- Supporting Information -

Ruthenium(II) Catalysis/Noncovalent Interaction Synergy for Cross-Dehydrogenative Coupling of Arene Carboxylic Acids

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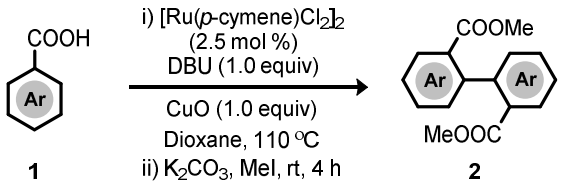
General information

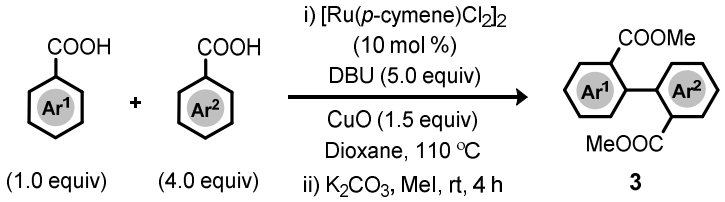
[Ru(*p*-cymene)Cl_2]$_2$ and CuO were purchased from Alfa Aesar company. Benzoic acids and DBU were purchased from Avra chemicals and Spectrochem. All reactions were monitored by thin layer chromatography (TLC) on Merck 60 F 254 precoated silica plates and visualized using a UV lamp (366 or 254 nm) or by use of potassium permanganate, 5 g K_2CO_3, / 100 mL water. Products were isolated by column chromatography (Merck silica gel 100-200μm). ^{13}C and ^{1}H NMR spectra were recorded on a Bruker 400 or Bruker 500 MHz spectrometers. Chemical shift values (δ) are reported in ppm and calibrated to the residual solvent peak $CDCl_3$ δ = 7.2600 ppm for ^{1}H, δ = 77.16 for ^{13}C; or calibrated to tetramethylsilane (δ = 0.00). All NMR spectra were recorded at ambient temperature (290 K) unless otherwise noted. ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constant, integration). The following abbreviations are used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet; dd, doublet of doublet; dt, doublet of triplet; dq, doublet of quartet; td, triplet of doublet; tt, triplet of triplet; dq, doublet of quartet; br, broad. Mass spectra were recorded by electron spray ionization (ESI) method on a Q-TOF Micro with lock spray source.

Typical ruthenium(II)-catalyzed *homo*-dimerization of benzoic acids (*isolated as ester*):



Procedure: To an oven dried screw cap reaction tube (10 × 1.5 cm), corresponding benzoic acid **1** (0.3 mmol, 1.0 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (2.5 mol %), CuO (1.0 equiv), and DBU (1.0 equiv) were taken. Then dry dioxane (0.4 mL) was added in it and the mixture was stirred at 110 °C for 24 h under air. After completion (monitored by TLC), K_2CO_3 (3.0 equiv) and iodomethane (3.0 equiv) were added to the reaction mixture and stirred for 4 h at room temperature. Then the solvent was evaporated under reduced pressure. In order to get pure 2,2′-biaryl acid methyl ester **2**, the resulting residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate.

Typical ruthenium(II)-catalyzed *cross*-dimerization of benzoic acids (*isolated as ester*):

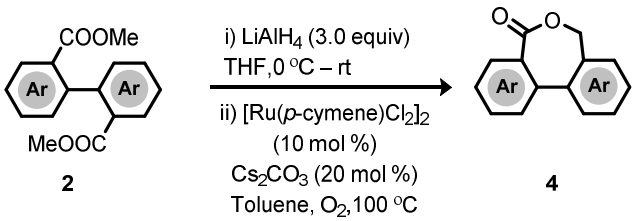


Procedure: To an oven dried screw cap reaction tube (10 × 1.5 cm), corresponding benzoic acid (**Ar**^{1}) (0.15 mmol, 1.0 equiv), benzoic acid (**Ar**^{2}) (4.0 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (10.0 mol %), CuO (1.5 equiv), and DBU (5.0 equiv) were taken. Then dry dioxane (0.5 mL) was added in it and the mixture was stirred at 110 °C for 24 h under air. After completion (monitored by TLC), K_2CO_3 (4.0 equiv) and iodomethane (8.0 equiv) were added to the reaction mixture and stirred for 4 h at room temperature. Then the solvent was evaporated under reduced pressure. In order to get pure 2,2′-biaryl acid methyl ester **3**, the resulting residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate.

Table for the Ar^1/Ar^2 acid ratio:

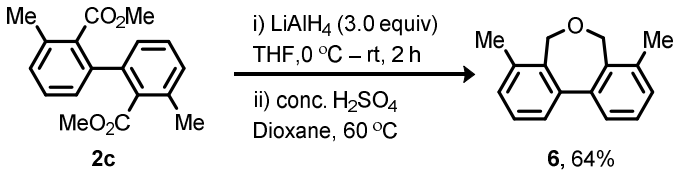
Compound	Ar^1 (1.0 equiv)	Ar^2 (4.0 equiv)
3a	2-Methoxybenzoic acid	2-Fluorobenzoic acid
3b	2,4-Dimethylbenzoic acid	3-Acetylbenzoic acid
3c	4-Methoxybenzoic acid	2-Fluorobenzoic acid
3d	1-Naphthoic acid	2-Benzoylbenzoic acid
3e	2-Methoxybenzoic acid	1-Naphthoic acid
3f	4-Methoxybenzoic acid	1-Naphthoic acid

Typical synthesis of biphenyl-tethered lactones (4a-e):



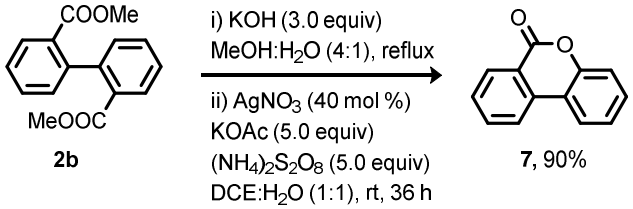
Procedure: A solution of corresponding 2,2′-biaryl acid methyl ester **2** (0.15 mmol, 1 equiv) in THF (1.0 mL) was slowly added to a suspension of $LiAlH_4$ (3.0 equiv) in THF (2.0 mL). After stirring for 2 h at room temperature, the mixture was hydrolyzed by careful addition of water (25 mL) and acidified with 2 N HCl. The organic solvent was evaporated, and the aqueous residue was diluted with water (5 mL) and extracted with dichloromethane. The organic extract was washed with water and dried over Na_2SO_4. After evaporation of the solvent, $[RuCl_2(p\text{-cymene})]_2$ (10.0 mol %) and Cs_2CO_3 (20.0 mol %) were added to the crude product. Next, Toluene (1.5 mL) was added in the reaction vessel and the reaction mixture was stirred at 100 °C under oxygen atmosphere (using an O_2 balloon) for 3 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. In order to get pure product **4**, the resulting residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate.

Typical synthesis of biphenyl-tethered ether (6):



Procedure: A solution of 2,2′-biaryl acid methyl ester **2c** (0.15 mmol, 1 equiv) in THF (1.0 mL) was slowly added to a suspension of $LiAlH_4$ (3.0 equiv) in THF (2.0 mL). After stirring for 2 h at room temperature, the mixture was hydrolyzed by careful addition of water (25 mL) and acidified with 2 N HCl. The organic solvent was evaporated, and the aqueous residue was diluted with water (5 mL) and extracted with dichloromethane. The combined organic extract was washed with water and dried over Na_2SO_4. After evaporation of the solvent conc. sulphuric acid (0.1 equiv) and 0.5 mL dioxane were added to the crude product and the reaction mixture was stirred at 60 °C for 24 h. Then solvent was evaporated under reduced pressure and DCM (10 mL) was added. The mixture was carefully washed with sodium bicarbonate solution. The solvent was evaporated under reduced pressure and resulting residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate.

Typical synthesis of 6*H*-benzo[c]chromen-6-one (7):

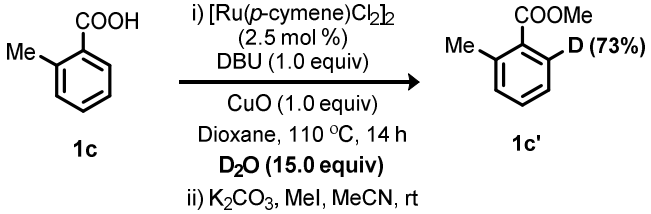


Procedure: 2,2′-Biaryl acid methyl ester **2b** (0.15 mmol, 1.0 equiv) and KOH (3.0 equiv) were taken in a 25 mL round bottom flask and 5 mL MeOH:water (4:1) was added in it. The mixture was refluxed until the consumption of the ester (monitored by TLC). Volatiles were removed under vacuo and the resulting solution was neutralized with 2N HCl. The acid was extracted using ethyl acetate, dried with $MgSO_4$, and evaporated to get the acid **2b′**. The crude acid **2b′** was taken in a screw cap reaction tube (10 × 1.5 cm). Then $AgNO_3$ (40 mol %), $(NH_4)_2S_2O_8$ (5.0 equiv), KOAc (5.0 equiv), dichloroethane (DCE, 1 mL), and H_2O (1 mL) were sequentially added in it. The reaction mixture was stirred at room temperature for 36 h. After completion, it was diluted with H_2O and extracted with CH_2Cl_2

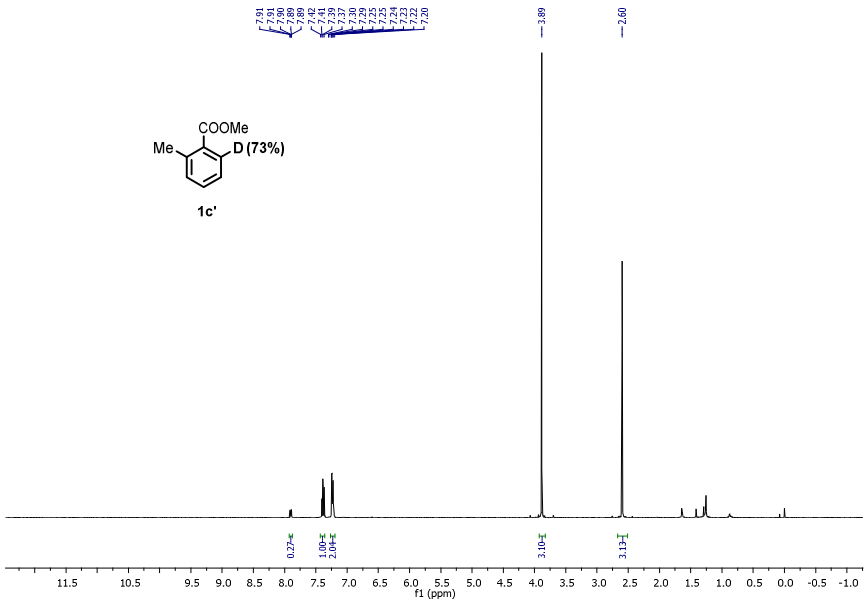
(3 × 20 mL). The organic extract was dried over $MgSO_4$ and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using ethyl acetate/hexane system afforded the desired product **7**.

Mechanistic studies:

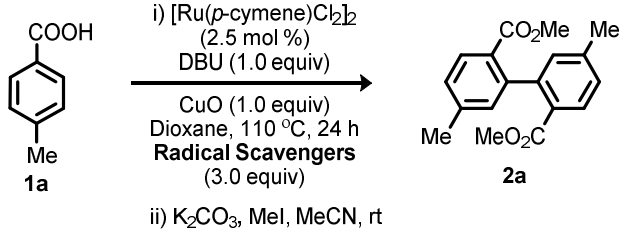
(a) H/D-Scrambling study:



Procedure: To an oven dried screw cap reaction tube (10 × 1.5 cm), benzoic acid **1c** (0.3 mmol, 1 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (2.5 mol %), CuO (1.0 equiv), and DBU (1.0 equiv) were taken. Then dry dioxane (0.4 mL) and D_2O (15.0 equiv) were added and the mixture was stirred at 110 °C for 14 h under air. Then, a spoon of sodium sulfate was added in the reaction mixture. The reaction mixture was diluted with DCM and transferred to a 25 mL round-bottom flask. Next, the volatiles were evaporated under reduced pressure and K_2CO_3 (3.0 equiv) and iodomethane (3.0 equiv) were added to the reaction mixture followed by the addition of acetonitrile (2.0 mL). The resulting solution was stirred at room temperature for 4 h. Then the solvent was evaporated under reduced pressure. In order to get pure product **1c′**, the resulting residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate. The deuterium scrambling was observed through ^{1}H NMR spectroscopy.



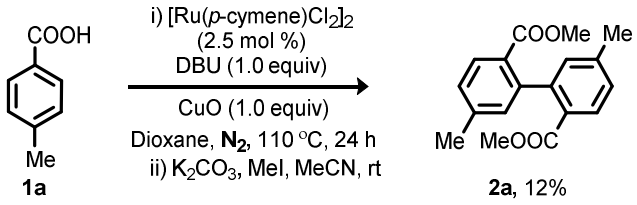
(b) Radical scavengers study:



Radical scavengers: ***TEMPO*** = 45%; ***BHT*** = 54%; ***1,1-diphenylethene*** = 41%

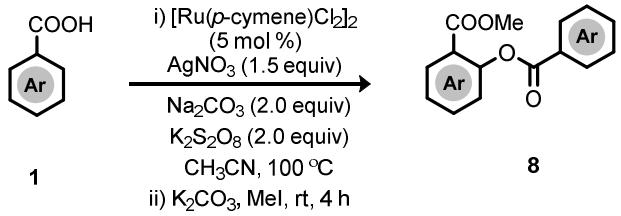
Procedure: To an oven dried screw cap reaction tube (10 × 1.5 cm) benzoic acid **1a** (0.3 mmol, 1.0 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (2.5 mol %), CuO (1.0 equiv), DBU (1.0 equiv), and radical scavenger (3.0 equiv) were taken. Then dry dioxane (0.4 mL) were added into the mixture and it was stirred at 110 °C for 24 h under air. After completion (monitored by TLC), K_2CO_3 (3.0 equiv) and iodomethane (3.0 equiv) were added to the reaction mixture and the resulting solution was stirred at room temperature for 4 h. Then the solvent was evaporated under reduced pressure. In order to get pure 2,2′-biaryl acid methyl ester **2a**, the resulting residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate.

(c) Studying the role of oxygen:



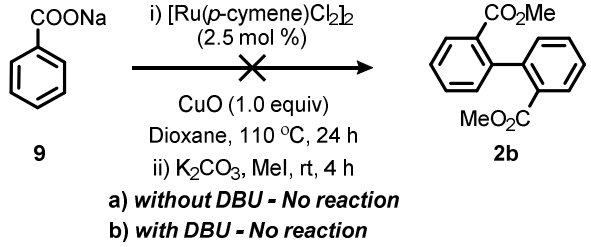
Procedure: To an oven dried reaction tube (10 × 1.5 cm) benzoic acid **1a** (0.3 mmol, 1 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (2.5 mol %), CuO (1.0 equiv), and DBU (1.0 equiv) were taken. Then the reaction tube was evacuated under vacuum and back-filled with nitrogen gas (three-times). Then dry dioxane (0.4 mL) were added into the mixture and it was stirred at 110 °C for 24 h under air. After completion (monitored by TLC), K_2CO_3 (3.0 equiv) and iodomethane (3.0 equiv) were added to the reaction mixture and the resulting solution was stirred at room temperature for 4 h. Then the solvent was evaporated under reduced pressure. In order to get pure 2,2′-biaryl acid methyl ester **2a**, the resulting residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate.

(d) Use of strong oxidant:



Procedure: To an oven dried screw cap reaction tube (10 × 1.5 cm) corresponding benzoic acid **1** (0.3 mmol, 1 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (5.0 mol %), $AgNO_3$ (1.5 equiv), Na_2CO_3 (2.0 equiv), and $K_2S_2O_8$ (2.0 equiv) were taken. Then dry acetonitrile (0.5 mL) was added into the mixture and it was stirred at 100 °C for 24 h under air. After completion (monitored by TLC), K_2CO_3 (3.0 equiv) and iodomethane (3.0 equiv) were added to the reaction mixture and the resulting solution was stirred at room temperature for 4 h. Then the solvent was evaporated under reduced pressure. In order to get pure product **8**, the resulting residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate.

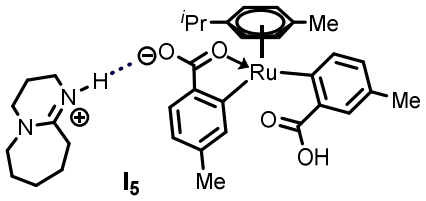
(e) Role of DBUH$^+$:



Procedure: To an oven dried screw cap reaction tube (10 × 1.5 cm) sodium benzoate (**9**, 0.3 mmol, 1 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (2.5 mol %), and CuO (1.0 equiv) were taken. Then dry dioxane (0.4 mL) was added into the mixture and it was stirred at 110 °C for 24 h under air. After completion (monitored by TLC), K_2CO_3 (3.0 equiv) and iodomethane (3.0 equiv) were added to the reaction mixture and the resulting solution was stirred at room temperature for 4 h. Same experiment was also performed in the presence of DBU (1.0 equiv). In both of the cases, the formation of 2,2′-biaryl acid methyl esters was not observed, indicating the decisive role of DBUH$^+$ in the transformation.

(f) ESI-HRMS analysis of reaction mixture:

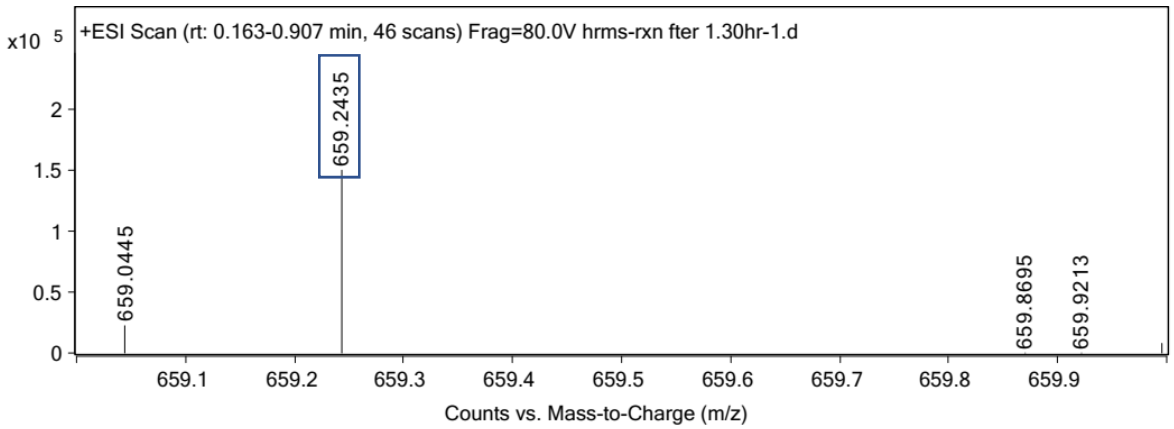
To an oven dried screw cap reaction tube (10 × 1.5 cm) [Ru(*p*-cymene)Cl_2]$_2$ (0.016 mmol), benzoic acid **1a** (2.0 equiv.), and DBU (2.0 equiv.) were taken. Then dry dioxane (0.3 mL) was added in it and the mixture was stirred at 110 °C under air. After 90 minutes, the crude reaction mixture was taken through a syringe and ESI-HRMS was recorded.



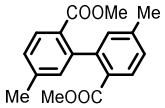
I_5

Detected in ESI-HRMS

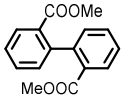
$[MH]^+$ = 659.2423 (*expected*)
659.2435 (*observed*)



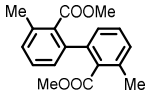
NMR spectroscopic data of synthesized compounds:



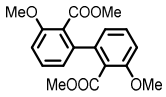
Dimethyl 4,4'-dimethyl-[1,1'-biphenyl]-2,2'-dicarboxylate (2a): yield = 32.3 mg (72%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.00 (s, 2H), 3.61 (s, 6H), 2.40 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.46, 143.77, 142.09, 131.02, 130.04, 127.91, 126.62, 51.78, 21.64 ppm.



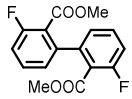
Dimethyl [1,1'-biphenyl]-2,2'-dicarboxylate (2b): yield = 23.4 mg (58%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.63 – 7.49 (m, 2H), 7.47 – 7.38 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 3.61 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.55, 143.41, 131.60, 130.33, 129.98, 129.49, 127.30, 51.94 ppm.



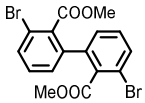
Dimethyl 3,3'-dimethyl-[1,1'-biphenyl]-2,2'-dicarboxylate (2c): yield = 27 mg (60%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 2H), 7.25 – 7.17 (m, 2H), 7.16 – 7.04 (m, 2H), 3.55 (s, 6H), 2.40 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.64, 139.26, 135.85, 133.12, 129.59, 129.02, 127.17, 51.80, 20.18 ppm.



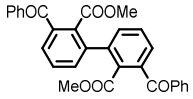
Dimethyl 3,3'-dimethoxy-[1,1'-biphenyl]-2,2'-dicarboxylate (2d): yield = 33.6 mg (68%), white solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 6.94 – 6.90 (m, 2H), 6.90 – 6.87 (m, 2H), 3.86 (s, 6H), 3.59 (s, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.85, 156.60, 139.32, 130.20, 123.32, 121.89, 110.48, 56.09, 52.12 ppm; **HRMS** (m/z) $C_{18}H_{18}O_6K^+$ 369.0735.



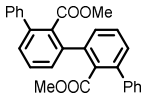
Dimethyl 3,3'-difluoro-[1,1'-biphenyl]-2,2'-dicarboxylate (2e): yield = 33 mg (72%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.37 (m, 2H), 7.19 – 7.13 (m, 2H), 7.06 (dd, *J* = 7.7, 0.5 Hz, 2H), 3.66 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.15, 160.05 (d, *J* = 253.6 Hz), 140.67, 131.52 (d, *J* = 9.3 Hz), 125.68 (d, *J* = 3.4 Hz), 121.11 (d, *J* = 15.5 Hz), 115.84 (d, *J* = 21.9 Hz), 52.52 ppm; **HRMS** (m/z) $C_{16}H_{12}F_2O_4Na^+$ 329.0591.



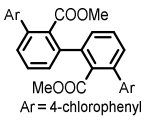
Dimethyl 3,3'-dibromo-[1,1'-biphenyl]-2,2'-dicarboxylate (2f): yield = 41.7 mg (65%), white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.3, 1.8 Hz, 2H), 7.26 – 7.14 (m, 4H), 3.57 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.29, 138.74, 135.47, 132.63, 130.22, 128.70, 119.88, 52.56 ppm; **HRMS** (m/z) $C_{16}H_{12}Br_2O_4K^+$ 464.8726.



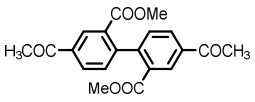
Dimethyl 3,3'-dibenzoyl-[1,1'-biphenyl]-2,2'-dicarboxylate (2g): yield = 57.4 mg (80%), white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.79 – 7.70 (m, 3H), 7.69 – 7.60 (m, 2H), 7.59 – 7.50 (m, 4H), 7.47 – 7.36 (m, 5H), 3.60 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.15, 166.47, 141.74, 137.22, 133.17, 132.51, 130.16, 129.72, 129.31, 129.27, 128.60, 127.85, 52.26 ppm.



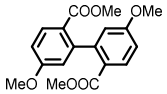
Dimethyl [1,1':3',1'':3'',1'''-quaterphenyl]-2',2''-dicarboxylate (2h): yield = 39.9 mg (63%), white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.35 – 7.20 (m, 14H), 3.25 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.29, 139.78, 139.60, 138.02, 131.85, 128.38, 128.06, 127.89, 127.45, 127.41, 126.60, 50.78 ppm; **HRMS** (m/z) $C_{28}H_{22}O_4Na^+$ 445.1411.



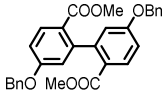
Dimethyl-4,4'''-dichloro-[1,1':3',1'':3'',1'''-quaterphenyl]-2',2''-dicarboxylate (2i): yield = 44.8 mg (61%), white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.30 (m, 12H), 3.35 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.01, 139.41, 139.19, 139.05, 133.86, 132.77, 129.82, 129.34, 129.22, 128.69, 128.66, 51.90 ppm.



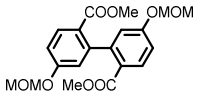
Dimethyl 4,4'-diacetyl-[1,1'-biphenyl]-2,2'-dicarboxylate (2j): yield = 29.7 mg (56%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.4 Hz, 2H), 8.15 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.68 (s, 6H), 2.68 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.92, 166.28, 147.35, 136.37, 131.27, 130.38, 130.27, 129.43, 52.34, 26.82 ppm; **HRMS** (m/z) $C_{20}H_{18}O_6Na^+$ 377.0990.



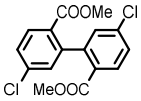
Dimethyl 5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-dicarboxylate (2k): yield = 32.7 mg (66%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.8 Hz, 2H), 6.91 (dd, *J* = 8.8, 2.7 Hz, 2H), 6.69 (d, *J* = 2.6 Hz, 2H), 3.84 (s, 6H), 3.61 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.79, 161.99, 146.05, 132.19, 121.57, 115.56, 112.38, 55.52, 51.70 ppm.



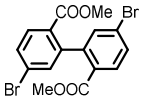
Dimethyl 5,5'-bis(benzyloxy)-[1,1'-biphenyl]-2,2'-dicarboxylate (2l): yield = 46.2 mg (64%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.59 – 7.32 (m, 10H), 7.00 (dd, *J* = 8.8, 2.6 Hz, 2H), 6.80 (d, *J* = 2.6 Hz, 2H), 5.10 (s, 4H), 3.62 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.78, 160.16, 144.98, 135.38, 131.19, 127.74, 127.28, 126.71, 120.88, 115.36, 112.29, 69.17, 50.68 ppm.



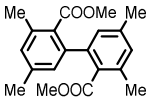
Dimethyl 5,5'-bis(methoxymethoxy)-[1,1'-biphenyl]-2,2'-dicarboxylate (2m): yield = 22.2 mg (38%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.7 Hz, 2H), 7.05 (dd, *J* = 8.7, 2.6 Hz, 2H), 6.82 (d, *J* = 2.5 Hz, 2H), 5.24 – 5.18 (m, 4H), 3.61 (s, 6H), 3.49 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.82, 159.69, 145.67, 132.08, 122.75, 117.78, 114.29, 94.39, 56.44, 51.72 ppm; **HRMS** (m/z) $C_{20}H_{22}O_8Na^+$ 413.1201.



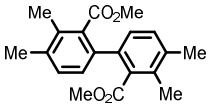
Dimethyl 5,5'-dichloro-[1,1'-biphenyl]-2,2'-dicarboxylate (2n): yield = 25.3 mg (50%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.42 (dd, *J* = 8.4, 2.1 Hz, 2H), 7.20 (d, *J* = 2.1 Hz, 2H), 3.65 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.24, 143.91, 138.07, 131.55, 130.14, 127.92, 127.67, 52.19 ppm.



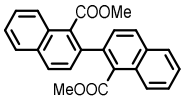
Dimethyl 5,5'-dibromo-[1,1'-biphenyl]-2,2'-dicarboxylate (2o): yield = 37.8 mg (59%), white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.58 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.36 (d, *J* = 2.0 Hz, 2H), 3.65 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.37, 143.85, 133.02, 131.59, 130.94, 128.16, 126.59, 52.21 ppm.



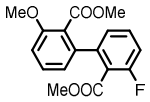
Dimethyl 3,3',5,5'-tetramethyl-[1,1'-biphenyl]-2,2'-dicarboxylate (2p): yield = 25.9 mg (53%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (s, 2H), 6.88 (s, 2H), 3.54 (s, 6H), 2.37 (s, 6H), 2.31 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.80, 139.99, 139.11, 136.00, 130.32, 129.97, 127.95, 51.66, 21.29, 20.27 ppm; **HRMS** (m/z) $C_{20}H_{22}O_4Na^+$ 349.1409.



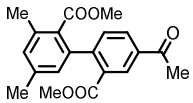
Dimethyl 3,3',4,4'-tetramethyl-[1,1'-biphenyl]-2,2'-dicarboxylate (2q): yield = 23.0 mg (47%), colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 3.57 (s, 6H), 2.30 (s, 6H), 2.25 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.39, 136.39, 136.23, 134.08, 133.53, 130.26, 127.04, 51.84, 20.22, 17.01 ppm.



Dimethyl [2,2'-binaphthalene]-1,1'-dicarboxylate (2r): yield = 46.6 mg (84%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 2H), 8.02 – 7.86 (m, 4H), 7.65 – 7.53 (m, 4H), 7.49 (d, *J* = 8.4 Hz, 2H), 3.61 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.14, 137.75, 132.63, 130.10, 129.77, 128.32, 127.64, 127.39, 126.65, 125.57, 52.19 ppm; **HRMS** (m/z) $C_{24}H_{18}O_4Na^+$ 393.1109.

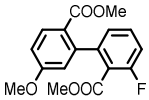


Dimethyl 3-fluoro-3'-methoxy-[1,1'-biphenyl]-2,2'-dicarboxylate (3a): yield = 25.3 mg (53%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.30 (m, 2H), 7.19 – 7.04 (m, 2H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 3.88 (s, 3H), 3.66 (s, 3H), 3.59 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.60, 165.33, 159.82 (d, *J* = 250.0 Hz), 156.63, 141.05, 138.92, 134.24, 131.24 (d, *J* = 9.1 Hz), 130.38, 125.77 (d, *J* = 3.4 Hz), 122.90, 121.81, 115.50 (d, *J* = 21.8 Hz), 110.73, 56.14, 52.41, 52.15 ppm; **HRMS** (m/z) $C_{17}H_{15}FO_5Na^+$ 341.0790.

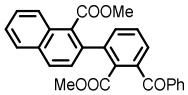


Dimethyl 4'-acetyl-3,5-dimethyl-[1,1'-biphenyl]-2,2'-dicarboxylate (3b): yield = 31.1 mg (61%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 1.9 Hz, 1H), 8.08 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.07 (s, 1H), 6.86 (s, 1H), 3.70 (s, 3H), 3.48 (s, 3H), 2.67 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.12, 169.32, 167.00, 147.11,

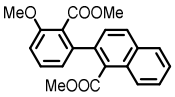
139.89, 139.53, 136.19, 136.10, 131.46, 130.92, 130.72, 130.16, 129.25, 127.27, 52.34, 51.70, 26.82, 21.39, 20.38 ppm; **HRMS** (m/z) $C_{20}H_{20}O_5Na^+$ 363.1196.



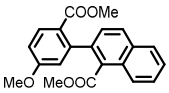
Dimethyl 3-fluoro-5'-methoxy-[1,1'-biphenyl]-2,2'-dicarboxylate (3c): yield = 23.9 mg (50%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.43 (dd, *J* = 5.0, 2.1 Hz, 1H), 7.22 – 6.89 (m, 3H), 6.73 (s, 1H), 3.84 (s, 3H), 3.76 – 3.55 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.87, 165.46, 162.00, 159.82 (d, *J* = 252.3 Hz), 143.40, 142.88, 132.61, 131.19 (d, *J* = 9.2 Hz), 125.18, 122.36, 120.79 (d, *J* = 15.3 Hz), 116.15, 114.97 (d, *J* = 22.0 Hz), 113.38, 55.64, 52.33, 51.88 ppm; **HRMS** (m/z) $C_{17}H_{15}FO_5Na^+$ 341.0788.



