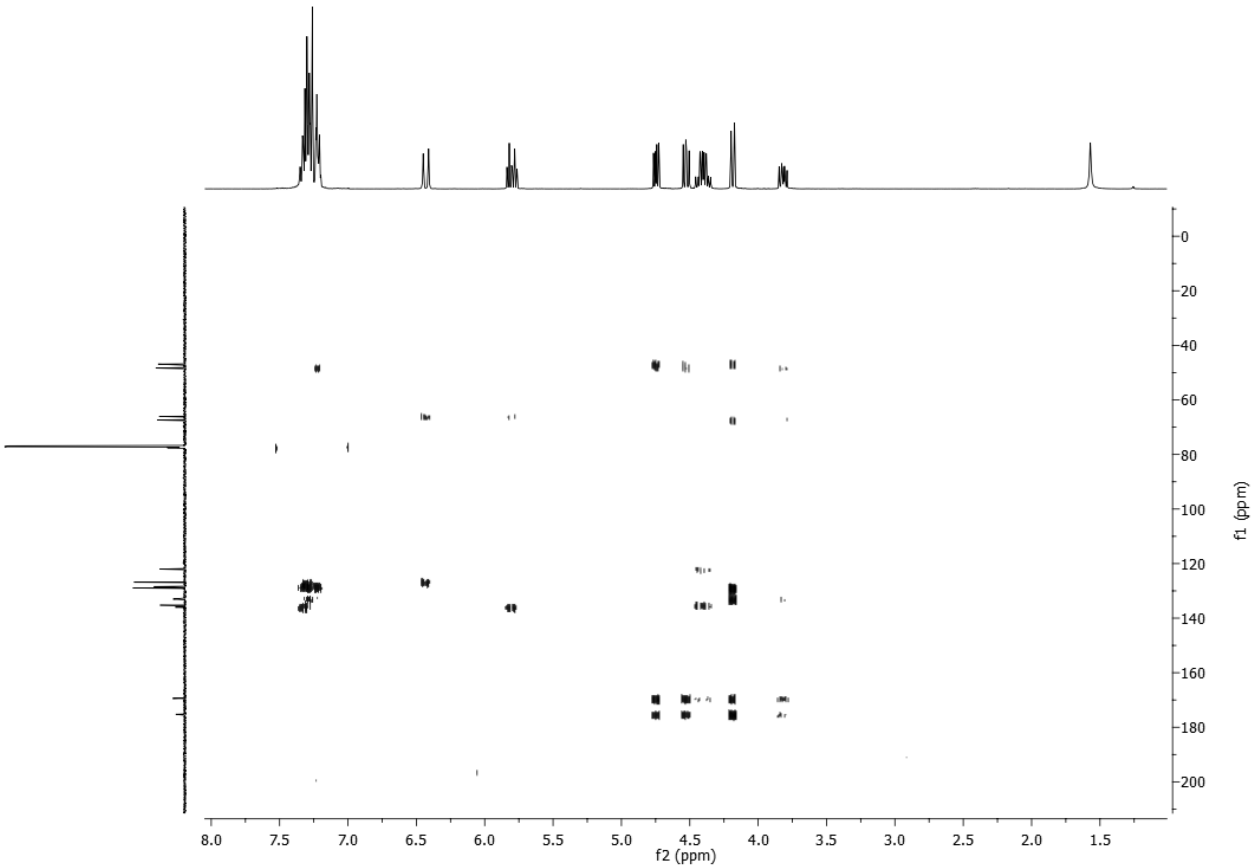


Figure S10 – HMBC NMR of the compound **6** (solvent: $CDCl_3$)

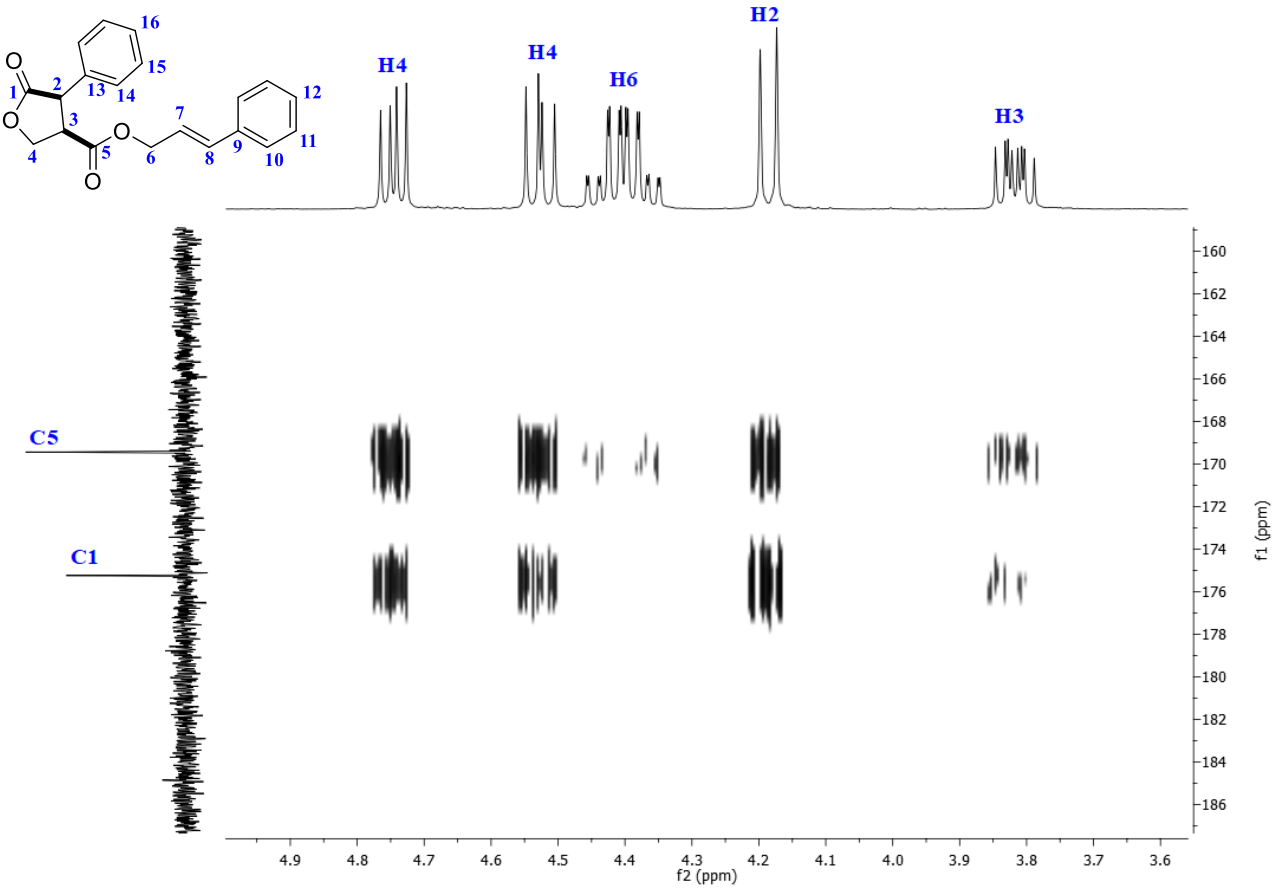
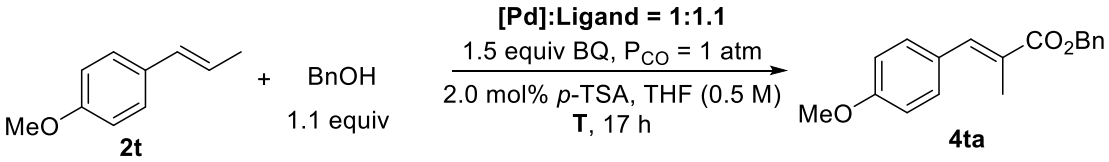


Figure S11 – Zoom of the HMBC NMR of the compound **6** (solvent: $CDCl_3$), highlighting the correlation of the carbonylic carbons C1 and C2 with H2, H3, H4 and H6. The analysis allows to assign the two different carbonyls, also excluding the formation of the β-lactone cinnamyl 2-(2-oxooxetan-3-yl)-2-phenylacetate, and confirming the proposed structure.

6. Optimization Reactions for the Oxidative Alkoxycarbonylation of Internal Olefins

Table S3 – Optimization of the oxidative alkoxycarbonylation of *trans* anethole **2t**



Entry[a]	[Pd]	Ligand	Catalyst Loading	T (°C)	Conversion (%)[b]	Yield 4ta (%)[b]
1	$Pd(TFA)_2$	**1e**	2 mol%	20	36	< 5
2[c]	$Pd(TFA)_2$	**1e**	5 mol%	60	85	44
3	$Pd(TFA)_2$	**1f**	5 mol%	20	55	< 5
4	$Pd(TFA)_2$	**1f**	5 mol%	60	100	90[d]
5	$Pd(TFA)_2$	**1f**	2 mol%	60	100	54
6	Pd_2dba_3	**1f**	2 mol%	20	13	5
7[e]	Pd_2dba_3	**1f**	2 mol%	20	10	10

[a]Reaction performed at 1 atm of CO pressure, with **2t** (0.25 mmol-scale), [Pd] : ligand = 1 : 1.1 at the indicated catalyst loading, using 1.1 equiv. of BnOH **3a**, 1.5 equiv. of *p*-BQ and 2.0 mol% of *p*-TSA in THF (0.5 M), for 17 h at the indicated temperature. [b]Determined by ^{1}H NMR analysis of the reaction crude. [c]Various by-products have been observed, including bis-alkoxycarbonylation products. [d]6% of benzyl 2-(4-methoxybenzyl)acrylate **7** is present. [e]MeOH is utilized in place of BnOH.

7. NMR Characterization of (N^1,N^2-bis(2,6-diisopropylphenyl)acenaphthylene-1,2-diimine)ditrifluoroacetato palladium(II) complex A

NMR Characterization

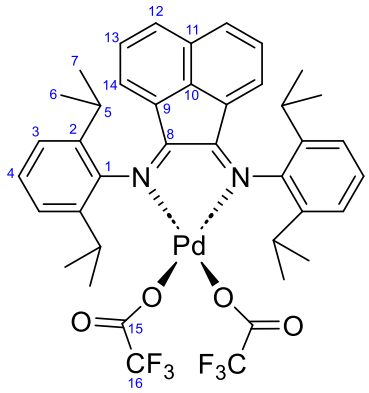


Figure S12 – Complex **A**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.3 Hz, 2H, *H12*), 7.59 – 7.51 (m, 4H, *H13* and *H4*), 7.35 (d, J = 7.8 Hz, 4H, *H3*), 6.72 (d, J = 7.3 Hz, 2H, *H14*), 3.63 (hept, J = 6.7 Hz, 4H, *H5*), 1.55 (d, J = 6.7 Hz, 12H, *H7* or *H6*), 0.99 (d, J = 6.7 Hz, 12H, *H7* or *H6*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2 (*C8*), 161.42 (q, J = 37.1 Hz, *C15*), 148.1 (*C10*), 140.6 (*C2*), 139.2 (*C1*), 133.4 (*C12*), 131.7 (*C11*), 130.1 (*C4*), 129.5 (*C13*), 126.5 (*C14*), 124.9 (*C3*), 124.2 (*C9*), 114.30 (q, J = 290.7 Hz, *C16*), 29.9 (*C5*), 24.4 (*C6* or *C7*), 23.4 (*C6* or *C7*).

^{19}F NMR (376 MHz, $CDCl_3$) δ -74.5.

Table S4 - Differences (Δδ) between the chemical shifts of the complex **A** free and the free ligand **1e** in the ^{1}H-NMR and ^{13}C-NMR (solvent: $CDCl_3$)

	^{1}H NMR			**^{13}C NMR**		
Signal	**δ ligand 1e**	**δ complex A**	**Δδ[a]**	**δ ligand 1e**	**δ complex A**	**Δδ[a]**
	ppm	ppm	ppm	ppm	ppm	ppm
3	7.22-7.30	7.35	+0.09	123.6	124.9	+1.3
4	7.22-7.30	7.59-7.51	+0.29	124.5	130.1	+5.6
5	3.03	3.63	+0.60	28.8	29.9	+1.1
6/7	1.22/0.97	1.55/0.99	+0.33/+0.02	23.6/23.3	24.4/23.4	+0.8/+0.1
12	7.87	8.18	+0.031	129.0	133.4	+4.4
13	7.36	7.59-7.51	+0.19	128.0	129.5	+1.5
14	6.63	6.72	+0.09	123.5	126.5	+3.0
1				147.6	139.2	-8.4
2				135.6	140.6	+5.0
8				161.1	176.2	+15.1
9				129.6	124.2	-5.4
10				141.0	148.1	+7.1
11				131.3	131.7	+0.4

[a]The δ differences (Δδ) are calculated by subtracting the chemical shifts of the ligand **1e** to the chemical shifts of complex **A**. A positive difference means that in the complex the signals are downfield shifted with respect to the ligand.

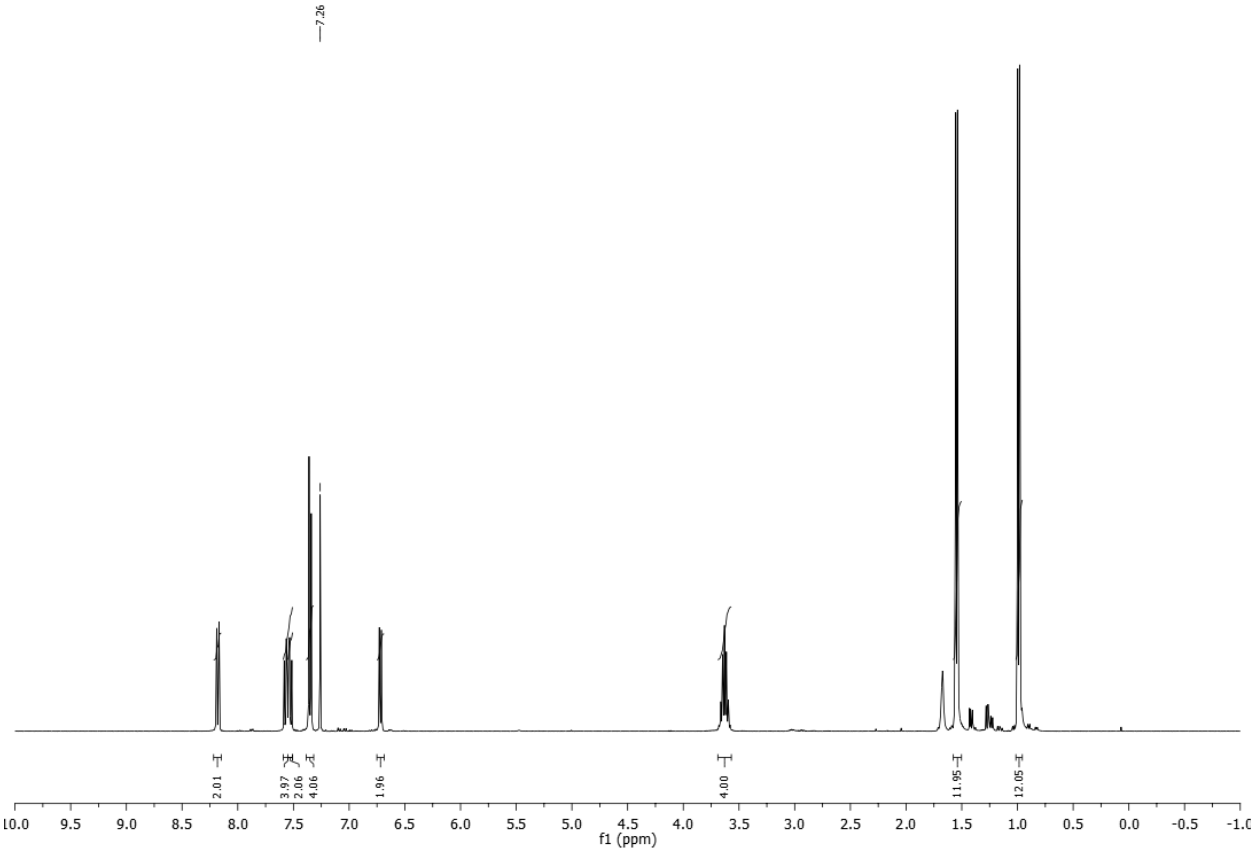


Figure S13 – ^{1}H NMR (from 10.0 ppm to -1.0 ppm) of the complex **A** (solvent: $CDCl_3$)

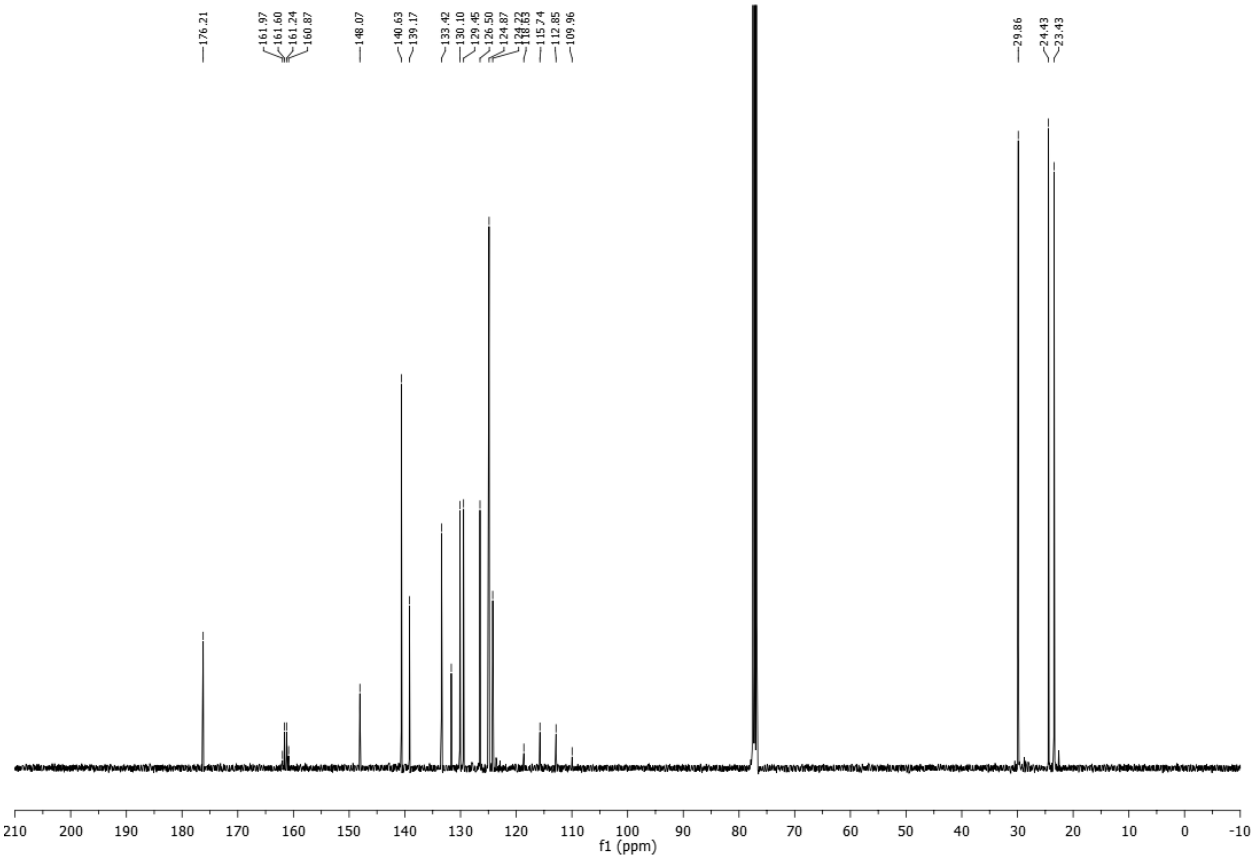


Figure S14 – ^{13}C NMR (from 210 ppm to -10 ppm) of the complex **A** (solvent: $CDCl_3$)

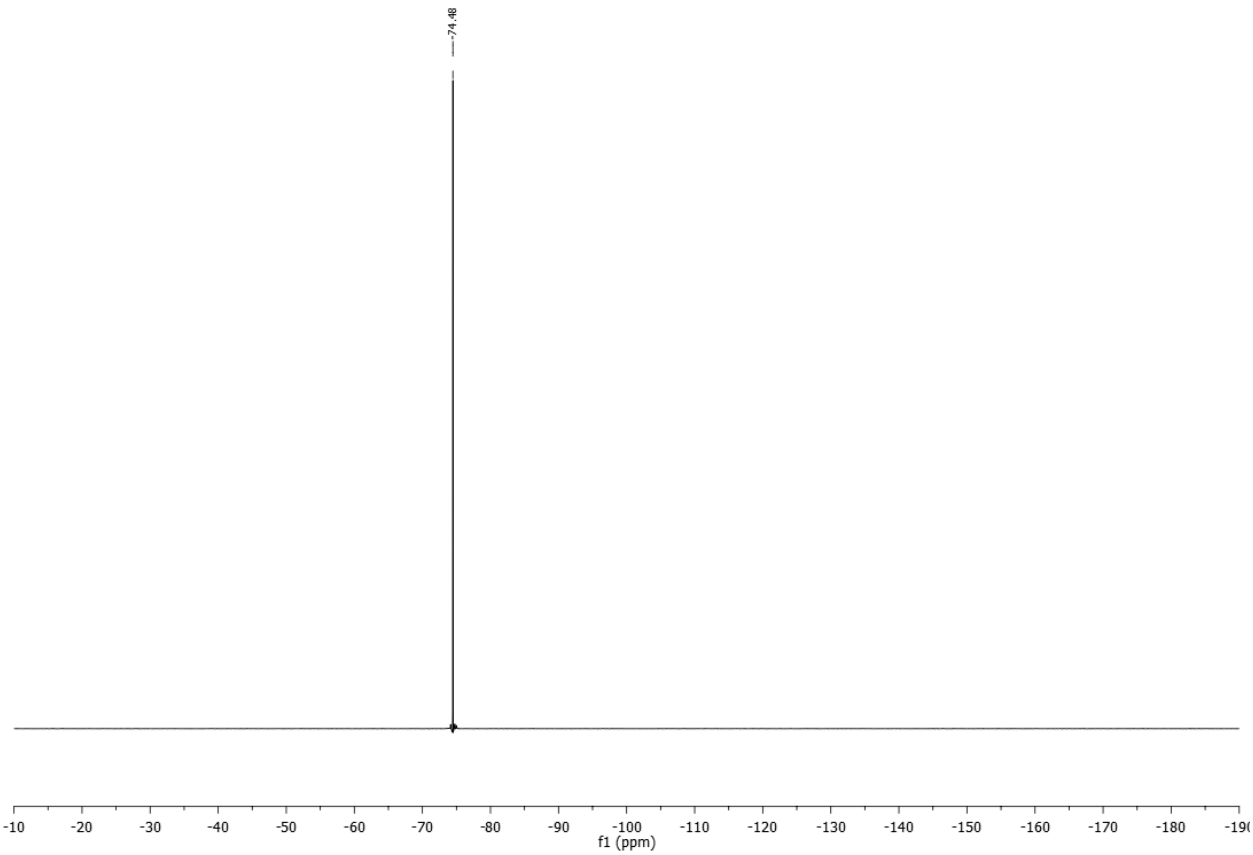


Figure S15 – ^{19}F NMR (from -10 ppm to -190 ppm) of the complex **A** (solvent: $CDCl_3$)

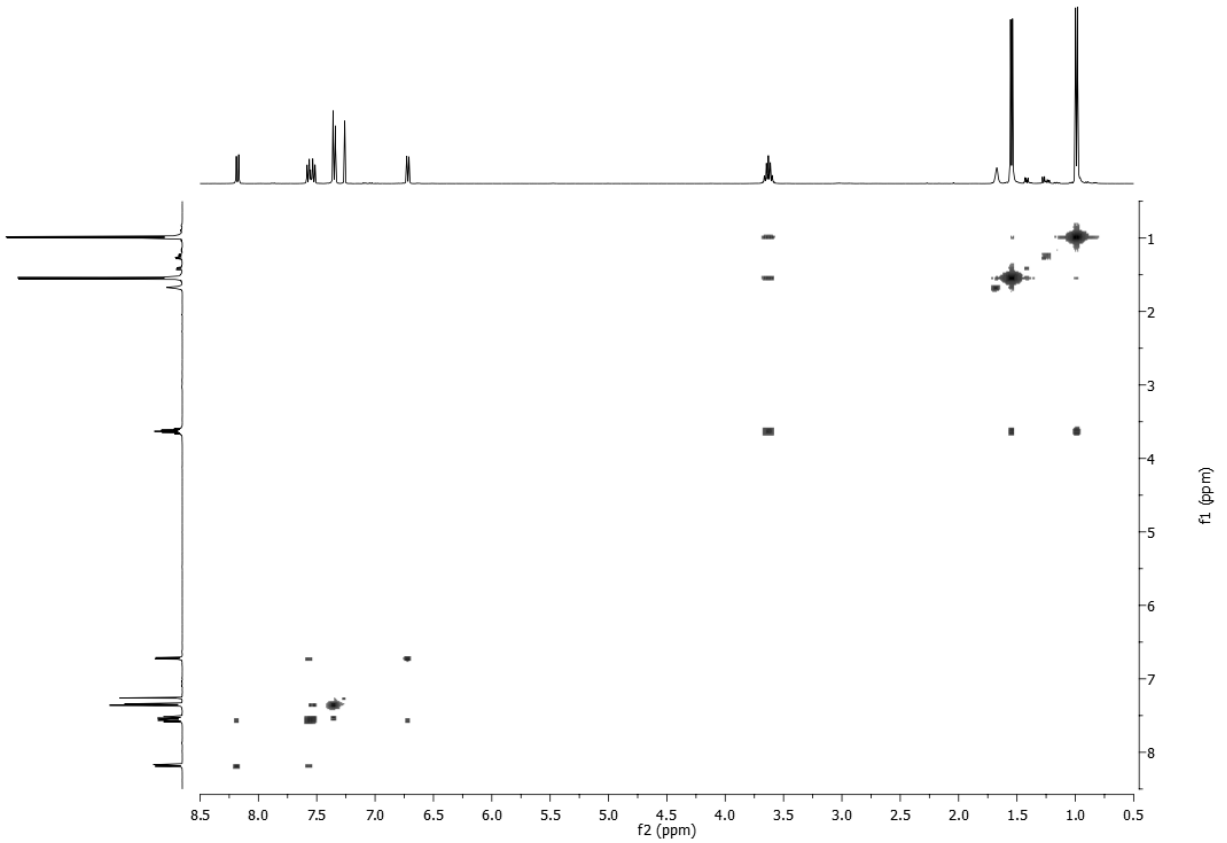


Figure S16 – ^{1}H-^{1}H COSY NMR of the complex **A** (solvent: $CDCl_3$)

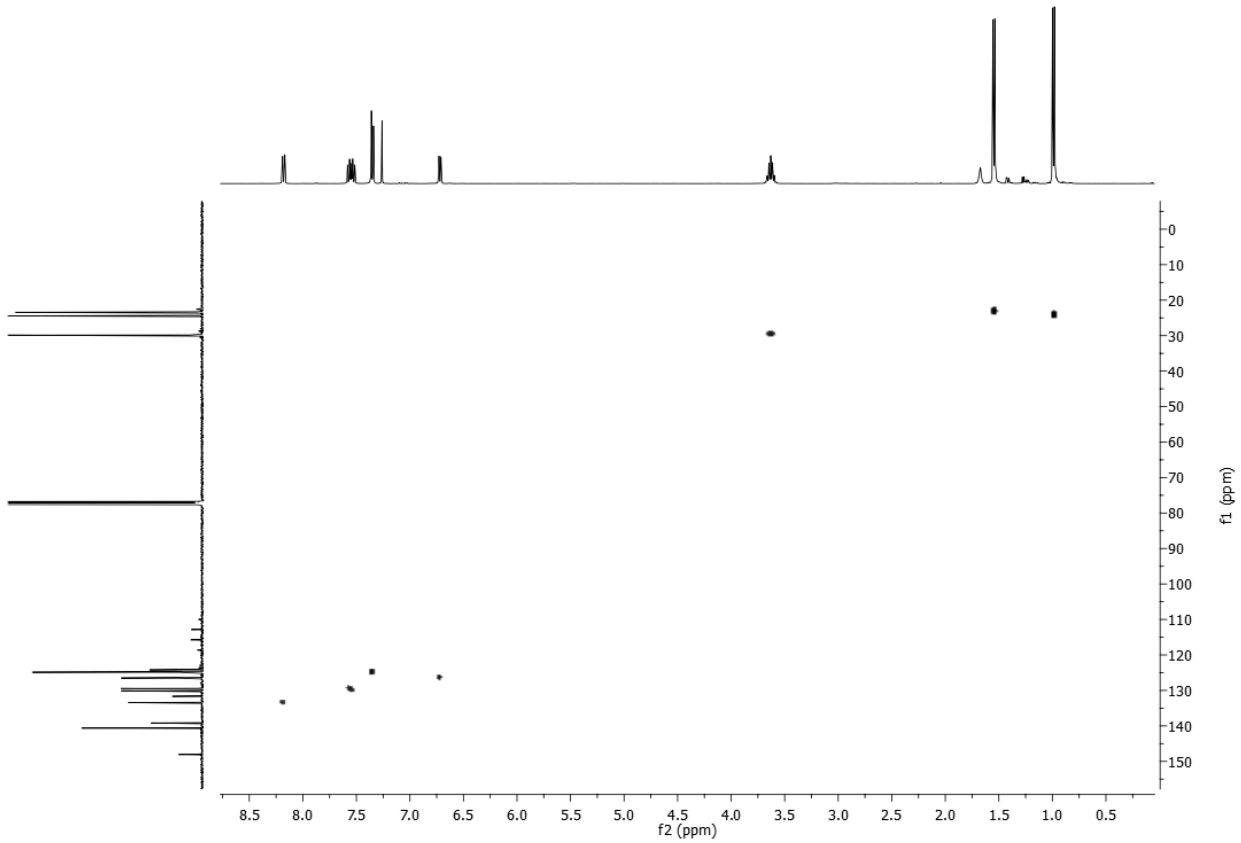


Figure S17 – HSQC NMR of the complex **A** (solvent: $CDCl_3$)

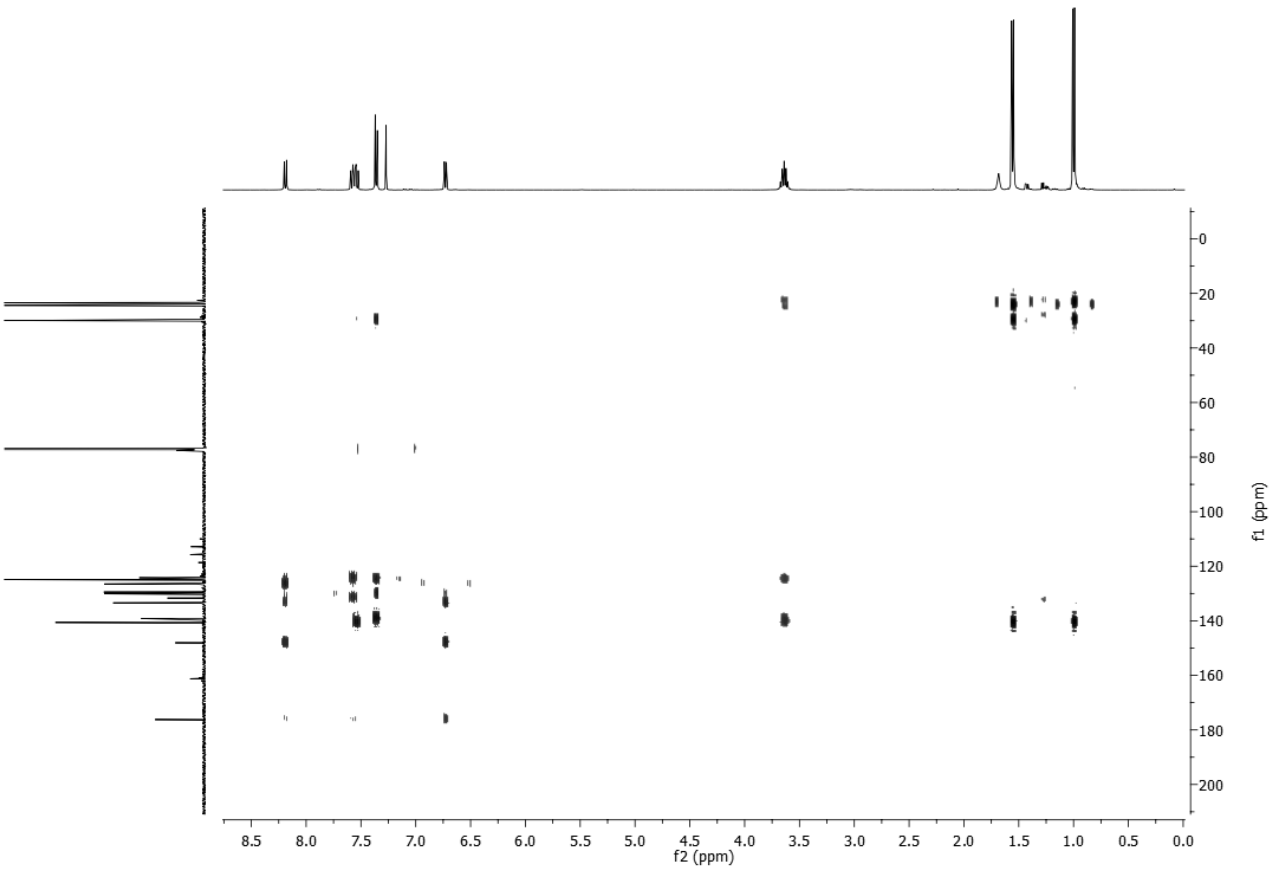
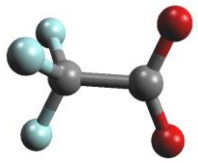


Figure S18 – HMBC NMR of the complex **A** (solvent: $CDCl_3$)

8. Computed Equilibrium Geometries and Energies for the Studied Compounds

The equilibrium geometries listed below have been obtained at the M06L-D0/def2-TZVP level of computation. At the same geometries, zero-point energies and thermal contributions were evaluated (ZPE+TC) and summed up to a single point energy E(el) calculated at the SMD(THF) M06-D0/def2-QZVPP level, to give the final free energy G. All energies in hartree. For transition states, the value of the transition state imaginary frequency ν (cm^{-1}) is also reported.



TFA^-

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7
ZPE+TC=0.00019766 E(el)=-526.39319482   G=-526.3929972
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C     1.587781933    -0.001264405     0.003016831
F    -0.497812752     1.252064608     0.020887657
F    -0.551766872    -0.607318581    -1.059284135
O     2.110692815    -0.574983697    -0.960449068
O     2.050989209     0.590108053     0.988367442
F    -0.495379199    -0.622920088     1.091467497
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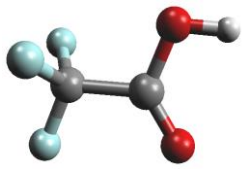

HTFA

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F    -0.464526710    -0.629519609    -1.065967188
O     2.200534804    -0.507920009    -0.858656243
O     1.987470119     0.640730973     1.074043968
F    -0.466740904    -0.611707972     1.089674009
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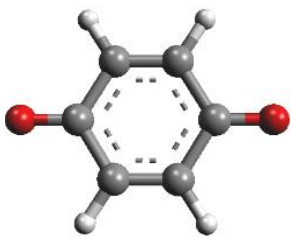

BQ

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C	0.770300852	-1.256924181	-0.000181331
C	2.105067661	1.256924308	0.000000000
C	0.770305000	1.256945742	0.000008532
C	0.000000000	0.000000000	0.000000000
O	4.092617474	0.000059627	-0.000170840
O	-1.217248992	-0.000059814	-0.000097089
H	2.687962946	-2.169956202	-0.000317758
H	0.187330158	-2.169887877	-0.000298263
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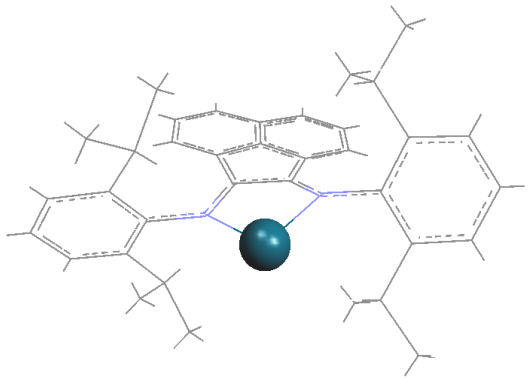
H	0.187405126	2.169956135	0.000029349



E

79
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N	0.303475531	2.064184251	-0.164011138
C	1.563364612	2.294710464	0.001400599
C	2.521789830	1.167634215	-0.019964545
C	-0.650492931	3.095380983	-0.171556248
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C	0.015078267	3.581690641	-2.568117854
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C	2.960657659	-1.143028554	0.171226006
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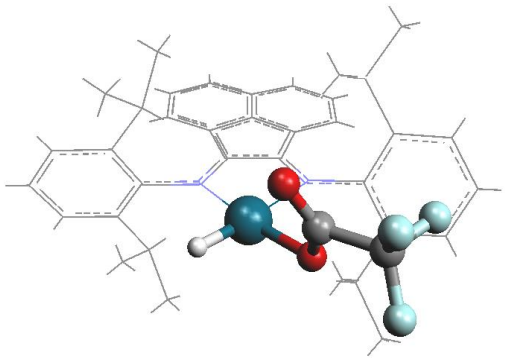

D

87

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C	2.596657605	1.198576826	-0.067768304
C	-0.647551594	3.033631212	-0.137265465
C	-0.902744846	3.762621562	-1.307996431
C	-1.910601317	4.718737415	-1.254135871
C	-2.634017781	4.936960966	-0.094007028
C	-2.375669921	4.184545604	1.036686365
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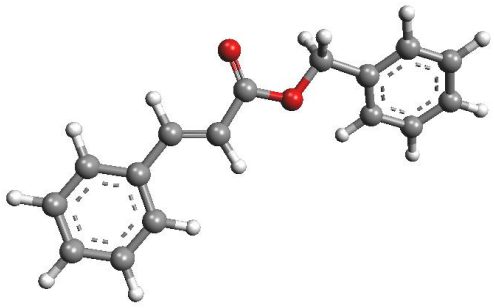

4aa

32

ZPE+TC= 0.21643621 E(el)=-768.40270978 G= -768.18627357

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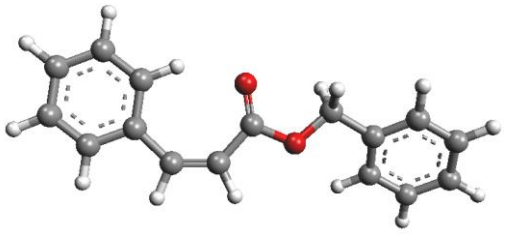
C	1.982066593	1.444828899	0.636125250
O	1.406498130	2.443631053	0.992812472
C	0.040760728	0.008484354	0.336065478
C	1.368469742	0.163046703	0.288481584
C	-0.903092453	-3.489655918	-0.675035045
C	-0.130398543	-2.383356401	-0.384376951
C	-0.723486151	-1.181417769	0.021319840
C	-2.287374030	-3.425997967	-0.568822354
C	-2.892268890	-2.245139882	-0.168367904
C	-2.117602218	-1.136533657	0.123223679
C	4.041732168	2.567993238	0.801193606
C	6.452167777	3.120751818	1.124570261
C	7.790803266	3.001855399	0.788716623
C	8.179941649	2.135344206	-0.221287613
C	5.482950865	2.383526422	0.452017303
C	5.881271215	1.517138969	-0.560587707
C	7.220963497	1.392384475	-0.892041416
H	2.038105803	-0.634899363	-0.005706443
H	-0.533318665	0.878412525	0.645090524
H	-0.427380960	-4.410342973	-0.986967014
H	0.946748597	-2.447003974	-0.470985191
H	-2.889475670	-4.295521288	-0.797865767
H	-3.969497696	-2.188142350	-0.083129156
H	-2.588128429	-0.212199317	0.436377420
H	3.914181474	2.813815398	1.858230618
H	3.591306525	3.393788167	0.241570058
H	6.153237594	3.790215347	1.923027496
H	8.532729932	3.580274052	1.323820105
H	9.225920348	2.035621423	-0.480227646
H	5.134589158	0.932325403	-1.080916141
H	7.516710939	0.709935292	-1.678614154



4aa′

32

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O	3.395624118	1.213993991	1.329747934
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O	1.875466158	2.857929751	1.163603184
C	0.148081804	0.572839553	-0.101035397
C	1.394962764	0.610238637	0.406330319
C	-2.002384238	3.684311659	-0.187564700
C	-0.904760918	2.879172093	0.055112147
C	-0.929516764	1.523389739	-0.299498982
C	-3.144918163	3.170090978	-0.784314382
C	-3.188029843	1.830710867	-1.142167654
C	-2.094691922	1.022337587	-0.901322763
C	4.299629066	2.156658473	1.904279025
C	6.470442840	1.910743766	3.112851671
C	7.730525114	1.353969438	3.262396930
C	8.169069597	0.379562363	2.379394350
C	5.635544302	1.508992456	2.075806269
C	6.083467363	0.531087348	1.193264031
C	7.340237514	-0.031116477	1.346489844
H	1.939155475	-0.325341493	0.393550172
H	-0.129573080	-0.416498807	-0.456580582
H	-1.965468789	4.728998417	0.093347685
H	-0.018634466	3.284009880	0.519416373
H	-3.998039584	3.810070503	-0.969420421
H	-4.073361223	1.418074182	-1.607914479
H	-2.127621642	-0.024572548	-1.180307803
H	3.900694042	2.512057247	2.857438848
H	4.353869163	3.033707703	1.251526846
H	6.125974042	2.662939417	3.813212534
H	8.366809592	1.674842026	4.076987453
H	9.149700657	-0.062236736	2.498963470
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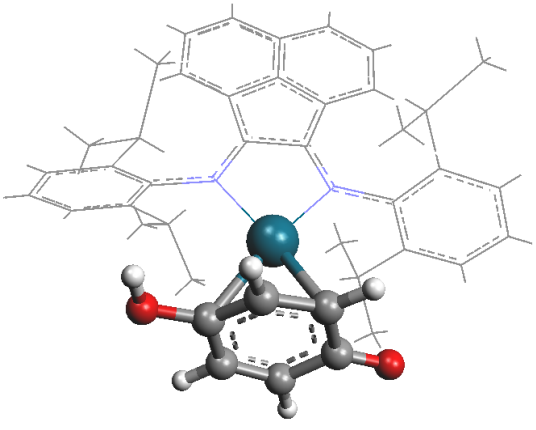
H	7.673450819	-0.795228767	0.655857458



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92
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N	0.434739539	2.117962338	0.083430545
C	2.627577081	1.188527736	0.190223812
C	1.693847417	2.349836405	0.213673989
C	2.870986275	-1.172987803	-0.151288723
C	3.449045065	-1.803828168	0.963329243
C	4.082637736	-3.019703252	0.741306684
C	4.139209022	-3.584814343	-0.522037207
C	3.557215863	-2.945445529	-1.599312378
C	2.900310267	-1.731744180	-1.441863598
C	3.339460697	-1.206357090	2.351075898
C	2.285083119	-0.996145399	-2.610788484
C	-0.529956974	3.142796296	-0.065251638
C	-0.622414846	3.818201134	-1.296440113
C	-1.615337261	4.782434204	-1.417829793
C	-2.483021203	5.063282139	-0.376405606
C	-2.391836747	4.361935387	0.811151433
C	-1.425801344	3.378870171	0.988945164
C	0.261266641	3.448644419	-2.470792460
C	-1.310910239	2.600612350	2.279797497
C	0.401738555	4.557521861	-3.500439746
C	-0.252875982	2.166839279	-3.125402493
C	3.182926916	0.154841891	-3.067487144
C	1.947344236	-1.887969292	-3.793944508
C	1.958005543	-1.462649589	2.951469113
C	4.426533960	-1.686105430	3.298948906
C	-2.615129984	2.519571418	3.061632782
C	-0.204690552	3.158102024	3.173070981
C	6.207257063	3.384360977	0.499008315
C	4.928620113	3.984721406	0.483474110
C	3.838053191	3.112618037	0.378240500
C	3.977125855	1.708475458	0.292880366
C	5.236982225	1.153646961	0.305284575
C	6.343427088	2.015935593	0.409795048
C	4.619931779	5.360923269	0.560154956
C	3.311155092	5.791442579	0.526512832
C	2.227413885	4.902263941	0.410722956
C	2.495032237	3.553247266	0.335520479
C	-2.286616727	-0.242266597	-0.164580925
C	-1.696098383	-1.092055426	0.793911335
C	-0.734208243	-2.008029288	0.327745318
C	-2.225607331	-0.570651039	-1.573060276
C	-1.464973153	-1.586863261	-2.019084951
C	-0.643592634	-2.385824929	-1.095042844
O	-3.123510638	0.756674659	0.141438209
O	0.098246934	-3.276965735	-1.474418191
H	3.455083535	-0.121954117	2.258059916
H	4.538924859	-3.538233228	1.573126363

H	4.636257871	-4.535012153	-0.663183324
H	3.597631360	-3.402067813	-2.578335095
H	1.342001816	-0.555032965	-2.251323632
H	1.266967847	3.239335530	-2.094319963
H	-1.715741005	5.321985757	-2.349411726
H	-3.242325931	5.823794330	-0.498407402
H	-3.086422148	4.577493767	1.611895003
H	-1.012446456	1.577010762	2.007111690
H	1.140292622	4.280108886	-4.250471580
H	0.720936062	5.495801926	-3.047605520
H	-0.532955687	4.742421200	-4.029627870
H	0.373924090	1.877636181	-3.968759793
H	-1.268699778	2.305652473	-3.498617546
H	-0.268787153	1.331309612	-2.422182426
H	3.379731760	0.881201498	-2.279639515
H	2.733071234	0.687253895	-3.905035436
H	4.147312722	-0.227927895	-3.403593250
H	2.846474125	-2.250320360	-4.293053648
H	1.384022469	-1.321505218	-4.535740797
H	1.884212697	-1.034364910	3.950832979
H	1.765978344	-2.533463351	3.033839582
H	1.163773079	-1.025061448	2.343193904
H	5.422561583	-1.553439733	2.877464096
H	4.308917639	-2.740512787	3.548466266
H	4.381699064	-1.131825865	4.234685015
H	-3.473471155	2.244250166	2.443782870
H	-2.871082274	3.474498666	3.520132556
H	-2.532745719	1.794827839	3.870410410
H	0.763608051	3.162232214	2.675238034
H	-0.107042647	2.570984913	4.085706679
H	-0.430567548	4.185338484	3.461394447
H	7.088466145	4.007996754	0.580938903
H	5.384251361	0.083244133	0.235995931
H	7.335231583	1.585197964	0.421451528
H	5.421480257	6.083747493	0.645369581
H	3.105569246	6.851300620	0.588168201
H	1.214149996	5.282642507	0.382352454
H	1.351167619	-2.747798747	-3.494229681
H	-3.149255336	0.902667993	1.097861363
H	-1.918982315	-0.971935703	1.848616195
H	-0.207691206	-2.651486606	1.020678062
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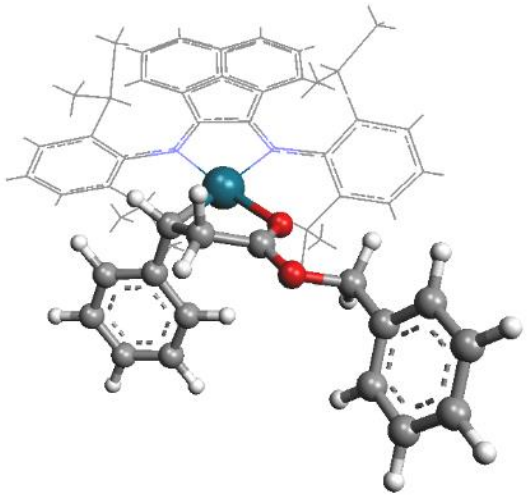
H	-1.434826554	-1.856778020	-3.066536621



C

112
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N	2.179082000	0.002028000	0.266676000
C	1.651172000	2.310499000	0.242453000
C	2.635719000	1.199394000	0.323249000
C	-0.586734000	3.004125000	-0.110137000
C	-0.693589000	3.529558000	-1.412060000
C	-1.715822000	4.446121001	-1.635039000
C	-2.583577000	4.825257001	-0.623770000
C	-2.450266000	4.293180001	0.646734000
C	-1.451478000	3.367862000	0.932053000
C	0.258371000	3.116861000	-2.520660000
C	-1.243274000	2.820422000	2.326845000
C	3.001864000	-1.149880000	0.235458000
C	3.539024000	-1.658215000	1.429564000
C	4.258887001	-2.844672000	1.348559000
C	4.439072001	-3.497498000	0.139679000
C	3.904175000	-2.968708000	-1.020426000
C	3.172482000	-1.786148000	-1.001412000
C	3.298549000	-0.958029000	2.751237000
C	2.576410000	-1.220844000	-2.273793000
O	-1.870747000	-3.598923000	0.986267000
C	-1.456058000	-2.373456000	0.841837000
O	-0.294025000	-2.108666000	0.497282000
C	-2.079032000	-0.021059000	0.338109000
C	-2.426441000	-1.286386000	1.126537000
C	-2.940930000	-0.928773000	-3.237318000
C	-2.466523000	-1.031540000	-1.942613000
C	-2.565060000	0.045489000	-1.050352000
C	-3.537496000	0.248033000	-3.674245000
C	-3.647865000	1.322677000	-2.804555000
C	-3.161329000	1.224999000	-1.511987000
C	-0.887410000	-4.659332001	0.694833000
C	-1.319227000	-6.756751001	1.977564000
C	-1.954389000	-7.979394001	2.128528000

C	-2.841492000	-8.422239001	1.159928000
C	-1.561352000	-5.971932001	0.855635000
C	-2.450883000	-6.426573001	-0.114971000
C	-3.090779000	-7.643889001	0.037763000
C	4.339660001	-1.287879000	3.808813000
C	1.890839000	-1.251895000	3.269717000
C	-0.197383000	3.645222000	3.075934000
C	-2.527583000	2.719048000	3.135085000
C	-0.033058000	1.708629000	-3.037071000
C	0.294680000	4.103211000	-3.677351000
C	1.319529000	-1.992000000	-2.669670000
C	3.580305000	-1.178447000	-3.418424000
C	4.434805001	5.478468001	0.290325000
C	4.806178001	4.116761000	0.345353000
C	3.757391000	3.187823000	0.323094000
C	2.394042000	3.558635000	0.240960000
C	2.065729000	4.896405001	0.187766000
C	3.107122000	5.842034001	0.216601000
C	6.112019001	3.581489000	0.419848000
C	6.311711001	2.218905000	0.465903000
C	5.246058001	1.298987000	0.444636000
C	3.961723000	1.790061000	0.372644000
H	1.266581000	3.102873000	-2.095953000
H	-1.834660000	4.873641001	-2.620849000
H	-3.365692000	5.544007001	-0.828183000
H	-3.128280000	4.602657001	1.430699000
H	-0.836030000	1.806584000	2.218013000
H	3.359345000	0.120171000	2.572294000
H	4.690282001	-3.264131000	2.247067000
H	5.005098001	-4.418473001	0.104126000
H	4.058435000	-3.478099000	-1.963293000
H	2.270756000	-0.190163000	-2.074159000
H	-2.336994000	-1.082856000	2.198505000
H	-3.451490000	-1.627982000	0.966262000
H	-2.386584000	0.868809000	0.885117000
H	-2.853413000	-1.772384000	-3.909247000
H	-2.004796000	-1.961091000	-1.626357000
H	-3.918144000	0.321049000	-4.683948001
H	-4.119502000	2.241059000	-3.130502000
H	-3.263531000	2.061510000	-0.829862000
H	-0.048690000	-4.526007001	1.377560000
H	-0.528458000	-4.481856001	-0.320441000
H	-0.625785000	-6.407935001	2.733526000
H	-1.756698000	-8.585785001	3.001988000
H	-3.337436000	-9.376467001	1.276435000
H	-2.640501000	-5.819278001	-0.992559000
H	-3.780046000	-7.990520001	-0.720258000
H	4.191393001	-0.666658000	4.690157001
H	5.353717001	-1.119541000	3.447132000
H	4.271154001	-2.325367000	4.135799000
H	1.712129000	-0.744599000	4.217549001

H	1.757258000	-2.322437000	3.433030000
H	1.123264000	-0.925215000	2.564678000
H	0.756843000	3.670729000	2.550501000
H	-0.019342000	3.236812000	4.070206000
H	-0.533586000	4.675987001	3.195622000
H	-3.310324000	2.185632000	2.594553000
H	-2.921670000	3.700543000	3.398138000
H	-2.345643000	2.191651000	4.070140000
H	0.720071000	1.408927000	-3.766608000
H	-1.005731000	1.666170000	-3.525622000
H	-0.038993000	0.963336000	-2.238224000
H	0.490827000	5.121334001	-3.342063000
H	-0.642930000	4.108286000	-4.233622001
H	1.078586000	3.825817000	-4.379498001
H	0.575646000	-1.974052000	-1.871982000
H	1.553686000	-3.035969000	-2.883472000
H	0.862787000	-1.562147000	-3.561536000
H	4.484537001	-0.637640000	-3.140788000
H	3.145943000	-0.684191000	-4.286652001
H	3.877637000	-2.177883000	-3.734834000
H	5.201721001	6.242476001	0.305790000
H	1.036612000	5.226458001	0.126337000
H	2.852055000	6.892094001	0.177275000
H	6.962509001	4.251000001	0.440612000
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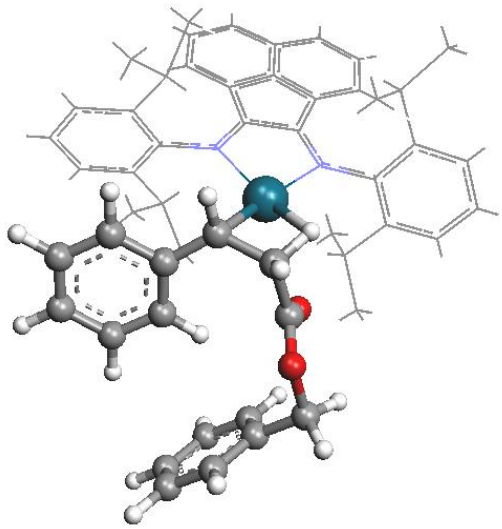

$CF_{TS,cis}$

112

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C	2.774138536	1.146098468	0.271387673
C	-0.720478724	2.371290344	-0.100343798

C	-1.137306108	2.425082770	-1.442898116
C	-2.272079463	3.177474893	-1.720356417
C	-2.951098417	3.856836247	-0.721897055
C	-2.524076664	3.776982555	0.590174738
C	-1.409940385	3.018932772	0.935268015
C	-0.377239138	1.695261459	-2.533321032
C	-0.922967592	2.918274181	2.363788431
C	3.515641355	-1.023455670	0.925244328
C	4.229574639	-0.974622429	2.134152538
C	5.119587532	-2.012221793	2.386688599
C	5.292293678	-3.049433184	1.485960045
C	4.567154507	-3.077087904	0.308369792
C	3.656715114	-2.072863886	0.003932991
C	3.986841585	0.131881016	3.140571419
C	2.876487848	-2.055071243	-1.290693998
O	-1.423319328	-4.264796483	1.185734132
C	-0.707328223	-3.174866884	0.983245497
O	0.067513784	-2.997231296	0.067951661
C	-1.537402699	-0.819207749	1.604577772
C	-0.901246512	-2.122506738	2.037482392
C	-3.885801759	-1.252685686	-1.336880859
C	-2.838309340	-1.498742102	-0.469606207
C	-2.609207946	-0.661179678	0.632194772
C	-4.718738723	-0.157704160	-1.150067635
C	-4.504500023	0.688847857	-0.072748603
C	-3.472547992	0.432667690	0.807362045
C	-1.276380903	-5.325614969	0.185648275
C	-1.548870518	-4.570925745	-2.187706954
C	-2.340586683	-4.311053165	-3.295580745
C	-3.708351087	-4.535051263	-3.239449030
C	-2.119203721	-5.057835317	-1.014895550
C	-3.494318323	-5.272705867	-0.965487118
C	-4.285547836	-5.012933363	-2.071475291
C	5.124630113	0.308631894	4.132458904
C	2.666707225	-0.082637137	3.880387290
C	0.218991579	3.896919618	2.635803856
C	-2.022754903	3.114206267	3.396162324
C	-0.654178749	0.193487407	-2.501669716
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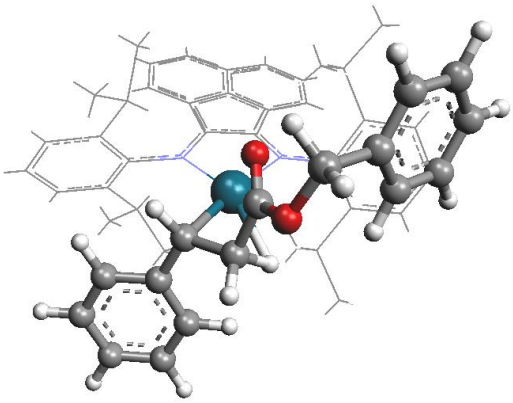

