Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Unlocking the Reactivity of Diazo Compounds on Red Light with the Use of Photochemical Tools

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1. General Information

Materials

All solvents and commercially available reagents were purchased from Sigma-Aldrich, TCI, Acros Organics and Alfa Aesar as reagent grade and were used without further purification, unless otherwise stated. Porphyrin catalysts were purchased from PorphyChem. Dry solvents were taken from Solvent Purification System (SPS) or purchased from Sigma Aldrich. All deuterated solvents used were purchased from Eurisotop.

General Procedures

Unless otherwise noted, reactions were performed without the exclusion of air or moisture. All the photochemical reactions were performed in 10 mL glassy vials sealed with aluminum caps containing a rubber septum. Reactions were monitored by thin layer chromatography (TLC), using 0.20 mm Merck silica plates (60F-254) and visualized using UV-light, potassium permanganate, cerium molybdate or anisaldehyde stain, with heat as a developing agent. Colum chromatography was performed on Merck silica gel 60 (230-400 mesh). GC yields were calibrated with dodecane as an internal standard. All yields determined by ^{1}H NMR analysis were obtained using dibromomethane or 1,3,5-trimethoxybenzene as the internal standard. Isolated yields refer to spectroscopically (^{1}H NMR) homogeneous materials. Structural assignments were made with additional information from gCOSY, gHSQC, and NOESY experiments.

Instrumentation

NMR spectra were recorded at ambient temperature (unless otherwise stated) on Bruker 400 MHz or Varian 500, 600 MHz. Chemical shifts are reported in ppm relative to the tetramethyl silane signal or a residual undeuterated solvent peak (TMS 0 ppm for ^{1}H and ^{13}C, $CHCl_3$ – 7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C, $(CD_3)_2CO$ – 2.05 ppm for ^{1}H and 29.8 ppm for ^{13}C, CD_2Cl_2 – 5.32 ppm for ^{1}H and 53.5 ppm for ^{13}C, $(CD_3)_2SO$ – 2.49 ppm for ^{1}H and 39.7 ppm for ^{13}C). Multiplicities are given as: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) broad singlet (brs).

LR and HRMS. Low-resolution mass spectra (LRMS) were recorded on an Applied Biosystems API 365 mass spectrometer using electrospray ionization (ESI) technique. High-resolution mass spectra (HRMS) were recorded on Waters SYNAPT G2-S HDMS instrument using electrospray ionization (ESI) or atmospheric-pressure chemical ionization (APCI) with time-of-flight detector (TOF).

Elemental analysis (C, H, N) were performed using a PERKIN-ELMER 240 Elemental Analyzer.

GC-MS analyses were performed using Shimadzu GCMS-QP2010 SE gas chromatograph with FID detector and Zebron ZB 5MSi column (length: 30.0 m; thickness: 0.25 um, diameter: 0.25 mm). **GC program:**

- time: 14.92 min;
- pressure: 90.8 kPa;
- total flow: 5.3mL/min;
- column flow: 1.11 mL/min;
- linear velocity: 27.5 cm/s;

- purge flow: 2.0 mL/min;
- split ratio: 2.0.

	Rate	Final Temperature	Hold Time
0	-	50.0	2.00
1	40.00	80.0	2.00
2	40.00	120.0	1.00
3	45.00	150.0	1.00
4	50.00	200.0	1.00
5	50.00	325.0	2.00

Flash column chromatography was performed on CombiFlash NextGen 300 Flash Chromatography System.

2. Photoreactor Setups

Red-light induced transformations were performed with the use of one of the following setups:

- **Studies on direct photolysis of diaryldiazoalkanes, photocatalyzed synthesis of γ-oximinoesters, phenantridines and hydrazones:**

The experiments were carried out in UOSlab Miniphoto photoreactor (Figure F1). Red (emission maximum at 655 nm) light was supplied to each reaction vial with the use of 7 LUMINUS LED units (of overall 25 W intensity when 100% power applied). The ambient temperature of LED block was maintained by cooling with Huber MiniChiller 300 ($T_{reaction}$ ~30°C).

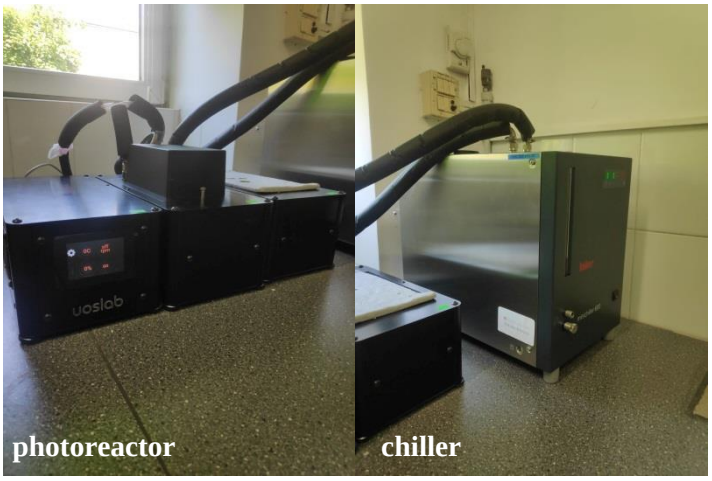


Figure F1. Standard photoreactor setup (655 nm, 25 W) with chiller.

- **Studies on photosensitized oxygenation of aryldiazoesters, photocatalyzed synthesis of β-amino-α-diazoesters:**

The experiments were carried out in a specially constructed photoreactor composed of cooling block (connected to Huber MiniChiller 300) and plate with red LEDs of 3 W power with maximum emission at 660 nm (Figure F2) ($T_{reaction}$ ~30°C).

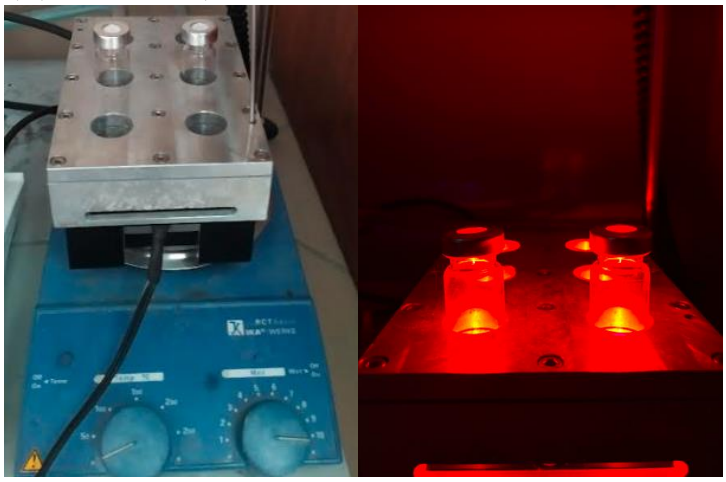


Figure F2. Standard photoreactor setup (660 nm, 3 W).

- **Studies on photosensitized O-H insertion of aryldiazoesters with benzoic acid and photosensitized cyclopropanation with aryldiazoesters:**

The experiments were carried out with the use of commercially available Kessil lamps. Red (emission maximum at 640 nm) light was supplied to each reaction vial with the use of two Kessil lamps, each of overall 40 W intensity (when 100% power applied), placed at opposite sites (Figure F3). The ambient temperature of LED block was maintained by cooling with the use of fans ($T_{reaction}$ ~30°C)

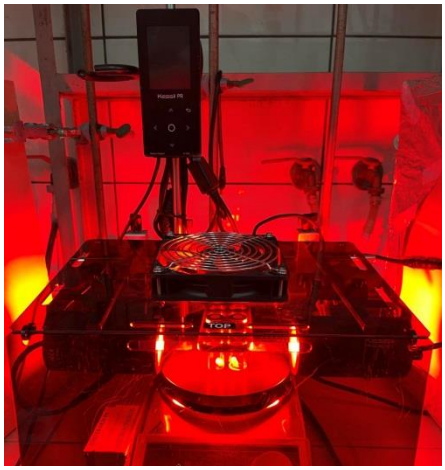


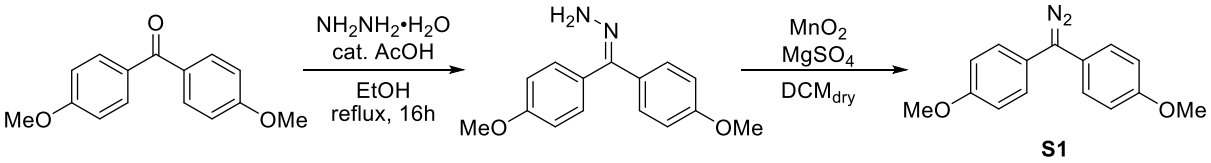
Figure F3. Standard photoreactor setup (640 nm, 2 x 40 W).

3. General synthetic procedures

3.1. Preparation of diazo compounds

Ethyl diazoacetate, *t*-butyl diazoacetate and benzyl diazoacetate are commercially available reagents (stab. with DCM) and were purchased from Sigma-Aldrich. All other diazo compounds were synthesized according to literature procedures. The observed characterization data (^{1}H and ^{13}C NMR) are consistent with those previously reported.[1-11]

3.1.1. Synthesis of 4,4'-(diazomethylene)bis(methoxybenzene) (S1)

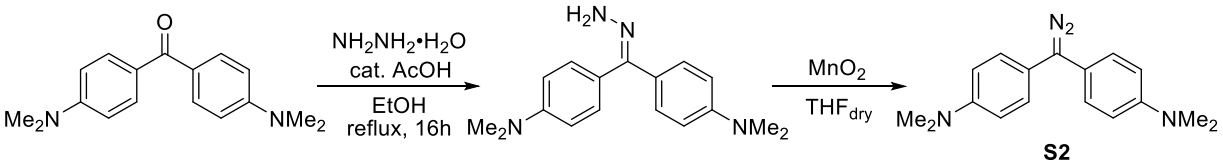


S1

Step 1: Following the reported literature.[1] Hydrazine monohydrate (100 mmol, 4.9 mL) was added to benzophenone derivative (10 mmol, 2.4 g) in EtOH (20 mL). Then AcOH (0.17 mL) was added and the mixture was heated at reflux for 16 h. After cooling to room temperature, benzophenone hydrazone precipitated. The crude mixture was filtrated and solid was washed with small amount of cold EtOH. Crystals were dried on vacuum pump to obtain pure benzophenone hydrazone derivative (2.3 g, 89% yield).

Step 2: Following the reported literature.[1] The suspension of benzophenone hydrazone derivative (5 mmol, 1.3 g) and anhydrous $MgSO_4$ (6.5 mmol, 0.8 g) in DCM (13 mL) was cooled to 0 °C. To this rapidly stirring mixture activated MnO_2 (25 mmol, 2.2 g) was added in one portion. The reaction mixture was warmed to room temperature and stirred for 3 h. The mixture was filtrated through Celite® and washed until the filtrate became colorless. After removal of the solvent under reduced pressure, the residue was purified by column chromatography using silica gel (neutralized by washing with Et_3N/PE = 1:10) with Et_3N/hexane = 1:20 as eluent to afford diaryldiazomethane **S1** (1.3 g, 99% yield) as a purple solid which was stored at -20 °C under argon. The characterization data (^{1}H and ^{13}C NMR) are consistent with those reported in literature.[1]

3.1.2. Synthesis of 4,4'-(diazomethylene)bis(N,N-dimethylaniline) (S2)



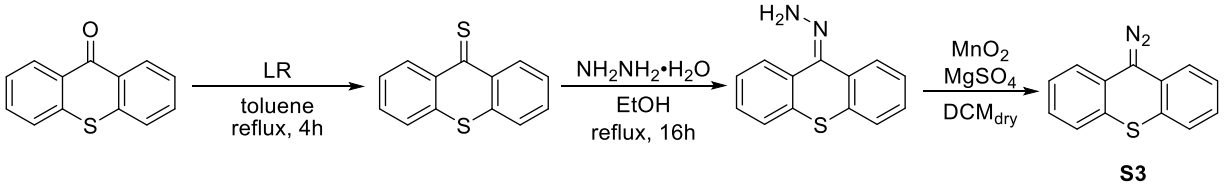
S2

Step 1: Following the reported literature,[1] analogously to Step 1 in 3.1.1. The product was obtained as a yellow needle-shaped crystals (2.4 g, yield 84%).

Step 2: Following the reported literature.[2] Activated MnO_2 (4.0 mmol, 350 mg) was added to rapidly stirred solution of the Michler's ketone hydrazone in THF (2 mL) cooled to -78 °C (0.4 mmol, 113 mg). The resulting mixture was stirred for 5 min -78 °C and then warmed to 0 °C and stirred an additional 20 min in in the absence of light (aluminum foil coated). Obtained solution of diazo compound **S2**

derivative was then transferred through a hydrophobic PTFE syringe filter into a glass vial equipped with a stirring bar (0.5 mL of THF was used for washing flask) and used to perform O-H insertion without further purification.

3.1.3. Synthesis of 9-diazo-9H-thioxanthene (S3)



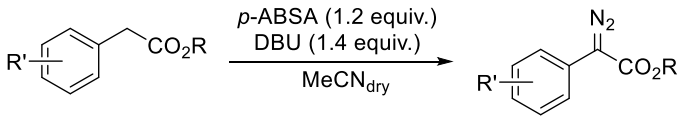
S3

Step 1: Following the modified procedure described in the literature.[12] In a round-bottomed flask equipped with reflux condenser with balloon and a magnetic stirrer ketone (6 mmol, 1.3 g) was dissolved in toluene (25 mL). Lawesson's reagent (LR, 3 mmol, 1.2 g) was added to the mixture. The reaction mixture was stirred in reflux for 4 h. After cooling to room temperature, the mixture was filtrated by silica plug using DCM/toluene = 1:10 as an eluent. After removal of the solvent under reduced pressure brown solid was obtained, used in the second step without further purification.

Step 2: Following the reported literature.[13] Crude thioxanthene-9-thione synthesized in *step 1* was dissolved in EtOH (22 mL) and hydrazine monohydrate (36 mmol, 1.7 mL) was added dropwise. Solution was heated under reflux for 2 h and filtered while hot. The filtrate was then cooled to room temperature and stored at -78 ^{o}C overnight. The resulting gray-yellow solid precipitated. After filtration and drying on vacuum pump pure thioxanthene-9-thione hydrazone was obtained (281 mg, 23% yield after 2 steps).

Step 3: Following the reported literature,[1] analogously to Step 2 in 3.1.1. Crude product was purified using alumina gel column chromatography and pentane as eluent to afford diaryldiazomethane **S3** as a green solid (131 mg, 47% yield) which was stored at -20 °C under argon. The observed characterization data (^{1}H and ^{13}C NMR) are consistent with those reported in the literature.[3]

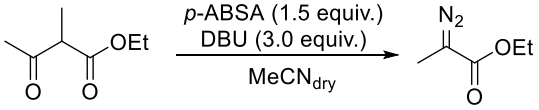
3.1.4. Synthesis of aryldiazoesters S4-S11



S4-S11

Following the reported literature.[4] A solution of a carbanion precursor (2 mmol) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA, 2.4 mmol, 0.6 g) in anhydrous MeCN (2.0 mL) was stirred under argon atmosphere at 0 °C. DBU (3.2 mmol, 0.5 mL) was added dropwise, then cooling bath was removed. The mixture was stirred until full conversion of the starting material was observed by the TLC. The reaction was quenched with sat. NH_4Cl and extracted with DCM (3 times), combined organic layers were washed with brine and dried over magnesium sulfate. The mixture was then filtered and evaporated *in vacuo*, crude product was purified by column chromatography (hexane:AcOEt as eluent**).**

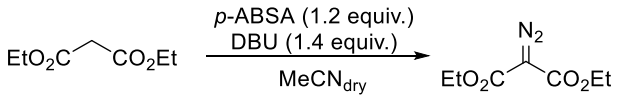
3.1.5. Synthesis of ethyl 2-diazopropanoate (S12)



S12

Following the reported procedure.[9] A solution of a ethyl 2-methyl-3-oxobutanoate (10 mmol, 1.2 mL) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA, 15 mmol, 3.6 g) in anhydrous MeCN (20 mL) was stirred under argon atmosphere at 0 °C. DBU (30 mmol, 4.5 mL) was added dropwise. The reaction mixture was then allowed to warm to room temperature and stirred overnight. Then, the reaction mixture was quenched with 1 M HCl (20 mL), and extracted with hexane (3 x 50 mL). The organic layers were combined and washed with saturated solution of $NaHCO_3$ (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the mixture was purified by flash column chromatography using Et_2O/pentane = 1:50 to give diazo compound **S12** as yellow oil (0.9 g, 70%). The observed characterization data (^{1}H and ^{13}C NMR) are consistent with those reported in the literature.[9]

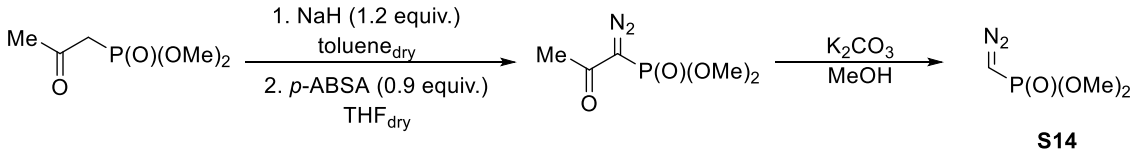
3.1.6. Synthesis of diethyl 2-diazomalonate (S13)



S13

Following the reported literature,[1] analogously to aryldiazoester synthesis (3.1.4). The observed characterization data (^{1}H and ^{13}C NMR) are consistent with those reported in the literature.[10]

3.1.7. Synthesis of dimethyl (diazomethyl)phosphonate (S14)



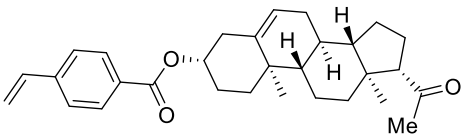
S14

Step 1: Following the reported literature.[11] To a solution of dimethyl (2-oxopropyl)phosphonate (20 mmol, 2.7 mL) in dry toluene (40 mL) cooled to 0 °C, NaH (24 mmol, 1.0 g of NaH 60% disp. in mineral oil) was added portionwise. The mixture was stirred at 0 °C for 1 hour and then a solution of *p*-acetamidobenzenesulfonyl azide (*p*-ABSA, 18 mmol, 4.3 g) in anhydrous THF (15 mL) was added dropwise. The mixture was stirred at room temperature for 24 h. Hexane (20 mL) was added and the precipitate was filtered off, washed with ether (3 x 20 mL). The filtrate was evaporated and the residue was purified by flash column chromatography on silica gel (hexane:ethyl acetate) to dimethyl (1-diazo-2-oxopropyl)phosphonate as a yellow liquid (3.4 g, 90 %).

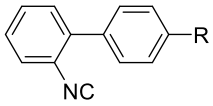
Step 2: Following the modified procedure described in the literature.[11] A solution of dimethyl (1-diazo-2-oxopropyl)phosphonate (18 mmol, 3.4 g) in methanol (20 mL) was stirred with potassium carbonate (9 mmol, 1.2 g) for 25 min. The precipitate was filtered off and the filtrate was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane:ethyl acetate) to give diazo compound **S14** as yellow liquid (2.2 g, 80 %).

3.2. Preparation of other starting materials

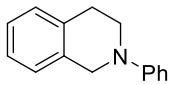
Along with diazo compounds, starting materials **S15-S23** were synthesized according to literature procedures. The observed characterization data (^{1}H and ^{13}C NMR) are consistent with those previously reported.[14-17]



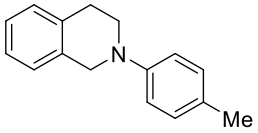
S15[14]



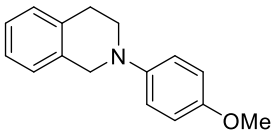
R = H, **S16**[15]
R = OMe, **S17**[15]



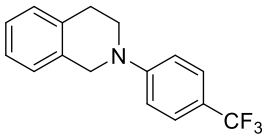
S18[16]



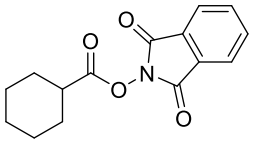
S19[16]



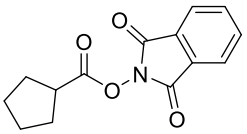
S20[16]



S21[16]

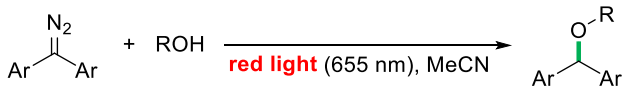


S22[17]

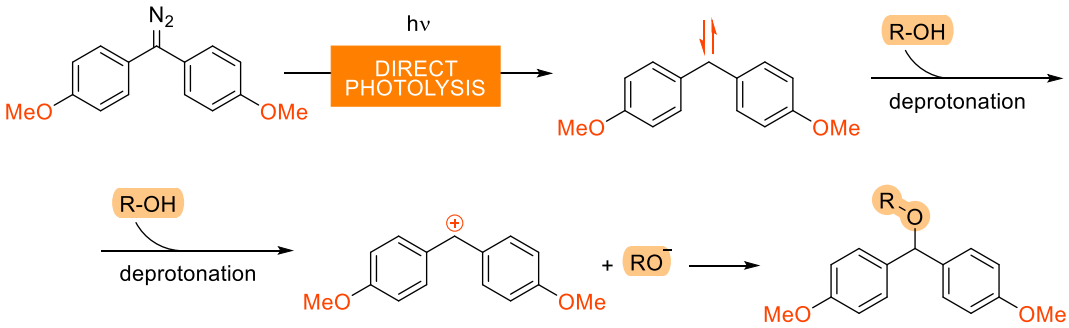


S23[17]

3.3. General procedure for the red light-induced O-H insertion of diaryldiazoalkanes with alcohols



Mechanism:



To a glass vial equipped with a stirring bar diazoalkane (0.2 mmol) was added. A vial was sealed with an aluminum cap with a rubber septum and charged with 2.0 mL of MeCN and alcohol (2 mmol, 10 equiv.). The reaction mixture was placed in a photoreactor and irradiated with red LEDs (25 W, 655 nm) until full discoloring of the purple solution was achieved (ca. 135 min). After that time, the crude reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel using hexane:AcOEt as eluent to afford final product.

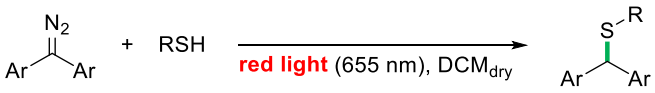
*Note: In the case of products **8**, **9**, **11** other substrates ratio was used. Additionally, for product **11** THF was used instead of MeCN at altered concentration.*

3.4. General procedure for the red light-induced N-H insertion of diaryldiazoalkanes with amines

To a glass vial equipped with a stirring bar 4,4'-(diazomethylene)bis(methoxybenzene) (**S1**, 0.4 mmol, 2 equiv.) was added. The vial was sealed with an aluminum cap with a rubber septum, purged with argon and charged with 2.0 mL of dry DCM and amine (0.2 mmol). The reaction mixture was placed in a photoreactor and irradiated with red LEDs (25 W, 655 nm) until full discoloring of the purple solution was achieved (ca. 135 min). After that time, the crude reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel using Et_3N:hexane as eluent to afford the final product.

*Note: In the case of product **13** other substrates ratio was used.*

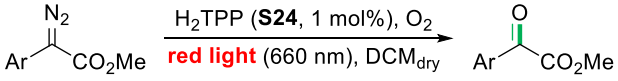
3.5. General procedure for the red light-induced S-H insertion of diaryldiazoalkanes with thiols



To a glass vial equipped with a stirring bar model diazo compound (0.4 mmol, 2 equiv.) was added. The vial was sealed with an aluminum cap with a rubber septum, purged with argon and charged with 2.0 mL of dry DCM and thiol (0.2 mmol). The reaction mixture was placed in a photoreactor and irradiated with red LEDs (25 W, 655 nm) until full discoloring of the purple solution was achieved (ca. 135 min). After that time, the crude reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel using hexane:AcOEt as an eluent to afford the final product.

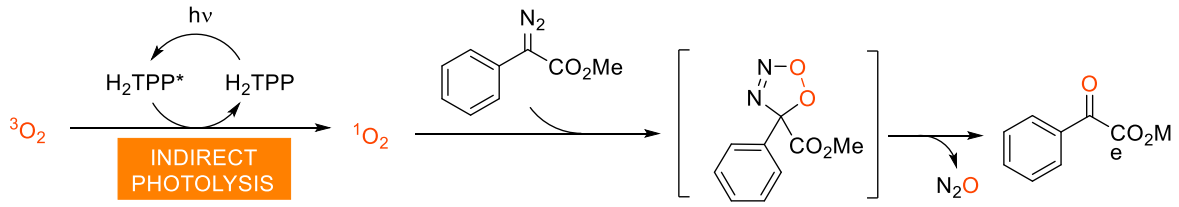
*Note: In the case of product **22** and **23** other substrates ratio was used.*

3.6. General procedure for the red light-induced, photosensitized oxygenation of aryldiazoesters



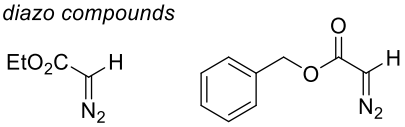
A glass vial equipped with a stirring bar was charged with tetraphenylporphyrin (H_2TPP, **S24**, 0.001 mmol, 0.6 mg), α-diazoester (0.1 mmol) and dry DCM (1.0 mL). A vial was sealed with an aluminum cap with a rubber septum and air was removed from the solution by freeze-pump-thaw technique, followed by refilling the vial with oxygen with O_2 balloon. The reaction mixture was placed in a photoreactor and irradiated with red LEDs (3 W, 660 nm) for 1 h. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel using hexane:AcOEt as eluent to afford the final product.

Mechanism:

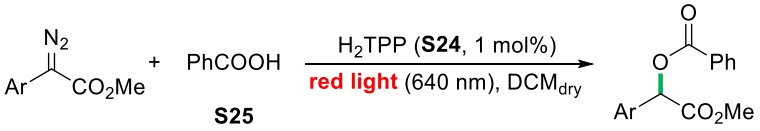


Failed substrates:

diazo compounds

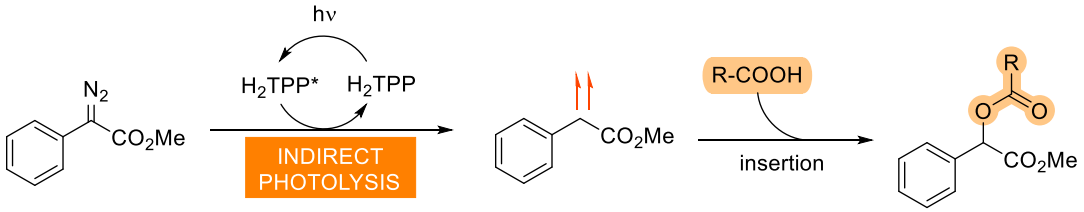


3.7. General procedure for the red light-induced, photosensitized O-H insertion of aryldiazoesters with benzoic acid



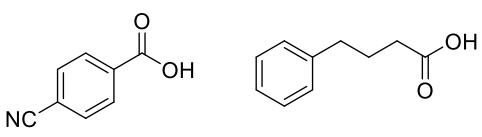
A glass vial equipped with a stirring bar was charged with tetraphenylporphyrin (H_2TPP, **S24**, 0.001 mmol, 0.6 mg), α-diazoester (0.1 mmol) and benzoic acid (**S25**, 0.2 mmol, 24.4 mg, 2 equiv.). A vial was sealed with an aluminum cap with a rubber septum impaled with a needle and placed in glovebox to remove air and maintain oxygen-free conditions. Dry DCM was added (1.0 mL) followed up by a needle removal. The vial was removed from glovebox and irradiated with two Kessil lamps (2 x 40 W, 640 nm) while stirring for 16 h. After that time, the crude mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel using hexane:AcOEt as eluent to afford final product.

Mechanism:

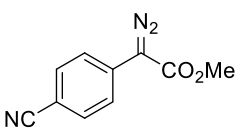


Failed substrates:

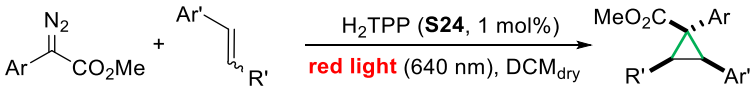
acids



arylodiazoester

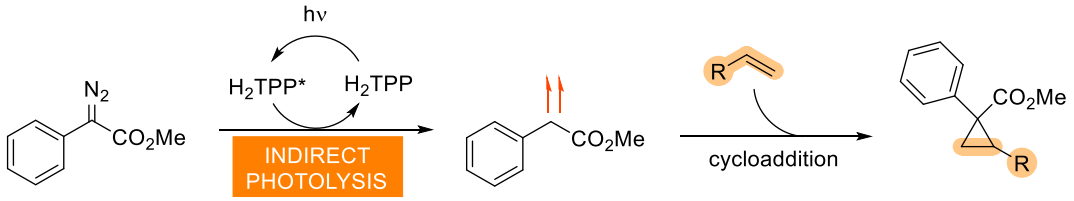


3.8. General procedure for the red light-induced, photosensitized cyclopropanation with aryldiazoesters

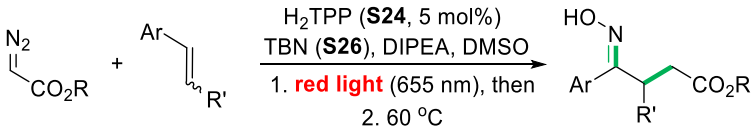


A glass vial equipped with a stirring bar was charged with tetraphenylporphyrin (H_2TPP, **S24**, 0.001 mmol, 0.6 mg) and α-diazoester (0.1 mmol). The vial was sealed with an aluminum cap with a rubber septum impaled with a needle and placed in glovebox to remove air and maintain oxygen-free conditions. Dry DCM (1.0 mL) and olefin (1.0 mmol, 10 equiv.) were added followed up by a needle removal. The vial was removed from glovebox and irradiated with two Kessil lamps (2 x 40 W, 640 nm) while stirring for 16 h. After that time, the crude mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel using hexane:AcOEt as eluent to afford final product.

Mechanism:



3.9. General procedure for the red light-induced, photocatalyzed synthesis of γ-oximinoesters

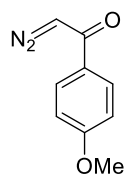


A glass vial equipped with a stirring bar was charged with tetraphenylporphyrin (H_2TPP, **S24**, 0.01 mmol, 6.2 mg) and DMSO (p.a. grade, 4.0 mL). The vial was sealed with an aluminum cap with a rubber septum and oxygen was removed from the solution by freeze-pump-thaw technique. Then, olefin (0.2 mmol - if liquid, solid is added prior the solvent), *N*,*N*-diisopropylethylamine (DIPEA, 0.6 mmol, 105 µL, 3 equiv.) and α-diazoester (0.4 mmol, 2 equiv.) were added under Ar atmosphere. The reaction mixture was stirred for 10 min. After that time, *t*-butyl nitrite (TBN, **S26**, 0.4 mmol, 48 µL, 2 equiv.) was added under Ar atmosphere and the vial was placed in a photoreactor and irradiated with red LEDs (25 W, 655 nm). After 17 h, the vial was placed in an oil bath and stirred at 60 °C for an additional 20 h. The reaction mixture washed with water (2 x 25 mL) and aqueous layers were washed with DCM (3 x 25 mL). Combined organic layers were dried over sodium sulfate, filtrated, and concentrated *in vacuo.* The residue was purified by flash column chromatography on silica gel using hexane:AcOEt as eluent to afford the final product.

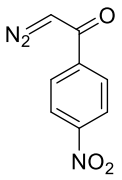
*Note: The synthesis of product **42** required prolonged irradiation time (66 h) and using MeCN as co-solvent for better olefin solubility, concentration was altered as well.*

Failed substrates:

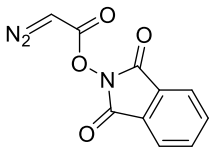
diazoesters



low conversion of diazo

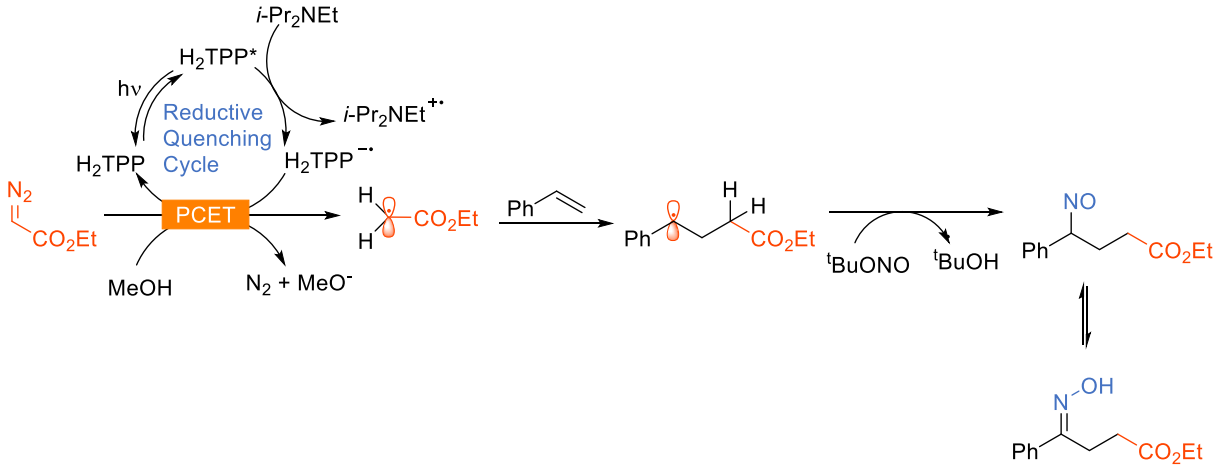


diazo fully converted, traces of product, low selectivity, messy



diazo fully converted, NHPI and Phtalimide present in high amount

Mechanism:

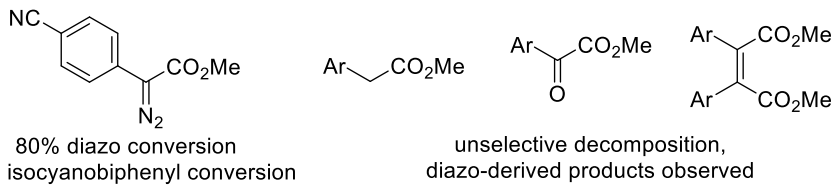


3.10. General procedure for the red light-induced, photocatalyzed synthesis of phenantridines

To a glass vial equipped with a stirring bar tetraphenylporphyrin (H_2TPP, **S24**, 0.01 mmol, 6.2 mg) was added. The vial was purged with argon, charged with dry DMSO (1.0 mL) and sealed with an aluminum cap with a rubber septum. Oxygen was removed from the solution by freeze-pump-thaw technique and isocyanate (0.2 mmol, if liquid – solid isocyanate is added prior the solvent), diazoalkane (1.0 mmol, 5 equiv.) and DIPEA (0.2 mmol, 35 µL, 1 equiv.) were added under Ar atmosphere. Then, the vial was placed in a photoreactor and irradiated with red LEDs (25 W, 655 nm) for 18 h. After that time, the crude reaction mixture was washed with water (2 x 25 mL) and aqueous layers were washed with DCM (3 x 25 mL). Combined organic layers were dried over sodium sulfate, filtrated, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel using hexane:acetone as eluent to afford the final product.

Failed substrates:

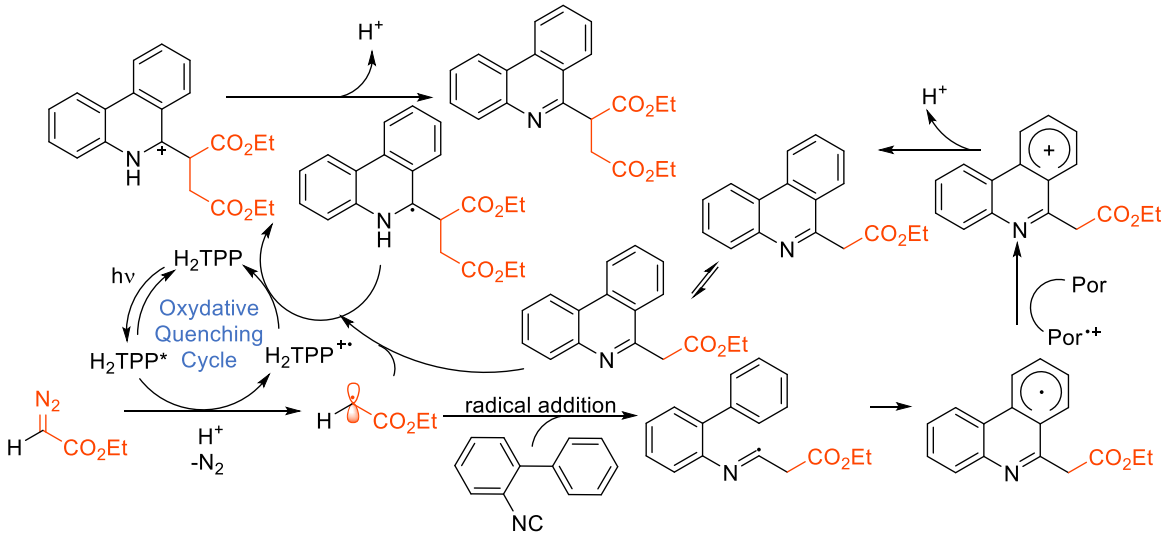
arylodiazoester



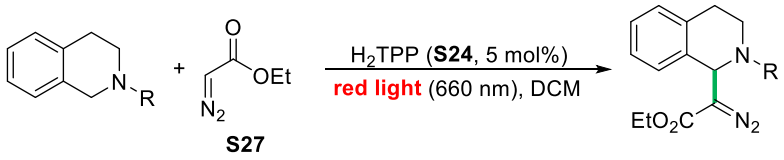
80% diazo conversion
75% isocyanobiphenyl conversion

unselective decomposition,
diazo-derived products observed

Mechanism:



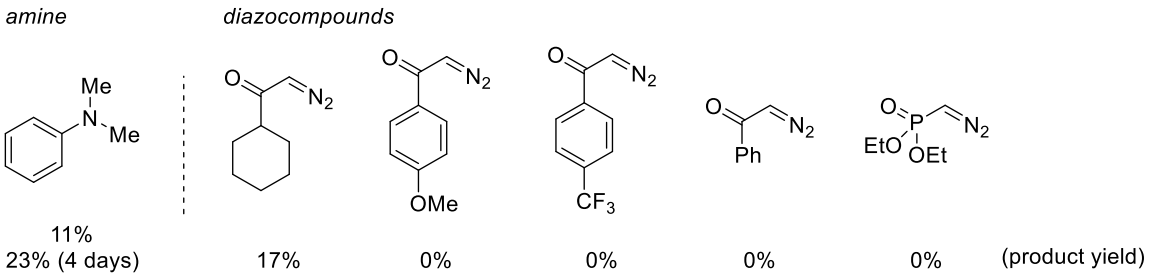
3.11. General procedure for the red light-induced, photocatalyzed synthesis of β-amino-α-diazo esters



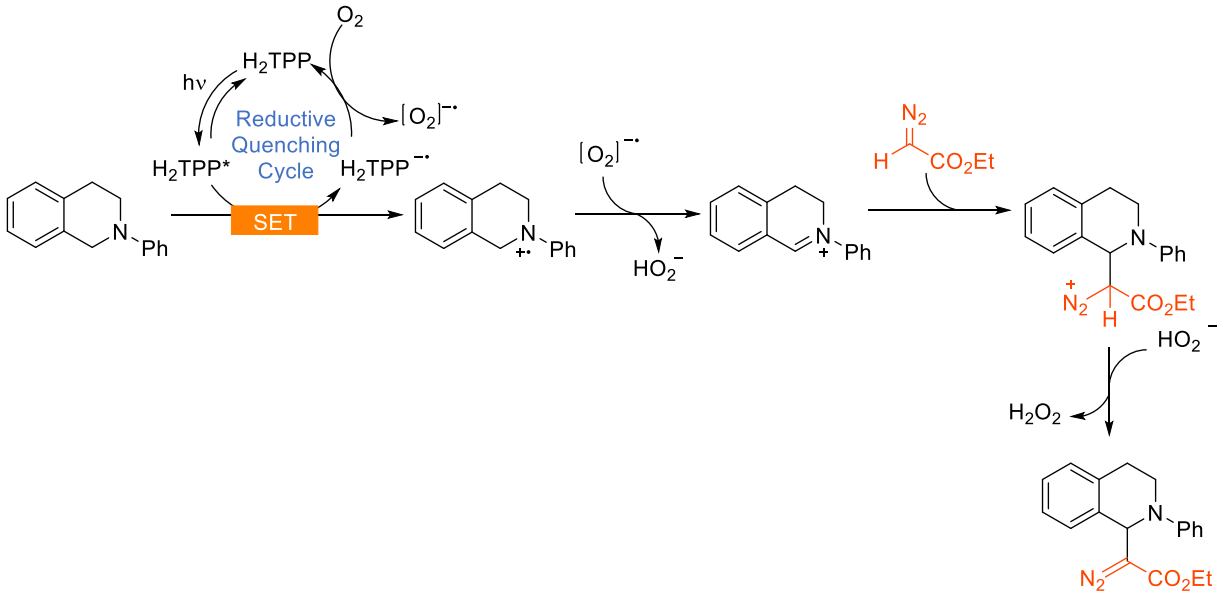
A glass vial equipped with a stirring bar was charged with tetrahydroisoquinoline (0.1 mmol) and 1/3 portion of tetraphenylporphyrin (H_2TPP, **S24**, 0.002 mmol, 1.0 mg). The vial was sealed with an aluminum cap with a rubber septum followed by the addition of DCM p.a. (0.5 mL) and ethyl diazoacetate solution (**S27**, 13% wt.in DCM, 0.3 mmol, 36 µL, 3 equiv.). The reaction mixture was placed in a photoreactor and irradiated with red LEDs (3 W, 660 nm) for 48 h at 30 °C. During that time, two additional portions of tetraphenylporphyrin were added in 12 h intervals.* After 48 h, the crude reaction mixture was concentrated *in vacuo* and purified by flash column chromatography on silica gel using hexane/AcOEt 99:1 to afford the final product.

*Note: *Tetraphenylporphyrin (H_2TPP) was added in 3 equal portions every 12 h (at 0, 12 and 24 h irradiation time). In total, 5 mol% of H_2TPP (0.05 mmol, 3.0 mg) was added into the vial.*

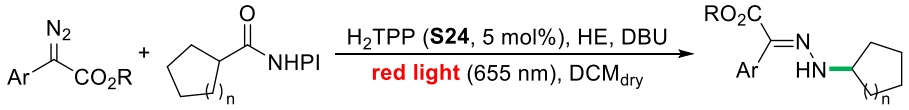
Failed substrates:



Mechanism:



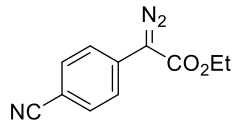
3.12. General procedure for the red light-induced, photocatalyzed synthesis of hydrazones



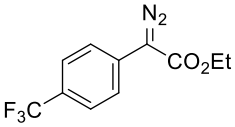
A glass vial equipped with a stirring bar was charged with tetraphenylporphyrin (H_2TPP, **S24**, 0.01 mmol, 6.2 mg), α-diazoester (0.2 mmol), NHPI ester (0.3 mmol, 1.5 equiv.) and Hantzsch ester (HE, 0.24 mmol mmol, 1.2 equiv.). A vial was sealed with an aluminum cap with a rubber septum impaled with a needle and placed in glovebox to remove air and maintain oxygen-free conditions. Dry DCM (2.0 mL) and DBU (0.46 mmol, 69 µL, 2.3 equiv.) were added followed up by a needle removal. The vial was removed from glovebox and was placed in a photoreactor for irradiation with red LEDs (25 W, 655 nm) for 18 h. After that time, the crude reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel using hexane:DCM:AcOEt as eluent to afford the final product.

Failed substrates:

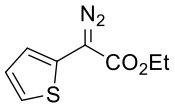
arylodiazoesters



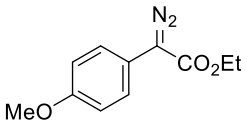
<20% of product (NMR)



product not obtained

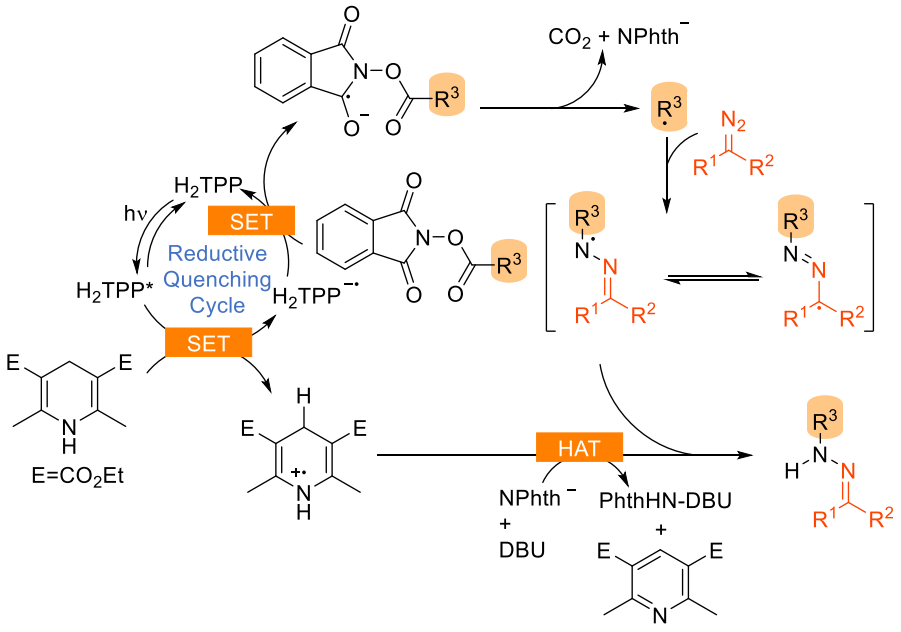


8% of product (NMR)



<30% of product (NMR)

Mechanism:



4. Optimization details

4.1. Optimization of the red light-induced O-H insertion of diaryldiazoalkanes with alcohols

Model reaction

Optimal reaction conditions: 4,4'-(diazomethylene)bis(methoxybenzene) (**S1**, 0.2 mmol), benzyl alcohol (**S28**, 2 mmol, 10 equiv.), MeCN (c = 0.1 M), red LEDs (655 nm, 25 W), air atmosphere, 25 °C, 135 min.

Background reactions

entry	deviation from reaction conditions	yield of **1** [%][a]
1	no light	0
2	none	64
3	dry DCM was used	67
4	air atmosphere	63

Reaction conditions: diazoalkane **S1** (0.2 mmol), benzyl alcohol (**S28**, 2.0 mmol, 10 equiv.), DCM (p.a. grade, c = 0.1 M), red LEDs (655 nm, 25 W), Ar atmosphere, T = 25 °C, 1 h; [a]isolated yield.

Solvent screening

entry	solvent	yield of **1** [%][a]
1	DCM	64
2	DCE	21
3*	benzene	47
4	$CHCl_3$	70
5	MeCN	67
6[c,d]	MeCN	79[b]
7[d,e]	MeCN	84

Reaction conditions: diazoalkane **S1** (0.2 mmol), benzyl alcohol (**S28**, 2.0 mmol, 10 equiv.), *solvent* (c = 0.1 M), red LEDs (655 nm, 25 W), Ar atmosphere, T = 25 °C, 1 h; [a]isolated yield. [b]GC yield. [c]0.1 mmol scale. [d]air atmosphere. [e] reaction time was prolonged to 135 min (to ensure full conversion of diazoalkane **S1**). *In $CHCl_3$ decomposition of diazo compound **S1** was observed over few hours without irradiation.

Concentration effects

entry	concentration [M]	yield of **1** [%][a]
1	0.05	75
2	0.1	79
3*	0.2	79

Reaction conditions: diazoalkane **S1** (0.1 mmol), benzyl alcohol (**S28**, 1.0 mmol, 10 equiv.), MeCN (c = *x* M), red LEDs (655 nm, 25 W), air atmosphere, T = 25 °C, 1 h; [a]GC yield. *not homogenous mixture.

Light intensity

entry	light intensity [W]	irradiation time* [min]	yield of **1** [%][a]
1	25	60	79
2	13	135	74
3	6	240	72

Reaction conditions: diazoalkane **S1** (0.1 mmol), benzyl alcohol (**S28**, 1.0 mmol, 10 equiv.), MeCN (c = 0.1 M), red LEDs (655 nm, *x* W), air atmosphere, T = 25 °C; [a]GC yield. *the reaction mixture was irradiated until full discoloring of violet solution.

Temperature

entry	temperature [°C]	irradiation time* [min]	yield of **1** [%][a]
1	25	60	79
2	16	145	74

Reaction conditions: diazoalkane **S1** (0.1 mmol), benzyl alcohol (**S28**, 1.0 mmol, 10 equiv.), MeCN (c = 0.1 M), red LEDs (655 nm, 25 W), air atmosphere, T = *x* °C; [a]GC yield. *the reaction mixture was irradiated until full discoloring of violet solution.

Substrates ratio

entry	**S1**:**S28** ratio [mol/mol]	yield of **1** [%][a]
1	5:1	81
2	2:1	81
3	1:1	56
4	1:2	64
5	1:5	74
6	1:10	79
7	1:15	75

Reaction conditions: diazoalkane **S1** (*x* mmol), benzyl alcohol (**S28**, *y* mmol), MeCN (c = 0.1 M), red LEDs (655 nm, 25 W), air atmosphere, T = 25 °C, 1 h; [a]GC yield.

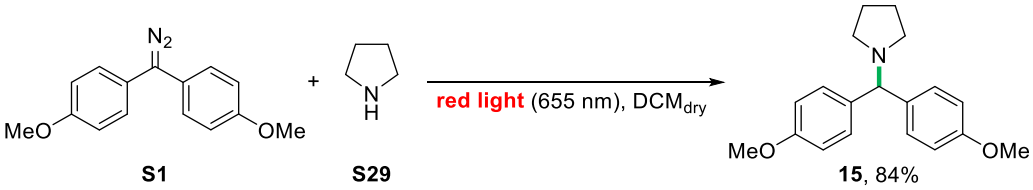
Addition of diazo compound

entry	diazo portions	irradiation time* [min]	yield of **1** [%][a]
1	one, before irradiation	60	79
2	two, second added after 30 min	130	78

Reaction conditions: diazoalkane **S1** (0.1 mmol), benzyl alcohol (**S28**, 1.0 mmol, 10 equiv.), MeCN (c = 0.1 M), red LEDs (655 nm, 25 W), air atmosphere, T = 25 °C; [a]GC yield. *the reaction mixture was irradiated until full discoloring of violet solution.

4.2. Optimization of the red light-induced N-H insertion of diaryldiazoalkanes with amines

Model reaction



Optimal reaction conditions: 4,4'-(diazomethylene)bis(methoxybenzene) (**S1**, 0.4 mmol, 2 equiv.), pyrrolidine (**S29**, 0.2 mmol), dry DCM (c = 0.1 M), red LEDs (655 nm, 25 W), Ar atmosphere, 25 °C, 135 min.

Background reactions

entry	deviation from reaction conditions	yield of **15** [%][a]
1	no light	0
2	none	44
3[b]	dry MeCN was used	45

Reaction conditions: diazoalkane **S1** (0.2 mmol), pyrrolidine (**S29**, 2.0 mmol, 10 equiv.), MeCN (c = 0.1 M), red LEDs (655 nm, 25 W), air atmosphere, T = 25 °C, 135 min; [a]isolated yield. [b]Ar atmosphere.

Solvent screening

entry	solvent	yield of **15** [%][a]
1	dry MeCN	46
2	dry DMF	54
3	dry DCM	70

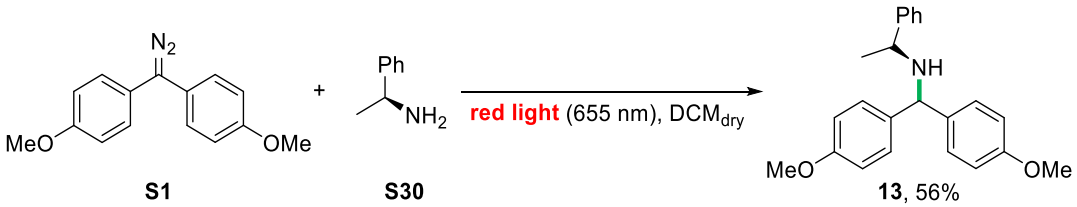
Reaction conditions: diazoalkane **S1** (0.2 mmol), pyrrolidine (**S29**, 2.0 mmol, 10 equiv.), *solvent* (c = 0.1 M), red LEDs (655 nm, 25 W), Ar atmosphere, T = 25 °C, 135 min; [a]isolated yield.

Substrates ratio

entry	**S1**:**S29** ratio [mol/mol]	yield of **15** [%][a]
1	2:1	84
2	1:2	74
4	1:4	77
4	1:5	74
5	1:10	70

Reaction conditions: diazoalkane **S1** (*x* mmol), pyrrolidine (**S29**, *y* mmol), dry DCM (c = 0.1 M), red LEDs (655 nm, 25 W), Ar atmosphere, T = 25 °C, 120 min; [a]isolated yield.

For primary amines, additional optimization of substrates ratio was undertaken, due to unsatisfactory yields observed when conditions optimal for secondary amines were used (entry 2, 44%, product **13**):



Substrates ratio – primary amine

entry	**S1**:**S30** ratio [mol/mol]	yield of **13** [%][a]
1	3:1	64 (56)
2	2:1	44
4	1:2	26
4	1:3	22
5	1:4	24

Reaction conditions: diazoalkane **S1** (*x* mmol), *(S)*-1-phenylethan-1-amine (**S30**, *y* mmol), dry DCM (c = 0.1 M), red LEDs (655 nm, 25 W), Ar atmosphere, T = 25 °C, 135 min; [a] yields determined by the ^{1}H NMR using 1,3,5-trimetoxybenzene as internal standard, isolated yields in parenthesis.

4.3. Optimization of the red light-induced S-H insertion of diaryldiazoalkanes with thiols

Model reaction

Optimal reaction conditions: 4,4'-(diazomethylene)bis(methoxybenzene) (**S1**, 0.4 mmol, 2 equiv.), benzyl mercaptan (**S31**, 0.2 mmol), dry DCM (c = 0.1 M), red LEDs (655 nm, 25 W), Ar atmosphere, 25 °C, 135 min.

Background reactions

entry	deviation from reaction conditions	yield of **19** [%][a]
1	no light	0
2	none	65
3	dry MeCN used as solvent	49

Reaction conditions: diazoalkane **S1** (0.2 mmol), benzyl mercaptan (**S31**, 2.0 mmol, 10 equiv.), dry DCM (c = 0.1 M), red LEDs (655 nm, 25 W), Ar atmosphere, T = 25 °C, 1 h; [a]isolated yield.

