Rapid Access to Carbon-Isotope Labeled Alkyl and Aryl Carboxylates Applying Palladacarboxylates

Stephanie J. Ton [†§], Anne K. Ravn[†§], Daniel Vrønning Hoffmann[†], Craig S. Day[†], Lee Kingston[‡], Charles S. Elmore[‡] and Troels Skrydstrup*[†]

[†]Carbon Dioxide Activation Center (CADIAC), The Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, Gustav Wieds Vej 14, 8000 Aarhus, Denmark

[‡]Isotope Chemistry, Early Chemical Development, Pharmaceutical Sciences, R&D, AstraZeneca Pharmaceuticals 43183 Gothenburg, Swede

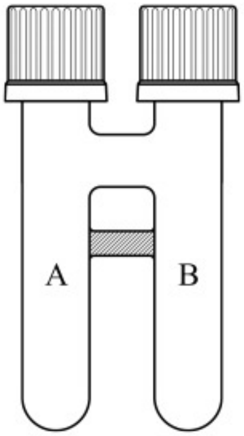
Table of Contents

General Methods

Solvents were dried according to standard procedures and degassed by bubbling with argon for a minimum of 30 minutes. Flash column chromatography was carried out utilizing Interchim puriflash system XS520Plus. NMR spectra were recorded on a Bruker 400 or 500 MHz spectrometer and chemical shifts are reported in ppm relative to solvent residual peak. Coupling patterns in the NMR spectra are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, sext = sextet, sep = septet, m = multiplet, br = broad, dd = double doublet, dt = double triplet, ddd = double double doublet. NMR spectra are reported as follows: (multiplicity; coupling constant(s) in Hz; integration). HRMS spectra were recorded on a LC TOF (ES) apparatus. All reagents were purchased commercially and used without further purification unless otherwise noted

Handling Of Carbon Monoxide

All carbonylation reactions were performed in a two-chamber system, in which gaseous CO was released in one chamber and utilized in a second chamber. The two-chamber system (COWare®) is depicted to the right and is composed of two glass vials (Chamber A and B) connected with a glass tube to allow gas-transfer. chambers can be sealed with a screw cap and a Teflon® coated silicone seal. CO-gas was released from methyldiphenylsilanecarboxylic acid (SilaCOgen) in a fluoride catalyzed decarbonylation with potassium fluoride in DMF at rt. Precise conditions are given in the general procedures.



WARNING: Glassware under pressure!

- Glass equipment should always be examined for damages to its surface, which may weaken its strength.
- One must abide to all laboratory safety procedures and always work behind a shield when working with glass equipment under pressure.
- COware is pressure tested to 224 psi, but should under no circumstances be operated above 60 psi (5 bar).

X-ray Crystallography Data

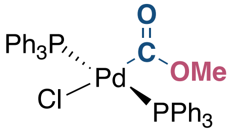
Crystallographic single crystal X-ray data were collected on XtaLAB Synergy S with a Photon-Jet sealed tube (Mo K-alpha radiation: lambda = 0.71073 Å). Absorption correction was done with SADABS. Cell refinement and data reduction were done in SAINT-plus. The structures were solved and refined with SHELXT and SHELXL, respectively, in Olex2.

Compound Pd-1

Item	**Value**
Molecular formula	$C_{38}H_{33}ClO_2P_2Pd$
Formula weight	725.43
Color of crystal	yellow
Crystal system	monoclinic
Space Group	P 2 1/n
a (Å)	12.0937(2)
b (Å)	22.8437(3)
c (Å)	12.7287(2)
α (°)	90
β (°)	113.675(2)
γ (°)	90
Volume (Å3)	3220.45 (10)
Z	4
T (K)	105
ρ (g cm-1)	1.496
λ (Å)	0.71073
µ (mm-1)	0.792
# measured refl	51822
# unique refl	9566
Rint	0.0336
# parameters	436
R(F2), all refl	0.0301
RW(F2), all refl	0.0617
Goodness of fit	1.051

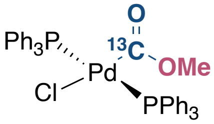
Synthesis of Palladium Complexes

***trans*-Chloro(methoxycarbonyl)bis(triphenylphosphine)palladium(II) (Pd-1)**



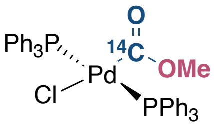
In a glove box under argon atmosphere to **chamber A** (volume = 30 mL) of a two-chamber system was added $Pd(PPh_3)_4$ (0.5 mmol, 578 mg, 1 equiv), LiCl (0.55 mmol, 1.1 equiv), triethylamine (1 mmol, 2 equiv), MeOH (1 mL) and THF (12 mL). To **chamber B** (volume = 10 mL) of the two-chamber system was added SilaCOgen (0.75 mmol, 1.5 equiv) and KF (0.75 mmol, 1.5 equiv). The reaction was removed from the glovebox and the reaction vessel was sparged with a balloon of O_2 for approximately 10 seconds. To Chamber B was added DMF (1 mL) and the chamber was quickly sealed. The entire two-chamber was allowed to stir at room temperature for 24 hours. After 24 h the reaction vessel was placed in the refrigerator to induce precipitation of the product. The white precipitate was collected by filtration, washed with MeOH (1 mL), pentane (3 x 1 mL) and dried overnight in vacuo affording Pd-1 as a white solid (347 mg, 96%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (dtd, *J* = 7.6, 5.6, 1.6 Hz, 12H), 7.48 – 7.31 (m, 18H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 184.74, 134.86 (t, *J* = 6.5 Hz), 131.61 (t, *J* = 23.1 Hz), 130.50, 128.34 (t, *J* = 5.2 Hz), 52.30. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.49. **HRMS** (ESI+) Calc. for $C_{36}H_{31}ClP_2Pd^+$; 666.0624, found 666.0575

***trans*-Chloro(methoxycarbonyl)bis(triphenylphosphine)palladium(II) (^{13}C Pd-1)**



Synthesized as above using ^{13}C-labelled SilaCOgen (0.75 mmol, 1.5 equiv) in place of unlabeled material. The product was obtained as a white solid (330 mg, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.66 (m, 12H), 7.50 – 7.31 (m, 18H), 2.39 (d, *J* = 4.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 184.74 (13C enriched), 134.86 (t, *J* = 6.6 Hz), 131.60 (t, *J* = 23.1 Hz), 130.50, 128.34 (t, *J* = 5.2 Hz), 52.30 (d, *J* = 4.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.48. **HRMS** (ESI+) Calc. for $C_{36}H_{31}ClP_2Pd^+$; 666.0624, found 666.0544

***trans*-Chloro(methoxycarbonyl)bis(triphenylphosphine)palladium(II) (^{14}C Pd-1)**



In a slight modification of the above procedure for the synthesis of **Pd-1,** to **chamber A** (volume = 30 mL) of a two-chamber system was added Pd(PPh$_3$)$_4$ (0.5 mmol, 578 mg, 1 equiv), LiCl (0.55 mmol, 1.1 equiv), triethylamine (1 mmol, 2 equiv), MeOH (1 mL) and THF (12 mL) under a flow of N$_2$. To **chamber B** (volume = 10 mL) of the two-chamber system was added Pd(dba)$_2$ (86 mg, 0.15 mmol) and tri-tert-butylphosphonium tetrafluoroborate (43.5 mg, 0.15 mmol), N,N-diisopropylethylamine (0.262 mL, 1.5 mmol). Seperately a stock solution of 9-methyl-9H-fluorene-9-carbonyl-14C chloride (^{14}C-Cogen) (221 MBq, 10% 9-methyl-9H-fluorene-9-carbonyl-14C chloride, diluted with unlabelled 9-methyl-9H-fluorene-9-carbonyl-chloride (367 mg, 1.5 mmol) in dioxane (1 mL) was prepared and added to the CO releasing chamber (Chamber B). Chamber B was then heated to 70 °C for 1 h in order to pre-release CO. After 1 h the reaction vessel was cooled to room temperature and a balloon of O$_2$ was added. The entire two-chamber was allowed to stir at room temperature for 24 hours. After 24 h the reaction vessel was placed in the refrigerator to induce precipitation of the product. The white precipitate was collected by filtration, washed with MeOH (1 mL), pentane (3 x 1 mL) and dried overnight in vacuo affording ^{14}C Pd-1 as a white solid (336 mg, 92%). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.85 – 7.67 (m, 12H), 7.47 – 7.30 (m, 18H), 2.39 (s, 3H). **13C NMR** (126 MHz, CDCl$_3$) δ 184.65, 134.90 (t, J = 6.5 Hz), 131.70 (t, J = 23.0 Hz), 130.50, 128.35 (t, J = 5.2 Hz), 52.26. **^{31}P NMR** (202 MHz, CDCl$_3$) δ 18.49. **Specific activity**: 158.4 GBq/mol. **Radioactivity:** 67 MBq.

General Procedures for the Synthesis of Methyl Ester Products

General Procedure A: Synthesis of Aryl Esters from Boronic Acid Derivatives

In a glove box under argon atmosphere to a 8 mL vial was added Pd-1 (0.1 mmol, 73 mg, 1 equiv.), ArB(OR)$_2$ (0.1 mmol, 1 equiv.), KF (0.1 mmol, 6 mg, 1 equiv.), Na_2CO_3 (0.2 mmol, 21 mg, 2 equiv.), dioxane (5.4 mL) and H_2O (0.6 mL). The vial was sealed, wrapped with parafilm and allowed to stir outside the glovebox overnight. After 16 hours, the reaction mixture was concentrated in vacuo onto celite and purified by flash column chromatography or concentrated, redissolved in DMSO (4 mL), and purified by high performance liquid chromatography (HPLC).

General Procedure B: Synthesis of ^{13}C Labelled Aryl Esters from Boronic Acid Derivatives

In a glove box under argon atmosphere to a 8 mL vial was added ^{13}C Pd-1 (0.1 mmol, 73 mg, 1 equiv.), ArB(OR)$_2$ (0.1 mmol, 1 equiv.), KF (0.1 mmol, 6 mg, 1 equiv.), Na_2CO_3 (0.2 mmol, 21 mg, 2 equiv.), dioxane (5.4 mL) and H_2O (0.6 mL). The vial was sealed, wrapped with parafilm and allowed to stir outside the glovebox overnight. After 16 hours, the reaction mixture was concentrated in vacuo onto celite and purified by flash column chromatography or concentrated, redissolved in DMSO (4 mL), and purified by HPLC.

General Procedure C: Synthesis of ^{14}C Labelled Aryl Esters from Boronic Acid Derivatives

To a 8 mL vial was added **^{14}C Pd-1** (0.1 mmol, 73 mg, 1 equiv.), ArB(OR)$_2$ (0.1 mmol, 1 equiv.), KF (0.1 mmol, 6 mg, 1 equiv.), Na_2CO_3 (0.2 mmol, 21 mg, 2 equiv.), dioxane (5.4 mL) and H_2O (0.6 mL). The solution was sparged with N_2 for 5 min, and then the vial was sealed, wrapped with parafilm, and allowed to stir overnight. After 16 hours, the reaction mixture was concentrated, redissolved in DMSO (4 mL), and purified by HPLC. The Radiochemical purity of the products was determined by Radio-HPLC.

Radio-HPLC setup: Waters Acquity UPLC with Waters Xbridge C18 3.5 µm, 4.6 × 100 mm column was used along with a Perkin-Elmer TRI-CARB 2500 liquid scintillation analyzer with Ultima Gold cocktail. A gradient method was used for radiochemical purity determination with mobile phase A (10 mM NH4HCO3 buffered with NH4OH) and mobile phase B (MeCN) with gradient elution (5% for 0–3 min, then ramp to 95% over 22 min and hold at 95% for 5 min).

General Procedure D: Synthesis of Aliphatic or Alkenyl Esters from Alkyl-9BBN Derivatives

In a glove box under argon atmosphere to a 4 mL vial was added 9-borabicyclo[3.3.1]nonane dimer (18 mg, 0.75 equiv) and the alkene or alkyne (1.6 equiv) in dioxane (2 mL). The vial was sealed and heated to 60 °C for 2 h under stirring. The alkyl-9BBN or alkenyl-9BBN solution was then added to an 8 mL vial containing **Pd-1** (0.1 mmol, 73 mg), KF (0.1 mmol, 6 mg), Na_2CO_3 (0.2 mmol, 21 mg). Lastly, dioxane (3.4 mL) and H_2O (0.6 mL) was added. The vial was sealed, wrapped with parafilm and allowed to stir vigorously outside the glovebox overnight. After 16 hours, the reaction mixture was concentrated onto silica and purified by flash column chromatography.

General Procedure E: Synthesis of ^{13}C Labelled Aliphatic or Alkenyl Esters Esters from Alkyl-9bbn Derivatives

In a glove box under argon atmosphere to a 4 mL vial was added 9-borabicyclo[3.3.1]nonane dimer (18 mg, 0.75 equiv) and the alkene or alkyne (1.6 equiv) in dioxane (2 mL). The vial was sealed and heated to 60 °C for 2 h under stirring. The alkyl-9BBN or alkenyl-9BBN solution was then added to an 8 mL vial containing **^{13}C Pd-1** (0.1 mmol, 73 mg), KF (0.1 mmol, 6 mg), Na_2CO_3 (0.2 mmol, 21 mg). Lastly, dioxane (3.4 mL) and H_2O (0.6 mL) was added. The vial was sealed, wrapped with parafilm and allowed to stir vigorously outside the glovebox overnight. After 16 hours, the reaction mixture was concentrated onto silica and purified by flash column chromatography.

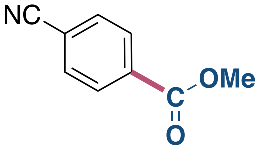
General Procedure F: Synthesis of ^{12}C or ^{13}C Labelled Aryl Esters from Aryl Carboxylic Acids

In a glove box under argon atmosphere to a 10 mL vial with a Teflon sealed screw cap was added the aryl carboxylic acid (0.1 mmol, 1.0 equiv), TFFH (1.0 equiv), and proton sponge (1.0 equiv). THF (0.2 mL) was added and the reaction allowed to stir for 20 min at room temperature to form the aryl acid fluoride. In a separate 4 mL vial, a standard solution of $Ni(cod)_2$ (6 mg) and PCy_3 (12 mg) in THF (0.2 mL) was prepared. After formation of the acyl fluoride, the Ni-catalyst was added from the standard solution (0.1 mL, 5 mol%) and, subsequently, B_2nep_2 (2 equiv) was added to the reactor vial. The reaction was sealed, transferred out of the glovebox and into a pre-heated block at 115 °C to stir for 24 h. The reaction was then allowed to cool to room temperature before being filtered through a silica plug using CH_2Cl_2 as the eluent. The filtrate was concentrated in an 8 mL vial and transferred back into the glovebox. To this vial was added **Pd-1** or **^{13}C Pd-1** (0.1 mmol, 73 mg), KF (0.1 mmol, 6 mg), Na_2CO_3 (0.2 mmol, 21 mg), dioxane (5.4 mL), and H_2O (0.6

mL). The vial was sealed, wrapped with parafilm, and allowed to stir outside the glovebox overnight. After 16 hours, the reaction mixture was concentrated onto silica and purified by flash column chromatography.

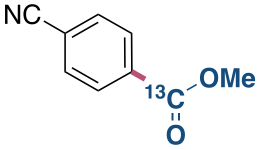
Synthesis and Characterization of Methyl Ester Products (1-24, Table 2)

Methyl 4-cyanobenzoate (1)



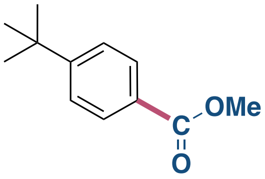
The title compound was prepared according to General Procedure A, employing 4-cyano-phenylboronic acid (0.1 mmol). Flash column chromatography (EtOAc 0-2% in heptane) yielded the product as a colourless solid (13.2 mg, 82%). **^{1}H NMR (**400 MHz, CDCl$_3$) δ 8.14 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 3.96 (s, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 165.59, 134.07, 132.38, 130.25, 118.12, 116.56, 52.89. **HRMS** (ESI+) calc. for $C_9H_9NO_2$ [M+H]$^+$ 162.0550, found 162.0548.

Methyl 4-cyanobenzoate (^{13}C-1)



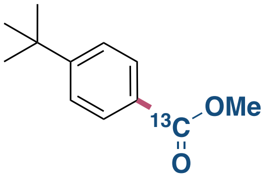
The title compound was prepared according to General Procedure B, employing 4-cyano-phenylboronic acid (0.1 mmol). Flash column chromatography (EtOAc 0-2% in heptane) yielded the product as a colourless solid (13.0 mg, 80%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.31 – 7.97 (m, 2H), 7.75 (dt, J = 7.9, 0.9 Hz, 2H), 3.96 (d, J = 3.8 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 165.58 (^{13}C enriched), 134.06 (d, J = 74.8 Hz), 130.26, 130.23, 118.11, 116.56, 52.88 (d, J = 2.3 Hz). **HRMS** (ESI+) calc. for $C_8{}^{13}CH_9NO_2$ [M+H]$^+$ 163.0584, found 163.0583.

Methyl 4-tert-butylbenzoate (2)



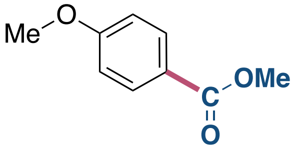
The title compound was prepared according to General Procedure A, employing 4-tert-butylphenylboronic acid (0.1 mmol). Flash column chromatography (EtOAc 0-2% in heptane) yielded the product as a colourless oil (17.0 mg 88%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.49 – 7.39 (m, 2H), 3.90 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.32, 156.70, 129.59, 127.52, 125.48, 52.10, 35.23, 31.27. **HRMS** (ESI+) calc. for $C_{12}H_{17}O_2$ $[M+H]^+$ 193.1223, found 193.1227.

Methyl 4-tert-butylbenzoate (^{13}C-2)



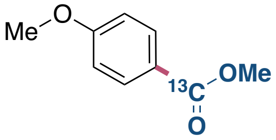
The title compound was prepared according to General Procedure B, employing 4-tert-butylphenylboronic acid (0.1 mmol). Flash column chromatography (EtOAc 0-2% in heptane) yielded the product as a colourless oil (17.2 mg, 89%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 – 7.86 (m, 2H), 7.57 – 7.34 (m, 2H), 3.90 (d, J = 3.8 Hz, 3H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.31 (^{13}C enriched), 156.69, 129.58 (d, *J* = 2.8 Hz), 127.50 (d, *J* = 75.5 Hz), 125.48 (d, J = 4.9 Hz), 52.11, 52.09, 35.22, 31.26. **HRMS** (ESI+) calc. for $C_{11}{}^{13}CH_{17}O_2$ $[M+H]^+$ 194.1257, found 194.1258.

Methyl 4-methoxybenzoate (3)



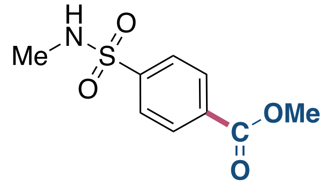
The title compound was prepared according to General Procedure A, 4-methoxyphenylboronic acid (0.1 mmol). Flash column chromatography (EtOAc 0-5% in heptane) yielded the product as a colourless solid (15.3 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 9.0 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.03, 163.46, 131.74, 122.75, 113.74, 55.57, 52.02. **HRMS** (ESI+) calc. for $C_9H_{11}O_3{}^+$ $[M+H]^+$ 167.0703, found 167.0703.

Methyl 4-methoxybenzoate (^{13}C-3)



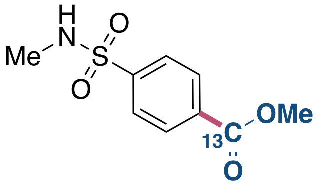
The title compound was prepared according to General Procedure B, 4-methoxyphenylboronic acid (0.1 mmol). Flash column chromatography (EtOAc 0-5% in heptane) yielded the product as a colourless solid (15.3 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 8.9, 3.8 Hz, 2H), 7.01 – 6.82 (m, 2H), 3.88 (d, J = 3.8 Hz, 3H), 3.86 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.02 (^{13}C enriched), 163.46, 131.73 (d, *J* = 2.9 Hz)., 122.73 (d, *J* = 77.1 Hz), 131.73 (d, J = 2.9 Hz), 55.56, 52.00 (d, J = 2.3 Hz). **HRMS** (ESI+) calc. for $C_8{}^{13}CH_{11}O_3{}^+$ $[M+H]^+$ 168.0737, found 168.0737.

Methyl 4-(N-methylsulfamoyl)benzoate (4)



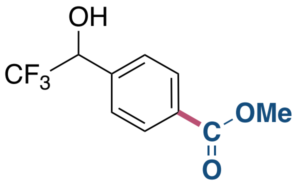
The title compound was prepared according to General Procedure A, employing (4-(N-methylsulfamoyl)phenyl)boronic acid (0.1 mmol). Preparatory HPLC (20–85% MeCN in H_2O/0.2% NH_3 over 22 min, wavelength of 220 nm, 15 mL/min) yielded the product as a white solid (20 mg, 87%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (d, J = 8.8 Hz, 2H), 7.93 (d, J = 8.8 Hz, 2H), 4.52 (s, 1H), 3.96 (s, 3H), 2.69 (d, J = 5.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.78, 142.97, 134.05, 130.50, 127.37, 52.83, 29.49. **HRMS** (ESI+) calc. for $C_9H_{12}NO_4S^+$ $[M+H]^+$ 230.0482, found 230.0485.

Methyl 4-(N-methylsulfamoyl)benzoate (^{13}C-4)



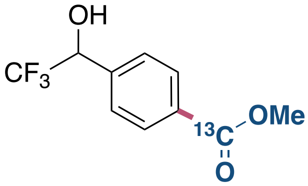
The title compound was prepared according to General Procedure B, employing (4-(N-methylsulfamoyl)phenyl)boronic acid (0.1 mmol). Preparatory HPLC (20–85% MeCN in H_2O/0.2% NH_3 over 22 min, wavelength of 220 nm, 15 mL/min) yielded the product as a white solid (21 mg, 91%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.5, 4.1 Hz, 2H), 7.93 (d, J = 7.9 Hz, 2H), 4.68 (dd, J = 5.5, 2.1 Hz, 1H), 3.96 (d, J = 3.8 Hz, 3H), 2.68 (d, J = 5.3 Hz, 3H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 165.79 (^{13}C enriched), 142.95, (d, J = 74.8 Hz), 134.02 (d, J = 74.8 Hz), 130.49 (d, J = 2.6 Hz), 127.36 (d, J = 4.8 Hz), 52.82 (d, J = 2.5 Hz), 29.46. $C_8{}^{13}CH_{12}NO_4S^+$ $[M+H]^+$ 231.0517, found 231.0504.

Methyl 4-(trifluoro-1-ethanol)benzoate (5)



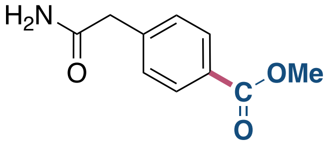
The title compound was prepared according to General Procedure A, employing 2,2,2-trifluoro-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol (0.1 mmol). Flash column chromatography (EtOAc 0-40% in heptane) yielded the product as a white crystalline solid (14 mg 60%). ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H), 5.11 (q, J = 6.6 Hz, 1H), 3.93 (s, 3H), 2.75 (s, 1H).^{19}**F NMR** (470 MHz, $CDCl_3$) δ -78.25. ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 166.73, 138.69, 131.37, 127.53 – 122.47 (m), 125.25, 123.01, 72.55 (q, *J* = 32.1 Hz), 52.45. **HRMS** (ESI+) calc. for $C_{10}H_{10}F_3O_3^+$ $[M+H]^+$ 235.0577, found 235.0580.

Methyl 4-(trifluoro-1-ethanol)benzoate (^{13}C-5)



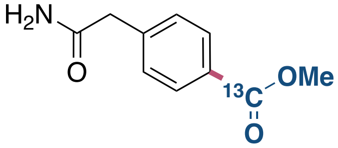
The title compound was prepared according to General Procedure B, employing 2,2,2-trifluoro-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol (0.1 mmol). Flash column chromatography (EtOAc 0-40% in heptane) yielded the product as a white crystalline solid (12 mg, 51%). ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.08 (dd, J = 8.4, 4.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 5.10 (q, J = 6.6 Hz, 1H), 3.93 (d, J = 3.8 Hz, 3H), 2.84 (s, 1H).^{19}**F NMR** (470 MHz, $CDCl_3$) δ -78.21. ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 166.73 (^{13}C enriched), 138.69, 131.37, 129.94 (d, *J* = 2.6 Hz), 127.63 (d, *J* = 4.5 Hz), 125.25, 123.01, 72.55 (q, J = 32.1), 52.45. **HRMS** (ESI+) calc. for $C_9{}^{13}CH_{10}F_3O_3^+$ $[M+H]^+$ 236.0610, found 236.0611.

Methyl 4-(2-amino-2-oxoethyl)benzoate (6)



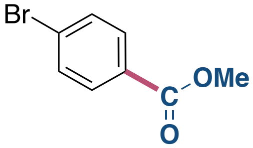
The title compound was prepared according to General Procedure A, employing (2- (4-(2-amino-2-oxoethyl)phenyl)boronic acid (0.1 mmol). Preparatory HPLC (20–85% MeCN in H_2O/0.2% NH_3 over 22 min, wavelength of 220 nm, 15 mL/min) yielded the product as a white solid (16 mg, 83%). Minimally soluble in $CDCl_3$. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 5.72 – 4.97 (m, 2H), 3.92 (s, 3H), 3.65 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.30, 166.85, 139.96, 130.43, 129.57, 129.53, 52.36, 43.27. **HRMS** (ESI+) calc. for $C_{10}H_{12}NO_3^+$ $[M+H]^+$ 194.0812, found 194.0814.

Methyl 4-(2-amino-2-oxoethyl)benzoate (^{13}C-6)



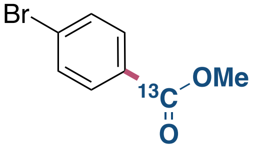
The title compound was prepared according to General Procedure B, employing (2-(4-(2-amino-2-oxoethyl)phenyl)boronic acid (0.1 mmol). Preparatory HPLC (20–85% MeCN in H_2O/0.2% NH_3 over 22 min, wavelength of 220 nm, 15 mL/min) yielded the product as a white solid (14 mg, 73%). Minimally soluble in $CDCl_3$. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.3, 4.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 5.60 – 5.21 (m, 2H), 3.92 (d, J = 3.8 Hz, 3H), 3.65 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.32, 166.86 (^{13}C enriched), 139.96, 130.43 (d, J = 2.6 Hz), 129.57 (d, J = 4.6 Hz), 129.52 (d, J = 75.4 Hz), 52.36 (d, J = 2.6 Hz), 43.27. **HRMS** (ESI+) calc. for $C_9{}^{13}CH_{12}NO_3^+$ $[M+H]^+$ 195.0846, found 195.0845.

Methyl 4-bromobenzoate (7)



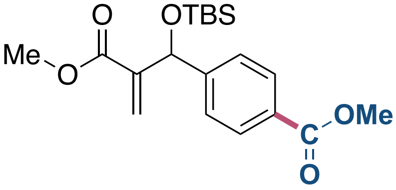
The title compound was prepared according to General Procedure A, employing 4-bromo-phenylboronic acid (0.1 mmol) with the addition of $PhIOAc_2$ (0.15 mmol, 1.5 equiv.) as an oxidant. Flash column chromatography (EtOAc 1-5% in heptane) yielded the product as a colourless solid (14.9 mg, 69%). **^{1}H NMR (**400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 3.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 131.8, 131.2, 129.2, 128.2, 52.4. **HRMS** (ESI+) calc. for $C_8H_7BrO_2$ $[M+H]^+$ 214.9702, found 214.9697.

Methyl 4-bromobenzoate (^{13}C-7)



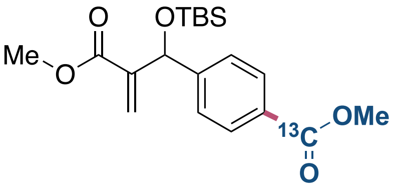
The title compound was prepared according to General Procedure B, employing 4-bromo-phenylboronic acid (0.1 mmol) with the addition of PhIOAc$_2$ (0.15 mmol, 1.5 equiv.) as an oxidant. Flash column chromatography (EtOAc 1-5% in heptane) yielded the product as a colourless solid (14.4 mg, 67%) with the addition of PhIOAc$_2$ (0.15 mmol, 1.5 equiv.) as an oxidant. **^{1}H NMR (**400 MHz, CDCl$_3$) δ 7.90 (dd, J = 8.6, 4.0 Hz, 2H), 7.70 – 7.49 (m, 2H), 3.91 (d, J = 3.8 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 166.5 (^{13}C enriched), 131.9 (d, J = 5.1 Hz), 131.3 (d, J = 76.8 Hz), 129.2, 128.2, 52.5 (d, J = 2.0 Hz). **HRMS** (ESI+) calc. for $C_7{}^{13}CH_7BrO_2$ [M+H]$^+$ 215.9736, found 215.9730.

Methyl 4-(1-((tert-butyldimethylsilyl)oxy)-2-(methoxycarbonyl)allyl)benzoate (8)



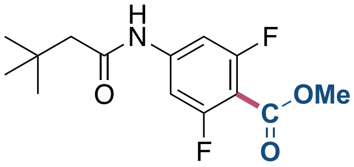
The title compound was prepared according to General Procedure A, methyl 2-(((tert-butyldimethylsilyl)oxy)(4-(5,5-dimethyl-1,3,2-dioxaborinan-2yl)phenyl)methyl)acrylate (0.1mmol). Flash column chromatography (0-6% ethyl acetate in heptane) yielded the product as a clear oil (24.4 mg, 67%).**^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.96 (d, J = 8.1 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 6.28 (s, 1H), 6.10 (s, 1H), 5.64 (s, 1H), 3.89 (s, 3H), 3.67 (s, 3H), 0.87 (s, 9H), 0.05 (s, 3H), -0.11 (s, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 167.13, 166.27, 148.03, 143.48, 129.63, 129.38, 127.14, 124.62, 72.47, 52.19, 51.87, 25.84, 18.31, -4.78, -4.90. **HRMS** (ESI+) calc. for $C_{19}H_{28}O_5SiNa^+$ [M$^+$Na$^+$] 387.1598, found: 387.1599.

Methyl 4-(1-((tert-butyldimethylsilyl)oxy)-2-(methoxycarbonyl)allyl)benzoate (^{13}C-8)



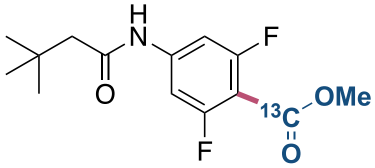
The title compound was prepared according to General Procedure B, methyl 2-(((tert-butyldimethylsilyl)oxy)(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)methyl)acrylate (0.100 mmol). Flash column chromatography (0-6% ethyl acetate in heptane) yielded the product as a clear oil (27.2 mg, 74%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.96 (dd, J = 8.2, 4.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 6.28 (s, 1H), 6.10 (s, 1H), 5.64 (s, 1H), 3.89 (d, J = 3.8 Hz, 3H), 3.67 (s, 3H), 0.87 (s, 9H), 0.05 (s, 3H), -0.11 (s, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 167.12 (^{13}C enriched), 166.26, 148.02, 143.48, 129.62 (d, J = 2.6 Hz), 129.36 (d, J = 75.2 Hz), 127.13 (d, J = 4.4 Hz), 124.61, 72.47, 52.17 (d, J = 2.6 Hz), 51.86, 25.84, 18.30, -4.78, -4.91. **HRMS** (ESI+) calc. for $C_{18}{}^{13}CH_{28}NaNO_5Si^+$ $[M+Na]^+$ 388.1632, found: 388.1640.

Methyl 4-(3,3-dimethylbutanamido)-3,5-difluorobenzoate (9)



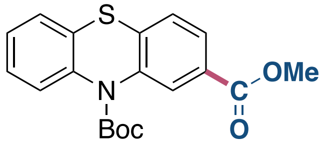
The title compound was prepared according to General Procedure A, N-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-2,6-difluorophenyl)-3,3-dimethylbutanamide (0.1 mmol). Flash column chromatography (5 – 20% ethyl acetate in heptane) yielded the product as yellow crystalline solid (23.1 mg, 91%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.60 (d, J = 8.3 Hz, 2H), 6.94 (s, 1H), 3.92 (s, 3H), 2.30 (s, 2H), 1.11 (s, 9H). **^{19}F NMR** (376 MHz, CDCl$_3$) δ -115.73. **^{13}C NMR** (101 MHz, CDCl$_3$) δ 169.90, 164.80 (t, J = 3.2 Hz), 157.10 (dd, J = 251.7, 5.2 Hz), 129.36 (t, J = 8.9 Hz), 118.63 (t, J = 16.7 Hz), 115.27 – 111.12 (m), 52.83, 50.30, 31.31, 29.82. **HRMS** (ESI+) calc. for $C_{14}H_{18}F_2NO_3^+$ $[M+H]^+$ 286.1249, found: 286.1245.

Methyl 4-(3,3-dimethylbutanamido)-3,5-difluorobenzoate (^{13}C-9)



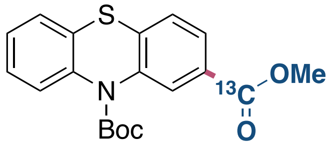
The title compound was prepared according to General Procedure B, N-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-2,6-difluorophenyl)-3,3-dimethylbutanamide (0.1 mmol). Flash column chromatography (5 – 20% ethyl acetate in heptane) yielded the product as yellow crystalline solid (26.5 mg, 93%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.50 (dd, J = 7.8 Hz, 4.42, 2H), 7.07 (s, 1H), 3.85 (d, J = 3.9 Hz, 3H), 2.23 (s, 2H), 1.03 (s, 9H).**^{19}F NMR** (376 MHz, CDCl$_3$) δ -115.58. **^{13}C NMR** (101 MHz, CDCl$_3$) δ 169.96, 164.79 (t, J = 3.1 Hz) (^{13}C enriched), 157.10 (ddd, J = 251.6, 7.7, 5.1 Hz), 129.32 (dt, J = 77.0, 8.8 Hz), 118.64 (t, J = 16.7 Hz), 115.87 – 109.91 (m), 52.82 (d, J = 2.6 Hz), 50.27, 31.31, 29.82. **HRMS** (ESI+) calc. for $C_{13}{}^{13}CH_{18}F_2NO_3^+$ $[M+H]^+$ 287.1283, found: 287.1279.

10-(*tert*-Butyl) 2-methyl 10H-phenothiazine-2,10-dicarboxylate (10)



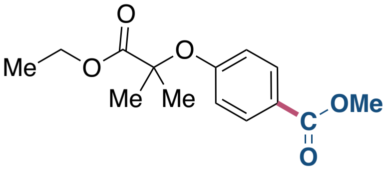
The title compound was prepared according to General Procedure A, employing tert-butyl 2-(neopentyl boronic ester)-10H-phenothiazine-10-carboxylate (0.1 mmol). Flash column chromatography (0-2% EtOAc in heptane) yielded the product as a colourless oil (29.3 mg, 82%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, J = 1.7 Hz, 1H), 7.82 (dd, J = 8.2, 1.8 Hz, 1H), 7.54 (dd, J = 8.1, 1.3 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.34-7.27 (m, 2H), 7.17 (td, J = 7.6, 1.3 Hz, 1H), 3.92 (s, 3H), 1.50 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.48, 152.27, 138.67, 138.30, 138.29, 131.05, 128.77, 128.42, 127.53, 127.38, 127.31, 127.08, 127.07, 126.46, 82.67, 52.40, 28.25. **HRMS** (ESI+) calc. for $C_{19}H_{19}NNaO_4S^+$ $[M+Na]^+$ 380.0927, found: 380.0928.

10-(*tert*-Butyl) 2-methyl 10H-phenothiazine-2,10-dicarboxylate (^{13}C-10)



The title compound was prepared according to General Procedure B, employing tert-butyl 2-(neopentyl boronic ester)-10H-phenothiazine-10-carboxylate (0.1 mmol). Flash column chromatography (0-2% EtOAc in heptane) yielded the product as a colourless oil (29.7 mg, 83%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 4.5, 1.7 Hz, 1H), 7.82 (ddd, J = 8.2, 3.9, 1.7 Hz, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.35-7.27 (m, 2H), 7.17 (t, J = 7.6 Hz, 1H), 3.92 (d, J = 3.8 Hz, 1H), 1.50 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.48 (^{13}C enriched), 152.28, 138.68 (d, J = 5.9 Hz), 138.31, 138.29, 131.06, 129.15, 128.42 (d, J = 3.0 Hz), 127.54, 127.39, 127.32 (d, J = 5.1 Hz), 127.08, 126.46, 82.68, 52.39 (d, J = 2.5 Hz), 28.25. **HRMS** (ESI+) calc. for $C_{18}{}^{13}CH_{19}NNaO_4S^+$ $[M+Na]^+$ 381.0961, found: 381.0960.

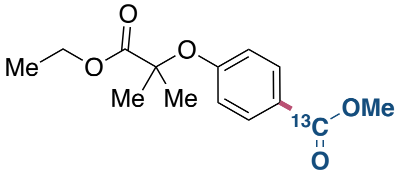
Methyl 4-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoate (11)



The title compound was prepared according to General Procedure A, Ethyl 2-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenoxy)-2-methylpropanoate (0.1 mmol). Flash column chromatography (EtOAc 0-10% in heptane) yielded the product as a colourless oil

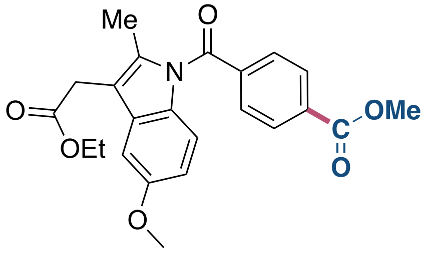
(16.4 mg, 62%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.93 (d, J = 8.9 Hz, 2H), 6.81 (d, J = 8.9 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.64 (s, 7H), 1.21 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 173.94, 166.89, 159.72, 131.35, 123.43, 117.48, 79.41, 61.81, 52.06, 25.51, 14.16 **HRMS** (ESI+) calc. for $C_{14}H_{19}O_5^+$ [M+H]$^+$ 267.1232, found 267.1227.

Methyl 4-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoate (^{13}C-11)



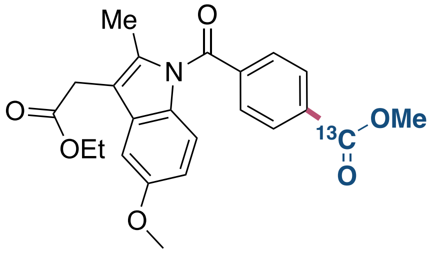
The title compound was prepared according to General Procedure B, Ethyl 2-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenoxy)-2-methylpropanoate (0.1 mmol). Flash column chromatography (EtOAc 0-10% in heptane) yielded the product as a colourless oil (20.0 mg, 71%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.93 (dd, *J* = 8.9, 3.9 Hz, 2H), 6.81 (dd, *J* = 9.0, 0.9 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.87 (d, *J* = 3.8 Hz, 3H), 1.64 (s, 6H), 1.20 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 173.92, 166.88 (^{13}C enriched), 159.71, 131.34 (d, *J* = 2.9 Hz), 123.42 (d, *J* = 77.0 Hz), 117.48 (d, *J* = 4.5 Hz), 79.40, 61.79, 25.50, 14.15. **HRMS** (ESI+) calc. for $C_{13}{}^{13}CH_{19}O_5^+$ [M+H]$^+$ 268.1265 found 268.1218.

Methyl 4-(3-(2-ethoxy-2-oxoethyl)-5-methoxy-2-methyl-1H-indole-1-carbonyl)benzoate (12)



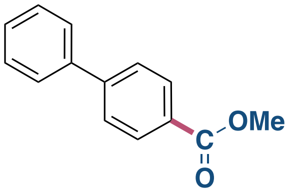
The title compound was prepared according to General Procedure A, ethyl 2-(1-(4-(neopentyl boronic ester)benzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (0.0893 mmol). Flash column chromatography (20-40% ethyl acetate in heptane) yielded the product as a yellow solid (28.1 mg, 77%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.15 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 6.97 (d, J = 2.6 Hz, 1H), 6.86 (d, J = 9.0 Hz, 1H), 6.64 (dd, J = 9.0, 2.6 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 3.97 (s, 3H), 3.83 (s, 3H), 3.65 (s, 2H), 2.36 (s, 3H), 1.26 (t, J = 7.1 Hz, 2H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 170.93, 168.68, 166.22, 156.28, 139.76, 135.95, 133.70, 130.96, 130.84, 130.06, 129.54, 115.26, 113.23, 111.84, 101.51, 61.17, 55.81, 52.68, 30.55, 14.37, 13.68. **HRMS** (ESI+) calc. for $C_{23}H_{24}NO_6^+$ $[M+H]^+$ 410.1598, found: 410.1600.

Methyl 4-(3-(2-ethoxy-2-oxoethyl)-5-methoxy-2-methyl-1H-indole-1-carbonyl)benzoate (^{13}C-12)



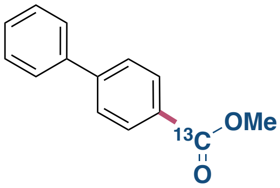
The title compound was prepared according to General Procedure B, ethyl 2-(1-(4-(neopentyl boronic ester)benzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (0.0893 mmol). Flash column chromatography (20-40% ethyl acetate in heptane) yielded the product as a yellow solid (24.6 mg, 67%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 8.4, 4.0 Hz, 2H), 7.76 (d, J = 8.7 Hz, 2H), 6.97 (d, J = 2.6 Hz, 1H), 6.86 (d, J = 8.9 Hz, 1H), 6.65 (dd, J = 9.0, 2.6 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 3.97 (d, J = 3.8 Hz, 3H), 3.83 (s, 3H), 3.65 (s, 2H), 2.36 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.93, 168.67, 166.22 (^{13}C enriched), 156.27, 139.75, 135.95, 133.67 (d, J = 74.8 Hz), 130.89 (d, J = 11.7 Hz), 130.05 (d, J = 2.5 Hz), 129.53 (d, J = 4.6 Hz), 115.25, 113.23, 111.83, 101.50, 61.17, 55.80, 52.67 (d, J = 2.6 Hz), 31.06, 30.53, 14.37, 13.67. **HRMS** (ESI+) calc. for $C_{22}{}^{13}CH_{24}NO_6^+$ $[M+H]^+$ 411.1632, found: 411.1633.

Methyl 4-phenylbenzoate (13)



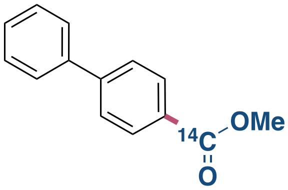
The title compound was prepared according to General Procedure A, employing 2-([1,1'-biphenyl]-4-yl)-5,5-dimethyl-1,3,2-dioxaborinane (0.1 mmol). Flash column chromatography (EtOAc 0-5% in heptane) yielded the product as a white solid (19.2 mg, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.8 Hz, 2H), 7.69 – 7.60 (m, 4H), 7.51 – 7.44 (m, 2H), 7.43 – 7.35 (m, 1H), 3.95 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.16, 145.78, 140.15, 130.24, 129.07, 128.29, 127.43, 127.20, 52.29. **HRMS** (ESI+) calc. for $C_{14}H_{13}O_2^+$ $[M+H]^+$ 213.0910, found 213.0913.

Methyl 4-phenylbenzoate (^{13}C-13)



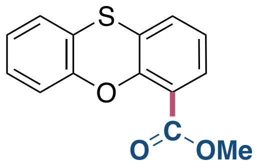
The title compound was prepared according to General Procedure B, employing 2-([1,1'-biphenyl]-4-yl)-5,5-dimethyl-1,3,2-dioxaborinane (0.1 mmol). Flash column chromatography (EtOAc 0-5% in heptane) yielded the product as a white solid (18.5 mg, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.73 – 7.60 (m, 3H), 7.60 – 7.42 (m, 1H), 7.42 – 7.31 (m, 1H), 3.95 (d, *J* = 3.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.15, 145.78, 140.15, 130.24 (d, *J* = 2.7 Hz), 129.07, 128.28, 127.42, 127.19 (d, *J* = 4.6 Hz), 52.28 (d, *J* = 2.3 Hz). **HRMS** (ESI+) calc. for $C_{13}{}^{13}CH_{13}O_2^+$ $[M+H]^+$ 214.0944, found 214.0945.

Methyl 4-phenylbenzoate (^{14}C-13)



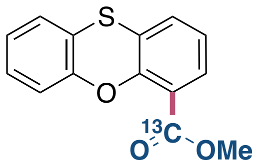
The title compound was prepared according to General Procedure C, employing 2-([1,1'-biphenyl]-4-yl)-5,5-dimethyl-1,3,2-dioxaborinane (0.1 mmol). Preparatory HPLC (20–85% MeCN in H_2O/0.2% NH_3 over 22 min, wavelength of 220 nm, 15 mL/min) yielded the product as a white solid (20 mg, 93%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.71 – 7.60 (m, 4H), 7.52 – 7.44 (m, 2H), 7.42 – 7.36 (m, 1H), 3.95 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.14, 145.80, 140.18, 130.25, 129.07, 128.28, 127.43, 127.19, 52.24. **Radiochemical purity**: 98%. **Specific activity:** 166.6 GBq/mol. **Radioactivity:** 15.6 MBq.

Methyl phenoxathiin-1-carboxylate (14)



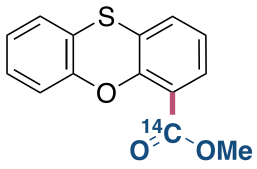
The title compound was prepared according to General Procedure A, employing phenoxathiin-1-boronic acid (0.1 mmol). Preparatory HPLC (20–85% MeCN in H_2O/0.2% NH_3 over 22 min, wavelength of 220 nm, 15 mL/min) yielded the product as a colourless oil (22 mg, 85%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.28 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.21 – 7.10 (m, 3H), 7.06 (td, *J* = 7.7, 2.2 Hz, 2H), 3.97 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.94, 152.39, 151.99, 130.64, 129.65, 128.15, 126.88, 125.27, 124.01, 123.19, 121.59, 120.75, 118.54, 52.46. **HRMS** (ESI+) calc. for $C_{14}H_{11}O_3S$ $[M+H]^+$ 259.0429, found 259.0478.

Methyl phenoxathiin-1-carboxylate (^{13}C-14)



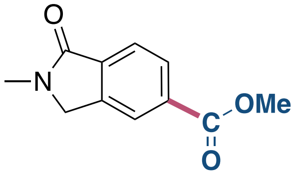
The title compound was prepared according to General Procedure B, employing phenoxathiin-1-boronic acid (0.1 mmol). Preparatory HPLC (20–85% MeCN in H_2O/0.2% NH_3 over 22 min, wavelength of 220 nm, 15 mL/min) yielded the product as a colourless oil (23 mg, 89%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (ddd, *J* = 7.7, 4.5, 1.6 Hz, 1H), 7.28 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.21 – 7.10 (m, 3H), 7.06 (ddt, *J* = 7.9, 7.0, 1.3 Hz, 2H), 3.97 (d, *J* = 4.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.95 (^{13}C enriched), 152.37, 151.98, 130.66, 129.65, 128.15, 126.87, 125.27, 124.02 (d, *J* = 4.6 Hz, 123.19 (d, *J* = 3.7 Hz, 121.86, 121.25, 120.74, 118.53, 77.41, 77.16, 76.91, 52.48 (d, *J* = 2.6 Hz). **HRMS** (ESI+) calc. for $C_{13}{}^{13}CH_{11}O_3S^+$ $[M+H]^+$ 260.0462, found 260.0462.