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112

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C	4.245555221	-3.331567779	-1.810193276
C	3.418517146	-2.659006704	-2.690587204
C	2.677075315	-1.559237968	-2.274745961
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C	1.213037484	-1.666682732	-4.343377296
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C	3.843294290	2.925118669	0.446363472
C	2.506734080	3.327038454	0.667794124
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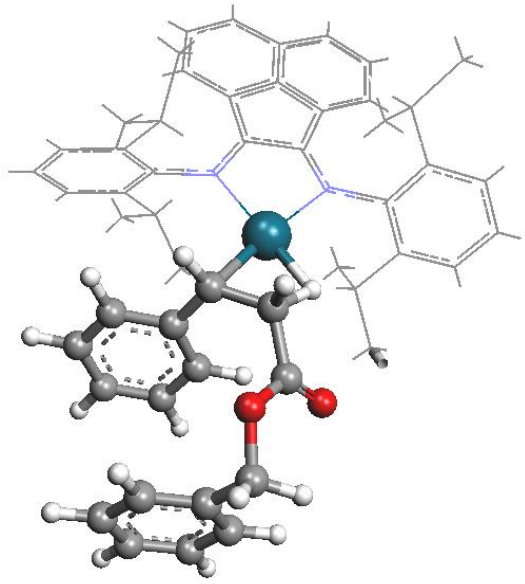

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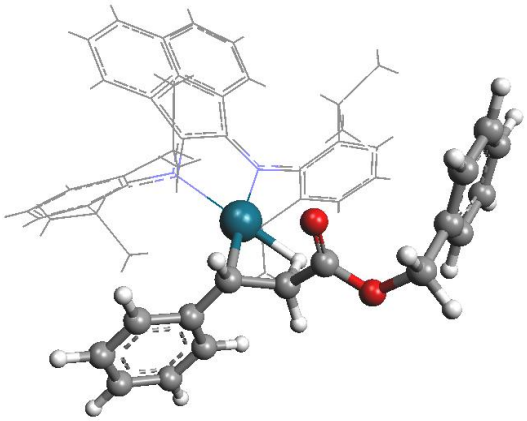

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C       3.101665010    -1.076523912    -0.108905717
C       3.607201591    -1.622914069     1.082340258
C       4.300250333    -2.824083781     0.981996170
C       4.490103808    -3.449260533    -0.238991650
C       3.991068175    -2.879835128    -1.395624669
C       3.281367340    -1.685288933    -1.358230724
C       3.371149930    -0.942102577     2.415841845
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C	1.924747606	-1.113198859	2.876437859
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C	3.875511436	3.251575267	0.202480286
C	2.514594284	3.634801920	0.178360655
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C	6.425418267	2.264019135	0.224013167
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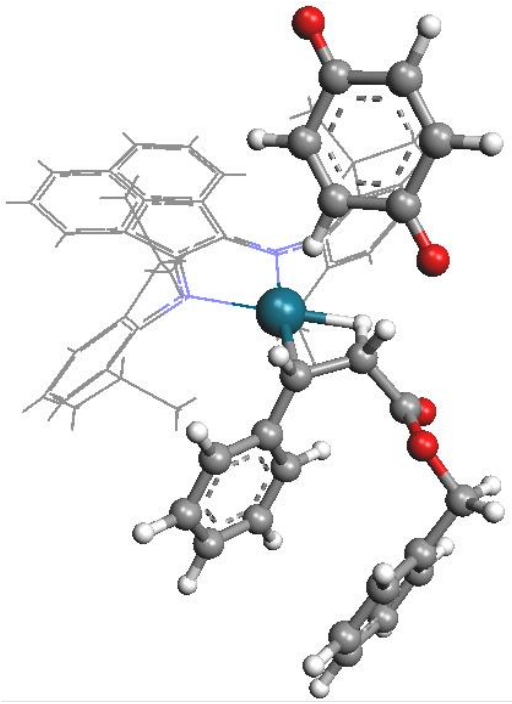

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C      2.713420596     1.174781040     0.373349945
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C	0.687295290	3.869457120	-2.092328823
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C	3.908876505	-1.148718586	-1.391545597
C	2.504086328	-1.953070107	2.086154003
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C	-1.362958868	-1.767624060	-0.699265553
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C	4.338826884	5.317012830	1.700749009
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C	3.013611762	5.676057068	1.580665651
C	6.065535092	3.473748502	1.494822543
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H	3.431164947	-0.106398737	2.793408241
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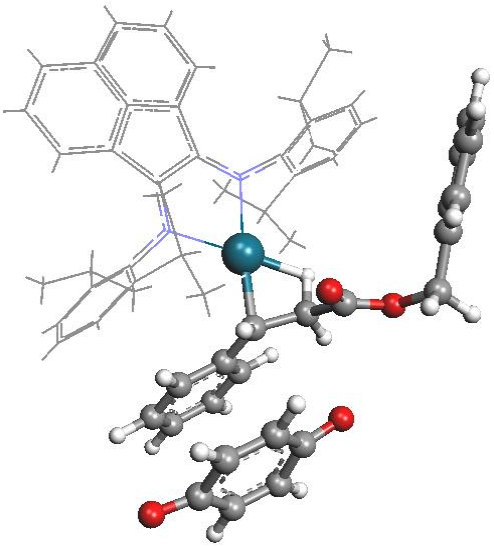

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124

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C	3.703172693	-1.355884131	1.291907279
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C	3.765397759	-3.142289001	-0.875408382
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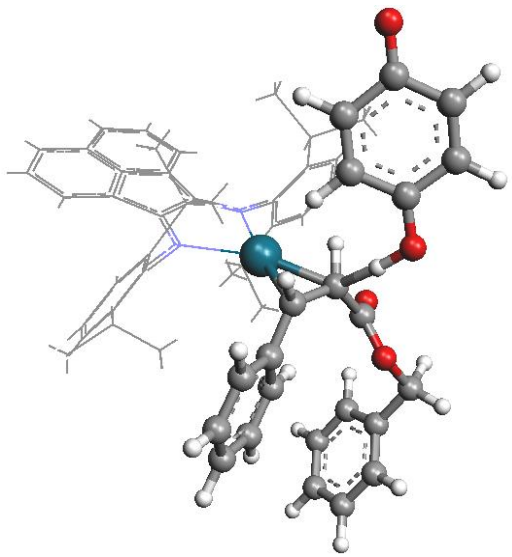
H	-1.991069651	-3.050278735	4.182763856
H	0.756096743	-4.805183596	2.320005052
H	3.076347139	-4.946736162	3.136945966
H	3.679291873	-3.974524376	5.331470501
H	-0.362673895	-2.666877286	5.848296810
H	1.956920291	-2.824988271	6.681132609
H	4.456604721	0.013299168	4.388986377
H	5.573206900	-0.712011425	3.236082665
H	4.373095178	-1.705724699	4.064466893
H	2.002365888	0.045892318	3.953574338
H	1.874414907	-1.587446015	3.312301313
H	1.363150602	-0.213565795	2.336092026
H	1.040547719	3.354526988	2.437103001
H	0.455787605	2.716006831	3.969666342
H	-0.163540574	4.246473947	3.356783772
H	-2.974042574	1.782966810	2.793864991
H	-2.508832021	3.201775000	3.732254714
H	-1.835369005	1.626764619	4.122849909
H	0.251401959	1.818384277	-4.004660689
H	-1.417774857	1.886819158	-3.447457759
H	-0.172799248	1.209815243	-2.406305293
H	-0.194997690	5.454640958	-3.278205947
H	-1.360934188	4.388793841	-4.059225212
H	0.336247270	4.279959677	-4.477601786
H	1.291859706	-3.509074548	-2.456232363
H	2.687191098	-3.349975492	-3.517272934
H	1.208375848	-2.493187775	-3.894233435
H	3.425130911	0.253354253	-2.618068304
H	2.584638198	-0.359417399	-4.039786205
H	4.059523305	-1.141715392	-3.480723521
H	5.178080843	6.401060692	-0.125753472
H	1.029273212	5.304696995	-0.085022370
H	2.814387607	7.007480454	-0.098508565
H	6.981216952	4.441015890	-0.143492990
H	7.387483196	2.034448241	-0.131113011
H	5.538792605	0.398306364	-0.072748782
H	-4.306128774	-0.341406145	2.636970311
H	-5.489280525	1.797812887	2.072865317
H	-5.864558574	-2.157190680	-0.982702093
H	-7.043479888	-0.023947067	-1.548967744



$JI_{TS,cis}$

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124
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cm**-1
Pd     0.070767456     0.083102044    -0.045473375
N      2.235119408     0.099724606    -0.007466826
N      0.572859202     2.230424526     0.046670242
C      1.836039417     2.442803774     0.132612303
C      2.755121253     1.268361849     0.070824344
C     -0.401316276     3.250223888    -0.002936278
C     -0.540342118     4.023921971    -1.171646972
C     -1.581476235     4.943466453    -1.203887851
C     -2.443187400     5.102446856    -0.132011402
C     -2.286863663     4.330044392     1.003608617
C     -1.273687920     3.382771055     1.090593802
C      0.381128221     3.830965951    -2.358913125
C     -1.054902136     2.564962527     2.342572139
C      2.978464348    -1.087552014    -0.158917456
C      3.057424765    -1.967213869     0.933064485
C      3.777232769    -3.142165449     0.760671076
C      4.362645695    -3.449464343    -0.454518409
C      4.212509877    -2.596643016    -1.534704764
C      3.513112510    -1.402922970    -1.421072693
C      2.395393747    -1.618931690     2.247566634
C      3.220416159    -0.541662628    -2.630267914
O     -2.603772450    -2.753808447    -1.604385993
C     -1.383444708    -2.492547744    -1.118526237
O     -0.365001115    -3.047845416    -1.458000138
C     -2.015608203    -0.173092096    -0.056306345
C     -1.456585996    -1.503607538    -0.017443369
C     -3.044181173     0.769990473    -3.554990507
C     -2.389985322     0.138939736    -2.515454367
C     -2.698005532     0.446298931    -1.185156334
C     -4.001525622     1.741635966    -3.291468713
C     -4.293173319     2.084761959    -1.979363622
C     -3.649727625     1.441788223    -0.937853374
C     -2.683868782    -3.718631682    -2.690168142
C     -1.386200894    -2.715623078    -4.583572217
C     -1.325466071    -2.050504914    -5.797326085
C     -2.494815666    -1.709555695    -6.463631023
C     -2.618262383    -3.034101758    -4.015268251
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C	-3.784115532	-2.681112327	-4.686679475
C	-3.724606074	-2.028093564	-5.907660116
C	3.275248732	-0.706279157	3.097926529
C	1.965915073	-2.846516335	3.035790240
C	0.045402695	3.176810518	3.208623771
C	-2.319839279	2.353549051	3.159009357
C	0.059498645	2.536204570	-3.099730136
C	0.381258596	5.006456086	-3.322301995
C	1.839798074	-0.904099514	-3.181143908
C	4.277556557	-0.639367780	-3.717747292
C	4.815892292	5.400561380	0.546110470
C	5.103398659	4.025192453	0.404433840
C	3.998981179	3.172553764	0.277215471
C	2.661999295	3.630851848	0.282519587
C	2.415267071	4.978083427	0.424847446
C	3.512698821	5.848255389	0.557647953
C	6.373684781	3.407638828	0.378402015
C	6.488401511	2.041758490	0.240403154
C	5.367895438	1.198840000	0.119357631
C	4.116017604	1.771132950	0.136936462
C	-0.896479837	-2.056270167	5.622653796
C	-0.852122587	-1.032263135	4.569392600
C	-1.426386518	-1.232782332	3.370443871
C	-1.604395505	-3.300285504	5.298663981
C	-2.157900531	-3.497978168	4.088457798
C	-2.105294621	-2.470553089	3.088250249
O	-0.357470490	-1.879781427	6.703284483
O	-2.683064363	-2.684233883	1.970146446
H	1.401985209	3.743217257	-1.977530067
H	-1.721132921	5.551250976	-2.086954954
H	-3.239406383	5.832927251	-0.184300369
H	-2.963263700	4.464861988	1.836818237
H	-0.691618610	1.578197957	2.015611393
H	1.485885690	-1.048820526	2.003850276
H	3.874349792	-3.833682588	1.586278166
H	4.917832907	-4.370721773	-0.568217865
H	4.636763151	-2.871753678	-2.490696789
H	3.182864063	0.504735923	-2.311999815
H	-0.608876749	-1.653453177	0.700176106
H	-2.249731841	-2.116746645	1.100444143
H	-2.331753555	0.243107769	0.902321374
H	-2.794924543	0.509186985	-4.575277058
H	-1.611455692	-0.580523372	-2.741285823
H	-4.511244670	2.236007916	-4.107885765
H	-5.027192825	2.850895691	-1.767093160
H	-3.884185245	1.703784913	0.087718233
H	-3.642292709	-4.209729222	-2.539352157
H	-1.878827857	-4.441001848	-2.564338457
H	-0.478802518	-2.998613639	-4.063838845
H	-0.363646327	-1.813556052	-6.234117468
H	-2.446857441	-1.204340479	-7.419496902
H	-4.744995667	-2.927690175	-4.250429430
H	-4.638502455	-1.770408701	-6.426657768
H	2.764366250	-0.418275281	4.017691889
H	3.549215457	0.206508063	2.569109423
H	4.199827079	-1.212110705	3.378791495

H	1.423887594	-2.550116138	3.933105602
H	2.818194747	-3.436353813	3.371463950
H	1.322510062	-3.501791236	2.446496562
H	0.984300180	3.282334293	2.666311042
H	0.238722255	2.564000855	4.089723838
H	-0.246273093	4.168869257	3.555608573
H	-3.131465142	1.936655846	2.560935180
H	-2.681237895	3.283559859	3.597214359
H	-2.131838696	1.673252750	3.989014522
H	0.766307321	2.370924453	-3.913303605
H	-0.941486048	2.578589946	-3.528469656
H	0.094003433	1.662882986	-2.443792491
H	0.586979858	5.949899052	-2.816866716
H	-0.572920492	5.105377235	-3.840281199
H	1.143717681	4.863724849	-4.085950506
H	1.055930277	-0.787593962	-2.426325057
H	1.819854146	-1.946649467	-3.500365854
H	1.580154060	-0.280628707	-4.036890001
H	5.277343383	-0.440190539	-3.332494707
H	4.073100857	0.081525814	-4.507570775
H	4.289888806	-1.624360668	-4.183991625
H	5.628937450	6.108410946	0.647309090
H	1.406377243	5.371293050	0.434551674
H	3.322435615	6.906880474	0.670433126
H	7.264764909	4.016007971	0.468954369
H	7.473929901	1.596650917	0.225488045
H	5.501264684	0.129249486	0.017156948
H	-0.335789161	-0.110645381	4.808948595
H	-1.392926343	-0.471509954	2.598609246
H	-1.644657156	-4.050737808	6.077089119
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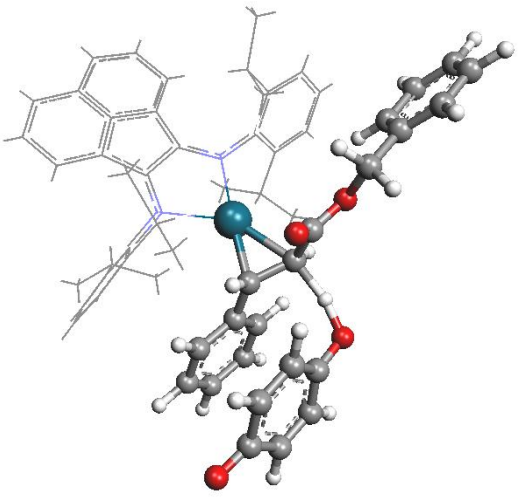

$JI_{TS,trans}$

124

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N	2.290114503	0.136591033	0.066551452
N	0.449973076	2.111644164	-0.133167810
C	1.684611153	2.439594946	-0.007848610
C	2.703909625	1.350822948	0.072421031

C	-0.615295872	3.019817879	-0.310137288
C	-0.779340142	3.656455932	-1.555264043
C	-1.894232059	4.473742903	-1.706443411
C	-2.806707282	4.651900885	-0.680555792
C	-2.631903543	3.997396817	0.525798059
C	-1.542749134	3.159327311	0.737026916
C	0.198972442	3.431372991	-2.691173373
C	-1.327843936	2.449622190	2.054356196
C	3.126959382	-0.994303701	0.164223400
C	3.761973376	-1.299266407	1.383063071
C	4.532958144	-2.454353879	1.423691320
C	4.659900478	-3.279112707	0.317972919
C	3.987861914	-2.981134805	-0.853101513
C	3.198371008	-1.842513263	-0.953448325
C	3.542515536	-0.444186013	2.614326971
C	2.475580843	-1.481906430	-2.231004858
O	-0.613843868	-2.802446476	1.997233375
C	-1.407629697	-1.767426652	1.700110686
O	-2.019721689	-1.115445223	2.516263395
C	-1.934515292	-0.265191099	-0.233207923
C	-1.511048624	-1.570859344	0.237106107
C	-2.580612515	-0.602036518	-3.935278324
C	-2.086576514	-0.859557702	-2.669569310
C	-2.394299913	-0.010982011	-1.595558482
C	-3.391786002	0.504106215	-4.159859173
C	-3.691680903	1.363356578	-3.110566281
C	-3.193484482	1.111374887	-1.844159905
C	-0.506904671	-3.132532676	3.390669115
C	1.624224774	-4.274084817	2.673915406
C	2.623397920	-5.209883695	2.894499866
C	2.582056841	-6.029698340	4.011025219
C	0.565867994	-4.155340943	3.569578813
C	0.528038327	-4.985962686	4.685112833
C	1.531083010	-5.913912148	4.908097050
C	4.575931532	-0.675739717	3.703811368
C	2.134155189	-0.654052422	3.171760100
C	-0.316150838	3.193700942	2.924081090
C	-2.614861595	2.197154995	2.822032082
C	0.040985474	2.037694896	-3.297391560
C	0.112715675	4.489521896	-3.778688267
C	2.103377165	-2.685768986	-3.080440926
C	3.276672782	-0.469759579	-3.047044781
C	4.363865427	5.688327133	0.183319281
C	4.781217797	4.339069324	0.176108028
C	3.763655399	3.377311485	0.122899963
C	2.391101568	3.707248518	0.059806170
C	2.016380858	5.032028460	0.068227080
C	3.024872719	6.010442953	0.135848746
C	6.103972172	3.845282794	0.215617291
C	6.347438097	2.489396352	0.202628731
C	5.312183588	1.537210152	0.161202640
C	4.011347672	1.986215204	0.123261861
C	-4.570999739	-1.933708951	-0.605314109
C	-4.848311835	-0.990299773	0.454850692
C	-5.751528680	-0.015532922	0.265383097
C	-5.326339398	-1.884035648	-1.831449468

C	-6.226443873	-0.909360929	-2.030655591
C	-6.468806383	0.125810829	-1.012373445
O	-3.653109516	-2.803582620	-0.486854620
O	-7.214383861	1.066138409	-1.222731103
H	1.209070695	3.492224596	-2.275582728
H	-2.052492840	4.982203459	-2.647340448
H	-3.659761720	5.301523392	-0.824558034
H	-3.353491092	4.138581431	1.319075725
H	-0.888987318	1.467406720	1.827220136
H	3.624789537	0.604901733	2.317422535
H	5.036061061	-2.722885388	2.342190963
H	5.275208117	-4.167272552	0.376718598
H	4.076404647	-3.642995302	-1.704049299
H	1.535582247	-0.987615562	-1.938081353
H	-2.666404495	-2.347074850	-0.029566509
H	-0.868338075	-2.189624346	-0.401034317
H	-2.420254227	0.346347769	0.525794830
H	-2.338587417	-1.269708670	-4.751712610
H	-1.465147960	-1.733327105	-2.505719565
H	-3.784947259	0.696331762	-5.149201298
H	-4.319524855	2.229747418	-3.276627795
H	-3.432877228	1.778184716	-1.021849556
H	-1.474135431	-3.494940140	3.745740043
H	-0.297646494	-2.213602212	3.946382243
H	1.660023039	-3.640310984	1.795513432
H	3.434314993	-5.300476418	2.183459140
H	3.360406995	-6.762345468	4.177689624
H	-0.298937927	-4.907871278	5.381390866
H	1.485574908	-6.555635520	5.777927185
H	4.432743575	0.035761362	4.514928205
H	5.594122860	-0.559585227	3.332850479
H	4.487869703	-1.673620253	4.135240608
H	1.948766088	0.008377378	4.017267761
H	2.019280588	-1.680977553	3.520581517
H	1.358476318	-0.465508051	2.423823826
H	0.640468328	3.330098345	2.419725651
H	-0.128998736	2.647501872	3.848332998
H	-0.689318897	4.183079285	3.192172081
H	-3.364340134	1.700322602	2.203282726
H	-3.053078865	3.121110246	3.200524517
H	-2.422040428	1.552309573	3.676639921
H	0.765767003	1.884665253	-4.096770325
H	-0.955048269	1.912149487	-3.722896243
H	0.185668694	1.244461317	-2.559966590
H	0.201480280	5.498469498	-3.376490901
H	-0.828082367	4.429615044	-4.326862982
H	0.912361027	4.347390262	-4.503263731
H	1.562064058	-3.437377032	-2.505522599
H	2.979685146	-3.168004020	-3.513602123
H	1.470836086	-2.377119320	-3.912246435
H	3.482693501	0.441729033	-2.485160568
H	2.739628828	-0.188002057	-3.952303826
H	4.235708312	-0.893140427	-3.348228910
H	5.105341641	6.476152930	0.226713896
H	0.975428314	5.326781143	0.023425184
H	2.734948056	7.052269904	0.146041211

H	6.932747451	4.540832515	0.256102663
H	7.370400331	2.139478254	0.230225214
H	5.546927721	0.480303861	0.161975078
H	-4.286831214	-1.089763765	1.378554643
H	-5.976561575	0.718874438	1.028424387
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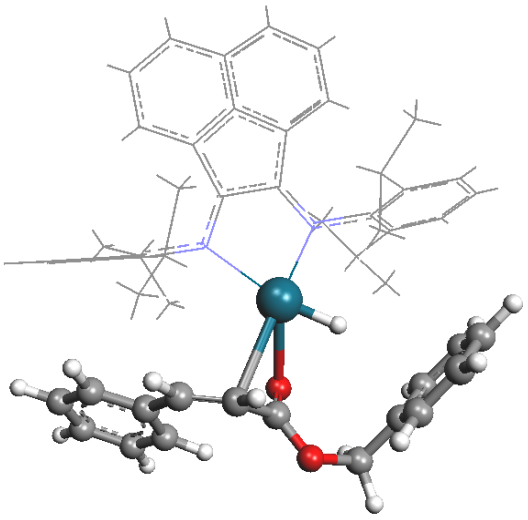

$FG_{TS,cis}$

112

ZPE+TC= 0.8527314 E(el)= -2401.82571618 G= -2400.97298478 v= -113.93 cm**-1

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N	1.700056983	-0.221601552	-0.082949277
N	0.276469442	2.106647588	-0.239408820
C	1.558732597	2.168952206	-0.163473178
C	2.333033909	0.902728776	-0.130308132
C	-0.460402872	3.318175240	-0.149707920
C	-0.598970632	4.130836497	-1.284354300
C	-1.220672069	5.362206957	-1.109587510
C	-1.693456850	5.761060830	0.130806197
C	-1.593315879	4.912713702	1.219437987
C	-0.980996440	3.667463680	1.103234387
C	-0.074598885	3.662566724	-2.624736973
C	-0.829514313	2.737953411	2.290510067
C	2.431914469	-1.443200460	-0.004900043
C	2.936986136	-1.838495124	1.242556917
C	3.692688304	-3.004327417	1.278240726
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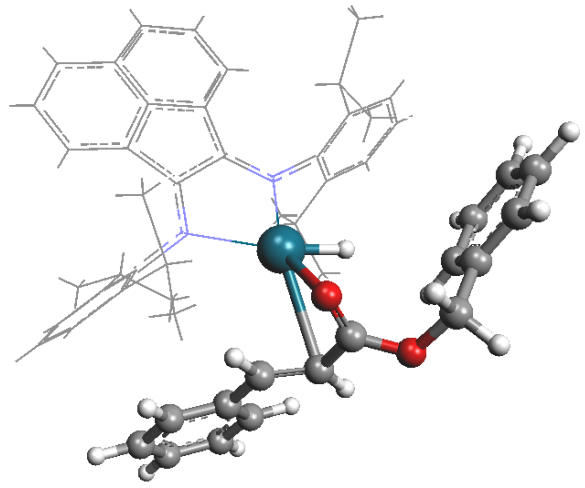

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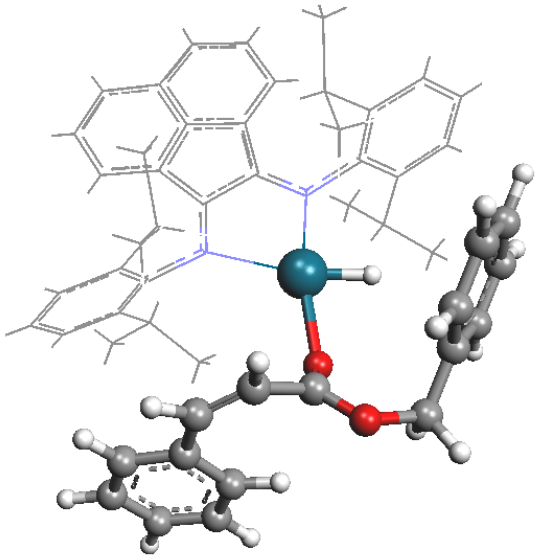

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H	3.106605584	-3.597067202	-3.593465281
H	1.693230818	-2.762726114	-4.199258688
H	3.712110209	0.041309472	-2.764070779
H	3.070306998	-0.648898952	-4.250070910
H	4.459260931	-1.389157268	-3.460707180
H	5.932978467	5.807424656	-0.533376944
H	1.679495776	5.315628551	-0.316871911
H	3.679043055	6.741280994	-0.415672856
H	7.434107015	3.620122979	-0.594484950
H	7.502198561	1.179138813	-0.580806017
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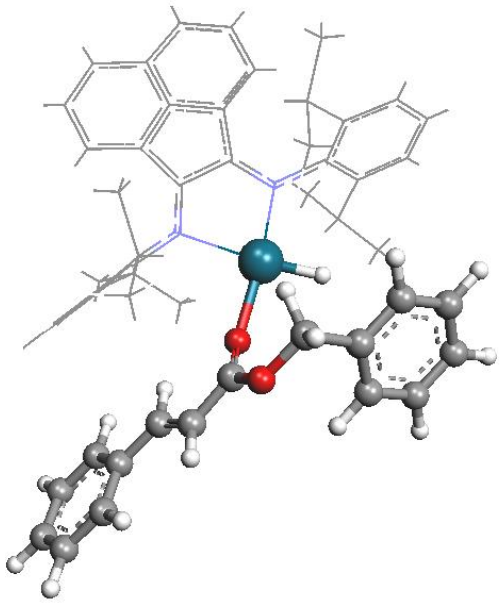

G_{trans}

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C      2.121263889     2.270568732     0.042368534
C      3.013195391     1.094623692     0.244662374
C     -0.053929823     3.033268977    -0.610133235
C      0.055905347     3.833493667    -1.761931663
C     -0.980034866     4.724474339    -2.018305274
C     -2.085283648     4.808774149    -1.187997359
C     -2.187651180     3.982687180    -0.083788765
C     -1.184391800     3.071269093     0.222548692
C      1.204139193     3.651155579    -2.732691123
C     -1.263756905     2.167888071     1.431700836
C      3.313778569    -1.264362102     0.268985832
C      3.485206516    -1.681420563     1.599152882
C      4.202402864    -2.854661531     1.804908543
C      4.722123312    -3.578133242     0.745406714
C      4.518558679    -3.151832407    -0.553743339
C      3.803119430    -1.991133247    -0.823797475
C      2.854967658    -0.934122863     2.757038834
C      3.591073142    -1.498002947    -2.235579401
O     -2.959085725    -0.946178329    -0.254813230
C     -2.481198968    -0.078576440    -1.139567532
O     -1.288620378     0.079939370    -1.410336606
C     -3.212609197     1.687008259    -2.624972620
C     -3.524256275     0.692021335    -1.775565990
C     -6.317588414     3.379463947    -3.877568675
C     -5.502903465     2.521525749    -3.168249517
C     -4.112535092     2.558010180    -3.336726319
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C	-1.534049041	-2.944038443	-0.346850442
C	-0.511139618	-3.720946323	0.195107446
C	0.031511709	-4.769400738	-0.526036017
C	3.567621668	-1.156858813	4.080981225
C	1.373487965	-1.289409491	2.874074830
C	-0.415760941	2.708213547	2.582007247
C	-2.685244410	1.900491576	1.899313492
C	1.013767530	2.367525328	-3.541714967
C	1.412849814	4.837922843	-3.658302216
C	3.524769727	-2.619573381	-3.258888977
C	4.653183964	-0.468247016	-2.616128373
C	4.889660212	5.223668578	1.221926863
C	5.193576391	3.844608706	1.192498202
C	4.161714596	2.992489547	0.778156399
C	2.884753046	3.456833607	0.392878344
C	2.619391725	4.806879194	0.431920813
C	3.641153067	5.676424519	0.855507694
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C	5.507384991	1.013686504	1.037972340
C	4.298611900	1.585905942	0.704954202
H	2.124666160	3.537332677	-2.153963231
H	-0.926423514	5.361108870	-2.891019853
H	-2.876482497	5.511406245	-1.414384925
H	-3.063500959	4.041343065	0.548314003
H	-0.823374894	1.204262348	1.134165588
H	2.913904152	0.137205787	2.546116997
H	4.354448693	-3.211112357	2.814300961
H	5.282741938	-4.483611281	0.935516255
H	4.918837349	-3.730025672	-1.375453354
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H	-4.541637032	0.430100923	-1.519402029
H	0.662383516	-1.639854168	-0.910010903
H	-2.152388600	1.859617988	-2.799419526
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H	-2.658077540	-2.150071444	1.309334160
H	-1.236891861	-1.202104219	0.868299128
H	-2.809471705	-2.651207101	-2.045856098
H	-1.838281943	-4.509492672	-3.329612653
H	-0.015263438	-5.870584645	-2.367623481
H	-0.128618184	-3.488997221	1.182818683
H	0.828576829	-5.361536195	-0.095653625
H	3.151965177	-0.503934630	4.846438079

H	4.634884089	-0.949553519	4.007148315
H	3.450601911	-2.179585347	4.438866449
H	0.893671204	-0.710250593	3.663116509
H	1.250695499	-2.346153999	3.115697153
H	0.839634695	-1.096995612	1.939552894
H	0.627359997	2.846053375	2.298355379
H	-0.442058893	2.031062573	3.435431261
H	-0.794495779	3.674936268	2.915707793
H	-3.334757052	1.585421877	1.082446532
H	-3.133758546	2.783369324	2.355166352
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H	1.516247429	5.772689921	-3.107638731
H	0.586266707	4.954079684	-4.360328219
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H	4.481768042	-0.087828415	-3.622818321
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H	1.653301901	5.202085264	0.144191840
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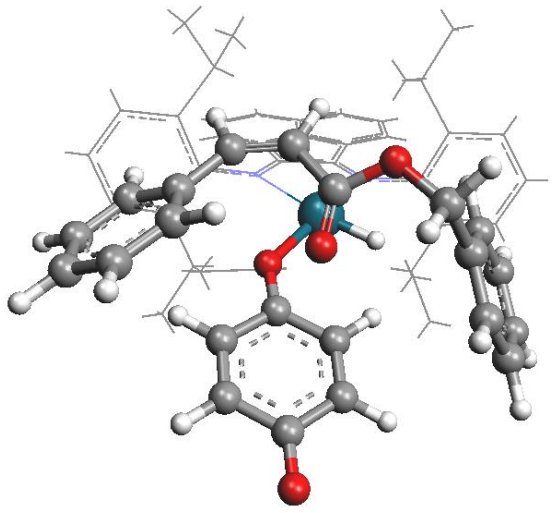

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124

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C	1.734054506	2.455243776	-0.150744935
C	2.630644782	1.272294251	-0.038852717

C	-0.421646155	3.376401299	-0.039994750
C	-1.167666199	3.525369227	-1.216993045
C	-2.005711327	4.629763495	-1.313543839
C	-2.112070218	5.537684239	-0.273830211
C	-1.420458793	5.324136555	0.906000625
C	-0.573986337	4.230328823	1.063230793
C	-1.031337226	2.526880158	-2.344959074
C	0.092934792	3.951714702	2.397521180
C	2.943705180	-1.047944768	0.167158090
C	3.540338336	-1.492433600	1.354004034
C	4.347234787	-2.621591846	1.276562515
C	4.564655783	-3.267815499	0.070363165
C	3.972176787	-2.794820723	-1.085355616
C	3.143504364	-1.676203156	-1.066414384
C	3.303342970	-0.766005757	2.659824832
C	2.498055989	-1.190034094	-2.346490264
O	-1.436020837	-2.594716712	3.213149088
C	-2.193020794	-1.652870079	2.615720873
O	-3.079192876	-1.919283776	1.831961093
C	-2.348508130	0.859524052	2.833558422
C	-1.739006303	-0.322350004	3.026036280
C	-6.038136812	0.822884952	2.061204114
C	-4.802216721	0.408261199	2.524202484
C	-3.669533943	1.205836885	2.335841597
C	-6.169376568	2.031237526	1.389856871
C	-5.055545564	2.838996596	1.201465413
C	-3.823924675	2.437351645	1.686303574
C	-1.740231228	-3.954946379	2.857692465
C	0.142040521	-3.978423540	1.198867568
C	0.687521417	-4.355980330	-0.017924003
C	-0.059943958	-5.111671401	-0.911076757
C	-1.162384411	-4.336804707	1.531314951
C	-1.904402168	-5.089260771	0.630049121
C	-1.353498996	-5.484953491	-0.580140394
C	4.462654718	-0.882983607	3.635585067
C	1.999315859	-1.237074847	3.297446450
C	1.417337555	4.690816601	2.574386342
C	-0.821796186	4.286386861	3.572632139
C	-2.341122396	2.293625177	-3.082267423
C	0.080133883	2.919737578	-3.314827939
C	1.486147040	-2.208196223	-2.860718004
C	3.537427101	-0.851210645	-3.408618322
C	4.705090064	5.227176928	-1.292675367
C	4.980551806	3.877662275	-0.982116878
C	3.881468650	3.088427069	-0.617679980
C	2.562504565	3.587321988	-0.543681097
C	2.325147761	4.906261399	-0.862685242
C	3.416227009	5.710632997	-1.237330517
C	6.234903002	3.229273725	-1.005346313
C	6.340040355	1.892190881	-0.690833423
C	5.225227668	1.107764291	-0.344002245

C	3.985265008	1.710133108	-0.310145300
C	-2.780837974	-0.636985638	-0.580065448
C	-2.412558554	-1.962771125	-1.050859751
C	-3.324751744	-2.751459339	-1.626235152
C	-4.166937192	-0.205754313	-0.705970510
C	-5.086385304	-1.003009042	-1.256600935
C	-4.734313119	-2.339425474	-1.762585452
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H	3.184150655	0.296975806	2.425448736
H	4.826630734	-2.991750030	2.172712306
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H	-1.301619936	-4.539945564	3.665959370
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H	0.369062585	-5.415741149	-1.857177032
H	-2.923348294	-5.363147197	0.877701282
H	-1.938979561	-6.082448020	-1.267423734
H	4.293025267	-0.245496876	4.501620260
H	5.407683689	-0.586001040	3.181190130
H	4.577814905	-1.900189316	4.009437475
H	1.764496652	-0.654128735	4.188460235
H	2.072621455	-2.283200782	3.599380867
H	1.159778405	-1.151002563	2.604017444
H	2.178561299	4.372263158	1.866977728
H	1.811285126	4.530282712	3.577479364
H	1.277493465	5.765304016	2.445034450
H	-1.830839256	3.895297187	3.445181420
H	-0.908614237	5.363330029	3.715699647
H	-0.414618432	3.878092240	4.496547362
H	-2.252289424	1.441293566	-3.755533542
H	-2.624898575	3.150408382	-3.693428811
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H	0.715516588	-2.408744523	-2.115049135
H	1.965847713	-3.158308063	-3.101253384
H	0.997706947	-1.846954170	-3.765726546
H	4.253963854	-0.112263831	-3.050041448
H	3.058313791	-0.448724580	-4.300482110
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H	5.355091135	0.057885378	-0.117997269
H	-1.381046300	-2.271888546	-0.913004413
H	-3.075084965	-3.736516468	-1.997438768
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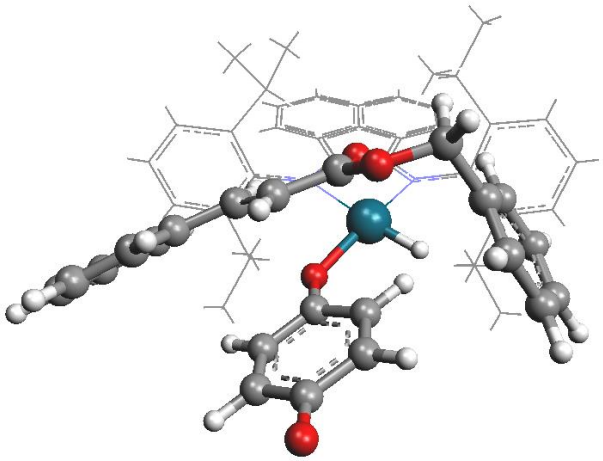

H_{trans}

124
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C	2.568969813	1.161618249	-0.237041588
C	-0.416804866	3.321492792	0.123127058
C	-1.035581946	3.873754608	-1.002689362
C	-1.761581165	5.048493032	-0.823791683
C	-1.898567004	5.622482772	0.427328259
C	-1.350228479	5.001654699	1.538010441
C	-0.604954749	3.834255120	1.416951507
C	-0.942870193	3.220391559	-2.363477611
C	-0.009710889	3.138259484	2.624216603
C	2.877779297	-1.134904403	0.235280217
C	3.567260372	-1.231026882	1.459153997
C	4.329482959	-2.375492712	1.662441668
C	4.429274333	-3.362289262	0.695198000
C	3.756249163	-3.227687255	-0.503394590

C	2.955508475	-2.117998288	-0.756625058
C	3.465879571	-0.156514300	2.525301273
C	2.266148050	-1.955378603	-2.091672166
O	-2.353235521	-1.702280358	3.988818242
C	-2.147939257	-0.617661338	3.225680453
O	-1.061437985	-0.317198744	2.769926476
C	-3.370630306	1.219834890	2.234007446
C	-3.388140034	0.119279955	2.999274225
C	-6.820303397	2.624434689	1.744143212
C	-5.790006507	1.869698365	2.268666688
C	-4.482220007	2.030989417	1.795601163
C	-6.569964420	3.553124950	0.738976642
C	-5.278389452	3.730367543	0.265933824
C	-4.244353784	2.978874214	0.794407000
C	-1.197408092	-2.543103666	4.215883369
C	-1.837901950	-4.482007454	2.763254509
C	-1.619662451	-5.319775927	1.681304626
C	-0.496339234	-5.147273273	0.883520643
C	-0.943910839	-3.453943569	3.056420093
C	0.177781335	-3.290007251	2.251155042
C	0.406139511	-4.136270209	1.175866681
C	4.636445448	-0.154168264	3.494990688
C	2.141612885	-0.254512589	3.275336869
C	1.407088697	3.626166140	2.923787971
C	-0.871208686	3.279306644	3.871728953
C	-2.328916053	3.005996357	-2.960768443
C	-0.055475447	4.014500507	-3.315917642
C	1.539578923	-3.217774902	-2.533756241
C	3.267103481	-1.489720865	-3.146408748
C	4.711412160	5.226291353	-0.889785501
C	4.961955672	3.839663181	-0.797858586
C	3.844182022	3.020445084	-0.588939385
C	2.527962672	3.520938168	-0.475626566
C	2.318498154	4.879779073	-0.559844222
C	3.429799559	5.716394808	-0.771073497
C	6.209599312	3.184521360	-0.885184920
C	6.293391874	1.814793033	-0.761973093
C	5.164487297	1.006841872	-0.538123460
C	3.930307377	1.614999399	-0.450797825
C	-2.984374051	-0.603835759	-0.256845539
C	-2.878114187	-1.913454140	0.364655925
C	-3.973702219	-2.655759683	0.562752301
C	-4.290098506	-0.139644221	-0.706796722
C	-5.387729505	-0.875107067	-0.505164158
C	-5.313929989	-2.184802314	0.165050530
O	-2.010995394	0.158678404	-0.415126007
O	-6.309319985	-2.846781538	0.385406905
H	-0.493331853	2.232280271	-2.225801506
H	-2.232201231	5.512533507	-1.682381062
H	-2.462488454	6.538380062	0.544325529
H	-1.506334881	5.427943624	2.520422734

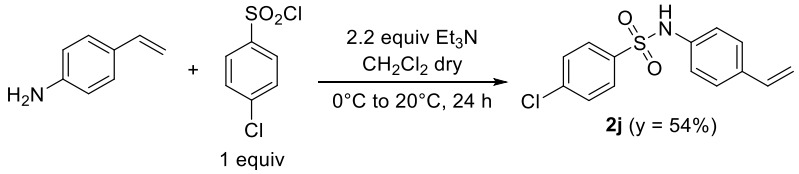
H	0.044464222	2.068360528	2.383872926
H	3.479245621	0.816313071	2.025590927
H	4.864893726	-2.493903176	2.594137925
H	5.041067904	-4.235362597	0.878597914
H	3.850628675	-3.994158435	-1.262197003
H	1.511141661	-1.171211136	-1.984111561
H	-4.294676850	-0.285971286	3.430995396
H	-0.053287325	-1.537181686	-0.055857868
H	-2.396501628	1.511796406	1.841411983
H	-7.827066718	2.493590486	2.117789107
H	-5.995222124	1.150278305	3.051589353
H	-7.382949037	4.139775540	0.332201574
H	-5.074370366	4.453802872	-0.513528122
H	-3.233376026	3.094340332	0.418430859
H	-1.455097237	-3.099011492	5.115257013
H	-0.332399849	-1.912467486	4.418289298
H	-2.709935842	-4.624063793	3.391925378
H	-2.319329343	-6.117498708	1.467094823
H	-0.320051767	-5.807820001	0.044344602
H	0.871460170	-2.485928901	2.461020283
H	1.293943688	-4.000001325	0.570780276
H	4.573542113	0.712175198	4.151596517
H	5.595685868	-0.114306175	2.979269479
H	4.636610161	-1.036904775	4.134501488
H	2.032269597	0.564735327	3.986644506
H	2.093609266	-1.186004437	3.842569813
H	1.278702601	-0.227471748	2.608169984
H	2.108723755	3.411167858	2.119373148
H	1.790831185	3.156689486	3.829309037
H	1.417486358	4.705531234	3.084133092
H	-1.917465790	3.045473518	3.679664687
H	-0.827300847	4.287983476	4.283536735
H	-0.515409190	2.601621633	4.647214273
H	-2.266438952	2.439273666	-3.888831285
H	-2.817919622	3.952530053	-3.192765261
H	-2.973830718	2.459886983	-2.272631880
H	0.959299268	4.120762373	-2.934102720
H	-0.453747517	5.017717179	-3.473932158
H	0.003938920	3.528379239	-4.289077692
H	0.803126746	-3.533095696	-1.794430385
H	2.225484724	-4.048461797	-2.699463743
H	1.015274857	-3.045030490	-3.472576112
H	3.753260299	-0.557736436	-2.856739291
H	2.775989812	-1.327433557	-4.105235362
H	4.049700763	-2.234532700	-3.296984390
H	5.536828588	5.908210964	-1.051082627
H	1.329565731	5.309444640	-0.468565965
H	3.266715540	6.783254297	-0.840035365
H	7.107921375	3.766587617	-1.048253540
H	7.261998817	1.339169991	-0.833669301
H	5.279776664	-0.064513643	-0.437929977

H	-1.887701503	-2.236737036	0.672974510
H	-3.926133434	-3.627459060	1.036551463
H	-4.320703781	0.831592781	-1.183297531
H	-6.370845763	-0.541932957	-0.812285099

9. Synthesis of the olefins 4-chloro-*N*-(4-vinylphenyl)benzenesulfonamide 2j and 4-chloro-N-((4-chlorophenyl)sulfonyl)-N-(4-vinylphenyl)benzenesulfonamide 2k

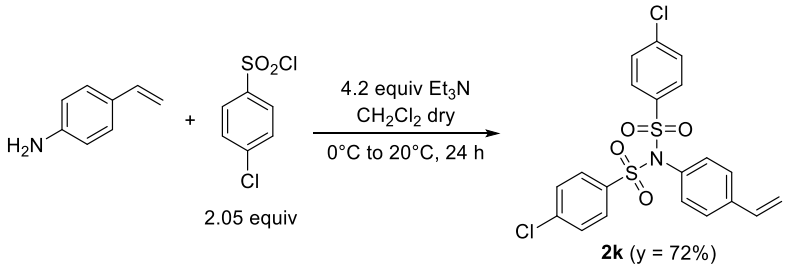
The synthesis of benzenesulfonamides **2j** and **2k** has been adapted from the literature.[17]

Synthesis of compound **2j**:



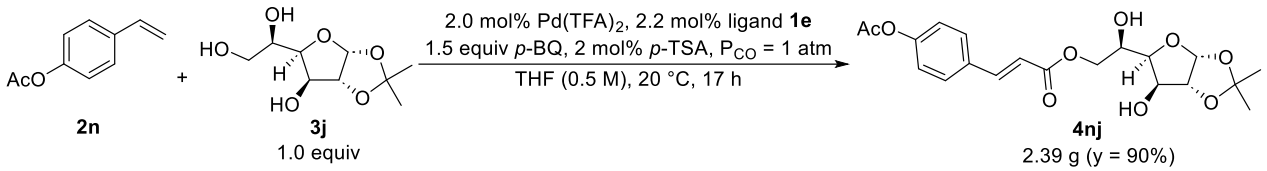
A solution 4-vinylaniline (238 g, 2 mmol) in dry dichloromethane (5 mL) was cooled at 0 °C and triethylamine (307 µL, 2.2 mmol) and 4-chlorobenzenesulfonyl chloride (422 mg, 2.0 mmol) were added in sequence to the stirred solution. The mixture was stirred for 1 hour at 0 °C and 24 hours at room temperature (20°C). The reaction mixture was diluted with dichloromethane (8 mL) and the organic phase was washed with HCl 1M (15 mL) and water (3 x 15 mL).
The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure.
The olefin **2j** has been eventually purified by flash column chromatography on silica gel (petroleum ether/EtOAc 95:5 to 85:15), obtaining a white solid; yield: 54% (320 mg). R_f = 0.37 (petroleum ether/EtOAc = 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 2H), 7.43 – 7.37 (m, 2H), 7.33 – 7.27 (m, 2H), 7.08 – 7.00 (m, 2H), 6.84 (br s, 1H), 6.63 (dd, J = 17.6, 10.9 Hz, 1H), 5.67 (dd, J = 17.6, 0.7 Hz, 1H), 5.22 (dd, J = 10.9, 0.7 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 137.6, 135.8, 135.5, 129.5, 128.8, 127.4, 122.2, 114.3.

Synthesis of compound **2k**:

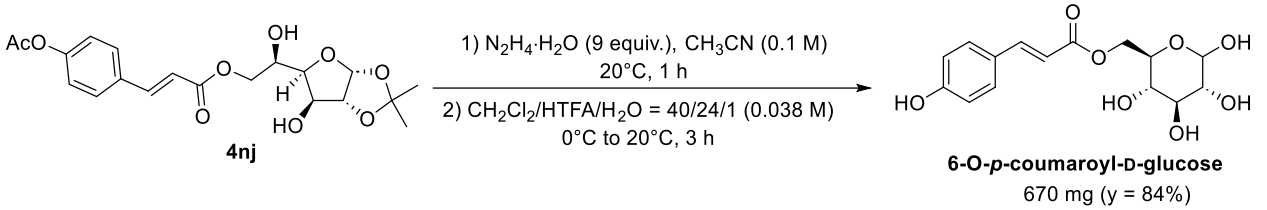


A solution 4-vinylaniline (238 g, 2 mmol) in dry dichloromethane (5 mL) was cooled at 0 °C and triethylamine (590 µL, 4.2 mmol) and 4-chlorobenzenesulfonyl chloride (866 mg, 4.1 mmol) were added in sequence to the stirred solution. The mixture was stirred for 1 hour at 0 °C and 24 hours at room temperature (20°C). The reaction mixture was diluted with dichloromethane (8 mL) and the organic phase was washed with HCl 1M (15 mL) and water (3 × 15 mL).
The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure.
The olefin **2k** has been eventually purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2 to 93:7), obtaining a white solid; yield: 72% (680 mg). R_f = 0.63 (petroleum ether/EtOAc = 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 4H), 7.56 – 7.51 (m, 4H), 7.42 – 7.38 (m, 2H), 7.00 – 6.95 (m, 2H), 6.72 (dd, J = 17.6, 10.9 Hz, 1H), 5.81 (dd, J = 17.6, 0.5 Hz, 1H), 5.37 (dd, J = 10.9, 0.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 140.0, 137.9, 135.6, 133.0, 131.6, 130.2, 129.6, 127.3, 116.7.

10.Procedure for the synthesis of the 6-O-*p*-coumaroyl-D-glucose

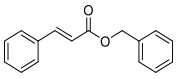


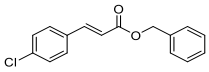
In a nitrogen flushed two-neck round-bottomed flask, equipped with a magnetic stirring bar, the $Pd(TFA)_2$ (43 mg, 0.13 mmol) and THF (13 mL) were added in sequence. After the mixture turned in a red/brown color (10 min), the ligand **1e** (71.6 mg, 0.143 mmol) was added. The mixture was left under stirring for 10 min, turning in a dark orange color. Then, *p*-benzoquinone (1.05 g, 9.75 mmol), *p*-TSA·H_2O (24.7 mg, 0.13 mmol), the glucofuranose **3j** (1.43 g, 6.5 mmol) and the olefin **2n** (995µL, 6.5 mmol) were added in sequence. The reaction was vigorously stirred at room temperature (20°C) under balloon pressure of CO, for 17 h. The crude was dried under reduced pressure and product **4nj** was eventually obtained after column chromatography on silica gel (cyclohexane/ EtOAc), obtaining an off-white solid; yield: 90% (2.39 g).

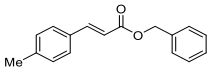


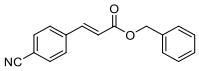
To a suspension of **4nj** (1 g, 2.45 mmol) in acetonitrile (25 mL), 580 µL of hydrazine monohydrate (12.25 mmol) were added. After 30 min additional 460 µL of hydrazine monohydrate (9.9 mmol) were added. The reaction was left under stirring until complete consumption of the starting material monitored by TLC (CH_2Cl_2/MeOH = 95:5). Then NH_4Cl sat. aq. (25 mL) was added and the mixture was left stirring for 10 min before adding 30 mL of H_2O. The solution was extracted with EtOAc (4 x 50 mL). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure, obtaining a white solid. Successively, CH_2Cl_2 (40 mL), H_2O (1 mL) and trifluoroacetic acid (24 mL) were added at 0°C and the reaction was left under stirring until complete consumption of the starting material monitored by TLC (CH_2Cl_2/MeOH = 90:10). The crude was dried under reduced pressure. Then, fresh Et_2O was added (30 mL) until the formation of a white precipitate is observed, which was collected by filtration, washing with fresh Et_2O, eventually affording the pure 6-O-p-coumaroyl-D-glucose with 84% isolated yield (670 mg), showing an α/β ratio = 0.35:0.65. ^{1}H NMR (400 MHz, CD_3OD) δ 7.63 (d, J = 16.0 Hz, 1H), 7.51 – 7.40 (m, 2H, ArH), 6.85 – 6.77 (m, 2H, ArH), 6.34 (d, J = 16.0 Hz, 0.35H), 6.33 (d, J = 16.0 Hz, 0.65H), 5.11 (d, J = 3.7 Hz, 0.35H, H1α), 4.51 (d, J = 7.8 Hz, 0.65H, H1β), 4.50 (dd, J = 11.8, 2.2 Hz, 0.65H, H6aβ), 4.45 (dd, J = 11.8, 2.2 Hz, 0.35H, H6aα), 4.31 (m, 1H, H6bβ, H6bα), 4.04 (ddd, J = 10.1, 5.5, 2.2 Hz, 0.35H, H5α), 3.70 (t, J = 9.3, 0.35H, H3α), 3.55 (ddd, J = 8.2, 5.8, 2.2 Hz, 0.65H, H5β), 3.43 – 3.33 (m, 2H, H4β, H3β, H2α, H4α), 3.23 – 3.11 (m, 0.65H, H2β). ^{13}C NMR (101 MHz, CD_3OD) δ 169.2 (α), 169.1 (β), 161.30 (β), 161.28 (α), 146.73 (β), 146.68 (α), 131.1 (2C, α+β), 127.14 (α), 127.13 (β), 116.8 (2C, α+β), 115.0 (α), 114.9 (β), 98.3 (β), 94.0 (α), 77.9 (β), 76.2 (β), 75.5 (β), 74.8 (α), 73.8 (α), 72.0 (α), 71.8 (β), 70.8 (α), 64.9 (α), 64.8 (β). ESI-MS: m/z = 325 $[M-H]^-$. Spectral data were in agreement with previously reported literature data.[18]

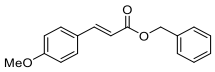
11. Experimental data for compounds 4-10

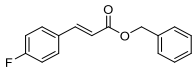
 **Benzyl cinnamate (4aa):** Compound **4aa** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining a white solid; yield: 94% (112 mg). R_f = 0.32 (petroleum ether/EtOAc 92:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 16.0 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.47 – 7.32 (m, 8H), 6.50 (d, J = 16.0 Hz, 1H), 5.26 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 145.3, 136.2, 134.5, 130.5, 129.0, 128.7, 128.39, 128.37, 128.2, 118.0, 66.5. ESI-MS: m/z = 239 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[19]

 **Benzyl (*E*)-3-(4-chlorophenyl)acrylate (4ba):** Compound **4ba** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining a white solid; yield: 96% (131 mg). R_f = 0.37 (petroleum ether/EtOAc 92:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 16.0 Hz, 1H), 7.48 – 7.32 (m, 9H), 6.46 (d, J = 16.0 Hz, 1H), 5.26 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 143.8, 136.4, 136.1, 133.0, 129.4, 129.3, 128.8, 128.4 (2C), 118.6, 66.6.
ESI-MS: m/z = 273 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[20]

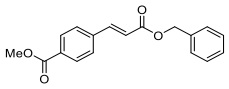
 **Benzyl (*E*)-3-(*p*-tolyl)acrylate (4ca):** Compound **4ca** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining a white solid; yield: 96% (121 mg). R_f = 0.47 (petroleum ether/EtOAc 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 16.0 Hz, 1H), 7.46 – 7.31 (m, 7H), 7.19 (app d, J = 8.0 Hz, 2H), 6.45 (d, J = 16.0 Hz, 1H), 5.26 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 145.3, 140.9, 136.3, 131.8, 129.8, 128.7, 128.40, 128.35, 128.2, 116.9, 66.4, 21.6. ESI-MS: m/z = 253 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[20]

 **Benzyl (*E*)-3-(4-cyanophenyl)acrylate (4da):** Compound **4da** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 95:5 to 90:10), obtaining colorless crystals; yield: 81% (107 mg). R_f = 0.16 (petroleum ether/EtOAc 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 16.0 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.63 – 7.58 (m, 2H), 7.45 – 7.32 (m, 5H), 6.56 (d, J = 16.0 Hz, 2H), 5.27 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 142.8, 138.8, 135.8, 132.8, 128.8, 128.59, 128.56, 128.52, 121.7, 118.5, 113.6, 66.9. ESI-MS: m/z = 264 $[M+H]^+$.

