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Supporting Information

Cooperative NHC/Photoredox Catalyzed Ring-Opening of Aryl Cyclopropanes to 1-Aroyloxylated-3-Acylated Alkanes

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Supporting Information

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A. General information:

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware using standard Schlenk techniques. All commercially available reagents were purchased from Sigma-Aldrich, Alfa Aesar, TCI Chemicals, Acros Organics or ABCR in the highest purity grade and used without further purification. DCE (99.8%, extra dry, AcroSeal) was used as received from Acros Organics.

Thin layer chromatography (TLC) was performed on Merck silica gel 60 F-254 plates and visualized by fluorescence quenching under UV light.

Column chromatography was performed on Merck or Fluka silica gel 60 (40-63 μm).

Melting points were measured on a Büchi M560 and are uncorrected.

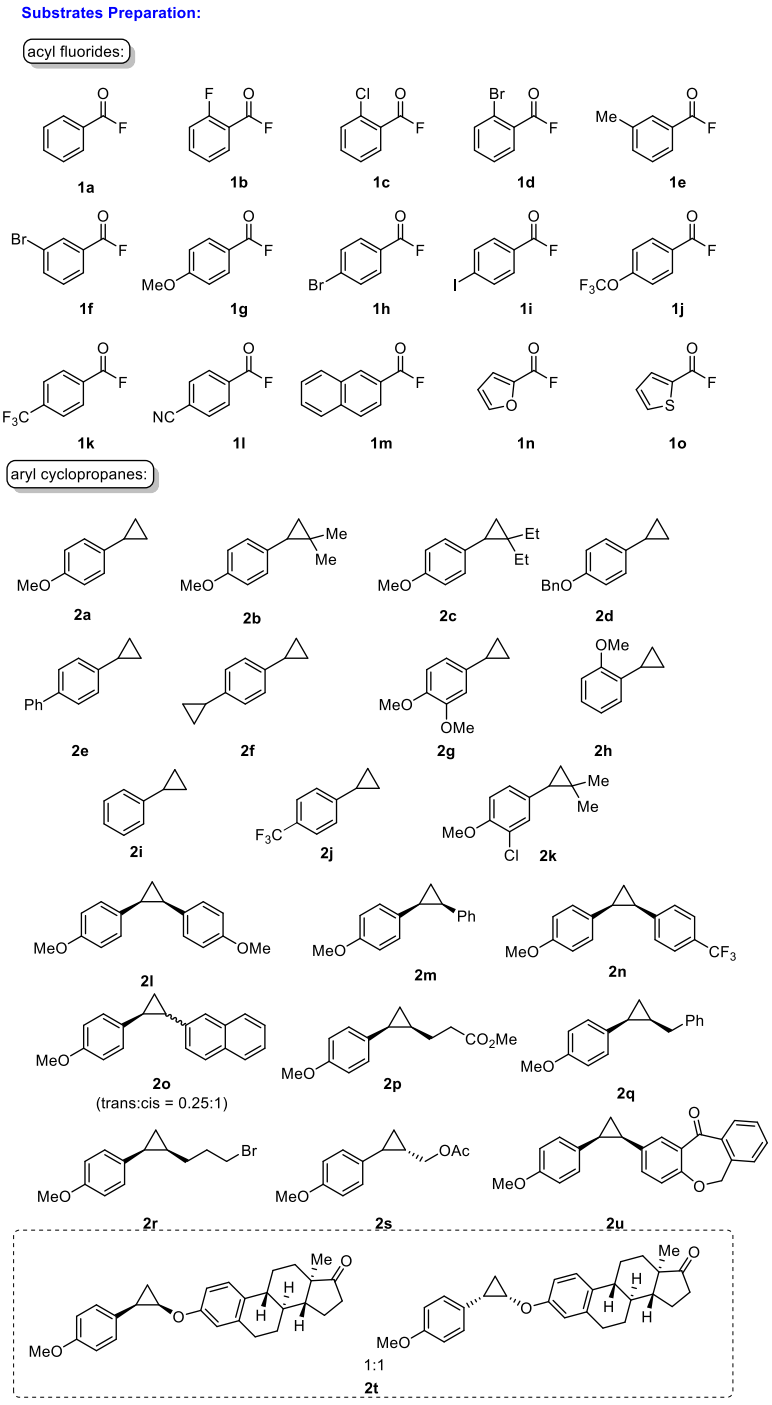
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 300, a Bruker AV 400 at 300 K, a Varian INOVA 500 or a Varian 600 UNITY plus spectrometer at 299 K. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: $CHCl_3$ (δ = 7.27 ppm for ^{1}H NMR and δ = 77.0 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constants (Hz) and integration.

Infrared spectra (IR) were measured on a Digilab 3100 FT-IR Excalibur Series spectrometer and the position of the absorption bands is given in wave numbers ν (cm^{-1}).

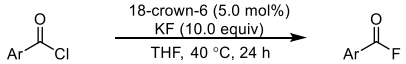
HRMS ESI (m/z) spectra were recorded on a Bruker MicroTof or an Orbitrap LTQ XL (Nanospray) of Thermo Scientific.

Chiral HPLC analysis was performed on a Hewlett Packard HP 1100 Series HPLC System using AD-H (0.46*25 cm, 5 μm silica-gel, DaicelTM) and IC (0.46*25 cm, 5 μm silica-gel, DaicelTM) chiral columns eluting with a mixture of cyclohexane and isopropyl alcohol.

B. Preparation of substrates:



General procedure for preparation of acyl fluorides:



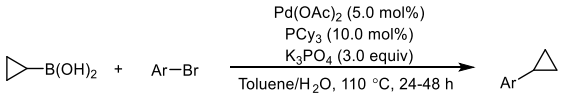
To a 100-mL Schlenk tube with a magnetic stir bar, were successively added an acyl chloride (1.0 equiv.), 18-crown-6 (5.0 mol %), KF (10.0 equiv.) and THF (0.2 M). After the reaction was stirred at 40 ºC for 24 hours, the insoluble inorganic solid was filtered, and the volatiles were removed using a

rotary evaporator. The crude product was purified by bulb-to-bulb distillation to afford the corresponding acyl fluorides.

All acyl fluorides are known compounds and spectroscopic data are in accordance with those described in literature.[1]

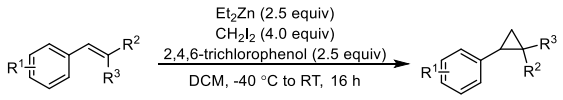
Preparation of cyclopropanes:

General procedure A:[2]



In a 50 mL Schlenk tube with magnetic stirring bar were added the corresponding aryl bromide (3.0 mmol, 1 equiv.), tricyclohexylphosphine (84.0 mg, 0.30 mmol, 0.1 equiv.), palladium acetate (33.7 mg, 0.15 mol, 0.05 equiv.), tripotassium phosphate (1.9 g, 9.0 mmol, 3.0 equiv.) and cyclopropylboronic acid (387.0 mg, 4.5 mmol, 1.5 equiv.). Then, toluene (10 mL) and 0.5 mL of water were added, and the tube was closed. The reaction mixture was shaken briefly and set under inert atmosphere by bubbling nitrogen gas through the vial for 5 minutes. Afterwards, the tube was placed into an oil bath and stirred at 110 °C for 24-48 h. Upon completion, the reaction mixture was poured into a separatory funnel, diluted with ethyl acetate and washed with 15 mL water twice. The organic layer was dried with Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to give the title compound. Compounds **2a**, **2d-j** were prepared following the General Procedure A.

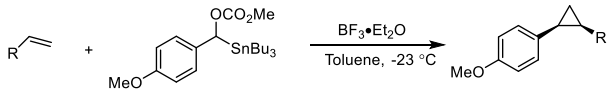
General procedure B:[3]



In a 100 mL oven-dried round-bottom flask with a stir bar, was added 2,4,6-trichlorophenol (1.18 g, 6.0 mmol, 2.5 equiv.) under nitrogen atmosphere. DCM (60 mL, 0.1 M) was added into the flask and the reaction mixture was cooled to -40 °C. $ZnEt_2$ (1.0 M, 6.0 mL, 6.0 mmol, 2.5 equiv.) was added slowly into the flask by syringe and the reaction mixture was stirred at this temperature for 15 min. CH_2I_2 (2.57 g, 9.6 mmol, 4.0 equiv.) was added slowly by syringe and the reaction mixture was stirred at this temperature for another 15 min. Next, the corresponding solution of alkene (2.4 mmol, 1.0 equiv.) in DCM (10 mL) was added by syringe and the reaction mixture was allowed to warm to room temperature and stirred for 16 h. After the reaction reached completion, the reaction mixture was

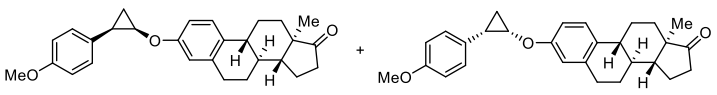
quenched with sat. NH_4Cl (30 mL) and extracted with DCM (100 mL) for 3 times. The combined organic layers were washed with aq. NaOH (1.0 M, 30 mL) and brine (20 mL), dried over Na_2SO_4 and filtered. After the volatile materials were removed under reduced pressure, the crude residue was purified by column chromatography to give the title compound. Compounds **2b**, **2c**, **2k, 2s** were prepared following the General Procedure B.

General procedure C:



To a 50 mL oven-dried round-bottom flask equipped with a stir bar was added a solution of (4-methoxyphenyl)(tributylstannyl)methyl methyl carbonate (972 mg, 2.0 mmol, 1.0 equiv.) and the corresponding alkene (2.2 mmol, 1.1 equiv.) in toluene (10 mL) under nitrogen atmosphere at room temperature. The reaction vessel was cooled to -23 °C. $BF_3 \cdot OEt_2$ (312 mg, 2.2 mmol, 1.1 equiv.) was added by syringe and the mixture was stirred at this temperature for 2 h. After the reaction reached completion according to the TLC analysis, the reaction mixture was quenched with sat. $NaHCO_3$ (10 mL) and extracted with EtOAc (30 mL) for 3 times. The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4 and filtered. After the volatile materials were removed under reduced pressure, the crude residue was purified by column chromatography to afford the desired compound. Compounds **2l-r**, **2t-u** were prepared following the General Procedure C.

The spectroscopic data of all known cyclopropanes are in accordance with those described in literature.[3-4]



1:1

(8S,9R,13R,14R)-3-(2-(4-Methoxyphenyl)cyclopropoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one +

(8S,9R,13R,14R)-3-((1S,2S)-2-(4-methoxyphenyl)cyclopropoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (2t)

Following procedure C to afford a white solid (668.1 mg, 73% yield).

MP: 54-55 °C.

^1H NMR (300 MHz, $CDCl_3$): δ 7.20 – 7.14 (m, 3H), 6.86 – 6.75 (m, 3H), 6.71 (dd, *J* = 4.9, 2.8 Hz, 1H),

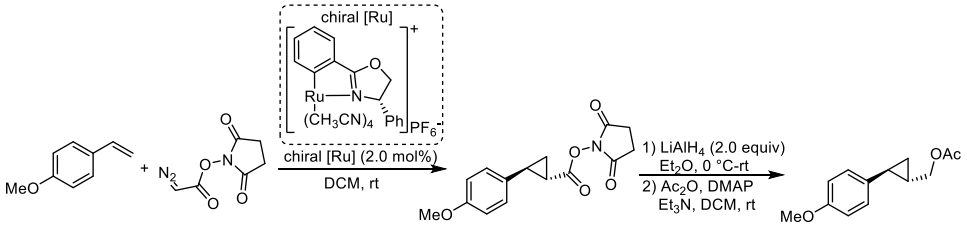
3.92 (td, *J* = 6.5, 3.7 Hz, 1H), 3.79 (s, 3H), 2.96 – 2.77 (m, 2H), 2.59 – 2.34 (m, 2H), 2.30 – 1.93 (m, 7H), 1.55 – 1.34 (m, 6H), 1.14 (dd, *J* = 6.9, 3.1 Hz, 1H), 0.92 (s, 3H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 221.1, 157.9, 156.7, 137.5, 132.4, 129.2, 128.9, 126.1, 115.4, 113.4, 112.7, 55.6, 55.2, 50.4, 48.0, 44.0, 38.3, 35.9, 31.6, 29.7, 26.6, 25.9, 22.2, 21.6, 13.9, 12.8.

FTIR (neat): υ (cm^{-1}) 3053, 2935, 1736, 1515, 1265, 1246, 732.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{28}H_{32}NaO_3$ 439.2249; found: 439.2238.

Synthesis of enantioenriched cyclopropane (S,S)-2s[5]

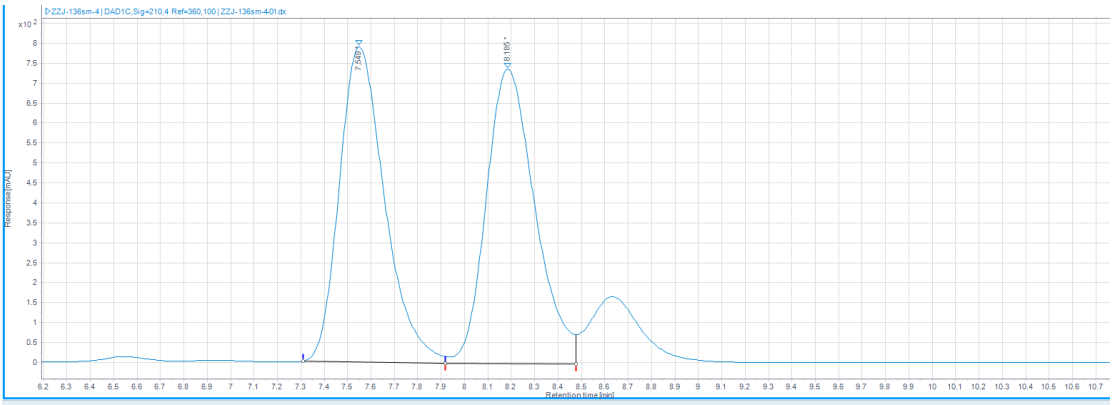


a) To an oven-dried 100 mL round-bottom flask equipped with a stir bar, succinimidyl diazocetate (183.0 mg, 1.0 mmol), 1-methoxy-4-vinylbenzene (114.6 μL, 5.0 mmol), chiral Ru(II)-Pheox catalyst (12.6 mg, 0.02 mmol) and CH_2Cl_2 (10.0 mL) were added at room temperature. After that we checked the TLC in less than 1 min, and we noticed the disappearance of the diazo compound. The residue was purified by column chromatography on silica gel (eluting with pentane/ethyl acetate = 3/1) to afford the white solid (263.0 mg, 91% yield).

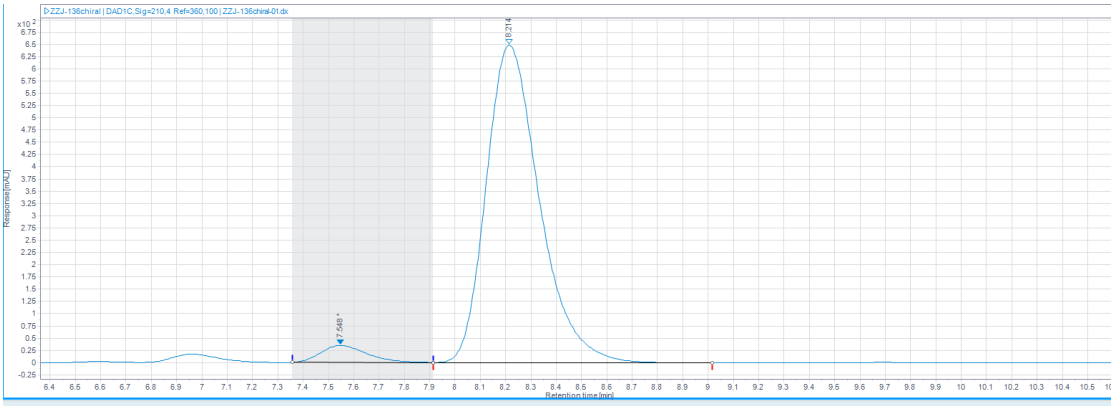
b) To the solution of succinimidyl cyclopropyl carboxylate derivatives (231.1 mg, 0.8 mmol) in Et_2O (10.0 mL) was added lithium aluminium hydride (60.8 mg, 1.6 mmol) at 0 ºC. After stirring for 2 h at same temperature, the reaction solution was quenched with water (0.5 mL), filtered, and evaporated under reduced pressure. The crude alcohol was used without further purification.

c) A solution of crude alcohol in CH_2Cl_2 (10.0 mL) was treated with Ac_2O (244.8 mg, 3.0 equiv.), Et_3N (242.4 mg, 3.0 equiv.), and 4-DMAP (10.0 mg, 0.1 equiv.) at 0 °C. The mixture was allowed to warm up to room temperature overnight. The volatile materials of the reaction mixture were removed under reduced pressure, the crude residue was purified by column chromatography (pentane/ethyl acetate = 10:1) to afford ((*1S*,*2S*)-2-(4-methoxyphenyl)cyclopropyl)methyl acetate as colorless oil (136.0 mg, 77% yield over 2 steps, 90% ee). HPLC Analysis: Chiralpak AD-H (Cyclohexane/iPrOH = 99/1, 1.0 mL/min, 25 °C).

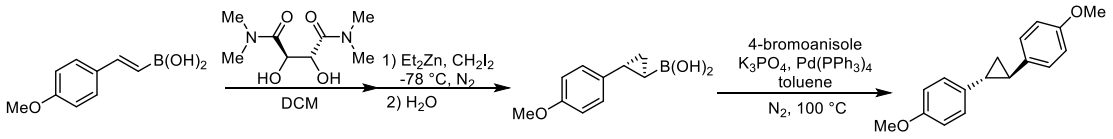
Racemic sample:



Chiral sample:



Synthesis of enantioenriched cyclopropane (R,R)-2l[4]



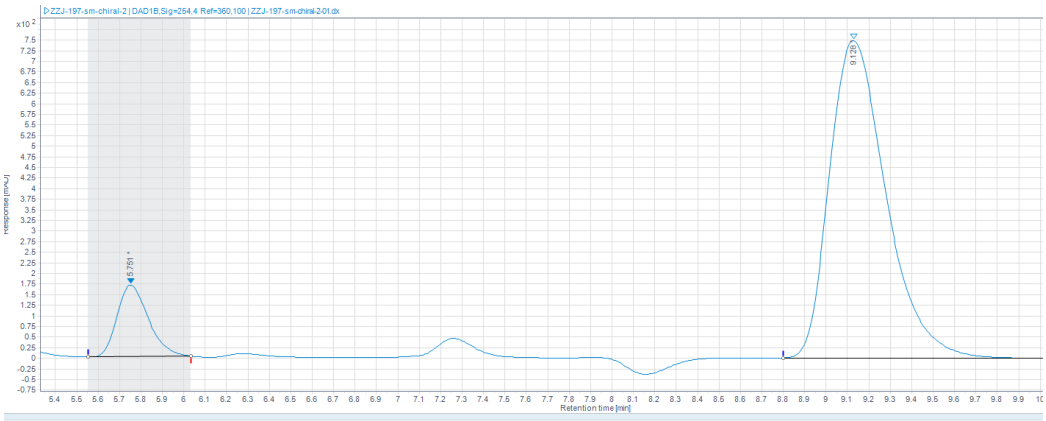
a) To an oven-dried 100mL round-bottom flask equipped with a stir bar, (*E*)-(4-methoxystyryl)boronic acid (0.86 g, 5 mmol, 1.0 equiv.), (+)-N,N,N',N'-Tetramethyl-L-tartaric acid diamide (1.05 g, 5 mmol, 1.0 equiv.) and dry DCM (20 mL) were added at room temperature. The reaction mixture was stirred for 2 h and then cooled to -78 °C. In a separate oven-dried 100 mL flask, Et_2Zn (1.0 M, 15 mL, 15 mmol, 3.0 equiv.) was dissolved in dry DCM (20 mL), cooled to -78 °C and treated dropwise with CH_2I_2 (1.0 mL, 12 mmol, 4.8 equiv.), then stirred vigorously for 10 min to generate the carbenoid

(ineffective stirring due to precipitation of zinc salt or CH_2I_2 did not affect the reaction). The pre-chilled -78 °C solution was then quickly added *via* syringe over 2 min. The mixture was stirred at -78 °C for 8 h. 20 mL of saturated aqueous NH_4Cl solution was carefully added to quench the reaction. After addition of NH_4Cl, the mixture was stirred at -78 °C for 5 min, taken out of the cooling bath and warmed to ambient temperature. After phase separation, 1M HCl was added just to dissolve precipitate in the aqueous phase (pH was 5-6 at this point). The aqueous phase was extracted with 50 mL of DCM three times. The combined organic phases were dried with $MgSO_4$, filtered and concentrated and pumped to afford crude ((*1R,2R*)-2-(4-methoxyphenyl)cyclopropyl)boronic acid (directly used for the next step).

b) To an oven-dried 50 mL round-bottom flask equipped with a stir bar, crude ((*1R,2R*)-2-(4-methoxyphenyl)cyclopropyl)boronic acid, 4-bromoanisole (864 mg, 4.5 mmol, 0.9 equiv.), K_3PO_4 (3.2 g, 15 mmol, 3.3 equiv.), $Pd(PPh_3)_4$ (156 mg, 0.03 equiv.) and toluene (20 mL) were added under nitrogen atmosphere. The reaction mixture was stirred at 100 °C for 16 h. Once the reaction was judged to be complete by TLC analysis, the reaction mixture was filtered to remove the solids and the volatile materials of the reaction mixture were removed under reduced pressure, the crude residue was purified by column chromatography (pentane:EA = 40:1) to (*1R,2R*)-1,2-bis(4-methoxyphenyl)cyclopropane as a white solid (381 mg, 30% yield over two steps, ee 78%). HPLC Analysis: Chiralpak AD-H (Cyclohexane/iPrOH = 98/2, 1.0 mL/min, 25 °C).

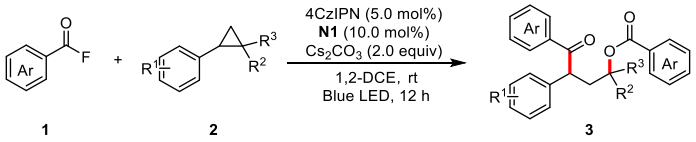
Racemic sample:

Chiral sample:



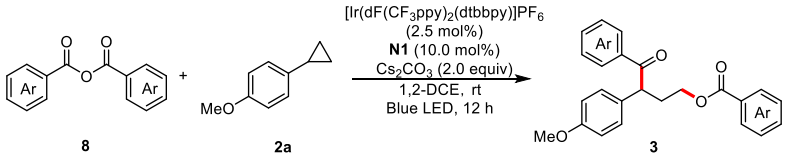
C. Results:

General procedure D for the reactions with acyl fluorides:



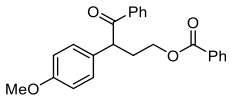
To an oven-dried 10 mL Schlenk tube equipped with a stir bar, an acyl fluoride **1** (0.50 mmol, 2.5 equiv.), an aryl cyclopropane **2** (0.20 mmol, 1.0 equiv.), photocatalyst 4CzIPN (7.9 mg, 5.0 mol%), **N1** (6.3 mg, 10.0 mol%) and Cs_2CO_3 (130.4 mg, 2.0 equiv.) were added. Then, the reaction tube was evacuated and backfilled with argon for three times. Subsequently, anhydrous DCE (2.0 mL, 0.1 M) was added. The resulting mixture was irradiated with blue LED at room temperature for 12 h. After solvent evaporation, the residue was purified by silica gel chromatography to afford the desired product **3**.

General procedure E for reactions with aryl anhydrides:



To an oven-dried 10 mL Schlenk tube equipped with a stir bar, an aryl anhydride **8** (0.20 mmol, 1.0 equiv.), the aryl cyclopropane **2a** (29.6 mg, 0.20 mmol, 1.0 equiv.), photocatalyst $[Ir(dF(CF_3ppy)_2(dtbbpy)]PF_6$ (5.6 mg, 2.5 mol%), **N1** (6.3 mg, 10.0 mol%) and Cs_2CO_3 (130.4 mg, 2.0 equiv.) were added. Then, the reaction tube was evacuated and backfilled with argon for three times. Subsequently, anhydrous DCE (2.0 mL, 0.1 M) was added. The resulting mixture was irradiated under

blue LEDs at room temperature for 12 h. After solvent evaporation, the residue was purified by silica gel chromatography to afford the desired product **3**.



3-(4-Methoxyphenyl)-4-oxo-4-phenylbutyl benzoate (3a)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

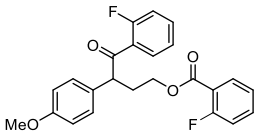
Colorless oil (60.6 mg, 81% yield)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (ddt, *J* = 16.3, 7.1, 1.4 Hz, 4H), 7.59 – 7.53 (m, 1H), 7.50 – 7.43 (m, 3H), 7.41 – 7.35 (m, 2H), 7.29 – 7.21 (m, 2H), 6.85 – 6.79 (m, 2H), 4.76 (t, *J* = 7.3 Hz, 1H), 4.36 (dt, *J* = 11.6, 5.9 Hz, 1H), 4.29 (ddd, *J* = 11.2, 7.8, 5.5 Hz, 1H), 3.75 (s, 3H), 2.70 – 2.60 (m, 1H), 2.30 (ddt, *J* = 13.9, 7.8, 5.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.1, 166.4, 158.9, 136.5, 132.9, 130.5, 130.2, 129.6, 129.3, 128.8, 128.5, 128.4, 114.6, 63.0, 55.2, 49.5, 32.7.

FTIR (neat): υ (cm^{-1}) 3066, 2837, 1714, 1680, 1511, 1449, 1266, 1248, 1110, 711.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{24}H_{22}NaO_4$ 397.1415; found: 397.1405.



4-(2-Fluorophenyl)-3-(4-methoxyphenyl)-4-oxobutyl 2-fluorobenzoate (3b)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

Colorless oil (41.8 mg, 51% yield)

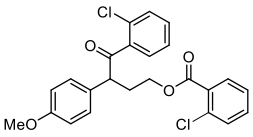
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (td, *J* = 7.5, 1.9 Hz, 1H), 7.74 (td, *J* = 7.5, 1.9 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.42 (dddt, *J* = 8.0, 5.9, 5.0, 1.3 Hz, 1H), 7.22 – 7.12 (m, 5H), 7.03 (ddd, *J* = 11.3, 8.3, 1.1 Hz, 1H), 6.81 (dd, *J* = 8.1, 1.3 Hz, 2H), 4.77 (dd, *J* = 8.3, 6.4 Hz, 1H), 4.41 (dt, *J* = 11.3, 5.7 Hz, 1H), 4.21 (ddd, *J* = 11.3, 8.1, 5.2 Hz, 1H), 3.75 (d, *J* = 0.8 Hz, 3H), 2.71 – 2.61 (m, 1H), 2.28 – 2.19 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) {^{19}F}: δ 198.3, 164.4, 161.9, 160.9, 158.9, 134.4, 134.2, 132.2, 131.1, 129.7, 129.4, 125.9, 124.4, 123.9, 118.8, 116.9, 116.6, 114.3, 63.1, 55.2, 53.2, 32.1.

^{19}F NMR (282 MHz, $CDCl_3$): δ -109.18 (d, *J* = 4.1 Hz), -109.65 (d, *J* = 4.5 Hz).

FTIR (neat): υ (cm^{-1}) 2904, 1717, 1685, 1610, 1511, 1452, 1249, 755.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{24}H_{20}F_2NaO_4$ 433.1227, found: 433.1216.



4-(2-Chlorophenyl)-3-(4-methoxyphenyl)-4-oxobutyl 2-chlorobenzoate (3c)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

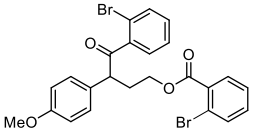
Colorless oil (67.2 mg, 76% yield)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 – 7.67 (m, 1H), 7.39 – 7.33 (m, 2H), 7.28 – 7.14 (m, 4H), 7.06 – 7.00 (m, 3H), 6.75 – 6.69 (m, 2H), 4.56 (dd, *J* = 8.4, 6.3 Hz, 1H), 4.34 (dt, *J* = 11.6, 5.9 Hz, 1H), 4.19 (ddd, *J* = 11.1, 7.7, 5.3 Hz, 1H), 3.68 (s, 3H), 2.73 – 2.47 (m, 1H), 2.23 (ddt, *J* = 14.3, 8.4, 5.8 Hz, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 202.6, 165.7, 159.1, 139.4, 133.6, 132.6, 131.5, 131.2, 131.1, 130.4, 130.2, 129.8, 128.9, 128.5, 126.6, 126.5, 114.5, 63.4, 55.2, 53.7, 31.2.

FTIR (neat): υ (cm^{-1}) 2962, 2837, 1728, 1700, 1510, 1434, 1246, 746.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{24}H_{20}Cl_2NaO_4$ 465.0636, found: 465.0629.



4-(2-Bromophenyl)-3-(4-methoxyphenyl)-4-oxobutyl 2-bromobenzoate (3d)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

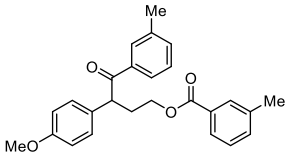
Colorless oil (75.5 mg, 71% yield)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 – 7.73 (m, 1H), 7.73 – 7.64 (m, 1H), 7.56 – 7.48 (m, 1H), 7.41 – 7.33 (m, 2H), 7.23 – 7.10 (m, 4H), 7.02 – 6.96 (m, 1H), 6.85 – 6.78 (m, 2H), 4.62 (dd, *J* = 8.5, 6.3 Hz, 1H), 4.45 (dt, *J* = 11.5, 5.9 Hz, 1H), 4.28 (ddd, *J* = 11.2, 7.8, 5.4 Hz, 1H), 3.78 (s, 3H), 2.73 (ddt, *J* = 13.9, 7.6, 5.9 Hz, 1H), 2.35 (ddt, *J* = 14.4, 8.6, 5.8 Hz, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 203.2, 166.1, 159.2, 141.5, 134.4, 133.3, 132.6, 132.3, 131.4, 131.1, 129.9, 128.8, 128.3, 127.2, 127.0, 121.6, 118.6, 114.5, 63.5, 55.2, 53.7, 31.0.

FTIR (neat): υ (cm^{-1}) 3059, 2839, 1728, 1701, 1511, 1465, 1248, 732.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{24}H_{20}Br_2NaO_4$ 552.9626, found: 552.9622.



3-(4-Methoxyphenyl)-4-oxo-4-(*m*-tolyl)butyl 3-methylbenzoate (3e)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

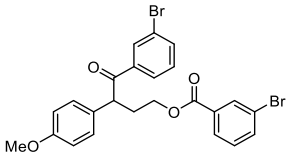
Colorless oil (54.7 mg, 81% yield)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 – 7.73 (m, 4H), 7.40 – 7.27 (m, 4H), 7.26 – 7.22 (m, 2H), 6.86 – 6.80 (m, 2H), 4.74 (t, *J* = 7.3 Hz, 1H), 4.38 – 4.23 (m, 2H), 3.75 (s, 3H), 2.75 – 2.56 (m, 1H), 2.40 (s 3H), 2.35 (s, 3H), 2.31 – 2.24 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.4, 166.6, 158.8, 138.3, 138.1, 136.6, 133.7, 133.7, 130.7, 130.2, 130.1, 129.3, 129.3, 128.4, 128.2, 126.7, 125.9, 114.5, 63.0, 55.2, 49.5, 32.7, 21.3, 21.2.

FTIR (neat): υ (cm^{-1}) 2958, 1715, 1678, 1510, 1462, 1276, 1197, 744.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{26}H_{26}NaO_4$ 425.1728, found: 425.1717.



4-(3-Bromophenyl)-3-(4-methoxyphenyl)-4-oxobutyl 3-bromobenzoate (3f)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

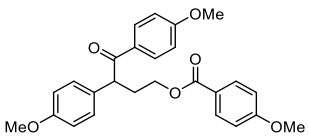
Colorless oil (72.4 mg, 68% yield)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (dt, *J* = 3.4, 1.8 Hz, 2H), 7.88 (ddt, *J* = 14.3, 7.8, 1.4 Hz, 2H), 7.71 – 7.57 (m, 2H), 7.39 – 7.20 (m, 4H), 6.89 – 6.77 (m, 2H), 4.65 (t, *J* = 7.2 Hz, 1H), 4.34 (tdd, *J* = 11.2, 9.6, 5.7 Hz, 2H), 3.76 (s, 3H), 2.72 – 2.61 (m, 1H), 2.37 – 2.20 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 197.6, 165.1, 159.0, 138.1, 135.9, 135.8, 132.5, 132.0, 131.8, 130.1, 129.9, 129.8, 129.3, 128.1, 127.2, 122.9, 122.5, 114.8, 63.5, 55.2, 49.9, 32.6.

FTIR (neat): υ (cm^{-1}) 2837, 1719, 1683, 1510, 1247, 745.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{24}H_{20}Br_2NaO_4$ 552.9626, found: 552.9623.



3,4-Bis(4-methoxyphenyl)-4-oxobutyl 4-methoxybenzoate (3g)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 5:1)

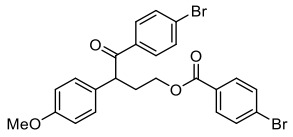
Colorless oil (68.6 mg, 79% yield)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 – 7.38 (m, 4H), 7.29 – 7.23 (m, 1H), 7.20 – 7.12 (m, 3H), 7.02 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 6.94 (ddd, *J* = 8.2, 2.7, 0.9 Hz, 1H), 6.79 – 6.72 (m, 2H), 4.64 (t, *J* = 7.3 Hz, 1H), 4.33 – 4.14 (m, 2H), 3.77 (s, 3H), 3.71 (s, 3H), 3.67 (s, 3H), 2.63 – 2.50 (m, 1H), 2.23 – 2.16 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 198.9, 166.3, 159.7, 159.6, 158.8, 137.9, 131.5, 130.5, 129.5, 129.4, 129.3, 121.9, 121.3, 119.4, 114.6, 114.1, 113.1, 63.2, 55.4, 55.3, 55.2, 49.6, 32.7.

FTIR (neat): υ (cm^{-1}) 2963, 1715, 1679, 1449, 1269, 1111, 710.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{26}H_{26}NaO_6$ 457.1627, found: 457.1618.



4-(4-Bromophenyl)-3-(4-methoxyphenyl)-4-oxobutyl 4-bromobenzoate (3h)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

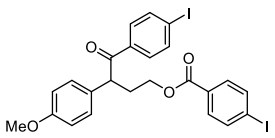
Colorless oil (72.4 mg, 68% yield)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 – 7.63 (m, 4H), 7.49 – 7.32 (m, 4H), 7.14 – 7.03 (m, 2H), 6.77 – 6.70 (m, 2H), 4.53 (t, *J* = 7.2 Hz, 1H), 4.28 – 4.11 (m, 2H), 3.65 (s, 3H), 2.62 – 2.44 (m, 1H), 2.29 – 2.10 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 197.9, 165.7, 158.9, 135.1, 131.9, 131.7, 131.1, 130.3, 130.1, 129.2, 129.0, 128.2, 128.1, 114.8, 63.3, 55.2, 49.8, 32.5.

FTIR (neat): υ (cm^{-1}) 2908, 1717, 1680, 1585, 1397, 1267, 1173, 755.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{24}H_{20}Br_2NaO_4$ 552.9626, found: 552.9622.



4-(4-Iodophenyl)-3-(4-methoxyphenyl)-4-oxobutyl 4-iodobenzoate (3i)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

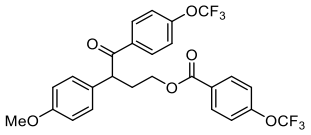
Colorless oil (73.9 mg, 59% yield)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 – 7.49 (m, 8H), 7.12 – 7.05 (m, 2H), 6.78 – 6.69 (m, 2H), 4.52 (t, *J* = 7.2 Hz, 1H), 4.28 – 4.12 (m, 2H), 3.66 (s, 3H), 2.60 – 2.45 (m, 1H), 2.27 – 2.09 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 198.2, 165.9, 158.9, 137.9, 137.7, 135.6, 130.9, 130.1, 130.1, 129.6, 129.2, 114.7, 101.0, 100.8, 63.3, 55.2, 49.7, 32.5.

FTIR (neat): υ (cm^{-1}) 2906, 1716, 1680, 1580, 1392, 1264, 1007, 817.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{24}H_{20}I_2NaO_4$ 648.9348, found: 648.9345.



3-(4-Methoxyphenyl)-4-oxo-4-(4-(trifluoromethoxy)phenyl)butyl 4-(trifluoromethoxy)benzoate (3j)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

Colorless oil (74.8 mg, 69% yield)

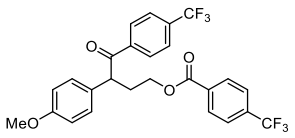
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 – 7.88 (m, 4H), 7.36 – 7.12 (m, 6H), 6.97 – 6.73 (m, 2H), 4.67 (t, *J* = 7.2 Hz, 1H), 4.43 – 4.27 (m, 2H), 3.76 (s, 3H), 2.75 – 2.60 (m, 1H), 2.35 – 2.22 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$) {^{19}F}: δ 197.3, 165.2, 159.0, 152.7, 152.4, 134.5, 131.5, 130.8, 130.1, 129.2, 128.5, 122.0, 120.2, 118.6, 114.8, 63.4, 55.2, 49.9, 32.6.

^{19}F NMR (282 MHz, $CDCl_3$): δ -57.65, -57.67.

FTIR (neat): υ (cm^{-1}) 2839, 1720, 1684, 1608, 1511, 1247, 1109, 738.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{26}H_{20}F_6NaO_6$ 565.1061, found: 565.1052.



3-(4-Methoxyphenyl)-4-oxo-4-(4-(trifluoromethyl)phenyl)butyl 4-(trifluoromethyl)benzoate (3k)

Performed with general procedure D and purified by flash silica column chromatography

(pentane/ethyl acetate = 20:1)

Colorless oil (67.3 mg, 66% yield)

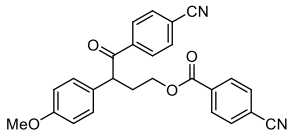
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 – 7.88 (m, 4H), 7.57 (dd, *J* = 19.1, 8.2 Hz, 4H), 7.16 – 7.05 (m, 2H), 6.79 – 6.69 (m, 2H), 4.60 (q, *J* = 7.6 Hz, 1H), 4.38 – 4.19 (m, 2H), 3.66 (s, 3H), 2.68 – 2.46 (m, 1H), 2.32 – 2.16 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$) {^{19}F}: δ 197.8, 165.2, 159.1, 139.1, 134.7, 134.4, 133.9, 133.3, 129.9, 129.7, 129.3, 129.0, 125.6, 125.4, 121.7, 114.9, 63.6, 55.2, 50.2, 32.5.

^{19}F NMR (282 MHz, $CDCl_3$): δ -63.15, -63.24.

FTIR (neat): υ (cm^{-1}) 3044, 2961, 1722, 1686, 1511, 1323, 1122, 775.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{20}H_{26}F_6NaO_4$ 533.1163, found: 533.1155.