Methyl phenoxathiin-1-carboxylate (^{14}C-14)



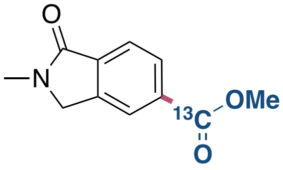
The title compound was prepared according to General Procedure C, employing phenoxathiin-1-boronic acid (0.05 mmol). Preparatory HPLC (20–85% MeCN in H_2O/0.2% NH_3 over 22 min, wavelength of 220 nm, 15 mL/min) yielded the product as a colourless oil (9 mg, 69%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.28 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.21 – 7.09 (m, 3H), 7.09 – 7.01 (m, 2H), 3.97 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.93, 152.41, 152.00, 130.62, 129.64, 128.15, 126.88, 125.26, 124.00, 123.20, 121.64, 120.77, 118.55, 77.41, 77.16, 76.91, 52.43. **Radiochemical purity** 97%. **Specific activity** 185.8 GBq/mol. **Radioactivity** 6.43 MBq

Methyl 2-methyl-1-oxoisoindoline-5-carboxylate (15)



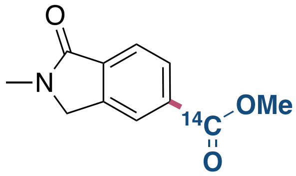
The title compound was prepared according to General Procedure A, employing (2-methyl-1-oxoisoindolin-5-yl)boronic acid (0.1 mmol). Preparatory HPLC (20–85% MeCN in H_2O/0.2% NH_3 over 22 min, wavelength of 220 nm, 15 mL/min) yielded the product as an off-white solid (18 mg, 88%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.9 Hz, 1H), 8.12 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 4.45 (s, 2H), 3.95 (s, 3H), 3.23 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.75, 166.66, 140.97, 136.97, 132.87, 129.72, 124.14, 123.72, 52.64, 52.07, 29.79. **HRMS** (ESI+) calc. for $C_{11}H_{12}NO_3^+$ $[M+H]^+$ 206.0812, found 206.0819.

Methyl 2-methyl-1-oxoisoindoline-5-carboxylate (^{13}C-15)



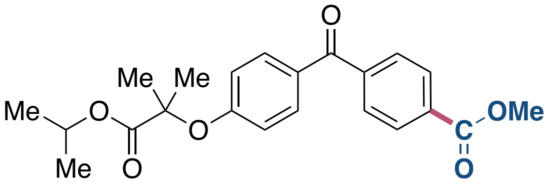
The title compound was prepared according to General Procedure B, employing (2-methyl-1-oxoisoindolin-5-yl)boronic acid (0.1 mmol). Preparatory HPLC (20–85% MeCN in H_2O/0.2% NH_3 over 22 min, wavelength of 220 nm, 15 mL/min) yielded the product as an off-white solid (18 mg, 87%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 – 8.12 (m, 1H), 8.13 – 8.10 (m, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 4.43 (s, 2H), 3.95 (d, *J* = 3.9 Hz, 3H), 3.22 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.72, 166.65 (^{13}C enriched), 140.97 (d, *J* = 5.2 Hz), 136.96, 132.85 (d, *J* = 74.4 Hz), 129.71 (d, *J* = 2.7 Hz), 124.13 (d, *J* = 2.7 Hz), 123.71 (d, *J* = 4.6 Hz), 52.63 (d, *J* = 2.5 Hz), 29.78. **HRMS** (ESI+) calc. for $C_{10}{}^{13}CH_{12}NO_3$ $[M+H]^+$ 207.0845, found 207.0854.

Methyl 2-methyl-1-oxo-2,3-dihydro-1H-isoindole-4-carboxylate (^{14}C-15)



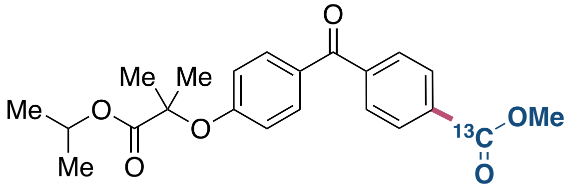
The title compound was prepared according to General Procedure C, employing (2-methyl-1-oxoisoindolin-5-yl)boronic acid (0.1 mmol). Preparatory HPLC (20–85% MeCN in H_2O/0.2% NH_3 over 22 min, wavelength of 220 nm, 15 mL/min) yielded the product as an off-white solid (17 mg, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.9 Hz, 1H), 8.12 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 4.43 (s, 2H), 3.96 (s, 3H), 3.23 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.74, 166.66, 141.02, 137.04, 132.96, 129.74, 124.15, 123.75, 52.60, 52.08, 29.78. **Radiochemical purity:** 97%. **Specific activity:** 129.7 GBq/mol. **Radioactivity:** 10.6 MBq.

Methyl 4-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)benzoate (16)



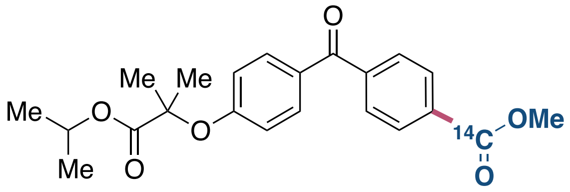
The title compound was prepared according to General Procedure A employing Isopropyl 2-(4-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoyl)phenoxy)-2-methylpropanoate (0.1 mmol). Flash column chromatography (EtOAc 0-30% in heptane) yielded the product as a white solid (26 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.91 – 7.57 (m, 4H), 6.86 (d, *J* = 8.9 Hz, 2H), 5.09 (p, *J* = 6.3 Hz, 1H), 3.96 (s, 3H), 1.66 (s, 6H), 1.20 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.92, 173.21, 166.53, 160.12, 142.14, 132.95, 132.27, 130.07, 129.59, 117.36, 79.59, 69.52, 52.59, 25.51, 21.67. **HRMS** (ESI+) calc. for $C_{22}H_{25}O_6^+$ [M+H]$^+$ 385.1651, found 385.1689.

Methyl 4-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)benzoate (^{13}C-16)



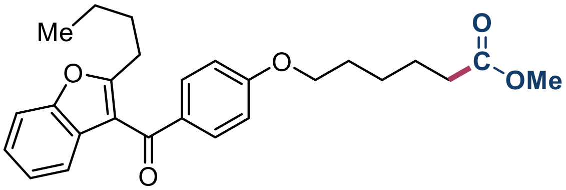
The title compound was prepared according to General Procedure B employing Isopropyl 2-(4-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoyl)phenoxy)-2-methylpropanoate (0.1 mmol). Preparatory HPLC (20–95% MeCN in H_2O/0.2% NH_3 over 35 min, wavelength of 220 nm, 15 mL/min) yielded the title compound as a pale-yellow solid (30 mg, 78%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.28 – 8.04 (m, 2H), 7.86 – 7.67 (m, 5H), 7.01 – 6.71 (m, 2H), 5.08 (p, *J* = 6.2 Hz, 1H), 3.96 (d, *J* = 3.8 Hz, 3H), 1.66 (d, *J* = 2.0 Hz, 7H), 1.20 (d, *J* = 6.3 Hz, 7H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.91, 173.20, 166.52 (^{13}C enriched), 160.11, 142.13, 132.92 (d, *J* = 74.6 Hz), 132.26, 129.97 (d, *J* = 22.6 Hz), 129.58 (d, *J* = 3.6 Hz), 117.34, 79.57, 69.51, 52.58 (d, *J* = 2.5 Hz), 25.50, 21.66. **HRMS** (ESI+) calc. for $C_{21}{}^{13}CH_{25}O_6^+$ [M+H]+ 386.16847, found 386.1700.

Methyl 4-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)benzoate (^{14}C-16)



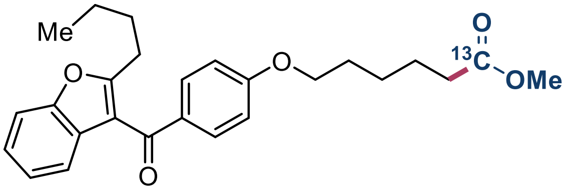
The title compound was prepared according to General Procedure C employing Isopropyl 2-(4-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoyl)phenoxy)-2-methylpropanoate (0.05 mmol). Preparatory HPLC (20–95% MeCN in H_2O/0.2% NH_3 over 35 min, wavelength of 220 nm, 15 mL/min) yielded the title compound as a pale-yellow solid (15 mg, 78%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.77 (dd, *J* = 12.9, 8.6 Hz, 4H), 6.87 (d, *J* = 8.9 Hz, 2H), 5.09 (p, *J* = 6.3 Hz, 1H), 3.96 (s, 3H), 1.66 (s, 6H), 1.20 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.88, 173.19, 166.53, 160.17, 159.74, 142.20, 133.00, 132.24, 130.18, 129.88, 129.58, 117.47, 79.65, 79.57, 69.51, 52.55, 25.55, 21.67. **Radiochemical purity**: >99%. **Specific Activity**: 148.9 GBq/mol. **Radioactivity**: 5.82 MBq

Methyl 6-(4-(2-butylbenzofuran-3-carbonyl)phenoxy)hexanoate (17)



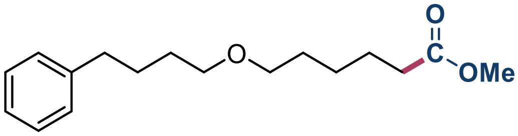
The title compound was prepared according to General Procedure D, employing (2-butylbenzofuran-3-yl)(4-(pent-4-en-1-yloxy)phenyl)methanone (58 mg, 1.6 equiv). Flash column chromatography (5% EtOAc in pentane) yielded the product as a colorless oil (30 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.30–7.24 (m, 1H), 7.21–7.15 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.05 (t, *J* = 6.4 Hz, 2H), 3.68 (s, 3H), 2.95–2.87 (m, 2H), 2.37 (t, *J* = 7.4 Hz, 2H), 1.89–1.81 (m, 2H), 1.80–1.68 (m, 4H), 1.59–1.48 (m, 2H), 1.41–1.29 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 190.7, 174.2, 164. 8, 163.1, 153.7, 131.9, 131.9, 127.4, 124.3, 123.4, 121.4, 116.9, 114.2, 111.1, 68.0, 51.7, 34.1, 30.3, 29.0, 28.0, 25.8, 24.8, 22.5, 13.9. **HRMS** (ESI+) calc. for $C_{26}H_{31}O_5$ $[M+H]^+$ 423.2166, found 423.2173.

Methyl 6-(4-(2-butylbenzofuran-3-carbonyl)phenoxy)hexanoate (^{13}C-17)



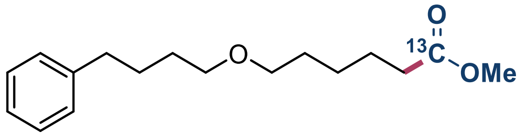
The title compound was prepared according to General Procedure E, employing (2-butylbenzofuran-3-yl)(4-(pent-4-en-1-yloxy)phenyl)methanone (58 mg, 1.6 equiv). Flash column chromatography (5% EtOAc in pentane) yielded the product as a colorless oil (31 mg, 73%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.49–7.45 (m, 1H), 7.37–7.33 (m, 1H), 7.30–7.24 (m, 1H), 7.21–7.15 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.05 (t, *J* = 6.4 Hz, 2H), 3.68 (d, *J* = 3.9 Hz, 3H), 2.96–2.86 (m, 2H), 2.37 (q, *J* = 7.3 Hz, 2H), 1.90–1.80 (m, 2H), 1.78–1.69 (m, 4H), 1.55–1.48 (m, 2H). 1.41–1.30 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 190.7, 174.2 (^{13}C-enriched), 164.8, 163.1, 153.7, 131.9, 131.8, 127.4, 124.3, 123.4, 121.4, 116.9, 114.2, 111.1, 68.0, 51.7 (d, *J* = 2.7 Hz), 34.1 (d, *J* = 57.5 Hz), 30.3, 29.0, 28.0, 25.8 (d, *J* = 3.7 Hz), 24.8 (d, *J* = 1.7 Hz), 22.5, 13.9. **HRMS** (ESI+) calc. for $C_{25}{}^{13}CH_{31}O_5$ $[M+H]^+$ 424.2200, found 424.2206.

Methyl 5-(4-phenylbutoxy)pentanoate (18)



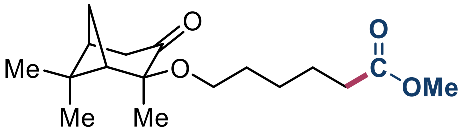
The title compound was prepared according to General Procedure D, employing (4-(but-3-en-1-yloxy)butyl)benzene (35 mg, 1.6 equiv). Flash column chromatography (gradient CH_2Cl_2 to 2% EtOAc in CH_2Cl_2) yielded the product as a yellow oil (18 mg, 67%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.30–7.24 (m, 2H), 7.20–7.14 (m, 3H), 3.66 (s, 3H), 3.45–3.35 (m, 4H), 2.63 (t, *J* = 7.4 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 1.73–1.52 (m, 8H), 1.43–1.31 (m, 2H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 174.3, 142.7, 128.6, 128.4, 125.8, 70.9, 70.8, 51.6, 35.9, 34.2, 29.6, 29.6, 28.2, 26.0, 24.9. **HRMS** (ESI+) calc. for $C_{17}H_{27}O_3$ $[M+H]^+$ 279.1955, found 279.1963.

Methyl 5-(4-phenylbutoxy)pentanoate (^{13}C-18)



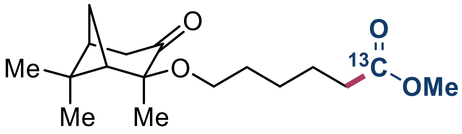
The title compound was prepared according to General Procedure E, employing (4-(but-3-en-1-yloxy)butyl)benzene (35 mg, 1.6 equiv). Flash column chromatography (gradient CH_2Cl_2 to 2% EtOAc in CH_2Cl_2) yielded the product as a yellow oil (21 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 2H), 7.20–7.14 (m, 3H), 3.66 (d, *J* = 3.9 Hz, 3H), 3.44–3.34 (m, 4H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.31 (q, *J* = 7.4 Hz, 2H), 1.74–1.51 (m, 8H), 1.43–1.32 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3 (^{13}C-enriched), 142.6, 128.6, 128.4, 125.8, 70.9, 70.8, 51.6 (d, *J* = 2.8 Hz), 35.9, 34.2 (d, *J* = 57.4 Hz), 29.6, 29.5, 28.2, 26.0 (d, *J* =3.8 Hz), 24.9 (d, *J* = 1.7 Hz). **HRMS** (ESI+) calc. for $C_{16}{}^{13}CH_{27}O_3$ $[M+H]^+$ 280.1988, found 280.1991.

Methyl 6-(((*1S,2S,5S*)-2,6,6-trimethyl-3-oxobicyclo[3.1.1]heptan-2-yl)oxy)hexanoate (19)



The title compound was prepared according to General Procedure D, employing (*1S,2S,5S*)-2,6,6-trimethyl-2-(pent-4-en-1-yloxy)bicyclo[3.1.1]heptan-3-one (38 mg, 1.6 equiv). Flash column chromatography (5% EtOAc in pentane) yielded the product as a yellow oil (22 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 3.41–3.27 (m, 2H), 2.64–2.51 (m, 2H), 2.41–2.33 (m, 1H), 2.29 (t, *J* = 7.5 Hz, 2H), 2.15 (t, *J* = 6.2 Hz, 1H), 2.11–2.03 (m, 1H), 1.80 (d, *J* = 10.6 Hz, 1H), 1.66–1.55 (m, 2H), 1.54–1.44 (m, 2H), 1.37–1.30 (m, 5H), 1.29 (s, 3H), 0.85 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.7, 174.3, 80.2, 61.8, 51.6, 50.2, 43.9, 39.3, 38.8, 34.2, 29.9, 28.3, 27.6, 26.0, 24.9, 22.8, 19.8. **HRMS** (ESI+) calc. for $C_{17}H_{29}O_4$ $[M+H]^+$ 297.2060, found 297.2966.

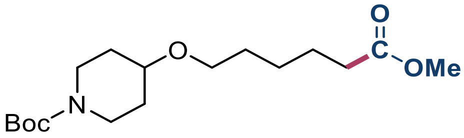
Methyl 6-(((*1S,2S,5S*)-2,6,6-trimethyl-3-oxobicyclo[3.1.1]heptan-2-yl)oxy)hexanoate (^{13}C-19)



The title compound was prepared according to General Procedure E, employing (*1S,2S,5S*)-2,6,6-trimethyl-2-(pent-4-en-1-yloxy)bicyclo[3.1.1]heptan-3-

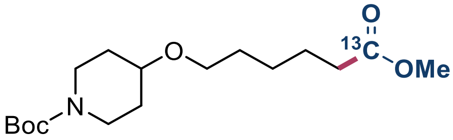
one (38 mg, 1.6 equiv). Flash column chromatography (5% EtOAc in pentane) yielded the product as a yellow oil (22 mg, 74%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.66 (d, *J* = 3.8 Hz, 3H), 3.41–3.27 (m, 2H), 2.63–2.54 (m, 2H), 2.41–2.33 (m, 1H), 2.29 (q, *J* = 7.4 Hz, 2H), 2.15 (t, *J* = 6.2 Hz, 1H), 2.11–2.04 (m, 1H), 1.80 (d, *J* = 10.7 Hz, 1H), 1.66–1.57 (m, 2H), 1.53–1.44 (m, 2H), 1.39–1.26 (m, 8H), 0.85 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.7, 174.3 (^{13}C-enriched), 80.2, 61.8, 51.6 (d, *J* = 2.8 Hz), 50.2, 43.9, 39.3, 38.8, 34.2 (d, *J* = 57.4 Hz), 29.9, 28.3, 27.6, 26.0 (d, *J* = 3.7 Hz), 24.9 (d, *J* = 1.6 Hz), 22.8, 19.8. **HRMS** (ESI+) calc. for $C_{16}{}^{13}CH_{29}O_4$ $[M+H]^+$ 298.2094, found 298.2097.

***tert*-Butyl 4-((6-methoxy-6-oxohexyl)oxy)piperidine-1-carboxylate (20)**



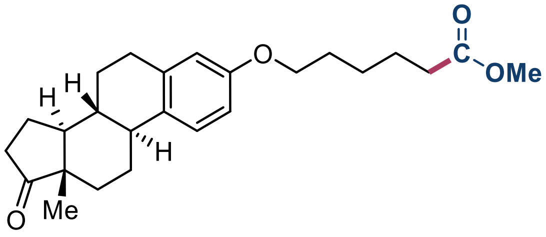
The title compound was prepared according to General Procedure D, employing *tert*-butyl 4-(pent-4-en-1-yloxy)piperidine-1-carboxylate (43 mg, 1.6 equiv). Flash column chromatography (25% Et_2O in pentane) yielded the product as a colorless oil (28 mg, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.81–3.70 (m, 2H), 3.66 (s, 3H), 3.49–3.35 (m, 3H), 3.13–3.00 (m, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.85–1.76 (m, 2H), 1.71–1.33 (m, 17H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 155.0, 79.6, 74.7, 67.8, 51.6, 41.5, 34.2, 31.2, 29.9, 28.6, 26.0, 24.9. **HRMS** (ESI+) calc. for $C_{17}H_{32}NO_5$ $[M+H]^+$ 330.2275, found 330.2273.

***tert*-Butyl 4-((6-methoxy-6-oxohexyl)oxy)piperidine-1-carboxylate (^{13}C-20)**



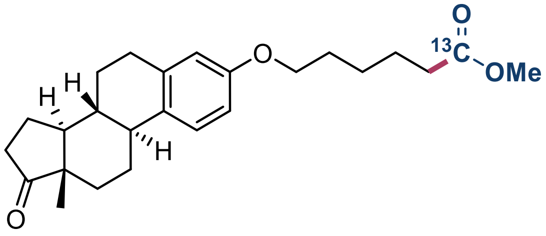
The title compound was prepared according to General Procedure E, employing *tert*-butyl 4-(pent-4-en-1-yloxy)piperidine-1-carboxylate (43 mg, 1.6 equiv). Flash column chromatography (25% Et_2O in pentane) yielded the product as a colorless oil (27 mg, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.82–3.70 (m, 2H), 3.66 (d, *J* = 3.8 Hz, 3H), 3.47–3.35 (m, 3H), 3.12–3.01 (m, 2H), 2.32 (q, *J* = 7.4 Hz, 2H), 1.85–1.74 (m, 2H), 1.70–1.33 (m, 17H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3 (^{13}C-enriched), 155.0, 79.5, 74.7, 67.8, 51.6 (d, *J* = 2.8 Hz), 41.4, 34.2 (d, *J* = 57.4 Hz), 31.3, 29.9, 28.6, 26.0 (d, *J* = 3.7 Hz), 24.9 (d, *J* = 1.7 Hz). **HRMS** (ESI+) calc. for $C_{16}{}^{13}CH_{32}NO_5$ $[M+H]^+$ 331.2309, found 331.2301.

Methyl 6-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)hexanoate (21)



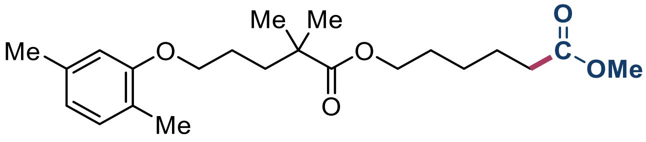
The title compound was prepared according to General Procedure D, employing (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(pent-4-en-1-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (54 mg, 1.6 equiv). Flash column chromatography (10% EtOAc in pentane) yielded the product as a colorless solid (30 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.6 Hz, 1H), 6.70 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.63 (d, *J* = 2.7 Hz, 1H), 3.93 (t, *J* = 6.4 Hz, 2H), 3.67 (s, 3H), 2.93–2.84 (m, 2H), 2.50 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.34 (t, *J* = 7.5 Hz, 2H), 2.30–1.91 (m, 5H), 1.83–1.36 (m, 13H), 0.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 221.0, 174.1, 157.1, 137.7, 131.9, 126.3, 114.5, 112.1, 67.6, 51.5, 50.4, 48.0, 44.0, 38.4, 35.9, 34.0, 31.6, 29.7, 29.0, 26.6, 25.9, 25.7, 24.7, 21.6, 13.9. **HRMS** (ESI+) calc. for $C_{25}H_{35}O_4$ $[M+H]^+$ 399.2530, found 399.2532.

Methyl 6-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)hexanoate (^{13}C-21)



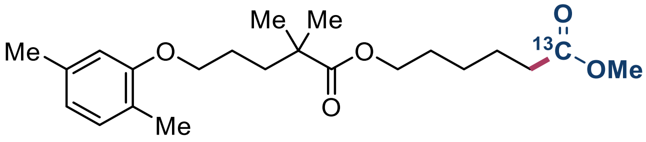
The title compound was prepared according to General Procedure E, employing (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(pent-4-en-1-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (54 mg, 1.6 equiv). Flash column chromatography (10% EtOAc in pentane) yielded the product as a colorless solid (29 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 1H), 6.70 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.63 (d, *J* = 2.4 Hz, 1H), 3.93 (t, *J* = 6.4 Hz, 2H), 3.67 (d, *J* = 3.9 Hz, 3H), 2.95 – 2.82 (m, 2H), 2.50 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.34 (q, *J* = 7.4 Hz, 2H), 2.29 – 1.83 (m, 5H), 1.83 – 1.36 (m, 13H), 0.91 (s, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 221.2, 174.2 (^{13}C-enriched), 157.2, 137.8, 132.0, 126.4, 114.6, 112.2, 67.7, 51.7 (d, *J* = 2.8 Hz), 50.5, 48.2, 44.1, 38.5, 36.0, 34.1 (d, *J* = 57.5 Hz), 31.7, 29.8, 29.1, 26.7, 26.1, 25.8 (d, *J* = 3.7 Hz), 24.8 (d, *J* = 1.8 Hz), 21.7, 14.0. **HRMS** (ESI+) calc. for $C_{24}{}^{13}CH_{35}O_4$ [M+H]$^+$ 400.2563, found 400.2563.

Methyl 6-((5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl)oxy)hexanoate (22)



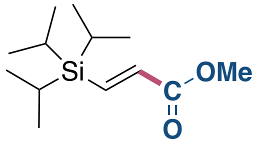
The title compound was prepared according to General Procedure D, employing pent-4-en-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (51 mg, 1.6 equiv). Flash column chromatography (2-5% EtOAc in pentane) yielded the product as a colorless oil (29 mg, 79%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.00 (d, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.61 (s, 1H), 4.06 (t, *J* = 6.6 Hz, 2H), 3.96–3.88 (m, 2H), 3.66 (s, 3H), 2.36–2.28 (m, 5H), 2.17 (s, 3H), 1.79–1.59 (m, 8H), 1.45–1.34 (m, 2H), 1.21 (s, 6H). **^{13}C NMR (**101 MHz, CDCl$_3$) δ 177.9, 174.1, 157.1, 136.6, 130.4, 123.7, 120.8, 112.1, 68.0, 64.3, 51.6, 42.2, 37.2, 34.0, 28.5, 25.7, 25.3, 25.3, 24.7, 21.5, 15.9. **HRMS** (ESI+) calc. for $C_{22}H_{35}O_5$ [M+H]$^+$ 379.2479, found 379.2481.

Methyl 6-((5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl)oxy)hexanoate (^{13}C-22)



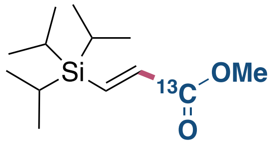
The title compound was prepared according to General Procedure E, employing pent-4-en-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (51 mg, 1.6 equiv). Flash column chromatography (2-5% EtOAc in pentane) yielded the product as a colorless oil (29 mg, 77%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.00 (d, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.61 (s, 1H), 4.06 (t, *J* = 6.6 Hz, 2H), 3.95–3.88 (m, 2H), 3.66 (d, *J* = 3.8 Hz, 3H), 2.46–2.26 (m, 5H), 2.17 (s, 3H), 1.77–1.60 (m, 8H), 1.45–1.34 (m, 2H), 1.21 (s, 6H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 177.9, 174.1 (^{13}C-enriched), 157.1, 136.6, 130.4, 123.7, 120.8, 112.0, 68.0, 64.3, 51.6 (d, *J* = 2.8 Hz), 42.2, 37.2, 34.0 (d, *J* = 57.5 Hz), 28.5, 25.7 (d, *J* = 3.7 Hz), 25.3, 25.3, 24.7 (d, *J* = 1.6 Hz), 21.5, 15.9. **HRMS** (ESI+) calc. for $C_{21}{}^{13}CH_{35}O_5$ [M+H]$^+$ 380.2513, found 380.2517.

Methyl (E)-3-(triisopropylsilyl)acrylate (23)



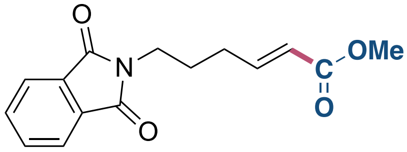
The title compound was prepared according to General Procedure D, employing triisobutylsilylethyne (29.2 mg, 0.16 mmol). Flash column chromatography (0-3% ethyl acetate in heptane) yielded the product as a colourless oil (12.9 mg, 53%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, J = 19.2 Hz, 1H), 6.33 (d, J = 19.2 Hz, 1H), 3.77 (s, 3H), 1.17 – 1.03 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.20, 145.82, 135.49, 51.81, 18.64, 10.86. **HRMS** (ESI+) calc. for $C_{13}H_{27}O_2Si^+$ $[M+H]^+$ 243.1775, found: 243.1770.

Methyl (E)-3-(triisopropylsilyl)acrylate (^{13}C-23)



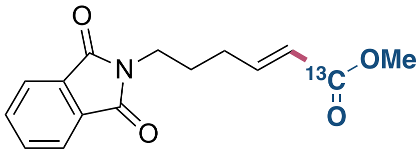
The title compound was prepared according to General Procedure E, employing triisobutylsilylethyne (29.2 mg, 0.16 mmol). Flash column chromatography (0-3% ethyl acetate in heptane) yielded the product as a colourless oil (16.2 mg, 67%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (dd, J = 19.1 Hz, 7.18 Hz, 1H), 6.32 (dd, J = 19.1 Hz, 5.1 Hz, 1H), 3.77 (d, J = 3.7 Hz, 3H), 1.19 – 1.03 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.20 (^{13}C enriched), 145.82, 135.48 (d, J = 70.8 Hz), 51.81 (d, J = 2.6 Hz), 18.64, 10.86. **HRMS** (ESI+) calc. for $C_{12}{}^{13}CH_{27}O_2Si^+$ $[M+H]^+$ 244.1808, found: 244.1809.

Methyl (*E*)-6-(1,3-dioxoisoindolin-2-yl)hex-2-enoate (24)



The title compound was prepared according to General Procedure D, employing 2-(pent-4-yn-1-yl)isoindoline-1,3-dione (34 mg, 1.6 equiv). Flash column chromatography (10% EtOAc in pentane) yielded the product as a light-yellow solid (16 mg, 57%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88–7.80 (m, 2H), 7.75–7.67 (m, 2H), 6.94 (dt, J = 15.7, 6.8 Hz, 1H), 5.86 (dt, J = 15.6, 1.6 Hz, 1H), 3.75–3.67 (m, 5H), 2.32–2.23 (m, 2H), 1.91–1.81 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 166.0, 147.8, 134.1, 132.2, 123.4, 121.8, 51.6, 37.5, 29.7, 27.0. **HRMS** (ESI+) calc. for $C_{15}H_{16}NO_4$ $[M+H]^+$ 274.1074, found 274.1073.

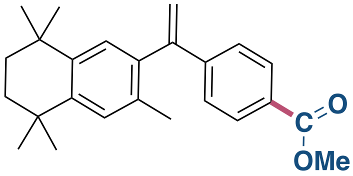
Methyl (*E*)-6-(1,3-dioxoisoindolin-2-yl)hex-2-enoate (^{13}C-24)



The title compound was prepared according to General Procedure E, employing 2-(pent-4-yn-1-yl)isoindoline-1,3-dione (34 mg, 1.6 equiv). Flash column chromatography (10% EtOAc in pentane) yielded the product as a light-yellow solid (15 mg, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88–7.82 (m, 2H), 7.75–7.69 (m, 2H), 6.94 (dq, *J* = 15.7, 6.8 Hz, 1H), 5.86 (ddt, *J* = 15.7, 3.2, 1.6 Hz, 1H), 3.76–3.67 (m, 5H), 2.32–2.22 (m, 2H), 1.92–1.81 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 167.0 (^{13}C-enriched), 147.8, 134.1, 132.2, 123.4, 121.8 (d, *J* = 74.9 Hz), 51.6 (d, *J* = 2.5 Hz), 37.5, 29.7 (d, *J* = 6.8 Hz), 27.0. **HRMS** (ESI+) calc. for $C_{14}{}^{13}CH_{16}NO_4$ $[M+H]^+$ 275.1107, found 275.1110.

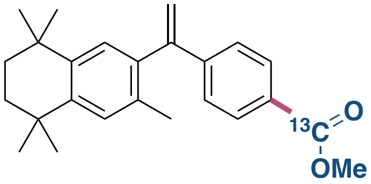
Synthesis and Characterization of Methyl Ester Products (25-27, Scheme 4)

Methyl 4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoate (25)



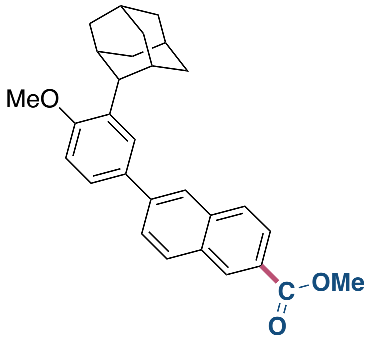
The title compound was prepared according to General Procedure F, employing bexarotene (17 mg, 0.05 mmol, 1.0 equiv). Flash column chromatography (1-2% EtOAc in pentane) yielded the product as a colorless solid (10 mg, 54%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.05 (s, 1H), 7.00 (s, 1H), 5.73 (d, *J* = 1.4 Hz, 1H), 5.25 (d, *J* = 1.3 Hz, 1H), 3.83 (s, 3H), 1.87 (s, 3H), 1.63 (s, 4H), 1.23 (s, 6H), 1.20 (s, 6H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 167.1, 149.3, 145.7, 144.5, 142.5, 138.1, 132.9, 129.8, 129.1, 128.2, 128.2, 126.7, 117.0, 52.2, 35.3, 35.3, 34.1, 34.0, 32.1, 32.0, 20.1. **HRMS** (ESI+) calc. for $C_{25}H_{31}O_2$ [M+H]$^+$ 363.2319, found 363.2324.

Methyl 4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoate (^{13}C-25)



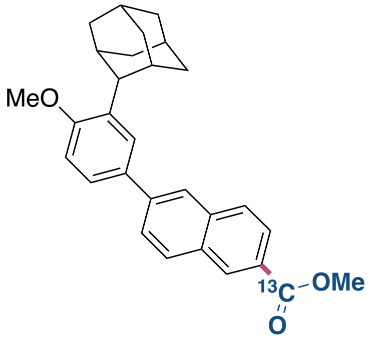
The title compound was prepared according to General Procedure F, employing Bexarotene (17 mg, 0.05 mmol, 1.0 equiv). Flash column chromatography (1-2% EtOAc in pentane) yielded the product as a colorless solid (10 mg, 55%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.95 (dd, *J* = 8.5, 4.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.13 (s, 1H), 7.08 (s, 1H), 5.81 (d, *J* = 1.3 Hz, 1H), 5.32 (d, *J* = 1.3 Hz, 1H), 3.91 (d, *J* = 3.8 Hz, 3H), 1.94 (s, 3H), 1.70 (s, 4H), 1.30 (s, 6H), 1.27 (s, 6H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 167.1 (^{13}C-enriched), 149.3, 145.7, 144.5, 142.5, 138.1, 132.9, 129.8 (d, *J* = 2.5 Hz), 129.4, 128.7, 128.2 (d, *J* = 4.6 Hz), 126.7 (d, *J* = 4.7 Hz), 117.0, 52.2 (d, *J* = 2.5 Hz), 35.3, 35.3, 34.1, 34.0, 32.1, 32.0, 20.1. **HRMS** (ESI+) calc. for $C_{24}{}^{13}CH_{31}O_2$ [M+H]$^+$ 364.2352, found 364.2348.

Methyl 6-(3-(1-adamantyl)-4-methoxyphenyl)-2-naphthoate (26)



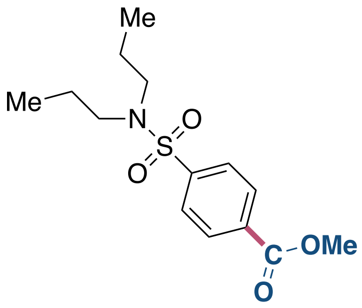
The title compound was prepared according to General Procedure F, employing Adapalene (0.1 mmol). Flash column chromatography (EtOAc 0-20% in heptane) yielded the product as a white solid (28.3 mg, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.01 (s, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.80 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.60 (d, *J* = 2.3 Hz, 1H), 7.55 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 3.99 (s, 3H), 3.91 (s, 3H), 2.18 (s, 6H), 2.10 (s, 3H), 1.80 (s, 6H). **^{13}C NMR** (101 MHz, CDCl3) δ 167.49, 159.06, 141.55, 139.15, 136.09, 132.71, 131.38, 130.99, 129.85, 128.37, 127.06, 126.64, 126.14, 125.87, 125.71, 124.88, 112.24, 55.32, 52.36, 40.74, 37.35, 37.27, 29.25. **HRMS** (ESI+) calc. for $C_{29}H_{31}O_3^+$ [M+H]$^+$ 427.226, found 427.2264.

Methyl 6-(3-(1-adamantyl)-4-methoxyphenyl)-2-naphthoate (^{13}C-26)



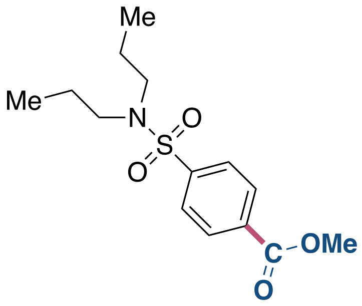
The title compound was prepared according to General Procedure F, employing Adapalene (0.1 mmol). Flash column chromatography (EtOAc 0-20% in heptane) yielded the product as a white solid (27.3 mg, 64%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 3.1 Hz, 1H), 8.07 (ddd, *J* = 8.6, 3.4, 1.7 Hz, 1H), 8.02 (s, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.80 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.55 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 3.99 (d, *J* = 3.8 Hz, 3H), 3.91 (s, 3H), 2.19 (s, 6H), 2.11 (s, 3H), 1.81 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.47 (^{13}C-enriched), 159.06, 141.54, 139.14, 136.08, 132.69, 131.37 (d, *J* = 4.4 Hz), 130.97 (d, *J* = 2.9 Hz), 129.83, 128.35 (d, *J* = 4.4 Hz), 127.41, 126.62, 126.12, 125.86, 125.71 (d, *J* = 2.9 Hz), 124.87, 112.24, 52.34 (d, *J* = 2.3 Hz), 40.74, 37.26, 29.24. **HRMS** (ESI+) calc. for $C_{28}{}^{13}CH_{31}O_3^+$ [M+H]$^+$ 428.230, found 428.2308.

Methyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (27)



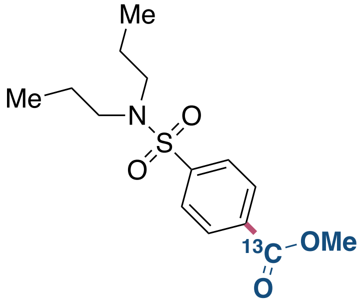
The title compound was prepared according to General Procedure F, employing probenecid (26 mg, 1.0 equiv). Flash column chromatography (7% EtOAc in pentane) yielded the product as a light-yellow solid (16 mg, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 3.96 (s, 3H), 3.15–3.05 (m, 4H), 1.62–1.47 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 144.4, 133.6, 130.4, 127.1, 52.8, 50.0, 22.1, 11.3. **HRMS** (ESI+) calc. for $C_{14}H_{22}NO_4S$ $[M+H]^+$ 300.1264, found 300.1264.

Methyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (27)



The title compound was prepared according to General Procedure A, employing 4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)-*N,N*-dipropylbenzenesulfonamide (35 mg, 1.0 equiv). Flash column chromatography (7% EtOAc in pentane) yielded the product as a light-yellow solid (23 mg, 79%).

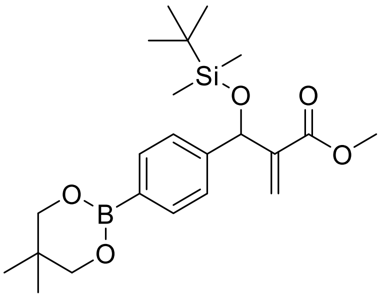
Methyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (^{13}C-27)



The title compound was prepared according to General Procedure F, employing probenecid (26 mg, 1.0 equiv). Flash column chromatography (7% EtOAc in pentane) yielded the product as a light-yellow oil (17 mg, 57%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18–8.12 (m, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 3.95 (d, *J* = 3.9 Hz, 3H), 3.14–3.05 (m, 4H), 1.61–1.48 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9 (^{13}C-enriched), 144.1 (d, *J* = 1.3 Hz), 133.5 (d, *J* = 74.8 Hz), 130.4 (d, *J* = 2.6 Hz), 127.1 (d, *J* = 4.7 Hz), 52.7 (d, *J* = 2.5 Hz), 50.0, 22.1, 11.3. **HRMS** (ESI+) calc. for $C_{13}{}^{13}CH_{22}NO_4S$ $[M+H]^+$ 301.1298, found 301.1298.

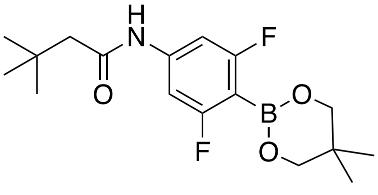
Synthesis and Characterization of Boronic Esters Applied in the Scope Presented in Table 2

Methyl 2-(((tert-butyldimethylsilyl)oxy)(4-(5,5-dimethyl-1,3,2-dioxaborinan-2 yl)phenyl)methyl)acrylate (A)

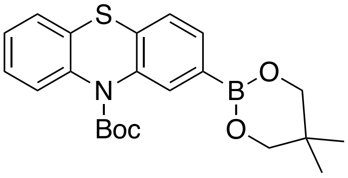


The title compound was prepared according to an adapted literature procedure[1] from methyl 2-((4-bromophenyl)((tert-butyldimethylsilyl)oxy)methyl)acrylate (1.0 mmol). In a glovebox under argon atmosphere, to a 20 mL COtube glassware were added anhydrous KOAc (3 mmol, 0.294 g, 3.0 equiv), $B_2(OH)_4$ (2 mmol, 180 mg, 2.0 equiv), Xphos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) (1 mol%), XPhos-Pd-G1 (2 mol%), and (hetero)aryl halide (1 mmol, 1.0 equiv) followed by dried EtOH (5 mL). The resulting mixture was then heated to 80 °C and stirred for 8 h. The reaction was then cooled to room temperature, transferred to a 100 mL roundbottom flask and concentrated *in vacuo*. The residue was then diluted with ethyl acetate (25 mL) and washed with saturated brine (25 mL). The organic layer was dried with $MgSO_4$ and concentrated. The residue was then dissolved in DCM (CH_2Cl_2, 5 mL), and neopentyl glycol (4 mmol, 208 mg, 2.0 equiv) was added and stirred at room temperature overnight. Afterwards the reaction mixture was concentrated and purification by flash column chromatography (0:100 to 10:90 ethyl acetate in heptane) yielded the product as brown oil (134 mg, 32%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 6.23 (s, 1H), 6.04 (s, 1H), 5.61 (s, 1H), 3.75 (s, 4H), 3.66 (s, 3H), 1.01 (s, 6H), 0.86 (s, 9H), 0.04 (s, 3H), -0.13 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$ δ 166.54, 145.19, 144.03, 133.76, 126.49*, 124.06, 72.91, 72.44, 51.75, 32.02, 25.90, 22.07, 18.33, -4.71, -4.93. **HRMS** (ESI+) calc. for $C_{17}H_{27}BNaO_5Si^+$ $[M+H]^+$ 373.1613, found: 373.1608.

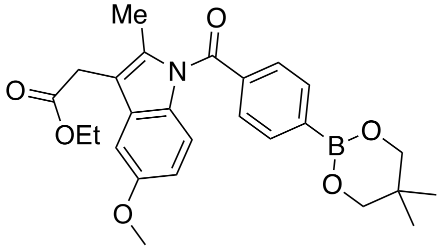
N-(4-(5,5-dimethyl-1,3,2-Dioxaborinan-2-yl)-2,6-difluorophenyl)-3,3-dimethylbutanamide (B)

The title compound was prepared according to an adapted literature procedure[1] from N-(4-bromo-2,6-difluorophenyl)-3,3-dimethylbutanamide (1.0 mmol). In a glovebox under argon atmosphere, to a 20 mL COtube glassware were added anhydrous KOAc (3 mmol, 0.294 g, 3.0 equiv), $B_2(OH)_4$ (2 mmol, 180 mg, 2.0 equiv), Xphos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) (1 mol%), XPhos-Pd-G1 (2 mol%), and (hetero)aryl halide (1 mmol, 1.0 equiv) followed by dried EtOH (5 mL). The resulting mixture was then heated to 80 °C and stirred for 8 h. The reaction was then cooled to room temperature, transferred to a 100 mL roundbottom flask and concentrated *in vacuo*. The residue was then diluted with ethyl acetate (25 mL) and washed with saturated brine (25 mL). The organic layer was dried with $MgSO_4$ and concentrated. The residue was then dissolved in DCM (CH_2Cl_2, 5 mL), and neopentyl glycol (4 mmol, 208 mg, 2.0 equiv) was added and stirred at room temperature overnight. Afterwards the reaction mixture was concentrated and purification by flash column chromatography (5:95 to 20:80 ethyl acetate in toluene) yielded the product as brown crystals (192.1 mg, 57%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.3 Hz, 2H), 6.68 (s, 1H), 3.75 (s, 4H), 2.28 (s, 2H), 1.12 (s, 9H), 1.01 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.19.**^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.96, 158.55 (t, J = 4.3 Hz), 156.05 (d, J = 4.1 Hz), 116.83 – 116.10 (m), 115.80 (d, J = 16.2 Hz), 72.50, 50.47, 32.02, 31.24, 29.86, 21.94. **HRMS** (ESI+) calc. for $C_{12}H_{17}BF_2NO_3^+$ $[M+H]^+$ 272.1264, found: 272,1263.

N-Boc-2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-10H-phenothiazine (C)

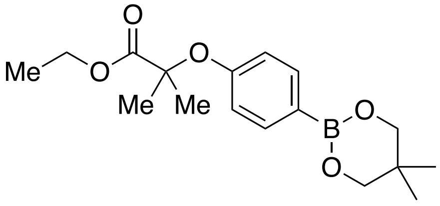
The substrate was synthesized in accordance with literature procedure on a 0.6 mmol scale.[1] The product was obtained as an off-white solid (90 mg, 36% yield). Spectral data is in accordance with previous reports. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.32 (d, J = 7.7 Hz, 2H), 7.26-7.23 (m, 1H), 7.13 (t, J = 7.6 Hz, 1H), 3.76 (s, 4H), 1.49 (s, 9H), 1.01 (s, 6H).

Methyl 2-(1-(4-(difluoromethyl)benzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (D)



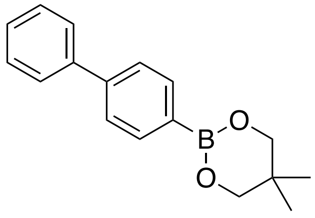
The substrate was synthesized in accordance with literature procedure on a 1.0 mmol scale.[2] The product was obtained as a white solid (322 mg, 72% yield). Spectral data is in accordance with previous reports. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 1H), 6.63 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.80 (s, 4H), 3.65 (s, 2H), 2.36 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.05 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.43, 170.21, 156.35, 137.83, 136.50, 134.50, 131.44, 131.05, 129.05, 115.64, 112.85, 112.00, 101.57, 72.89, 61.44, 56.15, 32.39, 30.95, 22.38, 14.71, 13.89.

Ethyl 2-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenoxy)-2-methylpropanoate (E)



The substrate was synthesized in accordance with literature procedure on a 2.5 mmol scale.[1] The product was obtained as an off-white solid (487 mg, 77% yield). Spectral data is in accordance with previous reports. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 4H), 1.61 (s, 6H), 1.22 (t, *J* = 7.1 Hz, 4H), 1.01 (s, 6H).

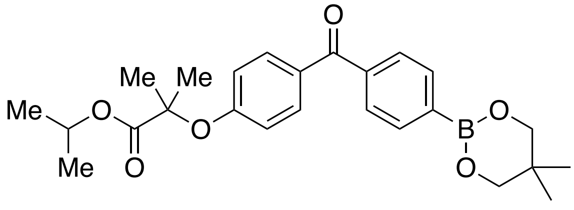
2-(Biphenyl-4-yl)-5,5-dimethyl-1,3,2-dioxaborinane (F)



To a flame-dried round-bottomed flask was added 4-biphenylboronic acid (2.97 g, 15 mmol) and Et_2O (40 mL) followed by 2,2-Dimethyl-1,3-propanediol (1.88 g, 18 mmol) under an argon atmosphere. The reaction mixture was stirred overnight at room temperature. After 16 hours, evaporation of the solvent and the 2,2-dimethyl-1,3-propanediol *in vacuo*, followed by washing with water afforded the product as a white solid (3.93 g, 98%). **^{1}H**

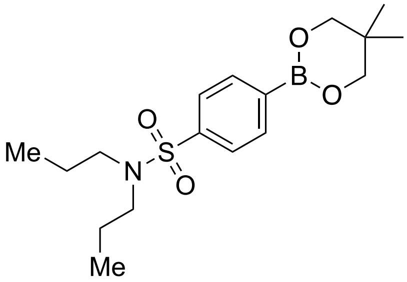
NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.64-7.59 (m, 4H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 3.80 (s, 4H), 1.04 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 141.4, 134.5, 128.9, 127.5, 127.3, 126.5, 72.5, 32.0, 22.1.