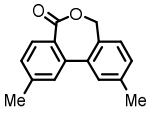
Methyl 2-(3-benzoyl-2-(methoxycarbonyl)phenyl)-1-naphthoate (3d): yield = 49.0 mg (77%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 1H), 7.97 – 7.92 (m, 1H), 7.92 – 7.88 (m, 1H), 7.86 – 7.79 (m, 2H), 7.62 – 7.41 (m, 9H), 3.66 (s, 3H), 3.25 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.51, 169.00, 167.34, 141.24, 139.86, 137.10, 137.06, 133.32, 132.75, 132.65, 131.87, 130.01, 129.86, 129.80, 129.77, 128.64, 128.38, 128.33, 127.68, 127.29, 126.71, 125.56, 52.16, 52.09 ppm; **HRMS** (m/z) $C_{27}H_{20}O_5Na^+$ 447.1194.



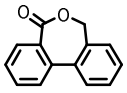
Methyl 2-(3-methoxy-2-(methoxycarbonyl)phenyl)-1-naphthoate (3e): yield = 29.4 mg (56%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 – 7.97 (m, 1H), 7.92 – 7.84 (m, 2H), 7.61 – 7.50 (m, 2H), 7.44 – 7.36 (m, 2H), 7.00 – 6.90 (m, 2H), 3.90 (s, 3H), 3.68 (s, 3H), 3.52 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.28, 167.81, 156.78, 140.48, 136.68, 132.68, 130.36, 130.27, 130.09, 129.61, 128.30, 127.56, 127.20, 126.62, 125.59, 123.35, 122.19, 110.59, 56.20, 52.21, 52.15 ppm; **HRMS** (m/z) $C_{21}H_{18}O_5Na^+$ 373.1043.



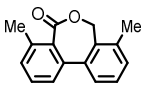
Methyl 2-(5-methoxy-2-(methoxycarbonyl)phenyl)-1-naphthoate (3f): yield = 30.5 mg (58%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 – 7.86 (m, 4H), 7.60 – 7.47 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 6.95 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.80 (d, *J* = 2.6 Hz, 1H), 3.83 (s, 3H), 3.61 (s, 3H), 3.57 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.37, 167.02, 161.92, 144.38, 138.92, 132.69, 132.49, 129.89, 129.29, 129.03, 128.34, 127.42, 127.24, 126.36, 125.42, 122.30, 116.03, 113.50, 55.65, 52.09, 51.83 ppm; **HRMS** (m/z) $C_{21}H_{18}O_5Na^+$ 373.1041.



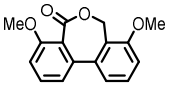
2,10-dimethyldibenzo[c,e]oxepin-5(7H)-one (4a): yield = 22.1 mg (62%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.45 (s, 1H), 7.41 (s, 1H), 7.35 – 7.30 (m, 2H), 7.25 – 7.20 (m, 1H), 5.05 – 4.87 (m, 2H), 2.49 (s, 3H), 2.45 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.70, 143.21, 140.12, 139.12, 137.54, 132.29, 132.23, 129.33 (4C), 128.59, 128.14, 69.07, 21.75, 21.58 ppm.



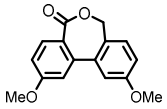
Dibenzo[c,e]oxepin-5(7H)-one (4b): yield = 21.4 mg (68%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 1H), 7.72 – 7.59 (m, 3H), 7.58 – 7.49 (m, 2H), 7.49 – 7.39 (m, 2H), 5.03 (d, *J* = 23.5 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.42, 139.13, 137.42, 134.97, 132.73, 132.10, 130.81, 130.29, 128.83 (2C), 128.72 (2C), 128.59, 69.34 ppm.



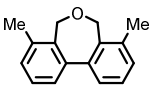
4,8-dimethyldibenzo[c,e]oxepin-5(7H)-one (4c): yield = 25.7 mg (72%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.38 (m, 2H), 7.37 – 7.28 (m, 2H), 7.24 – 7.19 (m, 1H), 5.10 – 4.81 (m, 2H), 2.49 (s, 3H), 2.46 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.68, 143.21, 140.14, 139.17, 137.57, 132.33, 132.26, 129.35 (2C), 129.31 (2C), 128.61, 128.20, 69.09, 21.76, 21.59 ppm; **HRMS** (m/z) $C_{16}H_{14}O_2Na^+$ 261.0894.



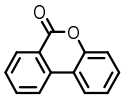
4,8-dimethoxydibenzo[c,e]oxepin-5(7H)-one (4d): yield = 23.1 mg (57%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (t, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 5.62 (d, *J* = 12.2 Hz, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 3.94 (s, 3H), 3.89 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.23, 158.42, 156.67, 140.75, 138.71, 132.12, 130.65, 124.33, 120.72 (2C), 111.49, 110.82, 60.89, 56.51, 56.06 ppm; **HRMS** (m/z) $C_{16}H_{14}O_4Na^+$ 293.0790.



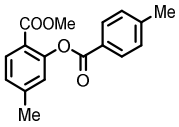
2,10-dimethoxydibenzo[c,e]oxepin-5(7H)-one (4e): yield = 28.3 mg (70%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.18 – 7.01 (m, 3H), 6.95 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.16 – 4.80 (m, 2H), 3.91 (d, *J* = 17.6 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.39, 162.79, 160.96, 140.55, 139.49, 134.57, 130.08, 127.74, 123.49, 114.51, 114.23, 113.84, 113.80, 68.76, 55.76, 55.70 ppm; **HRMS** (m/z) $C_{16}H_{14}O_4K^+$ 309.0525.



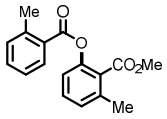
4,8-dimethyl-5,7-dihydrodibenzo[c,e]oxepine (6): yield = 21.5 mg (64%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.34 – 7.28 (m, 2H), 7.24 – 7.19 (m, 2H), 4.32 (s, 4H), 2.46 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.36, 138.77, 132.60, 129.76, 128.97, 128.25, 67.33, 21.52 ppm; **HRMS** (m/z) $C_{16}H_{17}O^+$ 225.1291.



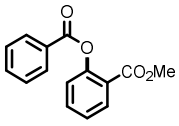
6H-benzo[c]chromen-6-one (7): yield = 26.5 mg (90%), white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.8 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 7.7 Hz, 1H), 7.82 (t, *J* = 7.3 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.41 – 7.29 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.28, 151.43, 134.95, 134.89, 130.69, 130.56, 128.99, 124.67, 122.88, 121.80, 121.40, 118.17, 117.90 ppm.



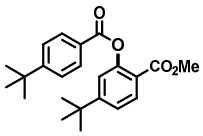
Methyl 4-methyl-2-((4-methylbenzoyl)oxy)benzoate (8a): yield = 17.4 mg (41%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.04 (s, 1H), 3.71 (s, 3H), 2.45 (s, 3H), 2.42 (s, 3H) ppm; **^{13}C NMR** (100MHz, $CDCl_3$) δ 165.71, 165.22, 150.98, 145.24, 144.42, 131.98, 130.41, 129.42, 126.98, 124.65, 120.64, 52.15, 21.90, 21.59 ppm; **HRMS** (m/z) $C_{17}H_{16}O_4Na^+$ 307.0931.



Methyl 2-methyl-6-((2-methylbenzoyl)oxy)benzoate (8b): yield = 14.5 mg (34%), colourless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 3.75 (s, 3H), 2.66 (s, 3H), 2.44 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.19, 165.55, 148.78, 141.66, 138.48, 132.95, 132.09, 131.34, 130.90, 128.25, 126.65, 126.08, 120.79, 52.29, 21.95, 20.18 ppm.



Methyl 2-(benzoyloxy)benzoate (8c): yield = 12.7 mg (33%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.0, 1.5 Hz, 2H), 8.08 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.69 – 7.58 (m, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.33 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 3.74 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.44, 165.09, 150.80, 133.89, 133.59, 131.96, 130.29, 129.51, 128.61, 126.12, 124.00, 123.49, 52.23 ppm.



methyl 4-(tert-butyl)-2-((4-(tert-butyl)benzoyl)oxy)benzoate (8d): yield = 21.0 mg (38%), colourless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 2H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.36 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.19 (d, *J* = 1.9 Hz, 1H), 3.73 (s, 3H), 1.37 (s, 9H), 1.34 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.67, 165.21, 158.38, 157.32, 150.95, 131.74, 130.26, 126.98, 125.72, 123.28, 121.08, 120.55, 52.19, 35.33, 35.29, 31.28, 31.11 ppm; **HRMS** (m/z) $C_{23}H_{28}O_4Na^+$ 391.1875.

Computational details:

Density functional theory calculations were performed employing the functional M06.[1] In all the calculations, Pople's basis set 6-31+G(d,p) was used for oxygen and nitrogen, while for carbon, hydrogen and ruthenium Ahlrichs basis set def2-SVP[2,3] with effective core potential[4] employed for ruthenium as the parameters provided in the EMSL website.[5] During the optimization of geometries, Grimme's D3 dispersion correction[6] was also employed. The absence of imaginary frequencies while performing analytical frequency calculations on the optimized geometries confirmed the obtained geometries are local minima (stationary points) for the intermediates. For transition states, the corresponding analytical frequency calculations on the optimized geometries result in only one imaginary frequency which show that the stationary points are saddle points. Further, the imaginary frequencies of the transition states show that the vibrations correspond to C-H-O stretching which is the reaction coordinate for the desired transition states. Unless otherwise stated, the reported energies in the manuscript are corrected enthalpies in kcal/mole obtained by adding electronic energy and thermal correction to enthalpy. All the calculations were performed in gas at 298.15 K using Linux version of Gaussian 16.

References:

1. Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
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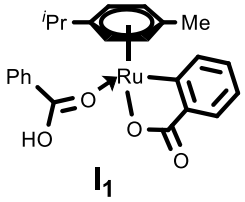
3. Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.
4. Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. Energy-Adjusted *ab initio* Pseudopotentials for the Second and Third Row Transition Elements. *Theor. Chim. Acta*, **1990**, *77*, 123–141.
5. https://bse.pnl.gov/bse/portal
6. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate *ab initio* Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys*. **2010**, *132*, 154104.

Cartesian coordinates



I_1

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Dispersion Correction = -0.013197983 Hartree

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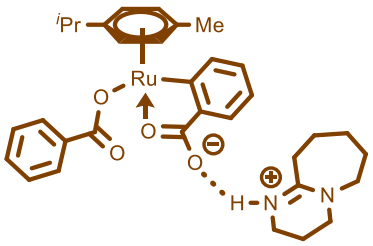

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Dispersion Correction = -0.026768825 Hartree

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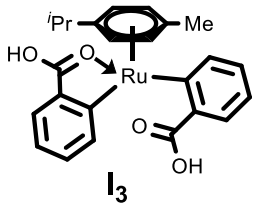

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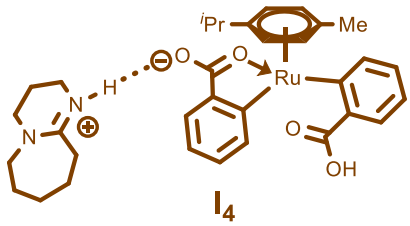
H	1.16287078	-2.90006937	-1.95425052
H	1.01396811	-3.75991415	-0.40090937
H	0.98641489	4.18623373	1.37048630
H	1.24111713	5.09011475	-0.91238871
H	0.67255178	3.66424159	-2.87478125
H	-0.05396191	1.33844696	-2.58220729
H	0.86908095	-1.74792993	2.37551883
H	3.10920337	-2.20338039	3.23594224
H	5.13507056	-1.52942659	1.91995271
H	4.81461732	-0.43598891	-0.30093334
H	2.02381839	-0.06958756	-3.31998047



I_4

Electronic Energy = -1784.91751645 Hartree

Sum of Electronic and Thermal Enthalpies = -1784.209577 Hartree

Dispersion Correction = -0.028412112 Hartree

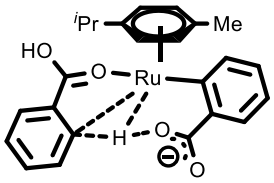
0 1

Ru	-1.72254944	-0.45816688	0.33470825
O	-0.59251524	1.04625053	1.32994414
C	-1.22141146	0.77692029	-1.23232512
C	0.11932134	-1.44854490	0.20343063
C	-3.77461019	0.24457655	0.93260664
C	-3.14959341	-0.47164719	2.00472461
C	-2.69930316	-1.80295486	1.87731240

C	-2.70698978	-2.42097920	0.59118531
C	-3.28798101	-1.72202617	-0.50387563
C	-3.81645633	-0.40865756	-0.31929728
C	-4.24645479	1.66011554	1.16529175
C	-5.55883010	1.65231204	1.94460216
C	-4.37585253	2.48363261	-0.10547630
C	-2.12477191	-3.78431431	0.40048501
O	0.46488004	2.99079458	1.06326423
C	-0.23403561	2.04898982	0.61359635
C	-0.62130067	1.98265302	-0.81348349
O	1.08206666	-1.68077784	-3.22132818
C	0.36128573	-1.99692788	-2.29451446
C	0.80161133	-2.05483944	-0.87619621
O	-0.89739339	-2.42578467	-2.51049829
C	-0.37053364	3.04101364	-1.69146505
C	-0.70737703	2.91887717	-3.03473632
C	-1.29271114	1.72945753	-3.47964277
C	-1.54812315	0.68240093	-2.59474441
C	0.75472925	-1.59724754	1.45914057
C	1.91970221	-2.33501131	1.64785598
C	2.55910808	-2.93228409	0.55930507
C	2.00512564	-2.76173785	-0.70082775
H	-3.46999276	2.13660952	1.79802576
H	-2.99041176	0.05528513	2.95374987
H	-2.21892101	-2.30817719	2.72086768
H	-3.29469528	-2.18346562	-1.49454169
H	-4.18357444	0.13103469	-1.19795838
H	-5.88611067	2.67718963	2.18550675
H	-6.35670974	1.17401368	1.34929653

H	-5.47189516	1.09314693	2.89069021
H	-5.18284324	2.10009357	-0.75480310
H	-4.63254617	3.52608345	0.14142421
H	-3.44082393	2.49651373	-0.69029383
H	-2.88316502	-4.55857596	0.60610544
H	-1.76787993	-3.91650101	-0.63158284
H	-1.27478923	-3.95392260	1.08056713
H	0.08542688	3.95508708	-1.29430834
H	-0.52324247	3.74004328	-3.73382742
H	-1.56311132	1.62133143	-4.53582629
H	-2.03184306	-0.22388799	-2.97888344
H	0.29222463	-1.12457284	2.33490661
H	2.32901379	-2.45494200	2.65981322
H	3.47197088	-3.52246375	0.69217765
H	2.49153731	-3.19531911	-1.58203468
H	-1.03034559	-2.34566633	-3.47183563
H	1.79580910	2.22418243	1.60464719
N	2.66179896	1.63640431	1.74911215
C	2.81896467	0.95803502	3.01930119
C	3.45289131	1.44933805	0.71445916
C	4.26883185	0.58259463	3.22324106
H	2.16334340	0.06790289	3.02339483
H	2.45312902	1.62837732	3.81137036
N	4.53736104	0.66703690	0.78570863
C	3.08135800	2.09209145	-0.58121226
C	4.80341995	-0.11664880	1.99193384
H	4.37974457	-0.07218112	4.10096354
H	4.86668638	1.49091031	3.41755411
C	5.36404805	0.38600068	-0.39471943

C	2.59917947	1.04799336	-1.59777592
H	2.28217411	2.81952301	-0.37240081
H	3.94320366	2.65684066	-0.97935186
H	4.34951284	-1.11973102	1.87209220
H	5.89348544	-0.25512987	2.06797306
C	4.67232347	-0.44546396	-1.46163161
H	6.25248214	-0.14059995	-0.01481951
H	5.73201753	1.33939040	-0.81574160
C	3.71147252	0.33436737	-2.34490742
H	1.95616151	0.31182062	-1.07703772
H	1.92943337	1.54806382	-2.31772998
H	4.14167569	-1.27855877	-0.96436336
H	5.45262502	-0.90721024	-2.09106335
H	3.25176015	-0.35239677	-3.07511199
H	4.28901210	1.07874397	-2.92941583



TS 1

Electronic Energy = -1323.30651951 Hartree

Sum of Electronic and Thermal Enthalpies = -1322.860757 Hartree

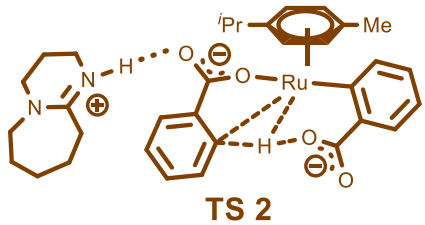
Dispersion Correction = -0.014833813 Hartree

0 1

Ru	-0.02187072	-0.52363567	-0.00740733
O	-0.59973103	0.36617040	1.89681966
C	1.88220898	-0.06221241	0.74340952
O	1.60582345	1.30031625	-1.82834463

C	-0.69178234	1.63244494	-0.58784808
H	0.46696599	1.26733316	-0.76923376
O	-1.28813604	2.14033530	2.98702742
O	3.79120652	0.93472490	-2.15981086
C	-1.03778267	1.51484983	1.84341396
C	-1.33828397	2.14875134	0.55762646
C	2.78172211	0.96537009	-1.44913690
C	2.91833778	0.53442218	0.00444785
C	-1.82339131	-1.90934444	-0.13295056
C	-0.68668786	-2.48151271	0.54827614
C	0.57668833	-2.60135552	-0.07162578
C	0.81002006	-2.02929582	-1.36297682
C	-0.28816018	-1.36973920	-1.97408032
C	-1.60615491	-1.38511871	-1.41065294
C	-3.14126610	-1.82525986	0.59450441
C	-4.04764659	-0.71445248	0.09171930
C	-3.84247560	-3.18014875	0.53960998
C	2.14945923	-2.09171739	-2.01457674
H	-2.88961690	-1.61037196	1.65246676
H	1.42062800	-3.01249053	0.49168792
H	-0.80541779	-2.80933610	1.58838398
H	-0.10377468	-0.82155390	-2.90369500
H	-2.40426217	-0.84263987	-1.92520518
H	-4.40867311	-0.91756650	-0.93135053
H	-3.53870735	0.26508122	0.08255114
H	-4.93856764	-0.62746155	0.73296320
H	-4.09715129	-3.44014878	-0.50241246
H	-3.20797833	-3.98795600	0.93866880
H	-4.77696985	-3.16481716	1.12286120

H	2.23818689	-3.02831179	-2.59048535
H	2.95968281	-2.07105845	-1.27006399
H	2.30616038	-1.24673071	-2.70140041
C	-2.36302899	3.09925132	0.44627360
C	-2.76896739	3.54411318	-0.80442058
C	-2.13778208	3.04560786	-1.94624076
C	-1.10499243	2.12125837	-1.83640905
C	4.17740008	0.70523796	0.59945896
C	4.42111173	0.31282220	1.90872852
C	3.40106893	-0.29462962	2.63867668
C	2.15064116	-0.48658711	2.05442934
H	-2.89293433	3.45819171	1.33675723
H	-3.57986266	4.27168822	-0.89137167
H	-2.44582033	3.39840244	-2.93469614
H	-0.55534178	1.78932508	-2.72190949
H	4.96540564	1.14879325	-0.01658149
H	5.40809009	0.46527663	2.35607824
H	3.57621964	-0.62781085	3.66704686
H	1.36728507	-0.97390624	2.64801111
H	-1.51607363	3.06913219	2.82338180



TS 2

Electronic Energy = -1784.89611675 Hartree

Sum of Electronic and Thermal Enthalpies = -1784.189305 Hartree

Dispersion Correction = -0.028362797 Hartree

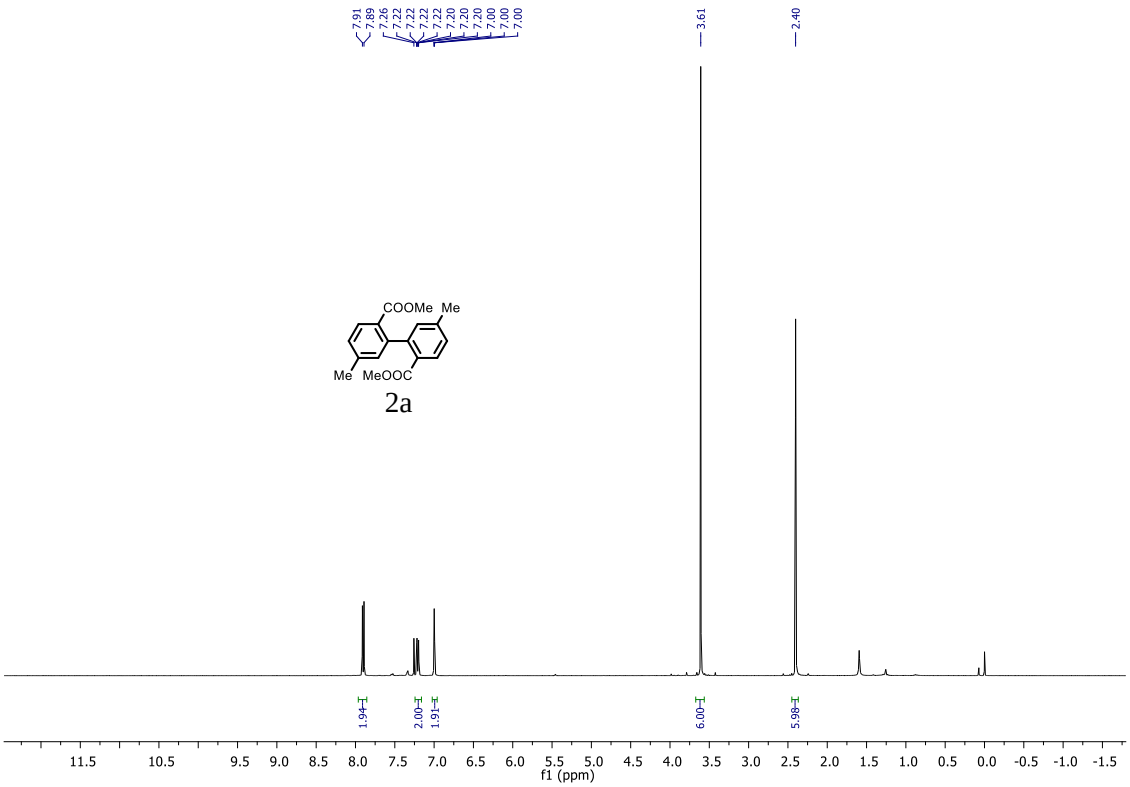
0 1

Ru	-1.71925965	0.60051347	0.14633983
O	-0.78316488	-0.10005645	-1.65231593
C	-0.30267040	2.09927348	-0.06417180
O	0.17696952	0.77728589	2.55441565
C	-0.36870082	-1.55992788	0.72368456
H	-0.05592113	-0.50171950	0.84465728
O	0.33559193	-1.70321012	-2.73250622
O	2.28587876	0.69743628	1.75396838
C	-0.29199681	-1.27957785	-1.74450338
C	-0.42124953	-2.15701044	-0.53608118
C	1.12042009	1.16583412	1.81899910
C	0.79541317	2.24627399	0.80455133
C	-3.82480514	-0.27235282	-0.28771979
C	-3.56939647	1.07665242	-0.73437356
C	-3.20426993	2.10856156	0.17504744
C	-2.88146045	1.80869006	1.53428576
C	-2.94761577	0.43942528	1.89806776
C	-3.51373101	-0.56420645	1.03919536
C	-4.29253599	-1.29065091	-1.29611012
C	-4.21808206	-2.72472690	-0.80500296
C	-5.71173089	-0.94997633	-1.74669141
C	-2.36049354	2.84374526	2.47386424
H	-3.61680947	-1.18300370	-2.16953451
H	-3.04018852	3.12443052	-0.19887447
H	-3.68746550	1.31709468	-1.79801034
H	-2.54636847	0.14400309	2.87310502
H	-3.54519131	-1.59747305	1.39548784
H	-4.91288977	-2.89481553	0.03619673

H	-3.20437645	-3.00265823	-0.47415036
H	-4.50729528	-3.41828363	-1.60991588
H	-6.41453357	-1.03142756	-0.89932644
H	-5.79069842	0.07284120	-2.14812982
H	-6.04915605	-1.64486806	-2.53209568
H	-3.15726310	3.19920539	3.14816881
H	-1.96132838	3.71015573	1.92396527
H	-1.54019305	2.41624649	3.07259869
C	-0.55456261	-3.54395205	-0.62962887
C	-0.68977294	-4.30354280	0.53080579
C	-0.65323894	-3.69139266	1.78835632
C	-0.47183545	-2.31402419	1.89099660
C	1.64905380	3.34918910	0.66948185
C	1.44104800	4.30638538	-0.31981655
C	0.39618450	4.13156064	-1.22759219
C	-0.45484775	3.03331870	-1.09988104
H	-0.56505848	-4.00841514	-1.62054383
H	-0.81941238	-5.38763517	0.45861609
H	-0.74400726	-4.30093565	2.69236350
H	-0.37829796	-1.80002006	2.85315552
H	2.48808901	3.44486447	1.36863356
H	2.09914849	5.17849761	-0.39292299
H	0.23873960	4.85311289	-2.03617605
H	-1.25286986	2.89706213	-1.84142096
H	1.86697417	-0.79752645	-2.36215218
N	2.60546435	-0.21042828	-1.93919969
C	3.48968817	-0.79497810	-1.15096861
N	4.45202824	-0.10345706	-0.54719831
C	4.41369122	1.36330986	-0.57572210

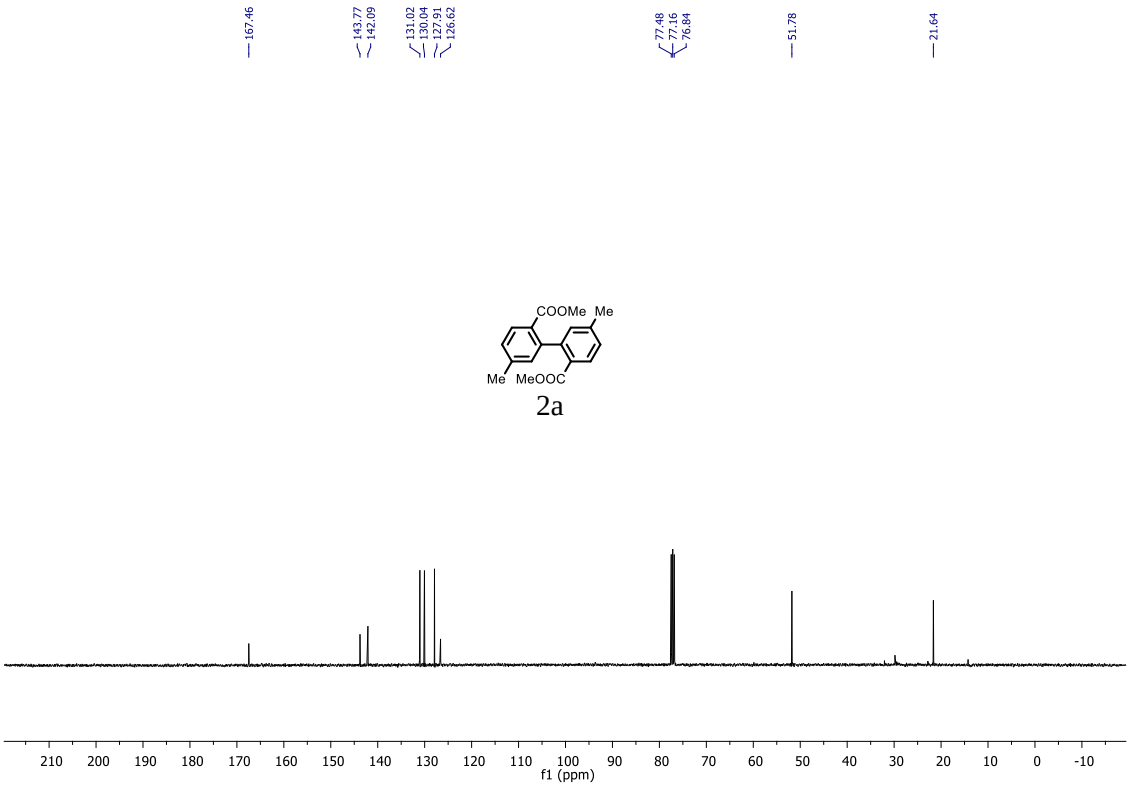
C	3.87695461	1.85413684	-1.90226484
C	2.53046191	1.22444942	-2.16735213
C	3.34685296	-2.26371119	-0.91776552
C	2.95355902	-2.57255802	0.53214664
C	4.11326286	-2.59458073	1.51254662
C	4.81796397	-1.25629203	1.66275568
C	5.41139126	-0.74029813	0.36302942
H	5.43921948	1.72514168	-0.40738779
H	3.77576296	1.68934950	0.26909926
H	4.58804480	1.60320488	-2.71039587
H	3.77310681	2.94960690	-1.87782100
H	2.18626153	1.38557381	-3.20020992
H	1.75895876	1.64435301	-1.50062644
H	4.28855814	-2.77716811	-1.18558363
H	2.57293783	-2.63440311	-1.60926206
H	2.43713820	-3.54724748	0.54268280
H	2.21538099	-1.82153774	0.86803402
H	4.84603384	-3.36535756	1.19571551
H	3.73714750	-2.91766704	2.49769572
H	5.64154595	-1.35742753	2.39035565
H	4.11418503	-0.50202879	2.06022537
H	5.93488425	-1.54916215	-0.18111124
H	6.17228676	0.02671748	0.56922285

NMR Spectra of Synthesized Compounds


7.91
7.89
7.26
7.22
7.22
7.22
7.22
7.20
7.20
7.20
7.00
7.00
7.00
3.61
2.40
1.94
2.00
1.91
6.00
5.98
f1 (ppm)