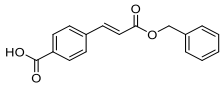
 **Benzyl (*E*)-3-(4-methoxyphenyl)acrylate (4ea):** Compound **4ea** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 95:5 to 90:10), obtaining an orange oil; yield: 79% (119 mg). R_f = 0.22 (petroleum ether/EtOAc 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 16.0 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.45 – 7.31 (m, 5H), 6.93 – 6.87 (m, 2H), 6.36 (d, J = 16.0 Hz, 1H), 5.25 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 161.6, 145.0, 136.4, 129.9, 128.7, 128.4, 128.3, 127.3, 115.5, 114.5, 66.3, 55.5. ESI-MS: m/z = 269 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[20]



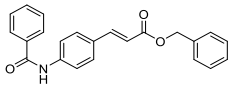
Benzyl (*E*)-3-(4-fluorophenyl)acrylate (4fa): Compound **4fa** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining a white solid; yield: 100% (128 mg). R_f = 0.41 (petroleum ether/EtOAc 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 16.0 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.44 – 7.31 (m, 5H), 7.12 – 7.03 (m, 2H), 6.41 (d, J = 16.0 Hz, 1H), 5.26 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 164.1 (d, J = 251.4 Hz), 144.0, 136.2, 130.8 (d, J = 3.4 Hz), 130.1 (d, J = 8.5 Hz), 128.8, 128.4 (2C), 117.8 (d, J = 2.4 Hz), 116.2 (d, J = 21.9 Hz), 66.6. ESI-MS: m/z = 257 $[M+H]^+$.



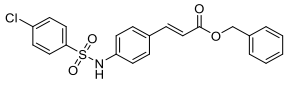
Benzyl (*E*)-3-(4-acetoxyphenyl)acrylate (4ga): Compound **4ga** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2 to 93:7), obtaining an off-white solid; yield: 87% (129 mg). R_f = 0.44 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.02 (m, 2H), 7.74 (d, J = 16.0 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.46 – 7.32 (m, 5H), 6.56 (d, J = 16.0 Hz, 1H), 5.27 (s, 2H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 166.5, 143.9, 138.7, 136.0, 131.6, 130.3, 128.8, 128.49, 128.46, 128.1, 120.4, 66.7, 52.4. ESI-MS: m/z = 297 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[21]



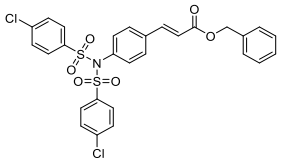
(*E*)-4-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)benzoic acid (4ha): Compound **4ha** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 90:10 to 60:40), obtaining a pale yellow crystals; yield: 71% (100 mg). R_f = 0.23 (Et_2O/CH_2Cl_2 50:50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (app d, J = 8.3 Hz, 2H), 7.75 (d, J = 16.0 Hz, 1H), 7.61 (app d, J = 8.3 Hz, 2H), 7.45 – 7.32 (m, 5H), 6.59 (d, J = 16.0 Hz, 1H), 5.27 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 166.4, 143.7, 139.5, 136.0, 130.9, 130.6, 128.8, 128.53, 128.49, 128.2, 120.9, 66.8. ESI-MS: m/z = 281 $[M-H]^-$.



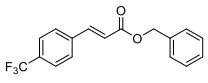
Benzyl (*E*)-3-(4-benzamidophenyl)acrylate (4ia): Compound **4ia** has been purified by flash column chromatography on silica gel (cyclohexane/EtOAc 85:15), obtaining a white solid; yield: 54% (96 mg). R_f = 0.30 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.84 (m, 3H), 7.75 – 7.66 (m, 3H), 7.60 – 7.46 (m, 5H), 7.44 – 7.32 (m, 5H), 6.44 (d, J = 16.0 Hz, 1H), 5.26 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 165.8, 144.5, 140.1, 136.4, 134.9, 132.2, 130.8, 129.3, 129.0, 128.7, 128.39, 128.37, 127.2, 120.3, 117.2, 66.5. ESI-MS: m/z = 358 $[M+H]^+$.



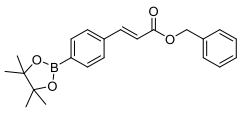
Benzyl (*E*)-3-(4-((4-chlorophenyl)sulfonamido)phenyl)acrylate (4ja): Compound **4ja** has been purified by flash column chromatography on silica gel (cyclohexane/EtOAc 85:15), obtaining a white solid; yield: 74% (158 mg). R_f = 0.15 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.63 (d, J = 16.0 Hz, 1H), 7.44 – 7.31 (m, 10H), 7.13 – 7.08 (m, 2H), 6.39 (d, J = 16.0 Hz, 1H), 5.24 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 144.1, 140.1, 138.1, 137.5, 136.1, 131.5, 129.7, 129.5, 128.8 (2C), 128.44, 128.39, 121.0, 117.8, 66.6. ESI-MS: m/z = 445 $[M+NH_4]^+$.



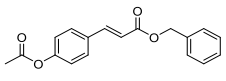
Benzyl (*E*)-3-(4-((4-chloro-N-((4-chlorophenyl)sulfonyl)phenyl)sulfonamido)phenyl)acrylate (4ka): Compound **4ka** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 95:5 to 90:10), obtaining a white solid; yield: 96% (290 mg). R_f = 0.53 (petroleum ether/EtOAc 85:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 4H), 7.70 (d, J = 16.0 Hz, 1H), 7.57 – 7.49 (m, 6H), 7.44 – 7.32 (m, 5H), 7.07 – 7.00 (m, 2H), 6.51 (d, J = 16.0 Hz, 1H), 5.27 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 143.3, 141.2, 137.7, 136.8, 136.0, 135.2, 132.0, 130.2, 129.6, 129.1, 128.8, 128.54, 128.48, 120.6, 66.8. ESI-MS: m/z = 602 $[M+H]^+$.



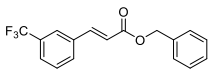
Benzyl (*E*)-3-(4-(trifluoromethyl)phenyl)acrylate (4la): Compound **4la** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining a white solid; yield: 96% (147 mg). R_f = 0.66 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 16.0 Hz, 1H), 7.65 (app d, J = 8.8 Hz, 2H), 7.62 (app d, J = 8.8 Hz, 2H), 7.46 – 7.32 (m, 5H), 6.56 (d, J = 16.0 Hz, 1H), 5.27 (s, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 166.3, 143.4, 137.9 (q, J = 1.2 Hz), 135.9, 132.0 (q, J = 32.7 Hz), 128.8, 128.54, 128.50, 128.4, 126.0 (q, J = 3.8 Hz), 123.9 (q, J = 272.2 Hz), 120.6, 66.8. ESI-MS: m/z = 307 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[20]



Benzyl (*E*)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (4ma): Compound **4ma** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 95:5 to 85:15), obtaining a pale yellow solid; yield: 72% (132 mg). R_f = 0.65 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (app d, J = 8.0 Hz, 2H), 7.74 (d, J = 16.0 Hz, 1H), 7.52 (app d, J = 8.0 Hz, 2H), 7.45 – 7.31 (m, 5H), 6.54 (d, J = 16.0 Hz, 1H), 5.26 (s, 2H), 1.35 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 145.1, 137.0, 136.2, 135.4, 128.7, 128.40, 128.38, 127.4, 118.9, 84.2, 66.5, 25.0. ESI-MS: m/z = 365 $[M+H]^+$.

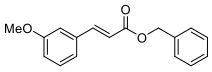


Benzyl (*E*)-3-(4-acetoxyphenyl)acrylate (4na): Compound **4na** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 95:5 to 90:10), obtaining a colorless solid; yield: 94% (139 mg). R_f = 0.44 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 16.0 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.45 – 7.31 (m, 5H), 7.15 – 7.10 (m, 2H), 6.45 (d, J = 16.0 Hz, 1H), 5.26 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 166.8, 152.3, 144.2, 136.1, 132.2, 129.4, 128.7, 128.43, 128.41, 122.3, 118.2, 66.6, 21.3. ESI-MS: m/z = 297 $[M+H]^+$.

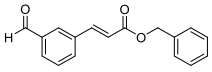


Benzyl (*E*)-3-(3-(trifluoromethyl)phenyl)acrylate (4oa): Compound **4oa** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining a

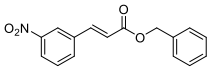
colorless oil; yield: 88% (135 mg). R_f = 0.21 (petroleum ether/EtOAc 95:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.74 (d, J = 16.0 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 7.46 – 7.32 (m, 5H), 6.56 (d, J = 16.0 Hz, 1H), 5.27 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 143.4, 136.0, 135.3, 131.6 (q, J = 32.6 Hz), 131.2 (q, J = 1.0 Hz), 129.6, 128.8, 128.51, 128.47, 126.9 (q, J = 3.7 Hz), 124.8 (q, J = 3.8 Hz), 123.9 (q, J = 272.5 Hz), 120.1, 66.8. ESI-MS: m/z = 307 $[M+H]^+$.



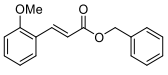
Benzyl (*E*)-3-(3-methoxyphenyl)acrylate (4pa): Compound **4pa** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 97:3), obtaining a pale yellow oil; yield: 100% (134 mg). R_f = 0.29 (petroleum ether/EtOAc 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 16.0 Hz, 1H), 7.44 – 7.32 (m, 5H), 7.30 (t, J = 7.9 Hz, 1H), 7.12 (d, J = 7.7 Hz, 1H), 7.05 – 7.03 (m, 1H), 6.94 (dd, J = 8.2, 2.4 Hz, 1H), 6.48 (d, J = 16.0 Hz, 1H), 5.26 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 160.1, 145.3, 136.2, 135.9, 130.0, 128.8, 128.44, 128.42, 121.0, 118.3, 116.5, 113.0, 66.5, 55.4. ESI-MS: m/z = 269 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[22]



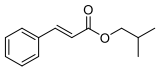
Benzyl (*E*)-3-(3-formylphenyl)acrylate (4qa): Compound **4qa** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 95:5), obtaining a colorless oil; yield: 94% (125 mg). R_f = 0.19 (petroleum ether/EtOAc 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.02 (t, J = 1.6 Hz, 1H), 7.89 (dt, J = 7.6, 1.3 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.57 (t, J = 7.7 Hz, 1H), 7.45 – 7.31 (m, 5H), 6.58 (d, J = 16.1 Hz, 1H), 5.27 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 166.4, 143.5, 137.1, 136.0, 135.5, 133.7, 131.2, 129.8, 129.1, 128.8, 128.5, 128.4, 120.0, 66.7. ESI-MS: m/z = 284 $[M+NH_4]^+$.

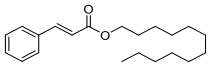


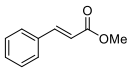
Benzyl (*E*)-3-(3-nitrophenyl)acrylate (4ra): Compound **4ra** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2 to 90:10), obtaining a pink solid; yield: 99% (140 mg). R_f = 0.47 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (t, J = 1.9 Hz, 1H), 8.23 (ddd, J = 8.2, 2.2, 1.0 Hz, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.75 (d, J = 16.0 Hz, 1H), 7.58 (t, J = 8.0 Hz, 1H), 7.46 – 7.32 (m, 5H), 6.61 (d, J = 16.0 Hz, 1H), 5.28 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 148.8, 142.4, 136.2, 135.8, 133.7, 130.1, 128.8, 128.6, 128.5, 124.7, 122.6, 121.3, 66.9. ESI-MS: m/z = 301 $[M+NH_4]^+$. Spectral data were in agreement with previously reported literature data.[23]

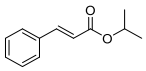


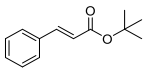
Benzyl (*E*)-3-(2-methoxyphenyl)acrylate (4sa): Compound **4sa** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 97:3), obtaining an orange oil; yield: 79% (106 mg). R_f = 0.32 (petroleum ether/EtOAc 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 16.1 Hz, 1H), 7.50 (dd, J = 7.7, 1.5 Hz, 1H), 7.45 – 7.30 (m, 6H), 6.96 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H), 6.59 (d, J = 16.1 Hz, 1H), 5.26 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 158.6, 140.8, 136.4, 131.7, 129.2, 128.7, 128.4, 128.3, 123.5, 120.8, 118.6, 111.3, 66.3, 55.6. ESI-MS: m/z = 269 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[24]

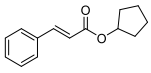
 **Isobutyl cinnamate (4ab):** Compound **4ab** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining a pale yellow oil; yield: 95% (97 mg). R_f = 0.45 (petroleum ether/EtOAc 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 16.0 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.43 – 7.35 (m, 3H), 6.46 (d, J = 16.0 Hz, 1H), 4.00 (d, J = 6.7 Hz, 2H), 2.02 (hept, J = 6.7 Hz, 1H), 0.99 (d, J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 144.7, 134.6, 130.4, 129.0, 128.2, 118.5, 70.8, 28.0, 19.3. ESI-MS: m/z = 205 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[19]

 **Dodecyl cinnamate (4ac):** Compound **4ac** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining a white solid; yield: 93% (147 mg). R_f = 0.61 (petroleum ether/EtOAc 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 16.0 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.43 – 7.35 (m, 3H), 6.44 (d, J = 16.0 Hz, 1H), 4.20 (t, J = 6.7 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.46 – 1.20 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 144.7, 134.7, 130.3, 129.0, 128.2, 118.5, 64.9, 32.1, 29.81, 29.79, 29.74, 29.69, 29.5, 29.4, 28.9, 26.1, 22.8, 14.3. ESI-MS: m/z = 317 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[25]

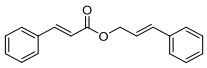
 **Methyl cinnamate (4ad):** Compound **4ad** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining a white solid; yield: 97% (79 mg). R_f = 0.38 (petroleum ether/EtOAc 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 16.0 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.42 – 7.36 (m, 3H), 6.45 (d, J = 16.0 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 145.0, 134.5, 130.4, 129.0, 128.2, 118.0, 51.9. ESI-MS: m/z = 163 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[26]

 **Isopropyl cinnamate (4ae):** Compound **4ae** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining a colorless oil; yield: 74% (70 mg). R_f = 0.52 (petroleum ether/EtOAc 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 16.0 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.42 – 7.35 (m, 3H), 6.42 (d, J = 16.0 Hz, 1H), 5.14 (hept, J = 6.3 Hz, 1H), 1.32 (d, J = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 144.4, 134.7, 130.3, 129.0, 128.2, 119.0, 67.9, 22.1. ESI-MS: m/z = 191 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[19]

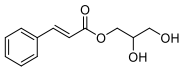
 ***tert*-Butyl cinnamate (4af):** Compound **4af** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining a colorless oil; yield: 53% (54 mg). R_f = 0.31 (petroleum ether/EtOAc 92:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 16.0 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.41 – 7.33 (m, 3H), 6.37 (d, J = 16.0 Hz, 1H), 1.54 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 143.7, 134.8, 130.1, 129.0, 128.1, 120.4, 80.7, 28.4. ESI-MS: m/z = 205 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[26]



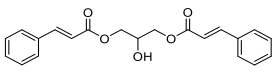
Cyclopentyl cinnamate (4ag): Compound **4ag** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining a pale pink oil; yield: 94% (102 mg). R_f = 0.45 (petroleum ether/EtOAc 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 16.0 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.42 – 7.34 (m, 3H), 6.42 (d, J = 16.0 Hz, 1H), 5.33 – 5.26 (m, 1H), 1.99 – 1.86 (m, 2H), 1.84 – 1.71 (m, 4H), 1.69 – 1.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 144.4, 134.7, 130.3, 129.0, 128.2, 119.0, 77. 3, 32.9, 24.0. ESI-MS: m/z = 217 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[27]



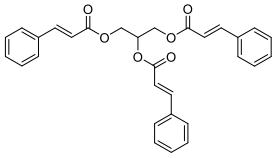
Cinnamyl cinnamate (4ah): Compound **4ah** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining an orange oil; yield: 84% (111 mg). R_f = 0.68 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 16.0 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.44 – 7.37 (m, 5H), 7.36 – 7.30 (m, 2H), 7.29 – 7.24 (m, 1H), 6.72 (d, J = 15.9 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 6.37 (dt, J = 15.9, 6.4 Hz, 1H), 4.88 (dd, J = 6.4, 1.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 145.3, 136.4, 134.6, 134.4, 130.5, 129.1, 128.8, 128.3, 128.2, 126.8, 123.5, 118.1, 65.3. ESI-MS: m/z = 265 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[28]



2,3-Dihydroxypropyl cinnamate (4ai$_1$): Compound **4ai$_1$** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 50:50 to 20:80), obtaining a yellow oil; yield: 72% (80 mg). R_f = 0.3 (petroleum ether/EtOAc 20:80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 16.0 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.45 – 7.35 (m, 3H), 6.47 (d, J = 16.0 Hz, 1H), 4.36 (dd, J = 11.7, 4.7 Hz, 1H), 4.30 (dd, J = 11.7, 6.1 Hz, 1H), 4.06 – 3.99 (m, 1H), 3.75 (dd, J = 11.5, 4.0 Hz, 1H), 3.66 (dd, J = 11.5, 5.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 146.1, 134.3, 130.8, 129.1, 128.3, 117. 3, 70.5, 65.6, 63.5. ESI-MS: m/z = 223 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[29]

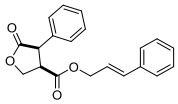


2-hydroxypropane-1,3-diyl (2*E*,2'*E*)-bis(3-phenylacrylate) (4ai$_2$): Compound **4ai$_2$** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 80:20 to 70:30), obtaining a pale yellow oil; yield: 95% (168 mg). R_f = 0.41 (petroleum ether/EtOAc 60:40). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 16.0 Hz, 2H), 7.56 – 7.49 (m, 4H), 7.43 – 7.34 (m, 6H), 6.49 (d, J = 16.0 Hz, 1H), 4.40 (dd, J = 11.6, 4.5 Hz, 2H), 4.35 (dd, J = 11.6, 5.6 Hz, 2H), 4.29 – 4.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 146.0, 134.3, 130.7, 129.1, 128.3, 117.4, 68.7, 65.6.E SI-MS: m/z = 375 $[M+Na]^+$.

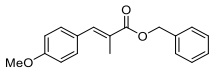


Propane-1,2,3-triyl (2*E*,2'*E*,2''*E*)-tris(3-phenylacrylate) (4ai$_3$): Compound **4ai$_3$** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 95:5 to 85:15), obtaining an off-white solid; yield: 44% (106 mg). R_f = 0.45 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 16.0 Hz, 1H), 7.72 (d, J = 16.0 Hz, 2H), 7.56 – 7.49 (m,

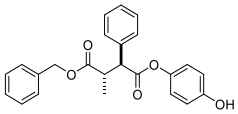
6H), 7.41 – 7.34 (m, 9H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 2H), 5.61 – 5.53 (m, 1H), 4.55 (dd, *J* = 12.0, 4.4 Hz, 2H), 4.48 (dd, *J* = 12.0, 5.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 166.2, 146.2, 145.9, 134.4 (2C), 130.7, 130.6, 129.1 (2C), 128.39, 128.36, 117.5, 117.4, 69.5, 62.8. ESI-MS: m/z = 483 $[M+H]^+$.



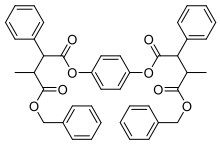
Cinnamyl (3*R,4*R**)-5-oxo-4-phenyltetrahydrofuran-3-carboxylate (6):** Compound **6** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 95:5 to 60:40), obtaining a white solid; yield: 72% (58 mg). R_f = 0.42 (petroleum ether/EtOAc 60:40). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 7H), 7.24 – 7.19 (m, 3H), 6.43 (d, *J* = 15.9 Hz, 1H), 5.80 (dt, *J* = 15.9, 6.8 Hz, 1H), 4.75 (dd, *J* = 9.6, 5.8 Hz, 1H), 4.53 (dd, *J* = 9.6, 7.5 Hz, 1H), 4.43 (ddd, *J* = 12.5, 6.9, 1.2 Hz, 1H), 4.37 (ddd, *J* = 12.5, 6.7, 1.2 Hz, 1H), 4.19 (d, *J* = 9.8 Hz, 1H), 3.82 (ddd, *J* = 9.8, 7.5, 5.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 169.4, 136.0, 135.2, 133.0, 129.1, 128.9, 128.7, 128.43, 128.41, 126.8, 122.0, 67.4, 66.0, 48.3, 46.9. ESI-MS: m/z = 323 $[M+H]^+$.



Benzyl (*E*)-3-(4-methoxyphenyl)-2-methylacrylate (4ta): Compound **4ta** (in a mixture **4ta**:**7** = 94:6) has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining a yellow oil; yield: 90% (127 mg). R_f = 0.56 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.45 – 7.30 (m, 7H), 6.95 – 6.90 (m, 2H), 5.26 (s, 2H), 3.84 (s, 3H), 2.16 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 159.9, 139.1, 136.6, 131.6, 128.7, 128.6, 128.23, 128.22, 126.2, 114.0, 66.7, 55.4, 14.3. ESI-MS: m/z = 283 $[M+H]^+$.

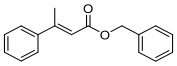


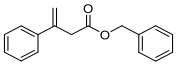
1-Benzyl 4-(4-hydroxyphenyl) (2*S,3*S**)-2-methyl-3-phenylsuccinate (5ua):** Compound **5ua** has been purified by flash column chromatography on silica gel (CH_2Cl_2/Et_2O 98:2 to 96:4), obtaining a pale yellow oil; yield: 51% (99 mg). R_f = 0.20 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.34 – 7.26 (m, 6H), 7.06 (dd, *J* = 4.4, 1.5 Hz, 2H), 6.85 – 6.78 (m, 2H), 6.78 – 6.71 (m, 2H), 4.92 (br s, 1H), 4.90 (s, 2H), 4.06 (d, *J* = 10.7 Hz, 1H), 3.39 (dq, *J* = 10.7, 6.8 Hz, 1H), 1.42 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 171.3, 153.5, 144.2, 136.3, 135.7, 128.9, 128.62, 128.59, 128.3, 128.2, 128.1, 122.4, 116.0, 66.6, 55.0, 43.9, 16.5. ESI-MS: m/z = 389 $[M-H]^-$. Spectral data were in agreement with previously reported literature data.[30]

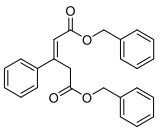


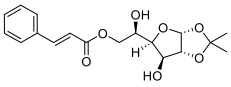
***O*'^{1},*O*^{1}-(1,4-phenylene) 4-dibenzyl bis(3-methyl-2-phenylsuccinate) (8):** Compound **8** has been purified by flash column chromatography on silica gel (CH_2Cl_2/Et_2O 100:0 to 99:1), obtaining an off-white solid; yield: 22% (37 mg). R_f = 0.40 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 4H), 7.33 – 7.26 (m, 12H), 7.08 – 7.03 (m, 4H), 6.91 (s, 4H), 4.89 (s, 4H), 4.05 (d, *J* = 10.6 Hz, 2H), 3.37 (dq, *J* = 10.6, 6.9 Hz, 2H), 1.40 (d, *J* = 6.9 Hz, 6H). ^{13}C

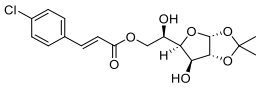
NMR (101 MHz, $CDCl_3$) δ 173.9, 170.7, 148.2, 136.1, 135.6, 128.9, 128.6 (2C), 128.3, 128.2 (2C), 122.3, 66.6, 54.9, 43.9, 16.5. ESI-MS: m/z = 671 $[M+H]^+$.

 **Benzyl (*E*)-3-phenylbut-2-enoate (4va):** Compound **4va** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 99:1 to 95:5), obtaining a colorless oil; yield: 15% (19 mg). R_f = 0.60 (petroleum ether/EtOAc 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.43 – 7.29 (m, 8H), 6.20 (q, J = 1.1 Hz, 1H), 5.22 (s, 2H), 2.60 (d, J = 1.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 156.4, 142.4, 136.6, 129.2, 128.72, 128.67, 128.4, 128.3, 126.5, 117.1, 65.9, 18.2. ESI-MS: m/z = 253 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[31]

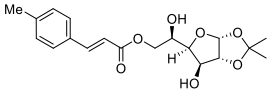
 **Benzyl 3-phenylbut-3-enoate (9):** Compound **9** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 99:1 to 95:5), obtaining a pale yellow oil; yield: 36% (46 mg). R_f = 0.48 (petroleum ether/EtOAc 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.34 – 7.24 (m, 6H), 7.24 – 7.20 (m, 2H), 5.53 (d, J = 0.7 Hz, 1H), 5.24 (dd, J = 1.0, 0.7 Hz, 1H), 5.10 (s, 2H), 3.57 (d, J = 1.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 141.1, 140.1, 136.0, 128.62, 128.55, 128.3, 128.2, 127.9, 126.1, 116.5, 66.7, 41.5. ESI-MS: m/z = 253 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[31]

 **Dibenzyl (*E*)-3-phenylpent-2-enedioate (10):** Compound **10** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 94:6 to 92:8), obtaining a pink oil; yield: 19% (37 mg). R_f = 0.60 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.40 – 7.28 (m, 11H), 7.27 – 7.22 (m, 2H), 6.35 (s, 1H), 5.18 (s, 2H), 5.10 (s, 2H), 4.27 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 166.2, 151.6, 140.6, 136.1, 135.9, 129.6, 128.9, 128.7, 128.6, 128.5, 128.4, 128.24, 128.19, 126.7, 119.9, 66.8, 66.3, 37.2. ESI-MS: m/z = 387 $[M+H]^+$.

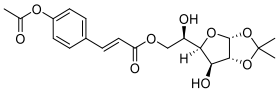
 (***R*)-2-hydroxy-2-((3a*R*,5*R*,6*S*,6a*R*)-6-hydroxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)ethyl cinnamate (4aj):** Compound **4aj** has been purified by flash column chromatography on silica gel (cyclohexane/EtOAc 70:30 to 50:50), obtaining a white solid; yield: 94% (164 mg). R_f = 0.29 (cyclohexane/EtOAc 50:50). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 – 7.67 (m, 2H), 7.68 (d, J = 16.0 Hz, 1H), 7.47 – 7.39 (m, 3H), 6.63 (d, J = 16.0 Hz, 1H), 5.82 (d, J = 3.7 Hz, 1H), 5.25 (d, J = 4.9 Hz, 1H), 5.09 (d, J = 5.9 Hz, 1H), 4.41 (d, J = 3.7 Hz, 1H), 4.35 (dd, J = 11.2, 2.0 Hz, 1H), 4.14 – 4.05 (m, 2H), 3.98 (m, 1H), 3.93 (dd, J = 8.8, 2.4 Hz, 1H), 1.39 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.2, 144.4, 134.0, 130.4, 129.0, 128.3, 118.2, 110.6, 104.5, 84.6, 80.3, 72.9, 66.9, 65.3, 26.7, 26.2. ESI-MS: m/z = 373 $[M+Na]^+$.



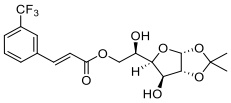
(*R*)-2-hydroxy-2-((3a*R*,5*R*,6*S*,6a*R*)-6-hydroxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)ethyl (*E*)-3-(4-chlorophenyl)acrylate (4bj): Compound **4bj** has been purified by flash column chromatography on silica gel (cyclohexane/ethyl acetate 70:30 to 50:50), obtaining a white solid; yield: 94% (180 mg). R_f = 0.27 (cyclohexane/ethyl acetate 50:50). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.80 – 7.71 (m, 2H), 7.67 (d, J = 16.0 Hz, 1H), 7.53 – 7.45 (m, 2H), 6.66 (d, J = 16.0 Hz, 1H), 5.81 (d, J = 3.6 Hz, 1H), 5.25 (d, J = 4.9 Hz, 1H), 5.08 (d, J = 5.9 Hz, 1H), 4.41 (d, J = 3.6 Hz, 1H), 4.35 (dd, J = 11.3, 2.2 Hz, 1H), 4.12 – 4.05 (m, 2H), 4.02 – 3.94 (m, 1H), 3.92 (dd, J = 8.7, 2.5 Hz, 1H), 1.38 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.2, 143.2, 135.1, 133.1, 130.1, 129.1, 119.1, 110.8, 104.6, 84.7, 80.4, 73.0, 67.1, 65.4, 26.8, 26.3. ESI-MS: m/z = 407 $[M+Na]^+$.



(*R*)-2-hydroxy-2-((3a*R*,5*R*,6*S*,6a*R*)-6-hydroxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)ethyl (*E*)-3-(*p*-tolyl)acrylate (4cj): Compound **4cj** has been purified by flash column chromatography on silica gel (cyclohexane/ EtOAc 70:30 to 50:50), obtaining a white solid; yield: 92% (167 mg). R_f = 0.31 (cyclohexane/ EtOAc 50:50). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.64 (d, J = 16.0 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.26 – 7.20 (m, 2H), 6.56 (d, J = 16.0 Hz, 1H), 5.82 (d, J = 3.7 Hz, 1H), 5.25 (d, J = 4.9 Hz, 1H), 5.08 (d, J = 5.9 Hz, 1H), 4.41 (d, J = 3.7 Hz, 1H), 4.34 (dd, J = 11.3, 2.0 Hz, 1H), 4.11 – 4.03 (m, 2H), 4.03 – 3.93 (m, 1H), 3.92 (dd, J = 8.7, 2.4 Hz, 1H), 2.33 (s, 3H), 1.38 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.3, 144.4, 140.4, 131.3, 129.6, 128.3, 117.1, 110.6, 104.5, 84.6, 80.3, 72.9, 66.8, 65.3, 26.7, 26.2, 21.0. ESI-MS: m/z = 387 $[M+Na]^+$.

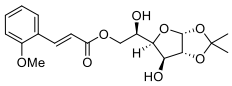


(*R*)-2-hydroxy-2-((3a*R*,5*R*,6*S*,6a*R*)-6-hydroxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)ethyl (*E*)-3-(4-acetoxyphenyl)acrylate (4nj): Compound **4nj** has been purified by flash column chromatography on silica gel (cyclohexane/ EtOAc 50:50), obtaining a white solid; yield: 90% (184 mg). R_f = 0.25 (cyclohexane/ EtOAc 40:60). ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR δ 7.73 (d, J = 16.0 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.16 – 7.11 (m, 2H), 6.43 (d, J = 16.0 Hz, 1H), 5.98 (d, J = 3.6 Hz, 1H), 4.62 – 4.54 (m, 2H), 4.43 – 4.36 (m, 2H), 4.31 (td, J = 6.3, 2.8 Hz, 1H), 4.14 (dd, J = 6.3, 2.8 Hz, 1H), 2.31 (s, 3H), 1.50 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 167.6, 152.5, 145.1, 132.0, 129.5, 122.4, 117.4, 112.0, 105.2, 85.4, 79.5, 75.9, 69.9, 66.5, 27.0, 26.3, 21.3. ESI-MS: m/z = 431 $[M+Na]^+$.

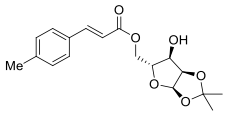


(*R*)-2-hydroxy-2-((3a*R*,5*R*,6*S*,6a*R*)-6-hydroxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)ethyl (*E*)-3-(3-(trifluoromethyl)phenyl)acrylate (4oj): Compound **4oj** has been purified by flash column chromatography on silica gel (cyclohexane/ EtOAc 70:30 to 50:50), obtaining a white solid; yield: 82% (171 mg). R_f = 0.33 (cyclohexane/ EtOAc 50:50). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.09 (s, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.78 (d, J = 16.0 Hz, 1H), 7.66 (t, J = 7.9 Hz, 1H), 6.83 (d, J = 16.0 Hz, 1H), 5.82 (d, J = 3.6 Hz, 1H),

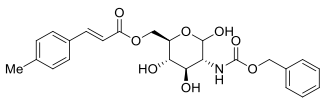
5.26 (d, *J* = 5.0 Hz, 1H), 5.08 (d, *J* = 5.9 Hz, 1H), 4.41 (d, *J* = 3.6 Hz, 1H), 4.36 (dd, *J* = 11.3, 2.0 Hz, 1H), 4.13 – 4.05 (m, 2H), 4.02 – 3.95 (m, 1H), 3.93 (dd, *J* = 8.8, 2.4 Hz, 1H), 1.38 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.9, 142.7, 135.2, 131.8, 130.0, 129.8 (q, *J* = 31.9 Hz), 126.6 (d, *J* = 3.7 Hz), 125.0 (d, *J* = 3.8 Hz), 124.0 (q, *J* = 272.4 Hz), 120.4, 110.6, 104.5, 84.6, 80.3, 72.9, 67.1, 65.3, 26.7, 26.2. ESI-MS: m/z = 441 $[M+Na]^+$.



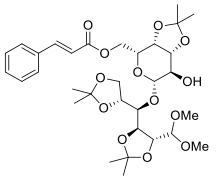
(*R*)-2-hydroxy-2-((3a*R*,5*R*,6*S*,6a*R*)-6-hydroxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)ethyl (*E*)-3-(2-methoxyphenyl)acrylate (4sj): Compound **4sj** has been purified by flash column chromatography on silica gel (cyclohexane/ EtOAc 70:30 to 50:50), obtaining a white solid; yield: 41% (78 mg). R_f = 0.24 (cyclohexane/ EtOAc 50:50). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.89 (d, *J* = 16.2 Hz, 1H), 7.69 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.42 (ddd, *J* = 8.7, 7.7, 1.6 Hz, 1H), 7.10 (dd, *J* = 8.7, 1.0 Hz, 1H), 6.99 (td, *J* = 7.7, 1.0 Hz, 1H), 6.61 (d, *J* = 16.2 Hz, 1H), 5.81 (d, *J* = 3.6 Hz, 1H), 5.24 (d, *J* = 5.0 Hz, 1H), 5.08 (d, *J* = 5.8 Hz, 1H), 4.40 (d, *J* = 3.6 Hz, 1H), 4.35 (dd, *J* = 11.3, 2.0 Hz, 1H), 4.10 – 4.01 (m, 2H), 4.01 – 3.93 (m, 1H), 3.92 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.87 (s, 3H), 1.39 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.5, 157.9, 139.2, 132.0, 128.8, 122.3, 120.7, 118.3, 111.8, 110.6, 104.5, 84.6, 80.3, 72.9, 66.8, 65.3, 55.6, 26.7, 26.2. ESI-MS: m/z = 403 $[M+Na]^+$.



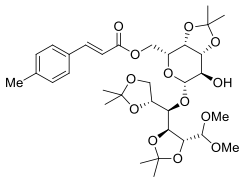
((3a*R*,5*R*,6*R*,6a*R*)-6-hydroxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)methyl (*E*)-3-(*p*-tolyl)acrylate (4ck): Compound **4ck** has been purified by flash column chromatography on silica gel (cyclohexane/EtOAc 70:30), obtaining a white solid; yield: 84% (140 mg). R_f = 0.30 (cyclohexane/ EtOAc 70:30). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.67 – 7.62 (m, 2H), 7.63 (d, *J* = 16.1 Hz, 1H), 7.27 – 7.18 (m, 2H), 6.61 (d, *J* = 16.1 Hz, 1H), 5.70 (d, *J* = 3.6 Hz, 1H), 5.29 (d, *J* = 7.0 Hz, 1H), 4.50 (t, *J* = 4.1 Hz, 1H), 4.43 (dd, *J* = 12.3, 2.1 Hz, 1H), 4.12 (dd, *J* = 12.3, 6.3 Hz, 1H), 3.96 (ddd, *J* = 8.6, 6.3, 2.1 Hz, 1H), 3.78 (ddd, *J* = 8.6, 7.0, 4.5 Hz, 1H), 2.33 (s, 3H), 1.45 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.2, 144.9, 140.6, 131.3, 129.6, 128.5, 116.7, 111.5, 103.5, 78.8, 77.0, 71.3, 63.3, 26.6, 26.3, 21.1. ESI-MS: m/z = 357 $[M+Na]^+$.



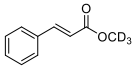
((2*R*,3*S*,4*R*,5*R*)-5-(((benzyloxy)carbonyl)amino)-3,4,6-trihydroxytetrahydro-2*H*-pyran-2-yl)methyl (*E*)-3-(*p*-tolyl)acrylate (4cl): Compound **4cl** has been purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH 95:5), obtaining an off white solid; yield: 39% (89 mg). α/β ratio 0.85:0.15. R_f = 0.19 (CH_2Cl_2/MeOH 95:5). ^{1}H NMR (400 MHz, CD_3OD) data for the α-anomer δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.40 – 7.26 (m, 5H), 7.25 – 7.19 (m, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 5.13 (d, *J* = 3.4 Hz, 1H), 5.09 (s, 2H), 4.48 (dd, *J* = 12.0, 2.2 Hz, 1H), 4.35 (dd, *J* = 12.0, 5.4 Hz, 1H), 4.05 (ddd, *J* = 9.4, 5.4, 2.2 Hz, 1H), 3.74 – 3.64 (m, 1H), 3.61 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.43 (t, *J* = 9.4, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CD_3OD) data for the α-anomer δ 168.8, 158.8, 146.5, 142.2, 138.3, 133.0, 130.7, 129.4, 129.3, 129.0, 128.9, 117.6, 93.0, 72.8, 72.5, 70.9, 67.6, 65.0, 57.6, 21.5. ESI-MS: m/z = 480 $[M+Na]^+$.



((3a*S*,4*R*,6*S*,7*R*,7a*R*)-6-((*R*)-((4*S*,5*R*)-5-(dimethoxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)-7-hydroxy-2,2-dimethyltetrahydro-4*H*-[1,3]dioxolo[4,5-*c*]pyran-4-yl)methyl cinnamate (4am): Compound **4am** has been purified by flash column chromatography on silica gel (cyclohexane/EtOAc 70:30), obtaining a colorless oil; yield: 56% (179 mg). R_f = 0.26 (cyclohexane/EtOAc 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 16.0 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.48 – 7.35 (m, 3H), 6.48 (d, J = 16.0 Hz, 1H), 4.54 – 4.48 (m, 2H), 4.47 – 4.42 (m, 2H), 4.42 – 4.37 (m, 1H), 4.29 (td, J = 6.7, 2.3 Hz, 1H), 4.19 – 4.13 (m, 2H), 4.13 – 4.08 (m, 2H), 4.07 – 3.99 (m, 2H), 3.91 (dd, J = 7.7, 1.6 Hz, 1H), 3.59 (t, J = 7.7 Hz, 1H), 3.41 (s, 3H), 3.40 (s, 3H), 1.53 (s, 3H), 1.50 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 145.5, 134.3, 130.5, 128.9, 128.1, 117.6, 110.4, 110.2, 108.3, 105.1, 103.8, 79.0, 77.9, 76.6, 75.1, 74.3, 73.4, 71.6, 64.7, 63.5, 56.2, 53.3, 29.7, 28.1, 27.2, 26.4, 26.3, 25.7, 24.6. ESI-MS: m/z = 656 $[M+NH_4]^+$.

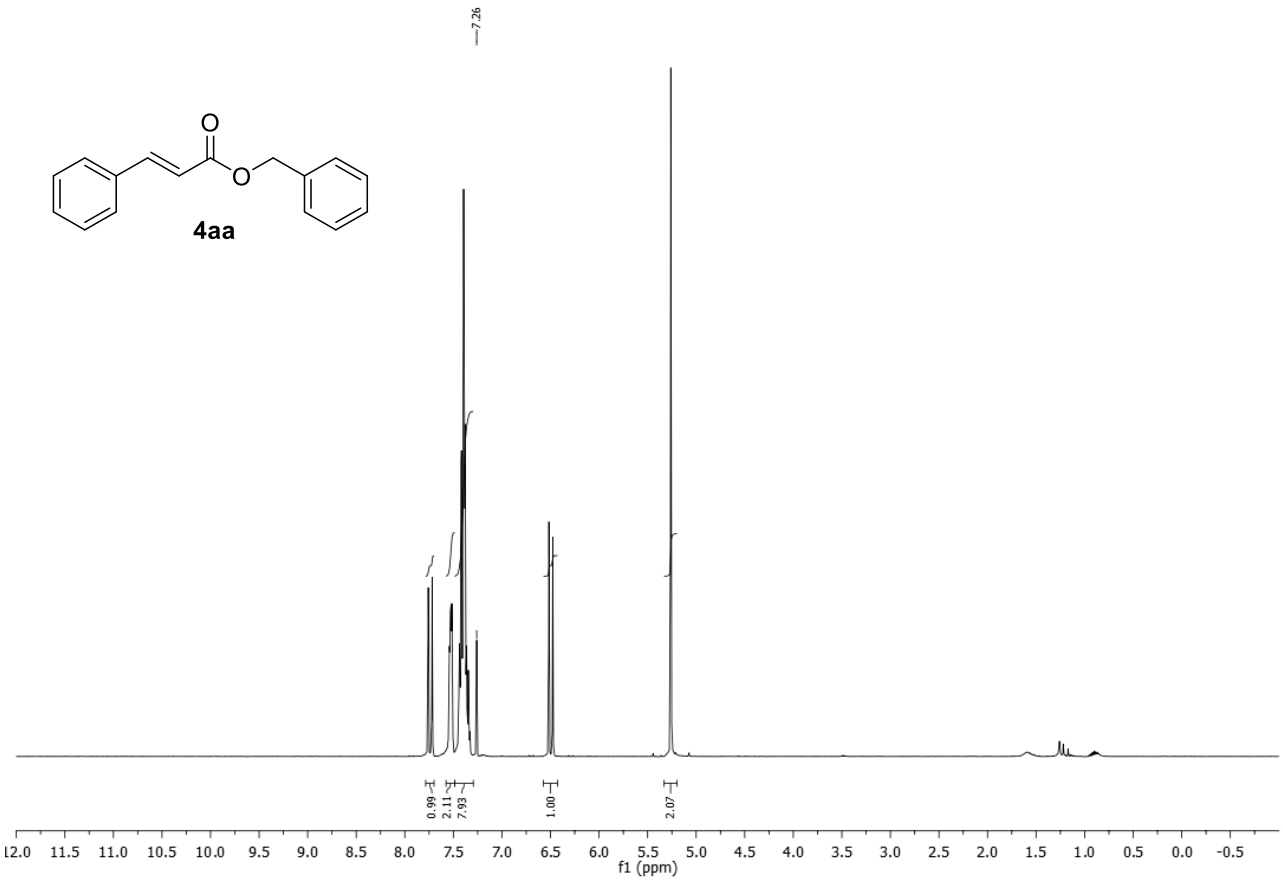


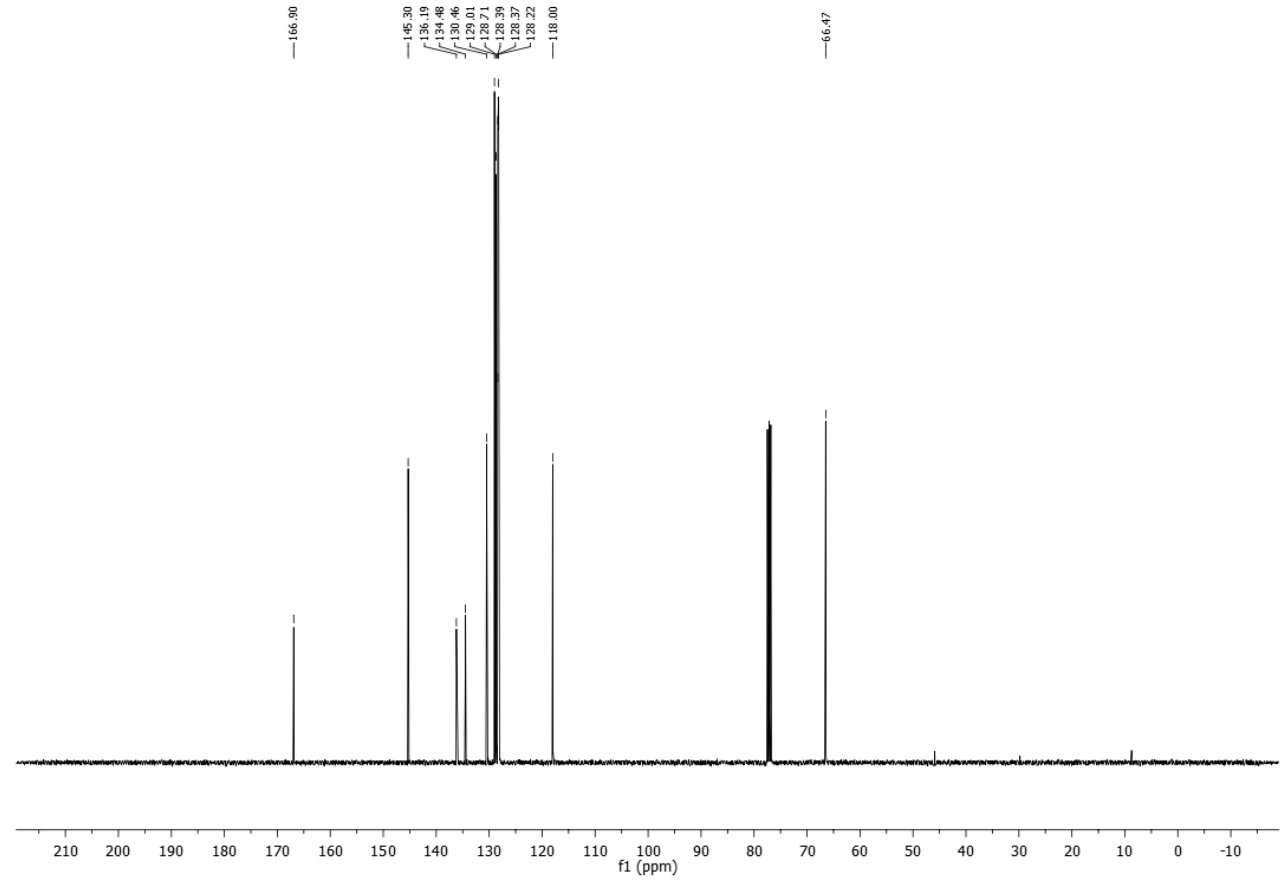
((3a*S*,4*R*,6*S*,7*R*,7a*R*)-6-((*R*)-((4*S*,5*R*)-5-(dimethoxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)-7-hydroxy-2,2-dimethyltetrahydro-4*H*-[1,3]dioxolo[4,5-*c*]pyran-4-yl)methyl (*E*)-3-(*p*-tolyl)acrylate (4cm): Compound **4cm** has been purified by flash column chromatography on silica gel (cyclohexane/ethyl acetate 70:30), obtaining a colorless oil; yield: 45% (147 mg). R_f = 0.24 (cyclohexane/ethyl acetate 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 16.0 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.23 – 7.17 (m, 2H), 6.42 (d, J = 16.0 Hz, 1H), 4.53 – 4.47 (m, 2H), 4.46 – 4.36 (m, 3H), 4.28 (td, J = 6.8, 2.4 Hz, 1H), 4.20 – 4.13 (m, 2H), 4.13 – 4.07 (m, 2H), 4.06 – 3.98 (m, 2H), 3.91 (dd, J = 7.7, 1.6 Hz, 1H), 3.58 (t, J = 7.7 Hz, 1H), 3.40 (s, 3H), 3.39 (s, 3H), 2.37 (s, 3H), 1.52 (s, 3H), 1.49 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 145.5, 141.1, 131.7, 129.8, 128.3, 116.6, 110.5, 110.3, 108.4, 105.2, 103.9, 79.2, 78.0, 76.7, 75.2, 74.4, 73.5, 71.8, 64.8, 63.7, 56.4, 53.4, 28.3, 27.4, 26.5, 26.4, 25.8, 24.7, 21.6. ESI-MS: m/z = 670 $[M+NH_4]^+$.

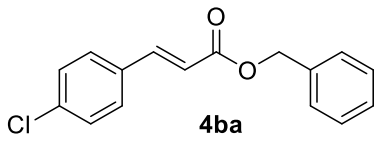


Methyl-d_3 cinnamate (4ad-*d*): Compound **4ad-*d*** has been purified by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2), obtaining a yellow solid; yield: 85% (36 mg). R_f = 0.77 (petroleum ether/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 16.0 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.43 – 7.35 (m, 3H), 6.45 (d, J = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 145.0, 134.5, 130.4, 129.0, 128.2, 118.0. ESI-MS: m/z = 166 $[M+H]^+$. Spectral data were in agreement with previously reported literature data.[32]