Isopropyl 2-(4-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoyl)phenoxy)-2-methylpropanoate (G)



The substrate was synthesized in accordance with literature procedure on a 1.25 mmol scale.[1] The product was obtained as a white solid (142 mg, 26% yield). Spectral data is in accordance with previous reports. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.9 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.08 (p, *J* = 6.3 Hz, 1H), 3.80 (s, 4H), 1.66 (s, 6H), 1.20 (d, *J* = 6.3 Hz, 6H), 1.04 (s, 6H).

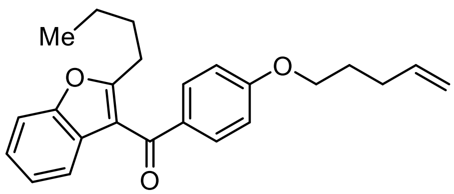
4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)-N,N-dipropylbenzenesulfonamide (H)



The title compound was prepared according to literature procedure.[3] In an argon filled glovebox, to a vial (10 mL) was added probenecid (0.3 mmol, 85.6 mg), TFFH (0.3 mmol, 79.2 mg), proton sponge (0.3 mmol, 64.3 mg), and THF (0.5 mL). The solution was stirred for 20 min resulting in formation of the acid fluoride. In a separate 4 mL vial, a standard solution of $Ni(cod)_2$ (0.03 mmol, 8.3 mg) and PCy_3 (0.06 mmol, 12 mg) in THF (0.2 mL) was prepared. After formation of the acyl fluoride, the Ni-catalyst was added from the standard solution (0.1 mL, 5 mol%) and, subsequently, B_2nep_2 (0.6 mmol, 136 mg, 2 equiv) was added to the reactor vial. The reaction was sealed, transferred out of the glovebox and into a pre-heated block at 115 °C to stir for 24 h. The reaction was allowed to cool to room tempertaure before Et_2O (10 mL) and saturated $NaHCO_3$ (10 mL) were added. The organic layer was collected, and the aqueous solution was further extracted with Et_2O (2 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel using EtOAc in hexanes afforded the title compound as a colorless solid (51 mg, 48%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 3.78 (s, 4H), 3.11–3.03 (m, 4H), 1.60–1.46 (m, 4H), 1.03 (s, 6H), 0.86 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 134.5, 126.1, 72.6, 50.1, 32.1, 22.1, 22.0, 11.3. The NMR data are in accordance with literature.[3]

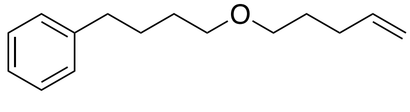
Synthesis and Characterization of Alkene and Alkynes Applied in the Scope Presented in Table 2

(2-Butylbenzofuran-3-yl)(4-(pent-4-en-1-yloxy)phenyl)methanone (I)



In a flame-dried round-bottomed flask under an inert atmosphere (2-butylbenzofuran-3-yl)(4-hydroxyphenyl)methanone (2.94 g, 10 mmol, 1.0 equiv) was dissolved in dry acetone (20 mL). Potassium carbonate (2.76 g, 2.0 equiv) was added followed by 5-bromopentene (1.64 g, 1.1 equiv) and the mixture was stirred at 60 °C for 16 h. The reaction was then cooled to room temperature before being filtered through a celite plug using acetone to wash, and then concentrated *in vacuo*. Flash column chromatography (10-20% EtOAc in pentane) afforded the title compound as a yellow oil (2.22 g, 61%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.50–7.45 (m, 1H), 7.38–7.33 (m, 1H), 7.30–7.24 (m, 1H), 7.21–7.15 (m, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.94–5.80 (m, 1H), 5.13–4.99 (m, 2H), 4.06 (t, *J* = 6.4 Hz, 2H), 2.96–2.86 (m, 2H), 2.32–2.22 (m, 2H), 1.98–1.87 (m, 2H), 1.81–1.70 (m, 2H), 1.36 (app. h, *J* = 7.4 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.6, 164.8, 163.1, 153.7, 137.7, 131.9, 131.8, 127.4, 124.3, 123.4, 121.4, 116.9, 115.6, 114.3, 111.1, 67.6, 30.3, 30.2, 28.4, 27.9, 22.5, 13.9. **HRMS** (ESI+) calc. for $C_{24}H_{27}O_3$ $[M+H]^+$ 363.1955, found 363.1961.

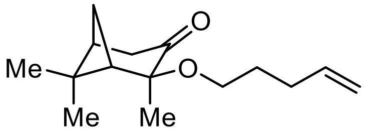
(4-(But-3-en-1-yloxy)butyl)benzene (J)



To a stirred solution of NaOH (2.00 g, 50.4 mmol, 7.0 equiv.) in H_2O (4.0 mL, 50 wt%) was added TBAB (464 mg, 1.44 mmol, 20 mol%), 4-phenylbutan-1-ol (1.10 mL, 7.20 mmol, 1.0 equiv,) and 5-bromo-1-pentene (2.60 mL, 21.6 mmol, 3.0 equiv.). After stirring vigorously overnight, the resulting reaction mixture was diluted with water (20 mL) and Et_2O (25 mL), the organic layer separated, and the aqueous layer further extracted with Et_2O (2 × 25 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude product which was purified by column chromatography (10% Et_2O in pentane) to give the title compound as a colorless oil (1.11 g, 5.10 mmol, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.12 (m, 5H), 5.91–5.71 (m, 1H), 5.09–4.90 (m, 2H), 3.42 (app. q, *J* = 6.4

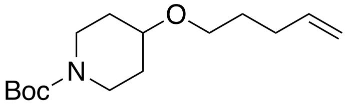
Hz, 4H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.17-2.07 (m, 2H), 1.76–1.55 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6, 138.5, 128.5, 128.4, 125.8, 114.8, 70.8, 70.3, 35.9, 30.5, 29.5, 29.1, 28.2. **HRMS** (ESI+) calc. for $C_{22}H_{15}NaO$ $[M+Na]^+$ 241.1563, found 241.1565.

(*1S,2S,5S*)-2,6,6-Trimethyl-2-(pent-4-en-1-yloxy)bicyclo[3.1.1]heptan-3-one (K)



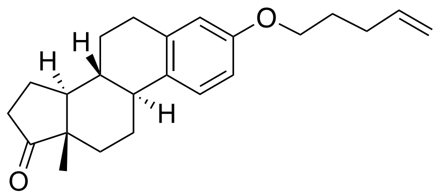
In a flame-dried round bottomed flask was added 2-hydroxy-3-pinanone (841 mg, 5 mmol) in DMF (20 mL) under an argon atmosphere. Under stirring was added NaH (240 mg, 1.2 equiv) portion wise (caution: gas evolution). The reaction was stirred at room temperature until end of gas evolution (15-30 min). Then, 5-bromopentene (745 mg, 1 equiv) was added dropwise and the reaction stirred at room temperature overnight. The reaction was quenched with water (caution: gas evolution) and extracted with diethyl ether (3 x 15 mL). The organic phases were washed with brine and dried over $MgSO_4$. Flash column chromatography (2% EtOAc in pentane) afforded the desired product as a colorless oil (480 mg, 41%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.78 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.05–4.88 (m, 2H), 3.43–3.28 (m, 2H), 2.62–2.56 (m, 2H), 2.42–2.33 (m, 1H), 2.16 (t, *J* = 6.1 Hz, 1H), 2.12–2.02 (m, 3H), 1.83 (d, *J* = 10.6 Hz, 1H), 1.63–1.53 (m, 2H), 1.35 (s, 3H), 1.30 (s, 3H), 0.85 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.7, 138.6, 114.7, 80.2, 61.4, 50.2, 43.9, 39.3, 38.8, 30.6, 29.5, 28.3, 27.6, 22.8, 19.8. **HRMS** (ESI+) calc. for $C_{15}H_{15}O_2$ $[M+H]^+$ 237.1849, found 237.1848.

***tert*-Butyl 4-(pent-4-en-1-yloxy)piperidine-1-carboxylate (L)**



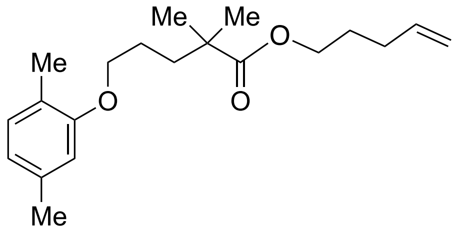
In a flame-dried round bottomed flask was added *tert*-butyl 4-hydroxypiperidine-1-carboxylate (1006 mg, 5 mmol) in DMF (20 mL) under an argon atmosphere. Under stirring was added NaH (240 mg, 1.2 equiv) portionwise (caution: gas evolution). The reaction was stirred at rt until end of gas evolution (15-30 min). To the solution was added 5-bromopentene (894 mg, 1.2 equiv) dropwise and the reaction stirred at rt overnight. The reaction was quenched with water (caution: gas evolution) and extracted with diethyl ether (3 x 15 mL). The organic phases were washed with brine and dried over $MgSO_4$. Flash column chromatography (10% EtOAc in pentane) afforded the desired product as a colorless oil (484 mg, 36%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.06–4.99 (m, 1H), 4.98–4.93 (m, 1H), 3.84–3.68 (m, 2H), 3.50–3.36 (m, 3H), 3.07 (ddd, *J* = 13.1, 9.2, 3.5 Hz, 2H), 2.17–2.08 (m, 2H), 1.87–1.75 (m, 2H), 1.71–1.62 (m, 2H), 1.55–1.47 (m, 2H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.0, 138.5, 114.9, 79.5, 74.7, 67.4, 41.6, 31.3, 30.5, 29.3, 28.6. The NMR data are in accordance with literature reports.[4]

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(pent-4-en-1-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H* cyclopenta[*a*]phenanthren-17-one (M)



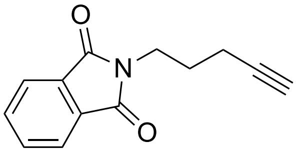
In a flame-dried round-bottomed flask under an inert atmosphere, estrone (1.35 g, 5 mmol, 1.0 equiv) was dissolved in dry DMF (20 mL). Potassium carbonate (2.07 g, 3.0 equiv) was added followed by 5-bromopentene (820 mg, 1.1 equiv) and the mixture was stirred at 50 °C for 16 h. The reaction was cooled to room temperature before being diluted with EtOAc (40 mL). The organic phase was washed with H_2O (3 x 30 mL) and brine (1 x 30 mL), before being dried over Na_2SO_4. Flash column chromatography (20% EtOAc in pentane) afforded the title compound as white solid (1.394 g, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 5.85 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.09–5.02 (m, 1H), 5.02–4.97 (m, 1H), 3.94 (t, *J* = 6.4 Hz, 2H), 2.93–2.86 (m, 2H), 2.50 (dd, *J* = 18.8, 8.4 Hz, 1H), 2.47–2.43 (m, 1H), 2.34–2.30 (m, 7H), 1.81–1.69 (m, 2H), 1.69–1.36 (m, 6H), 0.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 221.2, 157.2, 138.1, 137.9, 132.1, 126.4, 115.3, 114.7, 112.3, 67.2, 50.6, 48.2, 44.1, 38.5, 36.0, 31.7, 30.3, 29.8, 28.6, 26.7, 26.1, 21.7, 14.0. The NMR data are in accordance with literature reports.[5]

Pent-4-en-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (N)



In a flame-dried round-bottomed flask was added gemfibrozil (501 mg, 2 mmol) and K_2CO_3 (553 mg, 2 equiv) in dry acetonitrile (10 ml). To the suspension was added 5-bromo-1-pentene (473 *μ*L, 2.0 equiv.) and the reaction mixture was stirred at 80 °C overnight. After 16 hours, the reaction was cooled to room temperature, and the precipitate was filtered off and washed with EtOAc (3x 10 mL). The filtrate was concentrated under reduced pressure. Flash column chromatography (3% EtOAc in pentane) afforded the title compound as a colorless oil (560 mg, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 5.80 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.10–4.93 (m, 2H), 4.07 (t, *J* = 6.5 Hz, 2H), 3.96–3.87 (m, 2H), 2.30 (s, 3H), 2.20–2.08 (m, 5H), 1.81–1.67 (m, 6H), 1.22 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.0, 157.1, 137.6, 136.6, 130.4, 123.7, 120.8, 115.5, 112.1, 68.1, 63.9, 42.2, 37.3, 30.3, 28.0, 25.3, 21.6, 15.9. The NMR data are in accordance with literature reports.[6]

2-(Pent-4-yn-1-yl)isoindoline-1,3-dione (O)

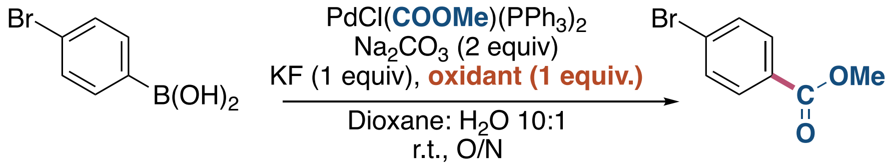


Prepared according to literature protocol.[7] In an argon-filled glovebox, to an 8 mL vial equipped with a screw cap was added phthalimide (621 mg, 1.2 equiv), K_2CO_3 (486 mg, 1.0 equiv), KI (10 mg), dry DMF (4 mL), and 5-chloropent-1-yne (344 mg, 1.0 equiv). The reaction was sealed and transferred out of the glovebox to stir at 70 °C overnight. The solution was allowed to cool to room temperature before being diluted with water and extracted with Et_2O (3x10 mL). The organic phases were washed with water (2x10 mL) and brine (3x10 mL) before being dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Flash column chromatography (CH_2Cl_2) afforded the title compound as a colorless solid (626 mg, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.82 (m, 2H), 7.74–7.69 (m, 2H), 3.80 (t, *J* = 7.0 Hz, 2H), 2.27 (td, *J* = 7.1, 2.7 Hz, 2H), 2.00–1.88 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 134.1, 132.3, 123.4, 83.1, 69.1, 37.3, 27.4, 16.43. The NMR data are in accordance with literature reports.[7]

Optimization of the Oxidative Reaction Conditions

In a glove box under argon atmosphere to a 8 mL vial was added Pd-1 (0.1 mmol, 73 mg, 1 equiv.), $ArB(OR)_2$ (0.1 mmol, 1 equiv.), KF (0.1 mmol, 6 mg, 1 equiv.), Na_2CO_3 (0.2 mmol, 21 mg, 2 equiv.), oxidant (0.1 mmol, 1 equiv.), dioxane (5.4 mL) and H_2O (0.6 mL). The vial was sealed, wrapped with parafilm and allowed to stir outside the glovebox overnight. After 16 hours, H_2O (2 ml) and EtOAc (4 ml) were added, followed by a stock solution of TMB (trimethoxybenzene, internal standard) in EtOAc (0.1 mmol). From this crude reaction mixture, 2 mL of the organic layer was removed, concentrated, and analyzed by quantitative ^1H NMR in which the integral ratio of TMB to product was determined.

Table S1. Optimization of oxidative conditions for aryl bromides



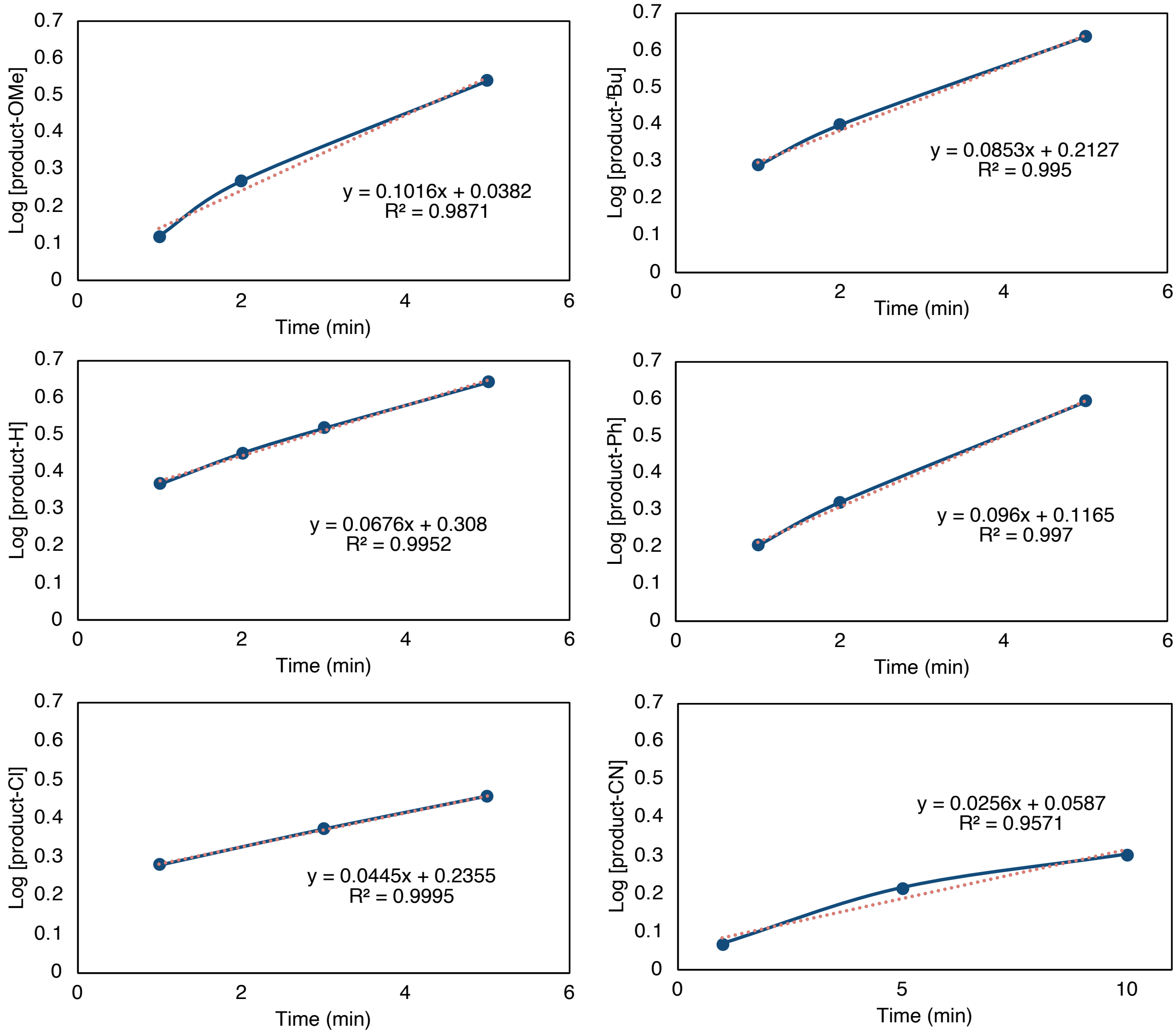
Entry	Deviation	Yield (%)
1	no oxidant	10
2	1,4-benzoquinone	11
3	DDQ	22
4	O_2	15
5	$K_2S_2O_8$	25
6	Togni Reagent II	34
7	$PhI(OAc)_2$	65
8	$PhI(OAc)_2$ (1.5 equiv.)	72
9	$PhI(OAc)_2$ (2 equiv.)	65

Hammet Analysis

Representative Procedure for Synthesis of Aryl Esters From Boronic Acids for Hammett Analysis.

In a glove box under argon atmosphere to a 4 mL vial equipped with a stir bar was added Pd-1 (0.025 mmol, 18.2 mg, 1 equiv.), $ArB(OH)_2$ (0.25 mmol, 10 equiv.), KF (0.025 mmol, 1.5 mg, 1 equiv.), Na_2CO_3 (0.05 mmol, 5.3 mg, 2 equiv.) and 1,3,5-trimethoxybenzene (0.025 mmol, 4.2 mg, 1 equiv) from a (1.0 mM stock solution prepared in dioxane). To the vial was then added dioxane (1.35 mL), and H_2O (0.15 mL); stirring was set to 800 rpm and a timer was started.

Aliquots (50 µl) were removed periodically, quenched with 4M HCl (100 µl) and pentane (0.5 mL) was added to ensure residual palladium precipitated. After the time-course of the reaction the quenched aliqouts were removed from the glovebox, diluted with EtOAc (~1 mL), filtered through celite and analysed by GC-FID. Product formation was determined by the ratio of product to internal standard (calibrated by pre-determined response factors).



Supplementary Figure 1. Kinetics data used for the Hammett Plot. R^2 determined from linear regression model in Excel

Comparative Conditions Using Stochiometric CO or CO_2 with Cu or Pd Catalysis

Cu-Catalyzed Carboxylation of Boronic Acids: An adapted literature procedure[8] was performed with the stochiometric release of CO_2. In a glovebox under argon atmosphere to chamber 1 of a two-chamber system was added boronic acid (0.13 mmol), IPrCuCl (1.9 mg, 3 mol %), KOMe (18.7 mg, 0.27 mmol, 2 equiv.), and THF or DMA (1 mL). The chamber was sealed with a screwcap fitted with a Teflon ® seal. To chamber 2 of the two-chamber system was added $BaCO_3$ (0.2 mmol, 39.5 mg, 1.5 equiv.), camphorsulfonic acid (0.4 mmol, 92.9 mg, 3 equiv.) and THF (1 mL). The chamber was quickly sealed with a screwcap fitted with a Teflon ® seal. The two-chamber was removed from the glovebox and allowed to stir at 70 °C for 24 h. After completion, the reaction was quenched with HCl (1 M, 1 mL), diluted with H_2O (2 mL) and extracted with EtOAc (2 ml x 3), followed by the addition of a stock solution of TMB (trimethoxybenzene, internal standard) in EtOAc (0.1 mmol). The organic crude reaction mixture was concentrated, dissolved in $CDCl_3$ and analyzed by quantitative ^1H NMR in which the integral ratio of TMB to product was determined.

Yield from [1,1'-biphenyl]-4-ylboronic acid, THF = 0.0013 mmol, 1 % yield

Yield from (4-cyanophenyl)boronic acid, DMA = 0.0247 mmol, 19 % yield

Yield from (4-(tert-butyl)phenyl)boronic acid, THF = 0.0026 mmol, 2 % yield

Pd-Catalyzed Alkoxycarbonylation of Boronic Acids: An adapted literature procedure[9] was performed with the stochiometric release of CO. In a glovebox under argon atmosphere to chamber 1 of a two-chamber system was added boronic acid (0.1 mmol), $Pd(OAc)_2$ (1.1 mg, 5 mol %), PPh_3 (2.7 mg, 10 mol %), *p*-benzoquinone (11.1 mg, 0.1 mmol, 1 equiv.) and MeOH (2 mL). The chamber was sealed with a screwcap fitted with a Teflon ® seal. To chamber 2 of the two-chamber system was added SilaCOgen (0.15 mmol, 36.4 mg, 1.5 equiv.), KF (0.15 mmol, 8.7 mg, 1.5 equiv.) and DMF (0.5 mL). The chamber was quickly sealed with a screwcap fitted with a Teflon ® seal. The two-chamber was removed from the glovebox and allowed to stir at room temperature for 24 h. After completion, a stock solution of TMB (trimethoxybenzene, internal standard) in EtOAc (0.1 mmol) was added, concentrated, and analyzed by quantitative ^1H NMR in which the integral ratio of TMB to product was determined.

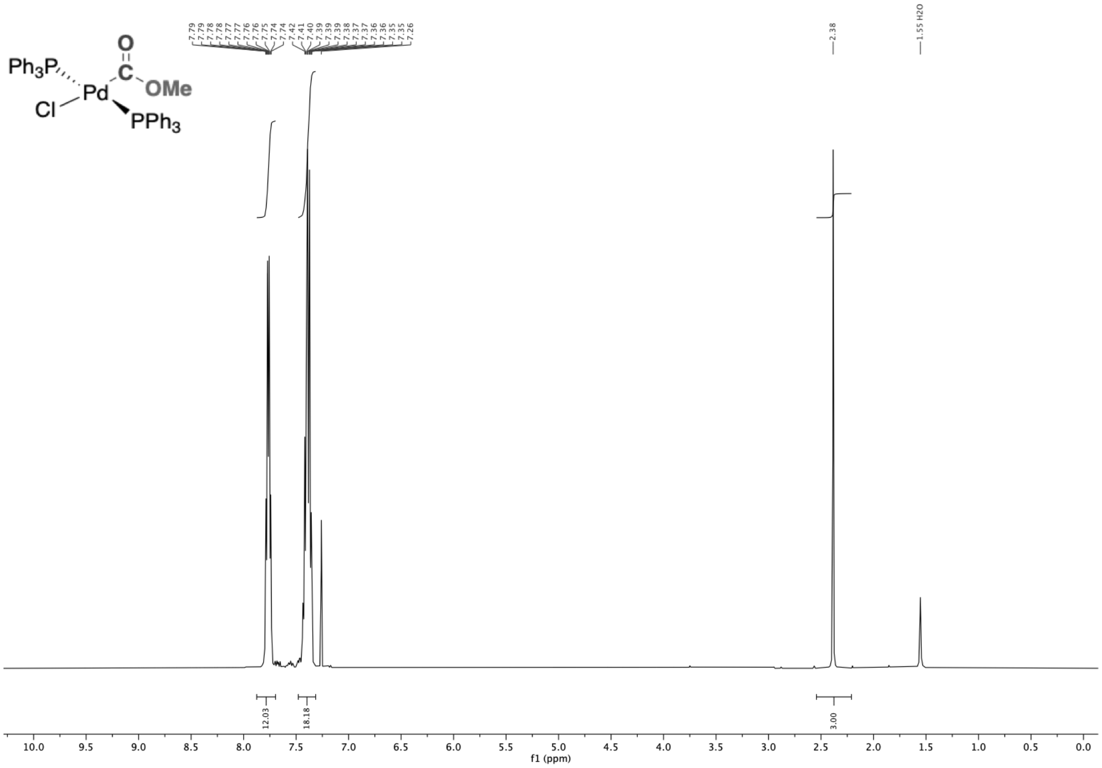
Yield from [1,1'-biphenyl]-4-ylboronic acid = 0.024 mmol, 24 % yield

Yield from (4-cyanophenyl)boronic acid = 0.027 mmol, 27 % yield

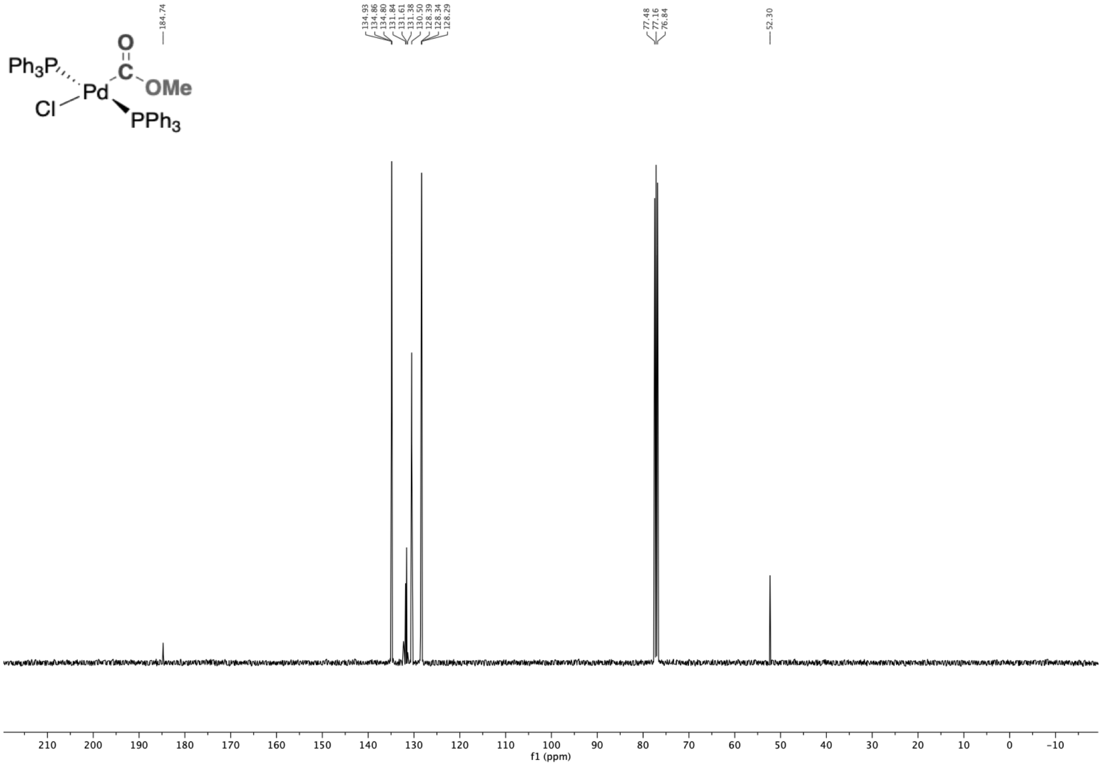
Yield from (4-(tert-butyl)phenyl)boronic acid = 0.054 mmol, 54 % yield

NMR Spectra of Palladium Complexes

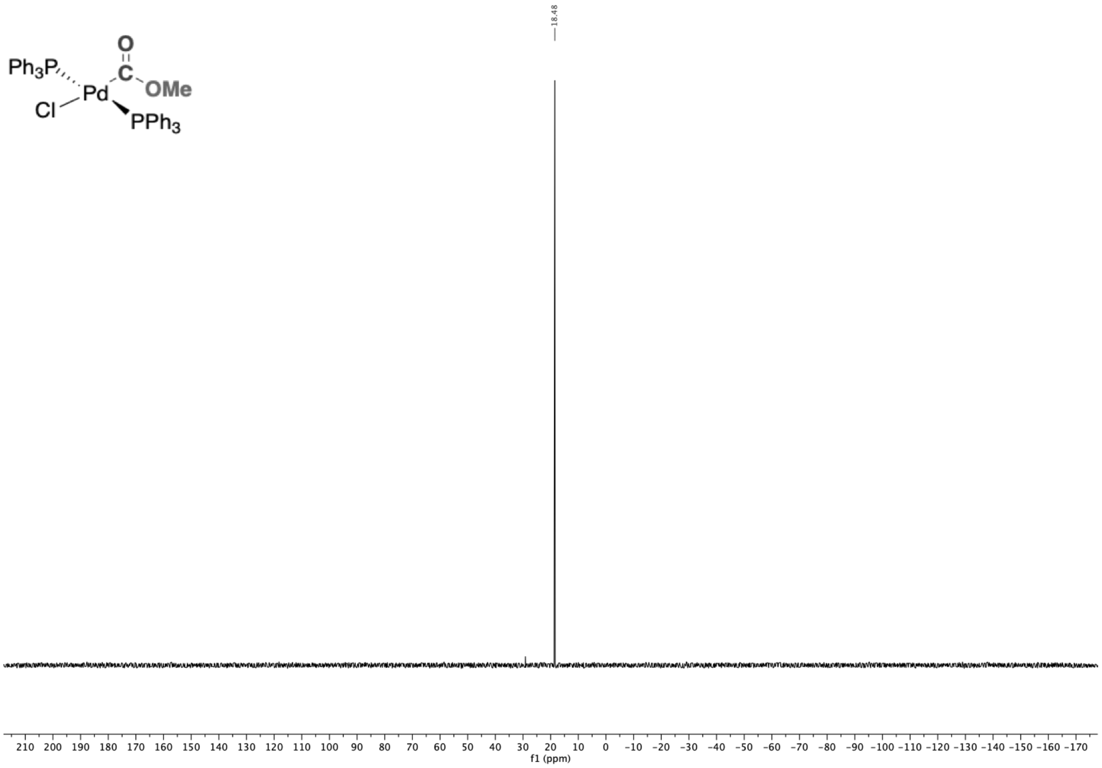
trans-chloro(methoxycarbonyl)bis(triphenylphosphine)palladium(II) (Pd-1) – ^{1}H NMR



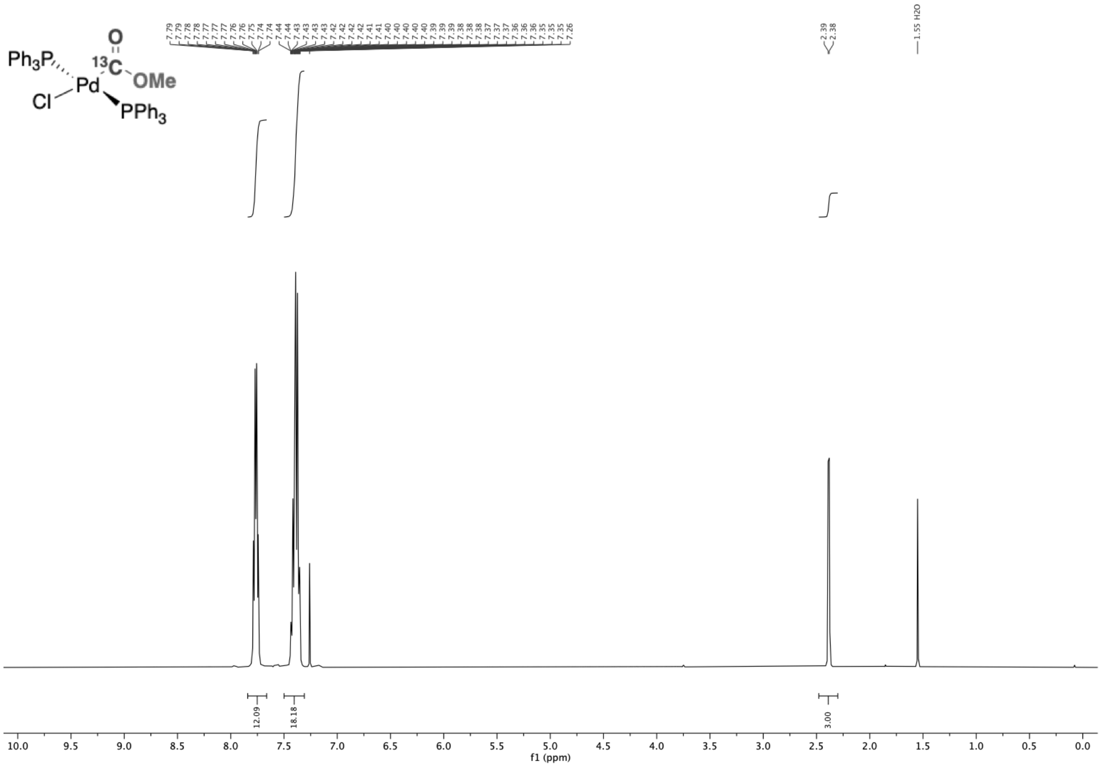
trans-chloro(methoxycarbonyl)bis(triphenylphosphine)palladium(II) (Pd-1) – ^{13}C NMR



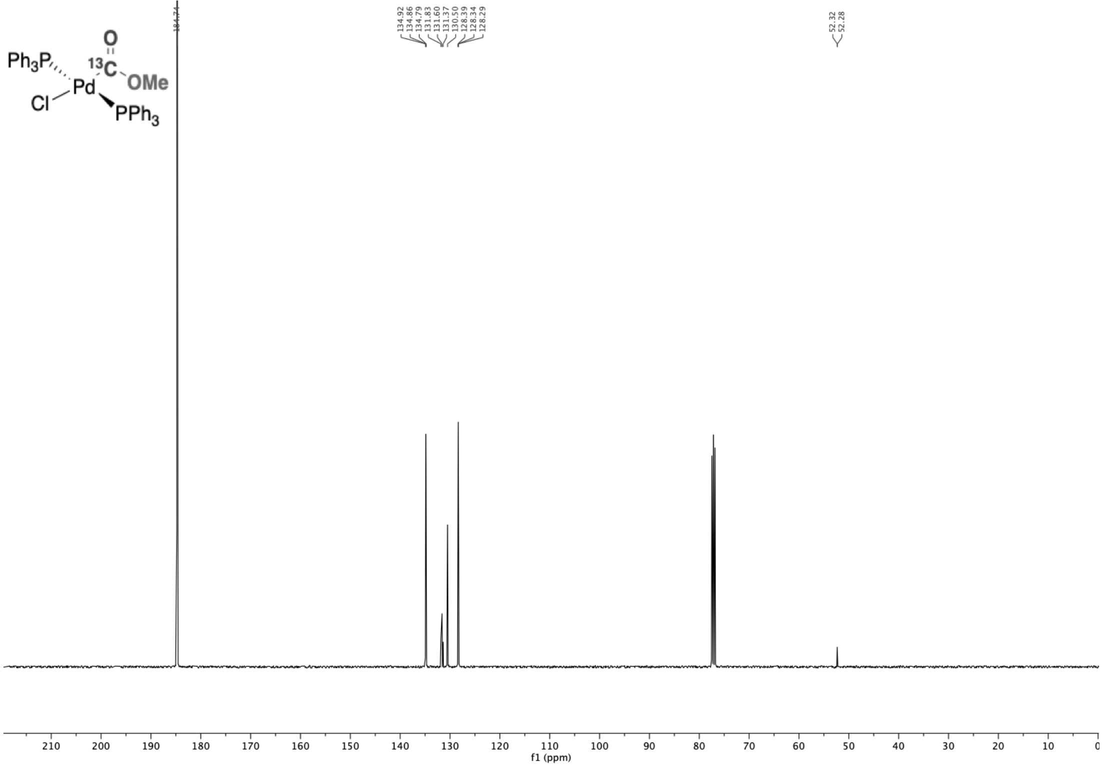
trans-chloro(methoxycarbonyl)bis(triphenylphosphine)palladium(II) (Pd-1) – ^{31}P NMR



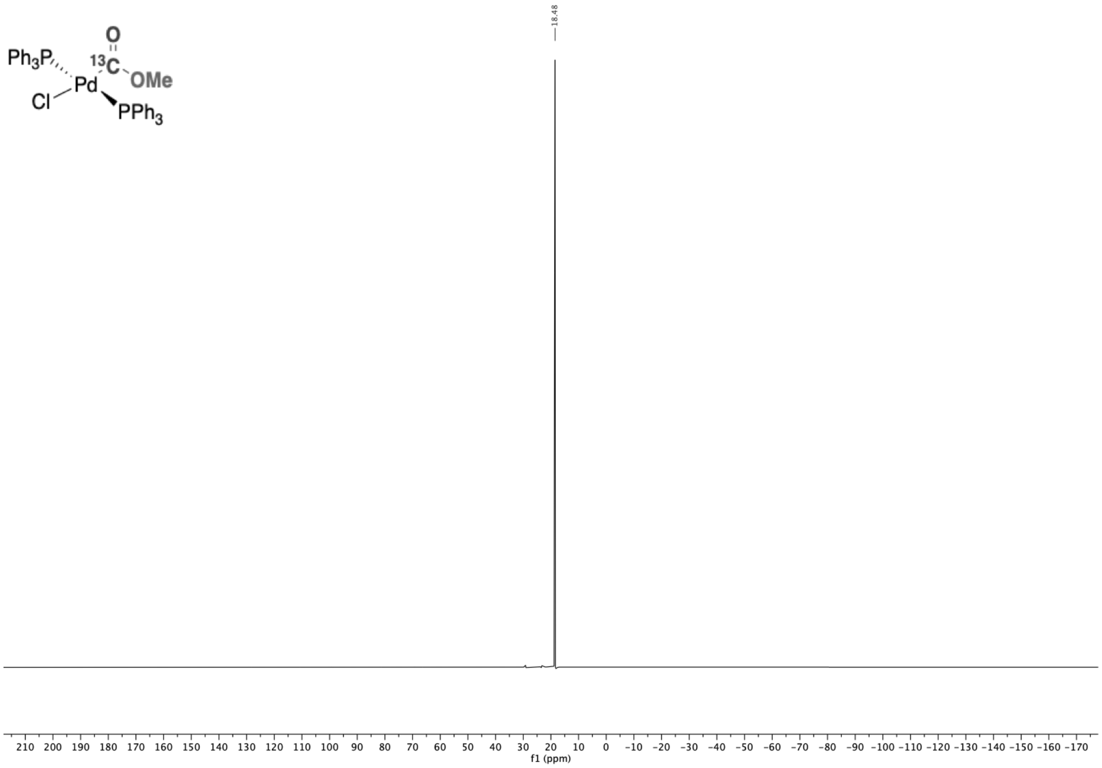
trans-chloro(methoxycarbonyl)bis(triphenylphosphine)palladium(II) (^{13}C Pd-1) – ^{1}H NMR



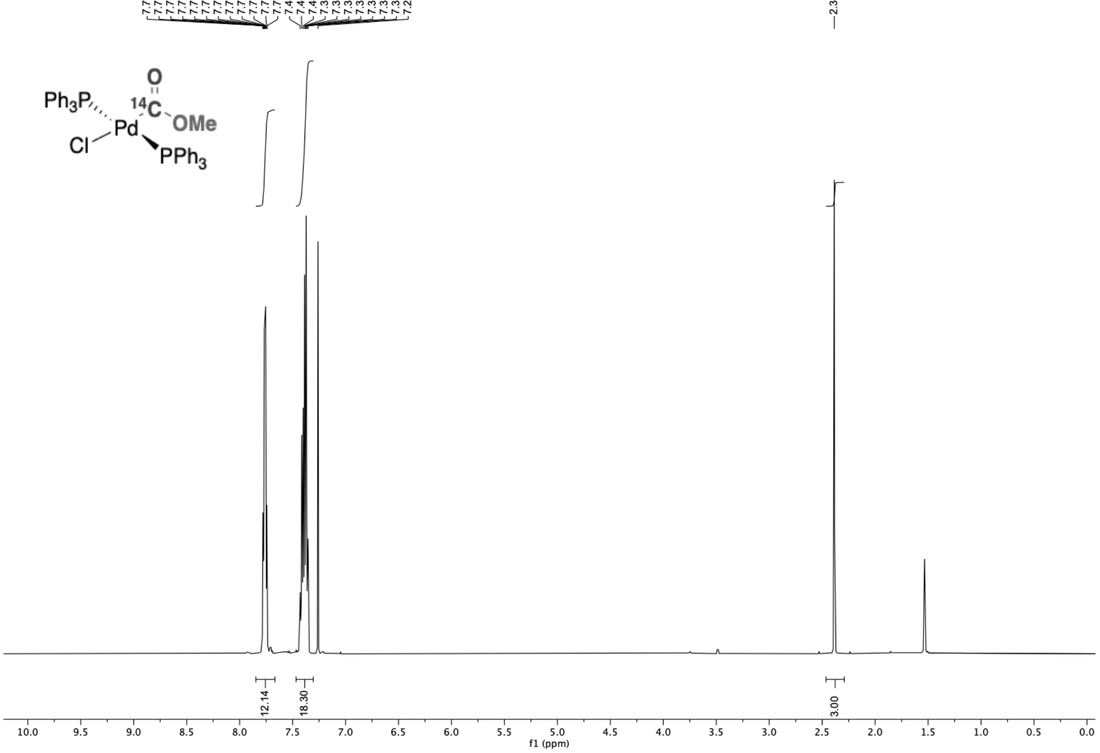
trans-chloro(methoxycarbonyl)bis(triphenylphosphine)palladium(II) (^{13}C Pd-1) – ^{13}C NMR



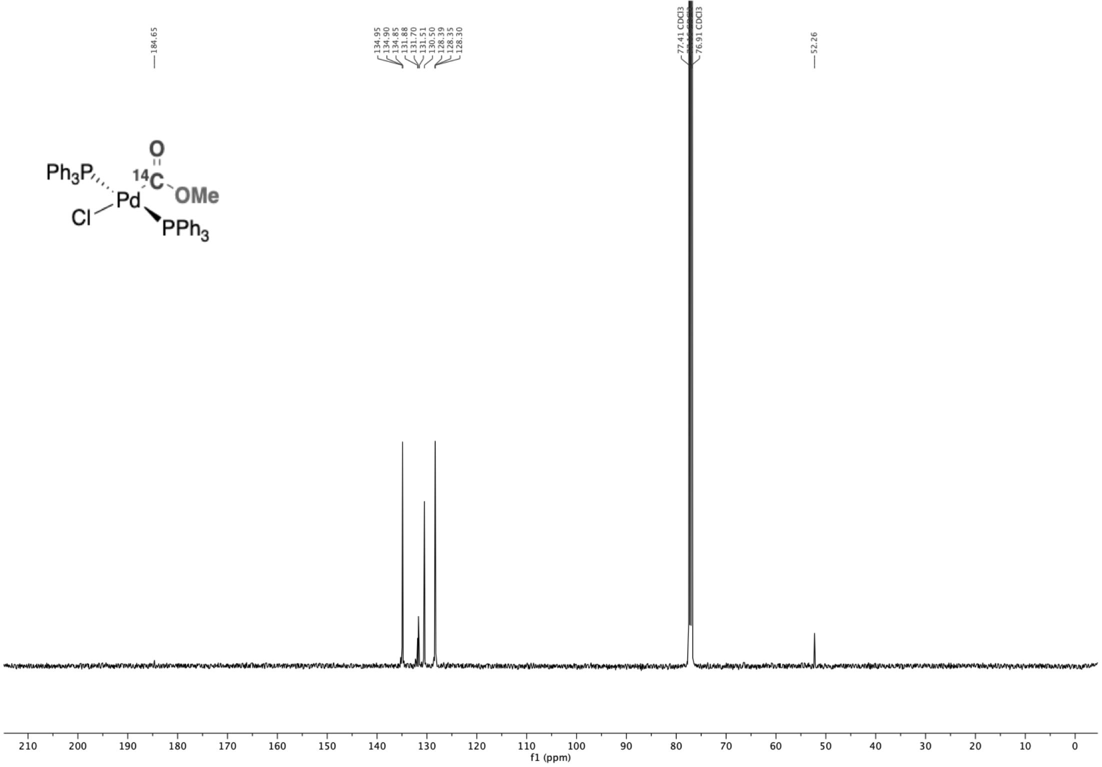
trans-chloro(methoxycarbonyl)bis(triphenylphosphine)palladium(II) (^{13}C Pd-1) – ^{31}P NMR



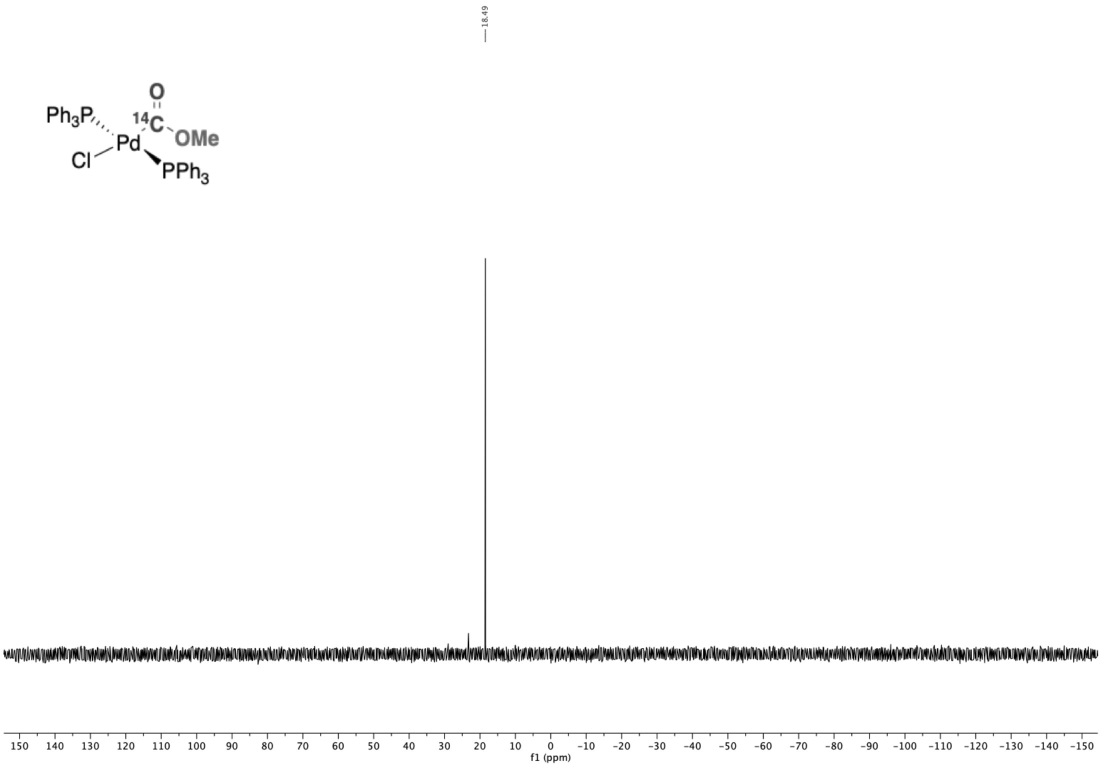
trans-chloro(methoxycarbonyl)bis(triphenylphosphine)palladium(II) (^{14}C Pd-1) – ^{1}H NMR



trans-chloro(methoxycarbonyl)bis(triphenylphosphine)palladium(II) (^{14}C Pd-1) – ^{13}C NMR