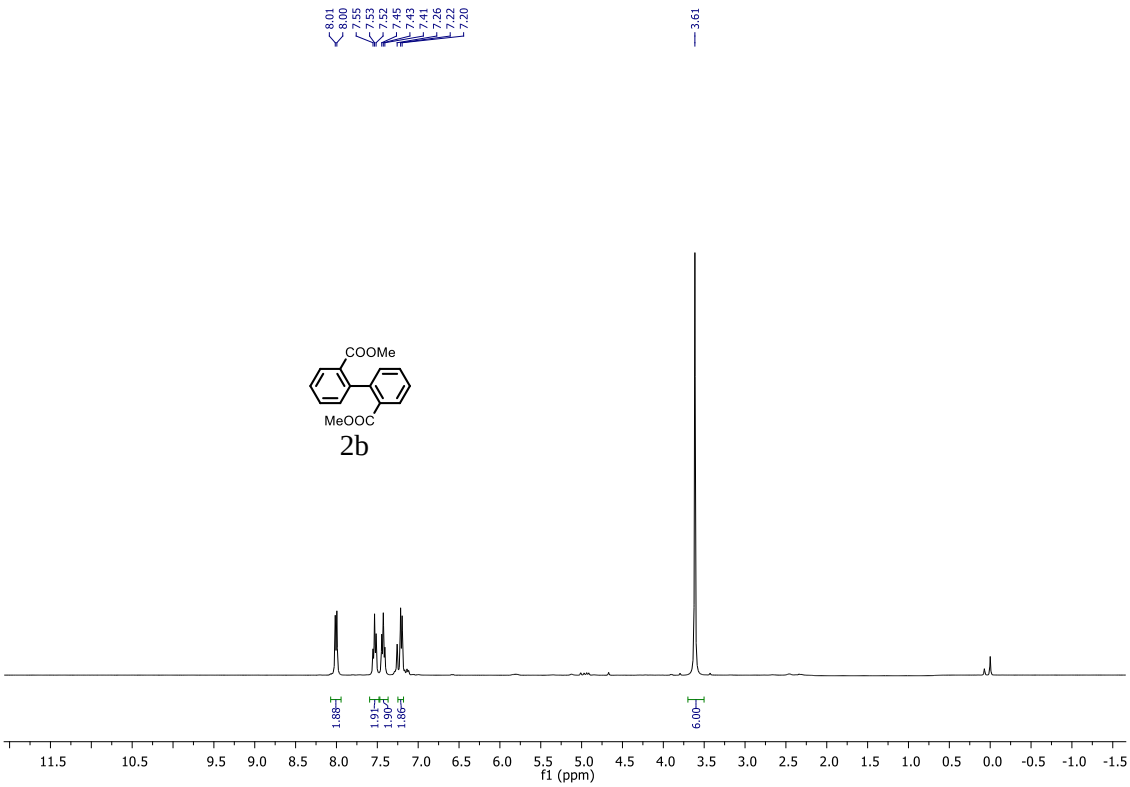
COOMe
Me
Me
MeOOC

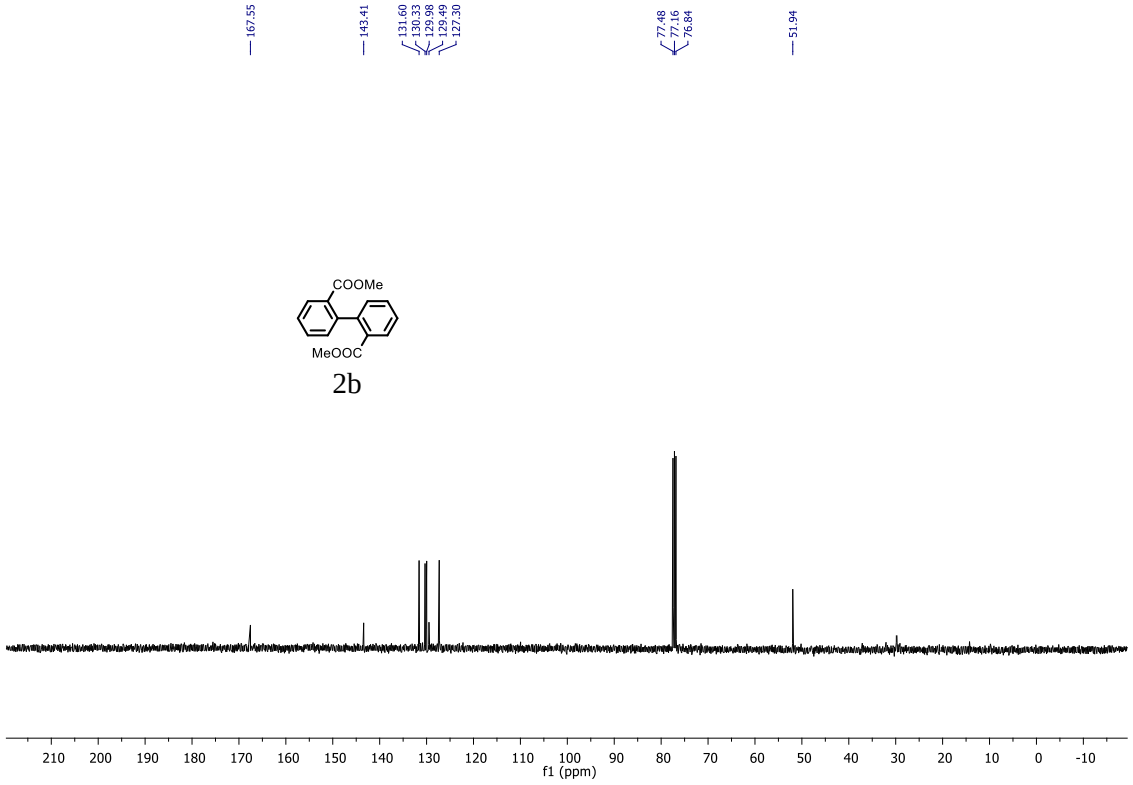
2a


167.46
143.77
142.09
131.02
130.04
127.91
126.62
77.48
77.16
76.84
51.78
21.64
f1 (ppm)

COOMe
Me
Me
MeOOC

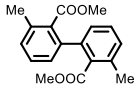
2a


8.01
8.00
7.55
7.53
7.52
7.45
7.43
7.41
7.26
7.22
7.20
3.61
COOMe
MeOOC
2b
1.88
1.91
1.90
1.86
6.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

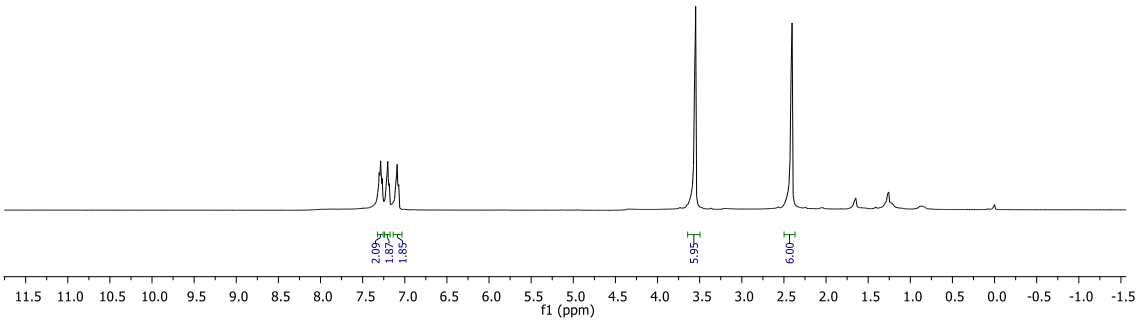

167.55
143.41
131.60
130.33
129.98
129.49
127.30
77.48
77.16
76.84
51.94
COOMe
MeOOC
2b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.30
7.29
7.28
7.27
7.20
7.18
7.09
7.07

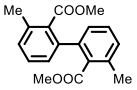

3.55
2.40


Me
COOMe
MeOOC
Me

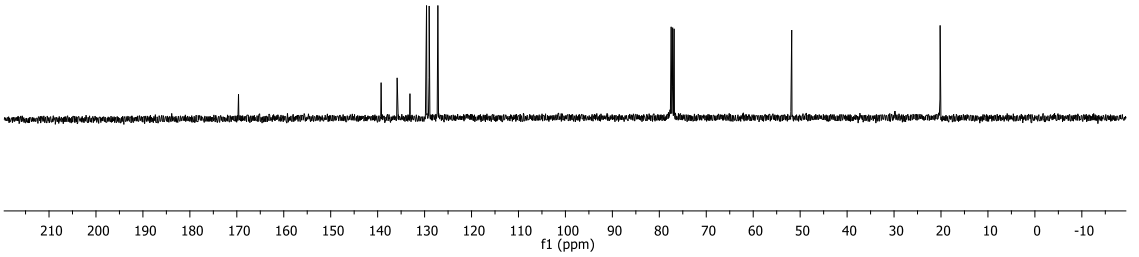
2c

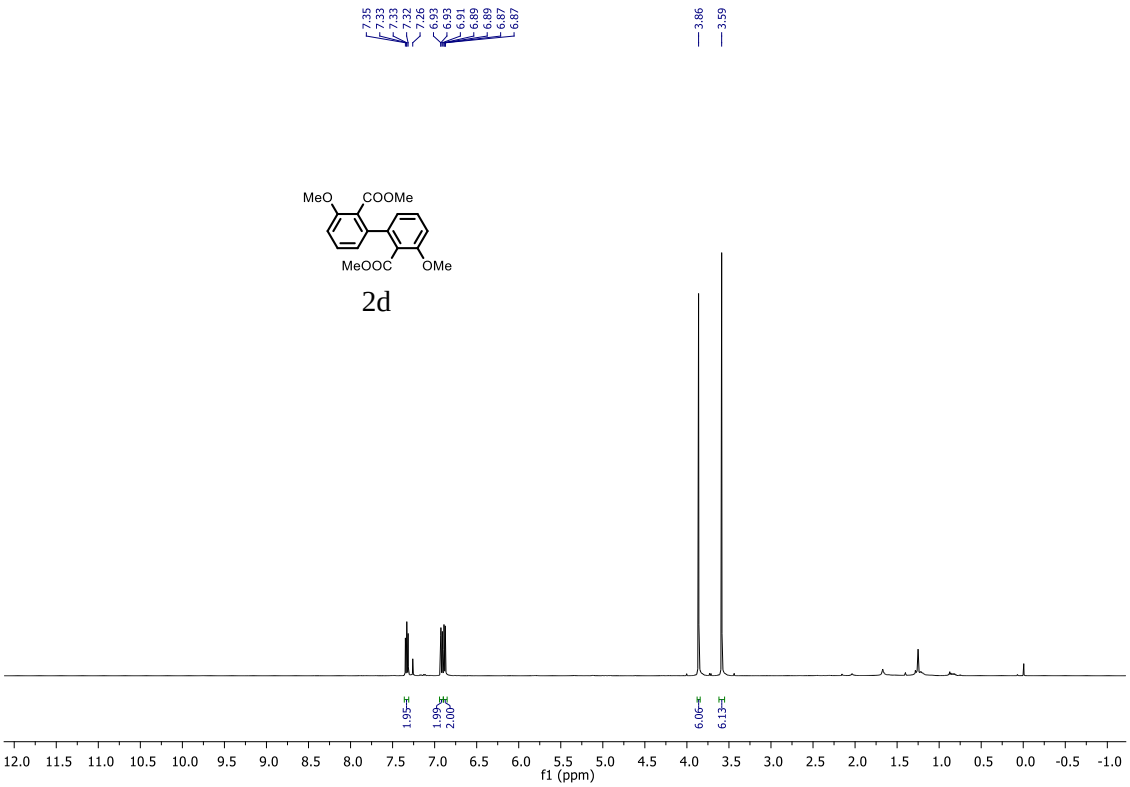

2.09
1.87
1.83
5.95
6.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


169.64
139.26
135.85
133.12
129.59
129.02
127.17
77.48
77.16
76.84
51.80
20.18


Me
COOMe
MeOOC
Me

2c


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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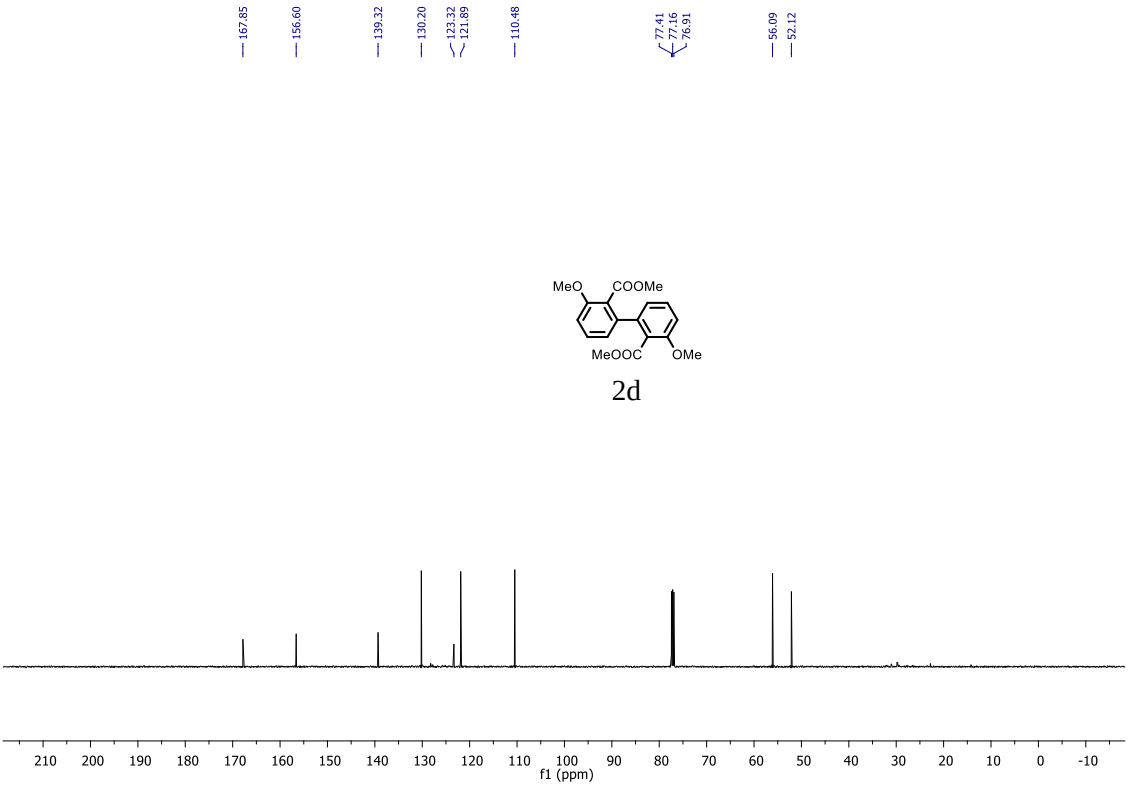
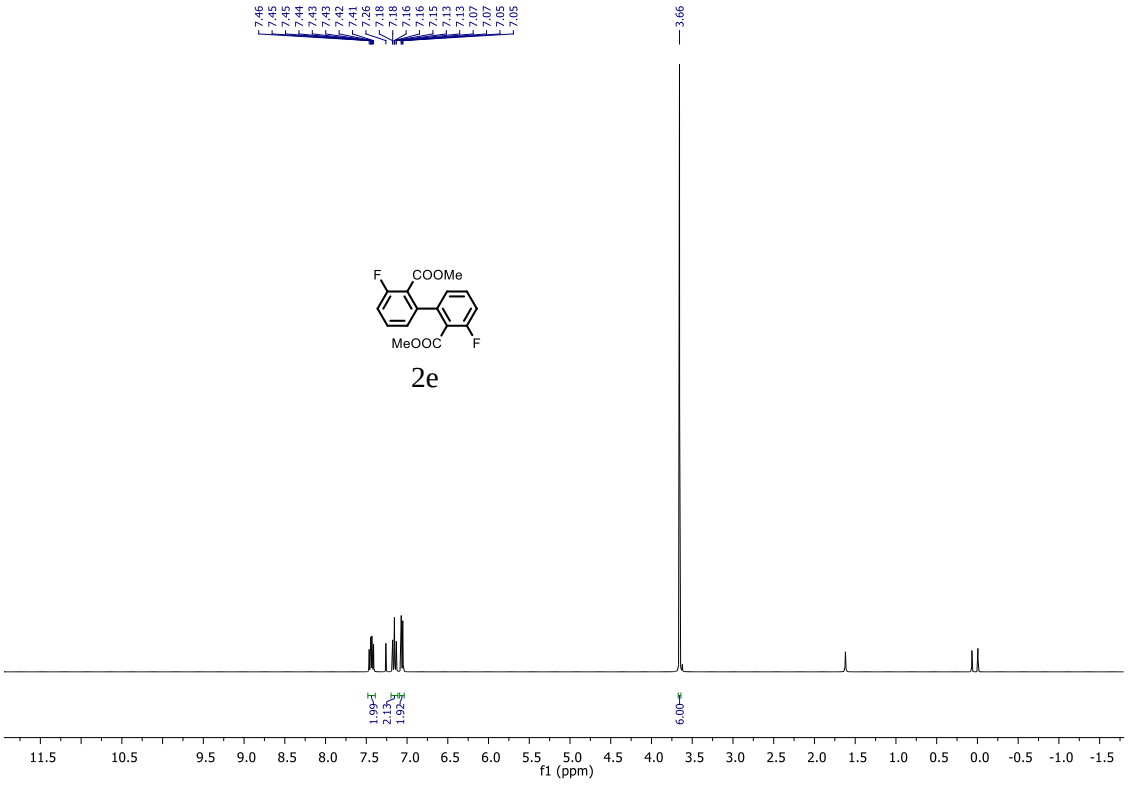
7.33
7.33
7.32
7.26
6.93
6.93
6.91
6.89
6.89
6.87
6.87
3.86
3.59
MeO
COOMe
MeOOC
OMe
1.95
1.99
2.00
6.06
6.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

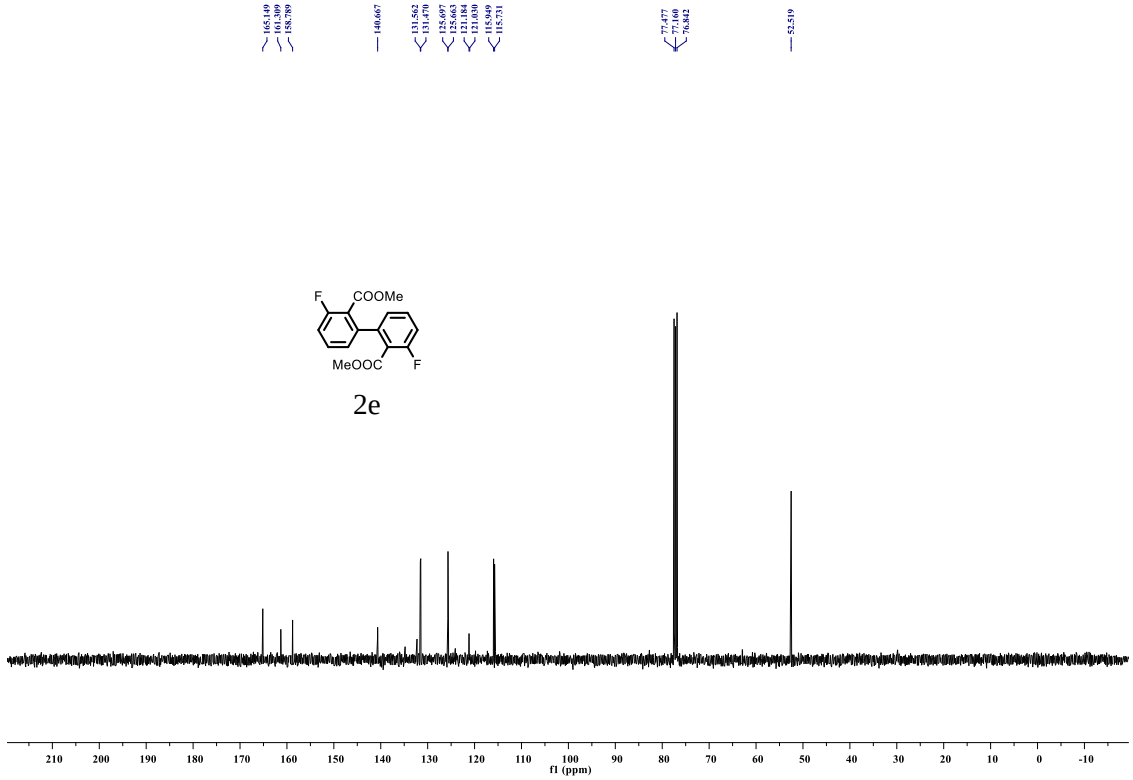
2d


167.85
156.60
139.32
130.20
123.32
121.89
110.48
77.41
77.16
76.91
56.09
52.12
MeO
COOMe
MeOOC
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

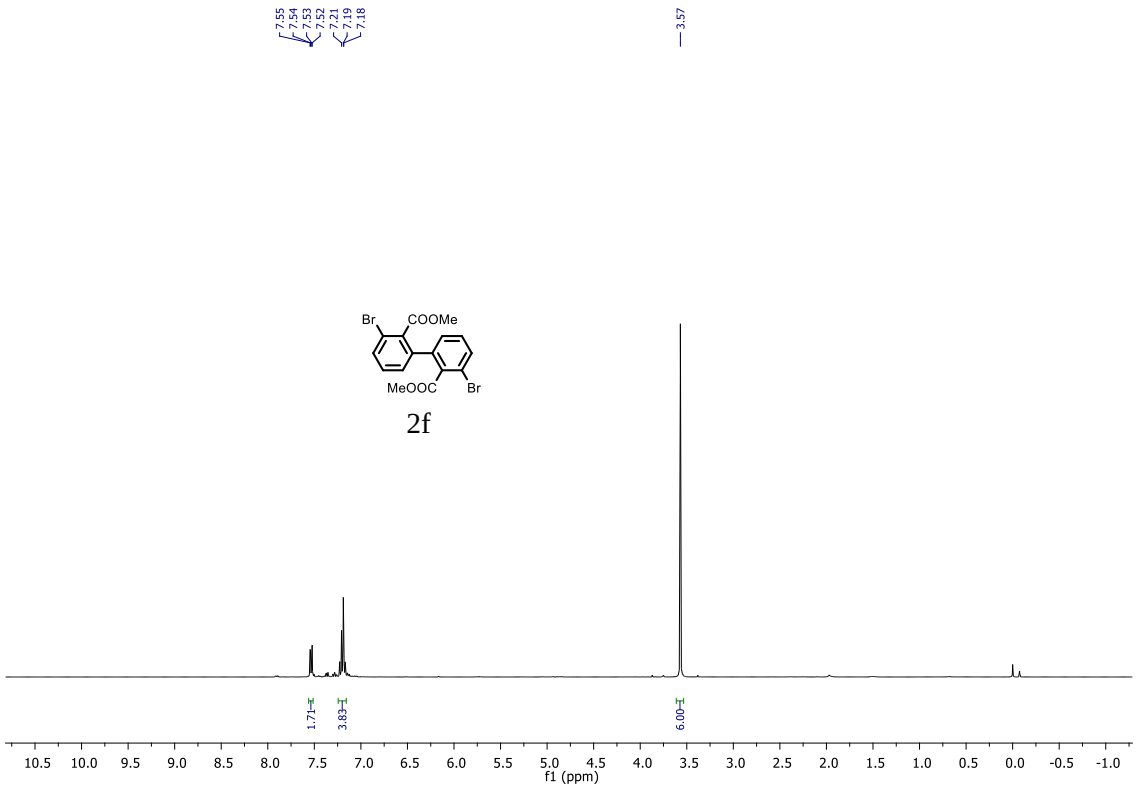
2d


7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.26
7.18
7.18
7.16
7.16
7.15
7.13
7.13
7.07
7.07
7.05
7.05
3.66
F
COOMe
MeOOC
F
1.99
2.13
1.92
6.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

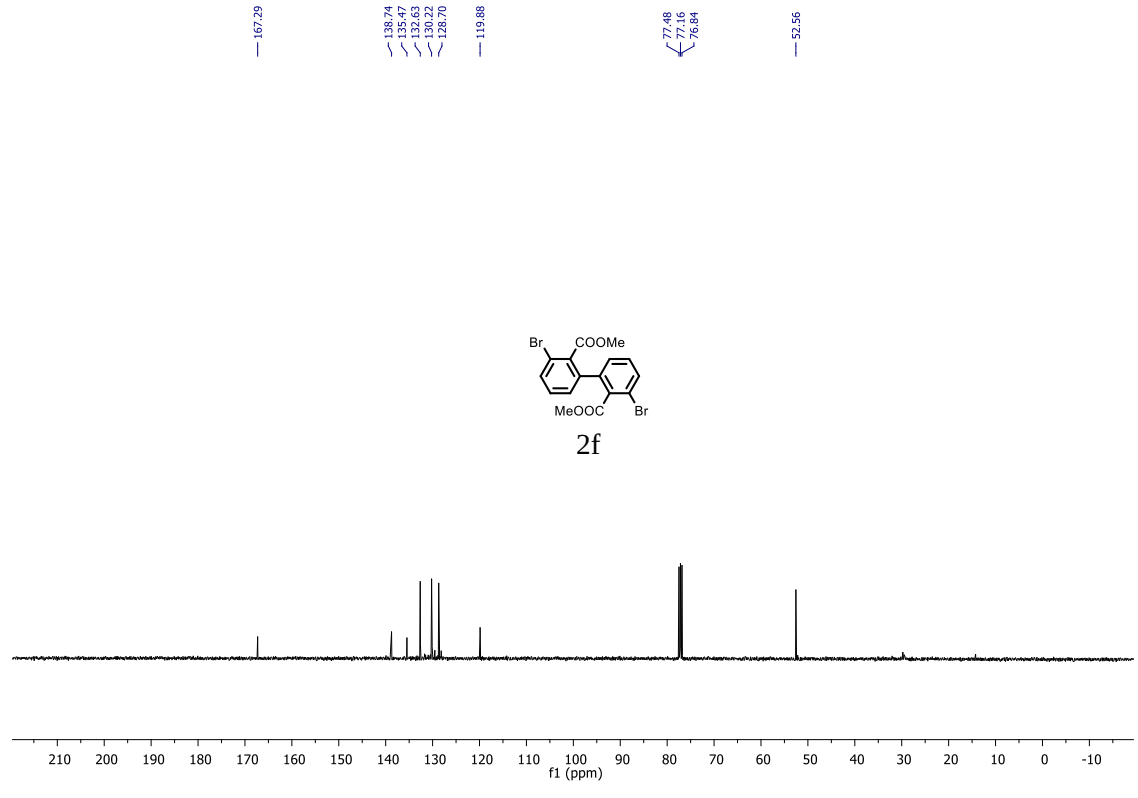
2e


165.149
161.309
158.789
140.667
131.562
131.470
126.497
125.665
121.184
121.030
115.949
115.731
77.477
77.160
76.842
52.519
F
COOMe
MeOOC
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

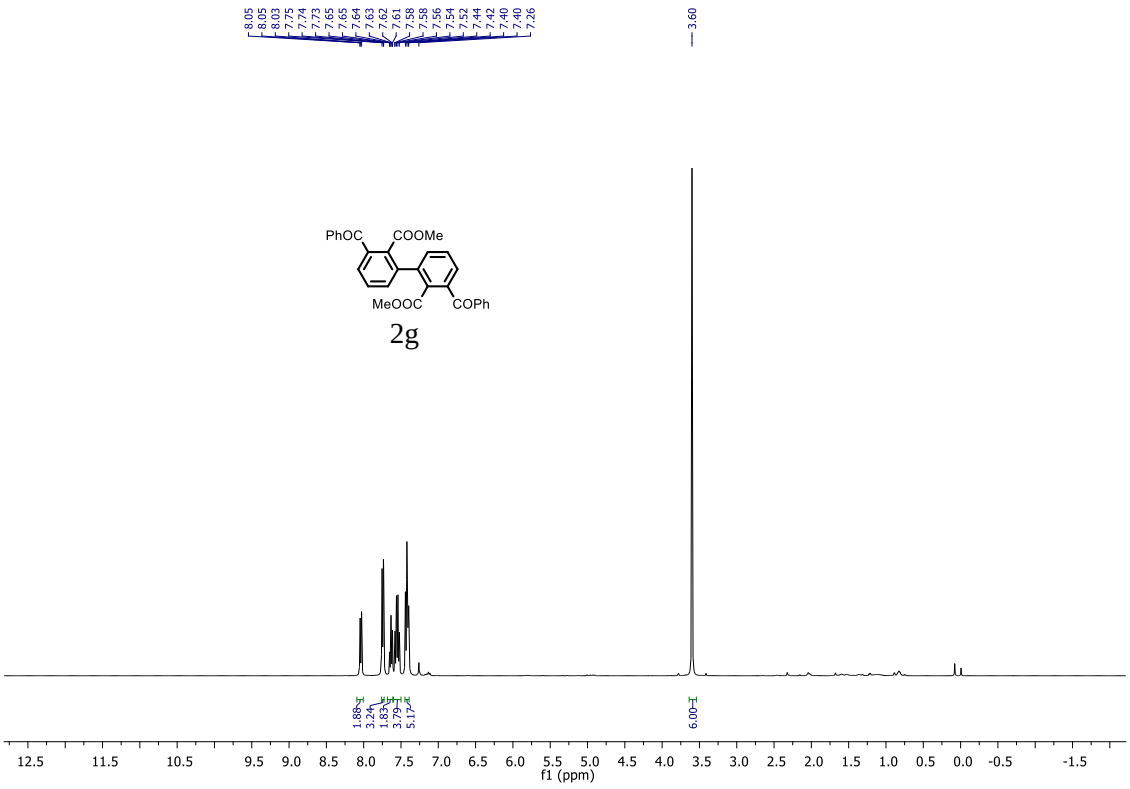
2e


7.55
7.54
7.53
7.52
7.21
7.19
7.18
3.57
Br
COOMe
MeOOC
Br
1.71
3.83
6.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

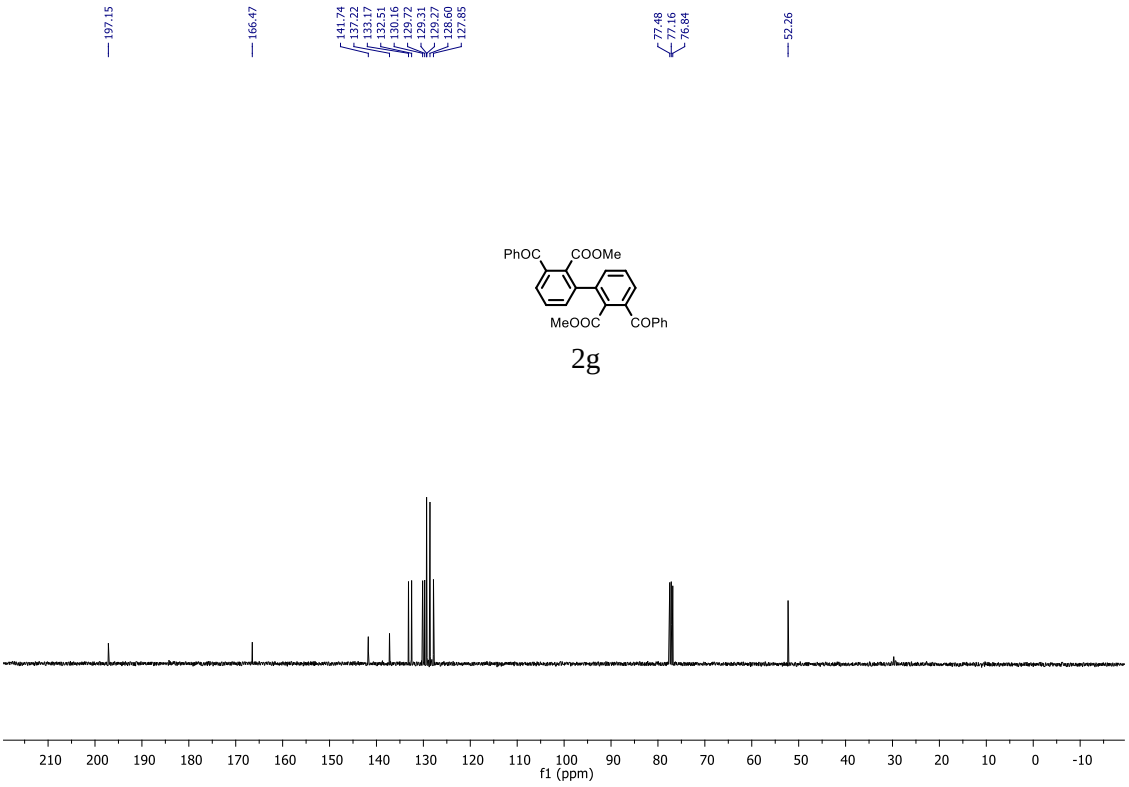
2f


167.29
138.74
135.47
132.63
130.22
128.70
119.88
77.48
77.16
76.84
52.56
Br
COOMe
MeOOC
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

