Transition Metal-Free Approach for the Late-Stage Benzylic C(sp^3)–H Etherifications and Esterifications

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1. Materials and methods

Commercial reagents were used without purification and reactions were run under N_2 atmosphere with exclusion of moisture from reagents using standard techniques for manipulating air-sensitive compounds.

^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (101 MHz) were recorded using Bruker Avance 400 spectrometer with $CDCl_3$ or DMSO-d_6 as solvent. NMR spectra were calibrated using the solvent residual signals ($CDCl_3$: δ ^{1}H = 7.26, δ ^{13}C = 77.16; DMSO-d_6: δ ^{1}H = 2.50, δ ^{13}C = 39.52). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublet, m = multiplet and br s = broad singlet.

Thin layer chromatography (TLC) was performed using pre-coated TLC sheets ALUGRAM® SIL G/UV254 (Machery-Nagel) and spots were visualized using UV light (254 nm).

Flash chromatography was performed on an automated chromatography system (Biotage® or Combiflash®Rf) with on-line UV detection using commercial SilicaFlash Cartridges and the indicated solvent and gradient system.

High-resolution mass spectrometry (HRMS) of samples were prepared by dissolving 0.1−5.0 mg of the product in methanol or in acetonitrile and further diluting to a concentration of 10^{-5}−10^{-6} M with 50% methanol (or acetonitrile)/50% H_2O/0.1% formic acid. The samples were injected in the MS, using a CapLC system and a nanoelectrospray source operated in positive ion mode at a potential of 1.5 or 1.7 kV. The eluent used was 30% A (0.1% formic acid in H_2O) and 70% B (0.1% formic acid in CH_3CN/H_2O 95/5) at a flow rate of 6.0 mL/min. Samples were injected with an interval of 3 min. Before analysis, 2.0 mL of a 0.025% H_3PO_4 solution (MeOH/H_2O-50/50) or 10.0 mL of 10^{-6} M deoxyadenosine solution (MeOH/H_2O-50/50) was injected as a lock mass. Positive-ion mode accurate mass spectra were acquired using a Q-TOF instrument.

Kessil lamps were purchased from Laser 2000 (UK) Ltd, with precise wavelengths (427nm, 456 nm). Blue LED setup was designed and made in workshop of University of Göttingen.

TLC-MS was analysed by TLC-plate express from advion, the MS is a single quad ZQ-Micromass from waters, the software is Masslynx 4.1 from Waters.

Fluorescence quenching experiments and Stern-Volmer analysis were conducted using a Cary Eclipse fluorescence spectrophotometer. The following parameters were employed: excitation bandwidth = 5 nm, emission bandwidth = 10 nm, data interval = 1 nm, scan speed = 120 nm/min, averaging time = 0.5 s. The samples were prepared in the same 1.4 mL quartz cuvette and capped with a rubber septum unless otherwise noted.

2. Setup for photocatalytic reactions

Kessil reaction setup

The reaction setup is depicted in **Figure S1**. The reaction setup consists of commercially available Kessil lamp which was purchased from Laser 2000 (UK) Ltd, with precise wavelengths (427nm, 456 nm), cooling of the setup was performed by commercially available 120 mm computer fans to keep the temperature around 30 °C. Magnetic stirring was performed at 500 rpm. The light intensity was measured by a lux meter and light intensity was higher than 100,000 lux.

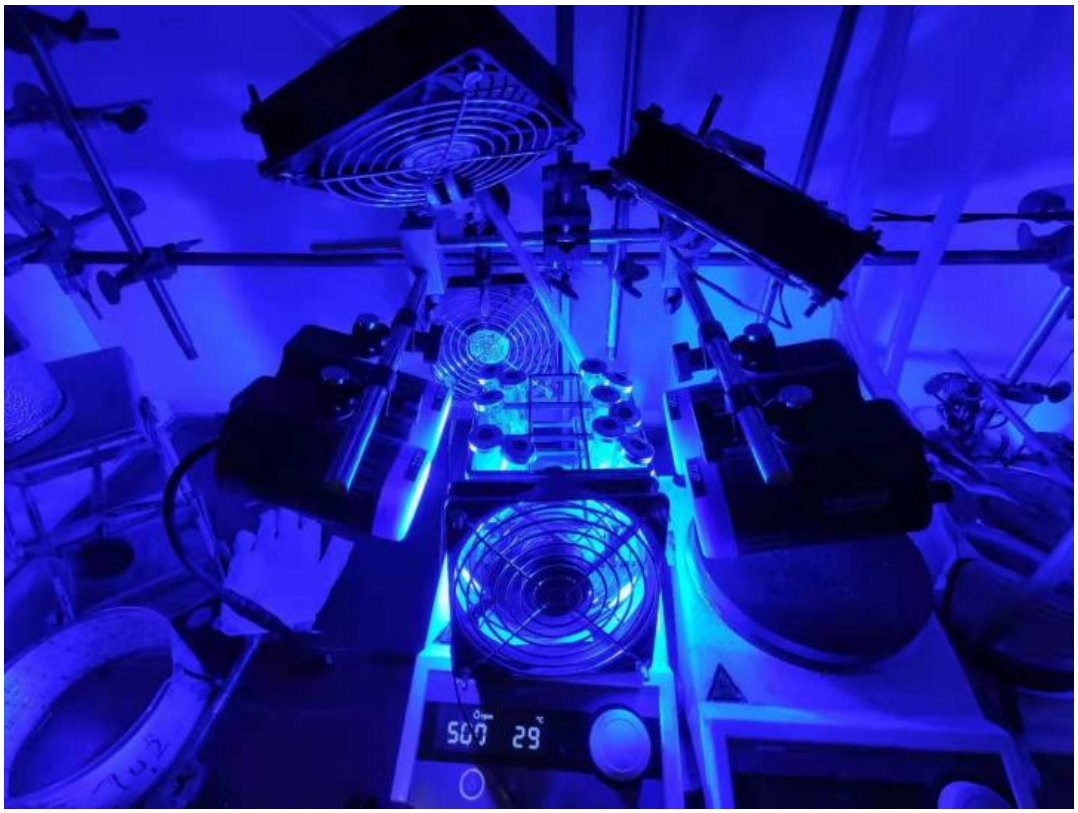


Figure S1: Kessil reaction setup

Blue LED setup

The reaction setup is depicted in **Figure S2**. The reaction setup consists of a self-constructed light source configuration, made up of a crystallizing dish with a diameter of 140 mm. Inside of the crystallizing dish, commercially available 5 m LED-Strip is glued with separable LED elements. In total, 3 m LED strip is used in a crystallizing dish, with a total power of 24 W. Light intensity of the light source can be adjusted by a self-constructed dimmer. Construction of the reaction setup and the dimmer was performed by the electronic services of the faculty for chemistry of the Georg-August-Universität Göttingen. Cooling of the setup is performed by a commercially available 120 mm computer fan. In this reaction, 24 W blue LED was used, and the light intensity was around 13,000 lux.

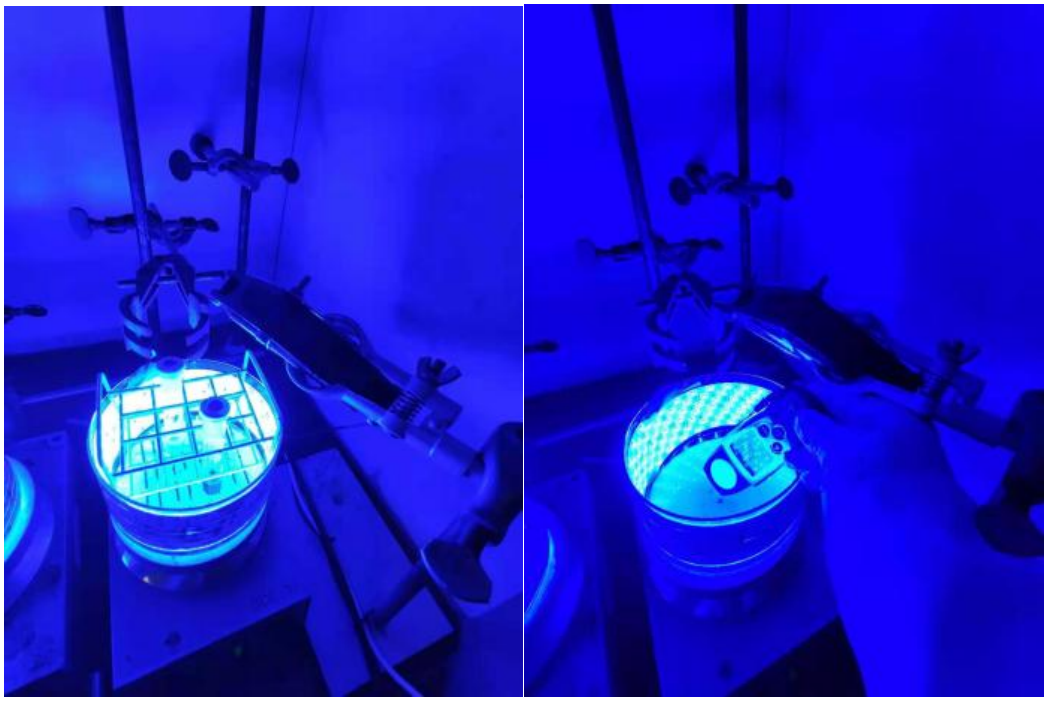


Figure S2: LED reaction setup.

The emission spectra of the light setup was measured with a UV-Vis probe from Ocean optics (P200-5-UV-Vis). The emission spectra showed the clear wavelength band between 404 and 553 nm with a maximum at 456 nm (**Figure S3**). The light intensity was measured by a lux meter, which can measure the value of different light intensity directly. Please note the distance between the sensor and light should be always same. In our case, we measured the light intensity in the center of the oil bath.

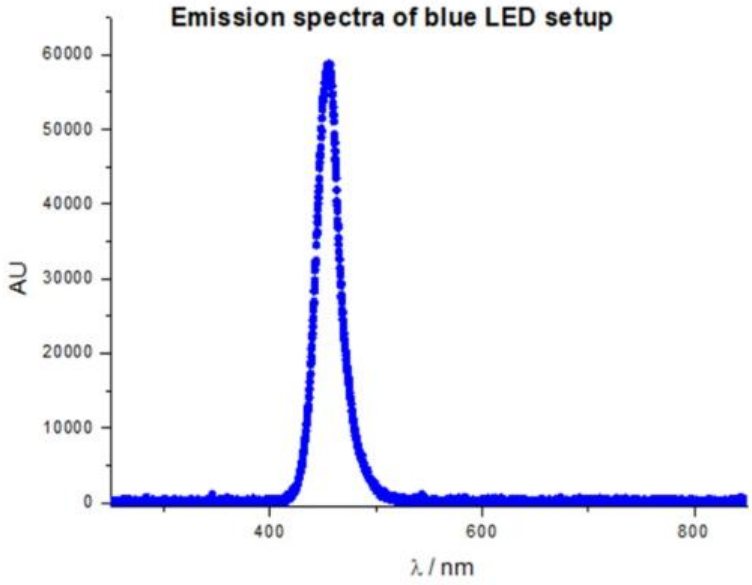
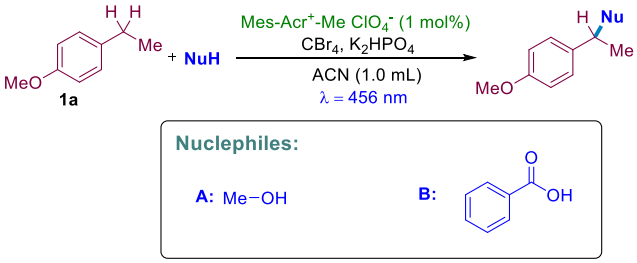


Figure S3: LED reaction setup.

3. Optimization

Table S1. Screening of reaction conditions.

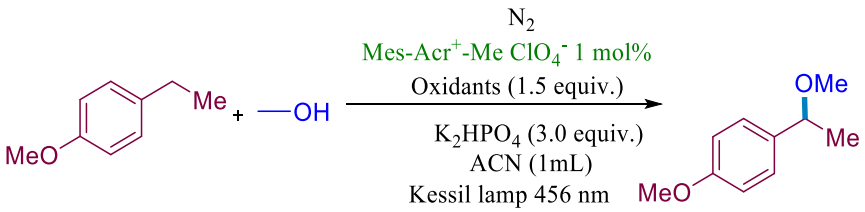


Entry	Variation of standards	NuH	Yield (%)[f]
1	/[a]	A	59 (57)
2	/[b]	B	73 (70)
3	No light[c]	A	0
4	No catalyst	A	2
5	No CBr_4[d]	A	0
6	No K_2HPO_4[e]	A	6

a. Reaction conditions: 1a (0.2 mmol, 1.0 equiv), catalyst (0.002 mmol, 1.0 mol%), K_2HPO_4 (0.6 mmol, 3.0 equiv), CBr_4 (0.3 mmol, 1.5 equiv), methanol (0.03 ml, 0.74 mmol, 3.7 equiv), acetonitrile (1 mL), room temperature (r.t.), 3 h. **b.** Reaction conditions: 1a (0.2 mmol), catalyst (0.002 mmol, 1.0 mol%), K_2HPO_4 (0.6 mmol, 3.0 equiv), CBr_4 (0.3 mmol, 1.5 equiv), benzoic acid (2.0 equiv, 0.40 mmol), acetonitrile (1 mL), r.t., 5.5 h. **c-e**. Control experiments for the etherification. **f**. The yield was determined by ^1H NMR using 1,3,5-trimethoxybenzene as the internal standard (the yield in bracket corresponds to the isolated yield).

Optimization of Etherification

Screening of oxidative quenchers

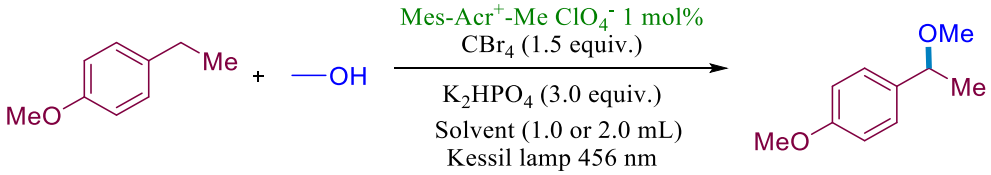


Entry	Oxidative quenchers	Yield [%][a]
1	$CBrCl_3$	20
2	NEt_3	0
3	iPr_2NEt	0

4	$PhI(OAc)_2$	0
5	$PhI(OTFA)_2$	18
6	$K_2S_2O_8$	4
7	Benzoyl Peroxide	19
8	Di-tert-butyl peroxide	trace

a. The yield was determined by NMR using the 1,3,5-trimethoxybenzene as the internal standard.

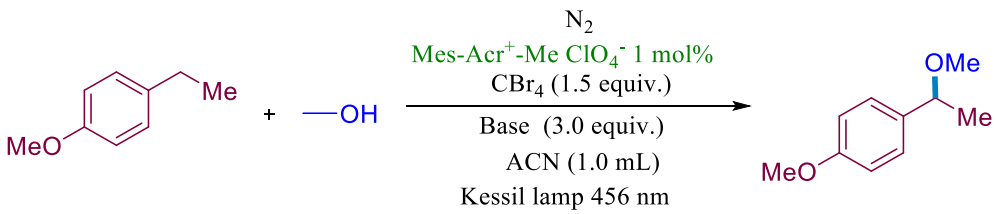
Screening of solvents



Entry	**Solvents**	**Yield [%][a]**
1	DCE	21
2	DCM	13
3	DCE+DCM(1.5 mL+0.5 mL)	0
4	DCM+HFIP (1.6 mL+0.4 mL)	0
5	Nitromethane (1.0 mL)	60[b]

a. The yield was determined by NMR using the 1,3,5-trimethoxybenzene as the internal standard; b. reaction time: 32h.

Screening of bases



Entry	**Base**	**Yield [%][a]**
1	2,6-Di-tert-butyl-4-methylpyridine	44
2	DBN	0
3	DBU	5

4	Cs_2CO_3	10
5	K_3PO_4	26
6	2,4-Lutidine	9

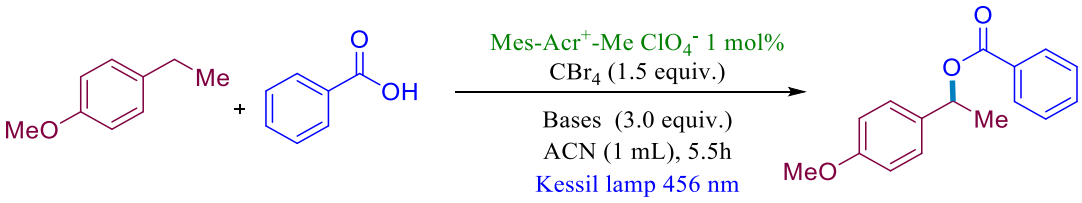
a. The yield was determined by NMR using the 1,3,5-trimethoxybenzene as the internal standard.

Control experiments

Entry	Controlled parameter	Yield [%][a]
1	Standard conditions	57
2	No CBr_4	0
3	No light	0
4	No catalyst	7
5	No base	6

Optimization of Esterification

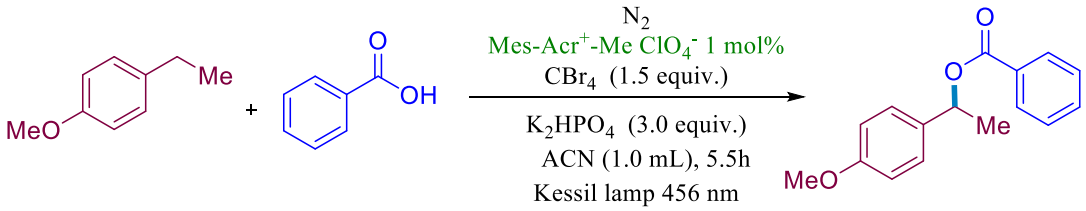
Screening of bases



Entry	Bases	Yield [%][a]
1	Cs_2CO_3	15
2	K_3PO_4	6
3	$NaHCO_3$	49
4	K_2CO_3	63

a. The yield was determined by NMR using the 1,3,5-trimethoxybenzene as the internal standard.

Screening the ratio between the reagents



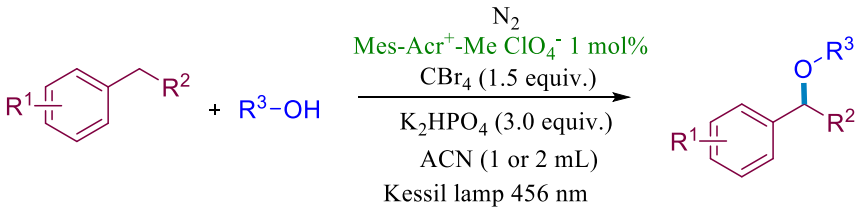
Entry	Benzoic acid	CBr_4	Base	Yield [%][a]
1	2.0 eq.	1.5 eq	3.0 eq.	73
2	2.0 eq.	1.5 eq	2.0 eq.	40
3	1.5 eq.	1.5 eq	2.0 eq.	42
4	1.5 eq.	1.5 eq	3.0 eq.	52
5	3.0 eq.	1.5 eq	3.0 eq.	73

a. The yield was determined by NMR using the 1,3,5-trimethoxybenzene as the internal standard.

Control experiments

Entry	Controlled parameter	Yield [%][a]
1	Standard conditions	73
2	No CBr_4	0
3	No light	0
4	No catalyst	2
5	No base	21

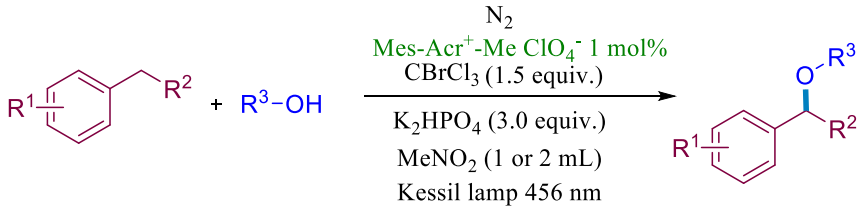
4. General procedure for the etherification



A dry 10 mL reaction tube containing a stirring bar was charged with 0.3 mmol of CBr_4 (1.5 equiv.), 0.6 mmol of K_2HPO_4 (3.0 equiv.) and 0.002 mmol (1 mol%) of catalyst. Then, the vial was closed with a pierceable Teflon cap. A needle was pierced through the cap to facilitate exchange of the vial headspace with the atmosphere. The vial was then transferred into the glovebox, where it was charged with dry acetonitrile (1.0 or 2.0 mL), 0.6 - 1.2 mmol of alcohols

(3.0 equiv.- 6.0 equiv.) and benzylic substrate (0.2 mmol, 1.0 equiv.). The reaction was kept for 3-6 h under 40 W Kessil lamp reaction setup (the progress can be monitored *via* GC-MS or TLC-MS). Then, the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Products were purified *via* Flash chromatography chromatography with ethyl acetate and *n*-heptane as solvents.

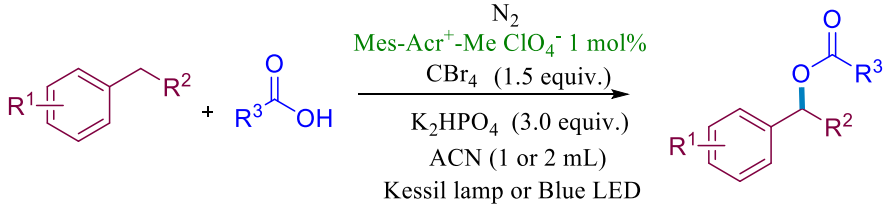
Modified conditions with $CBrCl_3$ and nitromethane



A dry 10 mL reaction tube containing a stirring bar was charged with 0.3 mmol of CBr_4 (1.5 equiv.), 0.6 mmol of K_2HPO_4 (3.0 equiv.) and 1 mol% of catalyst. Then, the vial was closed with a pierceable Teflon cap. A needle was pierced through the cap to facilitate exchange of the vial headspace with the atmosphere. The vial was then transferred into the glovebox, where it was charged with 1.2 mmol of alcohols (6.0 equiv.), 0.20 mmol of benzylic substrate (1.0 equiv.) and nitromethane (1.0 or 2.0 mL) The resulting mixture was stirred for 0.5 h under Kessil reaction setup. Then the benzylic substrate was added into the reaction mixture and kept for 32 h under 40 W Kessil lamp reaction setup (the progress can be monitored *via* GC-MS or TLC-MS). Then, the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Products were purified *via* Flash chromatography with ethyl acetate and *n*-heptane as solvents.

5. General procedure for the esterification

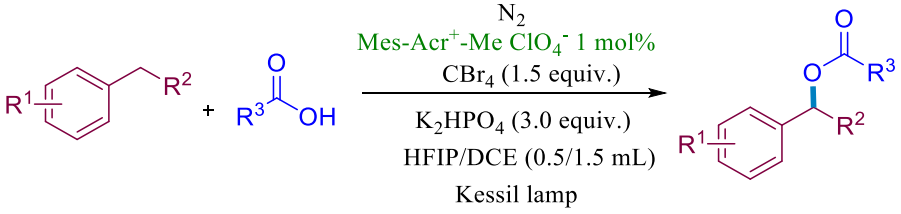
Procedure B



A dry 10 mL microwave vial containing a stirring bar was charged with 0.40 mmol of acids (2.0 equiv. if solid, otherwise it was added when the vial was moved out of the glovebox), 0.3 mmol of CBr_4 (1.5 equiv.), 0.6 mmol of K_2HPO_4 (3.0 equiv.) and 0.002 mmol (1 mol%) of catalyst. Then, the vial was closed with a pierceable Teflon cap. A needle was pierced through the cap to facilitate exchange of the vial headspace with the atmosphere. The vial was then transferred into the glovebox, where it was charged with dry acetonitrile (1.0 or 2.0 mL). The resulting mixture was

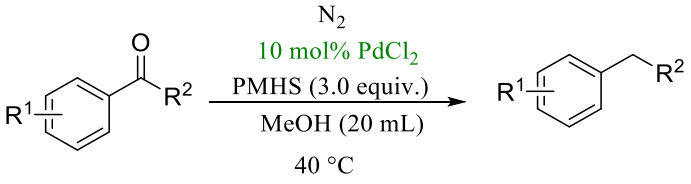
stirred for 0.5 h under 24 W blue LED irradiation (only used for a few reactions with amino acids) or 40W Kessil lamp reaction setup. Then the benzylic substrate was added into the reaction mixture and kept for 5-42 h under 24 W blue LED irradiation or Kessil reaction setup (the progress can be monitored *via* GC-MS or TLC). Then the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted for three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Products were purified *via* Flash chromatography with ethyl acetate and *n*-heptane as solvents.

Modified conditions with HFIP/DCE as a solvent



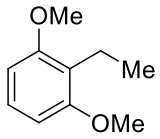
A dry 10 mL microwave vial containing a stirring bar was charged with 0.40 mmol of acids (2.0 equiv. if solid), 0.3 mmol of CBr_4 (1.5 equiv.), 0.6 mmol of K_2HPO_4 (3.0 equiv.) and 0.002 mmol (1 mol%) of catalyst. After purging the flask three times under vacuum and three times under nitrogen. The vial was charged with HFIP (0.5 ml), DCE (1.5 ml) and 0.4 mmol of acids (2.0 equiv., if it is liquid). The resulting mixture was stirred for 0.5 h under 40W Kessil lamp reaction setup. Then the benzylic substrate was added into the reaction mixture and kept for 24 h under irradiation of Kessil reaction setup (the progress can be monitored *via* GC-MS or TLC). Then the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Products were purified *via* Flash chromatography with ethyl acetate and *n*-heptane as solvents.

6. Procedure for the synthesis of substrate and characterization data.[1]



A 50 mL two-neck flask containing a stirring bar was charged with the catalyst (10.0 mol%). After purging the flask three times under vacuum and three times under nitrogen. Under the nitrogen atmosphere, the solvent (20 mL) and benzylic ketone were added subsequently. Finally, PMHS was added slowly under room temperature. The resulting mixture was stirred for 16 h at 40 °C. Then, the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted for three times with ethyl acetate. The combined organic

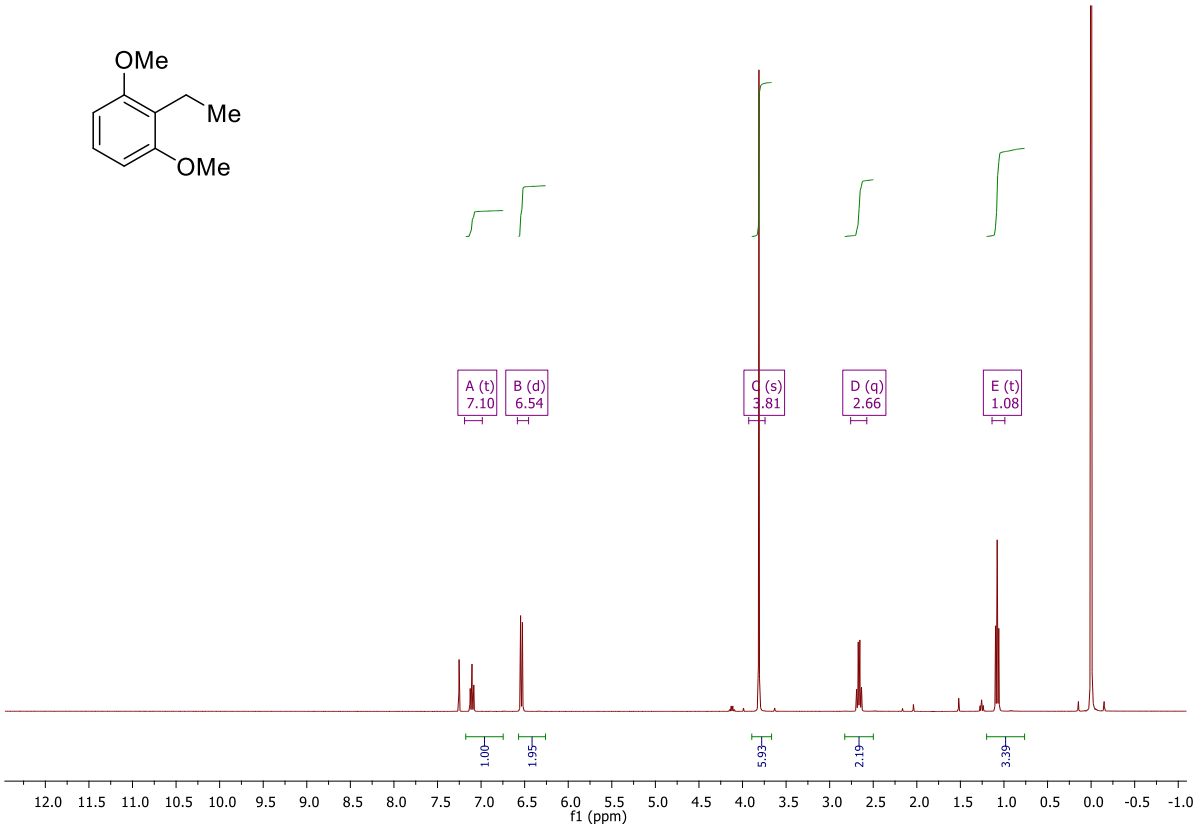
layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Products were purified *via* silica gel chromatography with ethyl acetate and *n*-hexane as solvents.



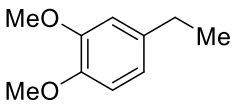
2-Ethyl-1,3-dimethoxybenzene (S1): Prepared according to the reduction of ketones. Following workup, the product was purified by flash column chromatography (gradient 0% to 3% EtOAc/heptane) to give the title compound as a white solid (isolated yield: 68%). Spectral data were consistent with the previously reported one.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 – 6.65 (m, 1H), 3.86 (s, 2H), 3.84 (s, 6H), 2.59 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H).

MS (TLC-MS) : m/z [M+Na]$^+$: 189.



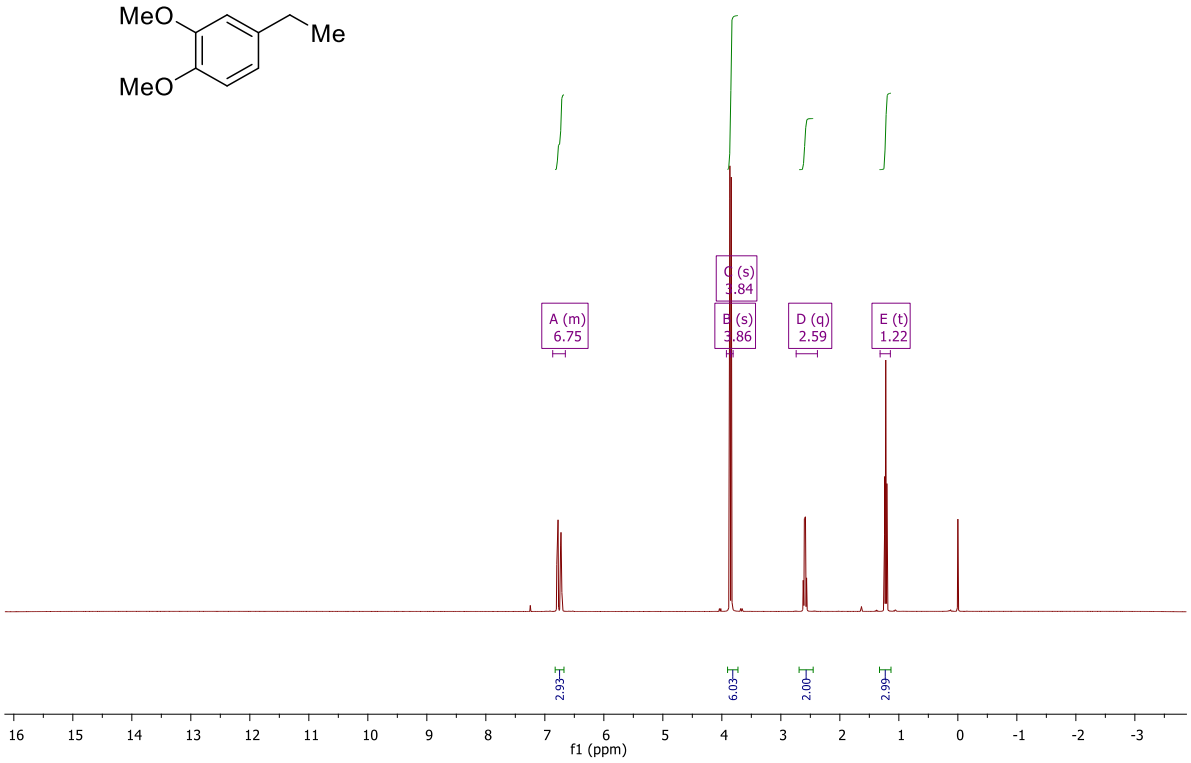
^{1}H NMR spectrum in $CDCl_3$.



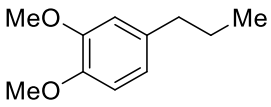
4-Ethyl-1,2-dimethoxybenzene (S2): Prepared according to the reduction of ketones. Following workup, the product was purified by flash column chromatography (gradient 0% to 3% EtOAc/heptane) to give the title compound as a white solid (isolated yield: 75%). Spectral data were consistent with the previously reported one.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 – 6.65 (m, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H);

MS (TLC-MS): m/z [M+Na]$^+$: 189.



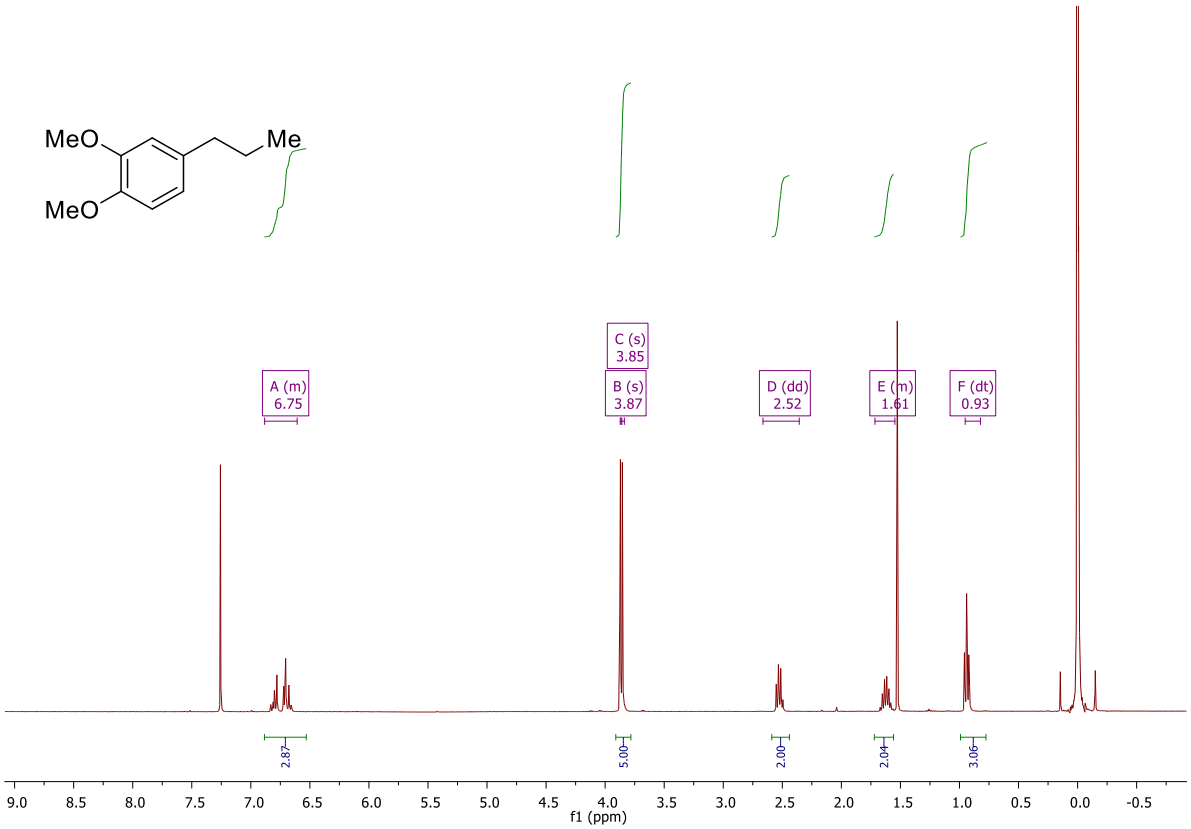
^{1}H NMR spectrum in $CDCl_3$.



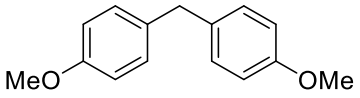
1,2-Dimethoxy-4-propylbenzene (S3): Prepared according to the reduction of ketones. Following workup, the product was purified by flash column chromatography (gradient 0% to 3% EtOAc/heptane) to give the title compound as a white solid (isolated yield: 48%). Spectral data were consistent with the previously reported one.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.61 (m, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 2.52 (dd, *J* = 15.2, 7.5 Hz, 2H), 1.72 – 1.55 (m, 2H), 0.93 (dt, *J* = 7.3, 3.7 Hz, 3H);

MS (TLC-MS): m/z [M+Na]$^+$: 203. However, the product formed from etherification is failed in the purification.

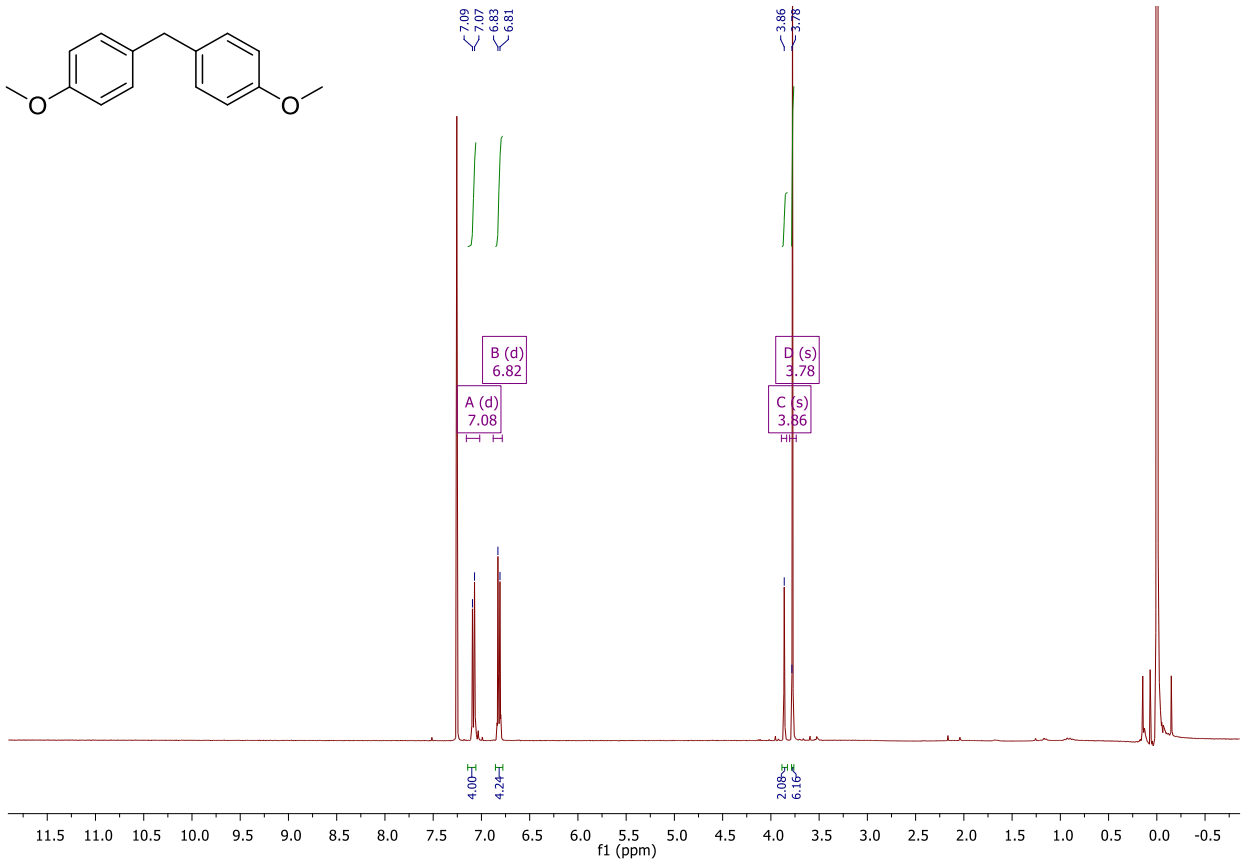


^{1}H NMR spectrum in $CDCl_3$.

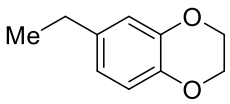


Bis(4-methoxyphenyl)methane (S4): Prepared according to the reduction of ketones. Following workup, the product was purified by flash column chromatography (gradient 0% to 3% EtOAc/heptane) to give the title compound as a white solid (isolated yield: 82%). Spectral data were consistent with the previously reported one.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 8.7 Hz, 4H), 6.82 (d, J = 8.7 Hz, 4H), 3.86 (s, 2H), 3.78 (s, 6H); **MS (TLC-MS):** m/z $[M+Na]^+$: 251. However, the yield of the product formed from etherification was lower than 25% with same amount of ketone. And the esterified product had good NMR yields (>60%), the purification was failed due to the by-product (ketone).



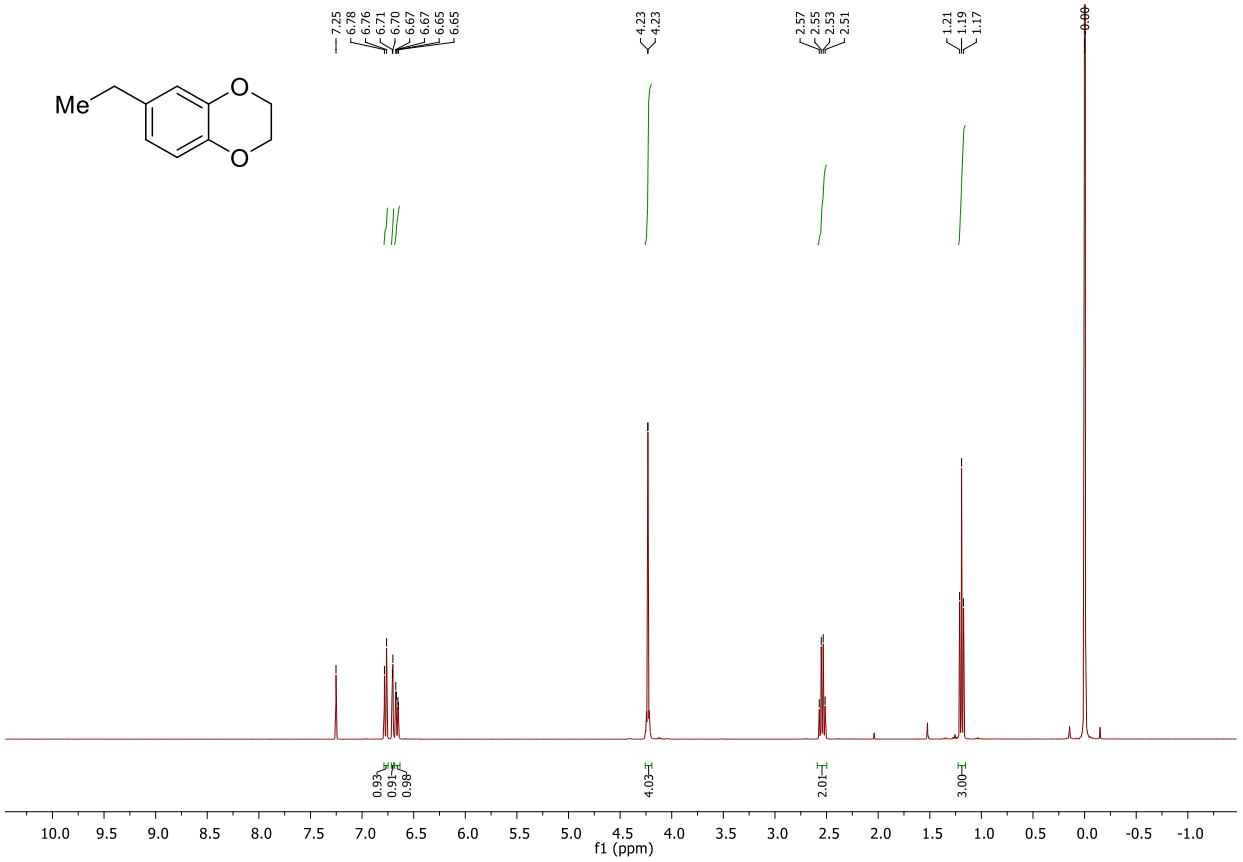
^{1}H NMR spectrum in $CDCl_3$.



6-Ethyl-2,3-dihydrobenzo[*b*][1,4]dioxine (S5): Prepared according to the reduction of ketones. Following workup, the product was purified by flash column chromatography (gradient 0% to 3% EtOAc/heptane) to give the title compound as a colourless oil (isolated yield: 86%).

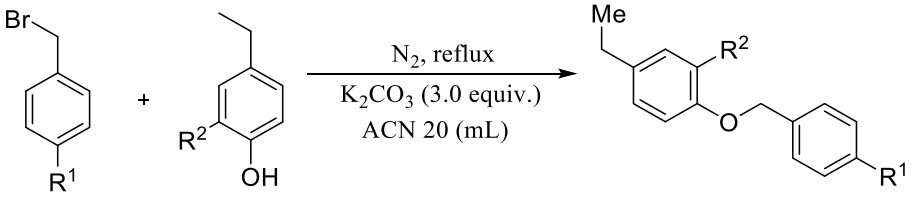
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (d, J = 8.2 Hz, 1H), 6.70 (d, J = 1.9 Hz, 1H), 6.66 (dd, J = 8.2, 2.0 Hz, 1H), 4.26 – 4.18 (m, 4H), 2.54 (q, J = 7.6 Hz, 2H), 1.19 (t, J = 7.6 Hz, 3H);

MS (TLC-MS): m/z $[M+Na]^+$: 187.

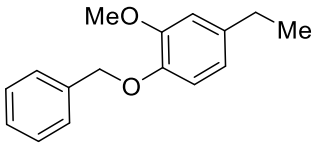


^{1}H NMR spectrum in $CDCl_3$.

Synthesis of ethers

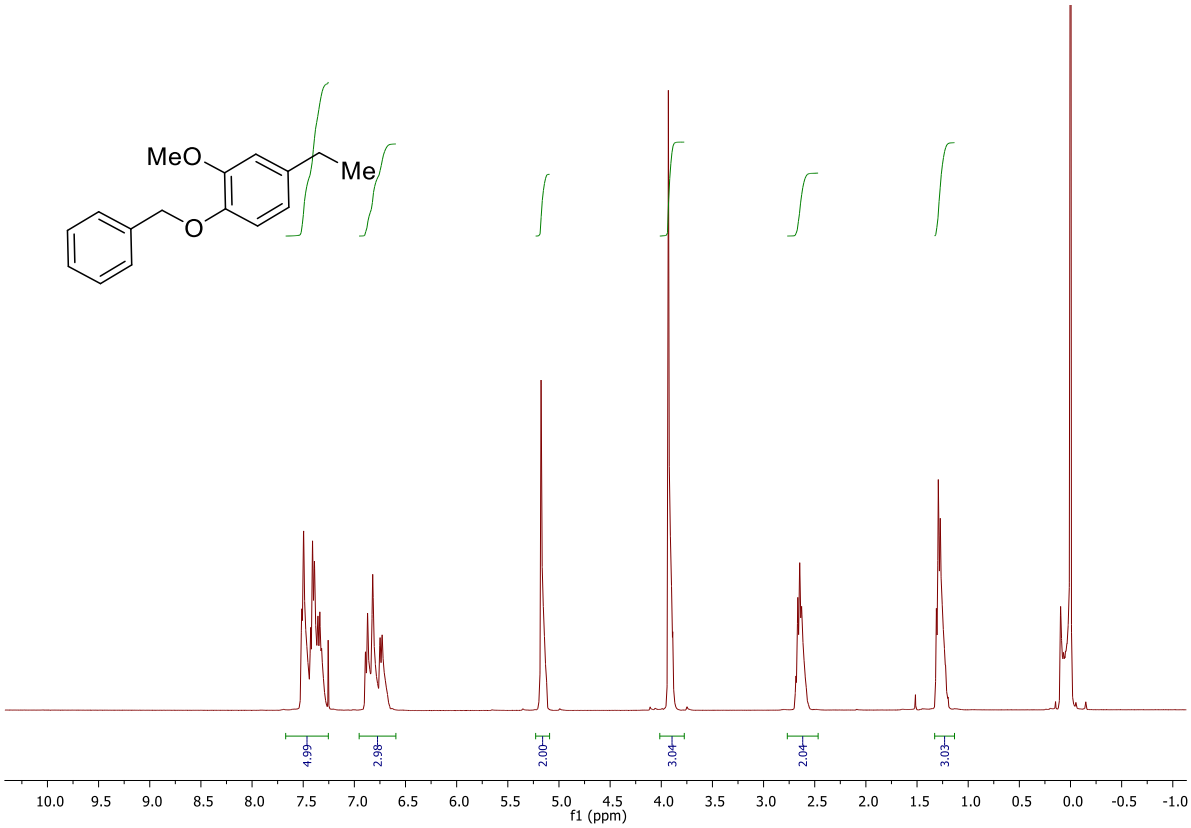


A 50 mL two-neck flask containing a stirring bar was charged with base (3.0 equiv, 30.0 mmol, 4.15 g), benzyl bromides (11.0 mmol, 1.1 equiv.) and phenols (10 mmol, 1.0 equiv.). After purging the flask three times under vacuum and three times under nitrogen. Under the nitrogen atmosphere, the solvent (20 mL) was added. The resulting mixture was stirred for 16 h at 105 °C. Then, the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted for three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Products were purified *via* silica gel chromatography with ethyl acetate and *n*-hexane as solvents.[5]

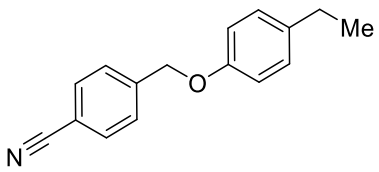


1-(benzyloxy)-4-ethyl-2-methoxybenzene (S6): Prepared according to the general synthesis procedure for ether. Following workup, the product was purified by flash column chromatography (gradient 0% to 15% EtOAc/heptane) to give the title compound as a colorlees oil (isolated yield: 57%). Spectral data were consistent with those reported previously.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.25 (m, 5H), 6.95 – 6.59 (m, 3H), 5.18 (s, 2H), 4.01 – 3.78 (m, 3H), 2.66 (dd, *J* = 14.9, 7.4 Hz, 2H), 1.33 – 1.13 (m, 3H); **MS (TLC-MS) :** m/z [M+Na]$^+$: 265.

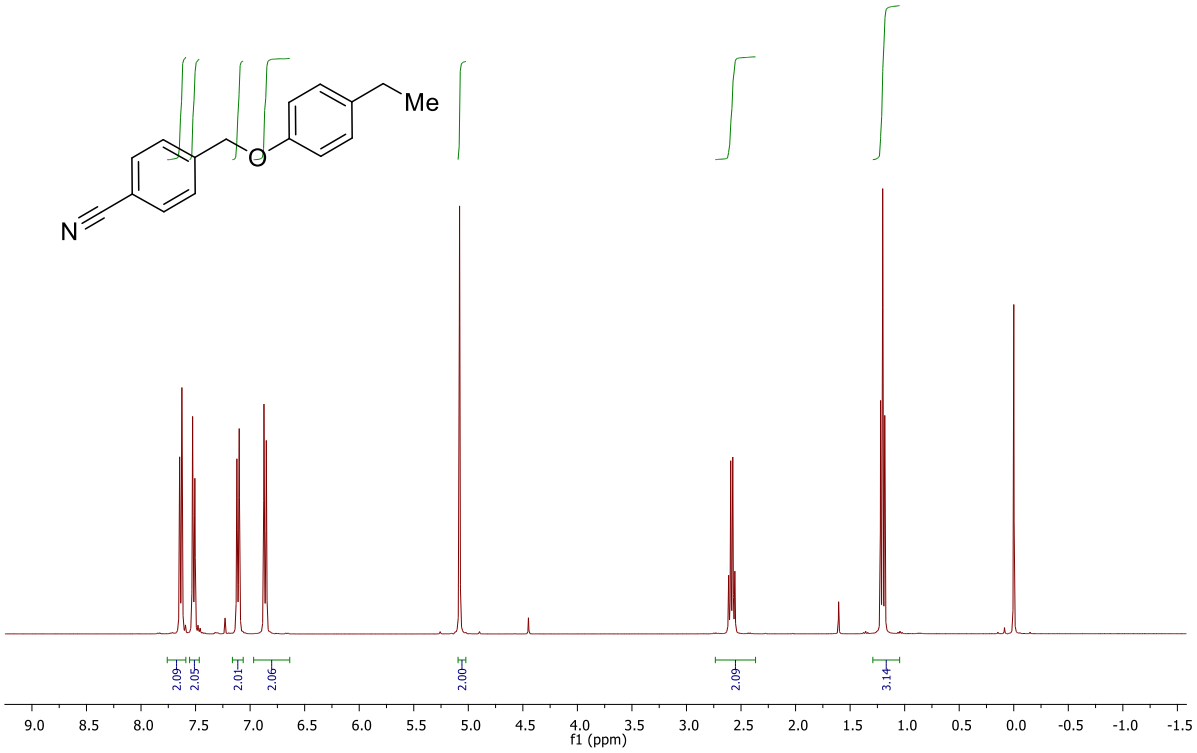


^{1}H NMR spectrum in $CDCl_3$.

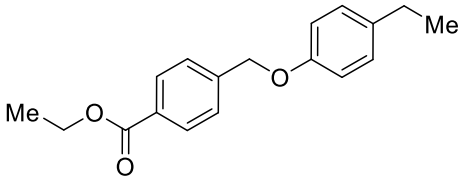


4-((4-ethylphenoxy)methyl)benzonitrile (S7): Prepared according to the general synthesis procedure for ether. Following workup, the product was purified by flash column chromatography (gradient 0% to 15% EtOAc/heptane) to give the title compound as a white solid (isolated yield: 48%).

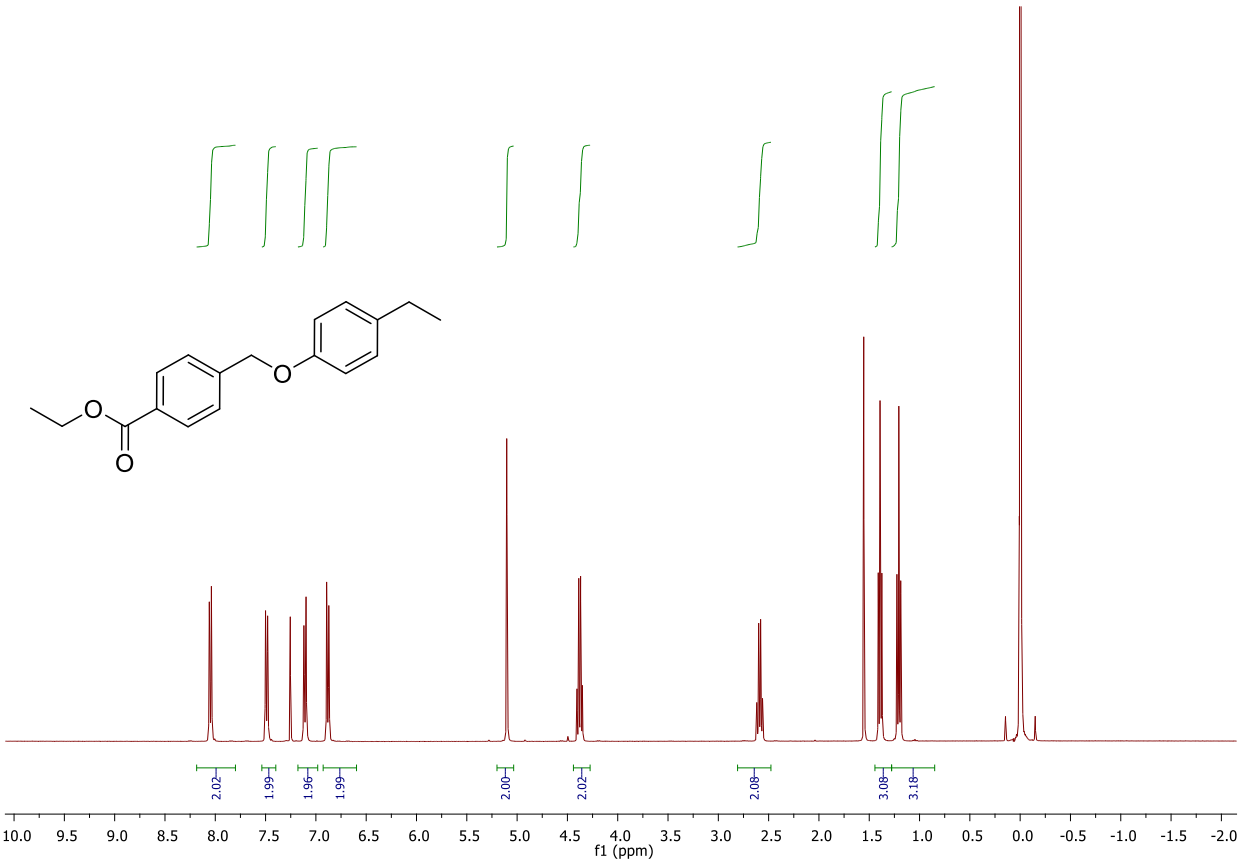
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.08 (s, 2H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H). **MS (TLC-MS) :** m/z [M+Na]$^+$: 260.



^{1}H NMR spectrum in $CDCl_3$.

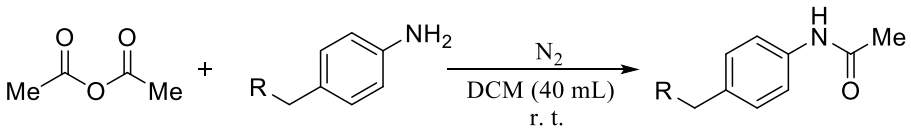


Ethyl 4-((4-ethylphenoxy)methyl)benzoate (S8): Prepared according to the general synthesis procedure for ether. Following workup, the product was purified by flash column chromatography (gradient 0% to 15% EtOAc/heptane) to give the title compound as a white solid (isolated yield: 48%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.10 (s, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.6 Hz, 3H). **MS (TLC-MS) :** m/z [M+Na]$^+$: 307.

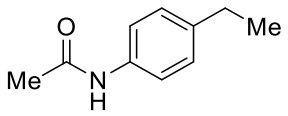


^{1}H NMR spectrum in $CDCl_3$.

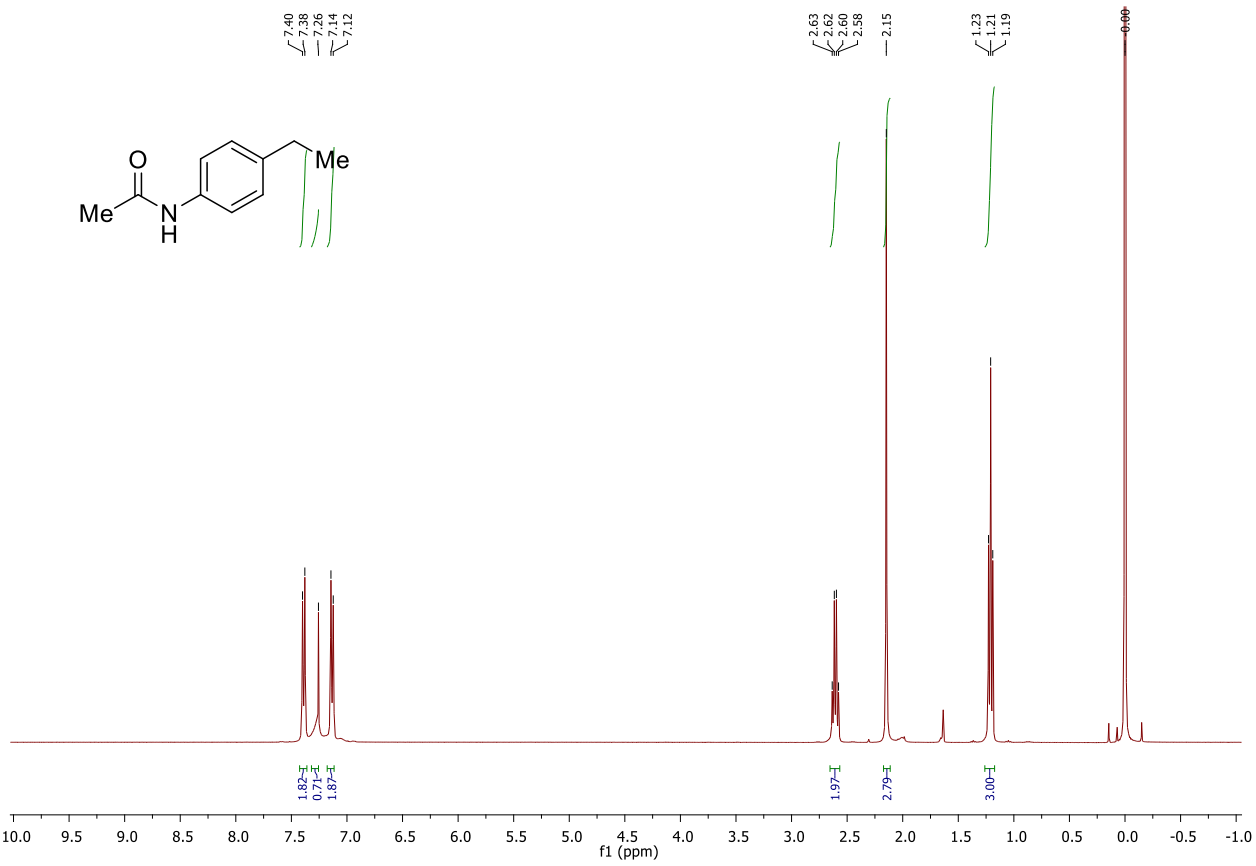
Protection of Amines[6]



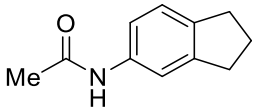
4-ethylaniline (1.21 g, 10 mmol, 1 eq) was added to a round-bottom flask. Then the flask was purged with argon and dry DCM (40 mL) was added. Acetic anhydride (1.14 mL, 12 mmol, 1.2 eq) was added and the reaction was stirred at room temperature and monitored by TLC. Upon completion, the reaction mixture was washed with a saturated solution of sodium carbonate, the organic layers dried with $MgSO_4$ and the solvent was removed under reduced pressure. Purification by column chromatography (ethyl acetate/petroleum ether) afforded the product.



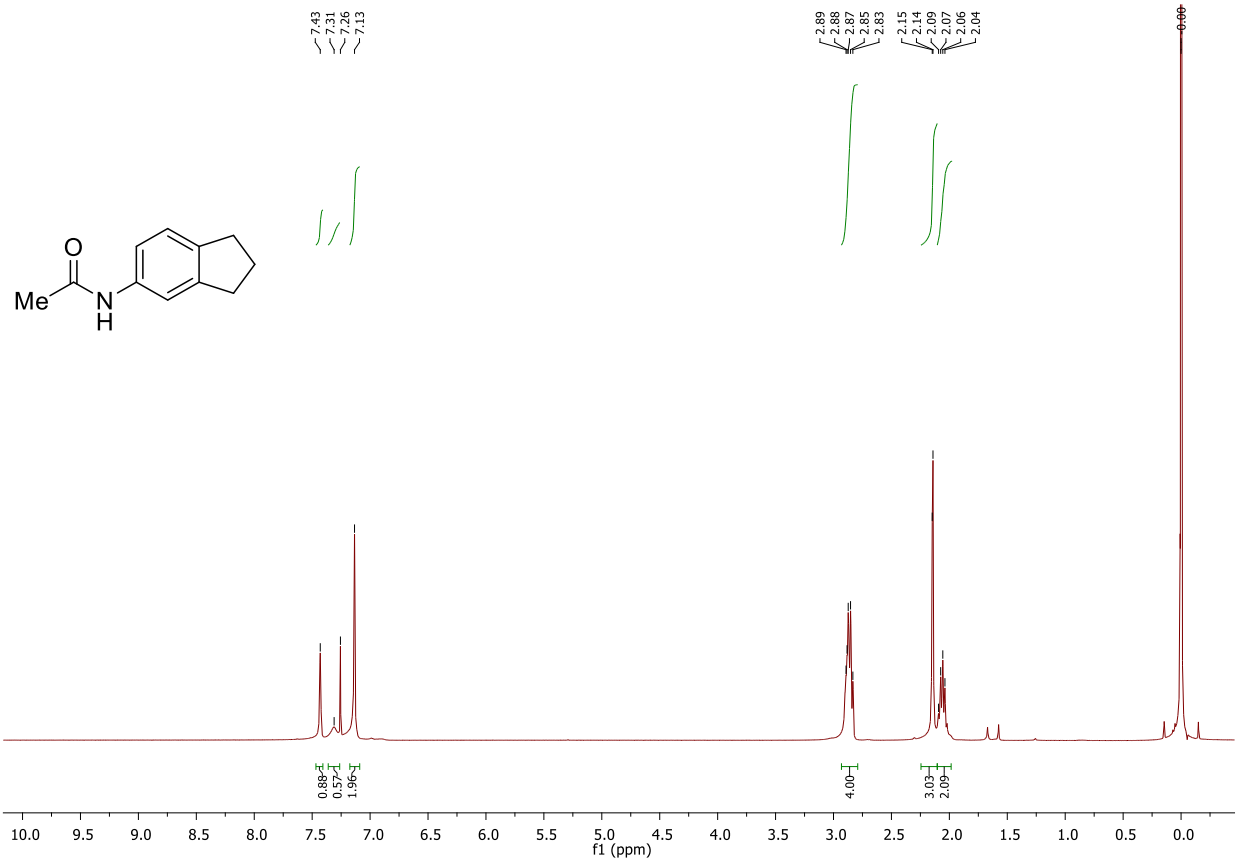
***N*-(4-ethylphenyl)acetamide (S9), ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.3 Hz, 2H), 7.26 (br-s, 1H), 7.13 (d, J = 8.3 Hz, 2H), 2.61 (q, J = 7.6 Hz, 2H), 2.15 (s, 3H), 1.21 (t, J = 7.6 Hz, 3H); **MS (TLC-MS):** m/z $[M+Na]^+$: 186. Spectral data were consistent with the previously reported one.[6]



^{1}H NMR spectrum in $CDCl_3$.

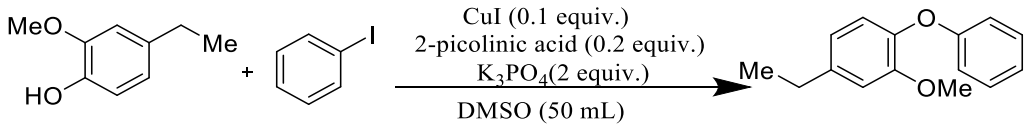


***N*-(2,3-dihydro-1H-inden-5-yl)acetamide (S10)**, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (br-s, 1H), 7.31 (b, 1H), 7.13 (s, 2H), 2.92 – 2.80 (m, 4H), 2.14 (d, J = 2.6 Hz, 3H), 2.08 – 2.02 (m, 2H). **MS (TLC-MS):** m/z $[M+Na]^+$:198. Spectral data were consistent with the previously reported one.[6]

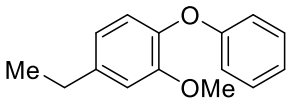


^{1}H NMR spectrum in $CDCl_3$.

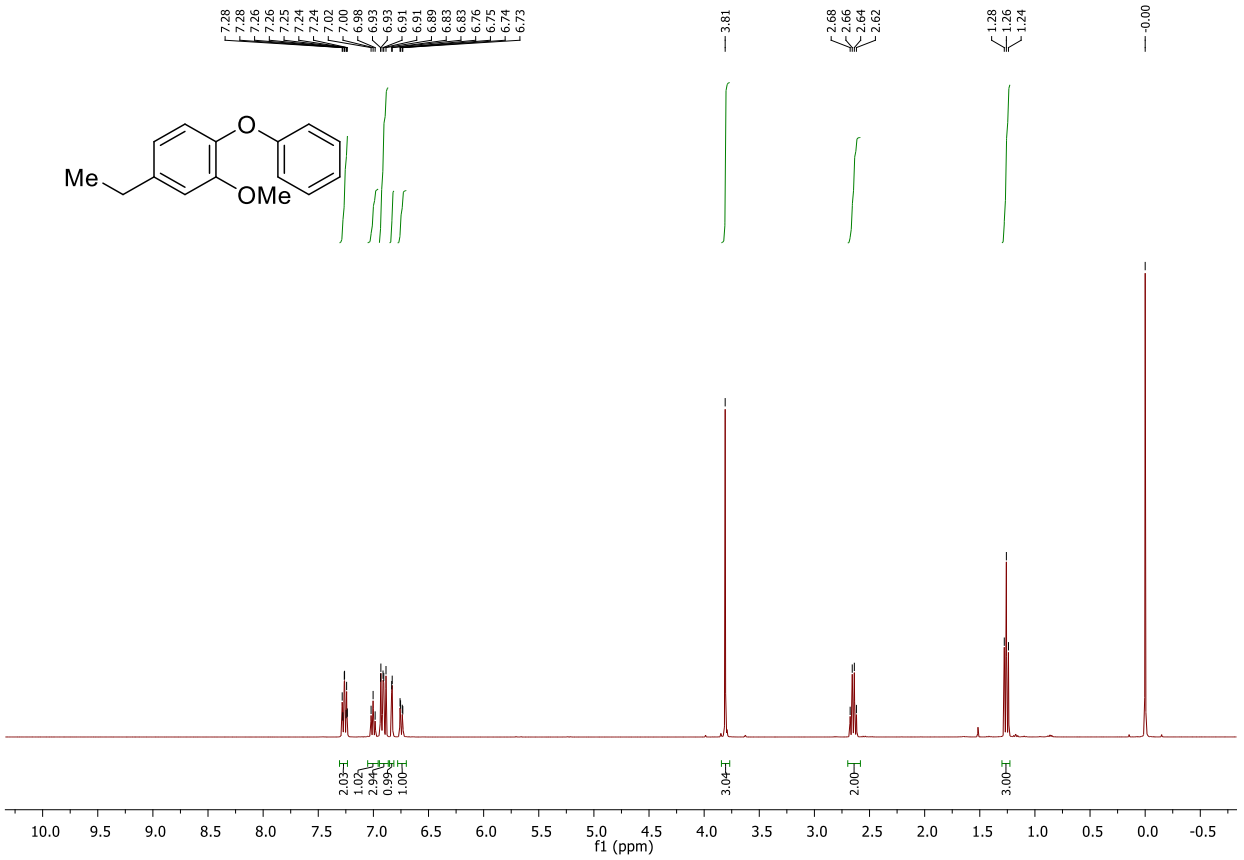
Phenoxy Group Protection



Under a flow of N_2, to an oven-dried 250 mL Schlenk flask, CuI (395 mg, 2.07 mmol), 2-picolinic acid (595 mg, 4.83 mmol), phenyl iodide (4.08 g, 20.5 mmol), 4-ethyl-2-methoxyphenol (26.0 mmol), K_3PO_4 (8.65 g, 40.7 mmol), a magnetic stir bar, and anhydrous DMSO (50 mL) were added. The reaction was heated at 100 ºC for 24 h under N_2 atmosphere. The reaction mixture was cooled to room temperature and diluted with dichloromethane (DCM) (150 mL) and transferred to a separatory funnel (500 mL). The organic mixture was washed with saturated NH_4Cl (aq) (100 mL x 3). The organic layer was collected and dried over anhydrous magnesium sulfate. The magnesium sulfate was filtered off on a glass frit. All volatiles were removed from the filtrate. The crude product was absorbed onto silica gel and purified by flash column chromatography.[7]

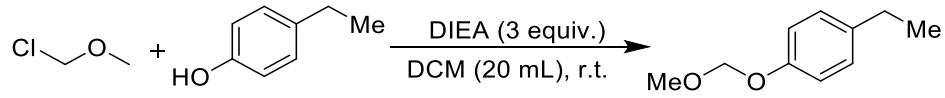


4-Ethyl-2-methoxy-1-phenoxybenzene (S12) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.00 (t, J = 7.4 Hz, 1H), 6.95 – 6.87 (m, 3H), 6.83 (d, J = 1.8 Hz, 1H), 6.75 (dd, J = 8.1, 1.9 Hz, 1H), 3.81 (s, 3H), 2.65 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.6 Hz, 3H); **MS (TLC-MS) :** m/z [M+Na]$^+$: 251. Spectral data were consistent with the previously reported one.[7]

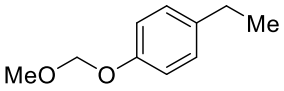


^{1}H NMR spectrum in $CDCl_3$.

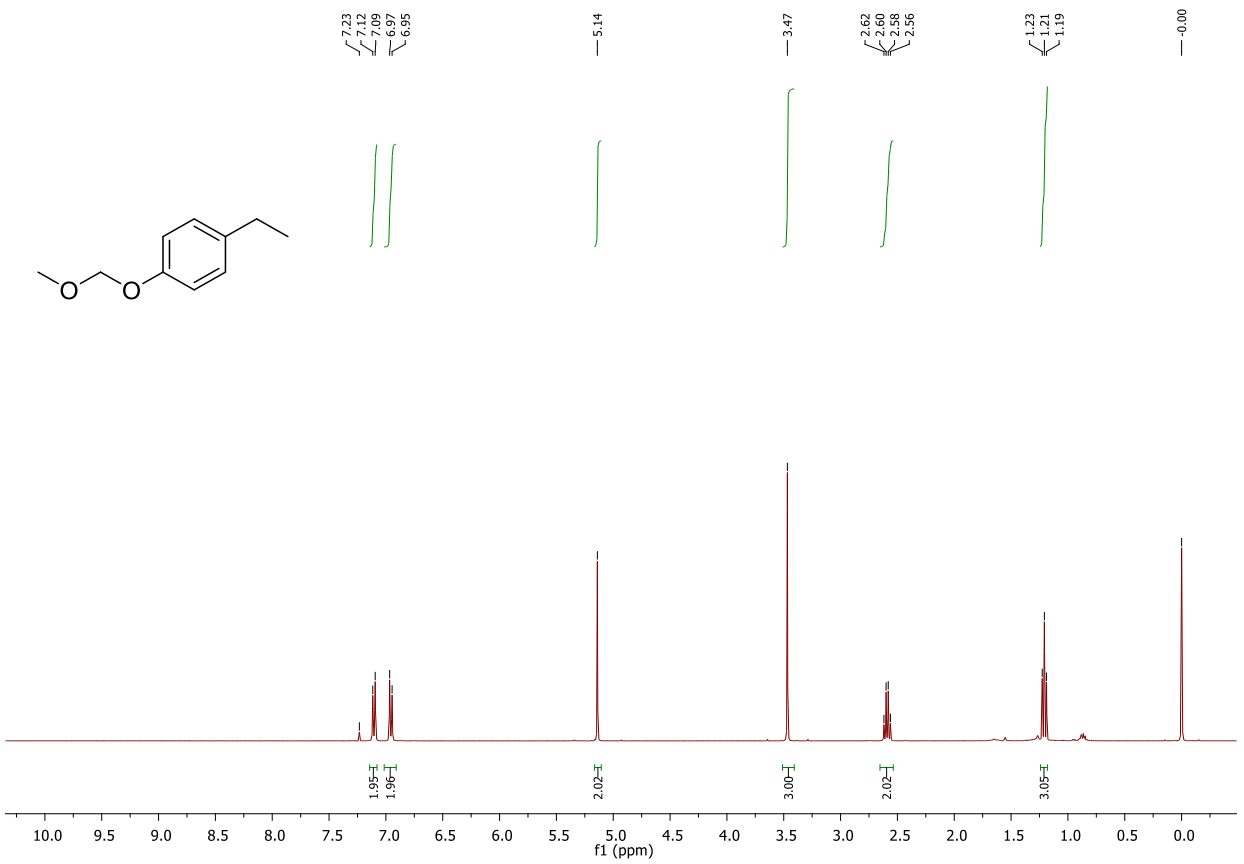
MOM Protection of Phenoxy Group



To a stirred solution of 4-ethylphenol (1.0 g, 8.19 mmol) in CH_2Cl_2(20 mL) at room temperature, DIEA (2.139 mL, 12.28 mmol) and MOMCl (0.311 mL, 4.09 mmol) over a 10 min period were successively added. The solution was stirred 11 h at room temperature after which a saturated aqueous NH_4Cl solution (5 mL) was added. The aqueous phase was segregated, and the organic one was washed with water (10 mL), brine (10 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated to give pure MOM ether in 90% yield (slightly yellowish oil).[8]

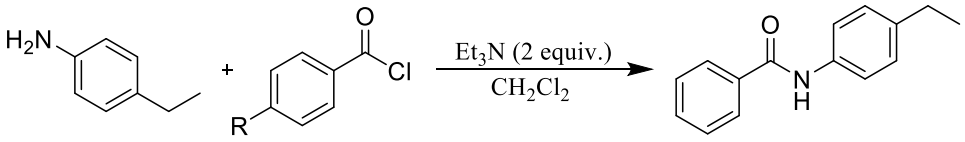


1-Ethyl-4-(methoxymethoxy)benzene (S13), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 5.14 (s, 2H), 3.47 (s, 3H), 2.59 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H). **MS (TLC-MS):** m/z $[M+Na]^+$: 189. Spectral data were consistent with those reported previously.[8]

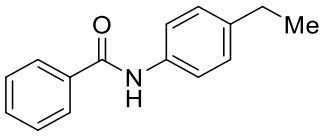


^{1}H NMR spectrum in $CDCl_3$.

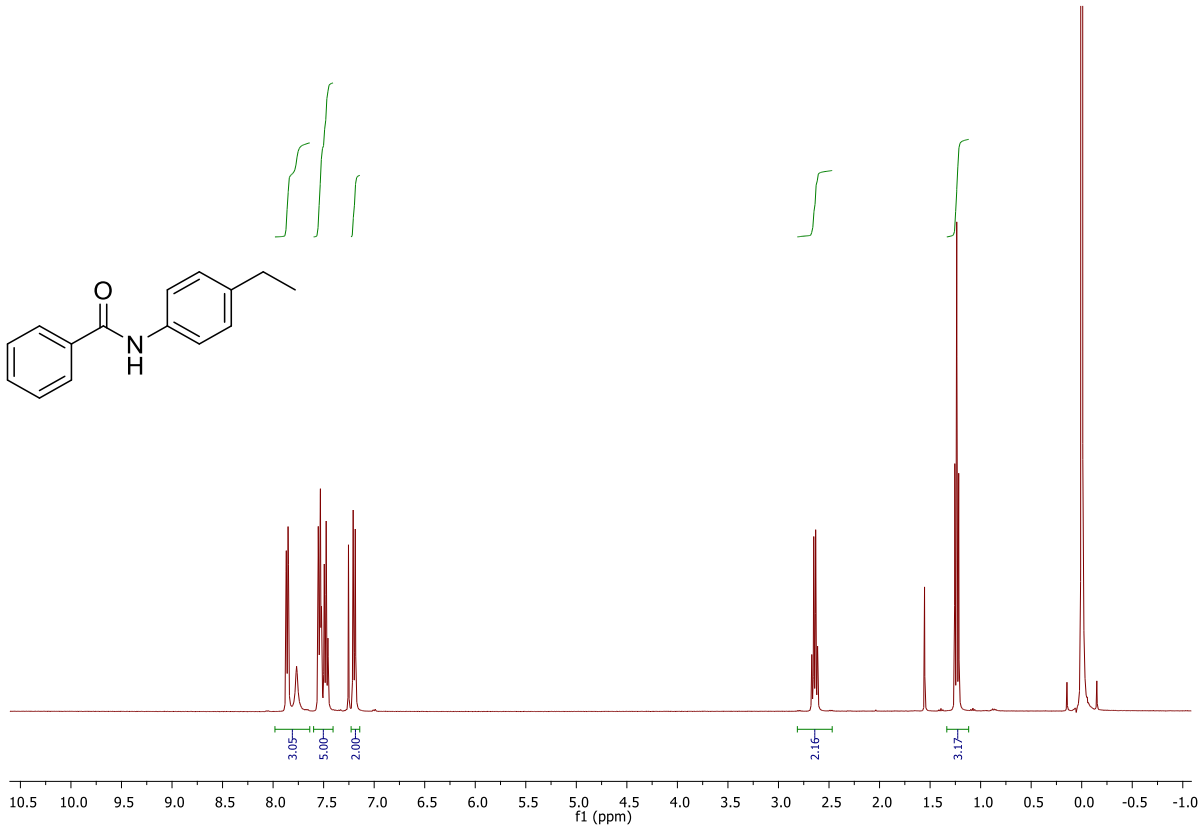
Synthesis of Amides



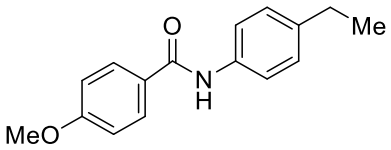
To a solution of 4-ethylaniline and Et_3N (2.0 equiv.) in CH_2Cl_2, benzoyl chloride (1.1 equiv) at 0 °C was added. After addition, the mixture was stirred at room temperature until TLC indicating 4-ethylaniline disappeared. The suspension was poured into H_2O and extracted with ethyl acetate (20 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo.* The crude material was purified by flash column chromatography to give desired amide products.[10]



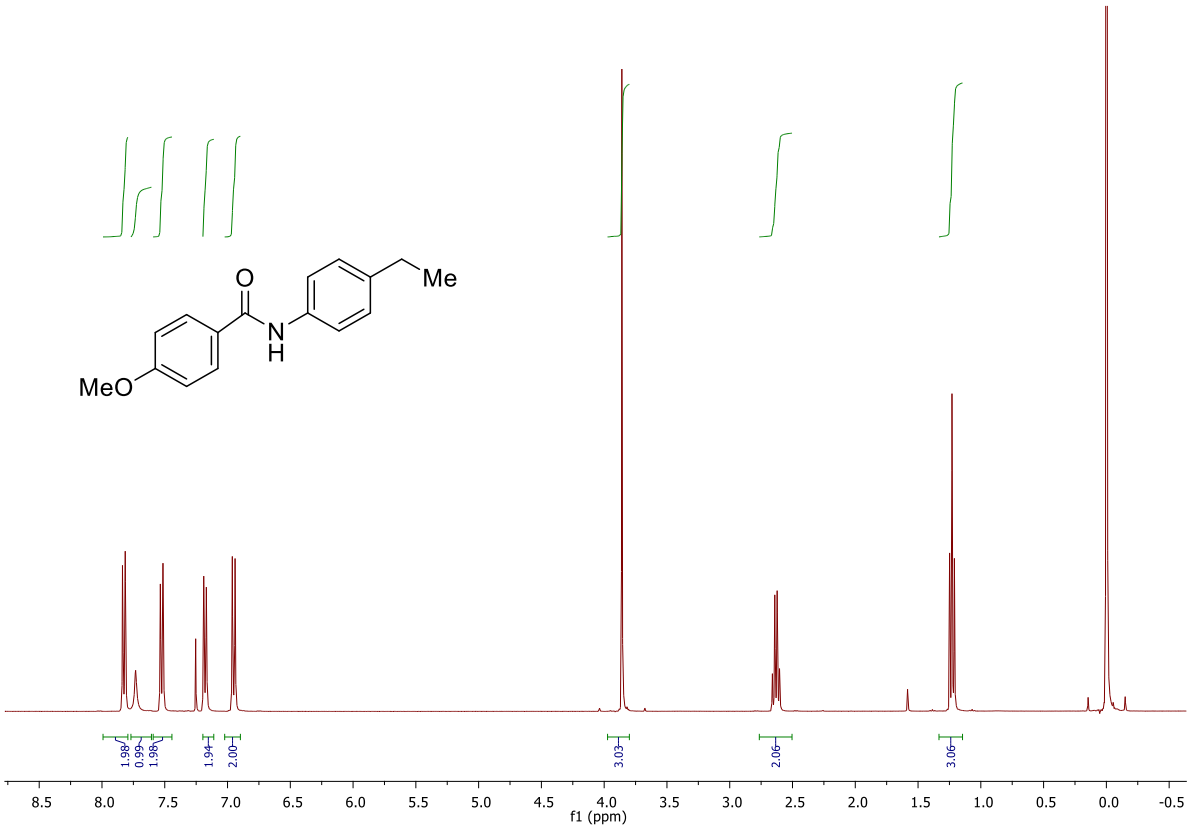
***N*-(4-ethylphenyl)benzamide (S14)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 2H), 7.77 (s, 1H), 7.51 (ddd, J = 25.6, 11.5, 6.4 Hz, 5H), 7.20 (d, J = 8.4 Hz, 2H), 2.64 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H). **MS (TLC-MS):** m/z $[M+Na]^+$: 248. Spectral data were consistent with the previously reported one.[10]



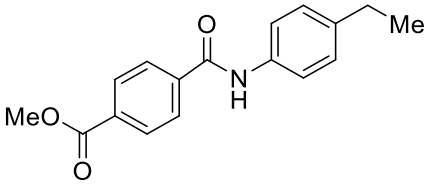
^{1}H NMR spectrum in $CDCl_3$.



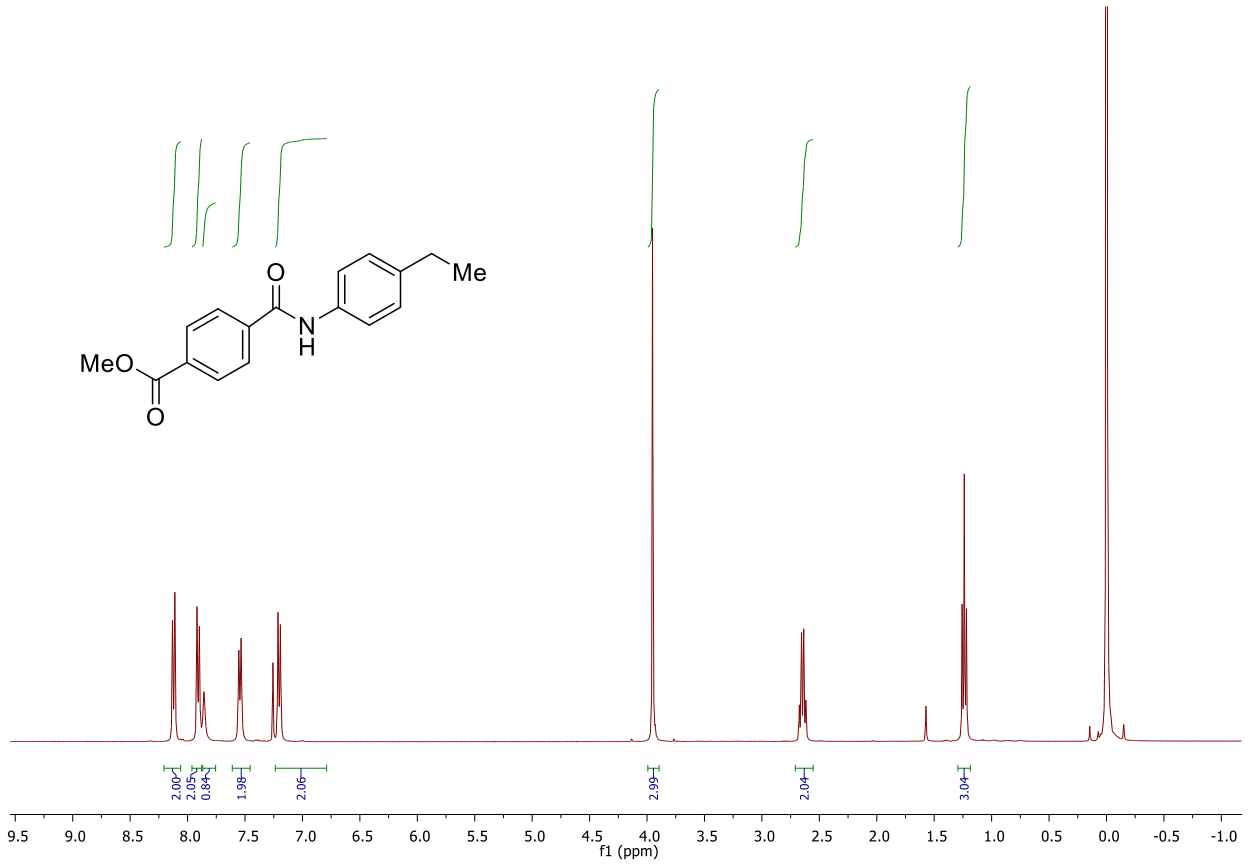
***N*-(4-ethylphenyl)-4-methoxybenzamide (S15)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 37.5 Hz, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 2.63 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.6 Hz, 3H). **MS (TLC-MS):** m/z $[M+Na]^+$: 278.



^{1}H NMR spectrum in $CDCl_3$.

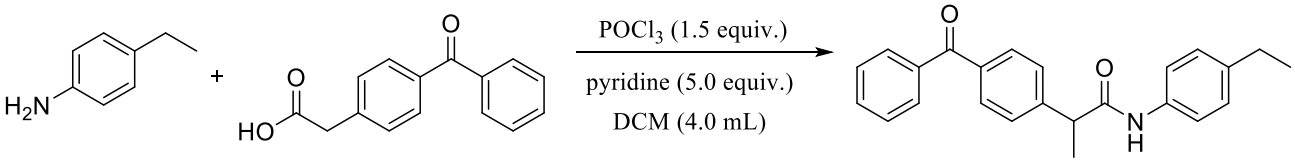


Methyl 4-((4-ethylphenyl)carbamoyl)benzoate (S16), ^{1}H NMR (400 MHz, $CDCl_3$) δ7.90 (t, J = 9.4 Hz, 2H), 7.91 (d, J = 8.2 Hz, 2H), 7.86 (s, 1H), 7.54 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 3.95 (s, 3H), 2.65 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H). **MS (TLC-MS):** m/z $[M+Na]^+$: 306.

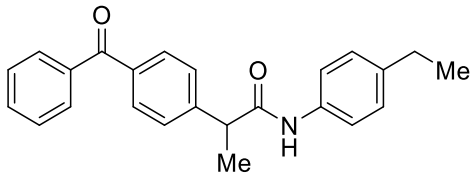


^{1}H NMR spectrum in $CDCl_3$.

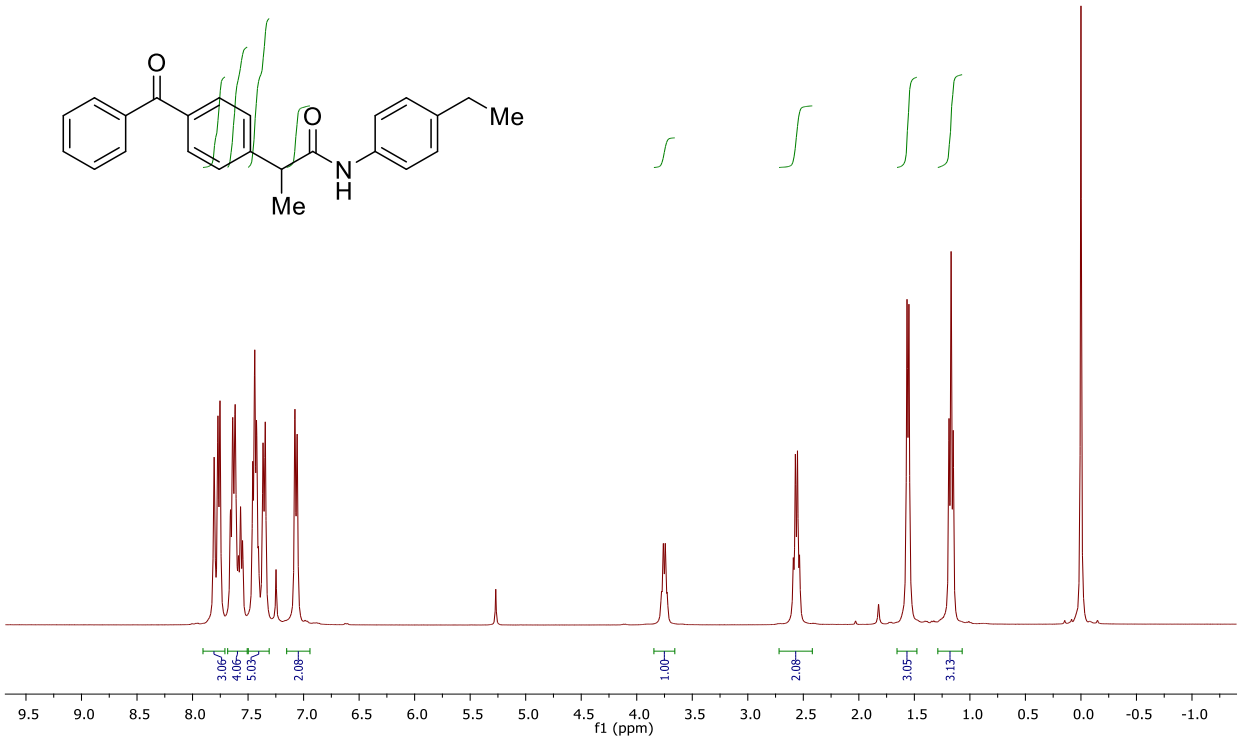
Carboxylic acids protection



To a round bottom flask containing a stirring bar under an atmosphere of argon was added the appropriate carboxylic acid (4 mmol, 1.017g, 1 equiv.) and 4-ethylaniline (6.0 mmol, 0.746 mL, 1.5 equiv.) followed by dichloromethane (4.0 mL) and pyridine (5 equiv.). Phosphoryl chloride (0.559 mL, 1.5 equiv.) was then added slowly to avoid the generation of excess heat. The resulting mixture was stirred at room temperature for 30 mins, before being quenched with water. The layers were separated, and the aqueous solution was extracted with CH_2Cl_2. The combined organic layers were then washed with sat. aq. NH_4Cl and sat. aq. $NaHCO_3$, dried over anhydrous $MgSO_4$, filtered and evaporated. Purification was carried out using an automated flash chromatography system.[11]



2-(4-Benzoylphenyl)-*N*-(4-ethylphenyl)propanamide (**S18**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.69 – 7.48 (m, 4H), 7.49 – 7.30 (m, 5H), 7.04 (t, *J* = 18.5 Hz, 2H), 3.75 (dd, *J* = 13.5, 6.6 Hz, 1H), 2.56 (q, *J* = 7.4 Hz, 2H), 1.56 (d, *J* = 6.9 Hz, 3H), 1.17 (t, *J* = 7.5 Hz, 3H). **MS (TLC-MS):** m/z $[M+Na]^+$: 380.



^{1}H NMR spectrum in $CDCl_3$.

7. Mechanistic investigations

Intermediate investigation

A dry 10 mL reaction tube containing a stirring bar was charged with 0.40 mmol of benzoic acid (2.0 equiv.), 0.3 mmol of CBr_4 (1.5 equiv.), 0.6 mmol of K_2HPO_4 (3.0 equiv.) and 1 mol% of catalyst. After purging the flask for three times under vacuum and three times under nitrogen. Finally dry acetonitrile (1.0 mL) was added. The resulting mixture was stirred for 0.5 h under 40W Kessil lamp reaction setup. Then the benzylic substrate was added into the reaction mixture and kept for 2.5 h under Kessil reaction setup. Then the resulting mixture underwent an aqueous workup (using distilled water; or brine in case of slurry phase separation) and was extracted three times with ethyl acetate. The combined organic layers were dried and measured by NMR using 1,3,5-trimethoxybenzene as an internal standard. From the NMR of the crude reaction mixture. There was no formation of brominated product which was basically 1-(1-bromoethyl)-4-methoxybenzene (**Figure S4-5**). However, in the esterification with primary benzylic substrate (4-methylanisole), there was a brominated intermediate which meant it involved the other pathway (**Figure S6**).

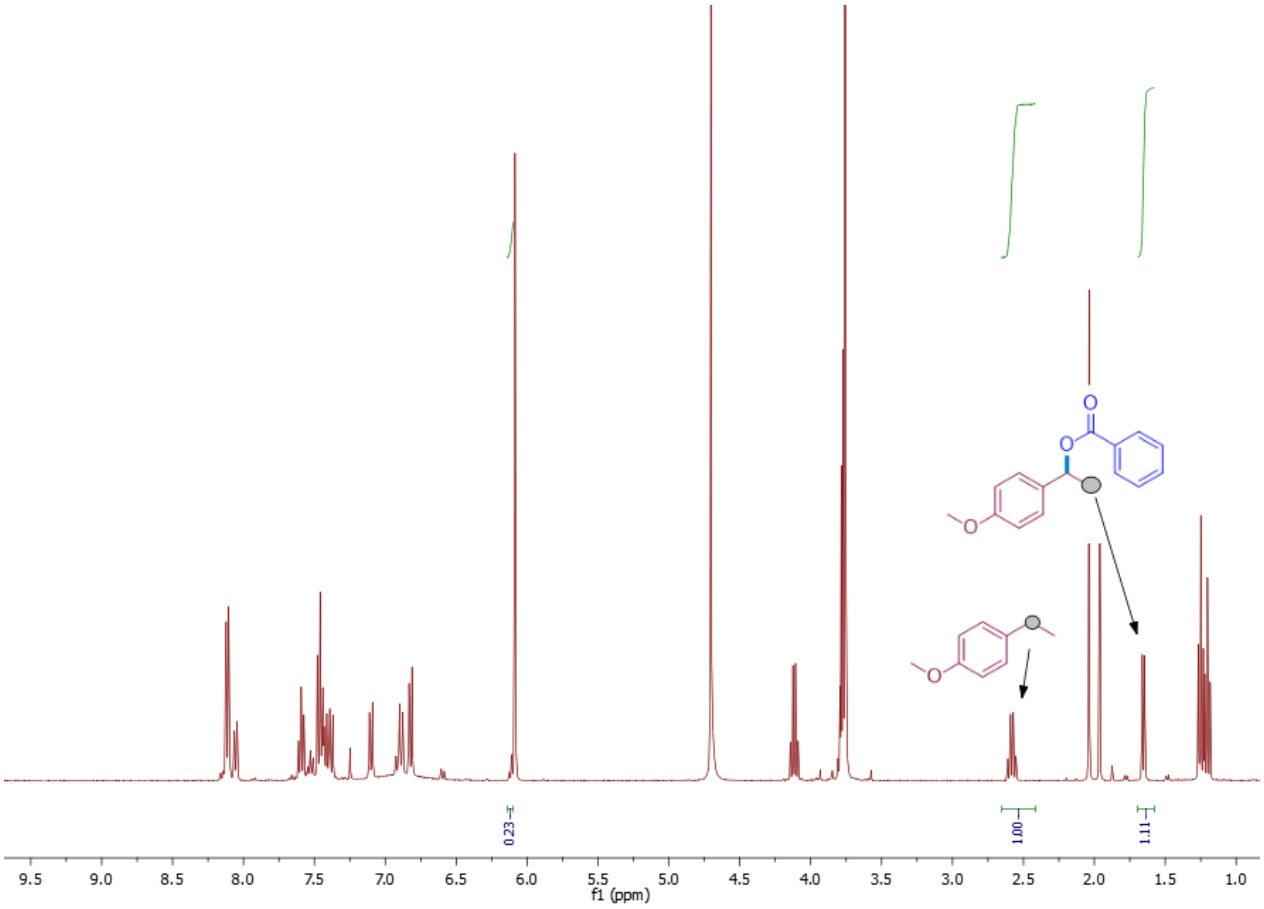


Figure S4: Reaction mixture after 2.5 h irradiation.

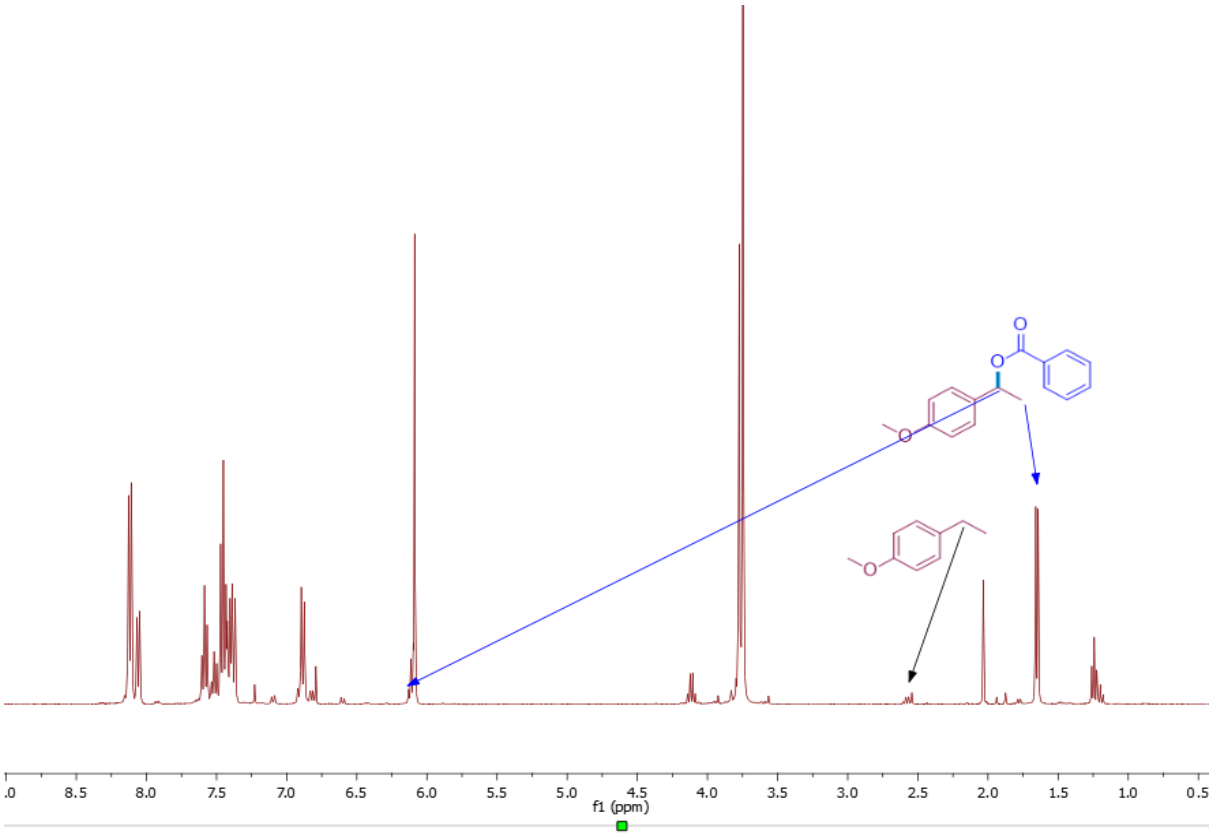


Figure S5: Reaction mixture after 5 h irradiation.

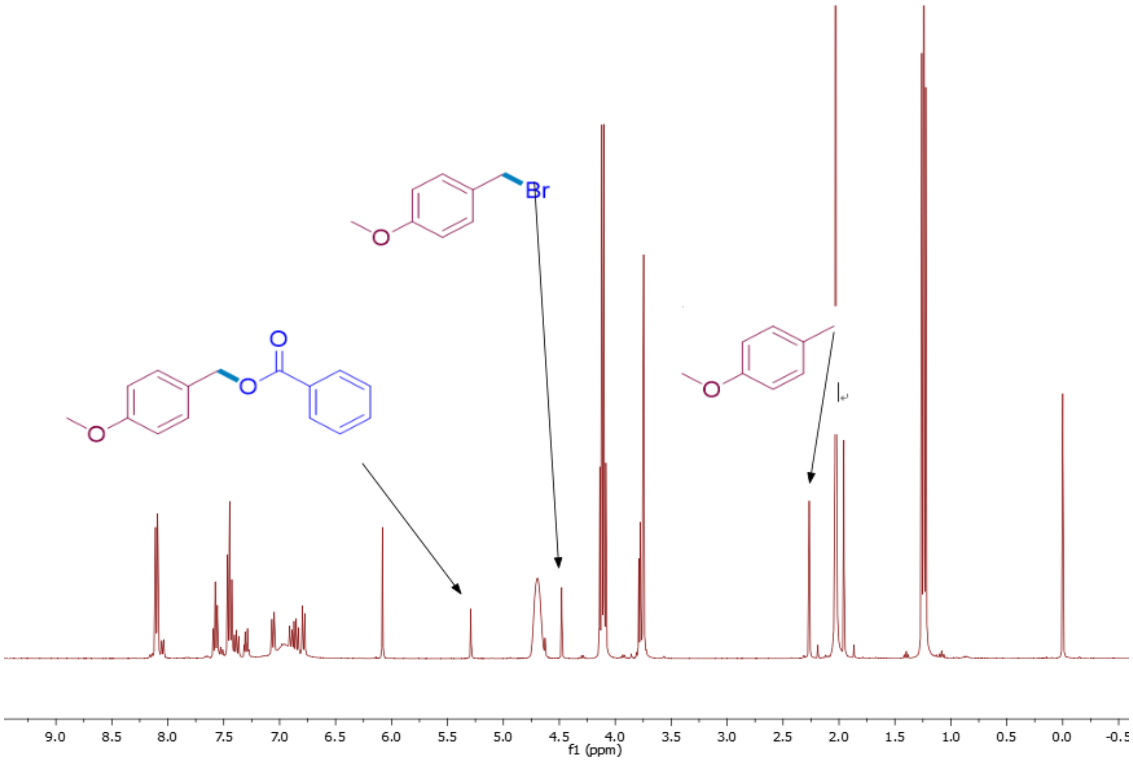
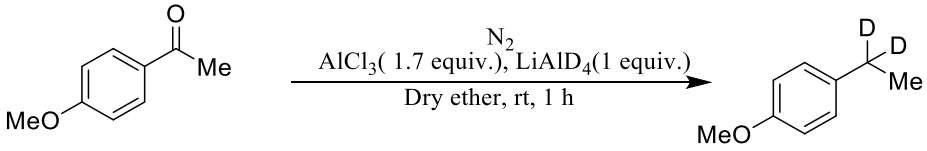


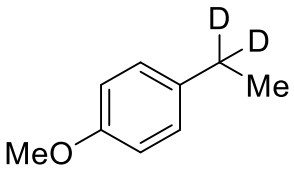
Figure S6: Reaction using 4-Methylanisole as benzylic substrate.

KIE experiment

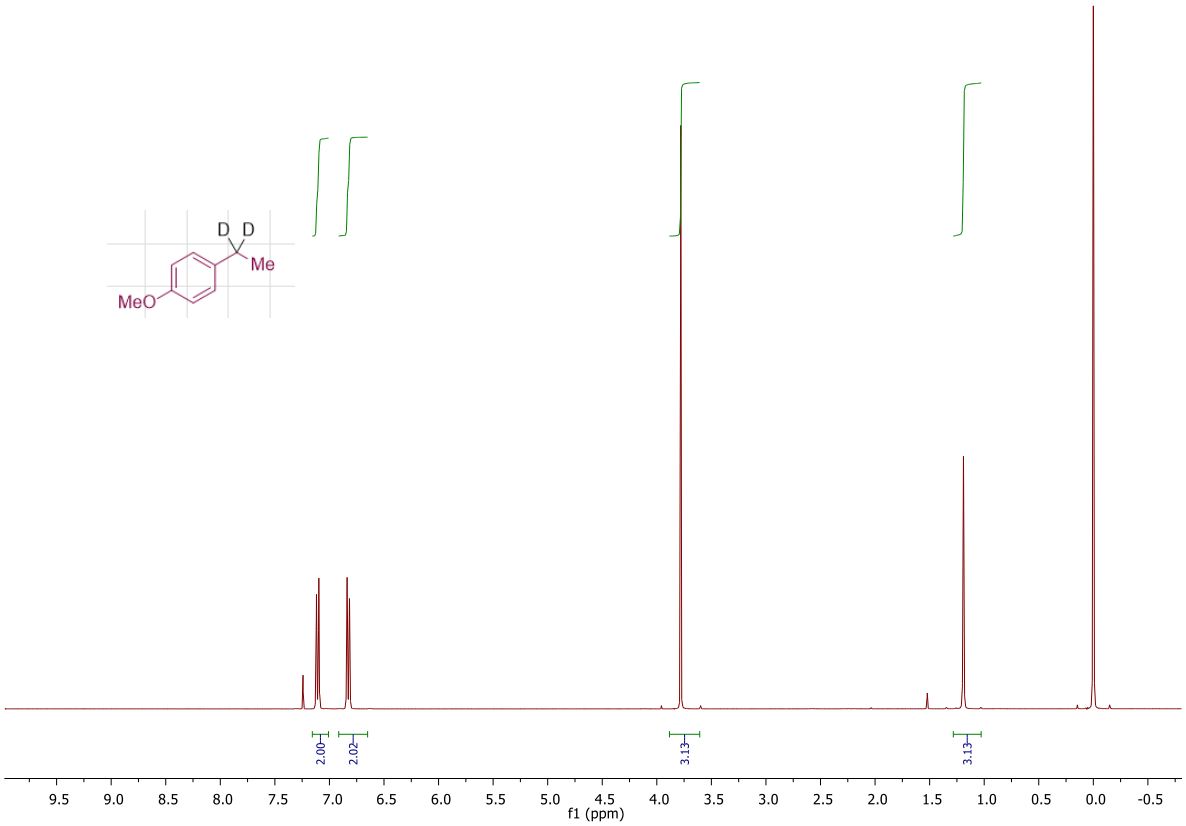
Synthesis of labelling substrate



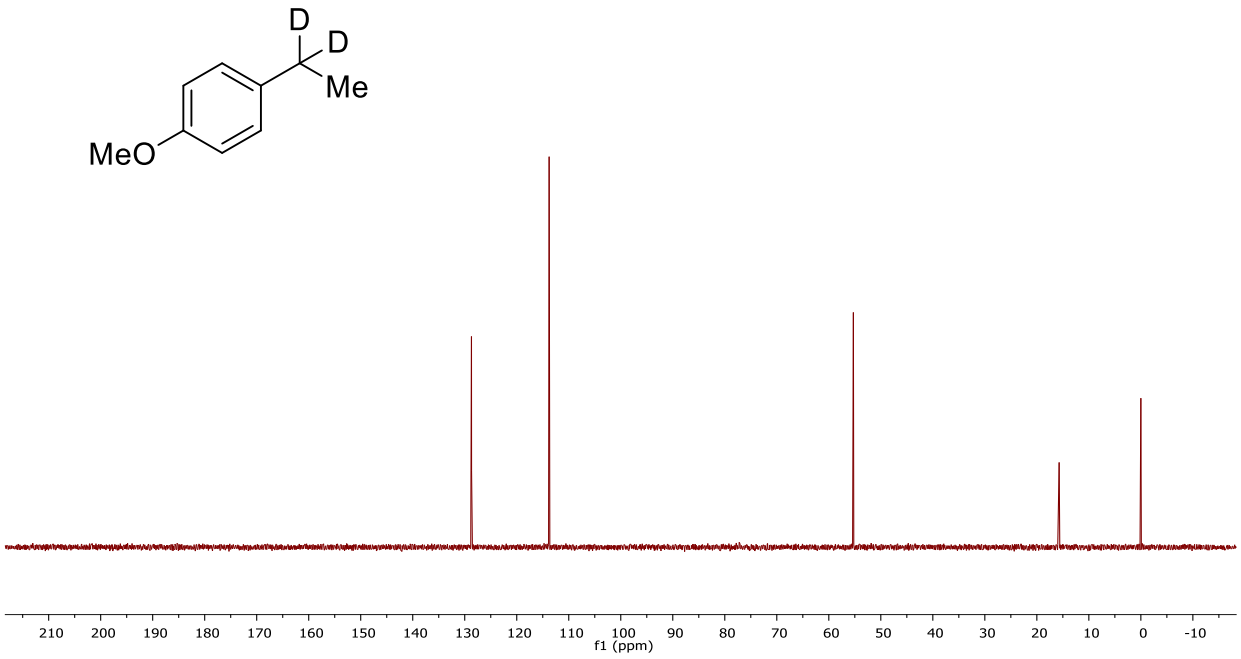
Following a reported procedure, a flame-dried vial was charged with water free $AlCl_3$ (453 mg, 3.4 mmol, 1.77equiv.) and lithium aluminum deuteride (84.0mg, 2.00 mmol, 1.0 equiv.) under nitrogen atmosphere. The mixture was carefully suspended in dry ether (8 mL). 1-(4-methoxyphenyl)ethan-1-one (300 mg, 2.0 mmol, 1.0 equiv.) was carefully added as solid (violent reaction) to the suspension. The mixture was stirred for 1 h at room temperature, diluted with ether (20 mL) and quenched by the addition of aqueous HCl (1 M). The phases where separated, and the aqueous phase was extracted with ether (3 x 10 mL). The organic phase was dried over sodium sulfate, filtered, and concentrated. After automated column chromatography (10 g SiO_2, pentane) the title compound was obtained as a white solid (268 mg, 1.45 mmol, 73% yield).[12]



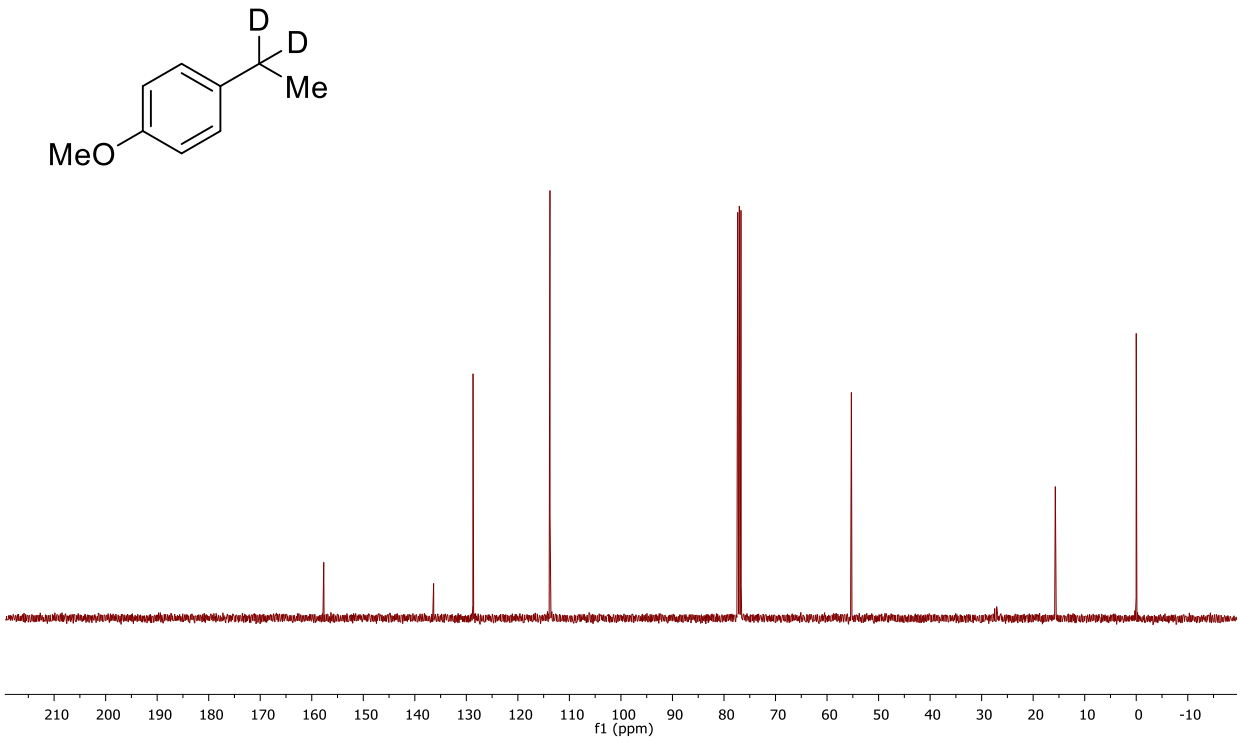
1-(ethyl-1,1-*d*$_2$)-4-methoxybenzene (S17). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 1.19 (s, 3H). **MS (TLC-MS):** m/z $[M+Na]^+$: 161.



^{1}H NMR spectrum in $CDCl_3$.



DEPT spectrum in $CDCl_3$.



^{13}C NMR spectrum in $CDCl_3$.

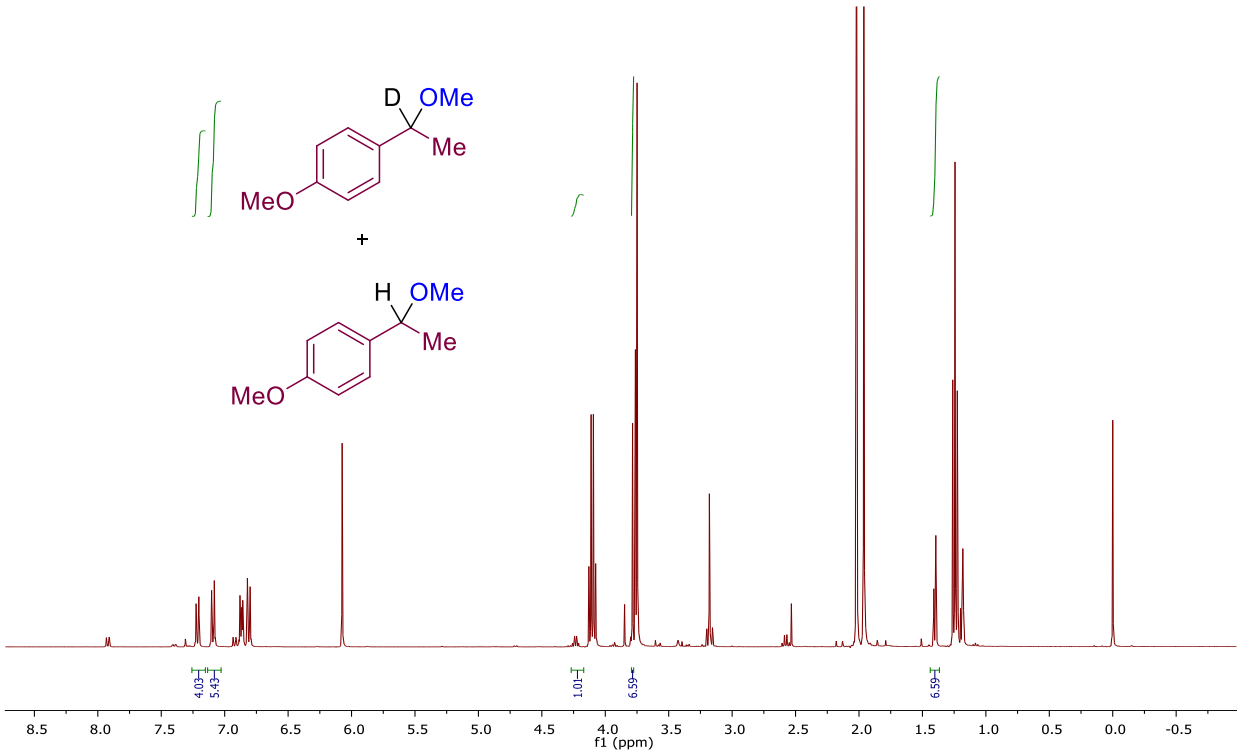


Figure S7: Spectrum of KIE experiment.

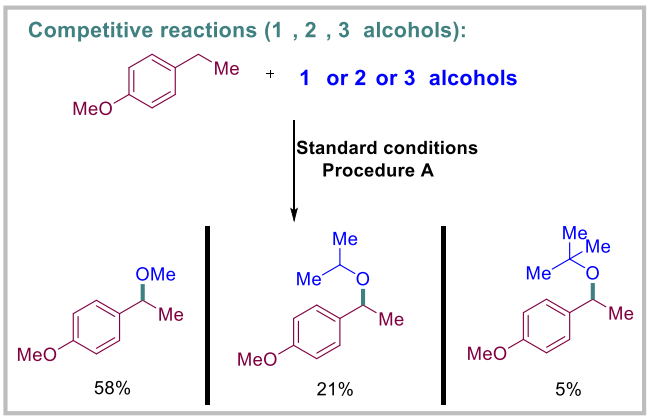
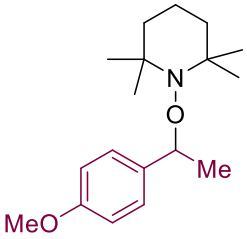


Figure S8: Competitive reactions.

HRMS of TEMPO with benzylic radical generated from 4-Ethyl anisole under the standard reaction conditions



The samples were used as delivered or acidified with 0.1% of formic acid. 10µl sample was infused using a gold coated borosilicate tapered needle. The needle was mounted in the nano-ESI source (Waters, Manchester, UK) and electrosprayed using an electrospray voltage delivering a stable spray (approx. 2 kV). Positive ion mode accurate mass spectra were acquired using a Q-TOF II instrument (Waters, Manchester, UK). The MS was calibrated prior to use with a 0.1% H_3PO_4 solution.

The spectra were lock mass corrected using the know mass of the nearest H_3PO_4 cluster or a known (background) ion.

Analytes were detected as protonated and/or sodiated molecule unless stated otherwise. The measured masses, best fitting elemental composition and corresponding calculated monoisotopic masses are given in the spectra. All the measured masses were within a difference of 5 ppm compared to the calculated mass unless specified otherwise. The presented MS data did allow to calculate the elemental composition of the analytes, but did not decide on structure or purity of the samples.

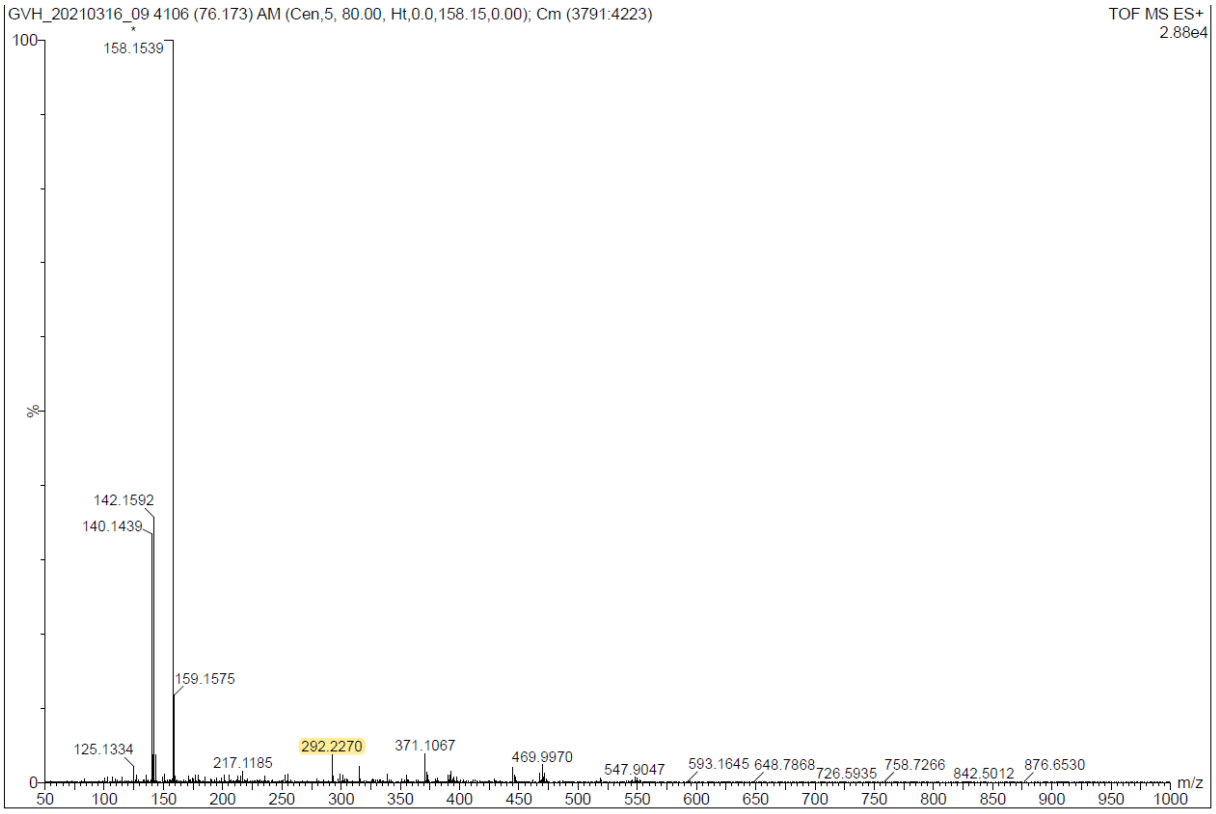


Figure S9: The HRMS spectra of TEMPO with benzyl radical.

Fluorescence quenching experiments

Stern-Volmer Emission Quenching Experiment: A quartz cuvette was charged with a 1 x 10^{-4} M solution of Mes-Acr+ -Me ClO4 – in dry MeCN (volume = 1 mL) and the initial fluorescence emission was measured. Then new samples were prepared by mixing Mes-Acr+ -MeClO4 – (1 x 10^{-4} M) and a known amount of 4-ethylanisole (**1a**, 0.001 M, 0.005 M, 0.01 M, 0.1 M) in MeCN (total volume = 1 mL). All samples were prepared in 1.4 mL quartz cuvettes capped with a rubber septum under N_2 atmosphere (all samples were prepared inside a nitrogen-filled glove box). The fluorescence emission of the samples was collected (an excitation beam with λex = 420 nm is employed) and the results are presented in **Figure S10**. A Stern-Volmer plot was generated for the quenching of the fluorescence of 9-mesityl-10-methylacridinium perchlorate with **1a** delivering a Stern-Volmer constant (K_q) of 109.23 (**Figure S11)**. Additionally, **Figure S12** indicates a similar quenching effect of the fluorescence intensity of 9-mesityl10-methylacridinium perchlorate in presence of other reagents like CBr4, Benzoic acid, Methanol and K_2HPO_4 and confirm that they have no involvement in the quenching of fluoroscence intensity of the catalyst.

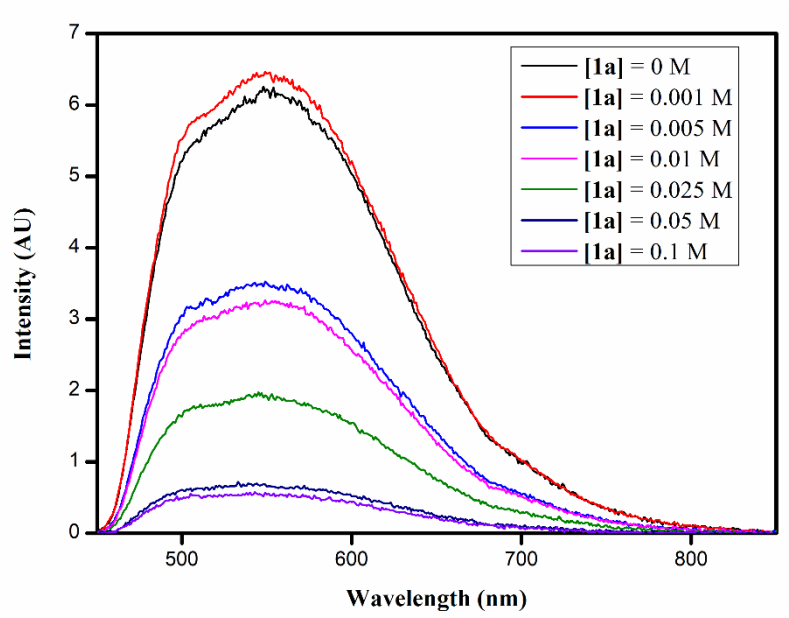


Figure S10: Fluorescence emission spectrum of Mes-Acr+ -Me ClO_4 – (1 x 10^{-4} M) in acetonitrile in the absence (**1a**, 0 M) (black line) and presence of various concentrations of 4-ethylanisole (**1a**). The fluorescence spectral intensities were uncorrected and an excitation beam with λex = 420 nm is employed.

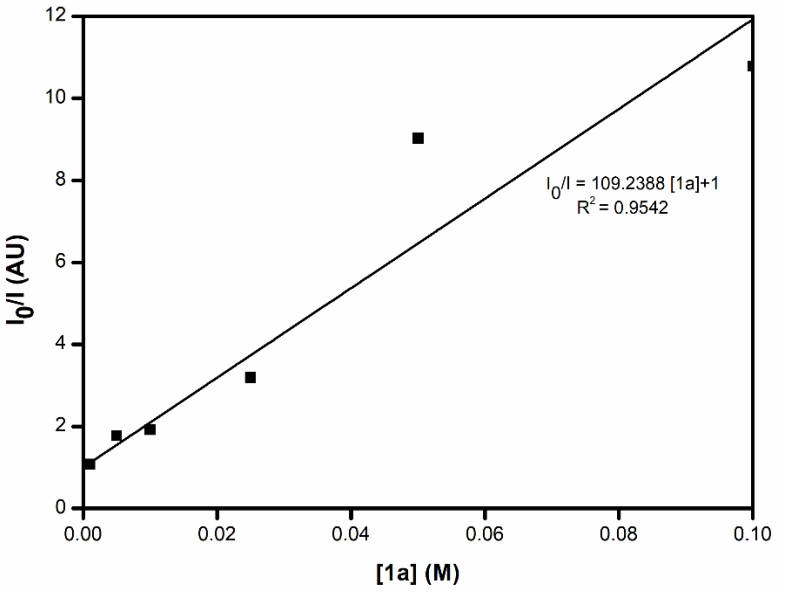


Figure S11: Stern-Volmer plot for the fluorescence quenching of 9-mesityl-10-methylacridinium perchlorate by **1a** in acetonitrile.

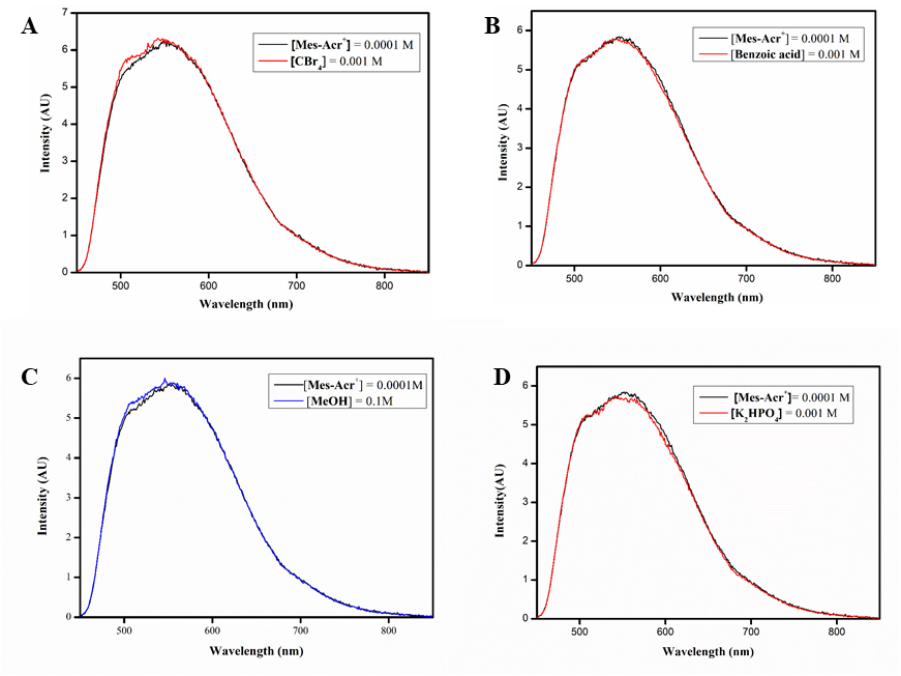


Figure S12: Fluorescence emission spectrum of Mes-Acr+ -Me ClO_4 – (1 x 10^{-4} M) in acetonitrile in the presence of CBr_4 (**A**), MeOH (**B**), Benzoic acid (**C**), and K_2HPO_4 (**D**). The fluorescence spectral intensities were uncorrected and an excitation beam with λex = 420 nm is employed.