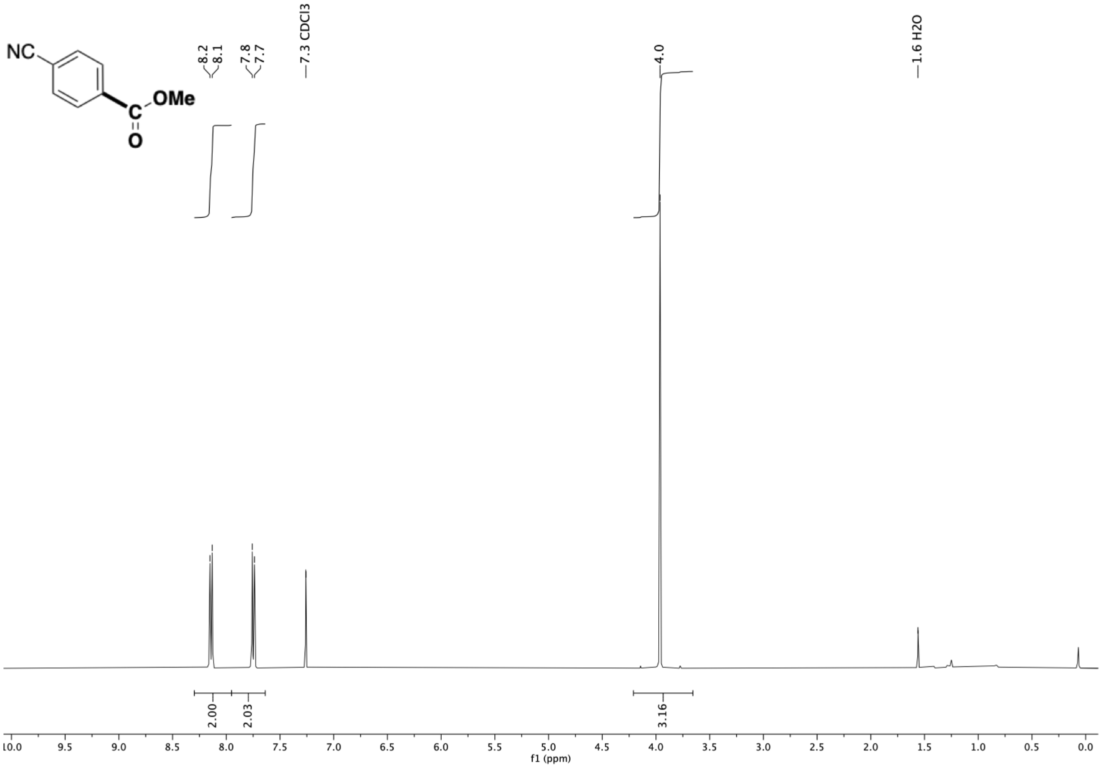


trans-chloro(methoxycarbonyl)bis(triphenylphosphine)palladium(II) (^{14}C Pd-1) – ^{31}P NMR

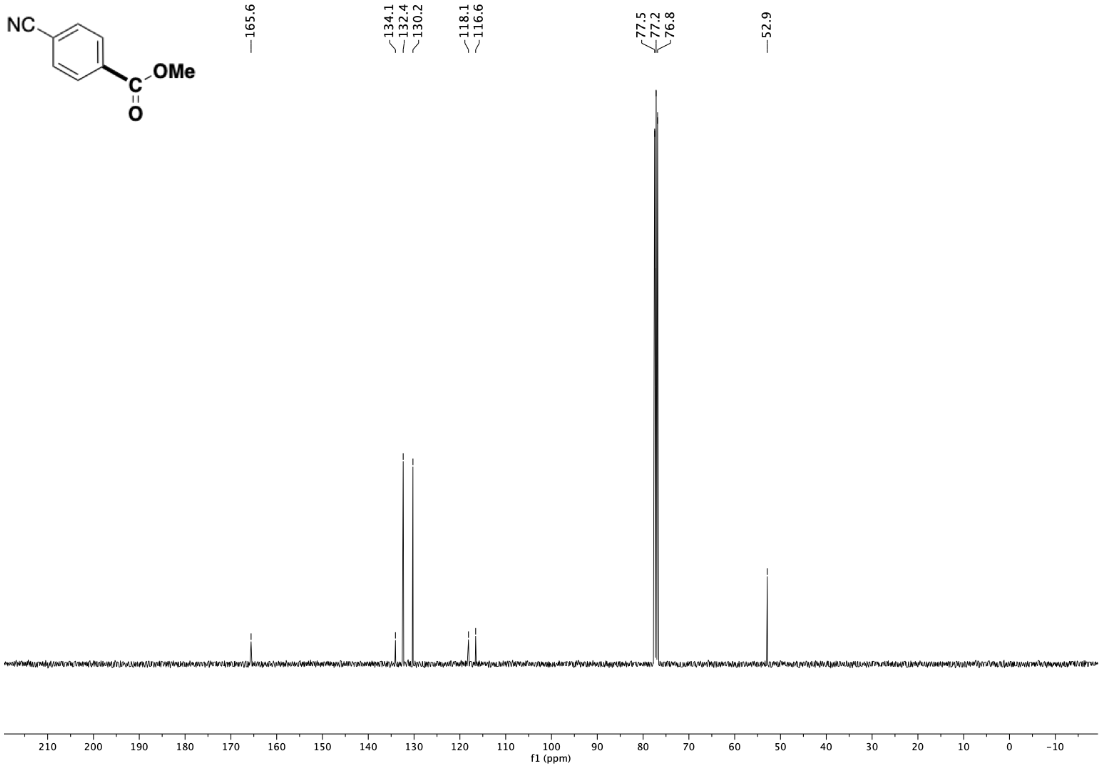

18.49
Ph3P
14C
O
OMe
Pd
Cl
PPh3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150
f1 (ppm)

NMR Spectra and Radio HPLC of ^{14}C compounds (1-27)

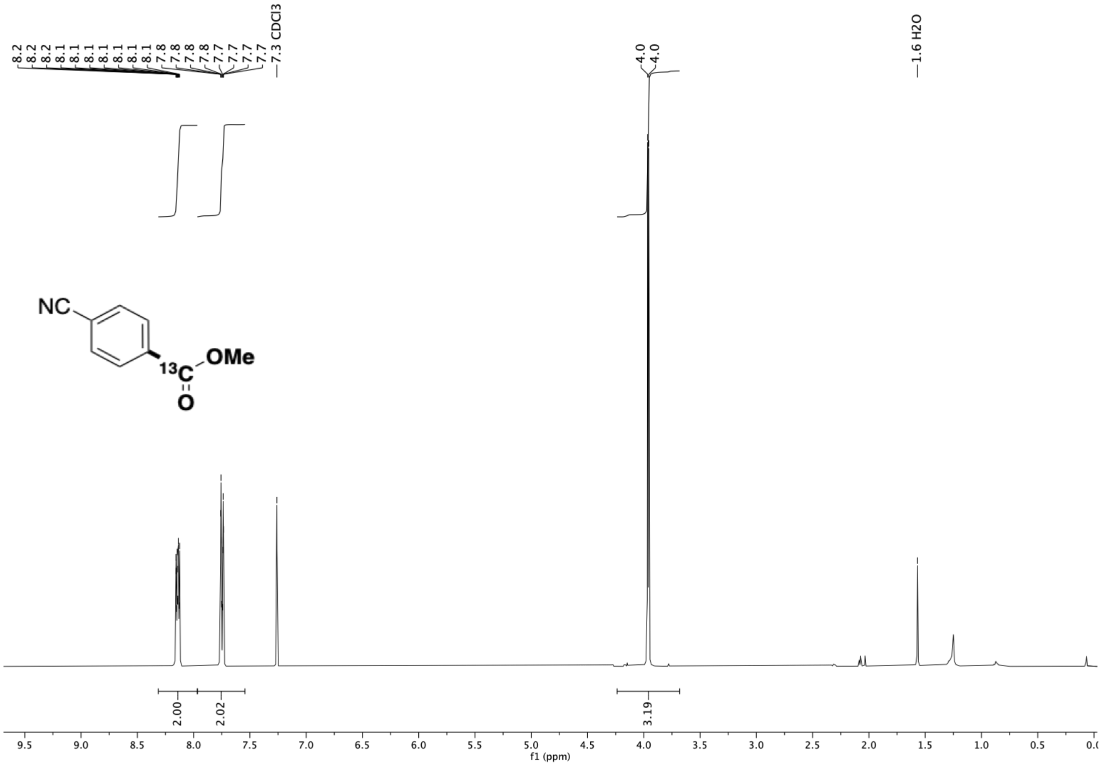
Methyl 4-cyanobenzoate (1) - ^{1}H NMR



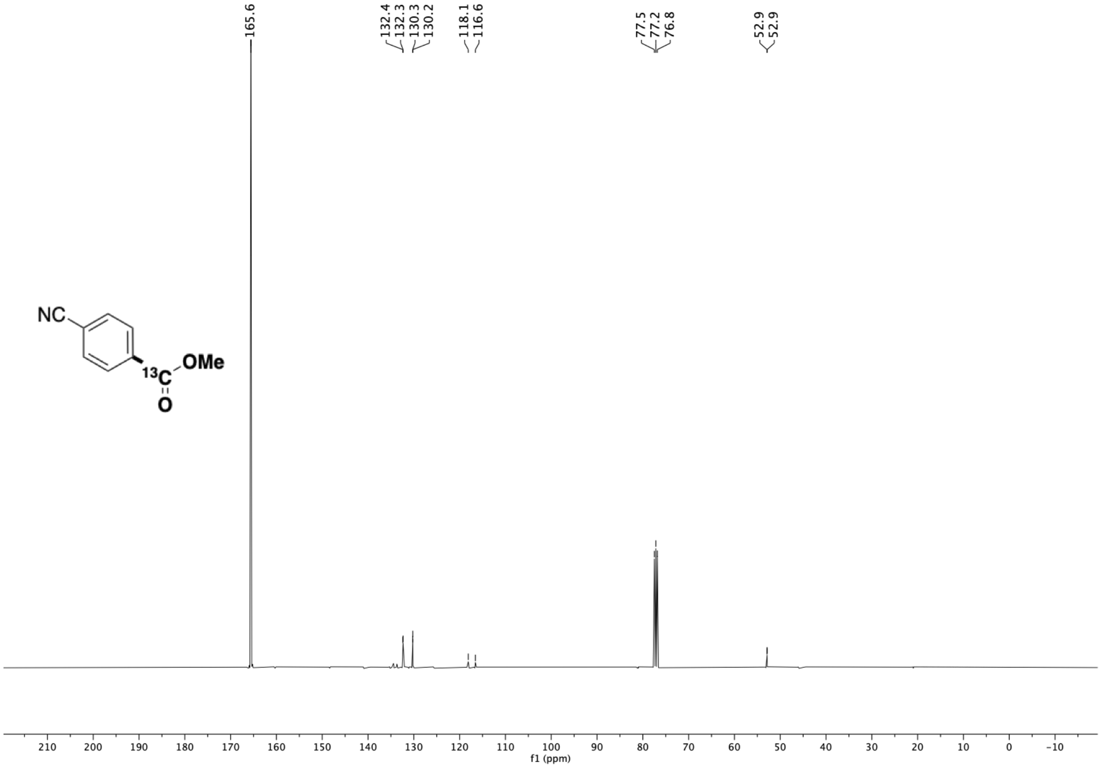
Methyl 4-cyanobenzoate (1) – ^{13}C NMR



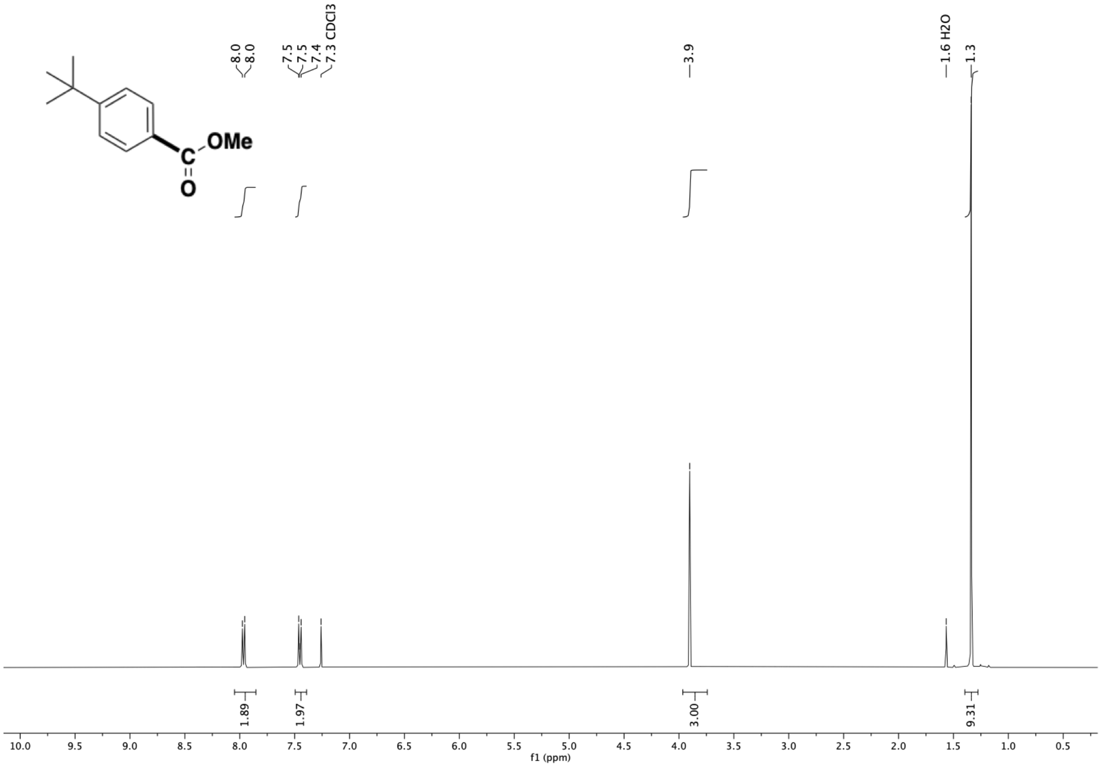
Methyl 4-cyanobenzoate (^{13}C-1) – ^{1}H NMR



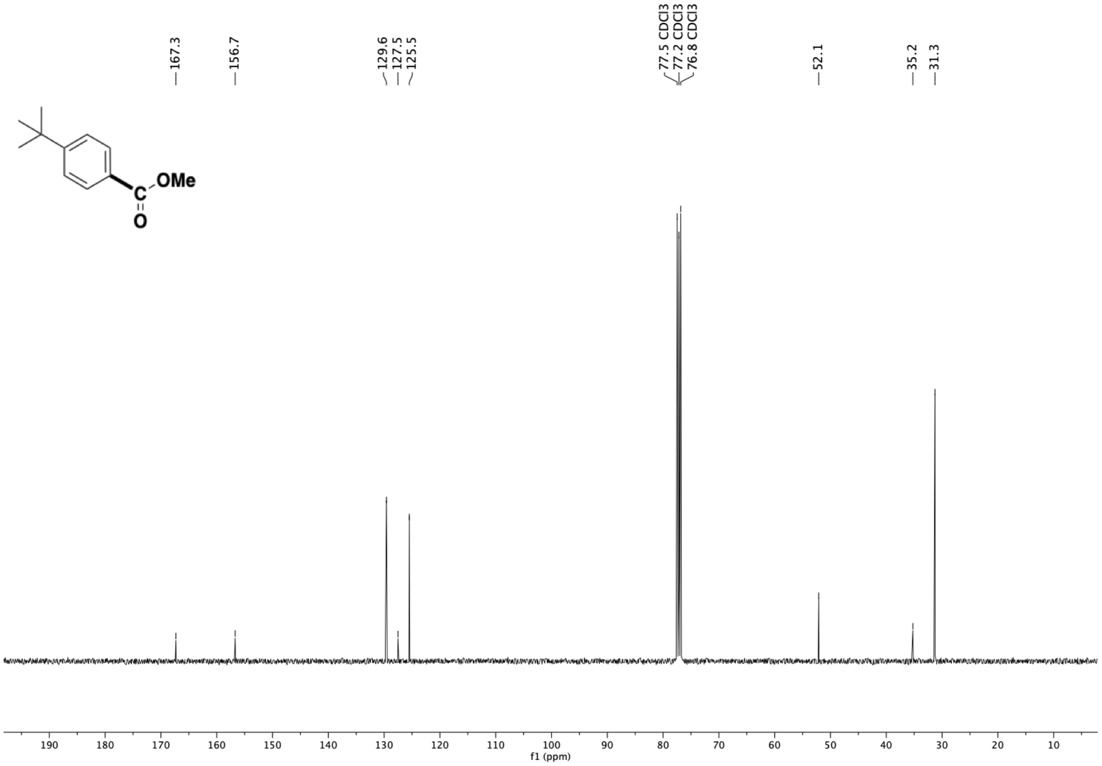
Methyl 4-cyanobenzoate (^{13}C-1) – ^{13}C NMR



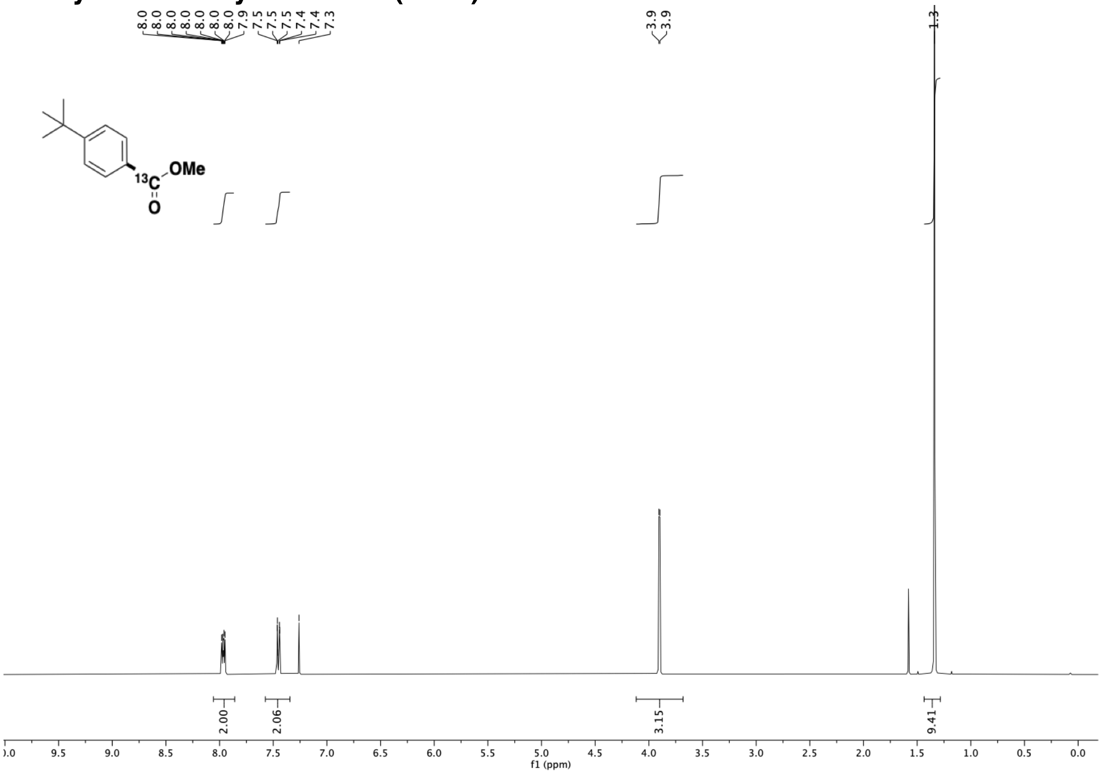
Methyl 4-tert-butylbenzoate (2) – ^{1}H NMR



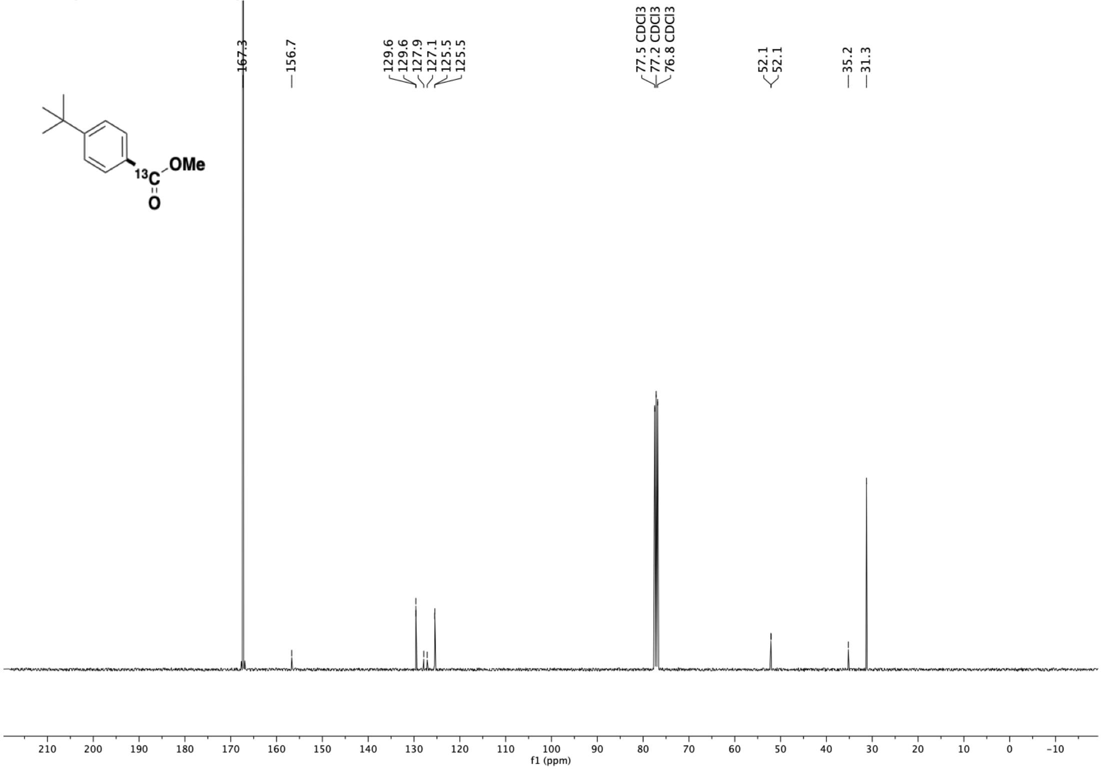
Methyl 4-tert-butylbenzoate (2) – ^{13}C NMR



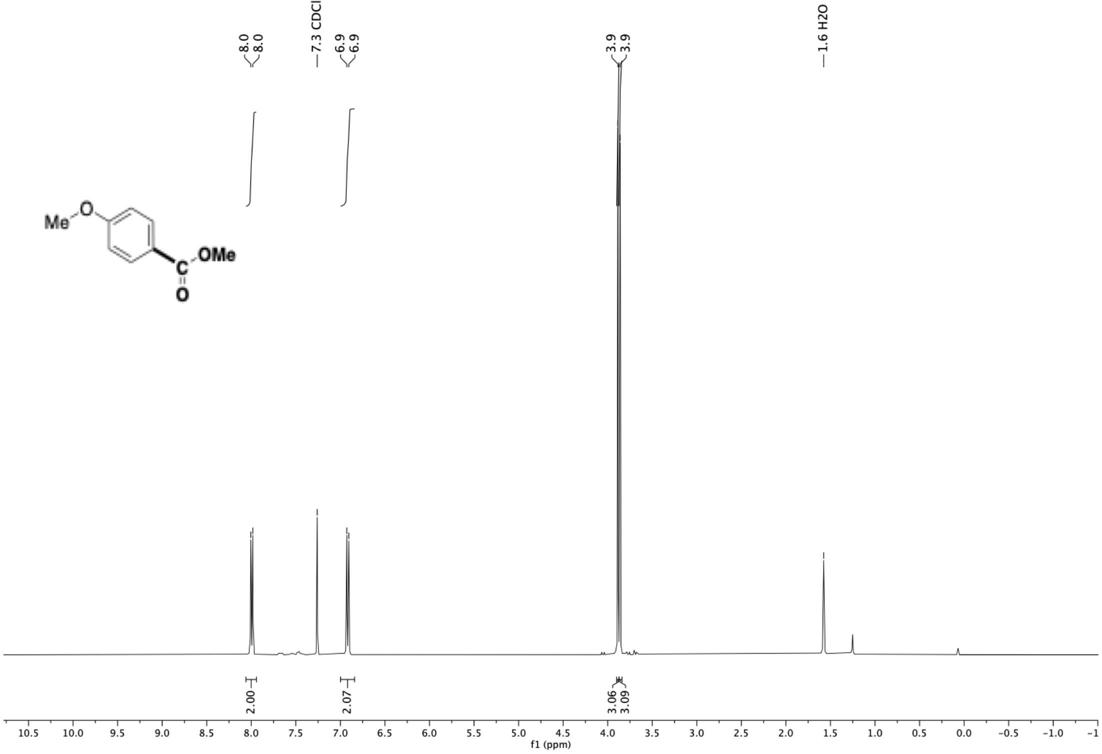
Methyl 4-tert-butylbenzoate (^{13}C-2) – ^{1}H NMR



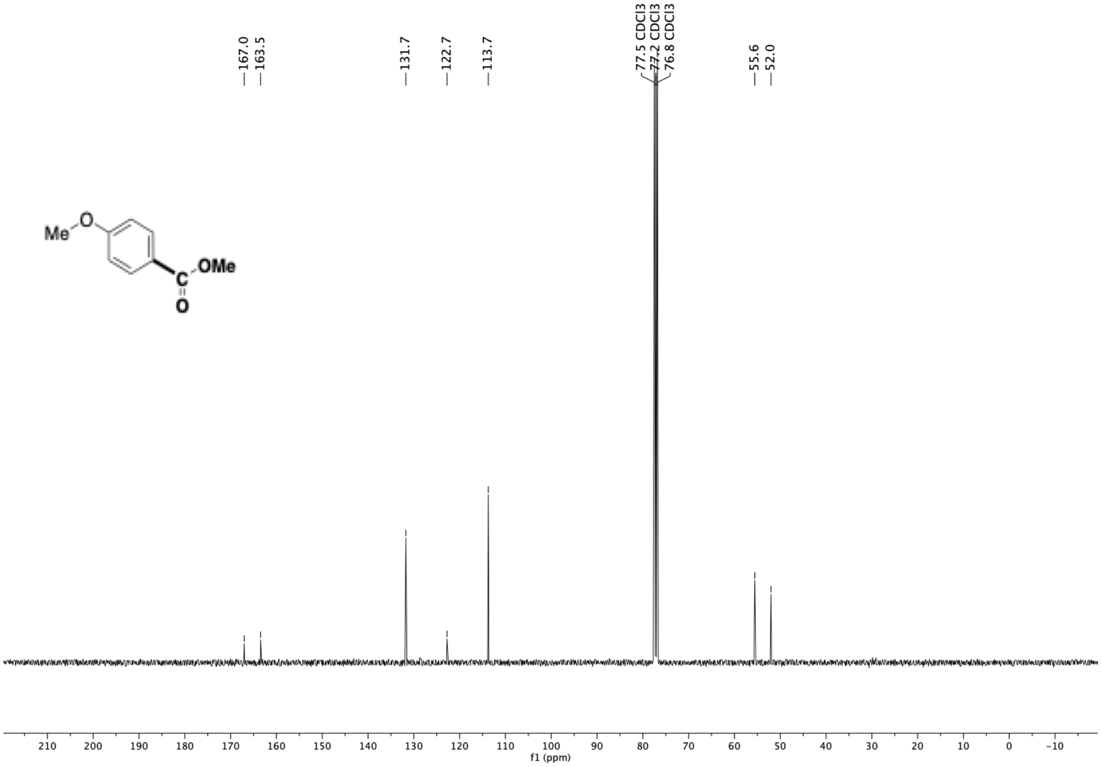
Methyl 4-tert-butylbenzoate (^{13}C-2) – ^{13}C NMR



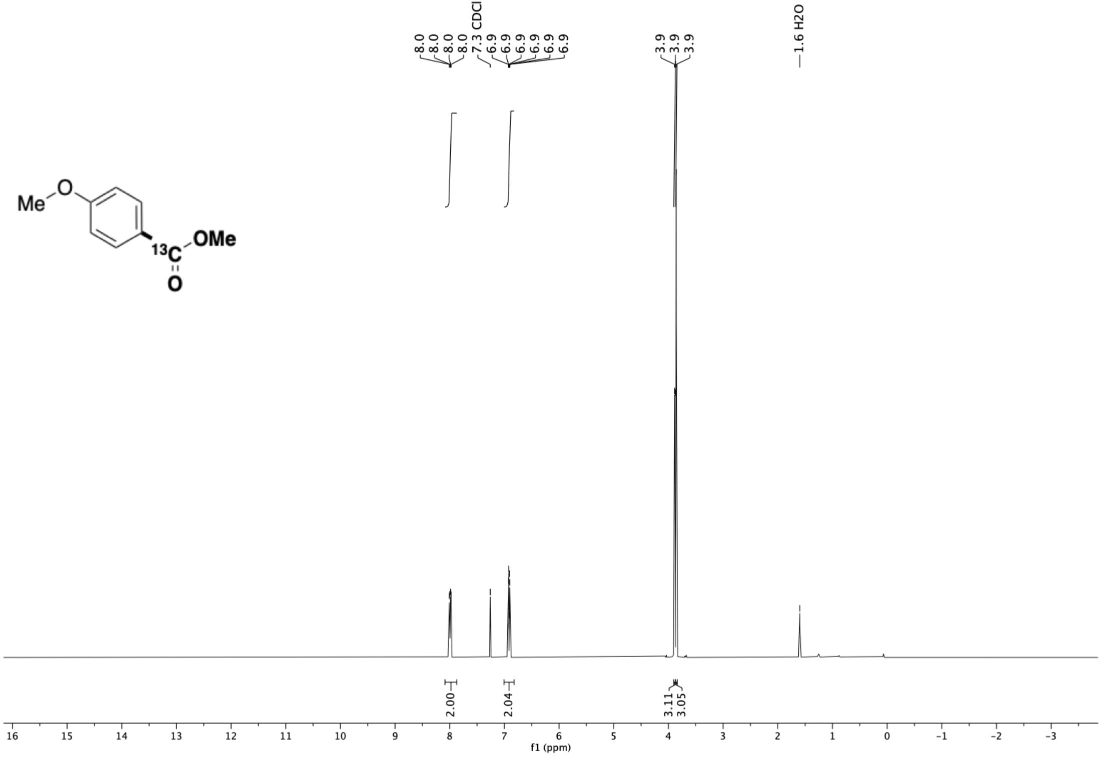
Methyl 4-methoxybenzoate (3) – ^{1}H NMR



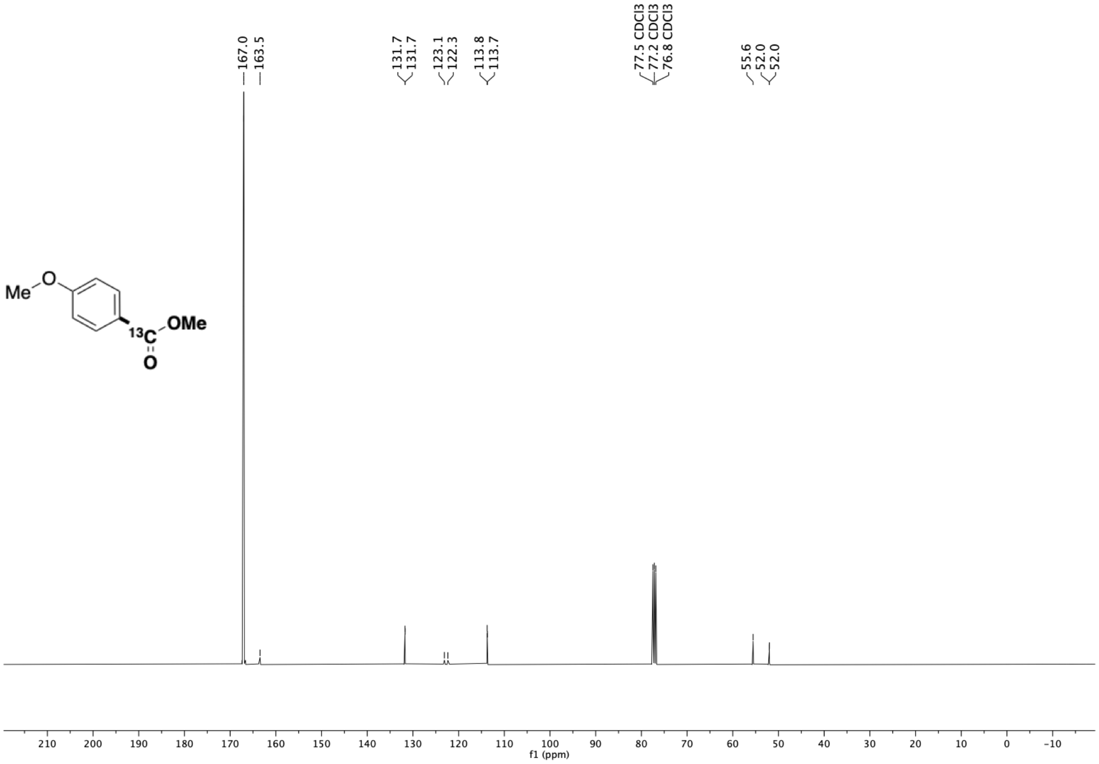
Methyl 4-methoxybenzoate (3) – ^{13}C NMR



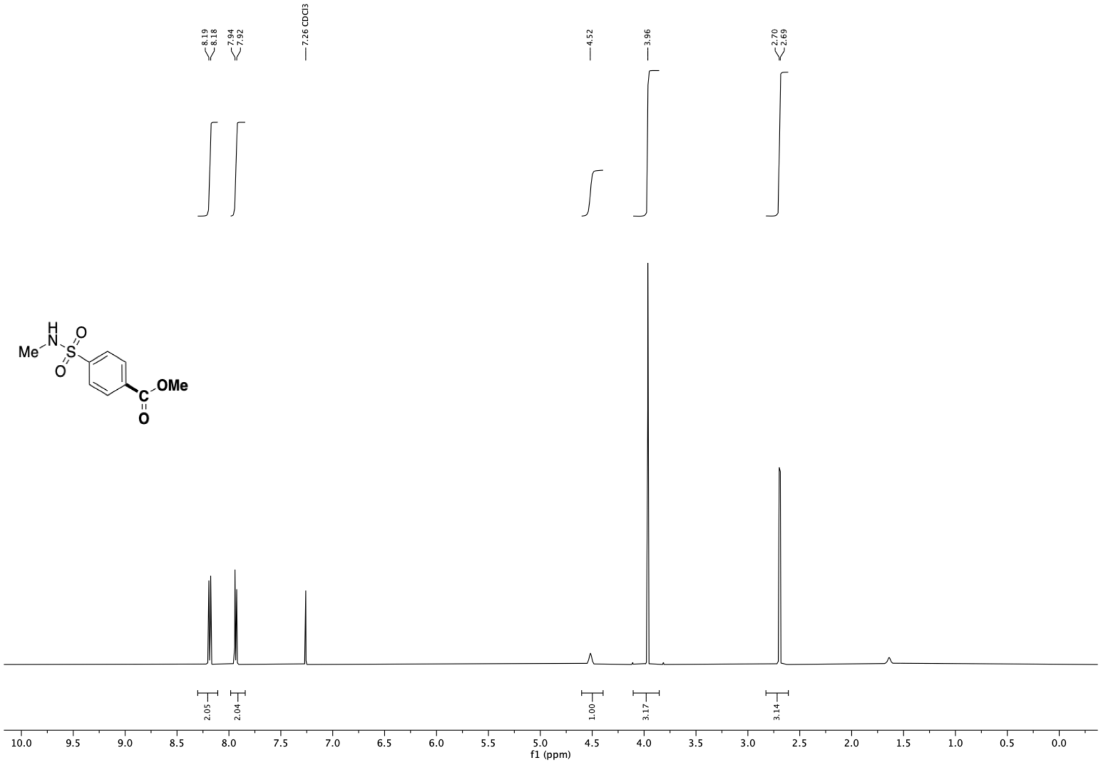
Methyl 4-methoxybenzoate (^{13}C-3) – ^{1}H NMR



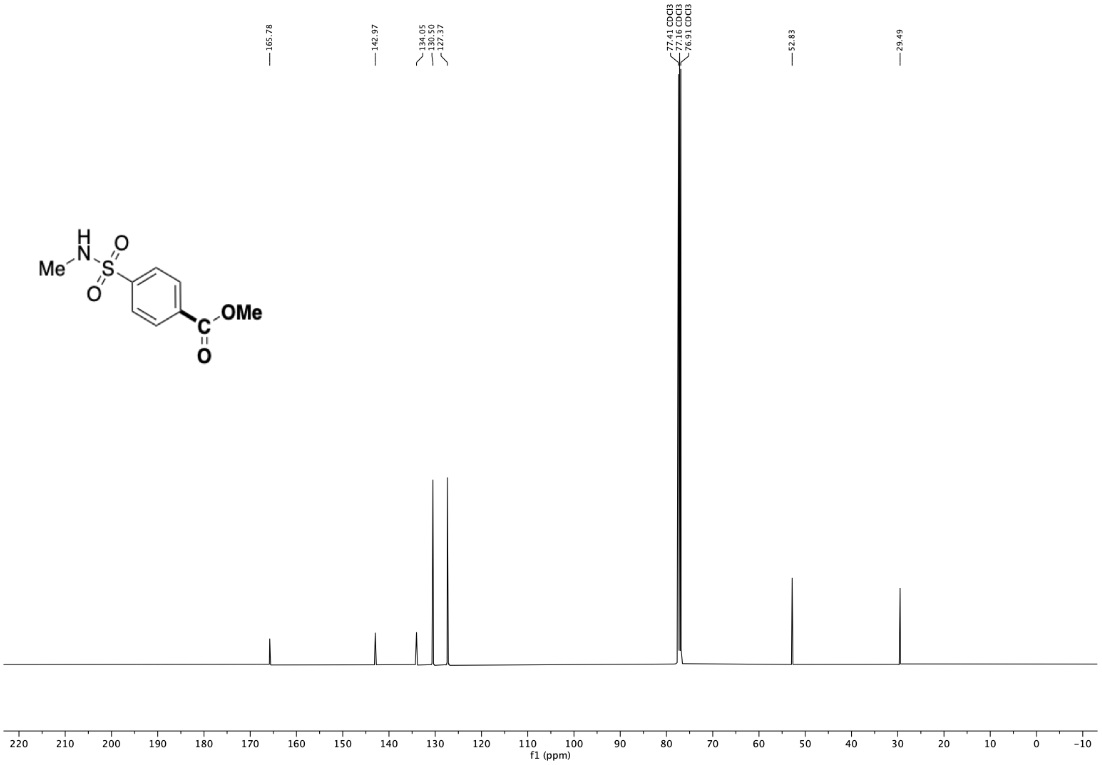
Methyl 4-methoxybenzoate (^{13}C-3) – ^{13}C NMR



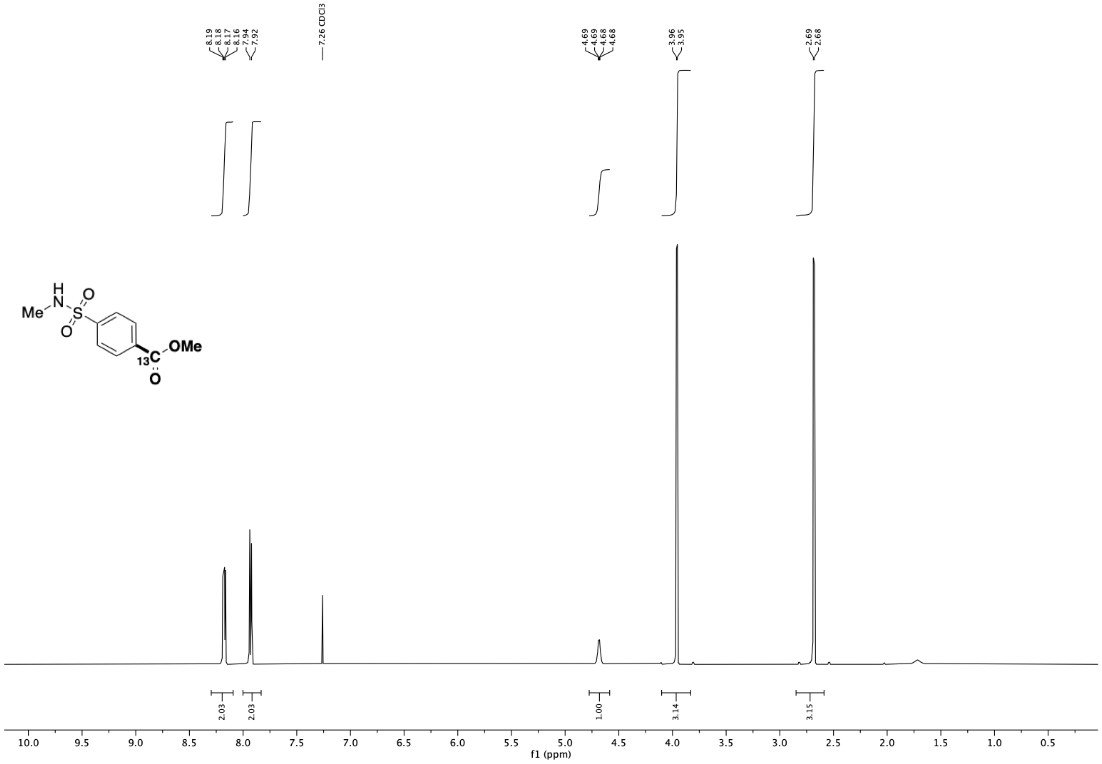
Methyl 4-(N-methylsulfamoyl)benzoate (4) – ^{1}H NMR



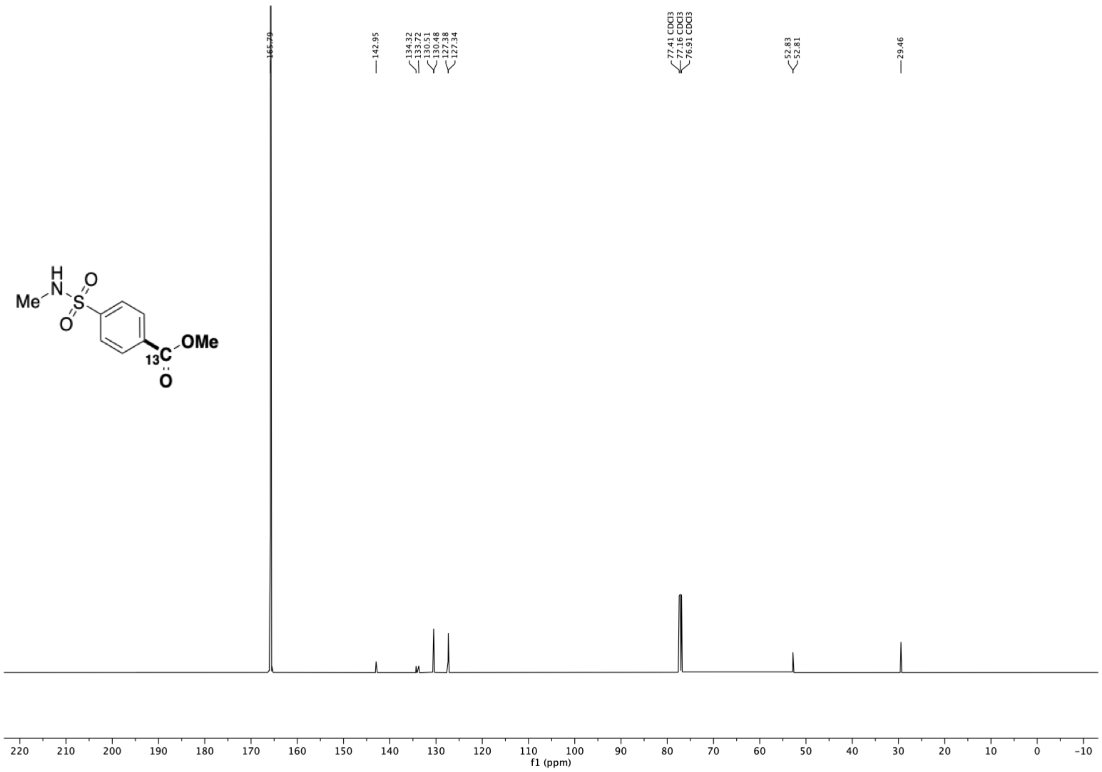
Methyl 4-(N-methylsulfamoyl)benzoate (4) – ^{13}C NMR



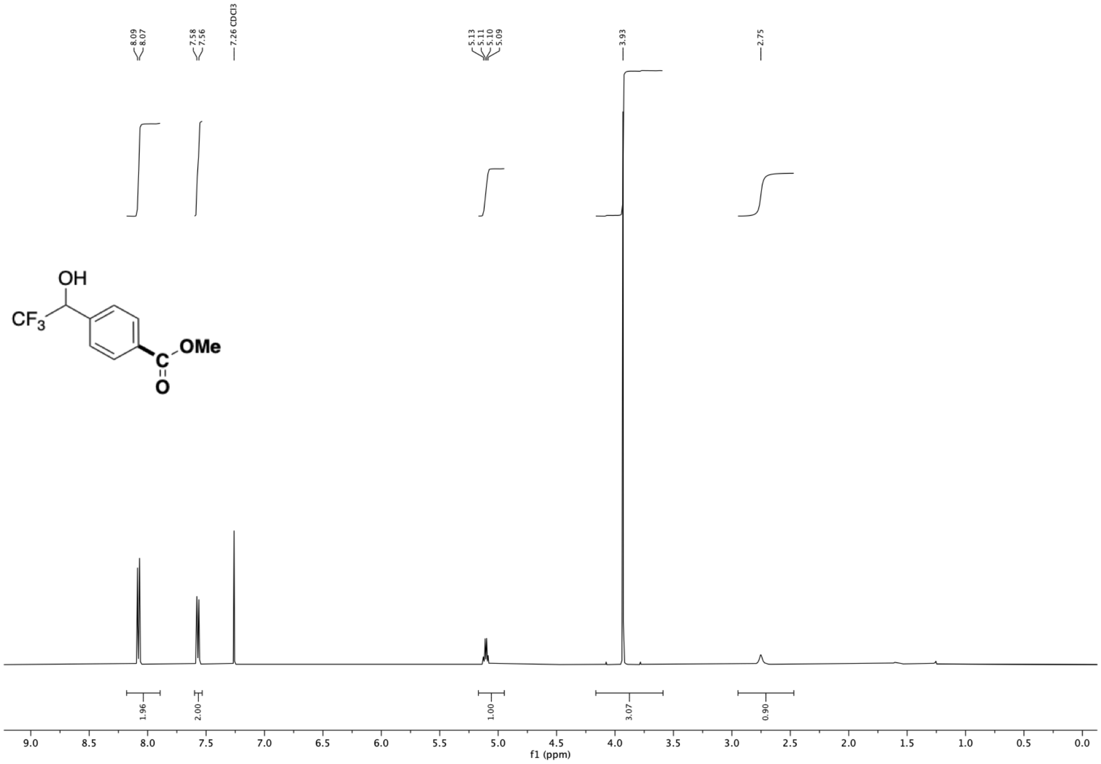
Methyl 4-(N-methylsulfamoyl)benzoate (^{13}C-4) – ^{1}H NMR