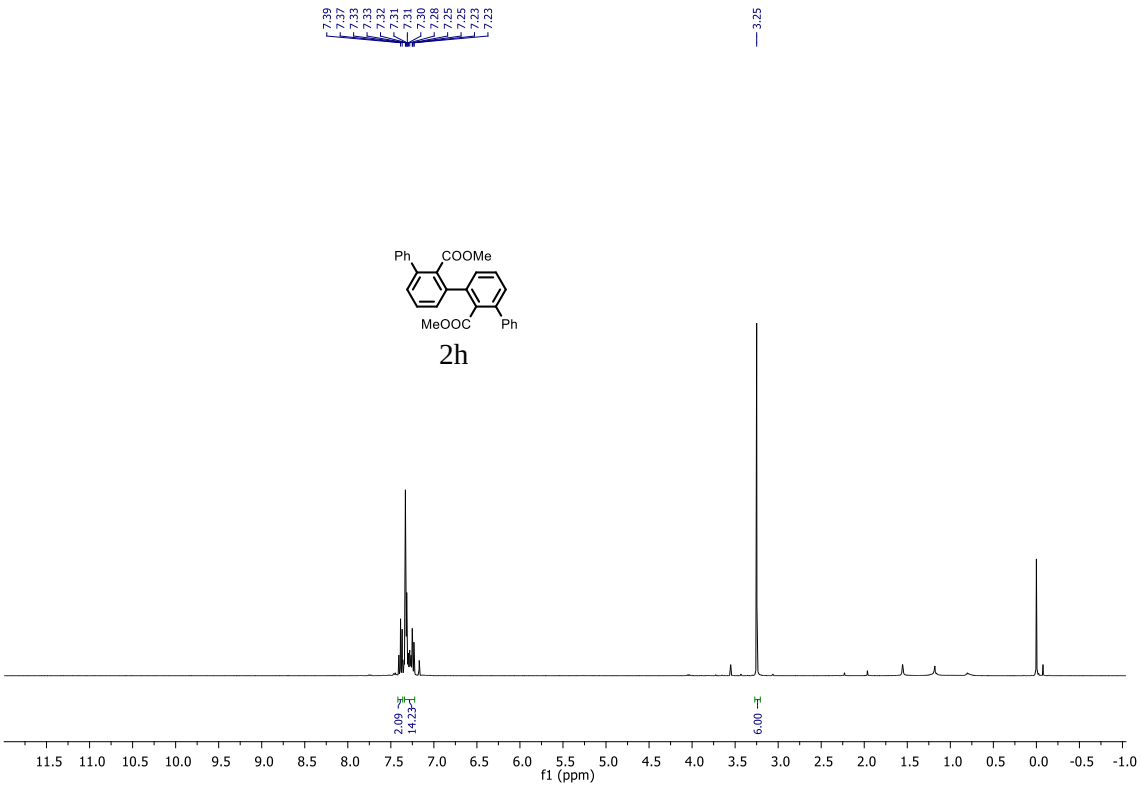
2f

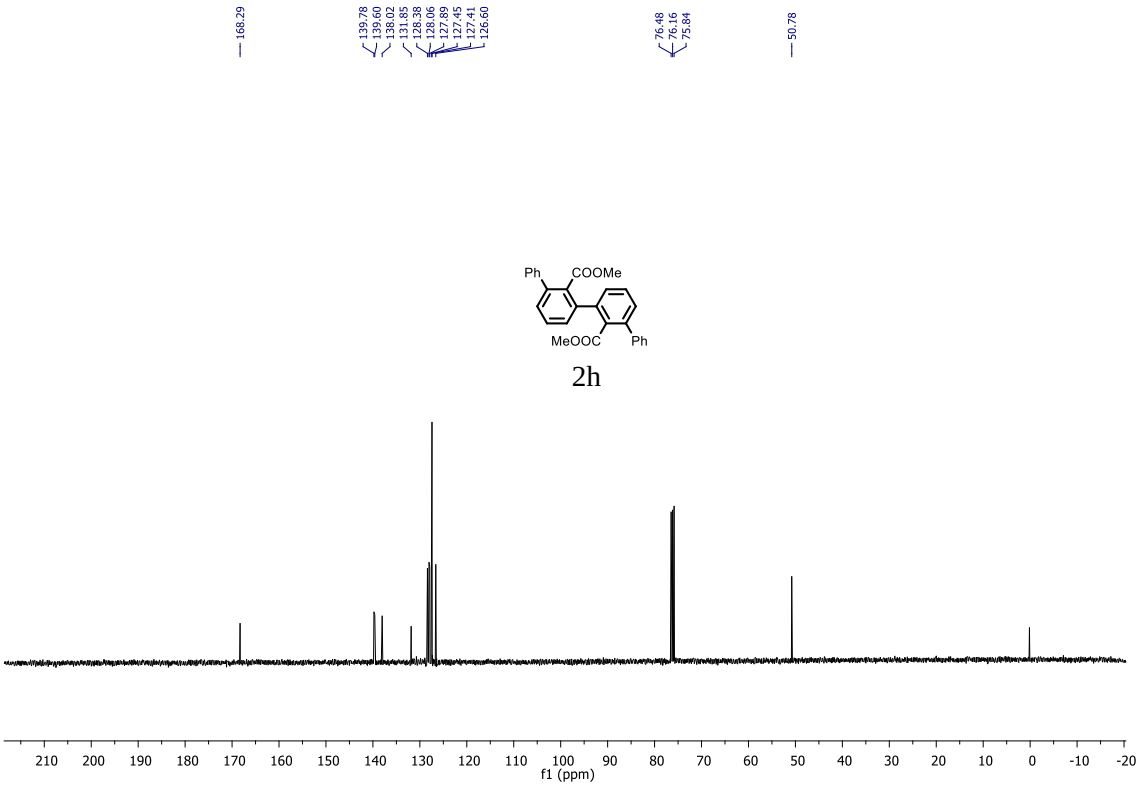

8.05
8.05
8.03
7.75
7.74
7.73
7.65
7.65
7.64
7.63
7.62
7.61
7.58
7.58
7.56
7.54
7.52
7.44
7.42
7.40
7.40
7.26
3.60
PhOC
COOMe
MeOOC
COPh
1.88
3.24
1.83
3.79
5.17
6.00
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.5
f1 (ppm)

2g


197.15
166.47
141.74
137.22
133.17
132.51
130.16
129.72
129.31
129.27
128.60
127.85
77.48
77.16
76.84
52.26
PhOC
COOMe
MeOOC
COPh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

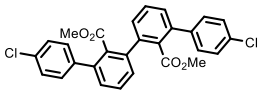
2g


7.39
7.37
7.33
7.33
7.32
7.31
7.31
7.30
7.28
7.25
7.25
7.23
7.23
3.25
Ph
COOMe
MeOOC
Ph
2h
2.09
14.23
6.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


168.29
139.78
139.60
136.02
131.85
128.38
128.06
127.89
127.45
127.41
126.60
76.48
76.16
75.84
50.78
Ph
COOMe
MeOOC
Ph
2h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.49
7.47
7.45
7.38
7.38
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.31
7.25

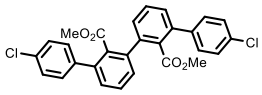
3.35


MeO2C
Cl
CO2Me
Cl

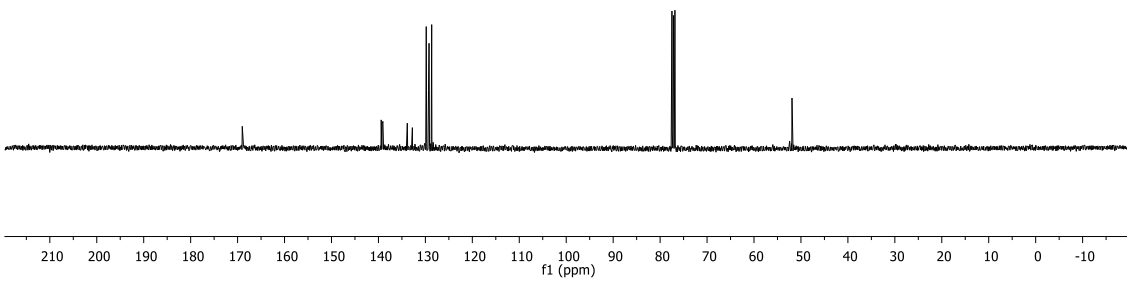
2i

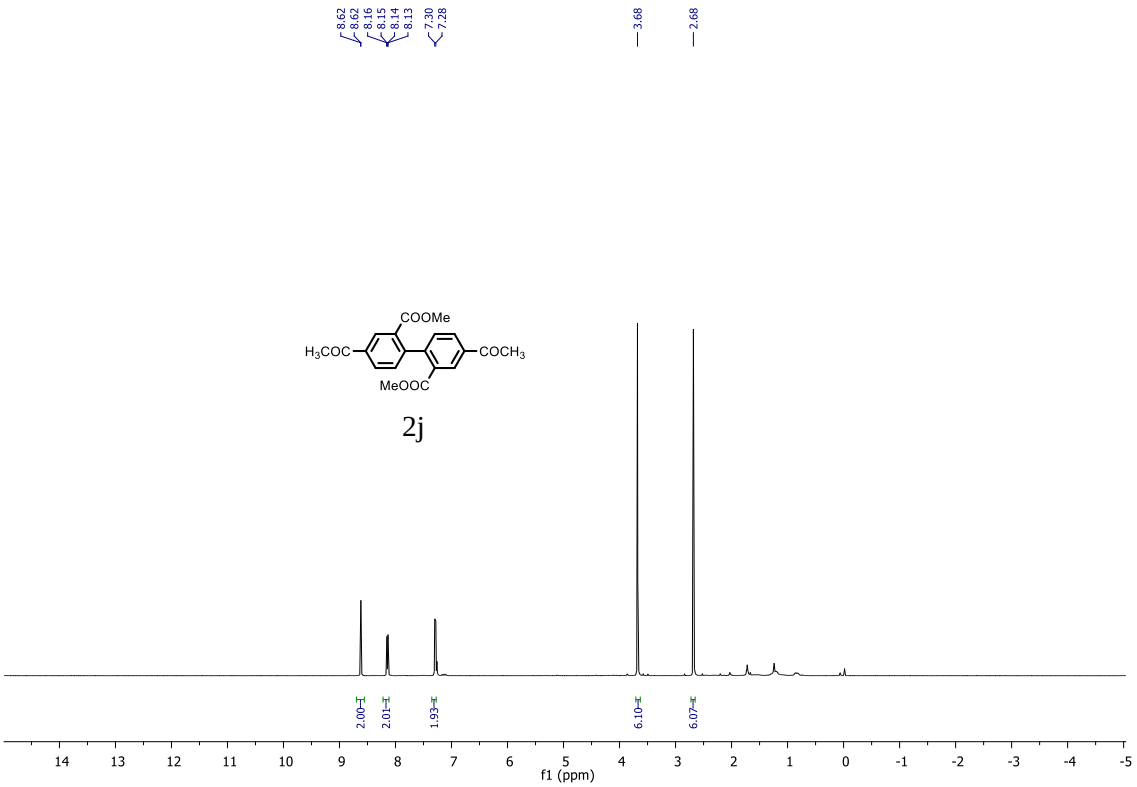
2.28
12.25
6.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

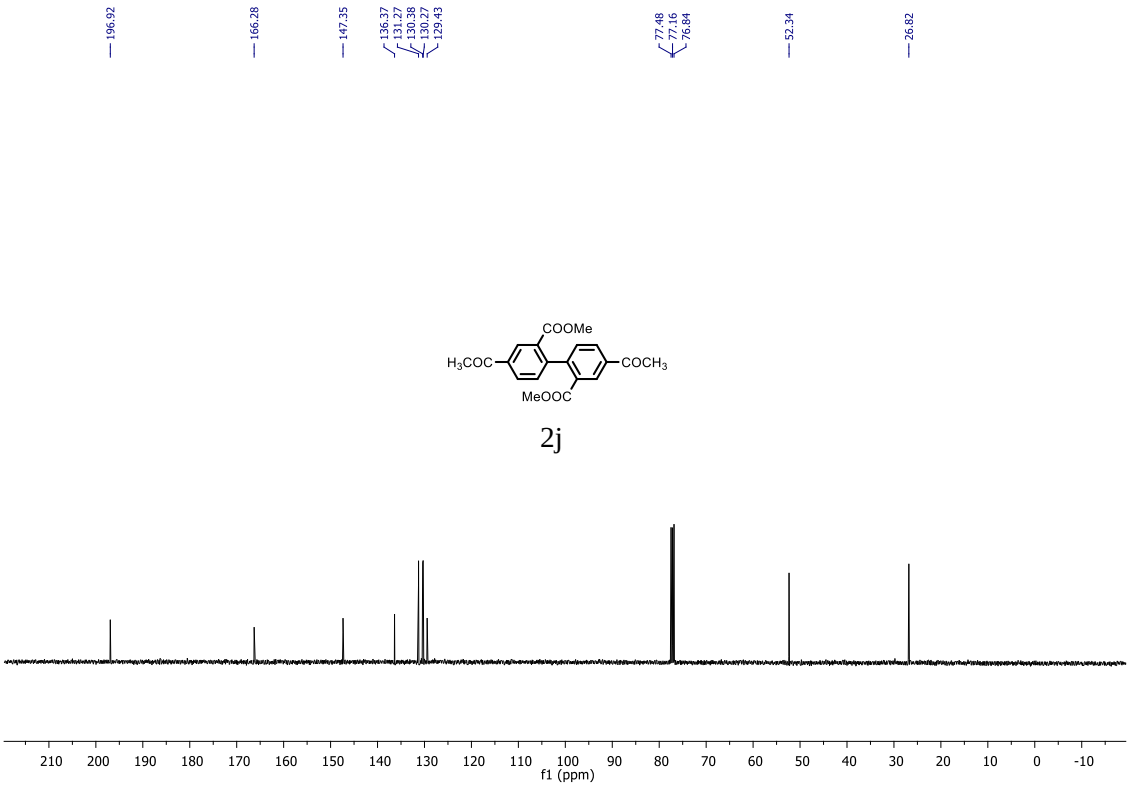

169.01
139.41
139.19
139.05
133.86
133.77
129.82
129.34
129.22
128.69
128.66
77.48
77.16
76.84
51.90

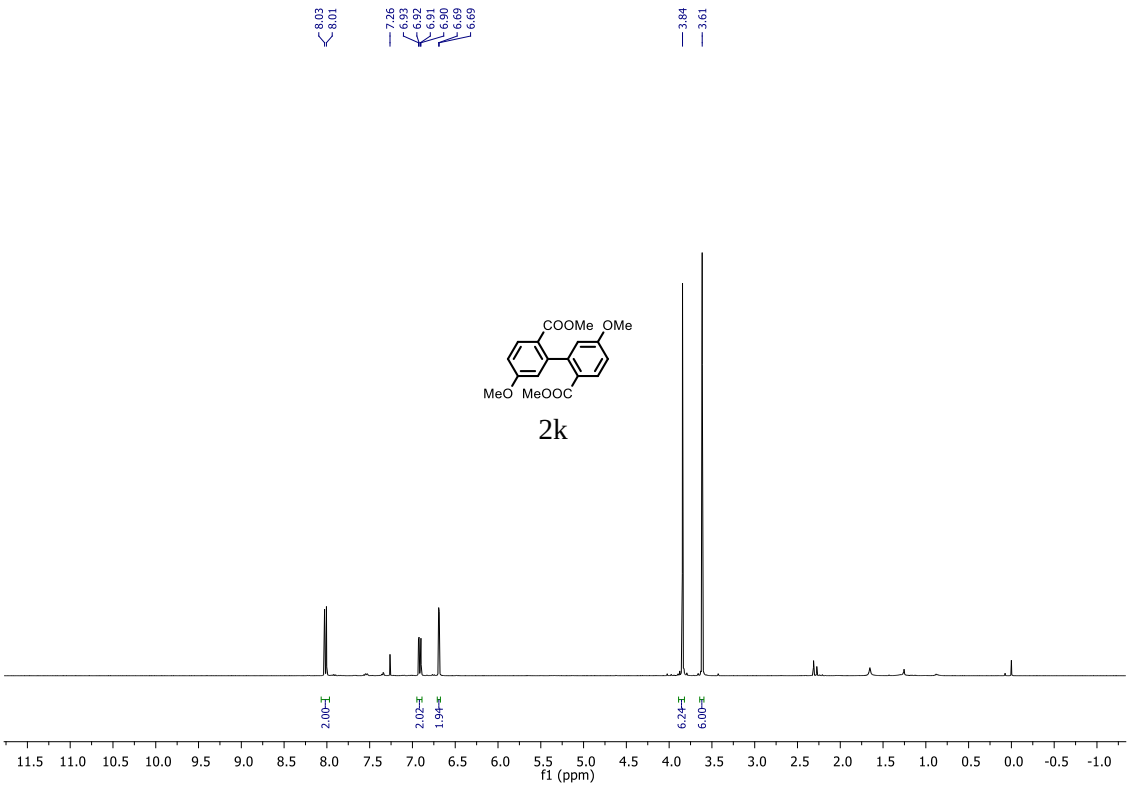

MeO2C
Cl
CO2Me
Cl

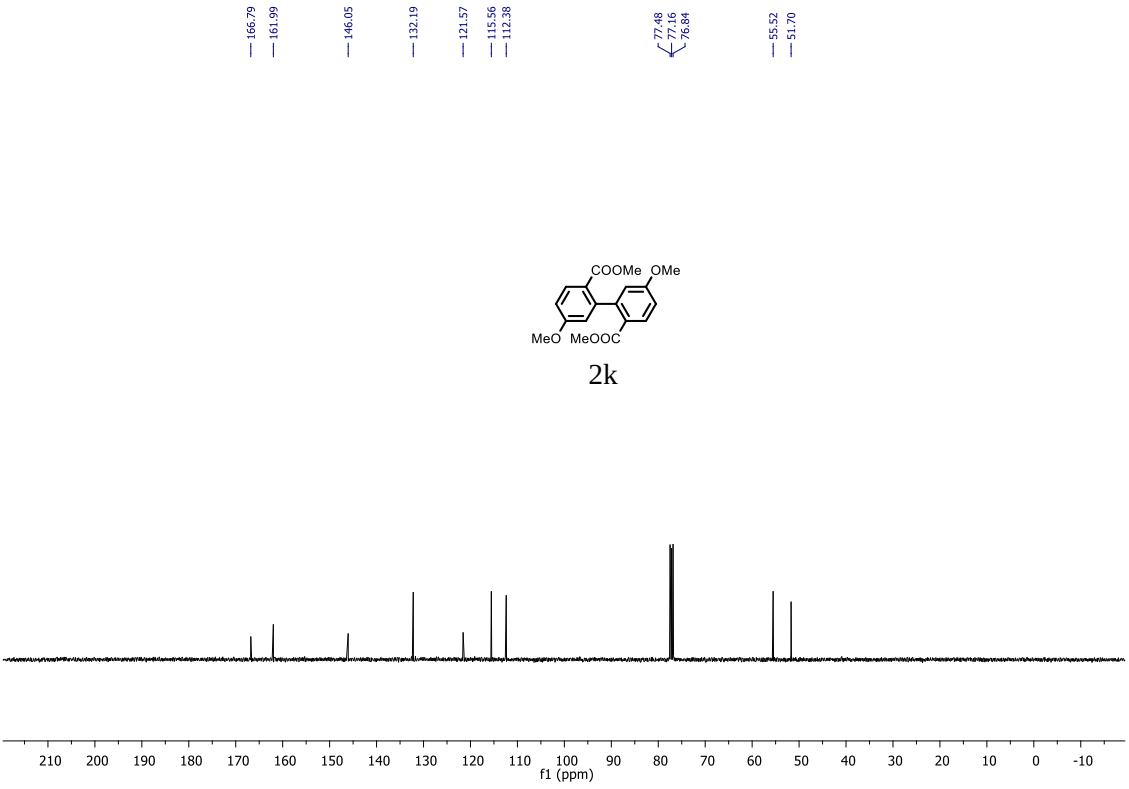
2i

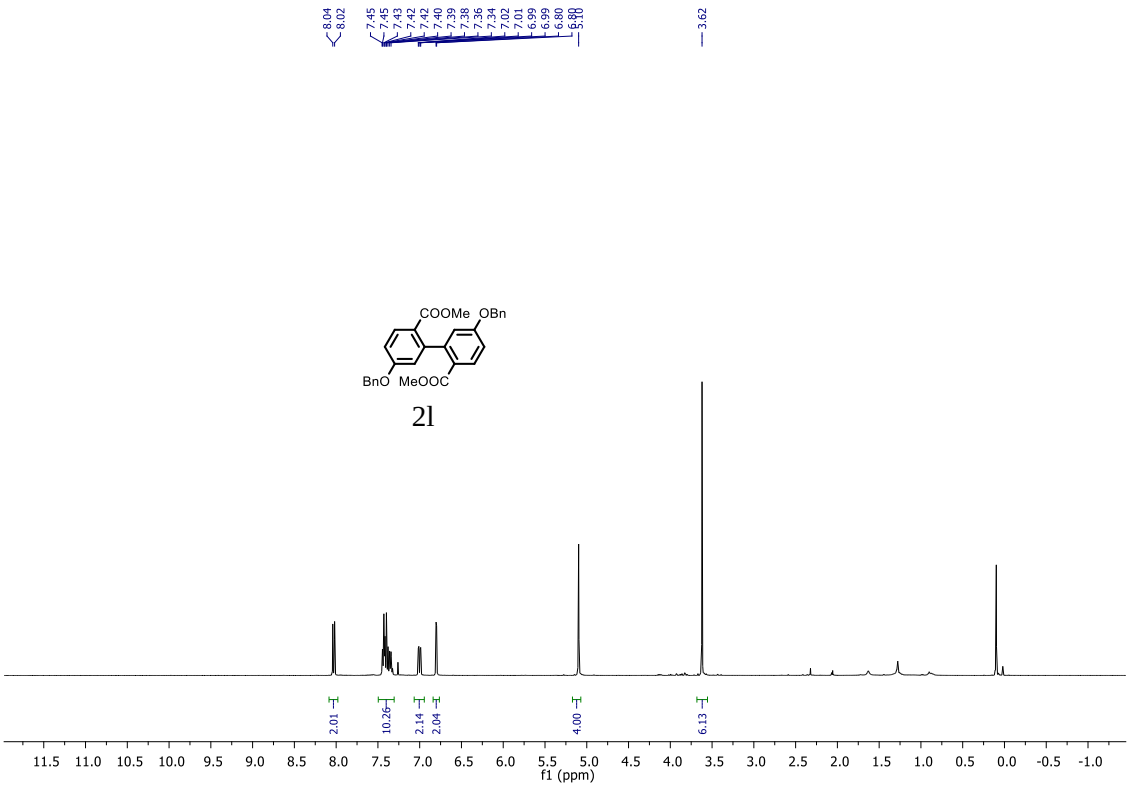

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

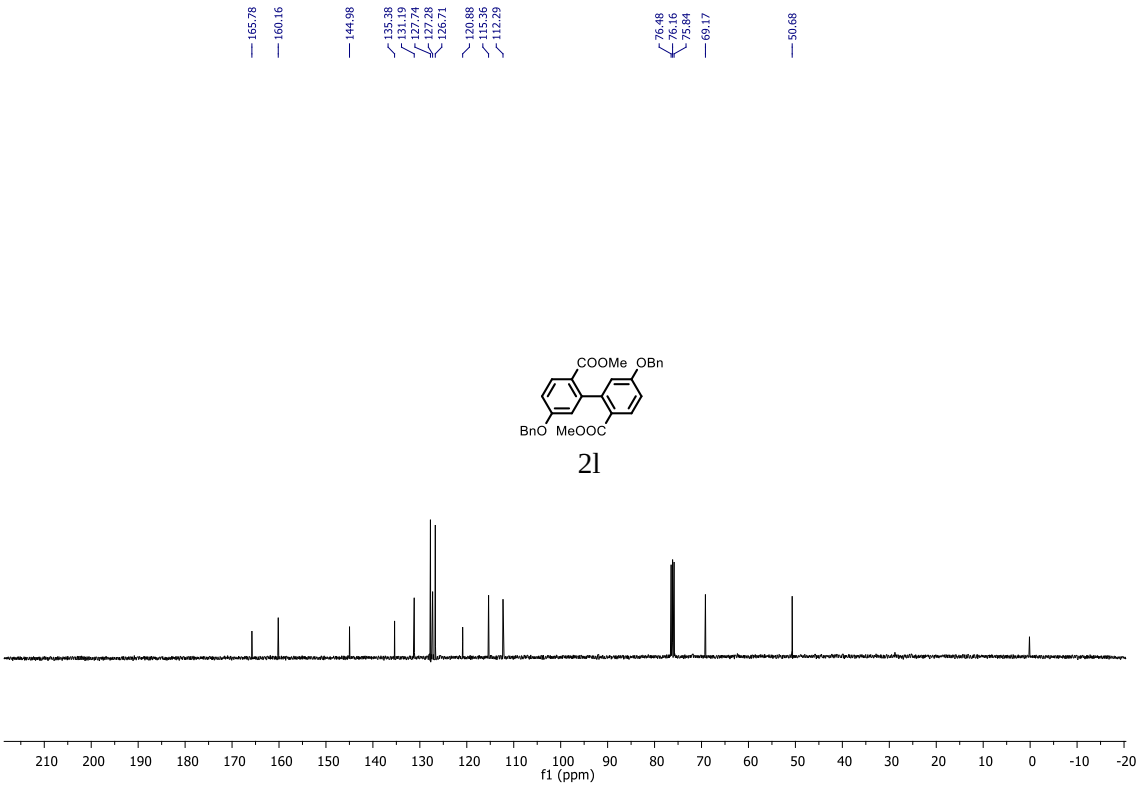

8.62
8.62
8.16
8.15
8.14
8.13
7.30
7.28
3.68
2.68
COOMe
H3COC
COCH3
MeOOC
2j
2.00
2.01
1.93
6.10
6.07
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5
f1 (ppm)

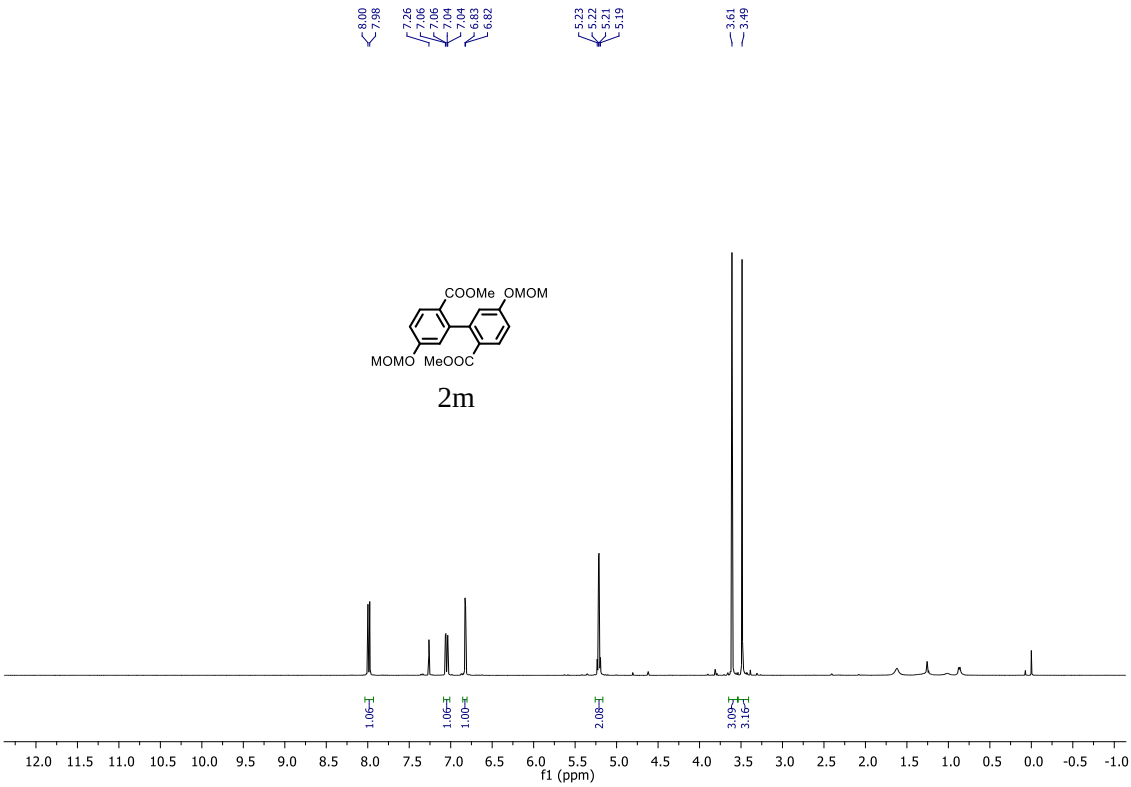

196.92
166.28
147.35
136.37
131.27
130.38
130.27
129.43
77.48
77.16
76.84
52.34
26.82
COOMe
H3COC
COCH3
MeOOC
2j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.03
8.01
7.26
6.93
6.92
6.91
6.90
6.69
6.69
3.84
3.61
COOMe OMe
MeO MeOOC
2k
2.00
2.02
1.94
6.24
6.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

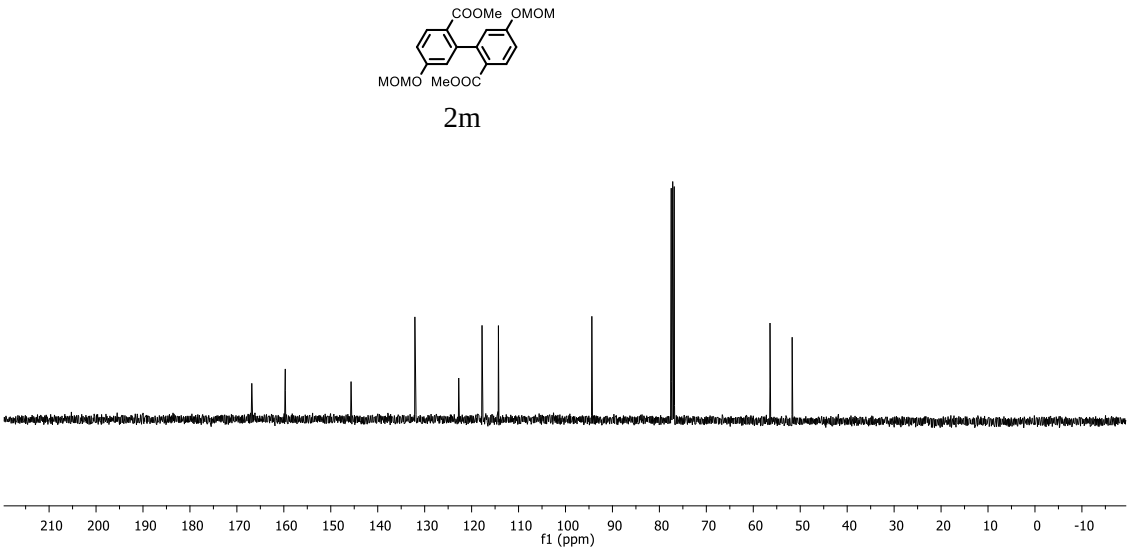

166.79
161.99
146.05
132.19
121.57
115.56
112.38
77.48
77.16
76.84
55.52
51.70
COOMe OMe
MeO MeOOC
2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.04
8.02
7.45
7.45
7.43
7.42
7.42
7.40
7.39
7.38
7.36
7.34
7.02
7.01
6.99
6.99
6.80
6.80
5.10
3.62
COOMe OBn
BnO MeOOC
2l
2.01
10.26
2.14
2.04
4.00
6.13
f1 (ppm)