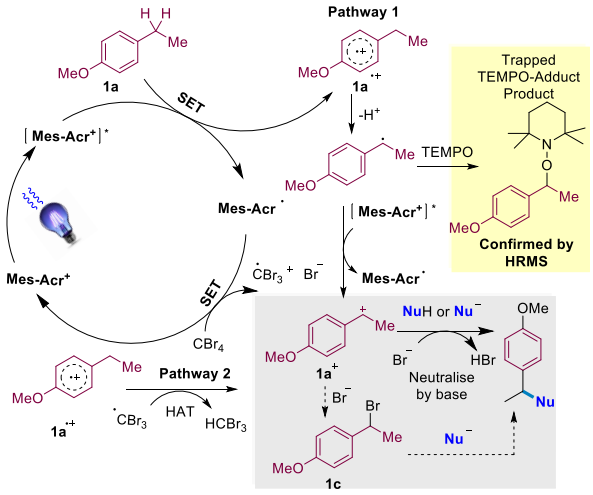
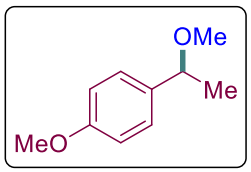


Figure S13: Proposed mechanism

8. Characterization data

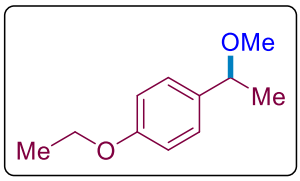


1-Methoxy-4-(1-methoxyethyl)benzene (1c):

Prepared according to the general procedure **A** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), methanol (0.03 ml, 0.74 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 ml), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 5% ethyl acetate). (Reaction time: 3 h; colorless liquid, isolated yield: 57%, 18.9 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 4.25 (q, J = 6.4 Hz, 1H), 3.80 (s, 3H), 3.19 (s, 3H), 1.42 (d, J = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1, 135.6, 127.4, 113.8, 79.1, 56.2, 55.3, 23.8.

MS (TLC-MS): m/z [M+Na]$^+$: 189. Spectral data were consistent with the previously reported one.[13]

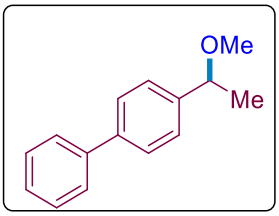


1-Ethoxy-4-(1-methoxyethyl)benzene (2c):

Prepared according to the general procedure **A** using 4-ethylphenetole (30.4 mg, 0.20 mmol), methanol (0.03 ml, 0.74 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 ml), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 5% ethyl acetate). (Reaction time: 3 h; colorless liquid, isolated yield: 50%, 18.0 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 4.24 (q, J = 6.4 Hz, 1H), 4.03 (q, J = 7.0 Hz, 2H), 3.19 (s, 3H), 1.41 (t, J = 7.0 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 135.4, 127.4, 114.4, 79.2, 77.3, 77.0, 76.7, 63.4, 56.2, 23.7, 14.9.

HRMS (ESI) [M+Na]$^+$ calculated for [$C_{11}H_{16}O_2$] requires m/z 203.1042, found m/z 203.1051.



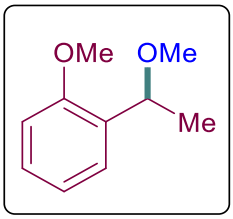
4-(1-Methoxyethyl)-1,1'-biphenyl (3c):

Prepared according to the modified procedure **A** using diphenylethyl (36.0 mg, 0.20 mmol), methanol (0.05 mL, 1.2 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), $CBrCl_3$ (0.03 mL, 0.30 mmol),

nitromethane (1.0 ml), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 5% ethyl acetate); (reaction time: 40 h; colorless liquid, isolated yield: 44%, 18.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 4H), 7.48 – 7.31 (m, 5H), 4.34 (q, *J* = 6.5 Hz, 1H), 3.27 (s, 3H), 1.47 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6, 141.0, 140.5, 128.8, 127.2, 127.1, 126.7, 79.4, 56.5, 23.8.

MS (TLC-MS): m/z $[M+Na]^+$: 235. Spectral data were consistent with the previously reported one.[14]

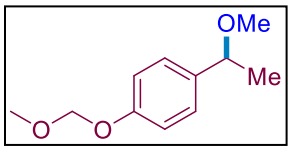


1-Methoxy-2-(1-methoxyethyl)benzene (4c):

Prepared according to the general procedure **A** using 2-ethyl-anisole (27.0 mg, 0.20 mmol), methanol (0.05 ml, 0.60 mmol), Mes-Acr$^+$-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 10% ethyl acetate). (Reaction time: 3 h; colorless liquid, isolated yield: 47%, 15.6 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.27 – 7.14 (m, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 4.75 (q, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 3.23 (s, 3H), 1.38 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 131.9, 128.0, 126.0, 120.8, 110.3, 73.3, 56.6, 55.3, 22.5.

MS (TLC-MS): m/z $[M+Na]^+$: 189. Spectral data were consistent with the previously reported one.[15]

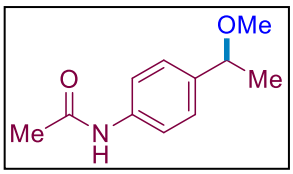


1-(1-Methoxyethyl)-4-(methoxymethoxy)benzene (5c):

Prepared according to the general procedure **A** using 1-ethyl-4-(methoxymethoxy)benzene (33.0 mg, 0.20 mmol), methanol (0.03 ml, 0.74 mmol), Mes-Acr$^+$-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 10% ethyl acetate). (Reaction time: 3 h; colorless liquid, isolated yield: 40%, 15.7 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 5.17 (s, 2H), 4.25 (q, J = 6.4 Hz, 1H), 3.48 (s, J = 3.9 Hz, 3H), 3.20 (s, 3H), 1.41 (d, J = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.7, 136.9, 127.4, 116.2, 94.6, 79.1, 56.3, 56.0, 23.8.

MS (TLC-MS): m/z $[M+Na]^+$: 219. Spectral data were consistent with the previously reported one.[13]

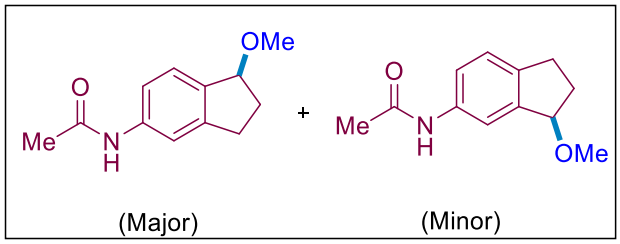


***N*-(4-(1-methoxyethyl)phenyl)acetamide (6c):**

Prepared according to the general procedure **A** using *N*-(4-ethylphenyl)acetamide (33.0 mg, 0.20 mmol), methanol (0.03 mL, 0.74 mmol), Mes-Acr^+-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 60% ethyl acetate); (Reaction time: 3 h; white solid, isolated yield: 55%, 21.24 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 9.0 Hz, 2H), 4.26 (q, *J* = 6.4 Hz, 1H), 3.20 (s, 3H), 2.16 (s, 3H), 1.41 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 139.5, 137.2, 126.9, 120.1, 79.2, 56.3, 24.5, 23.7.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{11}H_{15}NO_2]$ requires m/z 216.0994, found m/z 216.1001.

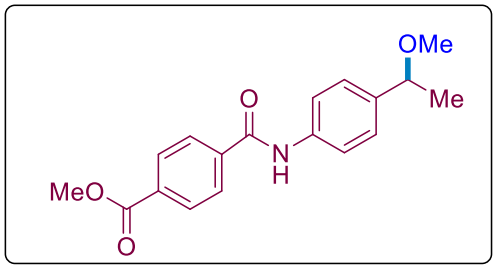


***N*-(1-methoxy-2,3-dihydro-1H-inden-5-yl)acetamide (7c):**

Prepared according to the modified procedure **A** using *N*-(2,3-dihydro-1H-inden-5-yl)acetamide (35.0 mg, 0.20 mmol), methanol (0.03 mL, 0.74 mmol), Mes-Acr^+-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), $CBrCl_3$ (0.03 mL, 0.30 mmol), nitromethane (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 60% ethyl acetate); (Reaction time: 32 h; white solid, isolated yield: 40%, 16.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.27 (m, 3H), 7.21 – 6.81 (m, 1H), 4.77 (dd, *J* = 6.3, 3.8 Hz, 1H), 3.39 (d, *J* = 5.4 Hz, 3H), 3.08 – 2.96 (m, 1H), 2.85 – 2.68 (m, 1H), 2.41 – 2.22 (m, 1H), 2.16 – 1.87 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 145.3, 143.5, 140.1, 138.6, 138.2, 136.3, 125.4, 125.1, 120.7, 118.2, 117.1, 116.5, 84.5, 84.1, 56.2, 55.9, 32.2, 32.1, 30.3, 29.7, 24.6.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{12}H_{15}NO_2]$ requires m/z 228.0994, found m/z 228.0997.

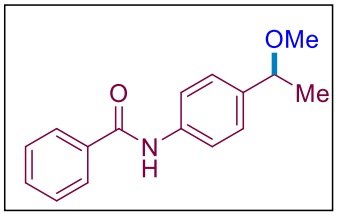


Methyl (S)-4-((4-(1-methoxyethyl)phenyl)carbamoyl)benzoate (8c):

Prepared according to the general procedure **A** using methyl 4-((4-ethylphenyl)carbamoyl)benzoate (56.6 mg, 0.20 mmol), methanol (0.05 mL, 1.2 mmol), Mes-Acr$^+$-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 60% ethyl acetate); (Reaction time: 4 h; white solid, isolated yield: 43%, 26.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 8.08 – 7.97 (m, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.29 (q, *J* = 6.4 Hz, 1H), 3.95 (s, 3H), 3.23 (s, 3H), 1.43 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 164.9, 140.3, 138.9, 136.9, 133.0, 130.0, 127.1, 127.0, 120.5, 79.2, 77.4, 77.0, 76.7, 56.4, 52.5, 23.8.

HRMS (ESI) $[M+H]^+$ calculated for $[C_{18}H_{19}NO_4]$ requires m/z 314.1387, found m/z 314.1375; $[M+Na]^+$ calculated for $[C_{18}H_{19}NO_4]$ requires m/z 336.1212, found m/z 336.1215.

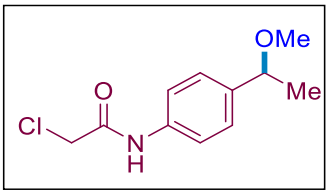


***N*-(4-(1-Methoxyethyl)phenyl)benzamide (9c):**

Prepared according to the general procedure **A** using N-(4-ethylphenyl)benzamide (45.0 mg, 0.20 mmol), methanol (0.03 mL, 0.74 mmol), Mes-Acr$^+$-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 60% ethyl acetate); (Reaction time: 3 h; white soild, isolated yield: 45%, 23.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.79 (m, 3H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.51 (m, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 4.29 (q, *J* = 6.4 Hz, 1H), 3.22 (s, 3H), 1.43 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 139.9, 137.2, 135.0, 131.8, 128.8, 127.0, 127.0, 120.4, 79.2, 56.4, 23.8.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{16}H_{17}NO_2]$ requires m/z 278.1151 found m/z 278.1157.

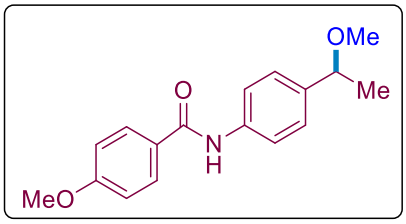


2-Chloro-*N*-(4-(1-methoxyethyl)phenyl)acetamide (10c):

Prepared according to general procedure **A** using2-chloro-N-(4-ethylphenyl)acetamide (40.0 mg, 0.20 mmol), methanol (0.05 mL, 1.2 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 60% ethyl acetate); (Reaction time: 7 h; white solid, isolated yield: 40%, 18.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.18 (br-s, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 4.28 (q, *J* = 6.4 Hz, 1H), 4.19 (s, 2H), 3.21 (s, 3H), 1.42 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.8, 140.7, 135.9, 127.0, 120.3, 79.1, 56.4, 42.9, 23.8.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{11}H_{14}NO_2Cl]$ requires m/z 250.0605, found m/z 250.0615

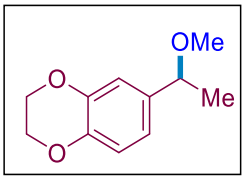


(*S*)-4-Methoxy-*N*-(4-(1-methoxyethyl)phenyl)benzamide (11c):

Prepared according to general procedure **A** using *N*-(4-ethylphenyl)-4-methoxybenzamide (50.1 mg, 0.20 mmol), methanol (0.03 mL, 0.74 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 60% ethyl acetate); (Reaction time: 3 h; white solid, isolated yield: 54%, 30.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.9 Hz, 3H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.28 (q, *J* = 6.4 Hz, 1H), 3.86 (s, 3H), 3.22 (s, 3H), 1.43 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3, 162.5, 139.6, 137.4, 128.9, 127.2, 126.9, 120.3, 114.0, 79.2, 56.4, 55.5, 23.8.

HRMS (ESI) $[M+H]^+$ calculated for $[C_{17}H_{19}NO_3]$ requires m/z 286.1438, found m/z 286.1432.

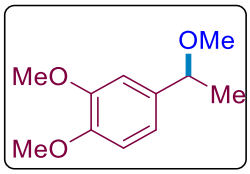


6-(1-Methoxyethyl)-2,3-dihydrobenzo[b][1,4]dioxine (12c):

Prepared according to general procedure **A** using 6-ethyl-2,3-dihydrobenzo[b][1,4]dioxine (33.0 mg, 0.20 mmol), methanol (0.03 mL, 0.74 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 60% ethyl acetate); (reaction time: 3 h; colorless liquid, isolated yield: 52%, 20.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 – 6.57 (m, 3H), 4.25 (s, 4H), 4.18 (q, J = 6.4 Hz, 1H), 3.20 (s, 3H), 1.40 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 142.9, 136.9, 119.3 117.1, 115.1 79.1, 77.3, 77.0, 76.7, 64.4, 64.4 56.3 23.8.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{17}H_{19}O_2F]$ requires m/z 217.0835, found m/z 217.0827.

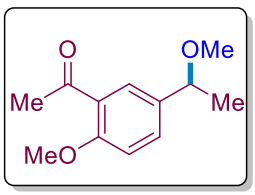


1,2-Dimethoxy-4-(1-methoxyethyl)benzene (13c):

Prepared according to general procedure **A** using 4-ethyl-1,2-dimethoxybenzene (33.2 mg, 0.20 mmol), methanol (19.0 mg, 0.025 ml, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 5% ethyl acetate). (reaction time: 3 h; colorless liquid, isolated yield: 50%, 19.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.83 (s, 2H), 4.24 (q, J = 6.4 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 1.43 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.3, 148.5, 136.2, 118.7, 111.0, 109.0, 79.4, 56.3, 55.9, 55.9, 23.8.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{11}H_{16}O_3]$ requires m/z 219.0991, found m/z 219.1012.

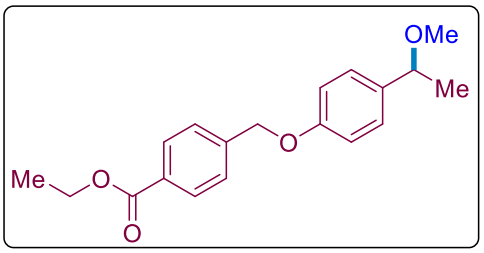


1-(2-Methoxy-5-(1-methoxyethyl)phenyl)ethan-1-one (14c):

Prepared according to general procedure **A** using 5-Ethyl-2-methoxyacetophenone (35.6 mg, 0.20 mmol), methanol (0.03 ml, 0.74 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 10% ethyl acetate). (Reaction time: 3 h; colorless liquid, isolated yield: 46%, 19.1 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2.3 Hz, 1H), 7.45 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 4.28 (q, *J* = 6.4 Hz, 1H), 3.92 (s, 3H), 3.20 (s, 3H), 2.62 (s, 3H), 1.41 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.8, 158.4, 135.7, 131.2, 128.6, 128.0, 111.9, 78.8, 56.4, 55.7, 31.8, 23.6.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{12}H_{16}O_3]$ requires m/z 231.0997, found m/z 231.1009.

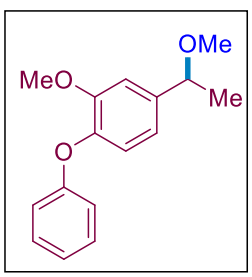


Ethyl (S)-4-((4-(1-methoxyethyl)phenoxy)methyl)benzoate (15c):

Prepared according to the general procedure **A** using 1-(benzyloxy)-4-ethyl-2-methoxybenzene (57.0 mg, 0.20 mmol), methanol (0.025 mL, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 15% ethyl acetate). (Reaction time: 3 h; white solid, isolated yield: 40%, 25.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 5.15 (s, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 4.27 (q, *J* = 6.4 Hz, 1H), 3.22 (s, 3H), 1.50 – 1.38 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 158.0, 142.2, 136.2, 130.1, 129.9, 127.5, 126.9, 114.8, 79.1, 69.4, 61.0, 56.2, 23.7, 14.3.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{22}O_4]$ requires m/z 337.1410, found m/z 337.1419.

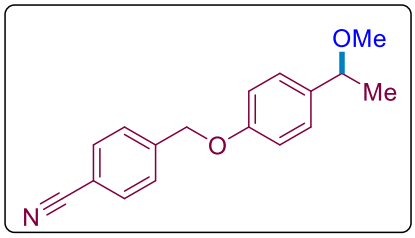


2-Methoxy-4-(1-methoxyethyl)-1-phenoxybenzene (16c):

Prepared according to the general procedure **A** using 4-ethyl-2-methoxy-1-phenoxybenzene (46.0 mg, 0.20 mmol), methanol (0.03 mL, 0.74 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 15% ethyl acetate); (Reaction time: 4 h; colorless liquid, isolated yield: 36%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.99 – 6.88 (m, 4H), 6.83 (dd, *J* = 8.1, 1.8 Hz, 1H), 4.28 (q, *J* = 6.4 Hz, 1H), 3.85 (s, 3H), 3.26 (s, 3H), 1.46 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 151.6, 144.4, 140.4, 129.5, 122.5, 120.7, 118.9, 117.3, 110.3, 79.4, 77.3, 77.0, 76.7, 56.5, 56.0, 23.8.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{16}H_{18}NO_3]$ requires m/z 281.1148, found m/z 281.1159.

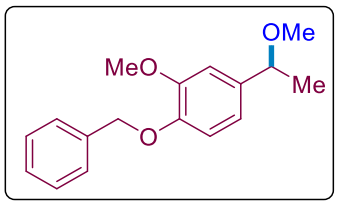


4-(1-methoxyethyl)phenoxy)methyl)benzonitrile (17c):

Prepared according to the modified procedure **A** using 4-((4-ethylphenoxy)methyl)benzonitrile (47.0 mg, 0.20 mmol), methanol (0.05 mL, 1.2 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), $CBrCl_3$ (0.03 ml, 0.30 mmol), nitromethane (1.5 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 15% ethyl acetate); (reaction time: 40 h; isolated yield: 33%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 9.9 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 5.12 (s, 2H), 4.25 (q, *J* = 6.4 Hz, 1H), 3.20 (s, 3H), 1.42 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.7, 142.6, 136.6, 132.4, 127.6, 127.6, 118.7, 114.7, 111.8, 79.1, 69.0, 56.3, 23.7.

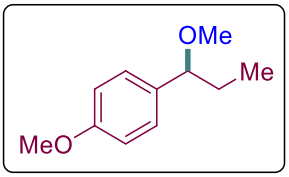
HRMS (ESI) $[2M+Na]^+$ calculated for $[C_{17}H_{17}NO_2]$ requires m/z 557.2410, found m/z 557.2384.



1-(Benzyloxy)-2-methoxy-4-(1-methoxyethyl)benzene (18c):

Prepared according to the general procedure **A** using 1-(benzyloxy)-4-ethyl-2-methoxybenzene (48.0 mg, 0.20 mmol), methanol (0.025 mL, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 15% ethyl acetate). (Reaction time: 3 h; colorless liquid, isolated yield: 38%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.33 (dt, *J* = 26.9, 7.2 Hz, 3H), 6.91 – 6.82 (m, 2H), 6.76 (dd, *J* = 8.2, 1.8 Hz, 1H), 5.14 (s, 2H), 4.22 (q, *J* = 6.4 Hz, 1H), 3.90 (s, 3H), 3.21 (s, 3H), 1.42 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.9, 147.6, 137.3, 136.8, 128.5, 127.8, 127.3, 118.7, 113.8, 109.6, 79.4, 77.3, 77.0, 76.7, 71.2, 56.3, 56.0, 23.8.
HRMS (ESI) $[M+Na]^+$ calculated for $[C_{17}H_{20}O_3]$ requires m/z 295.1304, found m/z 295.1300.

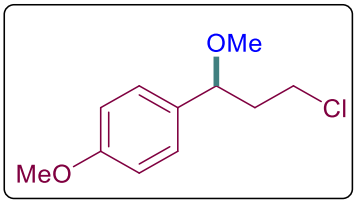


1-methoxy-4-(1-methoxypropyl)benzene (19c):

Prepared according to the general procedure **A** using 1-methoxy-4-propylbenzene (30.4 mg, 0.20 mmol), methanol (0.03 ml, 0.74 mmol), Mes-Acr$^+$-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 5% ethyl acetate). (Reaction time: 3 h; colorless liquid, isolated yield: 52%, 18.7 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.95 (t, *J* = 6.7 Hz, 1H), 3.81 (s, 3H), 3.18 (s, 3H), 1.85 – 1.60 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 134.3, 128.0, 113.7, 85.1, 56.4, 55.3, 30.8, 10.2.

MS (TLC-MS): m/z $[M+Na]^+$: 203. Spectral data were consistent with the previously reported one.[16]

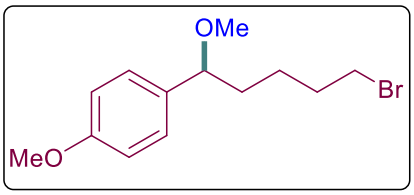


1-(1-(3-chloropropoxy)ethyl)-2-methoxybenzene (20c):

Prepared according to the general procedure **A** using 1-(3-chloropropyl)-4-methoxybenzene (36.9 mg, 0.20 mmol), methanol (0.05 ml, 1.2 mmol), Mes-Acr$^+$-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 10% ethyl acetate). (Reaction time: 6 h; colorless liquid, isolated yield: 61%, 26.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.31 (dd, *J* = 8.2, 5.2 Hz, 1H), 3.81 (s, 3H), 3.71 – 3.59 (m, 1H), 3.48 (dt, *J* = 10.9, 6.1 Hz, 1H), 3.20 (s, 3H), 2.24 (ddt, *J* = 14.2, 8.2, 5.9 Hz, 1H), 2.04 – 1.92 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 133.0, 127.8, 114.0, 79.9, 56.6, 55.1, 41.7, 40.7.

MS (TLC-MS): m/z $[M+Na]^+$: 237. Spectral data were consistent with the previously reported one.[13]

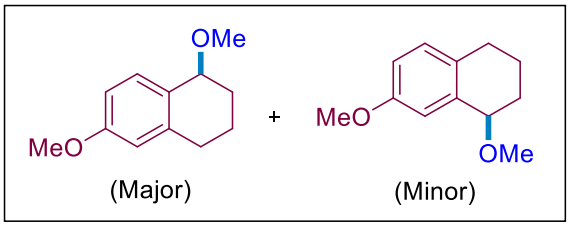


1-(4-Bromo-1-methoxybutyl)-4-methoxybenzene (21c):

Prepared according to the general procedure **A** using 1-(3-chloropropyl)-4-methoxybenzene (36.9 mg, 0.20 mmol), methanol (0.03 ml, 0.74 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 10% ethyl acetate). (Reaction time: 3 h; isolated yield: 46%, 26.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.03 (t, *J* = 6.9 Hz, 1H), (3.81 (s, 3H), 3.37 (t, *J* = 6.9 Hz, 2H), 3.17 (s, 3H), 1.94 – 1.79 (m, 3H), 1.68 – 1.32 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1, 134.1, 127.9, 113.8, 83.3, 56.4, 55.3, 37.2, 33.6, 32.8, 24.6.

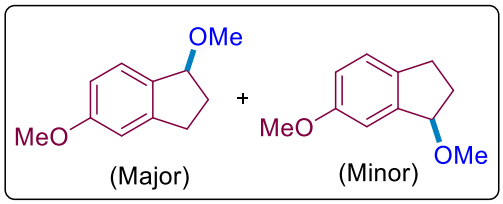
HRMS (ESI) $[M+Na]^+$ calculated for $[C_{13}H_{19}O_2Br]$ requires m/z 309.0460, found m/z 309.0469.



(S)-1,6-Dimethoxy-1,2,3,4-tetrahydronaphthalene (22c) (Major)
Prepared according to the modified procedure **A** using 6-methoxy-1,2,3,4-tetrahydronaphthalene (32.0 mg, 0.10 mmol), methanol (0.05 ml, 1.2 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.84 mg, 0.002 mmol), K_2HPO_4 (104.6 mg, 0.60 mmol), $CBrCl_3$ (0.03 ml, 0.30 mmol), nitromethane (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100 % heptane to 10 % ethyl acetate); (Reaction time: 32 h; colorless liquid, isolated yield: 60%, 23.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 3.2 Hz, 1H), 6.74 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.62 (d, *J* = 2.6 Hz, 1H), 4.26 (t, *J* = 4.5 Hz, 1H), 3.77 (s, 3H), 3.40 (s, 3H), 2.90 – 2.55 (m, 2H), 2.11 – 1.59 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 139.0, 130.7, 129.1, 113.4, 112.0, 76.4, 55.9, 55.2, 29.5, 27.6, 18.5.

MS (TLC-MS): m/z $[M+Na]^+$: 215. Spectral data were consistent with the previously reported one.[17]

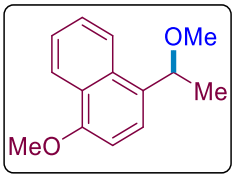


1,5-Dimethoxy-2,3-dihydro-1H-indene (23c) (major):

Prepared according to the modified procedure **A** using 5-methoxy-2,3-dihydro-1H-indene (30.0 mg, 0.20 mmol), methanol (0.05 mL, 1.2 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), $CBrCl_3$ (0.03 ml, 0.30 mmol), nitromethane (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 15% ethyl acetate); (Reaction time: 40 h; colorless liquid, isolated yield: 56%, 19.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.2 Hz, 1H), 6.99 – 6.68 (m, 2H), 4.76 (dd, *J* = 6.4, 3.3 Hz, 1H), 3.79 (s, 1H), 3.37 (s, 3H), 3.16 – 3.02 (m, 1H), 2.83 – 2.72 (m, 1H), 2.39 – 2.26 (m, 1H), 2.20 – 2.07 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.6, 160.3, 146.1, 134.9, 125.9, 112.6, 109.9, 84.0, 55.8, 55.4, 32.3, 30.5.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{11}H_{14}O_2]$ requires m/z 201.0886, found m/z 201.0893.

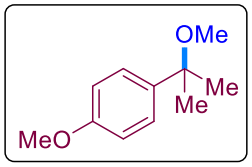


1-Methoxy-4-(1-methoxyethyl)naphthalene (24c):

Prepared according to the general procedure **A** using 1-ethyl-4-methoxynaphthalene (37.0 mg, 0.20 mmol), methanol (0.02 mL, 0.49 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 5% ethyl acetate). (Reaction time: 4 h; colorless liquid, isolated yield: 51%, 22.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.41 (m, 3H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.96 (p, *J* = 6.3 Hz, 1H), 4.00 (s, 3H), 3.29 (s, 3H), 1.60 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.0, 131.9, 130.8, 126.4, 126.0, 124.8, 123.7, 123.2, 122.7, 103.3, 77.4, 77.3, 77.0, 76.7, 56.4, 55.5, 23.2.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{14}H_{16}O_2]$ requires m/z 239.1042, found m/z 239.1037.

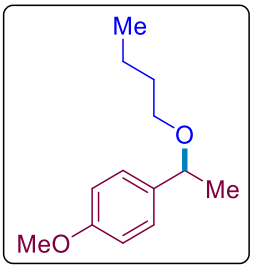


1-Methoxy-4-(2-methoxypropan-2-yl)benzene (25c):

Prepared according to the modified procedure **A** using 1-isopropyl-4-methoxybenzene (30.0 mg, 0.20 mmol), methanol (0.05 mL, 1.2 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), $CBrCl_3$ (0.03 ml, 0.30 mmol), nitromethane (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 5% ethyl acetate); (Reaction time: 36 h; isolated yield: 52%, 18.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.04 (s, 3H), 1.51 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.5, 137.9, 127.1, 113.5, 76.4, 55.2, 50.5, 28.0.

MS (TLC-MS): m/z [M+Na]$^{+}$: 203. Spectral data were consistent with the previously reported one.[13]

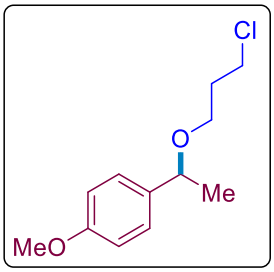


1-(1-Butoxyethyl)-4-methoxybenzene (26c):

Prepared according to the general procedure **A** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 1-butanol (0.05 ml, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 5% ethyl acetate). (Reaction time: 3 h; colorless liquid, isolated yield: 52%, 21.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.33 (q, *J* = 6.5 Hz, 1H), 3.80 (s, 3H), 3.27 (t, *J* = 6.6 Hz, 2H), 1.57 – 1.52 (m, 2H), 1.41 (d, *J* = 6.5 Hz, 3H), 1.36 – 1.15 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 136.4, 127.3, 113.8, 77.5, 68.3, 55.3, 32.1, 24.1, 19.4, 13.9.

MS (TLC-MS): m/z [M+Na]$^{+}$: 231. Spectral data were consistent with the previously reported one.[18]

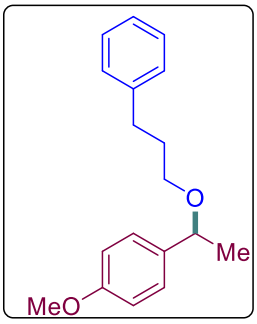


1-(1-(3-Chloropropoxy)ethyl)-4-methoxybenzene (27c):

Prepared according to the general procedure **A** using 2-ethyl-anisole (27.0 mg, 0.20 mmol), 3-chloropropan-1-ol (0.10 mL, 1.20 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 10% ethyl acetate). (Reaction time: 4 h; colorless liquid, isolated yield: 44%, 20.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.35 (q, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 3.70 – 3.55 (m, 2H), 3.45 – 3.34 (m, 2H), 2.11 – 1.83 (m, 2H), 1.41 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 135.9, 127.3, 113.8, 77.7, 64.8, 55.3, 42.1, 33.0, 23.9.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{12}H_{17}ClO_2]$ requires m/z 251.0809, found m/z 251.0857.

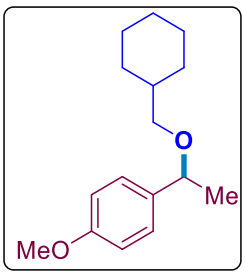


1-Methoxy-4-(1-(3-phenylpropoxy)ethyl)benzene (28c):

Prepared according to general procedure **A** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 2-phenylethan-1-ol (108.9 mg, 0.082 ml, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by flash chromatography using a heptane/ethyl acetate gradient (from 100% heptane to 10% ethyl acetate). (Reaction time: 2 h; colorless liquid, isolated yield: 45%, 24.3 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ7.13-7.26 (m, 7H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.33 (q, *J* = 6.5 Hz, 1H), 3.80 (s, 3H), 3.30 (t, *J* = 6.4 Hz, 2H), 2.66 (dtd, *J* = 21.6, 14.0, 7.8 Hz, 3H), 1.91 – 1.81 (m, 2H), 1.43 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 142.2, 136.2, 128.5, 128.3, 127.4, 125.7, 113.8, 77.5, 67.6, 55.3, 32.4, 31.5, 24.0.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{18}H_{22}O_2]$ requires m/z 293.1512, found m/z 293.1526.

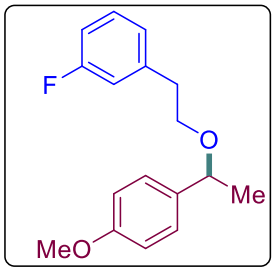


1-(1-(Cyclohexylmethoxy)ethyl)-4-methoxybenzene (29c):

Prepared according to the general procedure **A** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), cyclohexylmethanol (137.0 mg, 0.15 ml, 1.20 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 5% ethyl acetate). (Reaction time: 2 h; colorless liquid, isolated yield: 45%, 22.3 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 11.4 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.30 (q, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 3.06 (d, *J* = 6.5 Hz, 2H), 1.90 – 1.49 (m, 6H), 1.40 (d, *J* = 6.5 Hz, 3H), 1.31 – 1.07 (m, 3H), 1.03 – 0.71 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 136.5, 127.3, 113.7, 74.4, 55.3, 38.2, 30.3, 30.2, 26.7, 25.9, 25.9, 24.2.

MS (TLC-MS): m/z $[M+Na]^+$: 271. Spectral data were consistent with the previously reported one.[19]

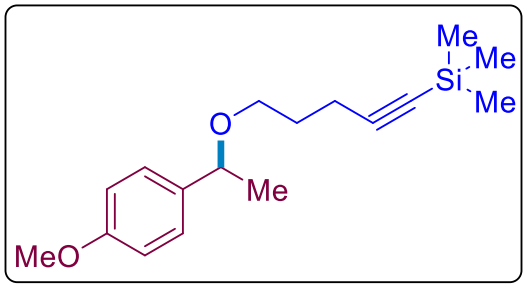


1-Methoxy-4-(1-phenethoxyethyl)benzene (30c):

Prepared according to the general procedure **A** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 2-(3-fluorophenyl)ethanol (84.1 mg, 0.074 ml, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by flash chromatography using a heptane/ethyl acetate gradient (from 100% heptane to 10% ethyl acetate). (Reaction time: 3 h; isolated yield: 48%, 26.3 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.23 (m, 1H), 7.17 (d, *J* = 8.7 Hz, 2H), 6. 87-6.96 (m, 3H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.35 (q, *J* = 6.4 Hz, 1H), 3.85 (s, 3H), 3.49 (dt, *J* = 14.0, 4.6 Hz, 2H), 2.84 (dd, *J* = 11.7, 6.9 Hz, 2H), 1.40 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.6, 159.1, 135.7, 129.6, 129.5, 127.2, 124.6, 115.8 (d, *J* = 20.9 Hz), 113.5, 113.0, 112.9 (d, *J* = 21.0 Hz), 77.7, 68.8, 55.4, 36.0, 24.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.08.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{17}H_{19}O_2F]$ requires m/z 297.1261, found m/z 297.1258.

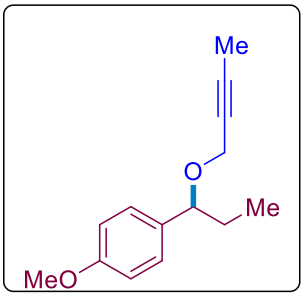


5-(1-(4-Methoxyphenyl)ethoxy)pent-1-yn-1-yl)trimethylsilane (31c):

Prepared according to general procedure **A** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 5-(trimethylsilyl)pent-4-yn-1-ol (0.109 mL, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 15% ethyl acetate); (Reaction time: 3 h; isolated yield: 42%, 24.4 mg). Note: Some 5-(trimethylsilyl)pent-4-yn-1-ol mixed with product which is difficult to remove.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 4.35 (q, J = 6.4 Hz, 1H), 3.80 (s, 3H), 3.35 (t, J = 6.3 Hz, 2H), 2.41 – 2.21 (m, 2H), 1.83 – 1.69 (m, 2H), 1.41 (d, J = 6.5 Hz, 3H), 0.12 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 136.1, 127.3, 113.8, 107.0, 84.6, 77.5, 66.8, 55.2, 29.0, 24.0, 16.8, 0.1.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{17}H_{26}O_2Si]$ requires m/z 313.2680, found m/z 313.2691.

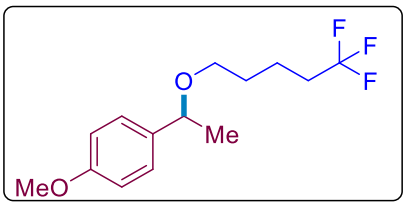


1-Methoxy-4-(1-(pent-3-yn-1-yloxy)propyl)benzene (32c):

Prepared according to general procedure **A** using 1-methoxy-4-propylbenzene (30.4 mg, 0.20 mmol), 3,3-dimethylbutan-1-ol (42.0 mg, 0.045 ml, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 10% ethyl acetate). (Reaction time: 3 h; colorless liquid, isolated yield: 42%, 18.3 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.26 (t, *J* = 6.8 Hz, 1H), 4.00 (dq, *J* = 15.0, 2.3 Hz, 1H), 3.81(s, 3H), 3.84 – 3.71 (m, 1H), 1.93 – 1.80 (m, 4H), 1.66 (tt, *J* = 14.5, 7.3 Hz, 1H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 133.5, 128.2, 113.8, 82.0, 81.8, 75.6, 56.1, 55.3, 30.6, 10.3, 3.7.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{14}H_{18}O_2]$ requires m/z 241.1199, found m/z 241.1193.

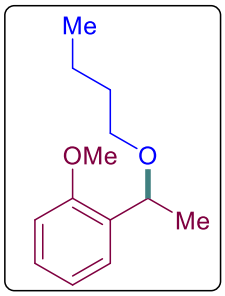


1-Methoxy-4-(1-((5,5,5-trifluoropentyl)oxy)ethyl)benzene (33c):

Prepared according to the general procedure **A** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 5,5,5-trifluoropentan-1-ol (0.063 mL, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 15% ethyl acetate); (Reaction time: 3 h; isolated yield: 38%, 21.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.32 (q, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 3.31 – 3.22 (m, 2H), 2.11 – 1.93 (m, 2H), 1.66 – 1.55 (m, 2H), 1.41 (d, *J* = 6.5 Hz, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 136.0, 127.3, 113.8, 77.7, 67.5, 55.3, 33.5 (q, *J* = 28.5 Hz), 28.9, 24.0, 18.9 (q, *J* = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.45 (dd, *J* = 14.0, 8.0 Hz).

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{14}H_{19}O_2F_3]$ requires m/z 299.1229, found m/z 299.1225.

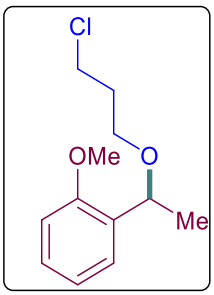


1-(1-Butoxyethyl)-2-methoxybenzene (34c):

Prepared according to the general procedure **A** using 2-ethyl-anisole (27.0 mg, 0.20 mmol), 1-butanol (0.05 ml, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 10% ethyl acetate). (reaction time: 4 h; isolated yield: 41%, 17.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.22 (td, *J* = 8.2, 1.7 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 4.82 (q, *J* = 6.4 Hz, 1H), 3.82 (s, 3H), 3.39 – 3.22 (m, 2H), 1.74 – 1.50 (m, 3H), 1.39 – 1.34 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.6, 132.8, 127.8, 126.0, 120.8, 110.2, 71.4, 68.6, 55.3, 32.2, 22.8, 19.5, 14.0.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{13}H_{20}O_2]$ requires m/z 231.1355, found m/z 231.1351

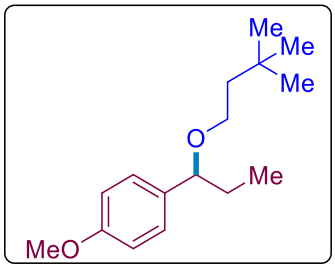


1-(1-(3-Chloropropoxy)ethyl)-2-methoxybenzene (35c):

Prepared according to the general procedure **A** using 2-ethyl-anisole (27.0 mg, 0.20 mmol), methanol (0.05 ml, 1.20 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 10% ethyl acetate). (reaction time: 3 h; isolated yield: 44%, 20.1 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 7.5, 1.6 Hz, 1H), 7.30 – 7.18 (m, 1H), 6.97 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 4.85 (q, J = 6.4 Hz, 1H), 3.82 (s, 3H), 3.73 – 3.59 (m, 2H), 3.47 (td, J = 5.9, 1.9 Hz, 2H), 2.07 – 1.90 (m, 2H), 1.38 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.6, 132.2, 128.0, 126.0, 120.8, 110.3, 77.4, 77.0, 76.7, 71.7, 65.2, 55.3, 42.2, 33.1, 22.6.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{12}H_{17}ClO_2]$ requires m/z 251.0809, found m/z 251.0855.



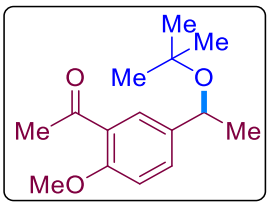
Na

1-(1-(3,3-Dimethylbutoxy)propyl)-4-methoxybenzene (36c):

Prepared according to general procedure **A** using 1-methoxy-4-propylbenzene (30.4 mg, 0.20 mmol), 3,3-dimethylbutan-1-ol (61.0 mg, 0.073 ml, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 10% ethyl acetate). (reaction time: 3 h; colorless liquid, isolated yield: 42%, 21.0 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 4.04 (t, J = 6.7 Hz, 1H), 3.79 (s, 3H), 3.39 – 3.31 (m, 1H), 3.29 – 3.21 (m, 1H), 1.88 – 1.72 (m, 1H), 1.69 – 1.42 (m, 4H), 0.97 – 0.82 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 135.1, 127.8, 113.6, 83.4, 65.9, 55.2, 43.2, 43.1, 31.2, 29.8, 10.4.

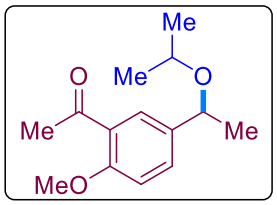
HRMS (ESI) $[M+Na]^+$ calculated for $[C_{16}H_{26}O_2]$ requires m/z 273.1825, found m/z 273.1820



1-(5-(1-(Tert-butoxy)ethyl)-2-methoxyphenyl)ethan-1-one (37c):

Prepared according to modified procedure **A** using 1-(5-ethyl-2-methoxyphenyl)ethan-1-one (36.0 mg, 0.20 mmol), *tert*-butanol (0.114 mL, 1.2 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), $CBrCl_3$ (0.03 ml, 0.30 mmol), nitromethane (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100 % heptane to 5 % ethyl acetate); (Reaction time: 30 h; colorless liquid, isolated yield: 44%, 22.0 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2.3 Hz, 1H), 7.53 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 4.65 (q, *J* = 6.5 Hz, 1H), 3.90 (s, 3H), 2.61 (s, 3H), 1.33 (d, *J* = 6.5 Hz, 3H), 1.15 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.9, 157.8, 139.8, 130.9, 127.7, 127.5, 111.6, 69.1, 55.6, 31.9, 28.6, 26.6.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{15}H_{22}O_3]$ requires m/z 273.1461, found m/z 273.1466.

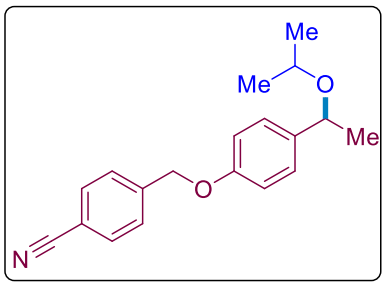


1-(5-(1-Isopropoxyethyl)-2-methoxyphenyl)ethan-1-one (38c):

Prepared according to the modified procedure **A** using 1-(5-ethyl-2-methoxyphenyl)ethan-1-one (36.0 mg, 0.20 mmol), isopropanol (0.092 mL, 1.2 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), $CBrCl_3$ (0.03 ml, 0.30 mmol), nitromethane (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100 % heptane to 5 % ethyl acetate); (Reaction time: 30 h; colorless liquid, isolated yield: 32%, 15.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2.3 Hz, 1H), 7.49 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 4.51 (q, *J* = 6.4 Hz, 1H), 3.91 (s, 3H), 3.56 – 3.17 (m, 1H), 2.61 (s, 3H), 1.38 (d, *J* = 6.5 Hz, 3H), 1.14 (d, *J* = 6.0 Hz, 3H), 1.08 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.8, 158.3, 137.1, 131.2, 128.4, 127.8, 111.9, 73.8, 68.5, 55.6, 31.8, 24.6, 23.3, 21.5.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{18}H_{21}NO_5S]$ requires m/z 259.1304, found m/z 259.1342.

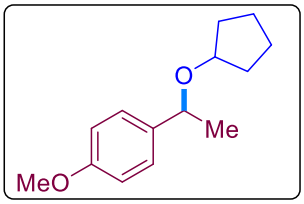


4-(1-Isopropoxyethyl)phenoxy)methyl)benzonitrile (39c):

Prepared according to the modified procedure **A** using 4-((4-ethylphenoxy)methyl)benzonitrile (47.0 mg, 0.20 mmol), isopropanol (0.092 mL, 1.2 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), $CBrCl_3$ (0.03 ml, 0.30 mmol), nitromethane (1.5 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 15% ethyl acetate); (Reaction time: 40 h; colorless liquid, isolated yield: 28%, 16.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 4.49 (q, *J* = 6.4 Hz, 1H), 3.48 (hept, *J* = 6.1 Hz, 1H), 1.38 (d, *J* = 6.5 Hz, 3H), 1.14 (d, *J* = 6.0 Hz, 3H), 1.08 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.5, 142.7, 137.9, 132.4, 127.6, 127.4, 118.7, 114.6, 111.7, 74.1, 69.0, 68.4, 24.7, 23.3, 21.5.

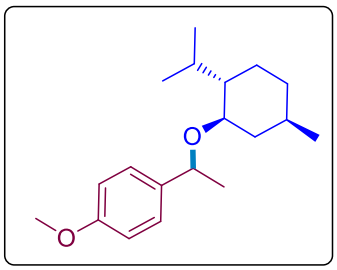
HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{21}NO_2]$ requires m/z 318.1464, found m/z 318.1460.



Methyl-9-isopropoxy-6-methoxy-1,4a-dimethyl-octahydrophenanthrene-1-carboxylate (40c):

Prepared according to the modified procedure **A** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), cyclopentanol (0.055 ml, 0.6 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.84 mg, 0.002 mmol), K_2HPO_4 (104.6 mg, 0.60 mmol), $CBrCl_3$ (0.03 ml, 0.3 mmol), nitromethane (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100 % heptane to 15 % ethyl acetate); (Reaction time: 40 h; colorless liquid, isolated yield: 40%, 17.6 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.41 (q, *J* = 6.5 Hz, 1H), 3.86 – 3.74 (m, 4H), 1.76 – 1.40 (m, 8H), 1.38 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 136.8, 127.4, 113.7, 78.4, 74.99, 55.3, 33.1, 31.9, 24.6, 23.5, 23.5.

MS (TLC-MS): m/z $[M+Na]^+$: 231. Spectral data were consistent with the previously reported one.[20]

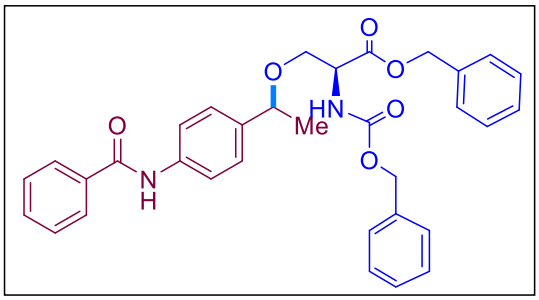


1-((S)-1-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)ethyl)-4-methoxybenzene (41c):

Prepared according to the modified procedure **A** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), L-menthol (188.0 mg, 1.2 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), $CBrCl_3$ (0.03 mL, 0.30 mmol), nitromethane (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 15% ethyl acetate); (reaction time: 40 h; isolated yield: 45%, dr 1.7:1, 26.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.14 (m, 2H), 6.86 (dt, *J* = 8.6, 4.3 Hz, 2H), 4.52 and 4.45 (q, *J* = 6.4 Hz, 1H), 3.80（s, 3H), 3.10 and 2.90 (td, *J* = 10.4, 4.1 Hz, 1H), 2.40 – 2.11 (m, 2H), 1.82 – 1.49 (m, 3H), 1.45 – 1.37 (m, 3H), 1.30 – 1.12 (m, 2H), 1.02 – 0.75 (m, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 158.8, 137.6, 136.3, 128.1, 127.4, 113.6, 113.6, 77.8, 76.3, 74.9, 73.3, 55.3, 49.1, 48.5, 47.6, 42.2, 40.4, 34.6, 34.5, 31.7, 31.5, 30.9, 25.4, 24.8, 24.6, 23.5, 23.2, 22.8, 22.5, 22.3, 21.3, 21.3, 19.4, 16.2, 15.5.

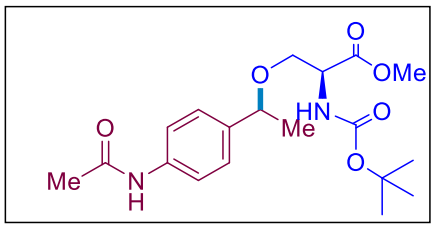
HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{30}O_2]$ requires m/z 313.2138, found m/z 313.2170.



Benzyl *O*-(1-(4-benzamidophenyl)ethyl)-*N*-((benzyloxy)carbonyl)-*L*-serinate (42c):

Prepared according to the general procedure **A** using *N*-(4-ethylphenyl)benzamide (45.0 mg, 0.20 mmol), benzyl ((benzyloxy)carbonyl)-*L*-serinate (0.03 mL, 0.74 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 60% ethyl acetate); (reaction time: 3 h; isolated yield: 44%, dr = 1:1, 49.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 23.4, 10.4 Hz, 3H), 7.60 – 7.43 (m, 5H), 7.37 – 7.25 (m, 9H), 7.15 (dd, *J* = 26.2, 8.4 Hz, 2H), 5.66 (m, 1H), 5.19 (m, 4H), 4.48 (dd, *J* = 8.7, 2.9 Hz, 1H), 4.29 (m, 1H), 3.87 – 3.65 (m, 1H), 3.57 – 3.28 (m, 1H), 1.46 – 1.22 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.4, 170.2, 165.7, 156.1, 156.0, 139.0, 137.4, 135.6, 135.4, 135.0, 131.9, 128.8, 128.6, 128.6, 128.4, 128.3, 128.2, 128.2, 128.2, 128.1, 127.0, 127.0, 126.9, 120.3, 120.3, 78.4, 78.3, 68.4, 68.3, 67.2, 67.2, 67.1, 67.0, 54.6, 54.6, 23.7, 23.5.
HRMS (ESI) $[M+Na]^+$ calculated for $[C_{33}H_{32}N2O_6]$ requires m/z 575.2158, found m/z 575.2165.

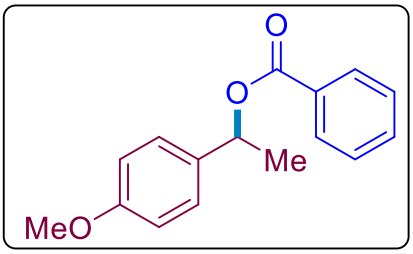


Benzyl *O*-(1-(4-benzamidophenyl)ethyl)-*N*-((benzyloxy)carbonyl)-*L*-serinate (43c):

Prepared according to the general procedure **A** using *N*-(4-ethylphenyl)benzamide (33.0 mg, 0.20 mmol), N-(tert-Butoxycarbonyl)-L-serine methyl (132.0 mg, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 60% ethyl acetate); (reaction time: 3 h; isolated yield: 41%, dr = 1:1, 31.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.19 (s, 1H), 7.16 (d, *J* = 8.3 Hz, 2H), 5.40 (d, *J* = 8.2 Hz, 1H), 4.40 – 4.28 (m, 2H), 3.72 – 3.61 (m, 4H), 3.51 (dd, *J* = 9.2, 2.6 Hz, 1H), 2.17 (s, 3H), 1.44 (s, 9H), 1.36 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 168.2, 155.6, 137.3, 126.8, 119.9, 80.0, 78.1, 68.4, 54.0, 52.3, 28.4, 24.6, 23.8.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{28}N_2O_6]$ requires m/z 403.1839, found m/z 403.1836.

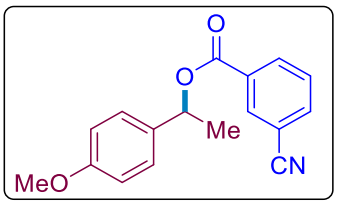


1-(4-Methoxyphenyl)ethyl benzoate (44c):

Prepared according to the general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), benzoic acid (48.4 mg, 0.040 mm ol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 5.5 h; isolated yield: 71%, 36.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.2 Hz, 2H), 7.58 – 7.47 (m, 1H), 7.44 – 7.32 (m, 4H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.10 (q, *J* = 6.6 Hz, 1H), 3.79 (s, 3H), 1.65 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 159.3, 133.9, 132.8, 130.7, 129.6, 128.3, 127.6, 113.9, 72.7, 55.3, 22.2.

MS (TLC-MS): m/z $[M+Na]^+$: 279. Spectral data were consistent with those reported previously.[13]

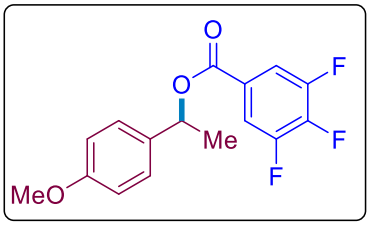


1-(4-Methoxyphenyl)ethyl 3-cyanobenzoate (45c):

Prepared according to the general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 3-cyanobenzoic acid (58.8 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 5.5 h; isolated yield: 78%, 43.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.3 Hz, 1H), 8.26 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.81 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.11 (q, *J* = 6.6 Hz, 1H), 3.81 (s, 3H), 1.68 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 159.6, 135.9, 133.7, 133.3, 133.1, 132.0, 129.4, 127.7, 118.0, 114.1, 112.9, 77.4, 77.0, 76.7, 73.8, 55.3, 21.9.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{17}H_{15}NO_3]$ requires m/z 304.0944, found m/z 304.0996.

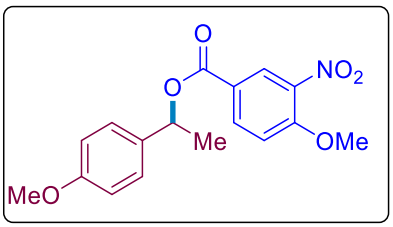


1-(4-Methoxyphenyl)ethyl 3,4,5-trifluorobenzoate (46c):

Prepared according to the general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 3,5-3,4,5-trifluorobenzoic acid (35.2 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 15% ethyl acetate). (reaction time: 5.5 h; isolated yield: 92%, 57.1 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.62 (m, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.07 (q, *J* = 6.6 Hz, 1H), 3.80 (s, 3H), 1.66 (d, *J* = 6.6 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -131.88 – -133.97 (m), -149.51 – -154.97 (m); **^{13}C NMR** (101 MHz, $CDCl_3$) 163.1, 159.6, 152.3 (dd, *J* = 10.3, 3.4 Hz), 149.8 (dd, *J* = 10.3, 3.5 Hz), 144.4 (d, *J* = 15.3 Hz), 141.8 (t, *J* = 15.3 Hz),133.0, 127.7, 126.7 (m), 114.3, 114.2, 114.1, 114.1, 74.0, 55.3, 21.9.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{13}H_{13}F_3O_3]$ requires m/z 333.0708, found m/z 333.0683.

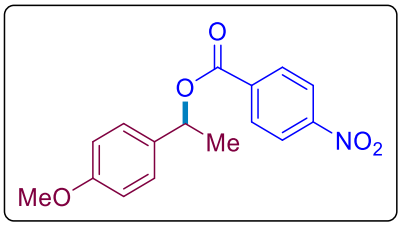


1-(4-Methoxyphenyl)ethyl 4-methoxy-3-nitrobenzoate (47c):

Prepared according to the general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 4-methoxy-3-nitrobenzoic acid (78.8 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 5.5 h; isolated yield: 90%, 59.6 mg)**.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 2.1 Hz, 1H), 8.21 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.90 (d, *J* = 6.8 Hz, 2H), 6.09 (q, *J* = 6.6 Hz, 1H), 4.01 (s, 3H), 3.80 (s, 3H), 1.66 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.8, 159.5, 156.0, 139.4, 135.4, 133.3, 127.7, 127.1, 123.1, 114.0, 113.1, 73.5, 56.9, 55.3, 22.0.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{17}H_{17}NO_6]$ requires m/z 354.0948, found m/z 354.0959.

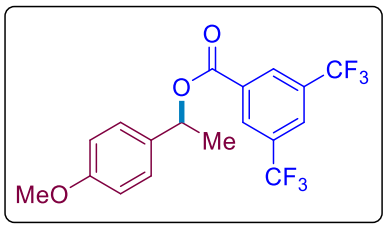


1-(4-Methoxyphenyl)ethyl 4-nitrobenzoate (48c):

Prepared according to the general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 4-nitrobenzonic acid (66.9 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 5.5 h; isolated yield: 80%, 48.2 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.27 (m, 2H), 8.27 – 8.17 (m, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.21 – 5.94 (m, 1H), 3.83 (s, 3H), 1.72 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.0, 159.6, 150.5, 136.0, 133.0, 130.7, 127.7, 123.5, 114.0, 74.0, 55.3, 21.9.

HRMS (ESI) $[2M+Na]^+$ calculated for $[C_{16}H_{15}NO_5]$ requires m/z 625.1792, found m/z 625.1786.

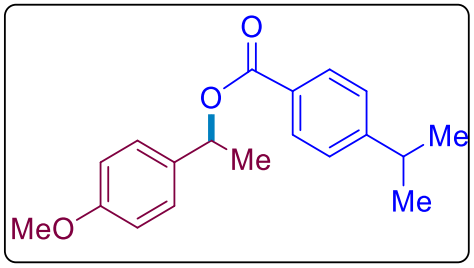


1-(4-Methoxyphenyl)ethyl 3,5-bis(trifluoromethyl)benzoate (49c):

Prepared according to the general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 3,5-bis(trifluoromethyl)benzoic acid (51.6 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 15% ethyl acetate). (reaction time: 5.5 h; isolated yield: 95%, 74.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 2H), 8.04 (s, 1H), 7.40 (d, *J* = 6.8 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.16 (q, *J* = 6.6 Hz, 1H), 3.80 (s, 3H), 1.72 (d, *J* = 6.6 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.00 (s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.3, 159.8, 132.9, 132.8, 132.7, 132.4, 132.0, 129.8 (d, *J* = 3.0 Hz), 127.9, 126.3 (dd, *J* = 7.4, 3.7 Hz), 126.2, 126.2, 124.3, 121.6, 118.9, 114.1, 74.4, 55.3, 21.8.

HRMS (ESI) $[2M+Na]^+$ calculated for $[C_{18}H_{14}F_6O_3]$ requires m/z 807.1586, found m/z 807.1729.

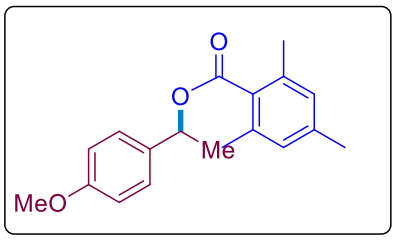


1-(4-Methoxyphenyl)ethyl 4-isopropylbenzoate (50c):

Prepared according to the general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 4-isopropylbenzonic acid (65.6 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 15% ethyl acetate). (Reaction time: 8.5 h; isolated yield: 30%, 17.9 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 6.7 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.09 (q, *J* = 6.6 Hz, 1H), 3.80 (s, 1H), 1.64 (d, *J* = 6.6 Hz, 3H), 1.26 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 159.3, 154.3, 134.1, 130.4, 129.8, 127.5, 126.4, 113.9, 72.4, 55.3, 34.3, 23.7, 22.2.

HRMS (**ESI**) $[M+Na]^+$ calculated for $[C_{19}H_{22}O_3]$ requires m/z 315.1716, found m/z 315.1732.

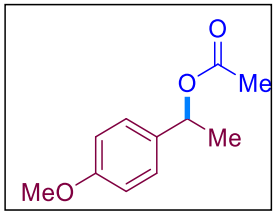


1-(4-Methoxyphenyl)ethyl 2,4,6-trimethylbenzoate (51c):

Prepared according to general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 2,4,6-trimethyl benzoic acid (53.8 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (Reaction time: 5.5 h; isolated yield: 27%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.13 (q, *J* = 6.6 Hz, 2H), 3.80 (s, 3H), 2.26 (s, 3H), 2.20 (s, 6H), 1.64 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.4, 159.4, 139.1, 134.9, 133.5, 131.3, 128.3, 127.9, 113.8, 72.7, 55.3, 21.9, 21.1, 19.6.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{22}O_3]$ requires m/z 321.1461, found m/z 321.1483.

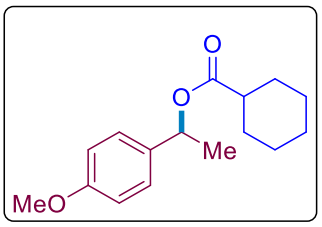


1-(4-methoxyphenyl)ethyl acetate (52c):

Prepared according to the modified procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), acetic acid (0.034 ml, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), HFIP (0.5 mL), DCE (1.5 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate); (Reaction time: 24.5 h; isolated yield: 62%, 24.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.85 (q, *J* = 6.6 Hz, 1H), 3.80 (s, 3H), 2.04 (s, 3H), 1.52 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.4, 159.3, 133.8, 127.6, 113.9, 77.3, 77.0, 76.7, 72.0, 55.3, 21.9, 21.4.

MS (TLC-MS): m/z $[M+Na]^+$: 217. Spectral data were consistent with those reported previously.[21]

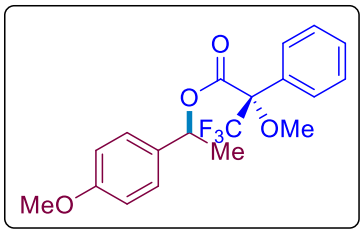


1-(4-Methoxyphenyl)ethyl cyclohexanecarboxylate (53c):

Prepared according to general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), cyclohexanecarboxylic acid (51.0 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 42.5 h; isolated yield: 53%, 27.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.84 (q, *J* = 6.6 Hz, 1H), 3.79 (s, 3H), 2.29 (tt, *J* = 11.2, 3.6 Hz, 1H), 1.99 – 1.55 (m, 5H), 1.50 (d, *J* = 6.6 Hz, 3H), 1.48 – 0.78 (m, 5H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.3, 159.2, 134.2, 127.4, 113.8, 71.4, 55.3, 43.4, 29.0, 25.8, 25.5, 22.1.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{16}H_{22}O_3]$ requires m/z 285.1461, found m/z 285.1458.

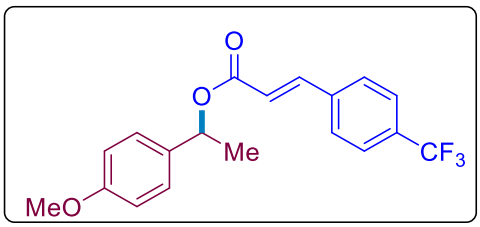


1-(4-Methoxyphenyl)ethyl 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (54c):

Prepared according to the general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 3,3,3-trifluoro-2-methoxy-2-phenylpropanoic acid (93.7 mg, 0.40 mmol, CAS No. 20445-31-2), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 42.5 h; isolated yield: 45%, dr: 1.3:1.0, 33.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.28 (m, 6H), 7.23 – 7.17 (m, 1H), 6.90 – 6.80 (m, 2H), 6.08 (dq, *J* = 17.0, 6.6 Hz, 1H), 3.80 (s, 3H), 3.50 (d, *J* = 1.0 Hz, 3H), 1.62 and 1.56 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 132.2, 129.5, 129.4, 128.3, 128.3, 128.0, 127.8, 127.4, 114.0, 113.8, 74.8, 74.7, 55.3, 21.9, 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.5, -71.7.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{19}F_3O_4]$ requires m/z 391.1127, found m/z 391.1123.

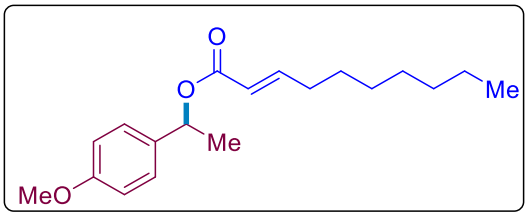


(*S*)-1-(4-Methoxyphenyl)ethyl (E)-3-(4-(trifluoromethyl)phenyl)acrylate (55c):

Prepared according to the general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 4-Trifluoromethylcinnamic acid (86.0 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 20.5 h; isolated yield: 75%, 52.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.65 – 7.53 (m, 4H), 7.35 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.00 (q, *J* = 6.6 Hz, 1H), 3.80 (s, 3H), 1.61 (d, *J* = 6.6 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.9; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 159.4, 142.8, 137.9, 133.6, 131.9, 131.6, 128.2, 127.7, 125.9 (q, *J* = 3.8 Hz), 121.2, 114.0, 72.6, 55.3, 21.9.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{17}F_3O_3S]$ requires m/z 373.1021, found m/z 373.1032.

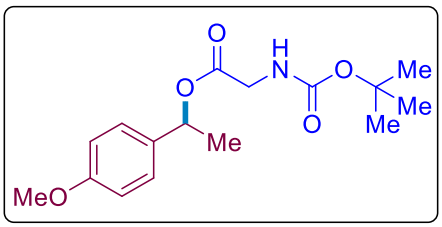


(S)-1-(4-Methoxyphenyl)ethyl (*E*)-dec-2-enoate (56c):

Prepared according to the general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 2-decenoic acid (69.0 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (Reaction time: 20.5 h; isolated yield: 63%, 38.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.7 Hz, 2H), 6.96 (dt, *J* = 15.6, 6.9 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.91 (q, *J* = 6.6 Hz, 1H), 5.82 (dt, *J* = 15.6, 1.4 Hz, 1H), 3.79 (s, 3H), 2.27 – 2.09 (m, 2H), 1.56 (dd, *J* = 11.5, 4.5 Hz, 3H), 1.42 (dt, *J* = 17.8, 9.0 Hz, 2H), 1.35 – 1.21 (m, 8H), 0.93 – 0.80 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1, 159.2, 149.6, 134.0, 127.6, 121.5, 113.9, 71.7, 55.3, 32.2, 31.7, 29.1, 29.1, 28.0, 22.6, 22.0, 14.1.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{28}O_3]$ requires m/z 327.1930, found m/z 327.1922.

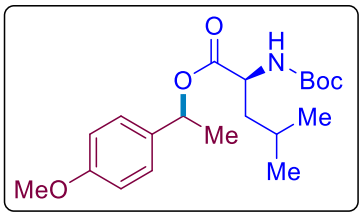


1-(4-methoxyphenyl)ethyl (tert-butoxycarbonyl)glycinate (57c):

Prepared according to the general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 3,5-(tert-butoxycarbonyl)glycine (35.2 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 20.5 h; isolated yield: 63%, 39.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 5.91 (q, J = 6.6 Hz, 1H), 4.97 (s, 1H), 4.03 – 3.82 (m, 5H), 3.80 (s, 2H), 1.55 (d, J = 6.6 Hz, 3H), 1.44 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 159.5, 155.8, 133.1, 127.7, 113.9, 79.9, 73.3, 55.3, 42.7, 28.3, 21.8.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{16}H_{23}NO_5]$ requires m/z 332.1468, found m/z 332.1456.

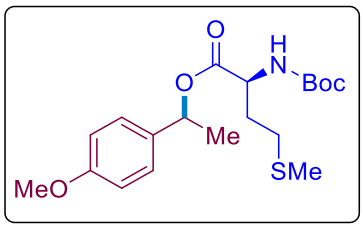


1-(4-Methoxyphenyl)ethyl (tert-butoxycarbonyl)-*L*-leucinate (58c):

Prepared according to the general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), Boc-Leu-OH (92.5 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 24 W blue LED (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (Reaction time: 48.5 h; isolated yield: 71%, dr = 1:1, 51.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, J = 8.9, 3.2 Hz, 2H), 6.92 – 6.83 (m, 2H), 5.92 – 5.76 (m, 1H), 4.85 (d, J = 10.3 Hz, 1H), 4.30 (d, J = 4.7 Hz, 1H), 3.80 (s, 3H), 1.77 – 1.48 (m, 6H), 1.43 (s, 9H), 0.96 (t, J = 10.7 Hz, 3H), 0.88 (dd, J = 11.2, 6.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.9, 159.4, 155.5, 133.3, 127.5, 113.8, 79.7, 73.2, 55.5, 55.3, 52.3, 42.0, 41.5, 28.3, 24.7, 22.9, 22.0.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{20}H_{31}NO_5]$ requires m/z 388.2094, found m/z 388.2099.

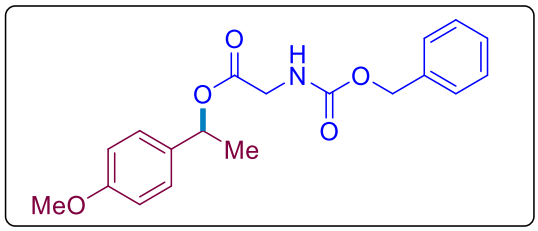


1-(4-Methoxyphenyl)ethyl (tert-butoxycarbonyl)-*L*-methioninate (59c):

Prepared according to the general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), Boc-Met-OH (99.7 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 24 W blue LED (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (Reaction time: 72.5 h; isolated yield: 40%, dr =1:1, 30.7 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.92 – 6.85 (m, 2H), 5.89 (q, *J* = 6.6 Hz, 1H), 5.11 (s, 1H), 4.39 (s, 1H), 3.80 (s, 3H), 2.56 – 2.49 (m, 1H), 2.45 – 2.20 (m, 1H), 2.21 – 1.72 (m, 5H), 1.55 (dt, *J* = 9.6, 4.8 Hz, 3H), 1.43 (m, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.5, 159.5, 155.3, 132.9, 127.7, 113.9, 79.9, 73.5, 73.5, 55.3, 52.9, 32.4, 32.2, 29.9, 29.7, 28.3, 21.8, 15.5, 15.4.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{29}NO_5S]$ requires m/z 406.1658, found m/z 406.1661.

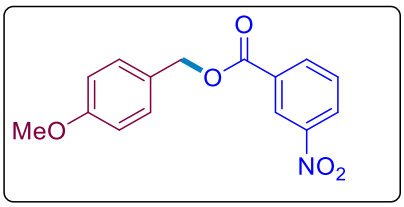


(1-(4-Methoxyphenyl)ethyl ((benzyloxy)carbonyl)glycinate (60c):

Prepared according to the general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), ((benzyloxy)carbonyl)glycine (53.8 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 24 W blue LED. The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (Reaction time: 42.5 h; isolated yield: 68%, 46.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 7.27 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.90 (q, *J* = 6.6 Hz, 1H), 5.24 (s, 1H), 5.11 (s, 2H), 4.17 – 3.81 (m, 2H), 3.79 (s, 3H), 1.54 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 159.5, 156.2, 136.3, 132.9, 128.5, 128.2, 128.1, 127.7, 114.0, 73.5, 67.1, 55.3, 43.1, 21.8.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{21}NO_5]$ requires m/z 366.1312, found m/z 366.1305.

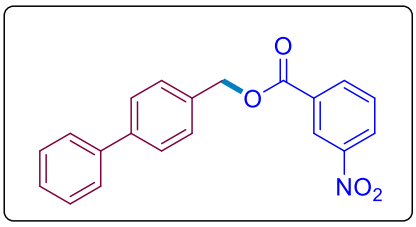


4-Methoxybenzyl 3-nitrobenzoate (61c):

Prepared according to the general procedure **B** using 1-methoxy-4-methylbenzene (24.4 mg, 0.20 mmol), 3-nitrobenzoic acid (66.8 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 42.5 h; isolated yield: 80%, 45.9 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 – 8.83 (m, 1H), 8.41 – 8.34 (m, 2H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 5.35 (s, 2H), 3.82 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.4, 160.0, 148.3, 135.4, 132.1, 130.4, 129.6, 127.4, 127.4, 124.7, 114.1, 67.5, 55.3.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{15}H_{13}NO_5]$ requires m/z 310.0685, found m/z 310.0780.

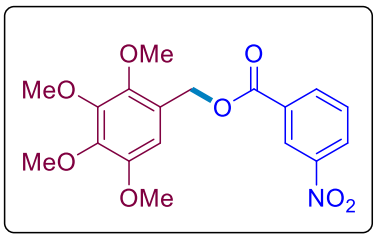


[1,1'-Biphenyl]-4-ylmethyl 3-nitrobenzoate (62c):

Prepared according to the general procedure **B** using 4-methylbiphenyl (33.6 mg, 0.20 mmol), 3-nitrobenzoic acid (66.8 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 42.5 h; isolated yield: 57%, 38.0 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (t, *J* = 1.8 Hz, 1H), 8.45 – 8.37 (m, 2H), 7.62 (ddd, *J* = 14.8, 9.0, 7.7 Hz, 5H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.45 (dd, *J* = 10.3, 4.7 Hz, 2H), 7.39 – 7.28 (m, 1H), 5.46 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.4, 148.4, 141.7, 140.6, 135.4, 134.2, 132.0, 129.7, 129.0, 128.9, 127.6, 127.5, 127.2, 124.7, 67.4.

HRMS (ESI) $[M]^+$ calculated for $[C_{20}H_{15}O_4N]$ requires m/z 333.0995, found m/z 333.0995.

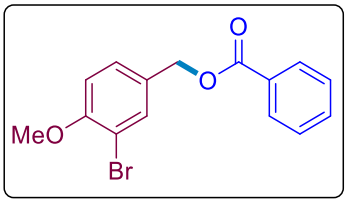


2,3,4,5-tetramethoxybenzyl 3-nitrobenzoate (63c):

Prepared according to general procedure **B** using 2,3,4,5-pentamethoxy-6-methylbenzene (42.4 mg, 0.20 mmol), 3-nitrobenzoic acid (66.8 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 42.5 h; isolated yield: 44%, 33.2 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 – 8.86 (m, 1H), 8.48 – 8.31 (m, 2H), 7.65 (t, J = 8.0 Hz, 1H), 6.74 (s, 1H), 5.41 (s, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.4, 149.6, 148.4, 147.2, 146.6, 143.9, 135.4, 132.1, 129.7, 127.4, 124.7, 122.9, 108.4, 63.2, 61.8, 61.2, 61.1, 56.4.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{17}H_{26}O_2Si]$ requires m/z 400.1002, found m/z 400.1018.

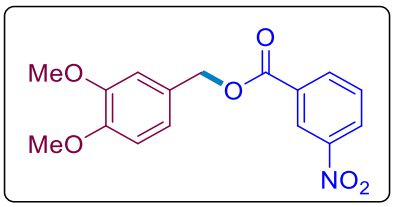


3-Bromo-4-methoxybenzyl benzoate(64c):

Prepared according to the general procedure **B** using 2-bromo-1-methoxy-4-methylbenzene (40.0 mg, 0.20 mmol), benzoic acid (48.4 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 42.5 h; isolated yield: 47%, 30.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 2H), 7.65 (d, J = 2.1 Hz, 1H), 7.55 (dd, J = 10.6, 4.3 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.36 (dd, J = 8.4, 2.1 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 5.26 (s, 2H), 3.89 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 156.0, 133.6, 133.1, 130.1, 129.7, 129.0, 128.4, 111.8, 111.7, 77.4, 77.1, 76.7, 65.7, 56.3.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{15}H_{13}O_3Br]$ requires m/z 342.9940, found m/z 342.9958.

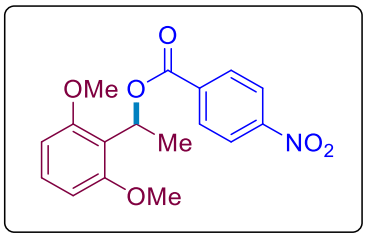


3,4-Dimethoxybenzyl 3-nitrobenzoate (65c):

Prepared according to general procedure **B** using 3,4-dimethoxy-toluene (30.4 mg, 0.20 mmol), 3-nitrobenzonic acid (66.8 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 42.5 h; isolated yield: 52%, 33.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 – 8.84 (m, 1H), 8.44 – 8.33 (m, 2H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.07 – 6.96 (m, 2H), 6.89 (d, *J* = 8.2 Hz, 1H), 5.35 (s, 2H), 3.91 (s, 3H), 3.90 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.4, 149.5, 149.2, 148.3, 135.4, 132.1, 129.6, 127.8, 127.4, 124.7, 121.7, 112.2, 111.2, 67.8, 56.0, 56.0.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{16}H_{15}NO_6]$ requires m/z 340.0791, found m/z 340.0786.

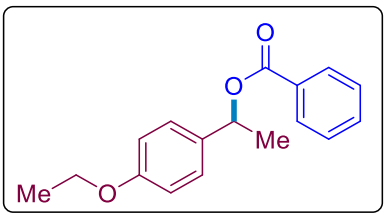


3,4-Dimethoxybenzyl 3-nitrobenzoate (66c):

Prepared according to the general procedure **B** using 2-ethyl-1,3-dimethoxybenzene (33.2 mg, 0.20 mmol), 3-nitrobenzonic acid (66.8 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate); (Reaction time: 5.5 h; isolated yield: 45%, 29.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.05 (m, 4H), 7.32 – 7.22 (m, 1H), 6.74 (q, *J* = 6.7 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 6H), 1.73 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.2, 158.7, 150.3, 136.8, 130.7, 129.5, 123.4, 116.6, 104.4, 67.2, 56.0, 19.1.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{17}H_{17}O_6N]$ requires m/z 354.0948, found m/z 354.0926.

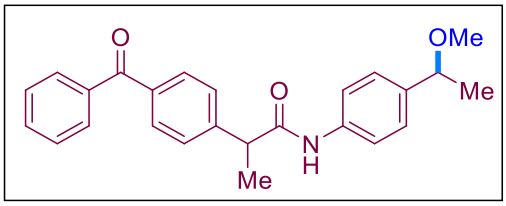


1-(4-Ethoxyphenyl)ethyl benzoate (67c):

Prepared according to general procedure **B** using 4-ethylphenetole (30.4 mg, 0.20 mmol), benzonic acid (48.4 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (Reaction time: 5.5 h; isolated yield: 83%, 44.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.64 – 7.50 (m, 1H), 7.47 – 7.39 (m, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.10 (q, *J* = 6.6 Hz, 1H), 4.02 (q, *J* = 7.0 Hz, 2H), 1.65 (d, *J* = 6.6 Hz, 3H), 1.40 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 158.7, 133.7, 132.8, 130.7, 129.6, 128.30, 127.6, 114.5, 72.7, 63.5, 22.2, 14.8.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{17}H_{18}O_3]$ requires m/z 293.1148, found m/z 293.1142.

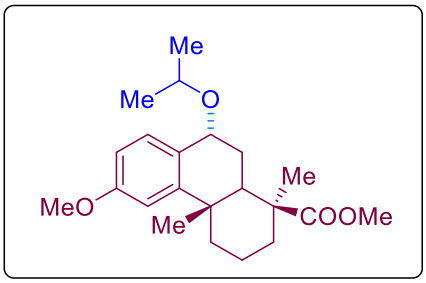


2-(4-Benzoylphenyl)-*N*-(4-ethylphenyl)propanamide (68c):

Prepared according to the general procedure **A** using 2-(4-benzoylphenyl)-*N*-(4-ethylphenyl)propanamide (71.0 mg, 0.20 mmol), methanol (0.03 mL, 0.74 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 60% ethyl acetate); (reaction time: 3 h; isolated yield: 51%, 39.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 12.7, 5.5 Hz, 3H), 7.71 – 7.54 (m, 3H), 7.45 (dd, *J* = 15.8, 8.1 Hz, 5H), 7.32 (s, 1H), 7.22 (d, *J* = 8.5 Hz, 2H), 4.23 (q, *J* = 6.4 Hz, 1H), 3.83 – 3.73 (m, 1H), 3.17 (s, 3H), 1.60 (d, *J* = 7.1 Hz, 3H), 1.38 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.6, 171.7, 141.6, 139.7, 138.2, 137.4, 137.1, 132.7, 131.5, 130.1, 129.4, 129.2, 129.0, 128.4, 126.8, 120.0, 79.1, 56.3, 47.9, 23.8, 18.8.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{25}H_{25}NO_3]$ requires m/z 410.1726, found m/z 410.1752.

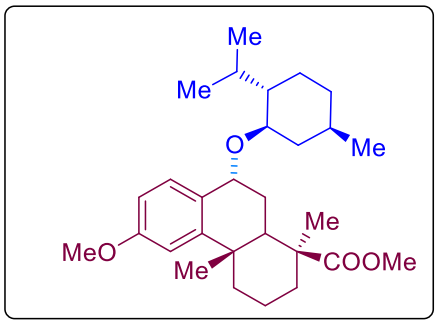


Methyl-9-isopropoxy-6-methoxy-1,4a-dimethyl-octahydrophenanthrene-1-carboxylate (69c):

Prepared according to the modified procedure **A** using *O*-methylpodocarpate (30.0 mg, 0.10 mmol), isopropanol (0.046 ml, 0.6 mmol), Mes-Acr$^+$-Me ClO_4^- (0.42 mg, 0.001 mmol), K_2HPO_4 (52.3 mg, 0.30 mmol), $CBrCl_3$ (0.015 ml, 0.15 mmol), nitromethane (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100 % heptane to 15 % ethyl acetate); (reaction time: 40 h; isolated yield: 37%, 26.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.3 Hz, 1H), 6.76 (dt, J = 8.3, 2.5 Hz, 2H), 4.47 – 4.37 (m, 1H), 3.90 – 3.79 (m, 1H), 3.76 (s, 3H), 3.67 (s, 3H), 2.40 – 2.11 (m, 3H), 2.08 – 1.87 (m, 3H), 1.72 – 1.39 (m, 2H), 1.33 – 1.26 (m, 6H), 1.21 (d, J = 6.3 Hz, 3H), 1.14 (td, J = 13.5, 4.2 Hz, 1H), 0.98 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.0, 159.3, 150.1, 132.0, 127.6, 112.0, 110.6, 72.5, 69.0, 55.3, 51.3, 45.6, 43.7, 38.9, 38.6, 37.4, 28.3, 26.1, 23.9, 22.2, 21.7, 19.9.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{17}H_{26}O_2Si]$ requires m/z 383.2192, found m/z 383.2199



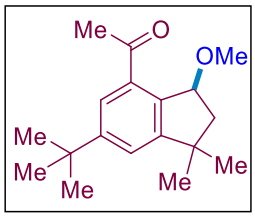
Methyl-9-((-2-isopropyl-5-methylcyclohexyl)oxy)-6-methoxy-1,4a-dimethyl-octahydrophenanthrene-1-carboxylate (70c):

Prepared according to modified procedure **A** using O-methylpodocarpate (30.0 mg, 0.10 mmol), L-Menthol (94.0 mg, 0.6 mmol), Mes-Acr$^+$-Me ClO_4^- (0.42 mg, 0.001 mmol), K_2HPO_4 (52.3 mg, 0.30 mmol), $CBrCl_3$ (0.015 ml, 0.15 mmol), nitromethane (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100 % heptane to 15 % ethyl acetate); (reaction time: 40 h; isolated yield: 43%, 39.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.3 Hz, 1H), 6.80 (dt, J = 8.3, 2.5 Hz, 2H), 4.52 (t, J = 8.7 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 3.34 (td, J = 10.3, 4.2 Hz, 1H), 2.57 – 2.35 (m, 2H), 2.34 – 2.17 (m, 3H), 2.15 – 1.88 (m, 3H), 1.77 – 1.38 (m, 6H), 1.32 – 1.23 (m, 4H), 1.15 (ddd, J = 18.9, 14.1, 5.4 Hz, 2H), 1.05 (dd, J = 8.3, 5.0 Hz, 3H), 0.99 – 0.95 (m, 3H), 0.94 – 0.85 (m, 4H), 0.82 (d, J = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.1, 159.1, 149.9, 132.1,

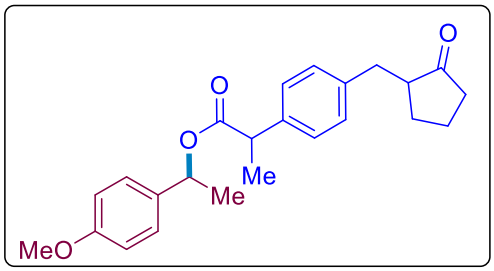
127.7, 112.2, 110.3, 76.5, 70.7, 55.2, 51.3, 48.1, 45.9, 44.0, 42.0, 38.9, 38.4, 37.7, 34.5, 31.7, 28.4, 27.0, 24.5, 23.1, 22.6, 21.9, 21.4, 19.9, 16.6.

MS (TLC-MS): m/z $[M+Na]^+$: 479. Spectral data were consistent with those reported previously.[13]



1-(6-(Tert-butyl)-3-methoxy-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)ethan-1-one (71c)
Prepared according to general procedure **A** using 1-(6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)ethan-1-one (49.0 mg, 0.10 mmol), methanol (0.05 ml, 1.2 mmol), Mes-Acr$^+$-Me ClO_4^- (0.84 mg, 0.002 mmol), K_2HPO_4 (104.6 mg, 0.60 mmol), $CBrCl_3$ (0.03 ml, 0.30 mmol), nitromethane (1.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100 % heptane to 10 % ethyl acetate); (reaction time: 48 h; isolated yield: 40%, 21.9 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 1.7 Hz, 1H), 7.35 (d, *J* = 1.7 Hz, 1H), 5.21 (dd, *J* = 5.5, 3.4 Hz, 1H), 3.42 (s, 3H), 2.61 (s, 3H), 2.08 (dd, *J* = 4.4, 2.7 Hz, 2H), 1.35 (d, *J* = 3.7 Hz, 12H), 1.30 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.7, 154.3, 152.6, 137.9, 135.4, 125.0, 123.1, 81.6, 57.1, 46.2, 42.6, 34.9, 31.2, 29.8, 28.8.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{18}H_{26}O_2]$ requires m/z 297.1825, found m/z 297.1818.

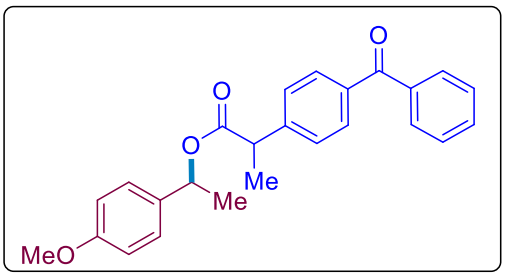


1-(4-Methoxyphenyl)ethyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (72c):

Prepared according to general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), loxoprofen (98.5 mg, 0.40 mmol), Mes-Acr$^+$-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 42.5 h; isolated yield: 59%, dr = 1:1, 44.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.02 (m, 6H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 5.86 – 5.74 (m, 1H), 3.84 – 3.75 (m, 3H), 3.71 – 3.59 (m, 1H), 3.16 – 3.01 (m, 1H), 2.51 (ddd, *J* = 13.9, 9.4, 4.7 Hz, 1H), 2.37 – 2.27 (m, 2H), 2.19 – 2.02 (m, 2H), 1.95 (tdd, *J* = 11.6, 6.3, 2.7 Hz, 1H), 1.80 – 1.67 (m, 1H), 1.62 – 1.53 (m, 2H), 1.51 – 1.36 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 173.7, 159.3, 159.1, 138.7, 138.7, 138.5, 138.4, 133.8, 133.8, 129.0, 129.0, 128.3, 128.2, 127.6, 127.6, 127.5, 127.2, 113.8, 113.6, 72.2, 72.2, 55.3, 55.2, 51.0, 45.3, 45.3, 38.2, 35.2, 35.2, 29.2, 29.2, 22.1, 21.8, 20.6, 18.4, 18.3, 18.3.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{24}H_{28}O_4]$ requires m/z 403.1879 found m/z 403.1899.

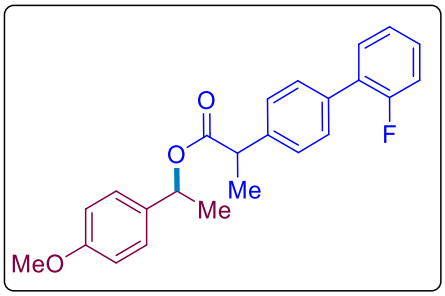


1-(4-Methoxyphenyl)ethyl 2-(4-benzoylphenyl)propanoate (73c):

Prepared according to general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), ketoprofen (102.0 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate). (reaction time: 42.5 h; isolated yield: 70%, dr = 1:1, 54.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 - 7.64 (m, 4H), 7.60 - 7.36 (m, 5H), 7.23 (d, *J* = 8.7 Hz, 1H), 7.07 (d, *J* = 8.7 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 1H), 5.88 – 5.77 (m, 1H), 3.89 – 3.67 (m, 4H), 1.49 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.5, 196.4, 173.3, 173.1, 159.3, 159.2, 140.9, 140.8, 137.9, 137.9, 137.6, 137.5, 133.5, 133.5, 132.5, 132.4, 131.6, 131.5, 130.0, 130.0, 129.2, 128.9, 128.8, 128.5, 128.5, 128.3, 128.3, 127.5, 127.2, 113.9, 113.7, 72.6, 72.5, 55.2, 55.2, 45.6, 45.6, 22.0, 21.8, 18.3, 18.2.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{25}H_{24}O_4]$ requires m/z 411.1566 found m/z 411.1559.

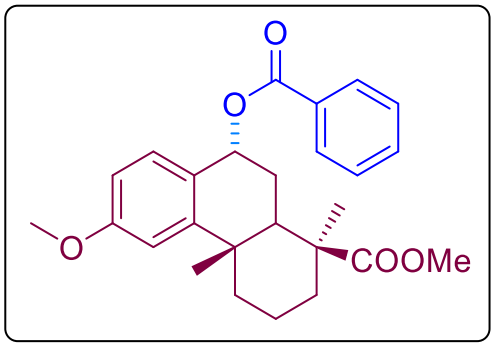


1-(4-Methoxyphenyl)ethyl 2-(2'-fluoro-[1,1'-biphenyl]-4-yl)propanoate (74c):

Prepared according to general procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), flubiprofen (97.7 mg, 0.40 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), ACN (2.0 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 15% ethyl acetate). Reaction time: 8.5 h; isolated yield: 64%; dr = 1:1, 48.4 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.30 (m, 6H), 7.25 (d, *J* = 0.9 Hz, 1H), 7.15 – 7.07 (m, 2H), 7.08 – 6.96 (m, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 1H), 5.85 (p, *J* = 6.5 Hz, 1H), 3.83 – 3.67 (m, 4H), 1.55 – 1.42 (m, 6H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.8 – -118.0 (m). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.2, 173.1, 160.9, 160.9, 159.4, 159.2, 142.0, 141.9, 141.9, 141.8, 135.6, 133.5, 133.5, 130.7, 130.8, 130.7, 130.6, 128.97, 129.0, 128.4, 127.6, 127.6, 127.3, 123.6, 123.6, 123.6, 123.5, 115.4, 115.4, 115.2, 115.1, 113.9, 113.7, 72.6, 72.6, 55.3, 55.2, 45.2, 22.0, 21.7, 18.3, 18.2.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{24}H_{23}O_4F]$ requires m/z 401.1523 found m/z 401.1533.

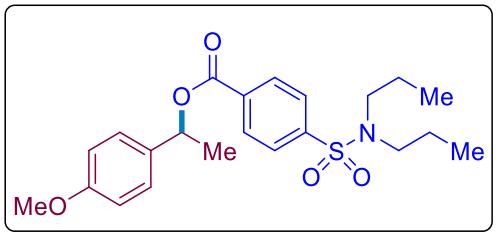


Methyl-9-(benzoyloxy)-6-methoxy-1,4a-dimethyl--octahydrophenanthrene-1-carboxylate (75c):

Prepared according to modified procedure **B** using O-methylpodocarpate (30.0 mg, 0.10 mmol), benzoic acid (37.0 mg, 0.3 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.42 mg, 0.001 mmol), K_2HPO_4 (52.3 mg, 0.30 mmol), CBr_4 (44.5 mg, 0.15 mmol), HFIP (0.5 mL), DCE (1.5 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100 % heptane to 15 % ethyl acetate); (reaction time: 40 h; isolated yield: 40%, 33.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.98 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 2.6 Hz, 1H), 6.74 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.30 – 6.23 (m, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 2.49 (d, *J* = 15.2 Hz, 1H), 2.39 – 2.22 (m, 3H), 2.10 (dd, *J* = 12.8, 1.5 Hz, 1H), 2.00 (ddd, *J* = 13.8, 10.3, 3.6 Hz, 1H), 1.69 (dd, *J* = 9.0, 5.2 Hz, 1H), 1.57 – 1.46 (m, 1H), 1.18 (s, 3H), 1.18 – 1.10 (m, 1H), 1.03 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.6, 166.1, 159.9, 150.9, 132.8, 132.3, 130.9, 129.6, 128.3, 124.9, 111.7, 110.9, 77.2, 71.3, 55.2, 51.3, 46.8, 43.5, 39.0, 38.7, 37.6, 28.4, 27.7, 21.8, 19.9.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{26}H_{30}O_5]$ requires m/z 445.1985 found m/z 445.2004.

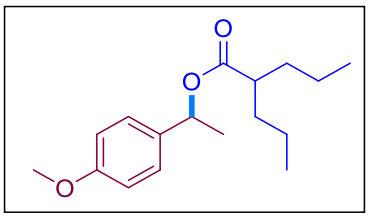


1-(4-Methoxyphenyl)ethyl 4-(N,N-dipropylsulfamoyl)benzoate (76c):

Prepared according to modified procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), probenecid (114.0 mg, 0.4 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), HFIP (0.5 mL), DCE (1.5 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 20% ethyl acetate). (reaction time: 8.5 h; isolated yield: 82%, 68.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.12 (q, *J* = 6.6 Hz, 1H), 3.80 (s, 3H), 3.09 (t, *J* = 6.9 Hz, 4H), 1.68 (d, *J* = 6.6 Hz, 3H), 1.59 – 1.41 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 159.5, 144.2, 134.0, 133.2, 130.2, 127.7, 127.0, 114.0, 73.6, 55.3, 50.1, 50.0, 22.0, 21.9, 11.2.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{22}H_{29}NO_5S]$ requires m/z 442.1658, found m/z 442.1658.

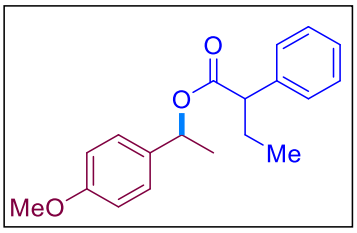


1-(4-methoxyphenyl)ethyl 2-propylpentanoate (77c):

Prepared according to the modified procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), valproic acid (0.096 ml, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), HFIP (0.5 mL), DCE (1.5 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate); (reaction time: 24.5 h; isolated yield: 80 %, 44.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.87 (q, *J* = 6.6 Hz, 1H), 3.80 (s, 3H), 2.48 – 2.22 (m, 1H), 1.74 – 1.53 (m, 2H), 1.51 (d, *J* = 6.6 Hz, 3H), 1.46 – 1.11 (m, 6H), 0.86 (dt, *J* = 15.9, 7.3 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.8, 159.2, 134.1, 127.5, 113.8, 77.4, 77.0, 76.7, 71.5, 55.3, 45.4, 34.7, 34.6, 22.0, 20.6, 20.5, 14.0, 14.0.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{17}H_{26}O_3]$ requires m/z 301.1774, found m/z 301.1765.

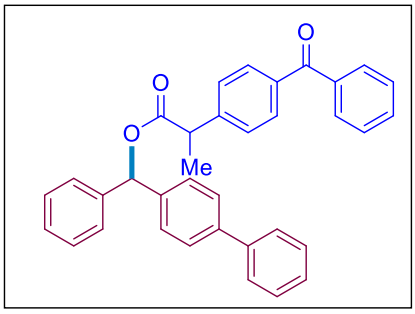


1-(4-Methoxyphenyl)ethyl 2-phenylbutanoate (78c):

Prepared according to the modified procedure **B** using 4-ethyl-anisole (27.0 mg, 0.20 mmol), 2-Phenylbutyricacid (99.0 mg, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^- (0.83 mg, 0.002 mmol), K_2HPO_4 (104.5 mg, 0.60 mmol), CBr_4 (99.5 mg, 0.30 mmol), HFIP (0.5 mL), DCE (1.5 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100% heptane to 25% ethyl acetate); (reaction time: 24.5 h; isolated yield: 71 %, dr 1:1, 42.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.18 (m, 6H), 7.07 (d, *J* = 8.6 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.76 (d, *J* = 8.7 Hz, 1H), 5.82 (qd, *J* = 6.5, 2.7 Hz, 1H), 3.83 – 3.72 (m, 3H), 3.45 (td, *J* = 7.7, 4.5 Hz, 1H), 2.16 – 1.99 (m, 1H), 1.91 – 1.69 (m, 1H), 1.48 (d, *J* = 6.6 Hz, 1.5H), 1.41 (d, *J* = 6.6 Hz, 1.5H), 0.86 (dt, *J* = 18.3, 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 173.1, 159.2, 159.1, 139.2, 139.9, 133.8, 133.8, 128.5, 128.4, 128.1, 128.0, 127.5, 127.2, 127.1, 127.0, 113.8, 113.7, 72.2, 72.1, 55.3, 55.2, 53.7, 53.7, 26.7, 26.5, 22.1, 21.7, 12.1.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{19}H_{22}O_3]$ requires m/z 321.1461, found m/z 321.1450.



(R)-[1,1'-Biphenyl]-4-yl(phenyl)methyl 2-(4-benzoylphenyl)propanoate (79c):

Prepared according to the modified procedure **B** using 4-benzyl-1,1'-biphenyl (49.0 mg, 0.20 mmol), ketonprofen (162.0 mg, 0.60 mmol), Mes-Acr^{+}-Me ClO_4^{-} (0.84 mg, 0.002 mmol), K_2HPO_4 (104.6 mg, 0.30 mmol), CBr_4 (99.0 mg, 0.15 mmol), HFIP (0.5 mL), DCE (1.5 mL), 40 W kessil lamp (456 nm). The product was purified by an automated flash chromatography system using a heptane/ethyl acetate gradient (from 100 % heptane to 15 % ethyl acetate); (reaction time: 40 h; isolated yield: 56%, dr = 1:1, 55.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.66 (m, 4H), 7.57 – 7.47 (m, 5H), 7.46 – 7.37 (m, 6H), 7.34 – 7.28 (m, 4H), 7.25 – 7.08 (m, 4H), 6.88 (s, 1H), 3.93 (q, *J* = 7.2 Hz, 1H), 1.57 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.4, 172.8, 141.0, 140.7, 140.6, 140.6, 140.5, 139.9, 139.9, 139.0, 138.9, 138.0, 137.5, 137.5, 132.5, 131.6, 131.6, 130.0, 130.0, 129.4, 129.4, 129.0, 128.8, 128.74, 128.6, 128.4, 128.3, 128.1, 127.9, 127.6, 127.4, 127.4, 127.3, 127.1, 127.1, 127.1, 126.7, 77.2, 77.1, 45.7, 45.6, 18.1, 18.1.

HRMS (ESI) $[M+Na]^+$ calculated for $[C_{35}H_{28}O_3]$ requires m/z 519.1930 found m/z 519.1919.

9. Details of DFT calculation

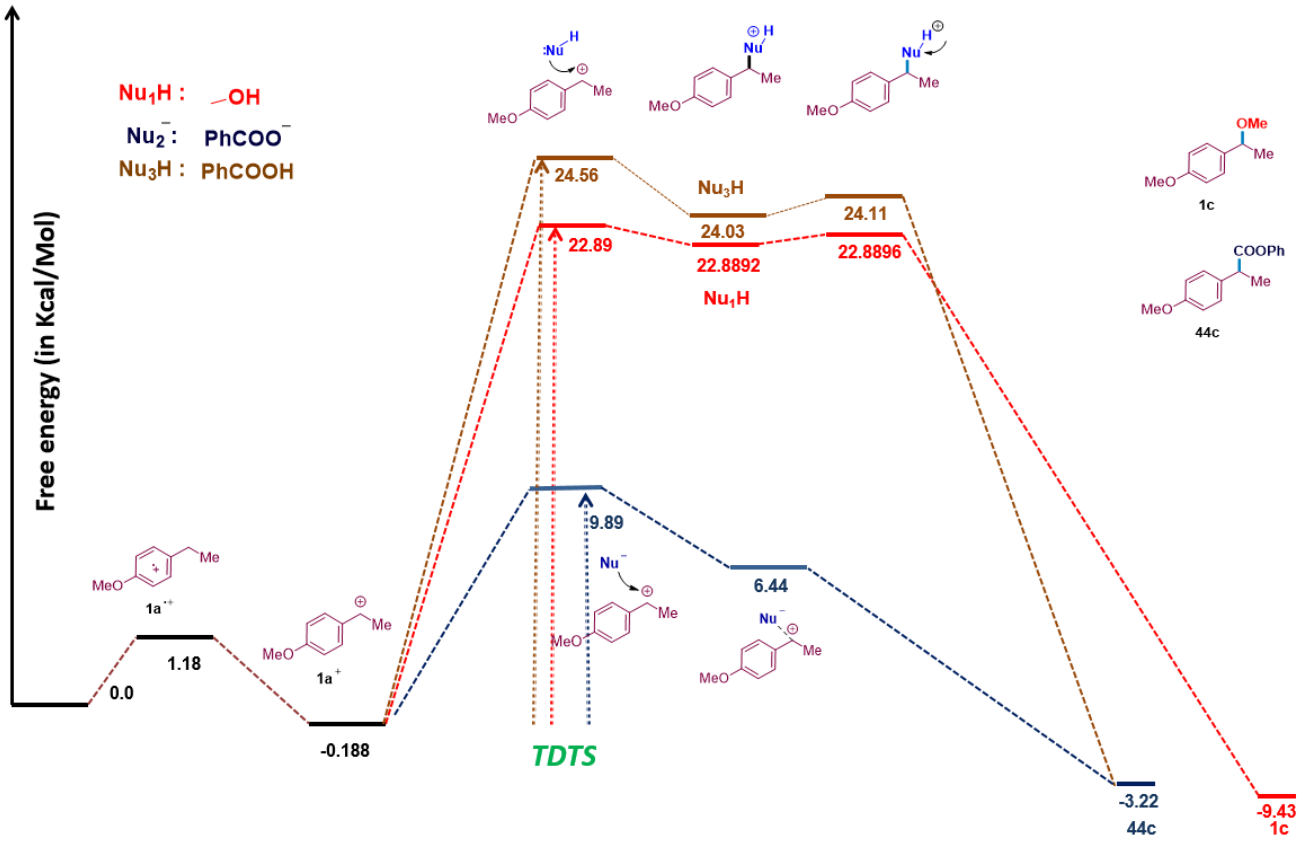


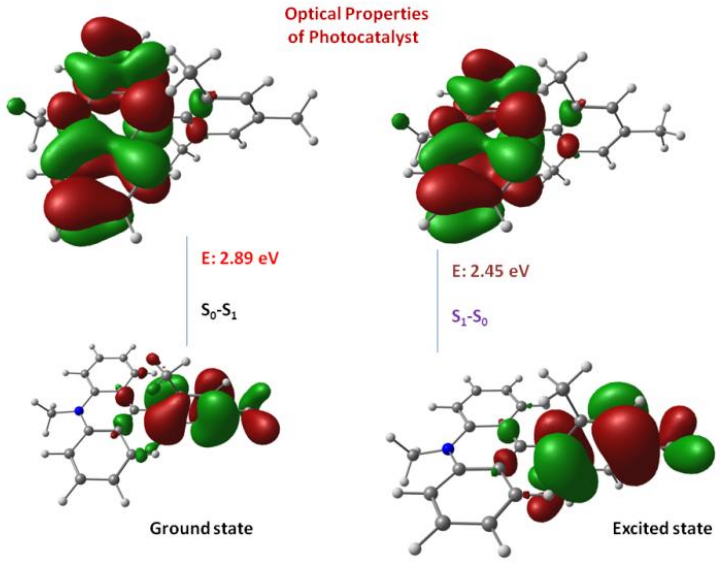
Figure S14: Gibbs free energy profile for the functionalization of benzylic C-H bonds catalyzed by the photocatalyst, based on B3LYP/6-311G. The relative Gibbs free energies (in kcal/mol) of intermediates and transition states are with respect to the reactant.

Methods :

DFT calculations were carried out with the Gaussian09 program package[22]. Ground state geometry optimizations and frequency calculations were performed at the gradient-corrected DFT level using B3LYP correlation functional sets. The excited state geometries optimized using time dependent –DFT (TDDFT) using aforementioned functional basis sets. Gibbs free energy calculations were carried out to confirm that the transition state structures connect the reactants and the respective products using IRC calculations using above mentioned sets (Fig. S12-S25). The excited state calculations in different solvents were carried out using PCM model. pKa calculations were carried out using PCM solvation models and Gibbs free energy has been calculated.

In order to study the photophysical behavior of acridine photocatalyst DFT calculations were carried out using Gaussian 09 program. The geometries of the acridine salt were optimized in ground state as well as excited state using 6-311G basis sets. FMO's obtained from the DFT calculations clearly revealed that the clear charge separation in the molecule both in ground state as well as excited state.

Figure S15: a: Frontier molecular orbitals of the photocatalyst acridine mesylate in ground state and excited state



To understand the solvent dependency of the photocatalyst acridine salt, we carried out the excited state calculations of the catalyst in different solvents using TDDFT methods. The strongest (S_1-S_0) transition with oscillator strength of (*f*= 1.482) in acetonitrile solvent was observed whereas other solvents showed only moderate transitions, it was providing the evidence for the enhanced catalytic ability of acridine salt photocatalyst in acetonitrile solvent.

Table-S2: The oscillator strength of the transitions occurred in acridinium cation in different solvents in excited state.

Sl. No	Solvent	Oscillator strength (*f*)
1	Methanol	0.96
2	Nitromethane	0.81
3	water	0.867
4	Acetonitrile	1.482
5	Hexane	0.782

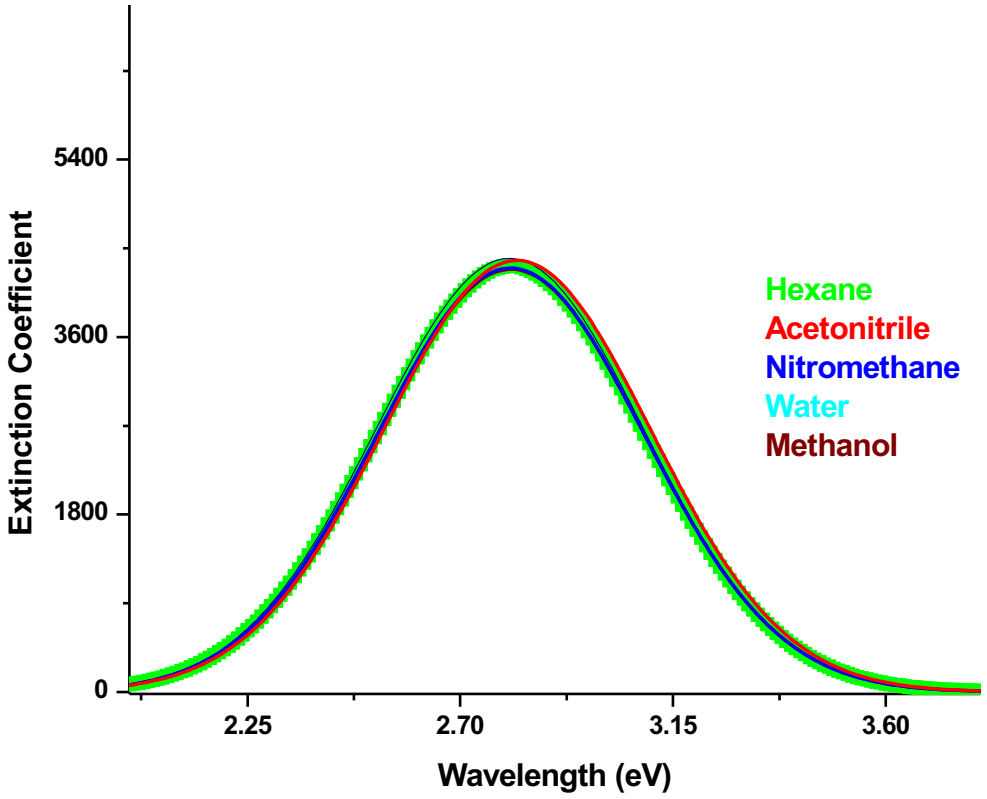


Figure S16: Stimulated emission spectra of Acridine cation in various solvents calculated by TDDFT /B3LYP method.

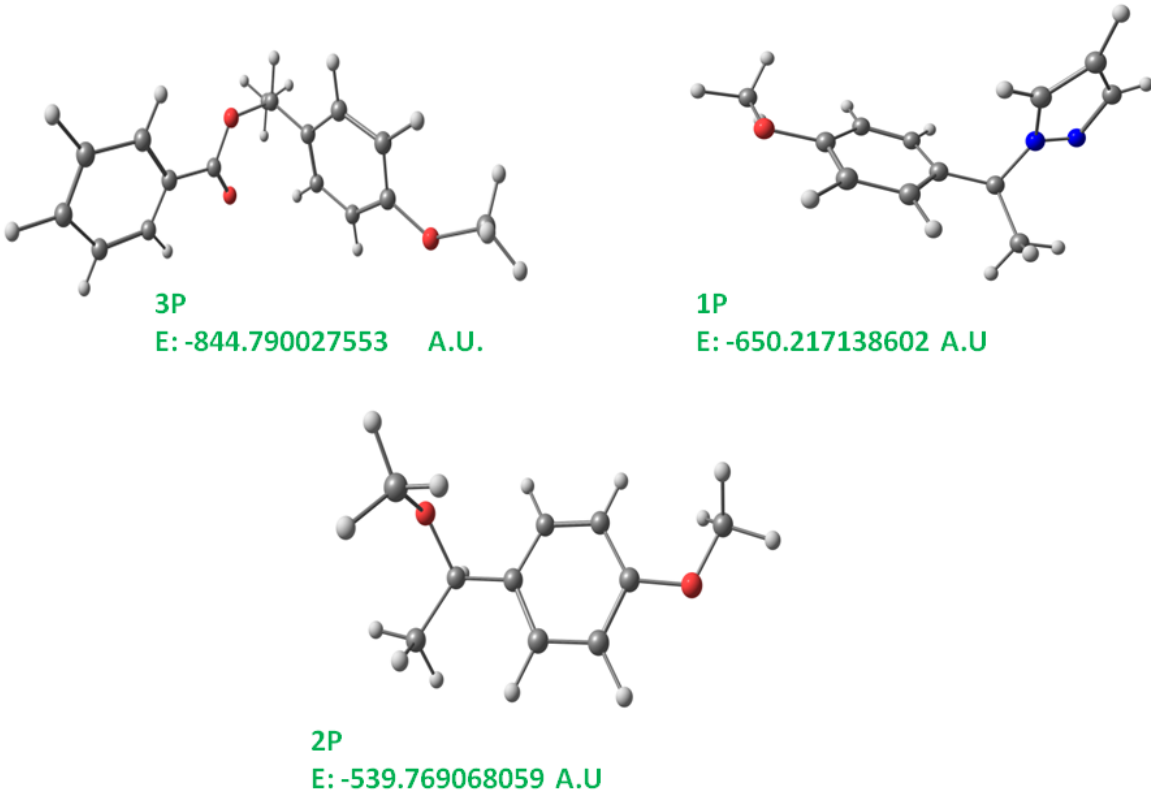


Figure S17: Energies of the products **1c**, **44c**.

Coordinates:

Catalyst ground state:

1	6	-7.402557000	-2.489727000	0.032881000
2	6	-6.028759000	-2.544530000	0.001724000
3	6	-5.241124000	-1.352516000	-0.068941000
4	6	-5.915883000	-0.082154000	-0.132898000
5	6	-7.333427000	-0.052177000	-0.076691000
6	6	-8.052497000	-1.230546000	0.005106000
7	6	-3.825062000	-1.408404000	-0.071959000
8	6	-3.783427000	1.066712000	-0.151230000
9	6	-3.092859000	-0.195130000	-0.087490000
10	6	-1.663296000	-0.192620000	-0.035986000
11	1	-1.155365000	-1.147964000	0.000859000
12	6	-0.953099000	0.984981000	-0.022716000
13	6	-1.647516000	2.220205000	-0.049953000
14	6	-3.028105000	2.267359000	-0.113634000
15	1	-7.988508000	-3.399105000	0.090031000
16	1	-5.509719000	-3.493872000	0.038573000
17	1	-7.870326000	0.884797000	-0.064327000
18	1	-9.134691000	-1.185466000	0.057263000
19	1	0.129322000	0.974429000	0.020015000
20	1	-1.089276000	3.149081000	-0.011831000
21	1	-3.515122000	3.231205000	-0.101581000

22	6	-3.115424000	-2.725083000	-0.040779000
23	6	-2.777619000	-3.365835000	-1.258332000
24	6	-2.783595000	-3.316604000	1.203330000
25	6	-2.109471000	-4.596667000	-1.204272000
26	6	-2.115199000	-4.548528000	1.201523000
27	6	-1.771511000	-5.207442000	0.012077000
28	1	-1.846106000	-5.088123000	-2.136340000
29	1	-1.856266000	-5.002275000	2.153745000
30	6	-3.118106000	-2.749828000	-2.600109000
31	1	-4.198830000	-2.605579000	-2.722985000
32	1	-2.642252000	-1.770375000	-2.734852000
33	1	-2.779335000	-3.392827000	-3.416215000
34	6	-3.130373000	-2.648231000	2.518314000
35	1	-2.656077000	-1.663764000	2.616717000
36	1	-4.211619000	-2.500103000	2.631179000
37	1	-2.794579000	-3.258291000	3.360523000
38	6	-1.076440000	-6.549005000	0.040738000
39	1	-1.806338000	-7.369014000	0.066498000
40	1	-0.452844000	-6.696682000	-0.846318000
41	1	-0.440389000	-6.652534000	0.925290000
42	7	-5.168232000	1.082017000	-0.240737000
43	6	-5.865888000	2.373226000	-0.475059000
44	1	-6.119628000	2.859086000	0.471242000
45	1	-5.229013000	3.026237000	-1.066239000

46	1	-6.769243000	2.196405000	-1.053171000

Catalyst –Excited state:

1	6	0.879747000	-3.687129000	-0.211745000
2	6	0.160624000	-2.503168000	-0.134871000
3	6	0.807583000	-1.237349000	-0.049427000
4	6	2.245529000	-1.223511000	-0.015817000
5	6	2.954812000	-2.433390000	-0.127084000
6	6	2.283381000	-3.652730000	-0.220102000
7	6	0.101841000	-0.000363000	-0.003034000
8	6	2.241335000	1.230157000	0.006974000
9	6	0.803333000	1.239675000	-0.026398000
10	6	0.152023000	2.504638000	-0.088325000
11	1	-0.930948000	2.541936000	-0.103058000
12	6	0.867064000	3.692289000	-0.143200000
13	6	2.270807000	3.662885000	-0.152210000
14	6	2.946440000	2.444347000	-0.081840000
15	1	0.357641000	-4.634948000	-0.277704000
16	1	-0.922213000	-2.543916000	-0.150343000
17	1	4.035199000	-2.431672000	-0.164707000
18	1	2.852931000	-4.570548000	-0.306215000
19	1	0.341699000	4.639370000	-0.191547000
20	1	2.837181000	4.584101000	-0.221304000
21	1	4.026822000	2.447040000	-0.119504000
22	6	-1.396431000	-0.003001000	0.005290000

23	6	-2.112558000	-0.016146000	1.290560000
24	6	-2.126254000	0.007072000	-1.208736000
25	6	-3.504889000	-0.018611000	1.309863000
26	6	-3.518737000	0.004248000	-1.143071000
27	6	-4.239827000	-0.008579000	0.116244000
28	1	-4.029207000	-0.028365000	2.257997000
29	1	-4.098702000	0.011816000	-2.060202000
30	6	-1.331012000	-0.026659000	2.564601000
31	1	-0.671354000	-0.901843000	2.606895000
32	1	-0.674768000	0.850159000	2.623380000
33	1	-1.985568000	-0.036125000	3.437631000
34	6	-1.421740000	0.020636000	-2.544011000
35	1	-0.783360000	0.903951000	-2.641135000
36	1	-0.779560000	-0.858004000	-2.657043000
37	1	-2.139811000	0.026531000	-3.367567000
38	6	-5.729329000	-0.010618000	0.098257000
39	1	-6.109487000	-0.881617000	-0.456204000
40	1	-6.157727000	-0.021231000	1.101033000
41	1	-6.111995000	0.870242000	-0.438649000
42	7	2.911688000	0.003147000	0.136822000
43	6	4.352927000	0.002714000	0.444107000
44	1	4.966912000	0.012077000	-0.463665000
45	1	4.594188000	0.876146000	1.048938000
46	1	4.597087000	-0.880910000	1.032764000

Radical cation:

1	6	-1.404025000	-0.273933000	-0.000252000
2	6	-0.443640000	-1.339895000	-0.001056000
3	6	0.901590000	-1.047394000	-0.001308000
4	6	1.353470000	0.304444000	-0.000969000
5	6	0.370624000	1.356805000	-0.000166000
6	6	-0.977806000	1.088854000	0.000169000
7	1	-0.815329000	-2.357570000	-0.001288000
8	1	1.624806000	-1.852078000	-0.001670000
9	1	0.713665000	2.386195000	0.000286000
10	1	-1.699621000	1.895679000	0.000716000
11	6	2.806827000	0.677400000	-0.001730000
12	1	2.979945000	1.340551000	0.864104000
13	1	2.980498000	1.333469000	-0.873000000
14	6	3.827731000	-0.465475000	0.002994000
15	1	4.839779000	-0.052197000	0.002966000
16	1	3.732912000	-1.094884000	0.894518000
17	1	3.735210000	-1.100388000	-0.884857000
18	8	-2.679744000	-0.668525000	-0.000036000
19	6	-3.828448000	0.274379000	0.001289000
20	1	-3.797064000	0.885230000	-0.903171000
21	1	-4.700446000	-0.373291000	0.003012000
22	1	-3.794342000	0.886375000	0.904862000

Benzyl cation:

1	6	-1.365044000	-0.279646000	-0.000009000
2	6	-0.425394000	-1.355224000	0.000055000
3	6	0.916716000	-1.090389000	0.000053000
4	6	1.402487000	0.271549000	0.000028000
5	6	0.424074000	1.334886000	0.000035000
6	6	-0.923876000	1.074385000	0.000040000
7	1	-0.814100000	-2.365709000	0.000108000
8	1	1.621537000	-1.912467000	0.000085000
9	1	0.773604000	2.362610000	0.000037000
10	1	-1.637791000	1.887306000	0.000075000
11	6	2.746095000	0.603837000	0.000007000
12	1	2.983780000	1.668405000	0.000041000
13	6	3.916872000	-0.300054000	-0.000073000
14	1	4.550915000	-0.081299000	-0.872802000
15	1	4.551154000	-0.081209000	0.872441000
16	1	3.675643000	-1.362682000	-0.000011000
17	8	-2.648483000	-0.650571000	-0.000041000
18	6	-3.762505000	0.325168000	-0.000051000
19	1	-3.718748000	0.937946000	-0.903091000
20	1	-4.655839000	-0.293262000	-0.000126000
21	1	-3.718832000	0.937856000	0.903051000

TS-1:

1	6	-3.268663000	-0.696259000	-0.456949000
2	6	-3.072925000	-1.868346000	0.334134000

3	6	-1.838689000	-2.138759000	0.860604000
4	6	-0.726929000	-1.248105000	0.624596000
5	6	-0.957335000	-0.070514000	-0.178829000
6	6	-2.197485000	0.202022000	-0.708947000
7	1	-3.924456000	-2.517619000	0.494082000
8	1	-1.698550000	-3.030290000	1.459539000
9	1	-0.114227000	0.593854000	-0.354146000
10	1	-2.350587000	1.088437000	-1.310482000
11	6	1.032889000	-2.576185000	1.954028000
12	1	1.466428000	-2.182181000	2.885714000
13	1	0.279323000	-3.322615000	2.206052000
14	1	1.870673000	-3.076879000	1.445127000
15	8	-4.516008000	-0.532881000	-0.921678000
16	6	-4.899049000	0.622141000	-1.759200000
17	1	-4.324075000	0.617066000	-2.688091000
18	1	-5.954803000	0.465269000	-1.963455000
19	1	-4.749919000	1.551786000	-1.205129000
20	6	3.860687000	2.674341000	-0.352620000
21	6	3.997619000	1.848609000	-1.459166000
22	1	4.413315000	3.547001000	-0.045454000
23	6	2.988659000	0.867663000	-1.322377000
24	1	4.721278000	1.938790000	-2.251616000
25	1	2.763329000	0.042034000	-1.978164000
26	6	0.552693000	-1.452953000	1.119510000

27	1	1.293737000	-0.691199000	0.854550000
28	7	2.257380000	1.058203000	-0.201033000
29	7	2.817739000	2.179915000	0.377495000
30	1	2.444639000	2.533240000	1.242167000

TS-2:

1	6	-2.981260000	0.168921000	0.147585000
2	6	-2.152238000	-0.364137000	1.156222000
3	6	-0.822032000	-0.649926000	0.886047000
4	6	-0.277032000	-0.411669000	-0.397078000
5	6	-1.119791000	0.117075000	-1.394499000
6	6	-2.459695000	0.407086000	-1.136236000
7	1	-2.586221000	-0.551582000	2.130677000
8	1	-0.212654000	-1.083217000	1.672571000
9	1	-0.732619000	0.281747000	-2.397499000
10	1	-3.084738000	0.797821000	-1.928662000
11	6	1.844877000	-1.857368000	-0.034325000
12	1	2.886172000	-1.946099000	-0.352637000
13	1	1.806415000	-1.789491000	1.055474000
14	1	1.330069000	-2.778477000	-0.326175000
15	8	-4.274829000	0.412243000	0.520062000
16	6	-5.235381000	0.934296000	-0.452842000
17	1	-5.359538000	0.236777000	-1.287087000
18	1	-6.167936000	1.023365000	0.099890000
19	1	-4.921881000	1.917012000	-0.819140000

20	6	2.243389000	1.026998000	0.994962000
21	6	3.573234000	1.100760000	1.191077000
22	1	1.400498000	1.148600000	1.656025000
23	6	4.210673000	0.841353000	-0.102165000
24	1	4.087103000	1.310879000	2.116224000
25	1	5.272134000	0.823636000	-0.307139000
26	6	1.150880000	-0.699182000	-0.728861000
27	1	1.307149000	-0.743699000	-1.809617000
28	7	3.366562000	0.617925000	-1.076617000
29	7	2.016345000	0.696565000	-0.415277000
30	1	1.483941000	1.420761000	-0.914438000

TS-3:

1	6	-2.796934000	-0.170757000	0.412013000
2	6	-1.962455000	-0.715579000	1.409784000
3	6	-0.631194000	-0.988927000	1.131954000
4	6	-0.090555000	-0.726022000	-0.148170000
5	6	-0.938684000	-0.185622000	-1.134755000
6	6	-2.279687000	0.092019000	-0.868769000
7	1	-2.393062000	-0.921795000	2.381937000
8	1	-0.017484000	-1.431571000	1.909852000
9	1	-0.554737000	-0.001832000	-2.135664000
10	1	-2.908795000	0.492381000	-1.653121000
11	6	2.040531000	-2.165137000	0.185453000
12	1	3.081635000	-2.242395000	-0.136454000

13	1	2.004010000	-2.115901000	1.276305000
14	1	1.530516000	-3.084214000	-0.120870000
15	8	-4.091139000	0.058417000	0.791319000
16	6	-5.057092000	0.591008000	-0.170432000
17	1	-5.178957000	-0.092952000	-1.016159000
18	1	-5.988934000	0.664881000	0.385730000
19	1	-4.750431000	1.581699000	-0.520648000
20	6	2.425069000	0.703765000	1.262081000
21	6	3.754964000	0.781898000	1.456102000
22	1	1.583207000	0.809308000	1.927196000
23	6	4.390528000	0.547987000	0.157090000
24	1	4.269943000	0.979551000	2.383376000
25	1	5.451523000	0.539873000	-0.050847000
26	6	1.338245000	-0.999524000	-0.487969000
27	1	1.492174000	-1.025001000	-1.569667000
28	7	3.545149000	0.336154000	-0.818863000
29	7	2.196335000	0.395850000	-0.153030000
30	1	1.658420000	1.125228000	-0.638524000

Product:

1	6	-4.409058000	-1.590590000	0.260152000
2	6	-3.110150000	-1.250132000	-0.144618000
3	6	-2.715208000	0.086218000	-0.167914000
4	6	-3.601098000	1.112171000	0.211582000
5	6	-4.896614000	0.750192000	0.609983000

6	6	-5.309826000	-0.585932000	0.638836000
7	1	-2.434343000	-2.045046000	-0.437355000
8	1	-1.708661000	0.327373000	-0.491319000
9	1	-5.596809000	1.525841000	0.907281000
10	1	-6.319288000	-0.825652000	0.949153000
11	6	-2.129431000	2.973241000	-0.813294000
12	1	-1.967367000	4.053309000	-0.767822000
13	1	-1.175127000	2.479654000	-0.602713000
14	1	-2.449011000	2.702958000	-1.825162000
15	8	-4.705508000	-2.948210000	0.248035000
16	6	-6.029857000	-3.380259000	0.657944000
17	1	-6.804508000	-2.966745000	0.001452000
18	1	-6.014902000	-4.465843000	0.570060000
19	1	-6.237343000	-3.095834000	1.696244000
20	7	-2.784244000	3.015449000	1.568457000
21	6	-2.204905000	2.294130000	2.579707000
22	6	-1.915698000	3.192128000	3.598460000
23	1	-2.060074000	1.229512000	2.509038000
24	6	-2.350092000	4.451756000	3.119299000
25	1	-1.465962000	2.968979000	4.552348000
26	1	-2.312099000	5.411075000	3.610647000
27	6	-3.205102000	2.582642000	0.213778000
28	1	-4.100597000	3.179122000	0.010788000
29	7	-2.878002000	4.356026000	1.881606000

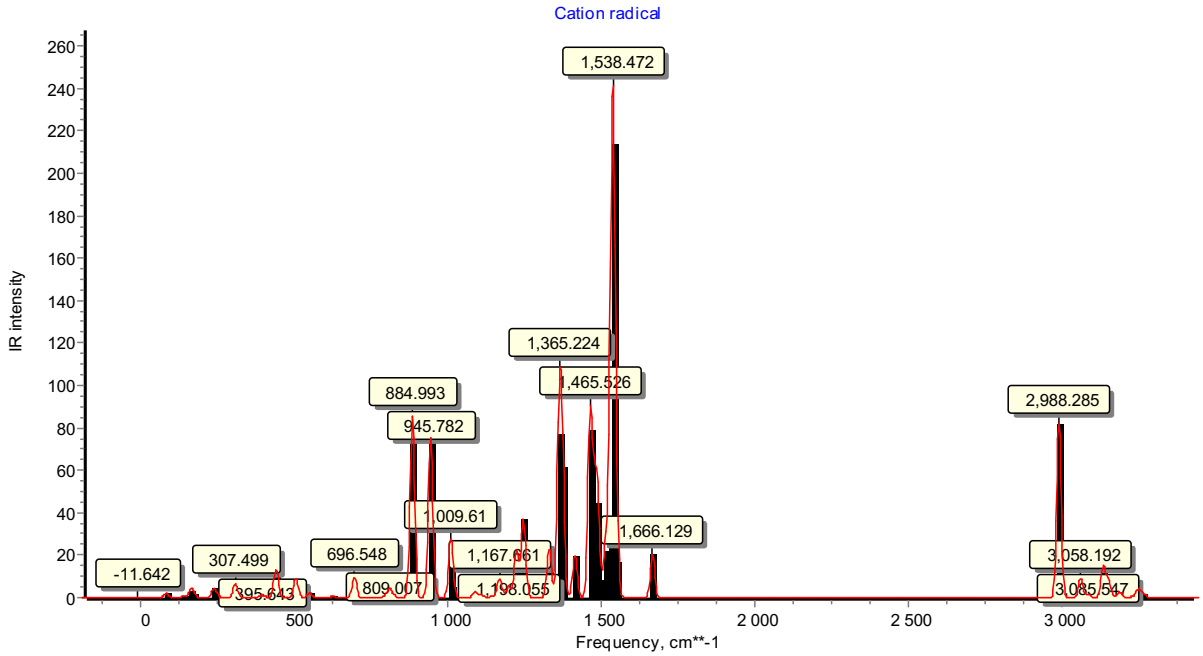


Figure S18: Stimulated IR spectrum of radical Cation.

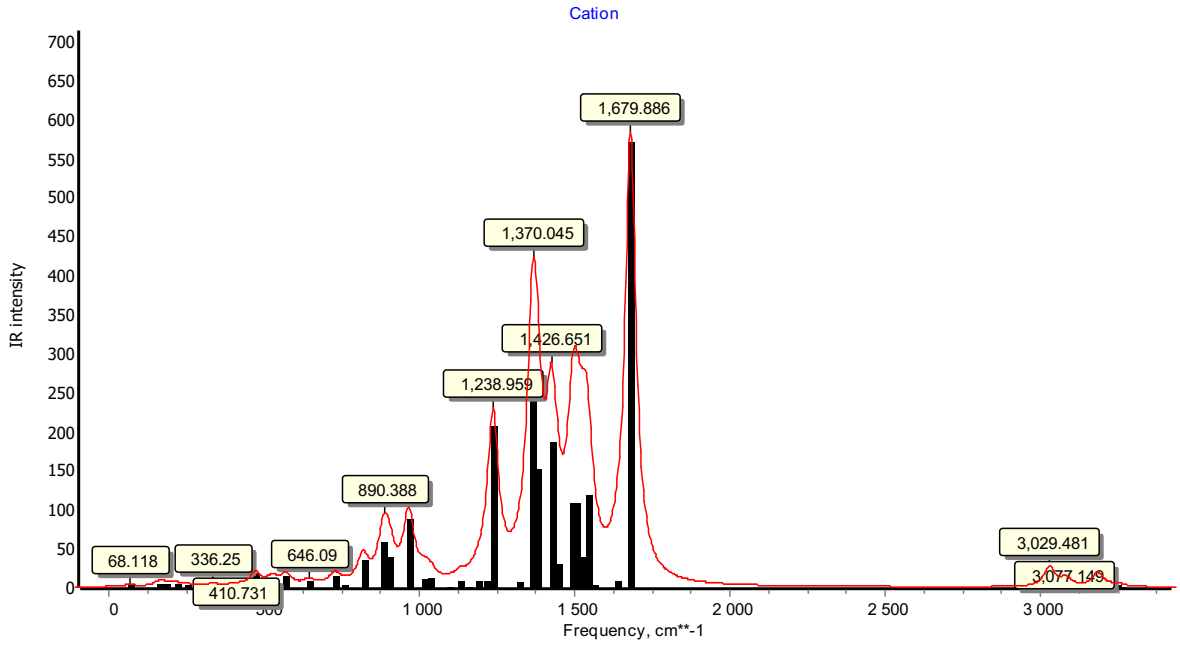


Figure S19: Stimulated IR spectrum of Cation.