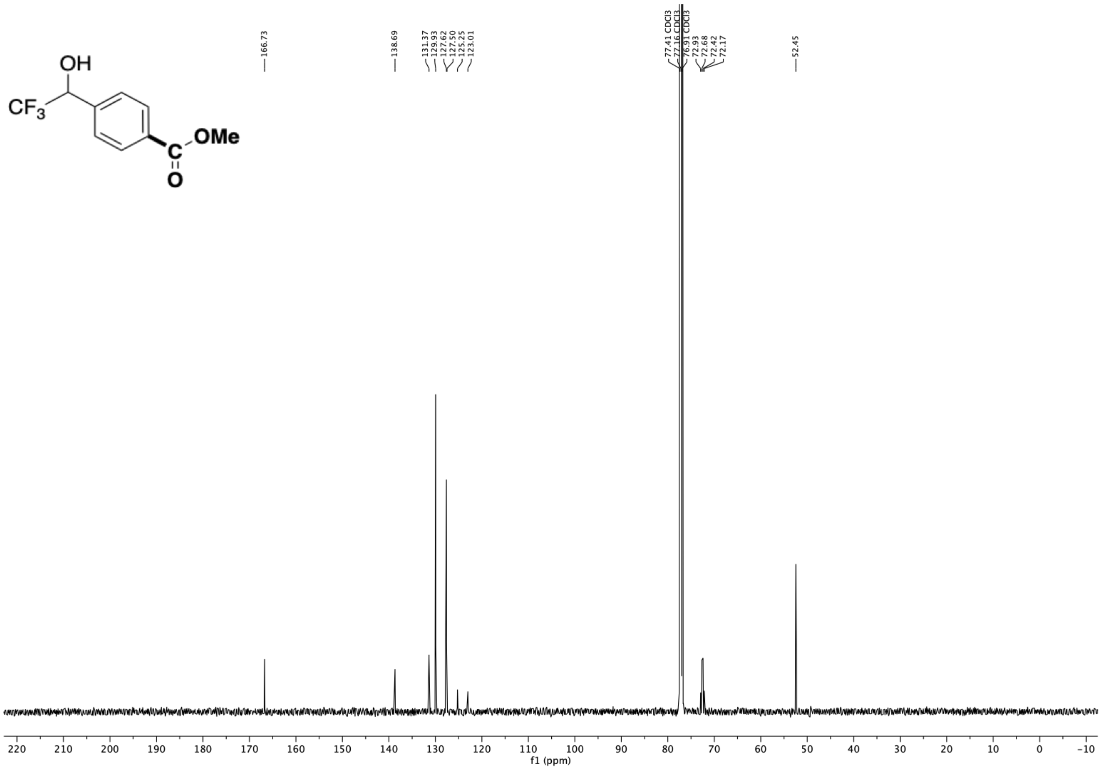
Methyl 4-(N-methylsulfamoyl)benzoate (^{13}C-4) – ^{13}C NMR



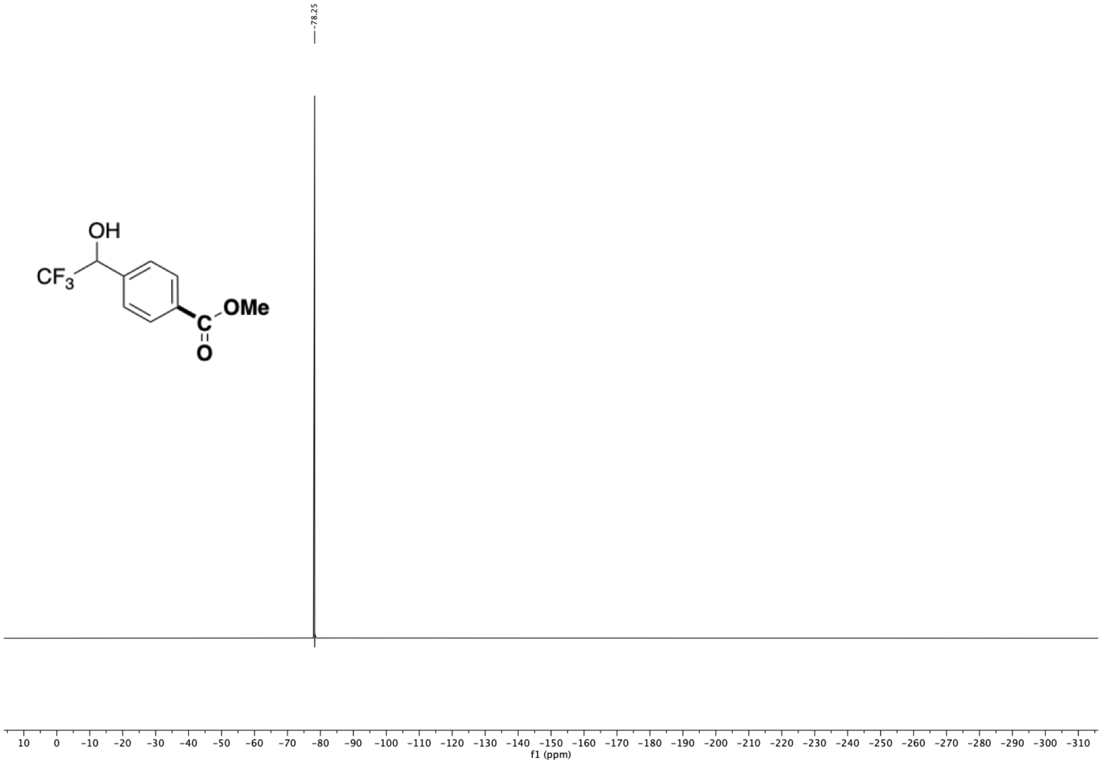
Methyl 4-(trifluoro-1-ethanol)benzoate (5) - ^{1}H NMR



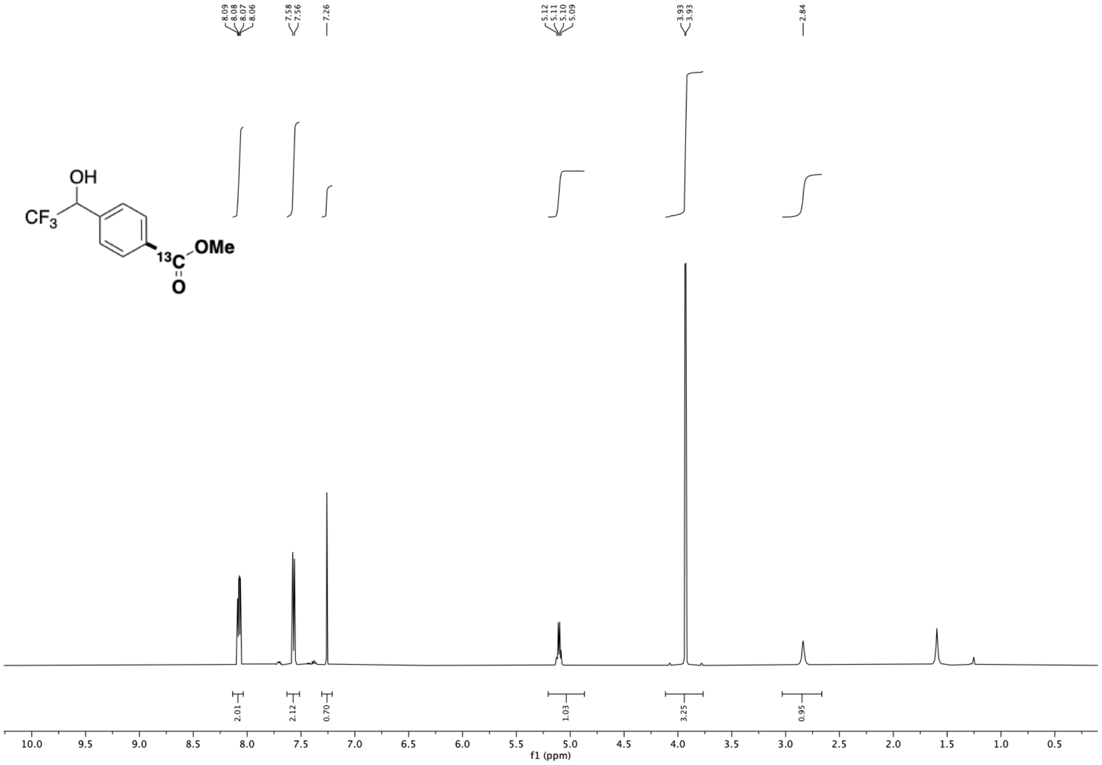
Methyl 4-(trifluoro-1-ethanol)benzoate (5) – ^{13}C NMR



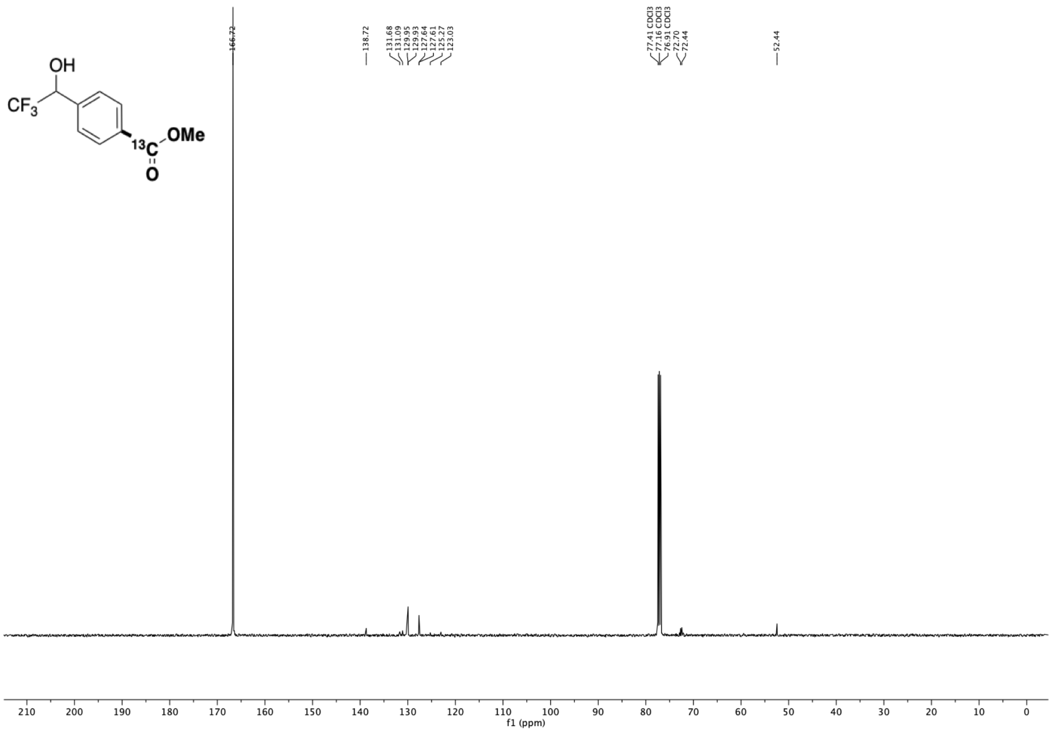
Methyl 4-(trifluoro-1-ethanol)benzoate (5) – ^{19}F NMR



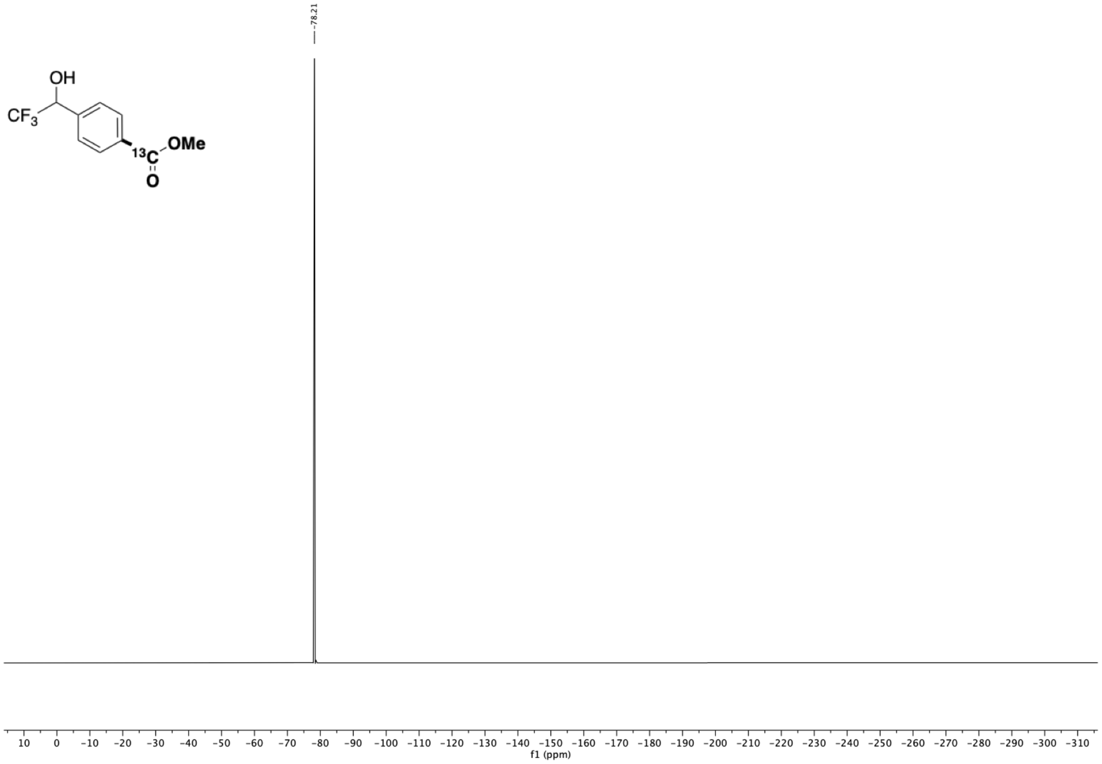
Methyl 4-(trifluoro-1-ethanol)benzoate (^{13}C-5) – ^{1}H NMR



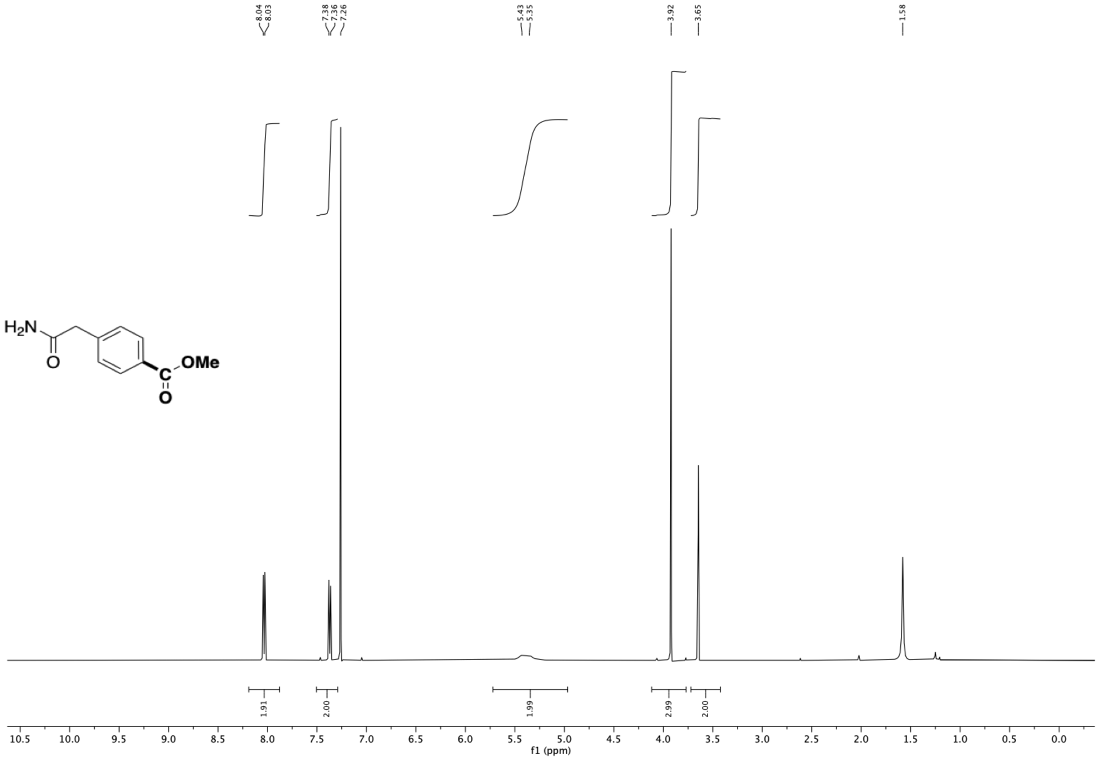
Methyl 4-(trifluoro-1-ethanol)benzoate (^{13}C-5) – ^{13}C NMR



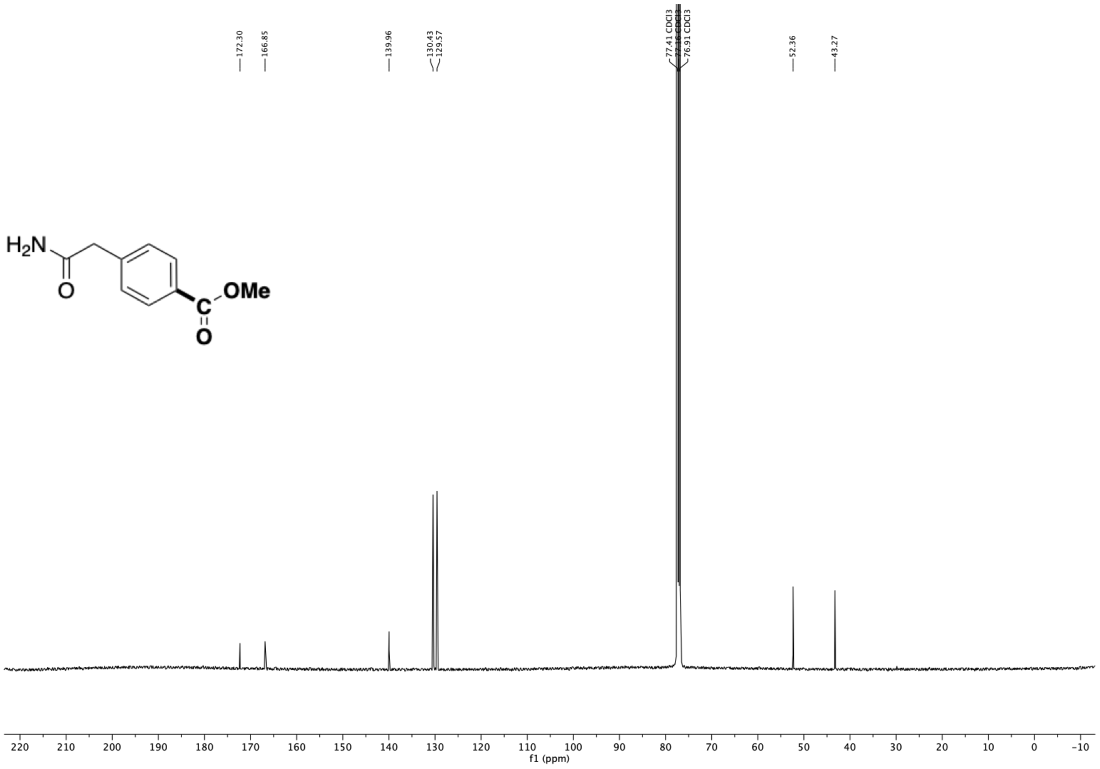
Methyl 4-(trifluoro-1-ethanol)benzoate (^{13}C-5) – ^{19}F NMR



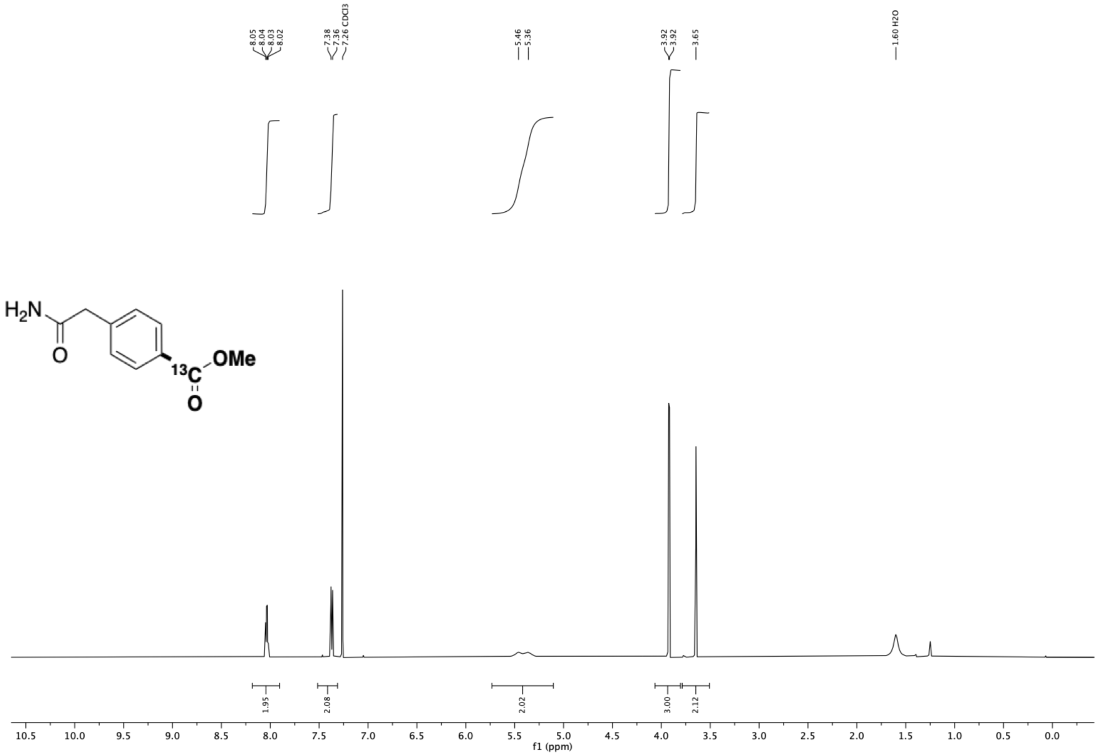
Methyl 4-(2-amino-2-oxoethyl)benzoate (6)- ^{1}H NMR



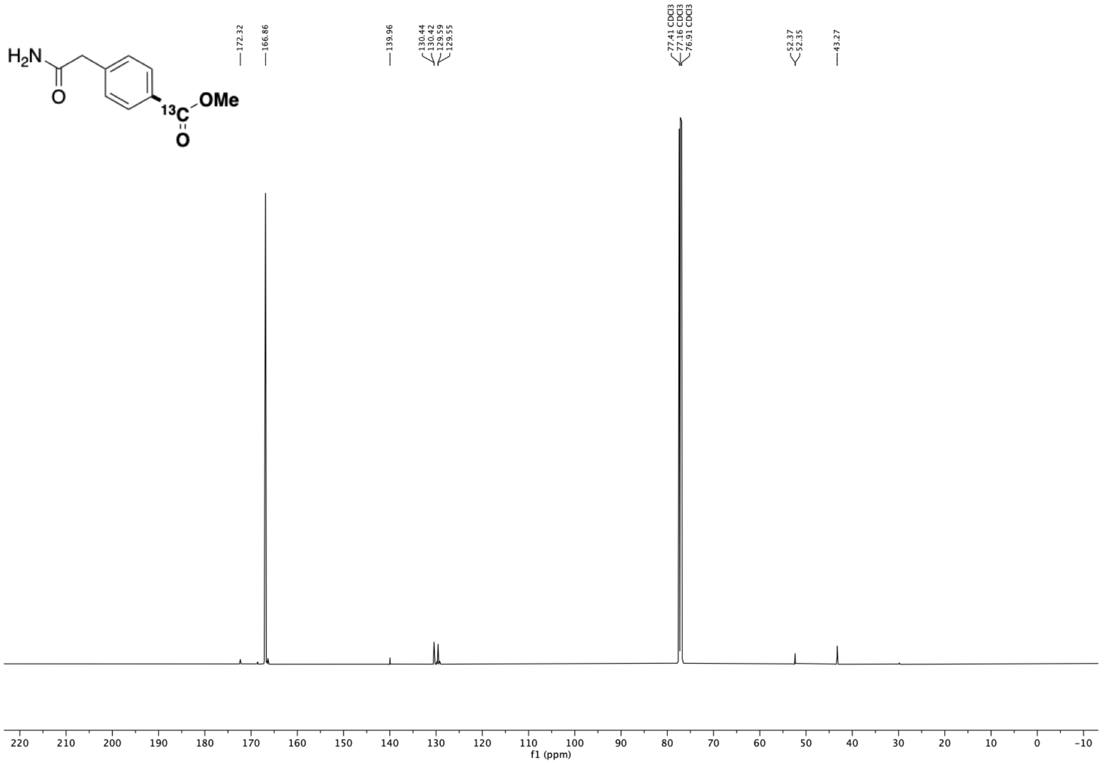
Methyl 4-(2-amino-2-oxoethyl)benzoate (6) – ^{13}C NMR



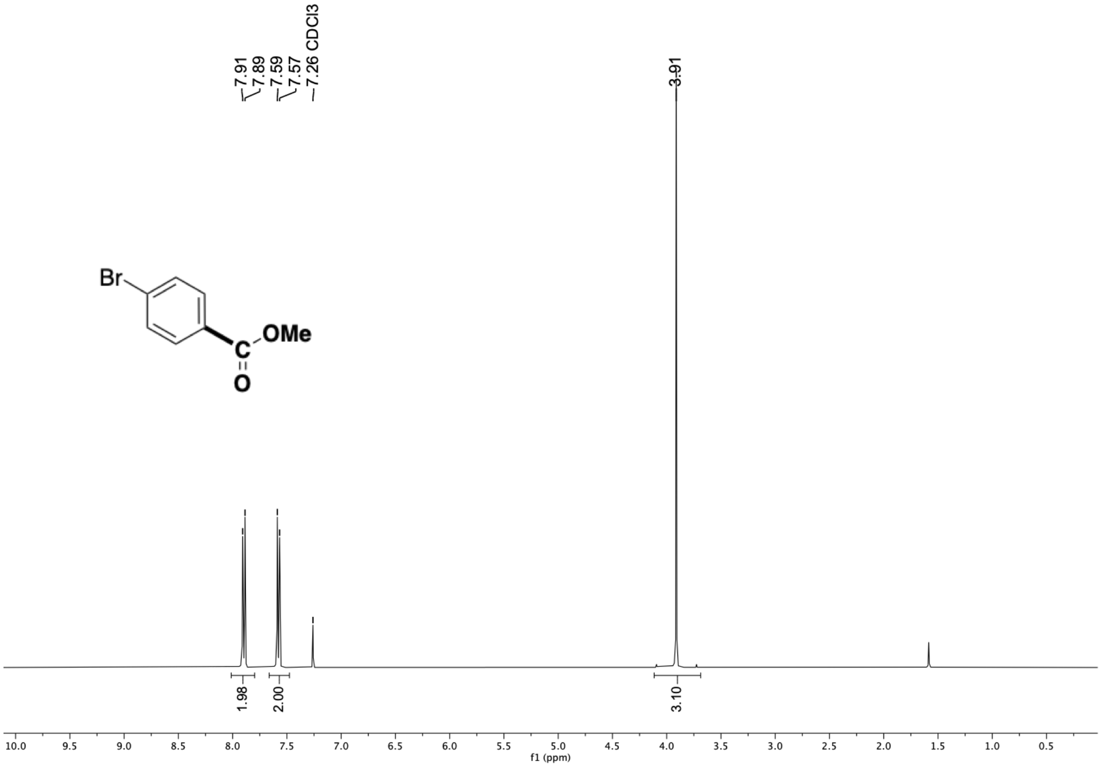
Methyl 4-(2-amino-2-oxoethyl)benzoate (13C-6)- ^{1}H NMR



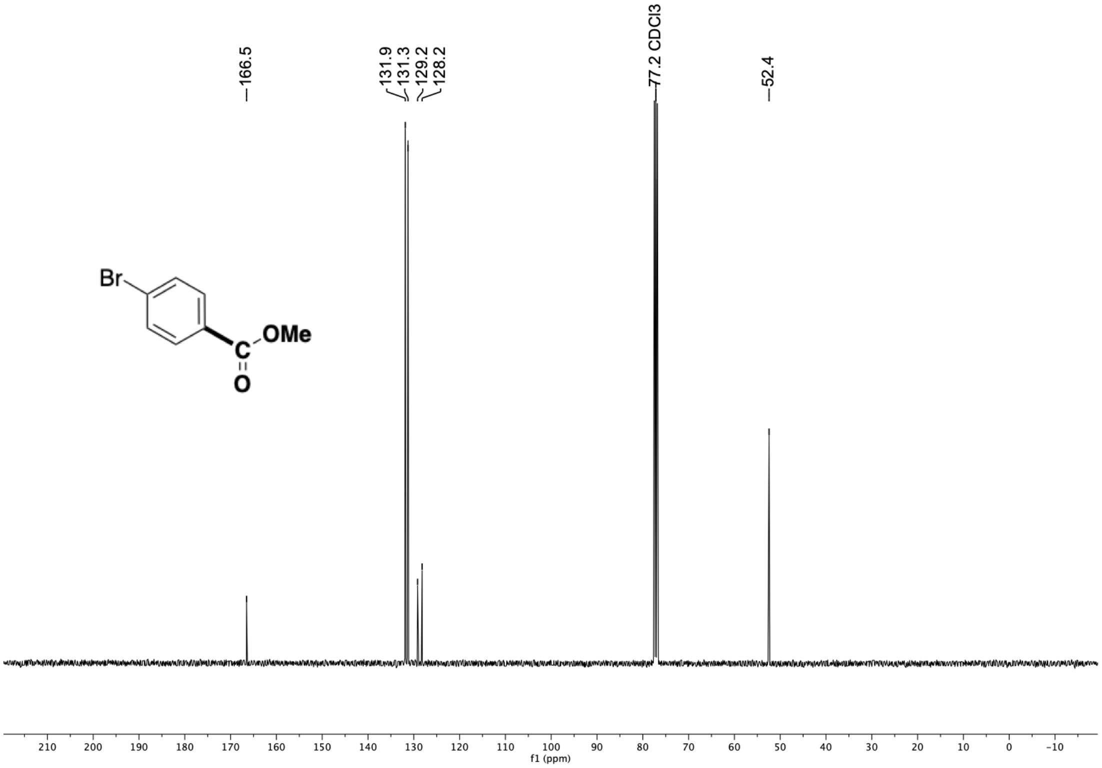
Methyl 4-(2-amino-2-oxoethyl)benzoate (13C-6)- ^{13}C NMR



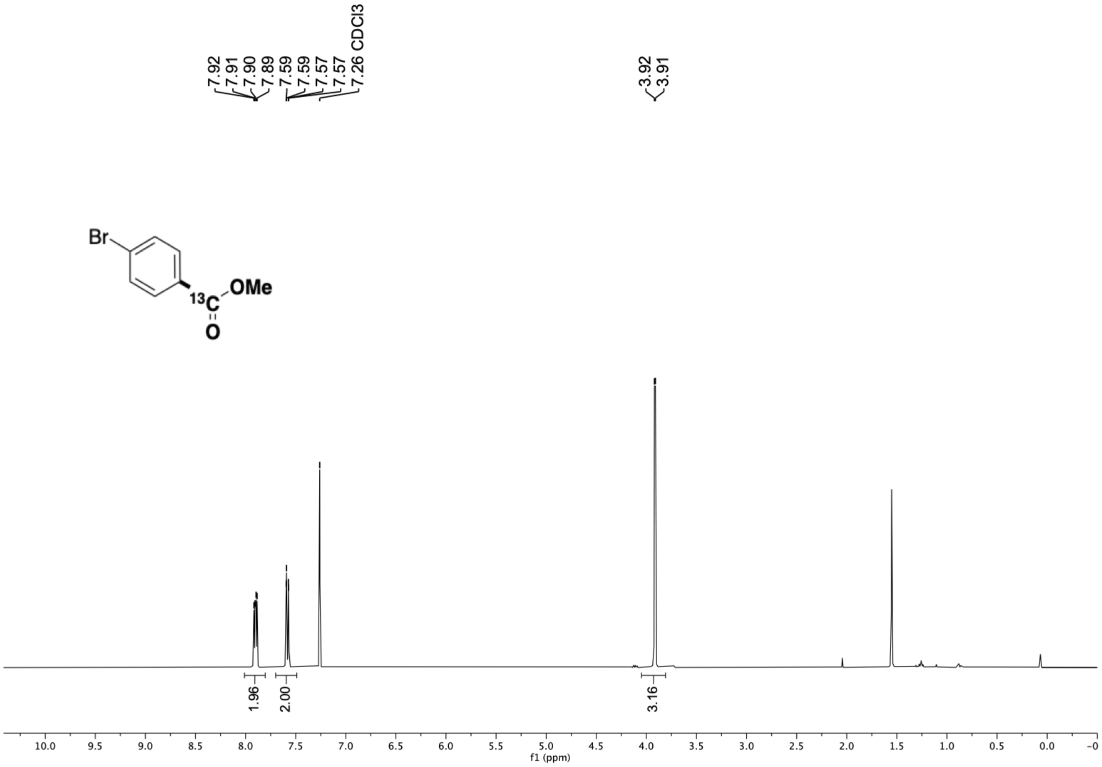
Methyl 4-bromobenzoate (7) – ^{1}H NMR



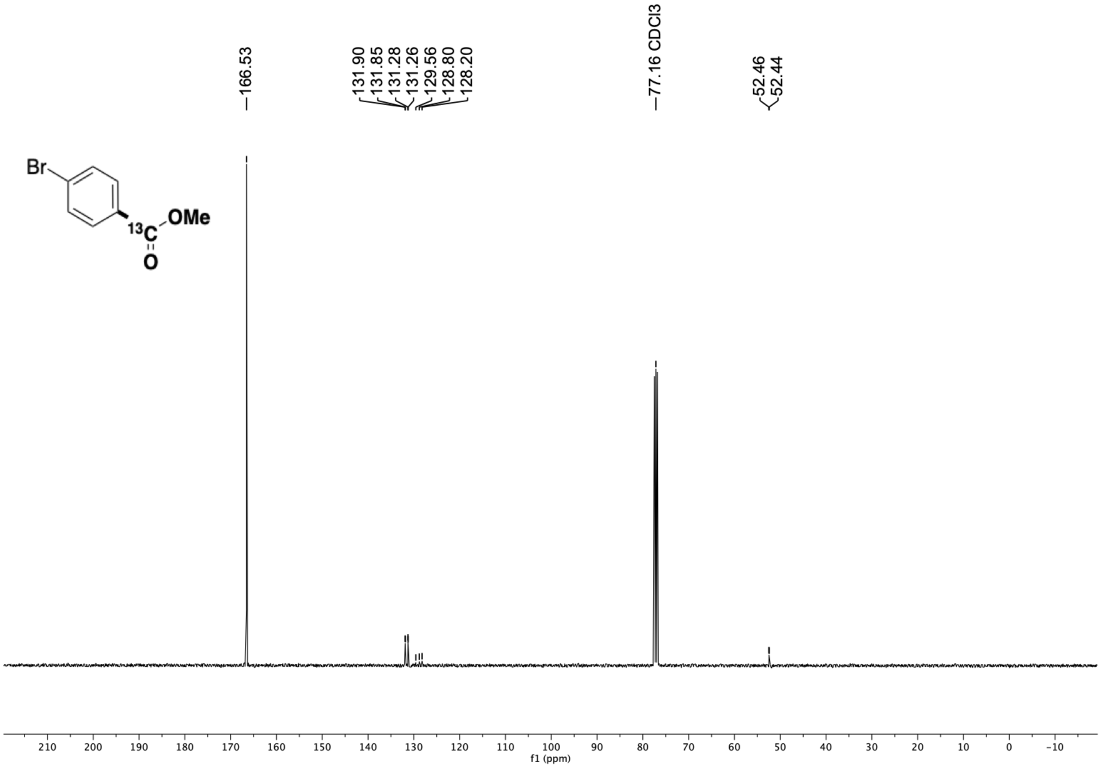
Methyl 4-bromobenzoate (7) – ^{13}C NMR



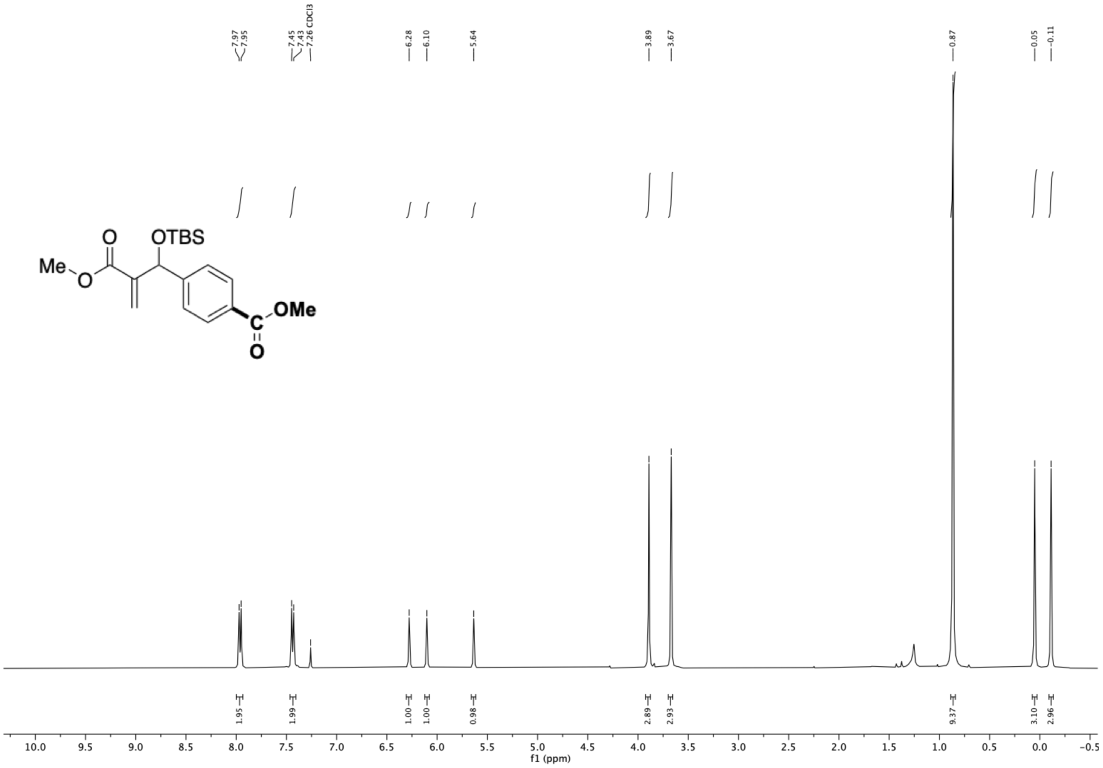
Methyl 4-bromobenzoate (^{13}C-7) – ^{1}H NMR



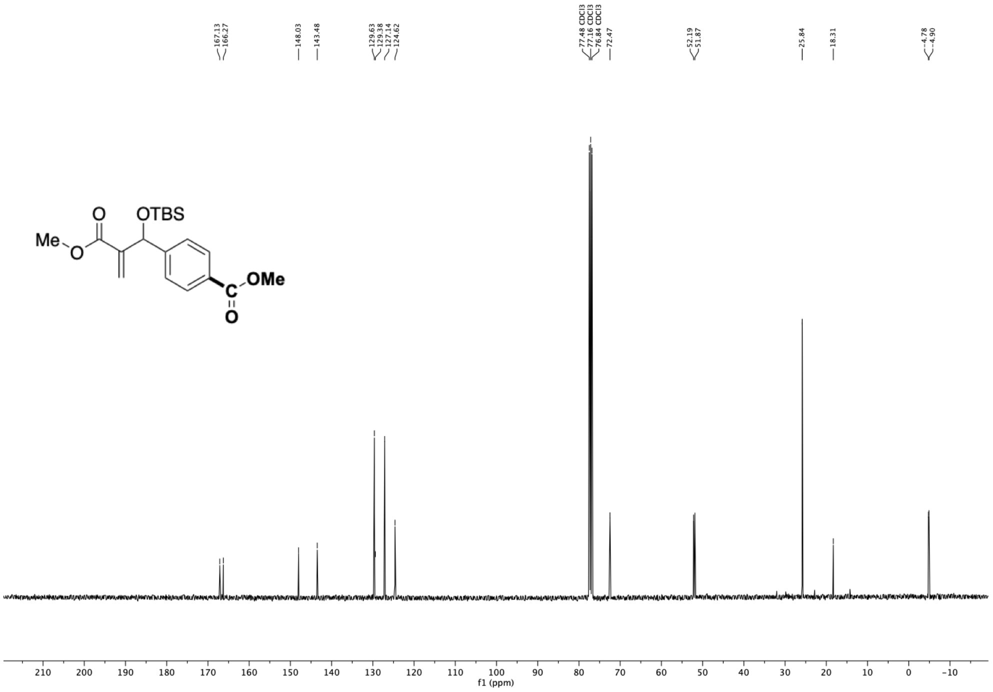
Methyl 4-bromobenzoate (^{13}C-7) – ^{13}C NMR



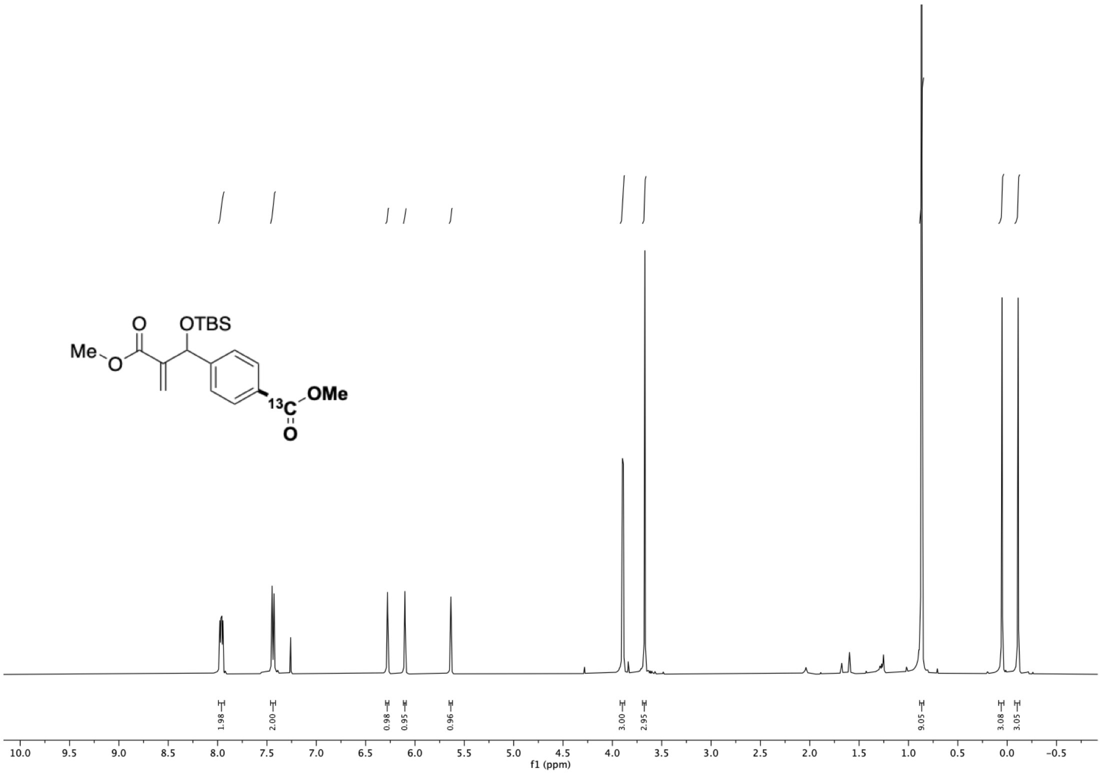
Methyl 2-(((tert-butyldimethylsilyl)oxy)(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)methyl)acrylate (8) – ¹H NMR



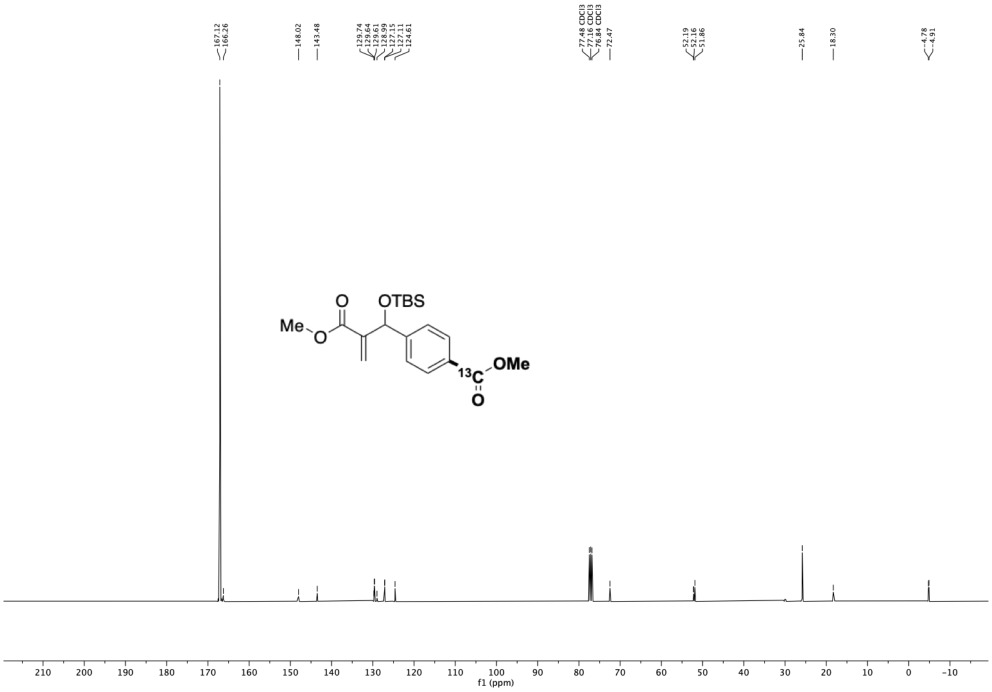
Methyl 2-(((tert-butyldimethylsilyl)oxy)(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)methyl)acrylate (8) – ¹³C NMR