12.Copies of ^{1}H NMR and ^{13}C NMR Spectra

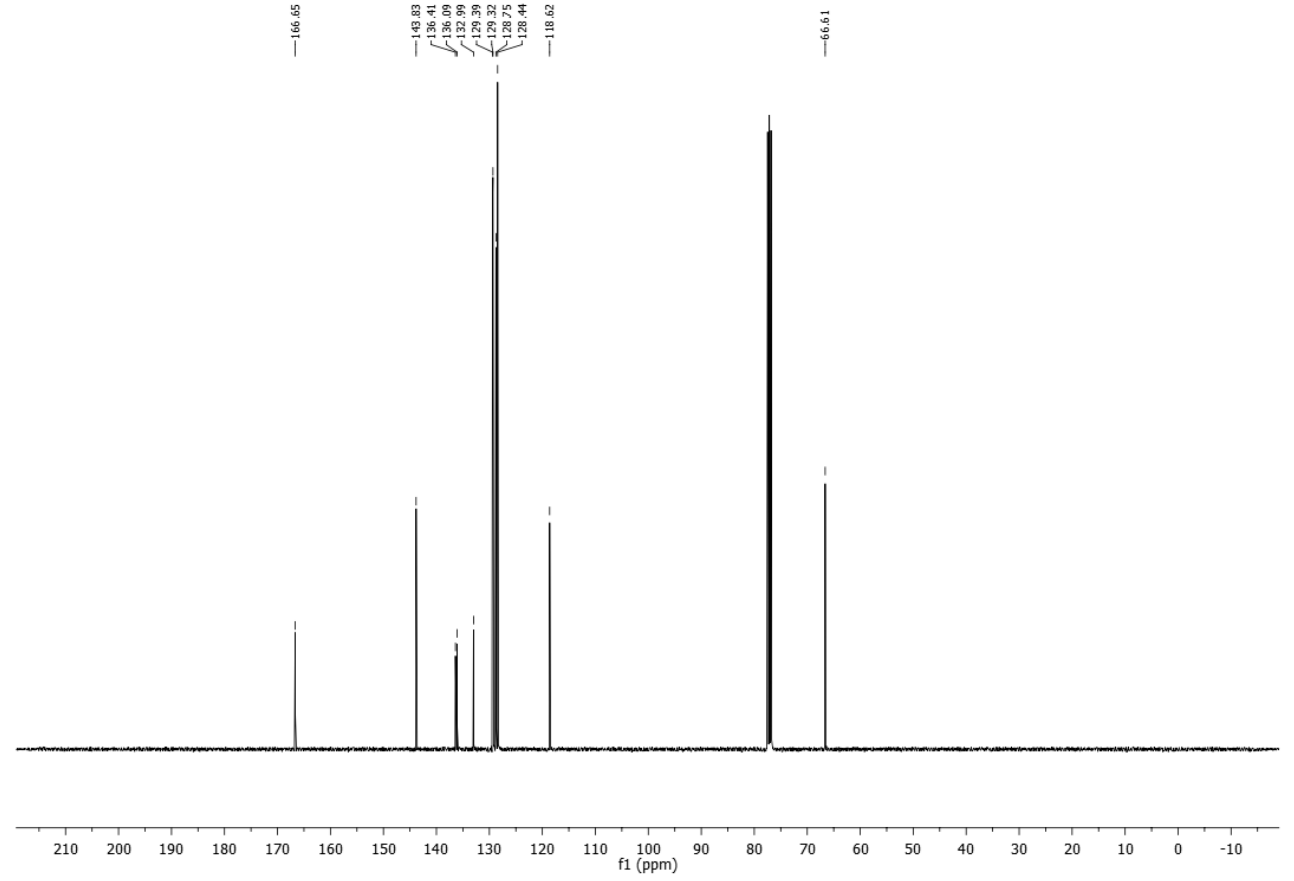


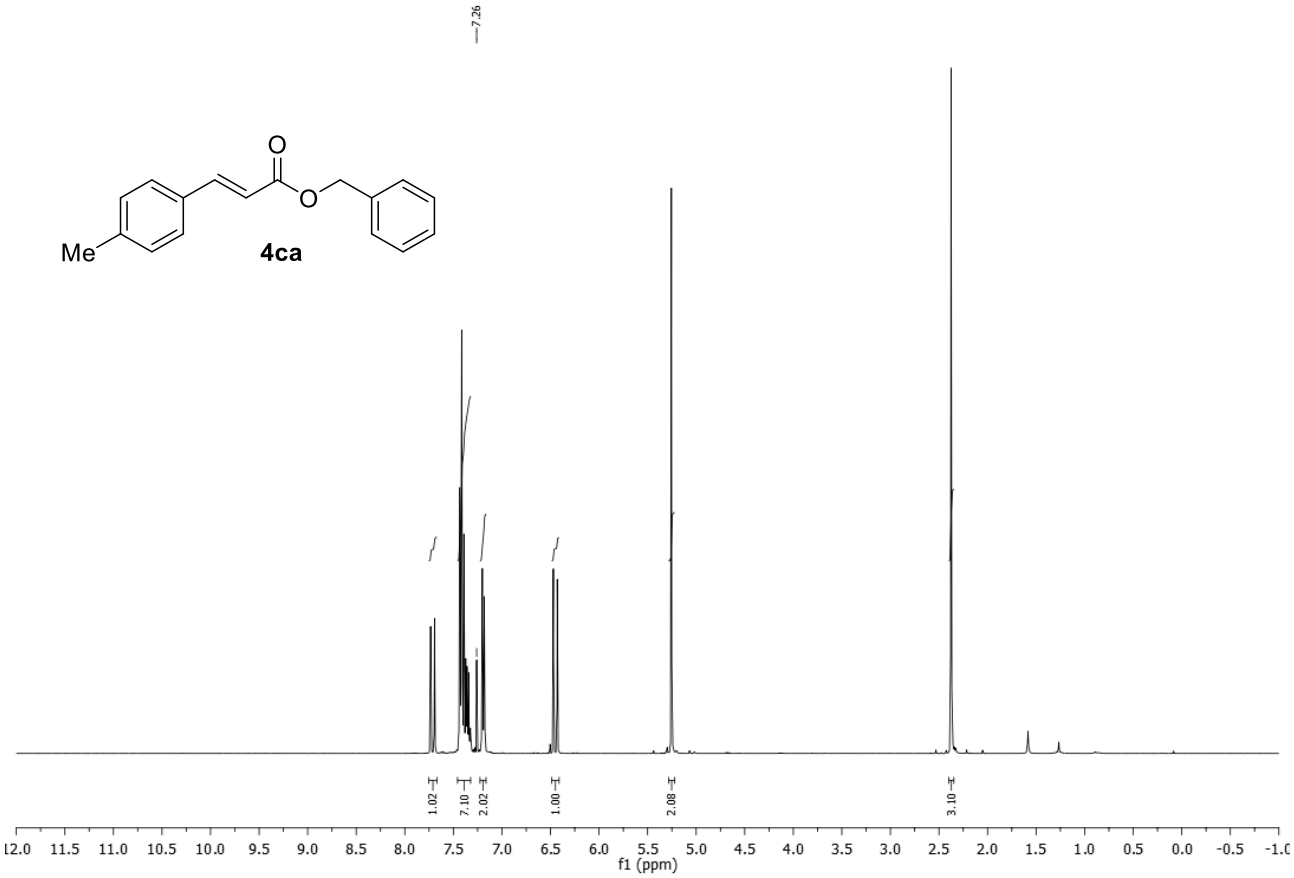


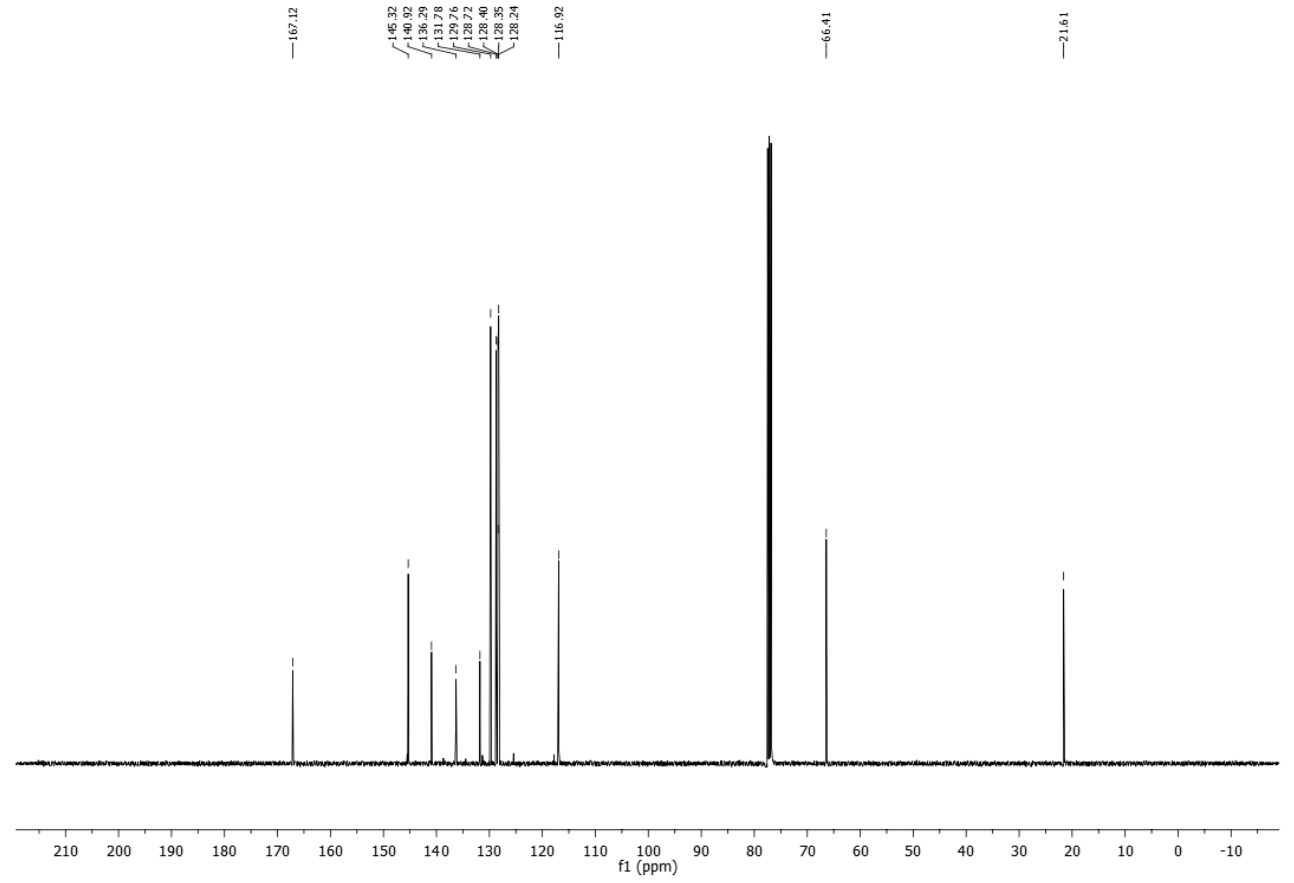

O
O
Cl

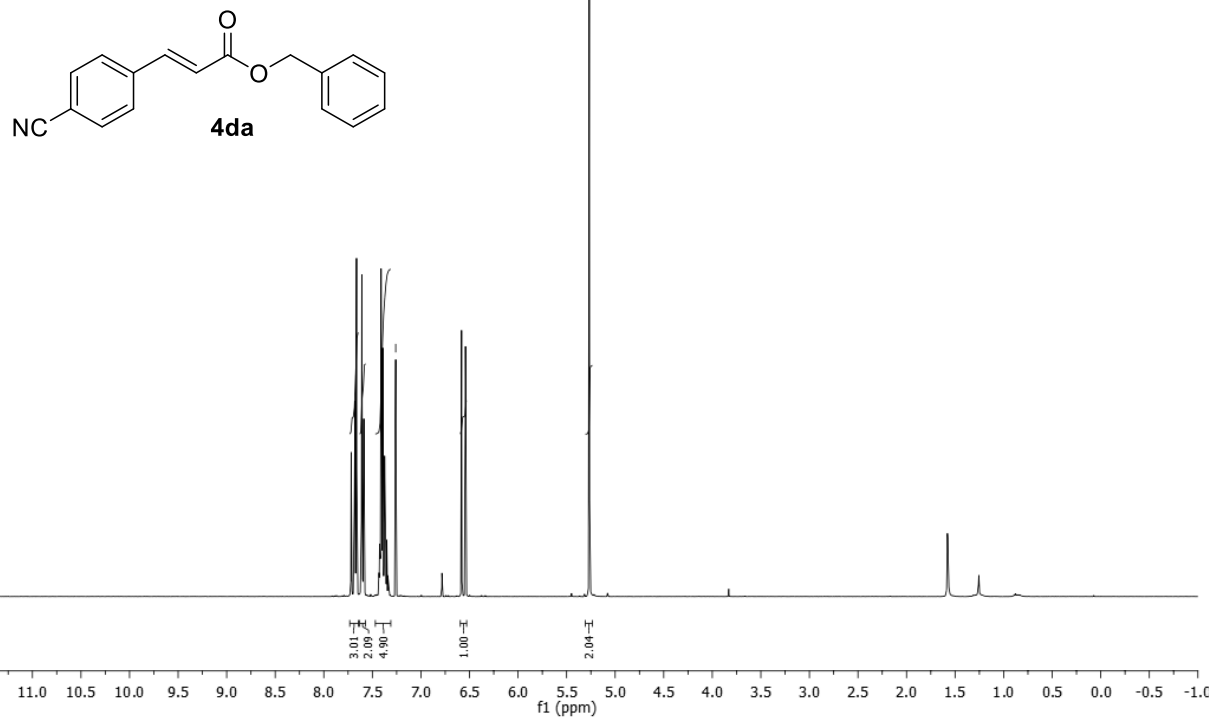
4ba

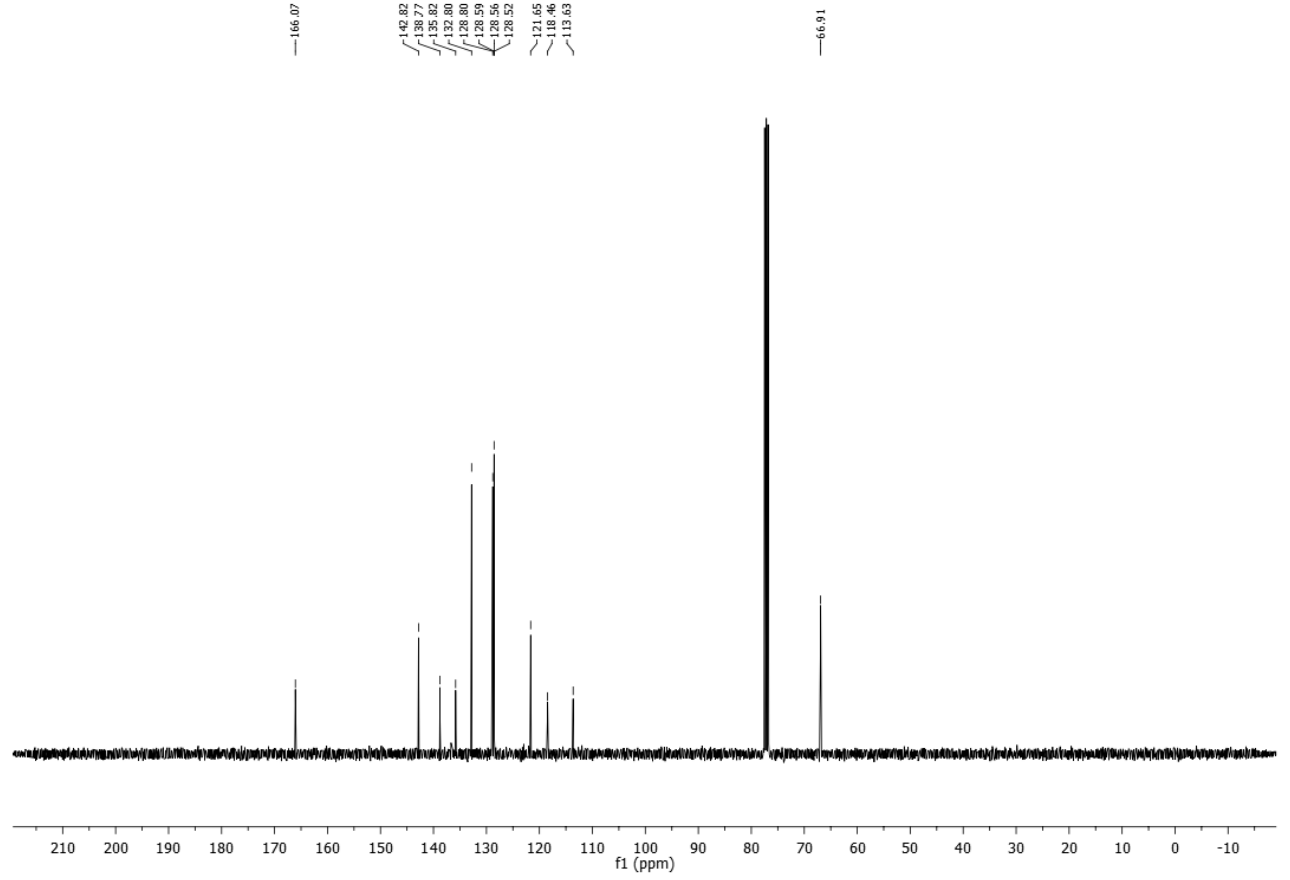
7.26
1.00
8.96
1.00
2.04
f1 (ppm)

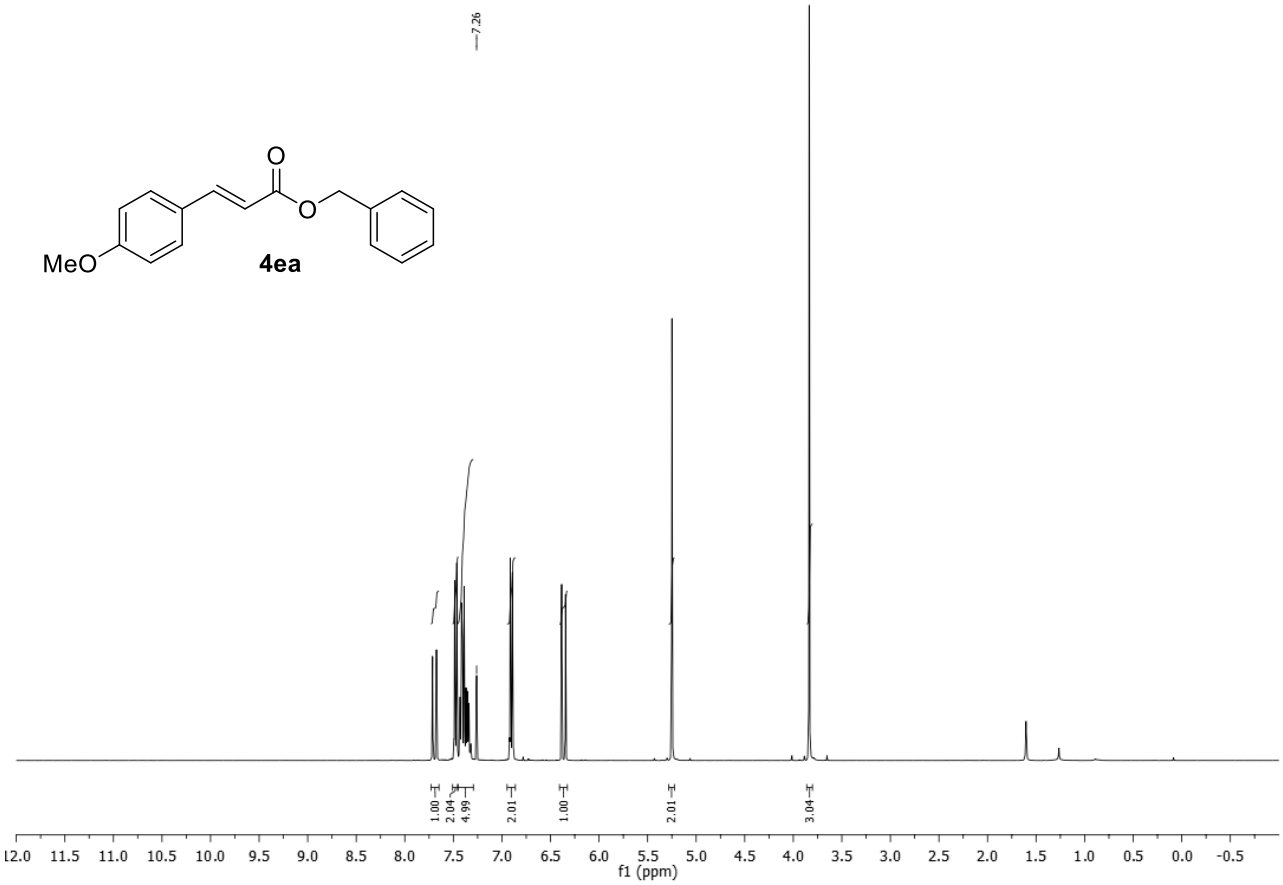

166.65
143.83
136.41
136.09
132.99
129.39
129.32
128.75
128.44
118.62
66.61
f1 (ppm)

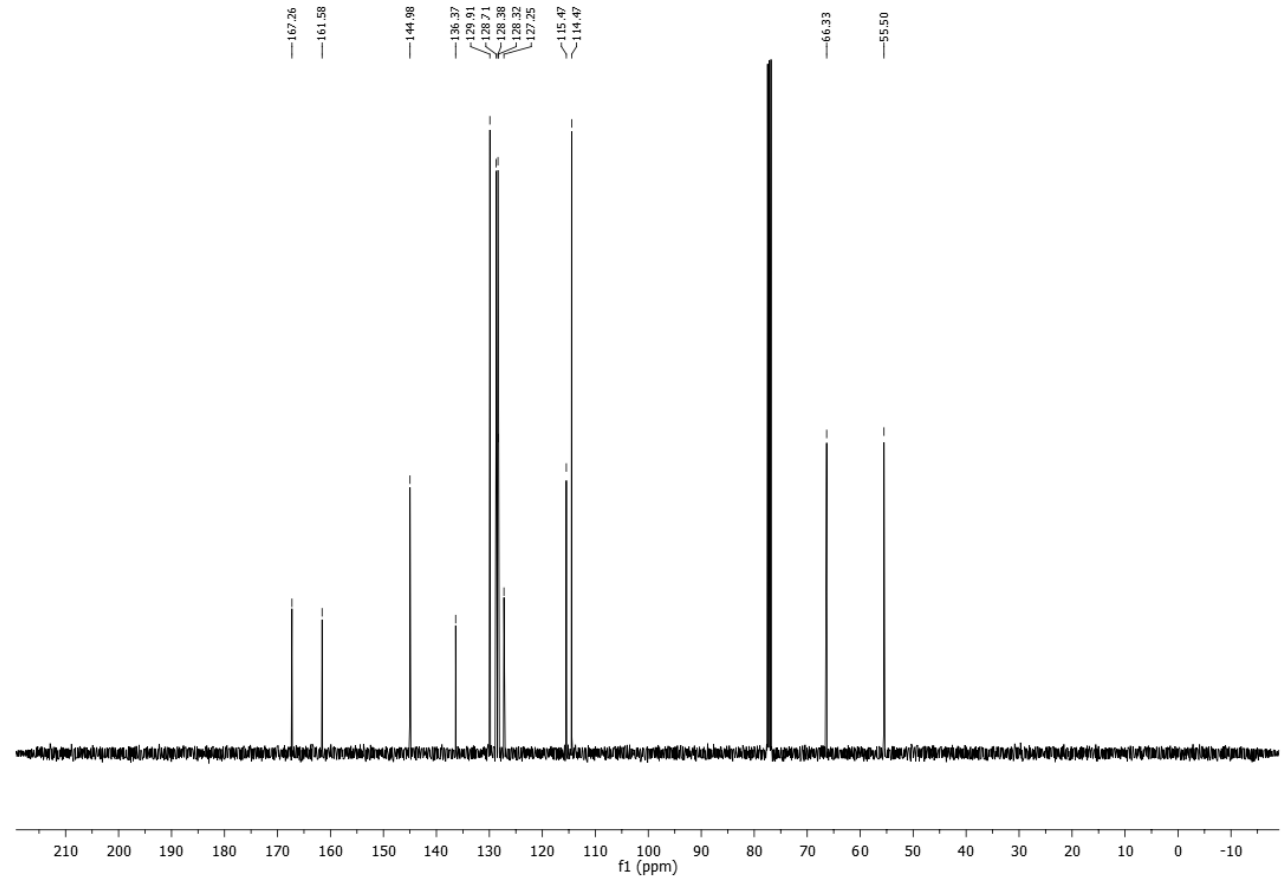

7.26
O
O
Me
4ca
1.02
7.10
2.02
1.00
2.08
3.10
f1 (ppm)

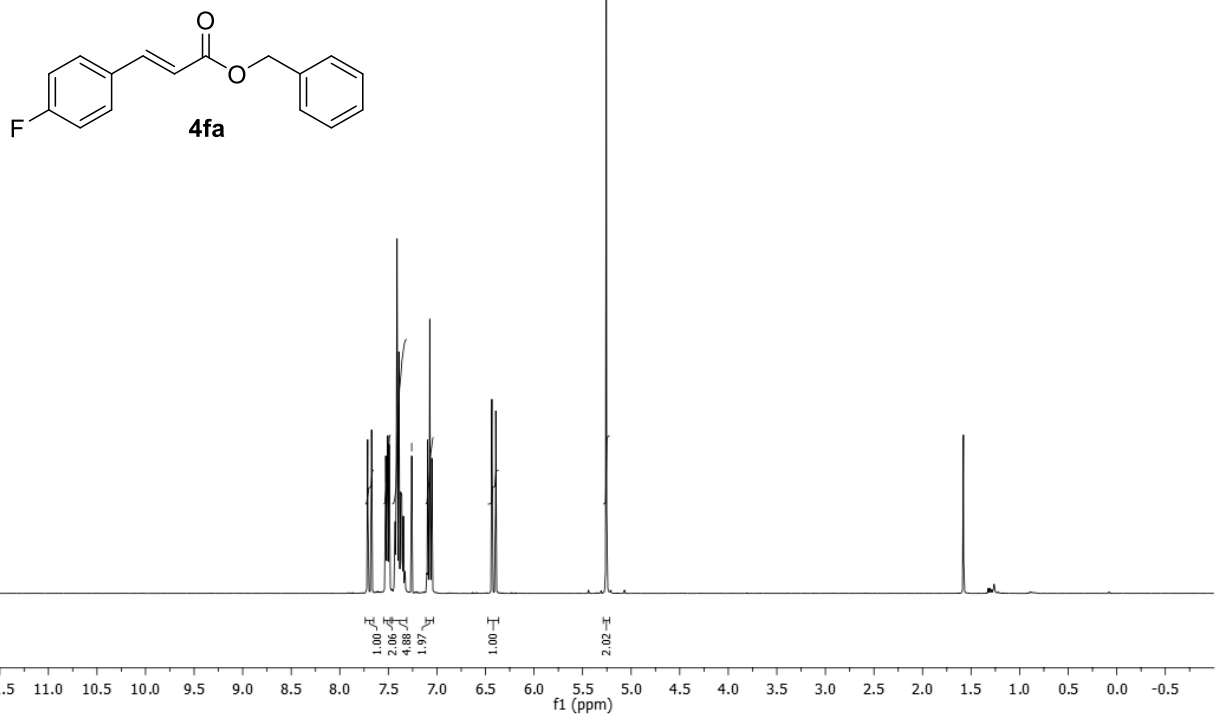

167.12
145.32
140.92
136.29
131.78
129.76
128.72
128.40
128.35
128.24
116.92
66.41
21.61
f1 (ppm)

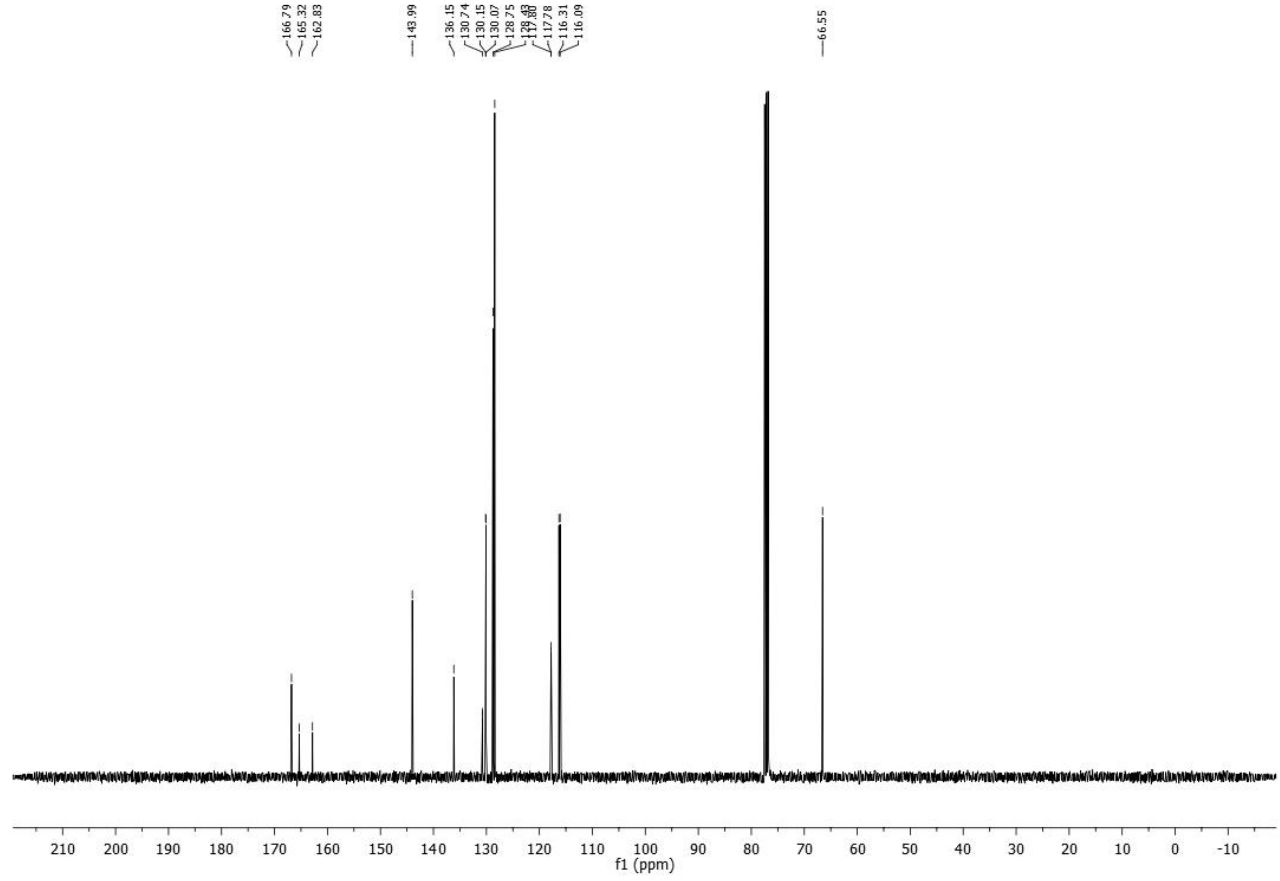

7.26
O
O
NC
4da
3.01
2.09
4.90
1.00
2.04
f1 (ppm)

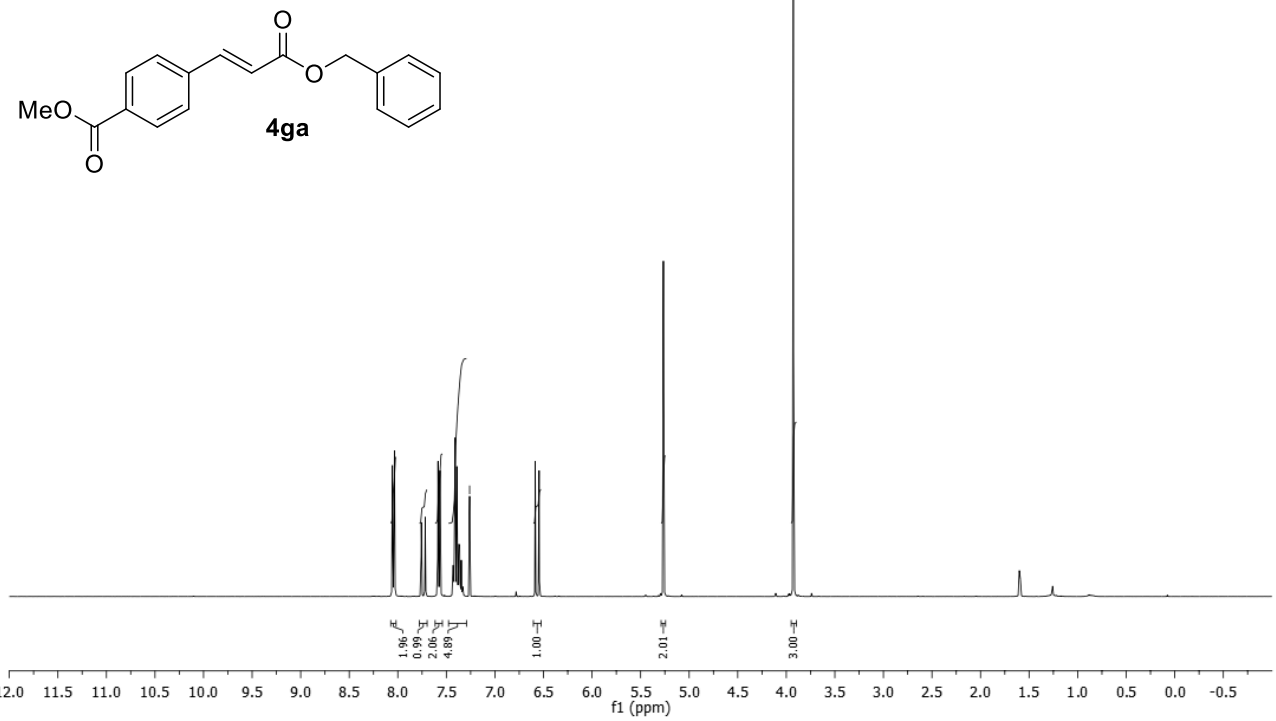

166.07
142.82
138.77
135.82
132.80
128.80
128.59
128.56
128.52
121.65
118.46
113.63
66.91
f1 (ppm)

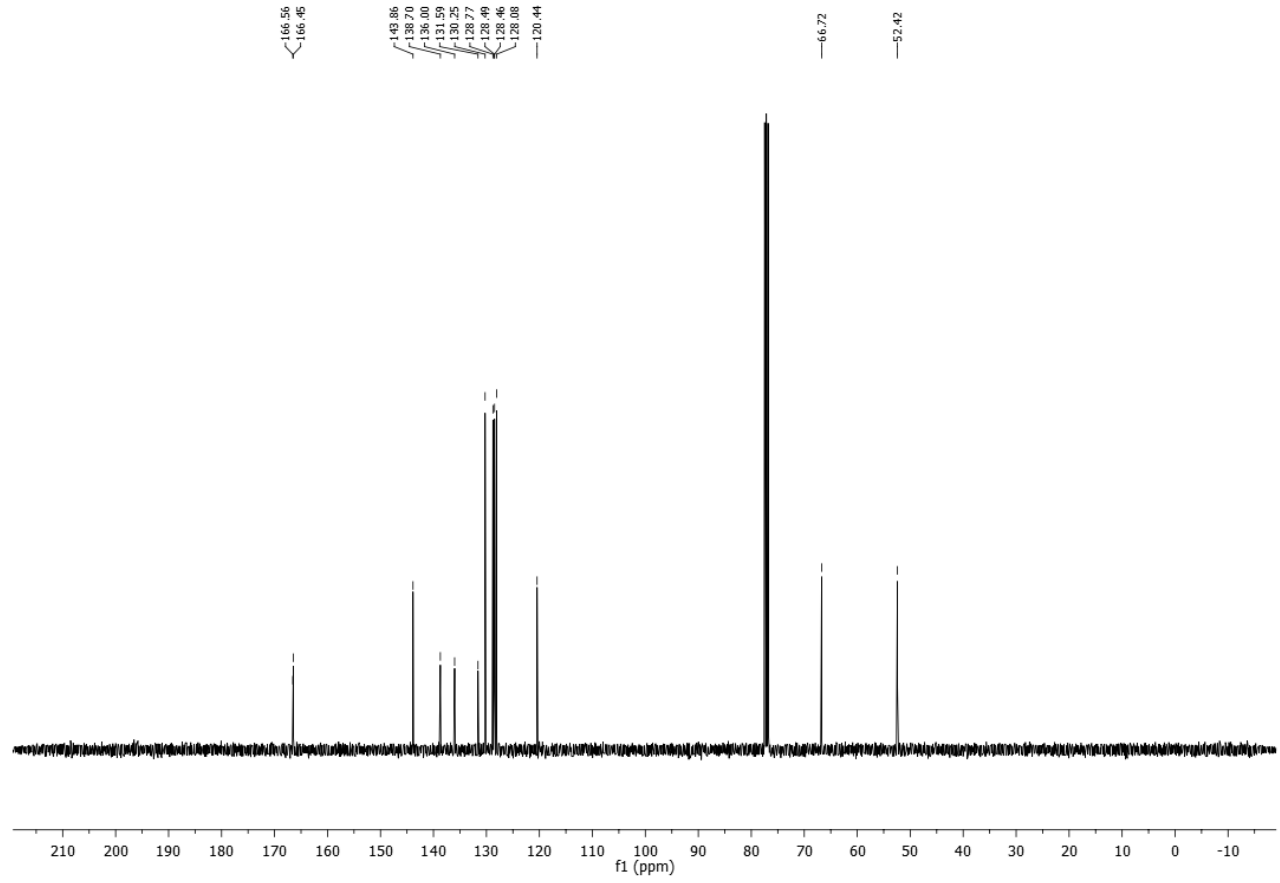

7.26
MeO
4ea
1.00
2.04
4.99
2.01
1.00
2.01
3.04
f1 (ppm)

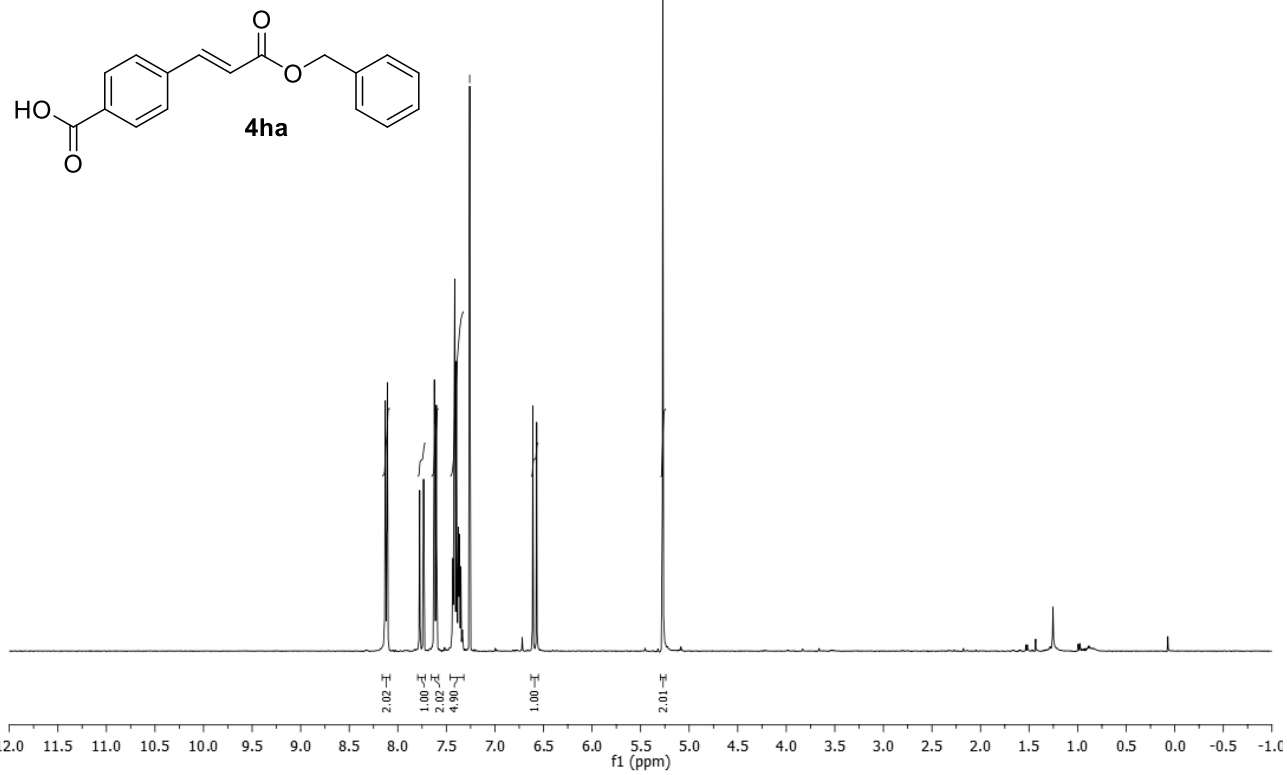

167.26
161.58
144.98
136.37
129.91
128.71
128.38
128.32
127.25
115.47
114.47
66.33
55.50
f1 (ppm)

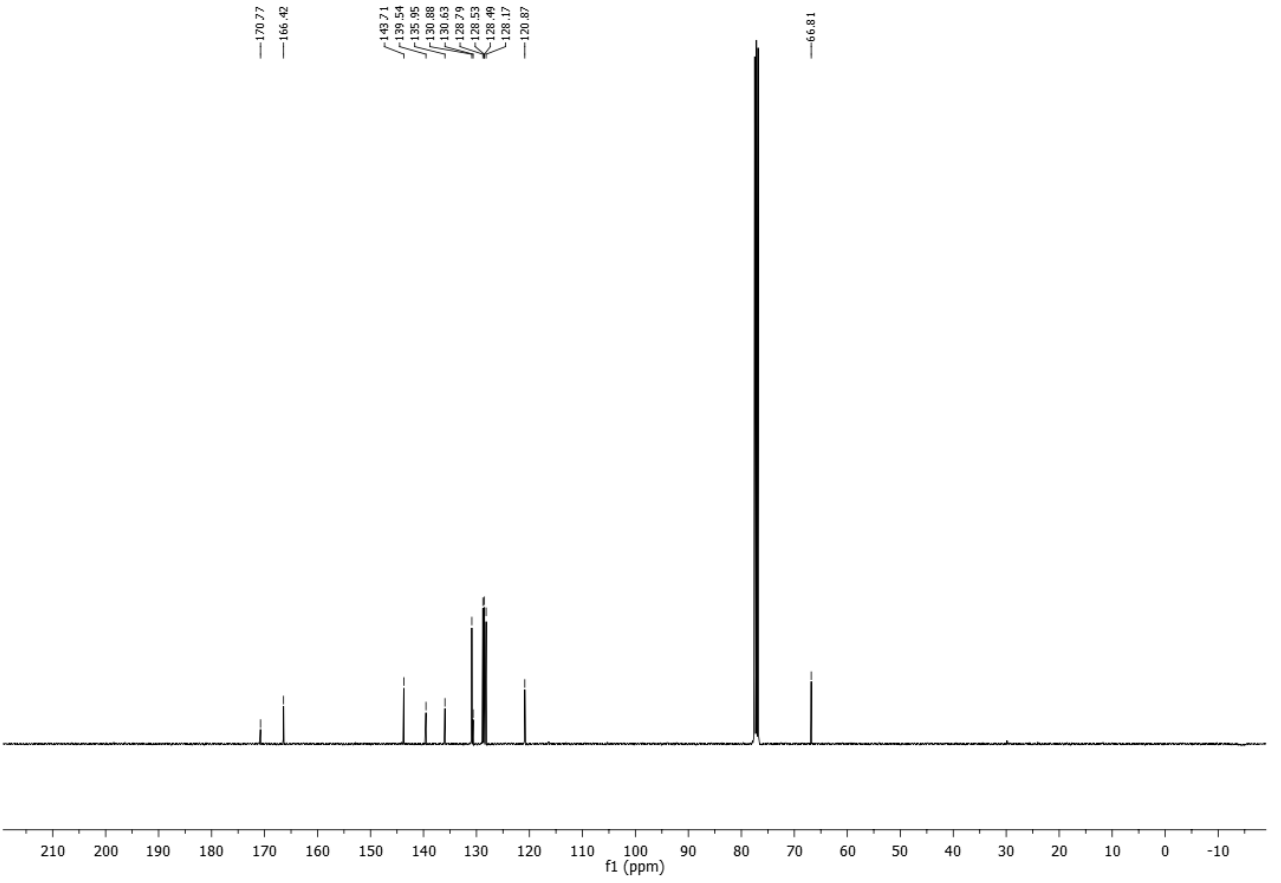

7.26
O
O
F
4fa
1.00
2.06
4.88
1.97
1.00
2.02
f1 (ppm)

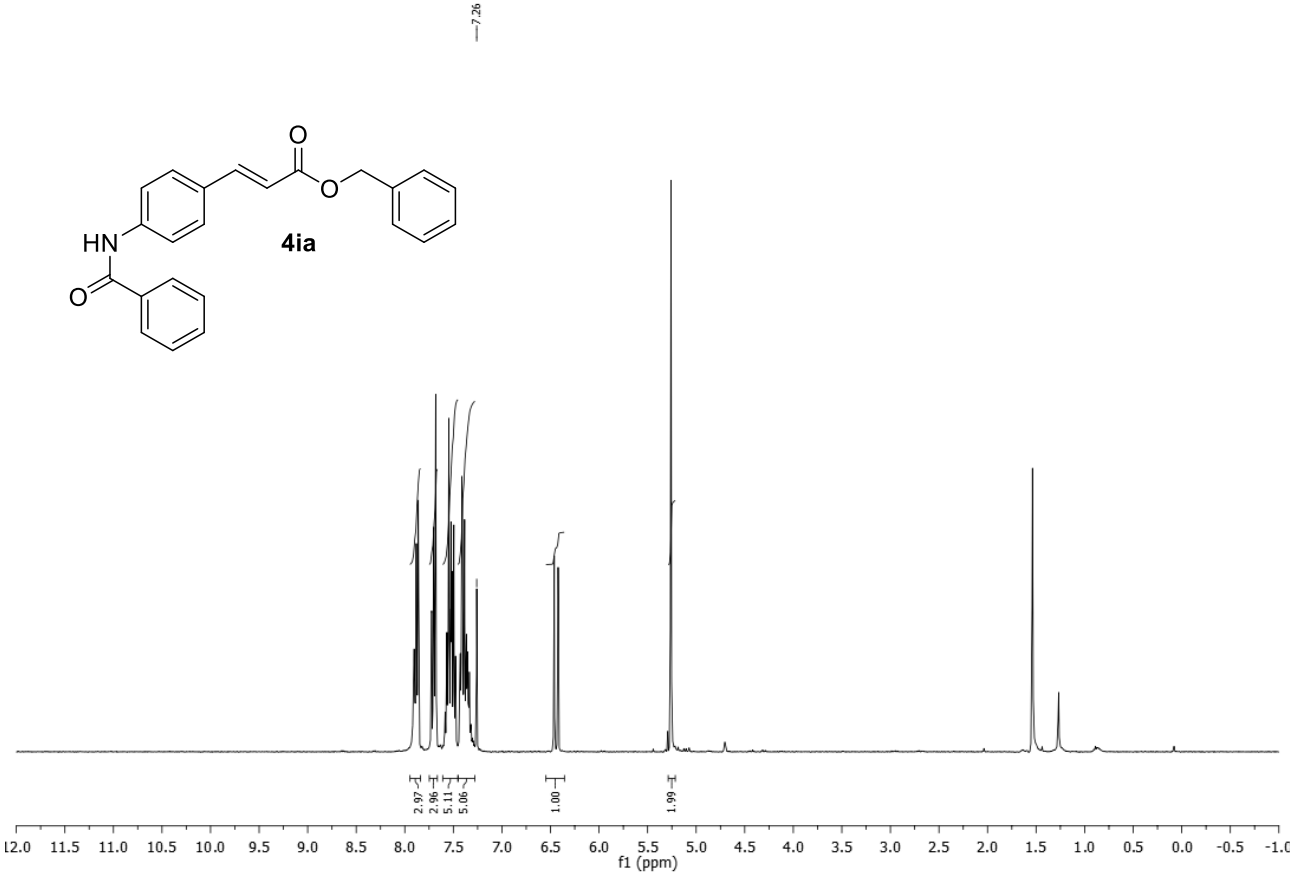

166.79
165.32
162.83
143.99
136.15
130.74
130.15
130.07
128.75
117.78
116.31
116.09
66.55
f1 (ppm)

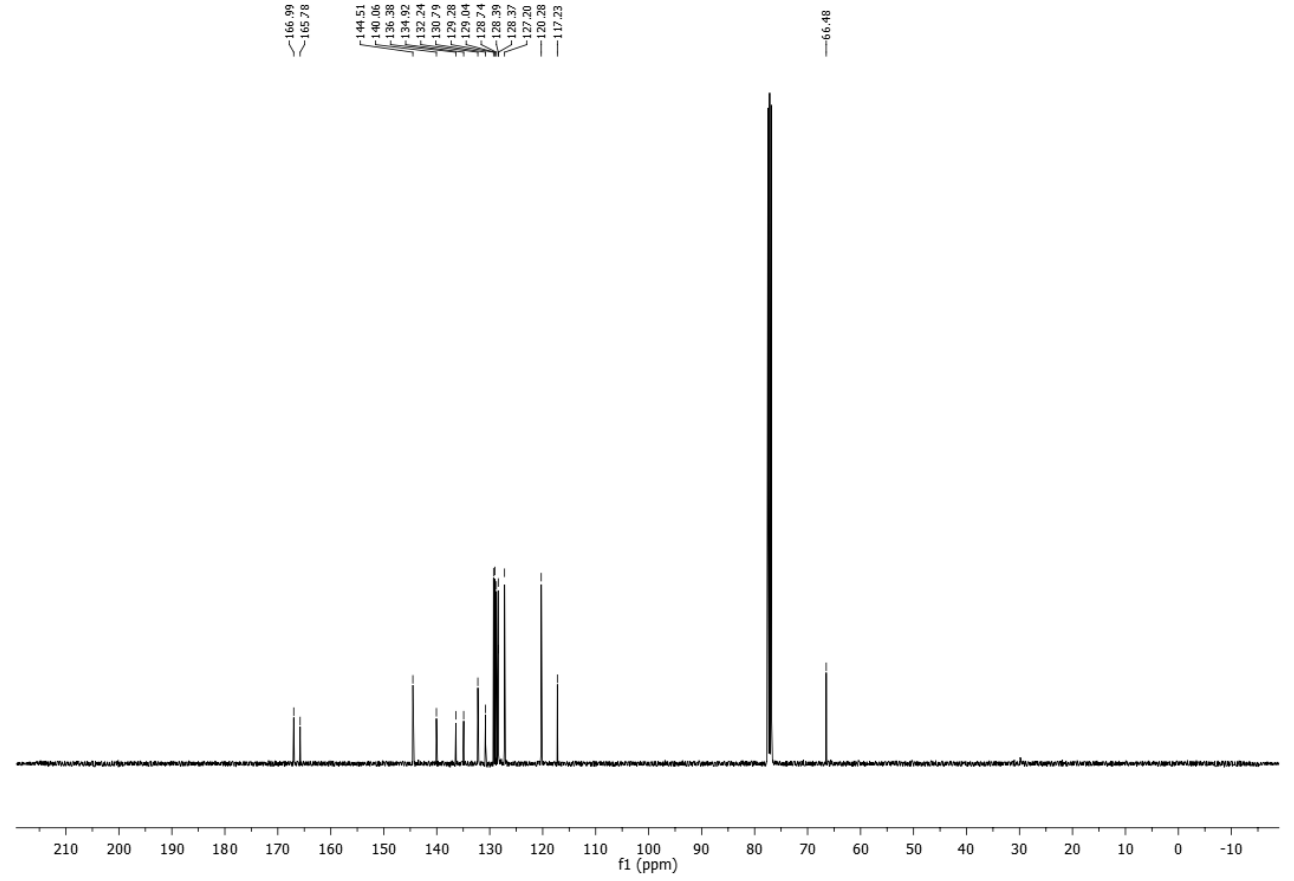

MeO
O
O
O
4ga
7.26
1.96
0.99
2.06
4.89
1.00
2.01
3.00
f1 (ppm)

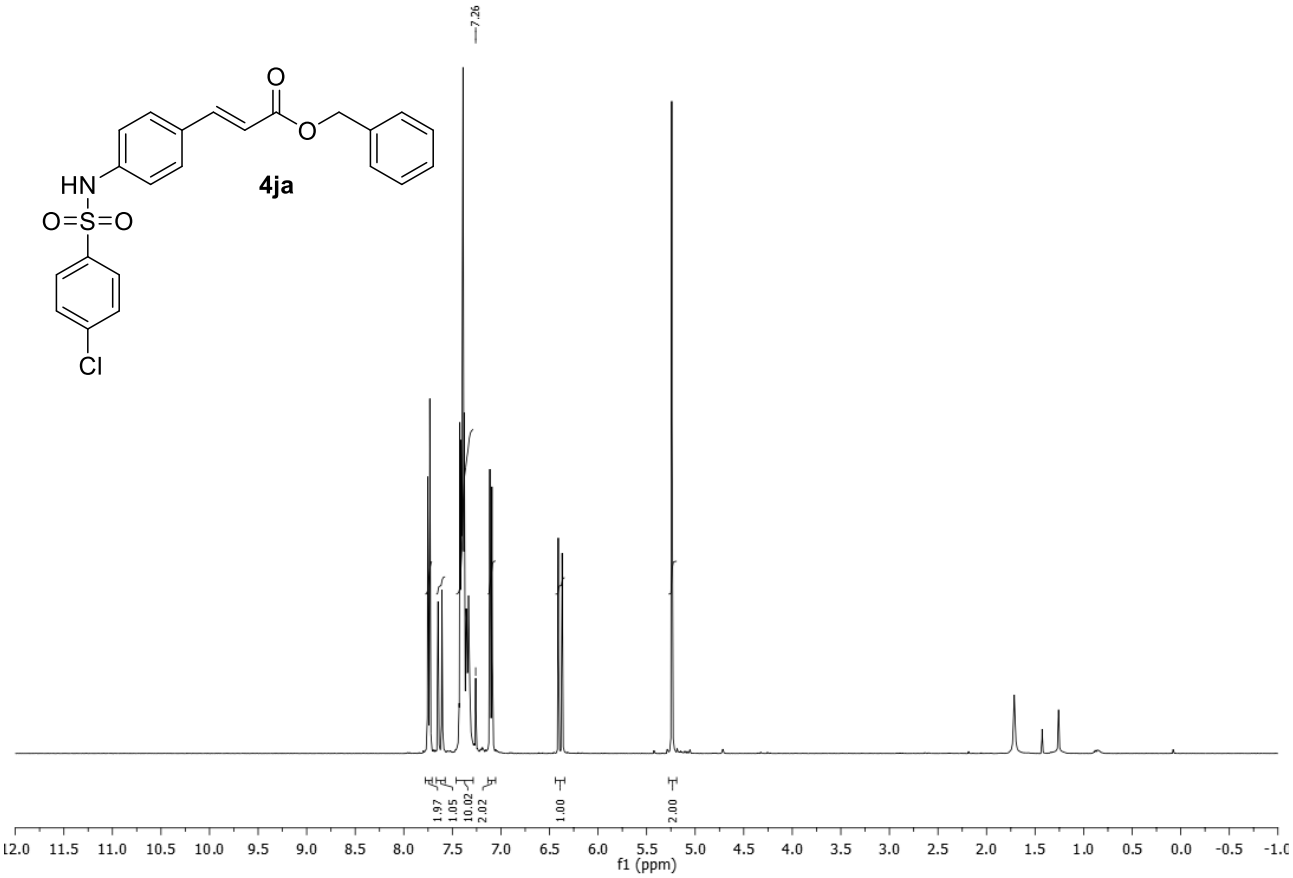

166.56
166.45
143.86
138.70
136.00
131.59
130.25
128.77
128.49
128.46
128.08
120.44
66.72
52.42
f1 (ppm)

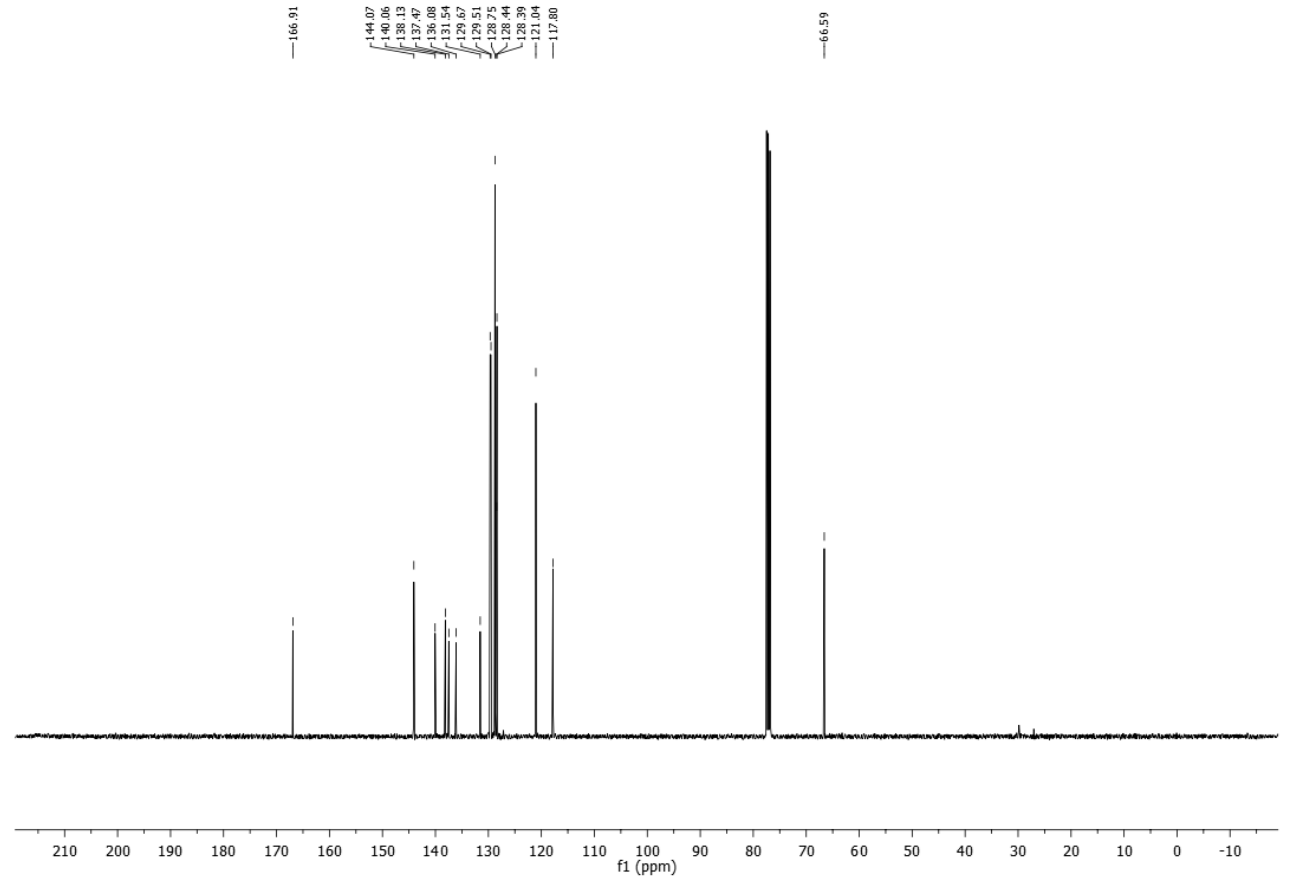

HO
O
O
O
4ha
7.26
2.02
1.00
2.02
4.90
1.00
2.01
f1 (ppm)

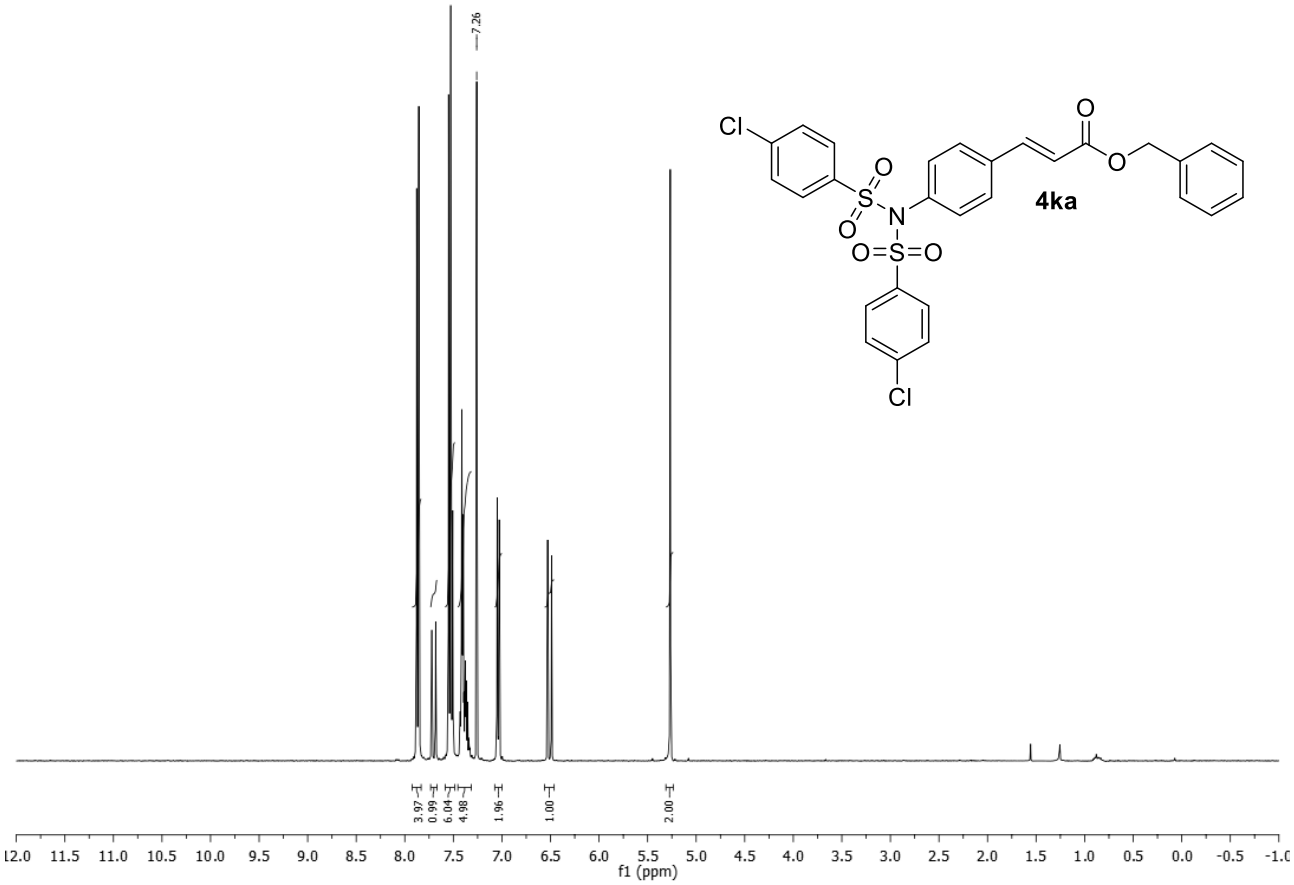

170.77
166.42
143.71
139.54
135.95
130.88
130.63
128.79
128.53
128.49
128.17
120.87
66.81
f1 (ppm)

