Supporting Information for

Versatile Dehydrogenation of Carbonyls Enabled by an Iodine(III) Reagent

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Contents

1. General information

Chemicals: All used reagents were purchased from common suppliers and used as received unless noted otherwise. Solvents used for syntheses were of puriss grade and technical grade solvents were used for column chromatography. All reactions were carried out in round-bottom flasks or glass vials under air unless stated otherwise.

TLC: Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 coated aluminum sheets (Merck). Visualization was achieved by ultraviolet fluorescence (λ = 254 nm) and/or staining with potassium permanganate ($KMnO_4$).

FCC: Flash column chromatography (FCC) was performed using silica gel 60 (pore size = 60 Å, mesh: 40-63 µm from Sigma-Aldrich or SiliCycle).

HRMS: High-resolution mass spectrometry (HRMS) data were obtained by the mass spectrometry service in the Laboratorium für Organische Chemie at ETH Zürich on a Varian IonSpec Spectrometer for electrospray ionization (ESI) and are reported as (m/z).

NMR: ^{1}H-, ^{13}C-, ^{15}N-, and ^{19}F-NMR spectra were recorded on a Bruker AVIII 400 MHz, a Bruker Neo 400 MHz or a Bruker Neo 500 MHz spectrometer and are reported in parts per million (ppm). ^{1}H-NMR spectra are calibrated with respect to the corresponding solvent residual peak ($CHCl_3$: 7.26 ppm; CH_3OH: 3.31 ppm; CH_2Cl_2: 5.32 ppm). ^{13}C-NMR spectra are calibrated with respect to the corresponding solvent residual peak ($CHCl_3$: 77.16 ppm; CH_3OH: 49.00 ppm; CH_2Cl_2: 53.84 ppm). Multiplet signals are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, or combinations thereof. ^{13}C signals are acquired with proton decoupling and are singlets unless stated otherwise. NMR yields were determined using 1,1,2,2-tetrachloroethane or mesitylene as an internal standard.

Safety Statement

General safety remarks on the use of PIFA (BTI) and its solvent compatibility:

We did not encounter any safety-related issues during the entirety of the project, however, the appropriate precautions are recommended to be taken when performing reactions with hypervalent iodine compounds.

Quote from Anastasios Varvoglis: Hypervalent Iodine in Organic Synthesis, 1997, Academic Press: "Pure BTI[a] is obtained by recrystallization from acetone-petroleum ether (m.p. 112-120 °C with decomposition, depending on the rate of heating). It is soluble in several organic solvents, such as acetone, acetonitrile, chloroform, dichloromethane, ethanol and ether. Most of them react slowly with BTI, even at room temperature; nevertheless, since its reactions do not require heating and are completed in a short time, by-products from reactions with the solvent are minimal and do not pose a problem. The reagent is fairly stable and can be kept without refrigeration for a long period of time, with light protection."

[a] BTI is an alternative abbreviation for (*bis*(trifluoroacetoxy)iodo)benzene (PIFA)

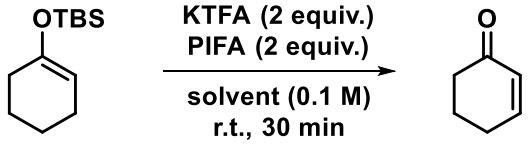
2. Optimisation of reaction conditions

General procedure for the optimisation of reaction conditions

In a 4 mL screw-cap vial equipped with a magnetic stirring bar, *tert*-butyl(cyclohex-1-en-1-yloxy)dimethylsilane (**1a**) (10.6 mg, 0.050 mmol, 1.0 equiv.) or *tert*-butyl(cyclopent-1-en-1-yloxy)dimethylsilane (**1b**) (9.9 mg, 0.050 mmol, 1.0 equiv.) was dissolved in the appropriate deuterated solvent, and cooled in an ice-water bath. Base was added in one portion followed by the oxidant and the mixture was stirred for 10 minutes at 0 °C, then for 30 minutes at room temperature, unless stated otherwise. The crude reaction mixture was concentrated and analysed by ^{1}H NMR after the addition of the mesitylene internal standard (5.00 µL, 0.1075 mmol, 2.15 equiv.) in acetone-d_6. The yield was determined by integration of the peak corresponding to the H at the 2-position of product **2a** at δ 5.89 ppm (dt, *J* = 10.2, 2.0 Hz, 1H) and for product **2b** at δ 6.10 ppm (dt, *J* = 5.7, 2.2 Hz, 1H) relative to the signal corresponding to the mesitylene internal standard at δ 6.76 ppm (q, *J* = 0.7 Hz, 3H).

Solvent optimisation

Table S1

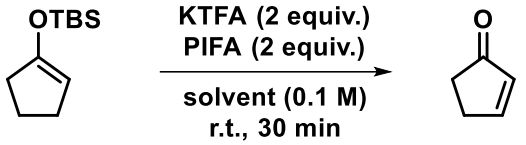


1a **2a**

Entry	Solvent	NMR yield of **2a** (%)
1	acetone	**53**
2	MeCN	**53**
3	DMSO	**44**
4	Et_2O	**32**
5	DMF	**31**
6	THF	**30**
7	toluene	**26**
8	DCM	**25**
9	$CDCl_3$	**22**
10	EtOH	**15**

11	dioxane	**4**
12	MeOH	**0**
13	HFIP	**0**

Table S2

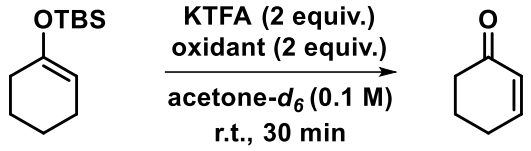


1b **2b**

Entry	Solvent	NMR yield of **2b** (%)
1	acetone	**62**
2	MeCN	**48**
3	THF	**41**
4	Et_2O	**31**
5	DMSO	**10**

Oxidant optimisation

Table S3

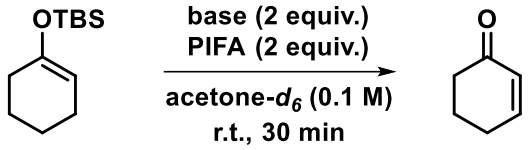


1a **2a**

Entry	Oxidant	NMR yield of **2a** (%)
1	**PIFA** Bis(trifluoroacetoxy) iodobenzene	**53**
2	**HTIB** Hydroxy(tosyloxy) iodobenzene	**45**
3	Hydroxy(methanesulfonyloxy) iodobenzene	**42**
4	Dess-Martin periodinane	**0**
5	Iodosobenzene	**0**
6	I_2	**0**
7	**PIDA** Diacetoxyiodobenzene	**0**
8	Togni reagent II	**0**
9	**FPIFA** Bis(trifluoroacetoxy) iodopentafluorobenzene	**0**
10	Bis(*tert*-butylcarbonyloxy) iodobenzene	**0**

Base optimisation

Table S4

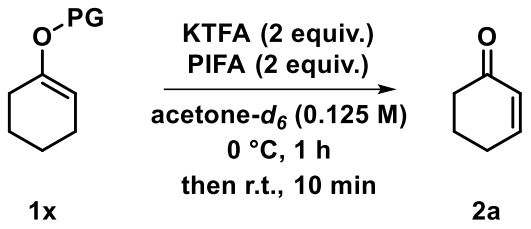


1a **2a**

Entry	Base	NMR yield of **2a** (%)
1	NaOAc	**55**
2	KTFA	**55**
3	NaTFA	**54**
4	NaOH	**54**
5	CsF	**52**
6	Na_2CO_3	**51**
7	K_3PO_4	**48**
8	K_2CO_3	**46**
9	$NaHCO_3$	**46**
10	KOH	**45**
11	Et_3N	**19**
12	No base	**18**
13	$Et(^iPr)_2N$	**17**
13	$(^iPr)_2NH$	**14**

Protecting group optimisation

Table S5

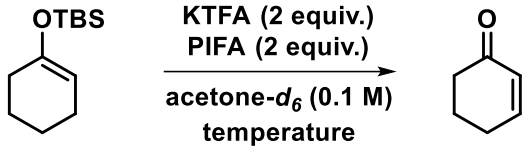


1x **2a**

Entry	Protecting group (PG)	NMR yield of **2a** (%)
1	*tert*-Butyldimethylsilyl (TBS)	**59**
2	Triisopropylsilyl (TIPS)	**27**
3	Triethylsilyl (TES)	**9**
4	Trimethylsilyl (TMS)	**3**
5	Diphenylphosphate	**0**

Temperature optimisation

Table S6

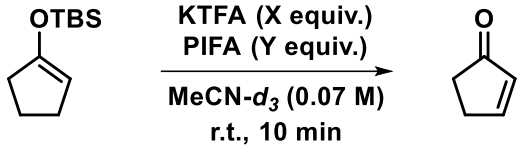


1a **2a**

Entry	Temperature	NMR yield of **2a** (%)
1	- 78 °C	**66**
2	0 °C	**59**
3	25 °C	**54**

Equivalent optimisation

Table S7

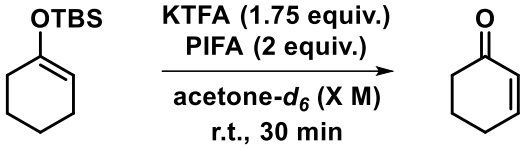


1b **2b**

Entry	KTFA (X equiv.)	PIFA (Y equiv.)	NMR yield of **2b** (%)
1	1	1	**28**
2	2	2	**45**
3	4	4	**45**
4	10	10	**52**
5	0.2	2	**11**
6	4	0	**0**
7	0	4	**0**

Concentration optimisation

Table S8



1a **2a**

Entry	Concentration (X M)	NMR yield of **2a** (%)
1	0.13 M	**56**
2	0.08 M	**56**
3	0.03 M	**51**

3. Synthesis and characterisation of starting materials

General procedure A1 for the silylation of ketones and aldehydes

The following procedure was adapted from literature.[1] A round bottom flask equipped with a magnetic stir bar was charged with the starting material ketone or aldehyde, which was dissolved in dichloromethane (0.4 M with respect to the starting material). Et_3N (1.5 equiv.) and TBSOTf (1.05 equiv.) were added at room temperature, and the mixture was stirred until all of the starting material was consumed (the reaction was monitored by TLC, in general 5-60 minutes reaction time). Then the mixture was diluted with dichloromethane, washed with saturated aq. $NaHCO_3$ solution, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was dissolved in Et_2O (in which Et_3NH^+ OTf^- is insoluble), filtered, and concentrated. The product was purified by flash column chromatography if required.

General procedure A2 for the silylation of ketones and aldehydes

A round bottom flask equipped with a magnetic stir bar was charged with the starting material ketone or aldehyde, which was dissolved in dichloromethane (0.4 M with respect to the starting material). Et_3N (1.5 equiv.) and TBSOTf (1.2 equiv.) were added at room temperature, and the mixture was stirred until all of the starting material was consumed (the reaction was monitored by TLC, in general 5-60 minutes reaction time). Then the mixture was diluted with dichloromethane, washed with saturated aq. $NaHCO_3$ solution, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was dissolved in Et_2O (in which Et_3NH^+ OTf^- is insoluble), filtered, and concentrated. The product was purified by flash column chromatography if required.

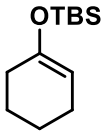
General procedure A3 for the silylation of ketones and aldehydes

A round bottom flask equipped with a magnetic stir bar was charged with the starting material ketone or aldehyde, which was dissolved in dry tetrahydrofuran (1.0 M with respect to the starting material). 2,6-Lutidine (3.0 equiv.) and TBSOTf (2.0 equiv.) were added at 0 °C, and the mixture was stirred until all of the starting material was consumed (the reaction was monitored by TLC, in general 5-60 minutes reaction time). Then the mixture was diluted with dichloromethane, washed with saturated aq. $NaHCO_3$ solution, dried over Na_2SO_4, filtered, and concentrated. The product was purified by flash column chromatography.

General procedure B for the phosphorylation of esters and amides

The following procedure was adapted from literature.[2] A flame-dried round bottom flask equipped with a magnetic stir bar was charged with the starting material ester or amide, which was dissolved in dry tetrahydrofuran (0.5 M with respect to the starting material) under N_2 atmosphere. To the solution LiHMDS (1.2 equiv., 1 M solution in tetrahydrofuran) was added dropwise at -78 °C, and the mixture was stirred for 15 minutes at -78 °C. Then $P(O)(OPh)_2Cl$ (1.2 equiv.) was added dropwise at -78 °C. The mixture was subsequently warmed to room temperature and stirred for additional 30 minutes. The mixture was quenched with saturated aq. $NaHCO_3$ solution and extracted with EtOAc two times. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The product was purified by flash column chromatography.

***tert*-Butyl(cyclohex-1-en-1-yloxy)dimethylsilane (1a)**



tert-Butyl(cyclohex-1-en-1-yloxy)dimethylsilane (**1a**) was prepared according to general procedure A2, using cyclohexanone (0.59 g, 0.62 mL, 6.0 mmol) as the starting material. The product was afforded as a colourless liquid in quantitative yield, and was used without further purification.

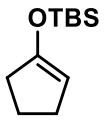
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (ddd, *J* = 3.9, 2.5, 1.3 Hz, 1H), 2.21 – 1.92 (m, 4H), 1.77 – 1.59 (m, 2H), 1.56 – 1.44 (m, 2H), 0.92 (s, 9H), 0.12 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 104.5, 30.1, 25.9, 24.0, 23.3, 22.5, 18.2, - 4.2.

HRMS (ESI, m/z): $[M+H]^+$ calc. 213.1669; found 213.1666.

The spectral data are consistent with those reported in the literature.[3]

***tert*-Butyl(cyclopent-1-en-1-yloxy)dimethylsilane (1b)**



tert-Butyl(cyclopent-1-en-1-yloxy)dimethylsilane (**1b**) was prepared according to general procedure A2, using cyclopentanone (0.50 g, 0.54 mL, 6.0 mmol) as the starting material. The product was afforded as a colourless liquid (1.07 g, 90% yield), and was used without further purification.

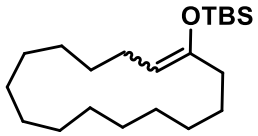
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66 – 4.57 (m, 1H), 2.37 – 2.11 (m, 4H), 1.94 – 1.74 (m, 2H), 0.92 (s, 9H), 0.15 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 102.6, 33.6, 28.8, 25.9, 21.6, 18.3, - 4.4.

HRMS (ESI, m/z): $[M+H]^+$ calc. 199.1513; found 199.1514.

The spectral data are consistent with those reported in the literature.[4]

tert-Butyl(cyclopentadec-1-en-1-yloxy)dimethylsilane (1c)



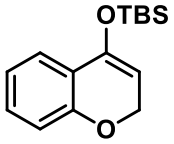
tert-Butyl(cyclopentadec-1-en-1-yloxy)dimethylsilane (**1c**) was prepared according to general procedure A1, using cyclopentadecanone (448 mg, 2.00 mmol) as the starting material. Flash column chromatography (pentane eluent) afforded the product as a colourless oil, as a mixture of *E* and *Z* isomers (495 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$, mixture of *E* and *Z* isomers) δ 4.58 (t, *J* = 7.6 Hz, 0.2H), 4.38 (t, *J* = 6.9 Hz, 0.8H), 2.15 – 1.78 (m, 4H), 1.42 – 1.19 (m, 22H), 0.95 (s, 7.2H), 0.92 (s, 1.8H), 0.13 (s, 1.2H), 0.11 (s, 4.8H).

^{13}C NMR (101 MHz, $CDCl_3$, mixture of *E* and *Z* isomers, overlapping signals) δ 151.9, 150.1, 109.0, 107.8, 35.8, 30.9, 29.5, 29.2, 27.7, 27.7, 27.5, 27.5, 27.3, 27.2, 27.1, 27.1, 27.0, 26.9, 26.9, 26.9, 26.6, 26.5, 26.4, 26.4, 26.0, 26.0, 25.7, 24.5, 18.4, 18.3, -3.8, -4.3.

HRMS (ESI, m/z): $[M+H]^+$ calc. 339.3078; found 339.3078.

((2*H*-Chromen-4-yl)oxy)(*tert*-butyl)dimethylsilane (1d)



((2*H*-Chromen-4-yl)oxy)(tert-butyl)dimethylsilane (**1d**) was prepared according to the general procedure A1 using chroman-4-one (370 mg, 2.50 mmol) as the starting material. The product was isolated as an orange oil (446 mg, 68% yield) and was used without further purification.

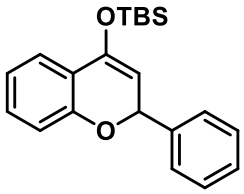
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.14 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 6.91 (td, *J* = 7.5, 1.2 Hz, 1H), 6.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.88 (dd, *J* = 4.2, 3.4 Hz, 1H), 4.84 (d, *J* = 4.1 Hz, 2H), 1.02 (s, 9H), 0.23 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 146.2, 129.7, 122.7, 122.5, 121.0, 116.0, 98.0, 65.9, 25.9, 18.4, - 4.4.

HRMS (ESI, m/z): $[M+H]^+$ calc. 263.1462; found 263.1459.

The spectral data are consistent with those reported in the literature.[5]

tert-Butyldimethyl((2-phenyl-2*H*-chromen-4-yl)oxy)silane (1e)



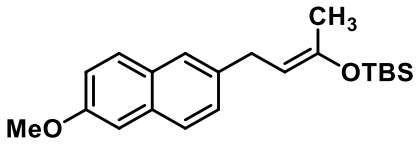
tert-Butyldimethyl((2-phenyl-2*H*-chromen-4-yl)oxy)silane (**1e**) was prepared according to general procedure A1, using 2-phenylchroman-4-one (673 mg, 3.00 mmol) as the starting material. Flash column chromatography (hexane:EtOAc = 100:0 to 90:10 eluent) afforded the product as a light yellow oil (901 mg, 89% yield).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.49 – 7.44 (m, 2H), 7.41 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.40 – 7.28 (m, 3H), 7.14 (ddd, *J* = 8.1, 7.4, 1.7 Hz, 1H), 6.90 (td, *J* = 7.5, 1.1 Hz, 1H), 6.75 (ddd, *J* = 8.1, 1.2, 0.4 Hz, 1H), 5.98 (d, *J* = 3.6 Hz, 1H), 5.00 (d, *J* = 3.6 Hz, 1H), 1.03 (s, 9H), 0.25 (d, *J* = 1.3 Hz, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 154.9, 146.2, 142.1, 130.2, 128.9, 128.7, 127.5, 122.9, 121.8, 121.1, 116.0, 102.2, 78.3, 25.9, 18.6, -4.4 (d, *J* = 3.7 Hz).

HRMS (ESI, m/z): $[M+H]^+$ calc. 339.1775; found 339.1773.

tert-Butyl((4-(6-methoxynaphthalen-2-yl)but-2-en-2-yl)oxy)dimethylsilane (1f)



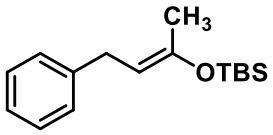
tert-Butyl((4-(6-methoxynaphthalen-2-yl)but-2-en-2-yl)oxy)dimethylsilane (**1f**) was prepared according to general procedure A3, using 4-(6-methoxynaphthalen-2-yl)butan-2-one (1.37 g, 6.00 mmol) as the starting material. Flash column chromatography (pentane:Et_2O = 98:2 eluent) afforded the product as a white solid (643 mg, 31% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 2H), 7.57 (dt, *J* = 1.8, 0.9 Hz, 1H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.20 – 7.09 (m, 2H), 4.70 (tq, *J* = 7.1, 1.0 Hz, 1H), 3.92 (J = 1.6 Hz, 3H), 3.52 (dt, *J* = 7.1, 1.2 Hz, 2H), 1.88 (q, *J* = 1.2 Hz, 3H), 1.00 (s, 9H), 0.21 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 147.6, 137.6, 133.1, 129.3, 129.0, 128.1, 126.8, 126.0, 118.6, 107.3, 105.8, 55.4, 31.6, 26.0, 23.0, 18.4, - 3.5.

HRMS (ESI, m/z): $[M+H]^+$ calc. 343.2088; found 343.2085.

***tert*-Butyldimethyl((4-phenylbut-2-en-2-yl)oxy)silane (1g)**



tert-Butyldimethyl((4-phenylbut-2-en-2-yl)oxy)silane (**1g**) was prepared according to general procedure A3, using 4-phenylbutan-2-one (888 mg, 6.00 mmol) as the starting material. Flash column chromatography (pentane eluent) afforded the product as a colourless oil (338 mg, 22% yield).

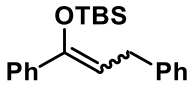
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.12 (m, 5H), 4.68 (tq, *J* = 7.1, 1.0 Hz, 1H), 3.45 (d, *J* = 7.0 Hz, 2H), 1.90 (q, *J* = 1.2 Hz, 3H), 1.04 (s, 9H), 0.24 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 142.4, 128.5, 128.4, 125.7, 107.3, 31.7, 25.9, 22.9, 18.4, - 3.6.

HRMS (ESI, m/z): $[M+H]^+$ calc. 263.1826; found 263.1827.

The spectral data are consistent with those reported in the literature.[6]

***tert*-Butyl((1,3-diphenylprop-1-en-1-yl)oxy)dimethylsilane (1h)**



tert-Butyl((1,3-diphenylprop-1-en-1-yl)oxy)dimethylsilane (**1h**) was prepared according to general procedure A1, using 1,3-diphenylpropan-1-one (1.05 g, 5.00 mmol) as the starting material. Flash column chromatography (pentane:Et_2O = 100:0 to 95:5 eluent) afforded the product as a colourless oil (979 mg, 60% yield), as a mixture of *E* and *Z* isomers.

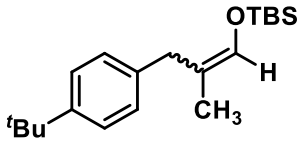
^{1}H NMR (400 MHz, $CDCl_3$, mixture of *E* and *Z* isomers) δ 7.62 – 7.44 (m, 2H), 7.42 – 7.18 (m, 8H), 5.35 (t, *J* = 7.2 Hz, 0.75H), 5.28 (t, *J* = 8.0 Hz, 0.25H), 3.63 (d, *J* = 7.2 Hz, 1.5H), 3.52 (d, *J* = 8.0 Hz, 0.5H), 1.06 (s, 6.8H), 0.97 (s, 2.2H), 0.11 (s, 1.4H), 0.04 (s, 4.5H).

^{13}C NMR (101 MHz, $CDCl_3$, mixture of *E* and *Z* isomers) δ 151.1, 150.2, 141.9, 141.7, 139.7, 137.8, 128.6, 128.5 (2C), 128.4, 128.3, 128.1, 128.0 (2C), 127.8, 126.2, 126.0, 125.9, 110.4, 109.0, 33.9, 32.5, 26.1, 25.9, 18.5, 18.3, - 3.8, - 4.3.

HRMS (ESI, m/z): $[M+H]^+$ calc. 325.1982; found 325.1979.

The spectral data of the *Z* isomer reported in the literature are consistent with the peaks attributed to the *Z* isomer in the mixture of *E* and *Z* isomers of **1h**.[7]

***tert*-Butyl((3-(4-(*tert*-butyl)phenyl)-2-methylprop-1-en-1-yl)oxy)dimethylsilane (1j)**



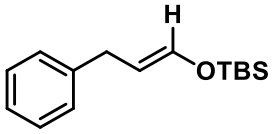
tert-Butyl((3-(4-(*tert*-butyl)phenyl)-2-methylprop-1-en-1-yl)oxy)dimethylsilane (**1j**) was prepared according to general procedure A1, using 3-(4-(*tert*-butyl)phenyl)-2-methylpropanal (1.02 g, 5.00 mmol) as the starting material. Flash column chromatography (hexane eluent) afforded the product as a colourless oil (895 mg, 58% yield), as a mixture of *E* and *Z* isomers.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 2H), 7.18 – 7.05 (m, 2H), 6.40 – 6.20 (m, 0.65H), 6.16 (dtt, *J* = 2.0, 1.5, 0.8 Hz, 0.28H), 3.39 (s, 0.55H), 3.15 (s, 1.3H), 1.52 (dt, *J* = 1.5, 0.7 Hz, 2H), 1.46 (t, *J* = 1.3 Hz, 1H), 1.32 (q, *J* = 0.7 Hz, 9H), 1.03 – 0.91 (m, 9H), 0.22 – 0.09 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 148.4, 138.1, 137.7, 135.5, 134.2, 128.6, 128.4, 125.2 (2C), 116.9, 116.2, 39.8, 34.6, 34.5, 34.5, 31.6, 31.6, 25.9, 25.9, 18.4, 18.3, 17.1, 12.8, -2.8, -5.1 (d, *J* = 5.2 Hz).

HRMS (ESI, m/z): $[M+Na]^+$ calc. 341.2271; found 341.2272.

***tert*-Butyldimethyl((3-phenylprop-1-en-1-yl)oxy)silane (1k)**



tert-Butyldimethyl((3-phenylprop-1-en-1-yl)oxy)silane (**1k**) was prepared according to general procedure A2, using 3-phenylpropanal (5.36 g, 40.0 mmol) as the starting material. Flash column chromatography (pentane eluent) afforded the product as a colourless oil (4.00 g, 40% yield).

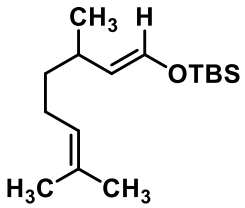
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.06 (m, 5H), 6.33 (dt, *J* = 5.8, 1.5 Hz, 1H), 4.69 (td, *J* = 7.3, 5.7 Hz, 1H), 3.47 (ddd, *J* = 7.4, 1.5, 0.7 Hz, 2H), 0.97 (s, 9H), 0.18 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 139.3, 128.5, 128.4, 125.8, 109.3, 30.1, 25.8, 18.4, - 5.2.

HRMS (ESI, m/z): $[M]^+$ calc. 248.1591; found 248.1595.

The spectral data are consistent with those reported in the literature.[8]

***tert*-Butyl((3,7-dimethylocta-1,6-dien-1-yl)oxy)dimethylsilane (1l)**



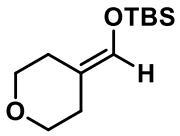
tert-Butyl((3,7-dimethylocta-1,6-dien-1-yl)oxy)dimethylsilane (**1l**) was prepared according to general procedure A1, using citronellal (463 mg, 3.00 mmol) as the starting material. Flash column chromatography (hexane:EtOAc = 100:0 to 90:10 eluent) afforded the product as a colorless oil (320 mg, 40% yield).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.15 (dd, *J* = 5.9, 1.0 Hz, 1H), 5.13 (tdt, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.25 (dd, *J* = 9.3, 5.9 Hz, 1H), 2.67 (dddd, *J* = 9.3, 8.2, 7.5, 6.3 Hz, 1H), 2.11 – 1.87 (m, 2H), 1.67 (d, *J* = 1.3 Hz, 3H), 1.59 (dt, *J* = 0.9, 0.4 Hz, 3H), 1.33 – 1.26 (m, 1H), 1.21 (dddd, *J* = 13.1, 9.5, 8.2, 6.1 Hz, 1H), 0.93 (s, 9H), 0.86 (d, *J* = 10.1 Hz, 3H), 0.12 (s, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 137.8, 131.2, 125.4, 117.2, 38.2, 28.7, 26.5, 25.8, 25.8, 21.3, 18.5, 17.7, -5.3 (d, *J* = 3.5 Hz).

HRMS (ESI, m/z): $[M+H]^+$ calc. 269.2295; found 269.2294.

***tert*-Butyldimethyl((tetrahydro-4*H*-pyran-4-ylidene)methoxy)silane (1m)**



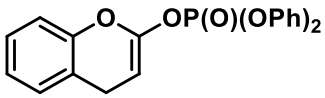
tert-Butyldimethyl((tetrahydro-4*H*-pyran-4-ylidene)methoxy)silane (**1m**) was prepared according to general procedure A1, using tetrahydro-2*H*-pyran-4-carbaldehyde (342 mg, 3.00 mmol) as the starting material. Flash column chromatography (pentane:Et_2O = 90:10 eluent) afforded the product as a colorless oil (213 mg, 31% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (t, *J* = 1.3 Hz, 1H), 3.63 (td, *J* = 5.5, 1.0 Hz, 4H), 2.32 (ddd, *J* = 6.5, 5.2, 1.3 Hz, 2H), 2.07 (ddd, *J* = 6.1, 5.0, 1.2 Hz, 2H), 0.91 (s, 9H), 0.12 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 116.2, 69.8, 68.6, 30.6, 26.5, 25.8, 18.4, - 5.2.

HRMS (ESI, m/z): $[M+H]^+$ calc. 229.1618; found 229.1618.

4*H*-Chromen-2-yl diphenyl phosphate (1n)



4*H*-Chromen-2-yl diphenyl phosphate (**1n**) was prepared according to the general procedure B using chroman-2-one (592 mg, 4.00 mmol) as the starting material. Filtration over alumina (hexane:EtOAc = 70:30 with 1% NEt_3 eluent) afforded the product as a yellow oil (1.22 g, 80% yield), which was used immediately in the corresponding desaturation reaction.

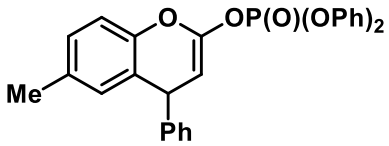
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 8H), 7.26 – 7.19 (m, 2H), 7.15 – 7.09 (m, 1H), 7.07 – 6.99 (m, 2H), 6.83 – 6.77 (m, 1H), 4.69 (td, *J* = 3.6, 2.6 Hz, 1H), 3.52 (td, *J* = 3.6, 0.9 Hz, 2H).

^{31}P NMR (122 MHz, $CDCl_3$) δ - 18.5.

Note: No ^{13}C NMR and HRMS were recorded due to the instability of the material.

The spectral data are consistent with those reported in the literature.[2]

6-Methyl-4-phenyl-4*H*-chromen-2-yl diphenyl phosphate (1o)



6-Methyl-4-phenyl-4*H*-chromen-2-yl diphenyl phosphate (**1o**) was prepared according to general procedure B, using 6-methyl-4-phenylchroman-2-one (1.19 g, 5.00 mmol) as the starting material. Flash column chromatography (pentane:Et_2O = 80:20 eluent) afforded the product as a white solid (1.70 g, 72% yield).

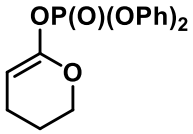
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.10 (m, 15H), 6.97 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.77 (dd, *J* = 2.0, 1.0 Hz, 1H), 4.83 (dd, *J* = 4.0, 2.4 Hz, 1H), 4.82 – 4.78 (m, 1H), 2.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5 (d, *J* = 5.9 Hz), 150.4 (d, *J* = 5.7 Hz), 148.1, 147.5 (d, *J* = 6.6 Hz), 146.1 (d, *J* = 1.6 Hz), 134.1, 130.1, 130.0 (2C), 129.9, 128.8, 128.7, 128.3, 127.0, 125.8, 122.5, 120.3 (d, *J* = 2.1 Hz), 120.3 (d, *J* = 2.1 Hz), 116.5, 86.3 (d, *J* = 5.4 Hz), 41.8, 20.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ - 18.5.

HRMS (ESI, m/z): $[M+Na]^+$ calc. 493.1175; found 493.1172.

3,4-Dihydro-2*H*-pyran-6-yl diphenyl phosphate (1p)



3,4-Dihydro-2*H*-pyran-6-yl diphenyl phosphate (**1p**) was prepared according to general procedure B, using tetrahydro-2*H*-pyran-2-one (400 mg, 4.00 mmol) as the starting material. Filtration through a silica plug afforded the product (192 mg, 14% yield), which was used immediately in the corresponding desaturation reaction.

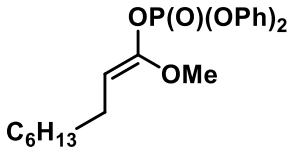
^{1}H NMR (400 MHz, $CDCl_3$) δ δ 7.41 – 7.33 (m, 4H), 7.31 – 7.19 (m, 6H), 4.47 (p, *J* = 3.3 Hz, 1H), 4.17 (q, *J* = 4.8 Hz, 2H), 2.17 – 2.08 (m, 2H), 1.89 – 1.79 (m, 2H).

^{31}P NMR (162 MHz, $CDCl_3$) δ – 18.3.

Note: No ^{13}C NMR and HRMS were recorded due to the instability of the material.

The spectral data are consistent with those reported in the literature.[2]

1-Methoxynon-1-en-1-yl diphenyl phosphate (1q)



1-Methoxynon-1-en-1-yl diphenyl phosphate (**1q**) was prepared using methyl nonanoate (516 mg, 3.00 mmol, 1.0 equiv.) as the starting material. In a flame-dried round bottom flask charged with a magnetic stir bar, *di*-isopropylamine (606 mg, 6.00 mmol, 2.0 equiv.) was dissolved in dry tetrahydrofuran (1 mL) under N_2 atmosphere. *n*-BuLi solution (2.8 mL, 4.5 mmol, 1.5 equiv., 1.6 M in hexanes) was added dropwise at -78 °C, and the resulting solution was stirred for 15 minutes at -78 °C. Then, methyl nonanoate (516 mg, 3.00 mmol, 1.0 equiv.) dissolved in dry tetrahydrofuran (3 mL) was added to the mixture dropwise at -78 °C, and it was stirred for additional 30 minutes at -78 °C. Then, a solution of diphenyl phosphoryl chloride (1.61 g, 6.00 mmol, 2.0 equiv.) in HMPA (5 mL) was added dropwise to the mixture at -78 °C, and the resulting solution was warmed up to room temperature, and was stirred for an additional hour. The mixture was quenched by the addition of saturated aq. $NaHCO_3$ solution and extracted with EtOAc three times. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and evaporated. Flash column chromatography (pentane:Et_2O = 90:10 to 80:20 eluent) afforded the product as a colourless oil (282 mg, 23% yield).

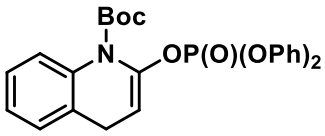
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.34 (m, 4H), 7.32 – 7.19 (m, 6H), 4.59 (td, *J* = 7.6, 2.7 Hz, 1H), 3.62 (s, 3H), 2.03 (qd, *J* = 7.3, 2.1 Hz, 2H), 1.46 – 1.26 (m, 9H), 0.98 – 0.79 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6 (d, *J* = 7.4 Hz), 150.4 (d, *J* = 8.3 Hz), 129.9 (d, *J* = 0.9 Hz), 125.7 (d, *J* = 1.3 Hz), 120.3 (d, *J* = 5.0 Hz), 95.4 (d, *J* = 4.8 Hz), 58.1 (d, *J* = 1.0 Hz), 32.0, 29.8 (d, *J* = 1.7 Hz), 29.2, 29.2, 24.5 (d, *J* = 1.2 Hz), 22.8, 14.2.

^{31}P NMR: (162 MHz, $CDCl_3$) δ - 18.1.

HRMS (ESI, m/z): $[M+H]^+$ calc. 405.1825; found 405.1824.

***tert*-Butyl 2-((diphenoxyphosphoryl)oxy)quinoline-1(4*H*)-carboxylate (1r)**



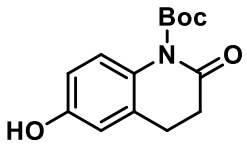
tert-Butyl 2-((diphenoxyphosphoryl)oxy)quinoline-1(4*H*)-carboxylate (**1r**) was prepared according to the general procedure B using *tert*-butyl 2-oxo-3,4-dihydroquinoline-1(2*H*)-carboxylate (990 mg, 4.00 mmol) as the starting material. Filtration over alumina (hexane:EtOAc = 70:30 with 1% NEt_3 eluent) afforded the product as a yellow oil, which was used immediately in the corresponding desaturation reaction.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.50 (m, 1H), 7.37 – 7.28 (m, 4H), 7.24 – 7.09 (m, 9H), 5.54 (td, *J* = 5.1, 2.9 Hz, 1H), 3.30 (dd, *J* = 5.2, 3.1 Hz, 2H), 1.47 (s, 9H).

^{31}P NMR (162 MHz, $CDCl_3$) δ - 18.6.

Note: No ^{13}C NMR and HRMS were recorded due to the instability of the material.