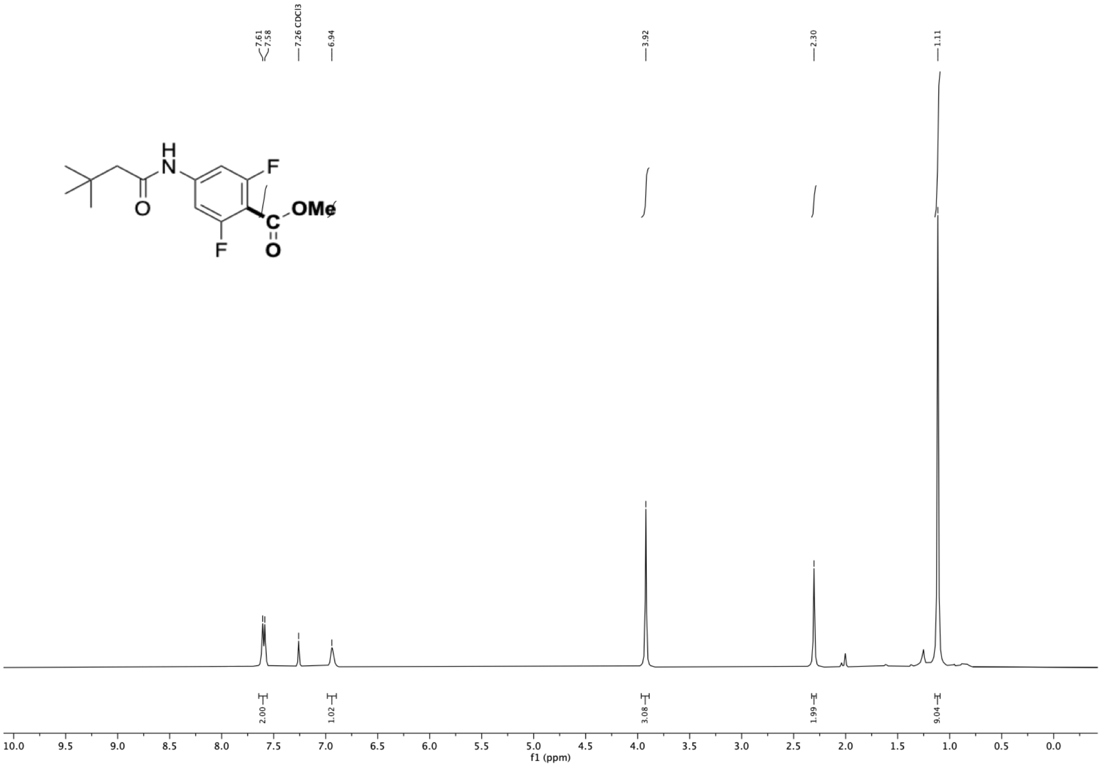
Methyl 2-(((tert-butyldimethylsilyl)oxy)(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)methyl)acrylate (^{13}C-8) – ^{1}H NMR



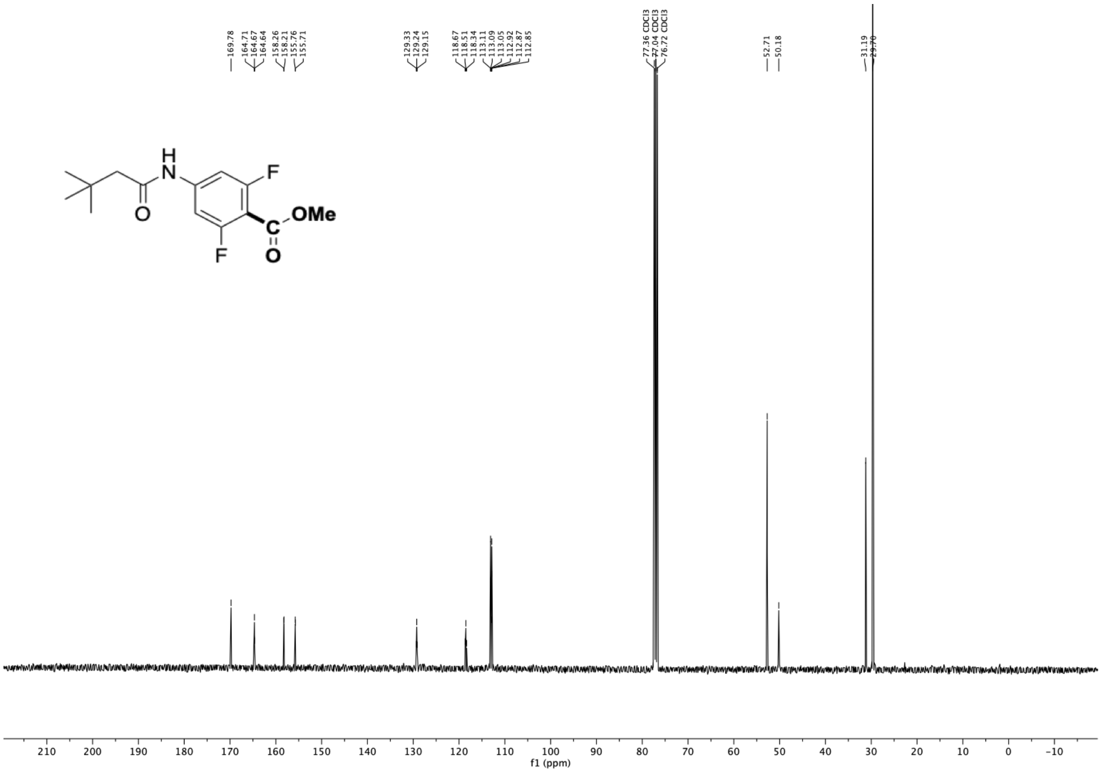
Methyl 2-(((tert-butyldimethylsilyl)oxy)(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)methyl)acrylate (^{13}C-8) – ^{13}C NMR



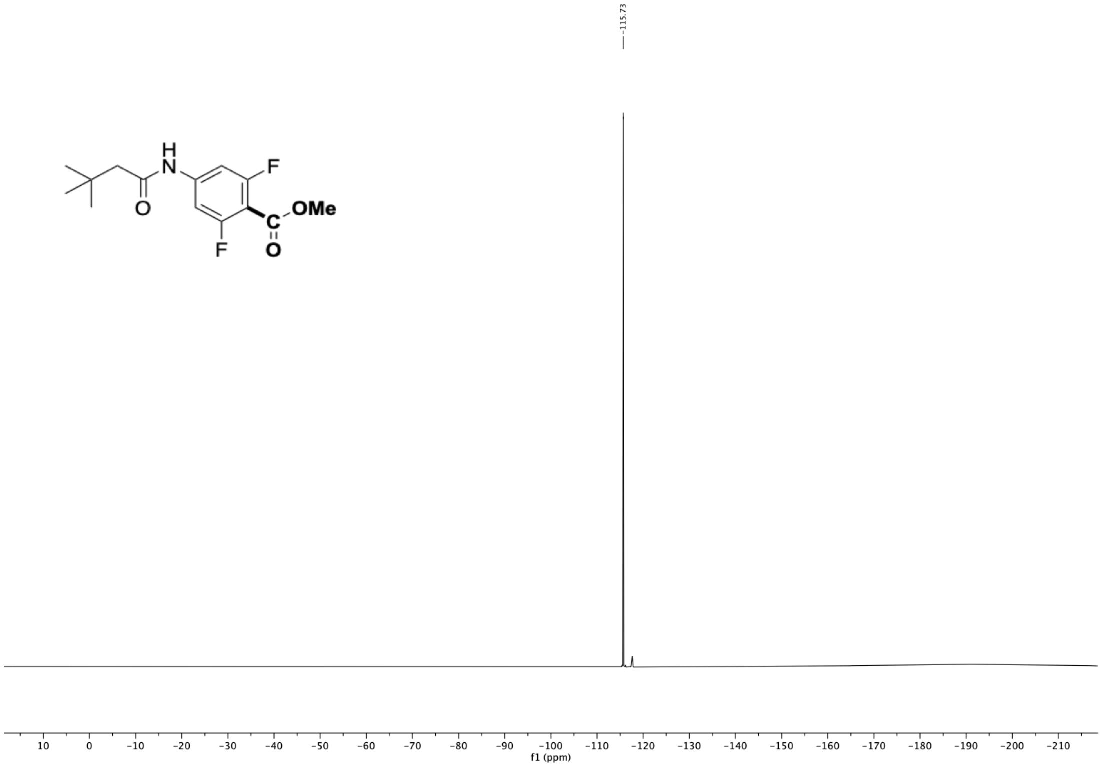
Methyl 4-(3,3-dimethylbutanamido)-3,5-difluorobenzoate (9) – ^{1}H NMR



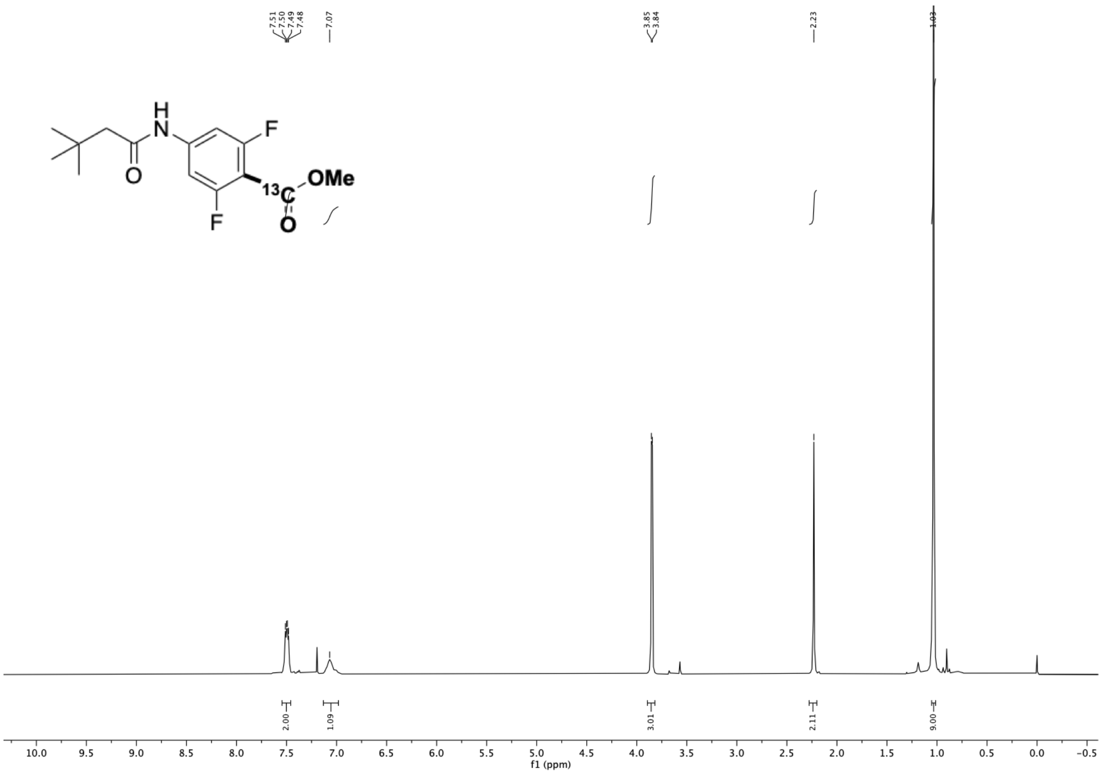
Methyl 4-(3,3-dimethylbutanamido)-3,5-difluorobenzoate (9) – ^{13}C NMR



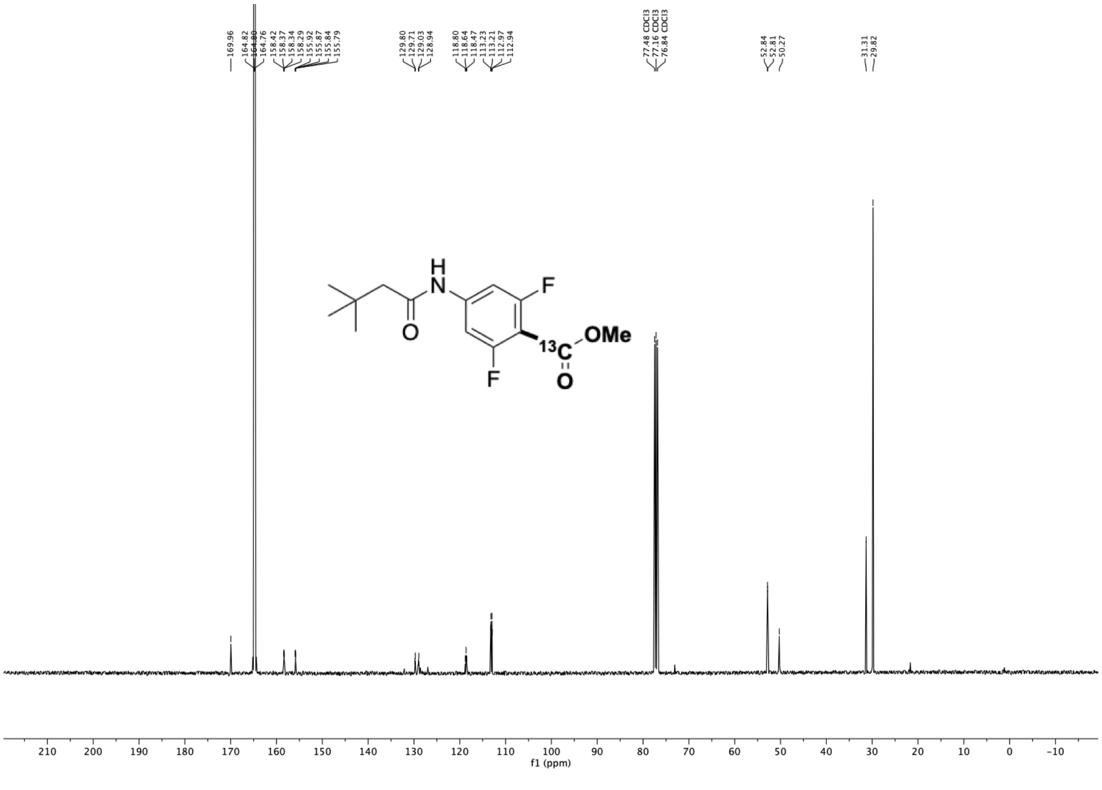
Methyl 4-(3,3-dimethylbutanamido)-3,5-difluorobenzoate (9) – ^{19}F NMR



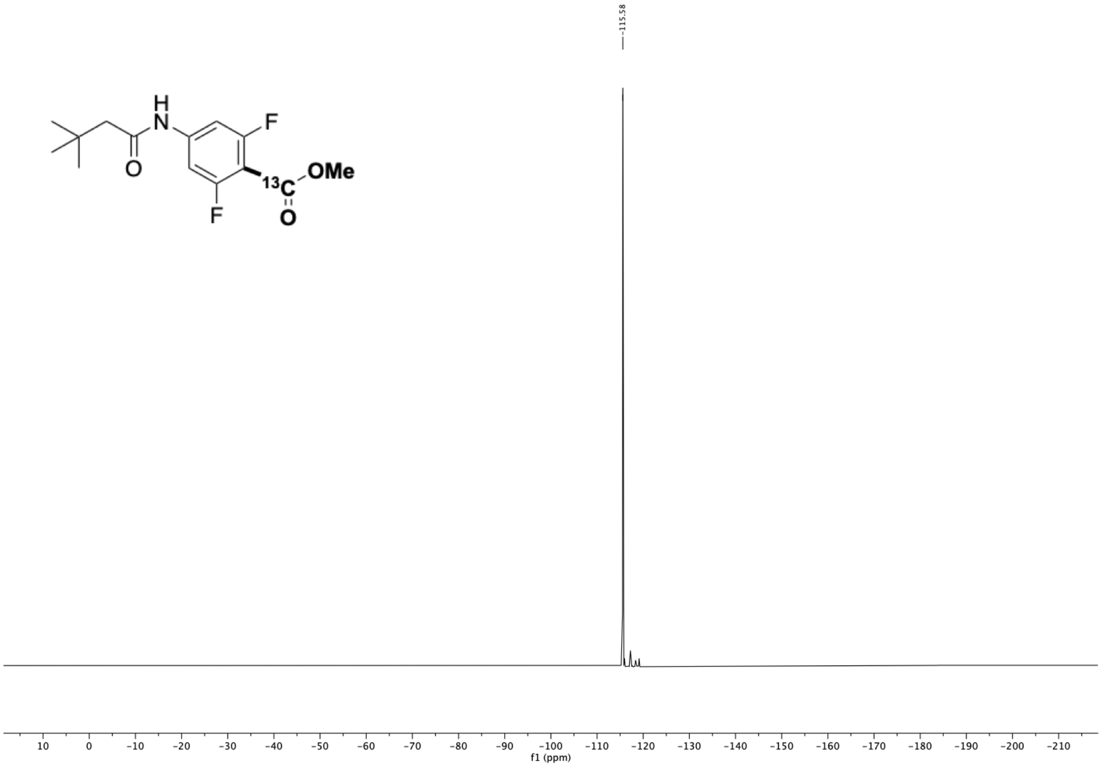
Methyl 4-(3,3-dimethylbutanamido)-3,5-difluorobenzoate (^{13}C-9) – ^{1}H NMR



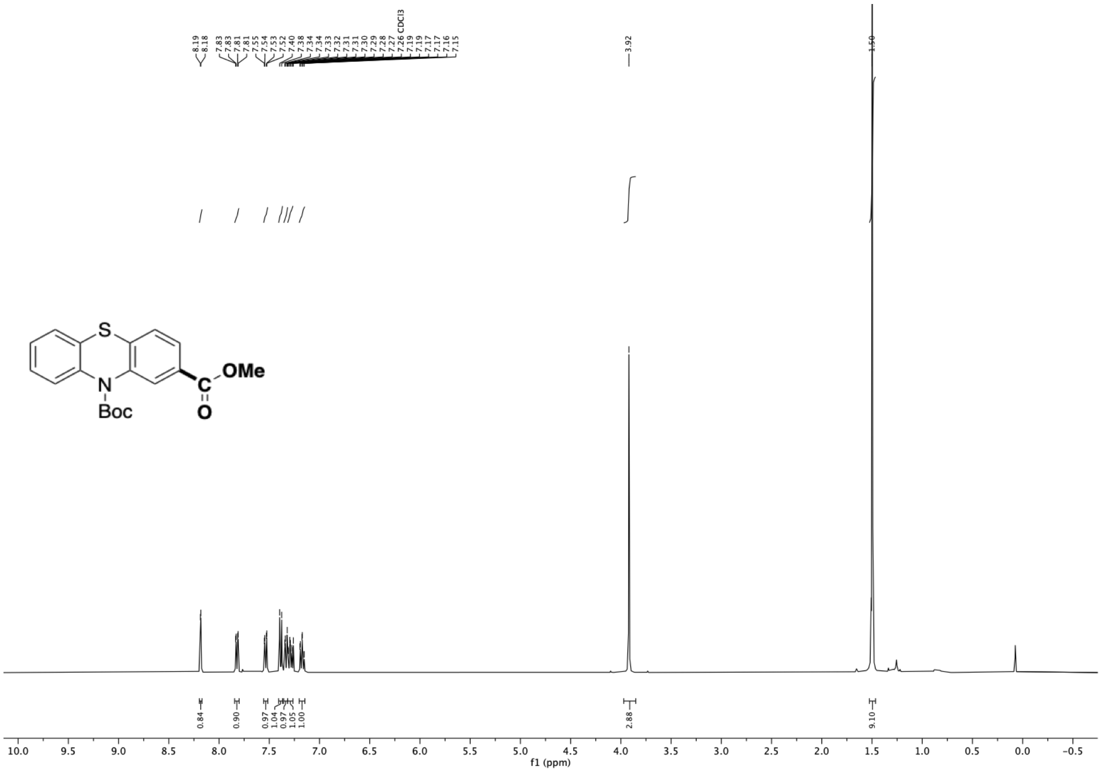
Methyl 4-(3,3-dimethylbutanamido)-3,5-difluorobenzoate (^{13}C-9) – ^{13}C NMR



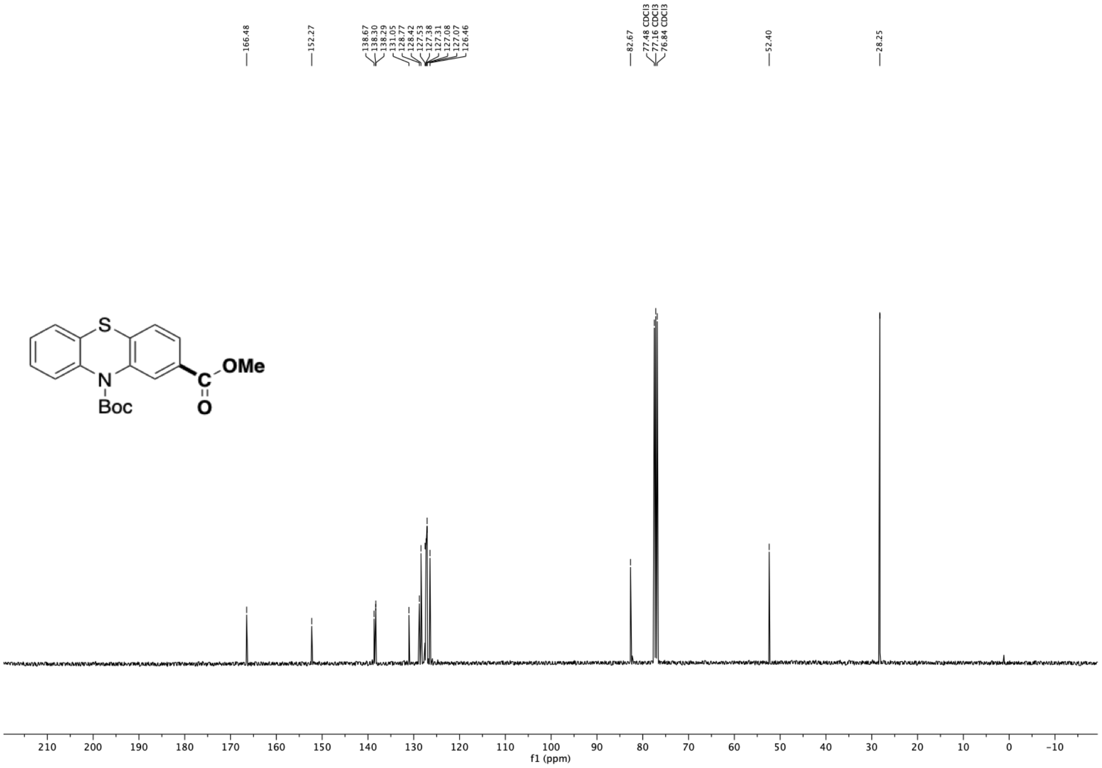
Methyl 4-(3,3-dimethylbutanamido)-3,5-difluorobenzoate (^{13}C-9) – ^{19}F NMR



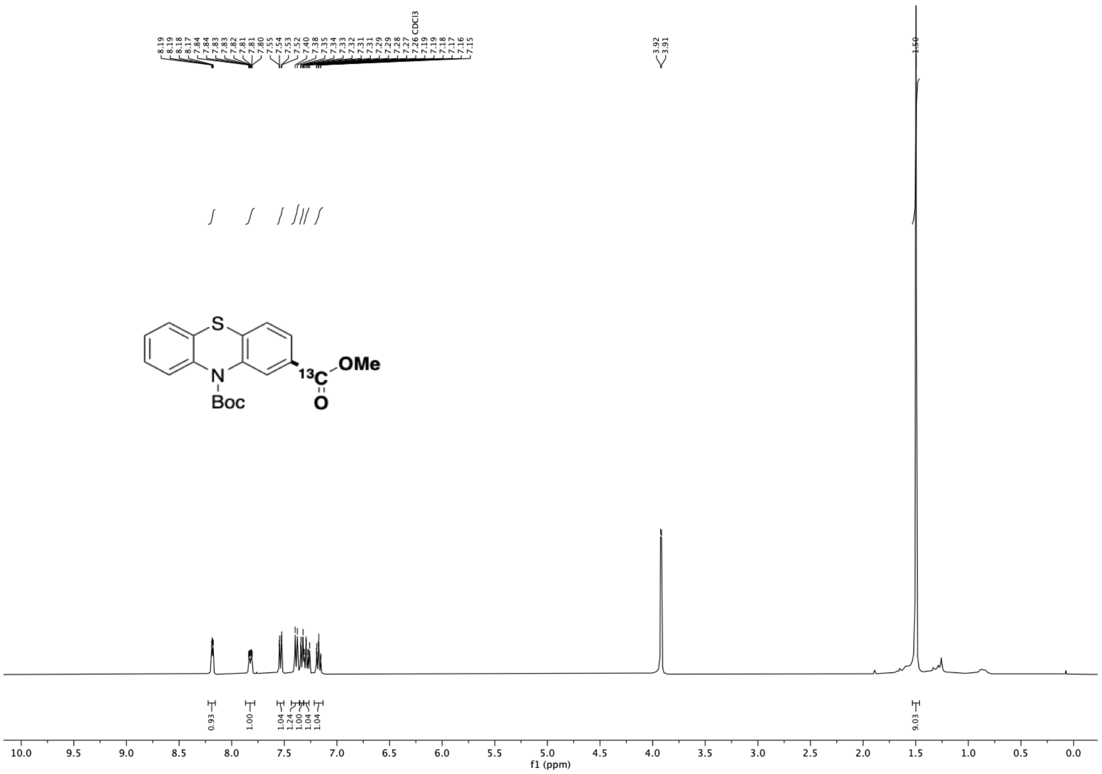
10-(tert-butyl) 2-methyl 10H-phenothiazine-2,10-dicarboxylate (10) – ^{1}H NMR



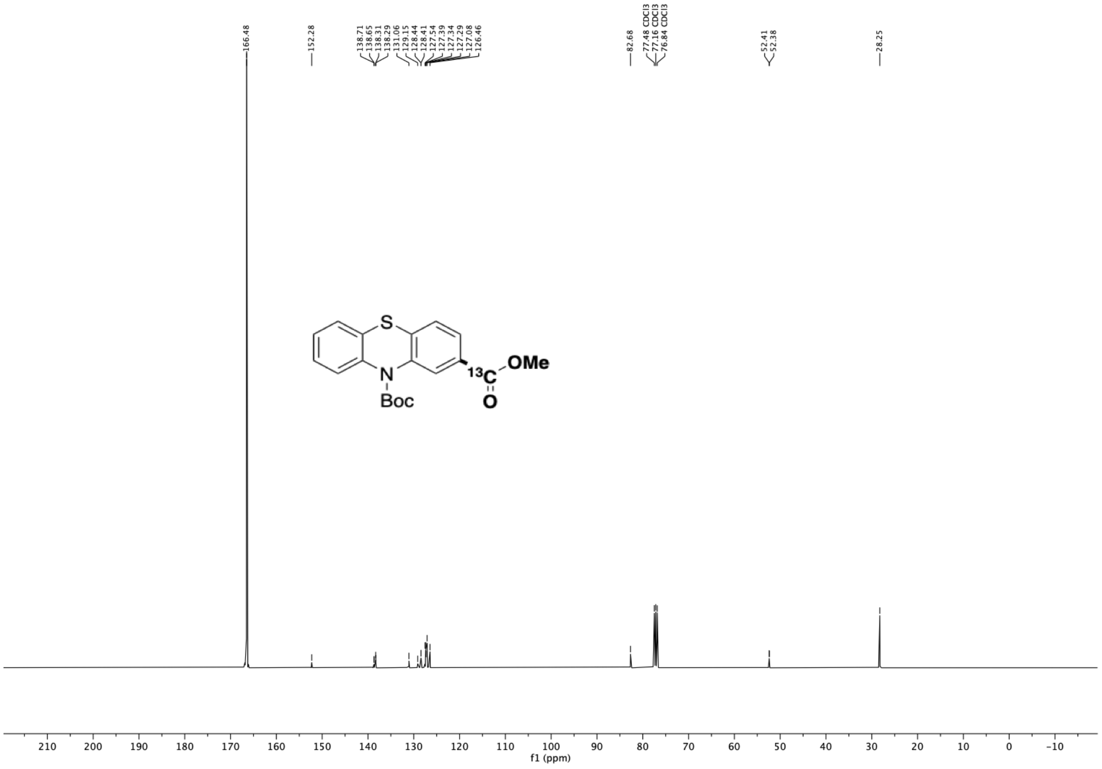
10-(tert-butyl) 2-methyl 10H-phenothiazine-2,10-dicarboxylate (10) – ^{13}C NMR



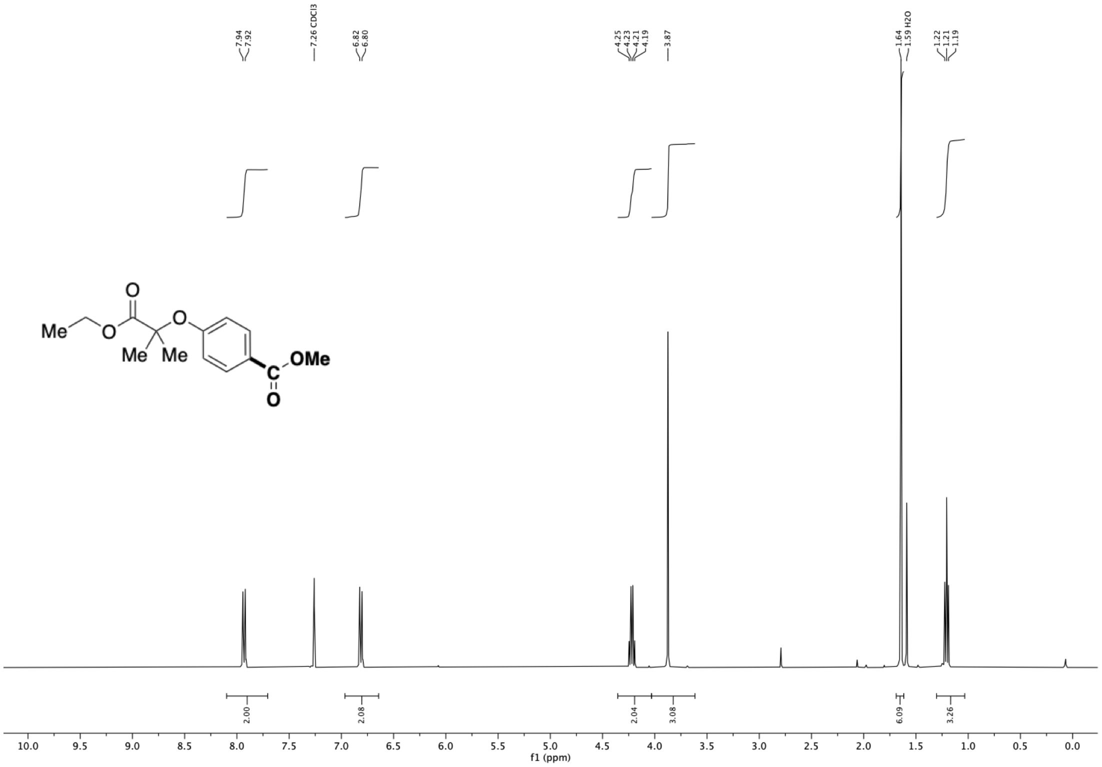
10-(tert-butyl) 2-methyl 10H-phenothiazine-2,10-dicarboxylate (^{13}C-10) – ^{1}H NMR



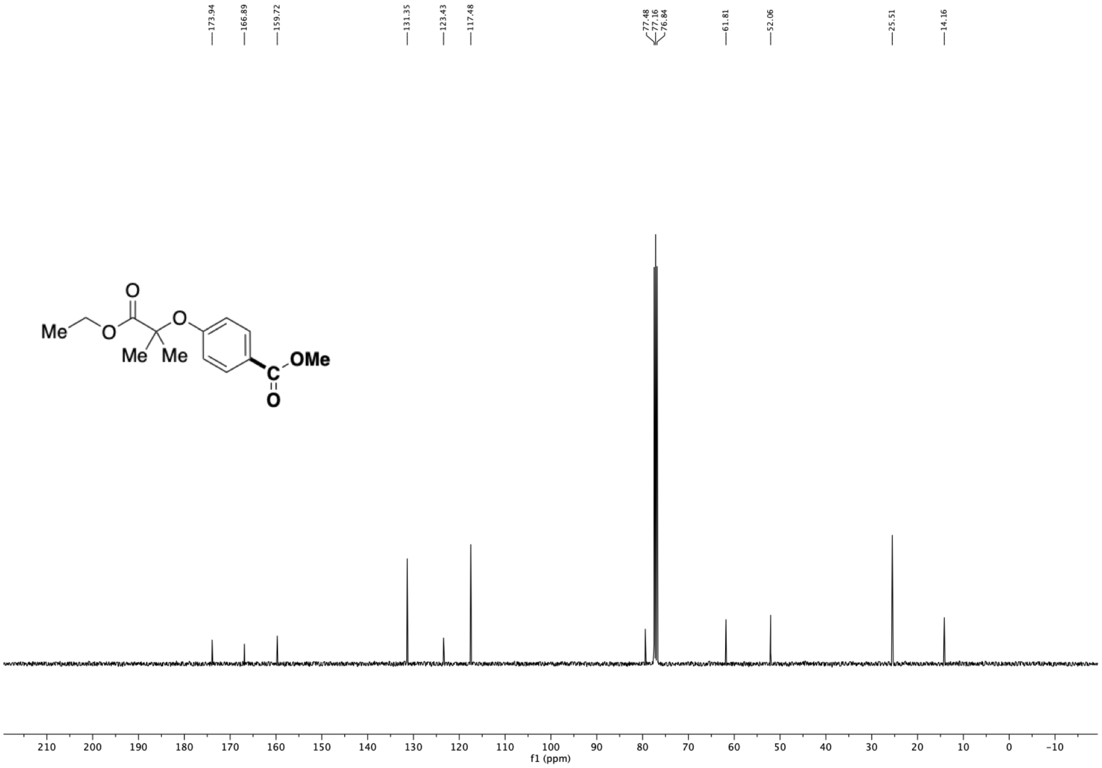
10-(tert-butyl) 2-methyl 10H-phenothiazine-2,10-dicarboxylate (^{13}C-10) – ^{13}C NMR



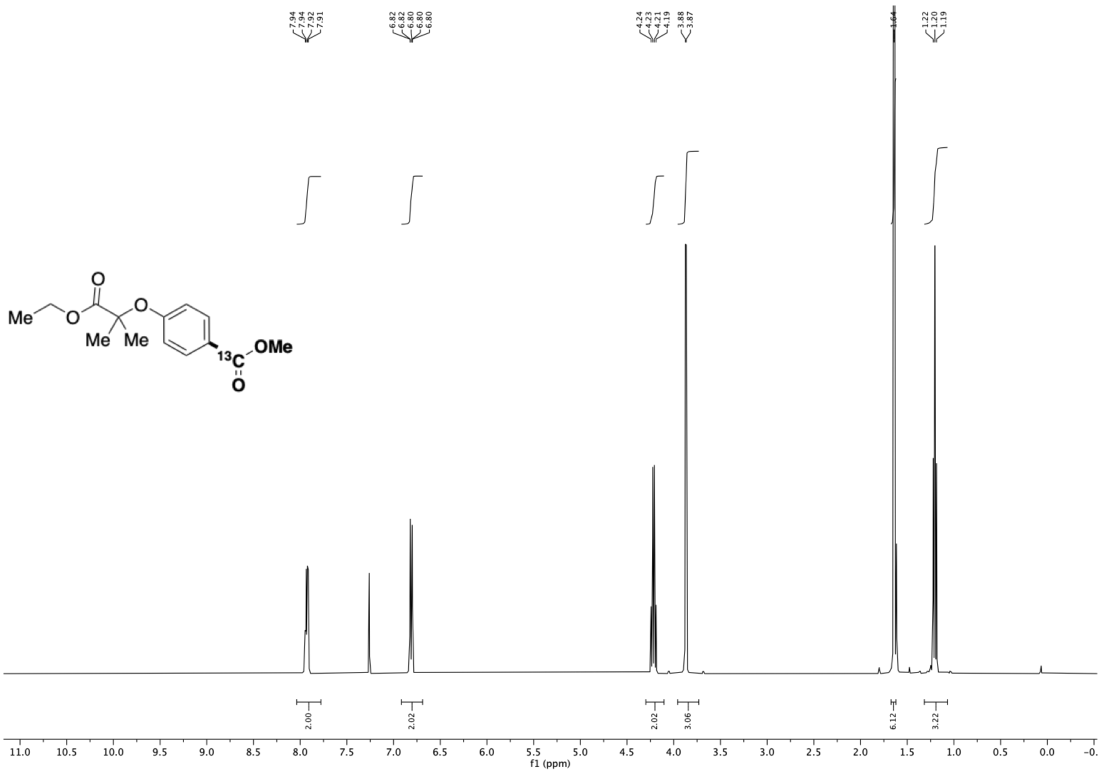
Methyl 4-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoate (11) – ^{1}H NMR



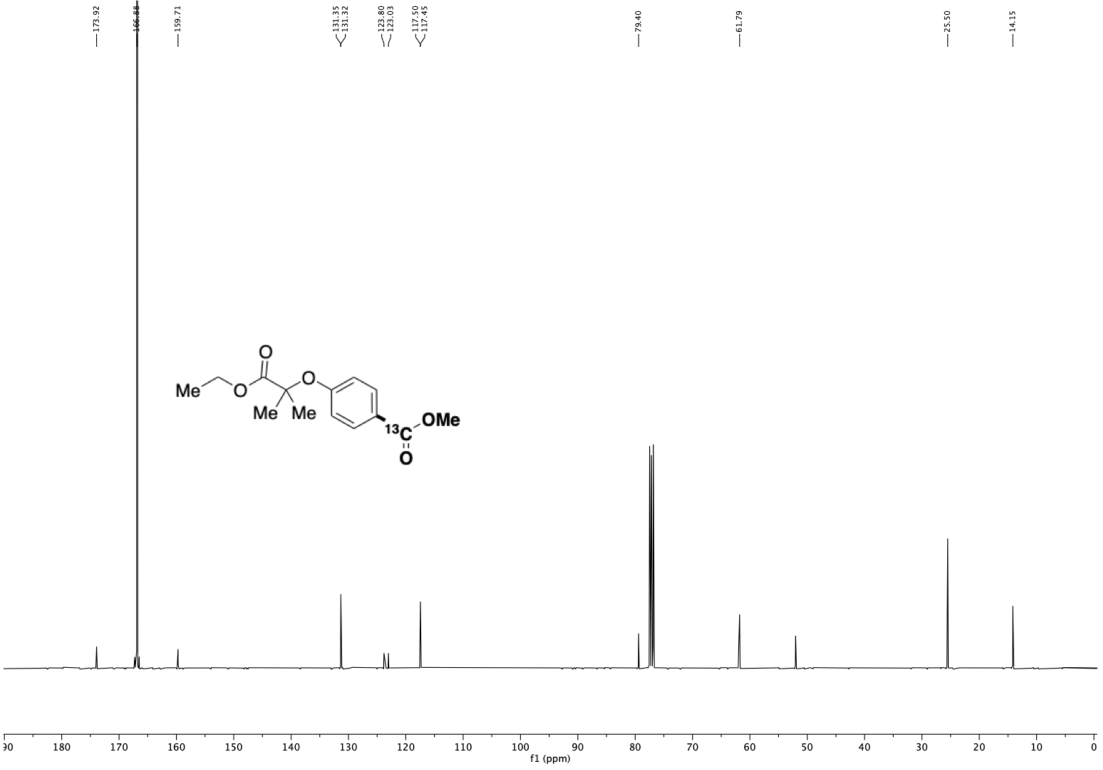
Methyl 4-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoate (11) – ^{13}C NMR



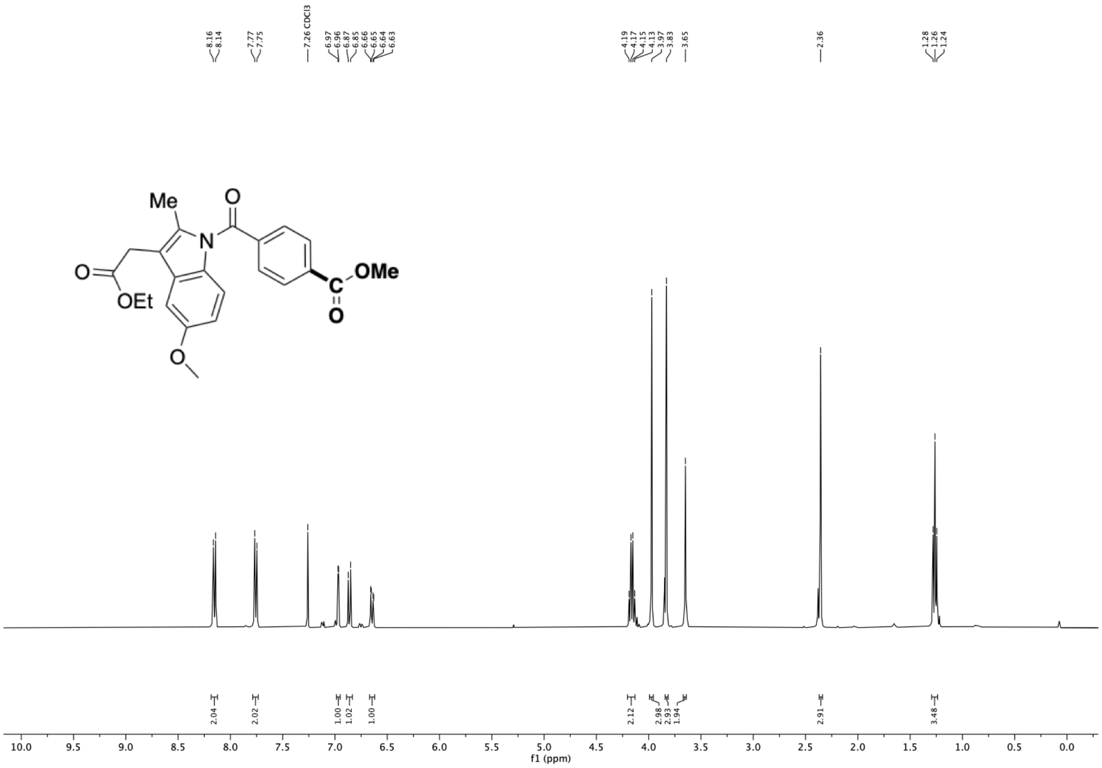
Methyl 4-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoate (^{13}C-11) – ^{1}H NMR



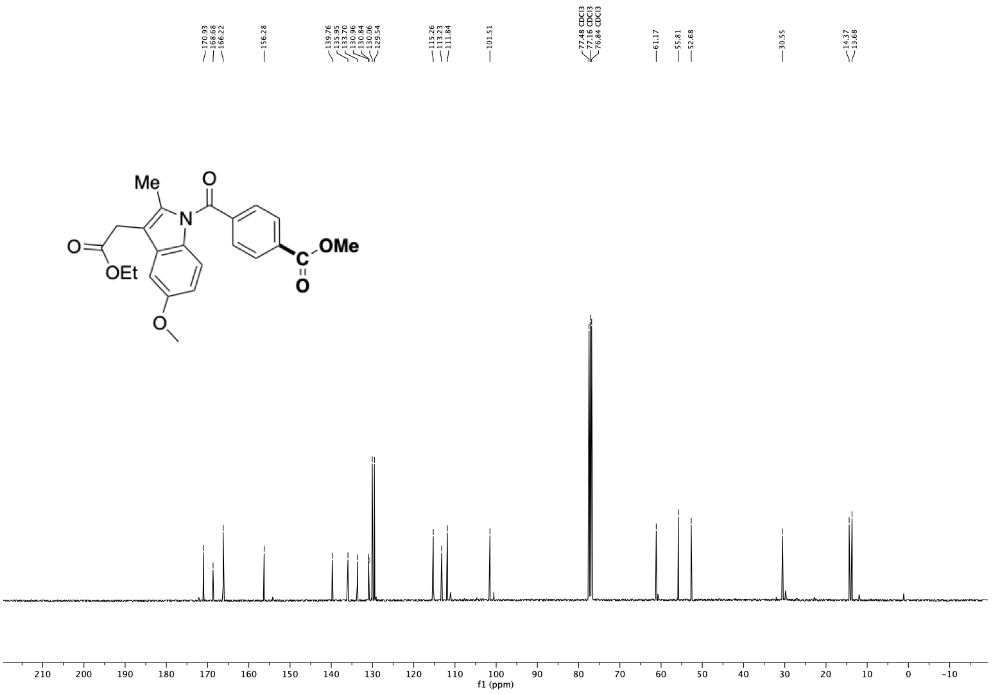
Methyl 4-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoate (^{13}C-11) – ^{13}C NMR



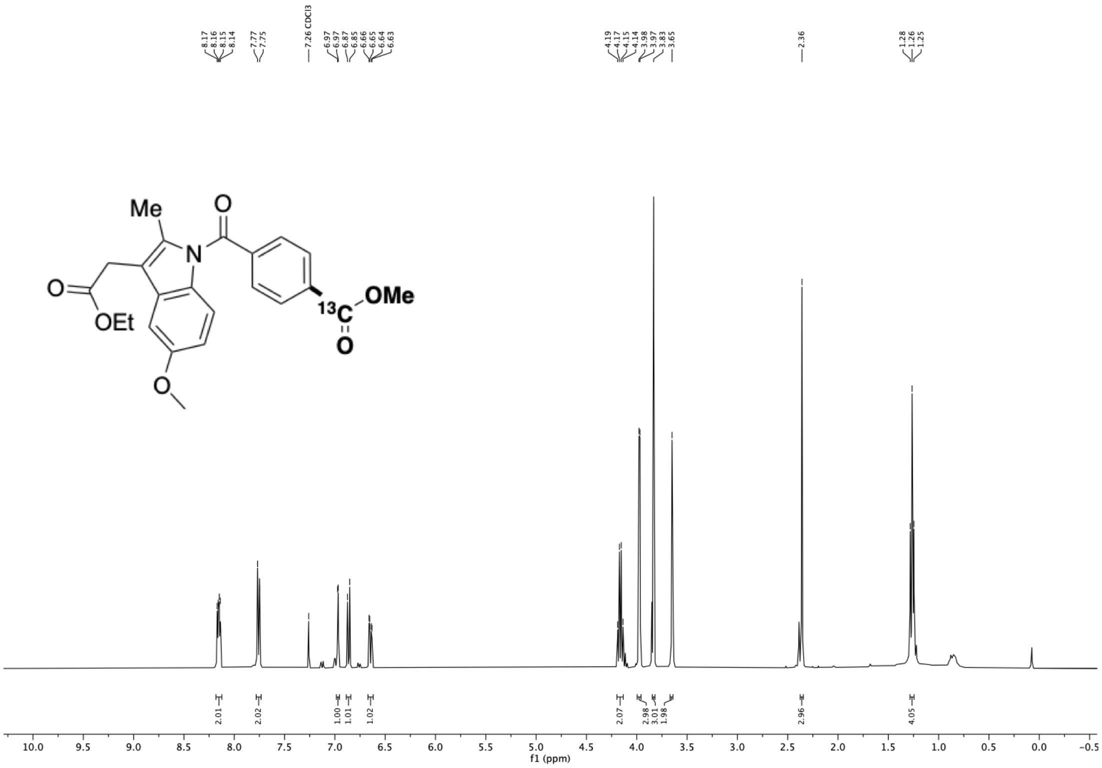
Methyl 4-(3-(2-ethoxy-2-oxoethyl)-5-methoxy-2-methyl-1H-indole-1-carbonyl)benzoate (12) – ^{1}H NMR