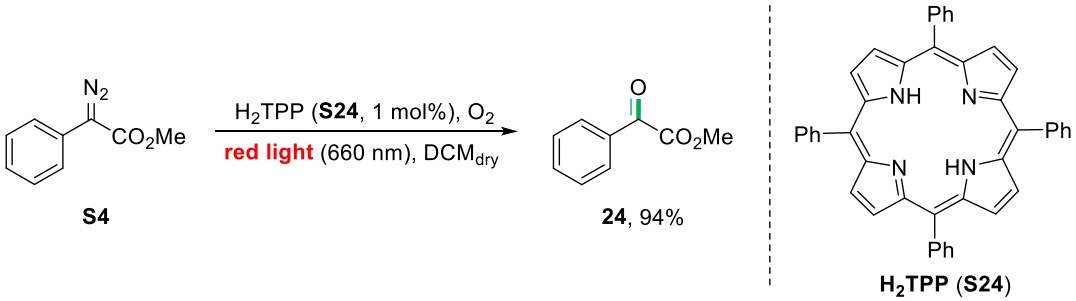
Substrates ratio

entry	**S1**:**S31** ratio [mol/mol]	yield of **19** [%][a]
1	2:1	>99 (89)
2	1:4	82
3	1:10	77

Reaction conditions: diazoalkane **S1** (*x* mmol), benzyl mercaptan (**S31**, *y* mmol), dry DCM (c = 0.1 M), red LEDs (655 nm, 25 W), Ar atmosphere, T = 25 °C, 135 min; [a] yields determined by the ^{1}H NMR using 1,3,5-trimetoxybenzene as internal standard, isolated yields in parenthesis.

4.4. Optimization of the red light-induced, photosensitized oxygenation of aryldiazoesters

Model reaction



Optimal reaction conditions: H_2TPP (**S24**, 1 mol%), methyl 2-diazo-2-phenylacetate (**S4**, 0.1 mmol), dry DCM (c = 0.1 M), red LEDs (660 nm, 3 W), O_2 atmosphere, 25 °C, 1 h.

Background reactions

entry	deviation from reaction conditions	yield of **24** [%]
1	none	60 (58)[a]
2	no light	0
3	no H_2TPP (**S24**)	0
4	no light, no H_2TPP (**S24**)	0
5	no light, heated to 35 °C, no H_2TPP (**S24**)	0

Reaction conditions: H_2TPP (**S24**, 1 mol%), diazoalkane **S4** (0.1 mmol), dry DCM (c = 0.1 M), red LEDs (660 nm, 3 W), Ar atmosphere, T = 25 °C, 18 h; [a]GC yield, isolated yield in parenthesis.

Solvent screening

entry	solvent	yield of **24** [%][a]
1	dry DCM	60
2	dry 1,4-dioxane	53
3	dry THF	49
4	dry acetone	45
5	dry MeCN	44
6	dry C_6F_6	47

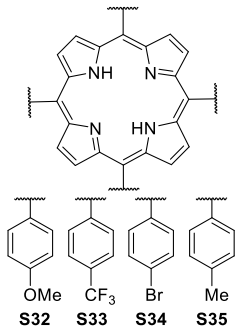
Reaction conditions: H_2TPP (**S24**, 1 mol%), diazoalkane **S4** (0.1 mmol), *solvent* (c = 0.1 M), red LEDs (660 nm, 3 W), Ar atmosphere, T = 25 °C, 1 h; [a]GC yield.

Concentration effects

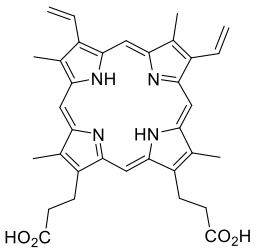
entry	concentration [M]	yield of **24** [%][a]
1	0.2	50
2	0.1	60
3	0.05	54
4	0.03	45
5	0.02	38

Reaction conditions: H_2TPP (**S24**, 1 mol%), diazoalkane **S4** (0.1 mmol), dry DCM (c = *x* M), red LEDs (660 nm, 3 W), Ar atmosphere, T = 25 °C, 1 h; [a]GC yield.

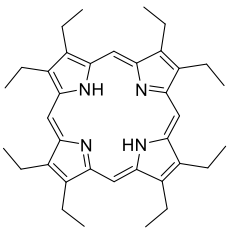
Photocatalyst screening



S32 **S33** **S34** **S35**



S36



S37

entry	photocatalyst	yield of **24** [%][a]
1	H_2TPP (**S24**)	60
2	H_2T(*p*-OMe)PP (**S32**)	62
3	H_2T(*p*-CF_3)PP (**S33**)	60
4	H_2T(*p*-Br)PP (**S34**)	59
5	H_2T(*p*-Me)PP (**S35**)	48
6	PPIX (**S36**)	37
7	octaethylporphyrin (**S37**)	60

Reaction conditions: photocatalyst (***x***, 1 mol%), diazoalkane **S4** (0.1 mmol), dry DCM (c = 0.1 M), red LEDs (660 nm, 3 W), Ar atmosphere, T = 25 °C, 1 h; [a]GC yield.

Photocatalyst loading

entry	catalyst **S24** loading [mol%]	yield of **24** [%][a]
1	0.2	28
2	0.5	55
3	1.0	60
4	1.5	61
5	2.0	60
6	5.0	22
7	10.0	17

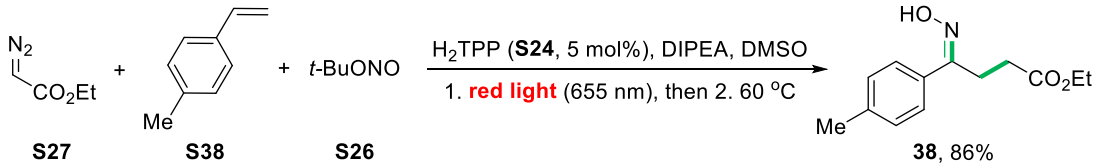
Reaction conditions: H_2TPP (**S24**, *x* mol%), diazoalkane **S4** (0.1 mmol), dry DCM (c = 0.1 M), red LEDs (660 nm, 3 W), Ar atmosphere, T = 25 °C, 1 h; [a]GC yield.

Oxygen access

entry	oxygen access via:	yield of **24** [%][a]
1	closed vial (air atmosphere)	60
2	closed vial with a needle (air atmosphere)	61
3	closed vial with O_2 balloon (O_2 atmosphere)	53
4[b]	closed vial with O_2 balloon (O_2 atmosphere)	79
5*	freeze-pump-thaw with O_2	94

Reaction conditions: H_2TPP (**S24**, 1 mol%), diazoalkane **S4** (0.1 mmol), dry DCM (c = 0.1 M), red LEDs (660 nm, 3 W), *x* atmosphere, T = 25 °C, 1 h; [a]GC yield. [b]catalyst **S24** added in 2 equal portions (0.5 mol% each, 2nd after 3 h). *air was removed from the vial by freeze-pump-thaw technique and the vial was purged with O_2.

4.5. Optimization of the red light-induced, photocatalyzed synthesis of γ-oximinoesters



S27 **S38** **S26** **38**, 86%

Optimal reaction conditions: H_2TPP (**S24**, 5 mol%), ethyl diazoacetate (**S27**, 0.4 mmol, 2 equiv.), 4-methyl-styrene (**S38**, 0.2 mmol), TBN (**S26**, 0.4 mmol, 2 equiv.), DIPEA (0.6 mmol, 3 equiv.), DMSO (c = 0.05 M), Ar atmosphere, irradiation with red LEDs (655 nm, 25 W) at 25 °C for 20 h, then heating (60 °C, 18 h).

Background reactions

entry	deviation from reaction conditions	yield of **38** [%][a]
1	none	42
2	no light	0
3	no H_2TPP (**S24**)	0
4	no light, no H_2TPP (**S24**)	0
5	dry solvents were used	36

Reaction conditions: H_2TPP (**S24**, 5 mol%), olefin **S38** (0.2 mmol), diazoalkane **S27** (0.4 mmol, 2 equiv.), TBN (**S26**, 0.4 mmol, 2 equiv.), DIPEA (0.6 mmol, 3 equiv.), MeOH/ DCM (1:1 v/v, c = 0.1 M), red LEDs (655 nm, 25 W), Ar atmosphere, T = 25 °C, 60 h; [a]isolated yield.

Solvent & catalyst screening

entry	photocatalyst	solvent system	yield of **38** [%][a]
1	H_2TPP (**S24**)	MeOH/DCM = 1/1 (v/v)	42
2		dry toluene	<5
3		dry DMSO	63
4		MeOH/dry DMSO = 1/1 (v/v)	64
5		dry MeOH/dry DMSO = 1/1 (v/v)	60
6		MeOH/dry DMF= 1/1 (v/v)	61
7	H_2T(*p*-OMe)PP (**S32**)	dry MeCN	40
8	Rose Bengal	MeOH	21

Reaction conditions: *catalyst* (5 mol%), olefin **S38** (0.2 mmol), diazoalkane **S27** (0.4 mmol, 2 equiv.), TBN (**S26**, 0.4 mmol, 2 equiv.), DIPEA (0.6 mmol, 3 equiv.), *solvent* (c = 0.1 M), red LEDs (655 nm, 25 W), Ar atmosphere, T = 25 °C, 60 h; [a]isolated yield.

Concentration effects

entry	concentration [M]	yield of **38** [%][a]
1	0.05	69
2	0.1	64
3	0.2	45

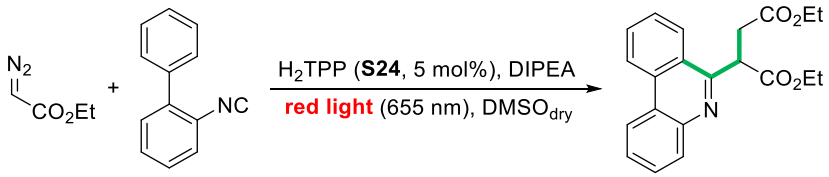
Reaction conditions: H_2TPP (**S24**, 5 mol%), olefin **S38** (0.2 mmol), diazoalkane **S27** (0.4 mmol, 2 equiv.), TBN (**S26**, 0.4 mmol, 2 equiv.), DIPEA (0.6 mmol, 3 equiv.), MeOH/dry DMSO (1:1 v/v, c = *x* M), red LEDs (655 nm, 25 W), Ar atmosphere, T = 25 °C, 60 h; [a]isolated yield.

Irradiation time & heating time

entry	irradiation time [h]	then heating time (at 60°C) [h]	yield of **38** [%][a]
1	20	no	53
2	60	no	64
3	115	no	55
4	20	2	56
5	20	6	60
6	20	18	76
7[b]	20	18	78
8[b,c]	20	18	67
9[b,d]	20	18	86

Reaction conditions: H_2TPP (**S24**, 5 mol%), olefin **S38** (0.2 mmol), diazoalkane **S27** (0.4 mmol, 2 equiv.), TBN (**S26**, 0.4 mmol, 2 equiv.), DIPEA (0.6 mmol, 3 equiv.), MeOH/dry DMSO (1:1, v/v, c = 0.1 M), Ar atmosphere, red LEDs (655 nm, 25 W), T = 25 °C, *x* h; then then the reaction vial (if noted) was placed in oil bath and stirred for *y* time at 60 °C. [a]isolated yield. [b]c = 0.05 M. [c]3.0 equiv. of EDA (**S27**) was used. [d]DMSO as solvent.

4.6. Optimization of the red light-induced, photocatalyzed synthesis of phenantridines



S27 **S16** **43**, 95%

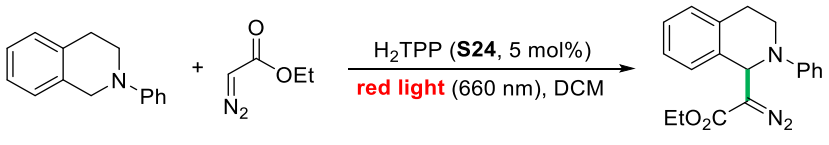
Optimal reaction conditions: H_2TPP (**S24**, 5 mol%), ethyl diazoacetate (**S27**, 1.0 mmol, 5 equiv.), 2-isocyano-1,1'-biphenyl (**S16**, 0.2 mmol), DIPEA (0.2 mmol, 1 equiv.), dry DMSO (c = 0.2 M), Ar atmosphere, red LEDs (655 nm, 25 W), 25 °C, 18 h.

Background & Optimization

entry	deviation from reaction conditions	yield of **38** [%][a]
1	none	59
2	no light	0
3	no H_2TPP (**S24**)	0
4	no light, no H_2TPP (**S24**)	0
5	DMSO as solvent	64
6	DMSO as solvent, 0.05 M	56
7	DMSO as solvent, 2 equiv. of DIPEA	67
8	dry DMSO as solvent	>99 (95)

Reaction conditions: H_2TPP (**S24**, 5 mol%), ethyl diazoacetate (**S27**, 1.0 mmol, 5 equiv.), 2-isocyano-1,1'-biphenyl (**S16**, 0.2 mmol), DIPEA (0.2 mmol, 1 equiv.), dry MeOH/dry DCM (1:1, v/v, c = 0.2 M), Ar atmosphere, red LEDs (655 nm, 25 W), 25 °C, 18 h. [a]yields determined by the ^1H NMR using dibromomethane as internal standard, isolated yield in parenthesis.

4.7. Optimization of the red light-induced, photocatalyzed synthesis of β-amino-α-diazo esters



S18 **S27** **48**, 70%

Optimal reaction conditions: H_2TPP (**S24**, 5 mol%), 2-phenyl-1,2,3,4-tetrahydroisoquinoline (**S18**, 0.1 mmol), ethyl diazoacetate (**S27**, 0.3 mmol, 3 equiv.), DCM (c = 0.2 M), air atmosphere, red LEDs (660 nm, 3 W), 25 °C, 48 h.

Background reactions

entry	deviation from reaction conditions	yield of **48** [%][a]
1	O_2 balloon	22
2	no light	0
3	no H_2TPP (**S24**)	traces
4	no light, no H_2TPP (**S24**)	0

Reaction conditions: H_2TPP (**S24**, 1 mol%), tetrahydroisoquinoline **S18** (0.1 mmol), diazoalkane **S27** (0.3 mmol, 3 equiv.), DCM (c = 0.1 M), air atmosphere, red LEDs (660 nm, 3 W), 25 °C, 20 h. [a]yields determined by the ^1H NMR using 1,3,5-trimetoxybenzene as internal standard.

Catalyst screening

entry	catalyst	yield of **48** [%][a]
1	H_2TPP (**S24**)	22
2	H_2T(*p*-OMe)PP (**S32**)	38
3	H_2T(*p*-CF_3)PP (**S33**)	34
4	PPIX (**S36**)	23

Reaction conditions: *catalyst* (1 mol%), tetrahydroisoquinoline **S18** (0.1 mmol), diazoalkane **S27** (0.3 mmol, 3 equiv.), DCM (c = 0.1 M), air atmosphere, red LEDs (660 nm, 3 W), 25 °C, 20 h. [a]yields determined by the ^{1}H NMR using 1,3,5-trimetoxybenzene as internal standard.

Solvent screening

entry	solvent	yield of **48** [%][a]
1	DCM	22
2[b]	DCM	42
3	MeCN	37
4	DMF	17

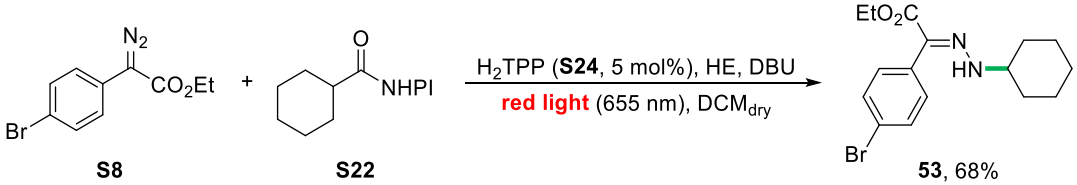
Reaction conditions: H_2TPP (**S24**, 1 mol%), tetrahydroisoquinoline **S18** (0.1 mmol), diazoalkane **S27** (0.3 mmol, 3 equiv.), *solvent* (c = 0.1 M), air atmosphere, red LEDs (660 nm, 3 W), 25 °C, 20 h. [a]yields determined by the ^{1}H NMR using 1,3,5-trimetoxybenzene as internal standard. [b]c = 0.2 M.

Light intensity

entry	light intensity [W]	yield of **48** [%][a]
1	3 W	42
2[b]	3 W	63
3[b,c]	3 W	51
4[b,d]	3 W	77 (70)
5	25 W	38
6	40 W	40

Reaction conditions: H_2TPP (**S24**, 1 mol%), tetrahydroisoquinoline **S18** (0.1 mmol), diazoalkane **S27** (0.3 mmol, 3 equiv.), DCM (c = 0.2 M), air atmosphere, red LEDs (660 nm, 3 W), 25 °C, 20 h. [a]yields determined by the ^{1}H NMR using 1,3,5-trimetoxybenzene as internal standard, isolated yield in parenthesis. [b]48 h. [c]1.5 equiv. of **S27**. [d]5 mol% of catalyst **S24** added in 3 portions.

4.8. Optimization of the red light-induced, photocatalyzed synthesis of hydrazones



S8 **S22** **53**, 68%

Optimal reaction conditions: H_2TPP (**S24**, 5 mol%), ethyl 2-(4-bromophenyl)-2-diazoacetate (**S8**, 0.2 mmol), NHPI ester **S22** (0.3 mmol, 1.5 equiv.), Hantzsch ester (0.24 mmol, 1.2 equiv.), DBU (0.46 mmol, 2.3 equiv.), dry DCM (c = 0.1 M), Ar atmosphere, red LEDs (655 nm, 25 W), 25 °C, 18 h.

Background & Optimization

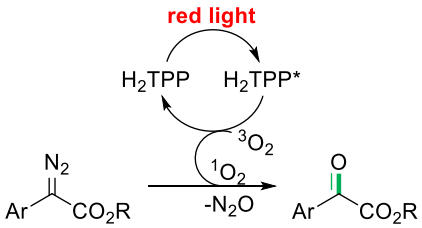
entry	deviation from reaction conditions	yield of **53** [%][a]
1	none	28
2	no light	0
3	no H_2TPP (**S24**)	0
4	no light, no H_2TPP (**S24**)	0
5	Rose Bengal instead of **S24**	24
6	reaction set in glove box*	66 (68)

Reaction conditions: H_2TPP (**S24**, 5 mol%), diazo compound **S8** (0.2 mmol), NHPI ester **S22** (0.3 mmol, 1.5 equiv.), Hantzsch ester (0.24 mmol, 1.2 equiv.), DBU (0.46 mmol, 2.3 equiv.), dry DCM (c = 0.1 M), Ar atmosphere, red LEDs (655 nm, 25 W), 25 ^{o}C, 18 h. [a] yields determined by the ^{1}H NMR using dibromomethane as internal standard, isolated yield in parenthesis. *entry 1-5: degassed with freeze-pump-thaw technique.

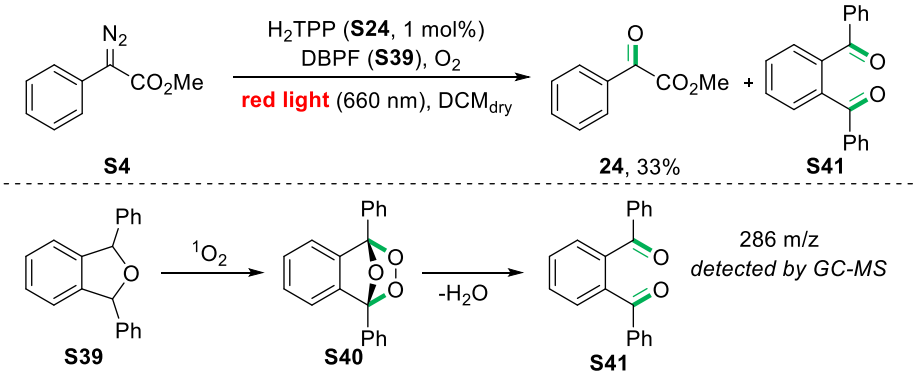
5. Mechanistic studies

5.1. Detection of $^1O_2$ - oxygen photosensitization by porphyrin catalyst

Porphyrins are known as efficient $^1O_2$ photosensitizers,[18-20] therefore when oxygen atmosphere is maintained in the reaction vial, $^1O_2$ is most likely generated by porphyrin catalyst in the excited state. Red light-induced, TPP-sensitized aryldiazoester indirect photolysis to carbenes is rather a slow process (see kinetics studies, section 5.2.), while the photooxygenation of arylodiazoesters is completed within 1 hour. Thus, the plausible mechanism assumes the aryldiazoester is attacked by generated $^1O_2$ and β-ketoester is formed upon the extrusion of N_2O, analogously to Wei's report.[21]



To confirm $^1O_2$ generation by H_2TPP sensitizer under red light irradiation, we performed an experiment with the addition of established $^1O_2$ probe, 1,3-diphenyl-1,3-dihydroisobenzofuran (**S39**).[22] The reaction was set up following the general oxygenation procedure (section 3.6.) on 0.1 mmol scale with the addition of probe **S39** (0.05 mmol, 14 mg). When diazo compound **S4** was irradiated with red light in the presence of H_2TPP (**S24**) and reagent **S39**, diminished yield of β-ketoester **24** was observed (33%). 56% of diazo ester **S4** remained unreacted and instead, 1,2-dibenzoylbenzene (**S41**) formed as a result of oxidation of probe **S39** followed by subsequent dehydratation of endoperoxide **S40** (detected by GC-MS analysis, Figure F4).



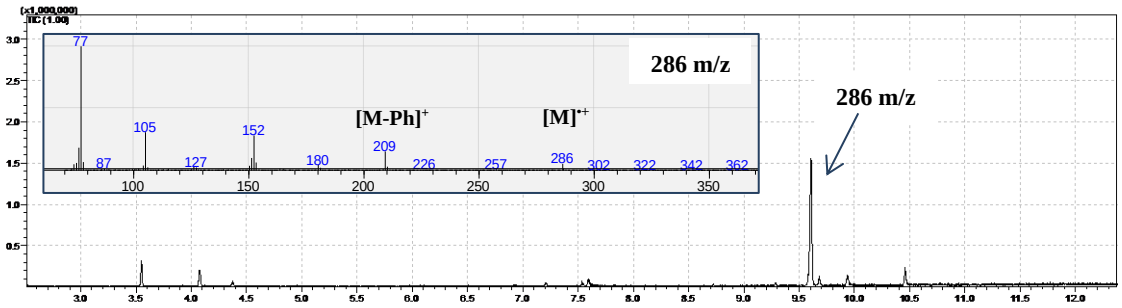
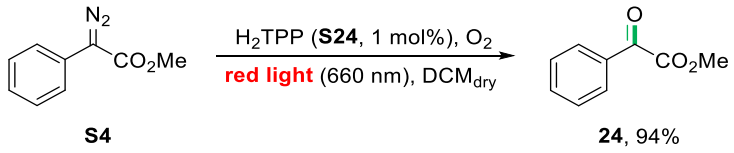


Figure F4. GC-MS chromatogram for the detection of product **S41** and the fragmentation of the 286 m/z peak.

5.2. Kinetic studies

Red light-induced, photosensitized oxygenation of aryldiazoesters



S4 **24**, 94%

The reaction was set up following the general photooxygenation procedure (section 3.3.) on 0.1 mmol scale with the addition of dodecane as an internal standard. The experiment was conducted for 1 h and the reaction progress over time was monitored with GC/FID. The kinetics studies reveal fast product **24** formation within ca. 30 min of irradiation (Charts C1).

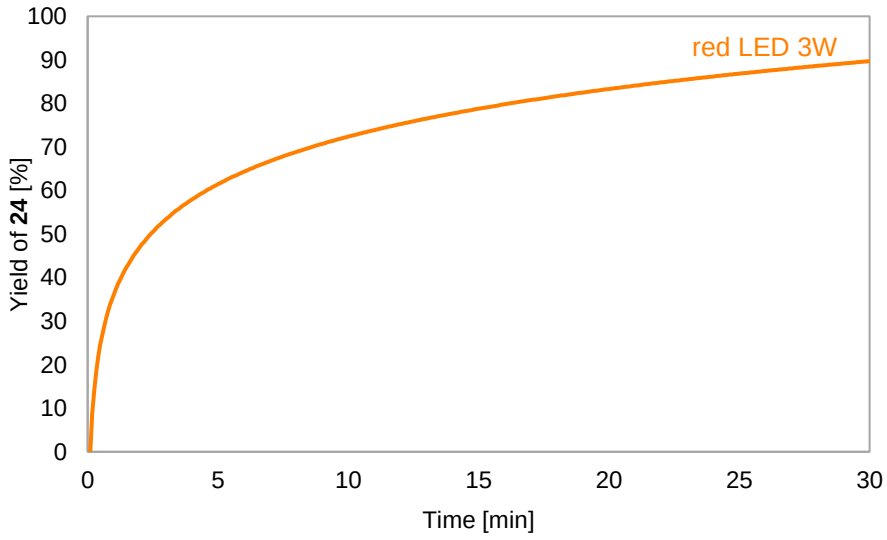
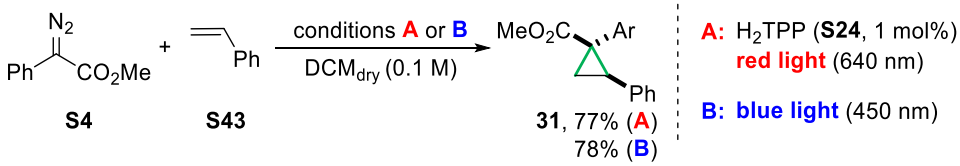


Chart C1. Kinetics of β-ketoester **24** formation.

Red light-induced, photosensitized cyclopropanation with aryldiazoesters



S4 **S43** **31**, 77% (**A**) 78% (**B**)

Two parallel experiments were performed to compare kinetics of TPP-sensitized red, light-mediated (conditions **A**) and catalyst-free, blue light-induced (conditions **B**) cyclopropanation reactions. Reaction A was set up following the general photosensitized cyclopropanation procedure (section 3.4.) on 0.1 mmol scale with the addition of dodecane as an internal standard. Reaction B was set up on 0.1 mmol scale without degassing reaction mixture with the addition of dodecane as an internal standard. The experiments were conducted for 18 h and the reaction progress over time was monitored with GC/FID. The kinetics studies reveal fast blue light-induced product **31** formation (78%) completed within 0.5 h of irradiation and slow photosensitized protocol yielding 77% of cyclopropane **31** within 18 h (Chart C2).

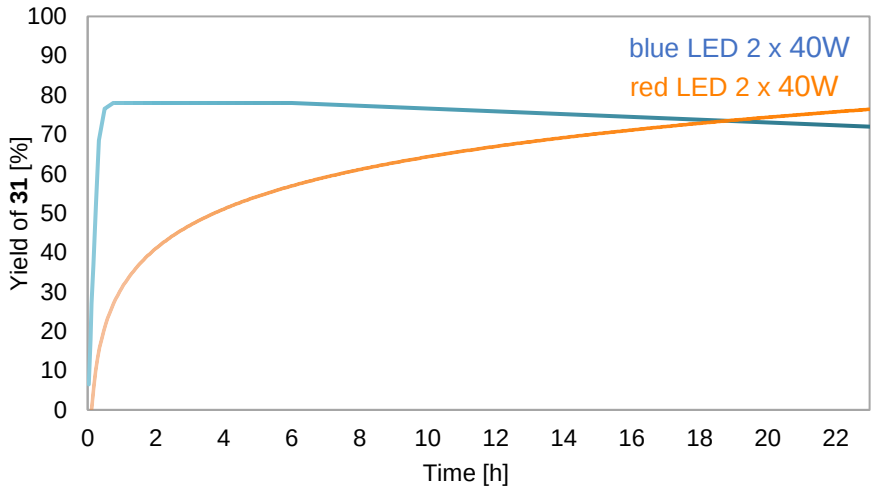
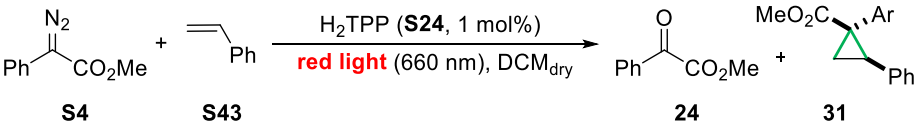


Chart C2. Kinetics of blue light and TPP-catalyzed, red light-induced cyclopropane **31** formation.

5.3. Competition between photooxygenation and cyclopropanation

Experiments on red light-induced, TPP-sensitized cyclopropanation revealed that depending on the oxygen concentration, photooxygenation of diazoalkane **S4** via $^1O_2$ to β-ketoester **24** competes with the cyclopropanation and results in decrease of yield of the desired product **31**. When oxygen-free conditions were maintained (entry 1), cyclopropane **31** formed exclusively in high yield (81%). On the other hand, even traces of oxygen diminished the cyclopropanation yield and side product **24** was observed. Reaction performed on air resulted in low reaction selectivity giving almost equal amounts of products **24** and **31**.



S4 **S43** **24** **31**

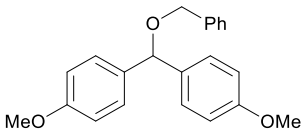
entry	oxygen access	yield of **24** [%][a]	yield of **31** [%][a]
1	set in glove box (<0.5 ppm O_2)	0	81
2	freeze-pump-thaw (Ar atmosphere)	14	58
3	air atmosphere	28	30

Reaction conditions: H_2TPP (**S24**, 5 mol%), diazoalkane **S4** (0.1 mmol), olefin **S43** (1.0 mmol, 10 equiv.), dry DCM (c = 0.1 M), red LEDs (660 nm, 3 W), T = 25 °C, 18 h. [a]GC yield.

6. Characterization of synthesized compounds

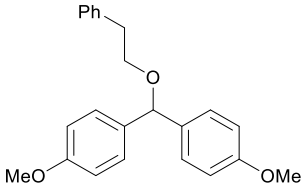
6.1. Photochemical O-H Insertion of diaryldiazoalkanes with alcohols

1-[bis(methoxyphenyl)methyl] benzyl ether (1)[23]



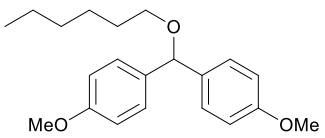
Synthesized according to the general procedure (section 3.3.).
Yield: 56 mg (84%), obtained as colorless oil from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37 – 7.32 (m, 4H), 7.29 – 7.24 (m, 5H), 6.87 – 6.84 (m, 4H), 5.36 (s, 1H), 4.51 (s, 2H), 3.78 (s, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 158.9, 138.6, 134.6, 128.3, 127.7, 127.4, 113.7, 81.5, 70.2, 55.3 ppm.

4,4'-(phenethoxymethylene)bis(methoxybenzene) (2)



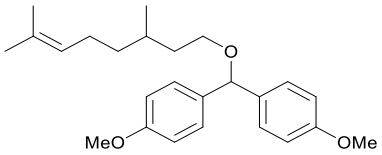
Synthesized according to the general procedure (section 3.3.).
Yield: 63 mg (90%), obtained as colorless oil from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.28 – 7.23 (m, 2H), 7.21 – 7.16 (m, 7H), 6.83 – 6.80 (m, 4H), 5.26 (s, 1H), 3.76 (s, 6H), 3.63 (t, *J* = 7.1 Hz, 2H), 2,94 (t, *J* = 7.1 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158.8, 139.2, 134.8, 129.0, 128.2, 128.1, 126.1, 113.7, 82.8, 69.8, 55.2, 36.5 ppm; **HRMS** (EI): m/z calcd for $C_{23}H_{24}O_3^{\bullet+}$: 348.1725 $[M]^{\bullet+}$; found: 348.1738; **elemental analysis** calcd (%) for $C_{23}H_{24}O_3$: C 79.28, H 6.94; found: C 79.24, H 6.98.

4,4'-((hexyloxy)methylene)bis(methoxybenzene) (3)



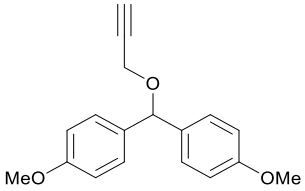
Synthesized according to the general procedure (section 3.3.).
Yield: 54 mg (82%), obtained as colorless oil from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.24 (m, 4H), 6.85 (m, 4H), 5,25 (s, 1H), 3.78 (s, 6H), 3.41 (t, *J* = 6.6 Hz, 2H), 1.65 – 1.60 (m, 2H), 1.40 – 1.35 (m, 2H), 1.34 – 1.24 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158.7, 135.1, 128.1, 113.6, 82.6, 69.0, 55.2, 31.7, 29.9, 25.9, 22.6, 14.1 ppm; **HRMS** (EI): m/z calcd for $C_{21}H_{28}O_3^{\bullet+}$: 328.2038 $[M]^{\bullet+}$; found: 328.2029; **elemental analysis** calcd (%) for $C_{21}H_{28}O_3$: C 76.79, H 8.59; found: C 76.56, H 8.63.

4,4'-(((3,7-dimethyloct-6-en-1-yl)oxy)methylene)bis(methoxybenzene) (4)



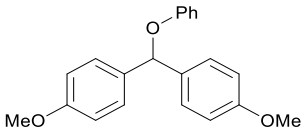
Synthesized according to the general procedure (section 3.3.).
Yield: 65 mg (85%), obtained as white solid from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.24 – 7.22 (m, 4H), 6.85 – 6.83 (m, 4H), 5.24 (s, 1H), 5.10 – 5.07 (m, 1H), 3.78 (m, 6H), 3.47 – 3.40 (m, 2H), 2.03 – 1.90 (m, 2H), 1.70 – 1.65 (m, 4H), 1.64 – 1.59 (m, 4H), 1.47 – 1.41 (m, 1H), 1.35 – 1.29 (m, 1H), 1.16 – 1.10 (m, 1H), 0.86 (d, *J* = 6.6 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158.7, 135.1, 131.0, 128.1, 124.9, 113.6, 82.7, 67.2, 55.2, 37.1, 36.9, 29.6, 25.7, 25.5, 19.6, 17.6 ppm; **HRMS** (ESI): m/z calcd for $C_{25}H_{34}O_3$+Na^+: 405.2406 $[M+Na]^+$; found: 405.2412; **elemental analysis** calcd (%) for $C_{25}H_{34}O_3$: C 78.49, H 8.96; found: C 78.23, H 8.97.

4,4'-((prop-2-yn-1-yloxy)methylene)bis(methoxybenzene) (5)



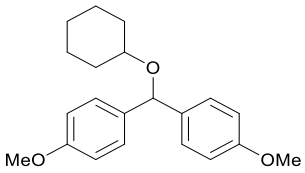
Synthesized according to the general procedure (section 3.3.).
Yield: 40 mg (71%), obtained as colorless oil from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.26 – 7.24 (m, 4H), 6.87 – 6.84 (m, 4H), 5.58 (s, 1H), 4.11 (d, *J* = 2.4 Hz, 2H), 3.78 (s, 6H), 2.44 (t, *J* = 2.4 Hz, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 159.0, 133.5, 128.5, 113.8, 80.8, 79.9, 74.4, 55.5, 55.2 ppm; **HRMS** (ESI): m/z calcd for $C_{18}H_{18}O_3$+Na^+: 305.1154 $[M+Na]^+$; found: 305.1154; **elemental analysis** calcd (%) for $C_{18}H_{18}O_3$: C 76,57, H 6,43; found: C 76,56, H 6,54.

4,4'-(phenoxymethylene)bis(methoxybenzene) (6)



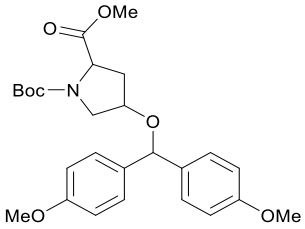
Synthesized according to the general procedure (section 3.3.).
Yield: 46 mg (72%), obtained as white solid from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.31 – 7.28 (m, 4H), 7.22 – 7.18 (m, 2H), 6.94 – 6.92 (m, 2H), 6.90 – 6.85 (m, 5H), 6.14 (s, 1H), 3.77 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 159.0, 158.2, 133.7, 129.3, 128.2, 120.8, 116.1, 113.9, 80.9, 55.2 ppm; **HRMS** (APCI): m/z calcd for $C_{21}H_{19}O_3^{\bullet-}$: 319.1334 $[M]^{\bullet-}$; found: 319.1335; **elemental analysis** calcd (%) for $C_{21}H_{20}O_3$: C 78,73, H 6,29; found: C 78,49, H 6,35.

4,4'-((cyclohexyloxy)methylene)bis(methoxybenzene) (7)



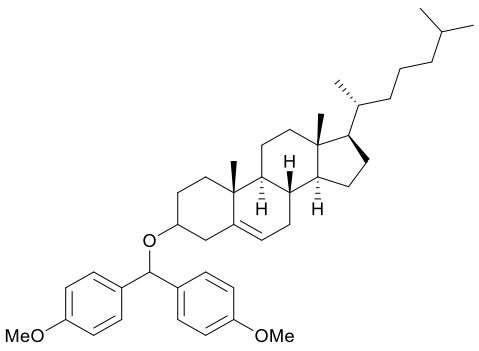
Synthesized according to the general procedure (section 3.3.).
Yield: 43 mg (66%), obtained as colorless oil from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.7 Hz, 4H), 6.86 (d, *J* = 8.7 Hz, 4H), 5.48 (s, 1H), 3.79 (s, 6H), 3.37 – 3.31 (m, 1H), 1.93 – 1.90 (m, 2H), 1.76 – 1.74 (m, 2H), 1.54 – 1.49 (m, 1H), 1.46 – 1.40 (m, 2H), 1.28 – 1.18 (m, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158.7, 135.6, 128.3, 113.6, 79.0, 74.7, 55.2, 32.4, 25.9, 24.2 ppm; **HRMS** (EI): m/z calcd for $C_{21}H_{26}O_3^{\bullet+}$: 326.1882 $[M]^{\bullet+}$; found: 326.1891; **elemental analysis** calcd (%) for $C_{21}H_{26}O_3$: C 77,27, H 8,03; found: C 77,36, H 8,02.

1-(tert-butyl) 2-methyl 4-(bis(4-methoxyphenyl)methoxy)pyrrolidine-1,2-dicarboxylate (8)



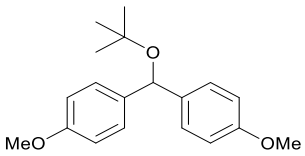
Synthesized according to the general procedure using 2.0 eq. of diazo compound and 2 mL of MeCN (section 3.3.). Product isolated as a mixture of diastereoisomers by silica gel column chromatography.
Yield: 53 mg (56%, d.r. 3:2), obtained as colorless oil from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.22 – 7.16 (m, 4H), 6.87 – 6.82 (m, 4H), 5.33 – 5,31 (m, 1H), 4.48 – 4.37 (m, 1H), 4.18 – 4.13 (m, 1H), 3.79 – 3.77 (m, 6H), 3.72 – 3.70 (m, 4H), 3.56 – 3.53 (m, 1H), 2.42 – 2.34 (m, 1H), 2.03 – 1.98 (m, 1H), 1.44 – 1.41 (m, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 173.6, 173.4, 159.1, 159.0, 154.4, 153.8, 134.2, 134.1, 133.9, 128.4, 128.3, 128.2, 113.8, 113.8, 113.77, 81.0, 80.9, 80.1, 80.1, 75.1, 74.1, 58.1, 57.7, 55.2, 52.1, 52.0, 51.6, 36.9, 35.9, 28.4, 28.2 ppm; **HRMS** (ESI): m/z calcd for $C_{23}H_{33}NO_7$+Na^+: 494.2155 $[M+Na]^+$; found: 494.2159; **elemental analysis** calcd (%) for $C_{26}H_{33}NO_7$: C 66.23, H 7.05, N 2.97; found: C 66.38, H 7.07, N 3.09.

(8S,9S,10R,13R,14S,17R)-3-(bis(4-methoxyphenyl)methoxy)-10,13-dimethyl-17-((R)-6-methyl heptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene (9)



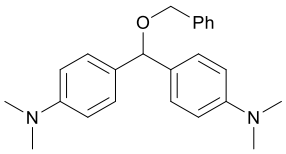
Synthesized according to the general procedure on 0.1 mmol scale using 5.0 eq. of diazo compound and 3 mL of MeCN (section 3.3.).
Yield: 59 mg (96%), obtained as white solid from flash column chromatography using hexanes/MTBE eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.24 – 7.22 (m, 4H), 6.84 – 6.83 (m, 4H), 5.48 (s, 1H), 5.29 (d, *J* = 5.3 Hz, 1H), 3.77 (s, 6H), 3.27 – 3.22 (m, 1H), 2.39 – 2.31 (m, 2H), 2.00 – 1.90 (m, 3H), 1.84 – 1.78 (m, 2H), 1.61 – 1.31 (m, 11H), 1.27 – 1.21 (m, 1H), 1.17 – 1.01 (m, 6H), 1.01 – 0.92 (m, 6H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 2.7 Hz, 6H), 0.66 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158,7, 141,1, 135,4, 128,2, 121,4, 113,7, 79,4, 76,6, 56,8, 56,1, 55,2, 50,2, 42,3, 39,8, 39,5, 39,4, 37,2, 36,9, 36,2, 35,8, 31,9, 31,9, 28,6, 28,2, 28,0, 24,3, 23,8, 22,8, 22,6, 21,0, 19,4, 18,7, 11,8 ppm; **HRMS** (ESI): m/z calcd for $C_{42}H_{60}O_3$+Na^+: 635.4440 $[M+Na]^+$; found: 635.4448; **elemental analysis** calcd (%) for $C_{42}H_{60}O_3$: C 82.30, H 9.87; found: C 82.24, H 9.89.

4,4'-(tert-butoxymethylene)bis(methoxybenzene) (10)



Synthesized according to the general procedure (section 3.3.).
Yield: 46 mg (77%), obtained as colorless oil from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.22 (d, *J* = 8.7 Hz, 4H), 6.81 (d, *J* = 8.7 Hz, 4H), 5.51 (s, 1H), 3.76 (s, 6H), 1.21 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158.3, 137.6, 128.0, 113.5, 74.8, 74.7, 55.2, 28.8 ppm; **HRMS** (EI): m/z calcd for $C_{42}H_{60}O_3^{\bullet+}$: 300.1725 $[M]^{\bullet+}$; found: 300.1722; **elemental analysis** calcd (%) for $C_{19}H_{24}O_3$: C 75.97, H 8.05; found: C 76.00, H 8.09.

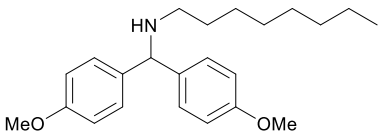
4,4'-((benzyloxy)methylene)bis(N,N-dimethylaniline) (11)



Synthesized according to the general procedure (section 3.3.).
Yield: 32 mg (45%), obtained as blue solid from flash column chromatography using hexanes/acetone eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.38 – 7.36 (m, 2H), 7.34 – 7.31 (m, 2H), 7.27 – 7.21 (m, 5H), 6.70 – 6.68 (m, 4H), 5.31 (s, 1H), 4.51 (s, 2H), 2.91 (s, 12H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 149.9, 139.1, 130.7, 128.2, 128.1, 127.7, 127.2, 112.4, 81.9, 70.0, 40.7 ppm; **HRMS** (ESI): m/z calcd for $C_{24}H_{29}N_2O^+$: 361.2280 $[M+H]^+$; found: 362.2286; **elemental analysis** calcd (%) for $C_{24}H_{28}N_2O$: C 79.96, H 7.83, N 7.77; found: C 79.74, H 7.87, N 7.98.

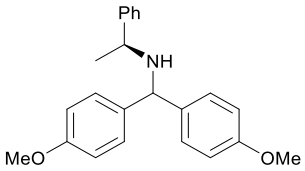
6.2. Photochemical N-H Insertion of diaryldiazoalkanes with alcohols

N-(bis(4-methoxyphenyl)methyl)octan-1-amine (12)



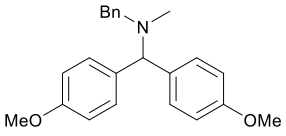
Synthesized according to the general procedure (section 3.4.).
Yield: 51 mg (72%), obtained as colorless oil from flash column chromatography using hexanes/Et_3N eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.2 Hz, 4H), 6.82 (d, *J* = 8.2 Hz, 4H), 4.72 (s, 1H), 3.76 (s, 6H), 2.53 (t, *J* = 7.0 Hz, 2H), 1.52 – 1.46 (m, 2H), 1.40 (bs, 1H), 1.31 – 1 .25 (m, 10H), 0.87 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158.4, 137.0, 128.2, 113.8, 66.3, 55.2, 48.3, 31.8, 30.3, 29.5, 29.3, 27.4, 22.6, 14.1 ppm; **HRMS** (EI): m/z calcd for $C_{23}H_{33}NO_2^{\bullet+}$: 355.2511 $[M]^{\bullet+}$; found: 355.2508; **elemental analysis** calcd (%) for $C_{23}H_{33}NO_2$: C 77.70, H 9.36, N 3.94; found: C 77.65, H 9.17, N 4.11.

(S)-N-(bis(4-methoxyphenyl)methyl)-1-phenylethan-1-amine (13)



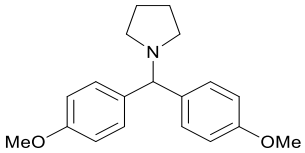
Synthesized according to the general procedure (section 3.4.) using 3 eq. of diazo compound.
Yield: 39 mg (56%), obtained as yellow oil from flash column chromatography using hexanes/Et_3N eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34 – 7.31 (m, 2H), 7.25 – 7.21 (m, 5H), 7.18 – 7.16 (m, 2H), 6.86 – 6.84 (m, 2H), 6.78 – 6.77 (m, 2H), 4.53 (s, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.65 (q, *J* = 6.7 Hz, 1H), 1.75 (bs, 1H), 1.35 (d, *J* = 6.7 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158.5, 158.4, 145.7, 137.3, 136.0, 128.5, 128.4, 128.3, 126.8, 126.7, 113.8, 113.7, 62.4, 55.2, 55.1, 24.4 ppm; **HRMS** (EI): m/z calcd for $C_{23}H_{25}NO_2^{\bullet+}$: 347.1885 $[M]^{\bullet+}$; found: 347.1886; **elemental analysis** calcd (%) for $C_{23}H_{25}NO_2$: C 79.51, H 7.25, N 4.03; found: C 79.54, H 7.20, N 3.91.

N-benzyl-1,1-bis(4-methoxyphenyl)-N-methylmethanamine (14)[24]



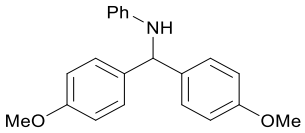
Synthesized according to the general procedure (section 3.4.).
Yield: 39 mg (65%), obtained as colorless oil from flash column chromatography using hexanes/acetone eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 – 7.39 (m, 6H), 7.35 – 7.31 (m, 2H), 7.26 – 7.23 (m, 1H), 6.87 – 6.85 (m, 4H), 4.42 (s, 1H), 3.78 (s, 6H), 3.49 (s, 2H), 2.06 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158.4, 140.1, 135.4, 129.0, 128.6, 128.2, 126.7, 113.8, 73.8, 59.6, 55.2, 40.1 ppm.

1-[bis(methoxyphenyl)methyl]pyrrolidine (15)[25]



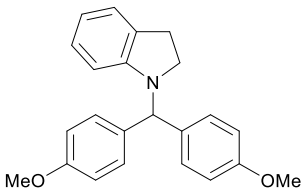
Synthesized according to the general procedure (section 3.4.).
Yield: 50 mg (84%), obtained as colorless oil from flash column chromatography using hexanes/acetone eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 – 7.32 (m, 4H), 6.81 – 6.78 (m, 4H), 4.07(s, 1H), 3.75 (s, 6H), 2.40 (bs, 4H), 1.76 (bs, 4H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158.3, 137.0, 128.3, 113.7, 75.0, 55.2, 53.7, 23.5 ppm.

N-(bis(4-methoxyphenyl)methyl)aniline (16)[24]



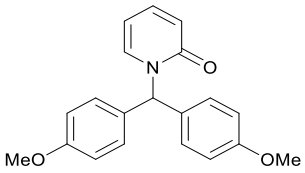
Synthesized according to the general procedure (section 3.4.).
Yield: 38 mg (59%), obtained as colorless oil from flash column chromatography using hexanes/THF eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.25 – 7.23 (m, 5H), 7.12 – 7.09 (m, 2H), 6.86 – 6.84 (m, 4H), 6.69 – 6.66 (m, 1H), 6.54 – 6.52 (m, 2H), 5.41 (s, 1H), 4.15 (bs, 1H), 3.78 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158.7, 147.4, 135.4, 129.1, 128.5, 117.5, 114.0, 113.4, 61.7, 55.3 ppm.

1-(bis(4-methoxyphenyl)methyl)indoline (17)



Synthesized according to the general procedure (section 3.4.).
Yield: 39 mg (57%), obtained as off-white solid from flash column chromatography using hexanes/THF eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.24 – 7.22 (m, 4H), 7.06 – 7.04 (m, 1H), 6.93 – 6.89 (m, 1H), 6.85 – 6.83 (m, 4H), 6.62 – 6.59 (m, 1H), 6.19 – 6.18 (m, 1H), 5.45 (s, 1H), 3.78 (s, 6H), 3.17 (t, *J* = 8.3 Hz, 2H), 2.91 (t, *J* = 8.3 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158.6, 152.0, 133.7, 130.4, 129.5, 127.1, 124.2, 117.3, 113.7, 108.1, 65.3, 55.2, 51.3, 28.3 ppm; **HRMS** (EI): m/z calcd for $C_{23}H_{23}NO_2^{\bullet+}$: 345.1729 $[M]^{\bullet+}$; found: 345.1730; **elemental analysis** calcd (%) for $C_{23}H_{23}NO_2$: C 79.97, H 6.71, N 4.05; found: C 79.97, H 6.73, N 3.93.

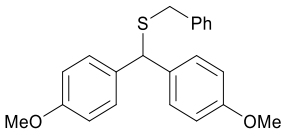
1-(bis(4-methoxyphenyl)methyl)pyridin-2(1H)-one (18)



Synthesized according to the general procedure for O-H insertion (section 3.3.). Crude NMR of reaction mixture reveals formation of both N-H and O-H insertion products (1:1.6 ratio) but the ether product converts to amine **18** on silica gel at the purification step.
Yield: 37 mg (58%), obtained as white solid from flash column chromatography using hexanes/acetone eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39 (s, 1H), 7.30 (ddd, *J* = 8.9, 6.5, 2.0 Hz, 1H), 7.15 (ddd, *J* = 7.0, 2.1, 0.7 Hz, 1H), 7.07 – 7.04 (m, 4H), 6.88 – 6.86 (m, 4H), 6.60 (ddd, *J* = 9.1, 1.5, 0.7 Hz, 1H), 6.10 (td, *J* = 6.8, 1.4 Hz, 1H), 3.79 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 162.5, 159.2, 138.9, 135.8, 131.1, 129.9, 120.8, 114.1, 105.6, 61.0, 55.3; **HRMS** (ESI): m/z calcd for $C_{20}H_{19}NO_3Na^+$: 344.1263 $[M+Na]^+$; found: 344.1264; **elemental analysis** calcd (%) for $C_{20}H_{19}NO_3$: C 74.75, H 5.96, N 4.36; found: C 74.76, H 5.87, N 4.49.

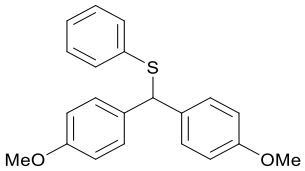
6.3. Photochemical S-H Insertion of diaryldiazoalkanes with alcohols

benzyl(bis(4-methoxyphenyl)methyl)sulfane (19)[26]



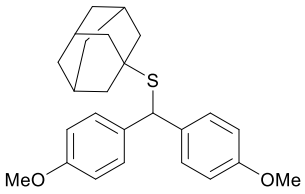
Synthesized according to the general procedure (section 3.5.).
Yield: 62 mg (89%), obtained as white solid from flash column chromatography using hexanes/acetone eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.30 – 7.26 (m, 6H), 7.24 – 7.20 (m, 3H), 6.84 – 6.82 (m, 4H), 4.87 (s, 1H), 3.77 (s, 6H), 3.52 (s, 2H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158.6, 138.1, 133.4, 129.4, 129.0, 128.4, 126.9, 113.9, 55.2, 51.9, 36.6 ppm.

(bis(4-methoxyphenyl)methyl)(phenyl)sulfane (20)[24]



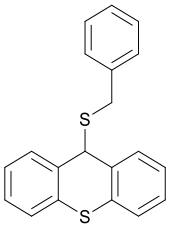
Synthesized according to the general procedure (section 3.5.).
Yield: 58 mg (86%), obtained as yellow solid from flash column chromatography using hexanes/Et_2O eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.7 Hz, 4H), 7.22 – 7.20 (m, 2H), 7.18 – 7.15 (m, 2H), 7.13 – 7.10 (m, 1H), 6.82 (d, *J* = 8.7 Hz, 4H), 5.48 (s, 1H), 3.77 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158.7, 136.5, 133.4, 130.3, 129.4, 128.7, 126.3, 113.9, 56.1, 55.2 ppm.

adamantan-1-yl(bis(4-methoxyphenyl)methyl)sulfane (21)



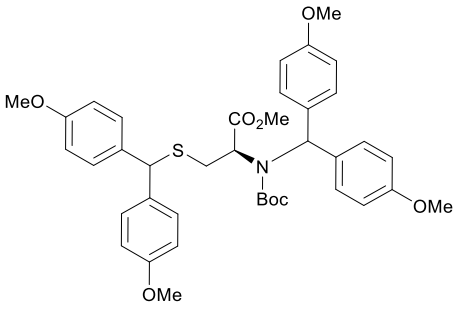
Synthesized according to the general procedure (section 3.5.).
Yield: 69 mg (88%), obtained as white solid from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33 – 7.30 (m, 4H), 6.82 – 6.79 (m, 4H), 5.23 (s, 1H), 3.76 (s, 6H), 1.96 (bs, 3H), 1.81 (m, 6H), 1.65 – 1.58 (m, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 158.2, 136.0, 129.3, 113.7, 55.2, 48.2, 46.8, 43.9, 36.3, 29.8 ppm; **HRMS** (ESI): m/z calcd for $C_{25}H_{30}O_2SNa^+$: 417.1864 $[M+Na]^+$; found: 417.1861; **elemental analysis** calcd (%) for $C_{25}H_{30}O_2S$: 76.10, H 7.66, S 8.13; found: C 75.99 H 7.63, S 7.96.