Methanol Nucleophile (Nu_2H):

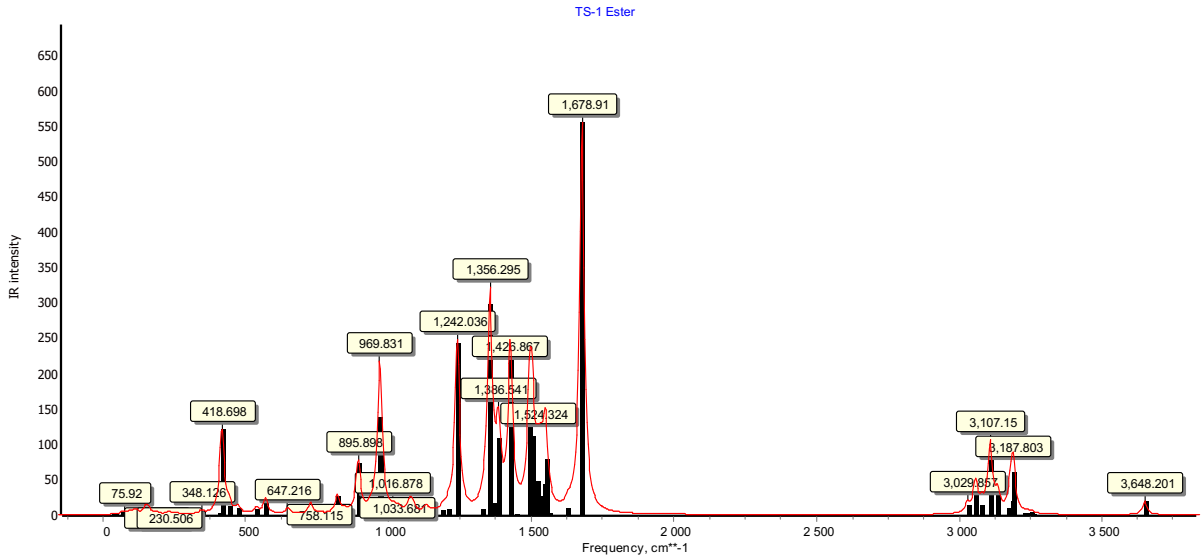


Figure S20: Stimulated IR spectrum of TS-1.

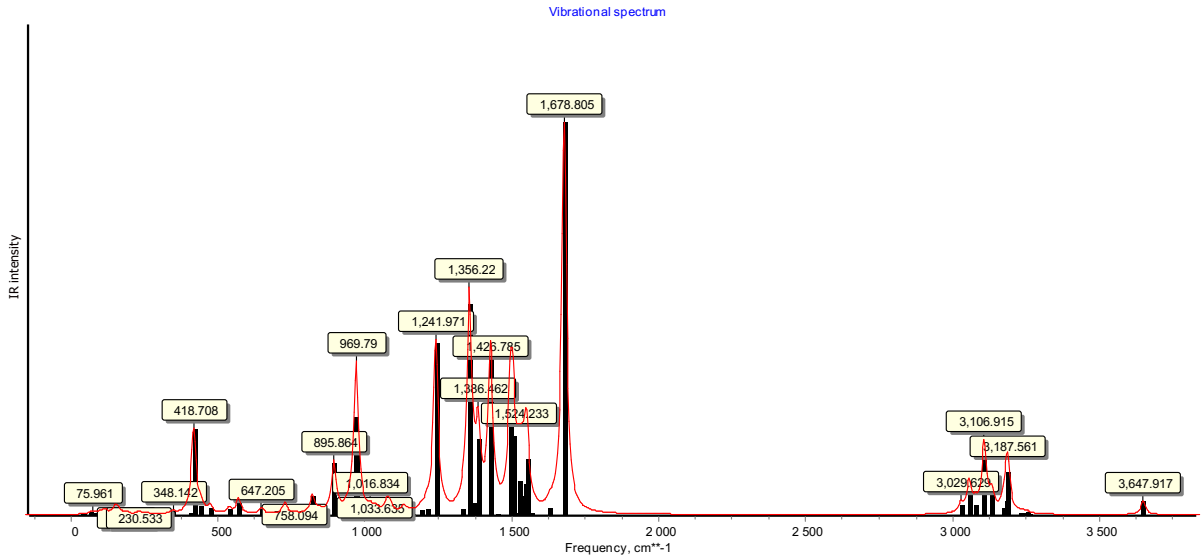


Figure S21: Stimulated IR spectrum of TS-2.

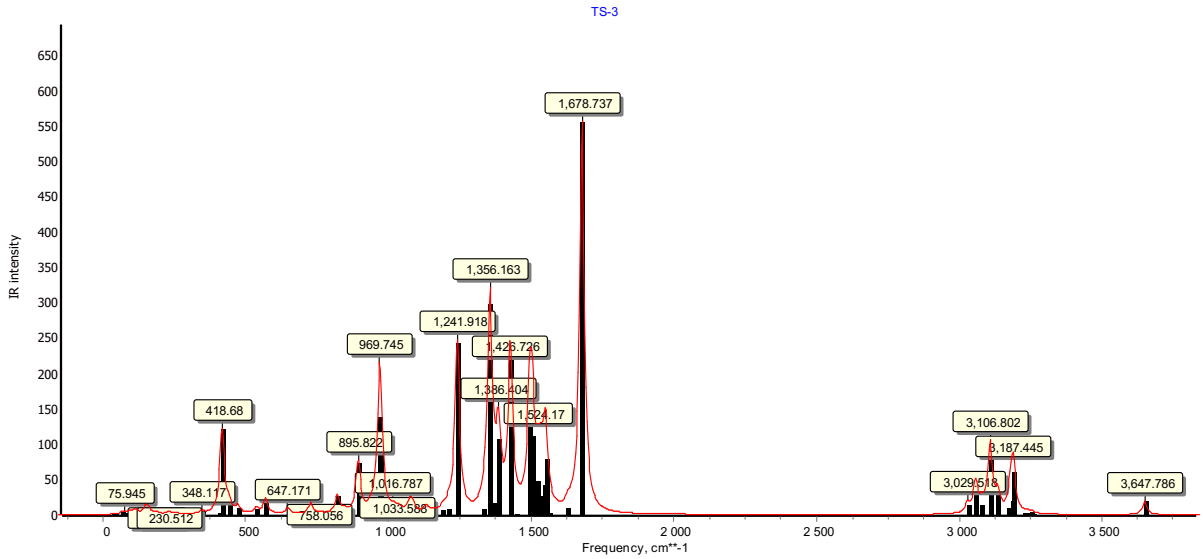


Figure S22: Stimulated IR spectrum of TS-3.

Benzoate Nucleophile (Nu_2) :

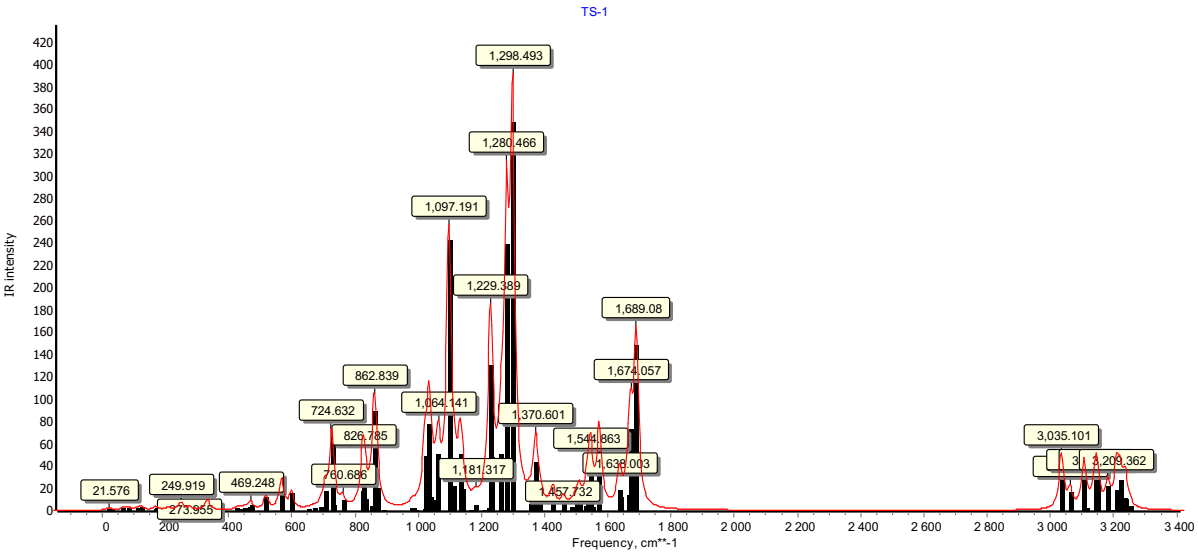


Figure S23: Stimulated IR spectrum of TS-1:

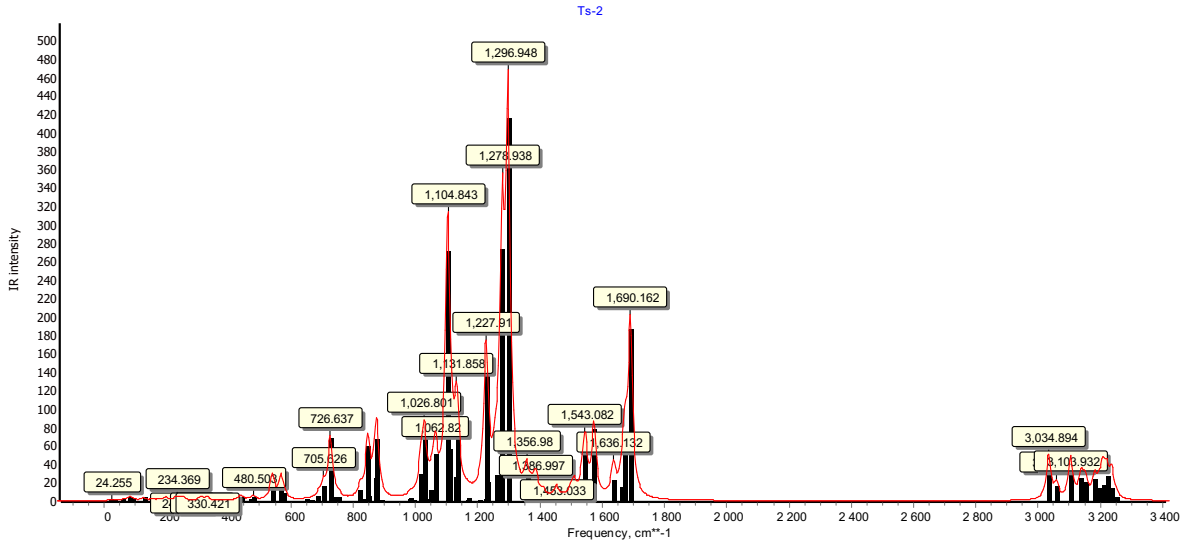


Figure S24: Stimulated IR spectrum of TS-2.

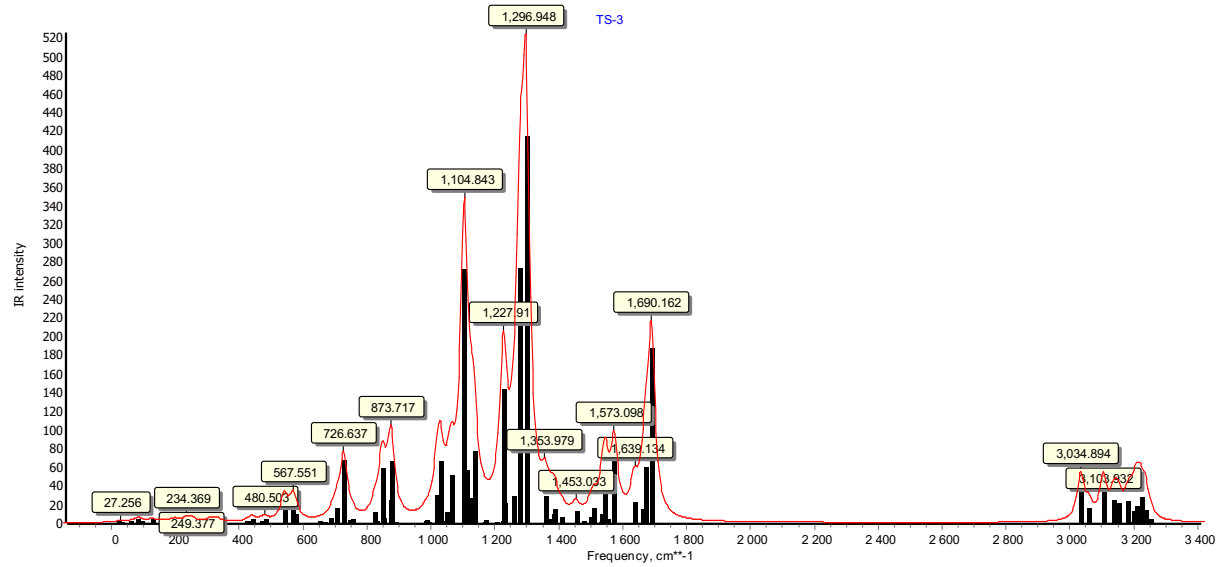


Figure S25: Stimulated IR spectrum of TS-3.

Benzoic acid nucleophile (Nu_3H) :

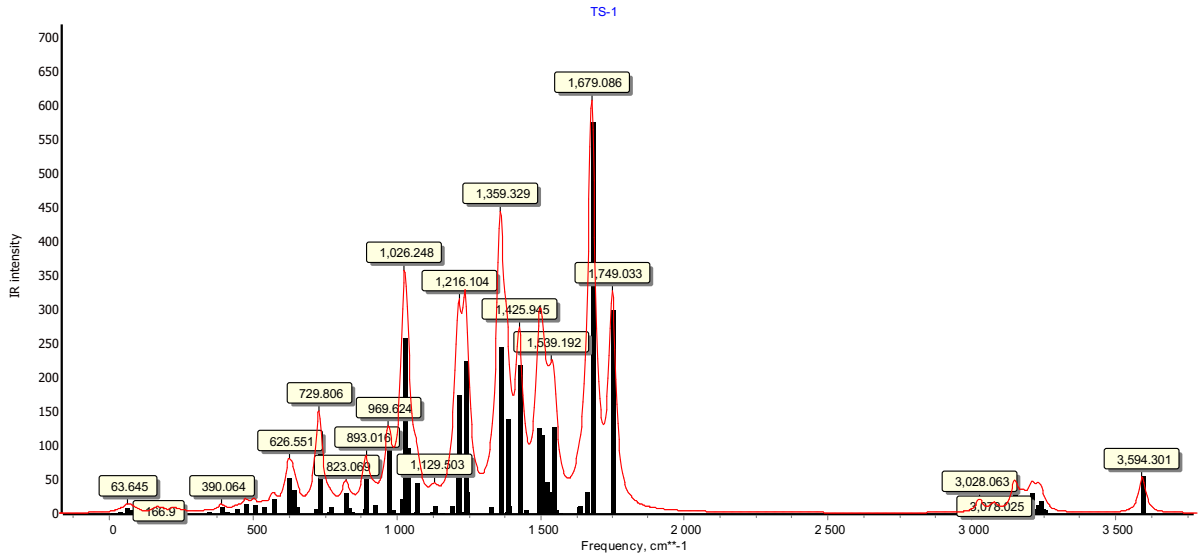


Figure S26: Stimulated IR spectrum of TS-1.

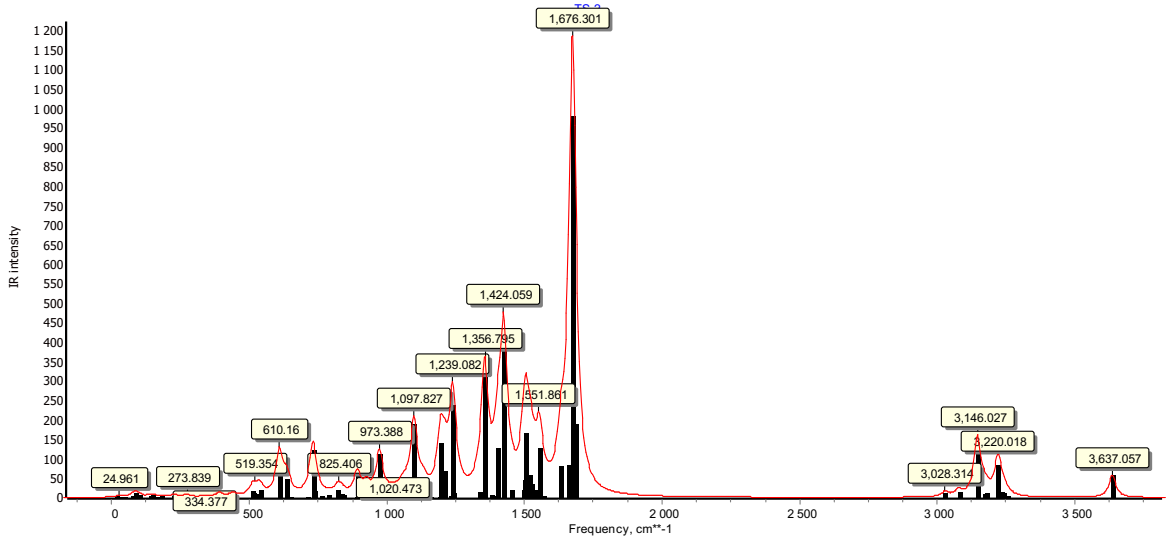


Figure S27: Stimulated IR spectrum of TS-2.

10. Details on cost estimation

An overview of the different steps for the three studied processes for the early stage technology cost estimation is presented in **Figure S22.** From this figure it becomes clear that the reaction step has the largest impact on the total process time.

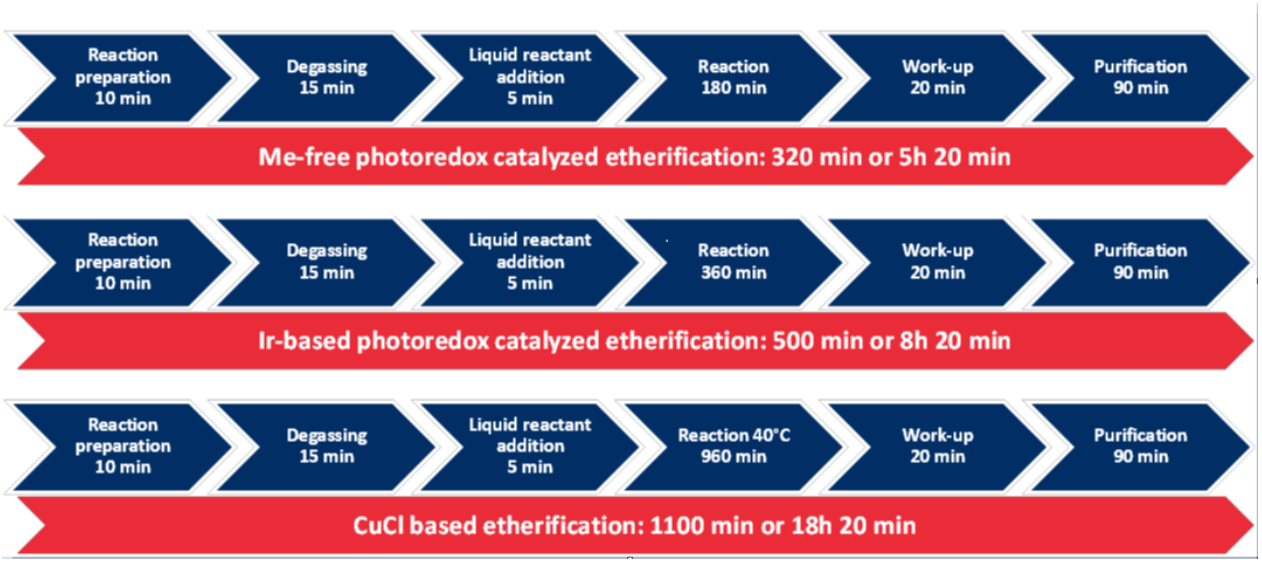


Figure S28: Overview of the different process steps for the etherification processes evaluated in the cost estimation.

As a first step, the mass balances for the first four steps (reaction preparation, degassing, liquid reactant addition and reaction) on a 1 g basis are constructed for the proposed transition metal-free photoredox catalyzed etherification, the Ir-based photoredox catalyzed etherification[5] and the copper-catalyzed etherification reaction[15]. For the Ir-based photoredox catalyzed etherification, two scenarios are studied for the cost estimation: (i) a scenario in which the price of a commercially available $Cu(TFA)_2$ is taken from Sigma Aldrich (denoted by IR based) and (ii) a scenario in which the cost of $Cu(TFA)_2$ is approximated by the cost of only the raw materials used to produce the oxidant as described by Lee et al., (2020)[5]. These are summarized in **Tables S3** – **S6**. The raw material costs per g are obtained from Sigma-Aldrich and are summarized in **Table S7**. The raw material costs are estimated by multiplying the costs summarized in **Table S7** with the global material inputs (second column) in **Table S3-S6**, respectively for the different studied protocols. This results in the material costs depicted in **Table S9**.

Table S3: Mass balance for the transition metal-free photoredox catalyzed etherification of 4-ethylanisole to 1 g of 1-methoxy-4-(1-methoxyethyl)benzene.

	Global material inputs (g/batch)	**Reaction preparation**		**Degassing**		**Liquid reactant addition**		**Reaction**	
		In	**Out**	**In**	**Out**	**In**	**Out**	**In**	**Out**
Substrate									
4-Ethylanisole	1.41					1.41	1.41	1.41	
Basic promoter									
K_2HPO_4	5.42	5.42	5.42	5.42	5.42	5.42	5.42	5.42	
Catalyst (homogeneous)									
Mes-Acr+-Me ClO_4-	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	
Oxidant									
CBr_4	5.16	5.16	5.16	5.16	5.16	5.16	5.16	5.16	
Alcohol									
Methanol	1.23					1.23	1.23	1.23	
Solvent									
Acetonitrile	0.05					0.05	0.05	0.05	

Product									
1-methoxy-4-(1-methoxyethyl)benzene									1.00
By-products/Waste streams									
Waste (generic)									12.31
In-out		**0.00**		**0.00**		**0.00**		**0.00**	

Table S4: Mass balance for the Ir-based photoredox catalyzed etherification of 4-ethylanisole to 1 g of 1-methoxy-4-(1-methoxyethyl)benzene (Ir-based).

	Global material inputs (g/batch)	**Reaction preparation**		**Degassing**		**Liquid reactant addition**		**Reaction**	
		In	**Out**	**In**	**Out**	**In**	**Out**	**In**	**Out**
Substrate									
4-Ethylanisole	1.12					1.12	1.12	1.12	
Basic promoter									
K_2HPO_4	4.31	4.31	4.31	4.31	4.31	4.31	4.31	4.31	
Catalyst (homogeneous)									
[Ir(dFCF_3ppy)2-(5,5'-dCF_3bpy)]PF_6	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	
Oxidant									
Cu(TFA)$_2$	2.86	2.86	2.86	2.86	2.86	2.86	2.86	2.86	
Alcohol									
Methanol	0.53					0.53	0.53	0.53	
Solvent									
Acetonitrile	39.48					39.48	39.48	39.48	
Product									
1-methoxy-4-(1-methoxyethyl)benzene									1.00
By-products/Waste streams									
Waste (generic)									47.33
In-out		**0.00**		**0.00**		**0.00**		**0.00**	

Table S5 Mass balance for Ir-based photoredox etherification reaction of 4-ethylanisole to 1 g of 1-methoxy-4-(1-methoxyethyl)benzene with the explicit use of reactants for the production of the oxidant (Ir-based RM).

	Global material inputs (g/batch)	**Reaction preparation**		**Degassing**		**Liquid reactant addition**		**Reaction**	
		In	**Out**	**In**	**Out**	**In**	**Out**	**In**	**Out**

Substrate									
4-Ethylanisole	1.12					1.12	1.12	1.12	
Basic promoter									
K_2HPO_4	4.31	4.31	4.31	4.31	4.31	4.31	4.31	4.31	
Catalyst (homogeneous)									
[Ir(dFCF$_3$ppy)2-(5,5'-dCF$_3$bpy)]PF$_6$	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	
Oxidant									
Cu(TFA)$_2$	2.86	2.86	2.86	2.86	2.86	2.86	2.86	2.86	
Basic copper carbonate	2.19								
Tetrafluoric acid	4.42								
3 Angstrom Molecular Sieves	1.97								
Acetonitrile	38.87								
Alcohol									
Methanol	0.53					0.53	0.53	0.53	
Solvent									
Acetonitrile	39.48					39.48	39.48	39.48	
Product									
1-methoxy-4-(1-methoxyethyl)benzene									1.00
By-products/Waste streams									
Waste (generic)									47.33
In-out		**0.00**		**0.00**		**0.00**		**0.00**	

Table S6: Mass balance for the copper-catalyzed etherification reaction of 4-ethylanisole to 1 g of 1-methoxy-4-(1-methoxyethyl)benzene. Note the triethylamine required after reaction for the quenching of unreacted NFSI.

	Global material inputs (g/batch)	**Reaction preparation**		**Degassing**		**Liquid reactant addition**		**Reaction**	
		In	**Out**	**In**	**Out**	**In**	**Out**	**In**	**Out**
Substrate									
4-Ethylanisole	1.19					1.19	1.19	1.19	
HAT promoter									
NFSI	3.04	3.04	3.04	3.04	3.04	3.04	3.04	3.04	
Catalyst (homogeneous)									
CuCl	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	
Ligand									
4,4'-5,5'-tetrahydro-2,2'-bioxazole	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	
Alcohol									
Methanol	1.40					1.40	1.40	1.40	
Solvent									

dimethyl phosphite	0.60					0.60	0.60	0.60	
Quenching of unreacted NFSI									
triethylamine	*4.41*								
Product									
1-methoxy-4-(1-methoxyethyl)benzene									1.00
By-products/Waste streams									
Waste (generic)									5.87
In-out		**0.00**		**0.00**		**0.00**		**0.00**	

Table S7*:* Prices used for the raw material cost estimation, obtained from Sigma-Aldrich.

Raw material	**Price [€/g]**
4-Ethylanisole	2.71
Methanol	0.04
$[Ir(dFCF_3ppy)_2$-(5,5'-dCF3bpy)]PF_6	858.00
Mes-Acr^+-Me ClO_4-	116.00
Acetonitrile	0.15
K_2HPO_4	0.16
$Cu(TFA)_2$	24.80
CBr_4	0.36
Ethyl acetate	0.10
n-heptane	0.08
1-methoxy-4-(1-methoxyethyl)benzene	83.38
Copper(i) chloride	6.69
N-Fluorobenzenesulfonimide (NFSI)	12.18
4,4′,5,5′-tetrahydro-2,2′- bioxazole	12.00
dimethyl phosphite	0.12
DCM	0.05
HFIP	5.18
4-Methoxy-α-methylbenzyl alcohol	8.67
$NaHSO_3$	0.13
Triethylamine	0.33
Basic Copper Carbonate	0.20
Tetrafluoric acid	0.34
3 Angstrom Molecular Sieves	0.11

Note: Sigma-Aldrich, https://www.sigmaaldrich.com/BE/en, visited on June 12, 2021.

As a second step, the energy costs are estimated based on the power consumption of the magnetic stirring+heating plate, power consumption of the Kessil lamp setup (lamp + fan) and assuming an electricity price of 74.2 €/MWh which corresponds to the electricity price for industrial users in Belgium. The energy costs are calculated by multiplying the electricity price with the electrical power consumption and the time of the reaction step as the main energy consumption takes place in this process step. For the different protocols studied, the reaction scale (i.e., the amount of product produced) and the reaction times differ (as depicted in **Table S8**). In order to be able to compare the different energy costs, the energy costs are divided by the mass of product produced such that the energy per gram of product can be compared. For all processes a 825 W stirring plate (with heating functionality) is considered, for the

transition metal-free photoredox catalyzed etherification and the Ir-based photoredox catalyzed etherficiation a 40 W Kessil-Lamp and a fan (12 V, 16 mA) are considered. To estimate the energy costs the maximum powers are assumed. For the Copper-based etherification only the energy consumption coming from the stirring plate is considered.

Table S8*:* Reaction scale (mmol of 4-ethylanisole) and reaction time for the studied protocols in literature.

	Metal-free	Ir-based	Ir-based RM	Copper-based
Substrate (4-Ethylanisole) [mmol]	0.2	0.5	0.5	0.1
Reaction time [h]	3	6	6	16

Early technology stage cost estimation

The costs of this transition metal-free photoredox catalyzed LSF processes have also been studied and compared with other state of the art LSF processes. The costs of the transition metal-free photoredox catalyzed etherification were compared with the costs of the Ir-based photoredox catalyzed etherification[5] and the costs for a copper-catalyzed etherification reaction.[15] For this purpose, the protocols for the conversion of 4-ethylanisole (**1a**) to 1-methoxy-4-(1-methoxyethyl)benzene (**1c**) were studied and raw material costs and energy costs were divided by the mass of product produced to compare the different processes in terms of raw material and energy costs. The raw material costs were estimated by constructing the mass balances for the reaction preparation, degassing, reactant addition and reaction steps. The prices for the raw materials per unit mass were obtained from Sigma Aldrich (see also **Table S7**). The energy costs were estimated based on the energy consumption of the stirring plate, illumination setup (for the photoredox catalyzed etherifications) and cooling (if applicable). From this study (see supporting information, section 12 for more details and **Fig. S26**), it became clear that the only substantial difference between these processes in terms of costs lied in the raw materials/chemicals that have been used, the energy consumption and the reaction time. The capital costs (costs for equipment and infrastructure) did not differ substantially, except that the photoredox processes required illumination by means of a Kessil lamp setup. This cost can be considered negligible compared to the costs related to other equipment as the glovebox and the BioTage® column for purifications. However, when scaling up the installation costs related to the illumination in the reactor design can become significant. The raw materials, energy costs and raw materials+energy costs per gram of product have been summarized in **Table S9**. Note that there are two entries for the Ir-based photoredox catalyzed process as two different manners have been considered for the calculations of the raw material and price of the oxidant. The entry Ir-based corresponds with the price of the commercially available $Cu(TFA)_2$ and the entry Ir-based RM corresponds to the raw material cost for the oxidant was approximated by the raw material costs needed to produce the oxidant according to the protocol for the synthesis of the oxidant.[13] From **Table S9**, it is clear that the transition metal-free catalyzed photoredox process (M-free) has the lowest raw material costs+energy costs per gm of product produced, compared with the Ir-based photoredox and copper-based etherifications. This indicates that this metal-free process is also more interesting from an economic point of view.

	M-free	Ir-based	Ir-based RM	Copper-based
Raw material costs [€/g product]	11.57	109.70	46.65	47.65

Energy costs [€/g product]	9.99	6.35	6.35	96.07
Raw material + energy costs [€/g product]	21.56	116.05	53.00	143.72

Table S9: Overview of the raw material costs, energy costs and raw material + energy costs for the production of 1 g of 1-methoxy-4-(1-methoxyethyl)benzene from 4-ethylanisole using metal-free photoredox etherification, Ir-based photoredox etherification (Ir-based: according to the protocol[13] assuming a commercially available oxidant $Cu(TFA)_2$, Ir-based RM: protocol using the raw material costs used for the production of the oxidant to approximate the cost of the oxidant $Cu(TFA)_2$) and Copper-based etherification.

11. References

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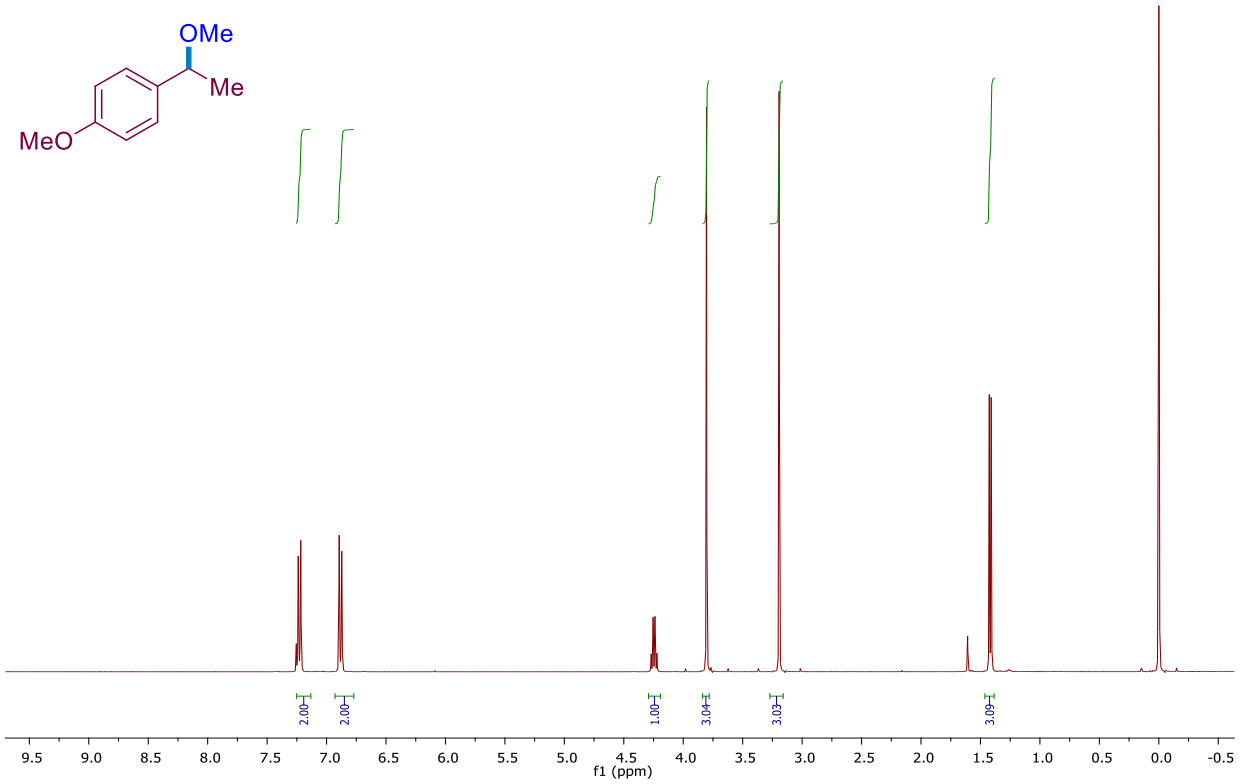
12. NMR data

1c



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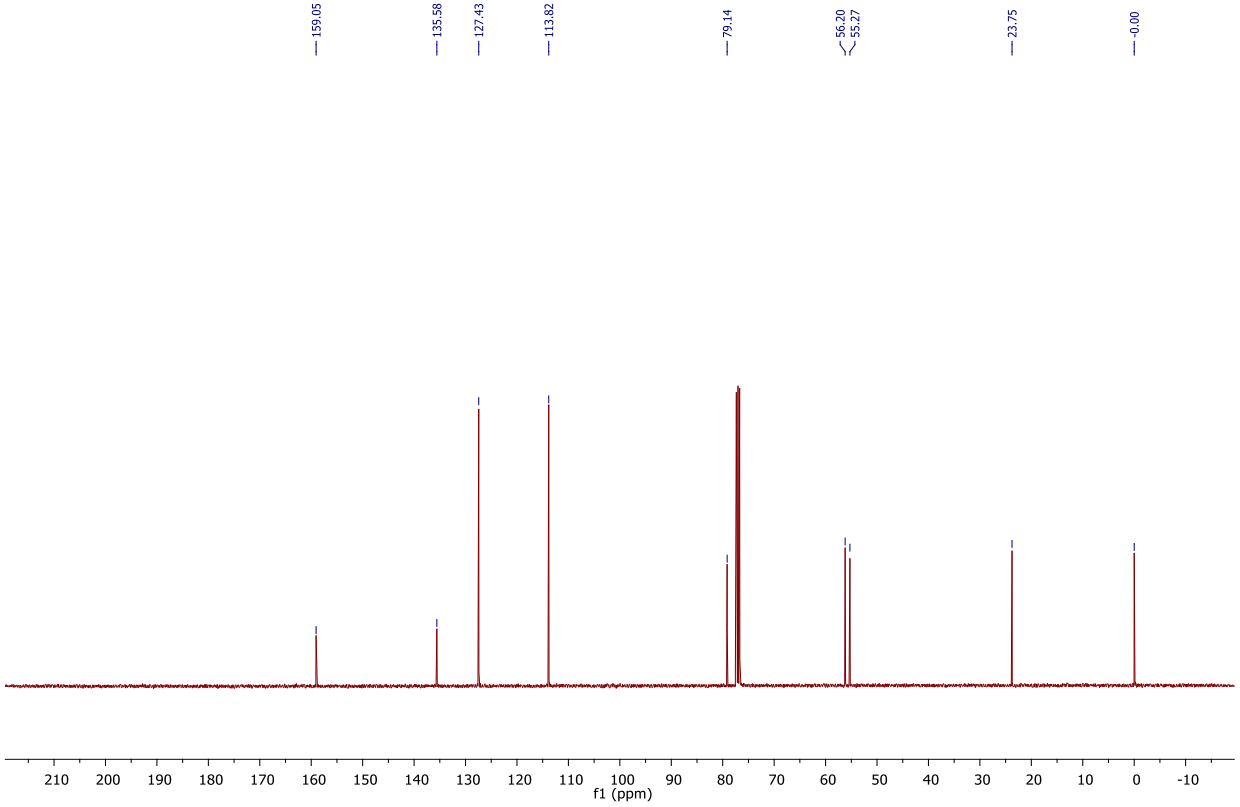

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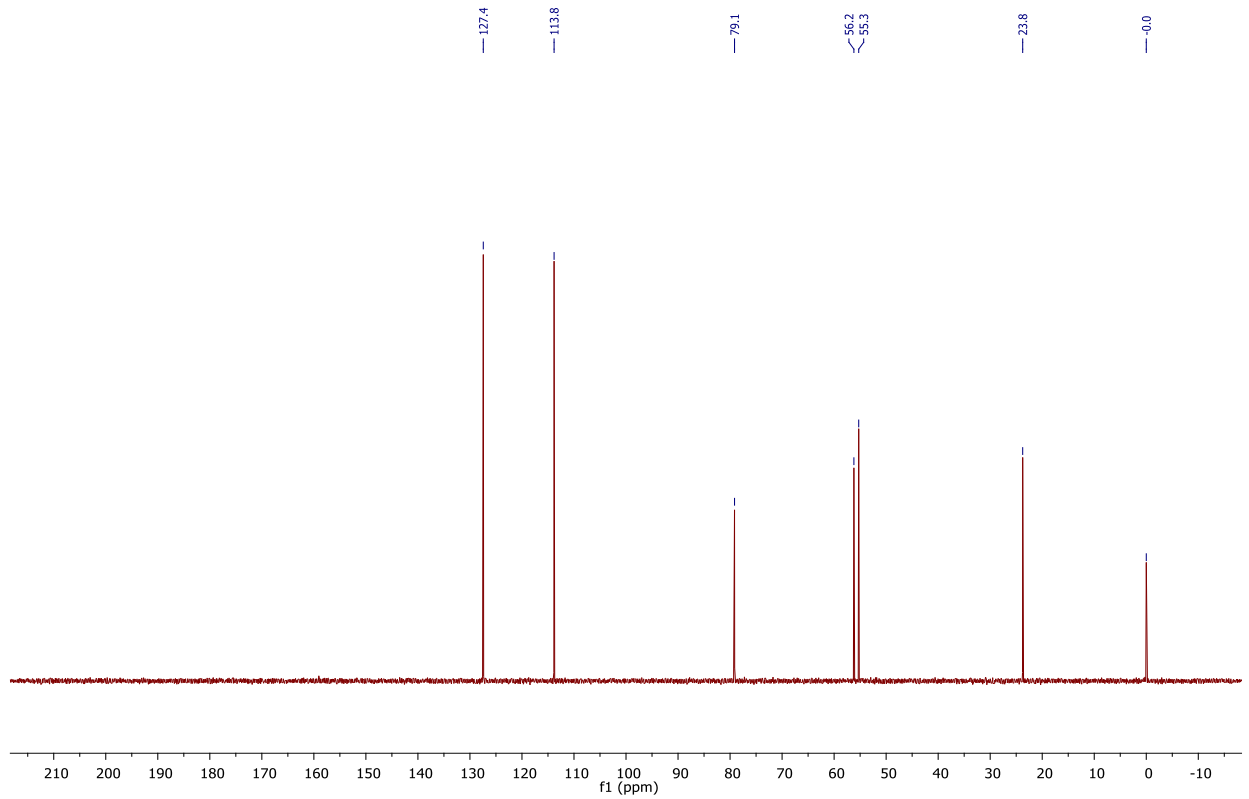

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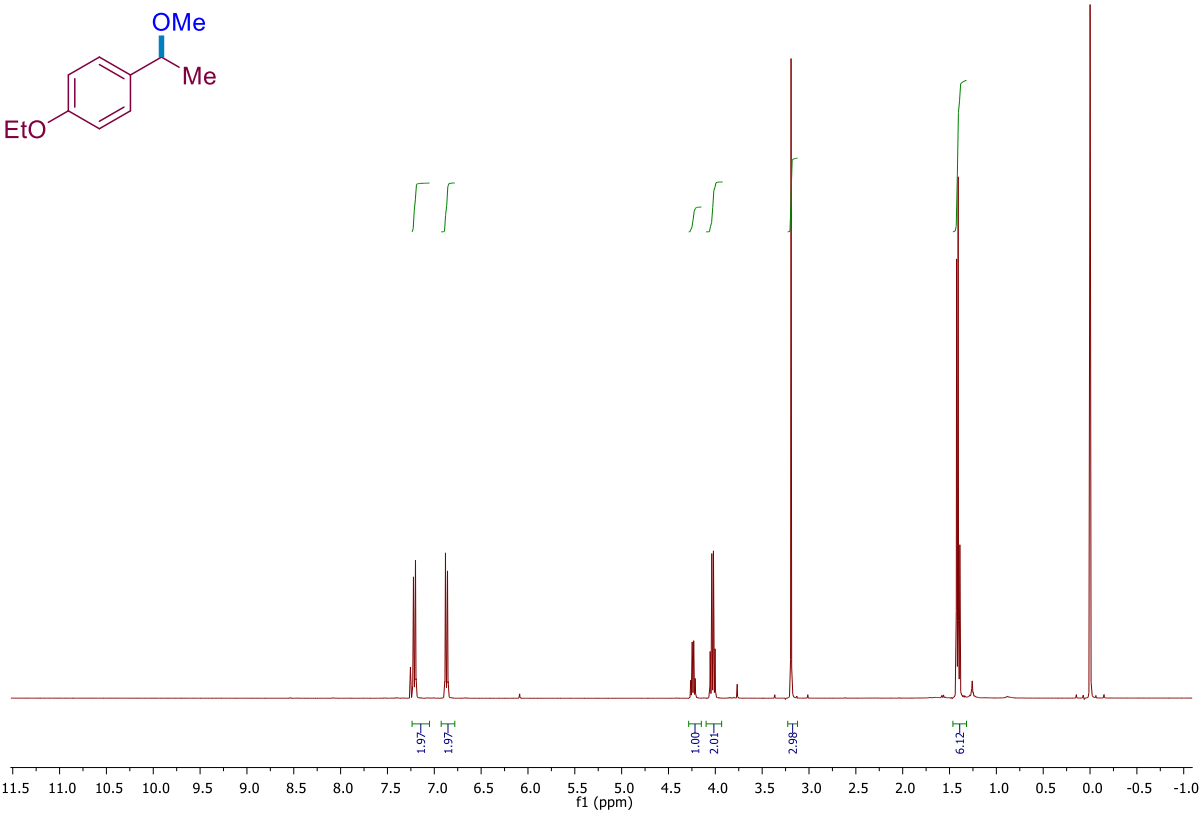

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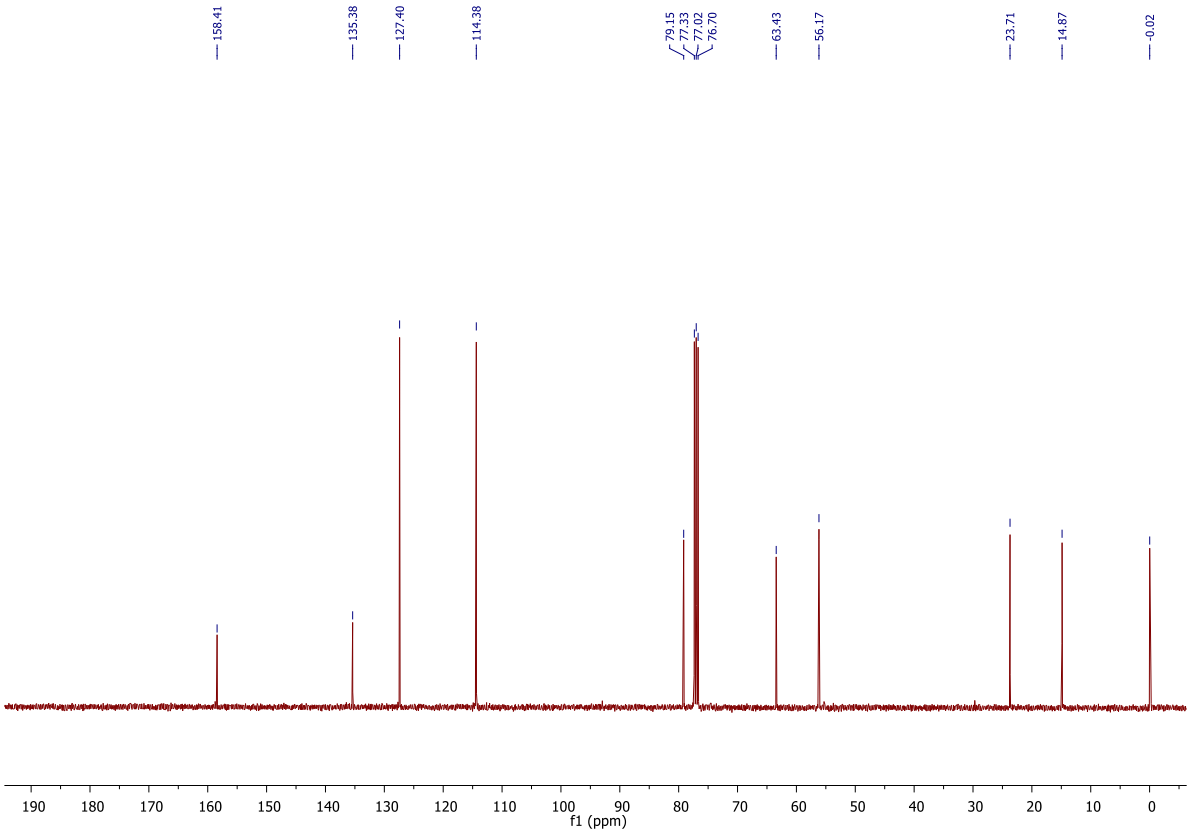

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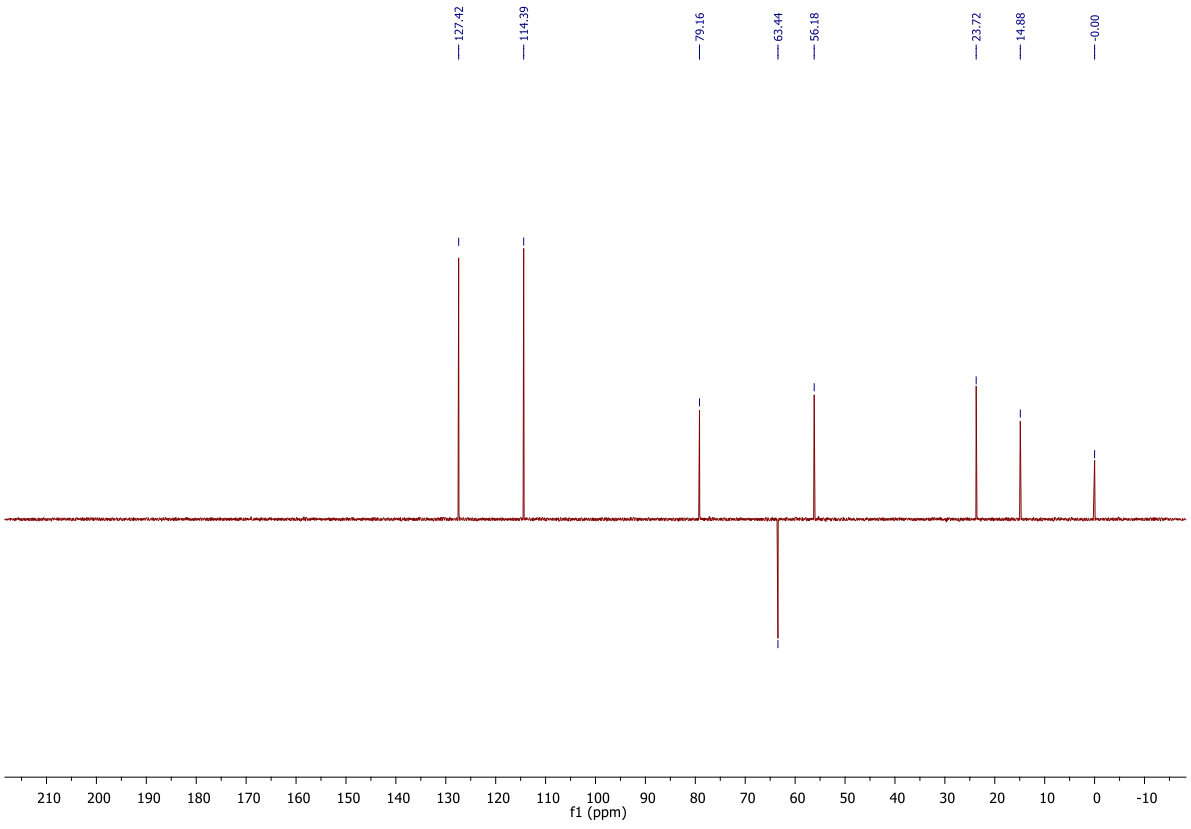

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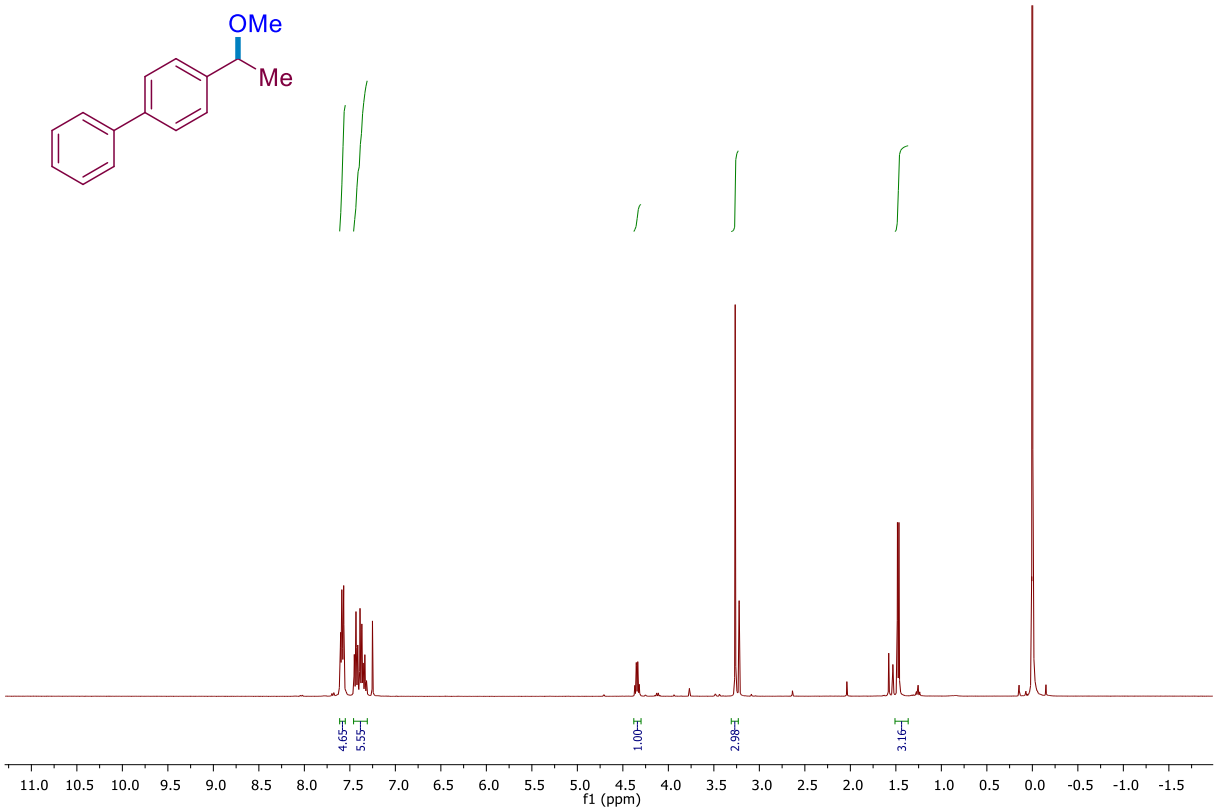

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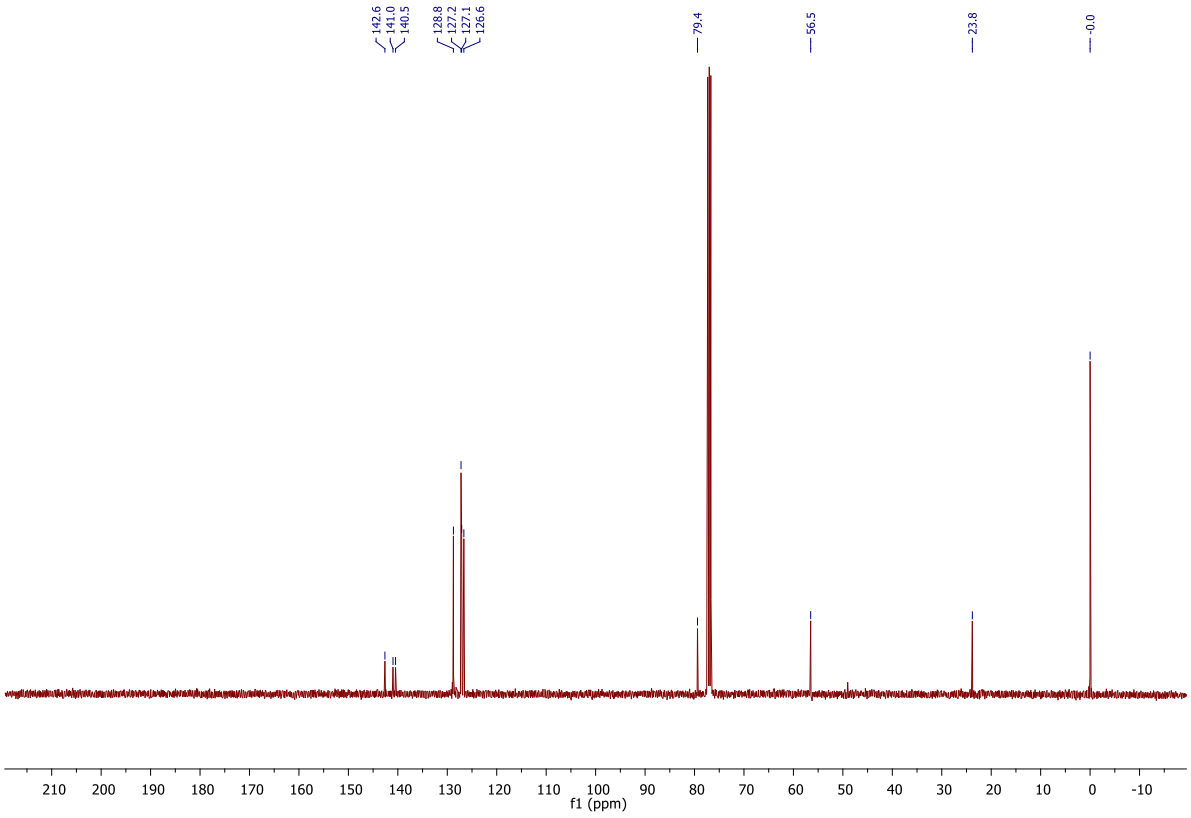

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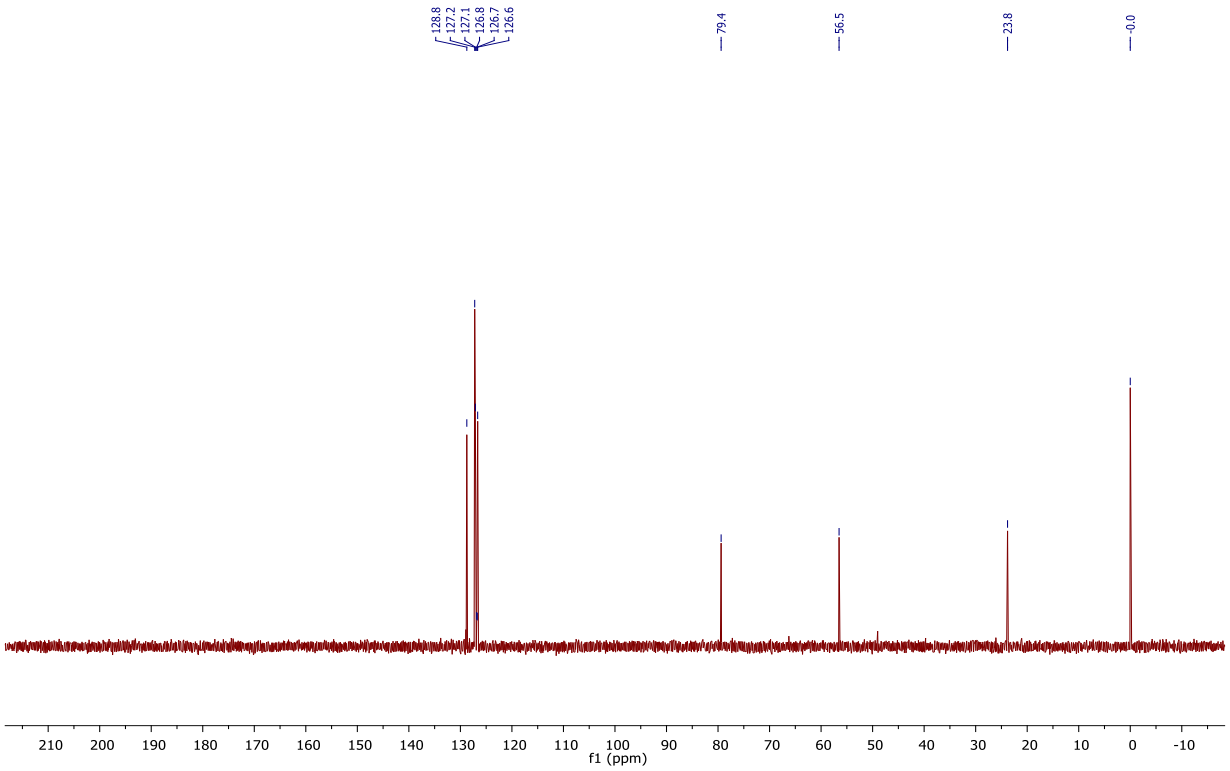

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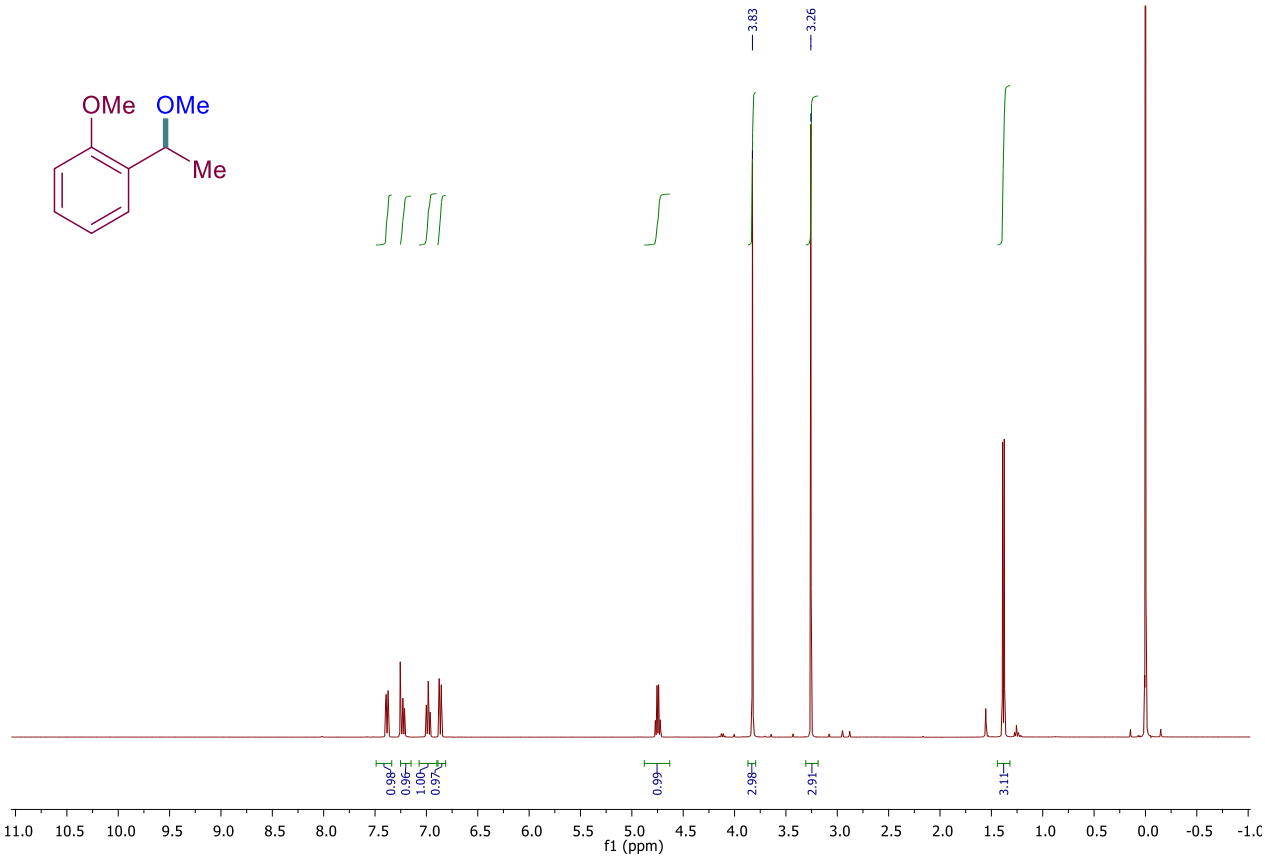

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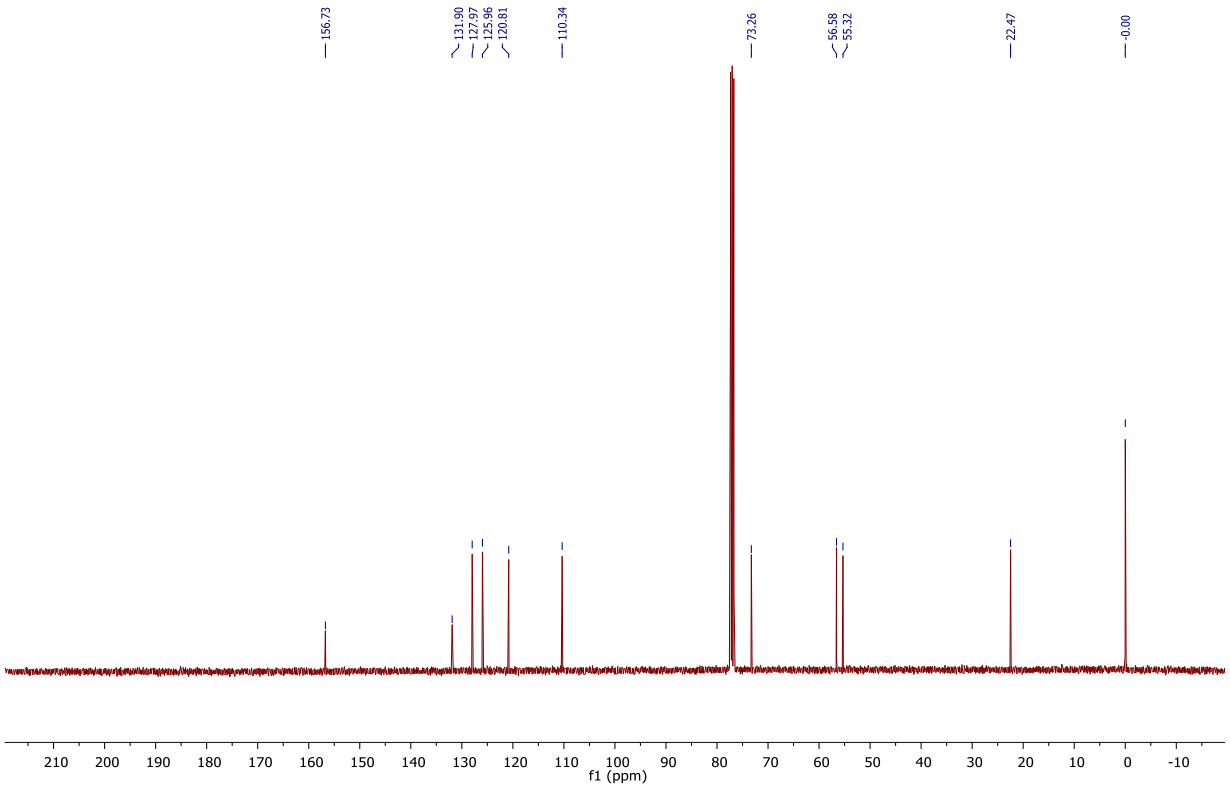

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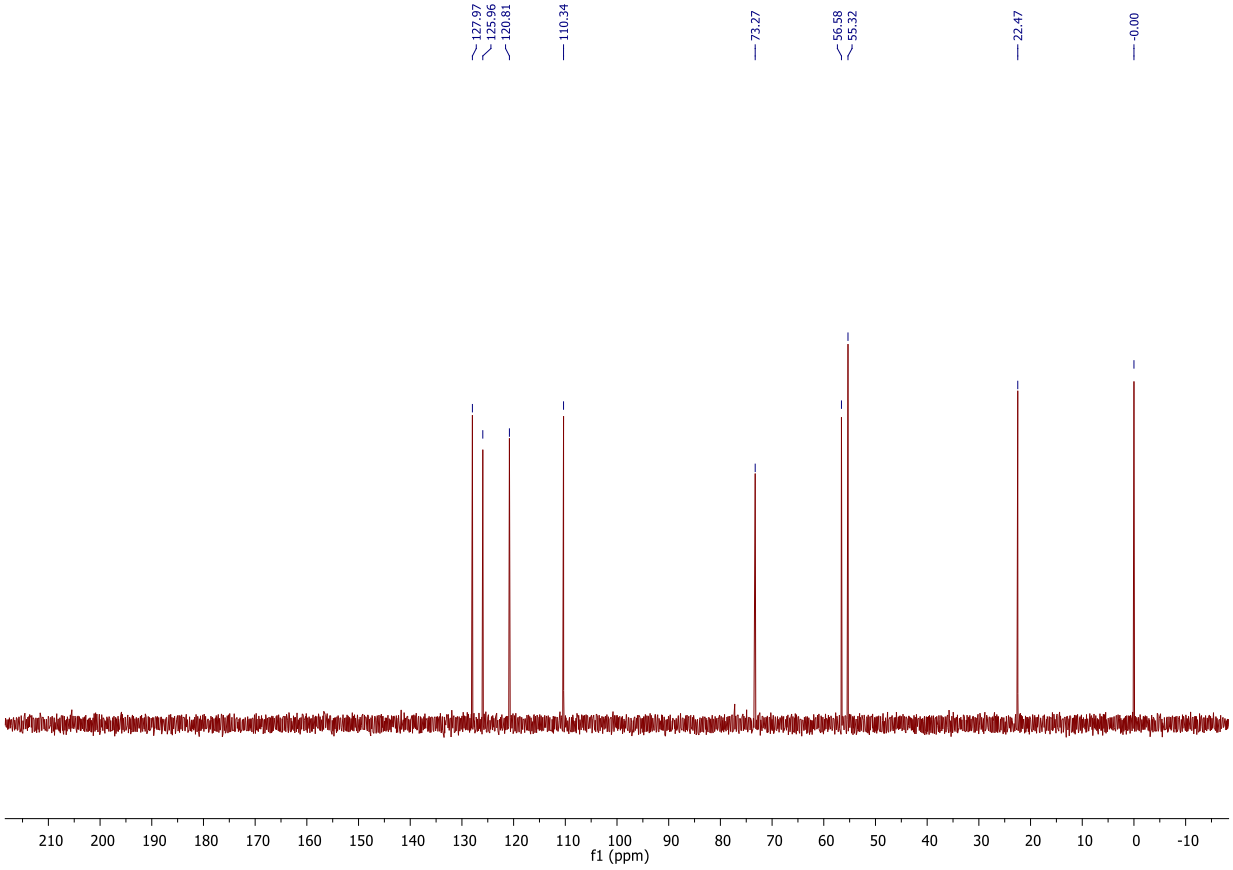

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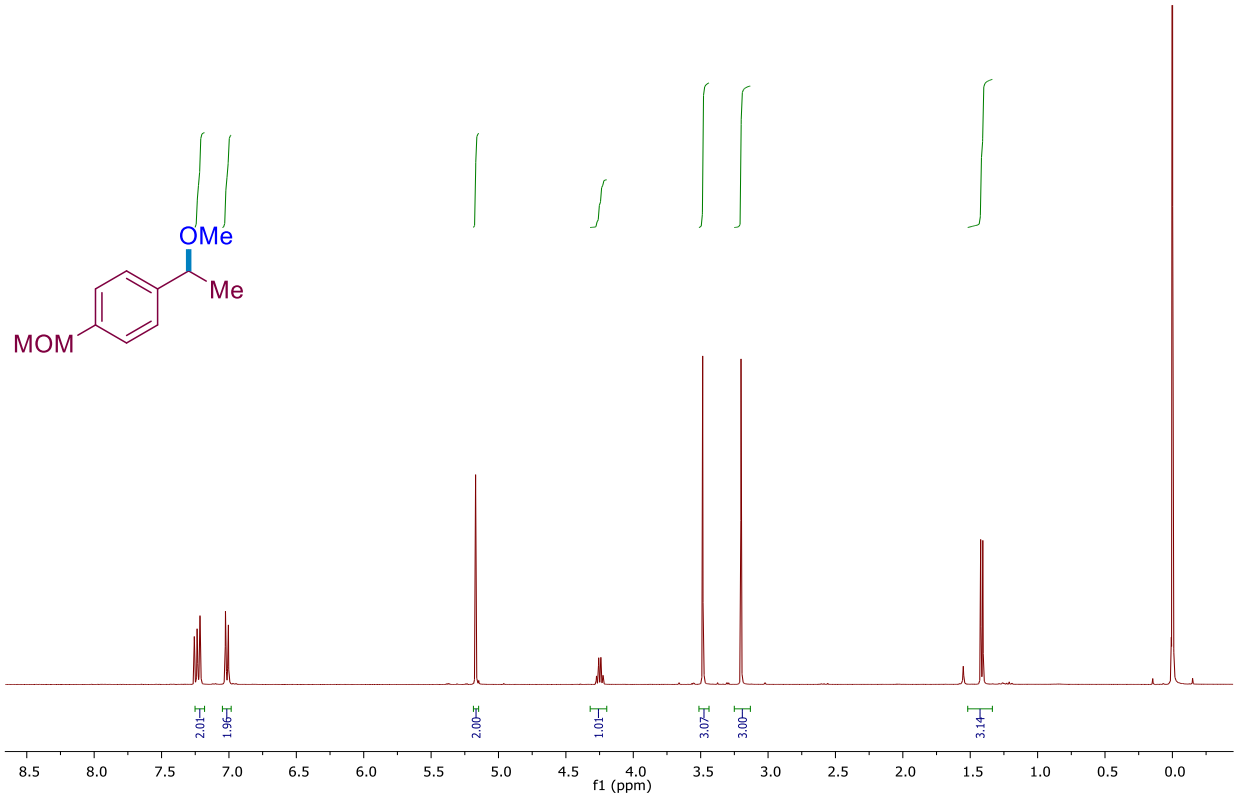

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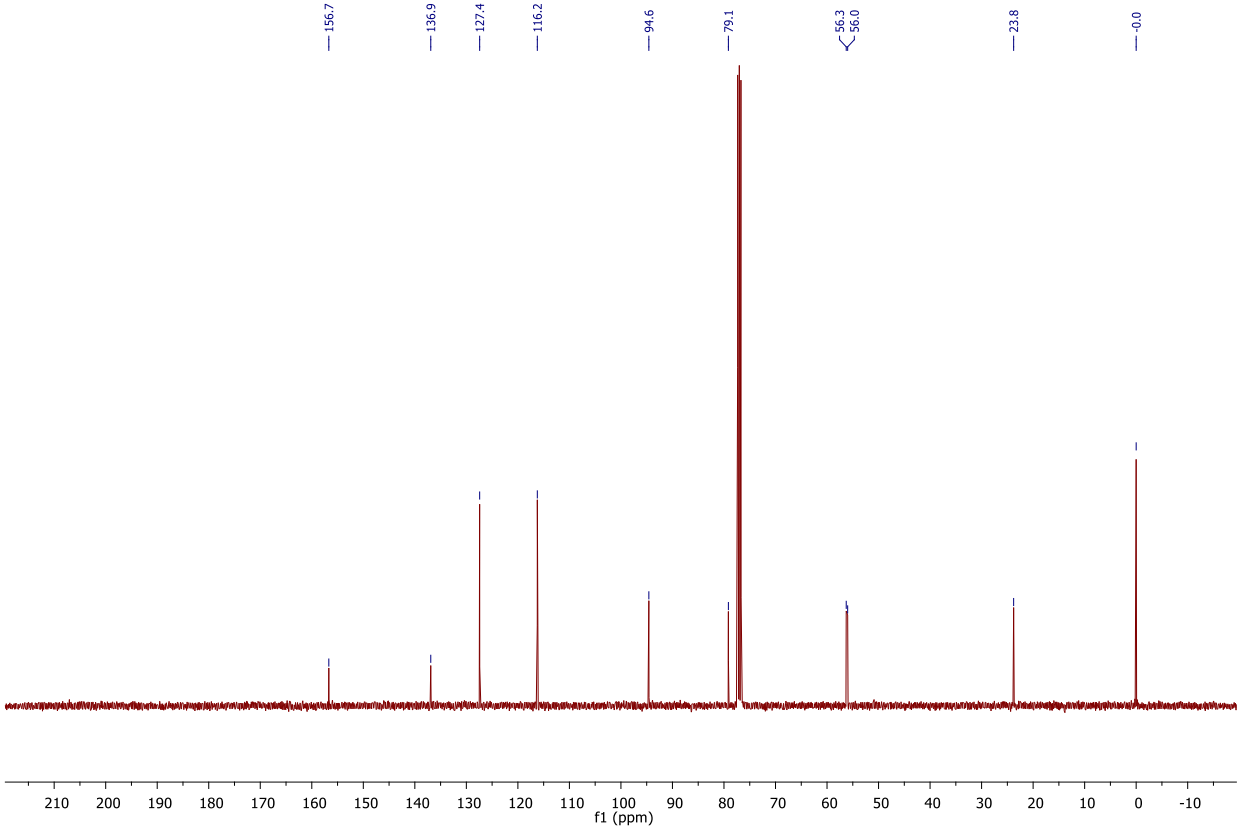

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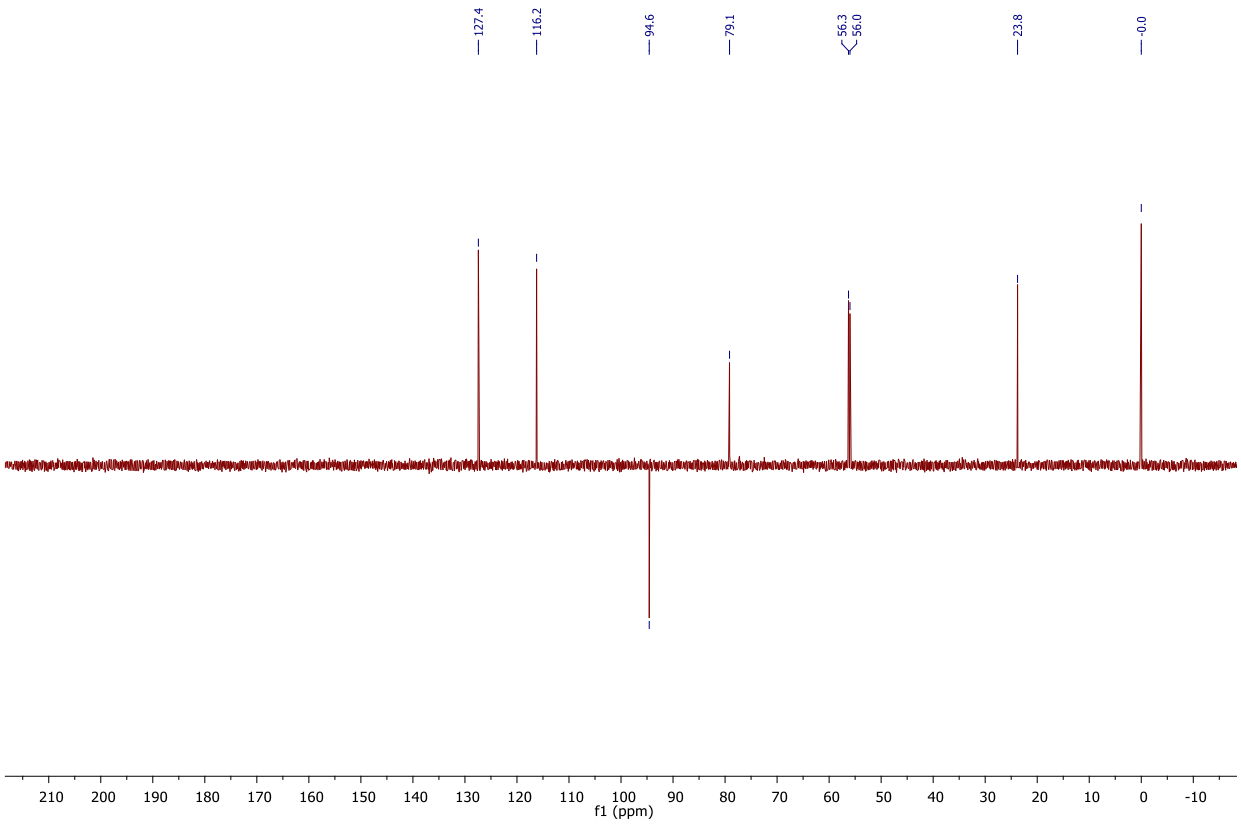

DEPT spectrum in $CDCl_3$.

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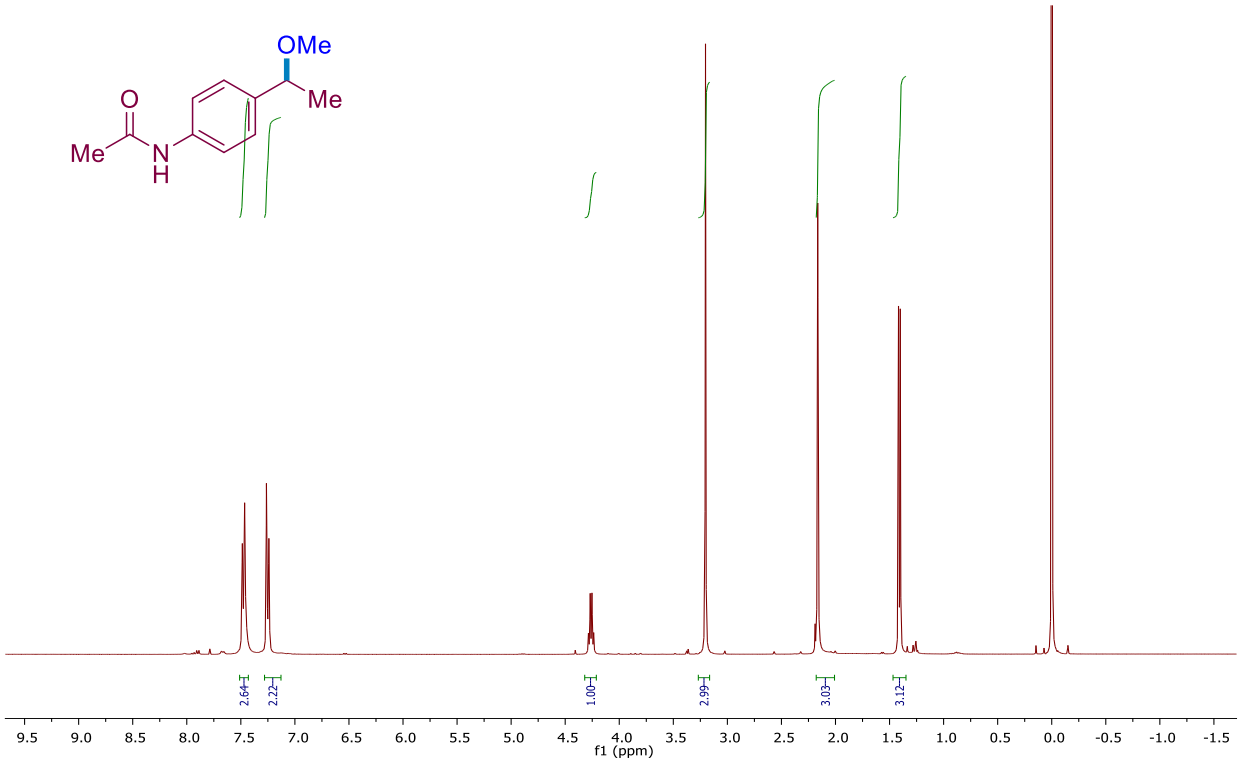

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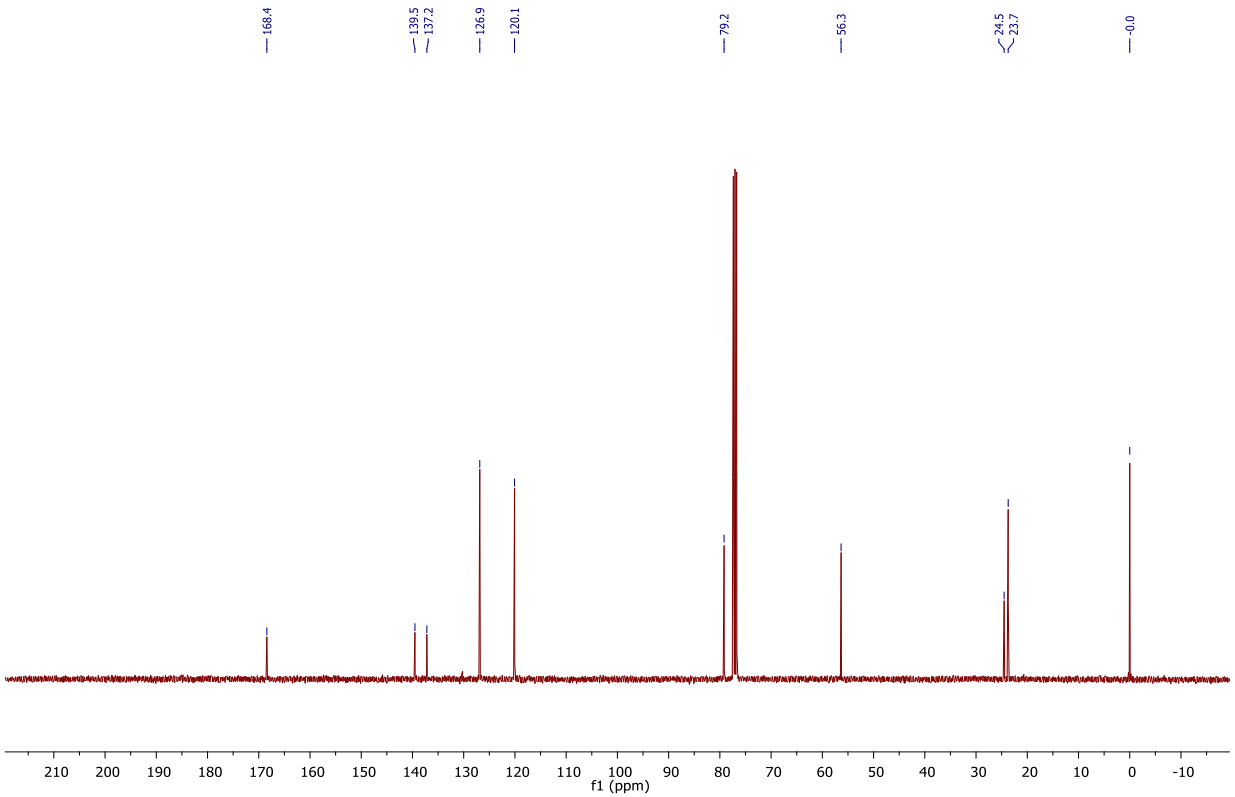

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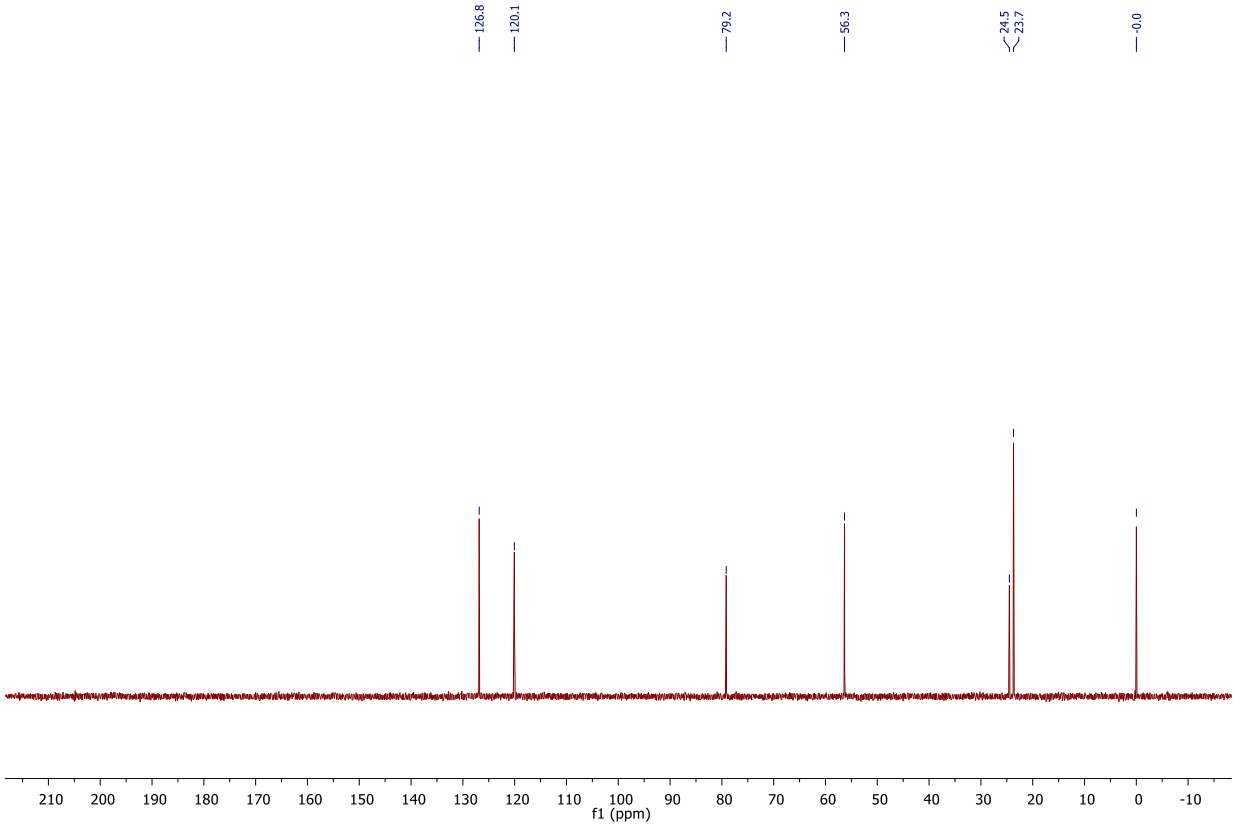

DEPT spectrum in $CDCl_3$.

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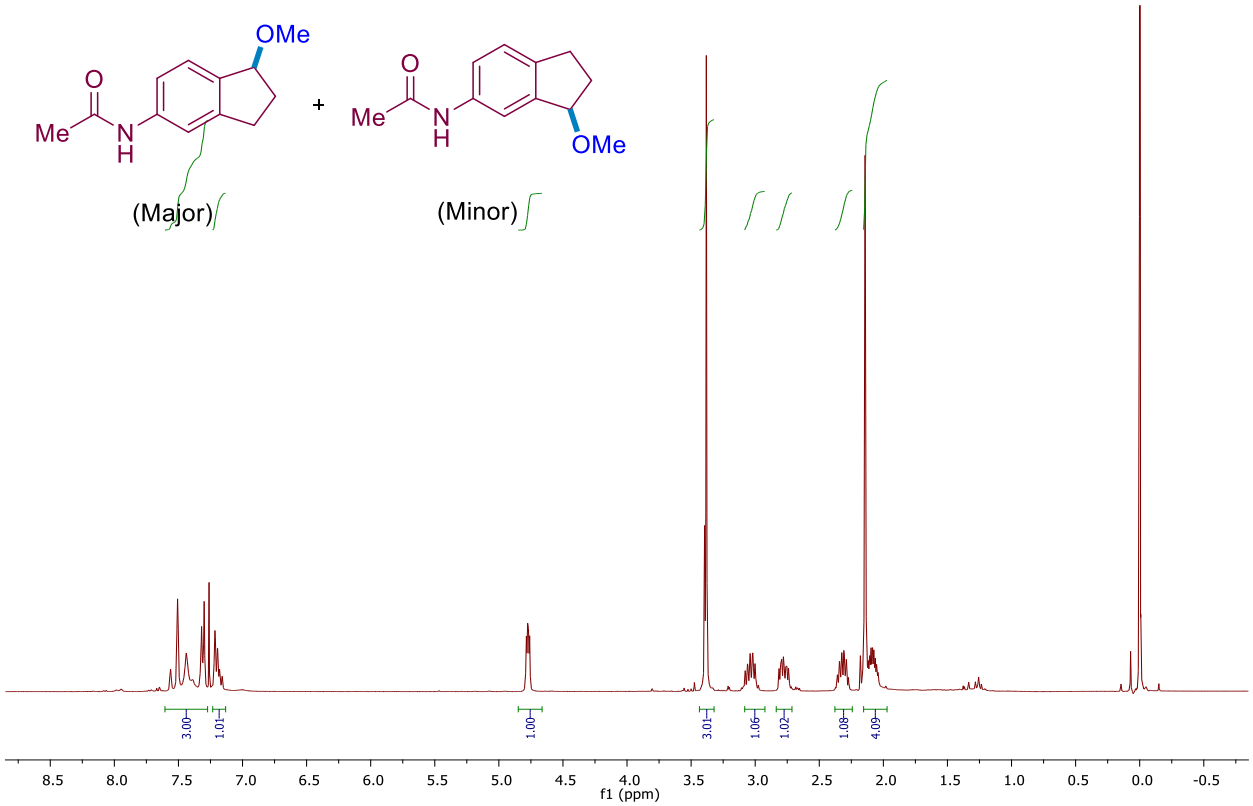

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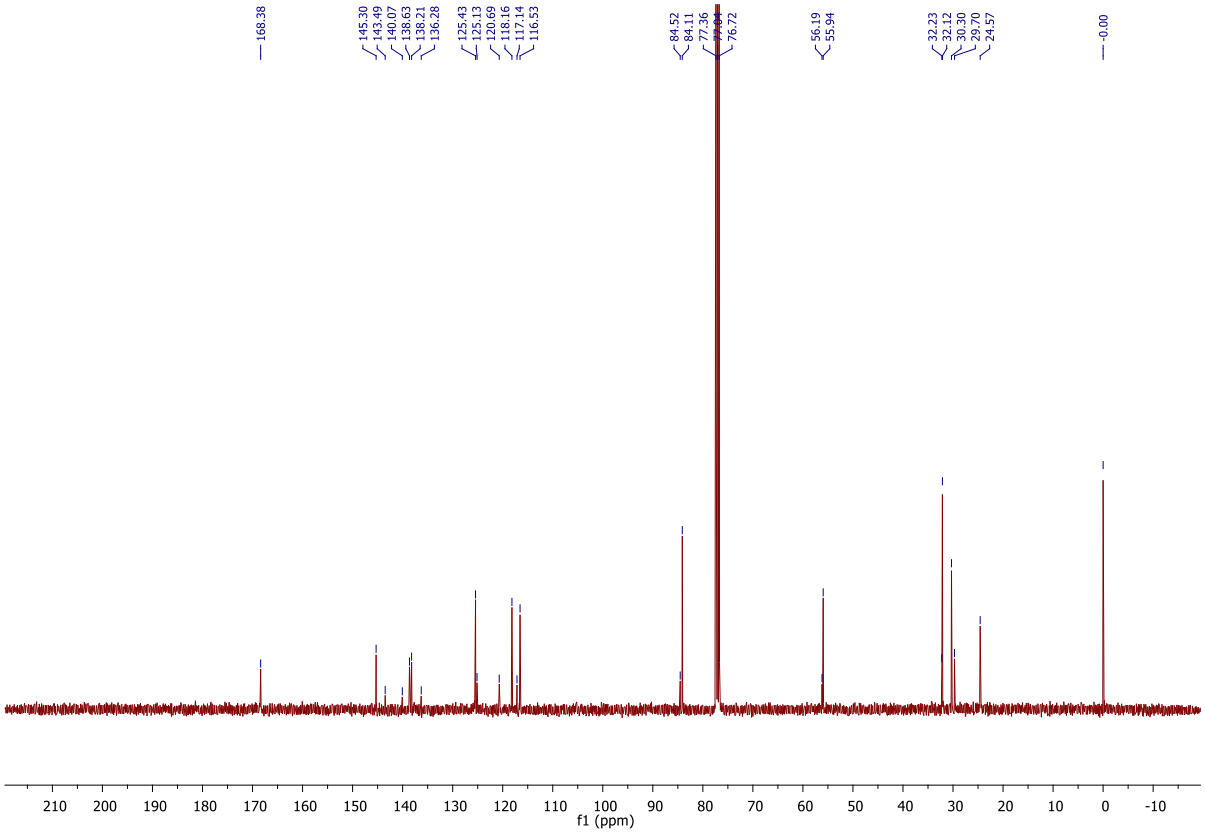

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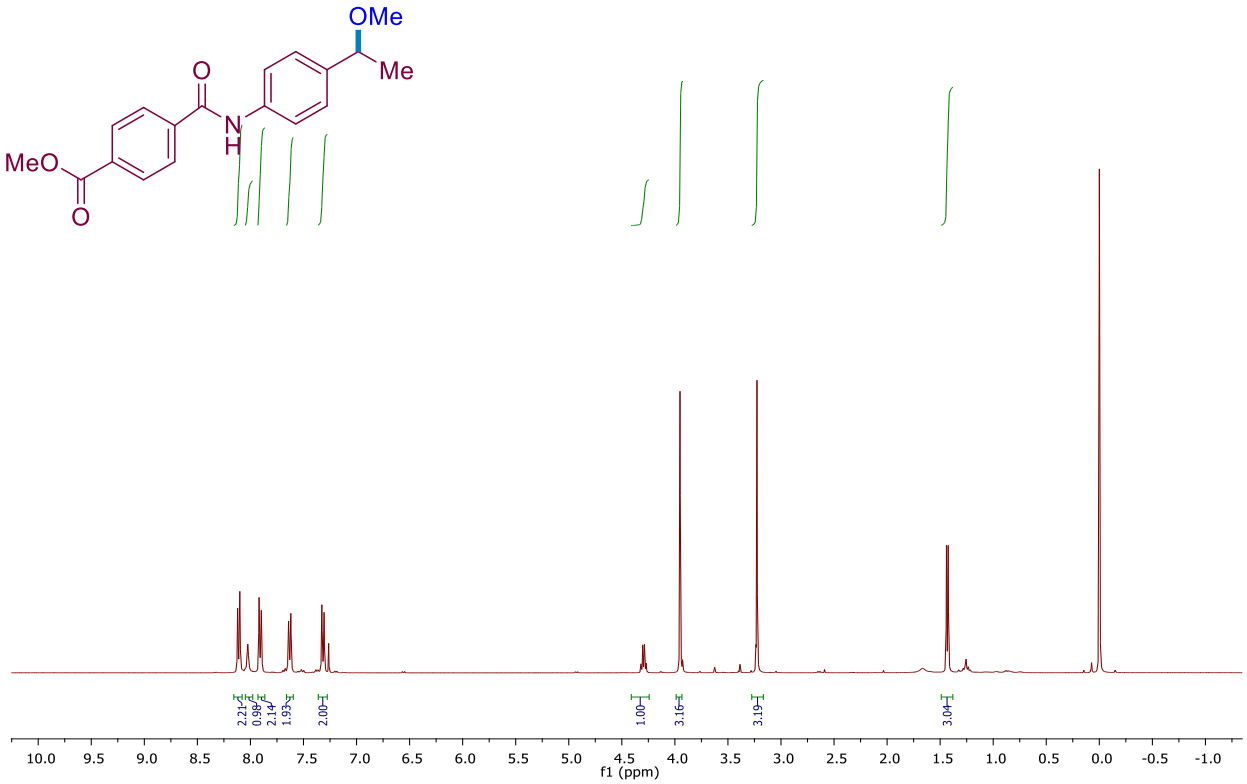

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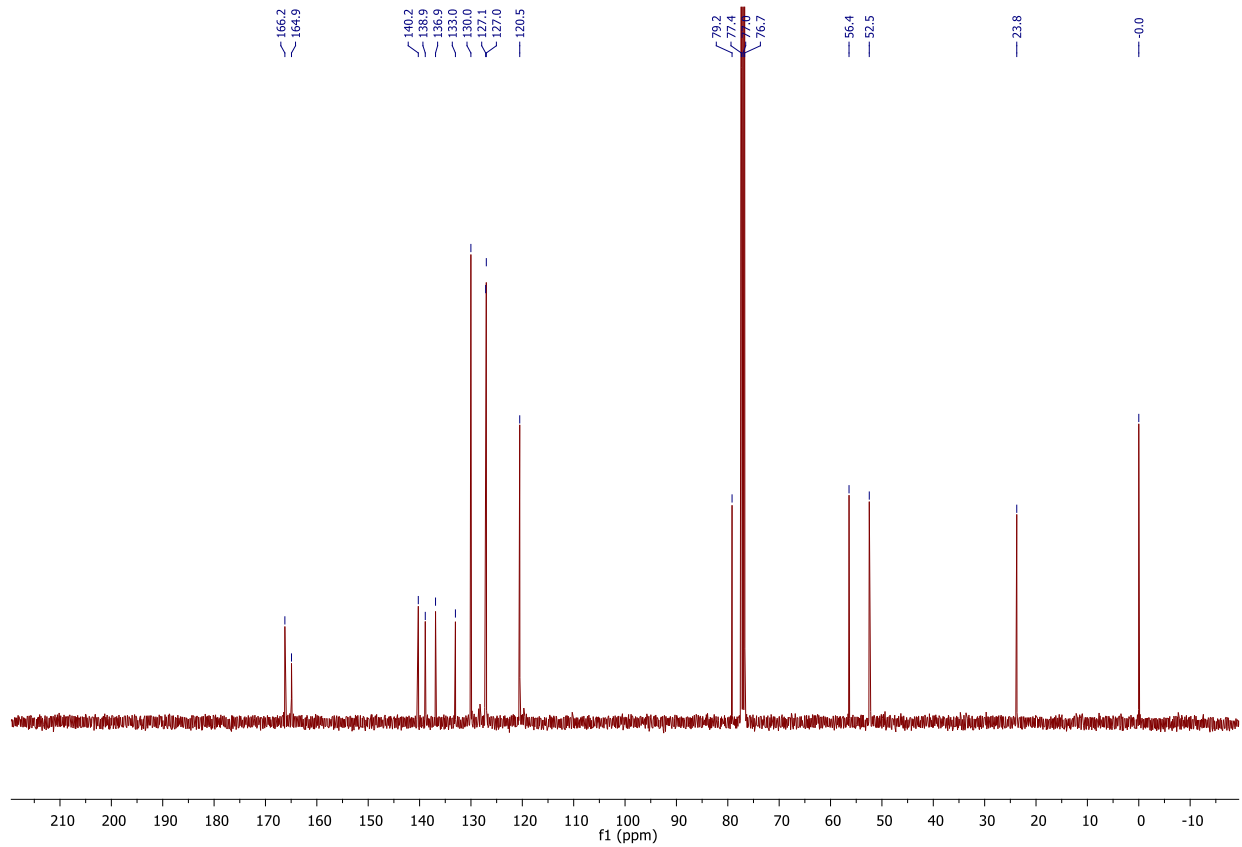

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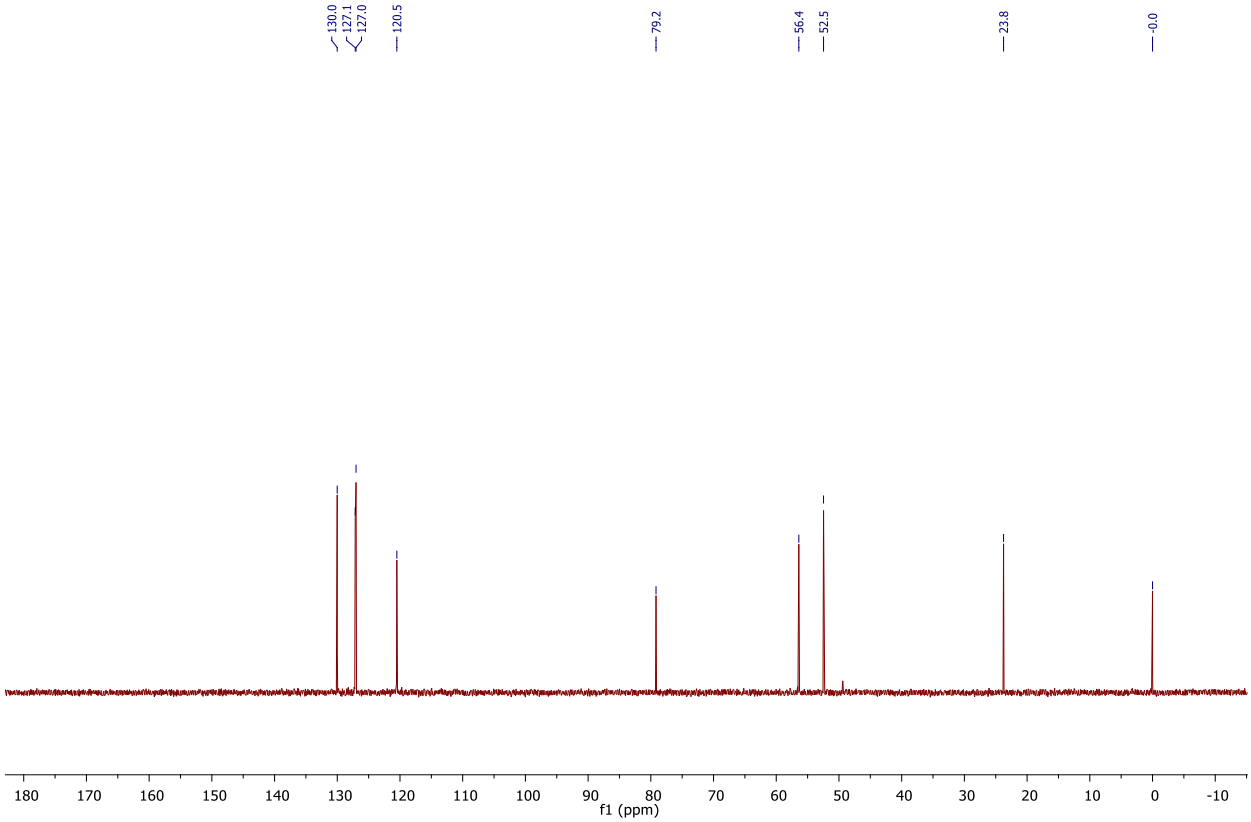
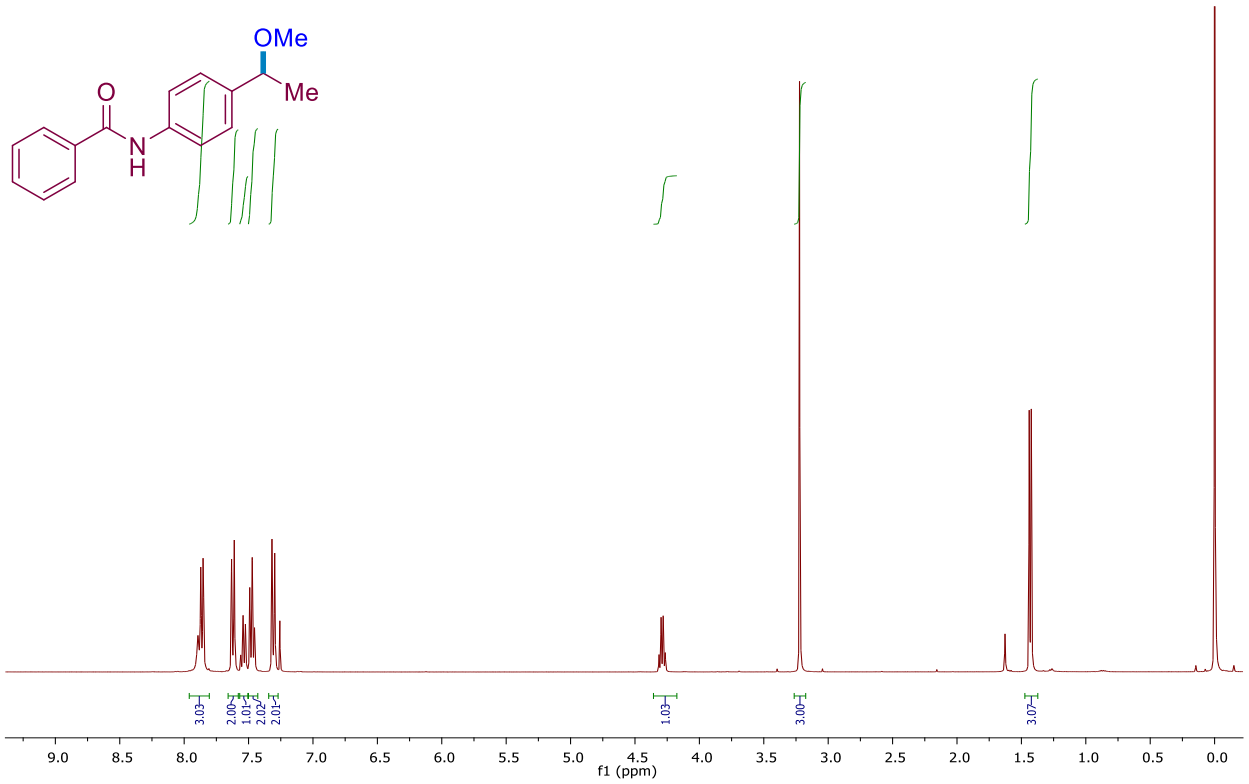


DEPT spectrum in $CDCl_3$.

9c



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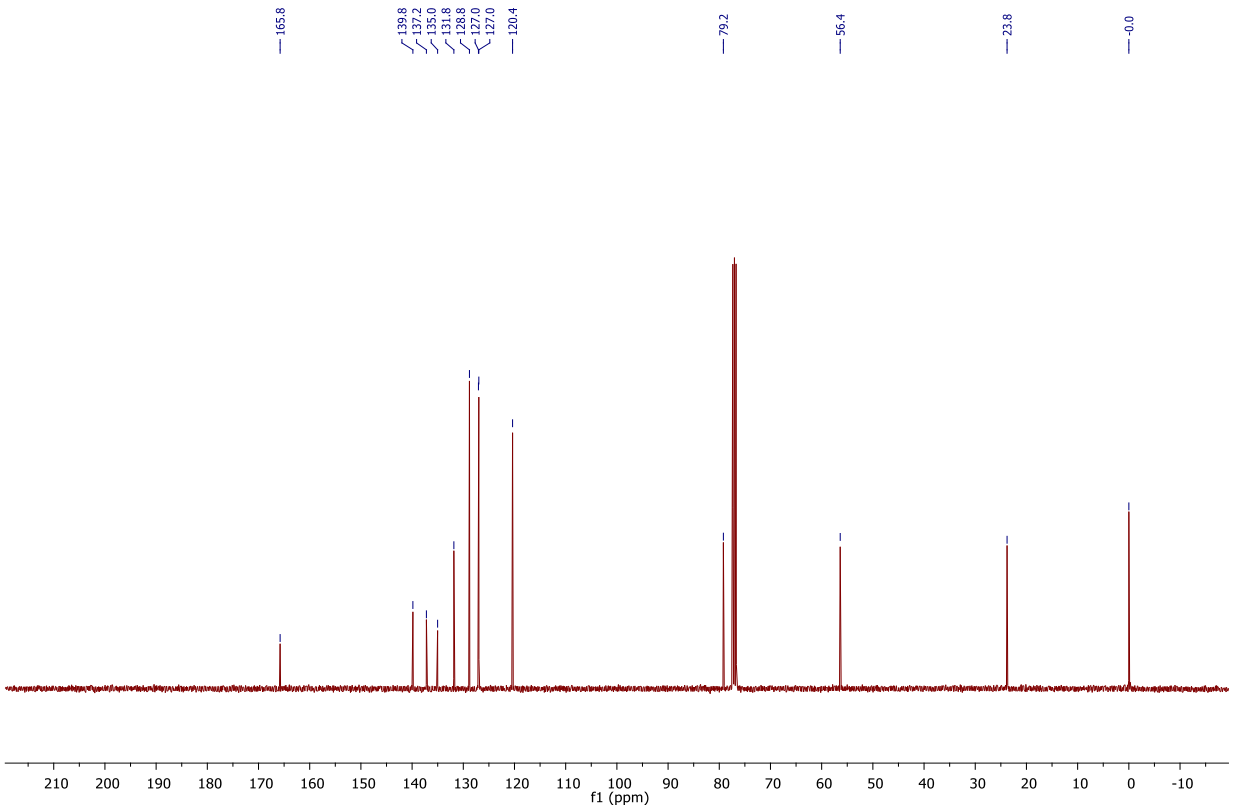

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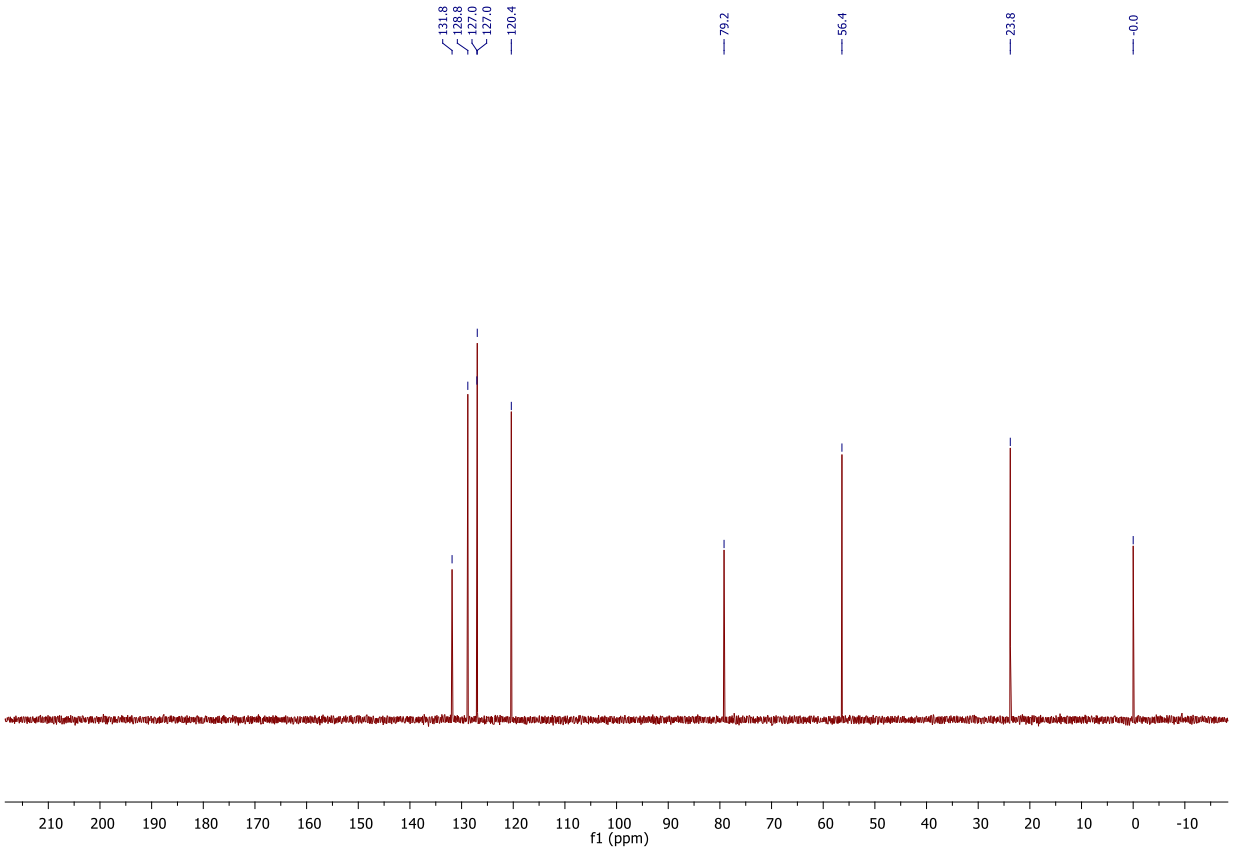

DEPT spectrum in $CDCl_3$.

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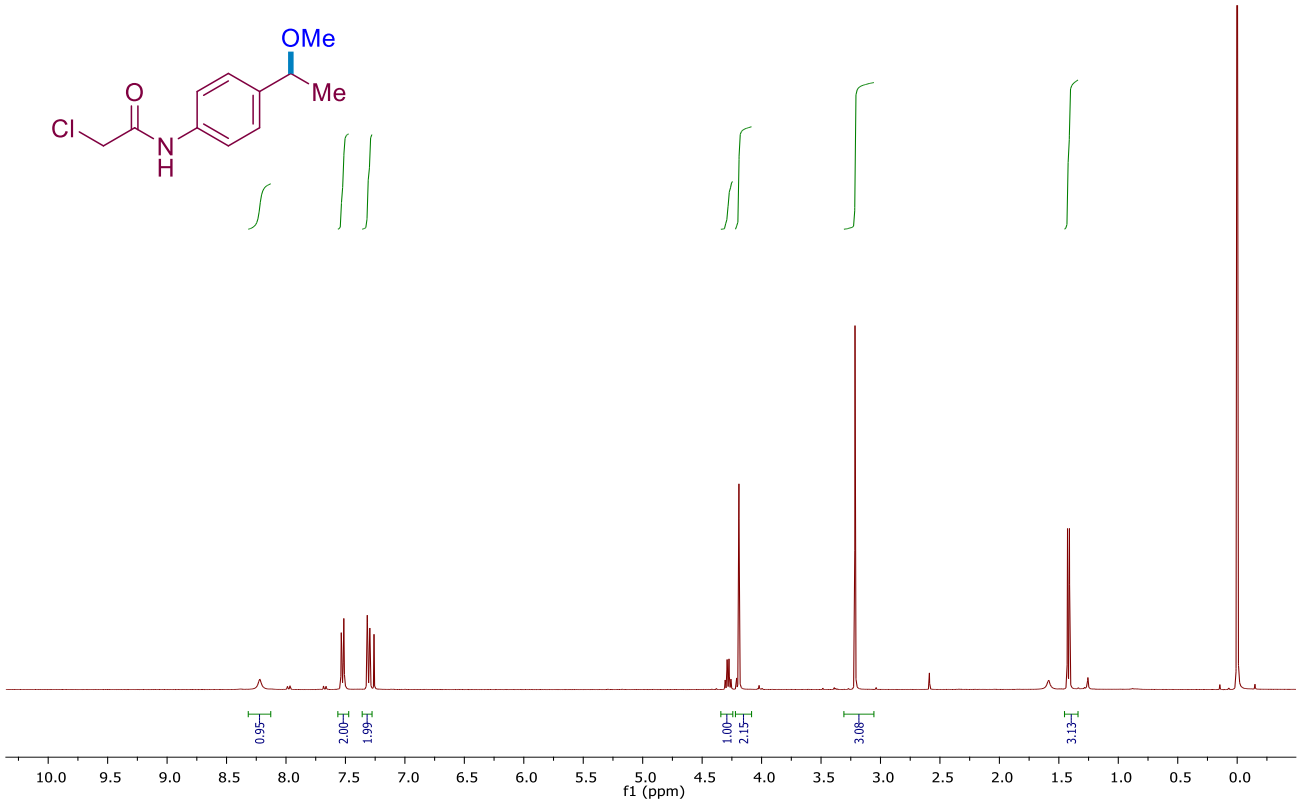

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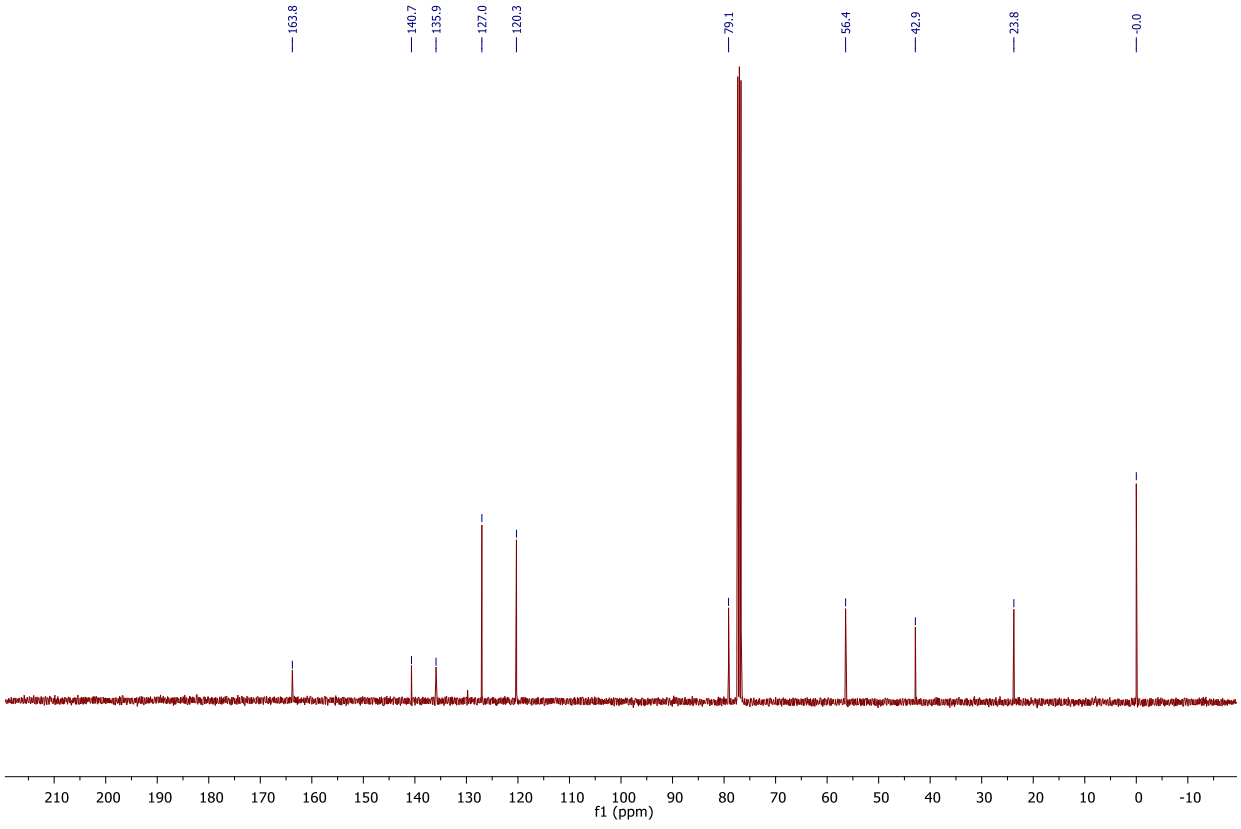

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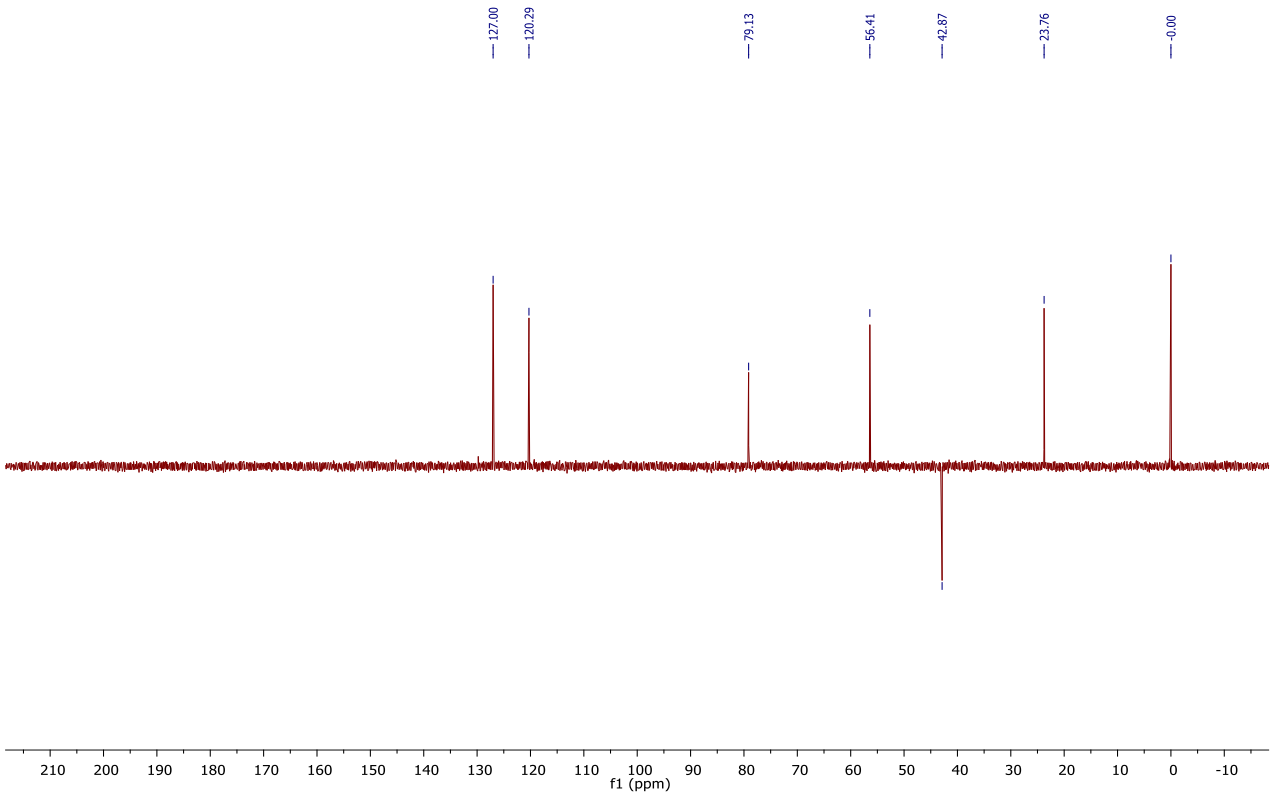

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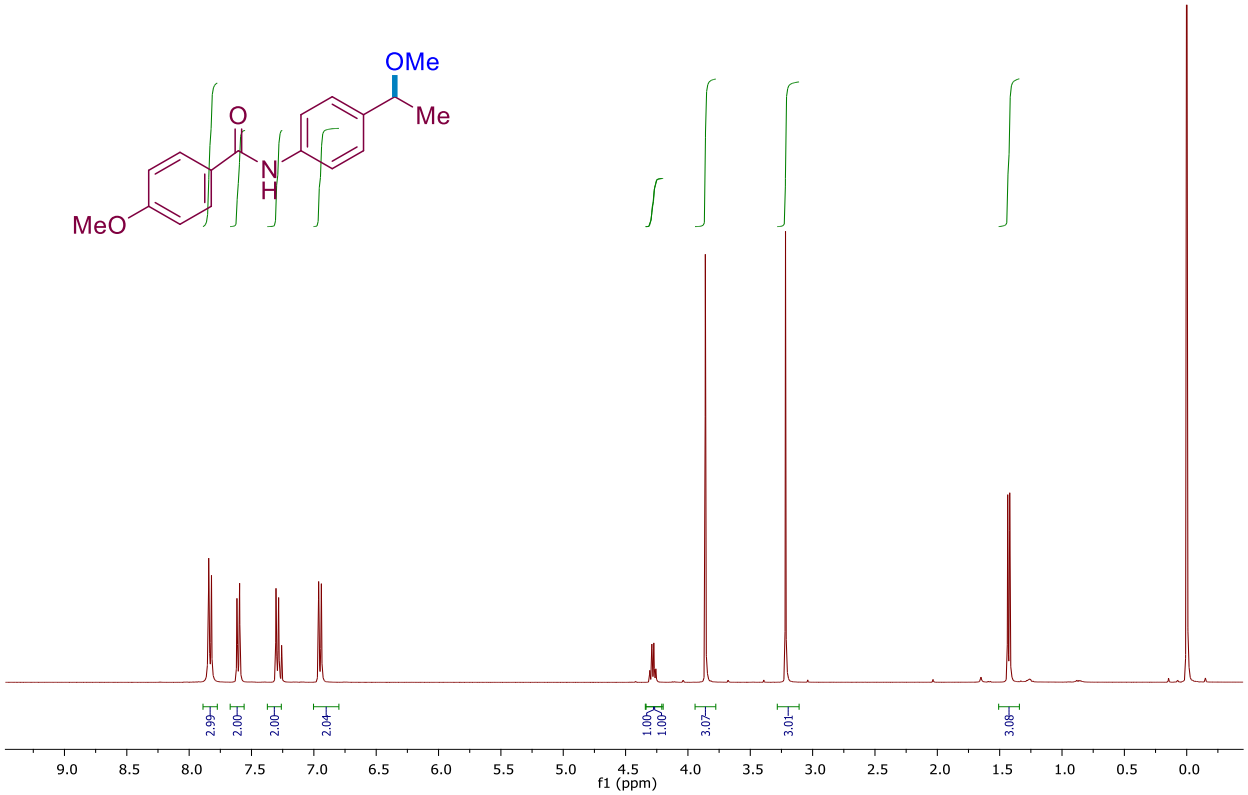

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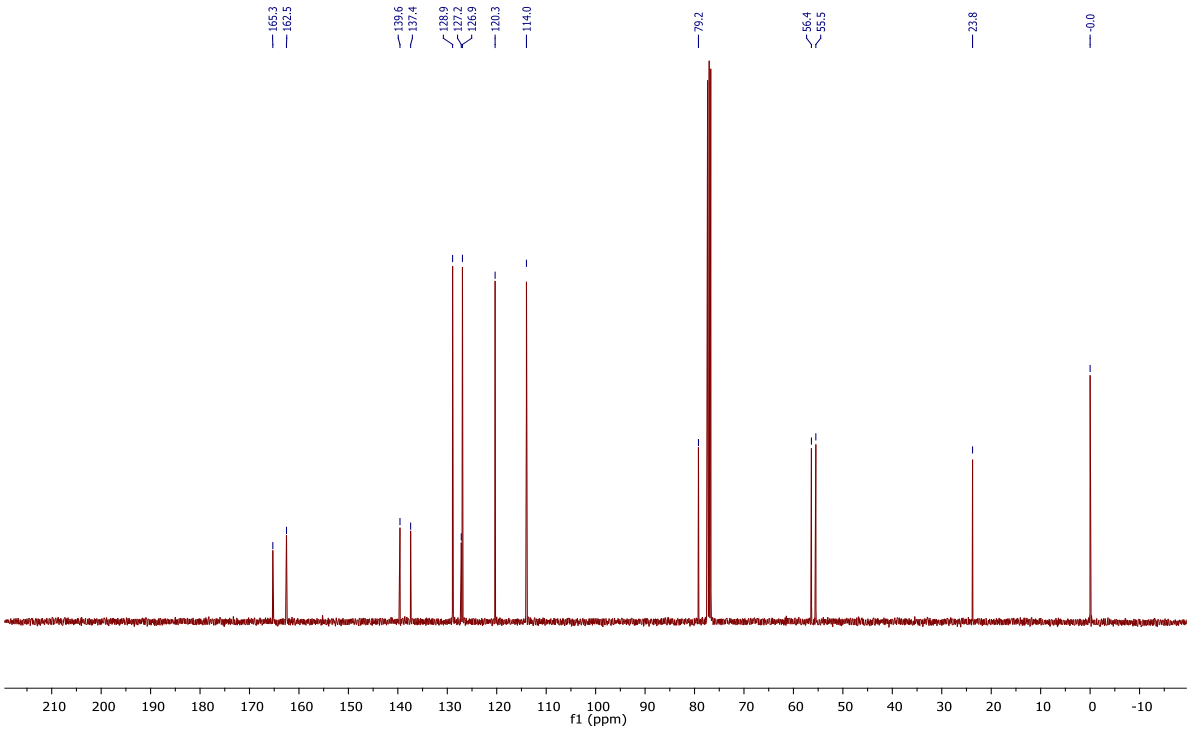

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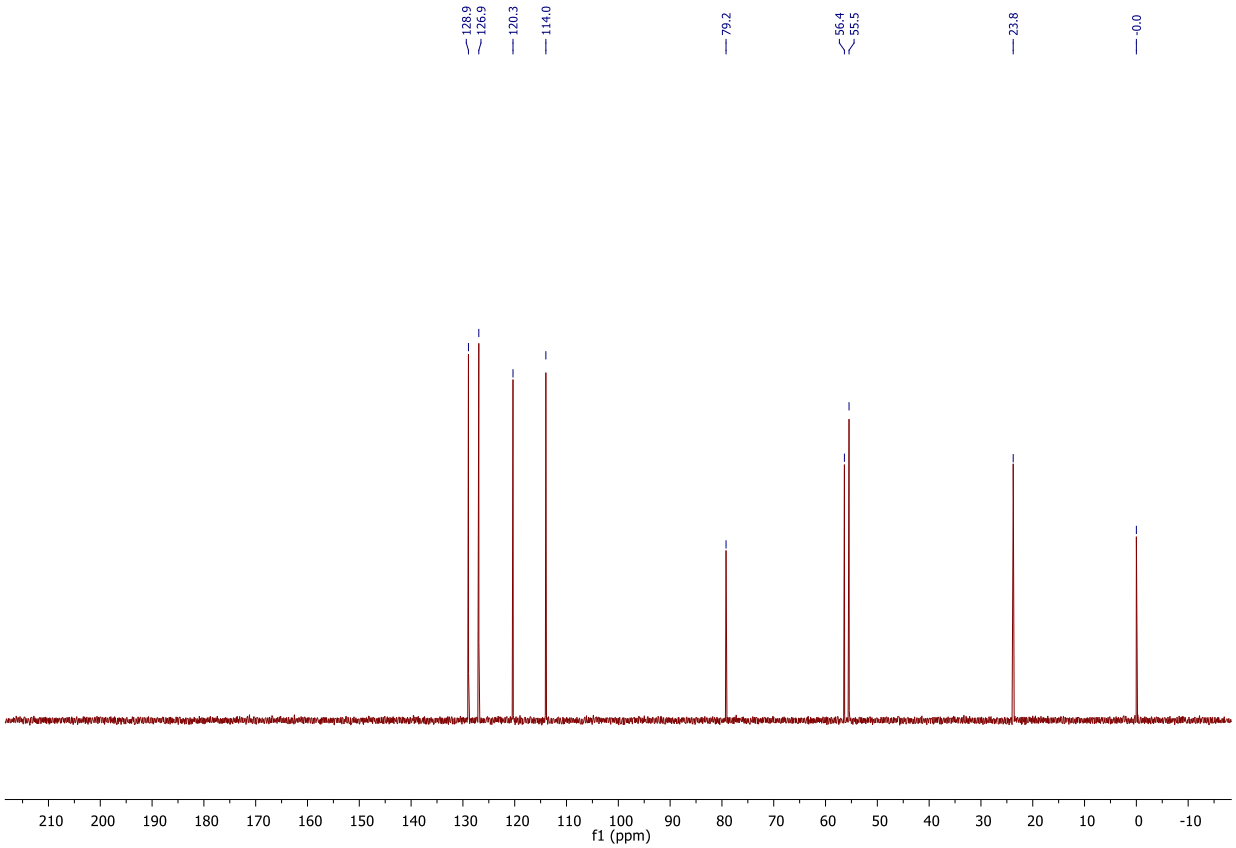
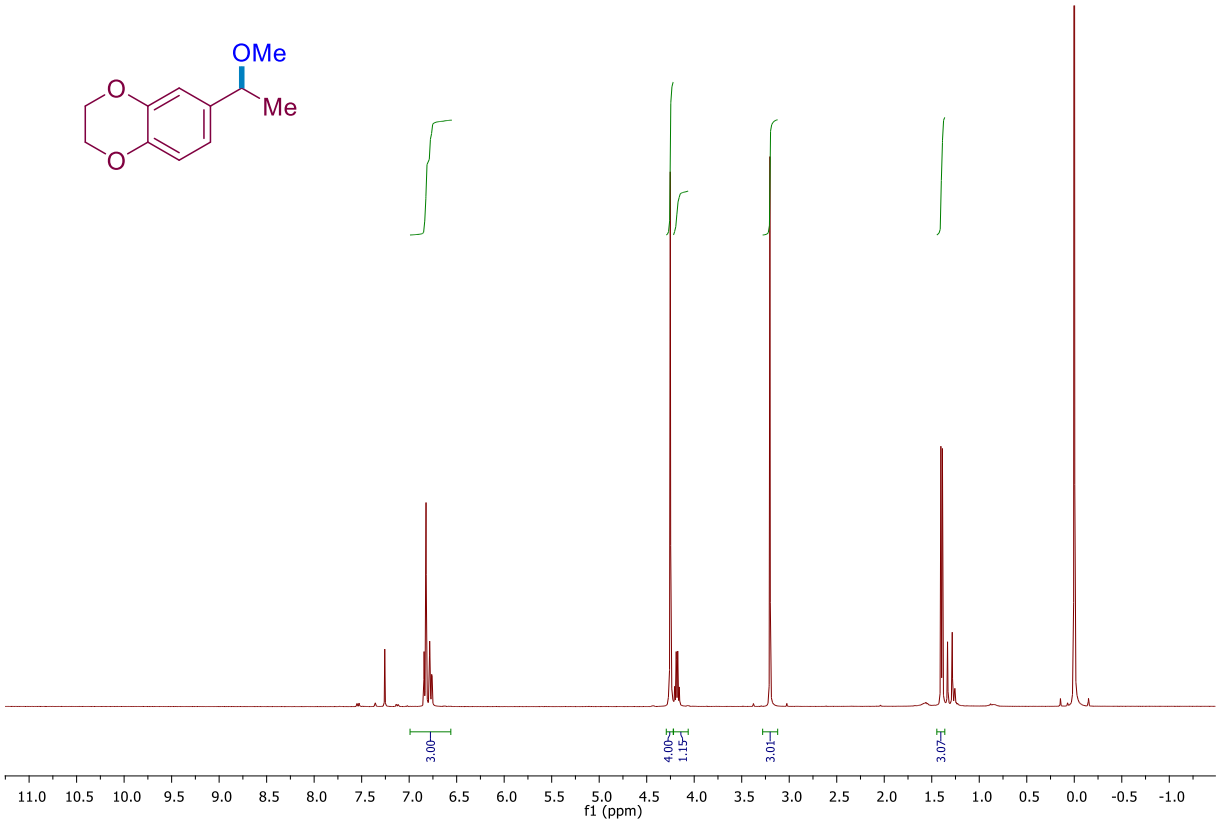
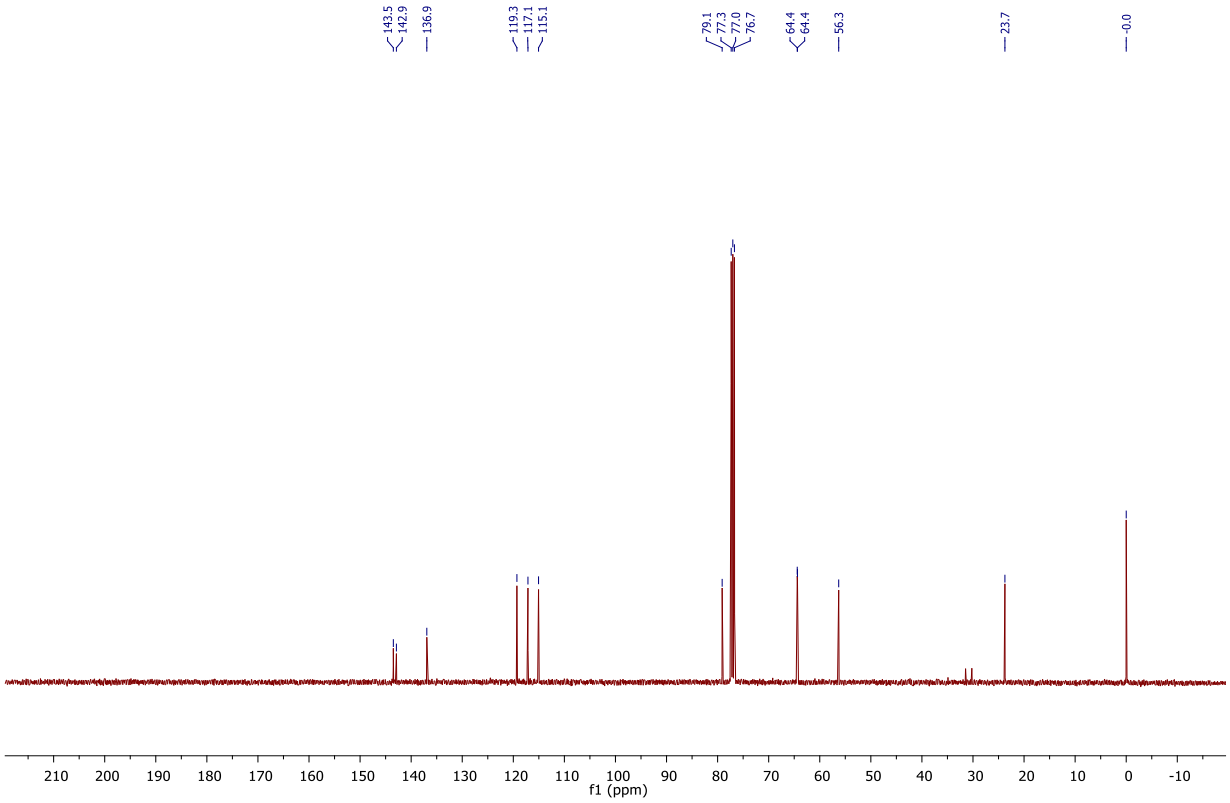


DEPT spectrum in $CDCl_3$.