***tert*-Butyl 6-hydroxy-2-oxo-3,4-dihydroquinoline-1(2*H*)-carboxylate (S1)**



6-Hydroxy-3,4-dihydroquinolin-2(1*H*)-one (816 mg, 5.00 mmol, 1.0 equiv.) was suspended in dichloromethane (40 mL) under N_2 atmosphere. Triethylamine (2.09 mL, 15.0 mmol, 3.0 equiv.) was added to the solution and it was cooled to 0 °C. At this temperature acetyl chloride (0.71 mL, 10.0 mmol, 2.0 equiv.) was added dropwise. The mixture was stirred for 2 hours at room temperature and then was quenched with water. The mixture was extracted with dichloromethane three times, the combined organic phases were dried over $MgSO_4$, filtered, and concentrated.

The resulting crude product was dissolved in MeCN (28 mL). DMAP (122 mg, 1.00 mmol, 0.2 equiv.) and di-*tert*-butyl dicarbonate (1.15 mL, 5.00 mmol, 1.0 equiv.) were added at room temperature, and the resulting mixture was stirred overnight. Saturated aq. NH_4Cl solution was

then added to the mixture, and it was extracted with dichloromethane three times. The combined organic phases were dried over $MgSO_4$, filtered and concentrated.

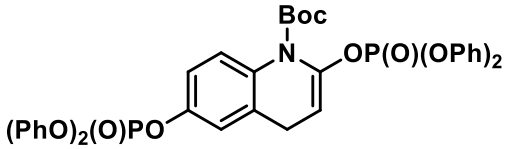
The resulting crude product was dissolved in a MeOH:H_2O = 1:1 mixture (42 mL), to which ammonia solution (5.7 mL, 40.0 mmol, 8.0 equiv., 7 M in MeOH) was added, and the resulting mixture was stirred at room temperature until the reaction went to completion. The mixture was then neutralised by 2 M aq. HCl solution, and it was extracted with dichloromethane three times. The combined organic phases were concentrated. Flash column chromatography (cyclohexane:EtOAc = 100:0 to 0:100 eluent) afforded the product *tert*-butyl 6-hydroxy-2-oxo-3,4-dihydroquinoline-1(2*H*)-carboxylate as a light yellow oil (301 mg, 23%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 – 6.83 (m, 1H), 6.70 – 6.64 (m, 2H), 3.66 (s, 1H), 2.90 – 2.85 (m, 2H), 2.66 – 2.61 (m, 2H), 1.59 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 152.5, 130.6, 128.4, 119.2, 114.9, 114.0, 85.0, 32.9, 28.5, 27.9, 25.8.

HRMS (ESI, m/z): $[M+Na]^+$ calc. 286.1050; found 286.1052.

***tert*-Butyl 2,6-bis((diphenoxyphosphoryl)oxy)quinoline-1(4*H*)-carboxylate (1s)**



tert-Butyl 2,6-bis((diphenoxyphosphoryl)oxy)quinoline-1(4*H*)-carboxylate (**1s**) was prepared according to a modified version of general procedure B using *tert*-butyl 6-hydroxy-2-oxo-3,4-dihydroquinoline-1(2*H*)-carboxylate (**S1**, 300 mg, 1.14 mmol) as the starting material, LiHMDS (2.2 equiv.), and $P(O)(OPh)_2Cl$ (2.2 equiv.) dissolved in THF (0.11 M with respect to the starting material). Flash column chromatography (pentane:EtOAC = 70:30 to 50:50 eluent) afforded the product as a yellow oil (213 mg, 26%).

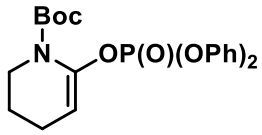
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.38 – 7.29 (m, 8H), 7.26 – 7.15 (m, 12H), 7.08 (dddd, *J* = 12.8, 8.9, 2.8, 1.3 Hz, 1H), 7.01 (dd, *J* = 2.8, 1.1 Hz, 1H), 5.51 (td, *J* = 5.1, 2.8 Hz, 1H), 3.26 (dd, *J* = 5.2, 3.1 Hz, 2H), 1.47 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 150.4 (d, *J* = 4.1 Hz), 150.4 (d, *J* = 4.1 Hz), 147.8 (d, *J* = 7.4 Hz), 141.5 (d, *J* = 7.5 Hz), 136.2 (d, *J* = 1.5 Hz), 134.3, 129.9 (d, *J* = 0.9 Hz), 129.9 (d, *J* = 0.8 Hz), 125.7, 125.6 (dd, *J* = 9.5, 1.3 Hz), 120.1 (d, *J* = 5.0 Hz), 120.0 (d, *J* = 5.1 Hz), 118.5 (d, *J* = 4.7 Hz), 117.6 (d, *J* = 5.2 Hz), 101.3 (d, *J* = 5.1 Hz), 83.2, 28.0, 27.3.

^{31}P NMR (202 MHz, $CDCl_3$) δ -17.7, -18.7.

HRMS (ESI, m/z): $[M+Na]^+$ calc. 750.1628; found 750.1609

***tert*-Butyl 6-((diphenoxyphosphoryl)oxy)-3,4-dihydropyridine-1(2*H*)-carboxylate (1t)**



tert-Butyl 6-((diphenoxyphosphoryl)oxy)-3,4-dihydropyridine-1(2*H*)-carboxylate (**1t**) was prepared according to a reported literature procedure.[2]

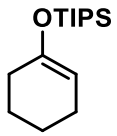
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 4H), 7.25 – 7.14 (m, 6H), 5.09 (td, *J* = 3.8, 3.0 Hz, 1H), 3.60 – 3.51 (m, 2H), 2.24 – 2.09 (m, 2H), 1.80 – 1.64 (m, 2H), 1.43 (s, 9H).

^{31}P NMR (162 MHz, $CDCl_3$) δ - 17.9 (d, *J* = 4.1 Hz, 1P).

Note: No ^{13}C NMR and HRMS were recorded due to the instability of the material.

The spectral data are consistent with those reported in the literature.[2]

(Cyclohex-1-en-1-yloxy)triisopropylsilane (1u)



(Cyclohex-1-en-1-yloxy)triisopropylsilane (**1u**) was prepared according to general procedure A2, using cyclohexanone (0.62 mL, 6.0 mmol) as the starting material, and TIPSOTf (1.90 mL, 7.20 mmol, 1.2 equiv.) as the silylating agent. The product was afforded as a colourless liquid in quantitative yield, and was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.88 (tt, *J* = 3.9, 1.3 Hz, 1H), 2.17 – 1.92 (m, 4H), 1.79 – 1.59 (m, 2H), 1.51 (ddt, *J* = 8.6, 6.0, 2.7 Hz, 2H), 1.12 – 1.06 (m, 18H), 1.08 – 1.03 (m, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 103.8, 30.1, 24.0, 23.4, 22.5, 18.1, 12.8

The spectral data are consistent with those reported in the literature.[3]

4. Substrate scope

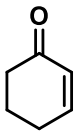
General procedure C for the dehydrogenation of silyl enol ethers

A round bottom flask equipped with a magnetic stir bar was charged with the indicated silyl enol ether (1 mmol), which was dissolved in acetone (0.125 M with respect to the staring material). The flask was cooled to 0 °C in an ice-water bath. Subsequently, NaOAc (160 mg, 2.00 mmol, 2.0 equiv.) was added, followed by the addition of PIFA (860 mg, 2.00 mmol, 2.0 equiv.) in one portion. After 10 minutes at 0 °C, the reaction mixture was warmed to room temperature and was stirred for additional 30 minutes at room temperature. The mixture was then concentrated under reduced pressure, and purified by flash column chromatography.

General procedure D for the desaturation of enol phosphates

A round bottom flask equipped with a magnetic stir bar was charged with the indicated enol phosphate (1 mmol), which was dissolved in the appropriate solvent (0.125 M with respect to the starting material; in acetone for the enol phosphates of lactones, in acetonitrile for the enol phosphates of lactams). The flask was cooled to 0 °C in an ice-water bath. Subsequently, NaOAc (160 mg, 2.00 mmol, 2.0 equiv.) was added, followed by the addition of PIFA (860 mg, 2.00 mmol, 2.0 equiv.) in one portion. After 10 minutes at 0 °C, the reaction mixture was warmed to room temperature and was stirred for additional 30 minutes at room temperature. The mixture was then concentrated under reduced pressure, and purified by flash column chromatography.

Cyclohex-2-en-1-one (2a)



Cyclohex-2-en-1-one (**2a**) was prepared according to general procedure C, using *tert*-butyl(cyclohex-1-en-1-yloxy)dimethylsilane (**1a**, 212 mg, 1.00 mmol) as the starting material. Microdistillation under vacuum, followed by flash column chromatography (hexane:EtOAc = 100:0 to 90:10 eluent) afforded the product as a yellow oil (60 mg, 62% yield).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.09 (dt, *J* = 10.1, 4.1 Hz, 1H), 6.03 (ddd, *J* = 10.1, 2.3, 1.8 Hz, 1H), 2.50 – 2.41 (m, 2H), 2.37 (tdd, *J* = 6.1, 4.0, 2.0 Hz, 2H), 2.05 – 1.97 (m, 2H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 201.8, 153.1, 129. 7, 38.2, 26.1, 23.0.

HRMS (ESI, m/z): $[M]^+$ calc. 96.0570; found 96.0567.

The spectral data are consistent with those reported in the literature.[9]

Cyclopent-2-en-1-one (2b)

Cyclopent-2-en-1-one (**2b**) was detected in a 0.05 mmol scale reaction using *tert*-butyl(cyclopent-1-en-1-yloxy)dimethylsilane (**1b**, 9.9 mg, 0.05 mmol) as the starting material. Mesitylene (5 µL, 0.1075 mmol, 2.15 equiv.) was used as an internal standard. 61% of the desired product **2b** were detected by ^{1}H NMR analysis of the crude reaction mixture.

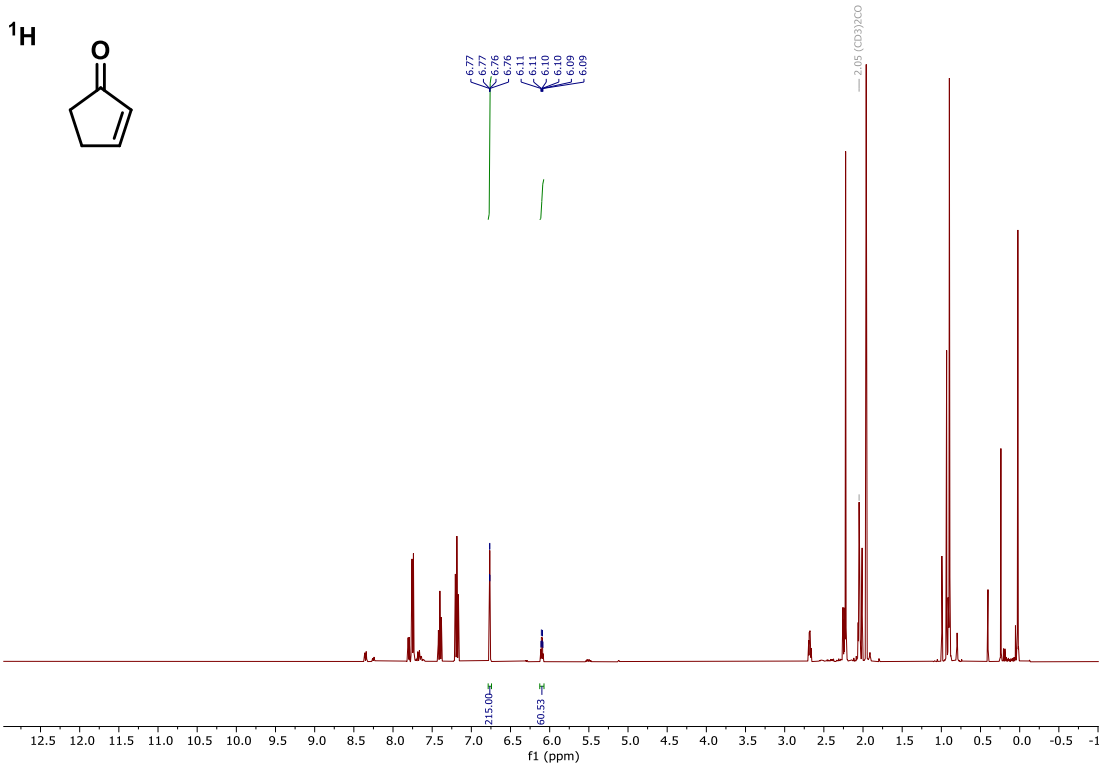
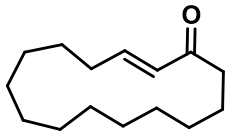


Figure S1: ^{1}H NMR of the crude reaction mixture using **1b** (acetone-d_6, 400 MHz). The peak at 6.10 ppm corresponds to the desired product (H-2 alkene peak). The peak at 6.77 ppm corresponds to the internal standard.

(*E*)-Cyclopentadec-2-en-1-one (2c)



(*E*)-Cyclopentadec-2-en-1-one (**2c**) was prepared according to general procedure C, using *tert*-butyl(cyclopentadec-1-en-1-yloxy)dimethylsilane (**1c**, 338 mg, 1.00 mmol) as the starting material. Flash column chromatography (pentane:Et_2O = 100:0 to 95:5 eluent) afforded the product as an off-white solid (99 mg, 45%).

(*E*)-Cyclopentadec-2-en-1-one (**2c**) was also prepared by a one-pot protocol. A round bottom flask equipped with a magnetic stir bar was charged with cyclopentadecanone (**1c"**, 224 mg, 1.00 mmol), which was dissolved in tetrahydrofuran (1 mL, 1.0 M with respect to the substrate). Et_3N (0.21 mL, 1.5 mmol, 1.5 equiv.) and TBSOTf (0.28 mL, 1.2 mmol, 1.2 equiv.) were added, and the resulting mixture was stirred for an hour at room temperature. Then acetone (9 mL) was added to the mixture, which was then cooled to 0 °C in an ice-water bath. Subsequently, NaOAc (160 mg, 2.00 mmol, 2.0 equiv.) was added, followed by the addition of PIFA (860 mg, 2.00 mmol, 2.0 equiv.) in one portion. After 10 minutes at 0 °C, the reaction mixture was warmed to room temperature and was stirred for additional 30 minutes. The reaction mixture was then concentrated. Flash column chromatography (pentane:Et_2O = 95:5 eluent) afforded the product as an off-white solid (76 mg, 34%).

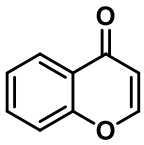
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (dt, *J* = 15.7, 7.4 Hz, 1H), 6.18 (dt, *J* = 15.7, 1.4 Hz, 1H), 2.57 – 2.38 (m, 2H), 2.32 – 2.21 (m, 2H), 1.75 – 1.61 (m, 2H), 1.54 (dtd, *J* = 12.0, 6.5, 2.8 Hz, 2H), 1.38 – 1.13 (m, 16H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 148.4, 131.0, 40.3, 31.9, 27.2, 27.1, 27.0, 26.9, 26.8, 26.7, 26.4, 26.2, 22.6, 22.5.

HRMS (ESI, m/z): $[M+H]^+$ calc. 223.2056; found 223.2056.

The spectral data are consistent with those reported in the literature.[10]

4*H*-Chromen-4-one (2d)



4*H*-Chromen-4-one (**2d**) was prepared according to the general procedure C using ((2*H*-chromen-4-yl)oxy)(*tert*-butyl)dimethylsilane (**1d**, 262 mg, 1.00 mmol) as the starting material. Flash column chromatography (hexane:EtOAc = 100:0 to 70:30 eluent) afforded the product as an off-white solid (113 mg, 77% yield).

4*H*-Chromen-4-one (**2d**) was also prepared by a one-pot protocol. A round bottom flask equipped with a magnetic stir bar was charged with chroman-4-one (**1d"**, 148 mg, 1.00 mmol), which was dissolved in tetrahydrofuran (1 mL, 1.0 M with respect to the substrate). Et_3N (0.21 mL, 1.5 mmol, 1.5 equiv.) and TBSOTf (0.28 mL, 1.2 mmol, 1.2 equiv.) were added, and the resulting mixture was stirred for an hour at room temperature. Then acetone (9 mL) was added to the mixture, which was then cooled to 0 °C in an ice-water bath. Subsequently, NaOAc (160 mg, 2.00 mmol, 2.0 equiv.) was added, followed by the addition of PIFA (860 mg, 2.00 mmol, 2.0 equiv.) in one portion. After 10 minutes at 0 °C, the reaction mixture was warmed to room temperature and was stirred for additional 30 minutes. The reaction mixture was then concentrated. Flash column

chromatography (pentane:Et_2O = 80:20 to 70:30 eluent) afforded the product as an off-white solid (75 mg, 51%).

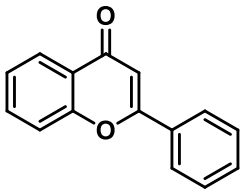
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.16 (m, 1H), 7.88 (dd, *J* = 6.0, 1.3 Hz, 1H), 7.67 (ddtd, *J* = 8.6, 7.1, 1.7, 0.9 Hz, 1H), 7.45 (dtd, *J* = 8.5, 1.3, 0.6 Hz, 1H), 7.43 – 7.36 (m, 1H), 6.44 – 6.36 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 156.7, 155.8, 134.1, 125.9, 125.5, 124.7, 118.3, 112.9.

HRMS (ESI, m/z): $[M+H]^+$ calc. 147.0441; found 147.0441.

The spectral data are consistent with those reported in the literature.[11]

2-Phenyl-4*H*-chromen-4-one (2e)



2-Phenyl-4*H*-chromen-4-one (**2e**) was prepared according to general procedure C, using *tert*-butyldimethyl((2-phenyl-2*H*-chromen-4-yl)oxy)silane (**1e**, 339 mg, 1.00 mmol) as the starting material. Flash column chromatography (hexane:EtOAc = 100:0 to 0:100 eluent) afforded the product as a light yellow solid (154 mg, 69% yield).

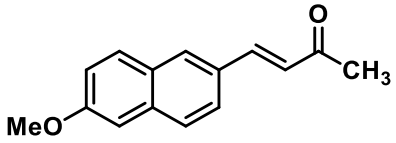
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (ddd, *J* = 7.9, 1.7, 0.5 Hz, 1H), 7.98 – 7.90 (m, 2H), 7.74 (ddd, *J* = 8.4, 7.1, 1.7 Hz, 1H), 7.61 (ddd, *J* = 8.5, 1.1, 0.5 Hz, 1H), 7.58 – 7.53 (m, 3H), 7.46 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.90 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.8, 163.7, 156.4, 134.0, 131.8, 131.8, 129.2, 126.5, 125.9, 125.4, 124.0, 118.2, 107.6.

HRMS (ESI, m/z): $[M+H]^+$ calc. 223.0754; found 223.0753.

The spectral data are consistent with those reported in the literature.[12]

(*E*)-4-(6-Methoxynaphtalen-2-yl)but-3-en-2-one (2f)



(*E*)-4-(6-Methoxynaphtalen-2-yl)but-3-en-2-one (**2f**) was prepared according to general procedure C, using *tert*-butyl((4-(6-methoxynaphthalen-2-yl)but-2-en-2-yl)oxy)dimethylsilane (**1f**, 342 mg, 1.00 mmol) as the starting material. Flash column chromatography (pentane:Et_2O = 80:20 to 50:50 eluent) afforded the product as an off-white solid (170 mg, 75%).

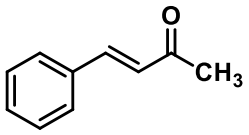
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 1H), 7.81 – 7.70 (m, 2H), 7.68 – 7.59 (m, 2H), 7.17 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.13 (d, *J* = 2.8 Hz, 1H), 6.79 (d, *J* = 16.2 Hz, 1H), 3.93 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 159.1, 143.9, 136.0, 130.3, 130.2, 129.9, 128.8, 127.7, 126.4, 124.3, 119.7, 106.1, 55.5, 27.7.

HRMS (ESI, m/z): $[M+H]^+$ calc. 227.1067; found 227.1069.

The spectral data are consistent with those reported in the literature.[13]

(*E*)-4-Phenylbut-3-en-2-one (2g)



(*E*)-4-Phenylbut-3-en-2-one (**2g**) was prepared according to general procedure C, using *tert*-butyldimethyl((4-phenylbut-2-en-2-yl)oxy)silane (**1g**, 262 mg, 1.00 mmol) as the starting material. Flash column chromatography (pentane:Et_2O = 100:0 to 90:10 eluent) afforded the product as an off-white solid (100 mg, 68%).

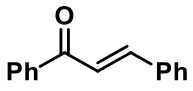
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 2H), 7.50 (d, *J* = 16.3 Hz, 1H), 7.45 – 7.35 (m, 3H), 6.71 (d, *J* = 16.3 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 143.5, 134.5, 130.6, 129.1, 128.4, 127.3, 27.6.

HRMS (ESI, m/z): $[M+H]^+$ calc. 147.0804; found 147.0806.

The spectral data are consistent with those reported in the literature.[14]

(*E*)-Chalcone (2h)



(*E*)-Chalcone (**2h**) was prepared according to general procedure C, using *tert*-butyl((1,3-diphenylprop-1-en-1-yl)oxy)dimethylsilane (**1h**, 324 mg, 1.00 mmol) as the starting material. Flash column chromatography (pentane:Et_2O = 100:0 to 90:10 eluent) afforded the product as an off-white solid (41 mg, 20%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.97 (m, 2H), 7.82 (d, *J* = 15.7 Hz, 1H), 7.69 – 7.57 (m, 3H), 7.54 (d, *J* = 15.8 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.46 – 7.39 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 145.0, 138.3, 135.0, 132.9, 130.7, 129.1, 128.8, 128.6, 128.5, 122.2.

HRMS (ESI, m/z): $[M+H]^+$ calc. 209.0961; found 209.0962.

The spectral data are consistent with those reported in the literature.[15]

(*E*)-3-(4-(*tert*-Butyl)phenyl)-2-methylacrylaldehyde (2j) + 2-(4-(*tert*-Butyl)benzyl)acrylaldehyde (2j')

2j **2j'**

(*E*)-3-(4-(*tert*-Butyl)phenyl)-2-methylacrylaldehyde (**2j**) and 2-(4-(*tert*-Butyl)benzyl)acrylaldehyde (**2j'**) were prepared according to general procedure C, using *tert*-butyl((3-(4-(*tert*-butyl)phenyl)-2-methylprop-1-en-1-yl)oxy)dimethylsilane (**1j**, 318 mg, 1.00 mmol) as the starting material. Flash column chromatography (hexane:EtOAc = 100:0 to 95:5 eluent) afforded the product as a pale yellow oil (113 mg, 56%, **2j:2j'** = 2:1).

For **2j**:

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.53 – 7.45 (m, 4H), 7.25 (d, *J* = 1.5 Hz, 1H), 2.10 (d, *J* = 1.3 Hz, 3H), 1.36 (s, 9H).

For **2j'**:

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.38 – 7.29 (m, 2H), 7.16 – 7.01 (m, 2H), 6.13 (td, *J* = 1.5, 0.7 Hz, 1H), 6.06 (q, *J* = 0.9 Hz, 1H), 3.54 (dq, *J* = 1.3, 0.7 Hz, 2H), 1.31 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ **195.8**, *194.2,* **153.3, 150.0**, *150.0, 149.4,* **137.8**, *135.3, 135.1,* **132.5, 130.2**, *128.9,* **125.8**, *125.6,* **35.0**, *34.5, 33.7, 31.5,* **31.3, 11.1.**

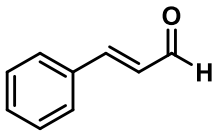
In bold: ^{13}C NMR signals attributed to **2j** upon comparison to literature spectra

In italics: ^{13}C NMR signals attributed to **2j'** upon comparison to literature spectra

HRMS (ESI, m/z): $[M+H]^+$ calc. 203.1430; found 203.1429

The spectral data are consistent with those reported in the literature.[16,17]

Cinnamaldehyde (2k)



Cinnamaldehyde (**2k**) was prepared according to general procedure C, using *tert*-butyldimethyl((3-phenylprop-1-en-1-yl)oxy)silane (**1k**, 248 mg, 1.00 mmol) as the starting material. Flash column chromatography (pentane:Et_2O = 90:10 eluent) afforded the product as a yellow oil (94 mg, 72%).

Cinnamaldehyde (**2k**) was also prepared by a one-pot protocol. A round bottom flask equipped with a magnetic stir bar was charged with 3-phenylpropanal (**1k"**, 134 mg, 1.00 mmol), which was dissolved in tetrahydrofuran (1 mL, 1.0 M with respect to the substrate). Et_3N (0.21 mL, 1.5 mmol, 1.5 equiv.) and TBSOTf (0.28 mL, 1.2 mmol, 1.2 equiv.) were added, and the resulting mixture was stirred for an hour at room temperature. Then acetone (9 mL) was added to the mixture, which was then cooled to 0 °C in an ice-water bath. Subsequently, NaOAc (160 mg, 2.00 mmol, 2.0 equiv.) was added, followed by the addition of PIFA (860 mg, 2.00 mmol, 2.0 equiv.) in one portion. After 10 minutes at 0 °C, the reaction mixture was warmed up to room temperature and was stirred for additional 30 minutes. The reaction mixture was then concentrated. Flash column chromatography (pentane:EtOAc = 90:10 eluent) afforded the product as an yellow liquid (64 mg, 48%).

Scale-up:

Cinnamaldehyde (**2k**) was also prepared on a 14-mmol scale according to general procedure C, using *tert*-butyldimethyl((3-phenylprop-1-en-1-yl)oxy)silane (**1k**, 3.47 g, 14.0 mmol) as the starting material. Flash column chromatography (pentane:Et_2O = 80:20 eluent) afforded the product as a yellow oil (1.35 g, 73%).

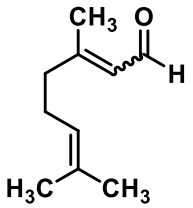
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, *J* = 7.7 Hz, 1H), 7.65 – 7.52 (m, 2H), 7.50 (d, *J* = 16.0 Hz, 1H), 7.47 – 7.36 (m, 3H), 6.72 (dd, *J* = 15.9, 7.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 152.9, 134.1, 131.4, 129.2, 128.7, 128.6.

HRMS (ESI, m/z): $[M+Na]^+$ calc. 155.0467; found 155.0466.

The spectral data are consistent with those reported in the literature.[18]

3,7-Dimethylocta-2,6-dienal (2l)



3,7-Dimethylocta-2,6-dienal (**2l**) was prepared according to general procedure C, using *tert*-butyl((3,7-dimethylocta-1,6-dien-1-yl)oxy)dimethylsilane (**1l**, 269 mg, 1.00 mmol) as the starting material. Flash column chromatography (hexane:EtOAc = 100:0 to 85:15 eluent) afforded the product as a light yellow solid (70 mg, 46%, *E/Z* = 63:37).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (dd, *J* = 8.1, 0.6 Hz, 0.63H), 9.89 (dd, *J* = 8.2, 0.5 Hz, 0.35H), 5.92 – 5.84 (m, 1H), 5.08 (dddd, *J* = 13.7, 6.8, 3.3, 1.4 Hz, 1H), 2.58 (t, *J* = 7.5 Hz, 1H), 2.28 – 2.19 (m, 3H), 2.16 (d, *J* = 1.3 Hz, 2H), 1.98 (dd, *J* = 1.3, 0.5 Hz, 1H), 1.70 – 1.66 (m, 3H), 1.61 (d, *J* = 1.4 Hz, 2H), 1.60 – 1.58 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, overlapping signals) δ 191.5, 191.0, 164.0, 133.9, 133.1, 128.8, 127.6, 122.7, 122.4, 40.8, 32.7, 27.2, 25.9, 25.8, 25.2, 17.9, 17.7.

HRMS (ESI, m/z): $[M+H]^+$ calc. 153.1274; found 153.1275.

The spectral data of the mixture of *E* and *Z* isomers are consistent with those reported in the literature.[19,20]

3,6-Dihydro-2*H*-pyran-4-carbaldehyde (2m)

3,6-Dihydro-2*H*-pyran-4-carbaldehyde (**2m**) was detected in a 0.05 mmol scale reaction using *tert*-butyldimethyl((tetrahydro-4*H*-pyran-4-ylidene)methoxy)silane (**1m**, 11.4 mg, 0.05 mmol) as the starting material. 1,1,2,2-Tetrachloroethane (5 µL, 0.095 mmol, 1.90 equiv.) was used as an internal standard. 41% of the desired product **2m** were detected by ^{1}H NMR analysis of the crude reaction mixture.

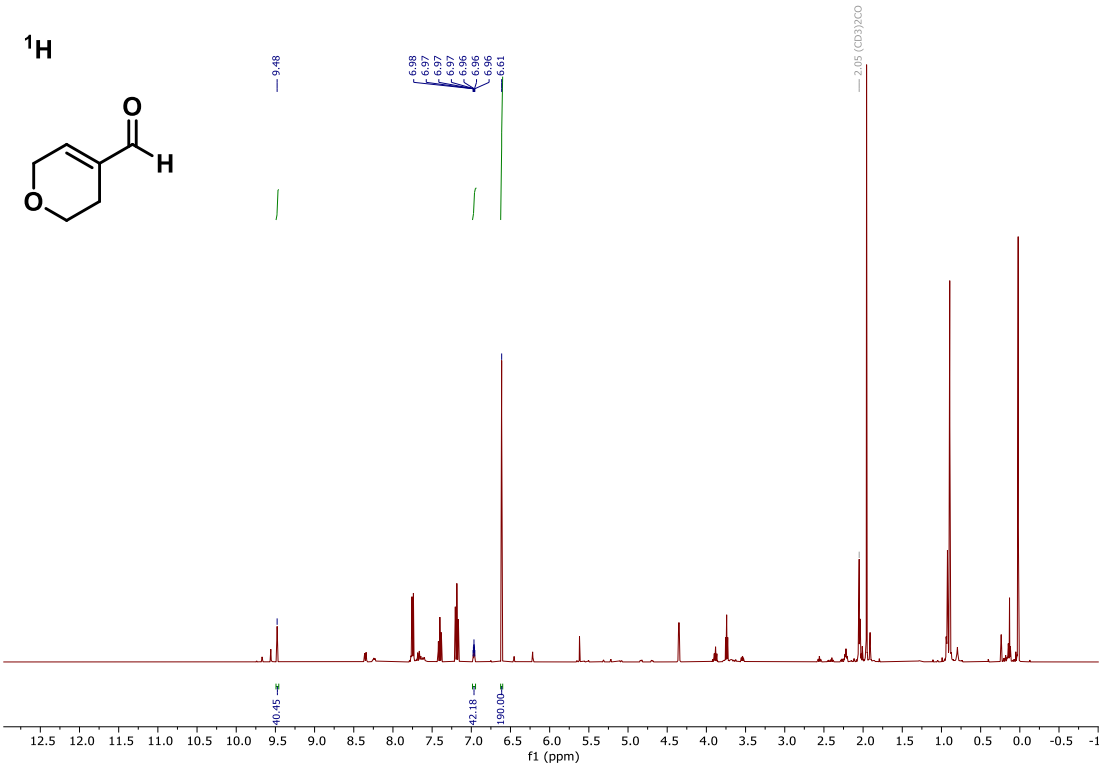
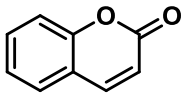


Figure S2: ^{1}H NMR of the crude reaction mixture using **1m** (acetone-d_6, 400 MHz). The peaks at 6.97 and 9.48 ppm correspond to the desired product (H-1 aldehyde and H-3 alkene peaks). The peak at 6.61 ppm corresponds to the internal standard.

2*H*-Chromen-2-one (2n)



2*H*-Chromen-2-one (**2n**) was prepared according to general procedure D, using 4*H*-chromen-2-yl diphenyl phosphate (**1n**, 380 mg, 1.00 mmol) as the starting material. Flash column chromatography (hexane:EtOAc = 100:0 to 80:20 eluent) afforded the product as an off-white solid (114 mg, 78% yield).

2*H*-Chromen-2-one (**2n**) was also prepared by a one-pot protocol. A flame-dried round bottom flask equipped with a magnetic stir bar was charged with chroman-2-one (**1n"**, 148 mg, 1.0 mmol), which was dissolved in dry tetrahydrofuran (8 mL, 0.125 M with respect to the substrate) under N_2 atmosphere. The resulting solution was cooled to – 78 °C. Then, LiHMDS (1.0 mL, 1.0 mmol, 1.0 equiv., 1 M in THF) was added dropwise at – 78 °C, and the mixture was stirred for 30 minutes at – 78 °C. Then, diphenyl phosphoryl chloride (0.21 mL, 1.0 mmol, 1.0 equiv.) was added dropwise at – 78 °C, the mixture was warmed to room temperature, and stirred for an additional hour. Then, KTFA (608 mg, 4.0 mmol, 4.0 equiv.) and PIFA (1.720 g, 4.0 mmol, 4.0 equiv.) were added to the mixture, which was stirred for 30 minutes at room temperature. The mixture was then concentrated under reduced pressure. Flash column chromatography (pentane:Et_2O = 90:10 to 80:20 eluent) afforded the product as an off-white solid (87 mg, 60% yield).

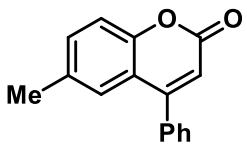
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 9.6, 7.2Hz, 1H), 7.59 – 7.40 (m, 2H), 7.35 – 7.18 (m, 2H), 6.46 – 6.34 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 154.1, 143.6, 131.9, 128.0, 124.6, 118.9, 116.9, 116.7.

HRMS (ESI, m/z): $[M+H]^+$ calc. 147.0441; found 147.0444.

The spectral data are consistent with those reported in the literature.[21]

6-Methyl-4-phenyl-2*H*-chromen-2-one (2o)



6-Methyl-4-phenyl-2*H*-chromen-2-one (**2o**) was prepared according to general procedure D, using 6-methyl-4-phenyl-4*H*-chromen-2-yl diphenyl phosphate (**1o**, 470 mg, 1.00 mmol) as the starting material. Flash column chromatography (pentane:Et_2O = 80:20 eluent) afforded the product as an off-white solid (101 mg, 43%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 3H), 7.48 – 7.40 (m, 2H), 7.35 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 6.34 (s, 1H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 155.8, 152.4, 135.5, 134.0, 133.0, 129.7, 129.0, 128.9, 126.8, 118.8, 117.2, 115.3, 21.1.

HRMS (ESI, m/z): $[M+Na]^+$ calc. 259.0730; found 259.0728.

The spectral data are consistent with those reported in the literature.[22]

5,6-Dihydro-2*H*-pyran-2-one (2p)

5,6-Dihydro-2*H*-pyran-2-one (**2p**) was detected in a 0.05 mmol scale reaction using 3,4-dihydro-2*H*-pyran-6-yl diphenyl phosphate (**1p**, 16.6 mg, 0.05 mmol) as the starting material. Mesitylene (5 µL, 0.1075 mmol, 2.15 equiv.) was used as an internal standard. 43% of the desired product **2p** were detected by ^{1}H NMR analysis of the crude reaction mixture.