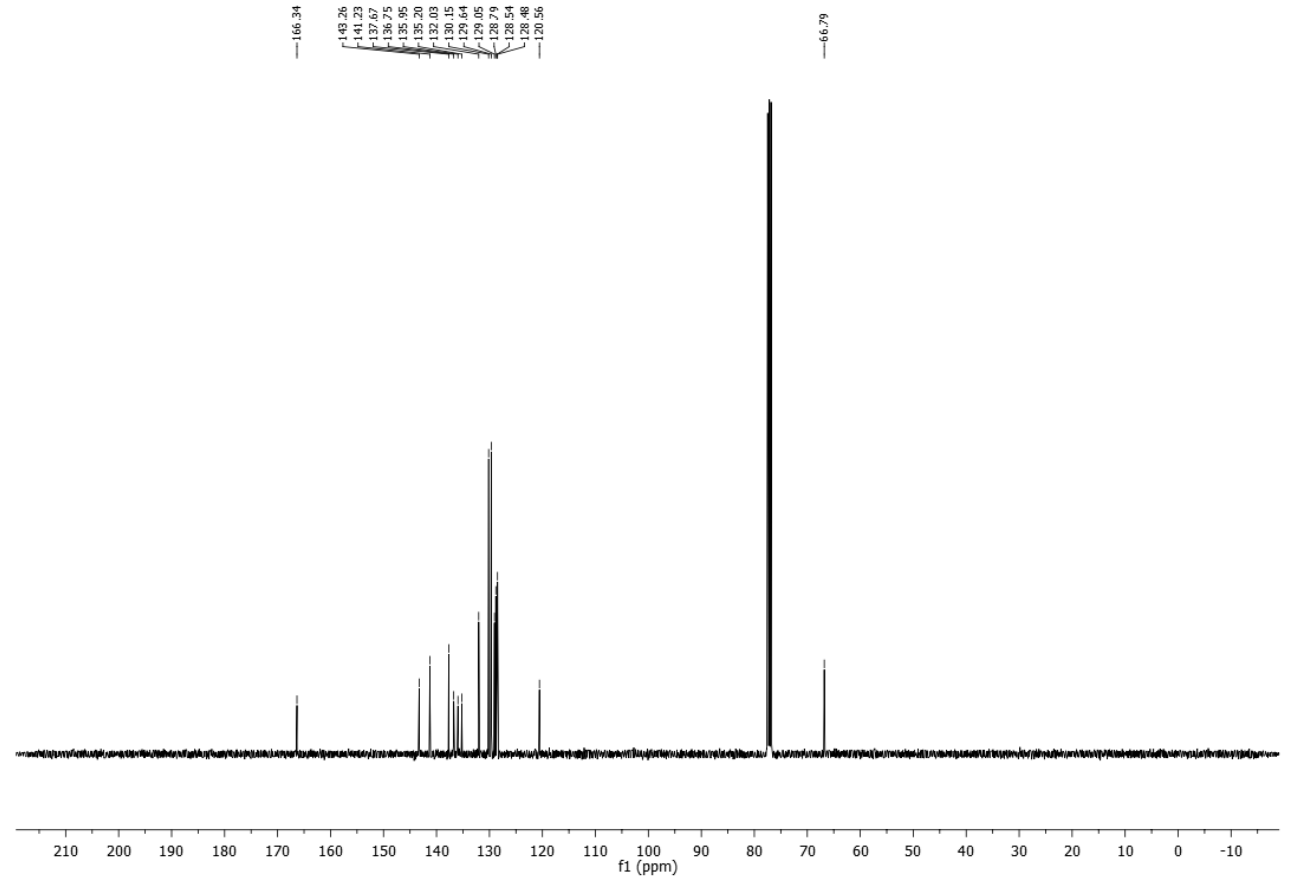

7.26
O
O
HN
O
4ia
2.97
2.96
5.11
5.06
1.00
1.99
f1 (ppm)

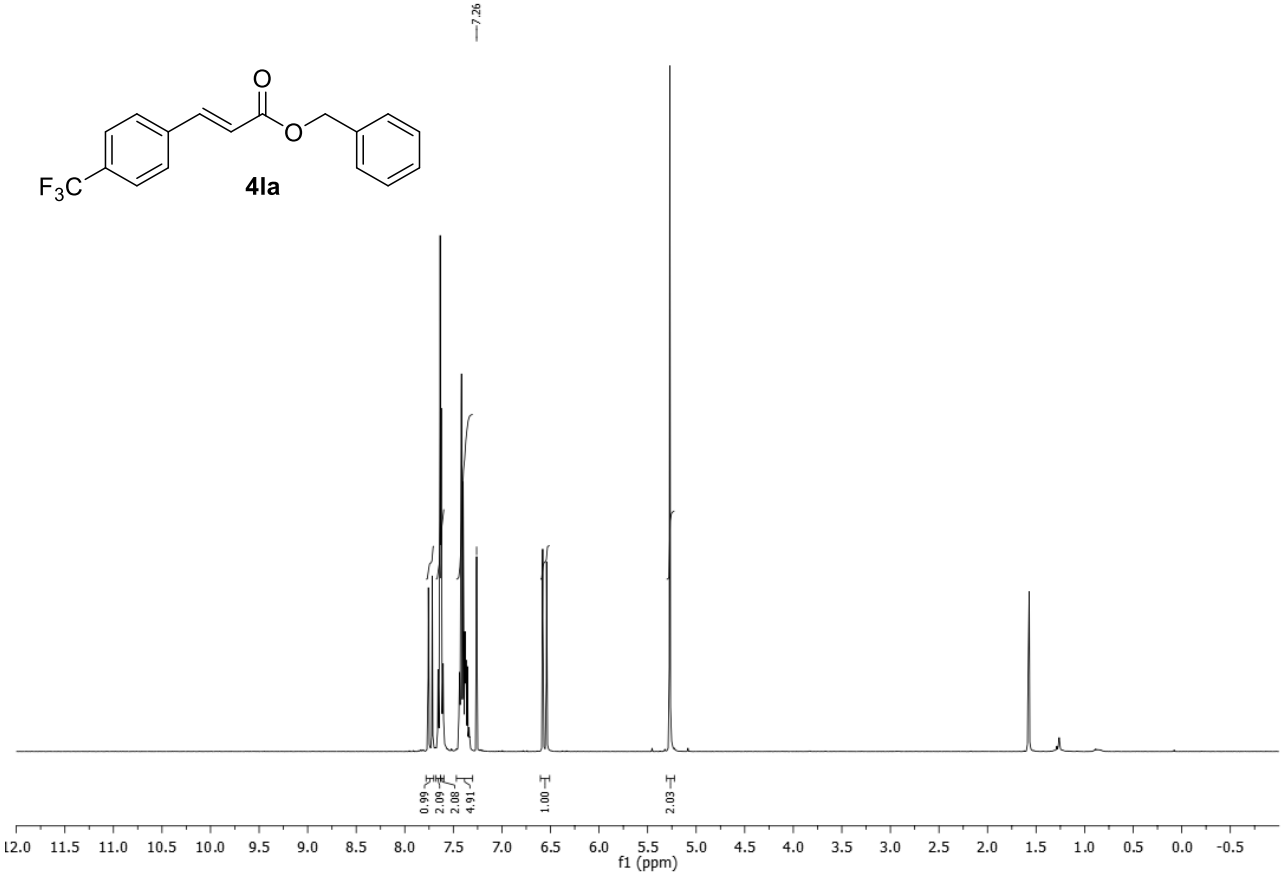

166.99
165.78
144.51
140.06
136.38
134.92
132.24
130.79
129.28
129.04
128.74
128.39
128.37
127.20
120.28
117.23
66.48
f1 (ppm)

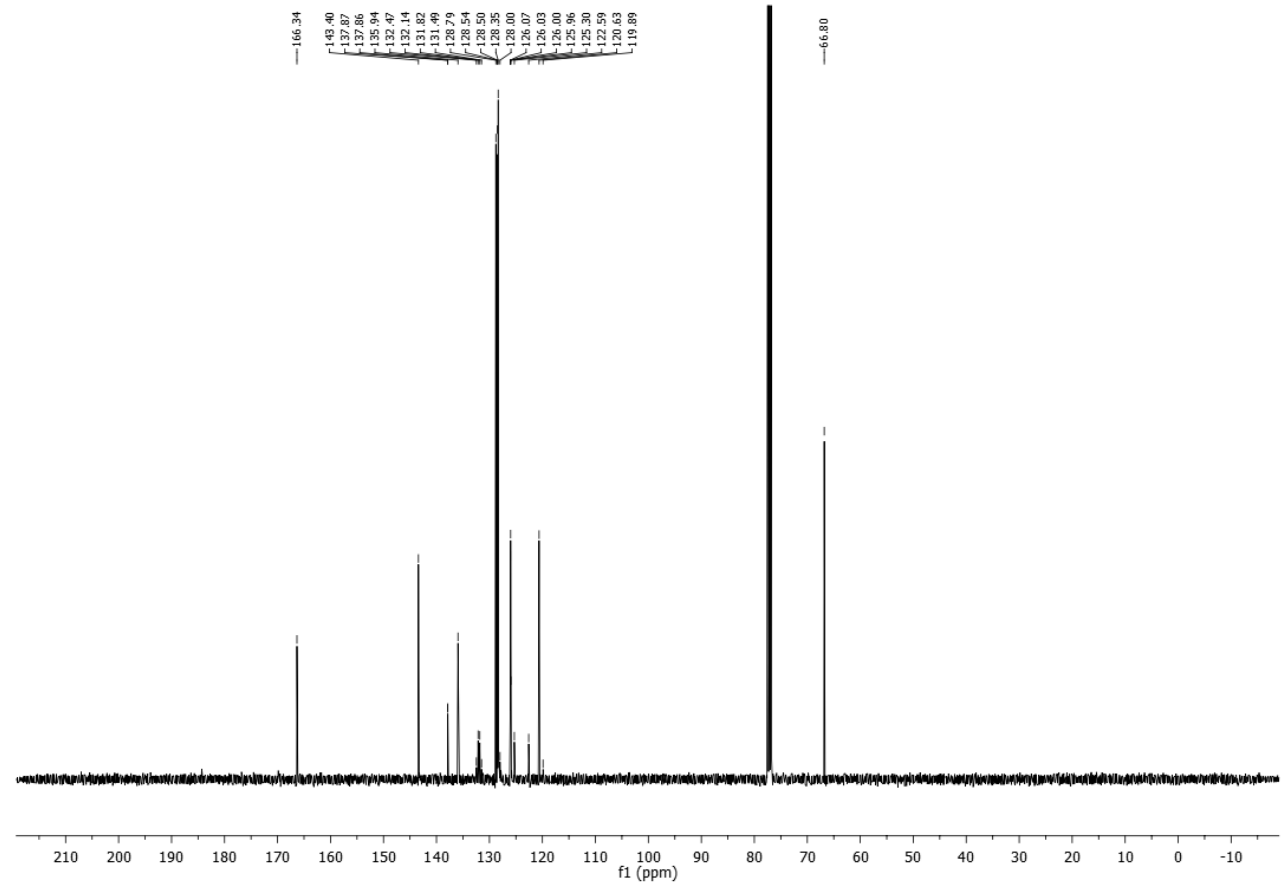

4ja
HN
O=S=O
Cl
O
O
7.26
1.97
1.05
10.02
2.02
1.00
2.00
f1 (ppm)


166.91
144.07
140.06
138.13
137.47
136.08
131.54
129.67
129.51
128.75
128.44
128.39
121.04
117.80
66.59
f1 (ppm)


7.26
Cl
O
O
S
N
O
O=S=O
O
O
4ka
Cl
3.97
0.99
6.04
4.98
1.96
1.00
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


166.34
143.26
141.23
137.67
136.75
135.95
135.20
132.03
130.15
129.64
129.05
128.79
128.54
128.48
120.56
66.79
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26
O
O
F3C
4la
0.99
2.09
2.08
4.91
1.00
2.03
f1 (ppm)


166.34
143.40
137.87
137.86
135.94
132.47
132.14
131.82
131.49
128.79
128.54
128.50
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128.00
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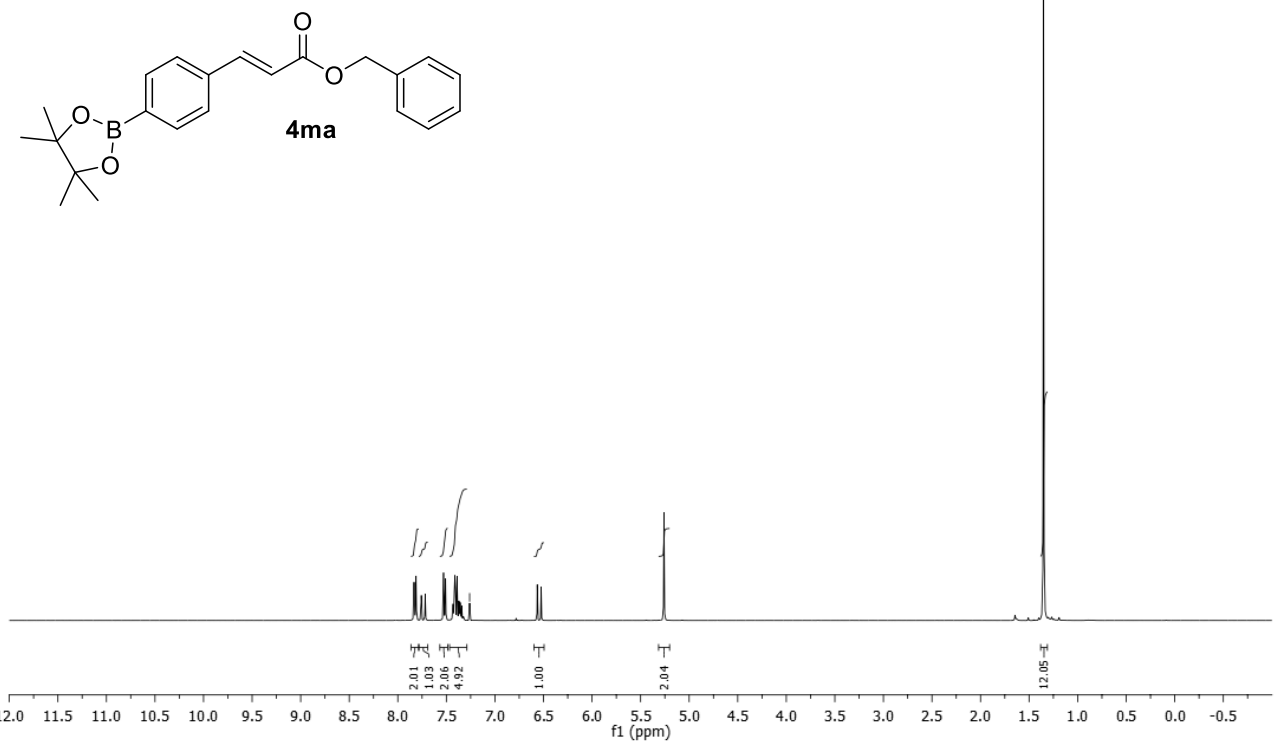
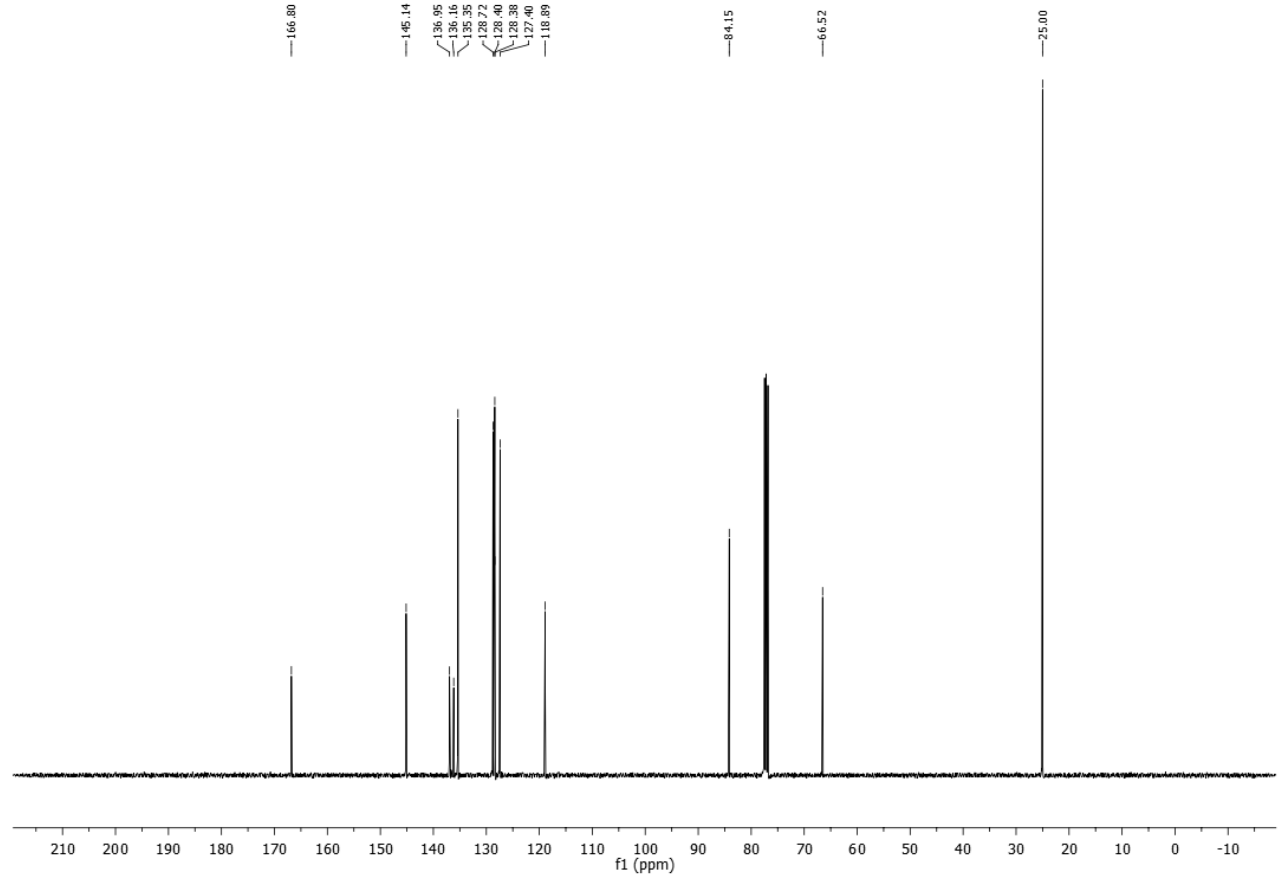
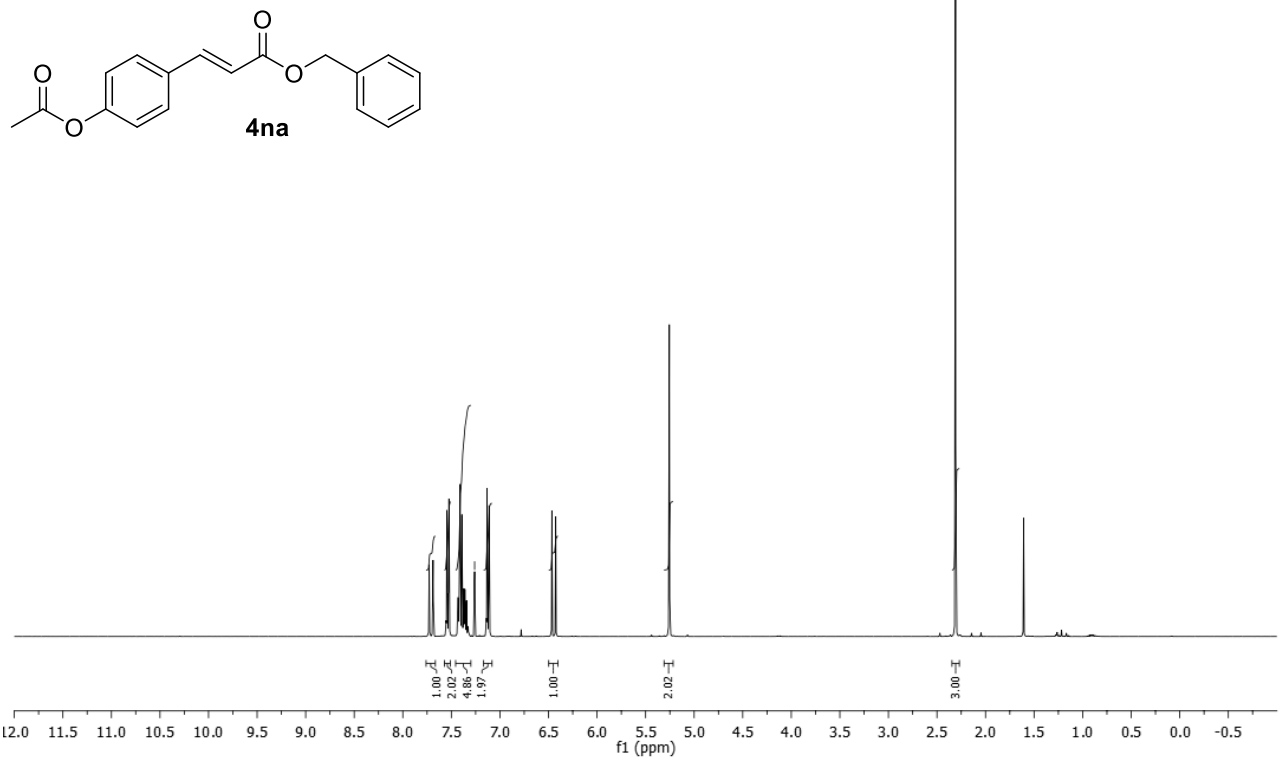
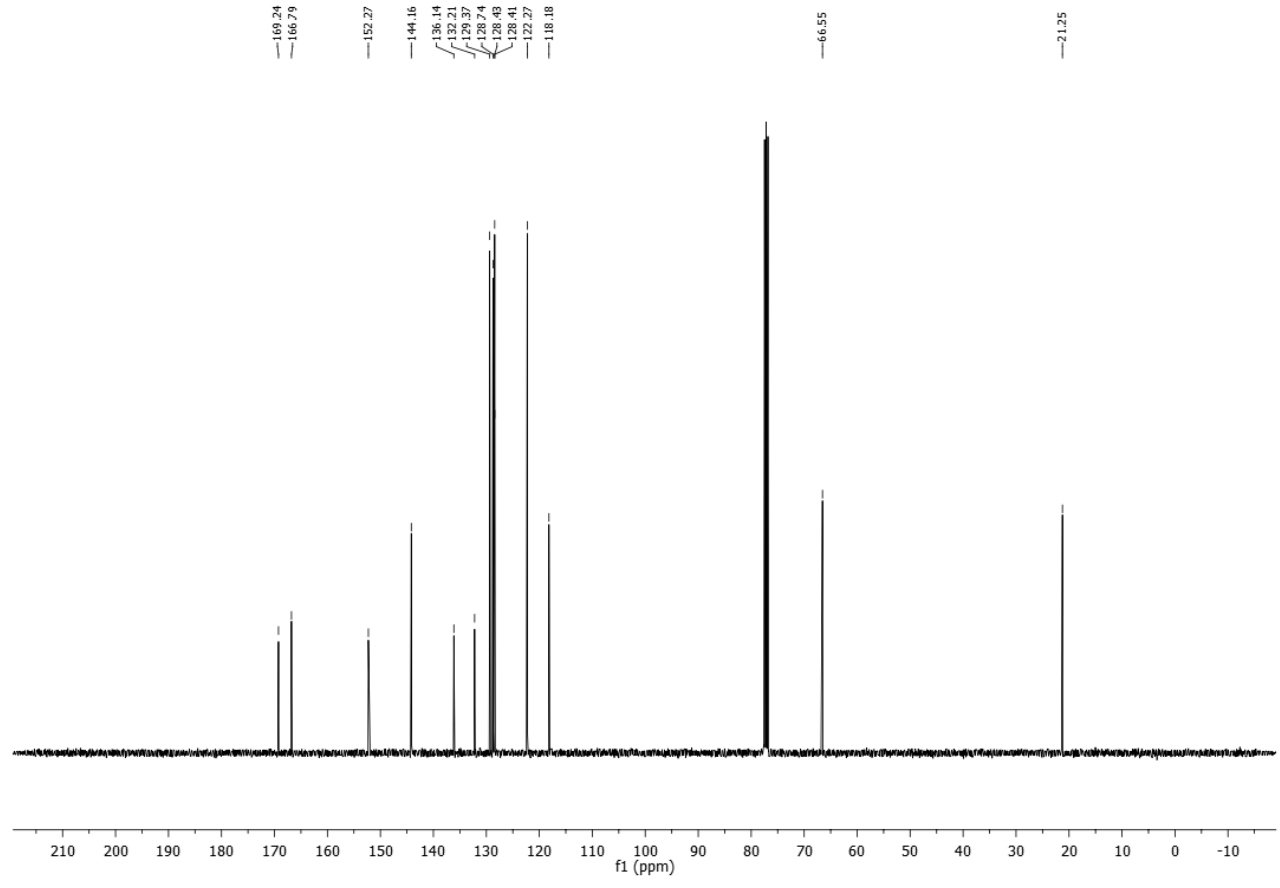
122.59
120.63
119.89
66.80
f1 (ppm)

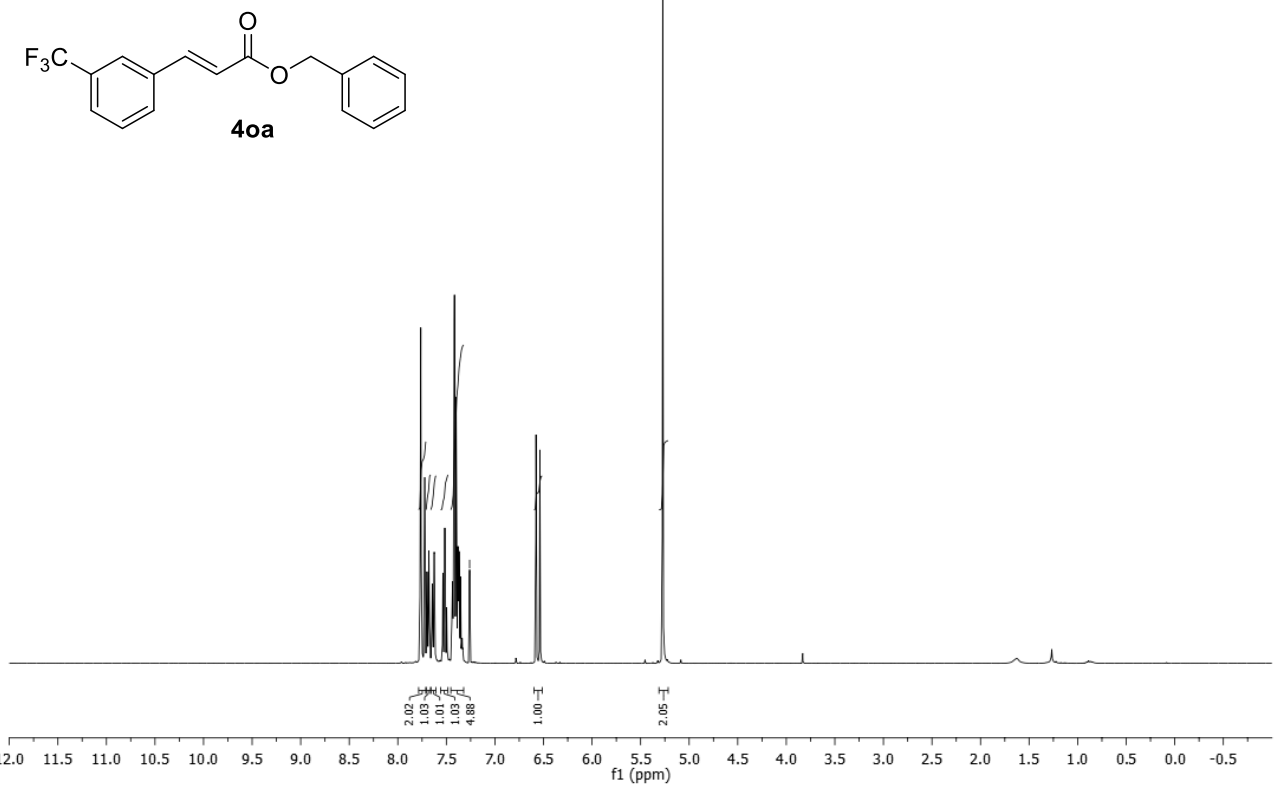

7.26
O
O
O
B
O
4ma
2.01
1.03
2.06
4.92
1.00
2.04
12.05
f1 (ppm)

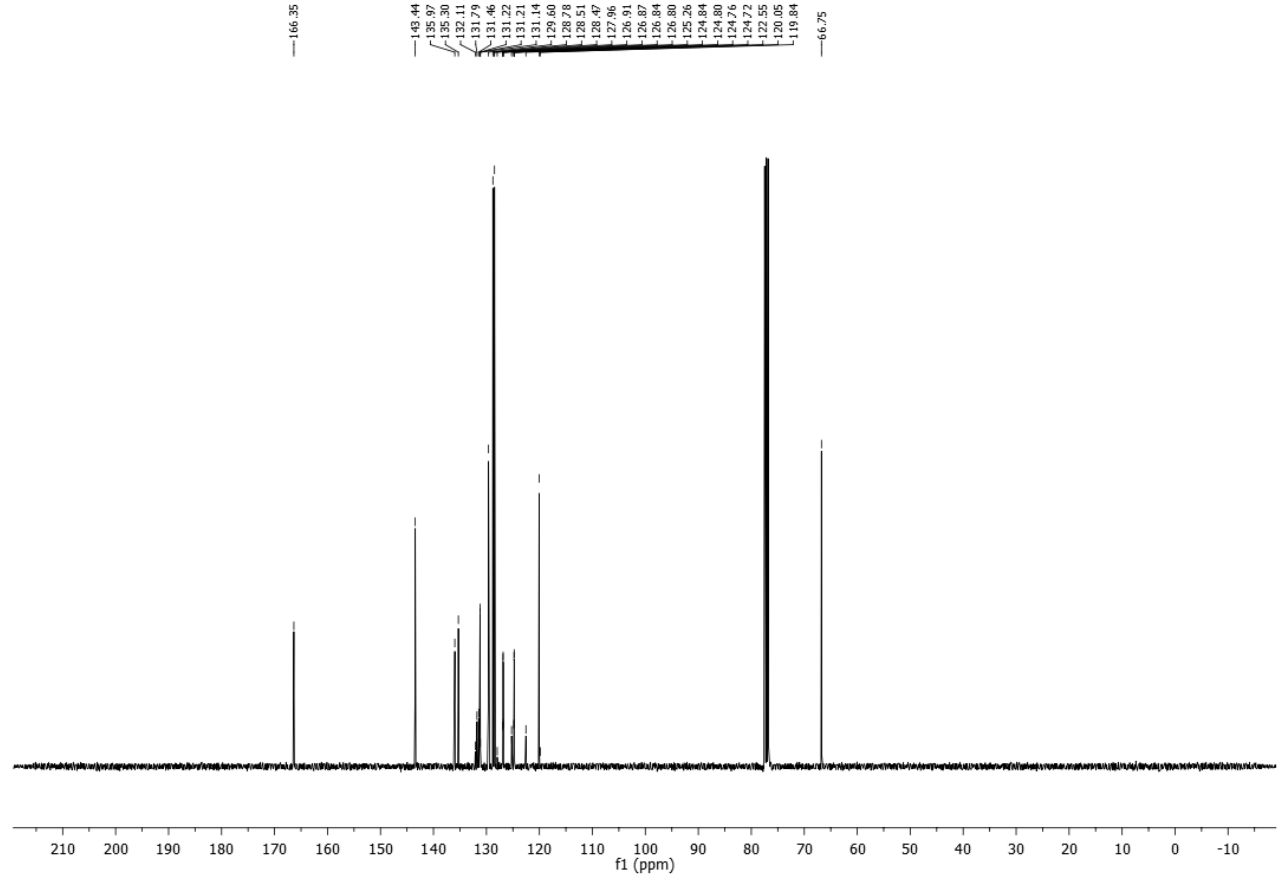

166.80
145.14
136.95
136.16
135.35
128.72
128.40
128.38
127.40
118.89
84.15
66.52
25.00
f1 (ppm)


7.26
1.00
2.02
4.86
1.97
1.00
2.02
3.00
f1 (ppm)

4na


169.24
166.79
152.27
144.16
136.14
132.21
129.37
128.74
128.43
128.41
122.27
118.18
66.55
21.25
f1 (ppm)


7.26
O
F3C
O
4oa
2.02
1.03
1.01
1.03
4.88
1.00
2.05
f1 (ppm)


166.35
143.44
135.97
135.30
132.11
131.79
131.46
131.22
131.21
131.14
129.60
128.78
128.51
128.47
127.96
126.91
126.87
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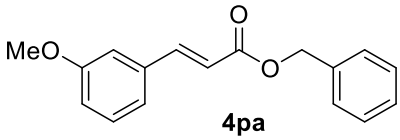
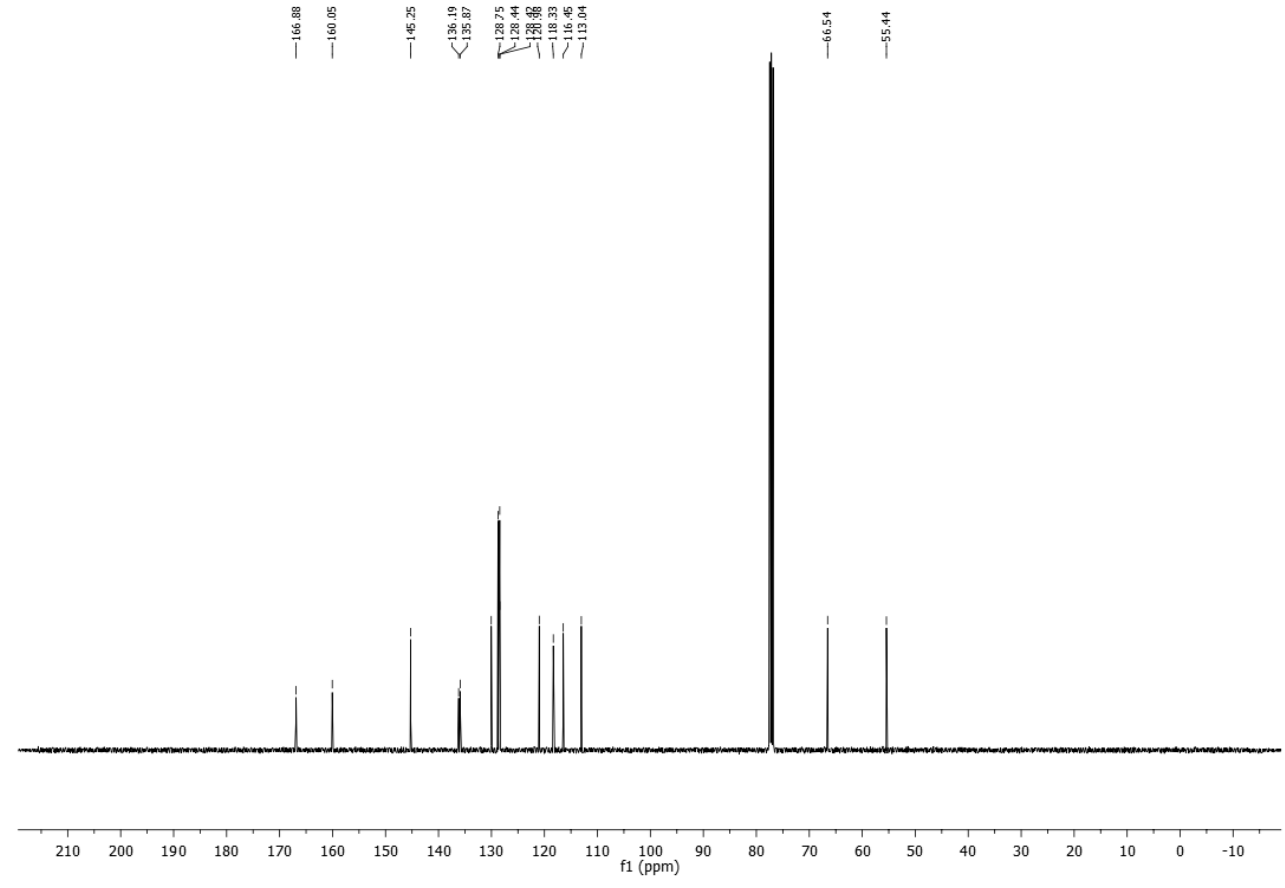
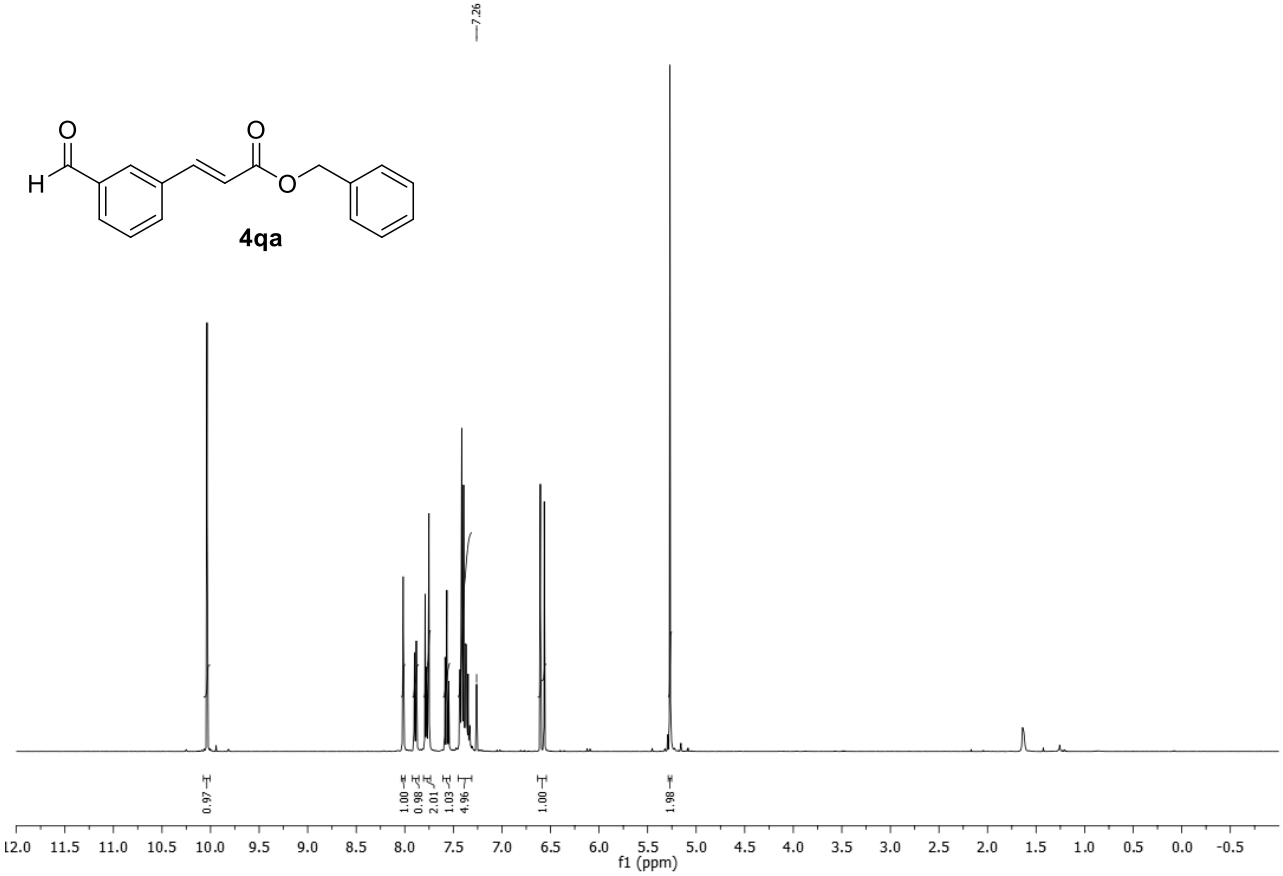
122.55
120.05
119.84
66.75
f1 (ppm)

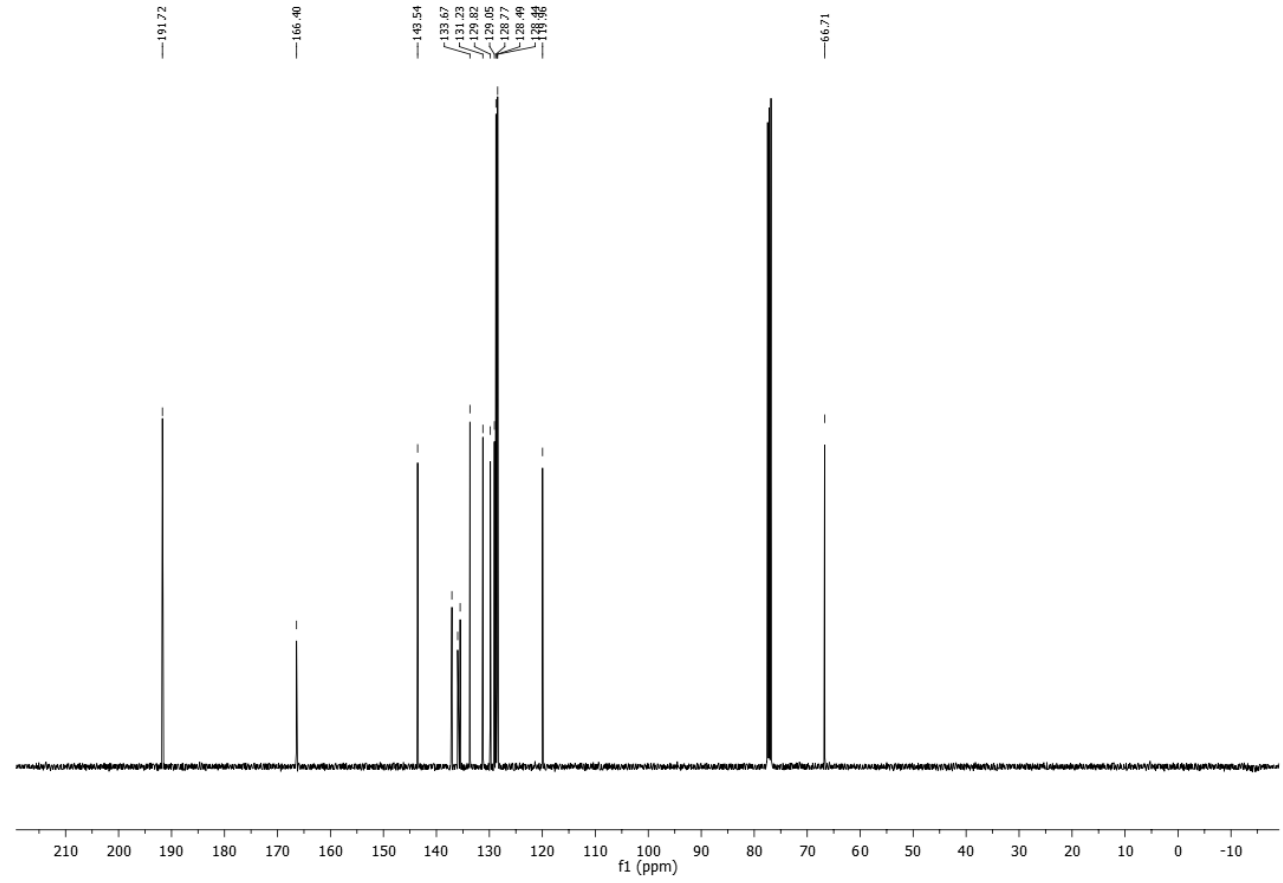

MeO
O
O

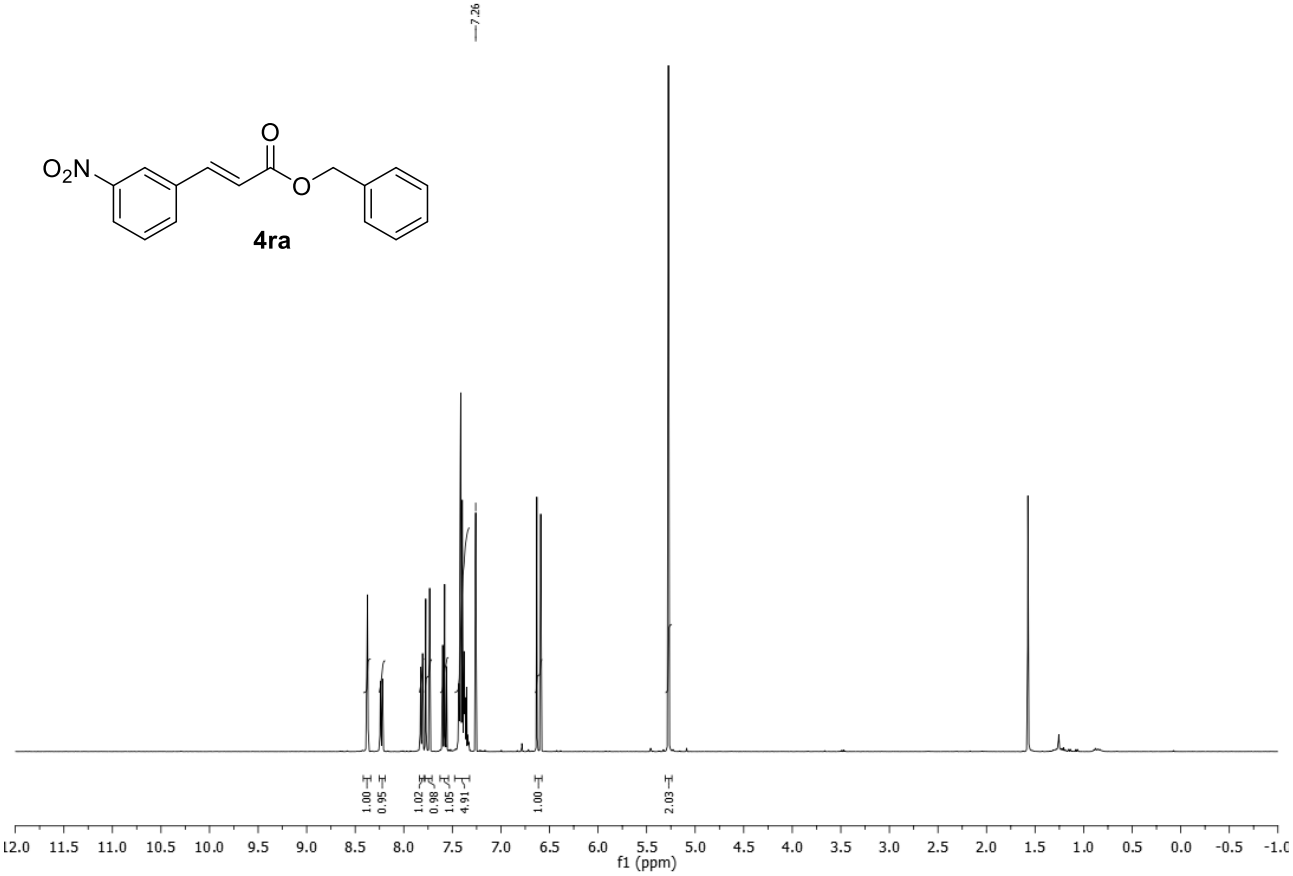
4pa

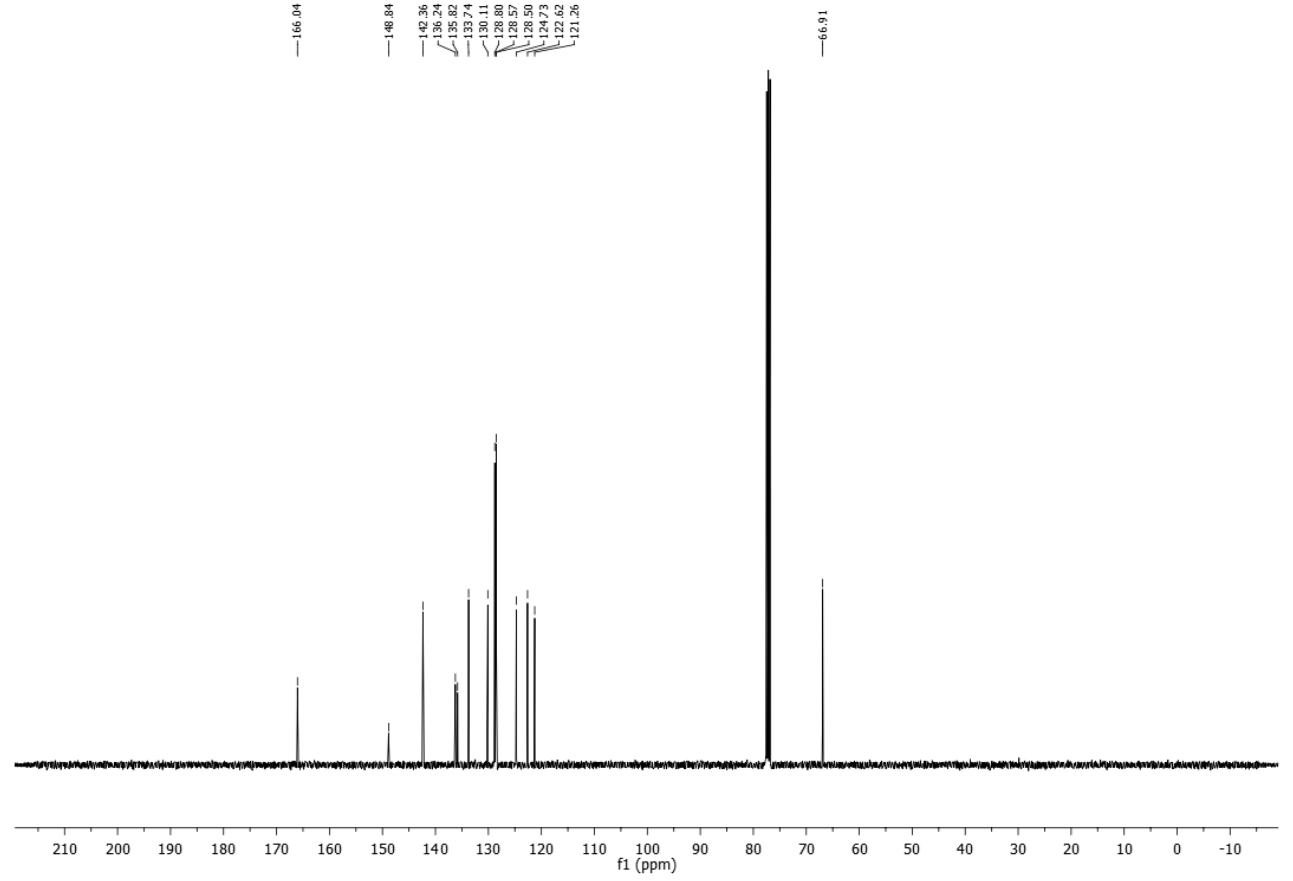
7.26
0.98
4.80
1.05
1.00
0.99
0.97
1.00
2.02
3.03
f1 (ppm)

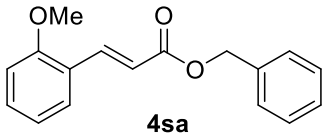

166.88
160.05
145.25
136.19
135.87
128.75
128.44
118.33
116.45
113.04
66.54
55.44
f1 (ppm)


7.26
O
O
H
O
4qa
0.97
1.00
0.98
2.01
1.03
4.96
1.00
1.98
f1 (ppm)


191.72
166.40
143.54
133.67
131.23
129.82
129.05
128.77
128.49
66.71
f1 (ppm)

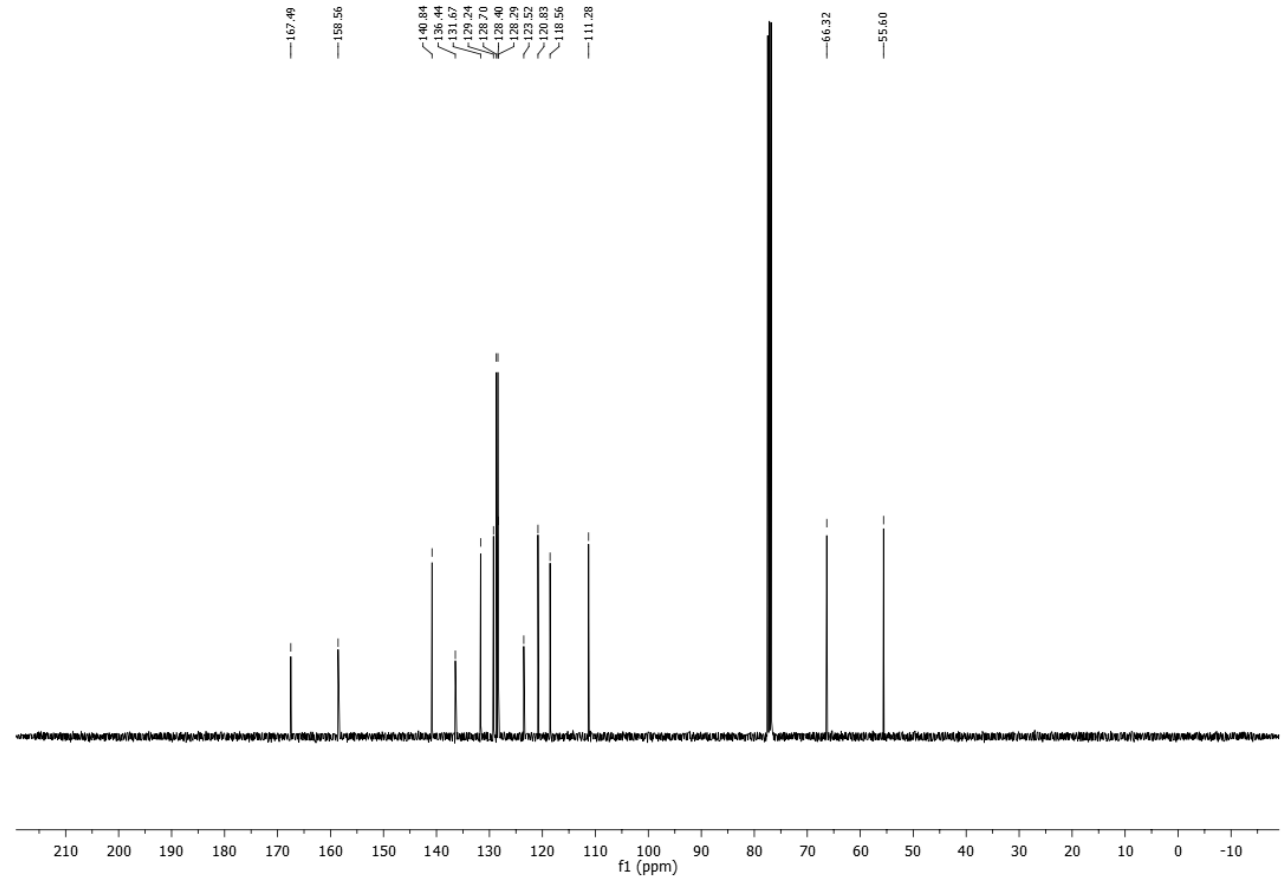

7.26
O2N
O
O
4ra
1.00
0.95
1.02
0.98
1.05
4.91
1.00
2.03
f1 (ppm)

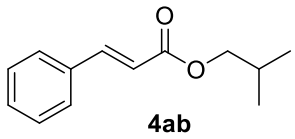

166.04
148.84
142.36
136.24
135.82
133.74
130.11
128.80
128.57
128.50
124.73
122.62
121.26
66.91
f1 (ppm)


OMe
O
O

4sa

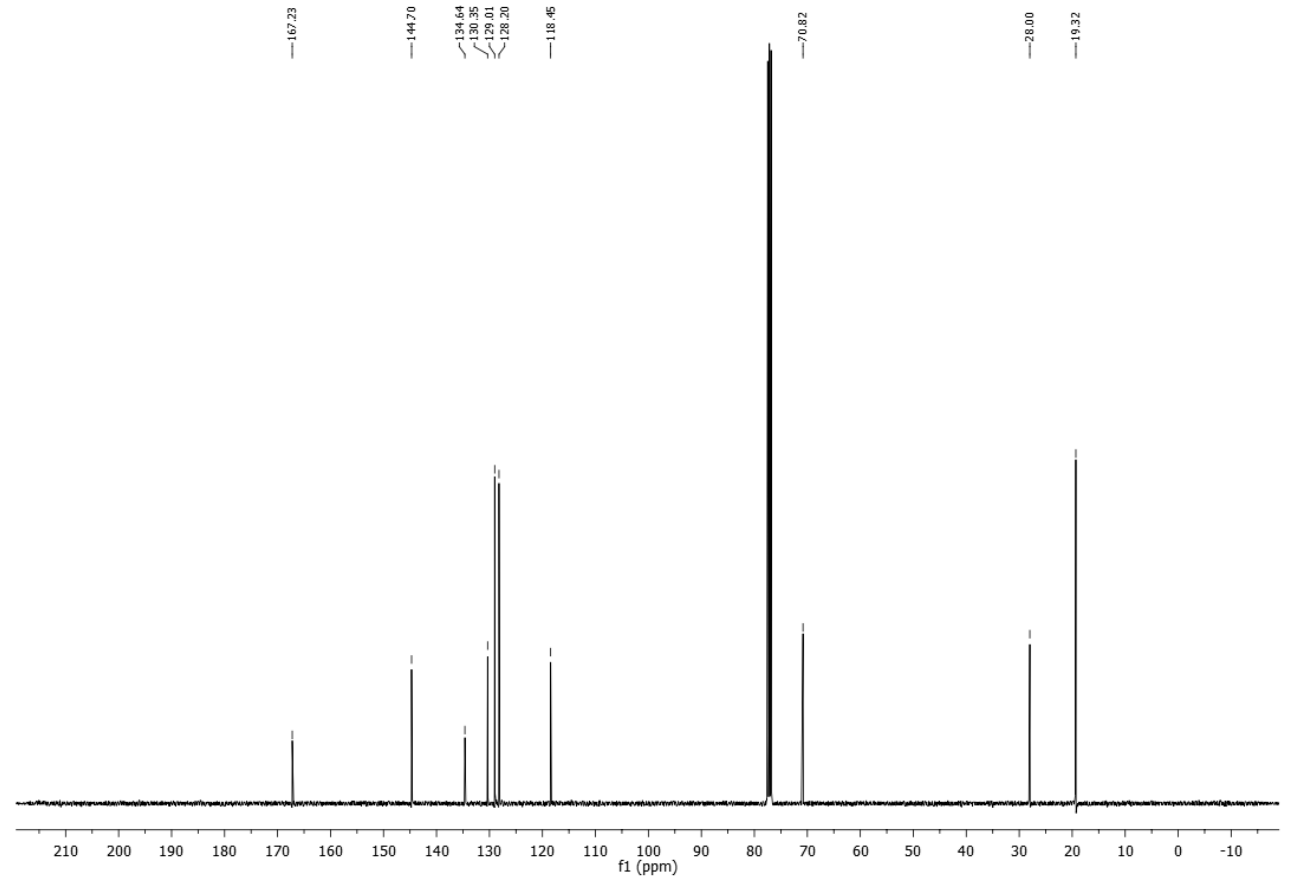
7.26
0.97
1.05
6.05
1.02
0.99
1.00
2.05
3.08
f1 (ppm)

