# Supporting Information

## Visible-Light-Driven C-H Functionalization of Double Bonds with Diazo Compounds under Mild Reaction Conditions

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# 1. General considerations

The $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on a *Bruker Avance 300 MHz spectrometer* running at 300 MHz for $^{1}H$, 75 MHz for $^{13}C$ and 282 MHz for $^{19}F$, respectively or on a *Bruker NEO-500 spectrometer* running at 500 MHz for $^{1}H$ and 126 MHz for $^{13}C$, respectively. The chemical shifts (δ) are reported relative to the tetramethylsilane signal at 0 ppm or relative to the residual signal of the solvent ($CDCl_3$ at 7.26 ppm), while for $^{13}C$ NMR are given in ppm relative to the residual signal of solvent ($CDCl_3$ at 77.16 ppm) $^{13}C$ and $^{19}F$ NMR spectra were acquired on a broadband decoupled mode. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublet of doublets; t, triplet; dt, doublet of triplets; td, triplet of doublets; tt, triplet of triplets; q, quartet; dq, doublet of quartets; p, pentuplet; m, multiplet; br, broad signal. The following abbreviations are used to indicate the solvents: Cy, Cyclohexane; DCM, dichloromethane, EtOH, Ethanol; EtOAc, Ethyl acetate; MeOH, Methanol; THF, Tetrahydrofuran; MeCN, Acetonitrile.

High-Resolution Mass Spectra (HRMS) were obtained on an *Agilent Technologies 6120 Quadrupole LC/MS* coupled with an *SFC Agilent technologies 1260 Infinity Series* instrument for the ESI-MS (Electrospray Ionization). *MassWorks* software version 4.0.0.0 (*Cerno Bioscience*) was used for the formula identification. *MassWorks* is an MS calibration software which calibrates isotope profiles to achieve high mass accuracy and enables elemental composition determination on conventional mass spectrometers of unit mass resolution allowing highly accurate comparisons between calibrated and theoretical spectra.[1] For determination of reaction intermediates in the presence of TEMPO, a high-resolution mass spectrometer (Electrospray Ionization) Bruker maXis IITM with quadrupole analyzer and QTOF time-of-flight was used.

Commercial grade reagents and solvent were purchased from *Sigma-Aldrich*, *Alfa Aesar*, *Fluorochem*, *TCI Chemicals* and used without further purifications while anhydrous solvents were taken from a SPS solvent dispenser. **4a** (Ethene-1,1-diyldibenzene), **4k** (styrene), **4l** (1-methoxy-4-vinylbenzene) and **4m** (1-bromo-4-vinylbenzene) are commercially available reagents and were used without further purification.

Analytical TLC was performed using pre-coated aluminium-backed plates (*Merck TLC Silicagel* 60 $F_{254}$) and visualized by ultraviolet irradiation. Chromatographic purification of products was accomplished using flash column chromatography (FC) on *Merck* Geduran® Si 60 silica gel (40 – 63 μm). *Celite® 512 medium* (*Sigma-Aldrich*) was used for filtration. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

A custom-made photoreactor setup was used for the photocatalytic reactions (Figure S1). The vial is placed inside the fitted well in which irradiation takes place at the desired

wavelengths (365, 385, 420, 460 or 540 nm) using 380 mW single LEDs (Figure S2). Reaction temperature is kept at 20-25 ºC using a recirculating chiller.

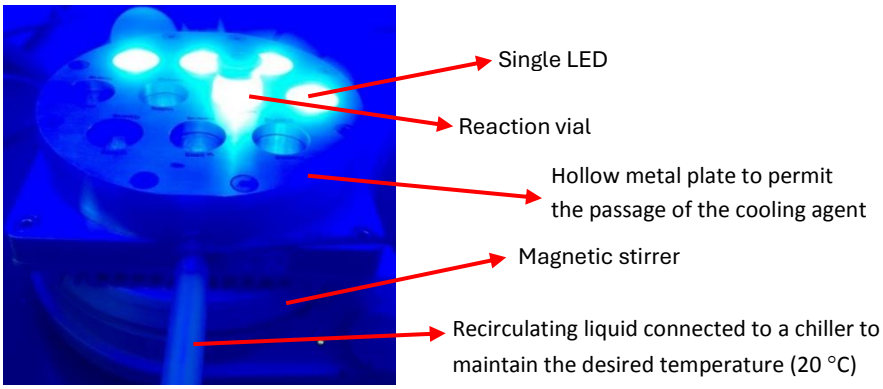



**Figure S1.** Experimental setup employed during photocatalytic reactions.

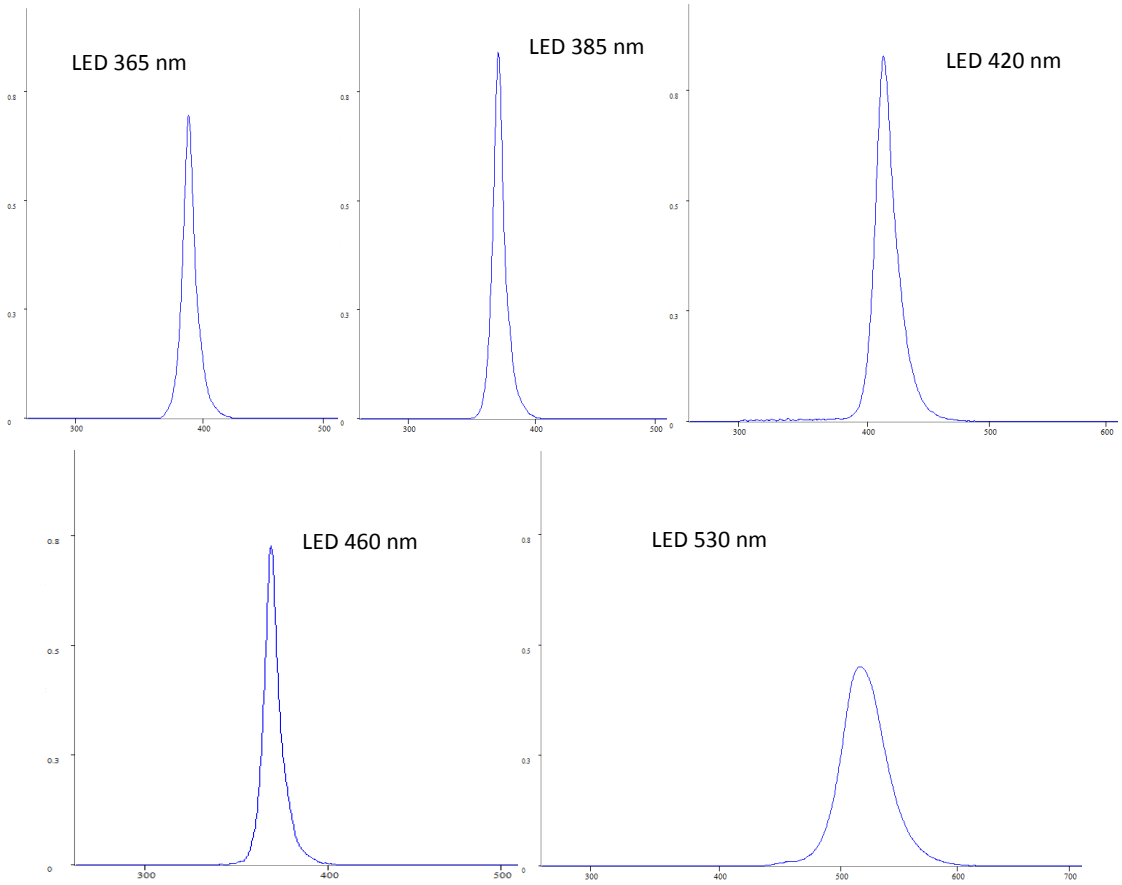


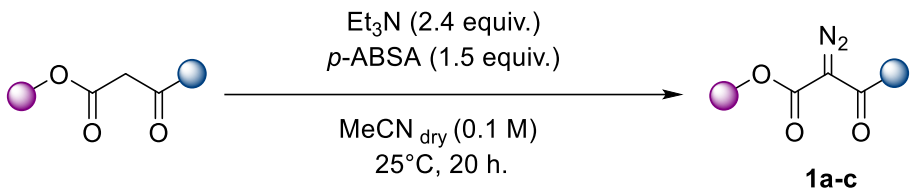

**Figure S2.** Emission spectrum of the LEDs used

UV-Vis measurements were carried out on an Agilent 8453 UV-Visible Spectroscopy System controlled by UV-Visible ChemStation Software. Emission intensities were recorded using a JASCO Spectrofluorometer FP-8600 equipped with a TC-815 Peltier thermostated single cell holder (water-cooled) controlled by Spectra Manager Version 2.10.01. Time

resolved emission spectra were recorded using an Edinburgh Instruments FS5 Spectrofluorometer, and a 460 nm EPL laser.

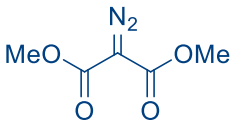
## 2. General procedures

### 2.1. General procedure GP1 for the synthesis of diazo compounds **1a-c**




Following a slightly modified procedure of Waser *al*:[2] To a stirred solution of the corresponding ester in dry acetonitrile (0.1 M), trimethylamine (2.4 equiv) and 4-acetoamidobenzensulfonyl azide (1.5 equiv) were added and further stirred for 20 hours at room temperature. At that time, the reaction was quenched with $NH_4Cl$ sat., extracted with EtOAc three times, washed with brine, dried over $MgSO_4$, filtered and concentrated under reduce pressure. The residue was purified by flash column chromatography on silica gel (Cy /EtOAc) to provide the corresponding diazoester **1**.

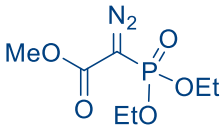
**Dimethyl 2-diazomalonate (1a)**




Following the general procedure **GP1**, from dimethyl malonate (3.0 mmol), compound **1a** was obtained as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 4 : 1). Spectroscopic data were consistent with the literature data for this compound.[2]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 3.83 (s, 6H).

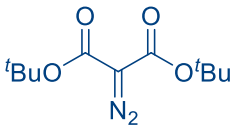
**Methyl 2-diazo-2-(diethoxyphosphoryl) acetate (1b)**




Following the general procedure **GP1**, from methyl 2-(diethoxyphosphoryl)acetate (3.0 mmol), compound **1b** was obtained as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 4 : 1). Spectroscopic data were consistent with the literature data for this compound.[3]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 4.15 – 4.07 (m, 1H), 3.72 (s, 1H), 1.30 – 1.25 (m, 6H).

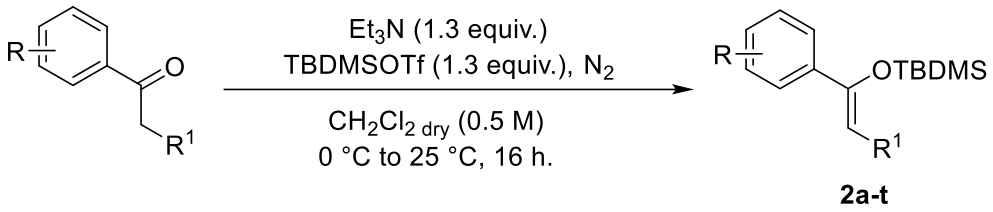
**di-*Tert*-butyl 2-diazomalonate (1c)**




Following the general procedure **GP1**, from di-*tert*-butyl malonate (3.0 mmol), compound **1c** was obtained as a yellow oil after purification by flash column chromatography (Cy : EtOAc = 4 : 1). Spectroscopic data were consistent with the literature data for this compound.[4]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 1.47 (s, 18 H).

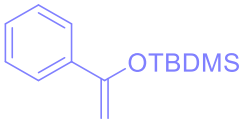
## 2.2. General procedure GP2 for the synthesis of TBDMS-Silyl-Enol Ethers **2a-t**




**2a-t**

Following a slightly modified procedure of Gademann *et al.*[5] To a flame-dried round bottom flask provided with a magnetic stirrer under nitrogen atmosphere, triethylamine (1.3 equiv.) was added to a solution of the corresponding ketone (3.0 mmol, 1.0 equiv) stirred in dry DCM (0.5 M) at 0 °C. After 1 hour of stirring at that temperature, TBDMSOTf (1.3 equiv.) was added dropwise. The reaction was allowed to warm to 25 °C and the reaction was monitored by TLC (usually 16 h). Then, $NH_4Cl$ sat. solution was added. The aqueous layer was extracted with $CH_2Cl_2$ three times, dried over $MgSO_4$, filtered and concentrated under reduce pressure. The crude product was purified by flash column chromatography on silica gel (Cy /EtOAc) to provide the corresponding protected ketone **2**.

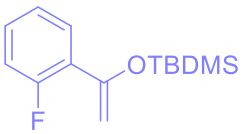
### *Tert*-butyldimethyl((1-phenylvinyl)oxy)silane (2a)




Following the general procedure **GP2**, from acetophenone (3.0 mmol), compound **2a** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[6]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.65 – 7.58 (m, 2H), 7.37 – 7.27 (m, 3H), 4.89 (d, *J* = 1.7 Hz, 1H), 4.43 (d, *J* = 1.8 Hz, 1H), 1.01 (s, 9H), 0.22 (s, 6H).

### *Tert*-butyl((1-(2-fluorophenyl)vinyl)oxy)dimethylsilane (2b)

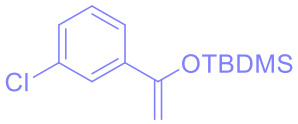



Following the general procedure **GP2**, from 1-(2-fluorophenyl)ethan-1-one (3.0 mmol), compound **2b** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.96 – 7.89 (m, 1H), 7.53 (dddd, *J* = 8.3, 7.2, 5.2, 1.9 Hz, 1H), 7.25 (td, *J* = 7.6, 1.1 Hz, 1H), 7.13 (ddd, *J* = 11.0, 8.3, 1.1 Hz, 1H), 4.85 (s, 1H), 4.84 (s, 1H), 0.93 (s, 9H), 0.13 (s, 6H). **$^{13}$C NMR** (76 MHz, $CDCl_3$): δ 196.5 (d, *J* = 5.6 Hz), 162.1 (d, *J* = 253.6 Hz), 134.8 (d, *J* = 8.9 Hz), 130.8 (d, *J* = 3.6 Hz), 124.8 (d, *J* = 3.1 Hz), 123.5 (d, *J* = 15.7 Hz), 116.5 (d, *J* = 23.8 Hz), 70.6 (d, *J* = 11.7 Hz), 26.0 (3C), 18.7, -5.2 (2C). **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ -108.08.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{14}H_{22}FOSi$: 253.1424; found: 253.1421.

***Tert*-butyl((1-(3-chlorophenyl)vinyl)oxy)dimethylsilane (2c)**

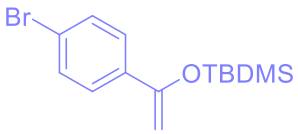



Following the general procedure **GP2**, from 1-(3-chlorophenyl)ethanone (3.0 mmol), compound **2c** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.61 – 7.58 (m, 1H), 7.52 – 7.47 (m, 1H), 7.28 – 7.23 (m, 2H), 4.90 (d, *J* = 1.9 Hz, 1H), 4.47 (d, *J* = 1.9 Hz, 1H), 1.02 (s, 9H), 0.23 (s, 6H). **$^{13}$C NMR** (76 MHz, $CDCl_3$): δ 154.8, 139.9, 134.3, 129.5, 128.3, 125.7, 123.5, 92.0, 26.0 (3C), 18.5, -4.5 (2C).

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{14}H_{22}ClOSi$: 269.1128; found: 269.1130.

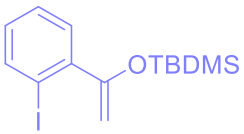
**((1-(4-Bromophenyl)vinyl)oxy)(*tert*-butyl)dimethylsilane (2d)**




Following the general procedure **GP2**, from 1-(4-bromophenyl)ethanone (3.0 mmol), compound **2d** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[7]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.52 – 7.42 (m, 4H), 4.88 (d, *J* = 1.8 Hz, 1H), 4.44 (d, *J* = 1.9 Hz, 1H), 1.01 (s, 9H), 0.22 (s, 6H).

***Tert*-butyl((1-(2-iodophenyl)vinyl)oxy)dimethylsilane (2e)**

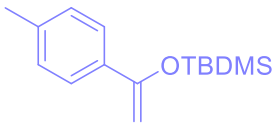



Following the general procedure **GP2**, from 1-(2-iodophenyl)ethanone (3.0 mmol), compound **2e** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.39 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.32 (td, *J* = 7.4, 1.2 Hz, 1H), 6.99 (ddd, *J* = 7.9, 7.3, 1.9 Hz, 1H), 4.67 (d, *J* = 1.3 Hz, 1H), 4.54 (d, *J* = 1.3 Hz, 1H), 1.01 (s, 9H), 0.21 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 158.4, 144.4, 139.8, 129.8, 129.4, 127.8, 96.3, 96.1, 25.9, 18.3, -4.4.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{14}H_{22}IOSi$: 361.0485; found: 361.0481.

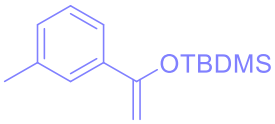
***Tert*-butyldimethyl((1-(*p*-tolyl)vinyl)oxy)silane (2f)**




Following the general procedure **GP2**, from 1-(*p*-tolyl)ethanone (3.0 mmol), compound **2f** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[6]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.51 and 7.15 (AA'BB' system, 4H), 4.84 (d, *J* = 1.6 Hz, 1H), 4.38 (d, *J* = 1.6 Hz, 1H), 2.35 (s, 3H), 1.01 (s, 9H), 0.21 (s, 6H).

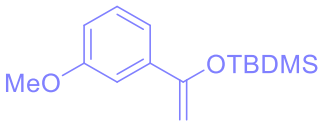
***Tert*-butyldimethyl((1-(*m*-tolyl)vinyl)oxy)silane (2g)**




Following the general procedure **GP2**, from 1-(*m*-tolyl)ethanone (3.0 mmol), compound **2g** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[6]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 5.00 (d, *J* = 1.6 Hz, 1H), 4.54 (d, *J* = 1.6 Hz, 1H), 2.48 (s, 3H), 1.14 (s, 9H), 0.34 (s, 6H).

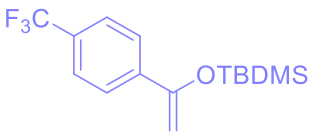
***Tert*-butyl((1-(3-methoxyphenyl)vinyl)oxy)dimethylsilane (2h)**




Following the general procedure **GP2**, from 1-(3-methoxyphenyl)ethanone (3.0 mmol), compound **2h** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[8]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.28 – 7.23 (m, 3H), 6.90 – 6.86 (m, 1H), 4.95 (d, *J* = 1.6 Hz, 1H), 4.47 (d, *J* = 1.7 Hz, 1H), 3.84 (s, 3H), 1.08 (s, 9H), 0.28 (s, 6H).

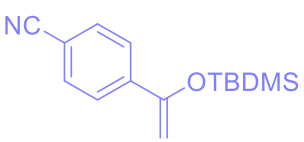
***Tert*-butyldimethyl((1-(3-(trifluoromethyl)phenyl)vinyl)oxy)silane (2i)**




Following the general procedure **GP2**, from 1-(4-(trifluoromethyl)phenyl)ethanone (3.0 mmol), compound **2i** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[6]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.73 y 7.60 (AA'BB' system, 4H), 4.99 (d, *J* = 2.0 Hz, 1H), 4.55 (d, *J* = 2.0 Hz, 1H), 1.03 (s, 9H), 0.25 (s, 6H).

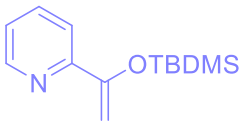
**3-(1-((*Tert*-butyldimethylsilyl)oxy)vinyl)benzonitrile (2j)**




Following the general procedure **GP2**, from 4-acetylbenzonitrile (3.0 mmol), compound **2j** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[9]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.69 y 7.60 (AA'BB' system, 4H), 4.99 (d, *J* = 2.3 Hz, 1H), 4.56 (d, *J* = 2.2 Hz, 1H), 0.99 (s, 9H), 0.22 (s, 6H).

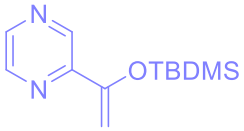
**2-(1-((*Tert*-butyldimethylsilyl)oxy)vinyl)pyridine (2k)**




Following the general procedure **GP2**, from 1-(pyridin-2-yl)ethanone (3.0 mmol), compound **2k** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[10]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.53 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.70 – 7.59 (m, 2H), 7.16 (ddd, *J* = 6.7, 4.7, 1.8 Hz, 1H), 5.64 (d, *J* = 1.1 Hz, 1H), 4.55 (d, *J* = 1.1 Hz, 1H), 1.00 (s, 9H), 0.23 (s, 6H).

**2-(1-((*Tert*-butyldimethylsilyl)oxy)vinyl)pyrazine (2l)**

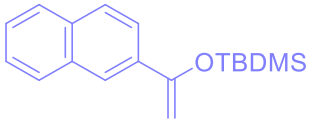



Following the general procedure **GP2**, from 1-(pyrazin-2-yl)ethanone (3.0 mmol), compound **2l** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.90 (d, *J* = 1.3 Hz, 1H), 8.51 – 8.46 (m, 4H), 5.66 (d, *J* = 1.5 Hz, 1H), 4.64 (d, *J* = 1.4 Hz, 1H), 1.02 (s, 9H), 0.26 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 152.6, 149.7, 143.5, 143.2, 140.7, 94.6, 25.5, 17.9, -5.0.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{12}H_{21}N_2OSi$: 237.1423; found: 237.1426.

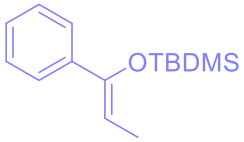
***Tert*-butyldimethyl((1-(naphthalen-2-yl)vinyl)oxy)silane (2m)**




Following the general procedure **GP2**, from 1-(naphthalen-2-yl)ethanone (3.0 mmol), compound **2m** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[11]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.11 (brs, 1H), 7.88 – 7.74 (m, 4H), 7.53 – 7.44 (m, 2H), 5.06 (d, *J* = 1.4 Hz, 1H), 4.57 (d, *J* = 1.6 Hz, 1H), 1.08 (s, 9H), 0.27 (s, 6H).

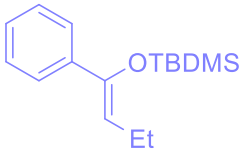
***Tert*-butyldimethyl((1-phenylprop-1-en-1-yl)oxy)silane (2n)**




Following the general procedure **GP2**, from propiophenone (3.0 mmol), compound **2n** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[5]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.43 – 7.37 (m, 2H), 7.28 – 7.16 (m, 3H), 5.17 (q, *J* = 6.9 Hz, 1H), 1.71 (d, *J* = 6.9 Hz, 3H), 0.96 (s, 9H), -0.07 (s, 6H).

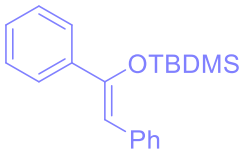
***Tert*-butyldimethyl((1-phenylbut-1-en-1-yl)oxy)silane (2o)**




Following the general procedure **GP2**, from 1-phenylbutan-1-one (3.0 mmol), compound **2o** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[12]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.47 – 7.41 (m, 2H), 7.32 – 7.19 (m, 3H), 5.10 (t, *J* = 7.1 Hz, 1H), 2.23 (p, *J* = 7.5 Hz, 2H), 1.04 (t, *J* = 7.5 Hz, 3H), 0.99 (s, 9H), -0.04 (s, 6H).

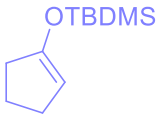
***Tert*-butyl((1,2-diphenylvinyl)oxy)dimethylsilane (2p)**




Following the general procedure **GP2**, from 1,2-diphenylethanone (3.0 mmol), compound **2p** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[13]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.68 – 7.55 (m, 4H), 7.40 – 7.23 (m, 5H), 7.21 – 7.12 (m, 1H), 6.11 (s, 1H), 0.97 (s, 9H), -0.22 (s, 6H).

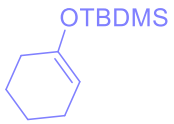
***Tert*-butyl(cyclopent-1-en-1-yloxy)dimethylsilane (2q)**




Following the general procedure **GP2**, from cyclopentanone (3.0 mmol), compound **2q** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[14]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 4.64 – 4.58 (m, 1H), 2.29 – 2.18 (m, 4H), 1.93 – 1.77 (m, 2H), 0.92 (s, 9H), 0.15 (s, 6H).

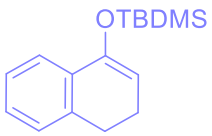
***Tert*-butyl(cyclohex-1-en-1-yloxy)dimethylsilane (2r)**




Following the general procedure **GP2**, from cyclohexanone (3.0 mmol), compound **2r** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[14]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 4.90 – 4.79 (m, 1H), 2.04 – 1.92 (m, 4H), 1.71 – 1.57 (m, 2H), 1.56 – 1.45 (m, 2H), 0.92 (s, 9H), 0.12 (s, 6H).

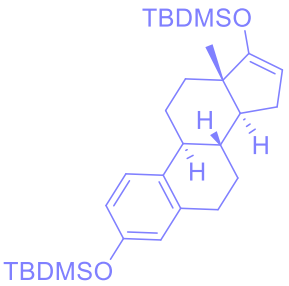
***Tert*-butyl((3,4-dihydronaphthalen-1-yl)oxy)dimethylsilane (2s)**




Following the general procedure **GP2**, from 3,4-dihydronaphthalen-1(2*H*)-one (3.0 mmol), compound **2s** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[15]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.47 (d, *J* = 6.9 Hz, 1H), 7.24 – 7.08 (m, 3H), 5.17 (t, *J* = 4.7 Hz, 1H), 2.76 (t, *J* = 7.9 Hz, 2H), 2.36 – 2.25 (m, 2H), 1.02 (s, 9H), 0.21 (s, 6H).

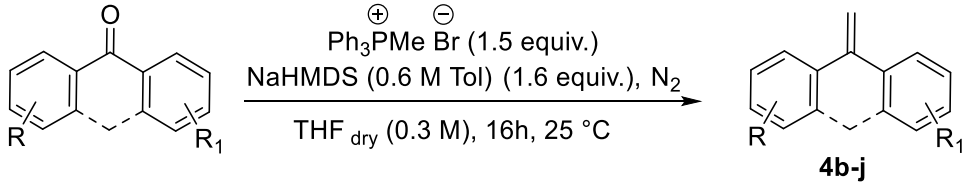
**(((8*R*,9*S*,13*S*,14*S*)-13-Methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*] phenanthrene-3,17-diyl)bis(oxy))bis(*tert*-butyldimethylsilane) (2t)**




Following the general procedure **GP2**, from (8*R*,9*S*,13*S*,14*S*)-3-hydroxy-13-methyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta [*a*]phenanthren-17(14*H*)-one (3.0 mmol), compound **2t** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[16]

**$^1$H NMR** (300 MHz, Chloroform-d)**:** δ 7.12 (d, *J* = 8.5 Hz, 1H), 6.62 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.57 (d, *J* = 2.5 Hz, 1H), 4.49 (dd, *J* = 3.1, 1.6 Hz, 1H), 2.92 – 2.76 (m, 2H), 2.40 – 2.18 (m, 2H), 2.18 – 2.04 (m, 1H), 1.97 – 1.76 (m, 3H), 1.67 – 1.49 (m, 5H), 1.00 (s, 9H), 0.96 (s, 9H), 0.88 (brs, 3H), 0.20 (s, 6H), 0.19 (s, 6H).

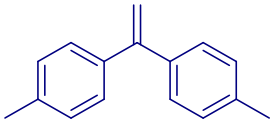
## 2.3. General procedure GP3 for the synthesis of 1,1-diarylalkenes **4b-j**




**4b-j**

Following a slightly modified procedure of Wangelin *et al.*[17] to a flame-dried round bottom flask provided with a magnetic stirrer, a solution of methyl triphenylphosphonium bromide (2.0 equiv) in dry THF (0.3 M) was stirred at room temperature. Dropwise addition of NaHMDS (0.6 M in toluene, 2.0 equiv) resulted in a yellow suspension that was further stirred at that temperature for 1 hour. At that time, the corresponding ketone (1.0 equiv.) was added (dropwise or portionwise) and the mixture was stirred at room temperature for 16 h. Next, $NH_4Cl$ sat. solution followed by distilled water were added and the resulting mixture was extracted with EtOAc three times. The organic layers were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (Cy / EtOAc) to afford the corresponding alkenes **4**.

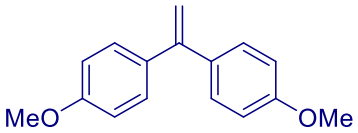
**4,4'-(Ethene-1,1-diyl)bis(methylbenzene) (4b)**



Following the general procedure **GP3**, from di-*p*-tolylmethanone (3.0 mmol), compound **4b** was obtained as a white solid after purification by flash column chromatography (Cy : EtOAc = 9.5 : 0.5). Spectroscopic data were consistent with the literature data for this compound.[18]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.28 and 7.14 (AA'BB' system, 8H), 5.41 (s, 2H), 2.37 (s, 6H).

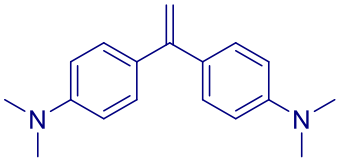
**4,4'-(Ethene-1,1-diyl)bis(methoxybenzene) (4c)**




Following the general procedure **GP3**, from bis(4-methoxyphenyl)methanone (3.0 mmol), compound **4c** was obtained as a white solid after purification by flash column chromatography (Cy : EtOAc = 9.5 : 0.5). Spectroscopic data were consistent with the literature data for this compound.[18]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.28 and 6.87 (AA'BB' system, 8H), 5.30 (s, 2H), 3.83 (s, 6H).

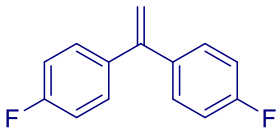
**4,4'-(Ethene-1,1-diyl)bis(*N*,*N*-dimethylaniline) (4d)**




Following the general procedure **GP3**, from bis(4-(dimethylamino)phenyl)methanone (3.0 mmol), compound **4c** was obtained as a white solid after purification by flash column chromatography (Cy : EtOAc = 9.5 : 0.5). Spectroscopic data were consistent with the literature data for this compound.[19]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.27 and 6.70 (AA'BB' system, 8H), 5.19 (s, 2H), 2.97 (s, 12H).

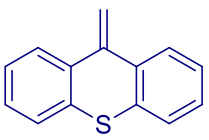
**4,4'-(Ethene-1,1-diyl)bis(fluorobenzene) (4e)**




Following the general procedure **GP3**, from bis(4-fluorophenyl)methanone (3.0 mmol), compound **4e** was obtained as a yellow oil after purification by flash column chromatography (Cy : EtOAc = 9.5 : 0.5). Spectroscopic data were consistent with the literature data for this compound.[18]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.33 – 7.23 (m, 4H), 7.05 – 6.94 (m, 4H), 5.37 (s, 2H).

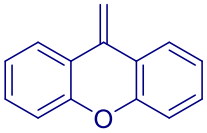
**9-Methylene-9*H*-thioxanthene (4f)**




Following the general procedure **GP3**, from 9*H*-thioxanthen-9-one (3.0 mmol), compound **4f** was obtained as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 9.5 : 0.5). Spectroscopic data were consistent with the literature data for this compound.[20]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.59 – 7.51 (m, 2H), 7.32 – 7.24 (m, 2H), 7.23 – 7.10 (m, 4H), 5.48 (s, 2H).

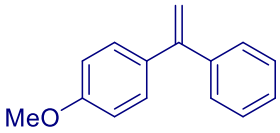
**9-Methylene-9*H*-xanthene (4g)**



Following the general procedure **GP3**, from 9*H*-xanthen-9-one (3.0 mmol), compound **4g** was obtained as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 9.5 : 0.5). Spectroscopic data were consistent with the literature data for this compound.[20]

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.7 Hz, 2H), 7.03 – 6.93 (m, 4H), 5.37 (s, 2H).

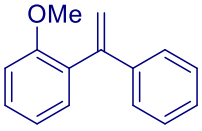
**1-Methoxy-4-(1-phenylvinyl)benzene (4h)**



Following the general procedure **GP3**, from (4-methoxyphenyl)(phenyl)methanone (3.0 mmol), compound **4h** was obtained as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 9.5 : 0.5). Spectroscopic data were consistent with the literature data for this compound.[21]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.31 – 7.22 (m, 5H), 7.21 and 6.79 (AA'BB' system, 4H), 5.33 (d, *J* = 1.4 Hz, 1H), 5.29 (d, *J* = 1.4 Hz, 1H), 3.75 (s, 3H).

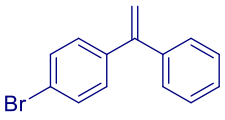
**1-Methoxy-2-(1-phenylvinyl)benzene (4i)**



Following the general procedure **GP3**, from (2-methoxyphenyl)(phenyl)methanone (3.0 mmol), compound **4i** was obtained as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9.5 : 0.5). Spectroscopic data were consistent with the literature data for this compound.[22]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.39 – 7.20 (m, 7H), 7.01 (td, *J* = 7.4, 1.2 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 5.75 (d, *J* = 1.5 Hz, 1H), 5.34 (d, *J* = 1.5 Hz, 1H), 3.66 (s, 3H).

**1-Bromo-4-(1-phenylvinyl)benzene (4j)**



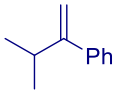
Following the general procedure **GP3**, from (4-bromophenyl)(phenyl)methanone (3.0 mmol), compound **4j** was obtained as colourless oil after purification by flash column chromatography (Cy : EtOAc = 9.5 : 0.5). Spectroscopic data were consistent with the literature data for this compound.[23]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.47 and 7.22 (AA'BB' system, 4H), 7.35 – 7.32 (m, 4H), 5.48 (d, *J* = 1.1 Hz, 1H), 5.46 (d, *J* = 1.1 Hz, 1H).

## 2.4. General procedure GP4 for the synthesis of **4l, 4m** and **4q**[24]

To a flame-dried round bottom flask provided with a magnetic stirrer, a solution of methyltriphenylphosphonium bromide (1.5 equiv) in diethyl ether (0.2 M) at 0 °C was treated dropwise with *n*-BuLi (1.4 equiv). The reaction mixture was stirred at 0 °C for 1 h before the corresponding ketone (4 mmol) was added dropwise. The reaction was then stirred at room temperature for 16 h. Distilled water was added, and the resulting mixture was extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (Cyclohexane) to afford the corresponding alkenes **4l, 4m and 4q**.

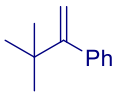
**(3-Methylbut-1-en-2-yl)benzene (4l)**




Following the general procedure **GP4**, from 2-methyl-1-phenylpropan-1-one (592.8 mg, 4.0 mmol), compound **4l** was obtained (376.3 mg, 64%) as colourless oil after purification by flash column chromatography (Cyclohexane). Spectroscopic data were consistent with the literature data for this compound.[24]

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 5.15 (s, 1H), 5.04 (s, 1H), 2.85 (p, *J* = 6.7 Hz, 1H), 1.11 (d, *J* = 6.8 Hz, 3H).

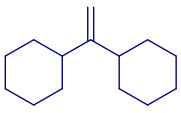
**(3,3-Dimethylbut-1-en-2-yl)benzene (4m)**




Following the general procedure **GP4**, from 2,2-dimethyl-1-phenylpropan-1-one (592.8 mg, 4.0 mmol), compound **4m** was obtained (384.6 mg, 60%) as a pale-yellow oil after purification by flash column chromatography (Cyclohexane). Spectroscopic data were consistent with the literature data for this compound.[25]

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.34 – 7.20 (m, 3H), 7.18 – 7.10 (m, 2H), 5.18 (d, *J* = 1.6 Hz, 1H), 4.77 (d, *J* = 1.7 Hz, 1H), 1.12 (s, 9H).

**Ethene-1,1-diyldicyclohexane (4q)**

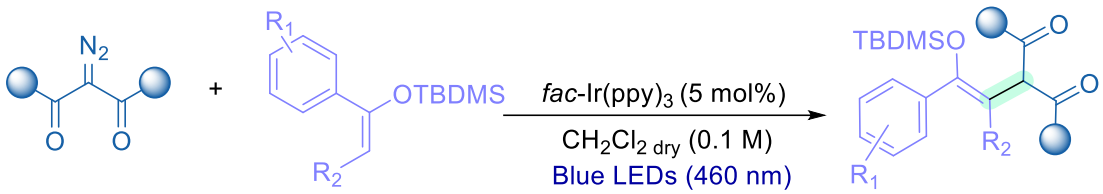


Following the general procedure **GP4**, from dicyclohexylmethanone (777.28 mg, 4 mmol), compound **4q** was obtained (436.6 mg, 57%) as colourless oil after purification by flash column chromatography (Cyclohexane). Spectroscopic data were consistent with the literature data for this compound.[26]

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 4.69 (s, 2H), 1.86 – 1.65 (m, 12H), 1.32 – 1.09 (m, 10H).

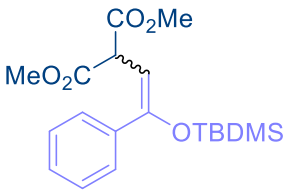
# 3. Synthesis and characterization of products 3, 5 and 6

## 3.1. General procedure GP5 for the TBDMS-Silyl-Enol Ethers **2** scope




In an oven-dried 6 mL vial, equipped with a magnetic stirring bar, was prepared a solution of diazo compound **1** (0.1 mmol), *tert*-butyldimethylsilane **2** (4.0 equiv.), and *fac*-$Ir(ppy)_3$ (5 mol%) in dry dichloromethane (0.1M). The vial was closed with a PTFE/rubber septum and pierced by a syringe. The reaction mixture was irradiated and stirred in the photoreactor setup at 460 nm for the time indicated in each case. After the reaction was complete, reaction mixture was concentrated under reduced pressure and the obtained crude purified by flash column chromatography to provide the products **3**.

**Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)-2-phenylvinyl)malonate (3aa)**



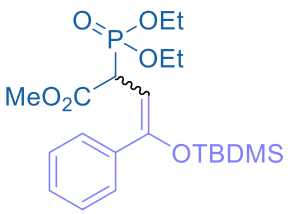

Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyldimethyl((1-phenylvinyl)oxy)silane (**2a**) (93.6 mg, 0.4 mmol), compound **3aa** was obtained as a 60:40 mixture of *Z*/*E* isomers after 1 hour reaction. Compound **3aa** was achieved in pure form (31.7 mg, 87% yield) as a pale-yellow solid after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

Major isomer (*Z*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.49 – 7.44 (m, 2H), 7.40 – 7.28 (m, 3H), 5.34 (d, *J* = 10.0 Hz, 1H), 4.64 (d, *J* = 10.0 Hz, 1H), 3.75 (s, 6H), 0.98 (s, 9H), -0.08 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.1, 153.7, 138.5, 128.7, 128.1, 126.8, 102.6, 52.8, 49.5, 25.9, 18.4, -4.0.

Minor isomer (*E*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.41 – 7.27 (m, 5H), 5.26 (d, *J* = 11.0 Hz, 1H), 4.17 (d, *J* = 11.0 Hz, 1H), 3.74 (s, 6H), 0.91 (s, 9H), 0.09 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.4, 155.0, 136.5, 128.8, 128.5, 128.3, 102.4, 52.8, 51.4, 25.8, 18.3, -4.5.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{19}H_{29}O_5Si$: 365.1784; found: 365.1788

**Methyl 4-((*tert*-butyldimethylsilyl)oxy)-2-(diethoxyphosphoryl)-4-phenylbut-3-enoate (3ba)**



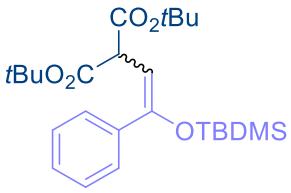

Following the general procedure **GP5**, from methyl 2-diazo-2-(diethoxyphosphoryl)acetate (**1b**) (23.6 mg, 0.1 mmol) and *tert*-butyldimethyl((1-phenylvinyl)oxy)silane (**2a**) (93.6 mg, 0.4 mmol), compound **3ba** was obtained as a 50:50 mixture of *Z*/*E* isomers after 6 hours reaction. Compound **3ba** was achieved in pure form (30.1 mg, 68% yield) as a white solid after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

Isomer (*Z*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.49 – 7.39 (m, 2H), 7.34 – 7.26 (m, 3H), 5.32 (dd, *J* = 10.7, 7.1 Hz, 1H), 4.32 (dd, *J* = 23.7, 10.6 Hz, 1H), 4.23 – 4.08 (m, 4H), 3.78 (s, 3H), 1.36 – 1.27 (m, 6H), 0.99 (s, 9H), -0.03 (s, 3H), -0.12 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.6 (d, *J* = 4.8 Hz), 153.2 (d, *J* = 13.3 Hz), 138.6 (d, *J* = 2.8 Hz), 128.7 (d, *J* = 8.0 Hz), 128.3, 128.1, 126.7, 100.7 (d, *J* = 10.7 Hz), 63.4 (d, *J* = 6.6 Hz), 63.0 (d, *J* = 6.3 Hz), 52.7, 44.1 (d, *J* = 133.2 Hz), 25.9, 18.4, 16.5 (d, *J* = 6.0 Hz), 16.5 (d, *J* = 6.6 Hz), -3.72, -4.32.

Isomer (*E*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.49 – 7.39 (m, 2H), 7.34 – 7.26 (m, 3H), 5.22 (dd, *J* = 11.6, 7.1 Hz, 1H), 4.16 – 4.03 (m, 4H), 3.90 (dd, *J* = 23.3, 11.6 Hz, 1H), 3.74 (s, 3H), 1.36 – 1.27 (m, 6H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.9 (d, *J* = 3.8 Hz), 136.6 (d, *J* = 2.6 Hz), 128.5, 128.4 (d, *J* = 7.8 Hz), 128.3, 126.7, 100.2 (d, *J* = 11.1 Hz), 63.2 (d, *J* = 6.7 Hz), 62.9 (d, *J* = 7.0 Hz), 45.6 (d, *J* = 134.5 Hz), 25.7, 18.2, -4.40, -4.50. The rest of the signals are overlapped with those of the *Z*-isomer.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{21}H_{36}O_6PSi$: 443.2013; found: 443.2015.

**Di-*tert*-butyl 2-(2-((*tert*-butyldimethylsilyl)oxy)-2-phenylvinyl)malonate (3ca)**

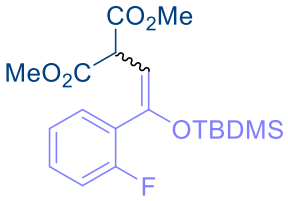



Following the general procedure **GP5**, from di-*tert*-butyl 2-diazomalonate (**1c**) (24.2 mg, 0.1 mmol) and *tert*-butyldimethyl((1-phenylvinyl)oxy)silane (**2a**) (93.6 mg, 0.4 mmol), compound **3ca** was obtained as a 45:55 mixture of *Z*/*E* isomers after 1 hour reaction. Compound **3ca** was achieved in pure form (25.8 mg, 58% yield) as a white solid after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Only **(*Z*)-4ca** could be separated in almost pure form after purification.

Major isomer (*Z*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.54 – 7.41 (m, 2H), 7.33 – 7.20 (m, 3H), 5.29 (d, *J* = 10.1 Hz, 1H), 4.38 (d, *J* = 10.1 Hz, 1H), 1.47 (s, 18H), 0.98 (s, 9H), -0.07 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.1, 153.0, 139.0, 128.4, 128.1, 126.8, 103.7, 81.6, 52.1, 28.1, 26.0, 18.4, -4.0.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{25}H_{41}O_5Si$: 449.2718; found: 449.2722.

**Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)-2-(2-fluorophenyl)vinyl)malonate (3ab)**



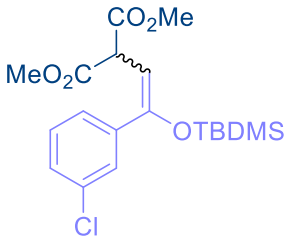

Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyl((1-(2-fluorophenyl)vinyl)oxy)dimethylsilane (**2b**) (100.8 mg, 0.4 mmol), compound **3ab** was obtained as a 63:37 mixture of *Z*/*E* isomers after 1 hour reaction. Compound **3ab** was achieved in pure form (35.5 mg, 93% yield) as a white solid after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

Major isomer (*Z*): **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.41 – 7.32 (m, 2H), 7.08 – 6.99 (m, 2H), 5.29 (dd, *J* = 9.8, 0.9 Hz, 1H), 4.68 (d, *J* = 9.8 Hz, 1H), 3.76 (s, 6H), 0.94 (s, 9H), -0.11 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.0, 161.5, 158.2, 148.2 (d, *J* = 1.0 Hz), 130.4 (d, *J* = 2.9 Hz), 130.3 (d, *J* = 8.2 Hz), 126.5 (d, *J* = 13.9 Hz), 123.8 (d, *J* = 3.8 Hz), 116.0 (d, *J* = 22.3 Hz), 105.7 (d, *J* = 3.3 Hz), 52.8, 49.3, 25.8, 18.3, -4.5. **$^{19}$F NMR** (282 MHz, $CDCl_3$): *δ* -113.4.

Minor isomer (*E*)*:* **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.41 – 7.32 (m, 2H), 7.08 – 6.99 (m, 2H), 5.38 (d, *J* = 10.8 Hz, 1H), 3.87 (dd, *J* = 10.8, 1.3 Hz, 1H), 3.72 (s, 6H), 0.89 (s, 9H), 0.10 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.1, 161.2, 157.9, 149.3, 131.0 (d, *J* = 3.3 Hz), 130.7 (d, *J* = 8.3 Hz), 124.5 (d, *J* = 15.9 Hz), 124.2 (d, *J* = 3.8 Hz), 116.1 (d, *J* = 22.0 Hz), 105.0, 51.5, 51.4, 25.7, 18.2, -4.6. **$^{19}$F NMR** (282 MHz, $CDCl_3$): *δ* -113.2.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{19}H_{28}FO_5Si$: 383.1685; found: 383.1689.

**Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)-2-(3-chlorophenyl)vinyl)malonate (3ac)**



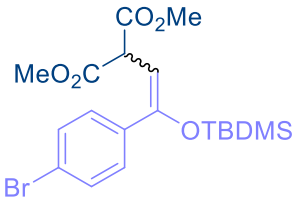

Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyl((1-(3-chlorophenyl)vinyl)oxy)dimethylsilane (**2c**) (107.2 mg, 0.4 mmol), compound **3ac** was obtained as a 34:66 mixture of *Z*/*E* isomers after 3 hours reaction. Compound **3ac** was achieved in pure form (35.0 mg, 88% yield) as a white solid after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

Major isomer (*E*)*:* **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.45 – 7.41 (m, 1H), 7.35 – 7.25 (m, 3H), 5.30 (d, *J* = 11.0 Hz, 1H), 4.13 (d, *J* = 11.0 Hz, 1H), 3.77 (s, 6H), 0.93 (s, 9H), 0.13 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.2, 153.6, 138.4, 134.3, 129.7, 129.0, 128.7, 126.7, 103.1, 52.9, 51.3, 25.7, 18.3, -4.5.

Minor isomer (*Z*): **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.50 – 7.47 (m, 1H), 7.40 – 7.35 (m, 1H), 7.35 – 7.25 (m, 2H), 5.40 (d, *J* = 10.0 Hz, 1H), 4.63 (d, *J* = 10.0 Hz, 1H), 3.78 (s, 6H), 1.00 (s, 9H), -0.04 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.9, 152.3, 140.3, 134.2, 129.5, 128.7, 126.9, 124.9, 103.7, 52.8, 49.5, 25.9, 18.4, -4.0.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{19}H_{28}ClO_5Si$: 399.1390; found: 399.1394.

**Dimethyl 2-(2-(4-bromophenyl)-2-((*tert*-butyldimethylsilyl)oxy)vinyl)malonate (3ad)**



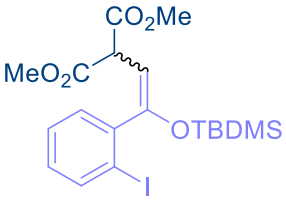

Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and ((1-(4-bromophenyl)vinyl)oxy)(*tert*-butyl)dimethylsilane (**2d**) (124.8 mg, 0.4 mmol), compound **3ad** was obtained as a 54:46 mixture of *Z*/*E* isomers after 1,5 hours reaction. Compound **3ad** was achieved in pure form (35.3 mg, 80% yield) as a white solid after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

Major isomer (*Z*): **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.44 and 7.34 (AA'BB' system, 4H), 5.34 (d, *J* = 10.0 Hz, 1H), 4.60 (d, *J* = 10.0 Hz, 1H), 3.75 (s, 6H), 0.98 (s, 9H), -0.07 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.0, 152.7, 137.6, 131.5, 128.4, 122.8, 103.4, 52.9, 49.6, 26.0, 18.5, -3.9.

Minor isomer (*E*)*:* **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.50 and 7.28 (AA'BB' system, 4H), 5.26 (d, *J* = 11.0 Hz, 1H), 4.09 (d, *J* = 11.0 Hz, 1H), 3.74 (s, 6H), 0.90 (s, 9H), 0.10 (s, 6H). ). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.3, 154.0, 135.6, 130.2, 128.4, 123.1, 103.0, 53.0, 51.4, 25.8, 18.4, -4.4.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{19}H_{28}BrO_5Si$: 443.0884; found: 443.0890, 445.0864.

**Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)-2-(2-iodophenyl)vinyl)malonate (3ae)**



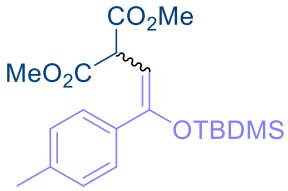

Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyl((1-(2-iodophenyl)vinyl)oxy)dimethylsilane (**2e**) (144 mg, 0.4 mmol), compound **3ae** was obtained as a 15:85 mixture of *Z*/*E* isomers after 1 hour reaction. Compound **3ae** was achieved in pure form (34.7 mg, 71% yield) as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

Major isomer (*E*): **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 4.4 Hz, 2H), 7.09 – 6.92 (m, 1H), 5.08 (d, *J* = 9.5 Hz, 1H), 4.66 (d, *J* = 9.5 Hz, 1H), 3.77 (s, 6H), 0.94 (s, 9H), -0.15 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.0, 154.4, 143.3, 139.76, 130.3, 130.1, 127.9, 104.6, 98.0, 52.7, 49.1, 25.8, 18.3, -4.2.

Minor isomer (*Z*)*:* **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 5.28 (d, *J* = 10.7 Hz, 1H), 3.72 (s, 6H), 0.90 (s, 9H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 156.1, 141.7, 139.82, 130.1, 128.1, 102.4, 97.8, 51.3, 25.7, -4.3. The rest of the signals are overlapped with those of the majority *E*-isomer.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{19}H_{28}IO_5Si$: 491.0746; found: 491.0746.

**Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)-2-(*p*-tolyl)vinyl)malonate (3af)**



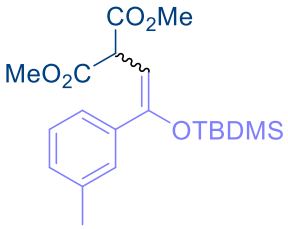

Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyldimethyl((1-(*p*-tolyl)vinyl)oxy)silane (**2f**) (99.3 mg, 0.4 mmol), compound **3af** was obtained as a 52:48 mixture of *Z*/*E* isomers after 1 hour reaction. Compound **3af** was achieved in pure form (13.6 mg, 36% yield) as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

*Z*-Isomer: **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.35 and 7.11 (AA'BB' system, 4H), 5.29 (d, *J* = 10.0 Hz, 1H), 4.63 (d, *J* = 10.0 Hz, 1H), 3.75 (s, 3H), 2.34 (s, 3H), 0.98 (s, 9H), -0.08 (s, 6H).**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.2, 153.7, 138.6, 135.7, 128.8, 126.8, 101.9, 52.7, 49.6, 26.0, 21.4, 18.5, -4.0.

*E*-isomer*:* **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.28 and 7.16 (AA'BB' system, 4H), 5.23 (d, *J* = 10.9 Hz, 1H), 4.17 (d, *J* = 11.0 Hz, 1H), 3.73 (s, 6H), 2.36 (s, 3H), 0.91 (s, 9H), 0.08 (s, 6H). (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.5, 155.1, 138.7, 133.7, 129.0, 128.5, 102.1, 52.8, 51.5, 25.8, 21.4, 18.3, -4.4.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{20}H_{31}O_5Si$: 379.1936; found: 379.1944.

**Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)-2-(*m*-tolyl)vinyl)malonate (3ag)**



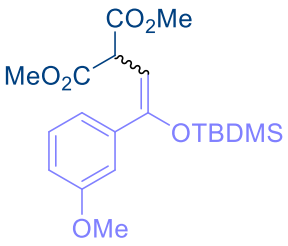

Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyldimethyl((1-(*m*-tolyl)vinyl)oxy)silane (**2g**) (99.3 mg, 0.4 mmol), compound **3ag** was obtained as a 64:36 mixture of *Z*/*E* isomers after 3 hours reaction. Compound **3ag** was achieved in pure form (20.4 mg, 54% yield) as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

Major isomer (*Z*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 1H), 7.22 – 7.14 (m, 2H), 7.14 – 7.08 (m, 1H), 5.33 (d, *J* = 10.0 Hz, 1H), 4.64 (d, *J* = 10.0 Hz, 1H), 3.75 (s, 6H), 2.34 (s, 3H), 0.98 (s, 9H), -0.08 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.2, 153.8, 138.4, 137.7, 129.4, 128.0, 127.5, 124.0, 102.3, 52.8, 49.5, 25.9, 21.5, 18.4, -4.0.

Minor isomer (*E*)*:* **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.27 – 7.23 (m, 1H), 7.26 – 7.12 (m, 3H), 5.24 (d, *J* = 11.0 Hz, 1H), 4.18 (d, *J* = 10.9 Hz, 1H), 3.74 (s, 6H), 2.36 (s, 3H), 0.91 (s, 9H), 0.09 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.5, 155.2, 137.9, 136.5, 129.6, 129.2, 128.2, 125.6, 102.2, 51.5, 25.8, 21.6, 18.3, -4.4. A signal is overlapped with those of the majority *Z*-isomer.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{20}H_{31}O_5Si$: 379.1936; found: 379.1932.

**Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)-2-(3-methoxyphenyl)vinyl)malonate (3ah)**



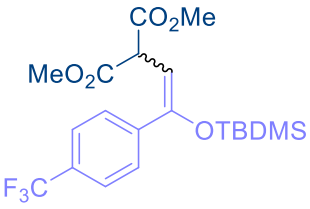

Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyl((1-(3-methoxyphenyl)vinyl)oxy)dimethylsilane (**2h**) (105.6 mg, 0.4 mmol), compound **3ah** was obtained as an 18:82 mixture of *Z*/*E* isomers after 3 hours reaction. Compound **3ah** was achieved in pure form (21.9 mg, 53% yield) as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

Major isomer (*E*)*:* **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.26 (t, *J* = 8.1 Hz, 1H), 7.02 – 6.96 (m, 2H), 6.88 (ddd, *J* = 8.4, 2.6, 1.0 Hz, 1H), 5.25 (d, *J* = 11.0 Hz, 1H), 4.22 (d, *J* = 11.0 Hz, 1H), 3.81 (s, 3H), 3.74 (s, 6H), 0.91 (s, 9H), 0.10 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.5, 159.5, 154.8, 137.8, 129.4, 120.9, 115.0, 113.7, 102.4, 55.4, 51.4, 25.8, 18.3, -4.5. A signal is overlapped with those of the majority *Z*-isomer.

Minor isomer (*Z*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.22 (ddd, *J* = 8.1, 7.6, 0.4 Hz, 1H), 7.06 (ddd, *J* = 7.6, 1.6, 1.0 Hz, 1H), 7.02 – 6.96 (m, 1H), 6.84 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 5.35 (d, *J* = 10.0 Hz, 1H), 4.63 (d, *J* = 10.0 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 6H), 0.98 (s, 8H), -0.06 (s, 6H).**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.1, 159.4, 153.5, 140.0, 129.2, 119.3, 114.6, 112.1, 102.7, 55.4, 52.8, 49.5, 25.9, 18.4, -4.0.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{20}H_{31}O_6Si$: 395.1885; found: 395.1891.

**Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)-2-(4-(trifluoromethyl)phenyl)vinyl) malonate (3ai)**



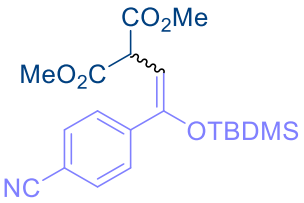

Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyldimethyl((1-(4-(trifluoromethyl)phenyl)vinyl)oxy)silane (**2i**) (120.9 mg, 0.4 mmol), compound **3ai** was obtained as a 50:50 mixture of *Z*/*E* isomers after 3 hours reaction. Compound **3ai** was achieved in pure form (34.0 mg, 79% yield) as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

*Z*-Isomer: **$^1$H NMR** (500 MHz, $CDCl_3$): δ 7.61 – 7.56 (m, 4H), 5.44 (d, *J* = 10.0 Hz, 1H), 4.63 (d, *J* = 10.0 Hz, 1H), 3.76 (s, 6H), 0.99 (s, 9H), -0.07 (s, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 168.8, 152.3, 142.0, 130.6 (q, *J* = 32.6 Hz), 126.9, 125.2 (q, *J* = 3.8 Hz), 124.2 (d, *J* = 271.6 Hz), 104.6, 52.9, 49.5, 25.8, 18.4, -4.0. **$^{19}$F NMR** (282 MHz, $CDCl_3$): -62.60.

*E*-isomer: **$^1$H NMR** (500 MHz, $CDCl_3$): δ 7.63 and 7.54 (AA'BB' system, 4H), 5.33 (d, *J* = 11.0 Hz, 1H), 4.08 (d, *J* = 11.1 Hz, 1H), 3.75 (s, 6H), 0.91 (s, 9H), 0.12 (s, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 169.1, 153.6, 140.1, 130.8 (q, *J* = 32.4 Hz), 128.8, 125.4 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.5 Hz), 103.5, 53.0, 51.2, 25.7, 18.3, -4.5. **$^{19}$F NMR** (282 MHz, $CDCl_3$): -62.73.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{20}H_{28}F_3O_5Si$: 433.1658; found: 433.1650.

**Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)-2-(4-cyanophenyl)vinyl)malonate (3aj)**



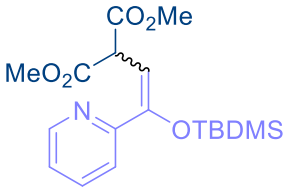

Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and 3-(1-((*tert*-butyldimethylsilyl)oxy)vinyl)benzonitrile (**2j**) (103.6 mg, 0.4 mmol), compound **3aj** was obtained as a 44:56 mixture of *Z*/*E* isomers after 2 hours reaction. Compound **3aj** was achieved in pure form (24.9 mg, 64% yield) as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

Major isomer (*E*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.67 and 7.54 (AA'BB' system, 4H), 5.35 (d, *J* = 11.1 Hz, 1H), 4.05 (d, *J* = 11.1 Hz, 1H), 3.75 (s, 6H), 0.90 (s, 9H), 0.12 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.8, 152.9, 140.9, 132.2, 129.0, 118.5, 112.5, 104.0, 52.9, 51.0, 25.6, 18.1, -4.6.

Minor isomer (*Z*)*:* **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.62 and 7.57 (AA'BB' system, 4H), 5.48 (d, *J* = 10.0 Hz, 1H), 4.61 (d, *J* = 10.0 Hz, 1H), 3.76 (s, 6H), 0.98 (s, 9H), -0.07 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.5, 151.7, 142.8, 132.0, 127.0, 118.6, 112.1, 105.5, 52.9, 49.3, 25.7, 18.3, -4.1.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{20}H_{28}NO_5Si$: 390.1731; found: 390.1737.

**Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)-2-(pyridin-2-yl)vinyl)malonate (3ak)**



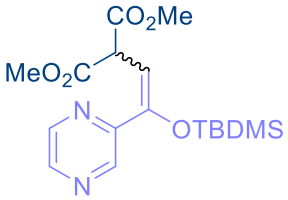

Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and 2-(1-((*tert*-butyldimethylsilyl)oxy)vinyl)pyridine (**2k**) (94.0 mg, 0.4 mmol), compound **3ak** was obtained as a 68:32 mixture of *Z*/*E* isomers after 1 hour reaction. Compound **3ak** was achieved in pure form (25.9 mg, 71% yield) as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

Major isomer (*Z*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.56 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.65 (td, *J* = 7.7, 1.8 Hz, 1H), 7.51 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.19 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 5.93 (d, *J* = 10.1 Hz, 1H), 4.71 (d, *J* = 10.1 Hz, 1H), 3.71 (s, 6H), 1.00 (s, 9H), 0.04 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.9, 155.1, 151.94, 152.1, 148.9, 136.3, 123.2, 120.9, 104.4, 52.9, 49.6, 26.0, 18.7, -3.6.

Minor isomer (*E*)*:* **$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.54 – 8.51 (m, 1H), 5.70 (d, *J* = 9.7 Hz, 1H), 5.45 (d, *J* = 9.7 Hz, 1H), 3.74 (s, 6H), 0.98 (s, 9H), 0.21 (s, 6H). The rest of the signals are overlapped with those of the majority *Z*-isomer. **$^{13}$C NMR** (75 MHz, $CDCl_3$): 169.8, 155.5, 150.4, 148.3, 136.4, 122.9, 122.0, 105.8, 52.7, 50.6, 25.9, 18.4, -4.4.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{18}H_{28}NO_5Si$: 366.1731; found: 366.1733.

**Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)-2-(pyrazin-2-yl)vinyl)malonate (3al)**




Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and 2-(1-((*tert*-butyldimethylsilyl)oxy)vinyl)pyrazine (**2l**) (94.4 mg, 0.4 mmol), compound **3al** was obtained as a 62:38 mixture of *Z*/*E* isomers after 2 hours reaction. Compound **3al** was achieved in pure form (30.0 mg, 82% yield) as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

**Reaction in large scale:**

Alternatively, from dimethyl 2-diazomalonate (**1a**) (158.1 mg, 1.0 mmol) and 2-(1-((*tert*-butyldimethylsilyl)oxy)vinyl)pyrazine (**2l**) (945.6 mg, 4.0 mmol), compound **3al** was obtained as a 70:30 mixture of *Z/E* isomers after 5 hours reaction after irradiation with two Kessil® LED PhotoReaction Lightning PR160L (455 nm, 100% intensity, 3.0 cm distance) and refrigerated with cooling fans (Figure S3). Compound **3al** was achieved in pure form (256.0 mg, 70% yield) as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

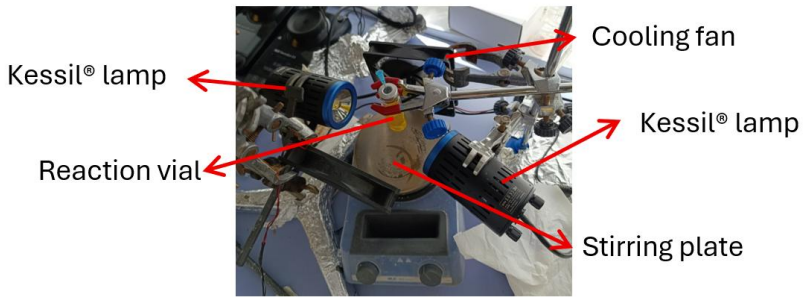


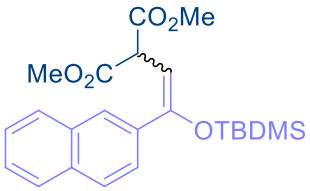

**Figure S3.** 1.0 mmol scale-up setup employed during photocatalytic reactions.

Major isomer (*Z*): **$^1$H NMR** (500 MHz, $CDCl_3$): δ 8.80 (brs, 1H), 8.52 – 8.50 (m, 1H), 8.50 – 8.46 (m, 1H), 6.05 (d, *J* = 10.1 Hz, 1H), 4.69 (d, *J* = 10.1 Hz, 1H), 3.76 (s, 6H), 1.01 (s, 9H), 0.05 (s, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 168.5, 150.6, 149.7, 143.9, 143.5, 142.4, 106.6, 53.0, 49.5, 25.9, 18.6, -3.7.

Minor isomer (*E*): **$^1$H NMR** (500 MHz, $CDCl_3$): δ 8.90 (brs, 1H), 8.50 – 8.46 (m, 2H), 5.59 (d, *J* = 9.9 Hz, 1H), 5.55 (d, *J* = 9.9 Hz, 1H), 3.74 (s, 6H), 0.99 (s, 9H), 0.24 (s, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 169.3, 150.9, 148.4, 143.8, 143.6, 142.7, 107.9, 52.9, 50.3, 25.9, 18.3, -4.4.

**HRMS (ESI) m/z:** $[M+H]^+$ Calculated for $C_{17}H_{27}N_2O_5Si$ 367.1684; found: 367.1688.

**Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)-2-(naphthalen-2-yl)vinyl)malonate (3am)**



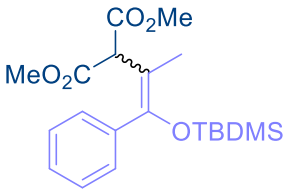

Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyldimethyl((1-(naphthalen-2-yl)vinyl)oxy)silane (**2m**) (113.6 mg, 0.4 mmol), compound **3am** was obtained as a 34:66 mixture of *Z*/*E* isomers after 3 hours reaction. Compound **3am** was achieved in pure form (23.2 mg, 56% yield) as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

Major isomer (*E*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.88 (d, *J* = 1.8 Hz, 1H), 7.83 – 7.74 (m, 3H), 7.54 – 7.45 (m, 3H), 5.35 (d, *J* = 11.0 Hz, 1H), 4.25 (d, *J* = 11.0 Hz, 1H), 3.76 (s, 6H), 0.92 (s, 9H), 0.11 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.5, 155.0, 133.9, 133.4, 132.9, 128.6, 128.1, 127.9, 126.7, 126.5, 126.1, 102.9, 52.83, 51.5, 25.8, 18.3, -4.4.

Minor isomer (*Z*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.94 (d, *J* = 1.7 Hz, 1H), 7.83 – 7.74 (m, 3H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.59 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.54 – 7.45 (m, 2H), 5.50 (d, *J* = 10.0 Hz, 1H), 4.71 (d, *J* = 10.0 Hz, 1H), 3.78 (s, 6H), 1.02 (s, 9H), -0.06 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.2, 153.6, 135.8, 133.5, 133.1, 128.4, 127.81, 127.78, 126.5, 125.9, 124.7, 103.2, 52.85, 49.6, 26.0, 18.5, -3.9.

**HRMS (ESI):** Calculated for $C_{23}H_{31}O_5Si$ $[M + H]^+$: 415.1936, found 415.1942.

**Dimethyl 2-(1-((*tert*-butyldimethylsilyl)oxy)-1-phenylprop-1-en-2-yl)malonate (3an)**



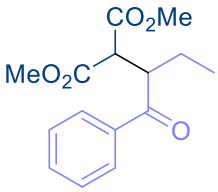

Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyldimethyl((1-phenylprop-1-en-1-yl)oxy)silane (**2n**) (99.3 mg, 0.4 mmol), compound **3an** was obtained as a 25:75 mixture of *Z*/*E* isomers after 1 hour reaction. Compound **3an** was achieved in pure form (20.8 mg, 55% yield) as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

Mayor isomer (*E*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.35 – 7.27 (m, 5H), 5.06 (s, 1H), 3.77 (s, 6H), 1.67 (s, 3H), 0.89 (s, 9H), -0.24 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.6, 148.8, 137.70, 129.6, 128.5, 128.3, 108.3, 52.8, 52.0, 25.8, 18.3, 14.9, -4.3.

Minor isomer (*Z*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.35 – 7.27 (m, 5H), 4.26 (s, 1H), 3.71 (s, 6H), 1.88 (s, 3H), 0.88 (s, 9H), -0.19 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.5, 150.5, 137.72, 129.3, 128.4, 128.0, 109.7, 52.5, 52.4, 25.8, 18.4, 13.2, -4.2.

**HRMS (ESI):** Calculated for $C_{20}H_{31}O_5Si$ $[M + H]^+$: 379.1941, found 379.1944.

**Dimethyl 2-(1-oxo-1-phenylbutan-2-yl)malonate (3ao')**

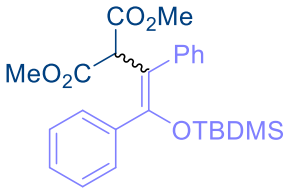



Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyldimethyl((1-phenylbut-1-en-1-yl)oxy)silane (**2o**) (104.8 mg, 0.4 mmol) compound **3ao** was obtained after 1 hour reaction. In this special case, detection of ketone derivative was observed in the reaction media. Thus, the crude was treated with TBAF (56 mg, 0.2 mmol, 2 equiv.) for 6 h, the reaction was quenched with water and extracted with dichloromethane, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. Compound **3ao'** was obtained (17.3 mg, 62% yield) as a white solid after purification by flash column chromatography (Cy : EtOAc = 8 : 2).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.05 – 7.96 (m, 2H), 7.62 – 7.53 (m, 2H), 7.53 – 7.44 (m, 2H), 4.23 (ddd, *J* = 11.1, 6.6, 4.6 Hz, 1H), 4.11 (d, *J* = 11.0 Hz, 1H), 3.80 (s, 3H), 3.64 (s, 3H), 1.80 – 1.57 (m, 2H), 0.79 (t, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 201.6, 169.3, 169.0, 137.0, 133.3, 128.8, 128.6, 53.1, 52.8, 46.3, 23.6, 10.3.

**HRMS (ESI):** Calculated for $C_{15}H_{19}O_5Si$ $[M + H]^+$: 279.1227, found 279.1233.

**Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)-1,2-diphenylvinyl)malonate (3ap)**




Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyl((1,2-diphenylvinyl)oxy)dimethylsilane (**2p**) (124.1 mg, 0.4 mmol), compound **3ap** was obtained as a 38:62 mixture of *Z*/*E* isomers after 1 hour reaction. Compound **3ap** was achieved in pure form (20.8 mg, 52% yield) as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

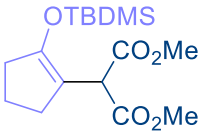
Major isomer (*E*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.47 – 7.00 (m, 10H), 4.40 (s, 1H), 3.58 (s, 6H), 0.54 (s, 9H), -0.37 (s, 6H).

Minor isomer (*Z*): **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.47 – 7.00 (m, 10H), 5.24 (s, 1H), 3.60 (s, 6H), 0.93 (s, 9H), -0.19 (s, 6H).

Isomer mixture: **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 169.5, 169.5, 152.2, 151.6, 137.7, 137.6, 137.5, 137.2, 131.4, 130.9, 130.2, 129.1, 128.8, 128.5, 128.0, 127.7, 127.6, 127.5, 126.9, 126.5, 115.2, 115.1, 56.1, 53.9, 52.4, 52.3, 25.8, 25.3, 18.3, 18.0, -4.0, -4.5.

**HRMS (ESI):** Calculated for $C_{25}H_{35}O_5Si$ $[M + H]^+$: 441.2097, found 441.2097.

**(*Z*)-Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)cyclopent-1-en-1-yl)malonate (3aq)**

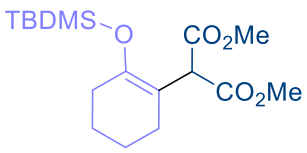



Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyl(cyclopent-1-en-1-yloxy)dimethylsilane (**2q**) (79.2 mg, 0.4 mmol), compound **3aq** was obtained after 1 hour reaction (22.3 mg, 68% yield) as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 4.57 (s, 1H), 3.72 (s, 6H), 2.46 – 2.27 (m, 4H), 1.93 – 1.81 (m, 2H), 0.93 (s, 9H), 0.13 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.0, 152.6, 108.3, 52.4, 49.4, 33.5, 28.7, 25.7, 20.0, 18.2, -3.9.

**HRMS (ESI):** Calculated for $C_{16}H_{29}O_5Si$ $[M + H]^+$: 329.1784, found 329.1787.

**(*Z*)-Dimethyl 2-(2-((*tert*-butyldimethylsilyl)oxy)cyclohex-1-en-1-yl)malonate (3ar)**

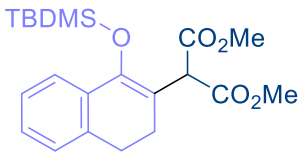



Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyl(cyclohex-1-en-1-yloxy)dimethylsilane (**2r**) (84.9 mg, 0.4 mmol), compound **3ar** was obtained after 1 hour reaction (25 mg, 73% yield) as a colourless oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 4.90 (s, 1H), 3.71 (s, 6H), 2.16 – 2.05 (m, 4H), 1.75 – 1.63 (m, 2H), 1.62 – 1.52 (m, 2H), 0.92 (s, 9H), 0.12 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.6, 148.5, 108.2, 52.3, 51.1, 30.5, 25.9, 25.0, 23.3, 22.7, 18.3, -3.6.

**HRMS (ESI):** Calculated for $C_{17}H_{31}O_5Si$ $[M + H]^+$: 343.1941, found 343.1946.

**(*Z*)-Dimethyl 2-(1-((*tert*-butyldimethylsilyl)oxy)-3,4-dihydronaphthalen-2-yl)malonate (3as)**

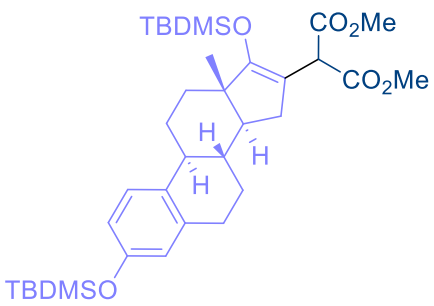



Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and *tert*-butyl((3,4-dihydronaphthalen-1-yl)oxy)dimethylsilane (**2s**) (104.1 mg, 0.4 mmol), compound **3as** was obtained after 1,5 hours reaction (25.8 mg, 66% yield) as a white solid after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.44 – 7.33 (m, 1H), 7.22 – 7.07 (m, 3H), 4.97 (s, 1H), 3.74 (s, 6H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.39 (dd, *J* = 8.7, 6.4 Hz, 2H), 1.05 (s, 9H), 0.02 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.1, 146.7, 137.4, 133.3, 127.7, 126.9, 125.9, 123.3, 112.6, 52.6, 51.6, 28.5, 26.1, 24.6, 18.6, -3.9.

**HRMS (ESI):** Calculated for $C_{21}H_{31}O_5Si$ $[M + H]^+$: 391.1941, found 391.1943.

**(*Z*)-Dimethyl2-((8*R*,9*S*,13*S*,14*S*)-3,17-bis((*tert*-butyldimethylsilyl)oxy)-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-16-yl)malonate (3at)**

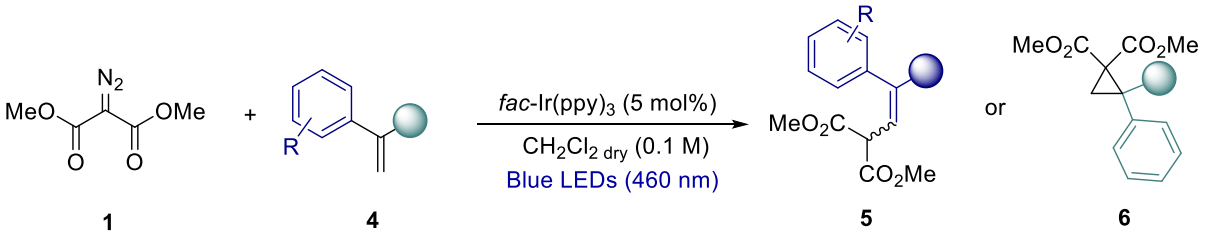



Following the general procedure **GP5**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and (((8*R*,9*S*,13*S*,14*S*)-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthrene-3,17-diyl)bis(oxy))bis(*tert*-butyldimethylsilane) (**2u**) (199.3 mg, 0.4 mmol), compound **3at** was obtained after 1 hour reaction (27 mg, 43% yield) as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.09 (d, *J* = 8.5 Hz, 1H), 6.61 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.56 (d, *J* = 2.7 Hz, 1H), 4.52 (s, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 2.87 – 2.77 (m, 2H), 2.37 – 2.23 (m, 3H), 2.04 (dd, *J* = 13.8, 10.7 Hz, 1H), 1.97 – 1.85 (m, 1H), 1.82 (dd, *J* = 8.0, 2.2 Hz, 1H), 1.68 – 1.34 (m, 5H), 0.98 (s, 18H), 0,91 (s, 3H), 0.19 (s, 6H), 0.18 (s, 3H), 0.18 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.2, 168.7, 162.3, 153.4, 138.0, 133.3, 125.7, 120.0, 117.1, 107.6, 52.4, 52.4, 52.2, 49.5, 45.7, 44.3, 37.0, 34.1, 29.5, 29.0, 27.0, 26.2, 25.9, 25.7, 18.5, 18.2, 15.3, -3.6, -3.6, -4.4.

**HRMS (ESI):** Calculated for $C_{35}H_{57}O_6Si$ $[M + H]^+$: 629.3689, found 629.3689.

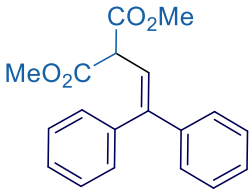
## 3.2. General procedure GP6 for 1,1-diarylalkenes **4** scope




**1** **4** **5** **6**

In an oven-dried 6 mL vial, equipped with a magnetic stirring bar, was prepared a solution of diazo compound **1a** (0.1 mmol), diarylalkene **4** (4.0 equiv.), and *fac*-Ir(ppy)$_3$ (5 mol%) in dry dichloromethane (0.1M). The vial was closed with a PTFE/rubber septum and pierced by a syringe. The reaction mixture was irradiated and stirred in the photoreactor setup at 460 nm for 1 hour. After the reaction was complete, reaction mixture was concentrated under reduced pressure and purified by flash column chromatography to provide the products **5** or **6**.

**Dimethyl 2-(2,2-diphenylvinyl) malonate (5aa)**

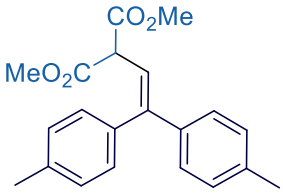


Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and ethene-1,1-diyldibenzene (**4a**) (72 mg, 0.4 mmol), compound **5aa** was obtained after 1 hour reaction (21.7 mg, 70% yield) as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 8 : 2).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.44 – 7.34 (m, 4H), 7.28 (br s, 4H), 7.22 – 7.16 (m, 2H), 6.32 (d, *J* = 10.5 Hz, 1H), 4.23 (d, *J* = 10.4 Hz, 1H), 3.75 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.8, 146.9, 141.4, 138.6, 129.9, 128.6, 128.4, 128.1, 128.0, 127.8, 119.6, 52.9, 52.8.