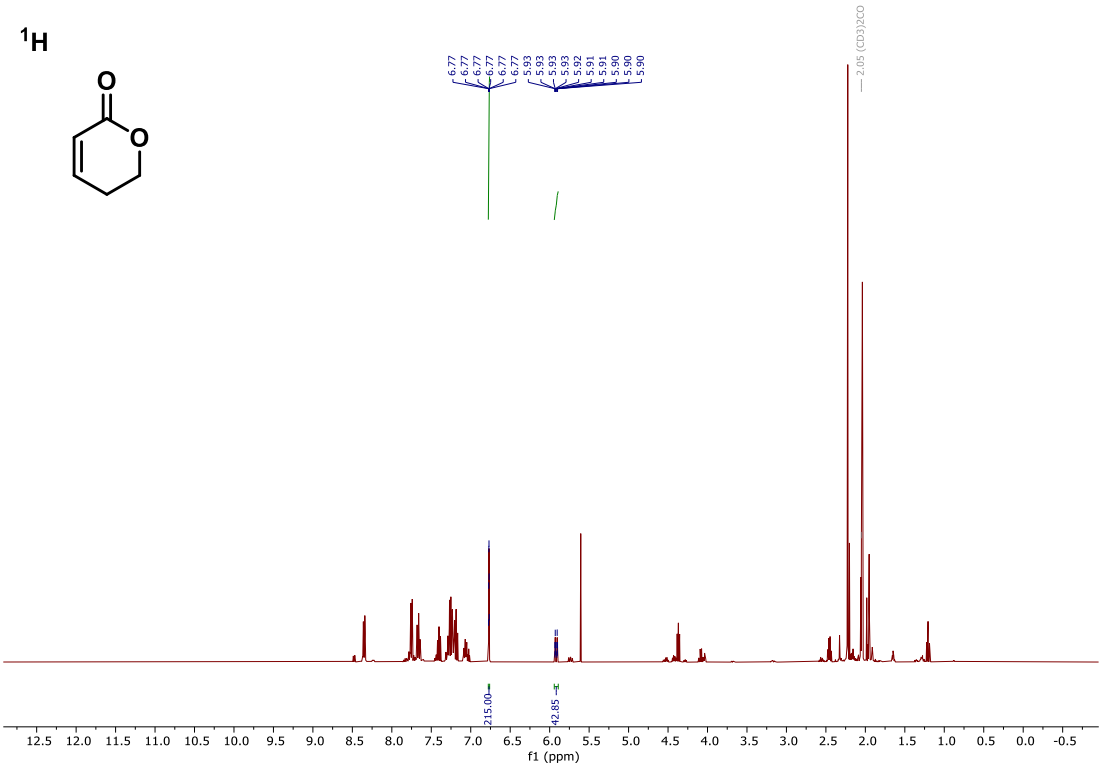
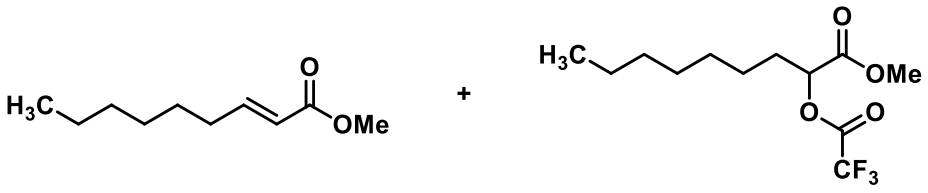


Figure S3: ^{1}H NMR of the crude reaction mixture using **1p** (acetone-d_6, 400 MHz). The peak at 5.92 ppm corresponds to the desired product (H-2 alkene peak). The peak at 6.77 ppm corresponds to the internal standard.

Methyl (*E*)-non-2-enoate (2q) + methyl 2-(2,2,2-trifluoroacetoxy)nonanoate (2q')



2q 2q'

Methyl (*E*)-non-2-enoate (**2q**) was prepared according to general procedure D, using 1-methoxynon-1-en-1-yl diphenyl phosphate (**1q**, 234 mg, 0.580 mmol) as the starting material. Flash column chromatography (pentane:Et_2O = 100:0 to 90:10 eluent) afforded the desired product (**2q**) as a yellow oil, co-isolated with side product methyl 2-(2,2,2-trifluoroacetoxy)nonanoate (**2q'**) (60.0 mg of the mixture of **2q** and **2q'**; **2q**:**2q'** = 43:57; corresponding to 25% yield of **2q**, and 34% yield of **2q'**). The ratio of **2q** and **2q'** was determined by ^{1}H NMR analysis.

^{1}H NMR: (400 MHz, $CDCl_3$) δ **6.97 (dt, *J* = 15.6, 7.0 Hz, 0.43H), 5.81 (dt, *J* = 15.6, 1.6 Hz, 0.43H)**, 5.17 (dd, J = 6.9, 5.6 Hz, 0.57H), 3.78 (s, 1.76H), **3.72 (s, 1.26H)**, **2.19 (qd, *J* = 7.1, 1.6 Hz, 0.87H)**, 2.04 – 1.88 (m, 1.16H), **1.55 – 1.39 (m, 2H), 1.34 – 1.19 (m, 8H), 1.11 – 0.84 (m, 3H).**

^{13}C NMR: (101 MHz, $CDCl_3$) δ 168.62, 167.35, 157.20 (d, *J* = 43.1 Hz), 149.97, 120.95, 114.56 (d, *J* = 285.0 Hz), 75.54, 52.90, 51.49, 32.36, 31.77, 31.73, 30.81, 29.03, 29.02, 28.94, 28.12, 24.92, 22.70, 22.68, 14.16 (d, *J* = 1.5 Hz).

^{19}F NMR: (376 MHz, $CDCl_3$) δ -75.02.

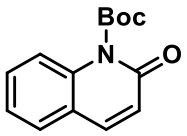
In bold: ^{1}H NMR signals attributed to **2q**.

Underlined*:* ^{1}H NMR signals attributed to **2q'**.

Underlined bold chemical shifts correspond to overlapping peaks of **2q** and **2q'**.

The peaks attributed to **2q** in the ^{1}H and ^{13}C spectra of the mixture of **2q** and **2q'** isomers are consistent with those reported in the literature for the isolated species.[23]

***tert*-Butyl 2-oxoquinoline-1(2*H*)-carboxylate (2r)**



tert-Butyl 2-oxoquinoline-1(2*H*)-carboxylate (**2r**) was prepared according to general procedure D, using *tert*-butyl 2-((diphenoxyphosphoryl)oxy)quinoline-1(4*H*)-carboxylate (**1r**, 440 mg, 0.92

mmol) as the starting material. Flash column chromatography (pentane:EtOAC = 80:20 to 66:33 eluent) afforded the product as a yellow oil (154 mg, 68%).

tert-Butyl 2-oxoquinoline-1(2*H*)-carboxylate (**2r**) was also prepared by a one-pot protocol. A flame-dried round bottom flask equipped with a magnetic stir bar was charged tert-butyl 2-oxo-3,4-dihydroquinoline-1(2*H*)-carboxylate (**1r"**, 247 mg, 1.0 mmol), which was dissolved in dry tetrahydrofuran (8 mL, 0.125 M with respect to the substrate) under N_2 atmosphere. The resulting solution was cooled to – 78 °C. Then, LiHMDS (1.1 mL, 1.1 mmol, 1.1 equiv., 1 M in THF) was added dropwise at – 78 °C, and the mixture was stirred for 30 minutes at – 78 °C. Then, diphenyl phosphoryl chloride (0.23 mL, 1.1 mmol, 1.1 equiv.) was added dropwise at – 78 °C, the mixture was warmed to room temperature, and stirred for an additional hour. Then, dry acetonitrile (8 mL) was added to the mixture, and it was cooled down to 0 °C. NaOAc (160 mg, 2.00 mmol, 2.0 equiv.) and PIFA (860 mg, 2.00 mmol, 2.0 equiv.) were added to the mixture, which was stirred for 10 minutes at 0 °C, then for 30 minutes at room temperature. The mixture was then concentrated under reduced pressure. Flash column chromatography (pentane:EtOAc = 66:33 eluent) afforded the product as a yellow oil (100 mg, 41% yield).

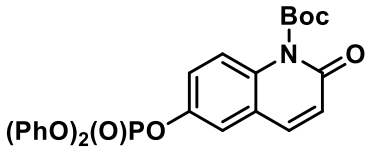
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dt, *J* = 9.5, 0.5 Hz, 1H), 7.64 – 7.44 (m, 2H), 7.34 – 7.20 (m, 1H), 7.19 – 7.06 (m, 1H), 6.67 (d, *J* = 9.6 Hz, 1H), 1.69 (s, 9H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 150.7, 141.1, 136.6, 131.1, 128.8, 123.4, 121.3, 119.7, 113.9, 87.1, 27.7

HRMS (ESI, m/z): $[M+Na]^+$ calc. 268.0944; found 268.0940.

The spectral data are consistent with those reported in the literature.[24]

tert-Butyl 6-((diphenoxyphosphoryl)oxy)-2-oxoquinoline-1(2*H*)-carboxylate (2s)



tert-Butyl 6-((diphenoxyphosphoryl)oxy)-2-oxoquinoline-1(2*H*)-carboxylate (**2s**) was prepared according to general procedure D, using *tert*-butyl 2,6-bis((diphenoxyphosphoryl)oxy)quinoline-1(4*H*)-carboxylate (**1s**, 182 mg, 0.250 mmol) as the starting material. Flash column chromatography (pentane:EtOAC = 66:33 eluent) afforded the product as a yellow oil (40 mg, 33%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 9.7 Hz, 1H), 7.44 (dd, *J* = 2.8, 1.3 Hz, 1H), 7.42 – 7.33 (m, 5H), 7.26 – 7.20 (m, 6H), 7.15 – 7.06 (m, 1H), 6.65 (d, *J* = 9.7 Hz, 1H), 1.68 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 150.7, 150.4 (d, *J* = 7.4 Hz), 145.8 (d, *J* = 7.2 Hz), 139.8, 134.4 (d, *J* = 1.2 Hz), 130.1 (d, *J* = 0.9 Hz), 126.0 (d, *J* = 1.4 Hz), 123.4 (d, *J* = 5.1 Hz), 123.0, 120.3 (d, *J* = 6.0 Hz), 120.2 (d, *J* = 4.9 Hz), 119.2 (d, *J* = 4.8 Hz), 115.4, 87.1, 27.7.

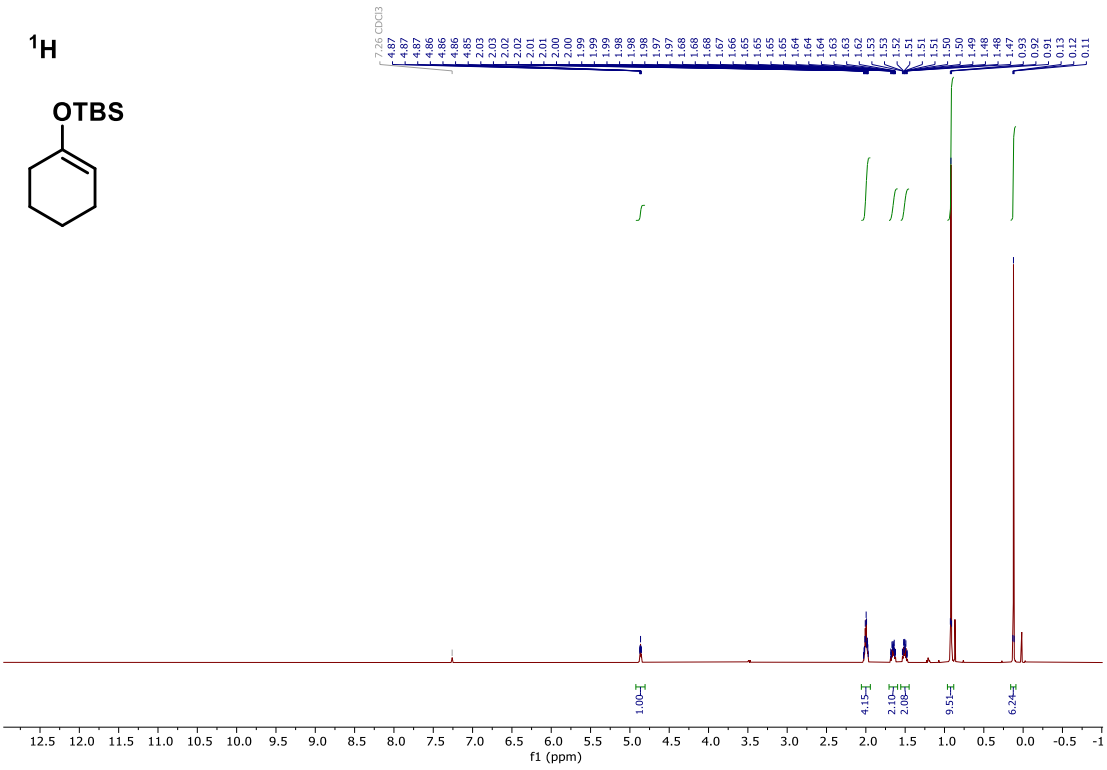
^{31}P NMR (162 MHz, $CDCl_3$) δ -17.4.

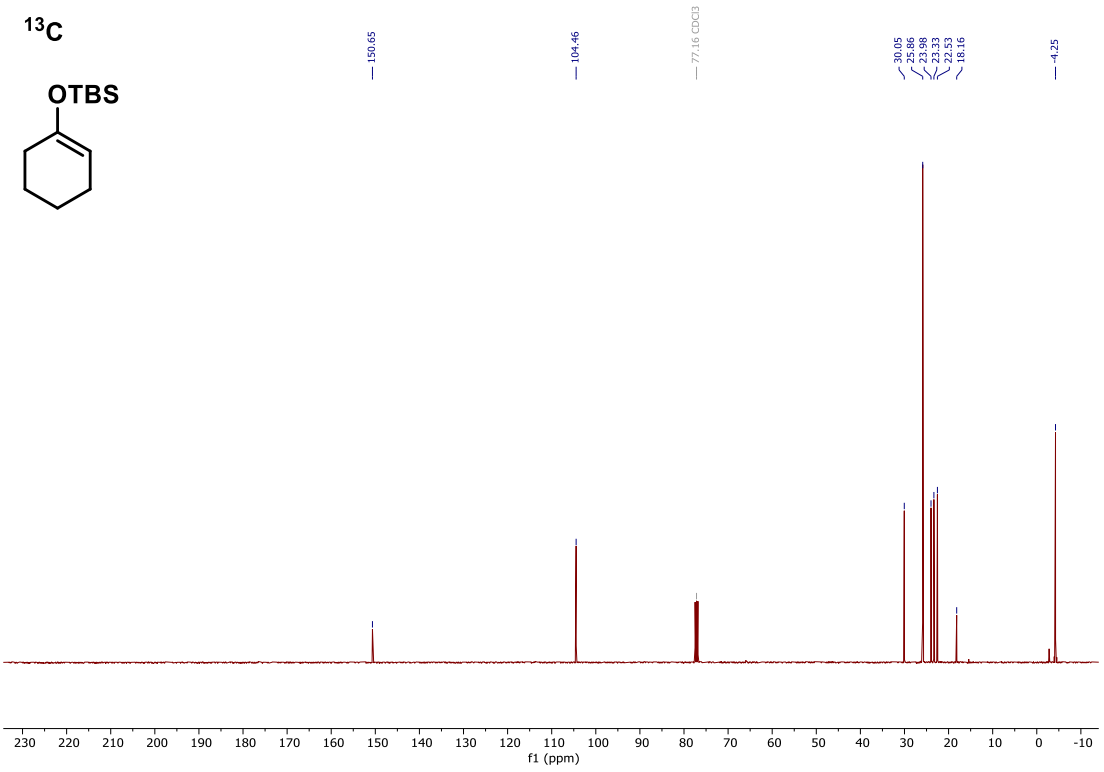
HRMS (ESI, m/z): $[M+Na]^+$ calc. 516.1183; found 516.1177

5. NMR Spectra

Starting materials

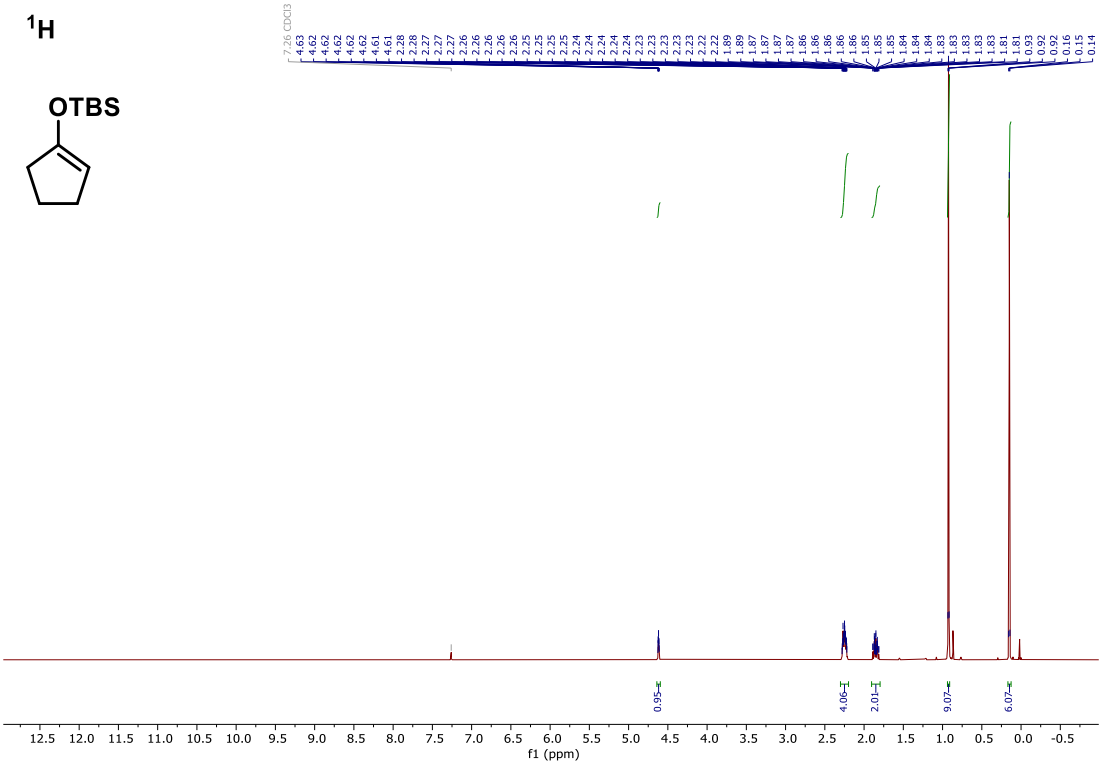
tert-Butyl(cyclohex-1-en-1-yloxy)dimethylsilane (1a)



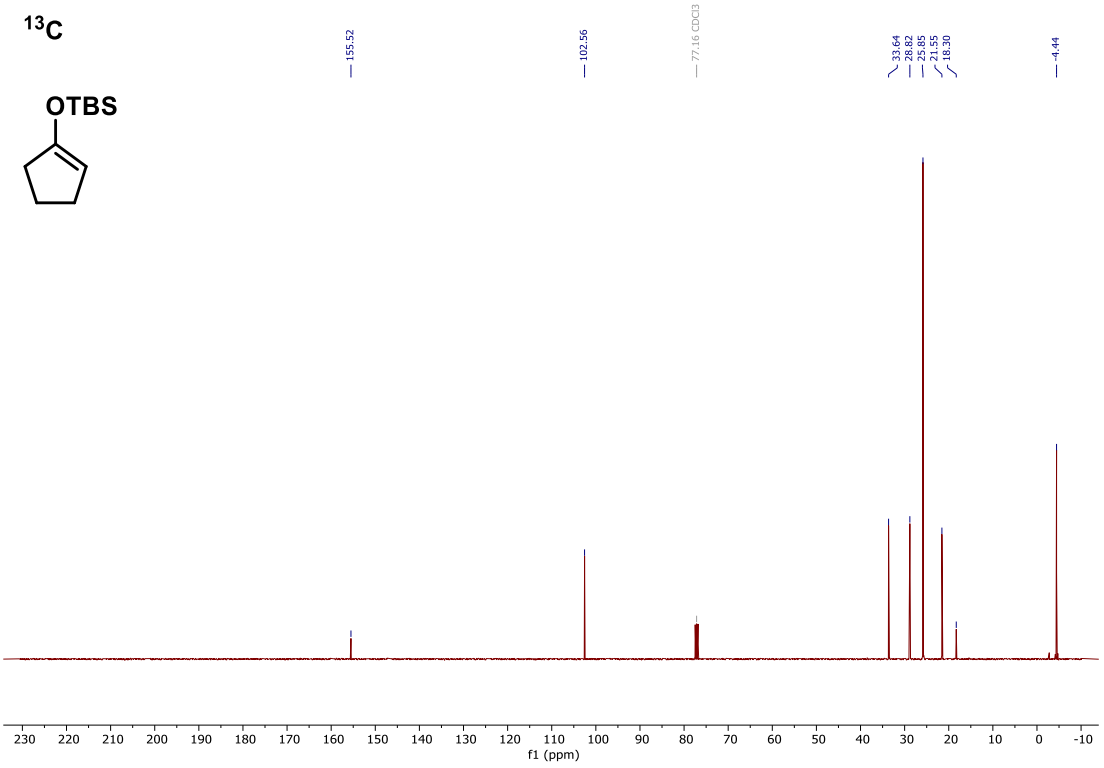

13C
OTBS
150.65
104.46
77.16 CDCl3
30.05
25.86
23.98
23.33
22.53
18.16
-4.25
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

tert-Butyl(cyclopent-1-en-1-yloxy)dimethylsilane (1b)

^{1}H

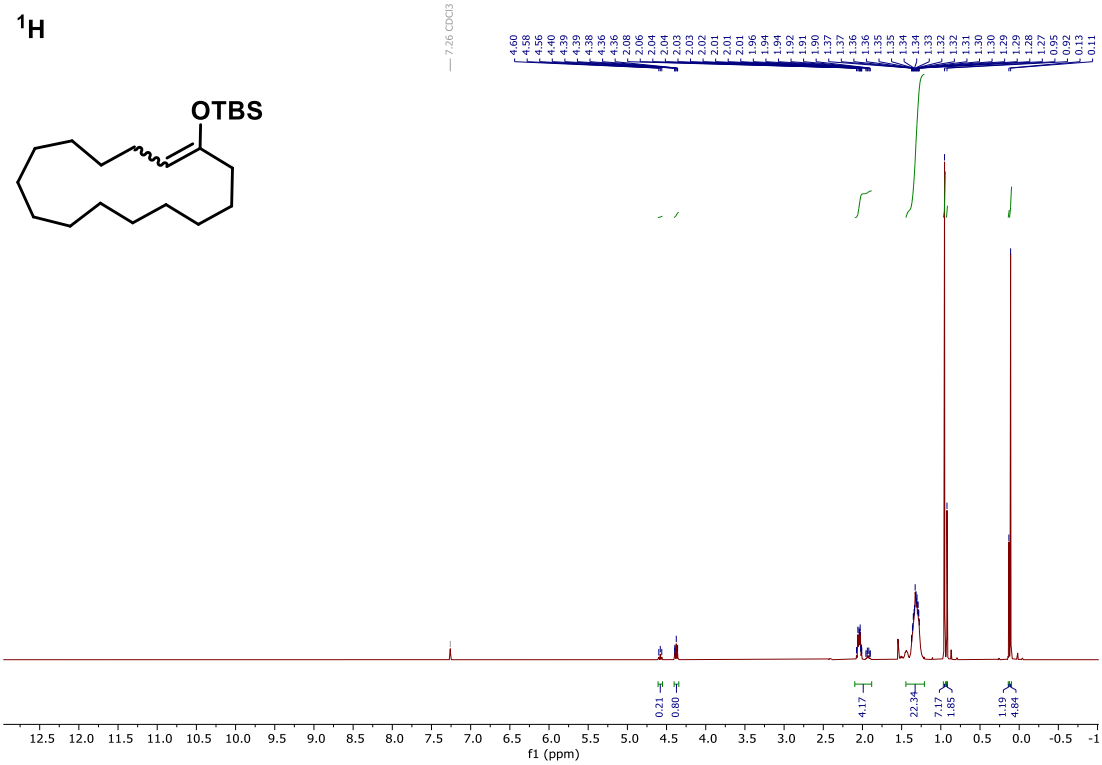


^{13}C

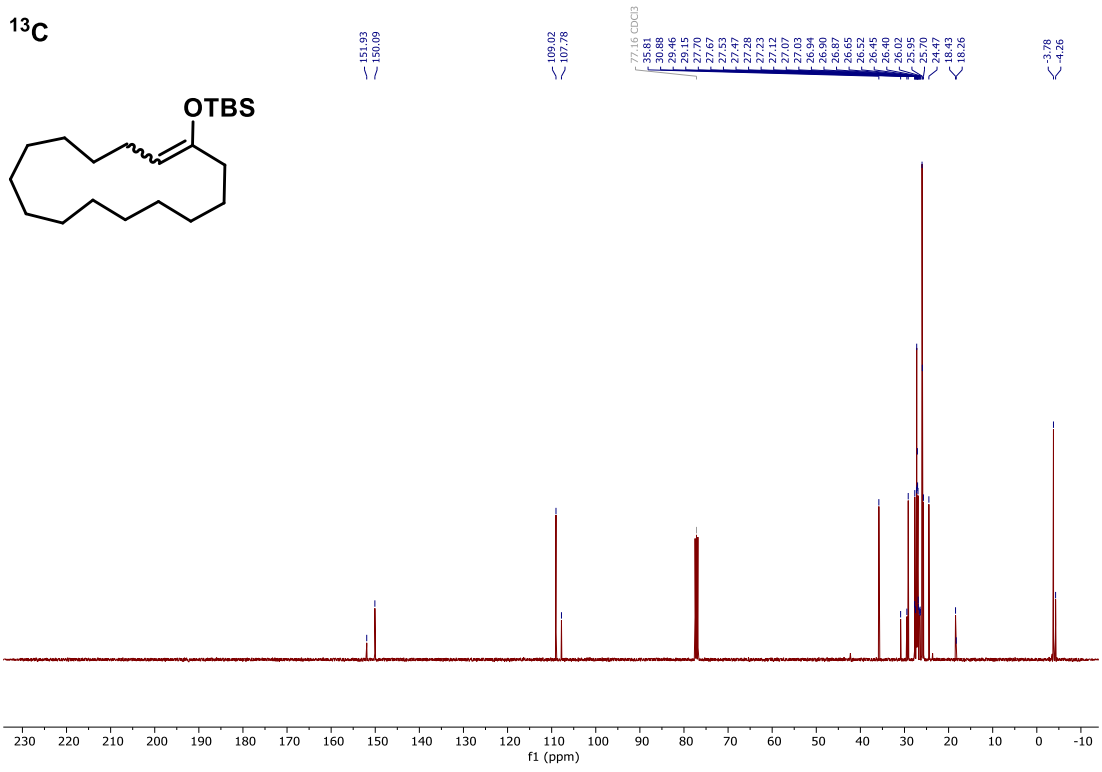


tert-Butyl(cyclopentadec-1-en-1-yloxy)dimethylsilane (1c)

^{1}H

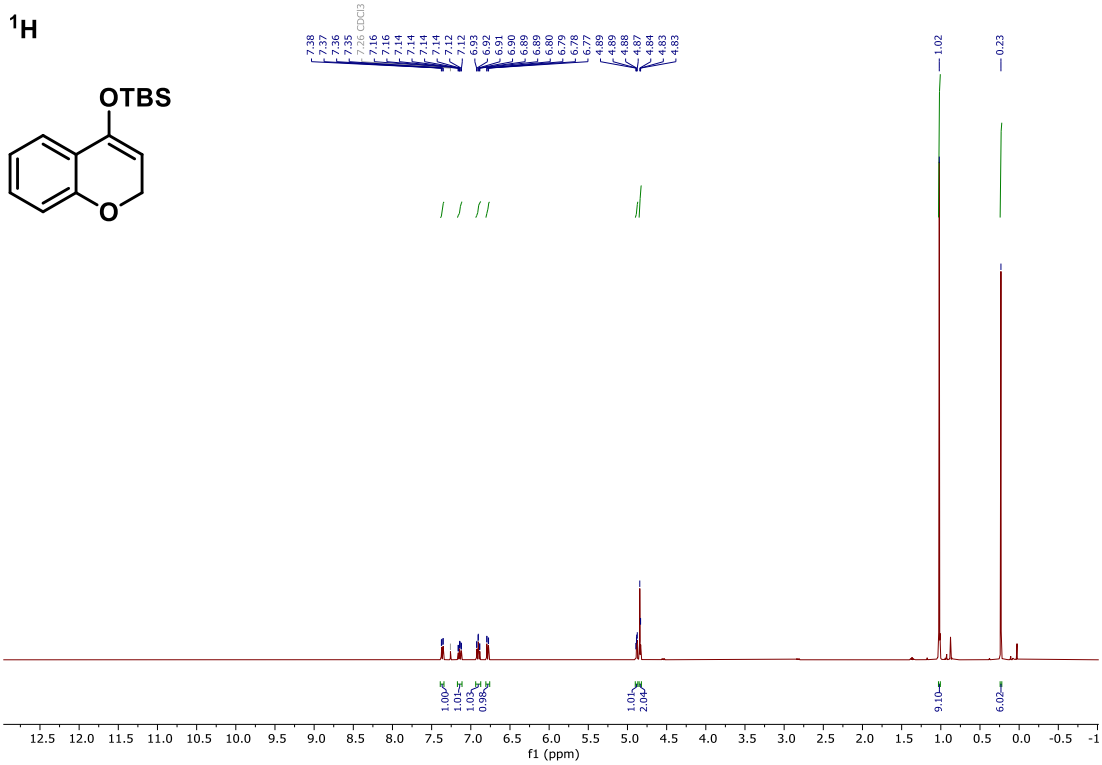


^{13}C

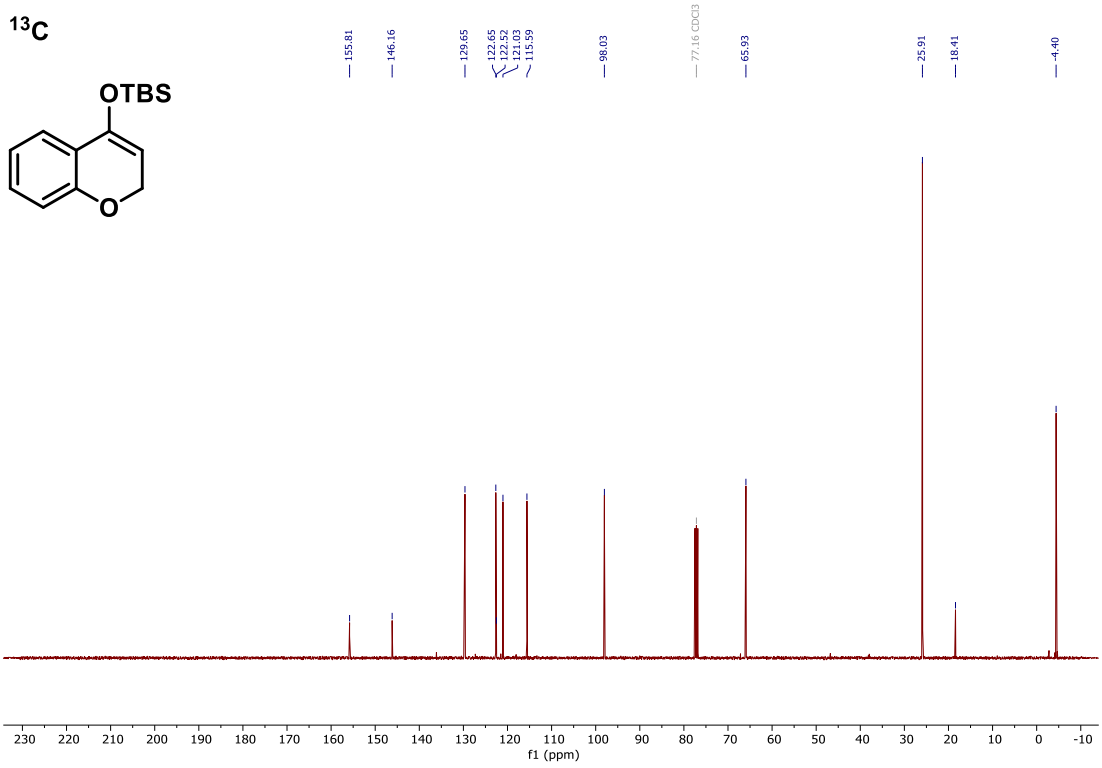


((2*H*-Chromen-4-yl)oxy)(*tert*-butyl)dimethylsilane (1d)

^{1}H

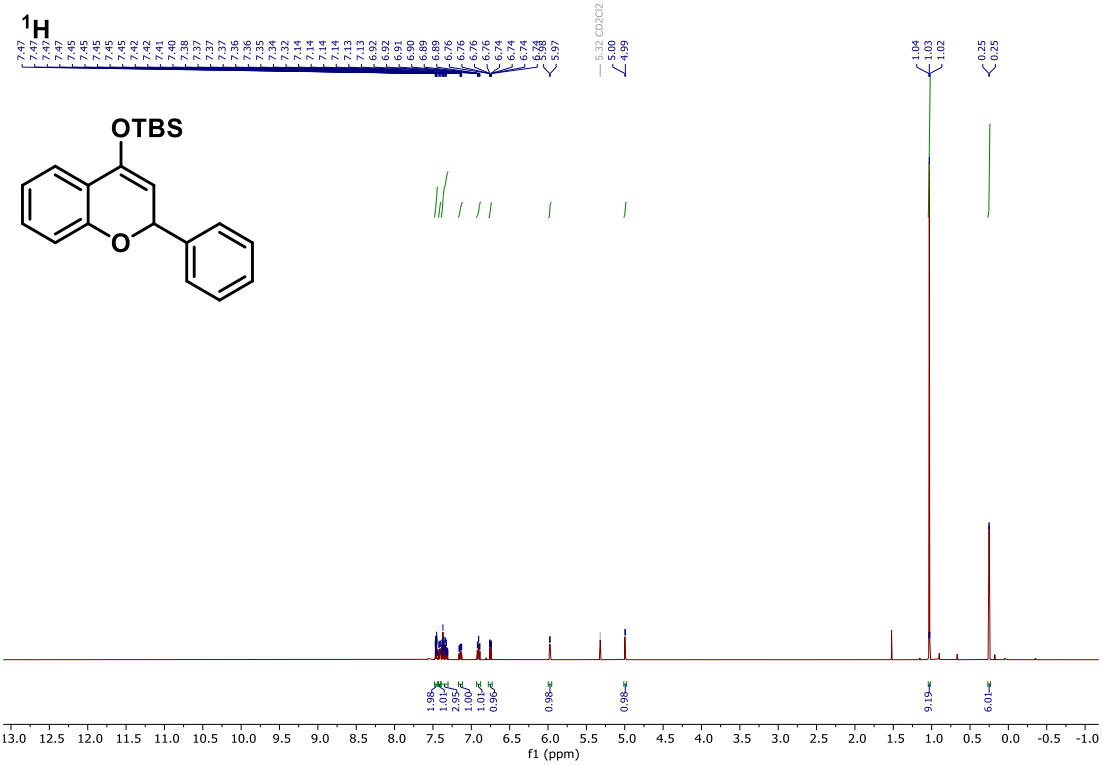


^{13}C

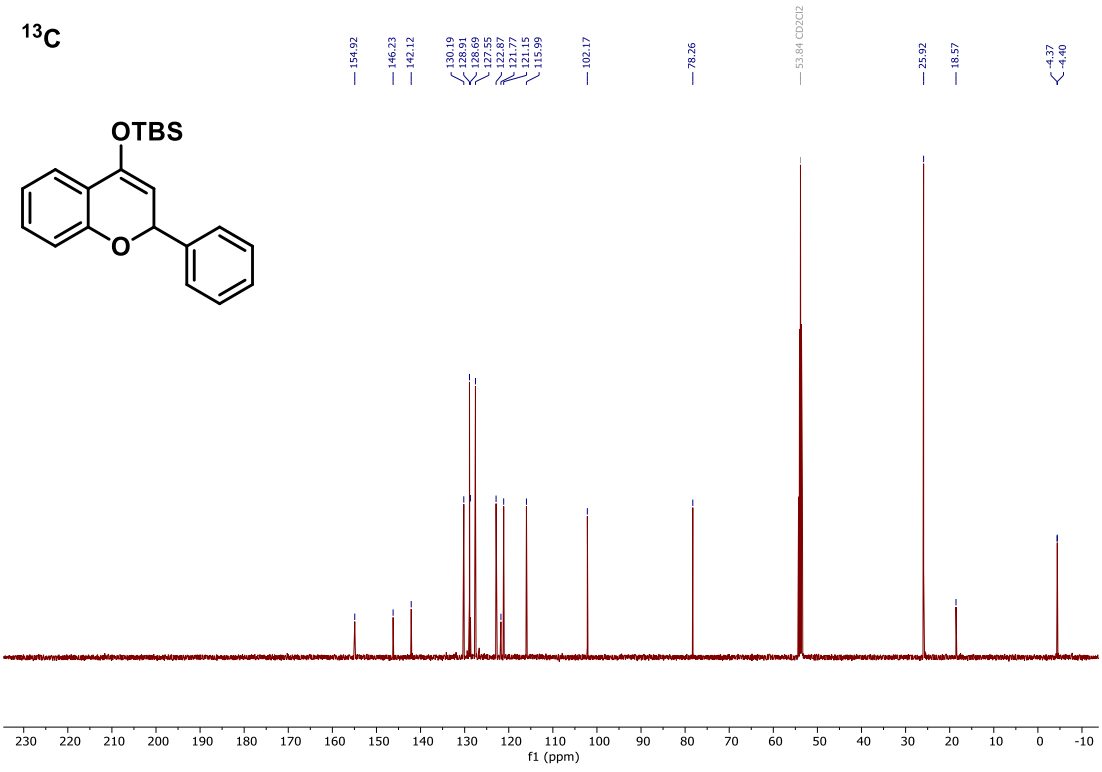


tert-Butyldimethyl((2-phenyl-2*H*-chromen-4-yl)oxy)silane (1e)