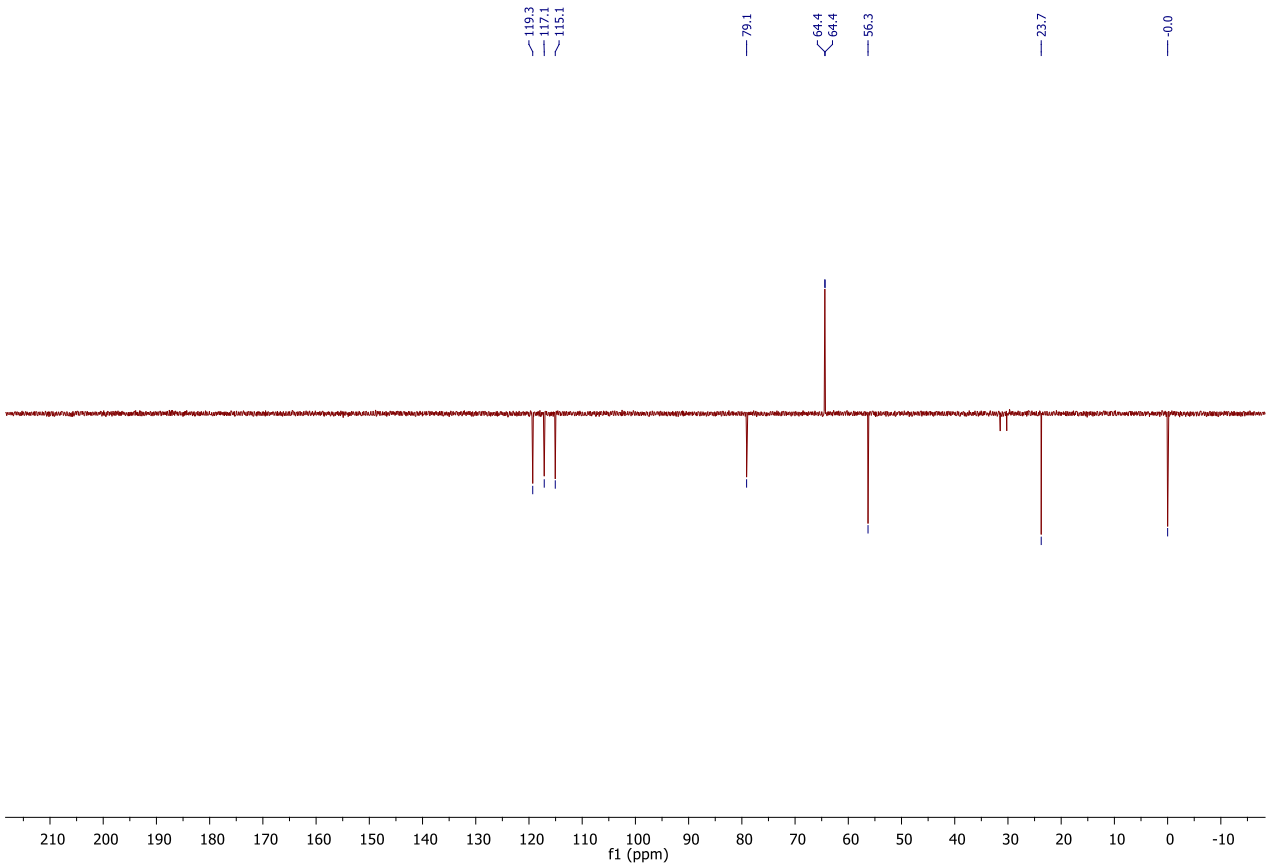
12c



^{1}H NMR spectrum in $CDCl_3$.

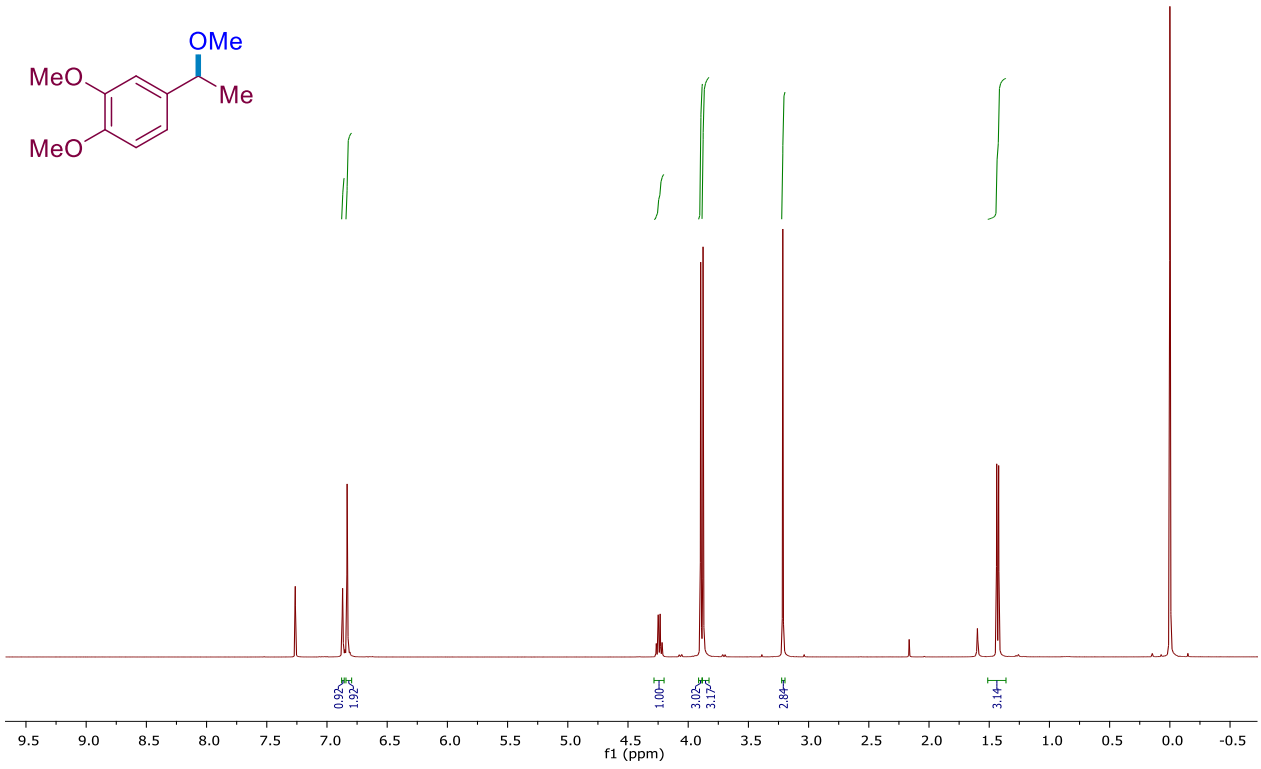


^{13}C NMR spectrum in $CDCl_3$

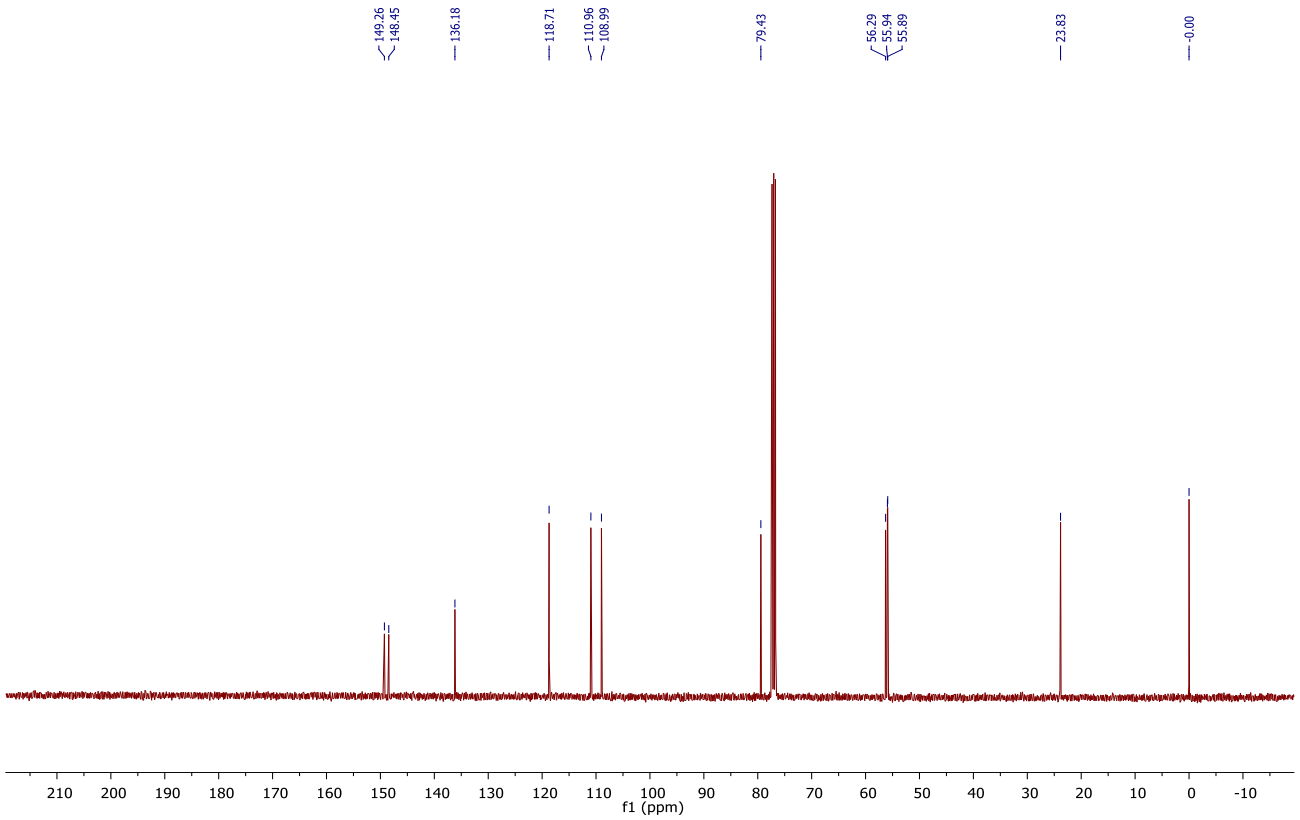


DEPT spectrum in $CDCl_3$.

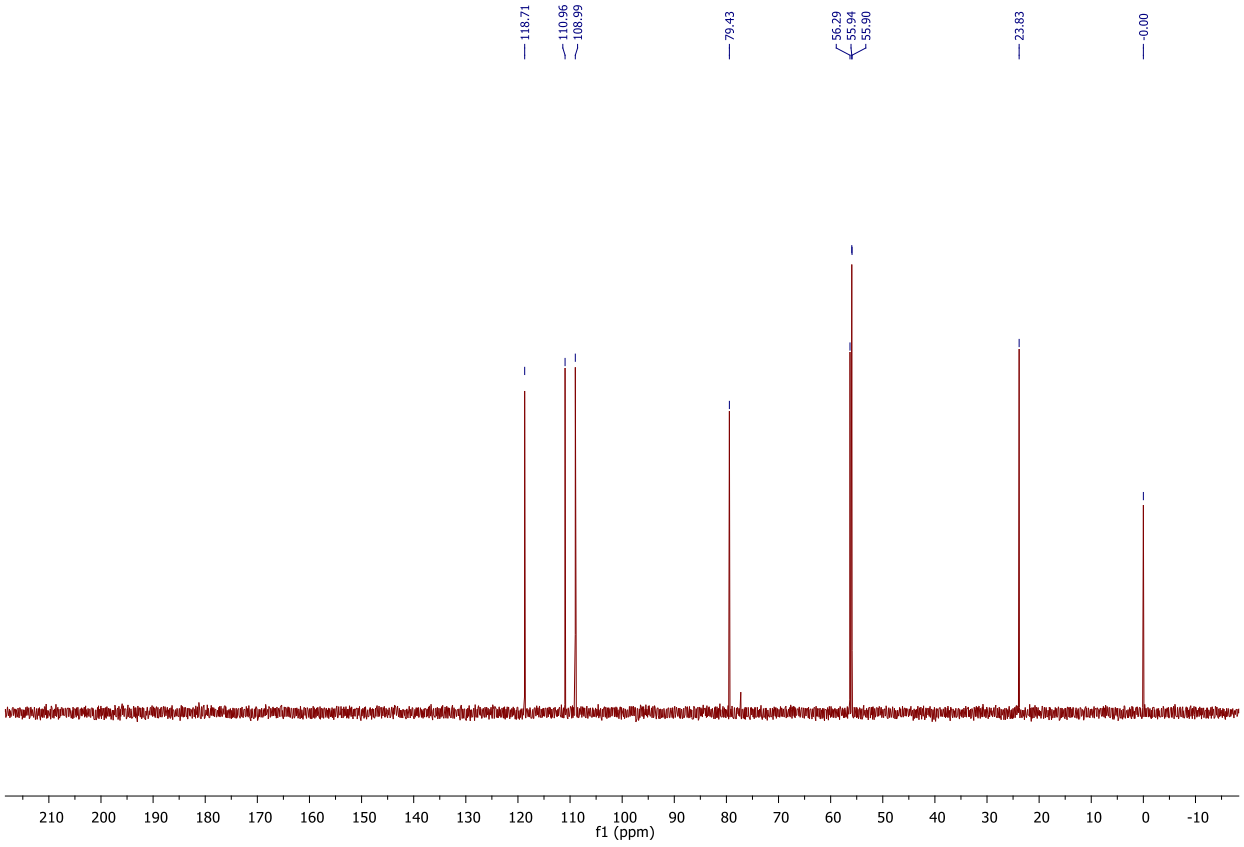
13c



^1H NMR spectrum in $CDCl_3$.

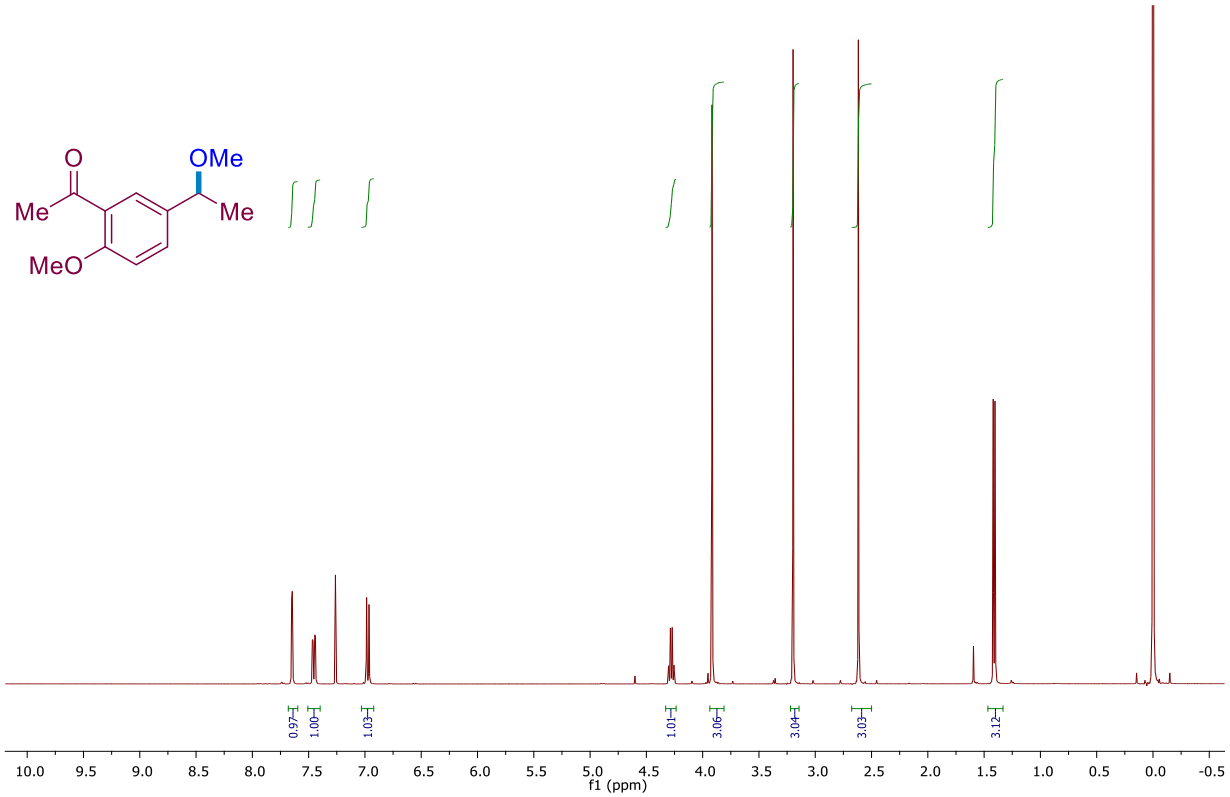


^{13}C NMR spectrum in $CDCl_3$

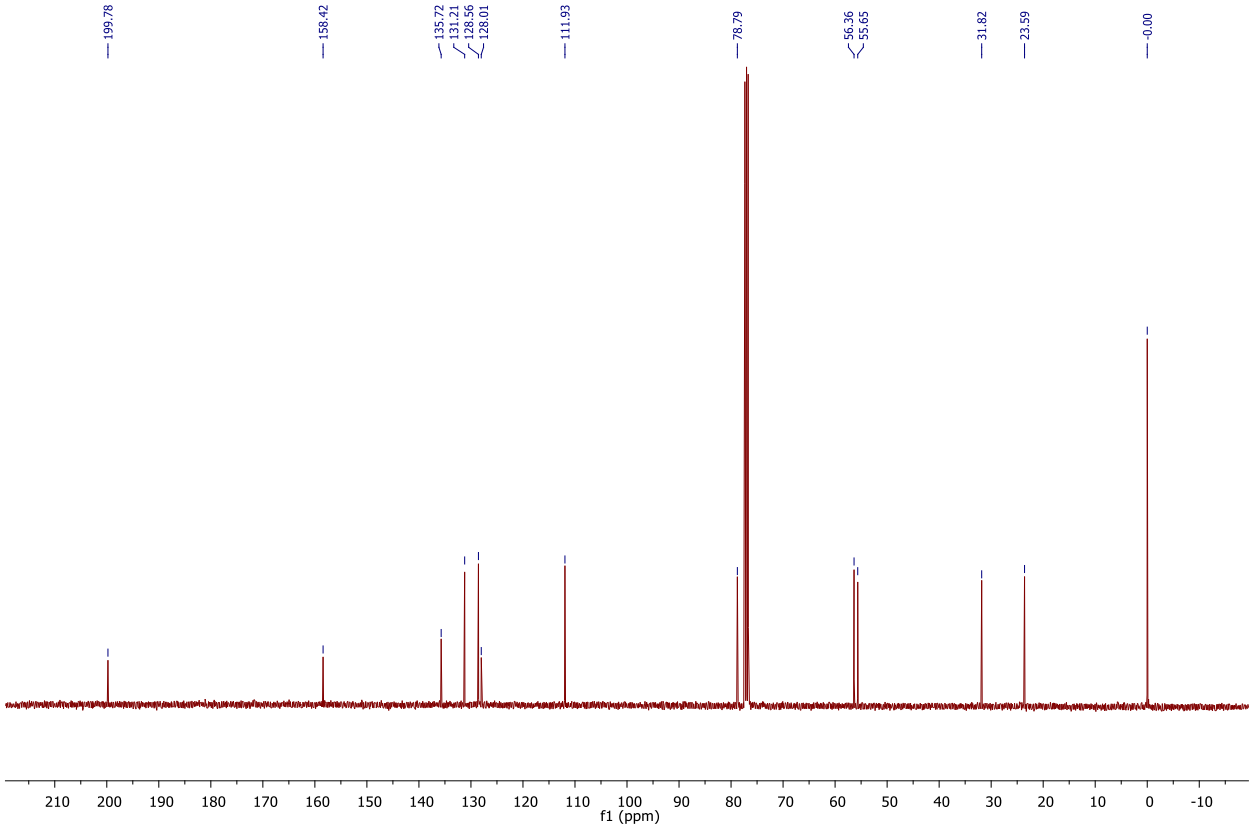


DEPT spectrum in $CDCl_3$.

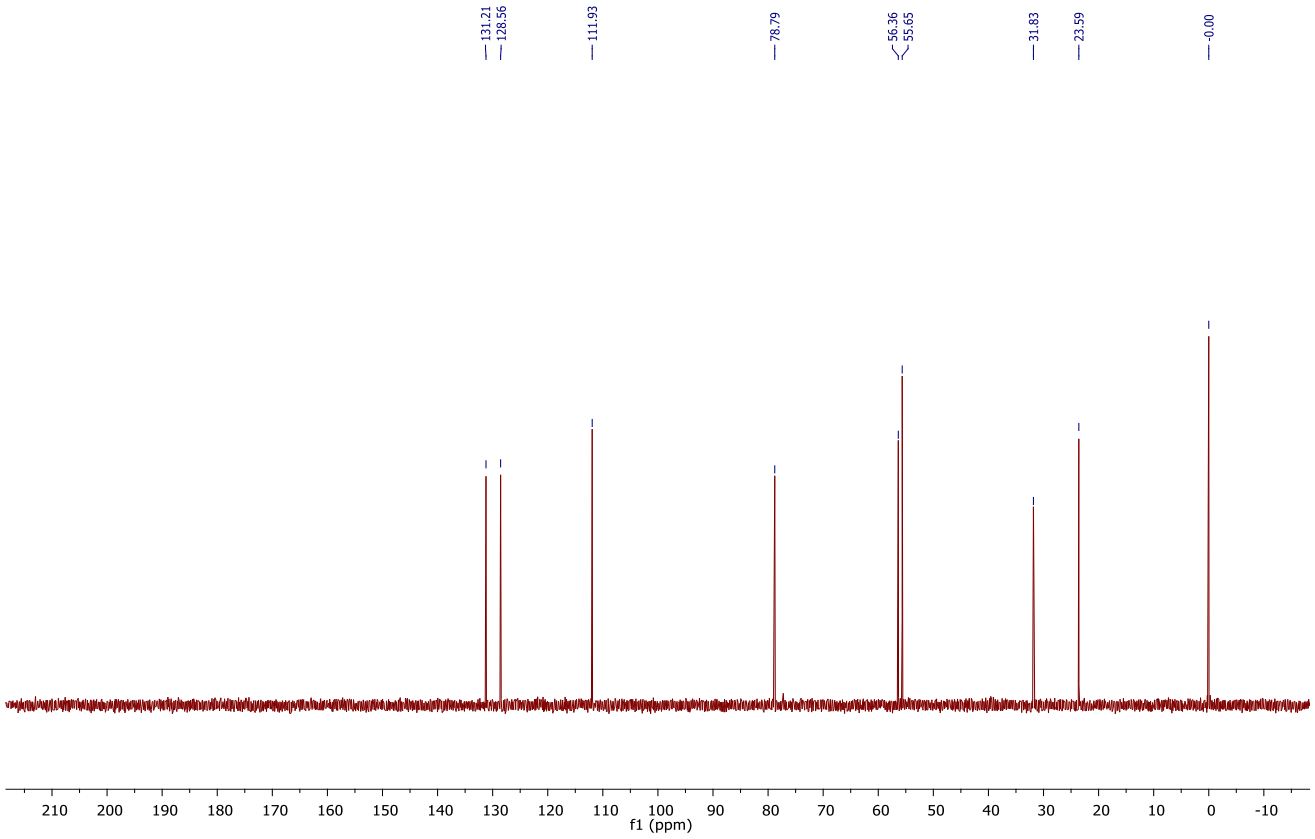
14c



^{1}H NMR spectrum in $CDCl_3$.

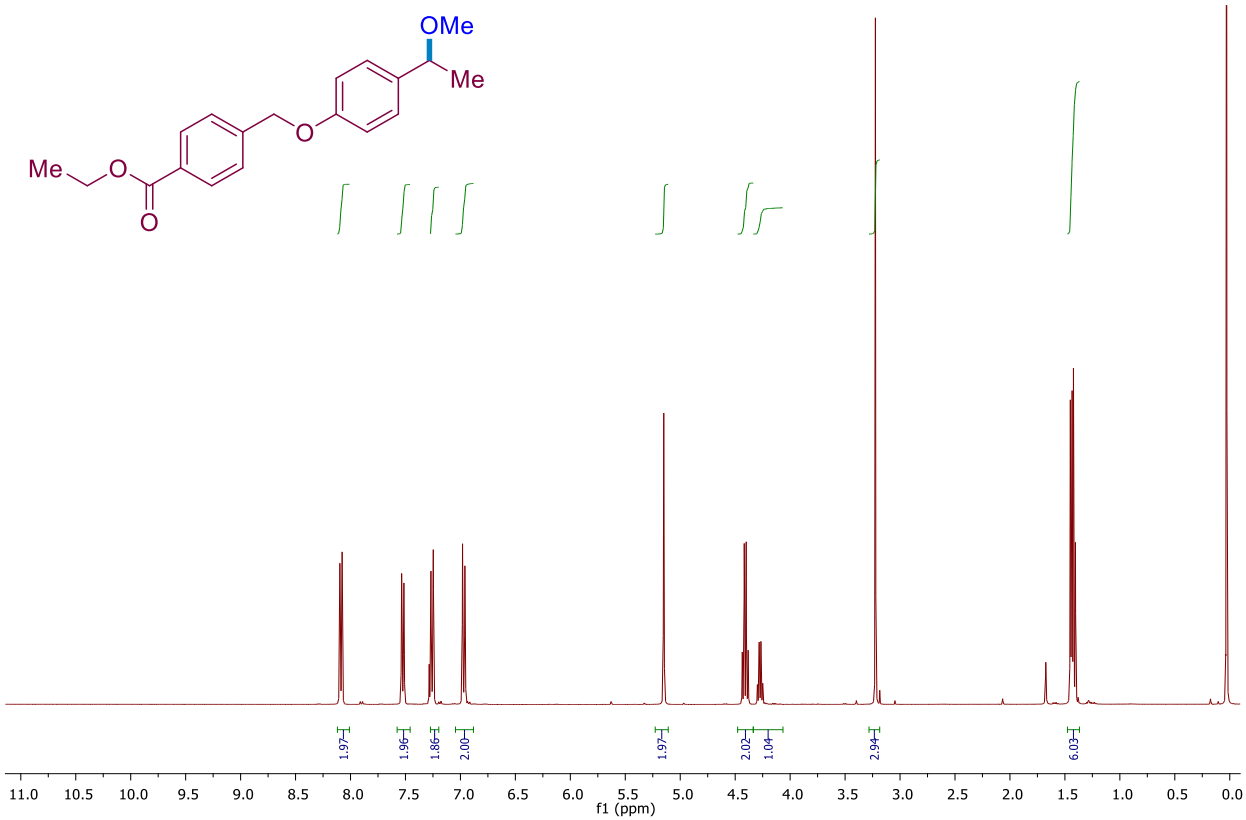


^{13}C NMR spectrum in $CDCl_3$

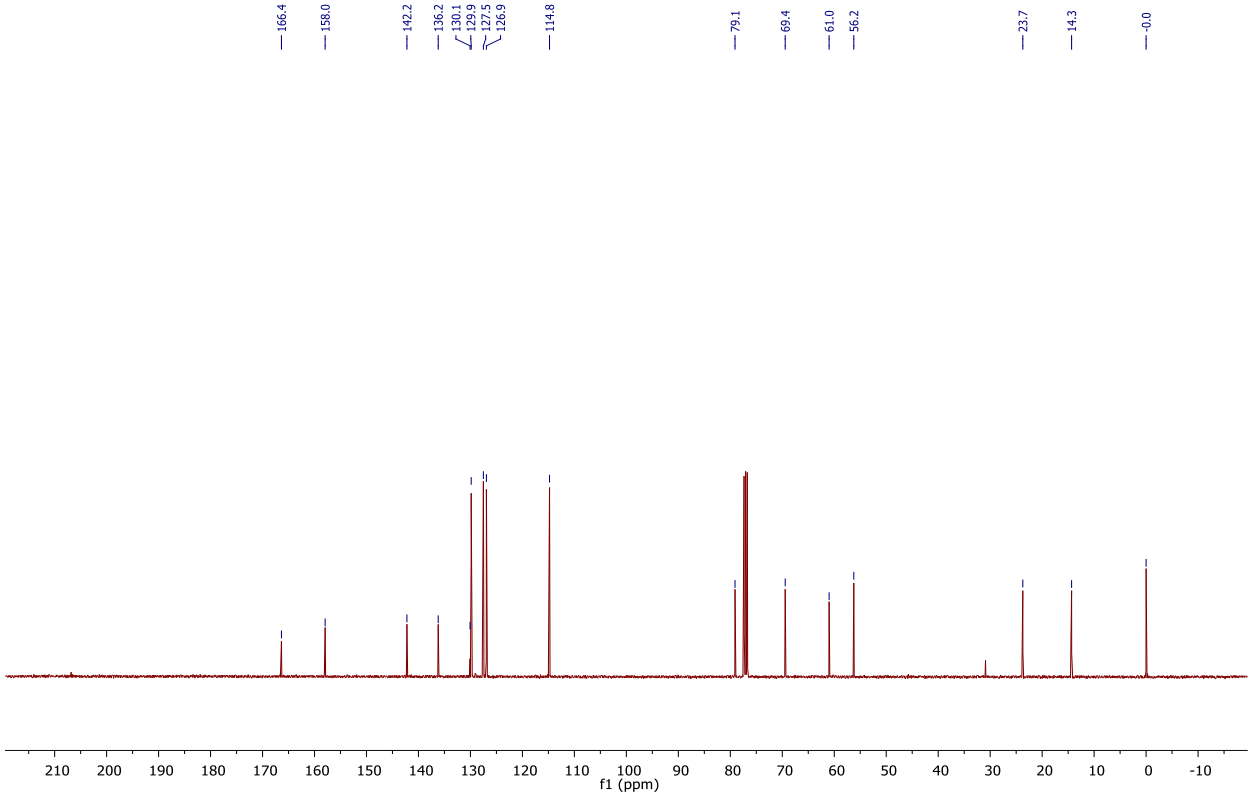


DEPT spectrum in $CDCl_3$.

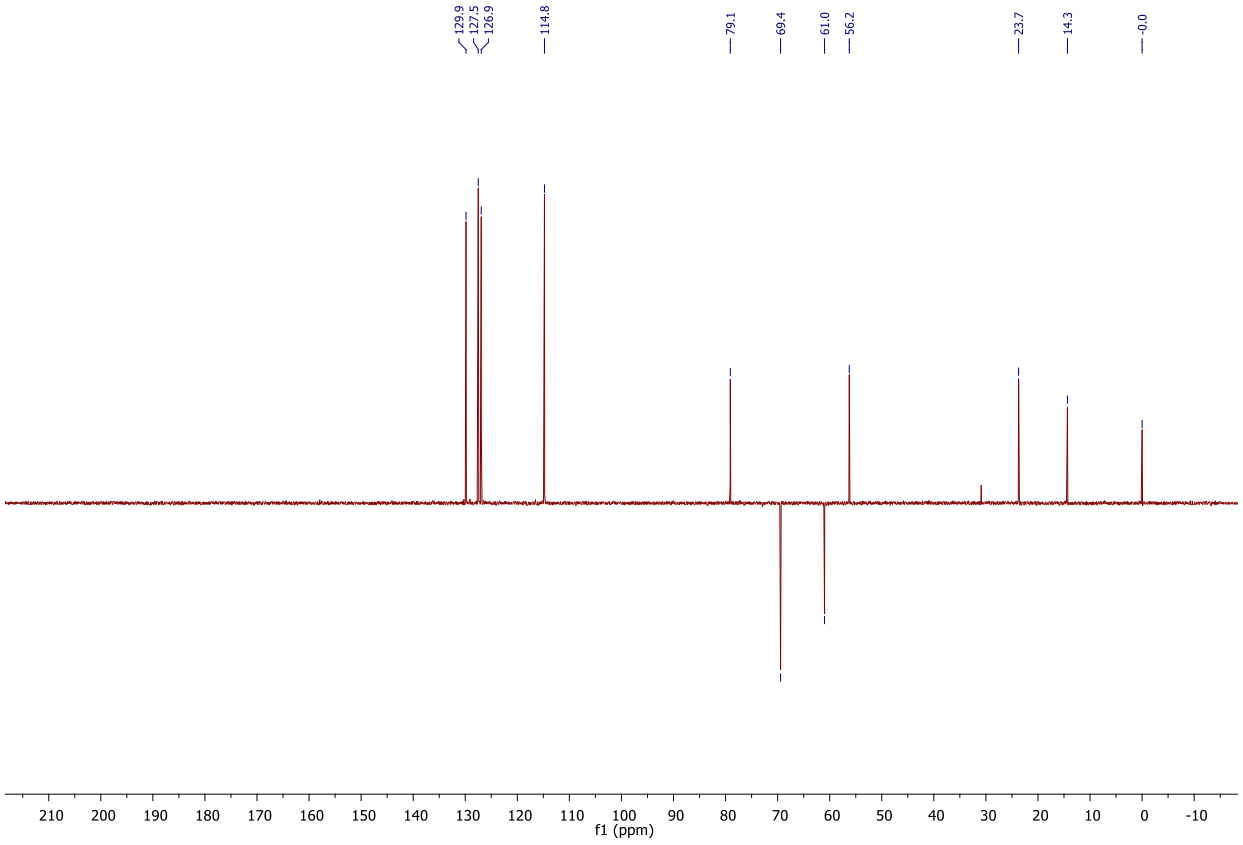
15c



^{1}H NMR spectrum in $CDCl_3$.

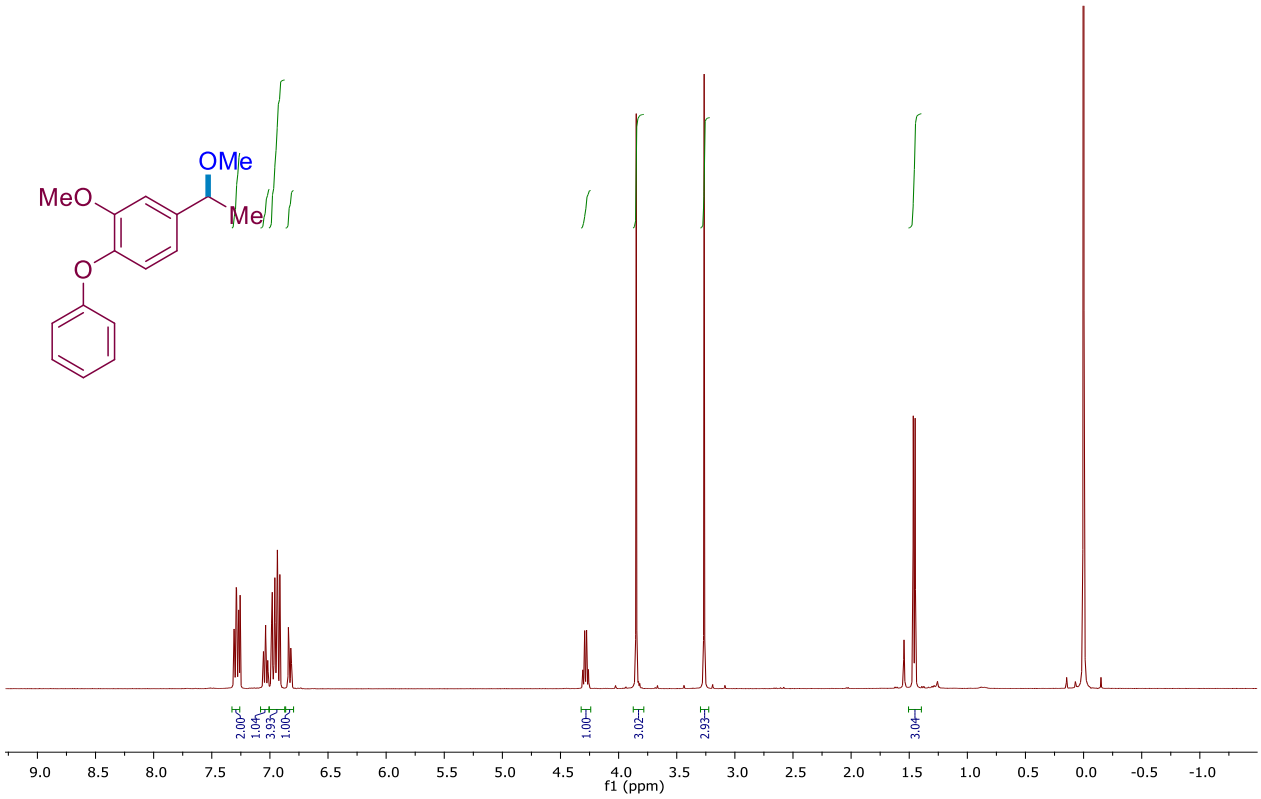


^{13}C NMR spectrum in $CDCl_3$

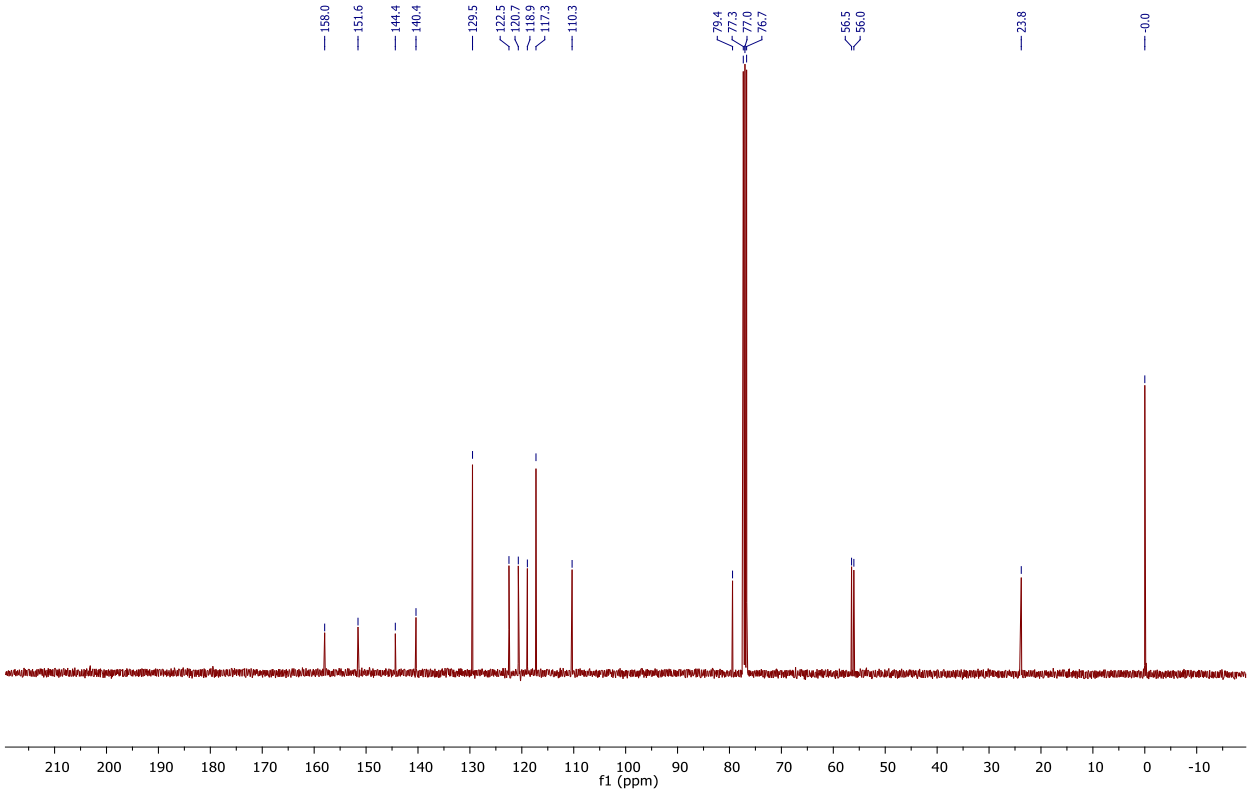


DEPT spectrum in $CDCl_3$.

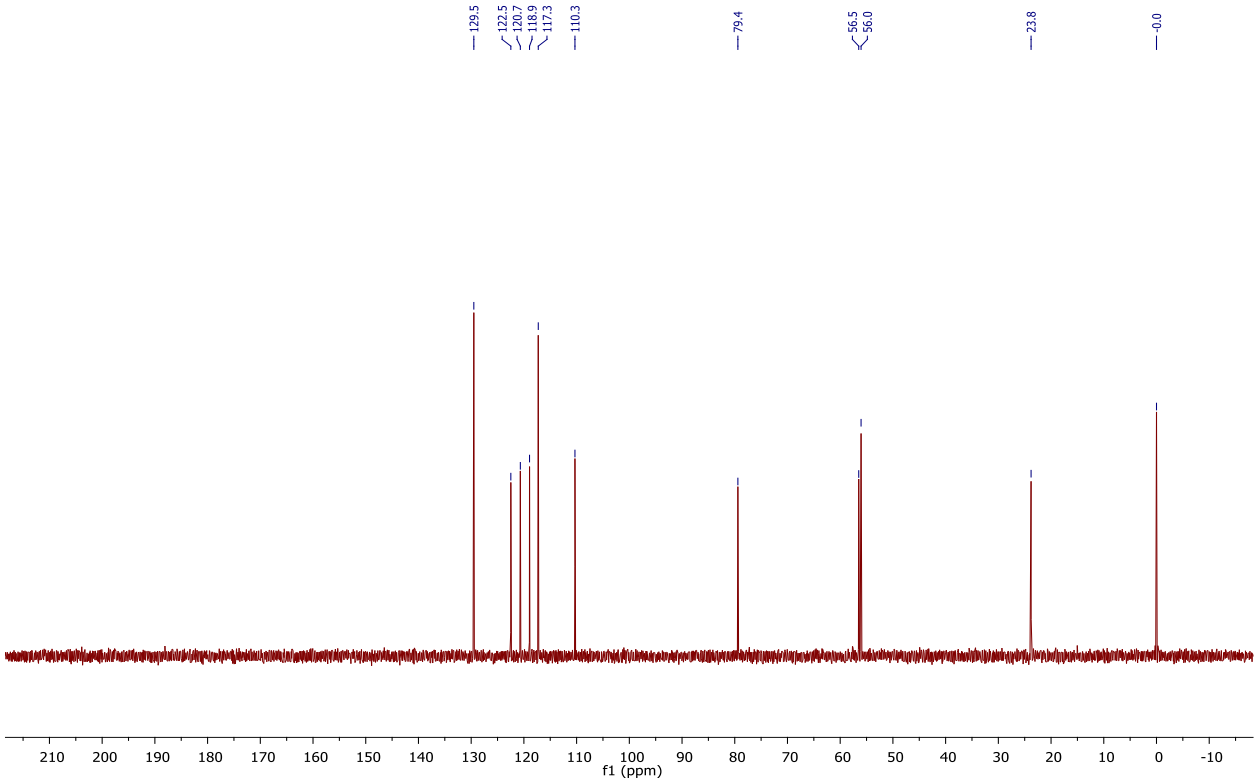
16c



^{1}H NMR spectrum in $CDCl_3$.

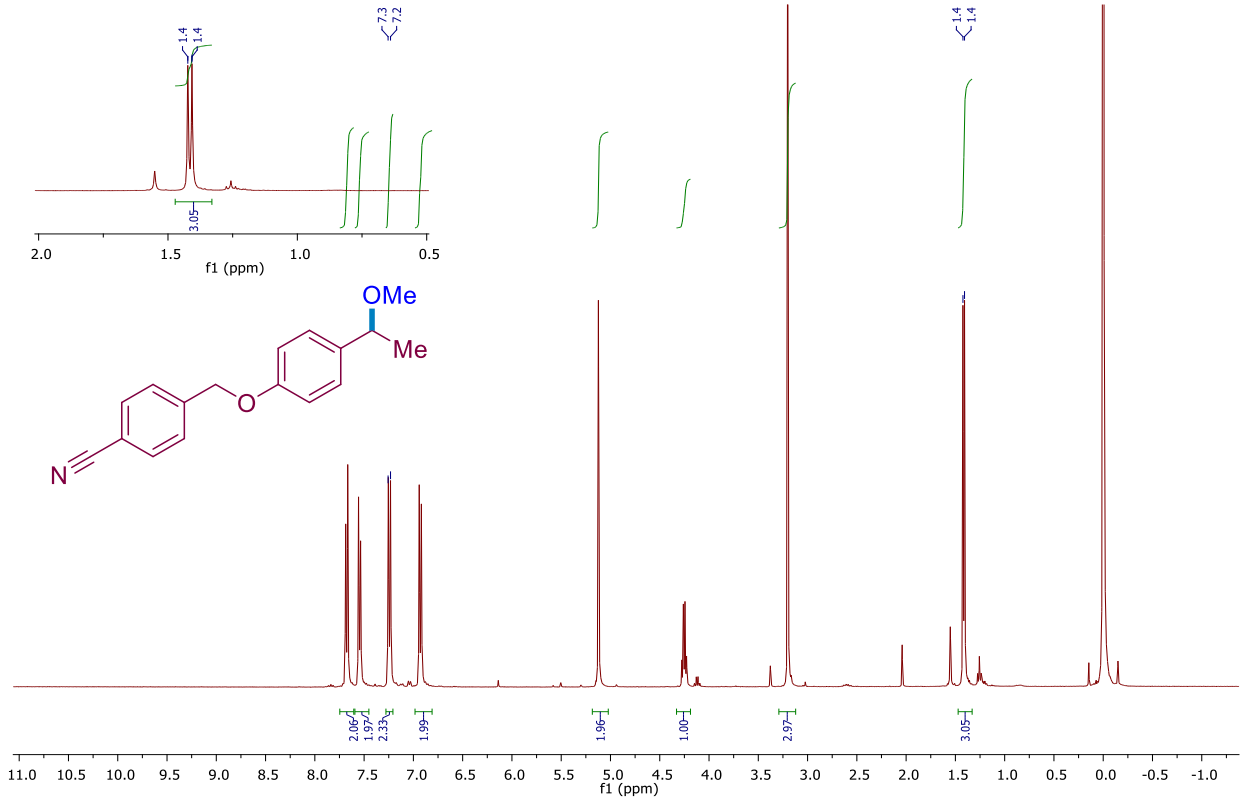


^{13}C NMR spectrum in $CDCl_3$

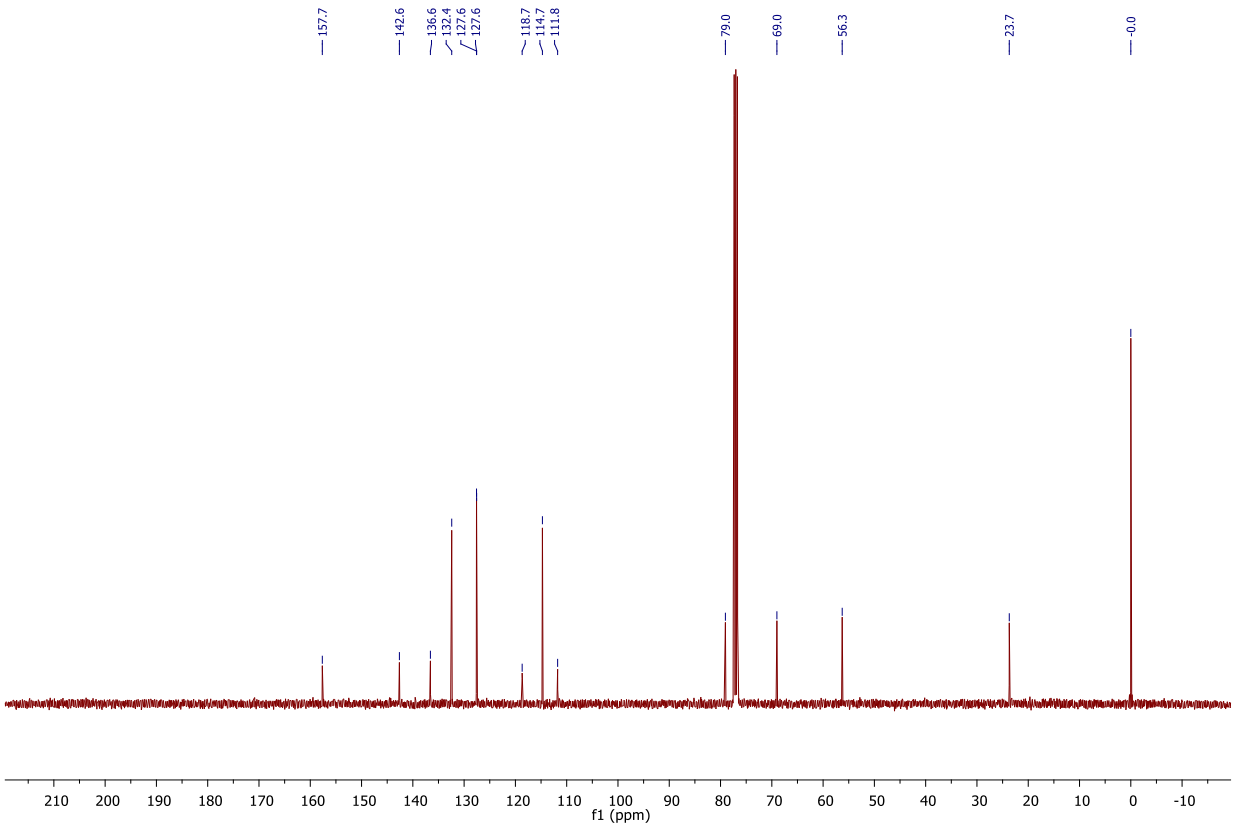


DEPT spectrum in $CDCl_3$.

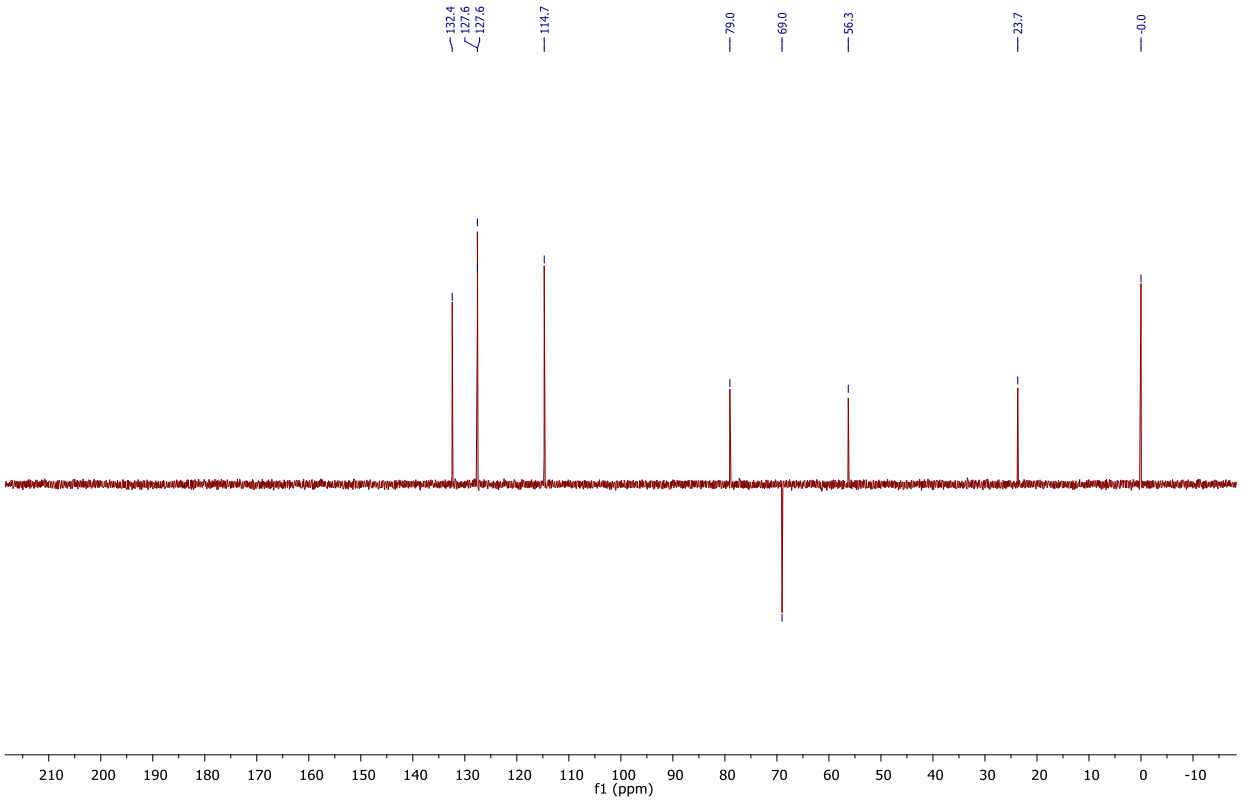
17c



^{1}H NMR spectrum in $CDCl_3$.

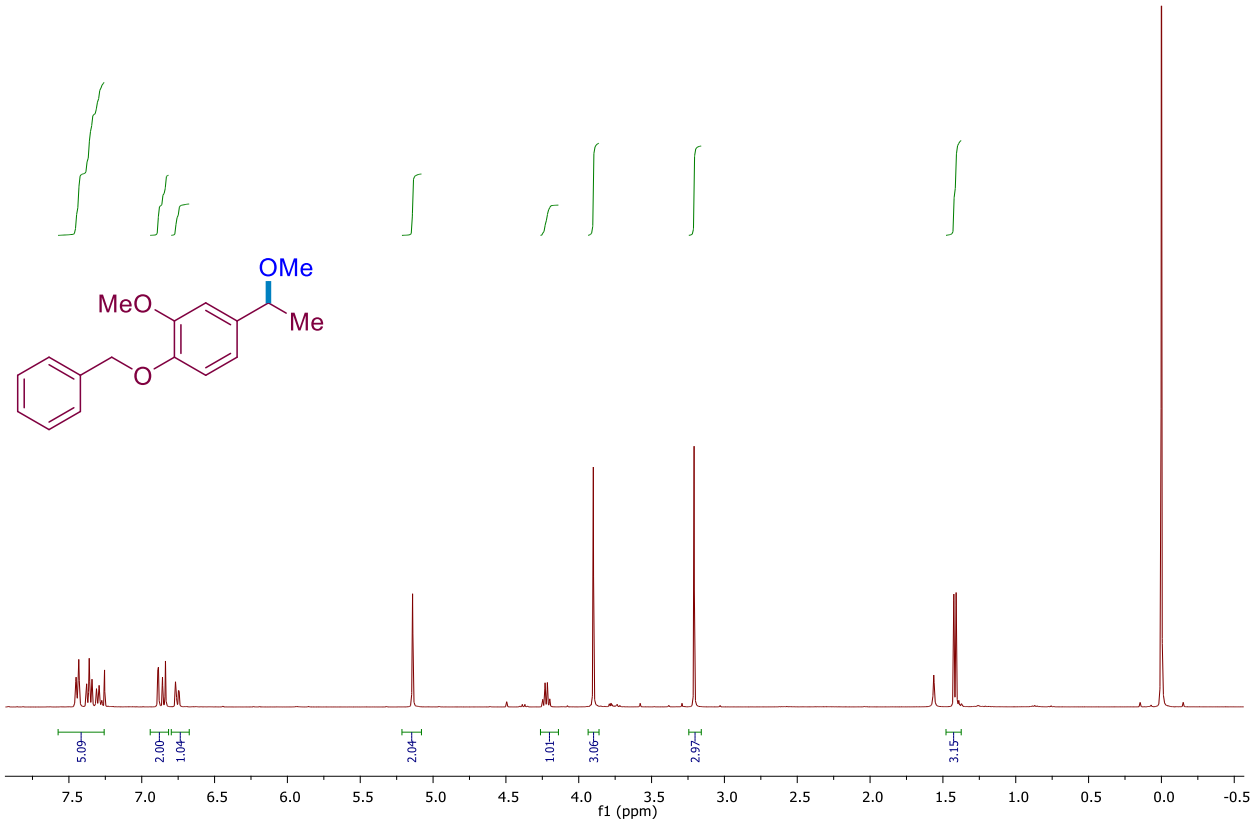


^{13}C NMR spectrum in $CDCl_3$

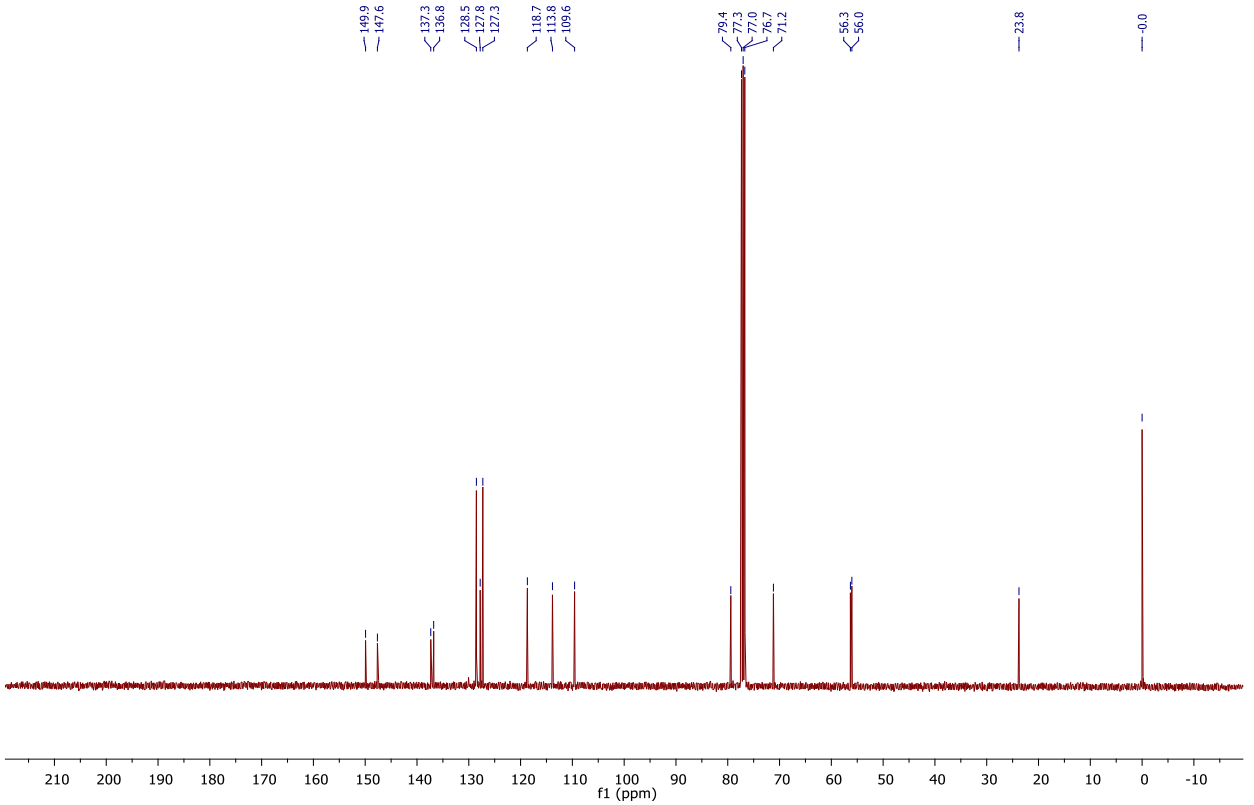


DEPT spectrum in $CDCl_3$.

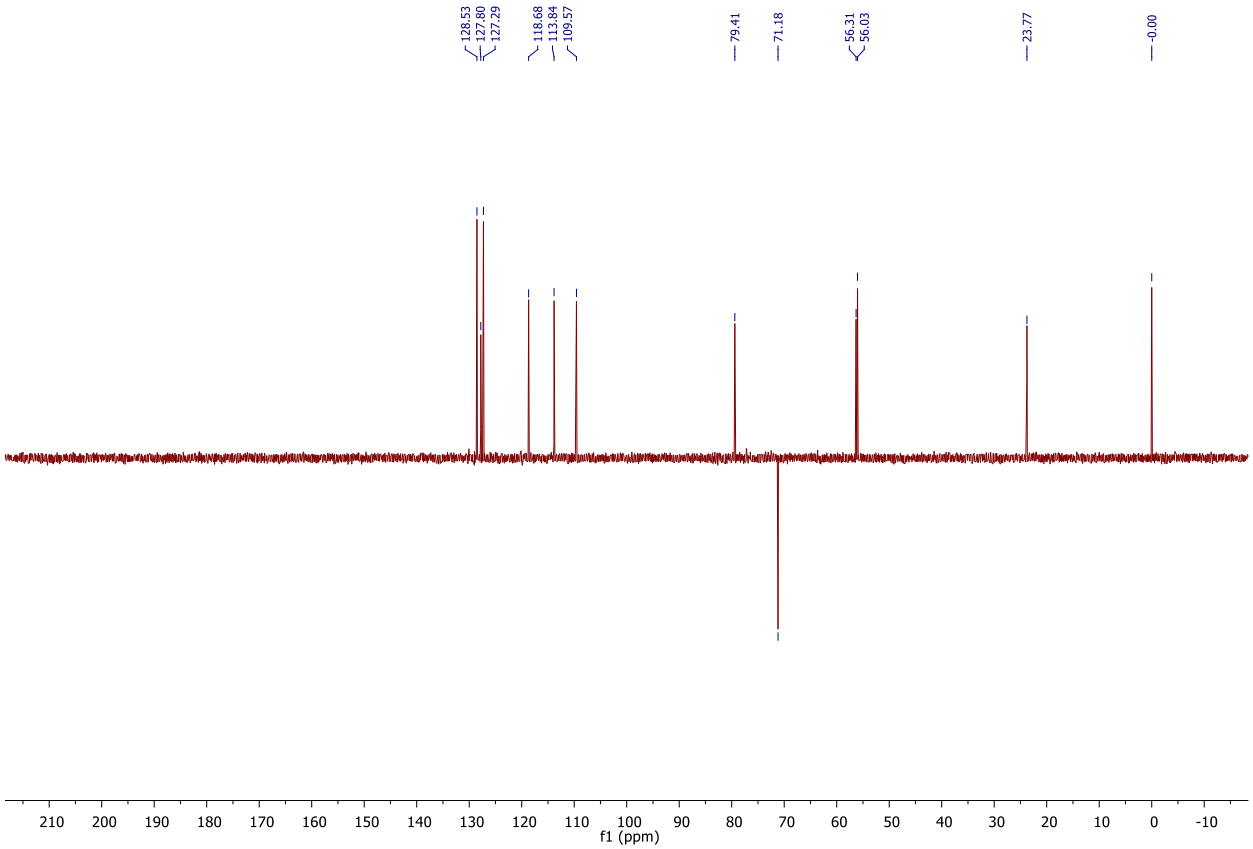
18c



^{1}H NMR spectrum in $CDCl_3$.

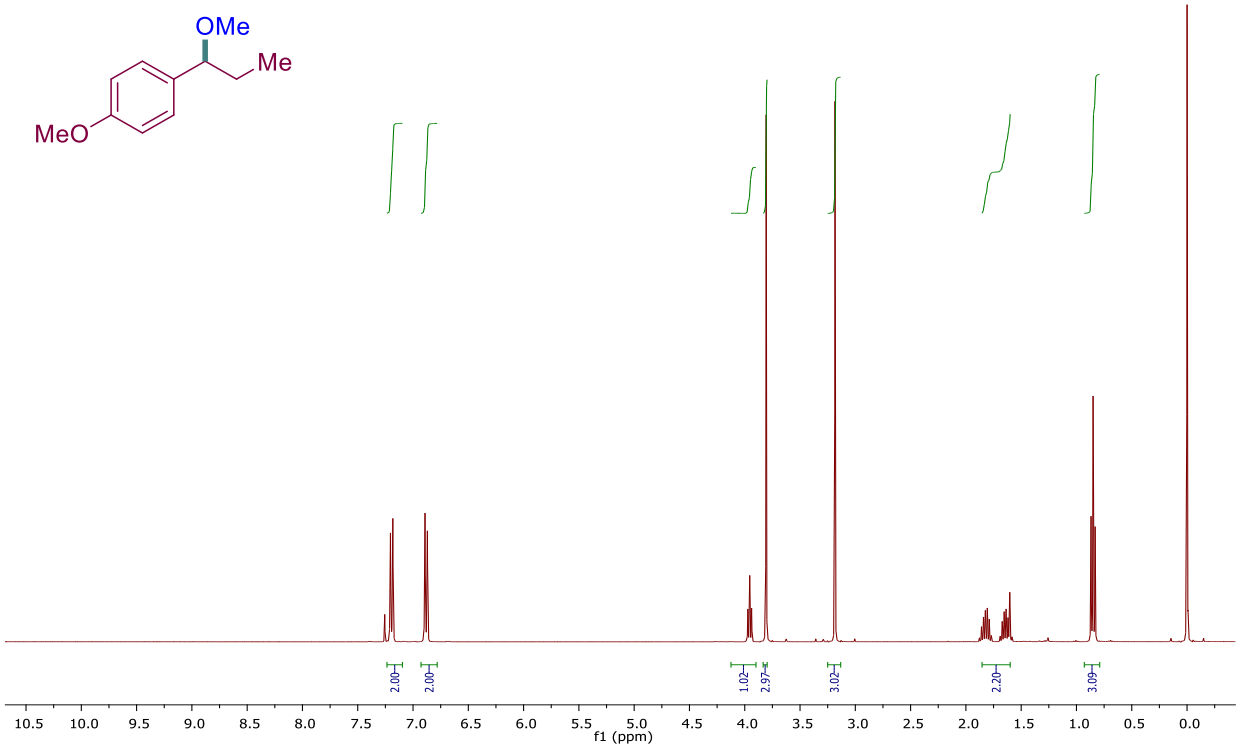


^{13}C NMR spectrum in $CDCl_3$

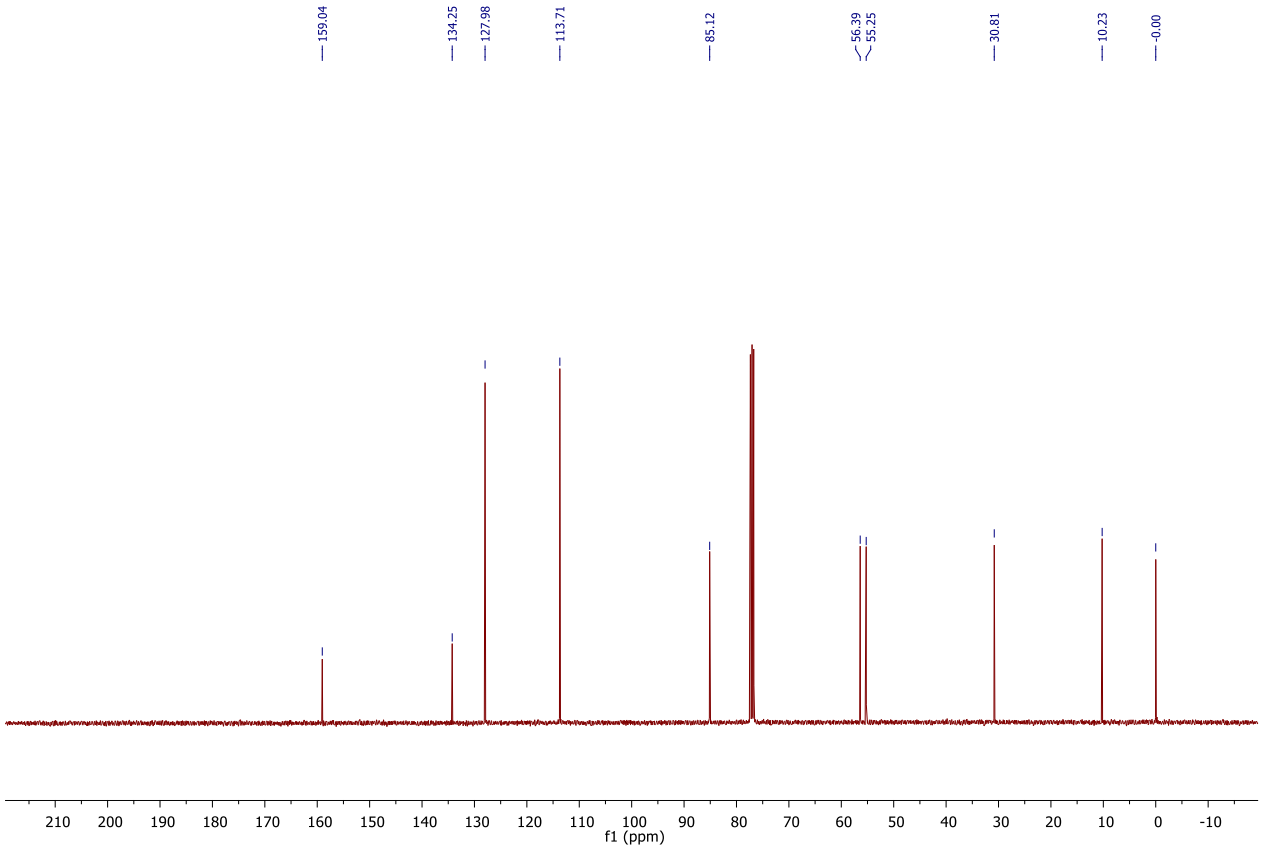


DEPT spectrum in $CDCl_3$.

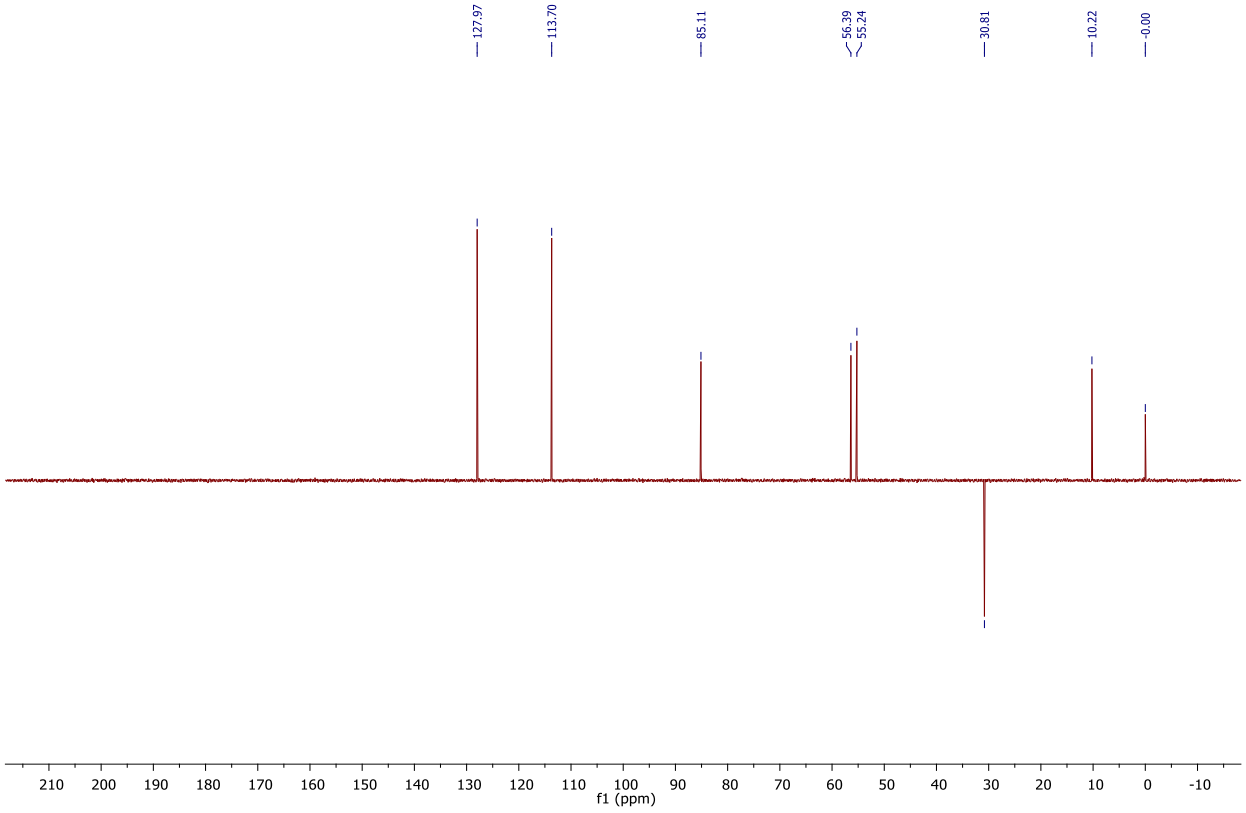
19c



^1H NMR spectrum in $CDCl_3$.

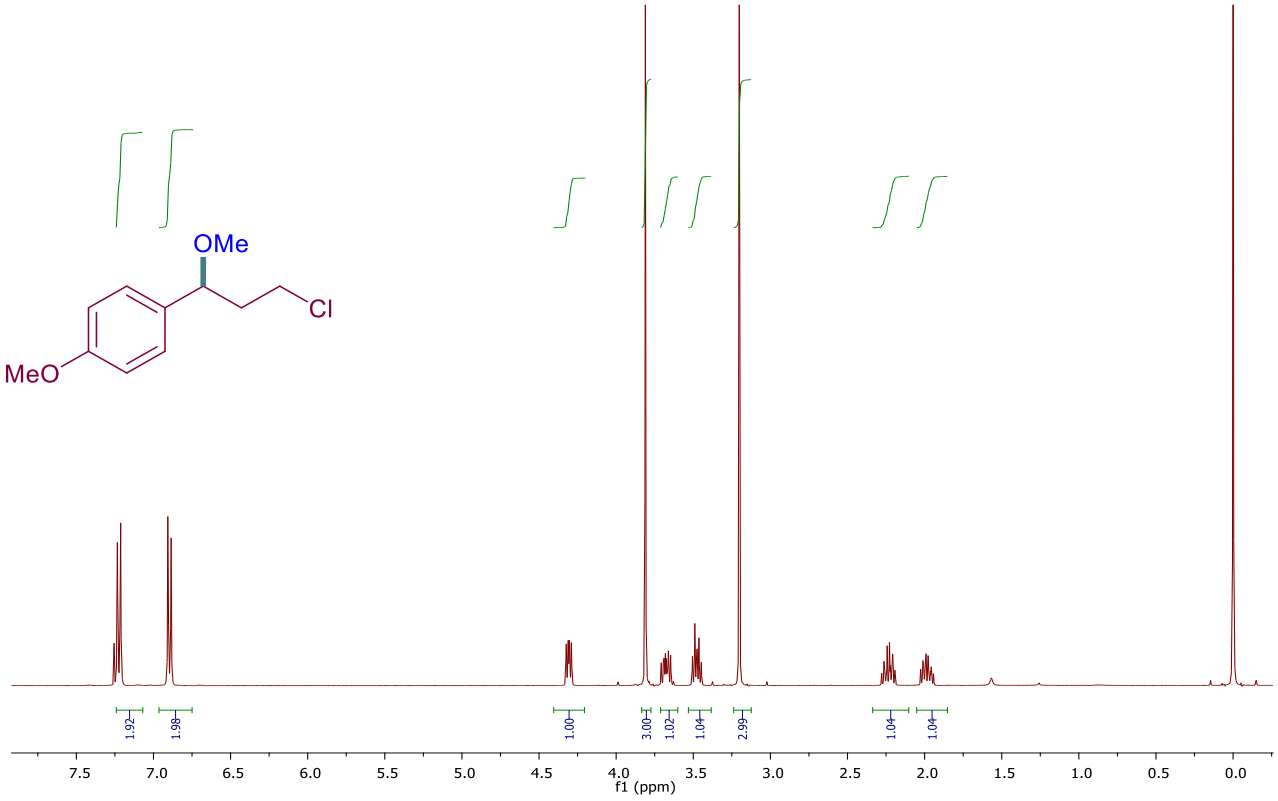


^{13}C NMR spectrum in $CDCl_3$

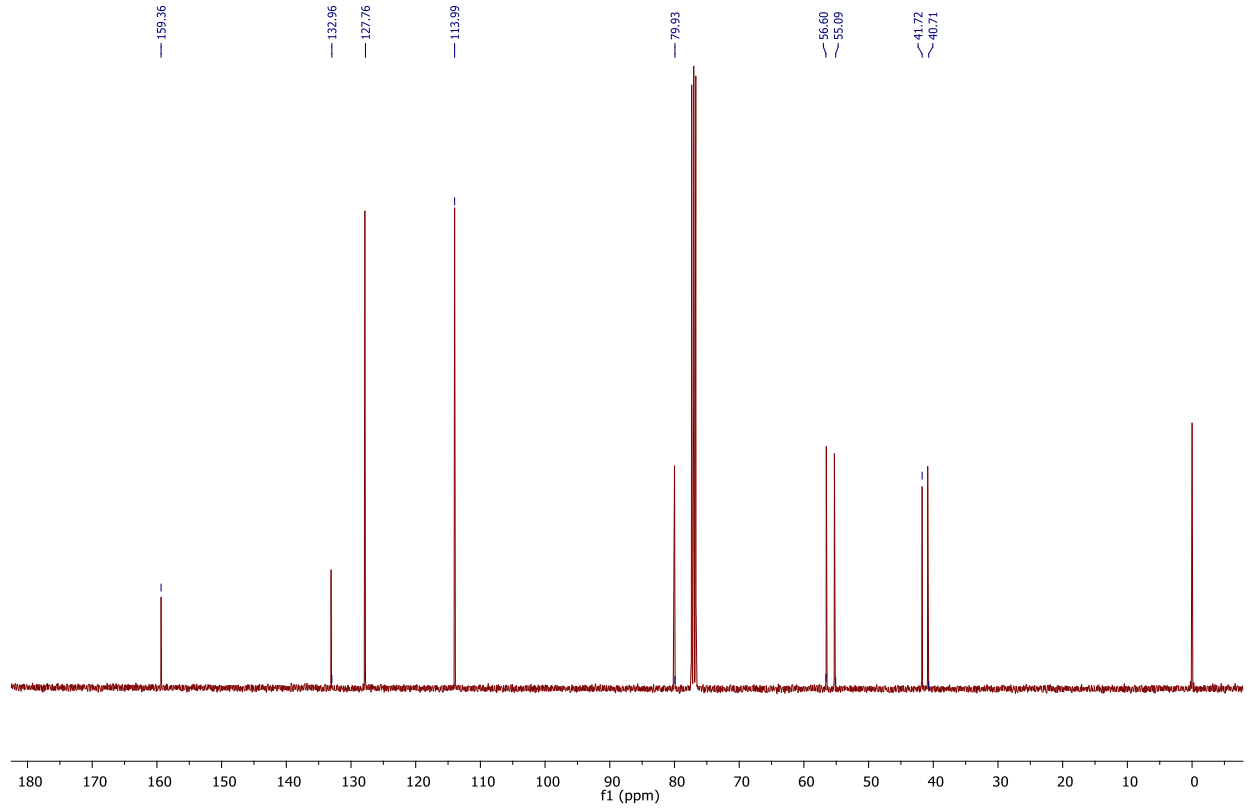


DEPT spectrum in $CDCl_3$.

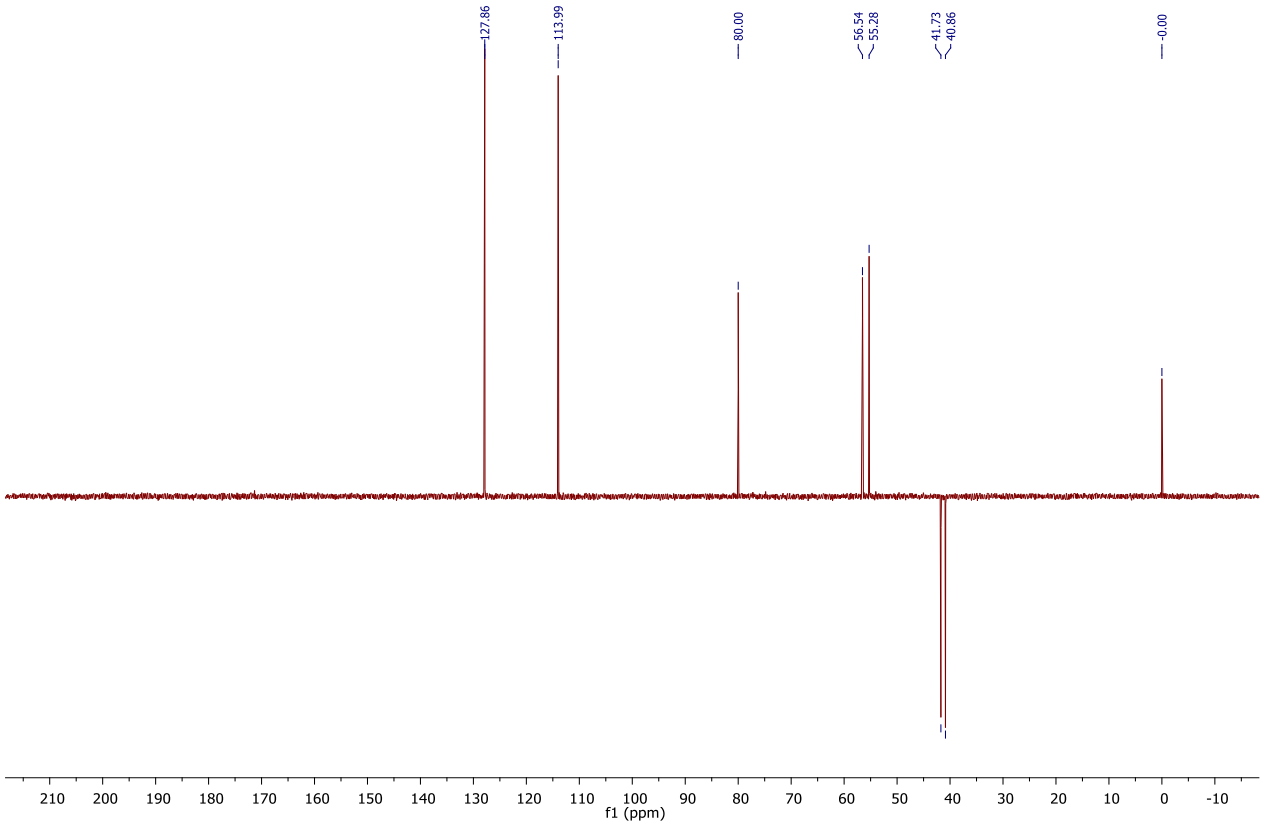
20c



^{1}H NMR spectrum in $CDCl_3$.

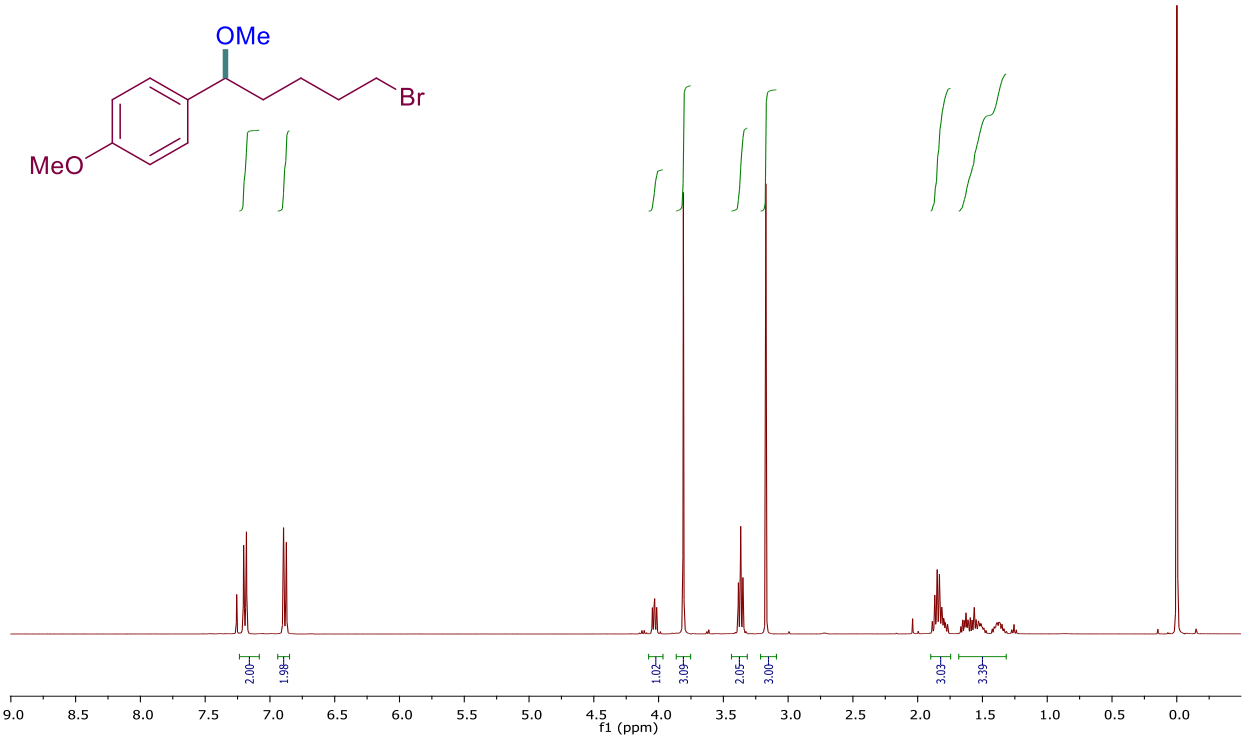


^{13}C NMR spectrum in $CDCl_3$.

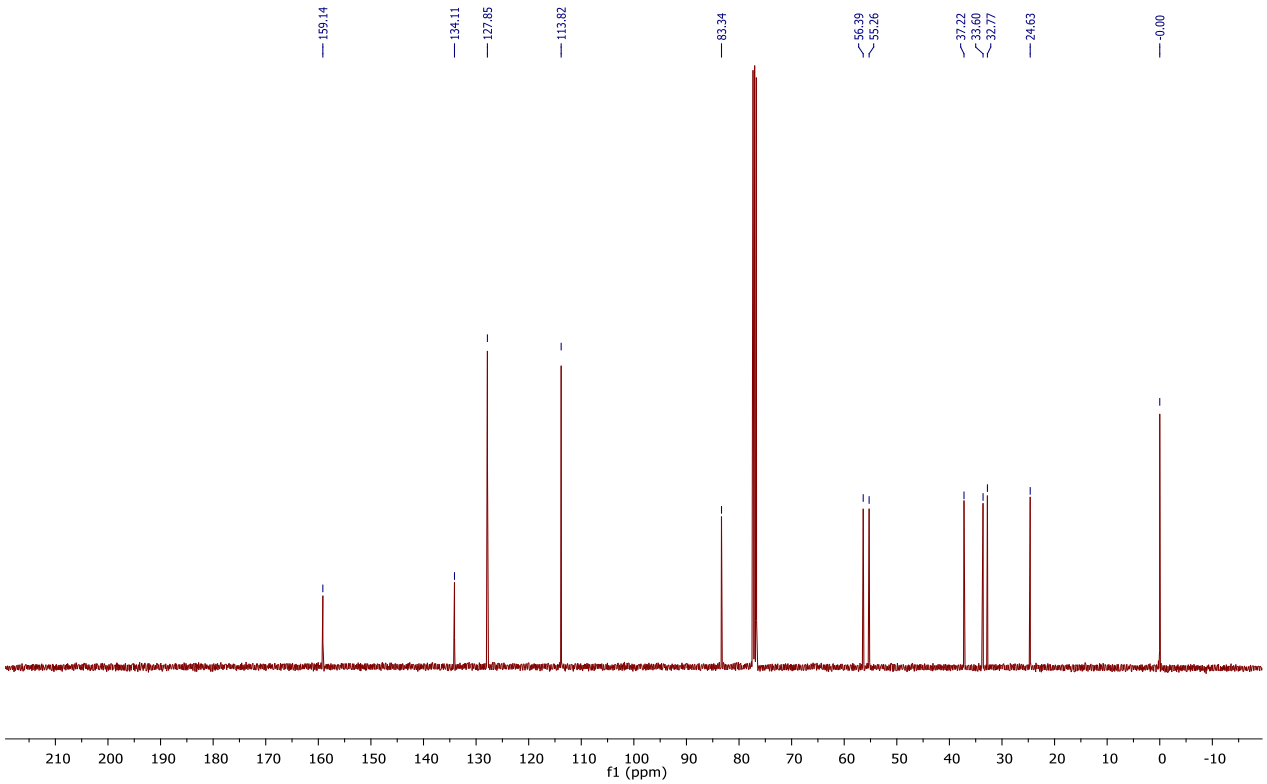


DEPT spectrum in $CDCl_3$.

21c

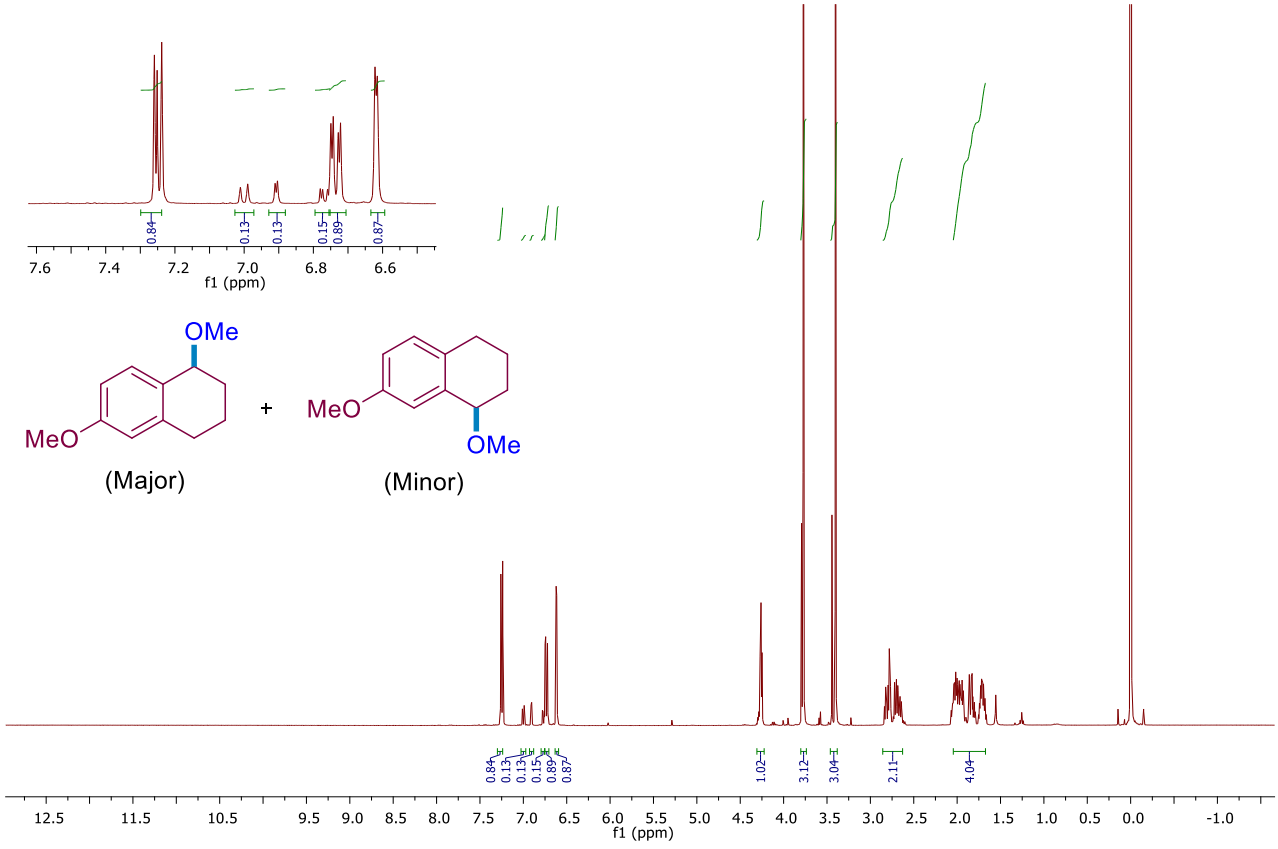


^{1}H NMR spectrum in $CDCl_3$.

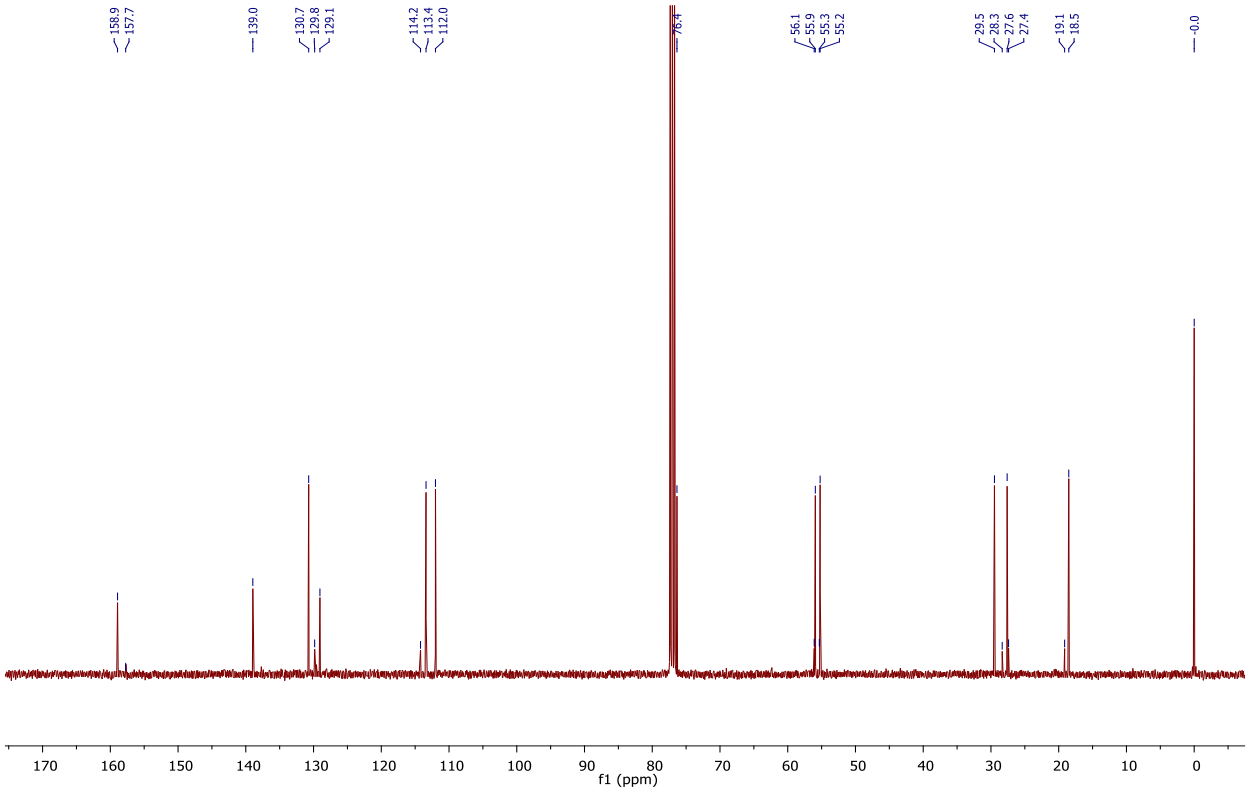


^{13}C NMR spectrum in $CDCl_3$

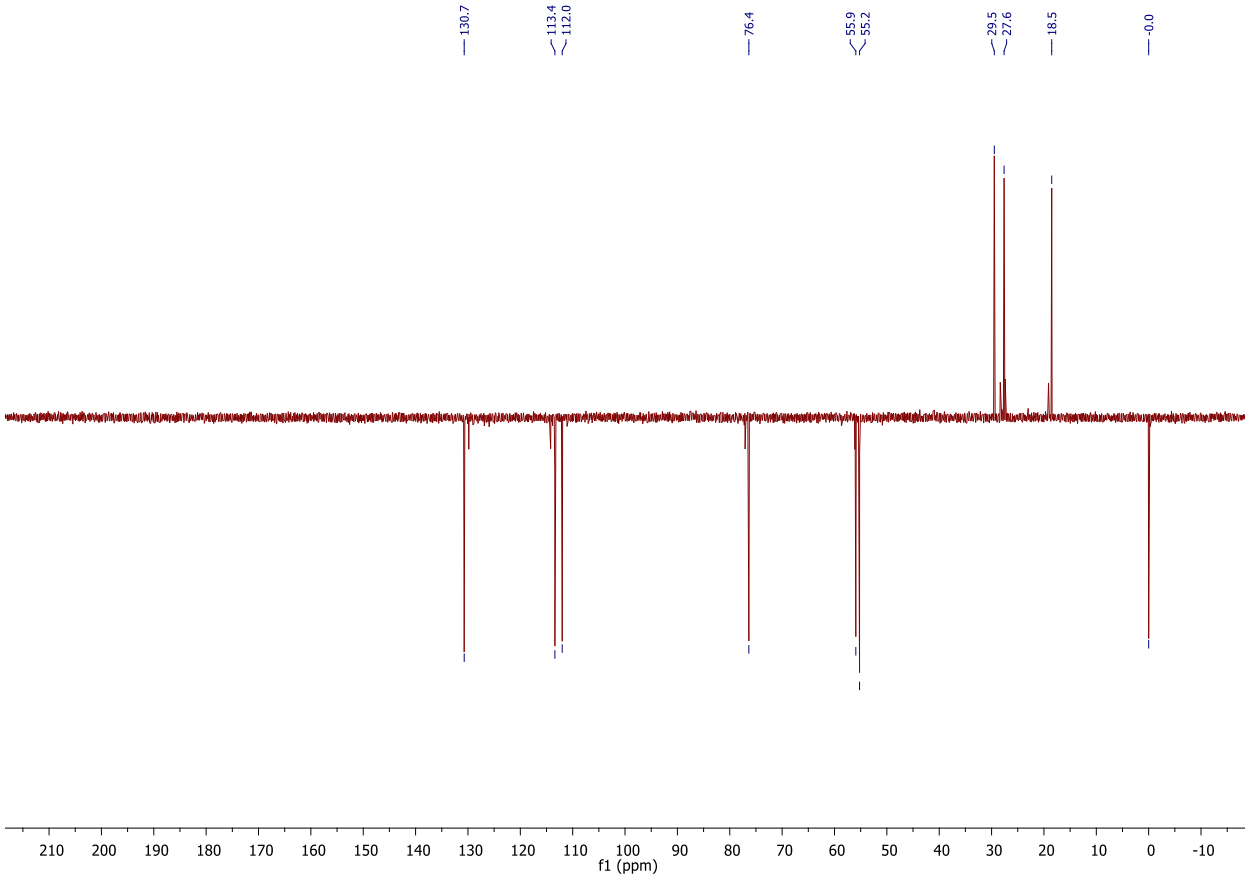
22c



^{1}H NMR spectrum in $CDCl_3$.

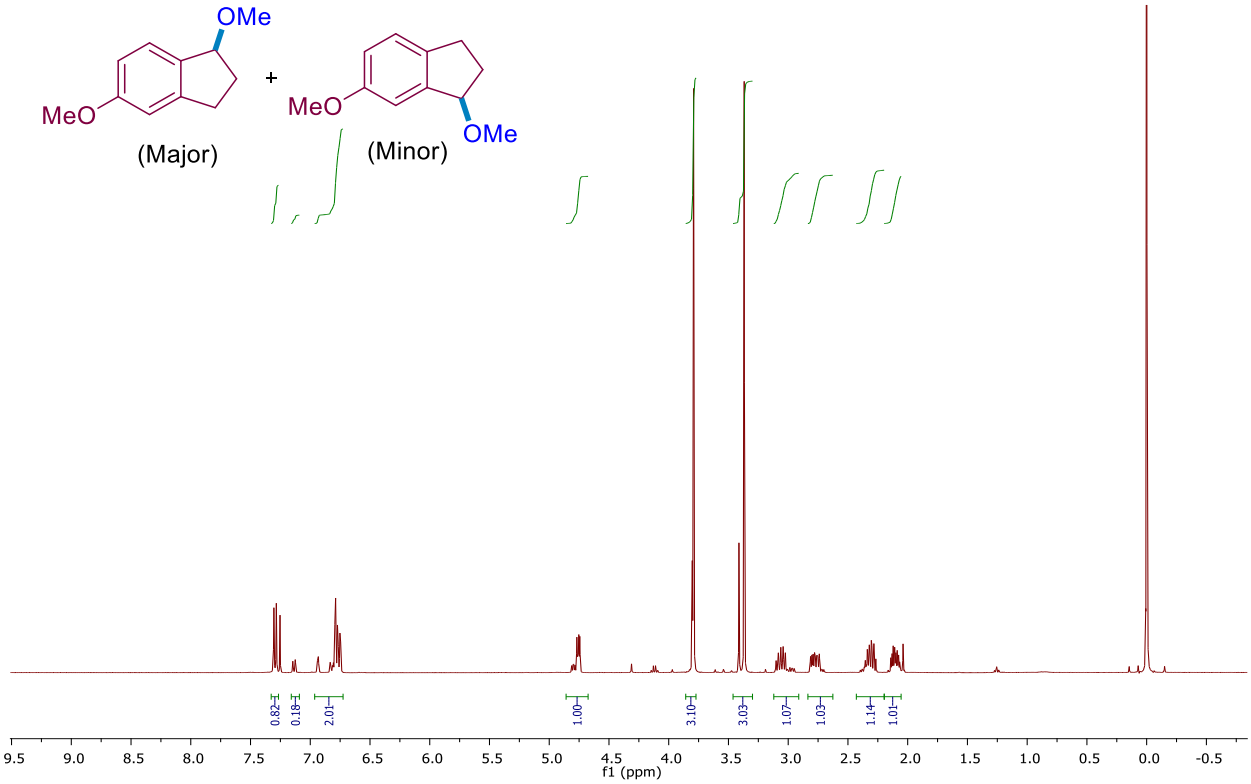


^{13}C NMR spectrum in $CDCl_3$

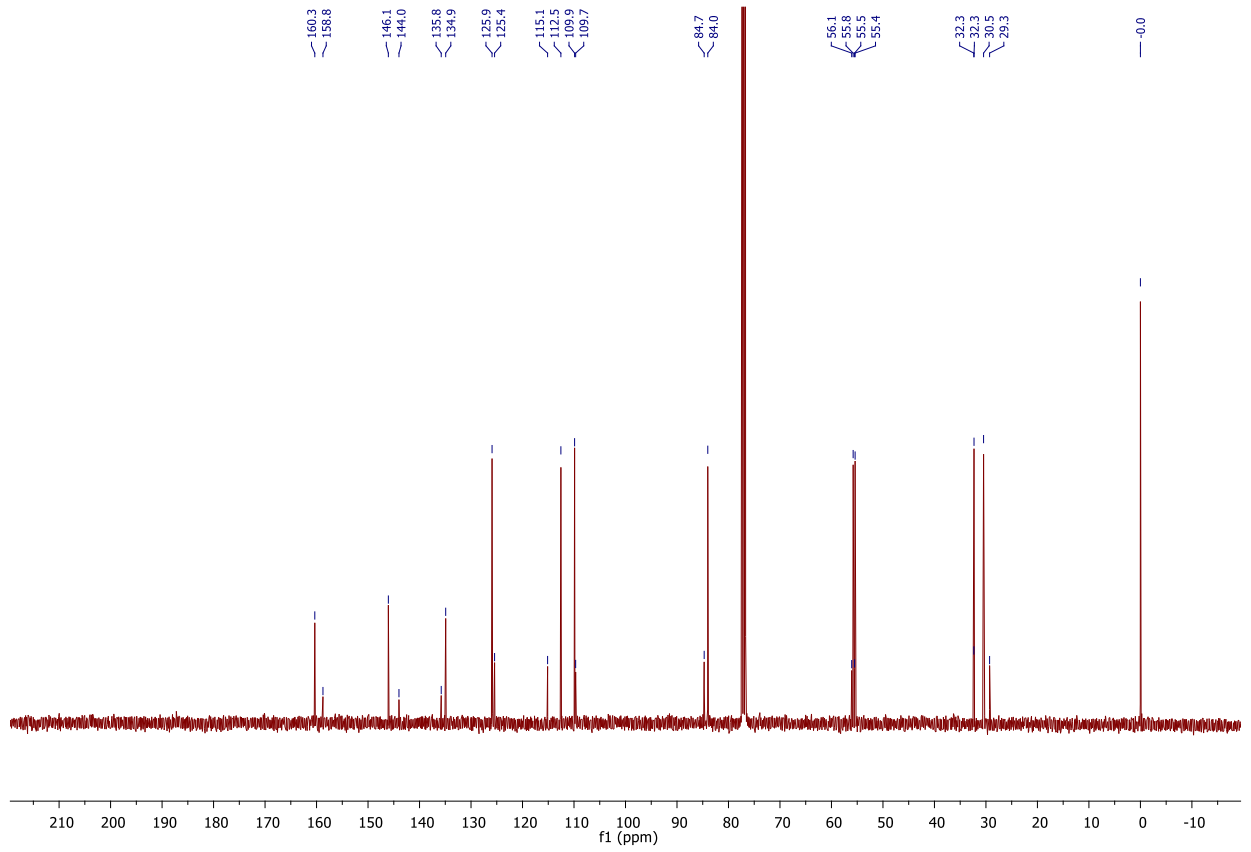


DEPT spectrum in $CDCl_3$.

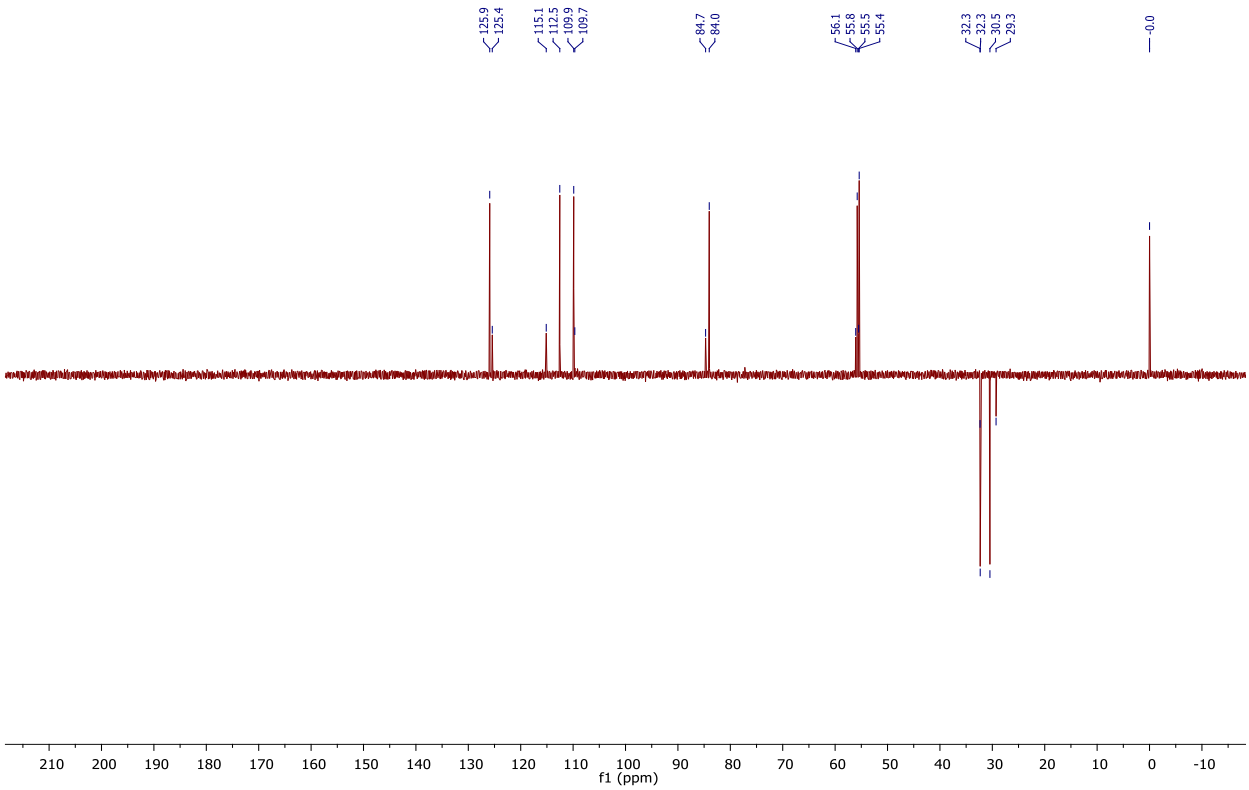
23c



^{1}H NMR spectrum in $CDCl_3$.

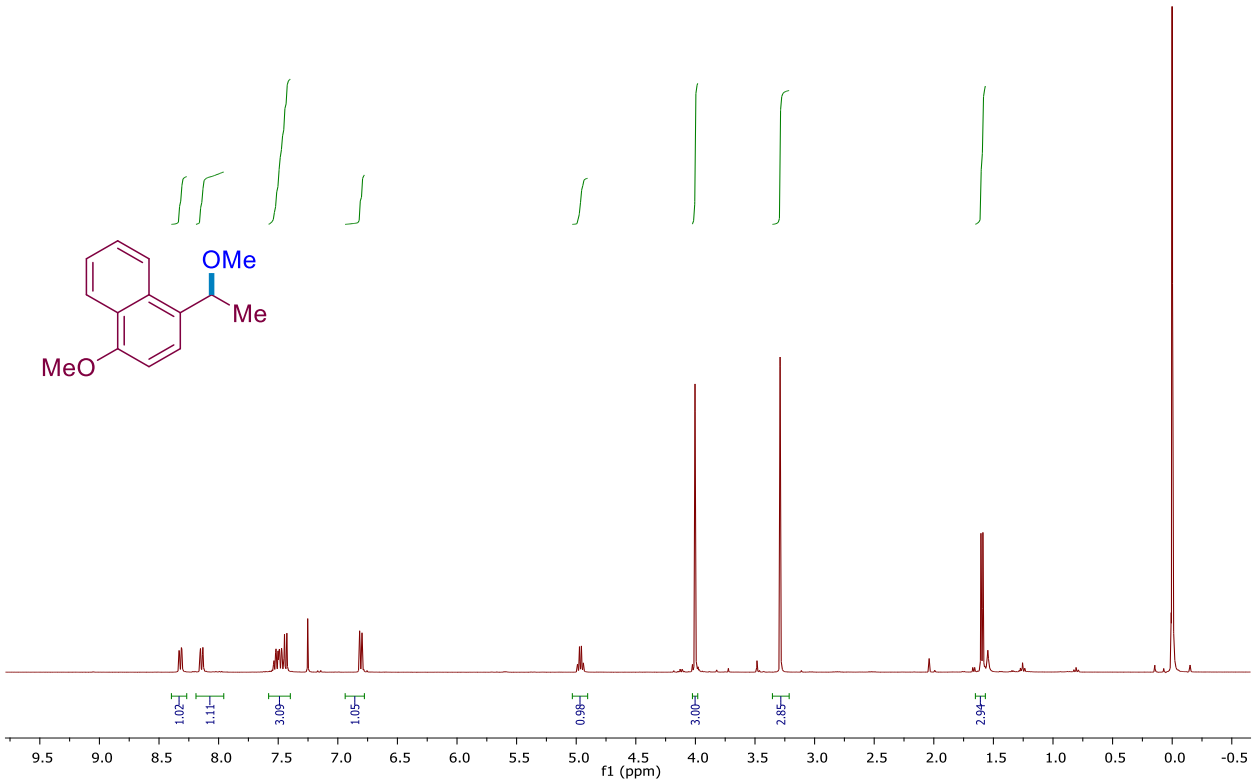


^{13}C NMR spectrum in $CDCl_3$

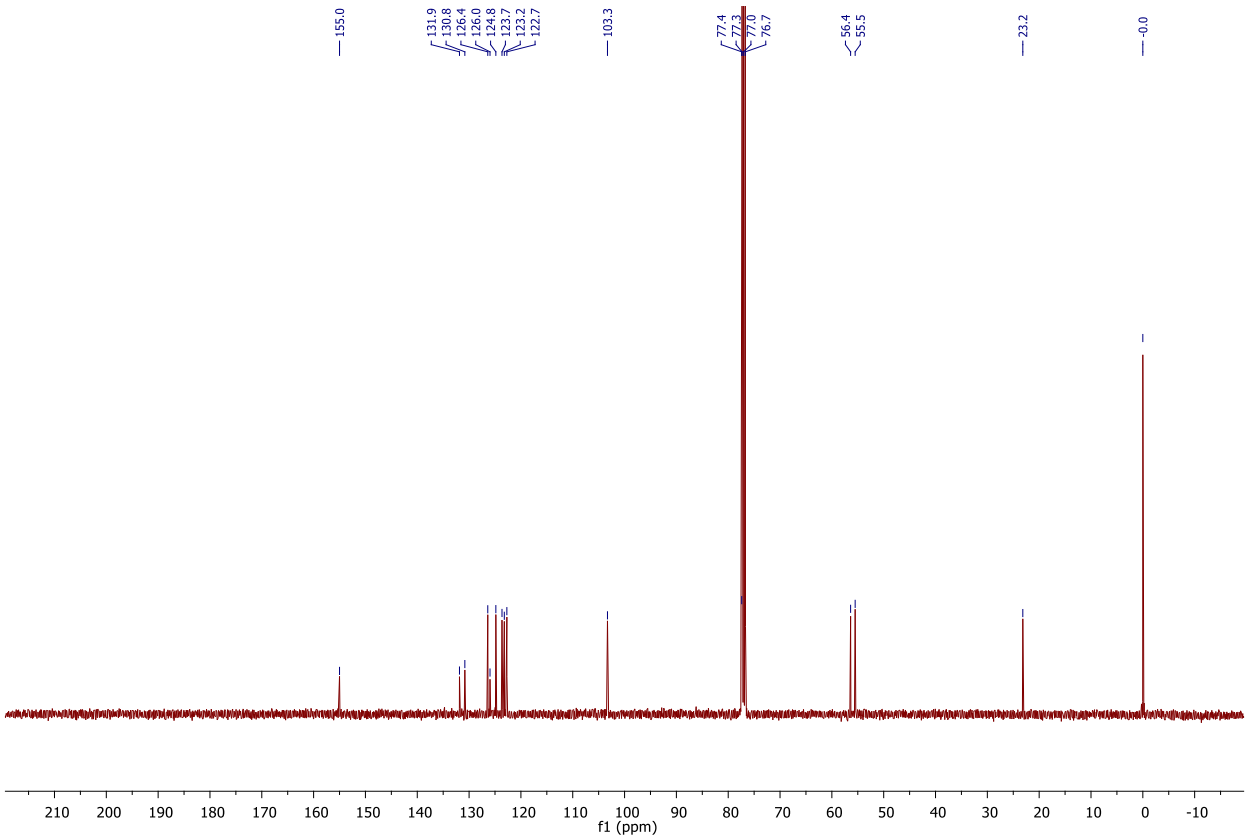


DEPT spectrum in $CDCl_3$.

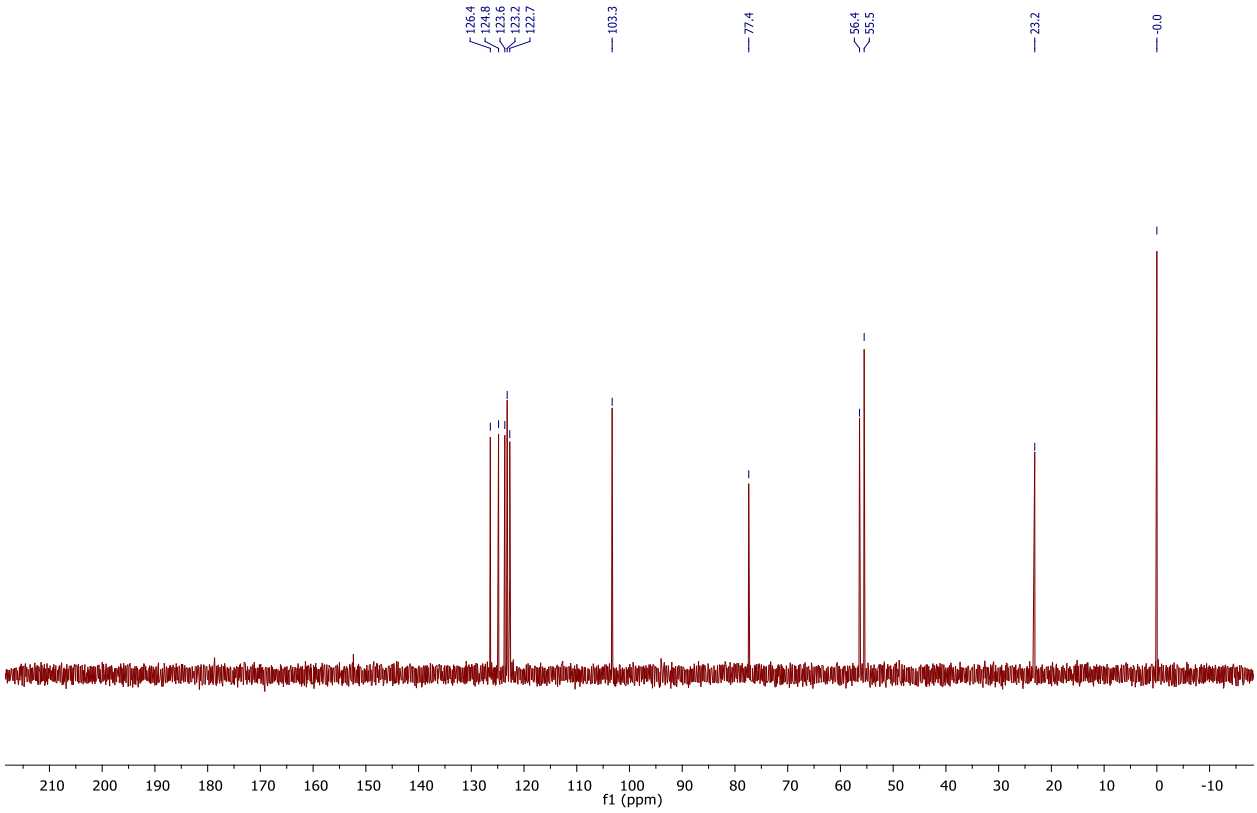
24c



^{1}H NMR spectrum in $CDCl_3$.

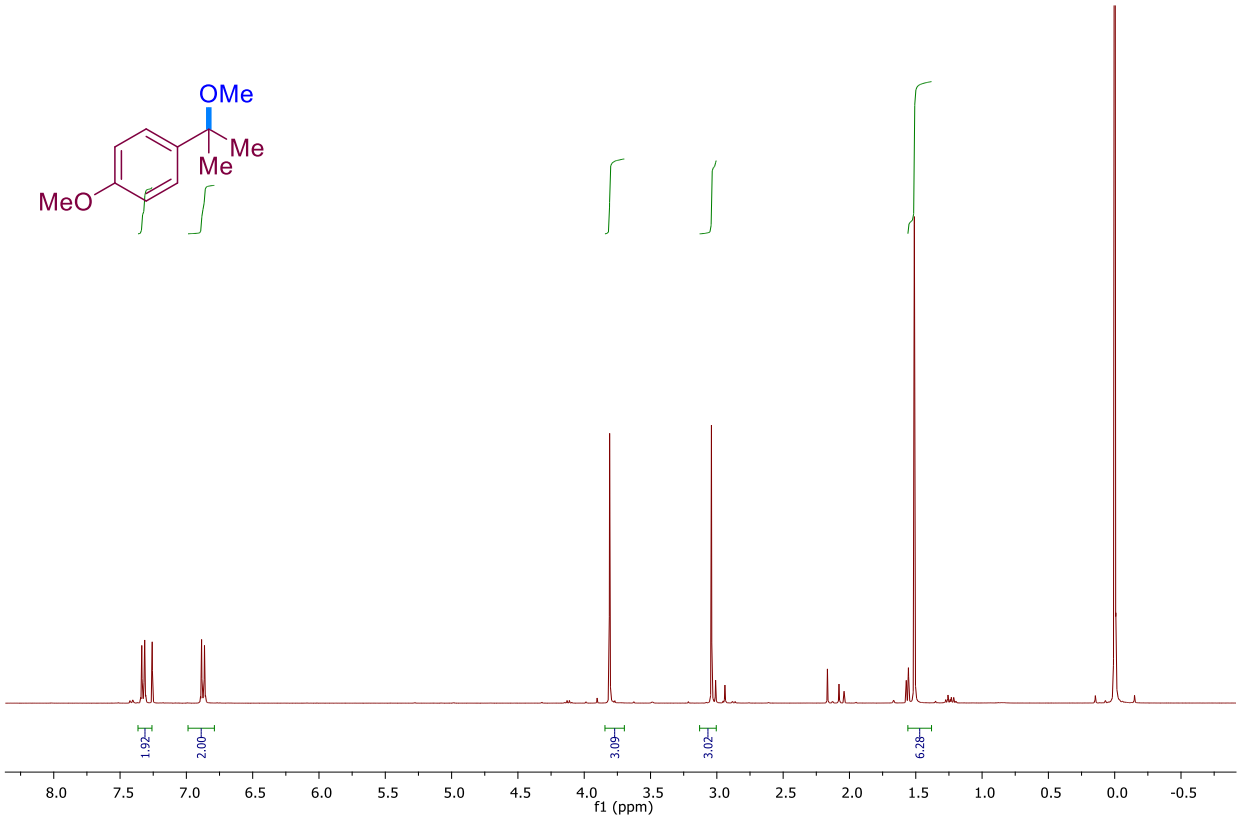


^{13}C NMR spectrum in $CDCl_3$

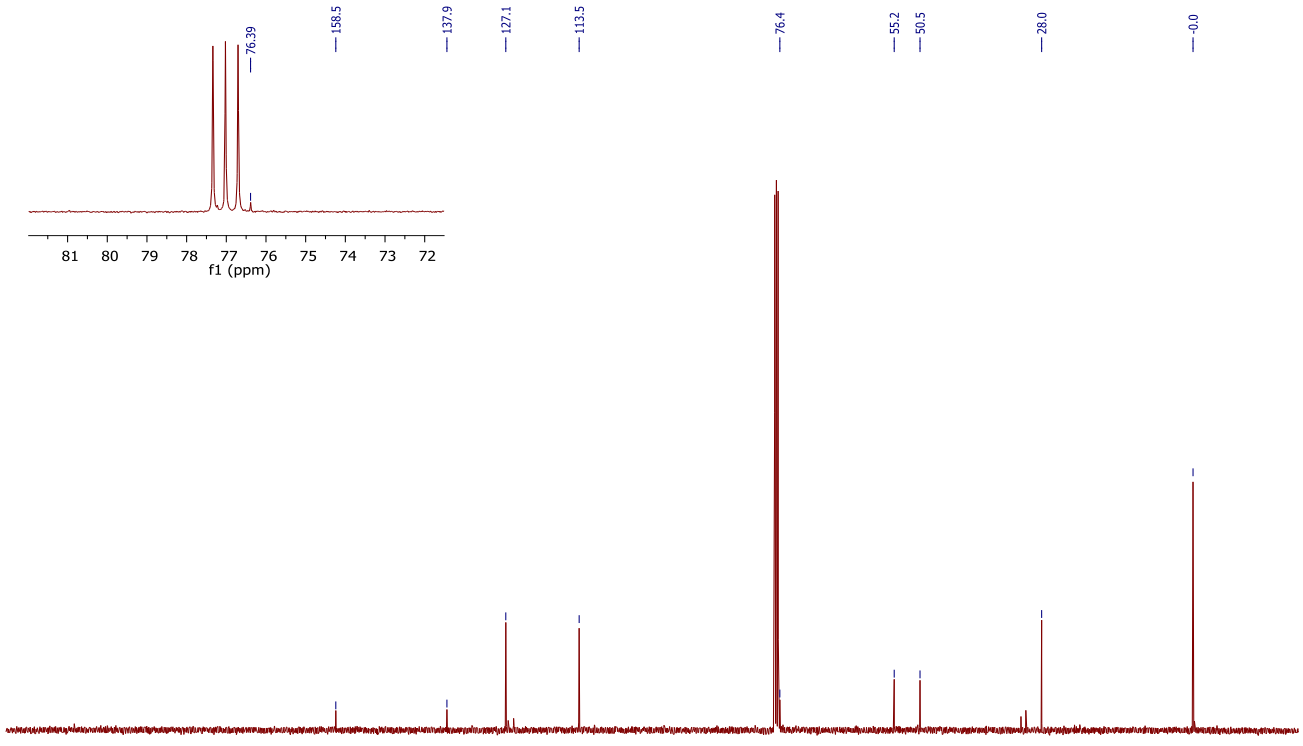


DEPT spectrum in $CDCl_3$.