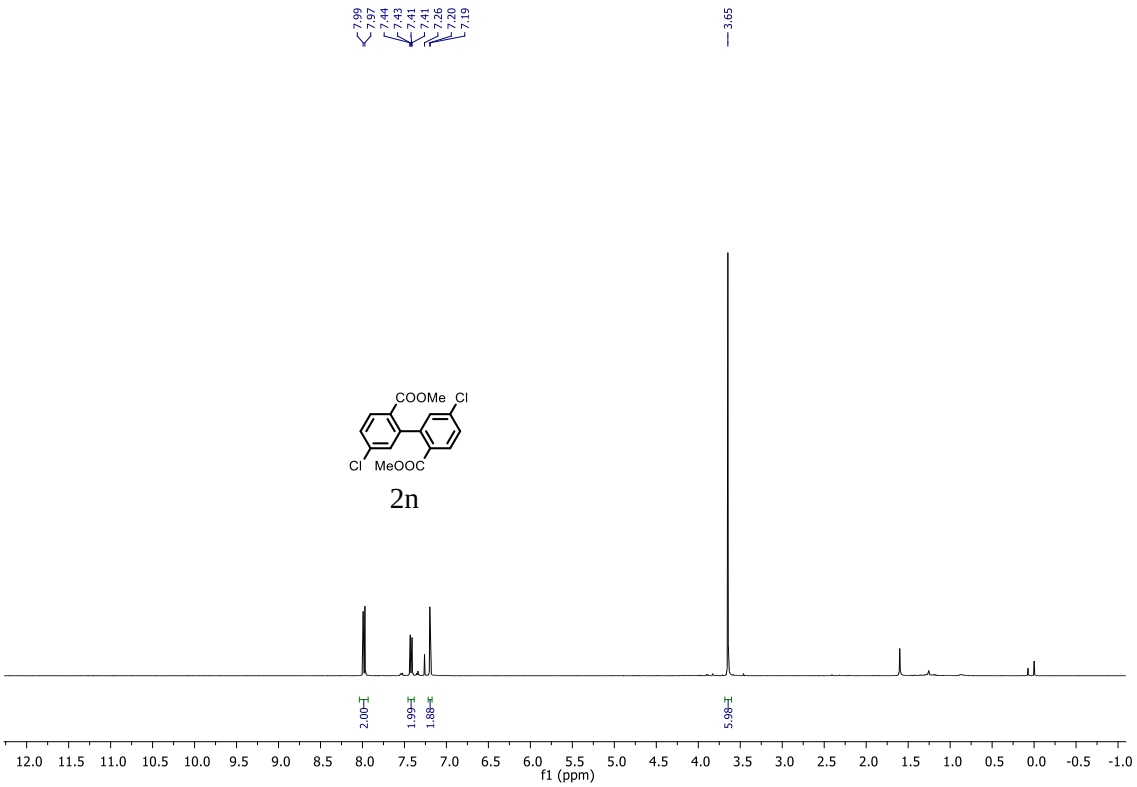

165.78
160.16
144.98
135.38
131.19
127.74
127.28
126.71
120.88
115.36
112.29
76.48
76.16
75.84
69.17
50.68
COOMe OBn
BnO MeOOC
2l
f1 (ppm)

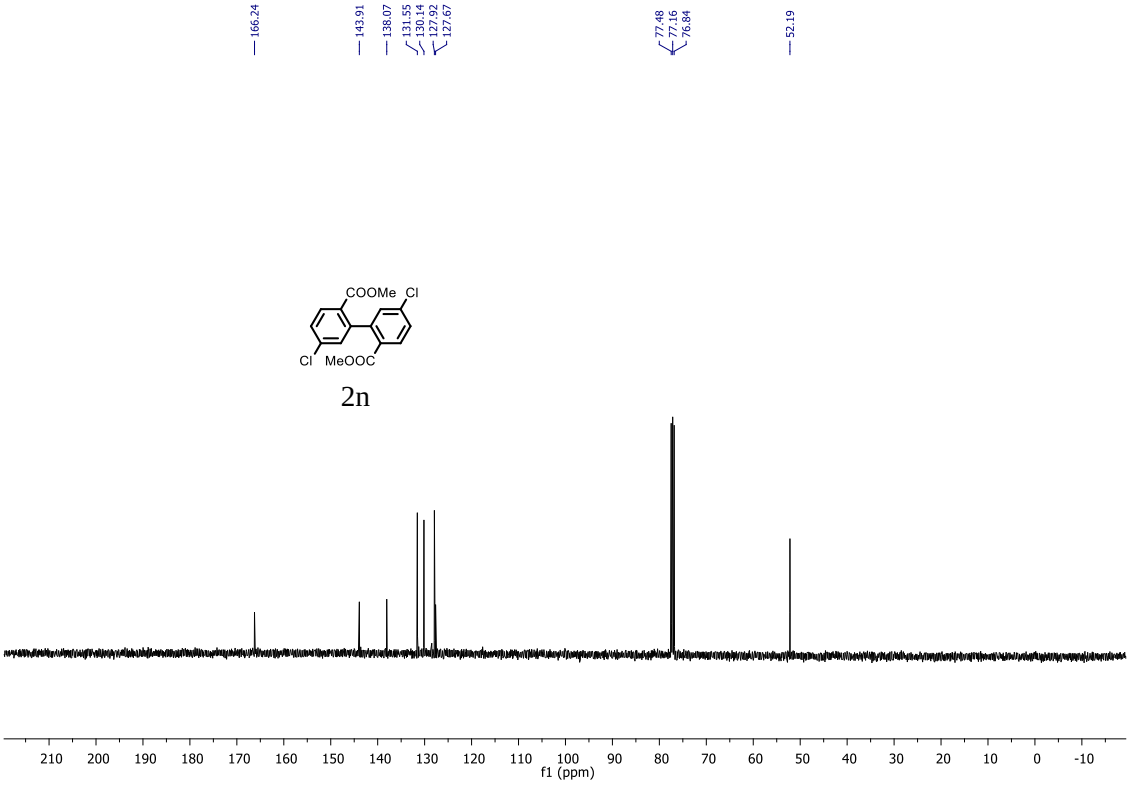

8.00
7.98
7.26
7.06
7.06
7.04
7.04
6.83
6.82
5.23
5.22
5.21
5.19
3.61
3.49
COOMe OMOM
MOMO MeOOC
1.06
1.06
1.00
2.08
3.09
3.16
f1 (ppm)

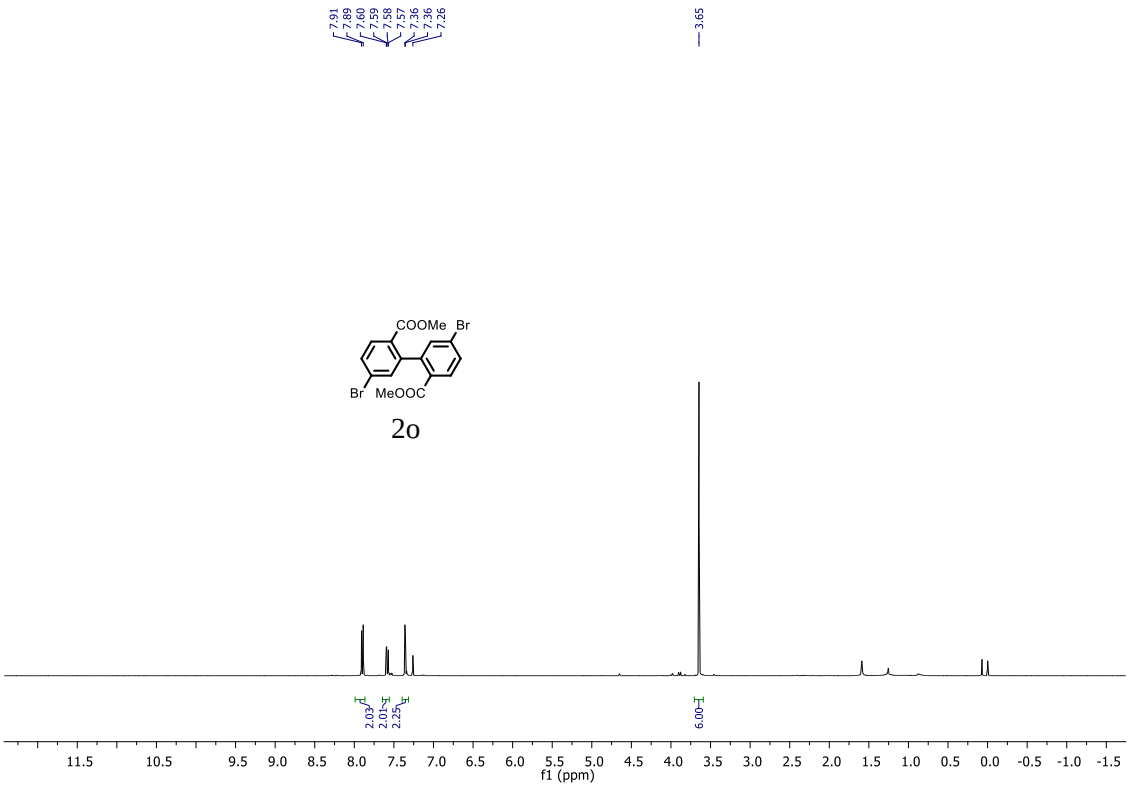
2m


166.82
159.69
145.67
132.08
122.75
117.78
114.29
94.39
77.48
77.16
76.84
56.44
51.72
COOMe OMOM
MOMO MeOOC
f1 (ppm)

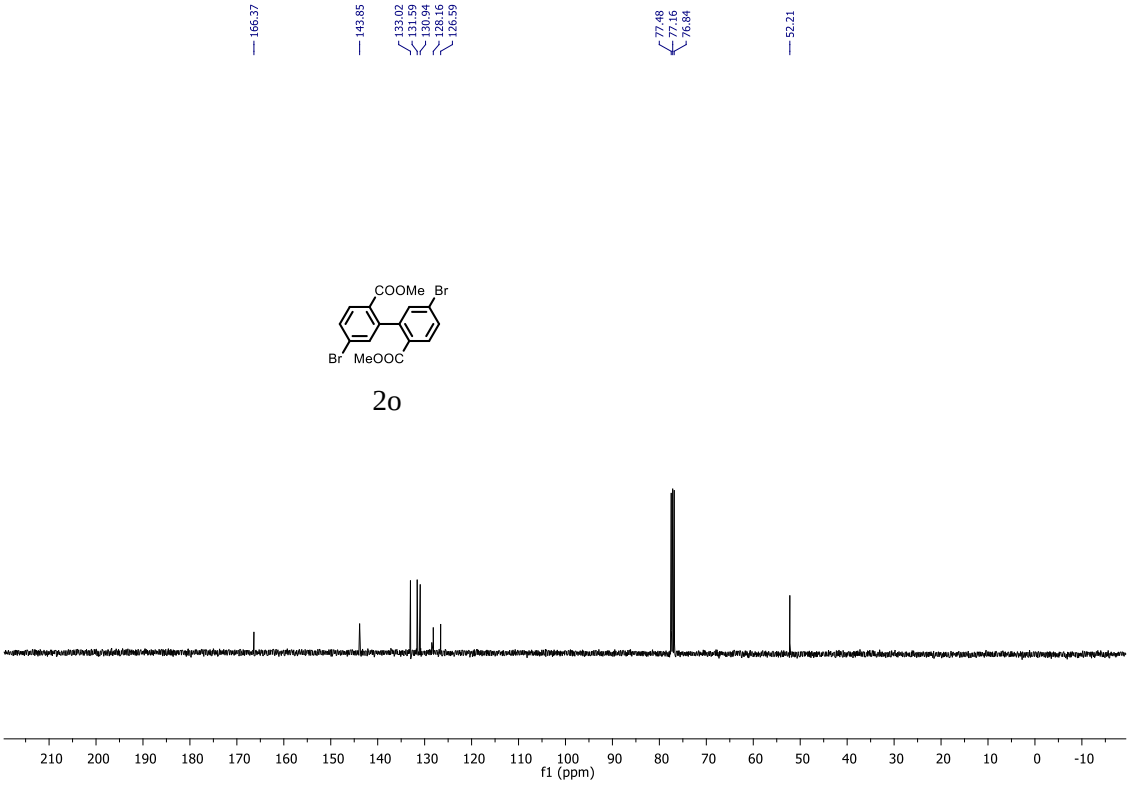
2m


7.99
7.97
7.44
7.43
7.41
7.41
7.26
7.20
7.19
3.65
COOMe Cl
Cl MeOOC
2n
2.00
1.99
1.88
5.98
f1 (ppm)

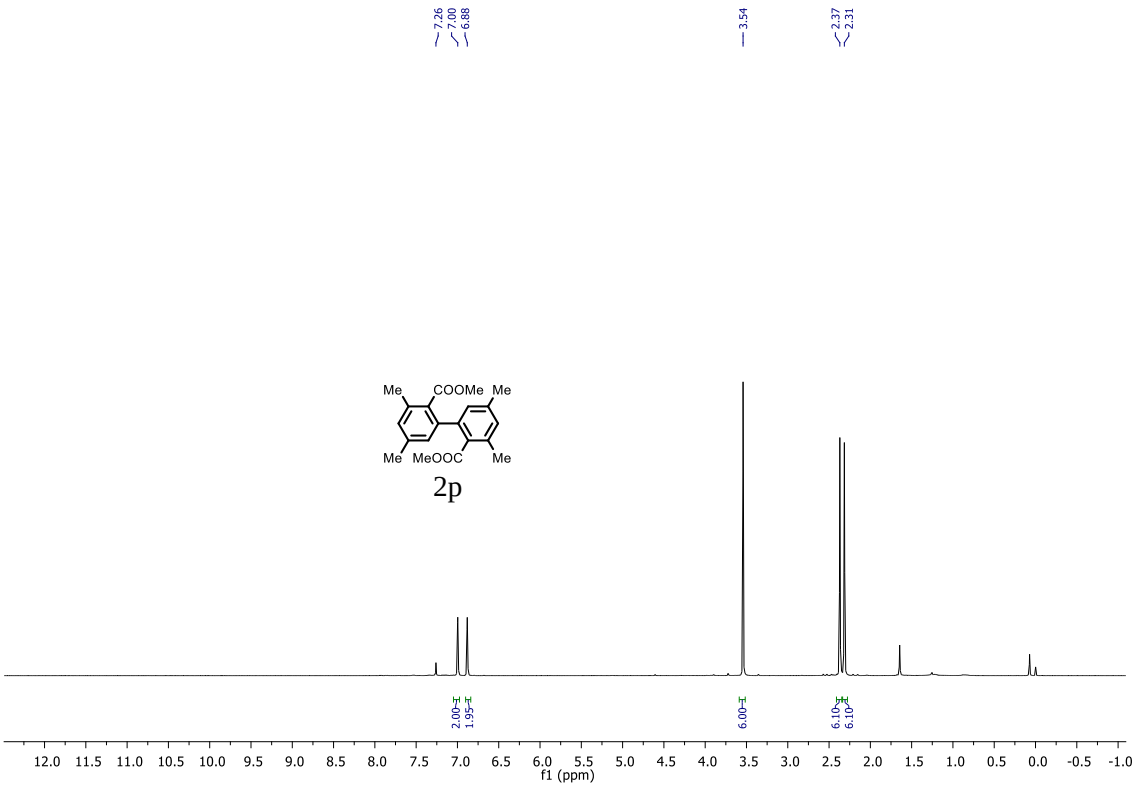

166.24
143.91
138.07
131.55
130.14
127.92
127.67
77.48
77.16
76.84
52.19
COOMe Cl
Cl MeOOC
2n
f1 (ppm)

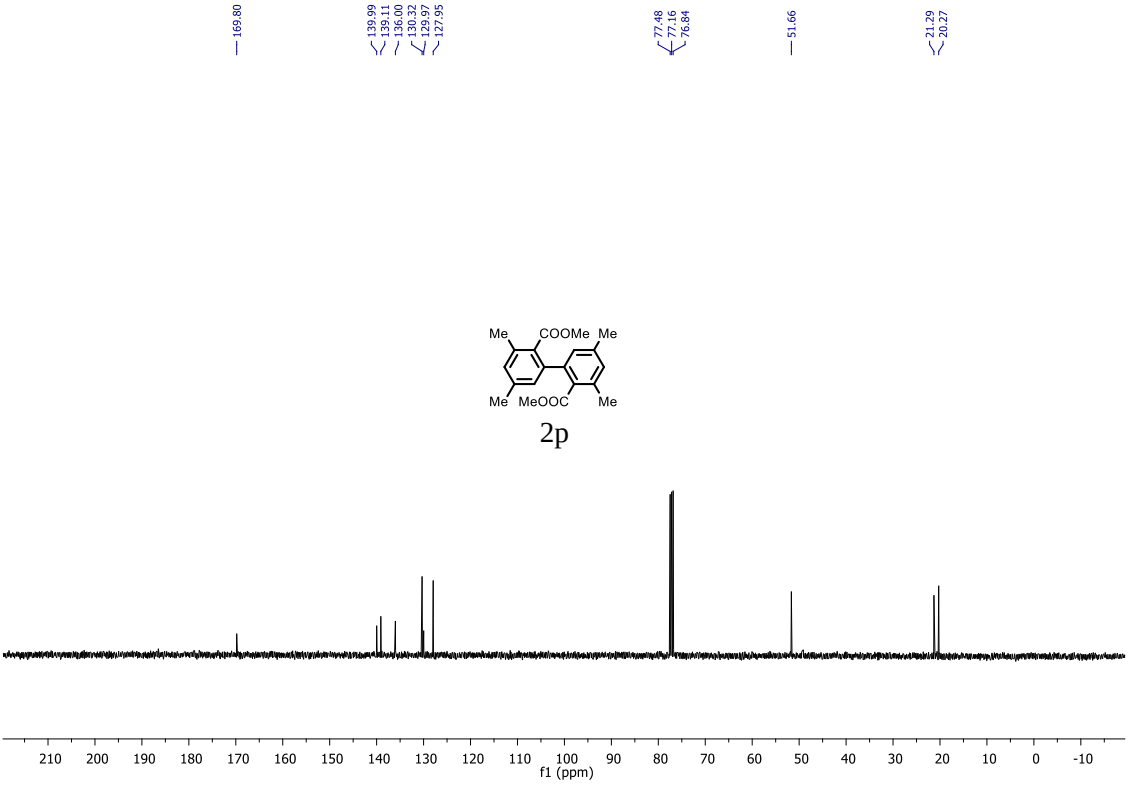

7.91
7.89
7.60
7.59
7.58
7.57
7.36
7.36
7.26
3.65
COOMe Br
Br MeOOC
2.03
2.01
2.25
6.00
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

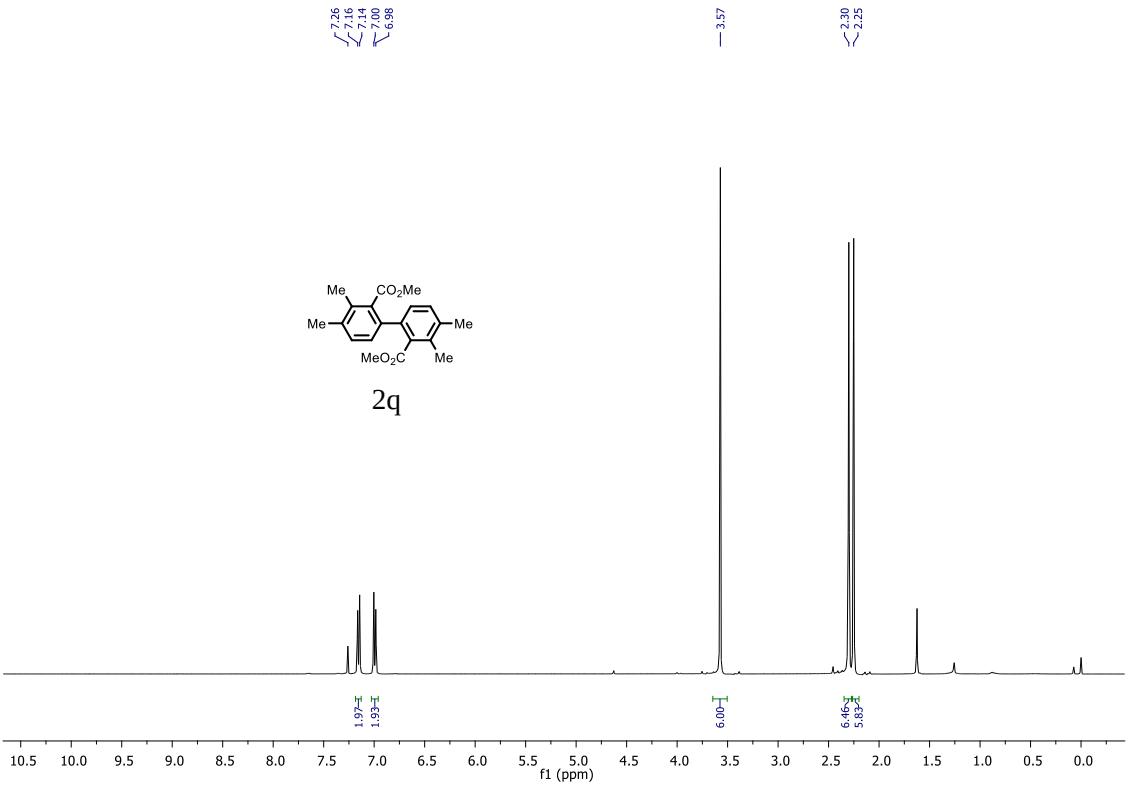
2o


166.37
143.85
133.02
131.59
130.94
128.16
126.59
77.48
77.16
76.84
52.21
COOMe Br
Br MeOOC
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

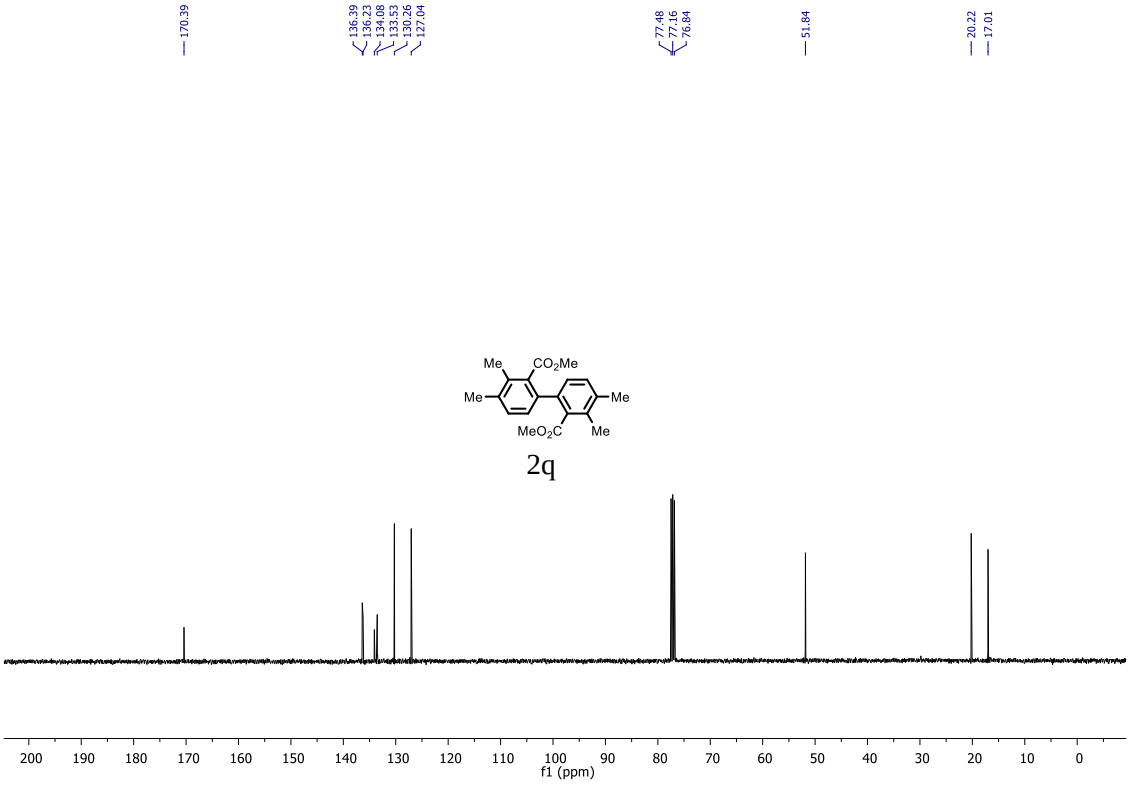
2o


7.26
7.00
6.88
3.54
2.37
2.31
Me
COOMe
Me
Me
MeOOC
Me
2p
2.00
1.95
6.00
6.10
6.10
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

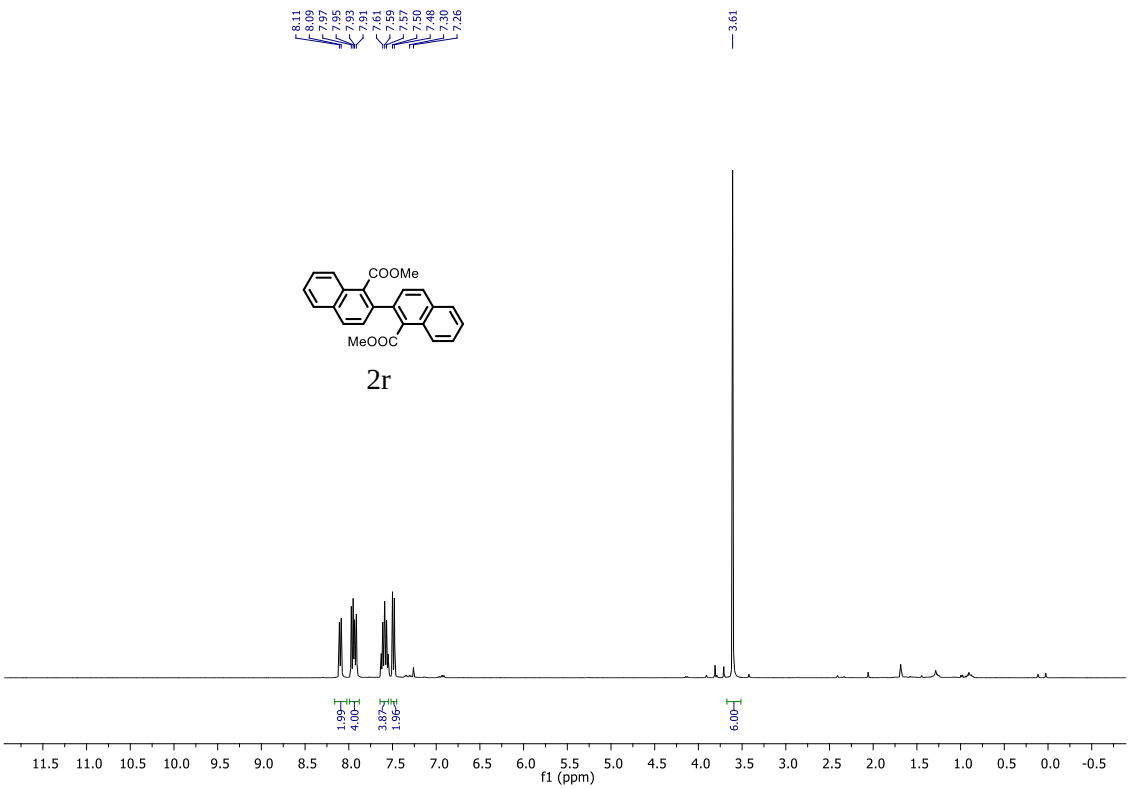

169.80
139.99
139.11
136.00
130.32
129.97
127.95
77.48
77.16
76.84
51.66
21.29
20.27
Me
COOMe
Me
Me
MeOOC
Me
2p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26
7.16
7.14
7.00
6.98
3.57
2.30
2.25
Me
CO2Me
Me
Me
MeO2C
Me
1.97
1.93
6.00
6.46
5.83
f1 (ppm)

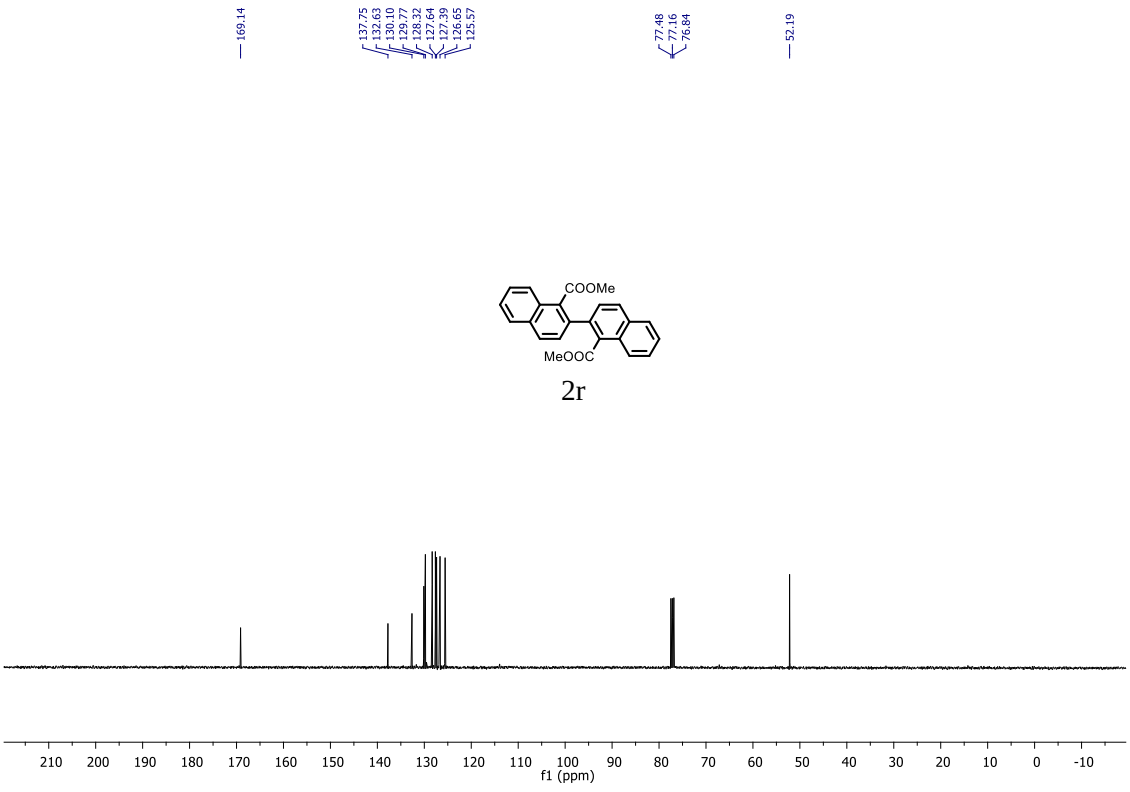
2q


170.39
136.39
136.23
134.08
133.53
130.26
127.04
77.48
77.16
76.84
51.84
20.22
17.01
Me
CO2Me
Me
Me
MeO2C
Me
f1 (ppm)