4-(4-Cyanophenyl)-3-(4-methoxyphenyl)-4-oxobutyl 4-cyanobenzoate (3l)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 5:1)

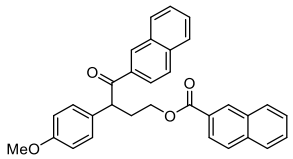
Colorless oil (45.0 mg, 53% yield)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 – 7.87 (m, 4H), 7.68 – 7.57 (m, 4H), 7.12 – 7.03 (m, 2H), 6.79 – 6.71 (m, 2H), 4.53 (t, *J* = 7.2 Hz, 1H), 4.37 – 4.21 (m, 2H), 3.67 (s, 3H), 2.56 (dt, *J* = 13.6, 7.0 Hz, 1H), 2.22 (dt, *J* = 13.9, 7.1 Hz, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 197.4, 164.8, 159.2, 139.4, 133.8, 132.4, 132.2, 130.0, 129.3, 129.2, 129.1, 117.9, 117.8, 116.5, 116.2, 114.9, 63.8, 55.3, 50.4, 32.3.

FTIR (neat): υ (cm^{-1}) 2837, 2232, 1721, 1686, 1511, 1325, 1249, 1108, 767.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{26}H_{20}N_2NaO_4$ 447.1320, found: 447.1314.



3-(4-Methoxyphenyl)-4-(naphthalen-2-yl)-4-oxobutyl 2-naphthoate (3m)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

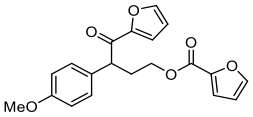
Colorless oil (70.2 mg, 74% yield)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.60 – 8.47 (m, 2H), 8.05 (dt, *J* = 8.6, 2.1 Hz, 2H), 7.93 – 7.79 (m, 6H), 7.63 – 7.46 (m, 4H), 7.40 – 7.32 (m, 2H), 6.89 – 6.80 (m, 2H), 4.97 (t, *J* = 7.2 Hz, 1H), 4.52 – 4.38 (m, 2H), 3.73 (s, 3H), 2.87 – 2.72 (m, 1H), 2.49 – 2.41 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 199.1, 166.6, 158.9, 135.5, 135.5, 133.9, 132.5, 132.4, 131.1, 130.8, 130.5, 129.6, 129.4, 128.5, 128.4, 128.3, 128.1, 127.8, 127.7, 127.5, 126.7, 126.6, 125.2, 124.5, 114.7, 63.4, 55.2, 49.7, 32.9.

FTIR (neat): υ (cm^{-1}) 3058, 2936, 1712, 1675, 1510, 1465, 1249, 779.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{32}H_{26}NaO_4$ 497.1728, found: 497.1721.



4-(Furan-2-yl)-3-(4-methoxyphenyl)-4-oxobutyl furan-2-carboxylate (3n)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1)

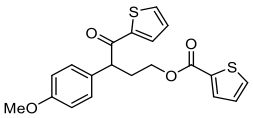
Colorless oil (31.9 mg, 45% yield)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 – 7.49 (m, 2H), 7.29 – 7.24 (m, 2H), 7.18 – 7.10 (m, 2H), 6.84 – 6.81 (m, 2H), 6.52 – 6.43 (m, 2H), 4.52 (q, *J* = 7.8 Hz, 1H), 4.35 – 4.18 (m, 2H), 3.77 (s, 3H), 2.66 – 2.58 (m, 1H), 2.30 – 2.22 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 188.1, 158.9, 158.6, 152.2, 146.4, 146.3, 144.6, 130.0, 129.4, 117.9, 117.8, 114.4, 112.3, 111.8, 62.9, 55.2, 49.5, 31.6.

FTIR (neat): υ (cm^{-1}) 2837, 1718, 1671, 1511, 1465, 1295, 1115, 734.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{20}H_{18}NaO_6$ 377.1001, found: 377.0994.



3-(4-Methoxyphenyl)-4-oxo-4-(thiophen-2-yl)butyl thiophene-2-carboxylate (3o)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1)

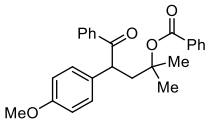
Yellow oil (47.1 mg, 61% yield)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (ddd, *J* = 16.9, 3.8, 1.2 Hz, 2H), 7.48 (dt, *J* = 5.0, 1.0 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.00 (ddd, *J* = 18.1, 5.0, 3.8 Hz, 2H), 6.82 – 6.69 (m, 2H), 4.48 (t, *J* = 7.4 Hz, 1H), 4.31 – 4.07 (m, 2H), 3.68 (s, 3H), 2.66 – 2.44 (m, 1H), 2.29 – 2.24 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 192.0, 162.0, 159.0, 143.7, 133.8, 133.7, 133.5, 132.5, 132.4, 130.5, 129.3, 128.1, 127.8, 114.5, 62.9, 55.2, 50.9, 32.4.

FTIR (neat): υ (cm^{-1}) 2997, 2836, 1703, 1656, 1510, 1414, 1247, 1099, 721.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{20}H_{18}NaO_4S_2$ 409.0544, found: 409.0538.



4-(4-Methoxyphenyl)-2-methyl-5-oxo-5-phenylpentan-2-yl benzoate (3p)

Purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

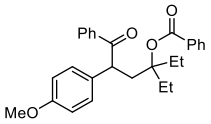
Colorless oil (68.3 mg, 85% yield)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 – 7.84 (m, 2H), 7.81 – 7.72 (m, 2H), 7.45 – 7.32 (m, 2H), 7.27 (td, *J* = 7.6, 3.3 Hz, 4H), 7.17 – 7.09 (m, 2H), 6.74 – 6.65 (m, 2H), 4.82 (dd, *J* = 8.1, 4.1 Hz, 1H), 3.62 (s, 3H), 2.96 (dd, *J* = 14.6, 8.0 Hz, 1H), 2.29 (dd, *J* = 14.6, 4.1 Hz, 1H), 1.56 (s, 3H), 1.47 (s, 3H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 199.4, 165.7, 158.6, 136.7, 132.9, 132.5, 132.0, 131.7, 129.4, 129.3, 128.7, 128.6, 128.1, 114.5, 82.7, 55.2, 47.9, 44.9, 26.7, 26.6.

FTIR (neat): υ (cm^{-1}) 3035, 1709, 1685, 1511, 1421, 1292, 1114, 833.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{26}H_{26}NaO_4$ 425.1728, found: 425.1719.



3-Ethyl-5-(4-methoxyphenyl)-6-oxo-6-phenylhexan-3-yl benzoate (3q)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

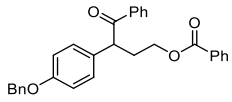
Colorless oil (49.1 mg, 57% yield)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 – 7.73 (m, 4H), 7.45 – 7.34 (m, 3H), 7.27 (dd, *J* = 7.1, 1.3 Hz, 3H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 4.75 (dd, *J* = 7.8, 4.3 Hz, 1H), 3.61 (s, 3H), 2.99 (dd, *J* = 14.3, 6.6 Hz, 1H), 2.36 (dd, *J* = 14.9, 4.3 Hz, 1H), 2.04 – 1.81 (m, 4H), 0.82 (t, *J* = 7.5, 3H), 0.78 (t, *J* = 7.5, 3H)

^{13}C NMR (76 MHz, $CDCl_3$): δ 199.2, 165.4, 158.5, 136.7, 132.8, 132.4, 131.9, 131.6, 129.4, 129.3, 128.7, 128.5, 128.1, 114.4, 88.4, 55.2, 47.4, 38.4, 27.9, 27.8, 8.0, 7.8.

FTIR (neat): υ (cm^{-1}) 2960, 1713, 1679, 1511, 1428, 1269, 1113, 711.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{28}H_{30}NaO_4$ 453.2042, found: 453.2035.



3-(4-(Benzyloxy)phenyl)-4-oxo-4-phenylbutyl benzoate (3r)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1)

White solid (71.1 mg, 79% yield)

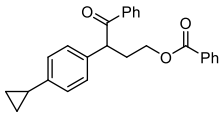
MP: 127-128 °C

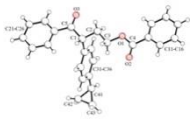
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 – 7.89 (m, 4H), 7.64 – 7.33 (m, 11H), 7.33 – 7.22 (m, 2H), 7.02 – 6.89 (m, 2H), 5.01 (s, 2H), 4.78 (t, *J* = 7.3 Hz, 1H), 4.51 – 4.24 (m, 2H), 2.69 – 2.65 (m, 1H), 2.36 – 2.29 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 199.1, 166.5, 158.2, 136.9, 136.5, 132.9, 130.8, 130.2, 129.6, 129.4, 128.8, 128.6, 128.5, 128.4, 128.0, 127.5, 115.5, 70.0, 63.1, 49.5, 32.7.

FTIR (neat): υ (cm^{-1}) 3055, 2920, 1737, 1612, 1515, 1496, 1245, 732.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{30}H_{26}NaO_4$ 473.1728, found: 473.1719.





CCDC: 2094400

3-(4-Cyclopropylphenyl)-4-oxo-4-phenylbutyl benzoate (3s)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 30:1)

White solid (49.2 mg, 64% yield)

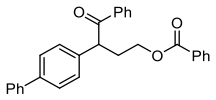
MP: 108-109 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (ddd, *J* = 8.6, 6.1, 1.4 Hz, 4H), 7.49 – 7.26 (m, 6H), 7.12 (d, *J* = 6.2 Hz, 2H), 6.99 – 6.86 (m, 2H), 4.67 (t, *J* = 7.3 Hz, 1H), 4.35 – 4.16 (m, 2H), 2.69 – 2.45 (m, 1H), 2.21 (ddt, *J* = 13.8, 7.8, 5.8 Hz, 1H), 1.72 (td, *J* = 8.4, 4.2 Hz, 1H), 0.83 (ddd, *J* = 8.6, 4.2, 1.5 Hz, 2H), 0.57 – 0.51 (m, 2H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 198.9, 166.5, 143.2, 136.5, 135.5, 132.9, 132.9, 130.2, 129.6, 128.8, 128.5, 128.4, 128.2, 126.4, 63.1, 50.0, 32.7, 15.0, 9.3, 9.2.

FTIR (neat): υ (cm^{-1}) 2837, 1721, 1686, 1511, 1375, 1249, 1108, 767.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{26}H_{24}NaO_3$ 407.1623, found: 407.1618.



3-([1,1'-Biphenyl]-4-yl)-4-oxo-4-phenylbutyl benzoate (3t)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 30:1)

White solid (57.2 mg, 68% yield)

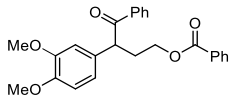
MP: 113-114 °C.

^{1}H NMR (599 MHz, $CDCl_3$): δ 8.03 – 7.93 (m, 4H), 7.56 – 7.47 (m, 6H), 7.44 – 7.36 (m, 8H), 7.36 – 7.28 (m, 1H), 4.84 (t, *J* = 7.2 Hz, 1H), 4.42 – 4.28 (m, 2H), 2.78 – 2.65 (m, 1H), 2.45 – 2.30 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.8, 166.4, 140.5, 140.3, 137.6, 136.4, 133.1, 132.9, 130.2, 129.5, 128.8, 128.7, 128.6, 128.5, 128.4, 127.9, 127.3, 126.9, 63.1, 50.1, 32.8.

FTIR (neat): υ (cm^{-1}) 3061, 3026, 2928, 1715, 1680, 1486, 1449, 1270, 1113, 710.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{29}H_{24}NaO_3$ 443.1623, found: 443.1616.



3-(3,4-Dimethoxyphenyl)-4-oxo-4-phenylbutyl benzoate (3u)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1)

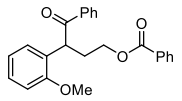
Colorless oil (49.3 mg, 61% yield)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 – 7.82 (m, 4H), 7.50 – 7.29 (m, 6H), 6.82 – 6.59 (m, 3H), 4.65 (t, *J* = 7.3 Hz, 1H), 4.31 – 4.16 (m, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 2.61 – 2.54 (m, 1H), 2.40 – 2.04 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 199.1, 166.4, 149.5, 148.4, 136.5, 132.9, 132.9, 129.7, 129.6, 129.5, 128.7, 128.5, 128.4, 120.9, 111.6, 110.8, 63.0, 55.9, 55.8, 50.0, 32.7.

FTIR (neat): υ (cm^{-1}) 2935, 1715, 1679, 1515, 1450, 1262, 1155, 712.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{25}H_{24}NaO_5$ 427.1521, found: 427.1512.



3-(2-Methoxyphenyl)-4-oxo-4-phenylbutyl benzoate (3v)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1)

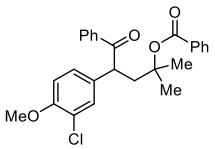
Colorless oil (53.9 mg, 72% yield)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 – 7.91 (m, 4H), 7.61 – 7.53 (m, 1H), 7.49 – 7.41 (m, 3H), 7.38 – 7.33 (m, 2H), 7.22 – 7.12 (m, 2H), 6.87 (ddd, *J* = 8.4, 5.9, 1.2 Hz, 2H), 5.32 (dd, *J* = 7.8, 6.4 Hz, 1H), 4.36 – 4.24 (m, 2H), 3.81 (s, 3H), 2.71 – 2.62 (m, 1H), 2.29 – 2.21 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.7, 166.5, 156.1, 136.4, 132.8, 132.7, 130.4, 129.5, 128.6, 128.5, 128.4, 128.3, 128.2, 127.4, 121.2, 110.9, 63.2, 55.5, 42.3, 31.8.

FTIR (neat): υ (cm^{-1}) 3066, 2837, 1721, 1682, 1603, 1511, 1249, 1176, 711.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{24}H_{22}NaO_4$ 397.1415; found: 397.1409.



4-(3-Chloro-4-methoxyphenyl)-2-methyl-5-oxo-5-phenylpentan-2-yl benzoate (3y)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1)

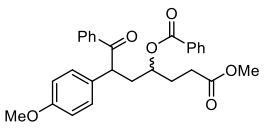
Colorless oil (51.6 mg, 59% yield)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 – 7.89 (m, 2H), 7.89 – 7.79 (m, 2H), 7.61 – 7.46 (m, 2H), 7.46 – 7.33 (m, 5H), 7.17 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 1H), 4.88 (dd, *J* = 7.7, 4.5 Hz, 1H), 3.80 (s, 3H), 2.98 (dd, *J* = 14.7, 7.8 Hz, 1H), 2.44 (dd, *J* = 14.7, 4.5 Hz, 1H), 1.66 (s, 3H), 1.57 (s, 3H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 198.9, 165.6, 154.0, 136.3, 133.1, 132.9, 132.6, 131.5, 130.2, 129.9, 129.4, 128.7, 128.5, 127.5, 122.8, 112.5, 82.5, 56.1, 47.5, 44.6, 26.8, 26.6.

FTIR (neat): υ (cm^{-1}) 3062, 2975, 1709, 1682, 1501, 1283, 1111, 771.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{26}H_{25}ClNaO_4$ 459.1339, found: 459.1330.



7-Methoxy-2-(4-methoxyphenyl)-1,7-dioxo-1-phenylheptan-4-yl benzoate (3z)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 5:1) as inseparable mixture of diastereoisomers (dr = 1.1:1)

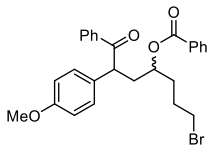
Yellow oil (50.7 mg, 55% yield)

^{1}H NMR (300 MHz, $CDCl_3$): (mixture of diastereoisomers) δ 8.03 – 7.82 (m, 4H), 7.61 – 7.53 (m, 1H), 7.47 – 7.30 (m, 5H), 7.23 – 7.15 (m, 2H), 6.87 – 6.78 (m, 1H), 6.79 – 6.71 (m, 1H), 5.26 – 5.07 (m, 1H), 4.67 (dt, *J* = 8.5, 5.8 Hz, 1H), [3.76 (s) + 3.69 (s), 3H] + [3.61 (s) + 3.58 (s), 3H], 2.72 – 2.55 (m, 1H), 2.47 – 2.33 (m, 2H), 2.26 – 1.99 (m, 3H).

^{13}C NMR (76 MHz, $CDCl_3$): (mixture of diastereoisomers) δ 199.1, 198.9, 173.4, 173.3, 166.1, 166.0, 158.8, 158.7, 136.5, 136.2, 133.0, 132.9, 132.8, 130.9, 130.4, 130.0, 129.9, 129.6, 129.5, 129.4, 129.1, 128.7, 128.5, 128.4, 128.4, 128.3, 128.2, 114.6, 114.5, 72.8, 72.0, 55.2, 55.1, 51.7, 51.6, 49.2, 49.1, 38.5, 38.2, 30.0, 29.9, 29.8.

FTIR (neat): υ (cm^{-1}) 2983, 1737, 1681, 1448, 1373, 1233, 1044, 711.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{28}H_{28}NaO_6$ 483.1783, found: 483.1778.



7-Bromo-2-(4-methoxyphenyl)-1-oxo-1-phenylheptan-4-yl benzoate (3aa)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1) as inseparable mixture of diastereoisomers (dr = 1.3:1)

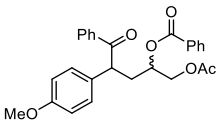
Colorless oil (56.5 mg, 57% yield)

^{1}H NMR (300 MHz, $CDCl_3$): (mixture of diastereoisomers) δ 7.99 – 7.74 (m, 4H), 7.53 – 7.17 (m, 6H), 7.15 – 7.04 (m, 2H), 6.75 – 6.62 (m, 2H), 5.18 – 4.95 (m, 1H), 4.62 – 4.56 (m, 1H), [3.66 (s) + 3.59 (s), 3H], 3.36 – 3.24 (m, 2H), 2.64 – 2.44 (m, 1H), 2.22 – 2.02 (m, 1H), 1.91 – 1.62 (m, 4H).

^{13}C NMR (76 MHz, $CDCl_3$): (mixture of diastereoisomers) δ 199.2, 199.0, 166.2, 166.1, 158.9, 158.7, 136.5, 136.2, 133.1, 132.9, 132.8, 131.1, 130.4, 130.2, 130.1, 129.6, 129.5, 129.4, 129.1, 128.7, 128.5, 128.4, 128.4, 128.3, 114.6, 114.5, 72.7, 72.1, 55.2, 55.1, 49.3, 49.2, 38.6, 38.3, 33.6, 33.5, 33.4, 33.3, 28.4, 28.3.

FTIR (neat): υ (cm^{-1}) 2837, 1712, 1678, 1510, 1269, 1178, 711.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{27}H_{27}BrNaO_4$ 517.0990, found: 517.0984.



1-Acetoxy-4-(4-methoxyphenyl)-5-oxo-5-phenylpentan-2-yl benzoate (3ab)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1) as inseparable mixture of diastereoisomers (dr = 1.4:1)

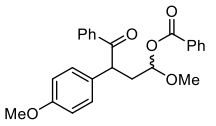
Yellow oil (36.6 mg, 41% yield)

^{1}H NMR (300 MHz, $CDCl_3$): (mixture of diastereoisomers) δ 7.95 – 7.78 (m, 5H), 7.34 – 7.28 (m, 5H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.76 – 6.67 (m, 2H), 5.33 – 5.08 (m, 1H), 4.62 (dt, *J* = 14.1, 7.7 Hz, 1H), 4.26 – 4.08 (m, 2H), 3.68 – 3.60 (m, 3H), 2.57 (dd, *J* = 13.0, 5.9 Hz, 1H), 2.23 – 2.08 (m, 1H), 1.96 – 1.91 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): (mixture of diastereoisomers) δ 198.9, 198.7, 170.7, 170.6, 165.9, 165.8, 158.9, 158.8, 136.3, 136.1, 133.1, 133.0, 132.9, 132.8, 130.7, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.5, 129.4, 129.1, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 114.7, 114.6, 114.6, 114.5, 71.0, 70.3, 65.3, 65.1, 55.2, 55.1, 49.1, 48.9, 35.0, 34.9, 20.8, 20.7.

FTIR (neat): υ (cm^{-1}) 2837, 1741, 1717, 1660, 1510, 1449, 1248, 1109, 712.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{27}H_{26}NaO_6$ 469.1627, found: 469.1620.



4-(4-Methoxyphenyl)-2-methyl-5-oxo-5-phenylpentan-2-yl benzoate (3ac)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1) as inseparable mixture of diastereoisomers (dr = 1.2:1)

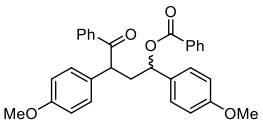
Colorless oil (42.9 mg, 53% yield)

^{1}H NMR (300 MHz, $CDCl_3$): (mixture of diastereoisomers) δ 8.03 – 7.76 (m, 4H), 7.57 – 7.24 (m, 6H), 7.16 – 7.08 (m, 2H), 6.89 – 6.62 (m, 2H), [5.95 (t, *J* = 5.3 Hz, minor diastereoisomers) + 5.76 (dd, *J* = 7.0, 4.0 Hz, major diastereoisomers) 1H], 4.75 (dt, *J* = 7.7, 6.1 Hz, 1H), 3.66 (s, 3H), [3.37 (s) + 3.32 (s) 3H), 2.85 – 2.50 (m, 1H), 2.38 – 2.20 (m, 1H).

^{13}C NMR (126 MHz, CD_2Cl_2+$CDCl_3$): (mixture of diastereoisomers) δ 198.8, 198.7, 165.9, 158.9, 136.4, 133.2, 133.1, 132.8, 132.7, 130.9, 130.3, 130.0, 129.9, 129.7, 129.6, 129.4, 129.3, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 114.4, 114.3, 99.1, 98.5, 56.7, 56.6, 48.3, 47.7, 47.6, 46.8, 38.3, 37.8.

FTIR (neat): υ (cm^{-1}) 3063, 2938, 1717, 1680, 1510, 1449, 1248, 1176, 711.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{25}H_{24}NaO_5$ 427.1521, found: 427.1509.



1,3-Bis(4-methoxyphenyl)-4-oxo-4-phenylbutyl benzoate (3ad)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1) as inseparable mixture of diastereoisomers (1.3:1 dr)

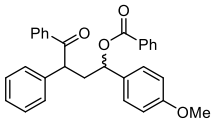
Colorless oil (63.4 mg, 66% yield)

^{1}H NMR (300 MHz, $CDCl_3$): (mixture of diastereoisomers) δ 8.09 – 7.93 (m, 2H), 7.87 (ddt, *J* = 11.3, 7.1, 1.4 Hz, 2H), 7.60 – 7.50 (m, 1H), 7.49 – 7.30 (m, 7H), 7.23 – 7.17 (m, 2H), 6.95 – 6.78 (m, 4H), 5.97 – 5.73 (m, 1H), 4.80 – 4.40 (m, 1H), [3.83 (s) + 3.79 (s), 3H], [3.77 (s) + 3.74 (s), 3H], 3.08 – 2.77 (m, 1H), 2.68 – 2.33 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): (mixture of diastereoisomers) δ 199.1, 198.9, 165.7, 165.6, 159.5, 159.4, 158.8, 158.7, 136.4, 132.9, 132.9, 132.8, 132.7, 132.2, 130.5, 130.5, 130.4, 130.3, 129.6, 129.6, 129.4, 128.7, 128.5, 128.3, 128.2, 128.1, 127.8, 114.6, 114.5, 114.0, 113.9, 74.9, 74.5, 55.3, 55.2, 55.1, 55.0, 49.4, 49.1, 40.6, 40.0.

FTIR (neat): υ (cm^{-1}) 3061, 2837, 1715, 1679, 1510, 1449, 1245, 711.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{31}H_{28}NaO_5$ 503.1834, found: 503.1830.



1-(4-Methoxyphenyl)-4-oxo-3,4-diphenylbutyl benzoate (3ae)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1) as inseparable diastereoisomeric (1.3:1 dr) and regioisomeric (3:1 rr) mixture.

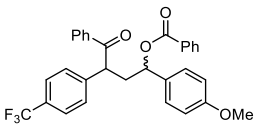
Colorless oil (53.2 mg, 59% yield)

^{1}H NMR (300 MHz, $CDCl_3$): (mixture of diastereoisomers and regioisomer) δ 8.23 – 7.63 (m, 5H), 7.59 – 7.30 (m, 10H), 7.24 – 6.77 (m, 4H), 6.02 – 5.73 (m, 1H), 4.78 – 4.59 (m, 1H), [3.83 (s, major diastereoisomer) + 3.79 (s, minor diastereoisomer) + 3.77 (s, regioisomer) + 3.74 (s, regioisomer), 3H], 3.13 – 2.81 (m, 1H), 2.67 – 2.30 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): (mixture of diastereoisomers and regioisomer) δ 198.9, 198.8, 165.7, 165.6, 159.5, 159.4, 138.7, 136.4, 132.9, 132.8, 132.5, 132.2, 130.3, 129.7, 129.6, 129.4, 129.3, 129.2, 129.1, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 127.8, 127.4, 127.3, 126.6, 114.5, 114.0, 113.9, 74.9, 74.6, 55.3, 55.2, 50.3, 49.9, 40.6, 40.2.

FTIR (neat): υ (cm^{-1}) 3062, 1715, 1679, 1513, 1448, 1247, 1175, 699.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{30}H_{26}NaO_4$ 473.1729, found: 473.1723.



1-(4-Methoxyphenyl)-4-oxo-4-phenyl-3-(4-(trifluoromethyl)phenyl)butyl benzoate (3af)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1) as inseparable diastereisomeric (1.2:1 dr) and regioisomeric (7:1 rr) mixture.

Yellow oil (63.2 mg, 61% yield)

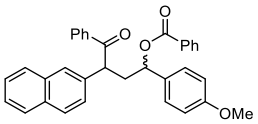
^{1}H NMR (300 MHz, $CDCl_3$): (mixture of diastereoisomers and regioisomer) δ 7.94 – 7.74 (m, 4H), 7.49 – 7.17 (m, 12H), 6.89 – 6.71 (m, 2H), 5.97 – 5.71 (m, 1H), 4.68 (dt, *J* = 22.3, 7.0 Hz, 1H), [3.72 (s, major diastereoisomer) + 3.68 (s, minor diastereoisomer) + 3.66 (s, regioisomer) + 3.62 (s, regioisomer), 3H], 3.07 – 2.71 (m, 1H), 2.62 – 2.27 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$) {^{19}F}: (mixture of diastereoisomers and regioisomer) δ 198.3, 198.2, 165.7, 165.6, 159.6, 159.5, 142.7, 135.9, 133.4, 133.3, 133.1, 133.0, 132.1, 131.8, 130.1, 130.0, 129.7, 129.6, 129.5, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.0, 127.8, 126.1, 126.0, 125.9, 114.1, 114.0, 74.8, 74.4, 55.3, 55.2, 49.9, 40.5, 40.1.

^{19}F NMR (282 MHz, $CDCl_3$): (mixture of diastereoisomers) δ -62.54, -62.56.

FTIR (neat): υ (cm^{-1}) 2963, 1717, 1681, 1514, 1450, 1327, 1247, 1109, 711.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{31}H_{25}F_3NaO_4$ 541.1603, found: 541.1597.



1-(4-Methoxyphenyl)-3-(naphthalen-2-yl)-4-oxo-4-phenylbutyl benzoate (3ag)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 20:1) as inseparable diastereoisomeric (dr = 1.2:1) and regioisomeric (4:1 rr)

mixture.

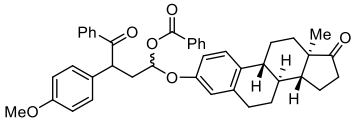
Yellow oil (55.1 mg, 55% yield)

^{1}H NMR (300 MHz, $CDCl_3$): (mixture of diastereoisomers and regioisomer) δ 7.93 – 7.88 (m, 1H), 7.84 – 7.66 (m, 6H), 7.47 – 7.19 (m, 12H), 6.85 – 6.79 (m, 1H), 6.77 – 6.70 (m, 1H), 5.83 (ddd, *J* = 13.9, 8.6, 5.2 Hz, 1H), 4.75 (dt, *J* = 23.5, 7.0 Hz, 1H), [3.71 (s, major diastereoisomer) + 3.66 (s, minor diastereoisomer) + 3.65 (s, regioisomer) + 3.62 (s, regioisomer) 3H], 3.11 – 2.81 (m, 1H), 2.70 – 2.34 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): (mixture of diastereoisomers and regioisomer) δ 198.9, 198.7, 165.7, 165.6, 159.5, 159.4, 136.4, 136.2, 136.1, 133.7, 133.6, 133.0, 132.9, 132.6, 132.5, 132.5, 132.2, 130.3, 130.2, 129.7, 129.6, 129.6, 129.5, 129.4, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 126.3, 126.2, 126.1, 126.0, 126.0, 114.6, 114.0, 113.9, 75.0, 74.6, 55.3, 55.3, 50.4, 50.3, 40.6, 40.2.

FTIR (neat): υ (cm^{-1}) 3061, 2962, 1716, 1680, 1513, 1267, 711.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{34}H_{28}NaO_4$ 523.1885, found: 523.1881.



3-(4-Methoxyphenyl)-1-(((8S,9R,13R,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)-4-oxo-4-phenylbutyl benzoate (3ah)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 5:1) as inseparable mixture of diastereoisomers (dr = 1:1)

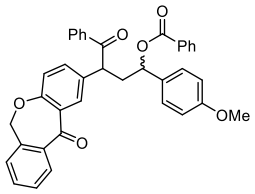
Brown oil (66.8 mg, 52% yield)

^{1}H NMR (300 MHz, $CDCl_3$): (mixture of diastereoisomers) δ 8.04 (dt, *J* = 7.1, 1.4 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.68 – 7.46 (m, 1H), 7.49 – 7.26 (m, 4H), 7.18 – 7.05 (m, 4H), 6.84 – 6.45 (m, 5H), [5.72 (td, *J* = 5.2, 1.9 Hz) + 5.50 (td, *J* = 5.2, 1.6 Hz) 1H], 4.80 (q, *J* = 7.5 Hz, 1H), [3.67 (s) + 3.66 (s), 3H], 2.76 (dq, *J* = 9.4, 4.3 Hz, 3H), 2.41 – 1.88 (m, 9H), 1.49 – 1.37 (m, 5H), 0.82 (d, *J* = 7.4 Hz, 3H).

^{13}C NMR (76 MHz, $CDCl_3$): (mixture of diastereoisomers) δ 221.2, 221.1, 221.0, 198.8, 198.7, 158.9, 154.4, 154.3, 138.1, 138.0, 138.0, 137.9, 136.3, 136.2, 134.9, 134.8, 133.7, 133.1, 133.0, 130.2, 130.1, 129.4, 129.3, 128.9, 128.8, 128.6, 128.5, 128.4, 126.5, 126.4, 117.3, 117.2, 115.3, 114.7, 114.6, 114.5, 112.9, 110.6, 107.7, 55.2, 50.4, 50.3, 48.1, 48.0, 48.0, 47.6, 47.5, 47.4, 44.1, 44.0, 43.9, 38.4, 38.2, 35.9, 31.6, 31.5, 29.6, 29.5, 29.5, 26.5, 26.4, 26.4, 25.9, 25.9, 25.8, 21.6, 21.6, 13.9, 13.8.

FTIR (neat): υ (cm^{-1}) 2931, 2837, 1722, 1680, 1511, 1448, 1246, 1176, 695.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{42}H_{42}NaO_6$ 665.2879, found: 665.2879.



1-(4-Methoxyphenyl)-4-oxo-3-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)-4-phenylbutyl benzoate (3ai)

Performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1) as inseparable inseparable diastereoisomeric (dr = 1.1:1) and regioisomeric (1.7:1 rr) mixture.

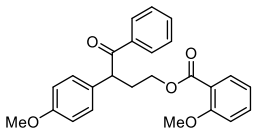
Yellow oil (66.8 mg, 61% yield)

^{1}H NMR (300 MHz, $CDCl_3$): (mixture of diastereoisomers and regioisomer) δ 8.39 – 7.86 (m, 6H), 7.61 – 7.31 (m, 12H), 7.07 – 6.77 (m, 3H), 6.01 – 5.79 (m, 1H), 5.16 (dd, *J* = 14.1, 7.7 Hz, 2H), 4.89 – 4.55 (m, 1H), [3.83 (s, major diastereoisomer) + 3.78 (s, minor diastereoisomer) + 3.76 (s, regioisomer) + 3.74 (s, regioisomer) 3H), 3.14 – 2.79 (m, 1H), 2.69 – 2.39 (m, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): (mixture of diastereoisomers and regioisomer) δ 198.9, 198.8, 198.7, 190.8, 190.7, 165.7, 165.6, 165.6, 161.1, 160.9, 160.6, 160.5, 159.5, 159.4, 158.9, 158.8, 140.5, 140.4, 140.3, 136.3, 136.1, 135.4, 135.4, 134.8, 134.7, 134.5, 134.1, 133.5, 133.1, 133.0, 132.9, 132.9, 132.8, 132.8, 132.7, 132.4, 132.3, 132.1, 131.9, 131.8, 130.6, 130.2, 130.1, 130.0, 129.9, 129.7, 129.7, 129.6, 129.6, 129.5, 129.5, 129.4, 129.3, 129.3, 129.2, 128.9, 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.9, 127.9, 127.8, 127.7, 125.5, 125.4, 125.2, 125.1, 121.8, 121.7, 121.2, 121.1, 114.7, 114.6, 114.1, 114.0, 74.8, 74.7, 74.6, 74.1, 73.6, 73.5, 73.5, 55.3, 55.2, 55.2, 49.4, 49.2, 49.0, 48.9, 40.5, 40.4, 40.2, 40.1.

FTIR (neat): υ (cm^{-1}) 2831, 1711, 1680, 1648, 1513, 1486, 1360, 1265, 1248, 1109, 711.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{38}H_{30}NaO_6$ 605.1940, found: 605.1939.



3-(4-Methoxyphenyl)-4-oxo-4-phenylbutyl 2-methoxybenzoate (3aj)

Performed with general procedure E and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1)

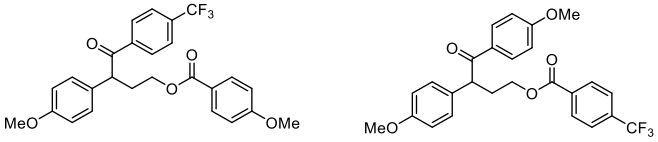
Colorless oil (29.1 mg, 36% yield)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 – 7.93 (m, 2H), 7.74 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.38 (dd, *J* = 8.3, 7.1 Hz, 2H), 7.27 – 7.20 (m, 2H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.87 – 6.82 (m, 2H), 4.81 (dd, *J* = 8.0, 6.5 Hz, 1H), 4.33 (dt, *J* = 11.3, 5.7 Hz, 1H), 4.25 – 4.22 (m, 1H), 3.90 (s, 3H), 3.76 (s, 3H), 2.73 – 2.53 (m, 1H), 2.35 – 2.21 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.3, 166.3, 159.1, 158.8, 136.6, 133.5, 132.8, 131.6, 130.6, 129.4, 128.8, 128.5, 120.3, 120.2, 114.6, 112,0, 62.7, 55.9, 55.2, 49.3, 32.7.

FTIR (neat): υ (cm^{-1}) 2963, 2831, 1727, 1685, 1512, 1180, 757.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{25}H_{24}NaO_5$ 427.1521, found: 427.1509.



3-(4-Methoxyphenyl)-4-oxo-4-(4-(trifluoromethyl)phenyl)butyl 4-methoxybenzoate or 3,4-bis(4-methoxyphenyl)-4-oxobutyl 4-(trifluoromethyl)benzoate (3ak)

Performed with general procedure E and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1) as inseparable mixture of regioisomer (1.8:1 rr).

Colorless oil (40.6 mg, 43% yield)

^{1}H NMR (300 MHz, $CDCl_3$): (mixture of regioisomer) δ 8.01 – 7.83 (m, 4H), 7.61 – 7.52 (m, 2H), 7.13 (t, *J* = 8.7 Hz, 2H), 6.86 – 6.73 (m, 4H), 4.60 (q, *J* = 7.8 Hz, 1H), 4.34 – 4.10 (m, 2H), [3.79 (s, major regioisomer) + 3.74 (s, minor regioisomer) + 3.67 (s, major regioisomer) + 3.66 (s, minor regioisomer), 6H], 2.61 – 2.54 (m, 1H), 2.25 – 2.51 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) {^{19}F}: (mixture of regioisomer) δ 198.1, 197.4, 166.2, 165.2, 163.4, 163.3, 159.0, 158.8, 139.2, 134.4, 134.0, 133.4, 131.5, 131.0, 130.9, 129.9, 129.9, 129.8, 129.8, 129.3, 129.2, 129.0, 125.5, 125.3, 125.2, 123.6, 123.5, 122.5, 114.8, 114.6, 113.7, 113.6, 63.9, 62.5, 55.4, 55.4, 55.2, 55.2, 50.1, 49.3, 32.7, 33.6.

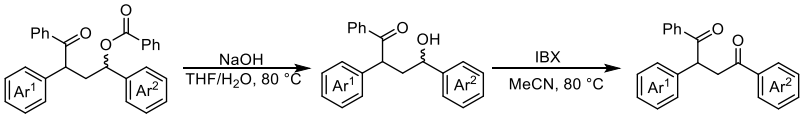
^{19}F NMR (564 MHz, $CDCl_3$): (mixture of regioisomer) δ -63.13, -63.23.

FTIR (neat): υ (cm^{-1}) 2909, 1718, 1686, 1606, 1512, 1325, 1168, 771.

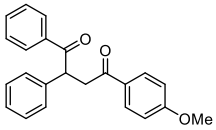
HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{26}H_{23}F_3NaO_5$ 495.1395, found: 495.1387.

Regioselectivities Determination of Unsymmetrical Diaryl Cyclopropanes

The regioselectivities of **3ae-3ag** was determinate by further derivatization (see below) and confirmed by comparison with the ^{1}H NMR of related known compounds or similar structures.[6-7]



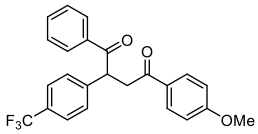
Major regioisomer of **3ae-s**



4-(4-Methoxyphenyl)-1,2-diphenylbutane-1,4-dione

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 – 8.00 (m, 4H), 7.55 – 7.34 (m, 8H), 7.01 – 6.90 (m, 2H), 5.38 – 5.33 (m, 1H), 4.30 – 4.18 (m, 1H), 3.90 (s, 3H), 3.35 – 3.26 (m, 1H).

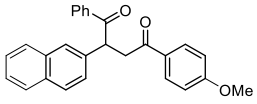
Major regioisomer of **3af-s**



4-(4-Methoxyphenyl)-1-phenyl-2-(4-(trifluoromethyl)phenyl)butane-1,4-dione

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (ddt, *J* = 16.5, 6.9, 2.0 Hz, 4H), 7.54 – 7.36 (m, 7H), 6.91 (dd, *J* = 9.1, 2.4 Hz, 2H), 5.39 (dd, *J* = 9.8, 4.0 Hz, 1H), 4.18 – 4.06 (m, 1H), 3.85 (s, 3H), 3.31 – 3.23 (m, 1H).