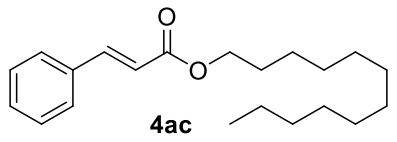

167.49
158.56
140.84
136.44
131.67
129.24
128.70
128.40
128.29
123.52
120.83
118.56
111.28
66.32
55.60
f1 (ppm)



4ab

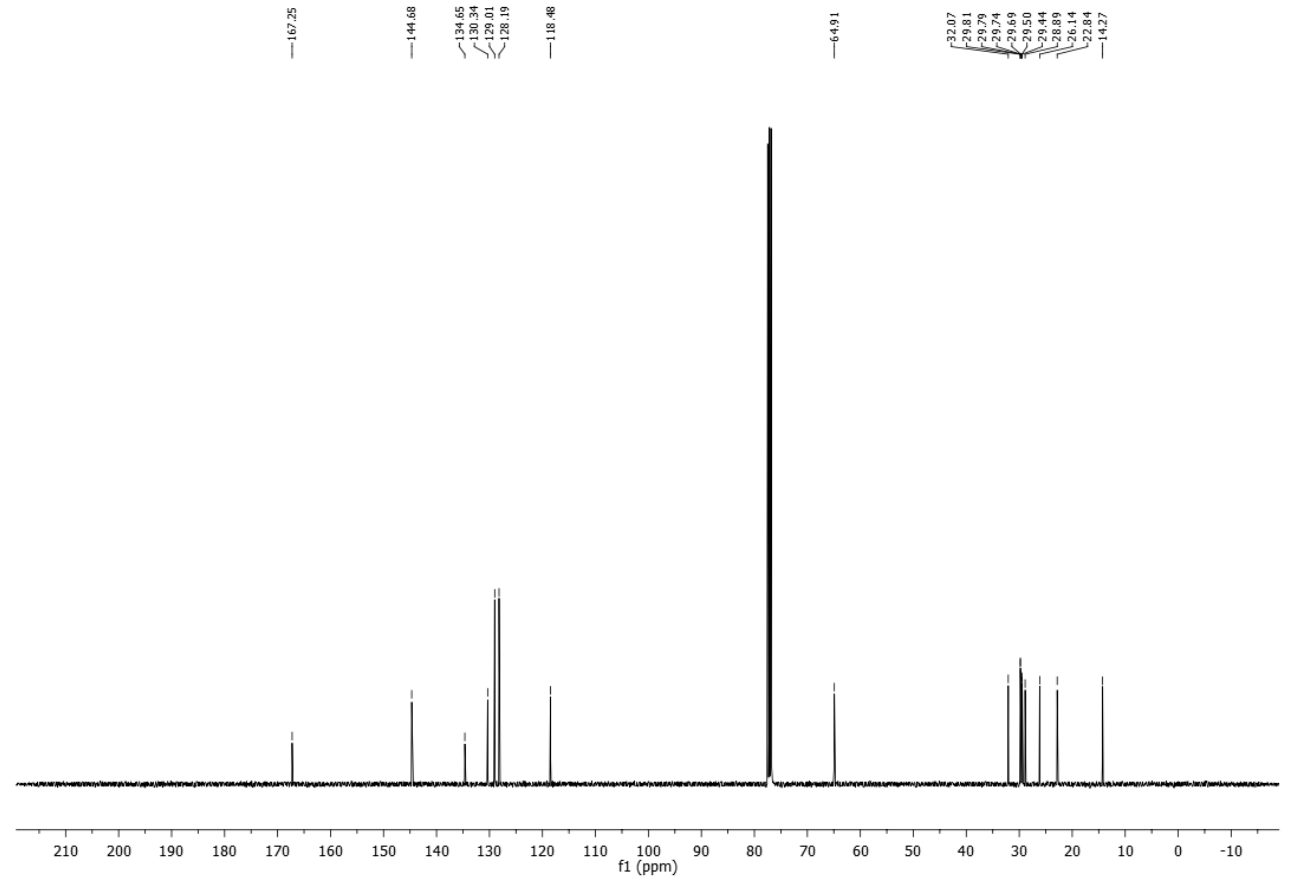
7.26
0.99
2.02
2.95
1.00
2.03
1.00
6.05
f1 (ppm)

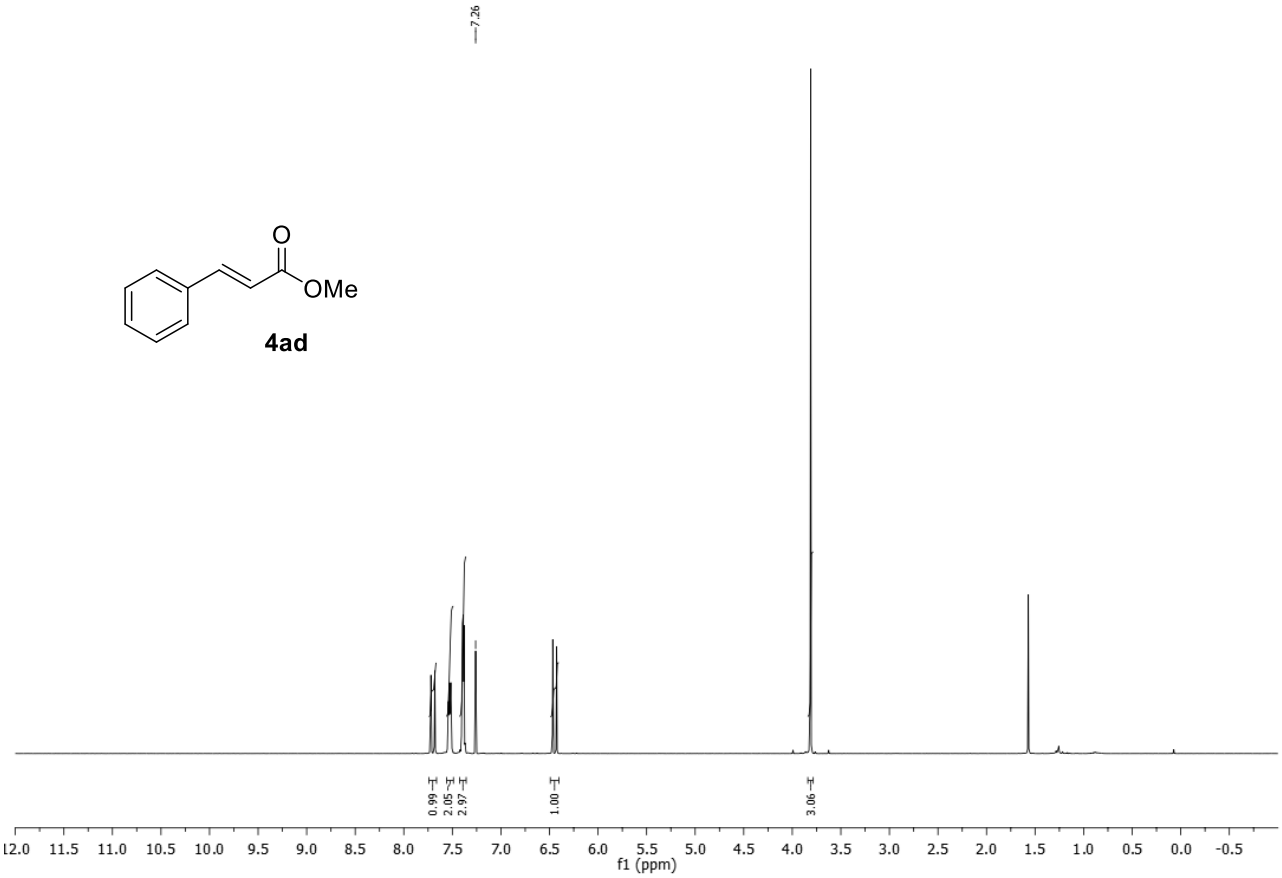

167.23
144.70
134.64
130.35
129.01
128.20
118.45
70.82
28.00
19.32
f1 (ppm)

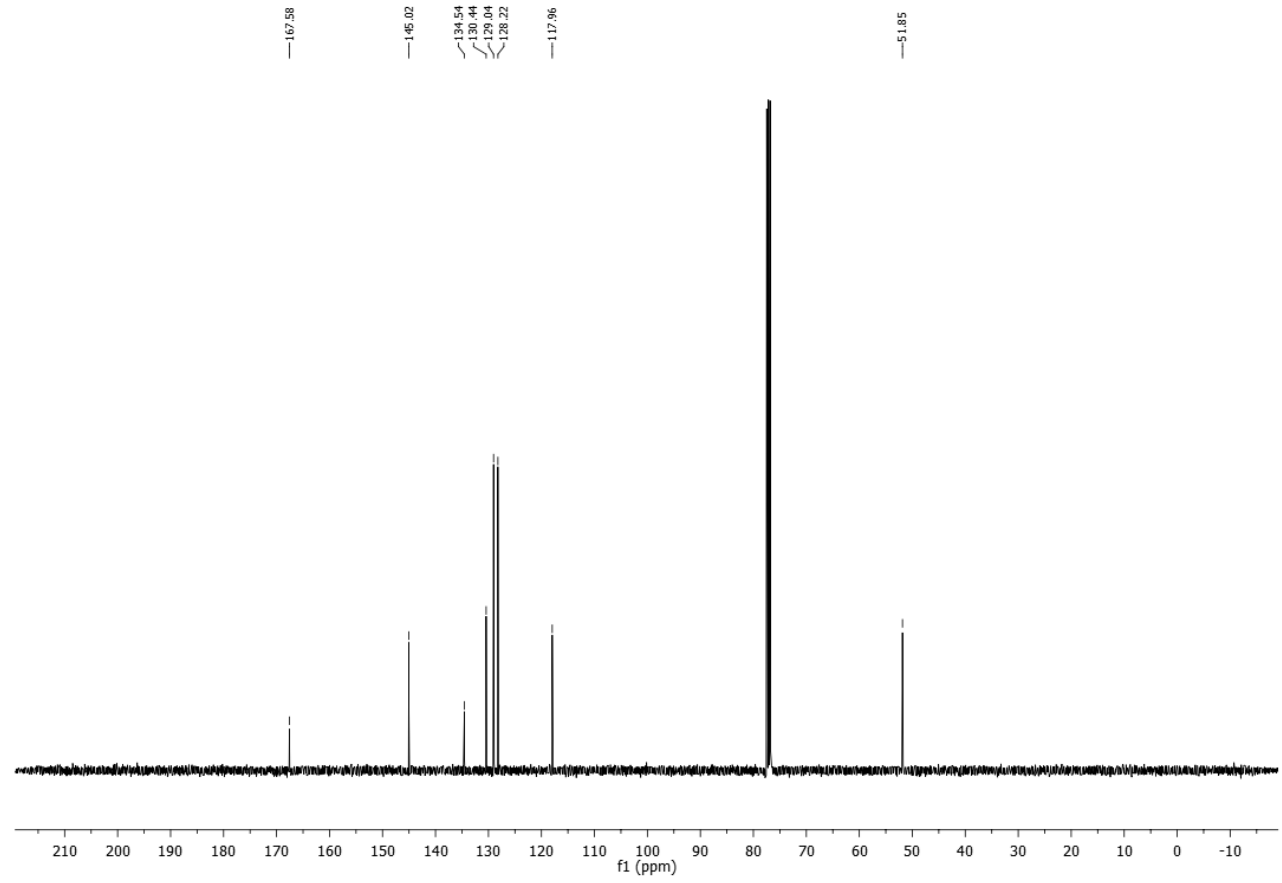


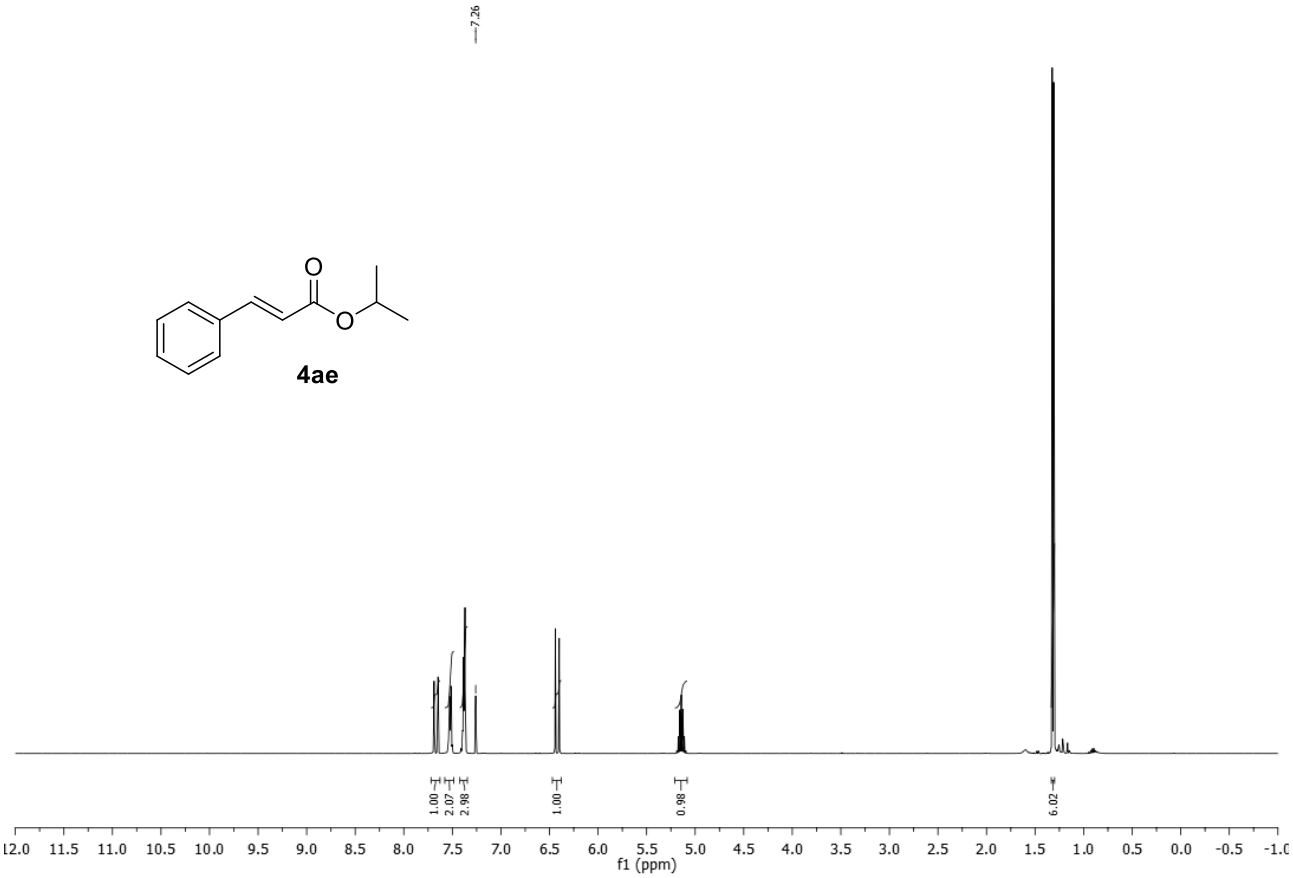
4ac

7.26
1.00
2.05
3.01
1.00
2.07
2.06
18.64
3.11
f1 (ppm)

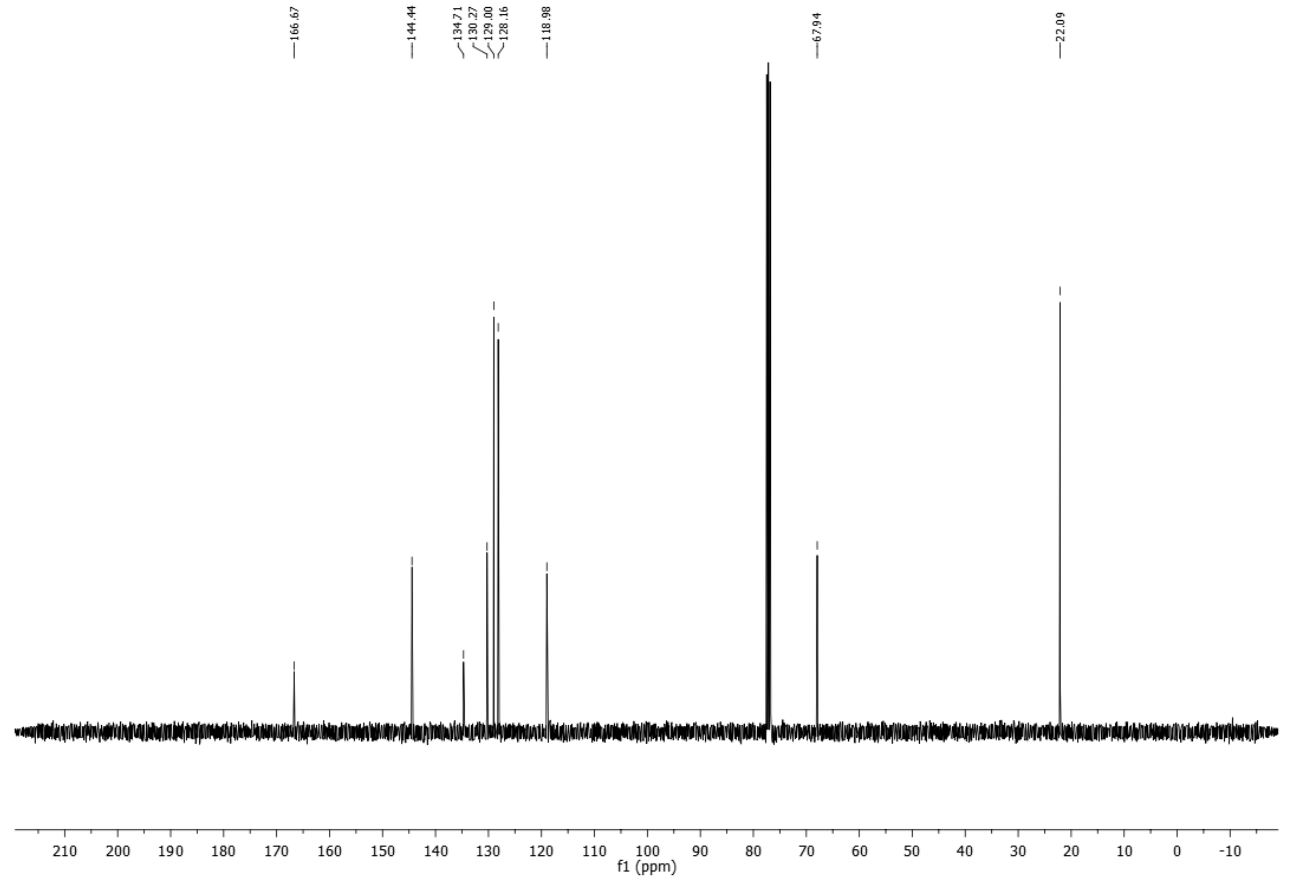

167.25
144.68
134.65
130.34
129.01
128.19
118.48
64.91
32.07
29.81
29.79
29.74
29.69
29.50
29.44
28.89
26.14
22.84
14.27
f1 (ppm)

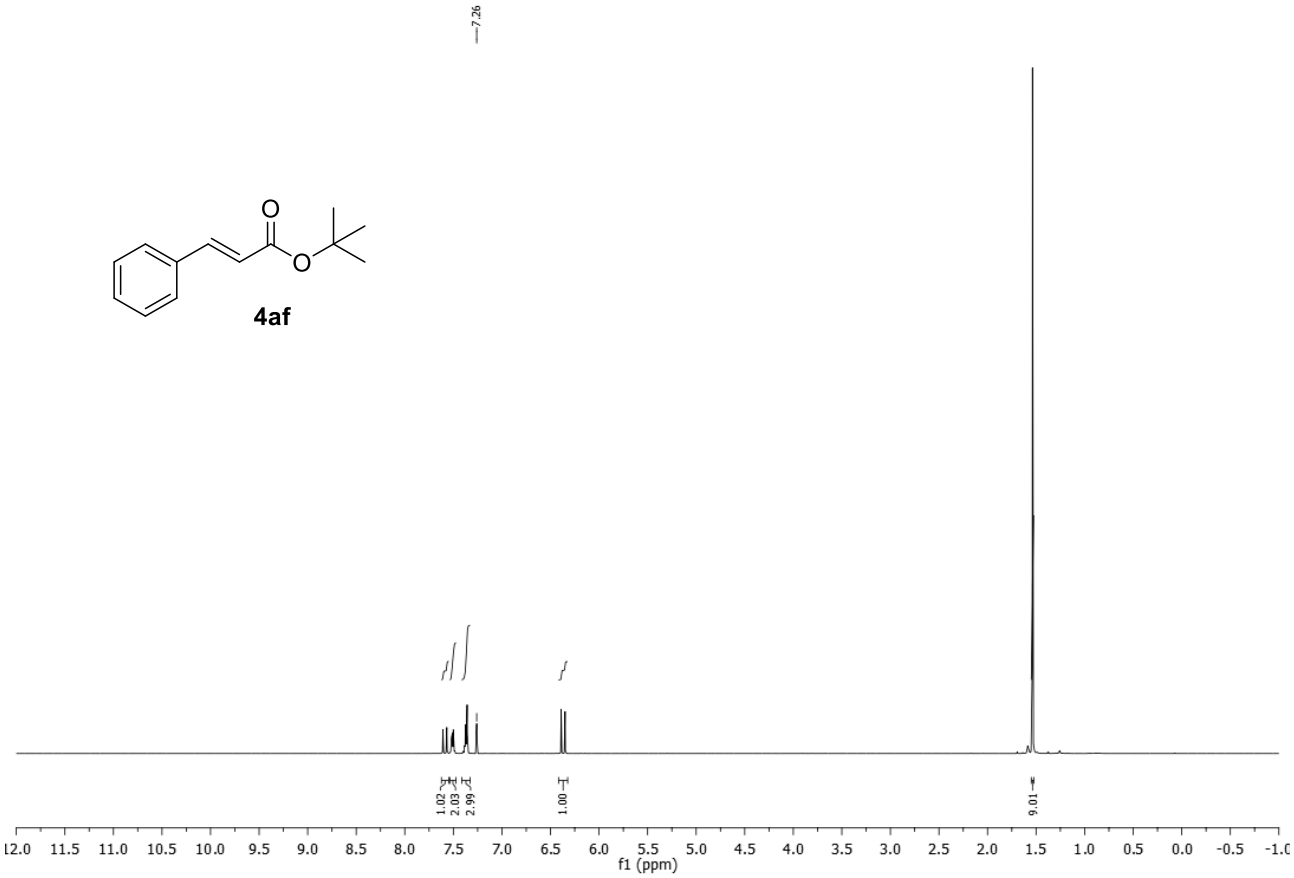

7.26
O
OMe
4ad
0.99
2.05
2.97
1.00
3.06
f1 (ppm)


167.58
145.02
134.54
130.44
129.04
128.22
117.96
51.85
f1 (ppm)

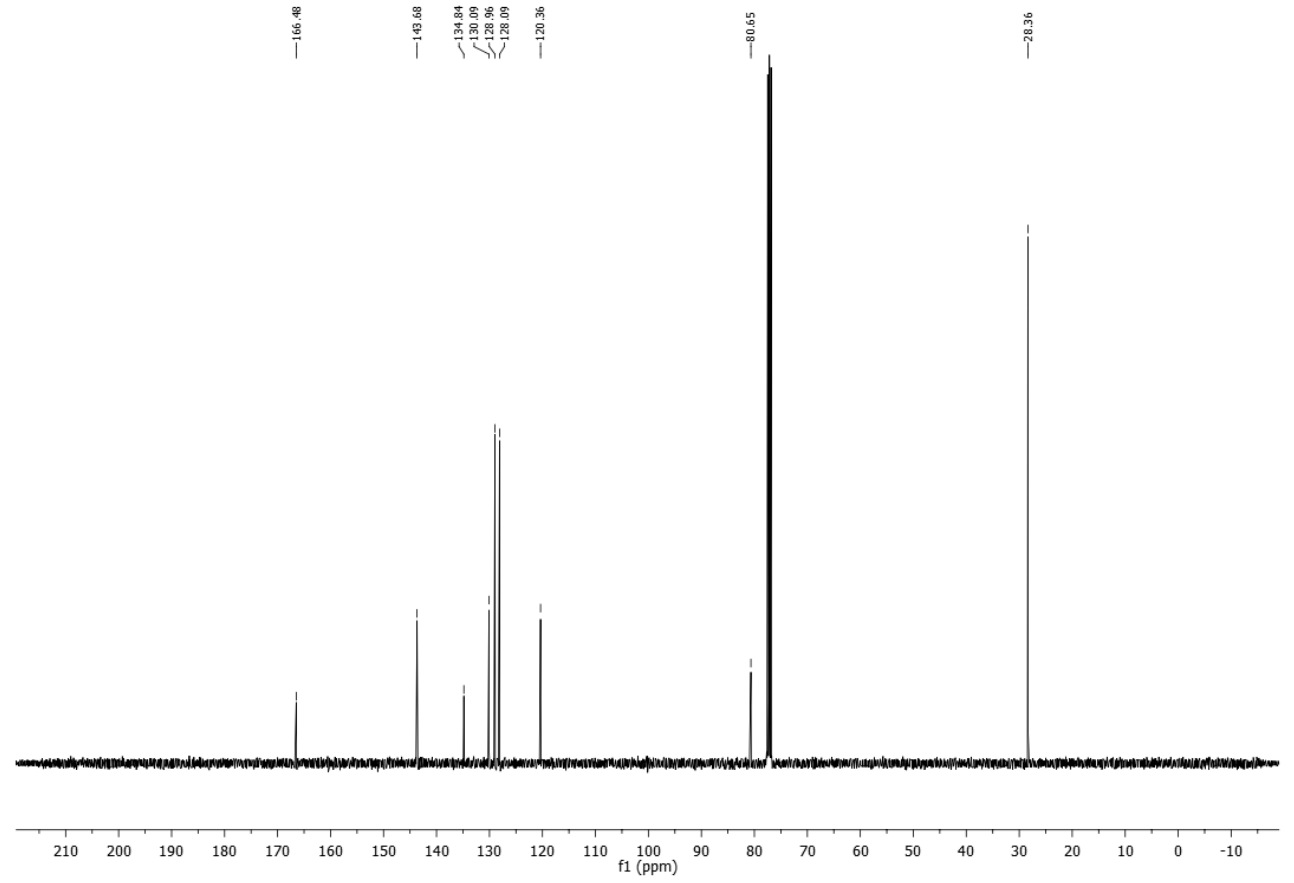

7.26
1.00
2.07
2.98
1.00
0.98
6.02
f1 (ppm)

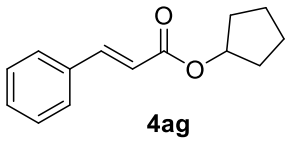
4ae


166.67
144.44
134.71
130.27
129.00
128.16
118.98
67.94
22.09
f1 (ppm)


7.26
1.02
2.03
2.99
1.00
9.01
f1 (ppm)

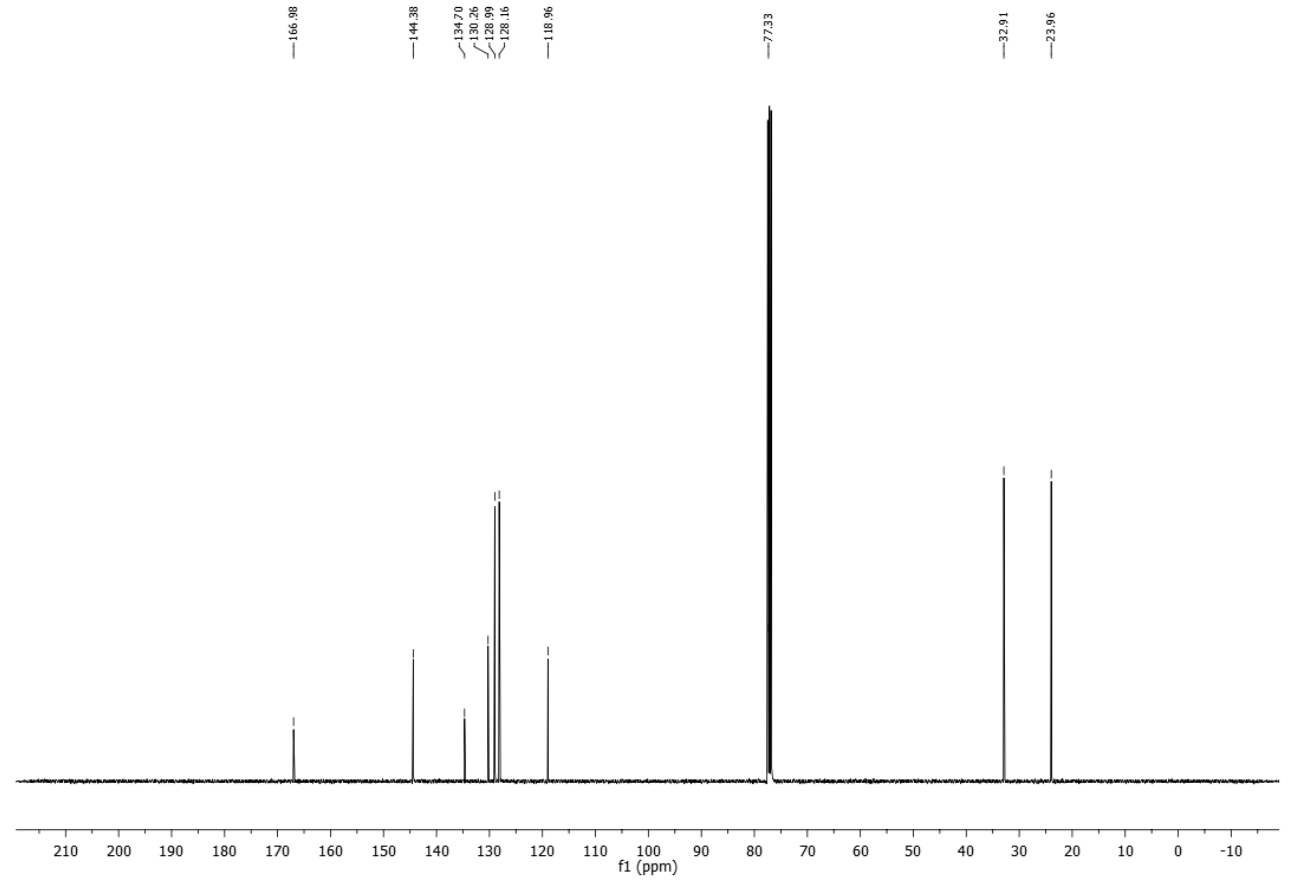
4af

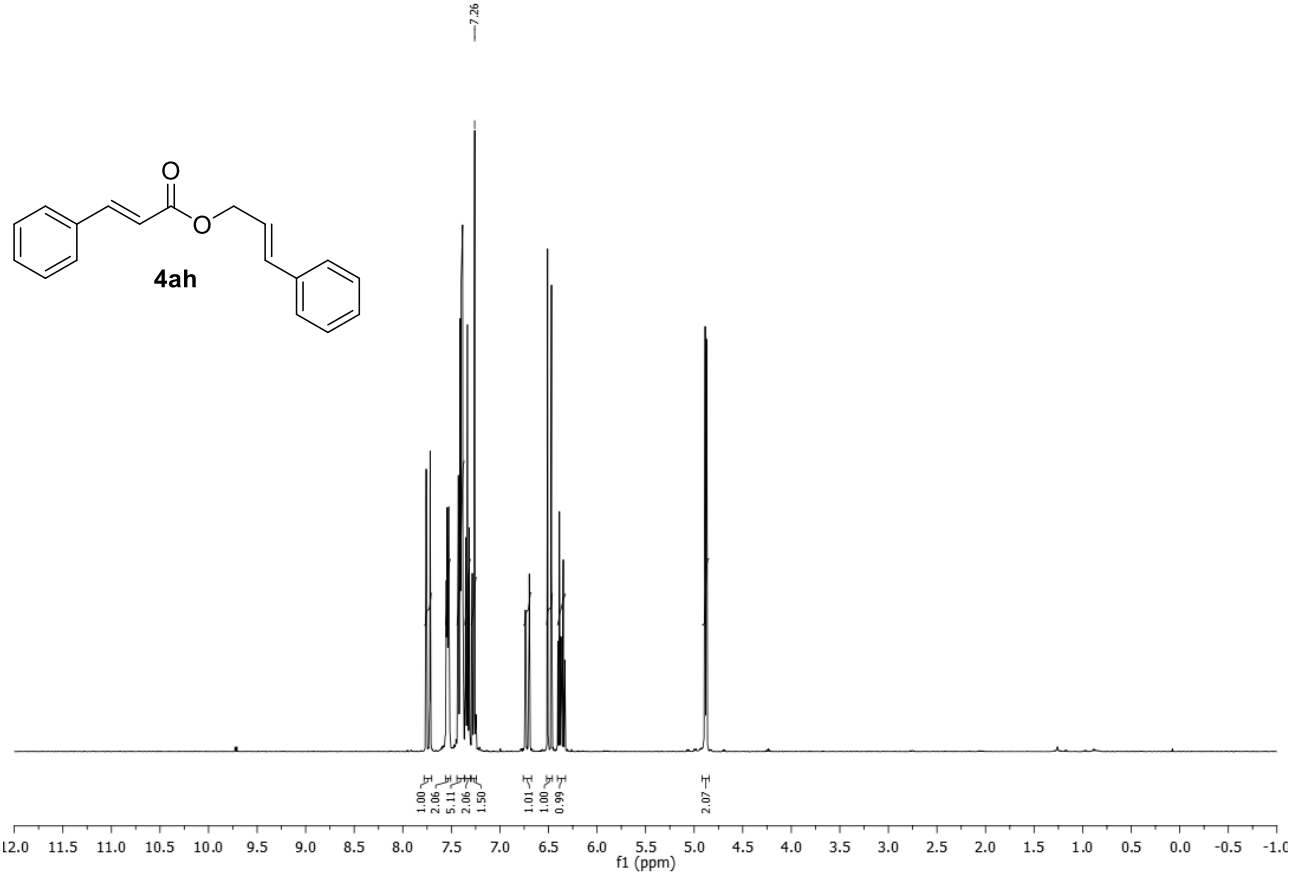

166.48
143.68
134.84
130.09
128.96
128.09
120.36
80.65
28.36
f1 (ppm)

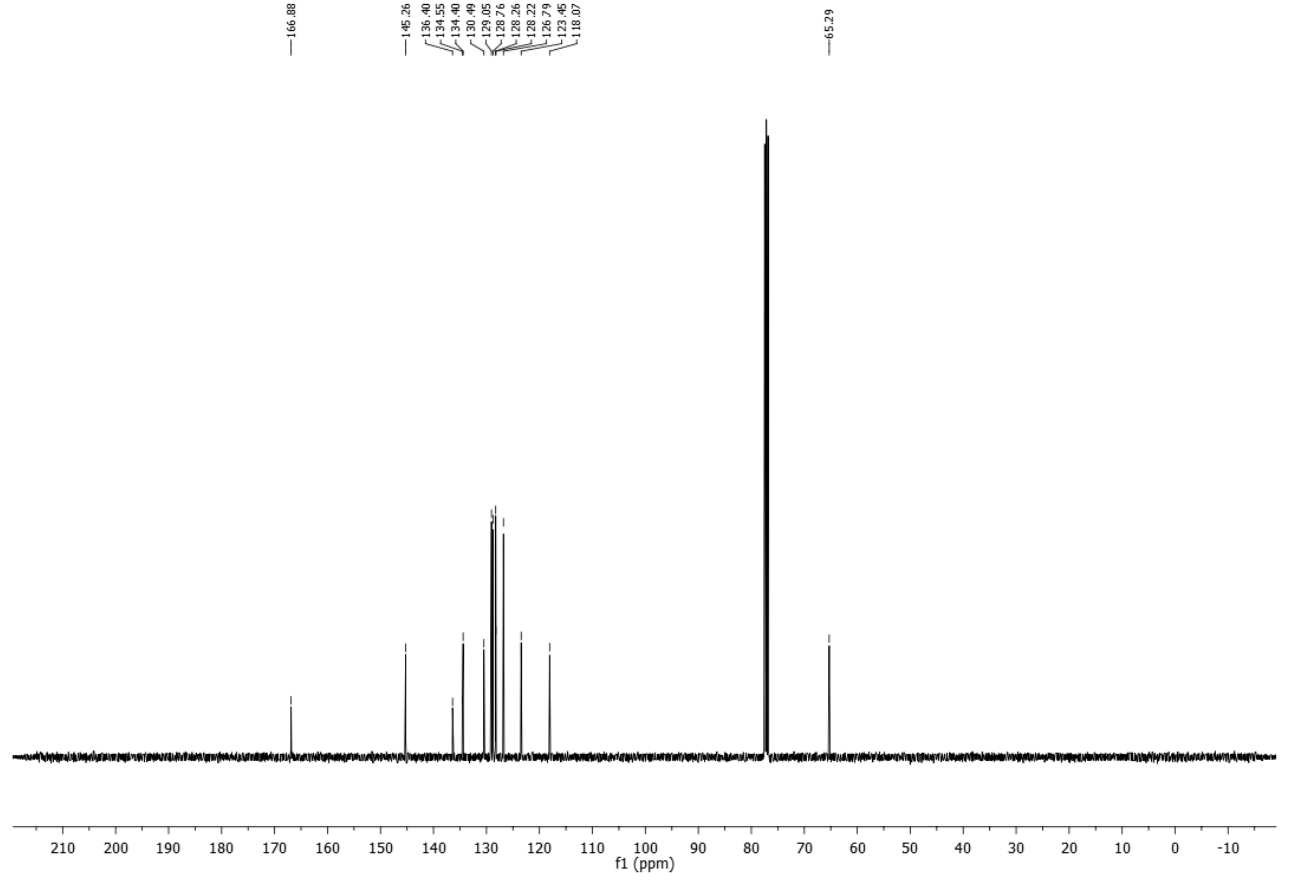


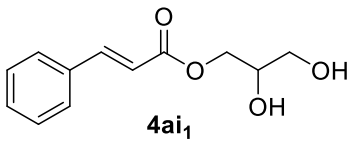
4ag

7.26
0.99
2.03
2.96
1.00
1.02
2.06
4.10
2.57
f1 (ppm)


166.98
144.38
134.70
130.26
128.99
128.16
118.96
77.33
32.91
23.96
f1 (ppm)

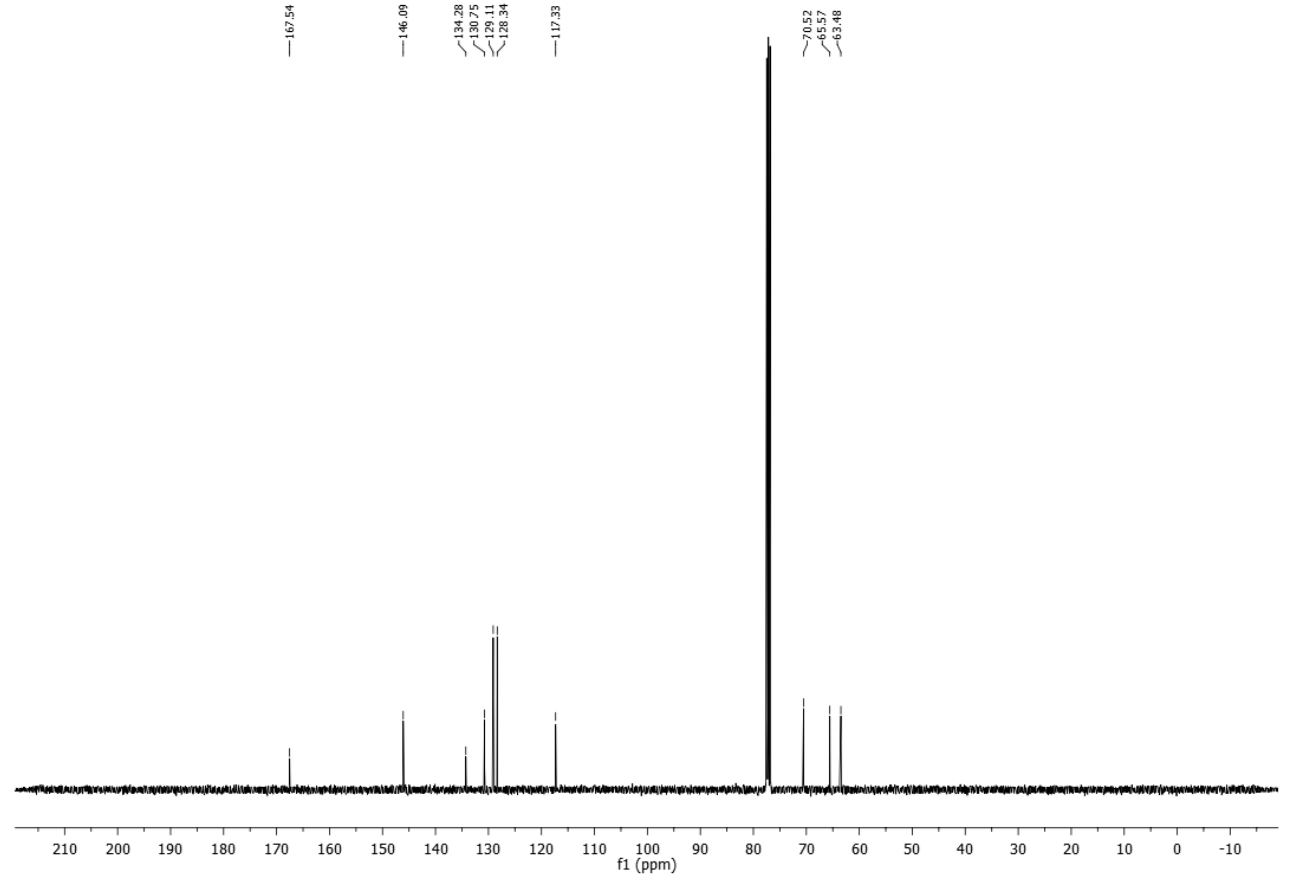

4ah
7.26
1.00
2.06
5.11
2.06
1.50
1.01
1.00
0.99
2.07
f1 (ppm)

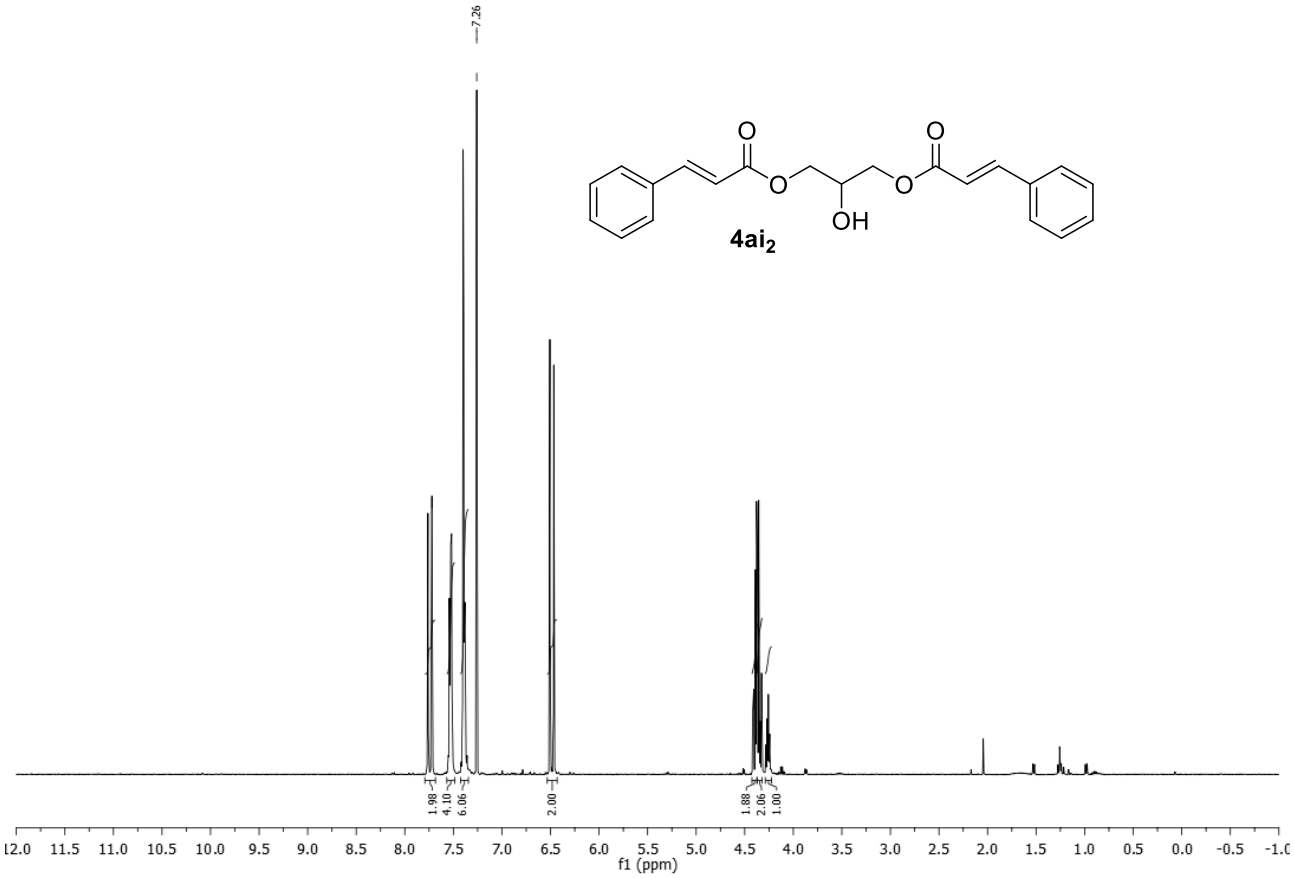

166.88
145.26
136.40
134.55
134.40
130.49
129.05
128.76
128.26
128.22
126.79
123.45
118.07
65.29
f1 (ppm)


O
O
OH
OH

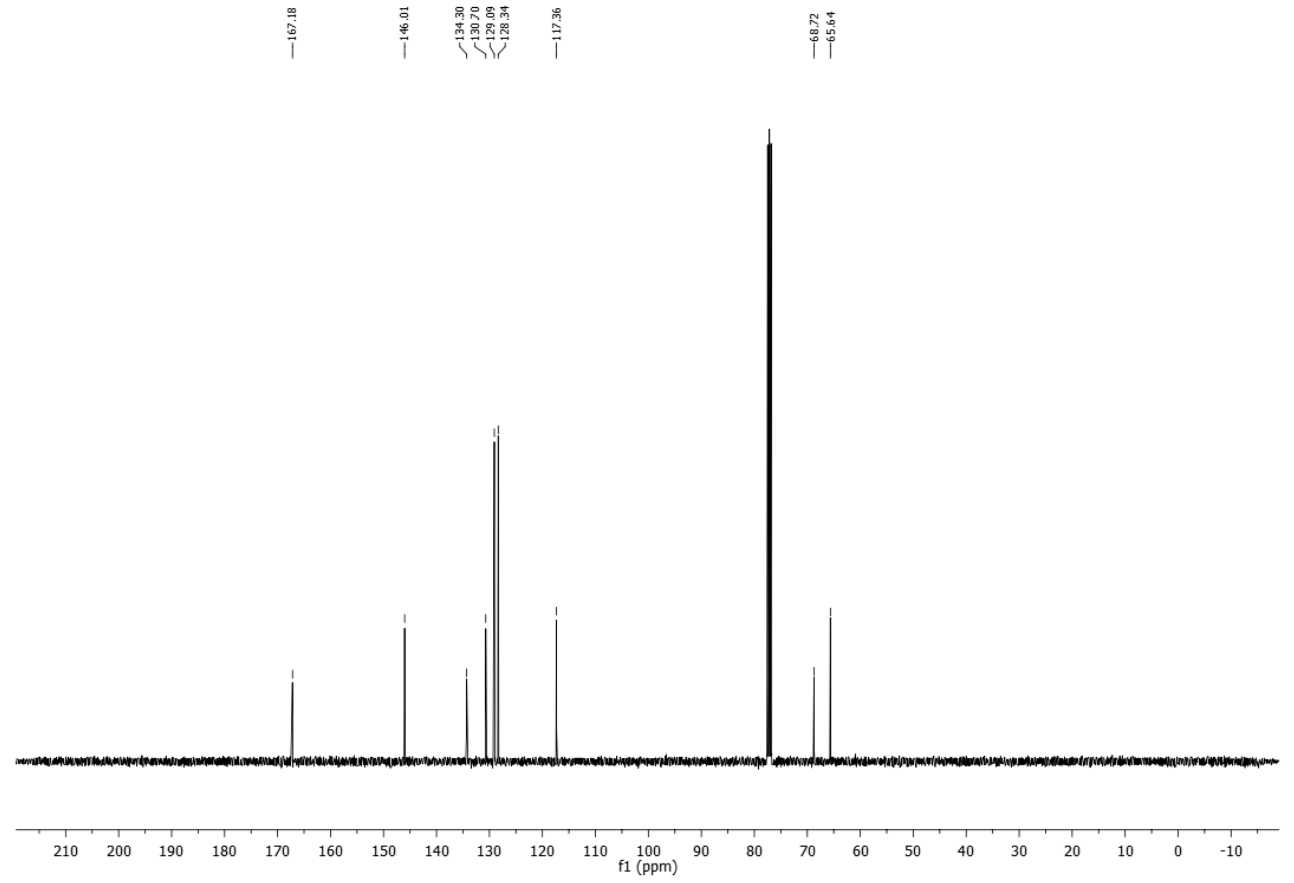
4ai$_1$

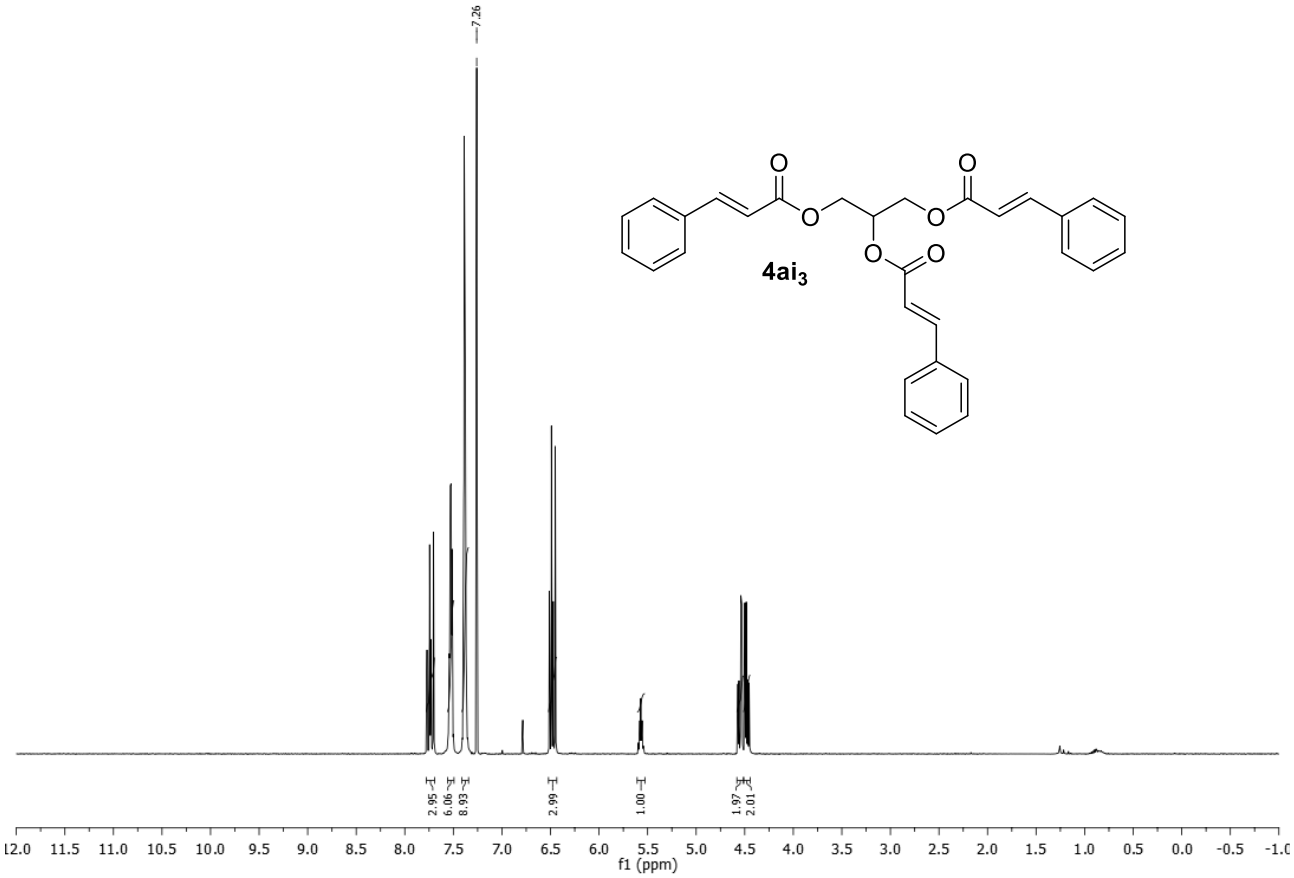
7.26
1.01
2.08
3.07
1.00
0.97
0.98
0.97
0.96
1.01
f1 (ppm)

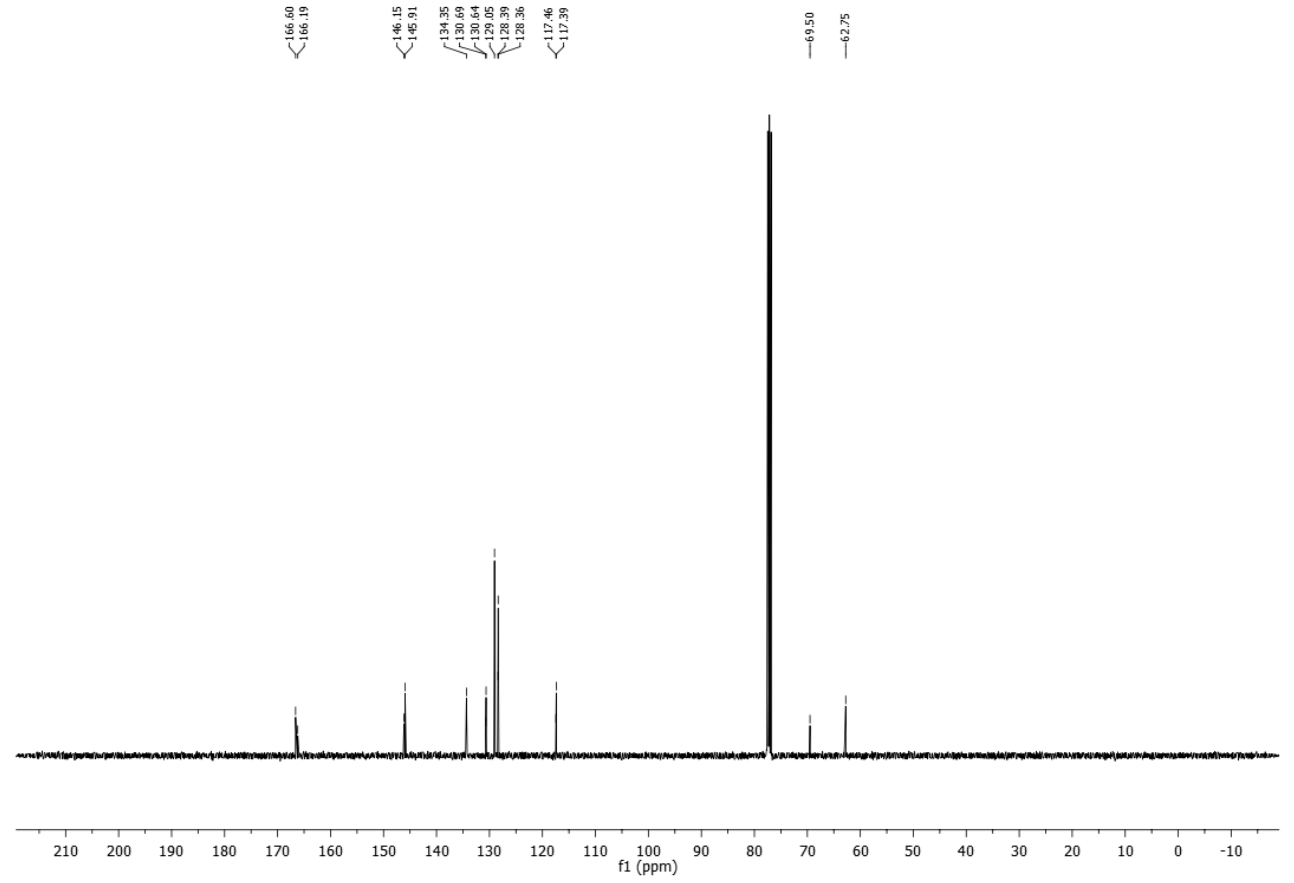

167.54
146.09
134.28
130.75
129.11
128.34
117.33
70.52
65.57
63.48
f1 (ppm)