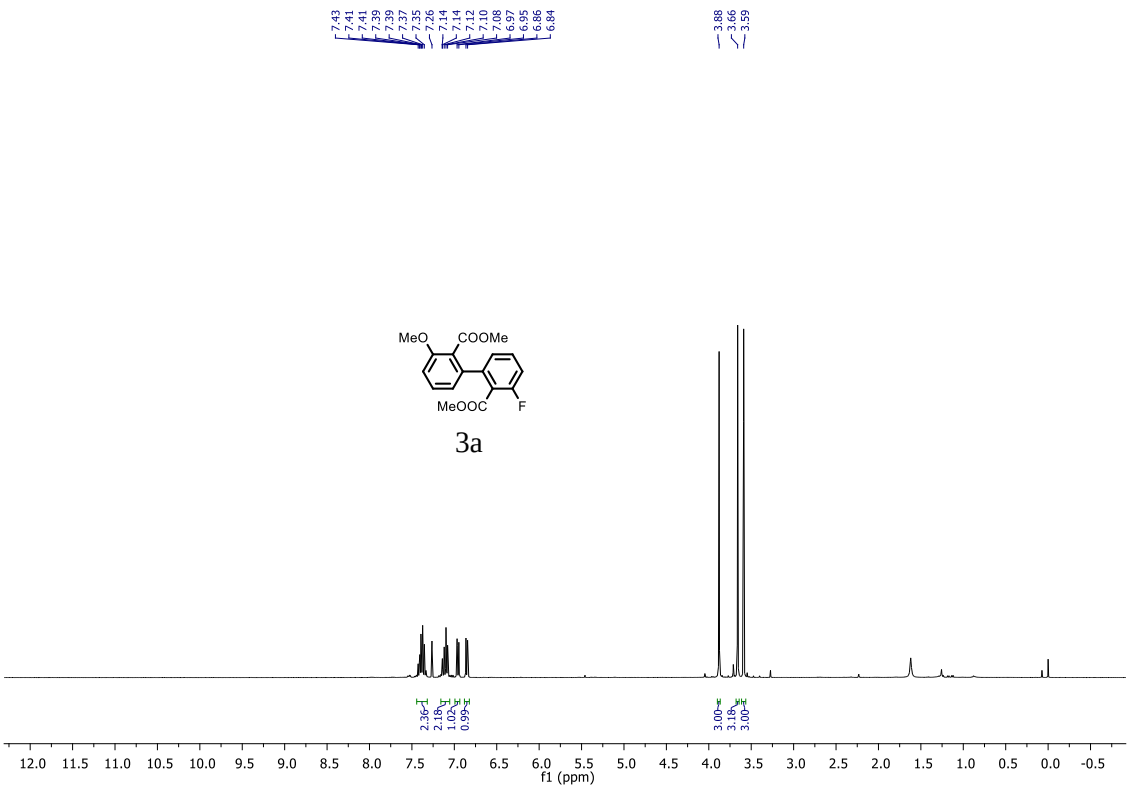
2q


8.11
8.09
7.97
7.95
7.93
7.91
7.61
7.59
7.57
7.50
7.48
7.30
7.26
3.61
COOMe
MeOOC
1.99
4.00
3.87
1.96
6.00
f1 (ppm)

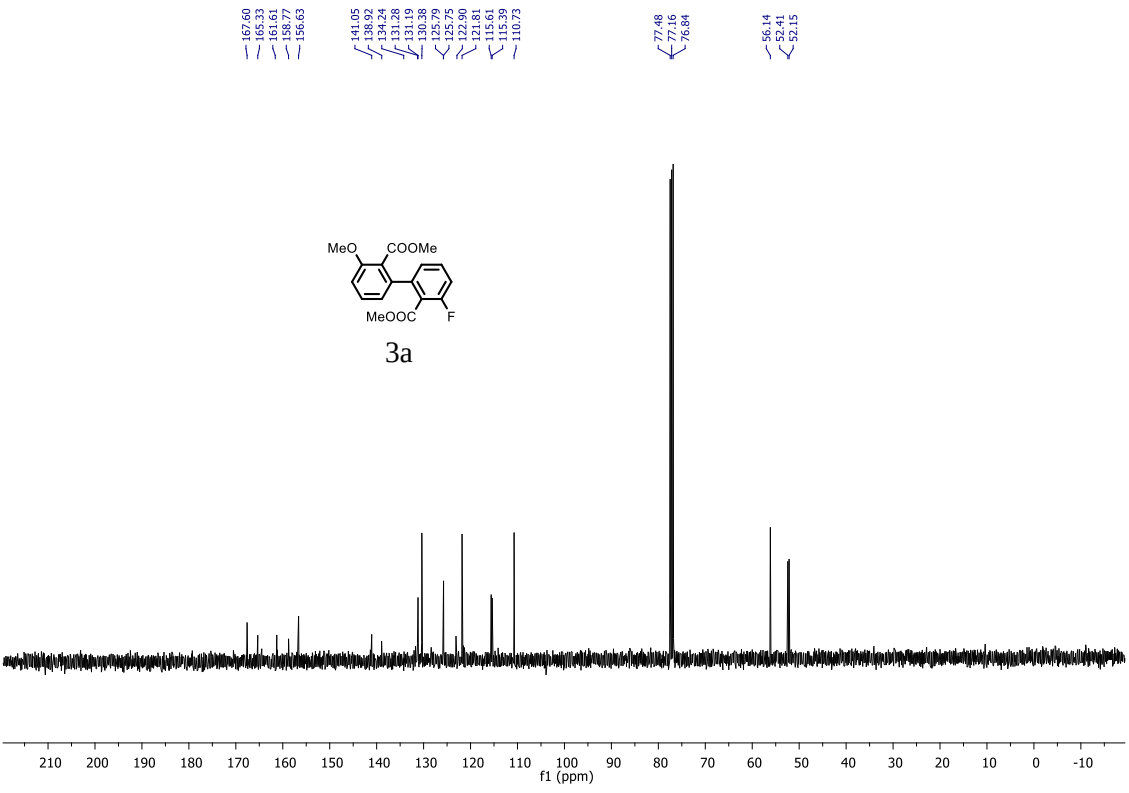
2r


169.14
137.75
132.63
130.10
129.77
128.32
127.64
127.39
126.65
125.57
77.48
77.16
76.84
52.19
COOMe
MeOOC
f1 (ppm)

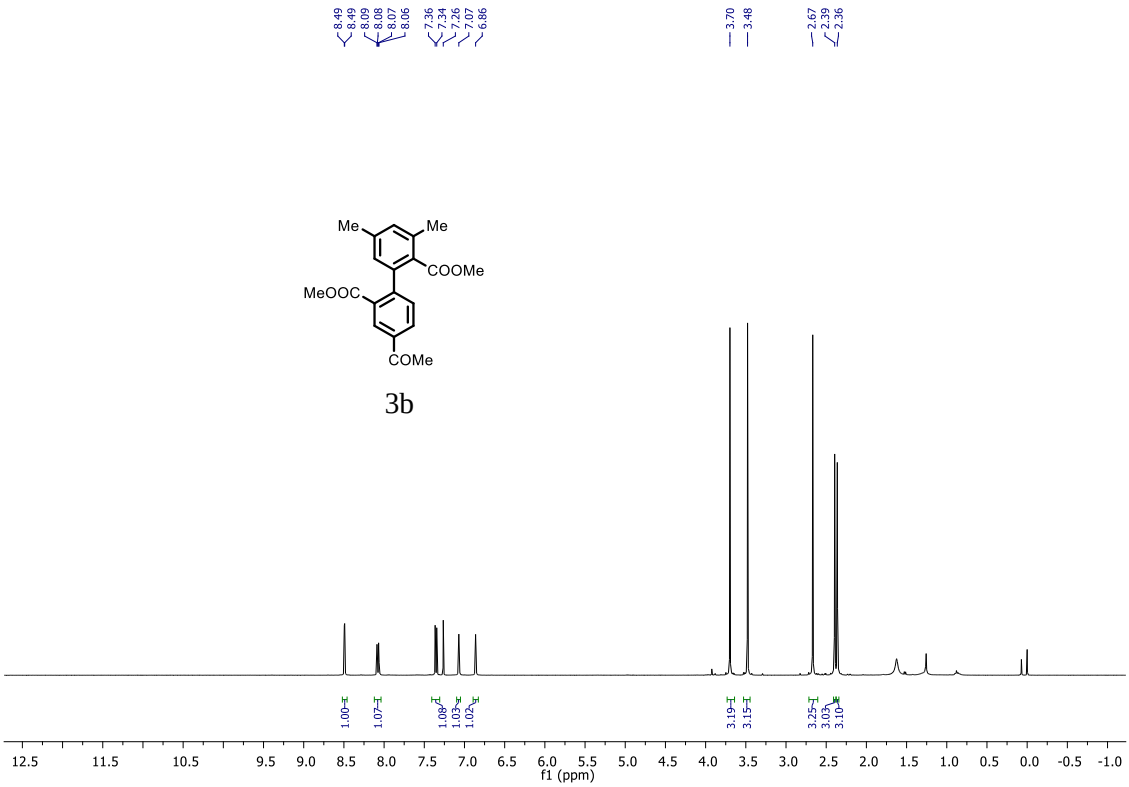
2r


7.43
7.41
7.41
7.39
7.39
7.37
7.35
7.26
7.14
7.14
7.12
7.10
7.08
6.97
6.95
6.86
6.84
3.88
3.66
3.59
MeO
COOMe
MeOOC
F
2.36
2.18
1.02
0.99
3.00
3.18
3.00
f1 (ppm)

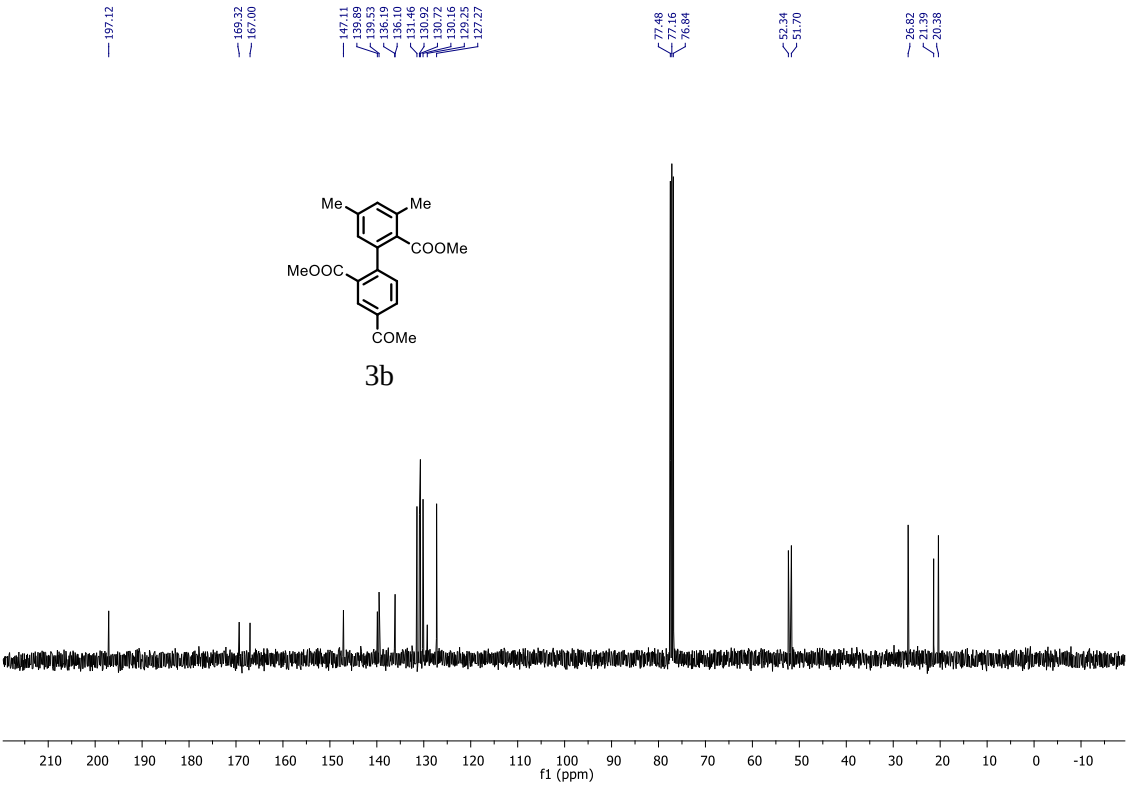
3a


167.60
165.33
161.61
158.77
156.63
141.05
138.92
134.24
131.28
131.19
130.38
125.79
125.75
122.90
121.81
115.61
115.39
110.73
77.48
77.16
76.84
56.14
52.41
52.15
MeO
COOMe
MeOOC
F
f1 (ppm)

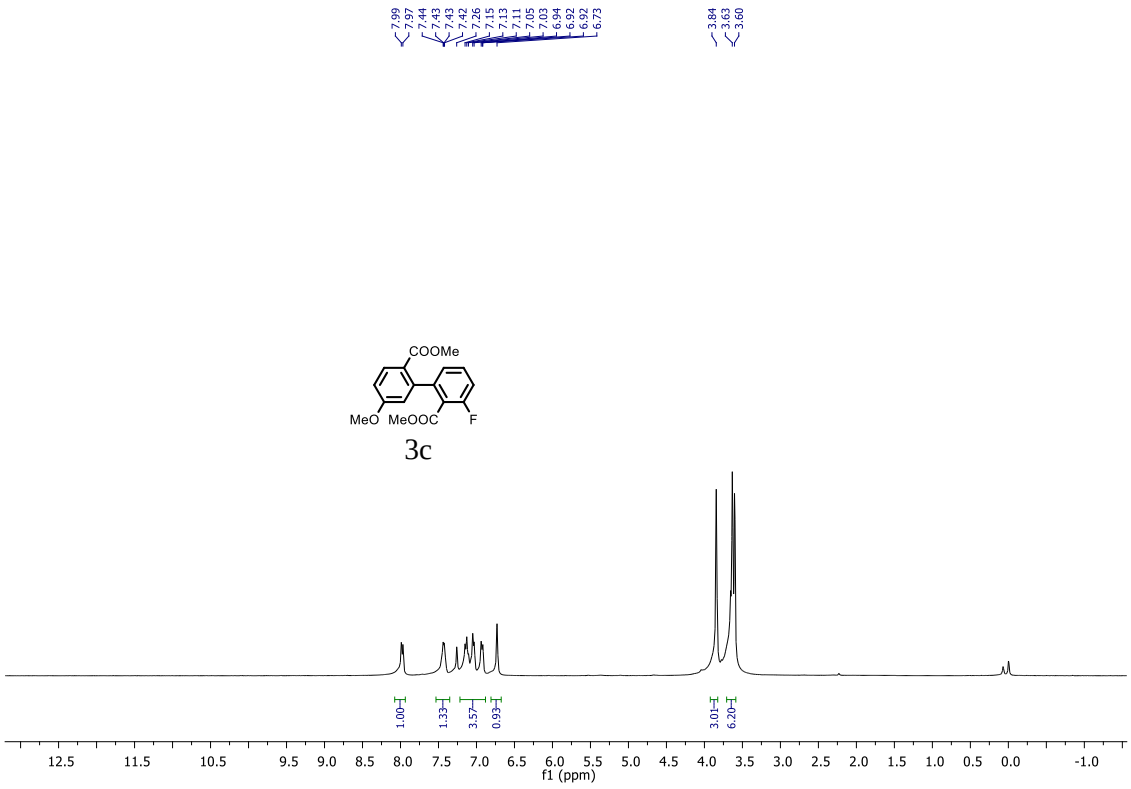
3a

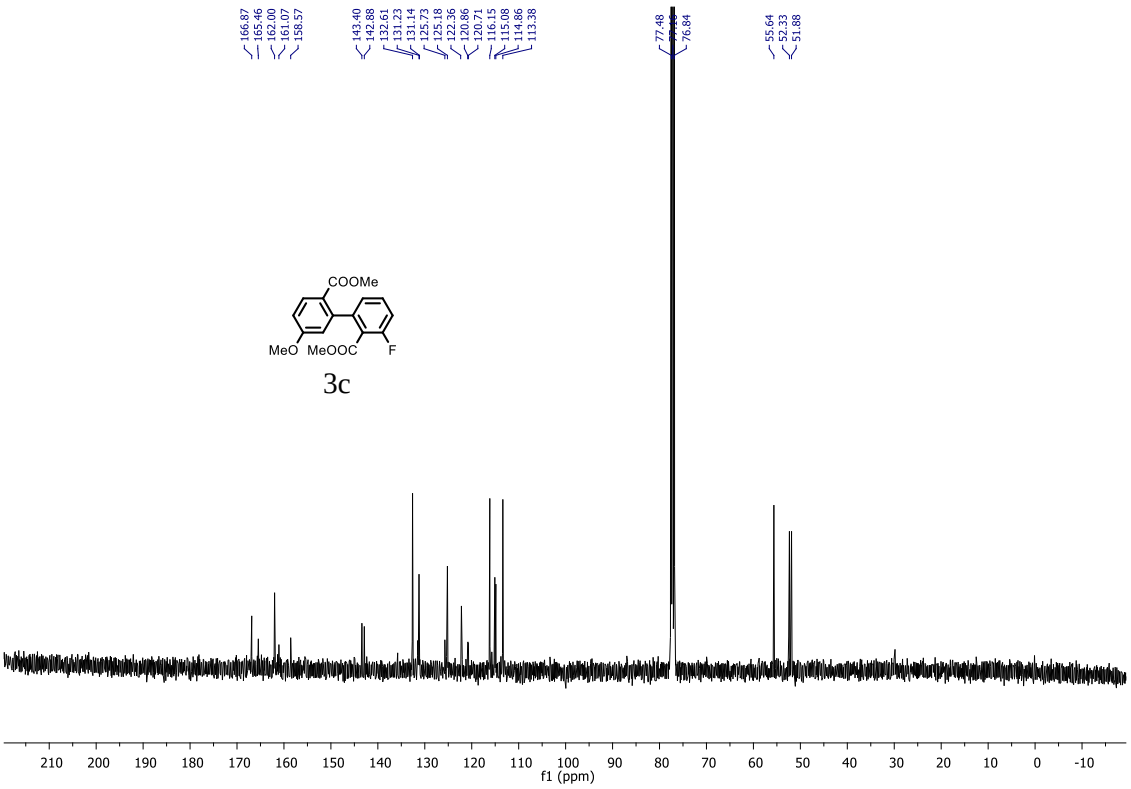

8.49
8.49
8.09
8.08
8.07
8.06
7.36
7.34
7.26
7.07
6.86
3.70
3.48
2.67
2.39
2.36
Me
Me
COOMe
MeOOC
COMe
1.00
1.07
1.08
1.03
1.02
3.19
3.15
3.25
3.03
3.10
f1 (ppm)

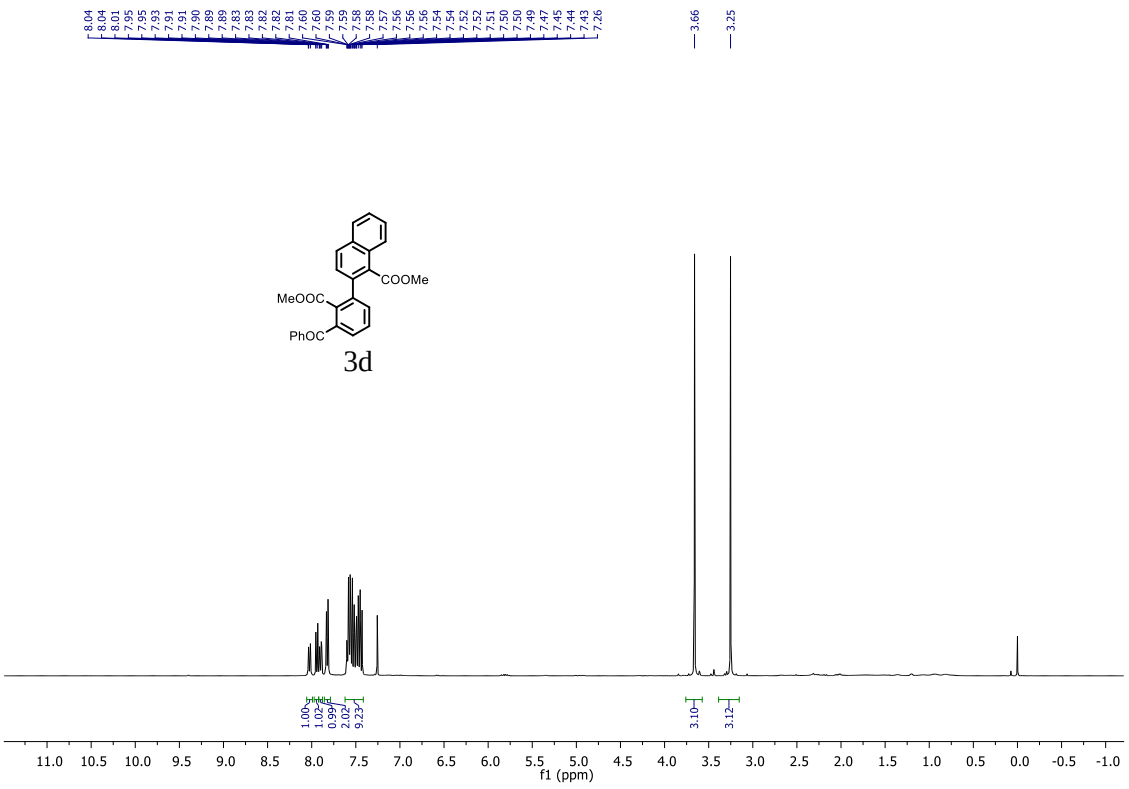
3b

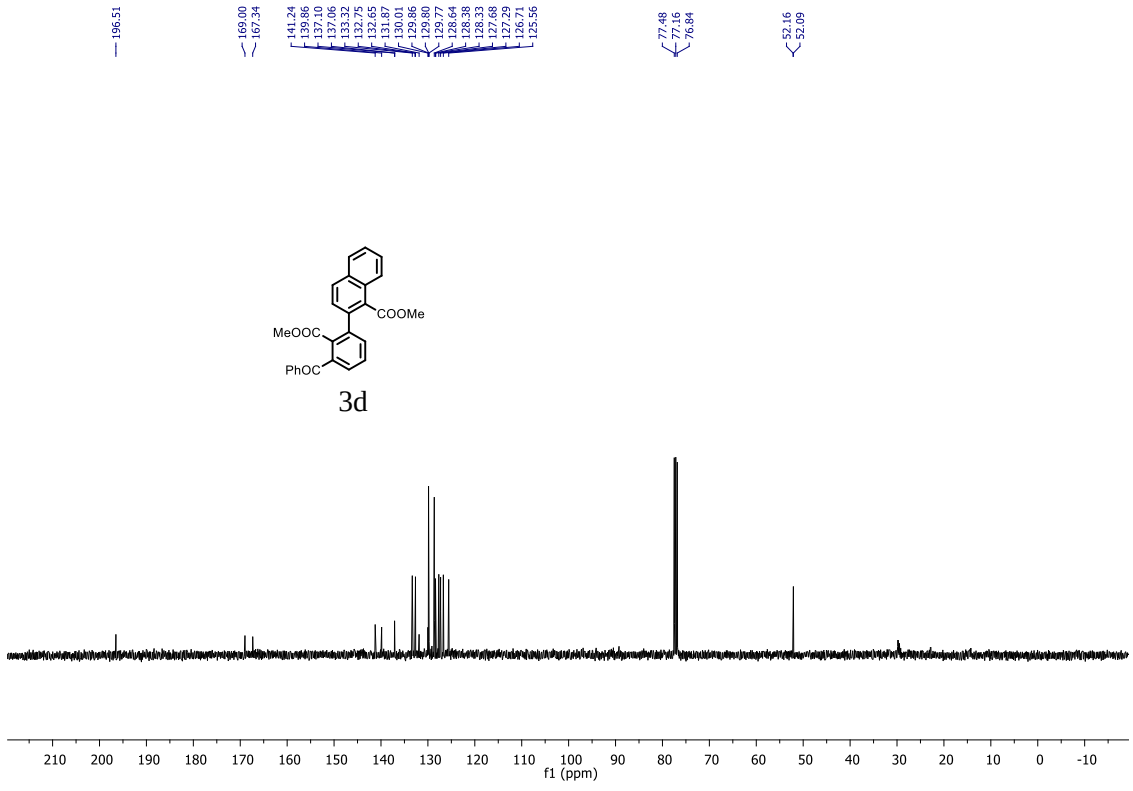

197.12
169.32
167.00
147.11
139.89
139.53
136.19
136.10
131.46
130.92
130.72
130.16
129.25
127.27
77.48
77.16
76.84
52.34
51.70
26.82
21.39
20.38
Me
Me
COOMe
MeOOC
COMe
f1 (ppm)

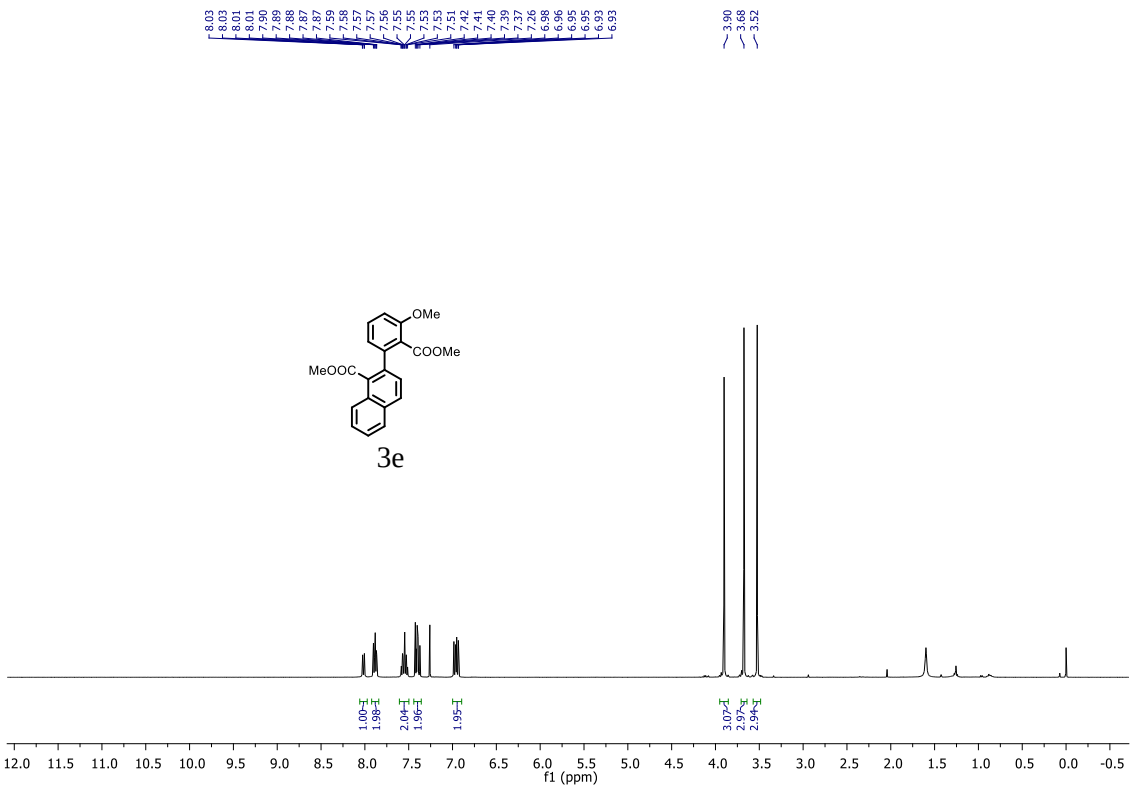
3b

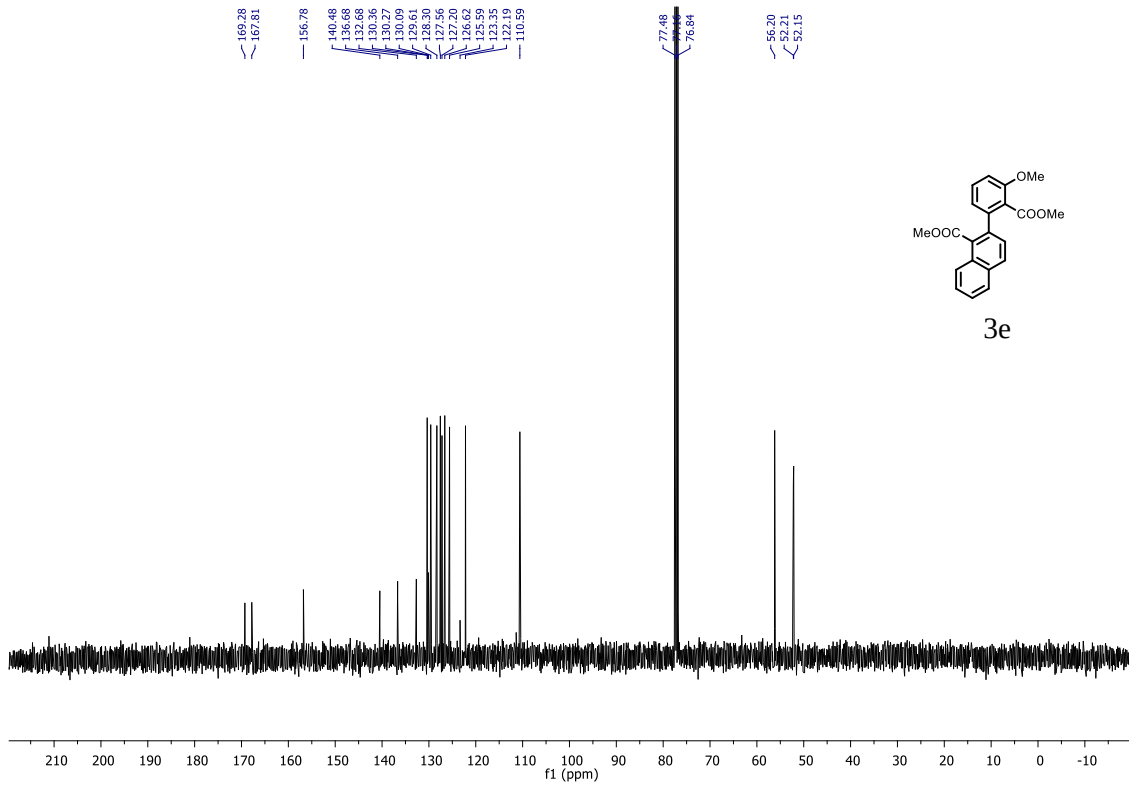

7.99
7.97
7.44
7.43
7.43
7.42
7.26
7.15
7.13
7.11
7.05
7.03
6.94
6.92
6.92
6.73
3.84
3.63
3.60
COOMe
MeO MeOOC F
3c
1.00
1.33
3.57
0.93
3.01
6.20
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)


166.87
165.46
162.00
161.07
158.57
143.40
142.88
132.61
131.23
131.14
125.73
125.18
122.36
120.86
120.71
116.15
115.08
114.86
113.38
77.48
76.84
55.64
52.33
51.88
COOMe
MeO MeOOC F
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.04
8.04
8.01
7.95
7.95
7.93
7.91
7.91
7.90
7.89
7.89
7.83
7.83
7.82
7.82
7.81
7.60
7.60
7.59
7.59
7.58
7.58
7.57
7.56
7.56
7.56
7.54
7.54
7.52
7.52
7.51
7.50
7.50
7.49
7.47
7.45
7.44
7.43
7.26
3.66
3.25
COOMe
MeOOC
PhOC
3d
1.00
1.02
0.99
2.02
9.23
3.10
3.12
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