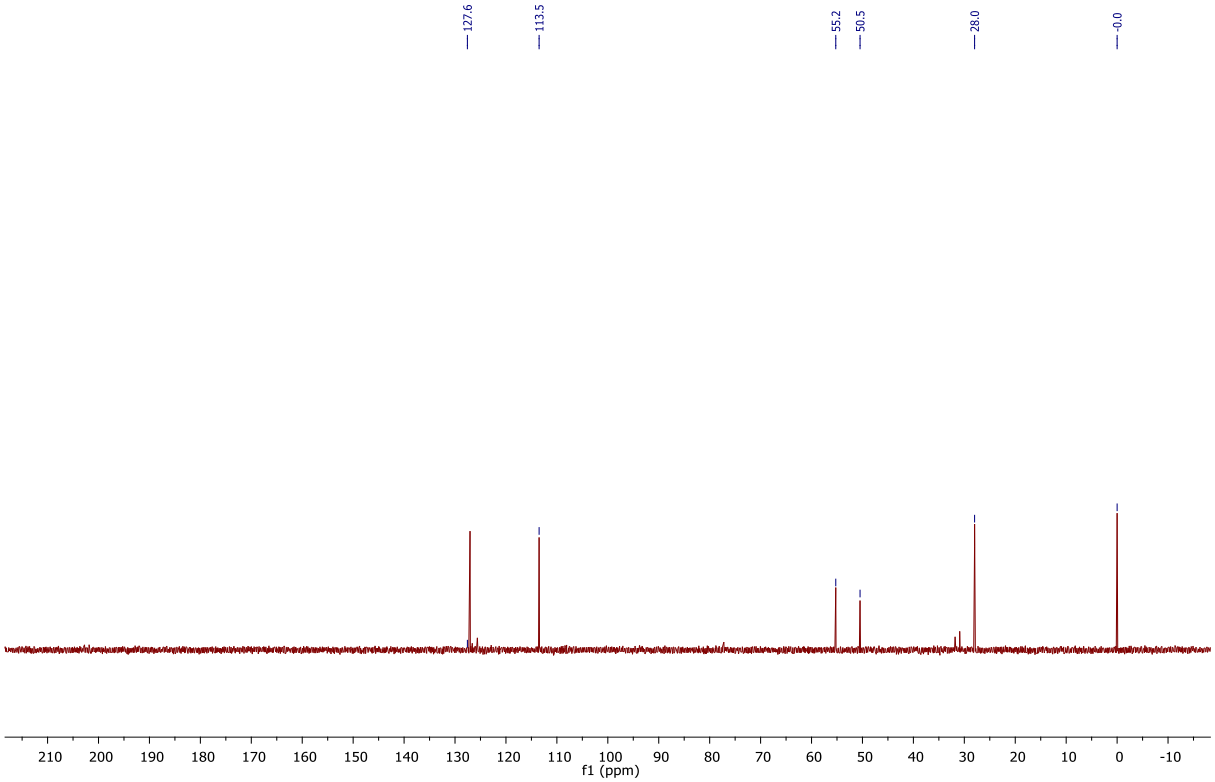
25c



^{1}H NMR spectrum in $CDCl_3$.

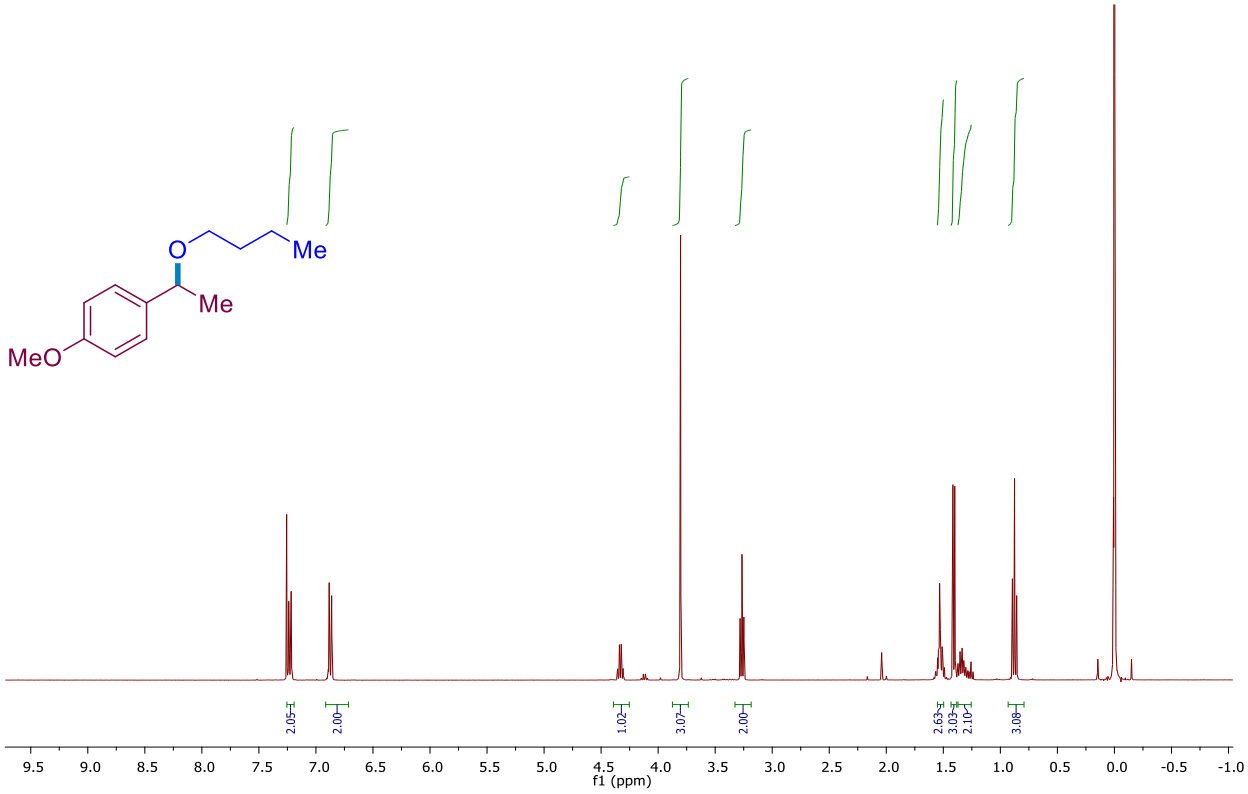


^{13}C NMR spectrum in $CDCl_3$

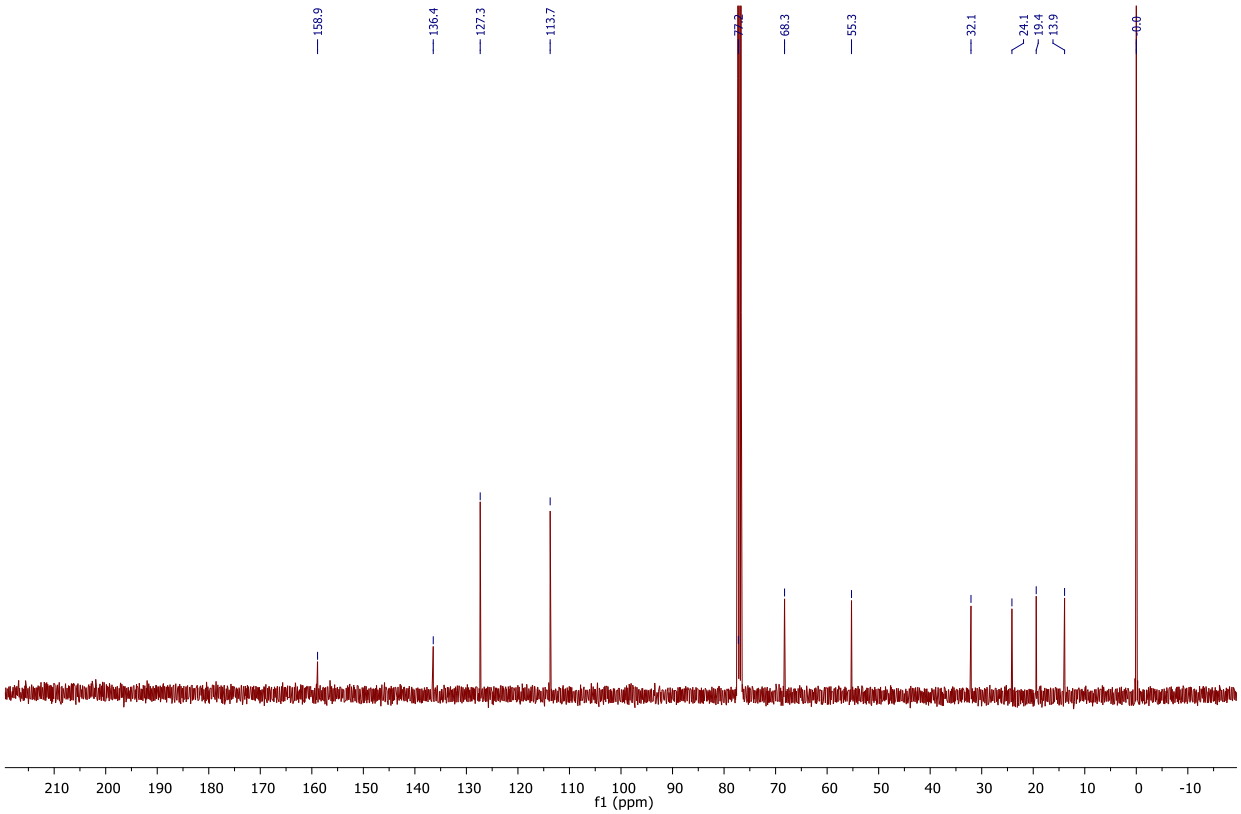


DEPT spectrum in $CDCl_3$.

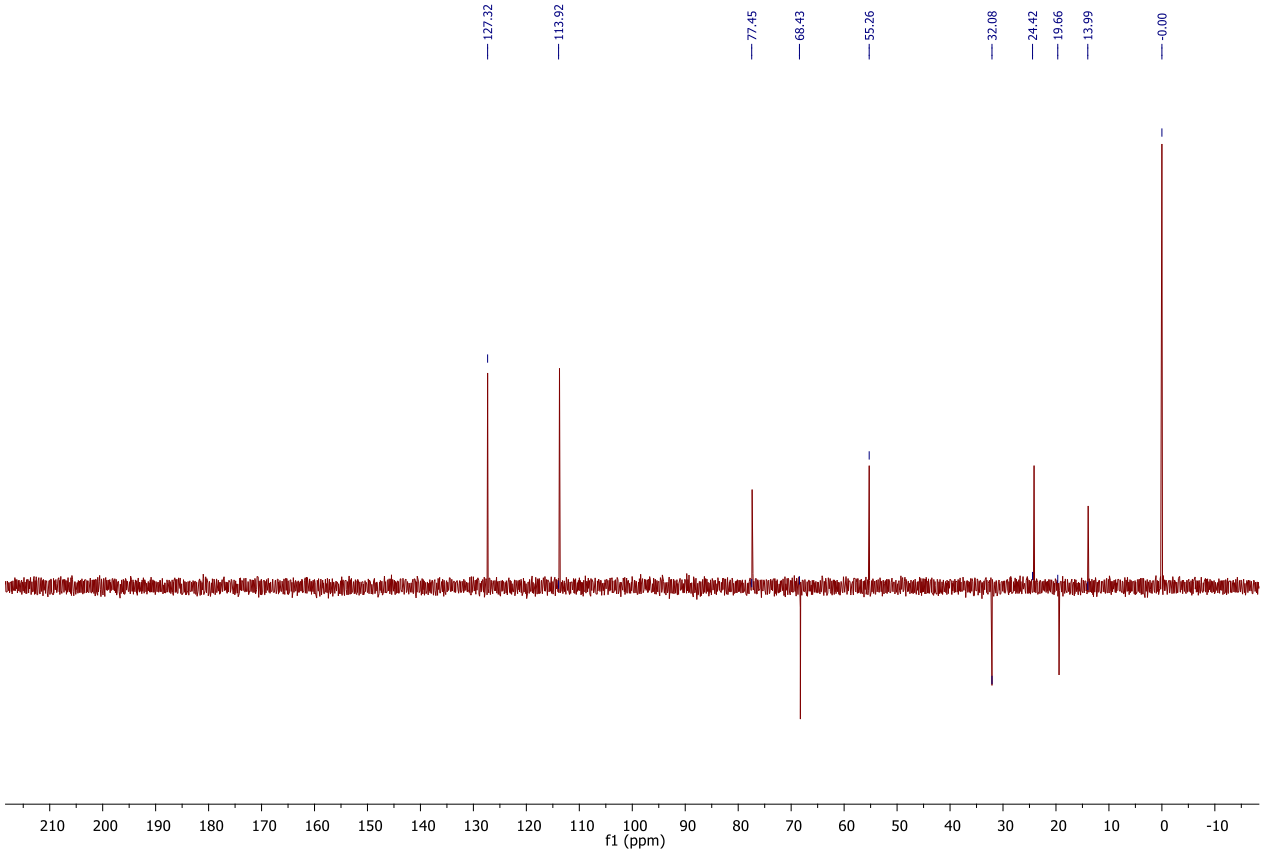
26c



^{1}H NMR spectrum in $CDCl_3$.

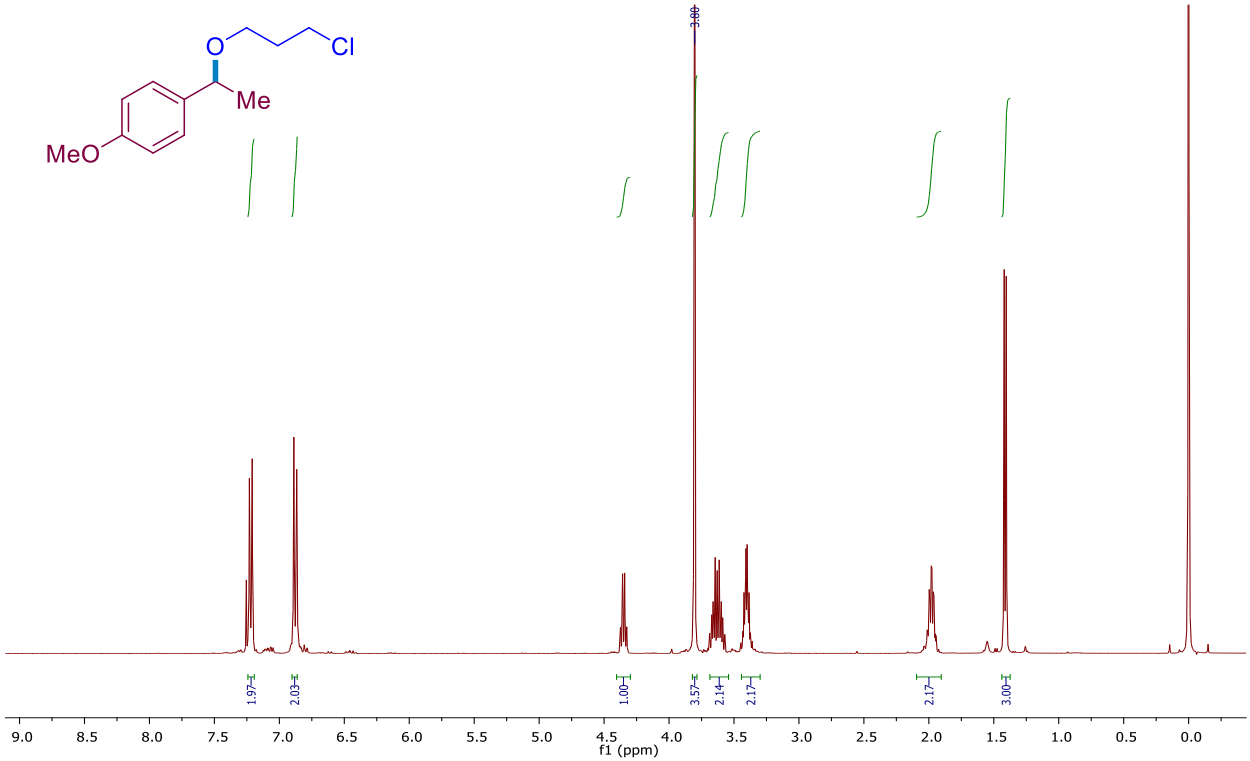


^{13}C NMR spectrum in $CDCl_3$

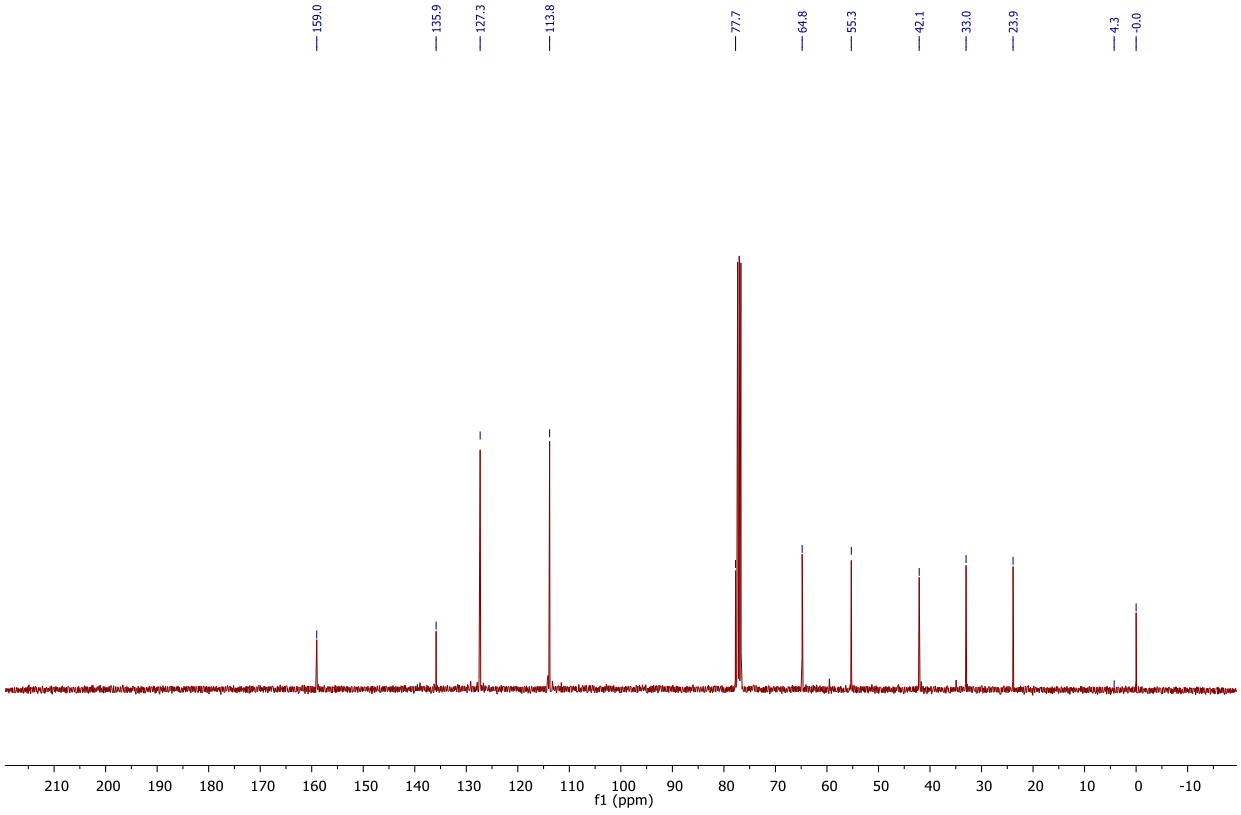


DEPT spectrum in $CDCl_3$.

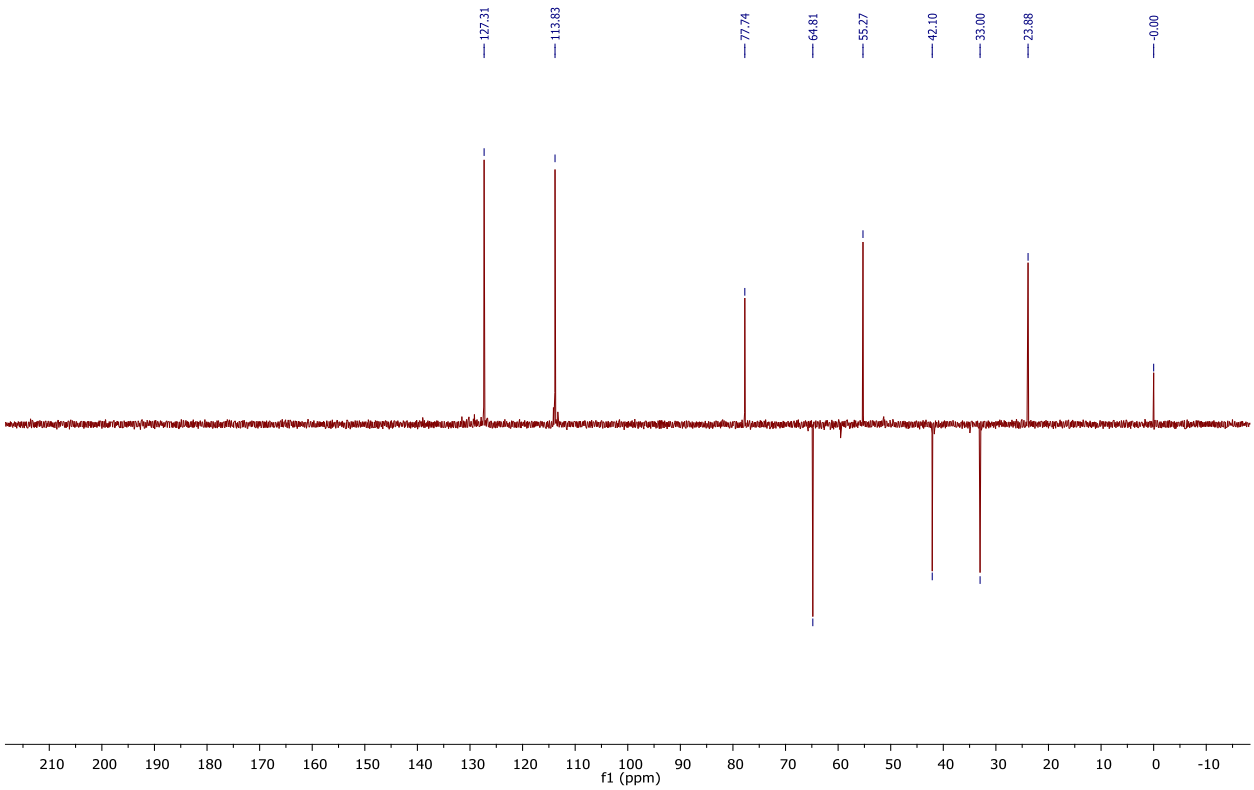
27c



^{1}H NMR spectrum in $CDCl_3$.

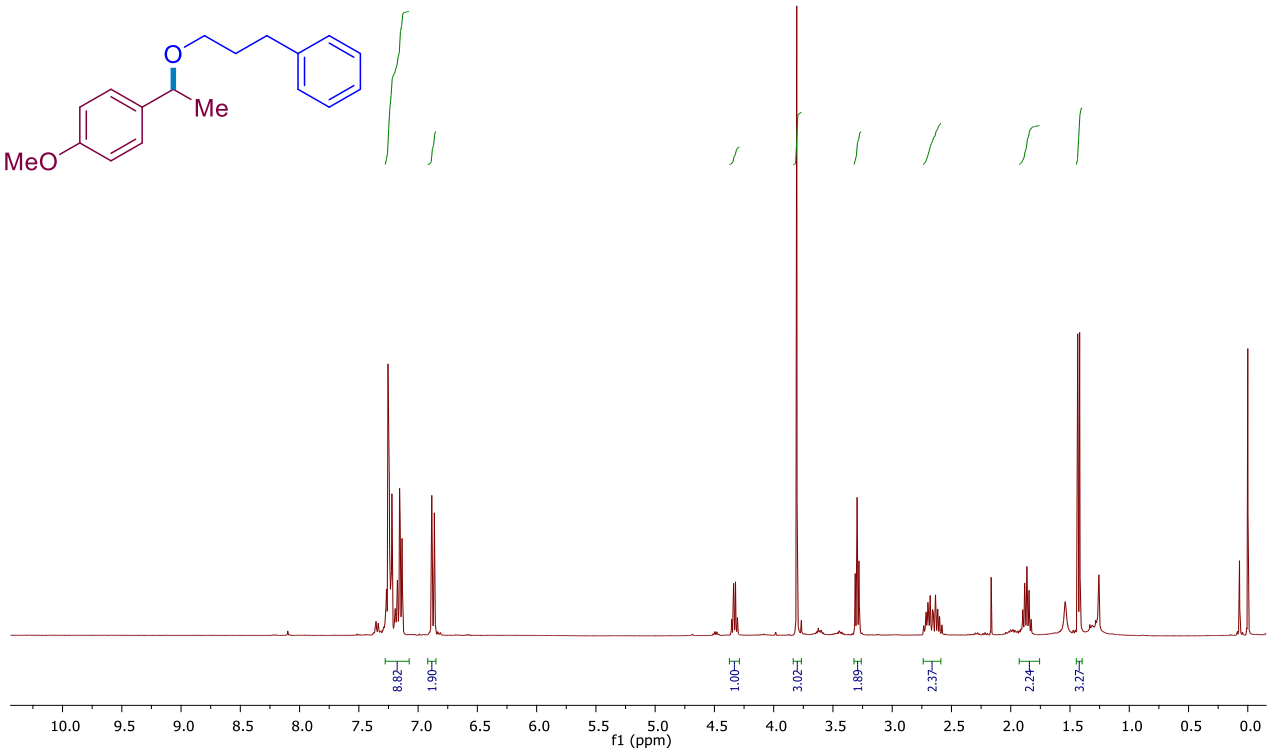


^{13}C NMR spectrum in $CDCl_3$

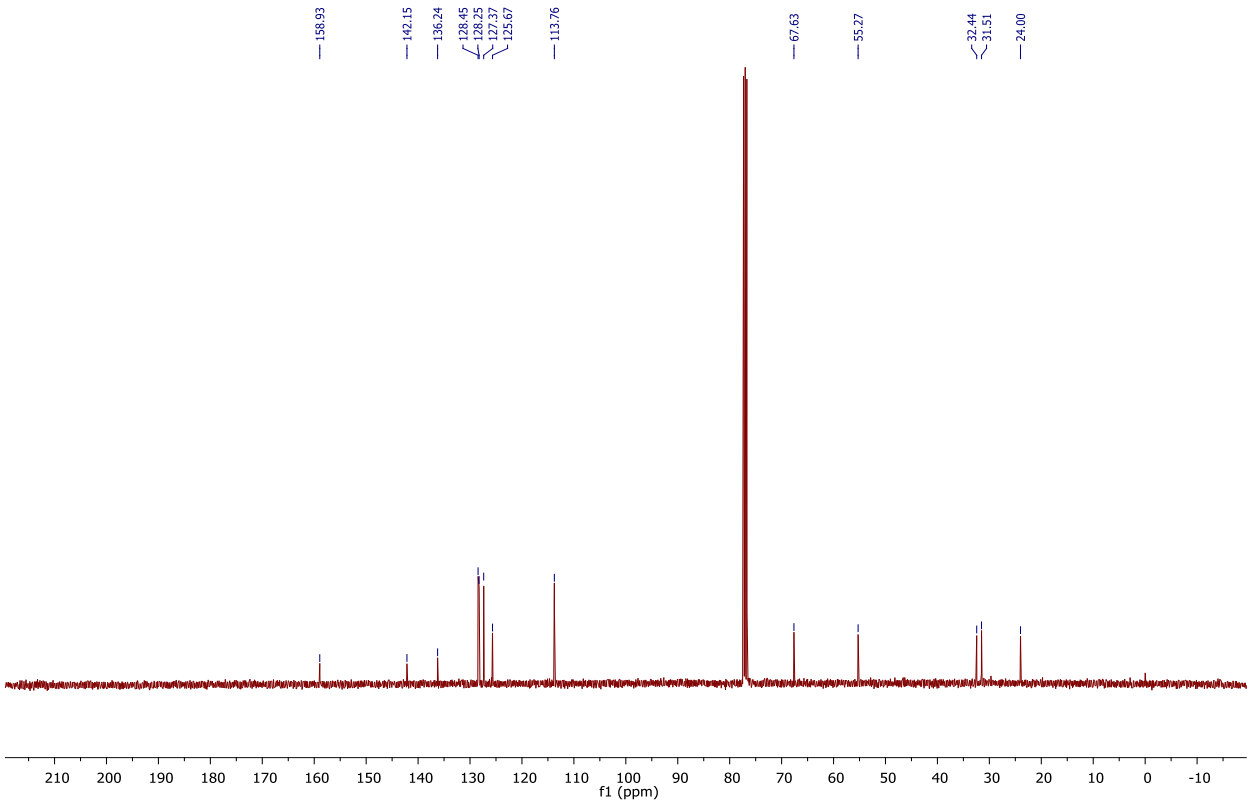


DEPT spectrum in $CDCl_3$.

28c

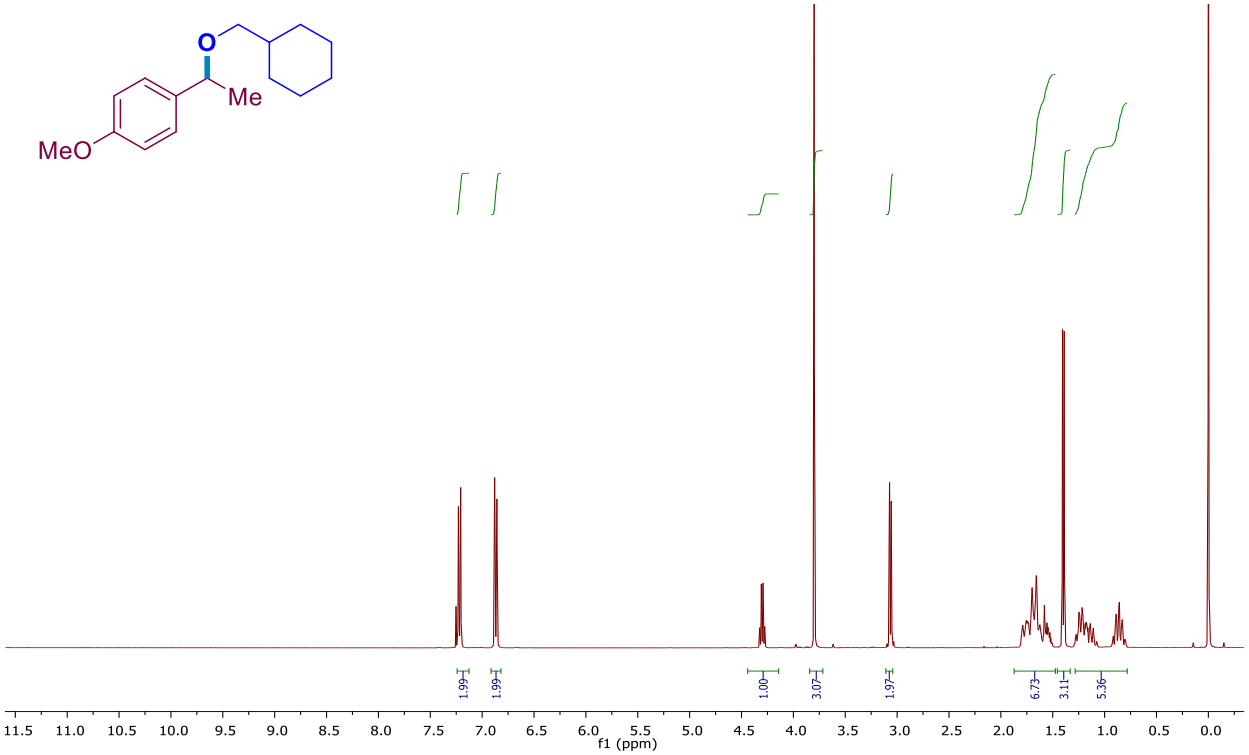


^{1}H NMR spectrum in $CDCl_3$.

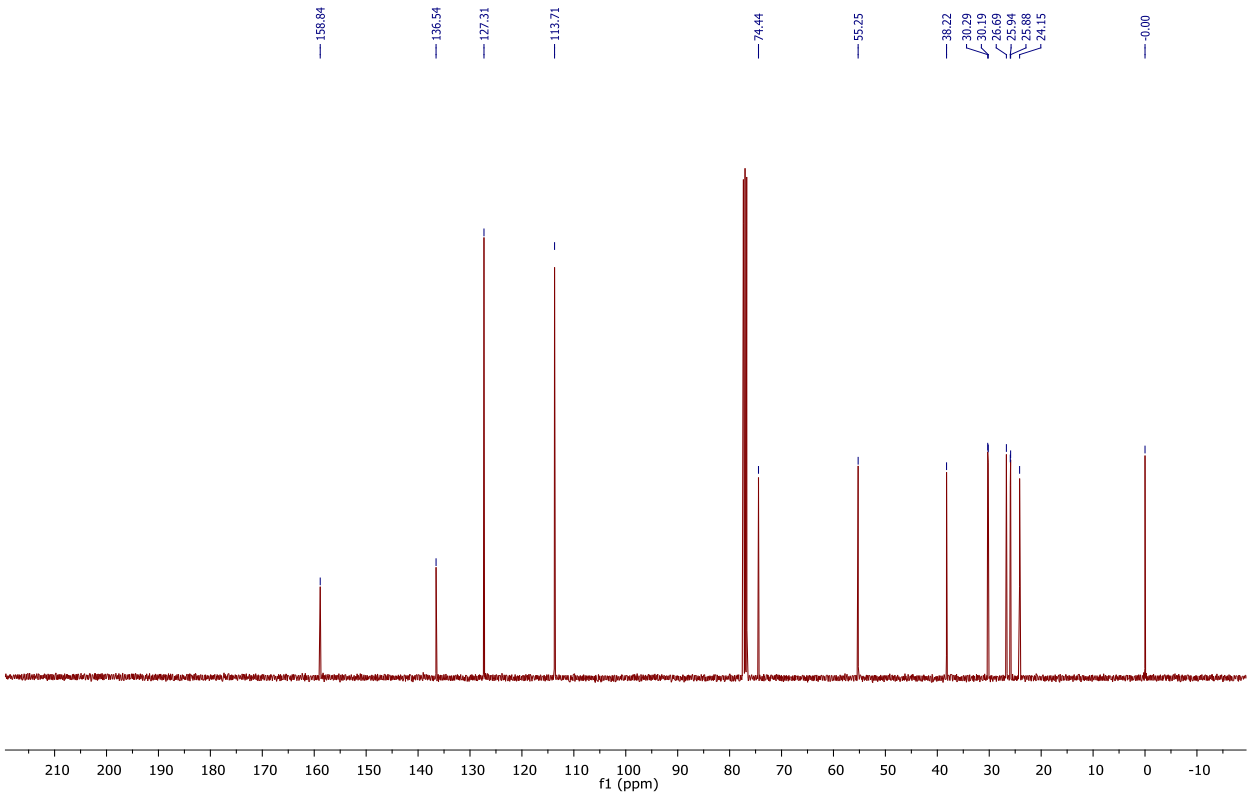


^{13}C NMR spectrum in $CDCl_3$

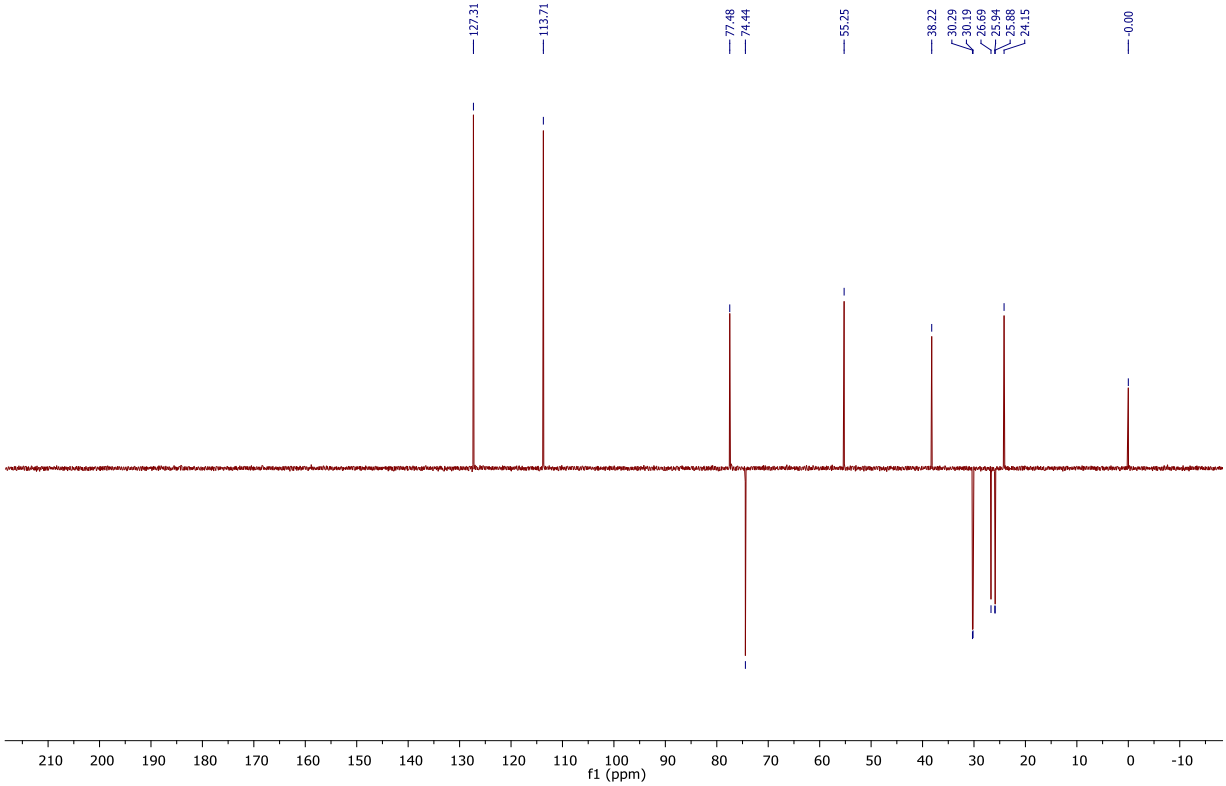
29c



^{1}H NMR spectrum in $CDCl_3$.

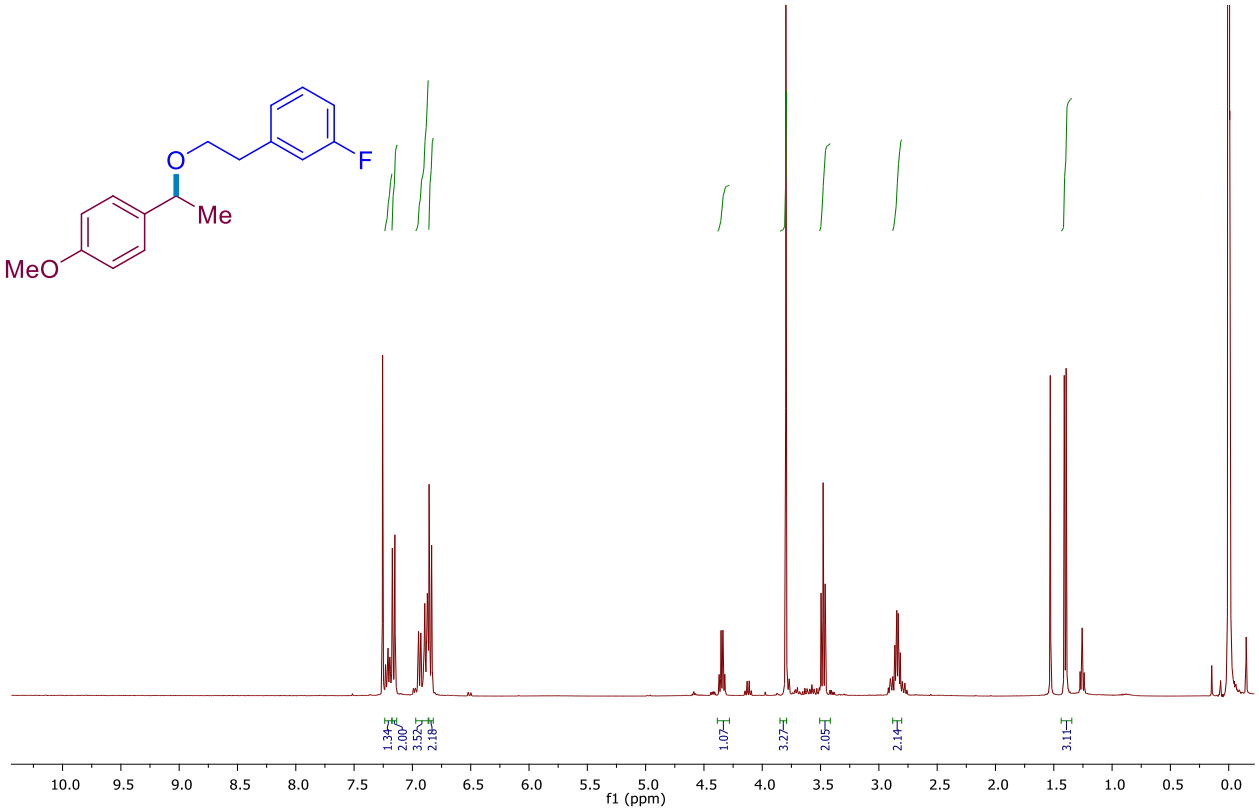


^{13}C NMR spectrum in $CDCl_3$

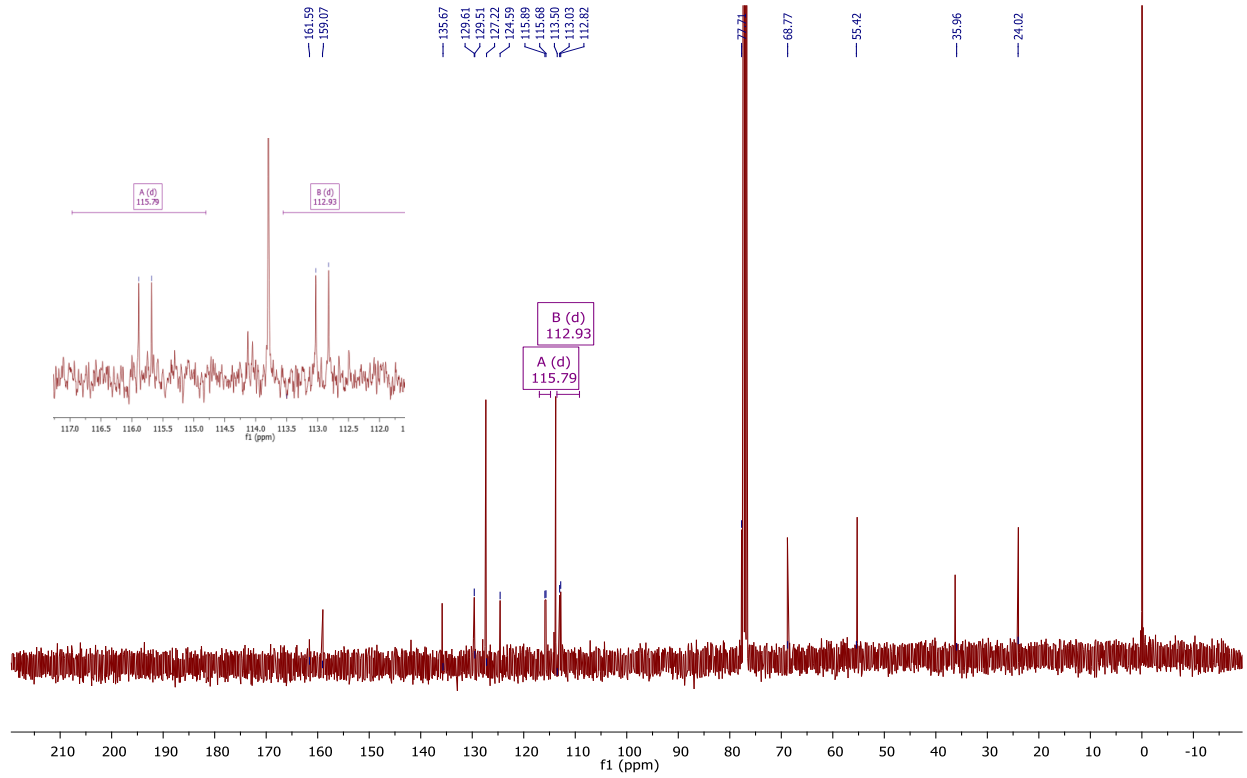


DEPT spectrum in $CDCl_3$.

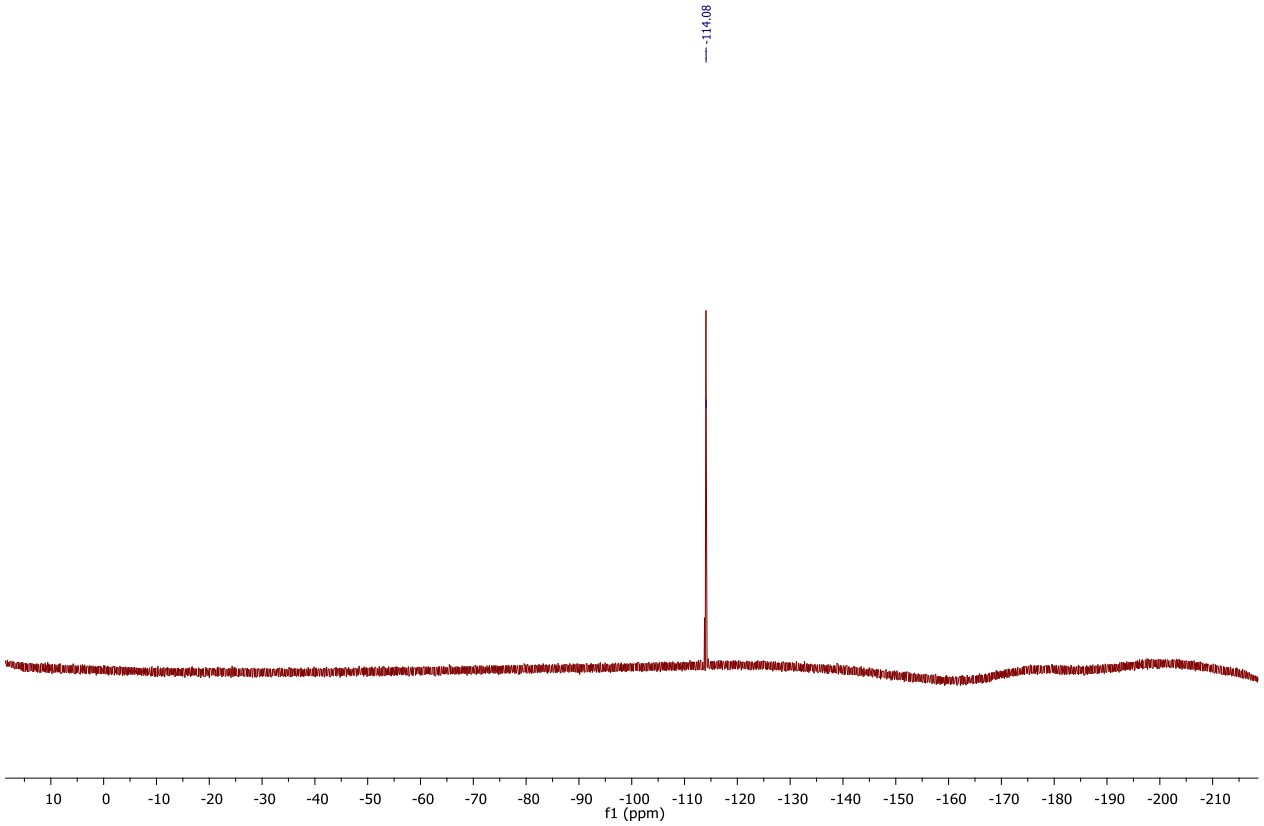
30c



^{1}H NMR spectrum in $CDCl_3$.

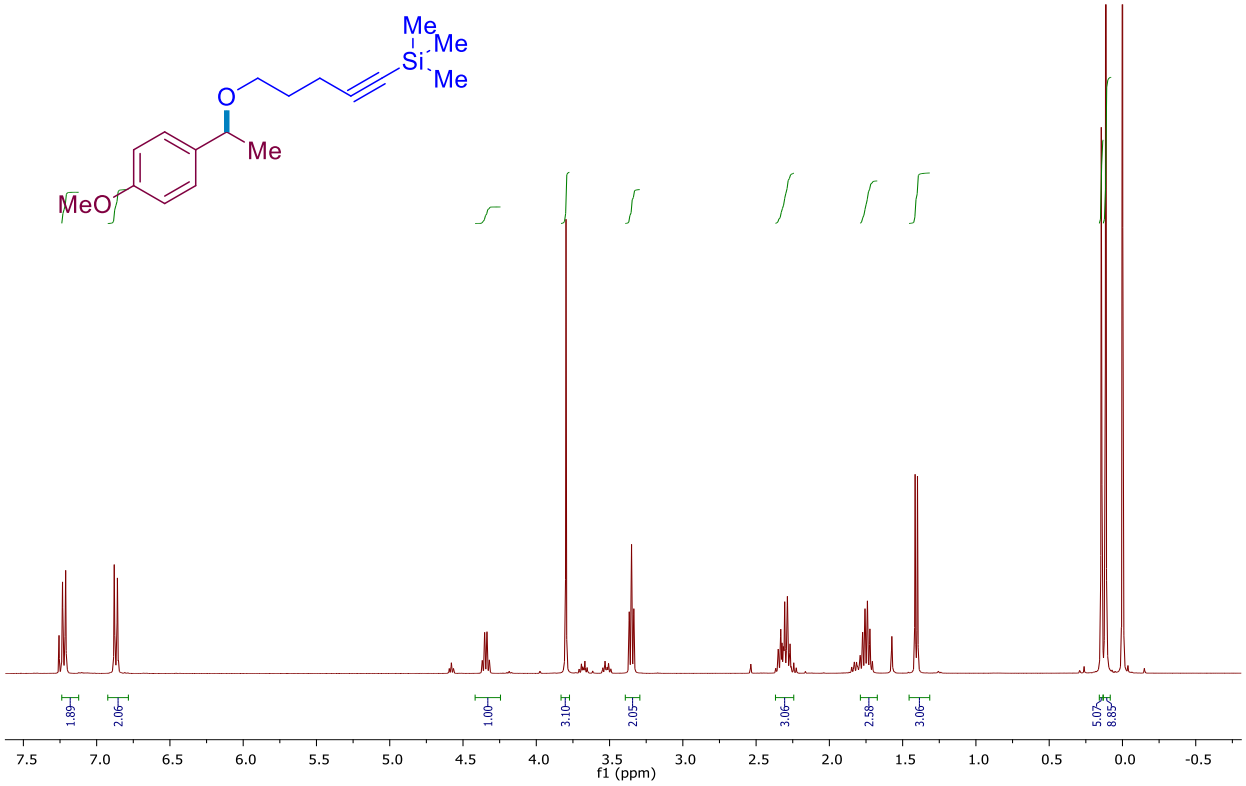


^{13}C NMR spectrum in $CDCl_3$

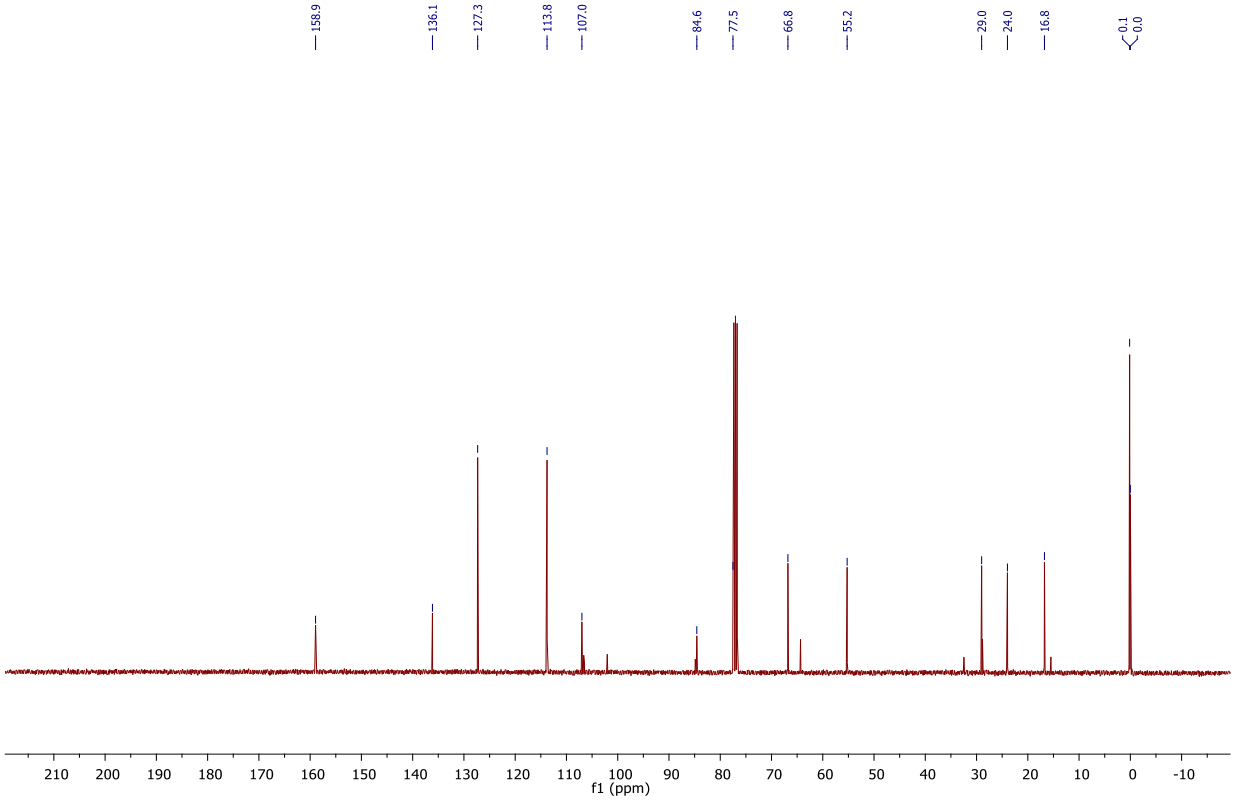


^{19}F NMR spectrum in $CDCl_3$.

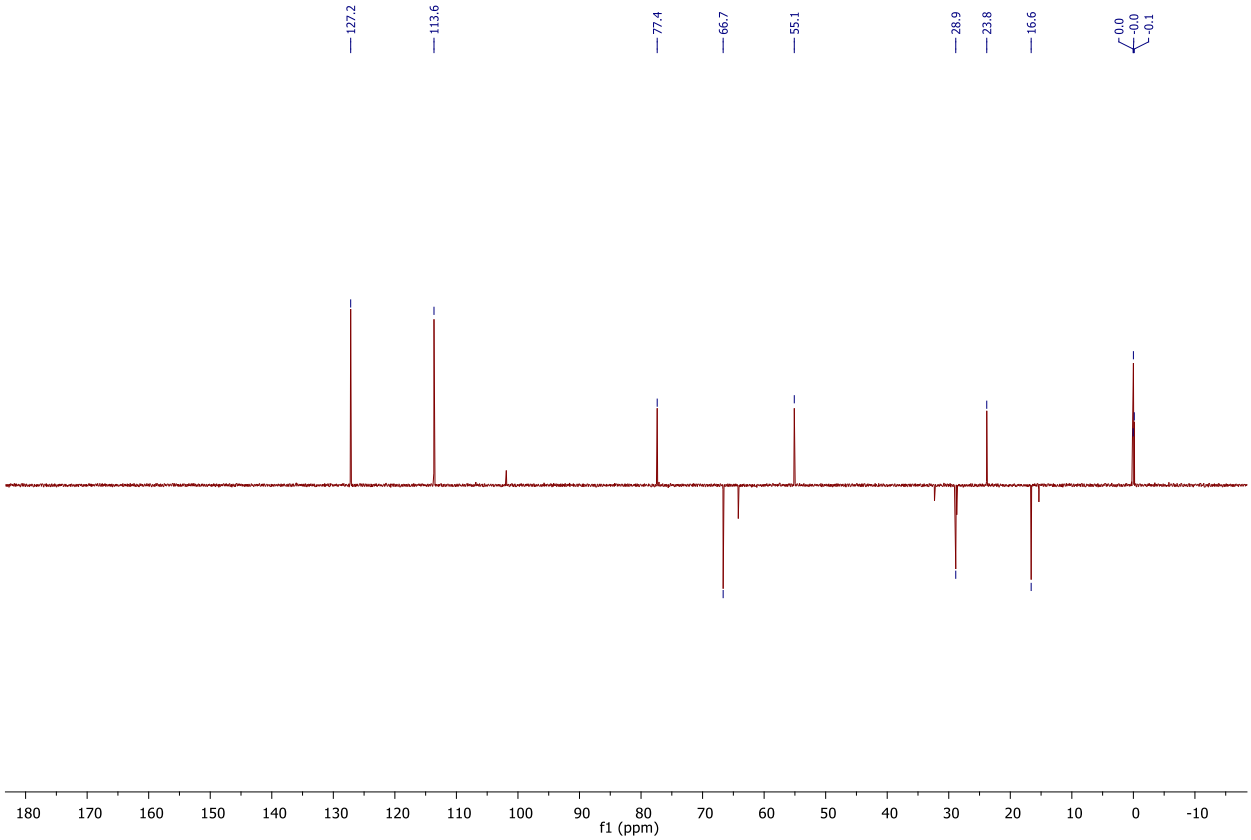
31c



^{1}H NMR spectrum in $CDCl_3$

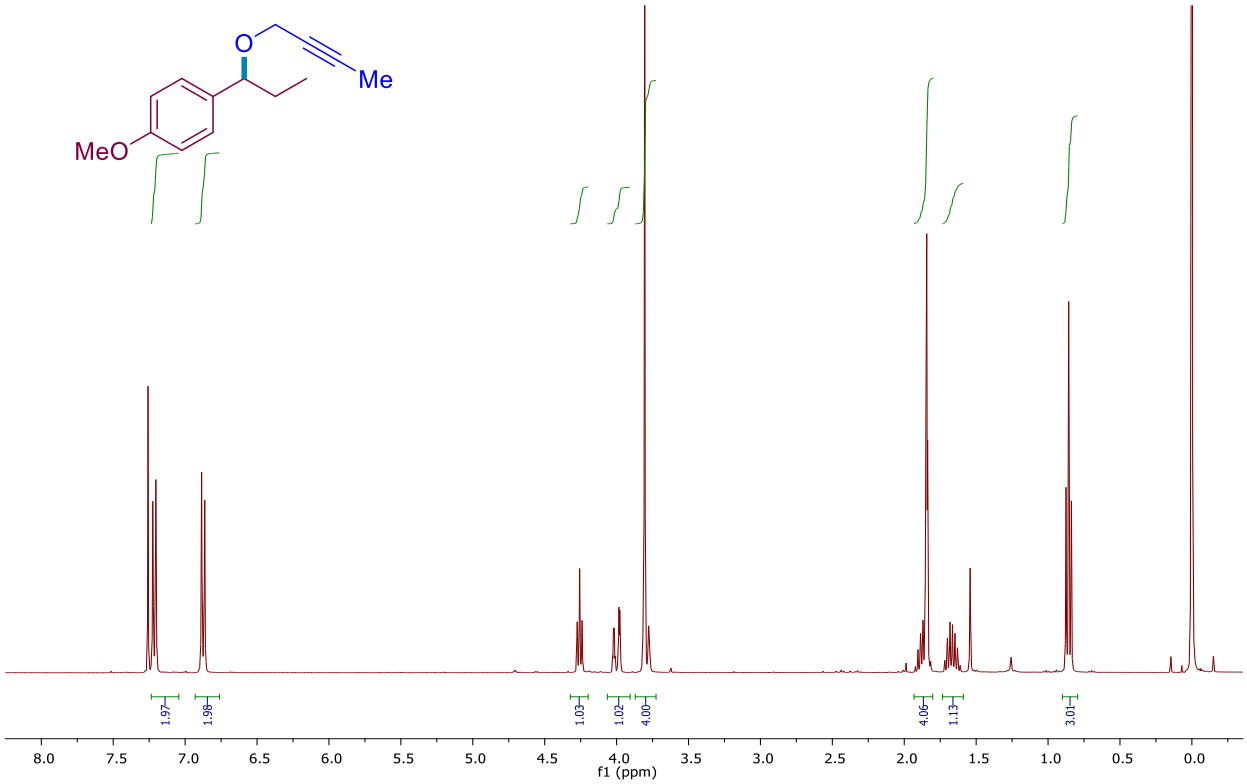


^{13}C NMR spectrum in $CDCl_3$

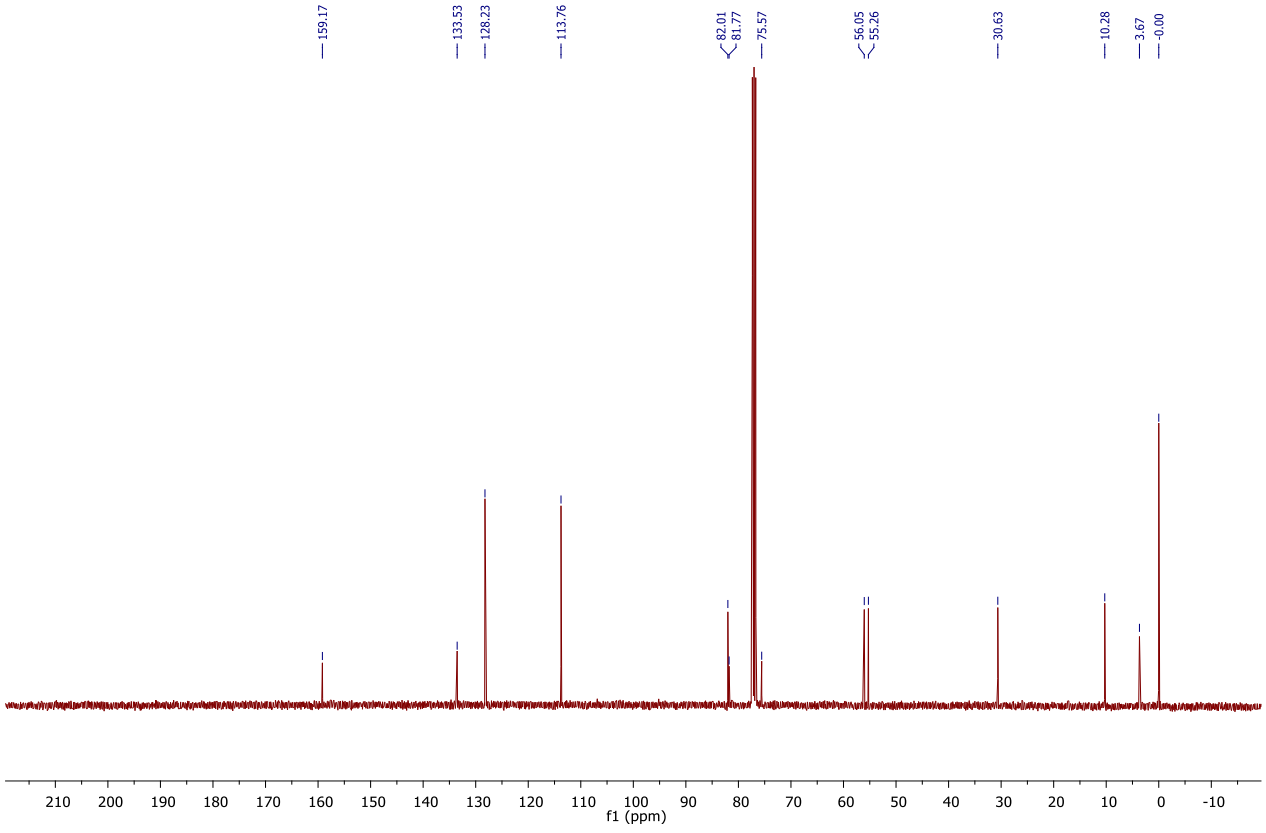


DEPT spectrum in $CDCl_3$.

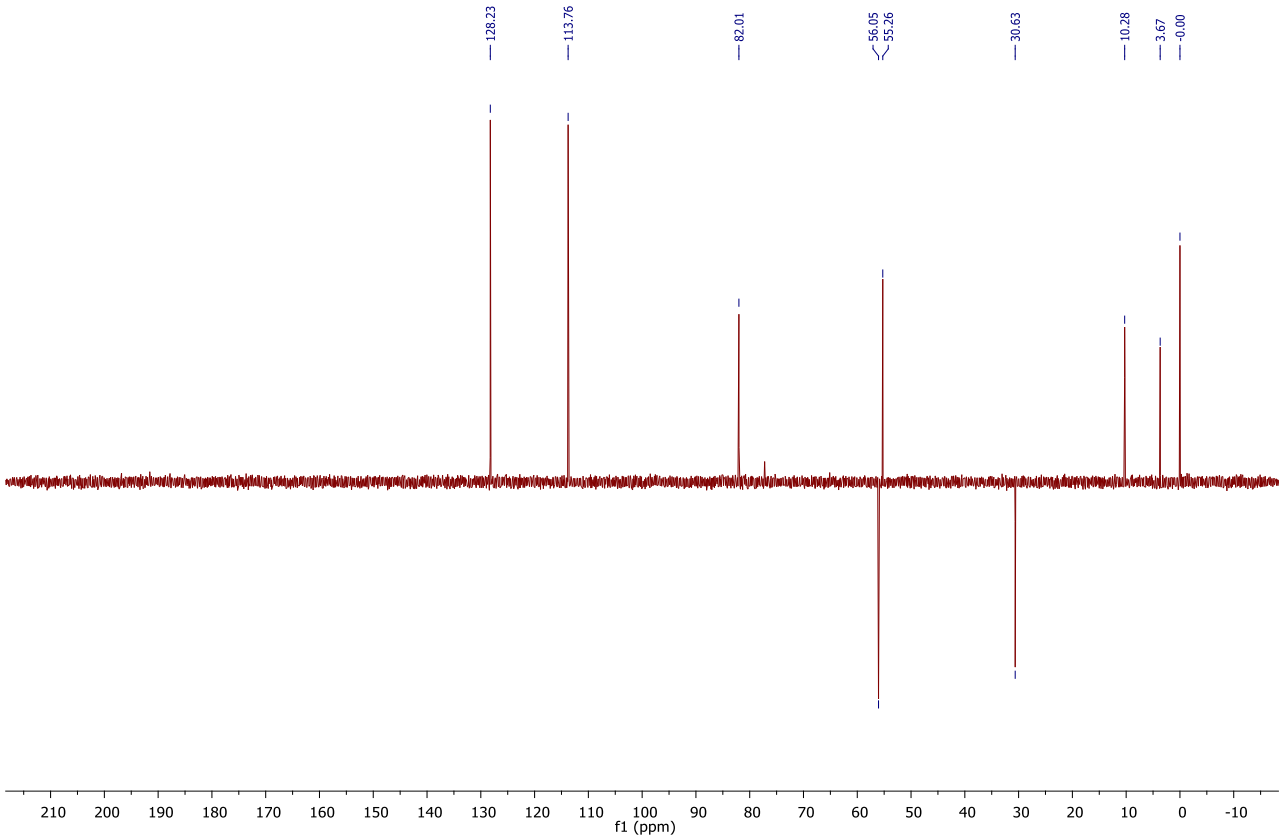
32c



^{1}H NMR spectrum in $CDCl_3$

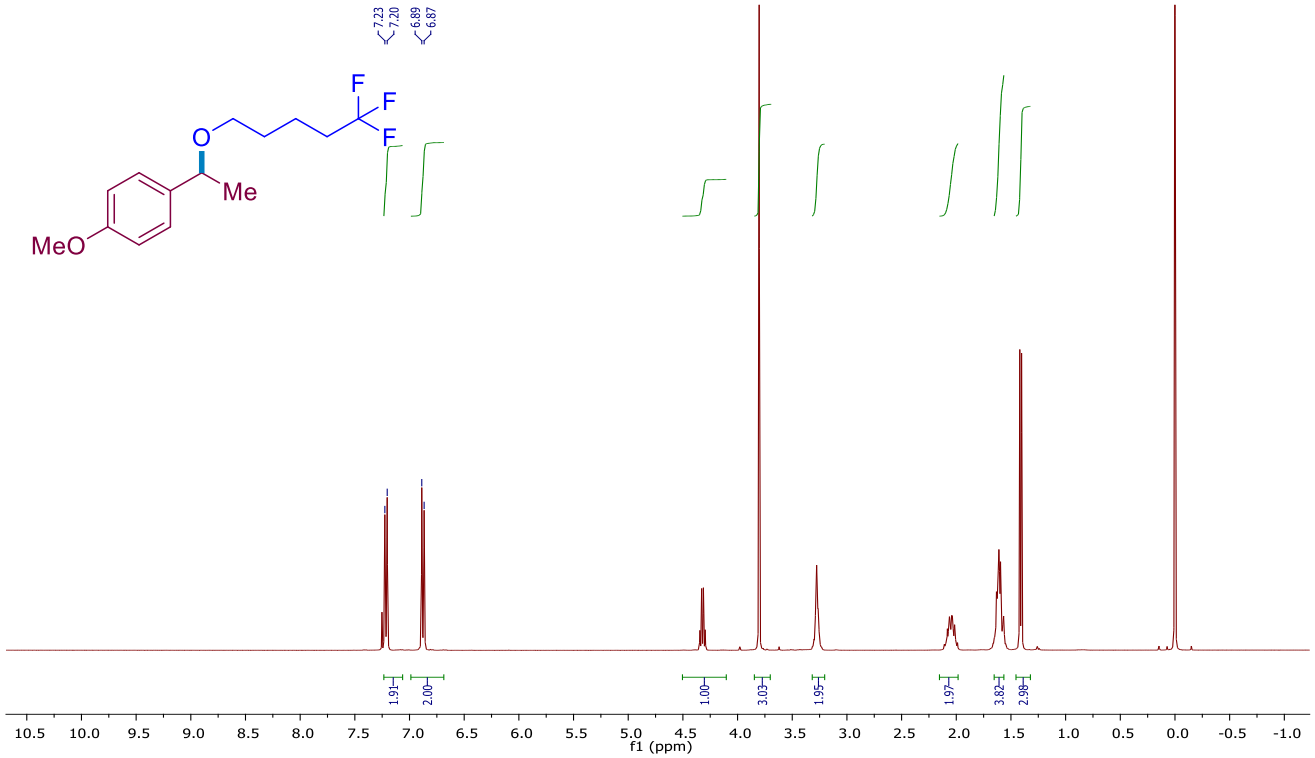


^{13}C NMR spectrum in $CDCl_3$

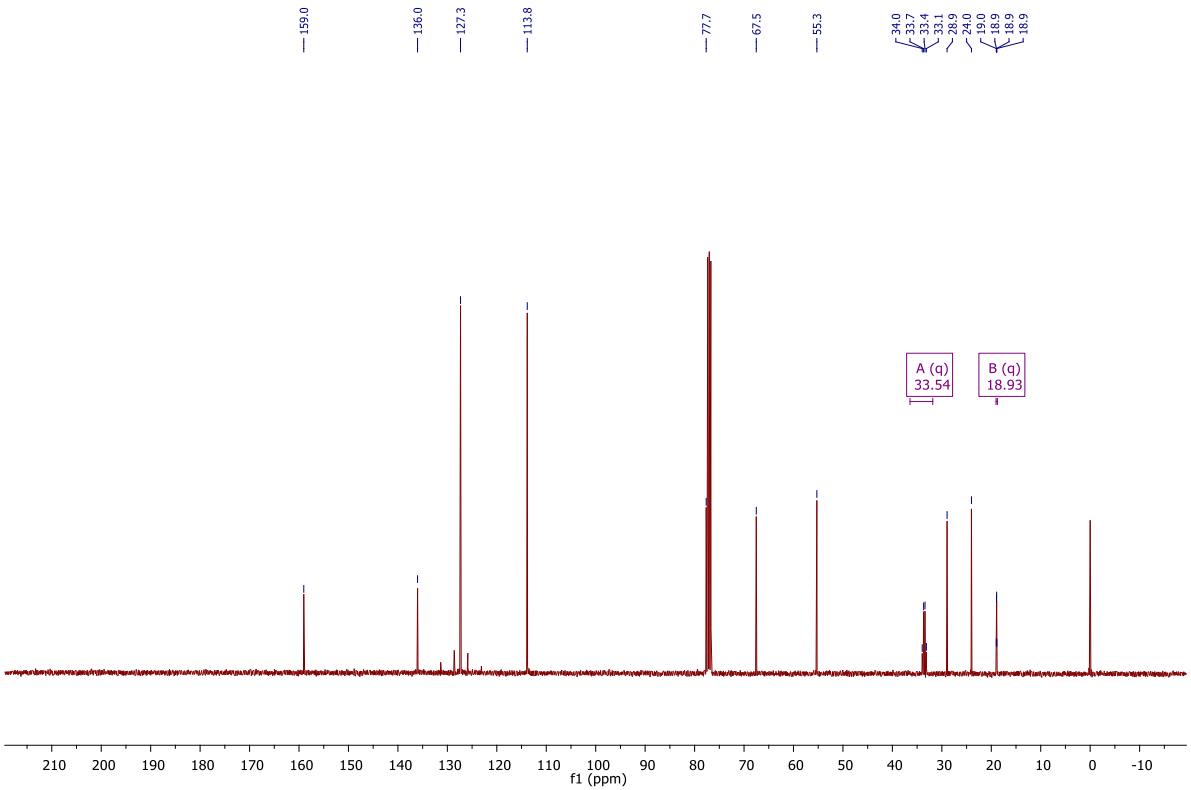


DEPT spectrum in $CDCl_3$.

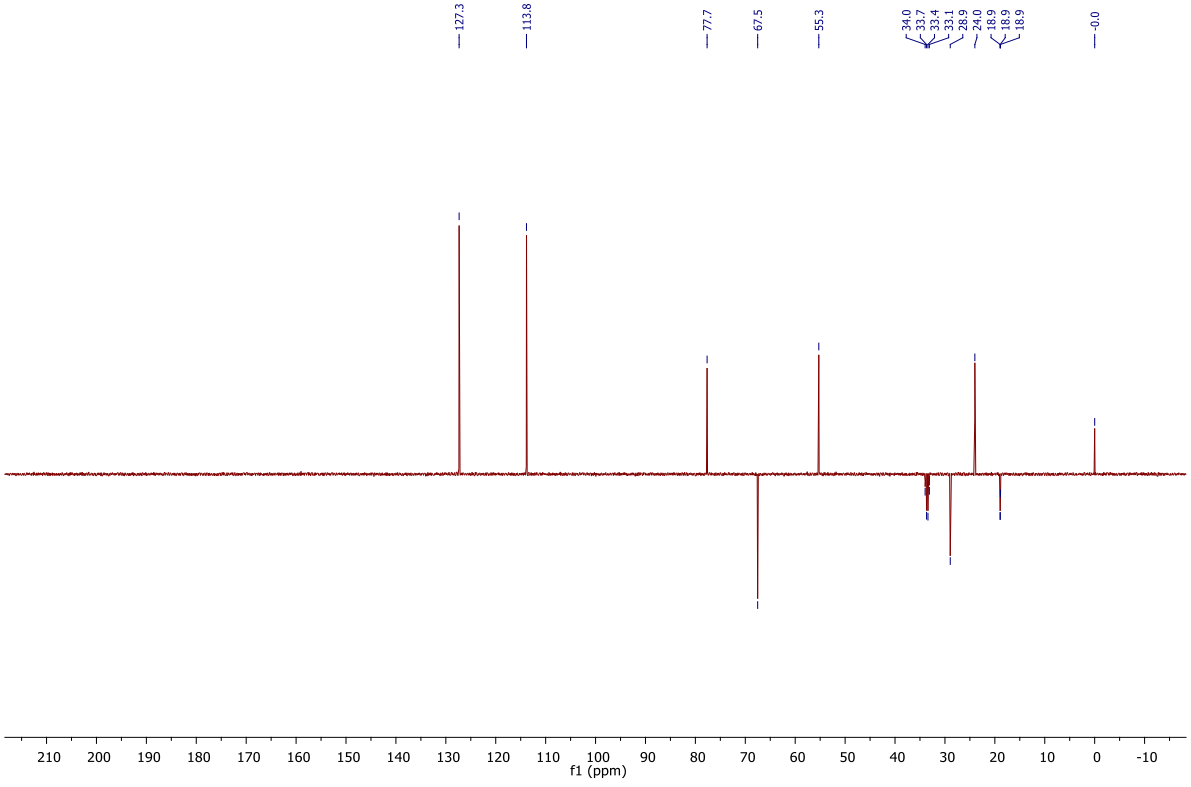
33c



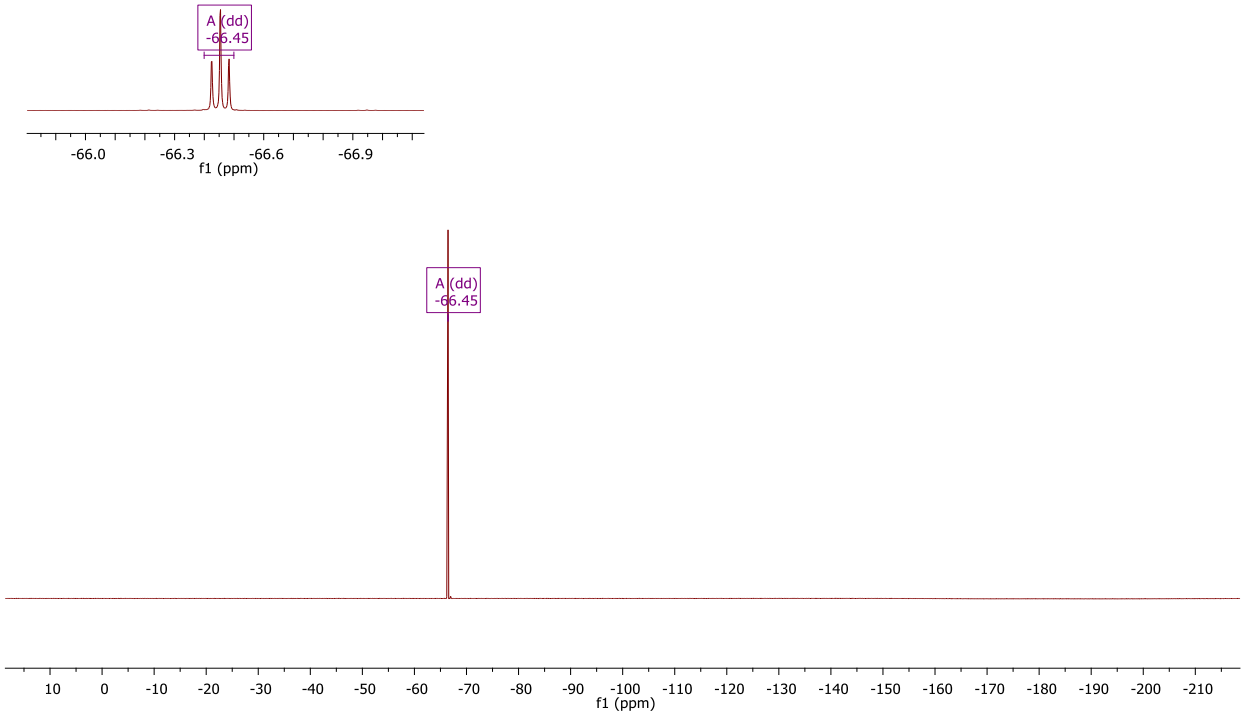
^1H NMR spectrum in $CDCl_3$.



^{13}C NMR spectrum in $CDCl_3$

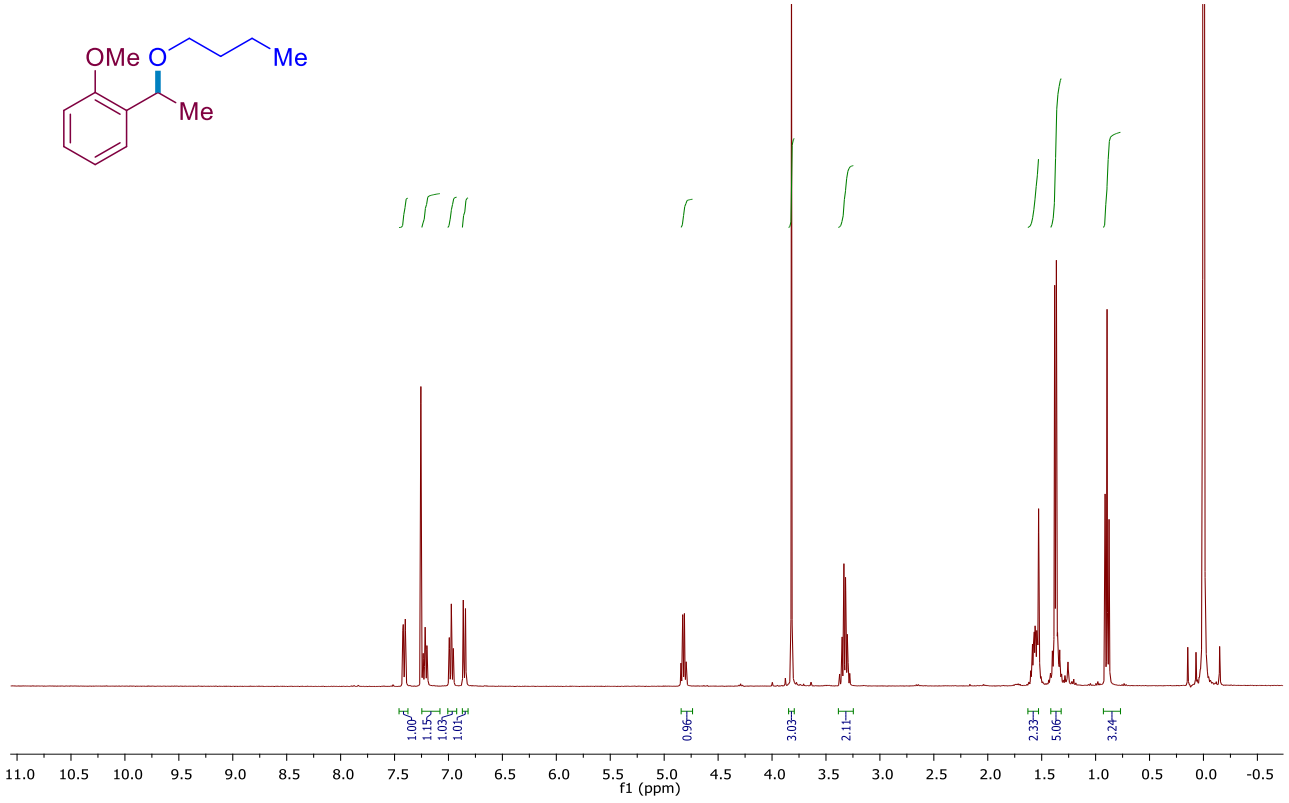


DEPT spectrum in $CDCl_3$.

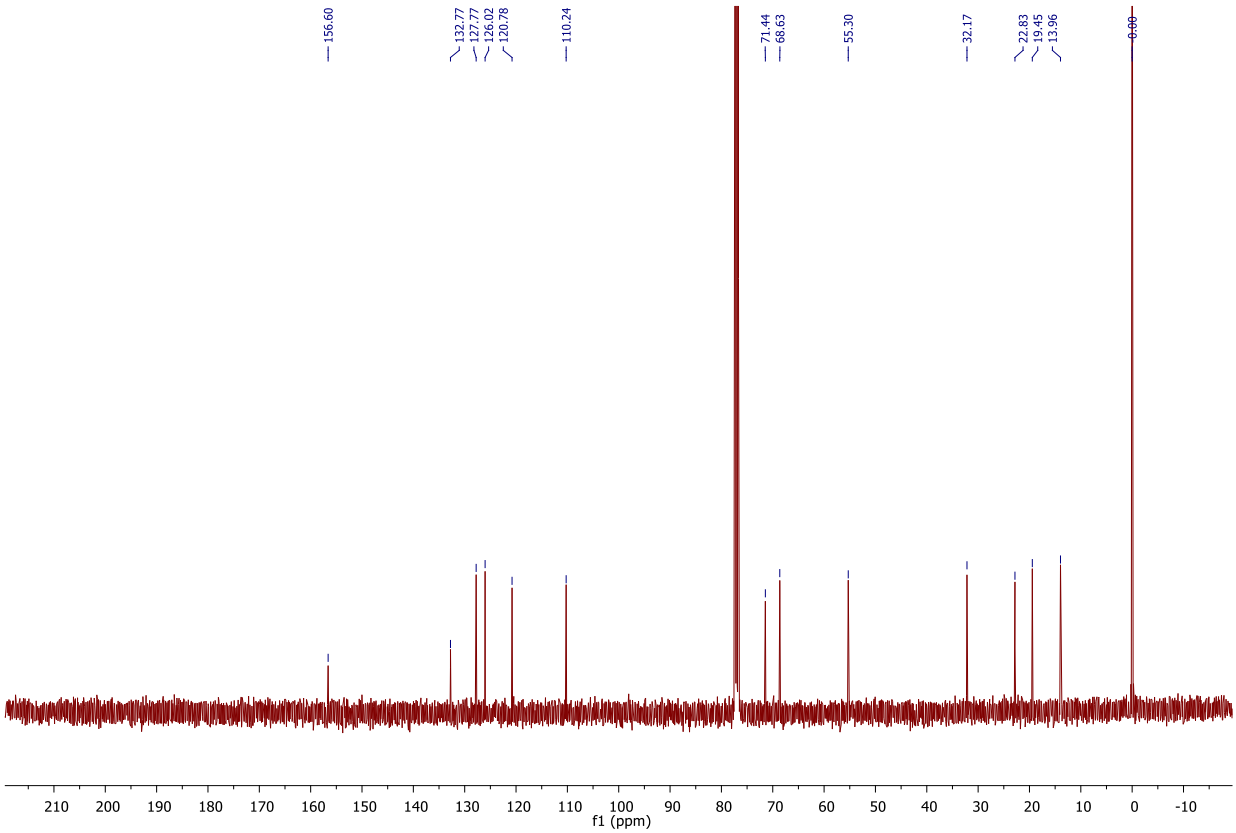


^{19}F NMR spectrum in $CDCl_3$.

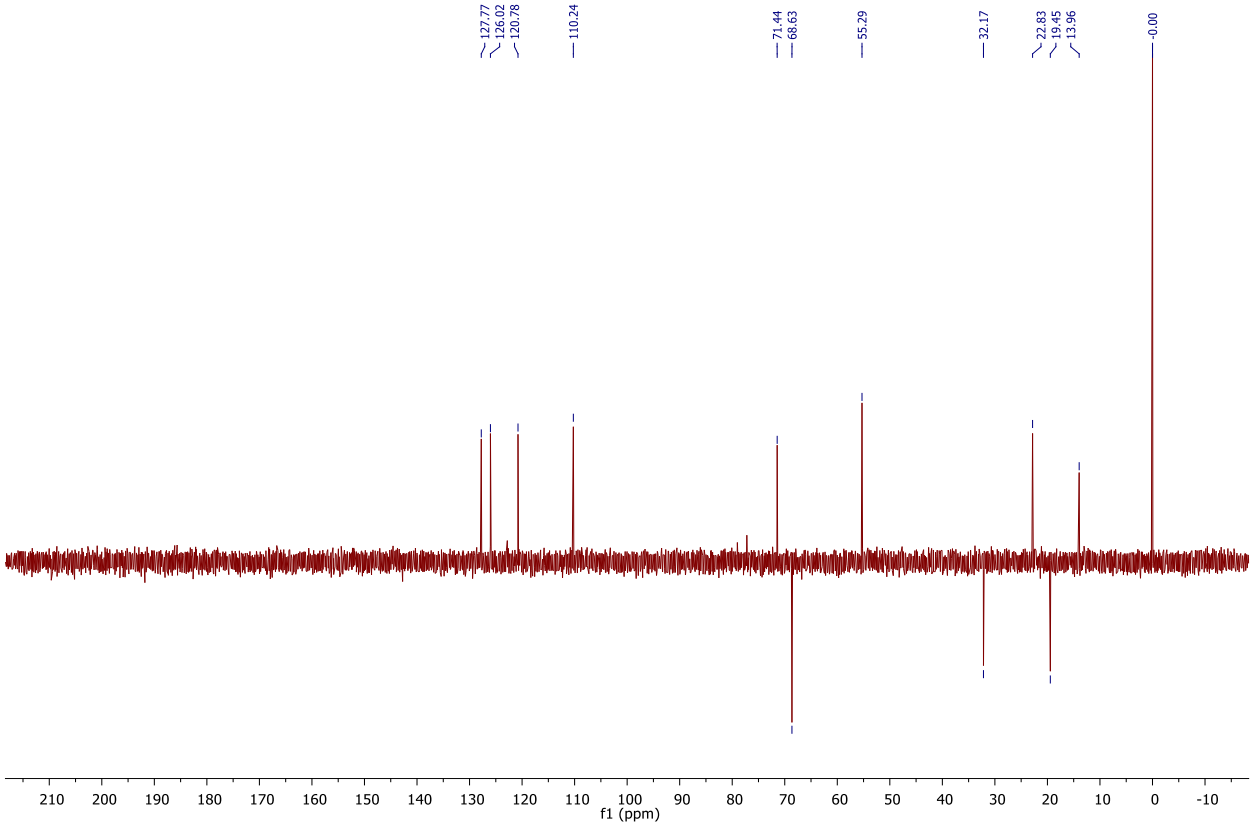
34c



^{1}H NMR spectrum in $CDCl_3$.

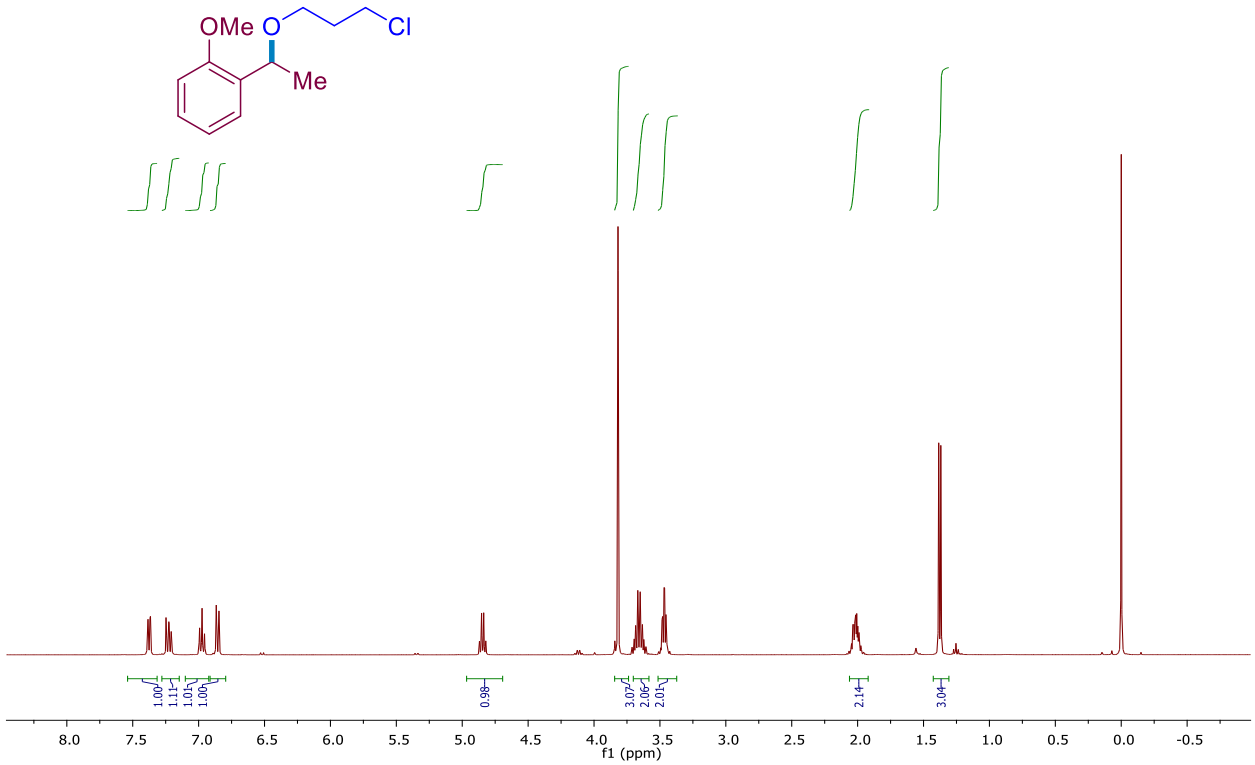


^{13}C NMR spectrum in $CDCl_3$

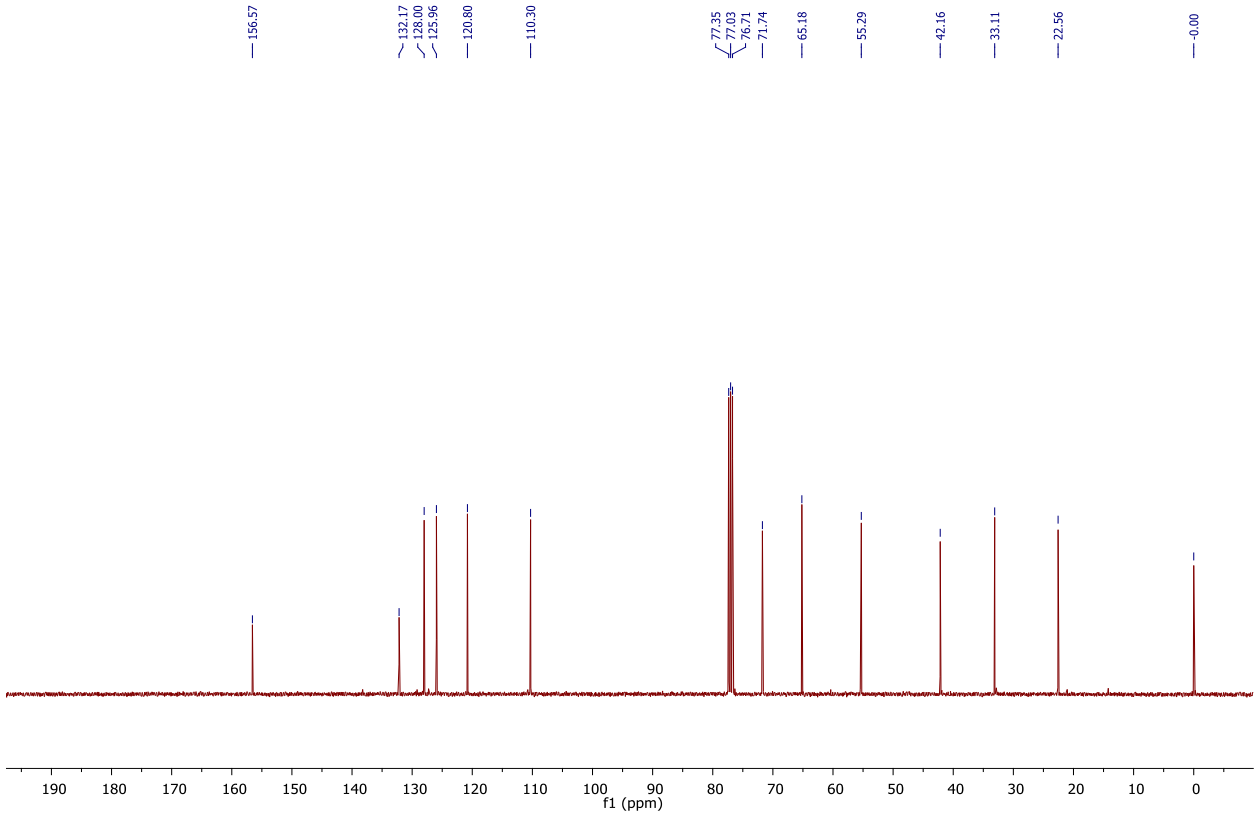


DEPT spectrum in $CDCl_3$.

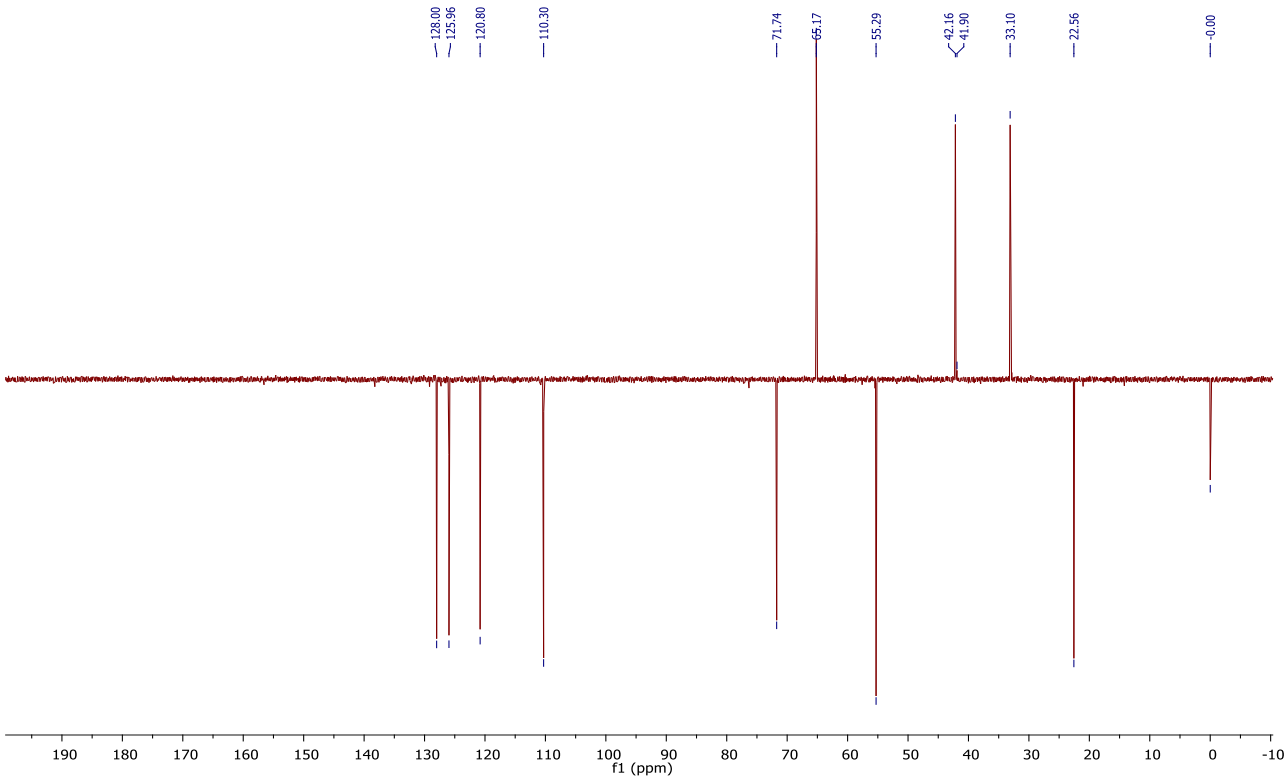
35c



^{1}H NMR spectrum in $CDCl_3$.

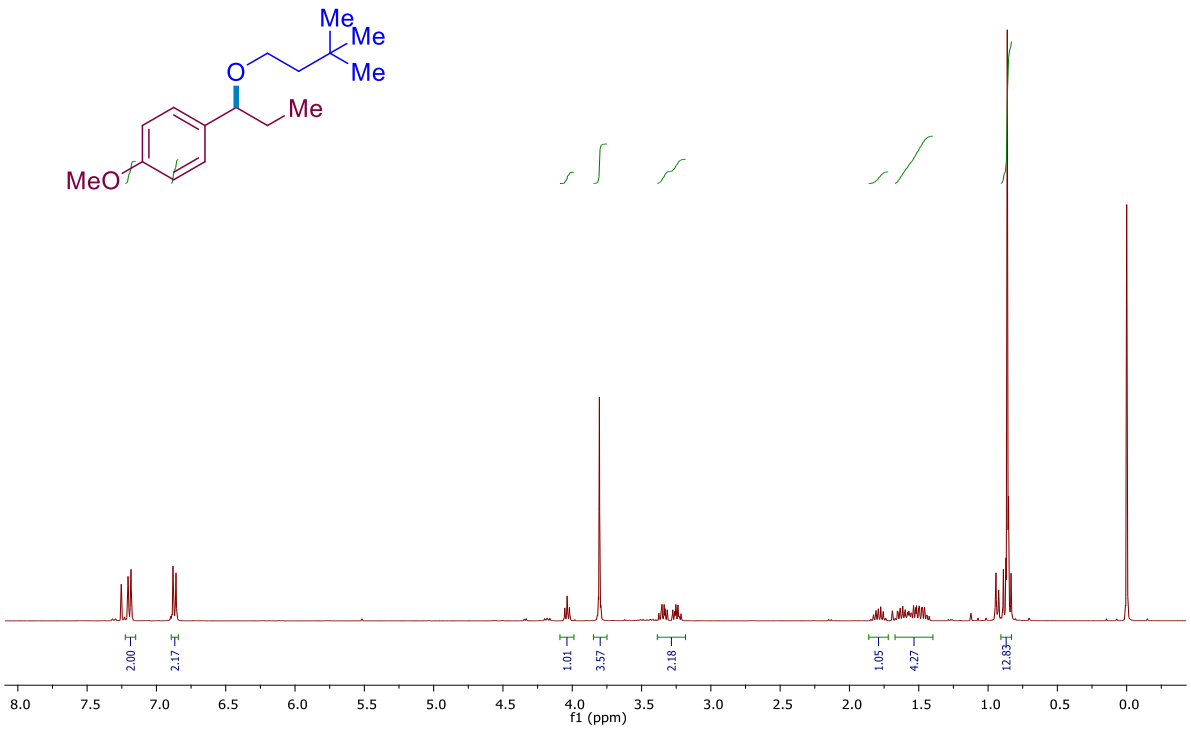


^{13}C NMR spectrum in $CDCl_3$

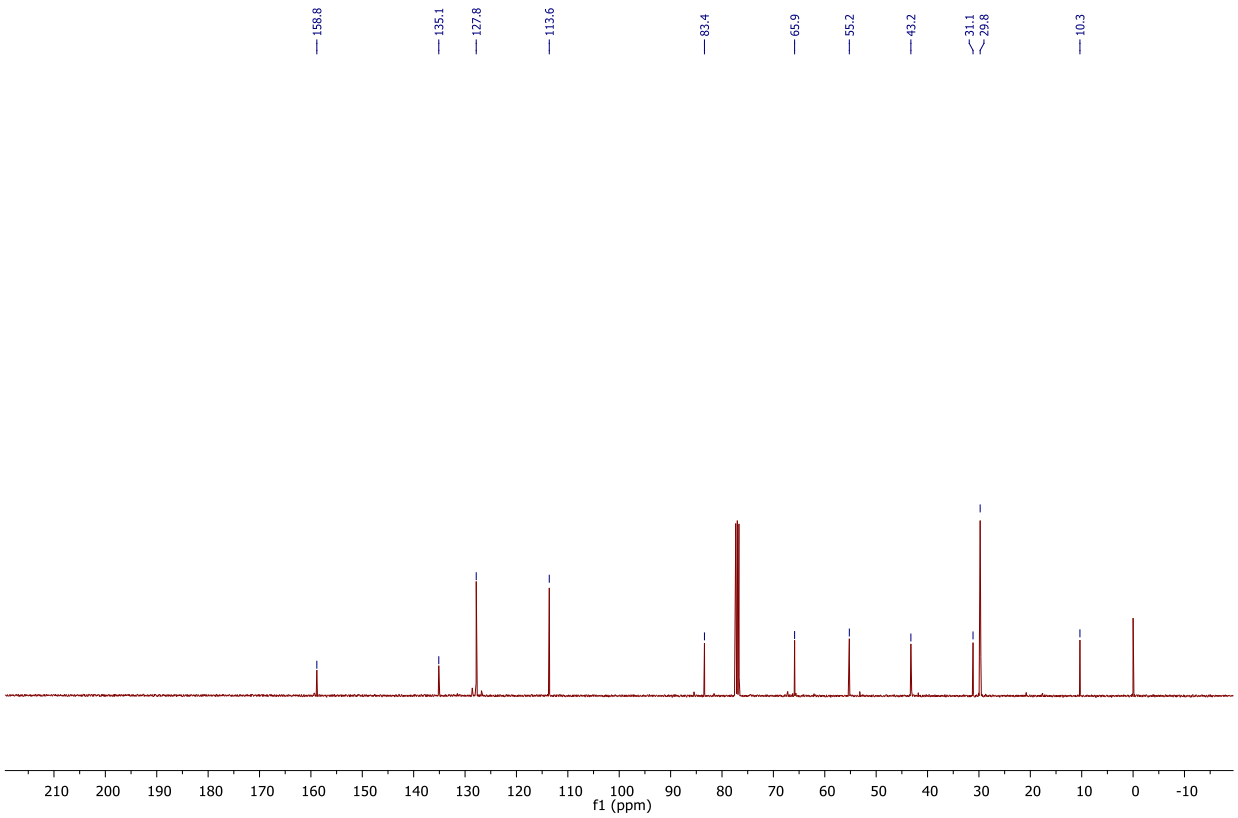


DEPT spectrum in $CDCl_3$.

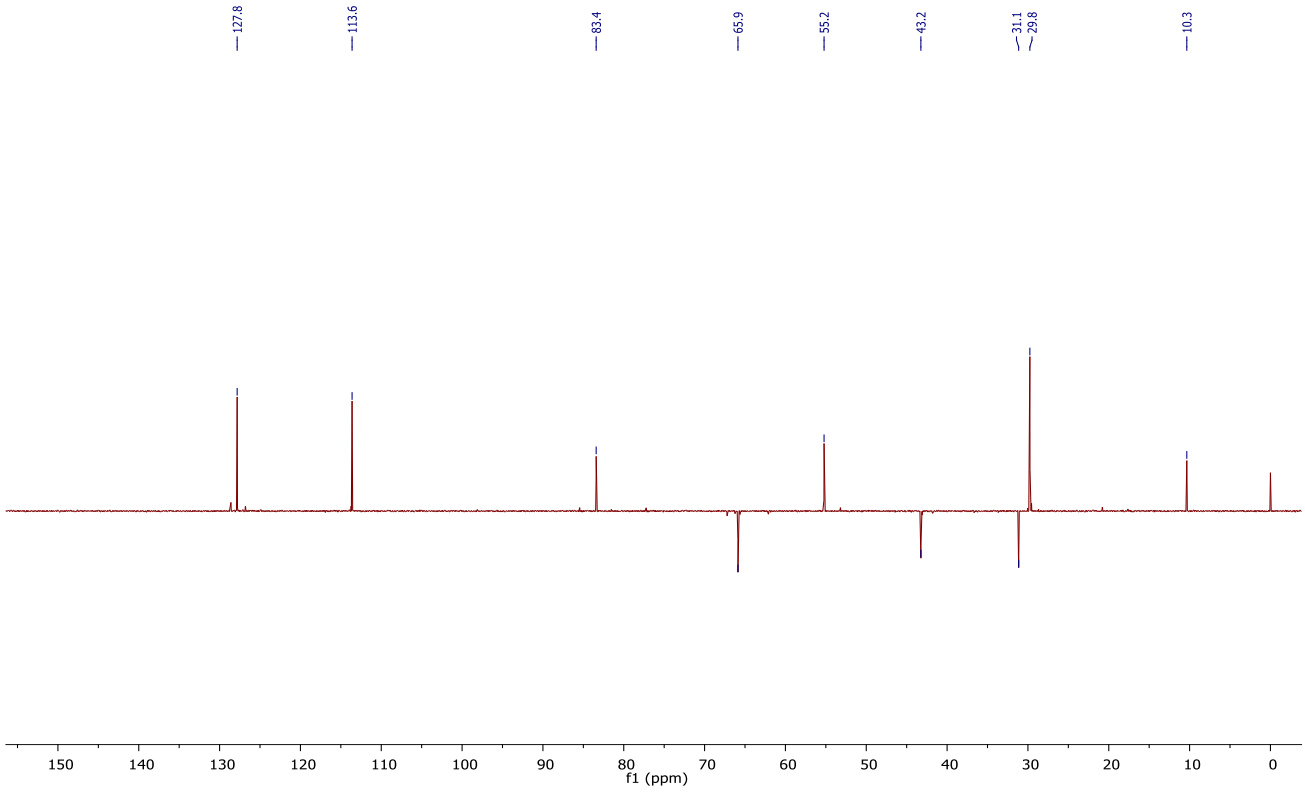
36c



^1H NMR spectrum in $CDCl_3$.

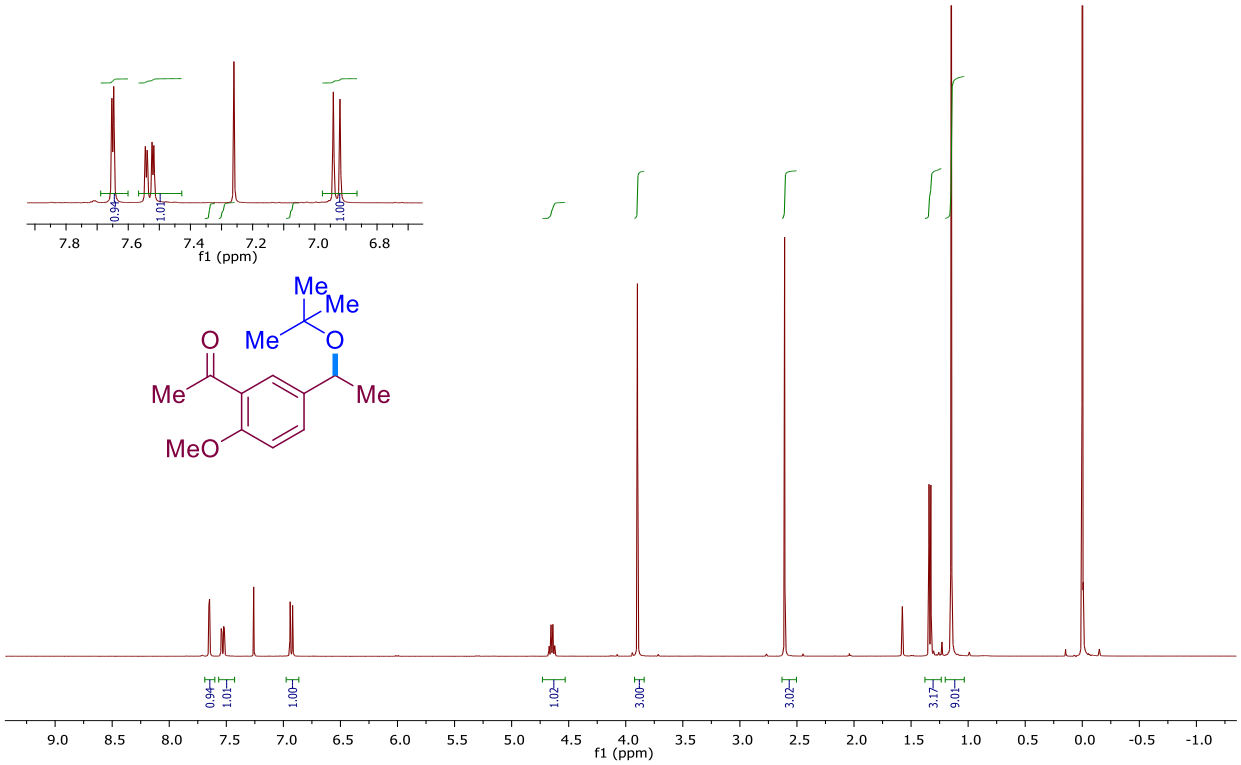


^{13}C NMR spectrum in $CDCl_3$

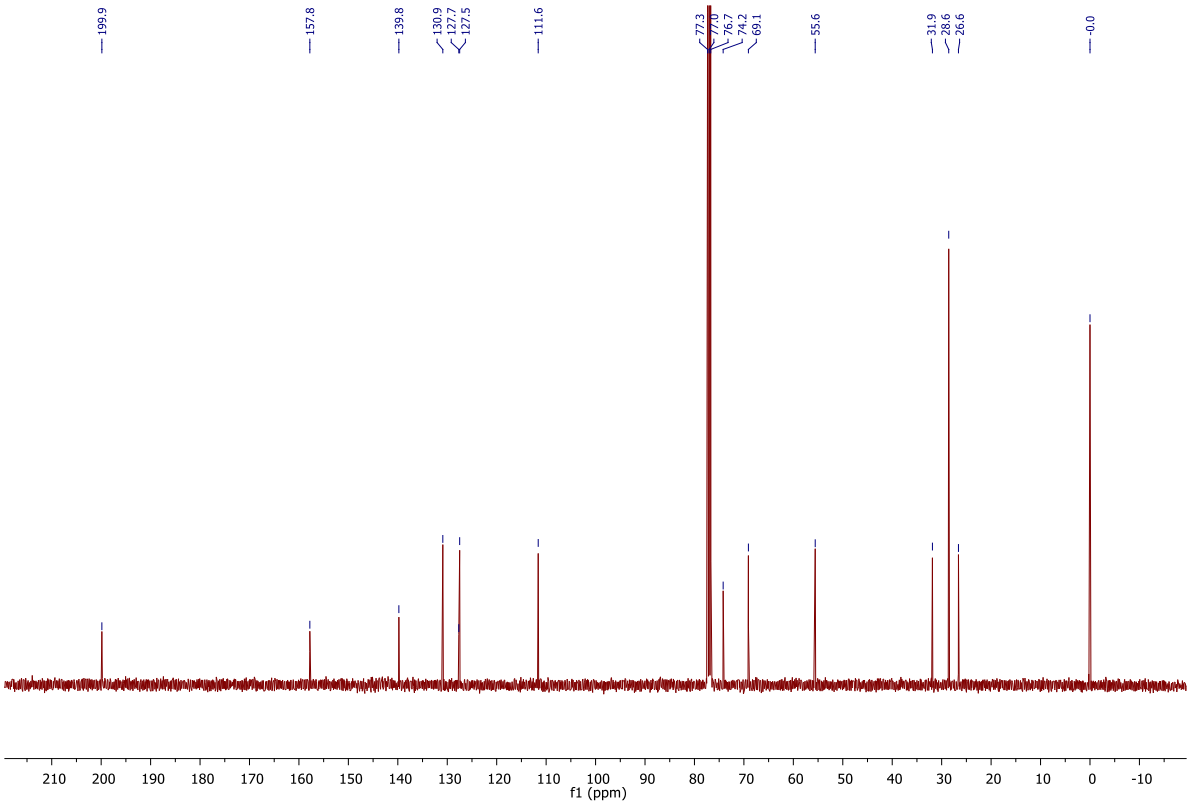


DEPT spectrum in $CDCl_3$.

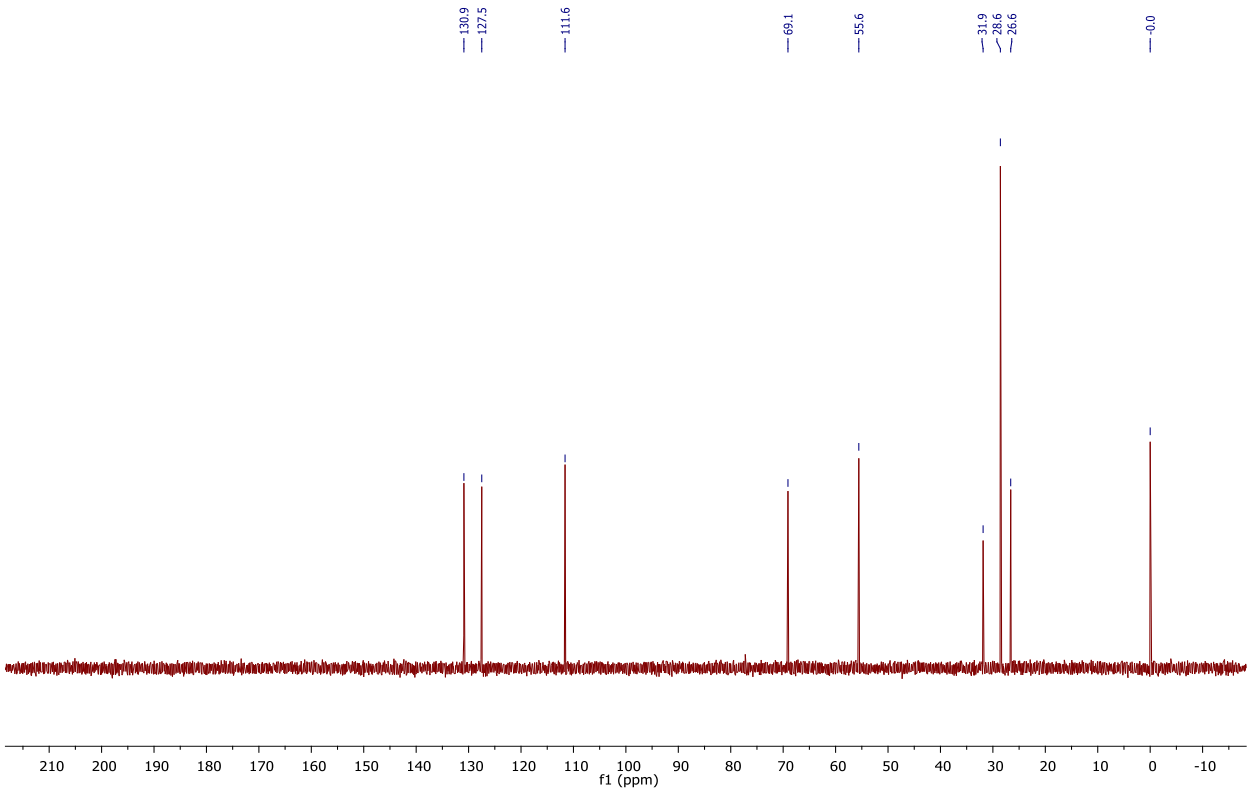
37c



^{1}H NMR spectrum in $CDCl_3$.

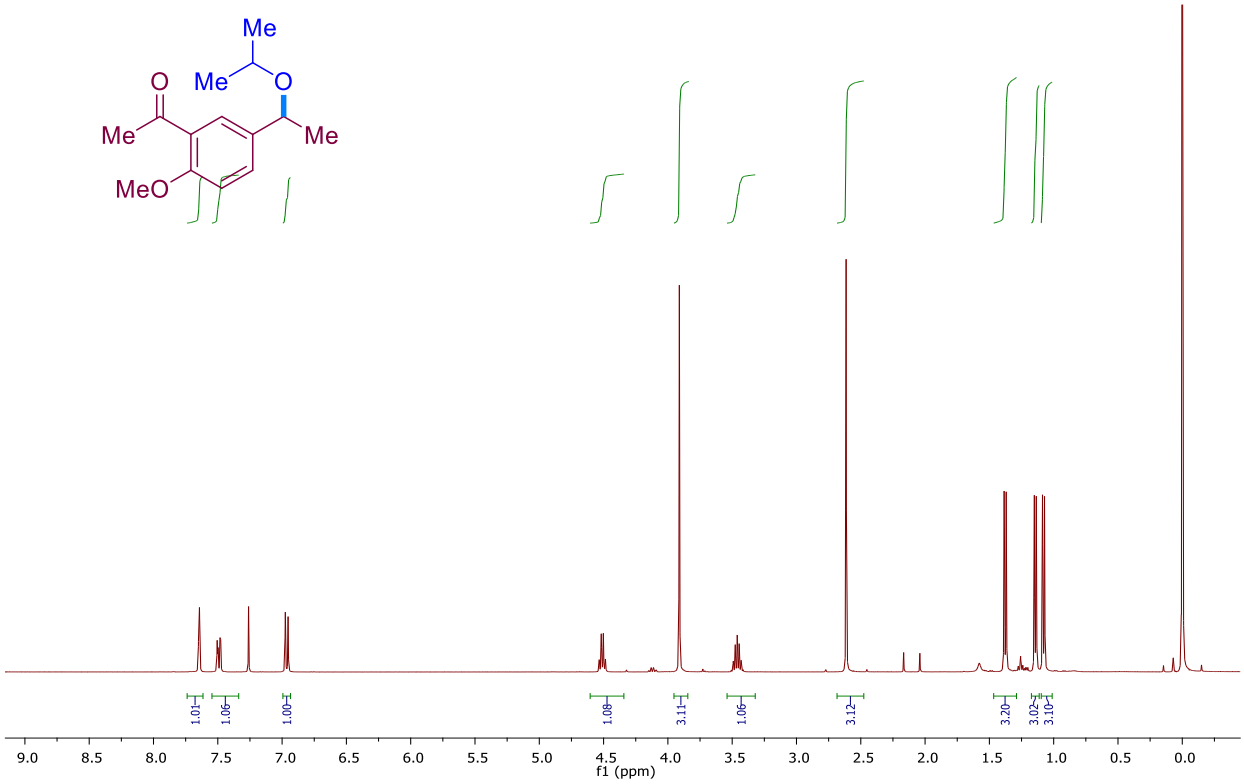


^{13}C NMR spectrum in $CDCl_3$

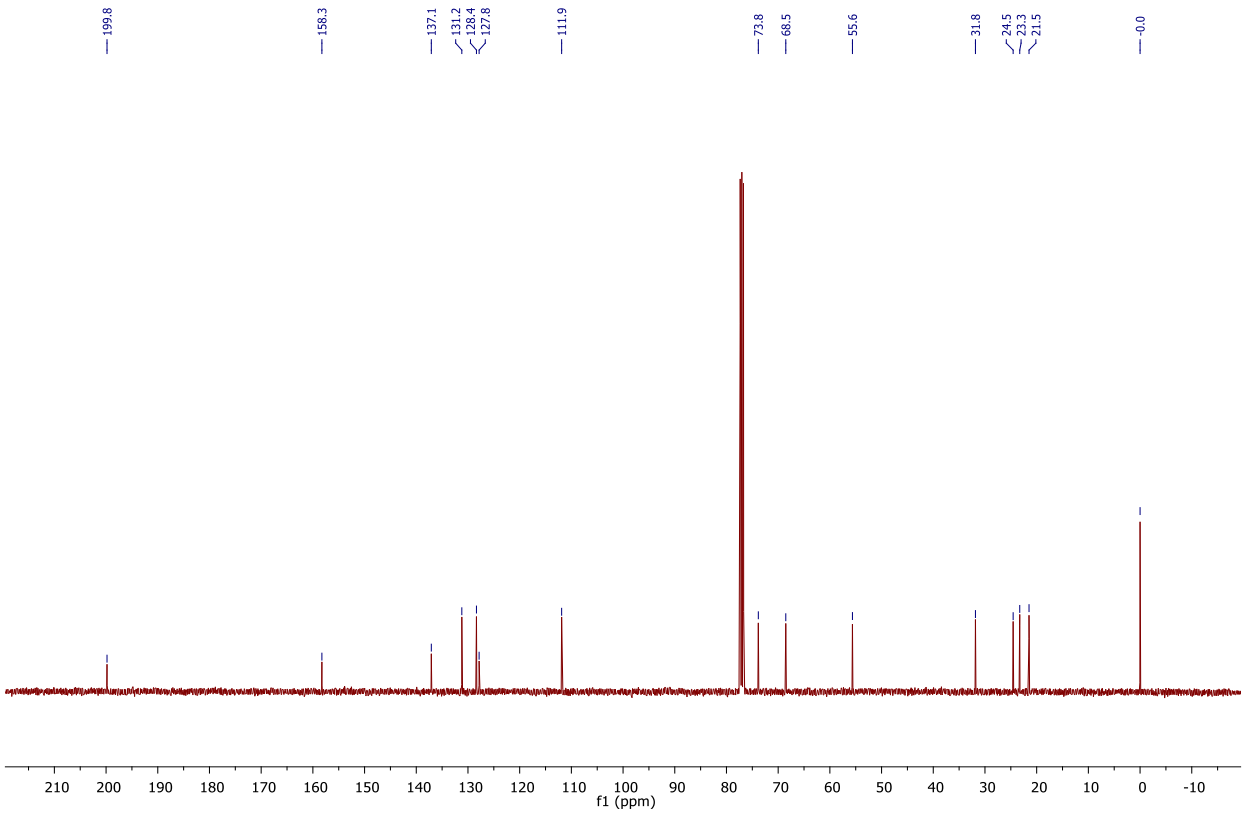


DEPT spectrum in $CDCl_3$.

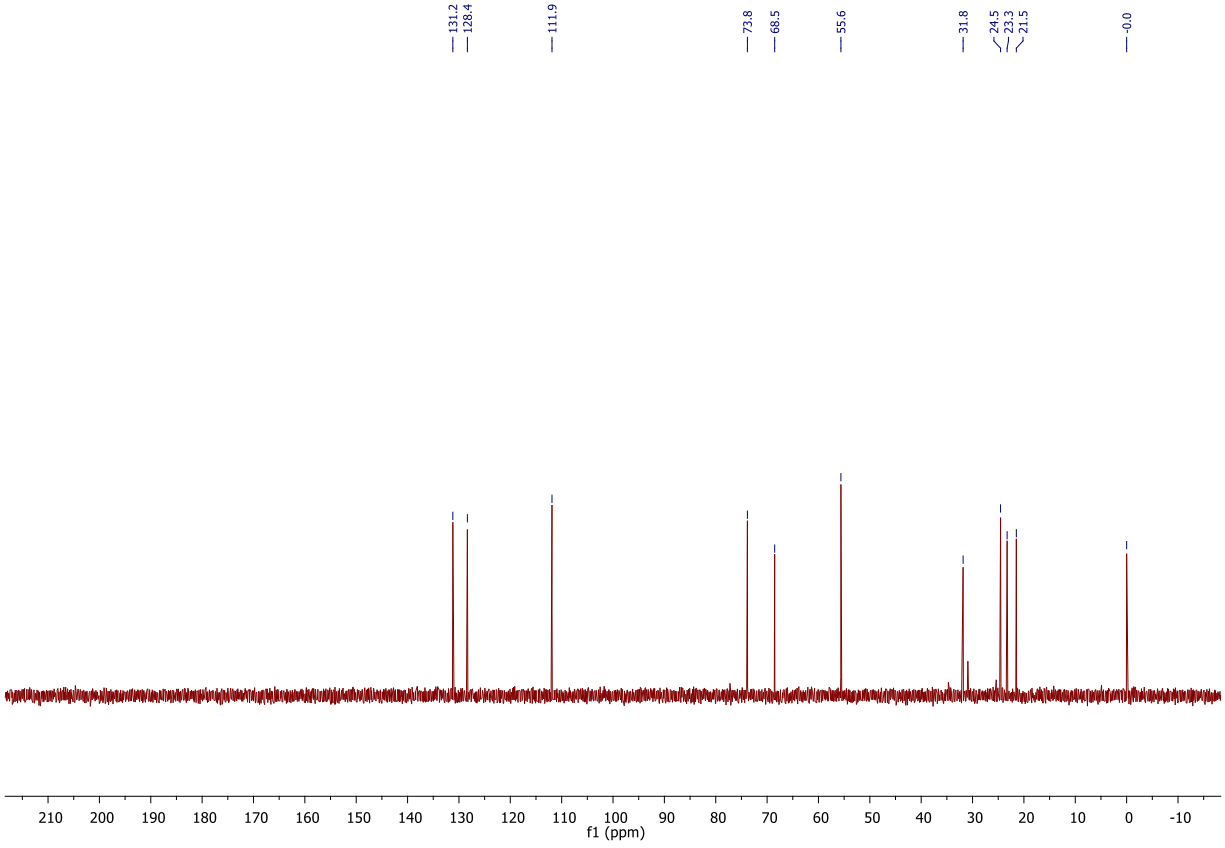
38c



^1H NMR spectrum in $CDCl_3$.