**HRMS (ESI):** Calculated for $C_{19}H_{19}O_4$ $[M + H]^+$: 311.1278; found: 311.1272.

**Dimethyl 2-(2,2-di-*p*-tolylvinyl)malonate (5ab)**

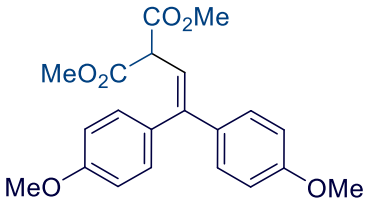


Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and 4,4'-(ethene-1,1-diyl)bis(methylbenzene) (**4b**) (83.2 mg, 0.4 mmol), compound **5ab** was obtained after 1 hour reaction (11.2 mg, 33% yield) as a yellowish solid after purification by flash column chromatography (Cy : EtOAc = 8 : 2).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.22 – 7.14 (m, 4H), 7.11 – 7.05 (m, 4H), 6.25 (d, *J* = 10.4 Hz, 1H), 4.24 (d, *J* = 10.5 Hz, 1H), 3.74 (s, 6H), 2.39 (s, 3H), 2.33 (s, 3H).**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.0, 146.8, 138.8, 137.9, 137.6, 135.7, 129.8, 129.3, 129.0, 127.7, 118.5, 52.9, 52.8, 21.4, 21.2.

**HRMS (ESI):** Calculated for $C_{21}H_{23}O_4$ $[M + H]^+$: 339.1591; found: 339.1599.

**Dimethyl 2-(2,2-bis(4-methoxyphenyl)vinyl)malonate (5ac)**

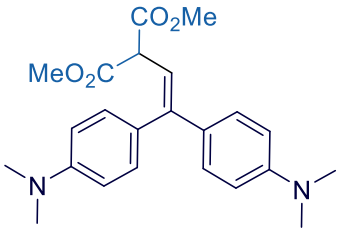


Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and 4,4'-(ethene-1,1-diyl)bis(methoxybenzene) (**4c**) (96 mg, 0.4 mmol), compound **5ac** was obtained after 1 hour reaction (34.4 mg, 93% yield) as a yellowish solid after purification by flash column chromatography (Cy : EtOAc = 8 : 2).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.21 and 6.81 (AA'BB' system, 4H), 7.12 and 6.92 (AA'BB' system, 4H), 6.18 (d, *J* = 10.4 Hz, 1H), 4.25 (d, *J* = 10.4 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.75 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.1, 159.6, 159.3, 146.1, 134.4, 131.1, 131.0, 129.1, 117.5, 114.0, 113.7, 55.4, 55.4, 52.9.

**HRMS (ESI):** Calculated for $C_{21}H_{23}O_6$ $[M + H]^+$: 371.1490; found: 371.1496.

**Dimethyl 2-(2,2-bis(4-(dimethylamino)phenyl)vinyl)malonate (5ad)**

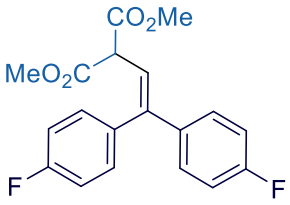


Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and 4,4'-(ethene-1,1-diyl)bis(*N,N*-dimethylaniline) (**4d**) (106.5 mg, 0.4 mmol), compound **5ad** was obtained after 1 hour reaction (22.6 mg, 57% yield) as a greenish solid after purification by flash column chromatography (Cy : EtOAc = 8 : 2).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.18 (d, *J* = 9.0 Hz, 2H), 7.08 (d, *J* = 8.9 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 6.06 (d, *J* = 10.4 Hz, 1H), 4.33 (d, *J* = 10.5 Hz, 1H), 3.74 (s, 6H), 2.98 (s, 6H), 2.94 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.5, 150.3, 150.0, 146.8, 130.9, 130.5, 128.9, 126.9, 115.0, 112.1, 112.0, 53.0, 52.8, 40.6.

**HRMS (ESI):** Calculated for $C_{23}H_{29}N_2O_4$ $[M + H]^+$: 397.2127, found 397.2124.

**Dimethyl 2-(2,2-bis(4-fluorophenyl)vinyl)malonate (5ae)**

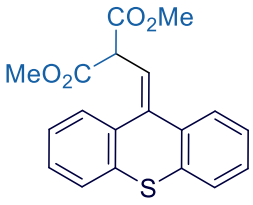


Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and 4,4'-(ethene-1,1-diyl)bis(fluorobenzene) (**4e**) (86.4 mg, 0.4 mmol), compound **5ae** was obtained after 1 hour reaction (8 mg, 23% yield) as a pale-yellow oil after purification by flash column chromatography (Cy : EtOAc = 8 : 2).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.25 – 7.13 (m, 4H), 7.11 and 7.08 (AA'BB' system, 2H), 6.99 and 6.96 (AA'BB' system, 2H), 6.26 (d, *J* = 10.4 Hz, 1H), 4.17 (d, *J* = 10.5 Hz, 1H), 3.76 (s, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.6, 162.9 (d, *J* = 248.1 Hz), 162.6 (d, *J* = 247.7 Hz), 145.0, 137.4 (d, *J* = 3.2 Hz), 134.2 (d, *J* = 3.5 Hz), 131.6 (d, *J* = 8.1 Hz), 129.5 (d, *J* = 8.2 Hz), 119.9, 115.8 (d, *J* = 21.5 Hz), 115.3 (d, *J* = 21.5 Hz), 53.0, 52.7. **$^{19}$F NMR** (282 MHz, CDCl3) δ -113.56, -113.91.

**HRMS (ESI):** Calculated for $C_{19}H_{17}F_2O_4$ $[M + H]^+$: 347.1090, found 347.1086.

**Dimethyl 2-((9*H*-thioxanthen-9-ylidene)methyl)malonate (5af)**

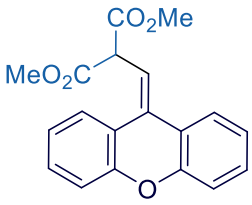


Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and 9-methylene-9*H*-thioxanthene (**4f**) (84 mg, 0.4 mmol), compound **5af** was obtained after 1 hour reaction (27.8 mg, 82% yield) as a yellow oil after purification by flash column chromatography (Cy : EtOAc = 8 : 2).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.56 – 7.49 (m, 2H), 7.48 – 7.43 (m, 1H), 7.40 – 7.34 (m, 1H), 7.33 – 7.19 (m, 4H), 6.09 (d, *J* = 10.8 Hz, 1H), 4.60 (d, *J* = 10.8 Hz, 1H), 3.77 (s, 6H).**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ 168.1, 140.4, 137.3, 134.1, 132.1, 132.0, 128.4, 128.0, 127.6, 127.2, 127.1, 126.6, 126.2, 125.9, 121.5, 53.2, 52.4.

**HRMS (ESI):** Calculated for $C_{19}H_{17}O_4S$ [M + H]$^+$: 341.0843, found 341.0850.

**Dimethyl 2-((9*H*-xanthen-9-ylidene)methyl)malonate (5ag)**

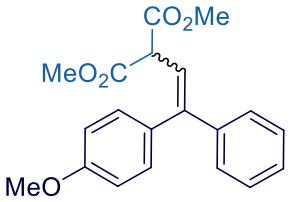



Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and 9-methylene-9*H*-xanthene (**4g**) (77.6 mg, 0.4 mmol), compound **5ag** was obtained after 1 hour reaction (21.7 mg, 67% yield) as a yellow oil after purification by flash column chromatography (Cy : EtOAc = 8 : 2).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.64 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.41 – 7.27 (m, 2H), 7.24 – 7.12 (m, 4H), 6.10 (d, *J* = 10.7 Hz, 1H), 4.80 (d, *J* = 10.6 Hz, 1H), 3.81 (s, 6H).**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.8, 153.1, 151.5, 131.6, 129.8, 129.2, 127.4, 124.8, 124.3, 124.1, 123.5, 121.1, 117.2, 116.6, 115.6, 53.2, 52.1.

**HRMS (ESI):** Calculated for $C_{19}H_{17}O_5$ [M + H]$^+$: 325.1071, found 325.1071.

**Dimethyl 2-(2-(4-methoxyphenyl)-2-phenylvinyl)malonate (5ah)**




Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and 1-methoxy-4-(1-phenylvinyl)benzene (**4h**) (84 mg, 0.4 mmol), compound **5ah** was obtained as a 70:30 mixture of two isomers after 1 hour reaction. Compound **5ah** was achieved in pure form (16.0 mg, 47% yield) as a yellow solid after purification by flash column chromatography (Cy : EtOAc = 8 : 2).

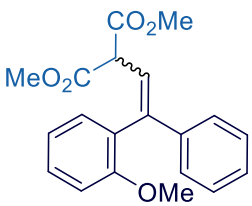
Major isomer: **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.28 (s, 5H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.26 (d, *J* = 10.5 Hz, 1H), 4.28 (d, *J* = 10.4 Hz, 1H), 3.84 (s, 3H), 3.75 (s, 6H).

Minor isomer: **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.41 – 7.35 (m, 3H), 7.23 – 7.16 (m, 4H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.23 (d, *J* = 10.4 Hz, 1H), 4.19 (d, *J* = 10.4 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 6H).

Isomers mixture: **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.1, 169.0, 159.8, 159.5, 146.7, 146.5, 141.9, 138.9, 134.1, 131.5, 131.3, 130.9, 130.3, 130.0, 130.0, 129.10 128.7, 128.4, 128.2, 128.0, 126.84, 119.4, 117.8, 114.1, 113.8, 55.55, 55.52, 53.1, 53.02, 52.97, 52.9.

**HRMS (ESI):** Calculated for $C_{20}H_{21}O_5$ [M + H]$^+$: 341.1384, found 341.1388.

**Dimethyl 2-(2-(2-methoxyphenyl)-2-phenylvinyl)malonate (5ai)**




Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and 1-methoxy-2-(1-phenylvinyl)benzene (**4i**) (84 mg, 0.4 mmol), compound **5ai** was obtained, after 1 hour reaction, as a 67:33 mixture of two isomeric olefins together with the corresponding cyclopropane in a ratio 15:85. Major isomeric olefin was only achieved in pure form (3.0 mg, 9% yield) as a yellow solid after purification by flash column

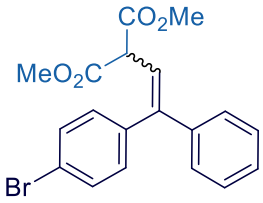
chromatography (Cy : EtOAc = 8 : 2). Low conversion was achieved due to the formation, mainly, of the corresponding cyclopropane derivative.

Major isomer: **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.33 – 7.27 (m, 3H), 7.25 – 7.18 (m, 4H), 6.96 – 6.89 (m, 1H), 6.83 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.17 (d, *J* = 10.6 Hz, 1H), 4.37 (d, *J* = 10.6 Hz, 1H), 3.75 (s, 6H), 3.57 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.9, 157.4, 144.8, 139.6, 132.0, 131.2, 129.3, 129.1, 128.1, 127.4, 122.0, 120.7, 112.0, 55.8, 52.9, 52.4.

**HRMS (ESI):** Calculated for $C_{20}H_{21}O_5$ $[M + H]^+$: 341.1384, found 341.1386.

Minor isomer: **$^1$H NMR** (300 MHz, CDCl3) δ 7.48 – 7.29 (m, 4H), 7.12 – 6.86 (m, 5H), 6.43 (d, *J* = 10.2 Hz, 1H), 4.05 (d, *J* = 10.2 Hz, 1H), 3.73 (s, 6H), 3.67 (s, 3H).

**Dimethyl 2-(2-(4-bromophenyl)-2-phenylvinyl)malonate (5aj)**

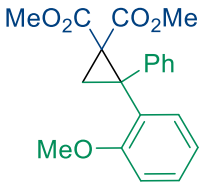



Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and 1-bromo-4-(1-phenylvinyl)benzene (**4j**) (103.2 mg, 0.4 mmol), compound **5aj** was obtained was obtained, after 1 hour reaction, as a mixture of two isomeric olefins together with the corresponding cyclopropane in a ratio 13:87. Compound **5aj** was achieved in pure form (4.5 mg, 12% yield) as a yellow oil after purification by flash column chromatography (Cy : EtOAc = 8 : 2). Low conversion was achieved due to the formation, mainly, of the corresponding cyclopropane derivative.

Isomers mixture: **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.58 – 7.49 (m, 2H), 7.46 – 7.32 (m, 7H), 7.33 – 7.25 (m, 2H), 7.21 – 7.00 (m, 7H), 6.33 (d, *J* = 10.5 Hz, 1H, one isomer), 6.31 (d, *J* = 10.4 Hz, 1H, one isomer), 4.21 (d, *J* = 10.6 Hz, 1H, one isomer), 4.18 (d, *J* = 10.2 Hz, 1H, one isomer), 3.75 (s, 3H, one isomer), 3.75 (s, 3H, one isomer). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.6, 168.6, 146.0, 140.4, 138.1, 131.9, 131.8, 131.6, 131.5, 129.8, 129.4, 129.1, 128.9, 128.8, 128.5, 128.4, 128.3, 127.8, 122.3, 120.2, 52.9, 52.8.

**HRMS (ESI):** Calculated for $C_{19}H_{18}BrO_4$ $[M + H]^+$: 389.0383, 391.0363, found 389.0388, 391.0388.

**Dimethyl 2-(2-methoxyphenyl)-2-phenylcyclopropane-1,1-dicarboxylate (6ai)**



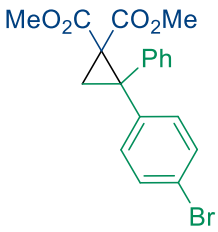

Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a)** (15.8 mg, 0.1 mmol) and 1-methoxy-2-(1-phenylvinyl)benzene (**4i**) (84 mg, 0.4 mmol), compound **6ai** was obtained, after 1 hour reaction, together with the corresponding mixture of isomeric olefins in a ratio 85:15. Compound **6ai** was achieved in pure form (21 mg, 62% yield) as a yellow oil after purification by flash column chromatography (Cy : EtOAc = 8 : 2).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.53 – 7.45 (m, 2H), 7.36 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.23 – 7.09 (m, 4H), 6.88 (td, *J* = 7.5, 1.1 Hz, 1H), 6.80 (dd, *J* = 8.3, 1.2 Hz, 1H), 3.85 (s, 3H), 3.54 (s, 3H),

3.38 (s, 3H), 2.61 (d, *J* = 5.3 Hz, 1H), 2.23 (d, *J* = 5.2 Hz, 1H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.8, 167.9, 157.4, 140.4, 130.6, 129.5, 129.0, 128.5, 128.1, 127.2, 120.7, 110.8, 55.2, 52.2, 52.2, 43.4, 41.0, 25.5.

**HRMS (ESI):** Calculated for $C_{20}H_{21}O_5$ $[M + H]^+$: 341.1384, found 341.1388.

**Dimethyl 2-(4-bromophenyl)-2-phenylcyclopropane-1,1-dicarboxylate (6aj)**

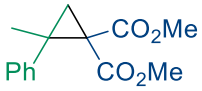



Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and 1-bromo-4-(1-phenylvinyl)benzene (**4j**) (103.2 mg, 0.4 mmol), compound **6aj** was obtained, after 1 hour reaction, together with the corresponding mixture of isomeric olefins in a ratio 87:13. Compound **6aj** was achieved in pure form (26.8 mg, 69% yield) as a yellow oil after purification by flash column chromatography (Cy : EtOAc = 8 : 2).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.37 – 7.30 (m, 2H), 7.28 – 7.10 (m, 3H), 3.45 (s, 1H), 3.39 (s, 1H), 2.45 (dd, *J* = 5.4, 0.7 Hz, 1H), 2.38 (dd, *J* = 5.4, 0.7 Hz, 1H).**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 167.6, 167.4, 139.9, 139.6, 131.6, 130.6, 128.8, 128.6, 127.6, 121.5, 52.6, 52.5, 46.5, 41.4, 23.7.

**HRMS (ESI):** Calculated for $C_{19}H_{18}BrO_4$ $[M + H]^+$: 389.0388, found 389.0381.

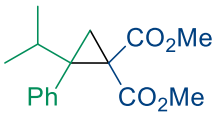
**Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (6ak)**




Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and prop-1-en-2-ylbenzene (**4k**) (52.0 µL, 0.4 mmol), compound **6ak** was obtained, after 1 hour reaction, as a yellow oil (16.3 mg, 66% yield) after purification by flash column chromatography (Cy : EtOAc = 9 : 1). Spectroscopic data were consistent with the literature data for this compound.[27]

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 7.30 – 7.25 (m, 4H), 7.25 – 7.20 (m, 1H), 3.83 (s, 3H), 3.33 (s, 3H), 2.22 (d, *J* = 5.2 Hz, 1H), 1.70 (d, *J* = 5.2 Hz, 1H), 1.52 (s, 3H).

**Dimethyl 2-isopropyl-2-phenylcyclopropane-1,1-dicarboxylate (6al)**

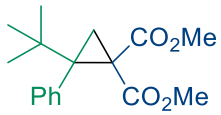



Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and (3-methylbut-1-en-2-yl)benzene (**4l**) (58.5 mg, 0.4 mmol), compound **6al** was obtained, after 1 hour reaction, as a yellow oil (16.6 mg, 60% yield) after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 7.28 – 7.22 (m, 3H), 7.22 – 7.17 (m, 2H), 3.83 (s, 3H), 3.34 (s, 3H), 2.07 (d, *J* = 5.0 Hz, 1H), 1.68 (d, *J* = 4.9 Hz, 1H), 1.55 (p, *J* = 6.8 Hz, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 168.9, 168.2, 136.1, 131.1, 127.2, 52.7, 52.2, 47.8, 41.5, 34.3, 25.3, 20.6, 19.4.

**HRMS (ESI):** Calculated for $C_{16}H_{20}O_4$ $[M + H]^+$: 277.1362, found. 277.1375.

**Dimethyl 2-(tert-butyl)-2-phenylcyclopropane-1,1-dicarboxylate (6am)**

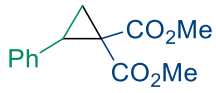



Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and (3,3-dimethylbut-1-en-2-yl)benzene (**4m**) (64.1 mg, 0.4 mmol), compound **6am** was obtained, after 1 hour reaction, as a yellow oil (11.6 mg, 40% yield) after purification by flash column chromatography (Cy : EtOAc = 9 : 1).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.30 – 7.22 (m, 3H), 7.22 – 7.16 (m, 2H), 3.80 (s, 3H), 3.28 (s, 3H), 1.99 (d, *J* = 5.7 Hz, 1H), 1.88 (d, *J* = 5.7 Hz, 1H), 0.94 (s, 9H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 169.0, 168.5, 140.0, 131.4, 131.2, 127.6, 126.8, 52.7, 52.6, 49.5, 40.5, 34.9, 28.2, 19.9.

**HRMS (ESI):** Calculated for $C_{17}H_{23}O_4$ $[M + H]^+$: 291.1591, found. 291.1598.

**Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (6an)**

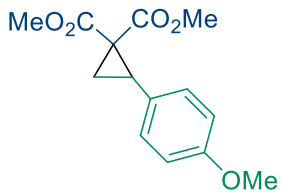



Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and styrene (**4n**) (41.6 mg, 0.4 mmol), compound **6an** was obtained after 1 hour reaction (22 mg, 93% yield) as a yellow oil after purification by flash column chromatography (Cy : EtOAc = 8 : 2). Spectroscopic data were consistent with the literature data for this compound.[28]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.27 – 7.14 (m, 5H), 3.76 (s, 3H), 3.33 (s, 3H), 3.20 (t, *J* = 8.6 Hz, 1H), 2.17 (dd, *J* = 8.0, 5.2 Hz, 1H), 1.71 (dd, *J* = 9.2, 5.2 Hz, 1H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.4, 167.2, 134.7, 128.6, 128.3, 127.5, 52.9, 52.3, 37.4, 32.7, 19.2.

**HRMS (ESI):** Calculated for $C_{13}H_{15}O_4$ $[M + H]^+$: 235.0965, found 235.0973.

**Dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (6ao)**

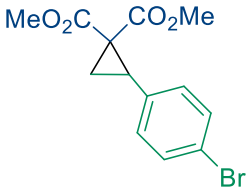



Following the general procedure **GP6**, from dimethyl 2-diazomalonate (**1a**) (15.8 mg, 0.1 mmol) and 1-methoxy-4-vinylbenzene (**4o**) (53.6 mg, 0.4 mmol), compound **6ao** was obtained after 1 hour reaction (25.6 mg, 97% yield) as a yellow oil after purification by flash column chromatography (Cy : EtOAc = 8 : 2).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.11 and 6.80 (AA'BB' system, 4H), 3.78 (s, 3H), 3.77 (s, 3H), 3.38 (s, 3H), 3.18 (t, *J* = 8.7 Hz, 1H), 2.15 (dd, *J* = 8.0, 5.1 Hz, 1H), 1.72 (dd, *J* = 9.3, 5.1 Hz, 1H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.5, 167.3, 159.1, 129.8, 126.6, 113.7, 55.3, 52.9, 52.4, 37.2, 32.4, 19.4.

**HRMS (ESI):** Calculated for $C_{14}H_{17}O_5$ $[M + H]^+$: 265.1071, found 265.1079.

**Dimethyl 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate (6ap)**




Following the general procedure **GP6**, from Dimethyl 2-diazomalonate **1a** (15.8 mg, 0.1 mmol) and 1-bromo-4-vinylbenzene (**4p**) (75.2 mg, 0.4 mmol), compound **6ap** was obtained after 1 hour reaction (30.3 mg, 97% yield) as a yellow oil after purification by flash column chromatography (Cy : EtOAc = 8 : 2).

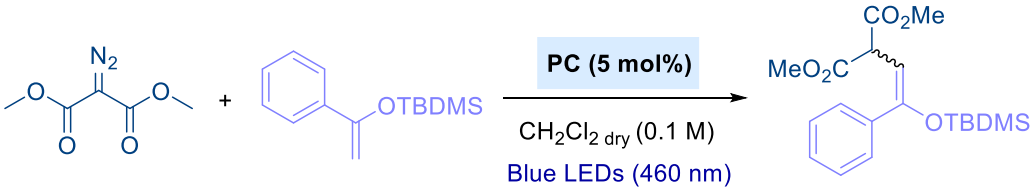
**$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.39 and 7.06 (AA'BB' system, 4H), 3.79 (s, 3H), 3.41 (s, 3H), 3.22 – 3.10 (m, 1H), 2.14 (dd, *J* = 8.0, 5.3 Hz, 1H), 1.74 (dd, *J* = 9.2, 5.3 Hz, 1H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 170.1, 167.0, 133.9, 131.5, 130.3, 121.6, 53.0, 52.5, 37.3, 31.9, 19.2.

**HRMS (ESI):** Calculated for $C_{13}H_{14}BrO_4$ $[M + H]^+$: 313.0070, 315.0050 found 313.0072, 315.0054.

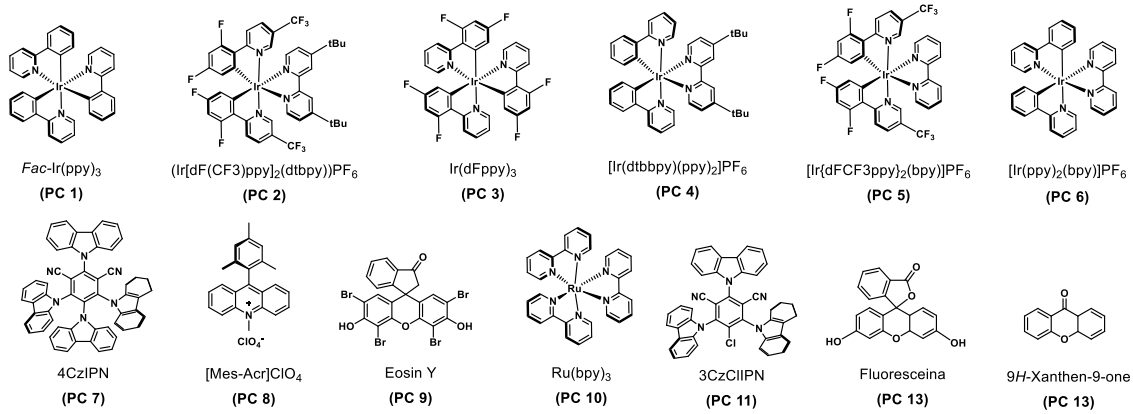
# 4. Screening of the reaction conditions

**Table S1.** Photocatalyst screening[a]




**1a** **2a** **3aa**

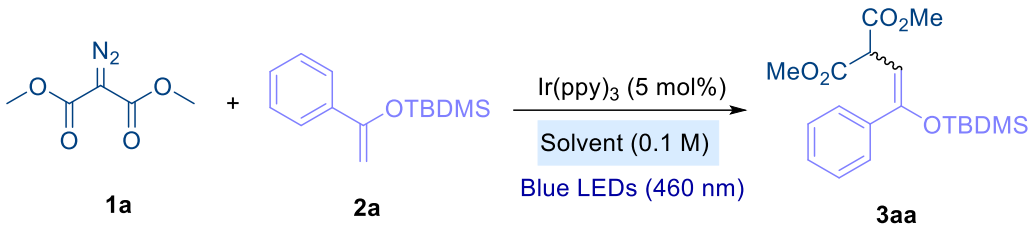
**Photocatalysts:**




| Entry | Photocatalyst (PC) | Yield[b] % |
|---|---|---|
| 1 | *fac*-Ir(ppy)$_3$ (**PC 1**) | 89 |
| 2 | Ir{dF[CF$_3$(ppy)$_2$(dtbpy)PF$_6$ (**PC 2**) | 71 |
| 3 | Ir(dF-ppy)$_3$ PF$_6$ (**PC 3**) | 68 |
| 4 | Ir(ppy)$_2$(dtbpy)PF$_6$ (**PC 4**) | 20 |
| 5 | IrdF[CF$_3$(ppy)$_2$(bpy)PF$_6$ (**PC 5**) | 13 |
| 6 | Ir(ppy)$_2$(bpy)PF$_6$ (**PC 6**) | 11 |
| 7 | 4CzIPN (**PC 7**) | Traces |
| 8 | [Acr$^+$-Mes] ClO$_4$ (**PC 8**) | n.r. |
| 9 | Eosin Y[c] (**PC 9**) | n.r. |
| 10 | [Ru(bpy)$_3$] (**PC 10**) | n.r. |
| 11 | 4CzClIPN (**PC 11**) | n.r. |
| 12 | Fluoresceina 5-isotiocianato (**PC 12**) | n.r. |
| 13 | 9H-Xanthen-9-one (**PC 13**) | n.r. |
| 14 | -- | decomposition |

[a] Reaction conditions: a mixture of **1a** (1.0 equiv, 0.1 mmol), **2a** (4.0 equiv, 0.4 mmol), **PC** (5 mol%, 0.005 mmol), in DCM (0.1M, 1.0mL) was irradiated with under blue LEDs in air at 25 °C for 1 h. [b] Determined by $^1$HNMR analysis using 1,3,5 Trimethoxybenzene as an internal standard. [c] Reactions were run both under blue and green LEDs.

**Table S2.** Solvent screening[a]

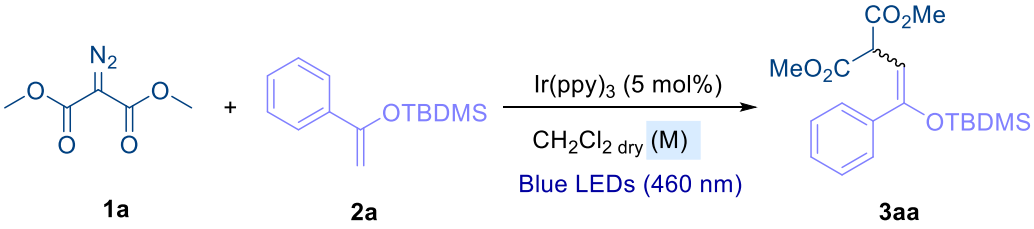



**1a** **2a** **3aa**

| Entry | Solvent (0.1M) | Yield[b] % |
|---|---|---|
| 1 | DCM dry | 89 |
| 2 | DCE | 83 |
| 3 | DCM | 62[c] |
| 4 | DCM:MeOH (3:1) | 61 |
| 5 | Chloroform | 38 |
| 6 | MeOH | n.r. |
| 7 | MeCN | n.r. |
| 8 | Neat | n.r. |

[a] Reaction conditions: a mixture of **1a** (1.0 equiv, 0.1 mmol), **2a** (4.0 equiv, 0.4 mmol), $Ir(ppy)_3$ (5 mol%, 0.005 mmol), in **Solvent** (0.1 M, 1.0mL) was irradiated with under blue LEDs in air at 25 °C for 1 h. [b] Determined by $^1$HNMR analysis using 1,3,5-Trimethoxybenzene as an internal standard. [c] Reaction time 16h.

**Table S3.** Solvent concentration screening[a]

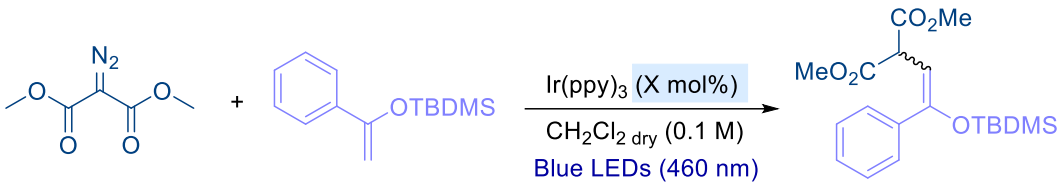



**1a** **2a** **3aa**

| Entry | Solvent concentration | Yield (%)[b] |
|---|---|---|
| 1 | 0.10 M (1 mL) | 89 |
| 2 | 0.20 M (0.5 mL) | 59 |
| 3 | 0.06 M (1.7 ml) | 44[c] |

[a] Reaction conditions: a mixture of **1a** (1.0 equiv, 0.1 mmol), **2a** (4.0 equiv, 0.4 mmol), $Ir(ppy)_3$ (5 mol%, 0.005 mmol), in $CH_2Cl_{2\ dry}$ (**X** M, **Y** mL) was irradiated with under blue LEDs in air at 25 ºC for 1 h. [b] Determined by $^1$HNMR analysis using 1,3,5-Trimethoxybenzene as an internal standard. [c] Isolated yield%

**Table S4.** Catalyst loading of *fac*-Ir(ppy)$_3$[a]



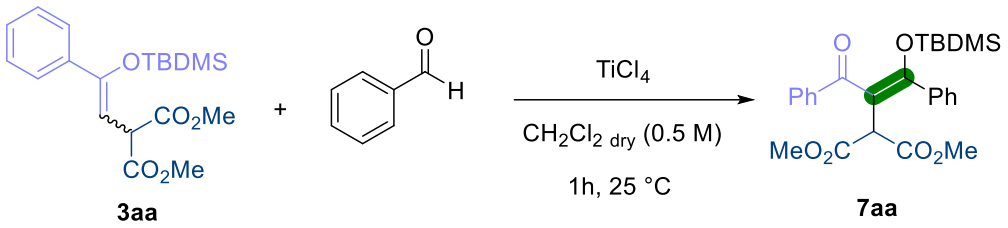

**1a** **2a** **3aa**

| Entry | Catalyst load (X mol%) | Yield[b] % |
|---|---|---|
| 1 | 5 | 86 % |
| 2 | 2,5 | 51 % |
| 3 | 1 | 27 % |

[a] Reaction conditions: a mixture of **1a** (1.0 equiv, 0.1 mmol), **2a** (4.0 equiv, 0.4 mmol), Ir(ppy)$_3$ (**X mol%**), in DCM dry (0.1M, 1.0 mL) was irradiated with under blue LEDs in air at 25 ºC for 1 h. [b] Determined by $^1$H NMR analysis using 1,3,5-Trimethoxybenzene as an internal standard.

## 5. Synthetic manipulation

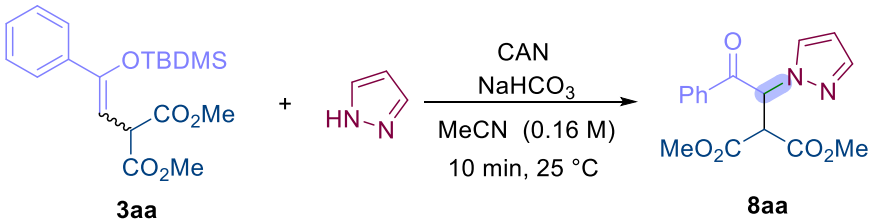
### 5.1. Mukaiyama aldol addition of benzaldehyde




To a solution of benzaldehyde (7.6 µL, 0.076 mmol, 1 equiv.) in $CH_2Cl_2$ (0.15 mL) was added a solution of $TiCl_4$ (1 M in $CH_2Cl_2$) (0.1 mL, 0.1 mmol, 1.3 equiv.). After being stirred for 15 min, a solution of silyl enol ether **3aa** (27.6 mg, 0.076 mmol, 1 equiv.) in $CH_2Cl_2$ (0.2 mL) was added dropwise and the reaction mixture was stirred for 1 h at room temperature. The resulting solution was diluted with water and extracted with $CH_2Cl_2$ twice. The combined organic extracts were dried over $MgSO_4$ and filtered. After concentration, the residue was purified by column chromatography on silica gel (Cy : EtOAc = 75 : 25) to give **7aa** (17.8 mg, 0.038 mmol, 50% yield) as a white solid.

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.87 – 7.82 (m, 2H), 7.49 – 7.44 (m, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.22 – 7.15 (m, 4H), 7.16 – 7.09 (m, 1H), 5.03 (d, *J* = 5.6 Hz, 1H), 4.69 (dd, *J* = 9.2, 5.7 Hz, 1H), 4.19 (d, *J* = 9.2 Hz, 1H), 3.63 (s, 3H), 3.59 (s, 3H), 0.82 (s, 9H), -0.09 (s, 3H), -0.29 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 200.1, 169.1, 168.7, 141.2, 137.7, 132.8, 128.9, 128.4, 128.1, 127.9, 126.9, 74.9, 54.6, 52.9, 52.7, 51.8, 25.9, 18.3, -4.6, -5.0.
**HRMS (ESI):** Calculated for $C_{26}H_{35}O_6Si$ $[M + H]^+$: 471.2198, found 471.2194.

### 5.2. Oxidative heteroarylation: acces to α-pyrazoleketone derivate



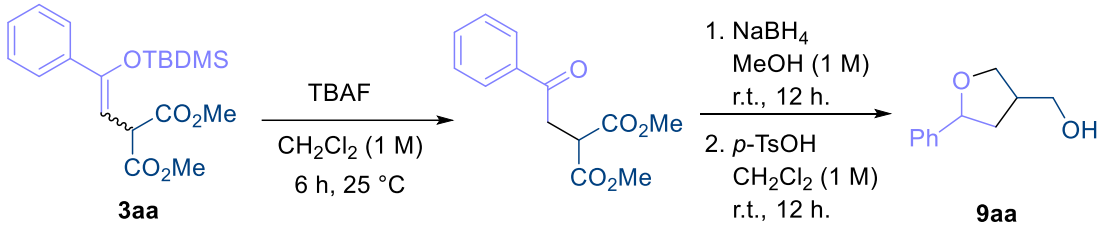

To a solution of CAN (137 mg, 0.25 mmol, 2.5 equiv) and $NaHCO_3$ (42 mg, 0.5 mmol, 5 equiv.) in acetonitrile (0.6 mL), pyrazole (20.5 mg, 0.3 mmol, 3 equiv.) was added. After being stirred for 5 min, silyl enol ether **3aa** (36.4 mg, 0.1 mmol, 1 equiv.) was added portionwise and the reaction mixture was stirred for 10 min at room temperature. The resulting solution was quenched with water and extracted with $CH_2Cl_2$ twice. The combined organic extracts were dried over $MgSO_4$ and filtered. After concentration, the residue was purified by column

chromatography on silica gel (Cy : EtOAc = 80 : 20) to give **8aa** (22.1 mg, 0.07 mmol, 70% yield) as a white solid.

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.96 – 7.90 (m, 2H), 7.57 – 7.46 (m, 3H), 7.45 – 7.36 (m, 2H), 6.52 (d, *J* = 10.8 Hz, 1H), 6.23 (t, *J* = 2.1 Hz, 1H), 4.64 (d, *J* = 10.9 Hz, 1H), 3.76 (s, 3H), 3.61 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 191.7, 167.3, 141.1, 134.6, 134.1, 129.8, 129.0, 128.9, 107.3, 63.6, 53.9, 53.23, 53.17.

**HRMS (ESI):** Calculated for $C_{16}H_{17}N_2O_5$ $[M + H]^+$: 317.1132, found 317.1132.

## 5.3. Intramolecular substitution: synthesis of tetrahydrofurane derivate




To a stirred solution of silyl enol ether **3aa** (72.8 mg, 0.2 mmol, 1 equiv.) in $CH_2Cl_2$ (0.2 mL), TBAF (104.6 mg, 0.4 mmol, 2 equiv.) was added and the reaction was stirred at room temperature for 6 hours achieving full conversion. At that time, the reaction was quenched with water and extracted with $CH_2Cl_2$ twice. The combined organic extracts were dried over $MgSO_4$, filtered and concentrated under vacuum. The crude product was used in the next step without further purification.

To a stirred solution of the crude ketone (50 mg, 0.2 mmol, 1 equiv.) in MeOH (0.2 mL) was added $NaBH_4$ (14.8 mg, 0.4 mmol, 2 equiv.) portionwise. The reaction was further stirred for 6 hours. At that time, water was added to quench the reaction, and the organic solvent was evaporated under vacuum. The water residue was extracted with $CH_2Cl_2$ twice. The combined organic extracts were dried over $MgSO_4$, filtered and concentrated under vacuum. Then, the reaction crude was dissolved in $CH_2Cl_2$ (0.2 mL) and catalytic amount of *p*-toluensulfonic acid (1 mg) was added, and the reaction mixture was stirred at room temperature 12 hours. The reaction was quenched with water and extracted with $CH_2Cl_2$ twice. The combined organic phases were dried over $MgSO_4$ and filtered. After concentration, the residue was purified by column chromatography on silica gel (Cy : EtOAc = 90 : 10) to give **9aa** as a mixture 56:44 of two diastereoisomers (19.6 mg, 0.11 mmol, 55% yield) as a colourless oil. Spectroscopic data were consistent with the literature data for this compound.[29]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.38 – 7.29 (m, 8H, two isomers), 7.29 – 7.22 (m, 2H, two isomers), 4.98 (t, *J* = 7.2 Hz, 1H, one isomer), 4.87 (dd, *J* = 9.4, 6.4 Hz, 1H, one isomer), 4.23

(dd, *J* = 8.8, 7.1 Hz, 1H, one isomer), 4.02 (dd, *J* = 8.8, 7.4 Hz, 1H, one isomer), 3.93 (dd, *J* = 8.8, 5.5 Hz, 1H, one isomer), 3.75 (dd, *J* = 8.7, 5.9 Hz, 1H, one isomer), 3.72 – 3.62 (m, 4H, two isomers), 2.73 – 2.54 (m, 2H, two isomers), 2.46 (ddd, *J* = 12.4, 8.1, 6.4 Hz, 1H, one isomer), 2.18 (ddd, *J* = 12.3, 7.2, 5.0 Hz, 1H, one isomer), 1.98 (ddd, *J* = 12.7, 8.5, 7.3 Hz, 1H, one isomer), 1.68 (brs, 2H) 1.54 (ddd, *J* = 12.4, 9.4, 7.8 Hz, 1H, one isomer). **$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ 143.3, 142.5, 128.51, 128.49, 127.5, 127.4, 125.8, 125.7, 81.4, 80.2, 71.2, 71.1, 65.4, 64.7, 42.5, 41.8, 37.9, 37.4.

**HRMS (ESI):** Calculated for $C_{11}H_{15}O_2$ $[M + H]^+$: 179.1067, found 179.1071.

# 6. Mechanistic investigations

## 6.1. Cyclic voltammetry

CV measurements were carried out under argon atmosphere. The measurements were performed in DCM containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate. A platinum electrode (working electrode), platinum wire counter electrode, and Ag/AgCl reference electrode were employed for the CV measurement. The scan rate was 100 mV/s, a step potential of 50 mV was applied.

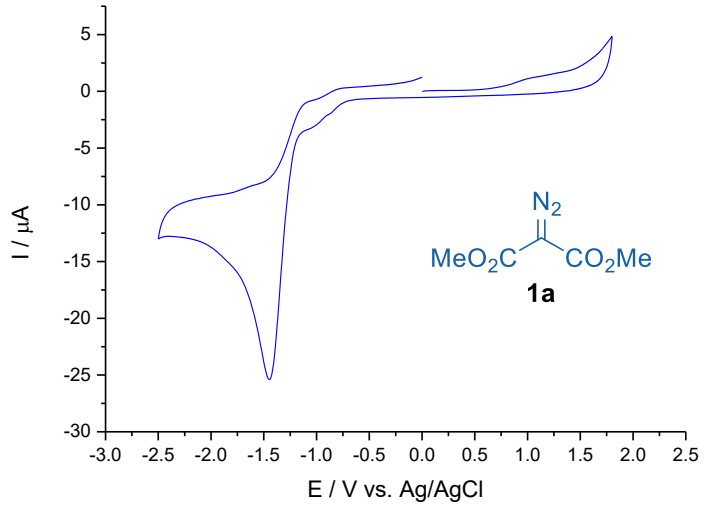



**Figure S4.** Cyclic voltammetry of **1a** (0.001 M in DCM), E=p/2 = -1.40 eV.[30]

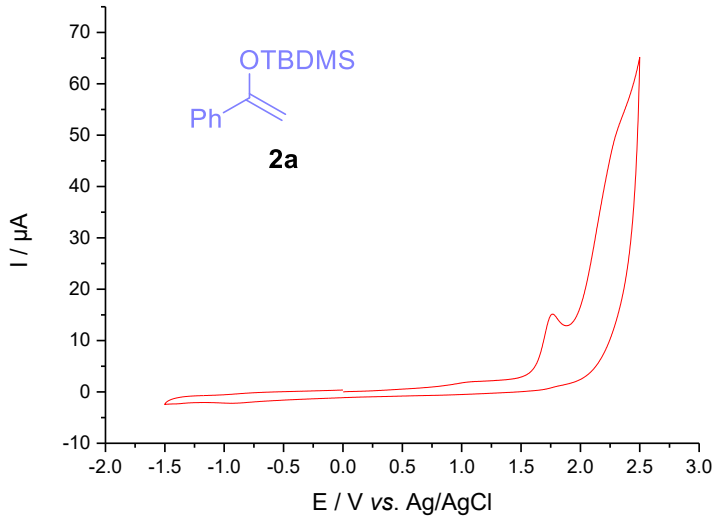



**Figure S5.** Cyclic voltammetry of **2a** (0.001 M in DCM), E=p/2 = +1.77 eV.[31]

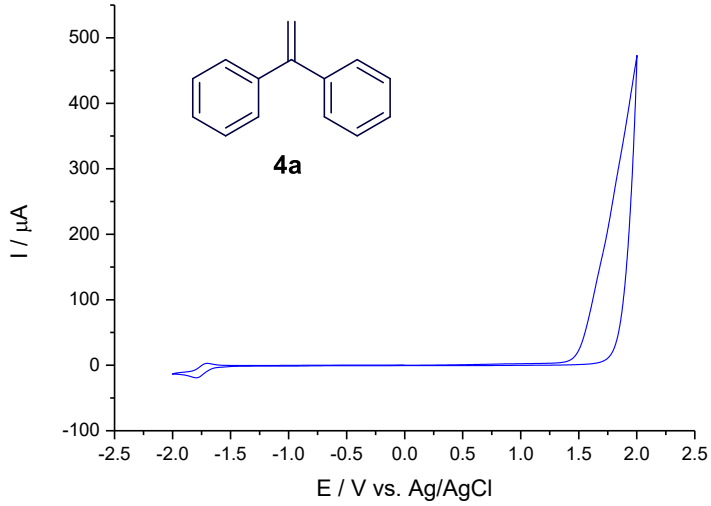



**Figure S6.** Cyclic voltammetry of **4a** (0.001 M in DCM), E=p/2 = +1.88 eV.[32]

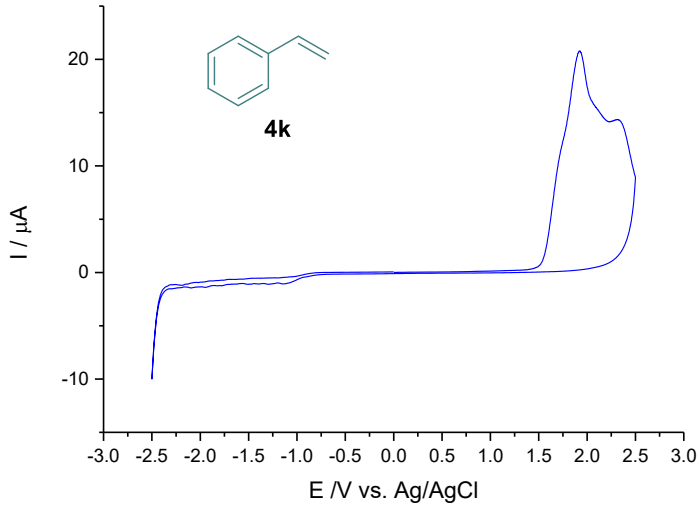



**Figure S7.** Cyclic voltammetry of **4k** (0.001 M in DCM), E=p/2 = +1.97 eV.[33]

## 6.2. Kinetic of the reaction

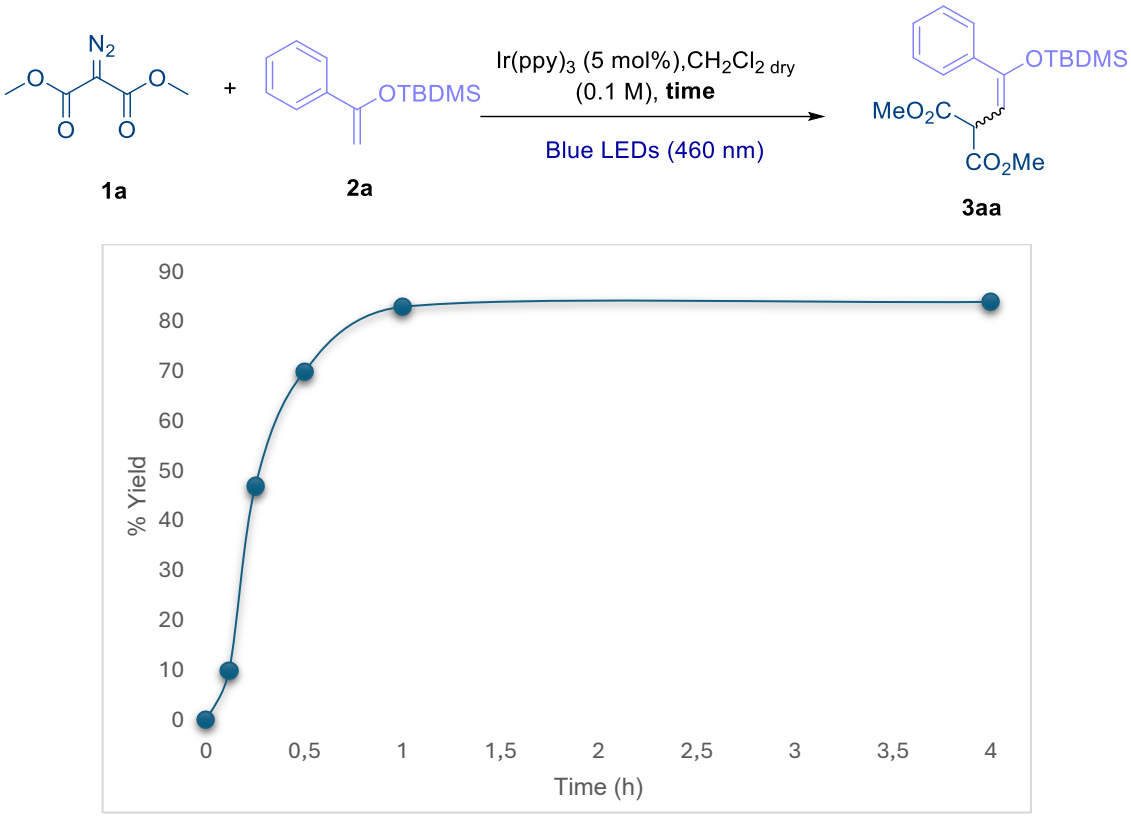
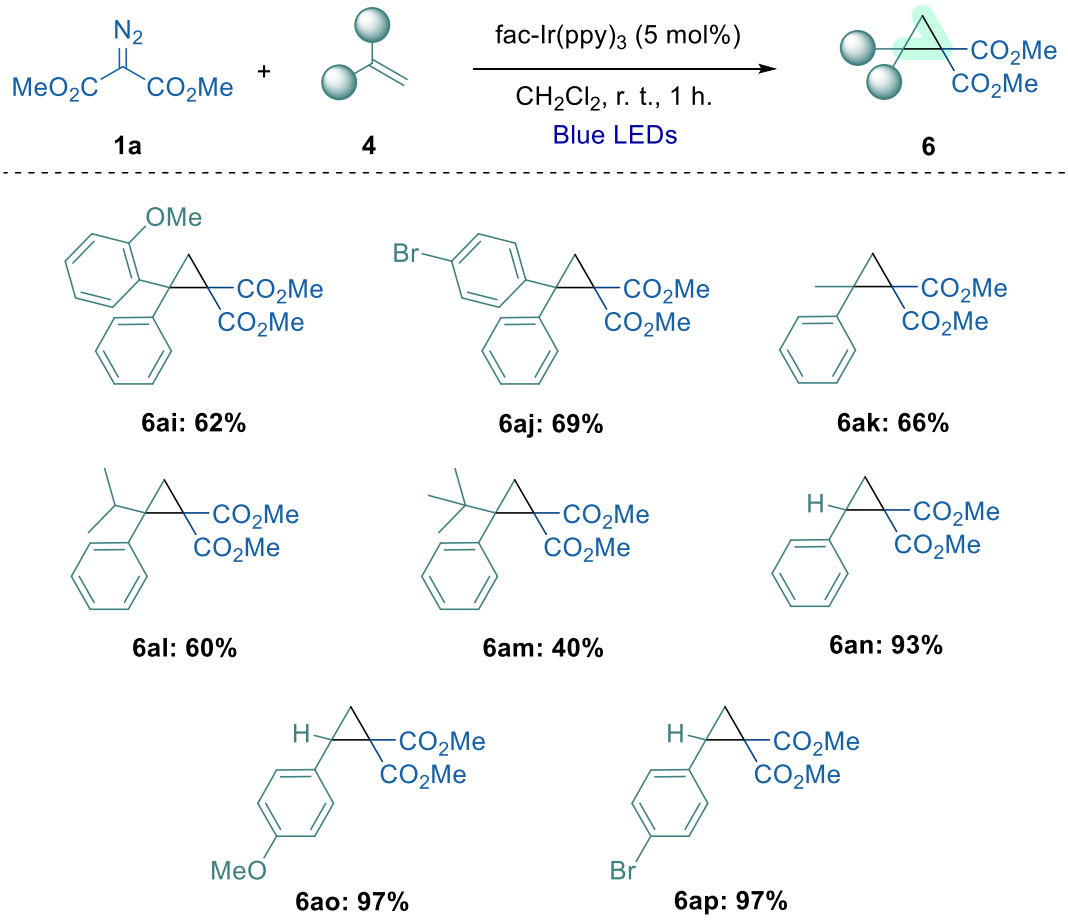



**Figure S8.** Kinetic of the reaction

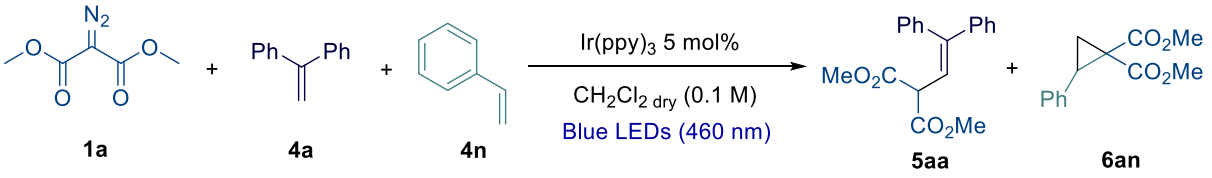
## 6.3. Selectivity towards cyclopropyl or double bond

As reported in Scheme S1, asymmetric double bonds mostly give cyclopropanated adducts (**6ai-6aj**) as major products, with minor Heck-type adducts. Efforts were directed toward elucidating the mechanisms that differentiate cyclopropanation from C-H functionalization when using the same catalyst. Testing styrene derivatives under photocatalytic conditions resulted in clean cyclopropanation products **6ak-6an**, with no C-H functionalized products, indicating that steric hindrance, rather than electronic properties, controls selectivity. Indeed, variations in electronic properties, such as with *para*-methoxy and *para*-bromo groups, also led to cycloaddition products (**6ao** and **6ap**) in nearly quantitative yields (97% both).




**Scheme S1.** Scope with asymmetric double bonds: Reaction conditions: **1a** (0.1 mmol), **4** (4 equiv.) *fac*-Ir(ppy)$_3$ (5 mol%), $CH_2Cl_2$ (1 mL), blue LED in air, 1 h. Isolated yield after flash column chromatography.

**Table S5.** Selectivity towards cyclopropyl or double bond




| Entry | Mmol of 4a | Mmol of 4n | Ratio 5aa/6an |
|---|---|---|---|
| 1 | 0.05 | 0.05 | 33/66 |
| 2 | 1 | 2 | 13/87 |
| 3 | 2 | 1 | 26/74 |
| 4 | 1 | 1 | 23/77 |
| 5 | 4 | 4 | 0/100 |

## 6.4. General procedure GP5 for the TBDMS-Silyl-Enol Ethers **2** in the presence of TEMPO

In an oven-dried 6 mL vial, equipped with a magnetic stirring bar, was prepared a solution of diazo compound **1** (0.1 mmol), *tert*-butyldimethylsilane **2** (4.0 equiv.), TEMPO (4.0 equiv.) and *fac*- $Ir(ppy)_3$ (5 mol%) in dry dichloromethane (0.1M). The vial was closed with a PTFE/rubber septum and pierced by a syringe. The reaction mixture was irradiated and stirred in the photoreactor setup at 460 nm for one hour. After the reaction was complete, reaction mixture was concentrated under reduced pressure and the obtained crude was directly analysis by $^1$H NMR and High-resolution Mass.

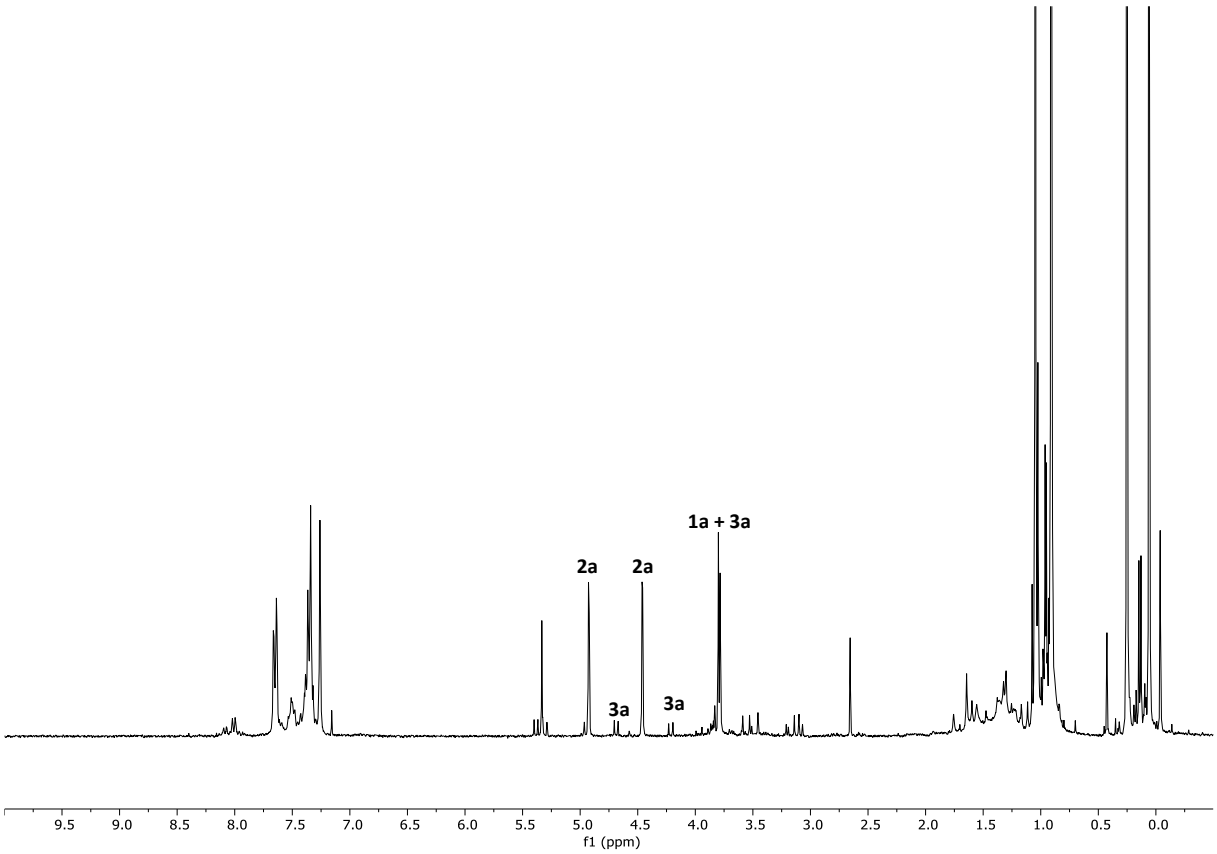



**Figure S9**. $^1$H NMR of reaction crude in the presence of TEMPO

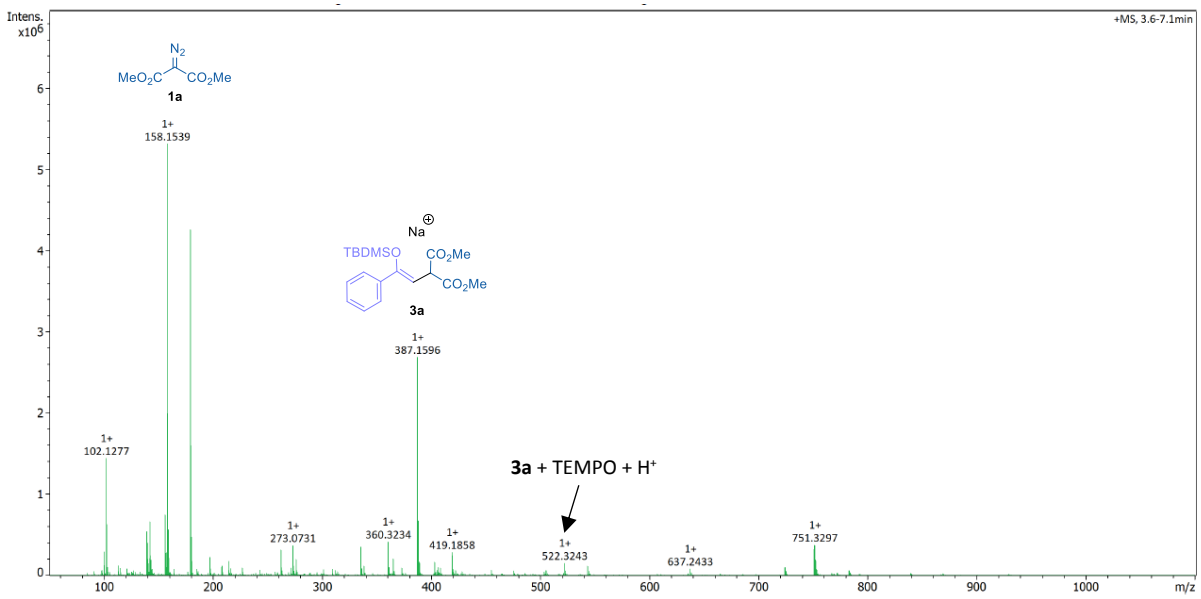



**Figure S10**. High-resolution mass of reaction crude in the presence of TEMPO

## 6.5. Study of the possible deactivation pathways of the photocatalyst and Luminescence quenching studies

For the steady-state and time resolved luminescence quenching studies, increasing concentrations of quencher were added to a solution of *fac*-Ir(ppy)$_3$ photocatalyst in $CH_2Cl_2$ with an absorption of 0.149 at 455 nm under air ($\lambda_{exc}$ = 455 nm). An efficient quenching of the excited photocatalyst is observed with **1a** with a rate constant of 2.67 x $10^9$ $s^{-1}$ $M^{-1}$, while the TBDMS protected enolate does not interact with the excited catalyst.

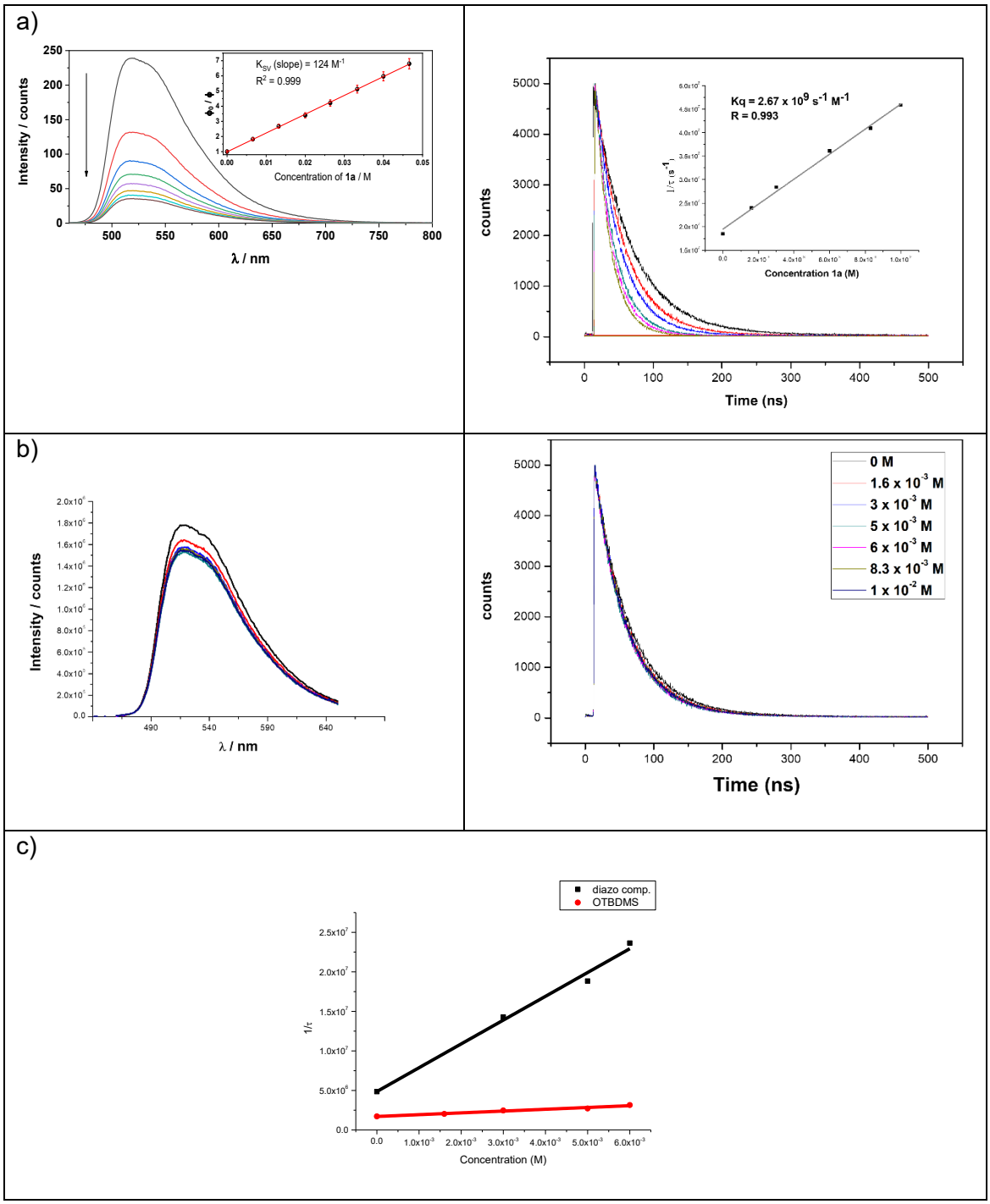



**Figure S11**. Steady-state and time resolved fluorescence quenching of Ir(ppy)$_3$ with increasing concentrations of a) **1a** and b) **2a**. c) Comparison between the quenching of **1a** and **2a**.

It is well-established that *fac*-Ir(ppy)$_3$ complex displays a characteristic phosphorescence band due to a ligand-centred triplet state ($T_1$) which is strongly disturbed by admixture with a state having metal-ligand charge-transfer (MLCT)[34] character ($^3$MLCT-LC). Furthermore, the fluorescence of these type of cyclometalated Ir complexes is virtually negligible since the intersystem crossing rate is found to be very fast (<100 fs), leading to triplet formation nearly quantitative.[35] Thus, *fac*-Ir(ppy)$_3$ complex exhibited a broad phosphorescence emission band in dichloromethane (See Figure S11a and b, black line) with maximum at 520 nm which fully agreed with previously reported data.[36] Interestingly, the intensity of this signal gradually decreased in the presence of increasing amounts of **1a** indicating significant quenching by the diazo derivative compound. The corresponding quenching rate constant $k_q$ could be also determined by the Stern-Volmer analysis (Equations E1 and E2).

$$\phi_0/\phi = 1 + K_{SV}\,[\mathbf{1a}] \qquad \text{(E1)}$$

$$K_{SV} = \tau_P\, k_q \qquad \text{(E2)}$$

The value of the Stern-Volmer constant ($K_{SV}$) was found to be 124 $M^{-1}$ and considering the phosphorescence lifetime ($\tau_P$) of *fac*-Ir(ppy)$_3$ complex in aerated dichloromethane (36 ns),[37] the rate constant for emission quenching was estimated as $k_q$ = 3.4 x 109 $M^{-1}$ $s^{-1}$. Therefore, compound **1a** quenches the luminescence emission of *fac*-Ir(ppy)$_3$ at a nearly diffusion-controlled rate. To discard other processes such as complex formation in the ground state between the photocatalyst and **1a** or filter effect by the addition of the quencher, absorptivity measurements of *fac*-Ir(ppy)$_3$ in the presence of different amounts of **1a** were carried out (Figure S12). Clearly, *fac*-Ir(ppy)$_3$ absorbed the same number of photons at the irradiation wavelength (450 nm), supporting that the luminescence quenching occurred by an electron transfer process.

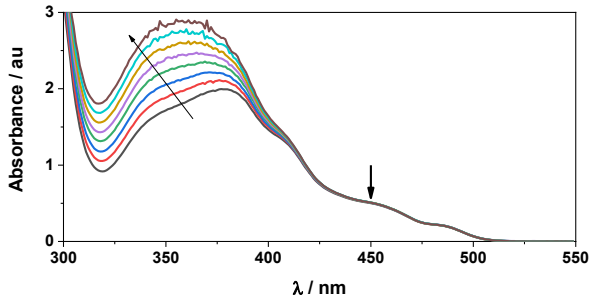



**Figure S12**. Absorbance spectra of *fac*-Ir(ppy)3 (0.1 mM) with **1a** (0, 6, 12, 20, 24, 33, 40 and 47 mM) in $CH_2Cl_2$/air.

Based on the $k_q$ value, the relative contributions of the competing pathways resulting in the deactivation of the phosphorescence of the *fac*-Ir(ppy)3 complex (Equation E3) in the presence of 1a were determined: radiative ($k_r$) and nonradiative decay rate constants ($k_{nr}$) as well as the

phosphorescence quenching. Competition between them should be governed by the respective rate constants and by the quencher concentration.

$$KD = k_r + k_{nr} + k_q[\mathbf{1a}] \qquad (E3)$$

Hence, the rate constant of radiative ($k_r$) and nonradiative ($k_{nr}$) are intrinsic properties of the photocatalyst. The values for *fac*-Ir(ppy)$_3$ complex were calculated from Equations E4 and E5, where the phosphorescence quantum yield ($\phi_P$) has been taken as 0.97.[36] The resulting values for the rate constants in aerobic conditions were $k_r$ = 2.7 x $10^7$ $s^{-1}$ and $k_{nr}$ = 7.7 x $10^5$ $s^{-1}$, respectively.

$$k_r = \phi_P / \tau_P \qquad (E4)$$

$$k_{nr} = (k_r / \phi_P) - k_r \qquad (E5)$$

Therefore, under preparative irradiation conditions ([**1a**] = 0.1 M), quenching of the phosphorescence emission of *fac*-Ir(ppy)$_3$ complex by **1a** is the major deactivation pathway (92.5% vs. 7.3% + 0.2% for radiative and nonradiative, respectively) which proves the high efficiency of catalytic reaction initiation.

## 7. Quantum yield determination

A solution of ferrioxalate was chosen as actinometer following the procedure described by the IUPAC (subcommittee on photochemistry).[38] The procedure is based on the decomposition under irradiation of ferric ions to ferrous ions which are complexed by 1,10-phenanthroline. This photochemical transformation has a known quantum yield and the complexation of $Fe^{2+}$ with 1,10-phenanthroline can be monitored by UV-Visible absorption since its extinction coefficient at 510 nm is known (ε =11100 $M^{-1}$ $cm^{-1}$ ). Therefore, the moles transformed can be related with the moles of photons absorbed by the Equation E6.

$$\Phi = \frac{mol\ transformed}{photons\ absorbed} \qquad \text{(E6)}$$

The complete procedure should be done under a red safe-light environment. At 460 nm ferroxilate has a Φ = 0.85.[39] 0.006, 0.012, or 0.15 M solutions of $K_3[Fe(C_2O_4)_3]$ $3H_2O$ can be used for actinometry. In this case, we chose a concentration of 0.15 M. The solutions were prepared and stored in a dark laboratory:

1. Potassium ferrioxalate solution (0.15 M): 368.4 mg of $K_3[Fe(C_2O_4)_3]$ $3H_2O$ (commercially available) and 26.6 µL of $H_2SO_4$ were added into a 5 mL volumetric flask and filled to the mark with Milli-Q water.
2. Phenanthroline solution (0.15 M): 1.35 g of 1,10-phenantroline monohydrate were added to 50 mL volumetric flask and filled to the mark with MilliQ water.
3. Buffer solution: 4.94 g of NaOAc and 1 mL of $H_2SO_4$ were added to 100 mL volumetric flask and filled to the mark with MilliQ water.
4. Model reaction solution: A dry vial equipped with a magnetic stir bar was charged with **1a** (0.1 mmol, 1 equiv.), **2a** (0.4 mmol, 4.0 equiv.), *fac*-$Ir(ppy)_3$ (2 mg, 0.005 mmol, 5 mol %) and 1.0 mL of $DCM_{dry}$ (0.1 M). The vial was then stirred under 460 nm LED irradiation (22.0216 W/m2 intensity; approximate distance was 2 cm from the vial) at 20ºC.

**Actinometry procedure**: Due to the reactor setup (**Figure S12**), the simultaneous irradiation of both the actinometer solution and model reaction is not feasible. However, the stability of the irradiation light was checked through radiometer measurements (from spectro-radiometer equipment Stellarnet model Blue-Wave UV-NB50). Therefore, we assumed that consecutive measurements of both actinometer and model reaction are comparable. In addition, using the same spectrometer, the LED source spectrum was measured, detecting a maximum wavelength of emission of 460 nm (**Figure S14)**.

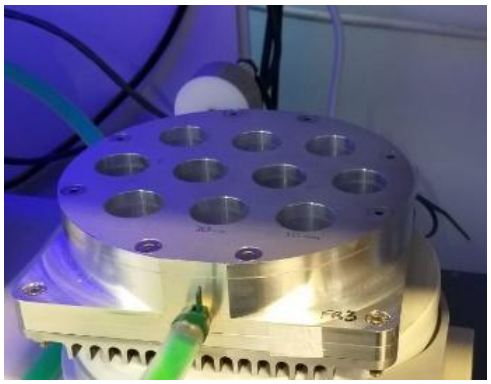


**Figure S13.** LED setup of the reaction

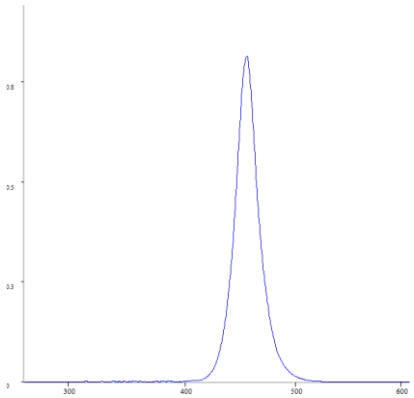


**Figure S14.** Emission spectrum of the blue LED of the photochemical reactor ($\lambda_{max}$= 460 nm).

2 mL of Potassium ferrioxalate solution (0.15 M) were introduced into the photoreactor under dark conditions while being stirred. Then, the LED was switched on. Every 5 s the light was switched off and a 0.1 mL aliquot was taken. To each aliquot, 2 mL of buffer solution and 0.5 mL of 1,10-phenanthroline 0.15 M were added and the final volume was raised to 10 mL with MilliQ water. Then 83 µL of this solution were diluted to 5 mL with MilliQ water. As a blank sample, a solution was prepared with 0.1 mL of potassium ferrioxalate solution (0.15 M) before irradiation, 2 mL of buffer solution and 0.5 mL of 1,10-phenanthroline 0.15 M in a 10 mL of volumetric flask filled with water until the mark, and 83 µL of this solution were diluted to 5 mL with MilliQ water. The absorbance spectrum of each sample was monitored at 510 nm. The absorbance to each time was related with the photochemically produced $Fe^{2+}$ ions across the Lambert-Beer Law (Equation E7), where V1 is the irradiated volume (noting that the initial volume is 2 mL but it changes as the aliquots are taken); V2 is the aliquot volume (0.1 mL), V3 is the final volume after addition of 1,10-phenanthroline and buffer (10 mL). b is referred to the optical pathway (1 cm), ΔA (510 nm) is the difference in absorbance between the irradiated solution and the blank sample, ε (510 nm) is the extinction coefficient of the complex formed by Fe(II) and 1,10-phenanthroline (ca. 11100 $M^{-1}$ $cm^{-1}$).

$$moles\ of\ Fe^{2+} = \frac{V_1 \cdot V_3 \cdot \Delta A_{(510\ nm)}}{10^3 \cdot V_2 \cdot b \cdot \varepsilon_{(510\ nm)}} \quad \text{(E7)}$$

The moles of $Fe^{2+}$ formed (x) are plotted as a function of time (t) (**Figure S15**).

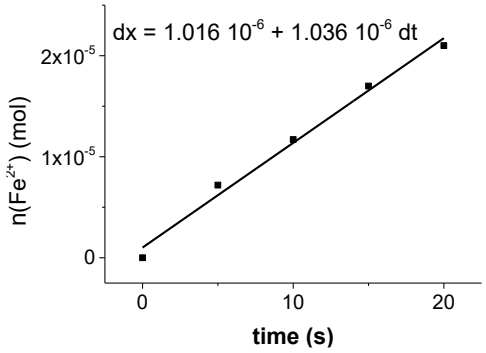



**Figure S15.** Actinometer.

The slope of this line (*dx*/*dt*) was correlated to the moles of incident photons by unit of time ($q^0_{n,p}$) using the following Equation E8:

$$q^0_{n,p} = \frac{dx/dt}{\Phi_{(\lambda)} \cdot [1-10^{-A(\lambda)}]} \quad \text{(E8)}$$

Where $\Phi_{(\lambda)}$ is the quantum yield of the actinometer reaction at the irradiated wavelength, in this case being 0.85 at 460 nm for 0.15 M dilution and $A_{(\lambda)}$ is the absorbance of the actinometer solution (ferrioxalate) at the irradiated wavelength (460 nm). The absorbance at 460 nm was measured with an Agilent 8453 UV-visible Spectroscopy System using a quartz cuvette with 1 cm of optical pathway. Therefore, the moles of incident photons by unit of time ($q^0_{n,p}$) was determined as 1.036 $10^{-5}$ einstein $s^{-1}$.

**The kinetic of the reaction under study was done as follows**: the photoreactor (blue LEDs) was switched on and the reaction mixture was stirred. At 10, 15, 20, 30 and 60 minutes an aliquot of 0.1 mL was taken from the reaction mixture under a positive flow of nitrogen, 0.05 mL of a solution of trimethoxybencene in $CDCl_3$ (0.2 M) were added, and the resulting solution diluted with 0.4 mL of $CDCl_3$. Thus, the conversion of the reaction at the different indicated time was determined by $^1H$ NMR. Knowing the initial molar concentration, the determination of the moles of photo-converted product is possible.

Plotting the moles of product versus the irradiation time, the slope *dx*/*dt* can be related with the quantum yield across the Equation E8 being equal to time ($q^0_{n,p}$) $\Phi_{(\lambda)} \cdot [1\text{-}10\text{-}A_{(\lambda)}]$. Therefore, the quantum yield at the wavelength of irradiation Φ (460 nm) can be calculated once A (460 nm) is determined. To measure A (460 nm), a model reaction solution was added to a 1 cm optical pathway cuvette, and the UV-Visible spectrum was recorded obtaining an absorbance of 2.1. Therefore, the quantum yield for the reaction is: Φ = 1.2

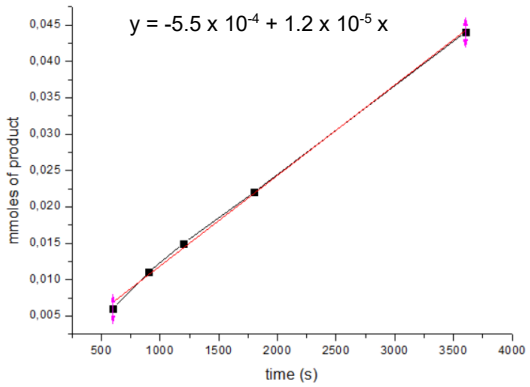



**Figure S16.** Kinetic of the reaction.

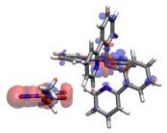
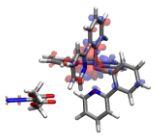
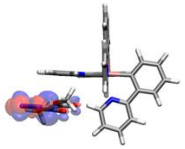
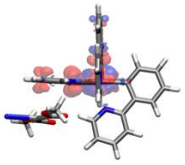
## 8. Computational details: DFT calculations

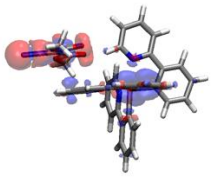
Method selection and ground state optimization: The ground state global minimum was optimized at the density functional theory (DFT) level with the classical B3LYP[40] functional combined with the 6-31g(d,p)[41] basis set and LANL2DZ[42] for the Ir in solution. This method, i.e. functional/basis set, was selected since it has been previously successfully applied to compute the excited states of Ir complexes.[43] However, since also M06 functionals have been proposed to accurate describe geometries and absorption spectra of this kind of complexes,[44] and usually performs better for systems where dispersion is important, we have double checked our results using also the M062X[45] functional for completeness.