^{1}H

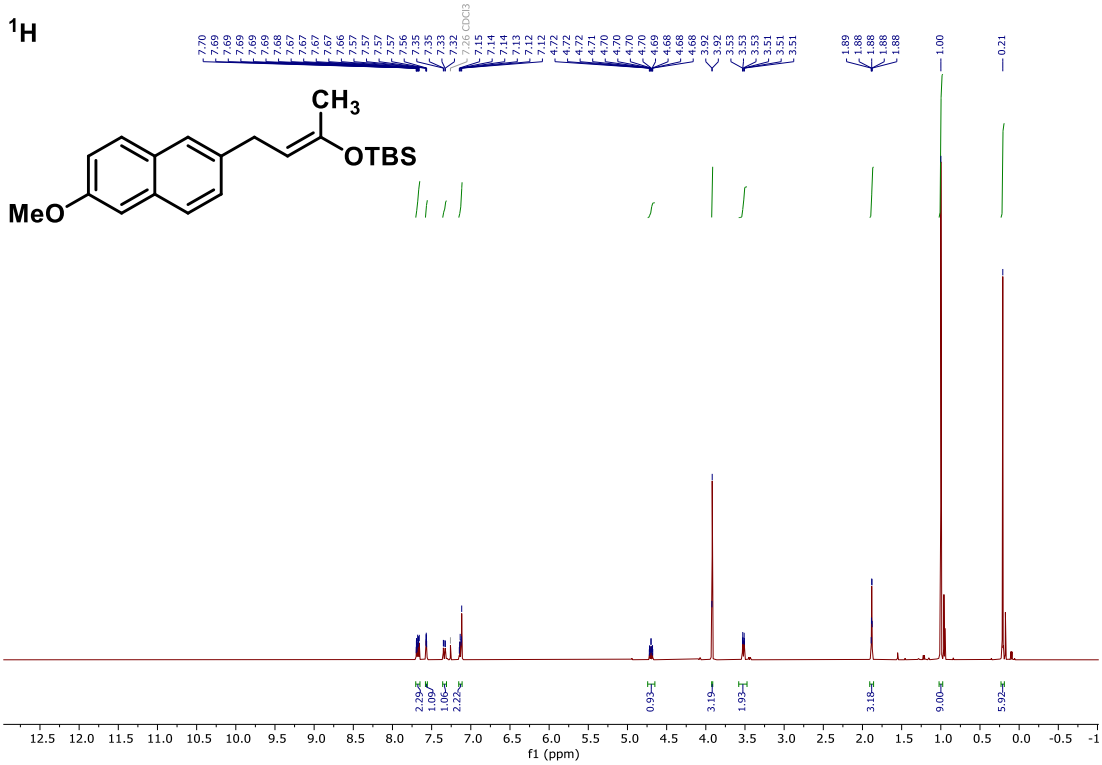


^{13}C

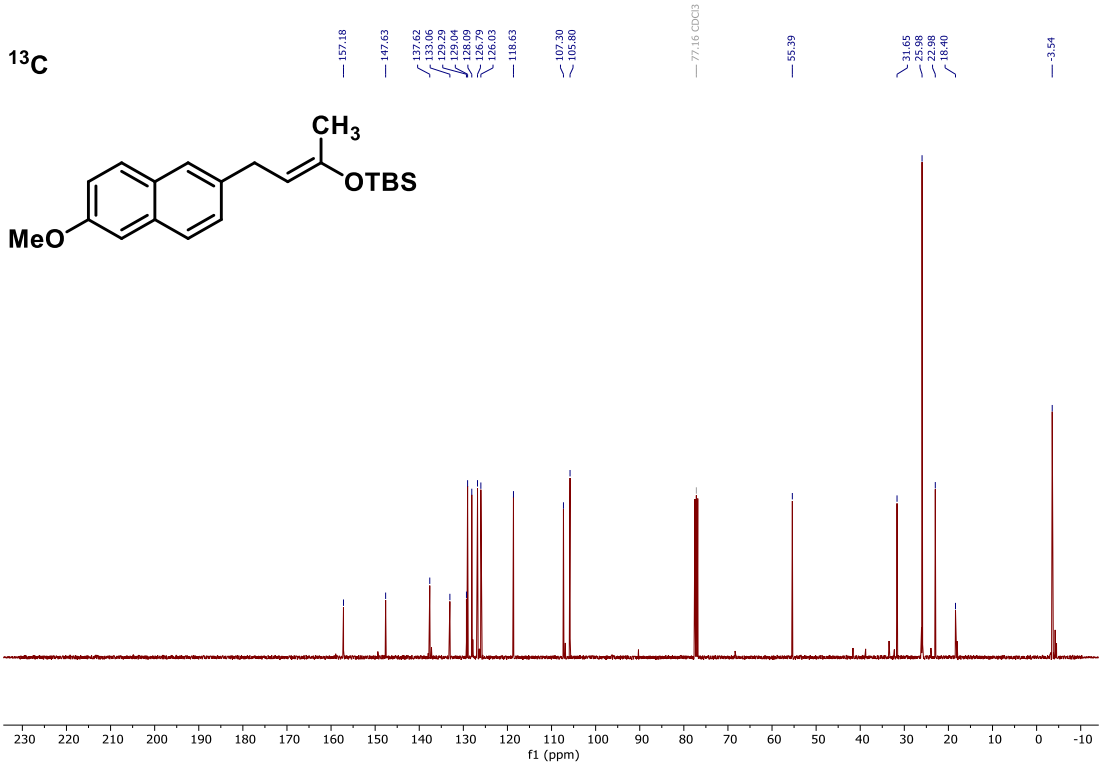


tert-Butyl((4-(6-methoxynaphthalen-2-yl)but-2-en-2-yl)oxy)dimethylsilane (1f)

^{1}H

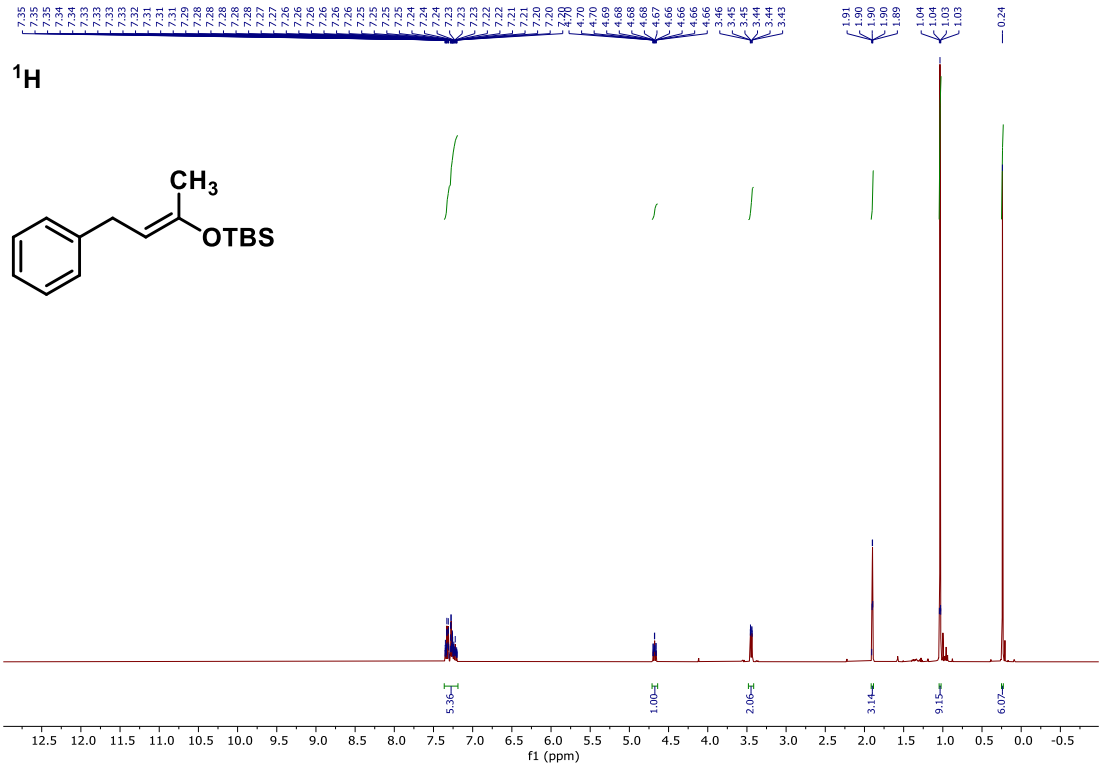


^{13}C

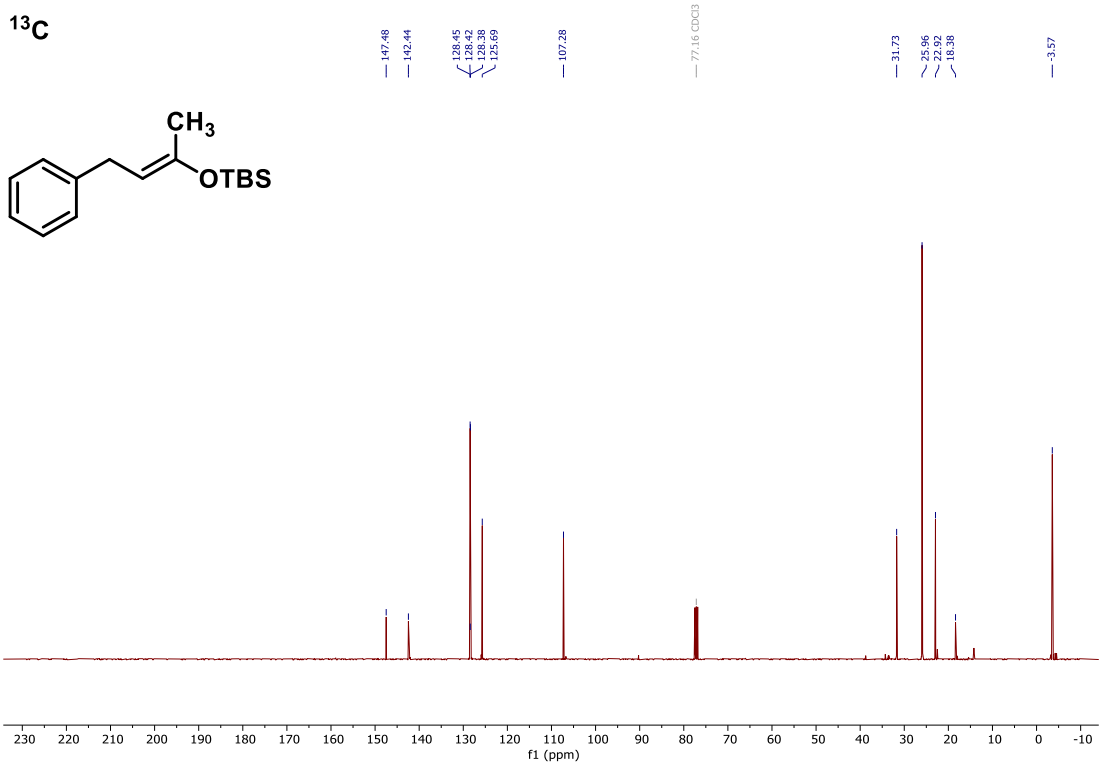


tert-Butyldimethyl((4-phenylbut-2-en-2-yl)oxy)silane (1g)

^{1}H

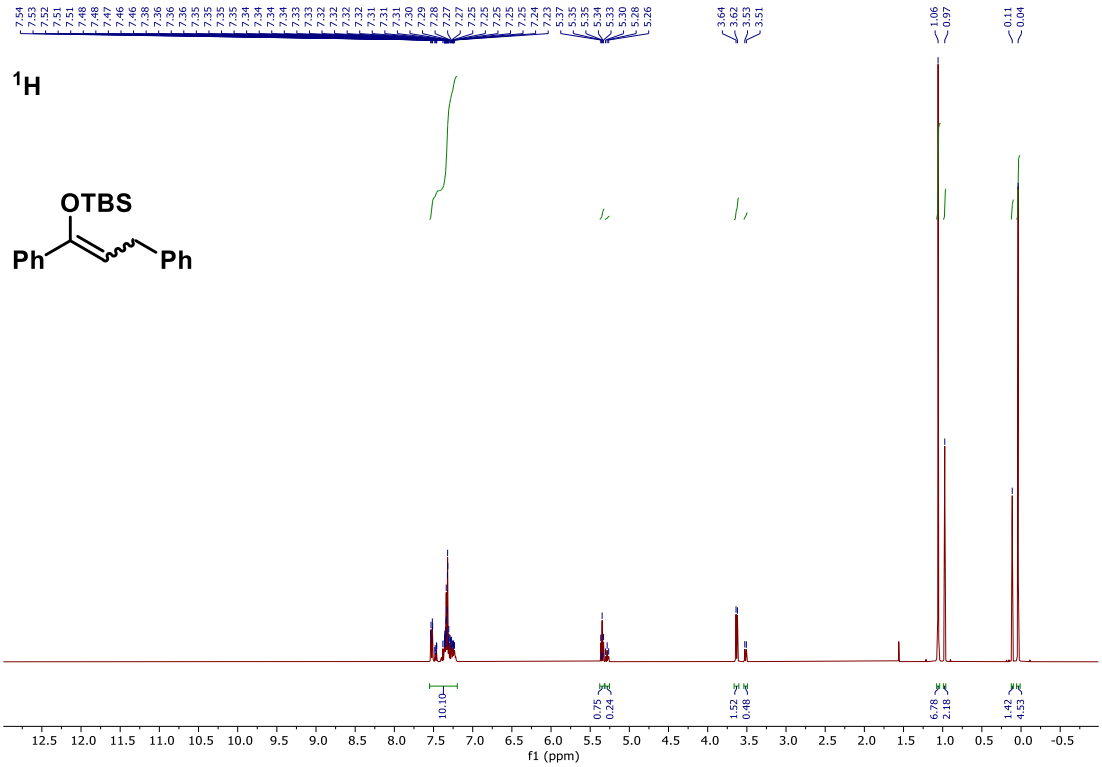


^{13}C

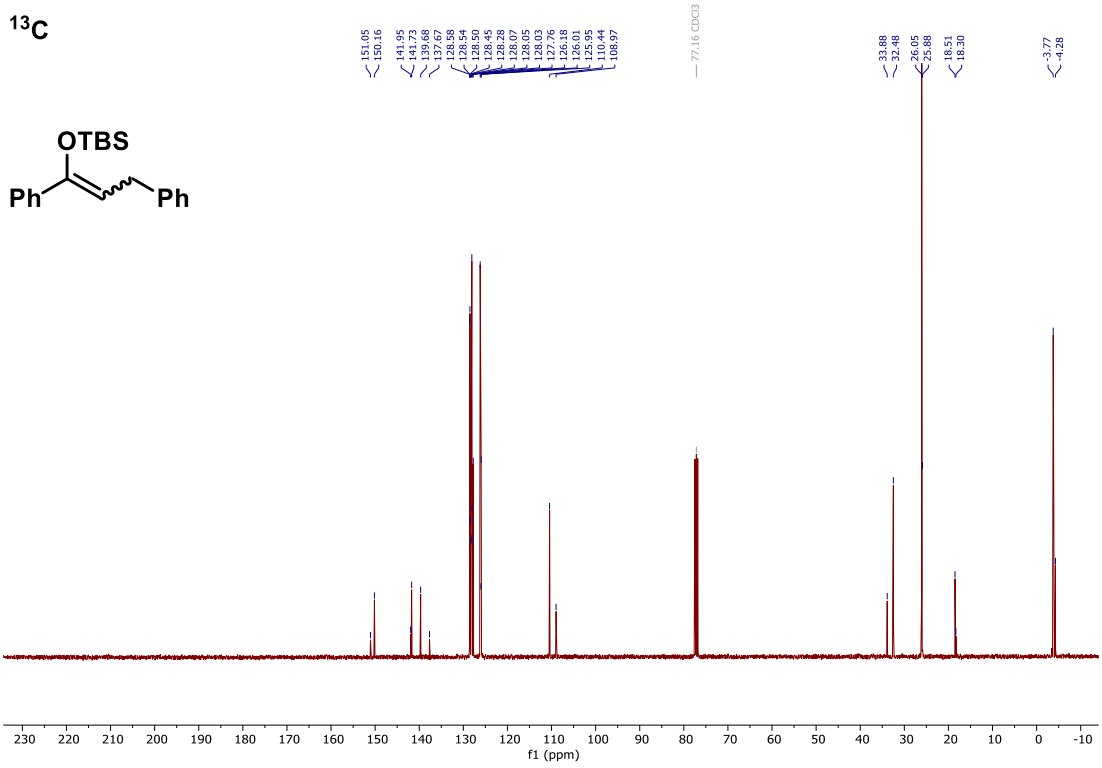


tert-Butyl((1,3-diphenylprop-1-en-1-yl)oxy)dimethylsilane (1h)

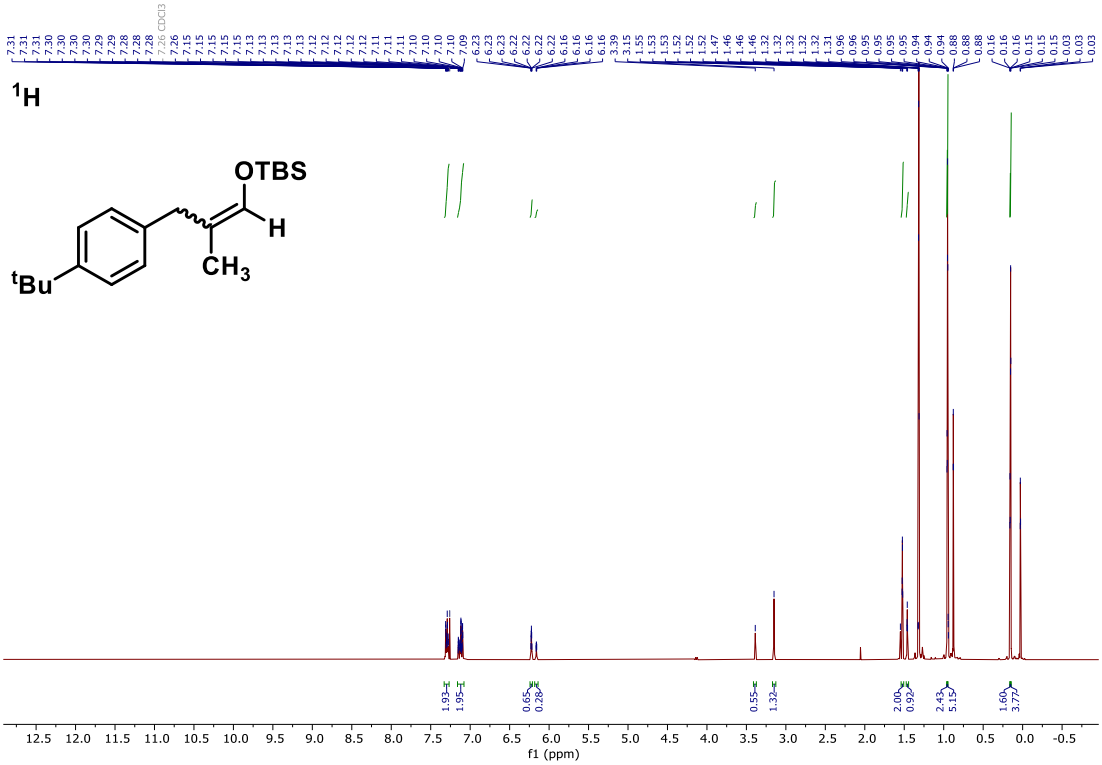
^{1}H

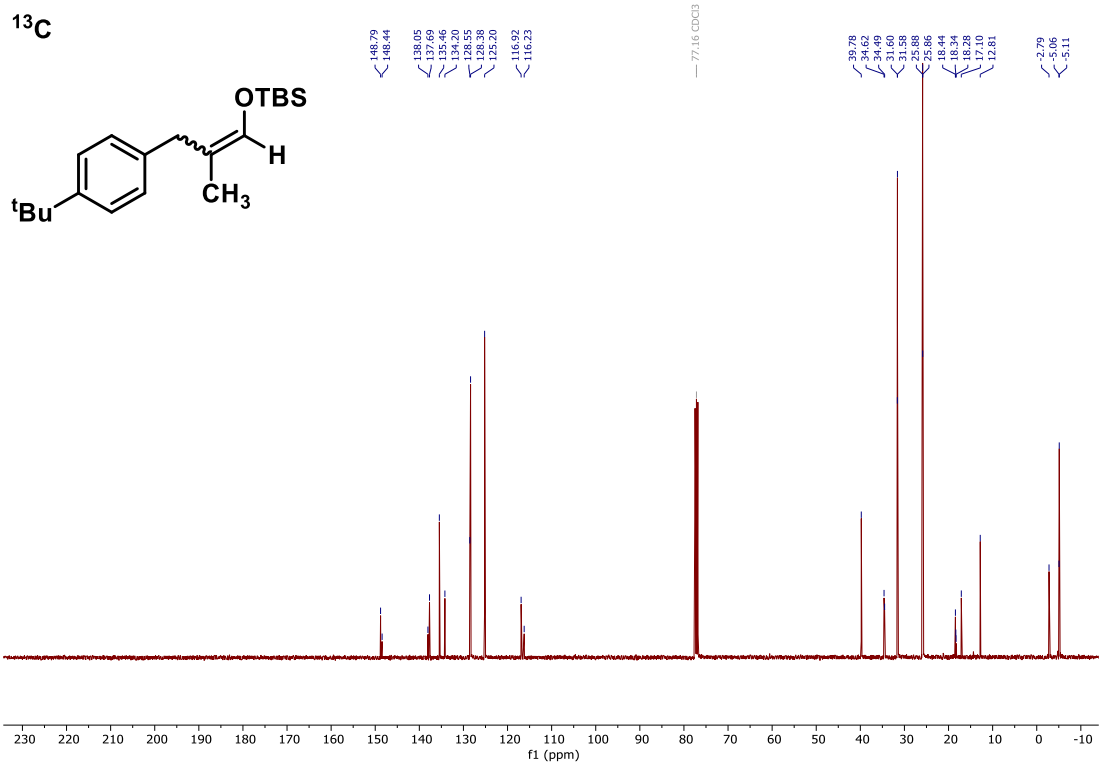


^{13}C



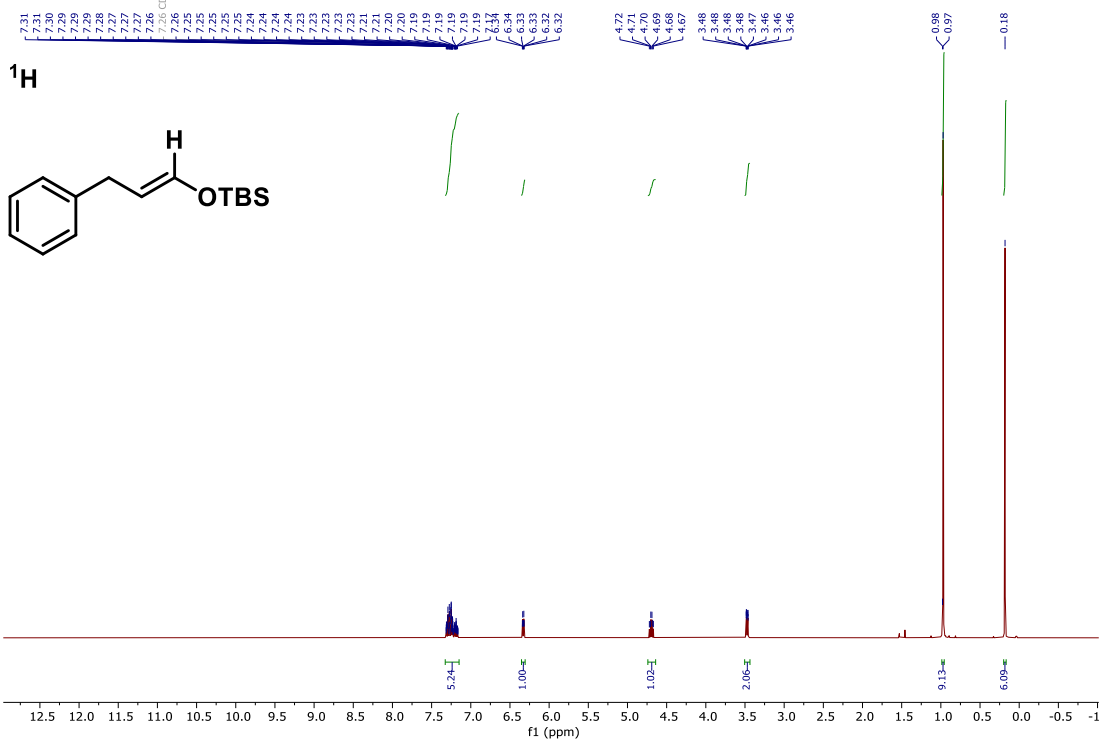
tert-Butyl((3-(4-(_tert_-butyl)phenyl)-2-methylprop-1-en-1-yl)oxy)dimethylsilane (1j)



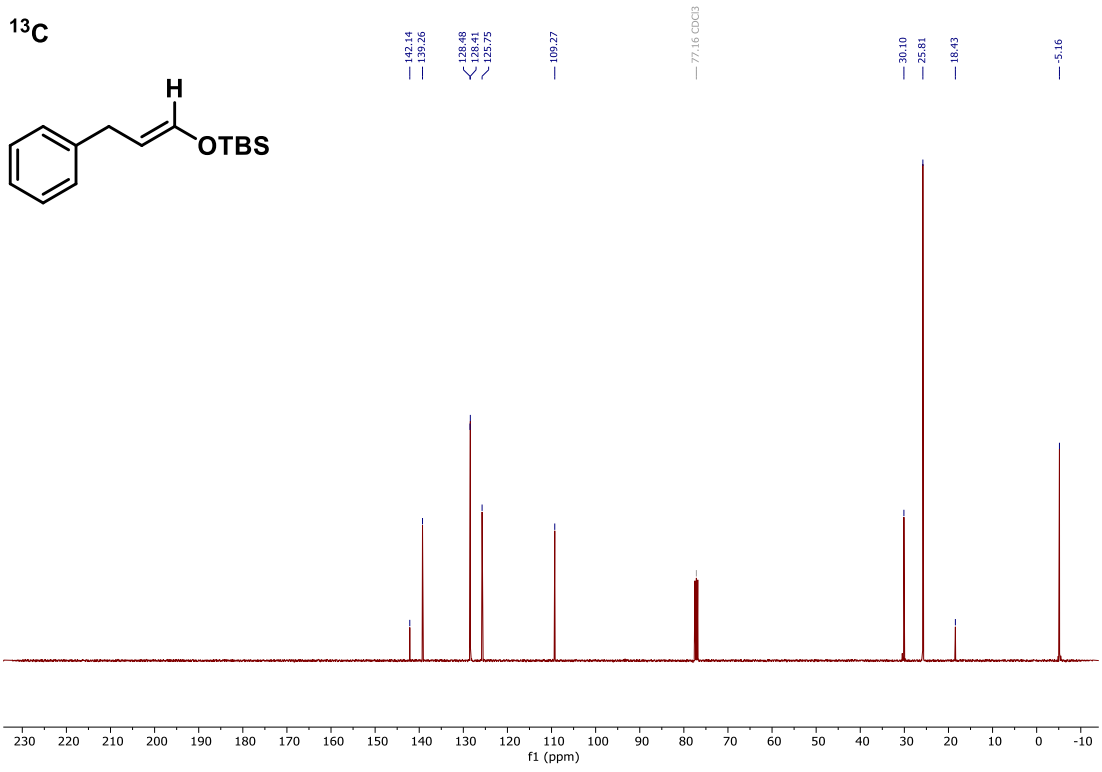


tert-Butyldimethyl((3-phenylprop-1-en-1-yl)oxy)silane (1k)

^{1}H

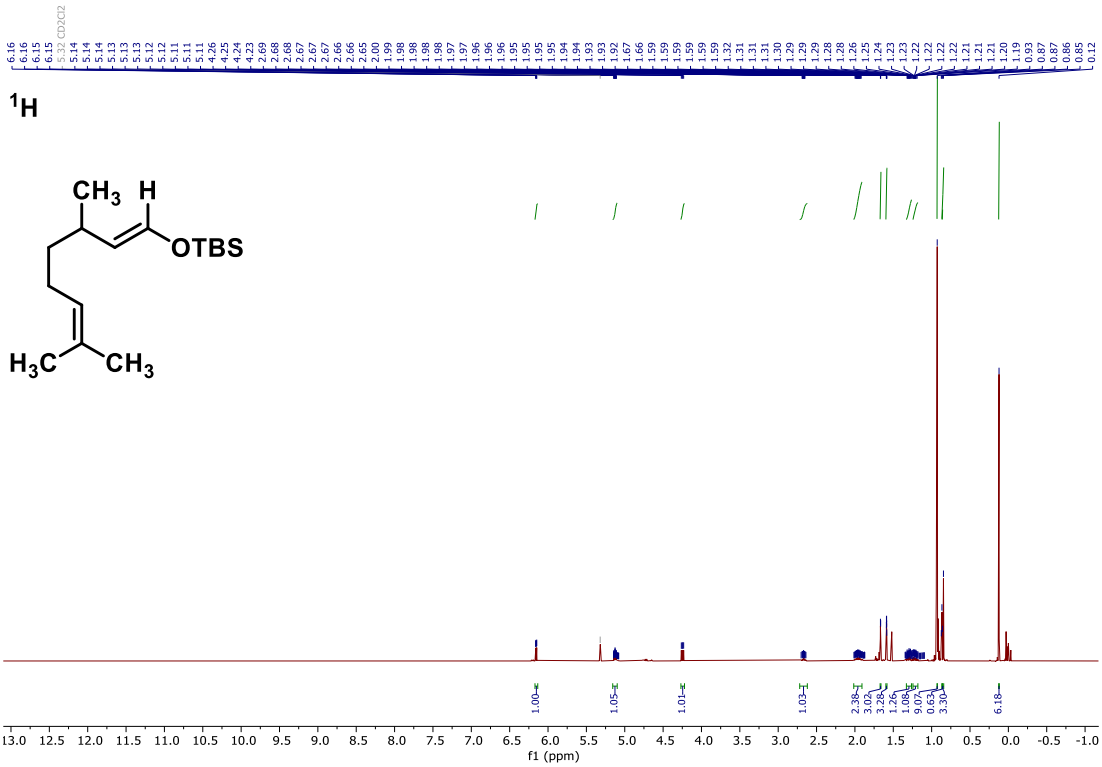


^{13}C

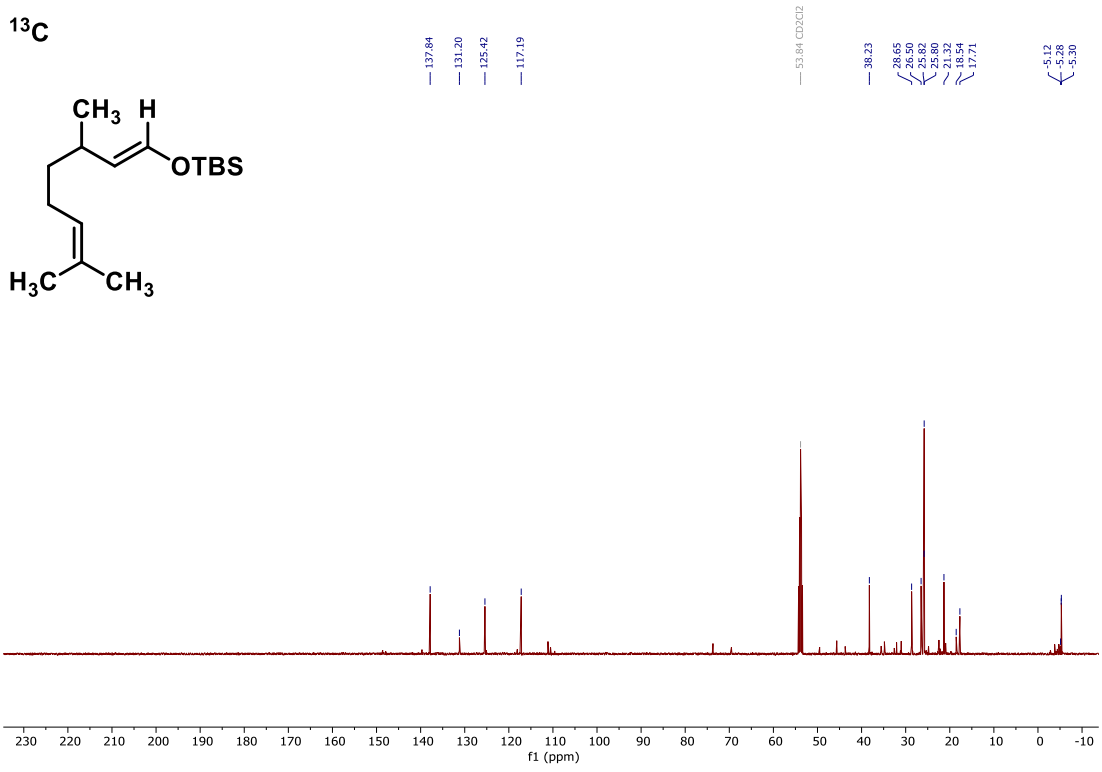


tert-Butyl((3,7-dimethylocta-1,6-dien-1-yl)oxy)dimethylsilane (1l)

^{1}H

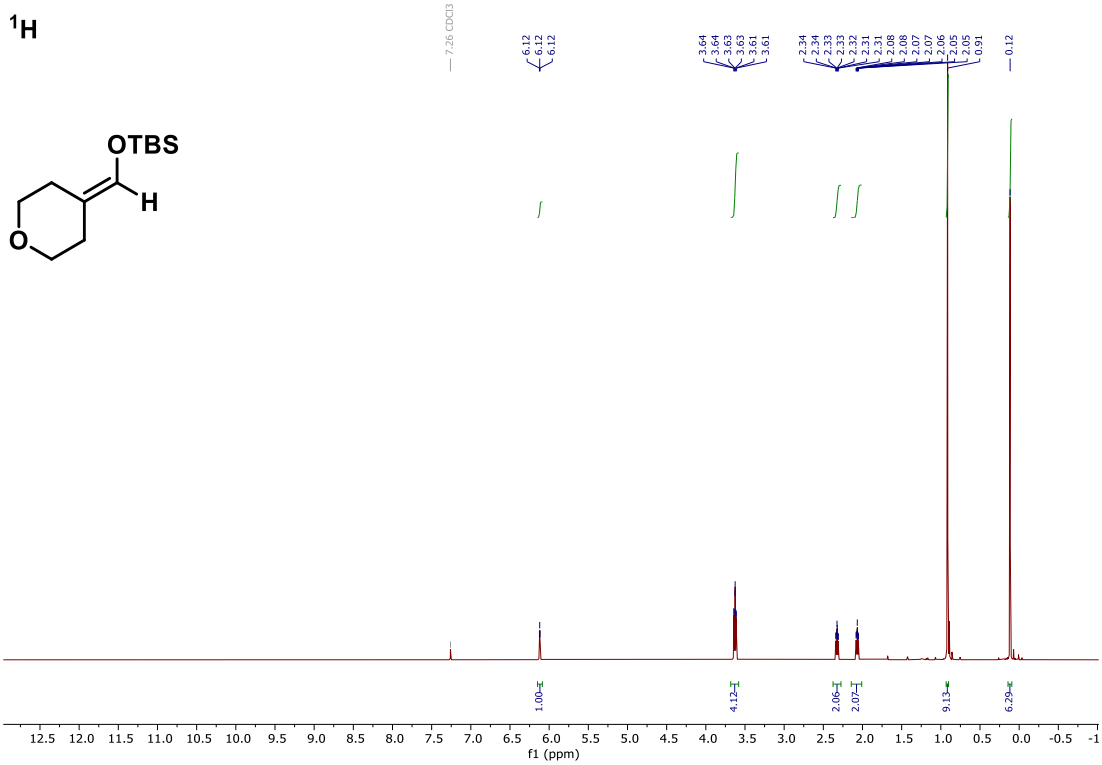


^{13}C

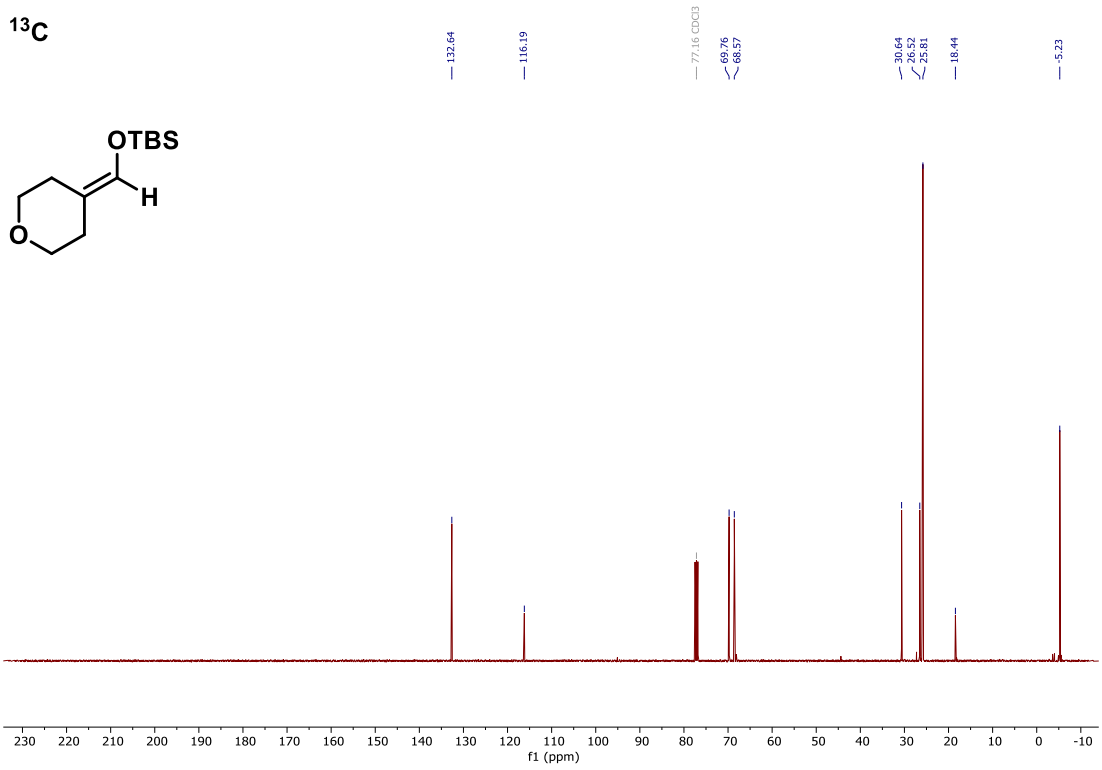


tert-Butyldimethyl((tetrahydro-4H-pyran-4-ylidene)methoxy)silane (1m)