9-(benzylthio)-9H-thioxanthene (22)



Synthesized according to the general procedure (section 3.5.) on 0.2 mmol scale using 4.0 eq. of benzyl mercaptan.
Yield: 24 mg (38%), obtained as white solid from flash column chromatography using hexanes/toluene eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45 – 7.43 (m, 2H), 7.38 – 7.32 (m, 4H), 7.27 – 7.19 (m, 7H), 5.12 (s, 1H), 3.54 (s, 2H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 137.7, 133.7, 133.4, 129.0, 128.8, 128.5, 127.4, 127.2, 127.0, 126.3, 50.1, 36.2 ppm; **HRMS** (ESI): m/z calcd for $C_{20}H_{16}S_2Na^+$: 343.0591 $[M+Na]^+$; found: 343.0594.

methyl N,S-bis(bis(4-methoxyphenyl)methyl)-N-(tert-butoxycarbonyl)-L-cysteinate (23)

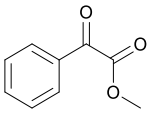


Synthesized according to the general procedure (section 3.5.) on 0.2 mmol scale using 2.0 eq. of diazo compound and 2 mL of dry DCM.
Yield: 66 mg (45%), obtained as white solid from flash column chromatography using hexanes/AcOEt eluent system.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.27 – 7.24 (m, 4H), 7.20 – 7.16 (m, 4H), 6.85 – 6.78 (m, 8H), 6.01 (bs, 1H), 4.83 (s, 1H), 4.05 (bs, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.75 (s, 3H), 3.64 (bs, 3H), 3.14 (dd, J = 13.6, 8.1 Hz, 1H), 2.40 (bs, 1H), 1.26 (bs, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 171.4, 158.7, 158.7, 158.5, 133.9, 133.6, 130.1, 129.4, 129.3, 113.8, 113.8, 113.7, 113.5, 81.0, 64.5, 59.5, 55.2, 55.2, 55.2, 53.6, 52.1, 28.11 ppm; **HRMS** (ESI): m/z calcd for $C_{39}H_{45}NO_8SNa^+$: 710.2764 $[M+Na]^+$; found: 710.2756; **elemental analysis** calcd (%) for $C_{39}H_{45}NO_8S$: C 68.10, H 6.59, N 2.04, S, 4.66; found: C 67.98, H 6.62, N 2.16, S 4.90.

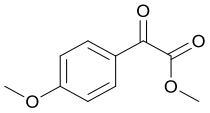
6.4. Photosensitized oxygenation of aryldiazoesters

methyl 2-oxo-2-phenylacetate (24) [21]



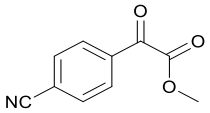
Synthesized according to the general procedure (section 3.6.).
Yield: 15 mg (94%), obtained as white solid from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 3.99 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 186.0, 135.0, 132.5, 130.1, 128.9, 52.8 ppm.

methyl 4-methoxybenzoate (25) [21]



Synthesized according to the general procedure (section 3.6.).
Yield: 14 mg (70%), obtained as white solid from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.05 – 7.96 (m, 2H), 7.01 – 6.93 (m, 2H), 3.96 (s, 3H), 3.90 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 184.4, 165.1, 164.3, 132.7, 125.5, 114.2, 55.6, 52.6 ppm.

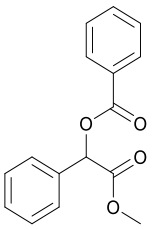
methyl 2-(4-cyanophenyl)-2-oxoacetate (26) [21]



Synthesized according to the general procedure (section 3.6.).
Yield: 8 mg (40%), obtained as white solid from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.6 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 2H), 4.00 (s, 3H) ppm.
^{13}C NMR (151 MHz, $CDCl_3$): δ = 184.0, 162.6, 135.5, 132.6, 130.5, 118.0, 117.5, 53.2 ppm.

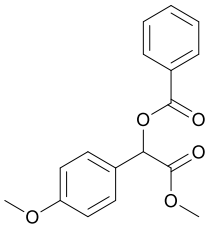
6.5. Photosensitized O-H insertion of aryldiazoesters with carboxylic acids

2-methoxy-2-oxo-1-phenylethyl benzoate (27)[27]



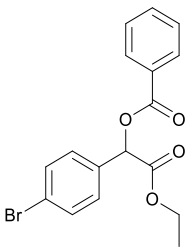
Synthesized according to the general procedure (section 3.7.).
Yield: 23 mg (84%), obtained as off-white solid from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.16 – 8.10 (m, 2H), 7.59 (d, *J* = 7.0 Hz, 3H), 7.44 (dt, *J* = 17.9, 6.9 Hz, 5H), 6.18 (s, 1H), 3.76 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 169.3, 165.9, 134.0, 133.5, 130, 129.3, 129.3, 128.9, 128.4, 127.6, 74.9, 52.6 ppm.

2-methoxy-1-(4-methoxyphenyl)-2-oxoethyl benzoate (28)[28]



Synthesized according to the general procedure (section 3.7.).
Yield: 15 mg (50%), obtained as off-white solid from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 6.12 (s, 1H), 3.83 (s, 3H), 3.75 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 169.5, 165.9, 160.4, 133.4, 129.9, 129.3, 129.1, 128.4, 126.1, 114.3, 74.5, 55.3, 52.6. ppm.

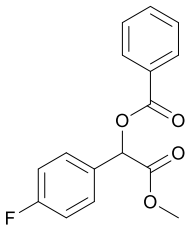
1-(4-bromophenyl)-2-ethoxy-2-oxoethyl benzoate (29)[27]



Synthesized according to the general procedure (section 3.7.).
Yield: 15 mg (42%), obtained as colorless oil from flash column chromatography using hexanes/AcOEt eluent system.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.1 Hz, 2H), 7.64 – 7.52 (m, 3H), 7.47 (dt, *J* = 7.4, 3.5 Hz, 4H), 6.11 (s, 1H), 4.30 – 4.15 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 168.3, 165.7, 133.5, 133.2, 132.0, 129.9, 129.2, 129.1, 128.5, 123.4, 74.3, 61.5, 14.0 ppm.

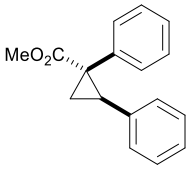
1-(4-fluorophenyl)-2-methoxy-2-oxoethyl benzoate (30)[27]



Synthesized according to the general procedure (section 3.7.).
Yield: 17 mg (55%), obtained as off-white solid from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.53 (m, 3H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 6.16 (s, 1H), 3.76 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 169.1, 165.7, 164.2, 133.6, 130.0, 129.6, 129.5, 129.1, 128.5, 116.0, 115.8, 74.1, 52.7ppm.

6.6. Photosensitized cyclopropanation of aryldiazoesters with olefins

methyl 1,2-diphenylcyclopropane-1-carboxylate (31)[7]



Synthesized according to the general procedure (section 3.8.).
Yield: 15 mg (68%), white solid obtained as mixture of diastereoisomers (d.r. 77:23) from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (minor, d, *J* = 7.8 Hz, 2H), 7.35 (minor, dt, *J* = 27.2, 7.4 Hz, 8H), 7.16 – 7.09 (m, 3H), 7.05 (ddd, *J* = 13.0, 5.4, 2.0 Hz, 5H), 6.81 – 6.73 (m, 2H), 3.67 (s, 3H), 3.31 (minor, s, 3H), 3.19 – 3.08 (m, 1H), 2.88 (minor, t, *J* = 8.2 Hz, 1H), 2.35 (minor, dd, *J* = 7.2, 5.2 Hz, 1H), 2.14 (dd, *J* = 9.3, 4.9 Hz, 1H), 1.89 (dd, *J* = 7.1, 5.1 Hz, 1H), 1.62 (minor, dd, *J* = 9.0, 5.0 Hz, 1H) ppm.

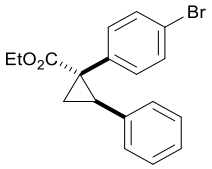
^{13}C NMR (151 MHz, $CDCl_3$) δ 174.3, 140.3, 136.5, 136.4, 134.7, 131.9, 130.2, 129.0, 128.3, 128.0, 127.7, 127.6, 127.3, 127.0, 126.8, 126.3, 52.6, 51.9, 37.4, 33.2, 33.1, 29.7, 20.4, 18.3 ppm.

methyl 1-(4-methoxyphenyl)-2-phenylcyclopropane-1-carboxylate (32)[29]

Synthesized according to the general procedure (section 3.8.).
Yield: 15 mg (70%), white solid, obtained as mixture of diastereoisomers (d.r. 98:2) from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (minor, d, 2H), 7.34 (minor, m, 5H), 7.22 (m, 2H), 7.07 (m, 3H), 6.94 (minor, d, *J* = 8.6 Hz, 2H), 6.82 – 6.72 (m, 2H), 6.67 (d, *J* = 8.6 Hz, 2H), 3.83 (minor, s, 3H), 3.73 (s, 3H), 3.67 (s, 3H), 3.30 (minor, s, 3H), 3.08 (dd, *J* = 9.1, 7.5 Hz, 1H), 2.82 (minor, m, 1H), 2.30 (minor,

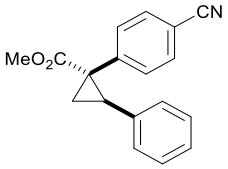
m, 1H), 2.13 (dd, *J* = 9.3, 4.8 Hz, 1H), 1.83 (dd, *J* = 7.2, 4.9 Hz, 1H), 1.60 (minor, m, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): (minor+major) δ = 158.4, 136.5, 132.9, 128.1, 127.7, 126.8, 126.2, 113.1, 55.0, 52.6, 36.6, 33.2, 20.2. ppm.

ethyl 1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylate (33)[7]

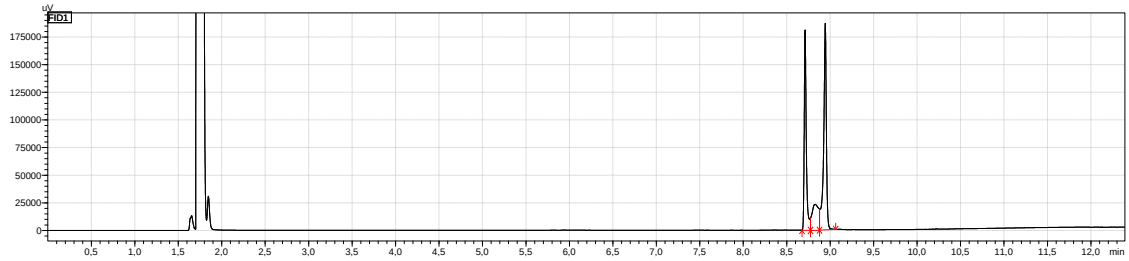


Synthesized according to the general procedure (section 3.8.).
Yield: 14 mg (40%), off-white solid obtained as single diastereoisomer (d.r. >99:1) from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.24 – 7.22 (m, 2H), 7.10 – 7.05 (m, 3H), 6.89 – 6.86 (m, 2H), 6.78 – 6.75 (m, 2H), 4.18 – 4.06 (m, 2H), 3.08 (dd, *J* = 9.3, 7.3 Hz, 1H), 2.12 (dd, *J* = 9.3, 5.0 Hz, 1H), 1.82 (dd, *J* = 7.3, 5.0 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 173.2, 136.0, 134.1, 133.5, 130.8, 128.0, 127.9, 126.5, 121.1, 61.4, 37.0, 32.9, 20.0, 14.1 ppm.

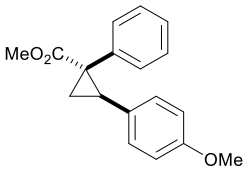
methyl 1-(4-cyanophenyl)-2-phenylcyclopropane-1-carboxylate (34)



Synthesized according to the general procedure (section 3.8.).
Yield: 25 mg (78%), off-white solid obtained as mixture of diastereoisomers (d.r. 61:39) from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$) both diastereoisomers: δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.31 (m, 4H), 7.27 (m, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 7.11 – 7.05 (m, 2H), 6.76 (dd, *J* = 6.5, 3.0 Hz, 2H), 3.68 (s, 3H), 3.31 (s, 3H), 3.18 (dd, *J* = 9.2, 7.5 Hz, 1H), 2.89 – 2.82 (m, 1H), 2.41 (dd, *J* = 7.6, 5.3 Hz, 1H), 2.23 – 2.17 (m, 1H), 1.91 (dd, *J* = 7.3, 5.2 Hz, 1H), 1.65 (dd, *J* = 9.2, 5.3 Hz, 1H) ppm. ppm.
^{13}C NMR (151 MHz, $CDCl_3$) both diastereoisomers: δ = 173.0, 169.9, 145.4, 140.5, 135.6, 135.2, 132.6, 132.2, 131.5, 130.9, 128.9, 128.2, 128.0, 127.9, 127.1, 126.9, 118.7, 118.7, 111.2, 110.9, 52.8, 52.1, 37.9, 37.2, 33.5, 33.4, 19.9, 18.4 ppm; **HRMS** (ESI): m/z calcd for $C_{18}H_{15}NO_2^+$: 278,1176 $[M+H]^+$; found: 278,1185. **GC chromatogram:** t_r = 8,717 min, (86% purity, 78% yield)



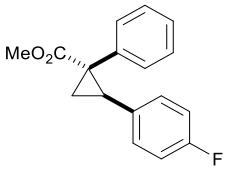
methyl 2-(4-methoxyphenyl)-1-phenylcyclopropane-1-carboxylate (35)[30]



Synthesized according to the general procedure (section 3.8.).
Yield: 20 mg (70%), white solid obtained as mixture of diastereoisomers (d.r. 78:22) from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (500 MHz,$CDCl_3$) δ 7.49 (minor, d, *J* = 7.3 Hz, 2H), 7.36 (minor, t, *J* = 7.5 Hz, 2H), 7.27 (minor, m, 3H), 7.14-7.12 (m, 3H), 7.02 (m, 2H), 6.85 (minor, d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 3.80 (minor, s, 3H), 3.69 (s, 3H), 3.65 (s, 3H), 3.32 (minor, s, 3H), 3.06 (dd, *J* = 9.2, 7.6 Hz, 1H), 2.81 (minor, m, 1H), 2.29 (minor, dd, *J* = 7.4, 5.1 Hz, 1H), 2.11 (dd, *J* = 9.4, 4.9 Hz, 1H), 1.80 (dd, *J* = 7.2, 4.9 Hz, 1H), 1.59 (minor, m, 1H) ppm.

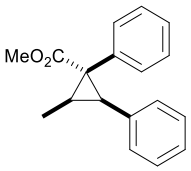
^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4 (minor + major), 158.5 (minor), 158.1, 134.9 (minor + major), 132.0 (minor + major), 130.2, 130.0, 129.0 (minor + major), 128.5, 128.3, 128.3, 127.7, 127.3, 126.9, 113.5, 113.2, 55.2, 55.1, 52.5, 52.0, 37.04 (minor + major), 32.7, 32.6, 20.5, 18.4 ppm.

methyl 2-(4-fluorophenyl)-1-phenylcyclopropane-1-carboxylate (36)[31]



Synthesized according to the general procedure (section 3.8.).
Yield: 11 mg (40%), yellowish oil obtained as single diastereoisomer (d.r. >99:1) from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.17 – 7.11 (m, 3H), 7.05 – 6.97 (m, 2H), 6.78 – 6.66 (m, 4H), 3.66 (s, 3H), 3.10 (dd, *J* = 9.3, 7.3 Hz, 1H), 2.14 (dd, *J* = 9.4, 5.0 Hz, 1H), 1.83 (dd, *J* = 7.2, 5.0 Hz, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 174.2, 162.4, 134.5, 132.1, 132.1, 131.9, 129.4, 129.4, 127.8, 127.1, 114.7, 114.5, 52.6, 37.2, 32.3, 20.5 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -116.48 (m, 1F).

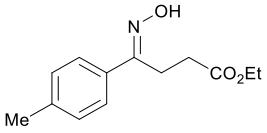
methyl 2-methyl-1,3-diphenylcyclopropane-1-carboxylate (37)[34]



Synthesized according to the general procedure (section 3.8.).
Yield: 15 mg (55%), white solid obtained as single diastereoisomer (d.r. >99:1) from flash column chromatography using hexanes/AcOEt eluent system. (Structure confirmed by NOE, see NMR section). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.34 – 7.26 (m, 3H), 7.13 (dt, *J* = 5.2, 2.9 Hz, 3H), 7.08 – 7.01 (m, 2H), 6.82 – 6.69 (m, 2H), 3.62 (s, 3H), 3.10 (d, *J* = 10.3 Hz, 1H), 2.38 (dq, *J* = 10.2, 6.8 Hz, 1H), 1.26 (d, *J* = 6.7 Hz, 4H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 13C NMR (150 MHz, $CDCl_3$) δ 175.5, 136.2, 133.2, 132.3, 130.6, 127.8, 127.5, 127.2, 52.7, 38.0, 36.5, 27.8, 10.8 ppm.

6.7. Photocatalyzed synthesis of γ-oximinoesters

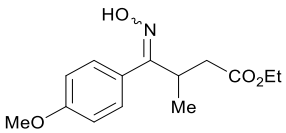
ethyl (E)-4-(hydroxyimino)-4-(p-tolyl)butanoate (38)[32]



Synthesized according to the general procedure (section 3.9.).
Yield: 41 mg (86%), obtained as white solid from flash column chromatography using hexanes/AcOEt eluent system.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.21 (s, 1 H), 7.50 (d, *J* = 8.1 Hz, 2 H), 7.17 (d, *J* = 8.1 Hz, 2 H), 4.01 (q, *J* = 7.1 Hz, 2 H), 2.91 (t, *J* = 7.9 Hz, 2 H), 2.44 (t, *J* = 7.9 Hz, 2 H), 2.31 (s, 3 H), 1.13 (t, *J* = 7.1 Hz, 3 H) ppm. **^{13}C NMR** (151 MHz, DMSO-d_6): δ = 172.0, 155.2, 138.2, 132.9, 129.0,125.7, 60.0, 30.4, 21.0, 20.8, 14.0 ppm.

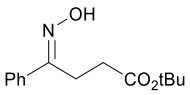
ethyl 4-(hydroxyimino)-5-(4-methoxyphenyl)-3-methylpentanoate (39)[32]



Synthesized according to the general procedure (section 3.9.).
Yield: from *trans*-anethole: 21 mg (38%, E/Z ratio: 2.2:1), from *cis*-anethole: 15 mg (26%, E/Z ratio: 2.1:1), yellowish oil obtained from flash column chromatography using hexanes/AcOEt eluent system. **^{1}H NMR** (600 MHz, $CDCl_3$): major isomer: δ = 8.81 (s, 1H), 7.46 – 7.40 (m, 2H), 6.91 – 6.86 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 3.78 – 3.71 (m, 1H), 2.88 (dd, *J* = 16.1, 7.2 Hz, 1H), 2.63 (dd, *J* = 16.1, 7.9 Hz, 1H), 1.33 (d, *J* = 7.1 Hz 3H), 1.20 (t, *J* = 7.1 Hz, 3H) ppm; minor isomer: δ = 8.34 (s, 1H), 7.38 – 7.33 (m, 2H), 6.96 – 6.92 (m, 2H), 4.17 – 4.14 (m, 2H), 3.83 (s, 3H), 3.28 – 3.19 (m, 1H), 2.72 (dd, *J* = 15.8, 7.3 Hz, 1H), 2.36 (dd, *J* = 15.8, 7.3 Hz, 1H), 1.25 (t, *J* = 7.2 Hz 3H), 1.14 (d, *J* = 7.0 Hz, 3H) ppm. The mixture of **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 172.4, 172.4, 161.5, 160.6, 160.1,

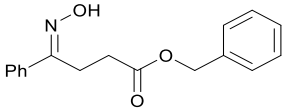
159.8, 129.4, 128.7, 128.5, 125.2, 113.8, 113.6, 60.4, 60.4, 55.3, 55.2, 38.8, 38.1, 36.4, 31.4, 18.4, 16.8, 14.2, 14.1.

tert-butyl (E)-4-(hydroxyimino)-4-phenylbutanoate (40)[32]



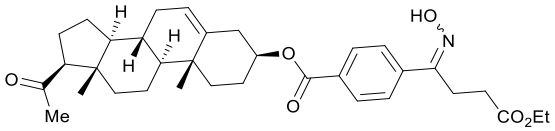
Synthesized according to the general procedure (section 3.9.).
Yield: 32 mg (64%), obtained as yellowish oil from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (600 MHz, DMSO-d_6): δ = 7 11.31 (s, 1H), 7.63 – 7.59 (m, 2 H), 7.40 – 7.34 (m, 3 H), 2.91 (t, *J* = 7.8 Hz, 2 H), 2.38 (t, *J* = 7.8 Hz, 2 H), 1.33 (s, 9 H). 1ppm. **^{13}C NMR** (151 MHz, DMSO-d_6): δ = 171.2, 155.5, 135.8, 128.6, 128.4, 125.9, 79.8, 31.5, 27.6, 21.2.

benzyl (E)-4-(hydroxyimino)-4-phenylbutanoate (41)[32]



Synthesized according to the general procedure (section 3.9.).
Yield: 40 mg (71%), obtained as yellowish oil from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.35 (s, 1H), 7.67 – 7.58 (m, 2 H), 7.41 – 7.28 (m, 8 H), 5.05 (s, 2 H), 2.98 (t, *J* = 7.5 Hz, 2 H), 2.56 (t, *J* = 7.8 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, DMSO-d_6): δ = 171.9, 155.3, 136.1, 135.7, 128.7, 128.4, 128.4, 128.0, 127.9, 125.8, 65.6, 30.3, 21.1 ppm.

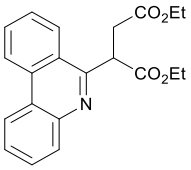
(3S,8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1H-cyclopenta[a]phenanthren-3-yl 4-(4-ethoxy-1-(hydroxyimino)-4-oxobutyl) benzoate (42)[32]



Synthesized according to the general procedure (section 3.9.).
Yield: 30 mg (27%), obtained as white solid from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (500 MHz, DMSO-d_6): δ = δ 11.64 (s, 1 H), 7.95 (d, *J* = 8.3 Hz, 2 H), 7.77 (d, *J* = 8.3 Hz, 2 H), 5.44 – 5.35 (m, 1 H), 4.77 – 4.68 (m, 1 H), 4.00 (q, *J* = 7.1 Hz, 2 H), 2.97 (t, *J* = 7.8 Hz, 2 H), 2.57 (t, *J* = 9.0 Hz, 1 H), 2.49 – 2.46 (m, 2 H), 2.45 – 2.40 (m, 2 H), 2.06 (s, 3 H), 2.05 – 1.85 (m, 5 H), 1.76 – 1.67 (m, 1 H), 1.66 – 1.50 (m, 4 H), 1.49 – 1.36 (m, 3 H), 1.19 – 1.09 (m, 6 H), 1.05 – 0.96 (m, 4 H), 0.54 (s, 3 H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 208.6, 172.0, 164.9, 154.8, 140.2, 139.5, 130.0, 129.4, 126.1, 122.3, 74.2, 62.6, 60.1, 56.1, 49.4, 43.3, 38.0, 37.7, 36.6, 36.2, 31.4, 31.3, 31.3, 30.2, 27.4, 24.1, 22.3, 21.0, 20.6, 19.1, 14.1, 13.0 ppm.

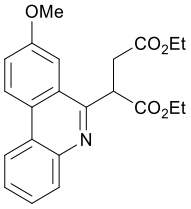
6.8. Photocatalyzed synthesis of phenantridines

diethyl 2-(phenanthridin-6-yl)succinate (43)[15]



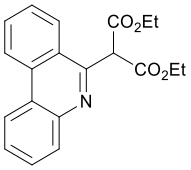
Synthesized according to the general procedure (section 3.10.).
Yield: 67 mg (95%), obtained as yellow oil from flash column chromatography using hexanes/acetone eluent system.
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.65 (d, *J* = 8.3 Hz, 1H), 8.54 (d, *J* = 7.8 Hz, 1H), 8.36 (d, *J* = 8.2 Hz, 1H), 8.11 (d, *J* = 7.4 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.75 – 7.66 (m, 2H), 7.66 – 7.60 (m, 1H), 5.23 (dd, *J* = 8.1, 6.3 Hz, 1H), 4.22 – 4.07(m, 4H), 3.44 (dd, *J* = 17.0, 8.1 Hz, 1H), 3.25 (dd, J = 17.0, 6.3 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 172.0, 171.7, 156.8, 143.3, 133.2, 130.4, 130.2, 128.5, 127.5, 127.0, 125.8, 124.9, 123.8, 122.5, 121.8, 61.3, 60.7, 46.0, 35.6, 14.1, 14.0 ppm.

diethyl 2-(8-methoxyphenanthridin-6-yl)succinate (44)[15]



Synthesized according to the general procedure (section 3.10.).
Yield: 61 mg (80%), obtained as yellow oil from flash column chromatography using hexanes/acetone eluent system.
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 9.1 Hz, 1H), 8.46 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.12 – 8.06 (m 1H), 7.71 (d, *J* = 2.5 Hz, 1H), 7.68 – 7.58 (m, 2H), 7.48 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.15 (dd, *J* = 8.1, 6,2 Hz, 1H), 4.24 – 4.09 (m, 4H), 4.00 (s, 3H), 3.47 (dd, *J* = 17.1, 8.1 Hz, 1H), 3.25 (dd, *J* = 17.1, 6.3 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 172.2, 171.8, 158.8, 155.8, 142.6, 130.2, 127.6, 127.6, 127.1, 126.3, 124.2, 123.9, 121.4, 121.2, 105.9, 61.3, 60.7, 55.6, 46.4, 35.5, 14.2, 14.1 ppm.

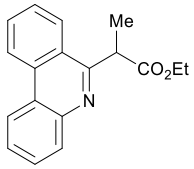
diethyl 2-(phenanthridin-6-yl)malonate (45)[15]



Synthesized according to the general procedure (section 3.10.).
Yield: 28 mg (42%), obtained as yellow solid from flash column chromatography using hexanes/acetone eluent system.

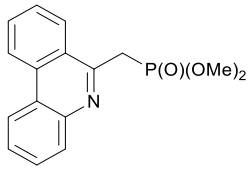
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.67 (d, *J* = 8.4 Hz, 1H), 8.57 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.85 (t, *J* = 7.3 Hz, 1H), 7.75 – 7.64 (m, 3H), 5.63 (s, 1H), 4.38 – 4.26 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 167.5, 153.6, 143.3, 133.2, 130.6, 130.5, 128.6, 127.6, 127.4, 125.2, 125.0, 124.0, 122.7, 121.9, 62.0, 59.5, 14.1. ppm.

ethyl 2-(phenanthridin-6-yl)propanoate (46)[15]



Synthesized according to the general procedure (section 3.10.).
Yield: 42 mg (75%), obtained as yellow oil from flash column chromatography using hexanes/acetone eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.67 (d, J = 8.3 Hzm 1H), 8.56 (d, *J* = 8.1, 1H), 8.22 (d, *J* = 8.2, 1H), 8.15 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.74 – 7.67 (m, 2H), 7.67 – 7.63 (m, 1H), 4.74 (q, *J* = 7.1 Hz, 1H), 4.26 – 4.13 (m, 2H), 1.78 (d, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 173.7, 159.5, 143.6, 133.3, 130.3, 130.2, 128.6, 127.4, 126.8, 125.6, 124.7, 123.7, 122.7, 121.8, 60.9, 45.6, 16.4, 14.1 ppm.

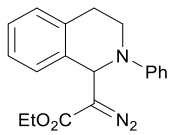
dimethyl (phenanthridin-6-ylmethyl)phosphonate (47)[15]



Synthesized according to the general procedure (section 3.10.).
Yield: 38 mg (63%), obtained as yellow oil from flash column chromatography using hexanes/acetone eluent system.
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.65 (d, *J* = 8.3 Hz, 1H), 8.56 (d, *J* = 7.8 Hz, 1H), 8.34 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.77 – 7.70 (m, 2H), 7.68 – 7.63 (m, 1H), 4.07 (s, 1H), 4.03 (s, 1H), 3.76 (s, 3H), 3.74 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 153.3 (d, *J* = 8.9 Hz), 143.6 (d, *J* = 2.7 Hz), 133.1, 130.8, 129.7, 128.7, 127.5, 127.1, 127.0, 125.4 (d, *J* = 3.4 Hz), 123.9, 122.3, 122.0, 53.0 (d, *J* = 6.5 Hz), 35.0, 33.9 ppm.

6.9. Photocatalyzed synthesis of β-amino-α-diazo esters

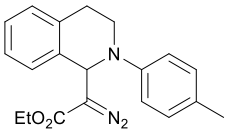
ethyl 2-diazo-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acetate (48)[33]



Synthesized according to the general procedure (section 3.11.).
Yield: 22 mg (70%), obtained as yellowish oil from flash column chromatography using hexanes/AcOEt eluent system.

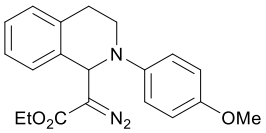
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33–7.13 (m, 6H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.90–6.82 (m, 1H), 5.79 (s, 1H), 4.26–4.14 (m, 2H), 3.66–3.53 (m, 2H), 3.03 (dt, *J* = 16.2, 6.5 Hz, 1H), 2.89 (dt, *J* = 16.1, 5.3 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 166.5, 149.1, 135.4, 134.7, 129.4, 128.8, 127.7, 127.6, 126.8, 119.8, 116.4, 61.1, 56.5, 43.9, 28.1, 14.6 ppm.

ethyl 2-diazo-2-(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetate (49)[33]



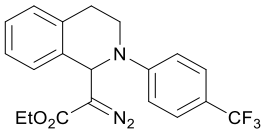
Synthesized according to the general procedure (section 3.11.).
Yield: 25 mg (78%), obtained as yellowish oil from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.27 (m, 1H), 7.24–7.18 (m, 2H), 7.19–7.14 (m, 1H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 5.74 (s, 1H), 4.25–4.15 (m, 2H), 3.60–3.50 (m, 2H), 3.06–2.97 (m, 1H), 2.90 (dt, *J* = 16.1, 5.3 Hz, 1H), 2.28 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.6, 147.0, 135.4, 134.8, 129.8, 129.6, 128.8, 127.7, 127.5, 126.7, 117.2, 61.0, 56.8, 44.6, 28.3, 20.6, 14.5 ppm.

ethyl 2-diazo-2-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetate (50)[33]



Synthesized according to the general procedure (section 3.11.).
Yield: 24 mg (67%), obtained as yellowish oil from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30–7.23 (m, 1H), 7.24–7.17 (m, 2H), 7.19–7.12 (m, 1H), 7.06 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 5.61 (s, 1H), 4.21–4.08 (m, 2H), 3.77 (s, 3H), 3.54–3.36 (m, 2H), 3.05–2.84 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.7, 154.7, 143.8, 135.4, 134.7, 128.9, 127.7, 127.5, 126.7, 120.6, 114.6, 61.0, 57.9, 55.7, 46.2, 28.7, 14.5 ppm.

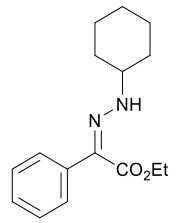
ethyl 2-diazo-2-(2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetate (51)[33]



Yield: 23 mg (53%), obtained as yellowish oil from flash column chromatography using hexanes/AcOEt eluent system.
^{1}H NMR (500 MHz, $CDCl_3$): δ = (d, *J* = 8.6 Hz, 2H), 7.33–7.27 (m, 1H), 7.27–7.21 (m, 2H), 7.21–7.15 (m, 1H), 7.08 (d, *J* = 8.6 Hz, 2H), 5.86 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.73 (dt, *J* = 12.8, 5.6 Hz, 1H), 3.63 (ddd, *J* = 12.8, 8.5, 4.5 Hz, 1H), 3.06 (ddd, *J* = 16.1, 8.5, 5.0 Hz, 1H), 2.88 (ddd, *J* = 16.1, 6.0, 4.4 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.3, 150.9, 135.0, 134.1, 128.0, 127.6, 127.1, 126.7 (q, *J* = 3.8 Hz), 124.9 (q, *J* = 270.4 Hz), 120.4 (q, *J* = 32.7 Hz), 114.1, 61.4, 55.8, 43.0, 27.6, 14.6 ppm.

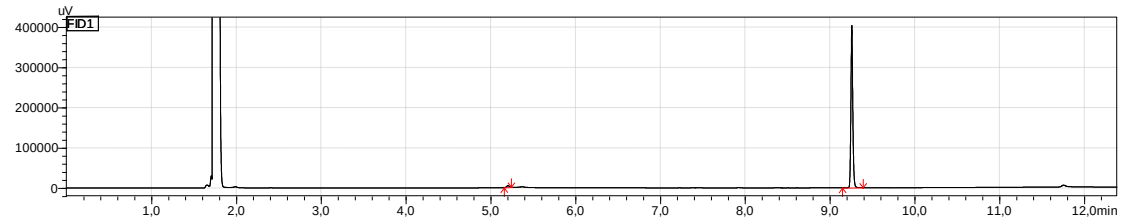
6.10. Photocatalyzed synthesis of hydrazones

ethyl (Z)-2-(2-cyclohexylhydrazineylidene)-2-phenylacetate (52)[17]

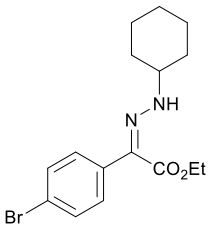


Exact Mass: 274,1681

Synthesized according to the general procedure (section 3.12.).
Yield: 43 mg (78%), obtained as colorless oil from flash column chromatography using hexanes/DCM/AcOEt eluent system.
^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.62 (s, 1H), 7.57– 6.49 (m, 2H), 7.35 – 7.27 (m, 2H), 7.27 – 7.19 (m, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.54 – 3.37 (m, 1H), 2.11 – 1.95 (m, 2H), 1.85 – 1.70 (m, 2H), 1.67 – 1.57 (m, 1H), 1.46 – 1.34 (m, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.29 – 1.15 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 163.9, 137.7, 128.4, 127.9, 126.7, 124.6, 60.3, 59.3, 32.7, 25.8, 24.7, 14.4 ppm; **HRMS** (ESI): m/z calcd for $C_{16}H_{23}N_2O_2^+$: 275.1760 $[M+H]^+$; found: 275.1759; **GC chromatogram:** t_r = 9.251 min, (98% purity).

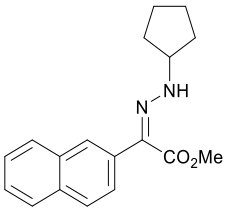


ethyl (Z)-2-(4-bromophenyl)-2-(2-cyclohexylhydrazineylidene)acetate (53)[17]



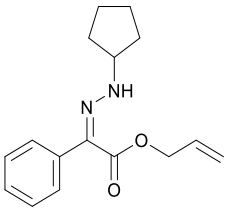
Synthesized according to the general procedure (section 3.12.).
Yield: 48 mg (68%), obtained as colorless oil from flash column chromatography using hexanes/DCM/AcOEt eluent system.
^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.70 (d, *J* = 5.1 Hz, 1H), 7.45 – 7.49 (m, 4H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.51 – 3.39 (m, 1H), 2.09 – 1.95 (m, 2H), 1.83 – 1.71 (m, 2H), 1.68 – 1.59 (m, 1H), 1.47 – 1.35 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.30 – 1.17 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 163.5, 136.5, 130.8, 129.8, 123.2, 120.5, 60.3, 59.3, 32.5, 25.6, 24.5, 14.3.ppm.

methyl (Z)-2-(2-cyclopentylhydrazineylidene)-2-(naphthalen-2-yl)acetate (54)[17]



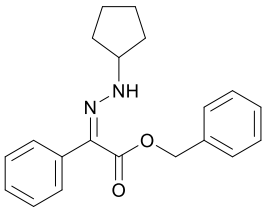
Synthesized according to the general procedure (section 3.12.).
Yield: 31 mg (53%), obtained as colorless oil from flash column chromatography using hexanes/DCM/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.67 (d, *J* = 4.0 Hz, 1H), 7.98 – 7.96 (m, 1H), 7.84 – 7.77 (m, 3H), 7.68 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.46 – 7.39 (m, 2H), 4.14 – 4.06 (m, 1H), 3.82 (s, 3H), 2.03 – 1.95 (m, 2H), 1.83 – 1.70 (m, 4H), 1.69 – 1.59 (m, 2H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 164.3, 134.7, 133.2, 132.4, 128.2, 127.5, 127.1, 126.8, 126.6, 125.8, 125.6, 124.3, 62.2, 51.2, 32.5, 23.9. ppm.

allyl (Z)-2-(2-cyclopentylhydrazineylidene)-2-phenylacetate (55)[17]



Synthesized according to the general procedure (section 3.12.).
Yield: 29 mg (53%), obtained as colorless oil from flash column chromatography using hexanes/DCM/AcOEt eluent system.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.61 (s, 1H), 7.56 – 7.51 (m, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.21 (m, 1H), 6.00 – 5.91 (m, 1H), 5.32 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.24 (d, *J* = 10.4, 1.4 Hz, 1H), 4.70 (d, *J* = 5.5 Hz, 2H), 4.10 – 4.03 (m, 1H), 1.99 – 1.93 (m, 2H), 1.79 – 1.71 (m, 4H), 1.65 – 1.59 (m, 2H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 163.3, 137.3, 132.0, 128.3, 127.7, 126.7, 124.3, 118.2, 64.7, 62.2, 32.5, 23.9 ppm.

benzyl (Z)-2-(2-cyclopentylhydrazineylidene)-2-phenylacetate (56)[17]



Synthesized according to the general procedure (section 3.12.).
Yield: 34 mg (52%), obtained as colorless oil from flash column chromatography using hexanes/DCM/AcOEt eluent system.
^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.61 (d, *J* = 2.7 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.35 (d, *J* = 4.3 Hz, 4H), 7.30 (t, *J* = 7.4 Hz 2H), 5.25 (s, 2H), 4.05 (d, J = 4.7 Hz, 1H), 2.00 – 1.89 (m, 2H), 1.80 – 1.69 (m, 4H), 1.66 – 1.57 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 163.4, 137.3, 135.9, 128.5, 128.3, 128.1, 127.9, 127.7, 126.7, 124.3, 65.7, 62.2, 32.5, 23.9. ppm.

7. References

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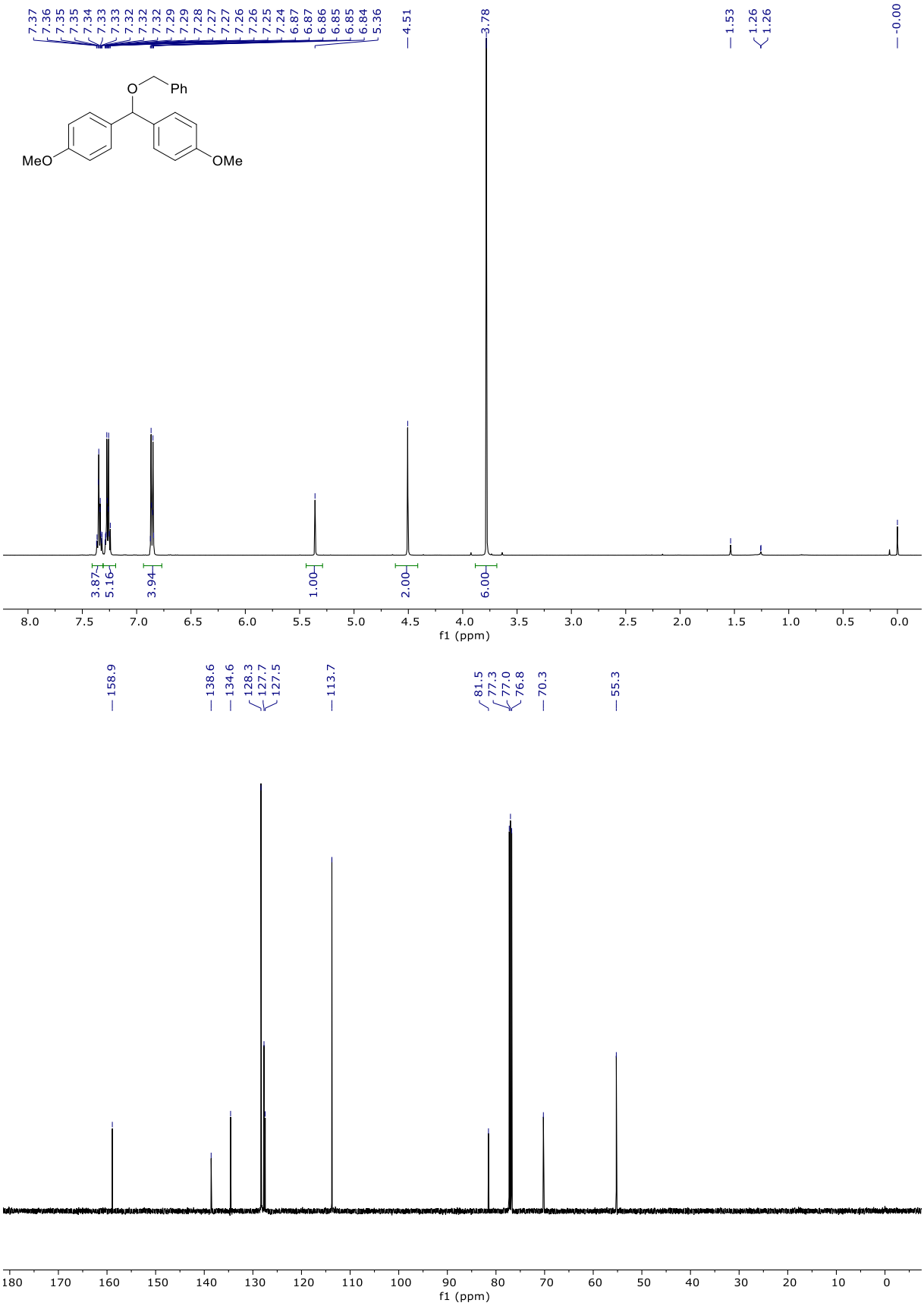
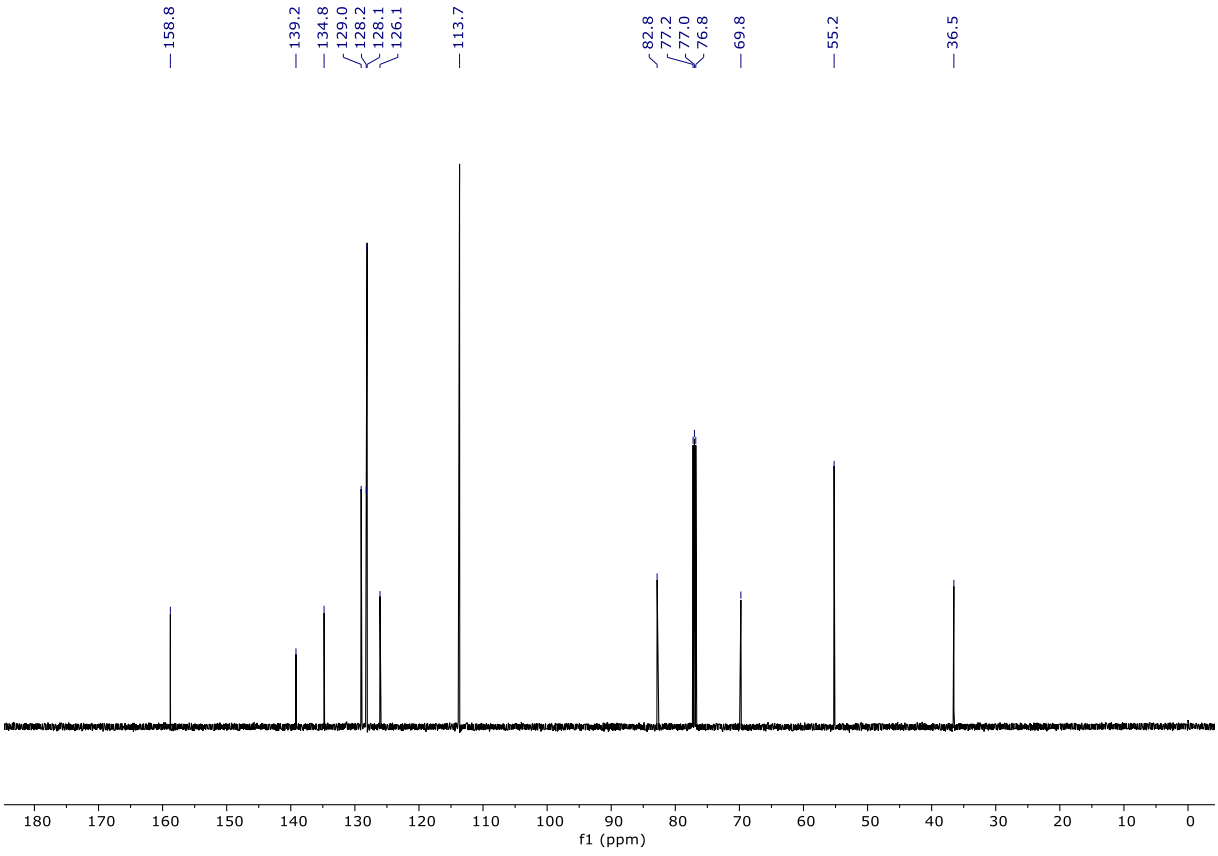
8. NMR spectra

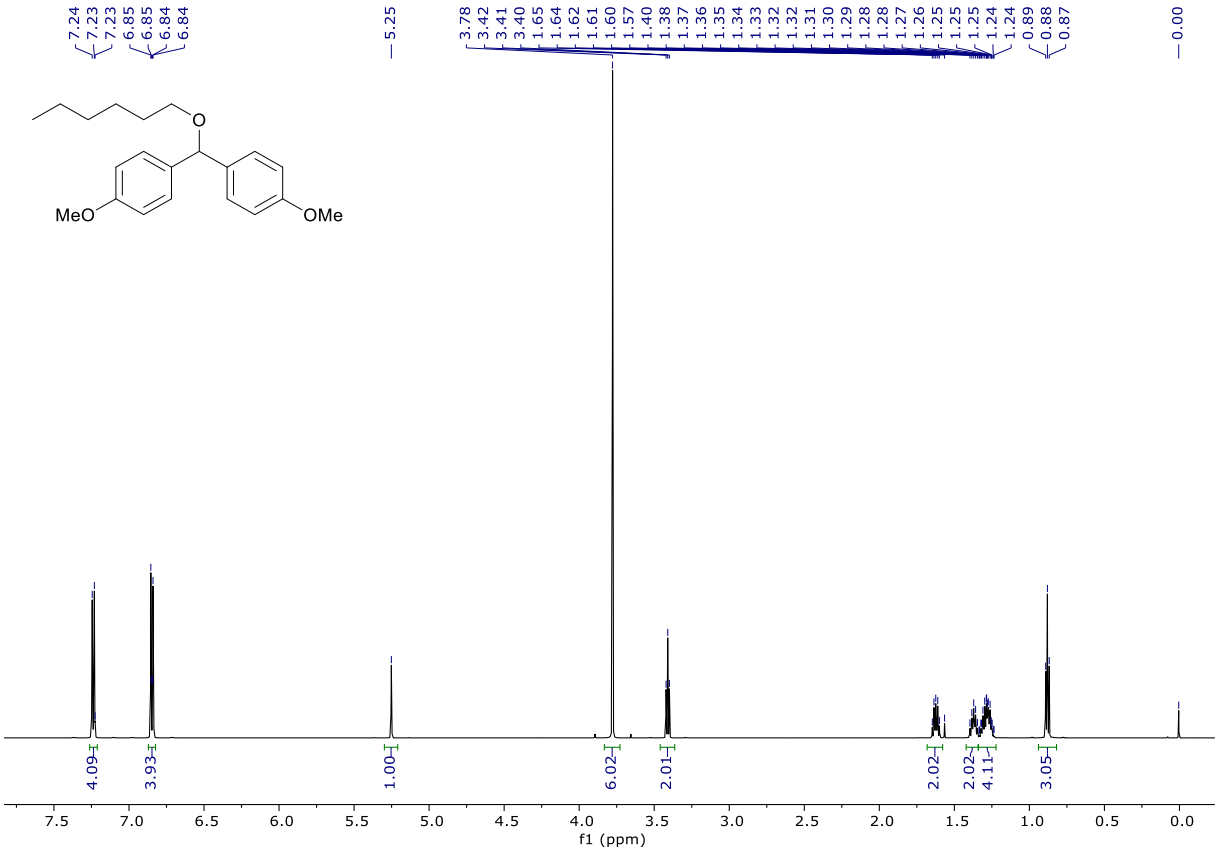
1-[bis(methoxyphenyl)methyl] benzyl ether (1)

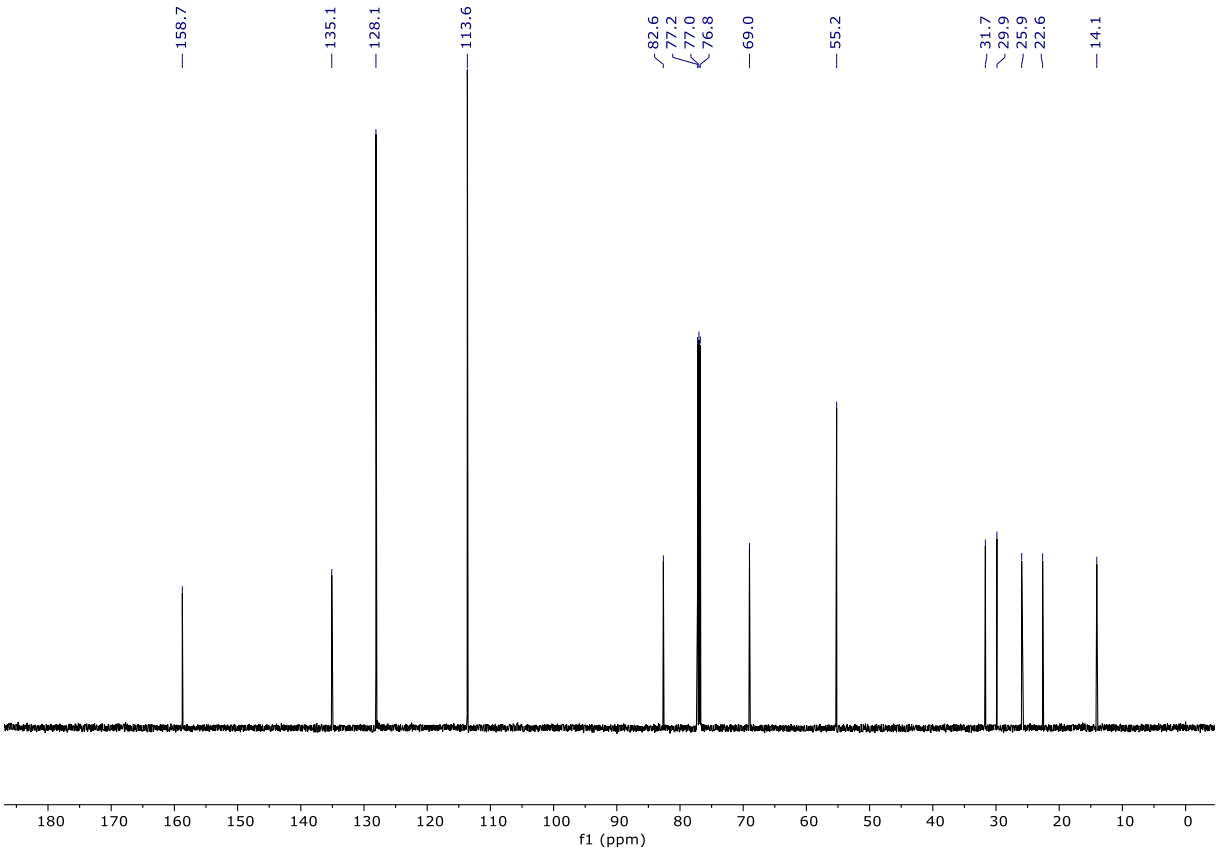


4,4'-(phenethoxymethylene)bis(methoxybenzene) (2)

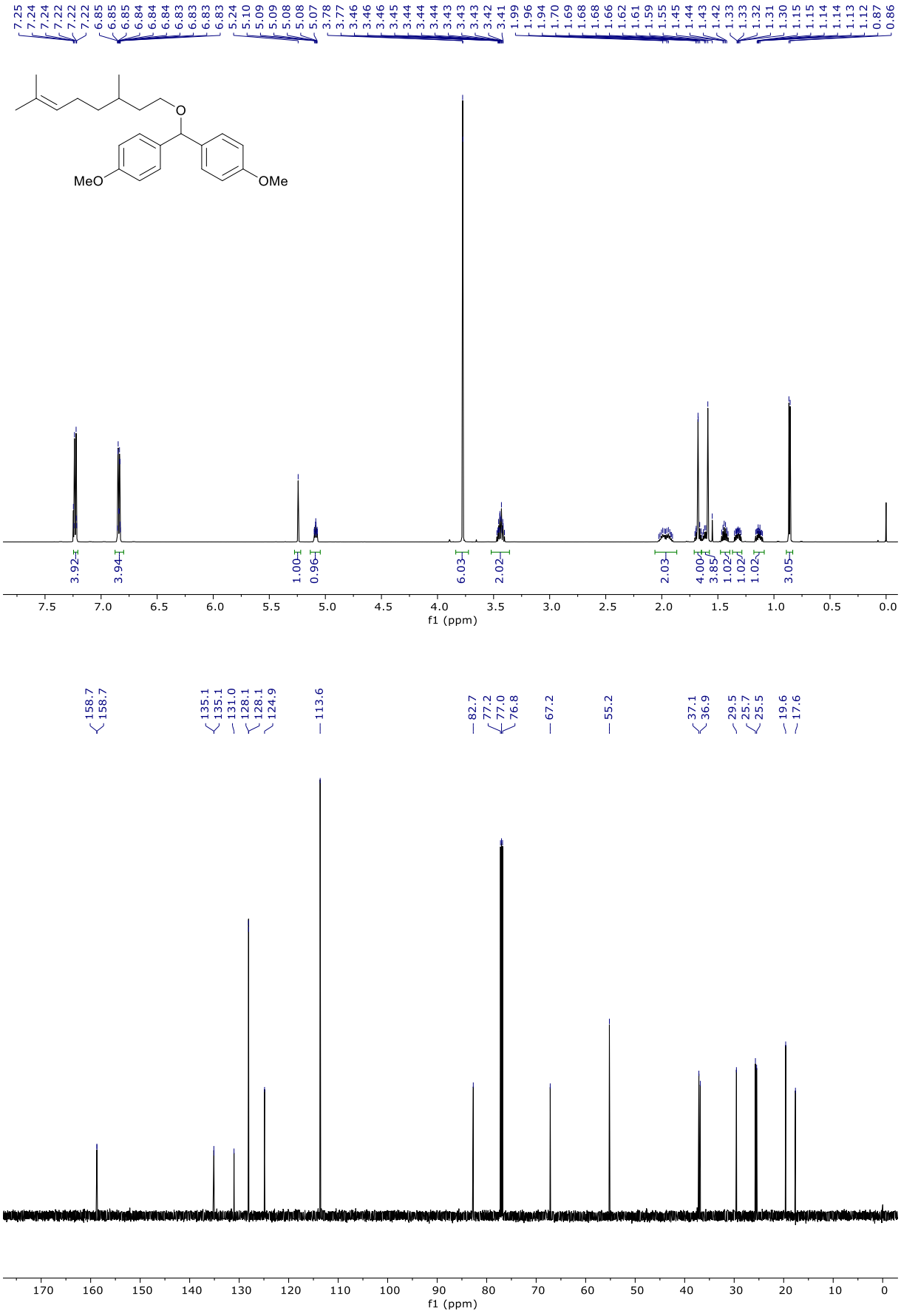


4,4'-((hexyloxy)methylene)bis(methoxybenzene) (3)