- **Excited States:** Time dependent density functional theory (TD-DFT) using B3LYP and M062X functionals combined with the 6-31g(d,p) basis set and LANL2DZ for the Ir was selected as method for the optimization of the excited states. All these calculations were done with the Gaussian16[46] program and within solution using the Polarizable Continuum Model.[47]
- **Franck-Condon region:** the B3LYP functional predicts that the first three states ($S_1$-$S_3$) have an important charge transfer (CT) character from the Ir(III) moiety to the 1a whereas $S_4$ and $S_5$ are mostly located at the Ir(III) (Table S6). Instead, M062X predicts mostly localized states in 1a and Ir (III) from $S_1$ to $S_5$. The first state with clear CT character is $S_{14}$ (Table S6) that is relatively close in energy ~0.7 eV respect to the spectroscopic states $S_3$/$S_4$.
- **Potential Energy Surfaces:** despite these discrepancies at the Franck-Condon region, the relaxation and potential energy surfaces (energies and geometries) of both functionals are similar (Figure S17 and S18). Optimization of excites states located on Ir(III) end up in an emissive minimum ($S_{min}$) similar to the one located when the Ir(III) is not in the presence of **1a**. Alternatively, optimization of states located in **1a** or with important CT, lead to a crossing region with the ground state ($S_1$/$S_0$). From there, if the ground state is optimized, the system relaxes back to the global $S_0$ minimum (path 1). Relax scan simulating the delivery of the $N_2$ molecule with the uncharged Ir(III) and **1a** species grow up in energy, being then unlikely (path 2). Alternatively, the same path (path 3) but considering that the Ir complex is positively charged and the **1a** is negatively charged deliver more stable products (see next point).
- **Charged Fragments:** Since the global charge of the system [Ir(III)+1a] is one both when the species are charged and when neutral, we resort to constrained DFT to specify the two different cases. We used it combined with the M062X/6-31g(d,p)/LANL2DZ functional and basis set with the NChem software.[48]

- **Spectra:** absorption spectra were computed at the M062X/ 6-31g(d,p)/LANL2DZ level of theory to obtain the vertical energies and intensities that have been convoluted using gaussian functions. For the Excited State Absorption spectra, for which excited-excited transition dipole moments are necessary we have coupled such calculations with multiwfn program.[49]
- **Triplets:** We have also analyzed the possibility for triplet population. From the $S_{min}$ we have optimized the closest in energy triplet state, $T_2$. This optimization led to a crossing region with the ground state ($T_1/S_0$) where the N=N moiety is twisted resembling the characteristics of the ($S_1/S_0$) geometry. From there, the system is expected to follow the most probable path in the ground state as above mentioned.

**Table S6**. Excitation energies, oscillator strengths (f) and charge transfer (a.u.) character of the lowest lying states computed at the specified level of theory. The excited-ground state density difference for the $S_n$ are shown (the electron moves from the blue regions towards the red)

| | **ΔE eV** | **ΔE nm** | **f** | **CT character** | |
|---|---|---|---|---|---|
| *B3LYP/ 6-31g(d,p)/LANL2DZ* | | | | | |
| **$S_1$** | 2.42 | 511 | 0.000 | 0.98 Ir (III)-> 1a |  |
| **$S_2$** | 2.55 | 486 | 0.000 | 0.98 Ir (III)-> 1a | |
| **$S_3$** | 2.56 | 484 | 0.000 | 0.98 Ir (III)-> 1a | |
| **$S_4$** | 2.99 | 414 | 0.011 | 0.30 Ir (III)* |  |
| **$S_5$** | 3.04 | 407 | 0.005 | 0.36 Ir (III)* | |
| *M062X/ 6-31g(d,p)/LANL2DZ* | | | | | |
| **$S_1$** | 3.38 | 367 | 0.000 | 0.02 1a* |  |
| **$S_2$** | 3.82 | 324 | 0.080 | 0.23 Ir (III)* |  |
| **$S_3$** | 3.85 | 322 | 0.120 | 0.23 Ir (III)* | |
| **$S_4$** | 3.93 | 315 | 0.111 | 0.26 Ir (III)* | |

| | | | | | |
|---|---|---|---|---|---|
| $S_5$ | 4.10 | 302 | 0.084 | 0.41 Ir (III)* | |
| $S_{14}$ | 4.69 | 264 | 0.001 | 0.86 Ir (III)-> 1a |  |

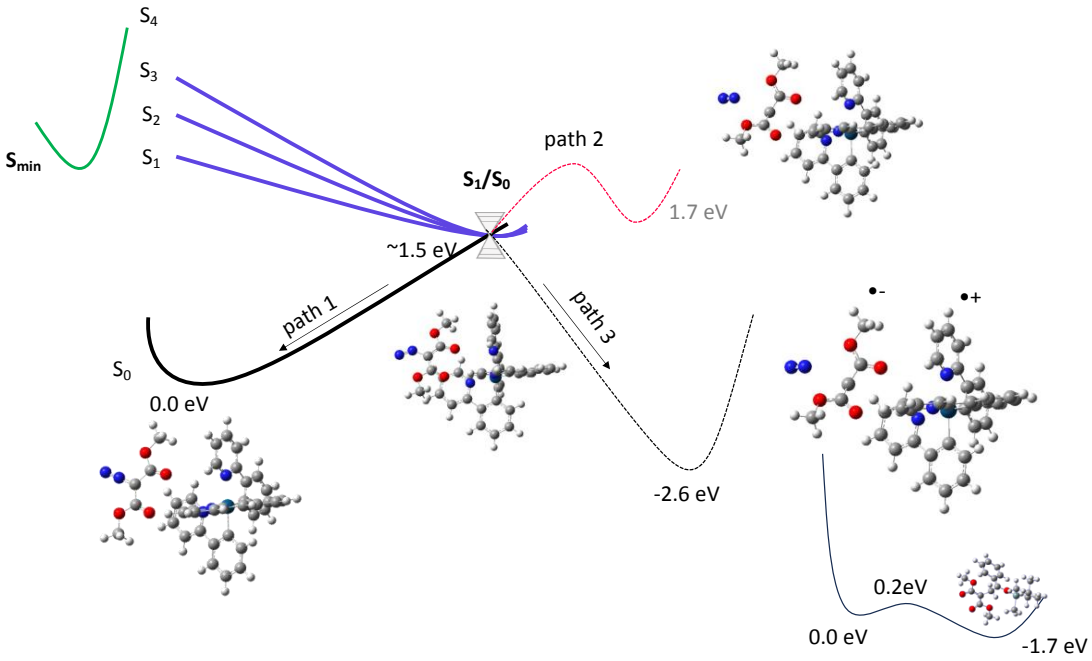



**Figure S17.** Potential Energy Surface at the M062X/ 6-31g(d,p)/LANL2DZ level of theory.

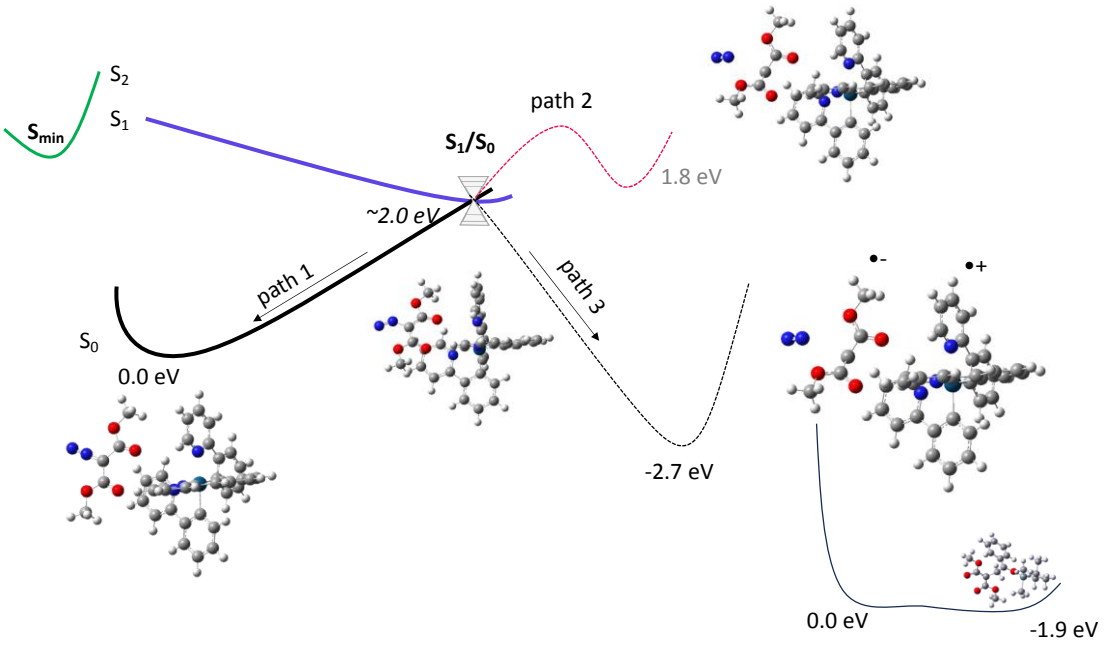



**Figure S18.** Potential Energy Surface at the B3LYP/ 6-31g(d,p)/LANL2DZ level of theory.

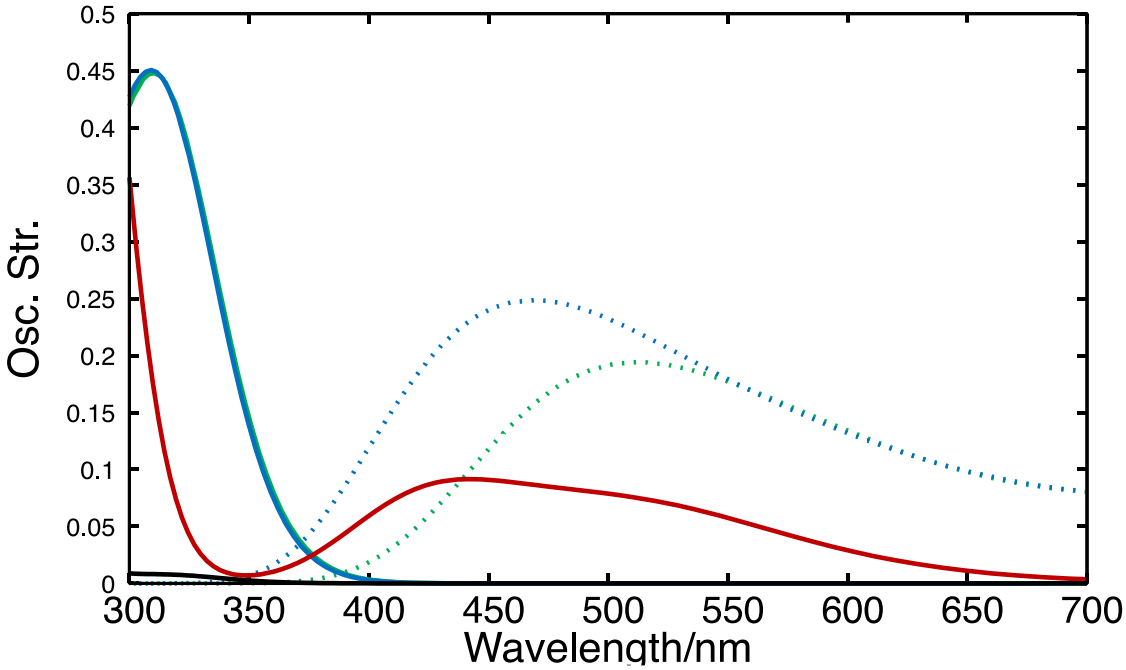



**Figure S19.** Absorption spectrum for the different optimized species computed at the M062X/ 6-31g(d,p)/LANL2DZ. Solid green= $S_0$ Ir (III)+ **1a**; dashed green= $S_{min}$ Ir (III)+ **1a**; solid blue= $S_0$ Ir (III); dashed blue= $S_{min}$ Ir (III); red= $S_0$ Ir (IV); black= $S_0$ **1a'**.

**Table S7.** Cartesian coordinates for the ground state optimized minimum at the *M062X/ 6-31g(d,p)/LANL2DZ* level of theory.

| | | | |
|---|---|---|---|
| Ir | 1.178601 | -0.117783 | -0.109513 |
| N | -0.741991 | -0.549789 | -1.079877 |
| C | -0.888605 | -1.849091 | -1.423947 |
| C | -2.030793 | -2.259454 | -2.124112 |
| H | -2.151566 | -3.298074 | -2.407938 |
| C | -2.994776 | -1.326969 | -2.477944 |
| H | -3.876788 | -1.637690 | -3.029287 |
| C | -2.813502 | 0.010628 | -2.128368 |
| H | -3.533934 | 0.774055 | -2.398604 |
| C | -1.670709 | 0.349216 | -1.417782 |
| H | -1.472195 | 1.370971 | -1.106407 |
| C | 0.237010 | -2.720146 | -1.041097 |
| C | 1.349614 | -2.085369 | -0.424872 |
| C | 2.434123 | -2.915334 | -0.091185 |
| H | 3.308187 | -2.471483 | 0.378281 |
| C | 2.423908 | -4.283592 | -0.348123 |
| C | 1.316302 | -4.884487 | -0.950487 |
| H | 1.305004 | -5.951524 | -1.147176 |
| C | 0.225556 | -4.098551 | -1.294664 |
| H | -0.635765 | -4.568208 | -1.761060 |

| | | | |
|---|---|---|---|
| H | 3.284099 | -4.890008 | -0.076680 |
| C | 2.911450 | 0.074783 | 0.874810 |
| C | 2.865552 | -0.150375 | 2.276918 |
| C | 4.014304 | -0.060666 | 3.073593 |
| H | 3.960304 | -0.239835 | 4.143653 |
| C | 5.240065 | 0.257063 | 2.504325 |
| H | 6.129046 | 0.324801 | 3.122903 |
| C | 5.310783 | 0.488924 | 1.129387 |
| H | 6.265316 | 0.738939 | 0.673588 |
| C | 4.168759 | 0.400353 | 0.337205 |
| H | 4.252691 | 0.579616 | -0.731570 |
| C | 1.546628 | -0.489768 | 2.842594 |
| N | 0.540368 | -0.529017 | 1.939009 |
| C | -0.708105 | -0.819364 | 2.318866 |
| H | -1.465340 | -0.815761 | 1.542845 |
| C | -1.031590 | -1.089511 | 3.641898 |
| C | -0.012325 | -1.057755 | 4.589787 |
| H | -0.222441 | -1.265549 | 5.634022 |
| C | 1.282943 | -0.756603 | 4.190123 |
| H | 2.084016 | -0.729487 | 4.918606 |
| H | -2.057020 | -1.317347 | 3.907203 |
| N | 0.859872 | 2.046734 | 0.000327 |
| C | 1.308968 | 2.712333 | -1.089267 |
| C | 1.197029 | 4.106828 | -1.147306 |
| H | 1.555906 | 4.646856 | -2.014733 |
| C | 0.627452 | 4.795853 | -0.086761 |
| H | 0.542852 | 5.876893 | -0.124511 |
| C | 0.167323 | 4.089226 | 1.023077 |
| H | -0.284667 | 4.589966 | 1.871023 |
| C | 0.301640 | 2.707906 | 1.019537 |
| H | -0.049119 | 2.095711 | 1.845027 |
| C | 1.883789 | 1.855785 | -2.143018 |
| C | 1.906874 | 0.459187 | -1.881896 |
| C | 2.450267 | -0.354842 | -2.890834 |
| H | 2.489883 | -1.429532 | -2.731974 |
| C | 2.949384 | 0.174384 | -4.077978 |
| C | 2.921635 | 1.551902 | -4.307708 |
| H | 3.311491 | 1.965919 | -5.231825 |
| C | 2.386379 | 2.388314 | -3.338098 |
| H | 2.365326 | 3.459126 | -3.519412 |
| H | 3.365675 | -0.488667 | -4.831904 |
| C | -3.810099 | 1.508515 | 0.875574 |
| O | -2.718642 | 1.309737 | 1.356726 |
| O | -4.327772 | 2.725949 | 0.653947 |
| C | -3.475446 | 3.820308 | 1.008734 |
| H | -4.051614 | 4.719734 | 0.804249 |
| H | -3.207595 | 3.764927 | 2.065339 |

| | | | |
|---|---|---|---|
| H | -2.565093 | 3.799223 | 0.405959 |
| C | -4.440584 | -0.976369 | 0.440909 |
| O | -3.481774 | -1.484295 | 0.972660 |
| O | -5.384563 | -1.659899 | -0.221930 |
| C | -5.205240 | -3.080854 | -0.234016 |
| H | -5.242280 | -3.473817 | 0.783257 |
| H | -6.026319 | -3.475162 | -0.828247 |
| H | -4.243437 | -3.331404 | -0.684612 |
| C | -4.731880 | 0.460254 | 0.432082 |
| N | -5.867433 | 0.846178 | -0.129782 |
| N | -6.829298 | 1.171358 | -0.599463 |

**Table S8.** Cartesian coordinates for the $S_1/S_0$ at the *M062X/ 6-31g(d,p)/LANL2DZ* level of theory.

| | | | |
|---|---|---|---|
| Ir | 1.143755 | -0.143743 | -0.142525 |
| N | -0.860248 | -0.231281 | -1.043207 |
| C | -1.162671 | -1.448615 | -1.553389 |
| C | -2.360758 | -1.632878 | -2.259060 |
| H | -2.597285 | -2.601371 | -2.681653 |
| C | -3.223777 | -0.564343 | -2.443934 |
| H | -4.149358 | -0.697719 | -2.994542 |
| C | -2.882859 | 0.687066 | -1.925005 |
| H | -3.517061 | 1.556506 | -2.064512 |
| C | -1.686435 | 0.799027 | -1.227974 |
| H | -1.362430 | 1.743845 | -0.799424 |
| C | -0.133905 | -2.478670 | -1.343732 |
| C | 1.071397 | -2.055328 | -0.719641 |
| C | 2.065007 | -3.036269 | -0.555687 |
| H | 3.004947 | -2.756963 | -0.086851 |
| C | 1.882156 | -4.349269 | -0.979071 |
| C | 0.685096 | -4.742093 | -1.583999 |
| H | 0.540320 | -5.767267 | -1.908241 |
| C | -0.319885 | -3.803645 | -1.763779 |
| H | -1.251370 | -4.111070 | -2.230707 |
| H | 2.676243 | -5.077319 | -0.835799 |
| C | 2.942902 | -0.262501 | 0.724993 |
| C | 2.958208 | -0.647870 | 2.091995 |
| C | 4.156840 | -0.765784 | 2.808067 |
| H | 4.149845 | -1.063588 | 3.852562 |
| C | 5.372285 | -0.506357 | 2.189639 |
| H | 6.299444 | -0.599692 | 2.745647 |
| C | 5.383704 | -0.124203 | 0.846805 |
| H | 6.329926 | 0.081113 | 0.353075 |
| C | 4.192598 | -0.004553 | 0.135180 |
| H | 4.229452 | 0.290854 | -0.910172 |
| C | 1.648248 | -0.928649 | 2.707996 |

| | | | |
|---|---|---|---|
| N | 0.590203 | -0.772456 | 1.878096 |
| C | -0.652440 | -1.014770 | 2.309203 |
| H | -1.448754 | -0.880730 | 1.587872 |
| C | -0.919820 | -1.414744 | 3.611457 |
| C | 0.152583 | -1.573040 | 4.485028 |
| H | -0.012032 | -1.886458 | 5.510897 |
| C | 1.442577 | -1.332748 | 4.031559 |
| H | 2.285334 | -1.459660 | 4.699735 |
| H | -1.943115 | -1.597115 | 3.917394 |
| N | 1.074677 | 2.003013 | 0.284932 |
| C | 1.522243 | 2.770189 | -0.736162 |
| C | 1.557833 | 4.163165 | -0.594931 |
| H | 1.915588 | 4.783982 | -1.406923 |
| C | 1.136282 | 4.745864 | 0.590974 |
| H | 1.165633 | 5.824224 | 0.706531 |
| C | 0.677569 | 3.936172 | 1.629366 |
| H | 0.338481 | 4.352568 | 2.570537 |
| C | 0.662240 | 2.563067 | 1.427615 |
| H | 0.309711 | 1.875224 | 2.191209 |
| C | 1.930762 | 2.020804 | -1.938478 |
| C | 1.818494 | 0.605520 | -1.872675 |
| C | 2.198850 | -0.102926 | -3.024980 |
| H | 2.128487 | -1.187660 | -3.020433 |
| C | 2.674566 | 0.539952 | -4.164728 |
| C | 2.785101 | 1.931735 | -4.200238 |
| H | 3.156814 | 2.434202 | -5.087143 |
| C | 2.409532 | 2.668034 | -3.085694 |
| H | 2.494139 | 3.750458 | -3.116558 |
| H | 2.963932 | -0.045380 | -5.033482 |
| C | -3.684888 | 1.571654 | 1.121529 |
| O | -2.769658 | 1.197819 | 1.814272 |
| O | -3.933998 | 2.845041 | 0.840004 |
| C | -3.016835 | 3.779935 | 1.424967 |
| H | -3.375550 | 4.763227 | 1.131339 |
| H | -3.011577 | 3.674032 | 2.511433 |
| H | -2.007198 | 3.607366 | 1.044154 |
| C | -4.446969 | -0.841778 | 0.485033 |
| O | -3.535729 | -1.386853 | 1.065608 |
| O | -5.377765 | -1.499117 | -0.188701 |
| C | -5.247698 | -2.927312 | -0.157226 |
| H | -5.339306 | -3.288478 | 0.868364 |
| H | -6.057653 | -3.307079 | -0.774500 |
| H | -4.278238 | -3.223944 | -0.560138 |
| C | -4.663277 | 0.661164 | 0.430998 |
| N | -5.682497 | 1.311994 | -0.187914 |
| N | -6.596193 | 0.734007 | -0.787169 |

**Table S9.** Cartesian coordinates for the 1a' optimized minimum at the *M062X/ 6-31g(d,p)/LANL2DZ* level of theory.

| | | | |
|---|---|---|---|
| Ir | 1.162390 | -0.094124 | -0.186665 |
| N | -0.840564 | -0.406607 | -1.014145 |
| C | -0.986026 | -1.586626 | -1.657036 |
| C | -2.208869 | -1.897182 | -2.269666 |
| H | -2.333378 | -2.839014 | -2.790102 |
| C | -3.254620 | -0.987910 | -2.221385 |
| H | -4.200963 | -1.219369 | -2.701149 |
| C | -3.078193 | 0.228839 | -1.561746 |
| H | -3.864079 | 0.973019 | -1.508045 |
| C | -1.846412 | 0.470721 | -0.973681 |
| H | -1.628929 | 1.397159 | -0.452484 |
| C | 0.218730 | -2.432545 | -1.665071 |
| C | 1.373837 | -1.893932 | -1.034746 |
| C | 2.530063 | -2.692850 | -1.071579 |
| H | 3.439788 | -2.320408 | -0.607936 |
| C | 2.547218 | -3.939852 | -1.689956 |
| C | 1.397381 | -4.447696 | -2.299353 |
| H | 1.409660 | -5.420975 | -2.778710 |
| C | 0.235429 | -3.690080 | -2.284158 |
| H | -0.658032 | -4.085191 | -2.759027 |
| H | 3.463271 | -4.524669 | -1.698380 |
| C | 2.989699 | -0.047966 | 0.629379 |
| C | 3.107281 | -0.599477 | 1.933520 |
| C | 4.336735 | -0.645010 | 2.603561 |
| H | 4.408887 | -1.076337 | 3.597966 |
| C | 5.482402 | -0.143444 | 2.000992 |
| H | 6.434300 | -0.181201 | 2.520506 |
| C | 5.392162 | 0.408020 | 0.721324 |
| H | 6.283566 | 0.803000 | 0.241050 |
| C | 4.169998 | 0.453729 | 0.055217 |
| H | 4.127084 | 0.880254 | -0.943760 |
| C | 1.868813 | -1.127303 | 2.535228 |
| N | 0.775592 | -1.031568 | 1.743962 |
| C | -0.415684 | -1.459844 | 2.172016 |
| H | -1.246419 | -1.339907 | 1.486064 |
| C | -0.595378 | -2.015153 | 3.430596 |
| C | 0.516628 | -2.127128 | 4.261876 |
| H | 0.422234 | -2.555837 | 5.254224 |
| C | 1.753557 | -1.682783 | 3.814087 |
| H | 2.623561 | -1.762014 | 4.454316 |
| H | -1.581639 | -2.342894 | 3.735951 |
| N | 0.784497 | 1.942812 | 0.536697 |
| C | 1.016091 | 2.895471 | -0.397515 |

| | | | |
|---|---|---|---|
| C | 0.842224 | 4.246153 | -0.069966 |
| H | 1.022317 | 5.014505 | -0.811532 |
| C | 0.454971 | 4.598821 | 1.215459 |
| H | 0.328369 | 5.644512 | 1.476026 |
| C | 0.235552 | 3.601994 | 2.164089 |
| H | -0.065692 | 3.834770 | 3.178257 |
| C | 0.407510 | 2.281289 | 1.774189 |
| H | 0.236725 | 1.457166 | 2.459432 |
| C | 1.463921 | 2.382487 | -1.705730 |
| C | 1.623603 | 0.974548 | -1.815958 |
| C | 2.077899 | 0.493483 | -3.056108 |
| H | 2.220720 | -0.576981 | -3.181428 |
| C | 2.357920 | 1.345108 | -4.121246 |
| C | 2.189424 | 2.725371 | -3.988907 |
| H | 2.405321 | 3.390400 | -4.818644 |
| C | 1.742549 | 3.239200 | -2.779720 |
| H | 1.615633 | 4.313273 | -2.679175 |
| H | 2.710559 | 0.933742 | -5.063416 |
| C | -3.472622 | 1.225295 | 1.563486 |
| O | -2.408473 | 1.068389 | 2.135205 |
| O | -3.861343 | 2.277964 | 0.868258 |
| C | -2.982398 | 3.421259 | 0.919593 |
| H | -3.536005 | 4.228509 | 0.447419 |
| H | -2.746353 | 3.660292 | 1.956935 |
| H | -2.057240 | 3.224264 | 0.373573 |
| C | -4.341113 | -1.092770 | 1.104647 |
| O | -3.468162 | -1.862460 | 1.457068 |
| O | -5.313537 | -1.337087 | 0.244252 |
| C | -5.362569 | -2.684165 | -0.265642 |
| H | -5.638154 | -3.368118 | 0.537971 |
| H | -6.127056 | -2.669708 | -1.038835 |
| H | -4.394710 | -2.966414 | -0.680065 |
| C | -4.431817 | 0.177053 | 1.796736 |
| N | -6.514026 | 1.182686 | -0.638920 |
| N | -6.819879 | 0.843609 | -1.638029 |