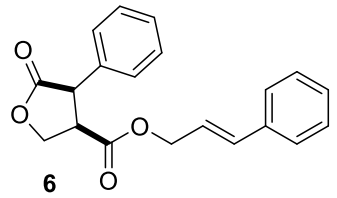

7.26
O
O
O
O
OH
1.98
4.10
6.06
2.00
1.88
2.06
1.00
f1 (ppm)

4ai$_2$


167.18
146.01
134.30
130.70
129.09
128.34
117.36
68.72
65.64
f1 (ppm)

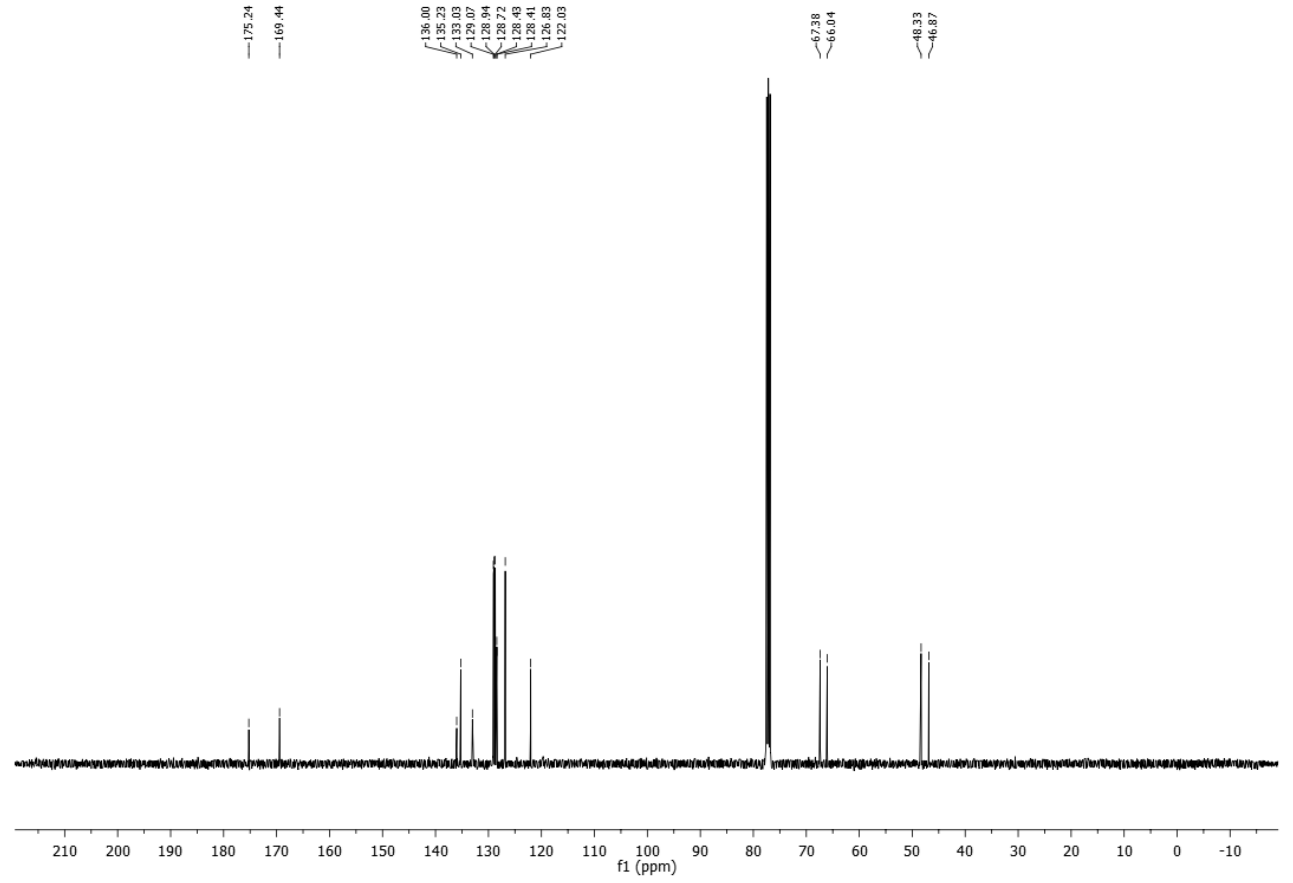

7.26
4ai3
2.95
6.06
8.93
2.99
1.00
1.97
2.01
f1 (ppm)

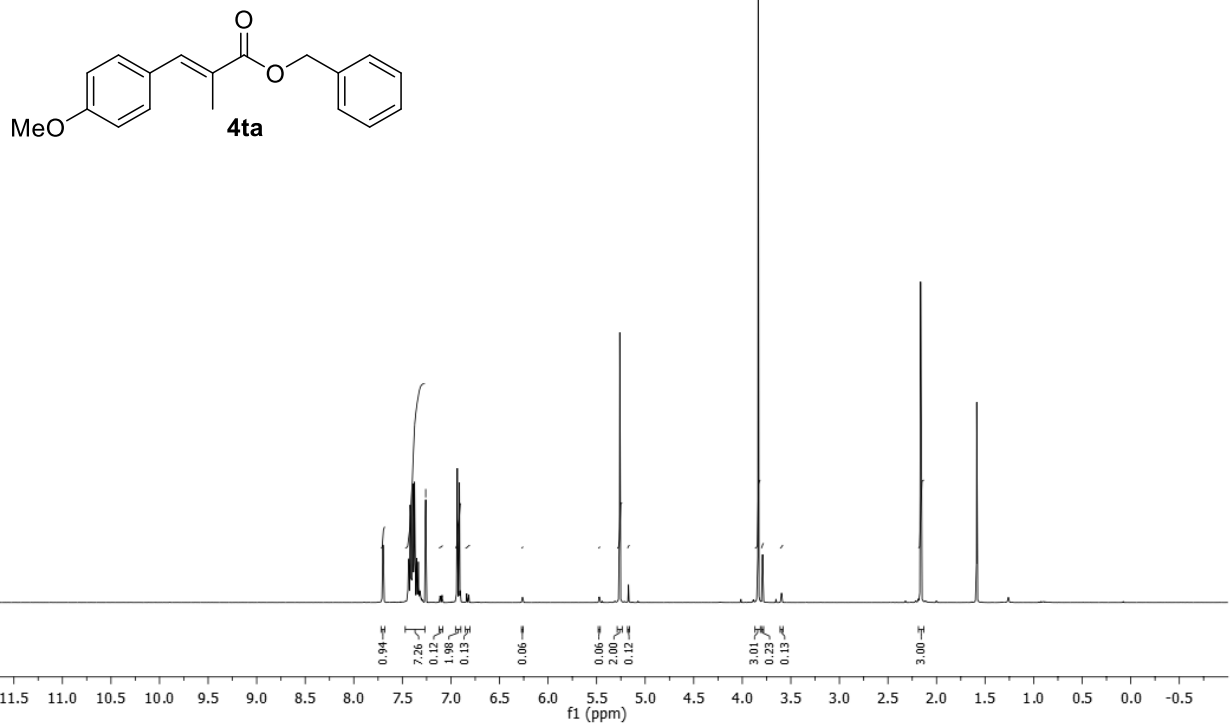

166.60
166.19
146.15
145.91
134.35
130.69
130.64
129.05
128.39
128.36
117.46
117.39
69.50
62.75
f1 (ppm)

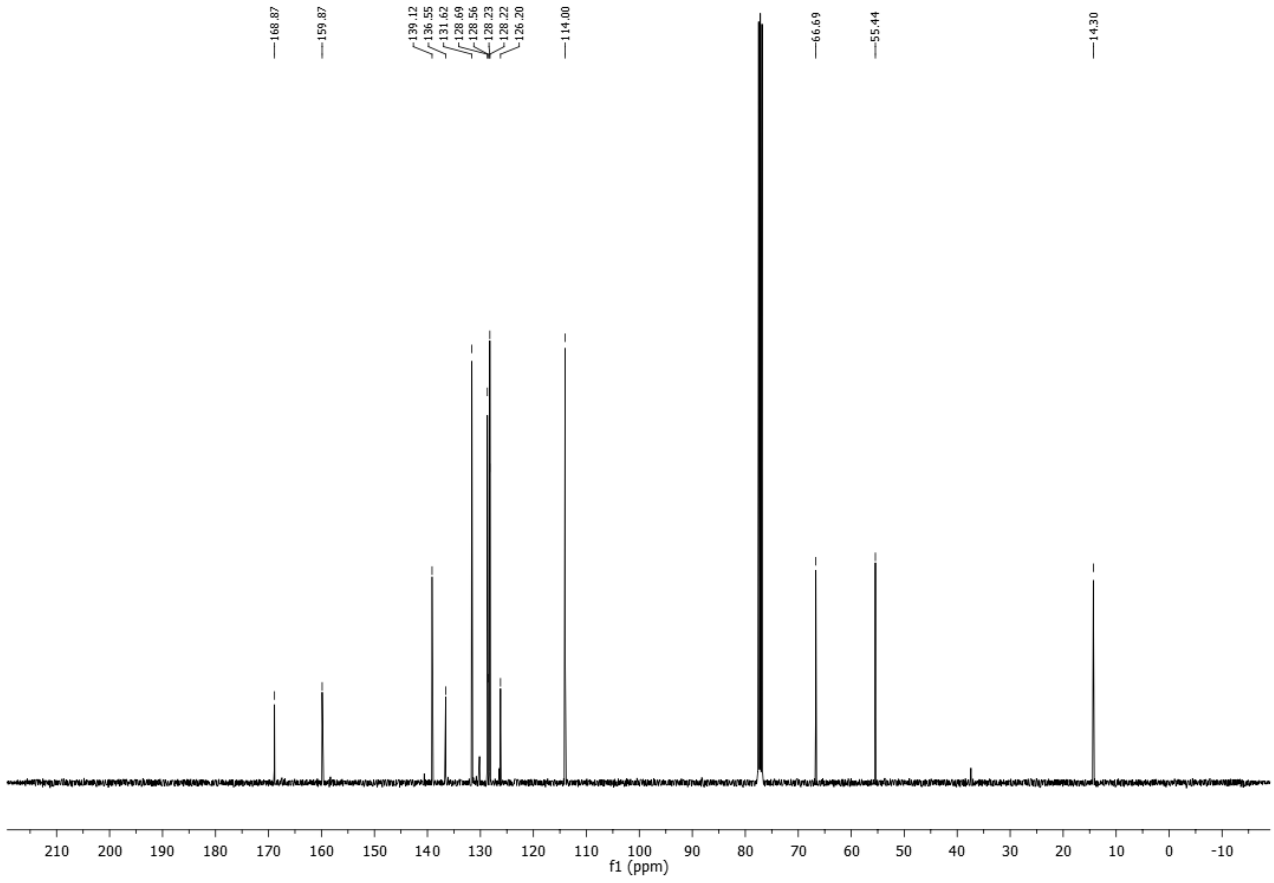

O
O
O
O
O

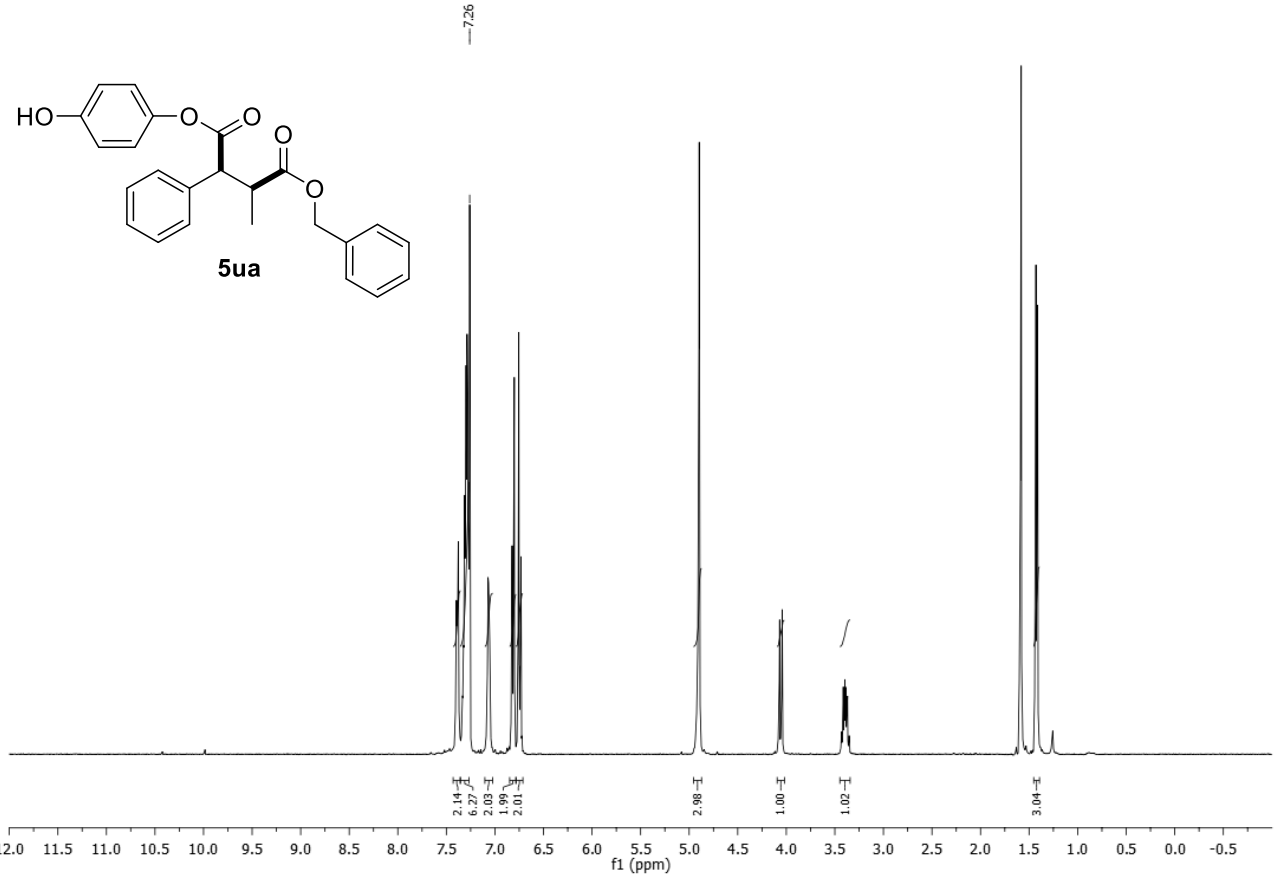
6

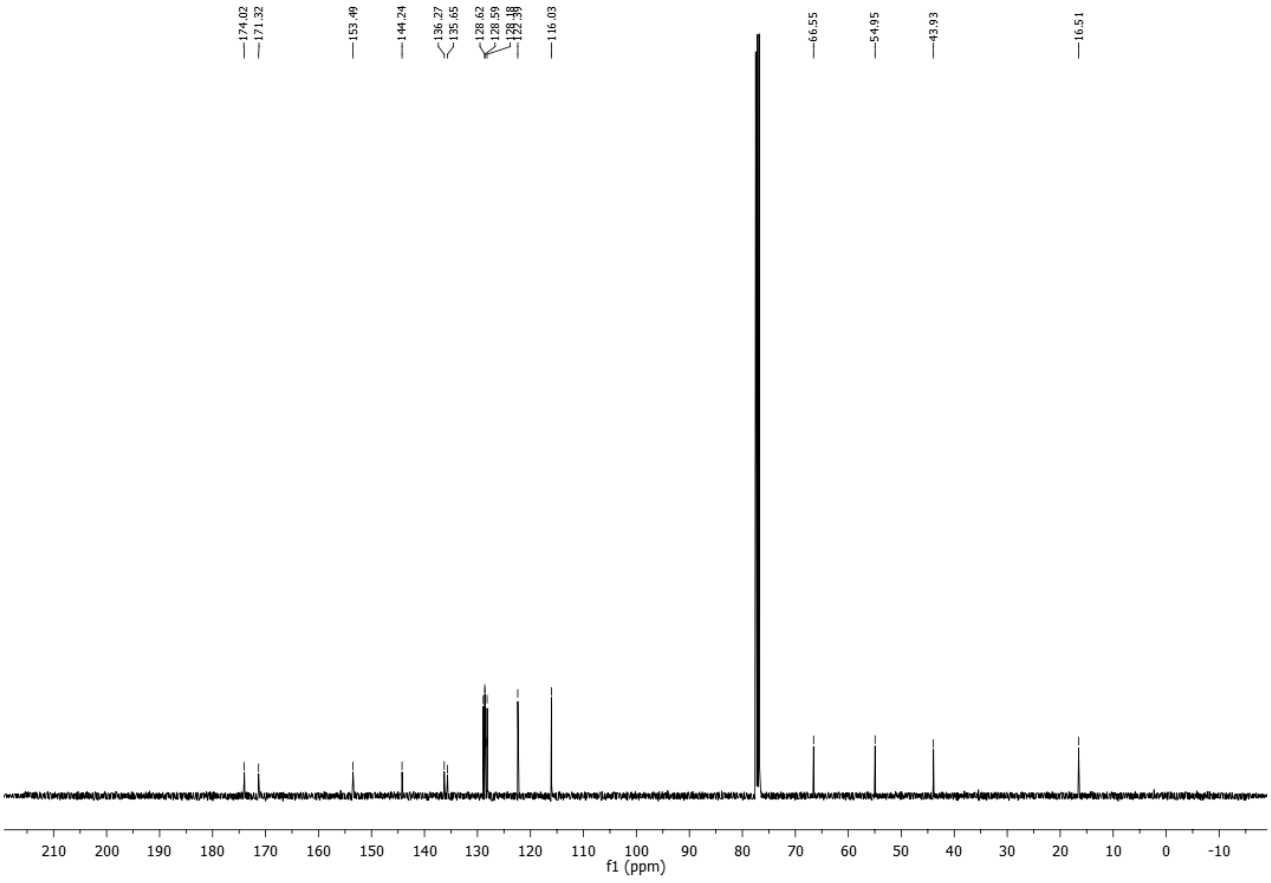
7.26
7.23
3.00
1.00
1.00
1.02
1.03
2.09
1.04
1.04
f1 (ppm)

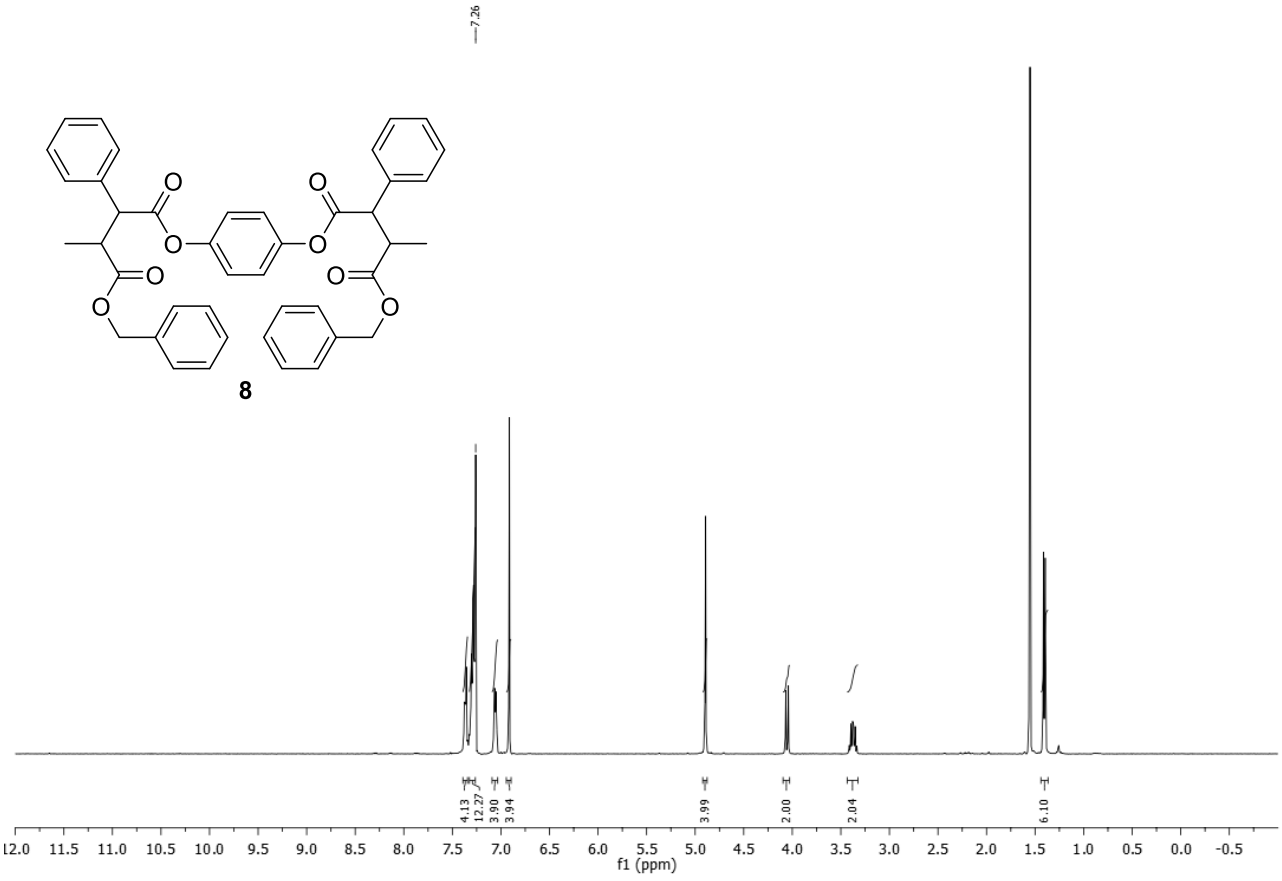

175.24
169.44
136.00
135.23
133.03
129.07
128.94
128.72
128.43
128.41
126.83
122.03
67.38
66.04
48.33
46.87
f1 (ppm)


MeO
4ta
7.26
0.94
7.26
0.12
1.98
0.13
0.06
0.06
2.00
0.12
3.01
0.23
0.13
3.00
f1 (ppm)

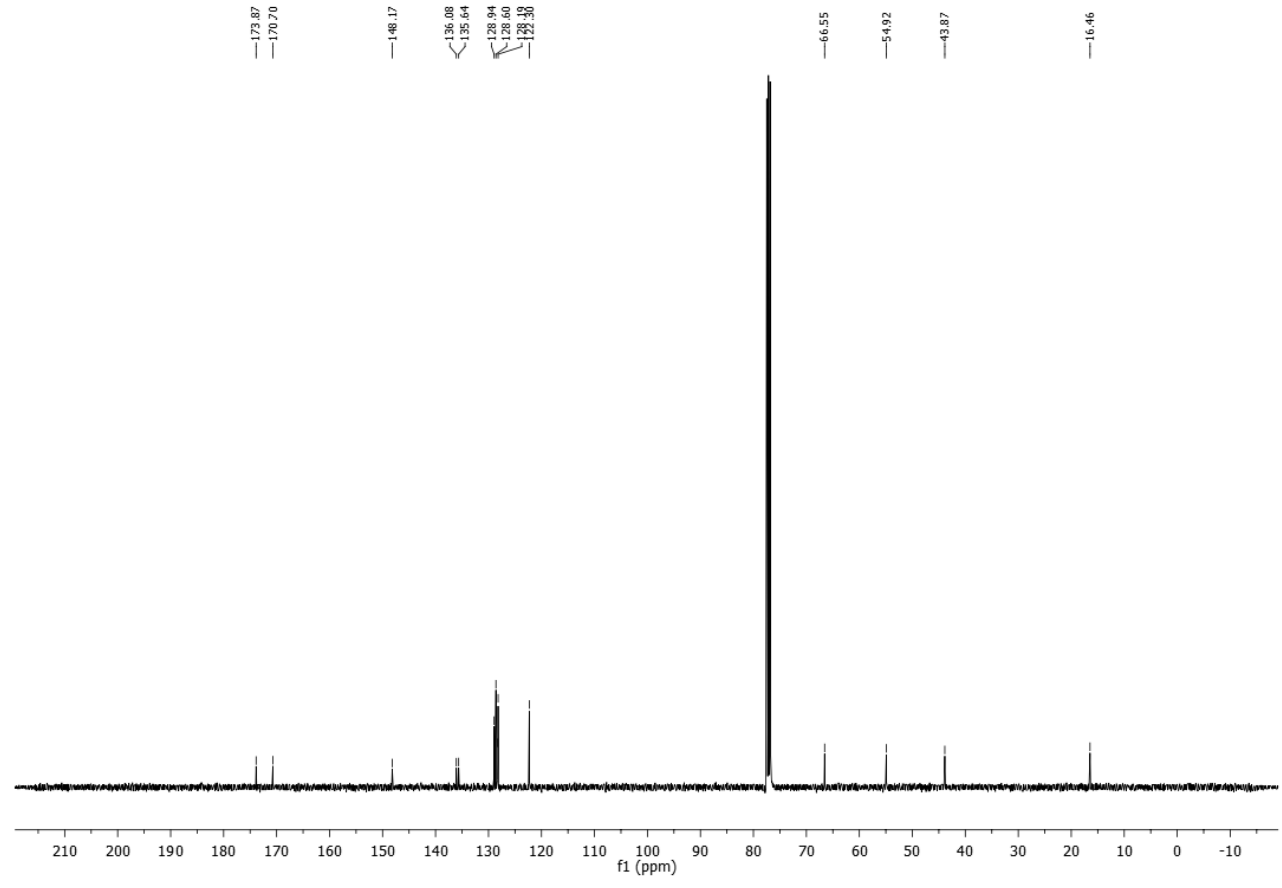

168.87
159.87
139.12
136.55
131.62
128.69
128.56
128.23
128.22
126.20
114.00
66.69
55.44
14.30
f1 (ppm)

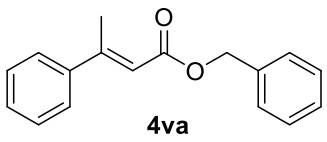

HO
O
O
O
O
5ua
7.26
2.14
6.27
2.03
1.99
2.01
2.98
1.00
1.02
3.04
f1 (ppm)


174.02
171.32
153.49
144.24
136.27
135.65
128.62
128.59
116.03
66.55
54.95
43.93
16.51
f1 (ppm)


7.26
4.13
12.27
3.90
3.94
3.99
2.00
2.04
6.10
f1 (ppm)

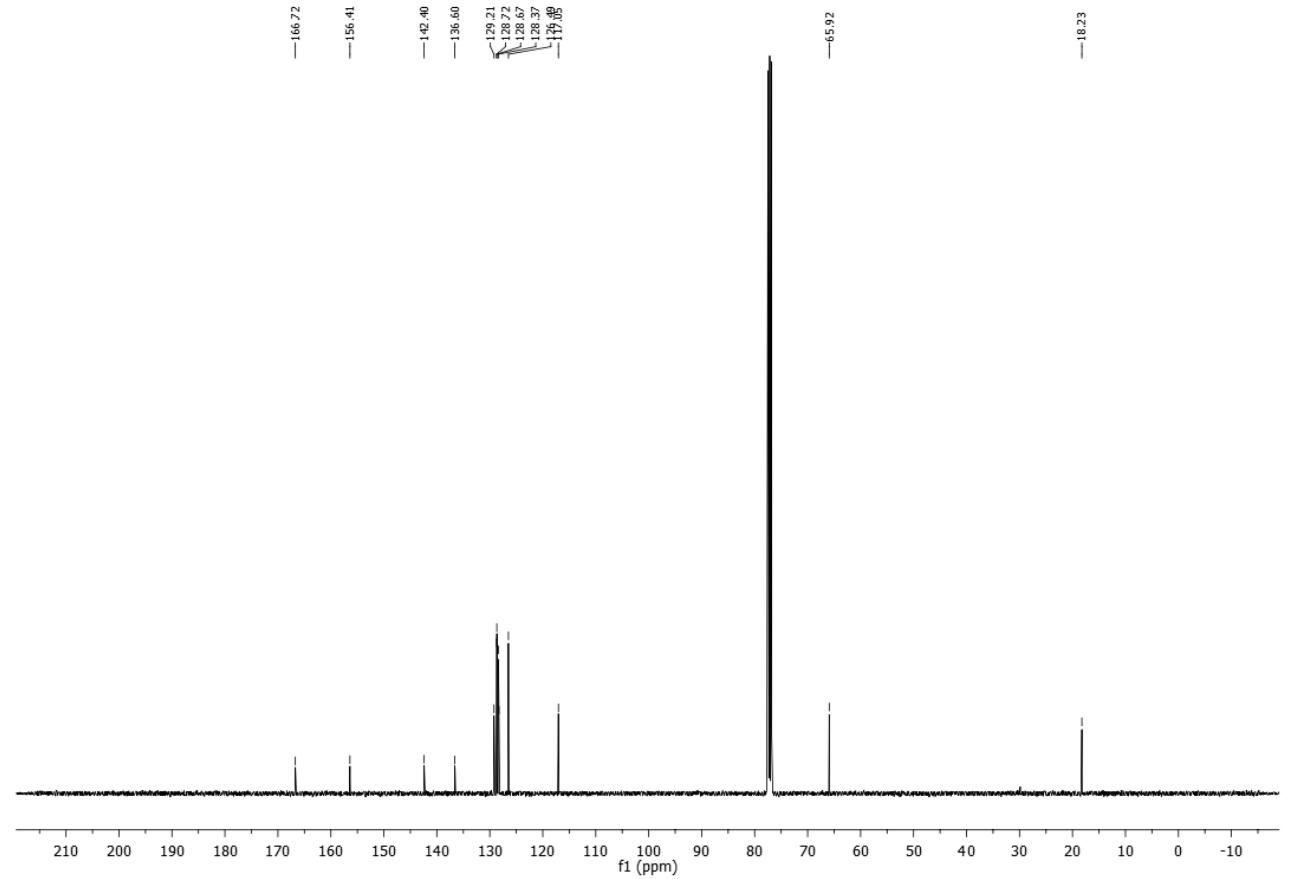
8

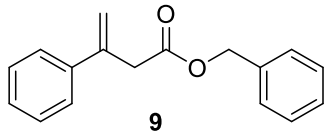

173.87
170.70
148.17
136.08
135.64
128.94
128.60
66.55
54.92
43.87
16.46
f1 (ppm)


O
O

4va

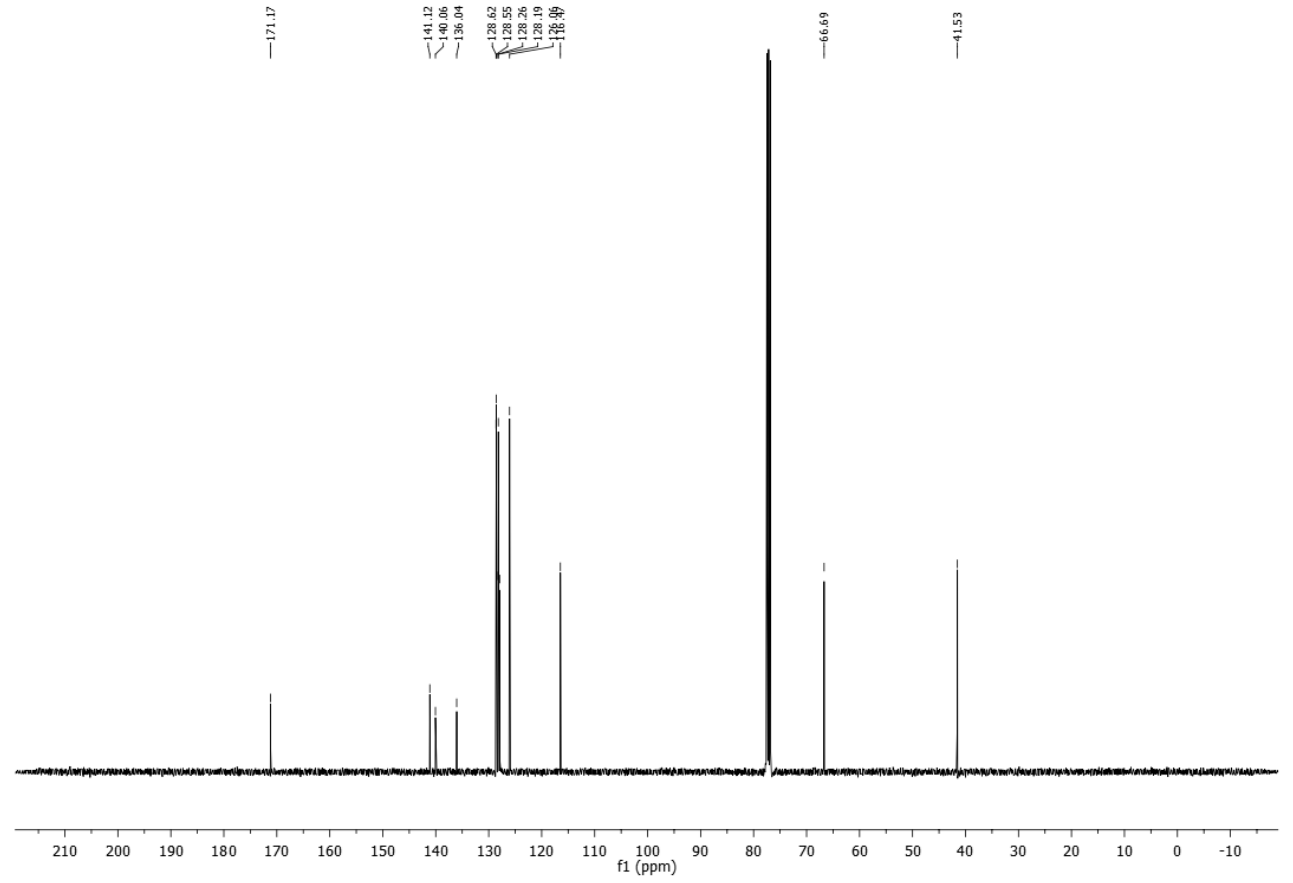
7.26
2.01
7.97
0.95
2.00
3.00
f1 (ppm)

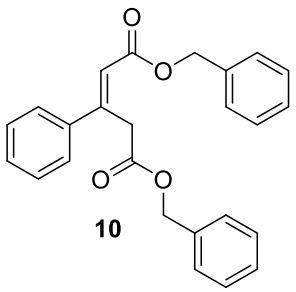

166.72
156.41
142.40
136.60
129.21
128.72
128.67
128.37
126.49
117.05
65.92
18.23
f1 (ppm)



9

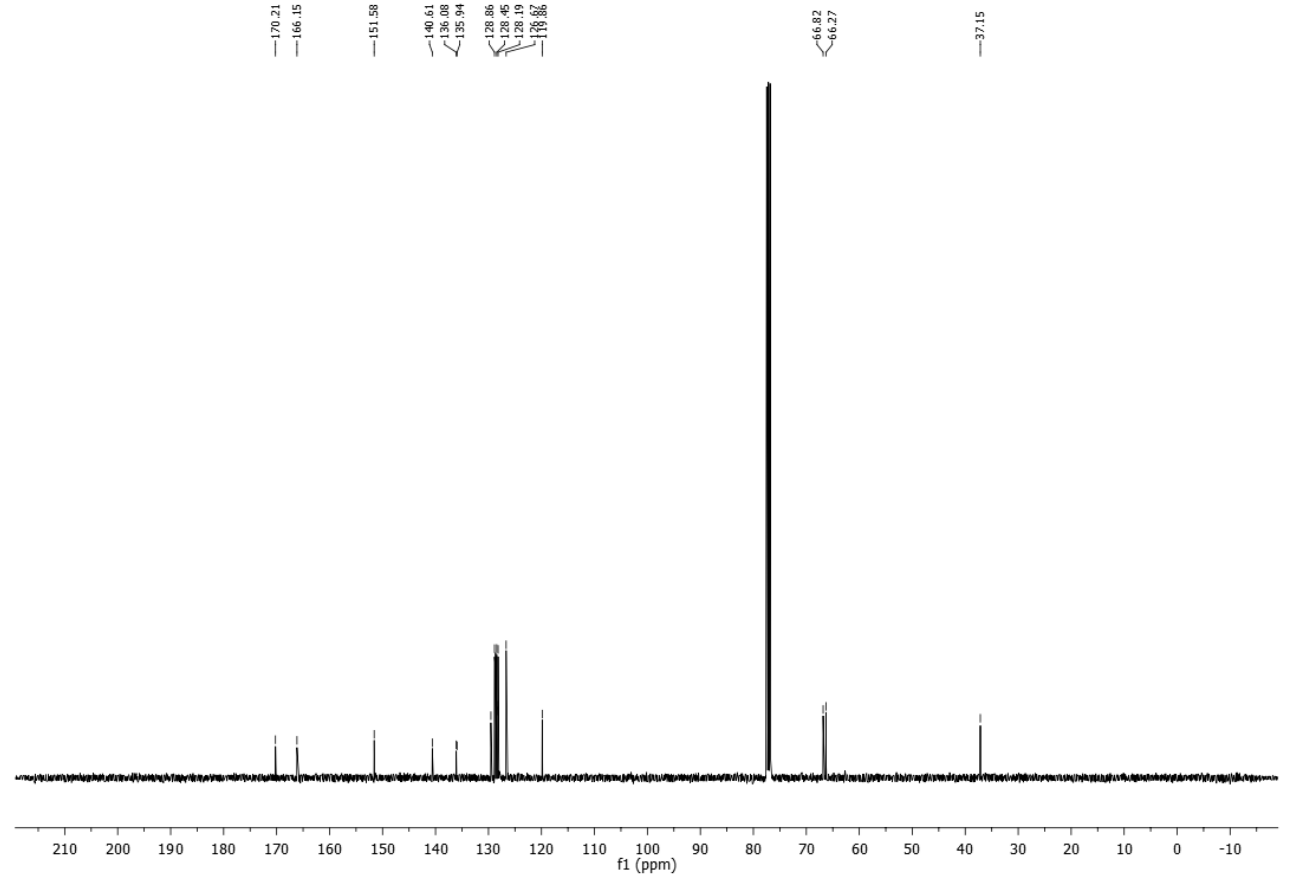
7.26
1.86
5.76
2.00
1.00
1.00
2.00
1.97
f1 (ppm)

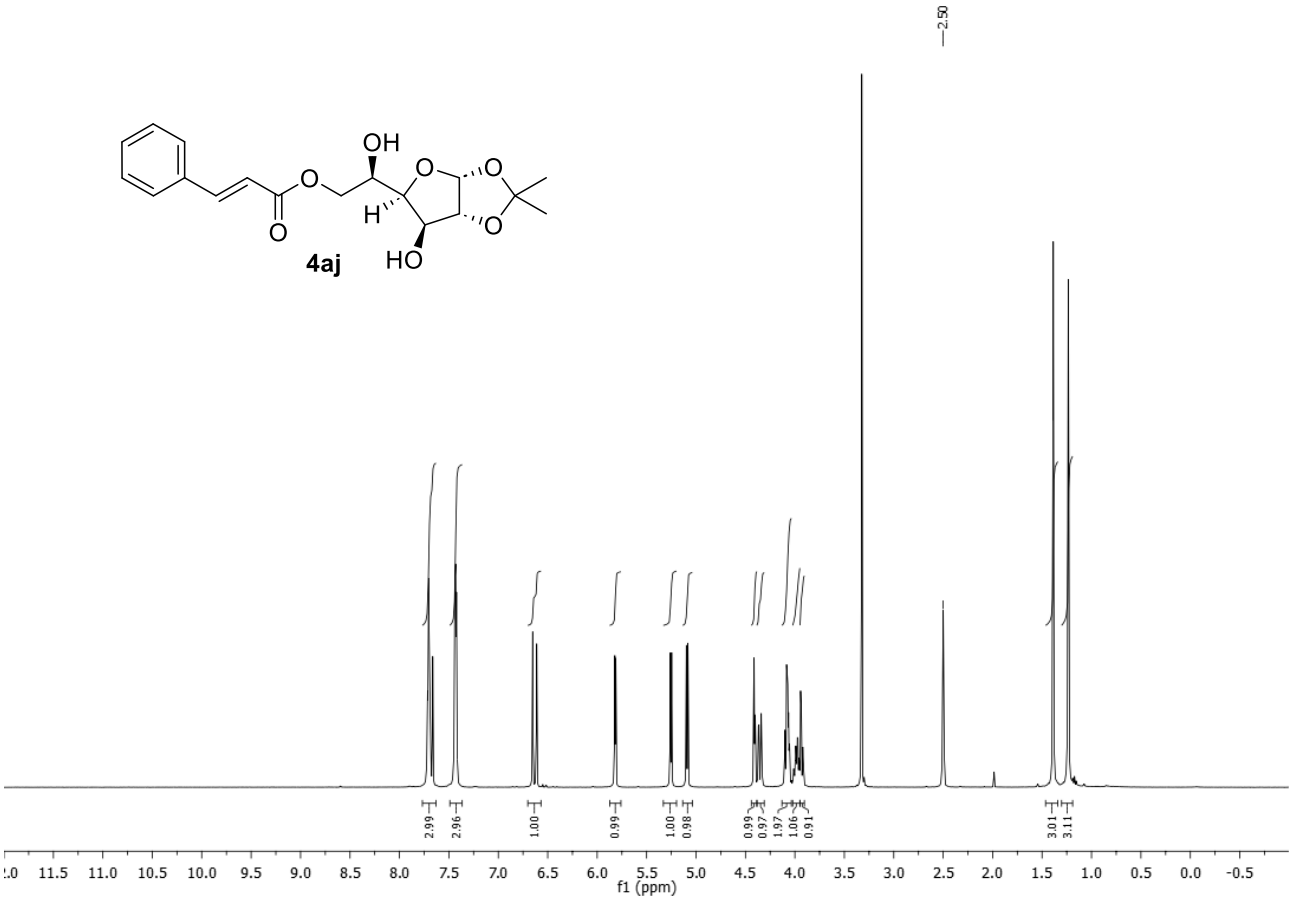

171.17
141.12
140.06
136.04
128.62
128.55
128.26
128.19
66.69
41.53
f1 (ppm)

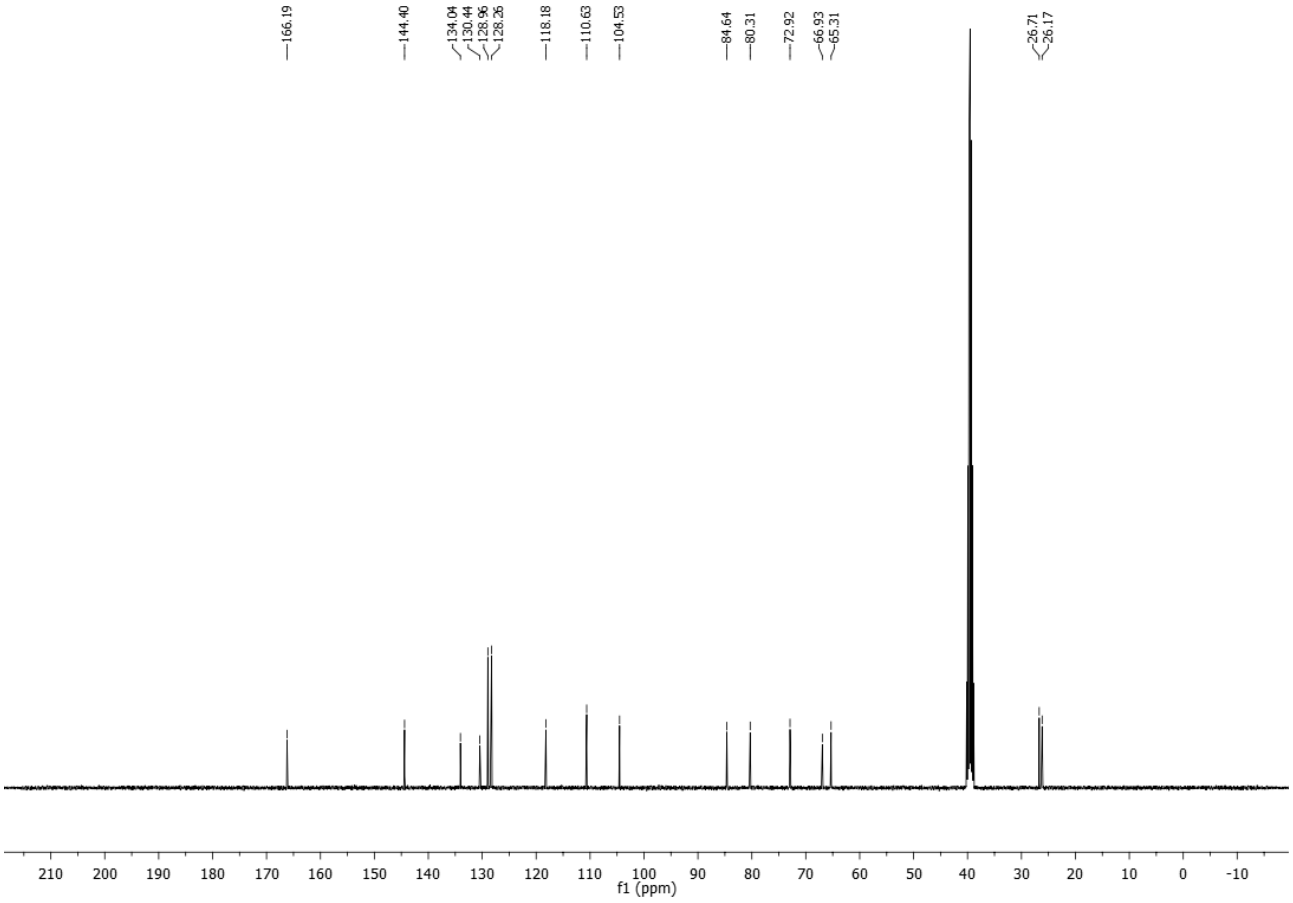

O
O
O
O

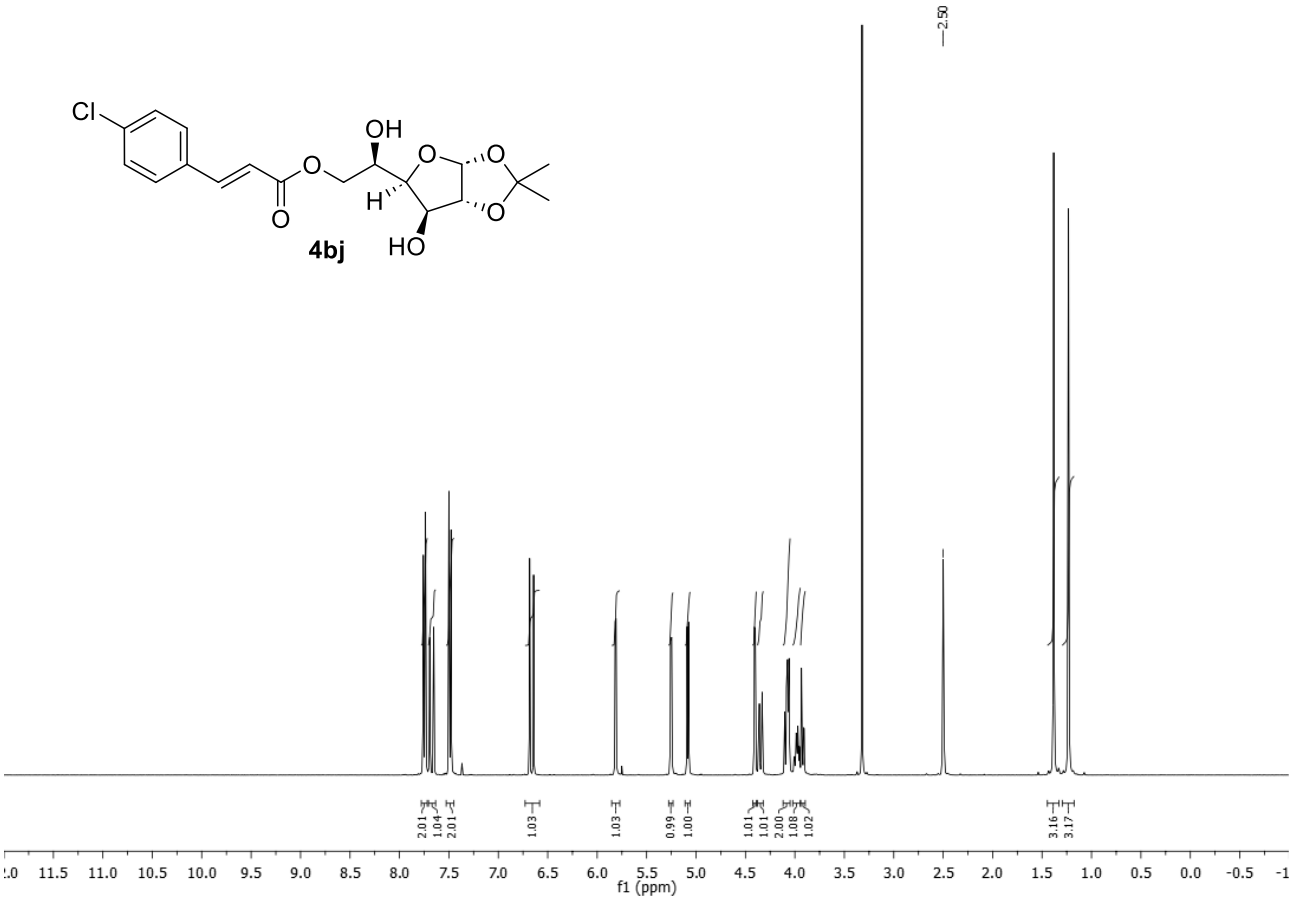
10

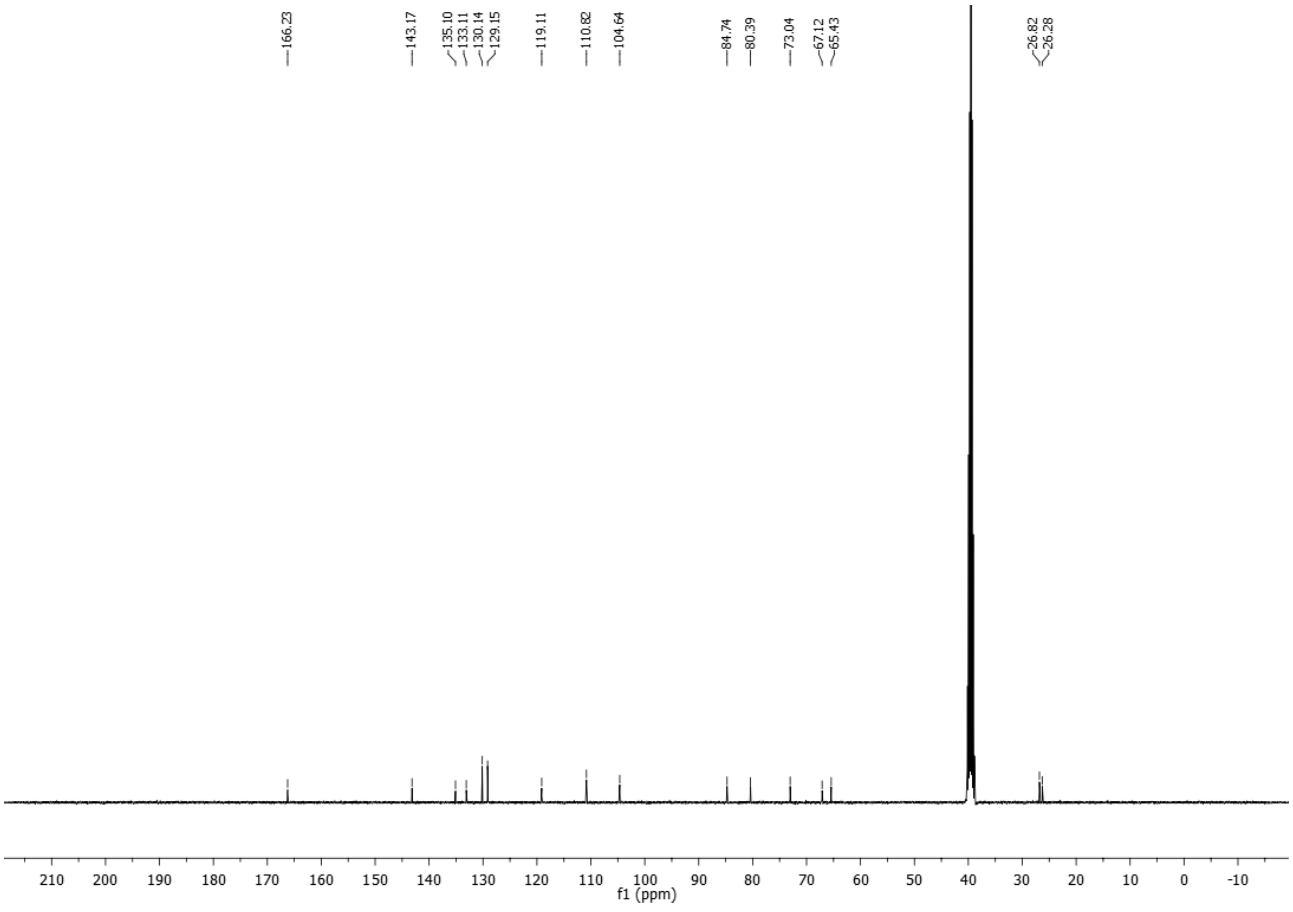
7.26
2.13
11.25
1.84
1.00
2.08
2.10
2.02
f1 (ppm)

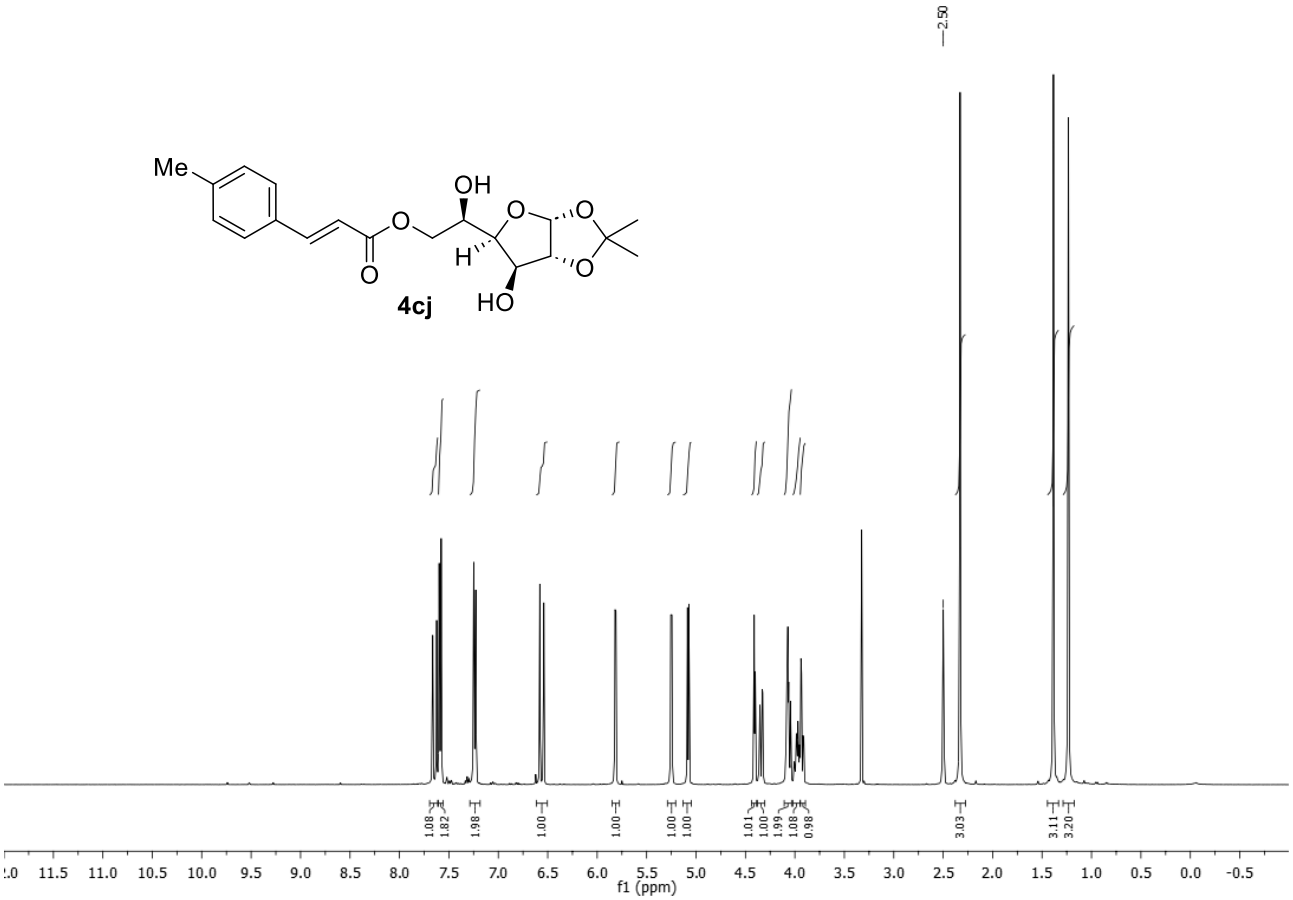

170.21
166.15
151.58
140.61
136.08
135.94
128.86
128.45
128.19
126.67
119.86
66.82
66.27
37.15
f1 (ppm)