Major regioisomer of **3ag-s**

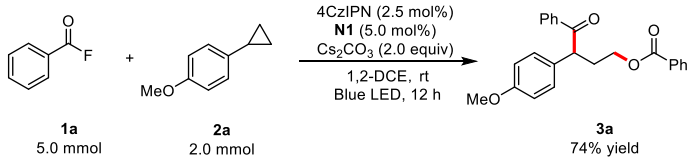


4-(4-methoxyphenyl)-2-(naphthalen-2-yl)-1-phenylbutane-1,4-dione

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 – 7.98 (m, 2H), 7.92 – 7.89 (m, 2H), 7.72 (d, *J* = 5.3 Hz, 3H), 7.44 – 7.30 (m, 7H), 6.85 (d, *J* = 8.9 Hz, 2H), 5.41 (dd, *J* = 10.0, 3.7 Hz, 1H), 4.19 (dd, *J* = 17.9, 10.1 Hz, 1H), 3.79 (s, 3H), 3.28 (dd, *J* = 17.9, 3.8 Hz, 1H).

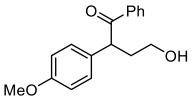
D. Large-scale preparation of 3a and its derivatization:

(a) Large-scale preparation of 3a



To an oven-dried 50 mL Schlenk tube equipped with a stir bar, acyl fluoride **1a** (620 mg, 5.0 mmol, 2.5 equiv.), aryl cyclopropane **2a** (370.5 mg, 2.0 mmol, 1.0 equiv.), photocatalyst 4CzIPN (39.5 mg, 2.5 mol%), **N1** (31.0 mg, 5.0 mol%) and Cs_2CO_3 (1.3 g, 2.0 equiv.) were added. Then, the reaction tube was evacuated and backfilled with argon for two times. Subsequently, anhydrous DCE (10.0 mL, 0.2 M) was added. The resulting mixture was irradiated with blue LED at room temperature for 12 h. The residue was purified by silica gel chromatography to afford the desired product **3a** (554 mg, 74% yield).

(b) Deprotection of 3a



4-Hydroxy-2-(4-methoxyphenyl)-1-phenylbutan-1-one (4a)

The NaOH aq (1 mL, 1 M) solution was added to a solution of **3a** (37.4 mg, 0.10 mmol) in THF (1.0 mL). The reaction mixture was stirred at 80 °C for 6 h. After completion, the mixture was extracted with ethyl acetate (3 × 3 mL). The organic layer was dried by Na_2SO_4, after filtration and evaporated under reduced pressure. Then, the residue was purified by column chromatography on silica gel (pentane/ethyl acetate = 6:1) to afford the desired product **4a** as colorless oil (20.5 mg, 76% yield).

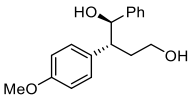
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 – 7.86 (m, 2H), 7.45 – 7.35 (m, 1H), 7.31 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.18 – 7.09 (m, 2H), 6.83 – 6.68 (m, 2H), 4.74 (t, *J* = 7.2 Hz, 1H), 3.68 (s, 3H), 3.64 – 3.45 (m, 2H), 2.33 (ddd, *J* = 14.5, 7.2, 5.2 Hz, 1H), 1.99 (tdd, *J* = 7.4, 6.1, 4.9 Hz, 1H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 200.3, 158.7, 136.7, 132.9, 131.0, 129.4, 128.8, 128.5, 114.5, 60.5, 55.2, 49.1, 36.4.

FTIR (neat): υ (cm^{-1}) 2957, 2930, 1710, 1512, 1248, 1178.

HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{17}H_{18}NaO_3$ 293.1154, found: 293.1148.

(c) Reduction of 3a



2-(4-Methoxyphenyl)-1-phenylbutane-1,4-diol (4b)

A solution of $LiAlH_4$ (19.0 mg, 0.50 mmol, 5.0 equiv.) in dry THF (3 mL) was stirred at 0 °C under N_2 atmosphere. Then, a solution of **3a** (37.4 mg, 0.10 mmol, 1.0 equiv.) in dry THF (2 mL) was added slowly. The reaction mixture was stirred at room temperature for 3 h and quenched with aqueous NaOH (2 mL, 2.5 M) solution. The mixture was extracted with ethyl acetate (3 × 3 mL). The organic layer was dried by Na_2SO_4, after filtration and evaporated under reduced pressure. The diastereoselectivity was determined by ^{1}H NMR on the crude product (>19:1 dr). Then, the residue was purified by column chromatography on silica gel (pentane/ethyl acetate = 2:1) to afford the desired product **4b** as colorless oil (26.4 mg, 97% yield). The relative configuration was confirmed by comparison with a related known compound.[8]

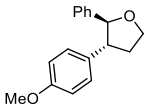
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.24 (m, 5H), 7.20 – 7.12 (m, 2H), 6.92 – 6.86 (m, 2H), 4.72 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 3H), 3.43 (ddd, *J* = 11.7, 6.9, 5.0 Hz, 1H), 3.32 (ddd, *J* = 10.6, 8.0, 6.3 Hz, 1H), 3.00 (ddd, *J* = 12.4, 8.1, 4.5 Hz, 1H), 1.81 – 1.62 (m, 2H).

^{13}C NMR (76 MHz, $CDCl_3$): δ 158.7, 142.4, 132.4, 129.7, 128.3, 127.8, 127.0, 114.2, 78.7, 60.9, 55.3, 49.9, 34.9.

FTIR (neat): υ (cm^{-1}) 3057, 1512, 1420, 1265, 702.

HRMS (ESI-TOF) m/z [M+Na^+] Calcd for $C_{17}H_{20}NaO_3$ 295.1310, found: 295.1302.

(c) Acid-catalyzed cyclization of 4b



3-(4-Methoxyphenyl)-2-phenyltetrahydrofuran (4c)

To a stirred solution of diol **4b** (27.2 mg, 0.10 mmol) in 1.0 mL dry 1,2-dichloroethane in a 5.0 mL reaction tube, TfOH (10.0 mol%) was added under inert atmosphere. The reaction vial was capped and put into an oil bath pre heated at 40 °C for overnight. After completion, the mixture was concentrated under reduced pressure and a column chromatographic purification was performed using silica gel (pentane/ethyl acetate = 50:1) to afford the desired product **4c** as colorless oil (22.6 mg, 89% yield). The relative configuration was confirmed by comparison with a related known compound.[9-10]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21 – 7.06 (m, 5H), 7.06 – 6.94 (m, 2H), 6.83 – 6.73 (m, 2H), 4.70 (d, *J* = 8.5 Hz, 1H), 4.17 (dd, *J* = 8.3, 5.8 Hz, 2H), 3.72 (s, 3H), 3.09 (dt, *J* = 9.6, 8.2 Hz, 1H), 2.42 – 2.30 (m, 1H), 2.23 – 2.10 (m, 1H).

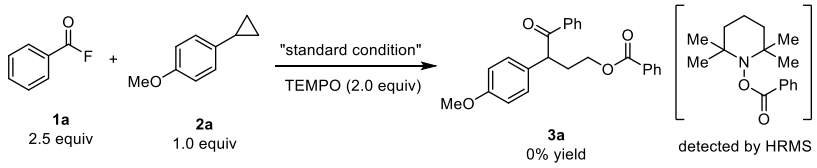
^{13}C NMR (76 MHz, $CDCl_3$): δ 158.4, 141.8, 132.7, 128.7, 128.2, 127.4, 125.8, 113.9, 87.7, 68.5, 55.3, 53.5, 35.6.

FTIR (neat): υ (cm^{-1}) 2968, 1582, 1514, 1339, 1215, 701.

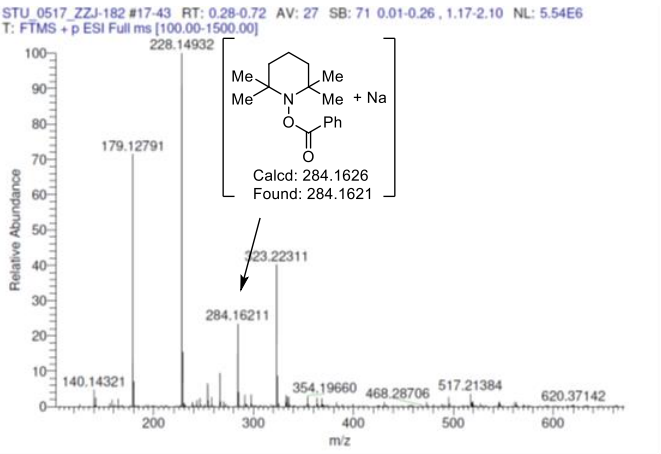
HRMS (ESI-TOF) m/z: [M+Na^+] Calcd for $C_{17}H_{18}NaO_2$ 277.1204, found: 277.1196.

E. Mechanistic studies:

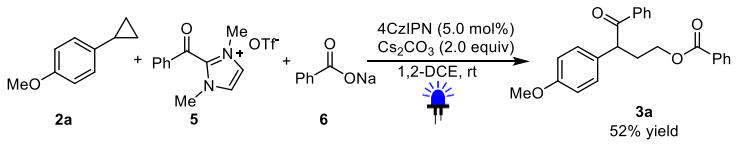
(a) Radical trapping experiment:



To an oven-dried 10 mL Schlenk tube equipped with a stir bar, acyl fluoride **1a** (62.1 mg, 0.50 mmol, 2.5 equiv), aryl cyclopropane **2a** (29.6 mg, 0.20 mmol, 1.0 equiv.), photocatalyst 4CzIPN (7.9 mg, 5.0 mol%), **N1** (6.2 mg, 10.0 mol%), Cs_2CO_3 (130.4 mg, 2.0 equiv.) and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (62.5 mg, 2.0 equiv.) were added. Then, the reaction tube was evacuated and backfilled with argon for two times. Subsequently, anhydrous DCE (2.0 mL, 0.1 M) was added. The resulting mixture was irradiated with blue LED at room temperature for 12 h. The mixture was analyzed by HRMS (see below).



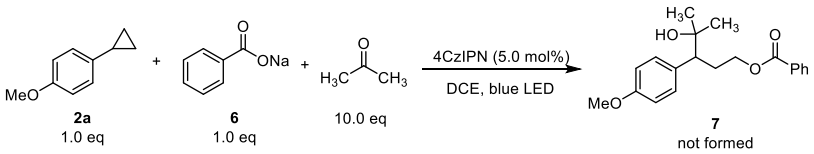
(b) The acyl azolium salt 5 as and Na-benzoate as competent substrates:



To an oven-dried 10 mL Schlenk tube equipped with a stir bar, aryl cyclopropane **2a** (29.6 mg, 0.20 mmol, 1.0 equiv.), acylazolium ion **5** (40.3 mg, 0.20 mmol, 1.0 equiv.), sodium benzoate **6** (28.8 mg, 0.20 mmol, 1.0 equiv.), photocatalyst 4CzIPN (7.9 mg, 5.0 mol%) and Cs_2CO_3 (130.4 mg, 2.0 equiv.)

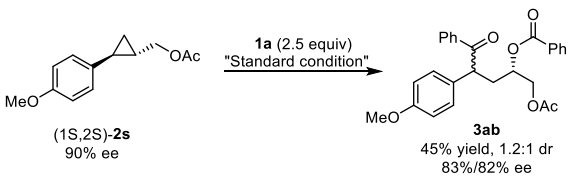
were added. Then, the reaction tube was evacuated and backfilled with argon for two times. Subsequently, anhydrous DCE (2.0 mL, 0.1 M) was added. The resulting mixture was irradiated with blue LEDs at room temperature for 12 h. The residue was purified by silica gel chromatography to afford the desired product **3a** in 52% yield.

(c) The benzyl anion trapping experiment by acetone:



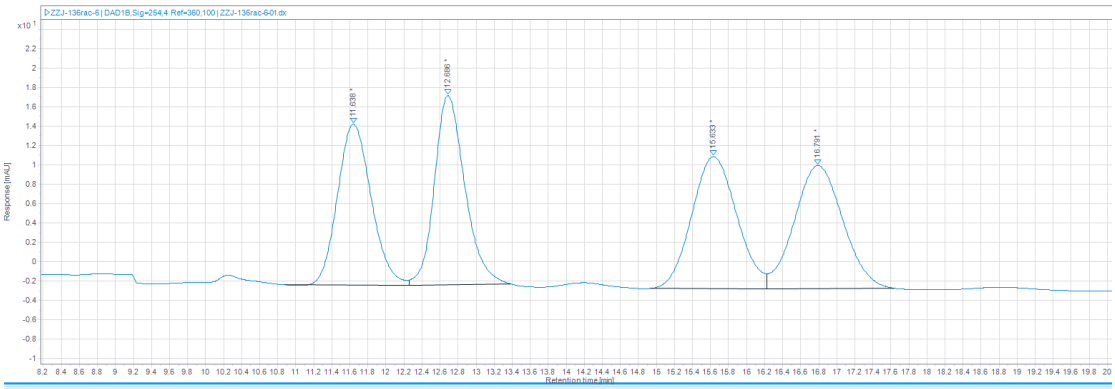
To an oven-dried 10 mL Schlenk tube equipped with a stir bar, aryl cyclopropane **2a** (29.6 mg, 0.20 mmol, 1.0 equiv.), sodium benzoate **6** (28.8 mg, 0.20 mmol, 1.0 equiv.), dry acetone (116 mg, 2.0 mmol, 10.0 equiv.) and photocatalyst 4CzIPN (7.9 mg, 5.0 mol%) were added. Then, the reaction tube was evacuated and backfilled with argon for two times. Subsequently, anhydrous DCE (2.0 mL, 0.1 M) was added. The resulting mixture was irradiated with blue LEDs at room temperature for 12 h. The alcohol **7** was not formed by HRMS measurement.

(d) Experiments with enantiomerically enriched 2s:



The reaction of **(1S,2S)-2s** with 90% ee was performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1) to afford the product **3ab** in 45% yield with 83%/82% ee and 1.2:1 dr. HPLC Analysis: Chiralpak IC (Cyclohexane/iPrOH = 93/7, 1.0 mL/min, 25 °C).

Racemic sample:

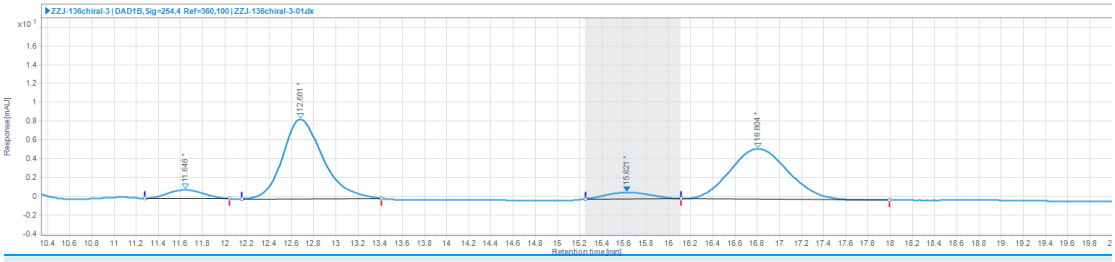


Injection Results

Peaks | Summary

#	Signal description	RT (min)	Area	Area%	Height
1	DAD1B,Sig=254,4 Ref=360,100	11.638	431.266	23.432	16.611
2	DAD1B,Sig=254,4 Ref=360,100	12.686	459.182	24.949	19.533
3	DAD1B,Sig=254,4 Ref=360,100	15.633	474.442	25.778	13.628
4	DAD1B,Sig=254,4 Ref=360,100	16.791	475.602	25.841	12.721

Chiral sample:

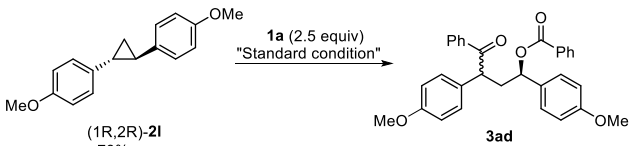


Injection Results

Peaks | Summary

#	Signal description	RT (min)	Area	Area%	Height
1	DAD1B,Sig=254,4 Ref=360,100	11.646	20.541	4.582	0.925
2	DAD1B,Sig=254,4 Ref=360,100	12.681	213.369	47.601	8.467
3	DAD1B,Sig=254,4 Ref=360,100	15.621	18.735	4.180	0.679
4	DAD1B,Sig=254,4 Ref=360,100	16.804	195.601	43.637	5.374

(e) Experiments with enantiomerically enriched 2l:

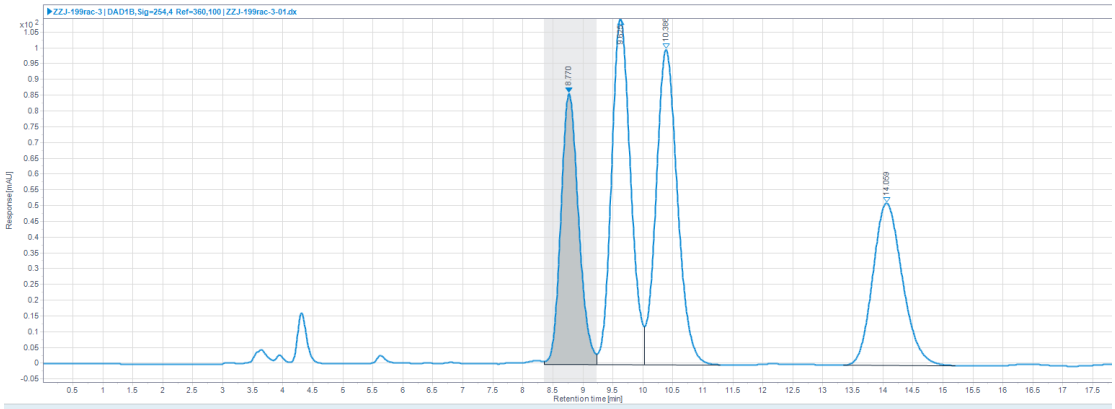


(1R,2R)-**2l**
78% ee

3ad
59% yield, 1.2:1 dr
14%/14% ee

The reaction of **(1R,2R)-2l** with 78% ee was performed with general procedure D and purified by flash silica column chromatography (pentane/ethyl acetate = 10:1) to afford the product **3ad** in 59% yield with 14%/14% ee and 1.2:1 dr. HPLC Analysis: Chiralpak AD-H (Cyclohexane/iPrOH = 90/10, 1.0 mL/min, 25 °C).

Racemic sample:

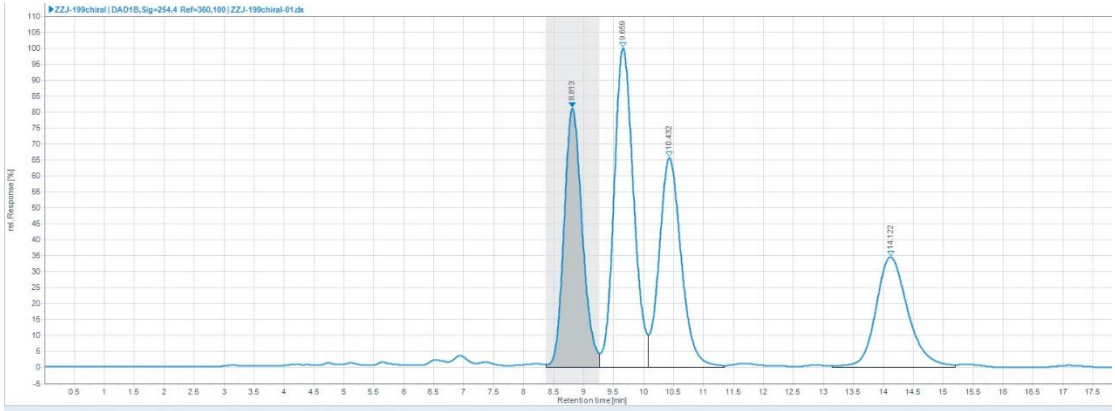


Injection Results

Peaks | Summary

#	Signal description	RT (min)	Area	Area%	Height
1	DAD1B,Sig=254,4 Ref=360,100	8.770	1760.800	20.868	85.787
2	DAD1B,Sig=254,4 Ref=360,100	9.625	2434.452	28.852	109.788
3	DAD1B,Sig=254,4 Ref=360,100	10.386	2475.032	29.333	99.868
4	DAD1B,Sig=254,4 Ref=360,100	14.059	1767.530	20.948	51.510

Chiral sample:

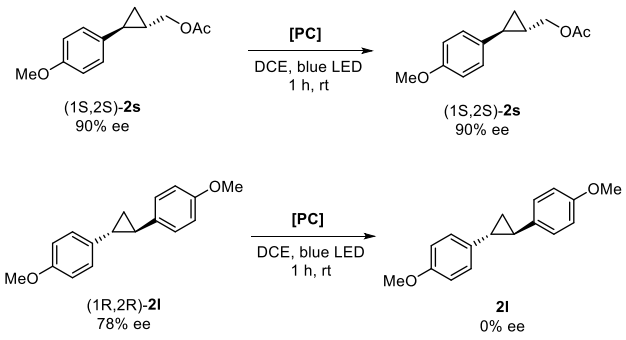


Injection Results

Peaks | Summary

#	Signal description	RT (min)	Area	Area%	Height
1	DAD1B,Sig=254,4 Ref=360,100	8.813	4569.813	24.727	216.154
2	DAD1B,Sig=254,4 Ref=360,100	9.659	6012.796	32.535	266.637
3	DAD1B,Sig=254,4 Ref=360,100	10.432	4464.945	24.160	174.910
4	DAD1B,Sig=254,4 Ref=360,100	14.122	3433.502	18.578	92.384

To our hypothesis of the erosion of stereochemistry due to the rapid ring opening/closing process of the diaryl radical cation, we treated the enantiomerically enriched **2s** and **2l** with blue LED irritation (see below). After one hour, the ee of **2s** would be retained but the diaryl cyclopropane **2l** would be racemization totally. These experimental results could support our assumption.



(1S,2S)-**2s**
90% ee

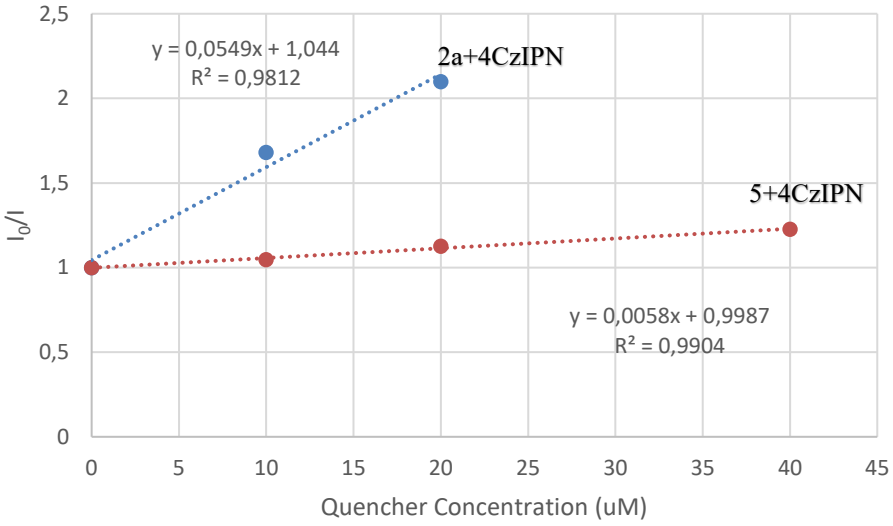
(1S,2S)-**2s**
90% ee

(1R,2R)-**2l**
78% ee

2l
0% ee

(f) Luminescence quenching experiments

Emission intensities were recorded using a Jasco FP-8300 spectrofluorometer. 4-CzIPN solutions were excited at 435 nm and the emission intensity was recorded at 590 nm. In a typical experiment, to a certain amount of a solution of 4-CzIPN in DCE (5 mL), the appropriate amount of quencher (1-cyclopropyl-4-methoxybenzene **2a**, acylazolium ion **5**) was added in a screw-top quartz cuvette, and the emission of the sample was recorded.



F. X-ray data for 3s:

X-Ray diffraction: Data sets for compound **3s** were collected with a Bruker APEXII Kappa CCD diffractometer. Programs used: data collection: APEX3 V2019.1-0[1] (Bruker AXS Inc., **2019**); cell refinement: SAINT V8.40A (Bruker AXS Inc., **2019**); data reduction: SAINT V8.40A (Bruker AXS Inc., **2019**); absorption correction, SADABS V2016/2 (Bruker AXS Inc., **2019**); structure solution *SHELXT-2015*[2] (Sheldrick, G. M. *Acta Cryst.,* **2015**, *A71*, 3-8); structure refinement *SHELXL-2015*[3] (Sheldrick, G. M. *Acta Cryst.,* **2015**, *C71* (1), 3-8) and graphics, *XP*[4] (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

X-ray crystal structure analysis of 3s: A colorless plate-like specimen of $C_{26}H_{24}O_3$, approximate dimensions 0.050 mm x 0.140 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Kappa CCD APEXII Bruker APEXII Diffractometer system equipped with a fine-focus sealed tube Cu sealed tube (CuKα, λ = 1.54178 Å) and a graphite monochromator. A total of 1558 frames were collected. The total exposure time was 21.01 hours. The

frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 12124 reflections to a maximum θ angle of 66.68° (0.84 Å resolution), of which 3457 were independent (average redundancy 3.507, completeness = 99.2%, R_{int} = 4.24%, R_{sig} = 3.80%) and 2728 (78.91%) were greater than $2\sigma(F^2)$. The final cell constants of a = 5.7053(2) Å, b = 9.3059(4) Å, c = 19.1323(7) Å, α = 89.576(2)°, β = 89.233(2)°, γ = 75.384(2)°, volume = 982.82(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 2945 reflections above 20 σ(I) with 9.245° < 2θ < 132.9°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.906. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9130 and 0.9680. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{26}H_{24}O_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 281 variables converged at R1 = 3.97%, for the observed data and wR2 = 10.31% for all data. The goodness-of-fit was 1.051. The largest peak in the final difference electron density synthesis was 0.170 $e^-/Å^3$ and the largest hole was -0.255 $e^-/Å^3$ with an RMS deviation of 0.044 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.299 g/cm^3 and F(000), 408 e^-. CCDC Nr.: 2094400.

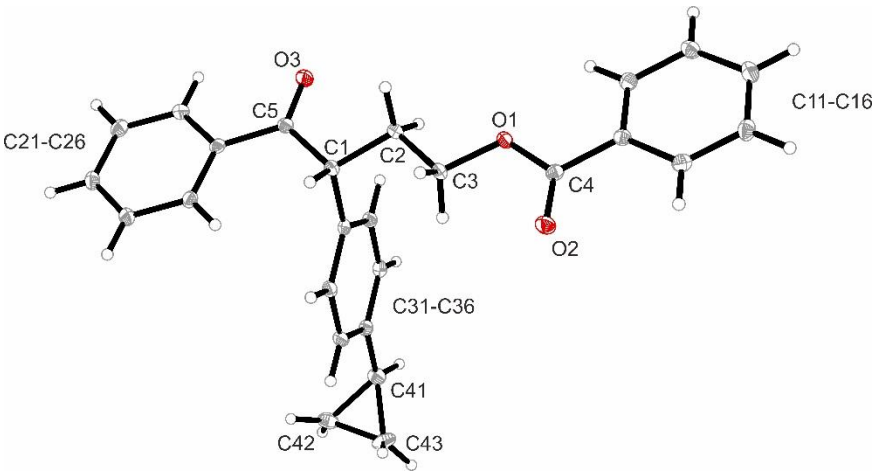


Figure 1: Crystal structure of compound 3s. Thermal ellipsoids are shown at 30% probability.

Table 1. Sample and crystal data for 3s.

Identification code	**3s**

Chemical formula	$C_{26}H_{24}O_3$	
Formula weight	384.45 g/mol	
Temperature	103(2) K	
Wavelength	1.54178 Å	
Crystal size	0.050 x 0.140 x 0.140 mm	
Crystal habit	colorless plate	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.7053(2) Å	α = 89.576(2)°
	b = 9.3059(4) Å	β = 89.233(2)°
	c = 19.1323(7) Å	γ = 75.384(2)°
Volume	982.82(7) $Å^3$	
Z	2	
Density (calculated)	1.299 g/cm^3	
Absorption coefficient	0.664 mm^{-1}	
F(000)	408	

Table 2. Data collection and structure refinement for 3s.

Diffractometer	Kappa CCD APEXII Bruker APEXII Diffractometer
Radiation source	fine-focus sealed tube Cu sealed tube (CuKα, λ = 1.54178 Å)
Theta range for data collection	4.62 to 66.68°
Index ranges	-6<=h<=6, -11<=k<=11, -22<=l<=22
Reflections collected	12124
Independent reflections	3457 [R(int) = 0.0424]
Coverage of independent reflections	99.2%

Absorption correction	Multi-Scan	
Max. and min. transmission	0.9680 and 0.9130	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3457 / 49 / 281	
Goodness-of-fit on F^2	1.051	
Final R indices	2728 data; I>2σ(I)	R1 = 0.0397, wR2 = 0.0964
	all data	R1 = 0.0528, wR2 = 0.1031
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0531P)^2+0.1073P]$where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.170 and -0.255 eÅ^{-3}	
R.M.S. deviation from mean	0.044 eÅ^{-3}	

Table 3. Bond lengths (Å) for 3s.

C1-C31	1.528(2)	C1-C5	1.530(2)
C1-C2	1.5372(19)	C1-H1	1.0
C2-C3	1.514(2)	C2-H2A	0.99
C2-H2B	0.99	C3-O1	1.4470(17)
C3-H3A	0.99	C3-H3B	0.99
C4-O2	1.2069(18)	C4-O1	1.3448(19)
C4-C11	1.490(2)	C5-O3	1.2187(18)
C5-C21	1.502(2)	C11-C12	1.388(2)
C11-C16	1.393(2)	C12-C13	1.388(2)
C12-H12	0.95	C13-C14	1.386(2)
C13-H13	0.95	C14-C15	1.389(2)

C14-H14	0.95	C15-C16	1.386(2)
C15-H15	0.95	C16-H16	0.95
C21-C22	1.394(2)	C21-C26	1.396(2)
C22-C23	1.386(2)	C22-H22	0.95
C23-C24	1.388(2)	C23-H23	0.95
C24-C25	1.388(2)	C24-H24	0.95
C25-C26	1.385(2)	C25-H25	0.95
C26-H26	0.95	C31-C36	1.392(2)
C31-C32	1.393(2)	C32-C33	1.386(2)
C32-H32	0.95	C33-C34	1.397(2)
C33-H33	0.95	C34-C35	1.397(2)
C34-C41	1.486(2)	C35-C36	1.387(2)
C35-H35	0.95	C36-H36	0.95
C41-C42A	1.497(10)	C41-C43	1.506(5)
C41-C42	1.516(5)	C41-C43A	1.528(11)
C41-H41	1.0	C41-H41A	1.0
C42-C43	1.490(6)	C42-H42A	0.99
C42-H42B	0.99	C43-H43A	0.99
C43-H43B	0.99	C42A-C43A	1.471(11)
C42A-H42C	0.99	C42A-H42D	0.99
C43A-H43C	0.99	C43A-H43D	0.99

Table 4. Bond angles (°) for 3s.

C31-C1-C5	107.88(12)	C31-C1-C2	111.92(12)
C5-C1-C2	111.15(12)	C31-C1-H1	108.6
C5-C1-H1	108.6	C2-C1-H1	108.6
C3-C2-C1	110.13(12)	C3-C2-H2A	109.6
C1-C2-H2A	109.6	C3-C2-H2B	109.6
C1-C2-H2B	109.6	H2A-C2-H2B	108.1
O1-C3-C2	107.52(11)	O1-C3-H3A	110.2
C2-C3-H3A	110.2	O1-C3-H3B	110.2
C2-C3-H3B	110.2	H3A-C3-H3B	108.5
O2-C4-O1	123.26(13)	O2-C4-C11	124.78(14)
O1-C4-C11	111.96(12)	O3-C5-C21	120.53(14)
O3-C5-C1	120.70(13)	C21-C5-C1	118.68(12)
C4-O1-C3	115.39(11)	C12-C11-C16	119.63(14)
C12-C11-C4	121.88(14)	C16-C11-C4	118.49(13)
C11-C12-C13	120.08(15)	C11-C12-H12	120.0
C13-C12-H12	120.0	C14-C13-C12	120.31(15)
C14-C13-H13	119.8	C12-C13-H13	119.8
C13-C14-C15	119.64(14)	C13-C14-H14	120.2
C15-C14-H14	120.2	C16-C15-C14	120.23(15)
C16-C15-H15	119.9	C14-C15-H15	119.9
C15-C16-C11	120.09(14)	C15-C16-H16	120.0
C11-C16-H16	120.0	C22-C21-C26	118.77(14)
C22-C21-C5	118.00(13)	C26-C21-C5	123.23(14)
C23-C22-C21	120.96(14)	C23-C22-H22	119.5
C21-C22-H22	119.5	C22-C23-C24	119.62(15)
C22-C23-H23	120.2	C24-C23-H23	120.2

C25-C24-C23	120.07(14)	C25-C24-H24	120.0
C23-C24-H24	120.0	C26-C25-C24	120.17(14)
C26-C25-H25	119.9	C24-C25-H25	119.9
C25-C26-C21	120.40(14)	C25-C26-H26	119.8
C21-C26-H26	119.8	C36-C31-C32	117.50(14)
C36-C31-C1	122.18(13)	C32-C31-C1	120.32(13)
C33-C32-C31	121.27(14)	C33-C32-H32	119.4
C31-C32-H32	119.4	C32-C33-C34	121.33(14)
C32-C33-H33	119.3	C34-C33-H33	119.3
C35-C34-C33	117.33(14)	C35-C34-C41	122.67(14)
C33-C34-C41	120.00(14)	C36-C35-C34	121.11(13)
C36-C35-H35	119.4	C34-C35-H35	119.4
C35-C36-C31	121.46(14)	C35-C36-H36	119.3
C31-C36-H36	119.3	C34-C41-C42A	123.8(5)
C34-C41-C43	121.4(3)	C34-C41-C42	118.2(3)
C43-C41-C42	59.1(2)	C34-C41-C43A	119.5(6)
C42A-C41-C43A	58.2(5)	C34-C41-H41	115.5
C43-C41-H41	115.5	C42-C41-H41	115.5
C34-C41-H41A	114.6	C42A-C41-H41A	114.6
C43A-C41-H41A	114.6	C43-C42-C41	60.2(3)
C43-C42-H42A	117.8	C41-C42-H42A	117.8
C43-C42-H42B	117.8	C41-C42-H42B	117.8
H42A-C42-H42B	114.9	C42-C43-C41	60.8(3)
C42-C43-H43A	117.7	C41-C43-H43A	117.7
C42-C43-H43B	117.7	C41-C43-H43B	117.7
H43A-C43-H43B	114.8	C43A-C42A-C41	62.0(6)
C43A-C42A-H42C	117.6	C41-C42A-H42C	117.6

C43A-C42A-H42D	117.6	C41-C42A-H42D	117.6
H42C-C42A-H42D	114.7	C42A-C43A-C41	59.8(5)
C42A-C43A-H43C	117.8	C41-C43A-H43C	117.8
C42A-C43A-H43D	117.8	C41-C43A-H43D	117.8
H43C-C43A-H43D	114.9		

Table 5. Torsion angles (°) for 3s.