# 9. NMR Spectra

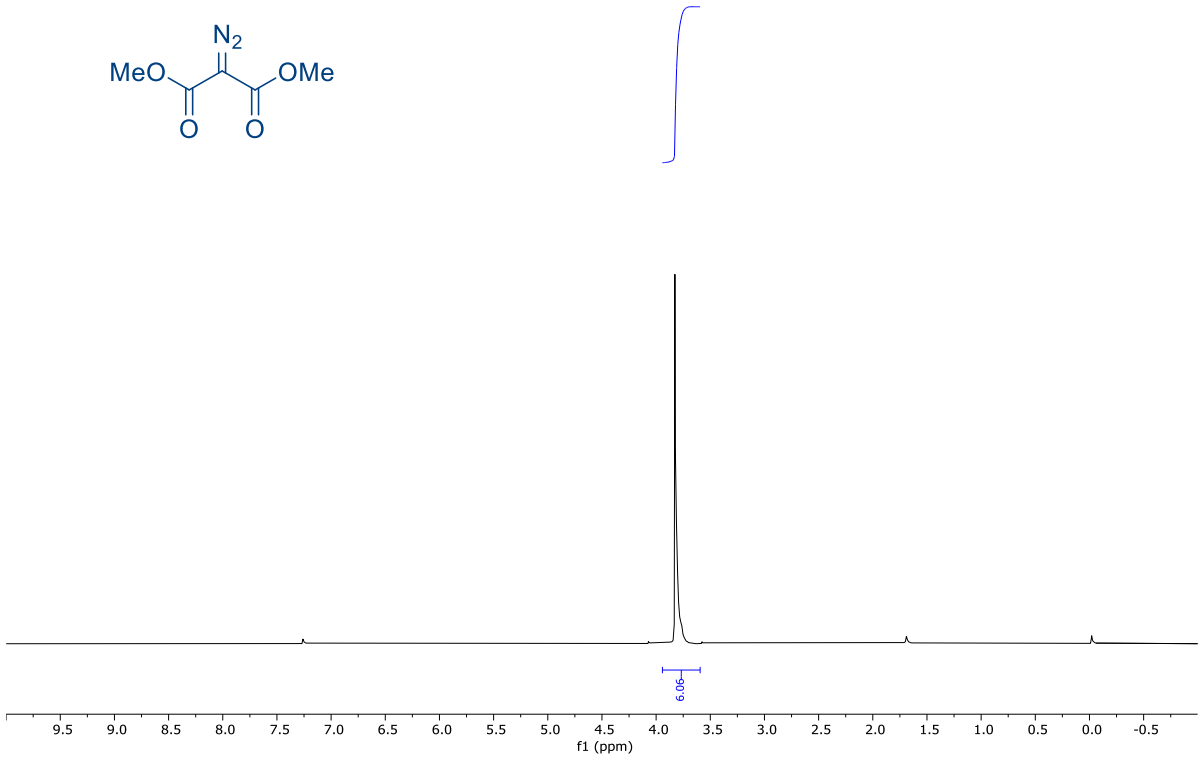



**Figure S20**. $^{1}H$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **1a**.

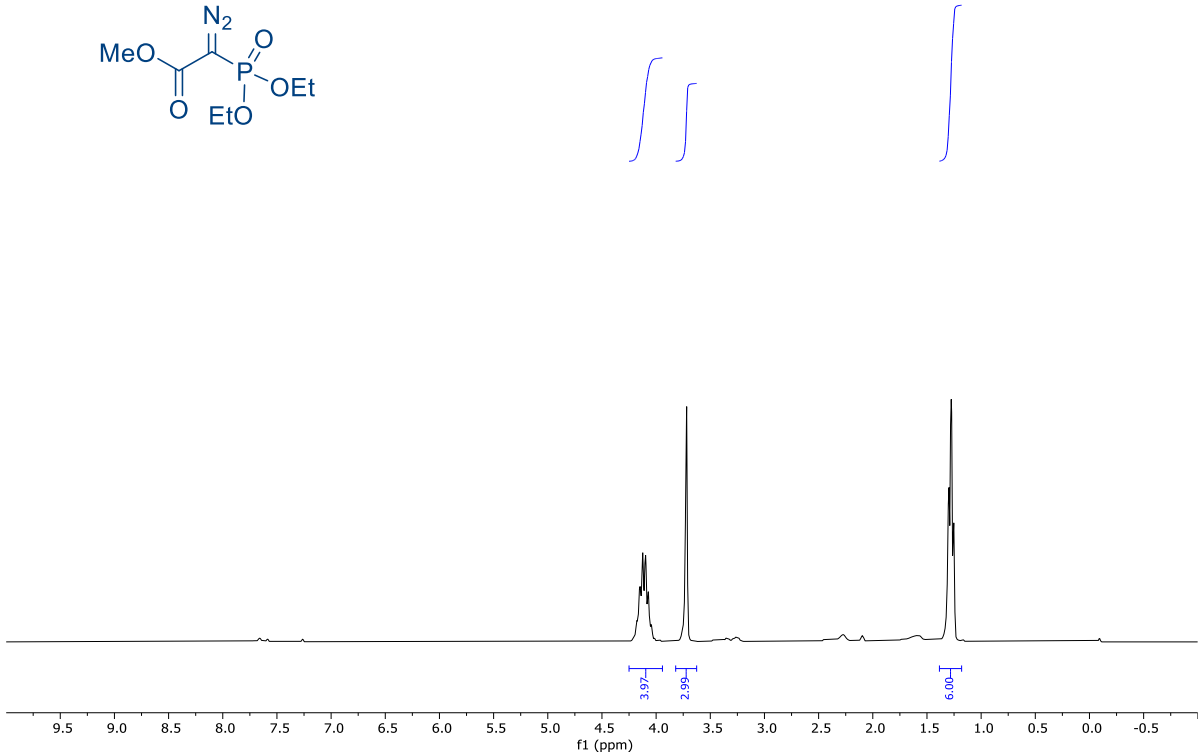



**Figure S21**. $^{1}H$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **1b**.

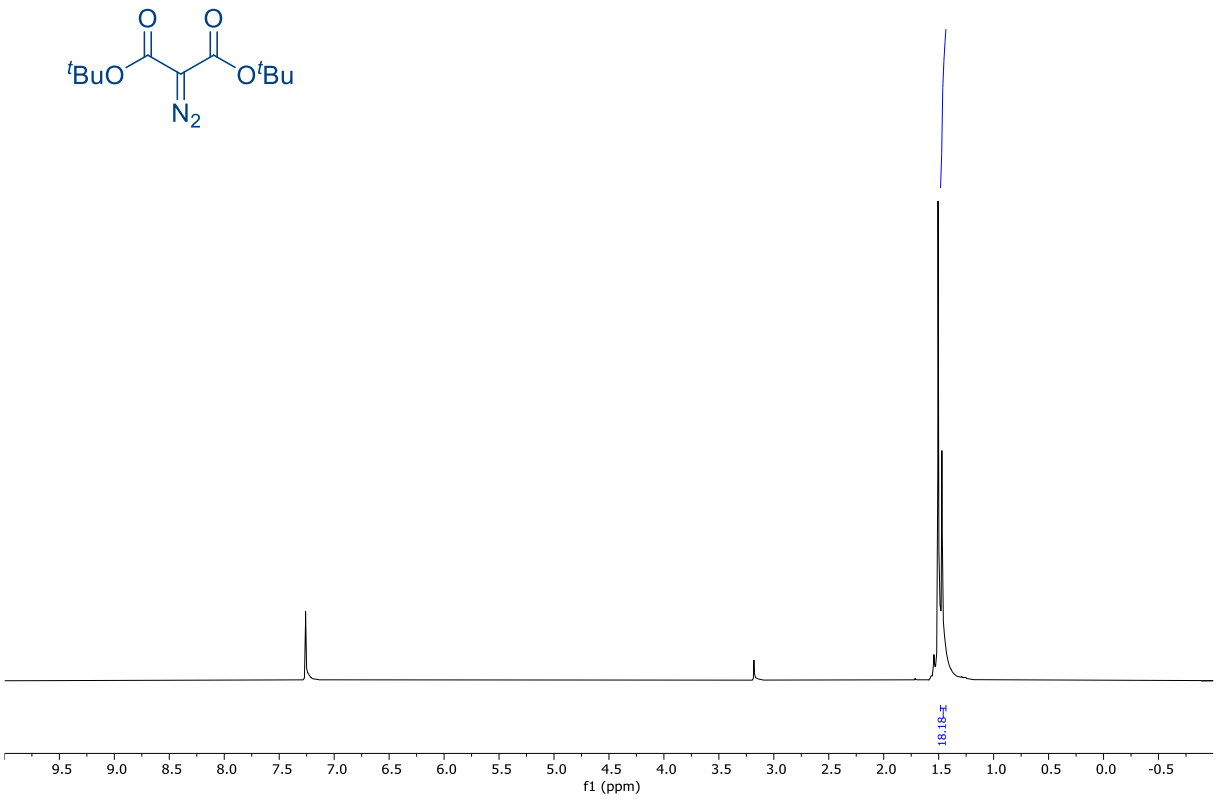



**Figure S22**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **1c**.

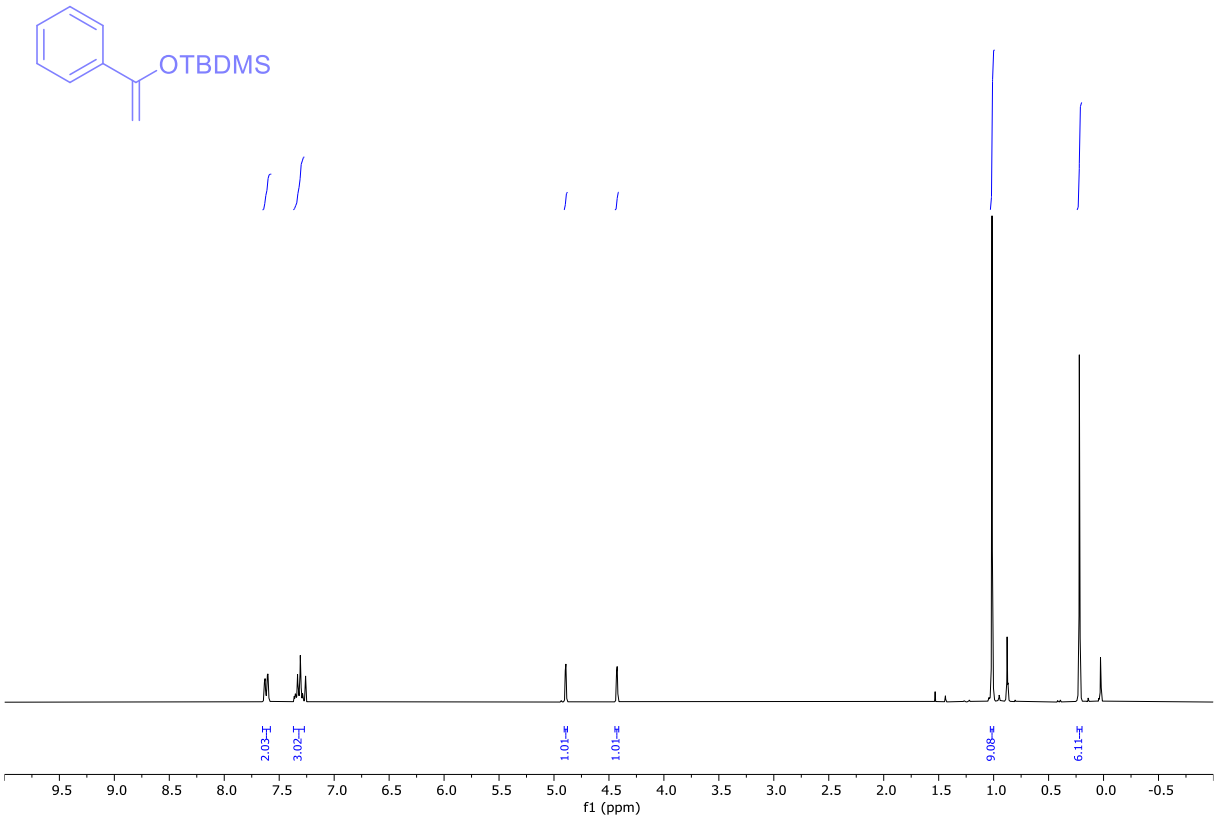



**Figure S23**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2a**.

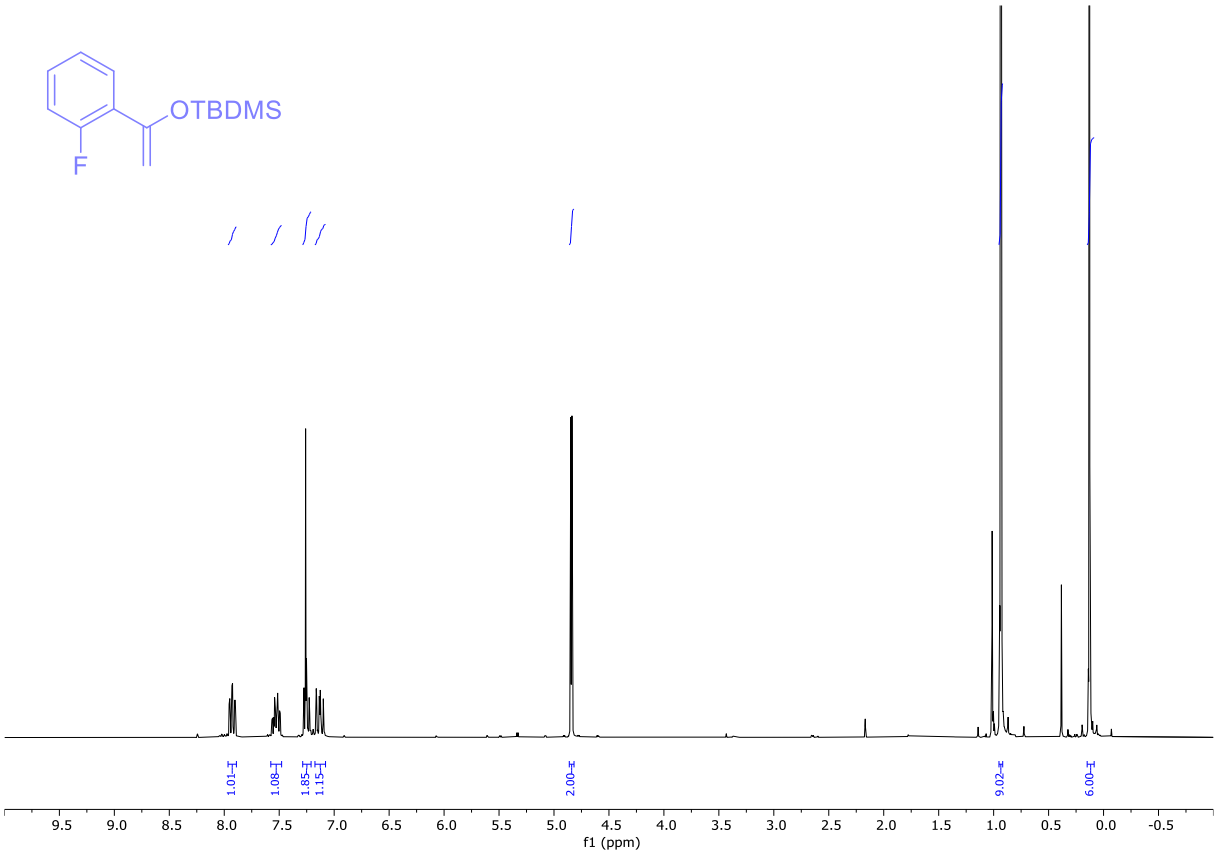



**Figure S24**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2b**.

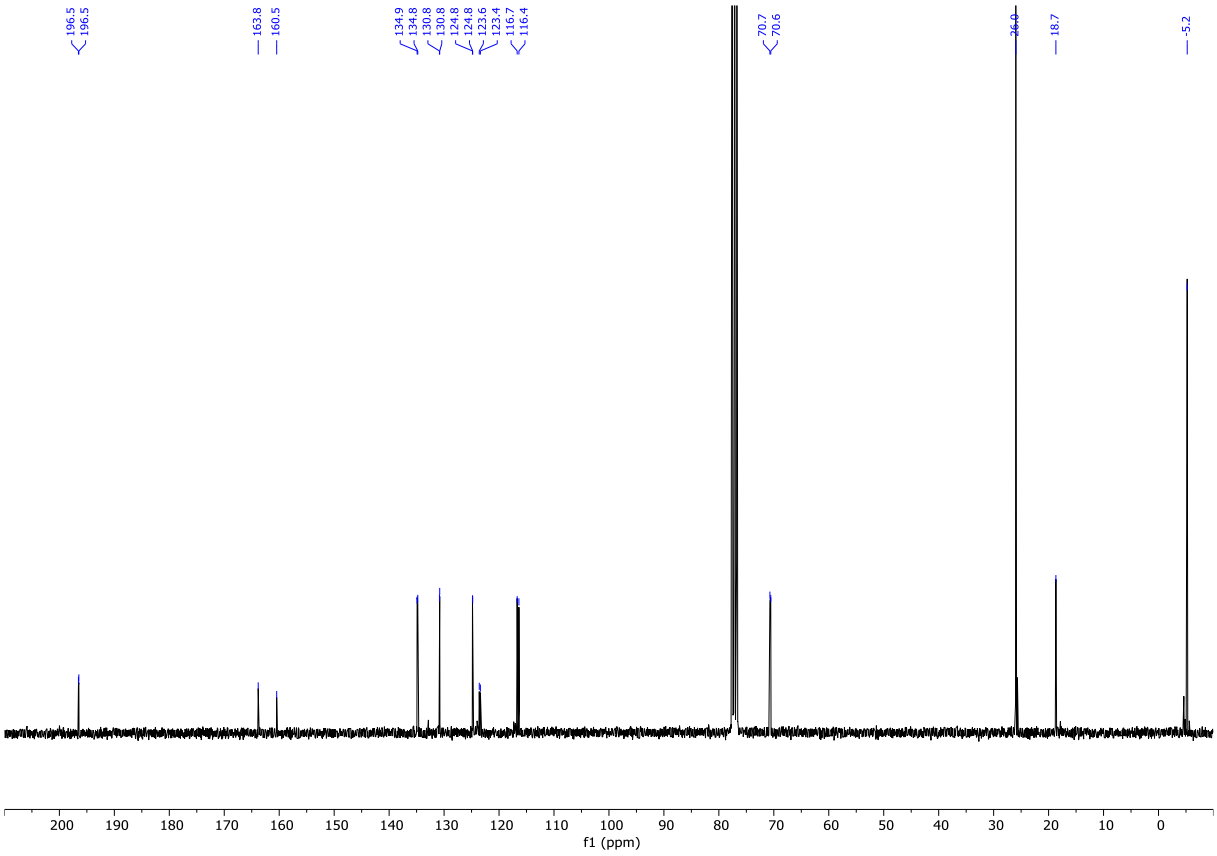



**Figure S25**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **2b**.

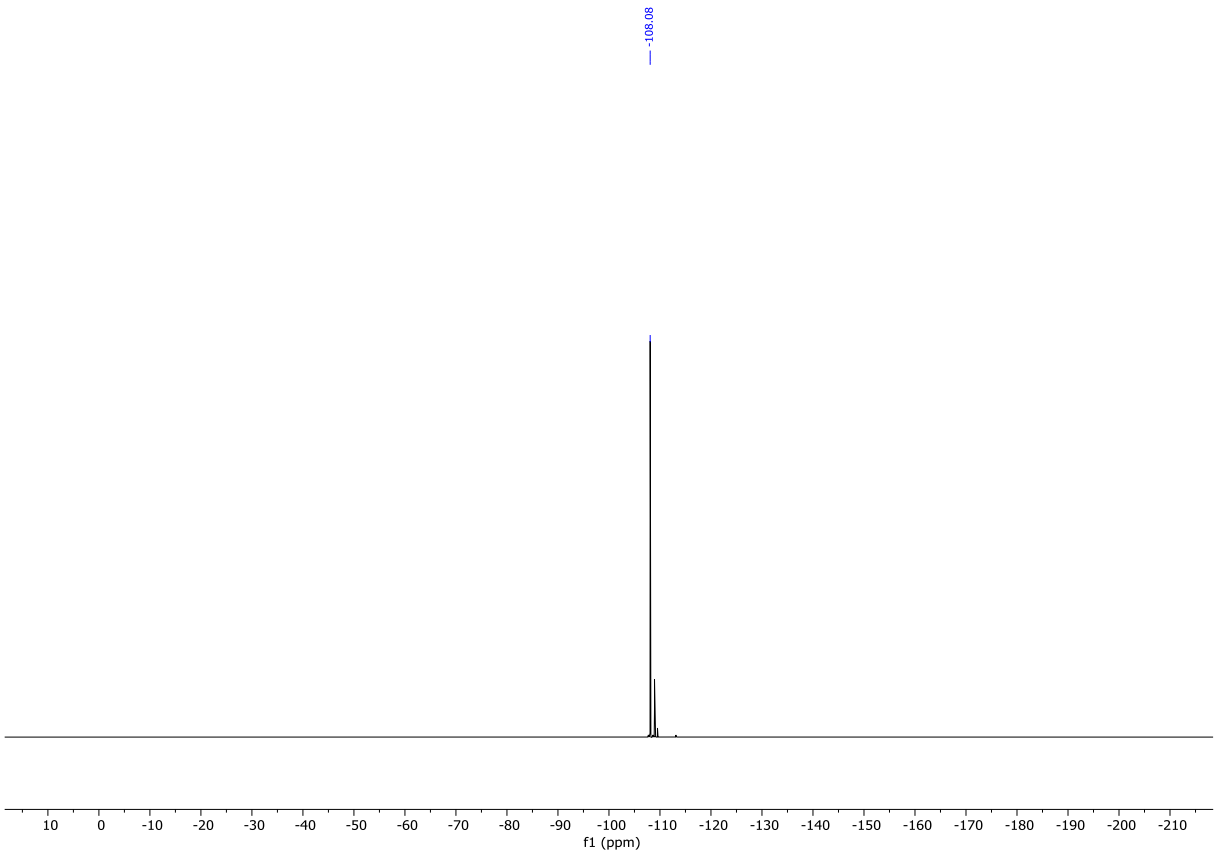



**Figure S26**. $^{19}F$ NMR spectrum (282 MHz, 298K, $CDCl_3$) of **2b**.

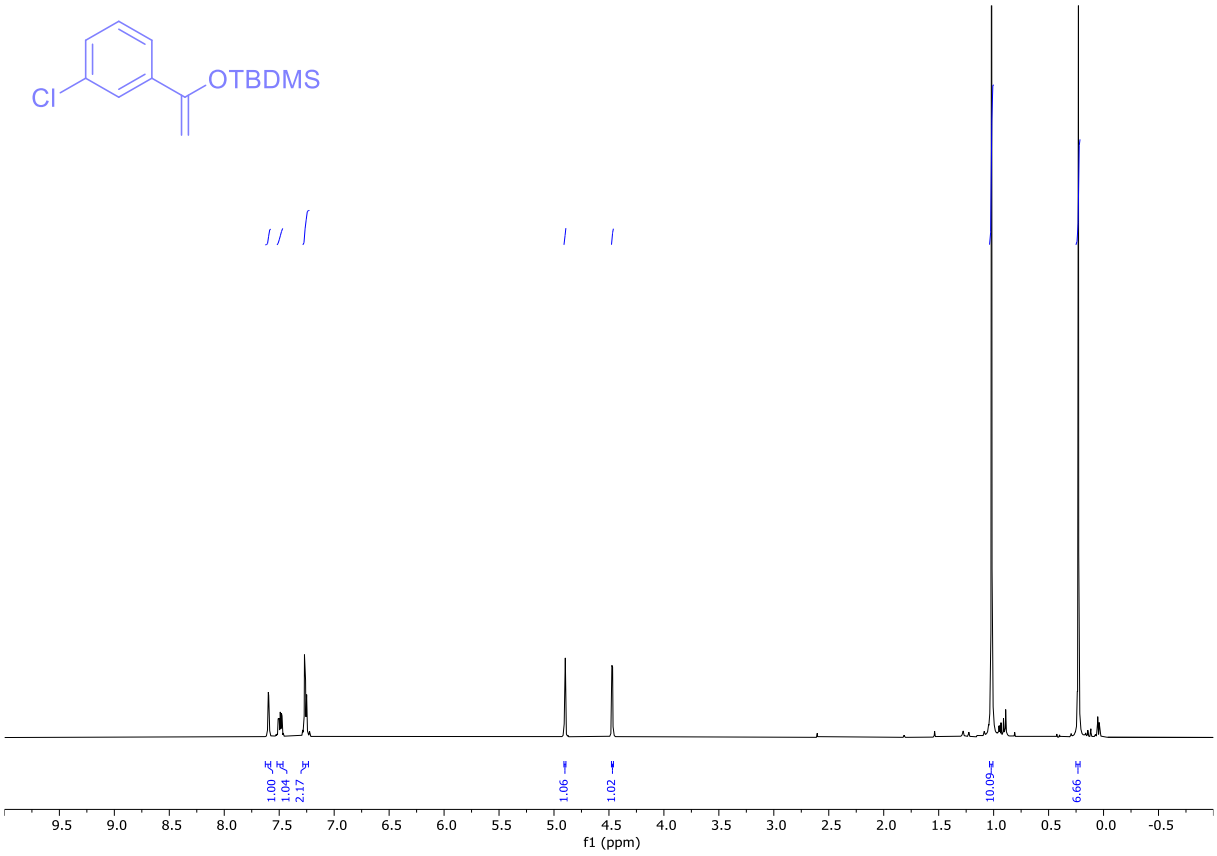



**Figure S27**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2c**.

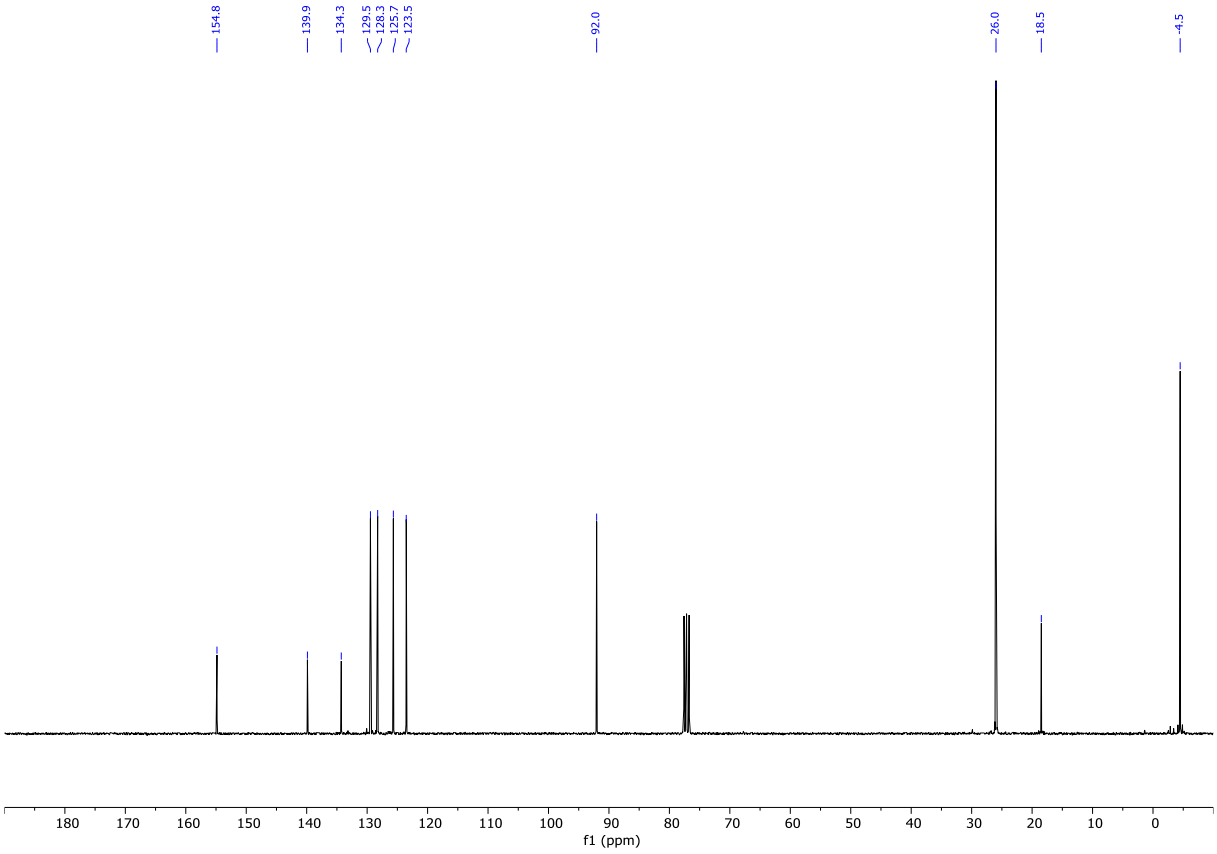



**Figure S28**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **2c**

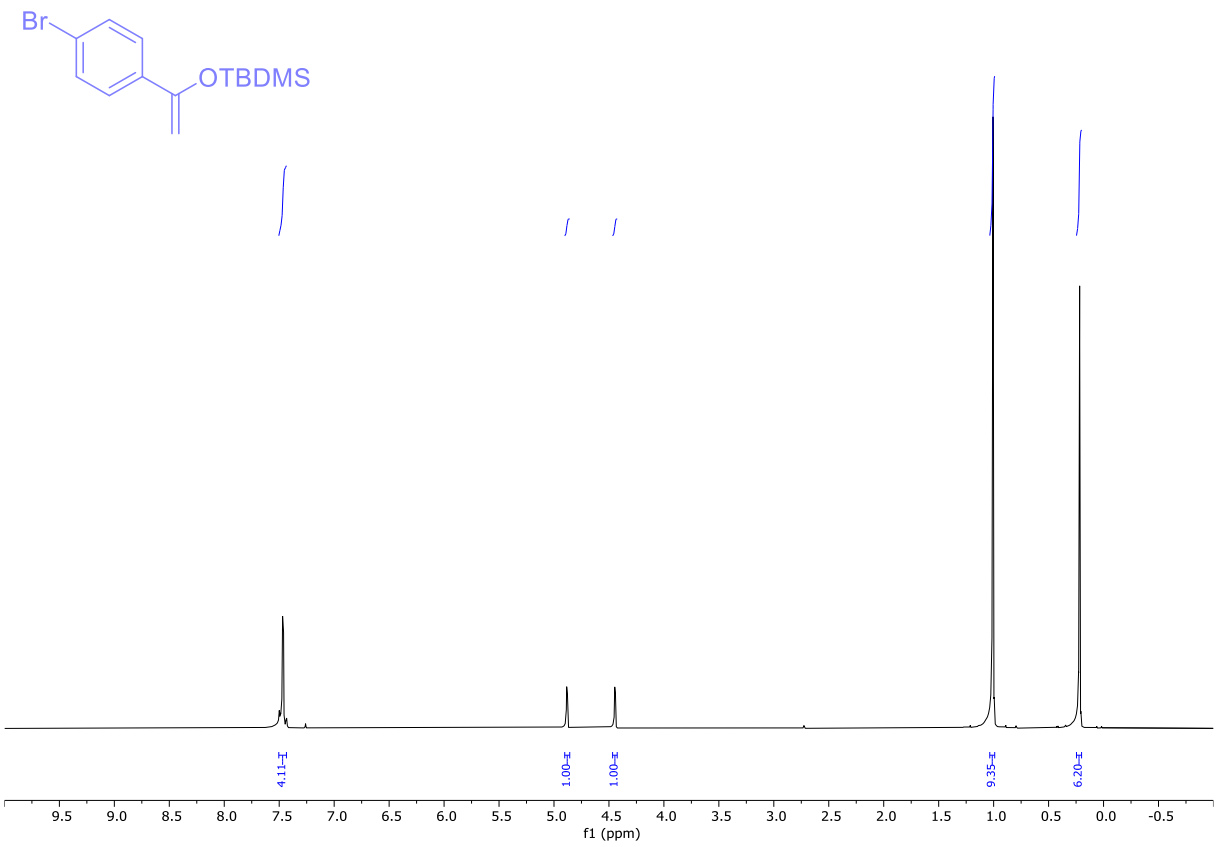



**Figure S29**. $^{1}H$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2d**.

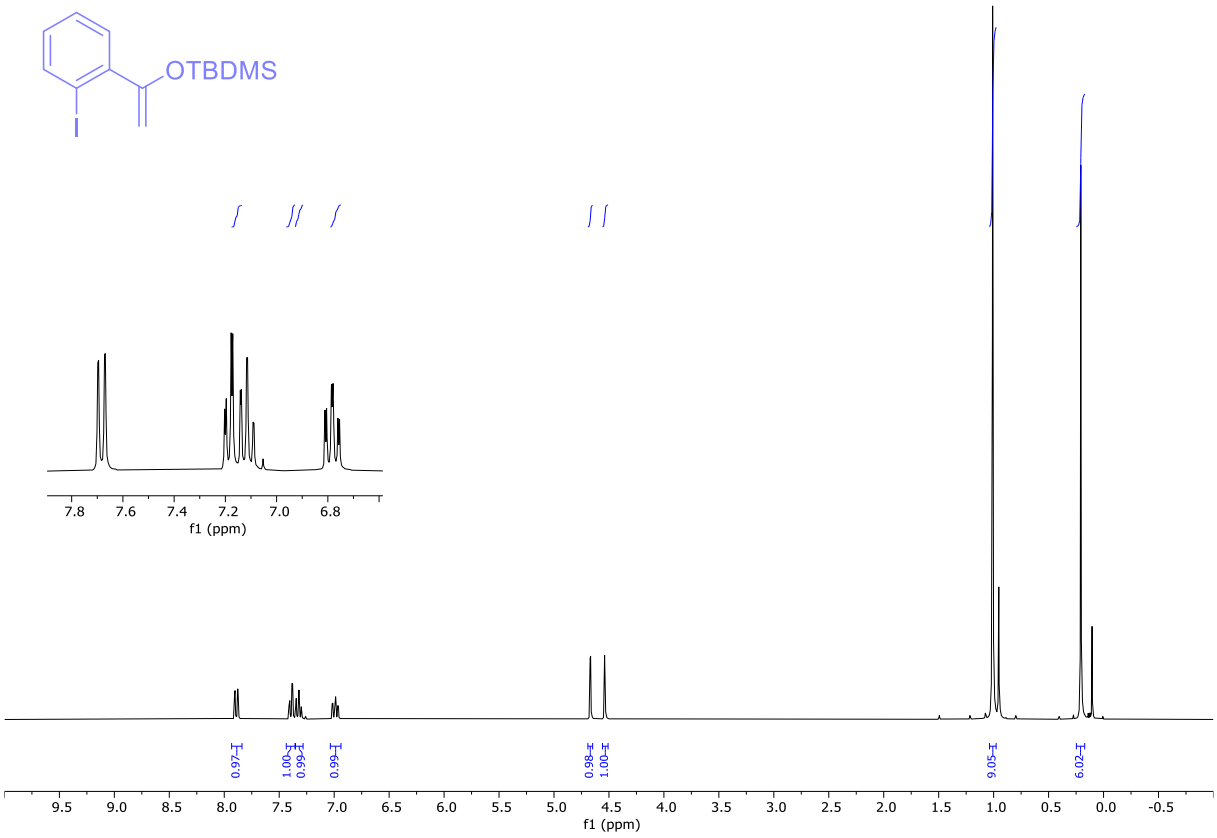



**Figure S30**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2e**.

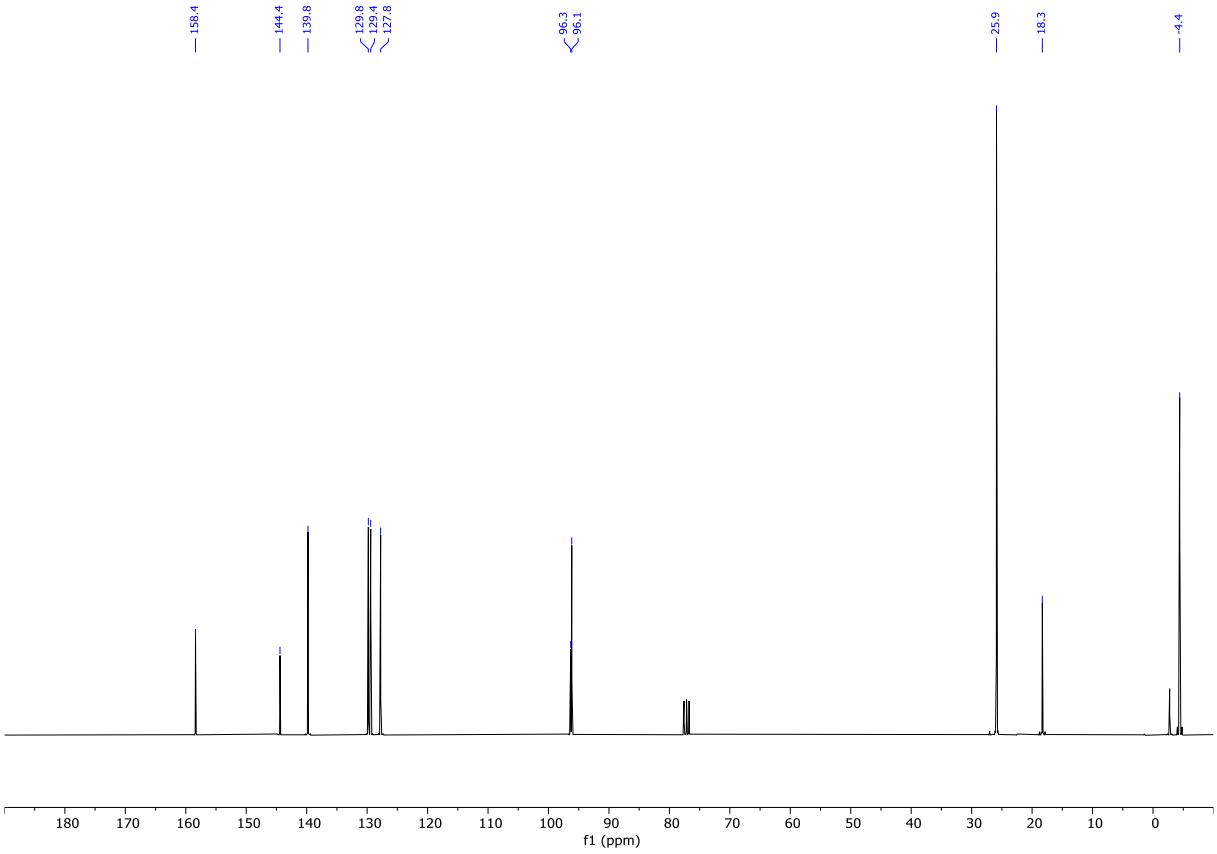



**Figure S31**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **2e**

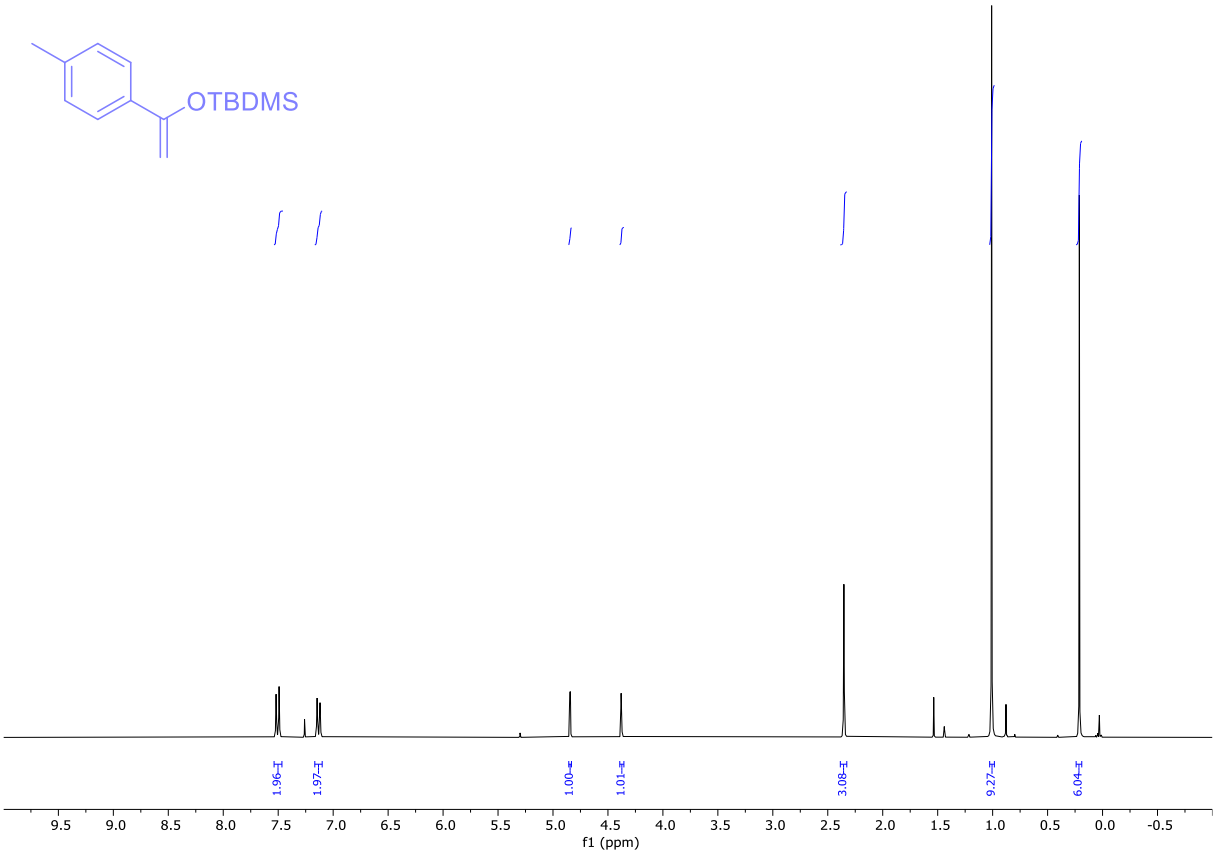



**Figure S32**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2f**.

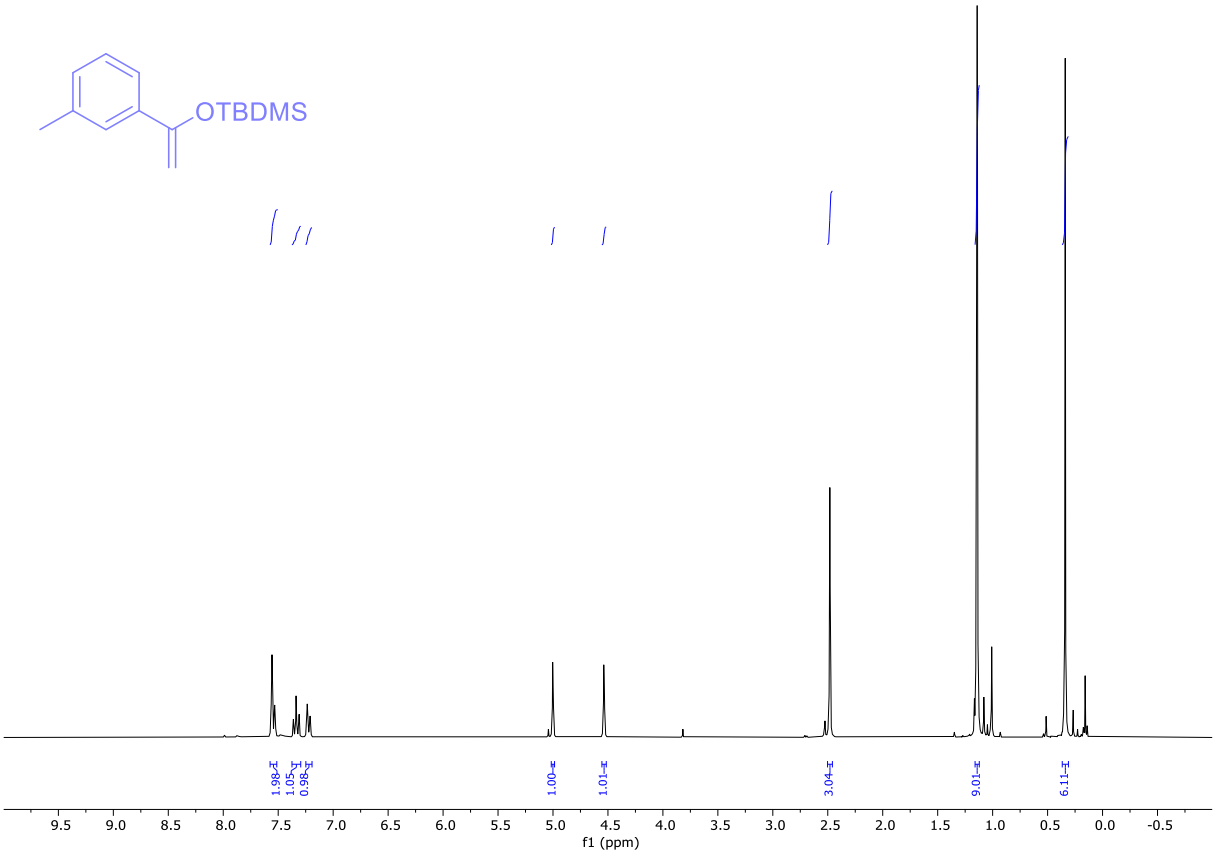



**Figure S33**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2g**.

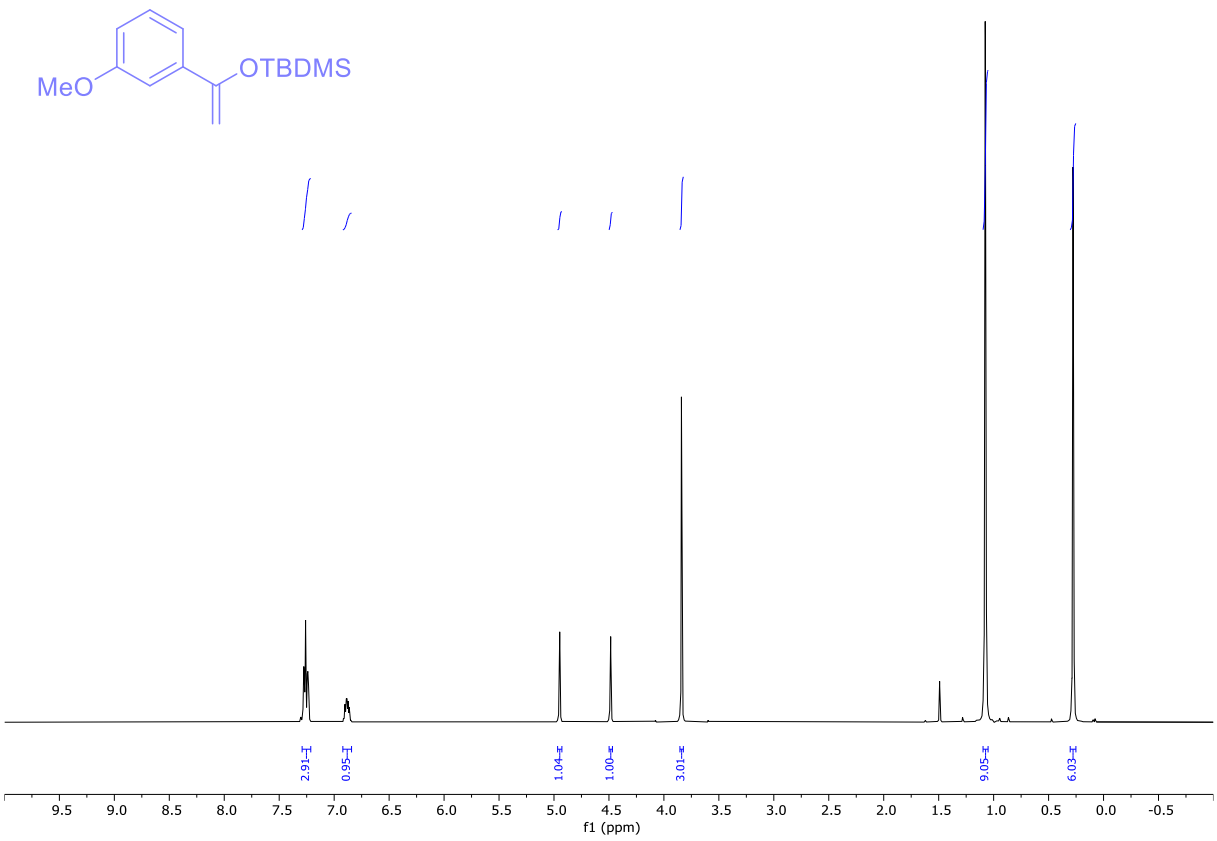



**Figure S34**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2h**.

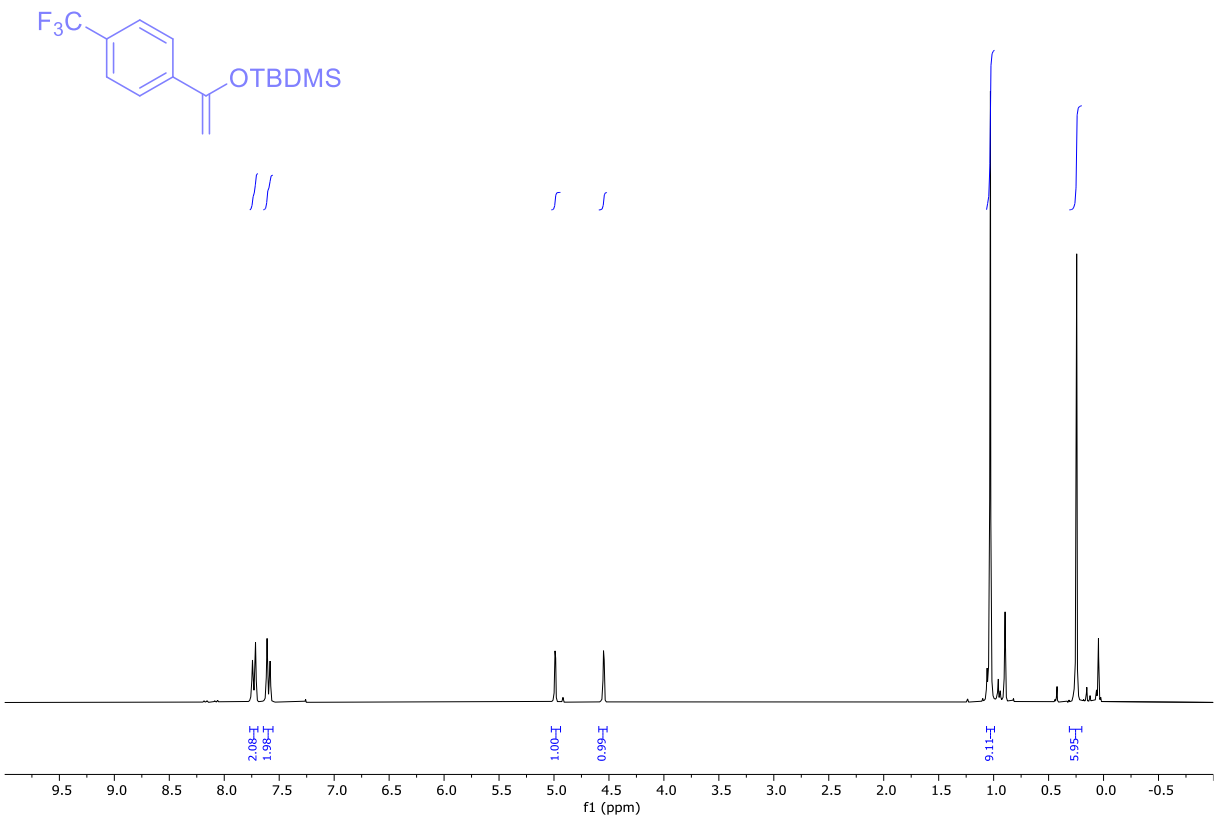



**Figure S35**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2i**.

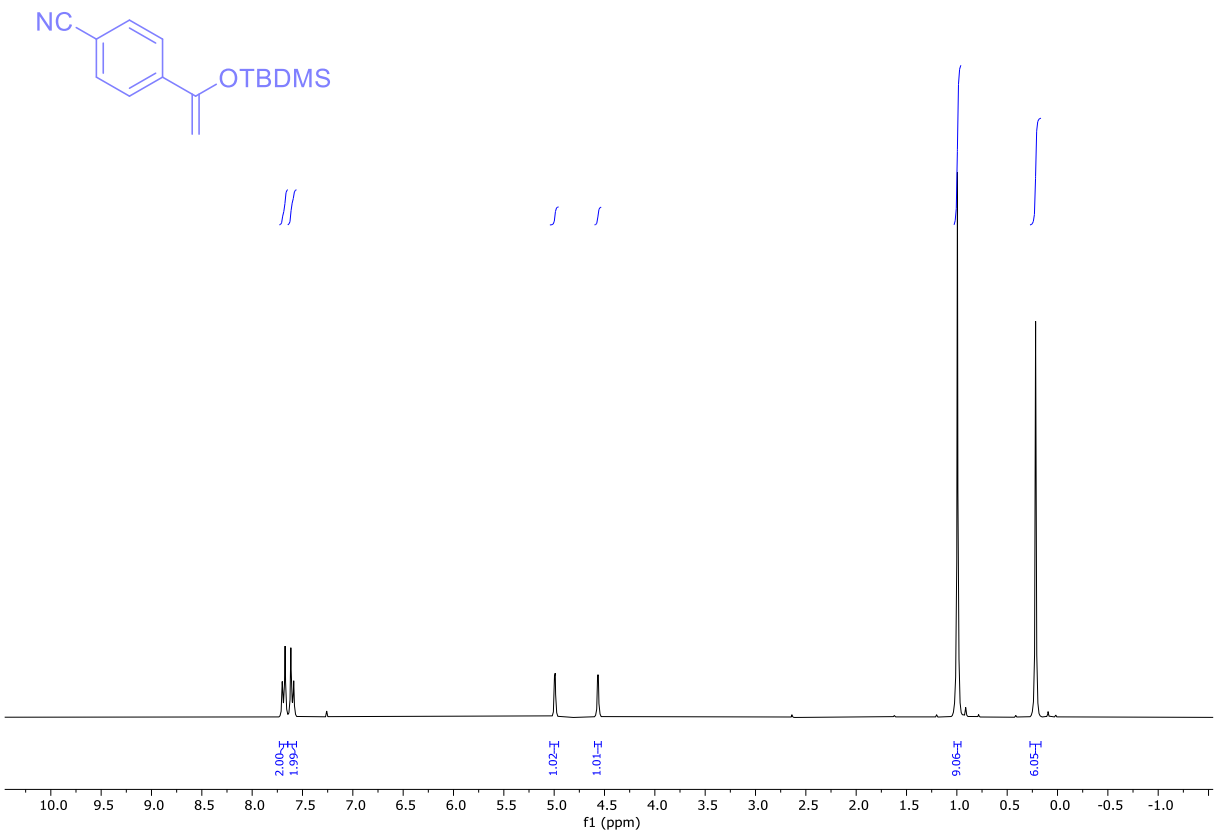



**Figure S36**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2j**.

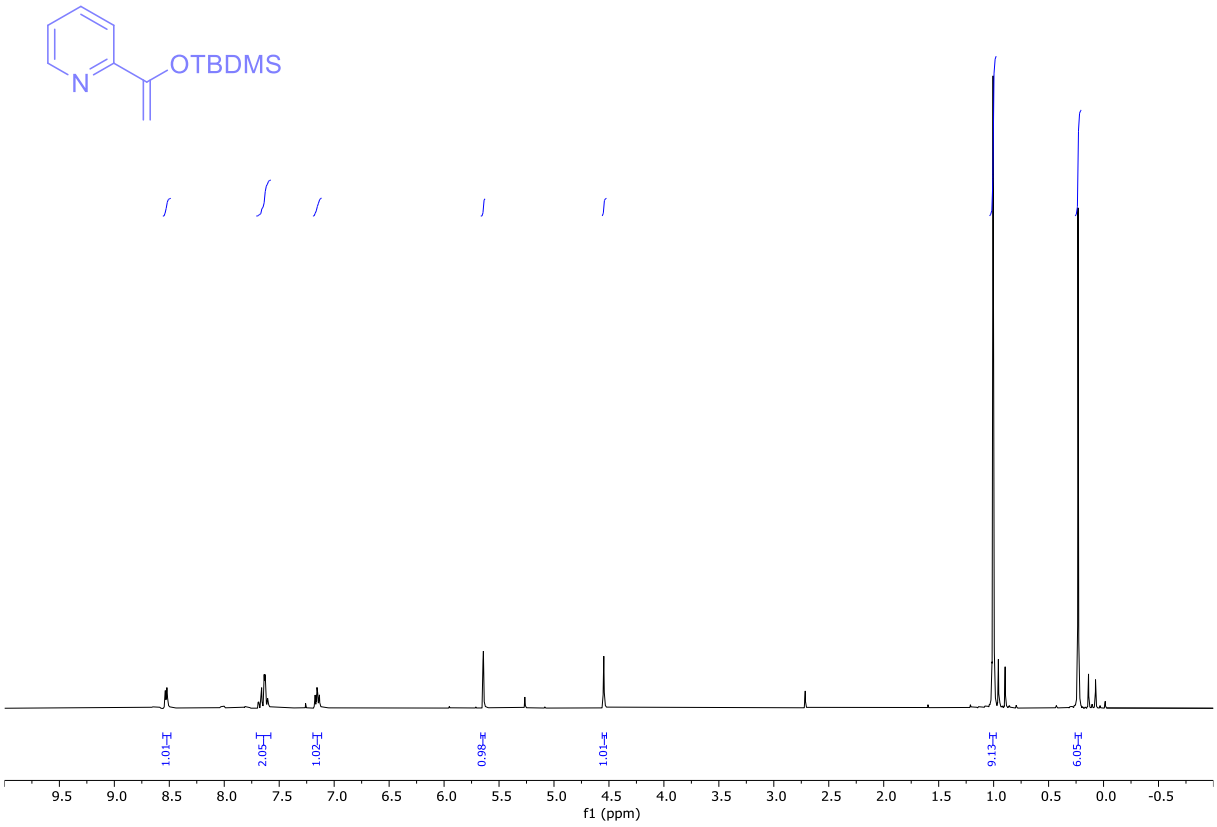



**Figure S37**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2k**.

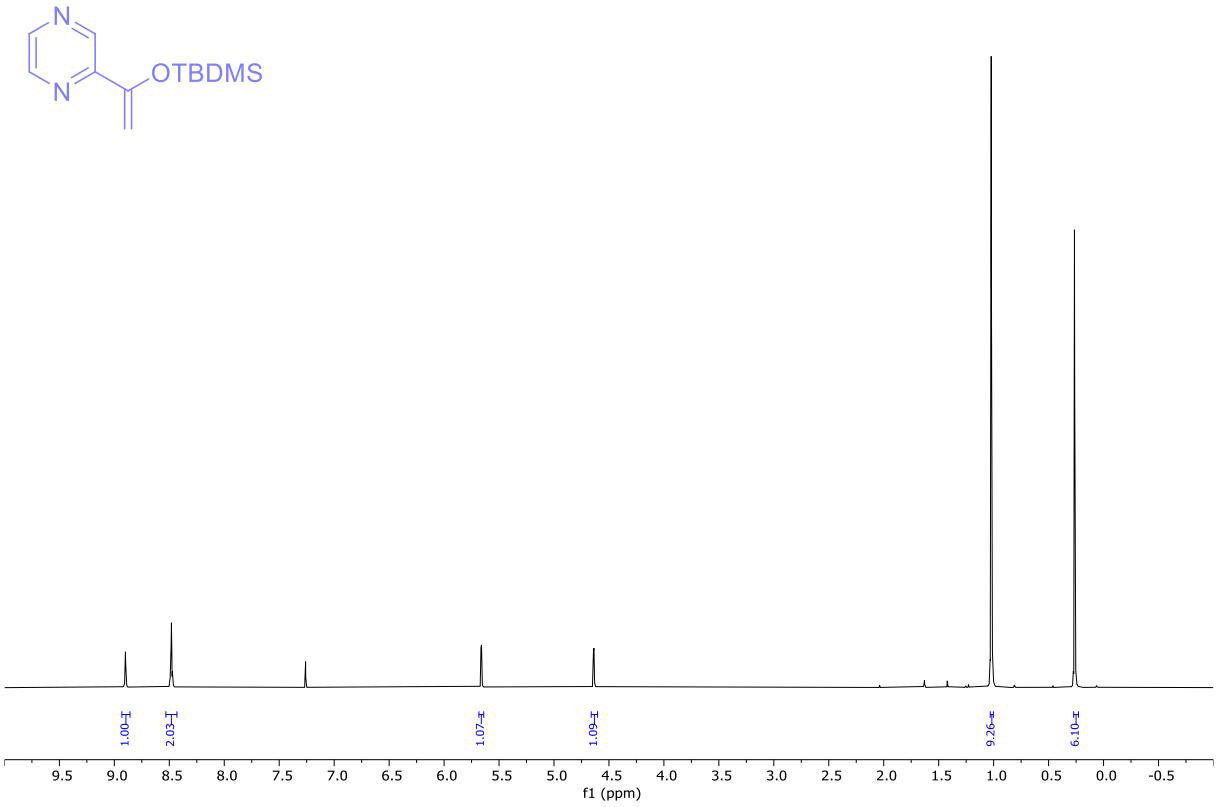



**Figure S38**. $^{1}H$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2l**.

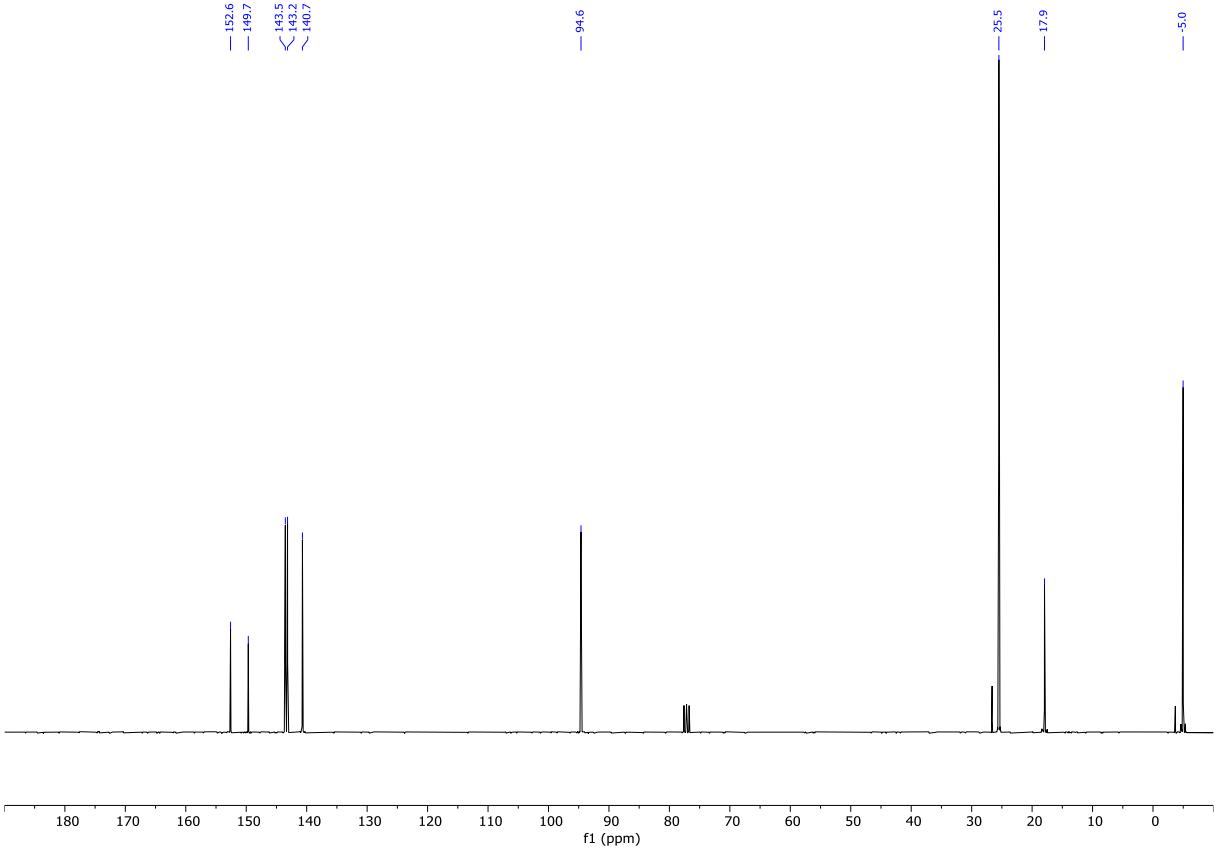



**Figure S39**. $^{13}C$ NMR spectrum (75 MHz, 298K, $CDCl_3$) of **2l**.

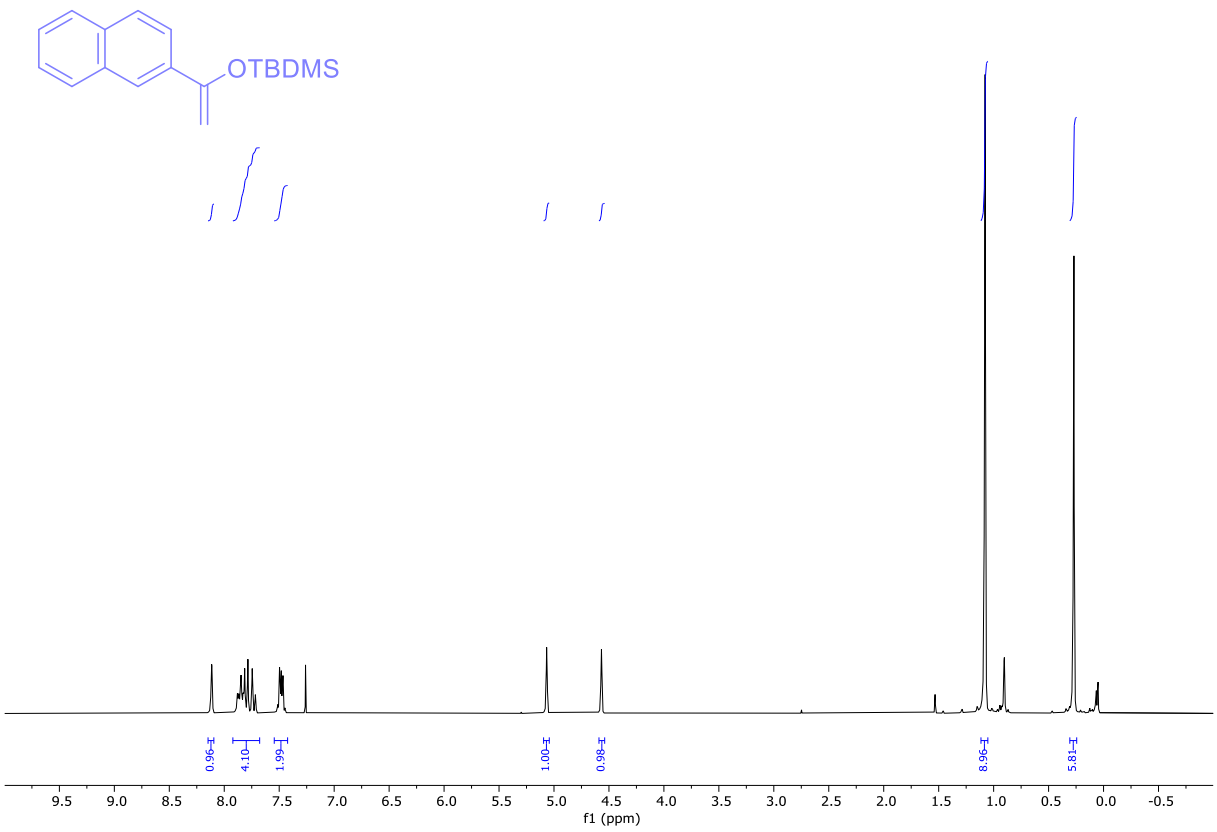



**Figure S40**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2m**.

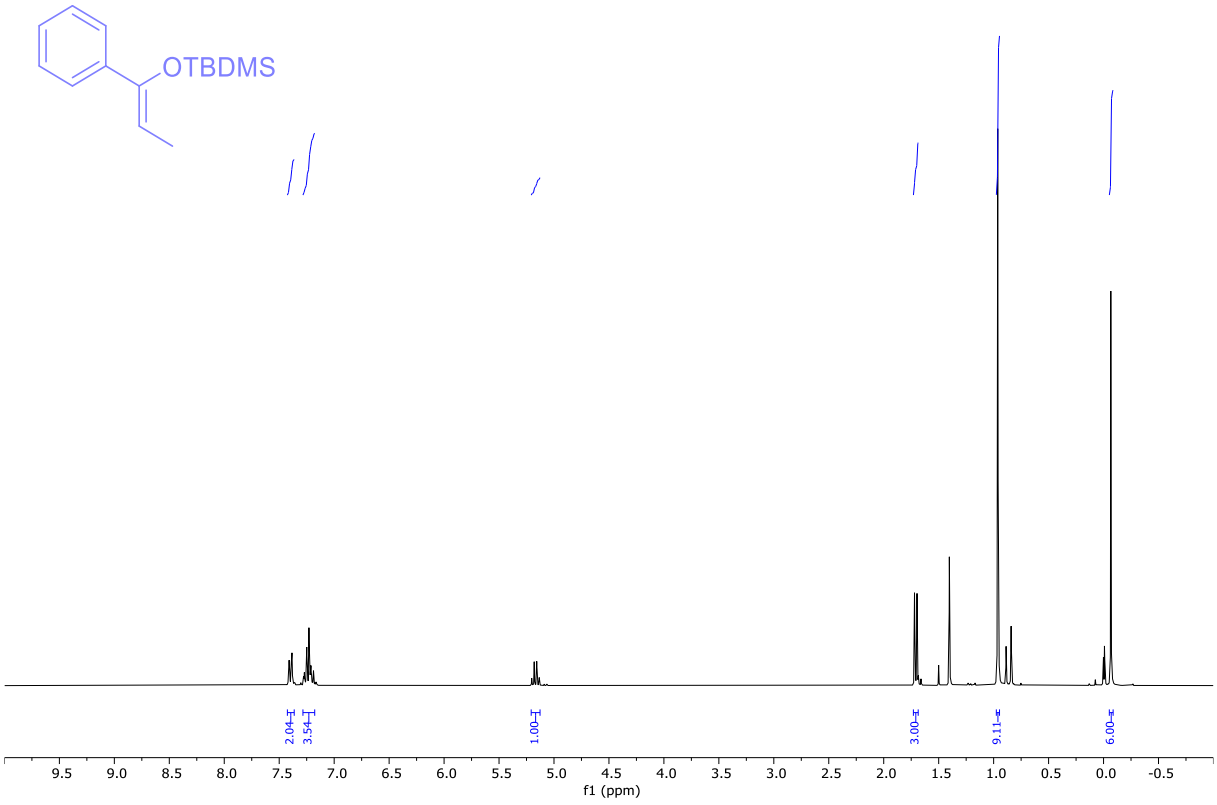



**Figure S41**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2n**.

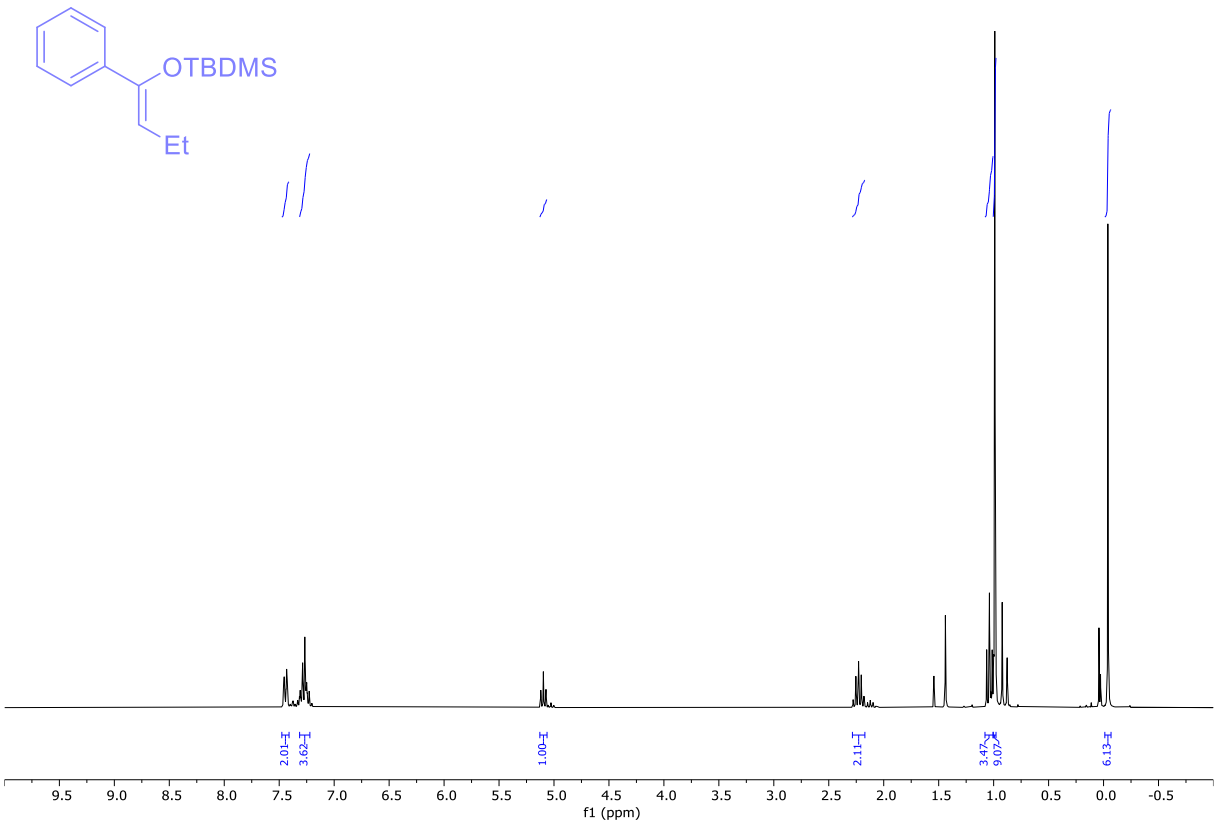



**Figure S42**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2o**.

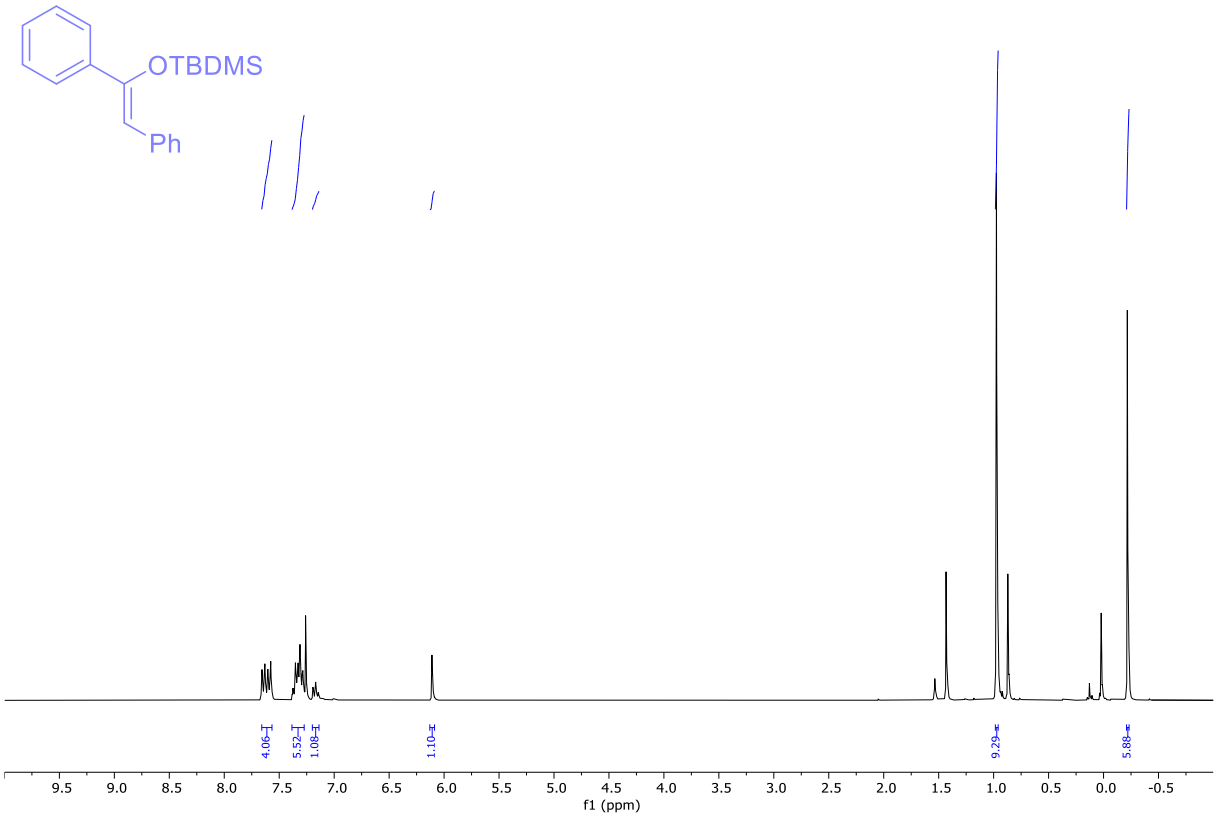



**Figure S43**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2p**.

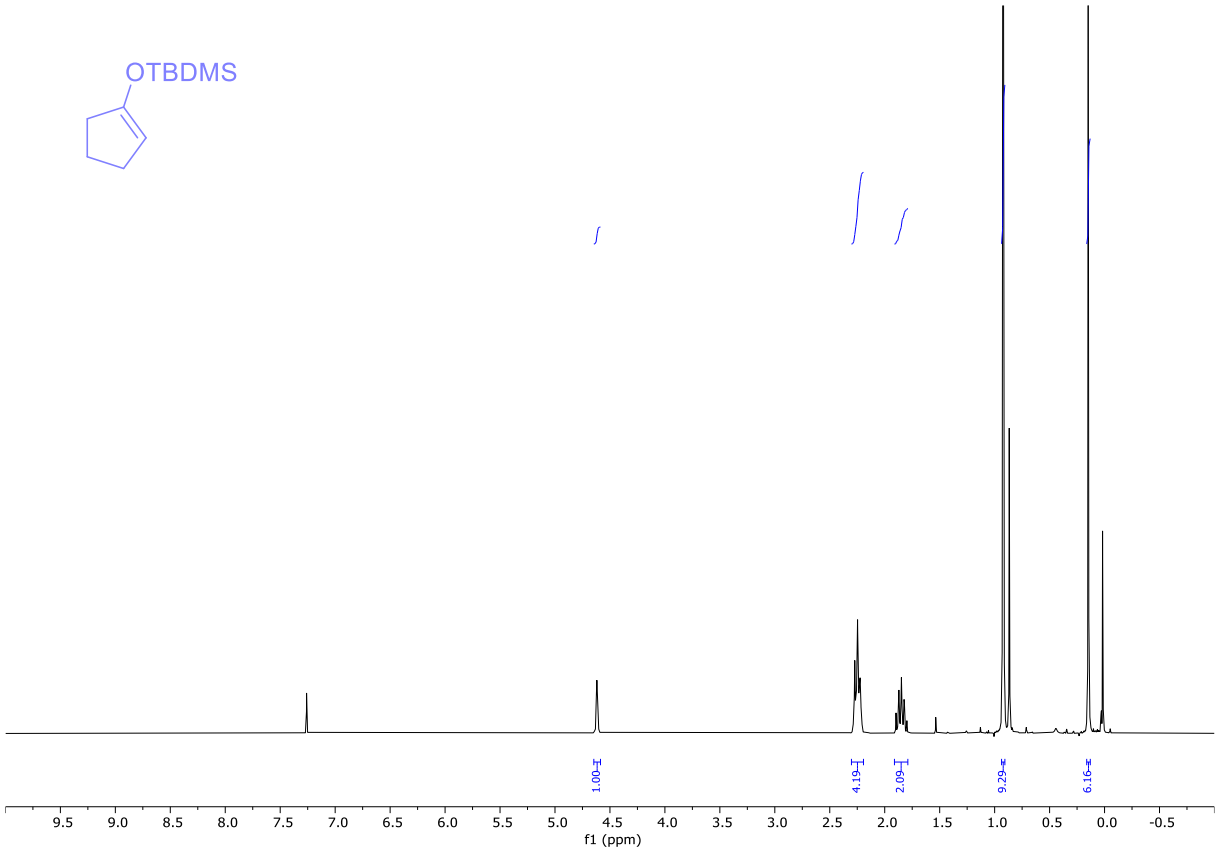



**Figure S44**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2q**.

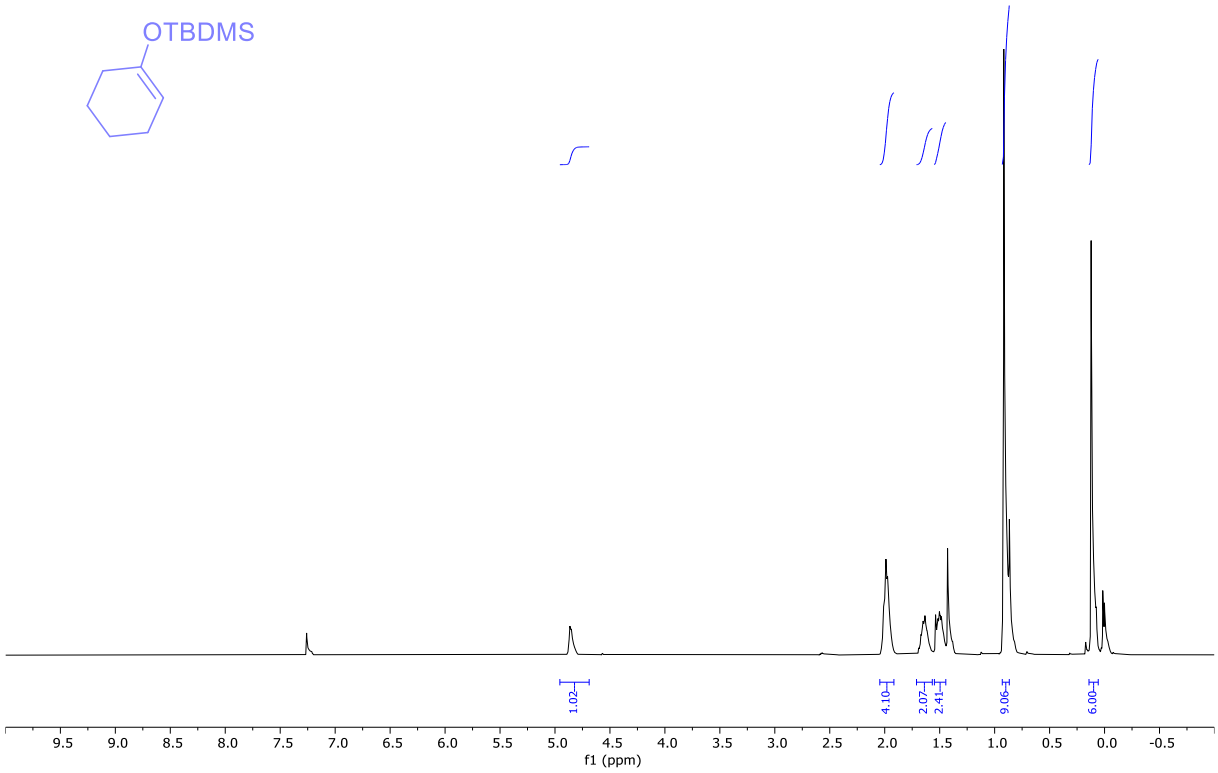



**Figure S45**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2r**.

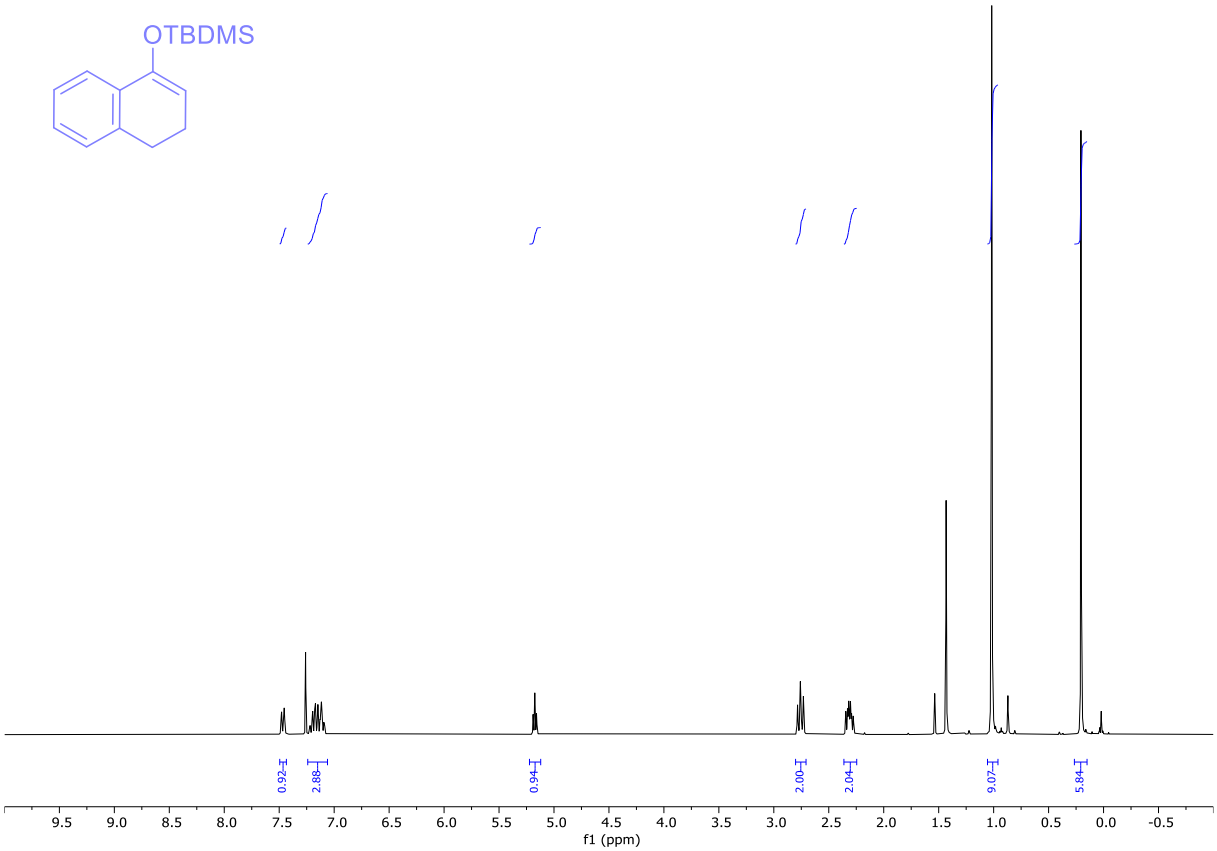



**Figure S46**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2s**.

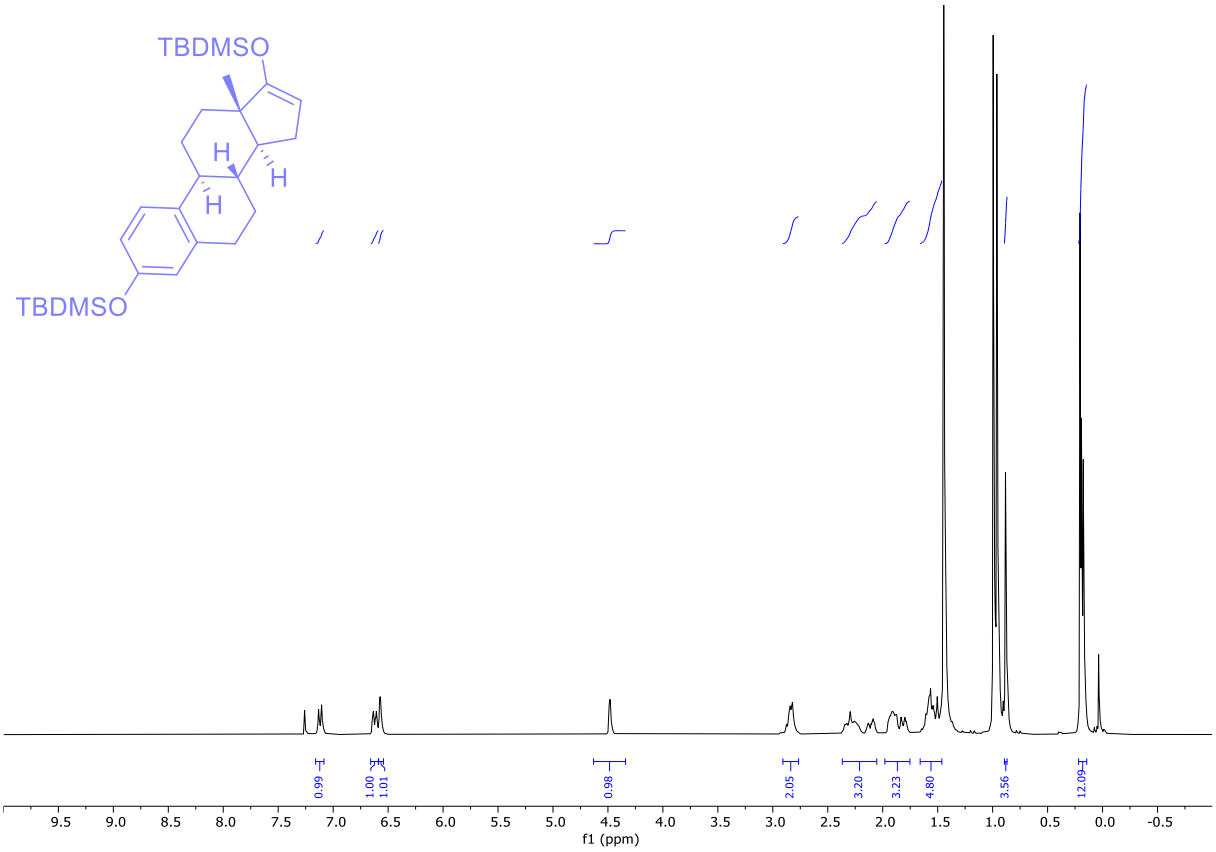



**Figure S47**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **2t**.

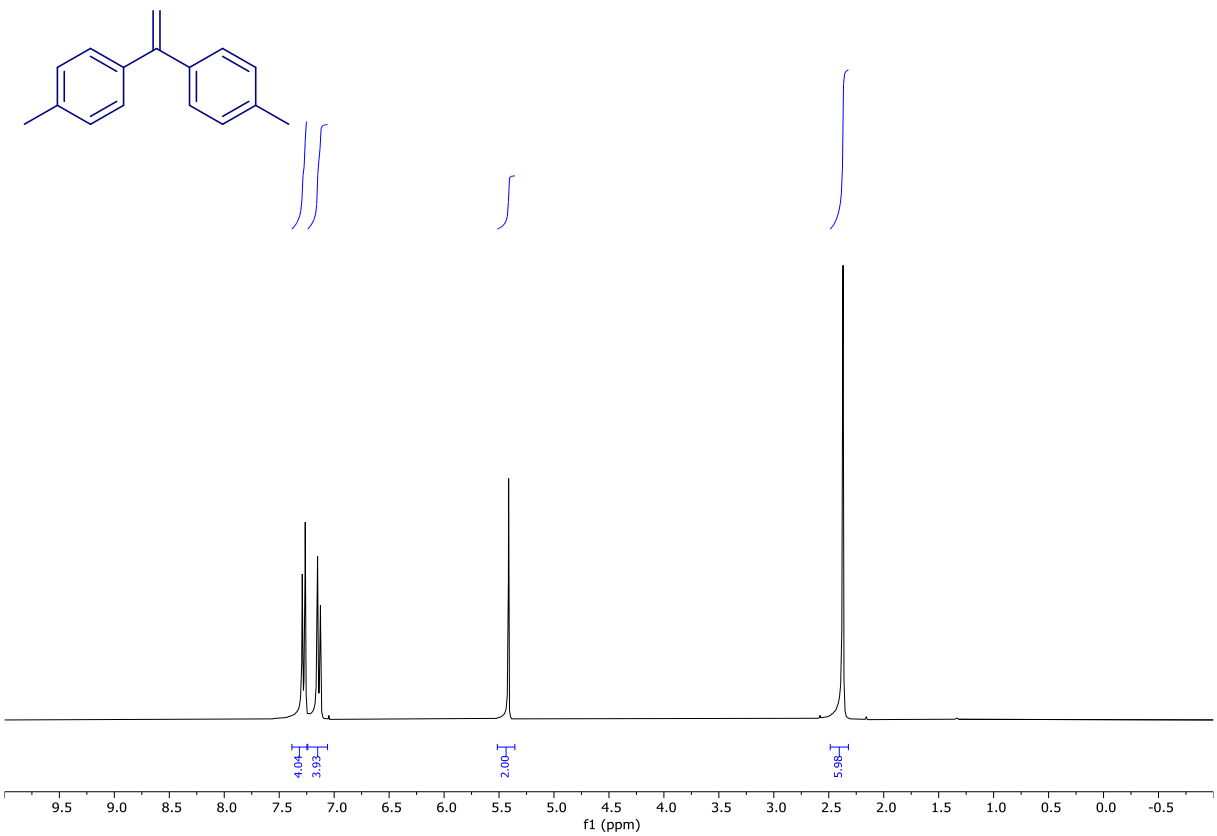