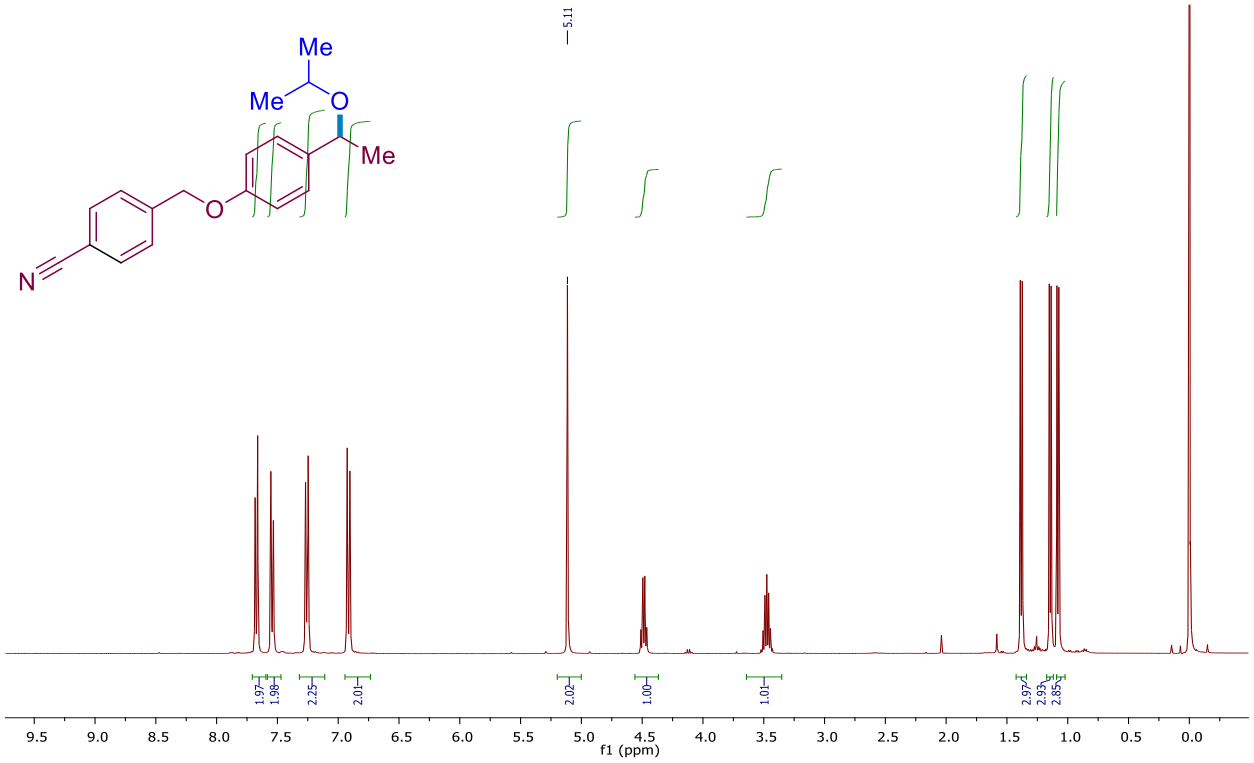


^{13}C NMR spectrum in $CDCl_3$

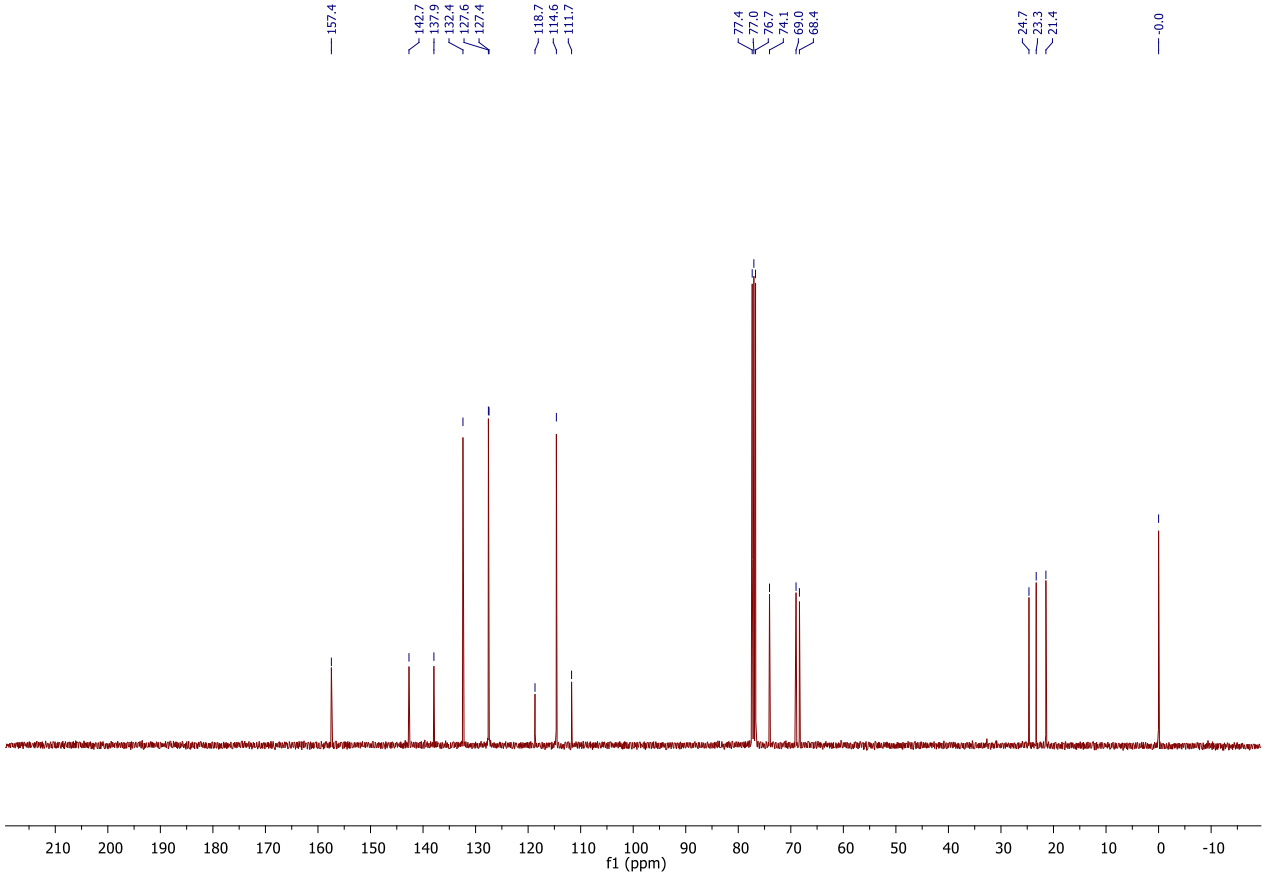


DEPT spectrum in $CDCl_3$.

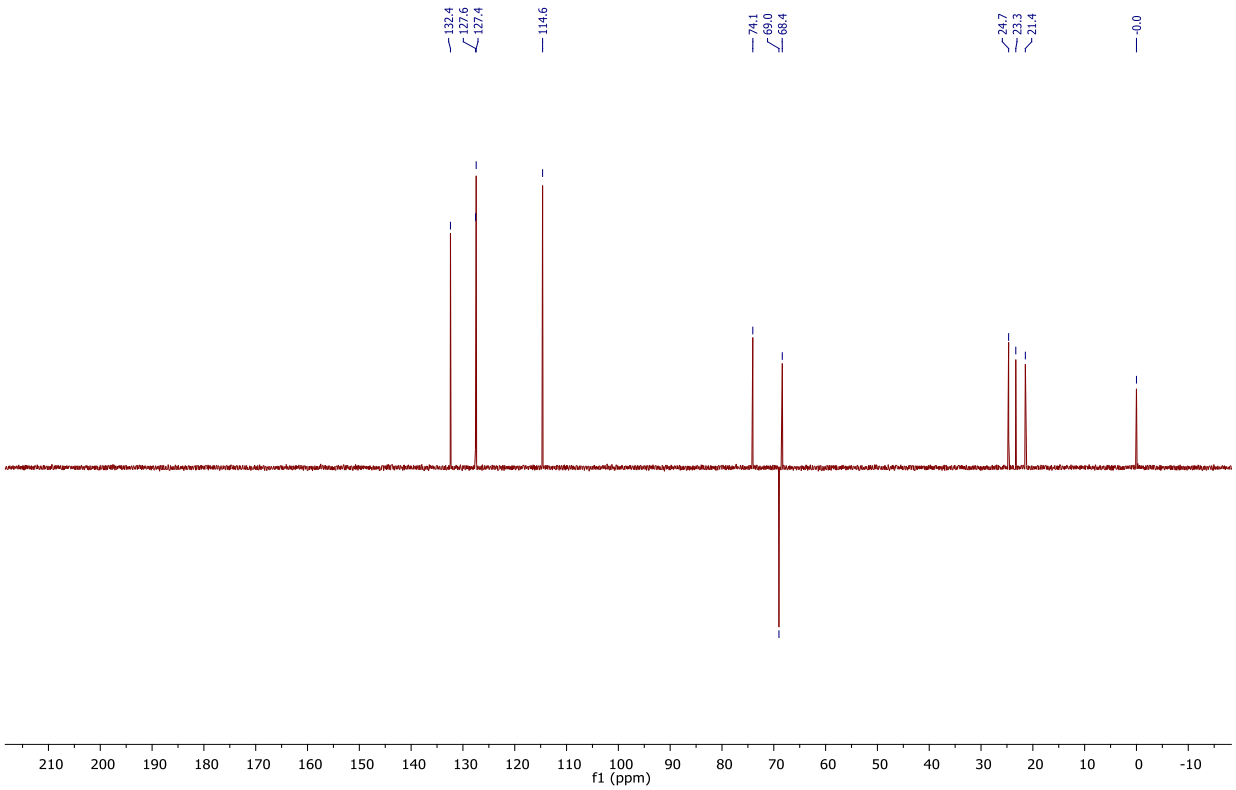
39c



^{1}H NMR spectrum in $CDCl_3$.

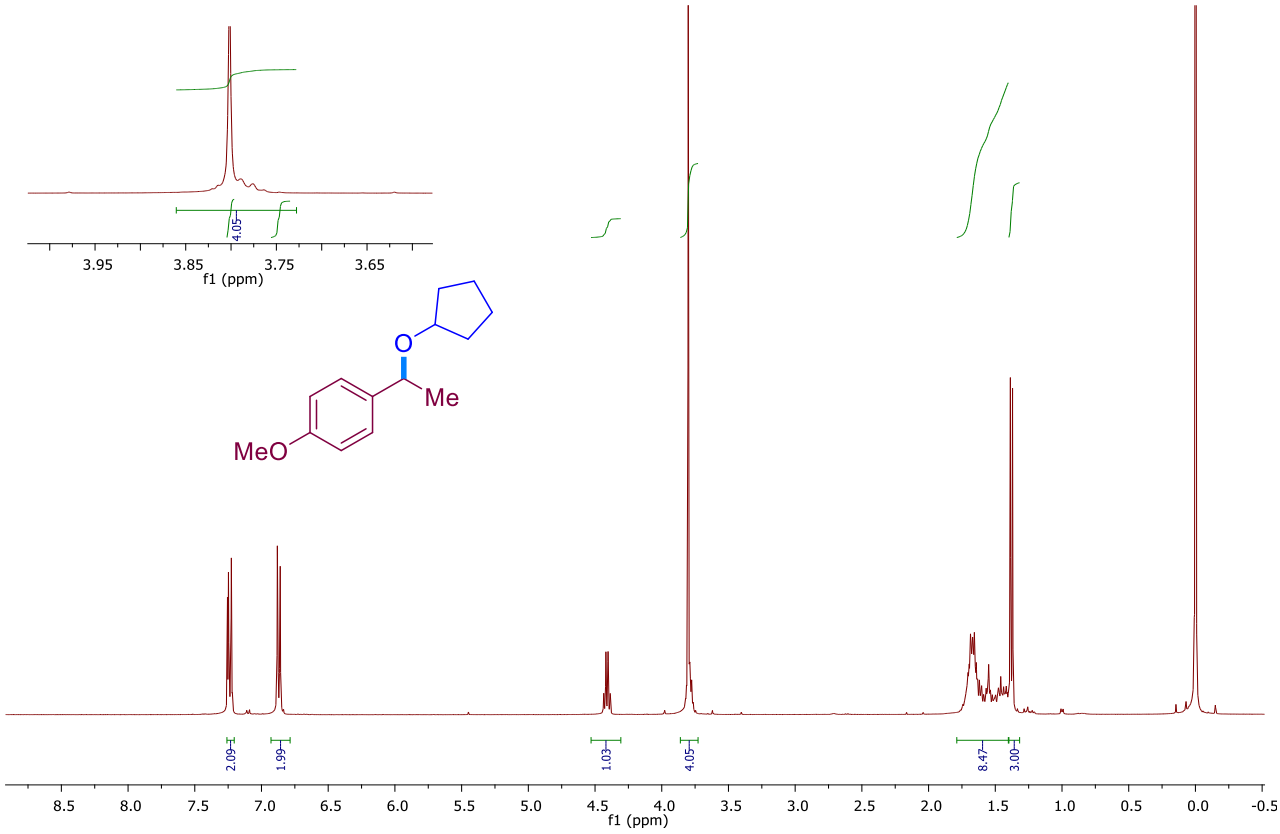


^{13}C NMR spectrum in $CDCl_3$

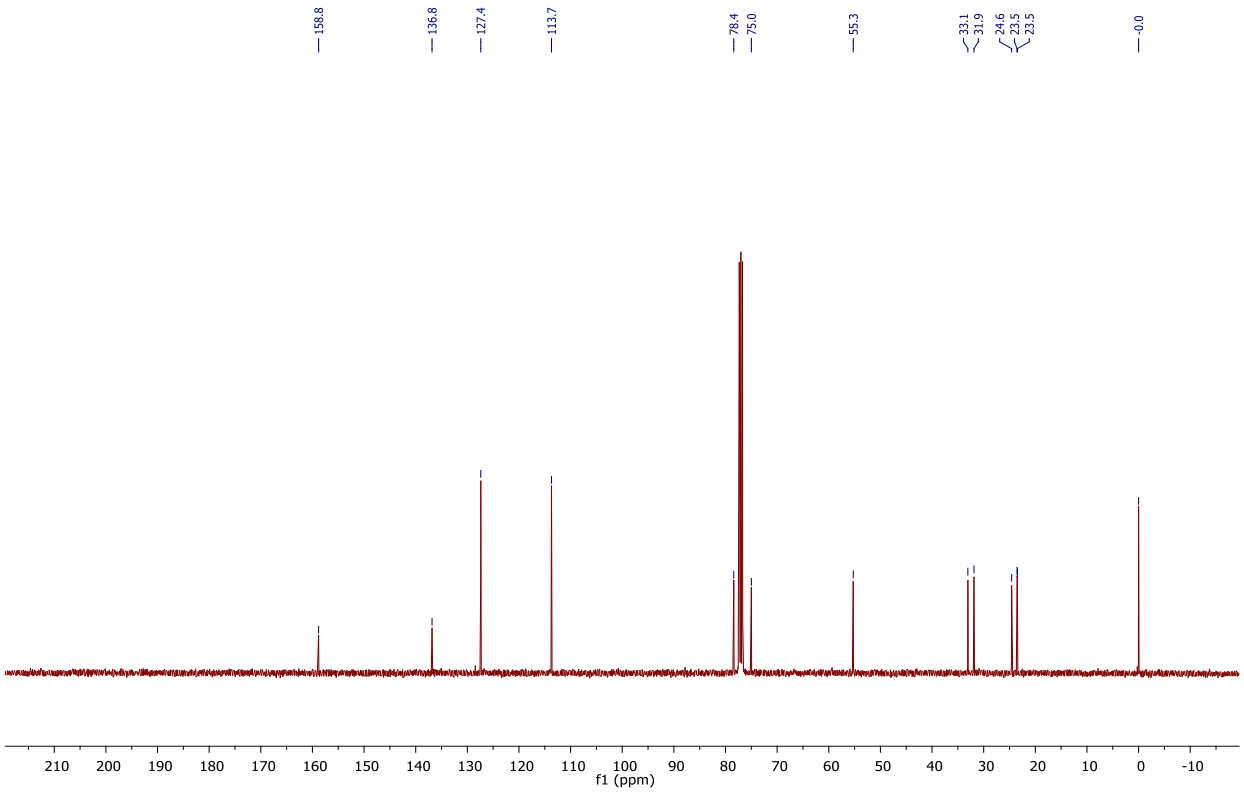


DEPT spectrum in $CDCl_3$.

40c

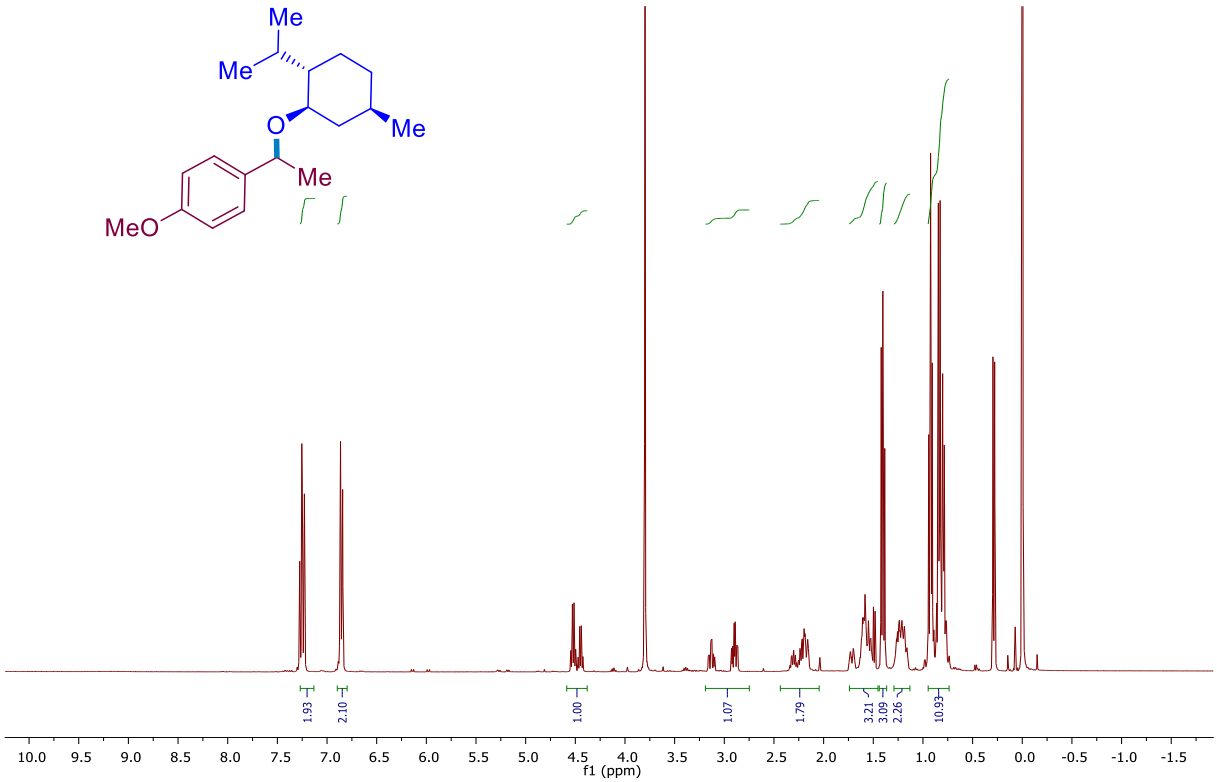


^{1}H NMR spectrum in $CDCl_3$.

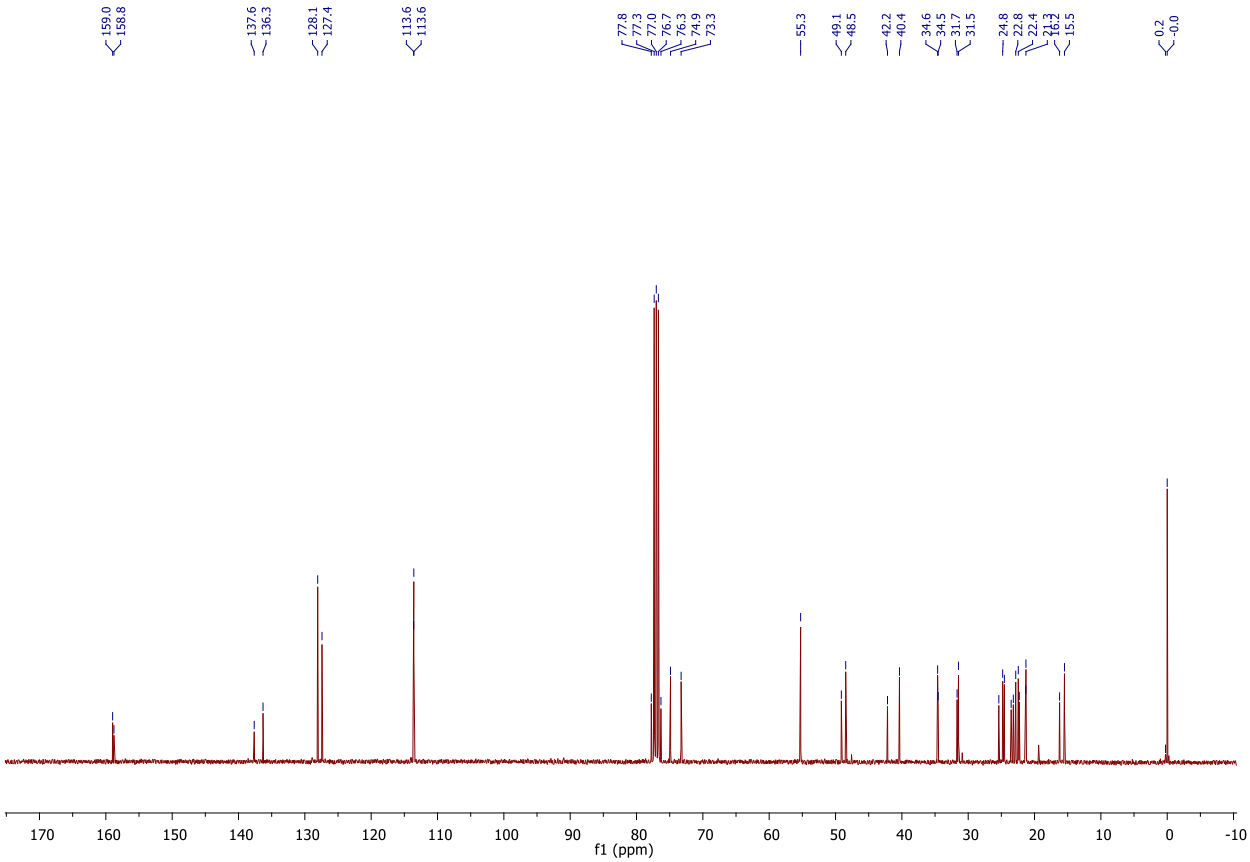


^{13}C NMR spectrum in $CDCl_3$

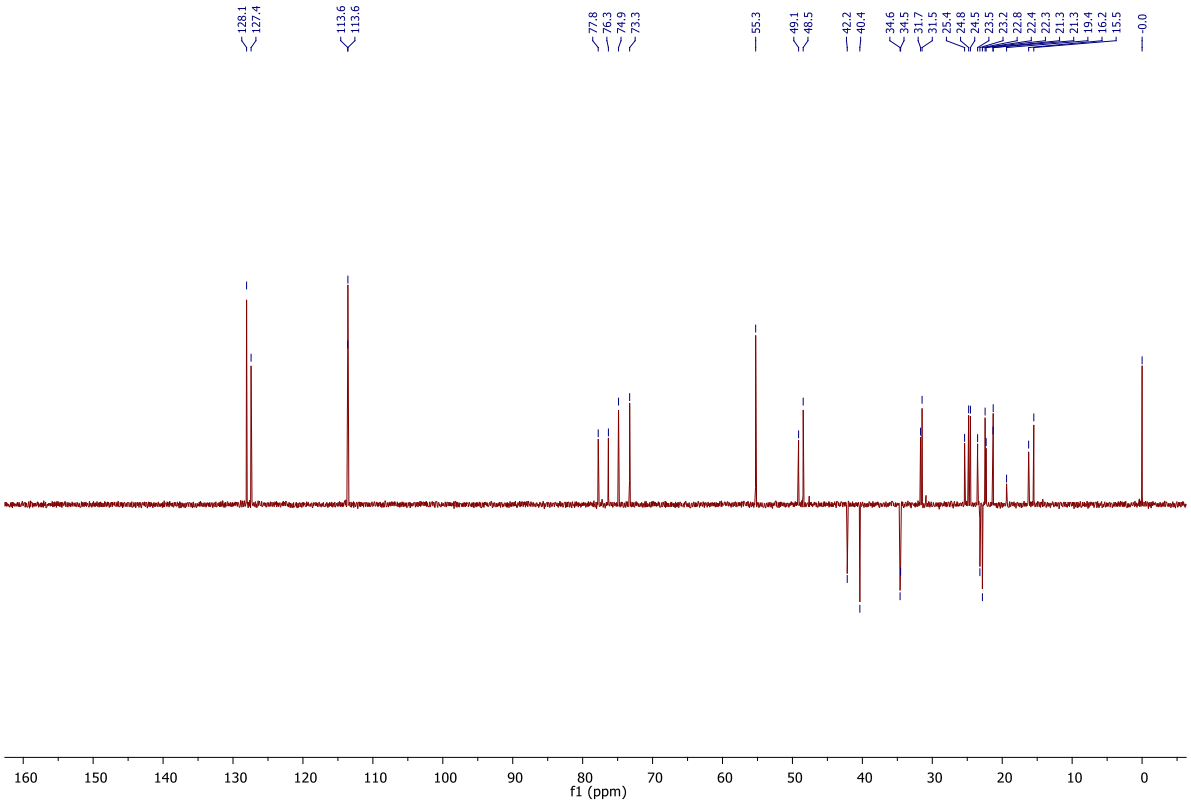
41c



^{1}H NMR spectrum in $CDCl_3$.

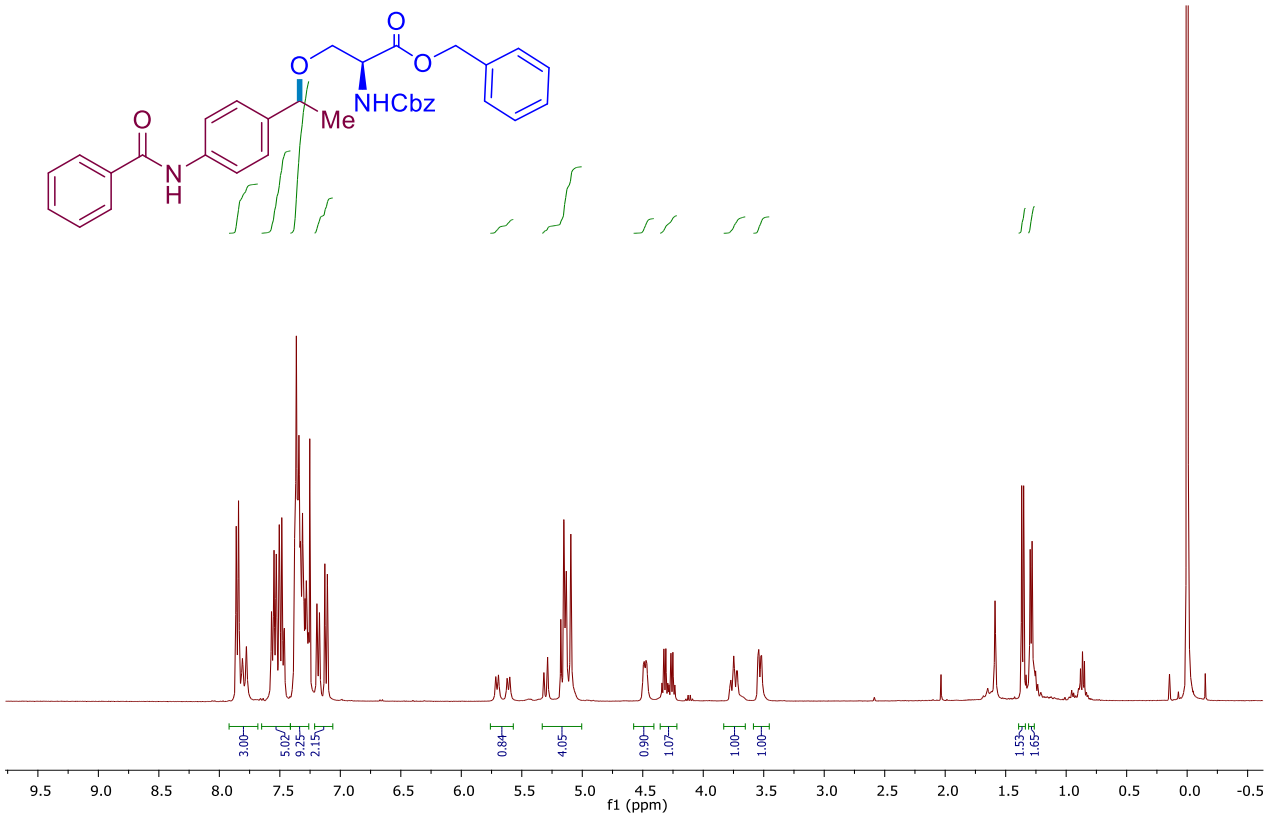


^{13}C NMR spectrum in $CDCl_3$

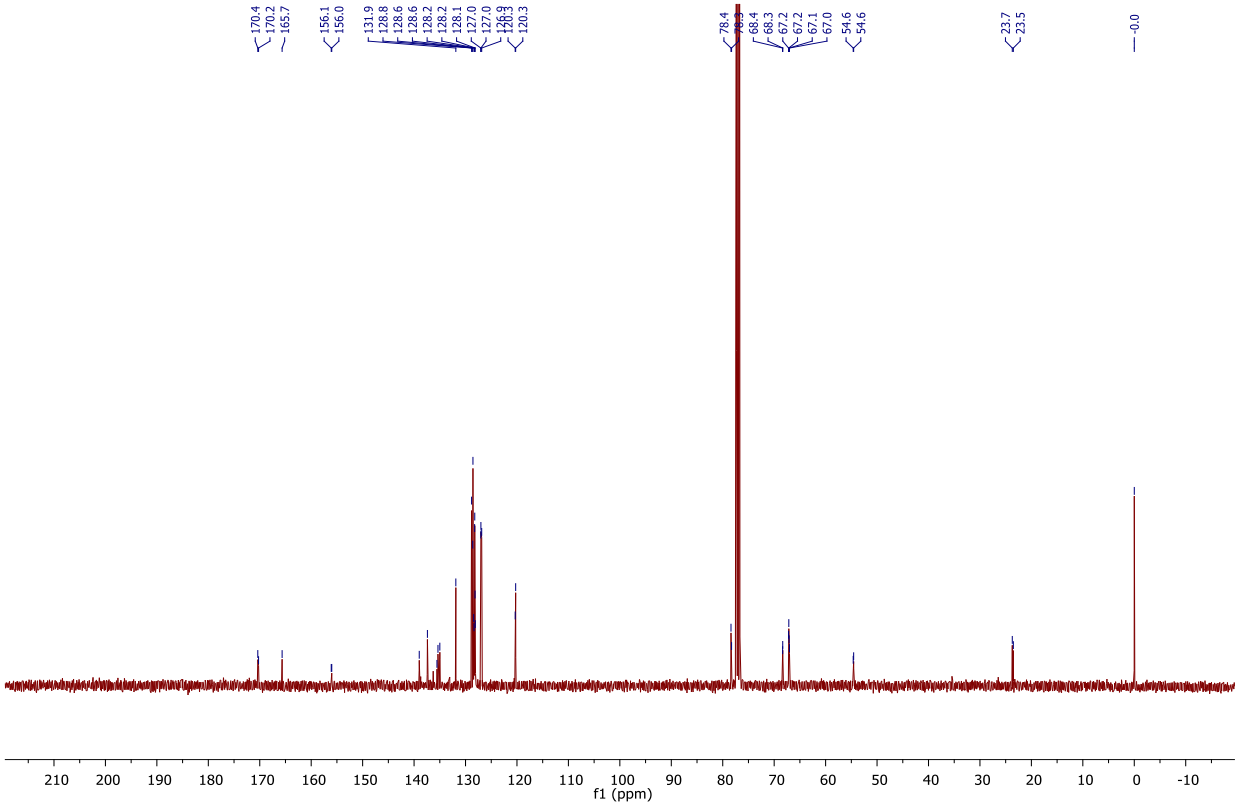


DEPT spectrum in $CDCl_3$.

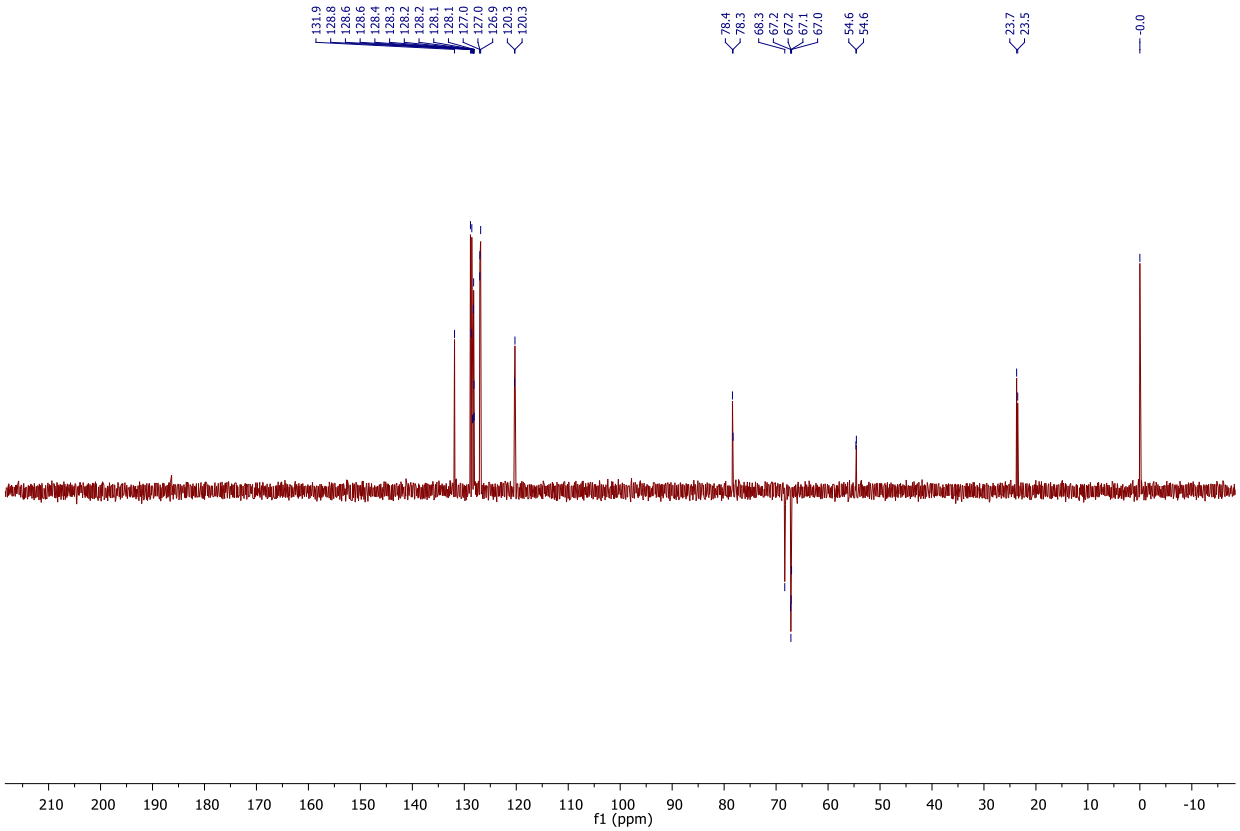
42c



^{1}H NMR spectrum in $CDCl_3$.

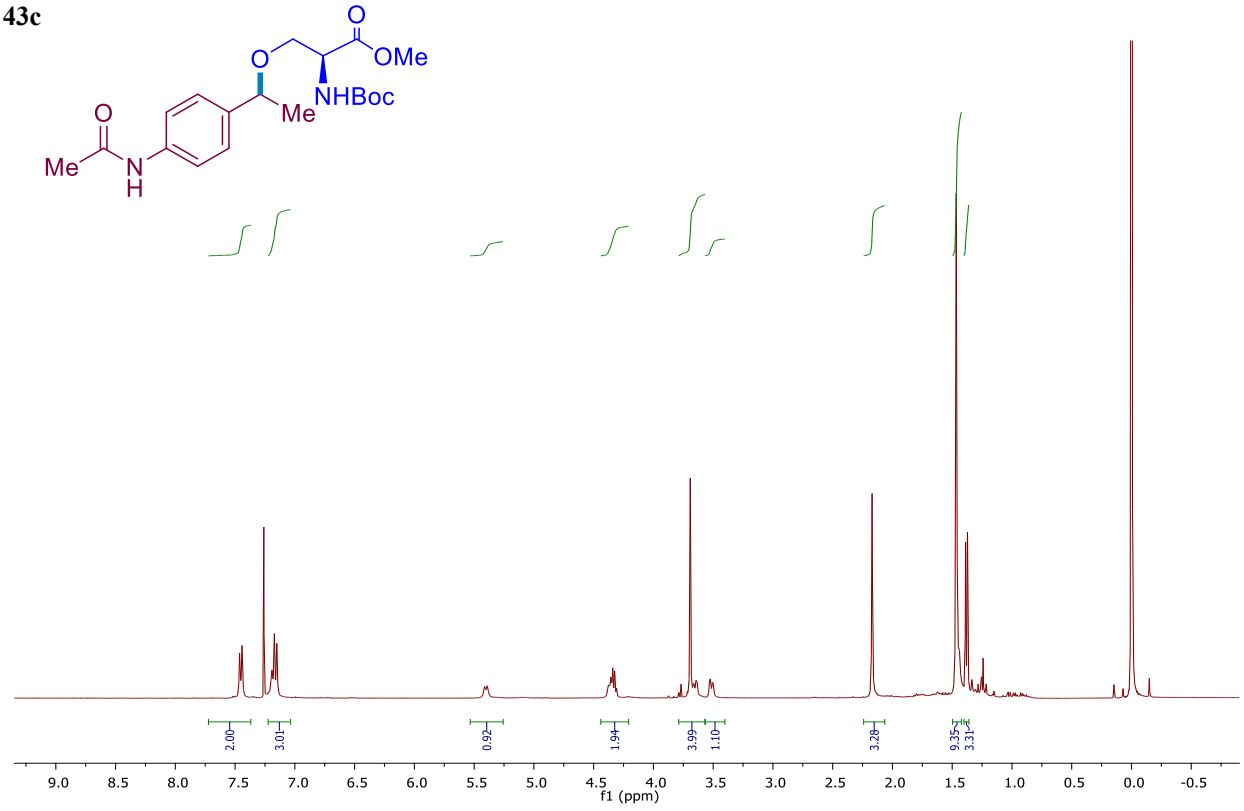


^{13}C NMR spectrum in $CDCl_3$

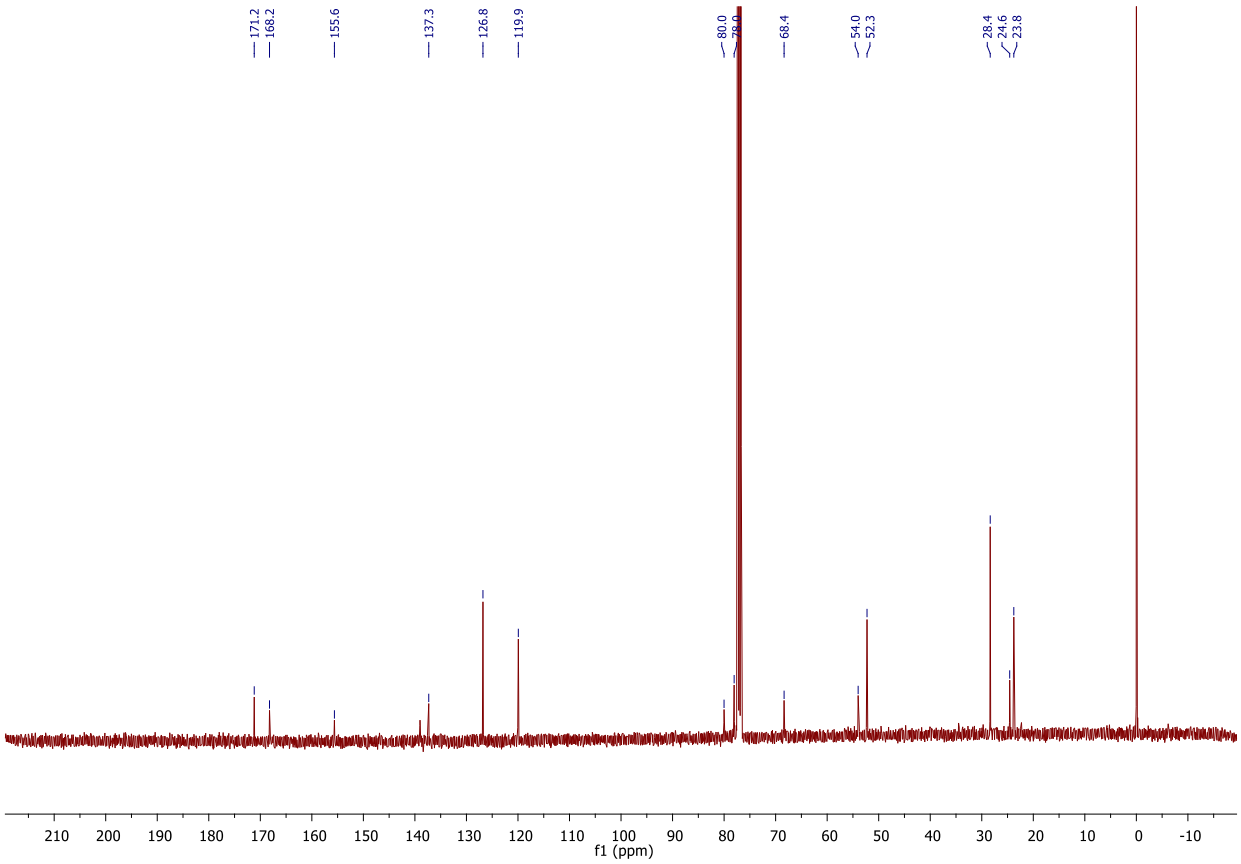


DEPT spectrum in $CDCl_3$.

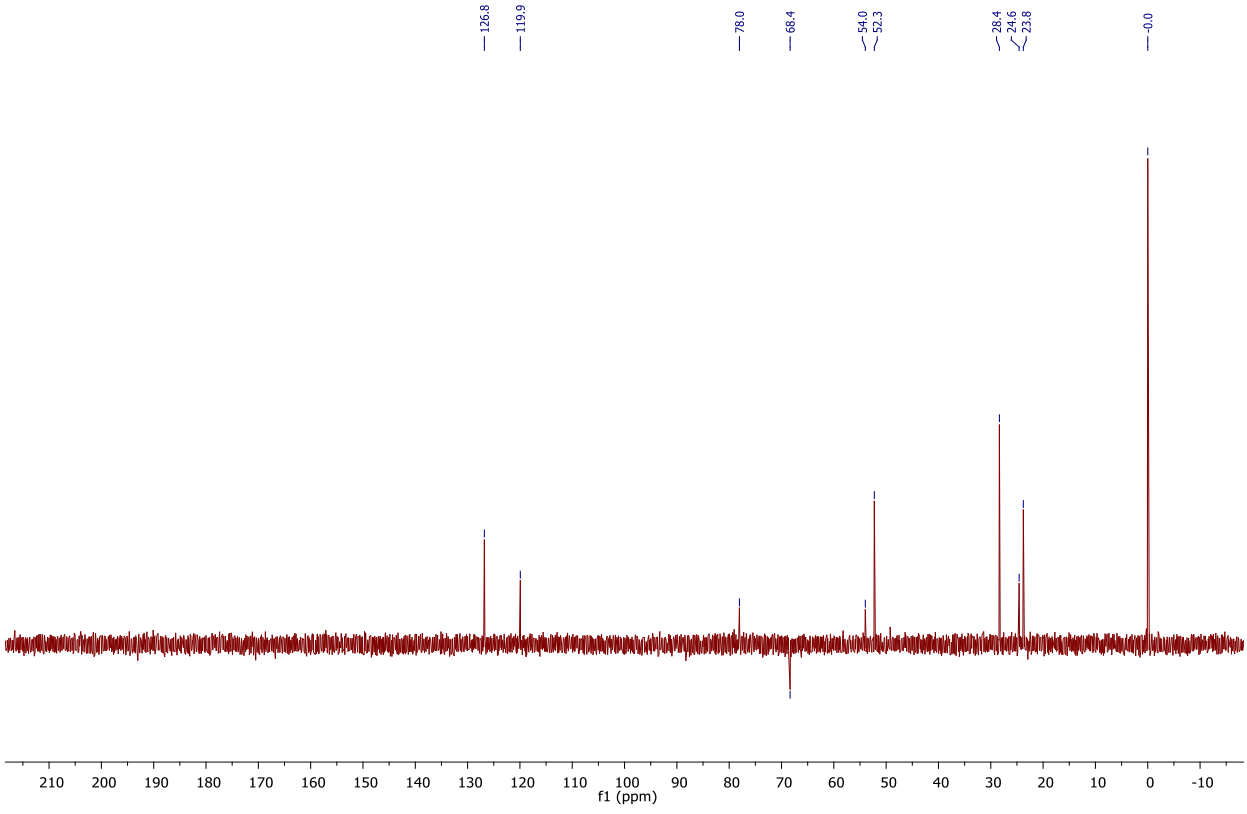
43c



^1H NMR spectrum in $CDCl_3$.

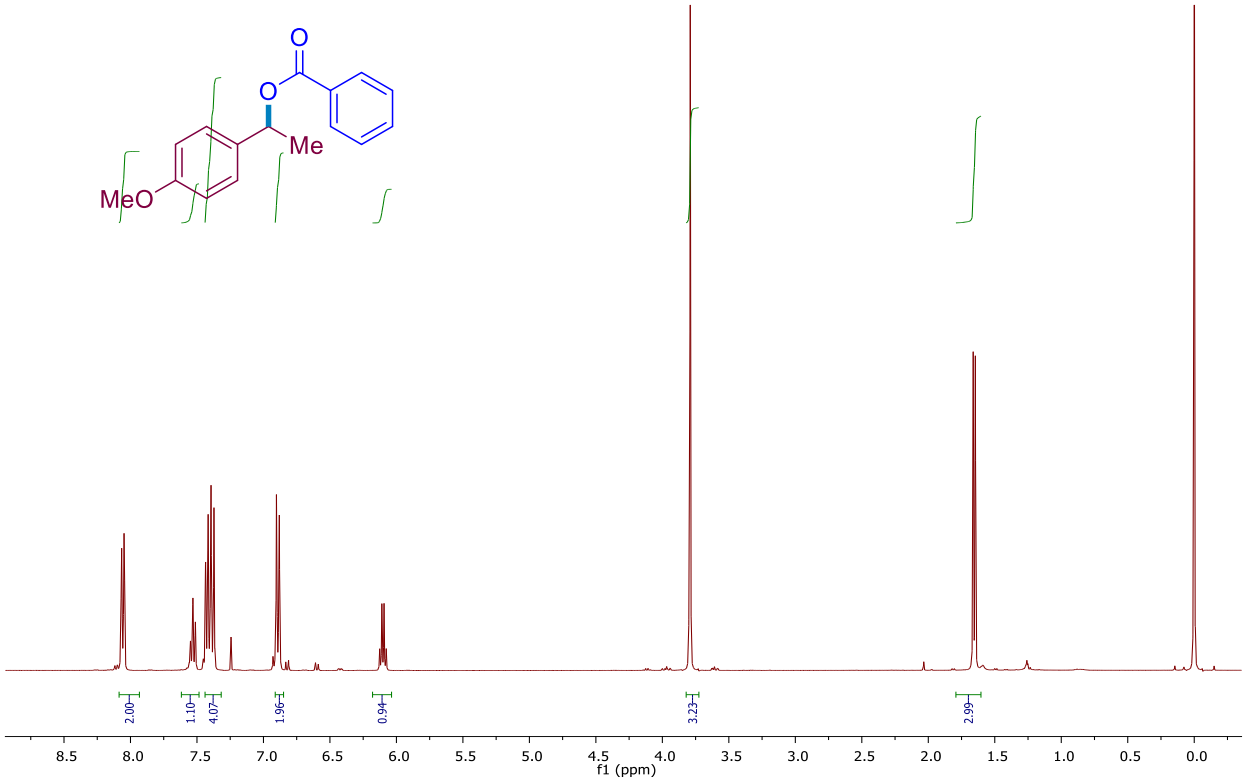


^{13}C NMR spectrum in $CDCl_3$

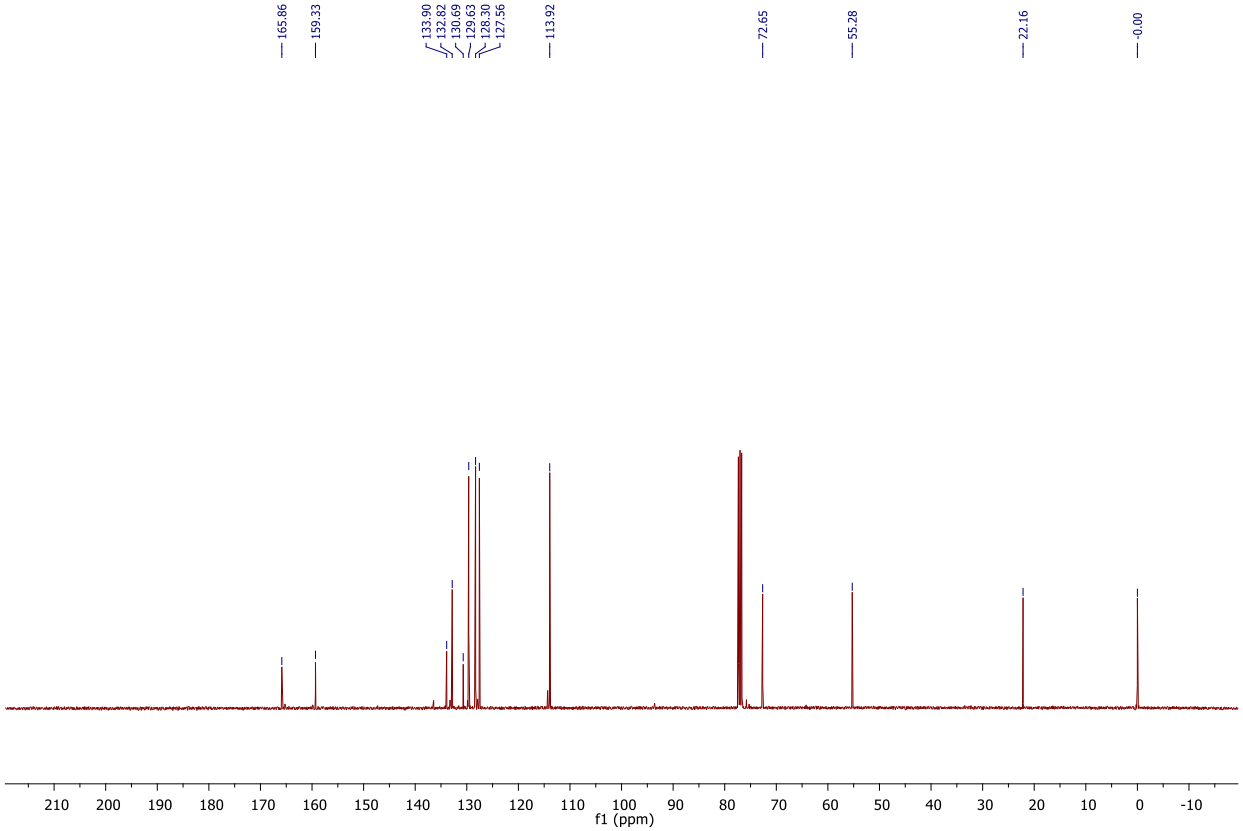


DEPT spectrum in $CDCl_3$.

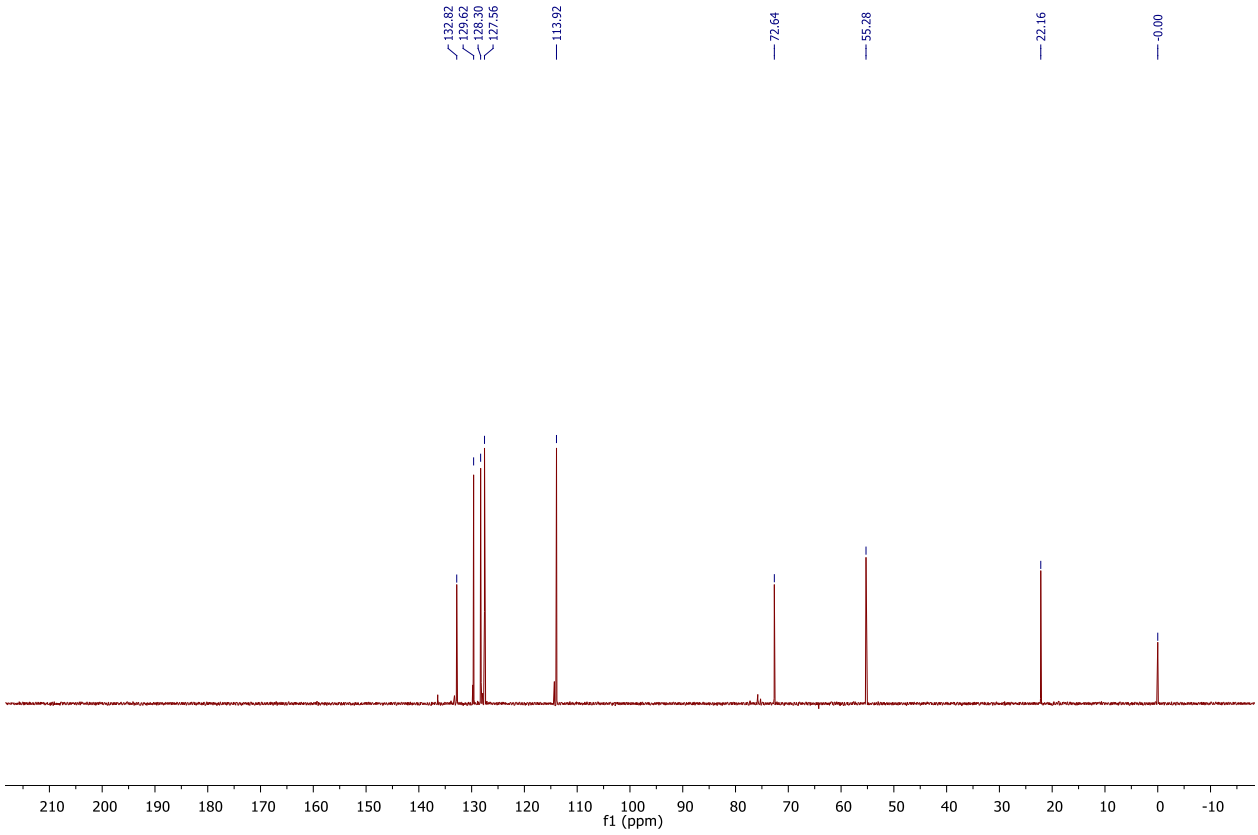
44c



^{1}H NMR spectrum in $CDCl_3$.

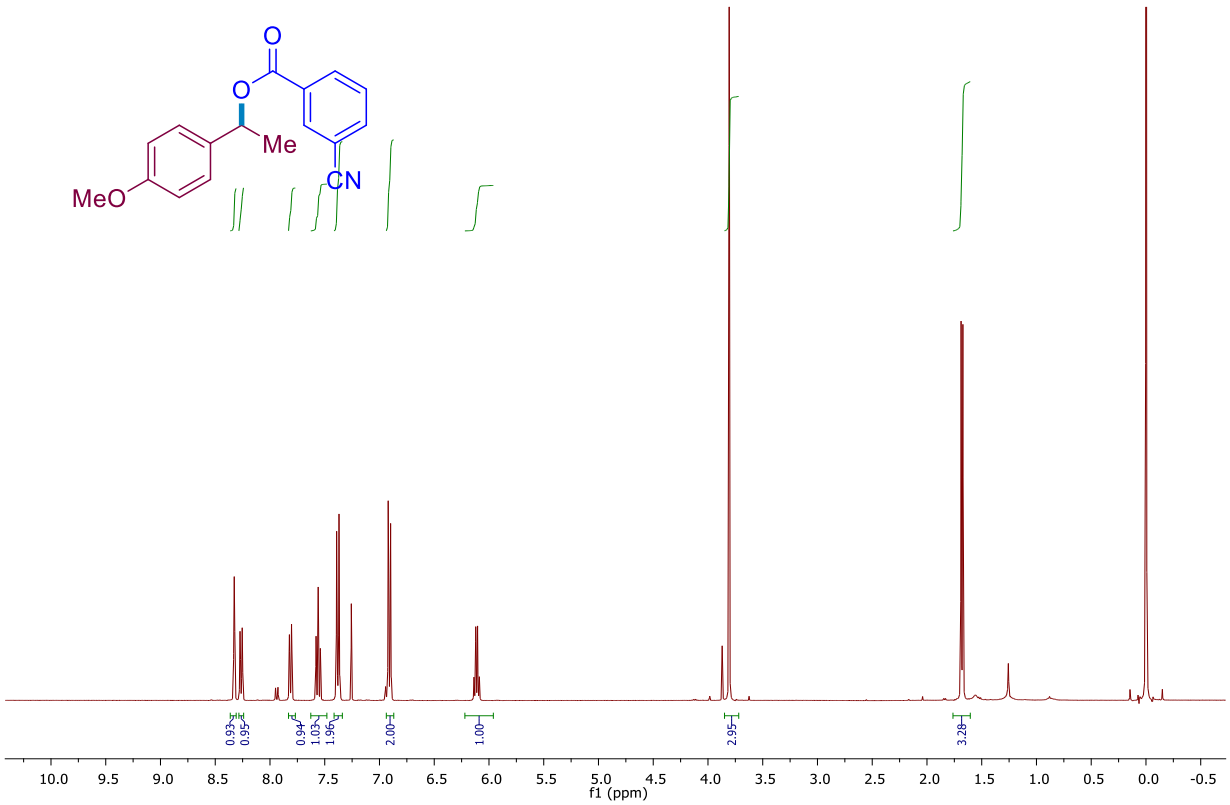


^{13}C NMR spectrum in $CDCl_3$

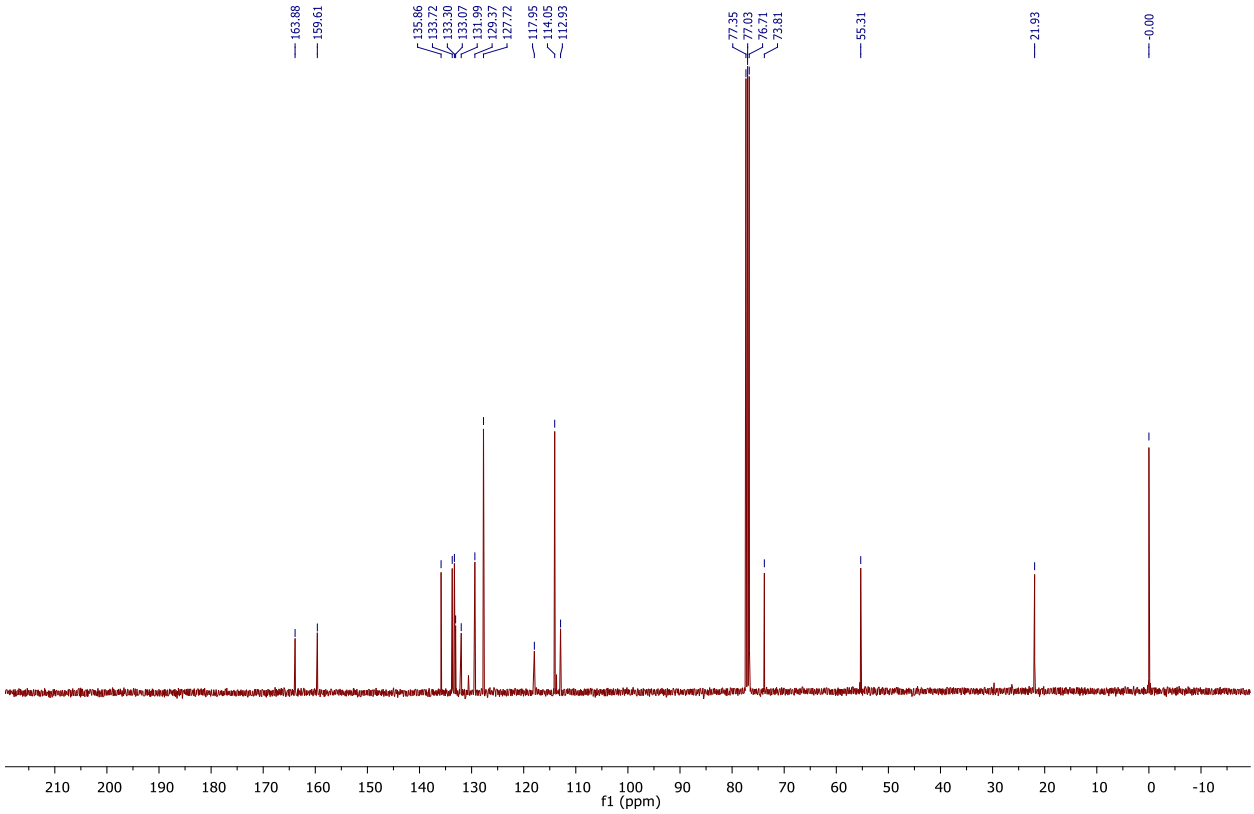


DEPT spectrum in $CDCl_3$.

45c

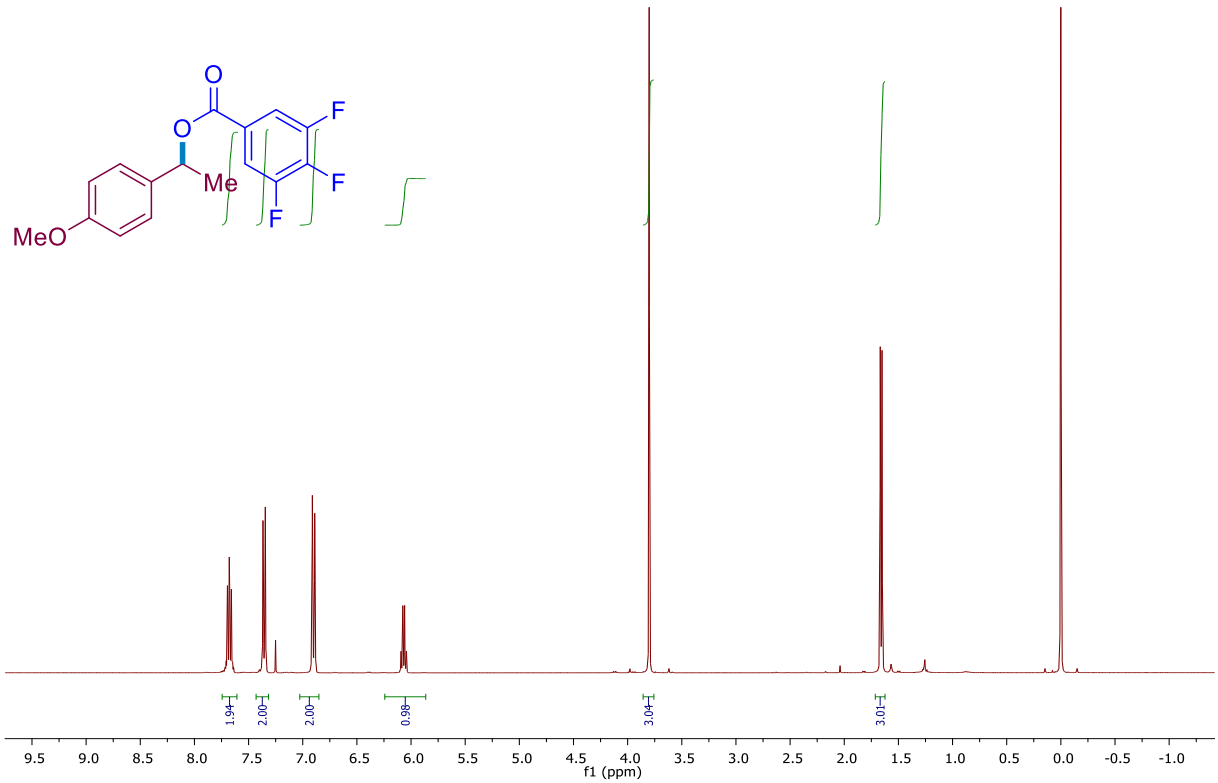


^1H NMR spectrum in $CDCl_3$.

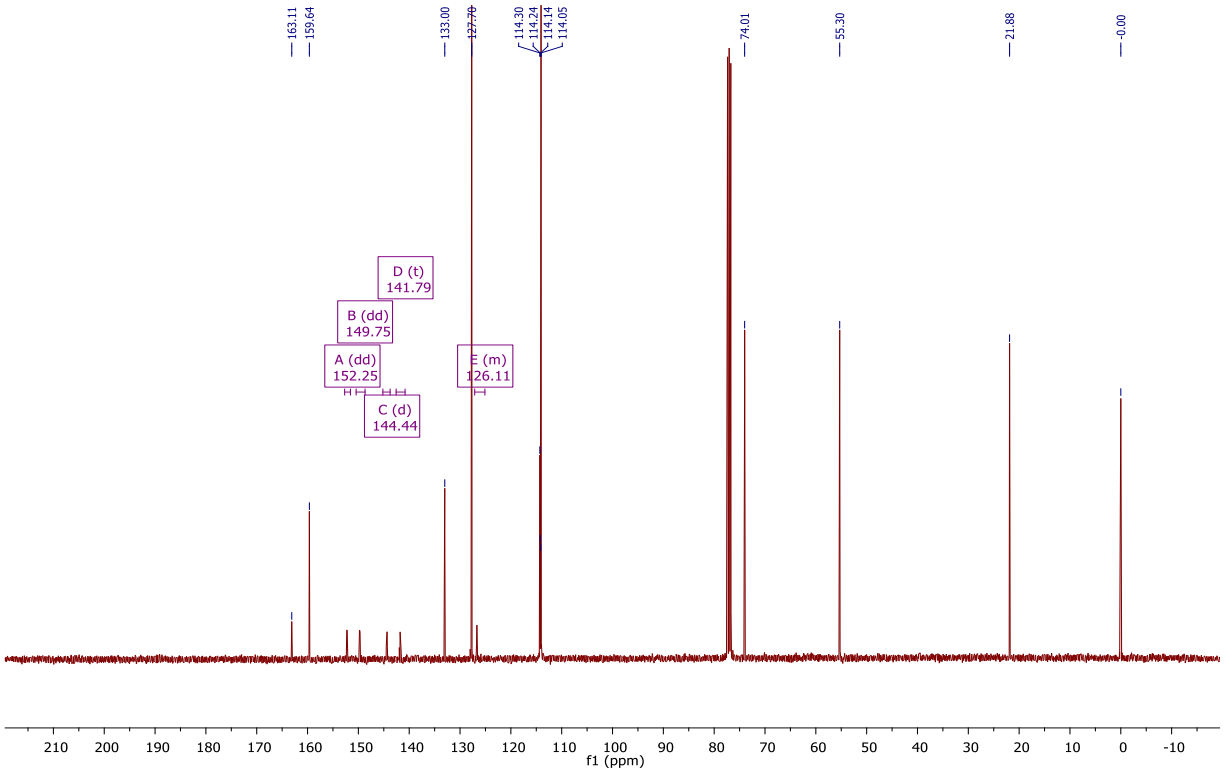


^{13}C NMR spectrum in $CDCl_3$

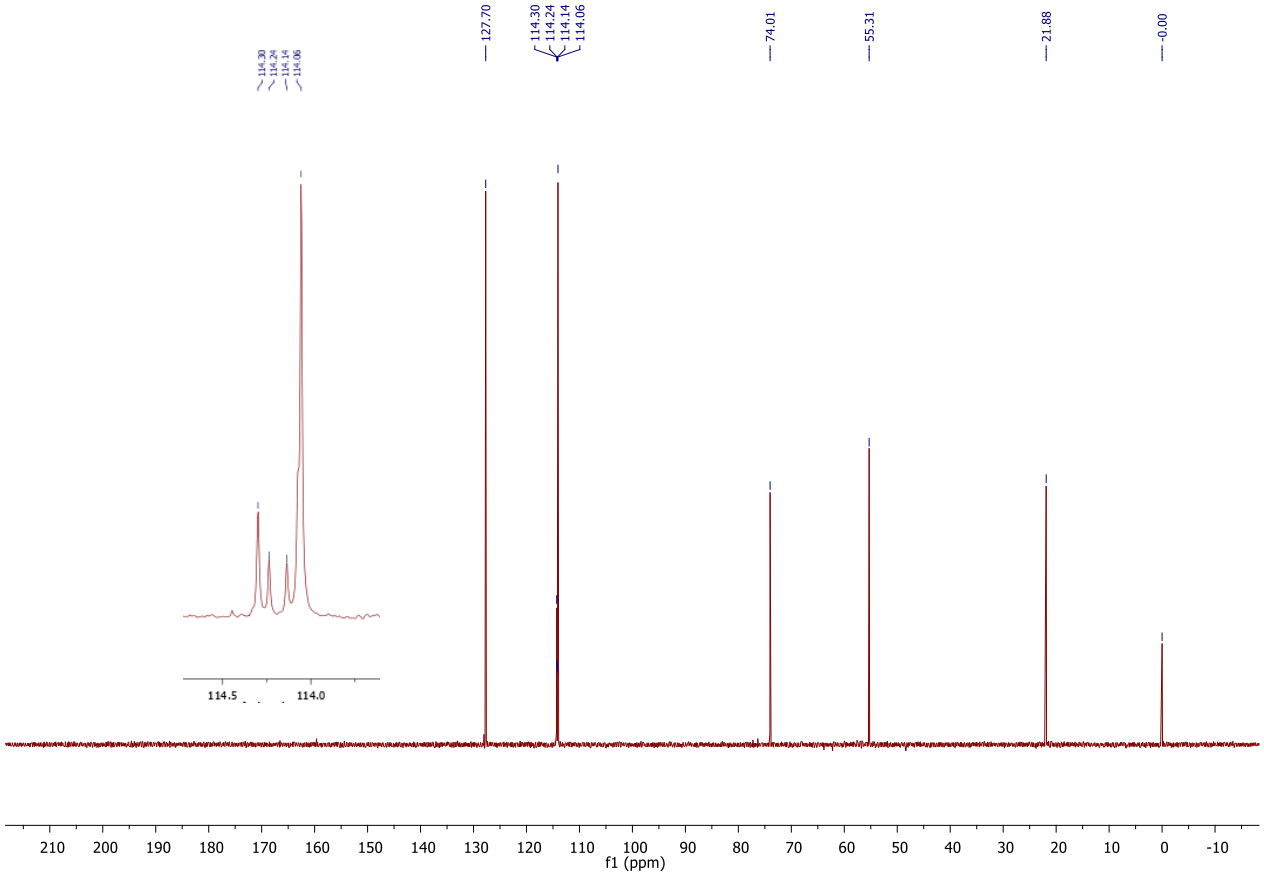
46c



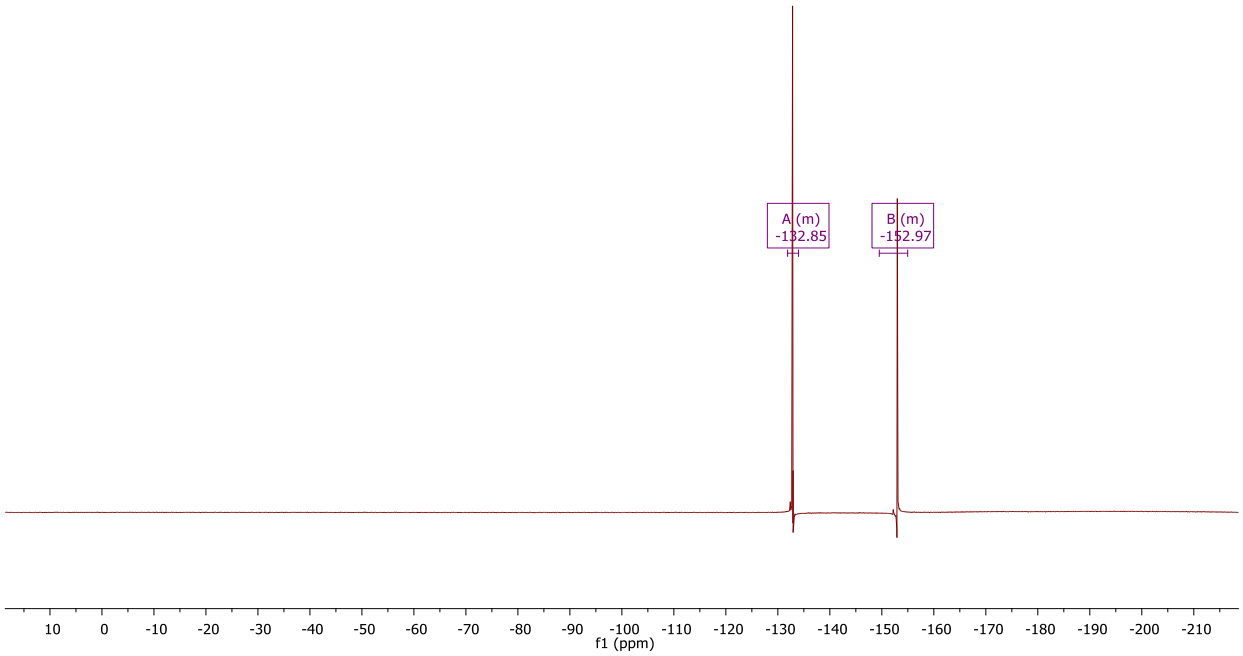
^{1}H NMR spectrum in $CDCl_3$.



^{13}C NMR spectrum in $CDCl_3$

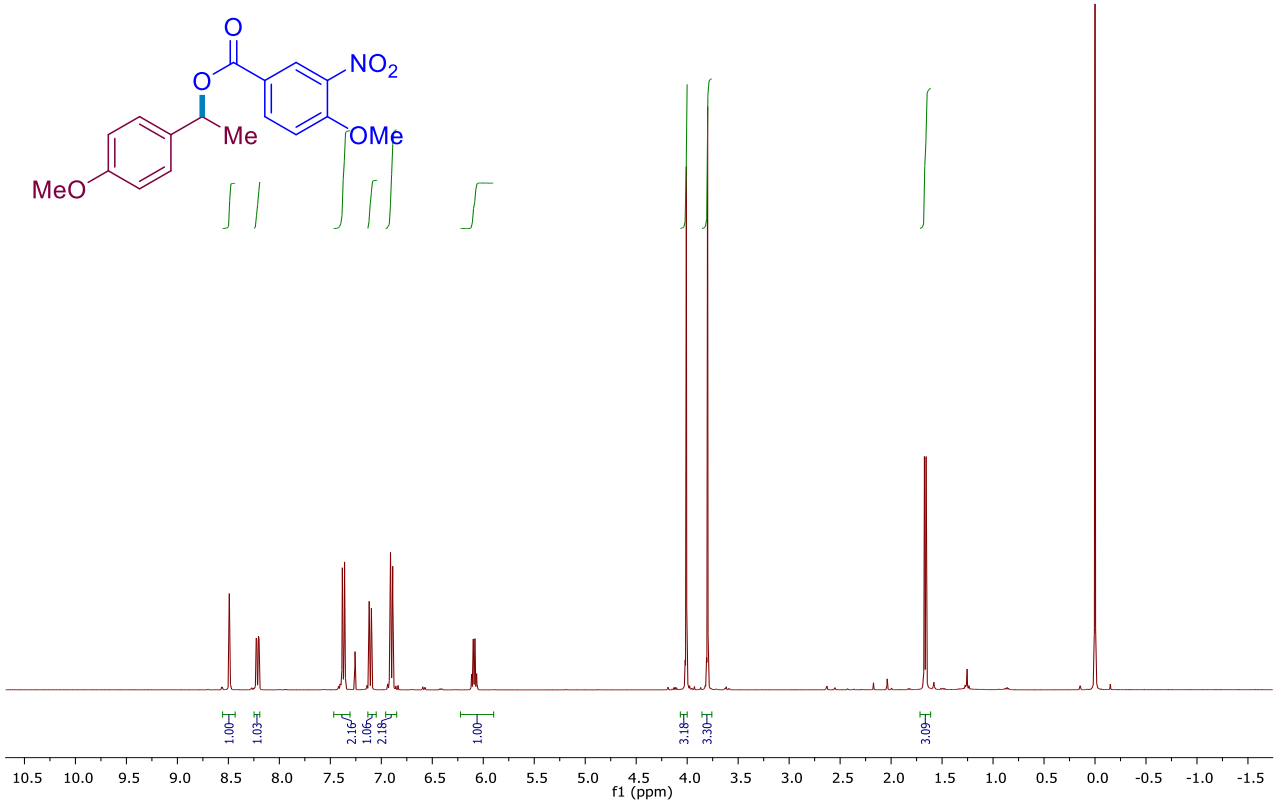


DEPT spectrum in $CDCl_3$.

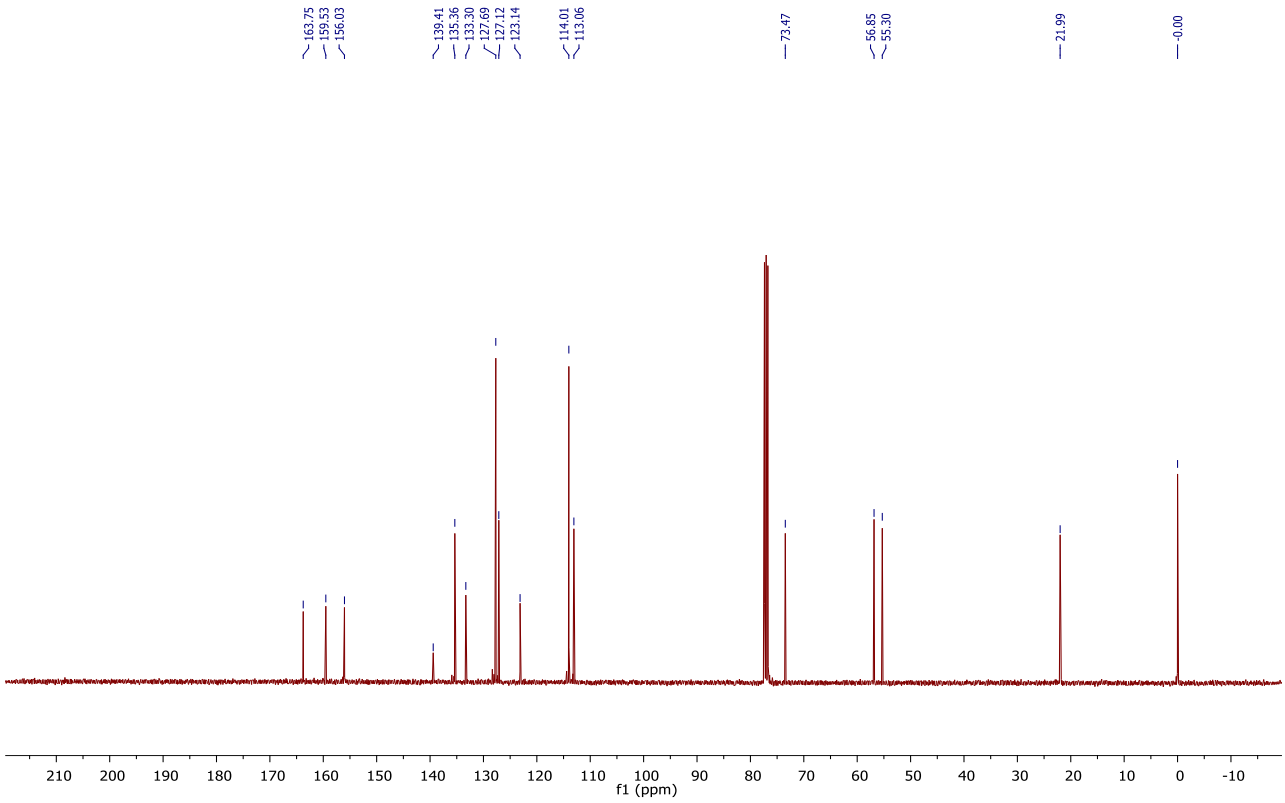


^{19}F NMR spectrum in $CDCl_3$

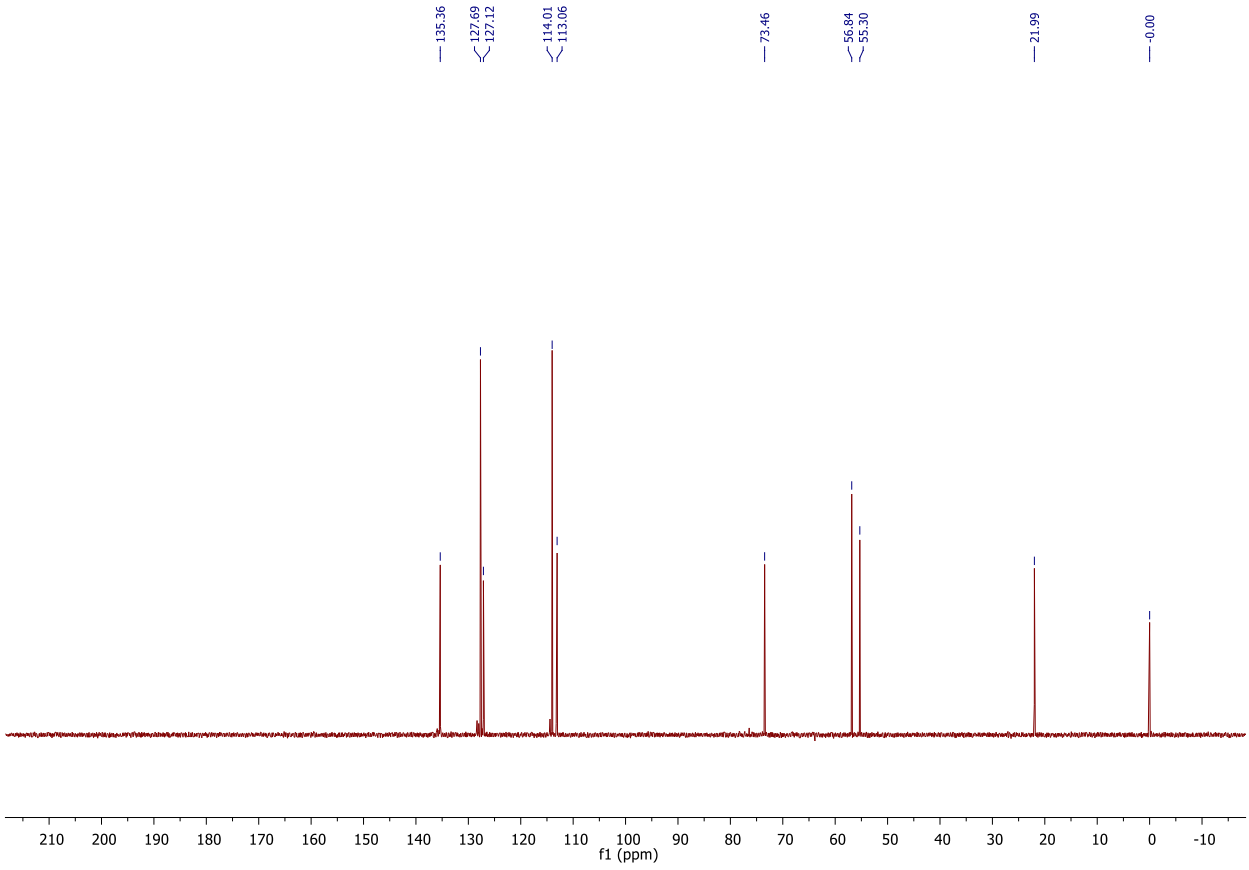
47c



^{1}H NMR spectrum in $CDCl_3$.

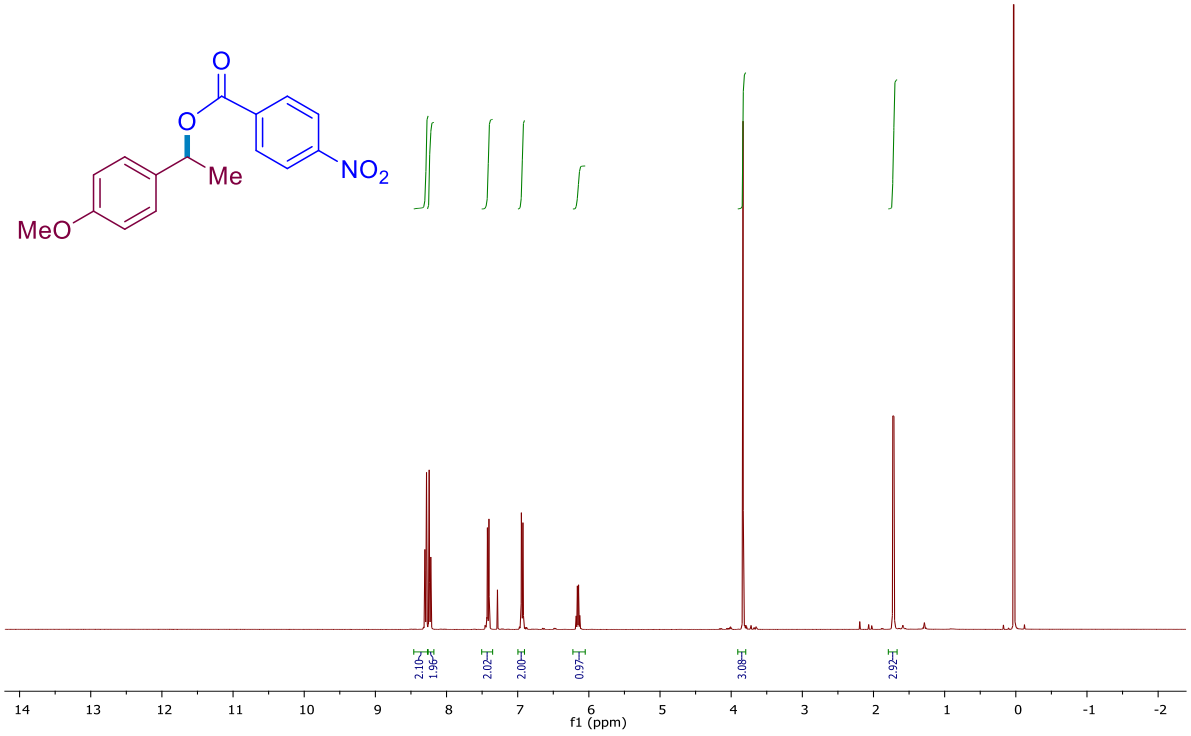


^{13}C NMR spectrum in $CDCl_3$

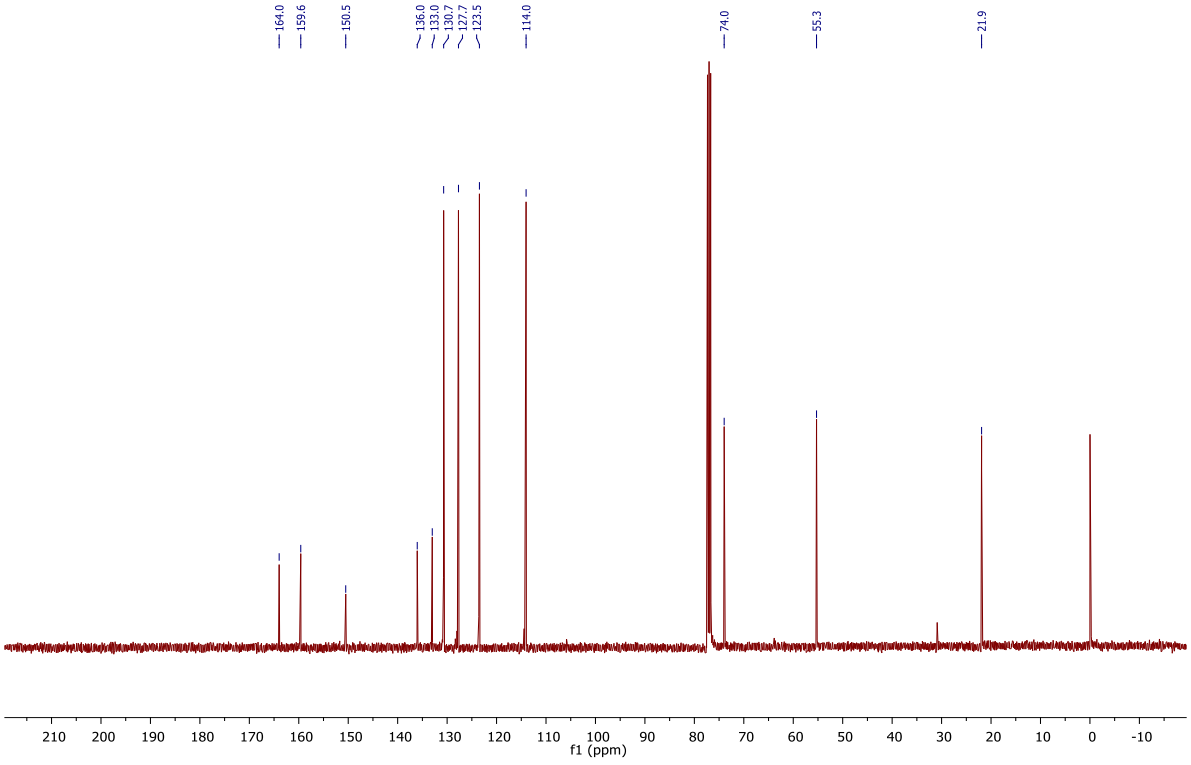


DEPT spectrum in $CDCl_3$.

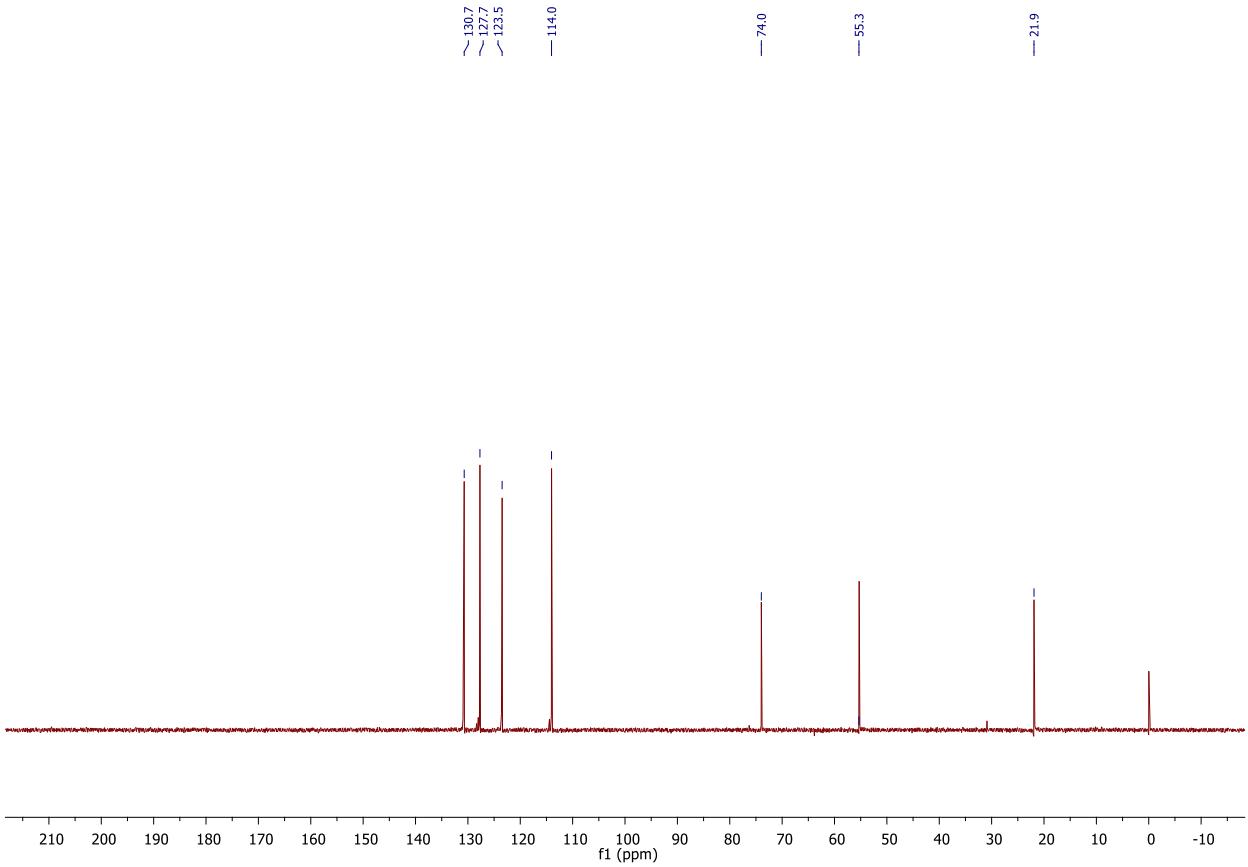
48c



^{1}H NMR spectrum in $CDCl_3$.

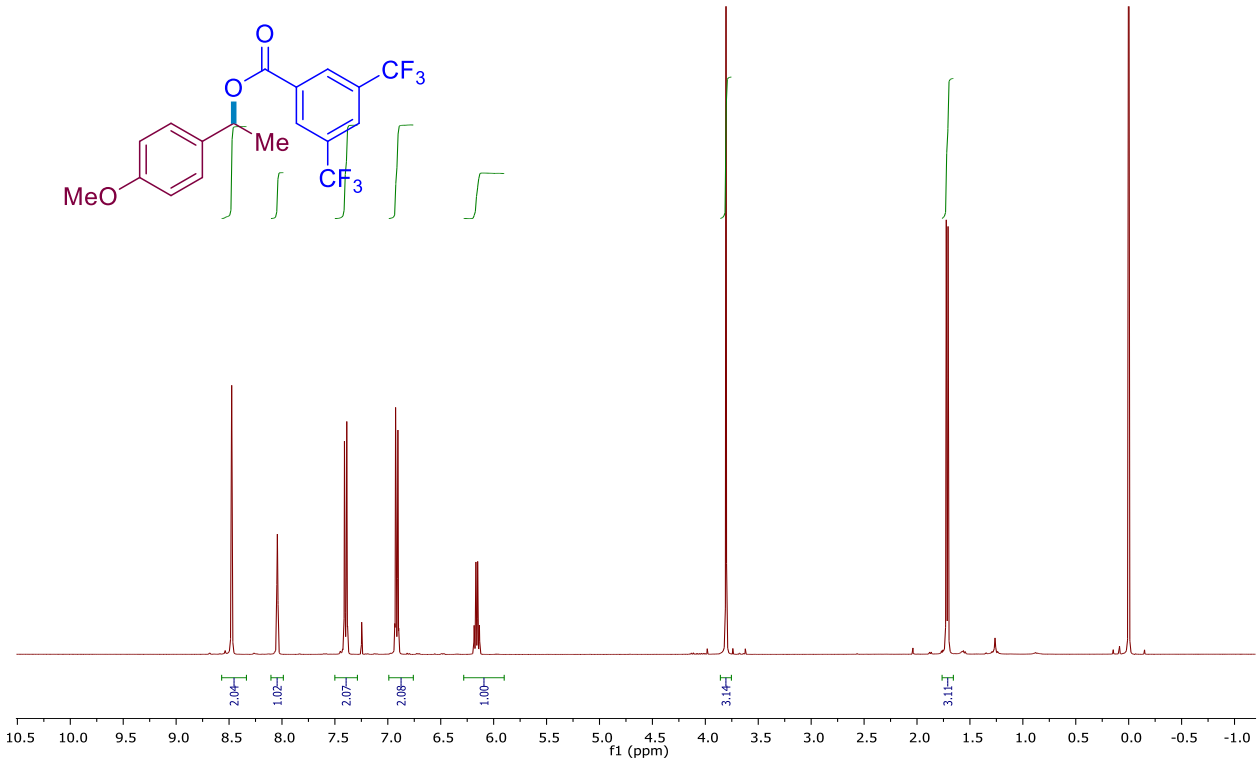


^{13}C NMR spectrum in $CDCl_3$

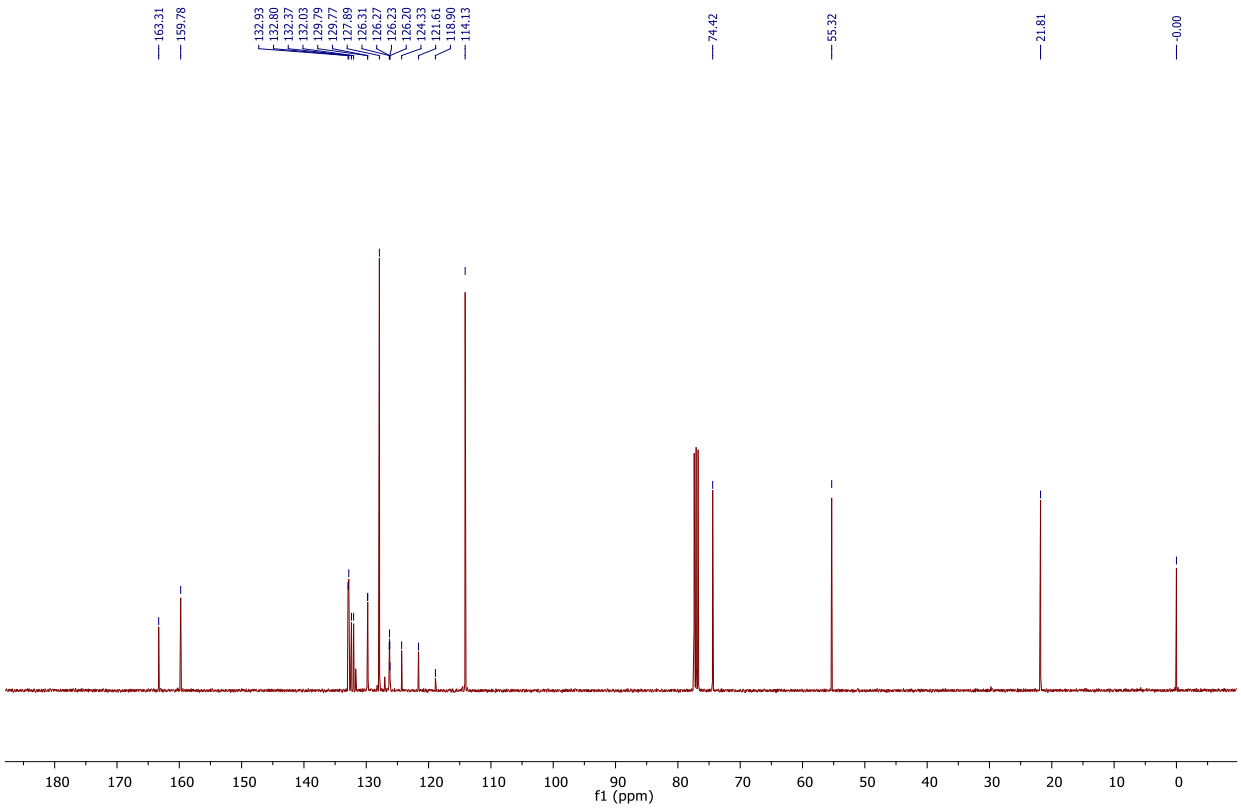


DEPT spectrum in $CDCl_3$.

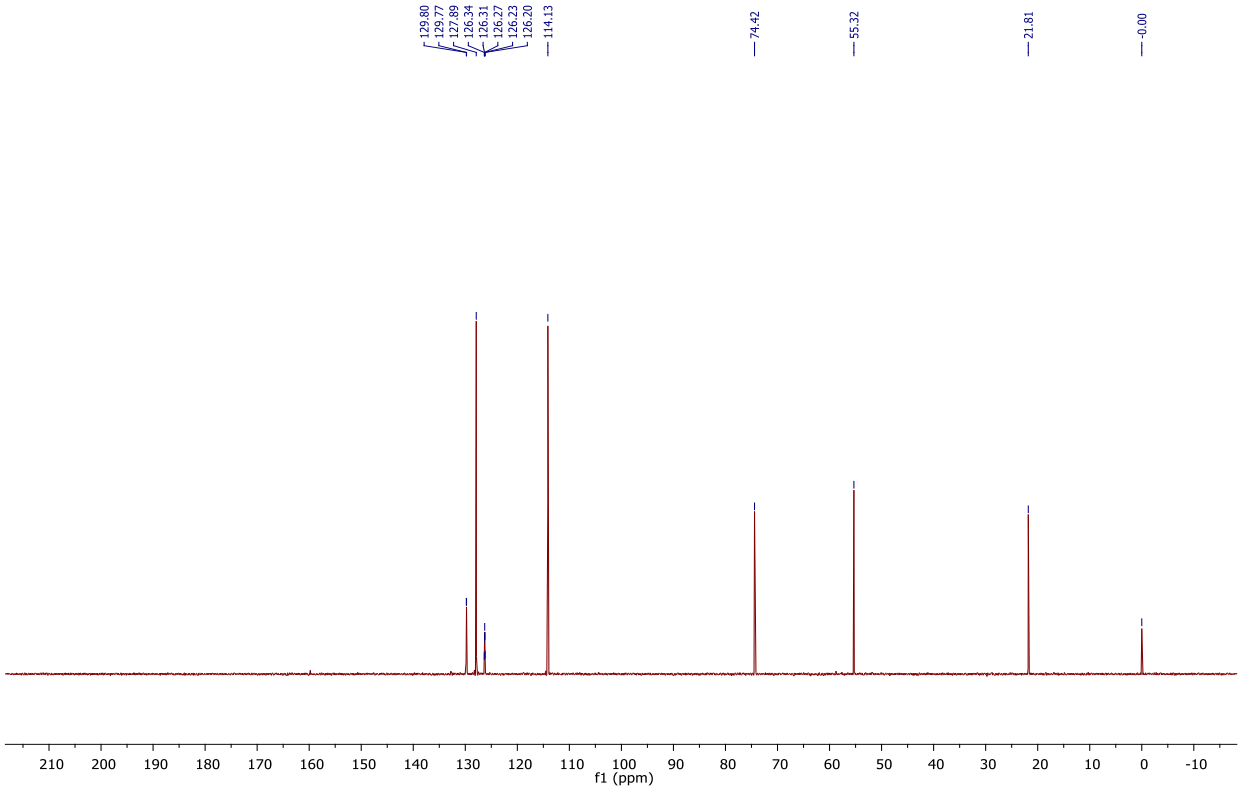
49c



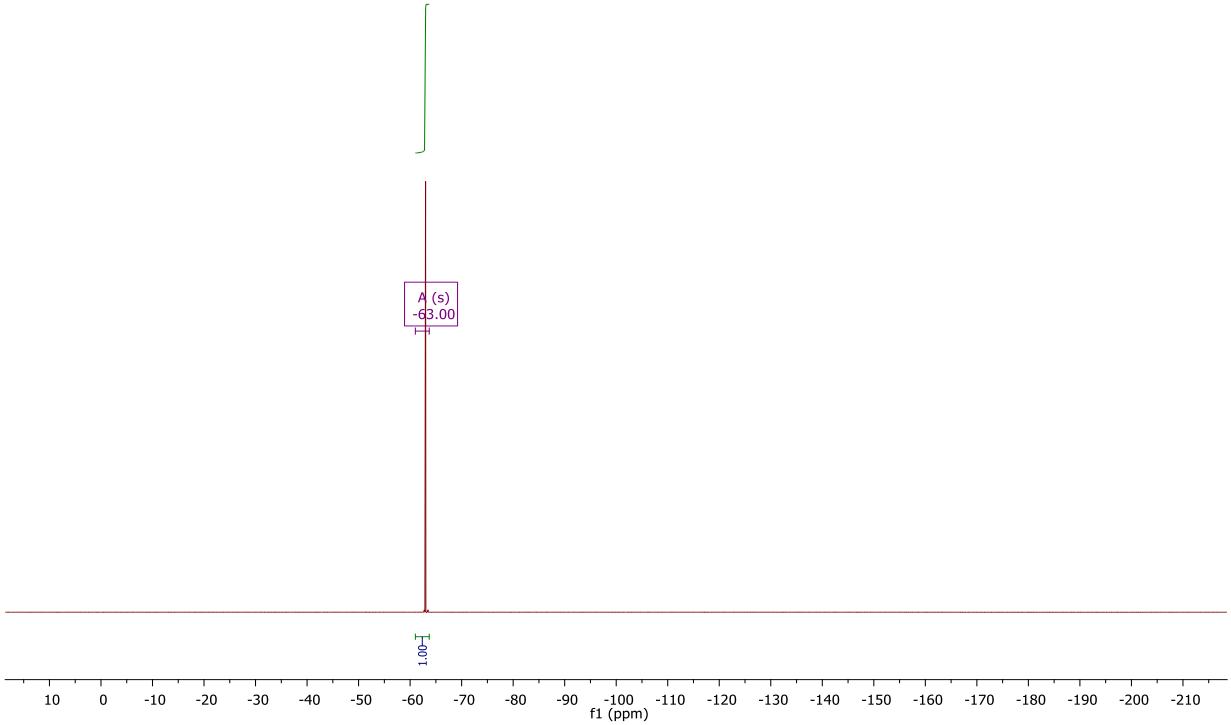
^{1}H NMR spectrum in $CDCl_3$.



^{13}C NMR spectrum in $CDCl_3$

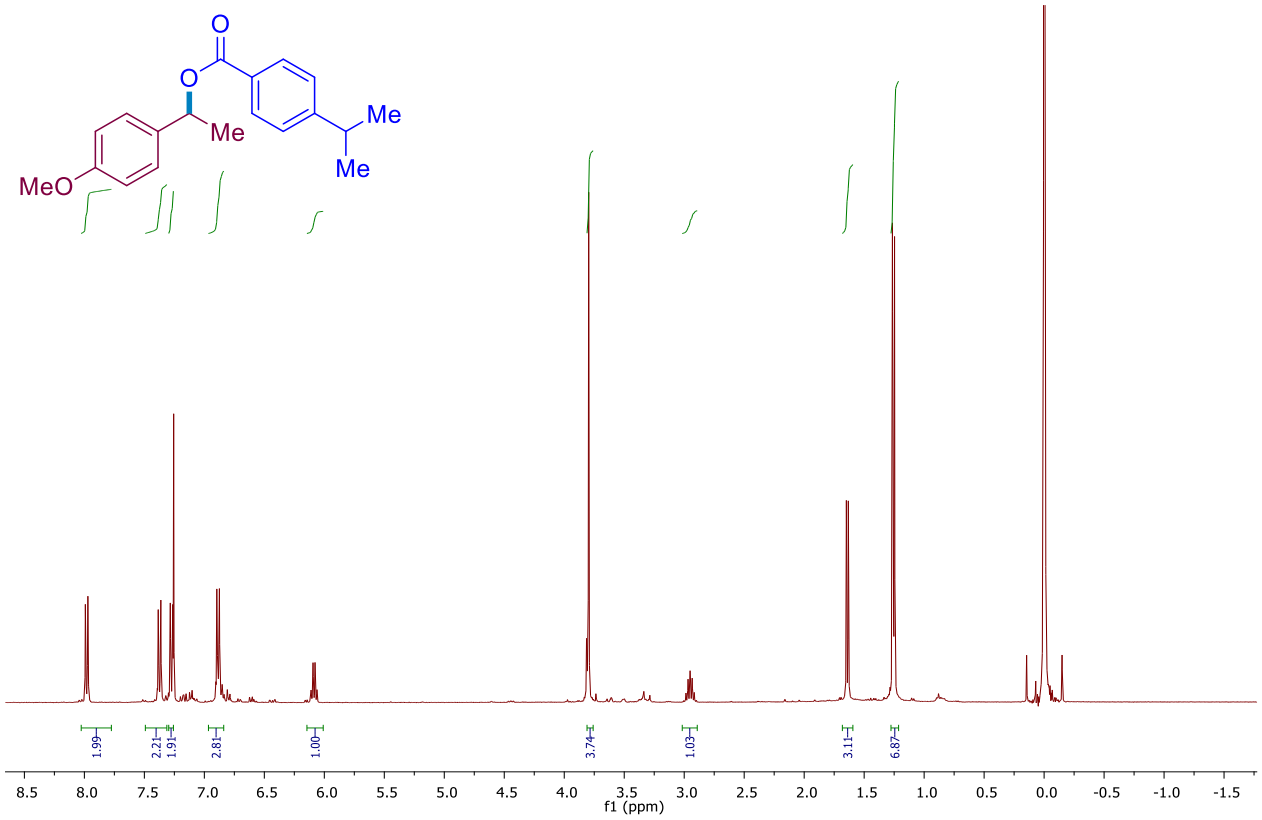


DEPT spectrum in $CDCl_3$.

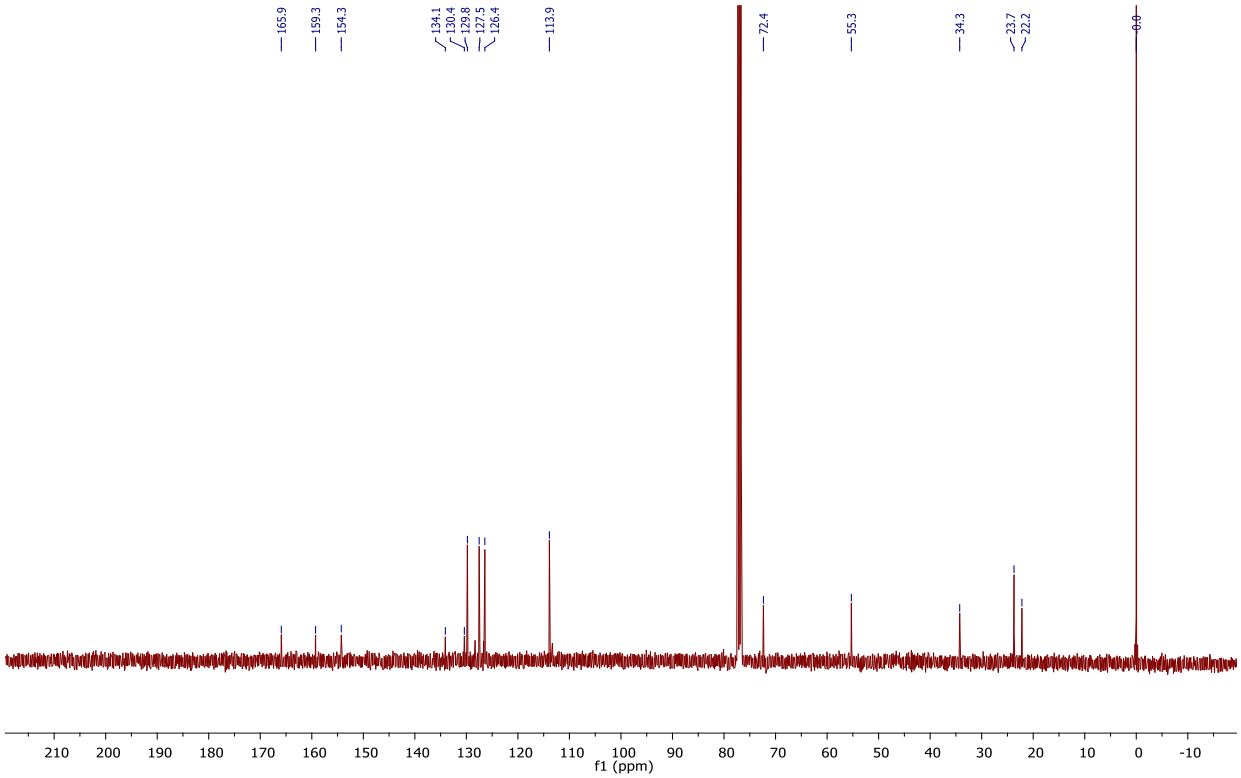


^{19}F NMR spectrum in $CDCl_3$

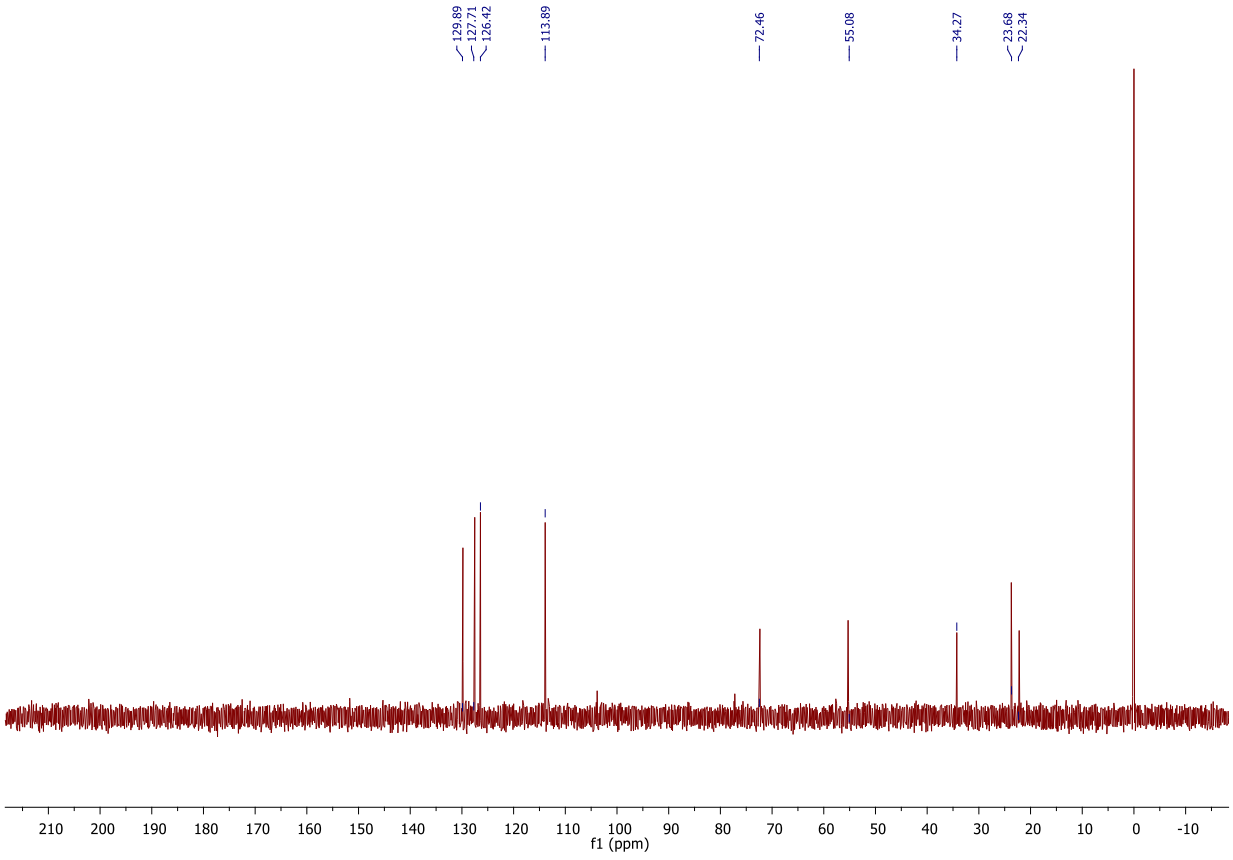
50c



^{1}H NMR spectrum in $CDCl_3$.

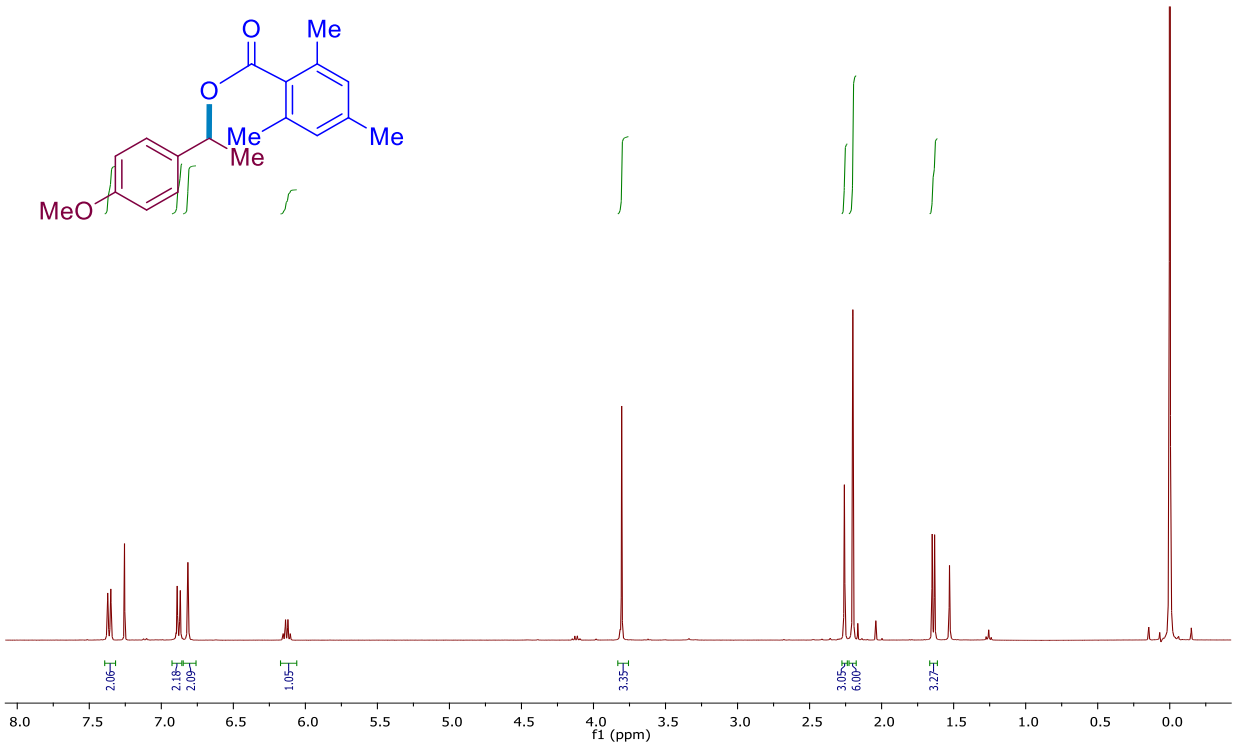


^{13}C NMR spectrum in $CDCl_3$

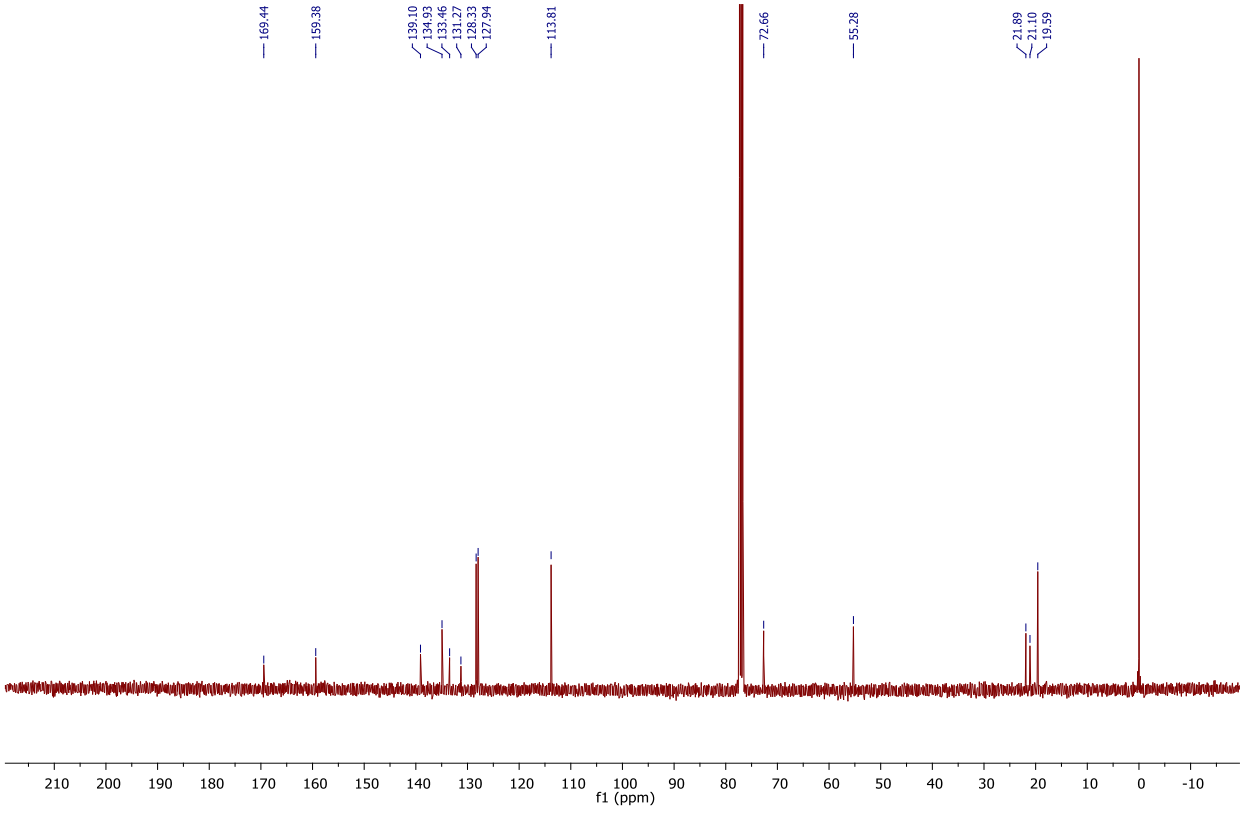


DEPT spectrum in $CDCl_3$.

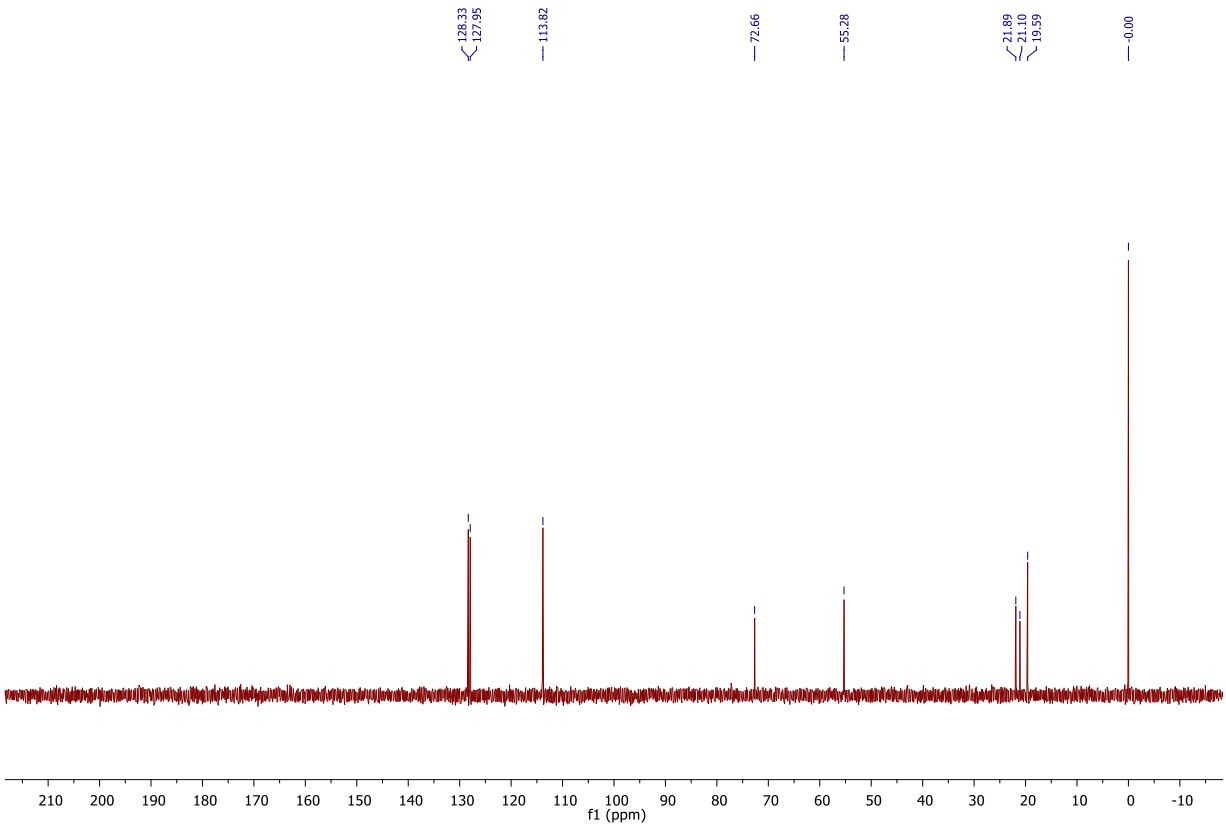
51c



^{1}H NMR spectrum in $CDCl_3$.

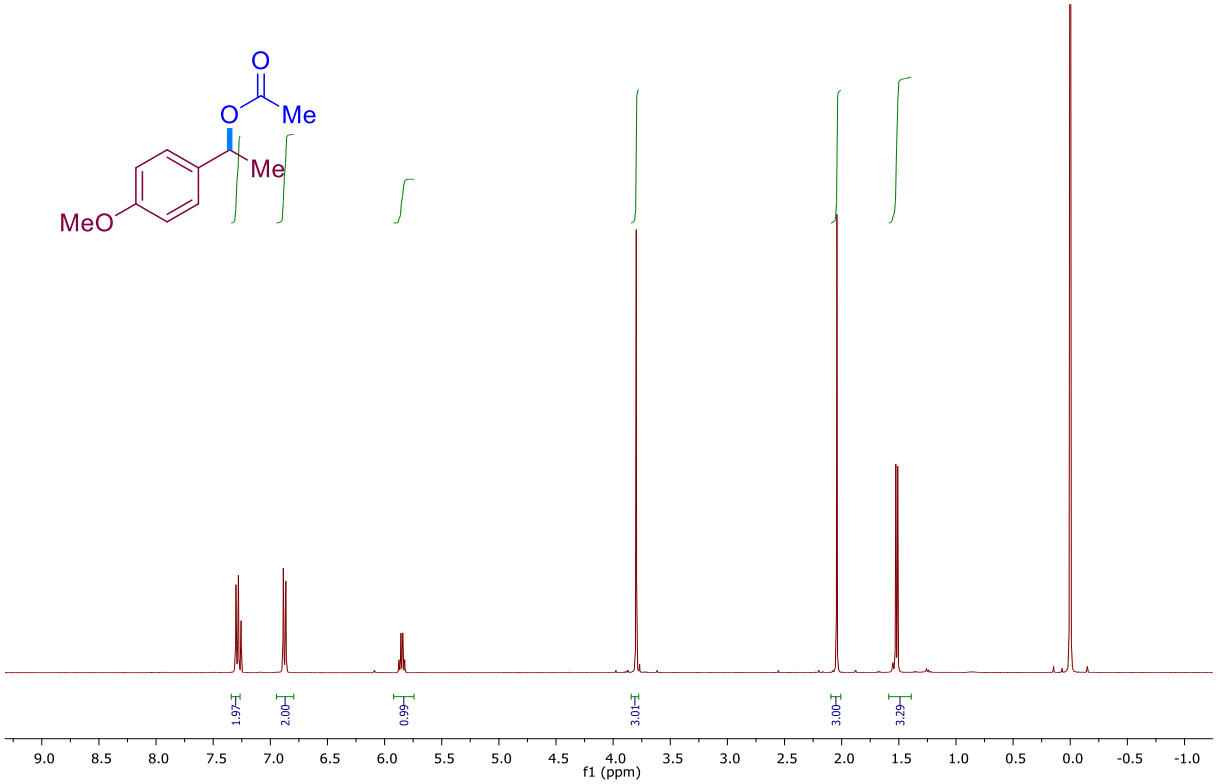


^{13}C NMR spectrum in $CDCl_3$

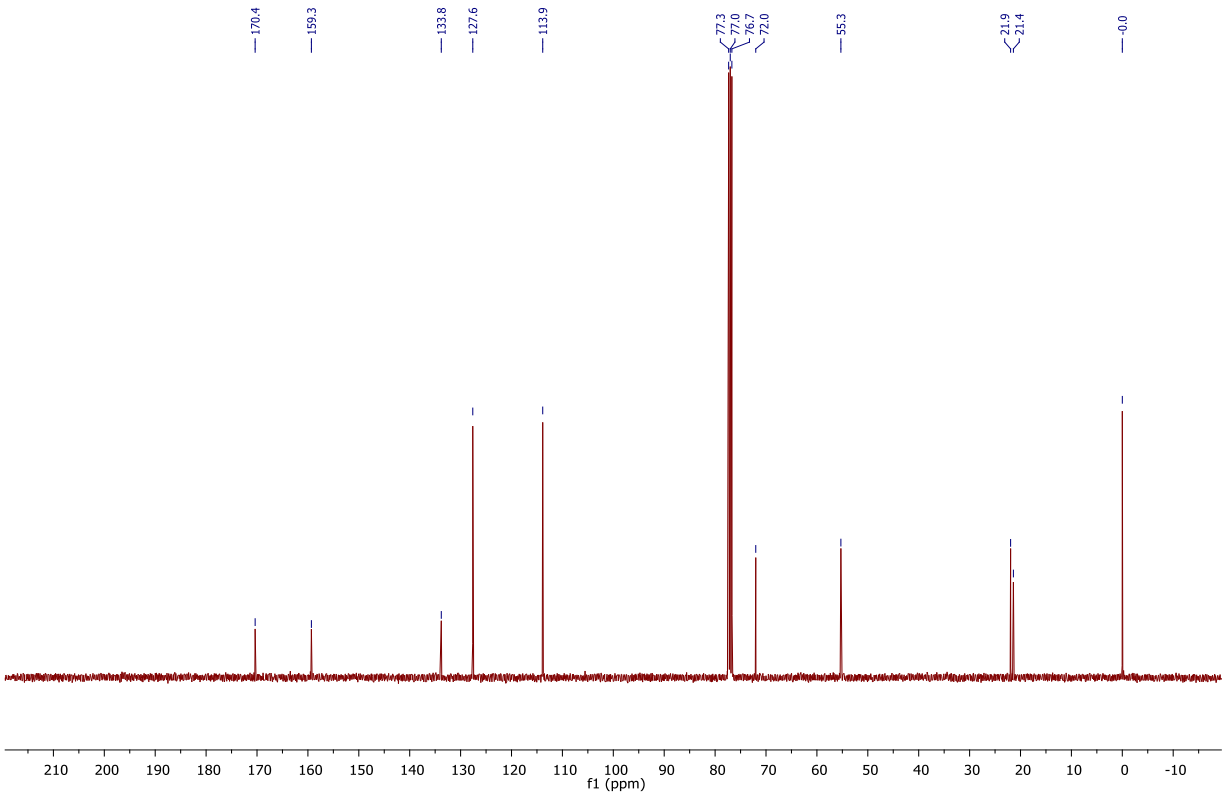


DEPT spectrum in $CDCl_3$.