C31-C1-C2-C3	-68.75(16)	C5-C1-C2-C3	170.56(13)
C1-C2-C3-O1	169.26(12)	C31-C1-C5-O3	-105.15(16)
C2-C1-C5-O3	17.9(2)	C31-C1-C5-C21	71.49(16)
C2-C1-C5-C21	-165.46(12)	O2-C4-O1-C3	-2.3(2)
C11-C4-O1-C3	178.12(12)	C2-C3-O1-C4	-176.84(12)
O2-C4-C11-C12	177.08(15)	O1-C4-C11-C12	-3.4(2)
O2-C4-C11-C16	-3.7(2)	O1-C4-C11-C16	175.90(13)
C16-C11-C12-C13	-1.6(2)	C4-C11-C12-C13	177.69(14)
C11-C12-C13-C14	1.1(2)	C12-C13-C14-C15	0.2(2)
C13-C14-C15-C16	-1.0(2)	C14-C15-C16-C11	0.5(2)
C12-C11-C16-C15	0.8(2)	C4-C11-C16-C15	-178.49(14)
O3-C5-C21-C22	3.9(2)	C1-C5-C21-C22	-172.79(13)
O3-C5-C21-C26	-176.41(15)	C1-C5-C21-C26	6.9(2)
C26-C21-C22-C23	-0.3(2)	C5-C21-C22-C23	179.46(14)
C21-C22-C23-C24	-1.0(2)	C22-C23-C24-C25	1.4(2)
C23-C24-C25-C26	-0.6(2)	C24-C25-C26-C21	-0.7(2)
C22-C21-C26-C25	1.1(2)	C5-C21-C26-C25	-178.63(14)
C5-C1-C31-C36	-119.40(15)	C2-C1-C31-C36	118.03(15)
C5-C1-C31-C32	60.20(17)	C2-C1-C31-C32	-62.37(18)
C36-C31-C32-C33	0.1(2)	C1-C31-C32-C33	-179.50(14)

C31-C32-C33-C34	0.3(2)	C32-C33-C34-C35	-0.6(2)
C32-C33-C34-C41	179.47(14)	C33-C34-C35-C36	0.5(2)
C41-C34-C35-C36	-179.59(15)	C34-C35-C36-C31	-0.1(2)
C32-C31-C36-C35	-0.2(2)	C1-C31-C36-C35	179.38(14)
C35-C34-C41-C42A	27.3(11)	C33-C34-C41-C42A	-152.8(11)
C35-C34-C41-C43	-22.0(6)	C33-C34-C41-C43	157.9(5)
C35-C34-C41-C42	47.1(4)	C33-C34-C41-C42	-133.0(4)
C35-C34-C41-C43A	-42.3(9)	C33-C34-C41-C43A	137.6(8)
C34-C41-C42-C43	-111.6(3)	C34-C41-C43-C42	106.3(4)
C34-C41-C42A-C43A	-106.4(9)	C34-C41-C43A-C42A	113.6(7)

G. References:

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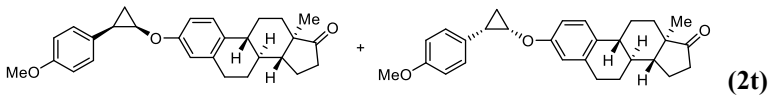
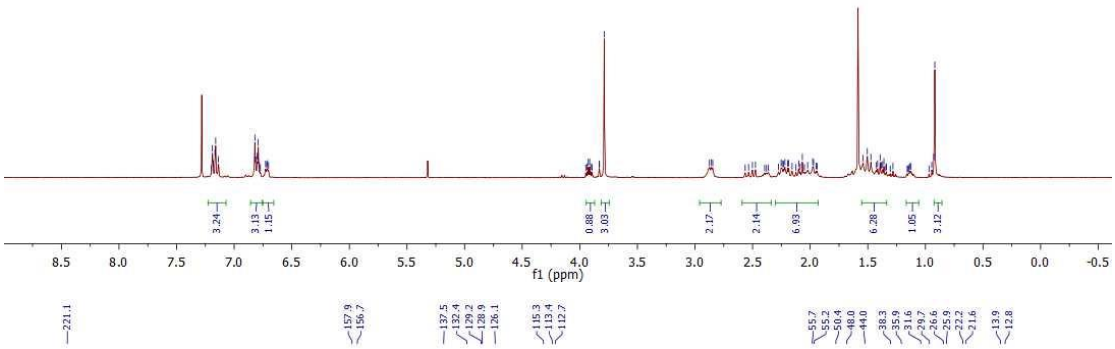
H. NMR spectrum:

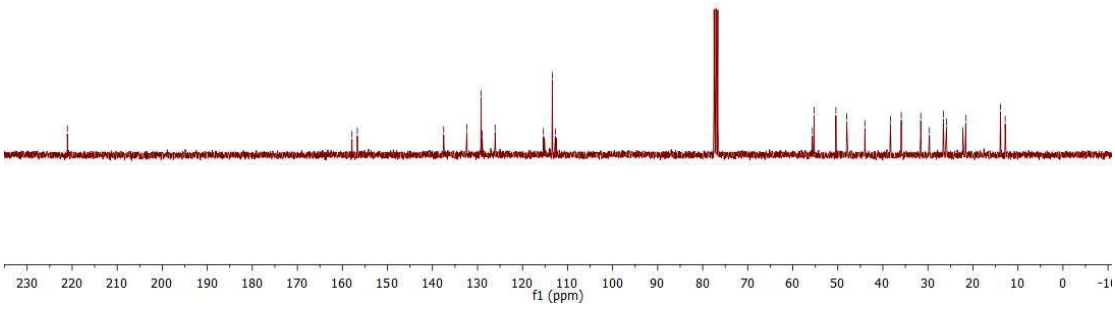


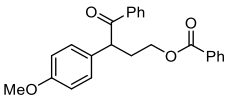
(2t)

300 MHz in $CDCl_3$



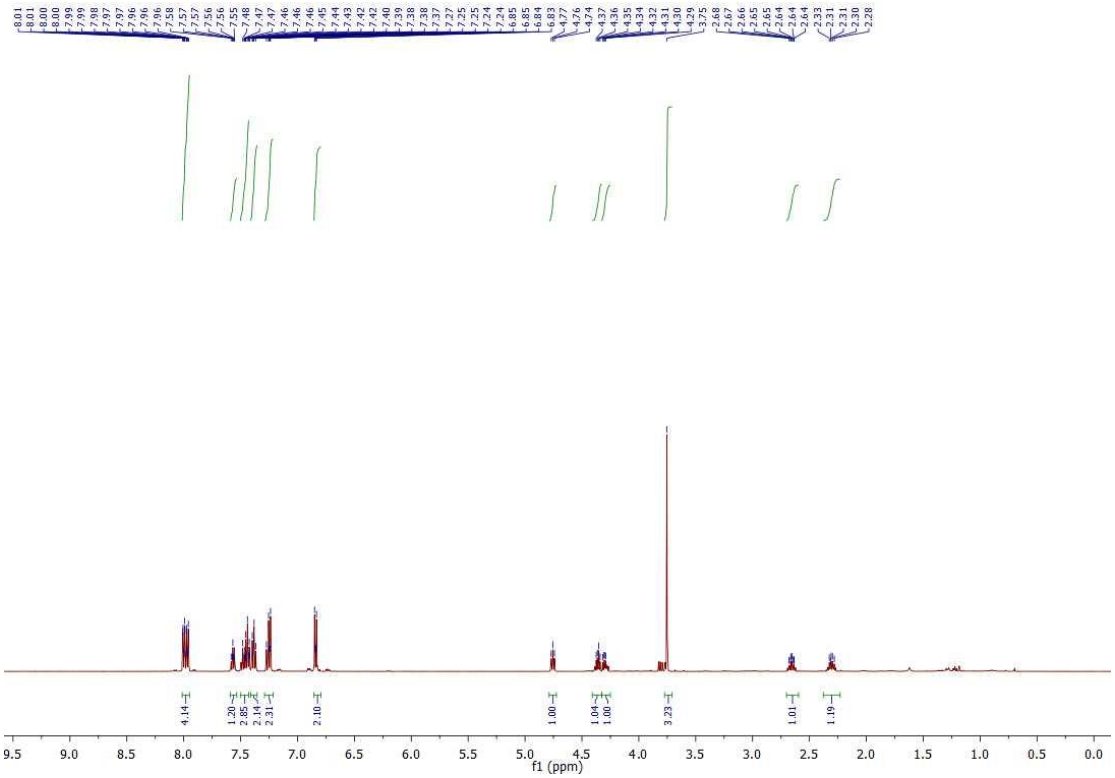
75 MHz in $CDCl_3$



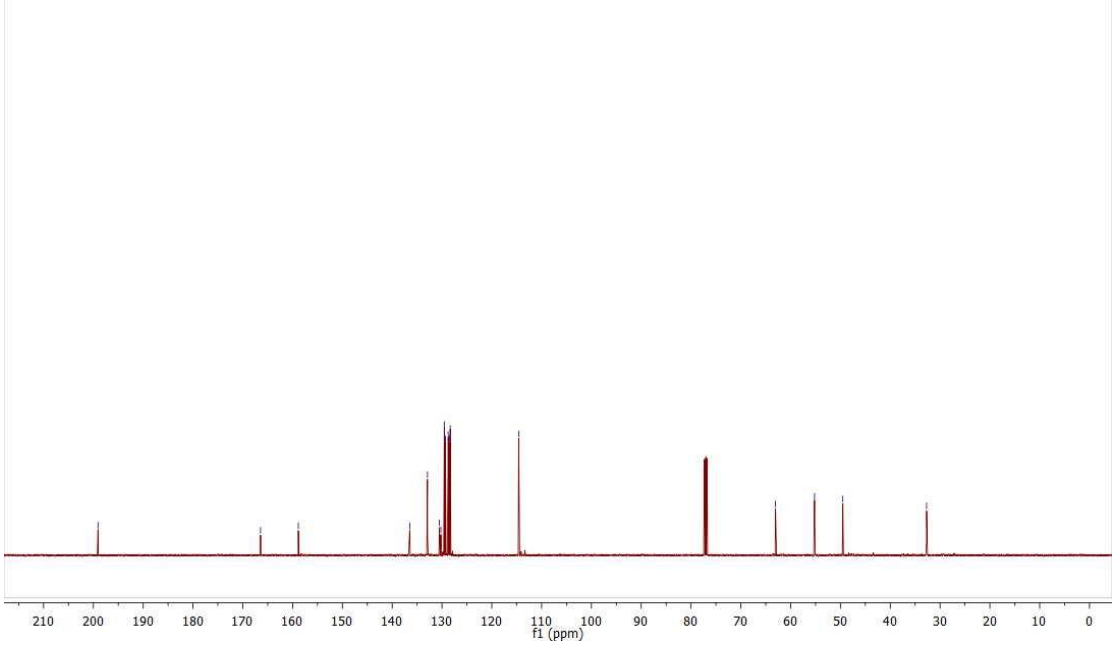


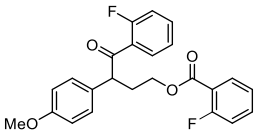
(3a)

500 MHz in $CDCl_3$



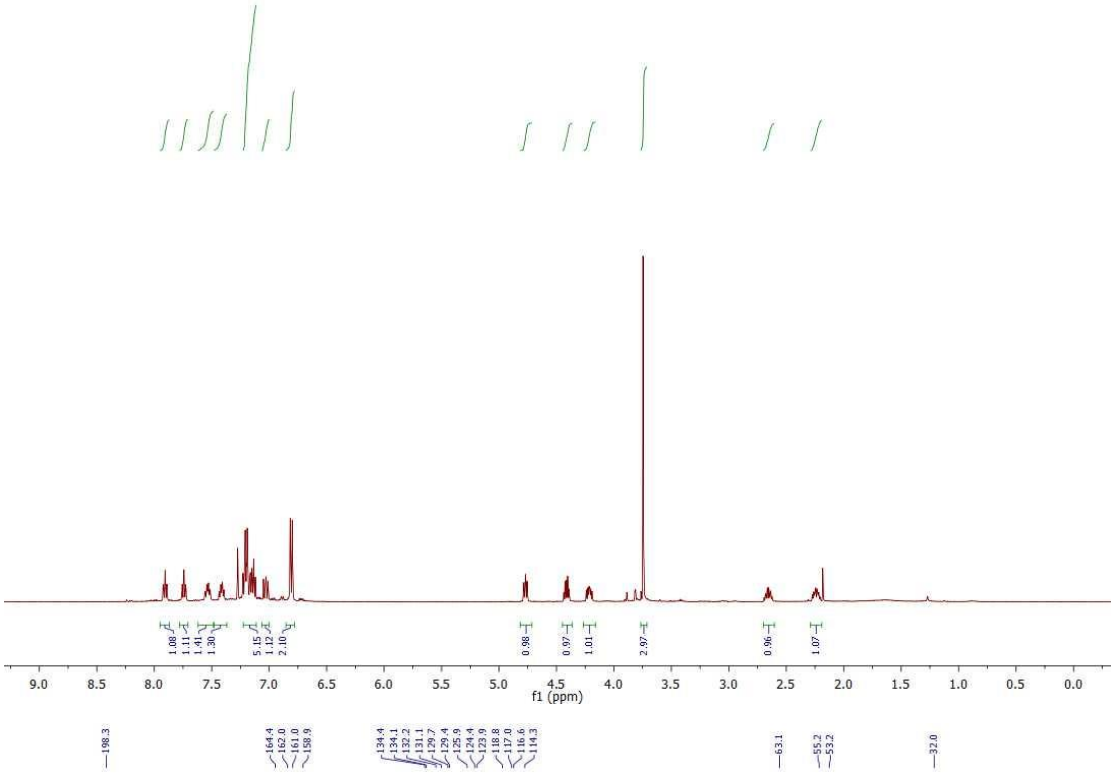
126 MHz in $CDCl_3$





(3b)

500 MHz in $CDCl_3$



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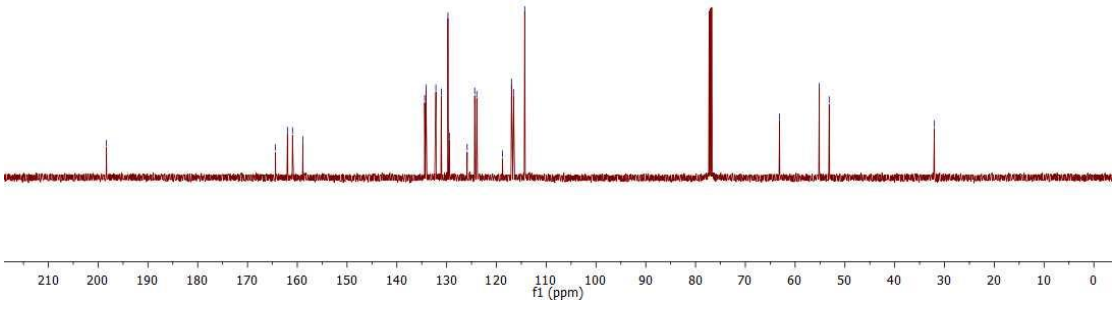

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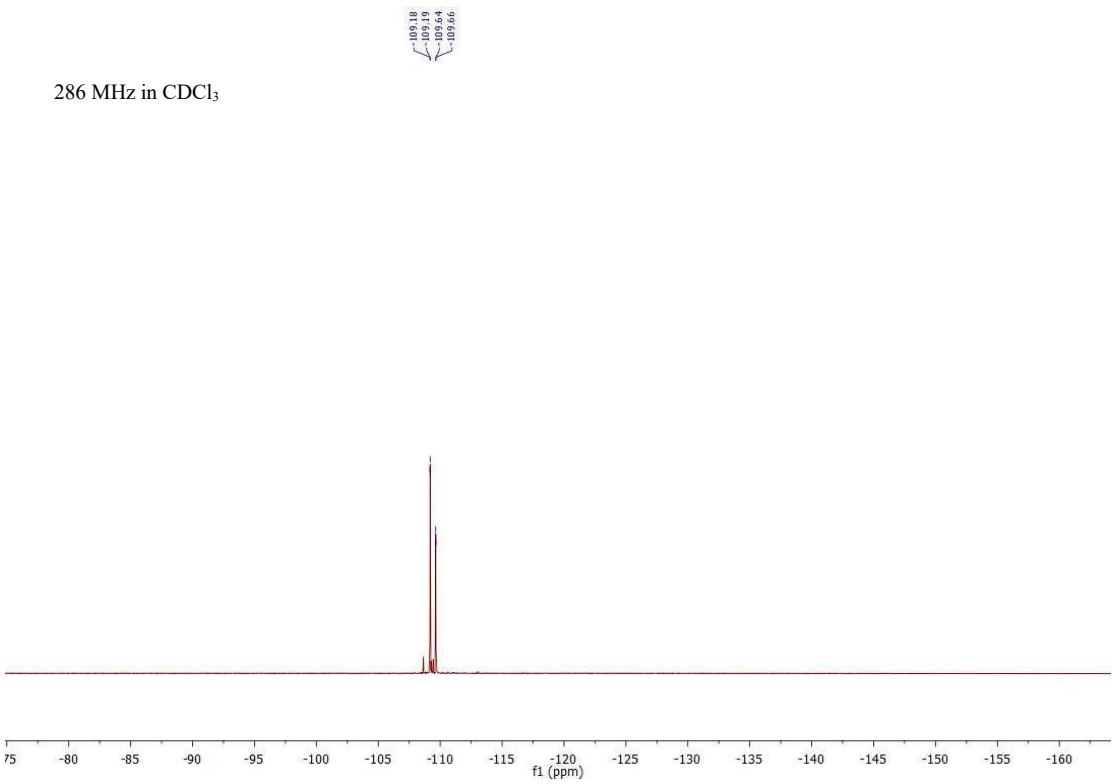
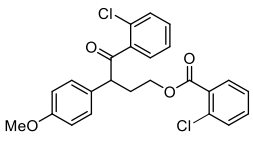
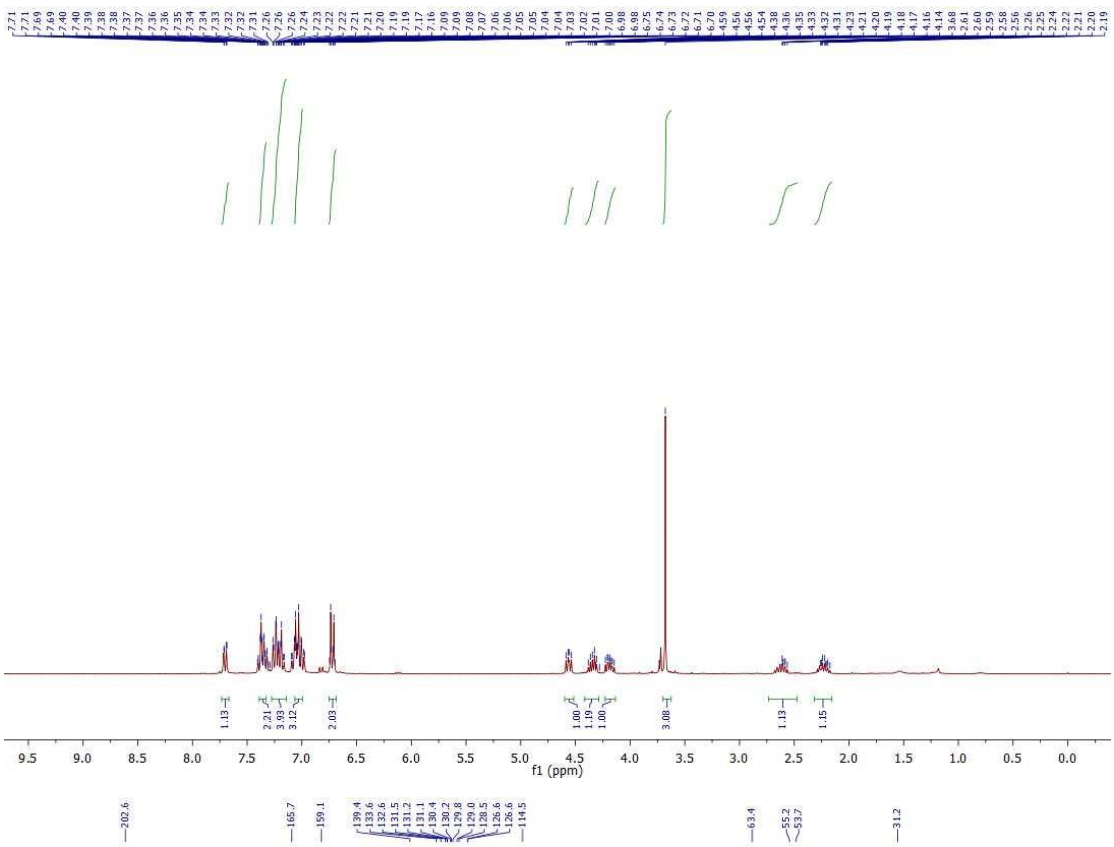


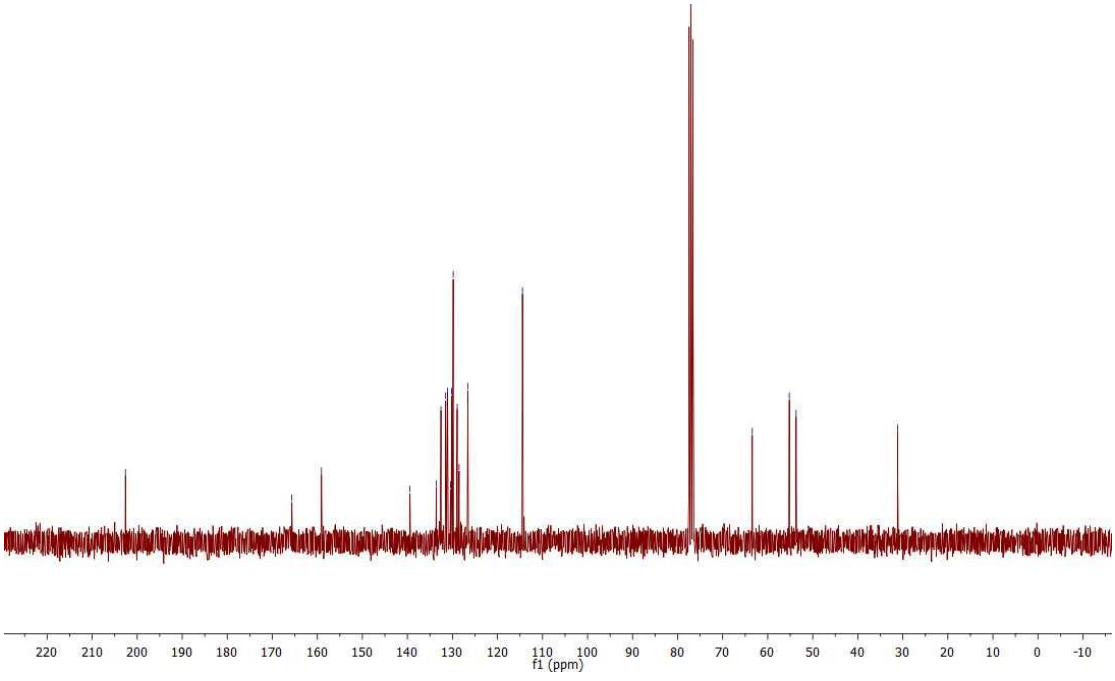


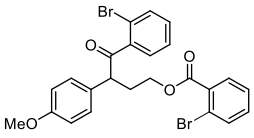
(3c)

300 MHz in $CDCl_3$



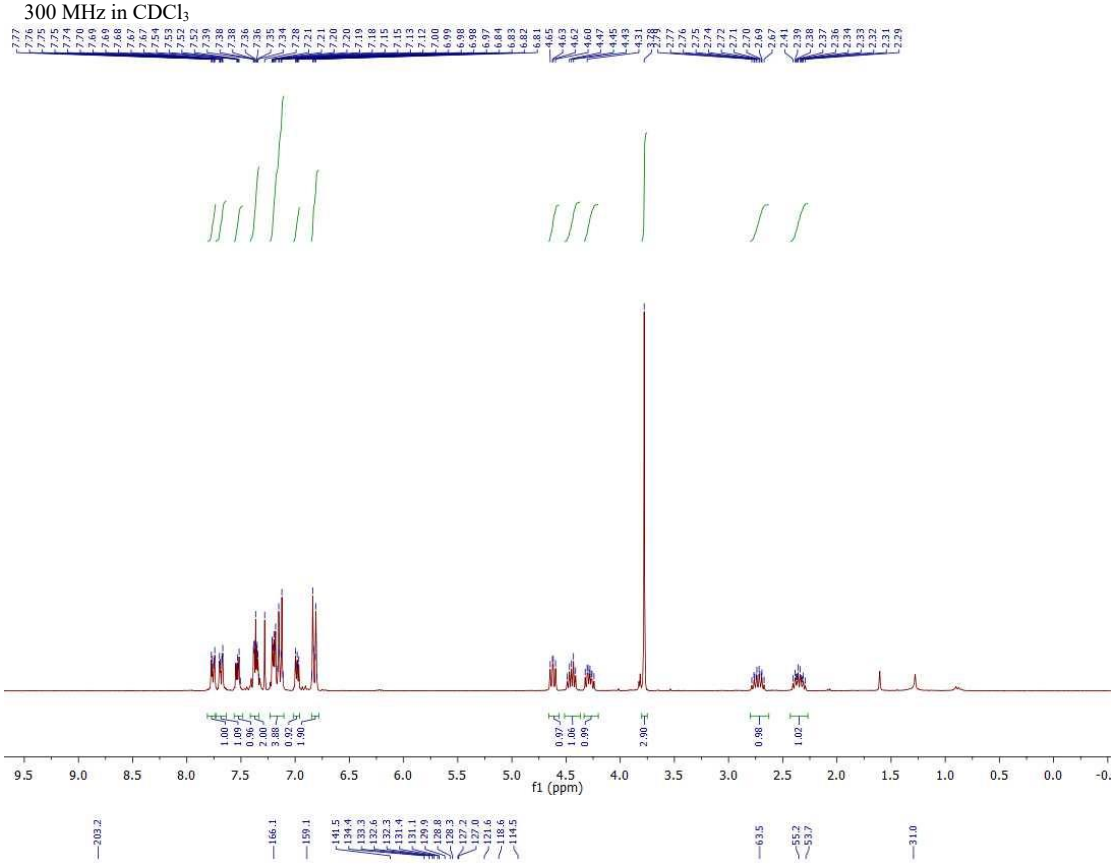
76 MHz in $CDCl_3$



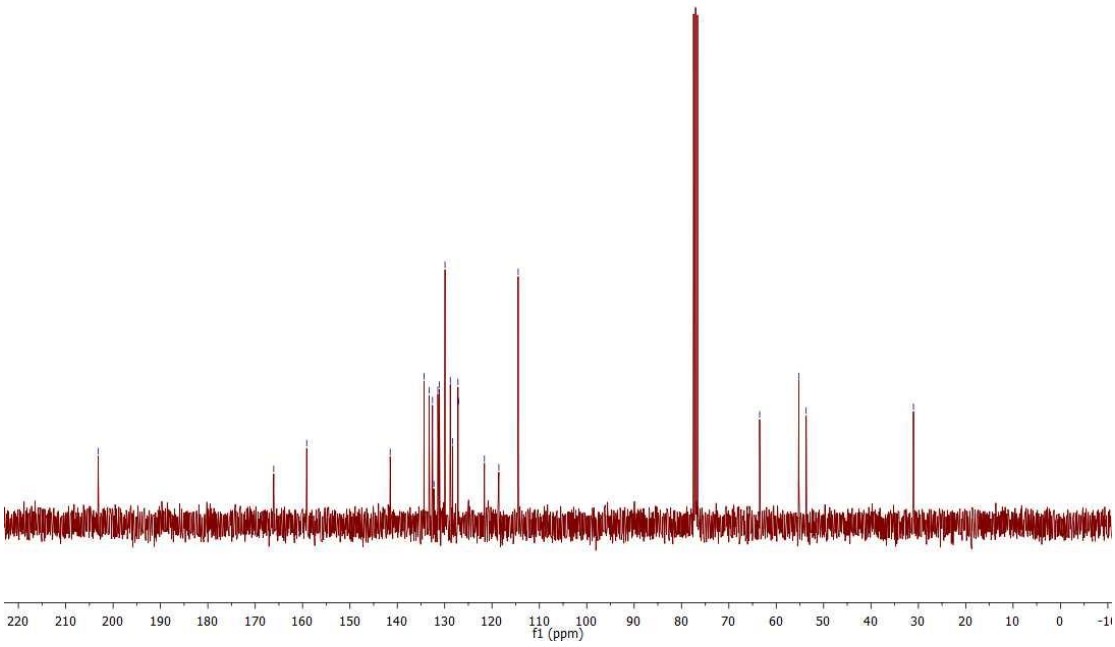


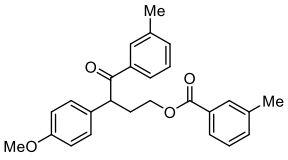
(3d)

300 MHz in $CDCl_3$



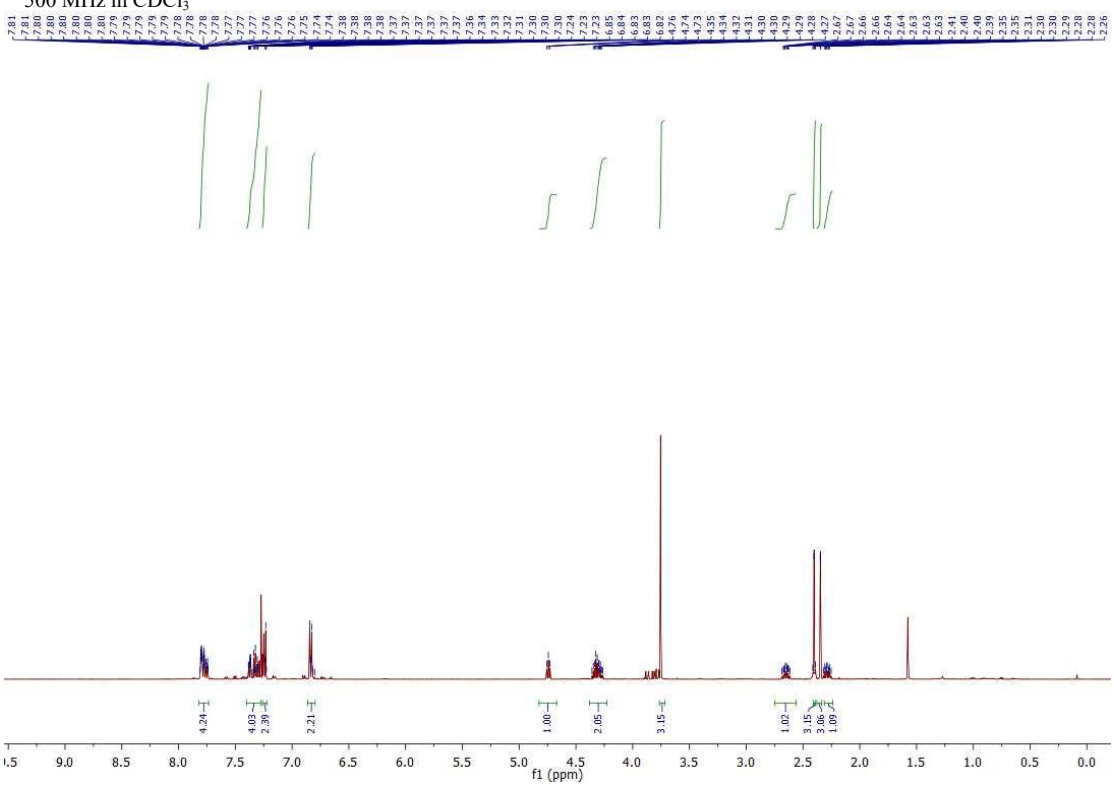
76 MHz in $CDCl_3$



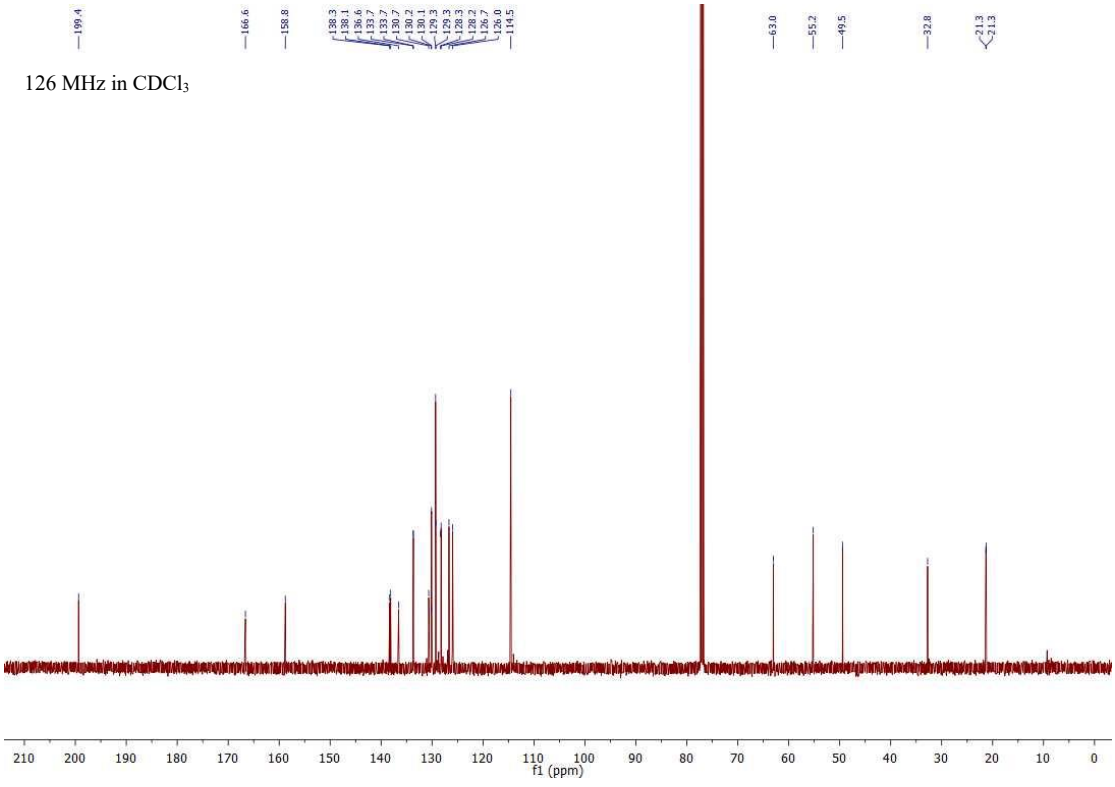


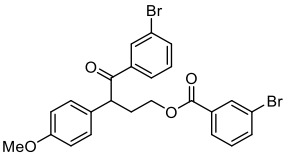
(3e)

500 MHz in $CDCl_3$



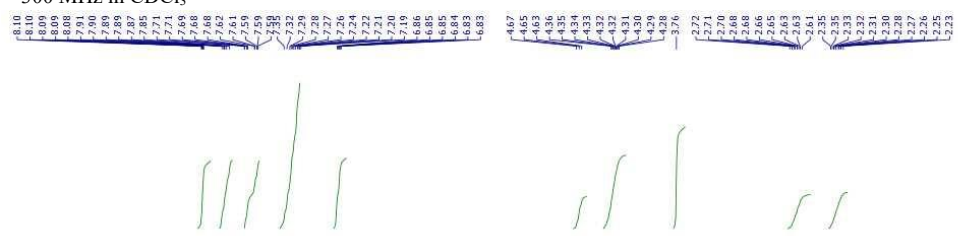
126 MHz in $CDCl_3$

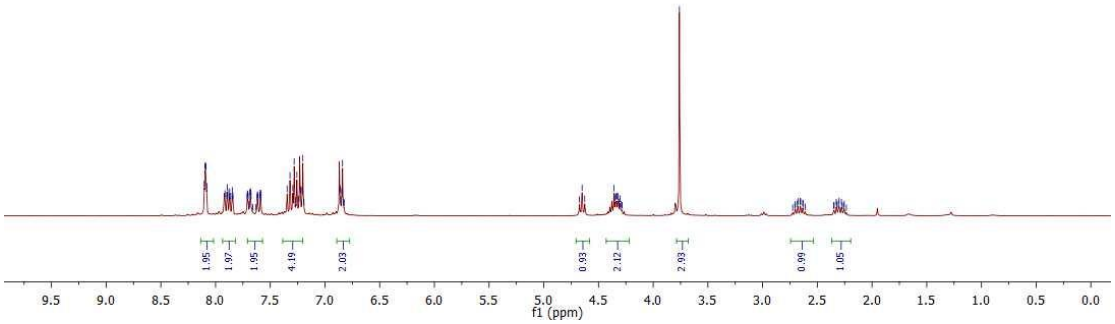




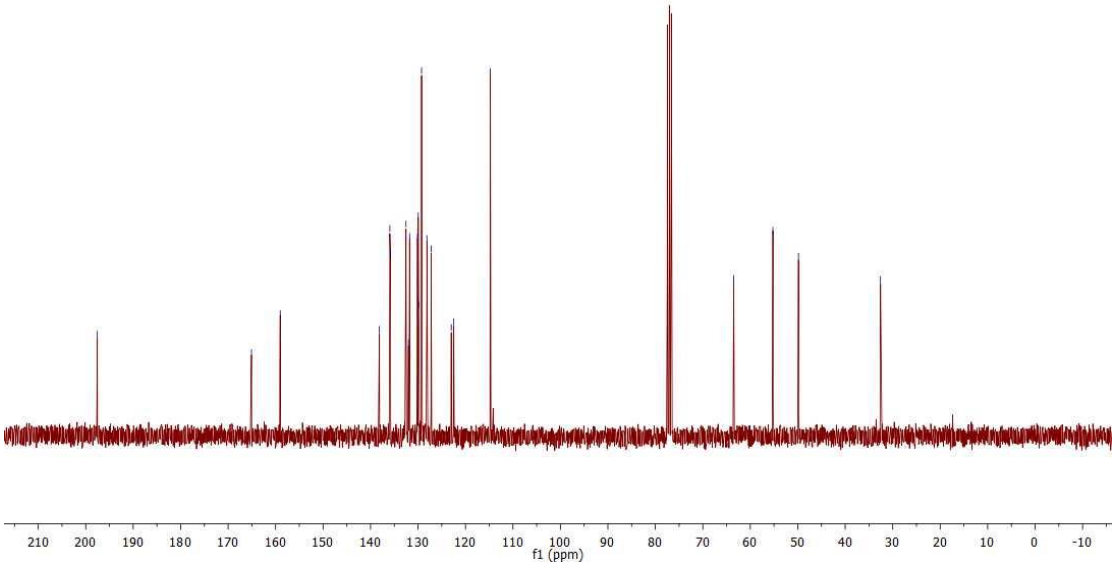
(3f)

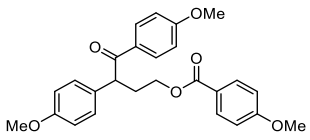
300 MHz in $CDCl_3$





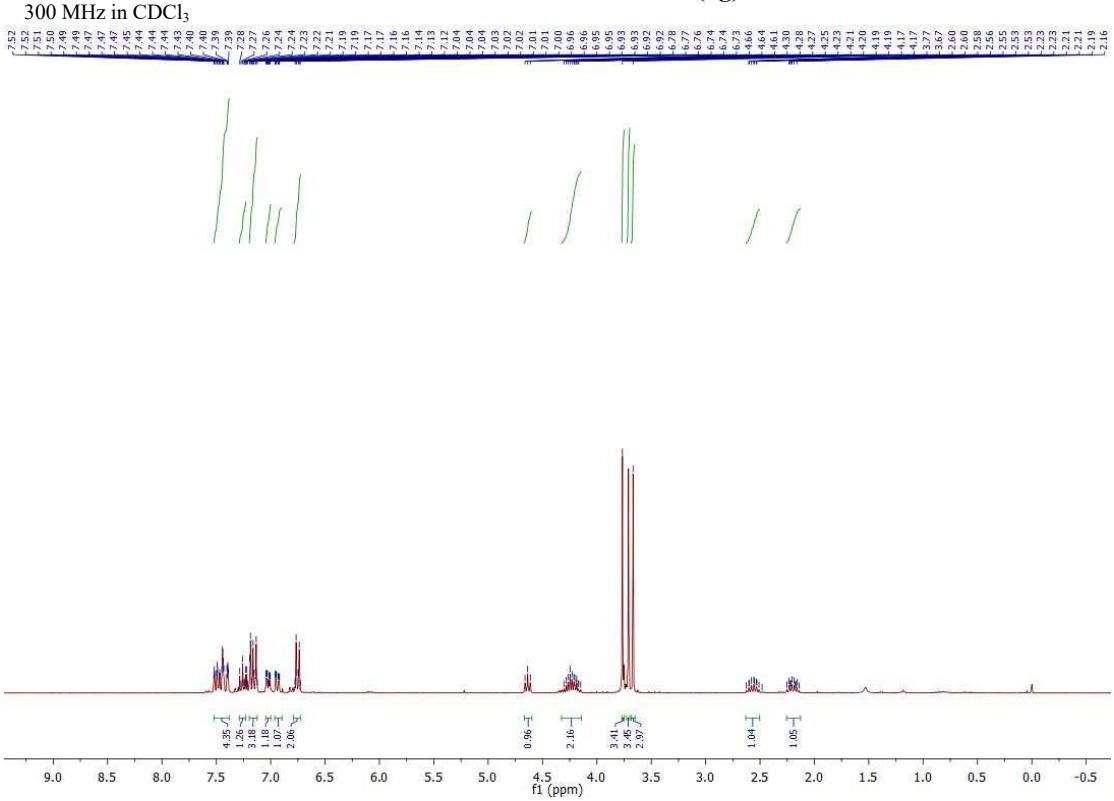
76 MHz in $CDCl_3$



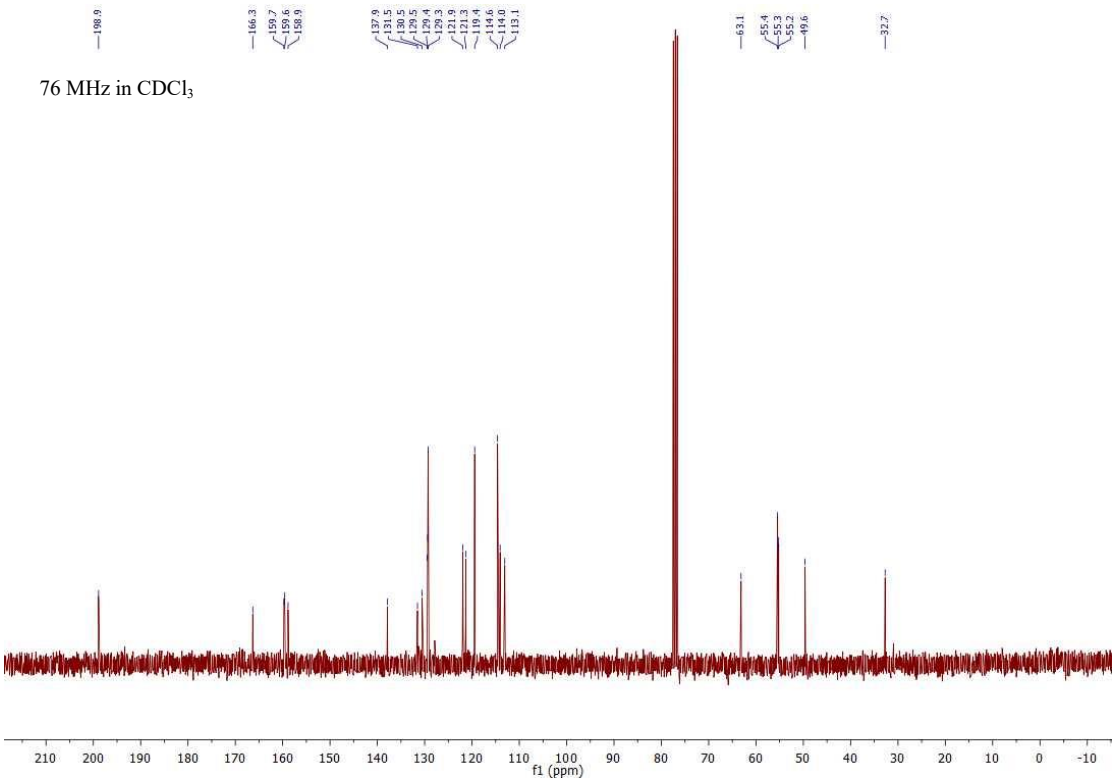


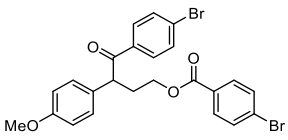
(3g)