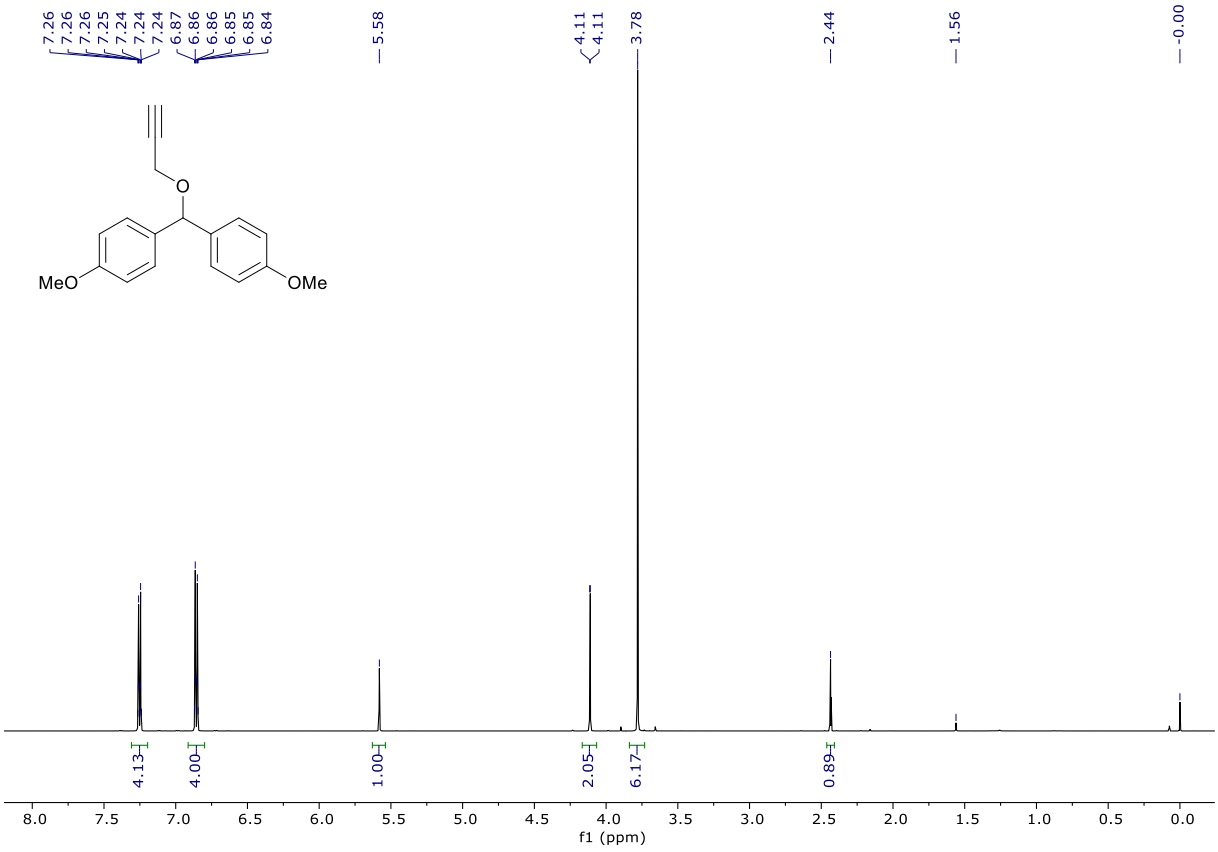


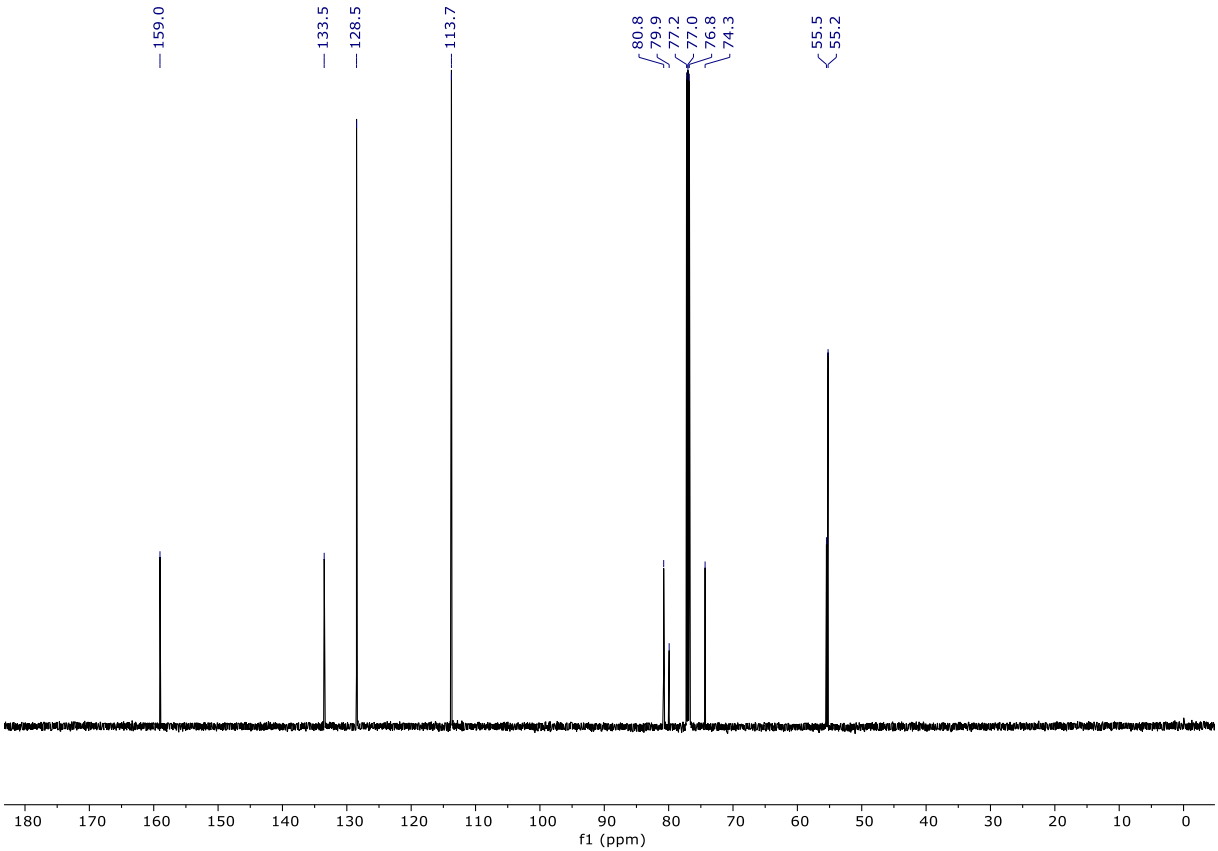


4,4'-(((3,7-dimethyloct-6-en-1-yl)oxy)methylene)bis(methoxybenzene) (4)

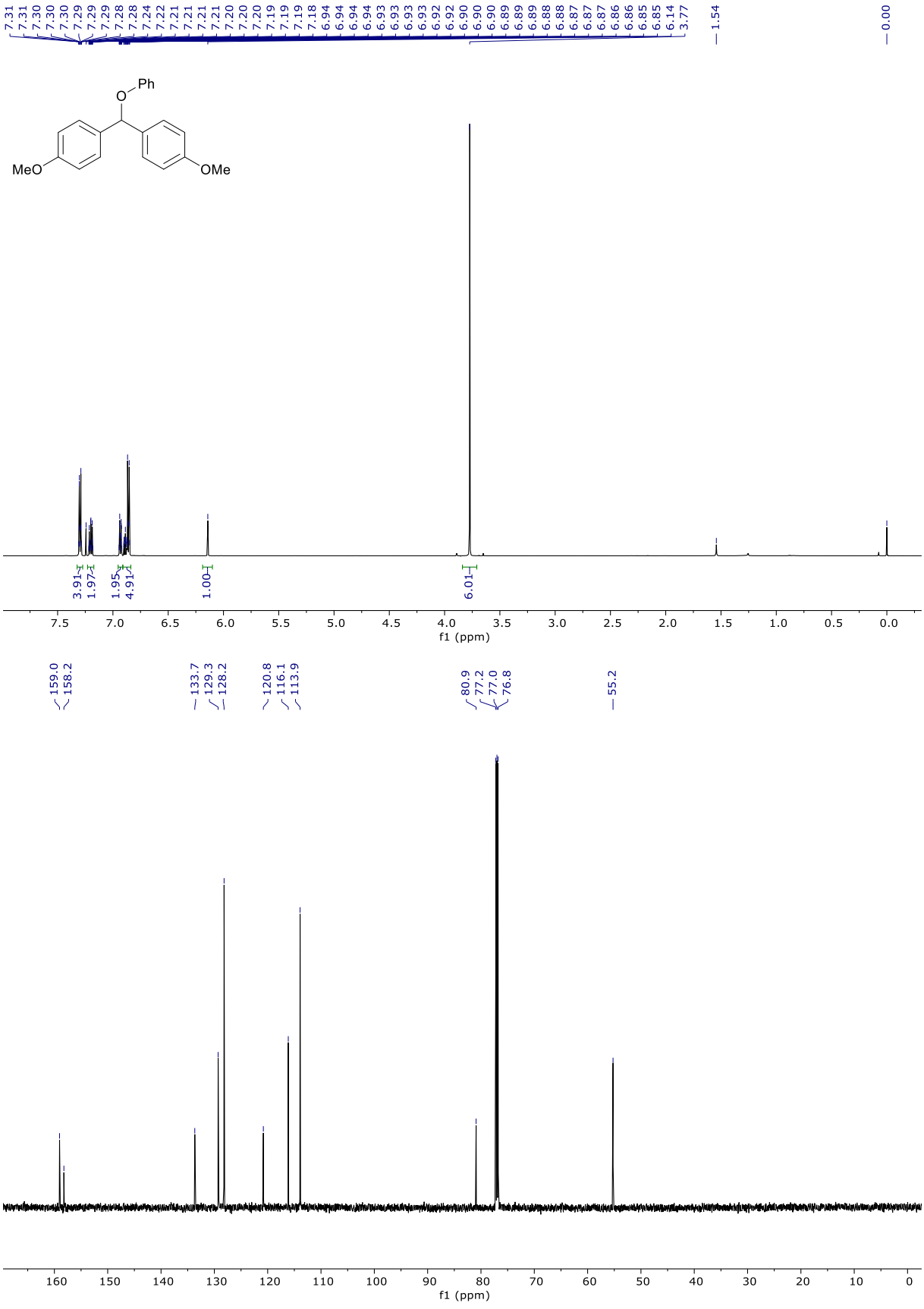


4,4'-((prop-2-yn-1-yloxy)methylene)bis(methoxybenzene) (5)

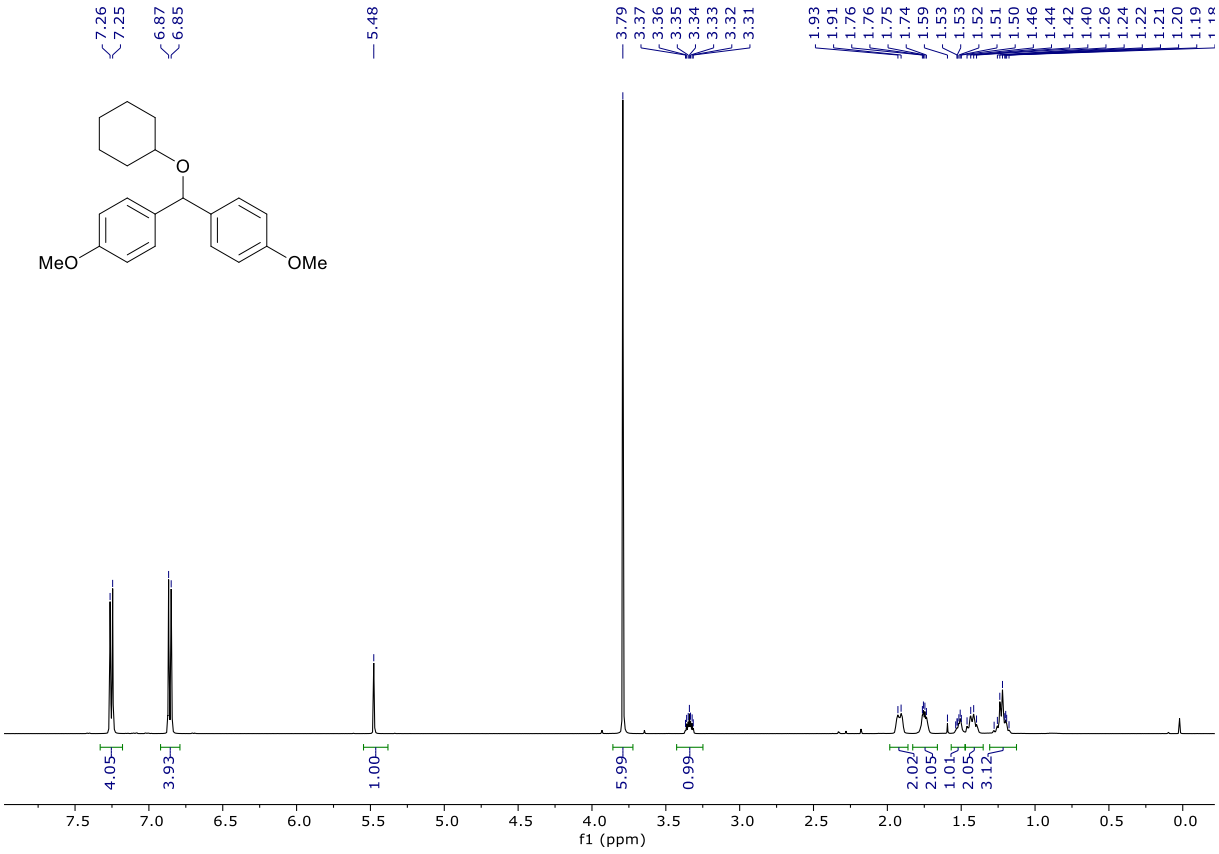


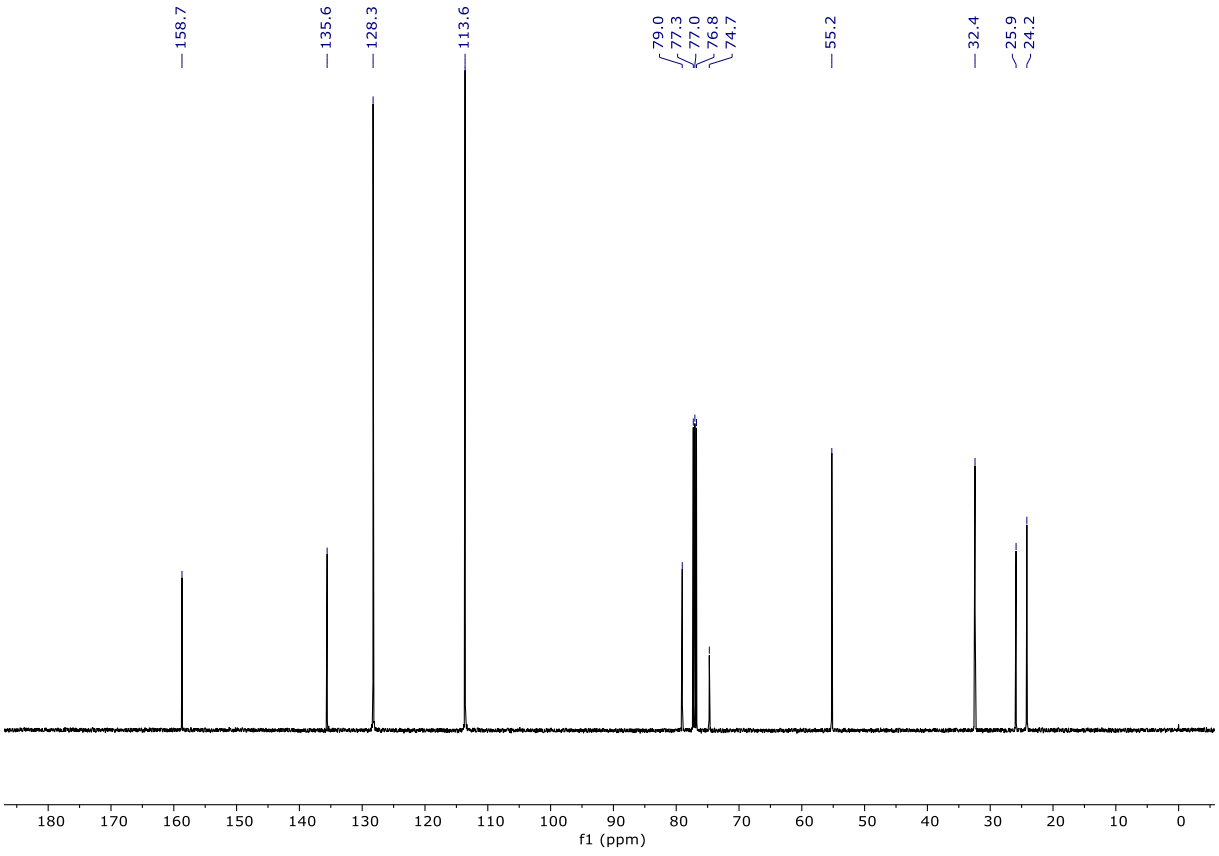


4,4'-(phenoxymethylene)bis(methoxybenzene) (6)

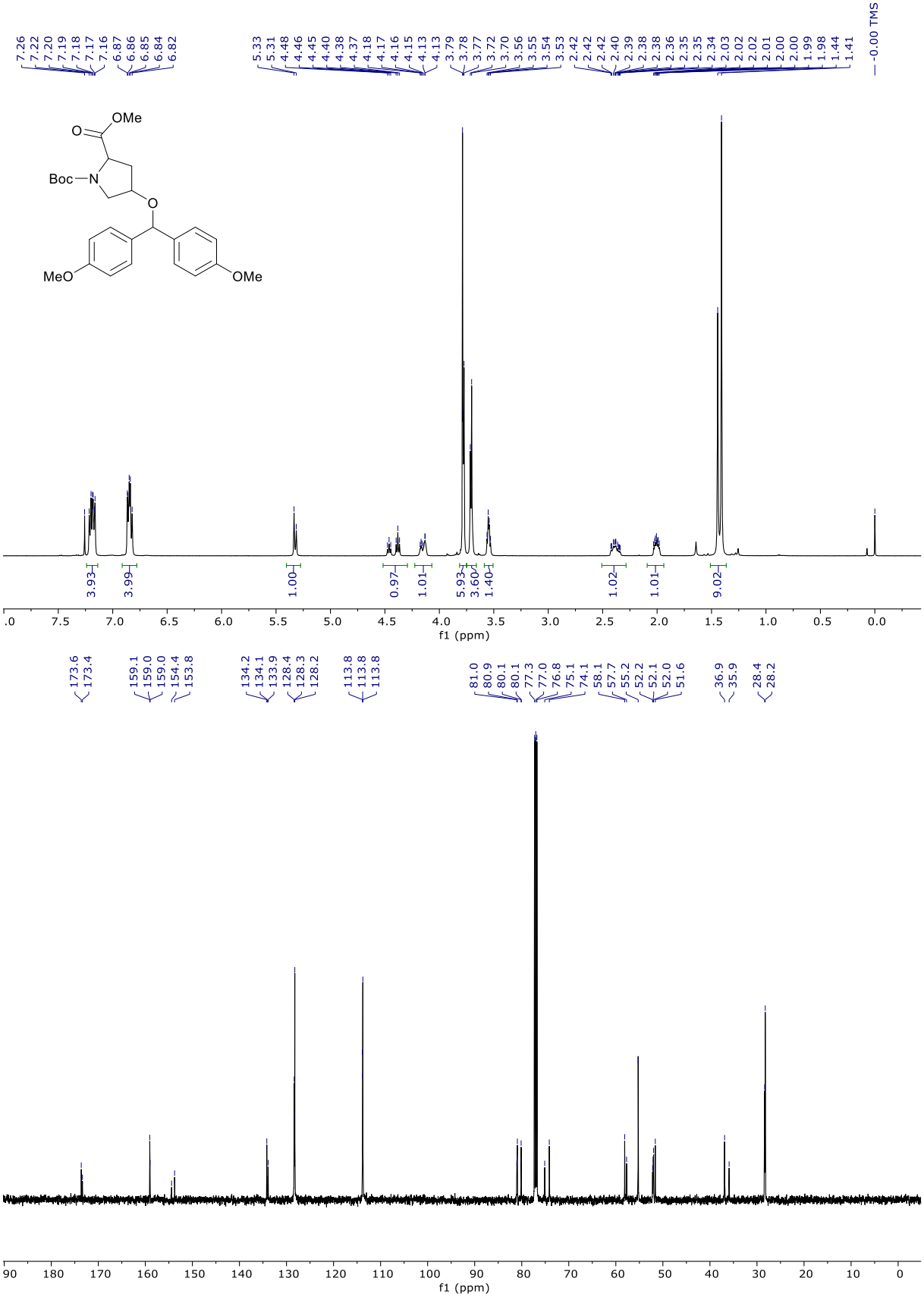


4,4'-((cyclohexyloxy)methylene)bis(methoxybenzene) (7)

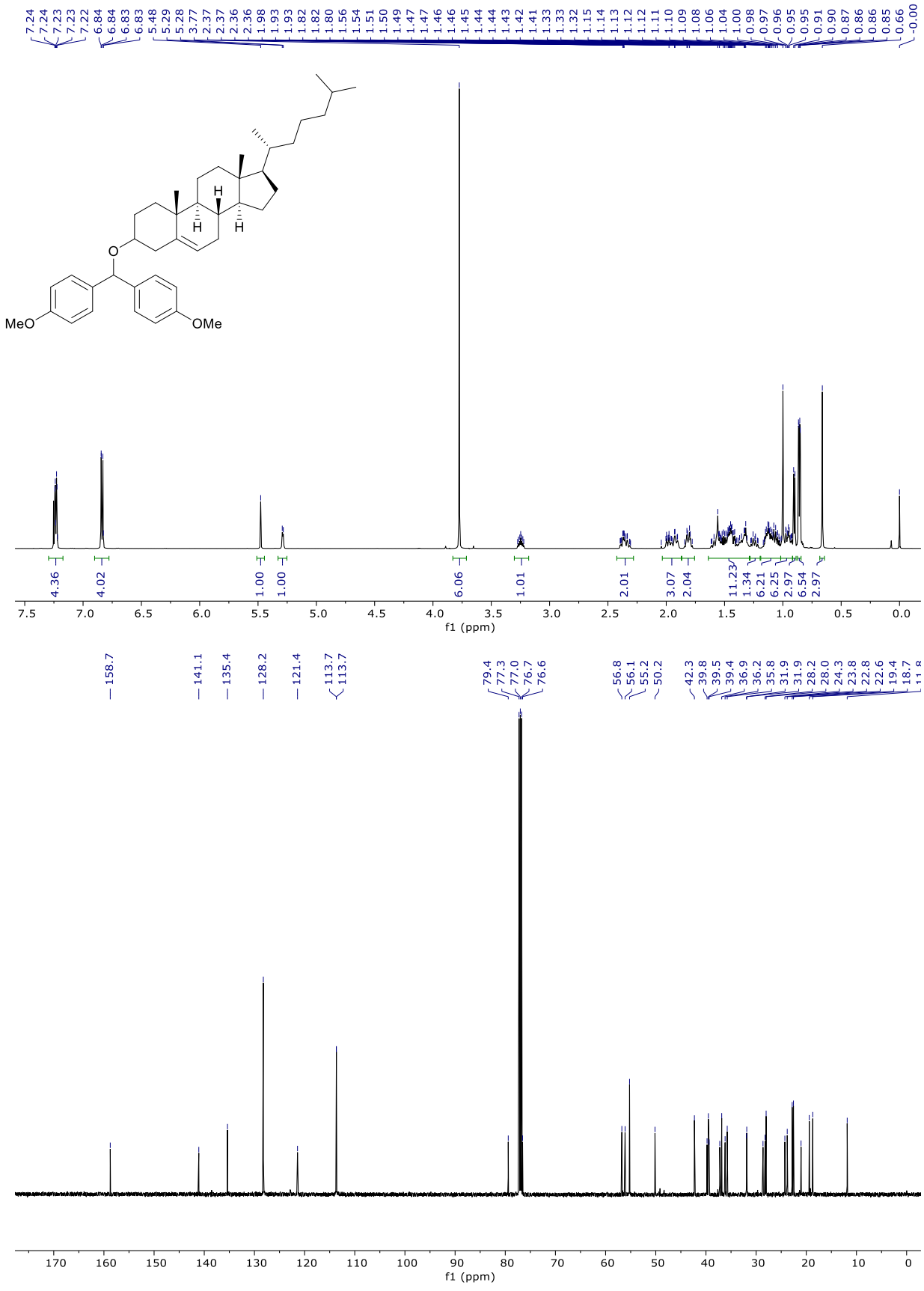


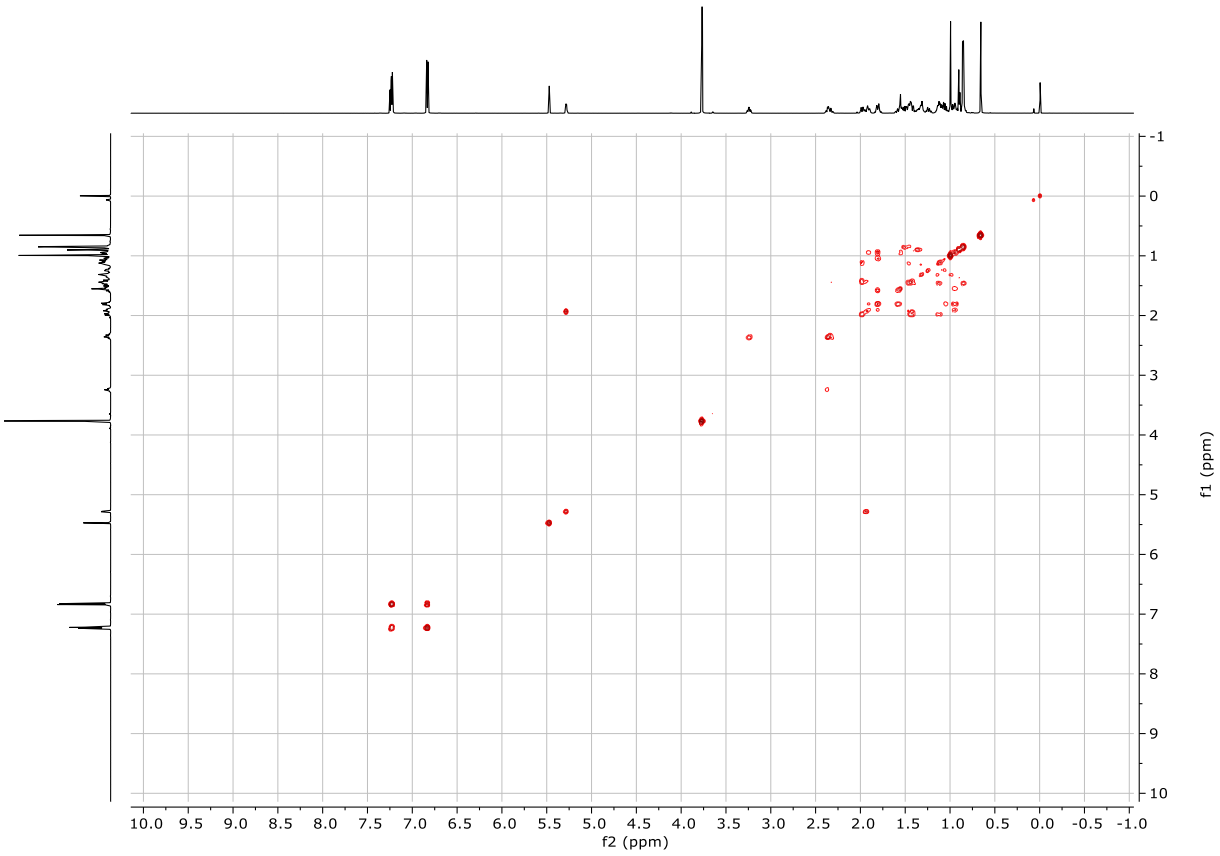


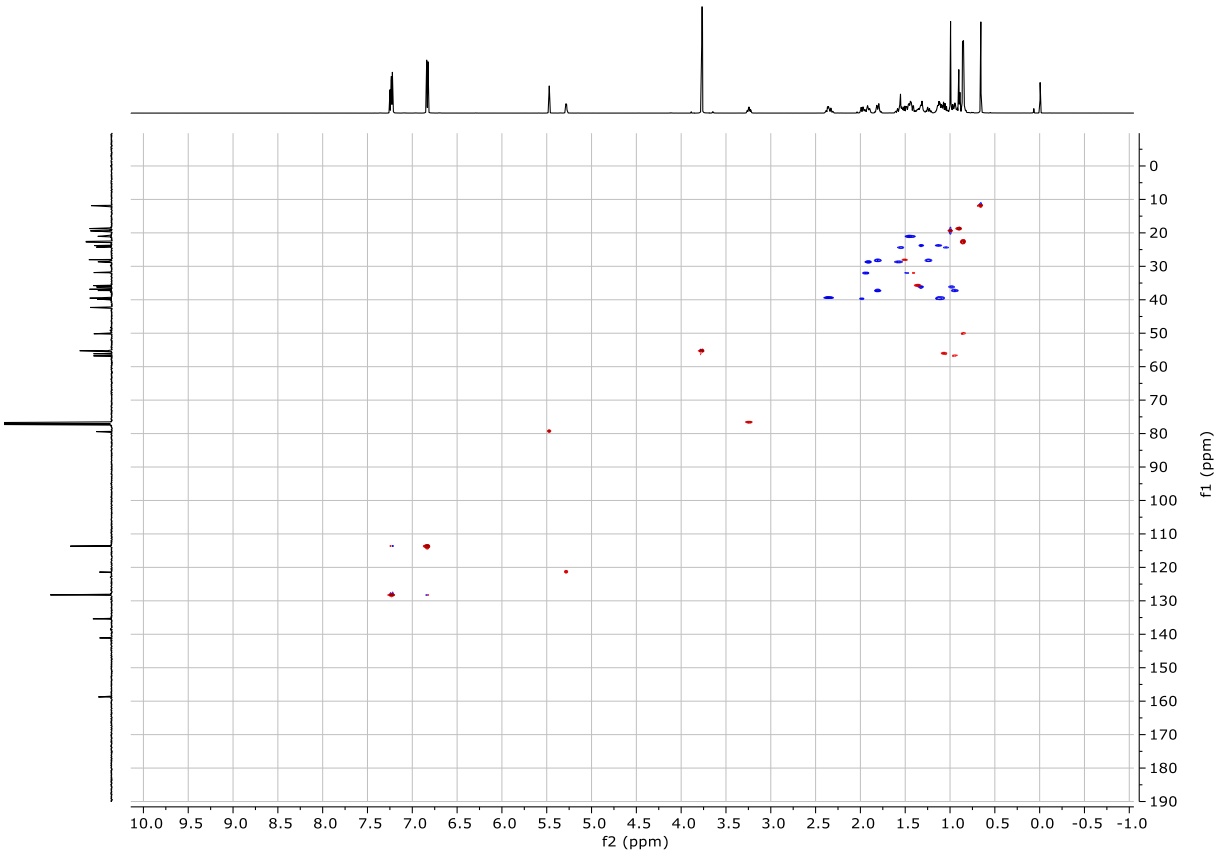
1-(tert-butyl) 2-methyl 4-(bis(4-methoxyphenyl)methoxy)pyrrolidine-1,2-dicarboxylate (8)



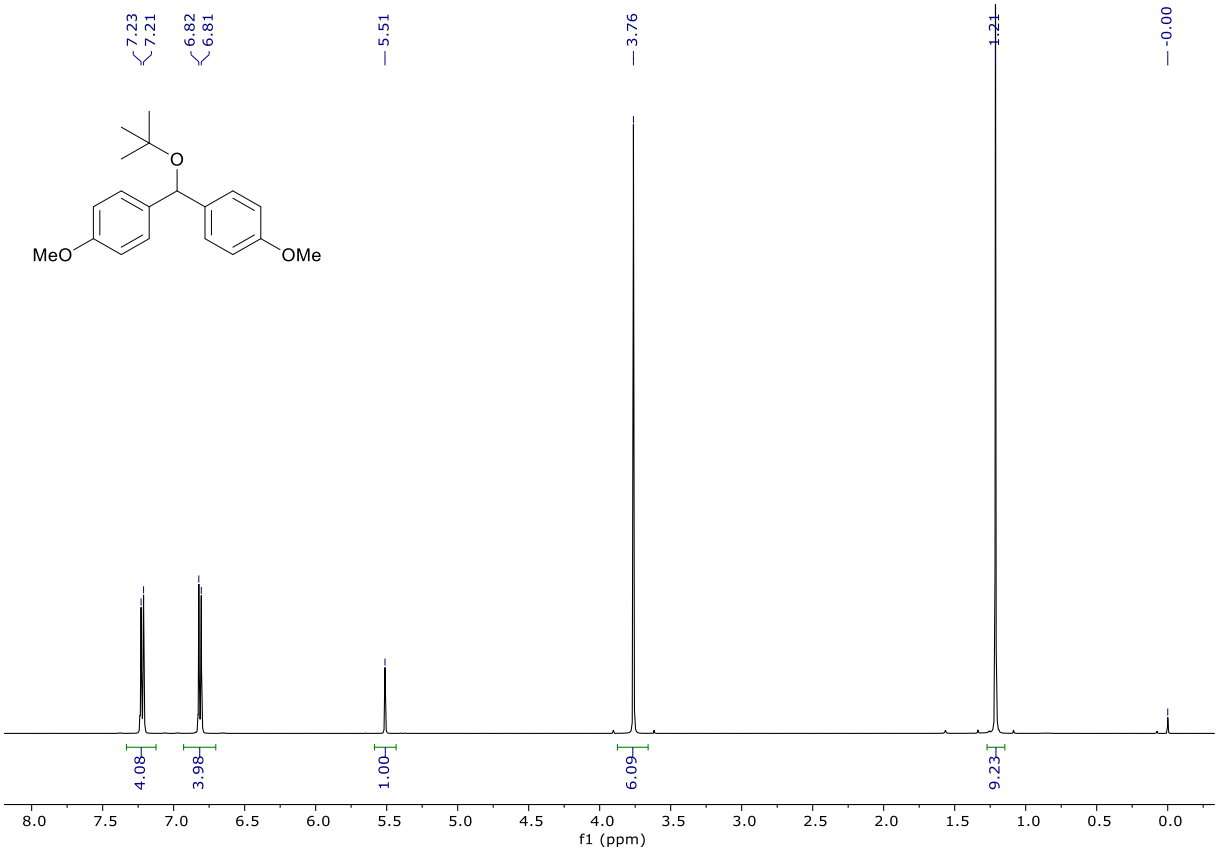
(8S,9S,10R,13R,14S,17R)-3-(bis(4-methoxyphenyl)methoxy)-10,13-dimethyl-17-((R)-6-methy lheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene (9)

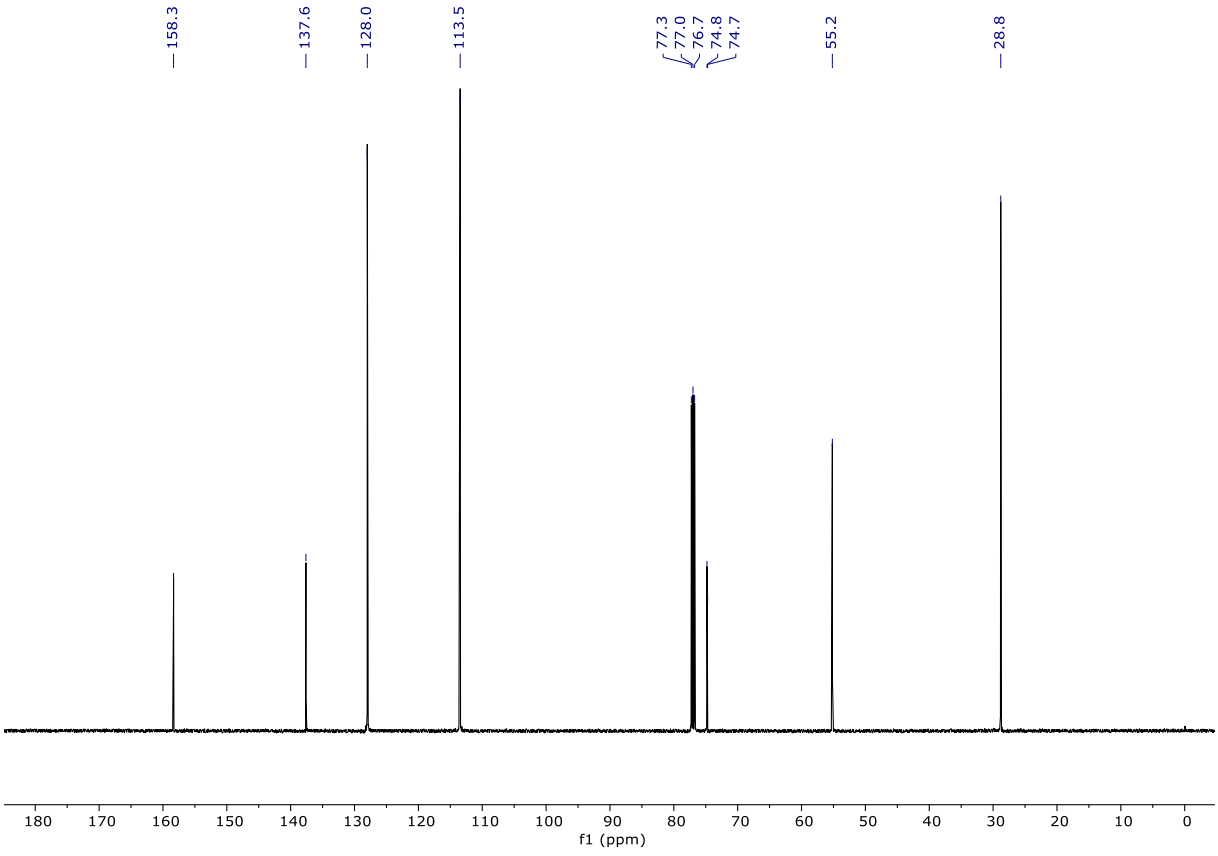



f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)

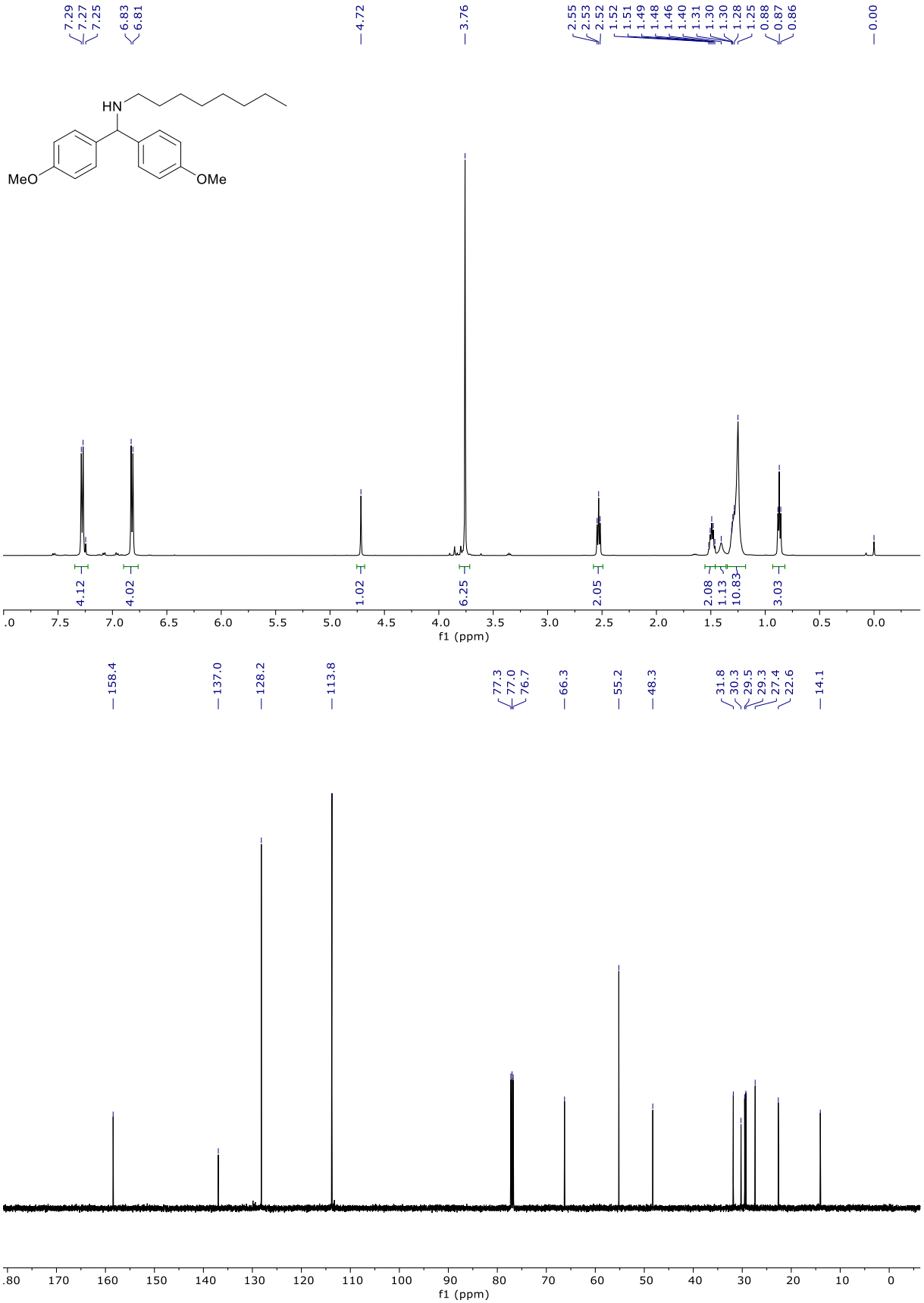
4,4'-(tert-butoxymethylene)bis(methoxybenzene) (10)



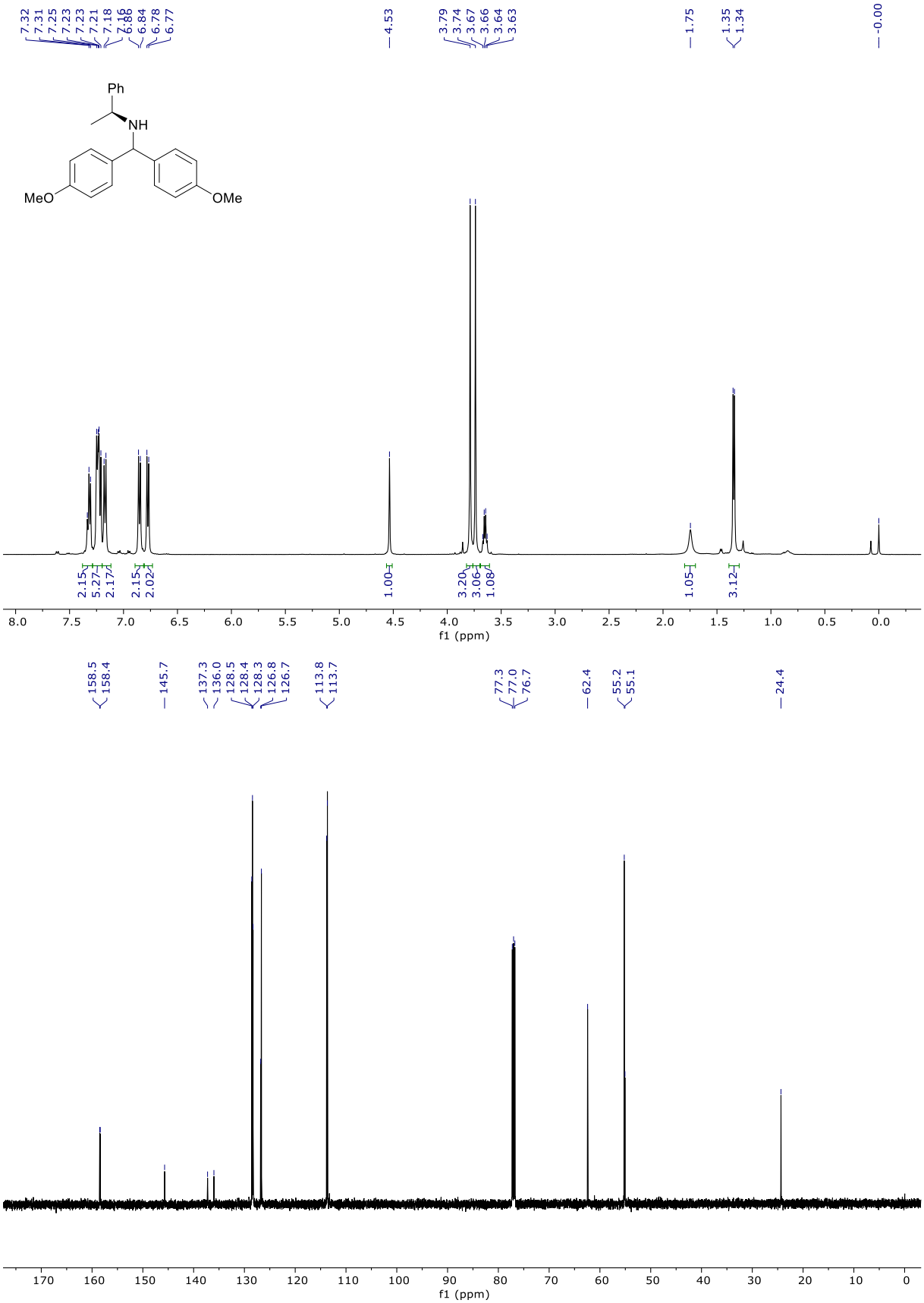


4,4'-((benzyloxy)methylene)bis(N,N-dimethylaniline) (11)

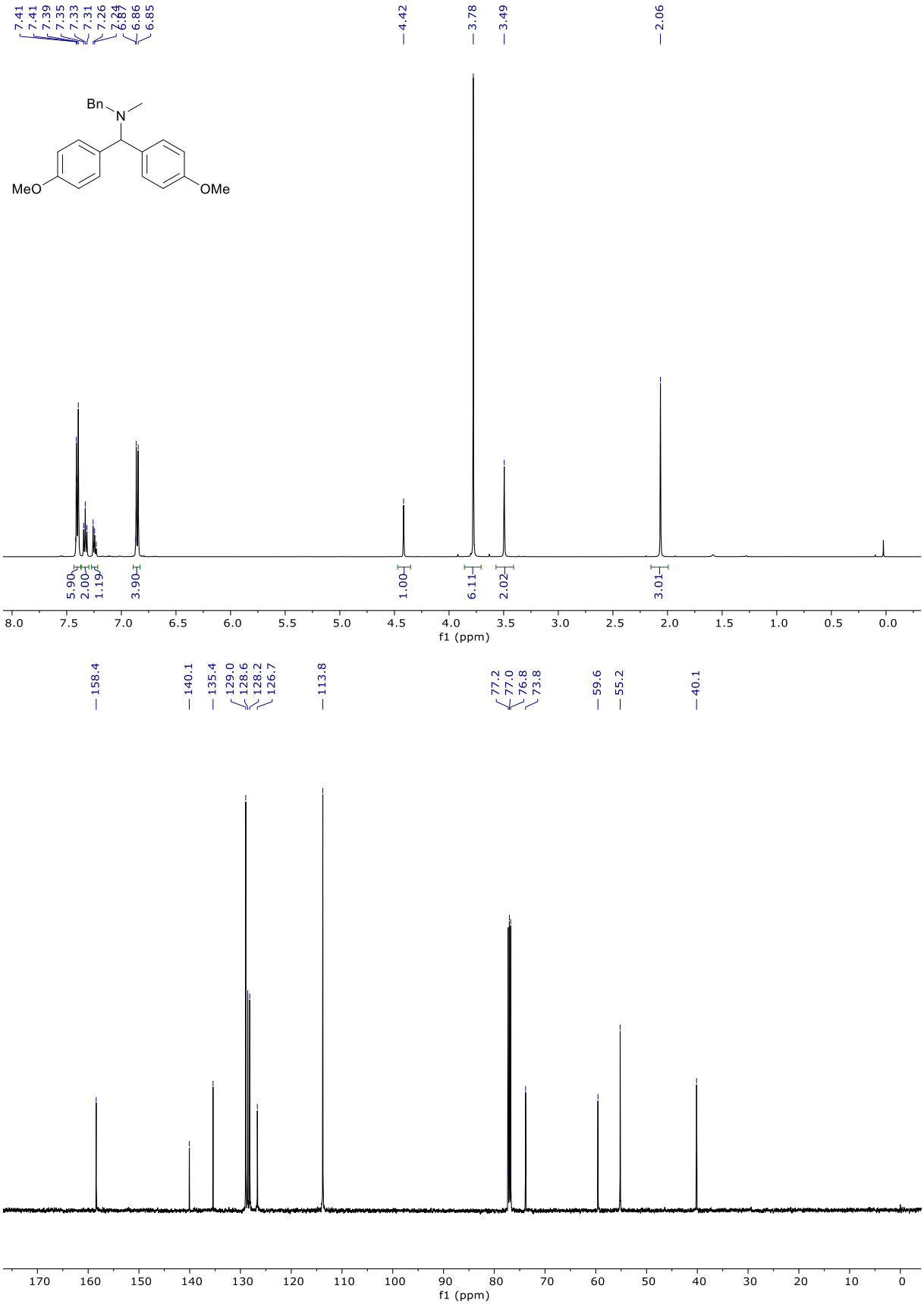
N-(bis(4-methoxyphenyl)methyl)octan-1-amine (12)



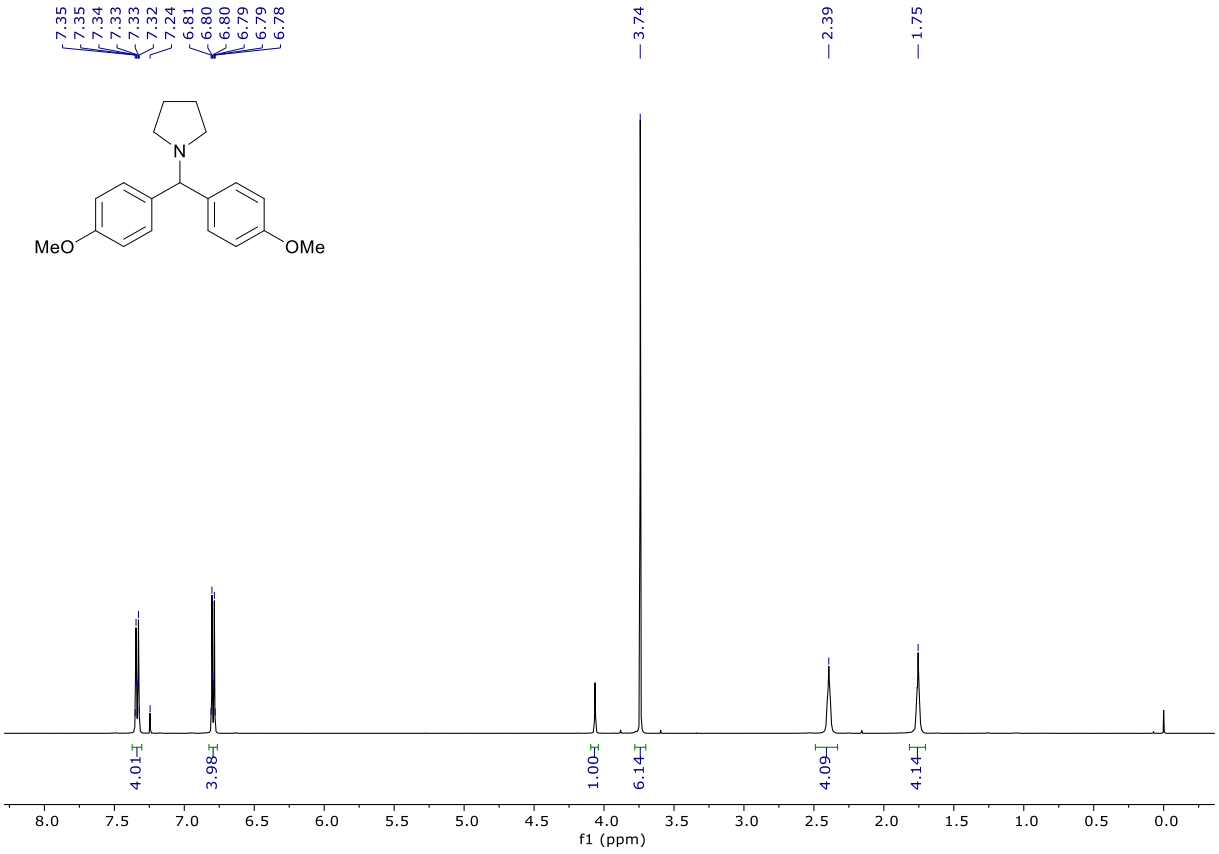
(S)-N-(bis(4-methoxyphenyl)methyl)-1-phenylethan-1-amine (13)