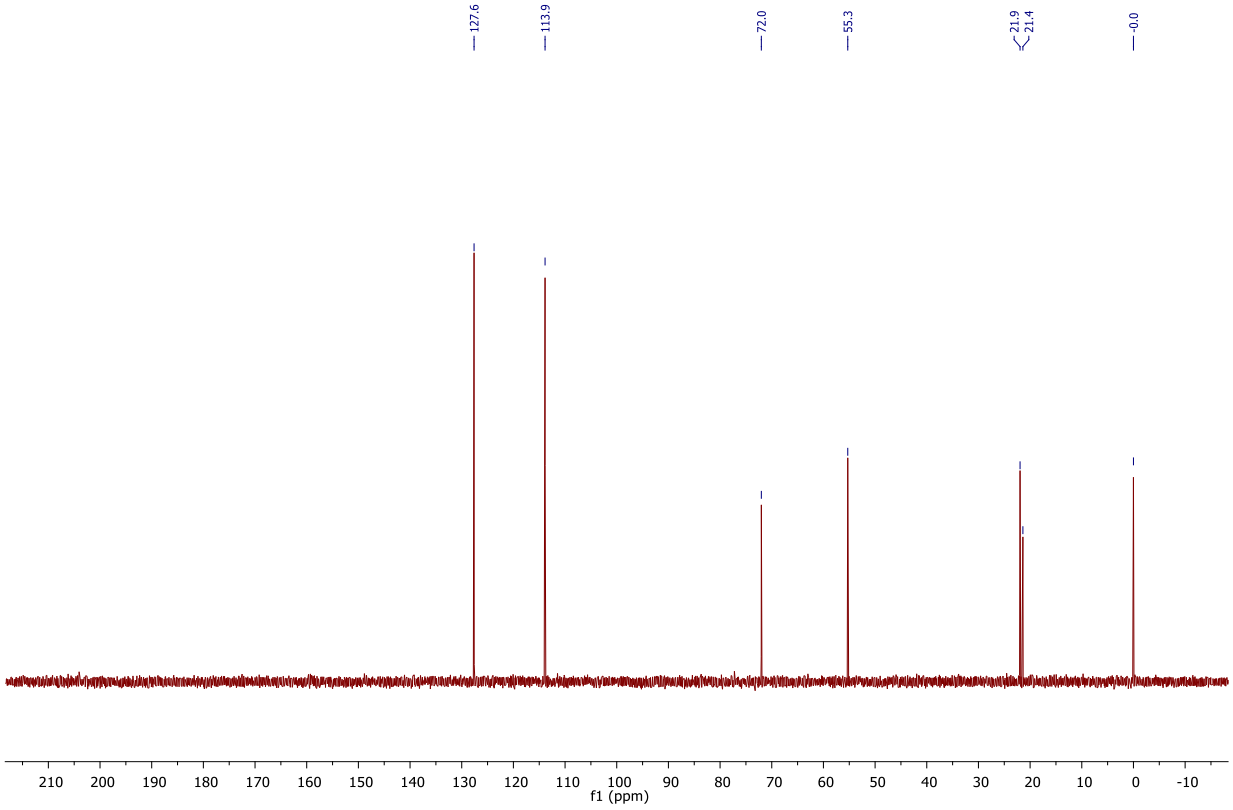
52c



^1H NMR spectrum in $CDCl_3$.

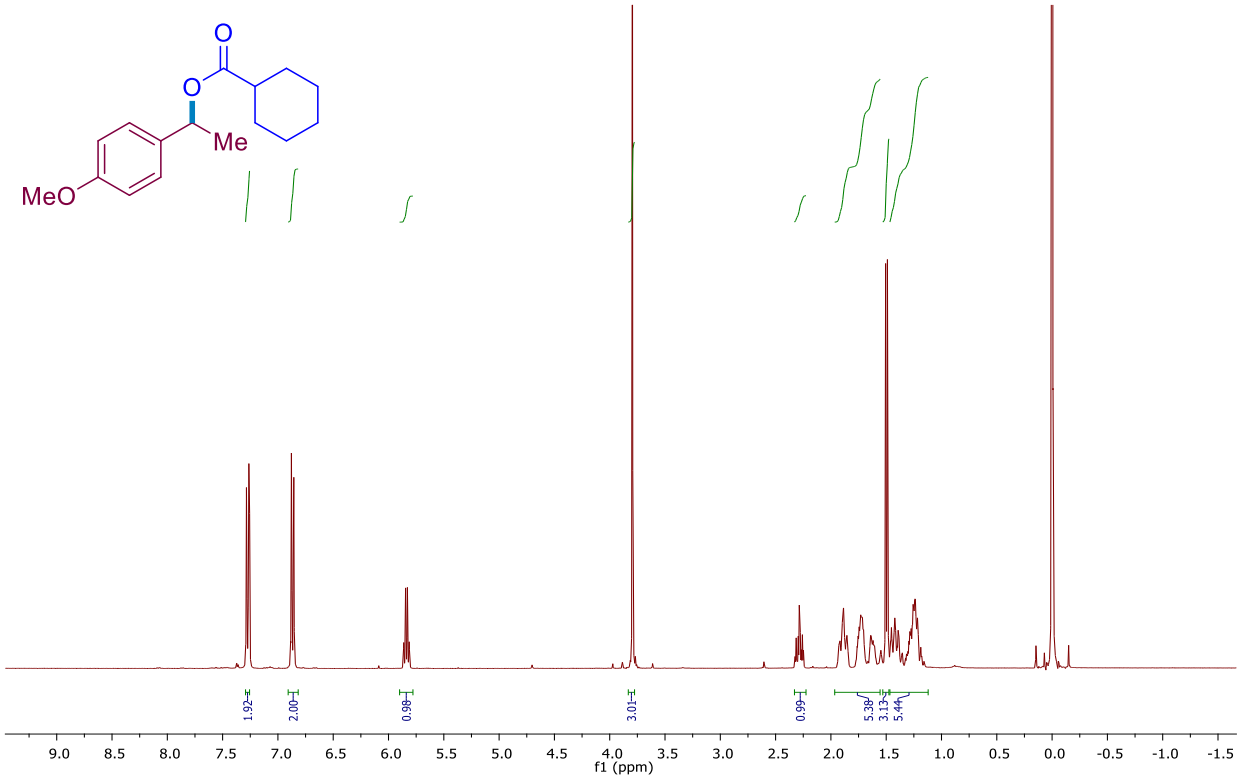


^{13}C NMR spectrum in $CDCl_3$

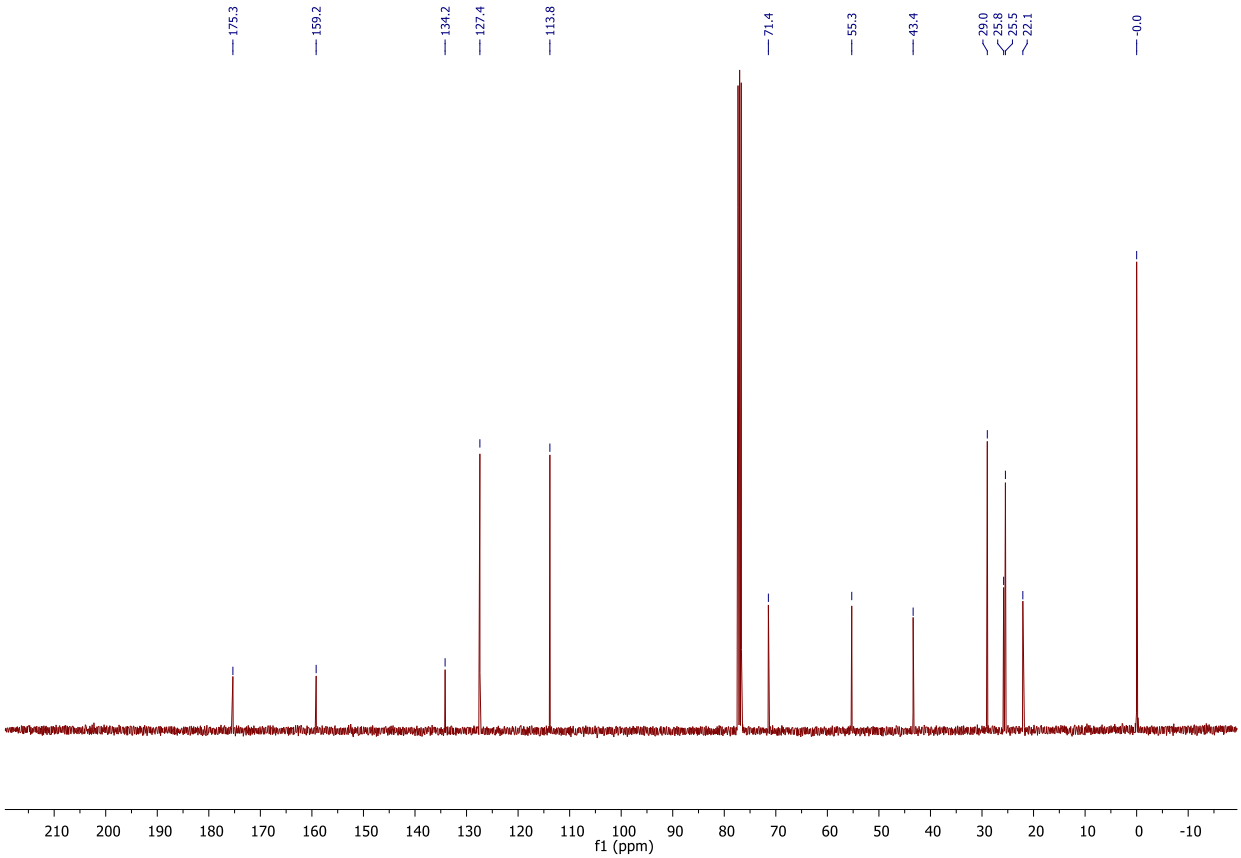


DEPT spectrum in $CDCl_3$.

53c

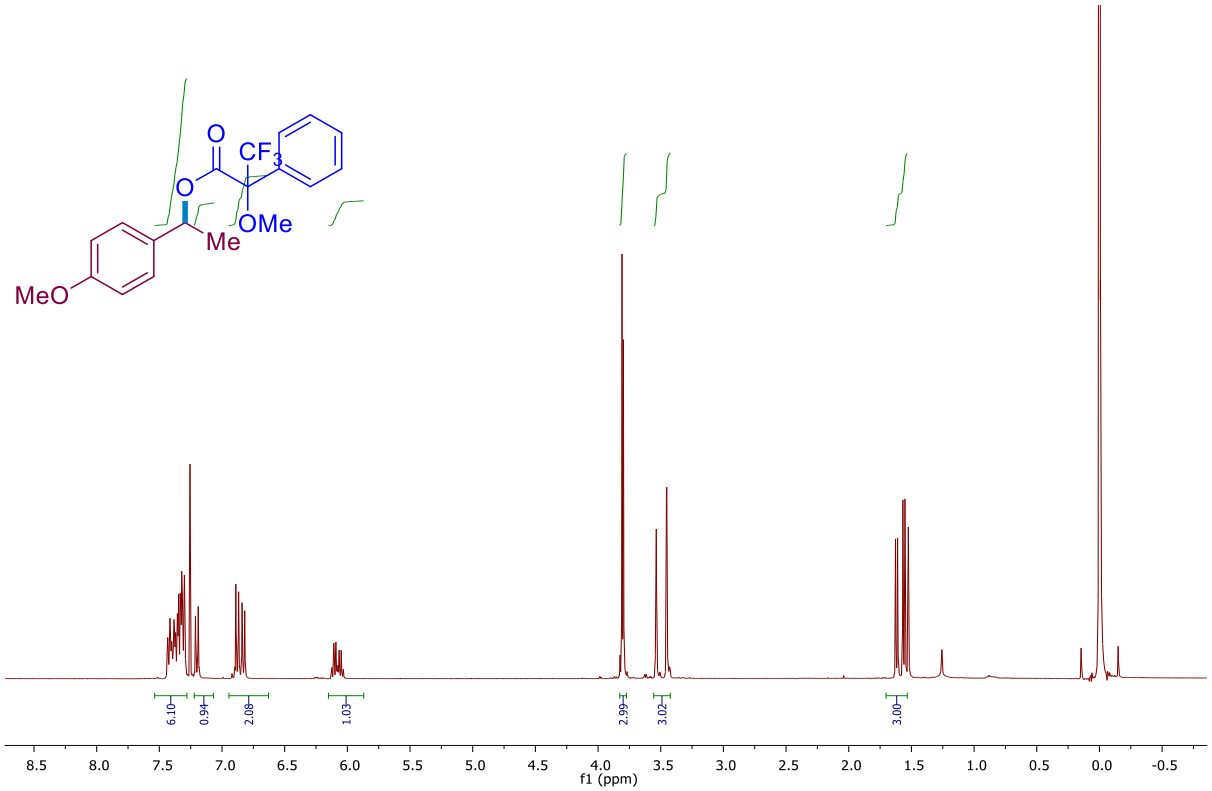


^{1}H NMR spectrum in $CDCl_3$.

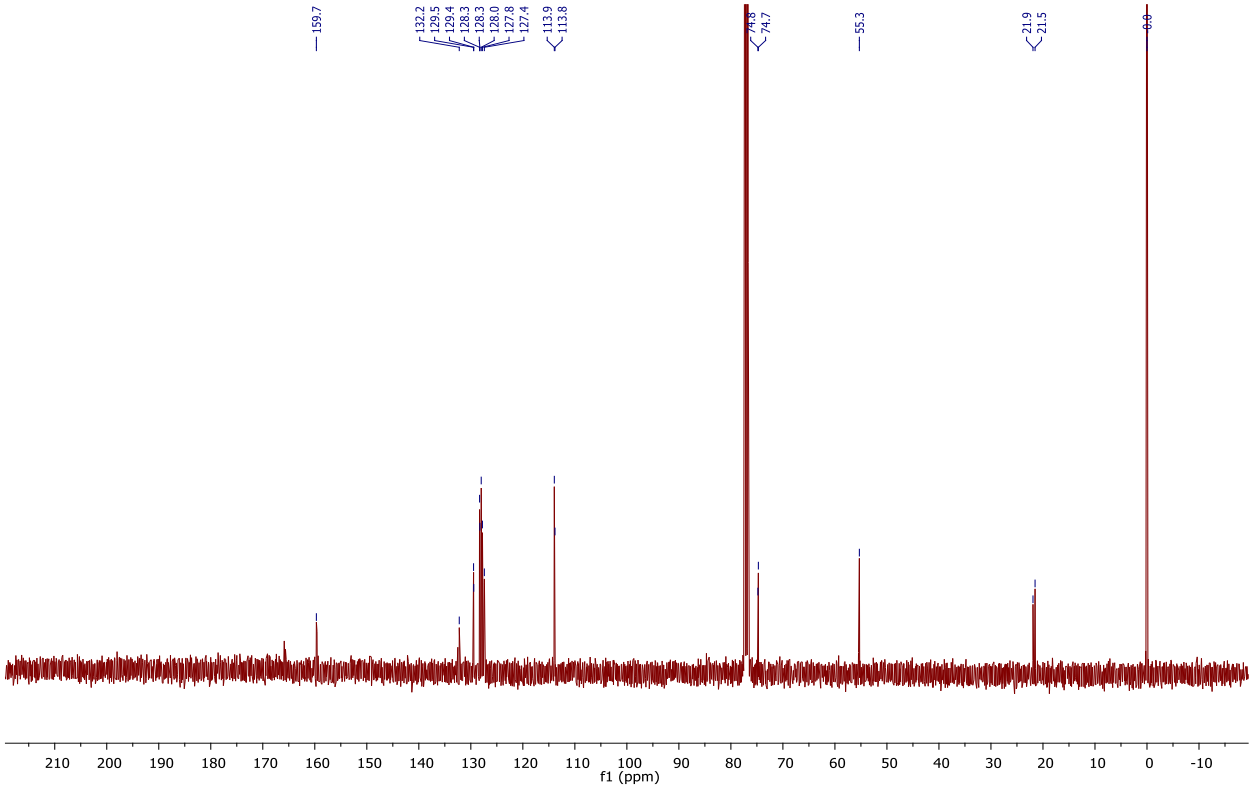


^{13}C NMR spectrum in $CDCl_3$

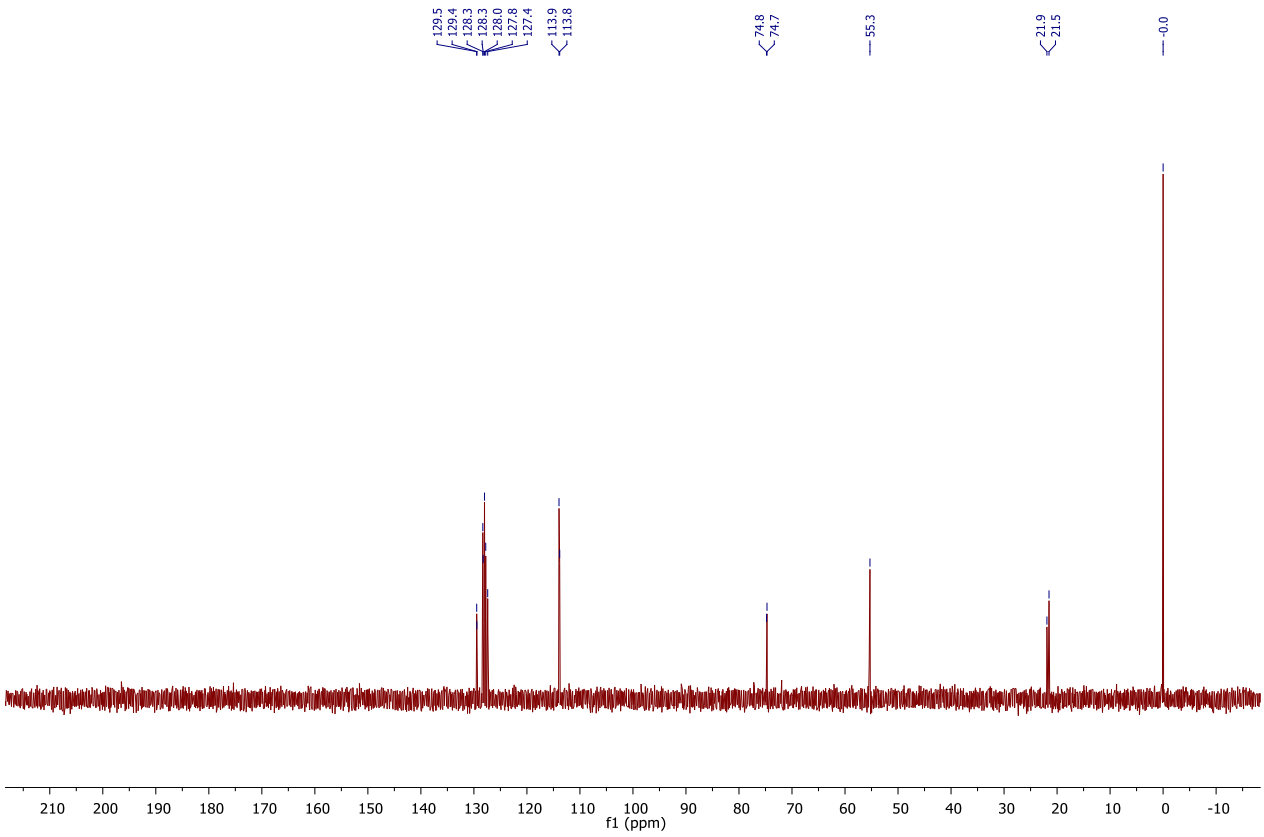
54c



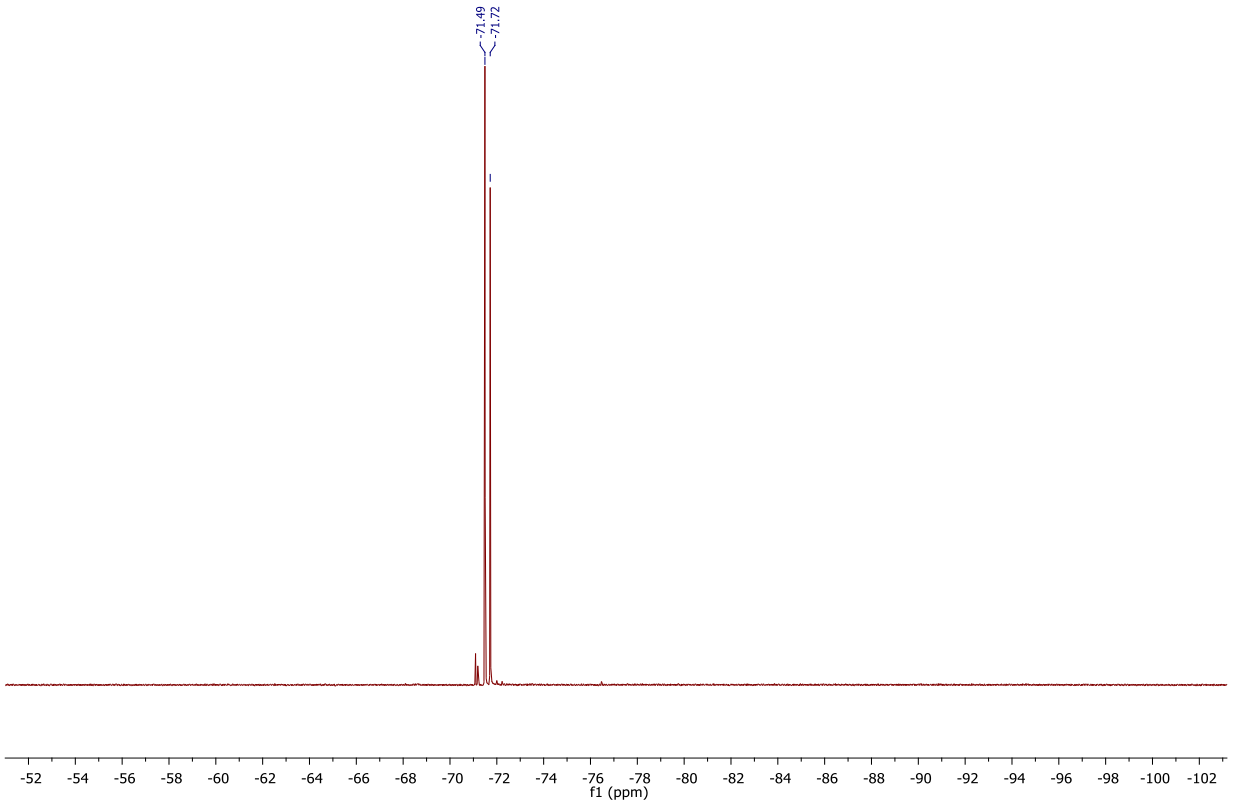
^{1}H NMR spectrum in $CDCl_3$.



^{13}C NMR spectrum in $CDCl_3$

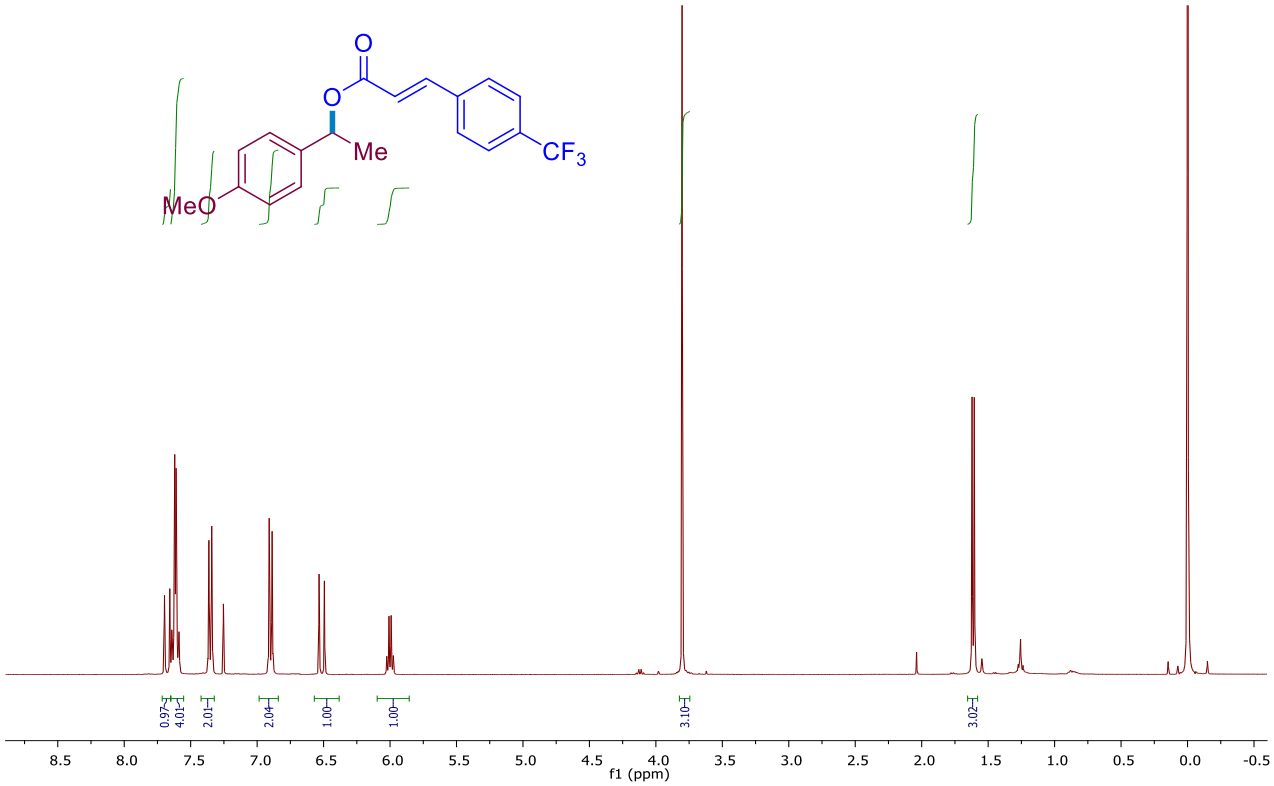


DEPT spectrum in $CDCl_3$.

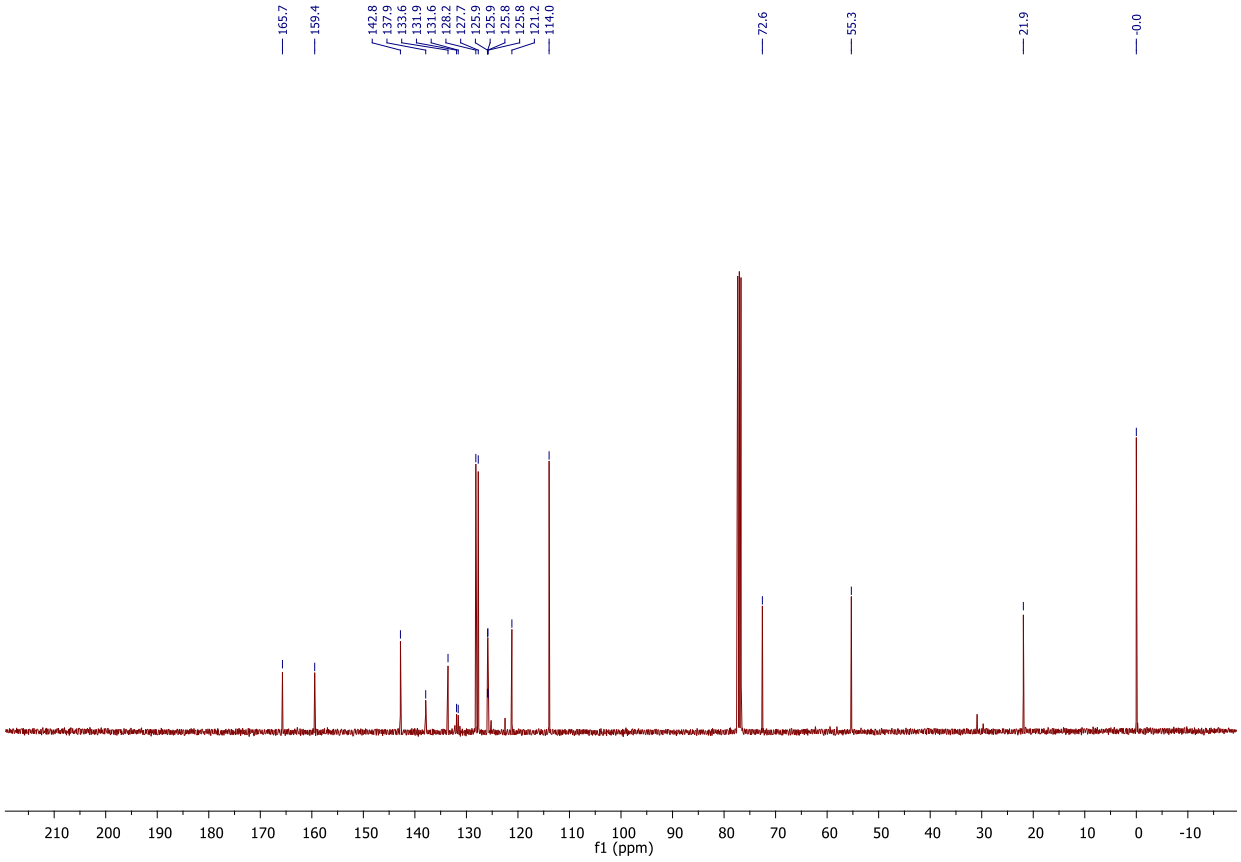


^{19}F NMR spectrum in $CDCl_3$

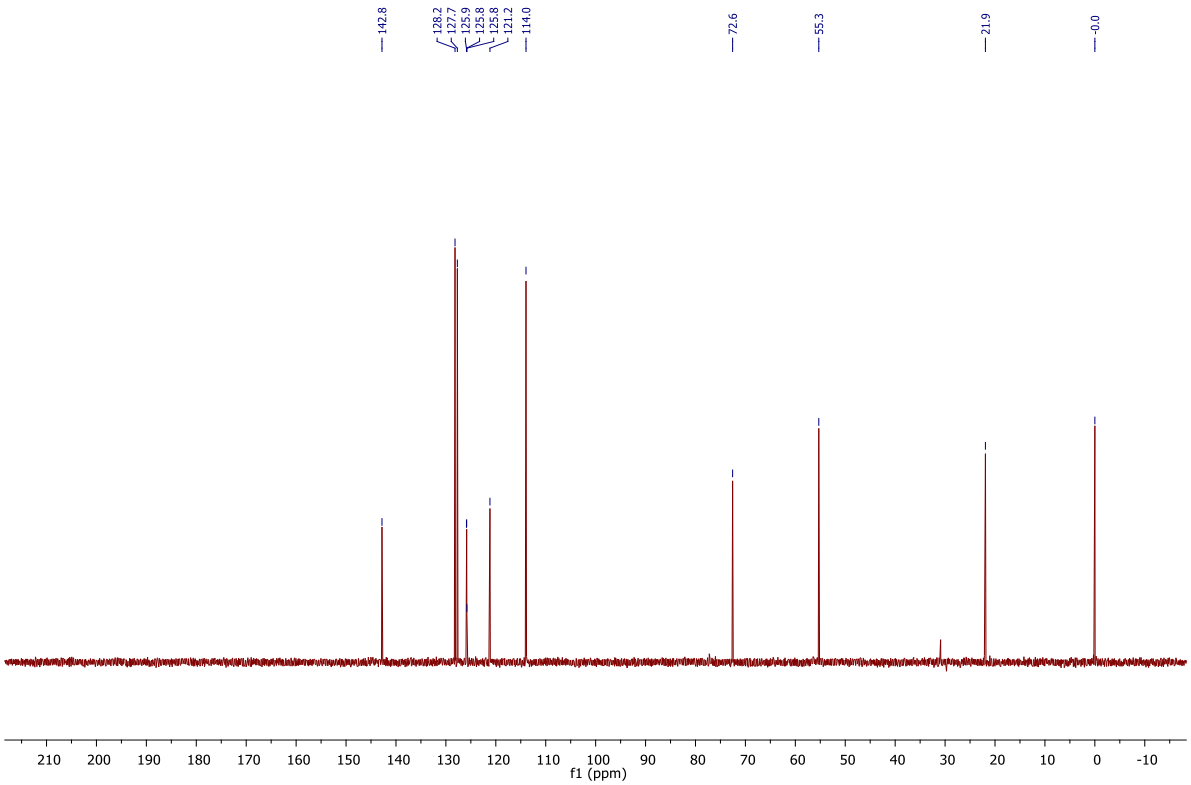
55c



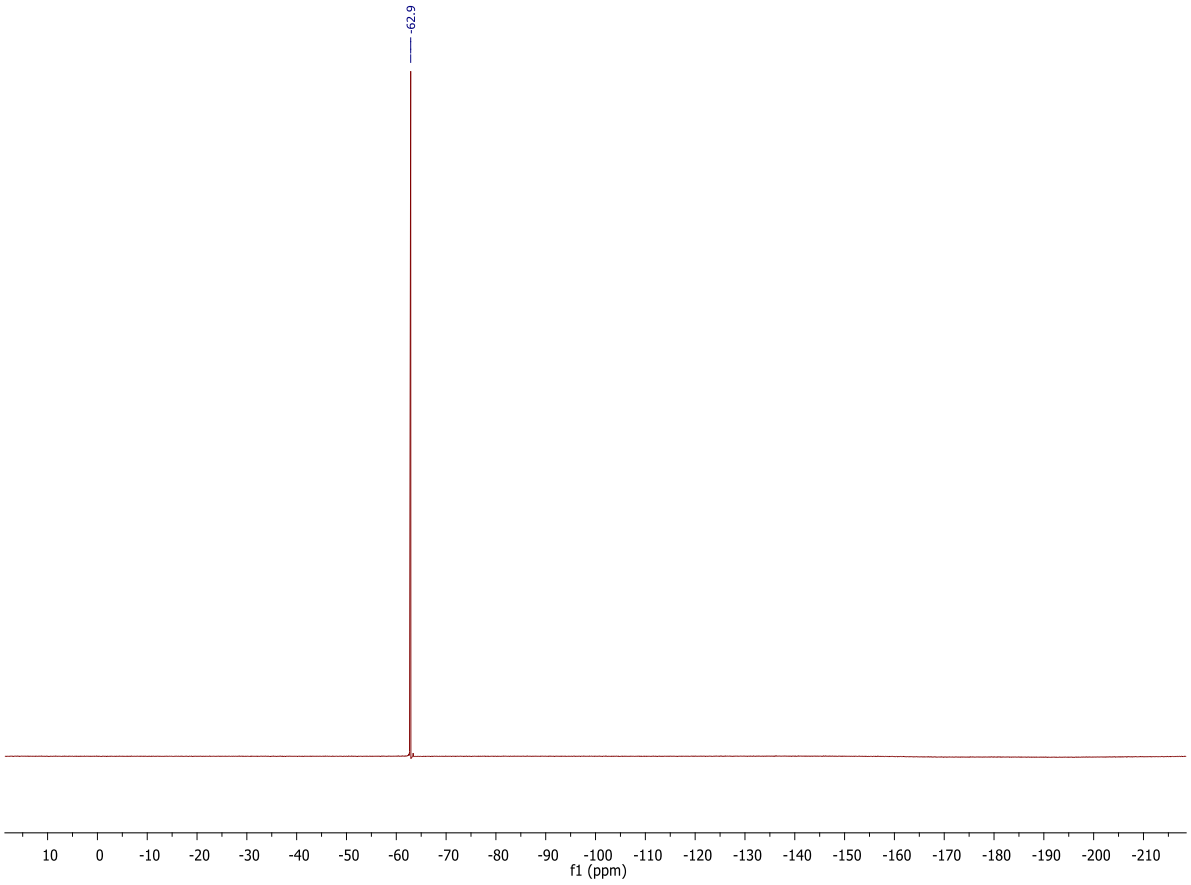
^{1}H NMR spectrum in $CDCl_3$.



^{13}C NMR spectrum in $CDCl_3$

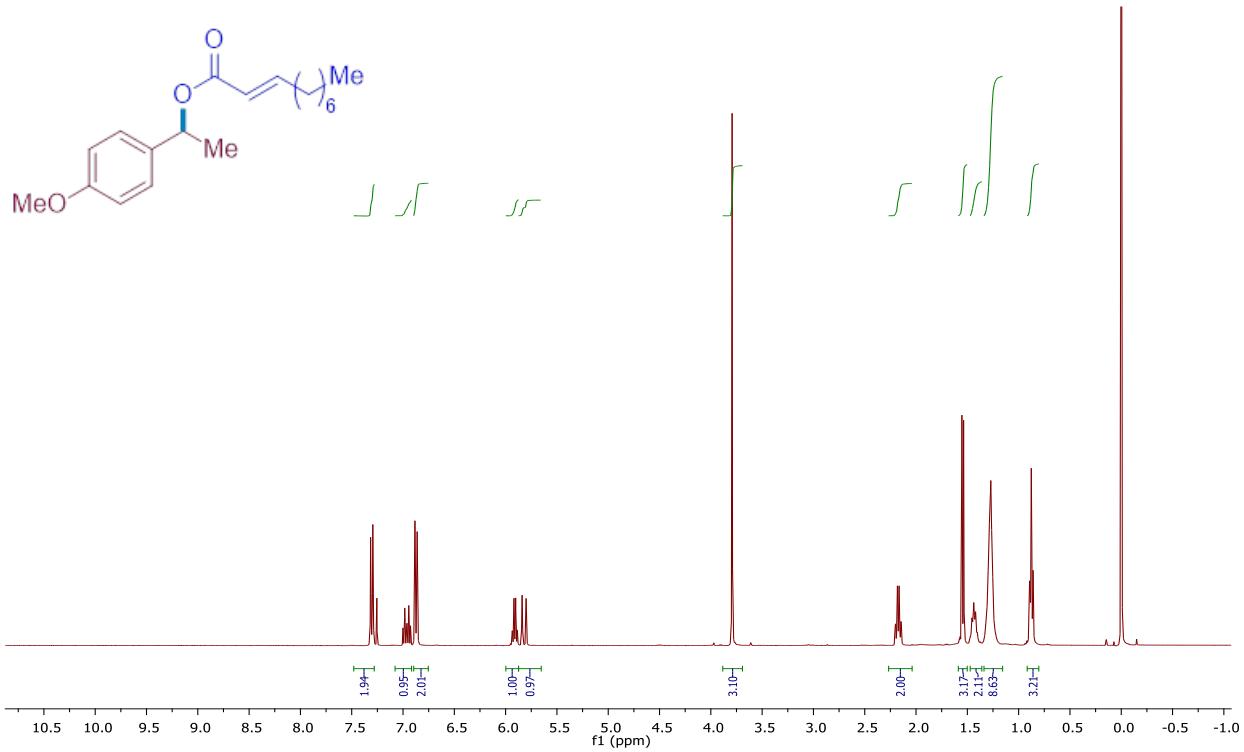


DEPT spectrum in $CDCl_3$.

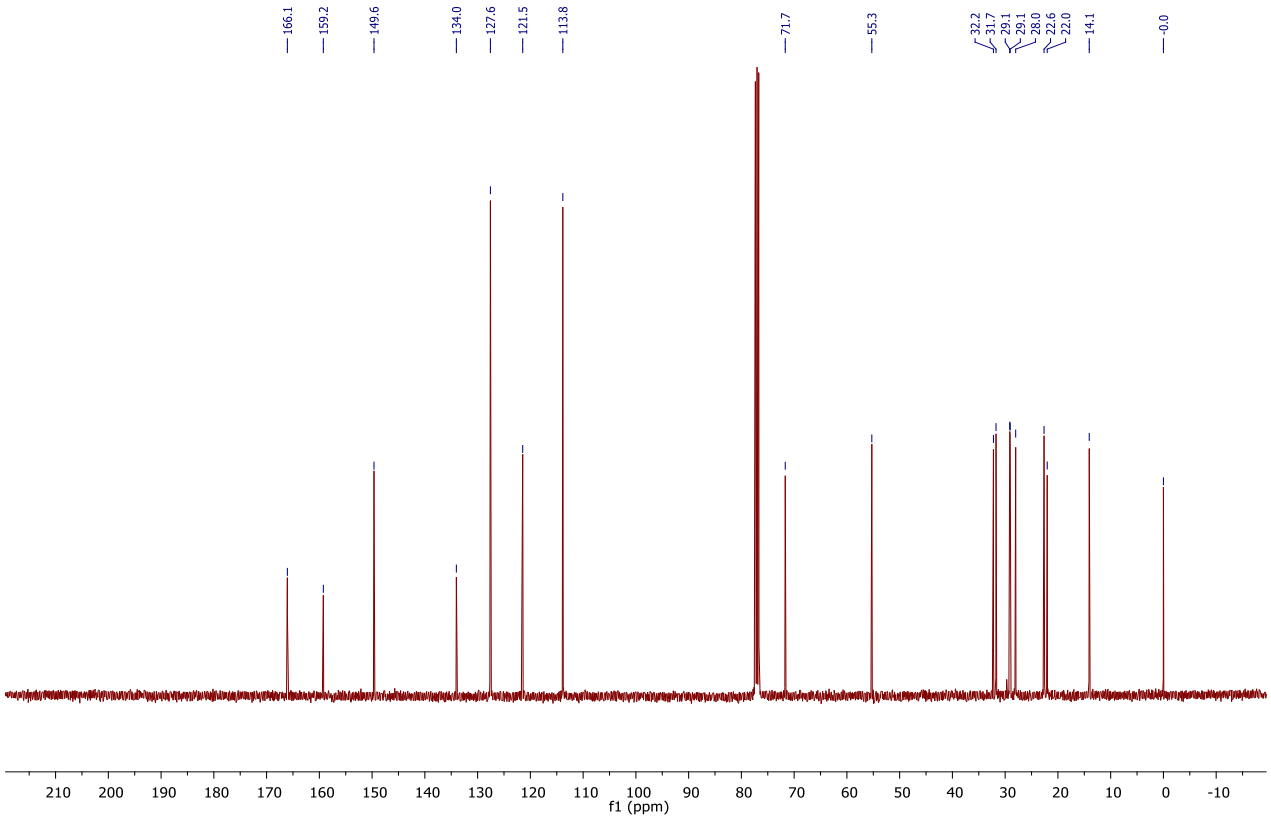


^{19}F NMR spectrum in $CDCl_3$

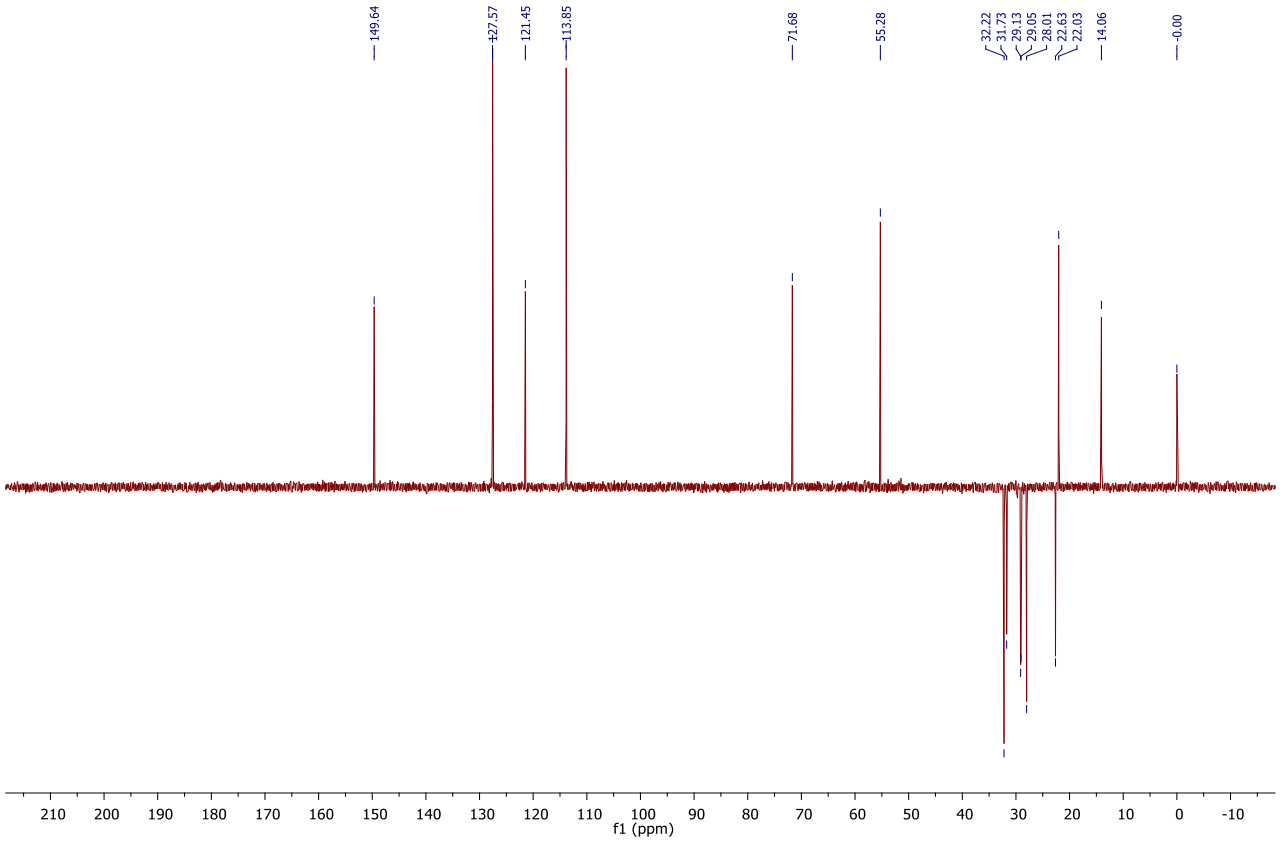
56c



^{1}H NMR spectrum in $CDCl_3$.

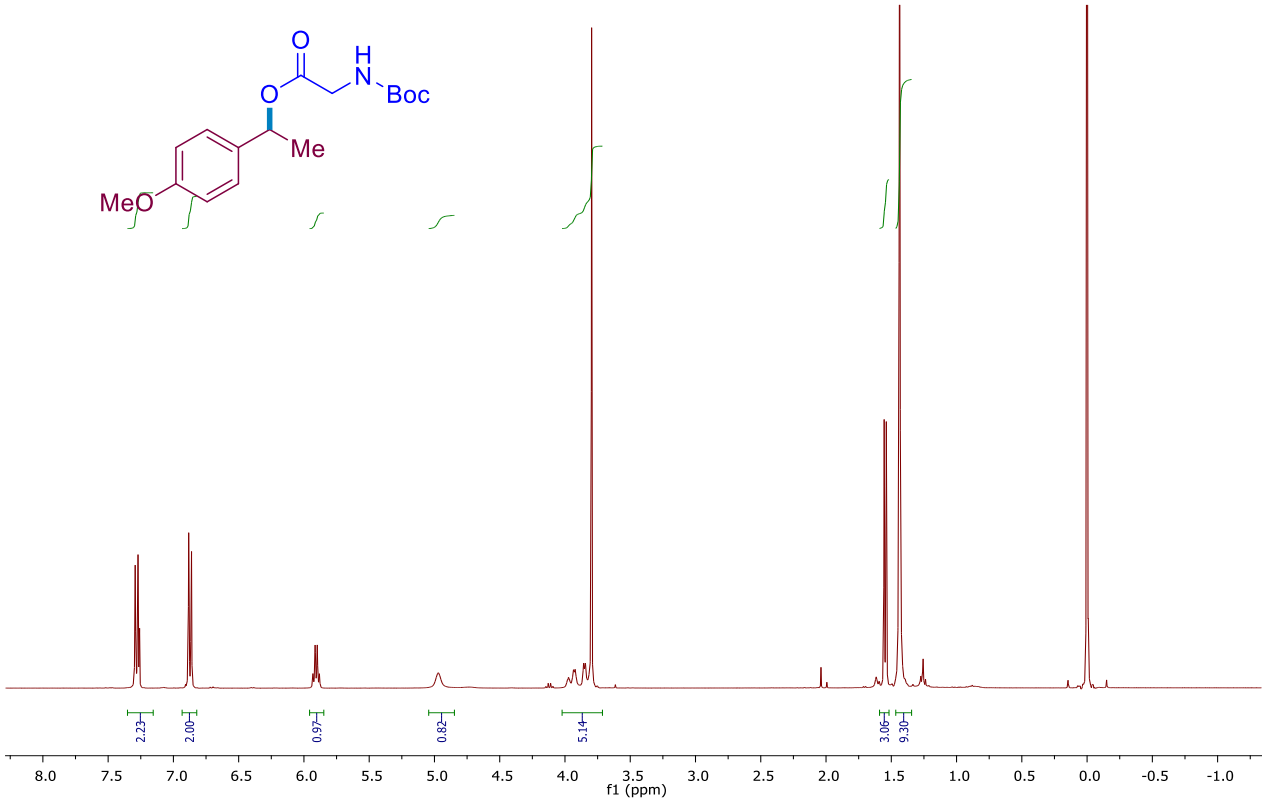


^{13}C NMR spectrum in $CDCl_3$

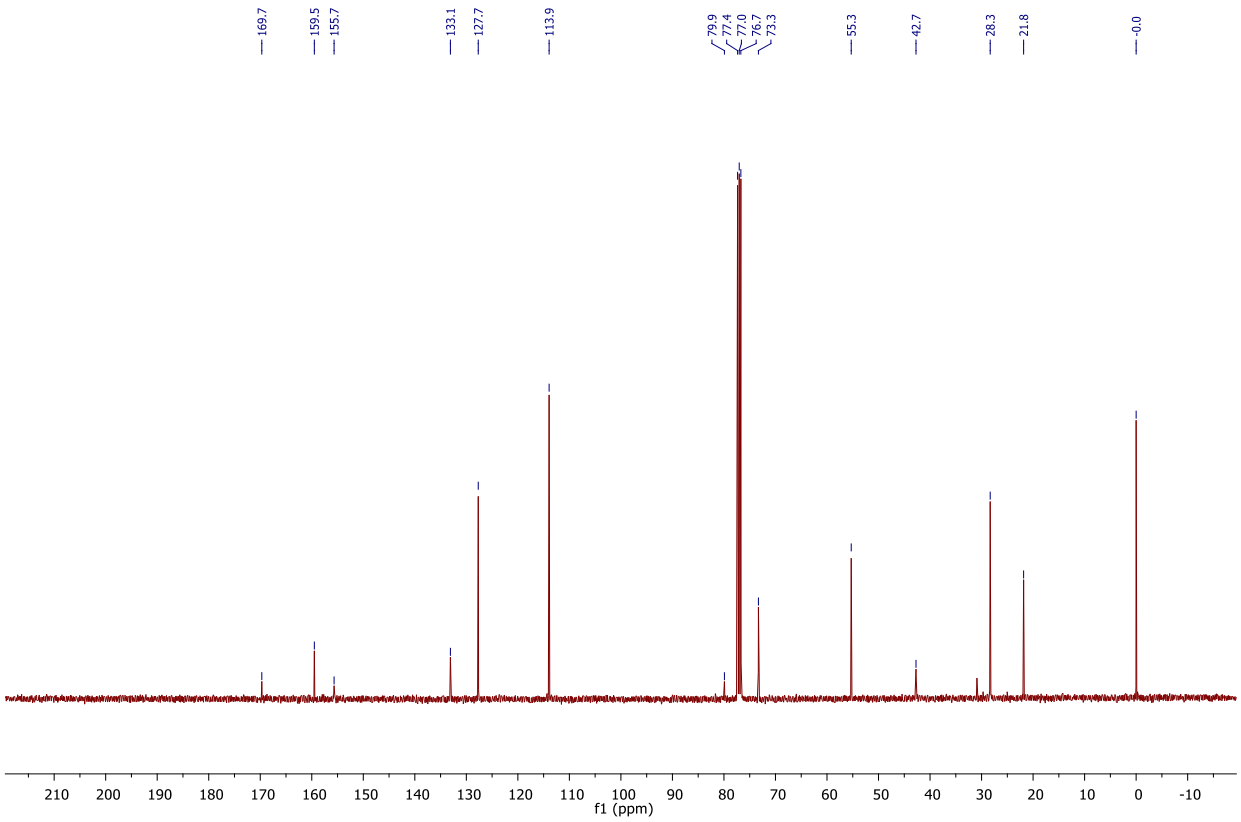


DEPT spectrum in $CDCl_3$.

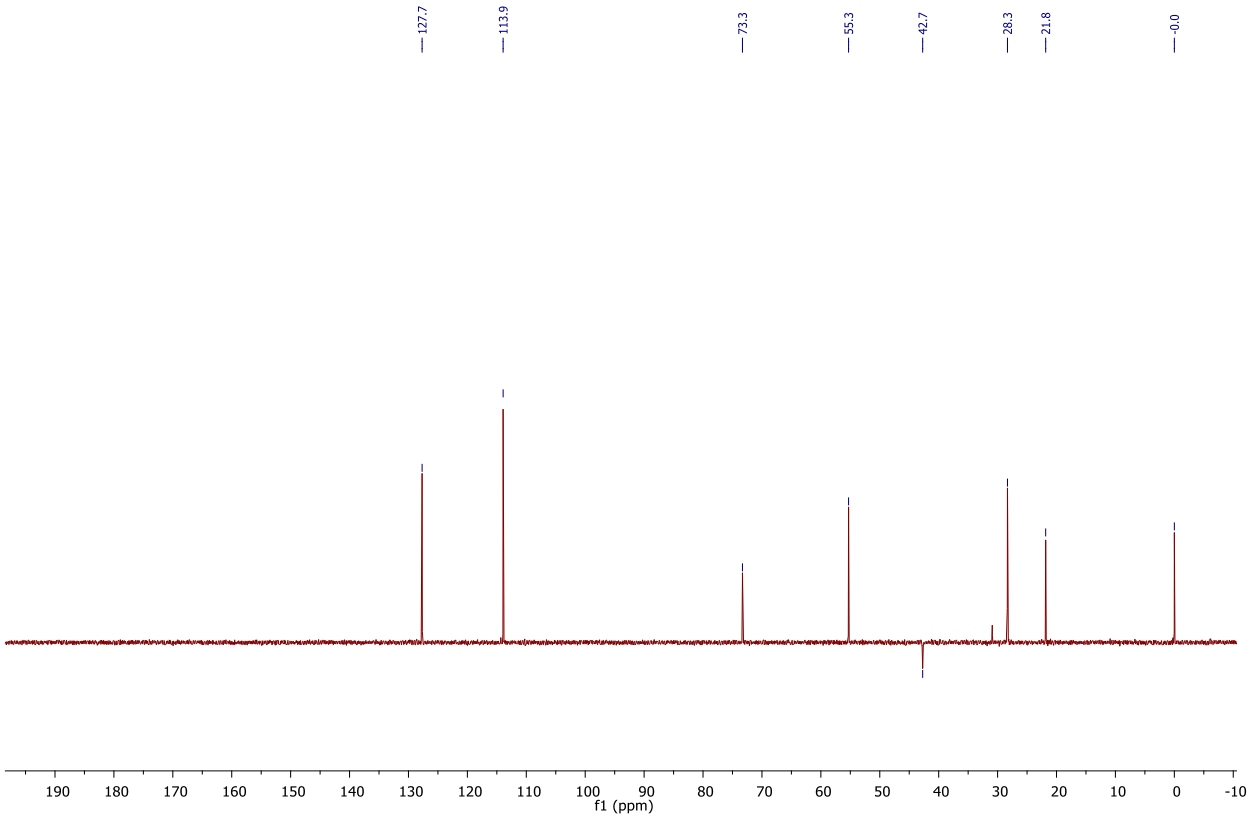
57c



^{1}H NMR spectrum in $CDCl_3$.

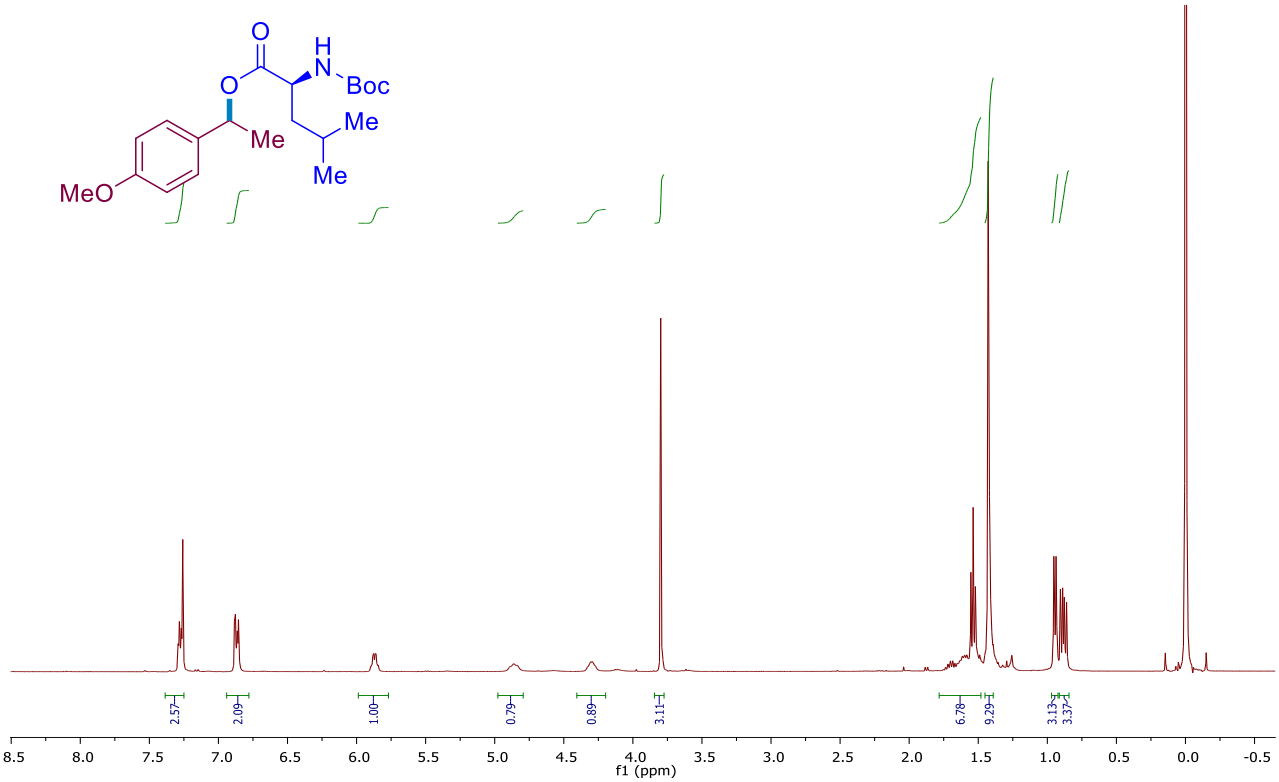


^{13}C NMR spectrum in $CDCl_3$

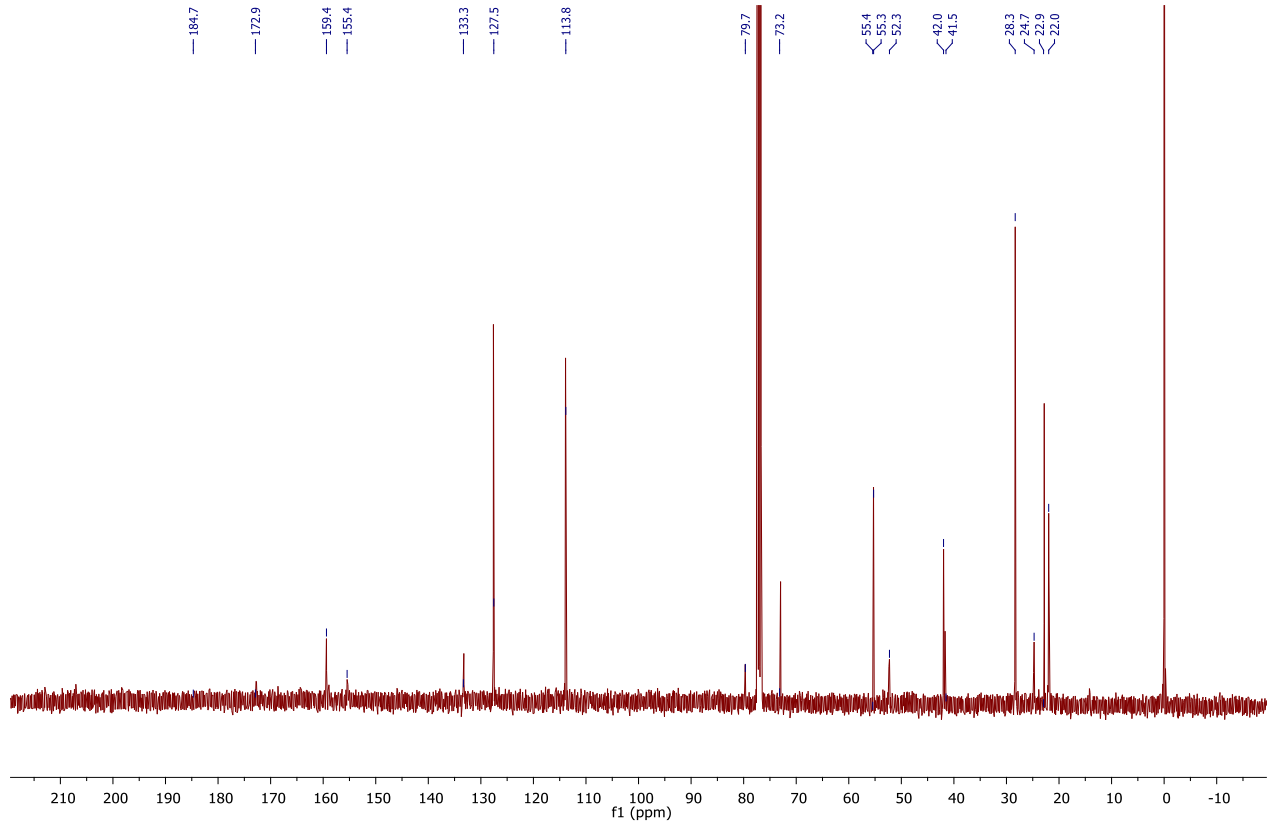


DEPT spectrum in $CDCl_3$.

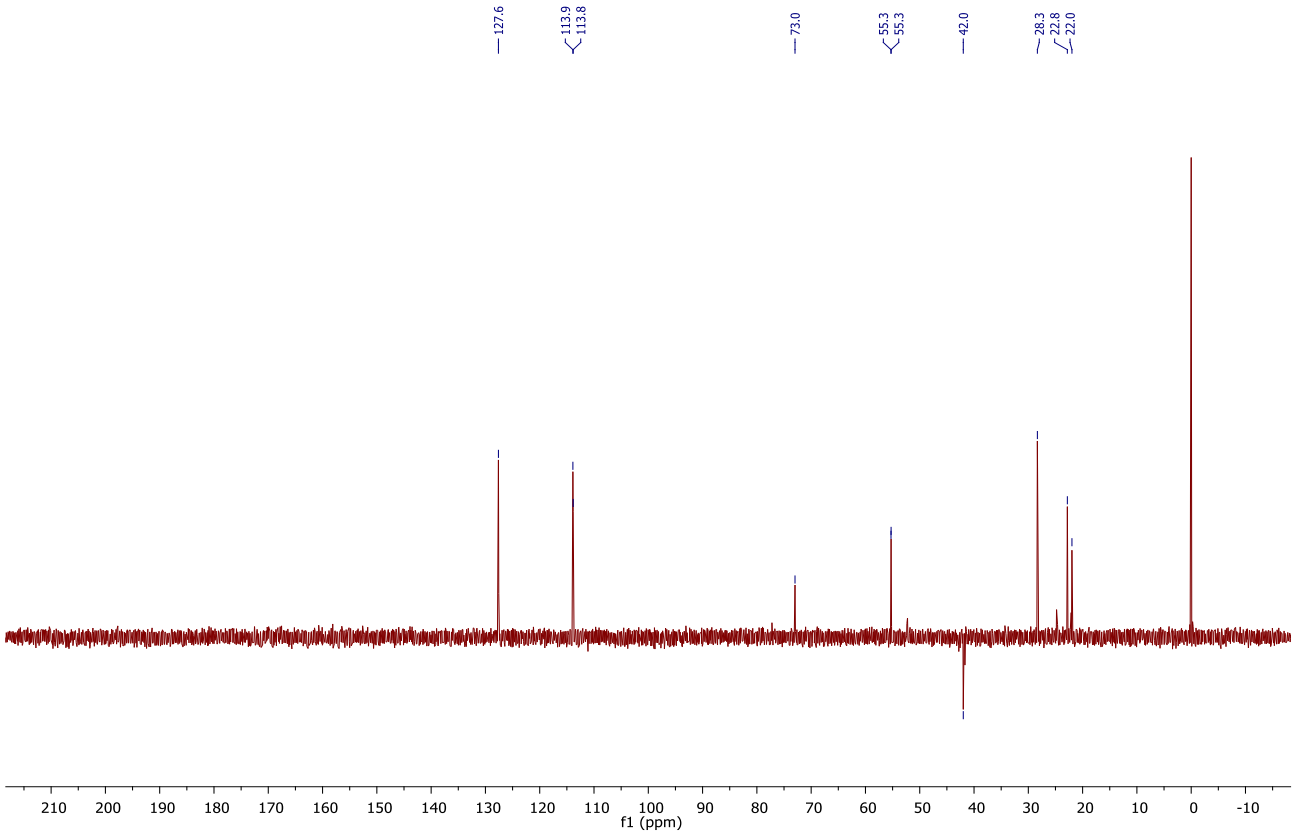
58c



^{1}H NMR spectrum in $CDCl_3$.

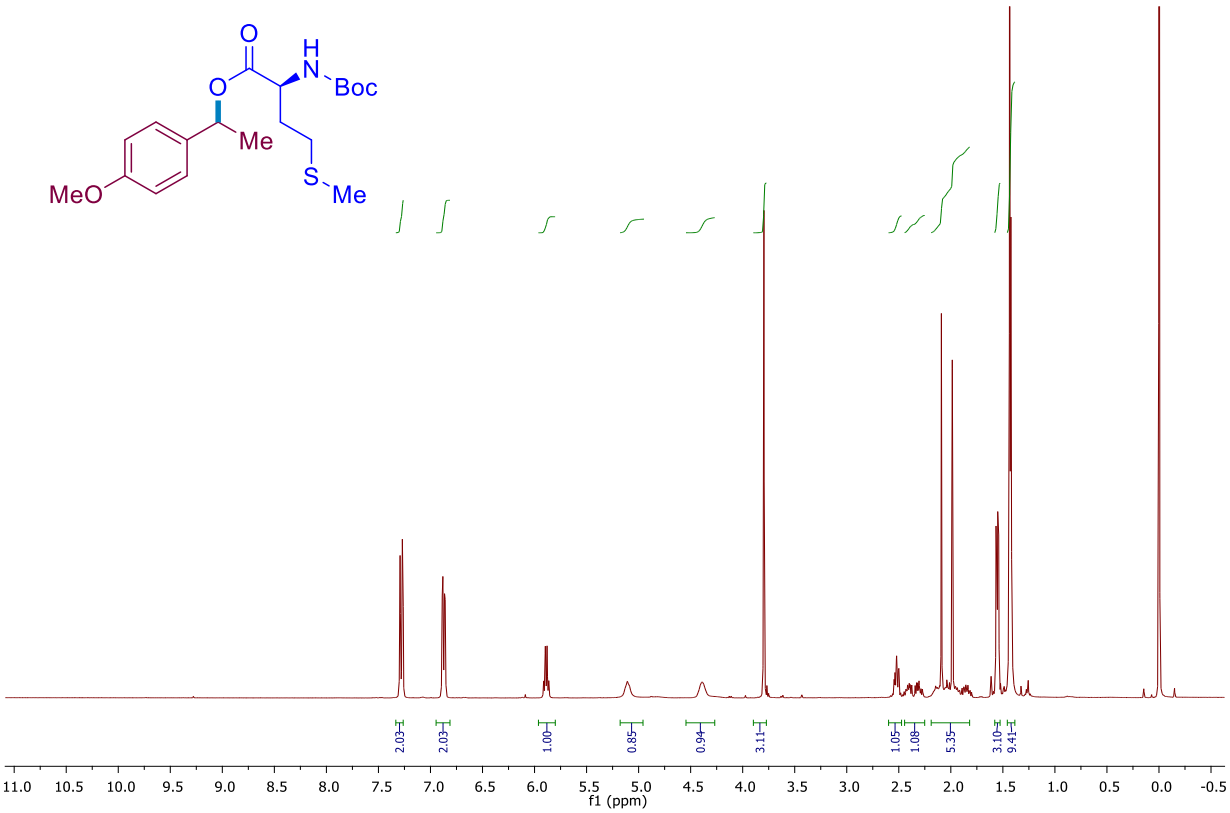


^{13}C NMR spectrum in $CDCl_3$

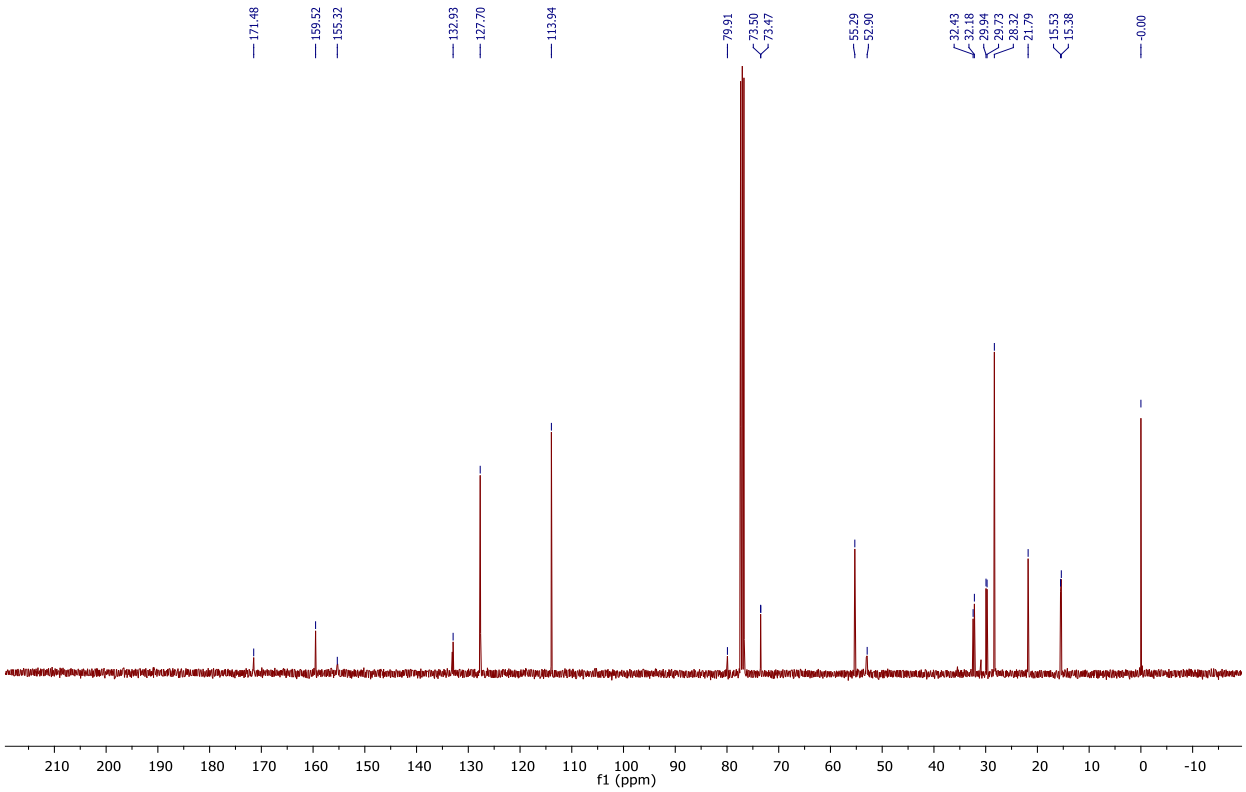


DEPT spectrum in $CDCl_3$.

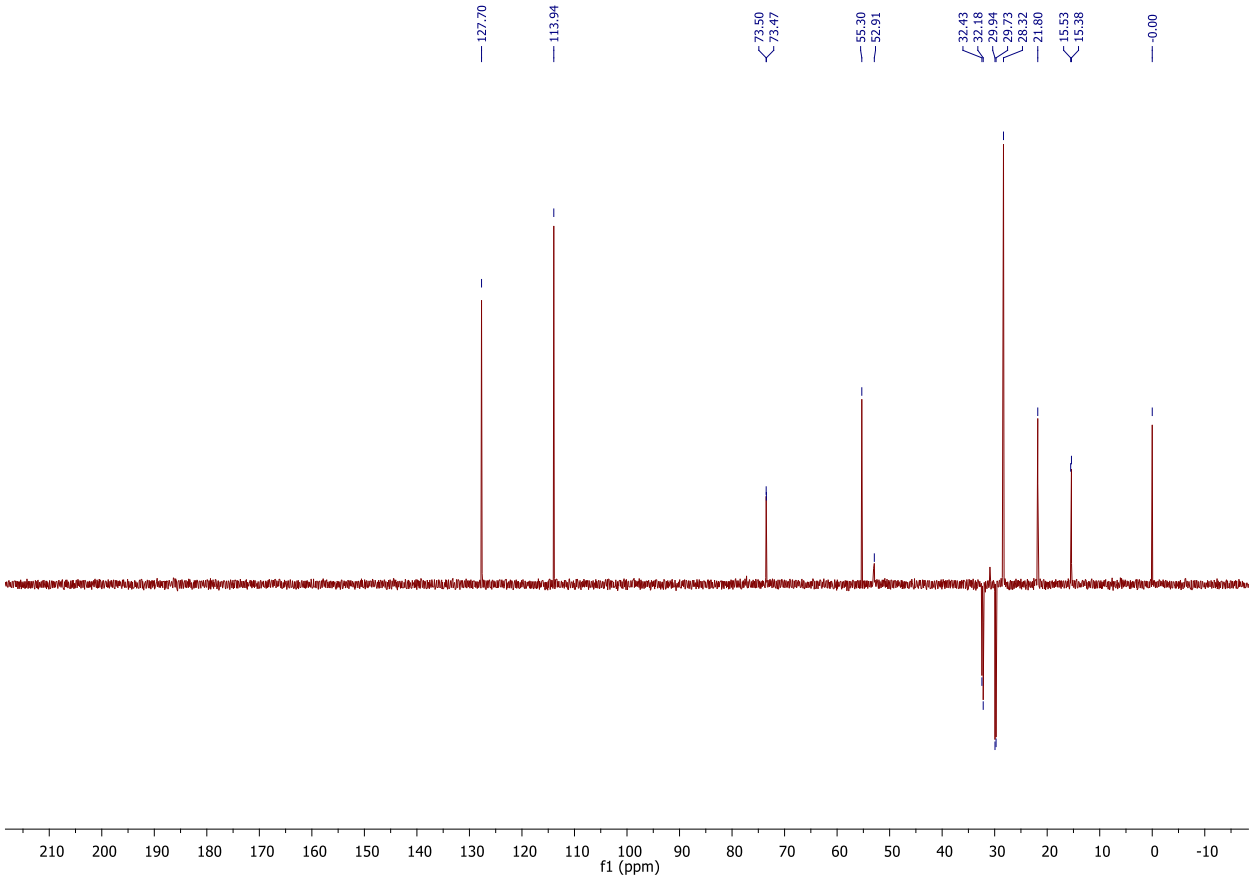
59c



^{1}H NMR spectrum in $CDCl_3$.

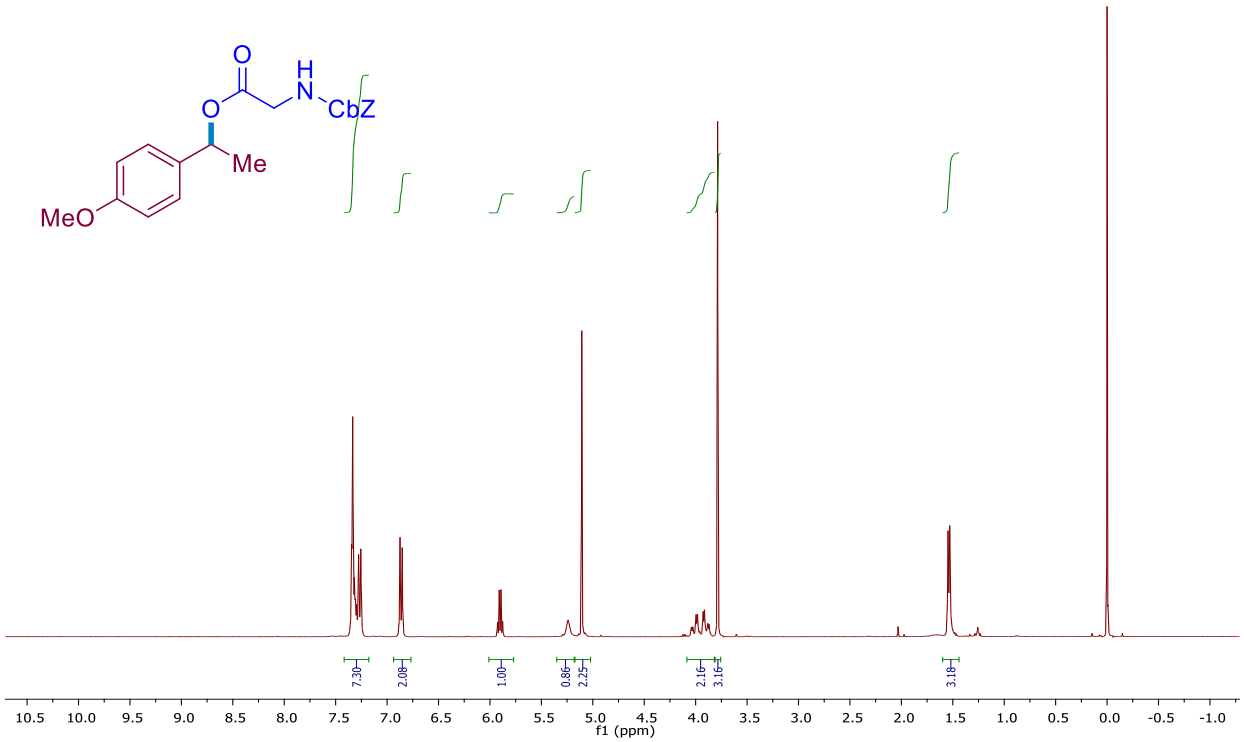


^{13}C NMR spectrum in $CDCl_3$

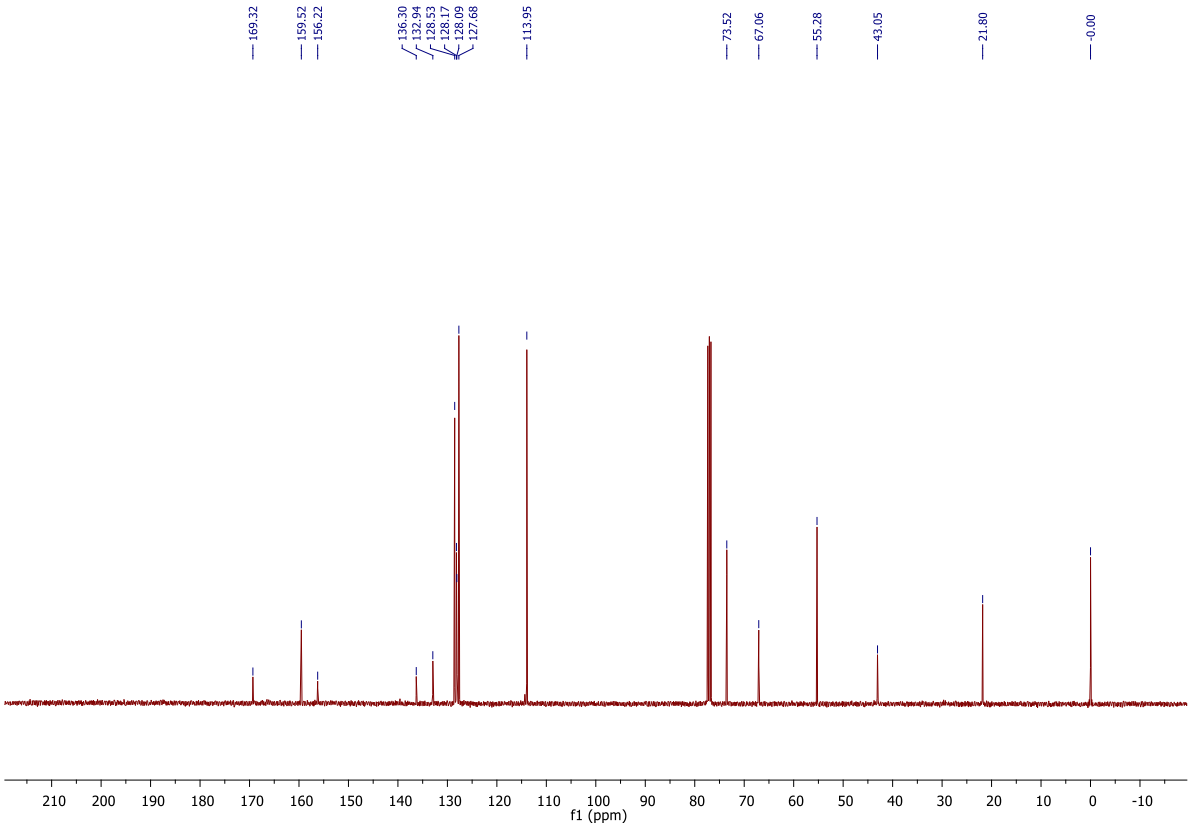


DEPT spectrum in $CDCl_3$.

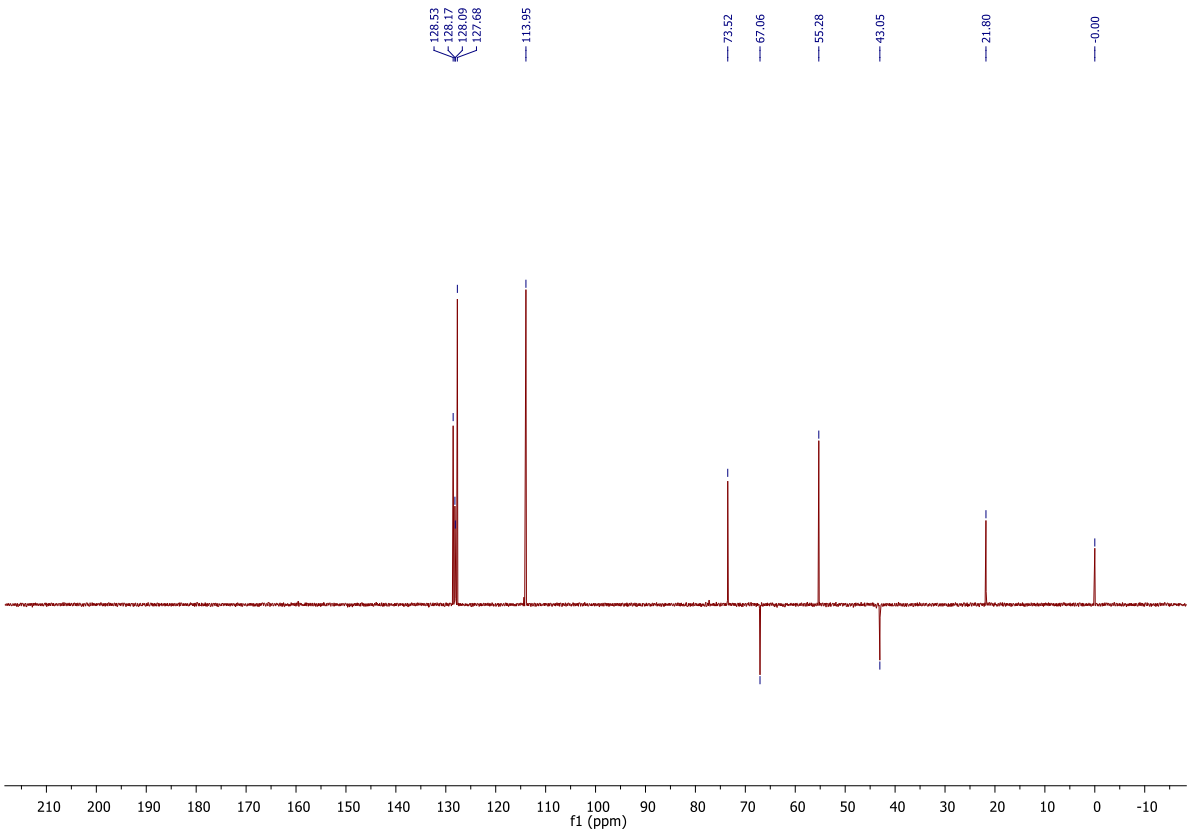
60c



^{1}H NMR spectrum in $CDCl_3$.

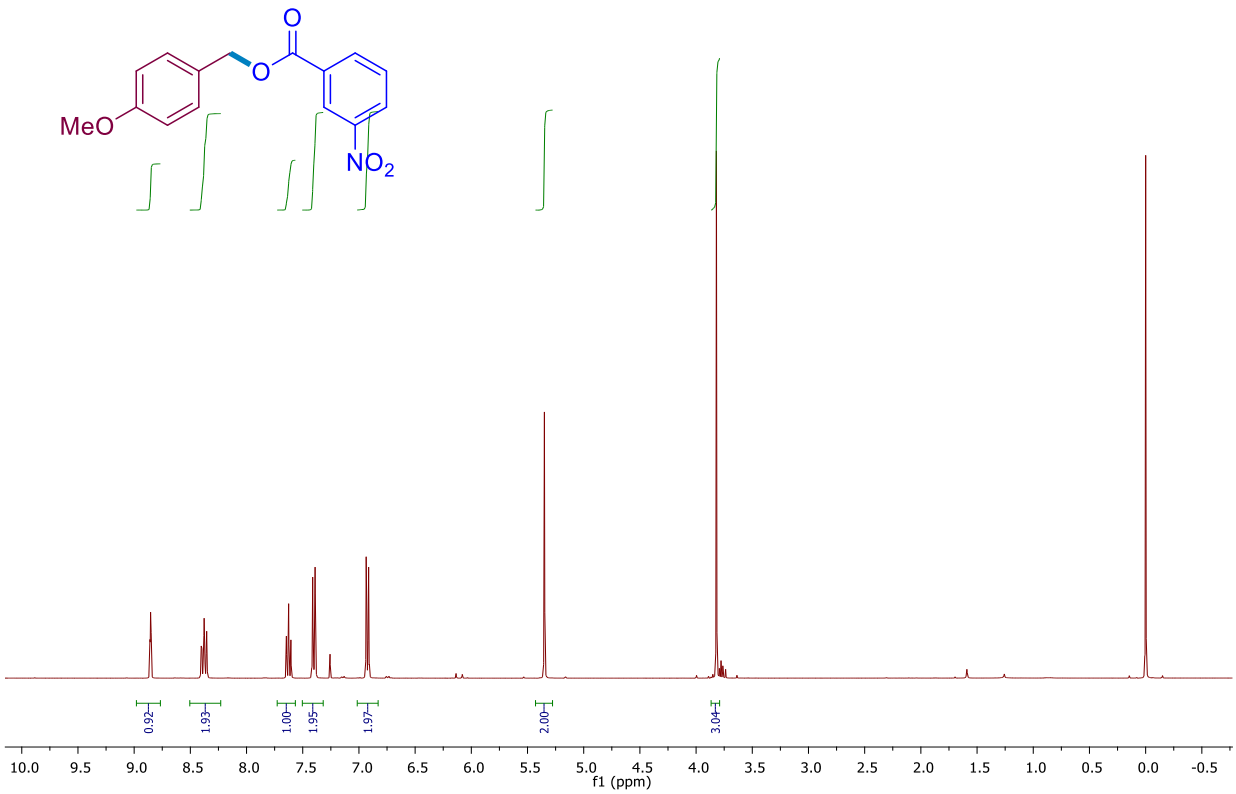


^{13}C NMR spectrum in $CDCl_3$

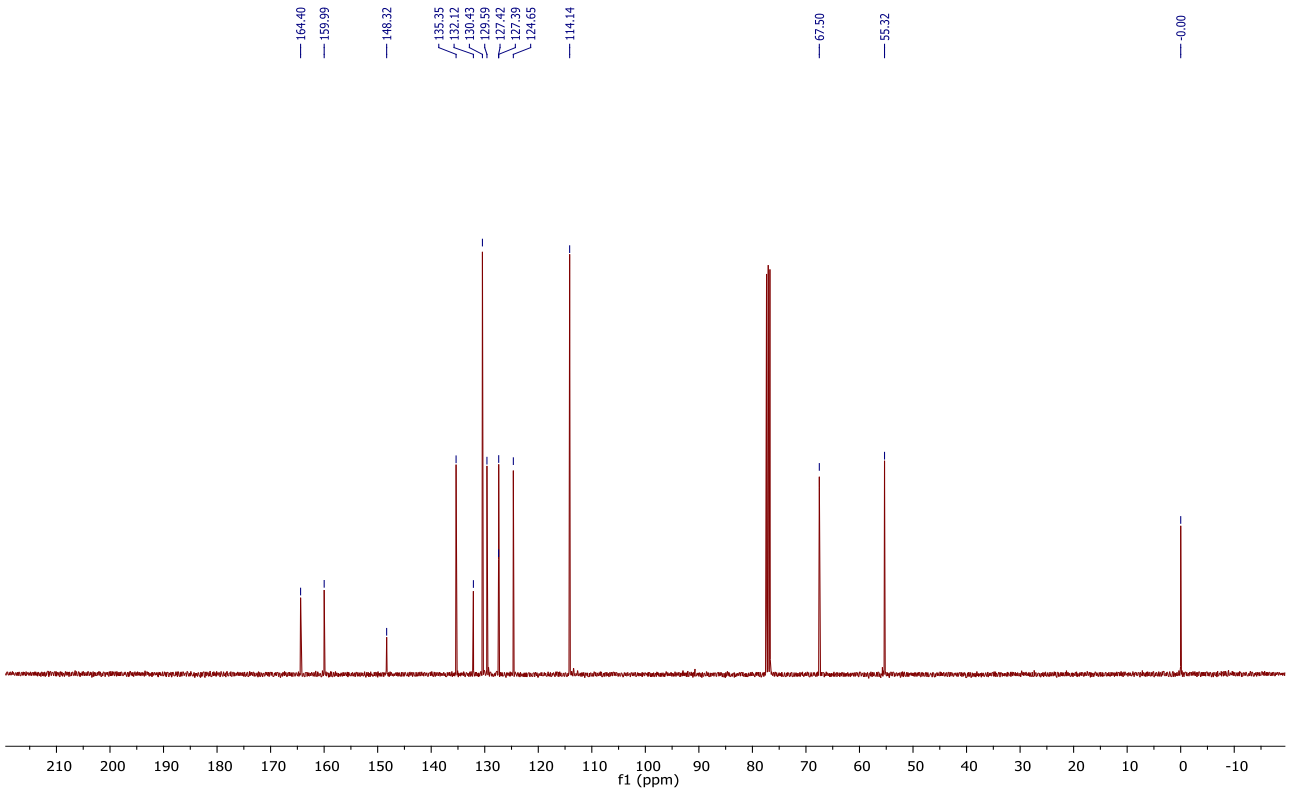


DEPT spectrum in $CDCl_3$.

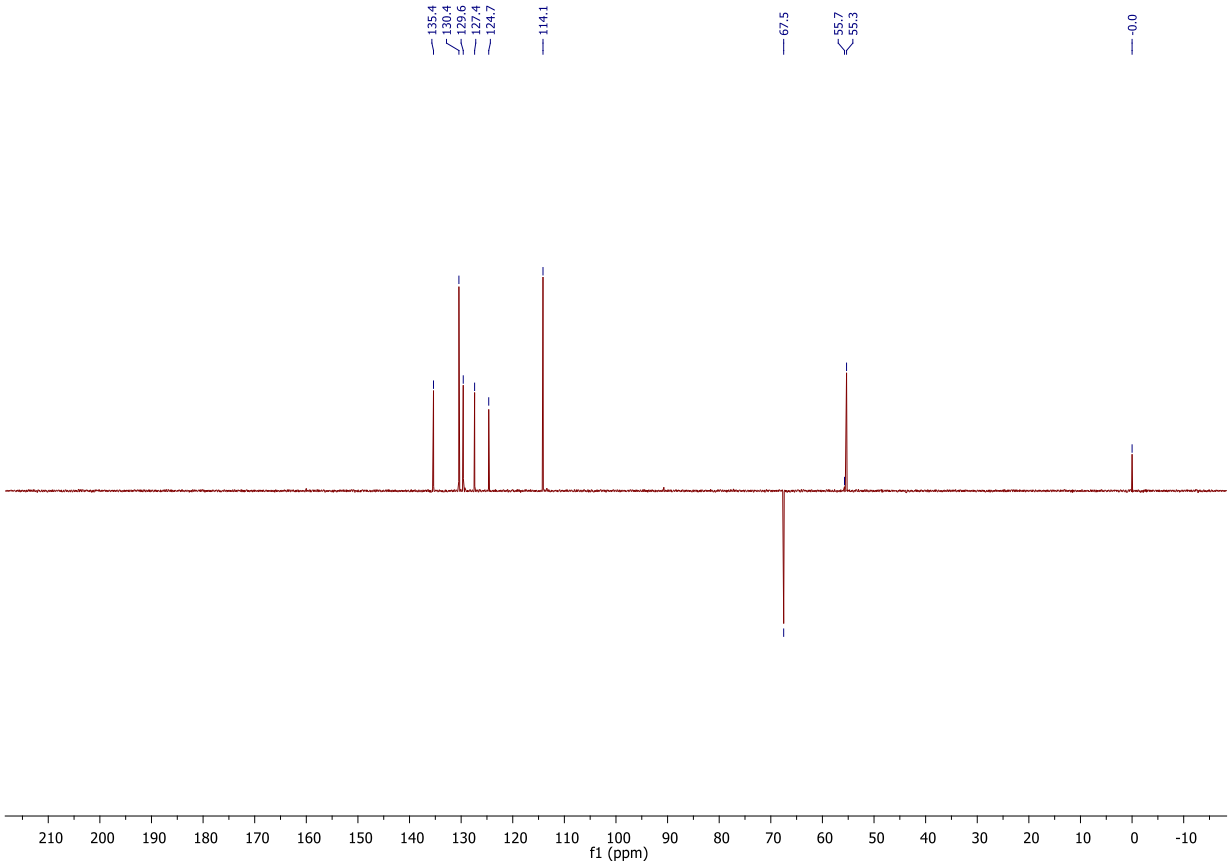
61c



^1H NMR spectrum in $CDCl_3$.

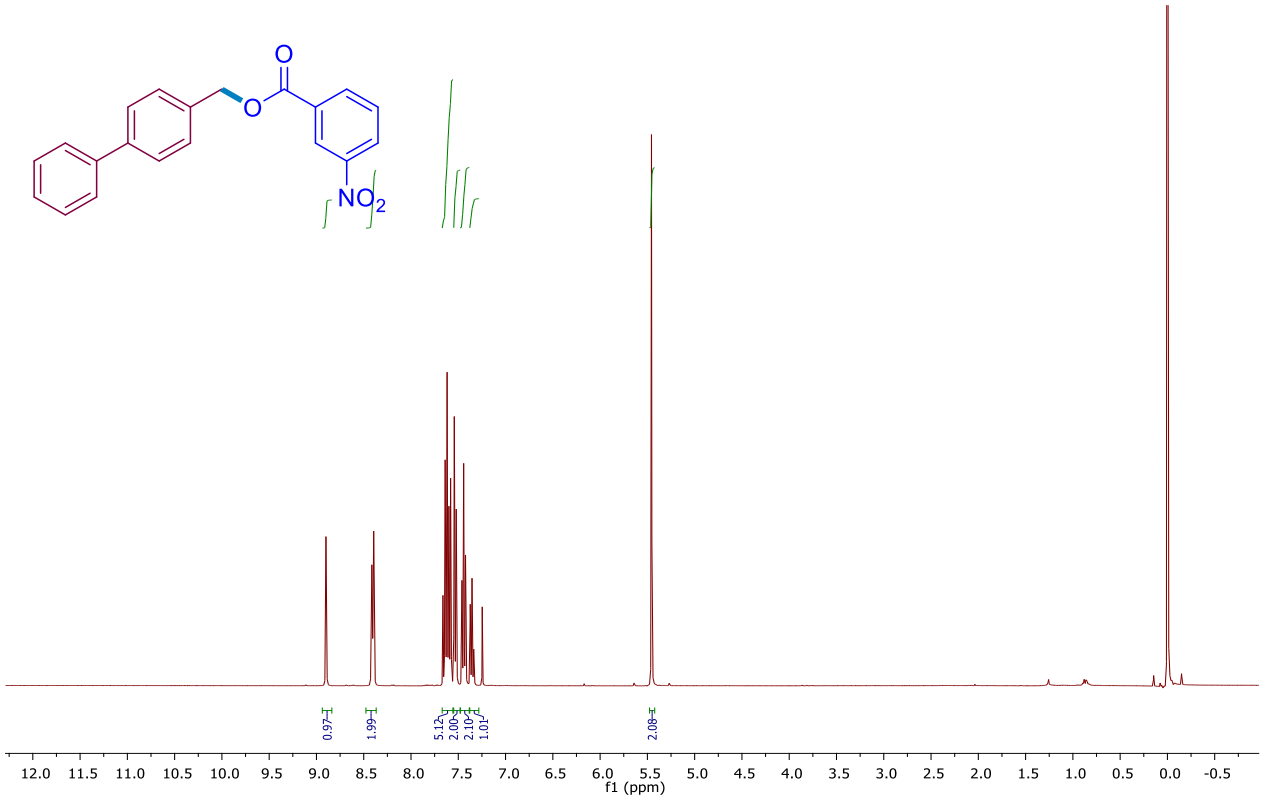


^{13}C NMR spectrum in $CDCl_3$

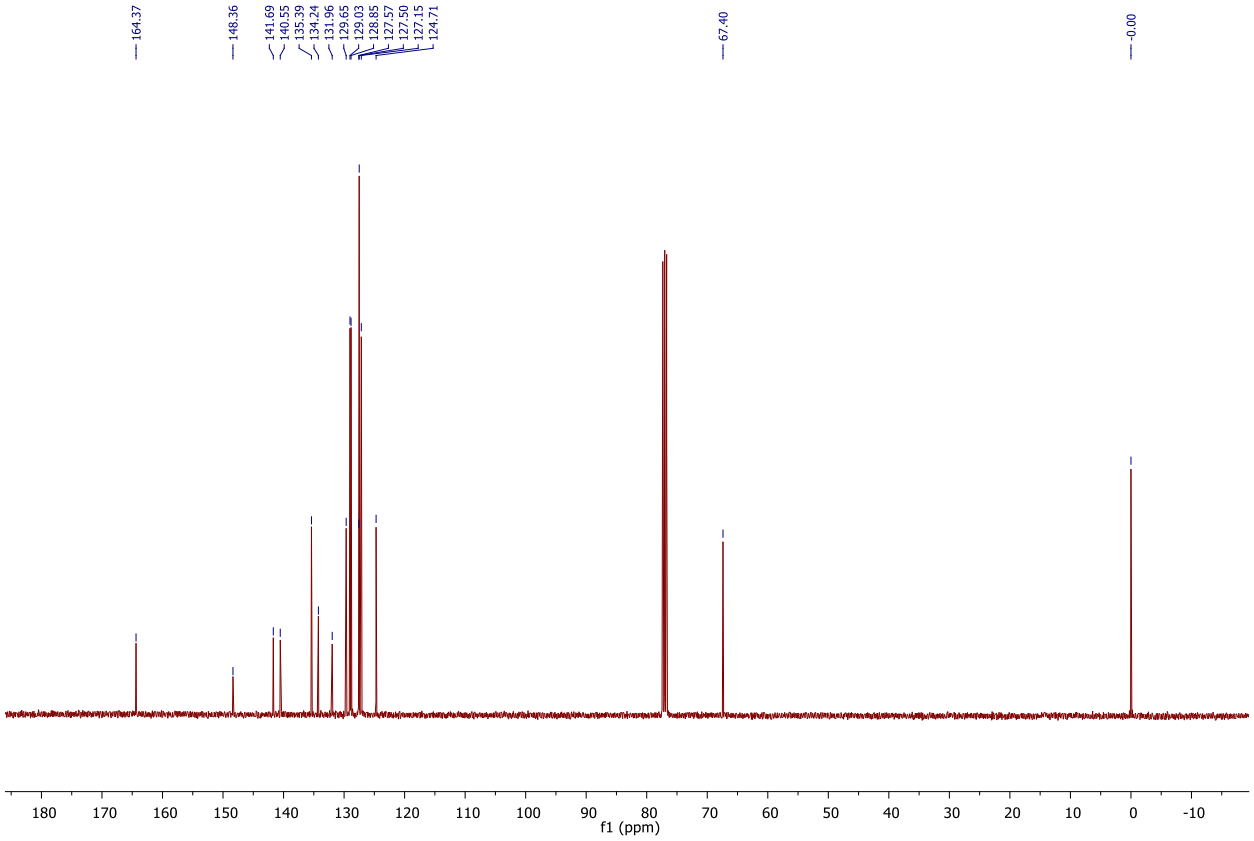


DEPT spectrum in $CDCl_3$.

62c

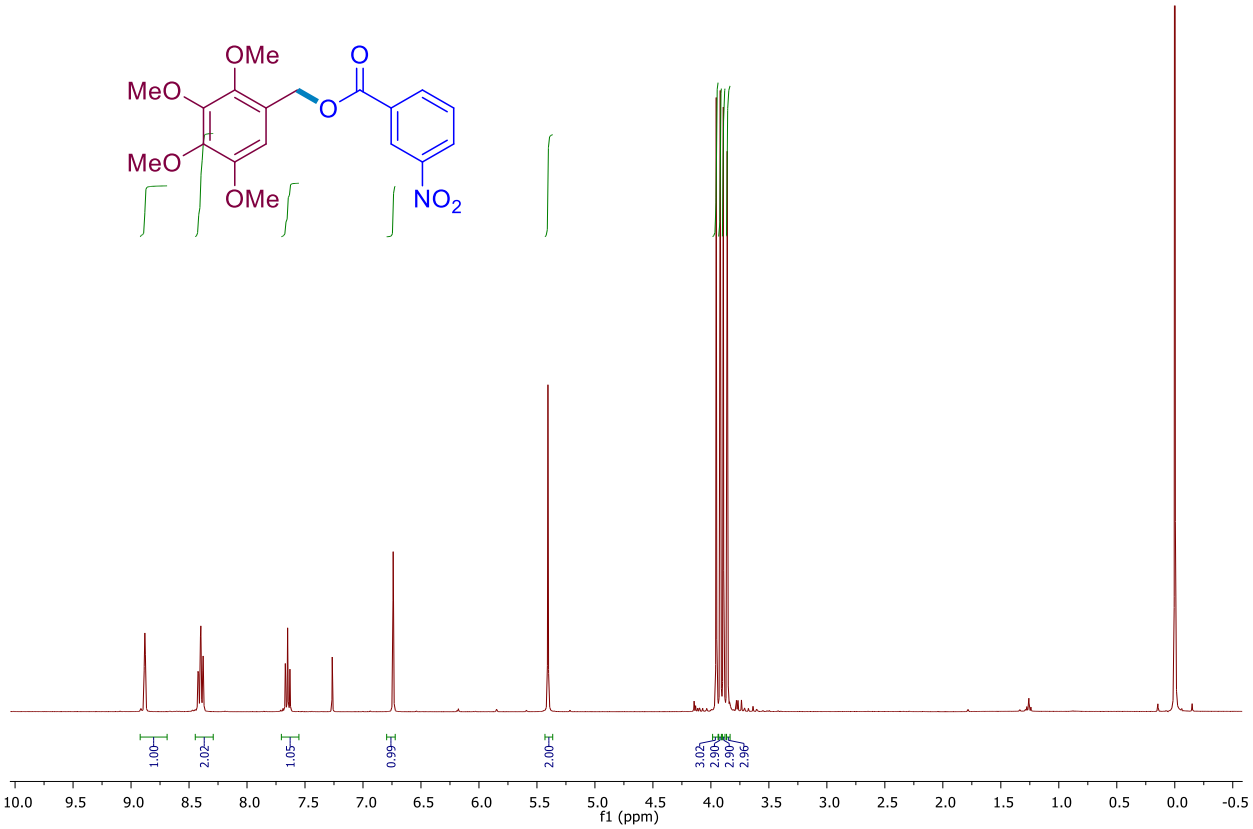


^{1}H NMR spectrum in $CDCl_3$.

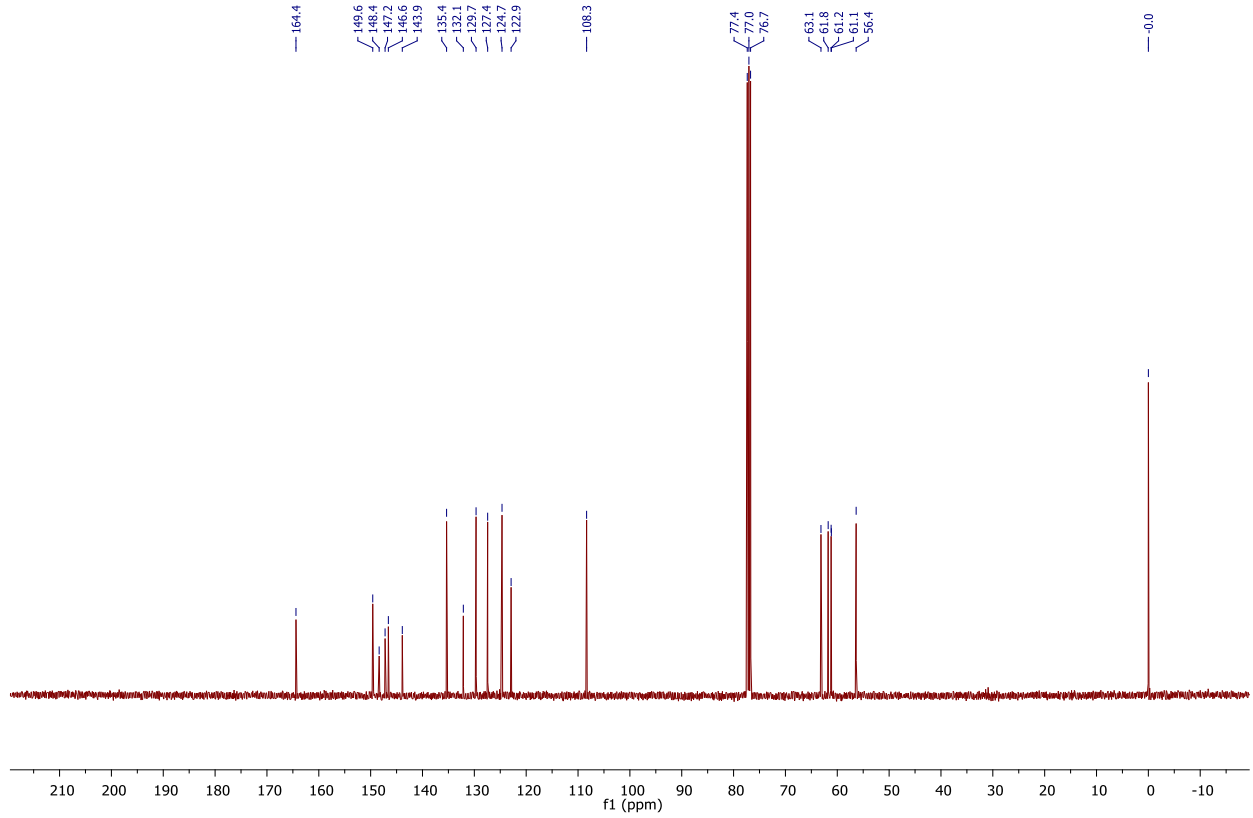


^{13}C NMR spectrum in $CDCl_3$

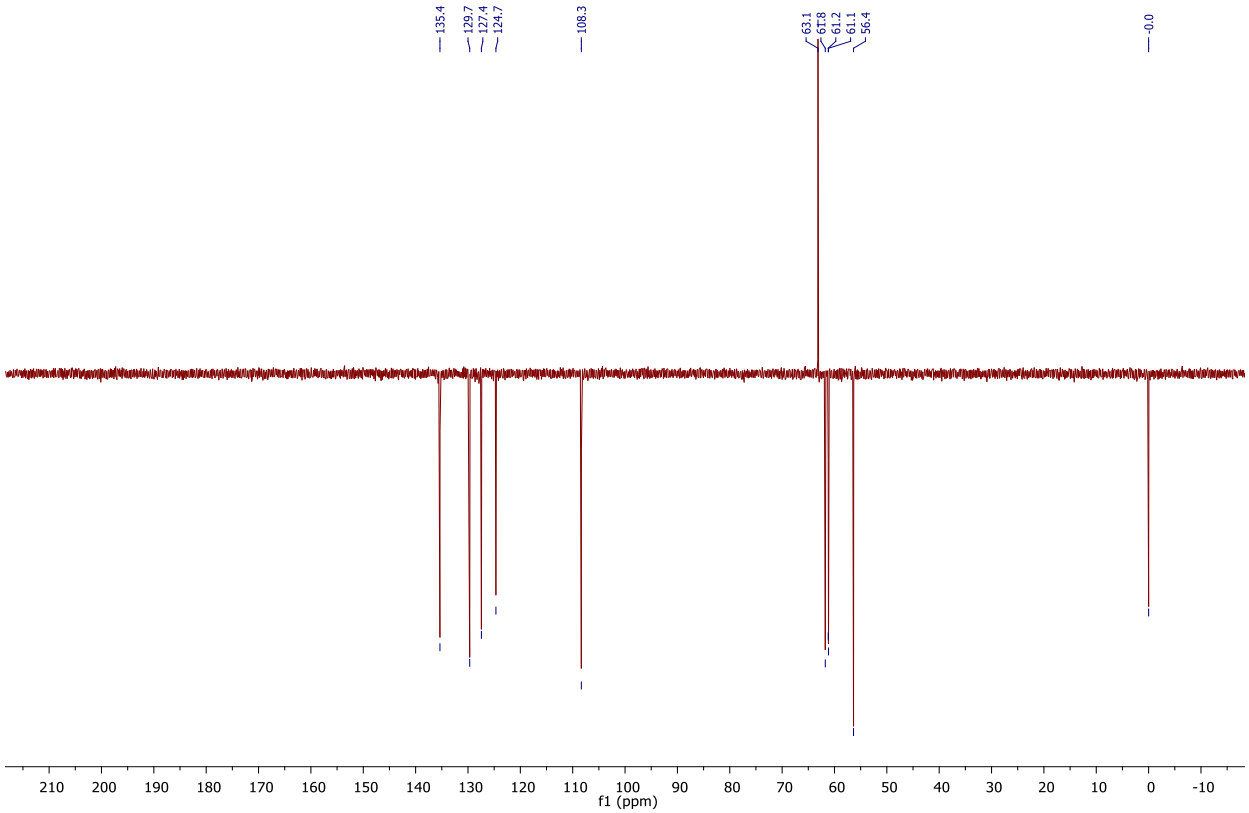
63c



^{1}H NMR spectrum in $CDCl_3$.

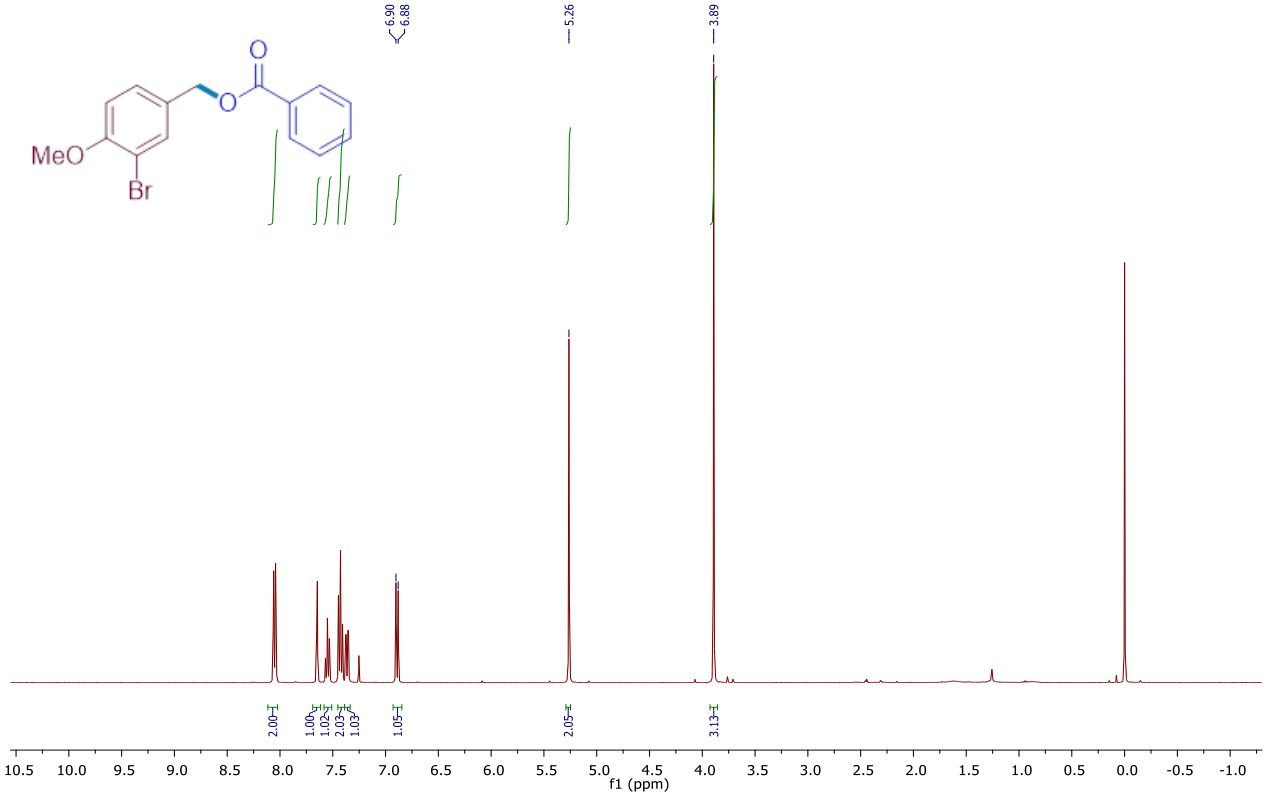


^{13}C NMR spectrum in $CDCl_3$

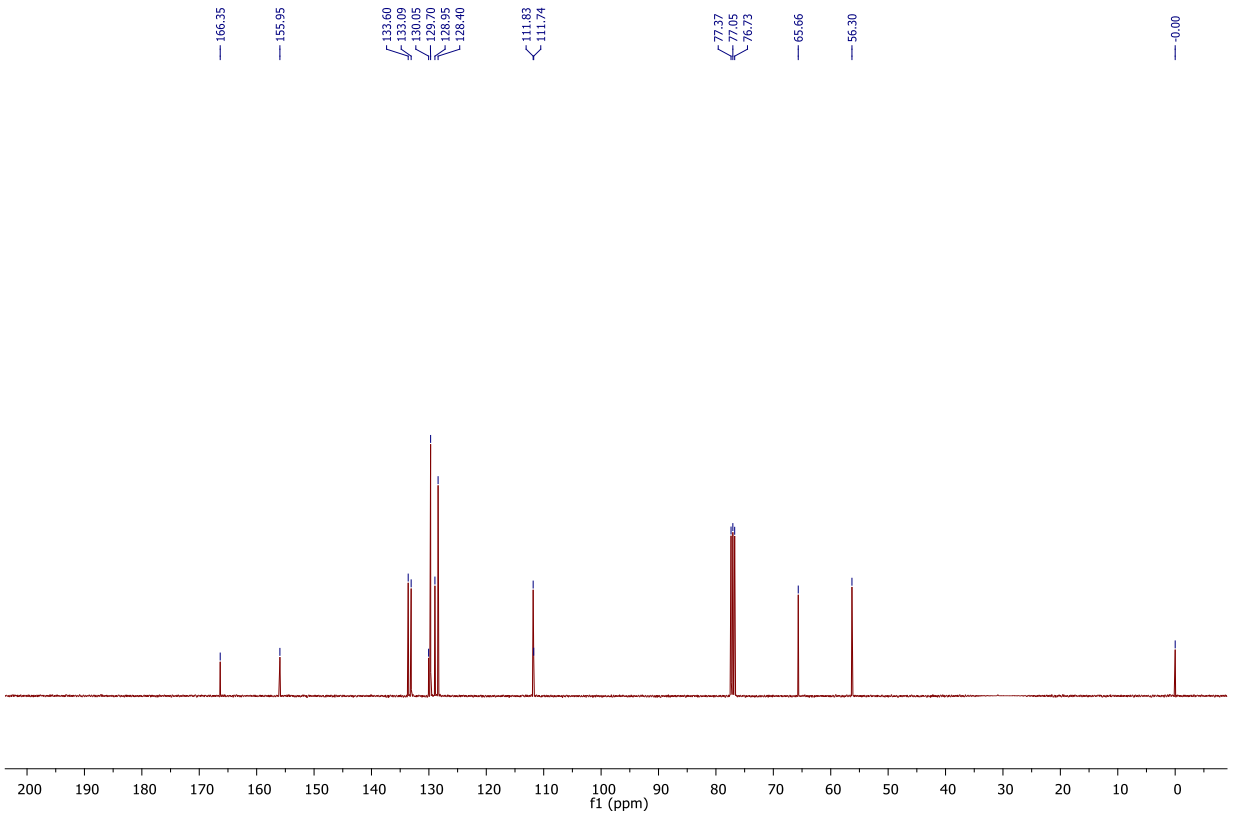


DEPT spectrum in $CDCl_3$.

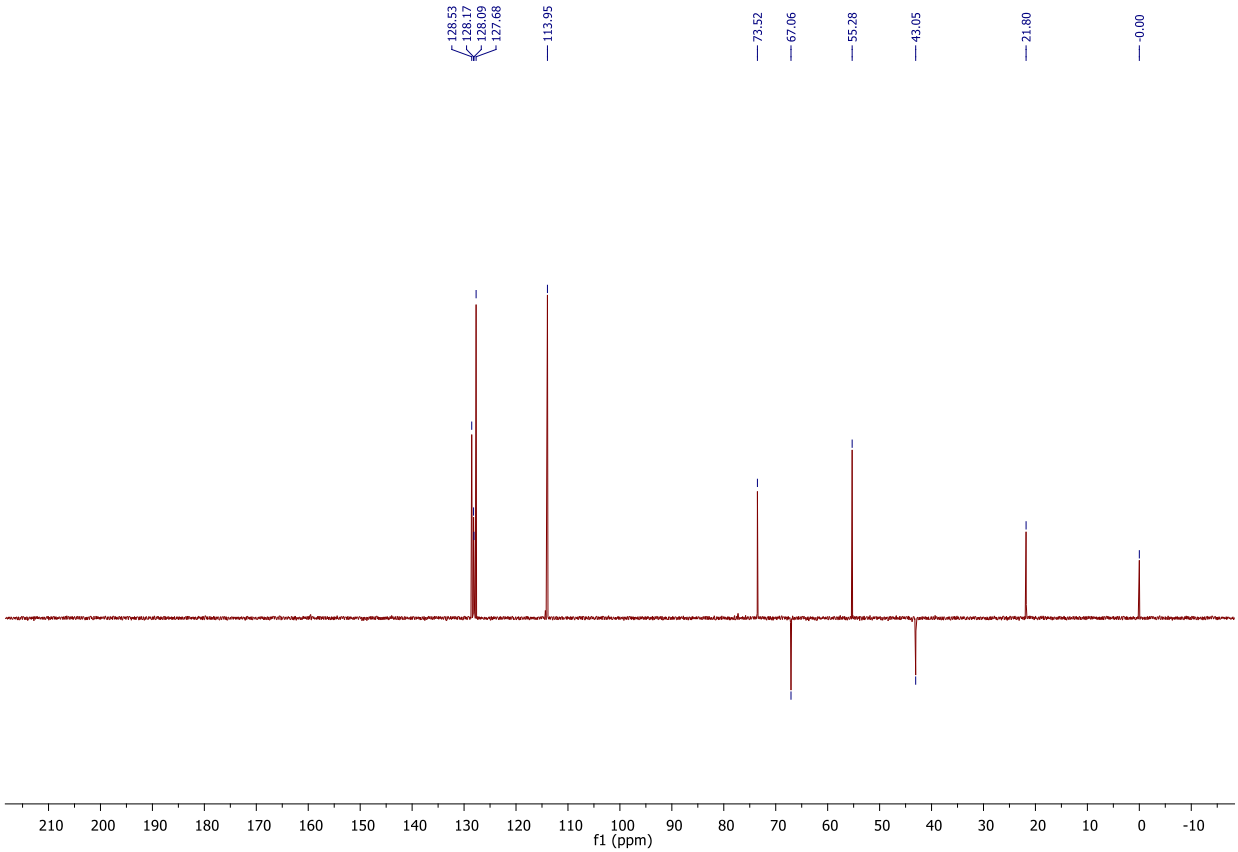
64c



^1H NMR spectrum in $CDCl_3$.

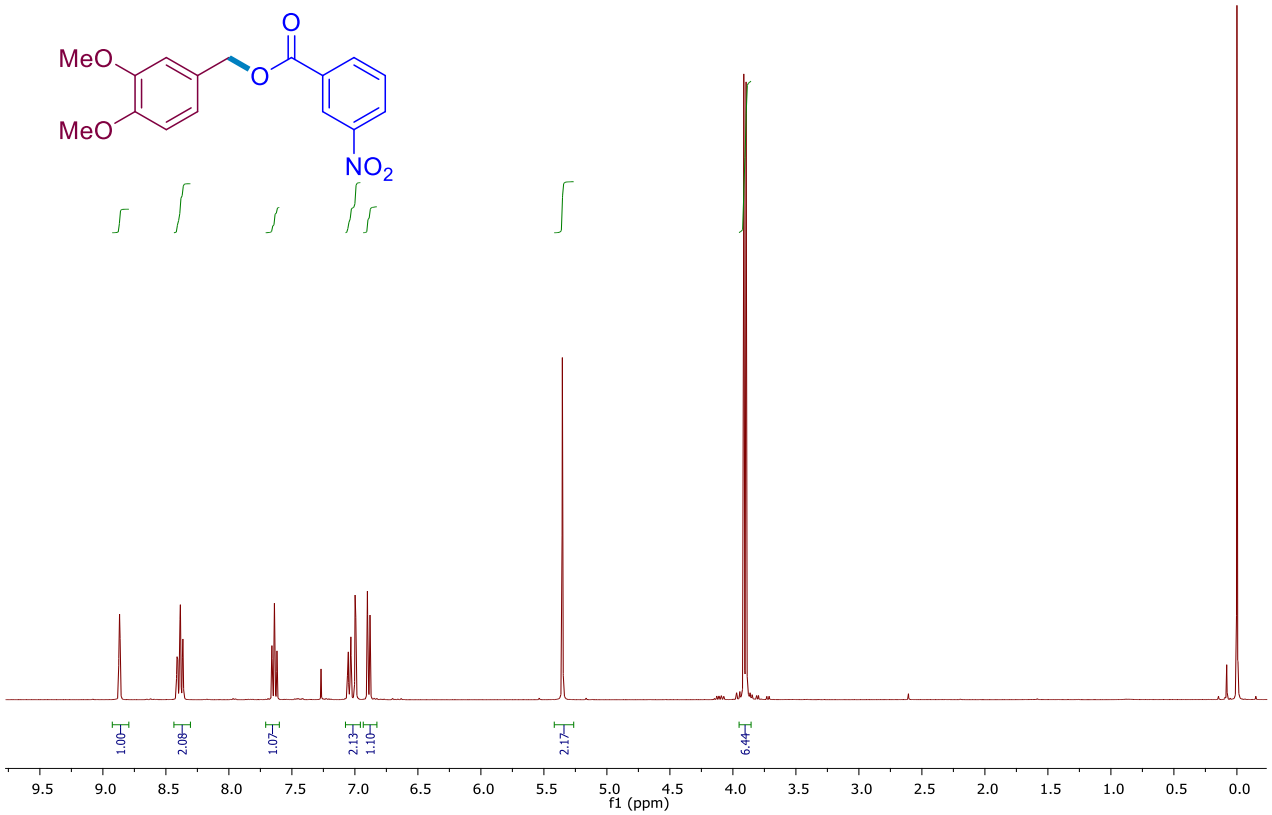


^{13}C NMR spectrum in $CDCl_3$

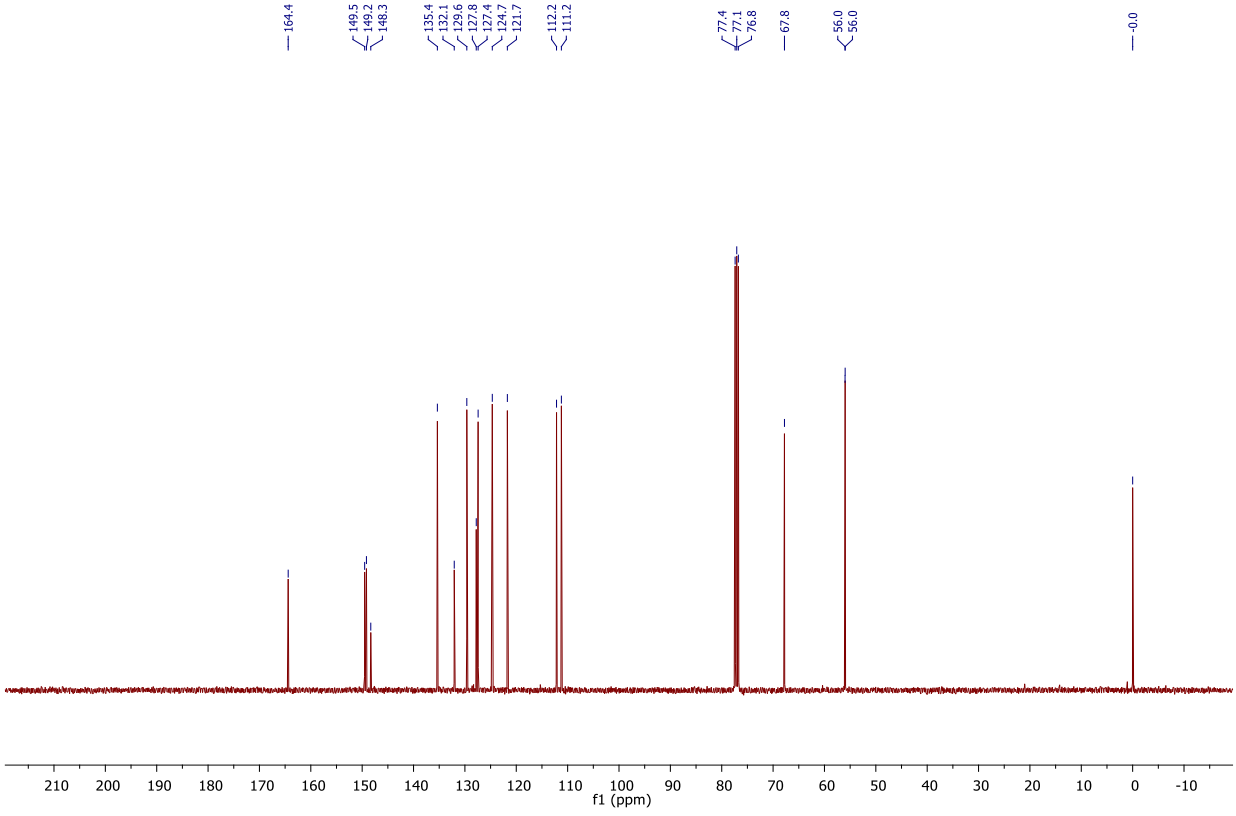


DEPT spectrum in $CDCl_3$.

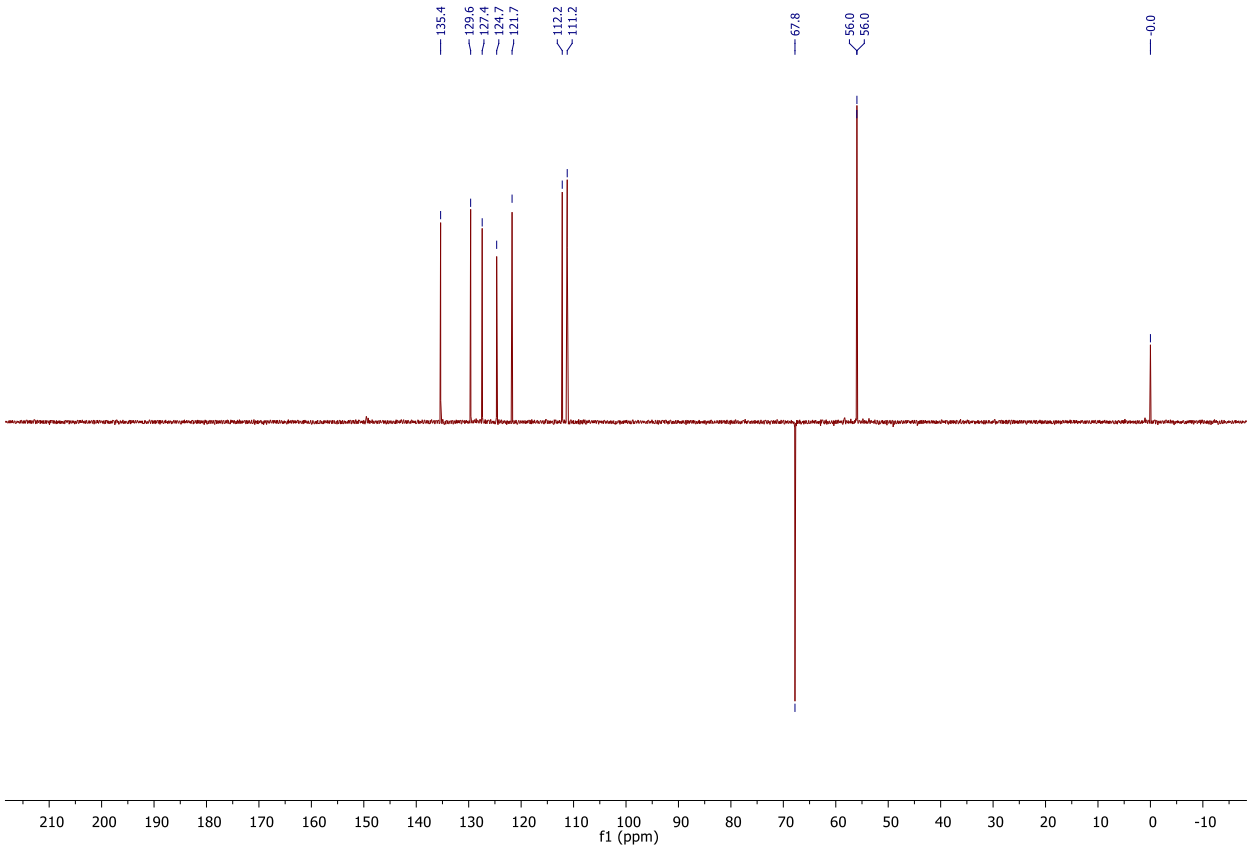
65c



^{1}H NMR spectrum in $CDCl_3$.