**Figure S48**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **4b**.

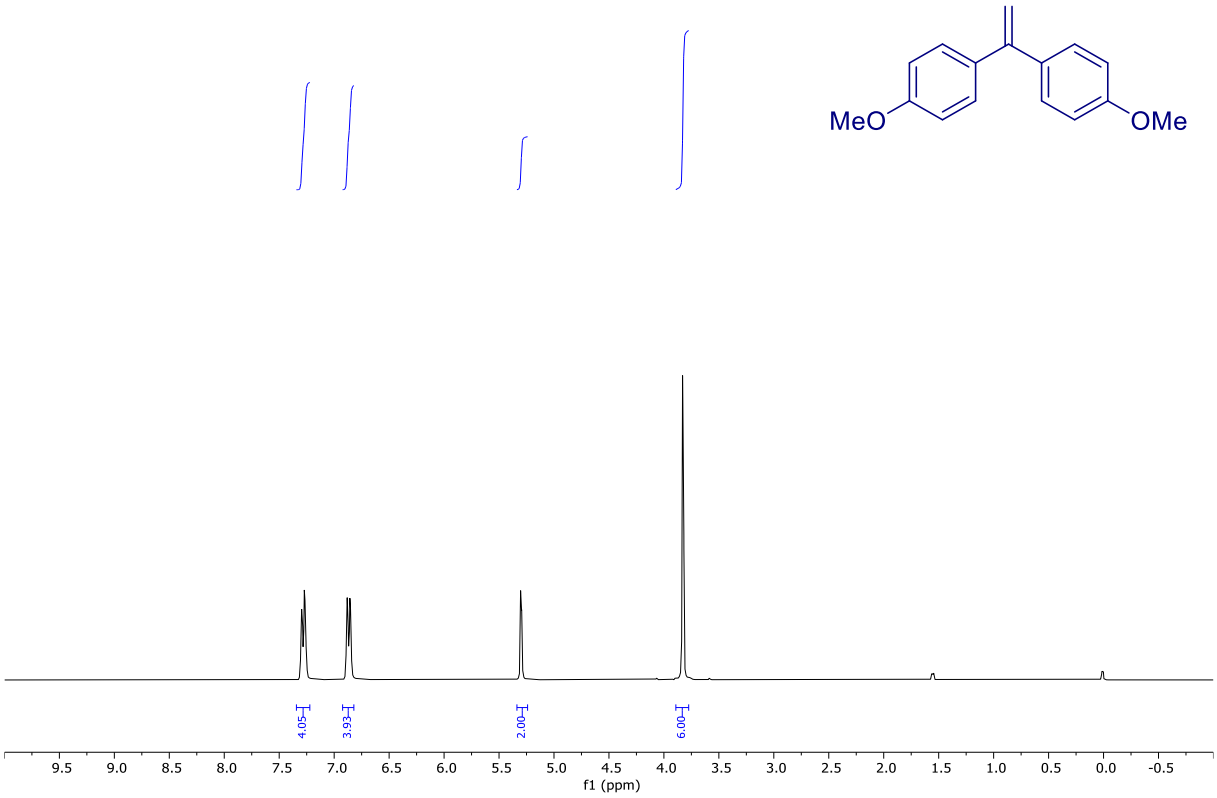



**Figure S49**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **4c**.

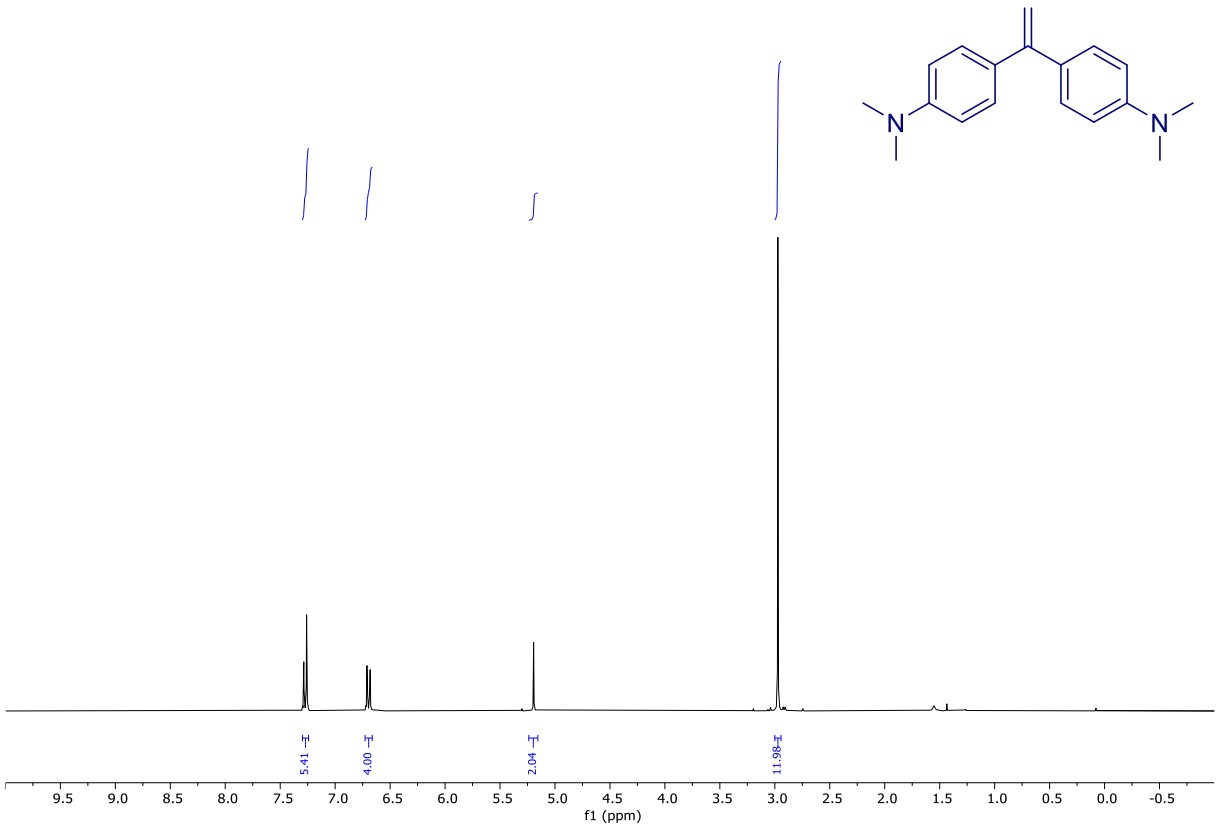



**Figure S50**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **4d**.

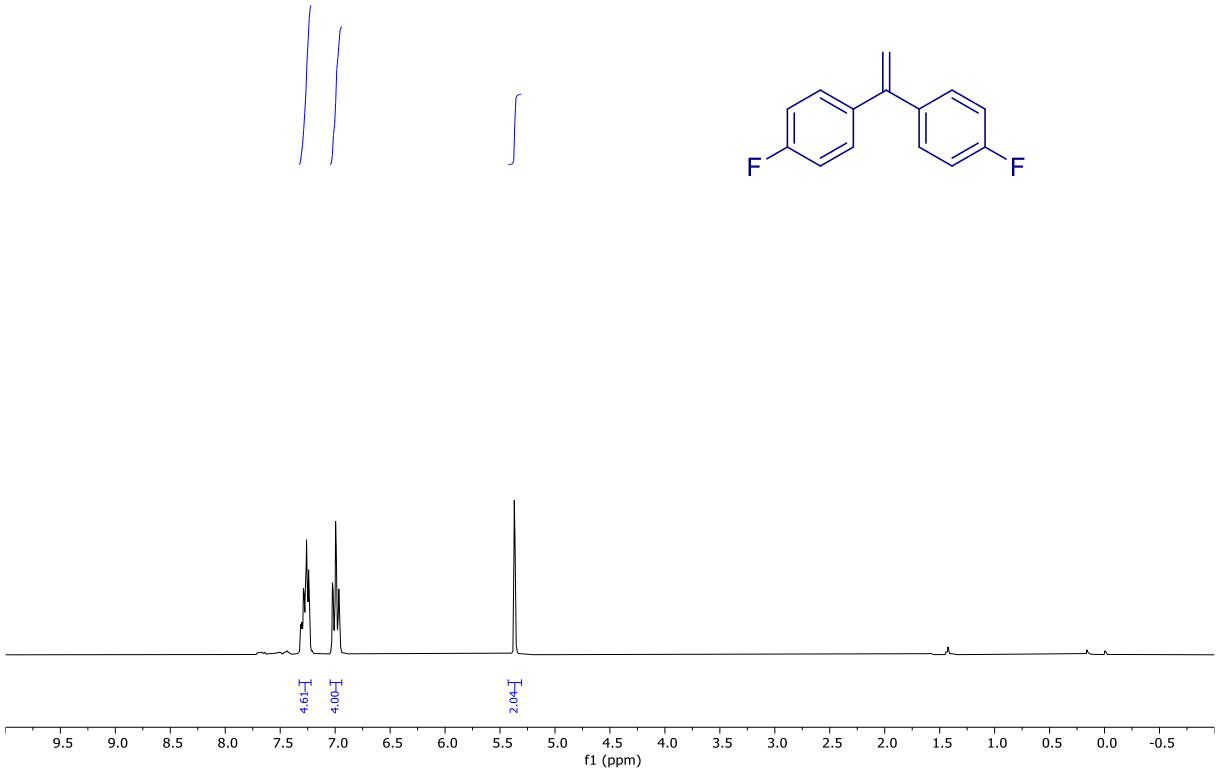



**Figure S51**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **4e**.

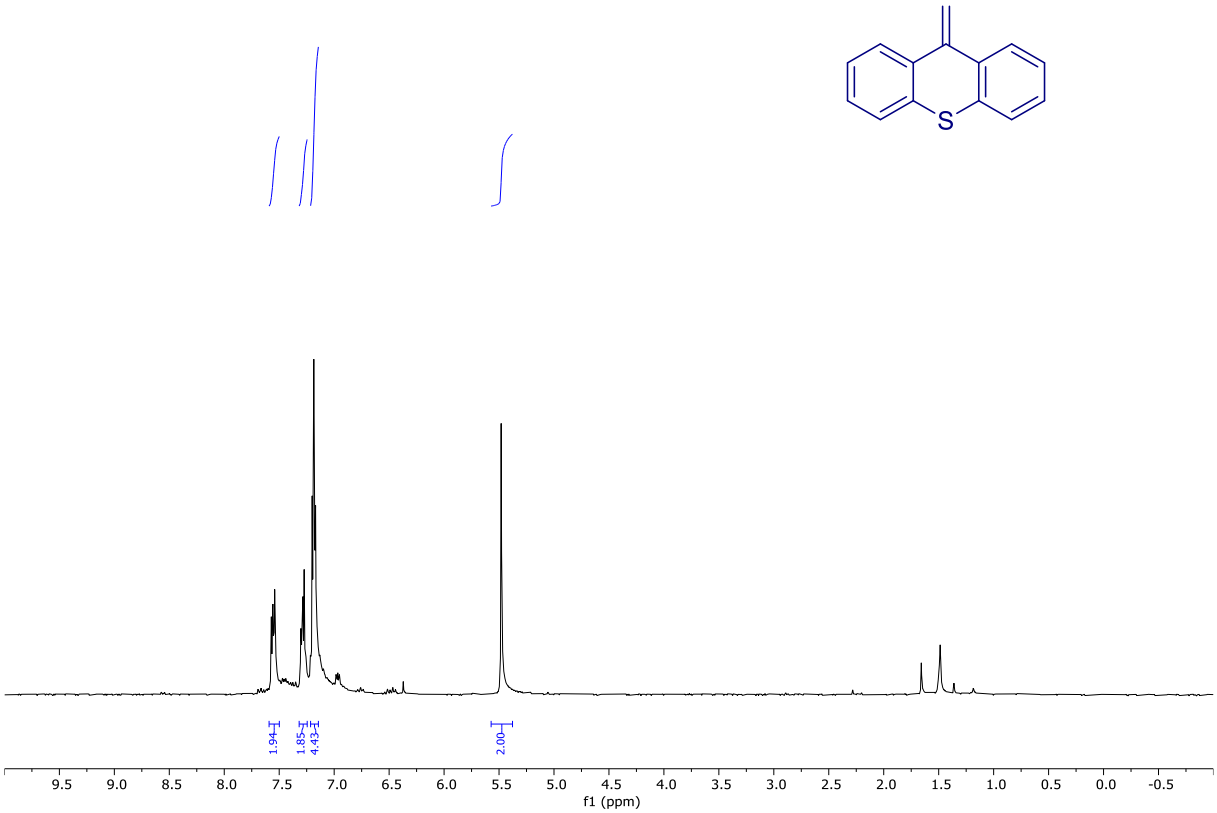



**Figure S52**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **4f**.

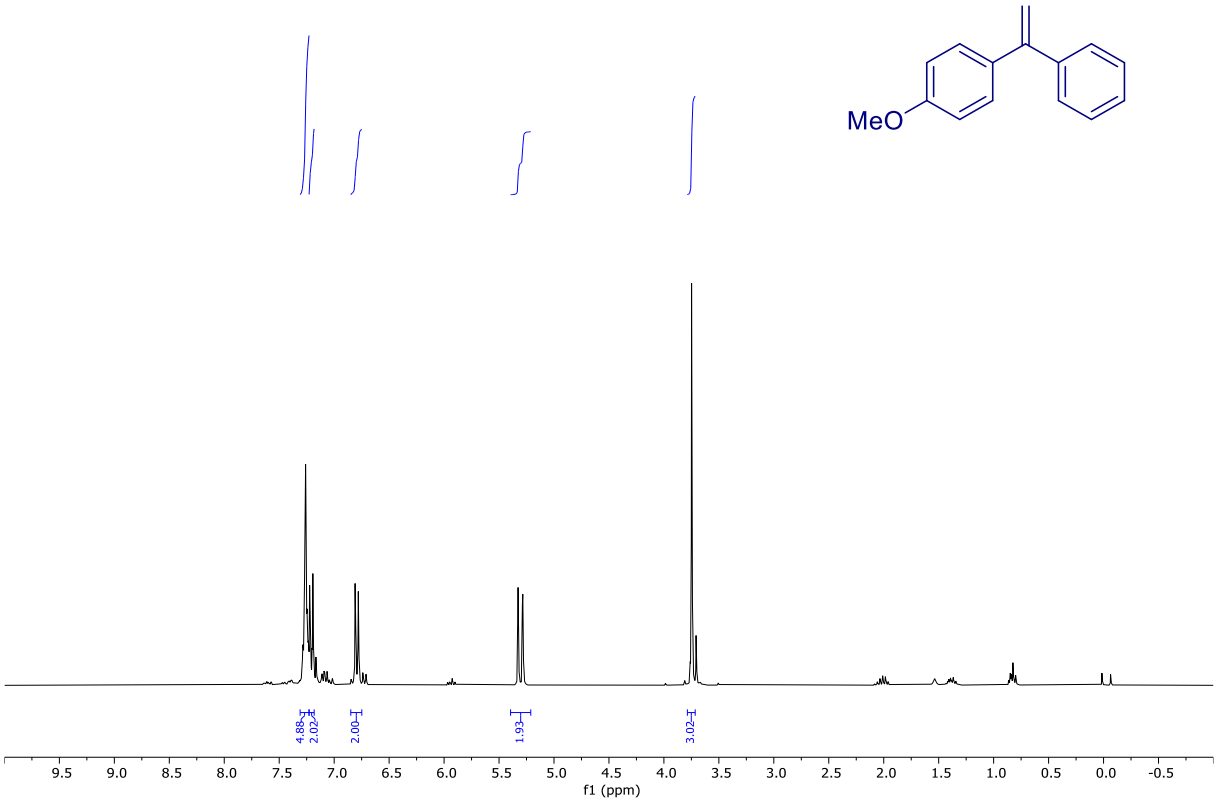



**Figure S53**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **4h**.

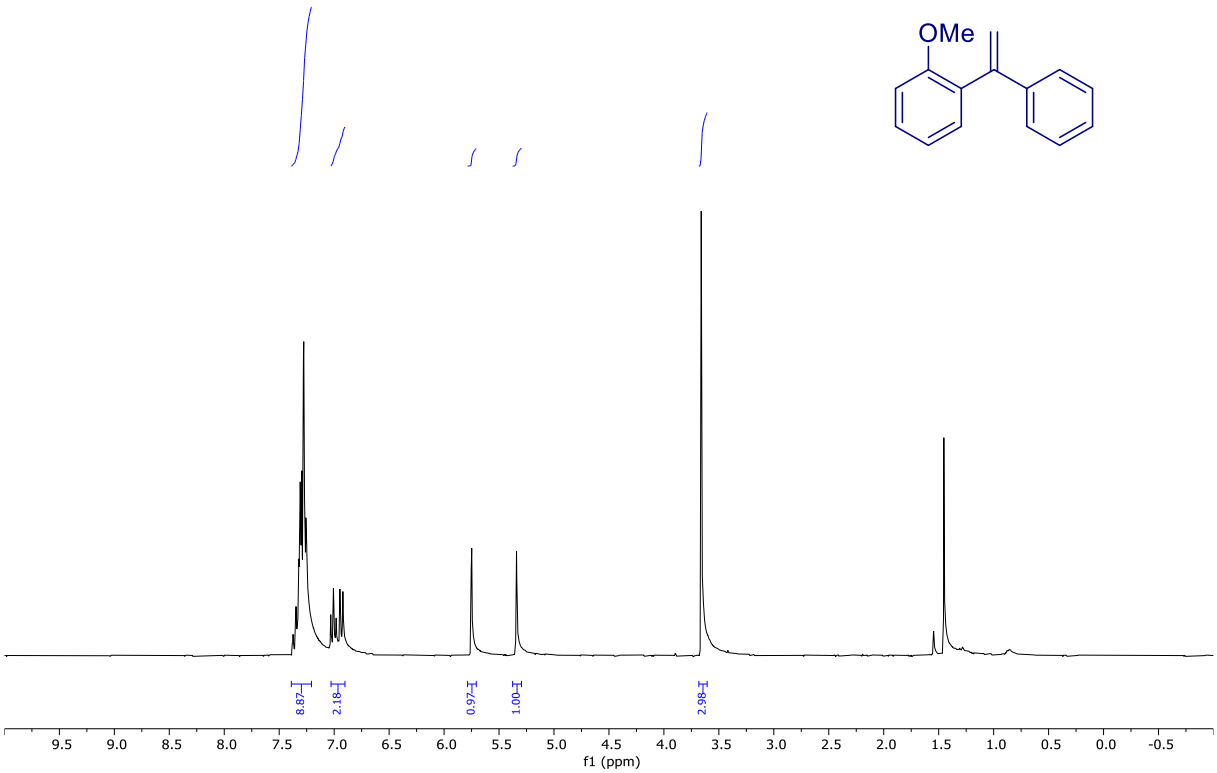



**Figure S54**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **4i**.

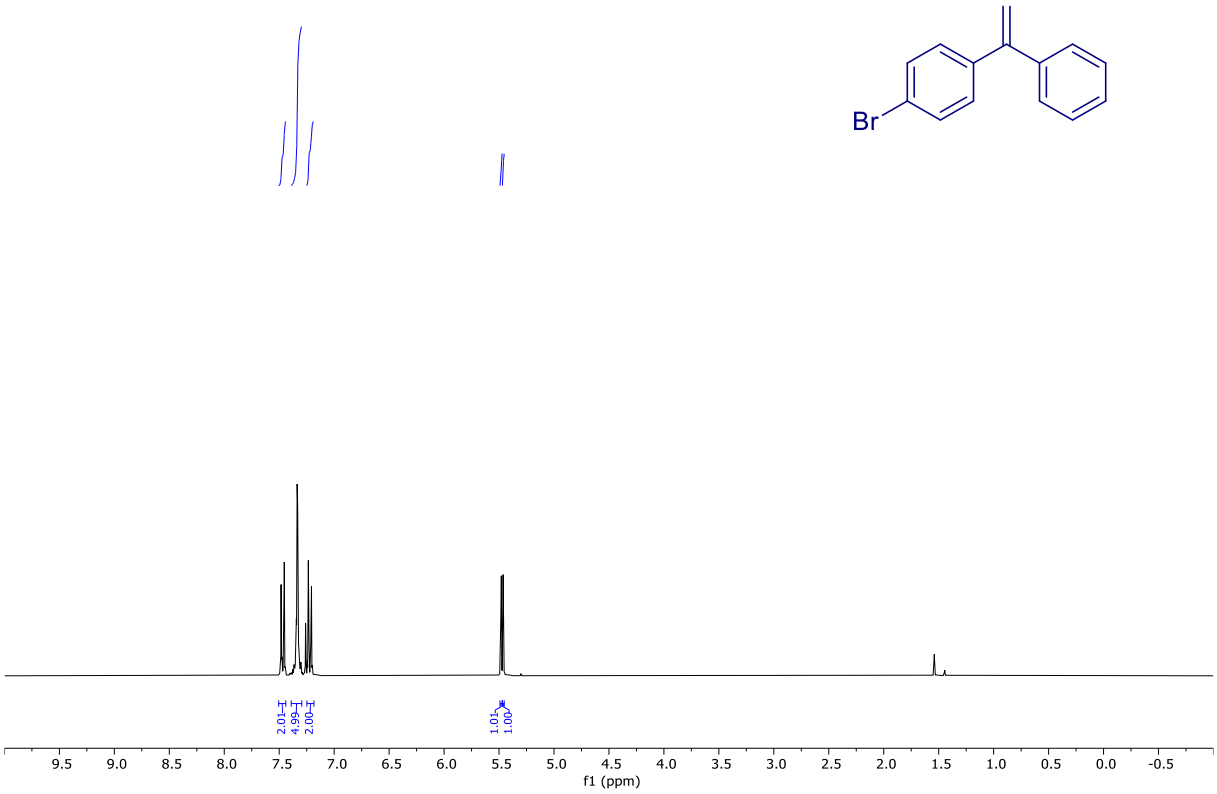



**Figure S55**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **4j**.

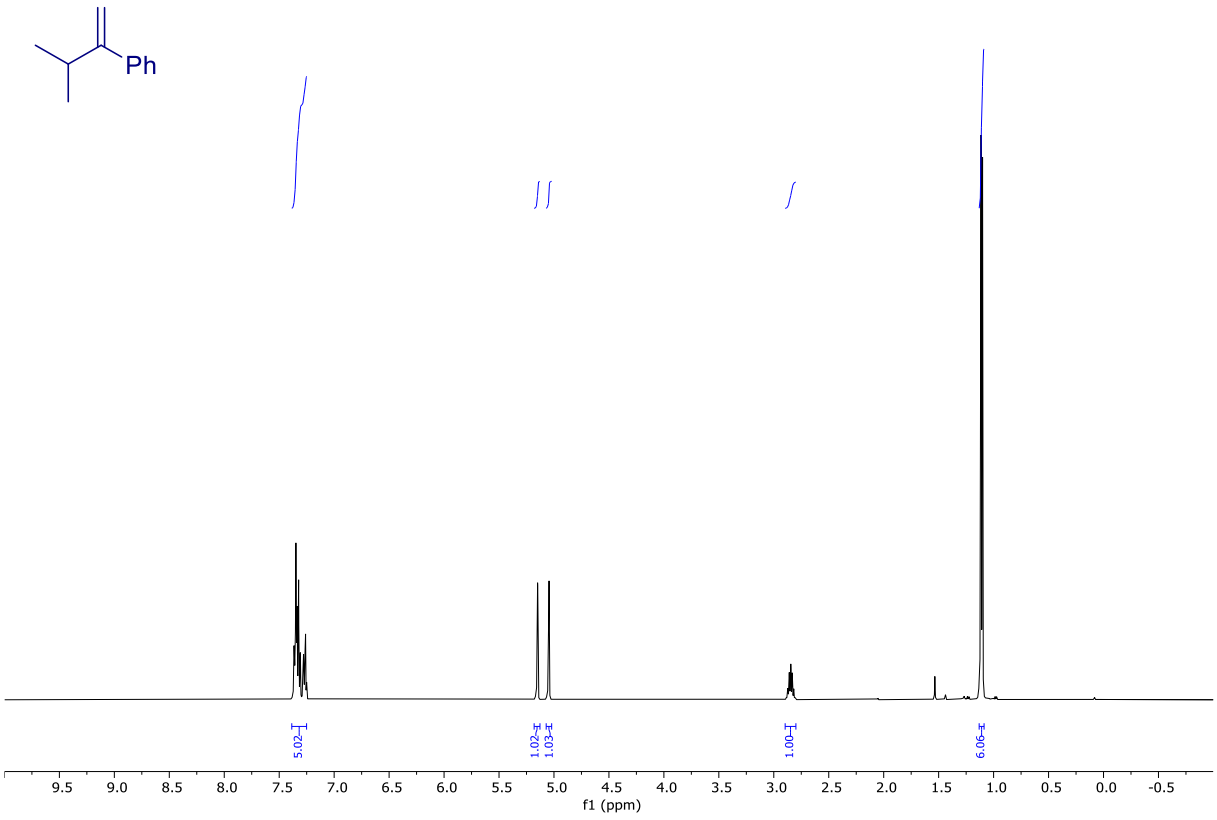



**Figure S56**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **4l**.

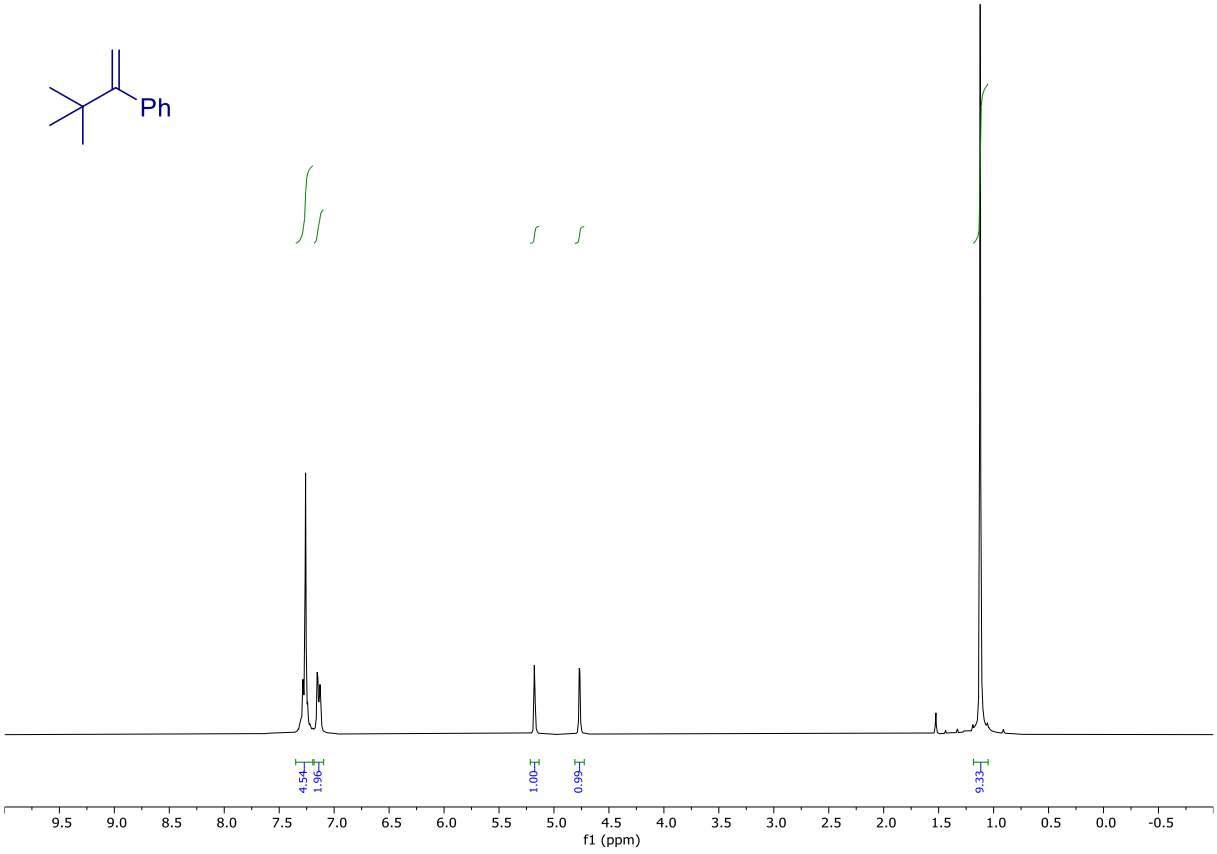



**Figure S57**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **4m**.

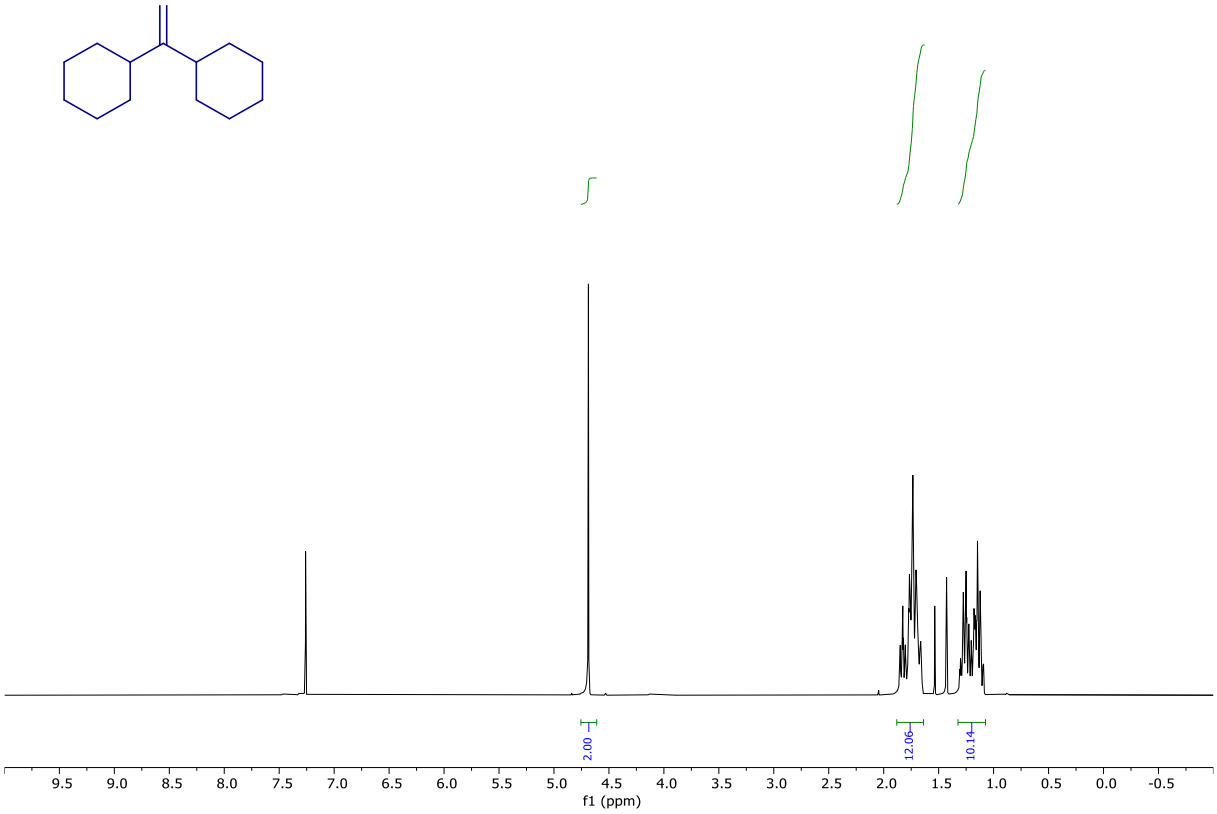



**Figure S58**. $^{1}$H NMR spectrum (500 MHz, 298K, $CDCl_3$) of **4q**.

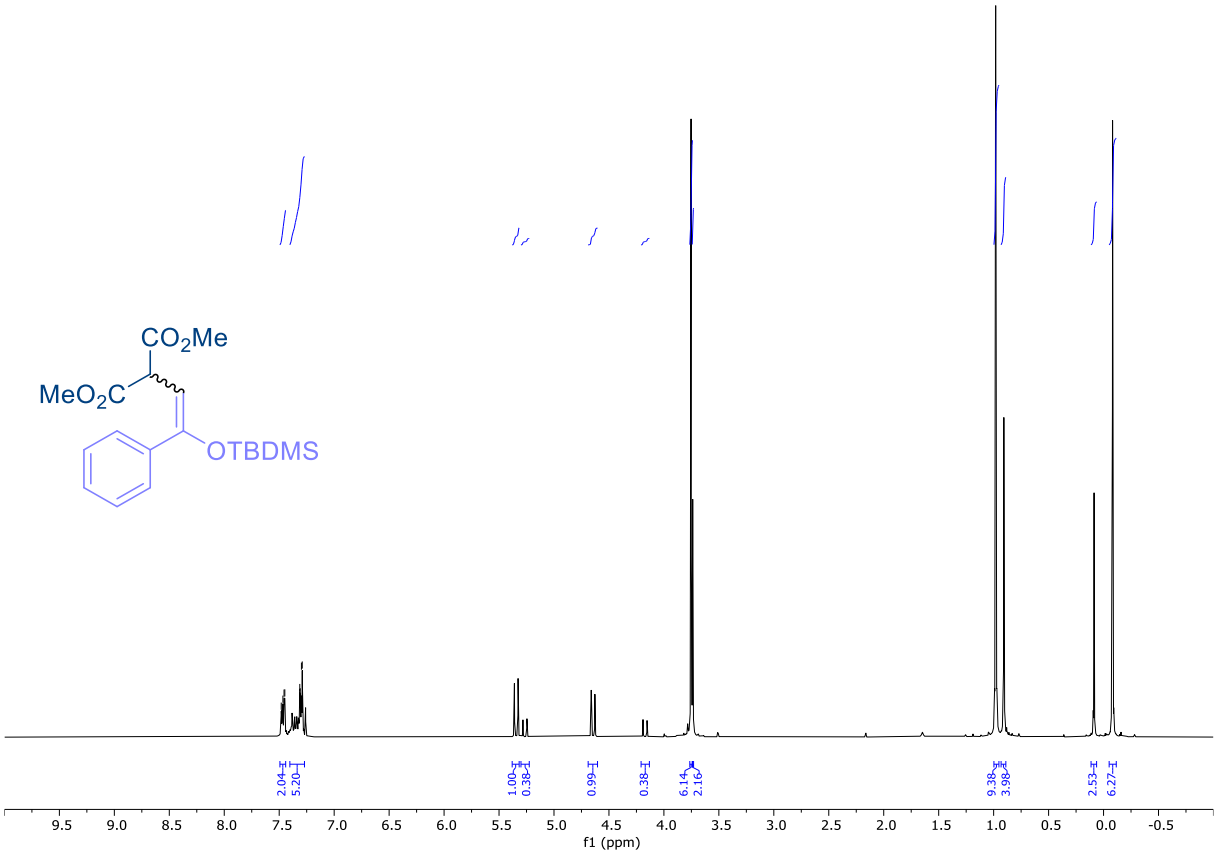



**Figure S59**. $^{1}H$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3aa (*Z*/*E* = 72:28)**.

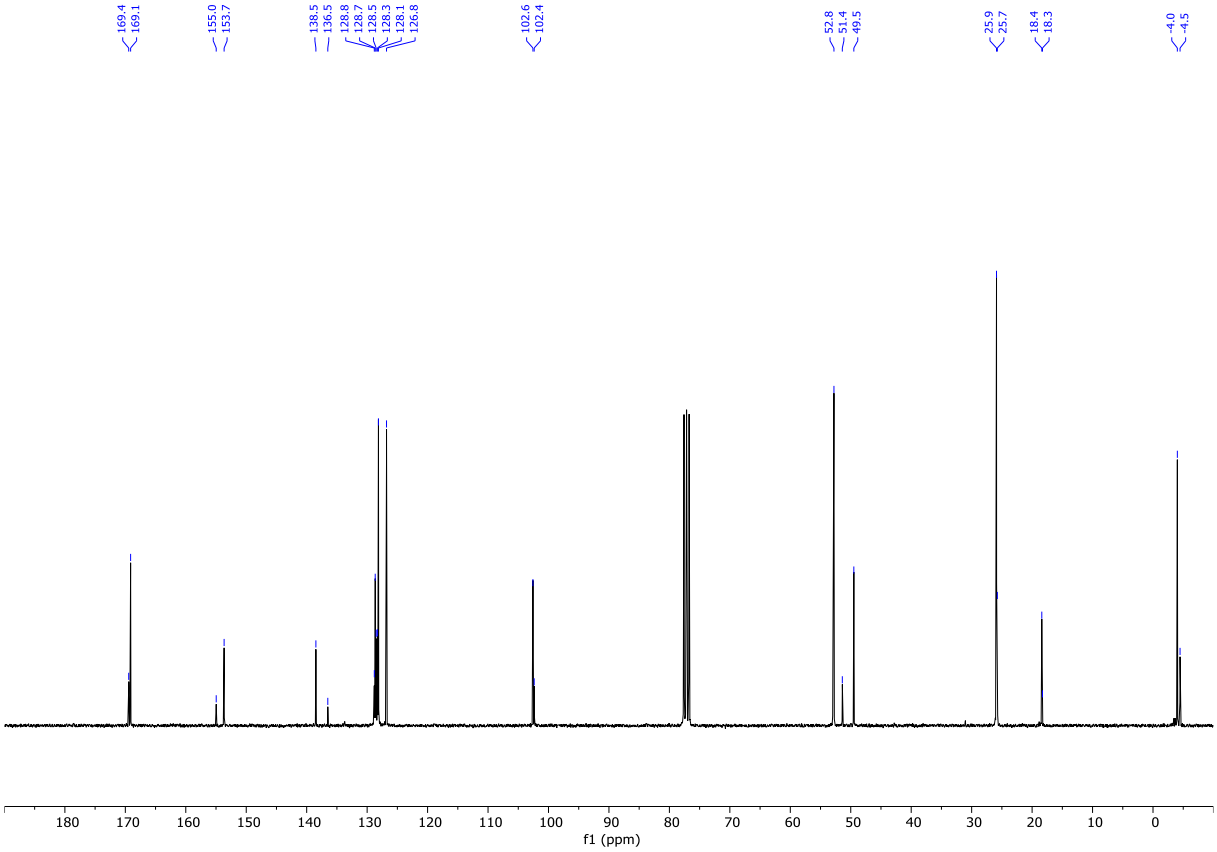



**Figure S60**. $^{13}C$ NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3aa (*Z*/*E* = 72:28)**.

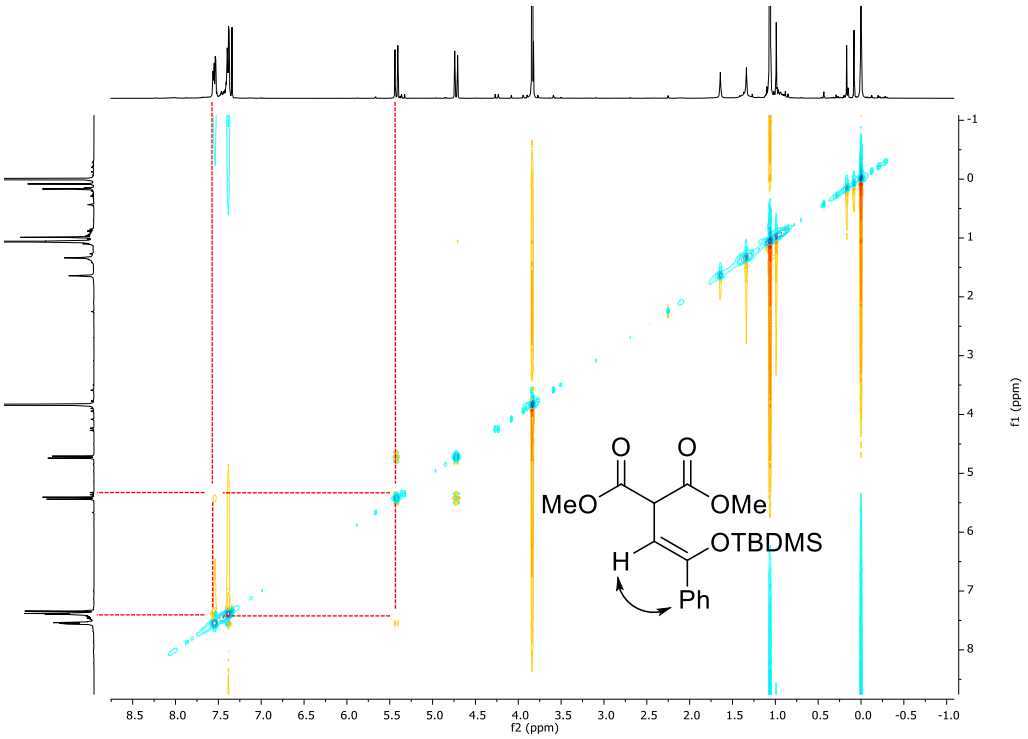



**Figure S61**. NOESY spectrum (300 MHz, 298K, $CDCl_3$) of (***Z***)-**3aa**.

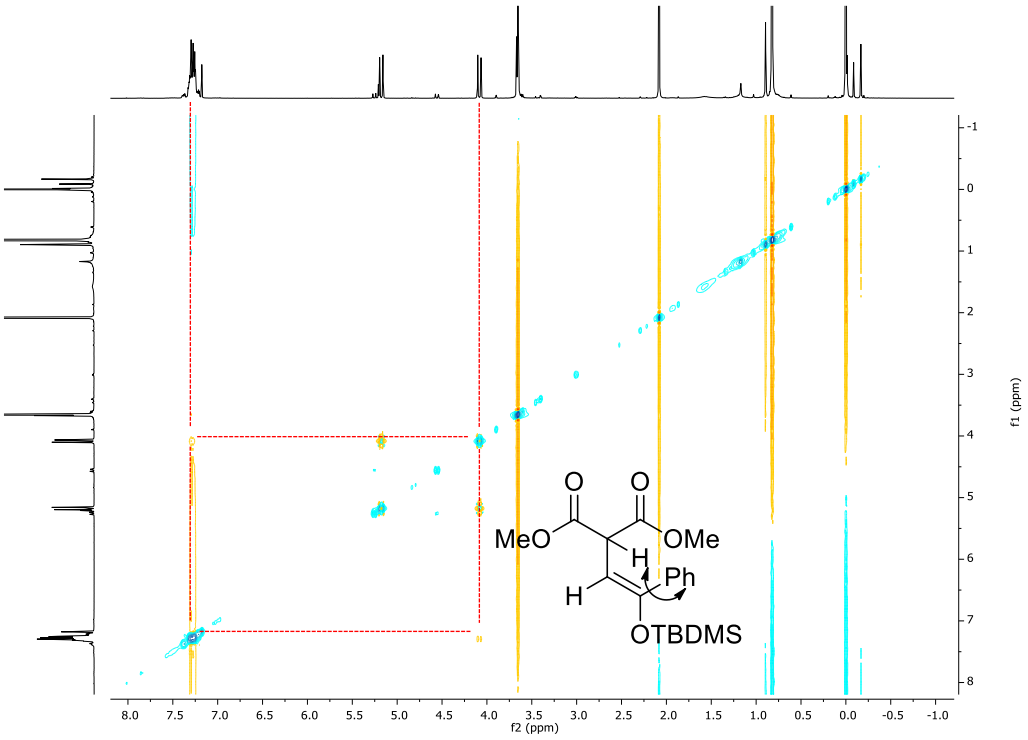



**Figure S62**. NOESY spectrum (300 MHz, 298K, $CDCl_3$) of (***E***)-**3aa**.

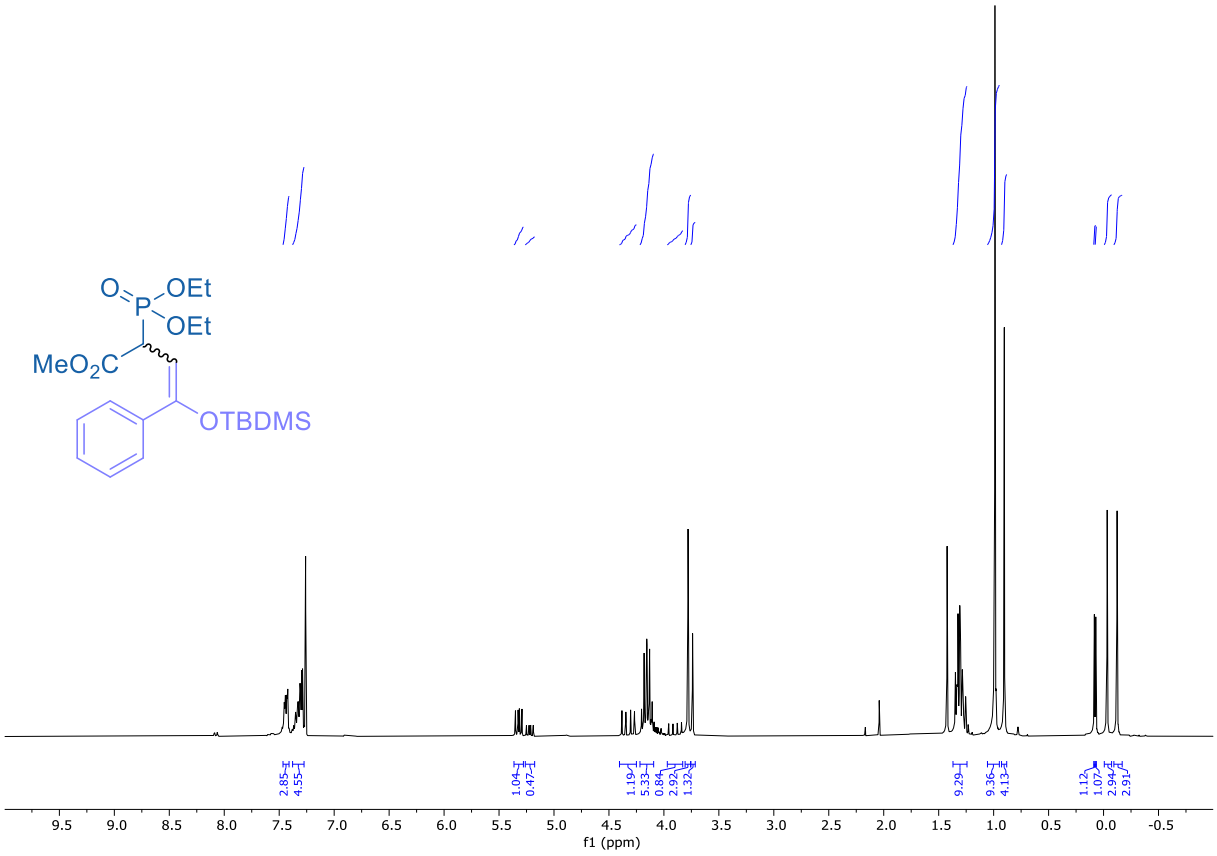



**Figure S63**. $^{1}H$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3ba (*Z*/*E* = 69:31)**.

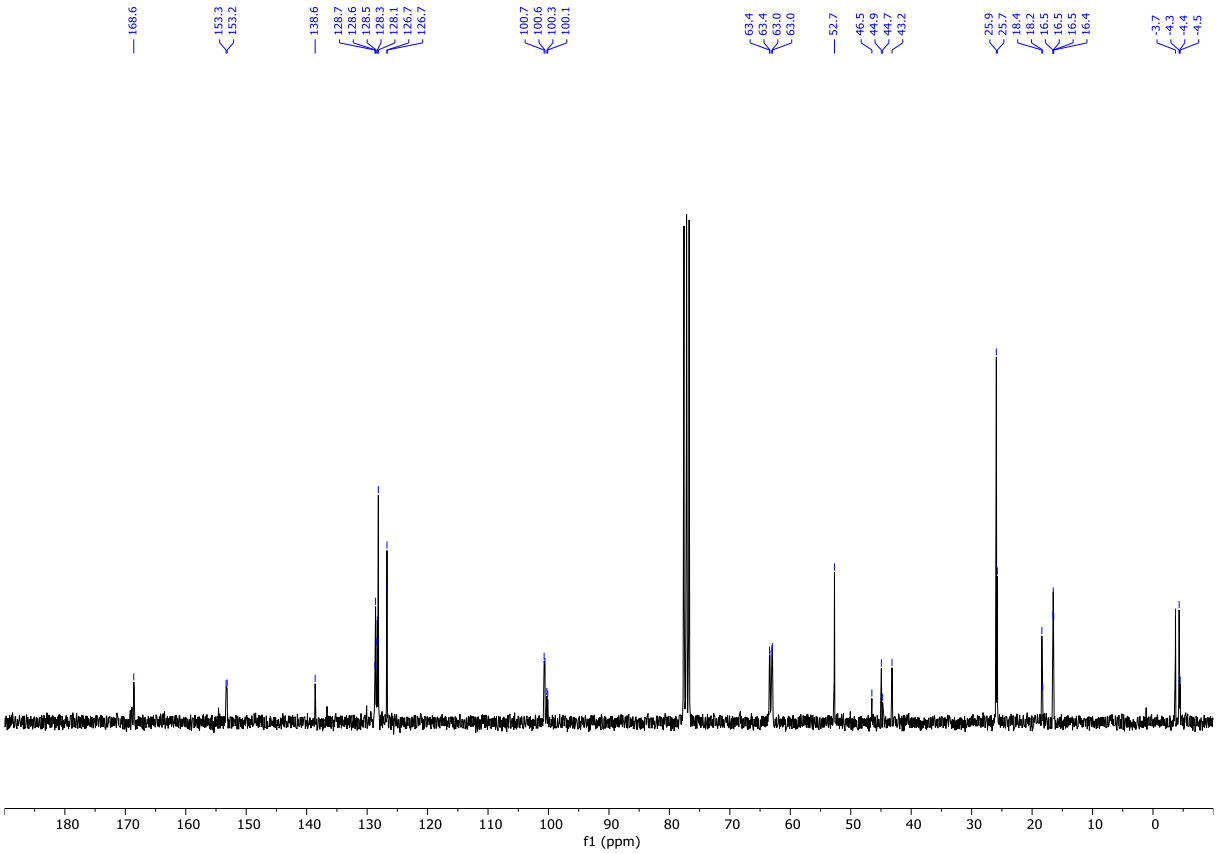



**Figure S64**. $^{13}C$ NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3ba (*Z*/*E* = 69:31)**.

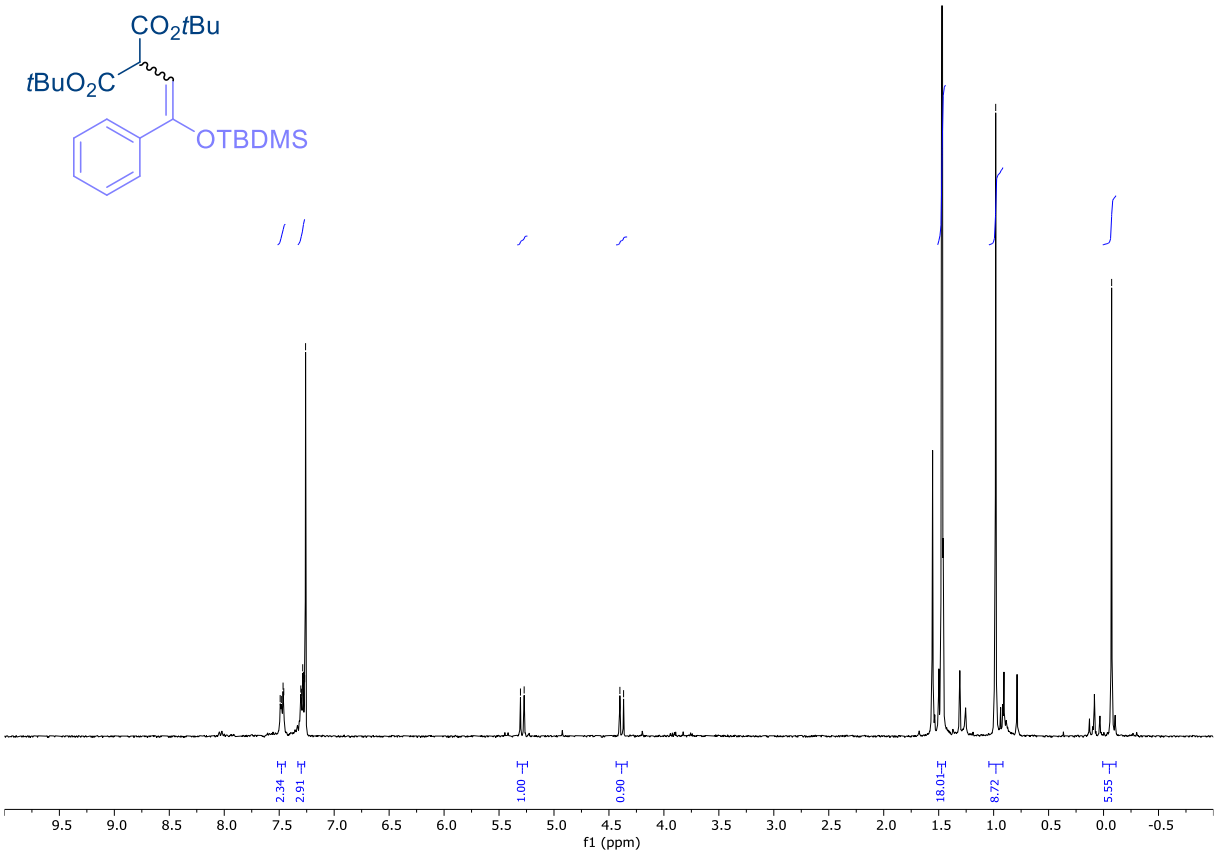



**Figure S65**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3ca (*Z*/*E* >95:5)**.

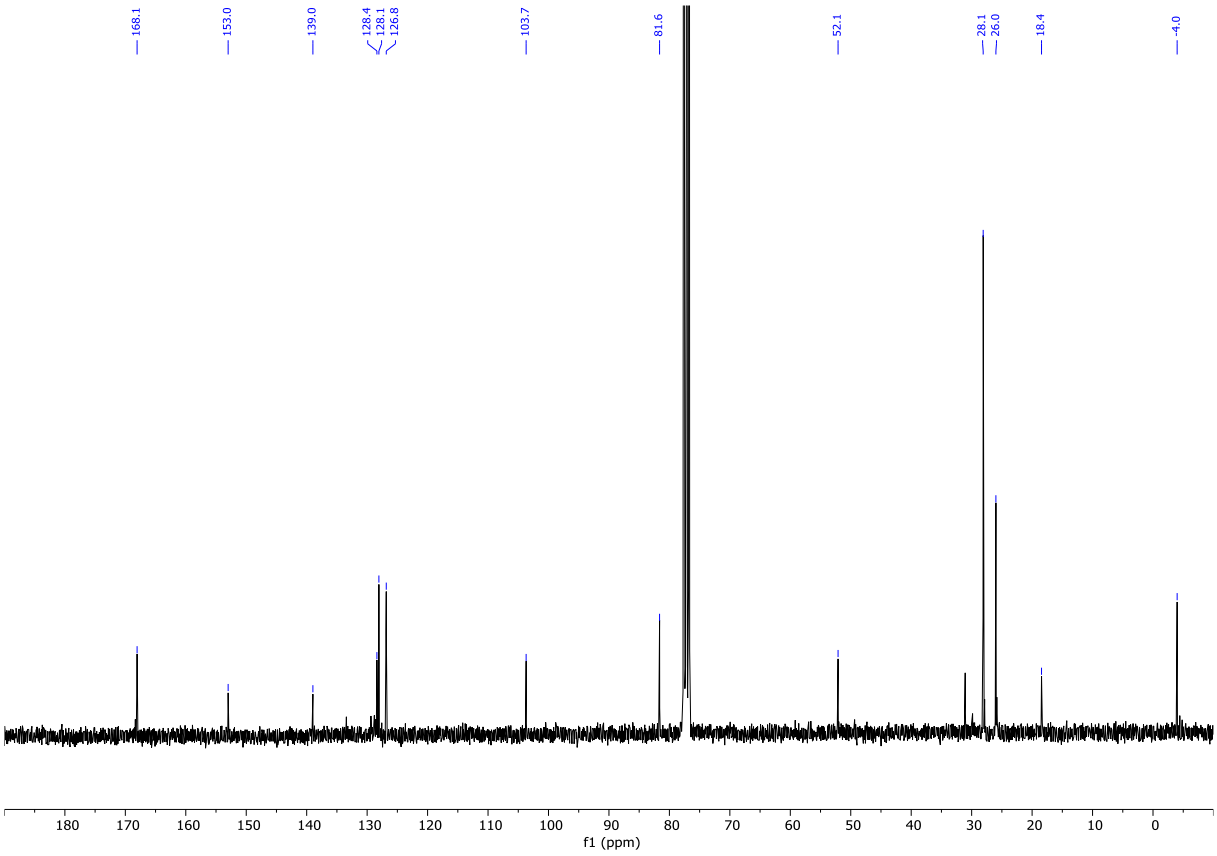



**Figure S66**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3ca (*Z*/*E* >95:5)**.

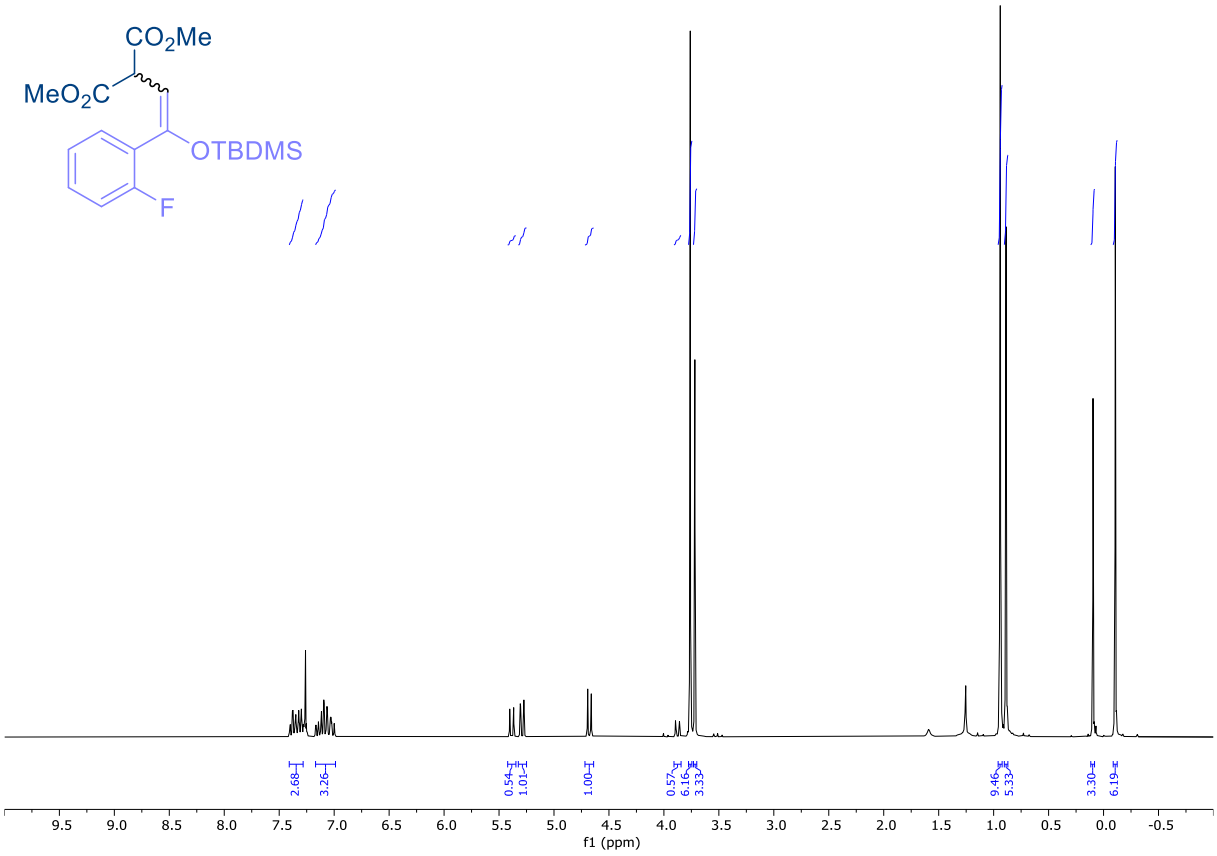



**Figure S67**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3ab (*Z*/*E* = 65:35)**.

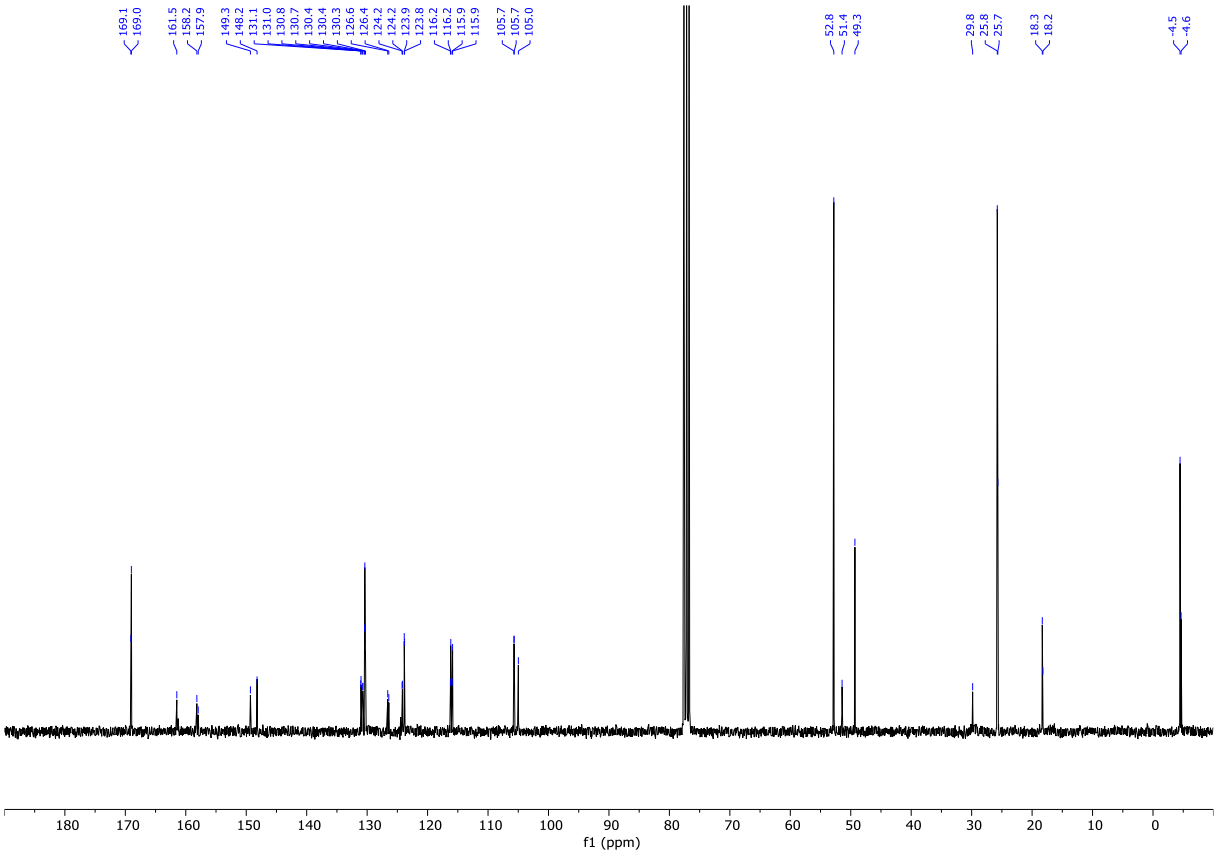



**Figure S68**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3ab (*Z*/*E* = 65:35)**.

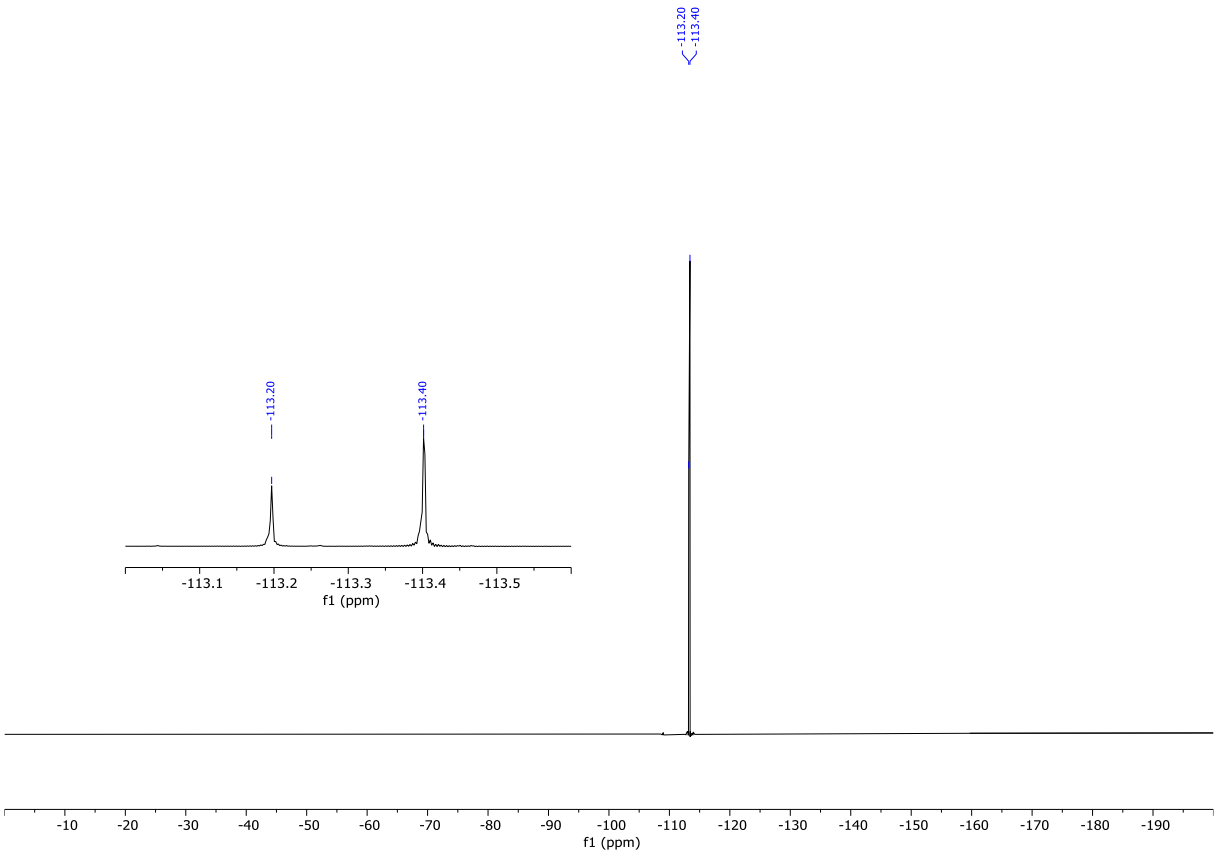



**Figure S69**. $^{19}F$ NMR spectrum (282 MHz, 298K, $CDCl_3$) of **3ab (*Z*/*E* = 65:35)**.

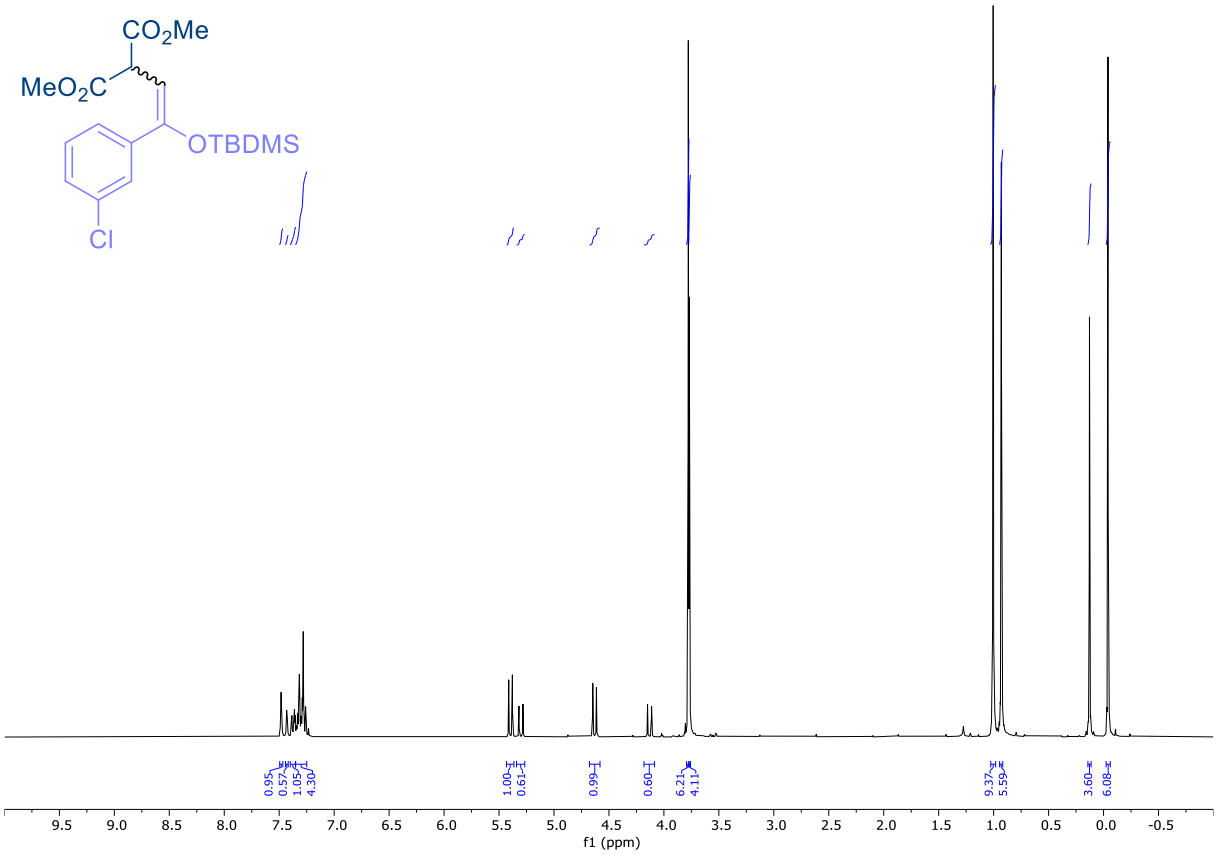



**Figure S70**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3ac (*Z*/*E* = 38:62)**.

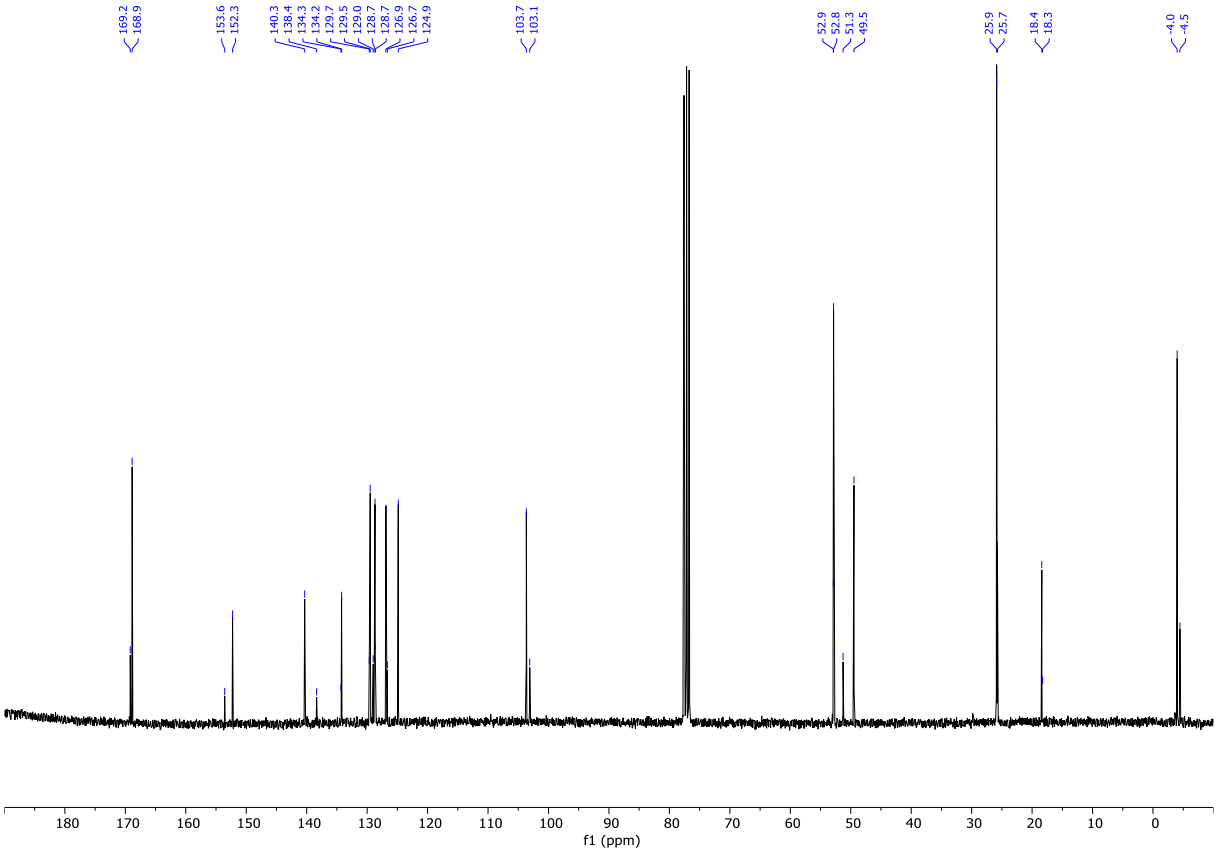



**Figure S71**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3ac (*Z*/*E* = 38:62)**.

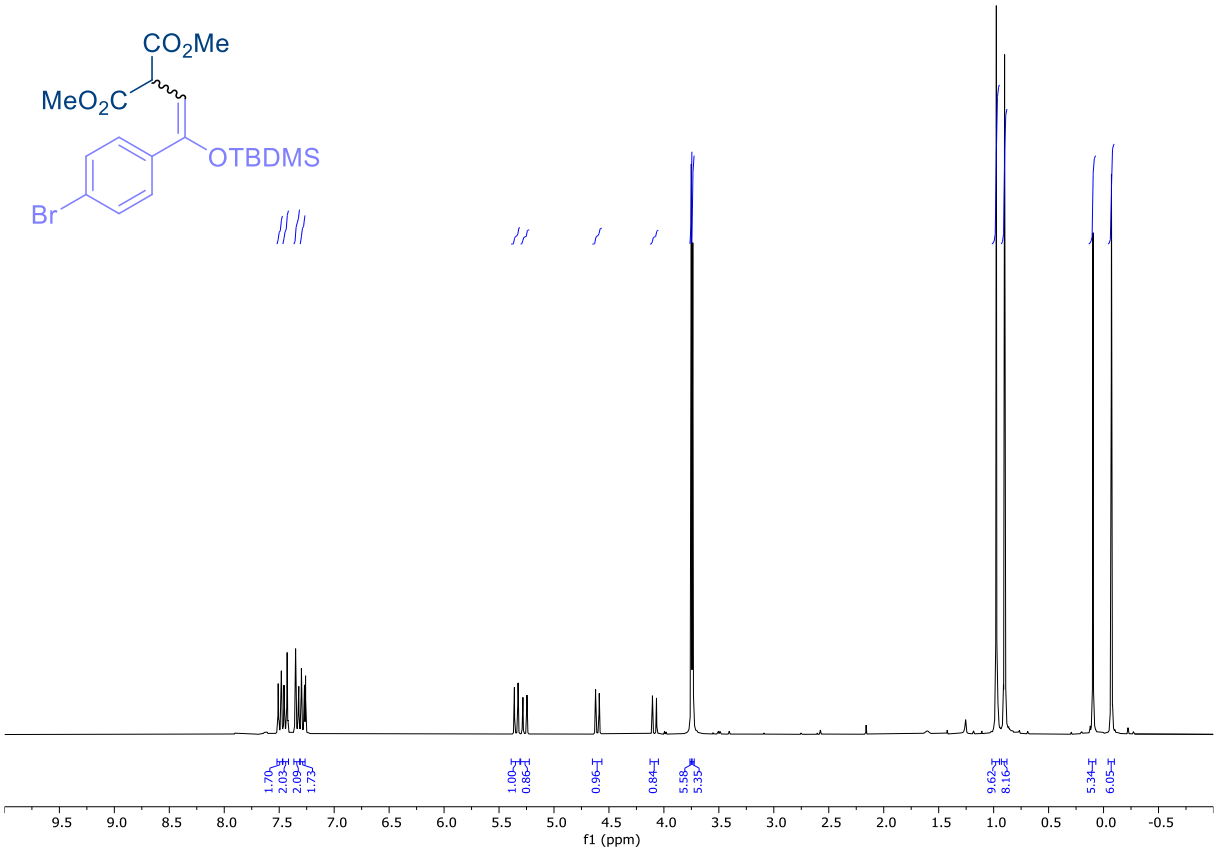



**Figure S72**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3ad (*Z*/*E* = 53:47)**.

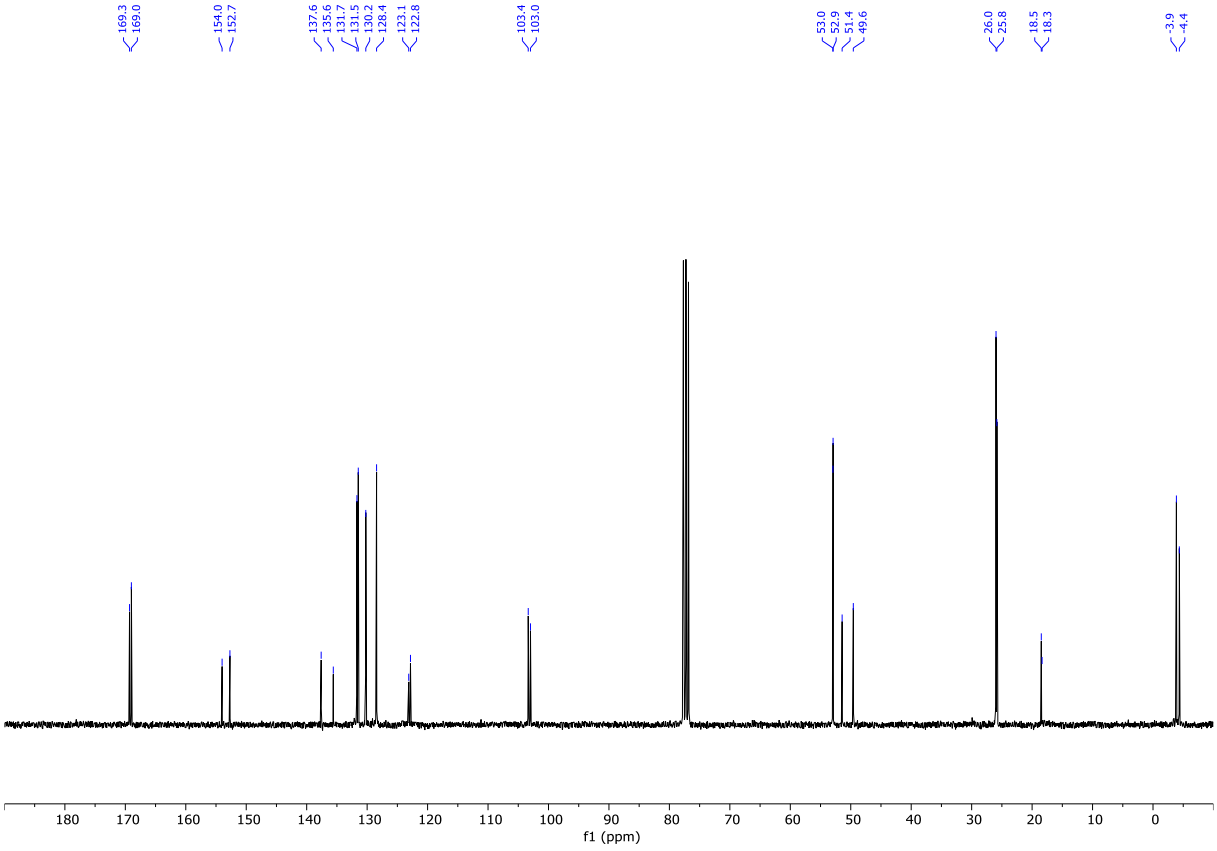



**Figure S73**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3ad (*Z*/*E* = 53:47)**.

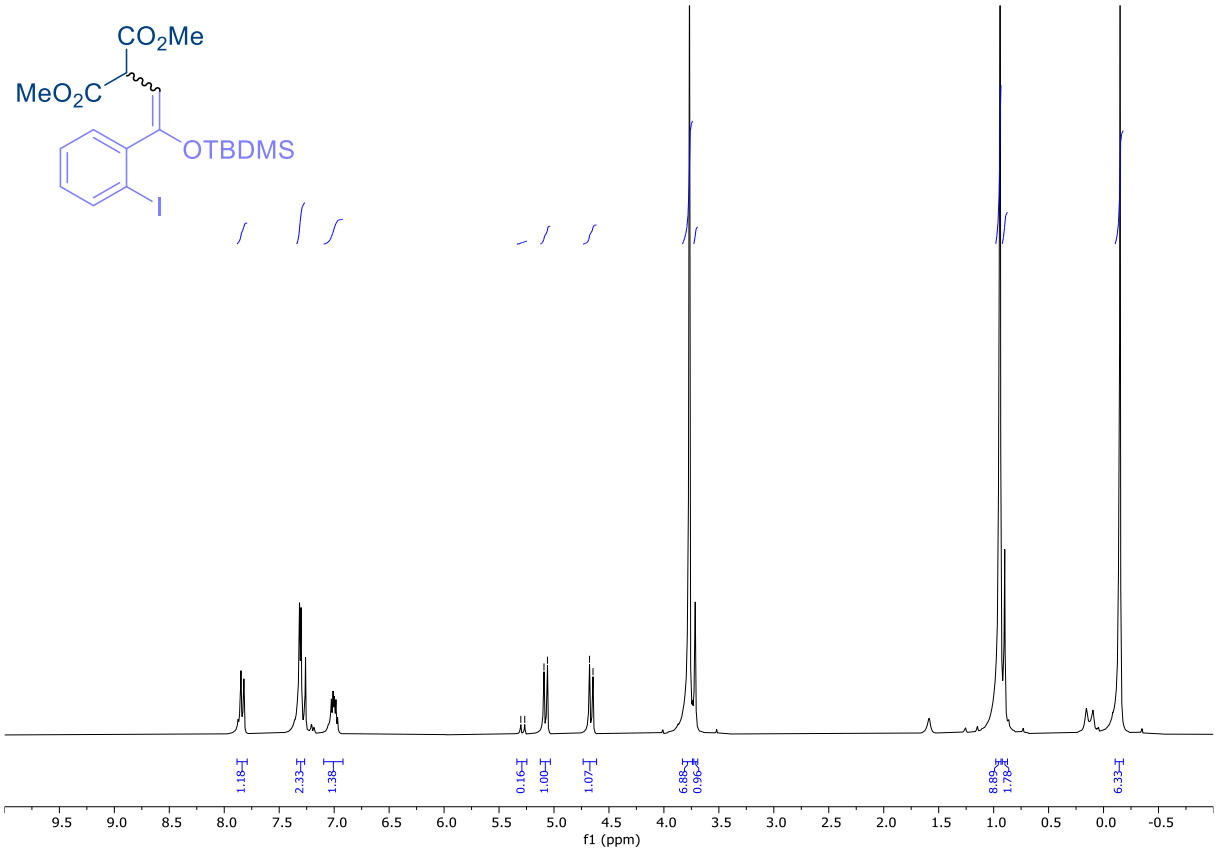



**Figure S74**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3ae (*Z*/*E* = 14:86)**.

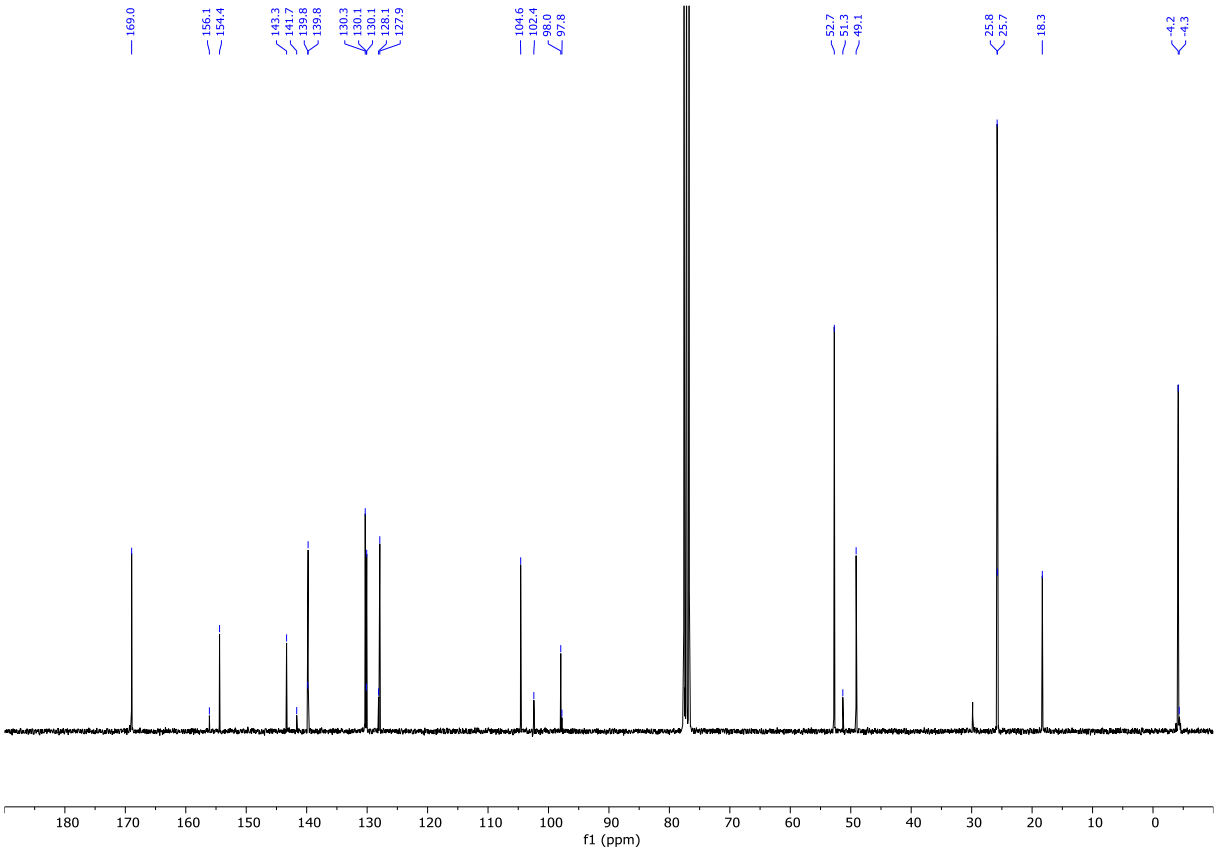