300 MHz in $CDCl_3$



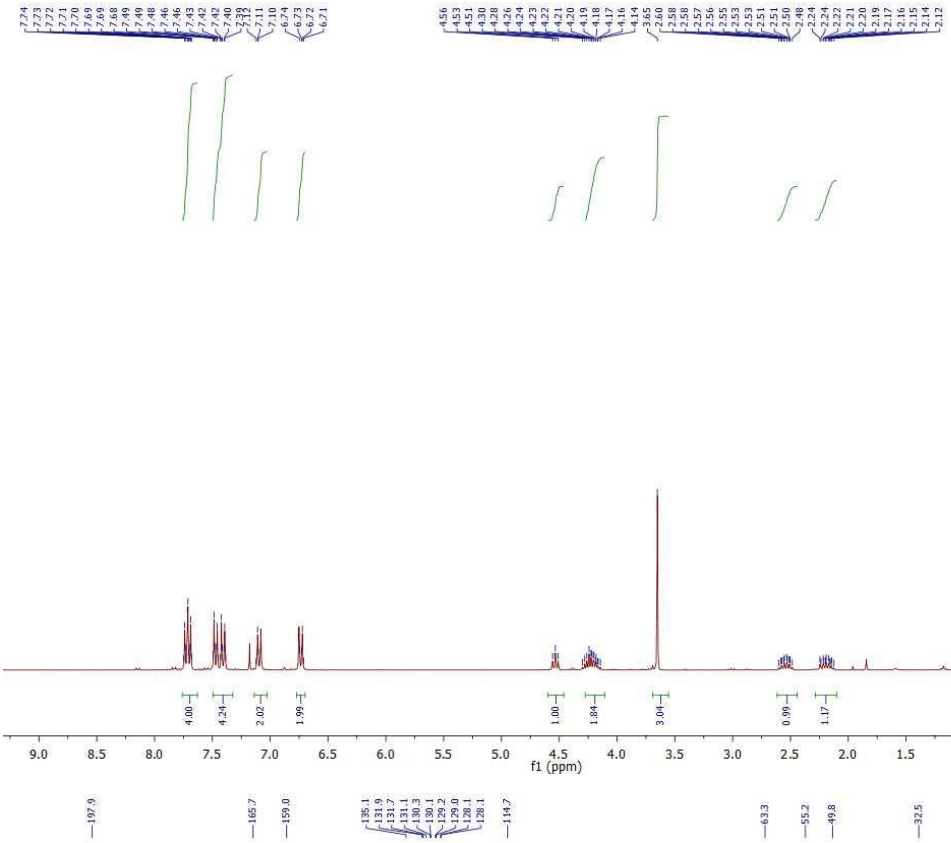
76 MHz in $CDCl_3$



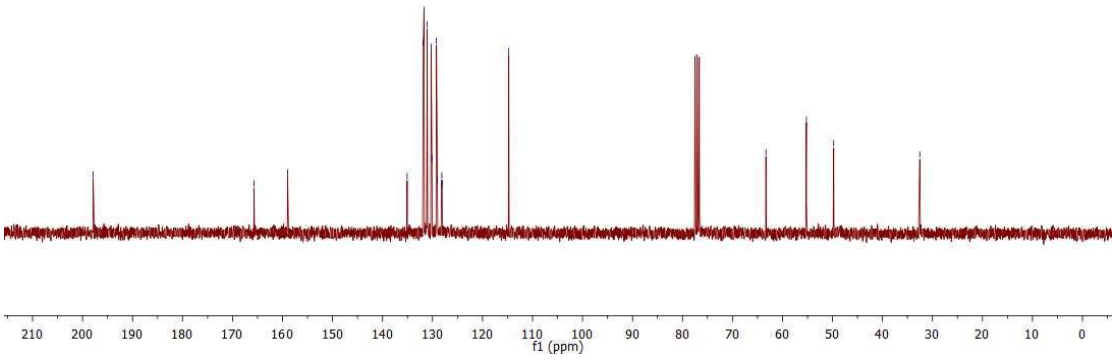


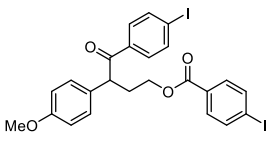
(3h)

300 MHz in $CDCl_3$



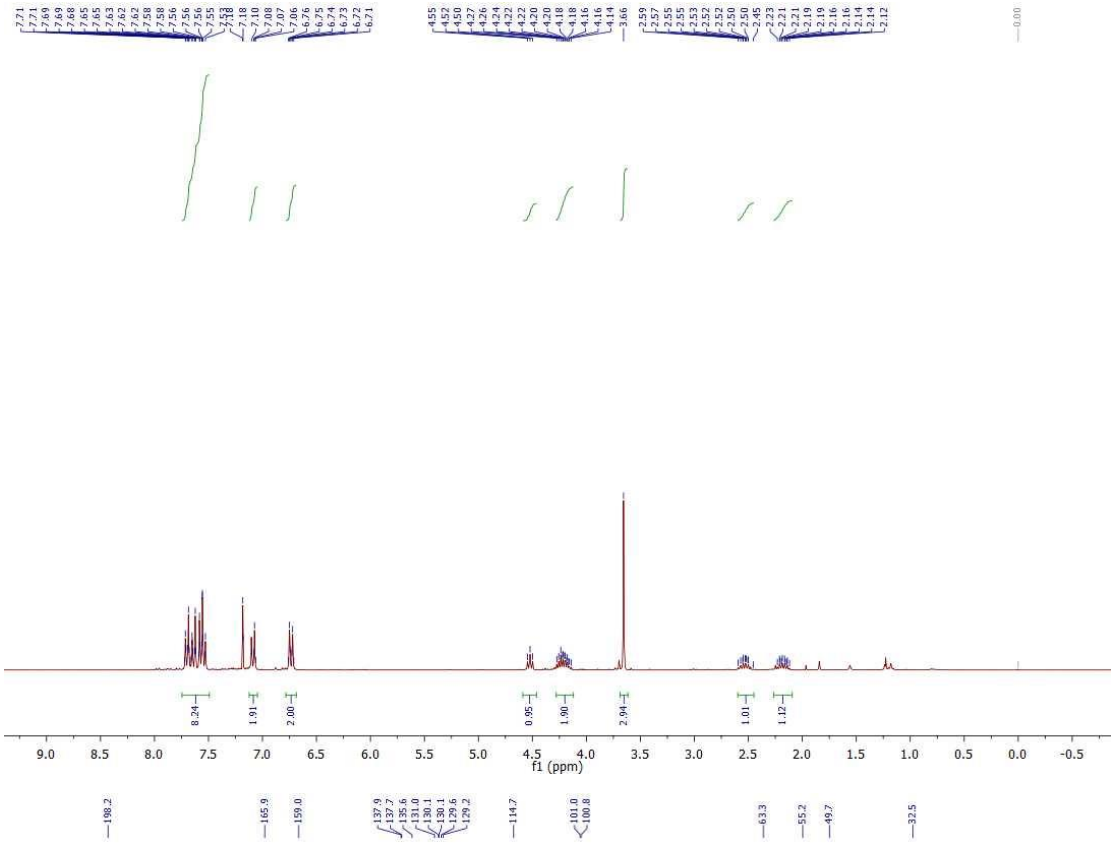
76 MHz in $CDCl_3$



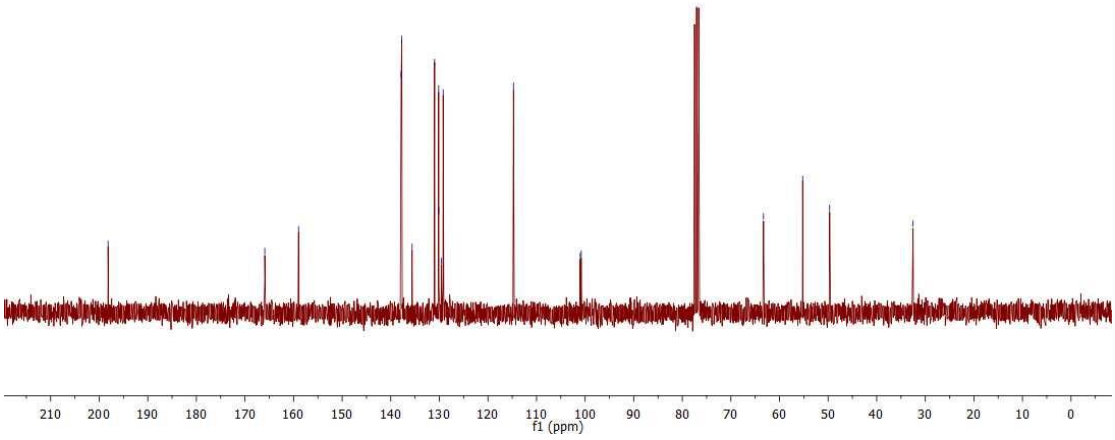


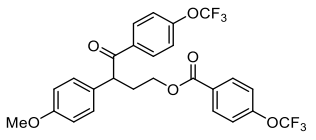
(3i)

300 MHz in $CDCl_3$



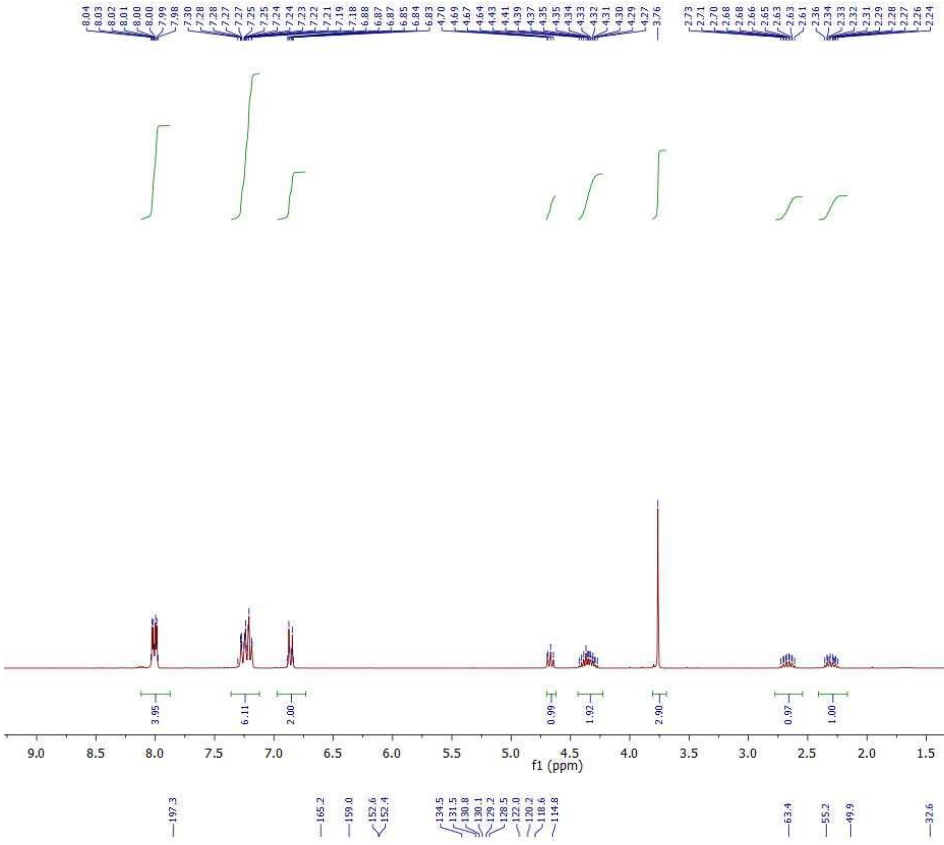
76 MHz in $CDCl_3$



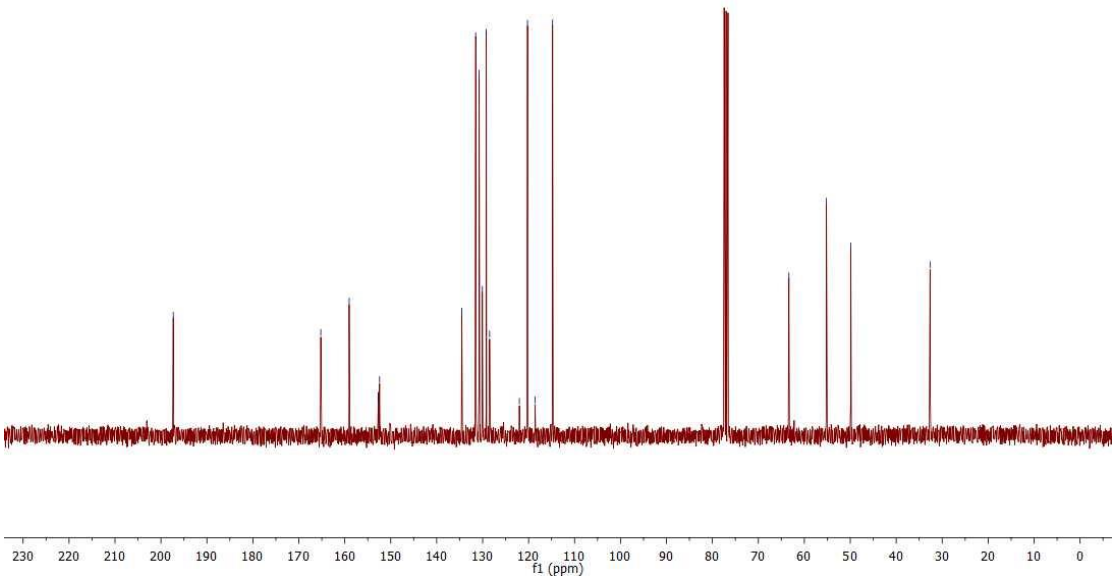


(3j)

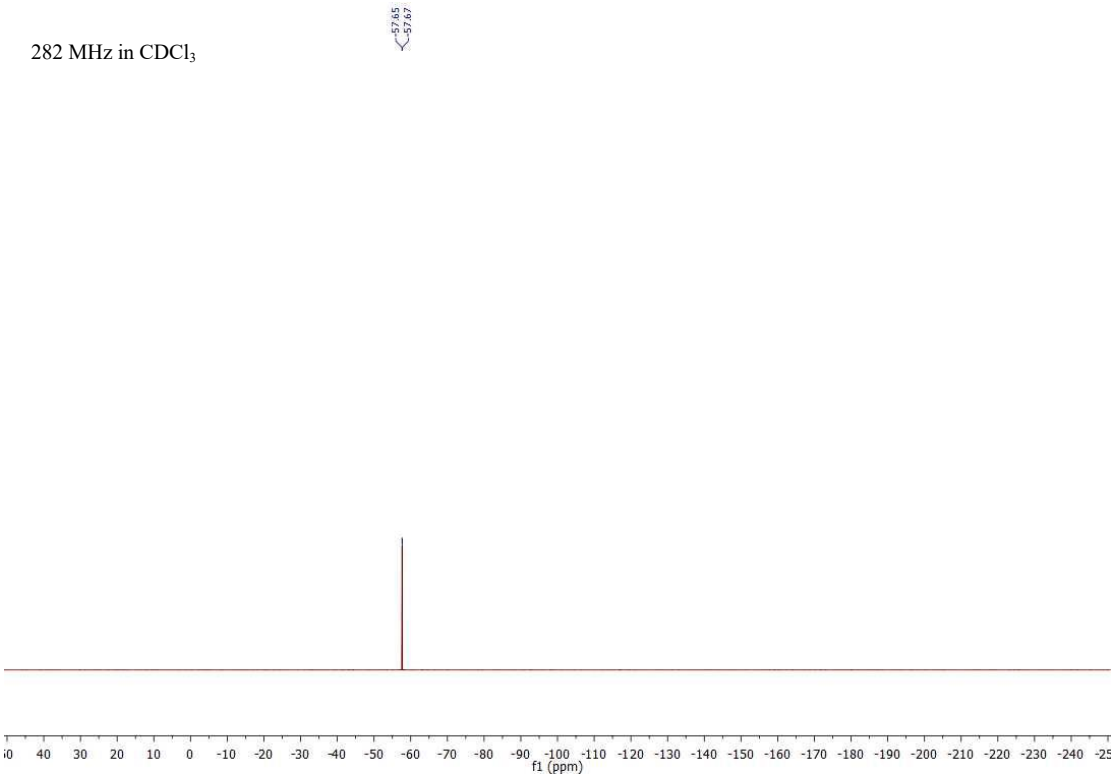
300 MHz in $CDCl_3$

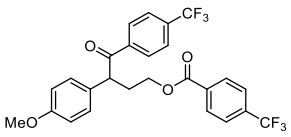


76 MHz in $CDCl_3$



282 MHz in $CDCl_3$





(3k)

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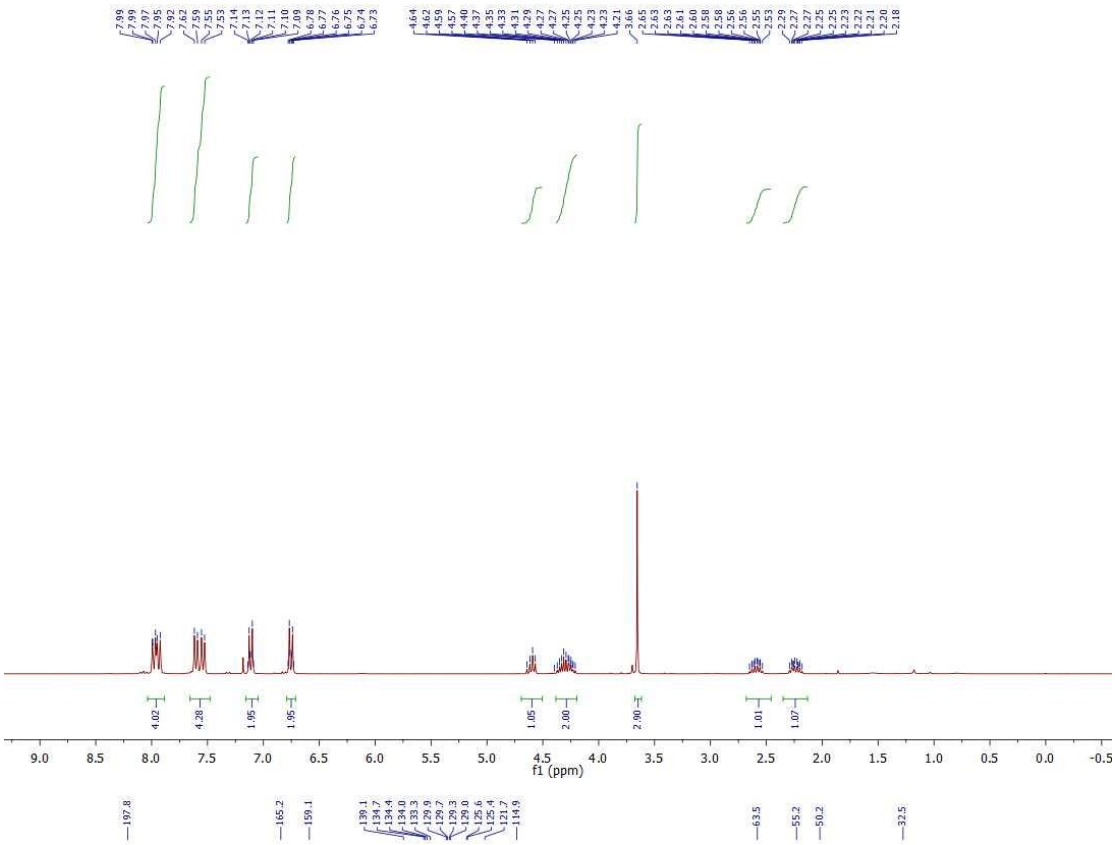
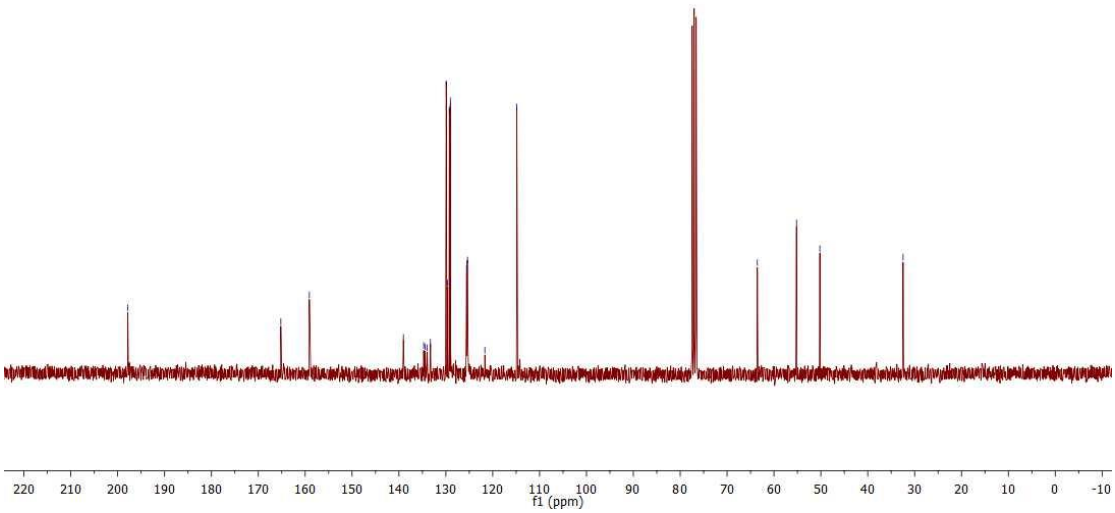
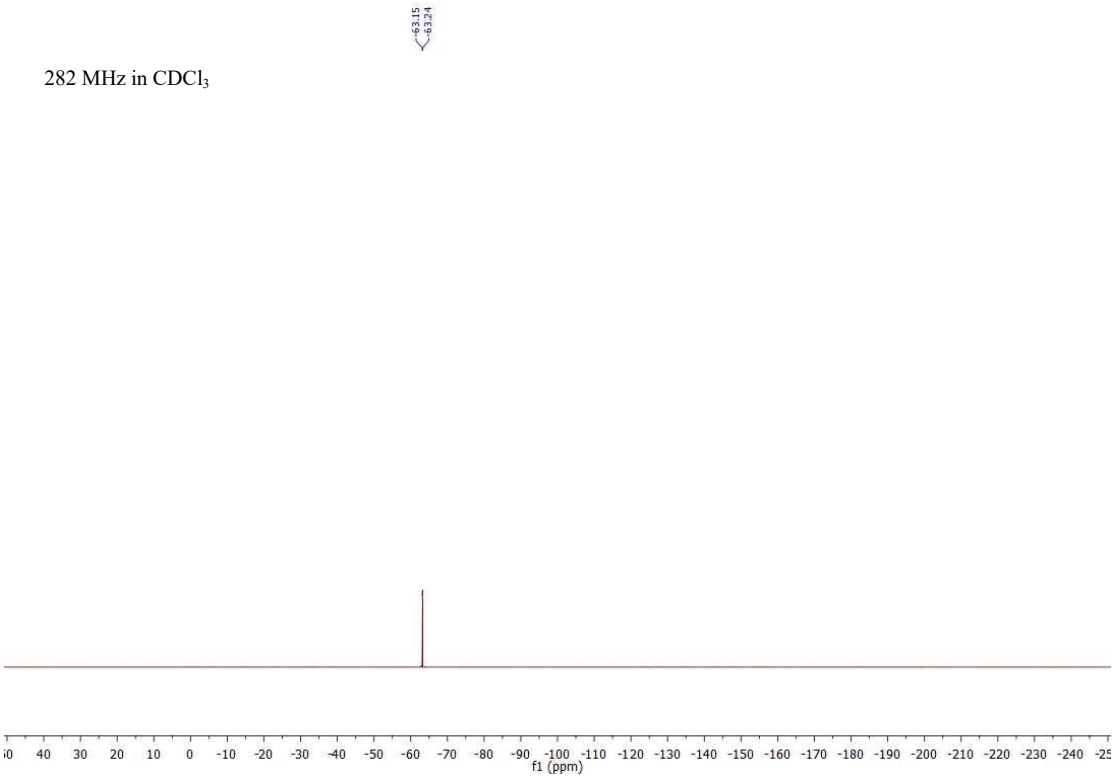
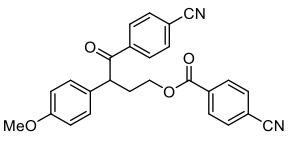


76 MHz in $CDCl_3$



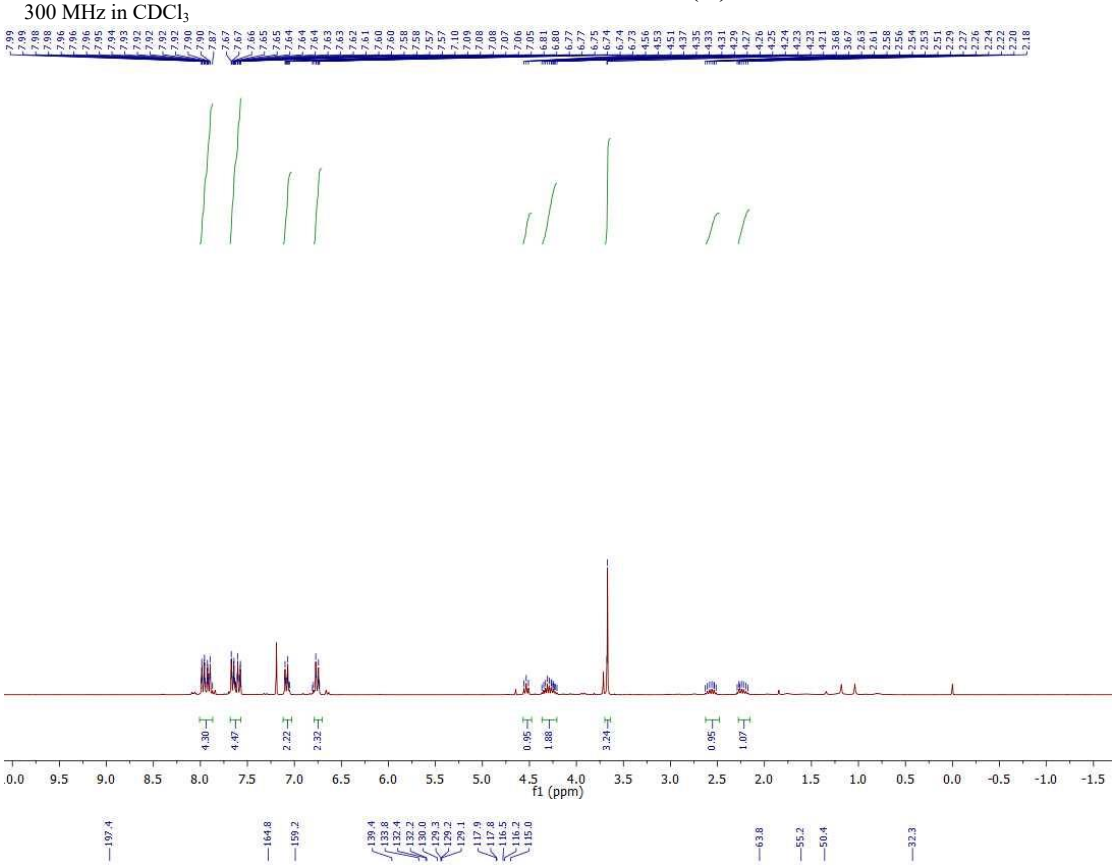
282 MHz in $CDCl_3$



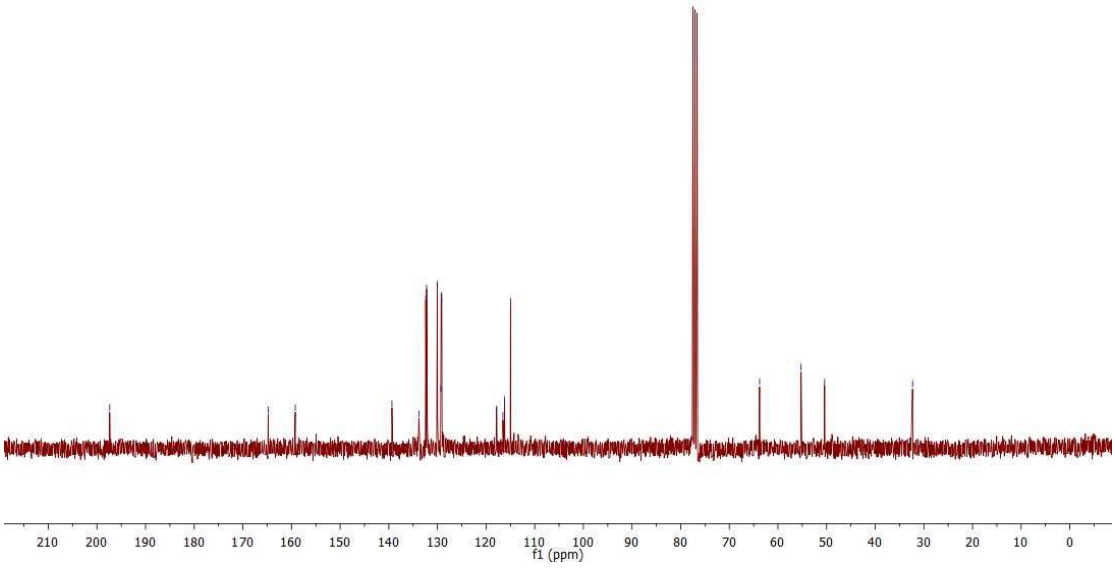


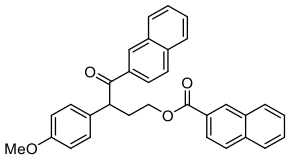
(3l)

300 MHz in $CDCl_3$



76 MHz in $CDCl_3$





(3m)

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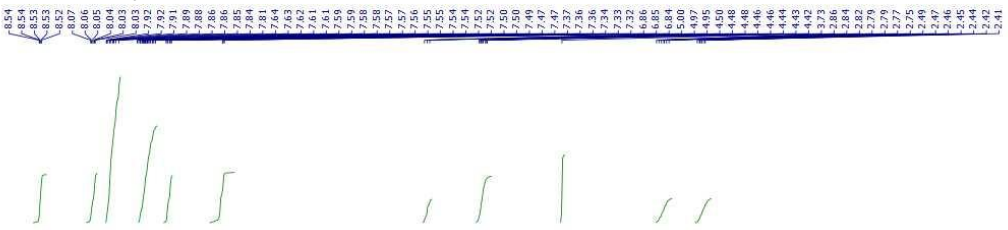
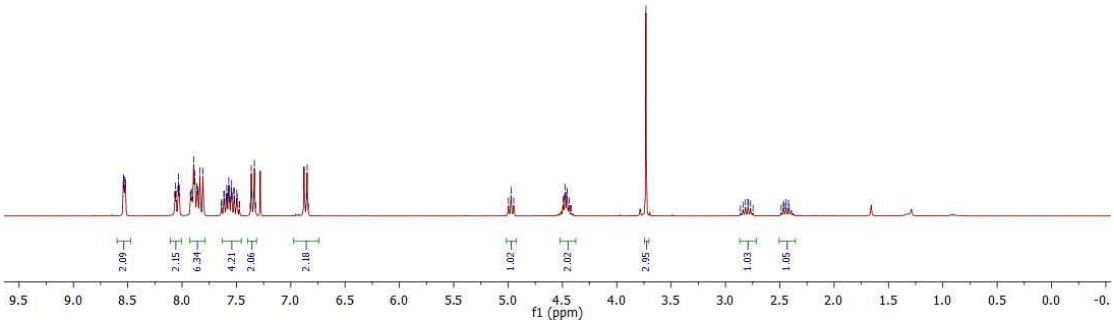
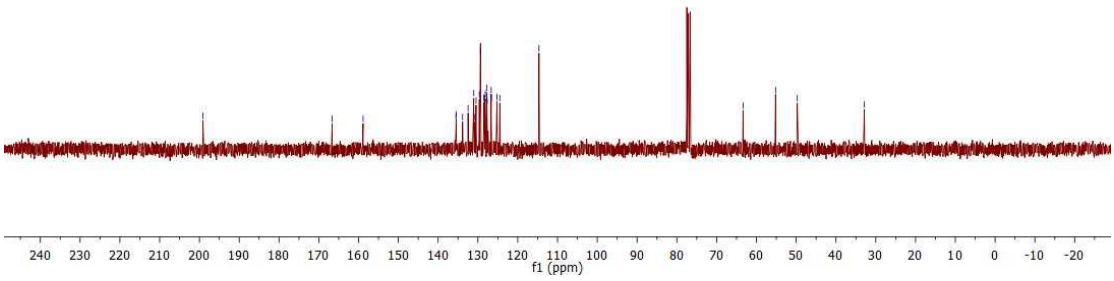
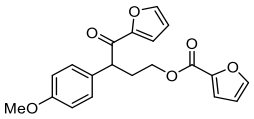




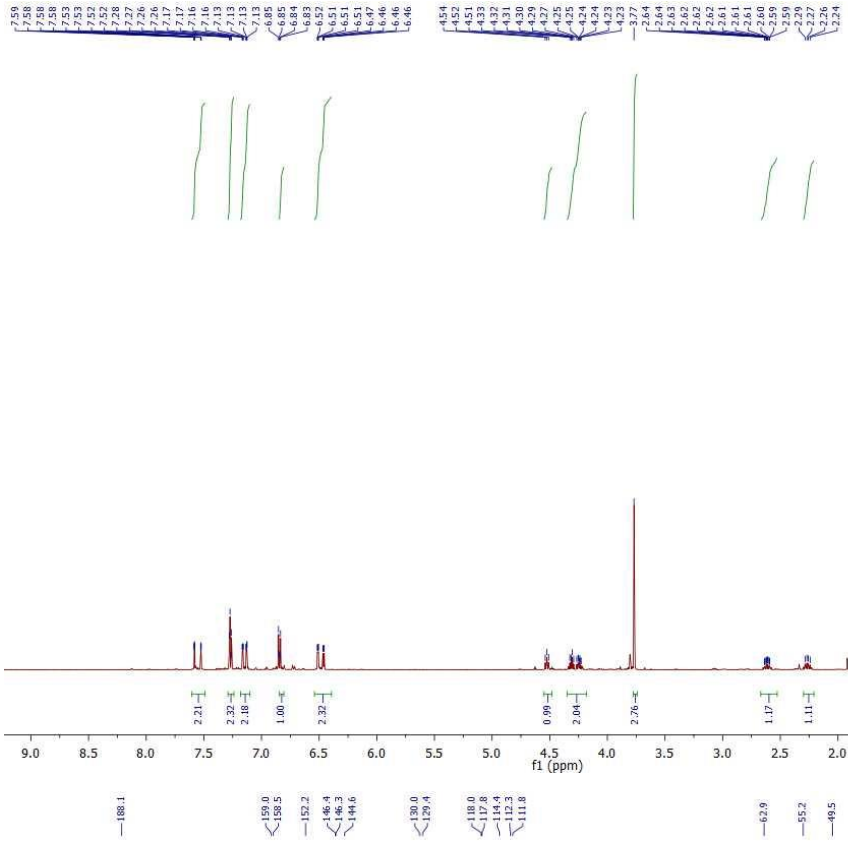
76 MHz in $CDCl_3$



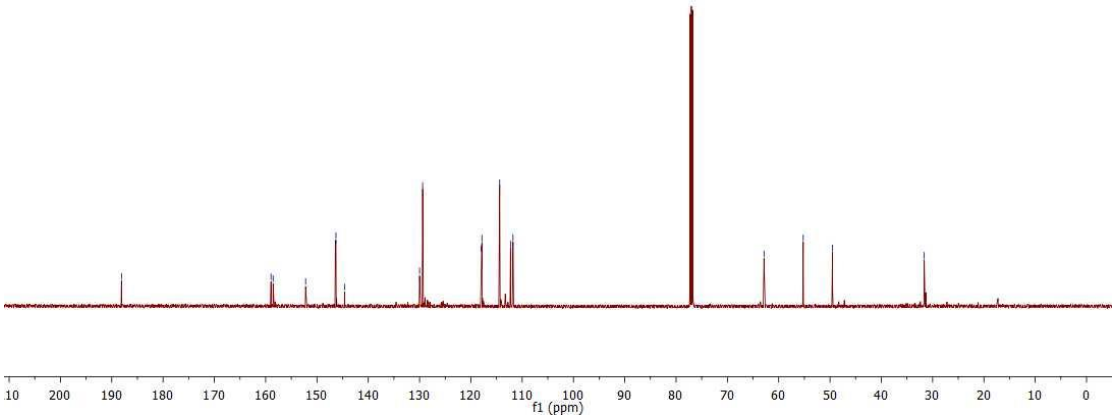


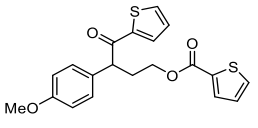
(3n)