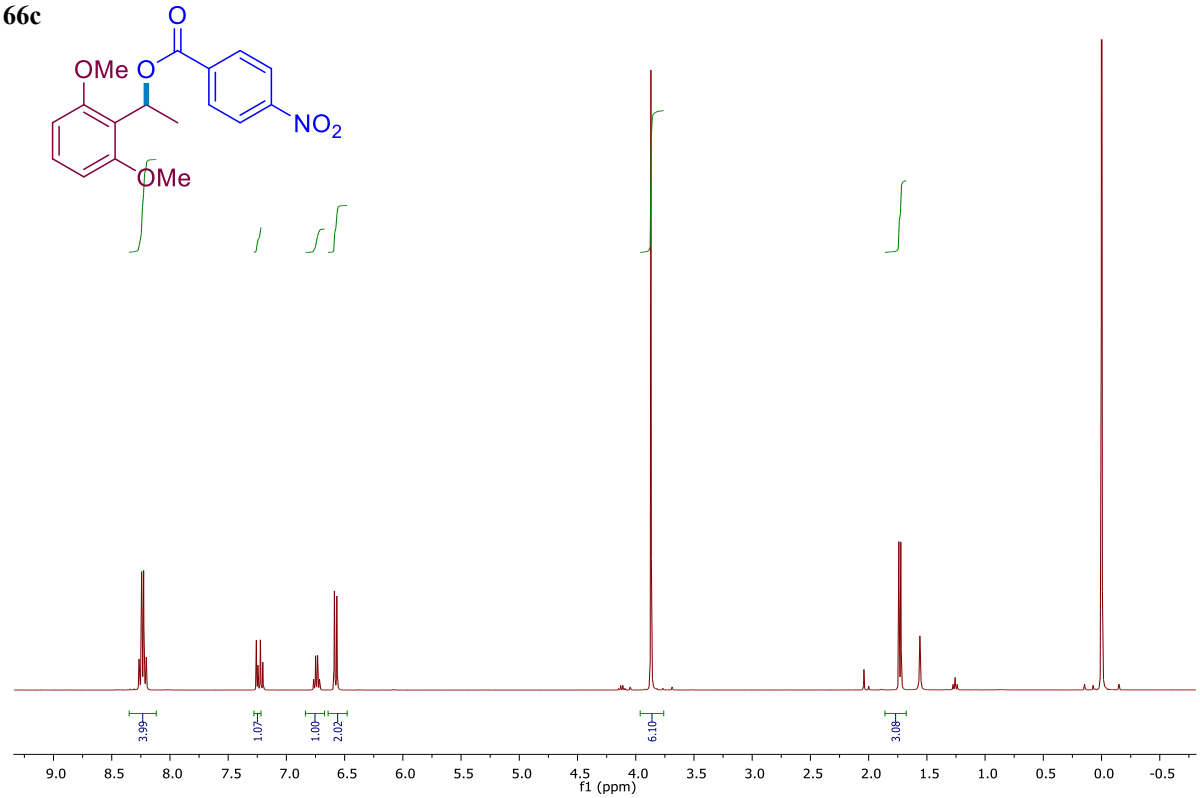


^{13}C NMR spectrum in $CDCl_3$

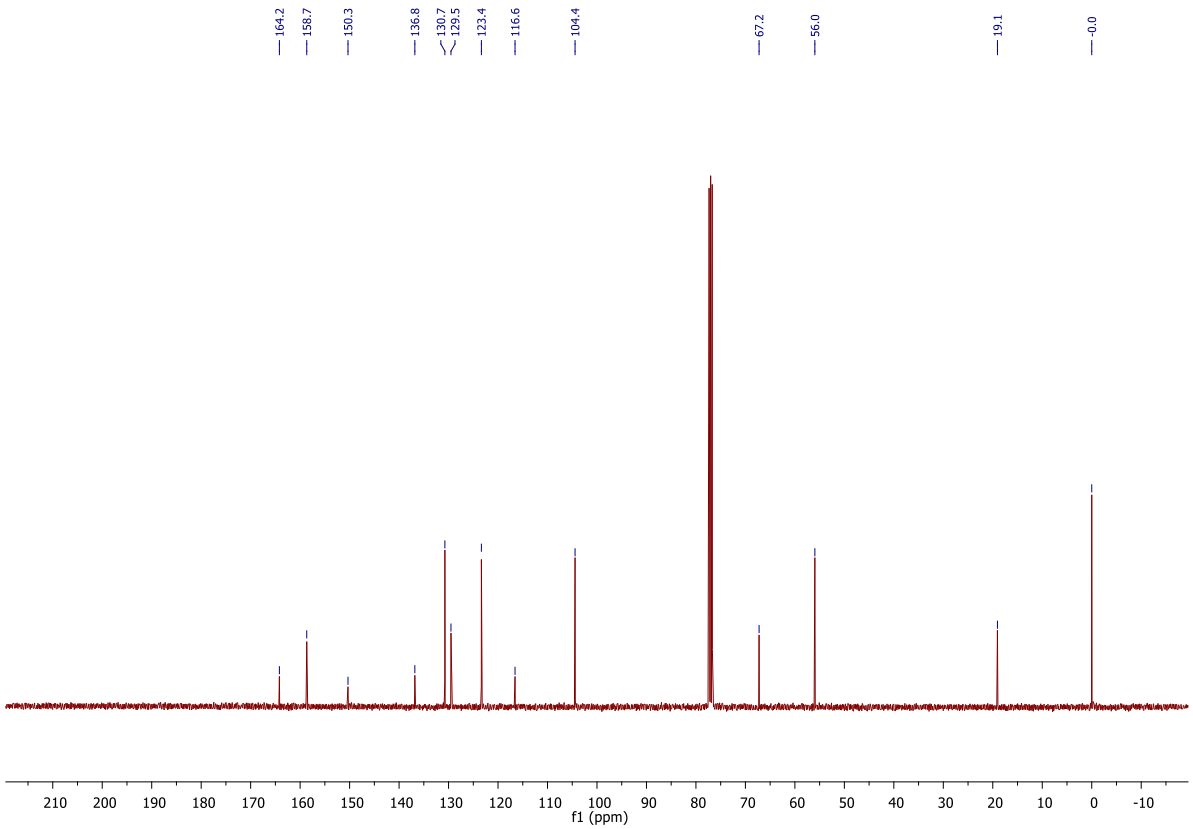


DEPT spectrum in $CDCl_3$.

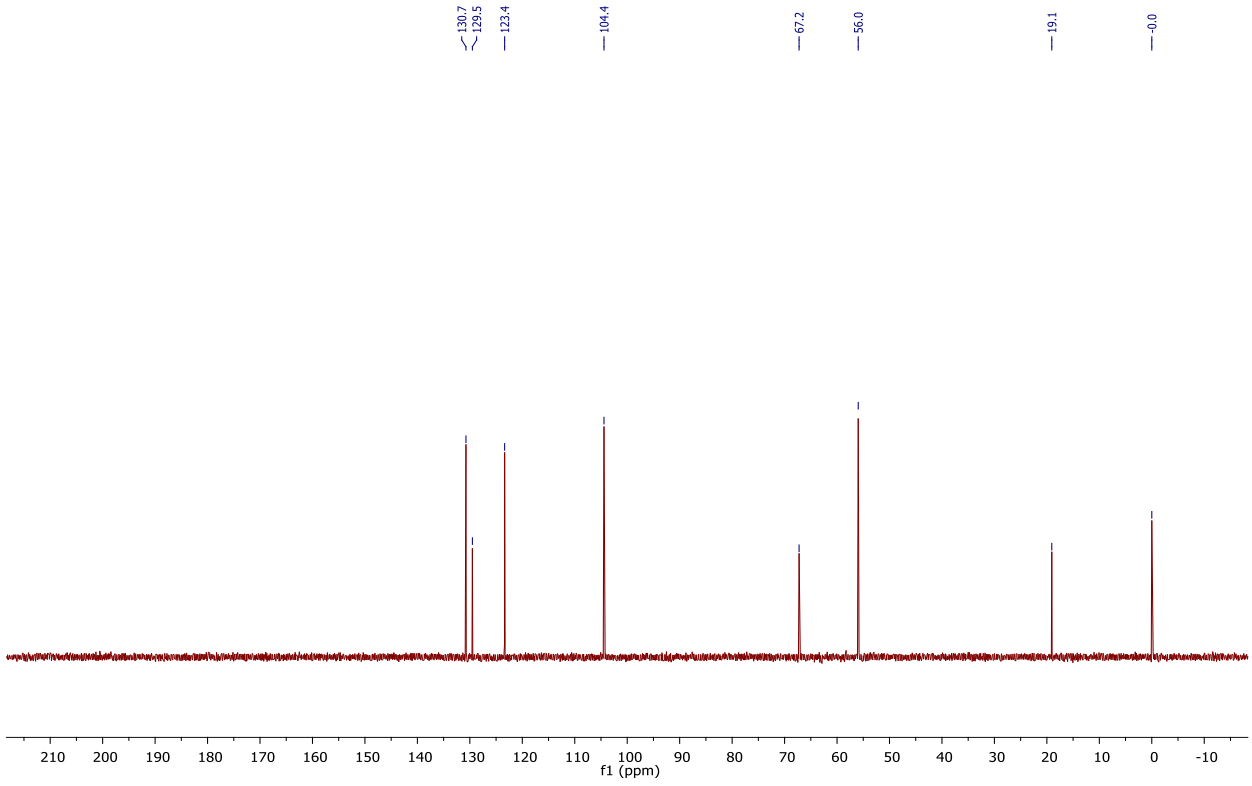
66c



^1H NMR spectrum in $CDCl_3$.

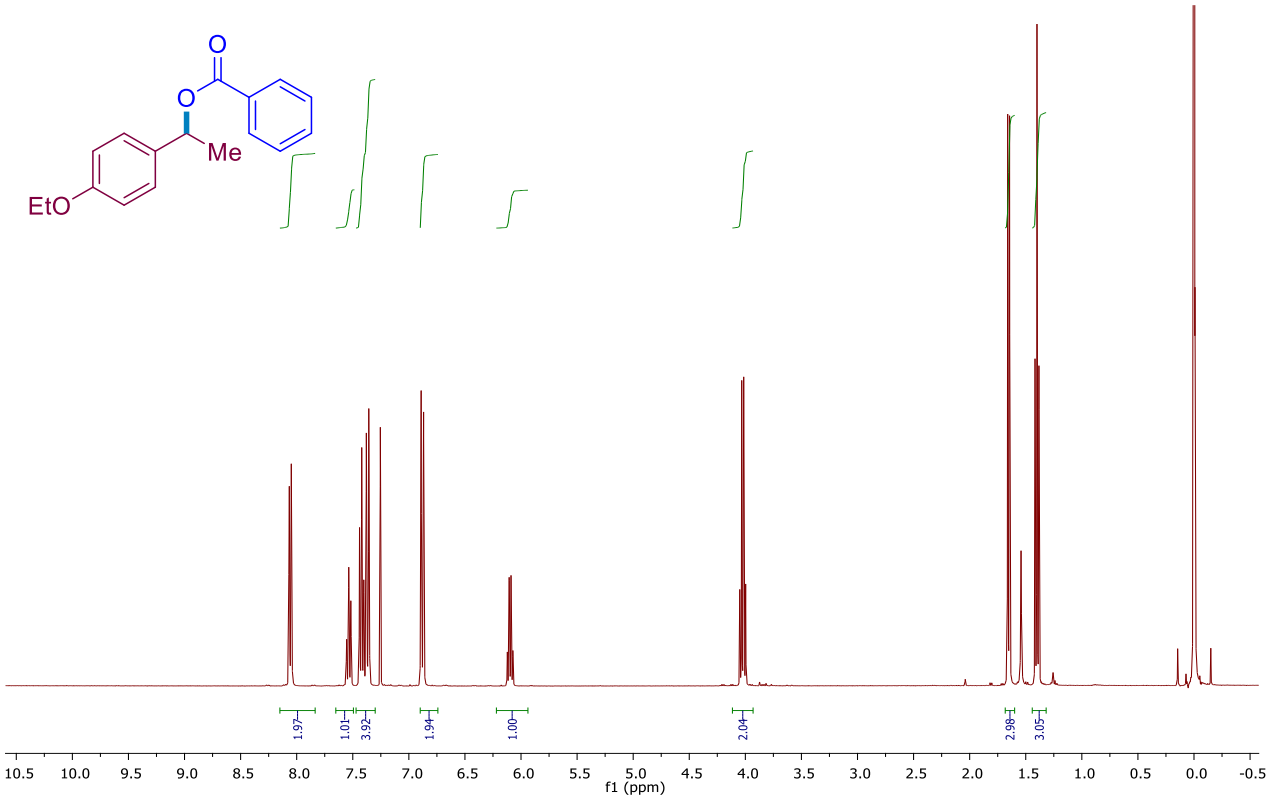


^{13}C NMR spectrum in $CDCl_3$

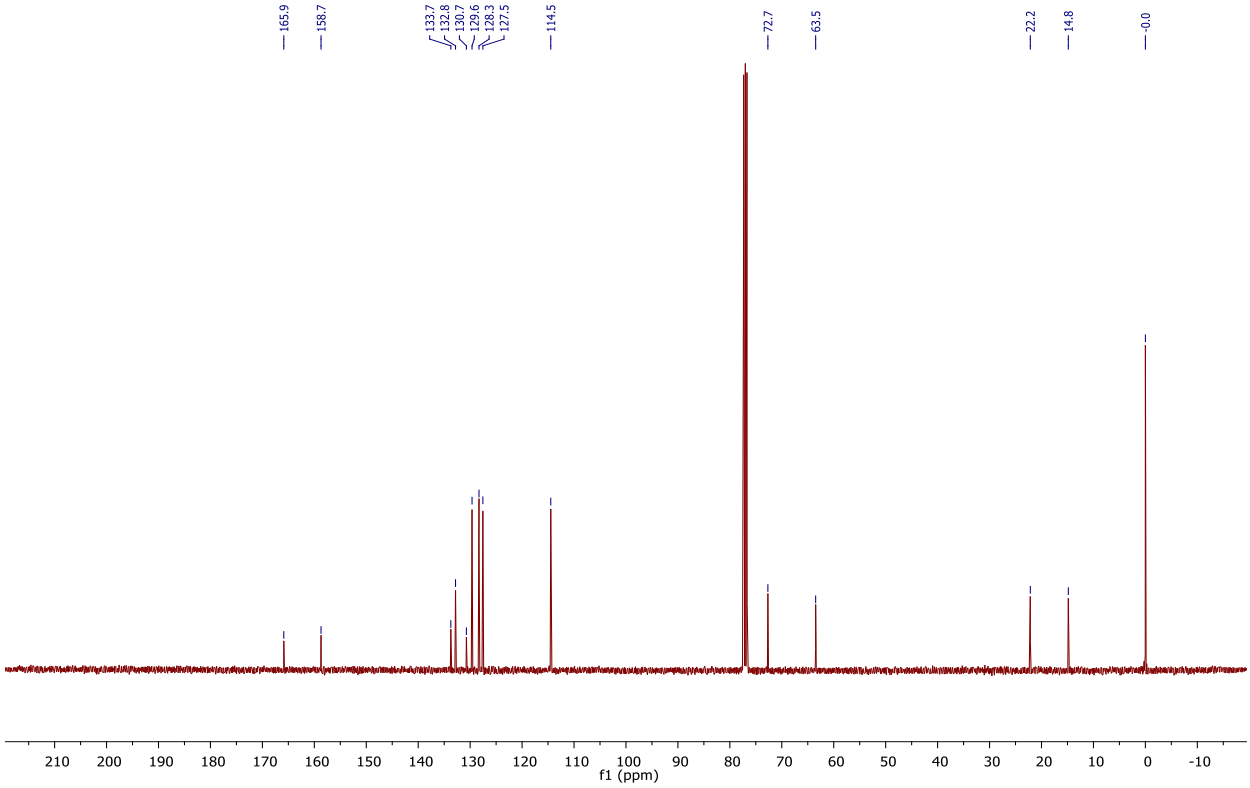


DEPT spectrum in $CDCl_3$.

67c

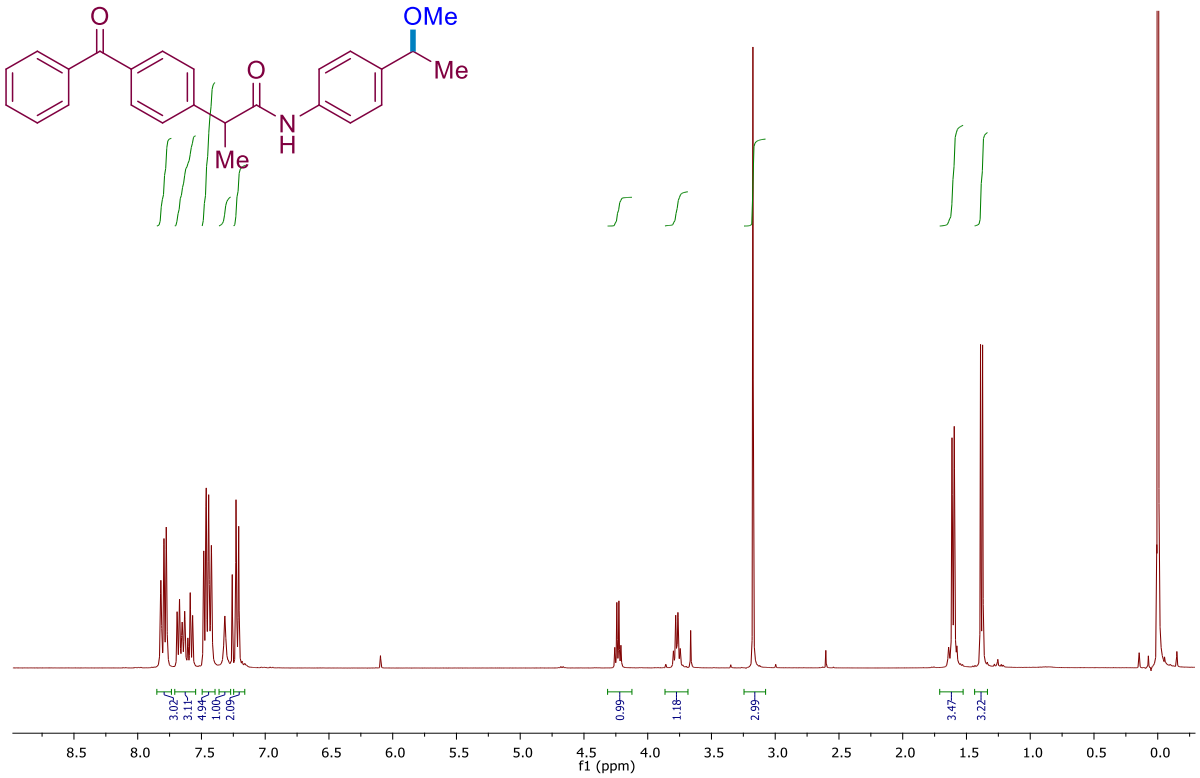


^{1}H NMR spectrum in $CDCl_3$.

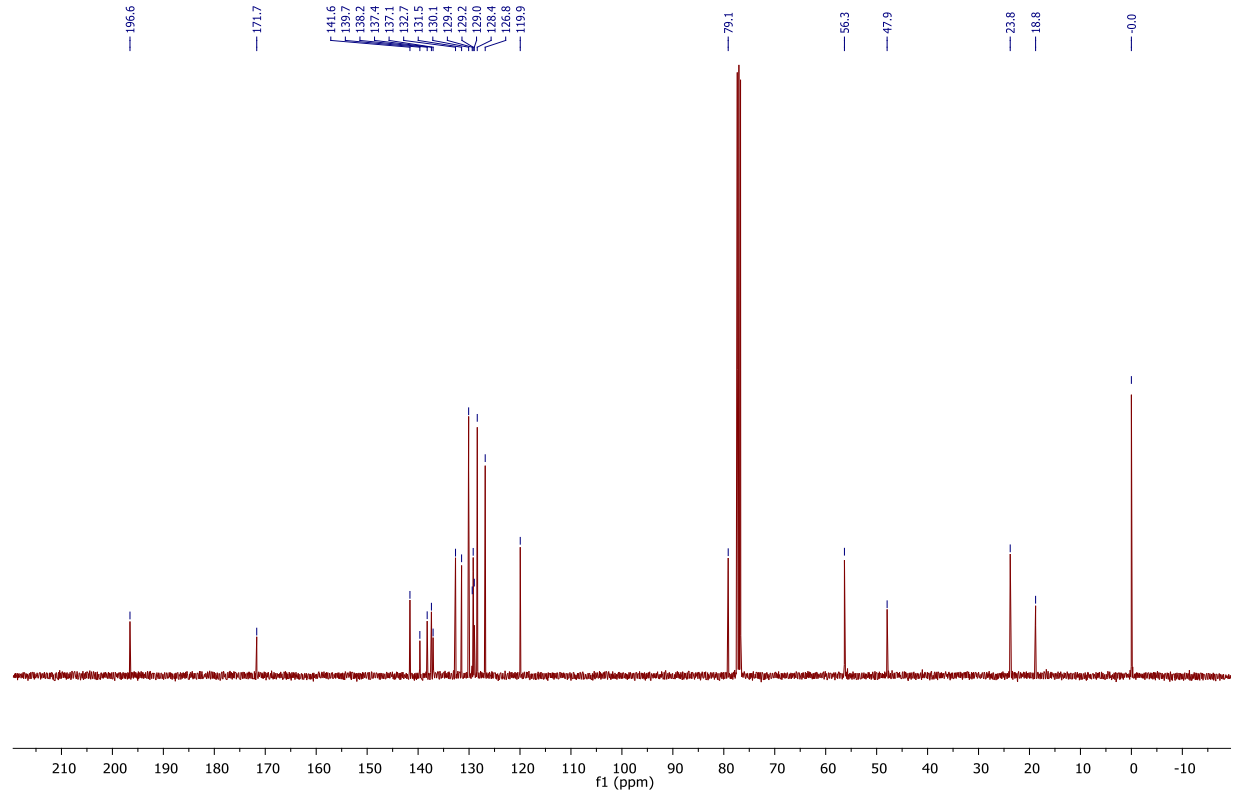


^{13}C NMR spectrum in $CDCl_3$

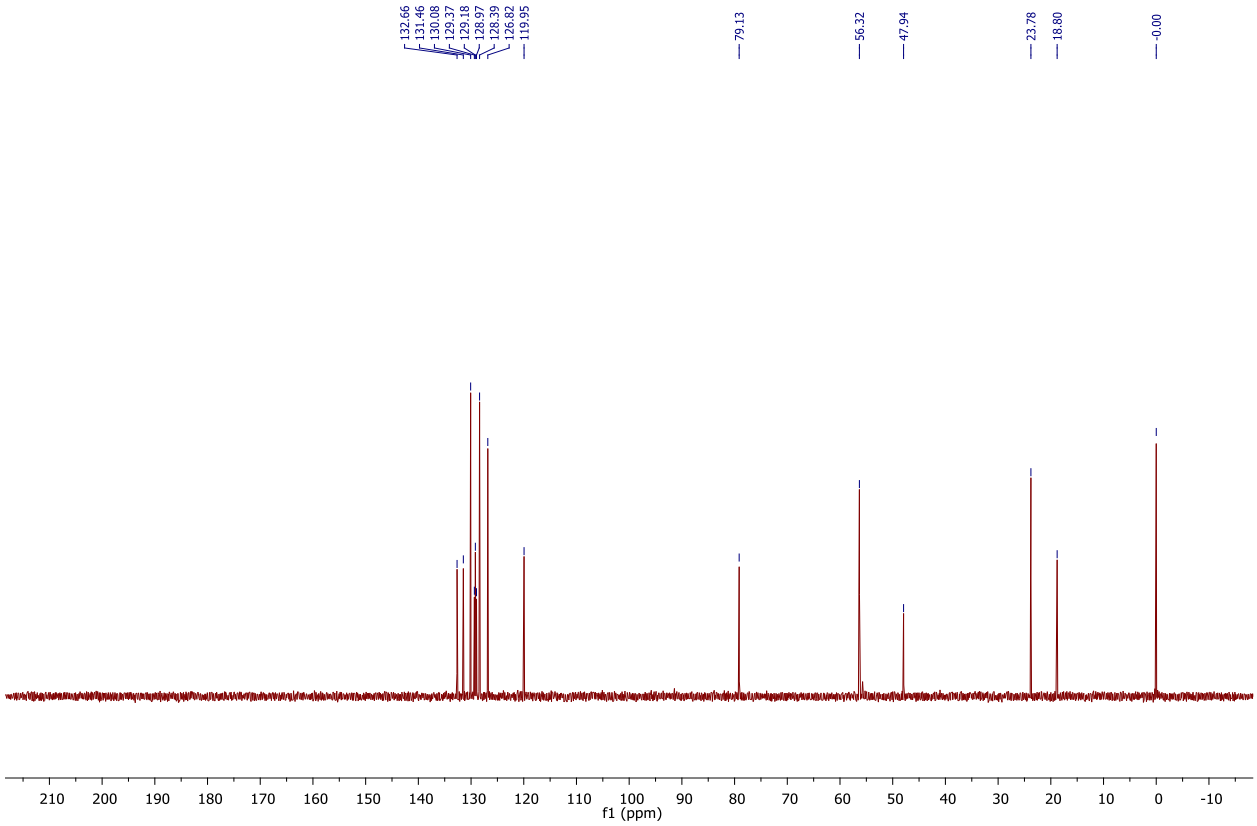
68c



^{1}H NMR spectrum in $CDCl_3$.

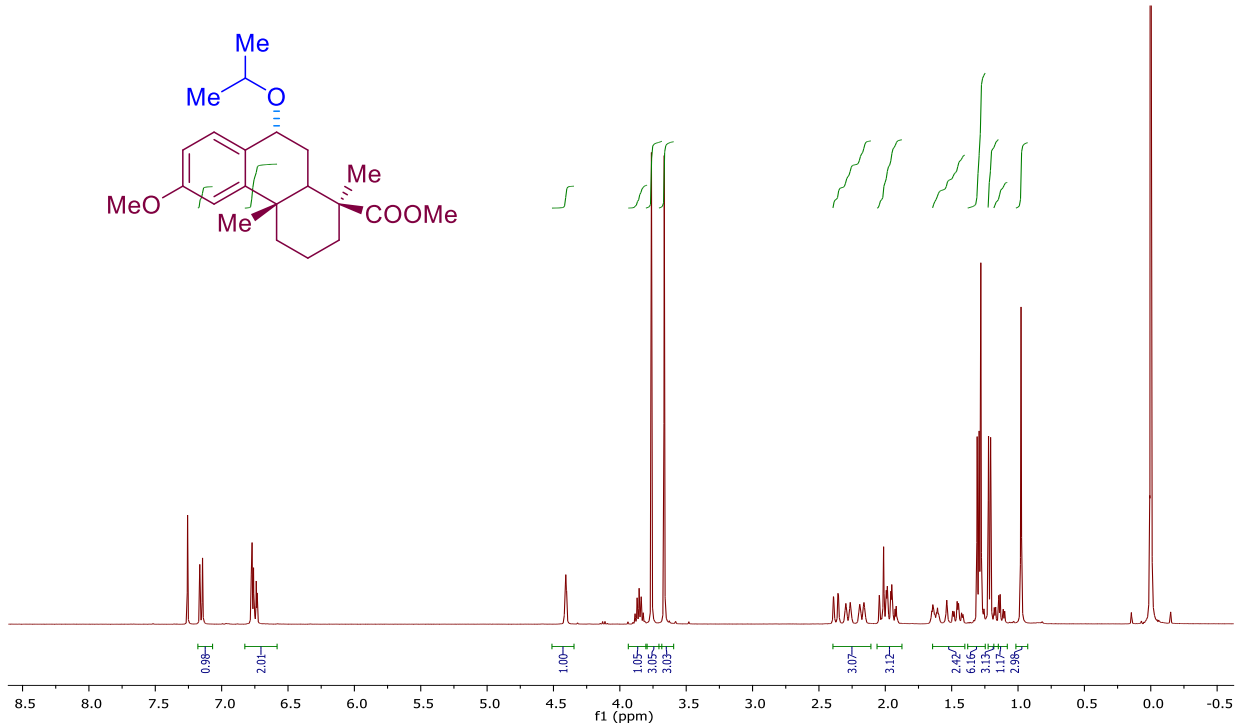


^{13}C NMR spectrum in $CDCl_3$

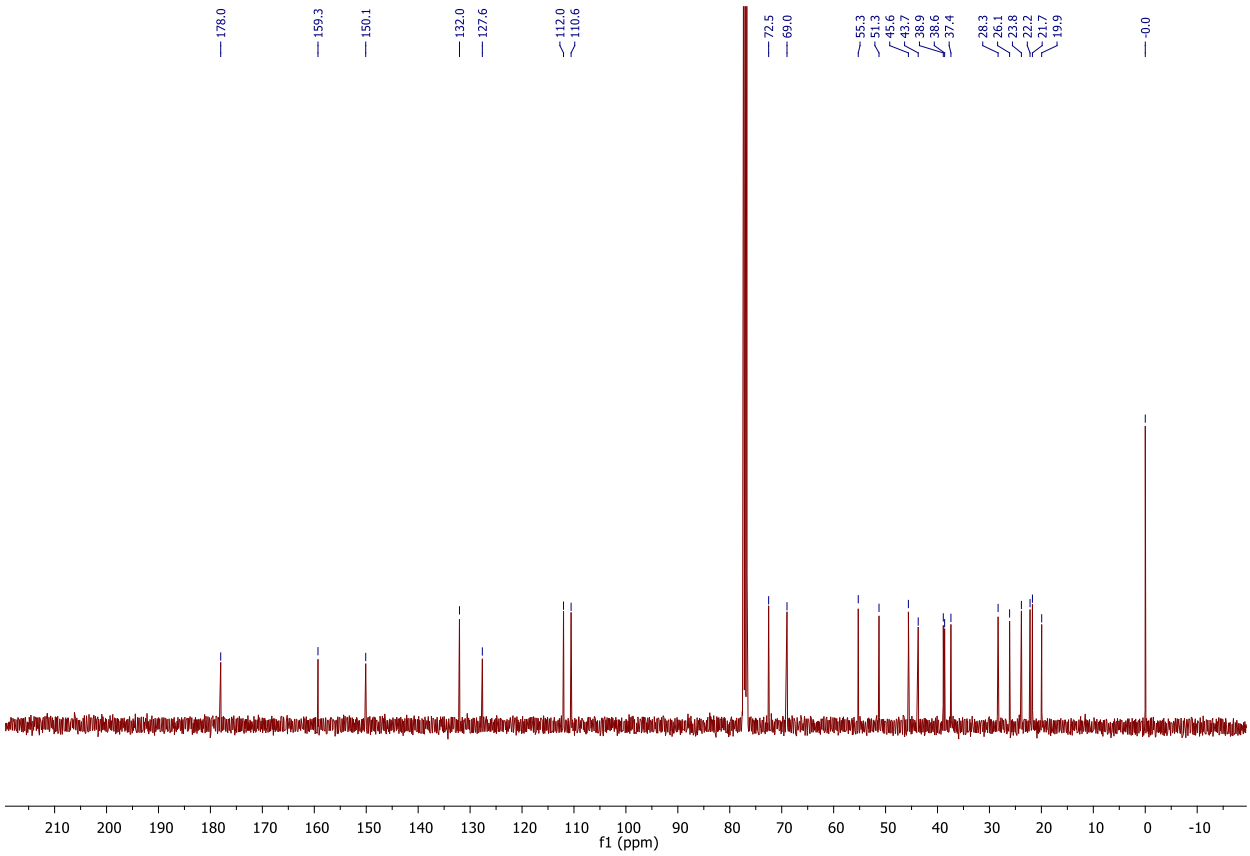


DEPT spectrum in $CDCl_3$.

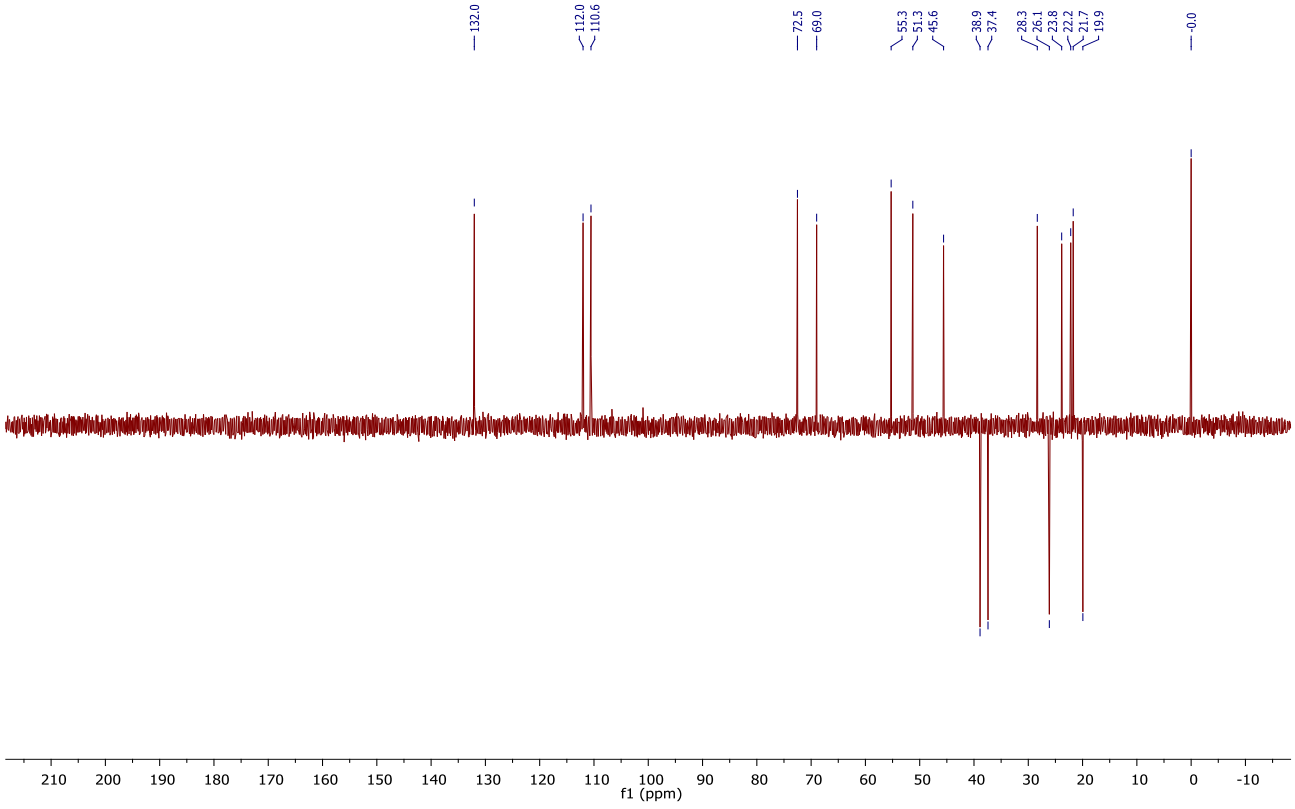
69c



^1H NMR spectrum in $CDCl_3$.

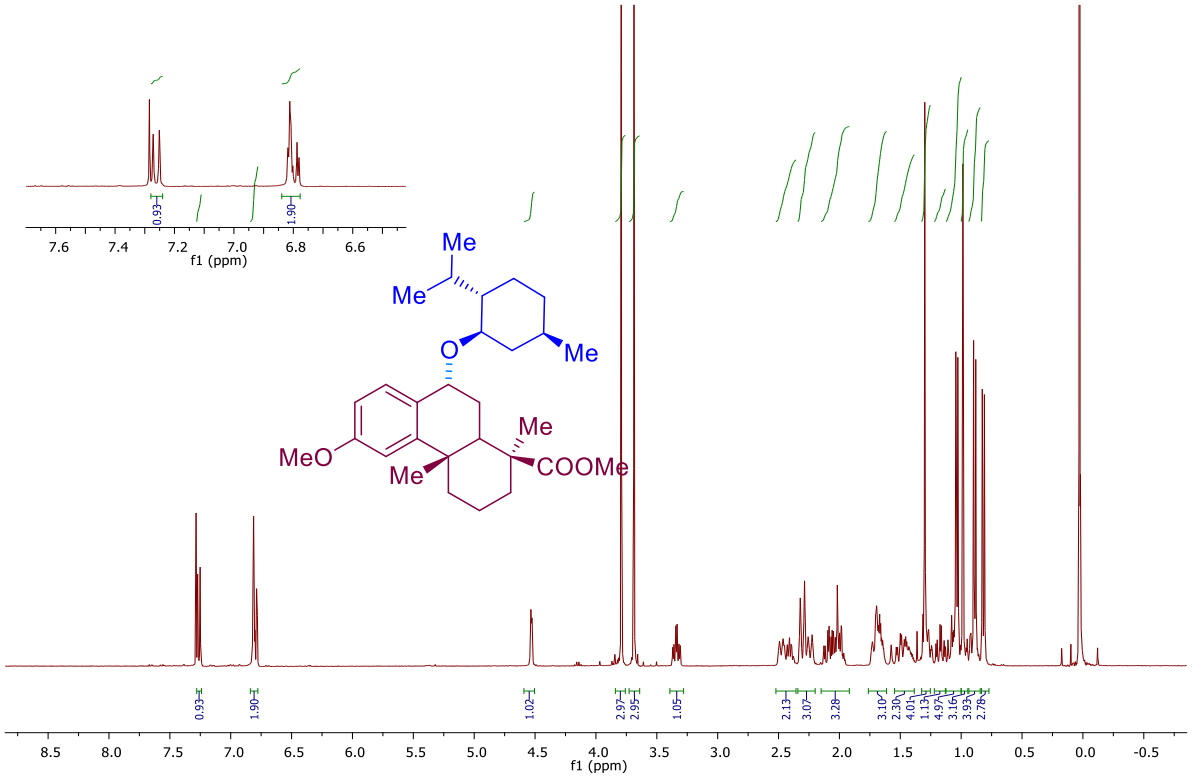


^{13}C NMR spectrum in $CDCl_3$

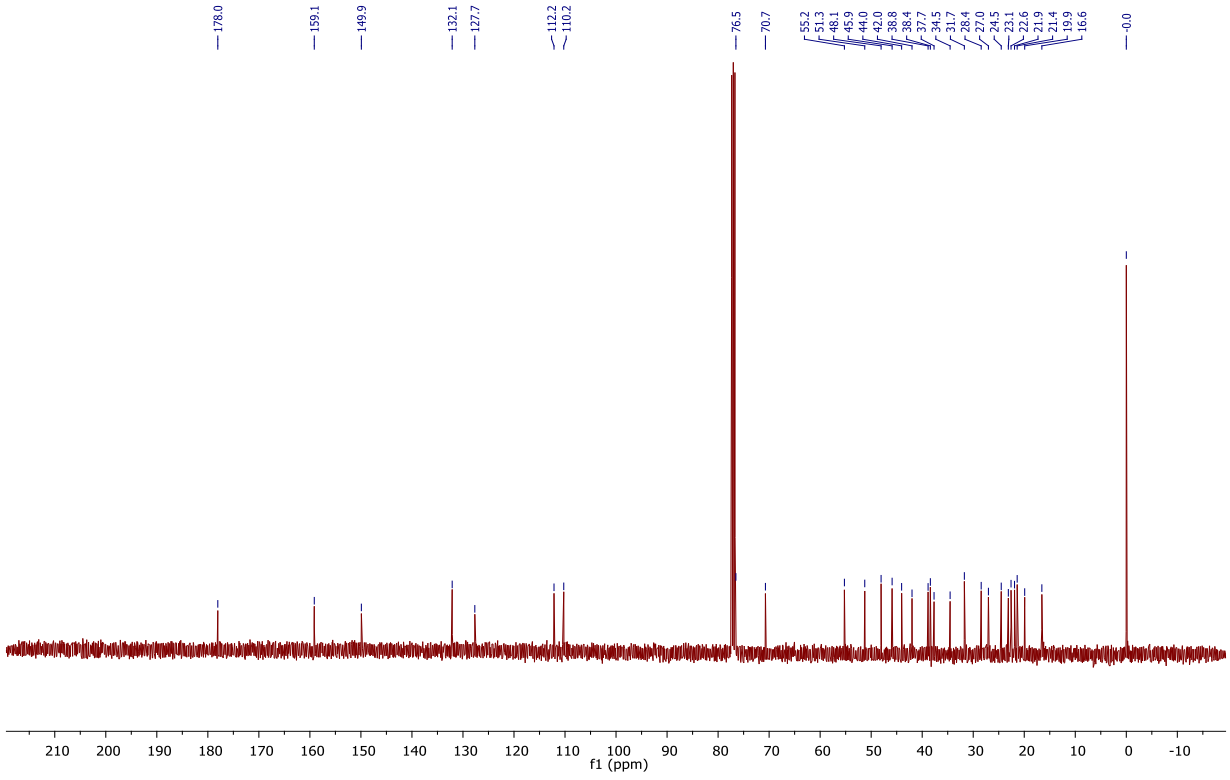


DEPT spectrum in $CDCl_3$.

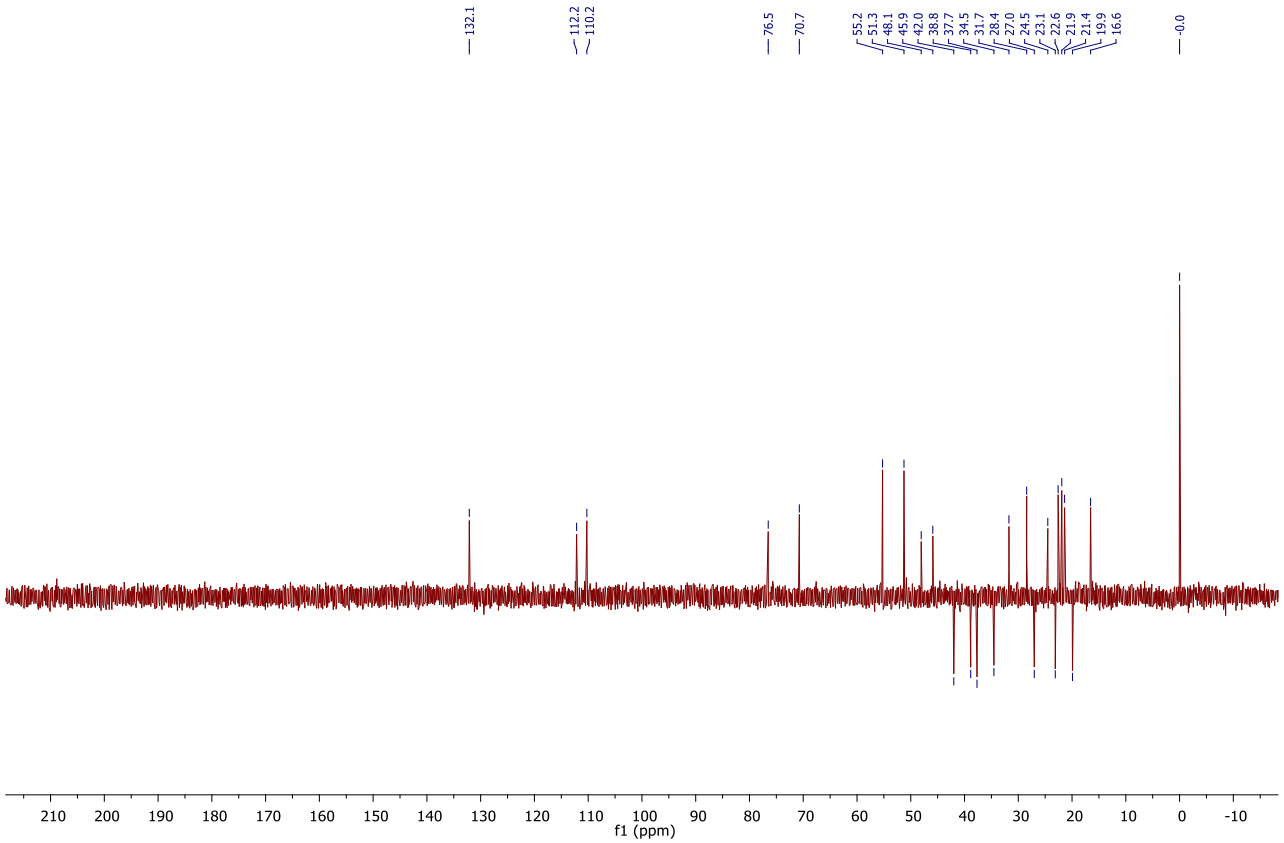
70c



^{1}H NMR spectrum in $CDCl_3$.

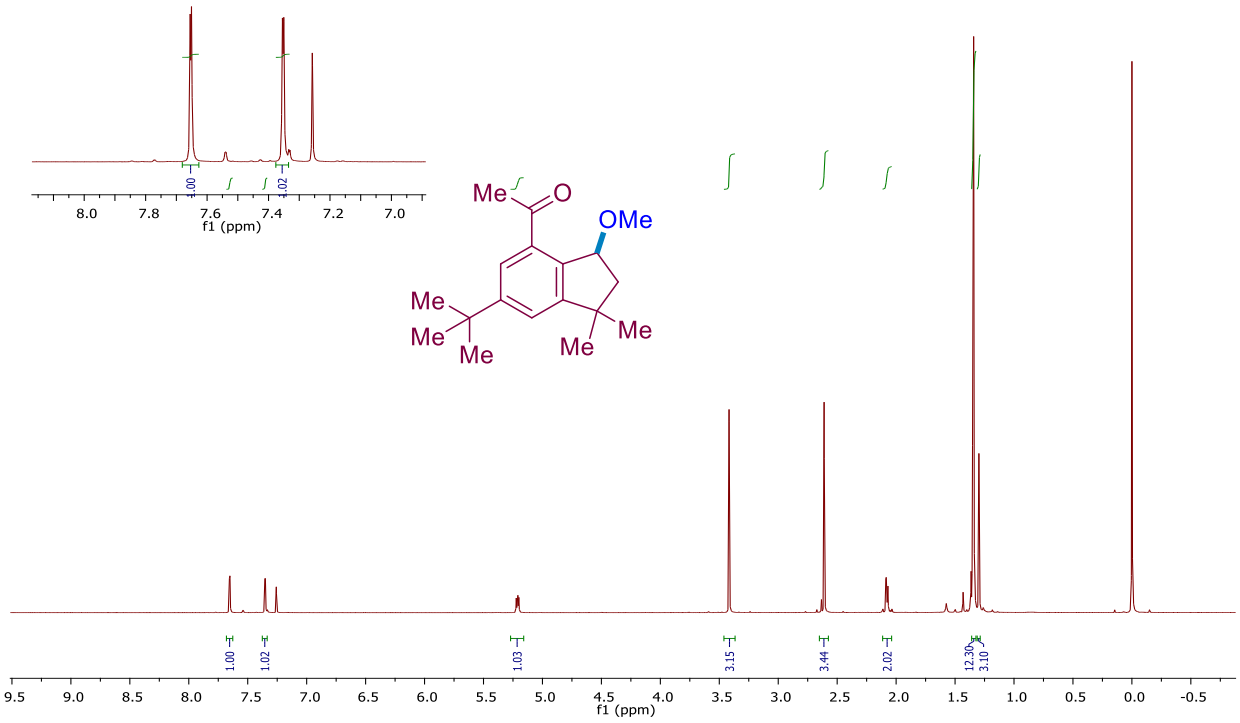


^{13}C NMR spectrum in $CDCl_3$

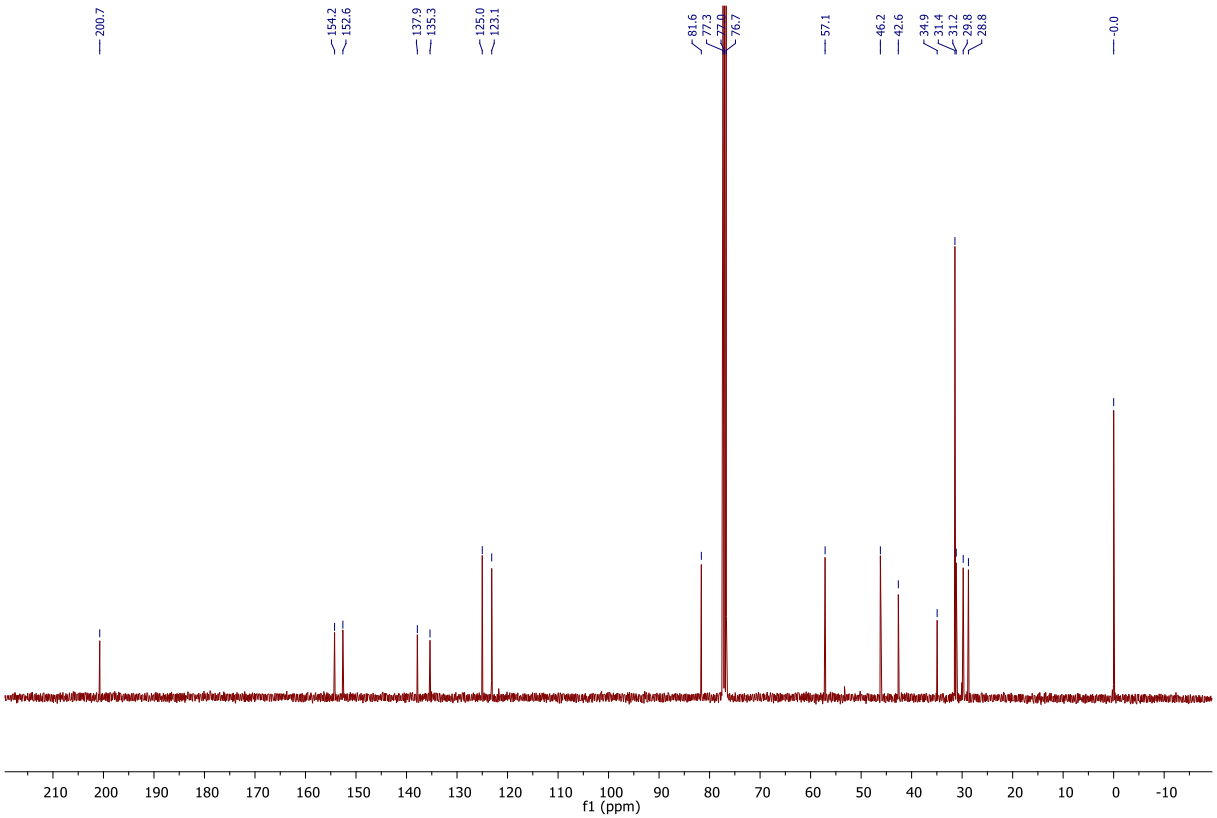


DEPT spectrum in $CDCl_3$.

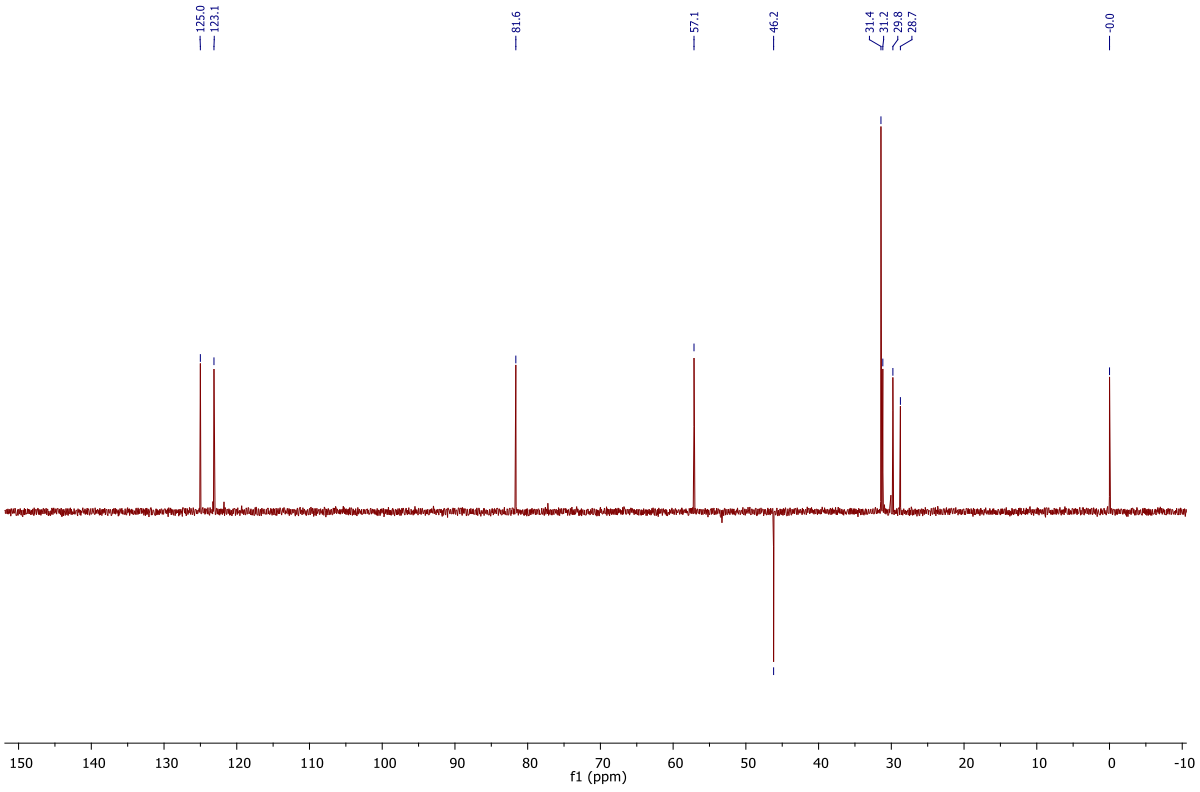
71c



^{1}H NMR spectrum in $CDCl_3$.

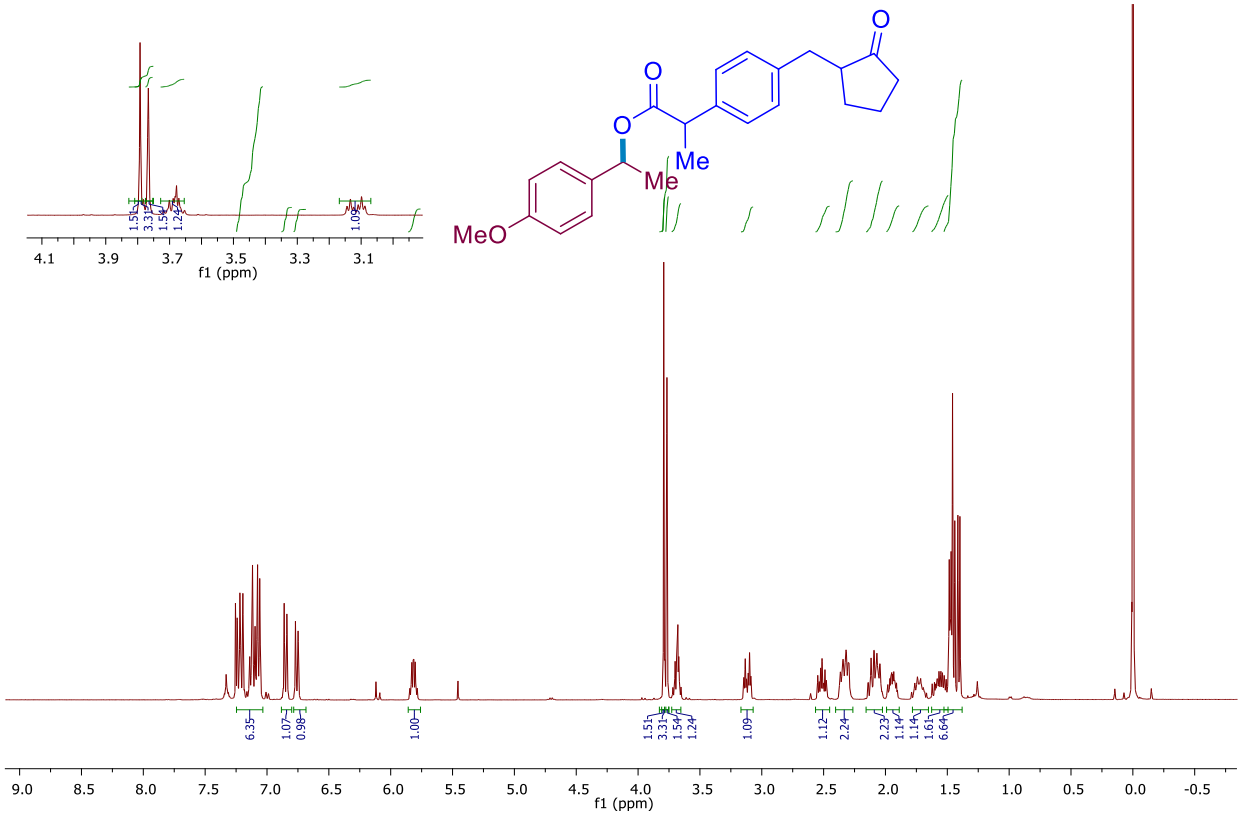


^{13}C NMR spectrum in $CDCl_3$

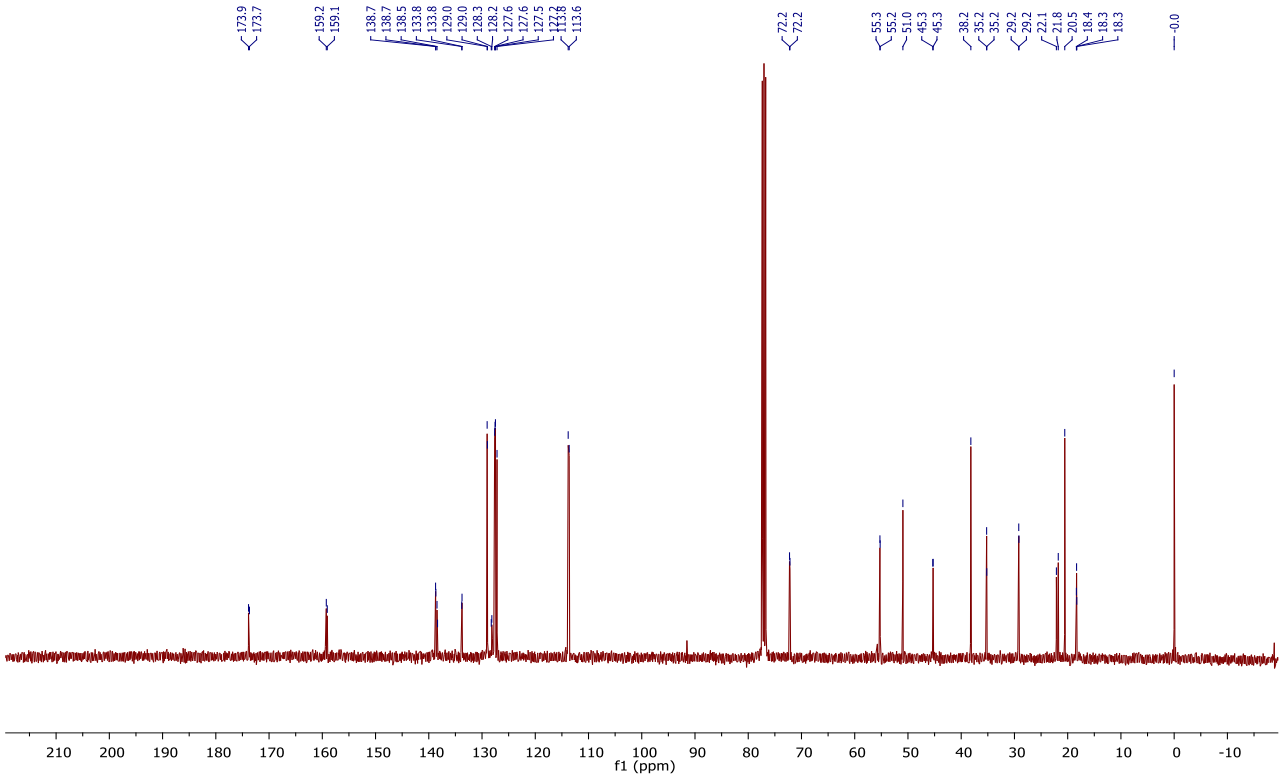


DEPT spectrum in $CDCl_3$.

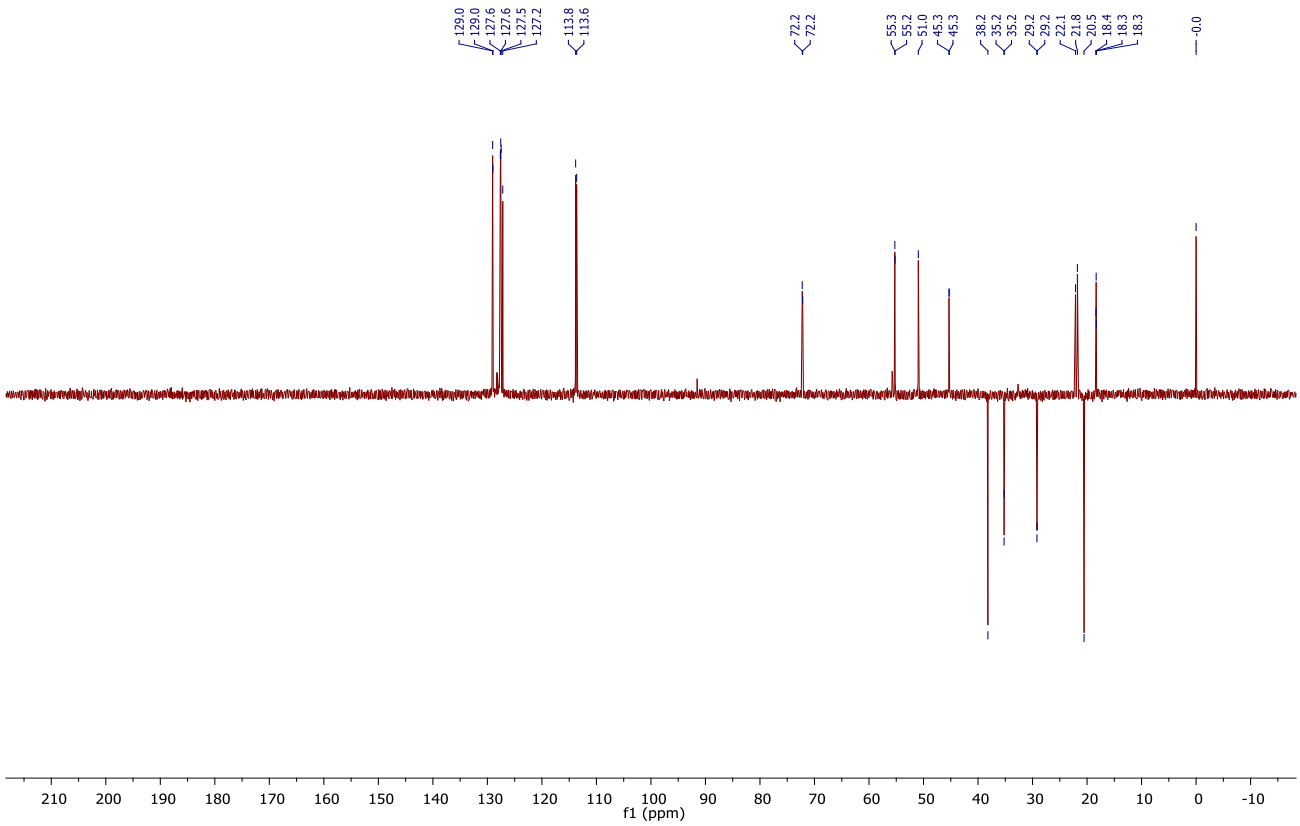
72c



^{1}H NMR spectrum in $CDCl_3$.

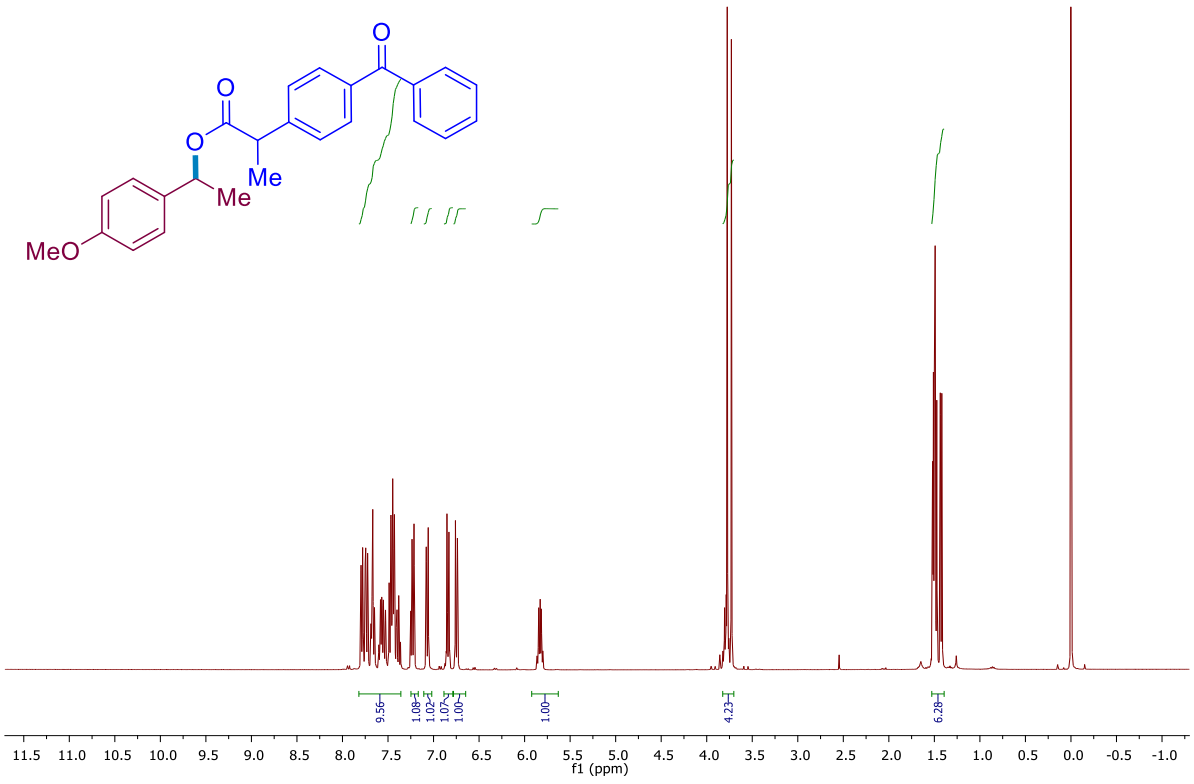


^{13}C NMR spectrum in $CDCl_3$

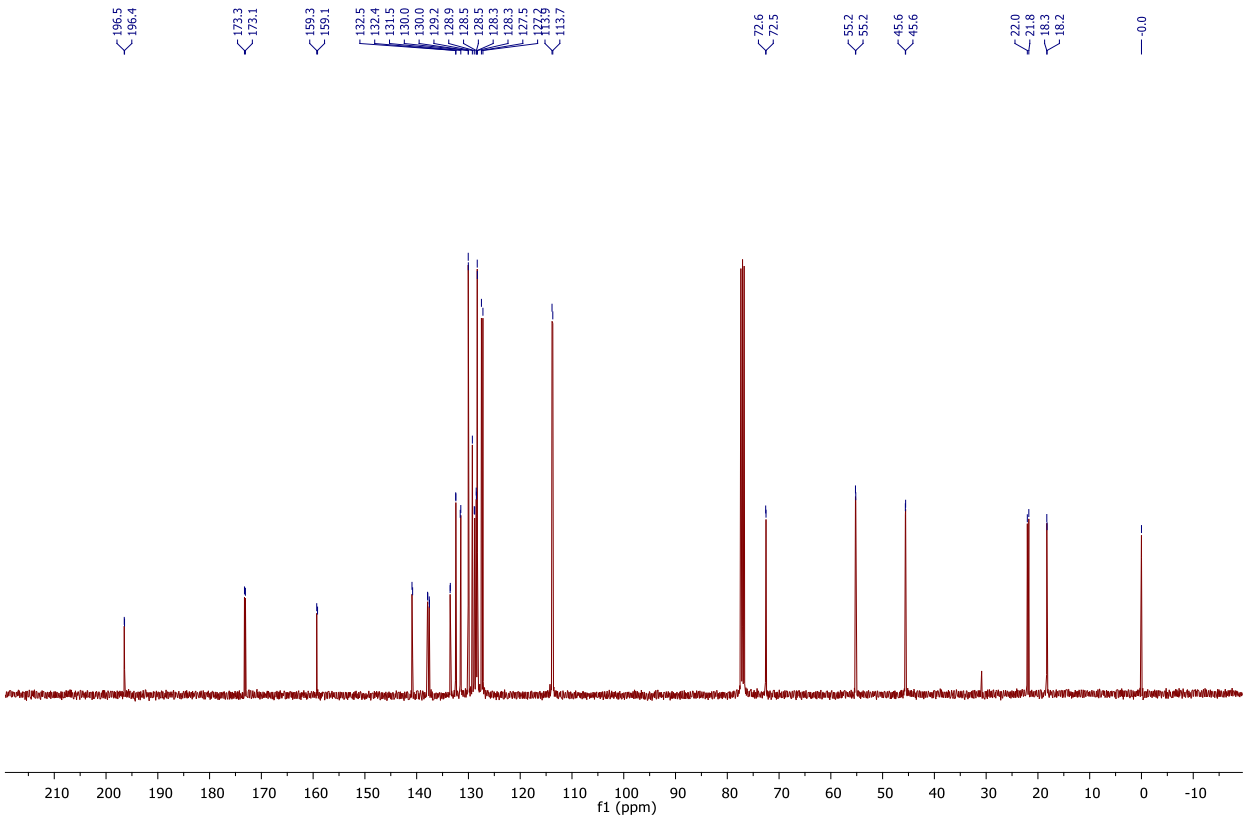


DEPT spectrum in $CDCl_3$.

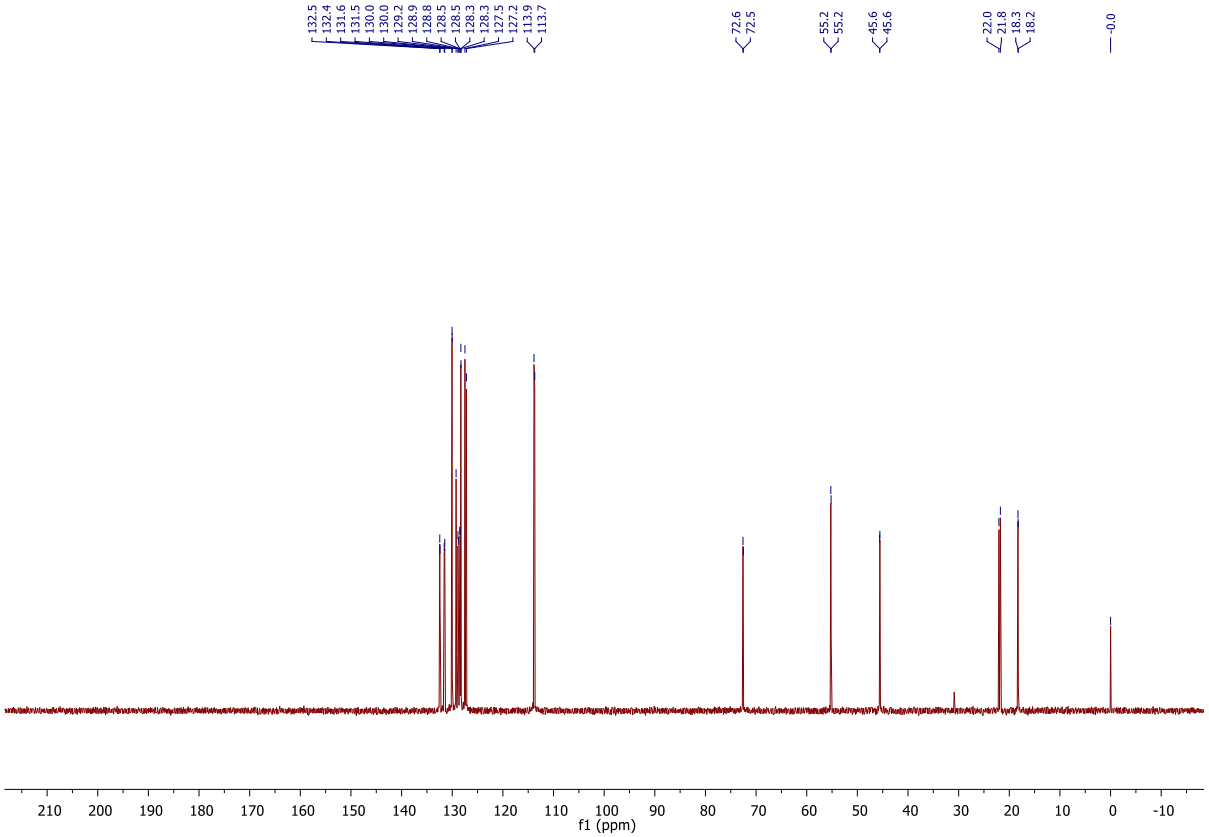
73c



^1H NMR spectrum in $CDCl_3$.

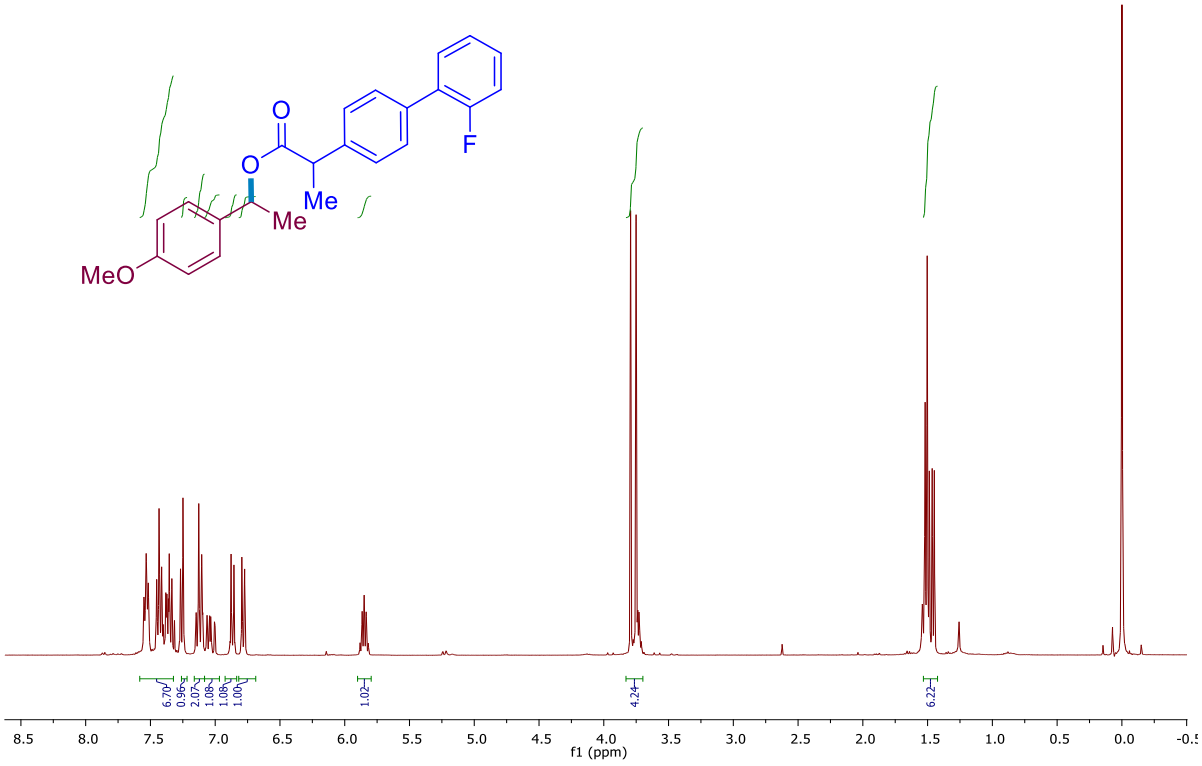


^{13}C NMR spectrum in $CDCl_3$

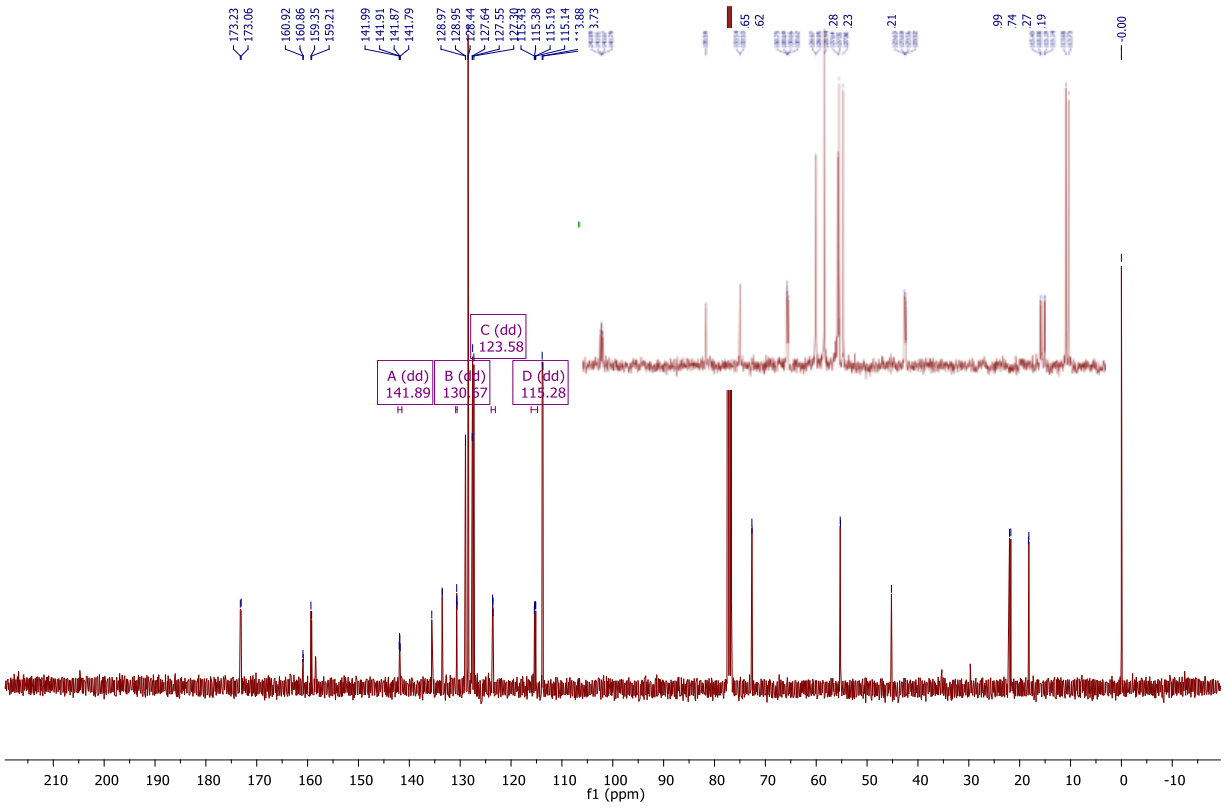


DEPT spectrum in $CDCl_3$.

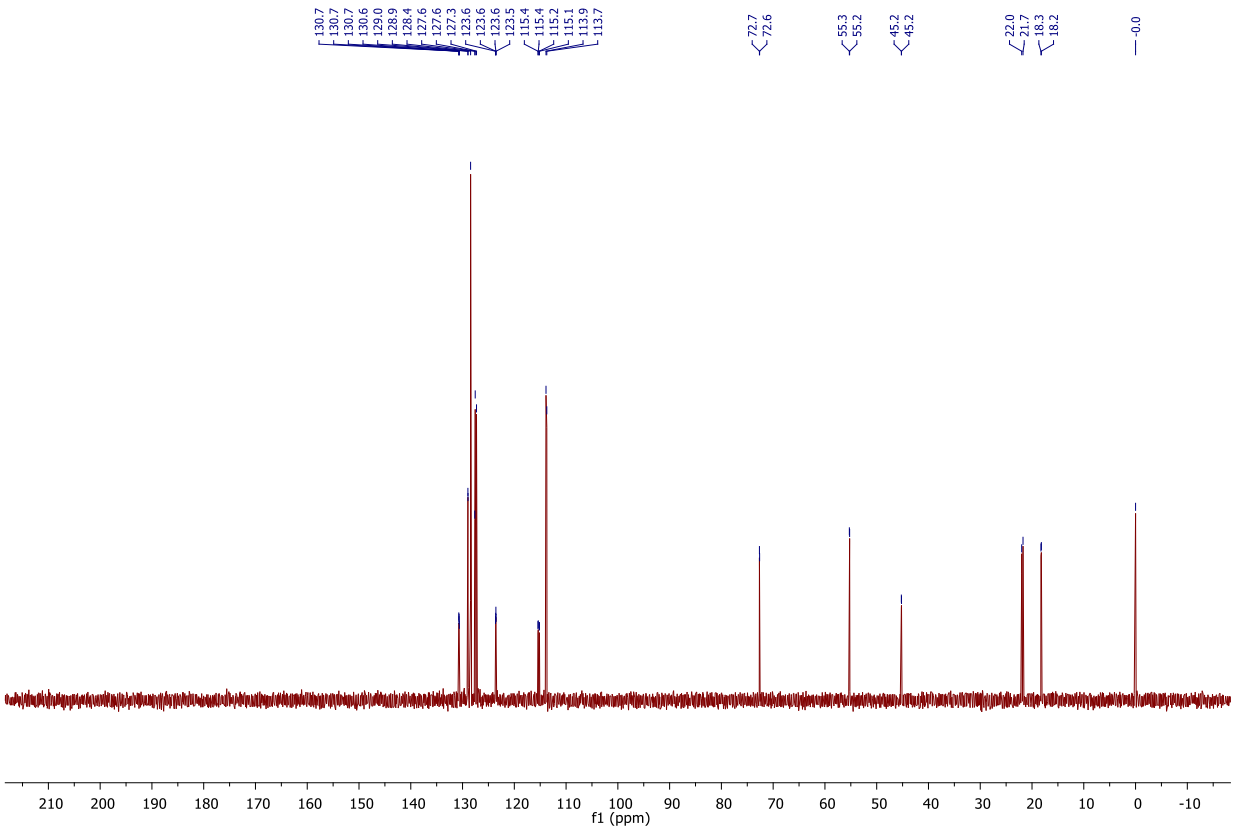
74c



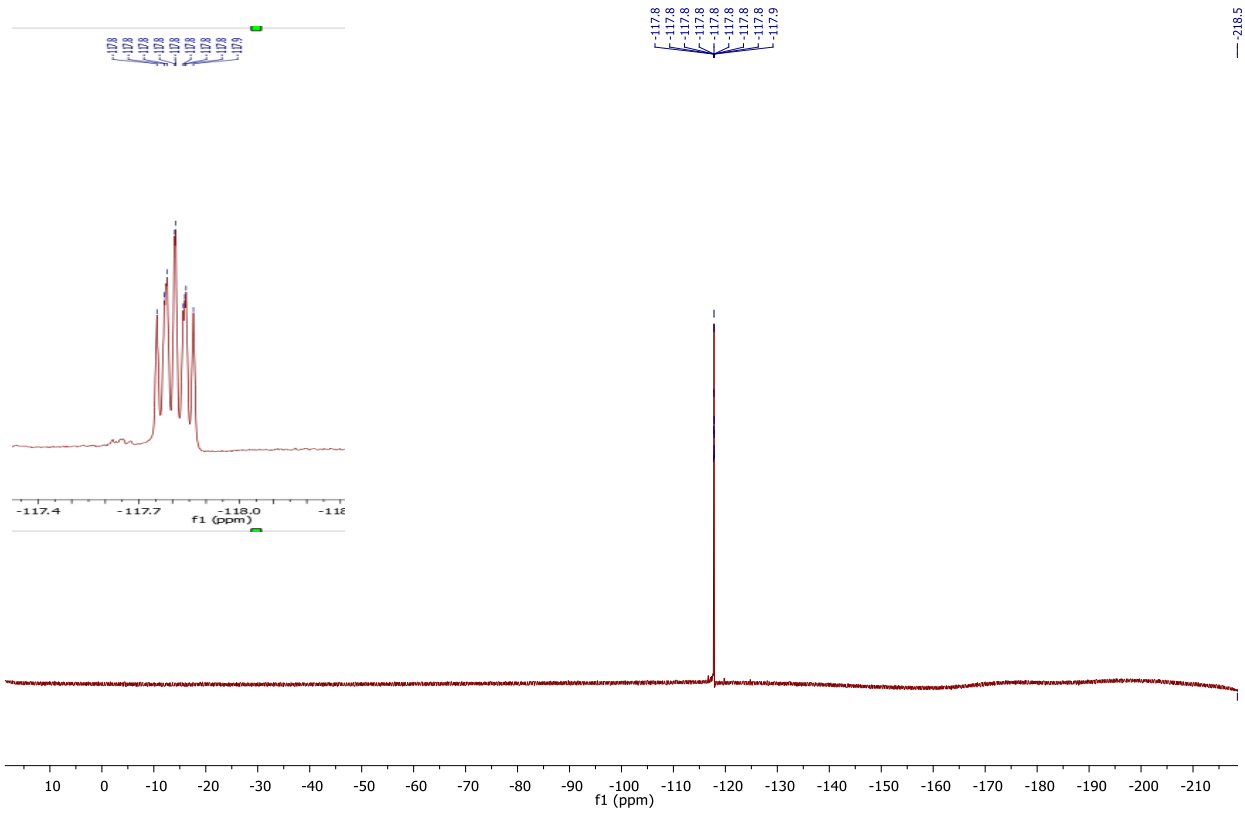
^{1}H NMR spectrum in $CDCl_3$



^{13}C NMR spectrum in $CDCl_3$

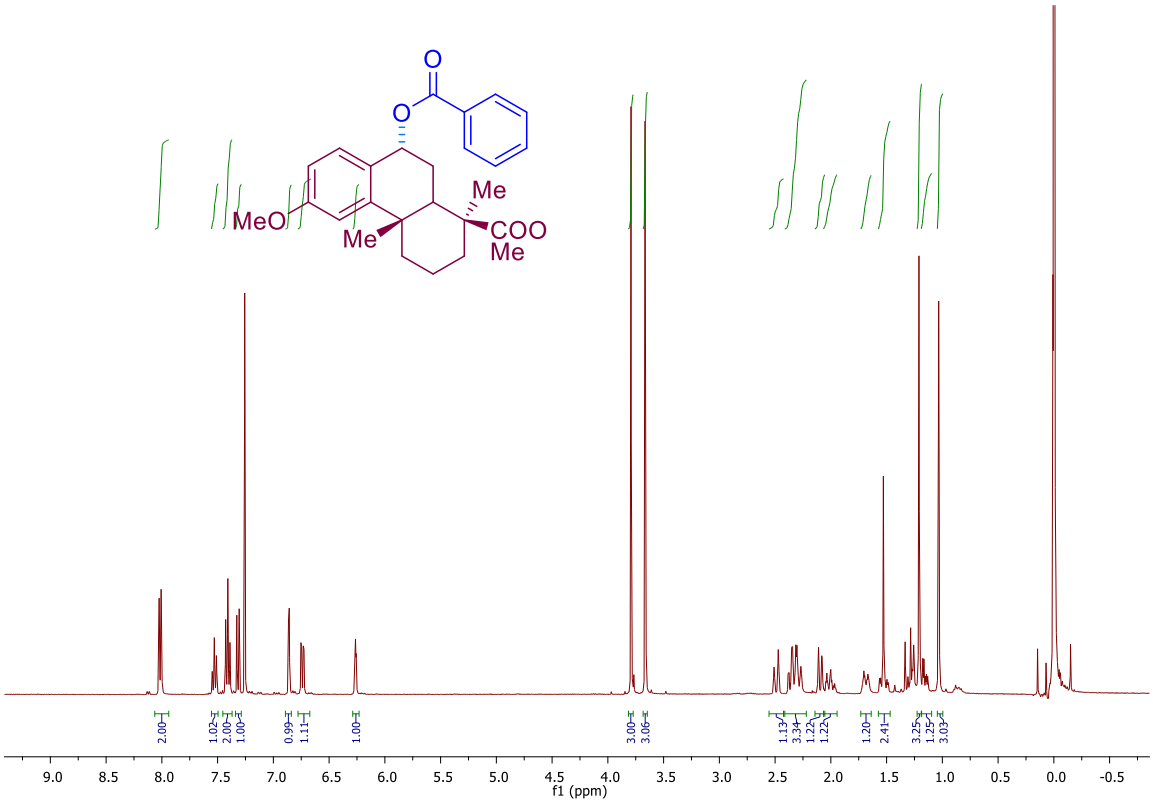


DEPT spectrum in $CDCl_3$.

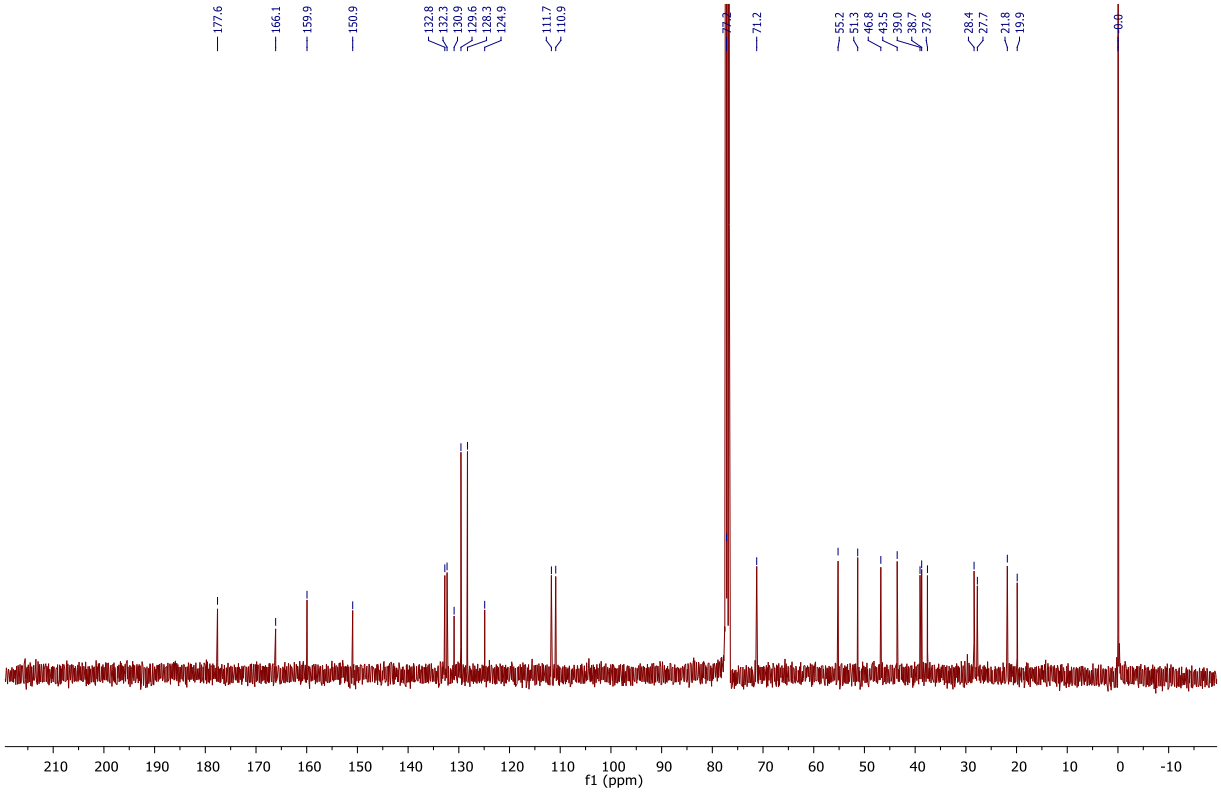


^{19}F NMR spectrum in $CDCl_3$.

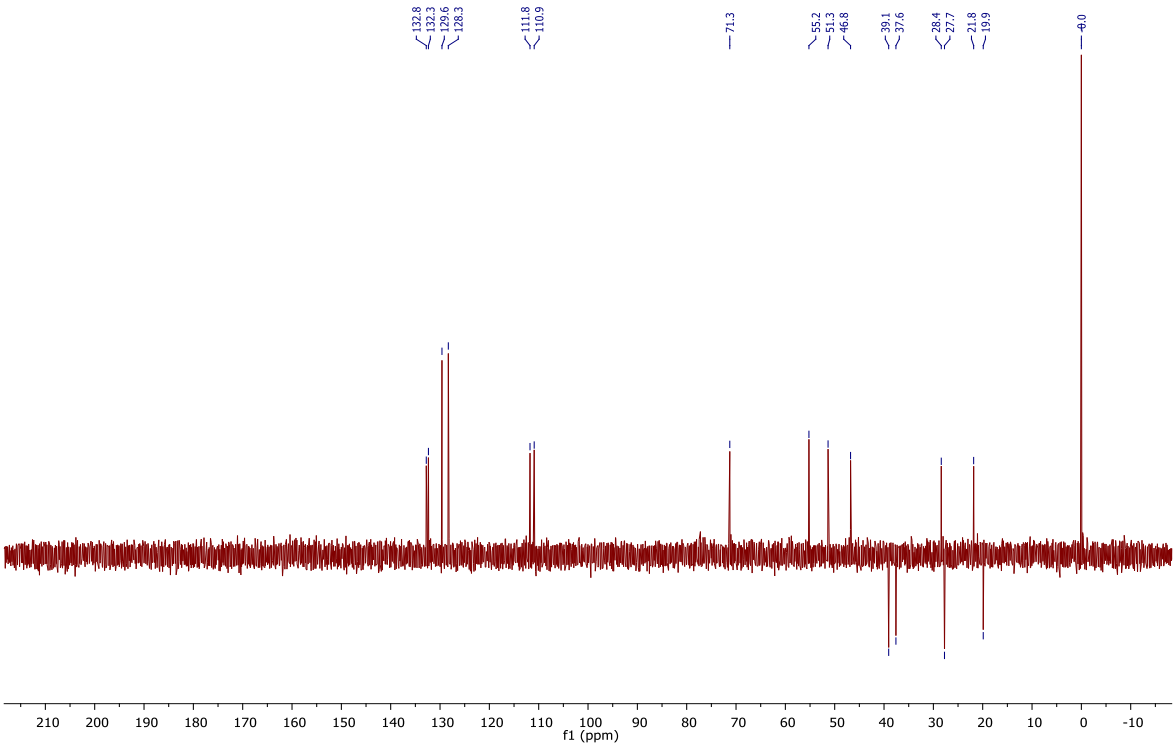
75c



^{1}H NMR spectrum in $CDCl_3$.

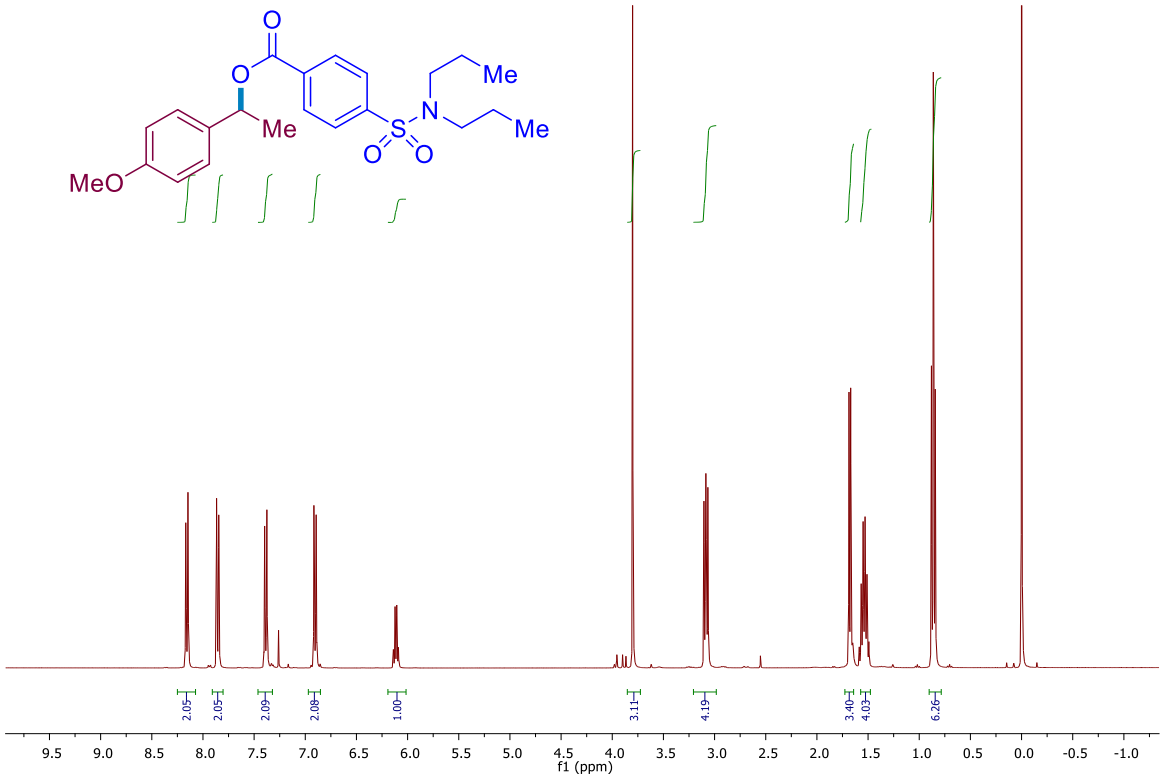


^{13}C NMR spectrum in $CDCl_3$

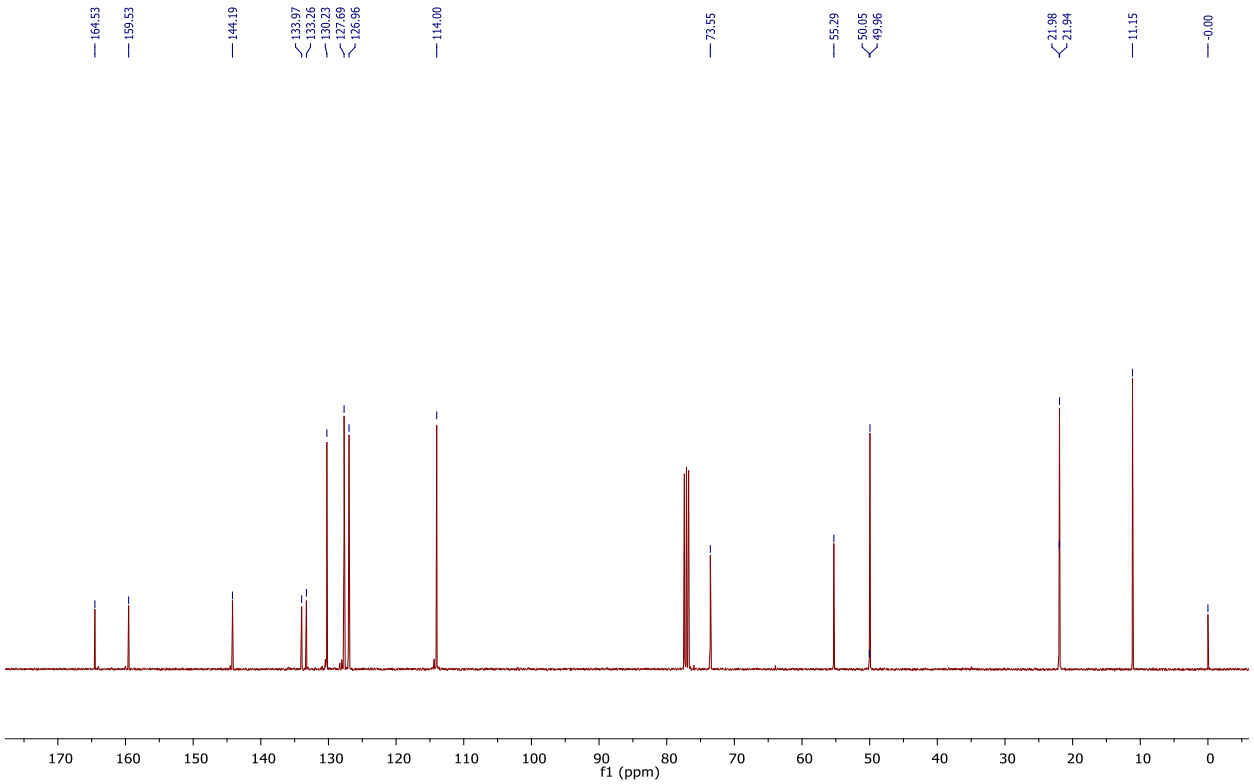


DEPT spectrum in $CDCl_3$.

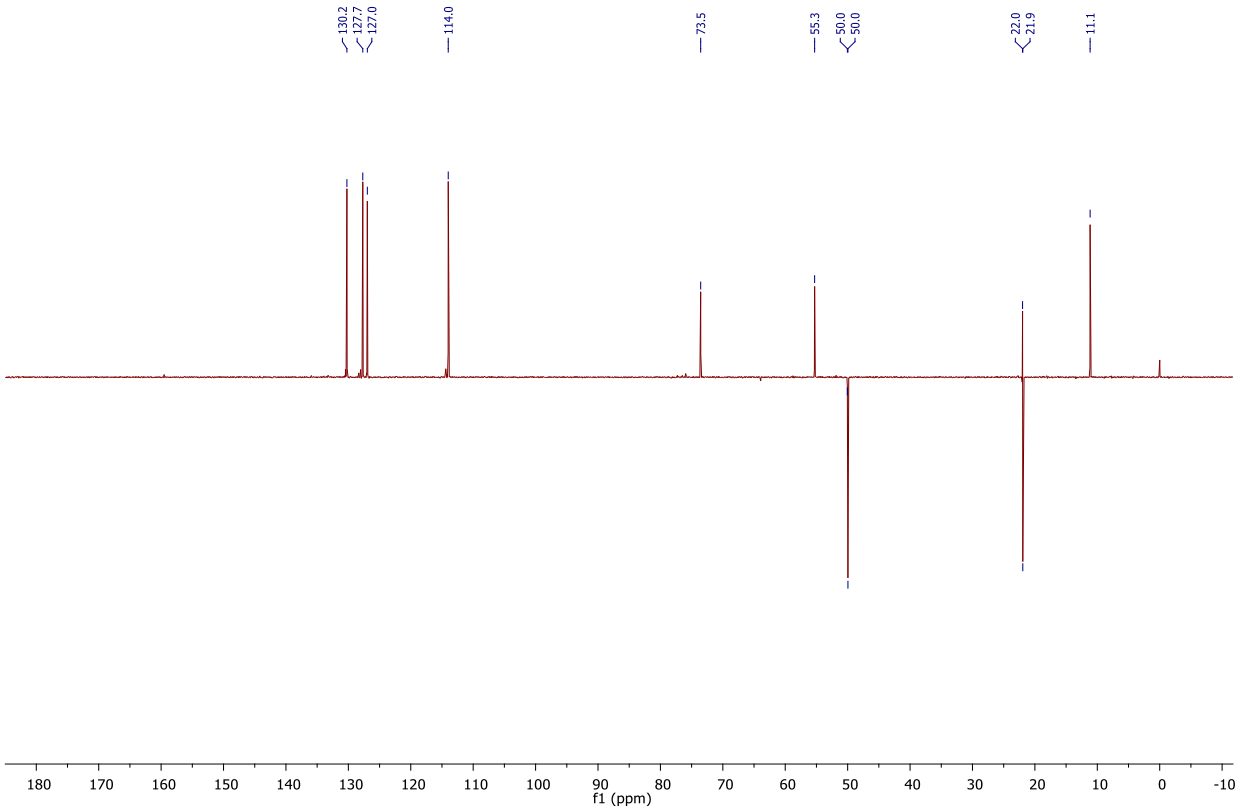
76c



^1H NMR spectrum in $CDCl_3$.

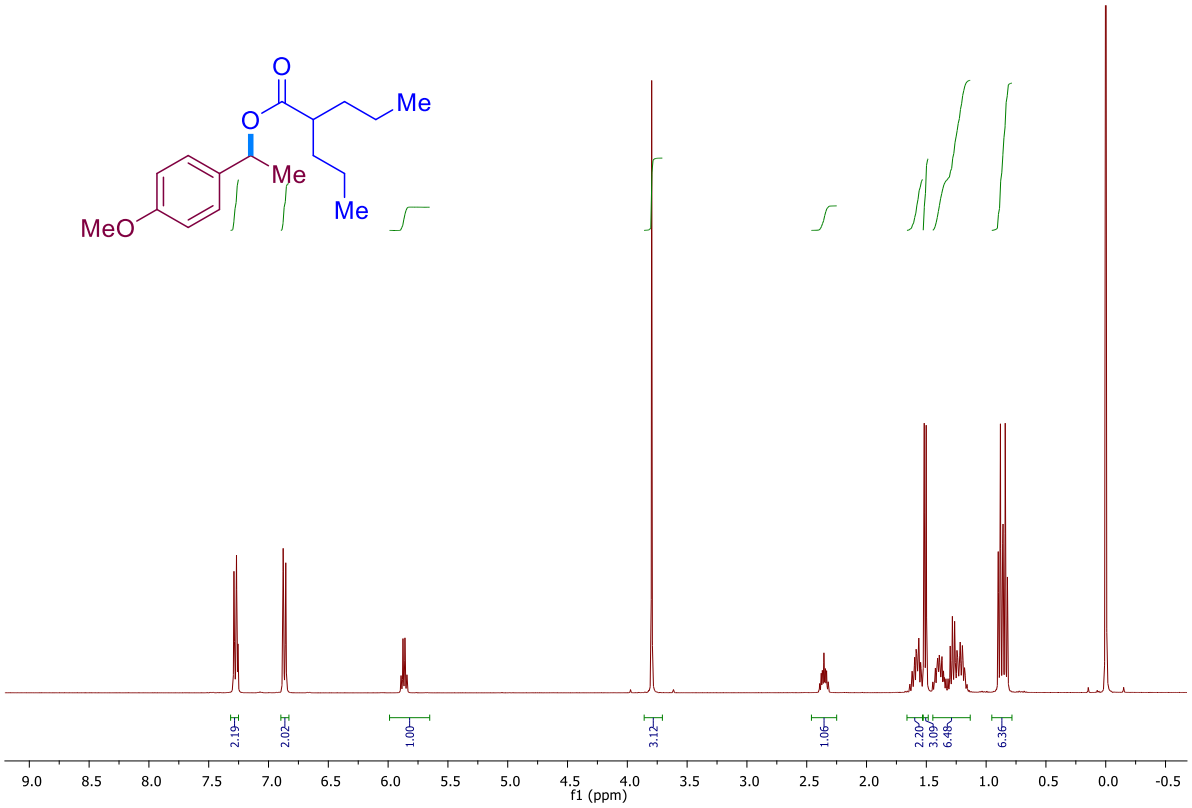


^{13}C NMR spectrum in $CDCl_3$

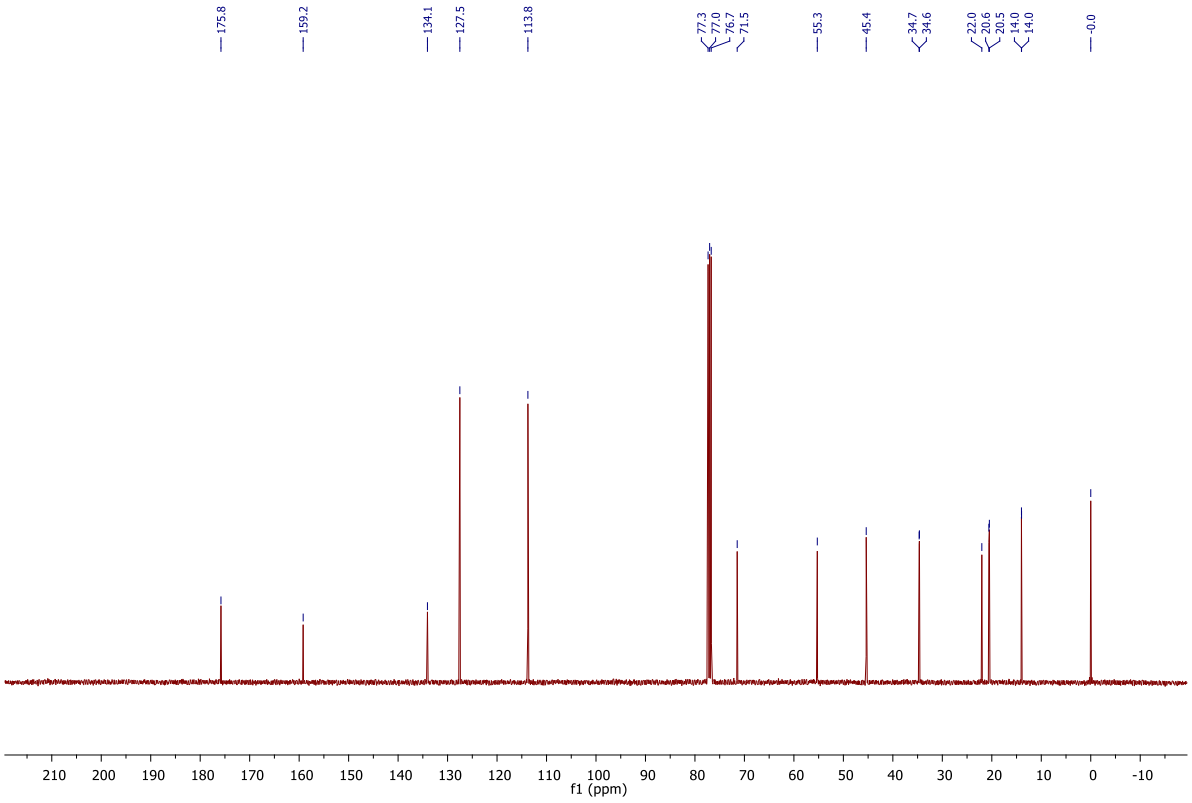


DEPT spectrum in $CDCl_3$.

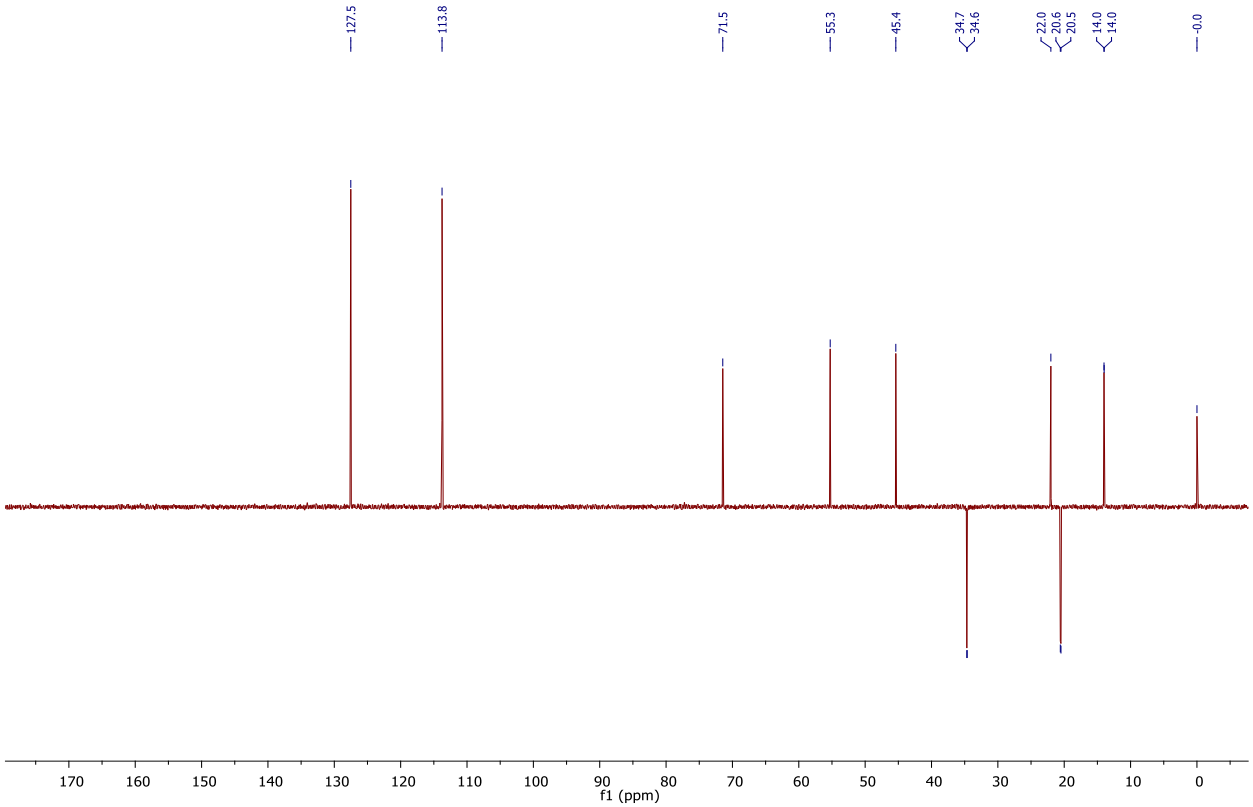
77c



^{1}H NMR spectrum in $CDCl_3$.

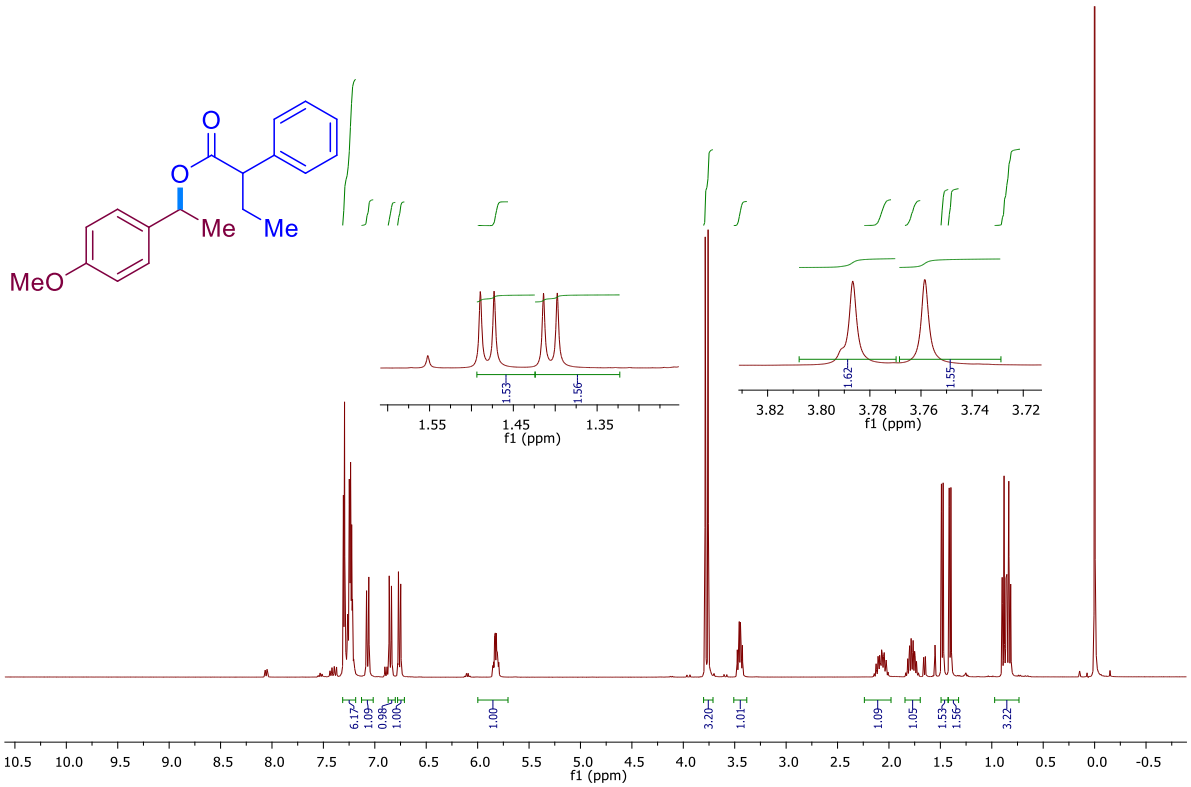


^{13}C NMR spectrum in $CDCl_3$

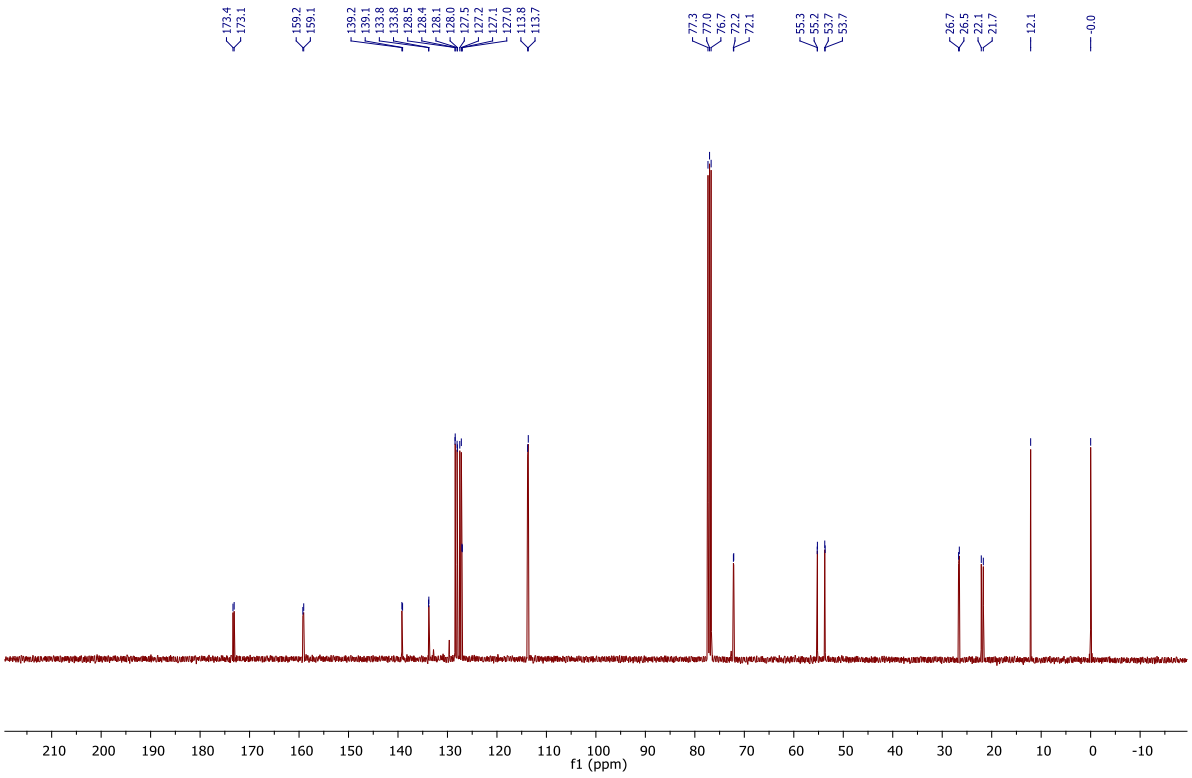


DEPT spectrum in $CDCl_3$.

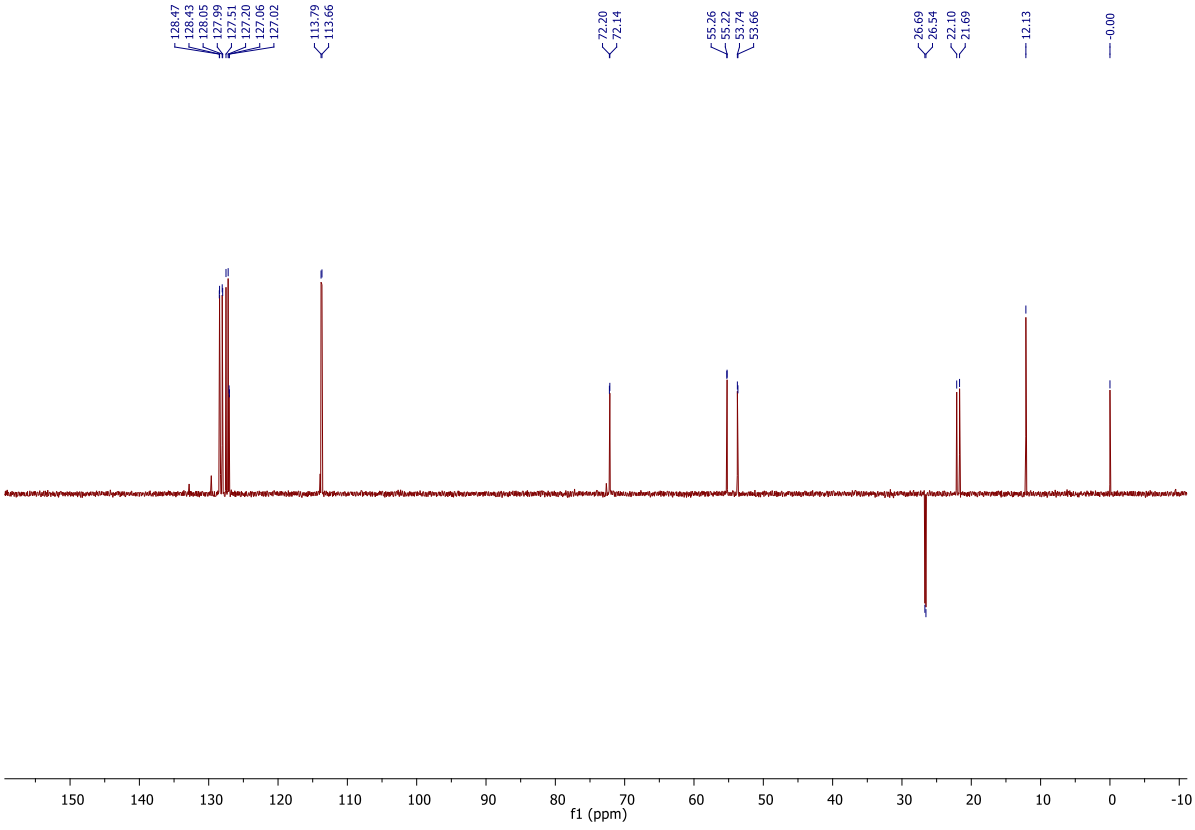
78c



^1H NMR spectrum in $CDCl_3$.

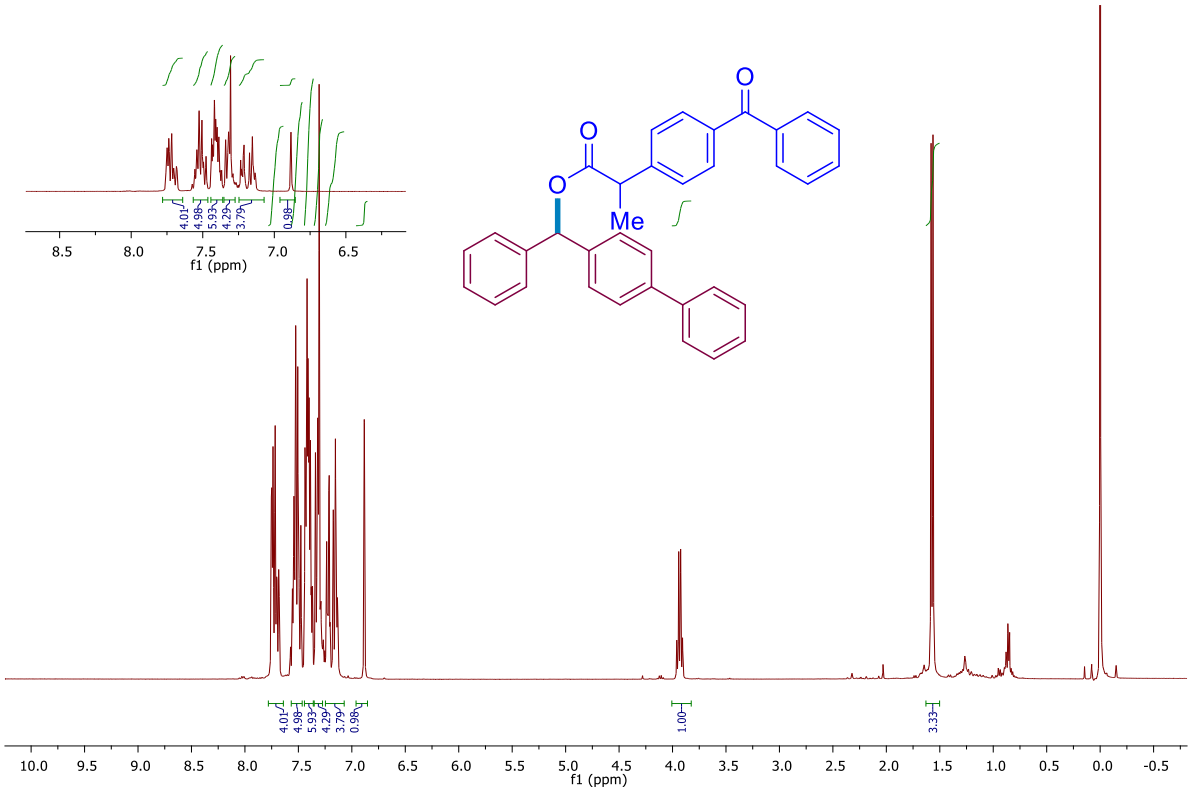


^{13}C NMR spectrum in $CDCl_3$

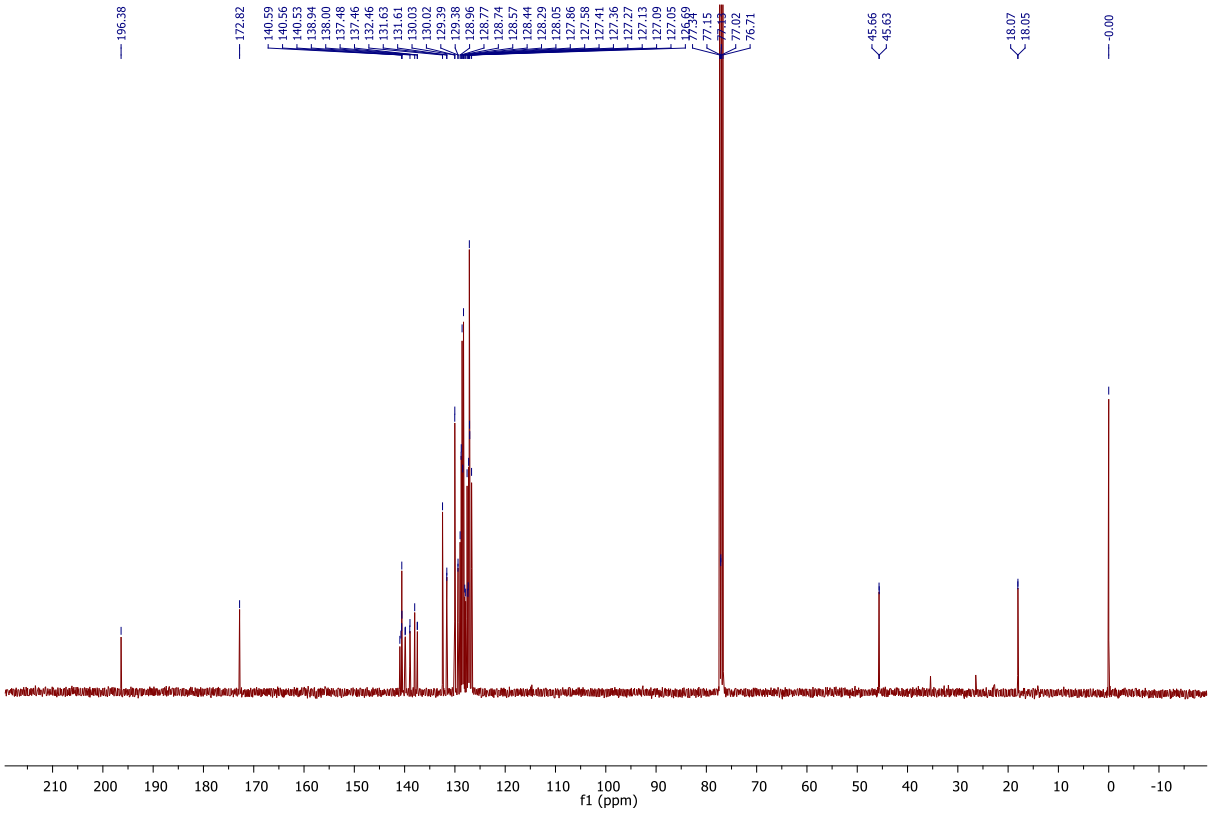


DEPT spectrum in $CDCl_3$.

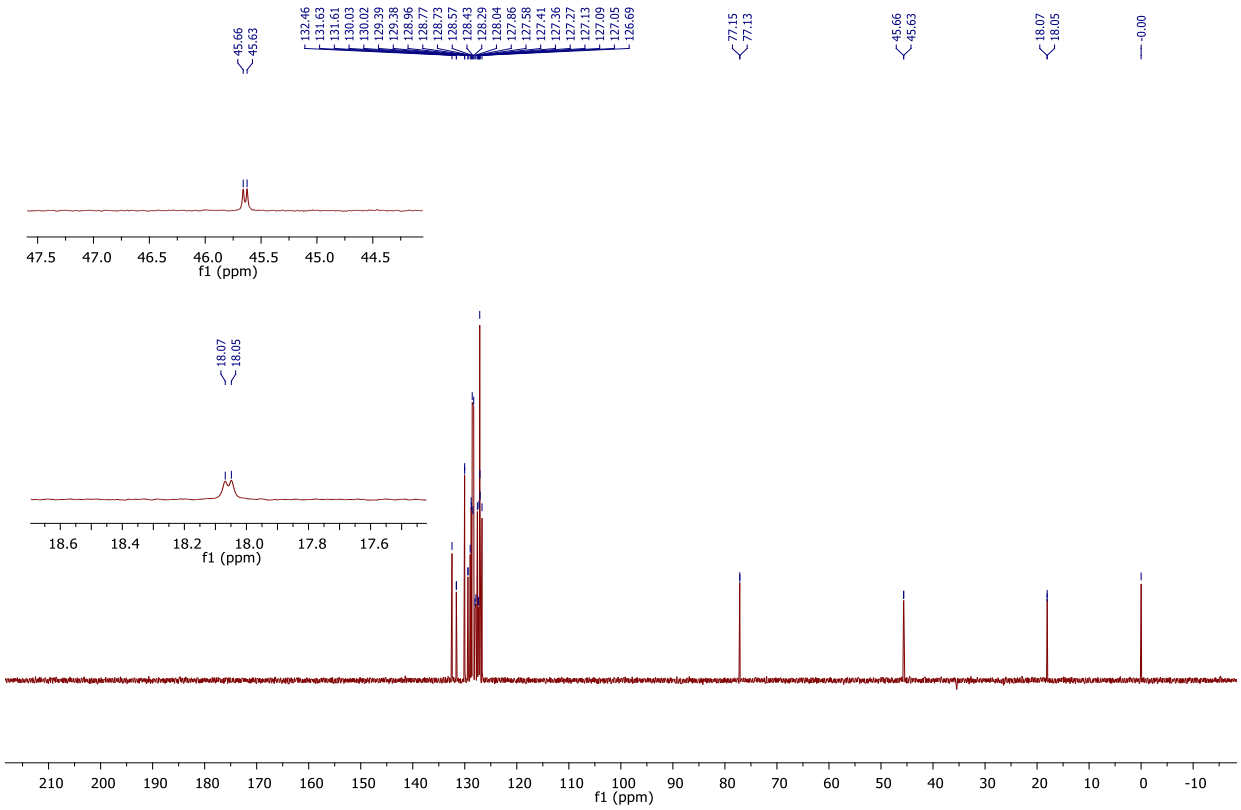
79c



^{1}H NMR spectrum in $CDCl_3$.



^{13}C NMR spectrum in $CDCl_3$



DEPT spectrum in $CDCl_3$.