**Figure S75**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3ae (*Z*/*E* = 14:86)**.

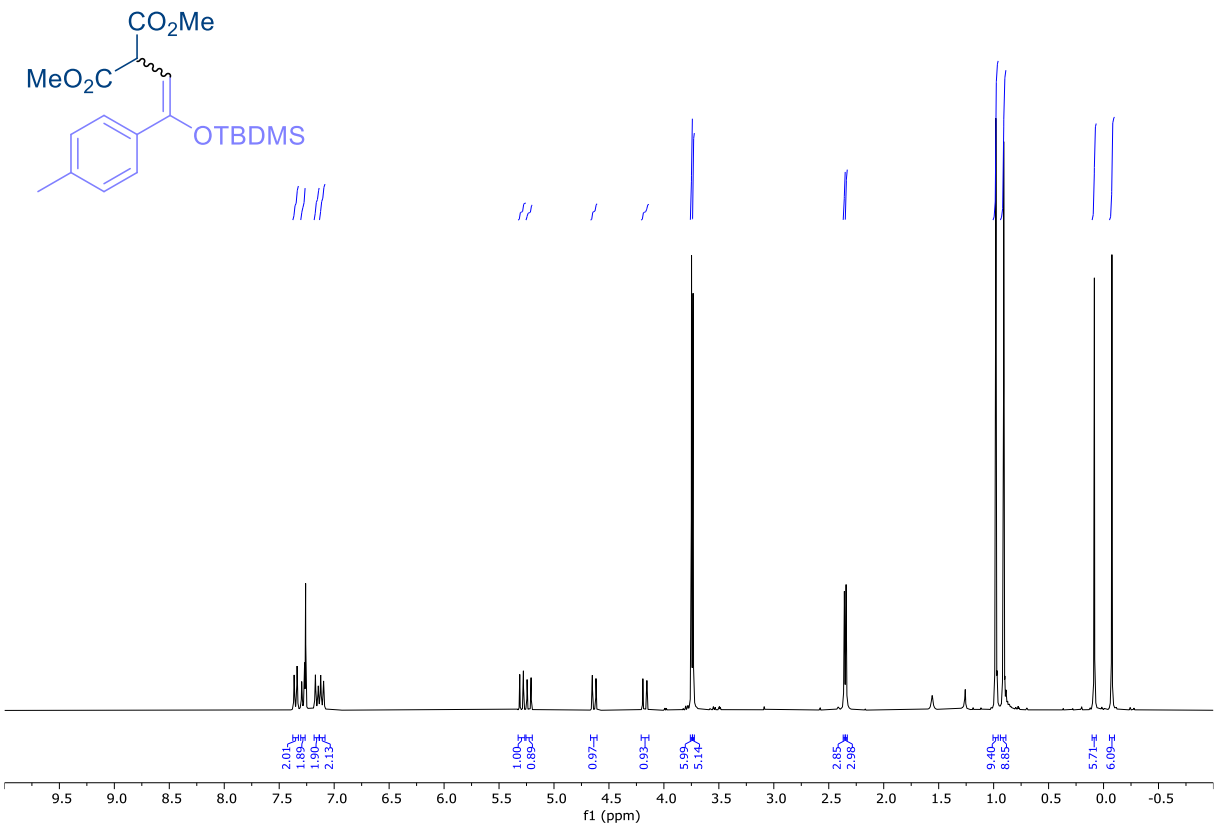



**Figure S76**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3af (*Z*/*E* = 53:47)**.

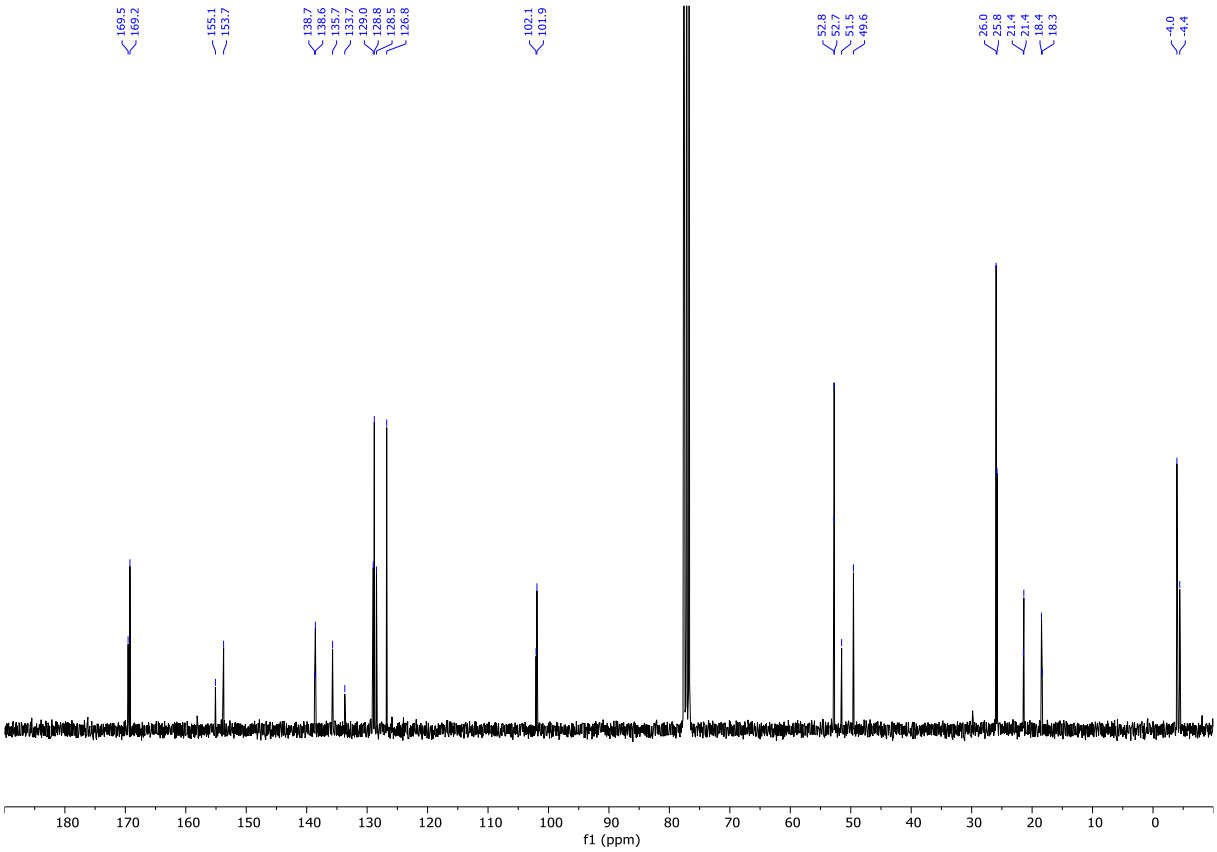



**Figure S77**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3af (*Z*/*E* = 53:47)**.

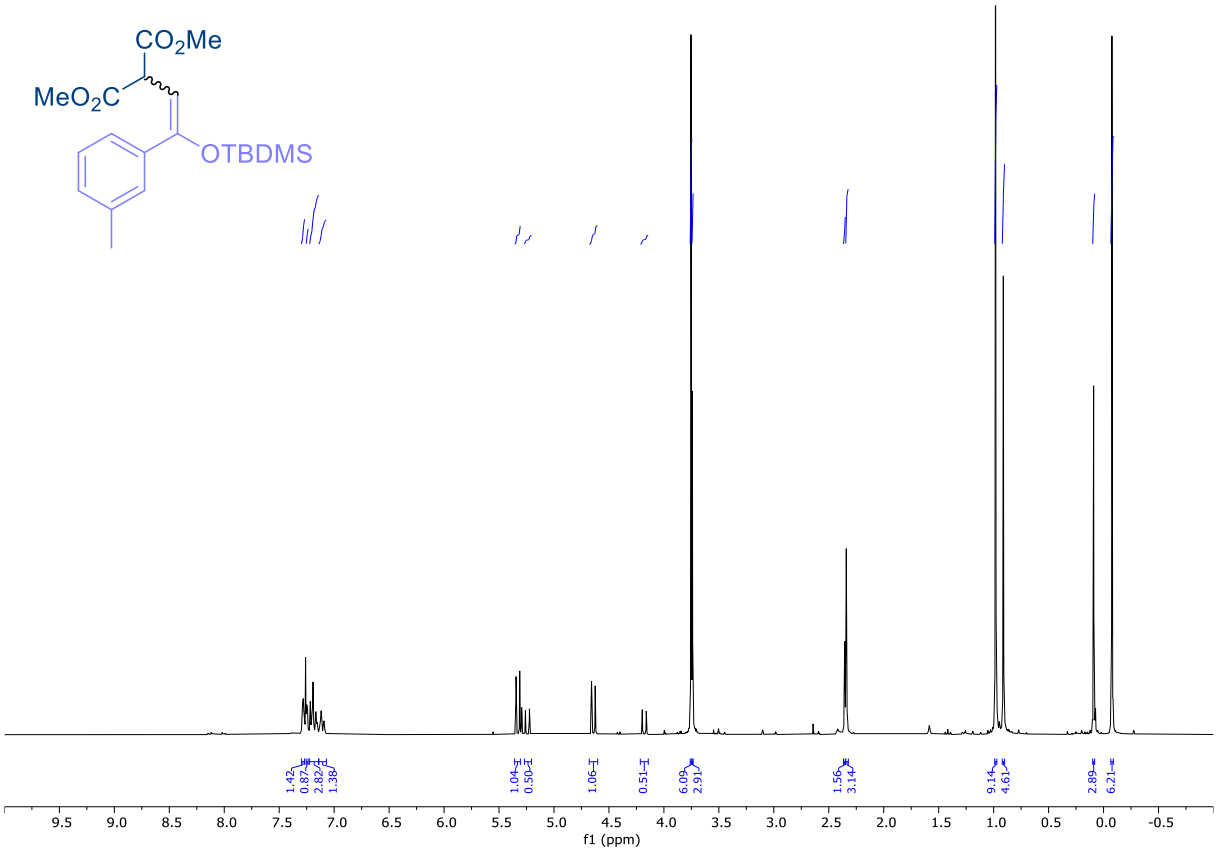



**Figure S78**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3ag (*Z*/*E* = 68:32)**.

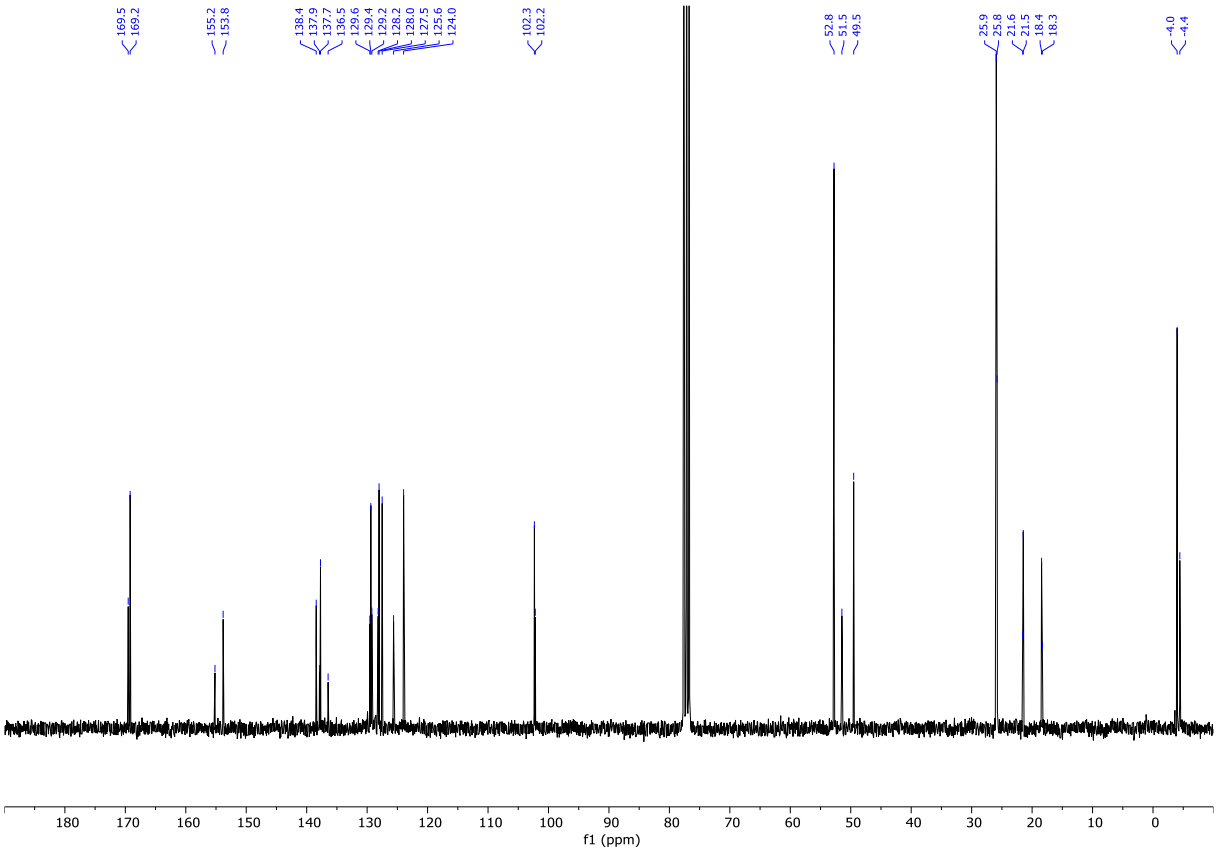



**Figure S79**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3ag (*Z*/*E* = 68:32)**.

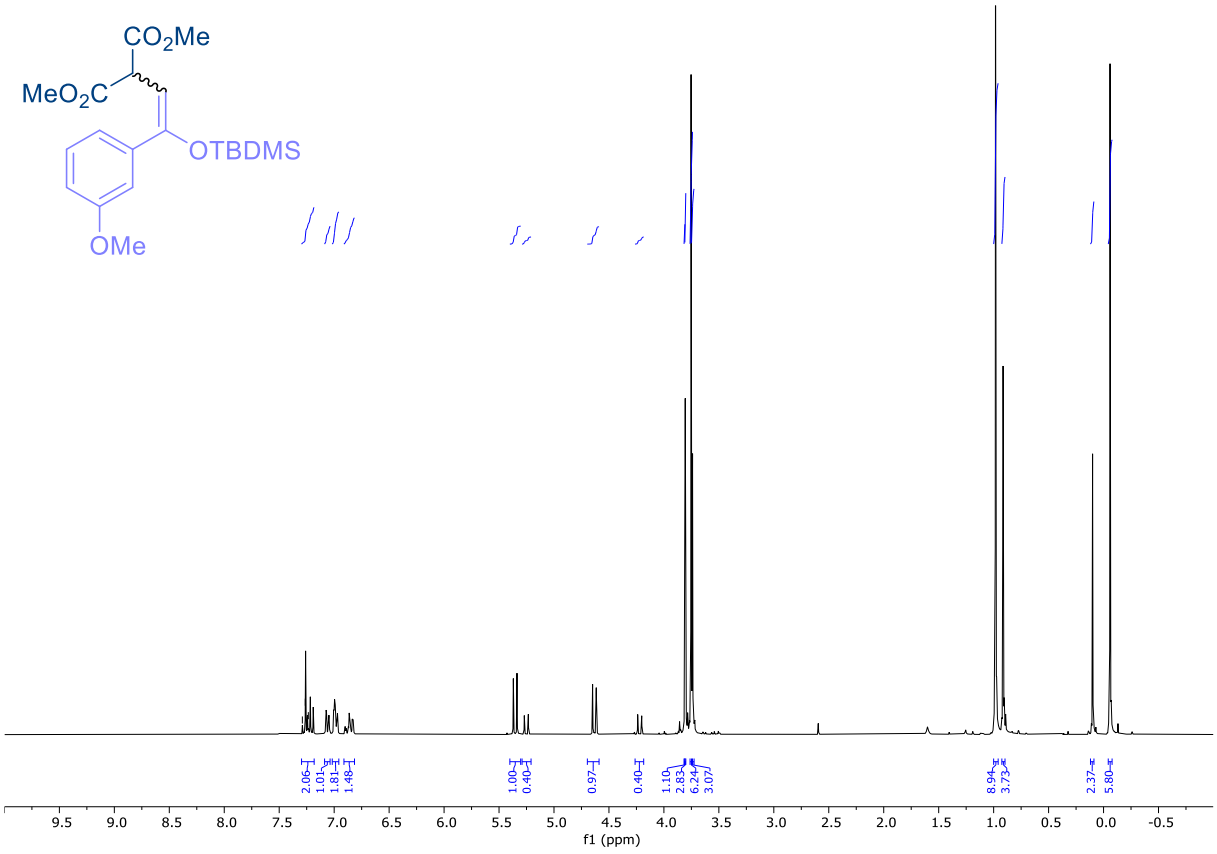



**Figure S80**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3ah (*Z*/*E* = 71:29)**.

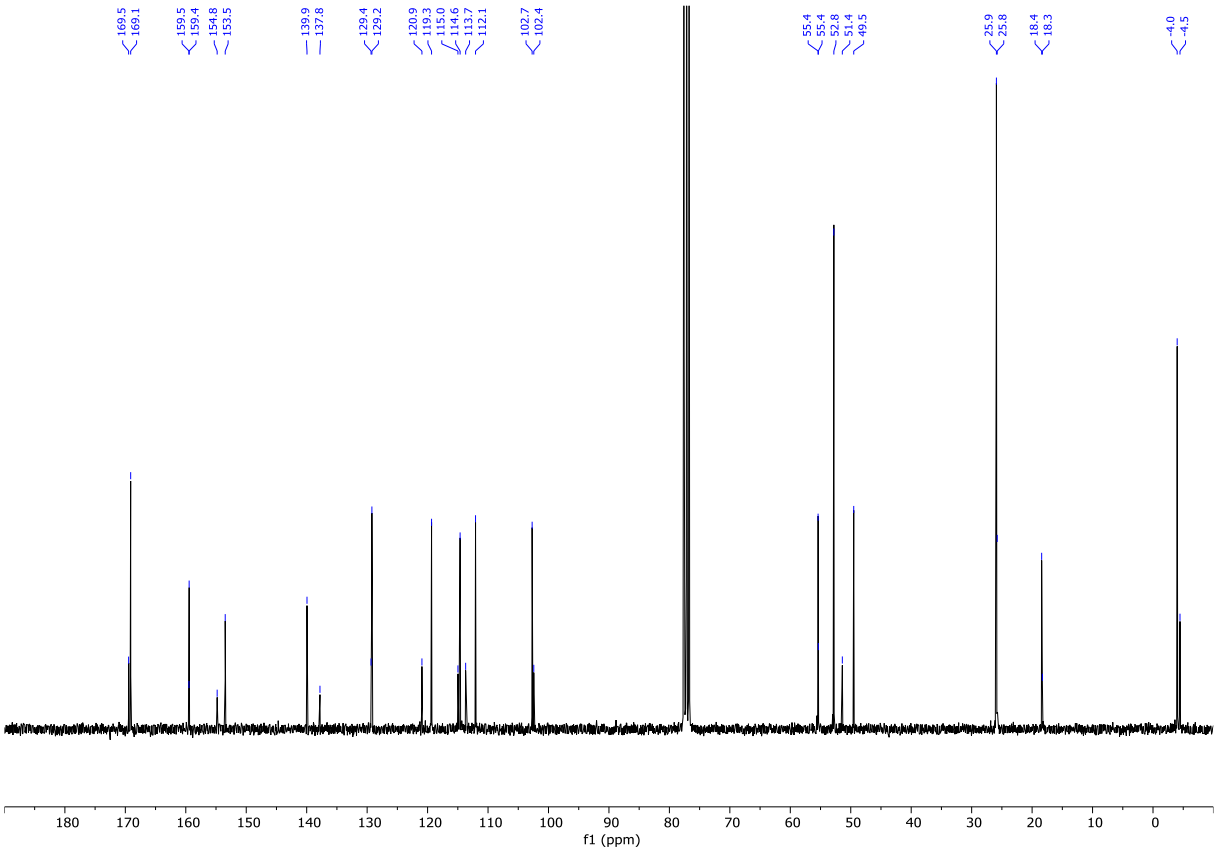



**Figure S81**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3ah (*Z*/*E* = 71:29)**.

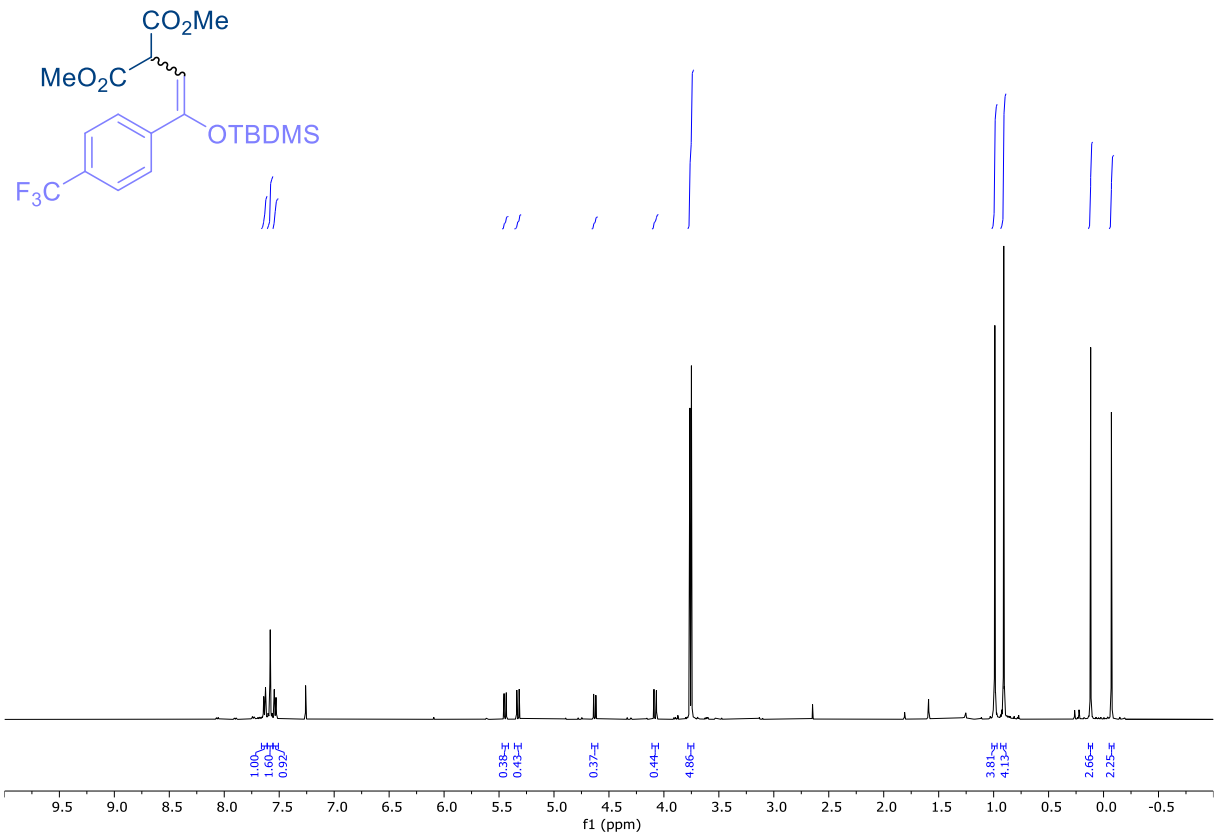



**Figure S82**. $^{1}$H NMR spectrum (500 MHz, 298K, $CDCl_3$) of **3ai (*Z*/*E* = 47:53)**.

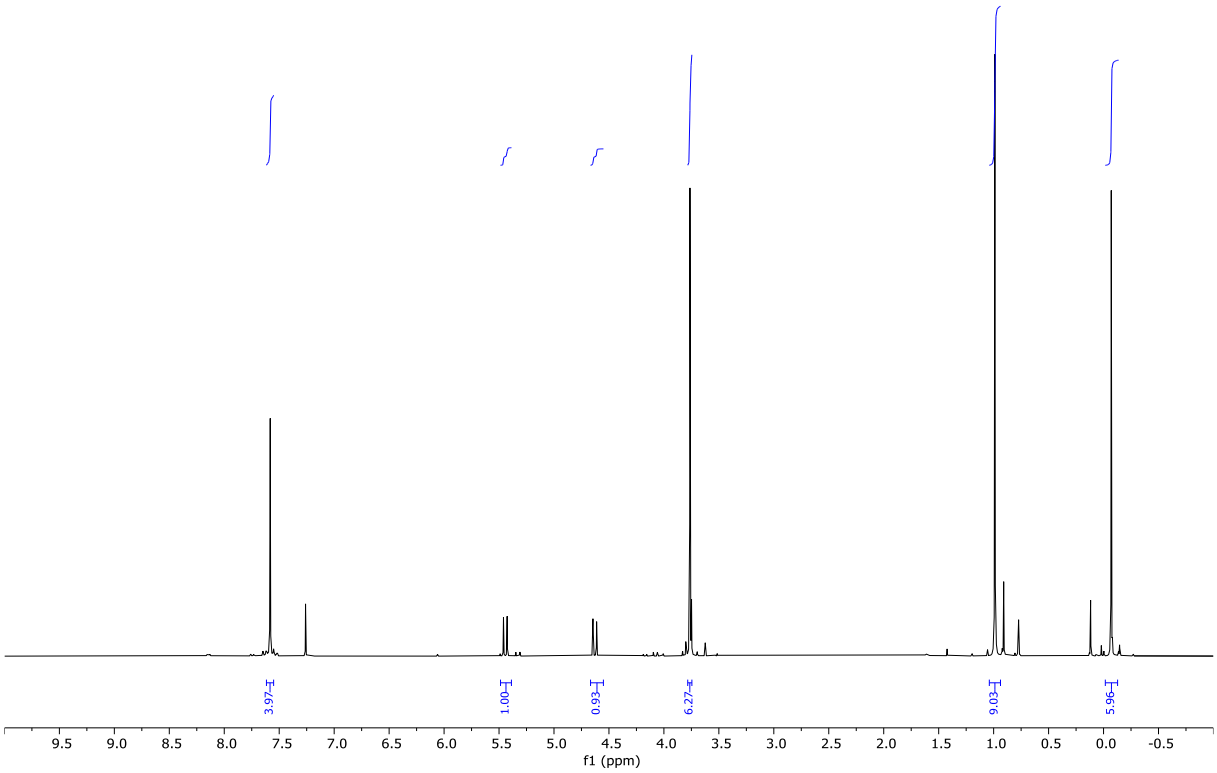



**Figure S83**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3ai (*Z-isomer*)**.

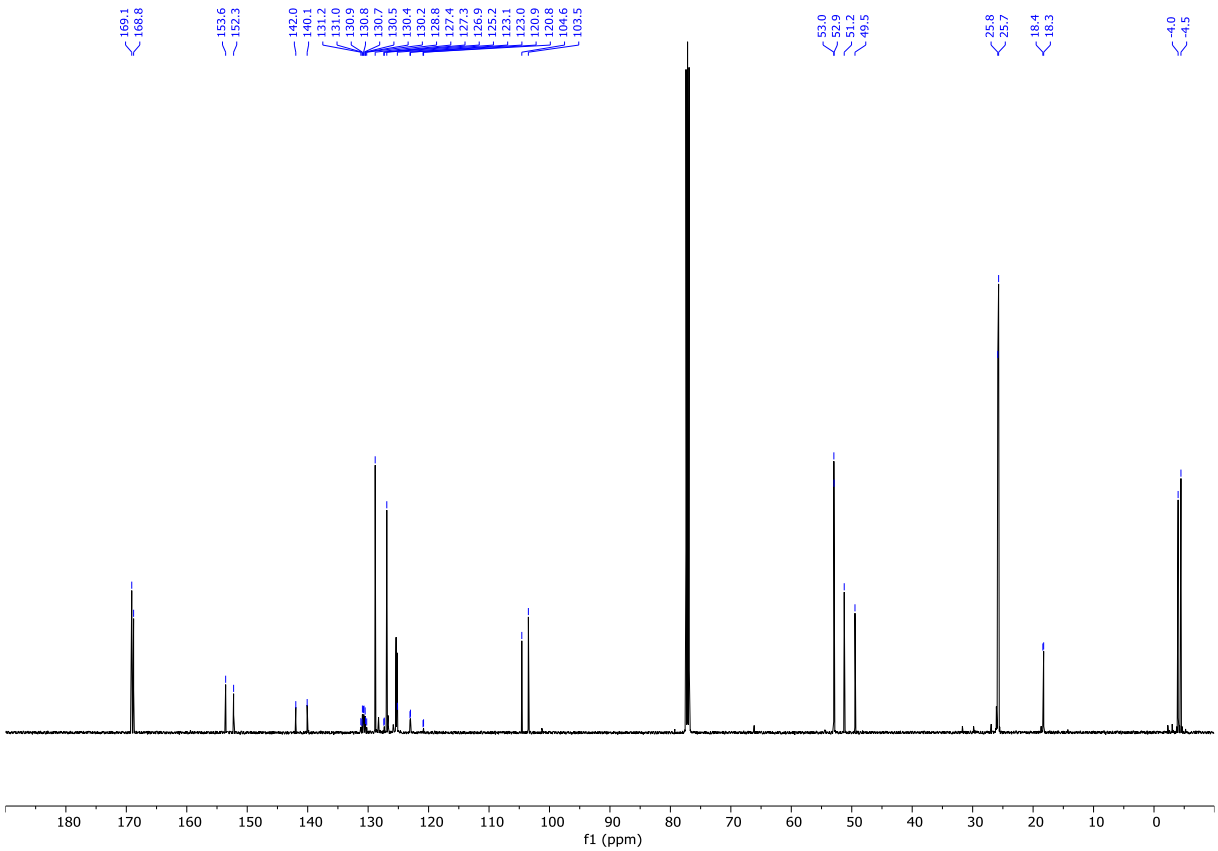



**Figure S84**. $^{13}C$ NMR spectrum (126 MHz, 298K, $CDCl_3$) of **3ai (*Z/E* = 47:53)**.

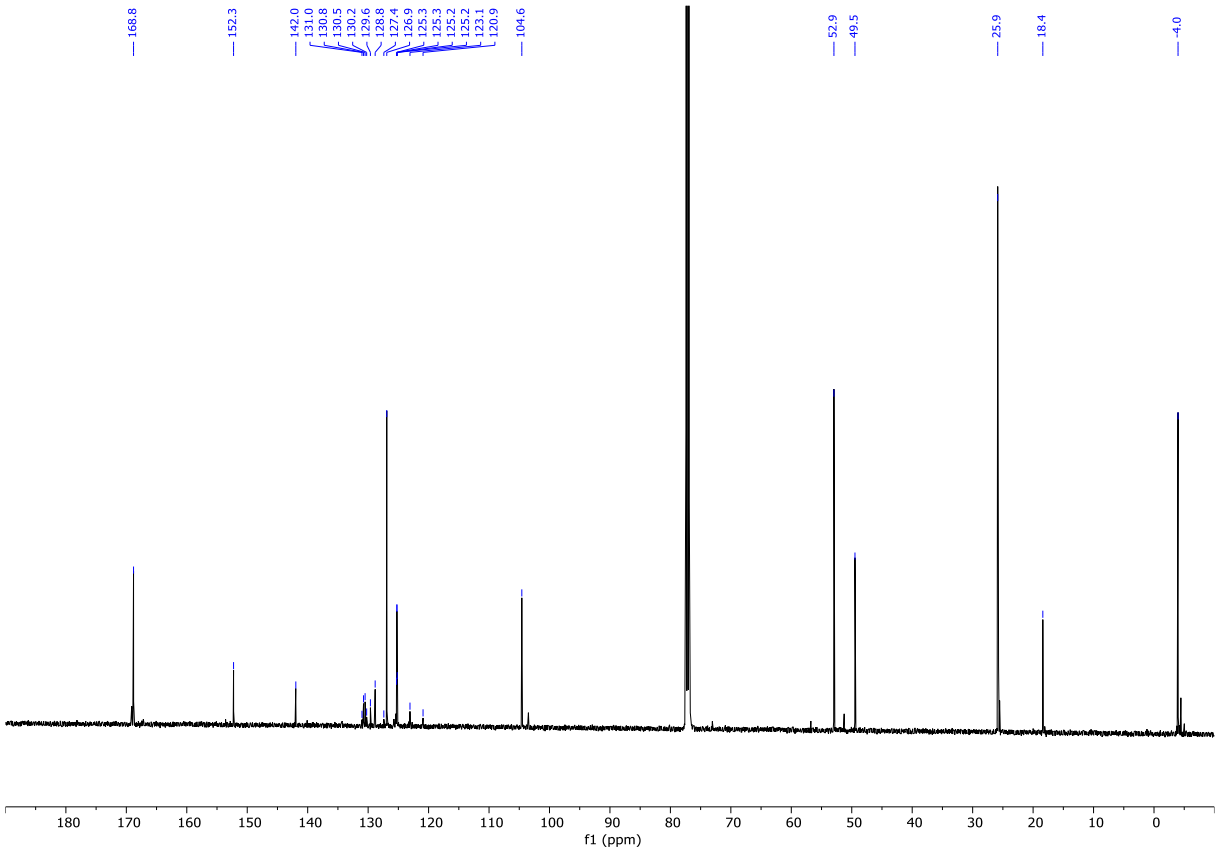



**Figure S85**. $^{13}C$ NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3ai (*Z-isomer*)**.

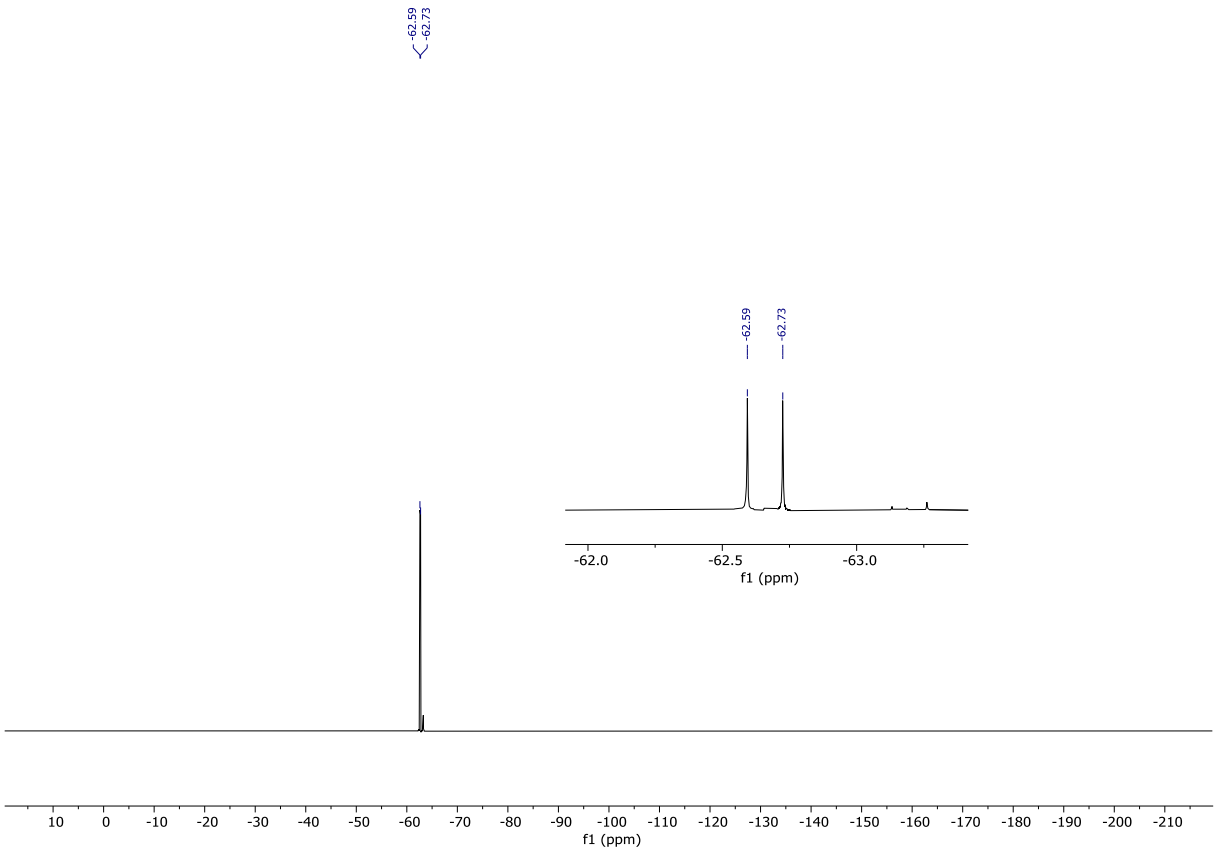



**Figure S86**. $^{19}F$ NMR spectrum (282 MHz, 298K, $CDCl_3$) of **3ai (*Z/E* = 47:53)**.

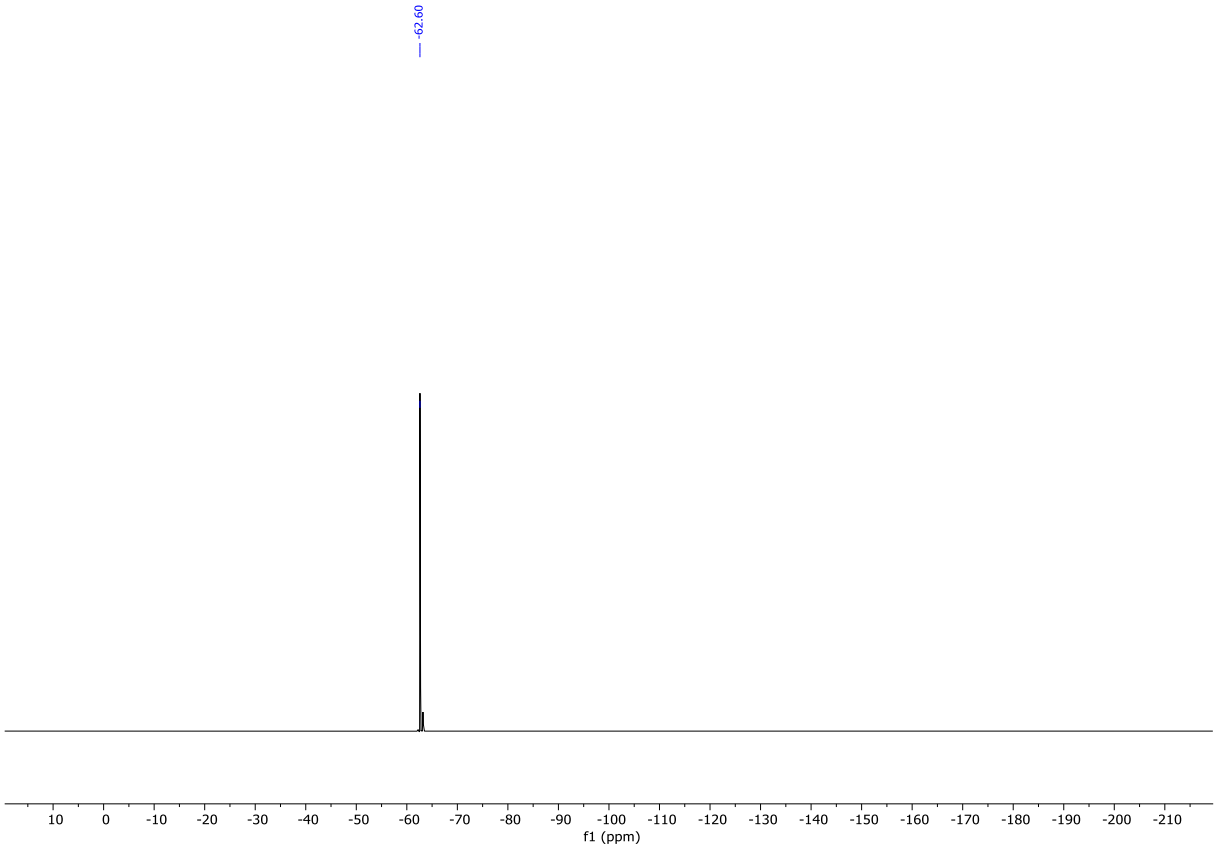



**Figure S87**. $^{19}F$ NMR spectrum (282 MHz, 298K, $CDCl_3$) of **3ai (*Z-isomer*)**.

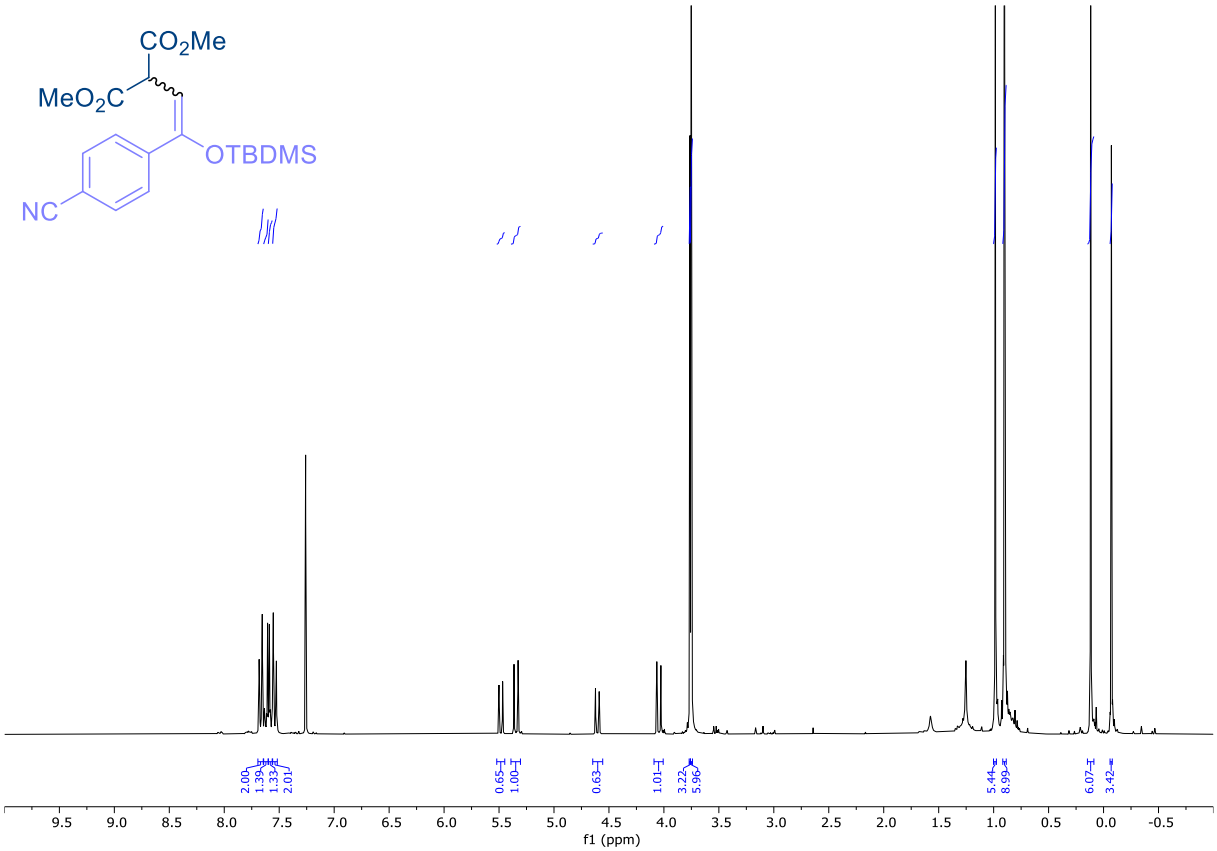



**Figure S88**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3aj (*Z*/*E* = 39:61)**.

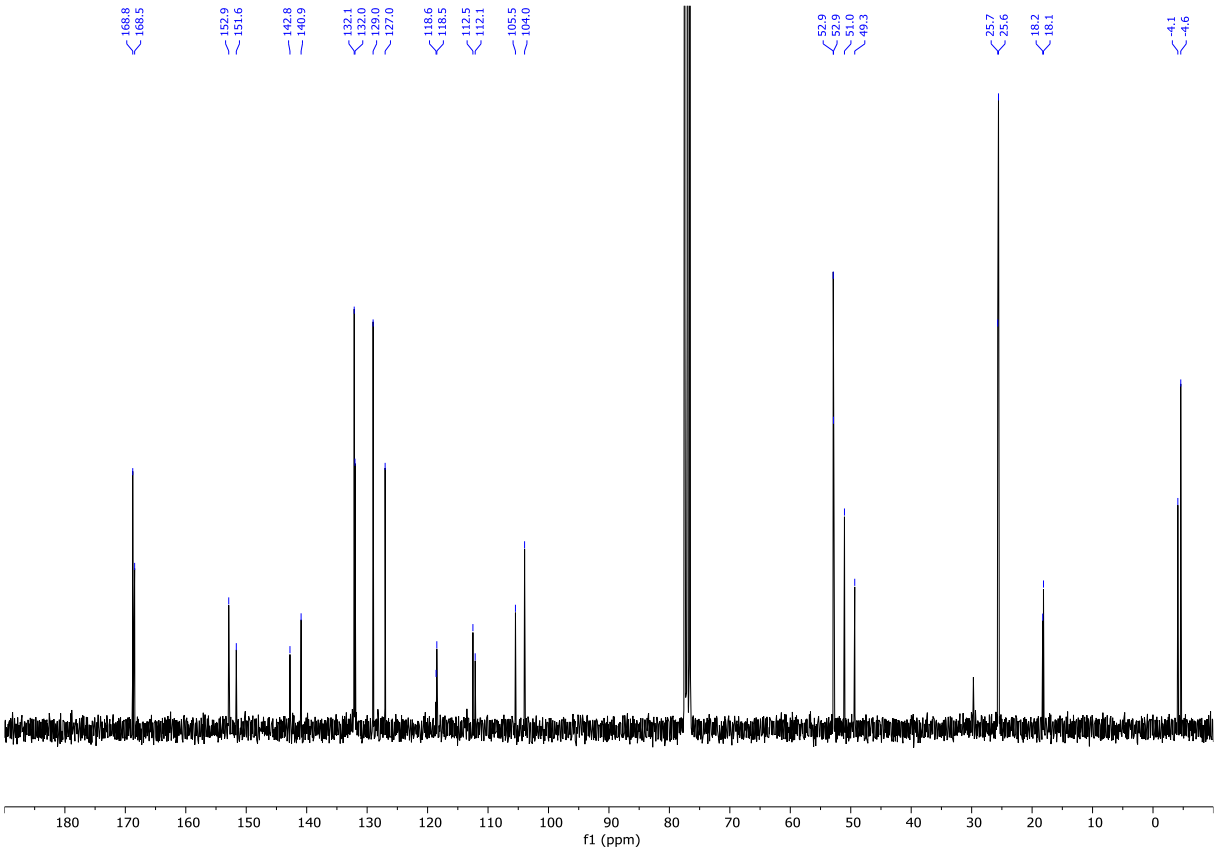



**Figure S89**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3aj (*Z*/*E* = 39:61)**.

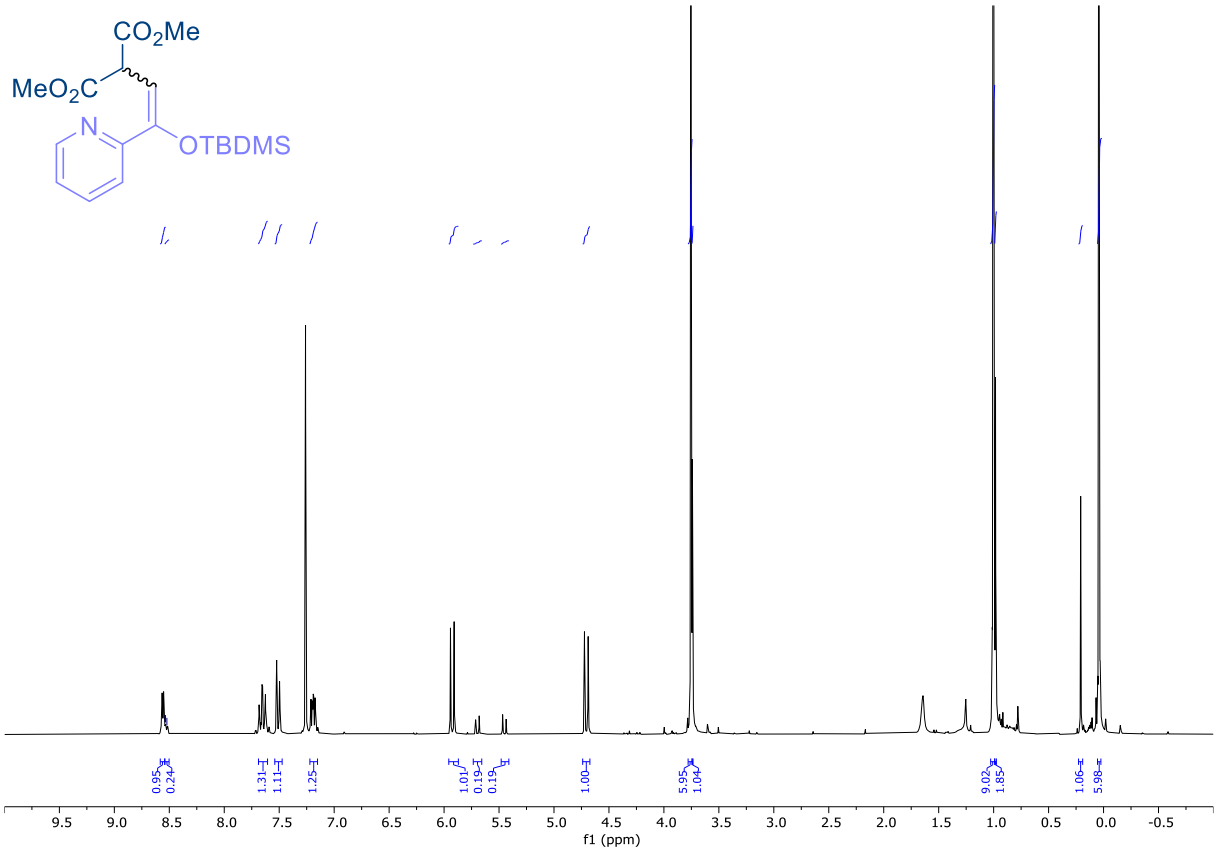



**Figure S90**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3ak (*Z*/*E* = 84:16)**.

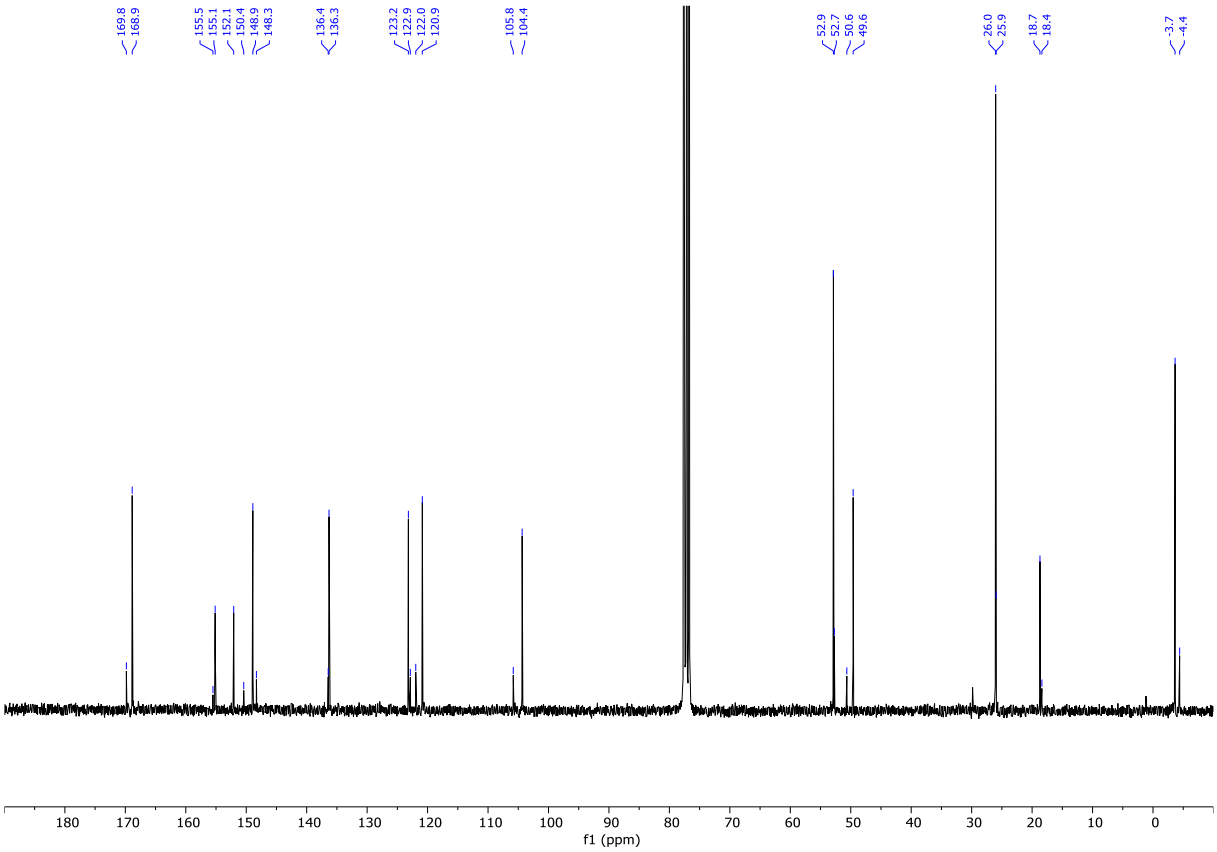



**Figure S91**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3ak (*Z*/*E* = 84:16)**.

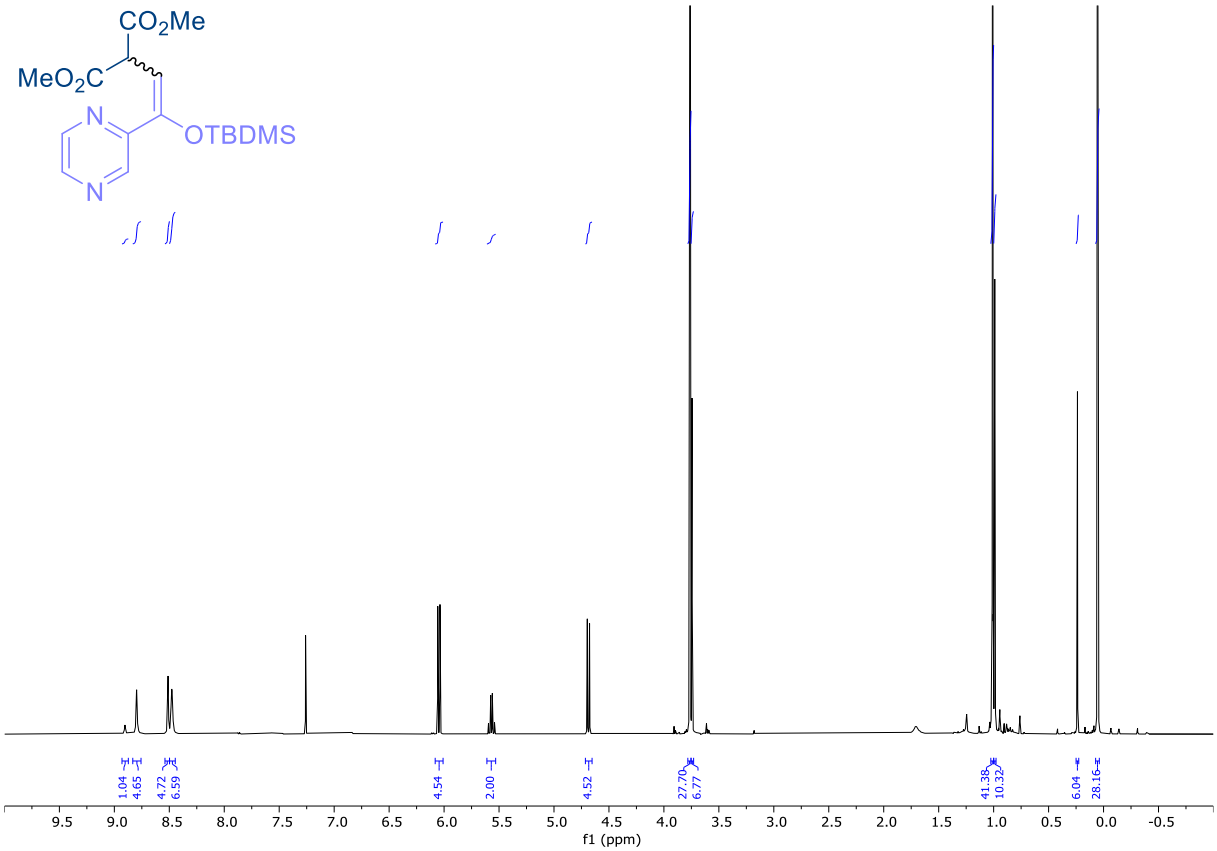



**Figure S92**. $^{1}$H NMR spectrum (500 MHz, 298K, $CDCl_3$) of **3al (*Z*/*E* = 78:22)**.

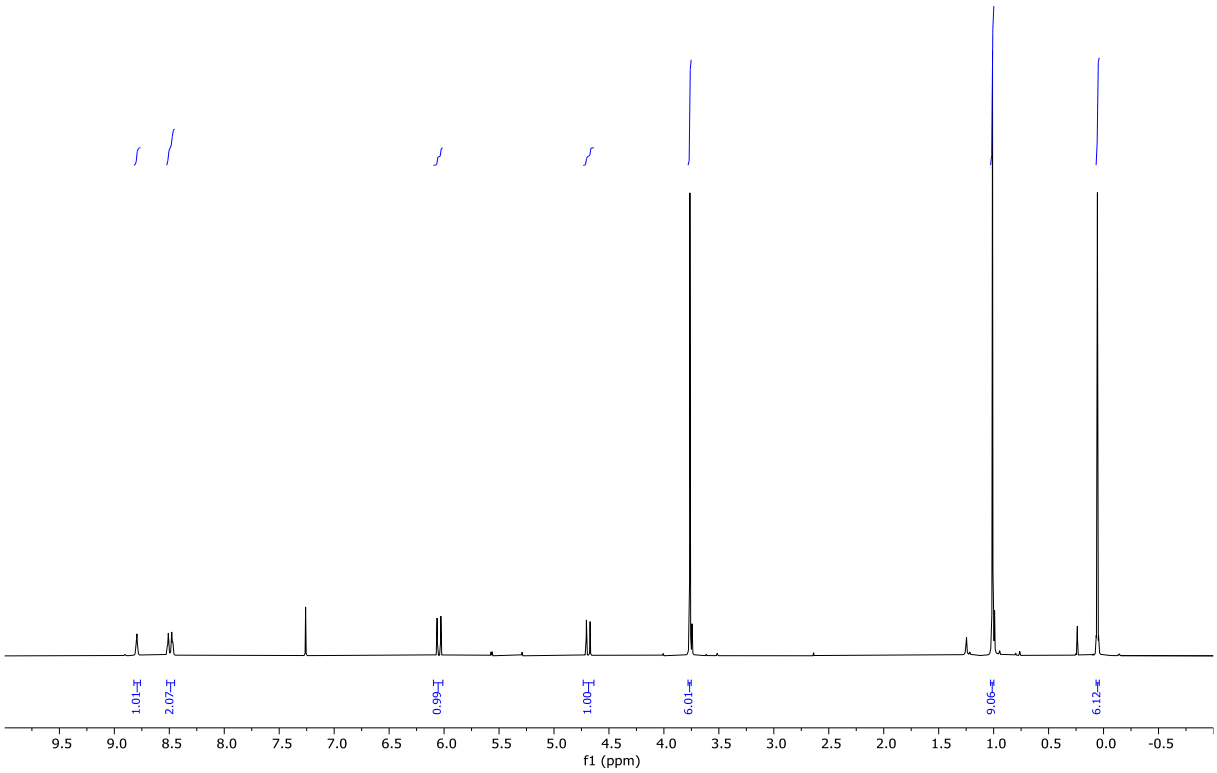



**Figure S93**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3al (*Z*/*E* = 94:6)**.

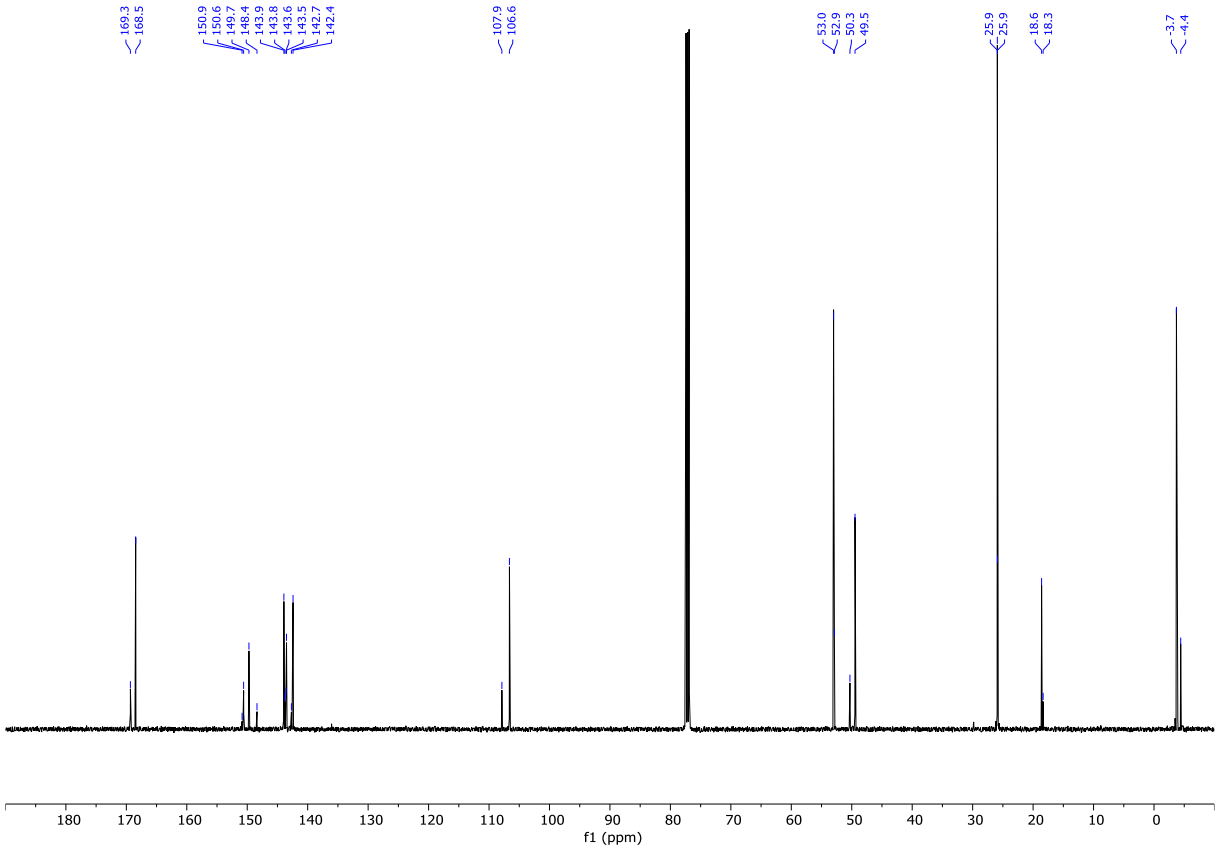



**Figure S94**. $^{13}C$ NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3al (*Z*/*E* = 78:22)**.

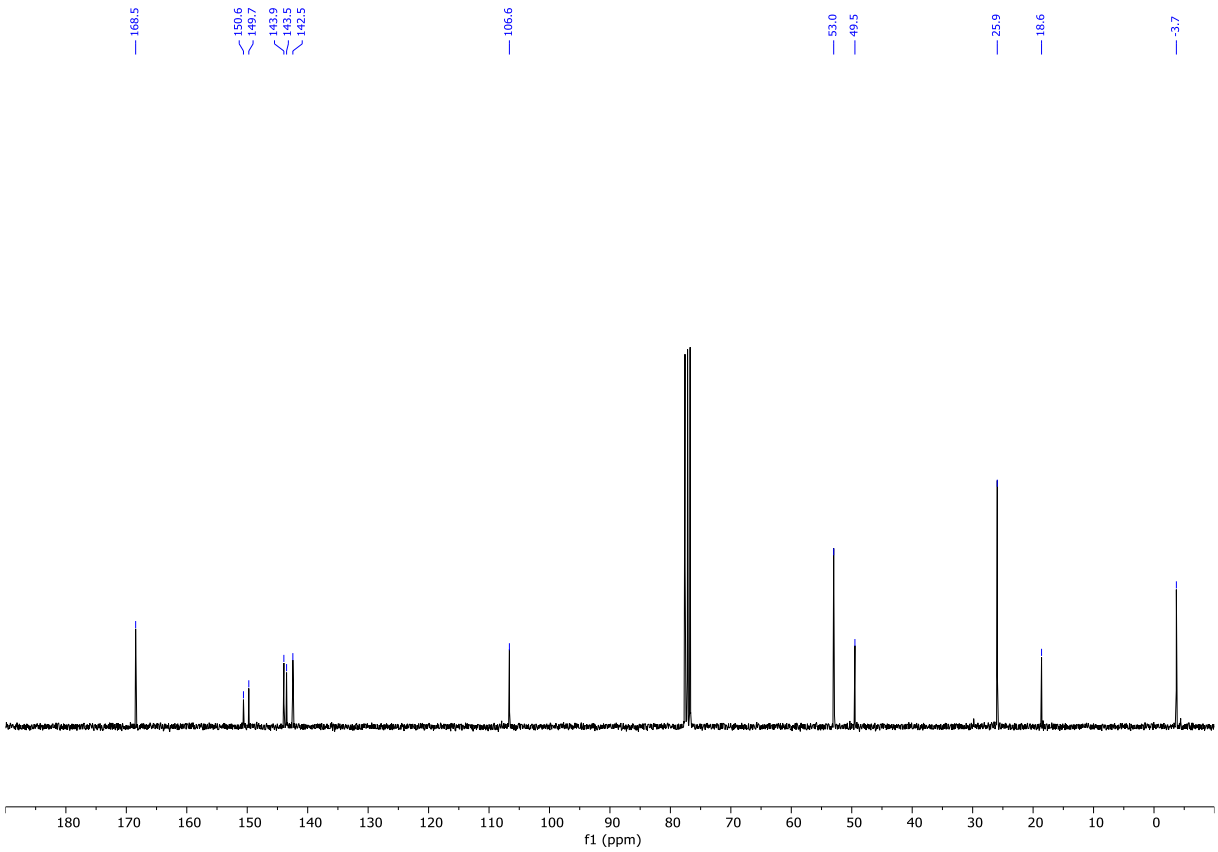



**Figure S95**. $^{13}C$ NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3al (*Z*/*E* = 94:6)**.

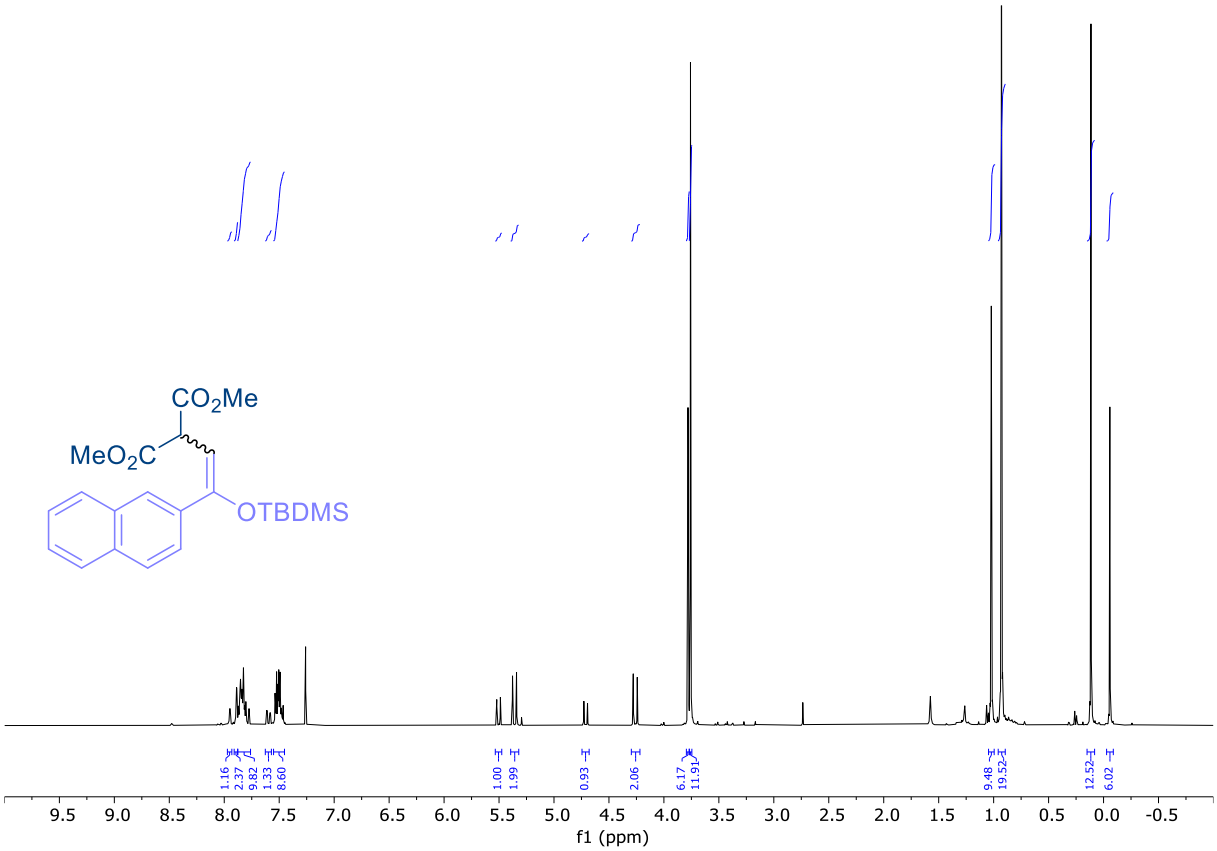



**Figure S96**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3am (*Z/E* = 34:66)**.

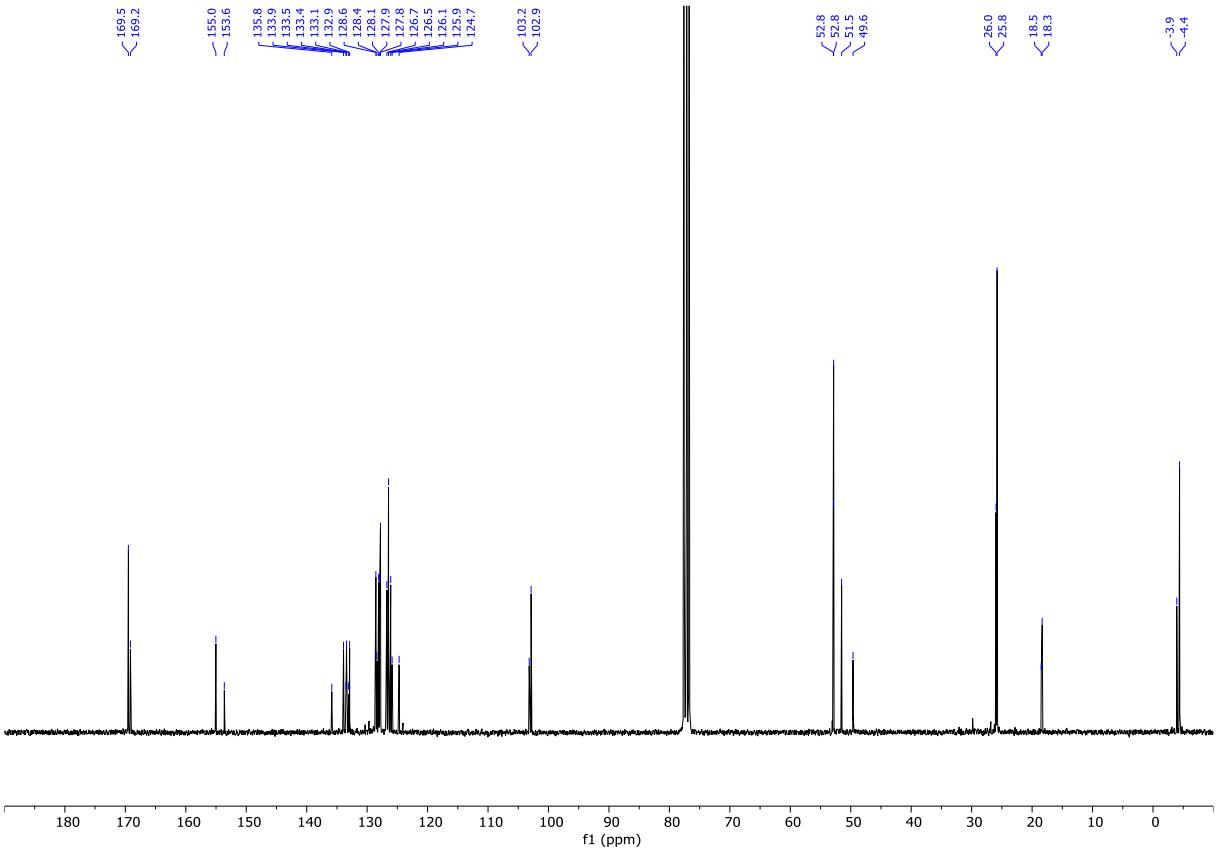



**Figure S97**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3am (*Z/E* = 34:66)**.

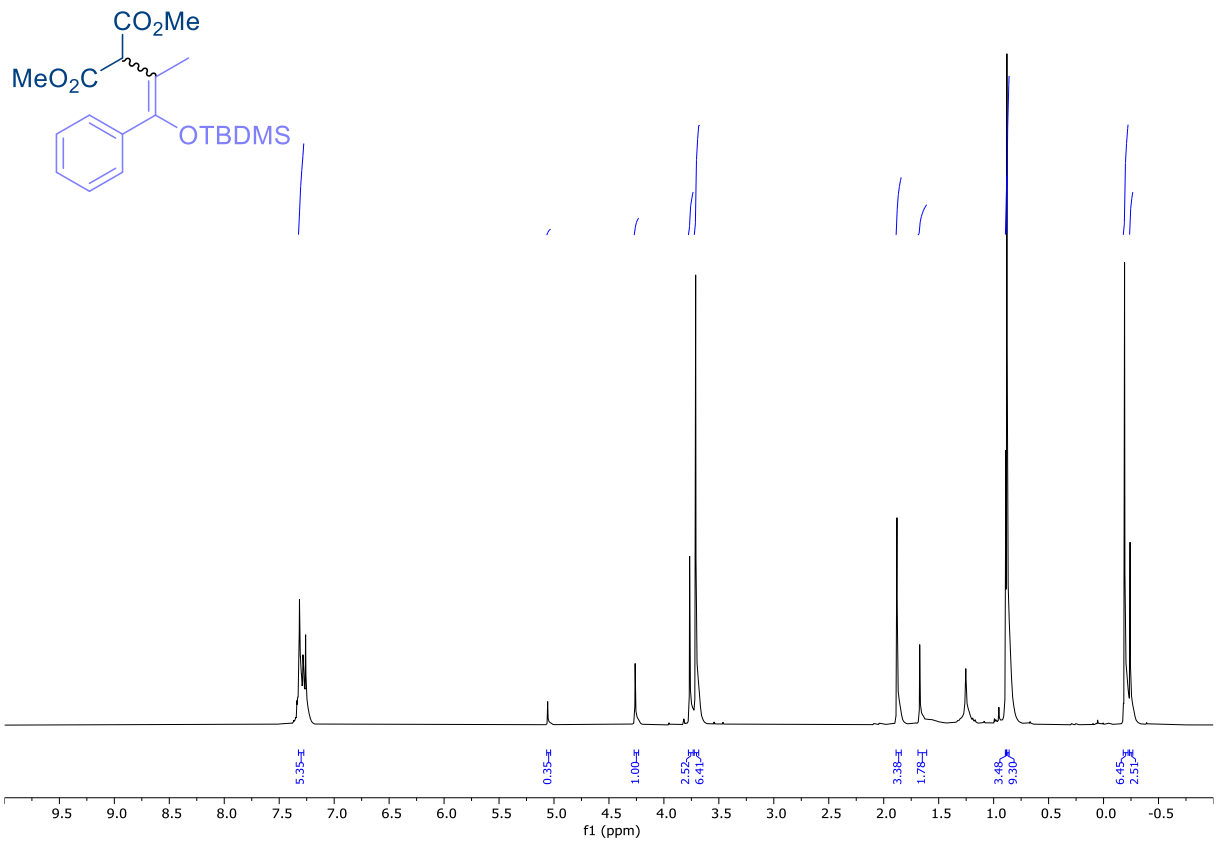



**Figure S98**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3an (*Z*/*E* = 26:74)**.

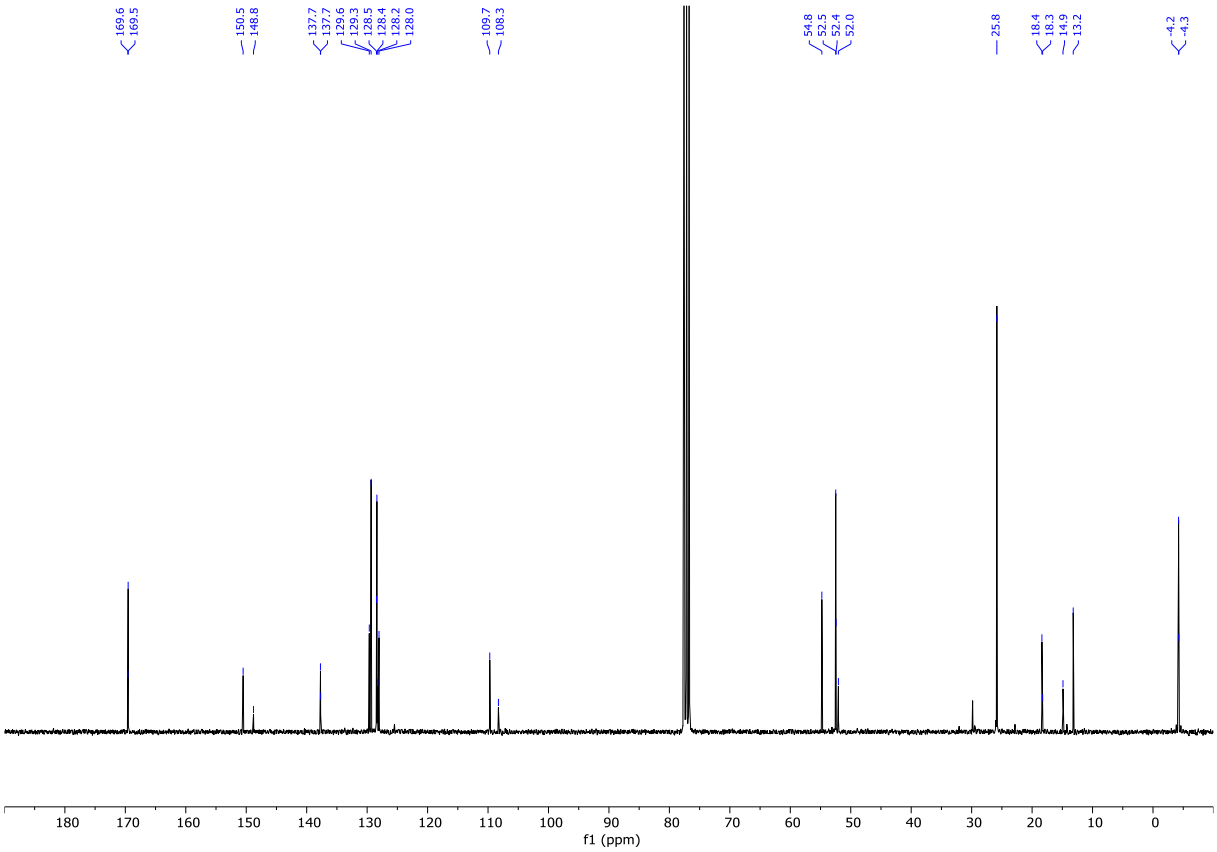



**Figure S99**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3an (*Z*/*E* = 26:74)**.

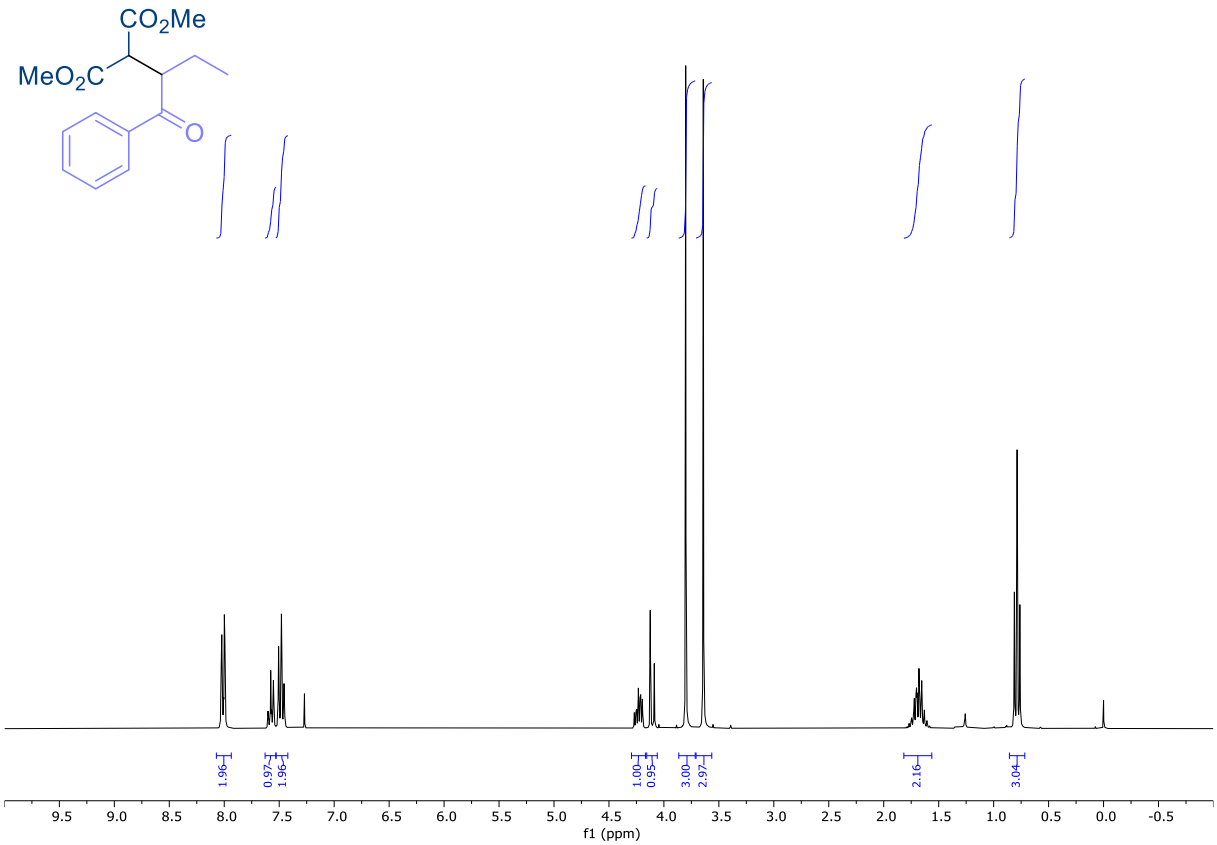