^{1}H

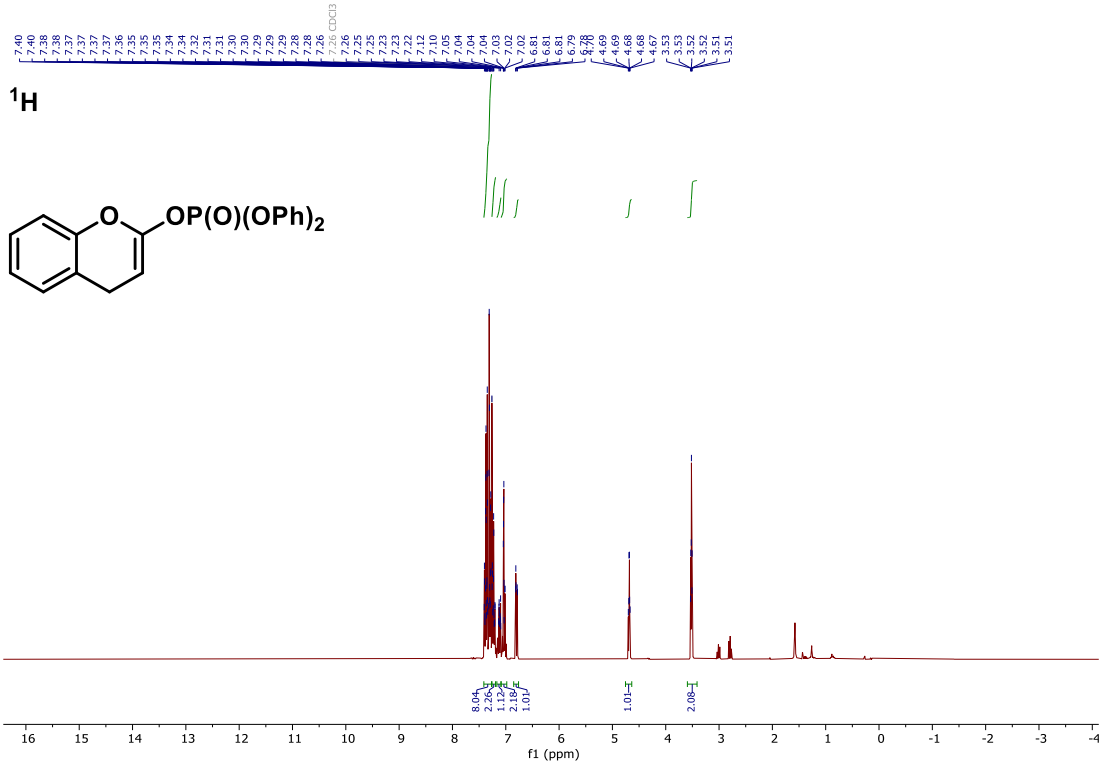


^{13}C

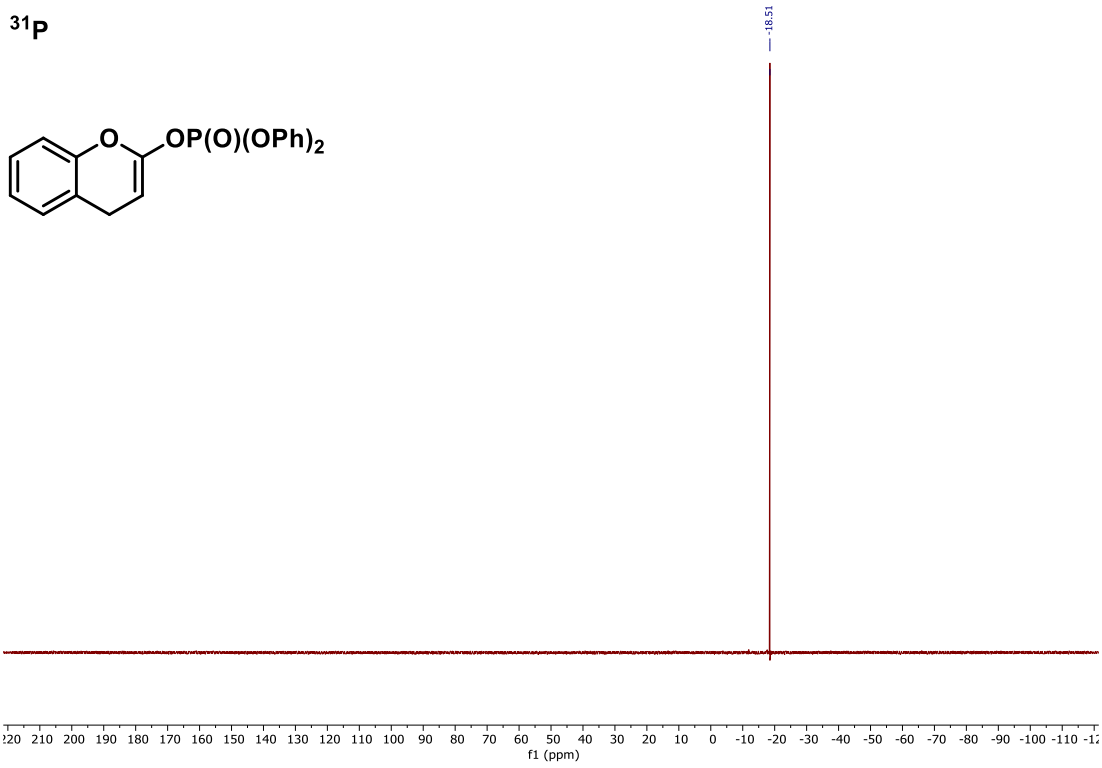


4*H*-Chromen-2-yl diphenyl phosphate (1n)

^{1}H

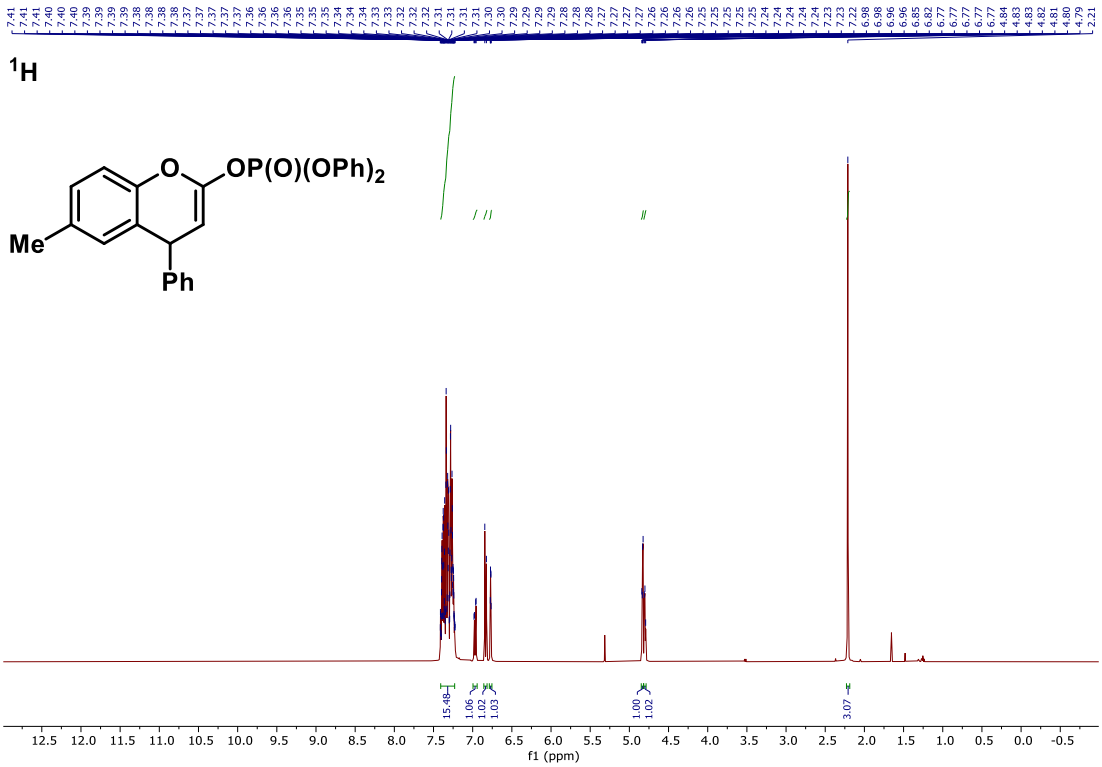


^{31}P

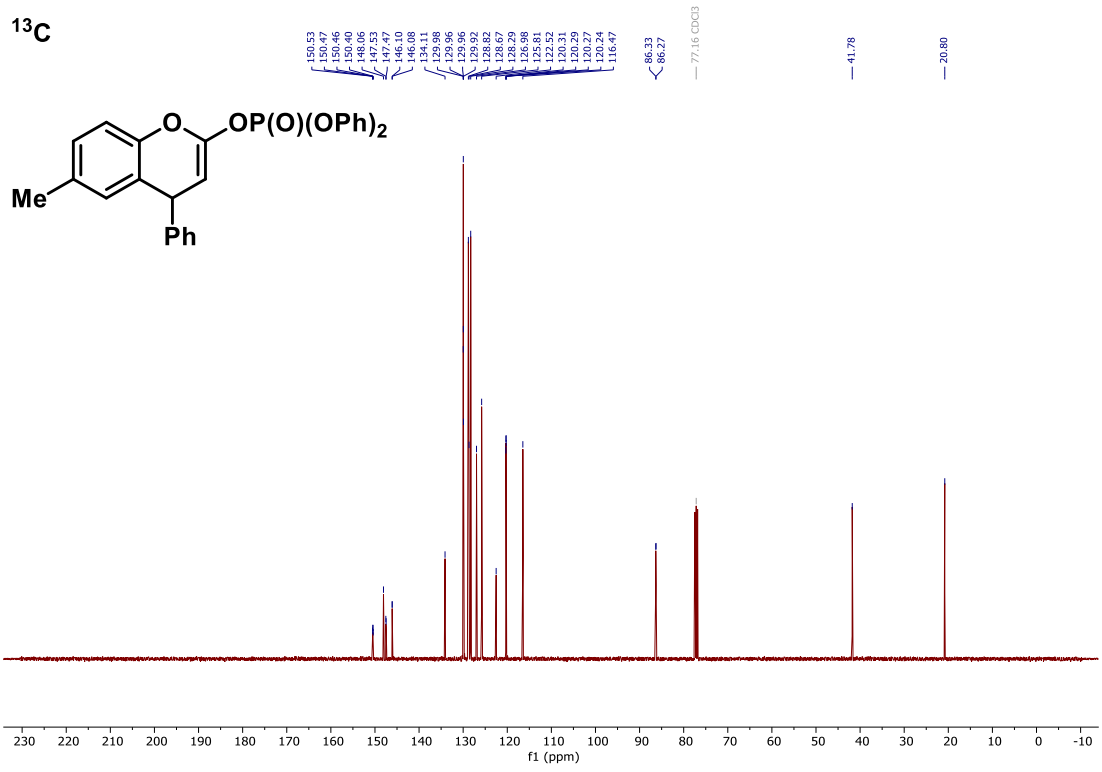


6-Methyl-4-phenyl-4*H*-chromen-2-yl diphenyl phosphate (1o)

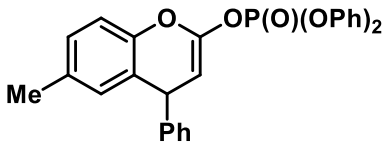
^{1}H



^{13}C



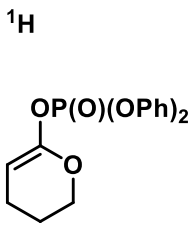
^{31}P


O
OP(O)(OPh)2
Me
Ph

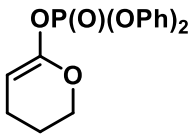
18.52
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -12
f1 (ppm)

3,4-Dihydro-2*H*-pyran-6-yl diphenyl phosphate (1p)

^{1}H

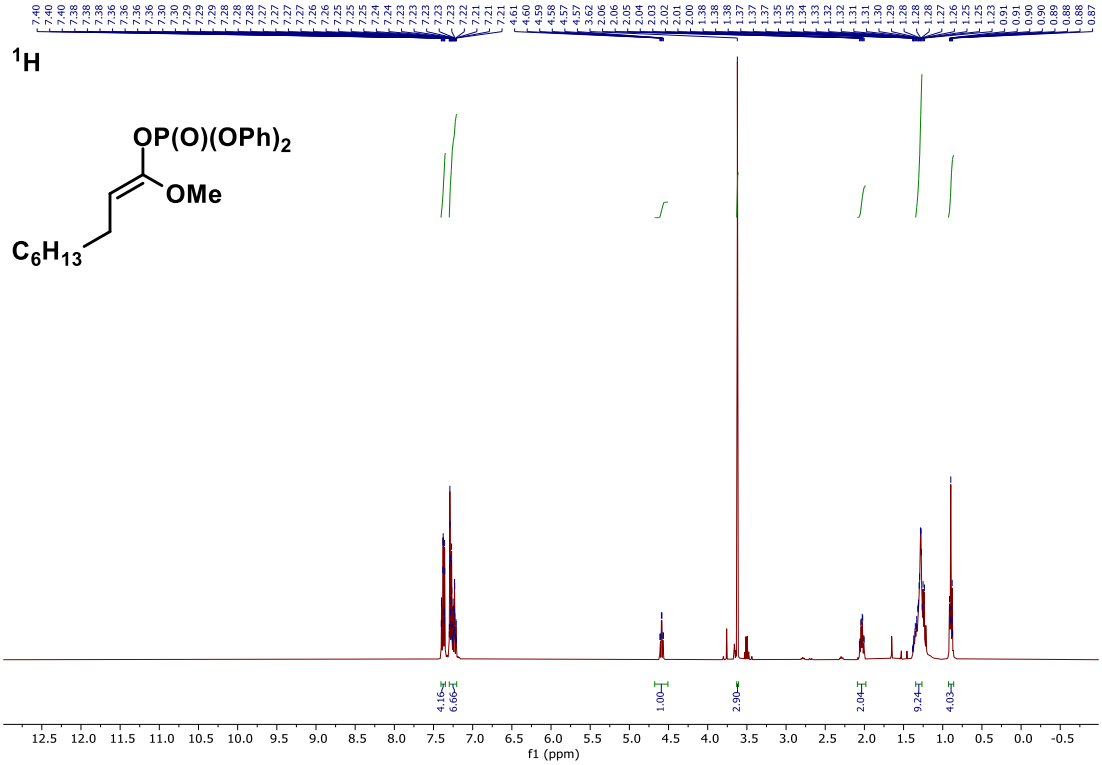


^{31}P

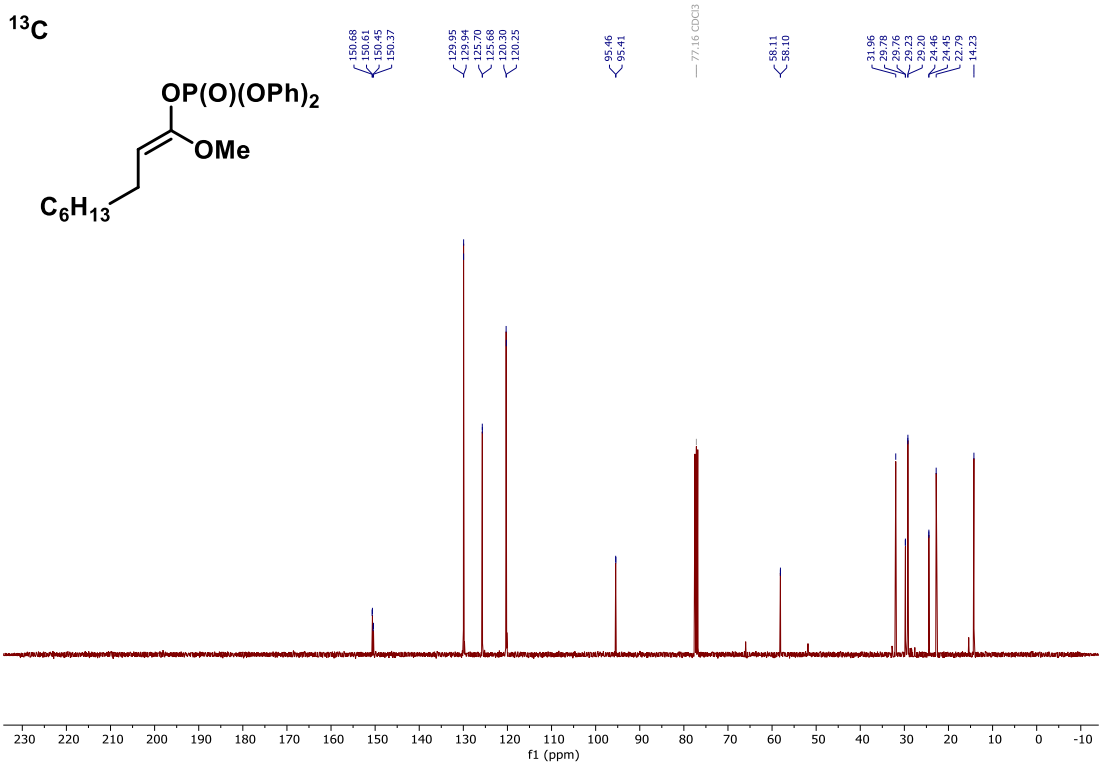


1-Methoxynon-1-en-1-yl diphenyl phosphate (1q)

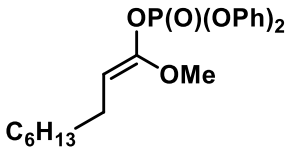
^{1}H



^{13}C



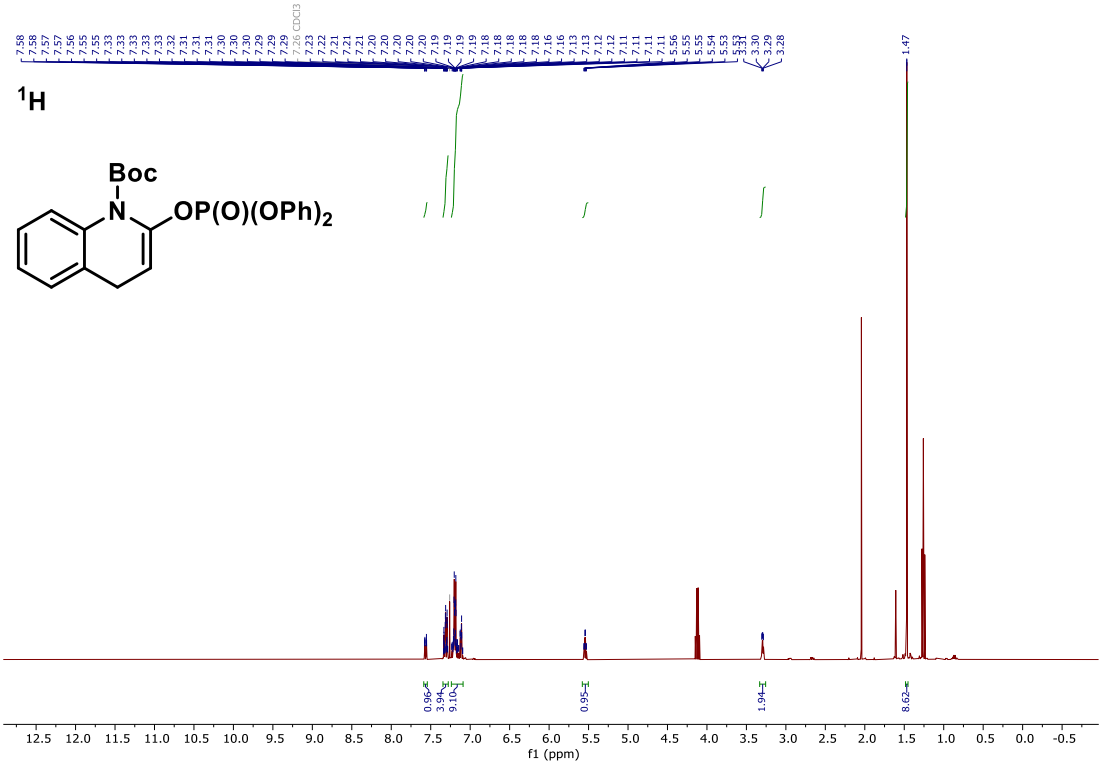
^{31}P


OP(O)(OPh)2
OMe
C6H13

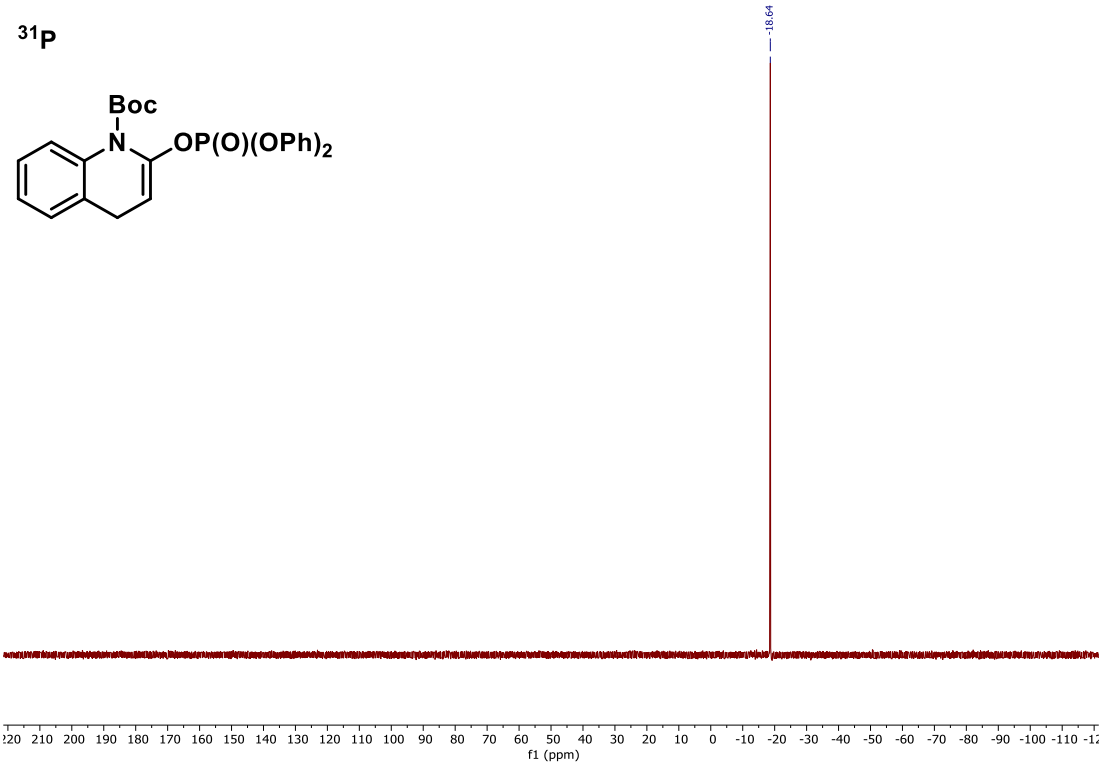
18.15
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

tert-Butyl 2-((diphenoxyphosphoryl)oxy)quinoline-1(4*H*)-carboxylate (1r)

^{1}H

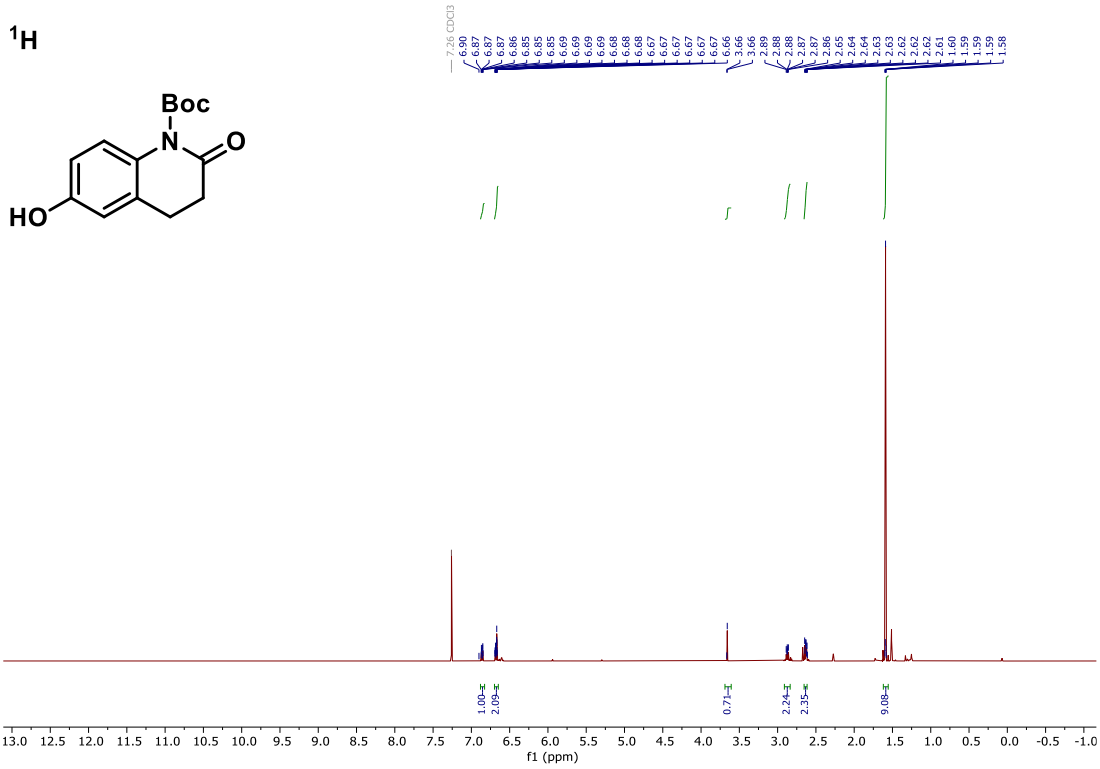


^{31}P

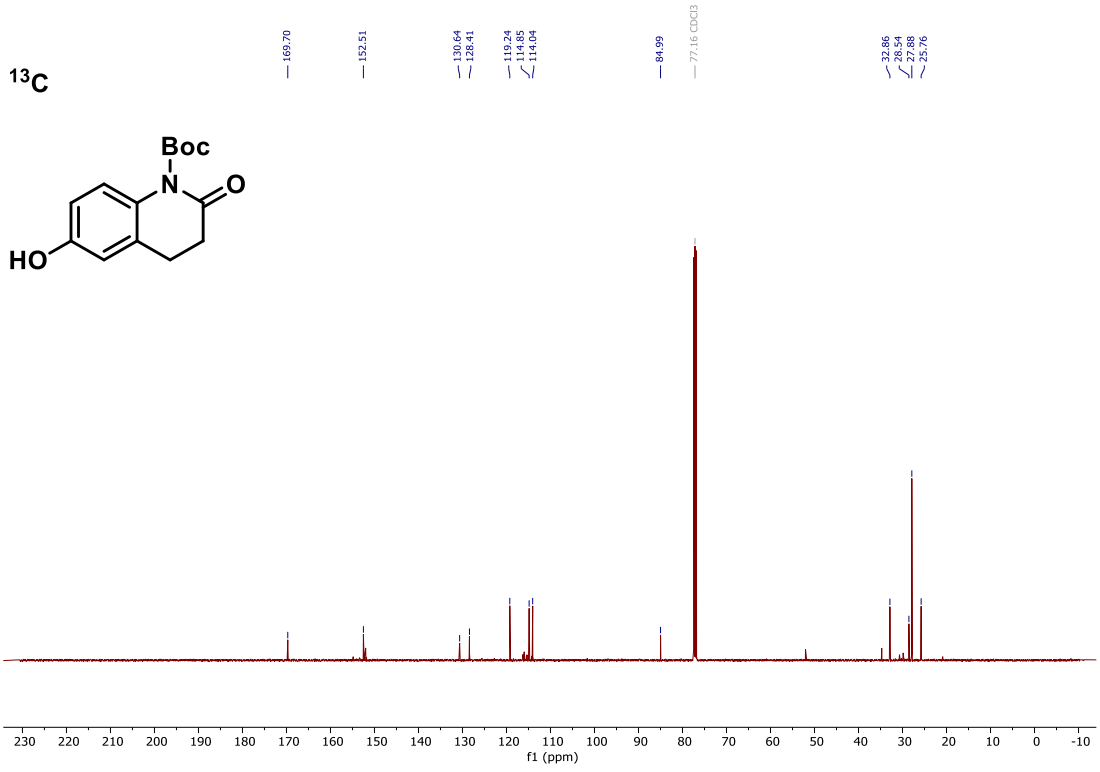


tert-Butyl 6-hydroxy-2-oxo-3,4-dihydroquinoline-1(2*H*)-carboxylate (S1)

^{1}H

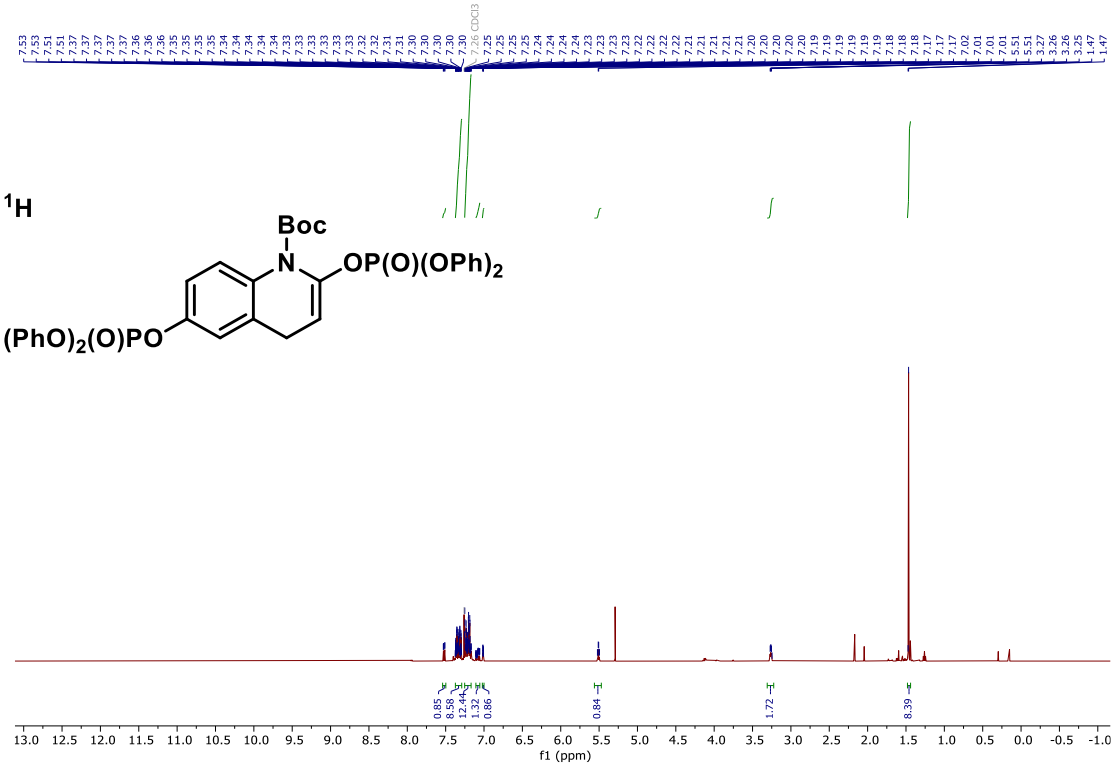


^{13}C

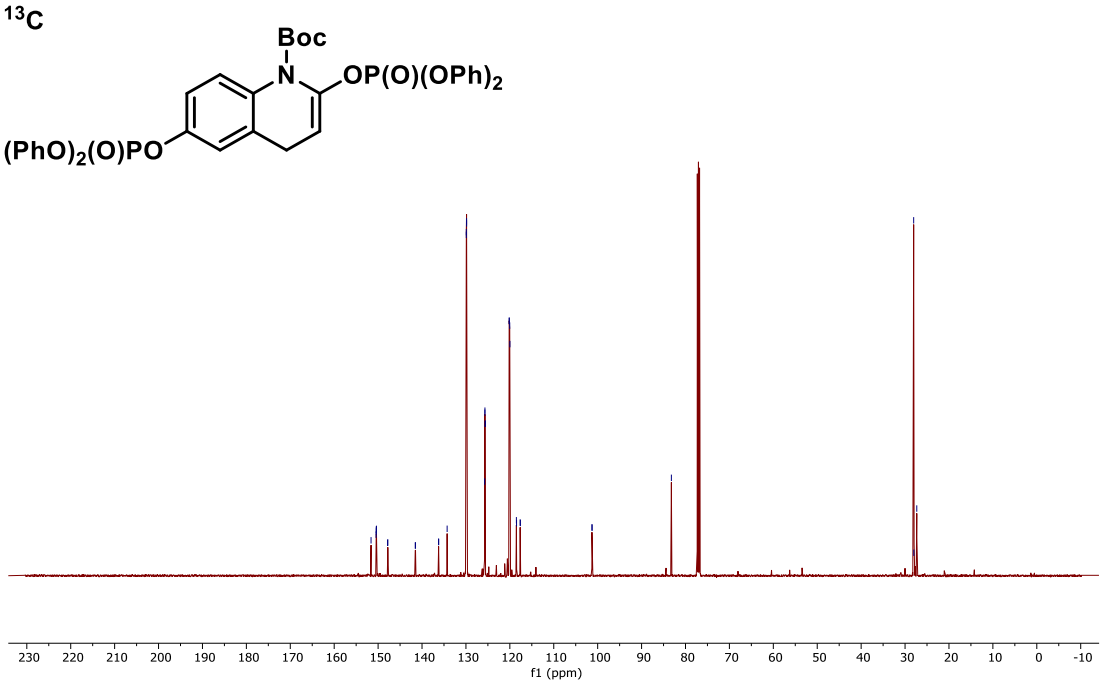


tert-Butyl 2,6-bis((diphenoxyphosphoryl)oxy)quinoline-1(4*H*)-carboxylate (1s)