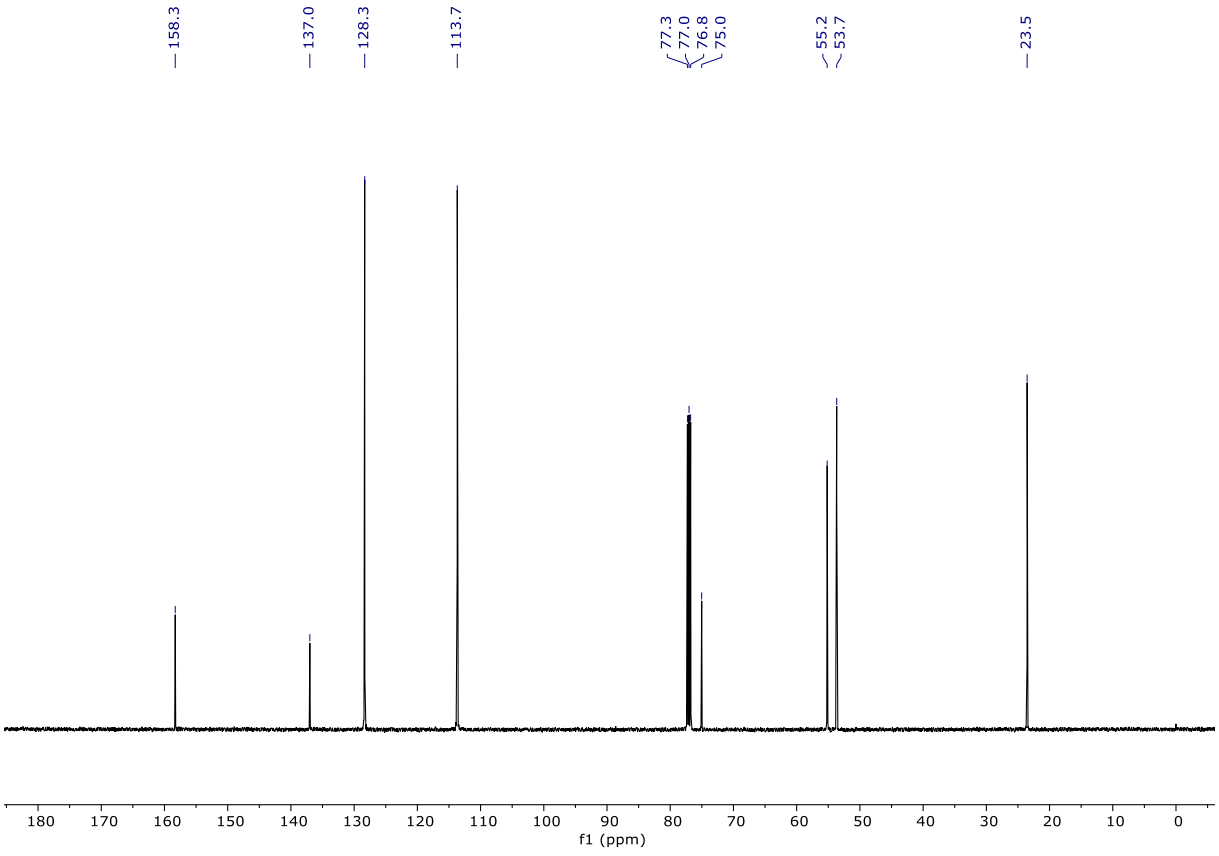


N-benzyl-1,1-bis(4-methoxyphenyl)-N-methylmethanamine (14)

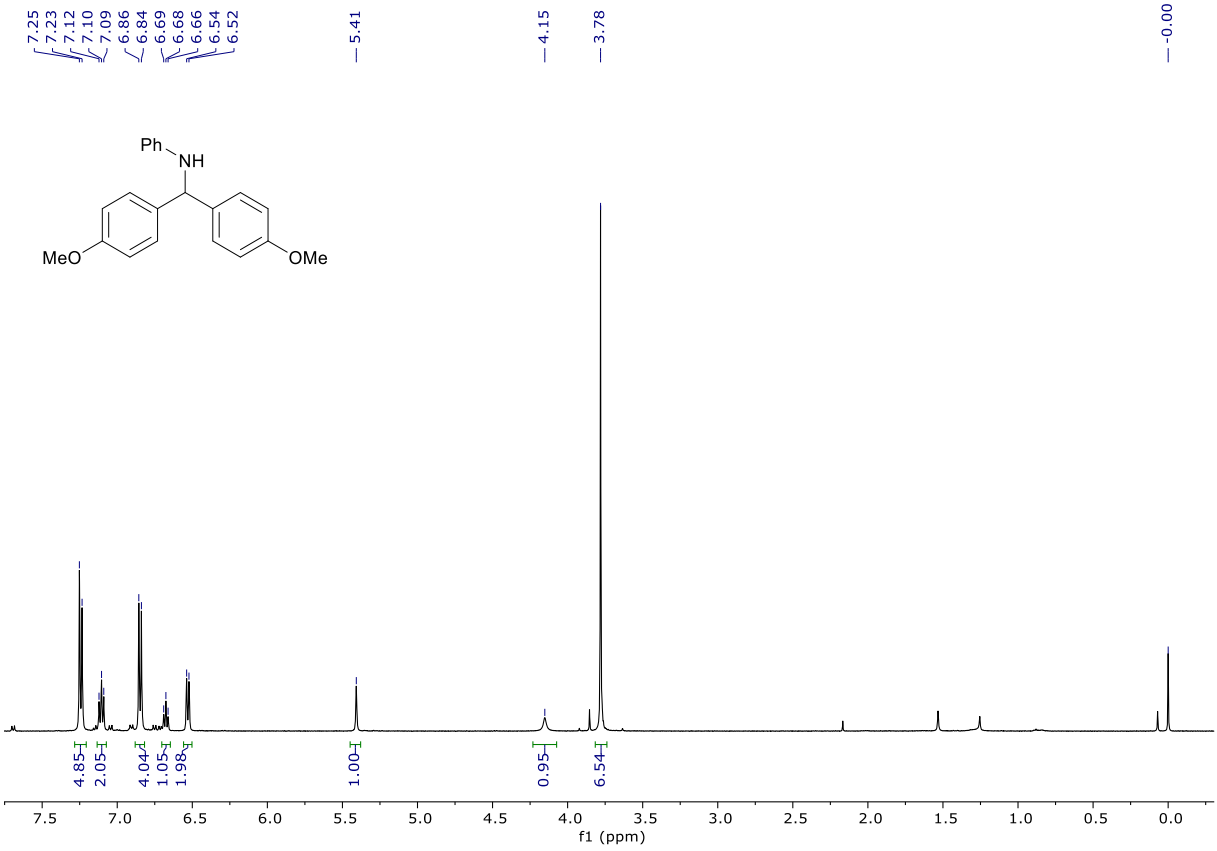


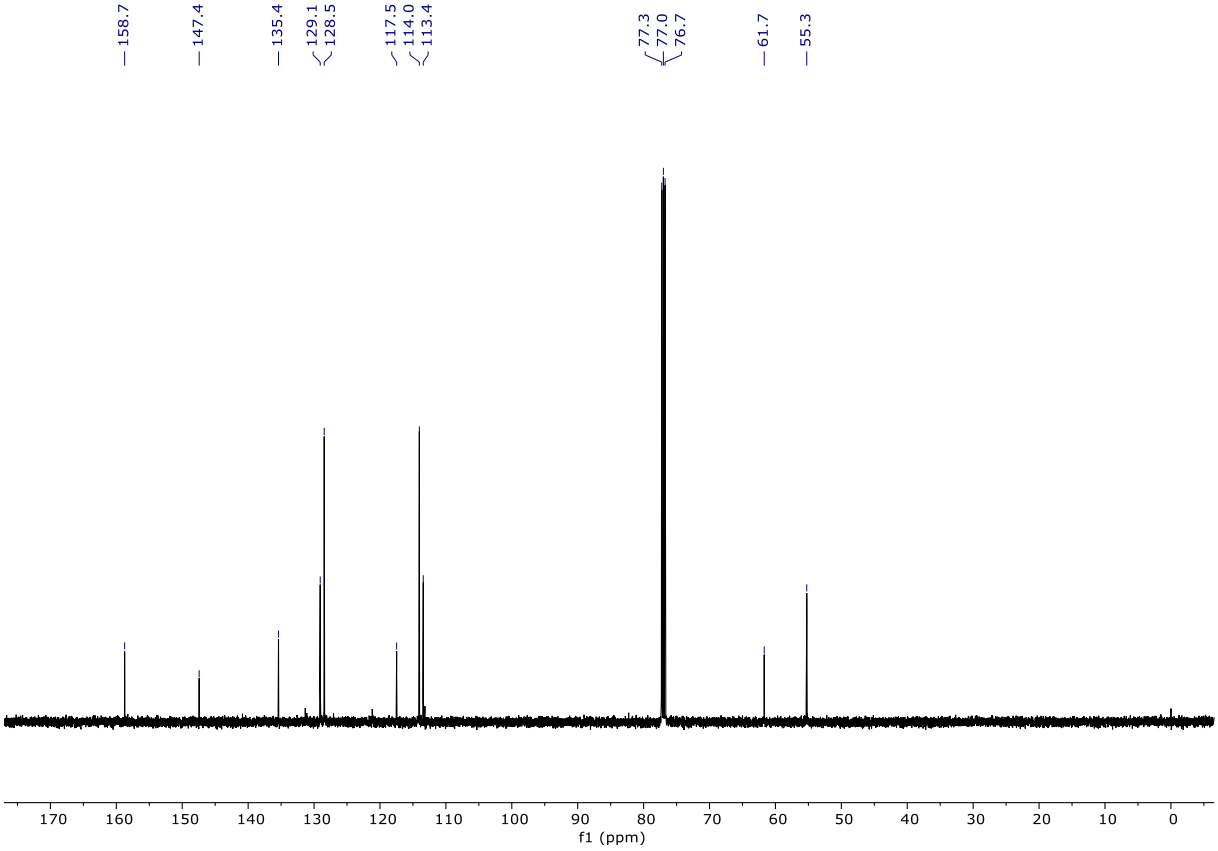
1-[bis(methoxyphenyl)methyl]pyrrolidine (15)



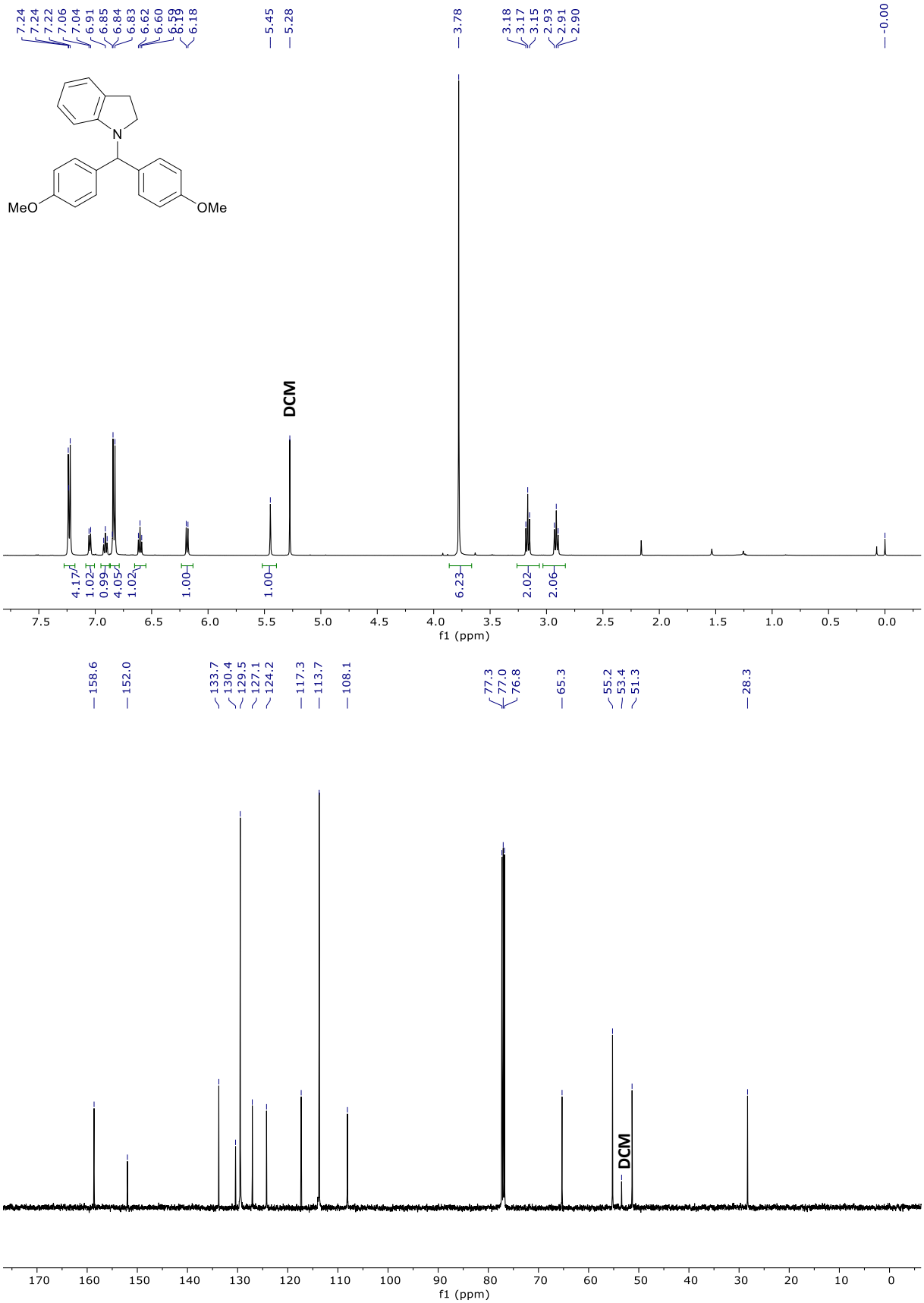


N-(bis(4-methoxyphenyl)methyl)aniline (16)

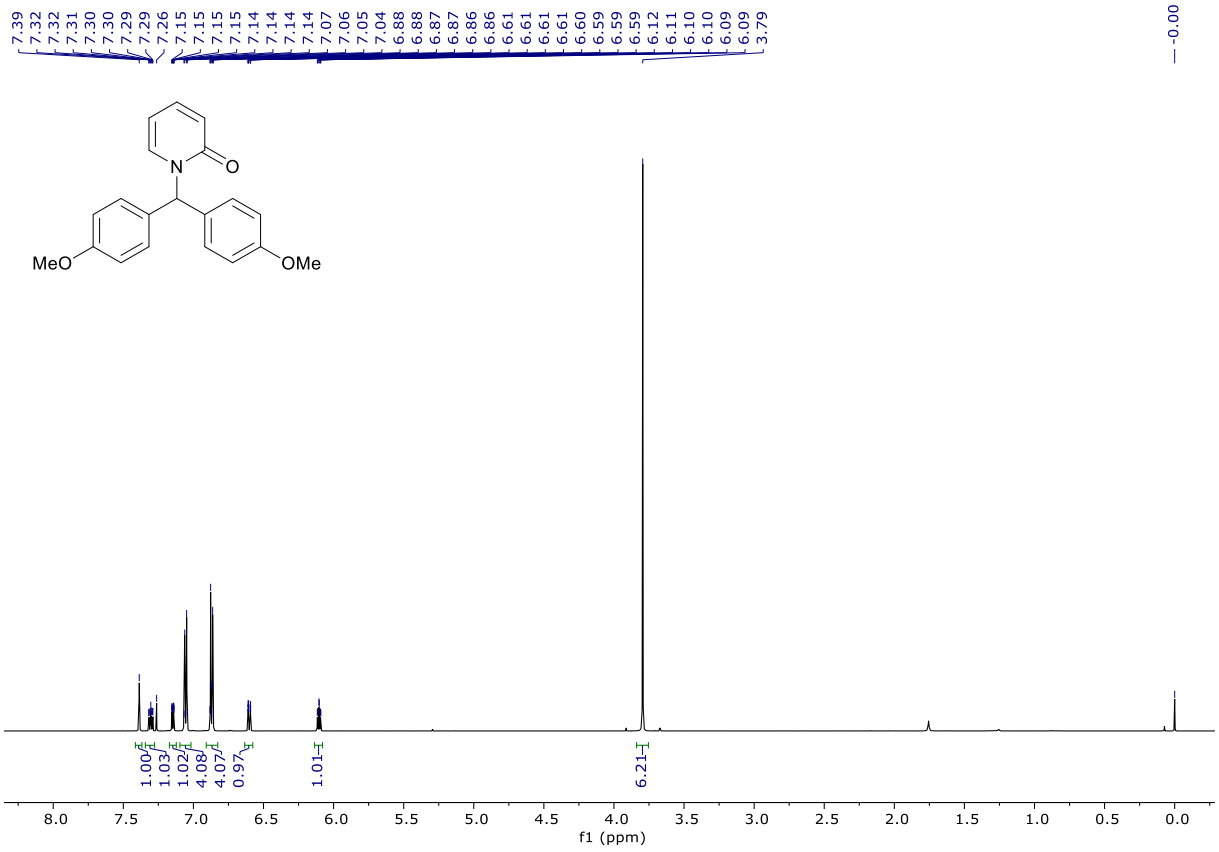


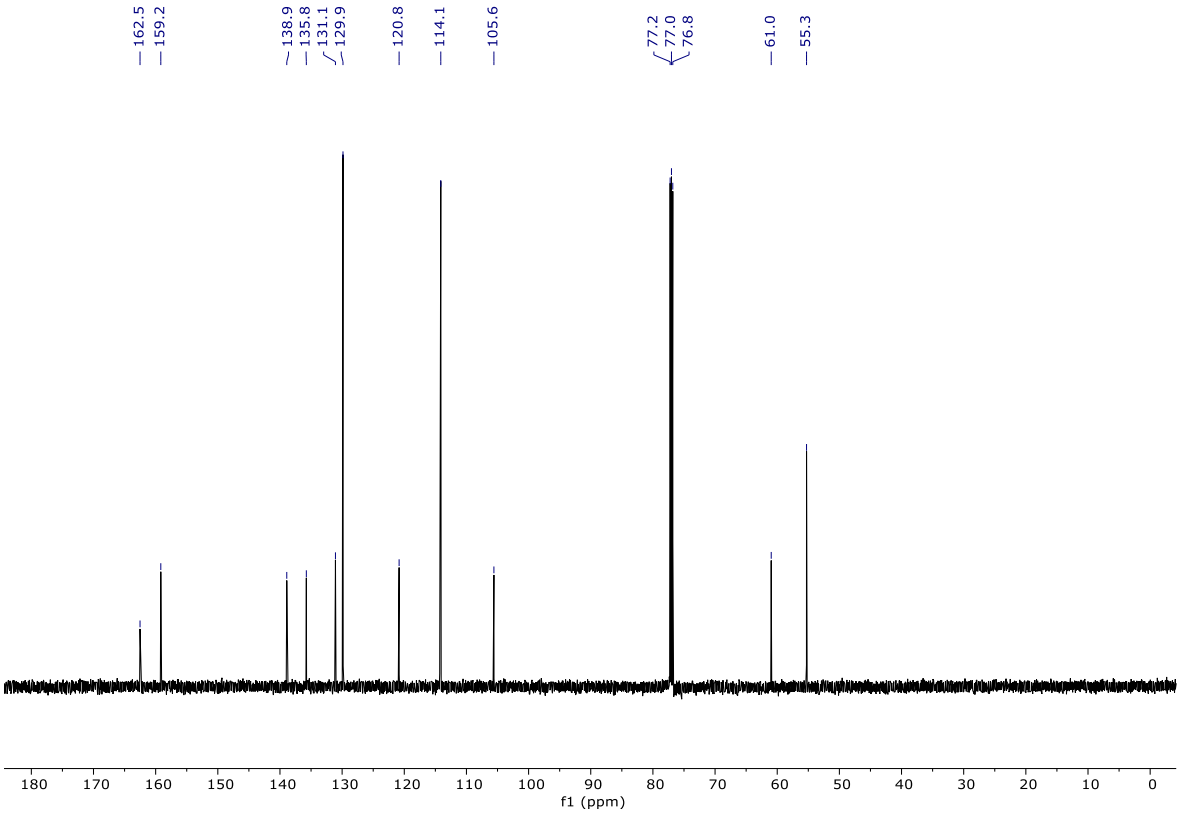


1-(bis(4-methoxyphenyl)methyl)indoline (17)

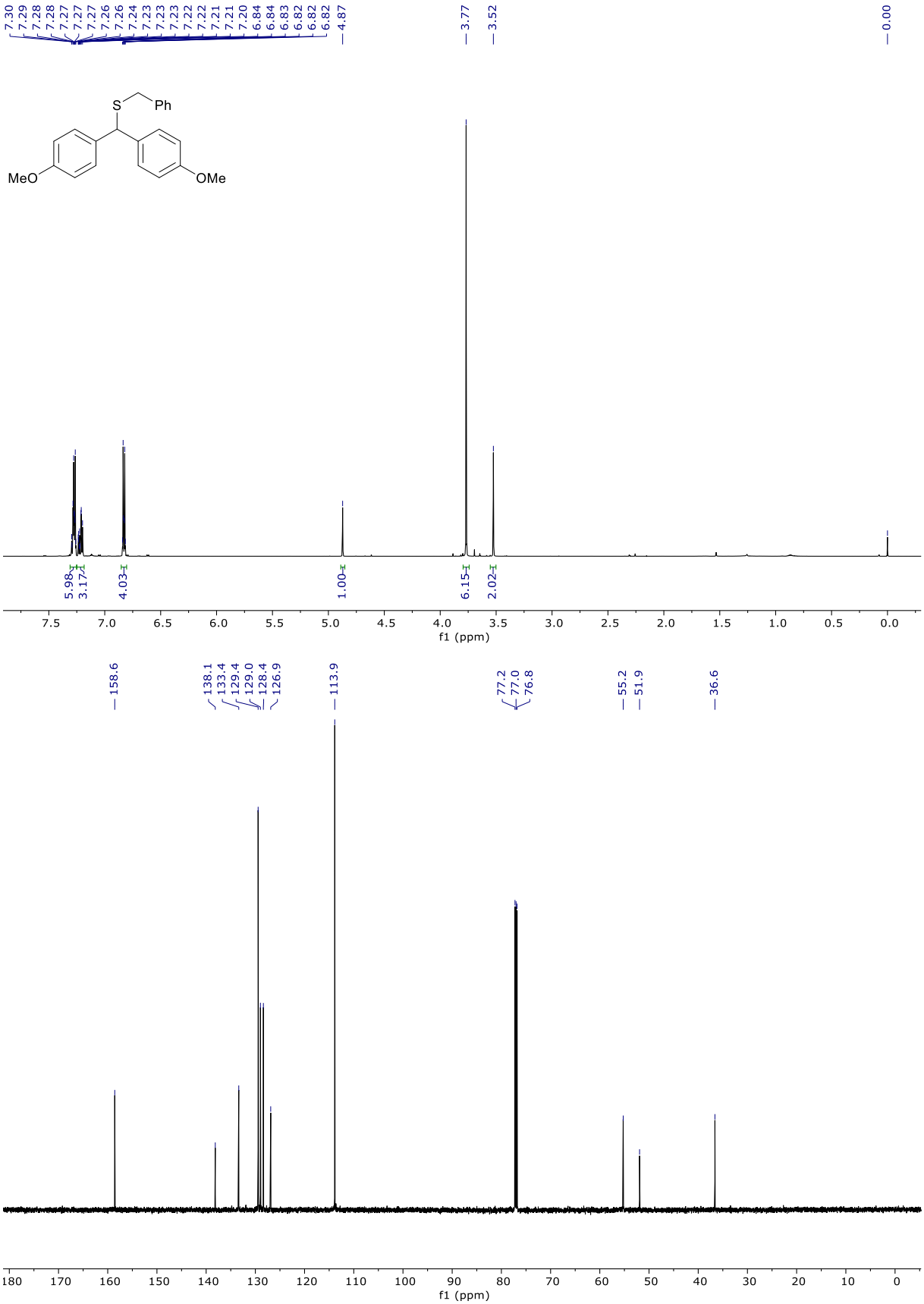


1-(bis(4-methoxyphenyl)methyl)pyridin-2(1H)-one (18)

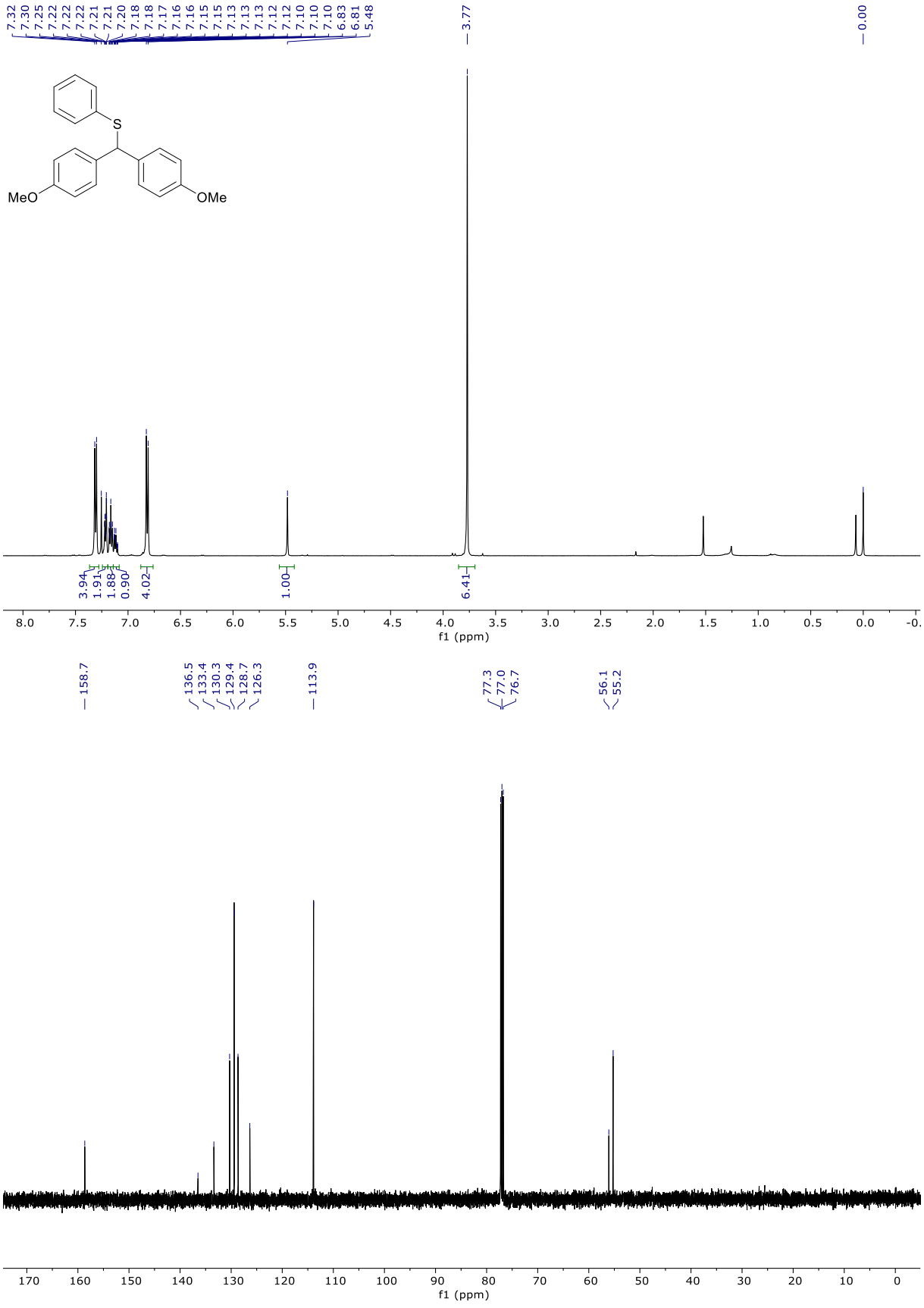




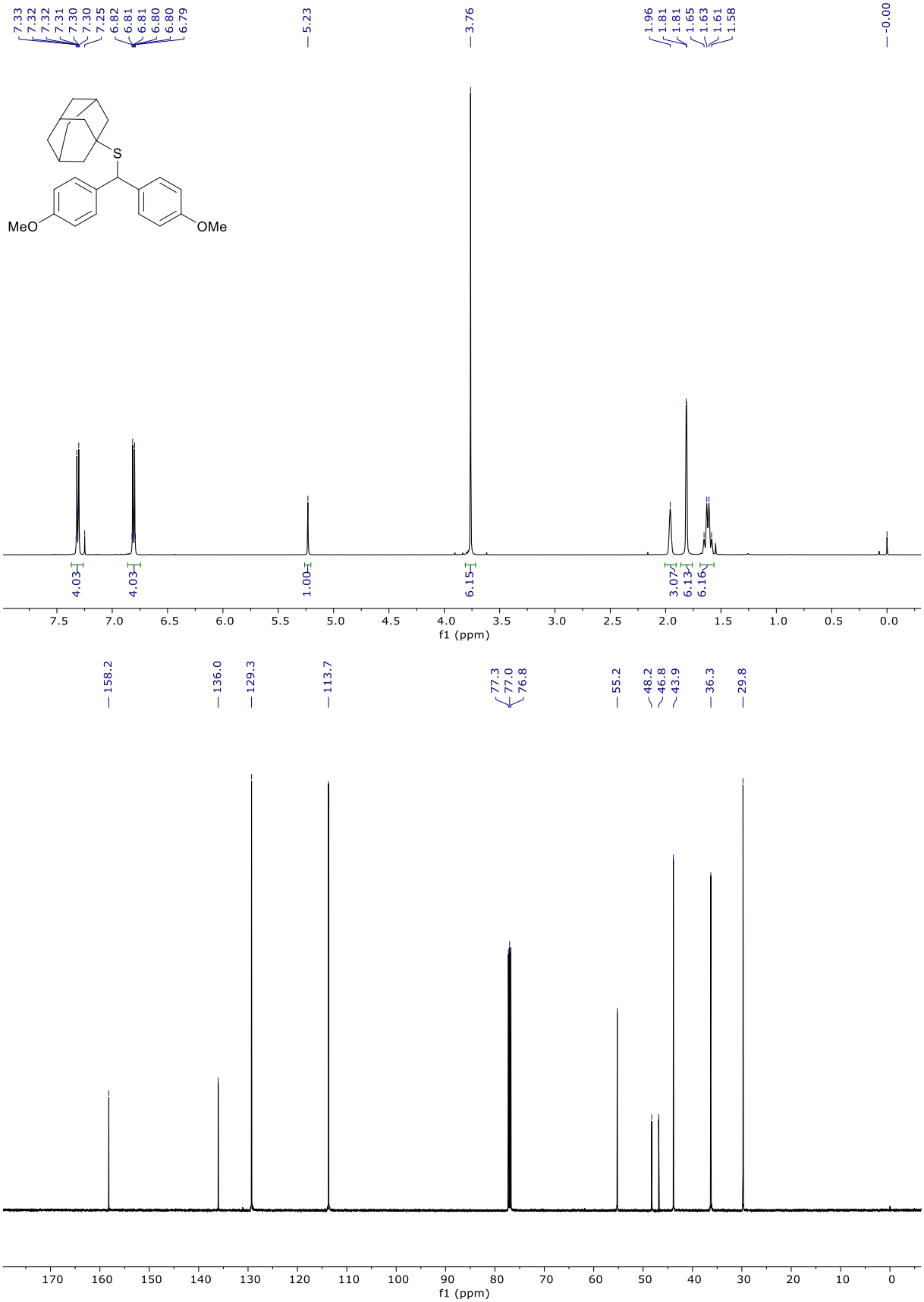
benzyl(bis(4-methoxyphenyl)methyl)sulfane (19)



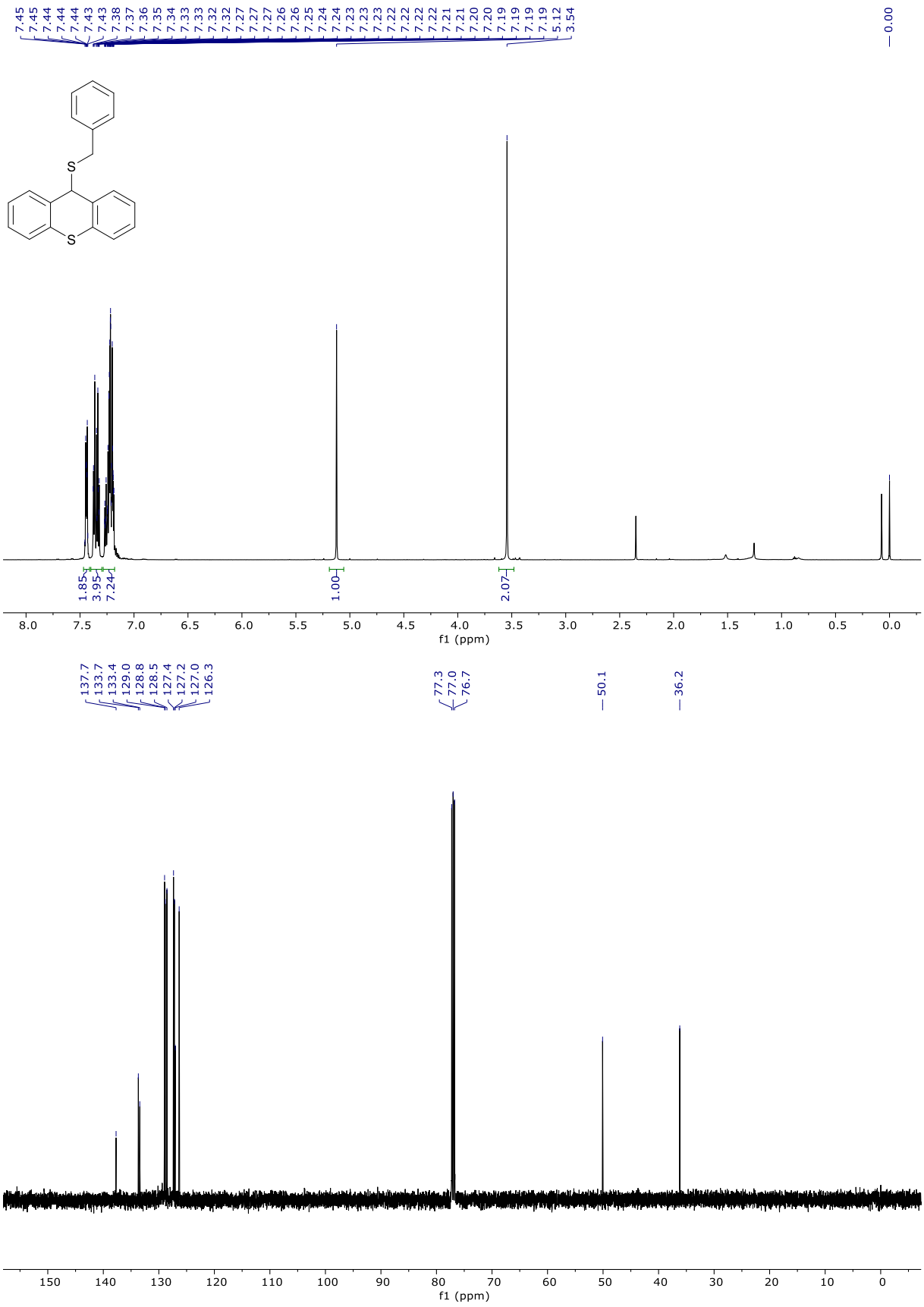
(bis(4-methoxyphenyl)methyl)(phenyl)sulfane (20)



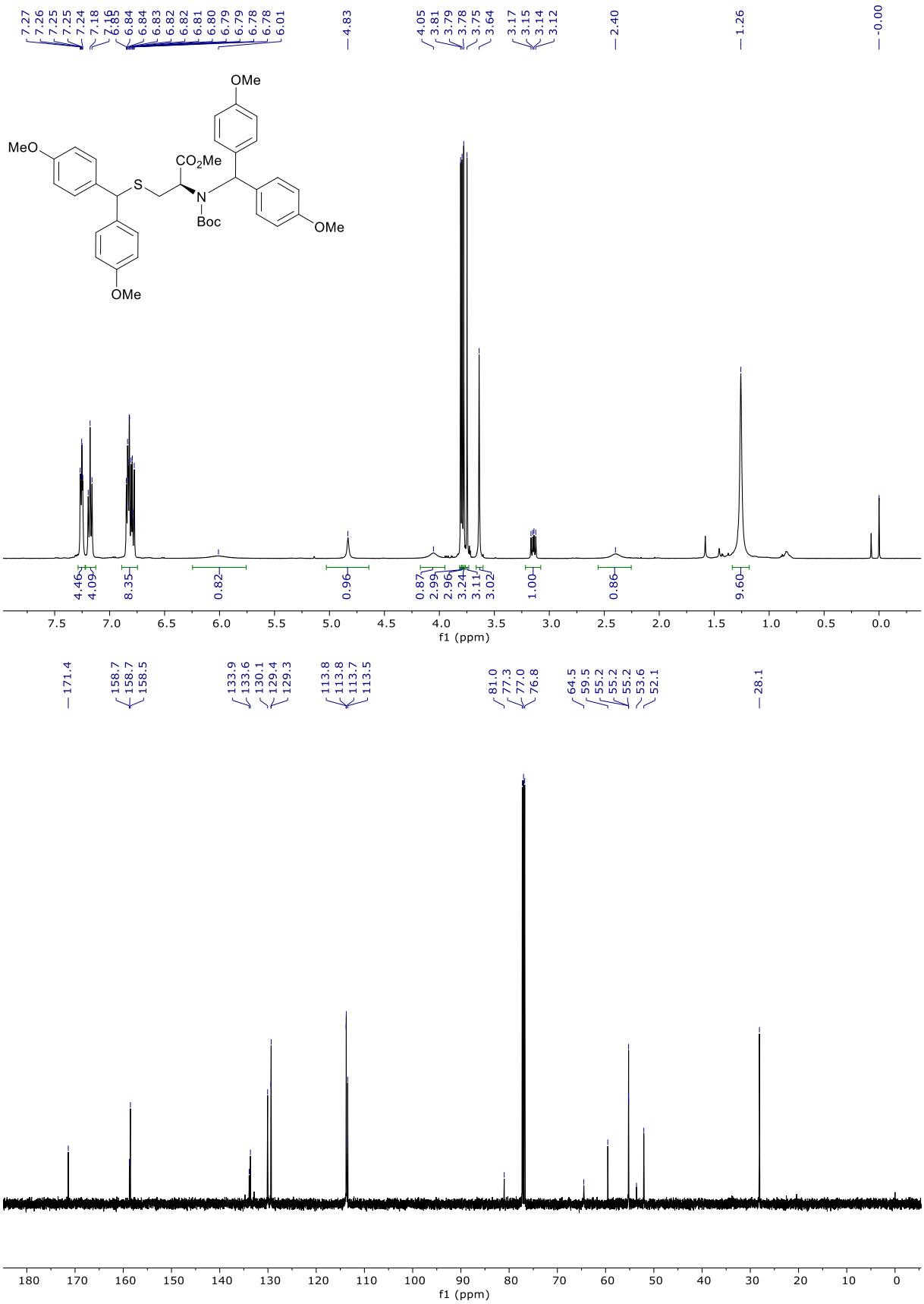
adamantan-1-yl(bis(4-methoxyphenyl)methyl)sulfane (21)



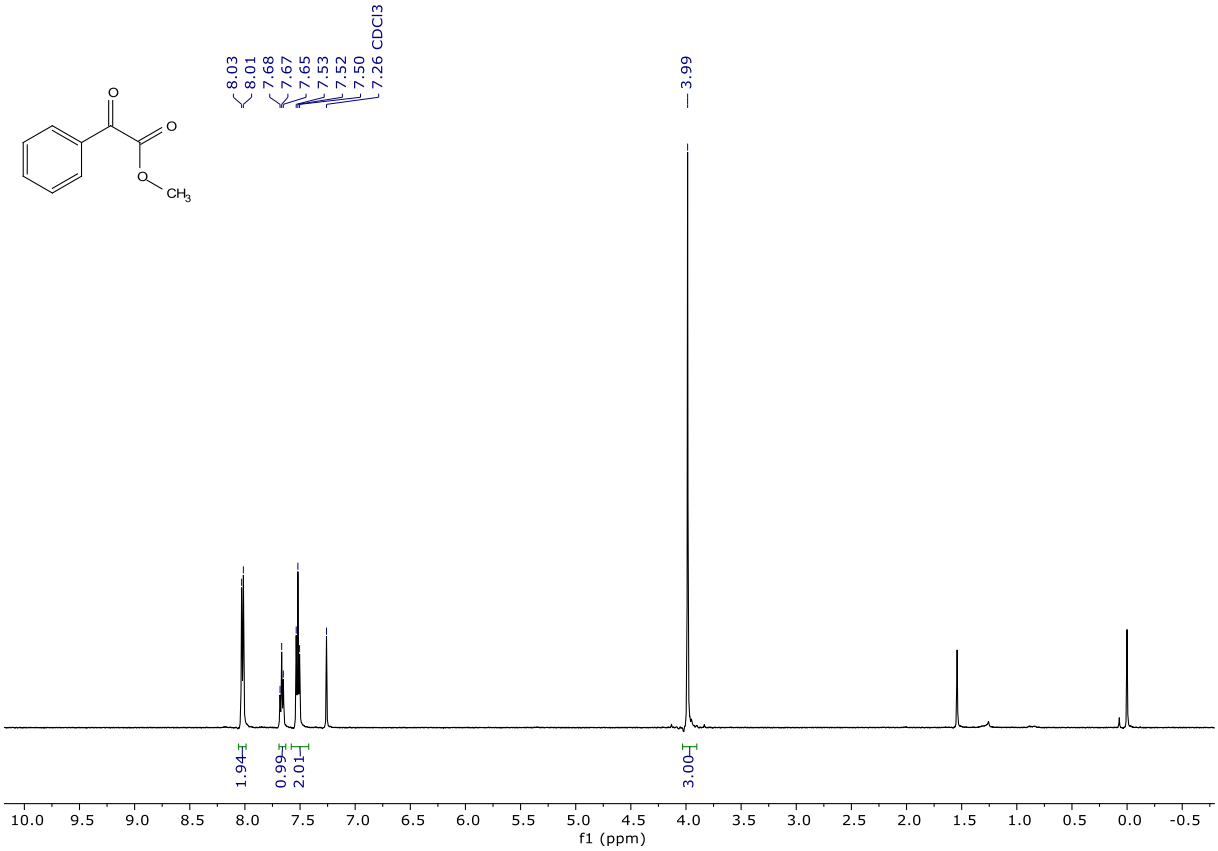
9-(benzylthio)-9H-thioxanthene (22)

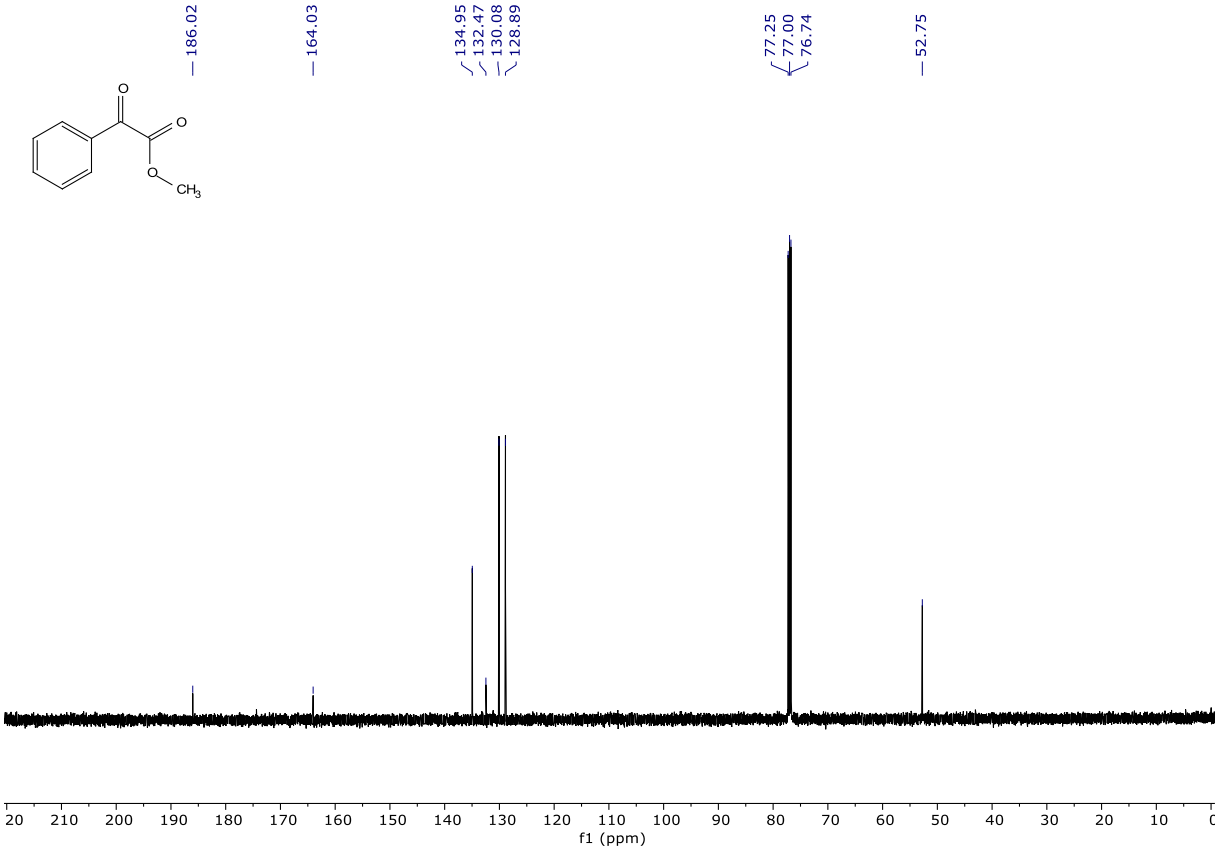


methyl N,S-bis(bis(4-methoxyphenyl)methyl)-N-(tert-butoxycarbonyl)-L-cysteinate (23)

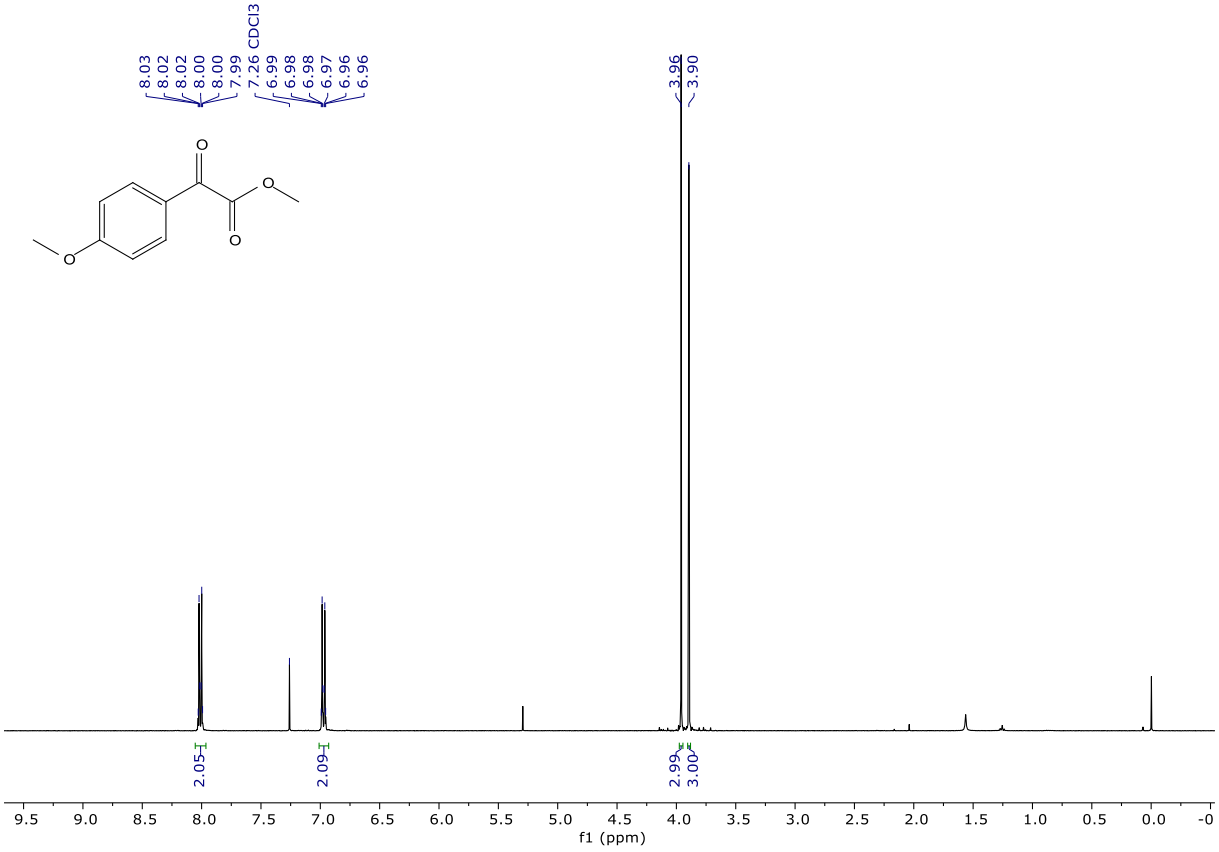


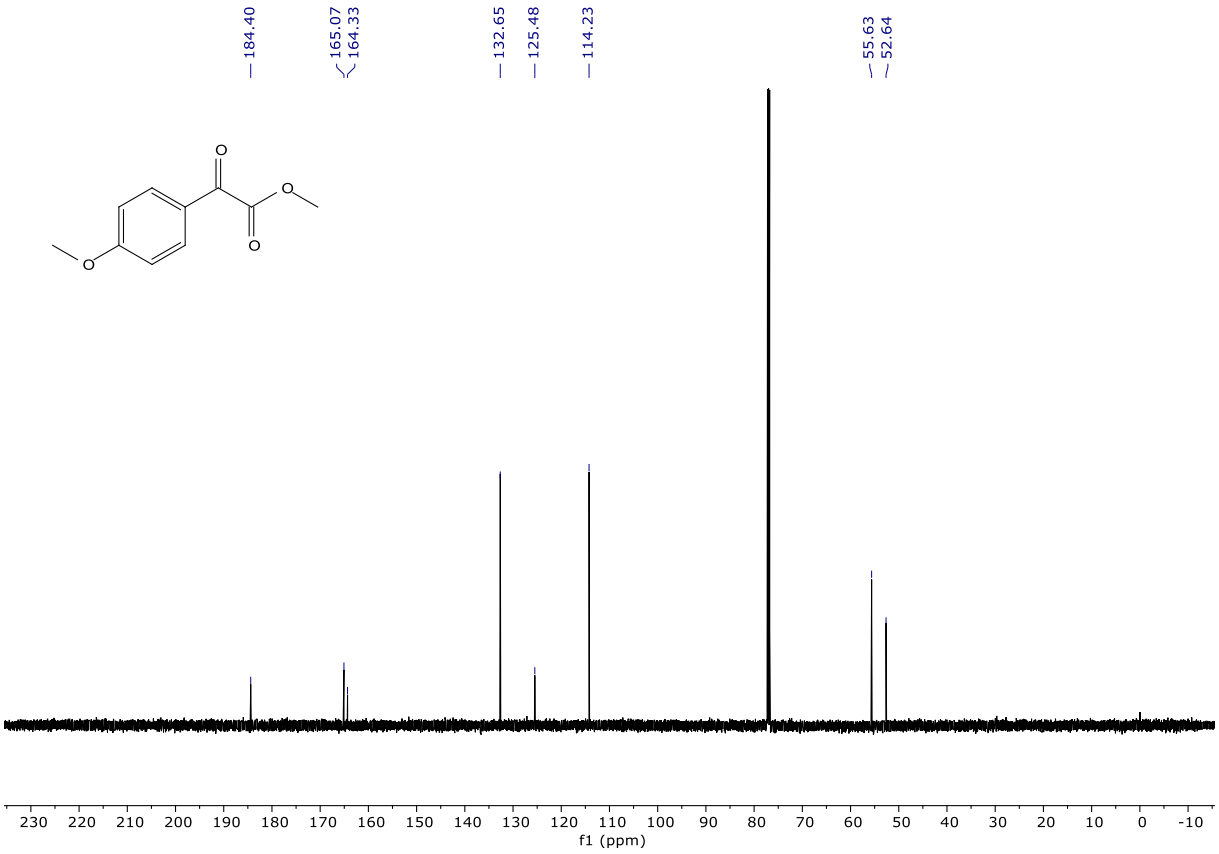
methyl 2-oxo-2-phenylacetate (24)



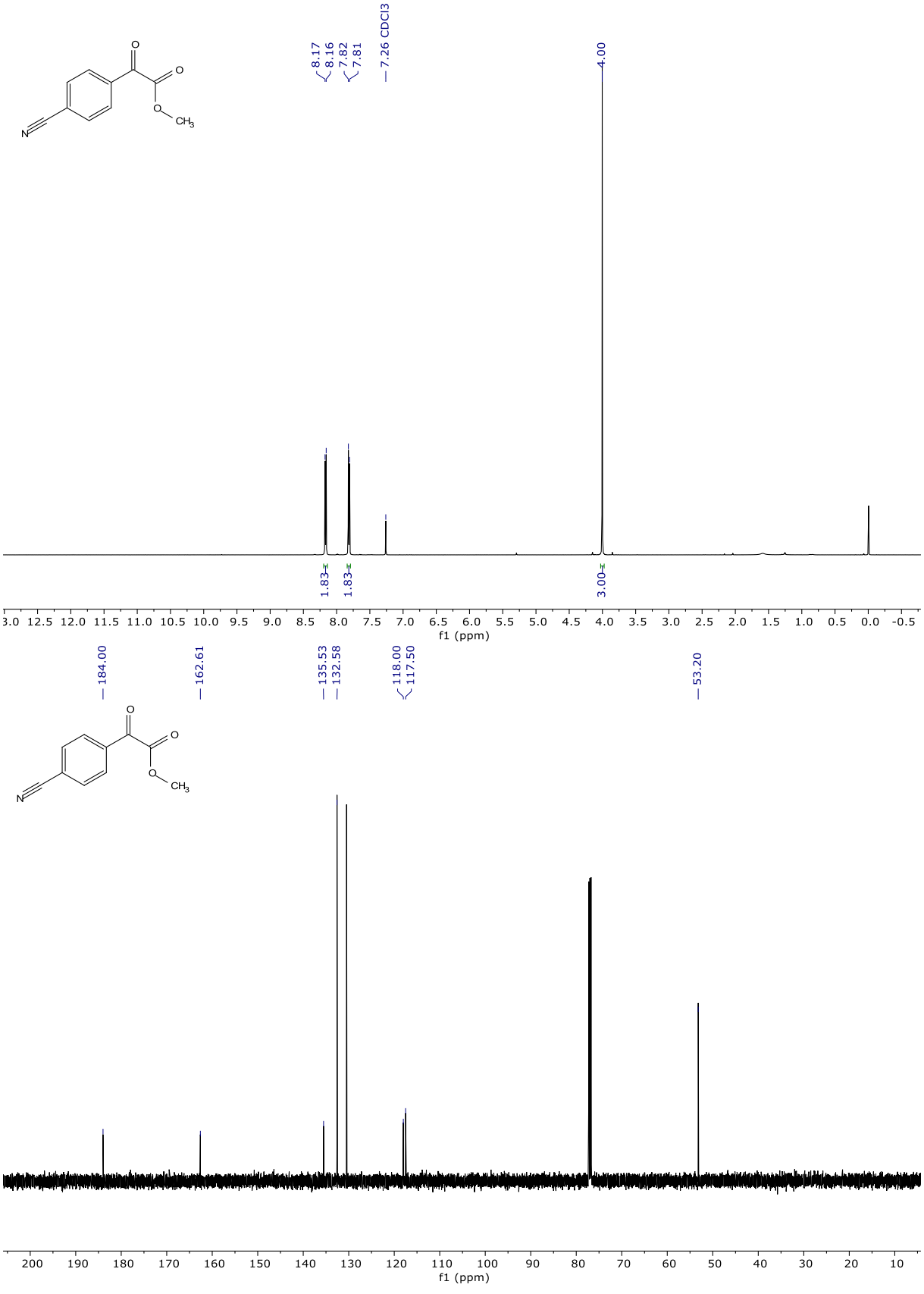


methyl 4-methoxybenzoate (25)