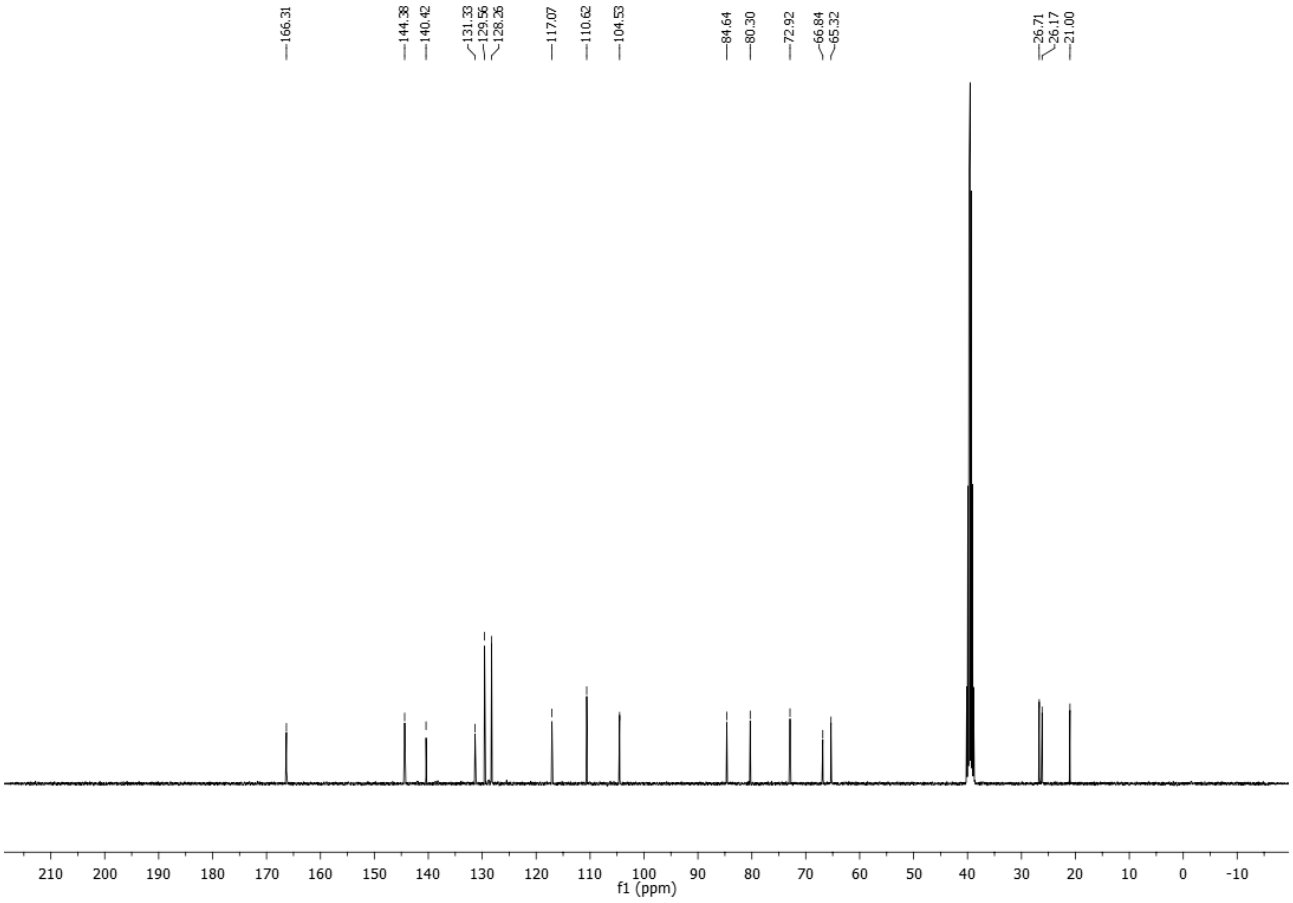

OH
O
O
O
O
H
HO
4aj
2.50
2.99
2.96
1.00
0.99
1.00
0.98
0.99
0.97
1.97
1.06
0.91
3.01
3.11
f1 (ppm)

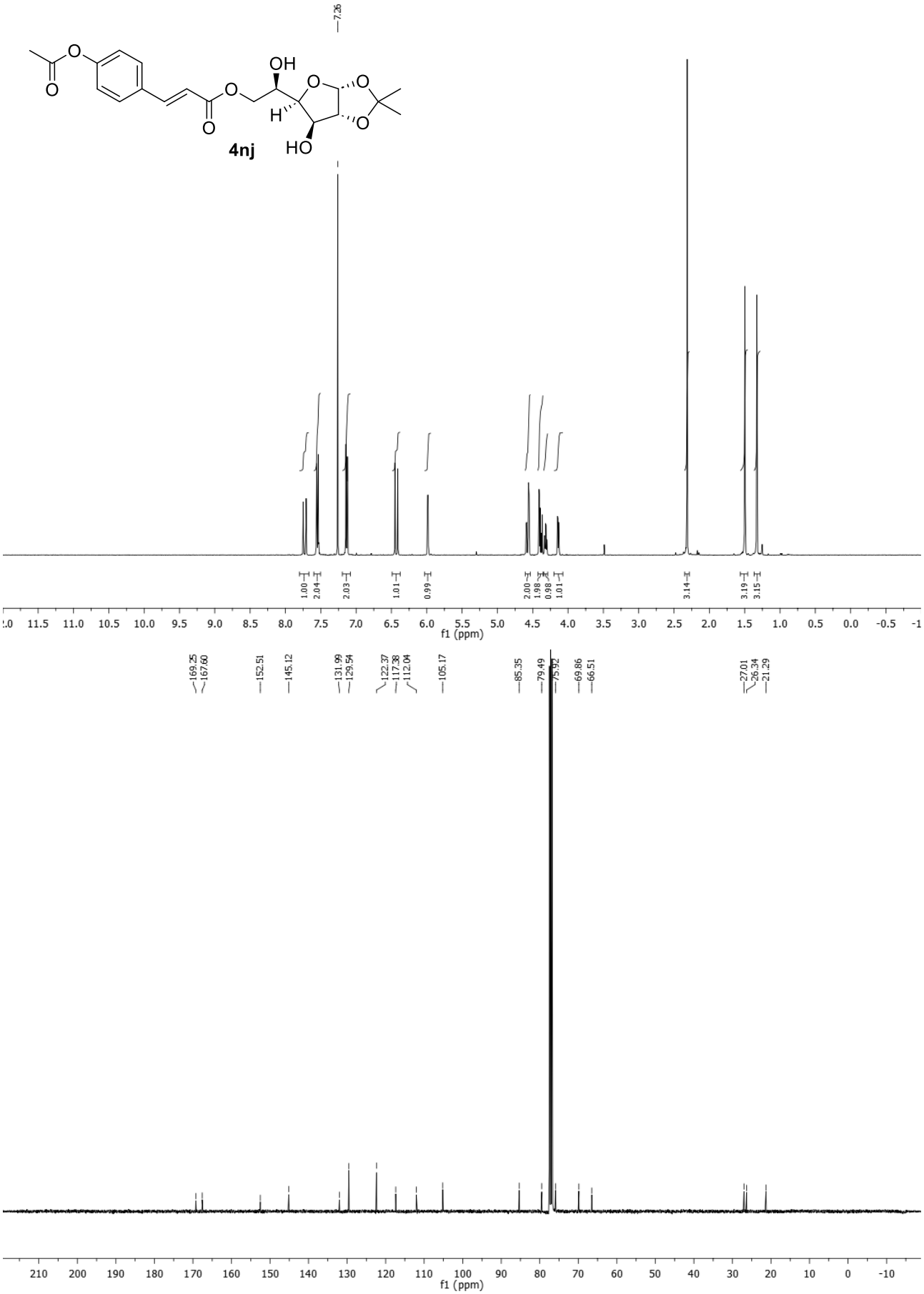

166.19
144.40
134.04
130.44
128.96
128.26
118.18
110.63
104.53
84.64
80.31
72.92
66.93
65.31
26.71
26.17
f1 (ppm)

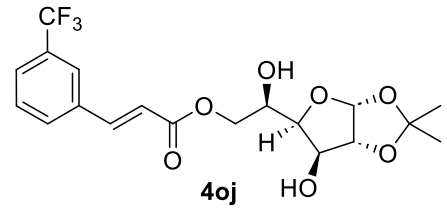

Cl
OH
O
O
O
H
O
O
HO
4bj
2.50
2.01
1.04
2.01
1.03
1.03
0.99
1.00
1.01
1.01
2.00
1.08
1.02
3.16
3.17
f1 (ppm)


166.23
143.17
135.10
133.11
130.14
129.15
119.11
110.82
104.64
84.74
80.39
73.04
67.12
65.43
26.82
26.28
f1 (ppm)


Me
OH
O
O
O
H
O
O
HO
4cj
2.50
1.08
1.82
1.98
1.00
1.00
1.00
1.00
1.01
1.00
1.99
1.08
0.98
3.03
3.11
3.20
f1 (ppm)

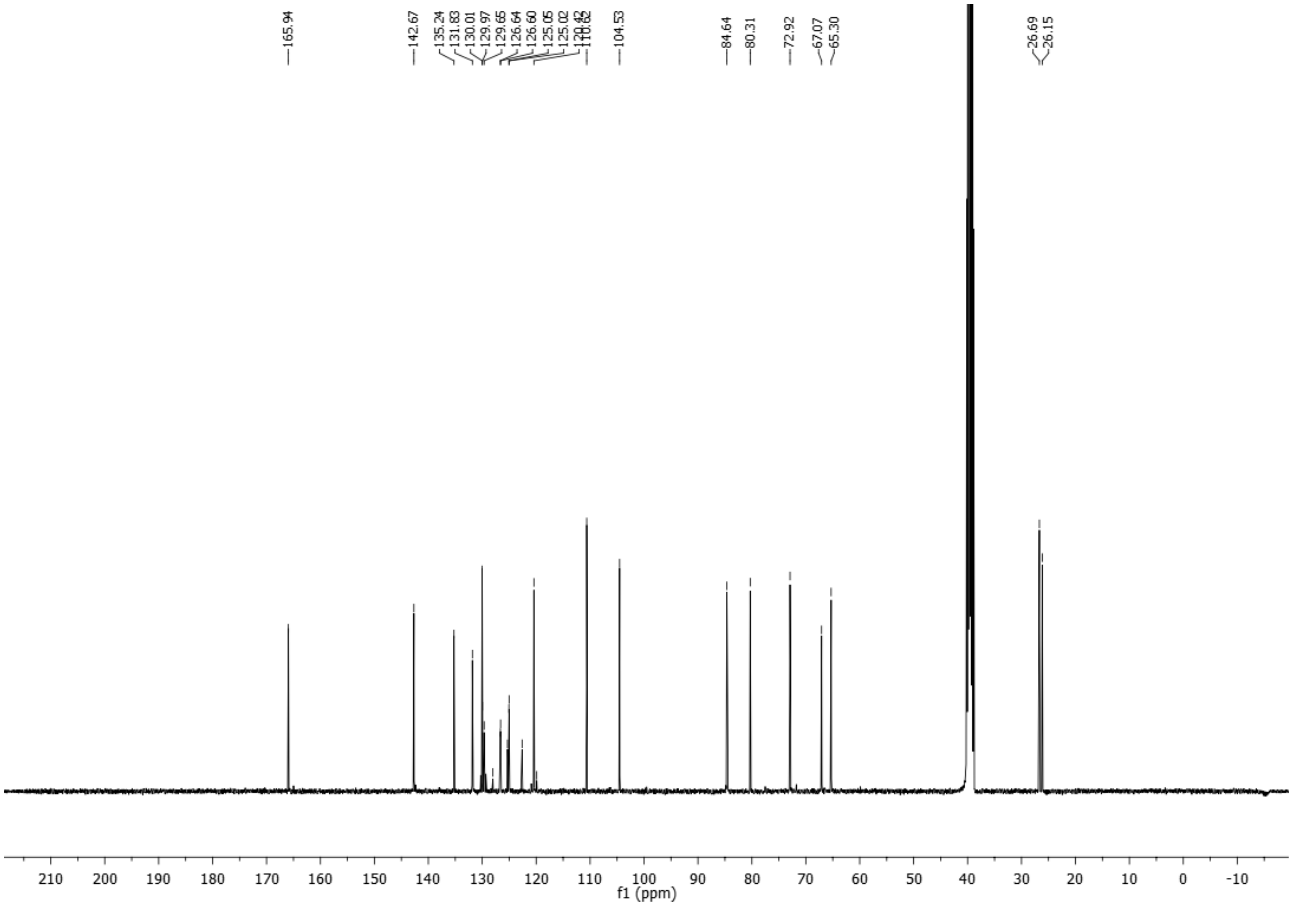

166.31
144.38
140.42
131.33
129.56
128.26
117.07
110.62
104.53
84.64
80.30
72.92
66.84
65.32
26.71
26.17
21.00
f1 (ppm)

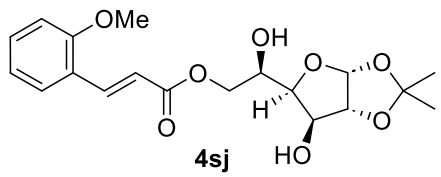

7.26
OH
O
O
O
O
O
O
H
HO
4nj
1.00
2.04
2.03
1.01
0.99
2.00
1.98
0.98
1.01
3.14
3.19
3.15
f1 (ppm)
169.25
167.60
152.51
145.12
131.99
129.54
122.37
117.38
112.04
105.17
85.35
79.49
75.92
69.86
66.51
27.01
26.34
21.29
f1 (ppm)


CF3
OH
O
O
O
H
O
O
HO

4oj

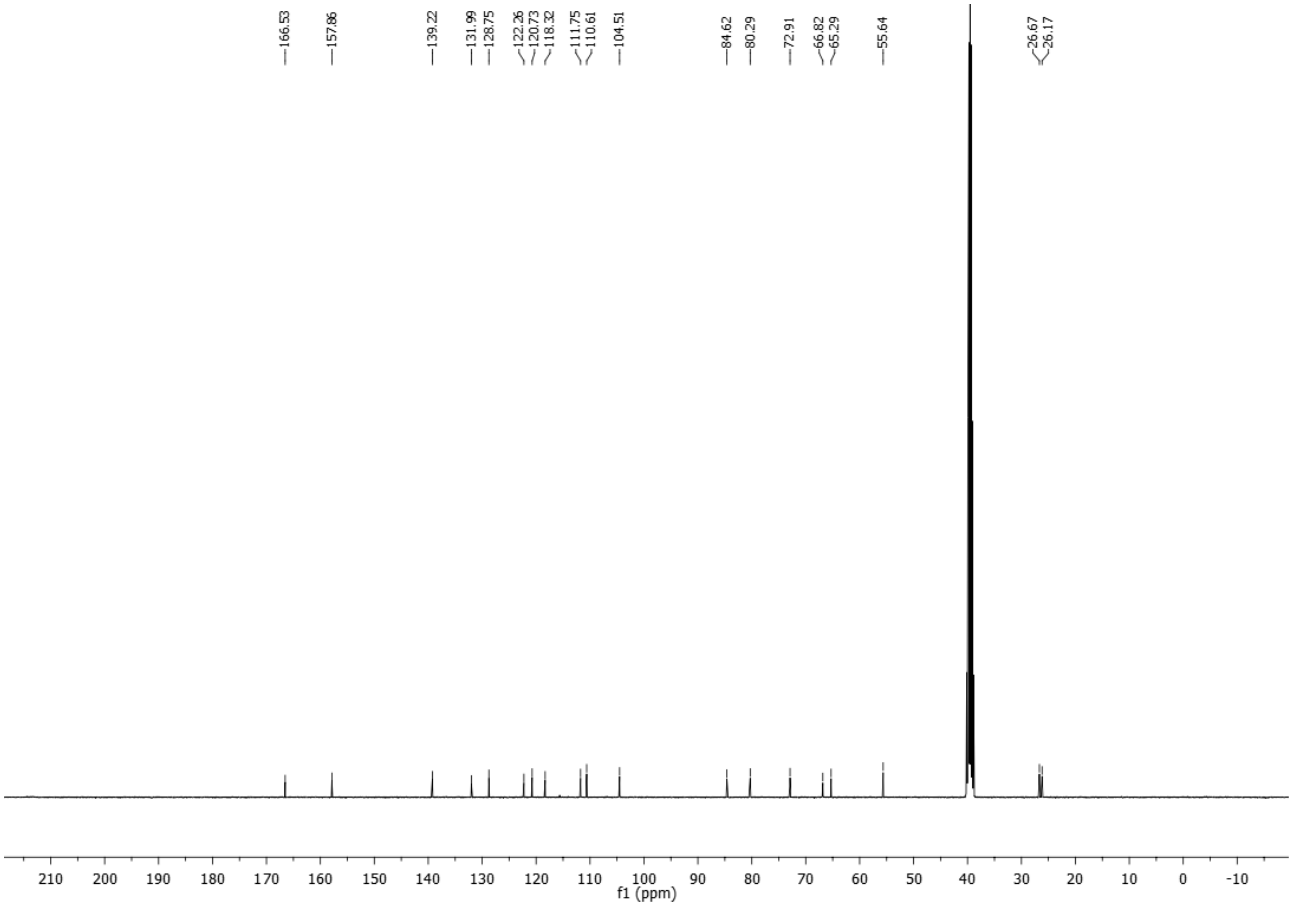
2.50
1.00
1.00
2.03
1.04
1.07
1.08
1.04
1.04
1.02
0.99
1.99
1.09
0.99
3.07
3.11
f1 (ppm)

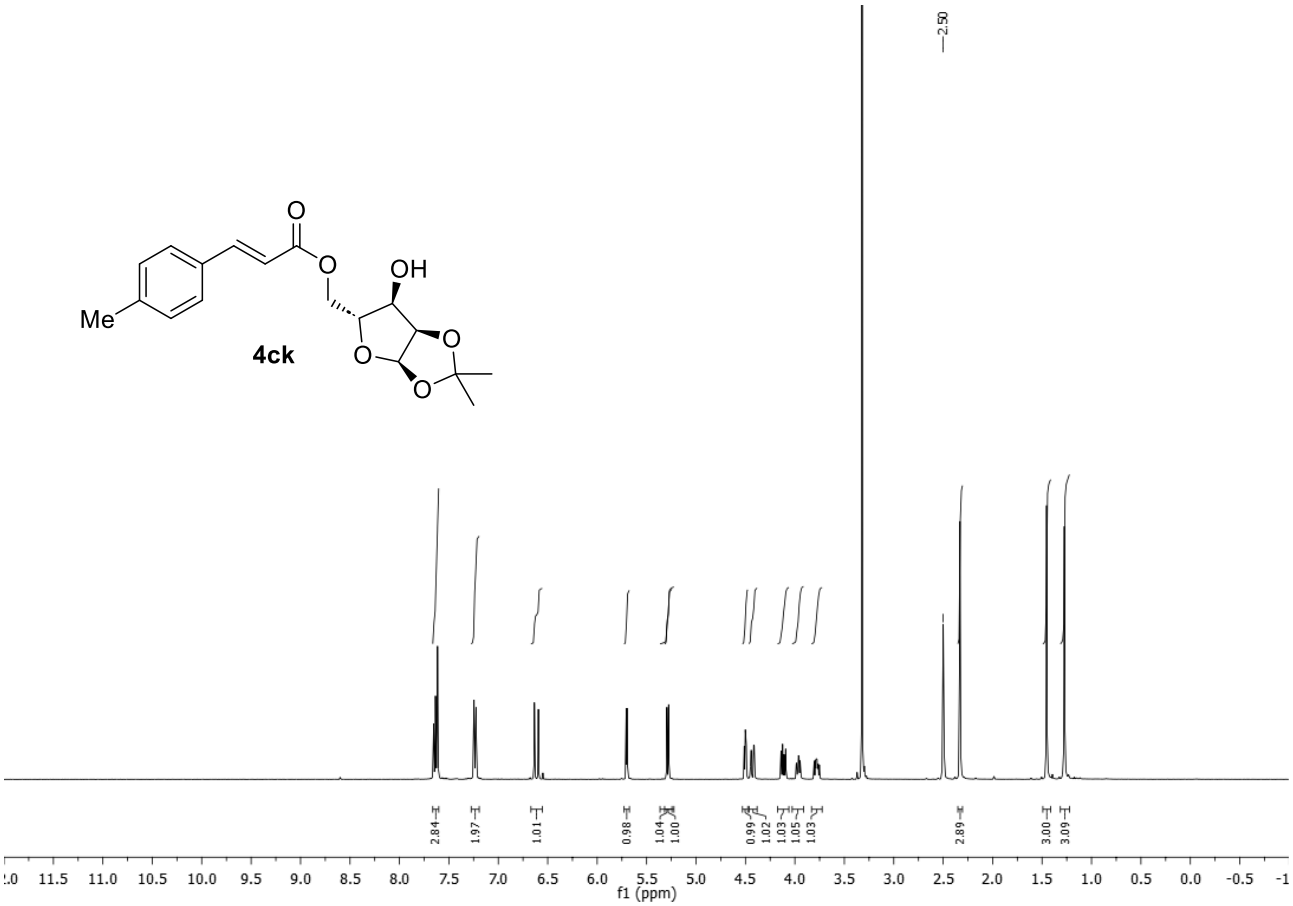

165.94
142.67
135.24
131.83
130.01
129.97
129.65
126.64
126.60
125.05
125.02
120.42
110.62
104.53
84.64
80.31
72.92
67.07
65.30
26.69
26.15
f1 (ppm)

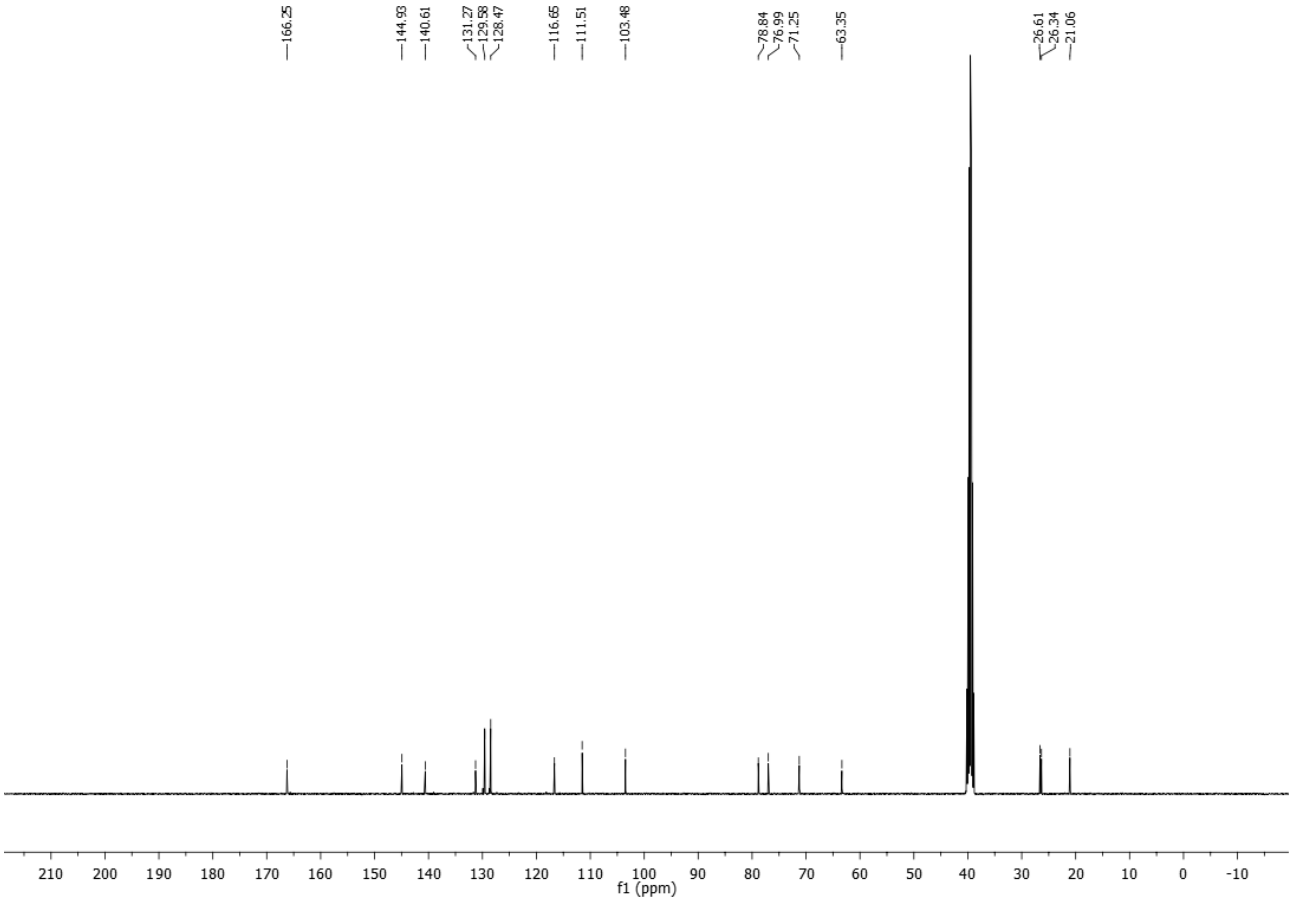

OMe
OH
O
O
O
O
H
O
HO

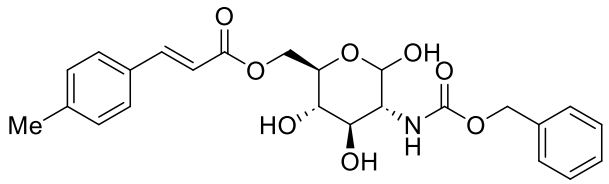
4sj

2.50
0.98
1.00
0.99
0.99
1.00
0.99
1.00
1.00
1.00
1.00
2.00
2.10
3.02
3.13
3.19
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


166.53
157.86
139.22
131.99
128.75
122.26
120.73
118.32
111.75
110.61
104.51
84.62
80.29
72.91
66.82
65.29
55.64
26.67
26.17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

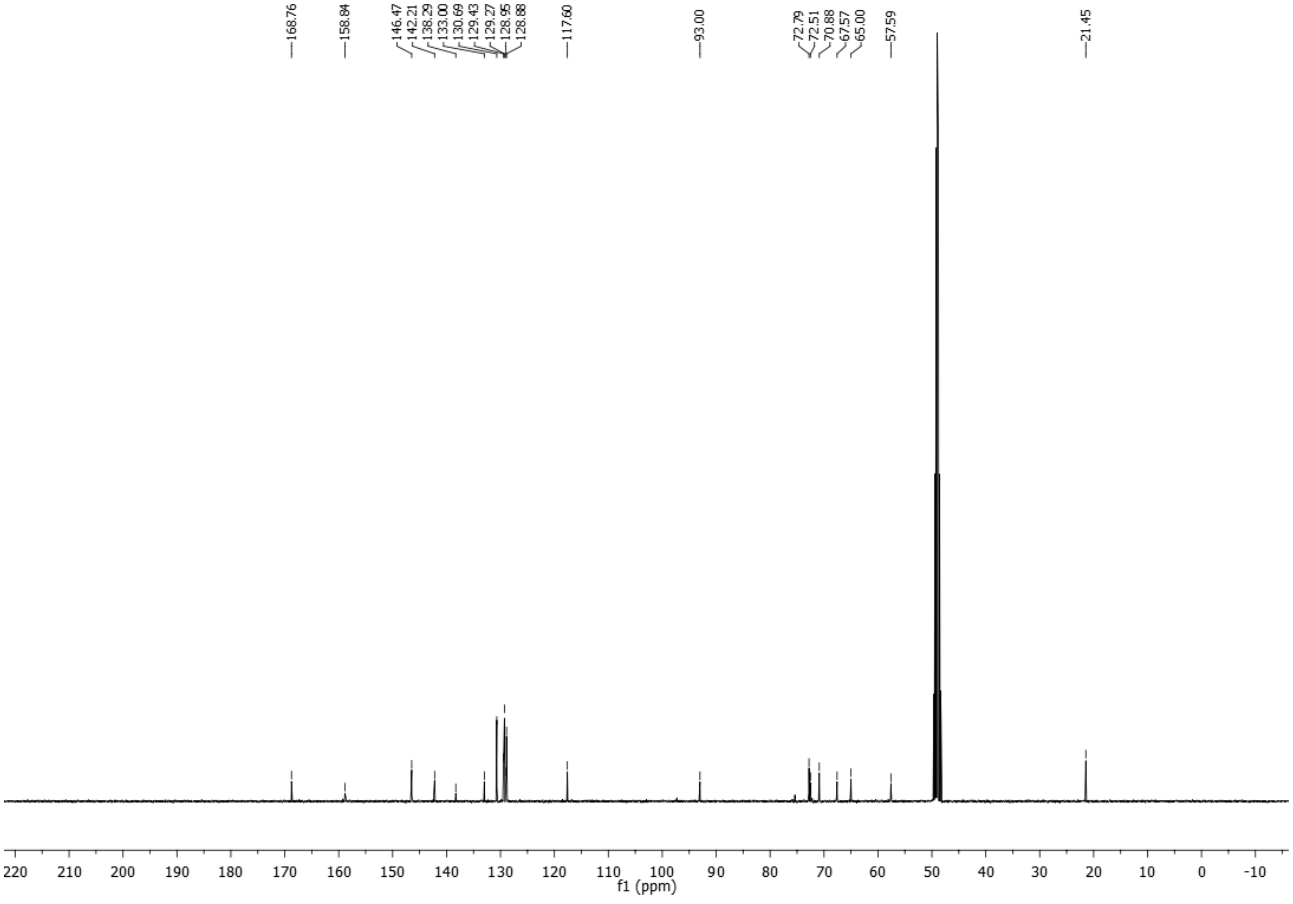

Me
O
O
OH
O
O
O
4ck
2.50
2.84
1.97
1.01
0.98
1.04
1.00
0.99
1.02
1.03
1.05
1.03
2.89
3.00
3.09
f1 (ppm)

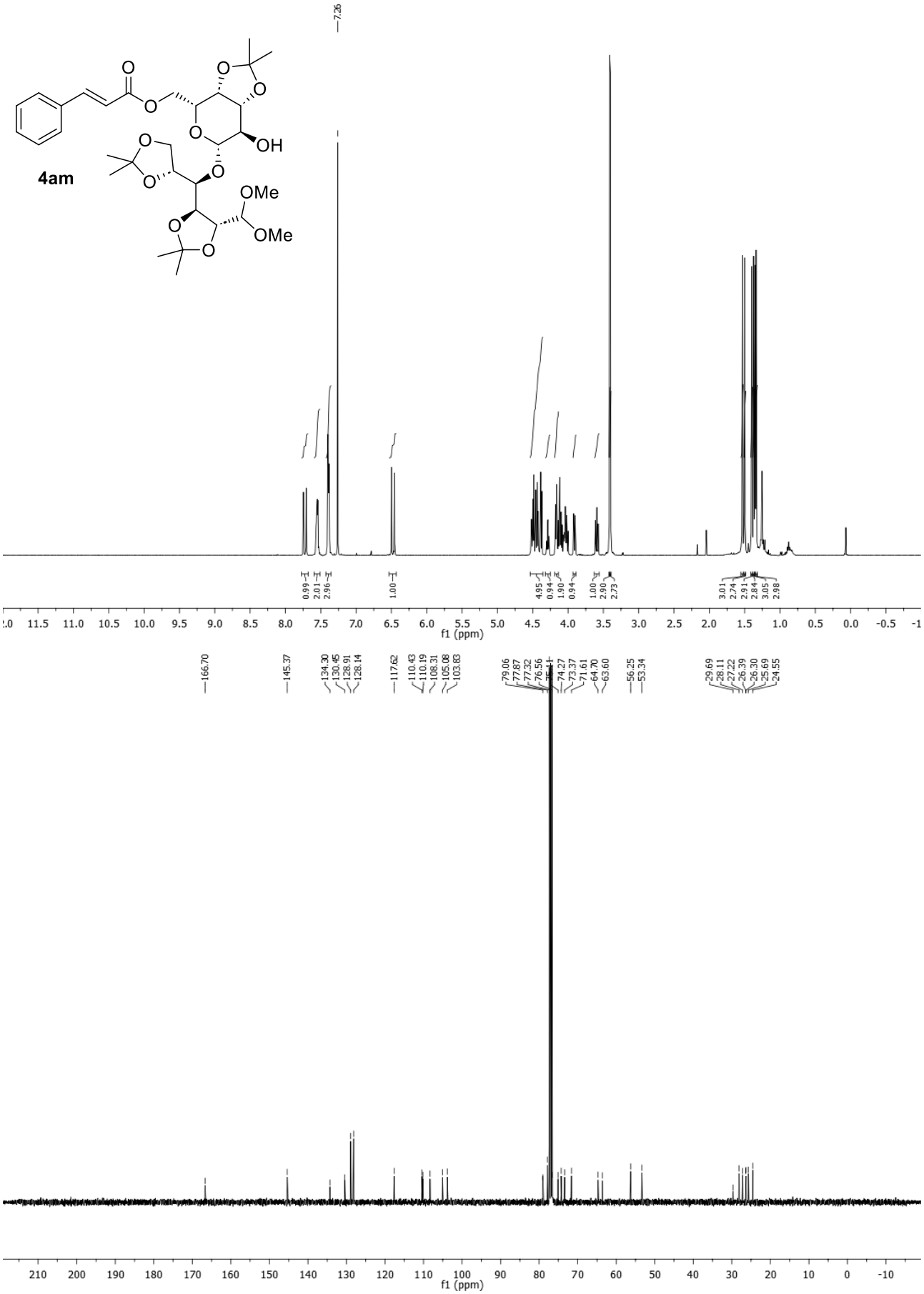

166.25
144.93
140.61
131.27
129.58
128.47
116.65
111.51
103.48
78.84
76.99
71.25
63.35
26.61
26.34
21.06
f1 (ppm)

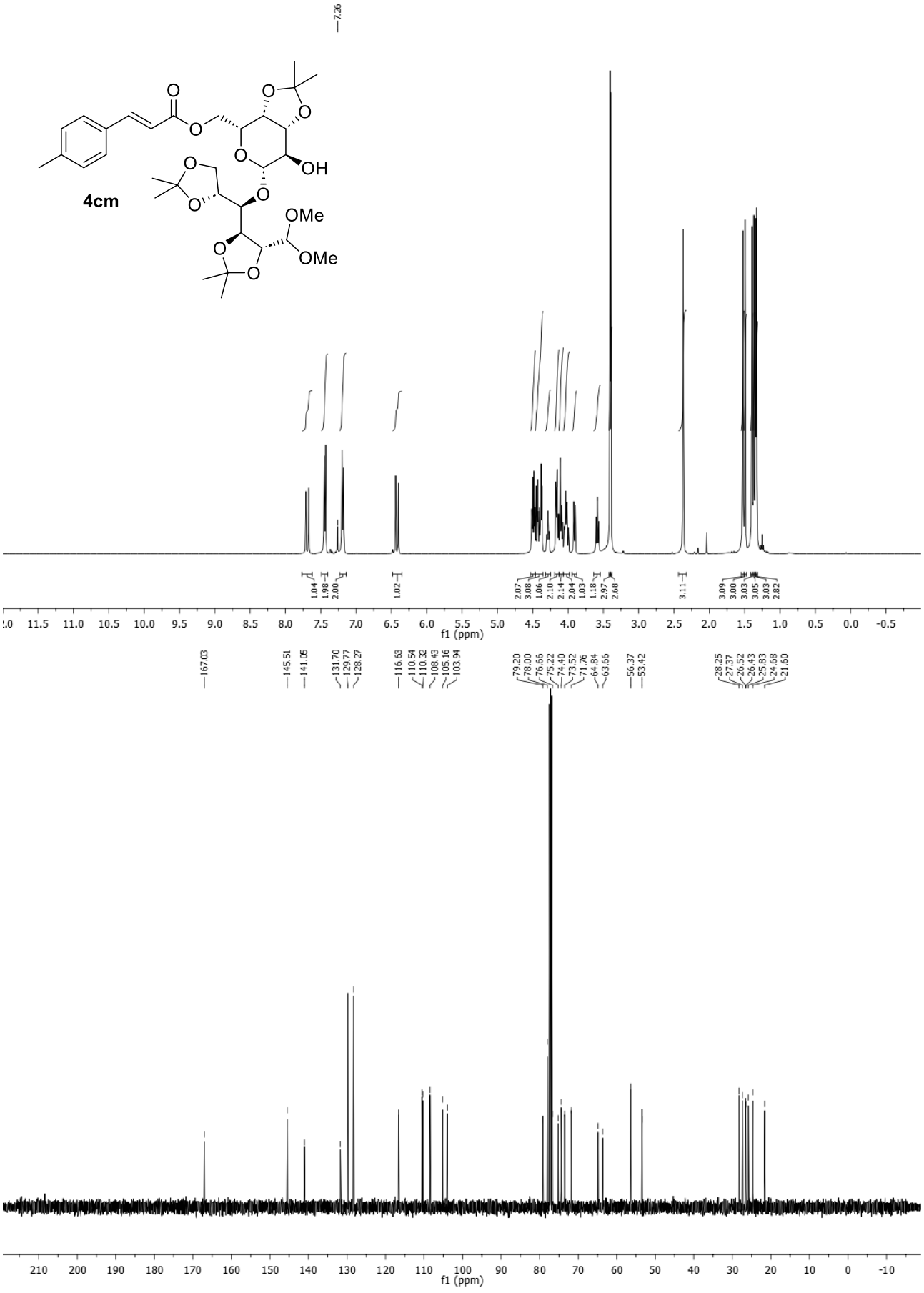


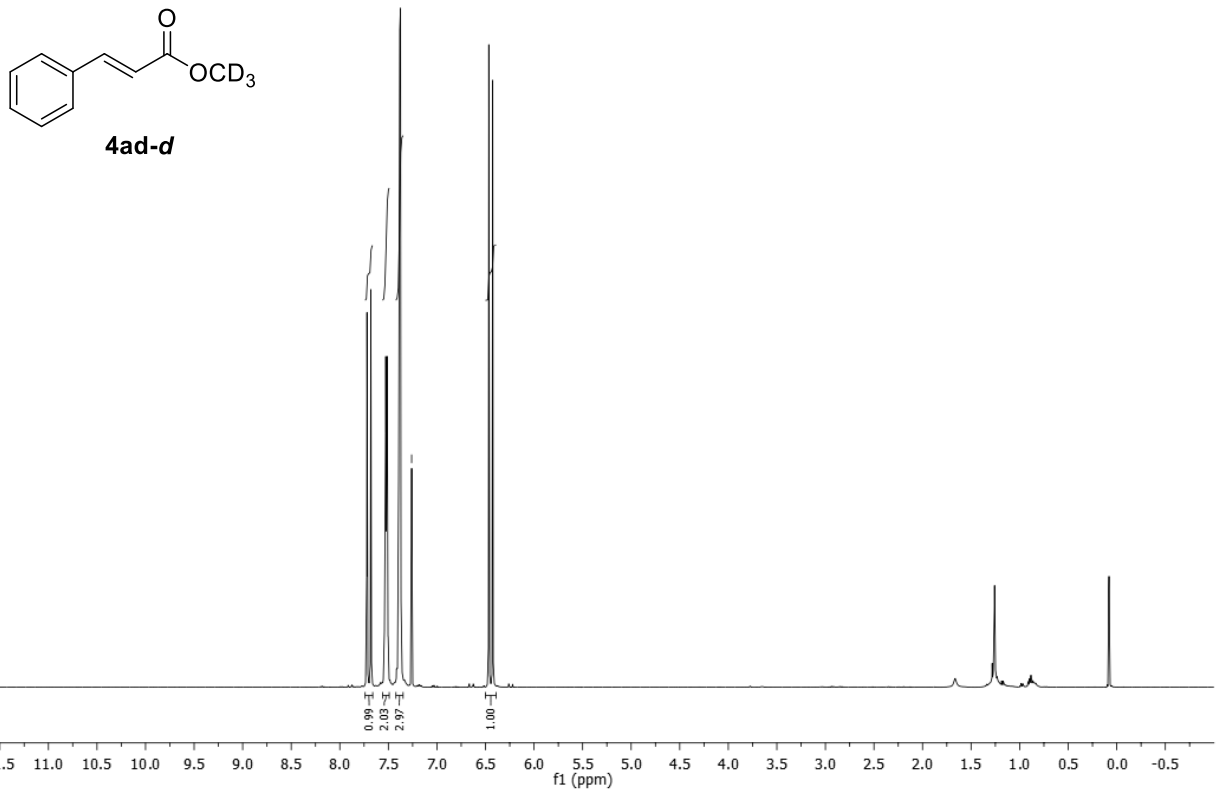
4cl

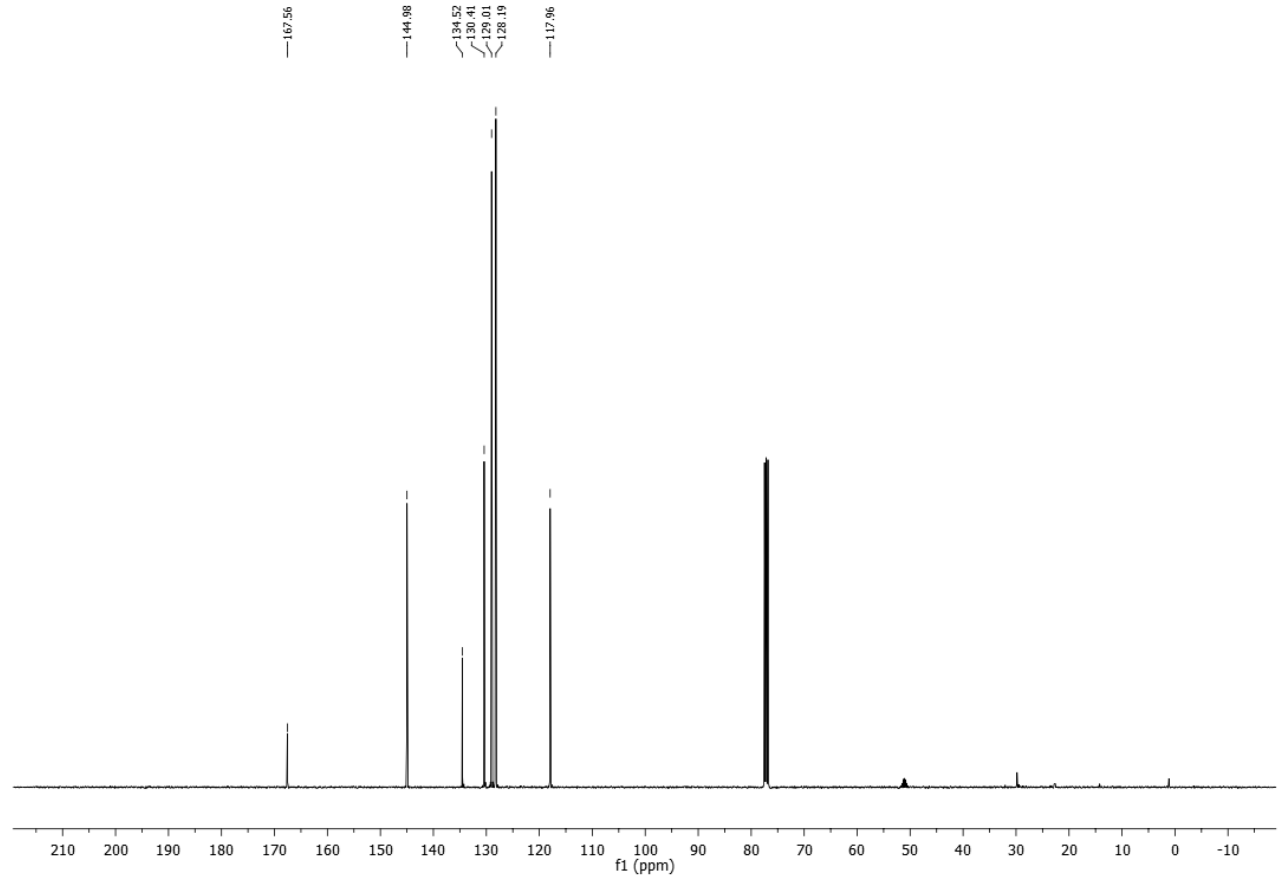
α/β = 0.85:0.15

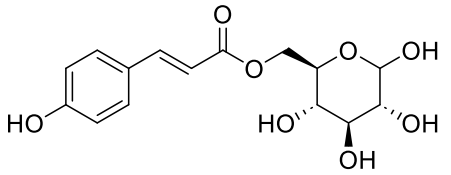



4am
OH
OMe
OMe
7.26
f1 (ppm)
166.70
145.37
134.30
130.45
128.91
128.14
117.62
110.43
110.19
108.31
105.08
103.83
79.06
77.87
77.32
76.56
74.27
73.37
71.61
64.70
63.60
56.25
53.34
29.69
28.11
27.22
26.39
26.30
25.69
24.55


4cm
OH
OMe
OMe
7.26
1.04
1.98
2.00
1.02
2.07
3.08
1.06
2.10
2.14
2.04
1.03
1.18
2.97
2.68
3.11
3.09
3.00
3.03
3.05
3.03
2.82
f1 (ppm)
167.03
145.51
141.05
131.70
129.77
128.27
116.63
110.54
110.32
108.43
105.16
103.94
79.20
78.00
76.66
75.22
74.40
73.52
71.76
64.84
63.66
56.37
53.42
28.25
27.37
26.52
26.43
25.83
24.68
21.60
f1 (ppm)

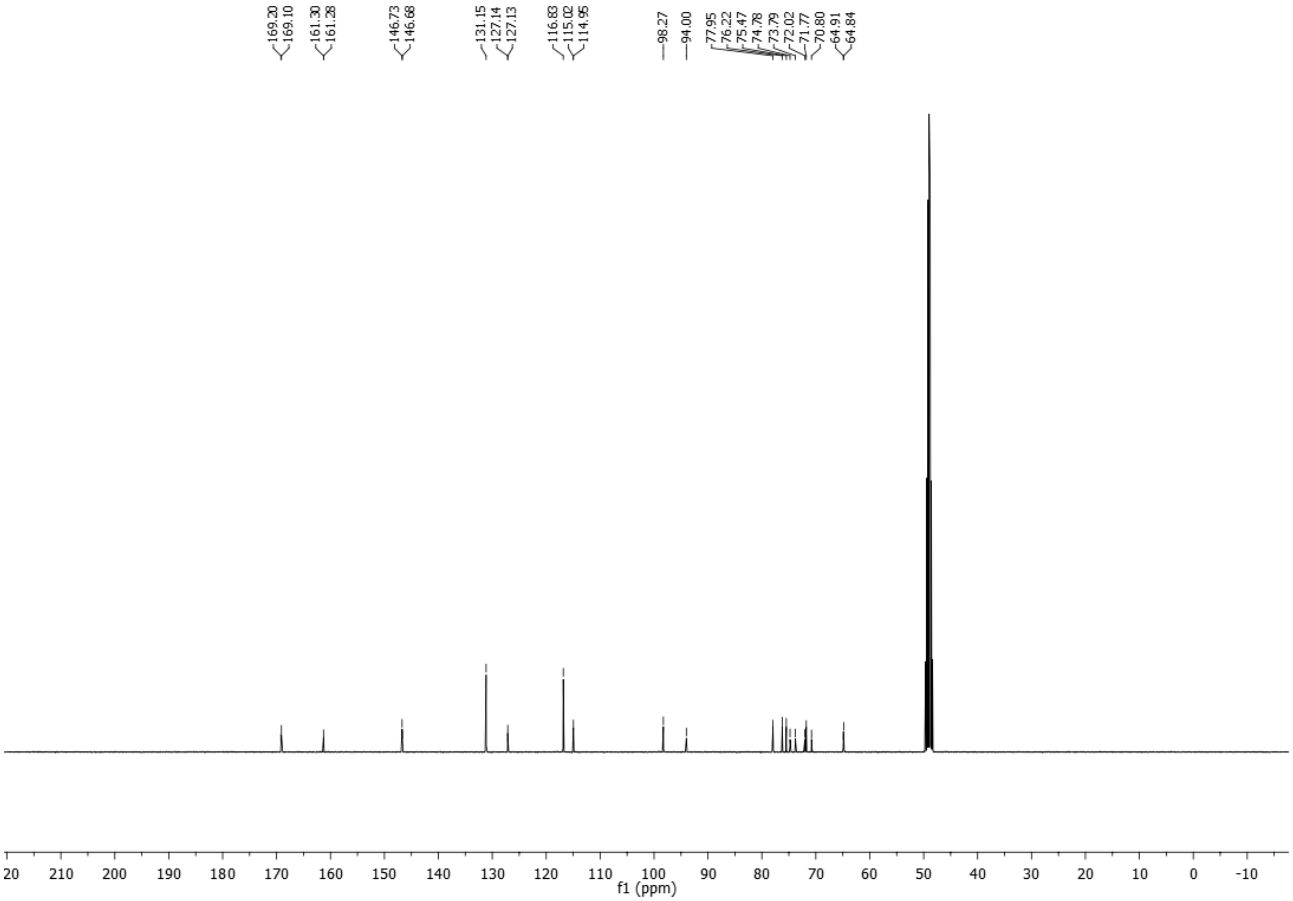

7.26
O
OCD3
4ad-d
0.99
2.03
2.97
1.00
f1 (ppm)


167.56
144.98
134.52
130.41
129.01
128.19
117.96
f1 (ppm)



6-O-*p*-coumaroyl-D-glucose

α/β = 0.35:0.65



13. References

[1] C. Q. O'Broin, P. J. Guiry, Org. Lett. 22 (2020) 879-883. https://doi.org/10.1021/acs.orglett.9b04413

[2] C. B. Baltus, I. S. Chuckowree, N. J. Press, I. J. Day, S. J. Coles, G. J. Tizzard, J. Spencer, Tetrahedron Lett. 54 (2013) 1211-1217. https://doi.org/10.1016/j.tetlet.2012.12.081

[3] D. C. Miller, B. Carbain, G. S. Beale, S. F. Alhasan, H. L. Reeves, U. Baisch, D. R. Newell, B. T. Golding, R. J. Griffin, Org. Biomol. Chem. 13 (2015) 5279-5284. https://doi.org/10.1039/C5OB00211G

[4] L. Hough, A. C. Richardson, L. A. W. Thelwall, Carbohydr. Res. 75 (1979) C11-C12. https://doi.org/10.1016/S0008-6215(00)84663-7

[5] S. D. Ittel, L. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169-1204. https://doi.org/10.1021/cr9804644

[6] a) F. Neese, WIRES-Comp Mol Sci. 2 (2012) 73-78. https://doi.org/10.1002/wcms.81; b) F. Neese, WIRES-Comp Mol Sci. 8 (2018) e1327. https://doi.org/10.1002/wcms.1327

[7] Y. Zhao, D. G. A. Truhlar, J. Chem. Phys. 125 (2006) 194101. https://doi.org/10.1063/1.2370993

[8] F. Weigend, R. Ahlrichs. Phys.Chem.Chem.Phys. 7 (2005) 3297-3305. https://doi.org/10.1039/B508541A

[9] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 132 (2010) 154104. https://doi.org/10.1063/1.3382344

[10] G. Henkelman, B. P. Uberuaga, H. A. Jónsson, J. Chem. Phys. 113 (2000) 9901. https://doi.org/10.1063/1.1329672

[11] K. Ishida, K. Morokuma, A. Komornicki, J. Chem. Phys. 66 (1977) 2153. https://doi.org/10.1063/1.434152

[12] M. K. Kesharwani, B. Brauer, J. M. L. Martin, J. Phys. Chem. A 119 (2015) 1701-1714. https://doi.org/10.1021/jp508422u

[13] R. L. Martin, P. J. Hay, L. R. Pratt, J. Phys. Chem. A 102 (1998) 3565-3573. https://doi.org/10.1021/jp980229p

[14] Y. Zhao, D. G. Truhlar, Theor. Chem. Acc. 120 (2008) 215-241. https://doi.org/10.1007/s00214-007-0310-x

[15] A. V. Marenich, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. B 113 (2009) 6378-6396. https://doi.org/10.1021/jp810292n

[16] G. M. Sheldrick, Acta Crystallogr. C 71 (2015) 3-8. https://doi.org/10.1107/S2053229614024218

[17] E. Molle, H. Mutlu, P. Theato, Macromol. Rapid Commun. 42 (2021) 2100063. https://doi.org/10.1002/marc.202100063

[18] H. Shimomura, Y. Sashida, T. Adachi, Phytochemistry 27 (1988) 641-644. https://doi.org/10.1016/0031-9422(88)83165-0

[19] M. Maffei, G. Giacoia, R. Mancuso, B. Gabriele, E. Motti, M. Costa, N. Della Ca*',* J. Mol. Cat. A: Chem. 426 (2017) 435-4432. https://doi.org/10.1016/j.molcata.2016.07.011.

[20] L. Wang, Y. Wang, C. Liu, A. Lei, Angew. Chem. Int. Ed. 53 (2014) 5657-5661. https://doi.org/10.1002/anie.201400612.

[21] A. A. Poeylaut-Palena, E. G. Mata, Org. Biomol. Chem. 8 (2010) 3947-3956. https://doi.org/10.1039/C004729E

[22] N. Y. P. Kumar, A. Bechtoldt, K. Raghuvanshi, L. Ackermann, Angew. Chem. Int. Ed. 55 (2016) 6929-6932. https://doi.org/10.1002/anie.201600490

[23] F. Valentini, F. Ferlin, S. Lilli, A. Marrocchi, L. Ping, Y. Gu, L. Vaccaro, Green Chem. 23 (2021) 5887-5895. https://doi.org/10.1039/D1GC01707A

[24] X.-X. He, H.-H. Chang, Y.-X. Zhao, X.-J. Li, S.-A. Liu, Z.-L. Zang, C.-H. Zhou, G.-X. Cai, Chem. Asian J. 18 (2023) e202200954. https://doi.org/10.1002/asia.202200954

[25] A. K. Sinha, A. Sharma, A. Swaroop, V. Kumar, Tetrahedron 63 (2007) 1000-1007. https://doi.org/10.1016/j.tet.2006.11.011

[26] A. V. Malkov, N. Derrien, M. Barłóg, P. Kočovský, Chem. Eur. J. 20 (2014) 4542-4547. https://doi.org/10.1002/chem.201304798.

[27] G. Reynard, E.-M. Joseph-Valcin, H. Lebel, Chem. Commun. 56 (2020) 10938-10941. https://doi.org/10.1039/D0CC03242E

[28] S. A. Morris, D. G. Gusev, Angew. Chem. Int. Ed. 56 (2017) 6228-6231. https://doi.org/10.1002/anie.201611186

[29] M. Abdullah, T. Kanwal, A. A. Shuja, K. Rao, K. Rehman, M. Kawish, S. U. Simjee, Sirajuddin, M. R. Shah, J. Mol. Struct. 1263 (2022) 133131. https://doi.org/10.1016/j.molstruc.2022.133131

[30] D. Olivieri, R. Tarroni, S. Zacchini, N. Della Ca', R. Mancuso, B. Gabriele, G. Spadoni, C. Carfagna, J. Catal. 421 (2023) 431-440. https://doi.org/10.1016/j.jcat.2023.03.008

[31] Y. Liu, M. Daka, M. Bandini, Synthesis 50 (2018) 3187-3196. https://dx.doi.org/10.1055/s-0037-1610023

[32] Z. Shen, S. Zhang, H. Geng, J. Wang, X. Zhang, A. Zhou, C. Yao, X. Chen, W. Wang, Org. Lett. 21 (2019) 448-452. https://doi.org/10.1021/acs.orglett.8b03641