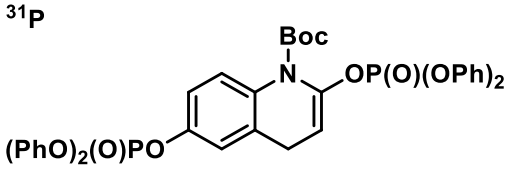
^{1}H



^{13}C



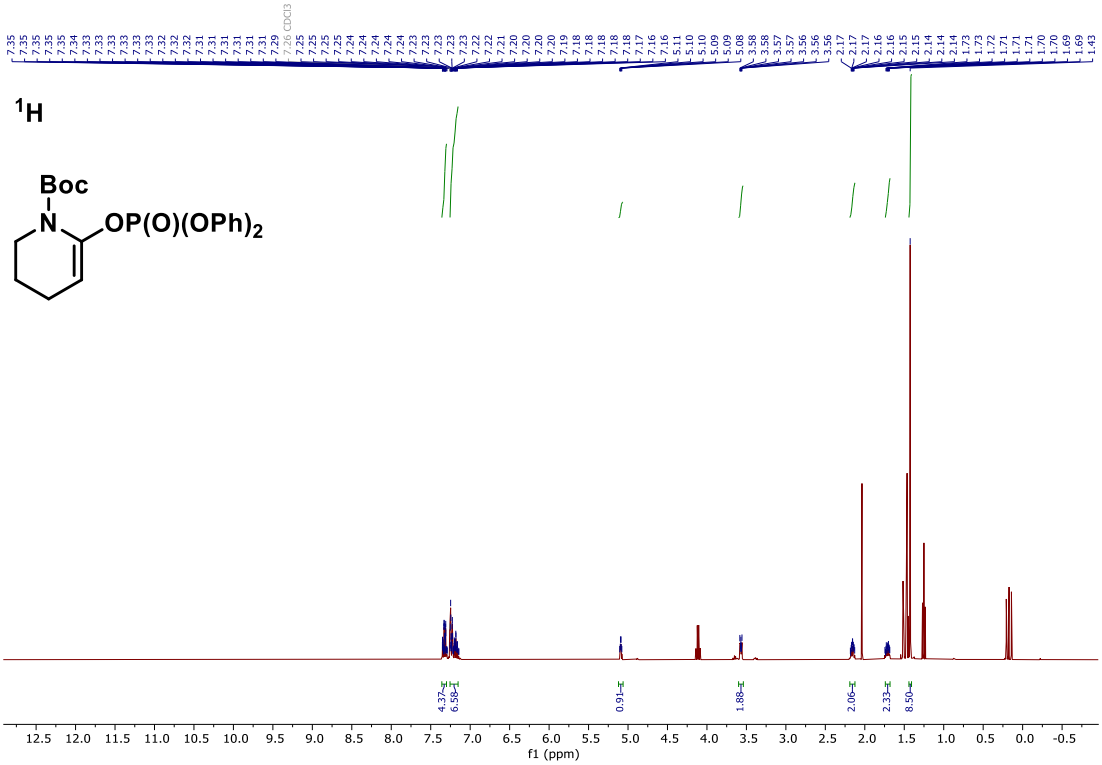
^{31}P


Boc
N
OP(O)(OPh)2
(PhO)2(O)PO

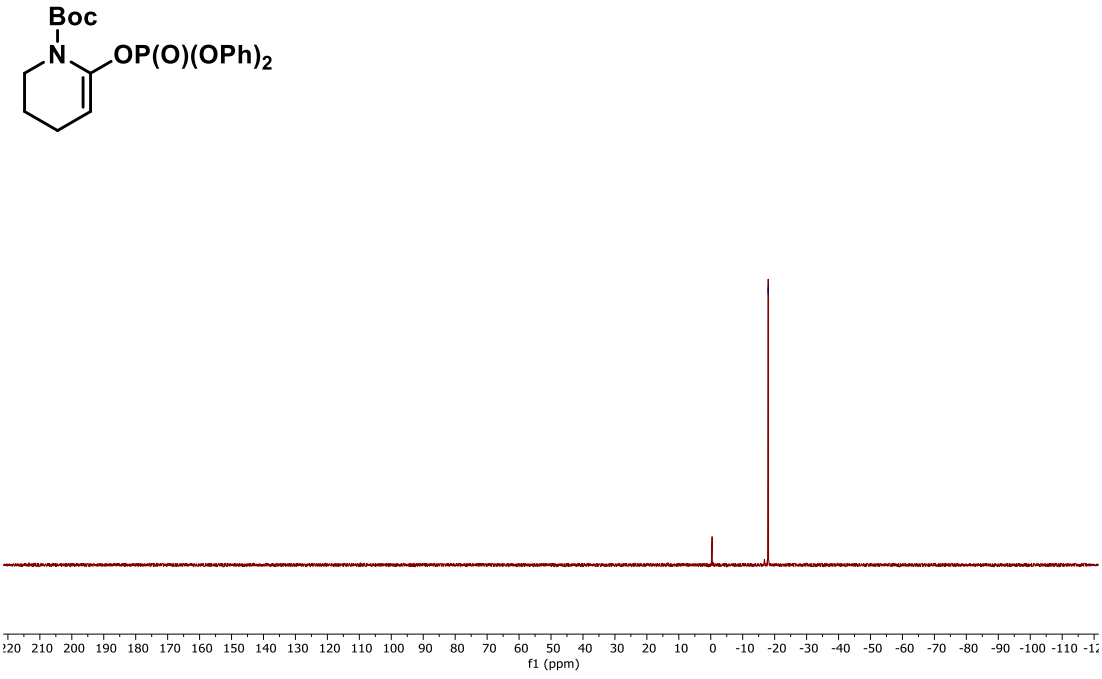
-17.68
-18.68
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

tert-Butyl 6-((diphenoxyphosphoryl)oxy)-3,4-dihydropyridine-1(2*H*)-carboxylate (1t)

^{1}H

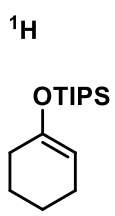


^{31}P

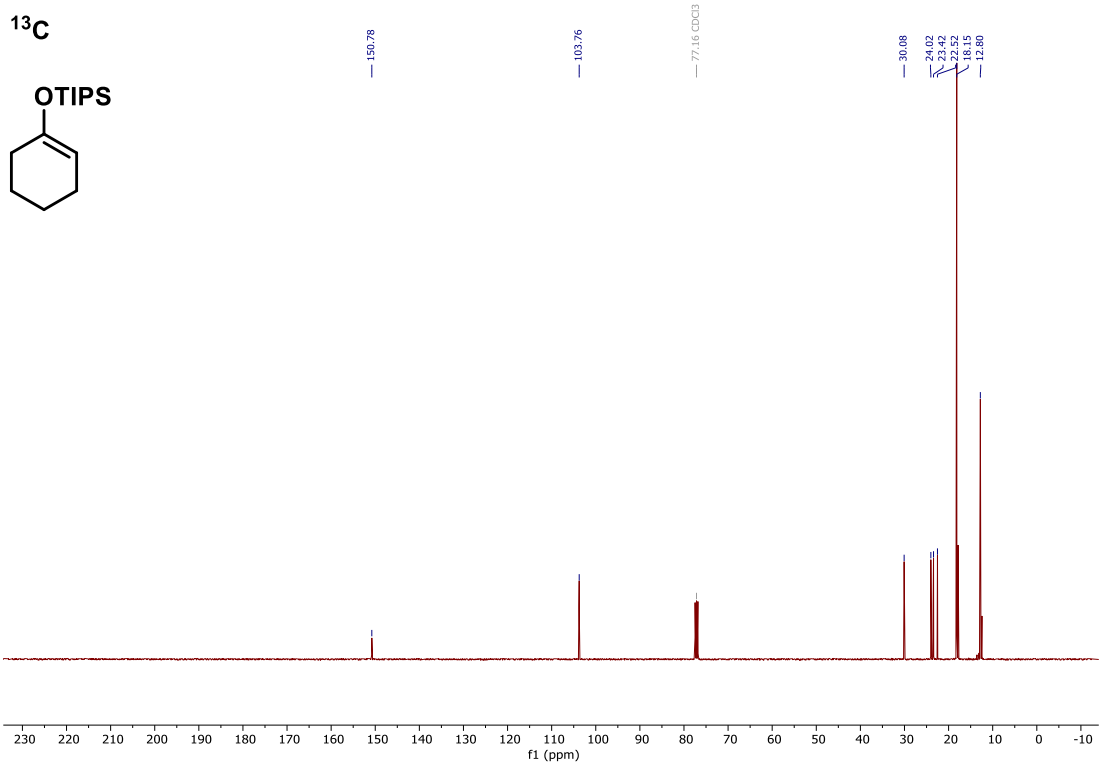


(Cyclohex-1-en-1-yloxy)triisopropylsilane (1u)

^{1}H



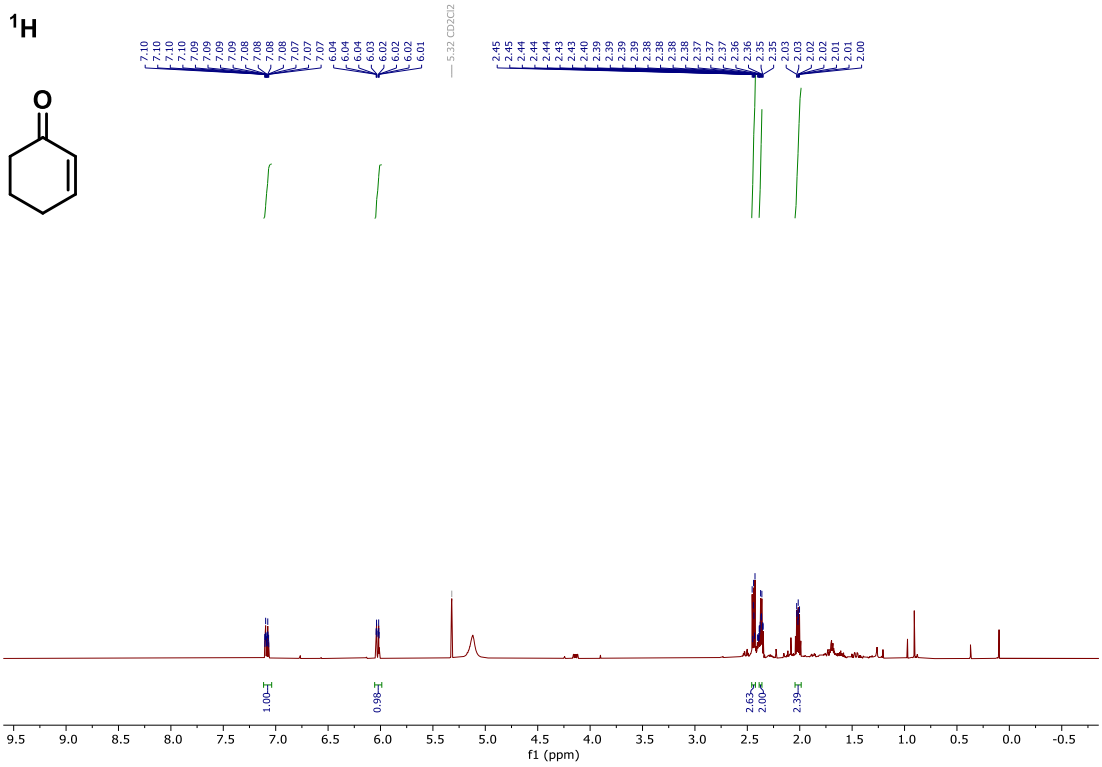
^{13}C



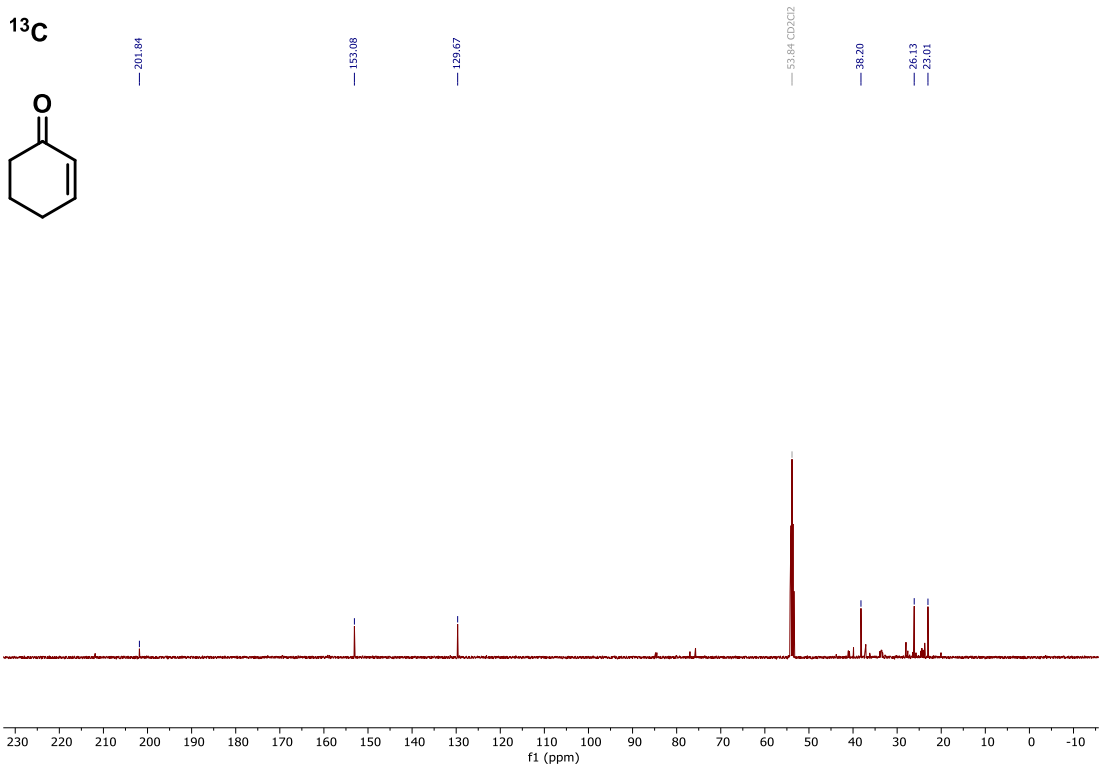
Products

Cyclohex-2-en-1-one (2a)

^{1}H

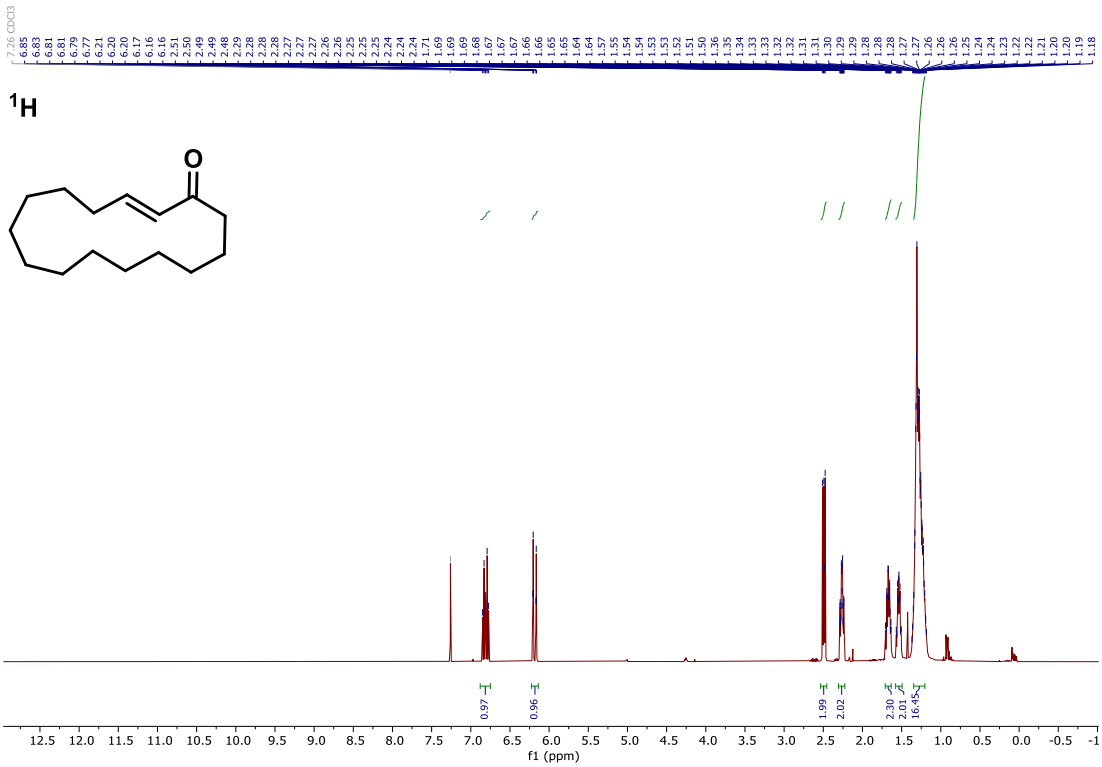


^{13}C

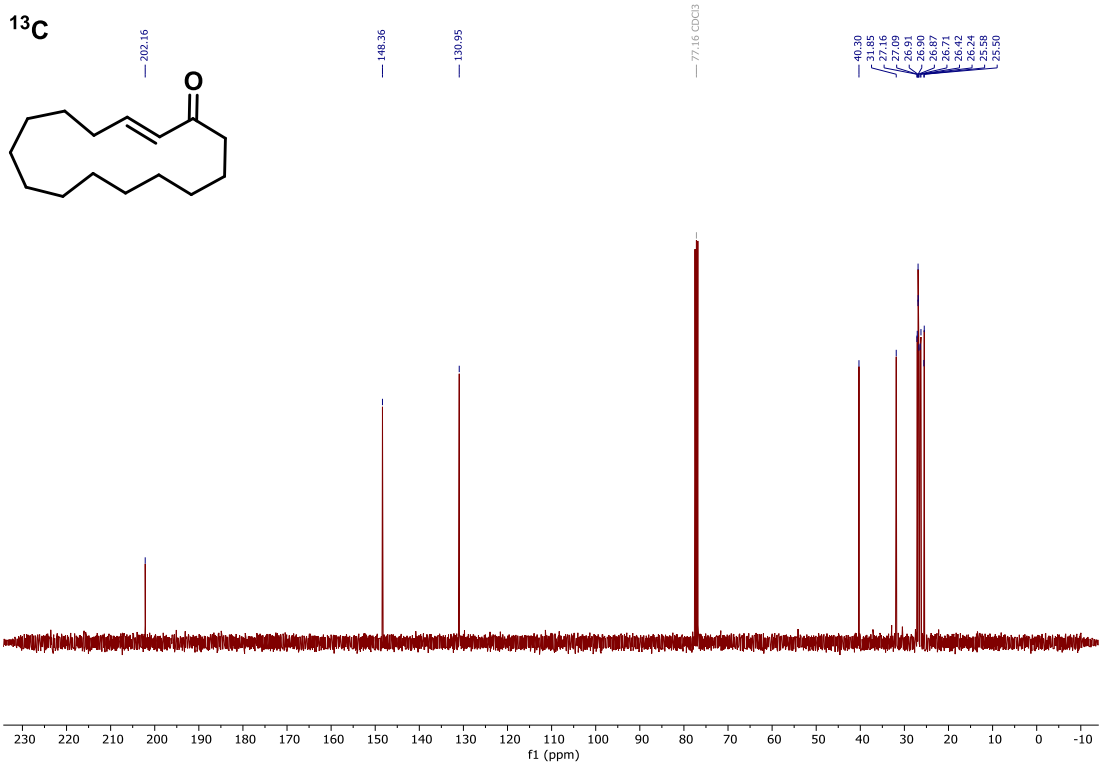


(*E*)-Cyclopentadec-2-en-1-one (2c)

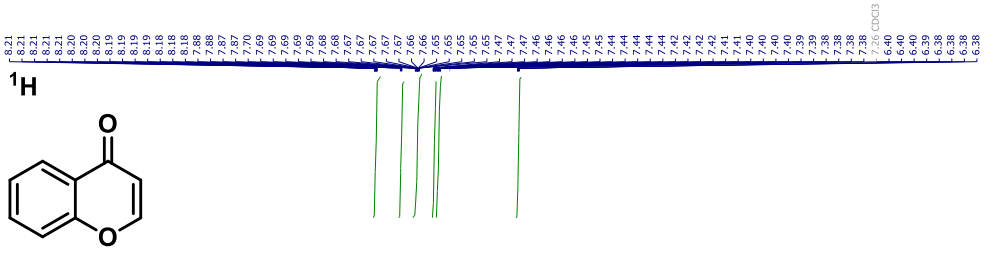
^{1}H

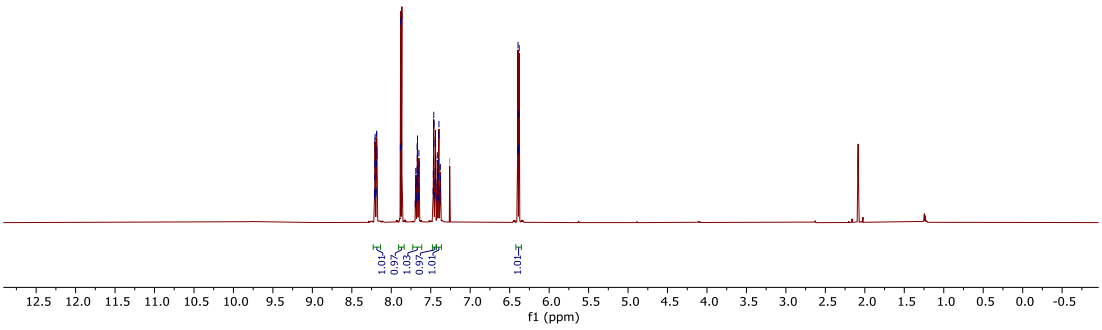


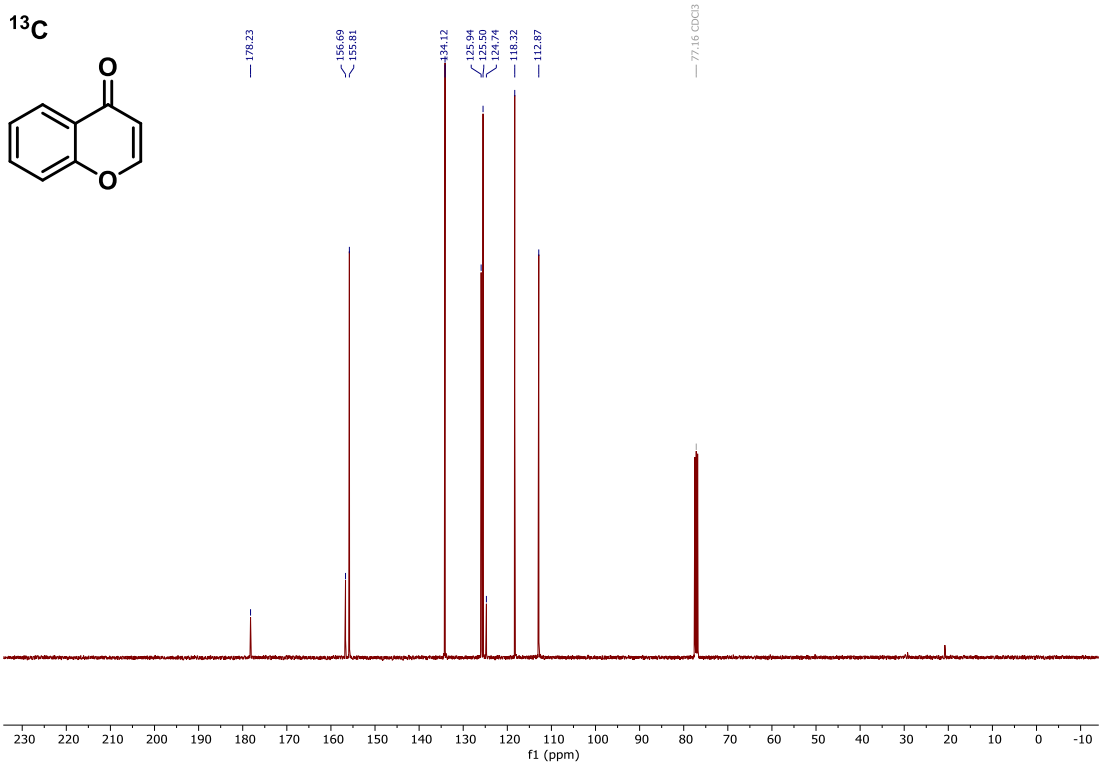
^{13}C



4*H*-Chromen-4-one (2d)

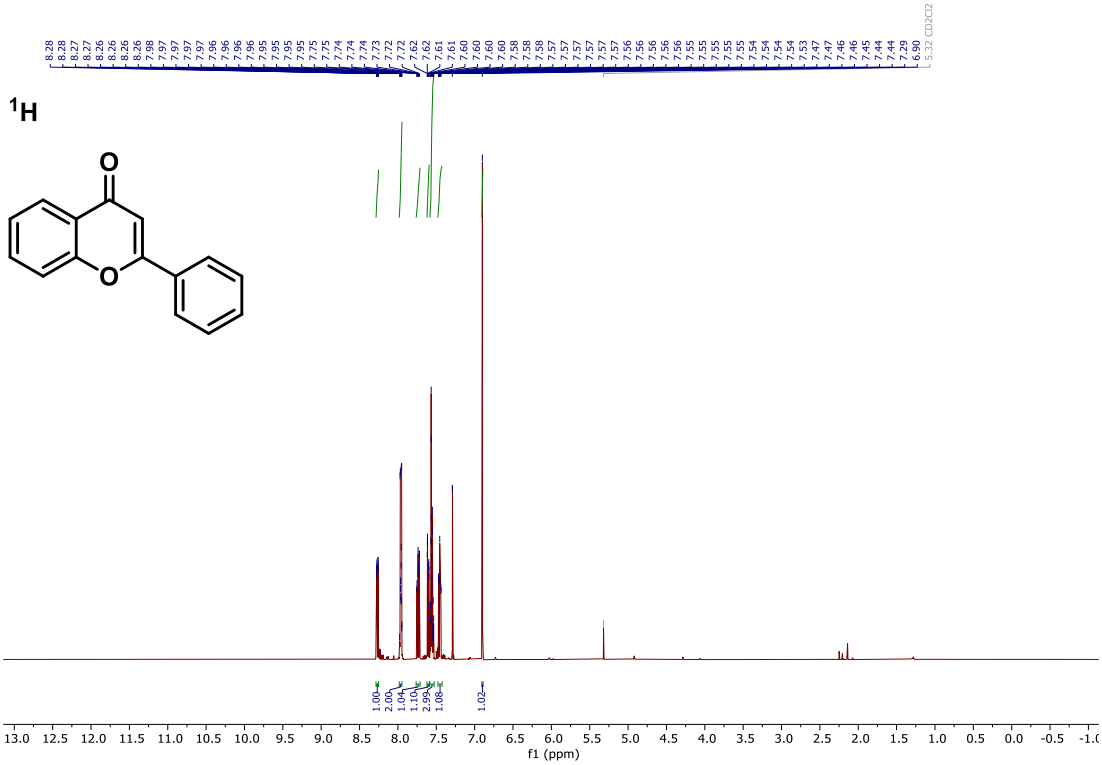




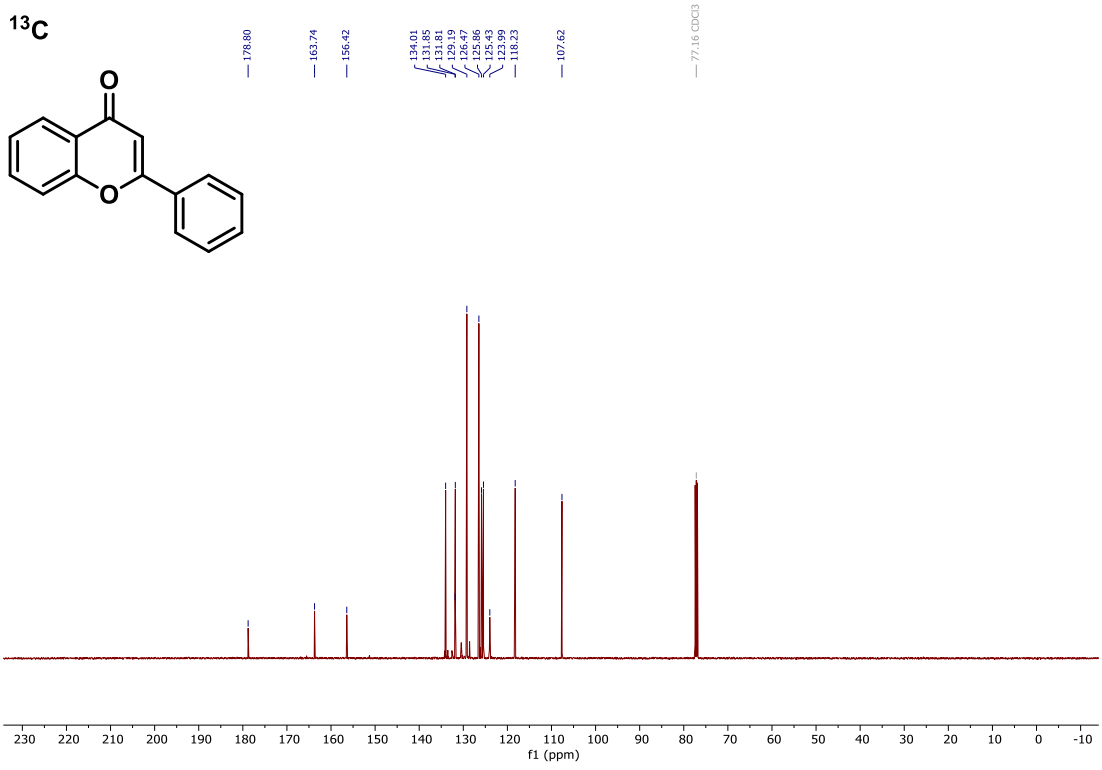


2-Phenyl-4*H*-chromen-4-one (2e)

^{1}H

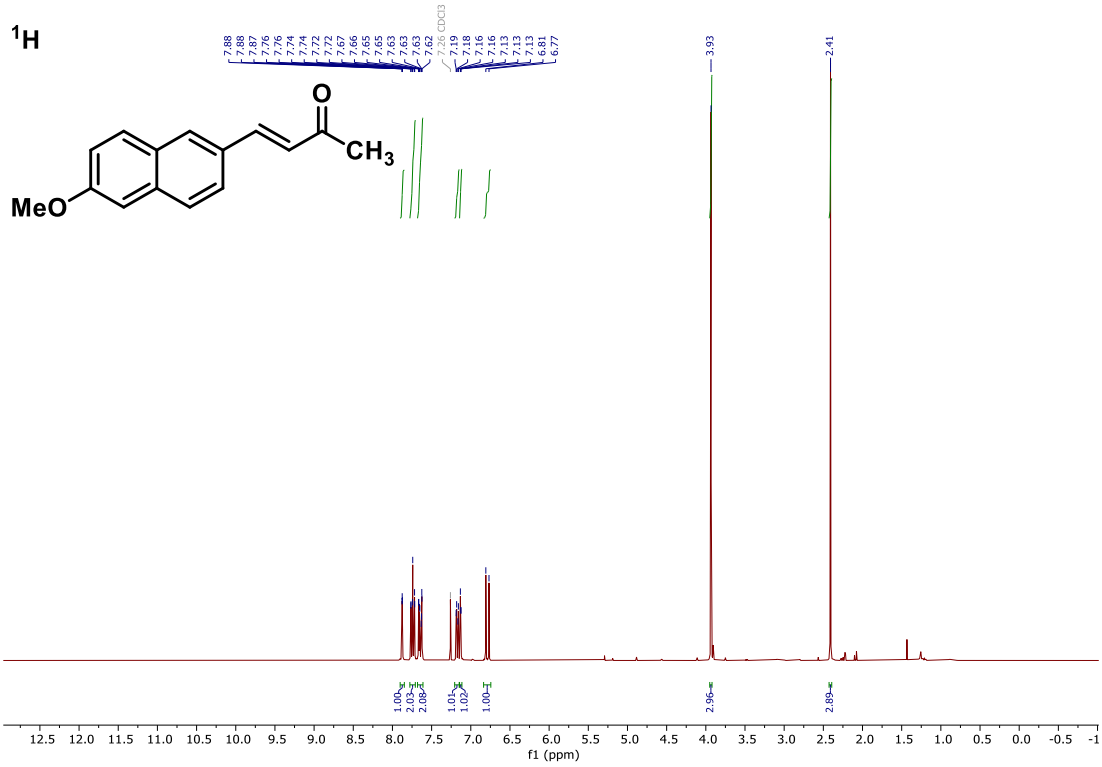


^{13}C

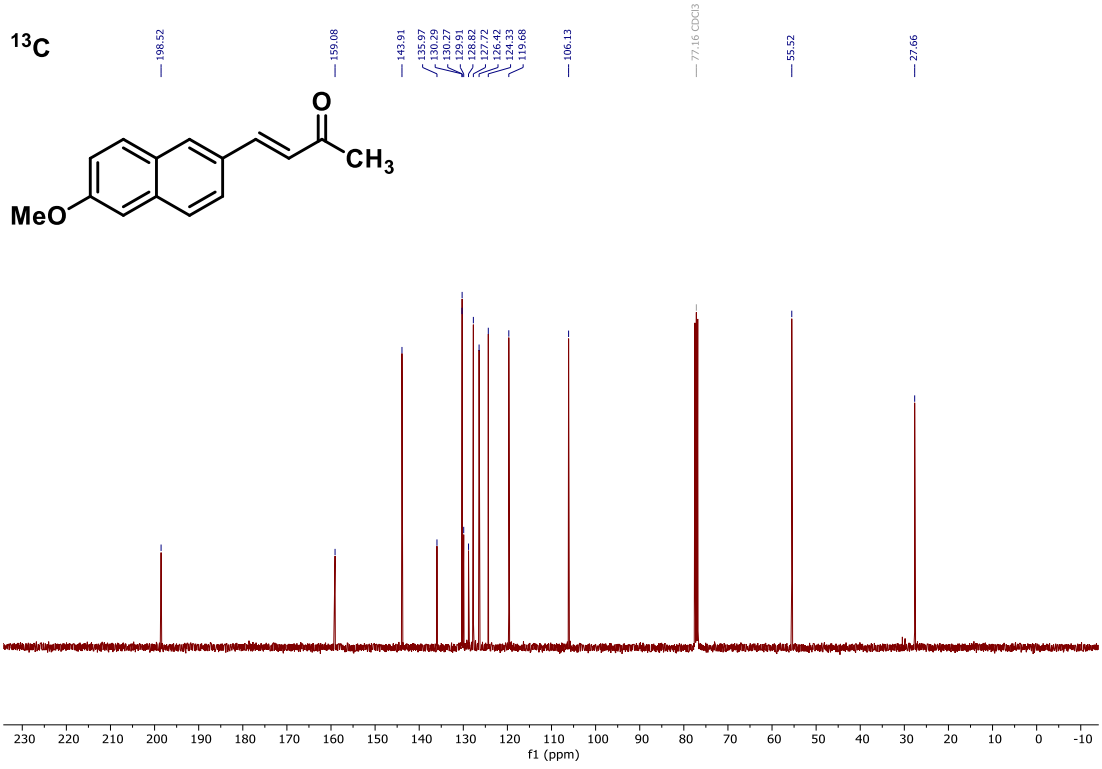


(*E*)-4-(6-Methoxynaphtalen-2-yl)but-3-en-2-one (2f)