300 MHz in $CDCl_3$



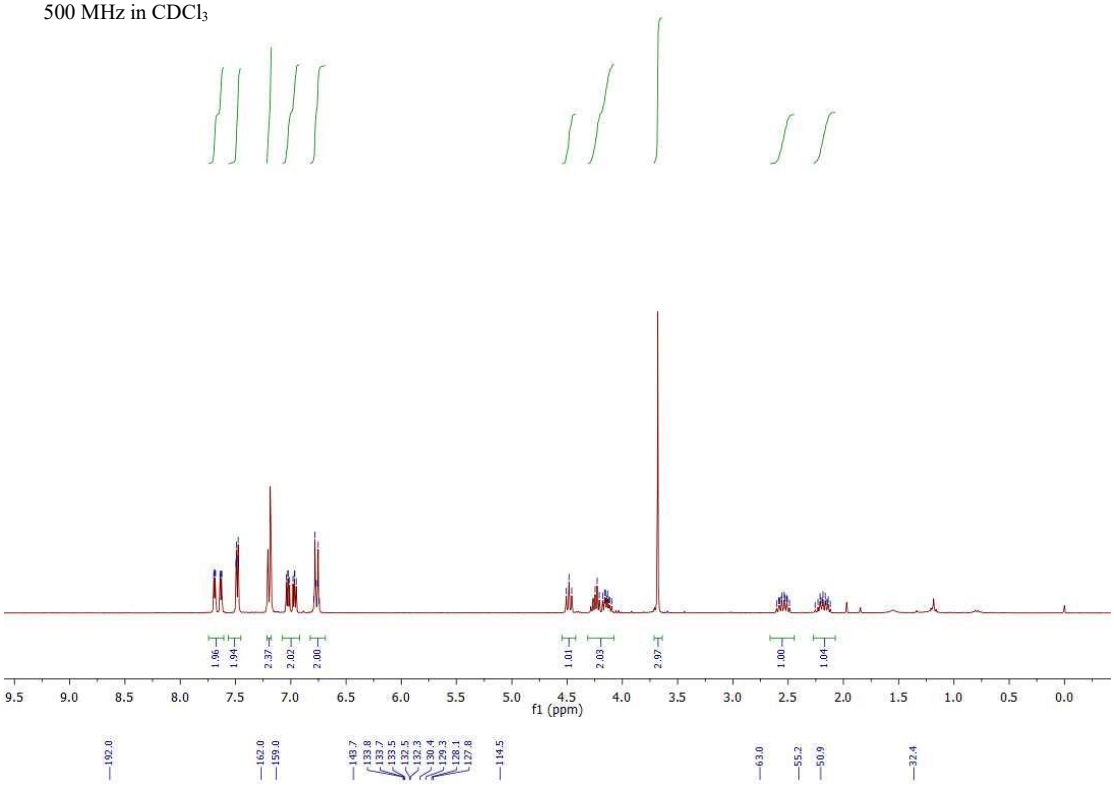
76 MHz in $CDCl_3$



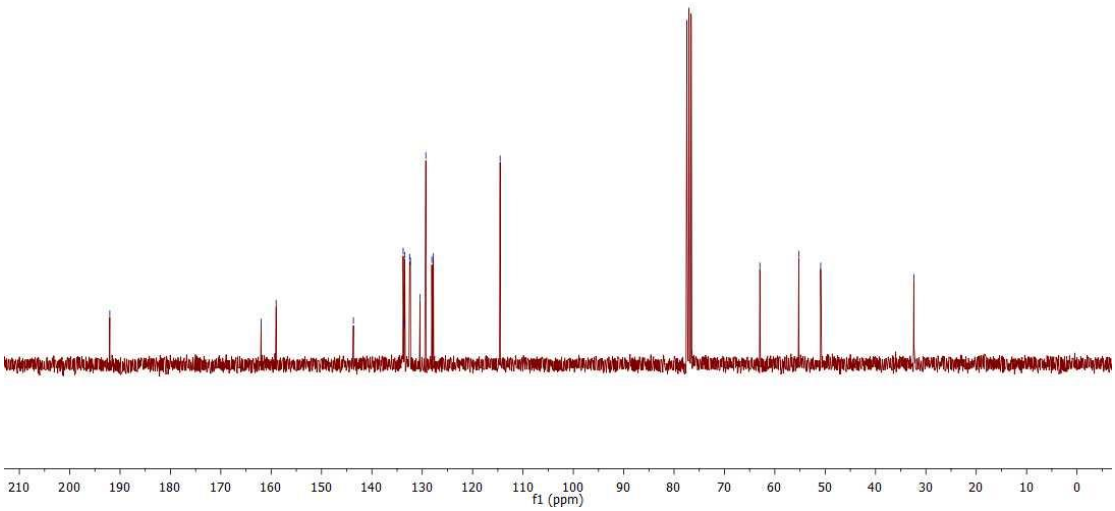


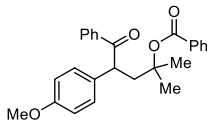
(3o)

500 MHz in $CDCl_3$



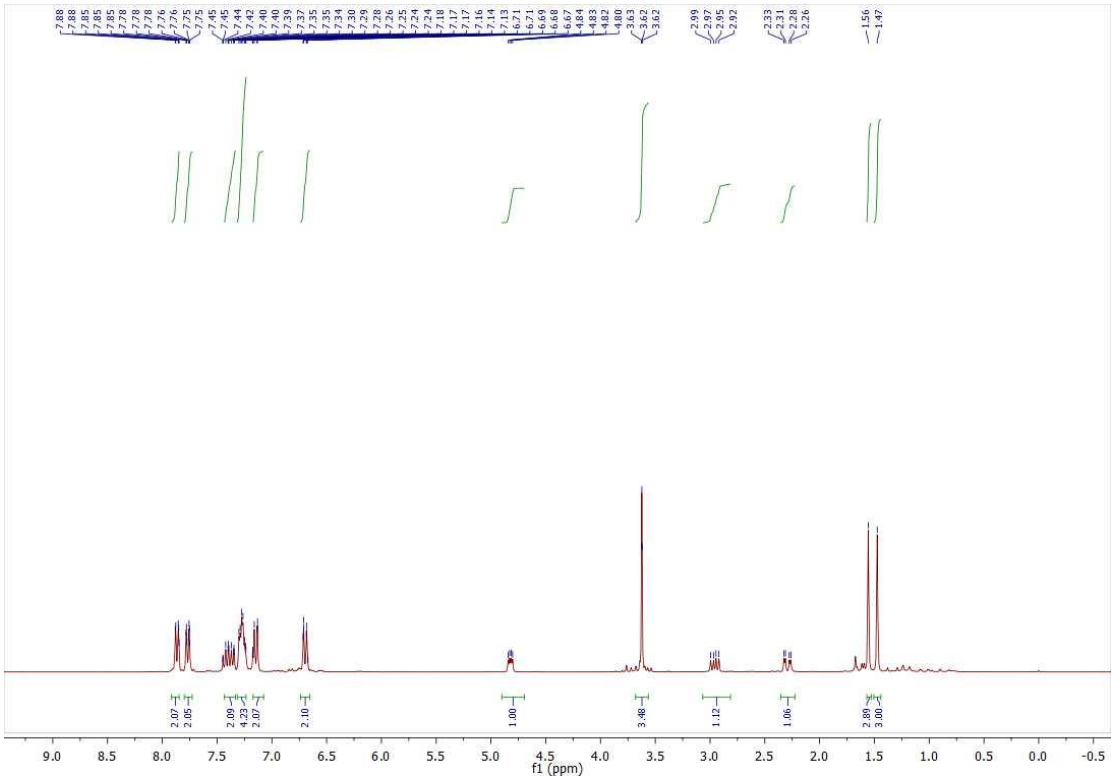
126 MHz in $CDCl_3$



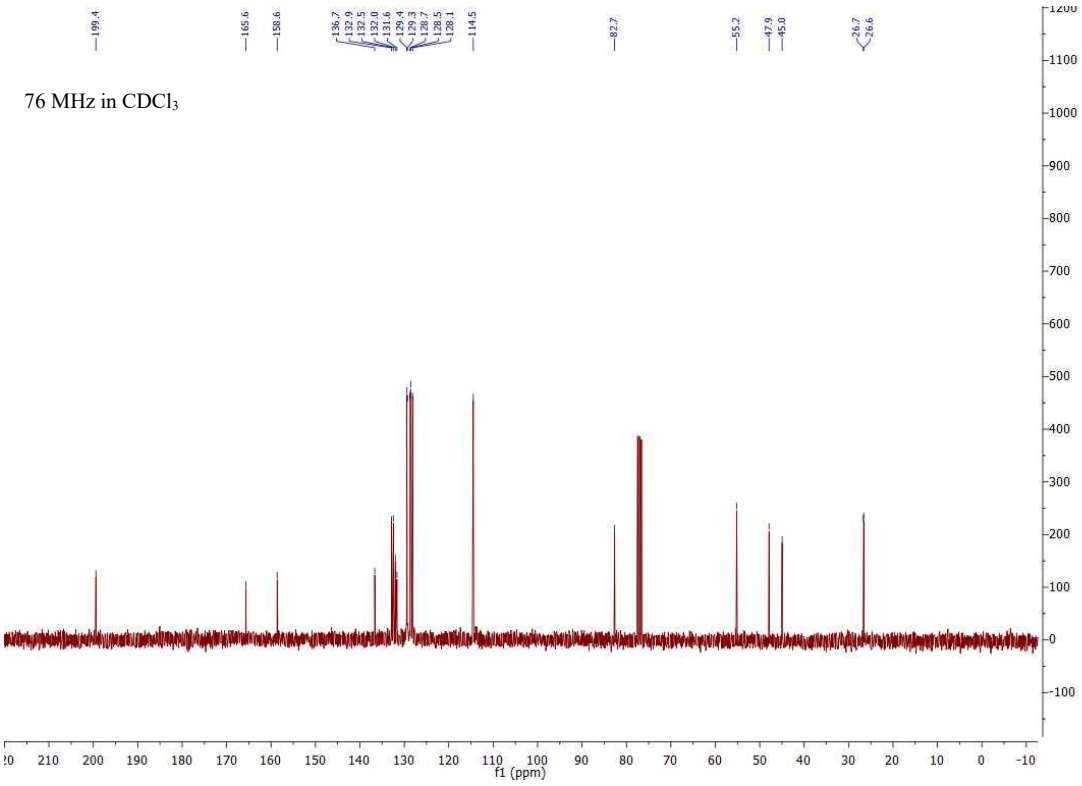


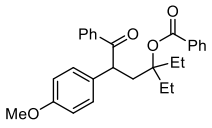
(3p)

300 MHz in $CDCl_3$



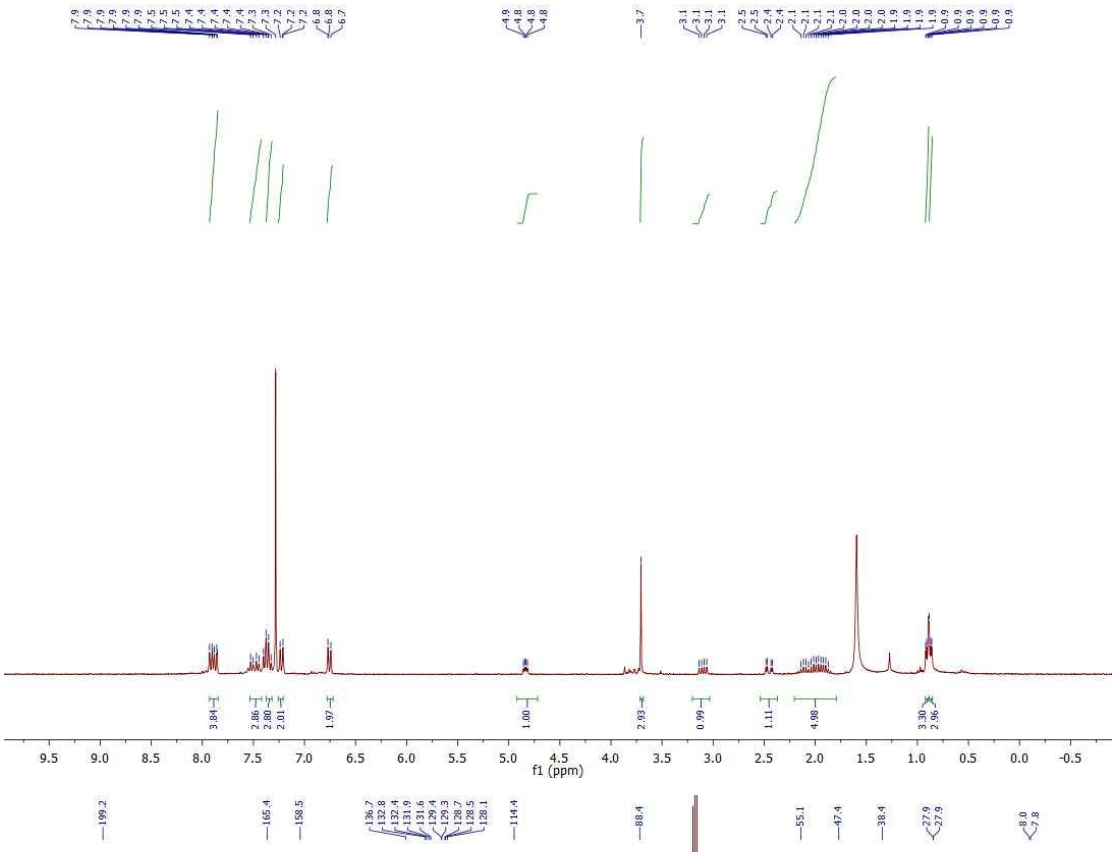
76 MHz in $CDCl_3$



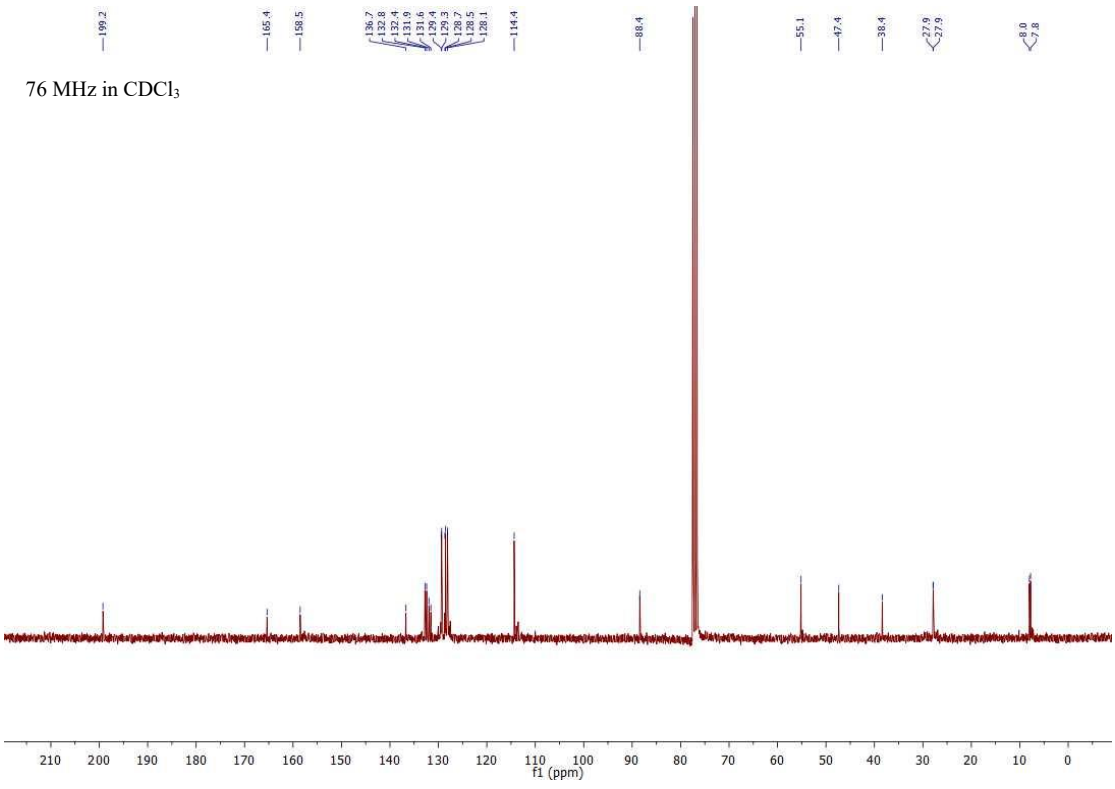


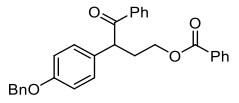
(3q)

300 MHz in $CDCl_3$



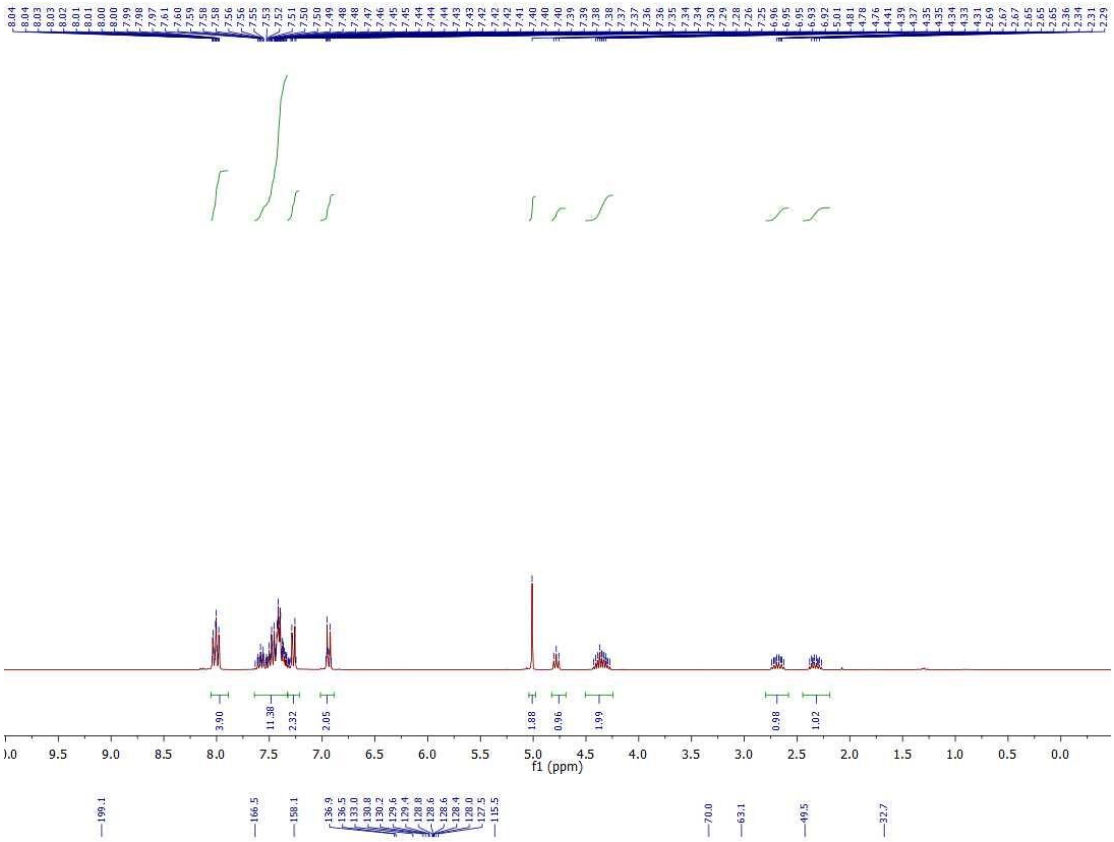
76 MHz in $CDCl_3$



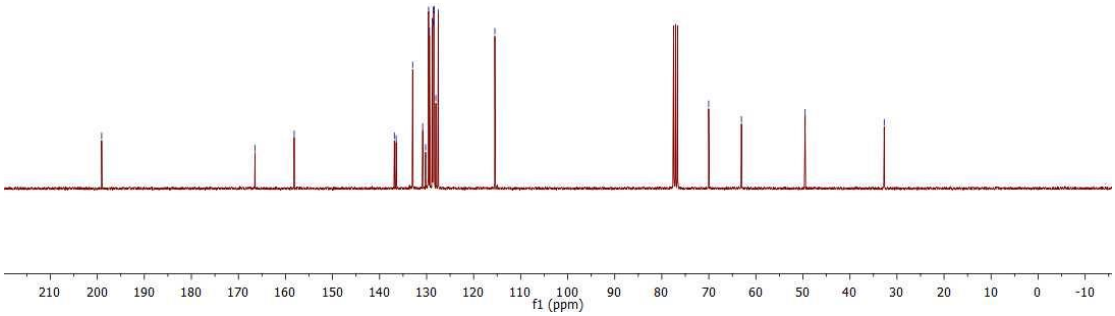


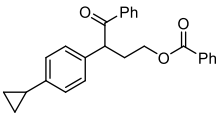
(3r)

300 MHz in $CDCl_3$



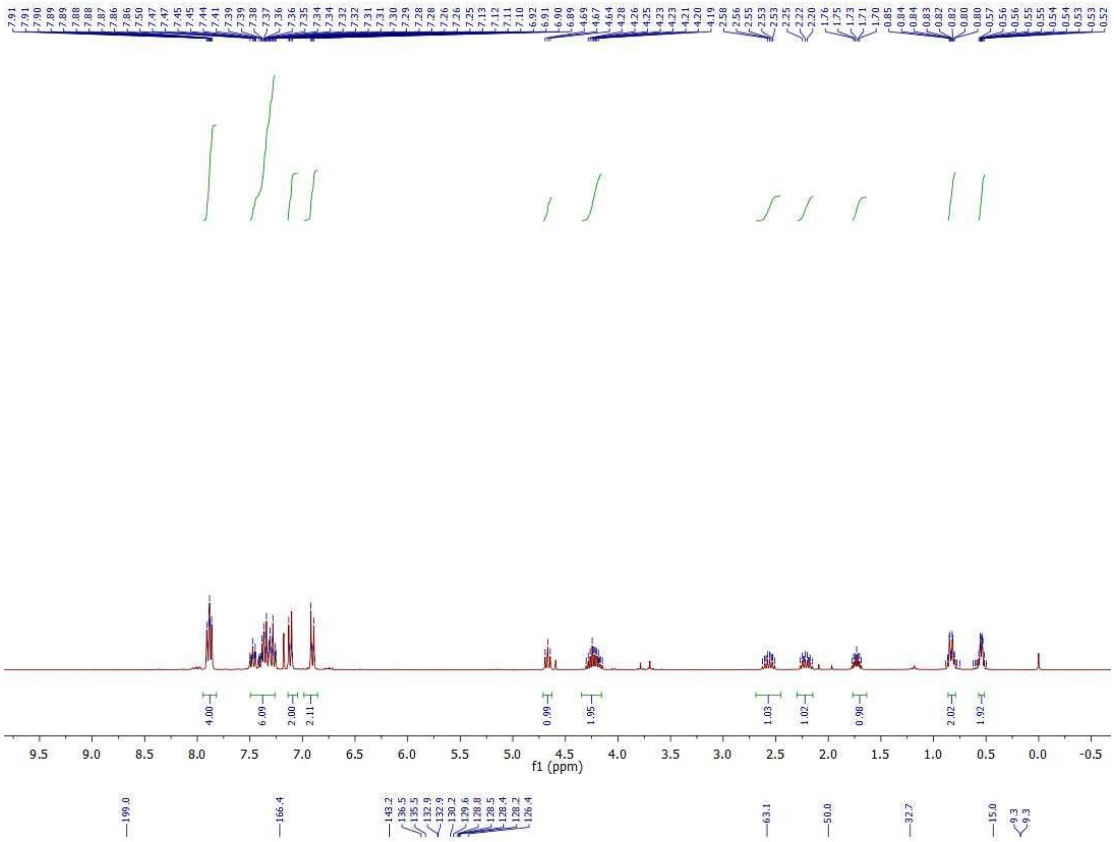
76 MHz in $CDCl_3$



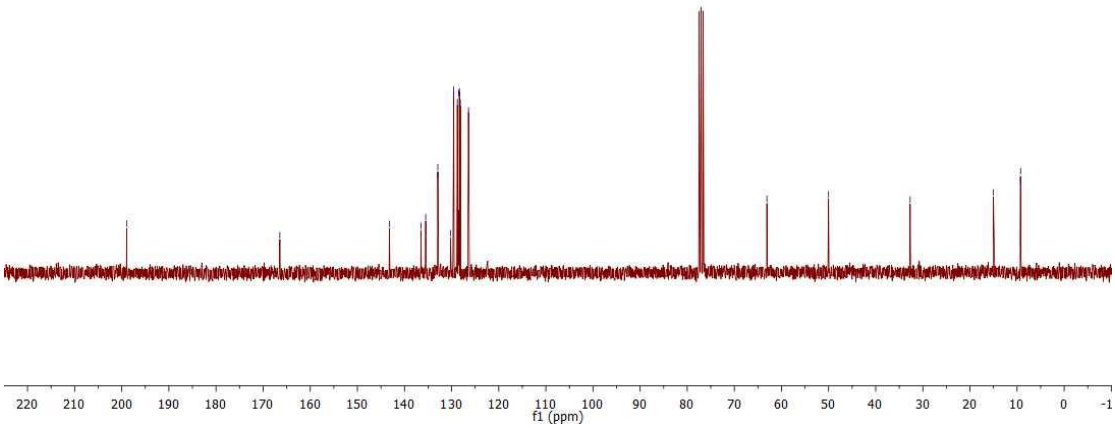


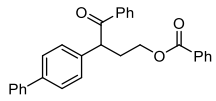
(3s)

300 MHz in $CDCl_3$



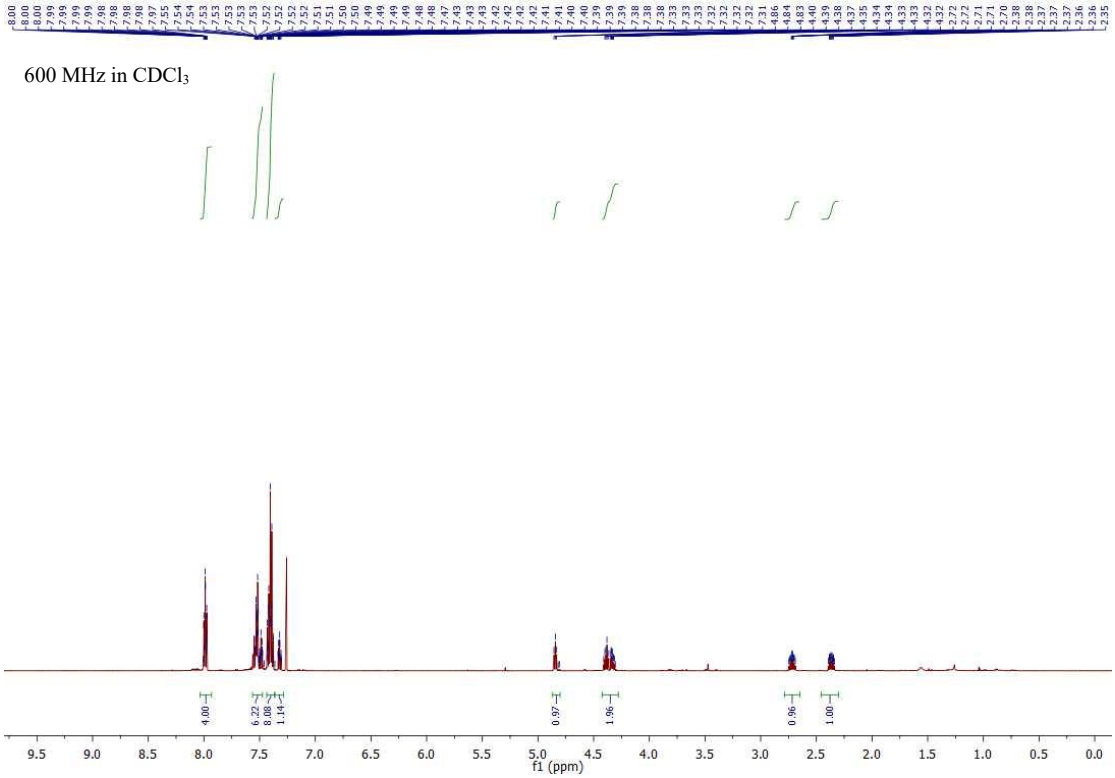
76 MHz in $CDCl_3$



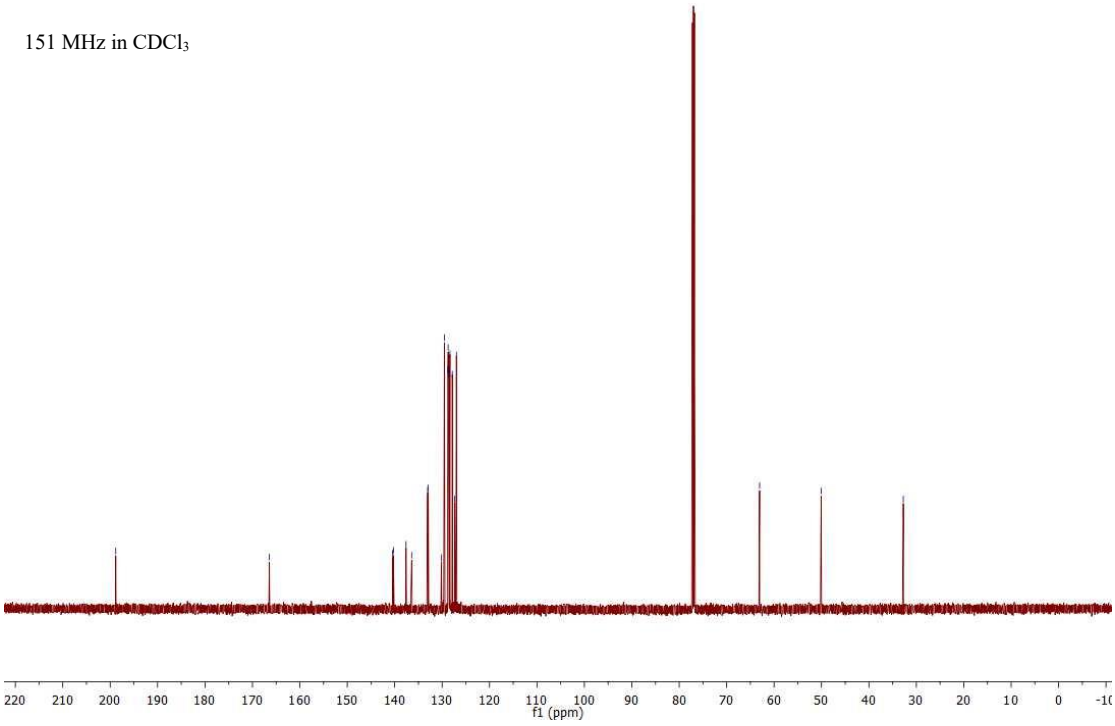


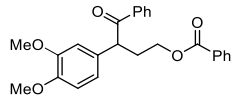
(3t)

600 MHz in $CDCl_3$



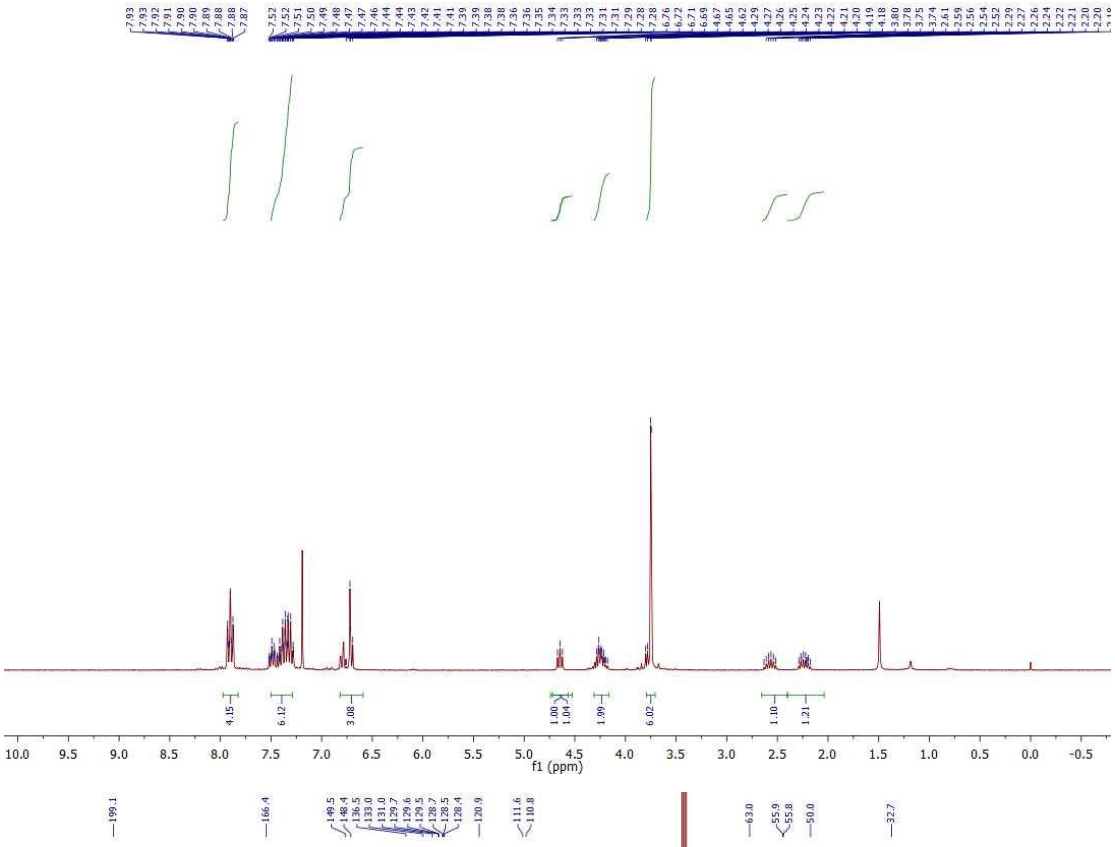
151 MHz in $CDCl_3$



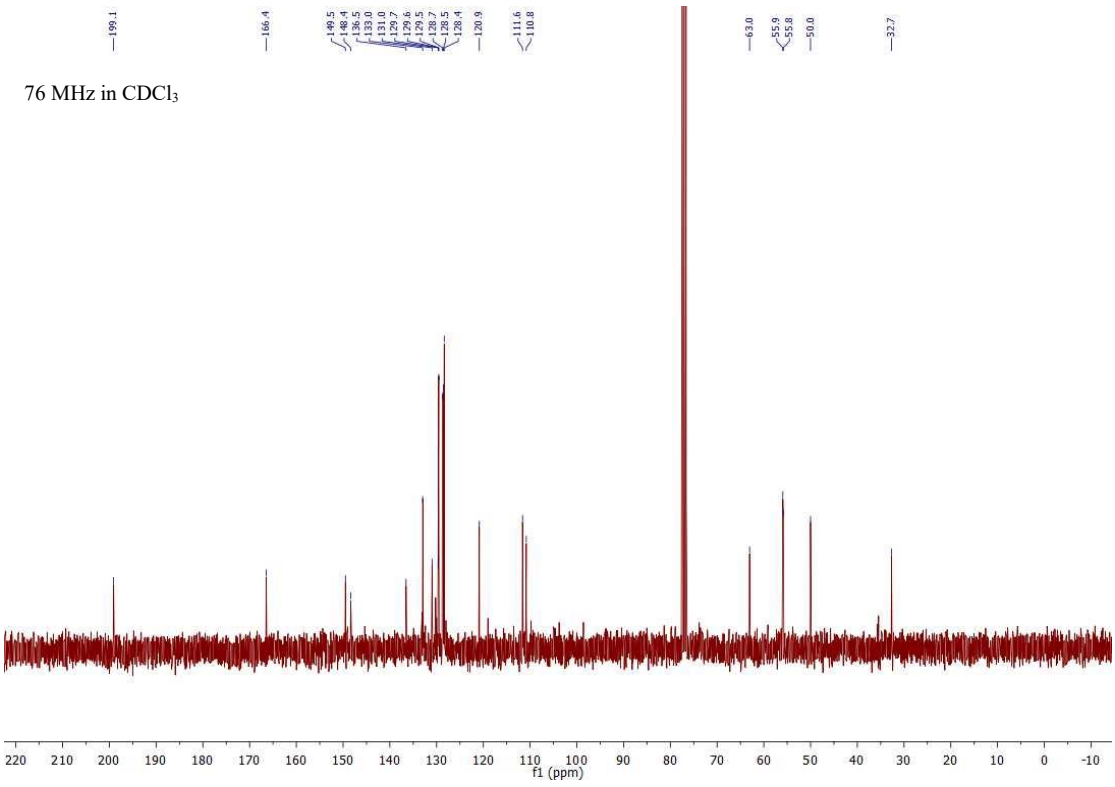


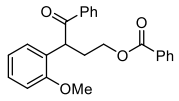
(3u)

300 MHz in $CDCl_3$



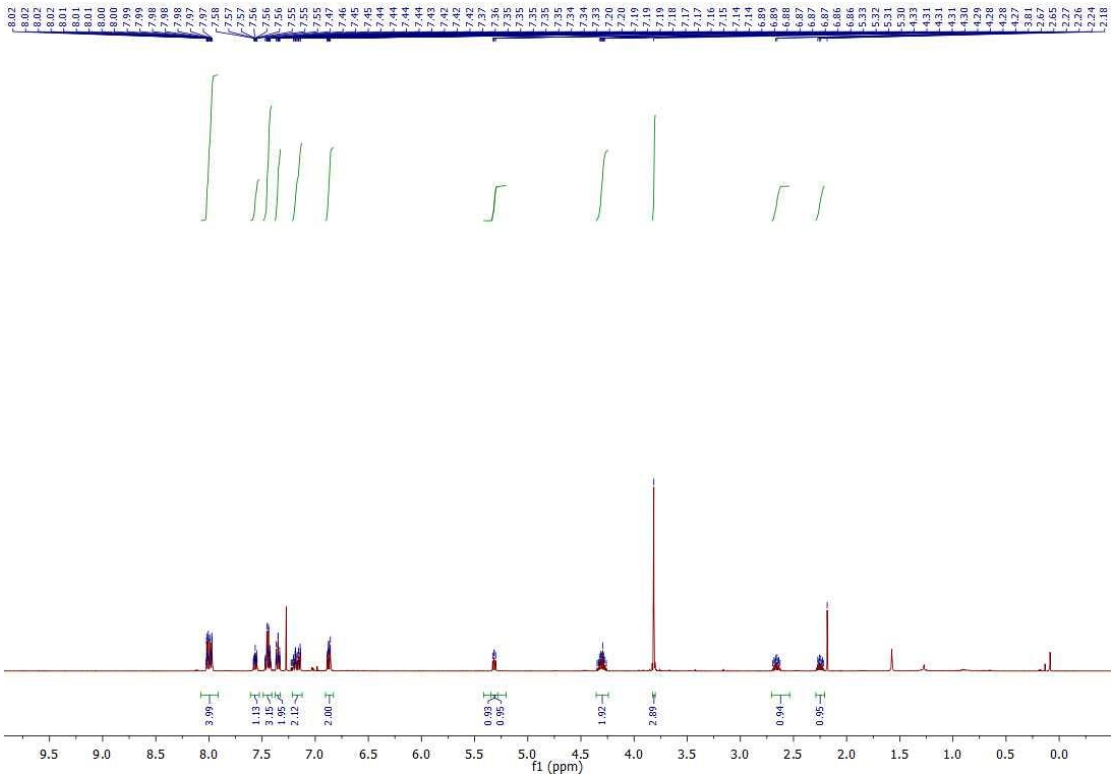
76 MHz in $CDCl_3$



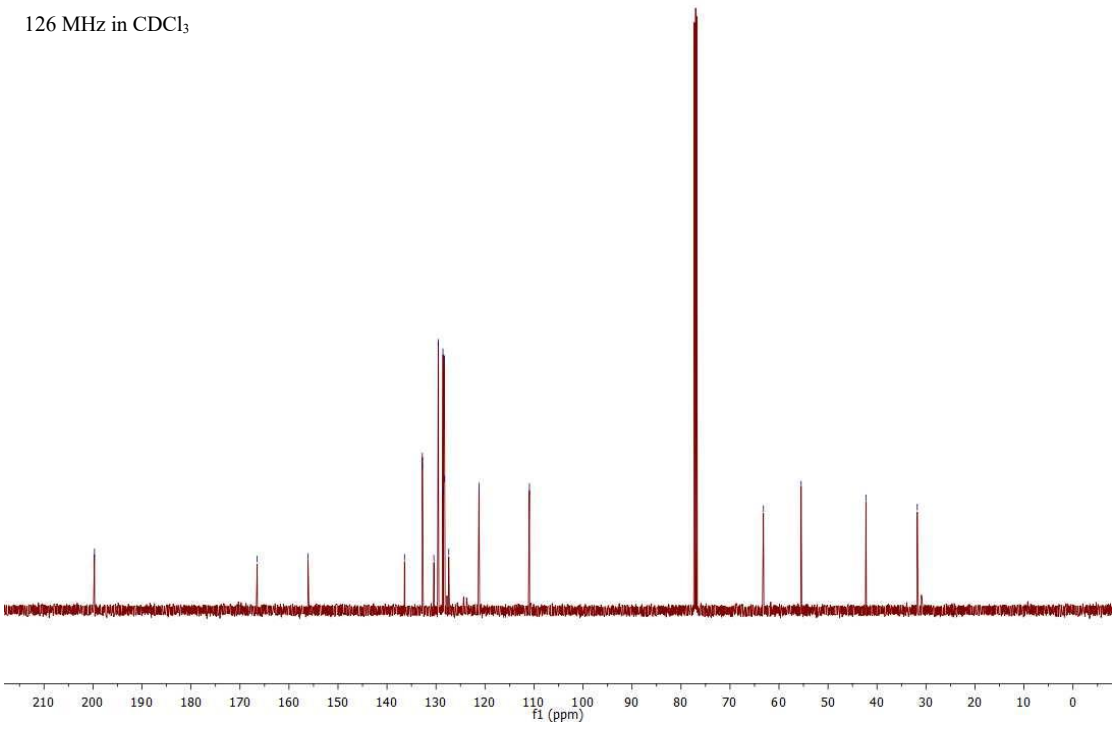


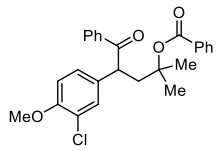
(3v)