196.51
169.00
167.34
141.24
139.86
137.10
137.06
133.32
132.75
132.65
131.87
130.01
129.86
129.80
129.77
128.64
128.38
128.33
127.68
127.29
126.71
125.56
77.48
77.16
76.84
52.16
52.09
COOMe
MeOOC
PhOC
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.03
8.03
8.01
8.01
7.90
7.89
7.88
7.87
7.87
7.59
7.58
7.57
7.57
7.56
7.55
7.55
7.53
7.53
7.51
7.42
7.41
7.40
7.39
7.37
7.26
6.98
6.96
6.95
6.95
6.93
6.93
3.90
3.68
3.52
OMe
COOMe
MeOOC
3e
1.00
1.98
2.04
1.96
1.95
3.07
2.97
2.94
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


169.28
167.81
156.78
140.48
136.68
132.68
130.36
130.27
130.09
129.61
128.30
127.56
127.20
126.62
125.59
123.35
122.19
110.59
77.48
76.84
56.20
52.21
52.15
OMe
COOMe
MeOOC
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.04
8.02
7.99
7.98
7.97
7.96
7.96
7.93
7.92
7.91
7.91
7.90
7.89
7.88
7.58
7.57
7.56
7.56
7.55
7.54
7.54
7.52
7.52
7.50
7.50
7.38
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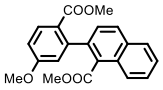
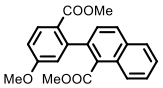
7.26
6.96
6.96
6.94
6.93
6.81
6.80
3.83
3.61
3.57


COOMe
MeO MeOOC

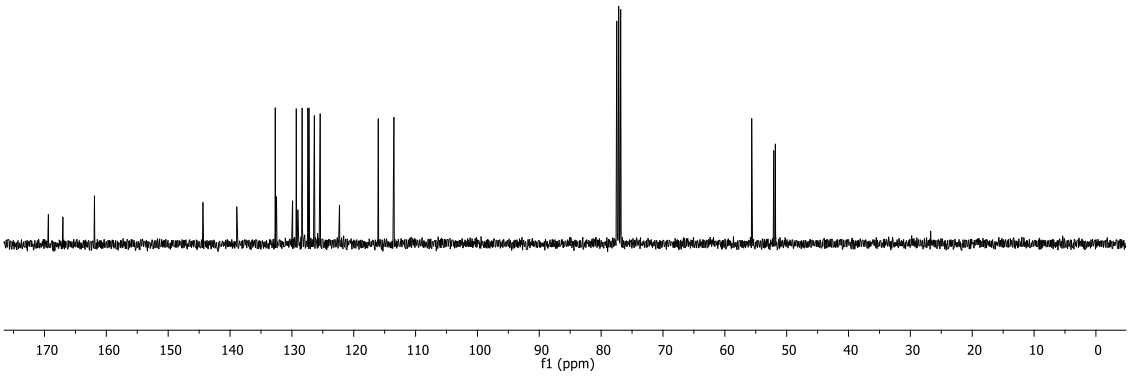
3f

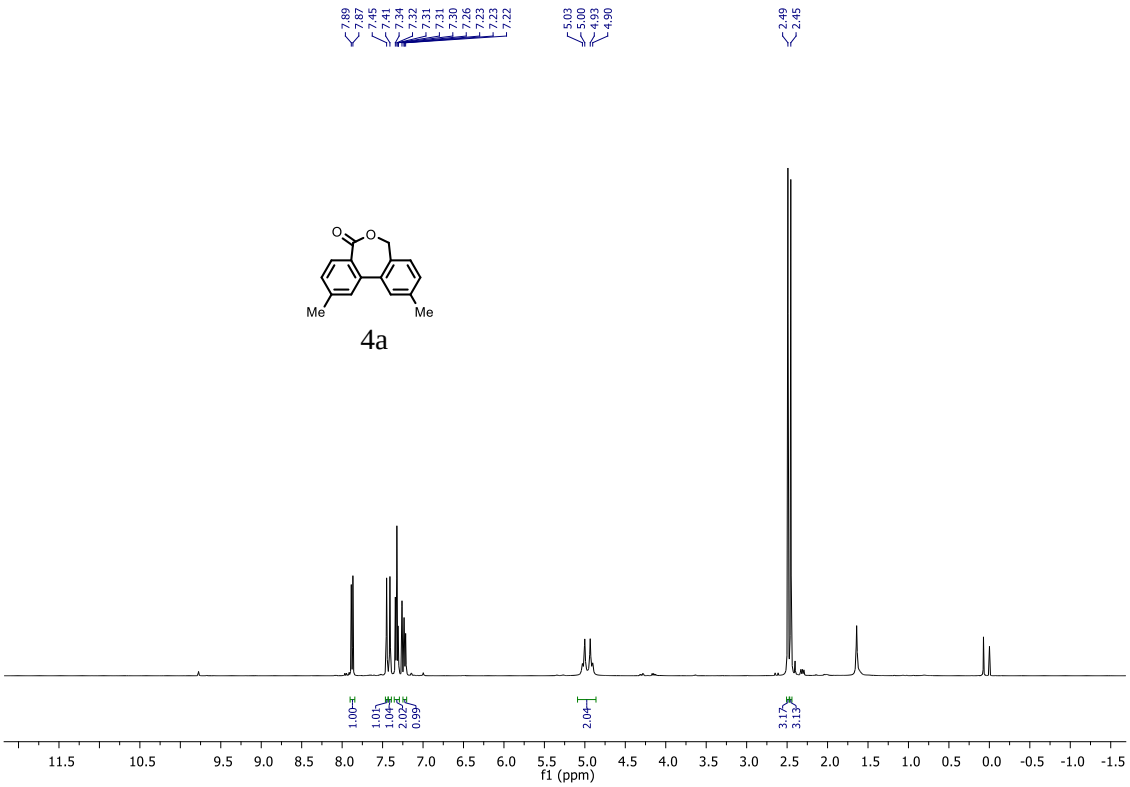
4.15
2.24
1.04
0.98
0.92
2.81
3.02
2.92
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.5
f1 (ppm)


169.37
167.02
161.92
144.38
138.92
132.69
132.49
130.80
129.29
129.03
128.34
127.42
127.24
126.36
125.42
122.30
116.03
113.50
77.48
77.16
76.84
55.65
52.09
51.83

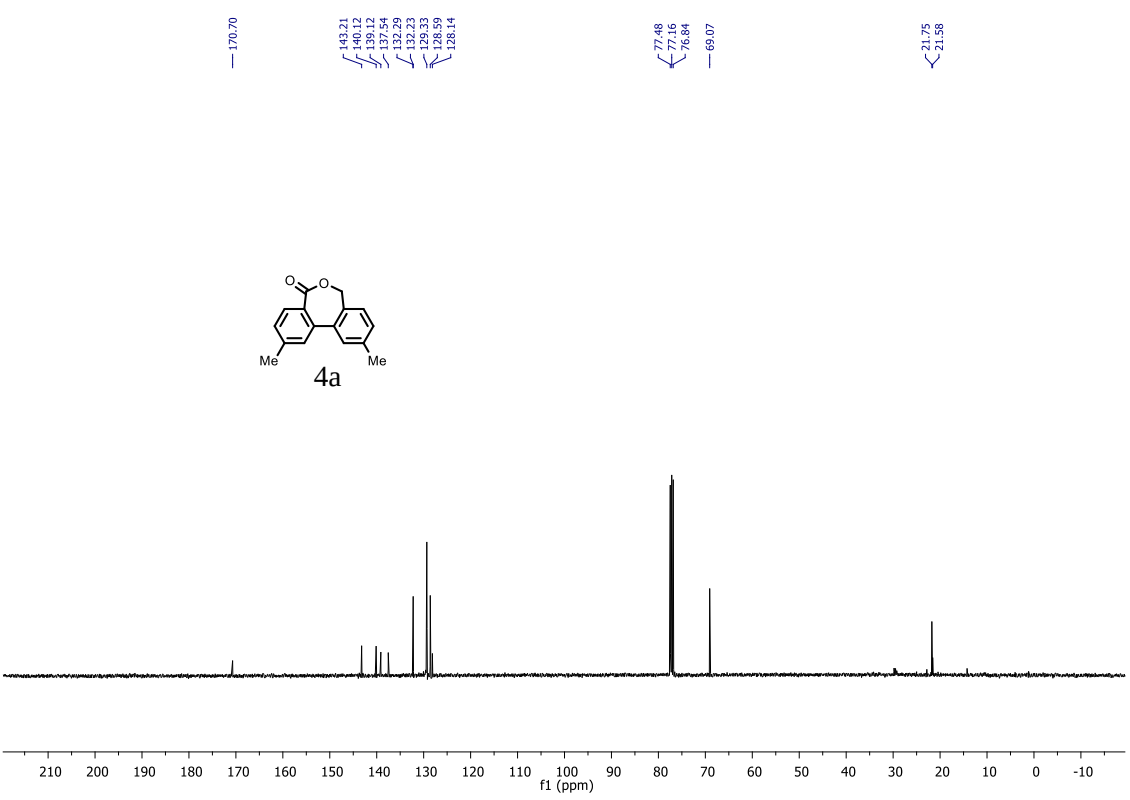

COOMe
MeO MeOOC

3f


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

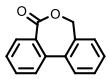

7.89
7.87
7.45
7.41
7.34
7.32
7.31
7.31
7.30
7.26
7.23
7.23
7.22
5.03
5.00
4.93
4.90
2.49
2.45
O
O
Me
Me
1.00
1.01
1.04
2.02
0.99
2.04
3.17
3.13
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

4a

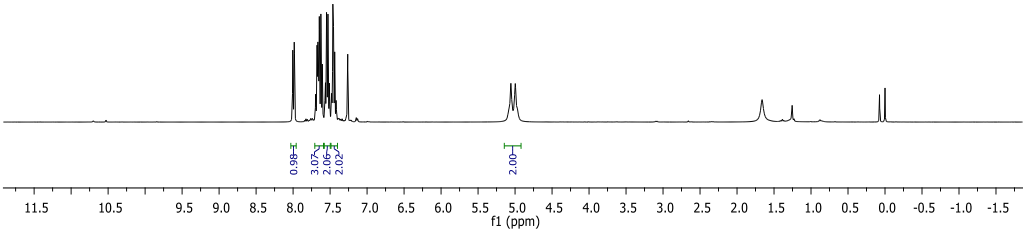

170.70
143.21
140.12
139.12
137.54
132.29
132.23
129.33
128.59
128.14
77.48
77.16
76.84
69.07
21.75
21.58
O
O
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4a

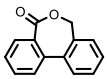

8.00
8.00
7.98
7.70
7.69
7.68
7.66
7.66
7.66
7.65
7.62
7.62
7.61
7.57
7.56
7.55
7.55
7.53
7.53
7.51
7.51
7.48
7.48
7.46
7.46
7.44
7.42
7.26
5.06
5.00



4b

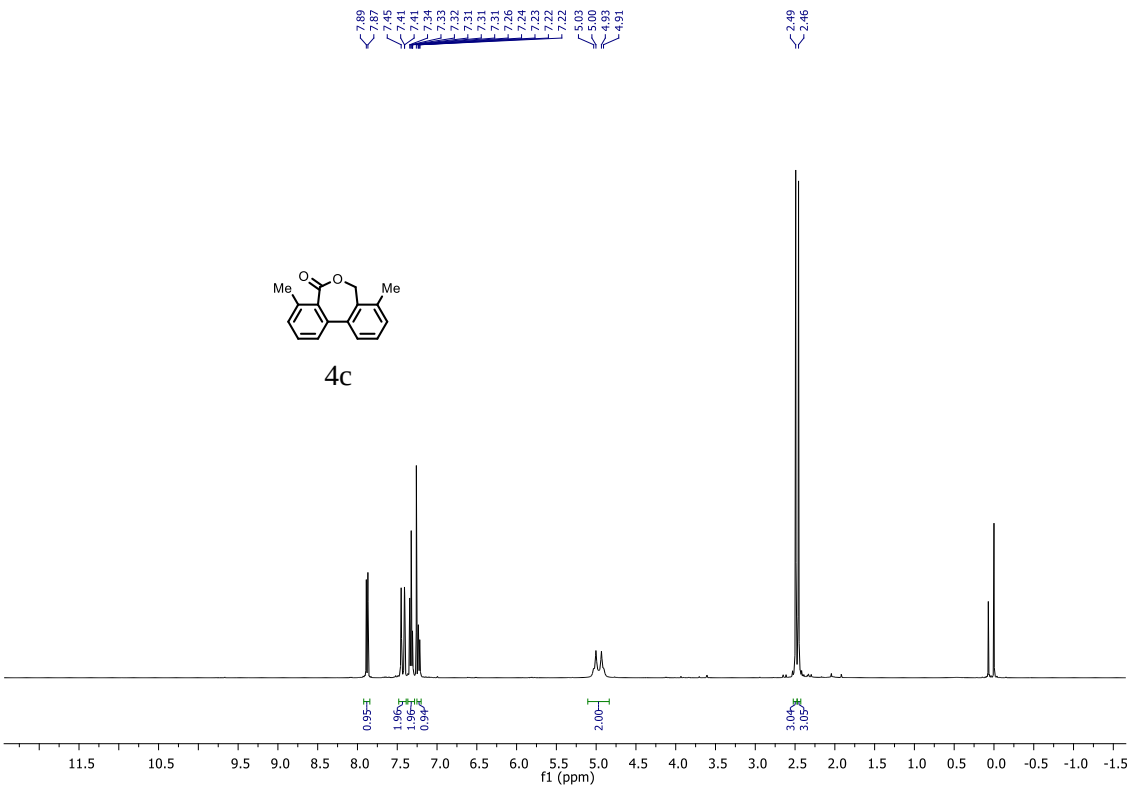

0.98
3.07
2.06
2.02
2.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

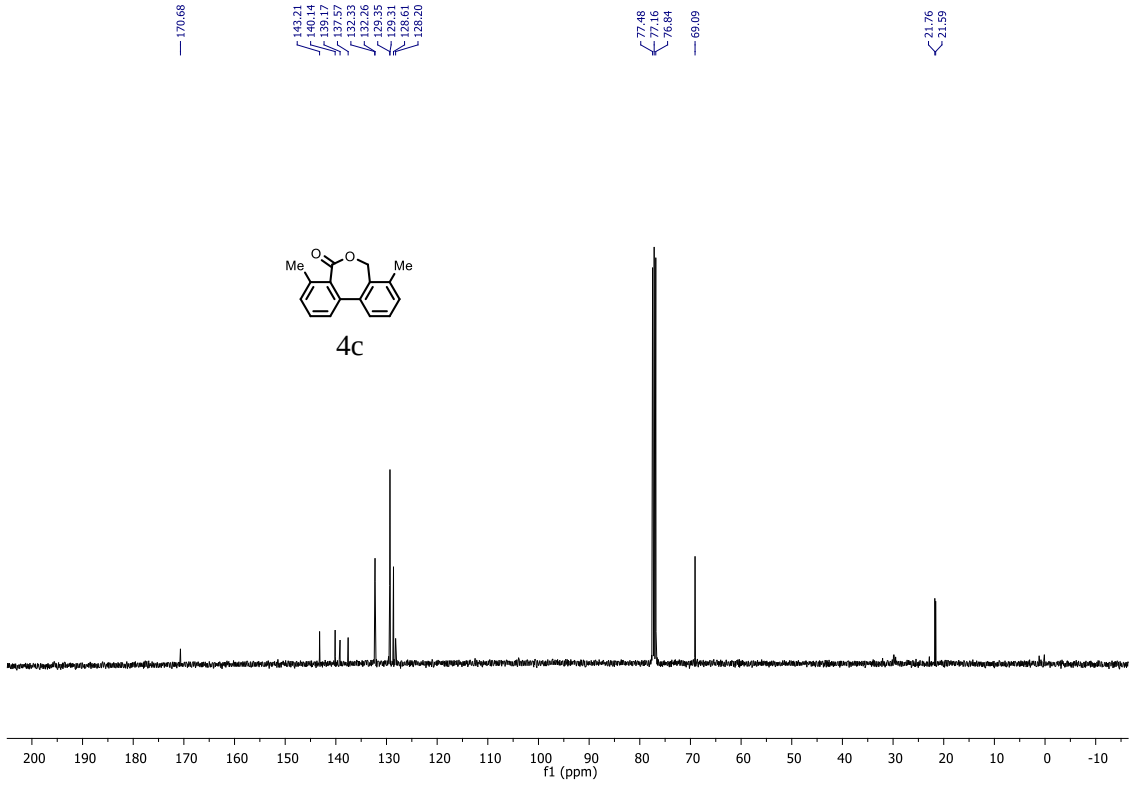

170.42
139.13
137.42
134.97
132.73
132.10
130.81
130.29
128.83
128.72
128.59
77.48
77.16
76.84
69.34

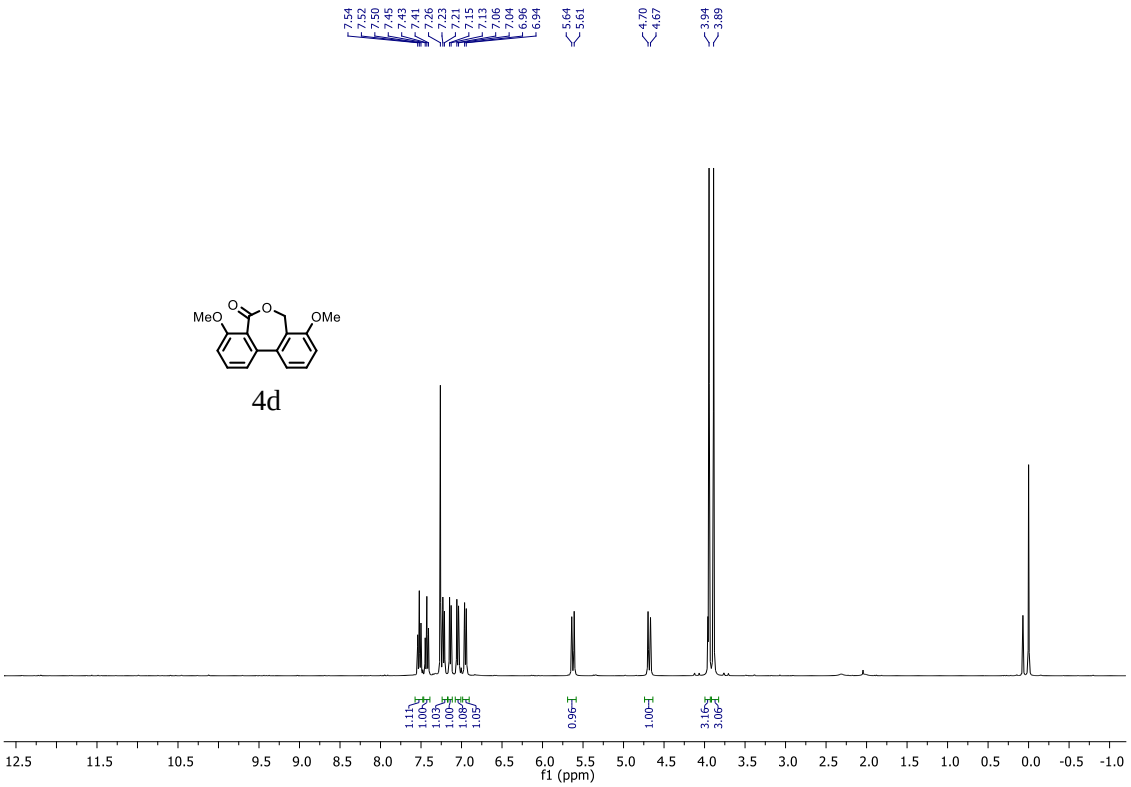


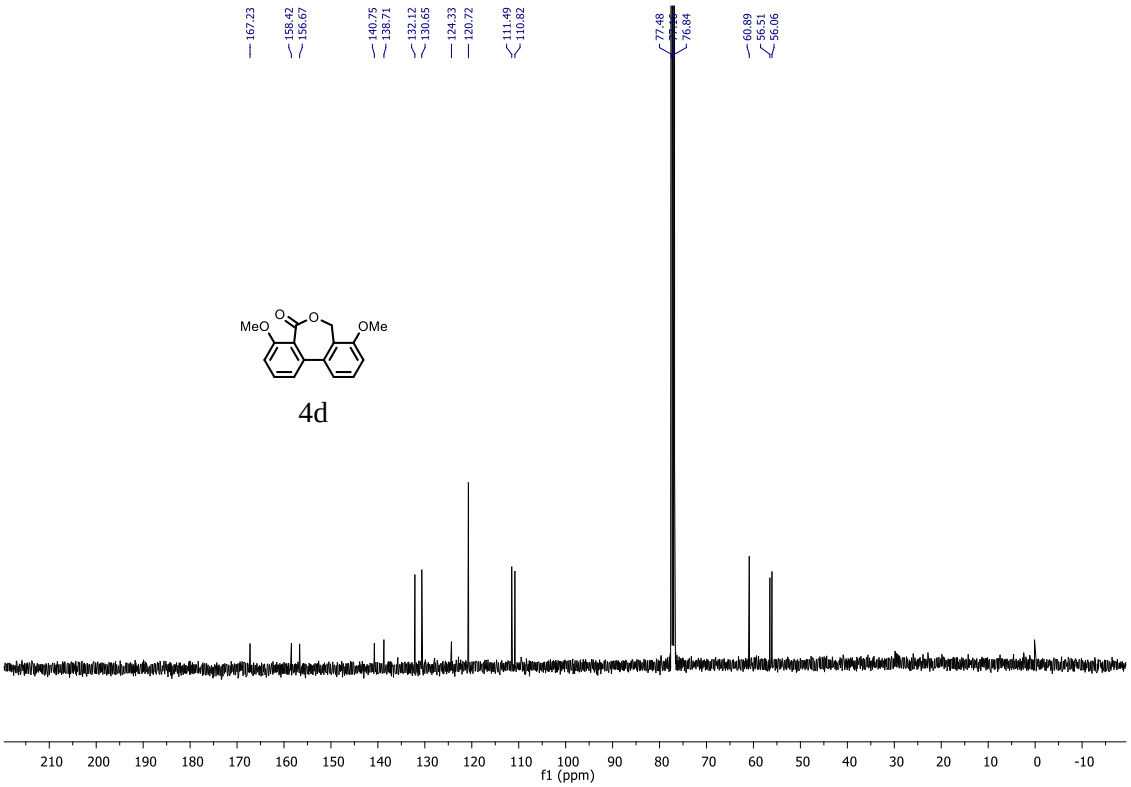
4b

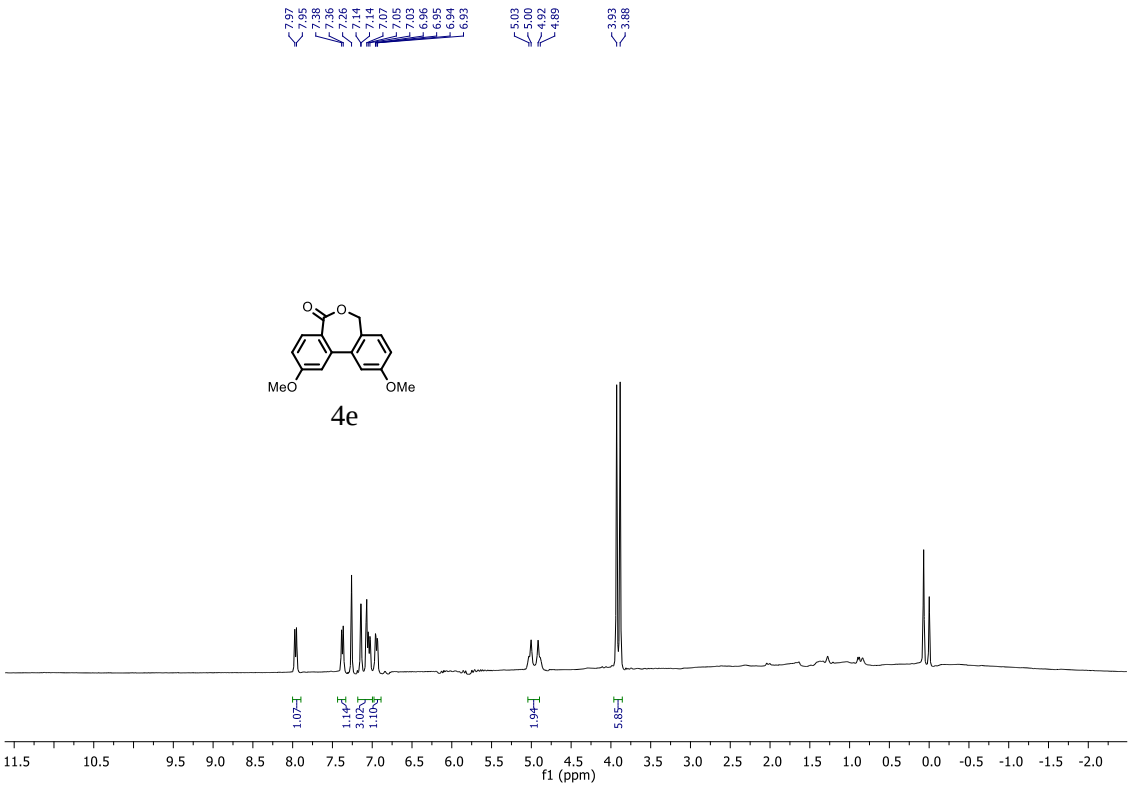
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

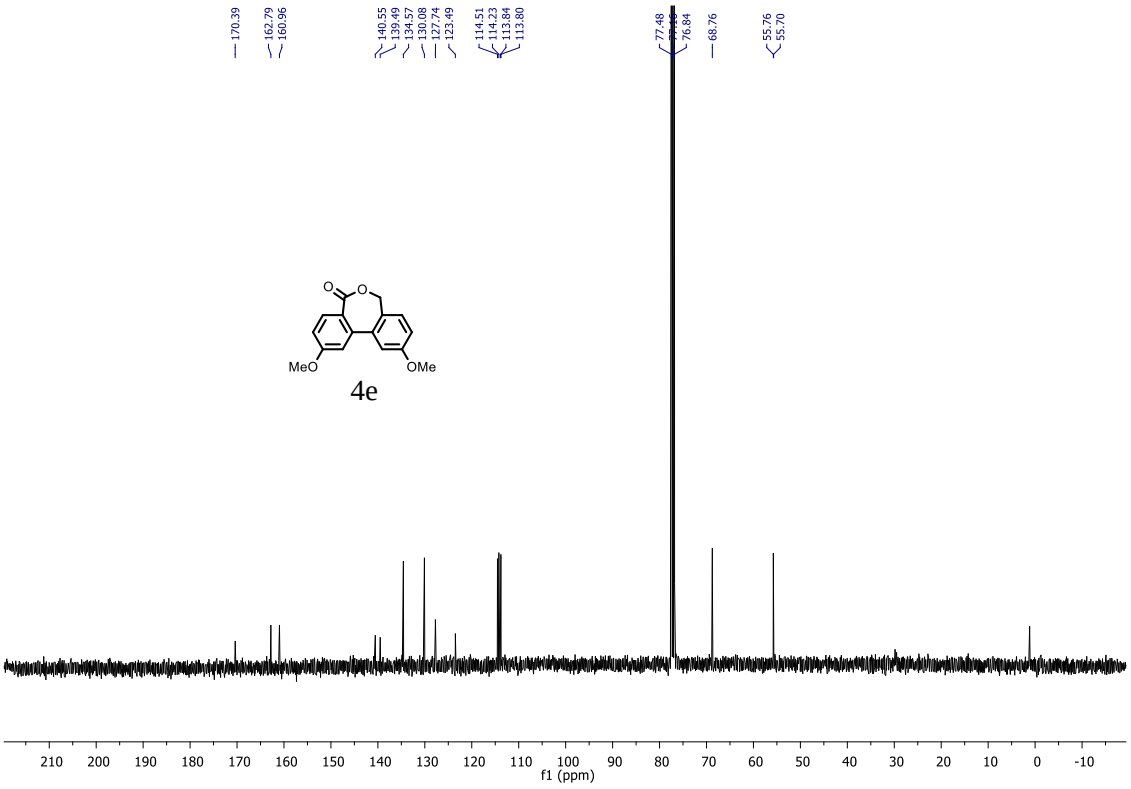

7.89
7.87
7.45
7.41
7.41
7.34
7.33
7.32
7.31
7.31
7.31
7.26
7.24
7.23
7.22
7.22
5.03
5.00
4.93
4.91
2.49
2.46
Me
O
O
Me
4c
0.95
1.96
1.96
0.94
2.00
3.04
3.05
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

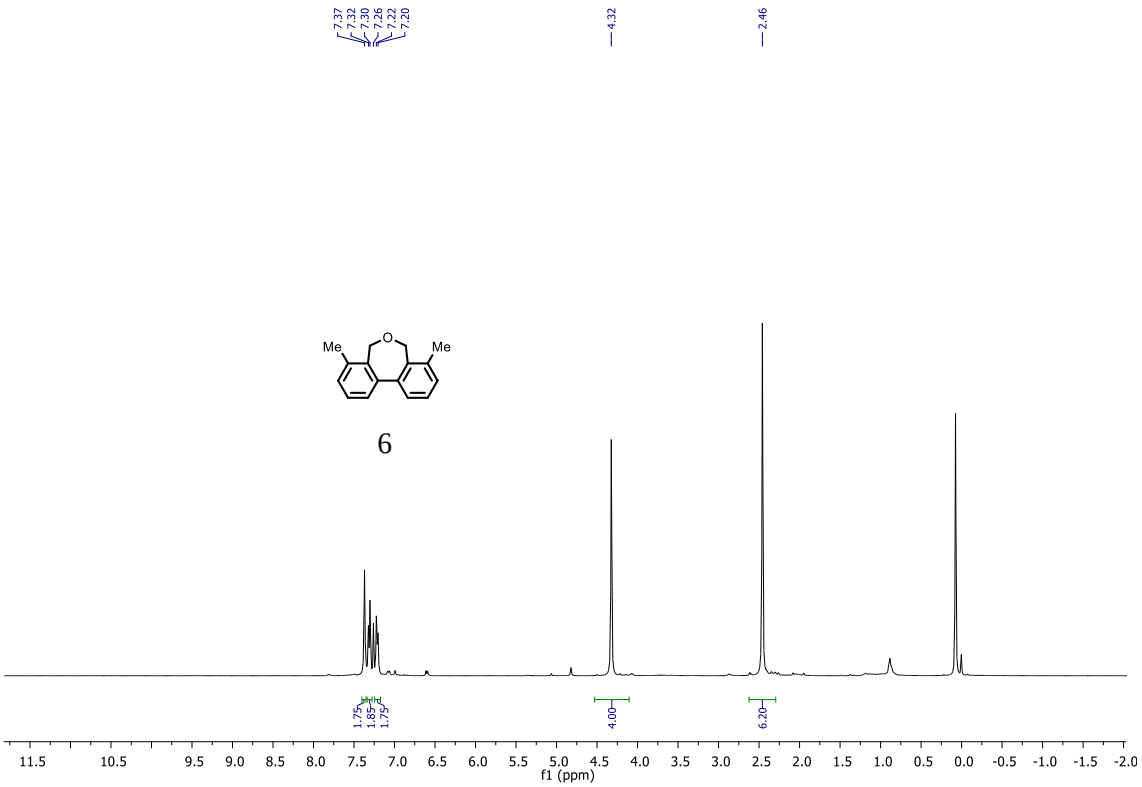

170.68
143.21
140.14
139.17
137.57
132.33
132.26
129.35
129.31
128.61
128.20
77.48
77.16
76.84
69.09
21.76
21.59
Me
O
O
Me
4c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