^{1}H

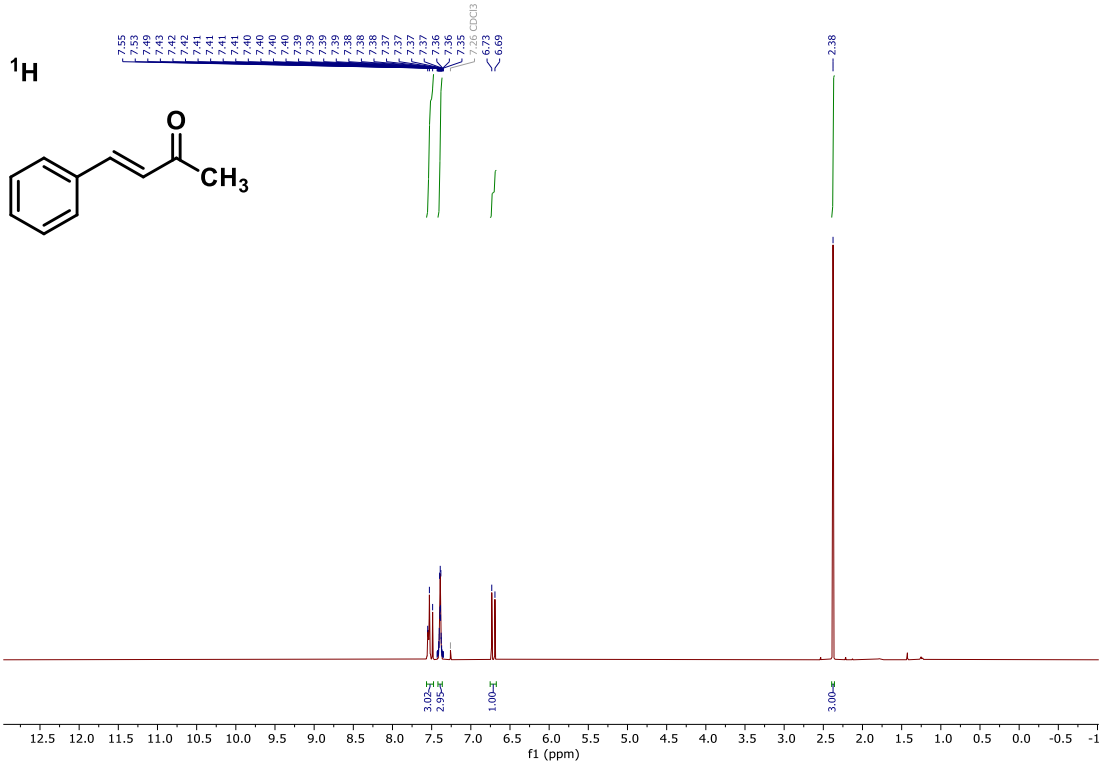


^{13}C

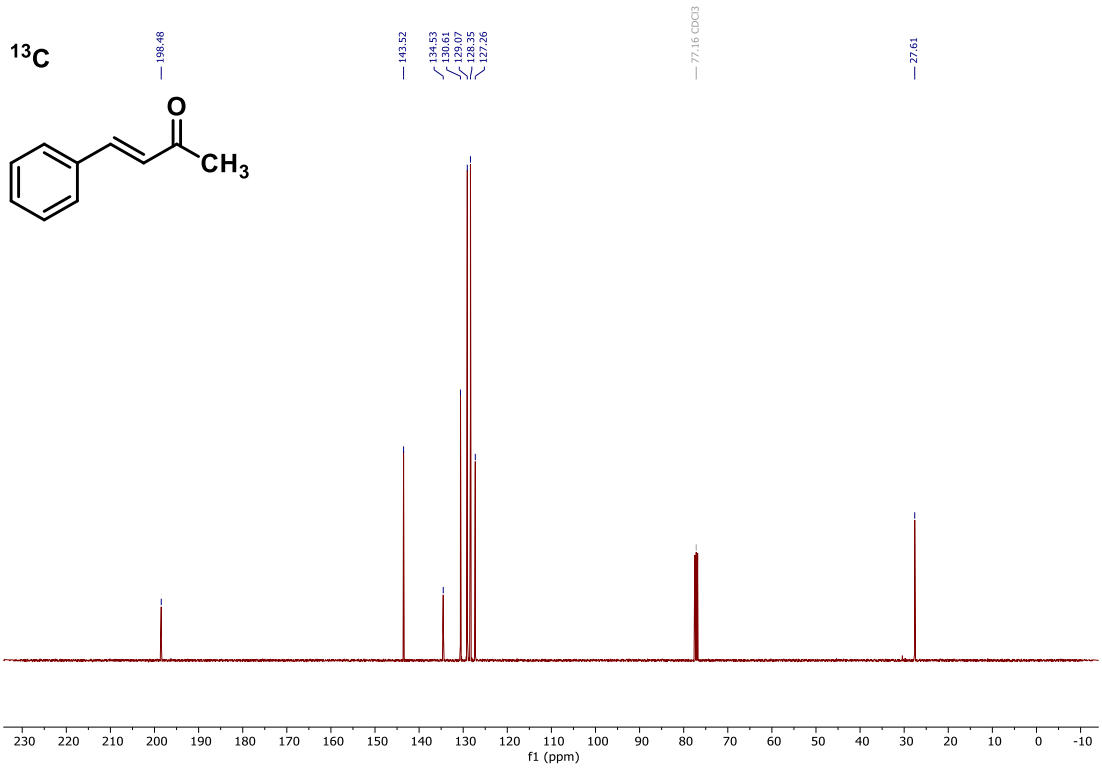


(*E*)-4-Phenylbut-3-en-2-one (2g)

^{1}H

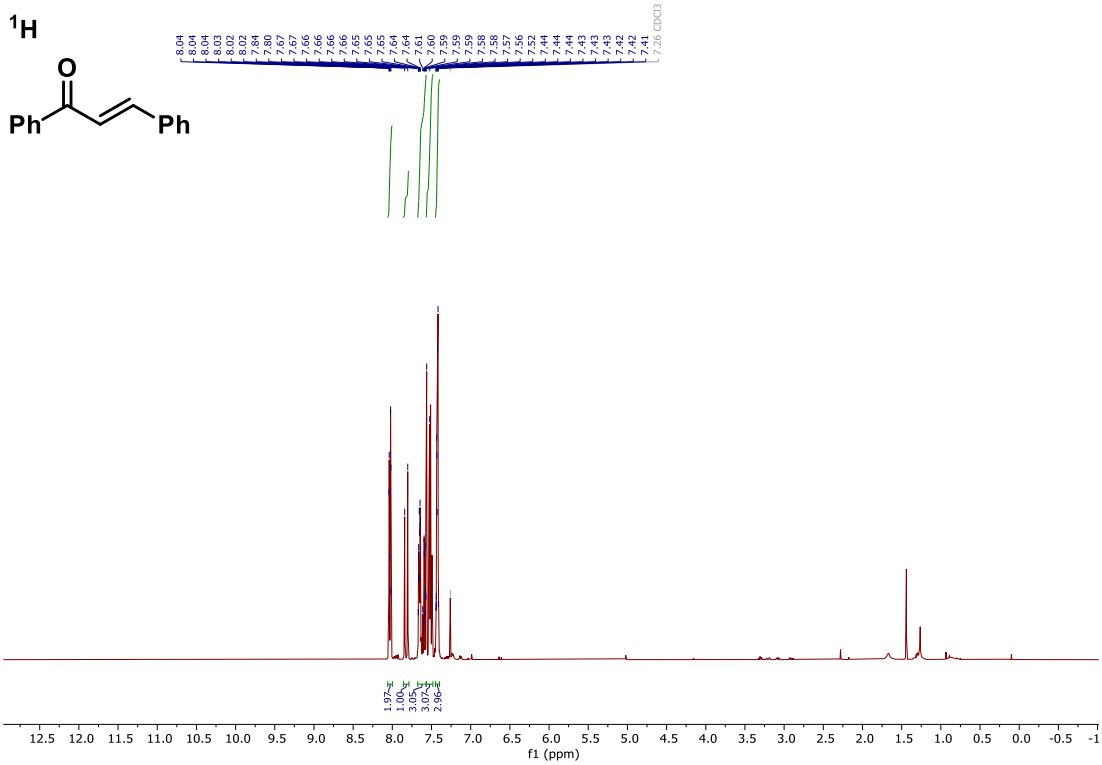


^{13}C

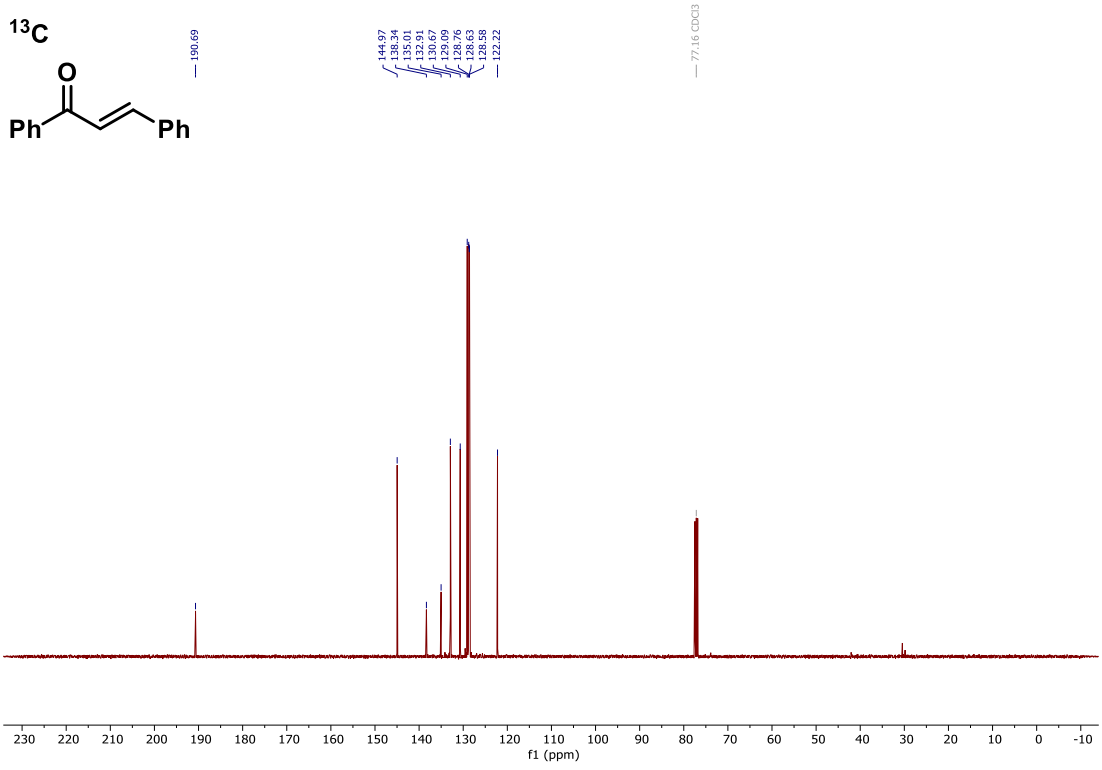


(*E*)-Chalcone (2h)

^{1}H

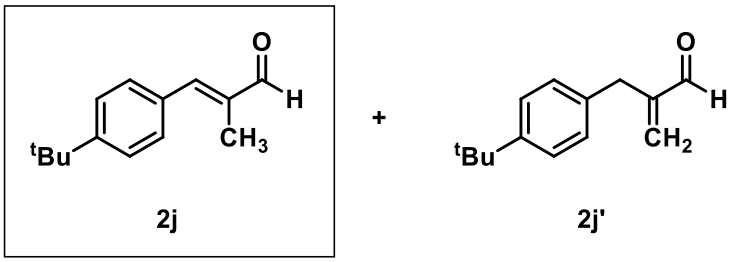


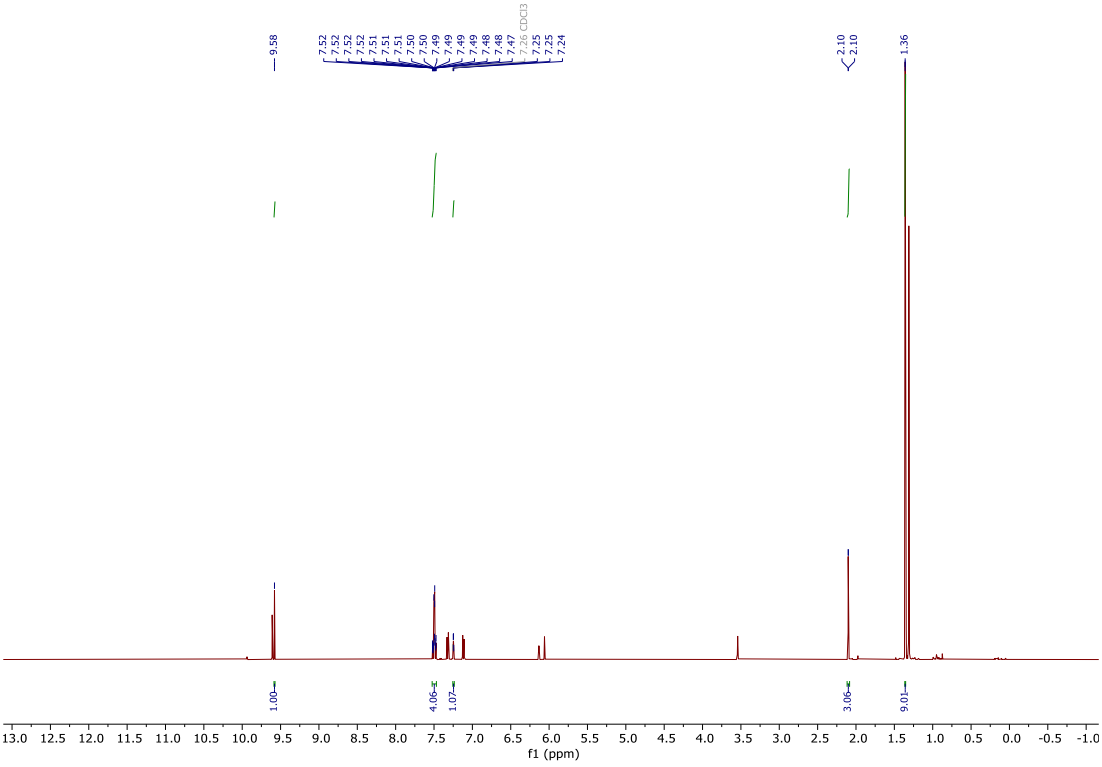
^{13}C



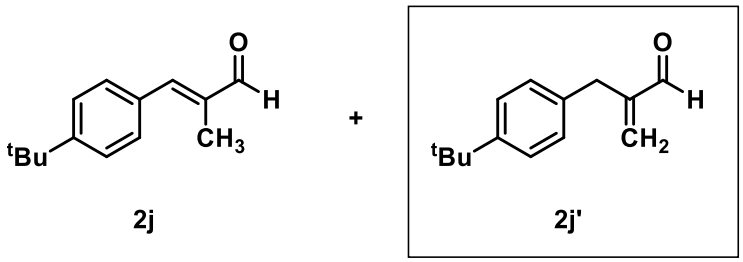
(*E*)-3-(4-(*tert*-Butyl)phenyl)-2-methylacrylaldehyde (2j) + 2-(4-(*tert*-Butyl)benzyl)acrylaldehyde (2j')

^{1}H



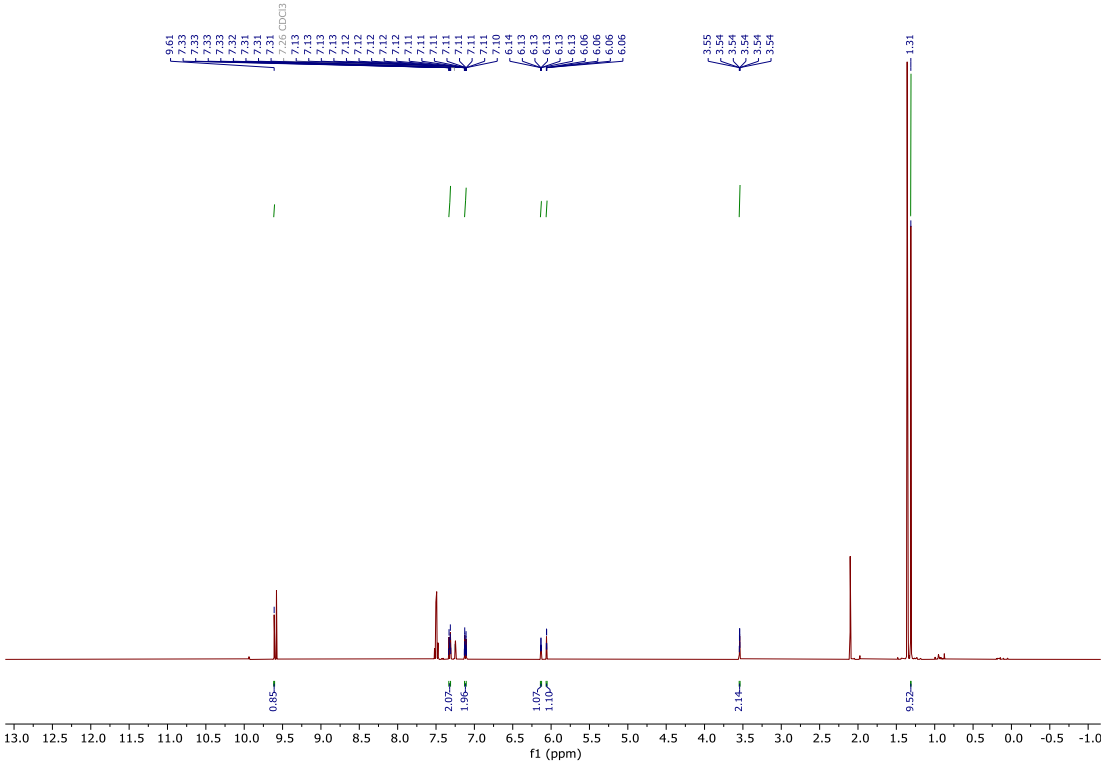


^{1}H


O
H
CH3
tBu
+
O
H
CH2
tBu

2j

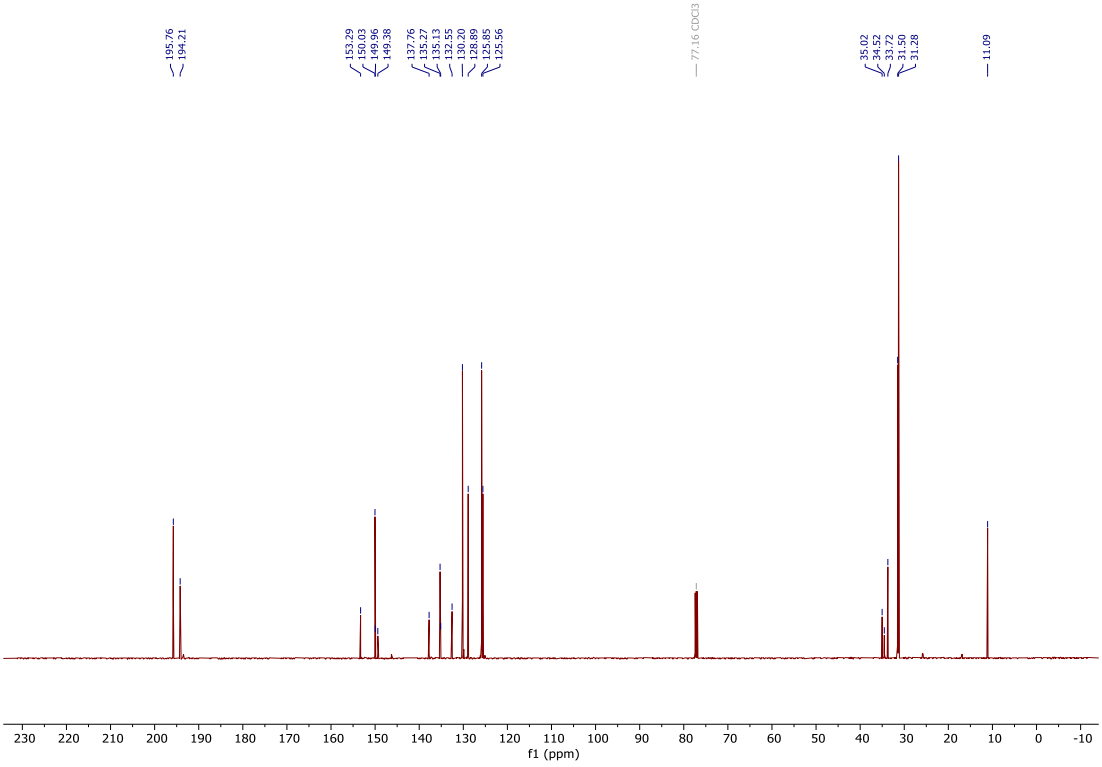
2j'


9.61
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.26 CDCl3
7.13
7.13
7.13
7.12
7.12
7.12
7.12
7.11
7.11
7.11
7.11
7.11
7.11
7.10
6.14
6.13
6.13
6.13
6.13
6.06
6.06
6.06
6.06
3.55
3.54
3.54
3.54
3.54
3.54
1.31
0.85
2.07
1.96
1.07
1.10
2.14
9.52
13.0 12.5 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)

^{13}C

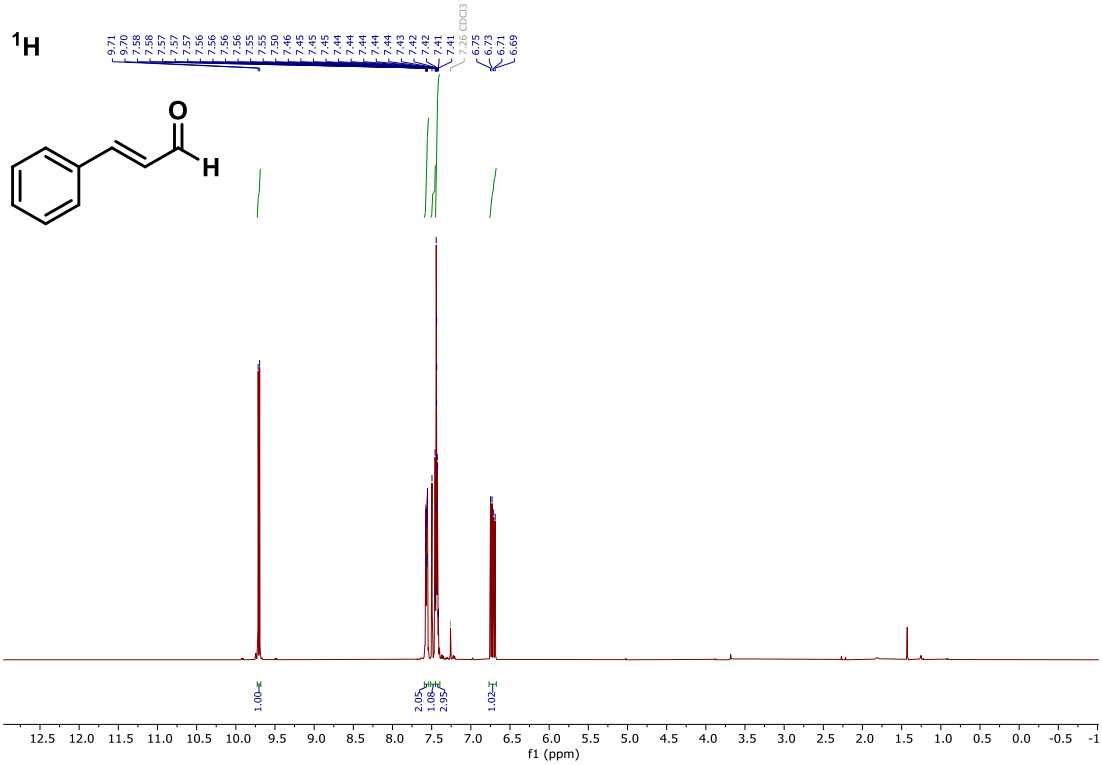

O
H
CH3
tBu
+
O
H
CH2
tBu

2j **2j'**

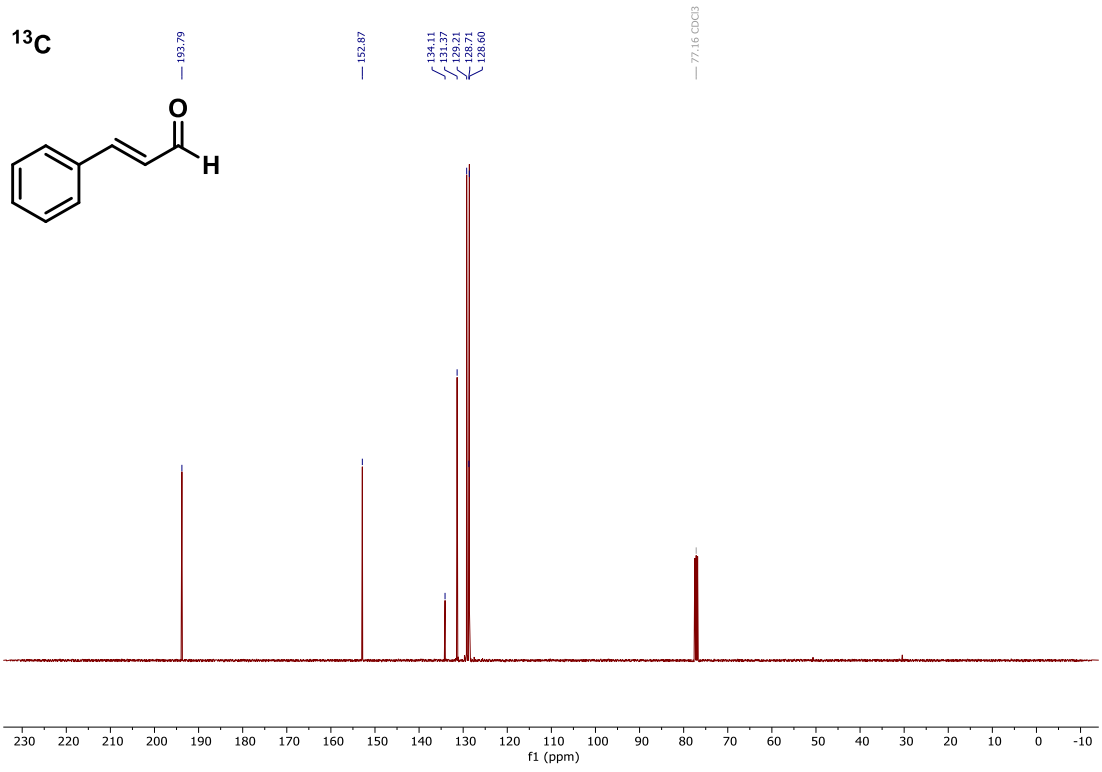

195.76
194.21
153.29
150.03
149.96
149.38
137.76
135.27
135.13
132.55
130.20
128.89
125.85
125.56
77.16 CDCl3
35.02
34.52
31.72
31.58
31.28
11.09
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Cinnamaldehyde (2k)

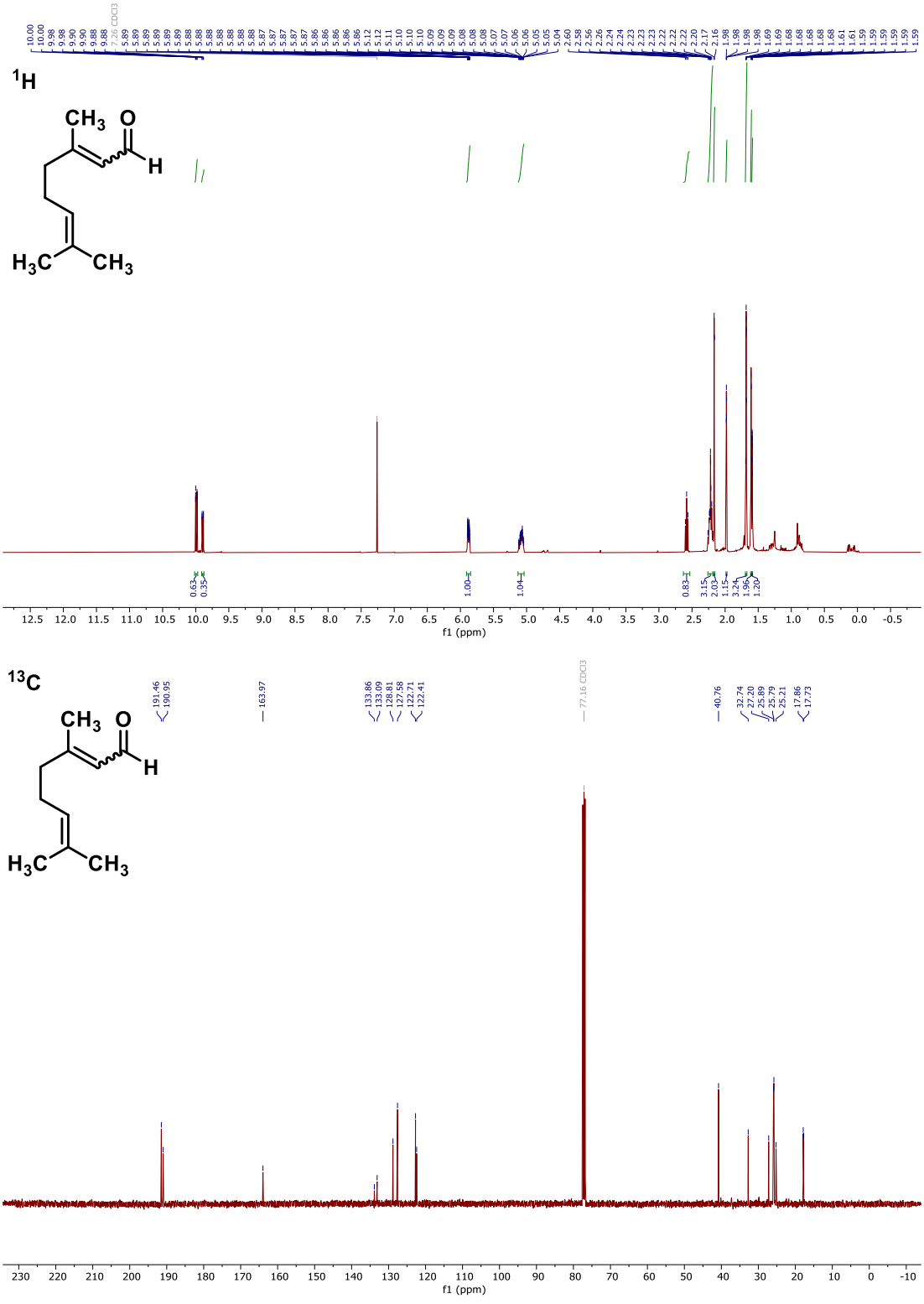
^{1}H



^{13}C

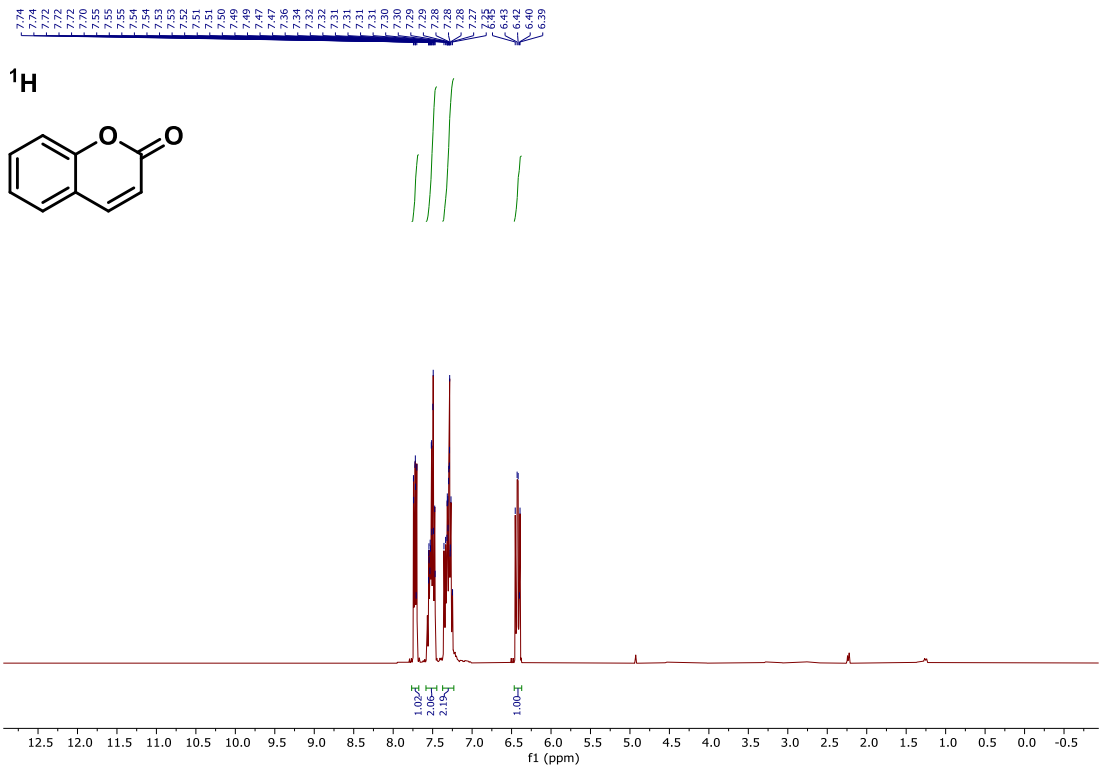


3,7-Dimethylocta-2,6-dienal (2l)

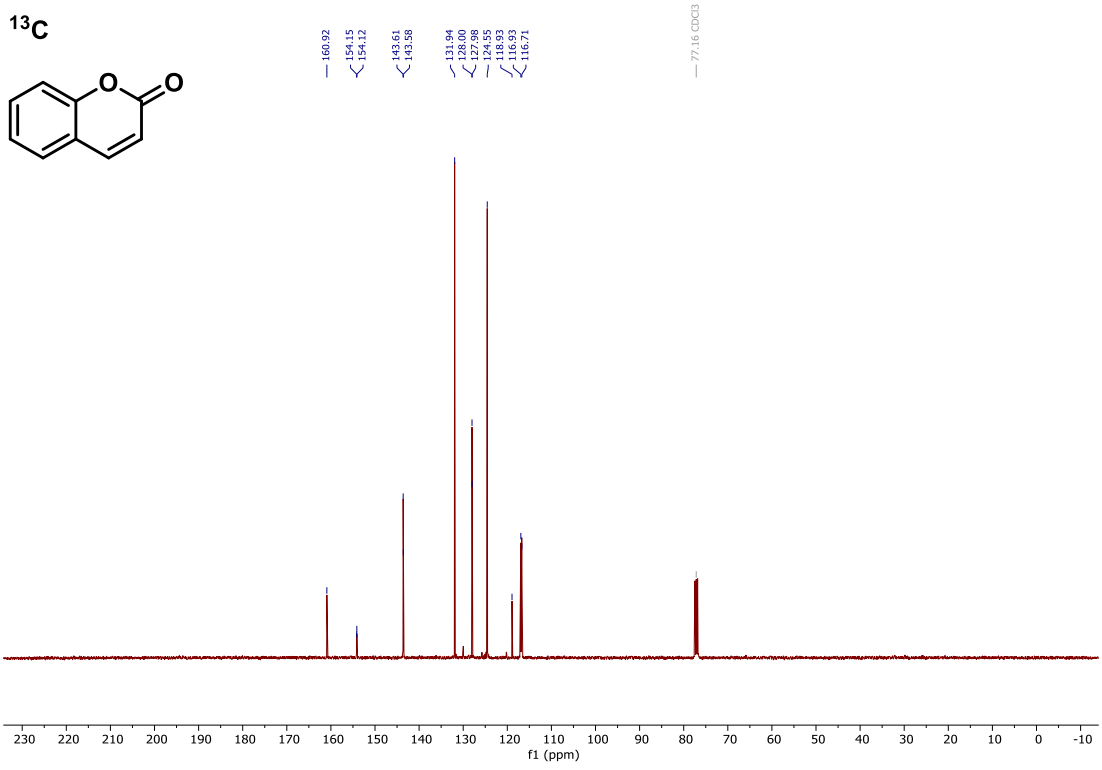


2*H*-Chromen-2-one (2n)