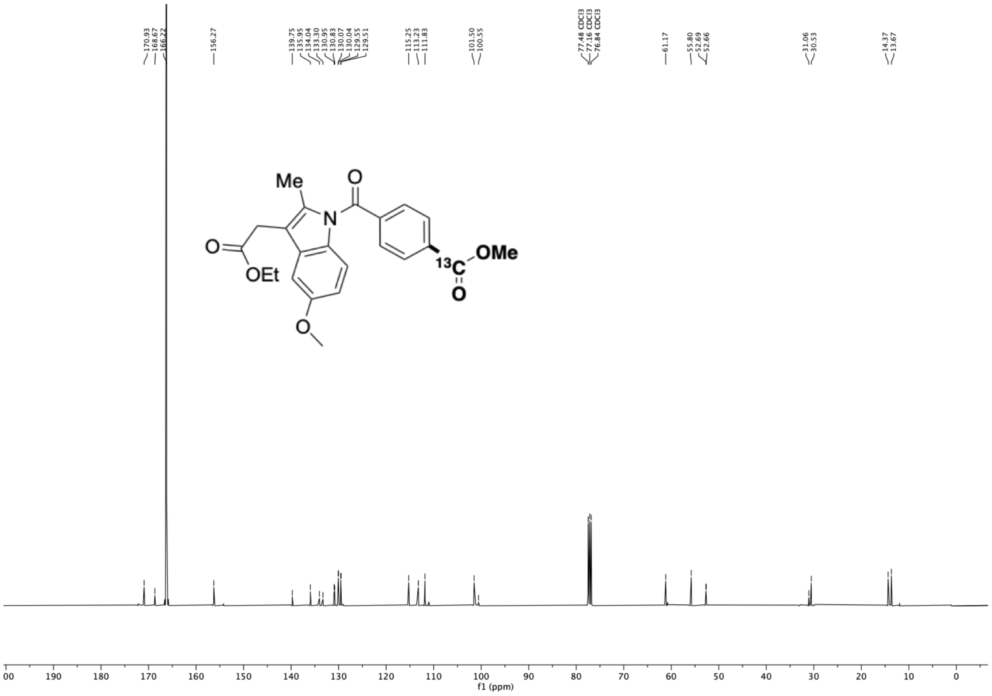
Methyl 4-(3-(2-ethoxy-2-oxoethyl)-5-methoxy-2-methyl-1H-indole-1-carbonyl)benzoate (12) – ^{13}C NMR



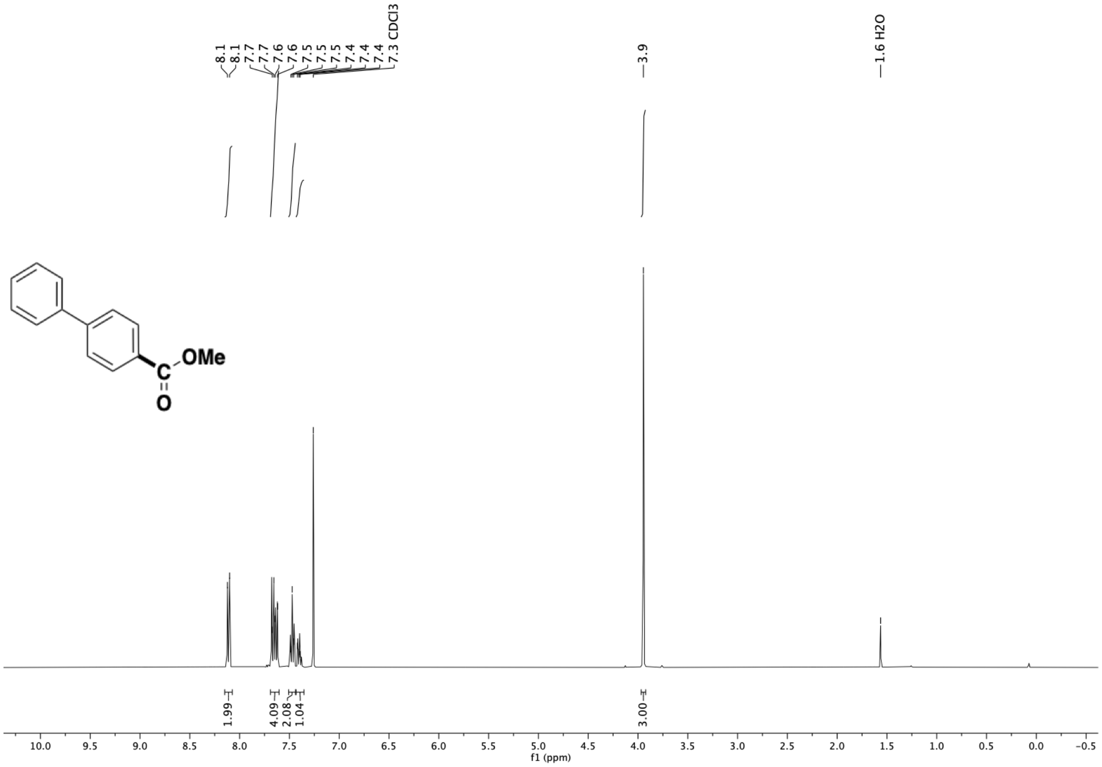
Methyl4-(3-(2-ethoxy-2-oxoethyl)-5-methoxy-2-methyl-1H-indole-1-carbonyl)benzoate (^{13}C-12) – ^{1}H NMR



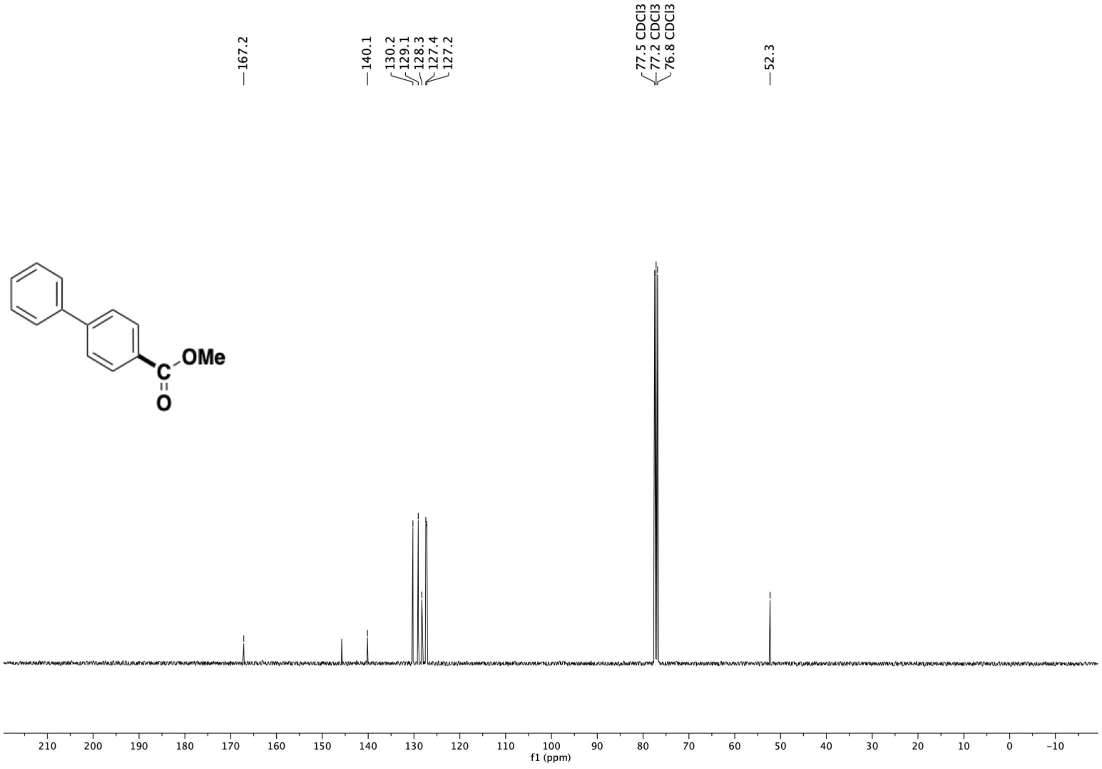
Methyl4-(3-(2-ethoxy-2-oxoethyl)-5-methoxy-2-methyl-1H-indole-1-carbonyl)benzoate (^{13}C-12) – ^{13}C NMR



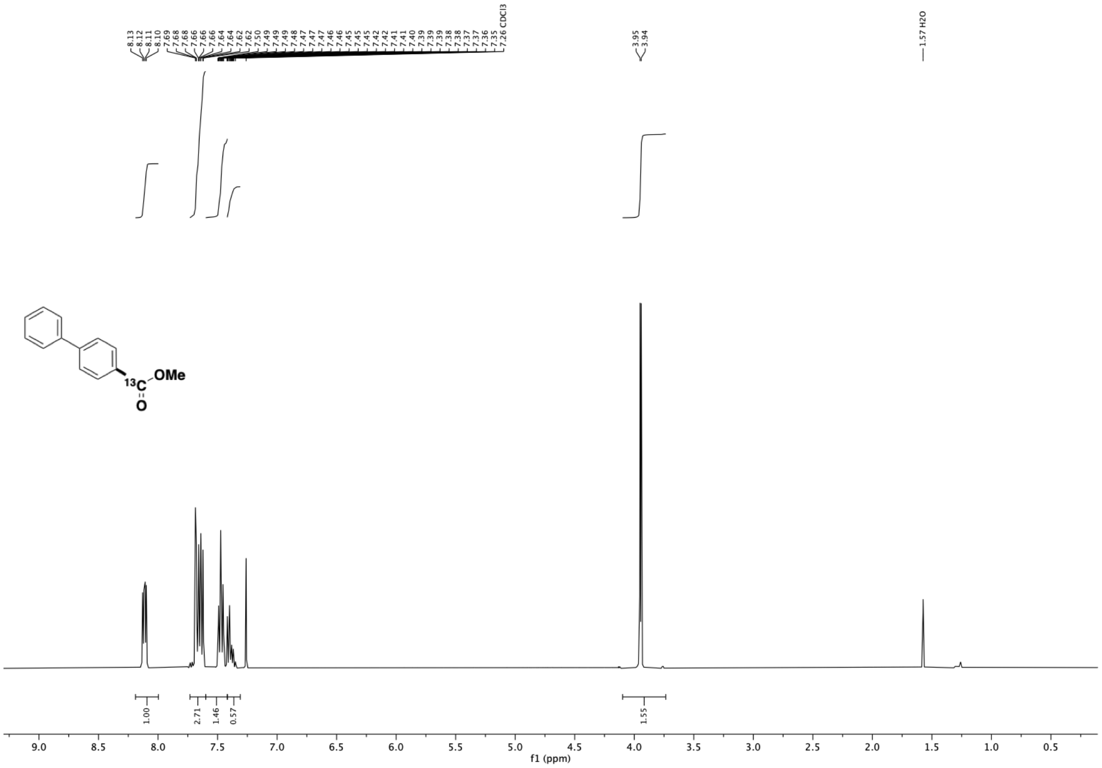
Methyl 4-phenylbenzoate (13) – ^{1}H NMR



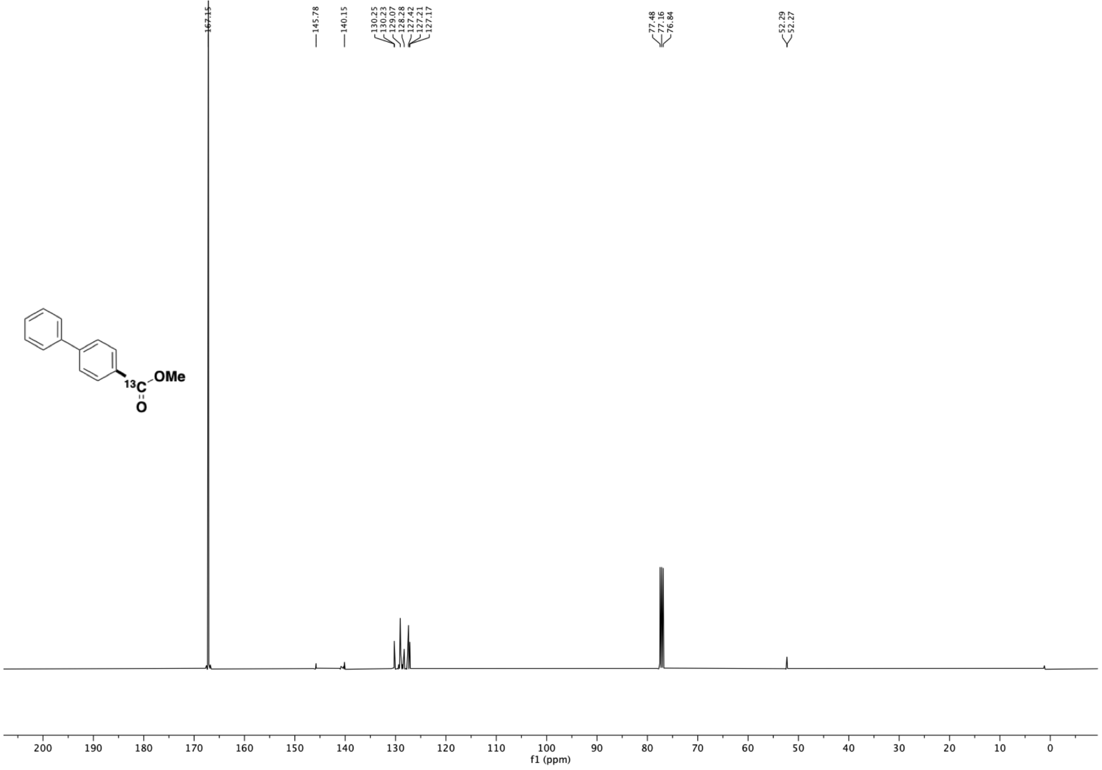
Methyl 4-phenylbenzoate (13) – ^{13}C NMR



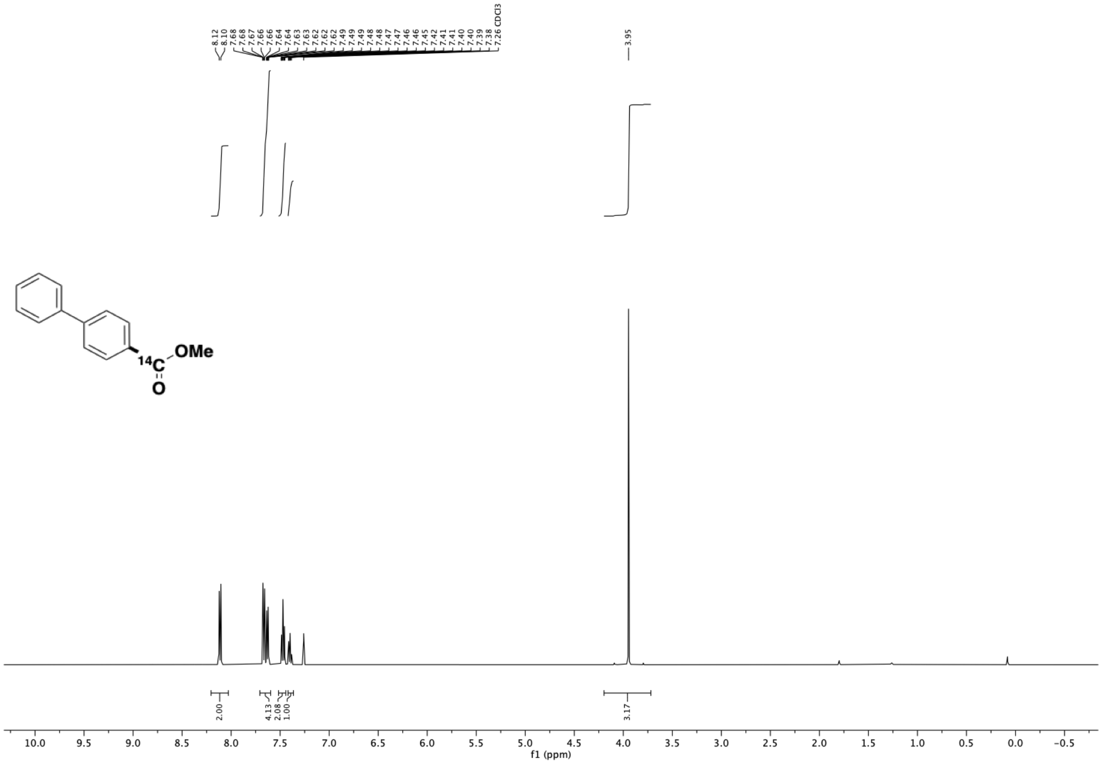
Methyl 4-phenylbenzoate (^{13}C-13) – ^{1}H NMR



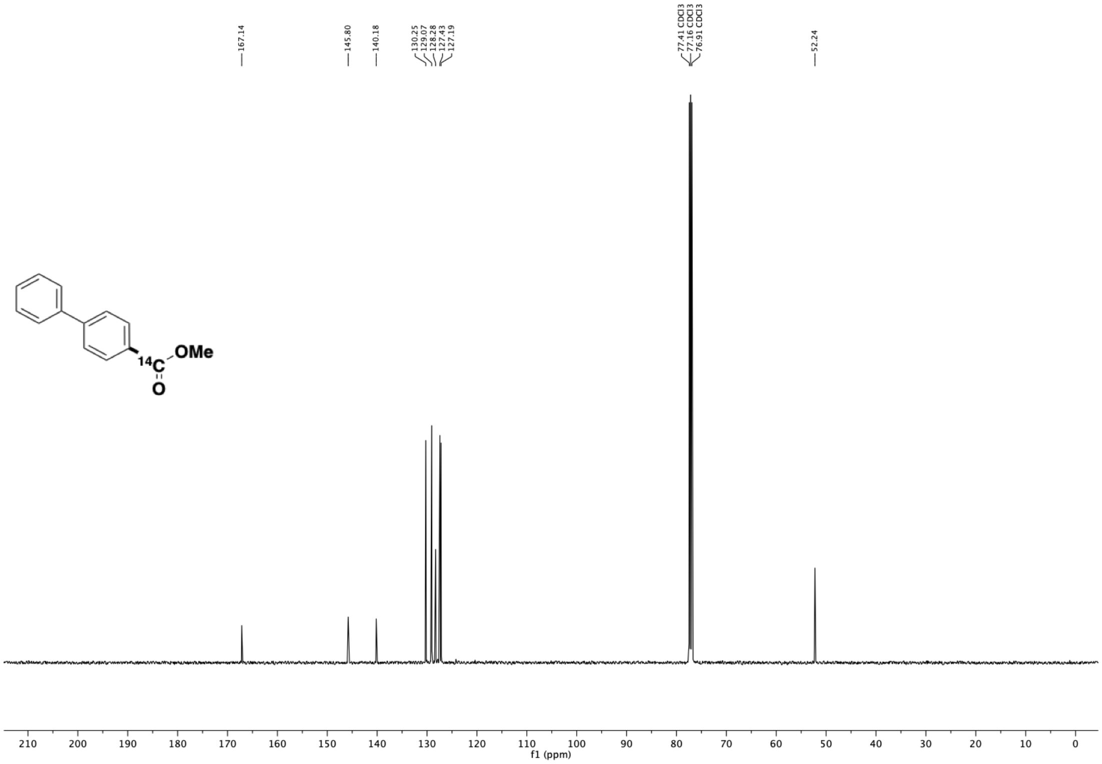
Methyl 4-phenylbenzoate (^{13}C-13) – ^{13}C NMR



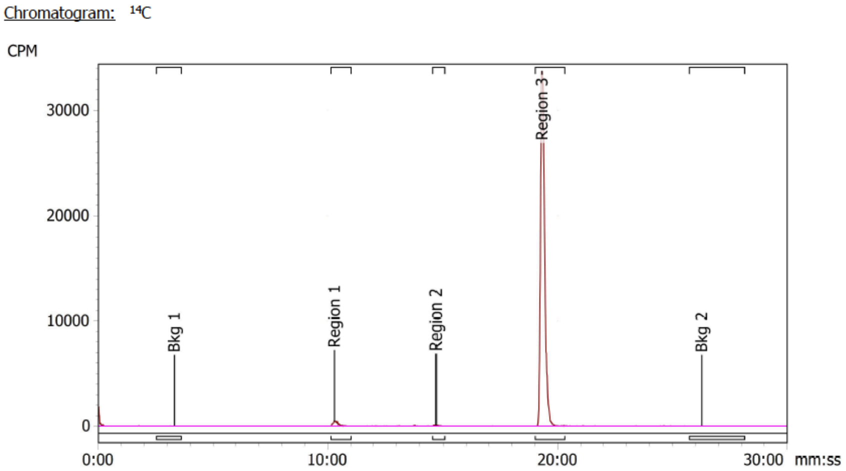
Methyl 4-phenylbenzoate (^{14}C-13) – ^{1}H NMR



Methyl 4-phenylbenzoate (^{14}C-13) – ^{13}C NMR



Methyl 4-phenylbenzoate (^{14}C-13) – Radio HPLC Injection 1



Regions: ^{14}C Detector: ß-RAM

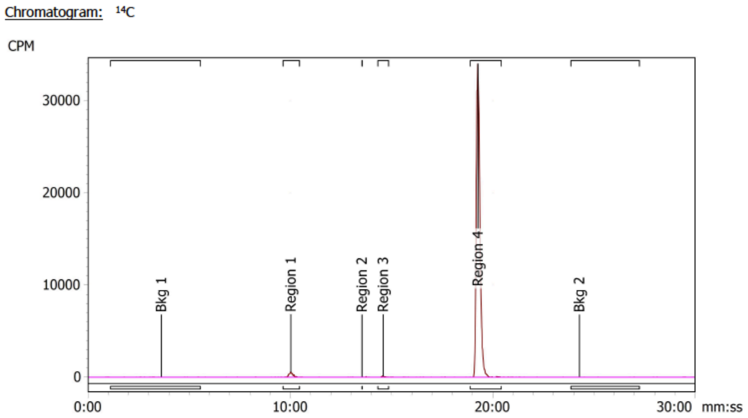
Name	Start (mm:ss)	End (mm:ss)	Retention (mm:ss)	Area (CPM)	%ROI (%)	%Total (%)
Bkg 1	2:32	3:37	3:19			
Region 1	10:09	11:01	10:18	6719	1,67	1,64
Region 2	14:35	15:04	14:43	1048	0,26	0,26
Region 3	19:01	20:18	19:19	394865	98,07	96,58
Bkg 2	25:44	28:09	26:17			
3 Peaks				402632	100,00	98,48

Total Area: 408849 CPM
Average Background: 1 CPM

Sample Details: EN13507-12 inj1 Ph10

Injection Volume:5 µL

Methyl 4-phenylbenzoate (^{14}C-13) – Radio HPLC Injection 2



Regions: ^{14}C Detector: ß-RAM

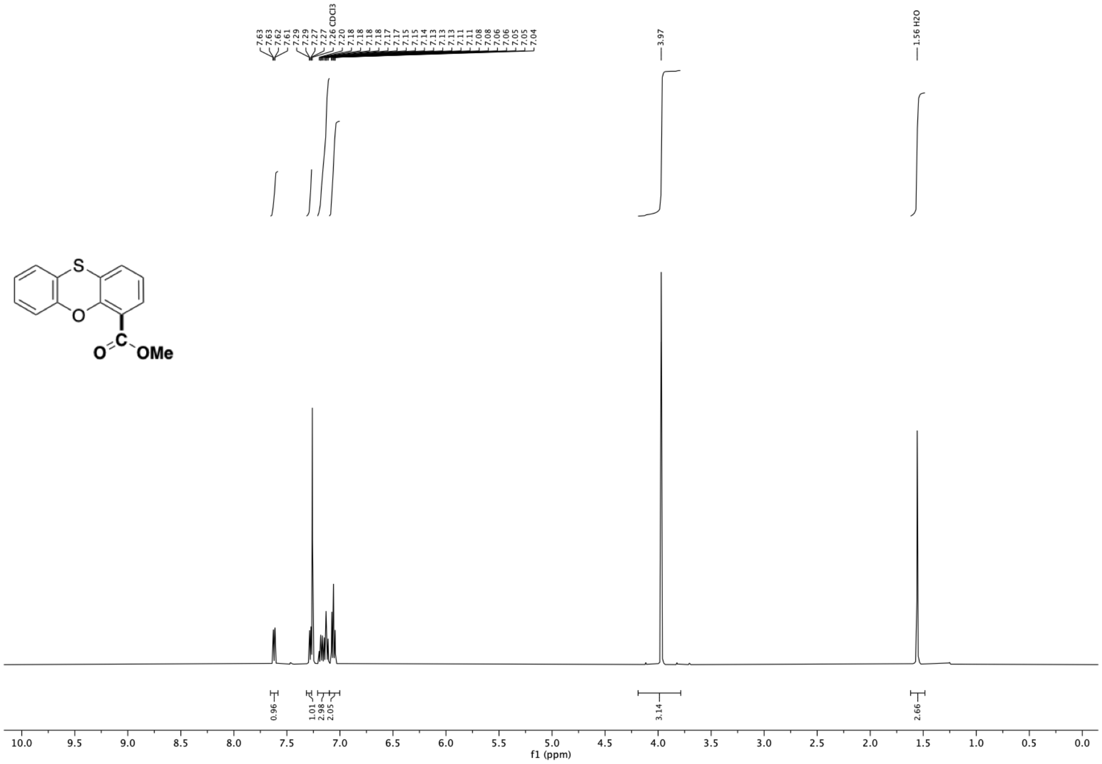
Name	Start (mm:ss)	End (mm:ss)	Retention (mm:ss)	Area (CPM)	%ROI (%)	%Total (%)
Bkg 1	1:06	5:33	3:37			
Region 1	9:38	10:27	10:01	6715	1,68	1,67
Region 2	13:32	13:33	13:32	-2	0,00	0,00
Region 3	14:19	14:51	14:35	1031	0,26	0,26
Region 4	18:53	20:25	19:16	392552	98,07	97,85
Bkg 2	23:52	27:15	24:17			
4 Peaks				400296	100,00	99,78

Total Area: 401171 CPM
Average Background: 2 CPM

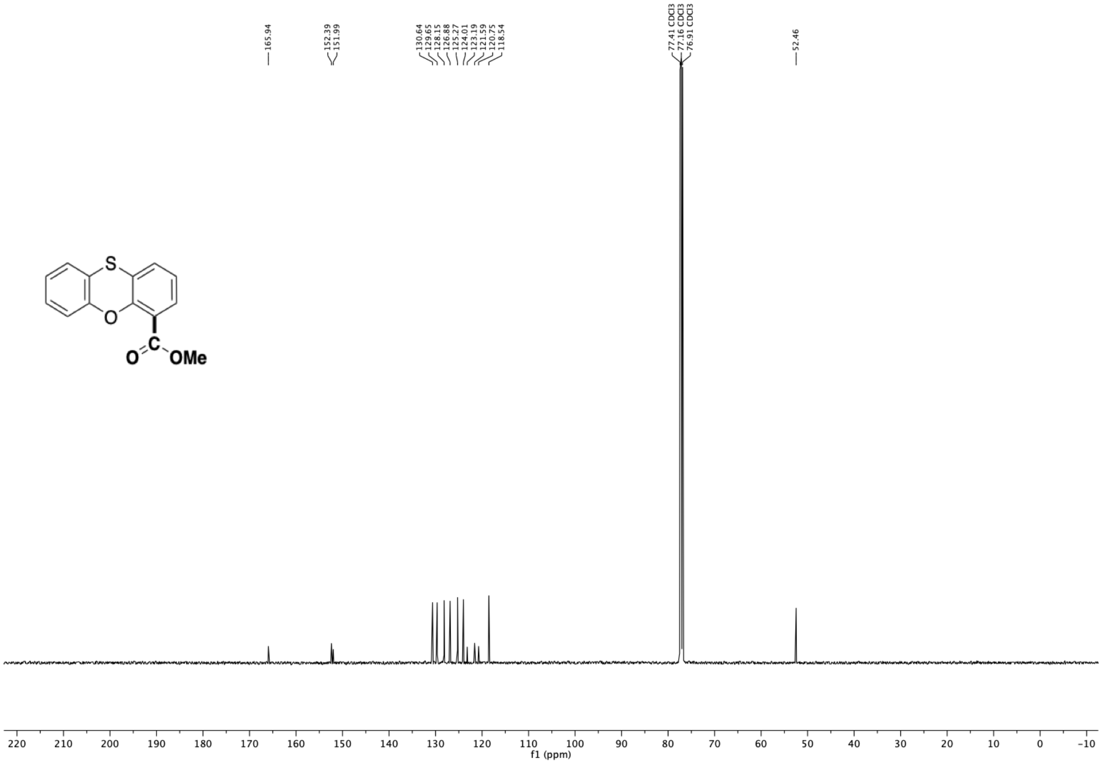
Sample Details: EN13507-12 inj2 Ph10

Injection Volume:5 µL

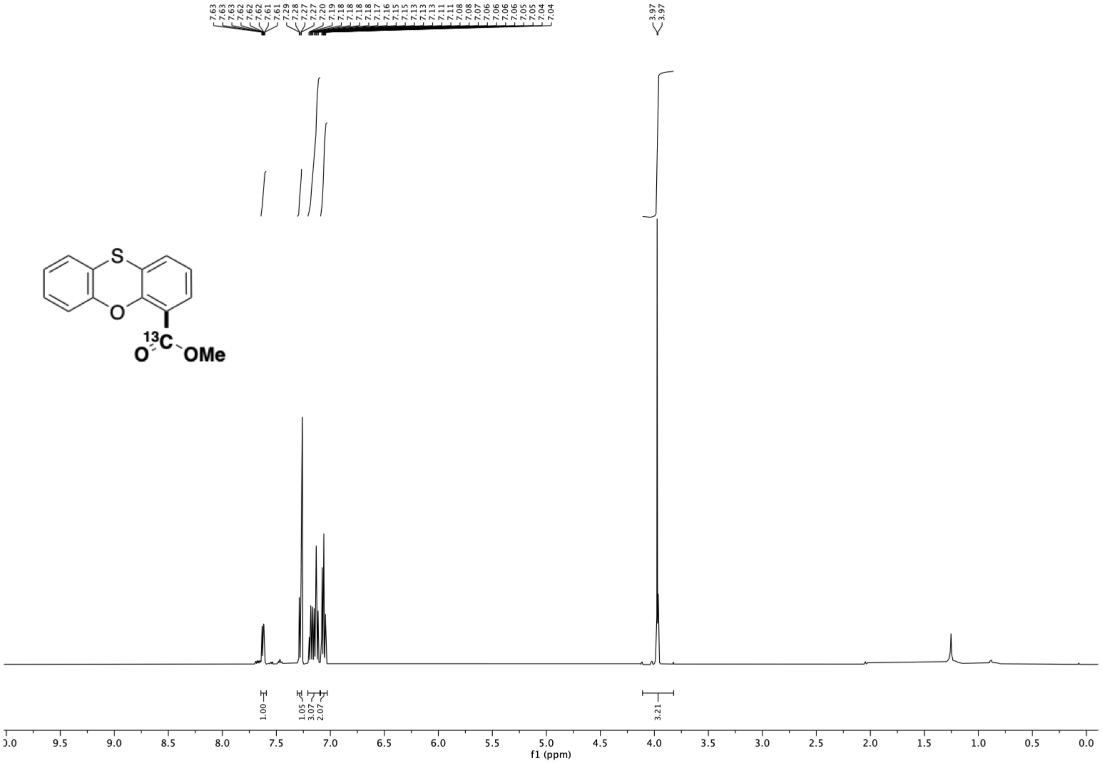
Methyl phenoxathiin-1-carboxylate (14) – ^{1}H NMR



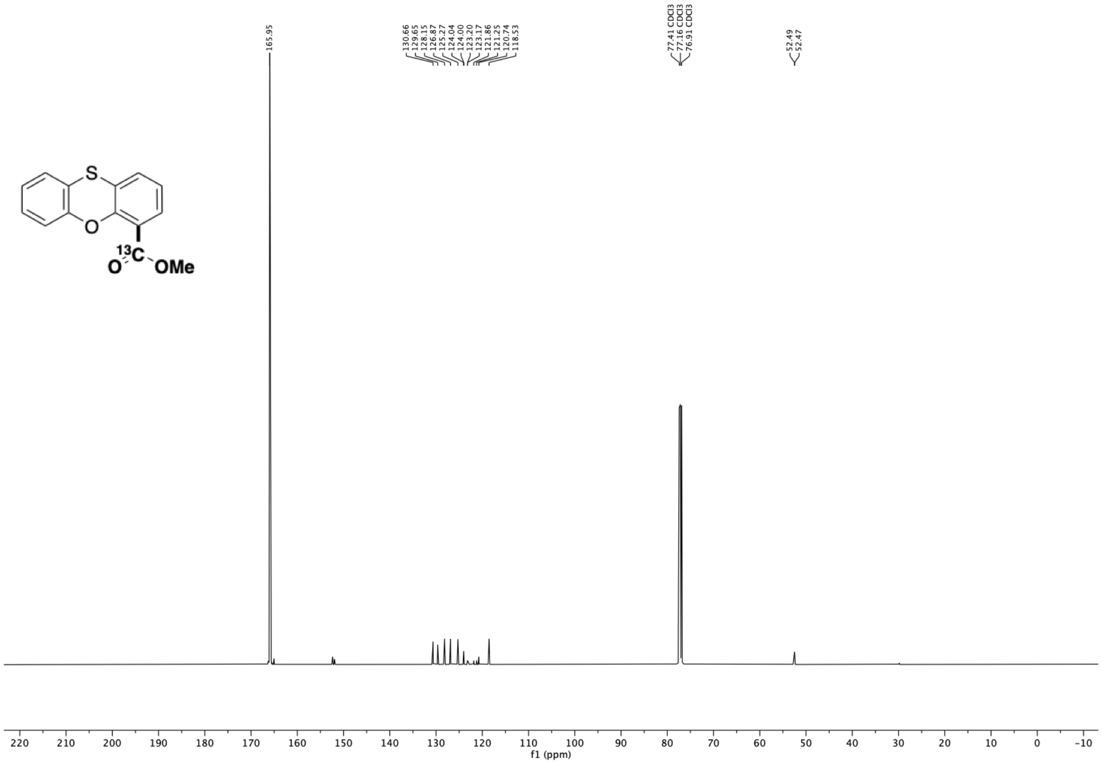
Methyl phenoxathiin-1-carboxylate (14) – ^{13}C NMR



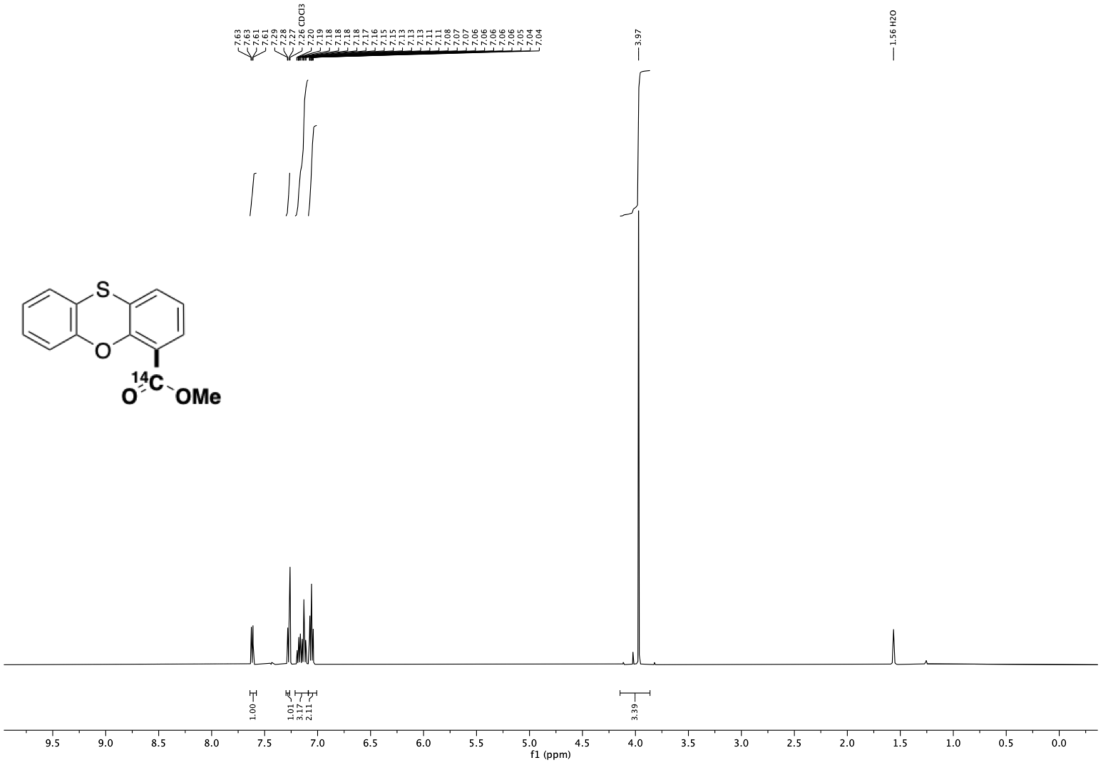
Methyl phenoxathiin-1-carboxylate (^{13}C-14) – ^{1}H NMR



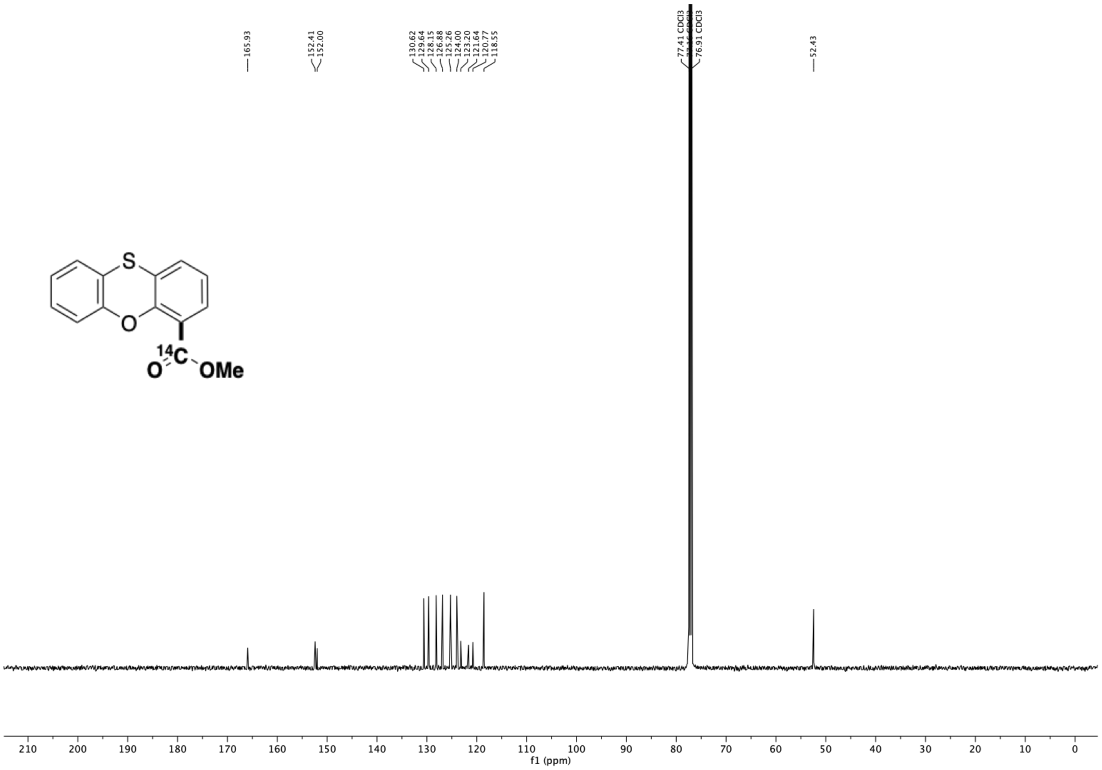
Methyl phenoxathiin-1-carboxylate (^{13}C-14) – ^{13}C NMR



Methyl phenoxathiin-1-carboxylate (^{14}C-14) – ^{1}H NMR

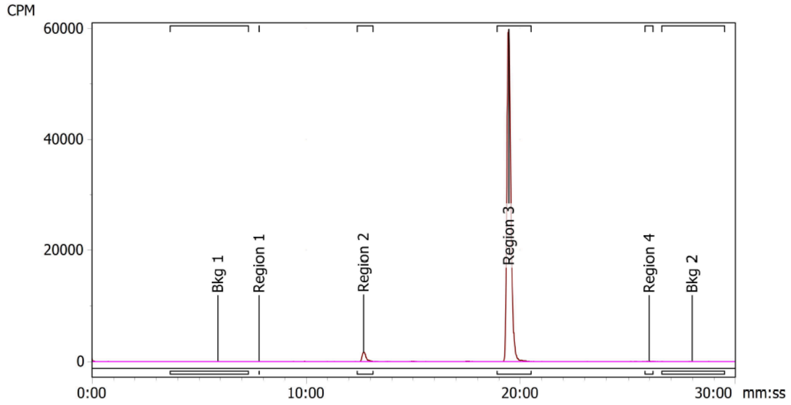


Methyl phenoxathiin-1-carboxylate (^{14}C-14) – ^{13}C NMR



Methyl phenoxathiin-1-carboxylate (^{14}C-14) – Radio HPLC Injection 1

Chromatogram: ^{14}C



Regions: ^{14}C Detector: ß-RAM

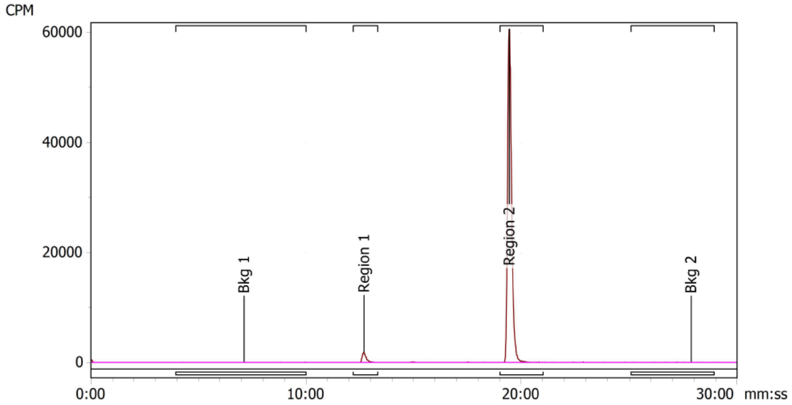
Name	Start (mm:ss)	End (mm:ss)	Retention (mm:ss)	Area (CPM)	%ROI (%)	%Total (%)
Bkg 1	3:39	7:18	5:53			
Region 1	7:48	7:49	7:48	10	0,00	0,00
Region 2	12:23	13:07	12:41	19597	2,65	2,64
Region 3	18:55	20:30	19:28	719180	97,28	96,78
Region 4	25:47	26:09	25:59	490	0,07	0,07
Bkg 2	26:34	29:30	27:59			
4 Peaks				739278	100,00	99,49

Total Area:	743083 CPM
Average Background:	3 CPM
Sample Details:	EN13507-31 inj1 pH10 1 mg per mL MeCN, 3.5 kBq/uL

Injection Volume:5 µL

Methyl phenoxathiin-1-carboxylate (^{14}C-14) – Radio HPLC Injection 2

Chromatogram: ^{14}C

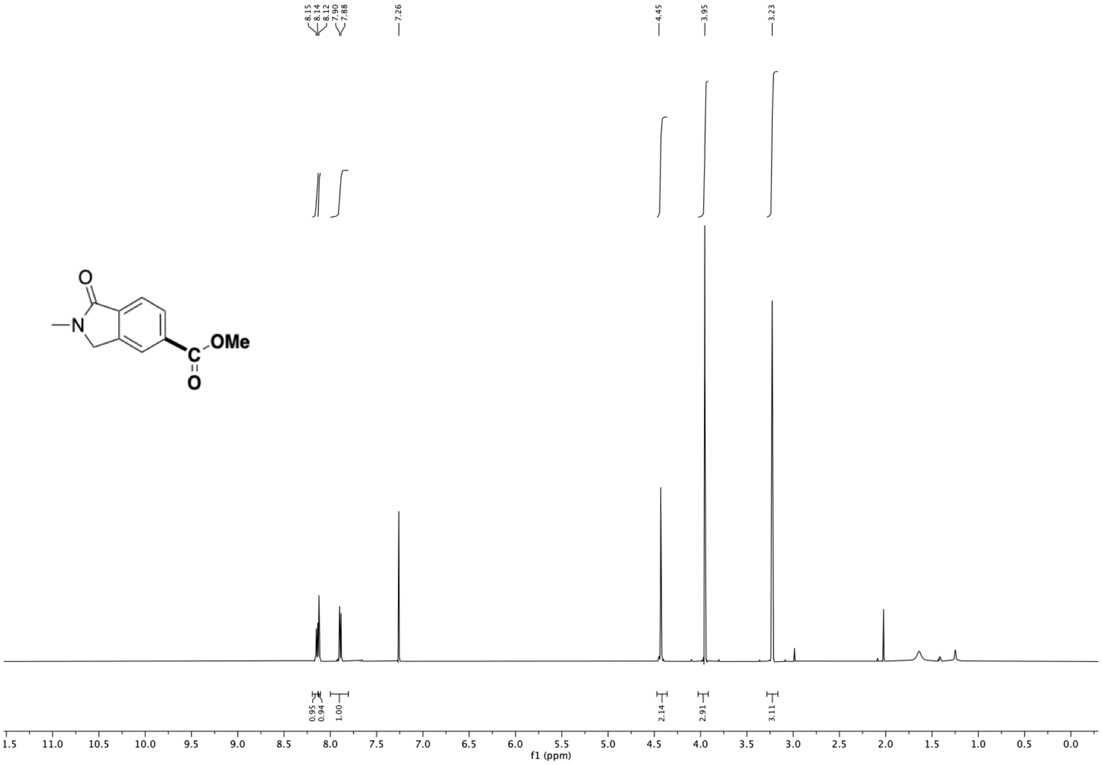


Regions: ^{14}C Detector: ß-RAM

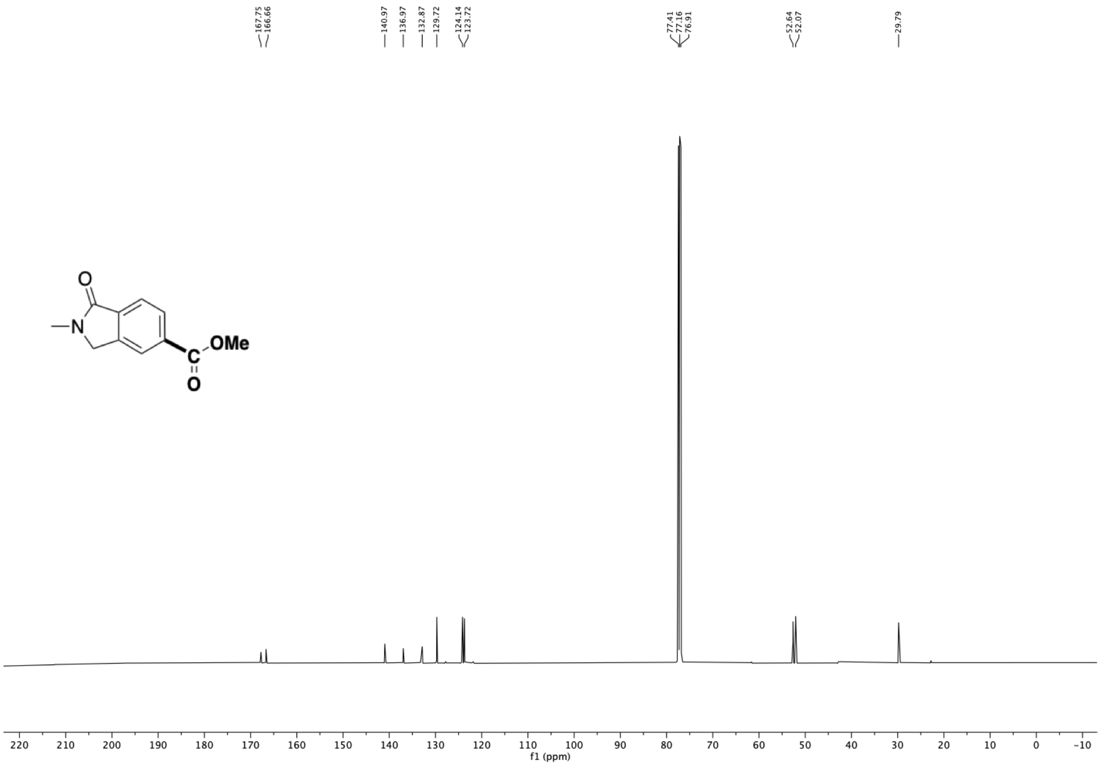
Name	Start (mm:ss)	End (mm:ss)	Retention (mm:ss)	Area (CPM)	%ROI (%)	%Total (%)
Bkg 1	3:57	10:00	7:07			
Region 1	12:12	13:20	12:42	20319	2,72	2,71
Region 2	19:01	21:01	19:27	727647	97,28	97,05
Bkg 2	25:04	28:56	27:52			
2 Peaks				747966	100,00	99,76