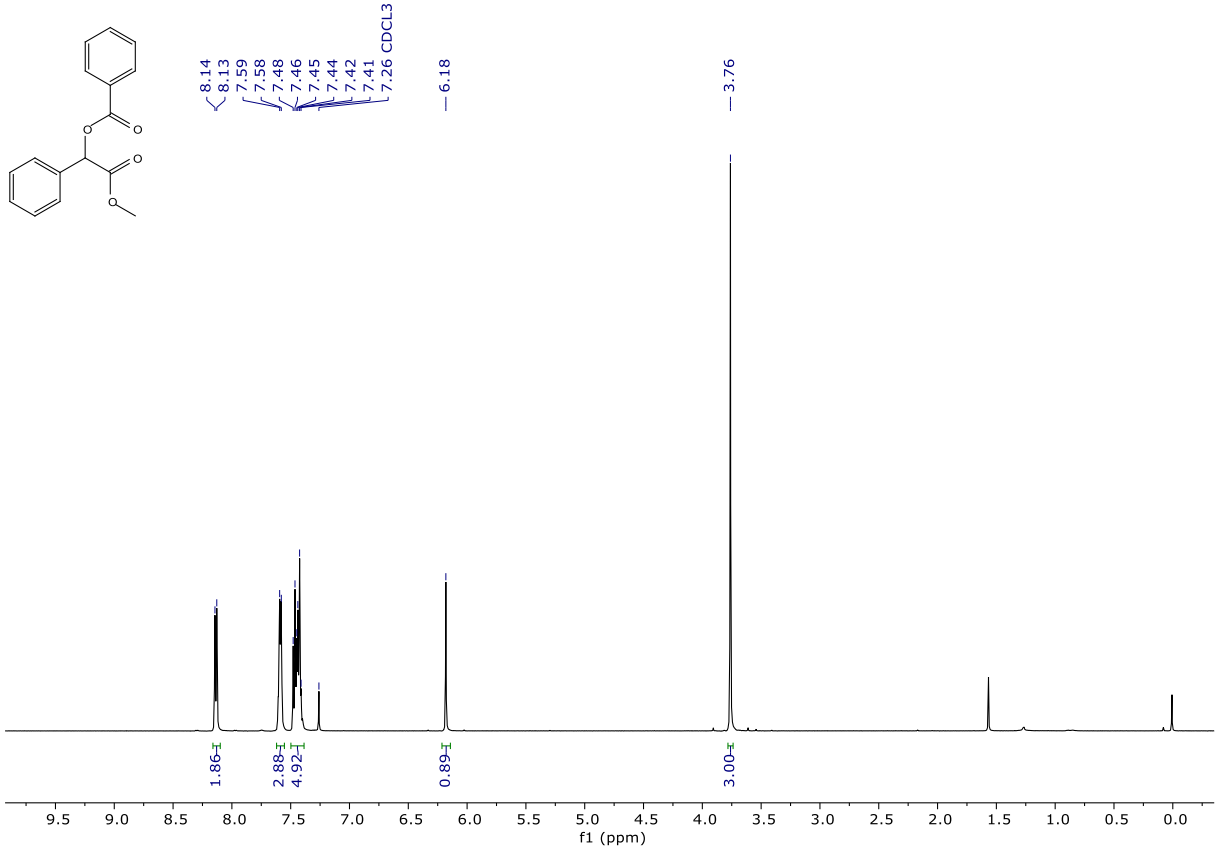


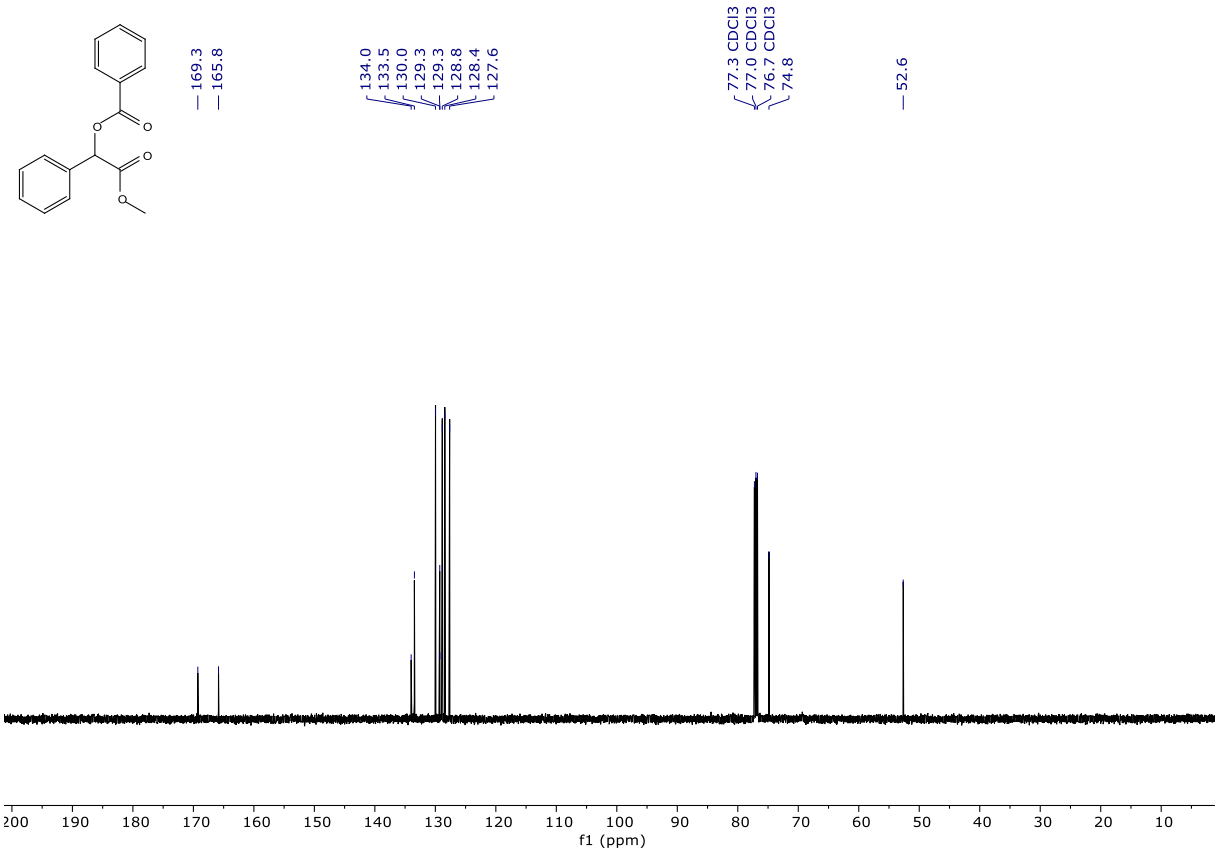


methyl 2-(4-cyanophenyl)-2-oxoacetate (26)

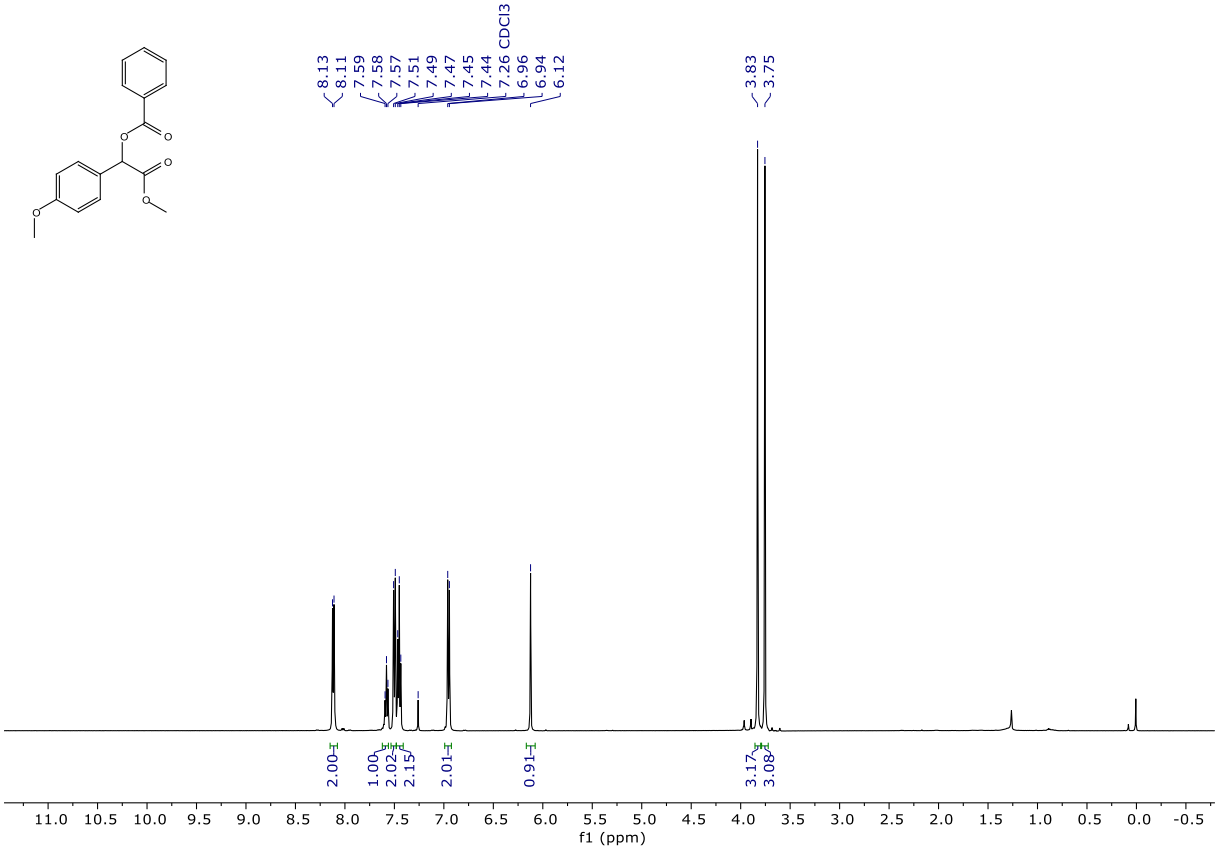


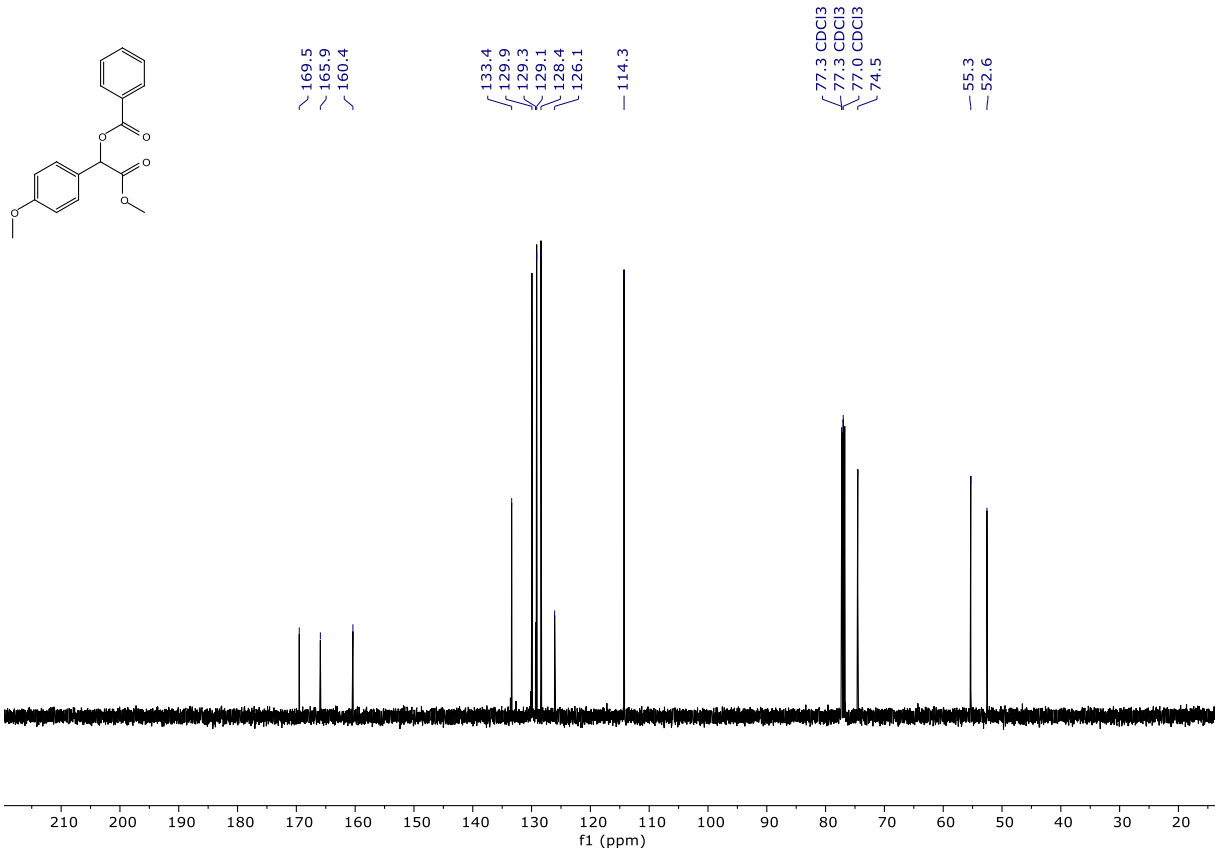
2-methoxy-2-oxo-1-phenylethyl benzoate (27)



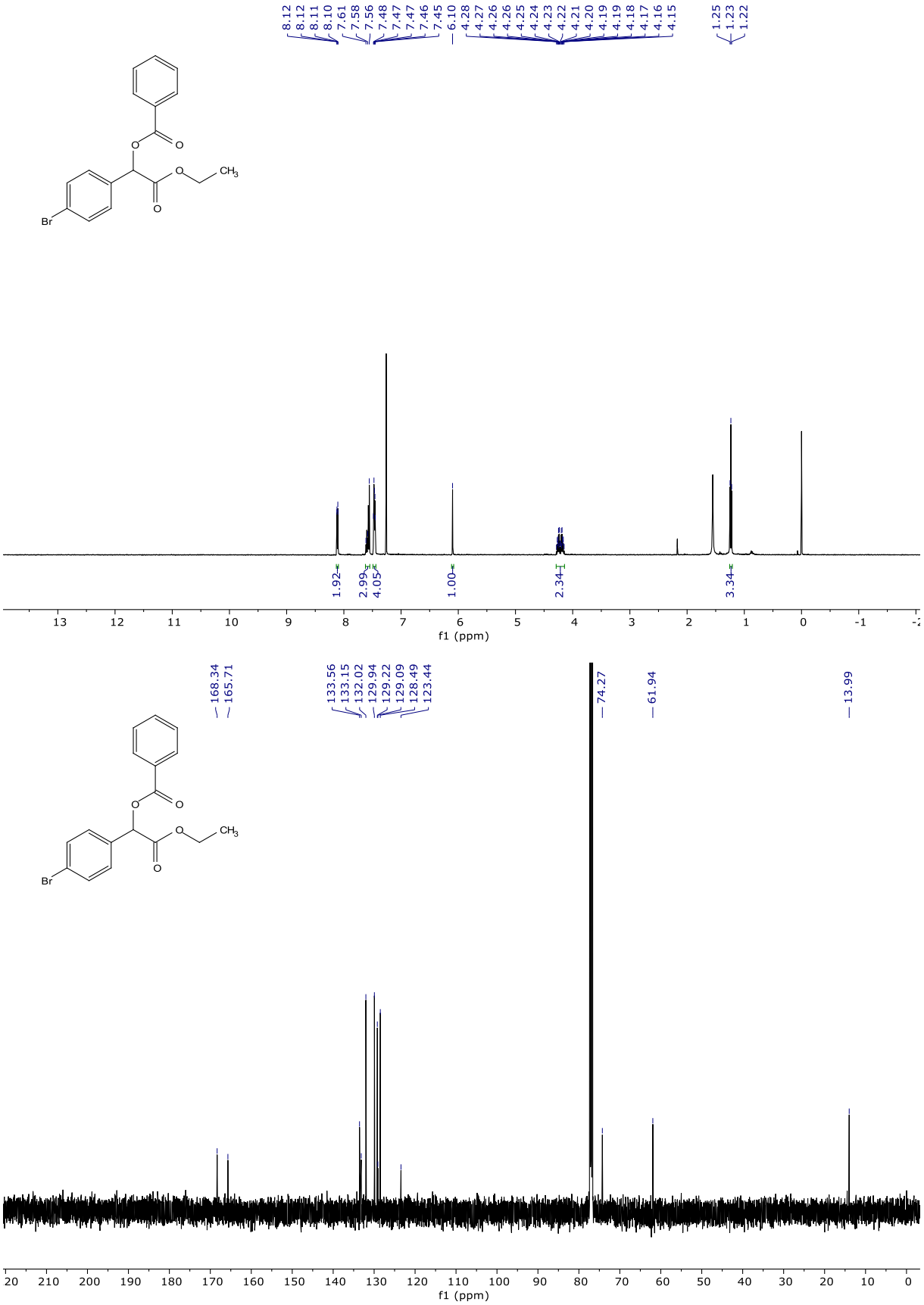


2-methoxy-1-(4-methoxyphenyl)-2-oxoethyl benzoate (28)

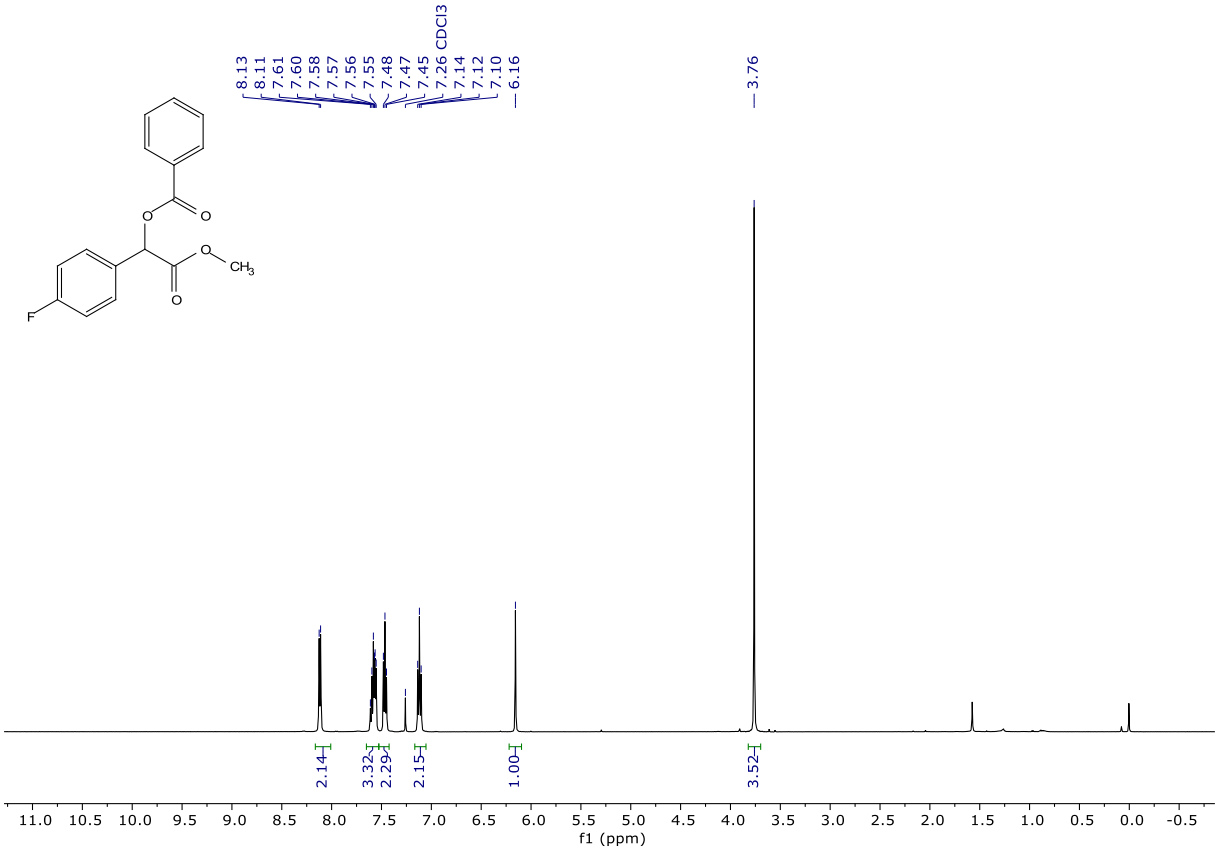


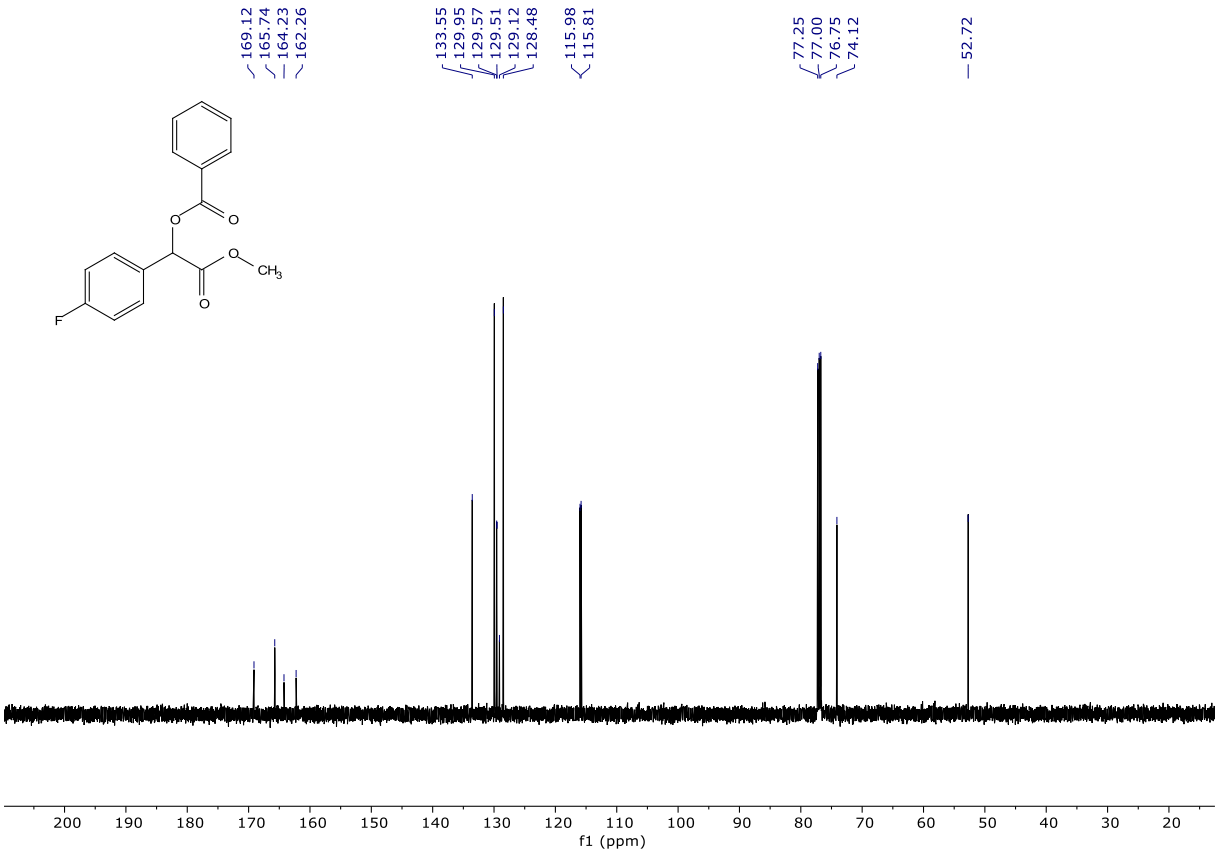


1-(4-bromophenyl)-2-ethoxy-2-oxoethyl benzoate (29)

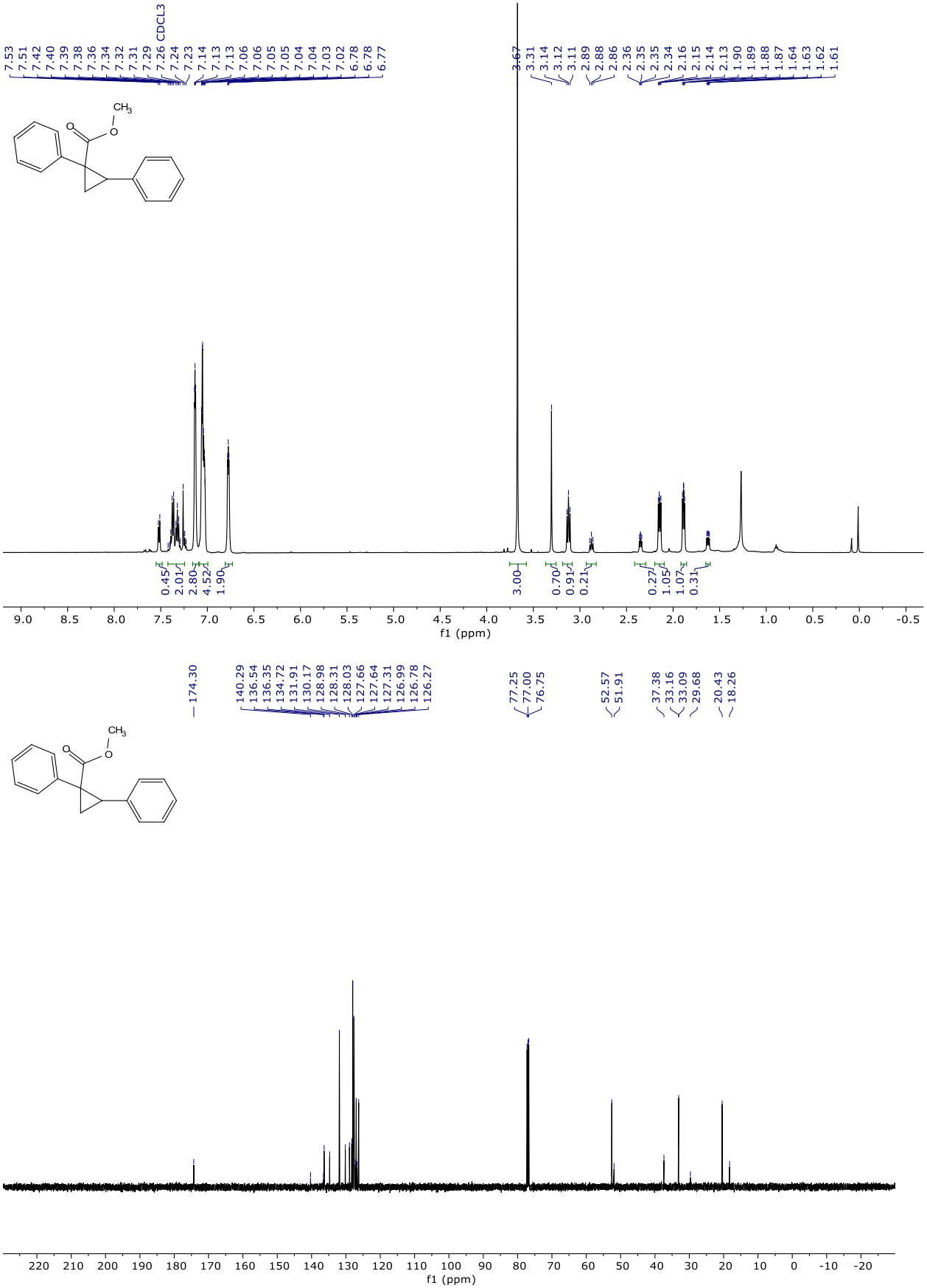


1-(4-fluorophenyl)-2-methoxy-2-oxoethyl benzoate (30)

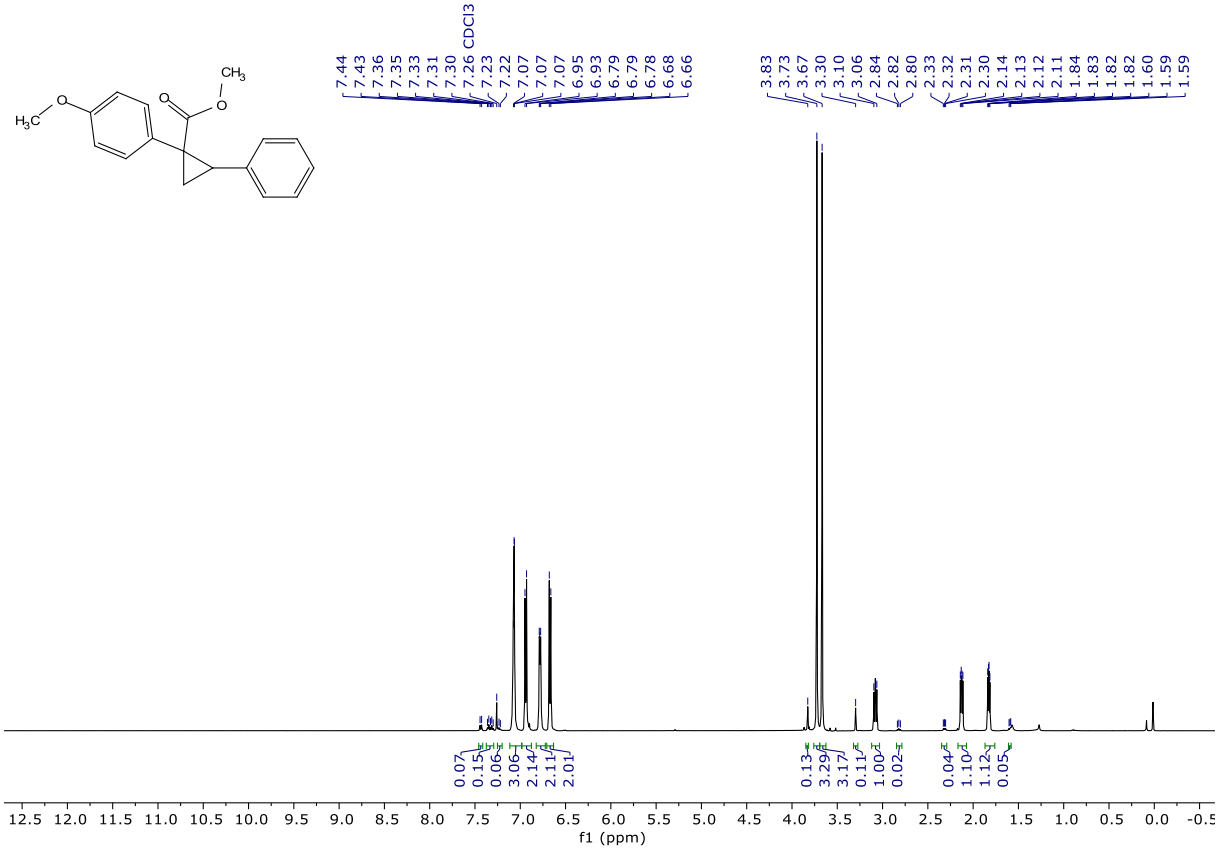


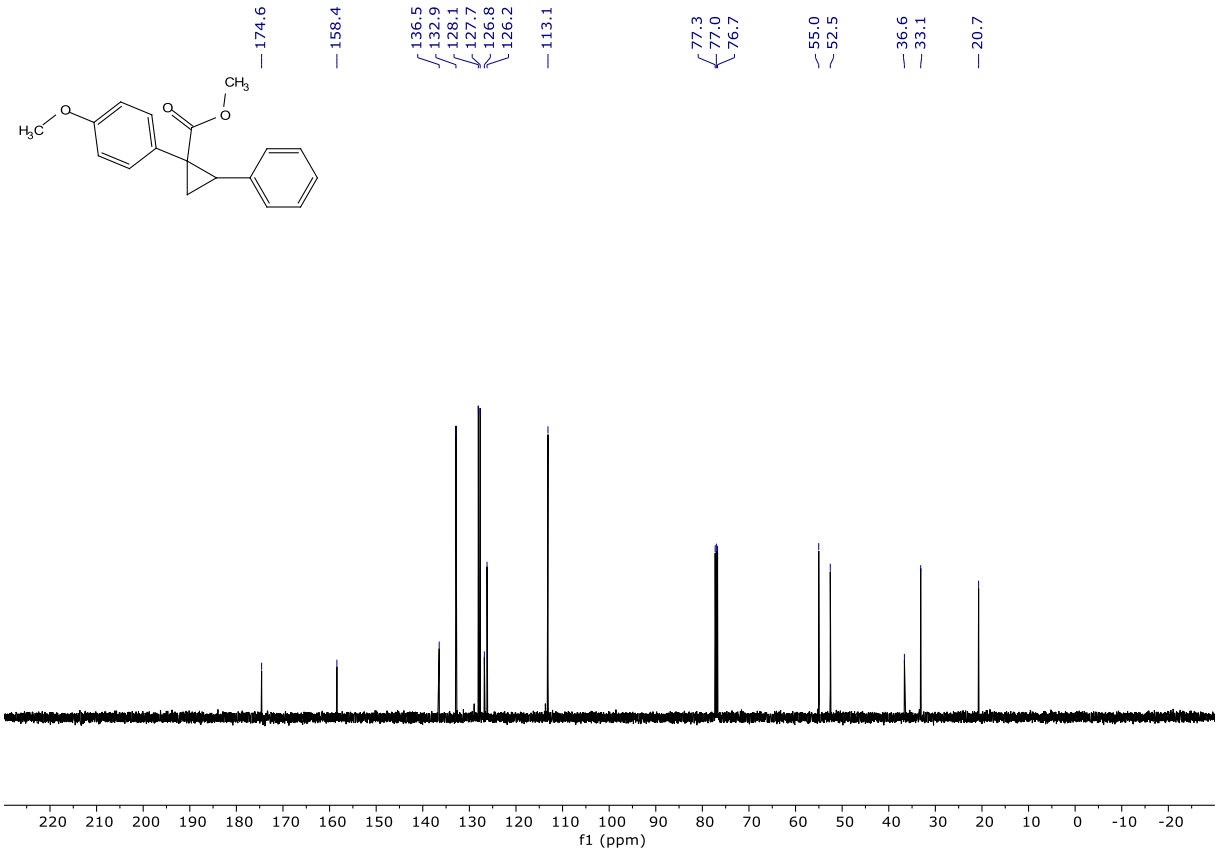


methyl 1,2-diphenylcyclopropane-1-carboxylate (31)

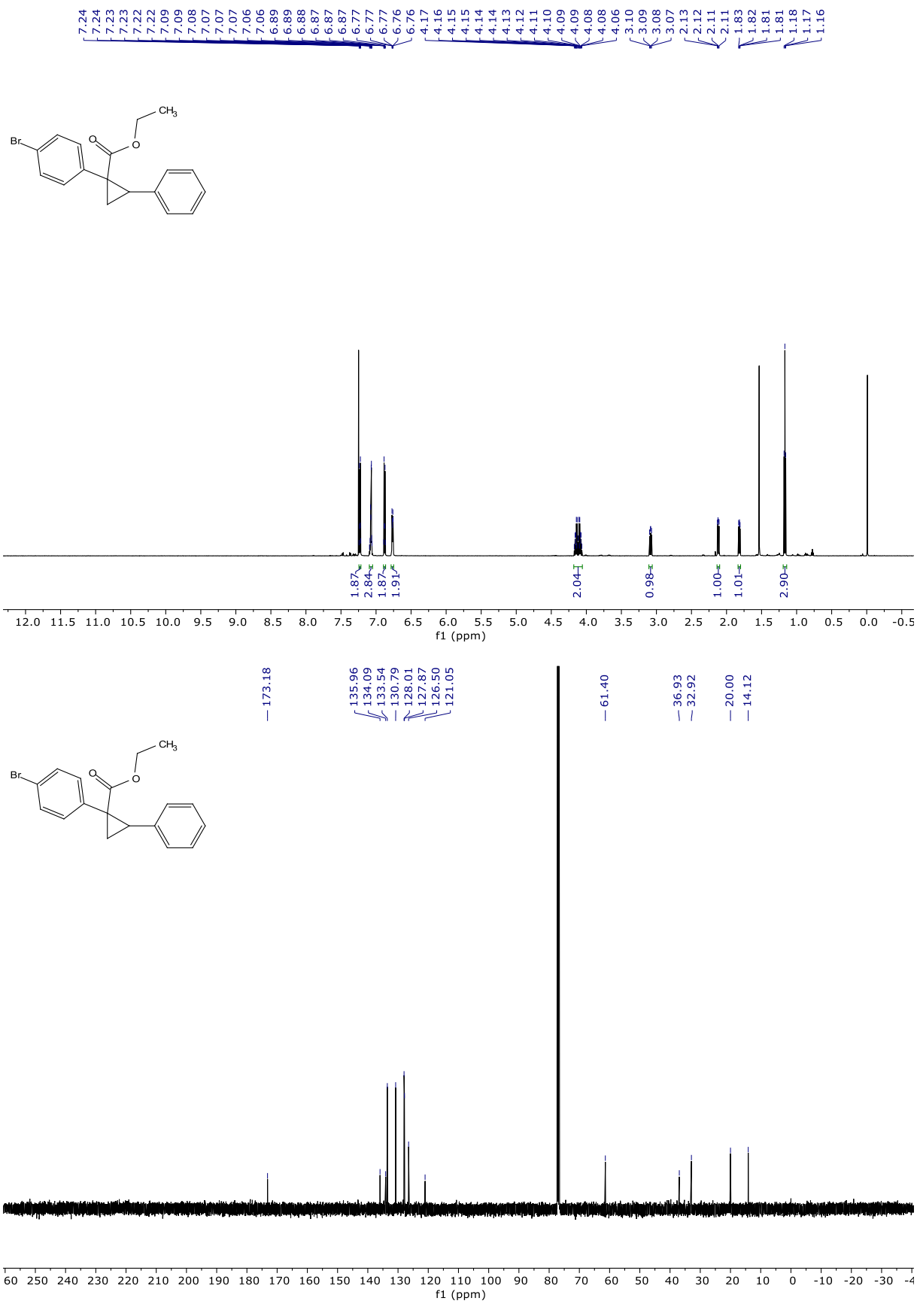


methyl 1-(4-methoxyphenyl)-2-phenylcyclopropane-1-carboxylate (32)

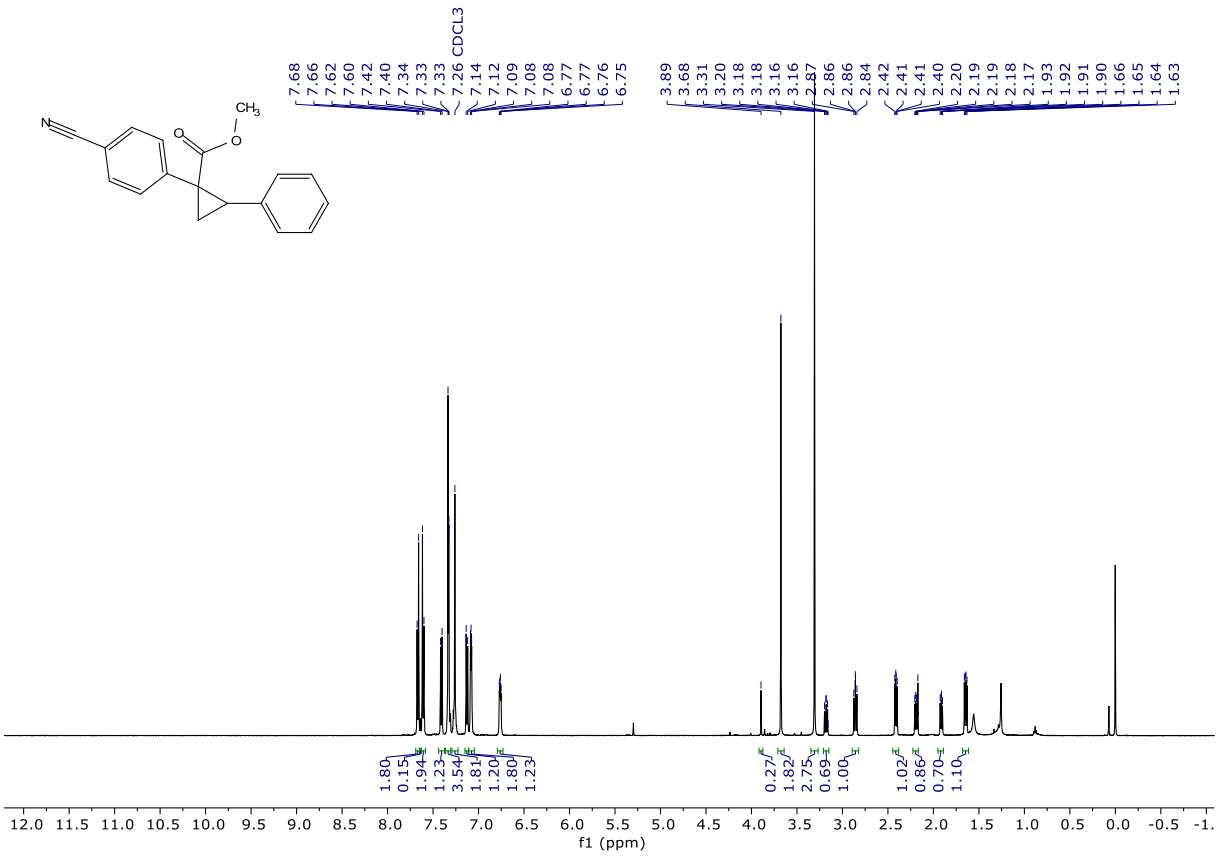


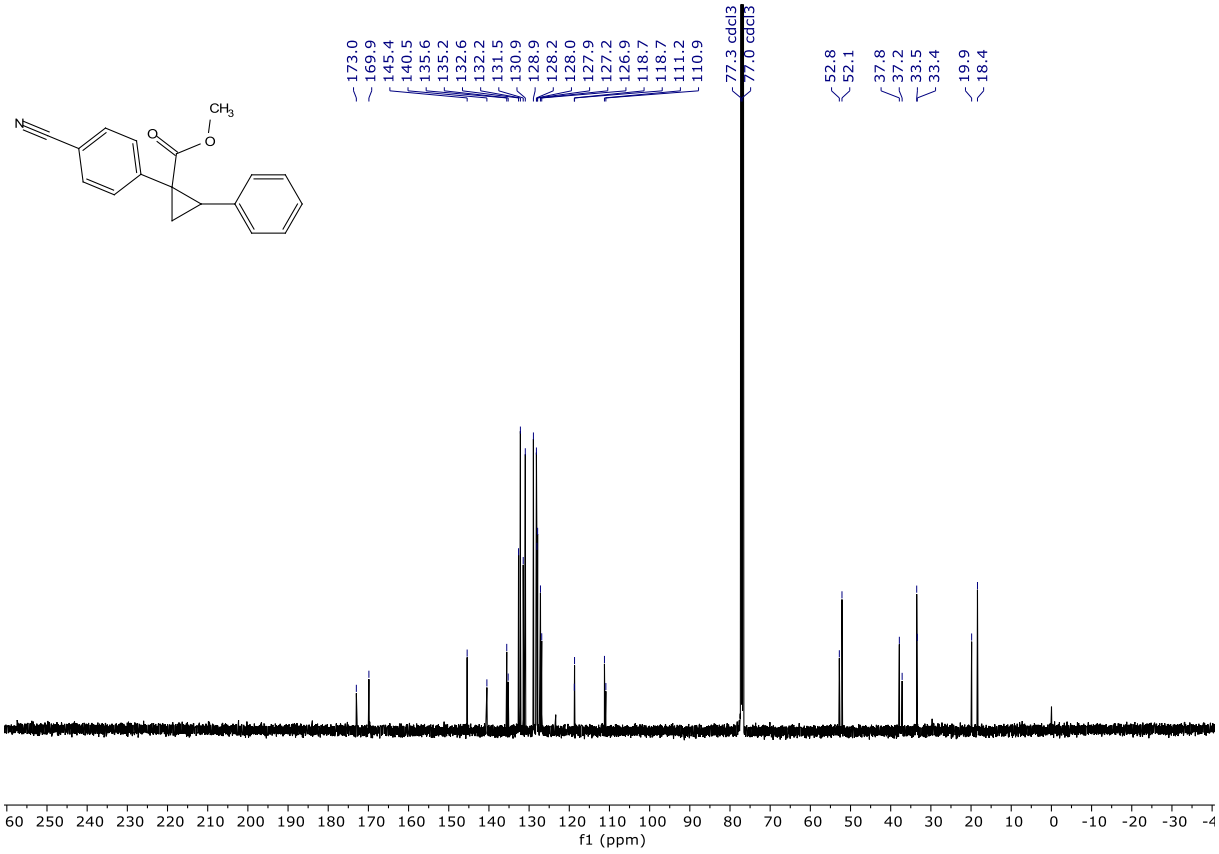


ethyl 1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylate (33)

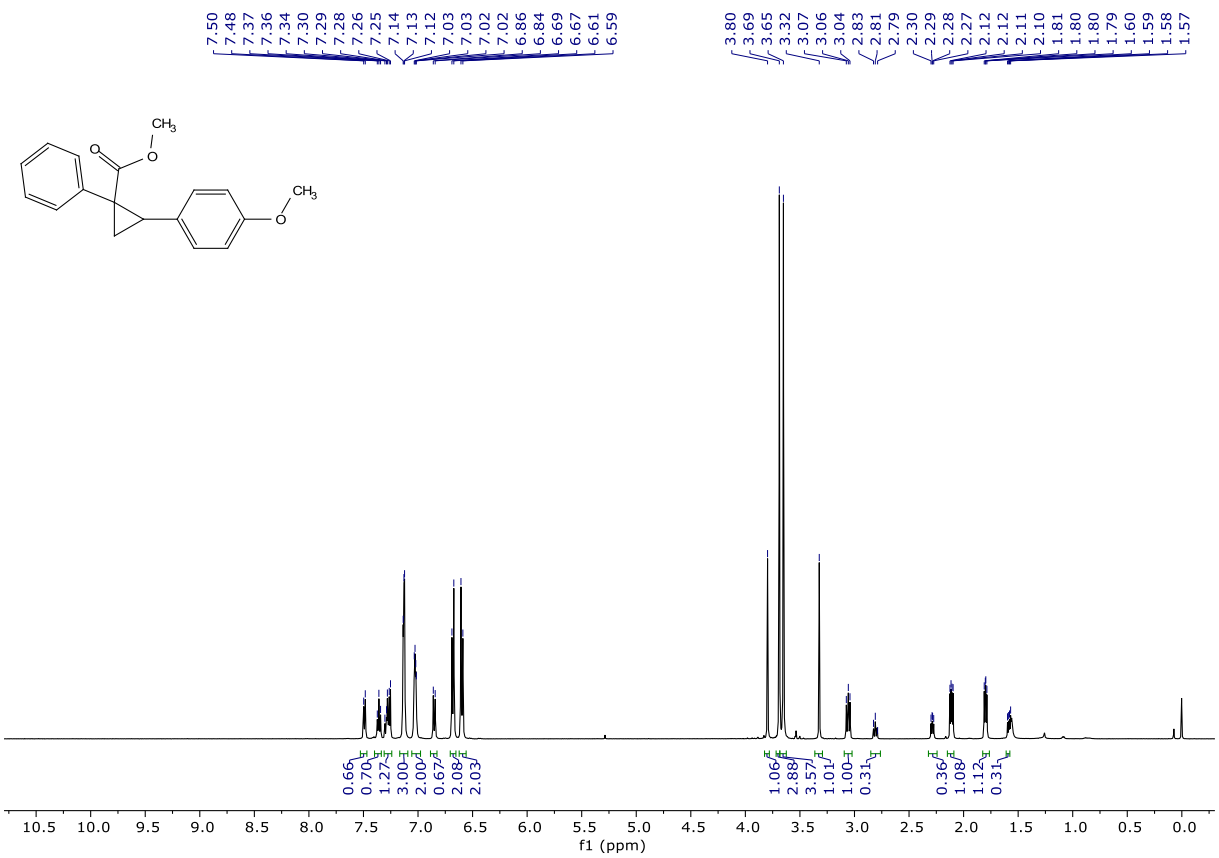


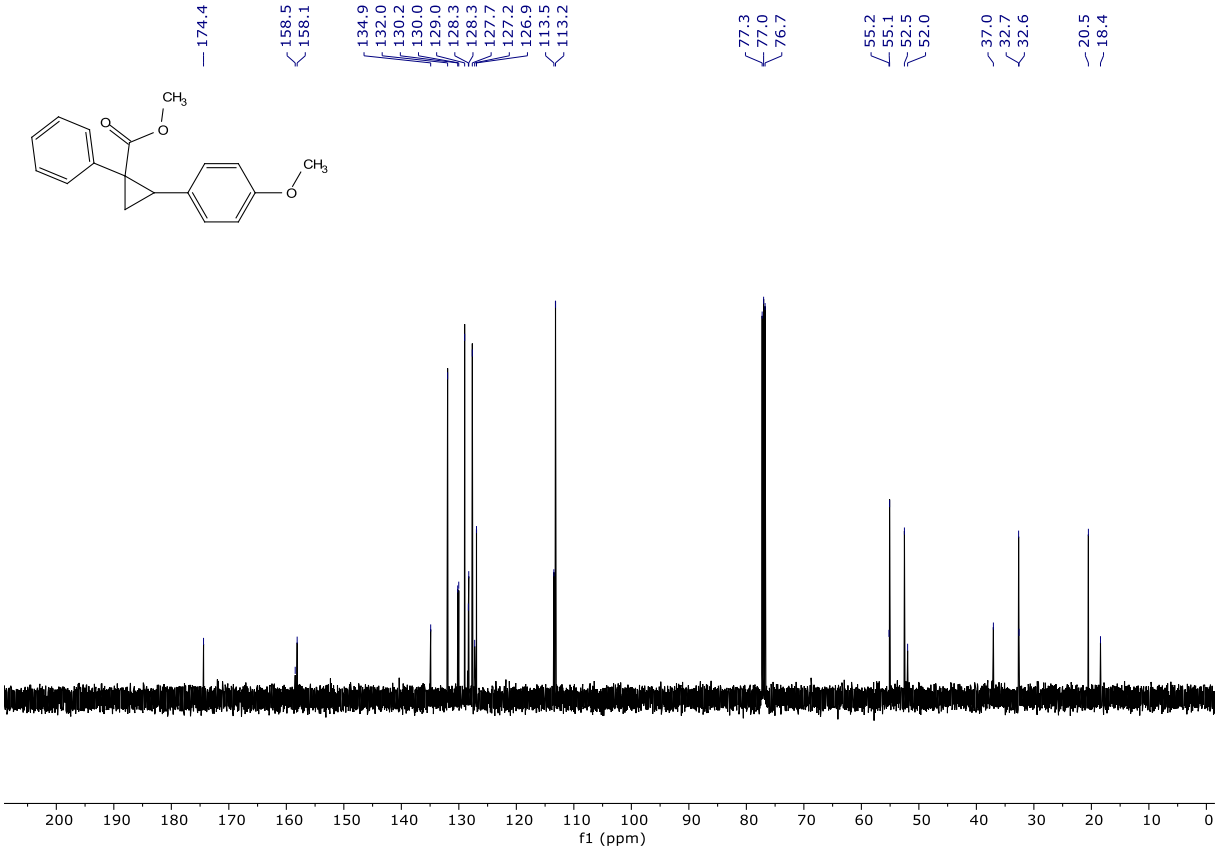
methyl 1-(4-cyanophenyl)-2-phenylcyclopropane-1-carboxylate (34) [86% purity]