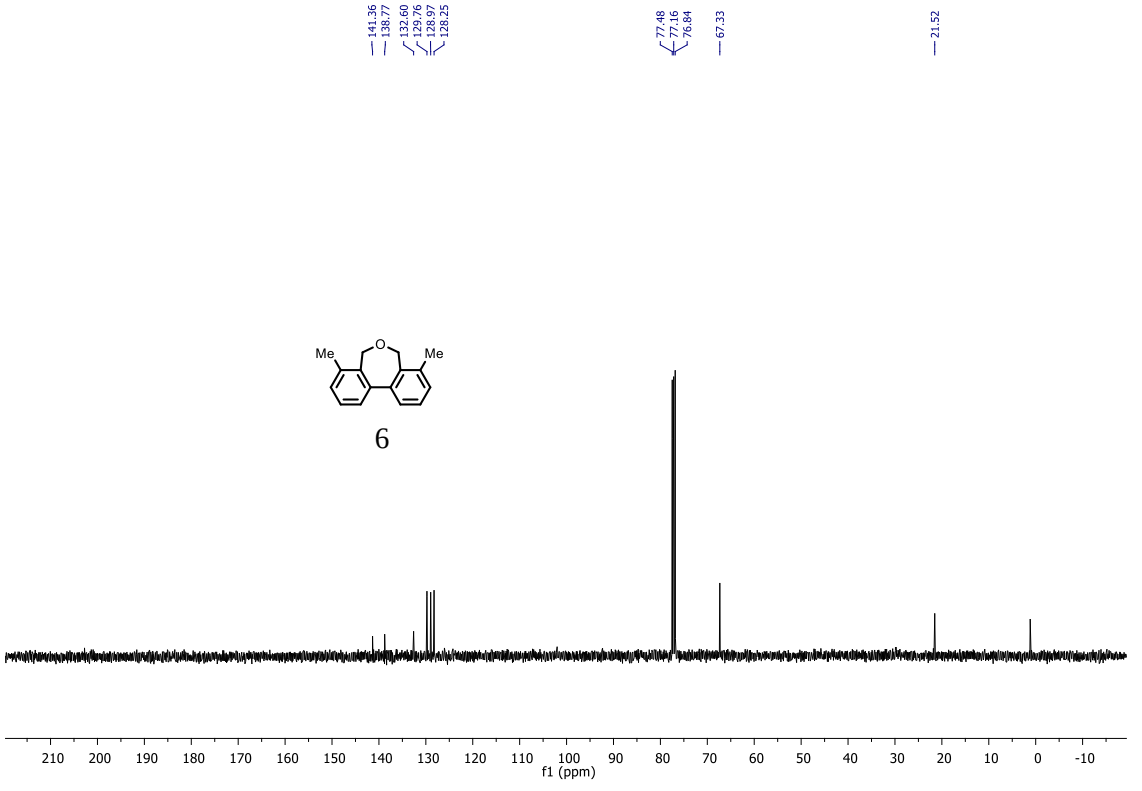

7.54
7.52
7.50
7.45
7.43
7.41
7.26
7.23
7.21
7.15
7.13
7.06
7.04
6.96
6.94
5.64
5.61
4.70
4.67
3.94
3.89
MeO
OMe
4d
1.11
1.00
1.03
1.00
1.08
1.05
0.96
1.00
3.16
3.06
f1 (ppm)


167.23
158.42
156.67
140.75
138.71
132.12
130.65
124.33
120.72
111.49
110.82
77.48
76.84
60.89
56.51
56.06
MeO
OMe
4d
f1 (ppm)

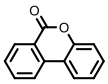

7.97
7.95
7.38
7.36
7.26
7.14
7.07
7.05
7.03
6.96
6.95
6.94
6.93
5.03
5.00
4.92
4.89
3.93
3.88
MeO
OMe
4e
1.07
1.14
3.02
1.16
1.94
5.85
f1 (ppm)


170.39
162.79
160.96
140.55
139.49
134.57
130.08
127.74
123.49
114.51
114.23
113.84
113.80
77.48
76.84
68.76
55.76
55.70
MeO
OMe
4e
f1 (ppm)


7.37
7.32
7.30
7.26
7.22
7.20
4.32
2.46
Me
O
Me
6
1.75
1.85
1.75
4.00
6.20
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
f1 (ppm)


141.36
138.77
132.60
129.76
128.97
128.25
77.48
77.16
76.84
67.33
21.52
Me
O
Me
6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.40
8.38
8.12
8.10
8.06
8.04
7.84
7.82
7.80
7.59
7.58
7.56
7.49
7.47
7.46
7.37
7.35
7.33
7.31
7.26



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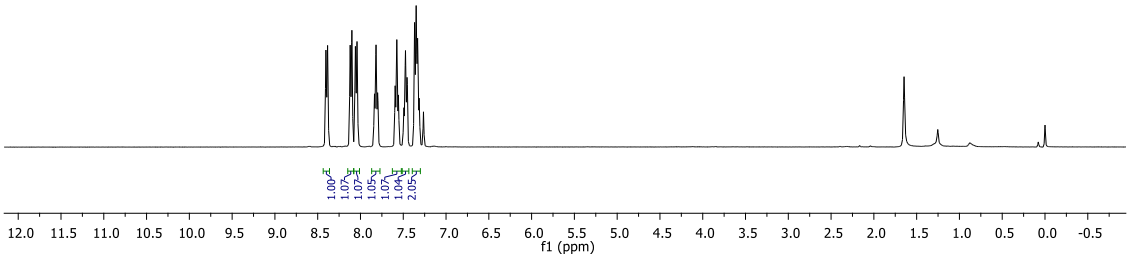
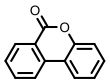
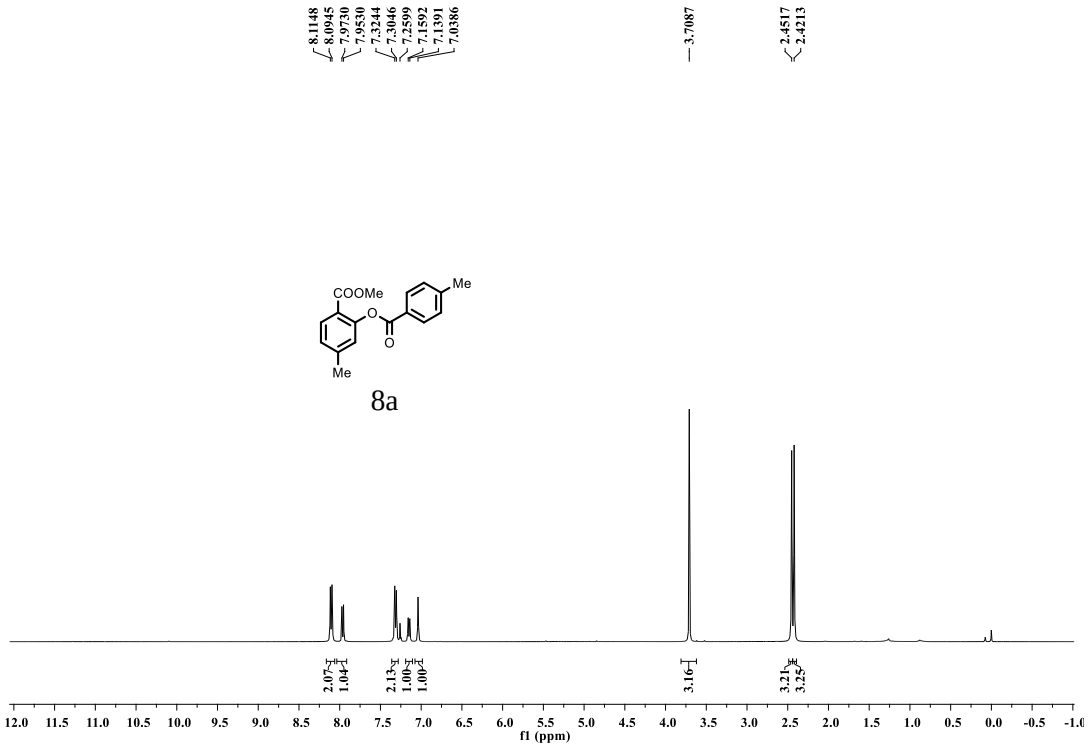

1.00
1.07
1.07
1.05
1.07
1.04
2.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


161.28
151.43
134.95
134.89
130.69
130.55
128.99
124.67
122.88
121.80
121.40
118.17
117.90
77.48
77.16
76.84



7

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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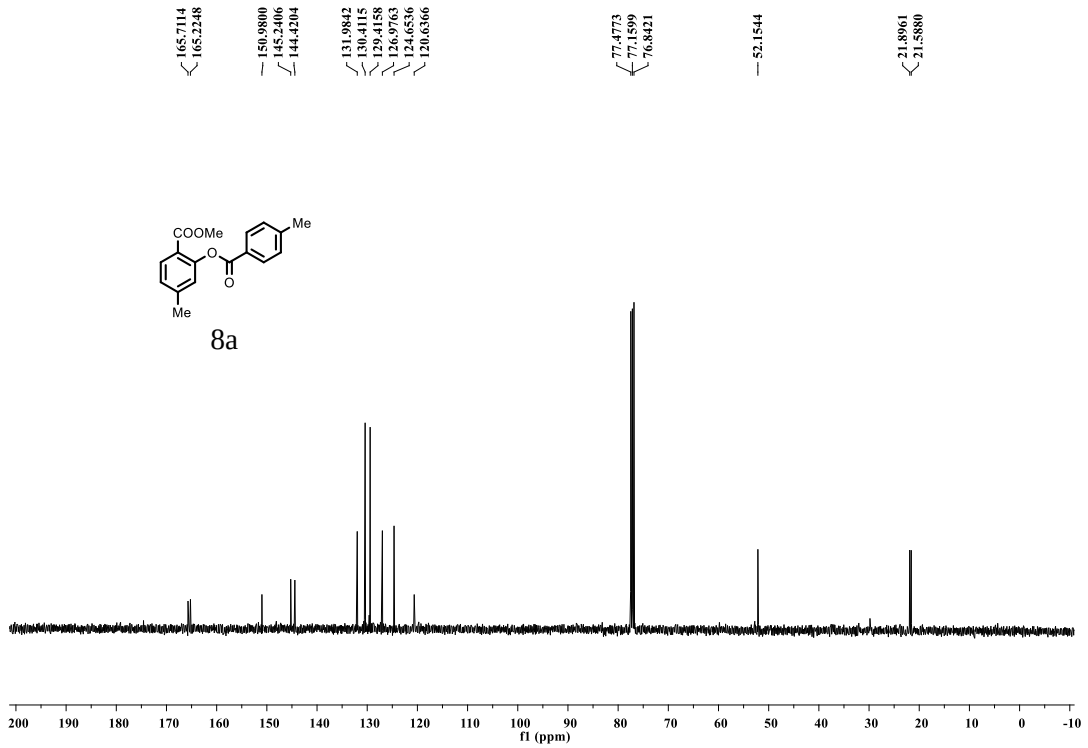
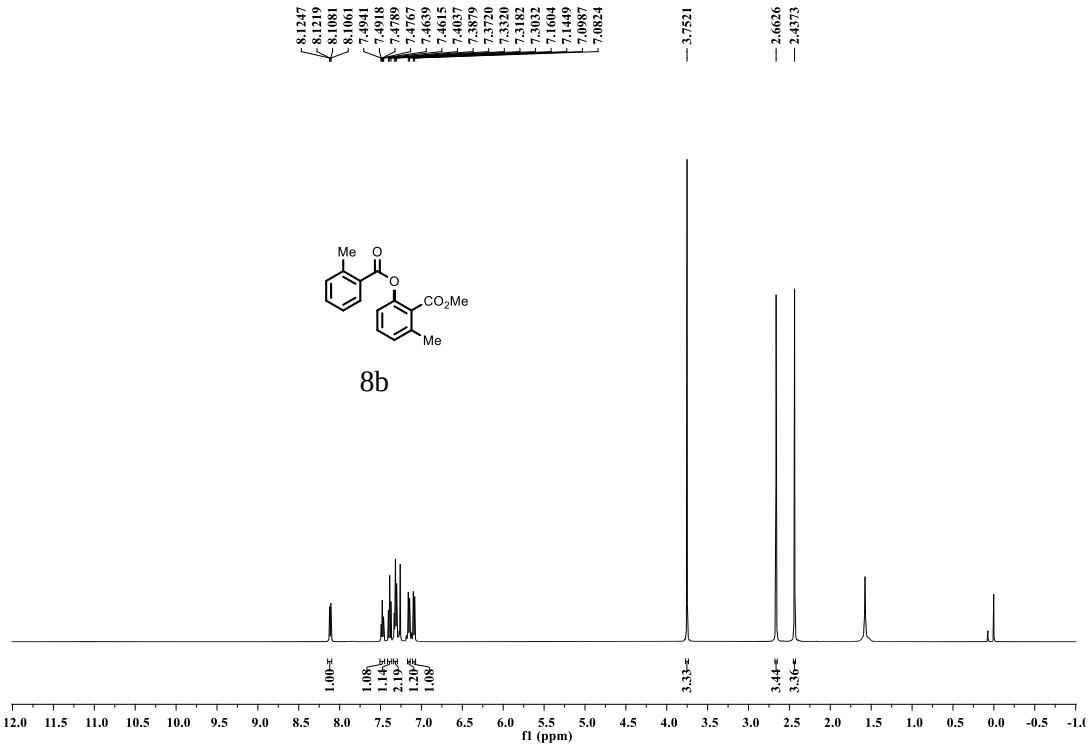
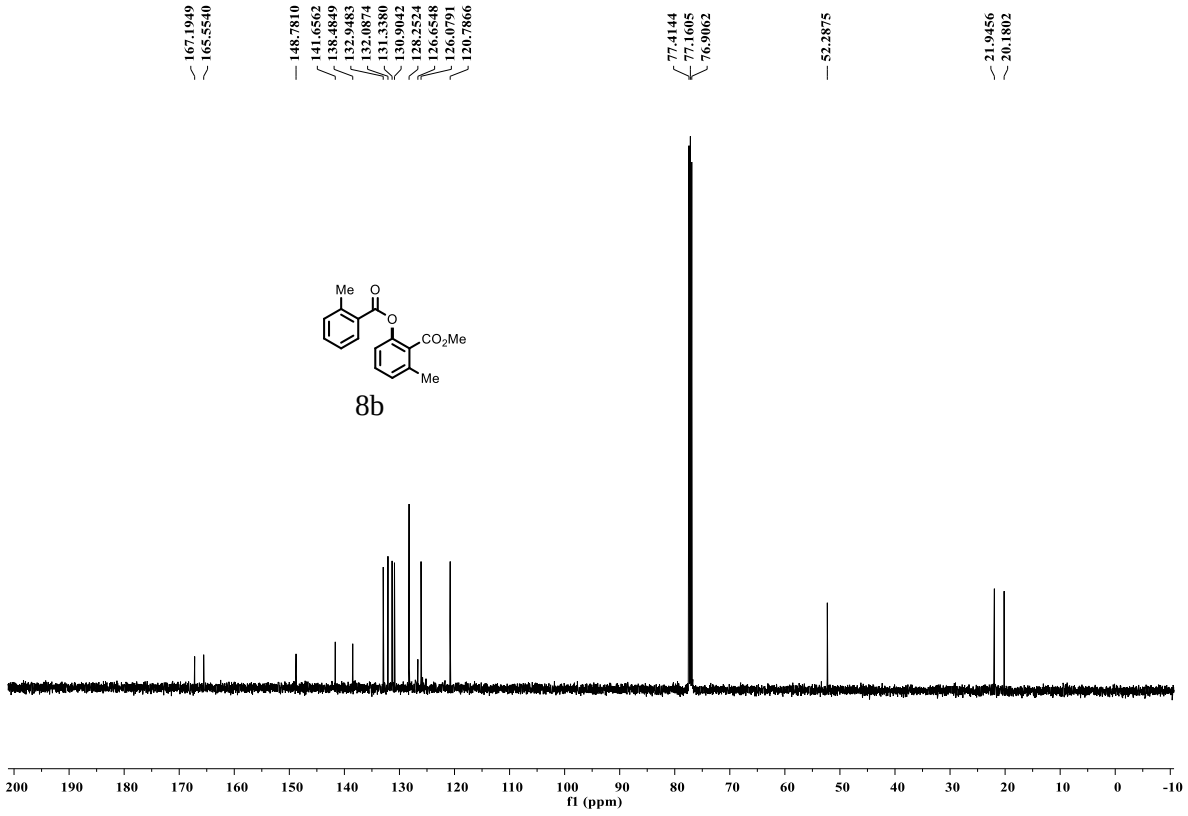
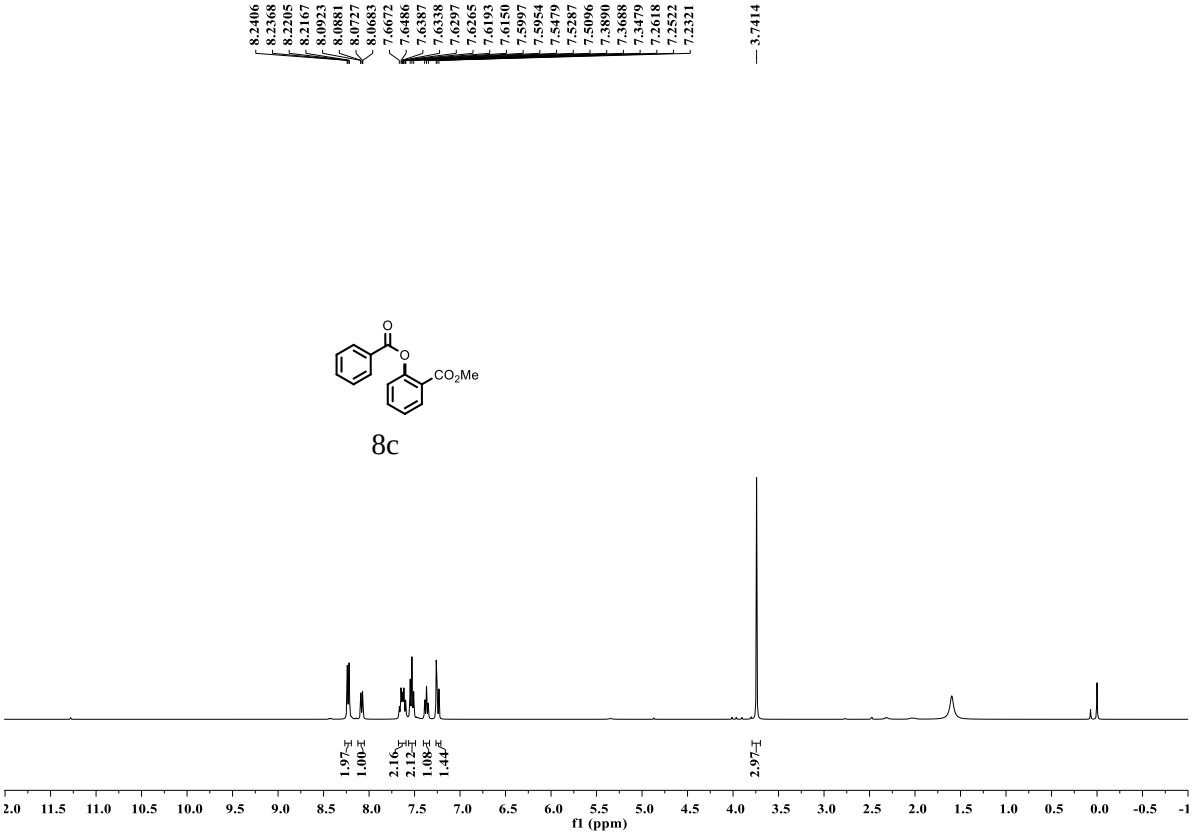
8.0945
7.9730
7.9530
7.3244
7.3046
7.2599
7.1592
7.1391
7.0386
3.7087
2.4517
2.4213
COOMe
Me
Me
8a
2.07
1.04
2.13
1.06
1.00
3.16
3.21
3.25
f1 (ppm)


165.7114
165.2248
150.9800
145.2406
144.4204
131.9842
130.4115
129.4158
126.9763
124.6536
120.6366
77.4773
77.1599
76.8421
52.1544
21.8961
21.5880
COOMe
Me
Me
8a
f1 (ppm)


8.1247
8.1219
8.1081
8.1061
7.4941
7.4918
7.4789
7.4767
7.4639
7.4615
7.4037
7.3879
7.3720
7.3320
7.3182
7.3032
7.1604
7.1449
7.0987
7.0824
3.7521
2.6626
2.4373
Me
O
O
CO2Me
Me
8b
1.00
1.08
1.14
2.19
1.20
1.08
3.33
3.44
3.36
f1 (ppm)


167.1949
165.5540
148.7810
141.6562
138.4849
132.9483
132.0874
131.3380
130.9042
128.2524
126.6548
126.0791
120.7866
77.4144
77.1605
76.9062
52.2875
21.9456
20.1802
Me
O
O
CO2Me
Me
8b
f1 (ppm)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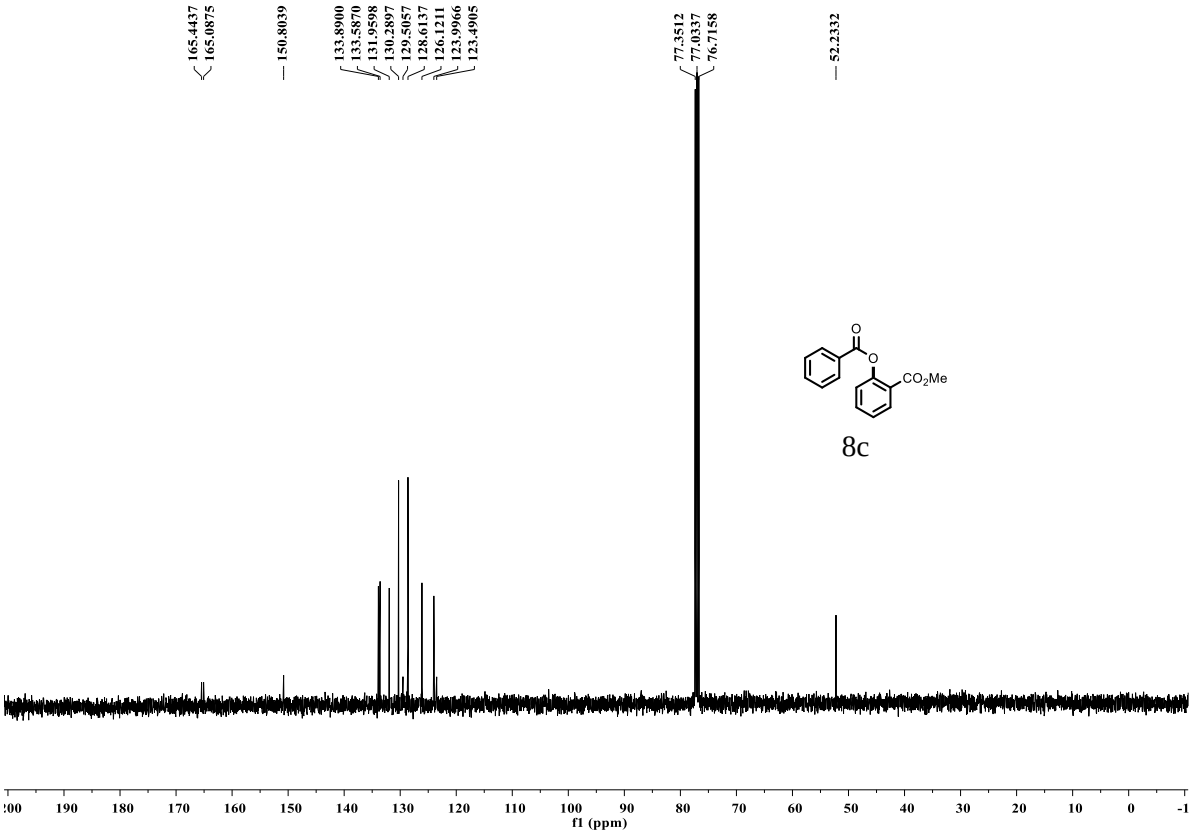
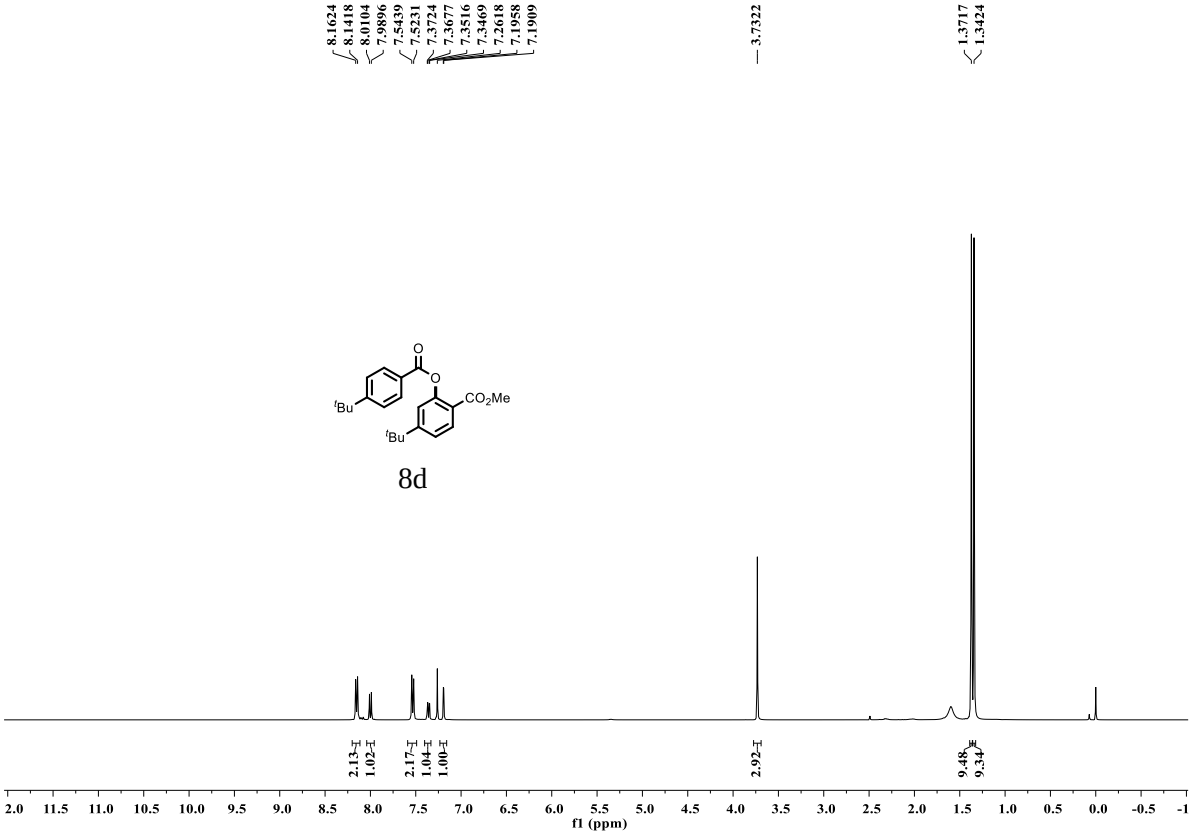
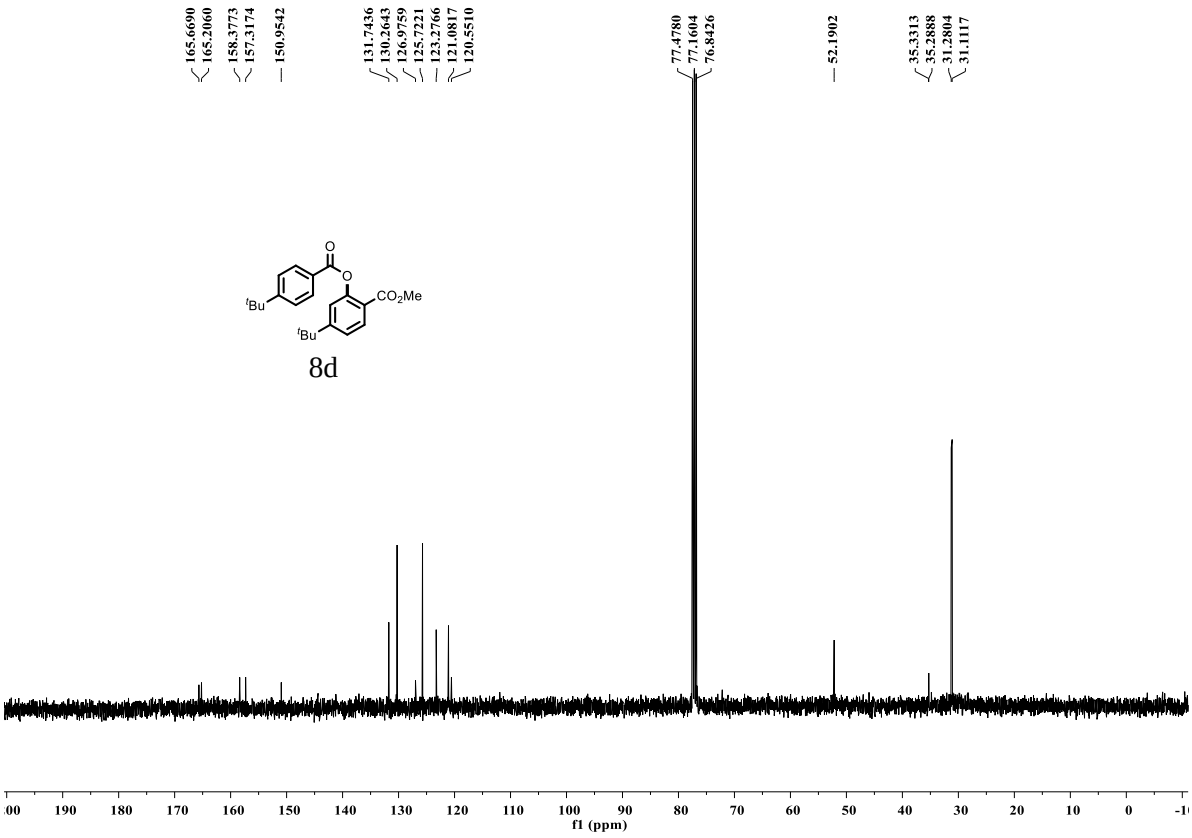
8.2368
8.2205
8.2167
8.0923
8.0881
8.0727
8.0683
7.6672
7.6486
7.6387
7.6338
7.6297
7.6265
7.6193
7.6150
7.5997
7.5954
7.5479
7.5287
7.5096
7.3890
7.3688
7.3479
7.2618
7.2522
7.2321
3.7414
CO2Me
8c
1.97
1.00
2.16
2.12
1.08
1.44
2.97
f1 (ppm)


165.4437
165.0875
150.8039
133.8900
133.5870
131.9598
130.2897
129.5057
128.6137
126.1211
123.9966
123.4905
77.3512
77.0337
76.7158
52.2332
CO2Me
8c
f1 (ppm)


8.1624
8.1418
8.0104
7.9896
7.5439
7.5231
7.3724
7.3677
7.3516
7.3469
7.2618
7.1958
7.1909
3.7322
1.3717
1.3424
O
O
CO2Me
tBu
tBu
8d
2.13
1.02
2.17
1.04
1.00
2.92
9.48
9.34
f1 (ppm)


165.6690
165.2060
158.3773
157.3174
150.9542
131.7436
130.2643
126.9759
125.7221
123.2766
121.0817
120.5510
77.4780
77.1604
76.8426
52.1902
35.3313
35.2888
31.2804
31.1117
O
O
CO2Me
tBu
tBu
8d
f1 (ppm)