**Figure S100**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3ao'**.

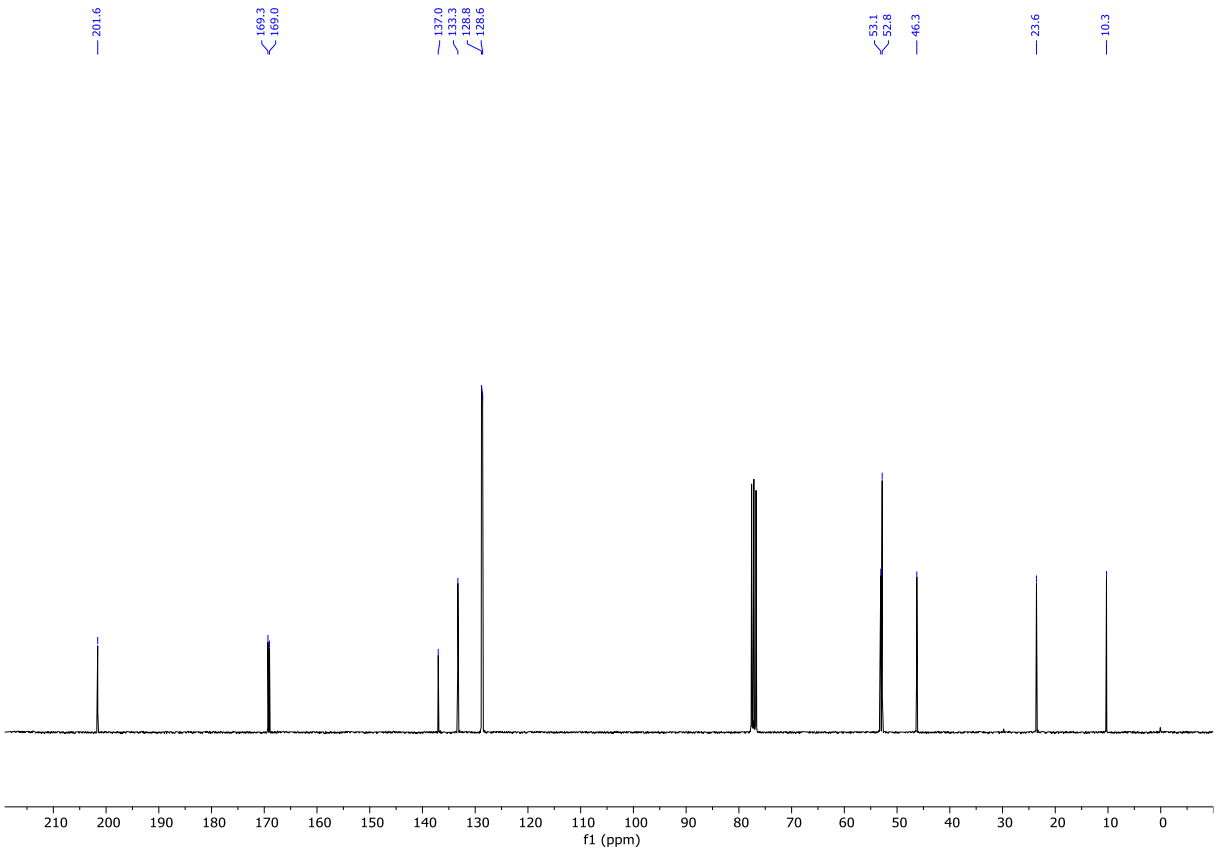



**Figure S101**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3ao'**.

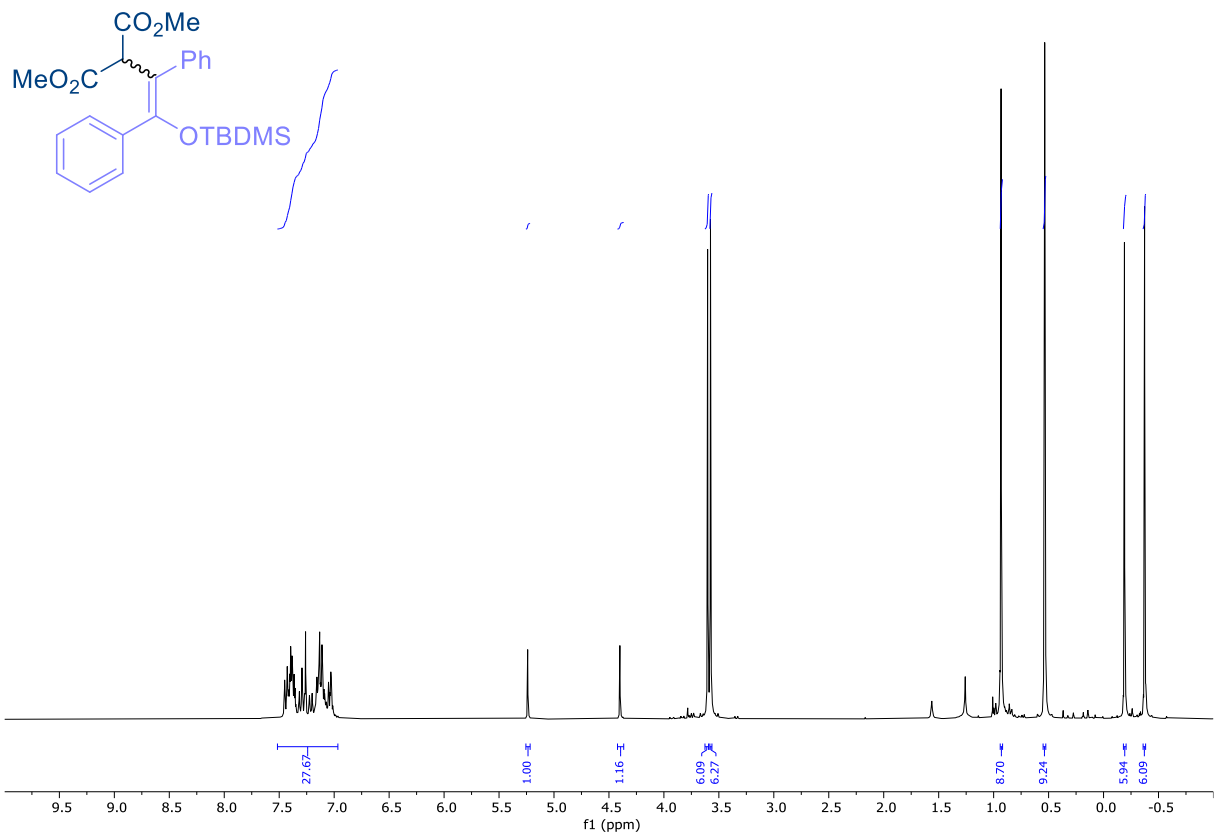



**Figure S102**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3ap (*Z*/*E* = 46:54)**.

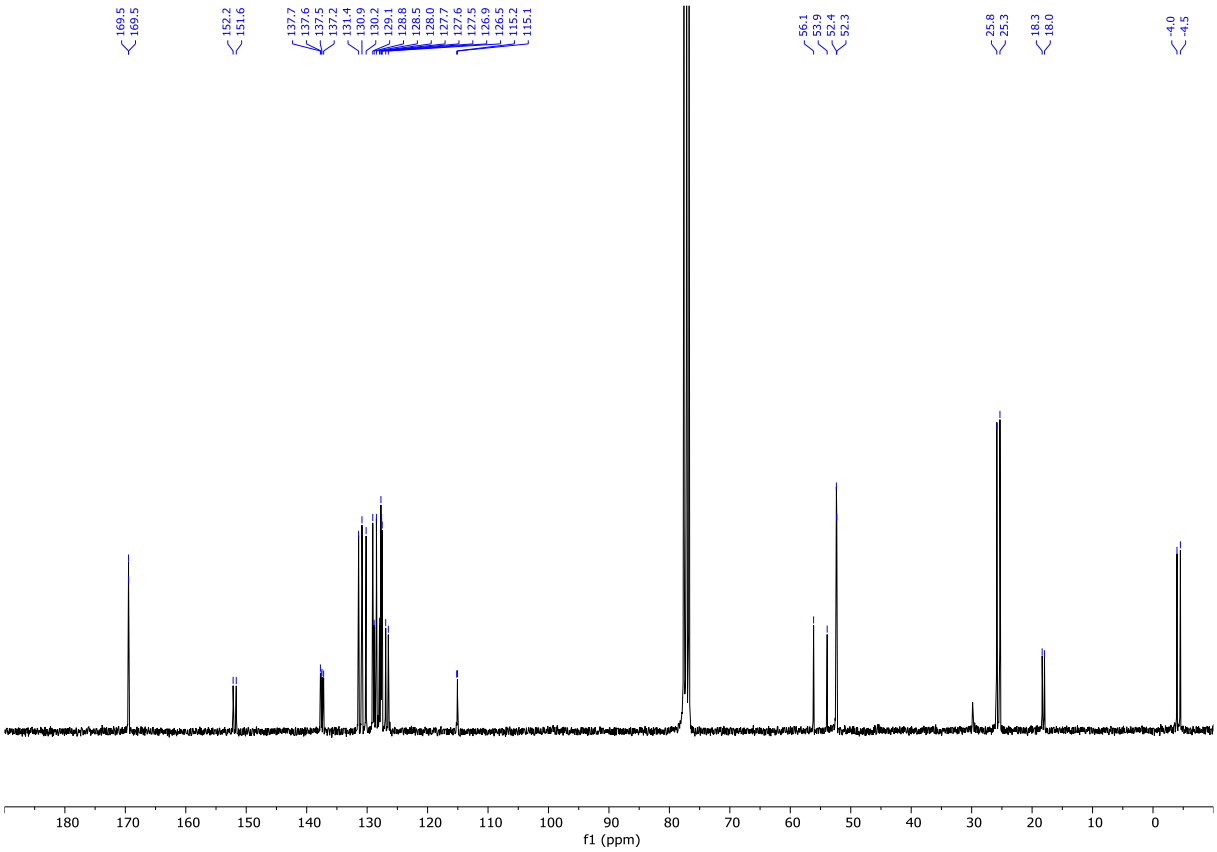



**Figure S103**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3ap (*Z*/*E* = 46:54)**.

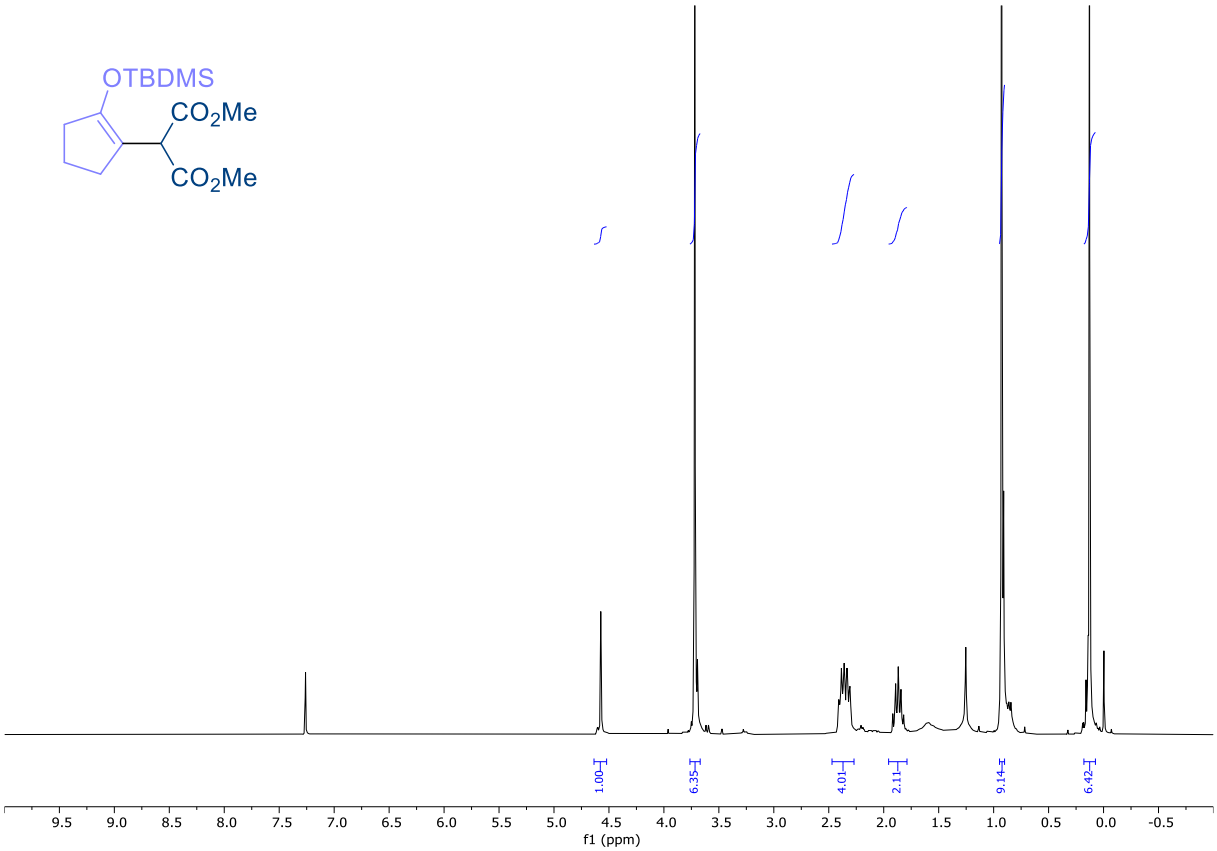



**Figure S104**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3aq**.

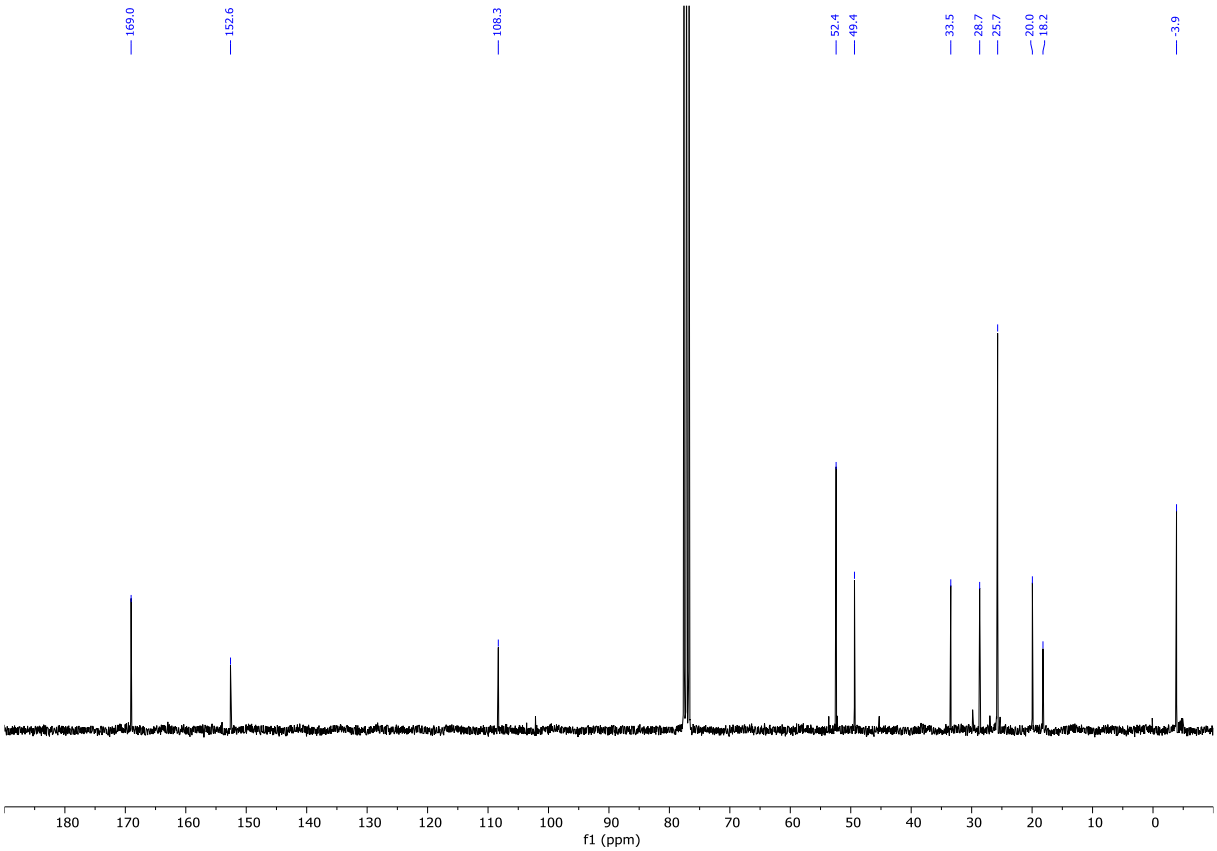



**Figure S105**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3aq**.

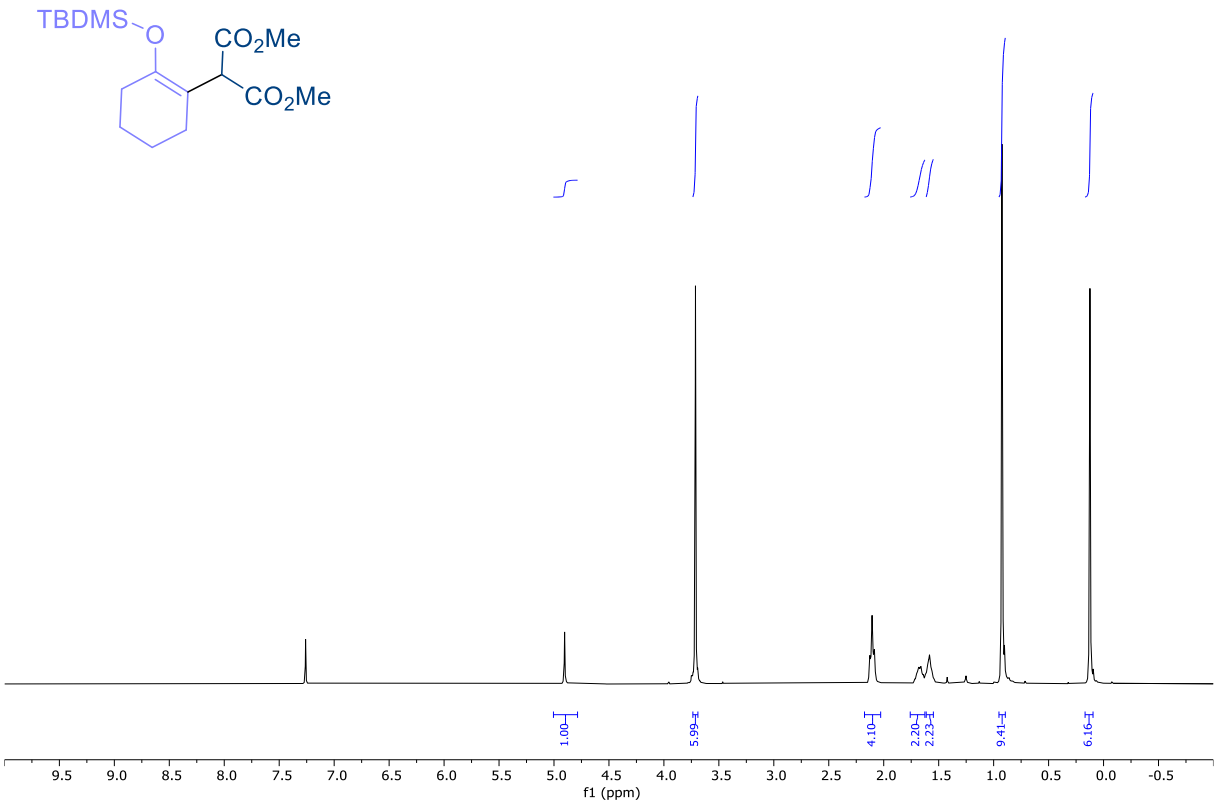



**Figure S106**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3ar**.

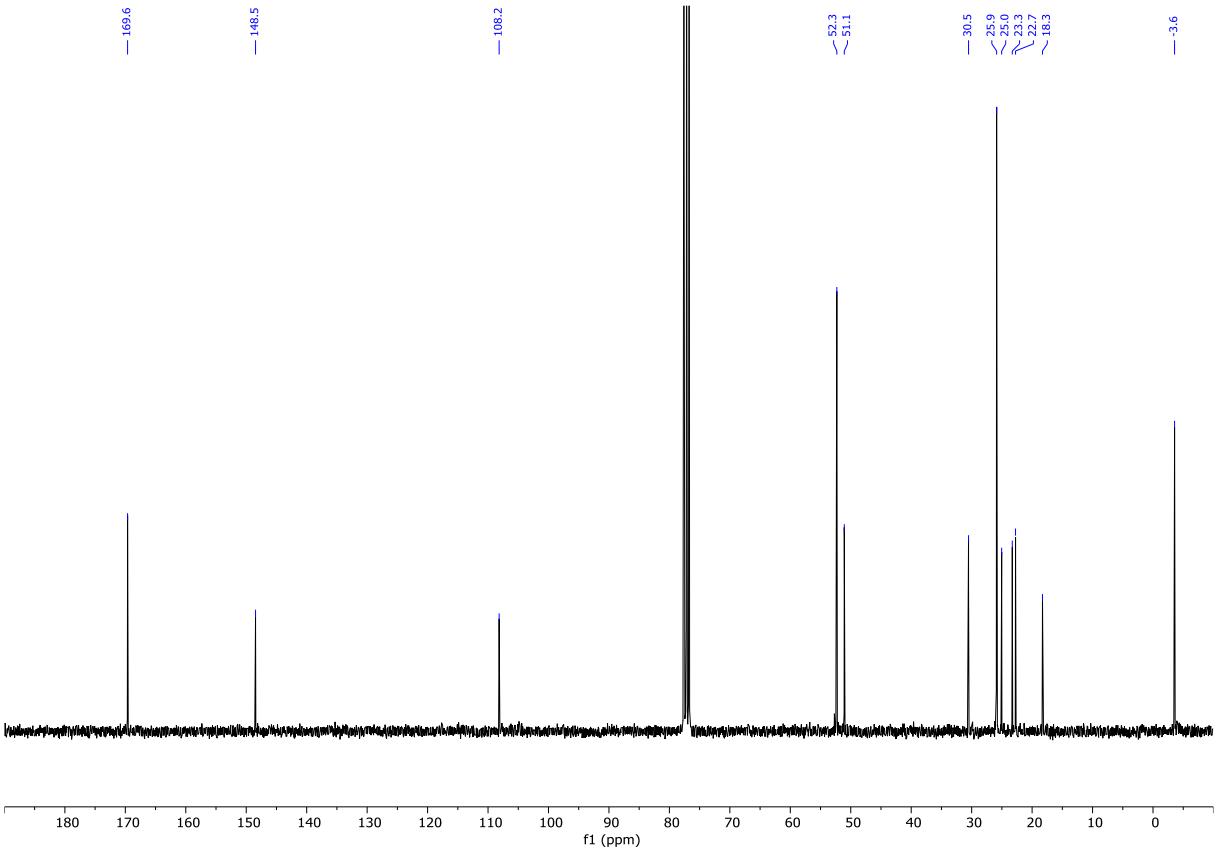



**Figure S107**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3ar**.

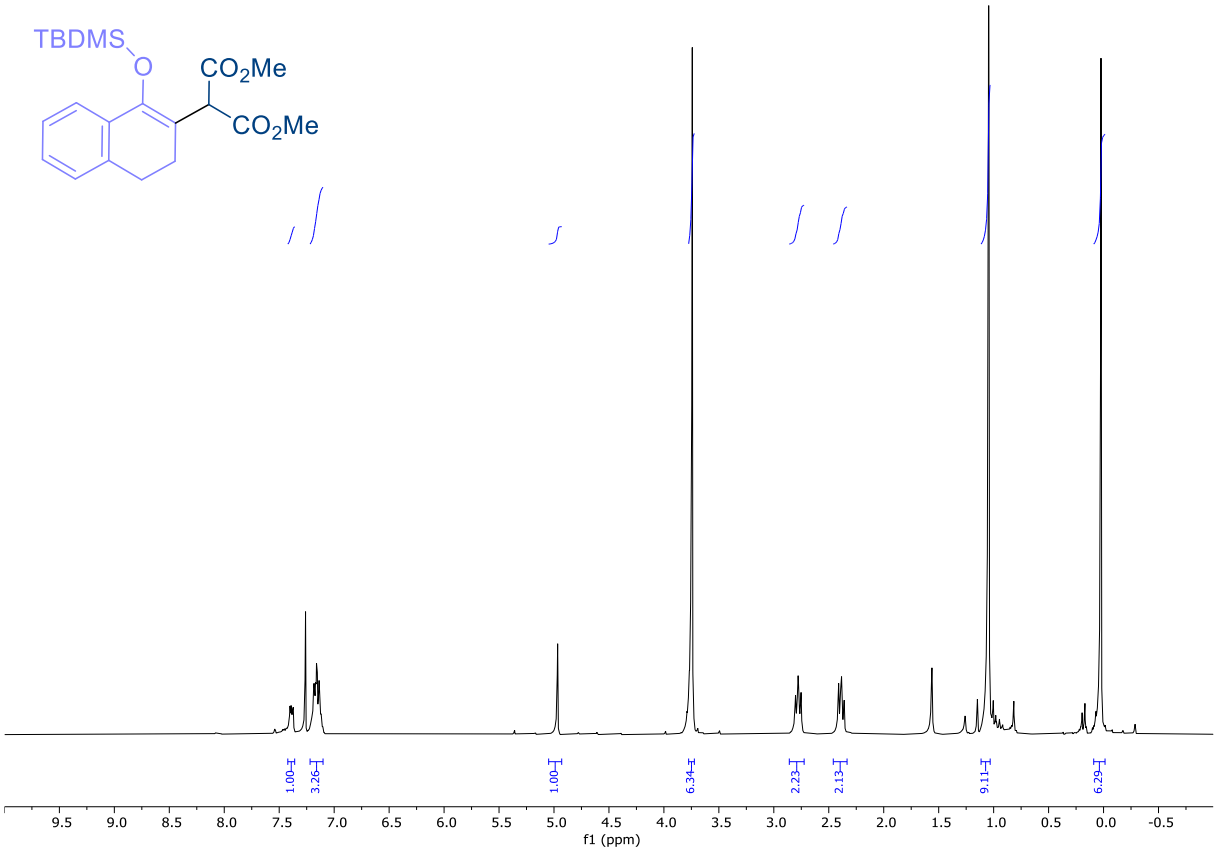



**Figure S108**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3as**.

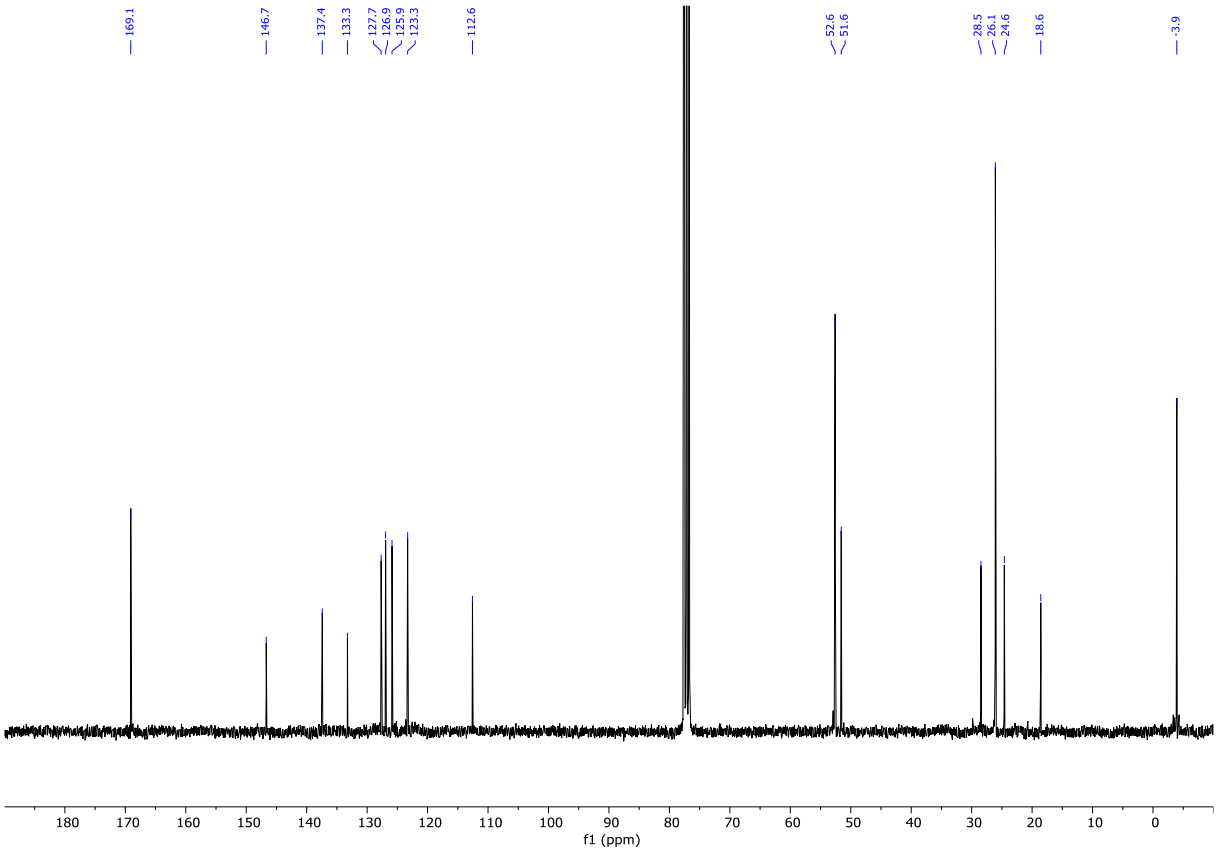



**Figure S109**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3as**.

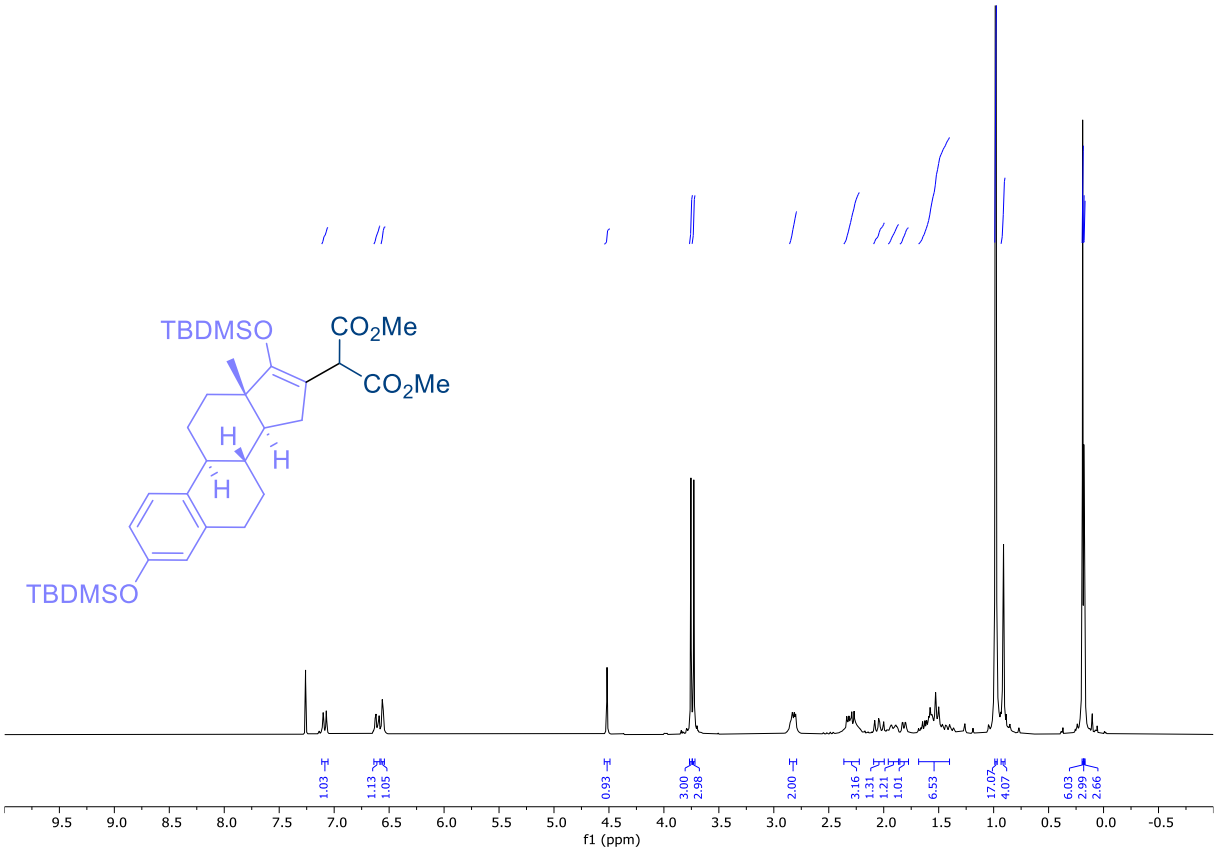



**Figure S110**. $^{1}H$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3at**.

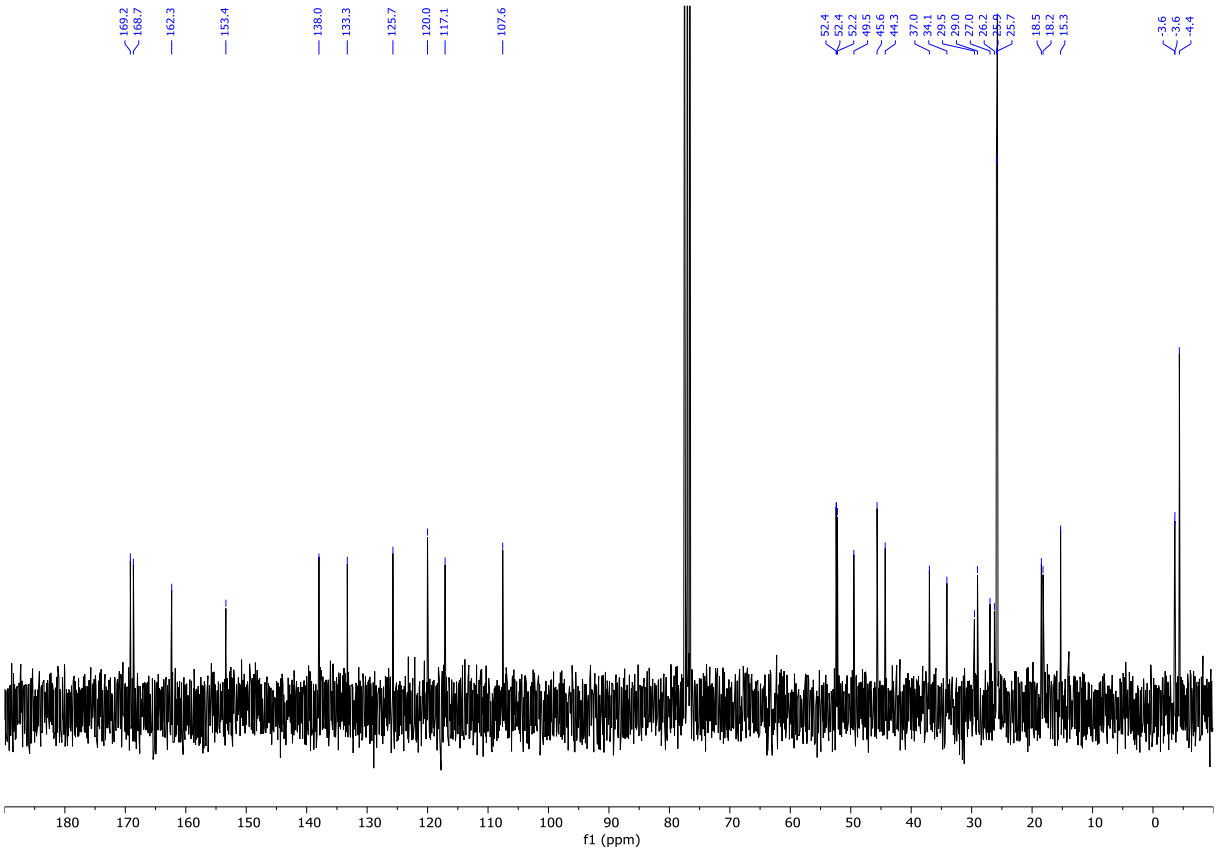



**Figure S111**. $^{13}C$ NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3at**.

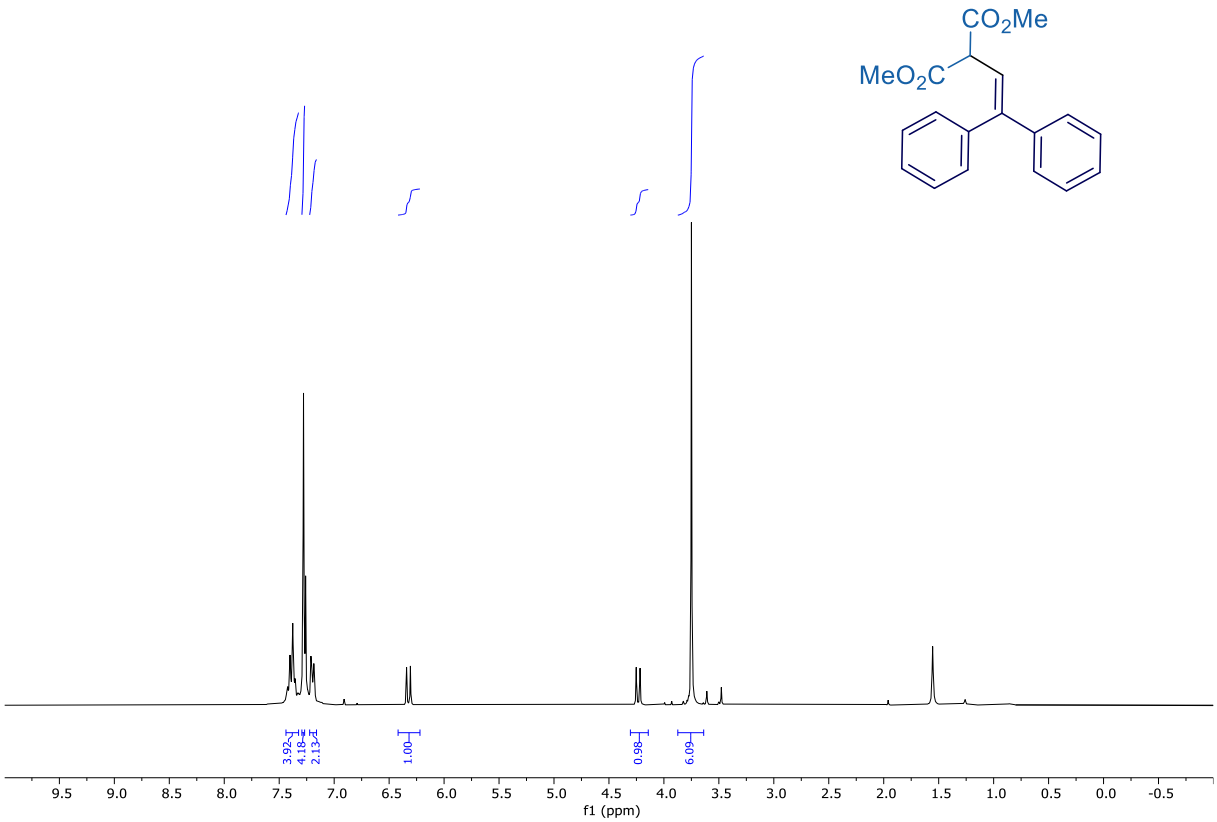



**Figure S112**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5aa**.

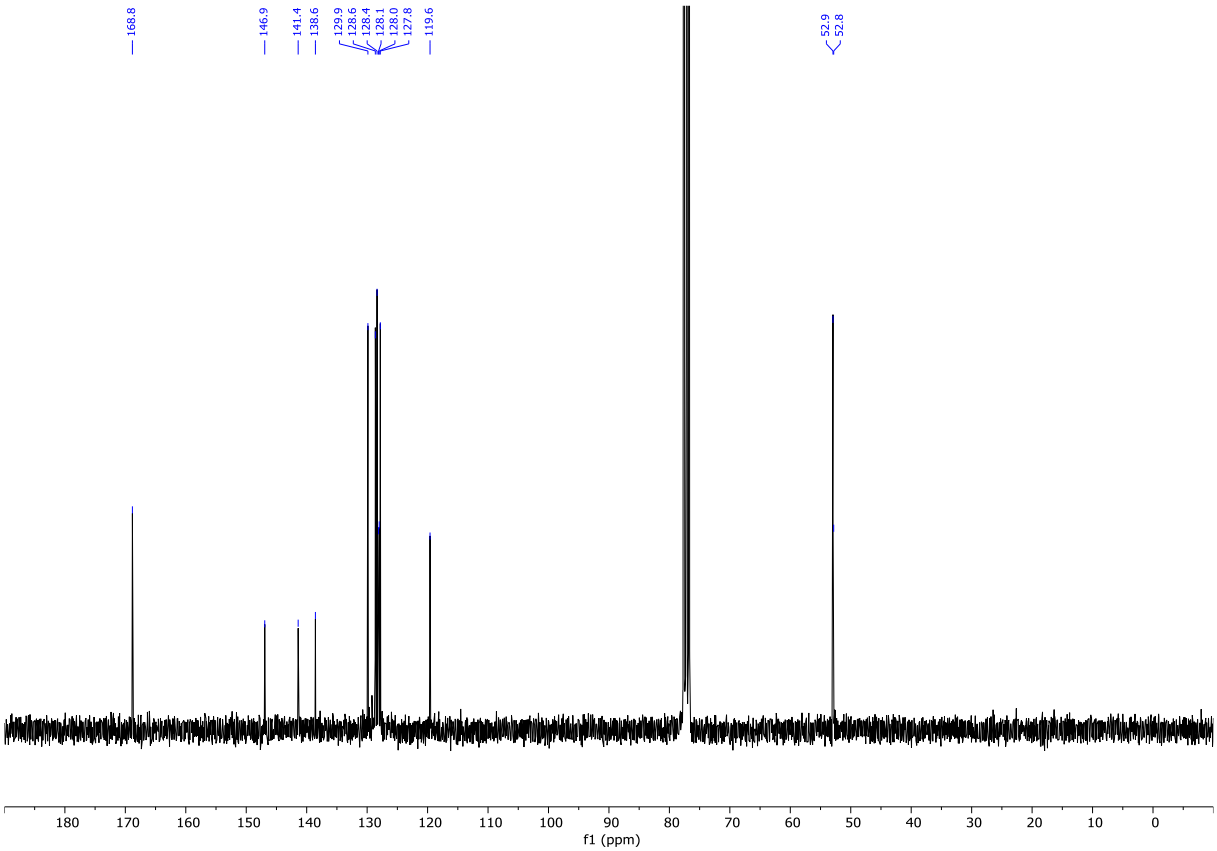



**Figure S113**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5aa**.

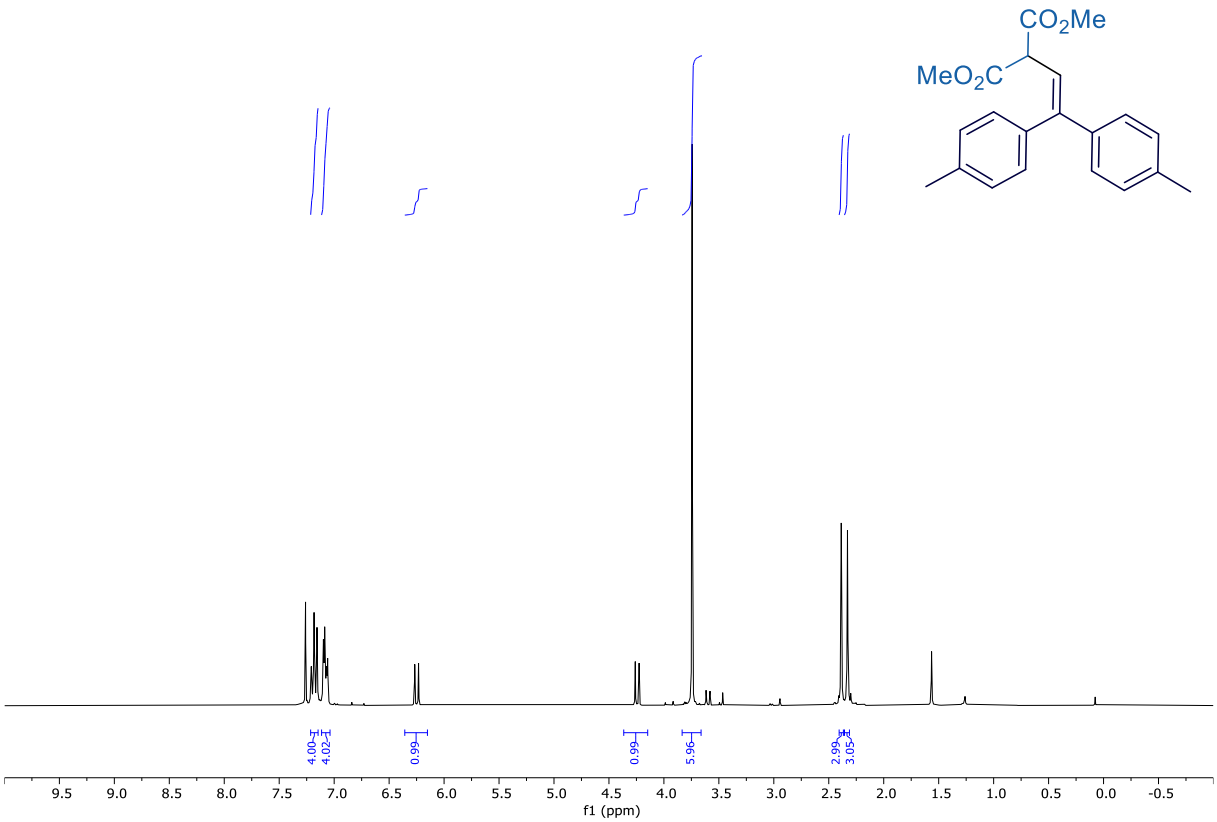



**Figure S114**. $^{1}H$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5ab**.

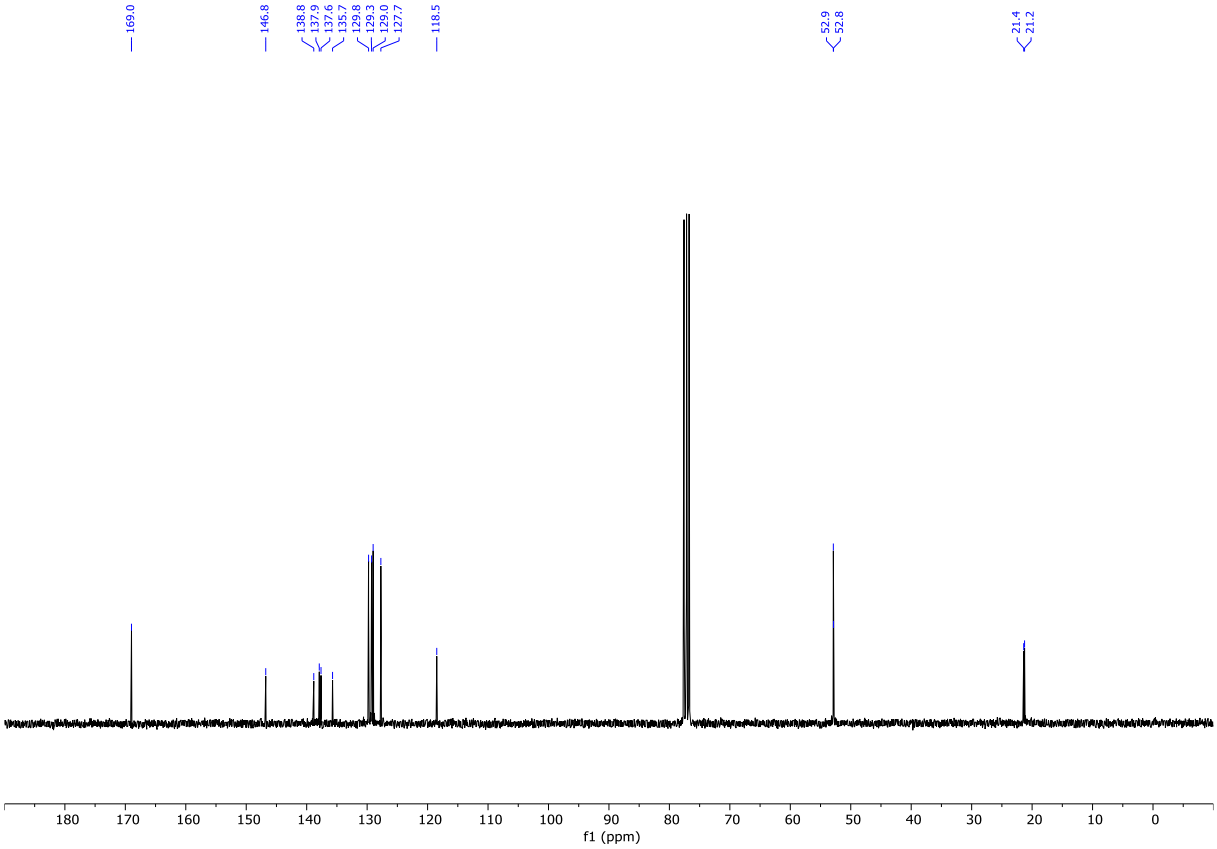



**Figure S115**. $^{13}C$ NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5ab**.

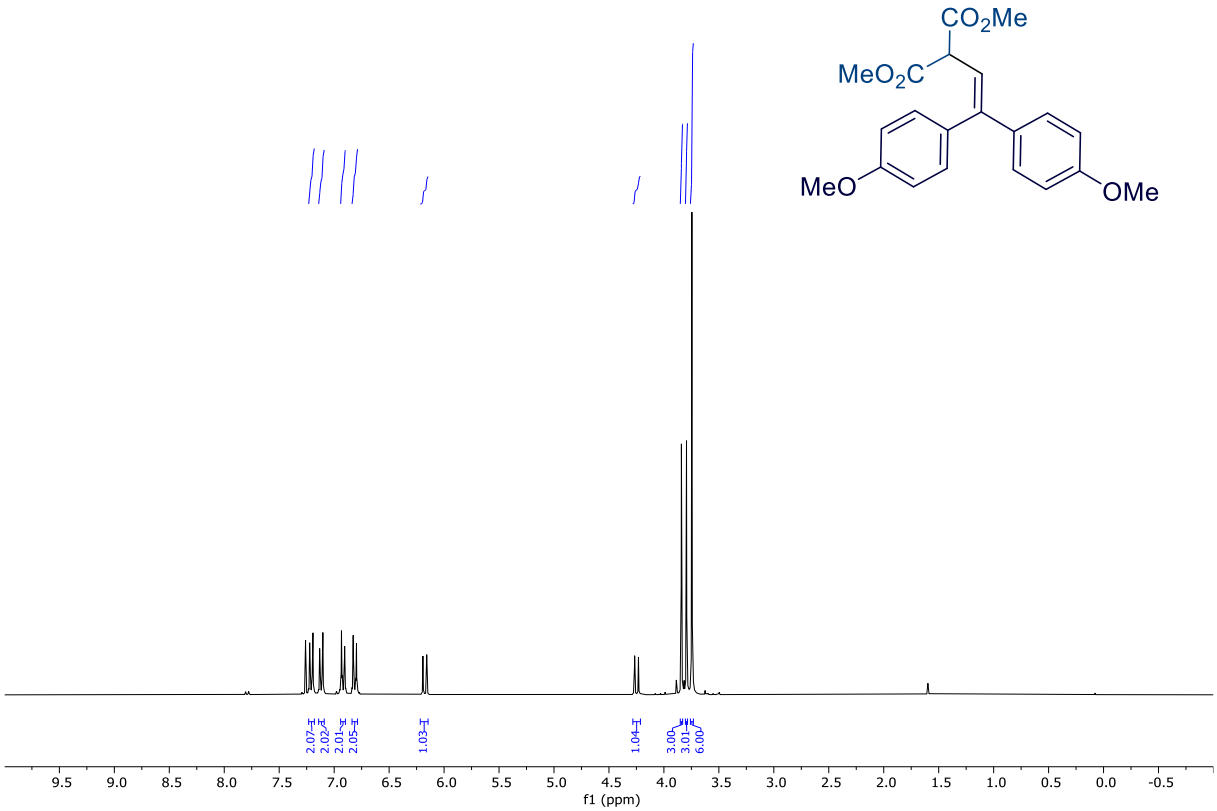



**Figure S116**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5ac**.

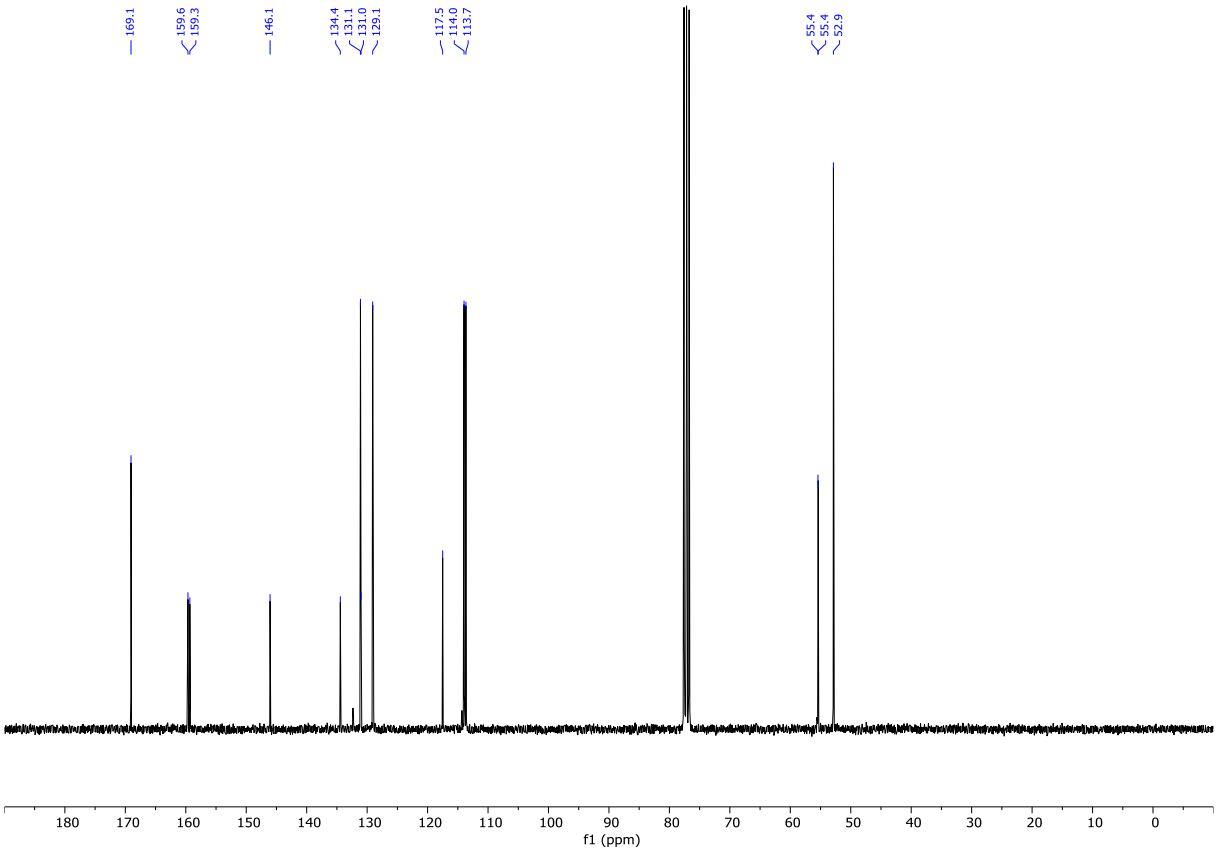



**Figure S117**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5ac**.

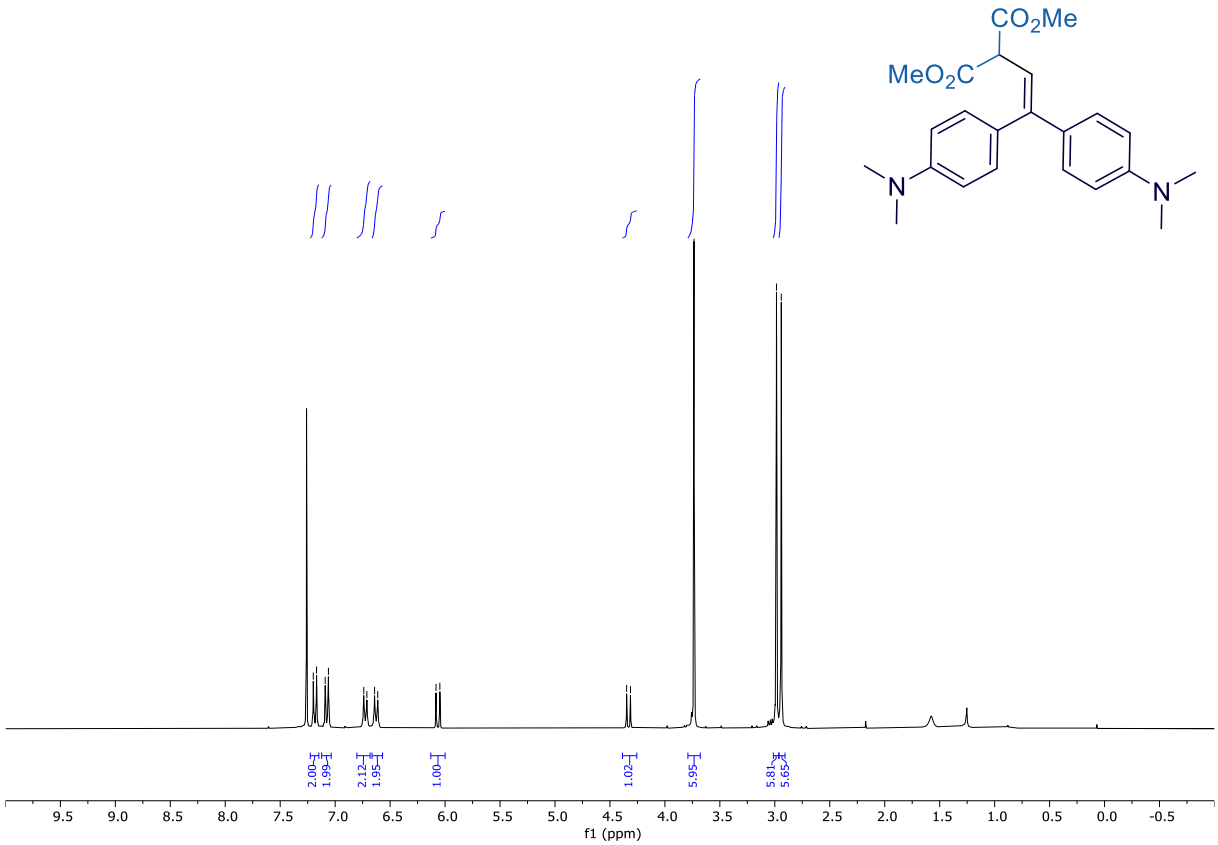



**Figure S118**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5ad**.

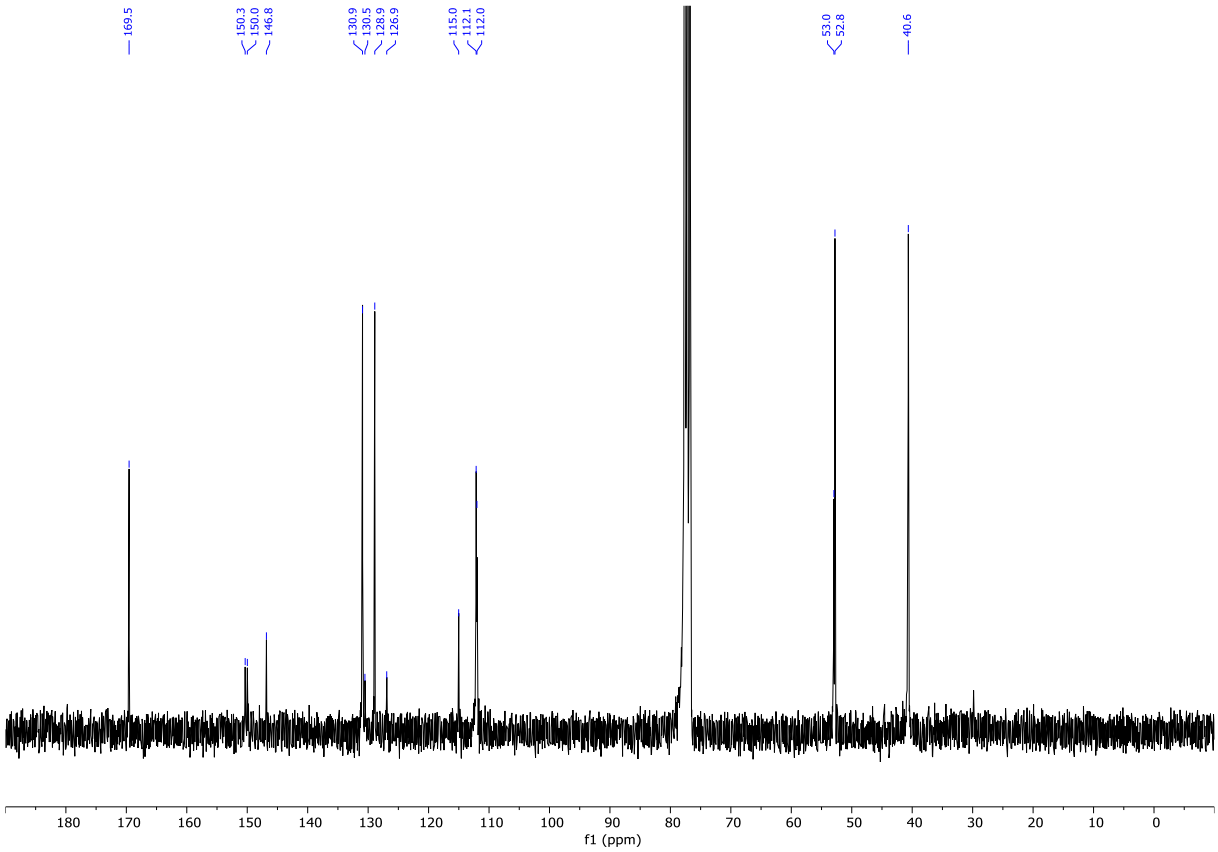



**Figure S119**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5ad**.

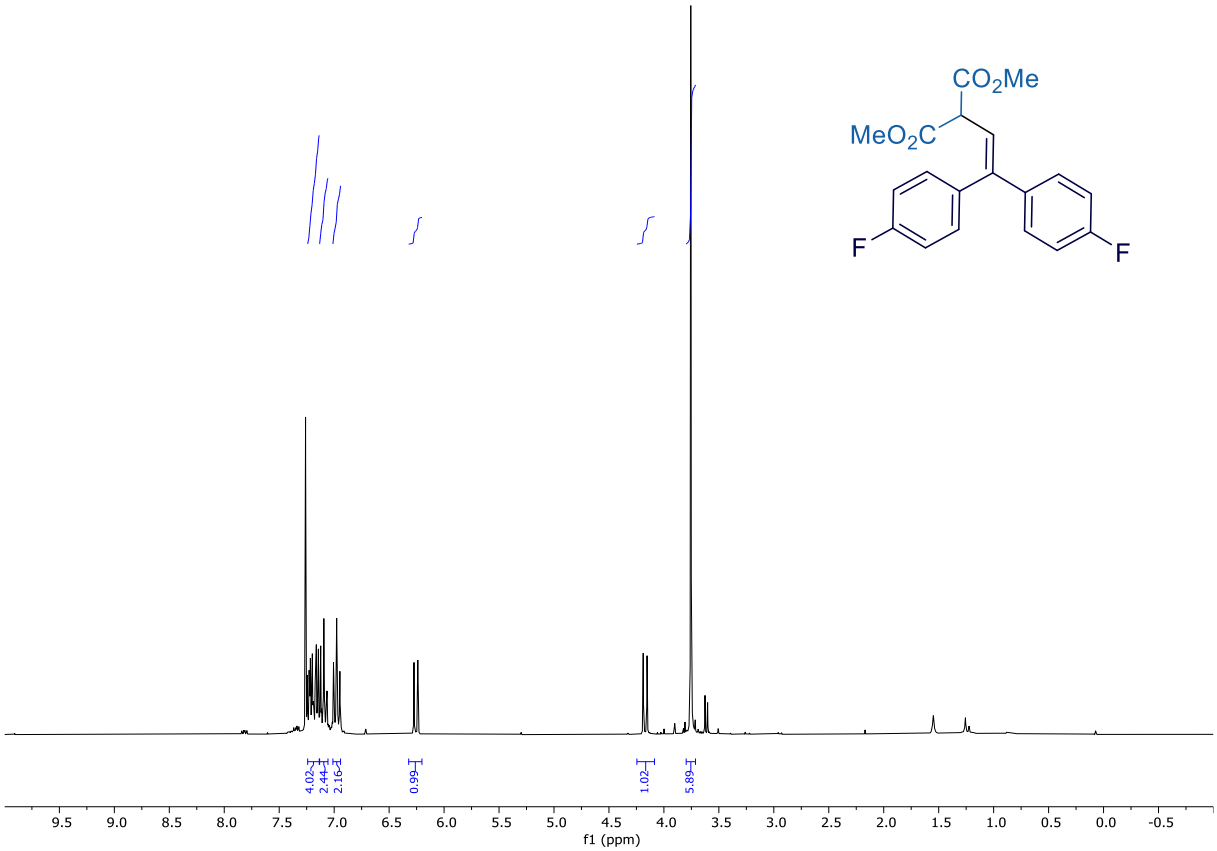



**Figure S120**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5ae**.

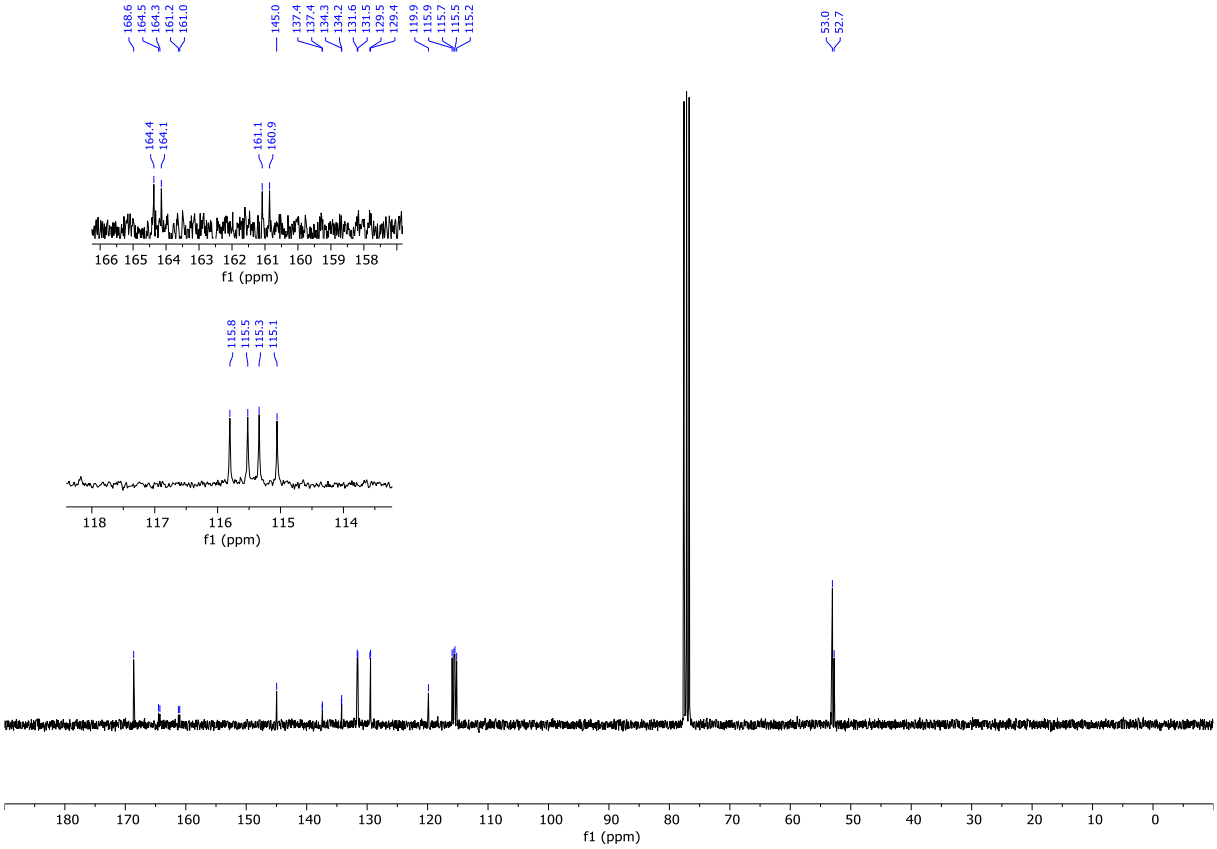



**Figure S121**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5ae**.

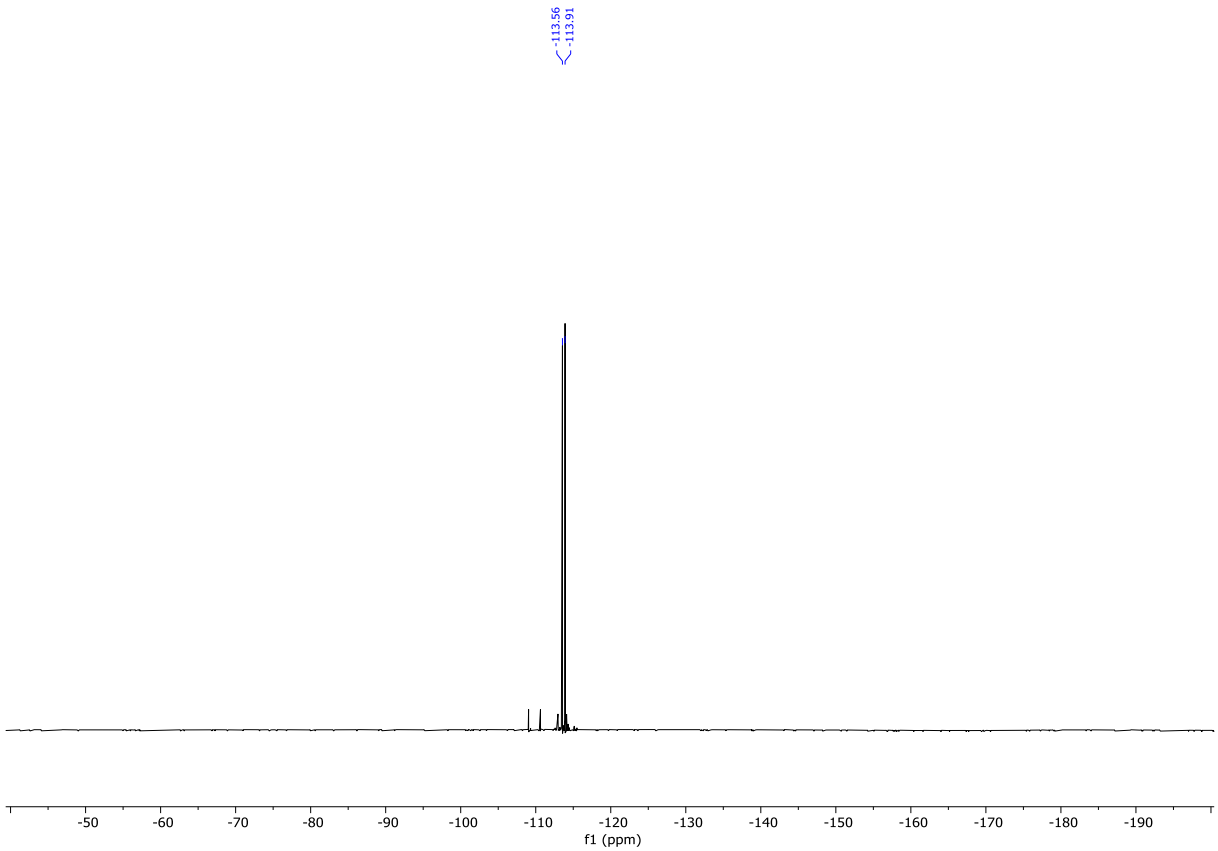



**Figure S122**. $^{19}F$ NMR spectrum (282 MHz, 298K, $CDCl_3$) of **5ae**.

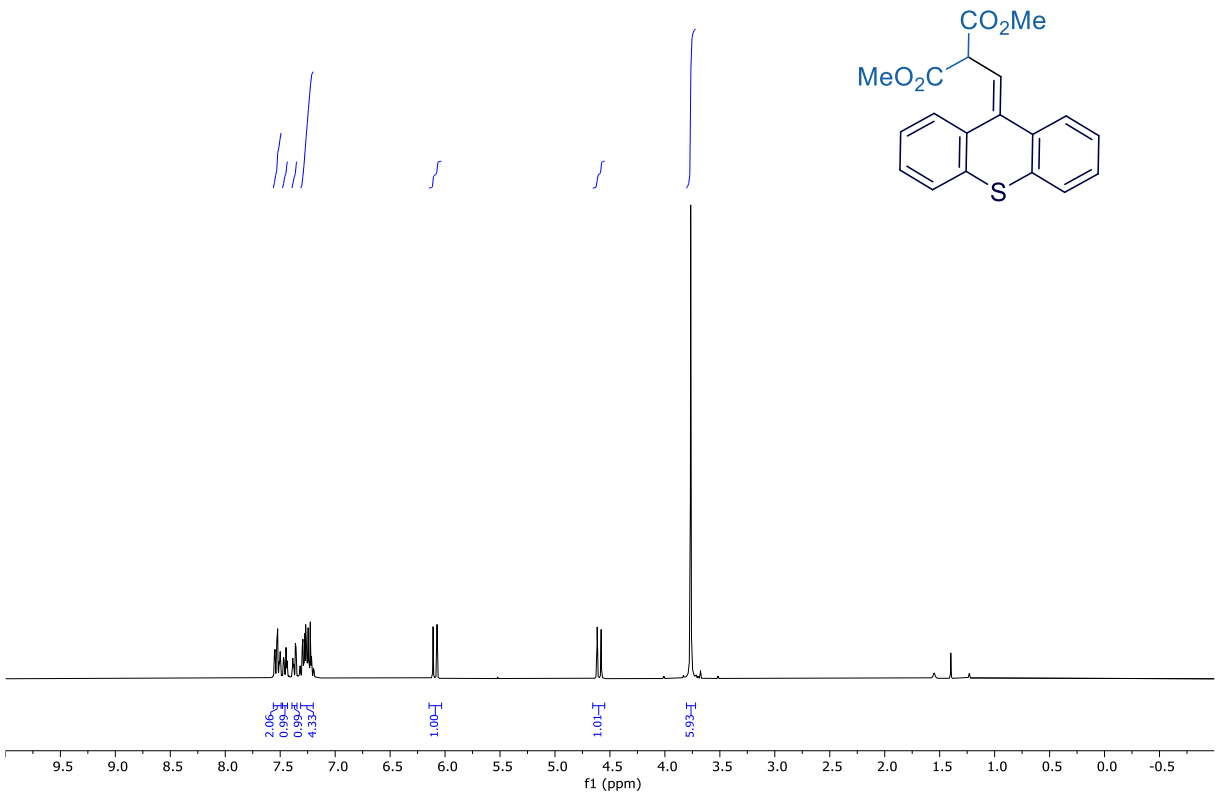



**Figure S123**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5af**.

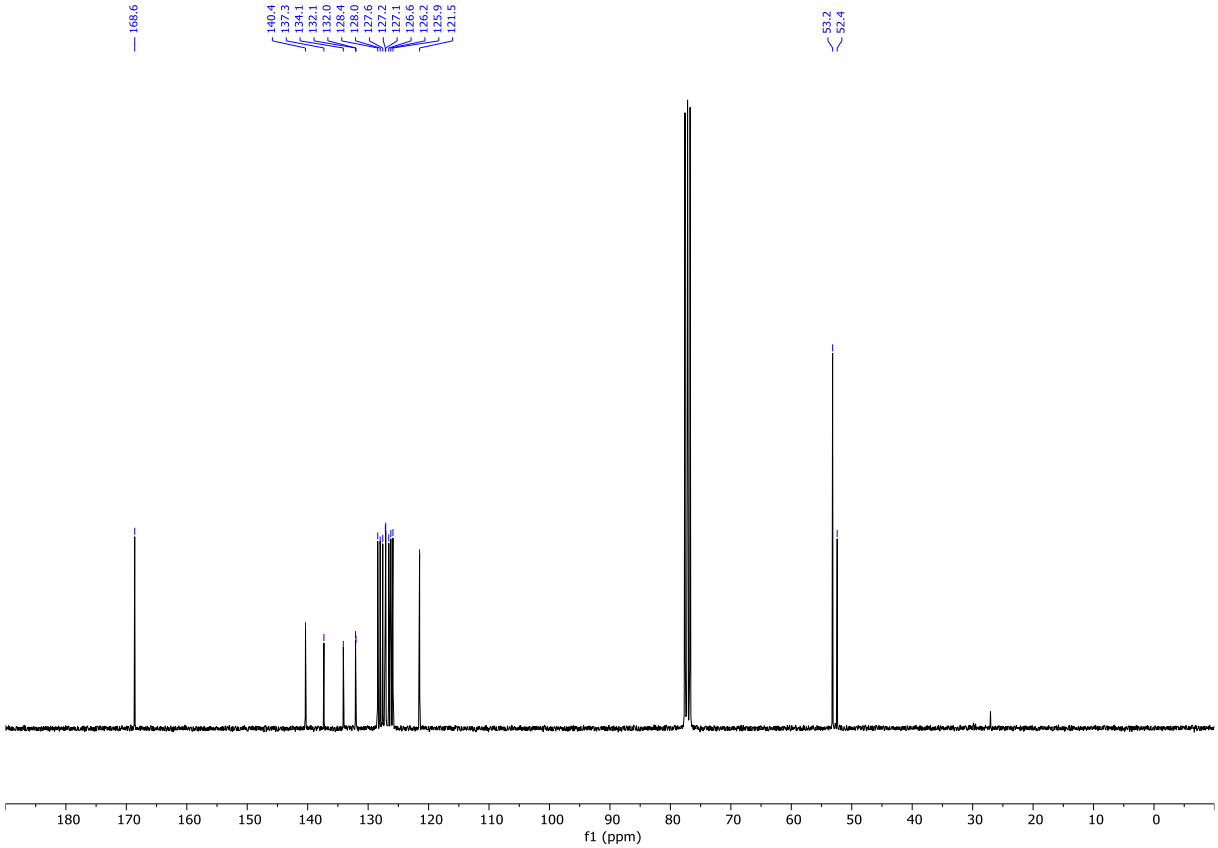



**Figure S124**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5af**.

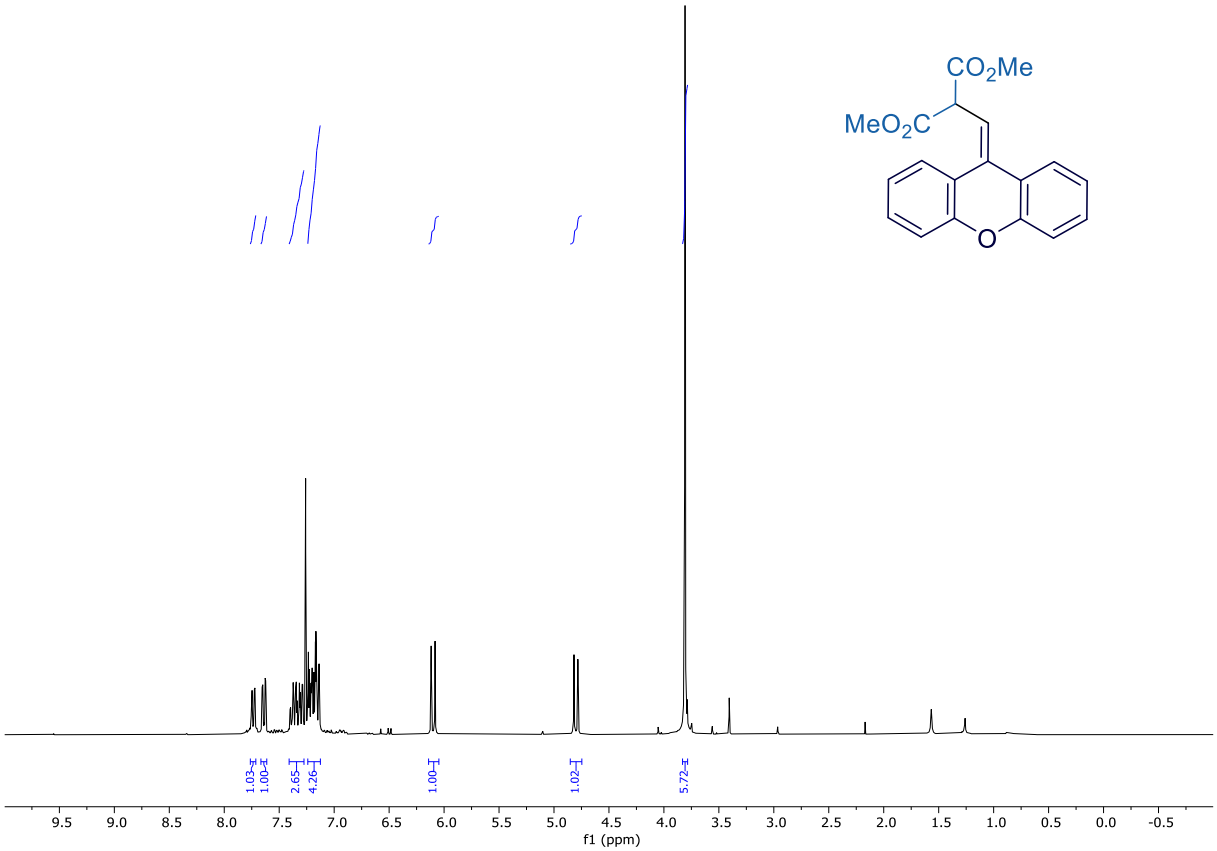



**Figure S125**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5ag**.

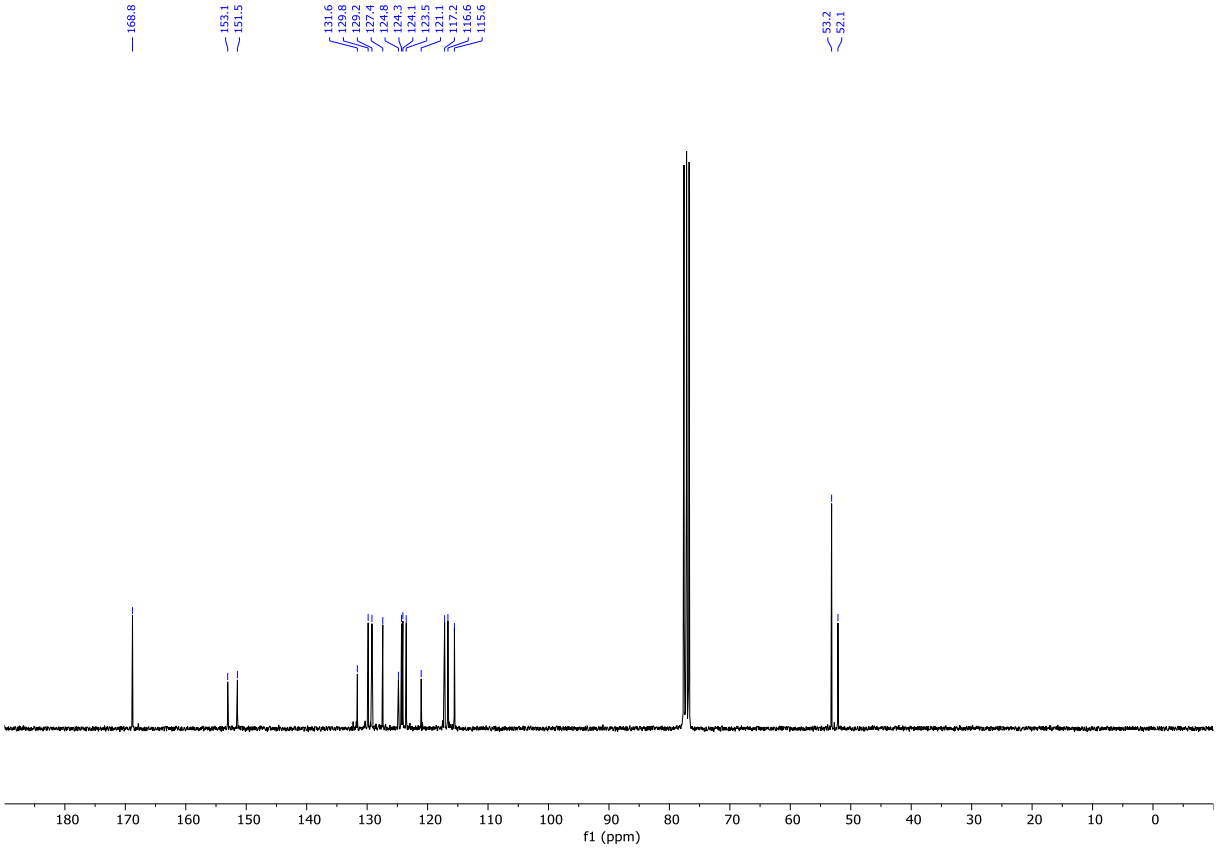



**Figure S126**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5ag**.

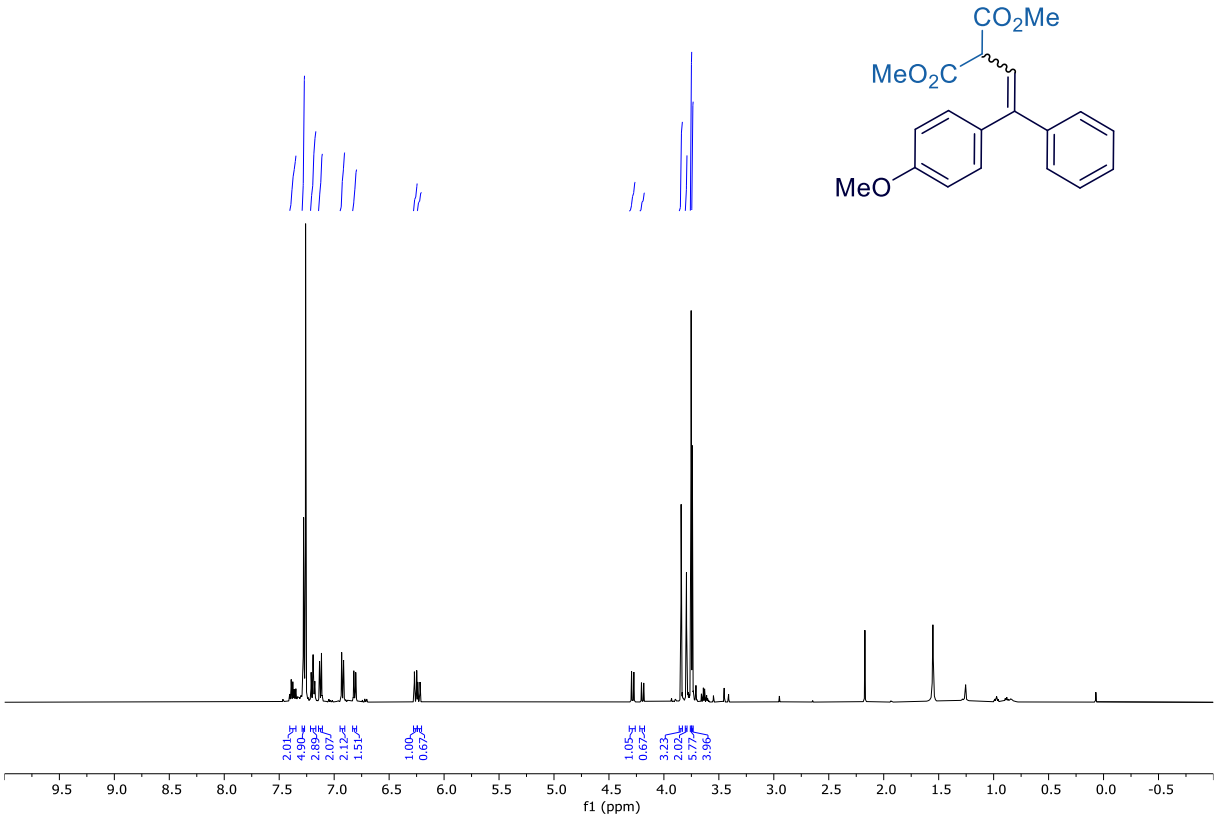



**Figure S127**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5ah (*Major/Minor* = 60:40)**.

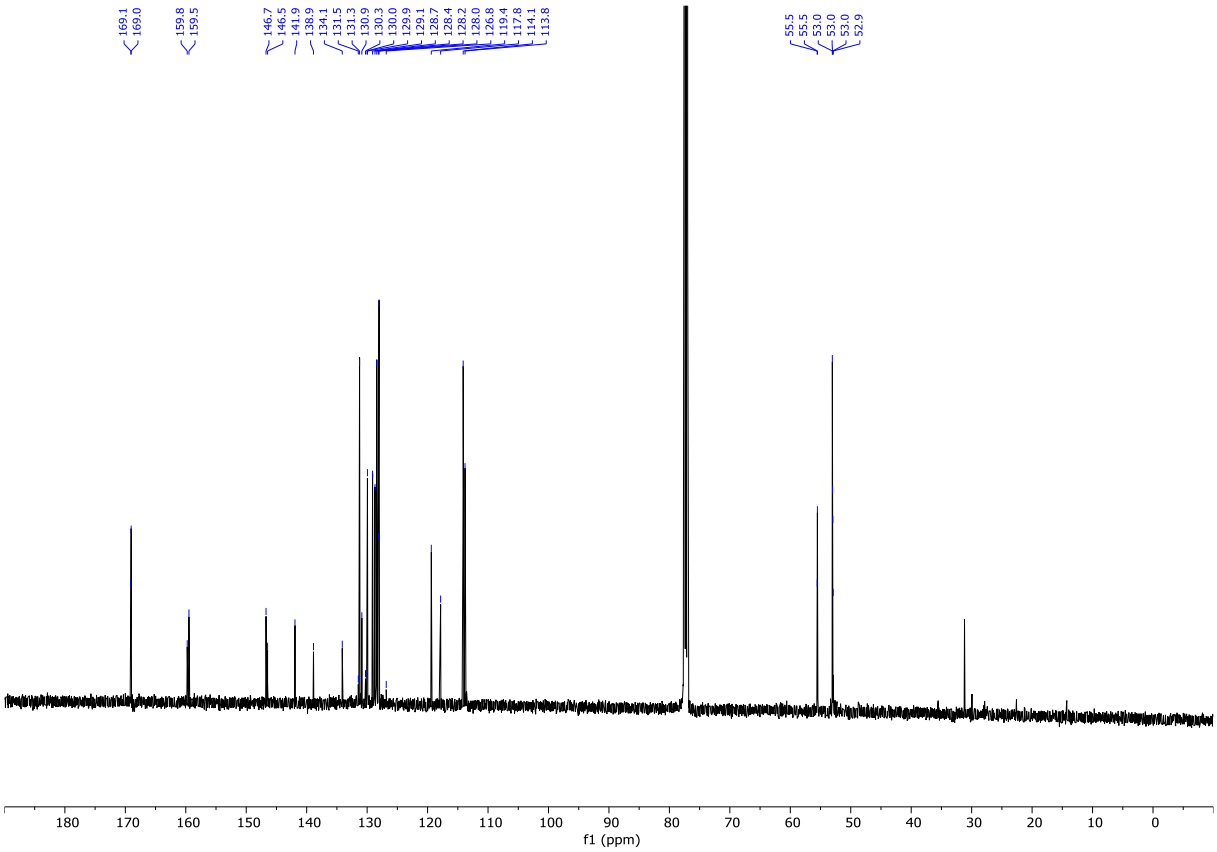