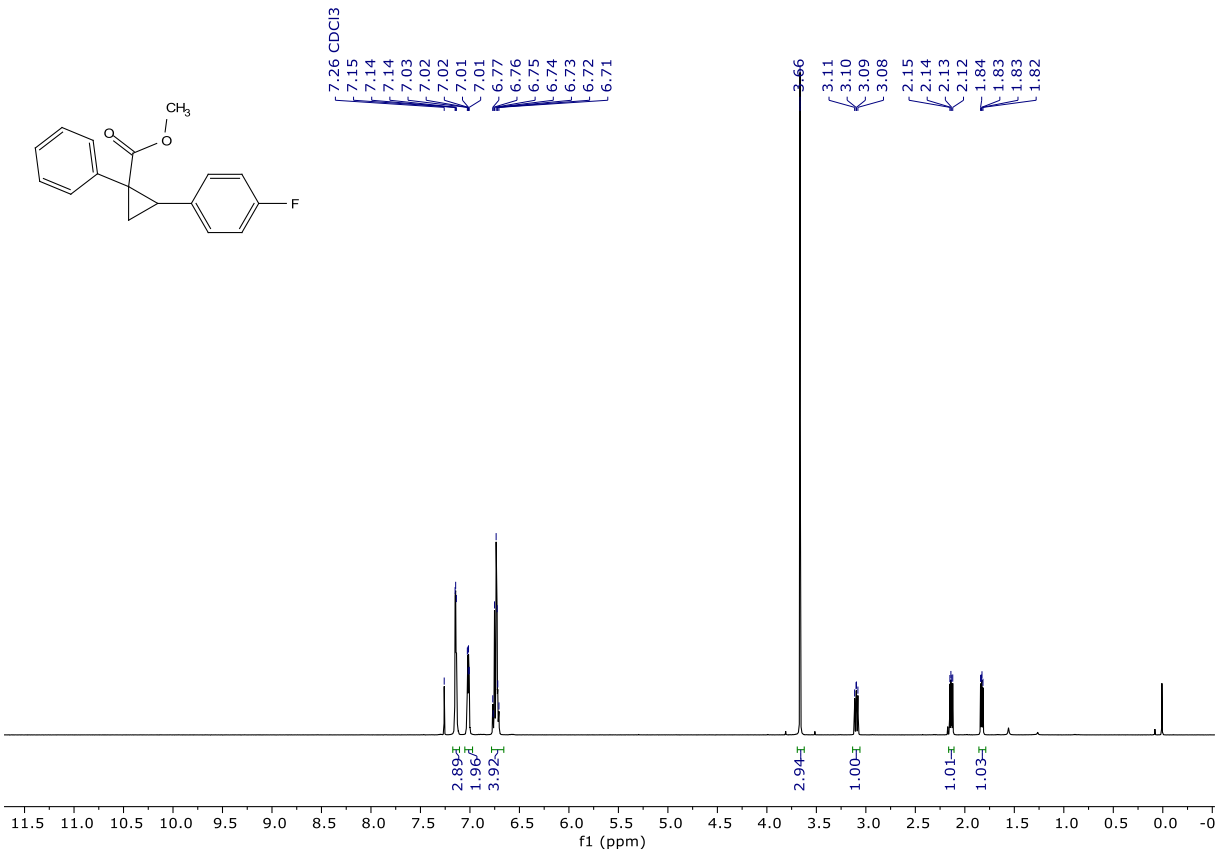


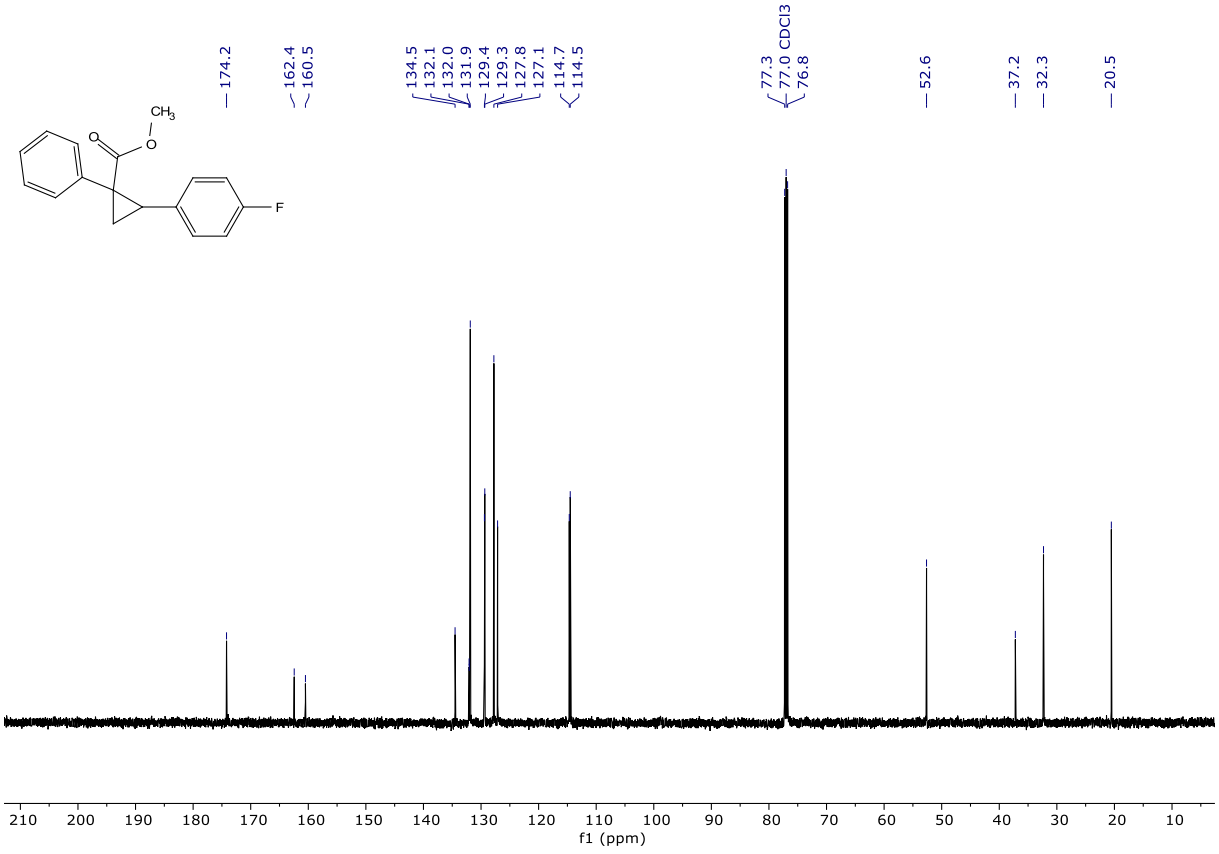
methyl 2-(4-methoxyphenyl)-1-phenylcyclopropane-1-carboxylate (35)

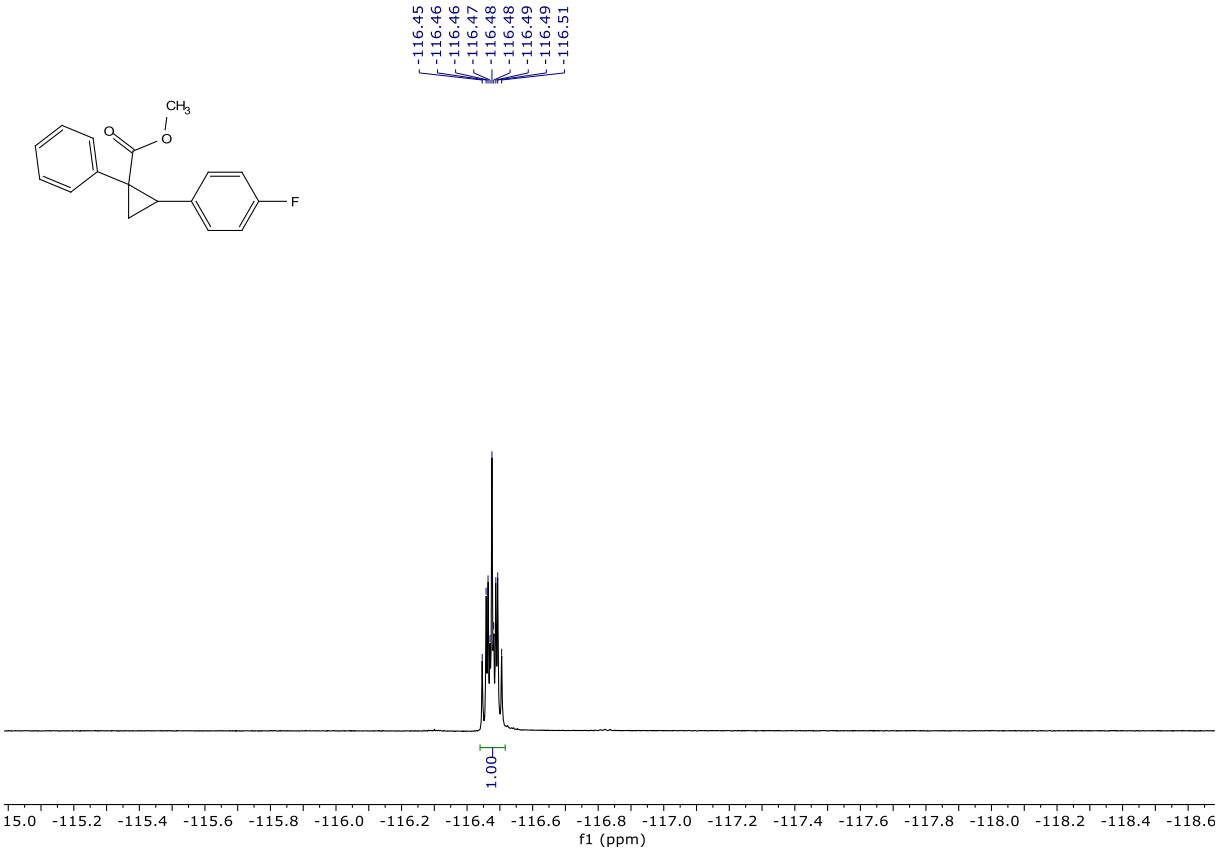




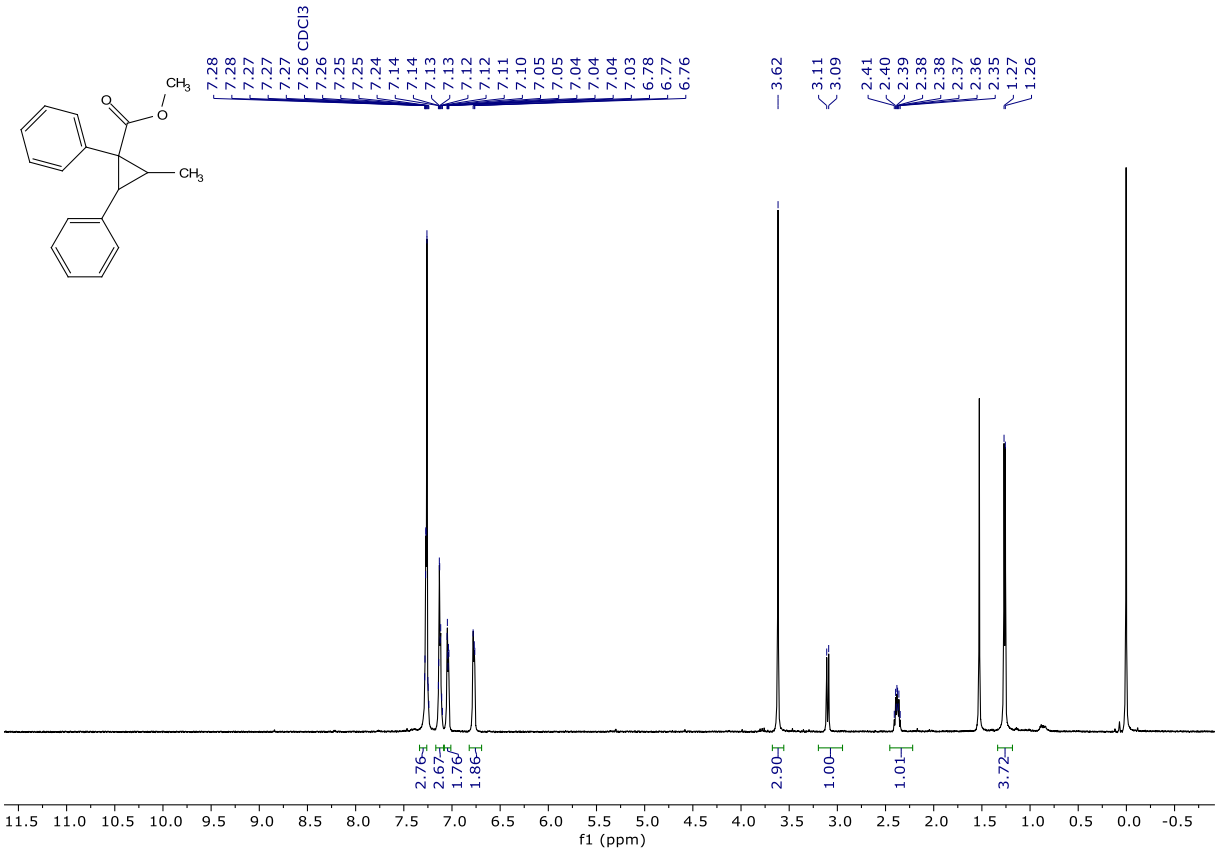
methyl 2-(4-fluorophenyl)-1-phenylcyclopropane-1-carboxylate (36)

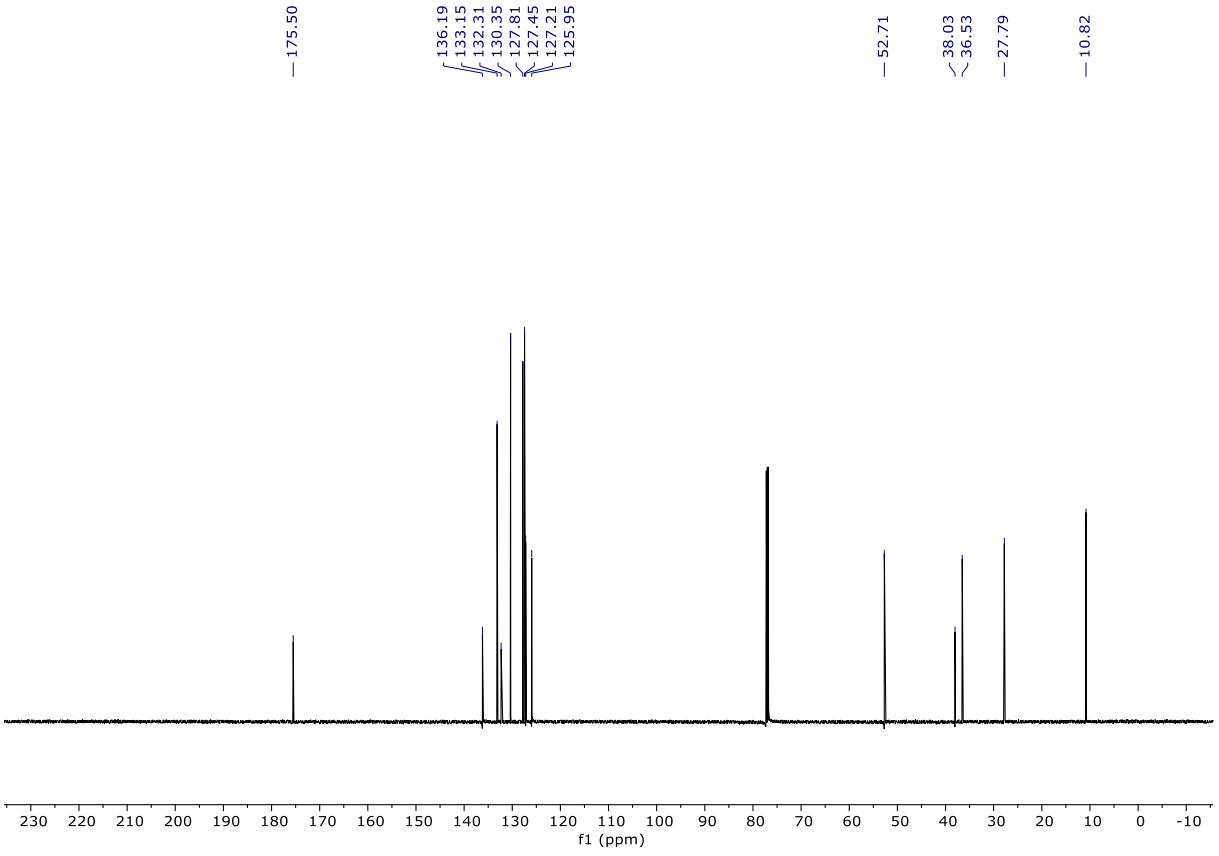


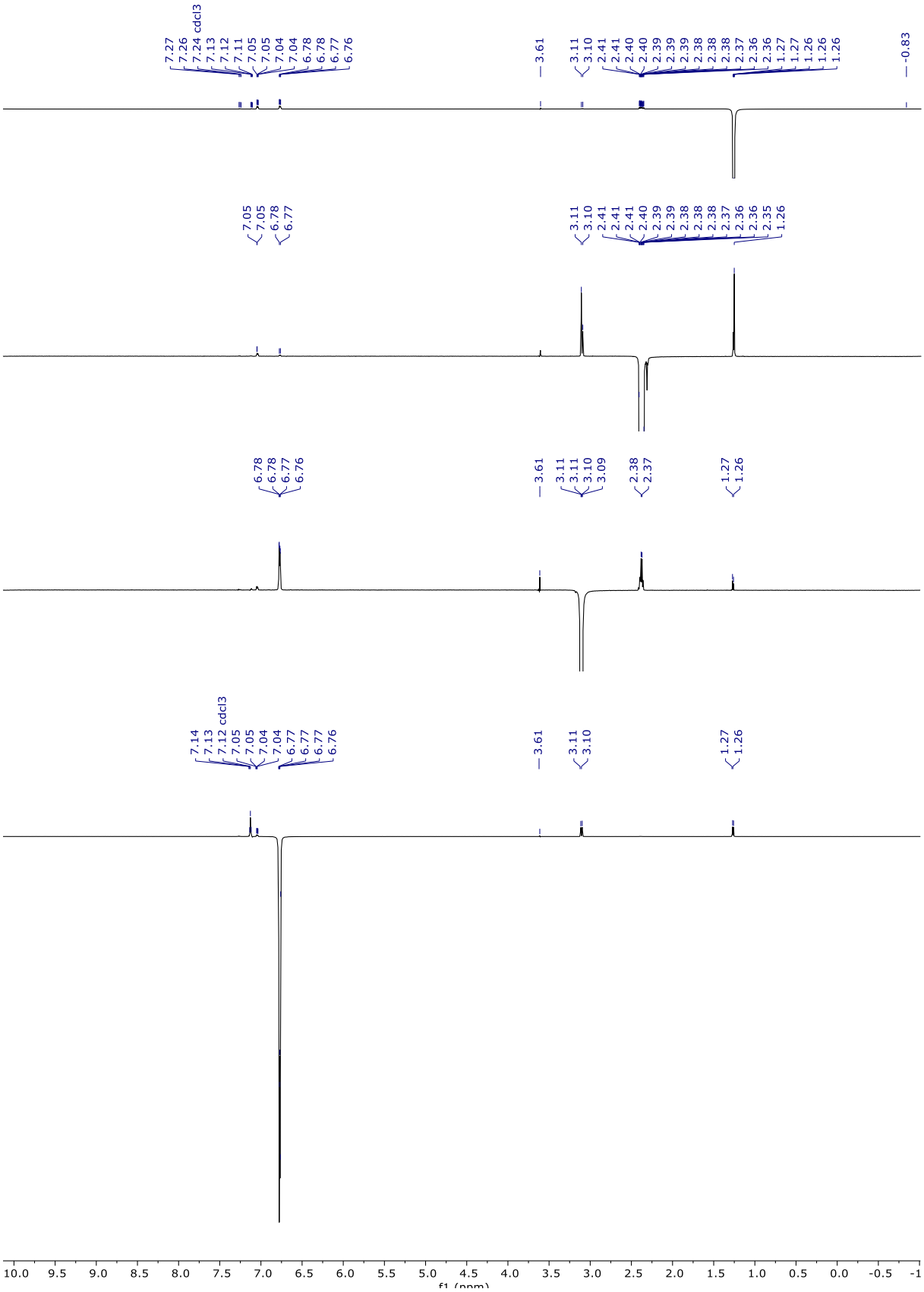


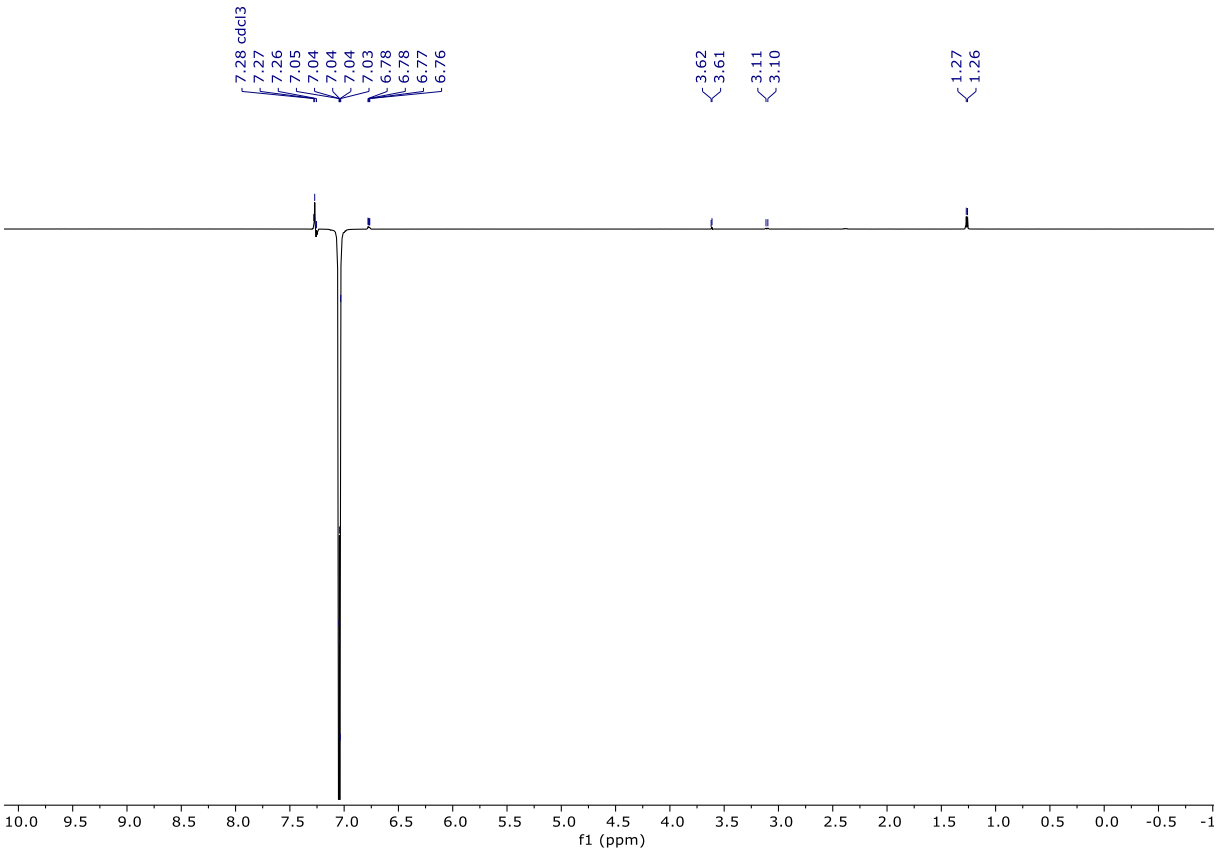

-116.45
-116.46
-116.46
-116.47
-116.48
-116.48
-116.49
-116.49
-116.51
CH3
O
O
F
1.00
15.0 -115.2 -115.4 -115.6 -115.8 -116.0 -116.2 -116.4 -116.6 -116.8 -117.0 -117.2 -117.4 -117.6 -117.8 -118.0 -118.2 -118.4 -118.6
f1 (ppm)

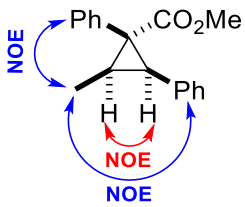
methyl 2-methyl-1,3-diphenylcyclopropane-1-carboxylate (37)



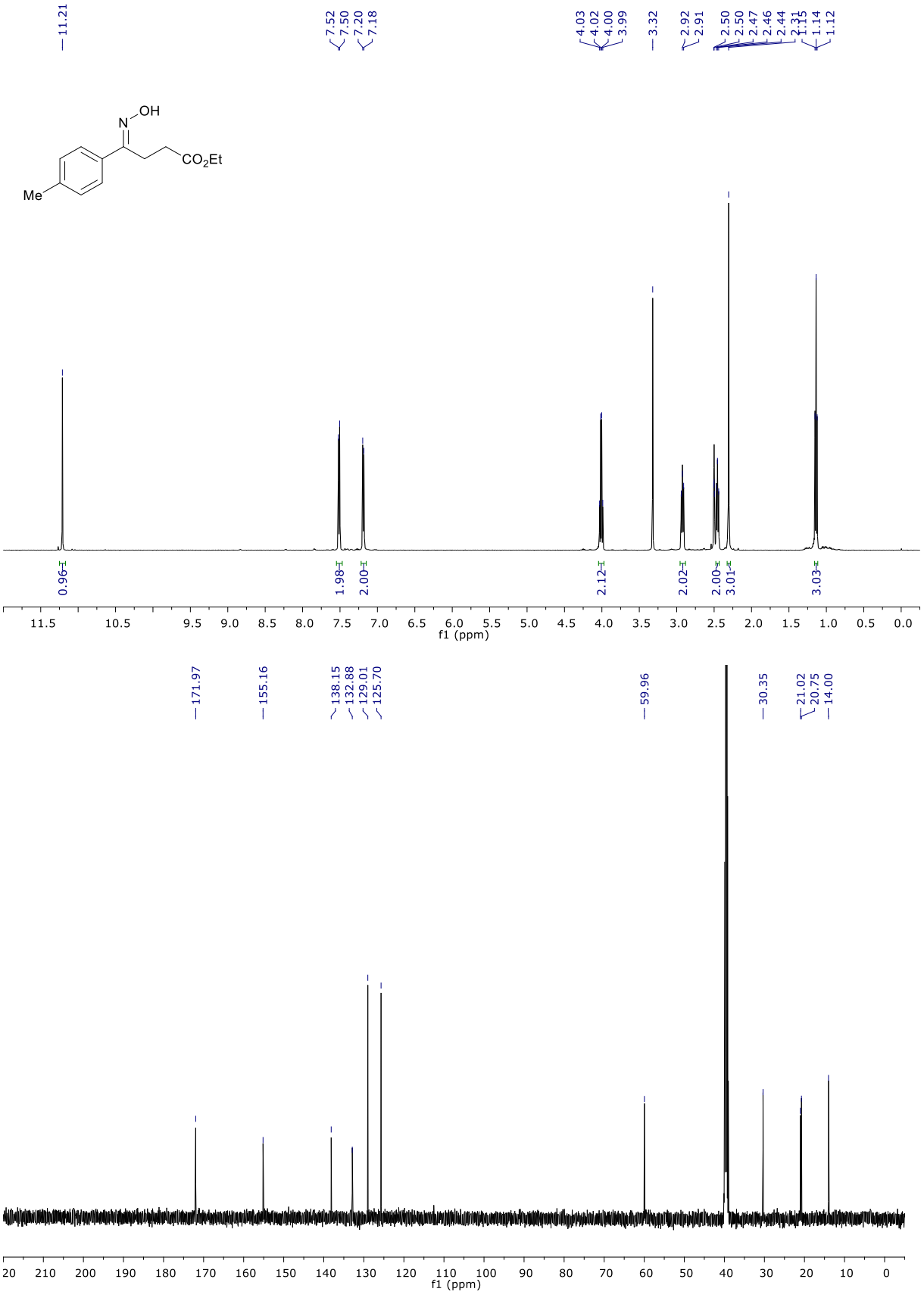



7.27
7.26
7.24 cdcl3
7.13
7.12
7.11
7.05
7.05
7.04
7.04
6.78
6.78
6.77
6.76
3.61
3.11
3.10
2.41
2.41
2.40
2.40
2.39
2.39
2.39
2.38
2.38
2.38
2.37
2.36
2.36
1.27
1.27
1.26
1.26
1.26
-0.83
7.05
7.05
6.78
6.77
3.11
3.10
2.41
2.41
2.41
2.40
2.39
2.39
2.38
2.38
2.38
2.37
2.36
2.35
1.26
6.78
6.78
6.77
6.76
3.61
3.11
3.11
3.10
3.09
2.38
2.37
1.27
1.26
7.14
7.13
7.12 cdcl3
7.05
7.05
7.04
7.04
6.77
6.77
6.77
6.76
3.61
3.11
3.10
1.27
1.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

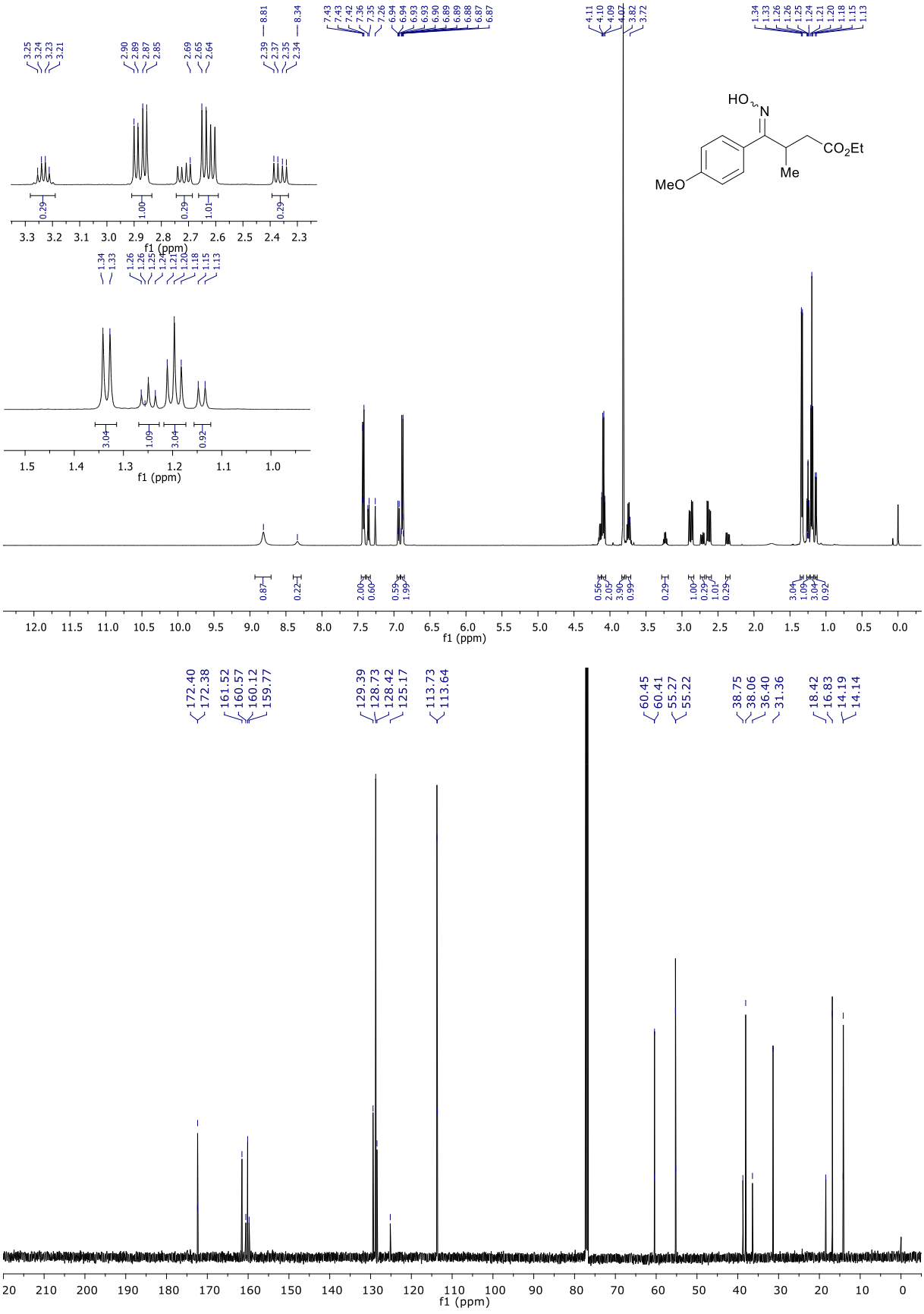

7.28 cdcl3
7.27
7.26
7.05
7.04
7.04
7.04
7.03
6.78
6.78
6.77
6.76
3.62
3.61
3.11
3.10
1.27
1.26
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


NOE
Ph
CO2Me
Ph
H H
NOE
NOE

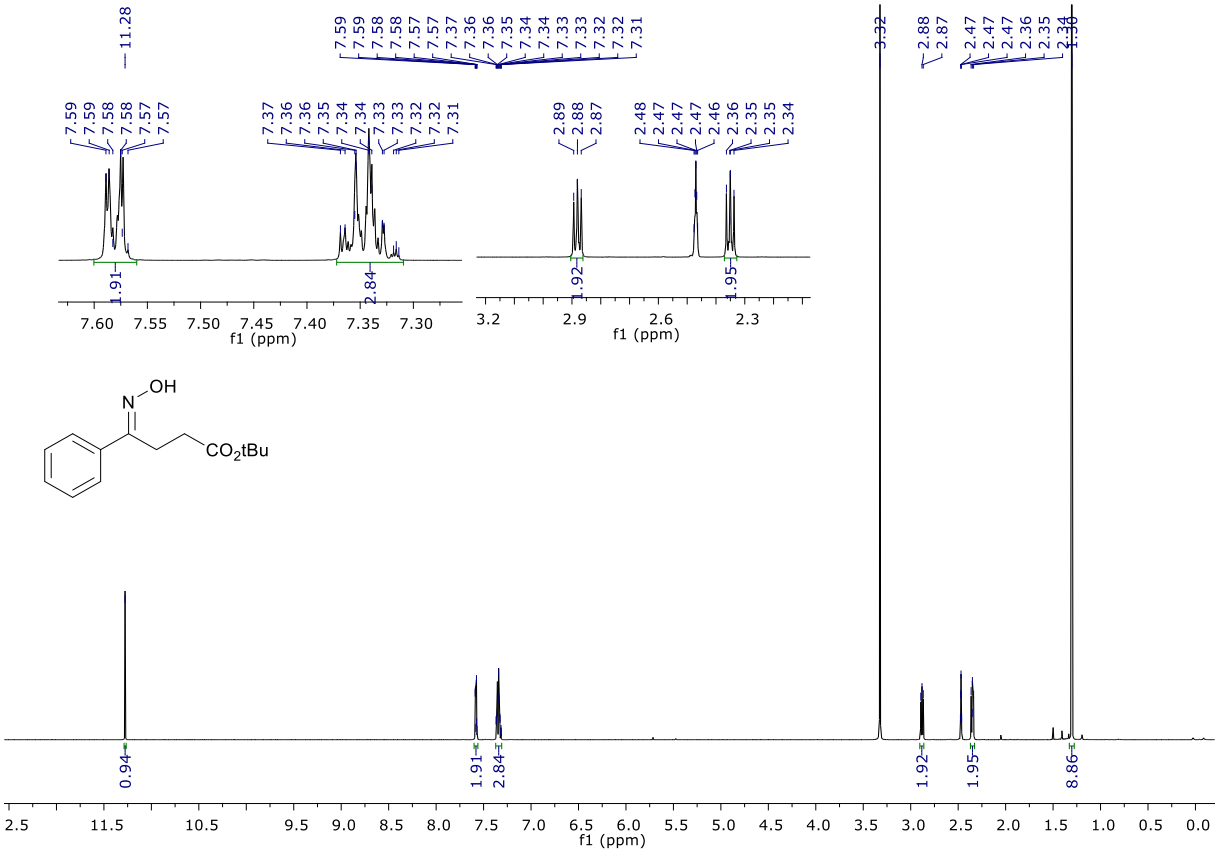
ethyl (E)-4-(hydroxyimino)-4-(p-tolyl)butanoate (38)

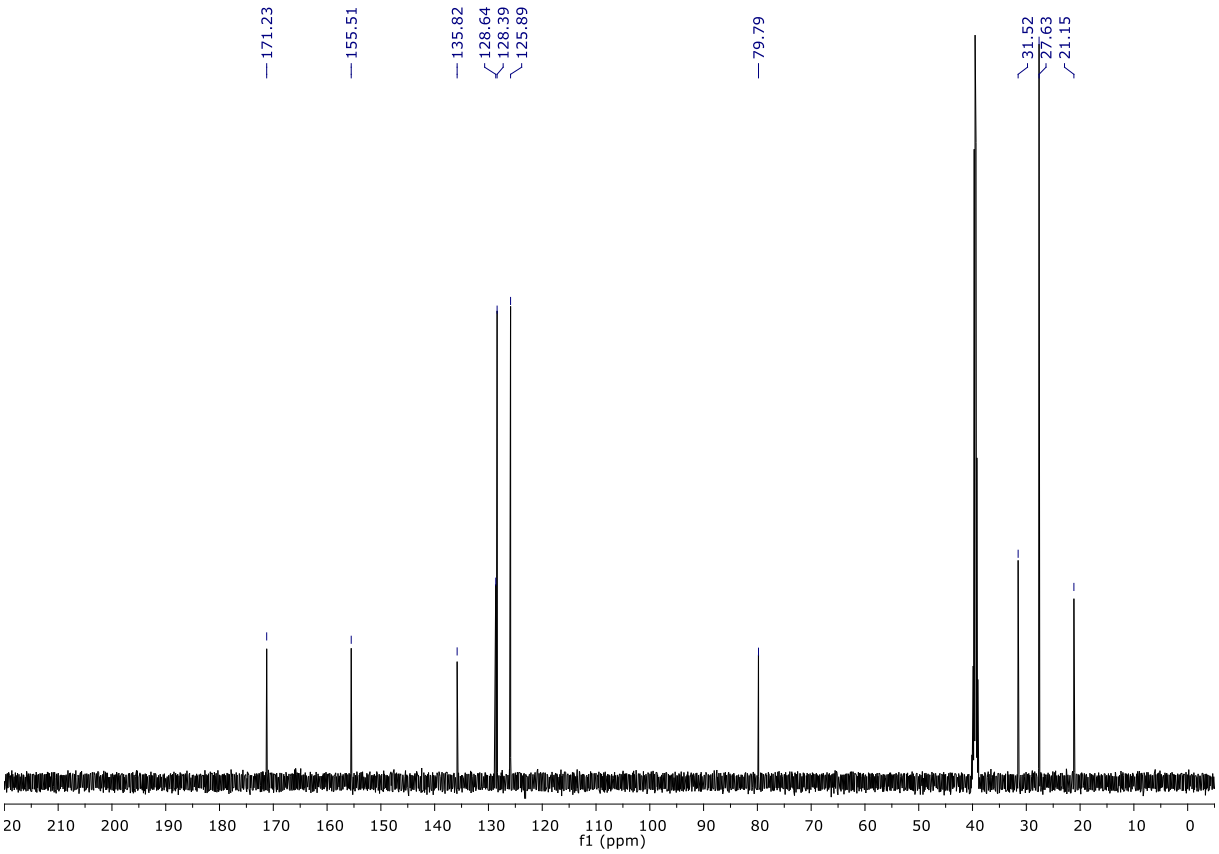


ethyl 4-(hydroxyimino)-5-(4-methoxyphenyl)-3-methylpentanoate (39)

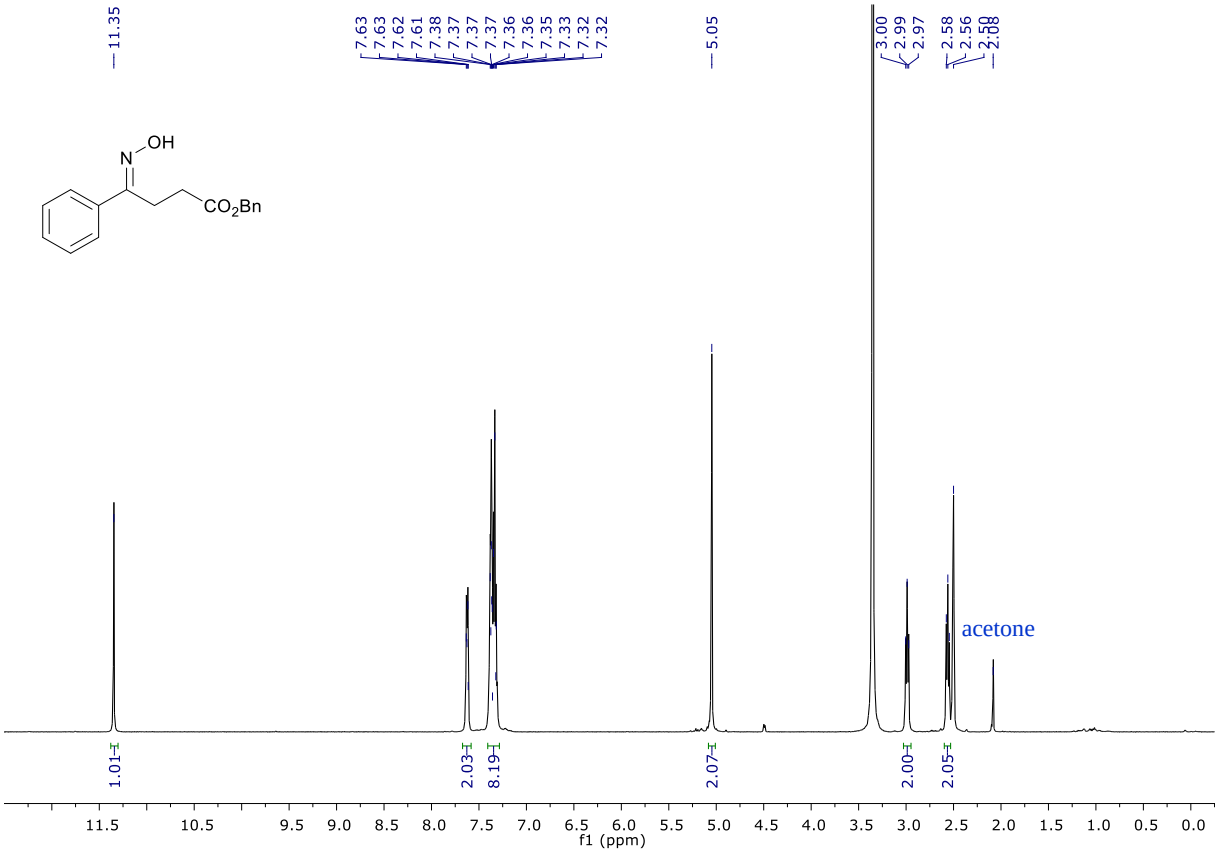


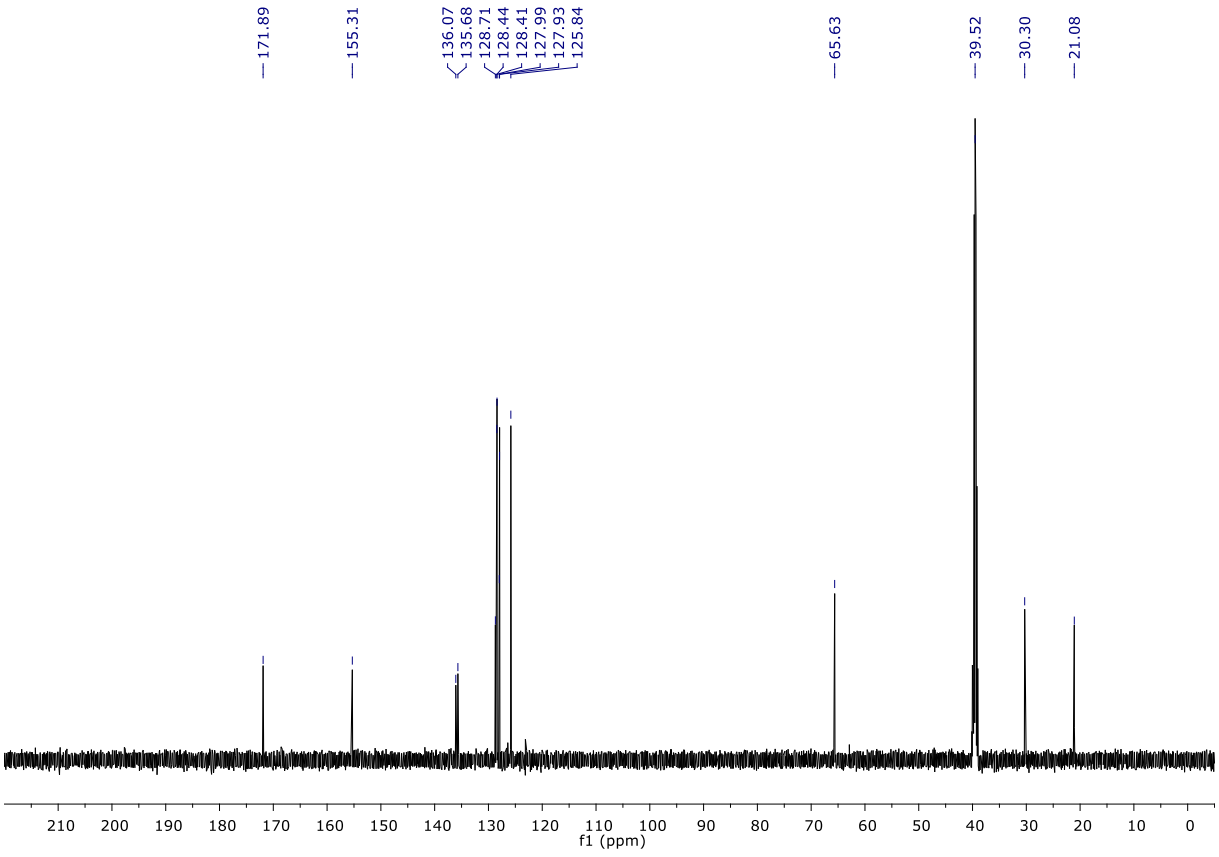
tert-butyl (E)-4-(hydroxyimino)-4-phenylbutanoate (40)



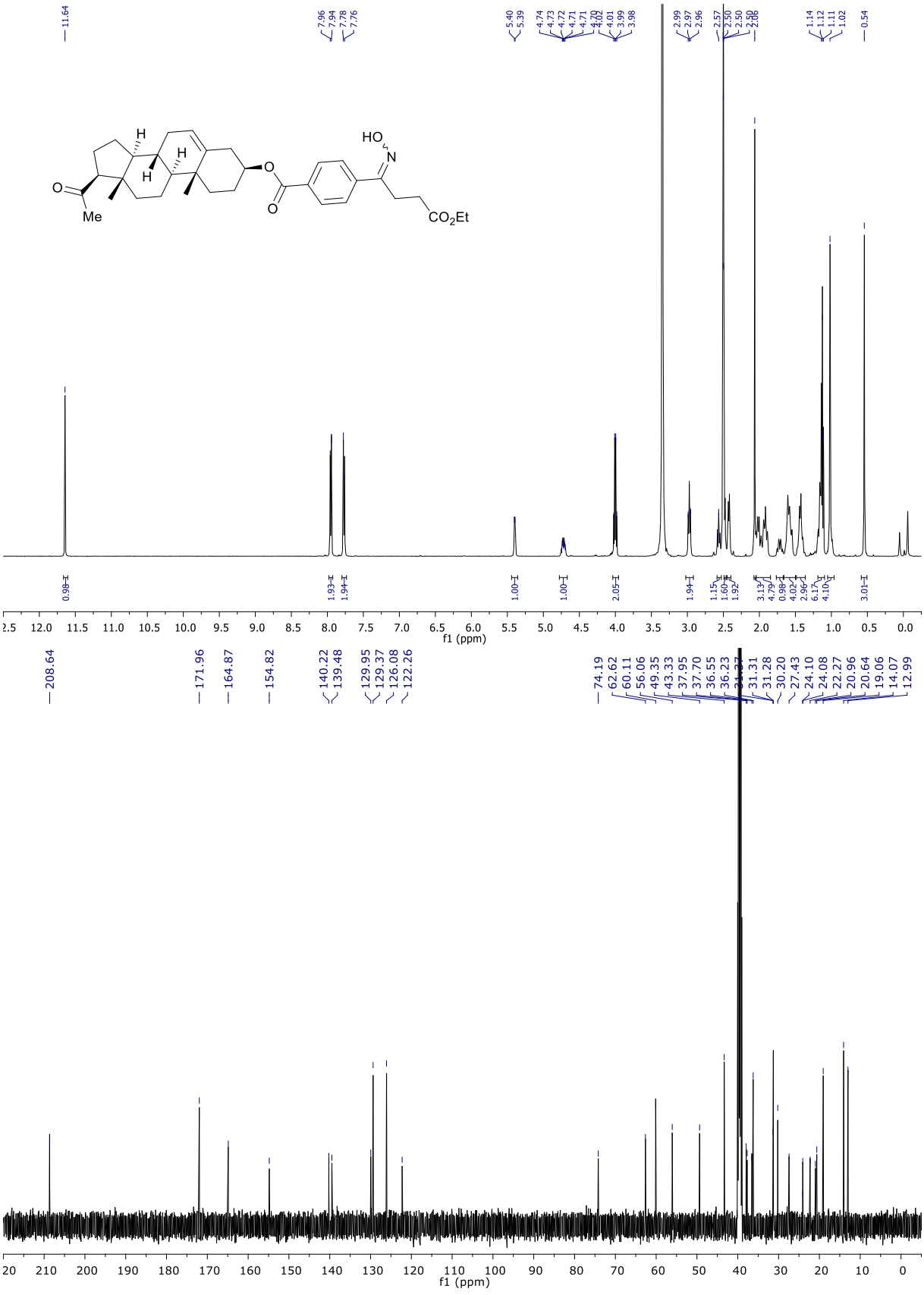


benzyl (E)-4-(hydroxyimino)-4-phenylbutanoate (41)

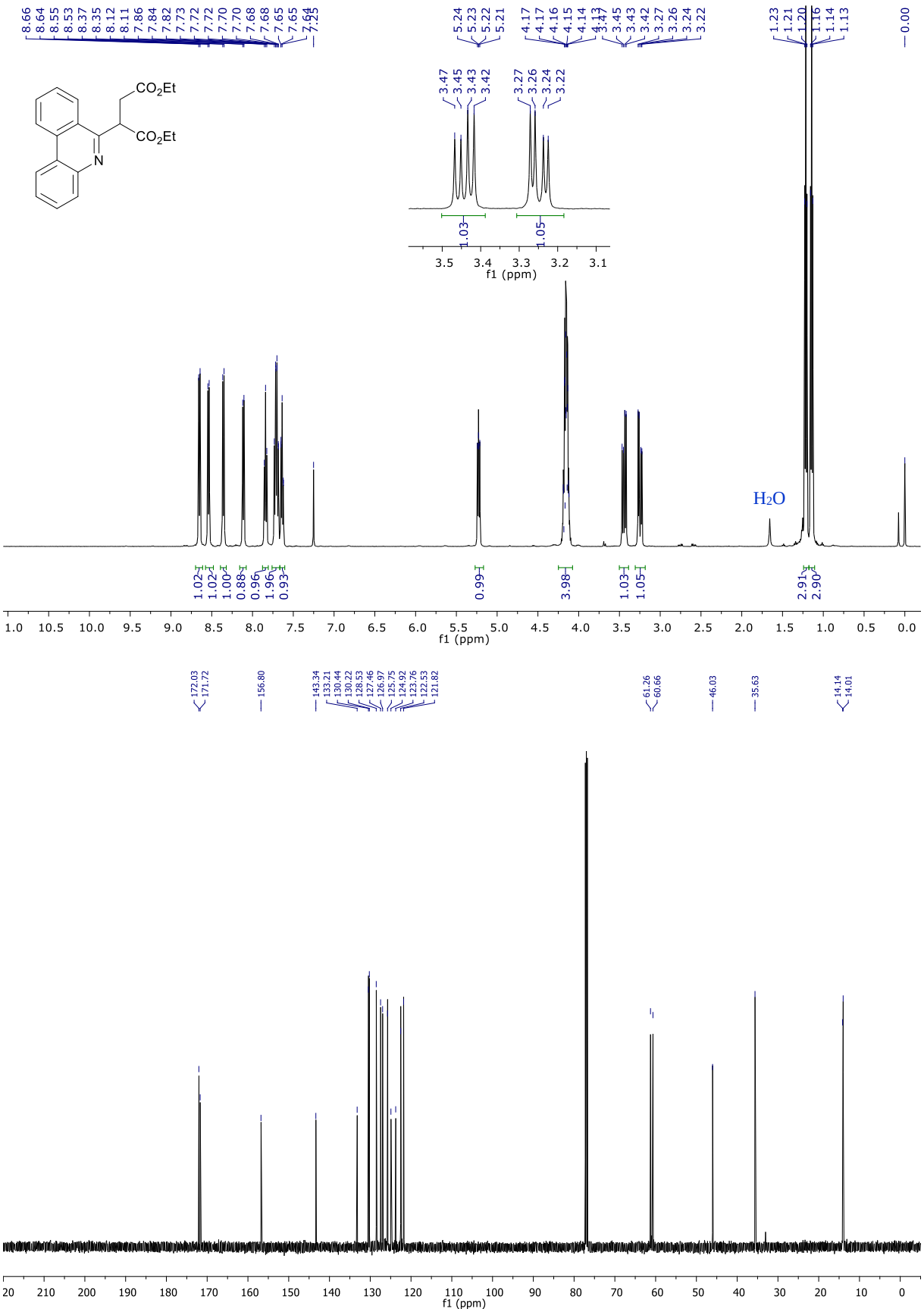




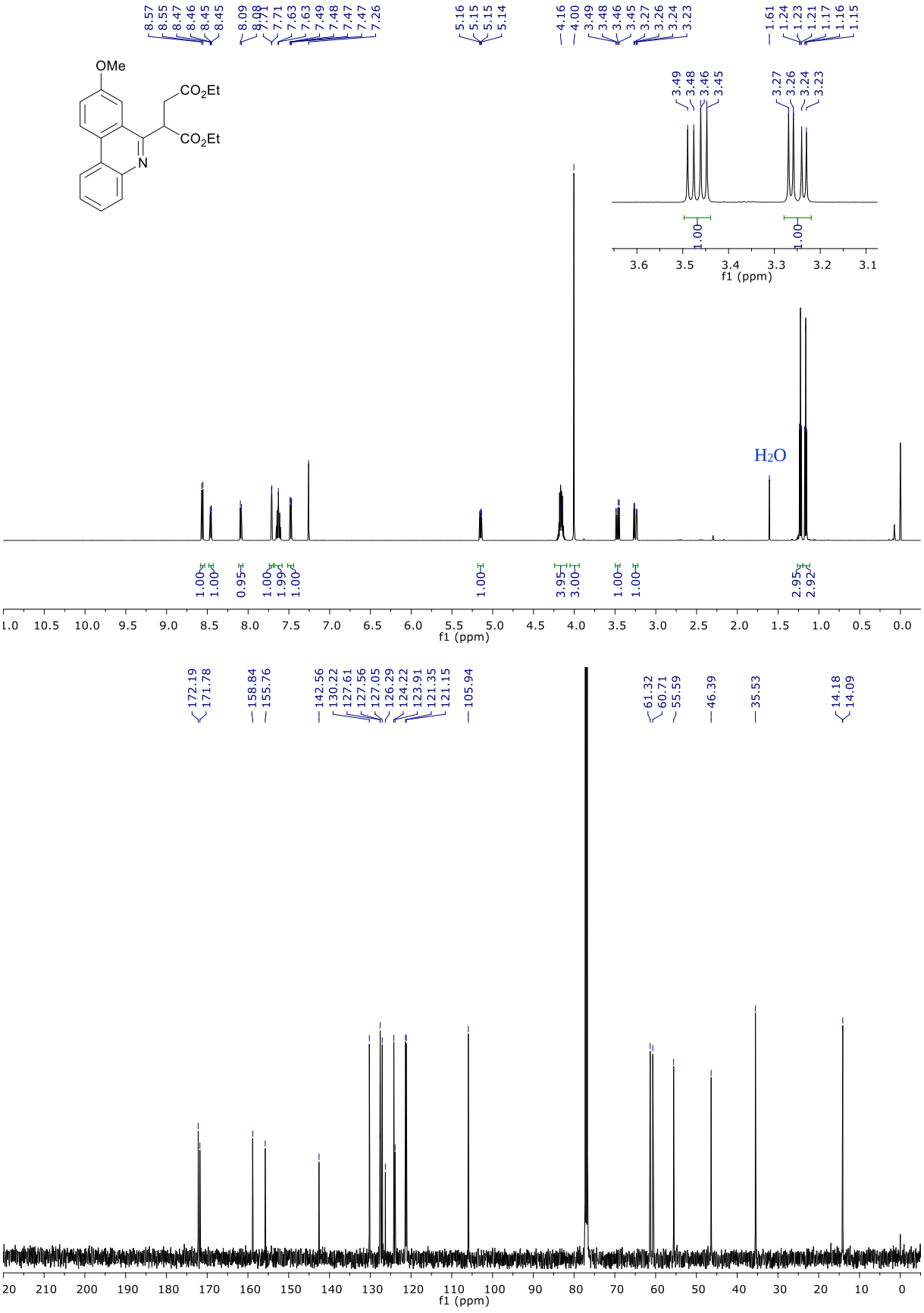
(3S,8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1H-cyclopenta[a]phenanthren-3-yl 4-(4-ethoxy-1-(hydroxyimino)-4-oxobutyl) benzoate (42)