500 MHz in $CDCl_3$



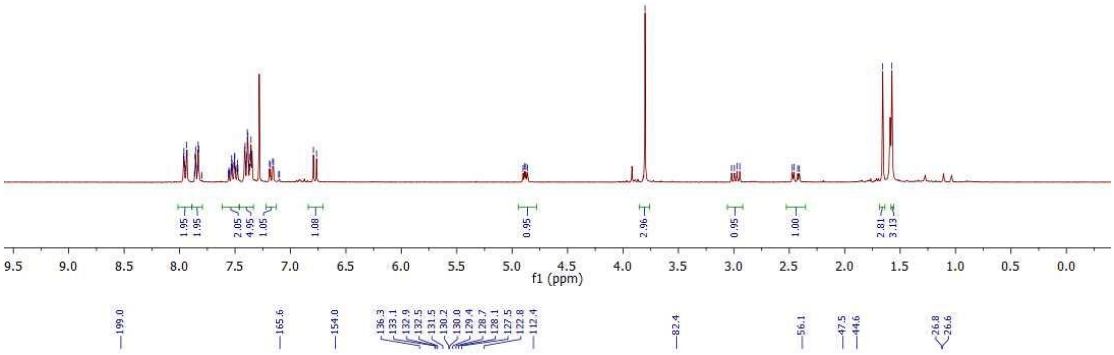
126 MHz in $CDCl_3$



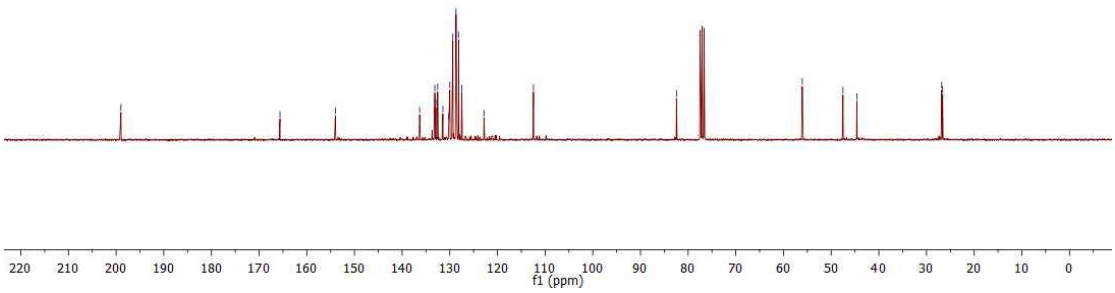


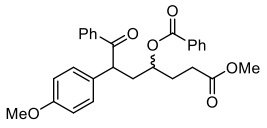
(3y)

300 MHz in $CDCl_3$



76 MHz in $CDCl_3$

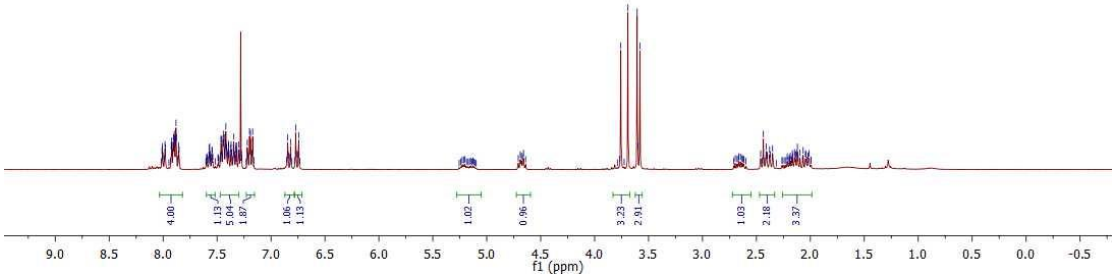




(3z)

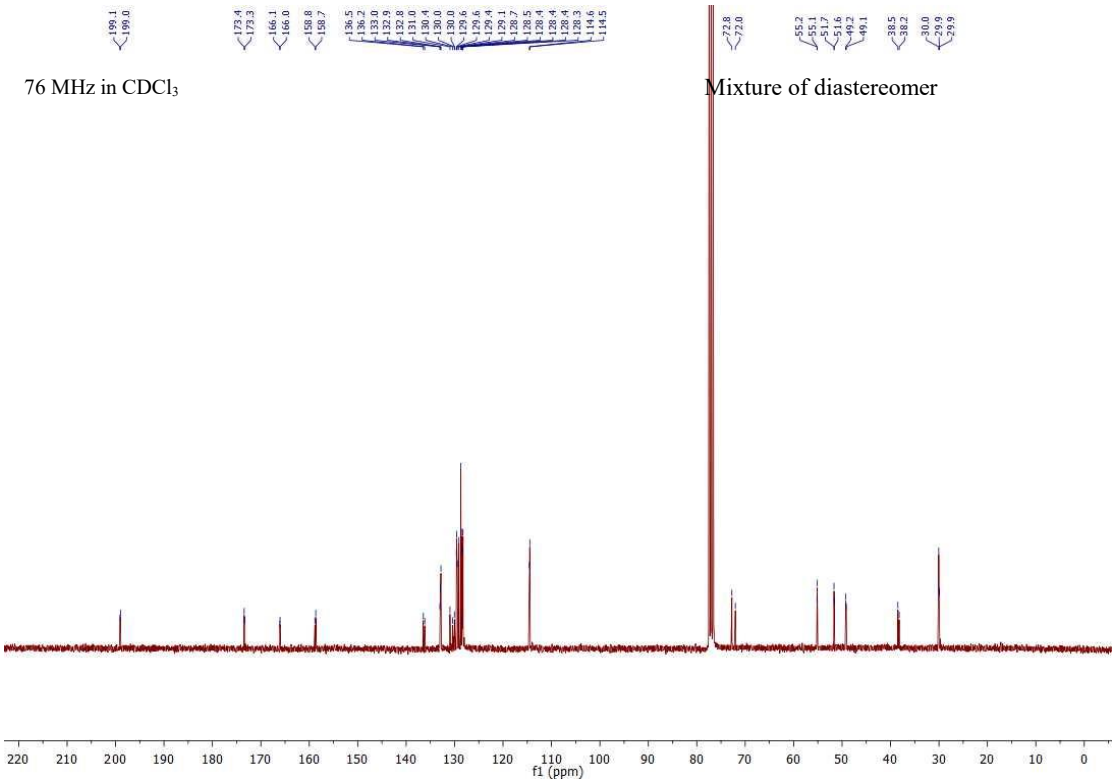
300 MHz in $CDCl_3$

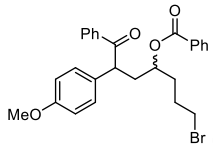
Mixture of diastereomer



76 MHz in $CDCl_3$

Mixture of diastereomer

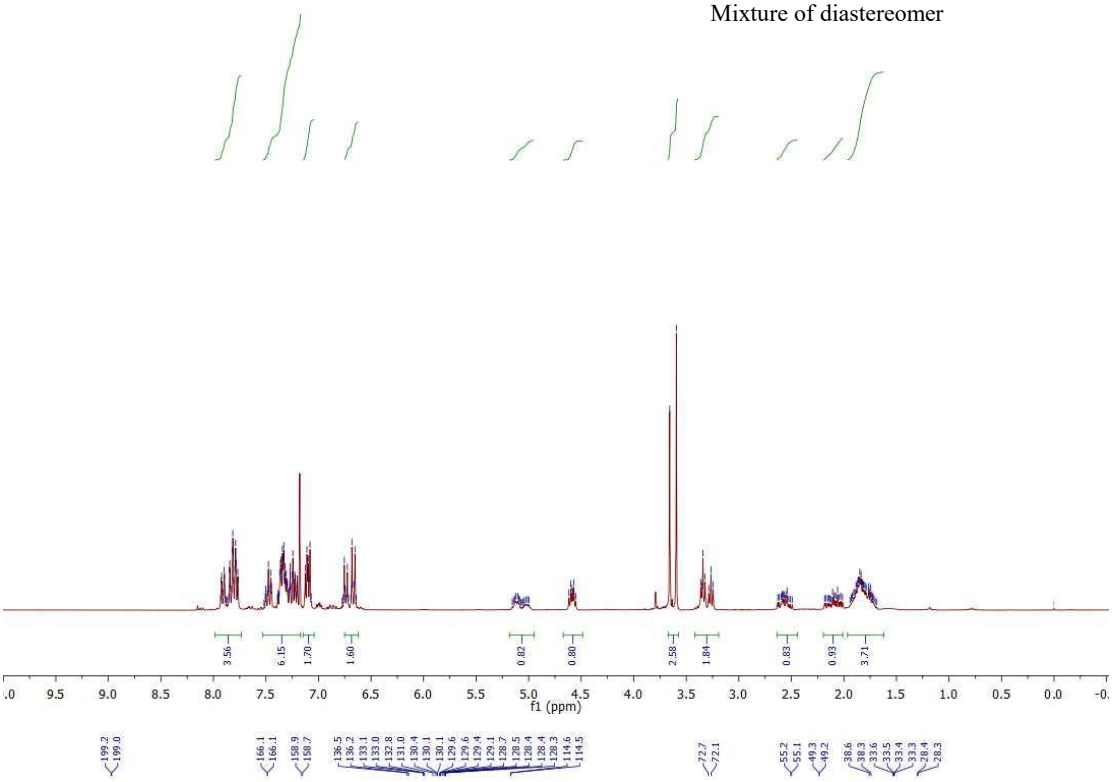




(3aa)

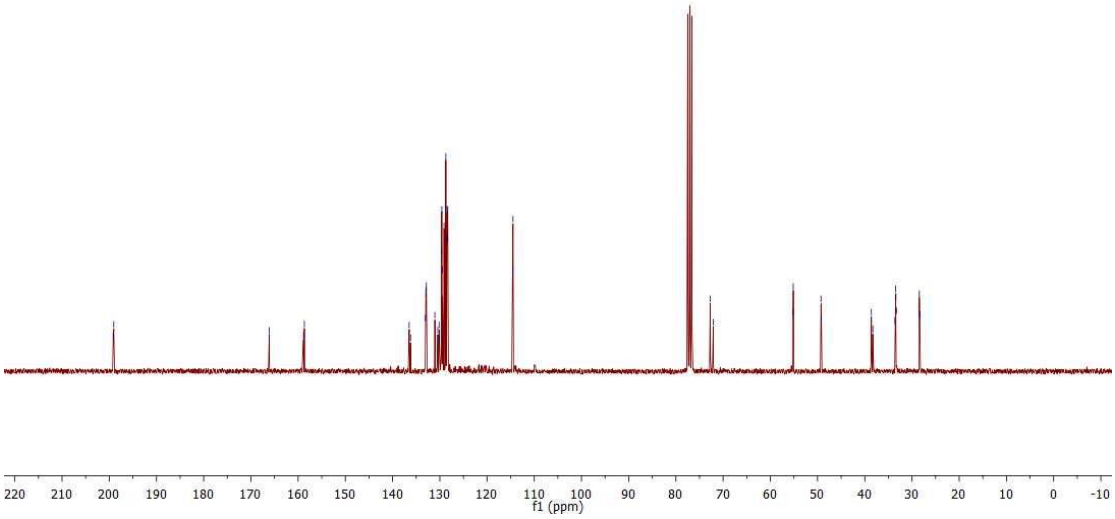
300 MHz in $CDCl_3$

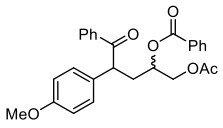
Mixture of diastereomer



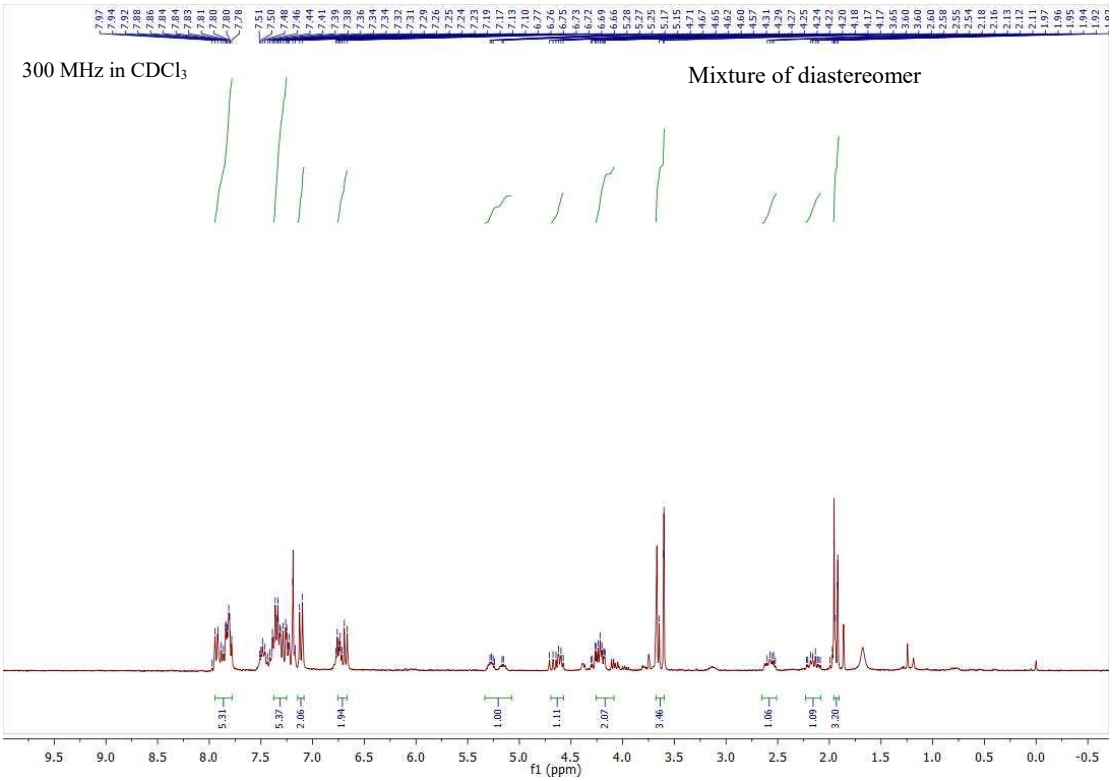
76 MHz in $CDCl_3$

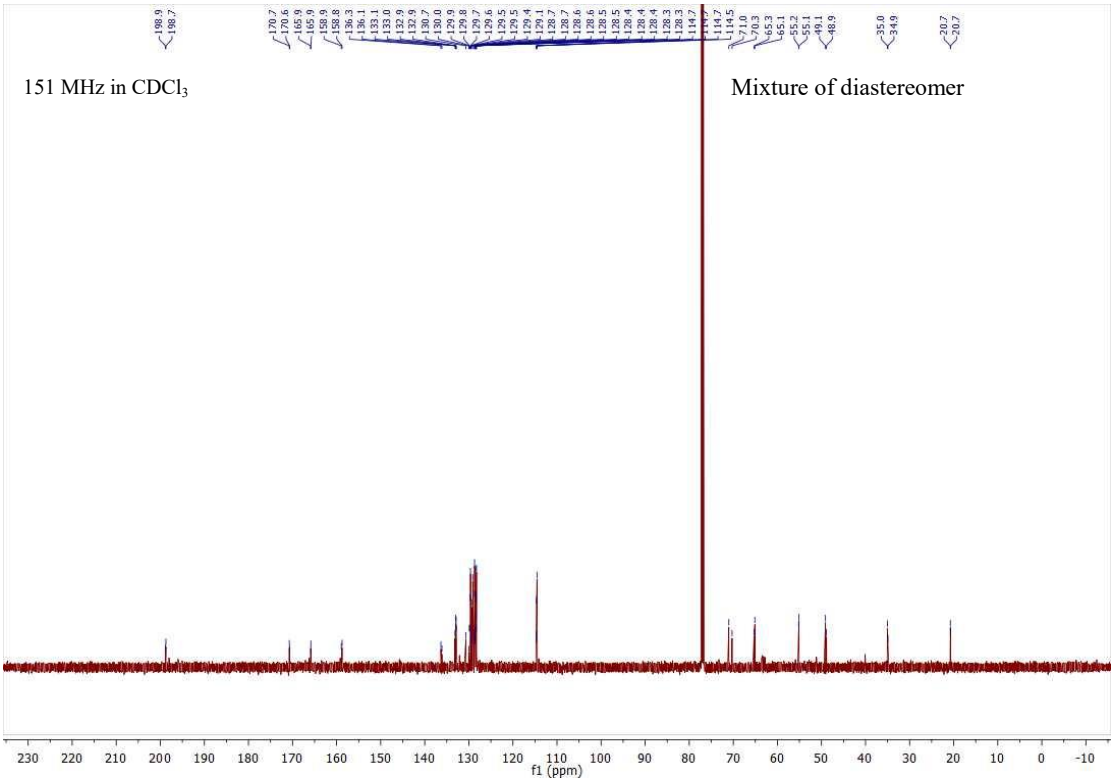
Mixture of diastereomer

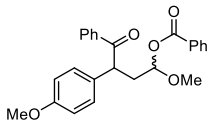



Ph
O
O
O
Ph
OAc
MeO

(3ab)


300 MHz in CDCl3
Mixture of diastereomer
f1 (ppm)

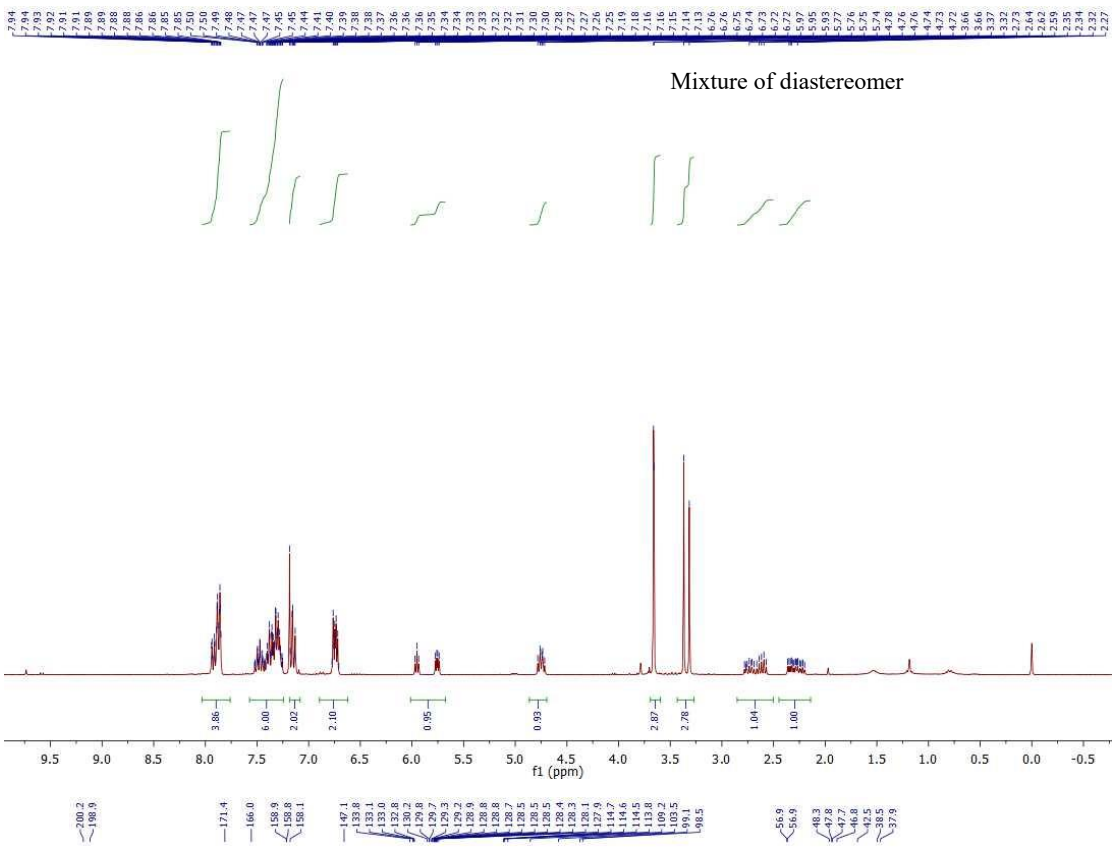

151 MHz in CDCl3
Mixture of diastereomer
f1 (ppm)



(3ac)

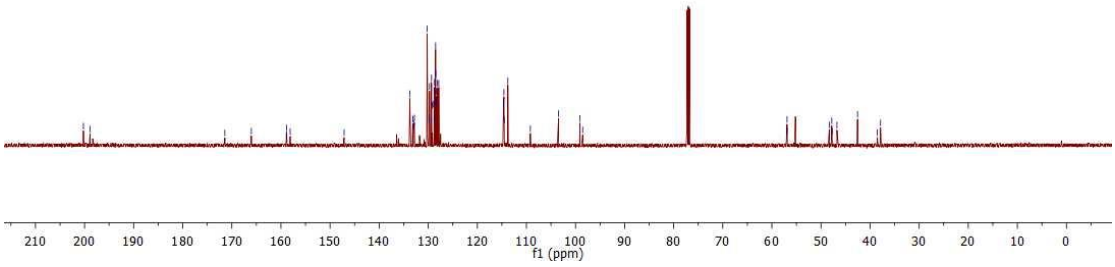
300 MHz in $CDCl_3$

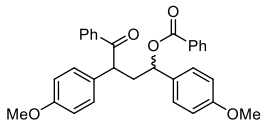
Mixture of diastereomer



126 MHz in CD_2Cl_2+$CDCl_3$

Mixture of diastereomer

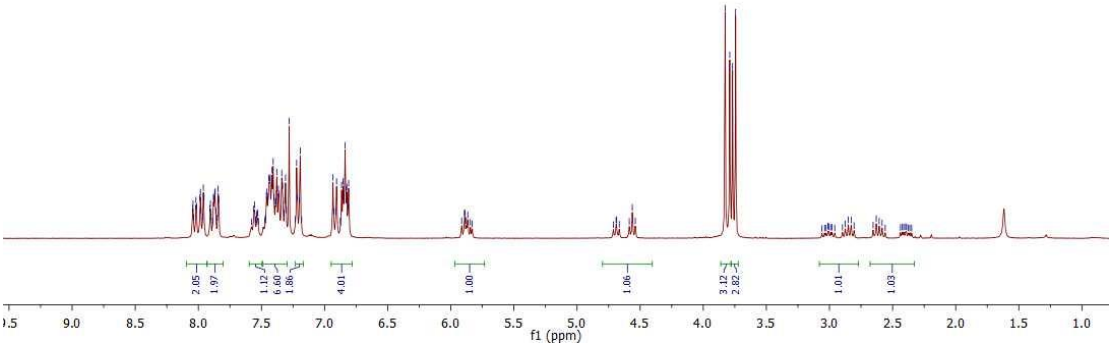




(3ad)

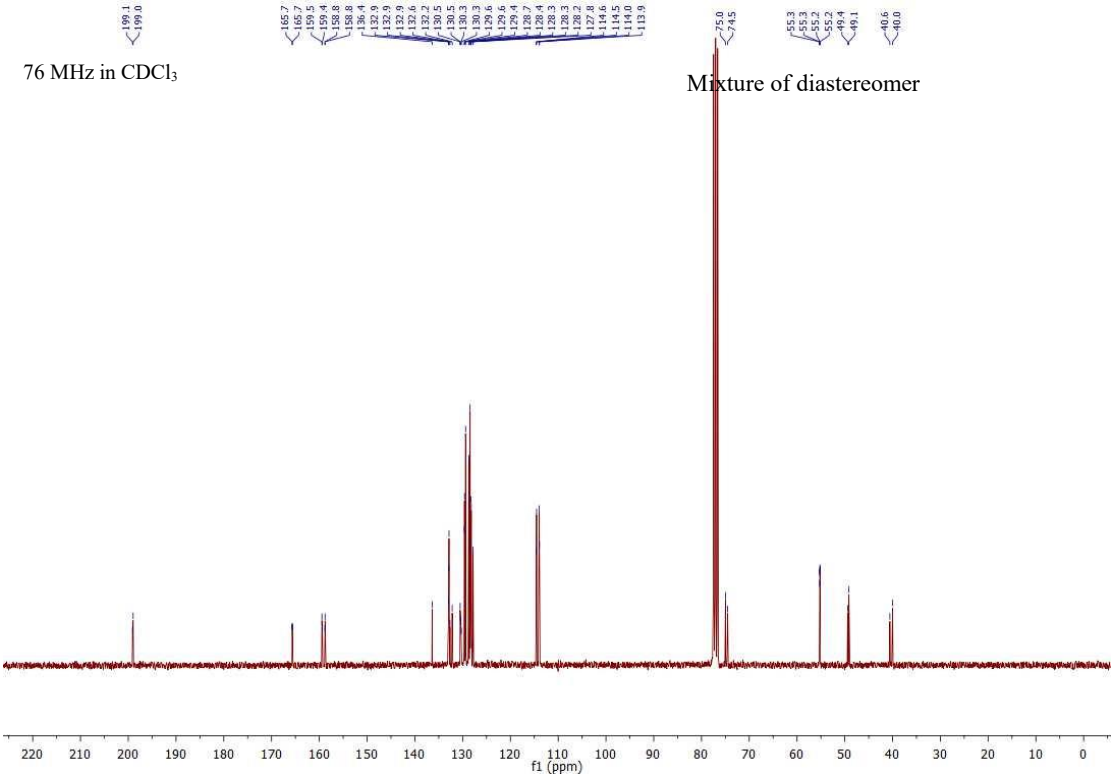
300 MHz in $CDCl_3$

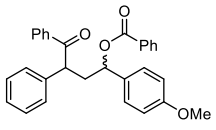
Mixture of diastereomer



76 MHz in $CDCl_3$

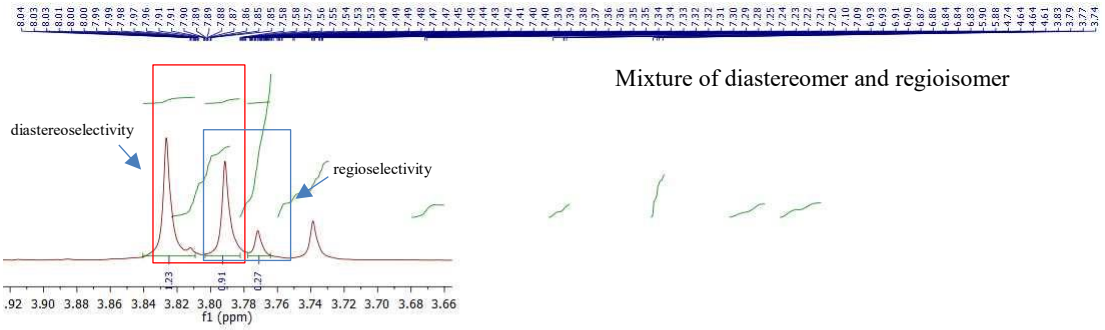
Mixture of diastereomer



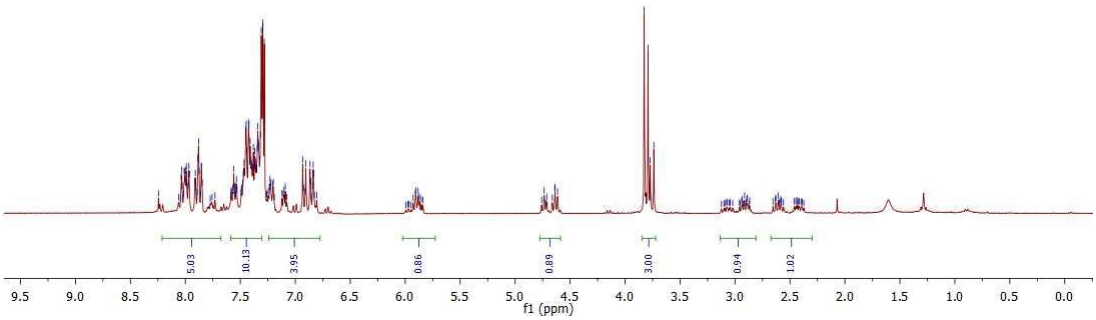


(3ae)

300 MHz in $CDCl_3$

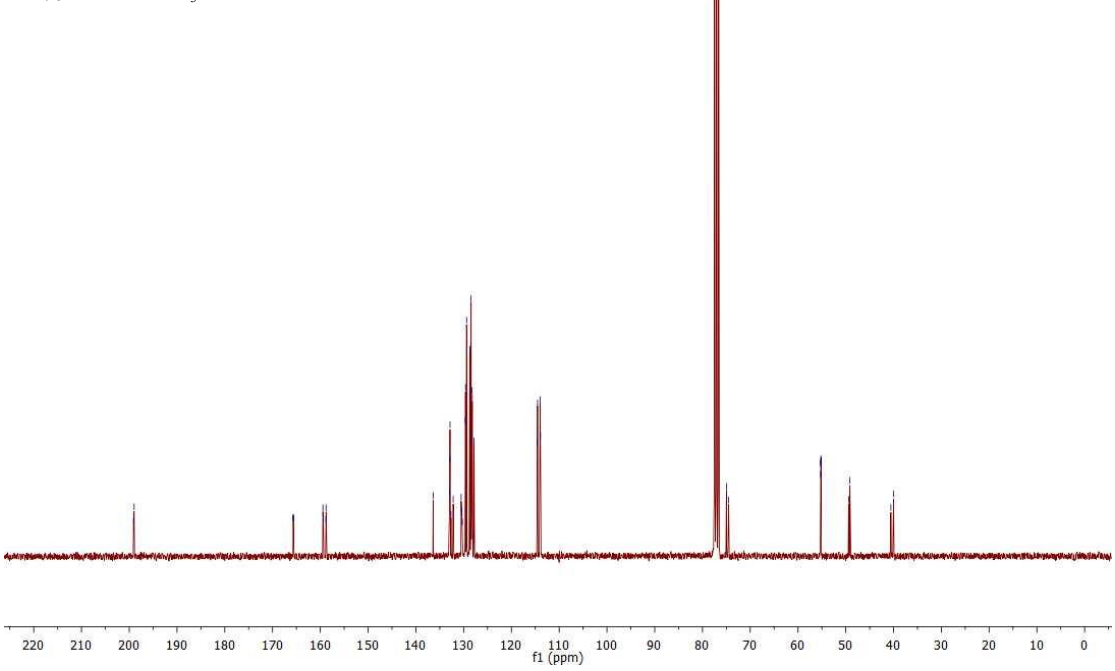


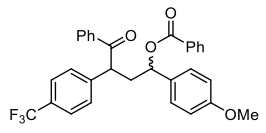
Mixture of diastereomer and regioisomer



Mixture of diastereomer and regioisomer

76 MHz in $CDCl_3$

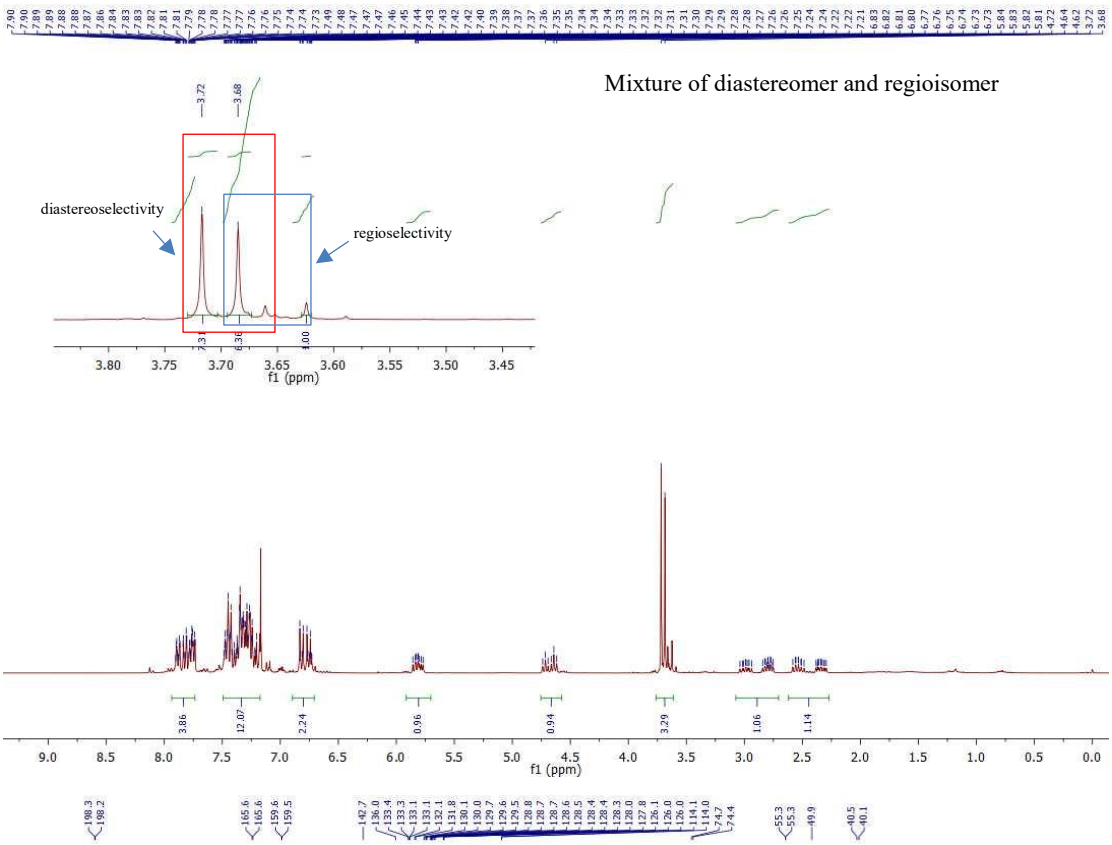




(3af)