**Figure S128**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5ah (*Major/Minor* = 60:40)**.

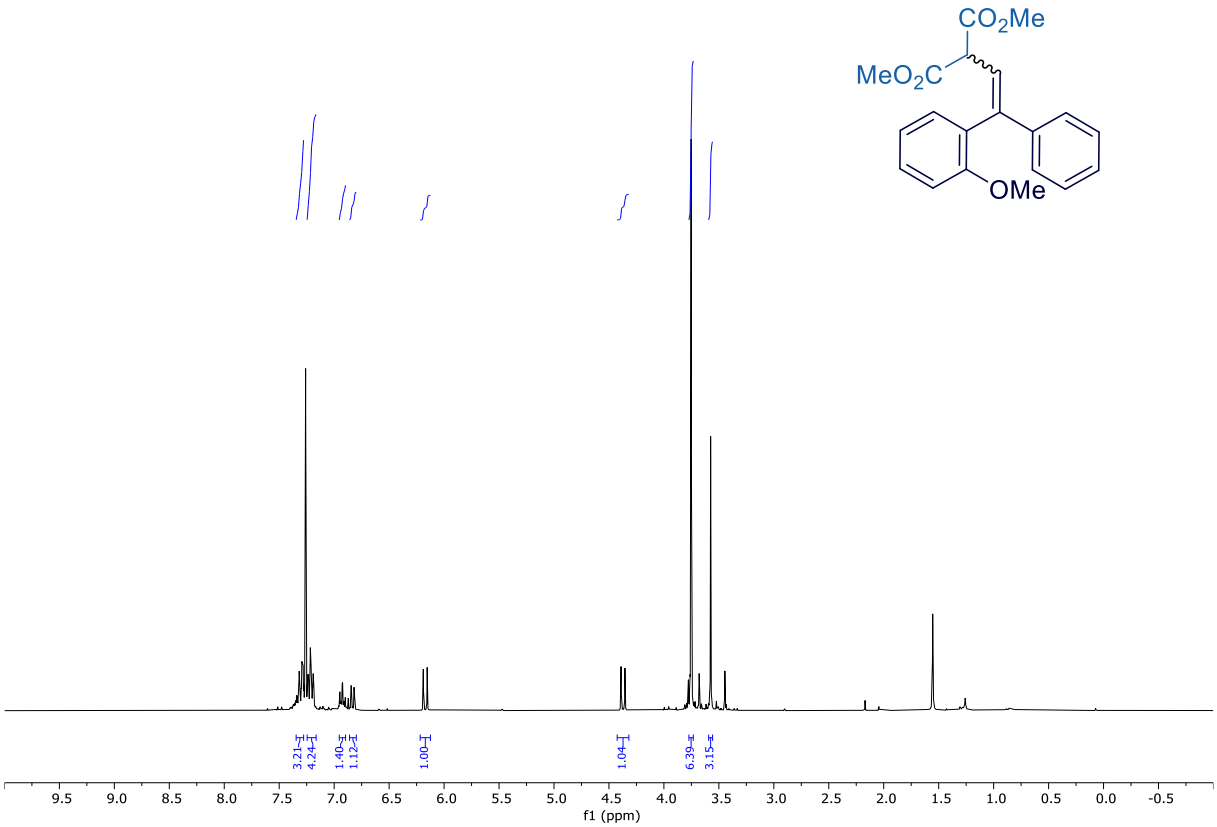



**Figure S129**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5ai (Major isomer)**.

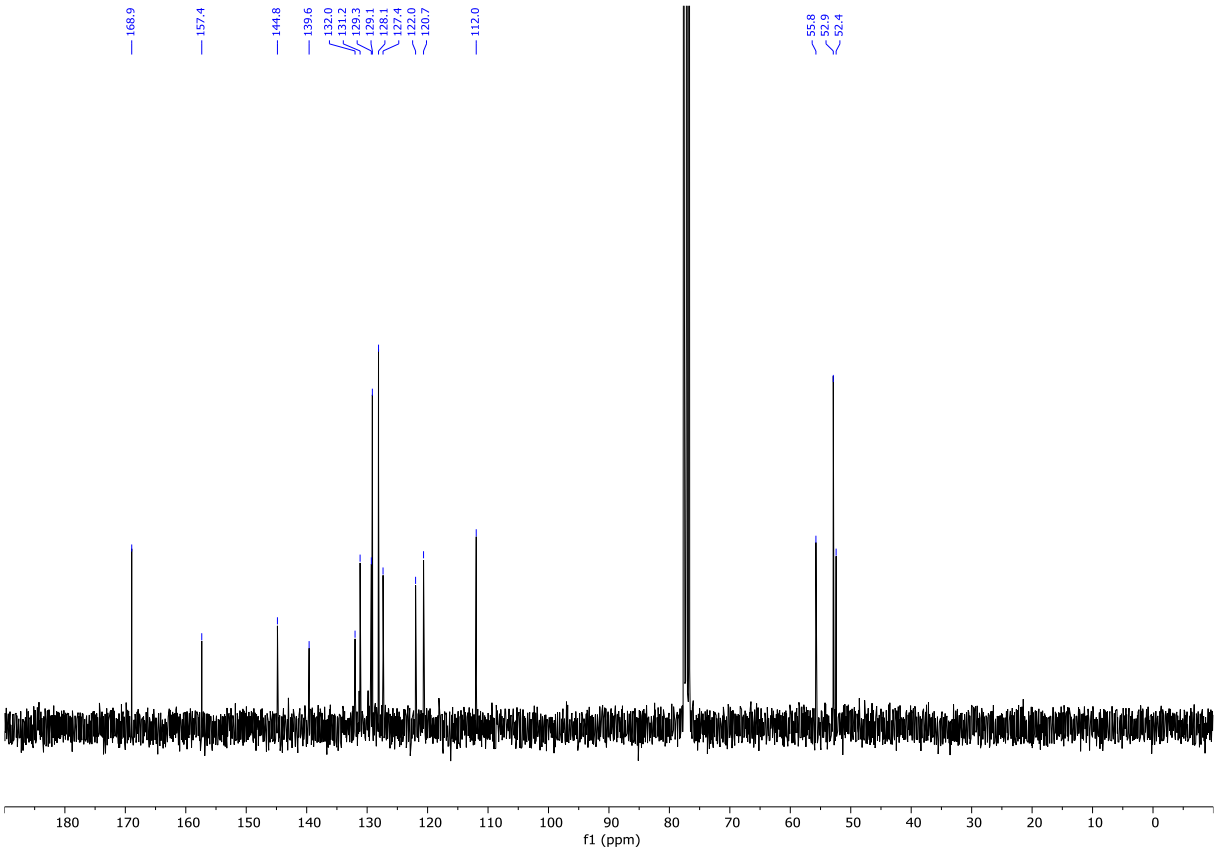



**Figure S130**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5ai (Major isomer)**.

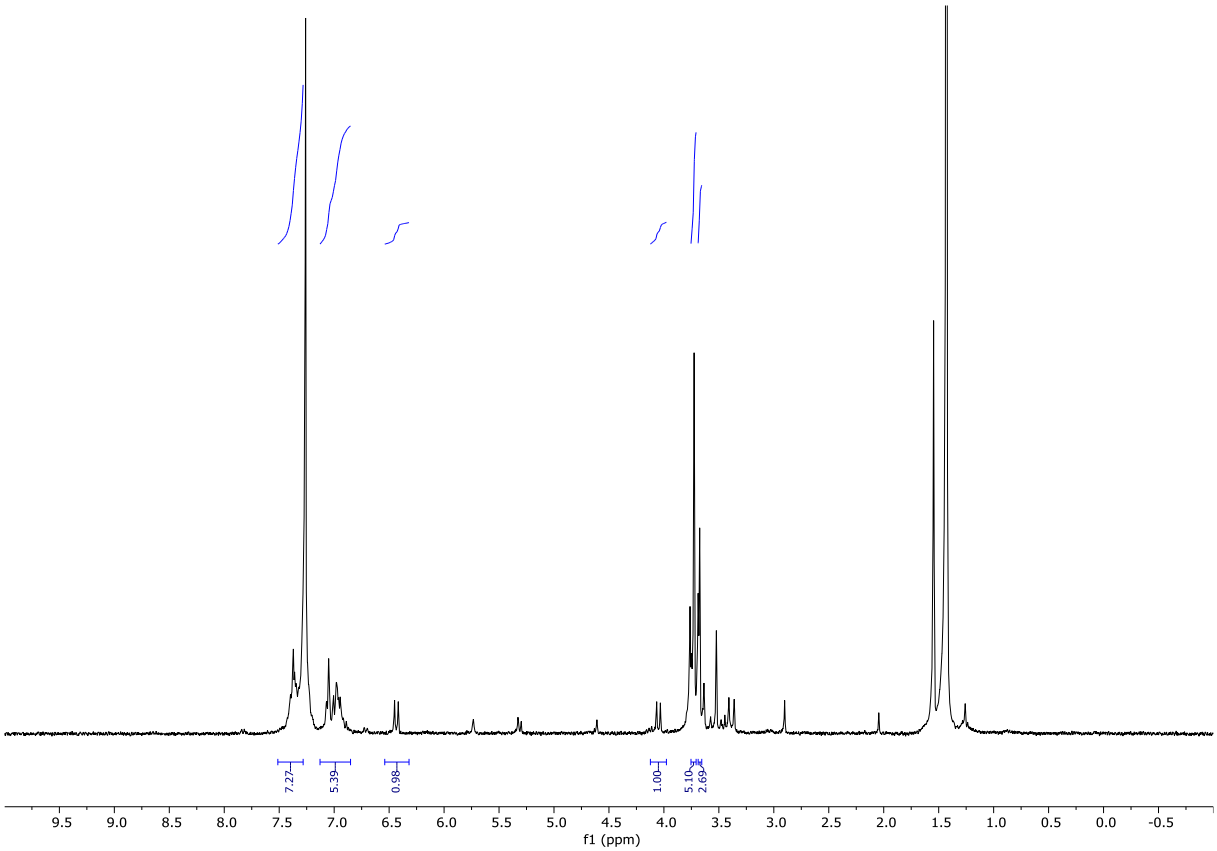



**Figure S131**. $^{1}H$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5ai (Minor isomer)**.

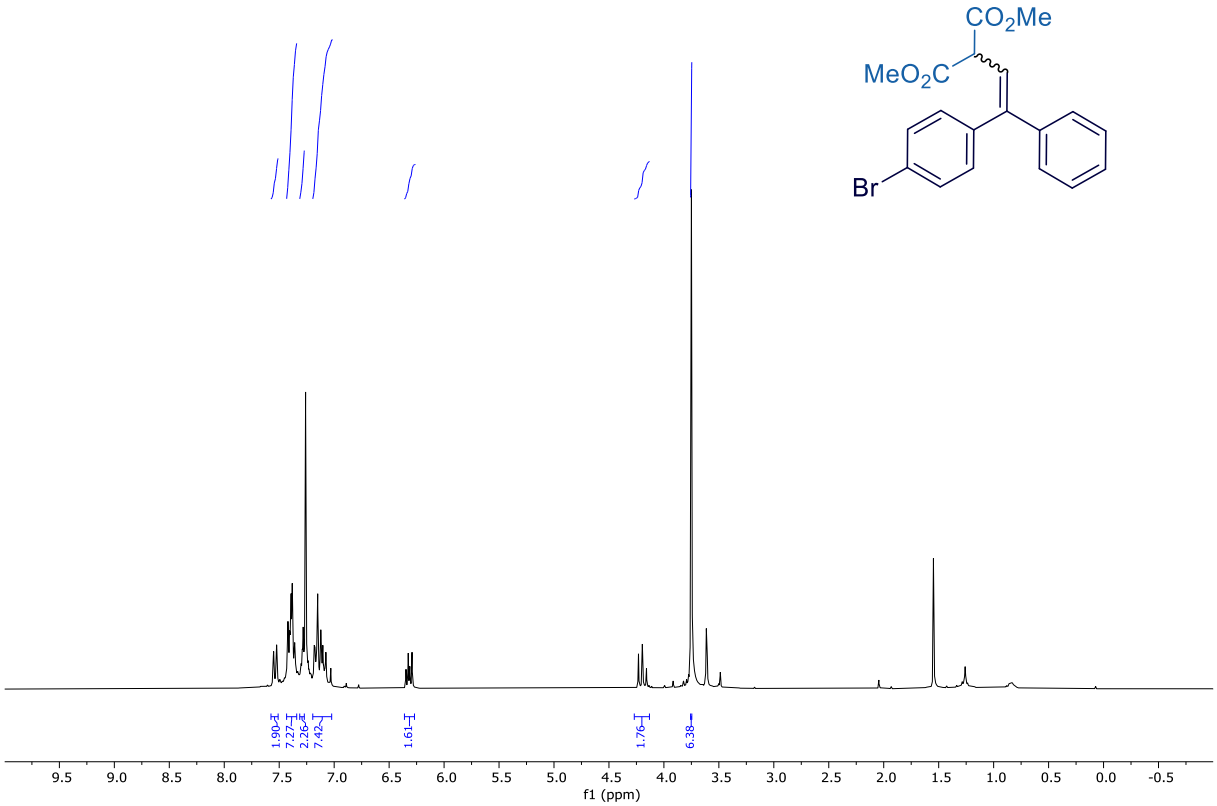



**Figure S132**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5aj (isomers mixture)**.

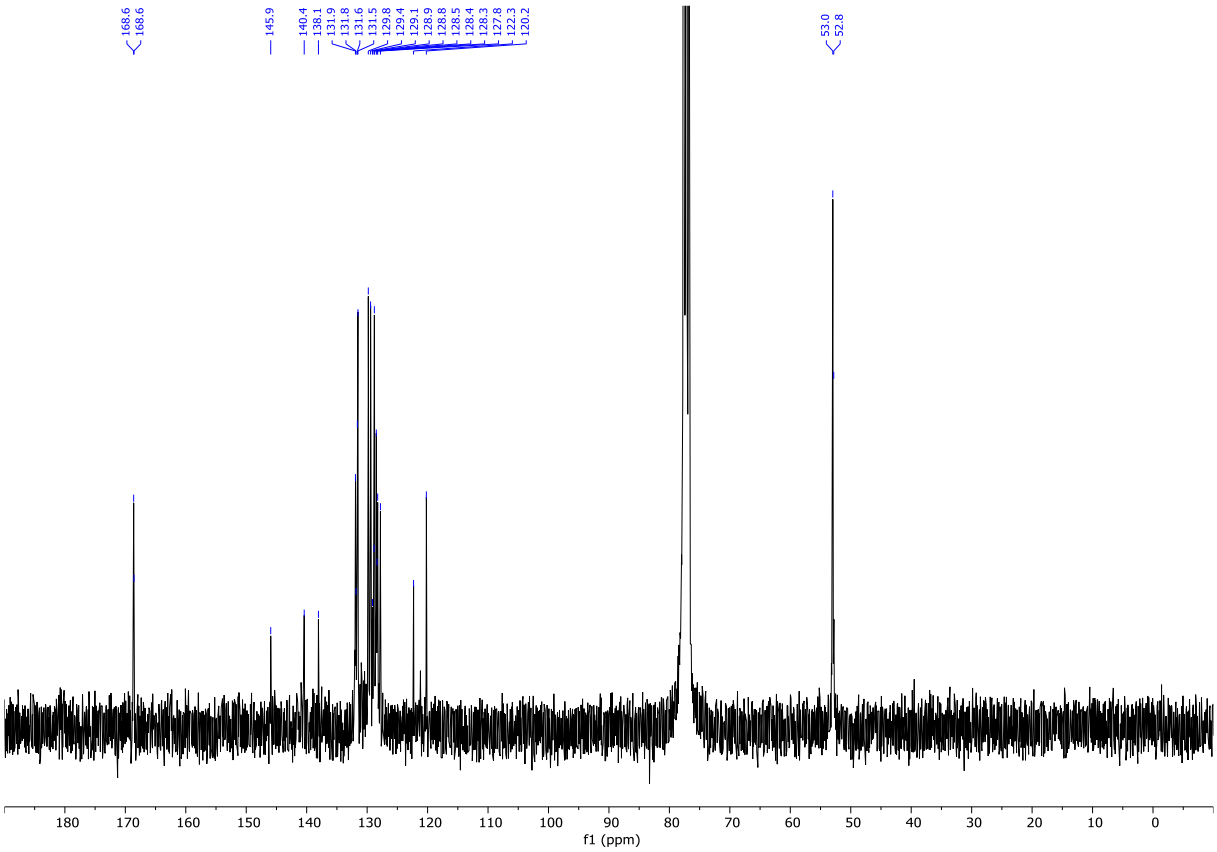



**Figure S133**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5aj (isomers mixture)**.

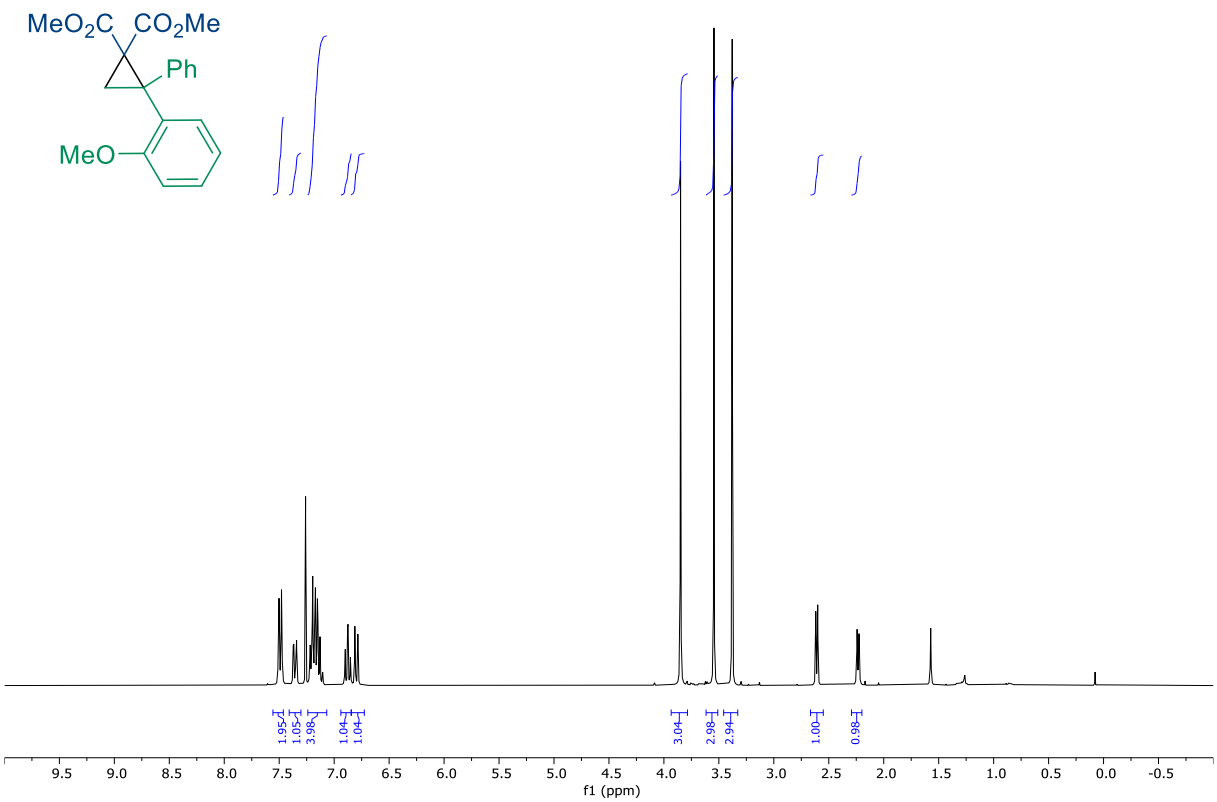



**Figure S134**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **6ai**.

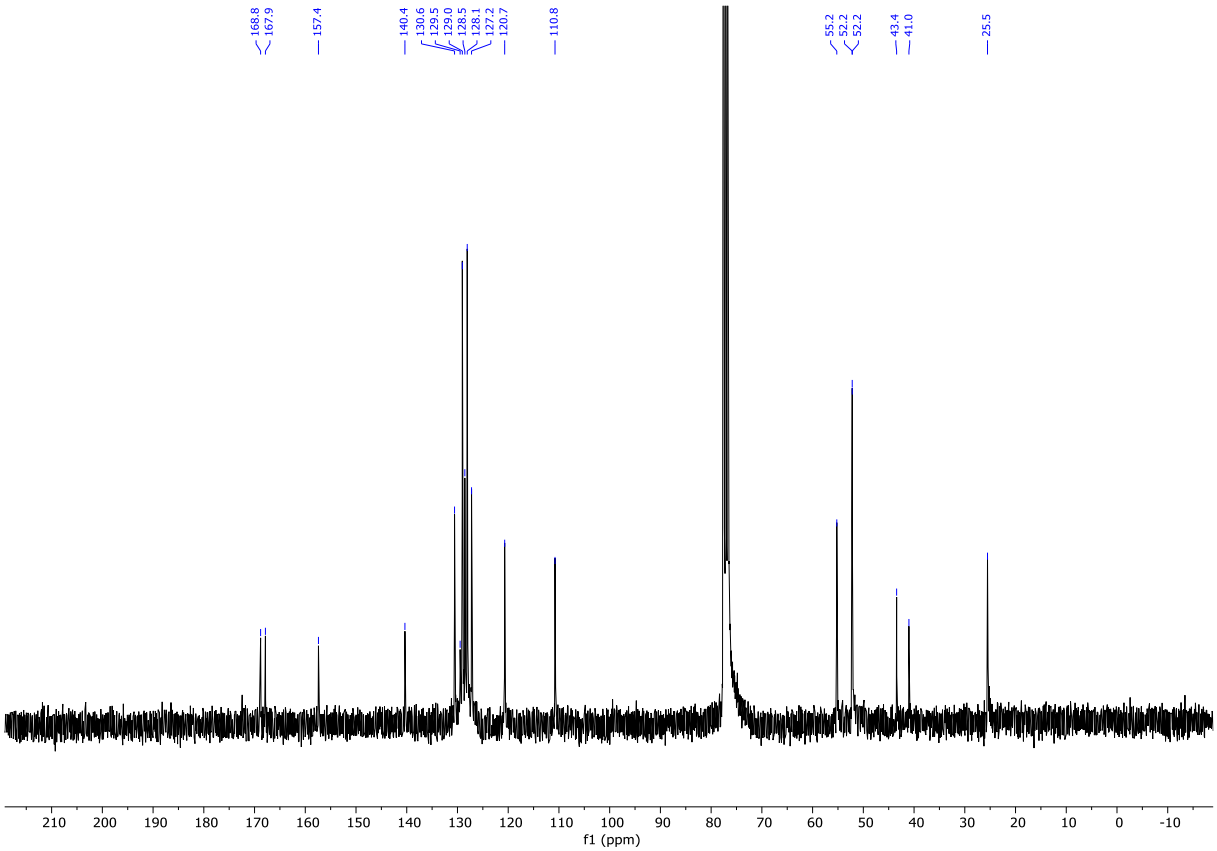



**Figure S135**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **6ai**.

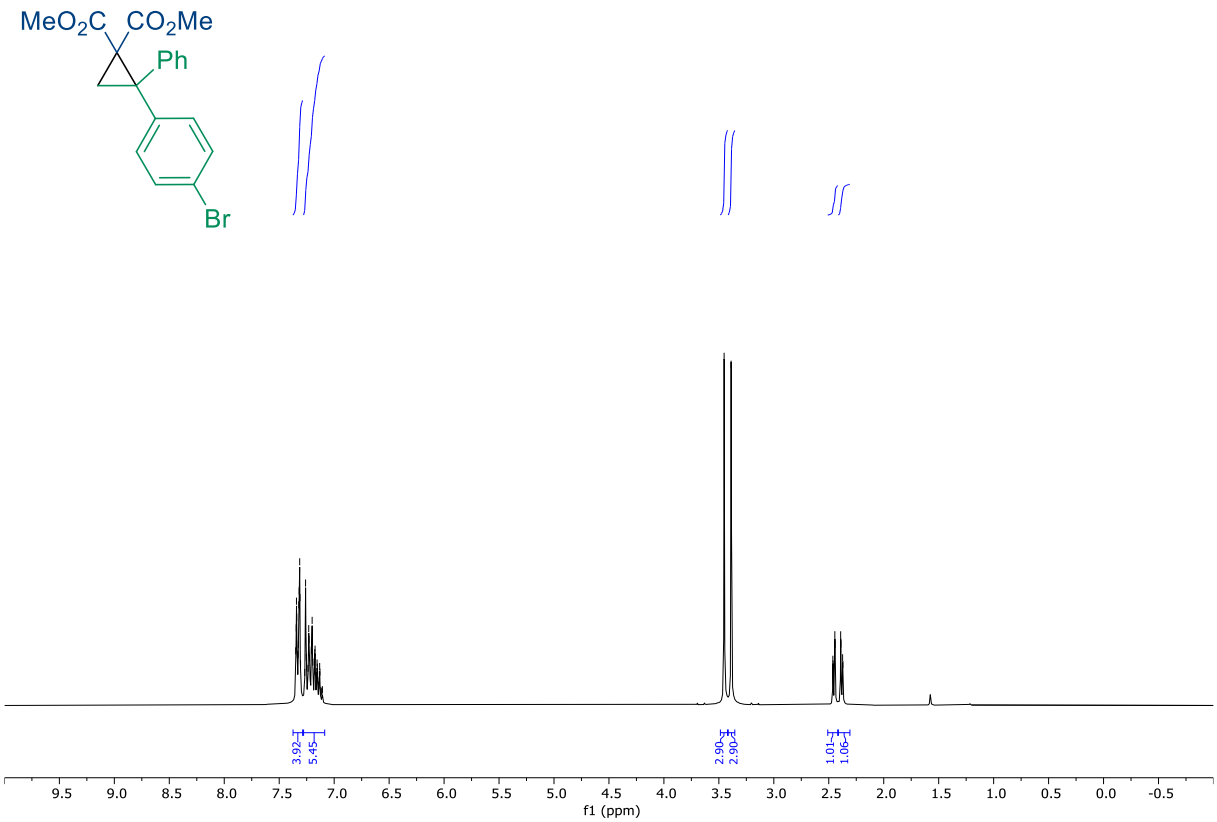



**Figure S136**. $^{1}H$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **6aj**.

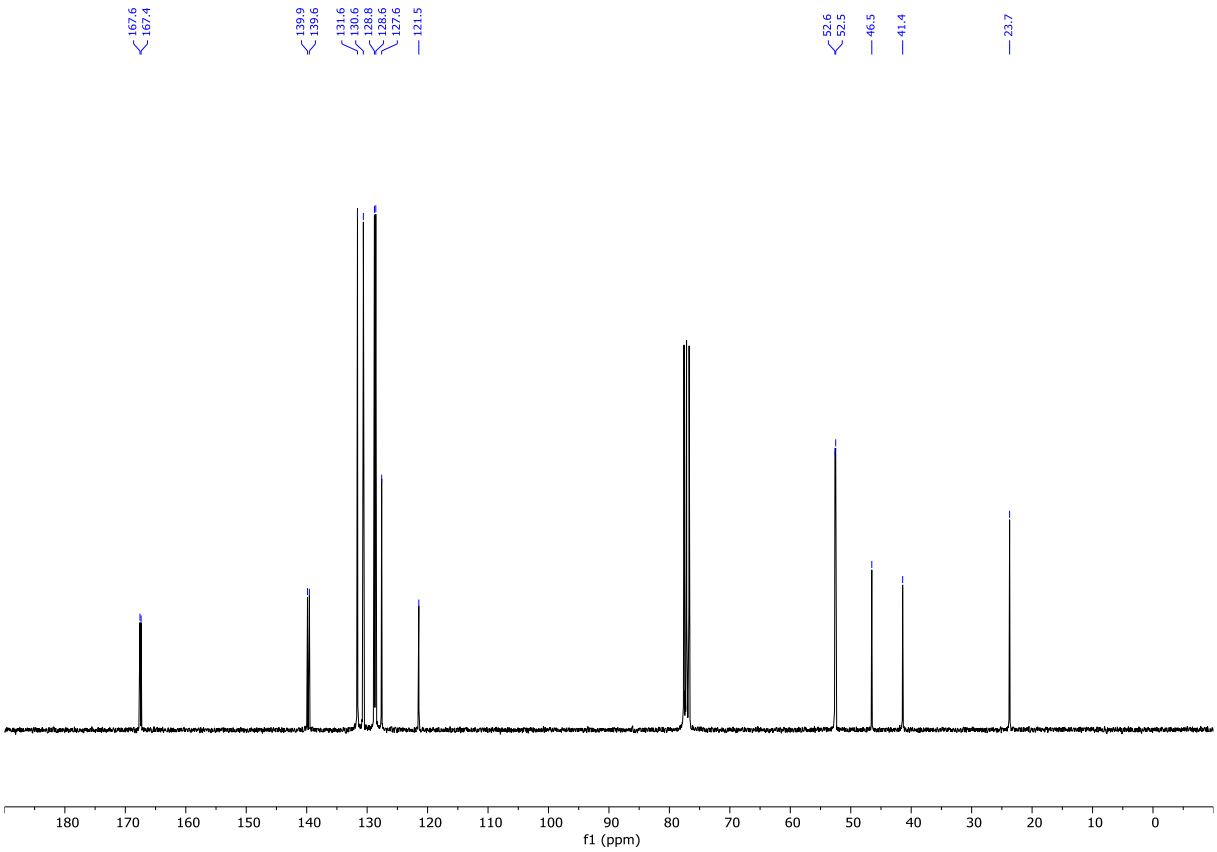



**Figure S137**. $^{13}C$ NMR spectrum (75 MHz, 298K, $CDCl_3$) of **6aj**.

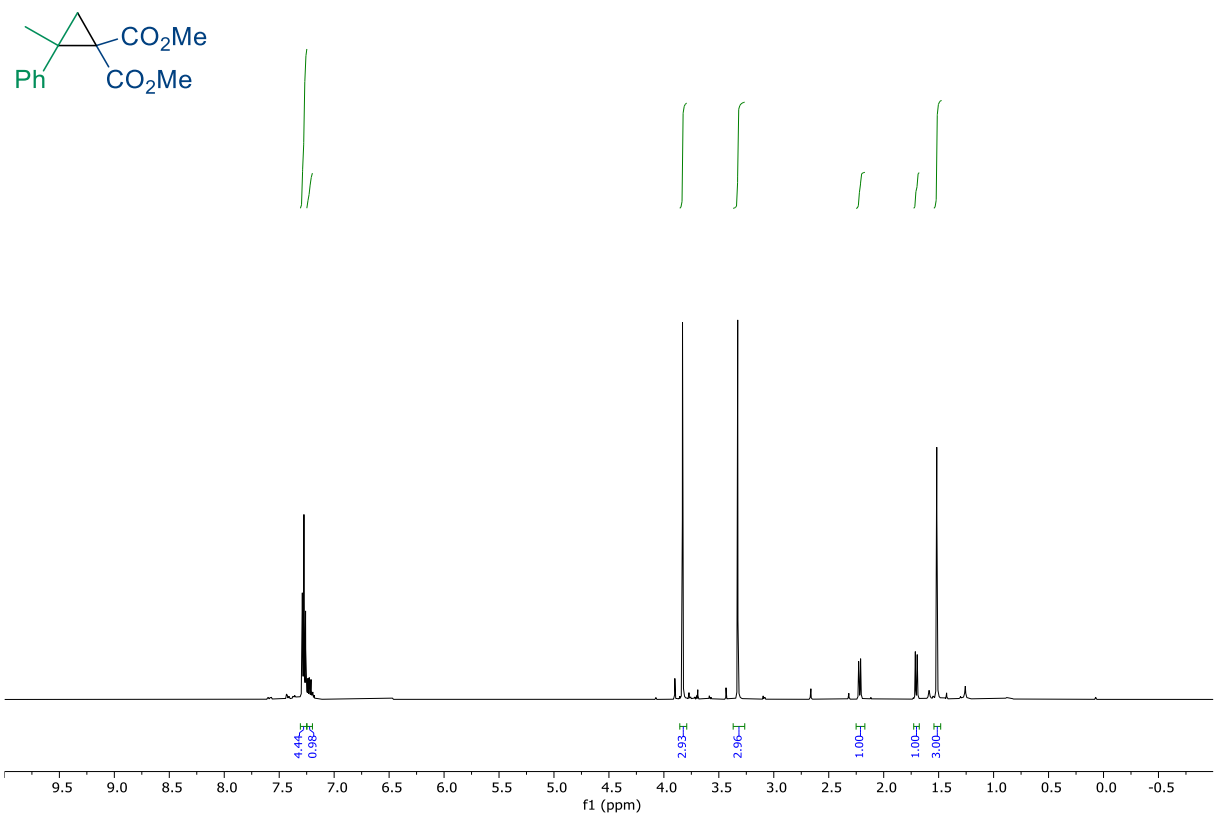



**Figure S138**. $^{13}C$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **6ak**.

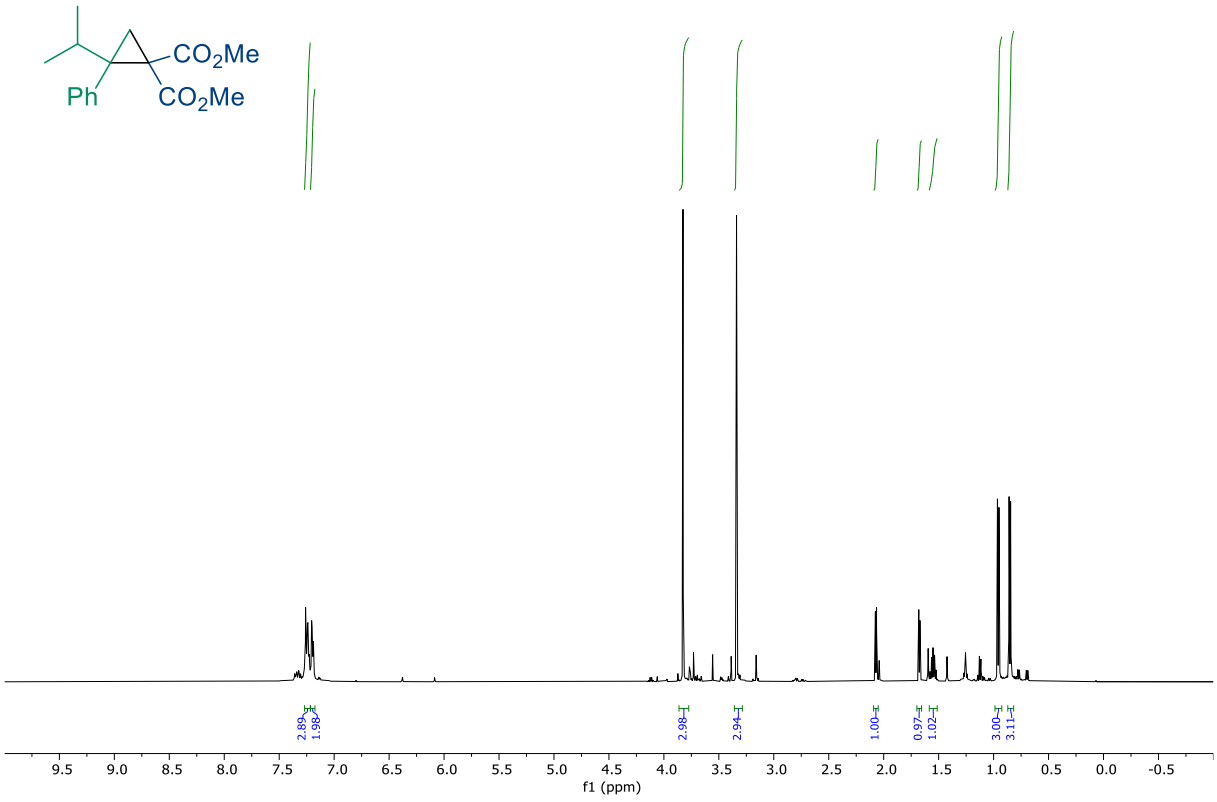



**Figure S139**. $^{13}C$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **6al**.

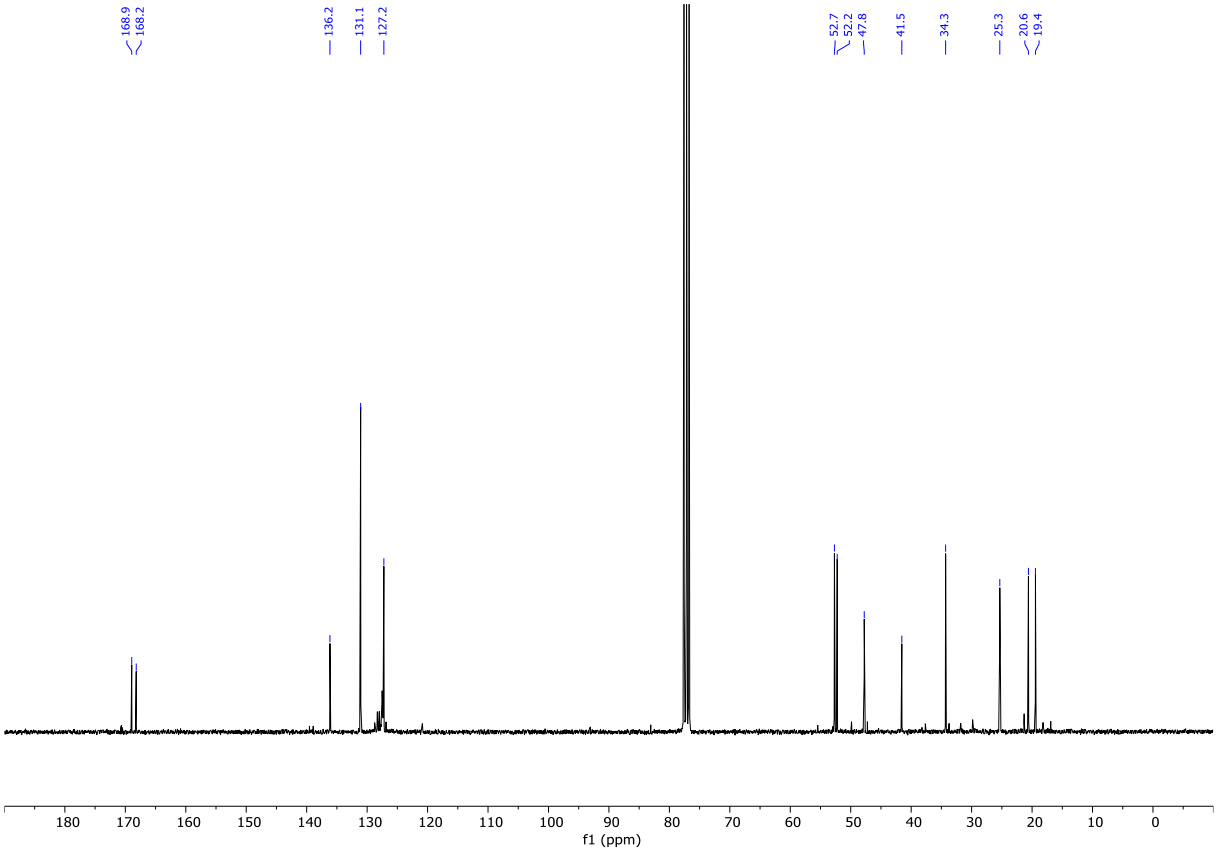



**Figure S140**. $^{13}C$ NMR spectrum (75 MHz, 298K, $CDCl_3$) of **6al**.

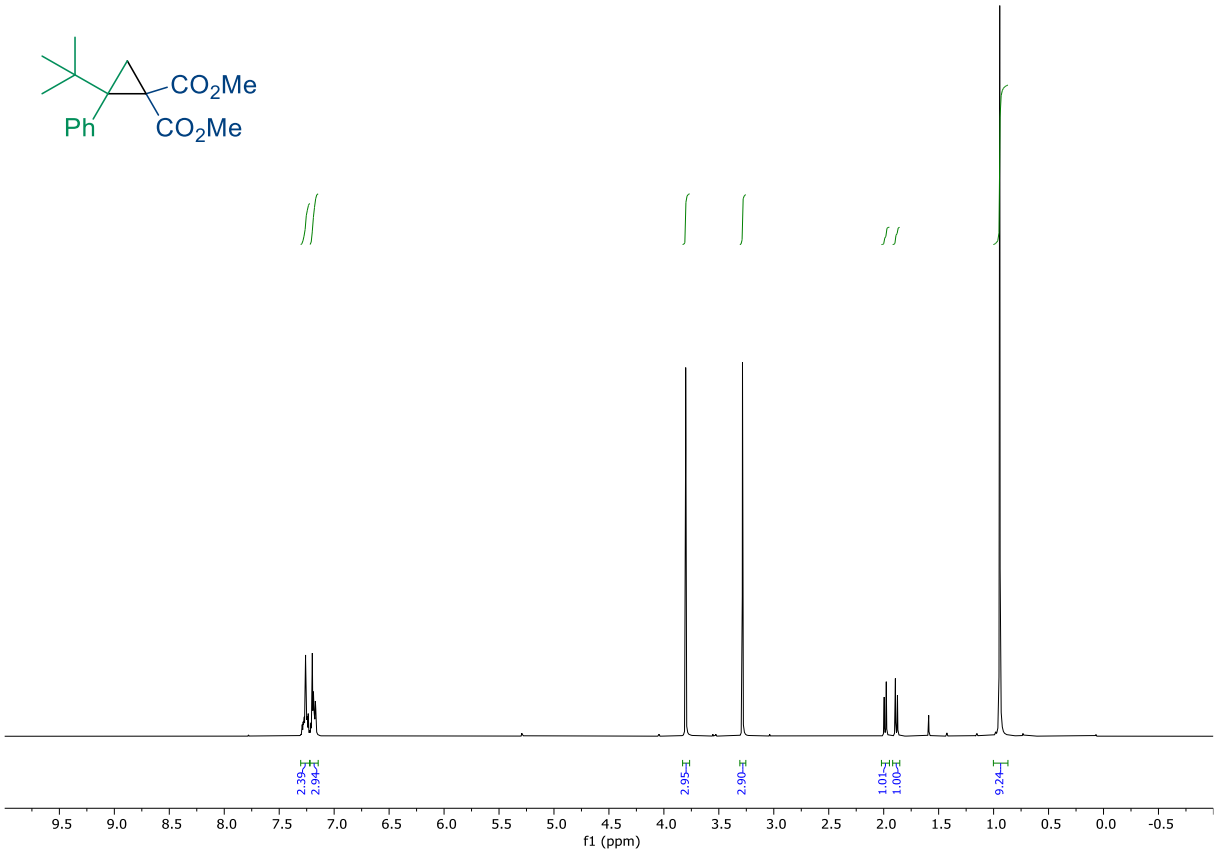



**Figure S141**. $^{13}C$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **6am**.

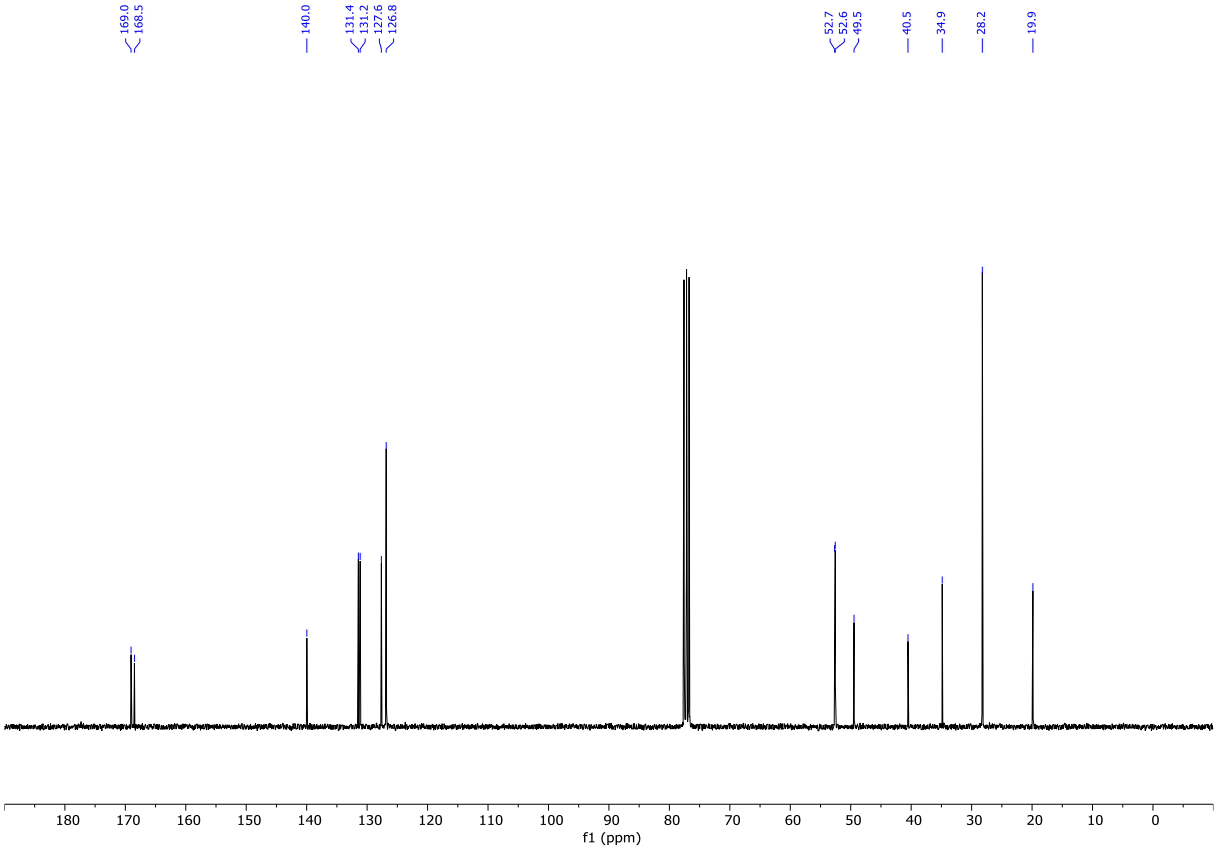



**Figure S142**. $^{13}C$ NMR spectrum (75 MHz, 298K, $CDCl_3$) of **6am**.

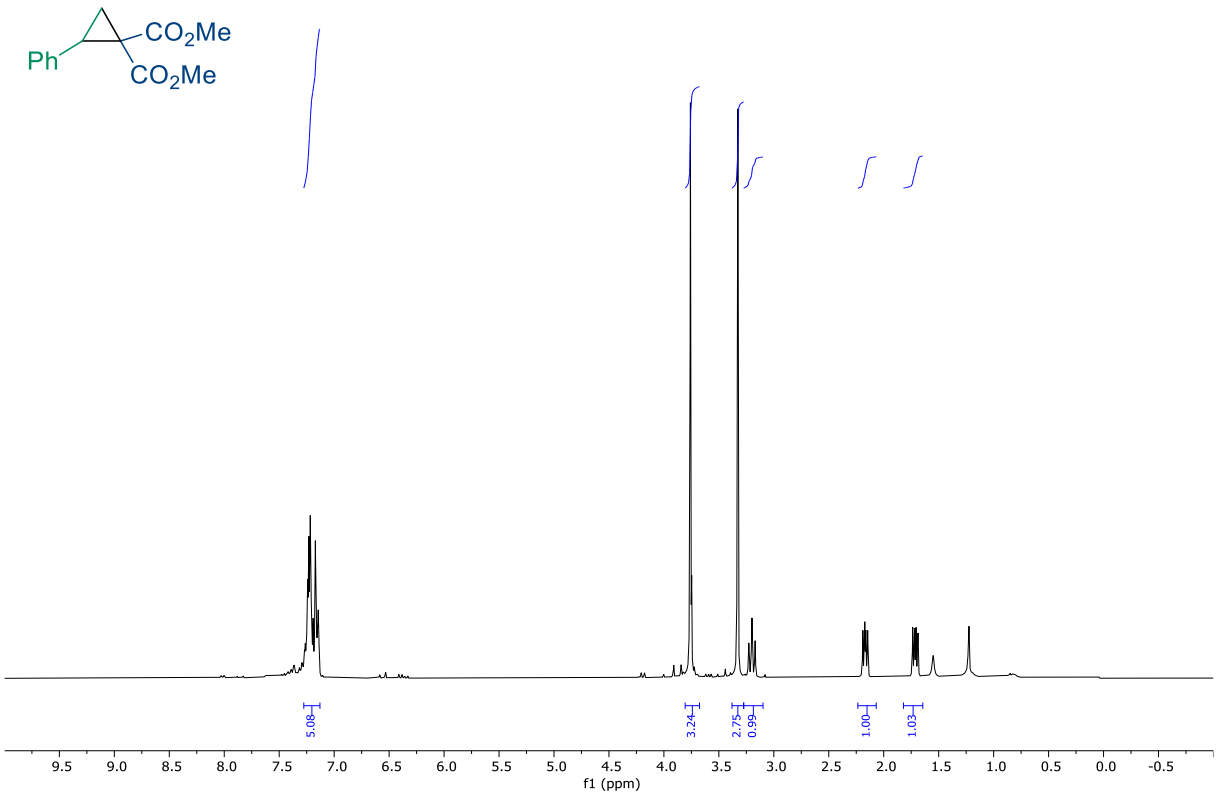



**Figure S143**. $^{1}H$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **6an**.

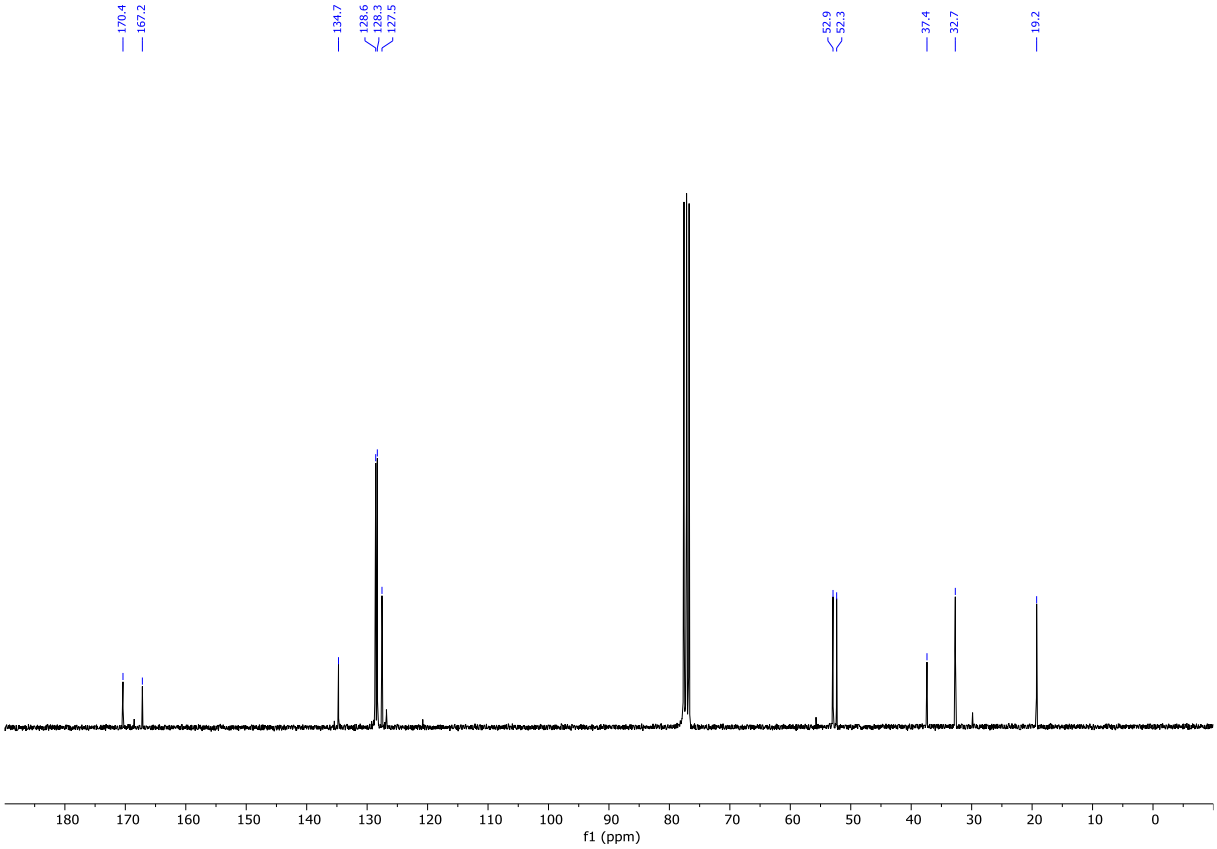



**Figure S144**. $^{13}C$ NMR spectrum (75 MHz, 298K, $CDCl_3$) of **6an**.

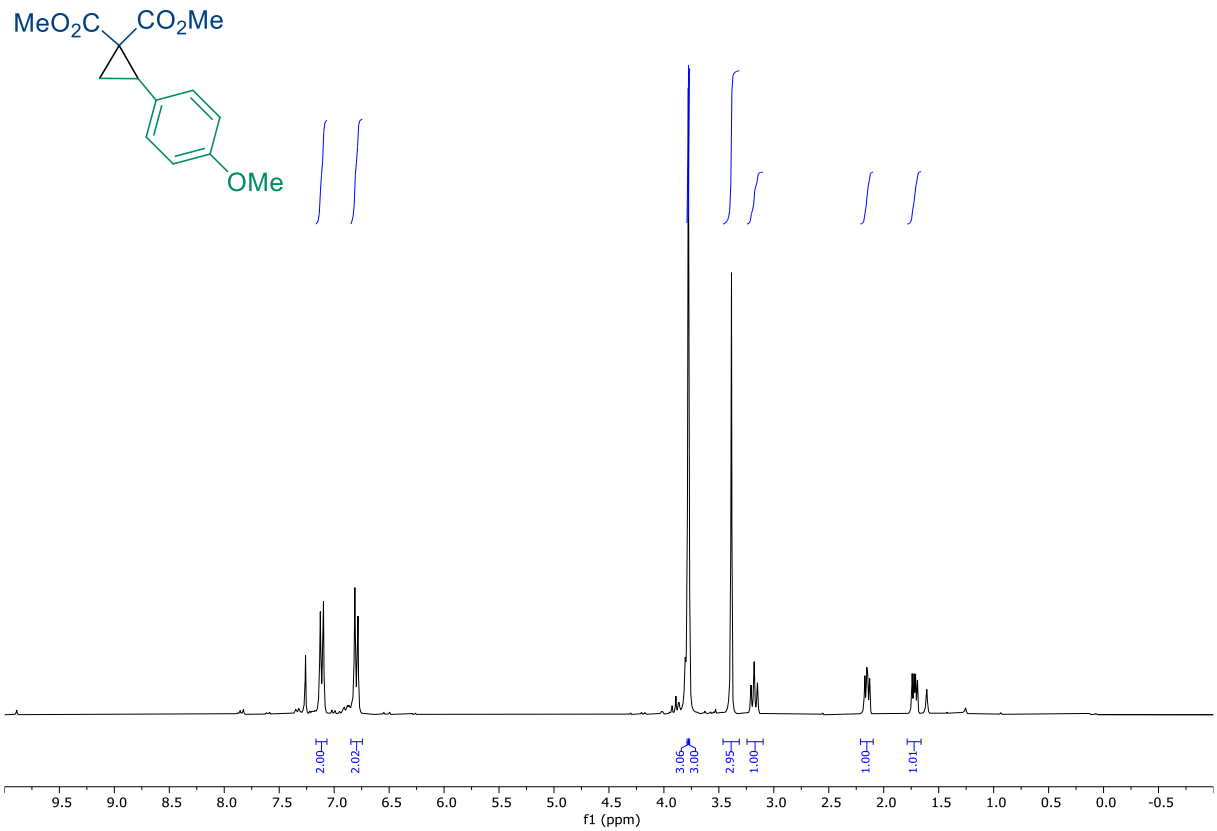



**Figure S145**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **6ao**.

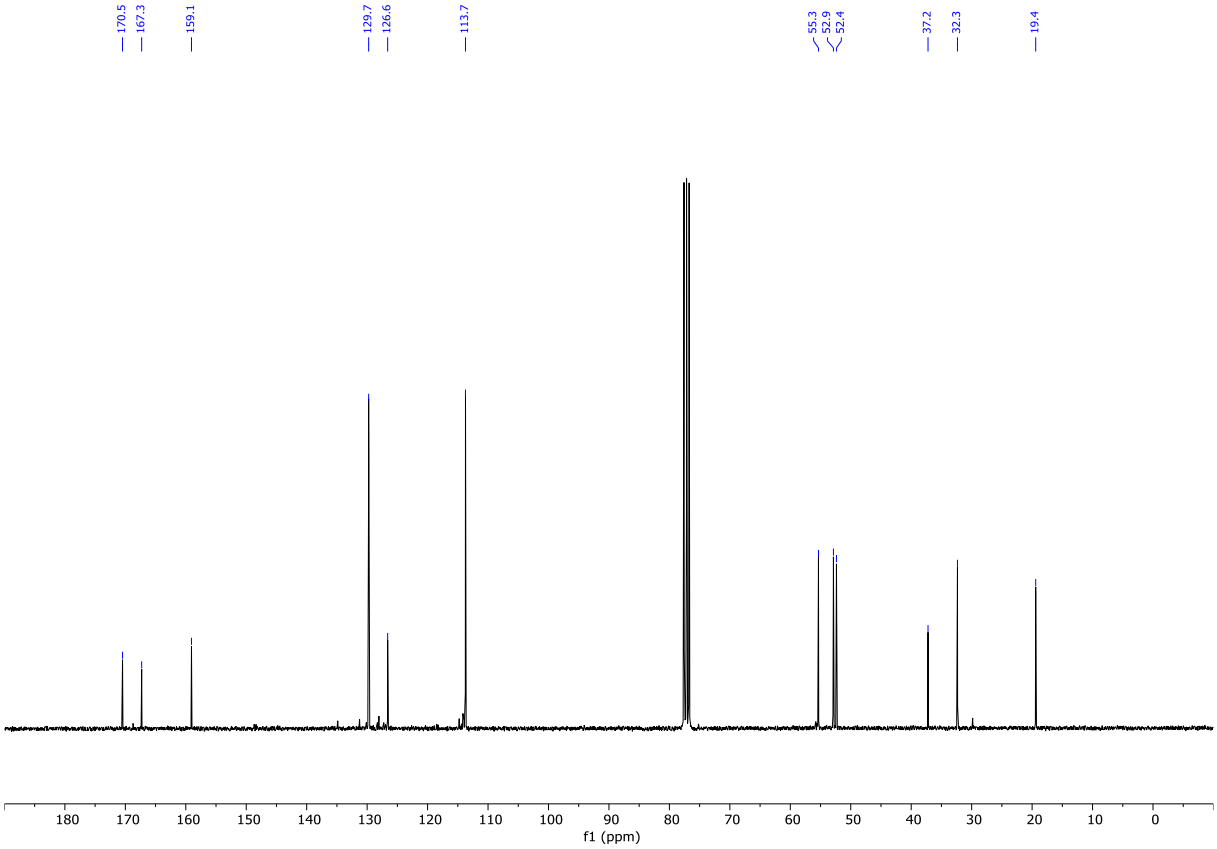



**Figure S146**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **6ao**.

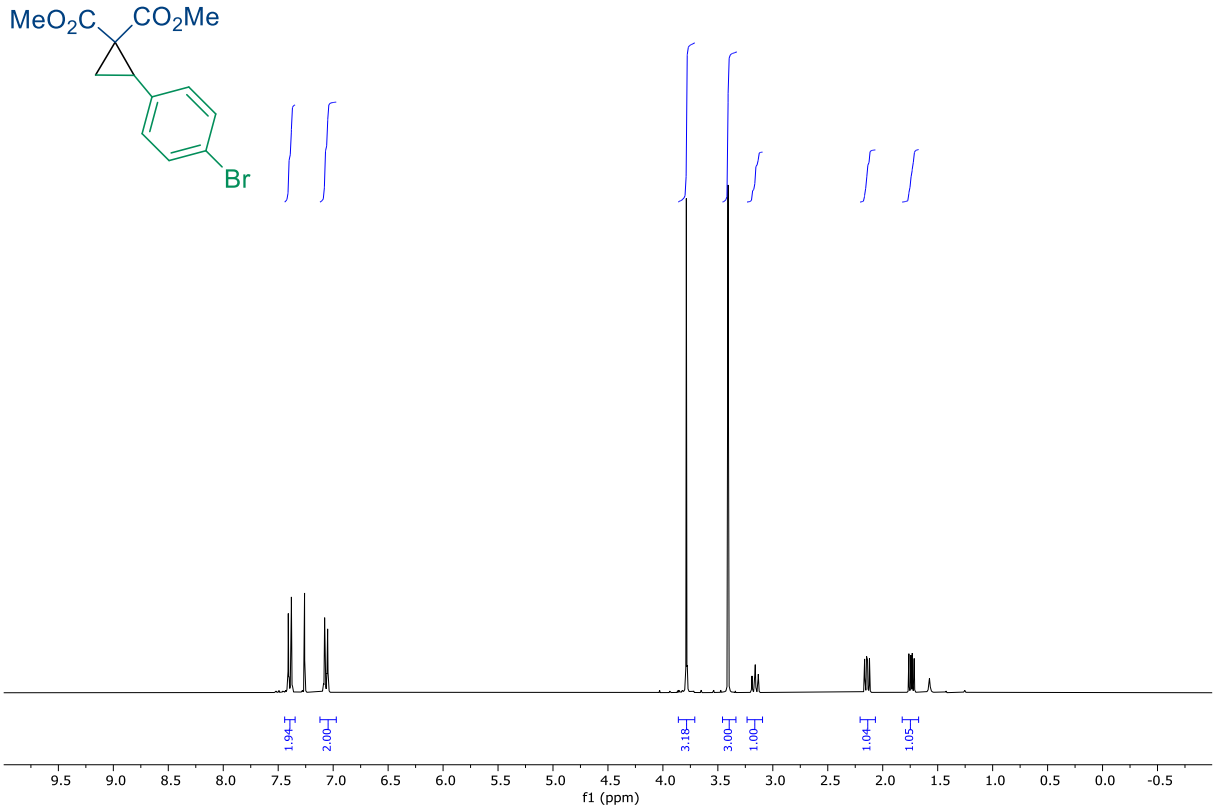



**Figure S147**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **6ap**.

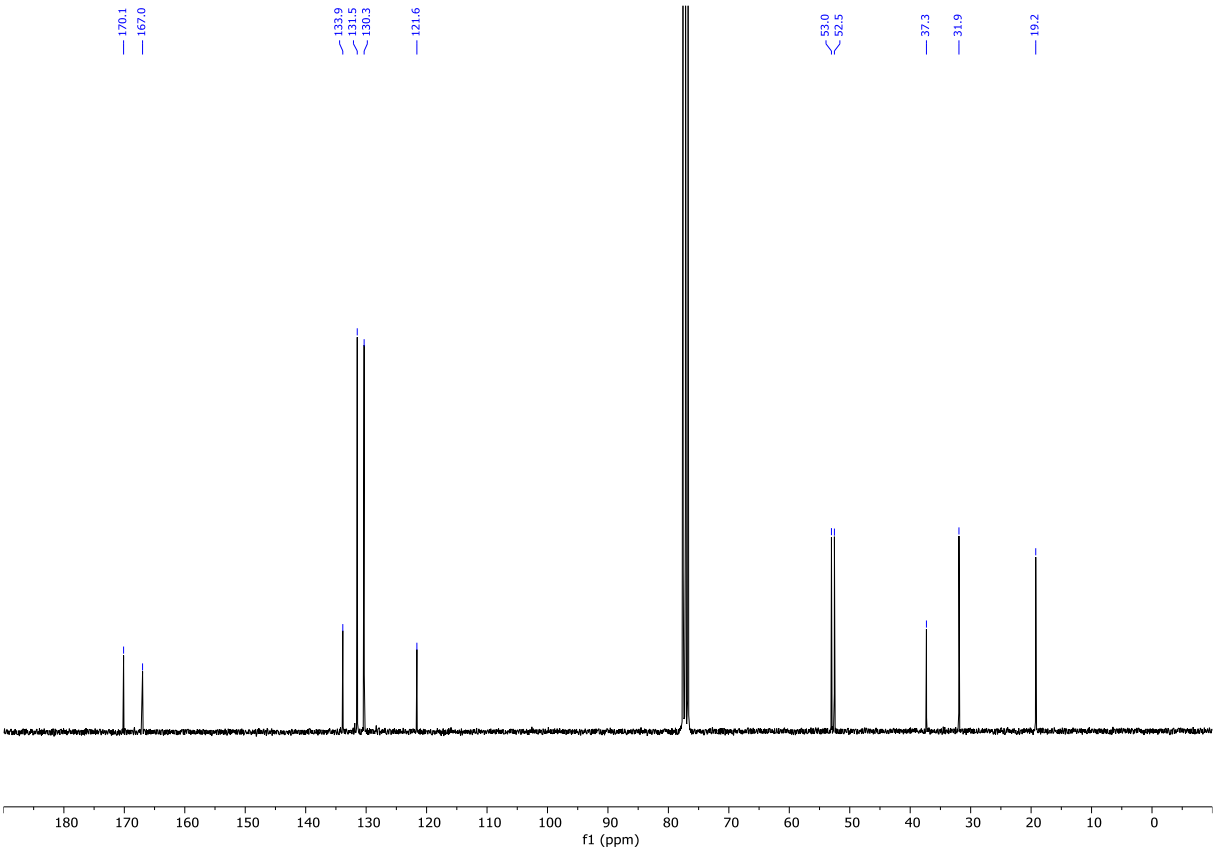



**Figure S148**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **6ap**.

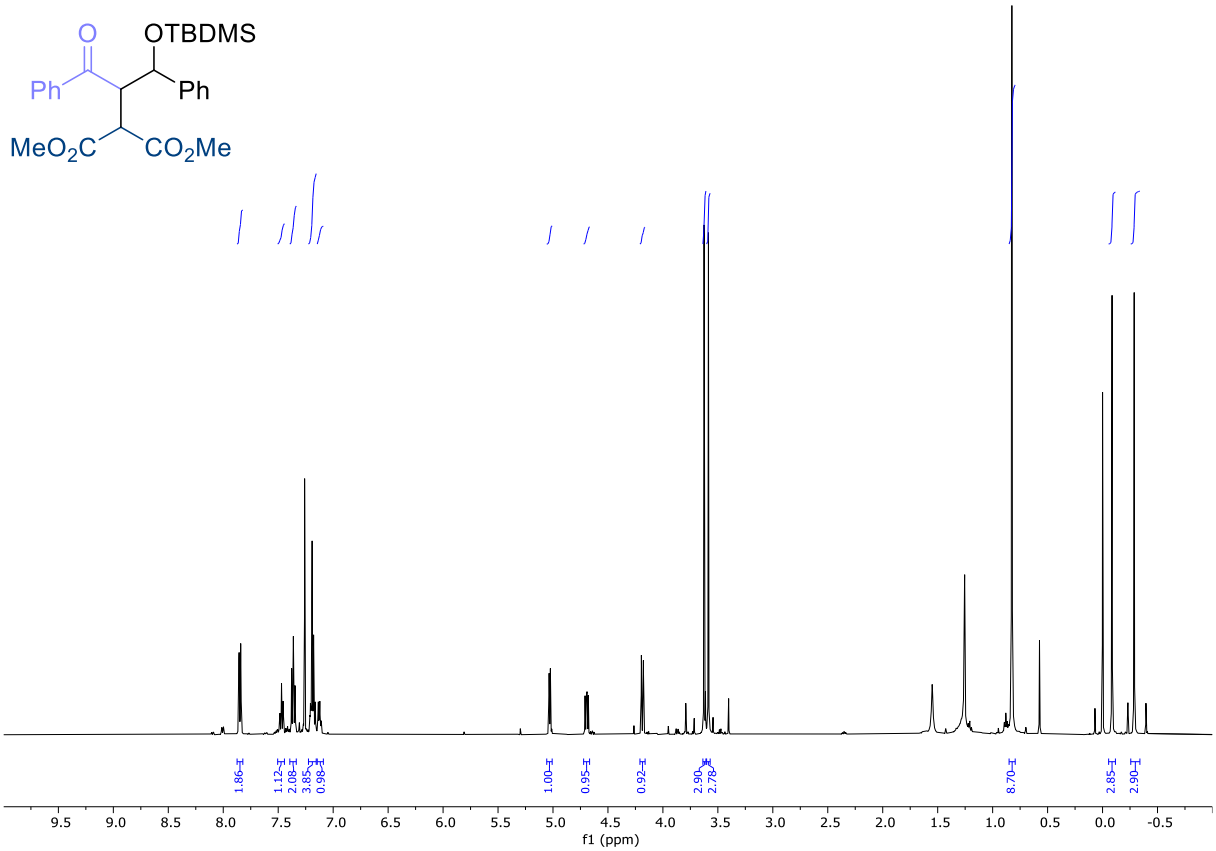



**Figure S149**. $^{1}H$ NMR spectrum (300 MHz, 298K, $CDCl_3$) of **7aa**.

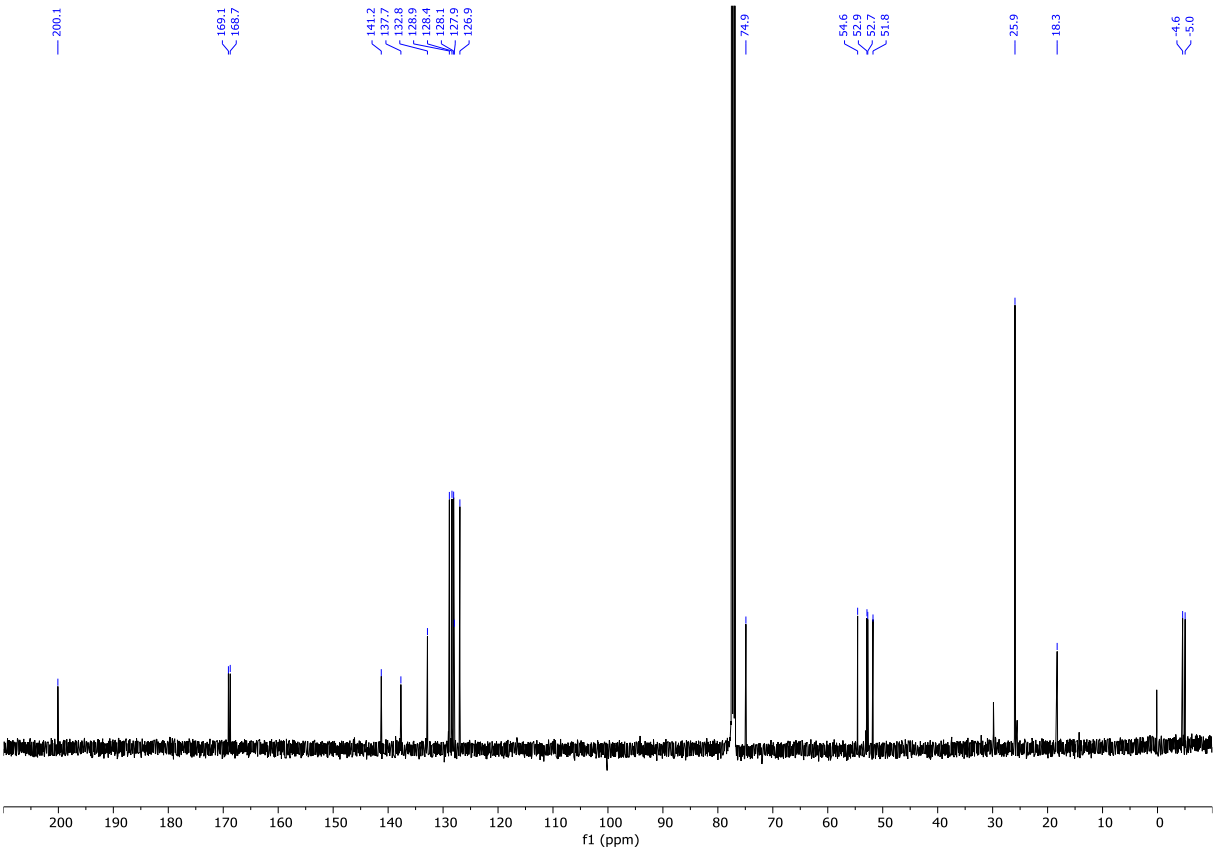



**Figure S150**. $^{13}C$ NMR spectrum (75 MHz, 298K, $CDCl_3$) of **7aa**.

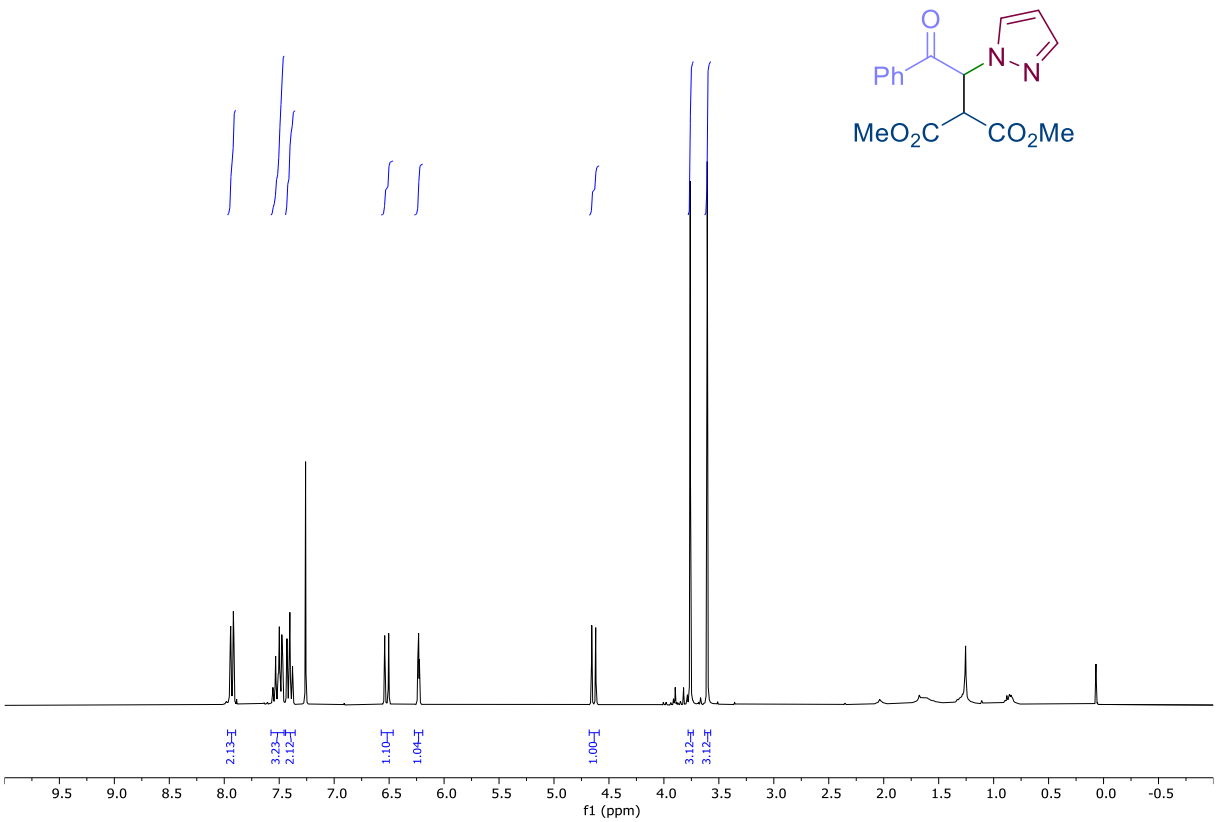



**Figure S151**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **8aa**.

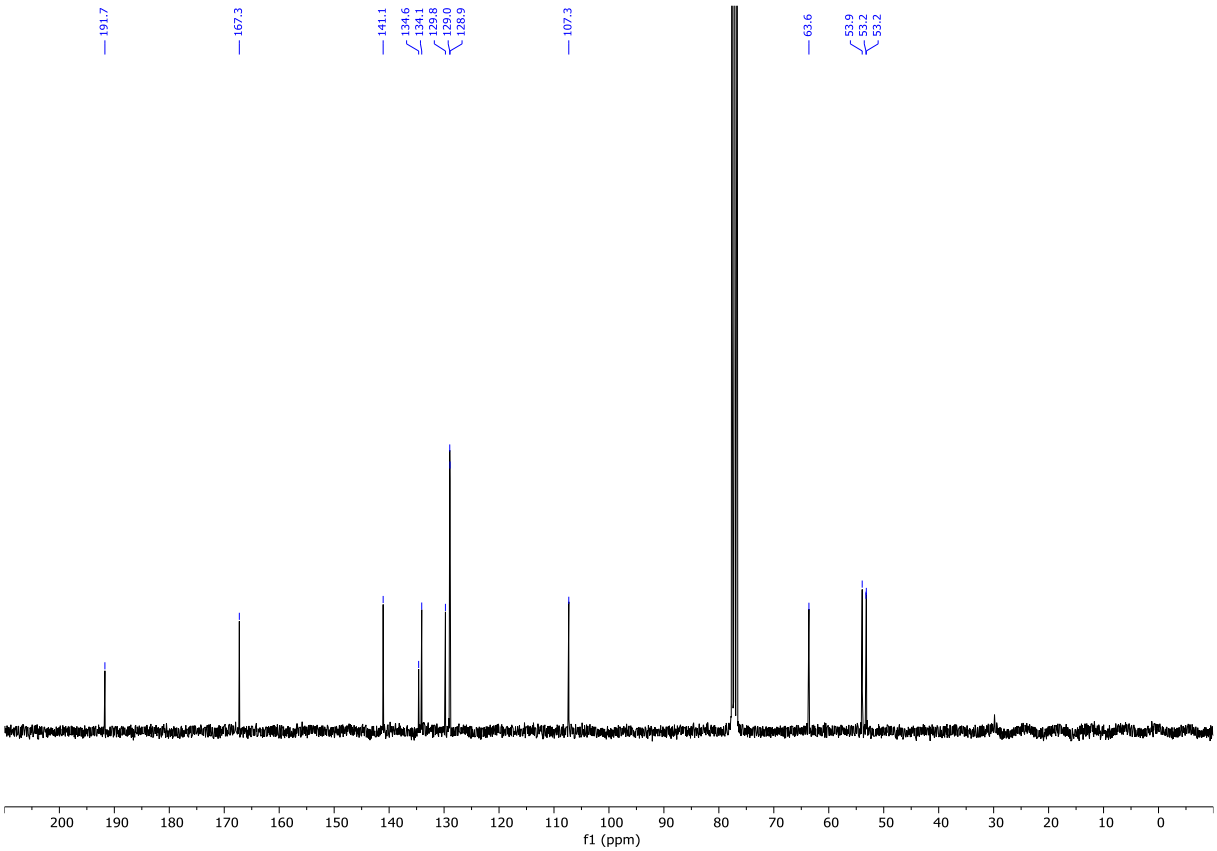



**Figure S152**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **8aa**.

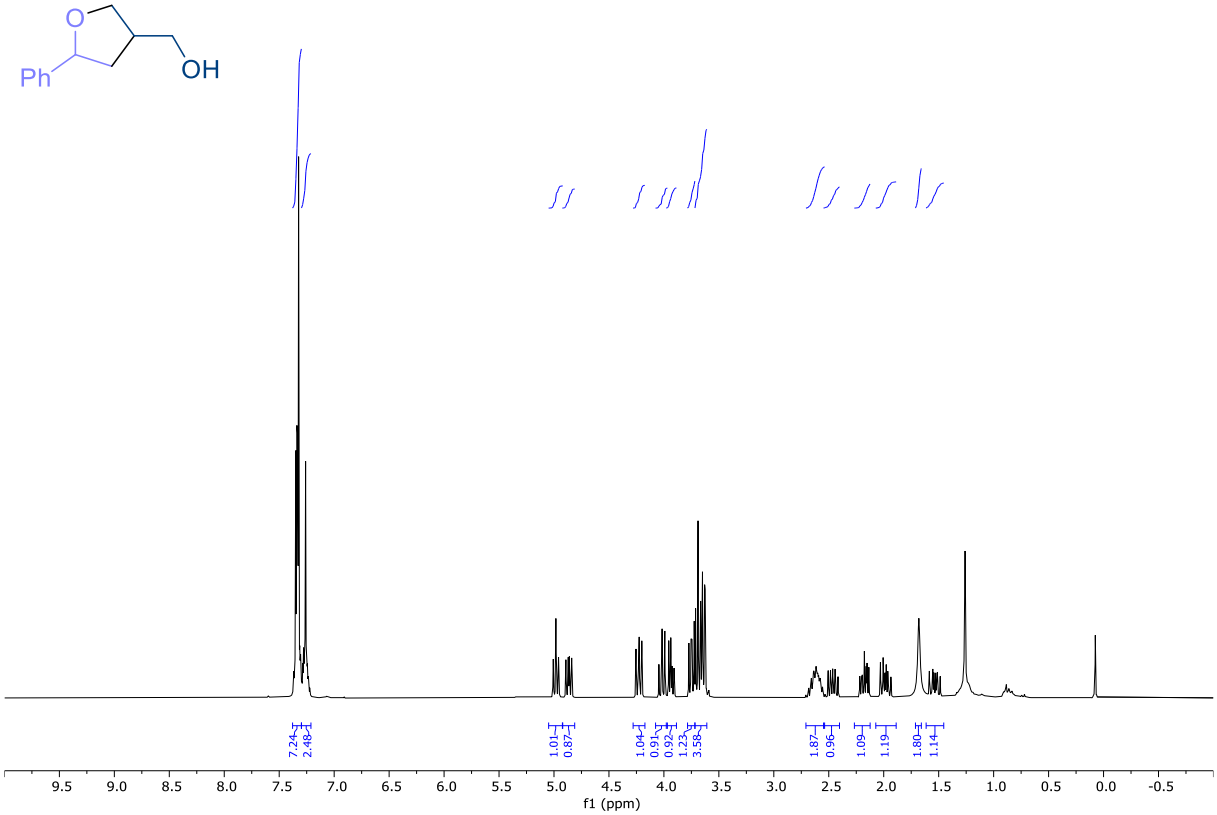



**Figure S153**. $^{1}$H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **9aa**.

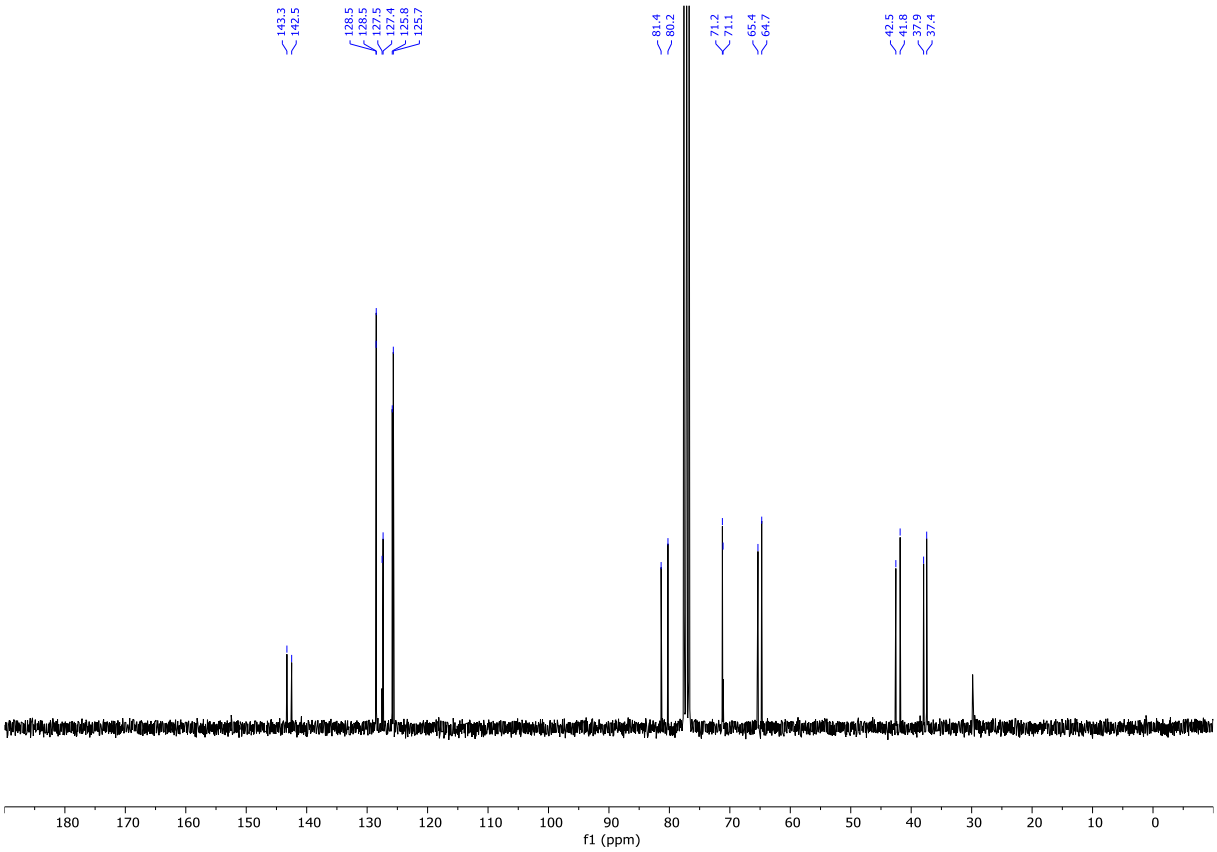



**Figure S154**. $^{13}$C NMR spectrum (75 MHz, 298K, $CDCl_3$) of **9aa**.

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