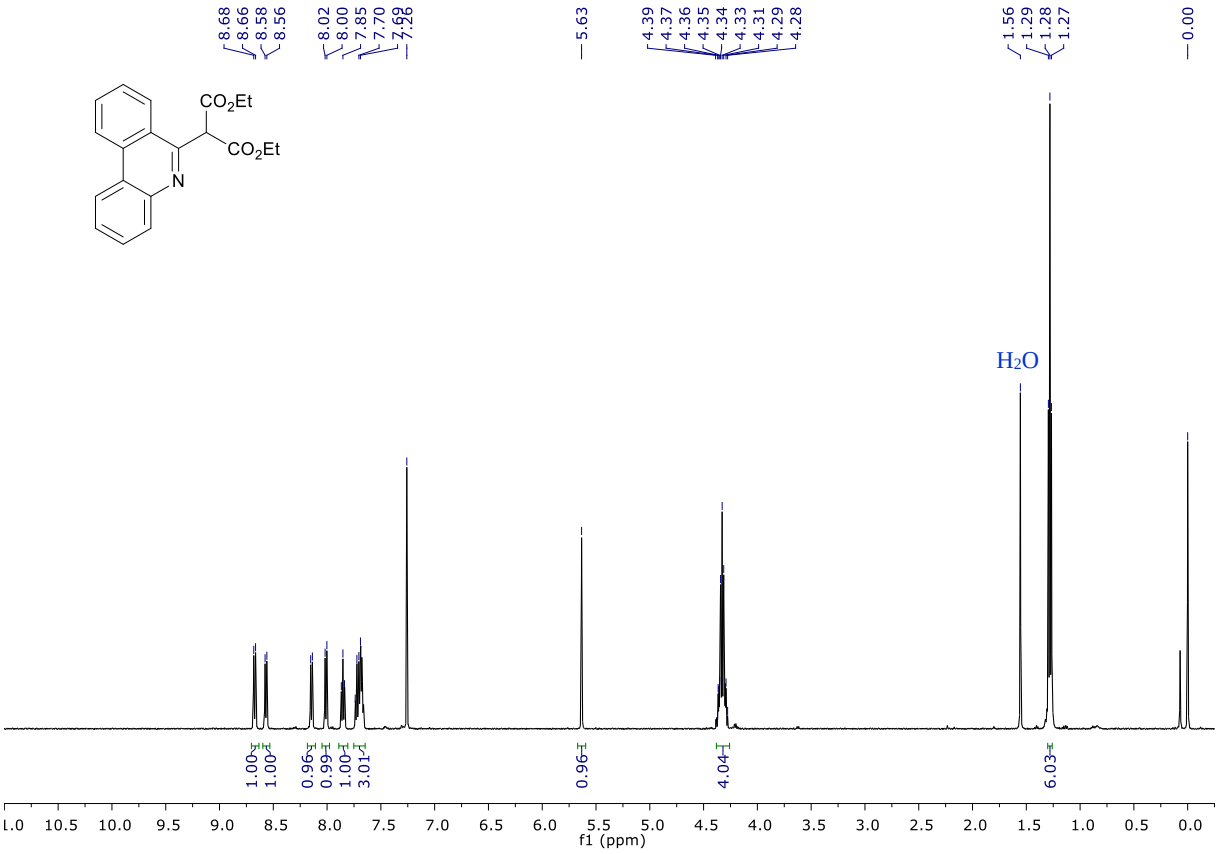
diethyl 2-(phenanthridin-6-yl)succinate (43)

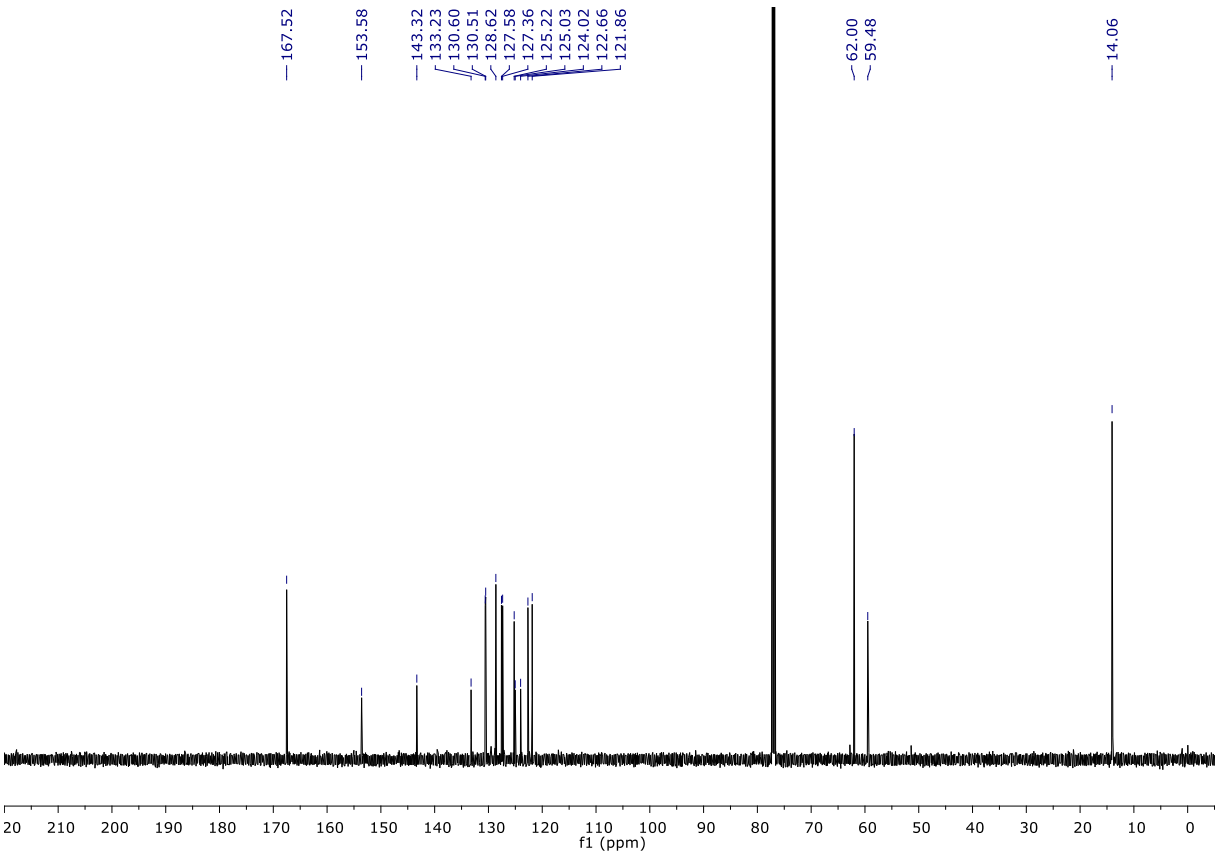


diethyl 2-(8-methoxyphenanthridin-6-yl)succinate (44)

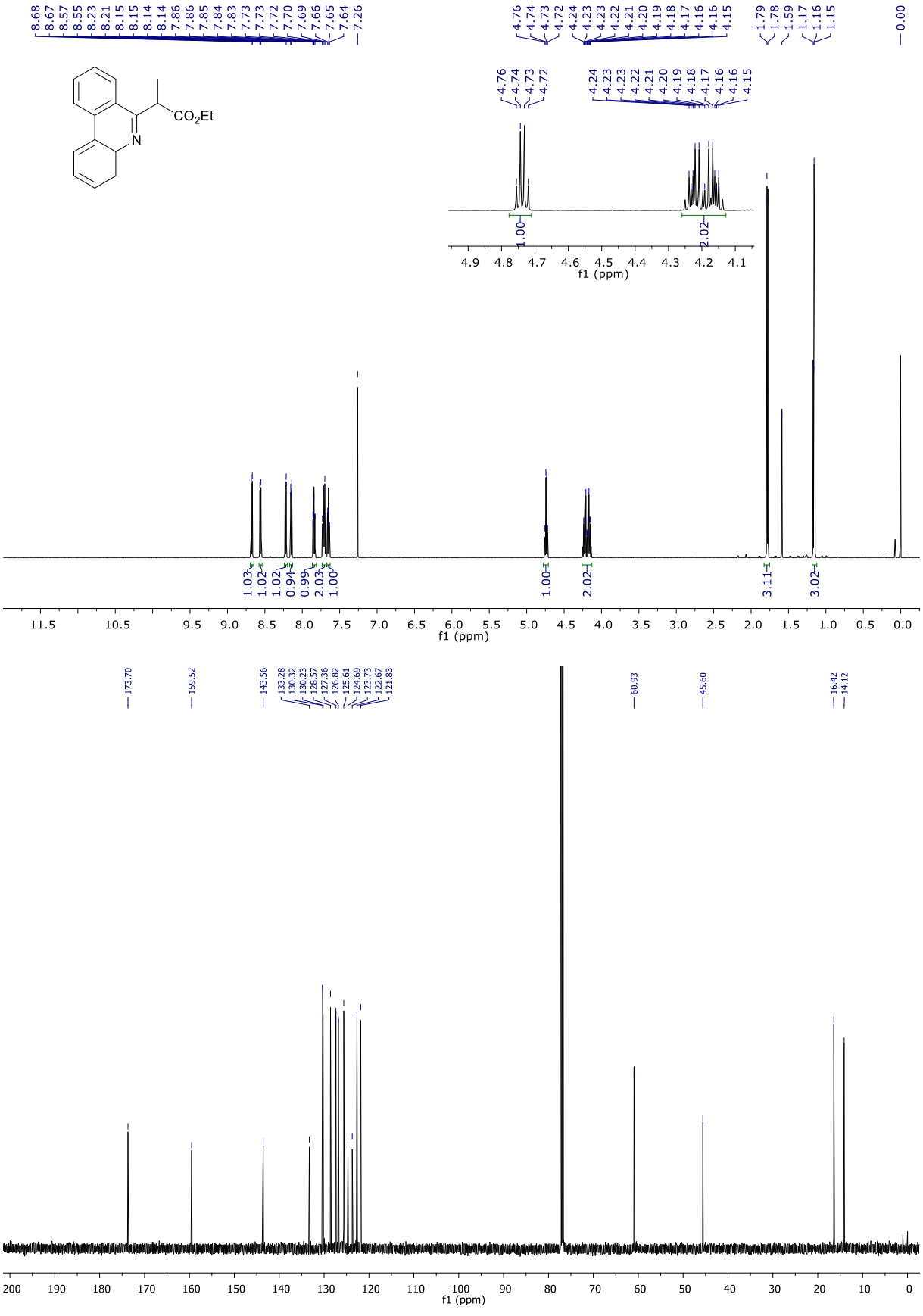


diethyl 2-(phenanthridin-6-yl)malonate (45)

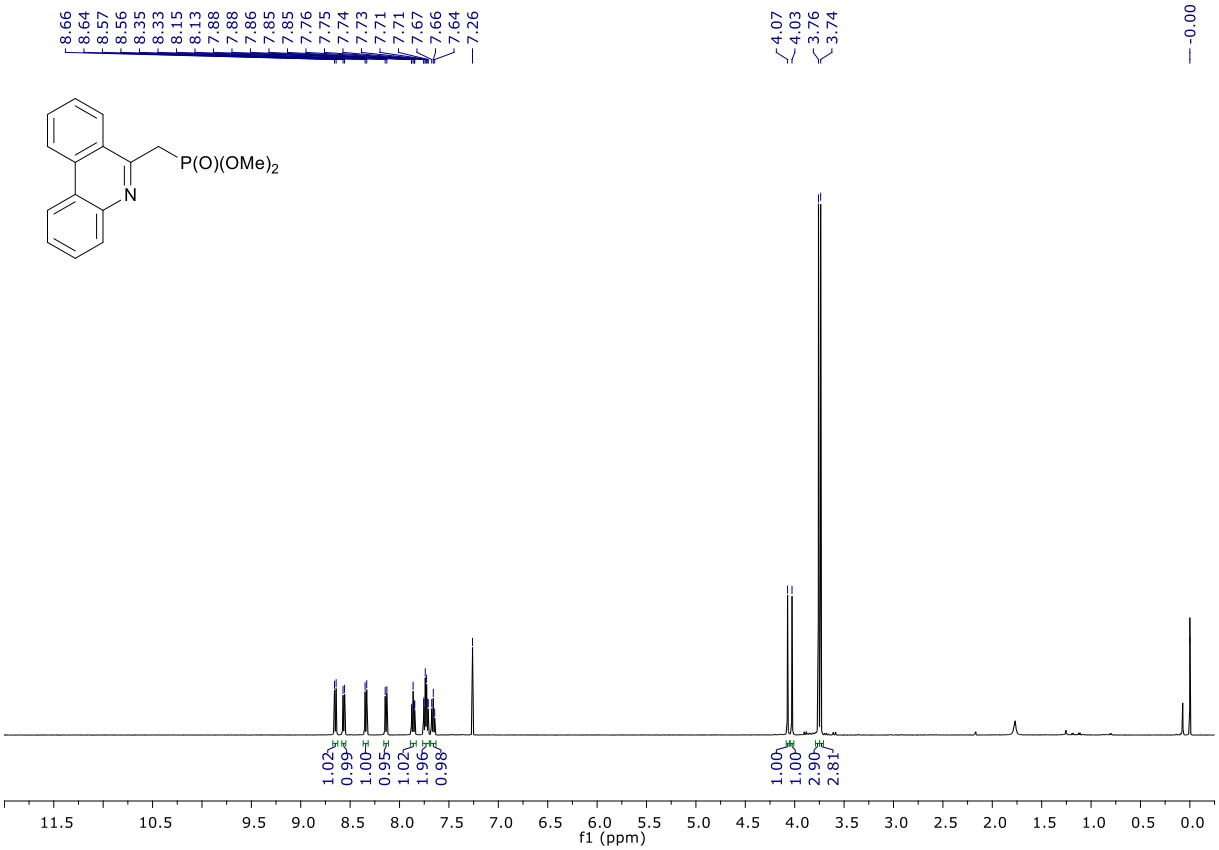


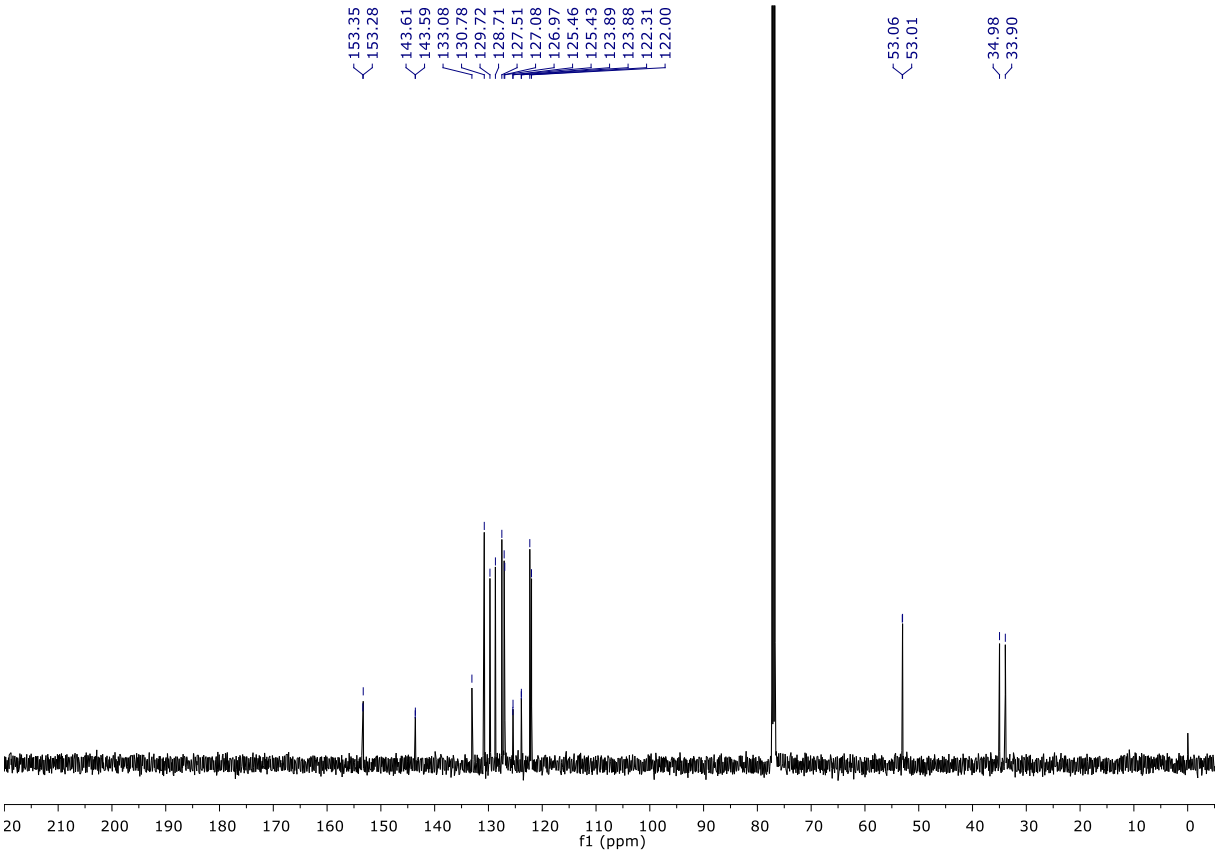


ethyl 2-(phenanthridin-6-yl)propanoate (46)

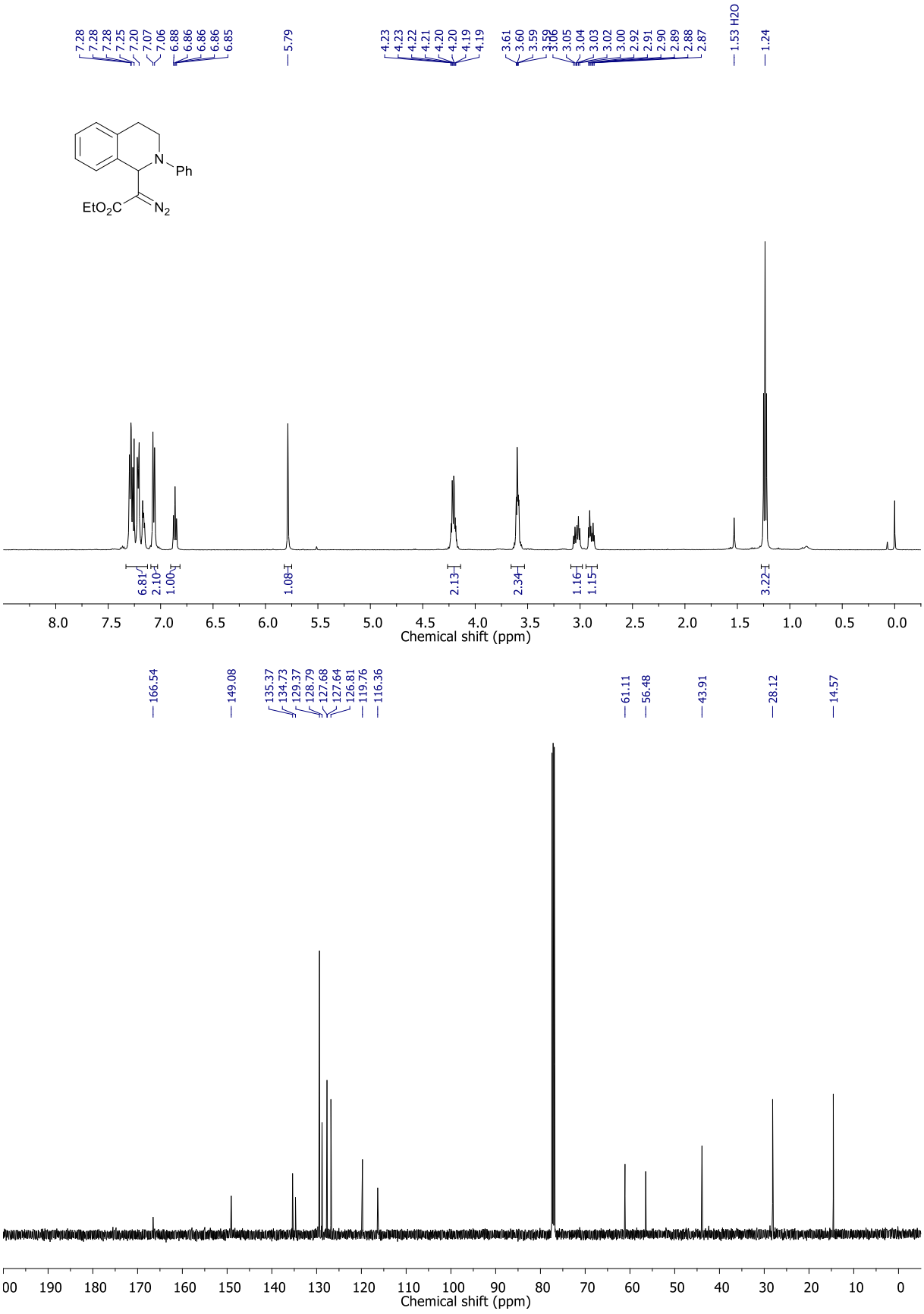


dimethyl (phenanthridin-6-ylmethyl)phosphonate (47)

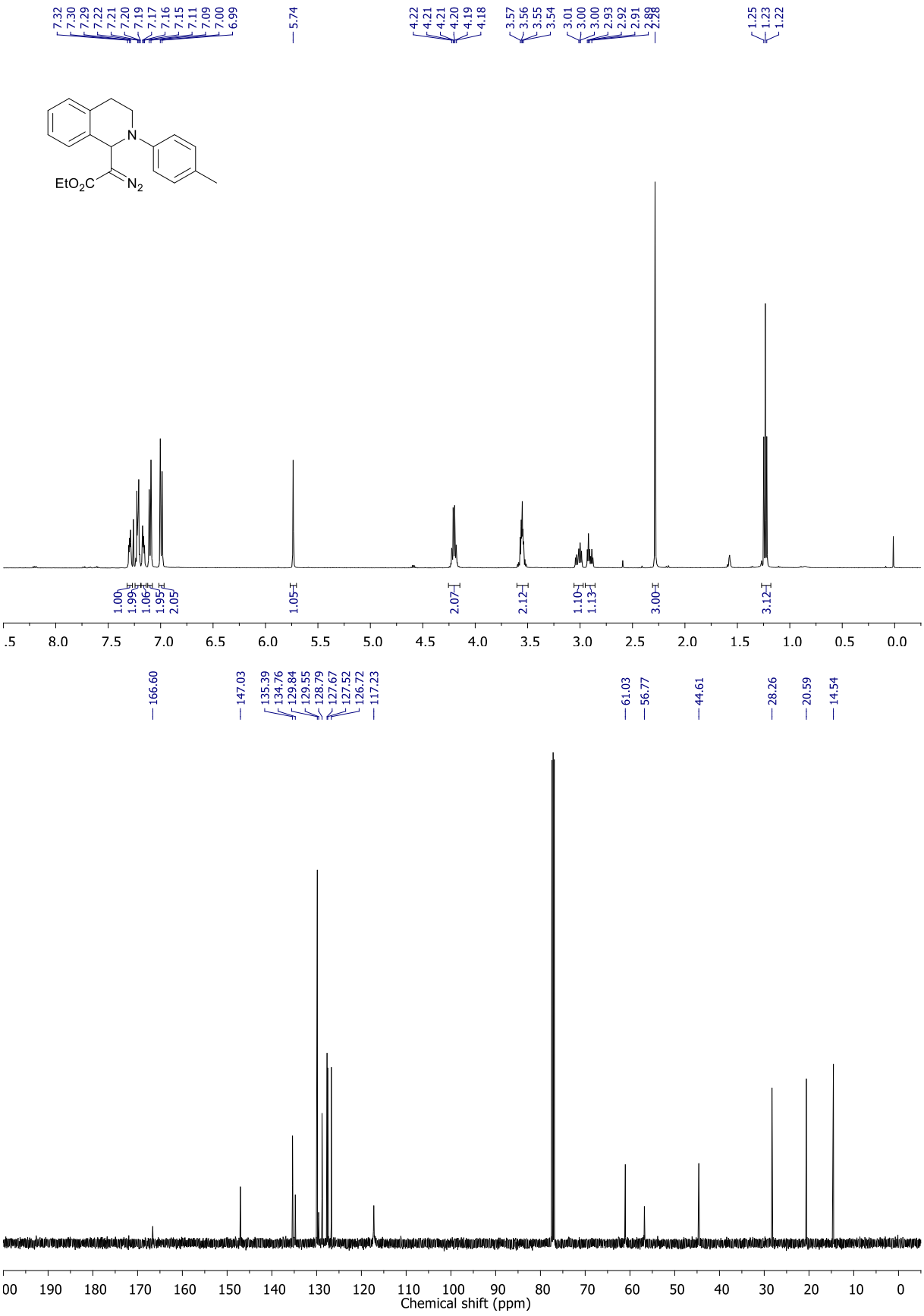




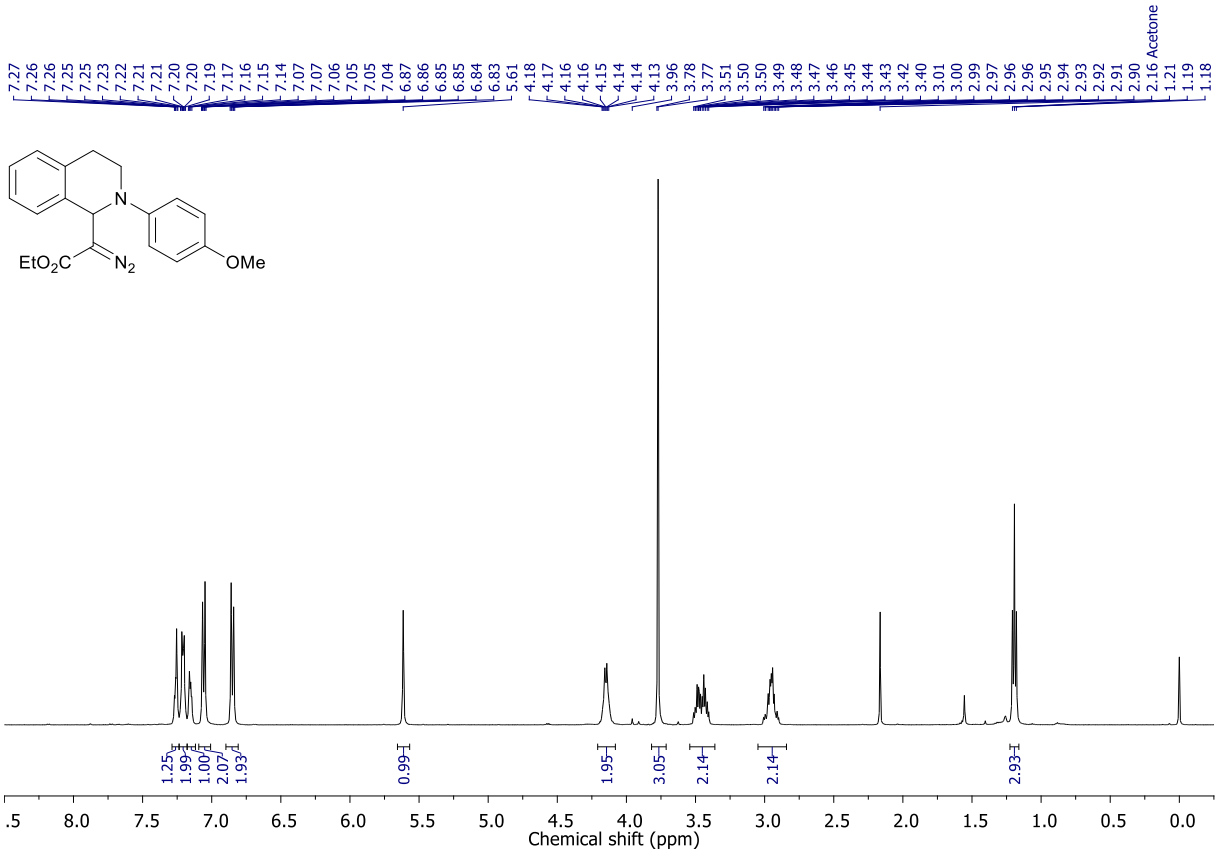
ethyl 2-diazo-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acetate (48)

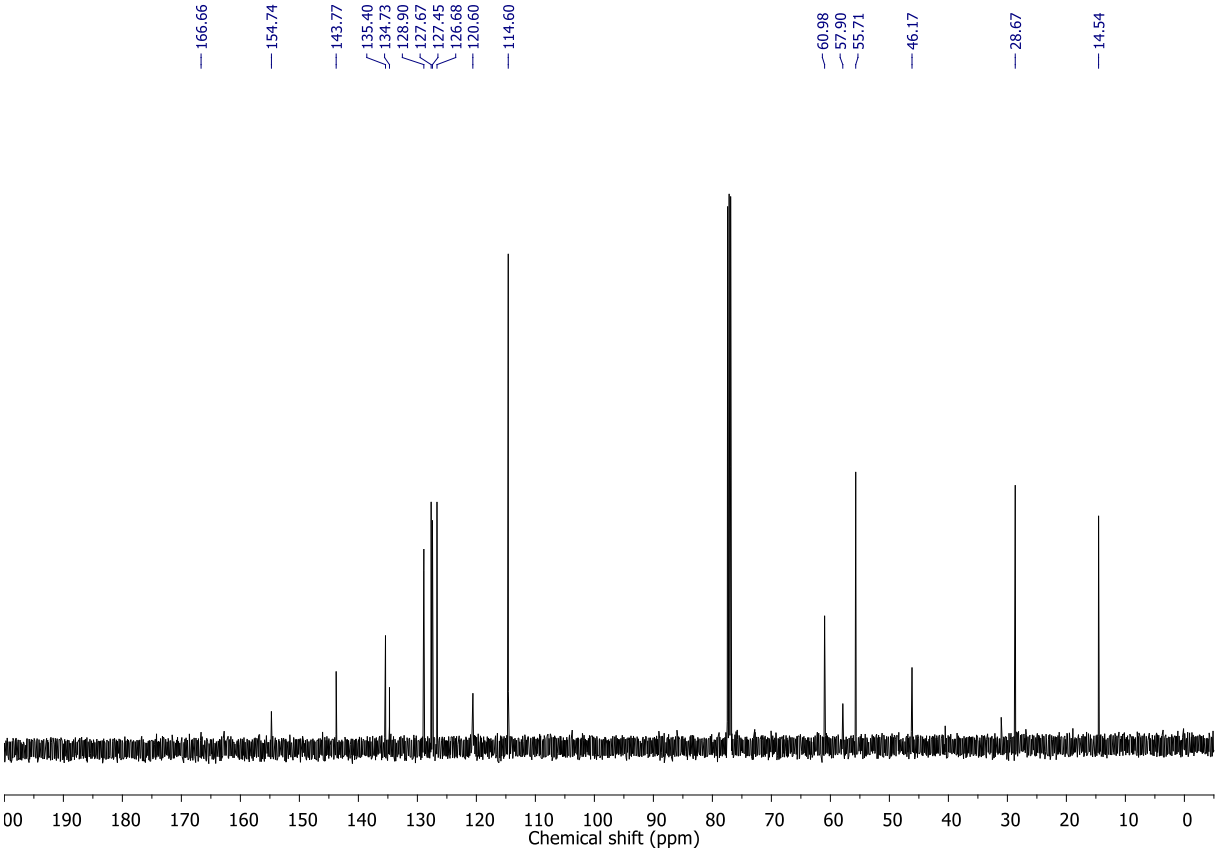


ethyl 2-diazo-2-(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetate (49)

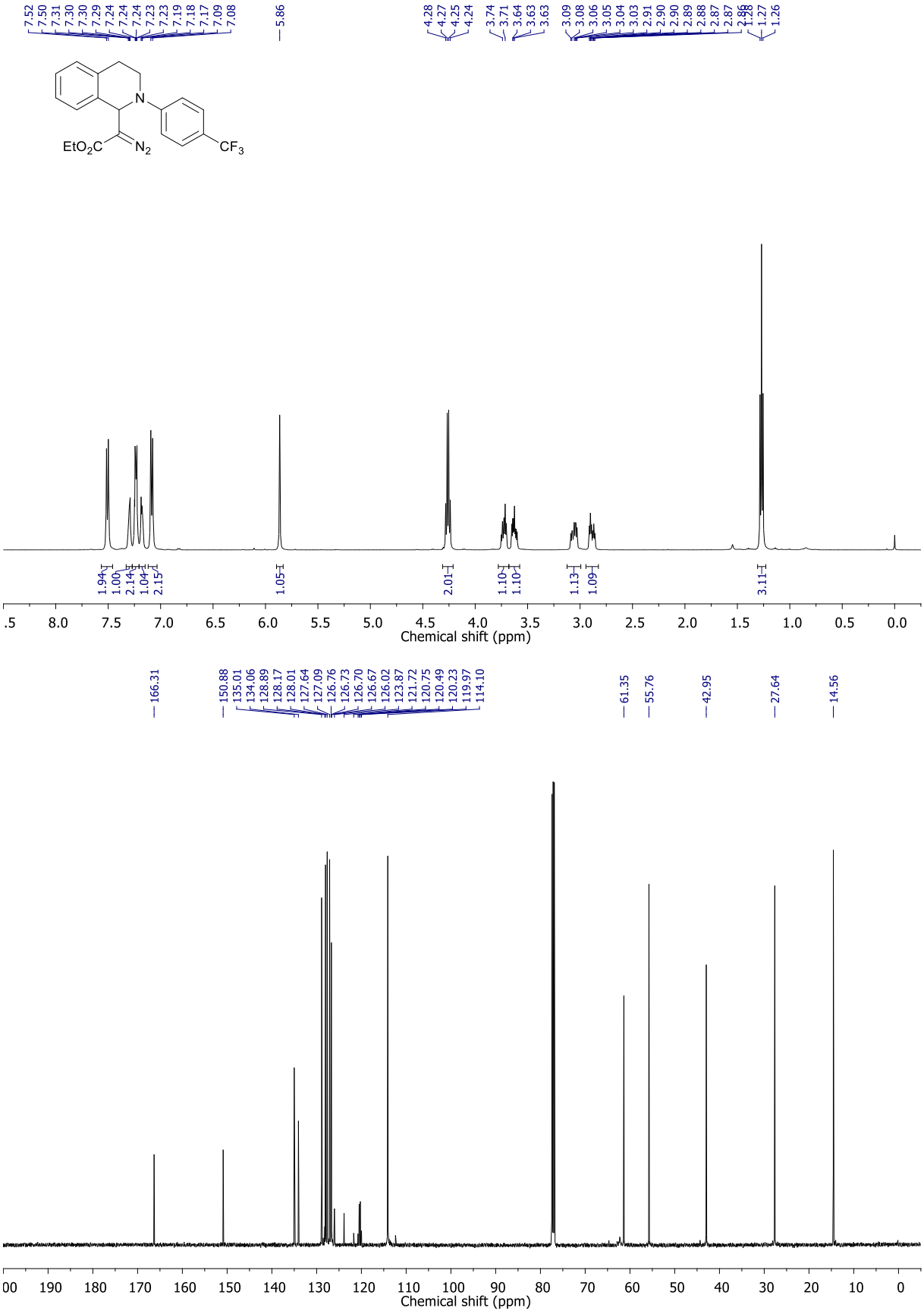


ethyl 2-diazo-2-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetate (50)

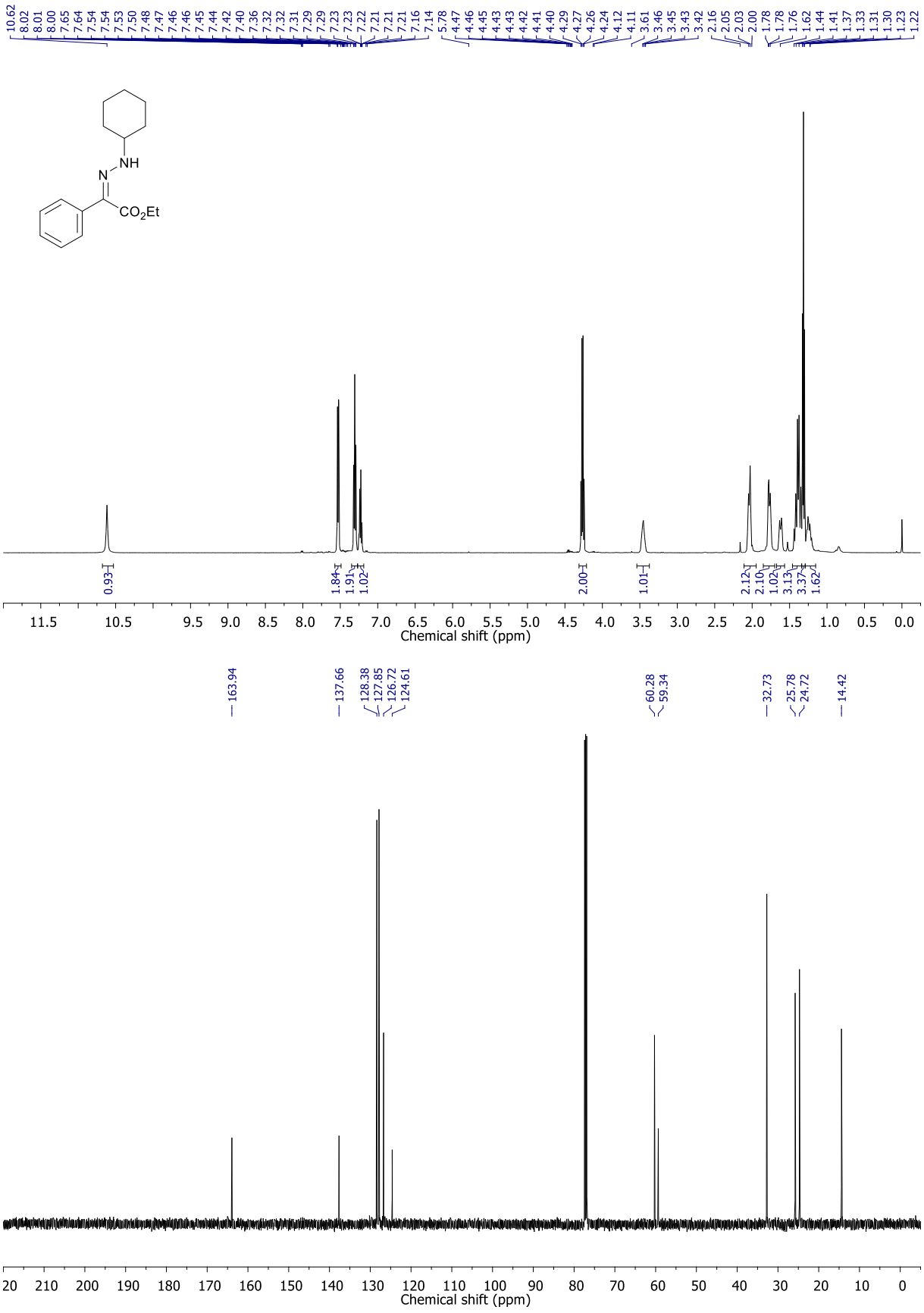




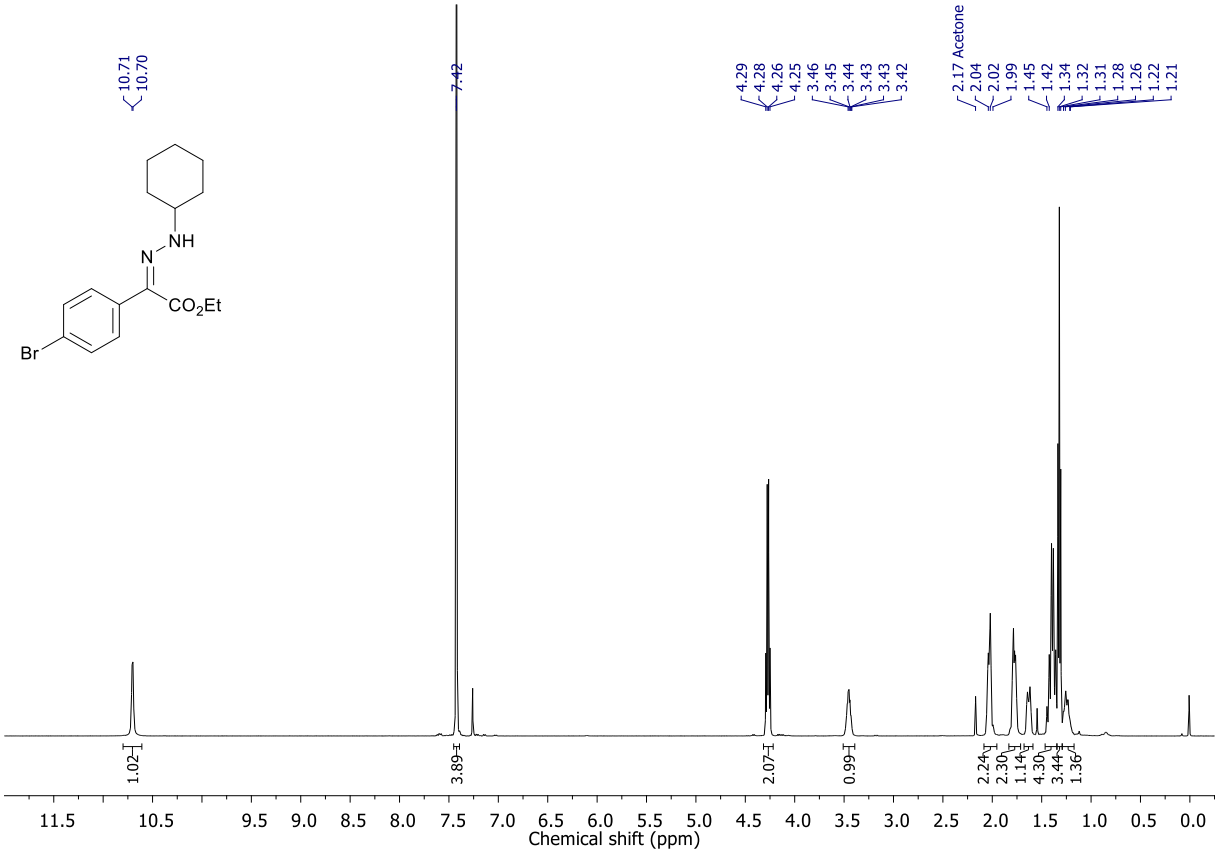
ethyl 2-diazo-2-(2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetate (51)

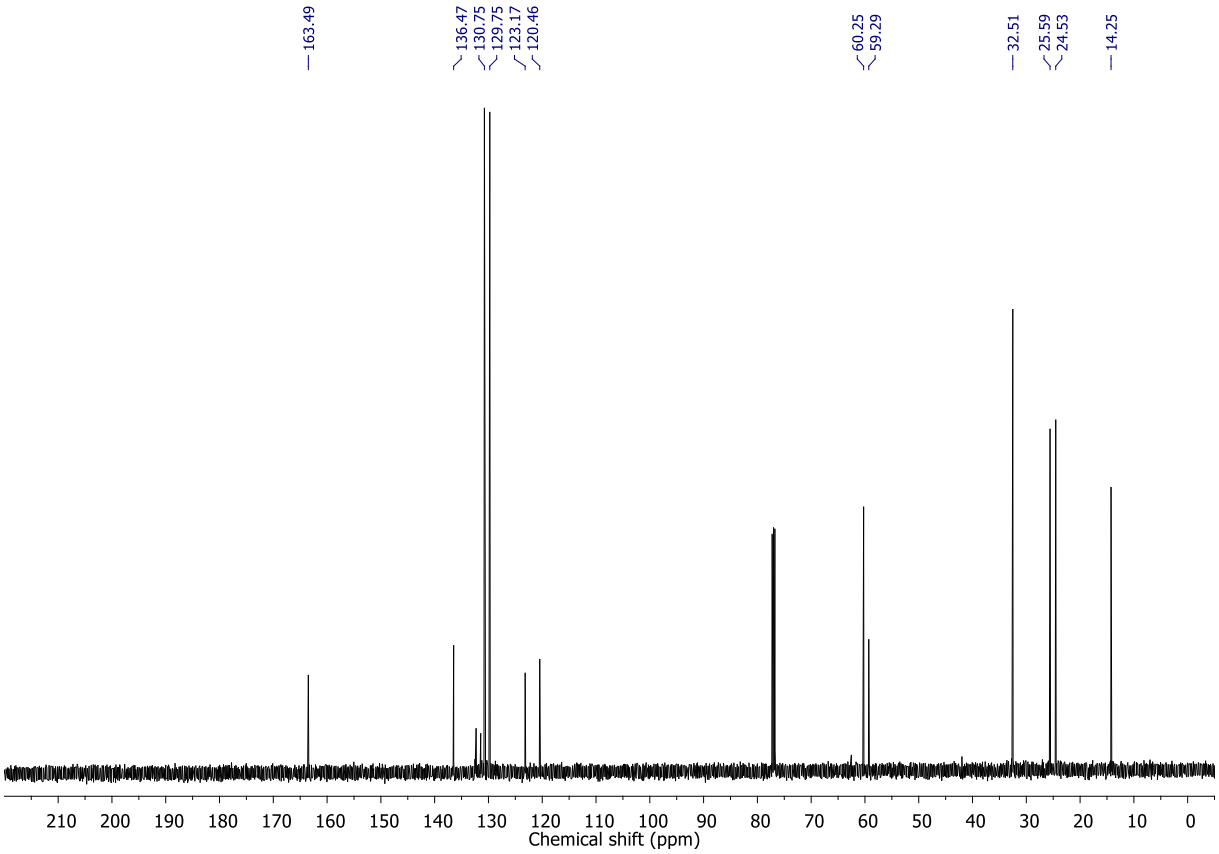


ethyl (Z)-2-(2-cyclohexylhydrazineylidene)-2-phenylacetate (52)

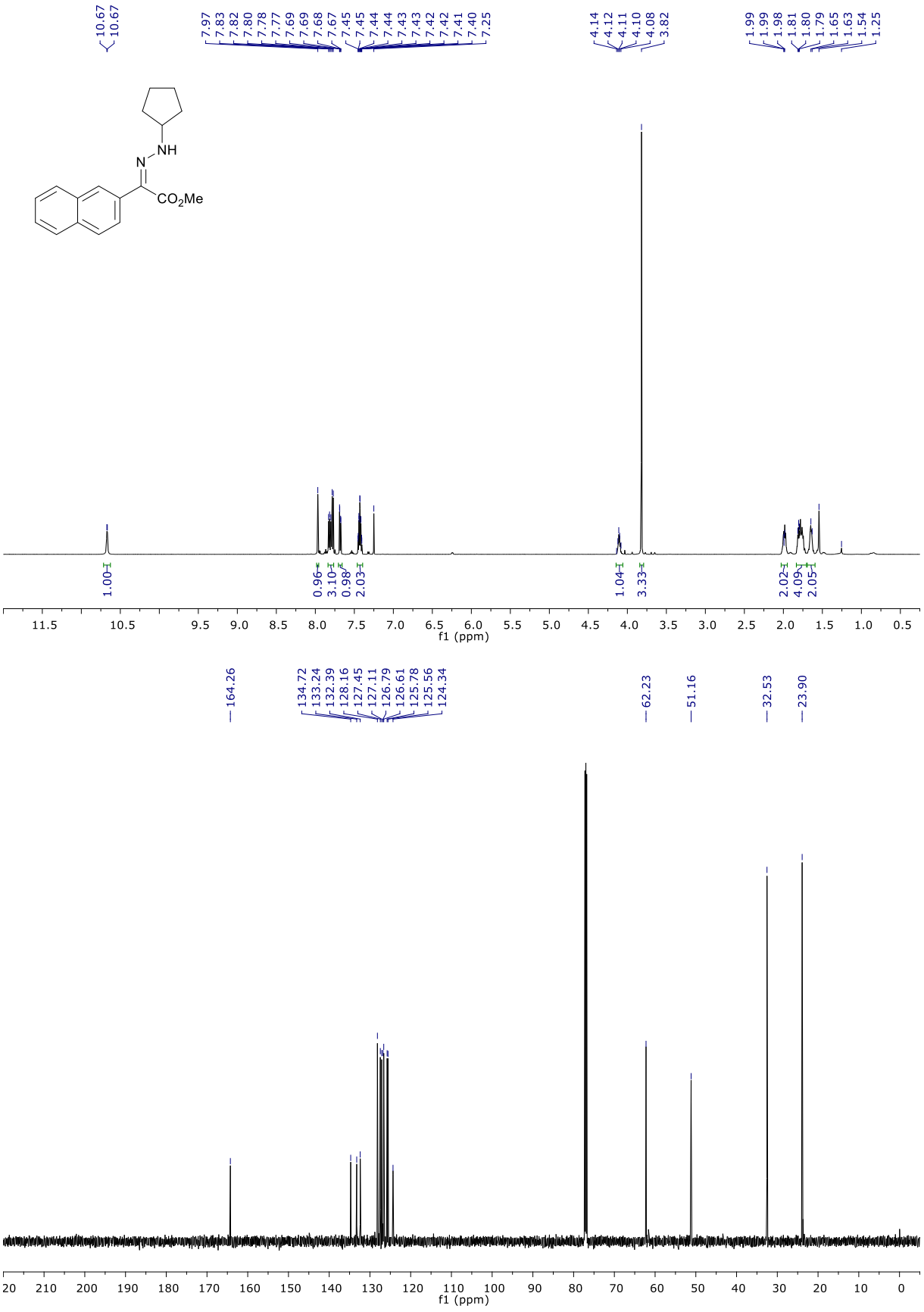


ethyl (Z)-2-(4-bromophenyl)-2-(2-cyclohexylhydrazineylidene)acetate (53)

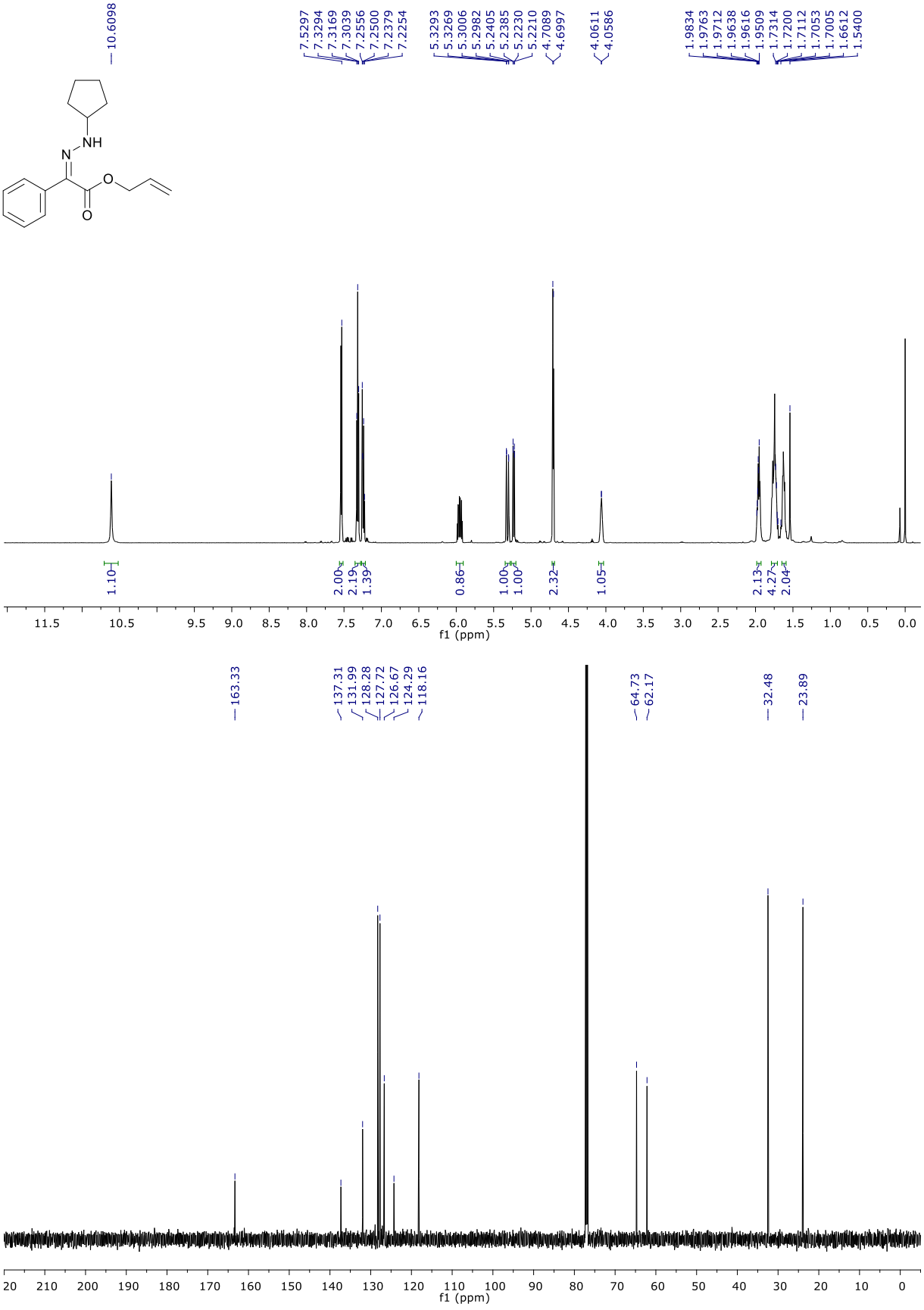




methyl (Z)-2-(2-cyclopentylhydrazineylidene)-2-(naphthalen-2-yl)acetate (54)



allyl (Z)-2-(2-cyclopentylhydrazineylidene)-2-phenylacetate (55)



benzyl (Z)-2-(2-cyclopentylhydrazineylidene)-2-phenylacetate (56)