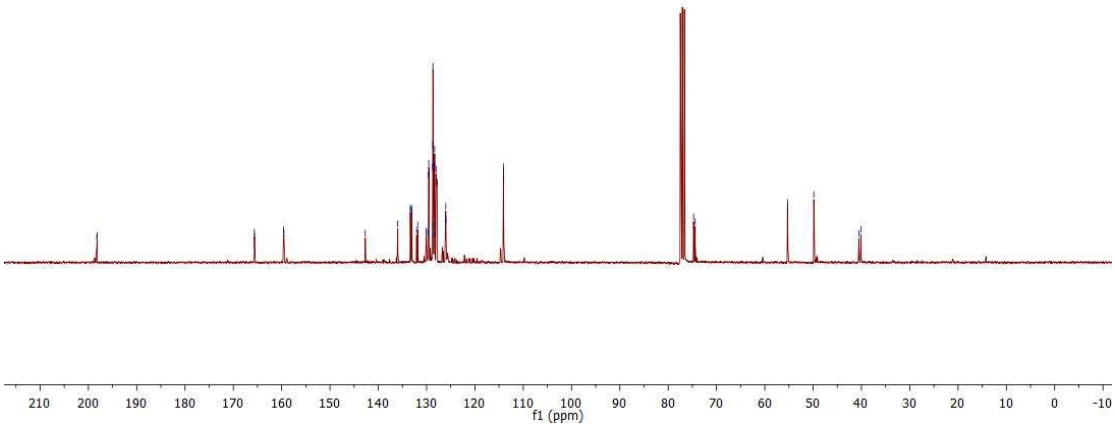
300 MHz in $CDCl_3$

Mixture of diastereomer and regioisomer

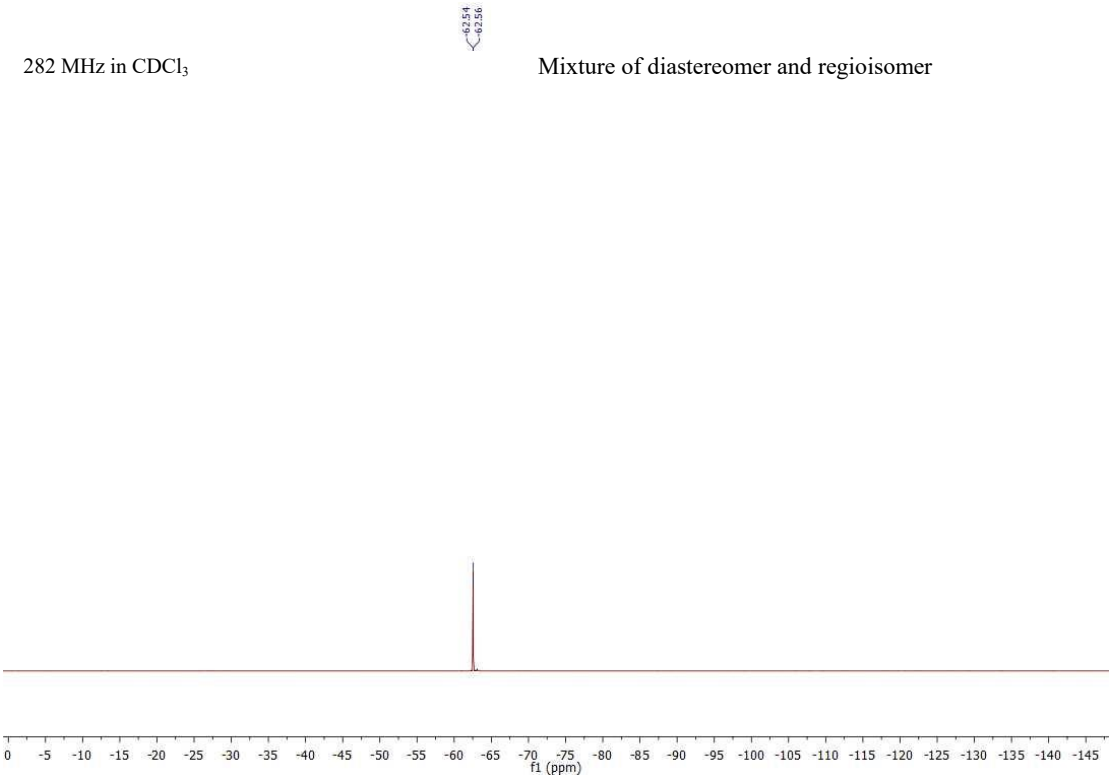


76 MHz in $CDCl_3$

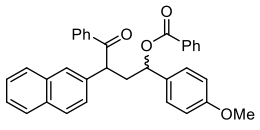
Mixture of diastereomer and regioisomer



282 MHz in $CDCl_3$ Mixture of diastereomer and regioisomer

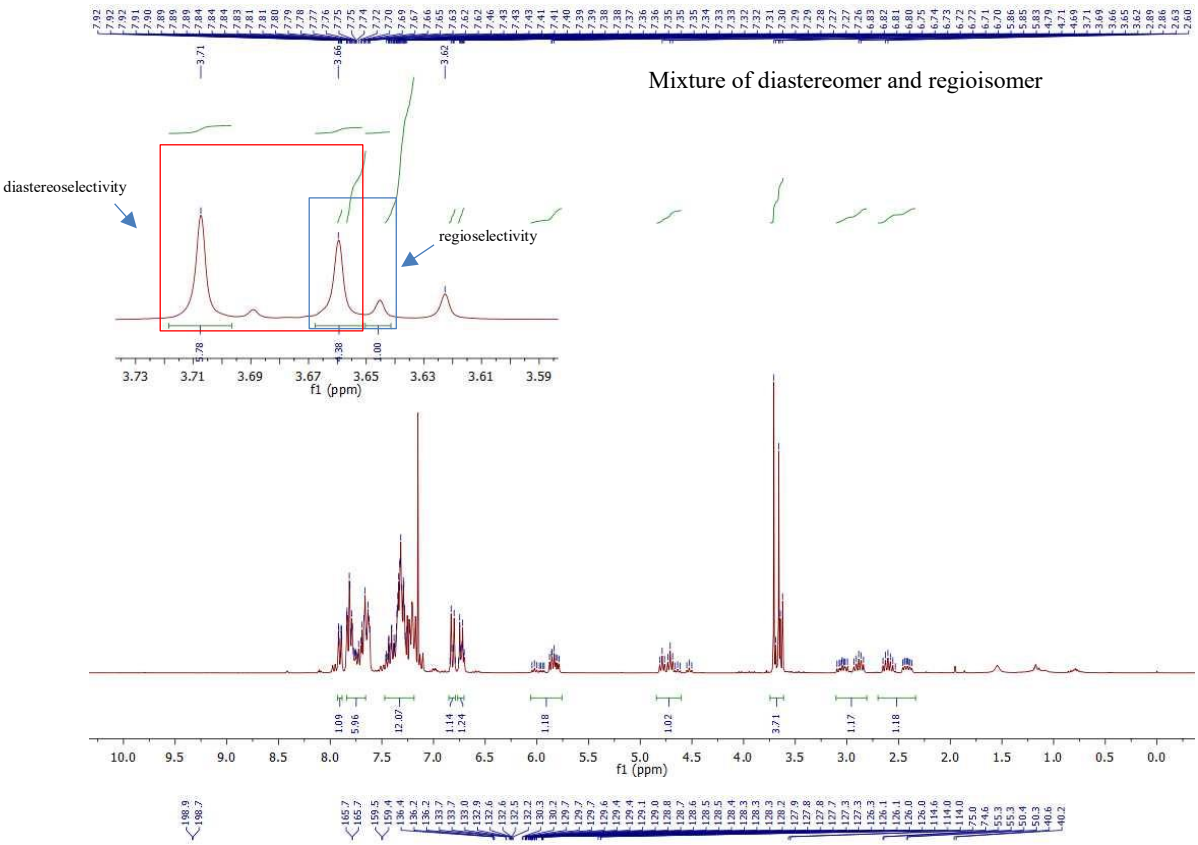


300 MHz in $CDCl_3$



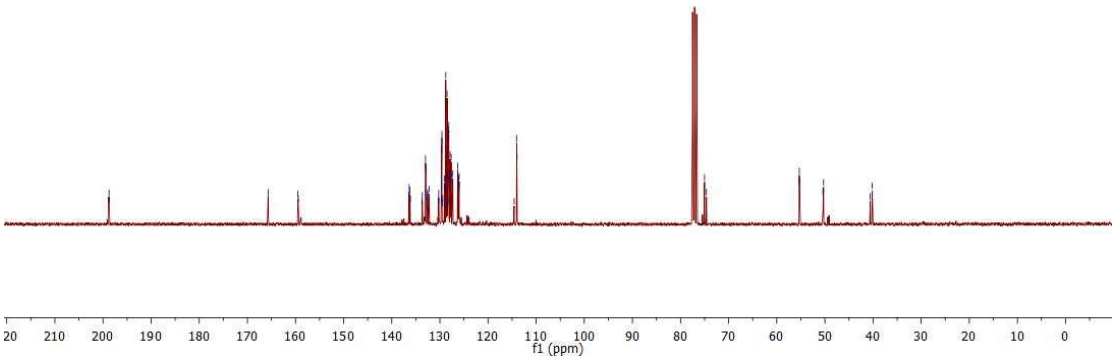
(3ag)

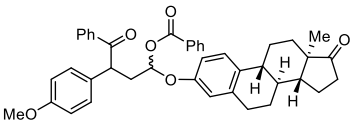
Mixture of diastereomer and regioisomer



76 MHz in $CDCl_3$

Mixture of diastereomer and regioisomer

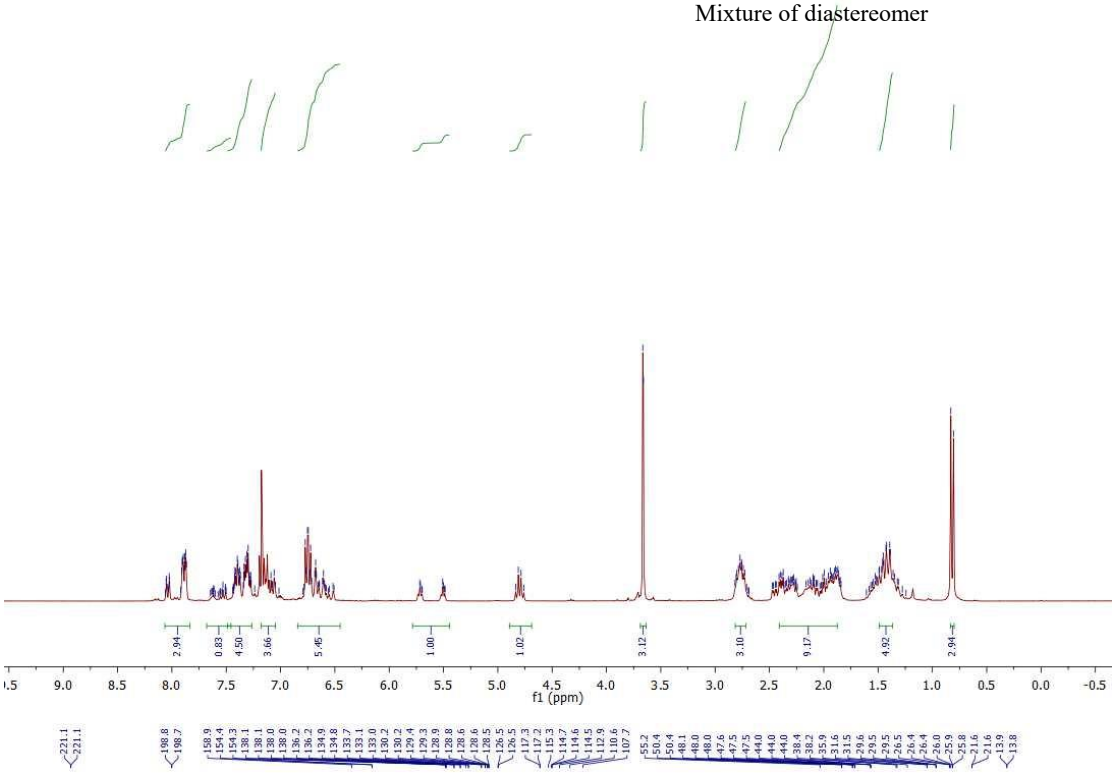




(3ah)

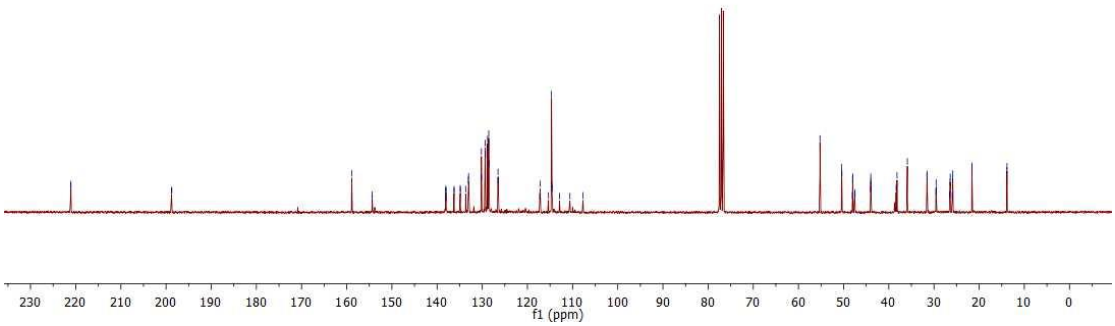
300 MHz in $CDCl_3$

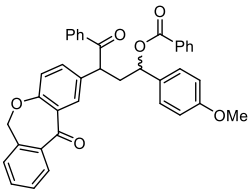
Mixture of diastereomer



76 MHz in $CDCl_3$

Mixture of diastereomer

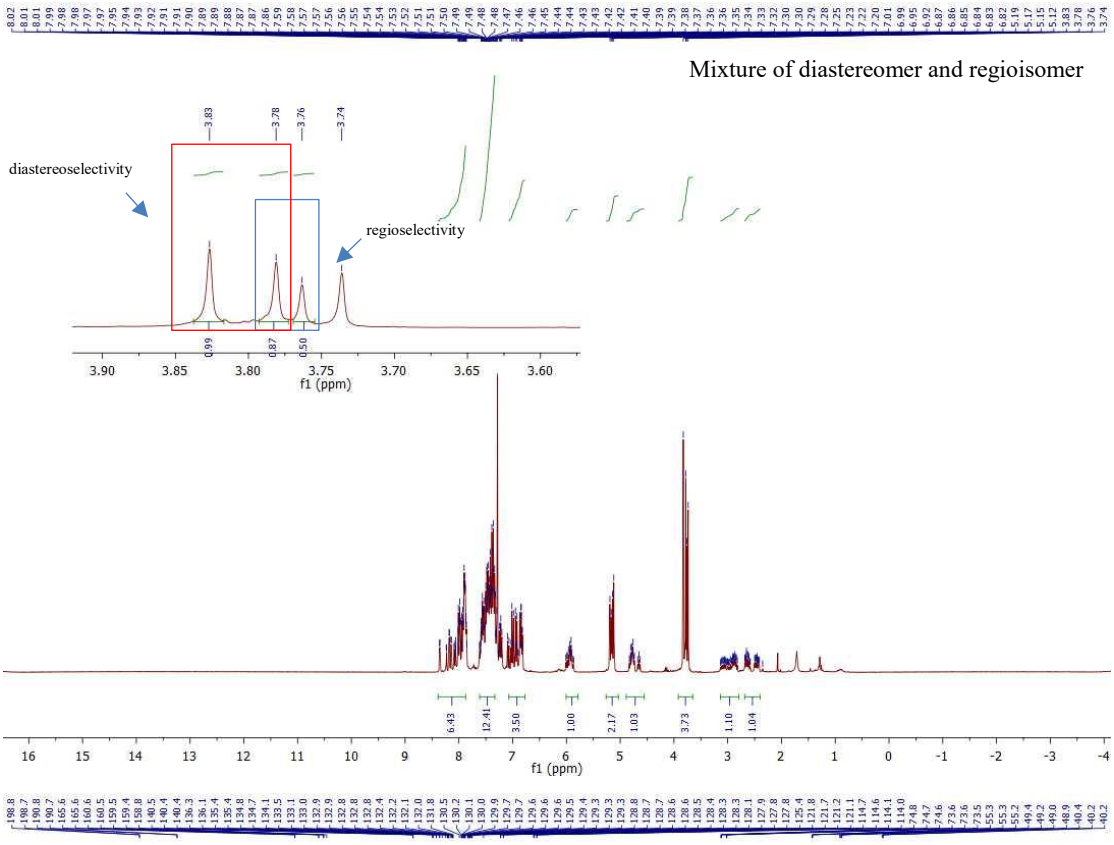




(3ai)

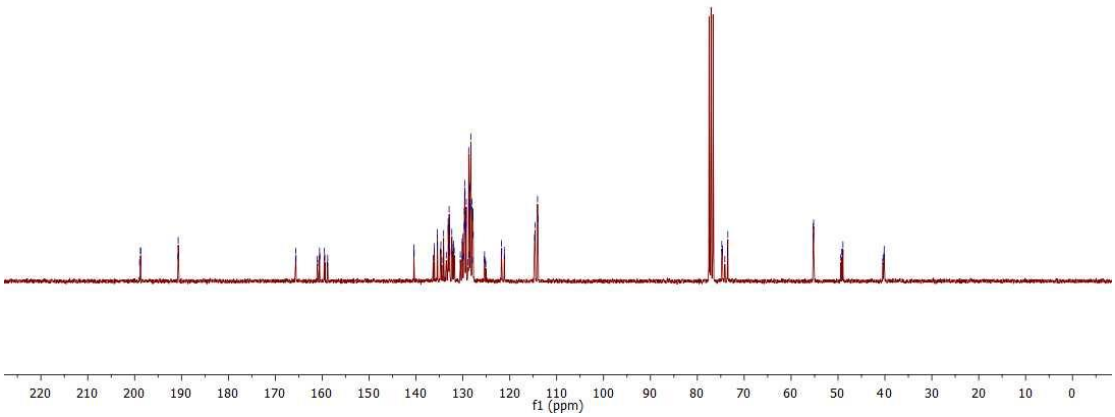
300 MHz in $CDCl_3$

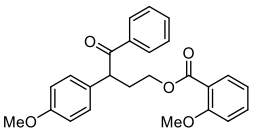
Mixture of diastereomer and regioisomer



76 MHz in $CDCl_3$

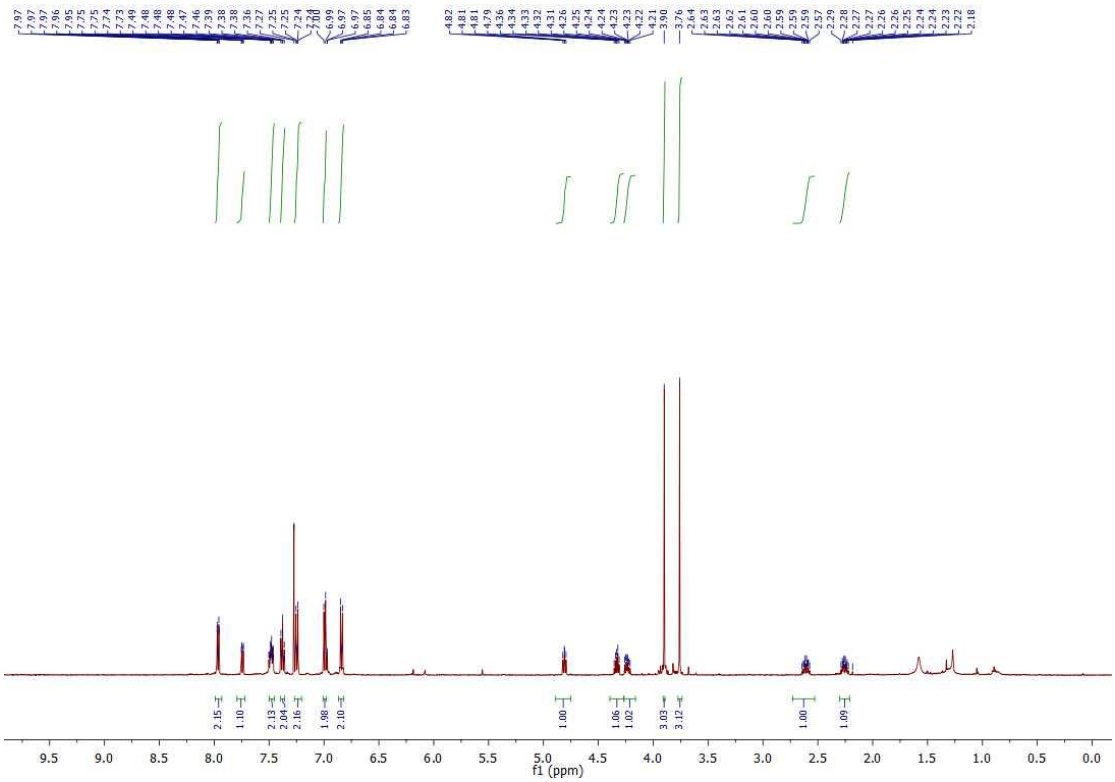
Mixture of diastereomer and regioisomer



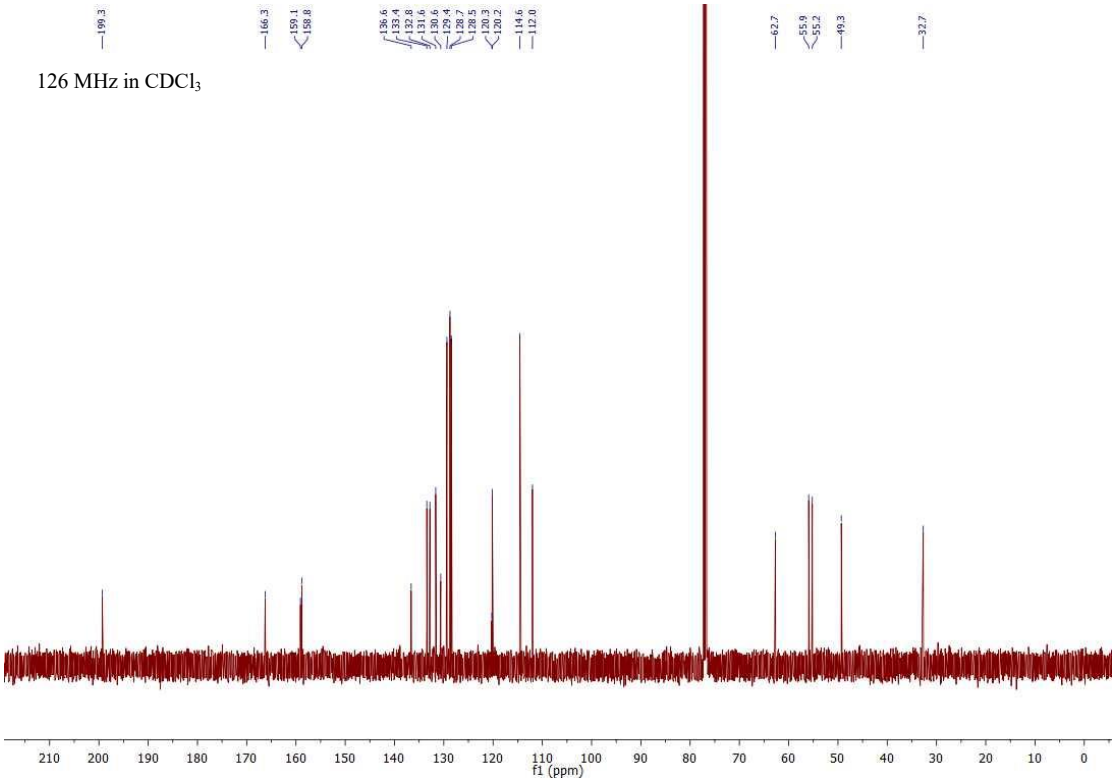


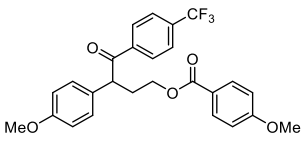
(3aj)

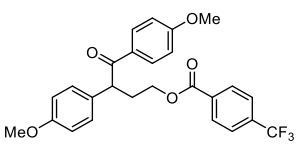
500 MHz in $CDCl_3$



126 MHz in $CDCl_3$



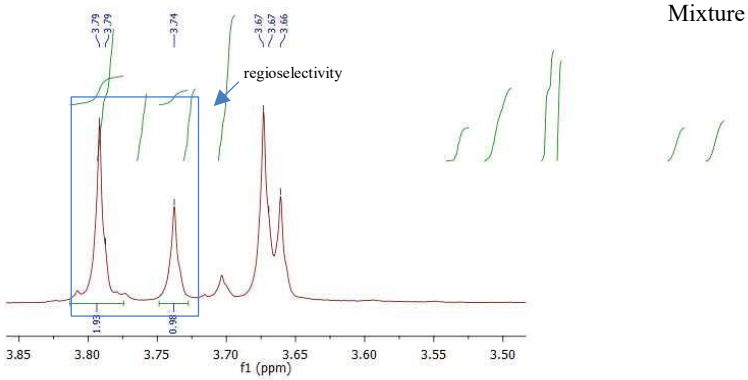


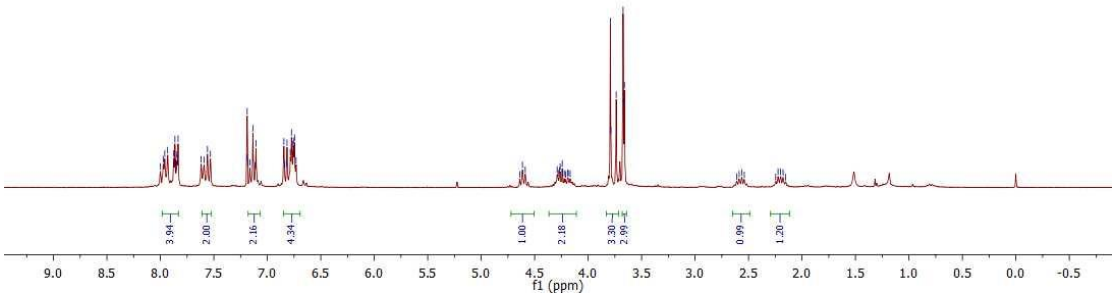


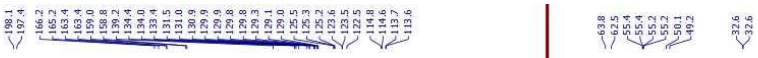
(3ak)

300 MHz in $CDCl_3$

Mixture of regioisomer

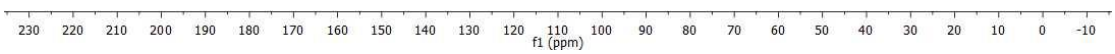






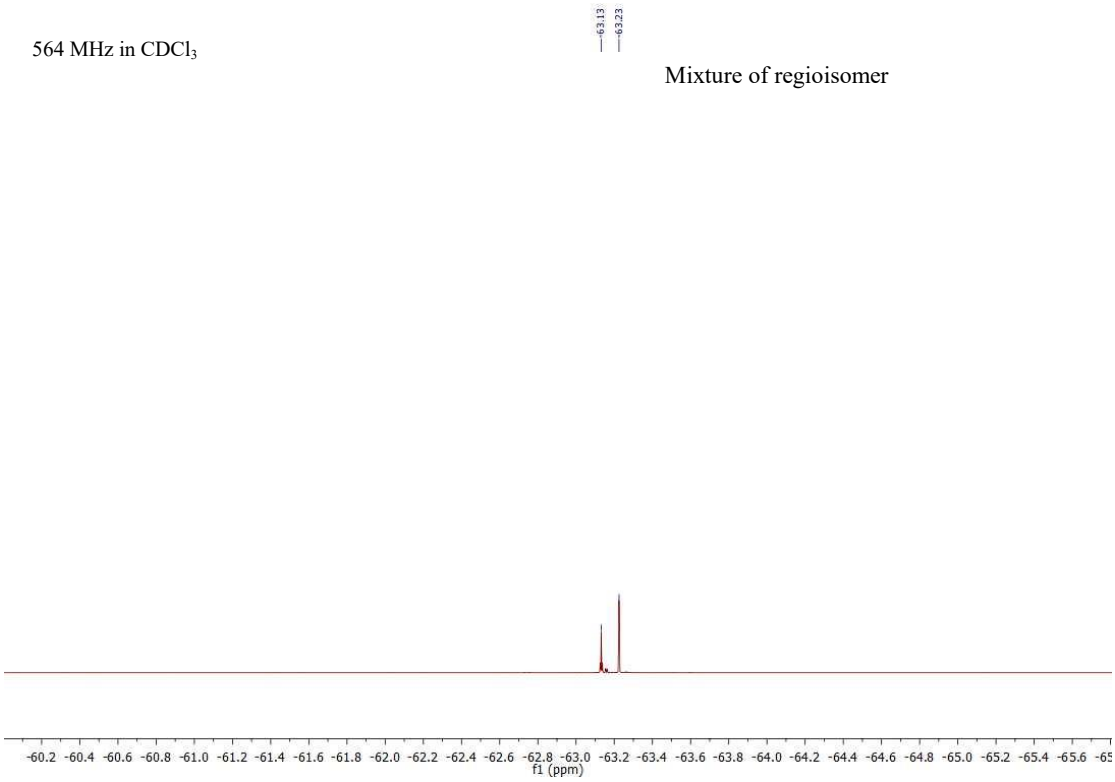
151 MHz in $CDCl_3$

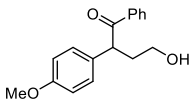
Mixture of regioisomer



564 MHz in $CDCl_3$

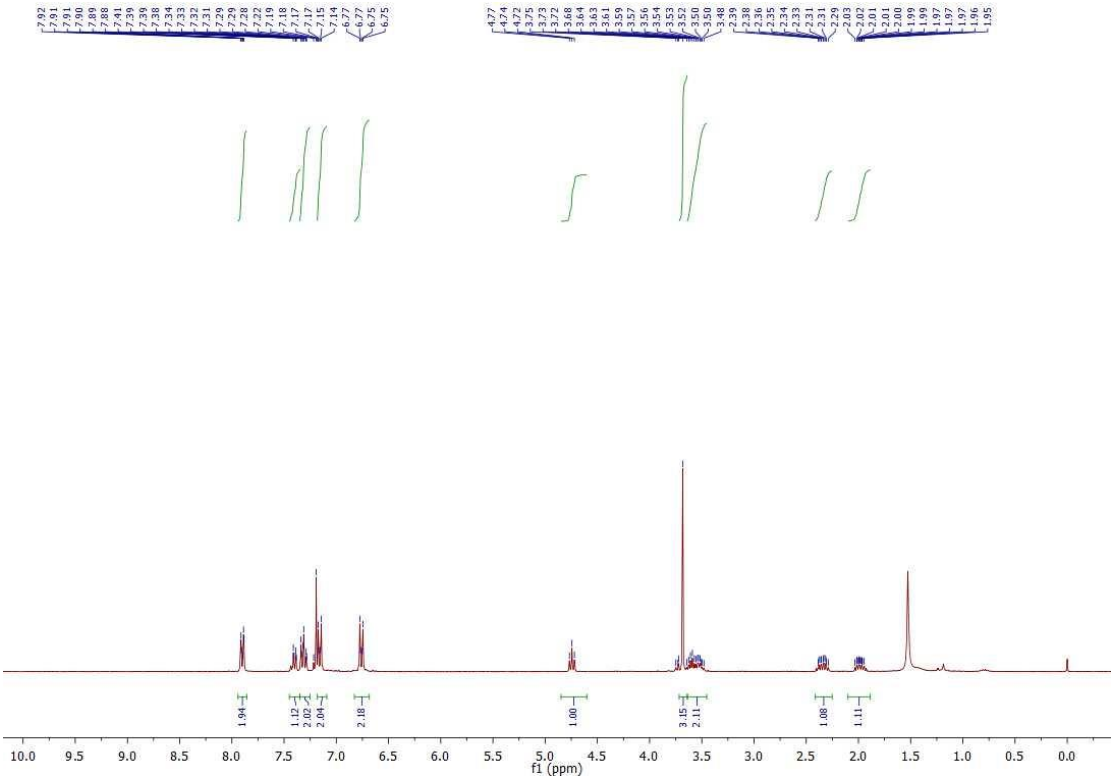
Mixture of regioisomer



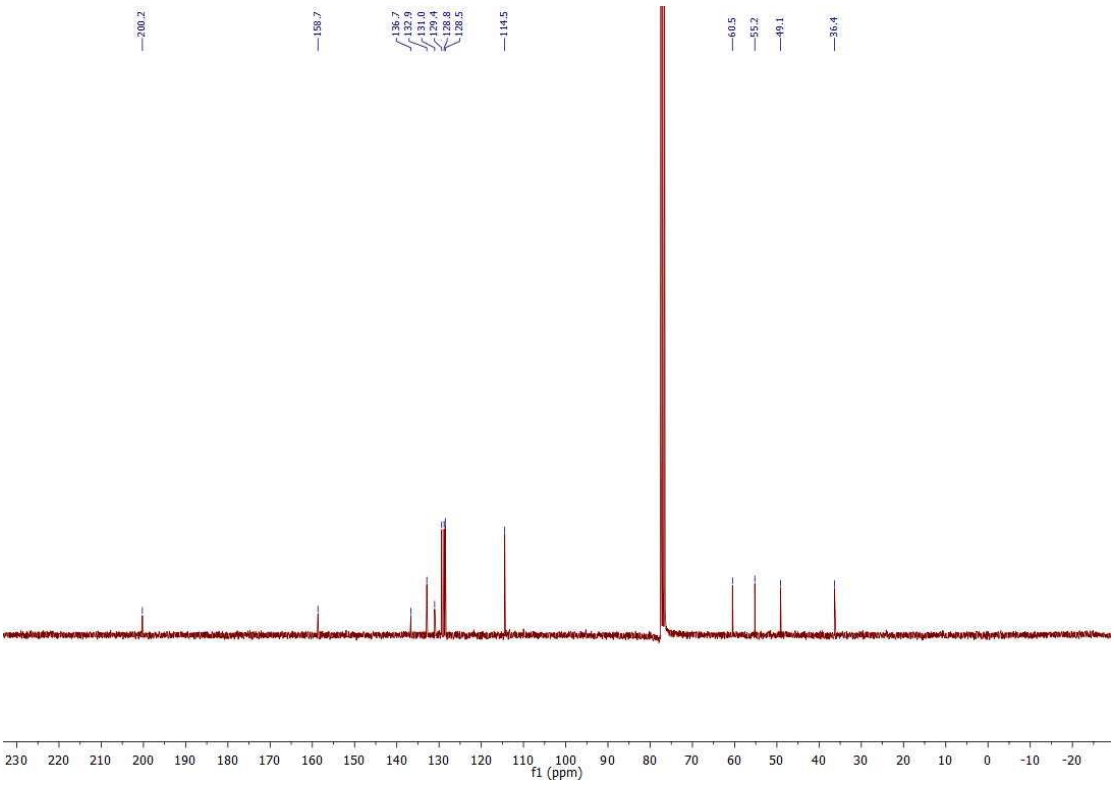


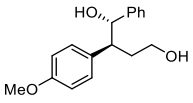
(4a)

300 MHz in $CDCl_3$



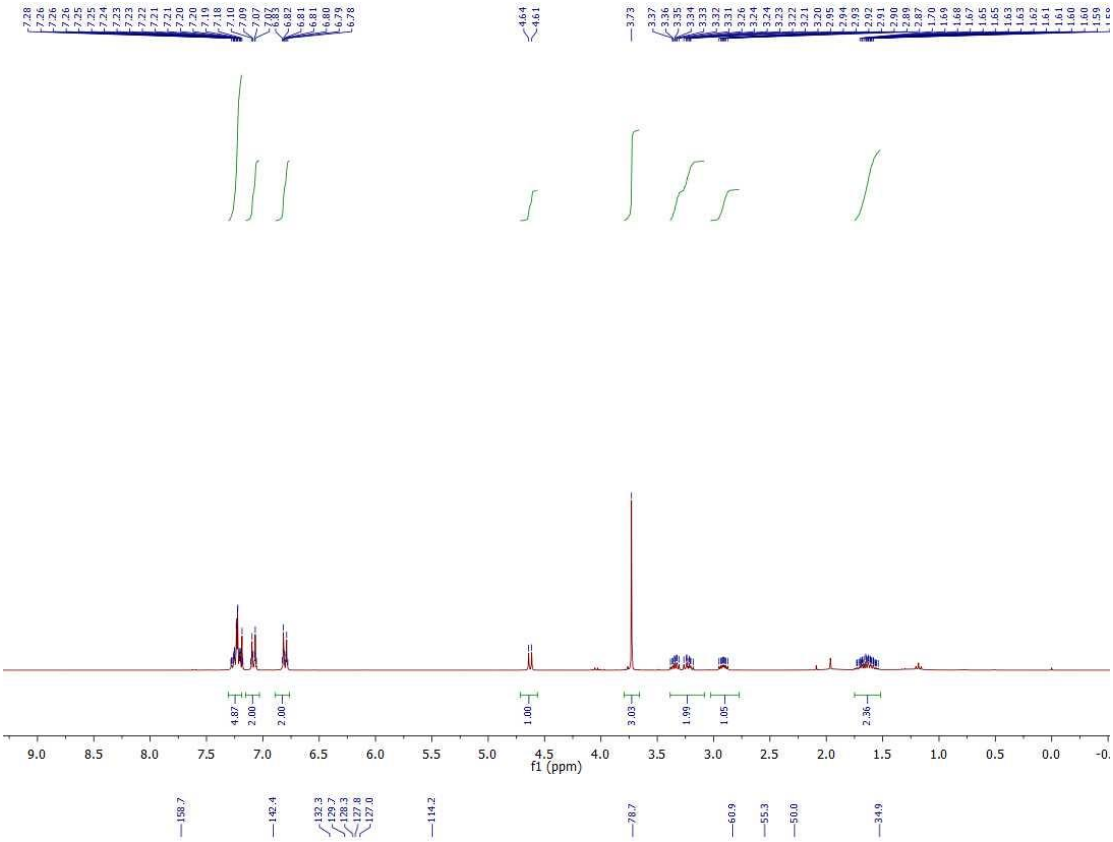
75 MHz in $CDCl_3$



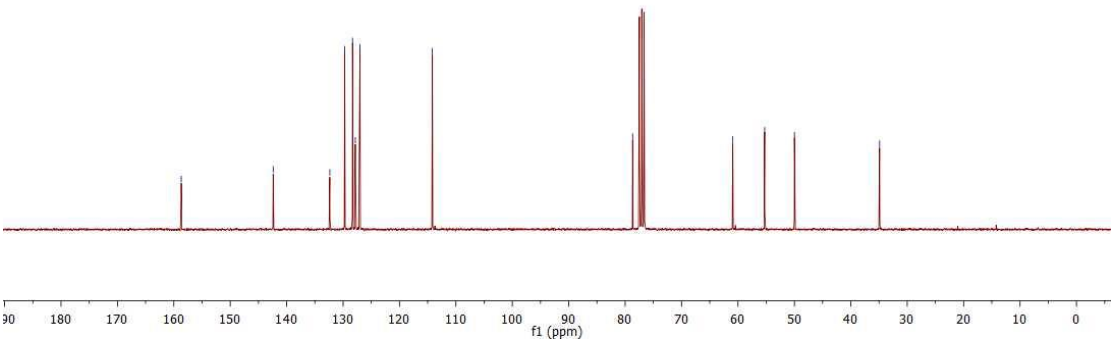


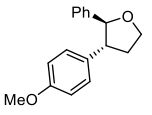
(4b)

500 MHz in $CDCl_3$



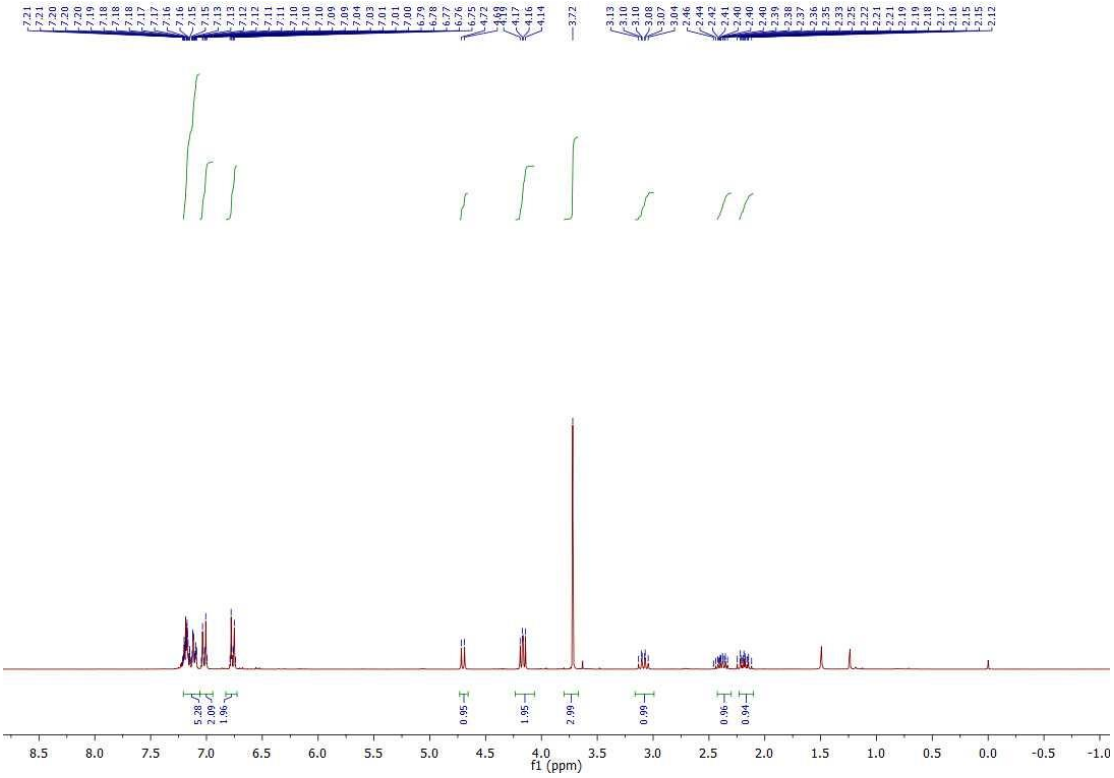
76 MHz in $CDCl_3$





(4c)

300 MHz in $CDCl_3$



76 MHz in $CDCl_3$