^{1}H

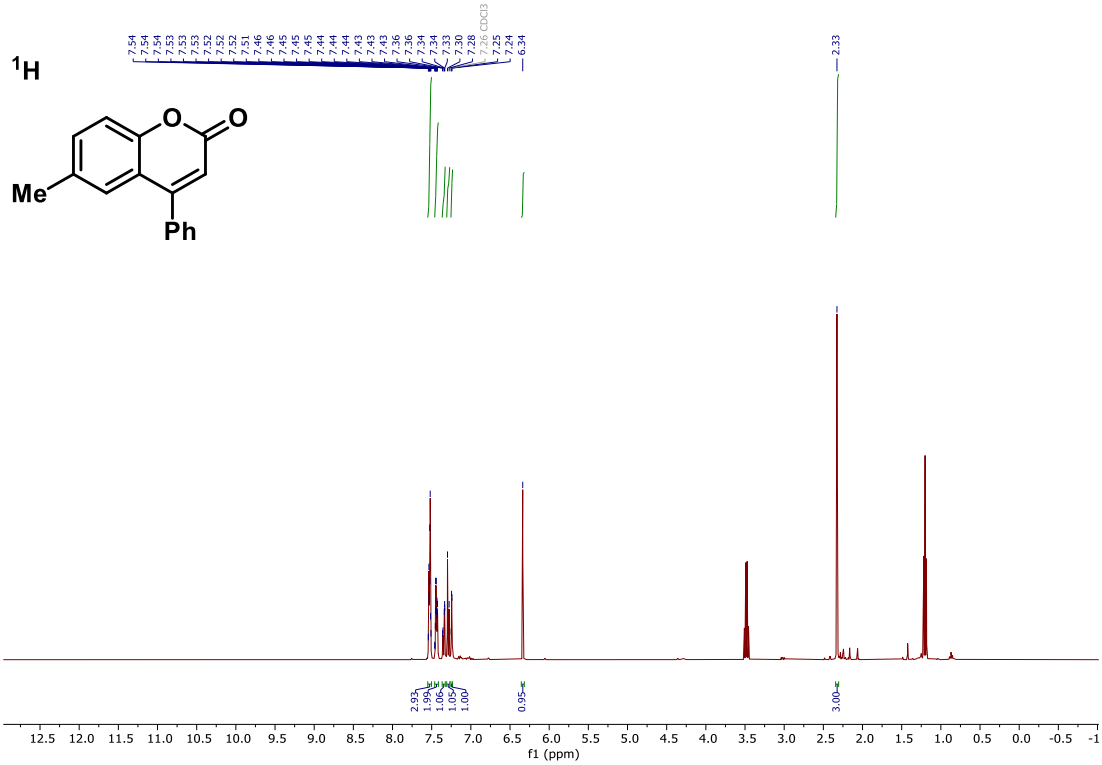


^{13}C

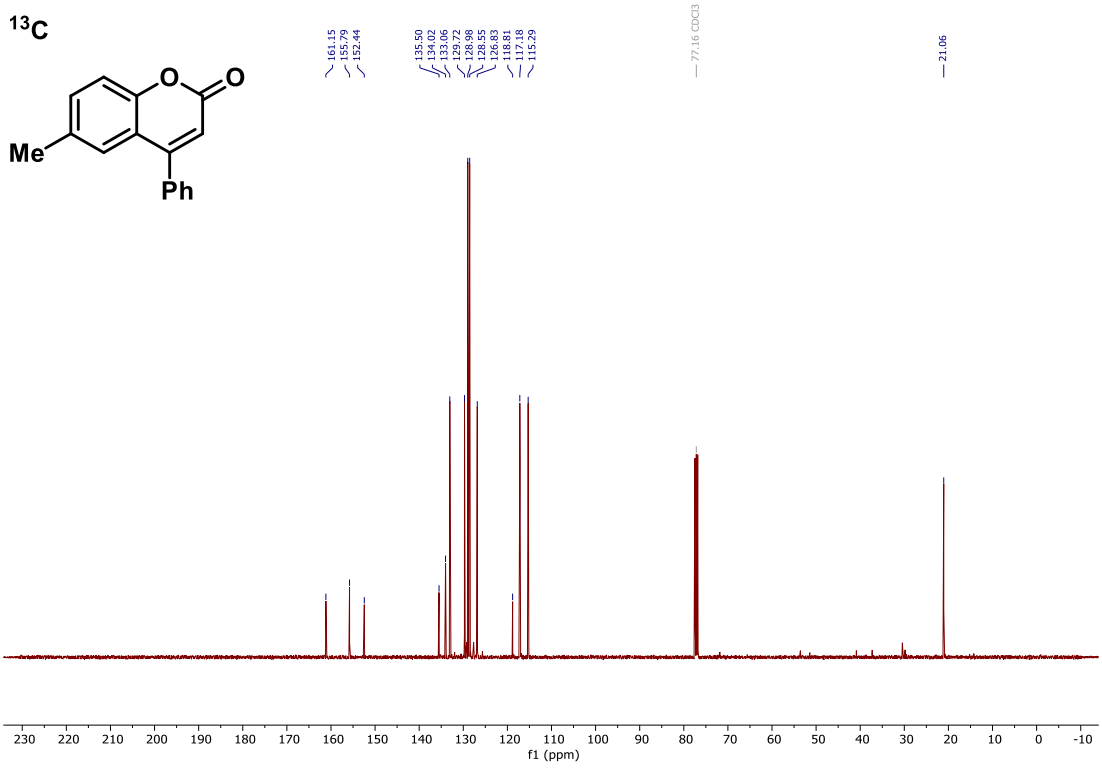


6-Methyl-4-phenyl-2*H*-chromen-2-one (2o)

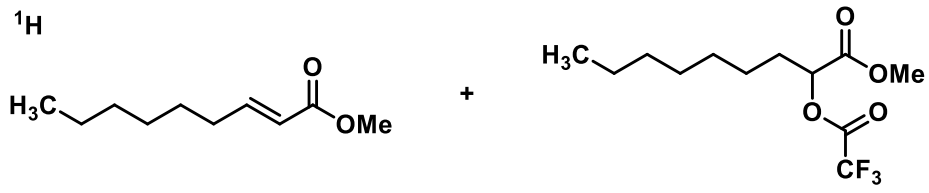
^{1}H



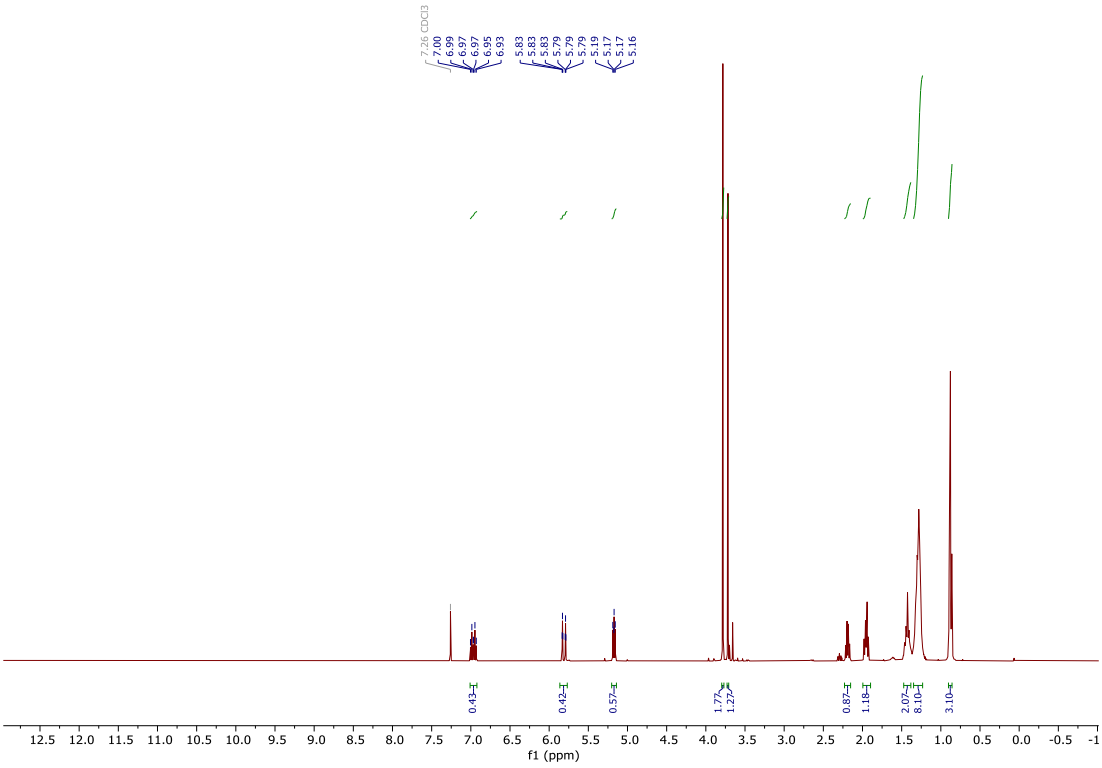
^{13}C



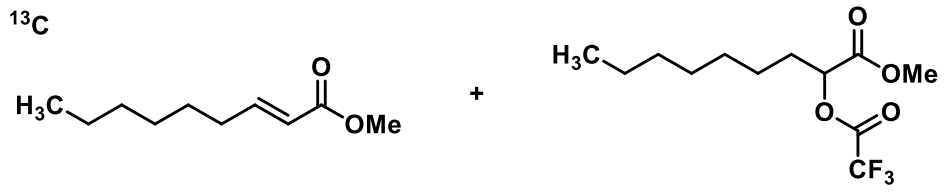
Methyl (*E*)-non-2-enoate (2q) + methyl 2-(2,2,2-trifluoroacetoxy)nonanoate (2q')



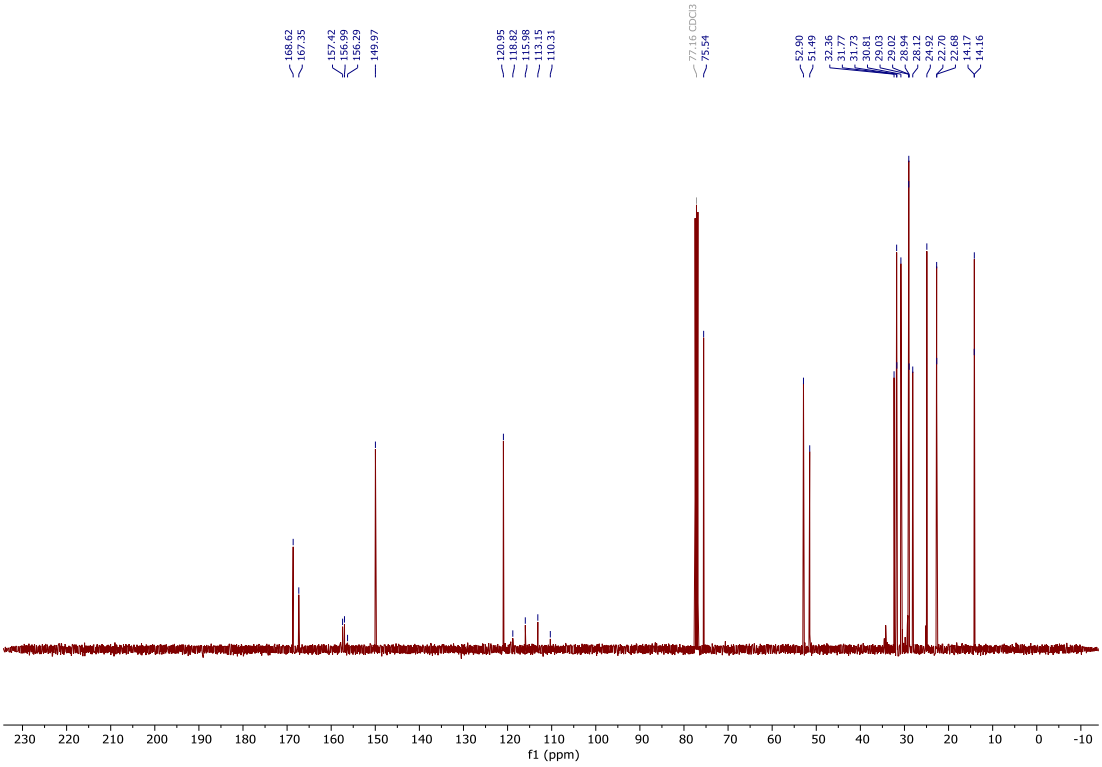
2q **2q'**



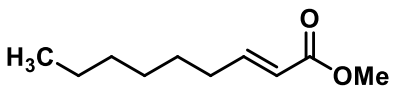
^{1}H NMR of the isolated mixture of **2q** and **2q'** ($CDCl_3$, 400 MHz). The peaks at 5.81 and 6.97 ppm correspond to the desired product **2q** (H-2 and H-3 alkene peak). The peak at 5.17 ppm corresponds to the side product **2q'**.


13C
H3C
O
OMe
+
H3C
O
OMe
O
O
CF3

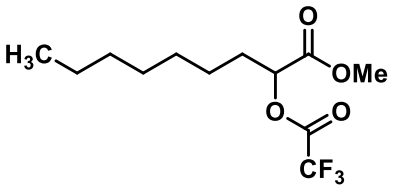
2q **2q'**


168.62
167.35
157.42
156.99
156.29
149.97
120.95
118.82
115.98
113.15
110.31
77.16 CDCl3
75.54
52.90
51.49
32.36
31.77
31.73
30.81
29.03
29.02
28.94
28.13
24.92
22.70
22.68
14.17
14.16
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

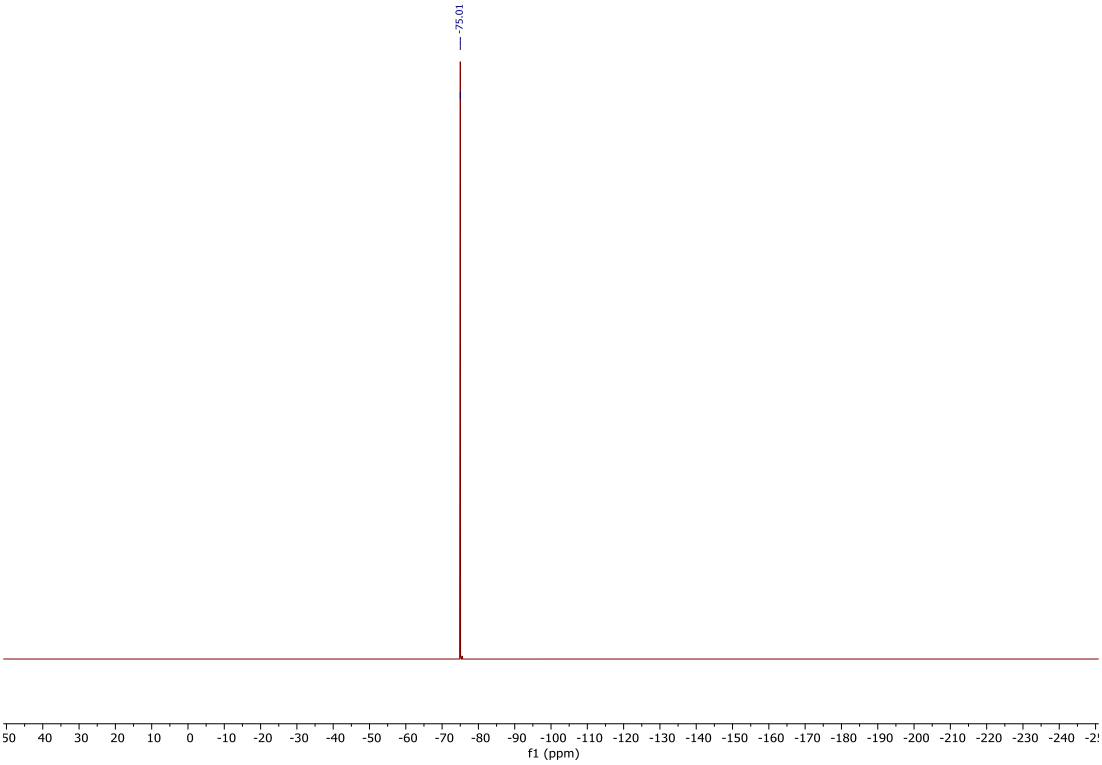
^{19}F


H3C
O
OMe

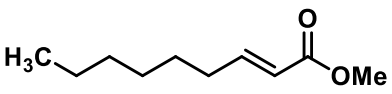
+


H3C
O
OMe
O
O
CF3

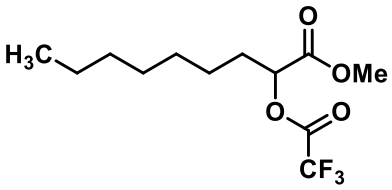
2q **2q'**


-75.01
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

COSY

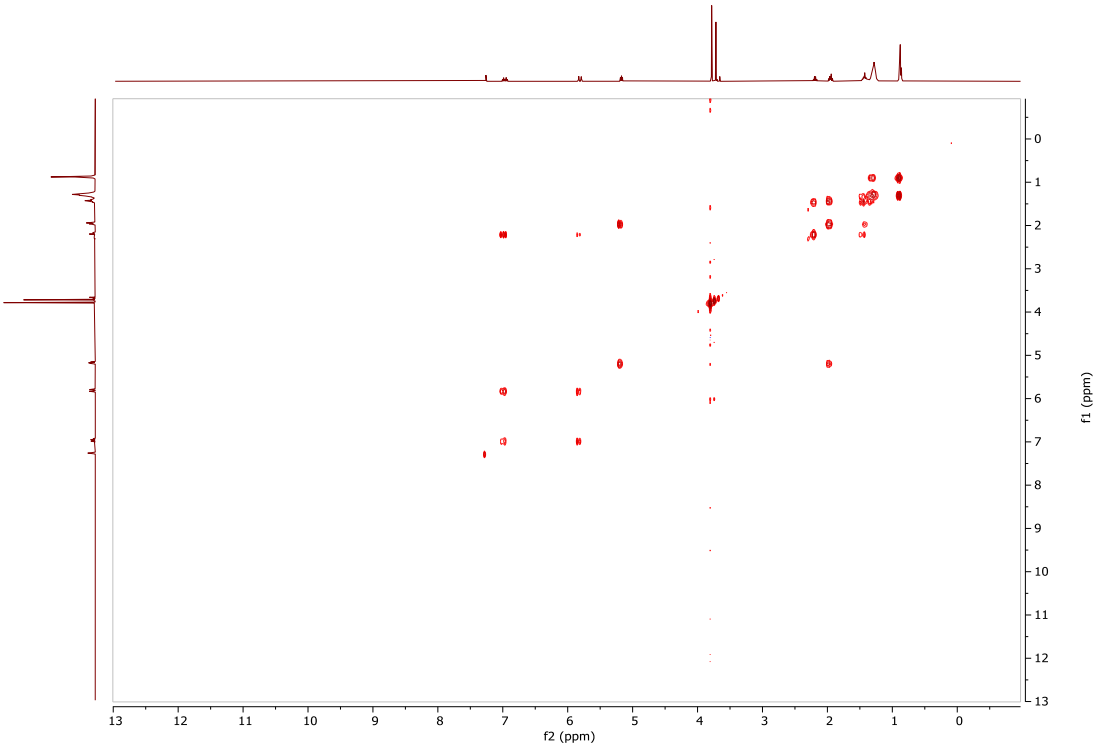


+

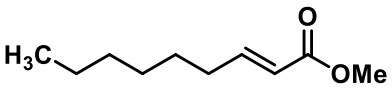


2q

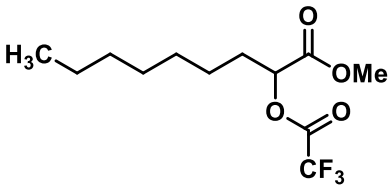
2q'



HSQC

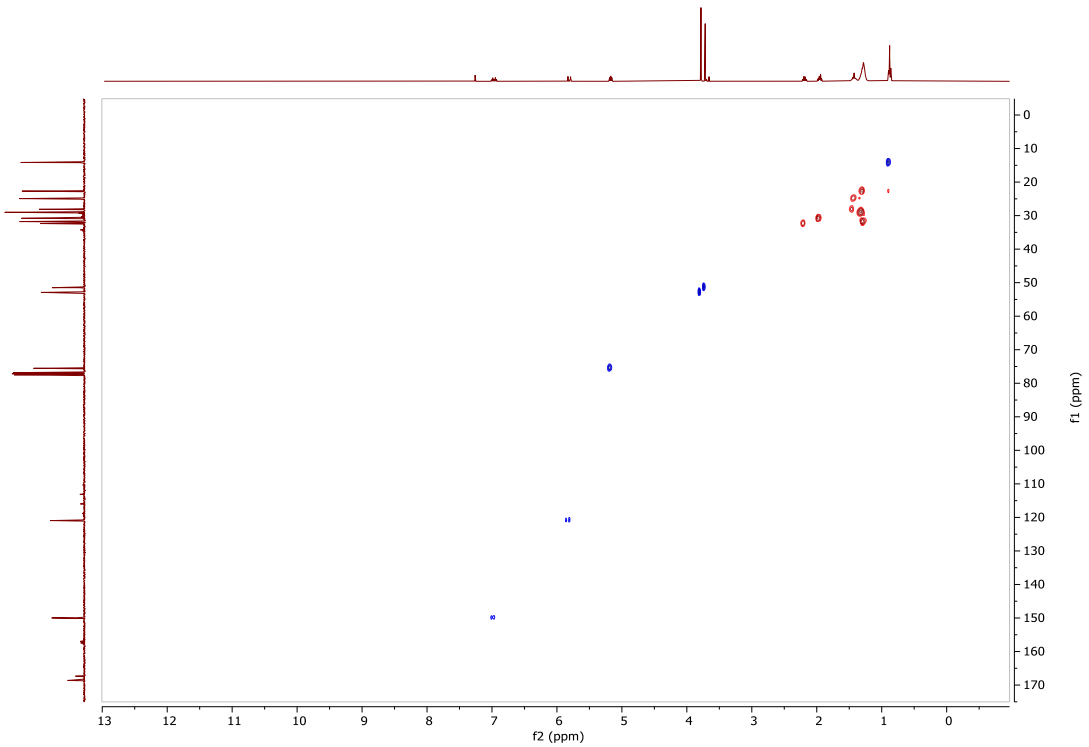


+

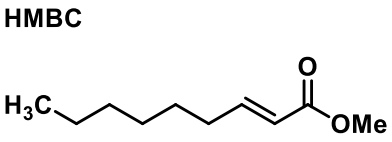


2q

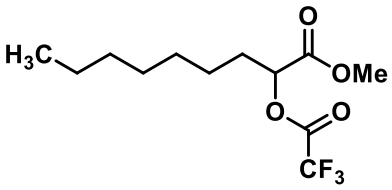
2q'



HMBC

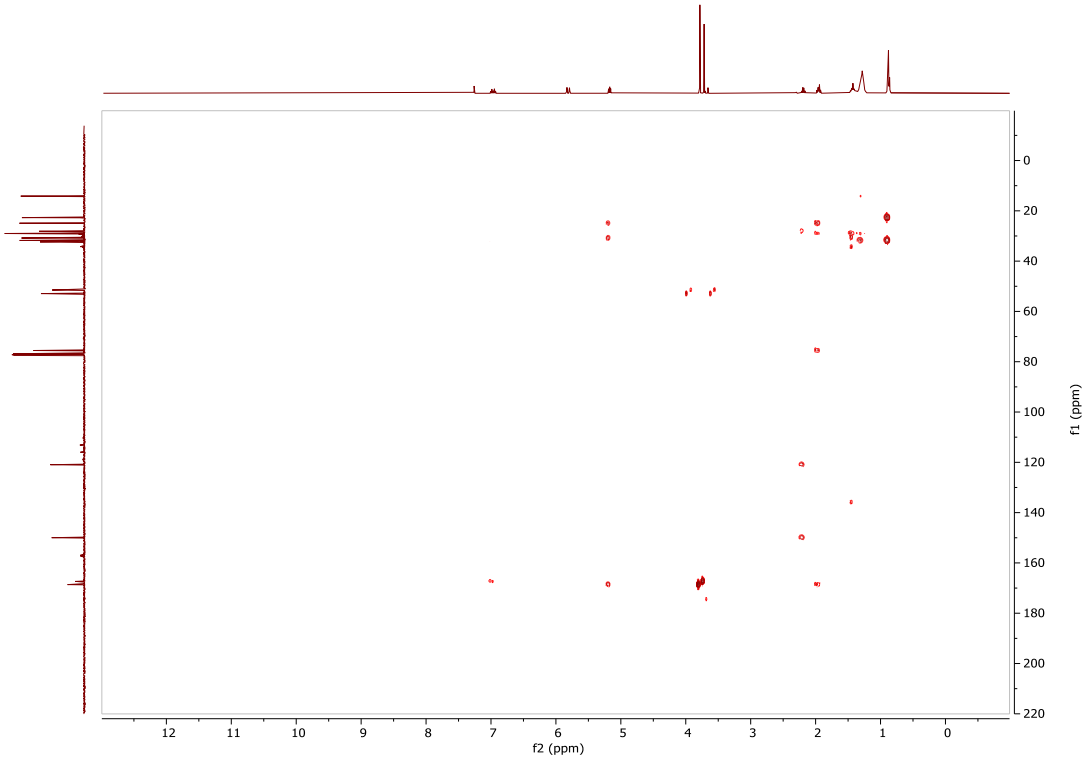


+



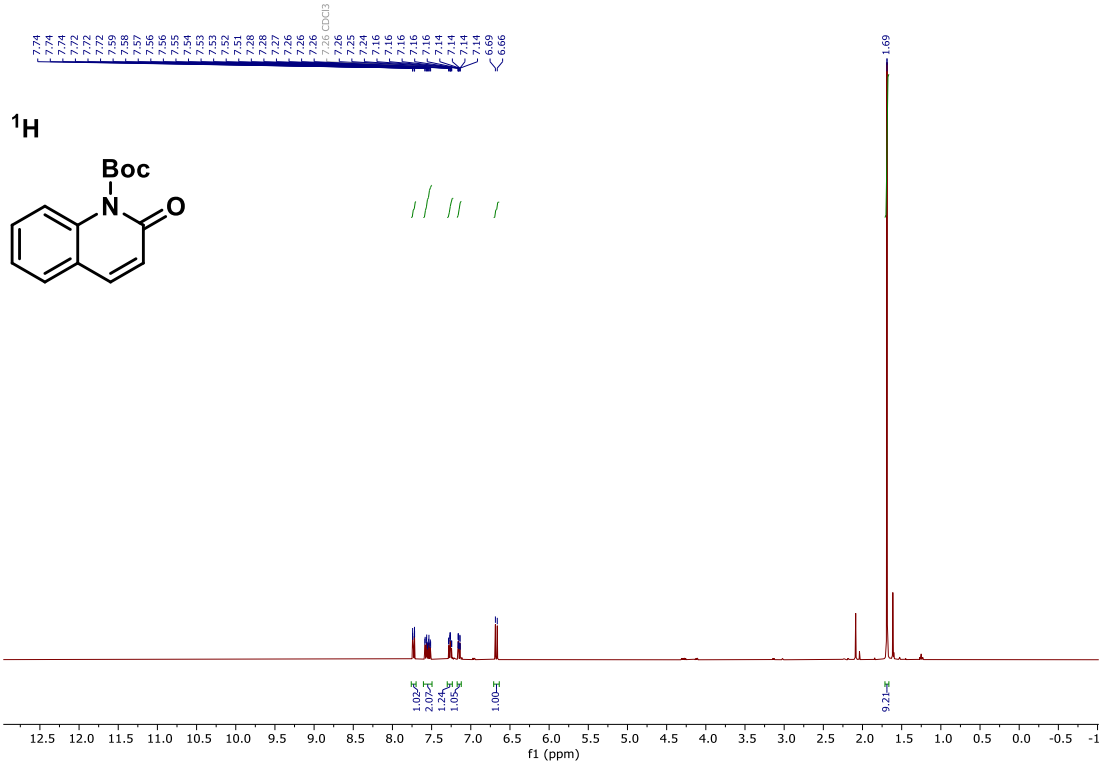
2q

2q'

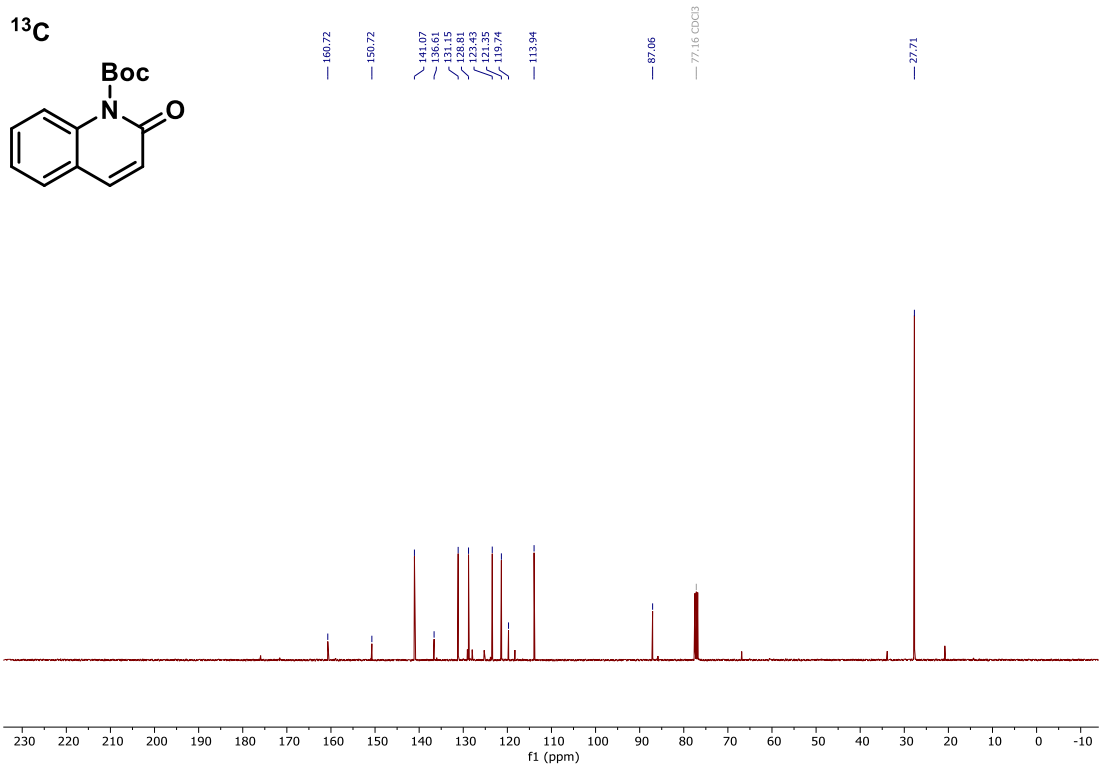


tert-Butyl 2-oxoquinoline-1(2*H*)-carboxlate (2r)

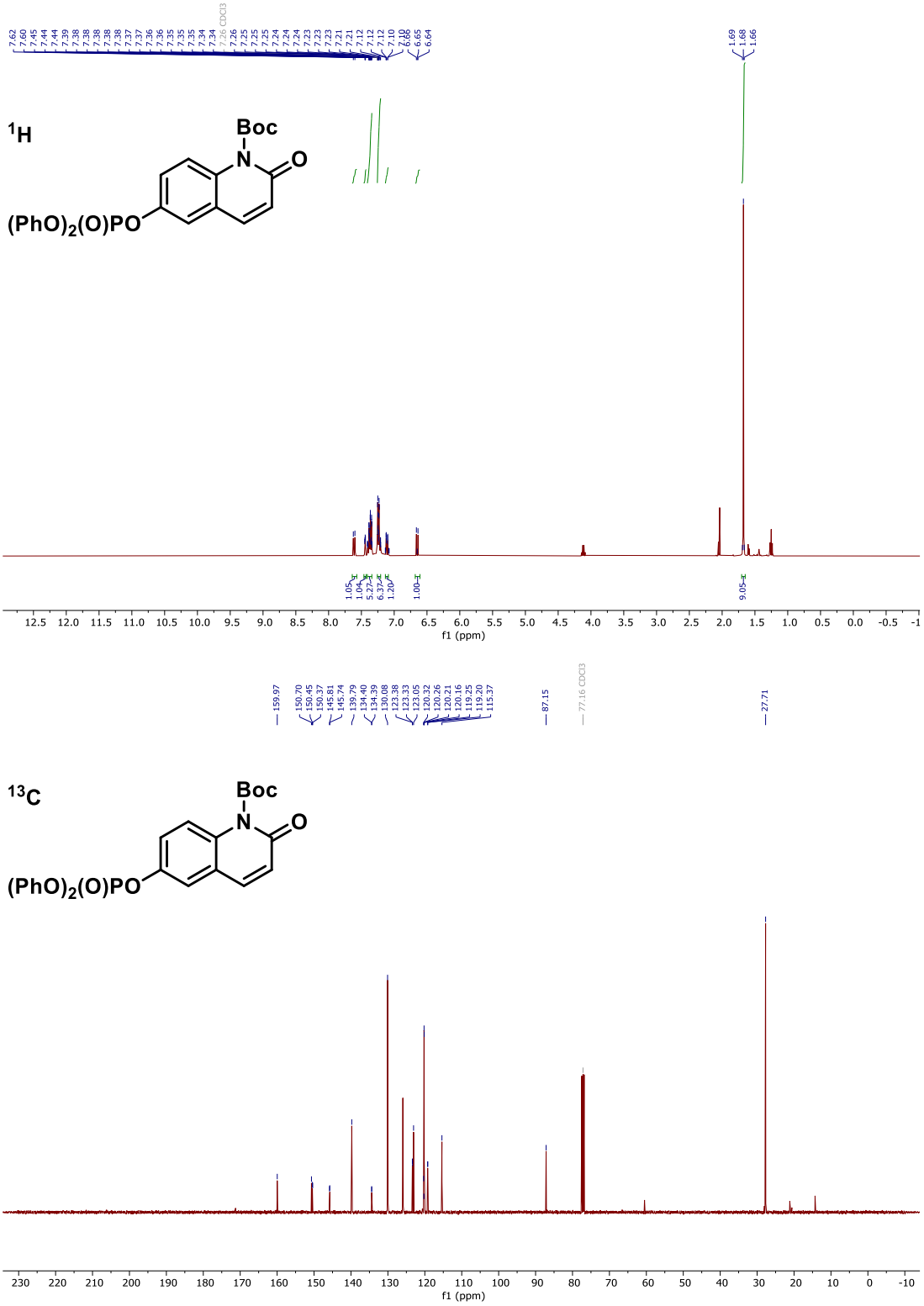
^{1}H

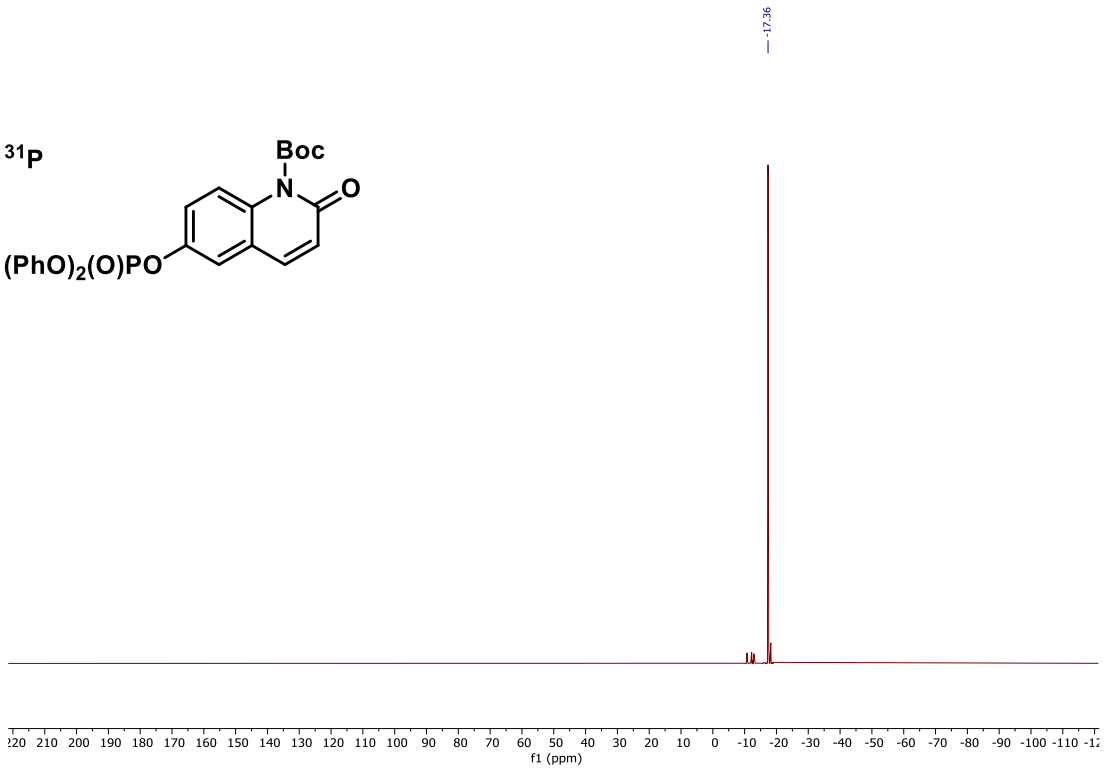


^{13}C



tert-Butyl 6-((diphenoxyphosphoryl)oxy)-2-oxoquinoline-1(2*H*)-carboxylate (2s)




31P
Boc
N
O
(PhO)2(O)PO
-17.36
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -12
f1 (ppm)

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