Total Area:	749800 CPM
Average Background:	3 CPM

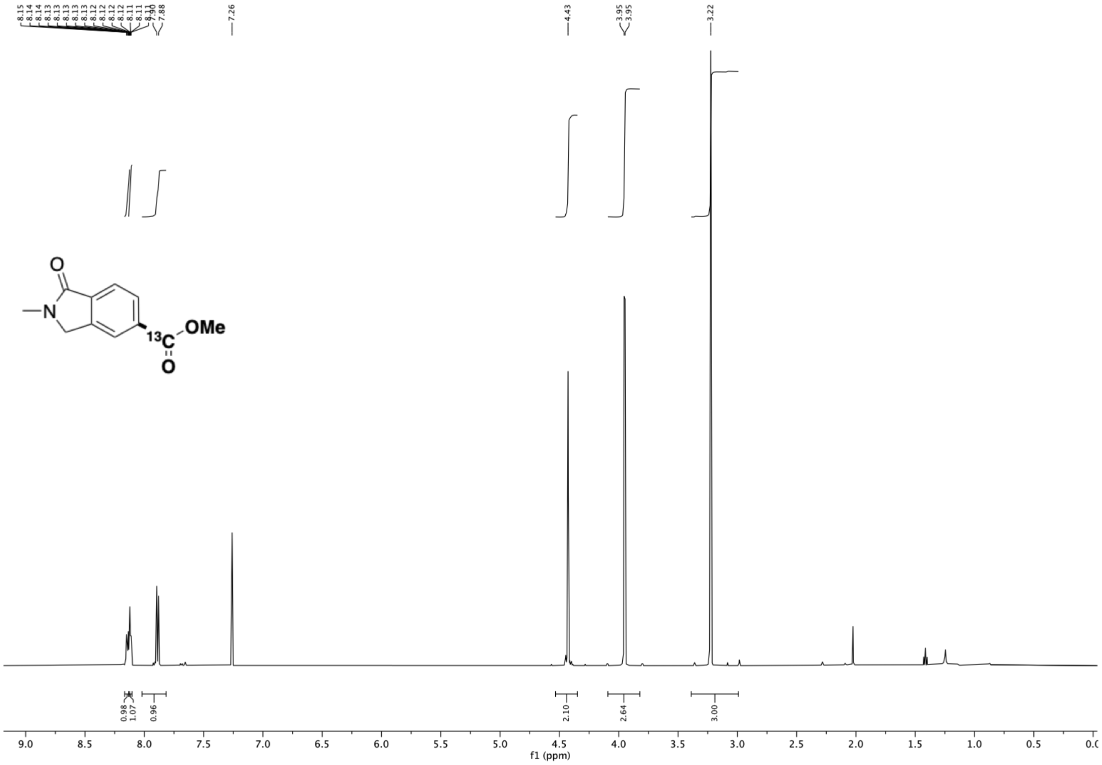
Methyl 2-methyl-1-oxoisoindoline-5-carboxylate (15) – ^{1}H NMR



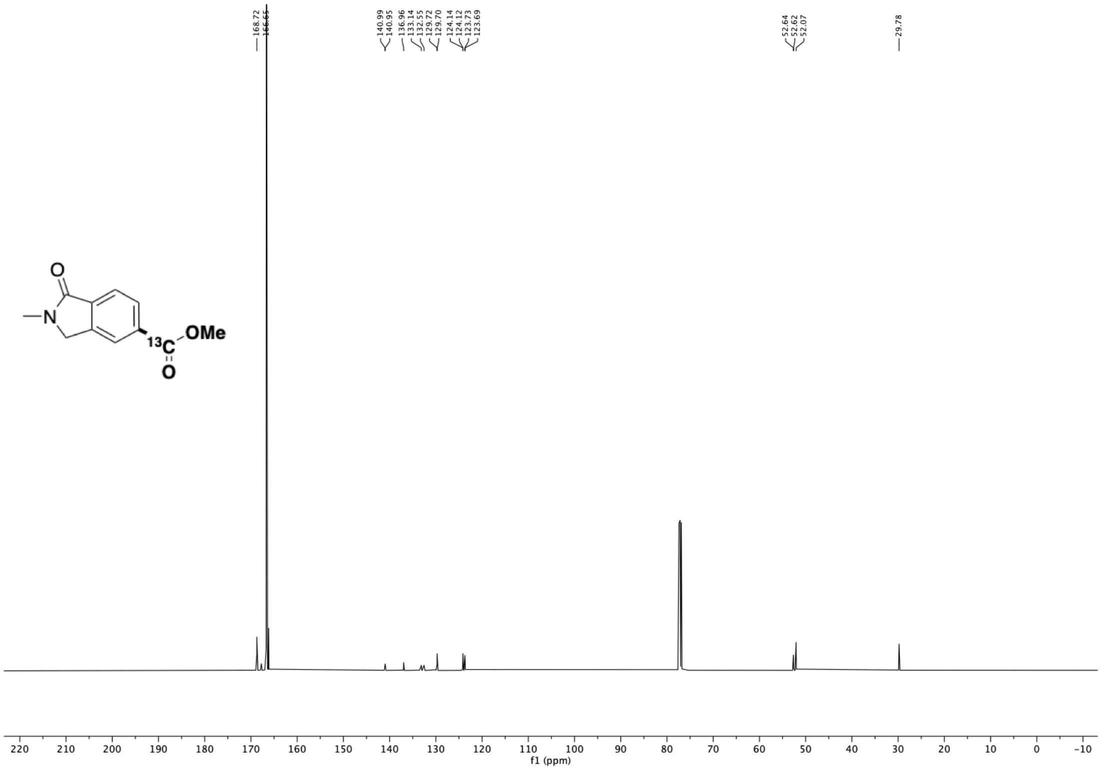
Methyl 2-methyl-1-oxoisoindoline-5-carboxylate (15) – ^{13}C NMR



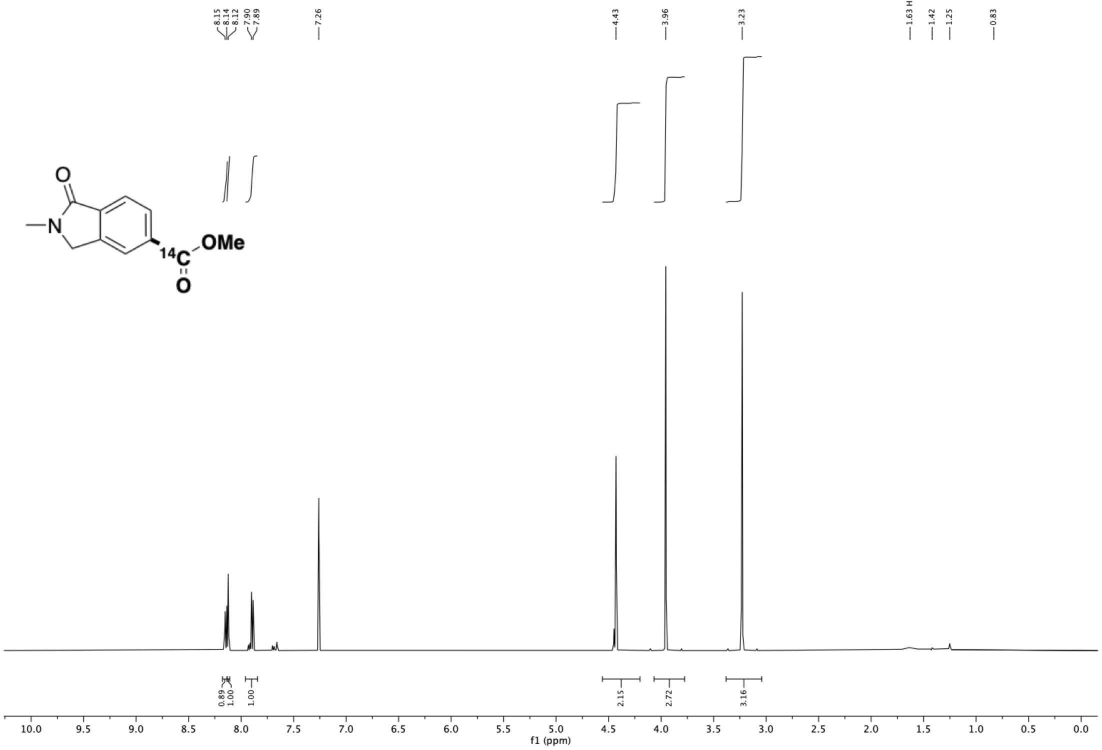
Methyl 2-methyl-1-oxoisoindoline-5-carboxylate (^{13}C-15) – ^{1}H NMR



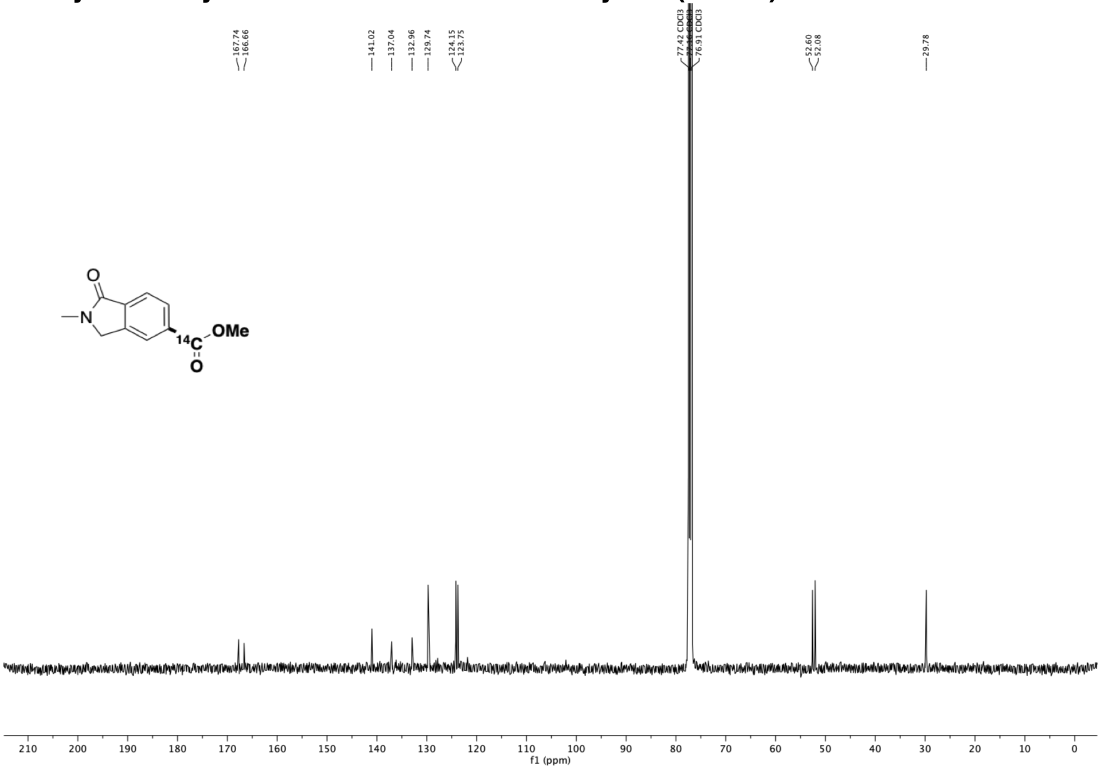
Methyl 2-methyl-1-oxoisoindoline-5-carboxylate (^{13}C-15) – ^{13}C NMR



Methyl 2-methyl-1-oxoisoindoline-5-carboxylate (^{14}C-15) – ^{1}H NMR

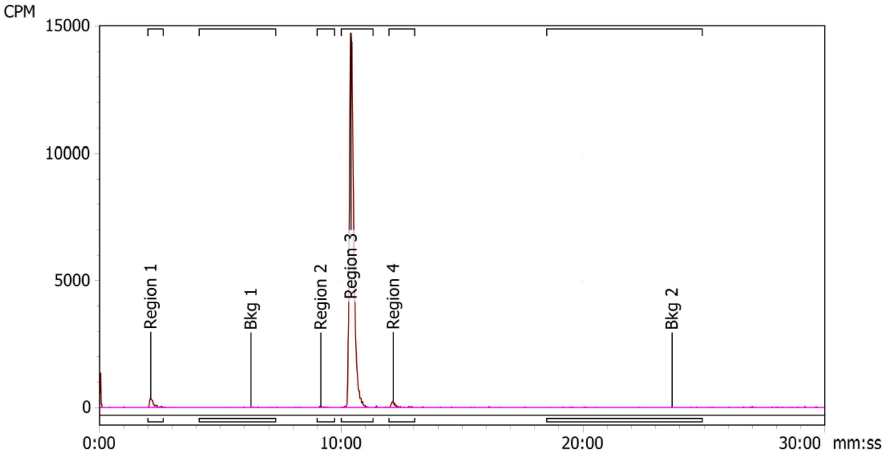


Methyl 2-methyl-1-oxoisoindoline-5-carboxylate (^{14}C-15) – ^{13}C NMR



Methyl 2-methyl-1-oxoisoindoline-5-carboxylate (^{14}C-15) – Radio HPLC Injection 1

Chromatogram: ^{14}C



Regions: ^{14}C Detector: ß-RAM

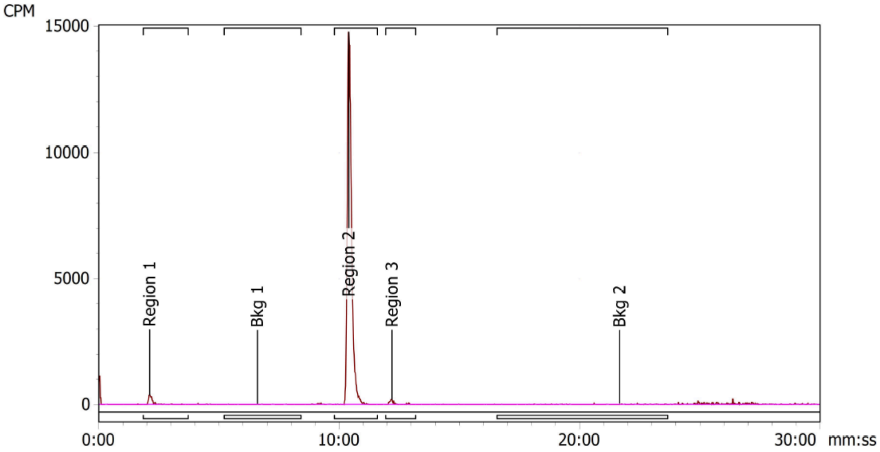
Name	Start (mm:ss)	End (mm:ss)	Retention (mm:ss)	Area (CPM)	%ROI (%)	%Total (%)
Region 1	2:00	2:38	2:07	3634	2,07	2,03
Bkg 1	4:07	7:17	6:16			
Region 2	9:00	9:43	9:09	399	0,23	0,22
Region 3	10:00	11:19	10:24	169460	96,32	94,76
Region 4	11:58	13:02	12:09	2450	1,39	1,37
Bkg 2	18:30	24:56	23:41			
4 Peaks				175943	100,00	98,39

Total Area:	178825 CPM
Average Background:	2 CPM
Sample Details:	EN13507-32 inj1 pH10 1 mg per mL MeCN, 3.5 kBq/uL

Injection Volume:5 µL

Methyl 2-methyl-1-oxoisoindoline-5-carboxylate (^{14}C-15) – Radio HPLC Injection 2

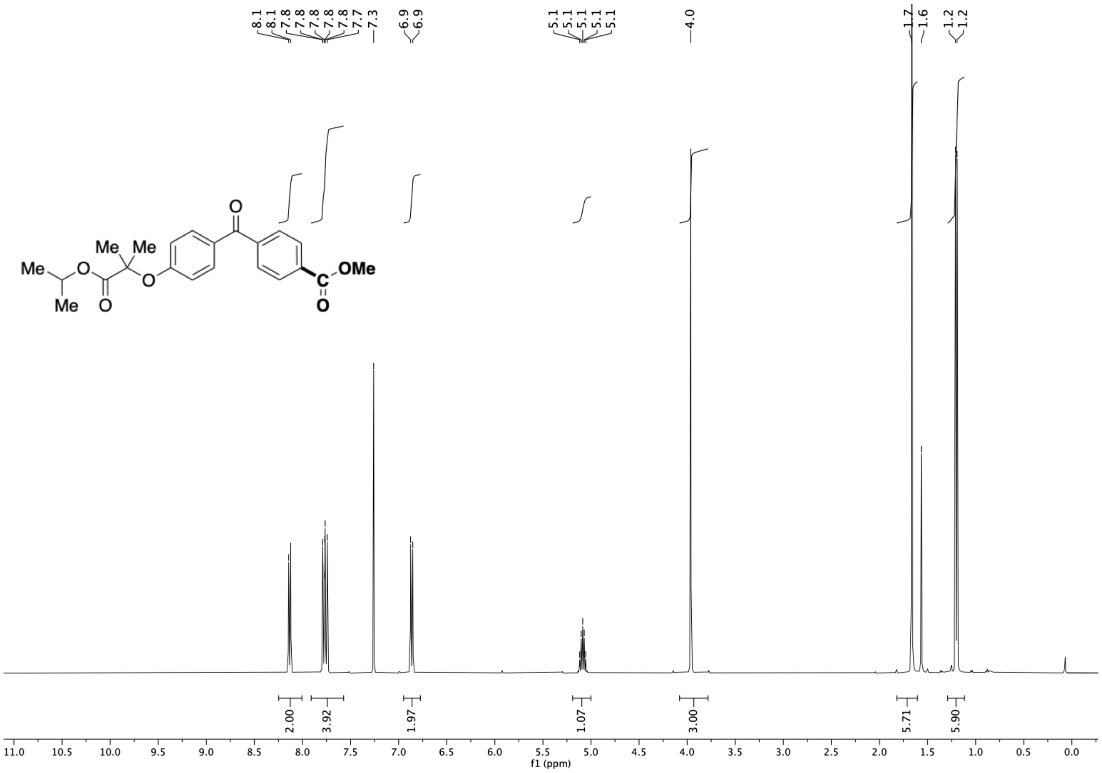
Chromatogram: ^{14}C



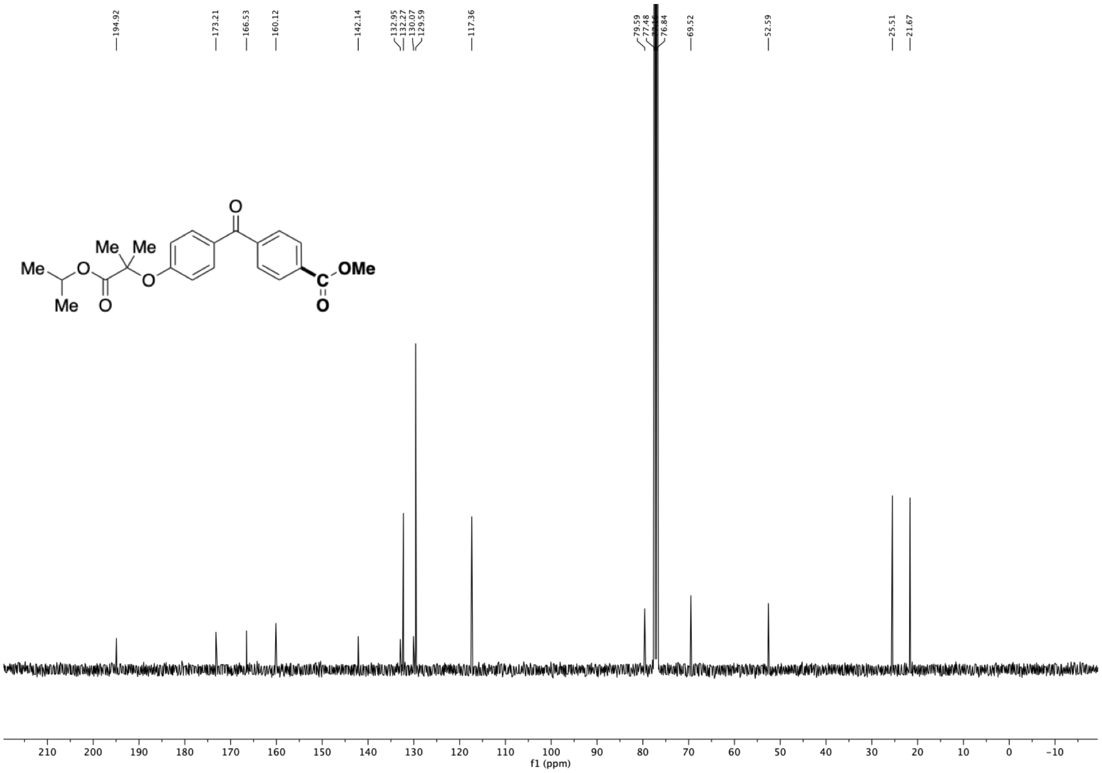
Regions: ^{14}C Detector: ß-RAM

Name	Start (mm:ss)	End (mm:ss)	Retention (mm:ss)	Area (CPM)	%ROI (%)	%Total (%)
Region 1	1:51	3:43	2:07	3677	2,11	2,02
Bkg 1	5:13	8:25	6:36			
Region 2	9:48	11:35	10:24	168411	96,76	92,67
Region 3	11:56	13:11	12:12	1971	1,13	1,08
Bkg 2	16:34	23:40	21:40			
3 Peaks				174059	100,00	95,77

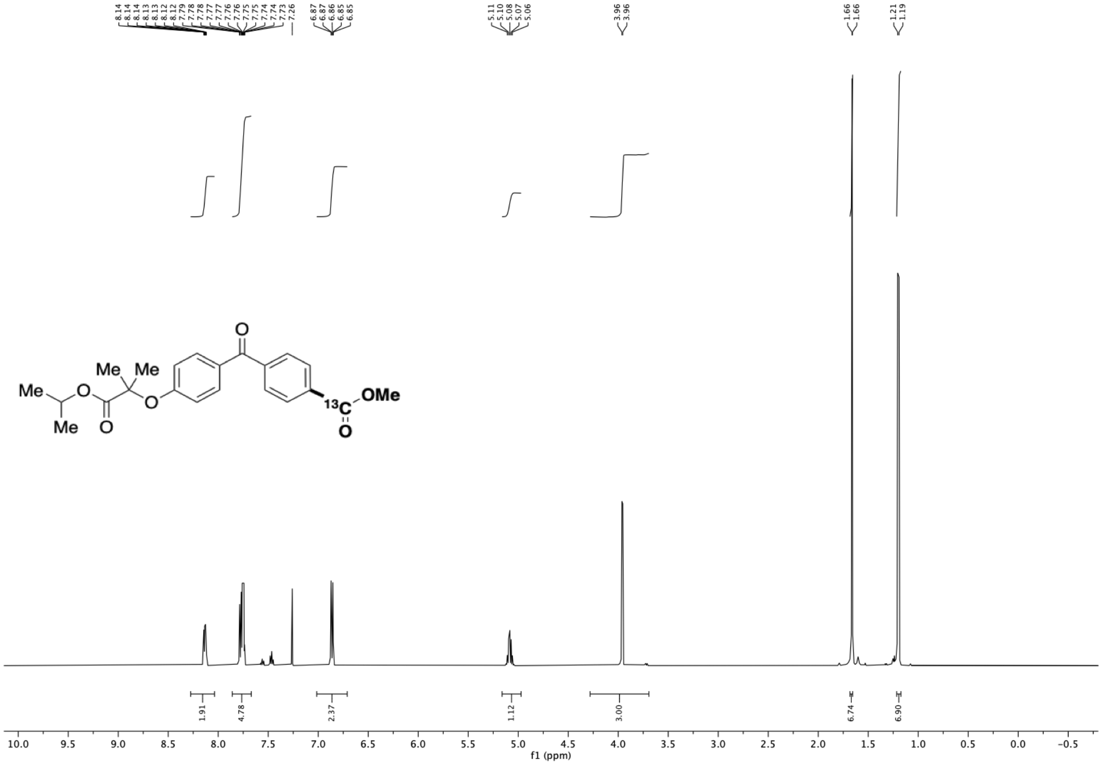
Methyl 4-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)benzoate (16) – ^{1}H NMR



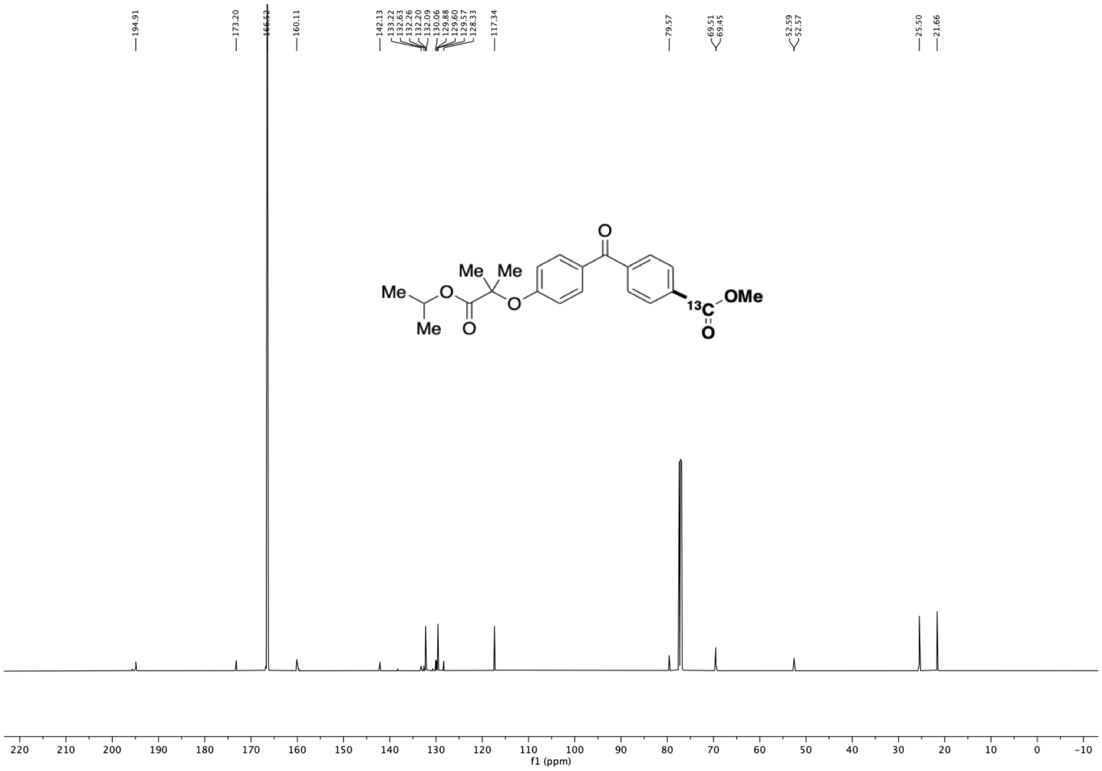
Methyl 4-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)benzoate (16) – ^{13}C NMR



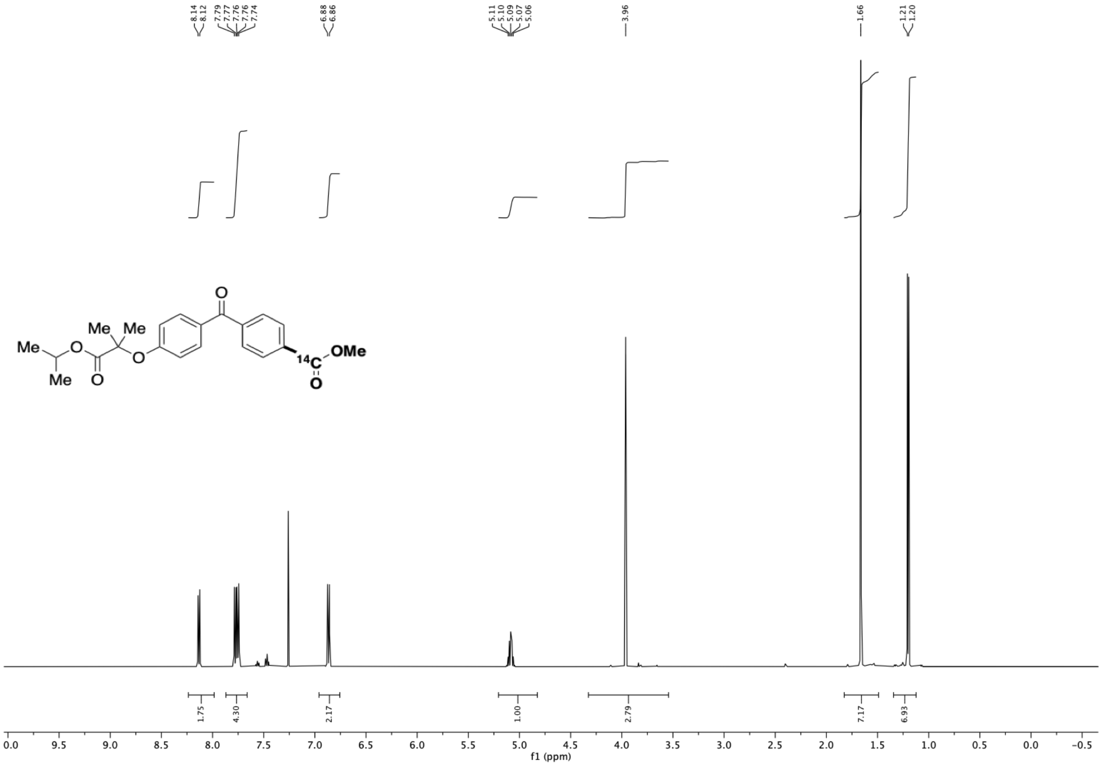
Methyl 4-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)benzoate (^{13}C-16) – ^{1}H NMR



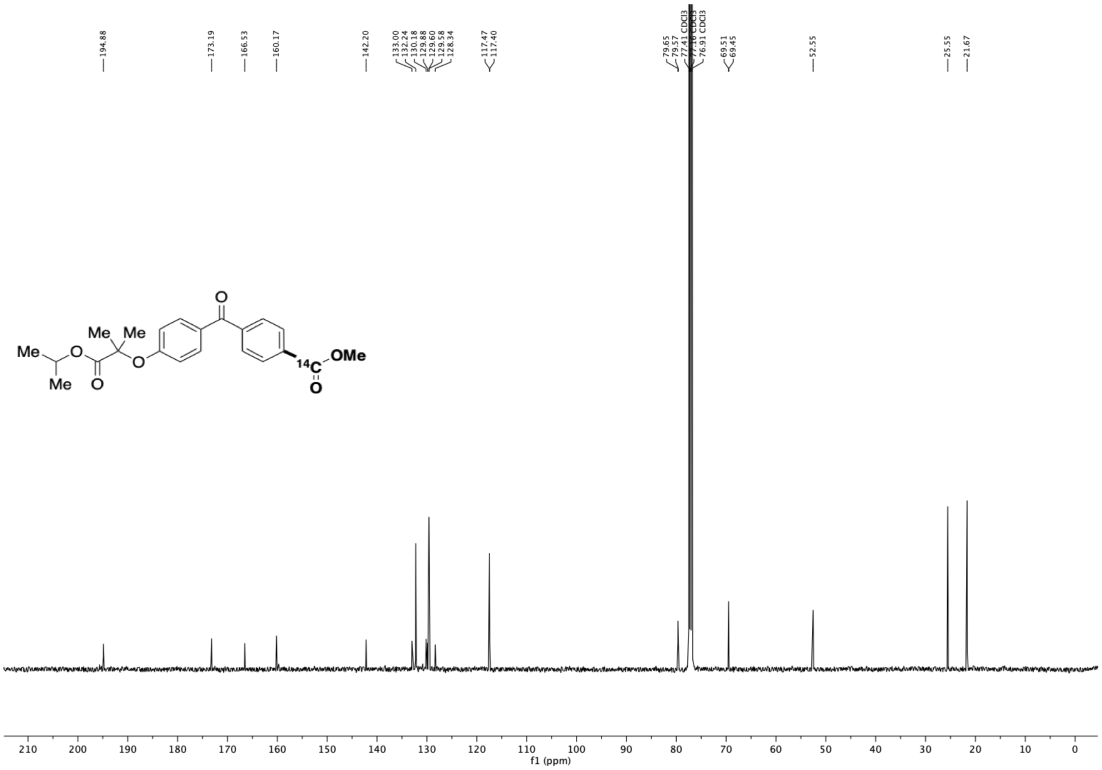
Methyl 4-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)benzoate (^{13}C-16) – ^{13}C NMR



Methyl 4-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)benzoate (^{14}C-16) – ^{1}H NMR

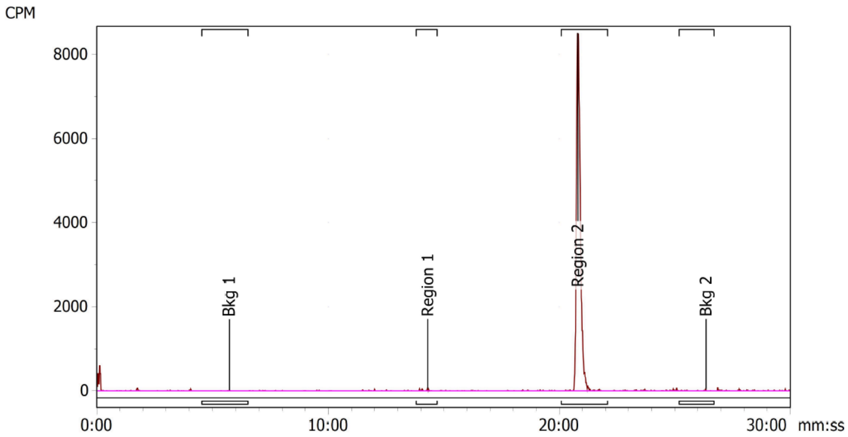


Methyl 4-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)benzoate (^{14}C-16) – ^{13}C NMR



Methyl 4-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)benzoate (^{14}C-16) – Radio HPLC Injection 1

Chromatogram: ^{14}C



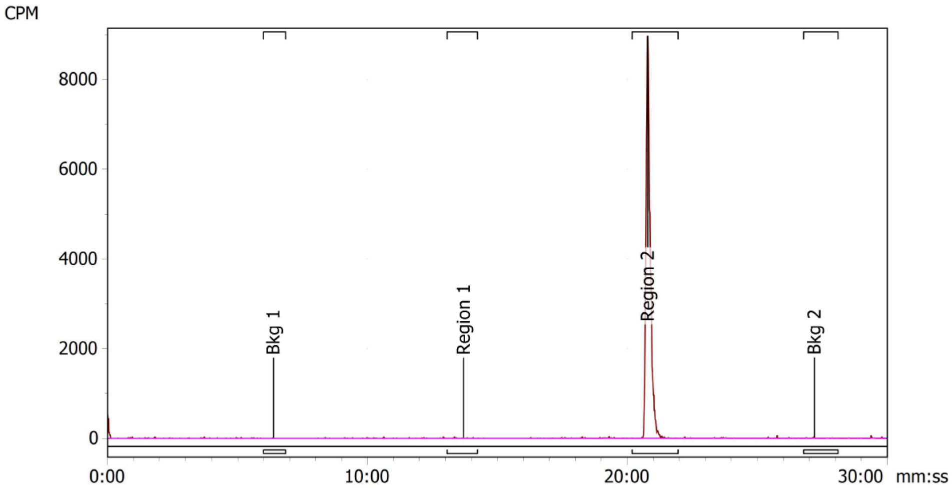
Regions: ^{14}C Detector: ß-RAM

Name	Start (mm:ss)	End (mm:ss)	Retention (mm:ss)	Area (CPM)	%ROI (%)	%Total (%)
Bkg 1	4:33	6:31	5:43			
Region 1	13:48	14:42	14:18	319	0,34	0,33
Region 2	20:05	22:05	20:48	93077	99,66	95,96
Bkg 2	25:11	26:42	26:21			
2 Peaks				93396	100,00	96,29

Total Area: 96998 CPM
Average Background: 2 CPM

Methyl 4-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)benzoate (^{14}C-16) – Radio HPLC Injection 2

Chromatogram: ^{14}C

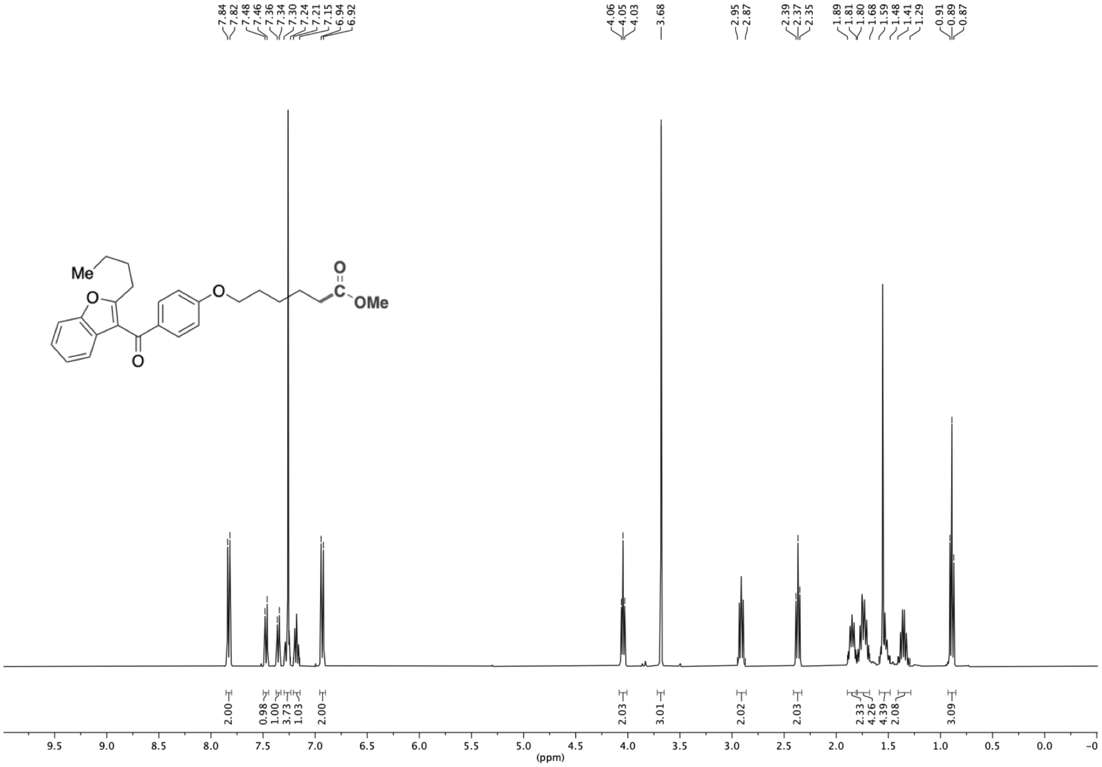


Regions: ^{14}C Detector: ß-RAM

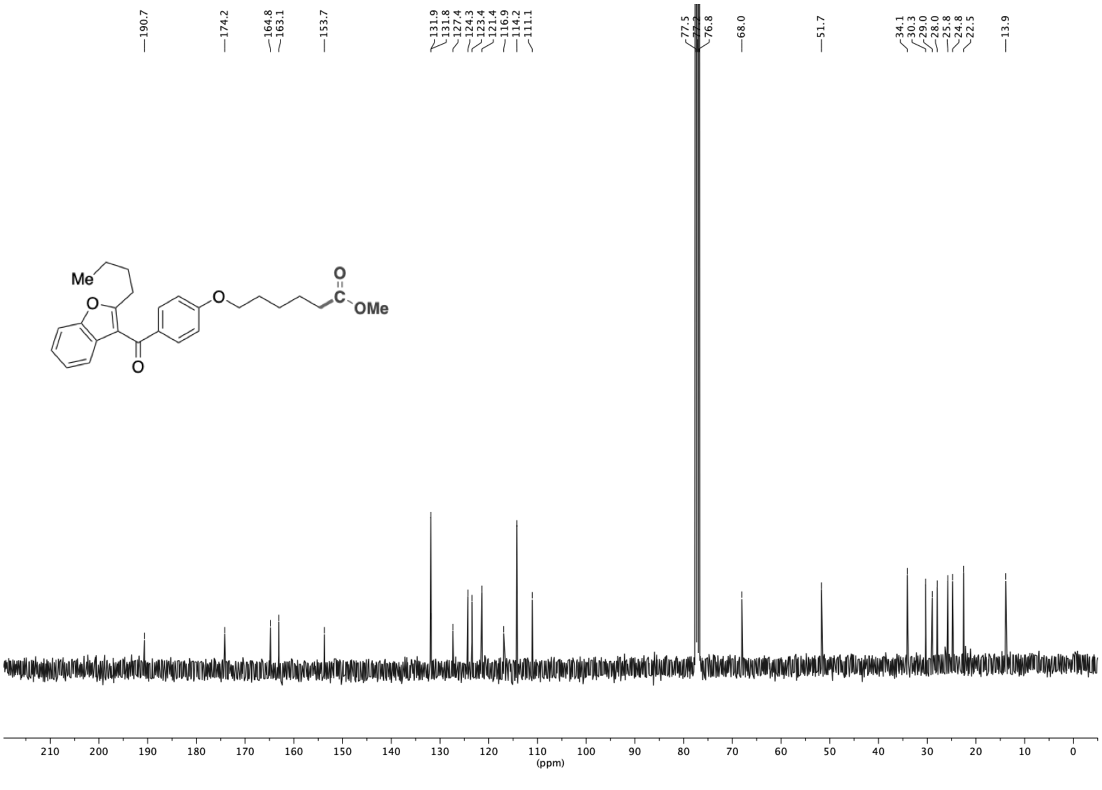
Name	Start (mm:ss)	End (mm:ss)	Retention (mm:ss)	Area (CPM)	%ROI (%)	%Total (%)
Bkg 1	6:00	6:51	6:23			
Region 1	13:04	14:14	13:42	127	0,14	0,13
Region 2	20:11	21:57	20:47	93019	99,86	97,98
Bkg 2	26:47	28:06	27:12			
2 Peaks				93146	100,00	98,12

Total Area: 94932 CPM
Average Background: 2 CPM

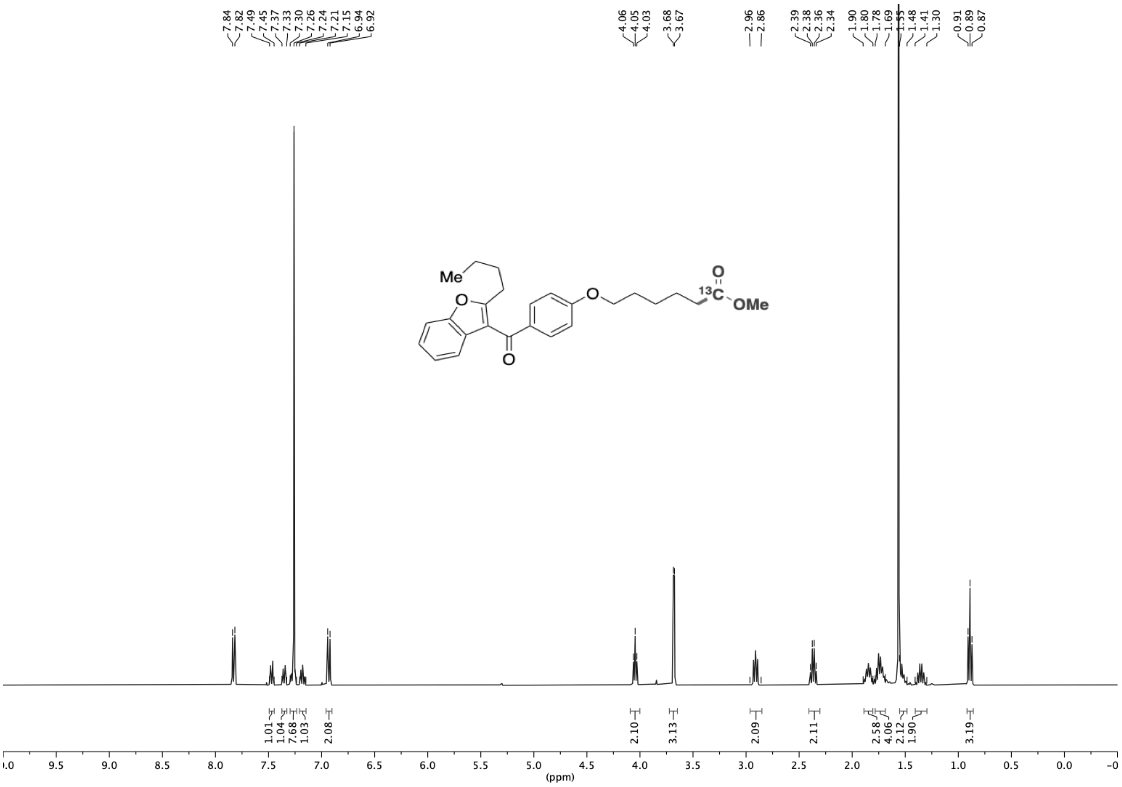
Methyl 6-(4-(2-butylbenzofuran-3-carbonyl)phenoxy)hexanoate (17) – ^{1}H NMR



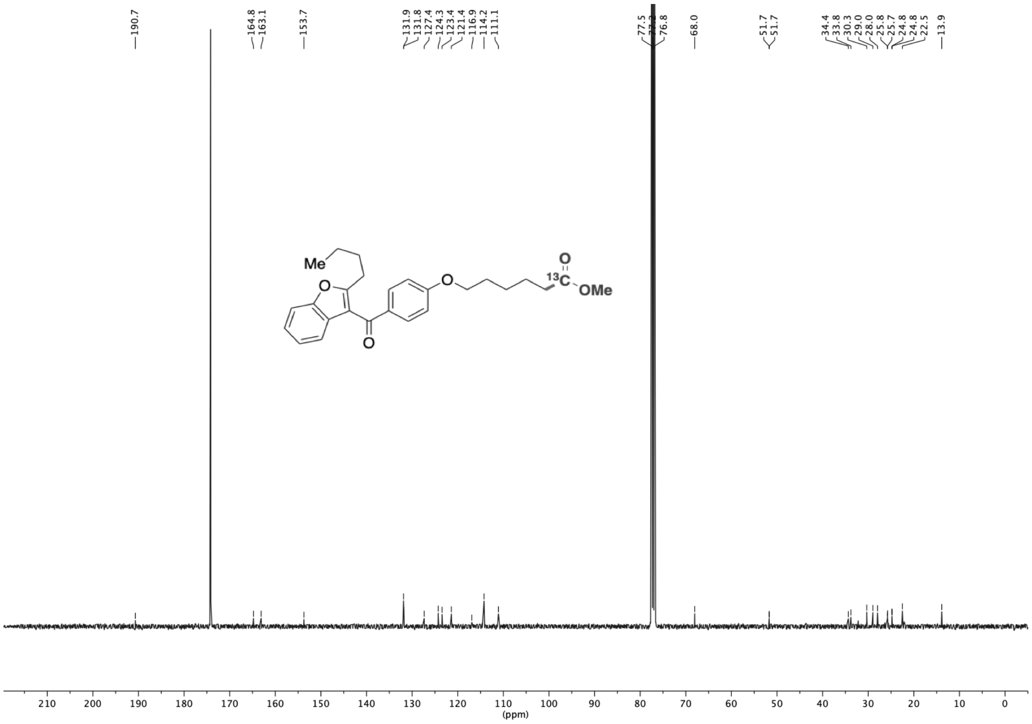
Methyl 6-(4-(2-butylbenzofuran-3-carbonyl)phenoxy)hexanoate (17) – ^{13}C NMR



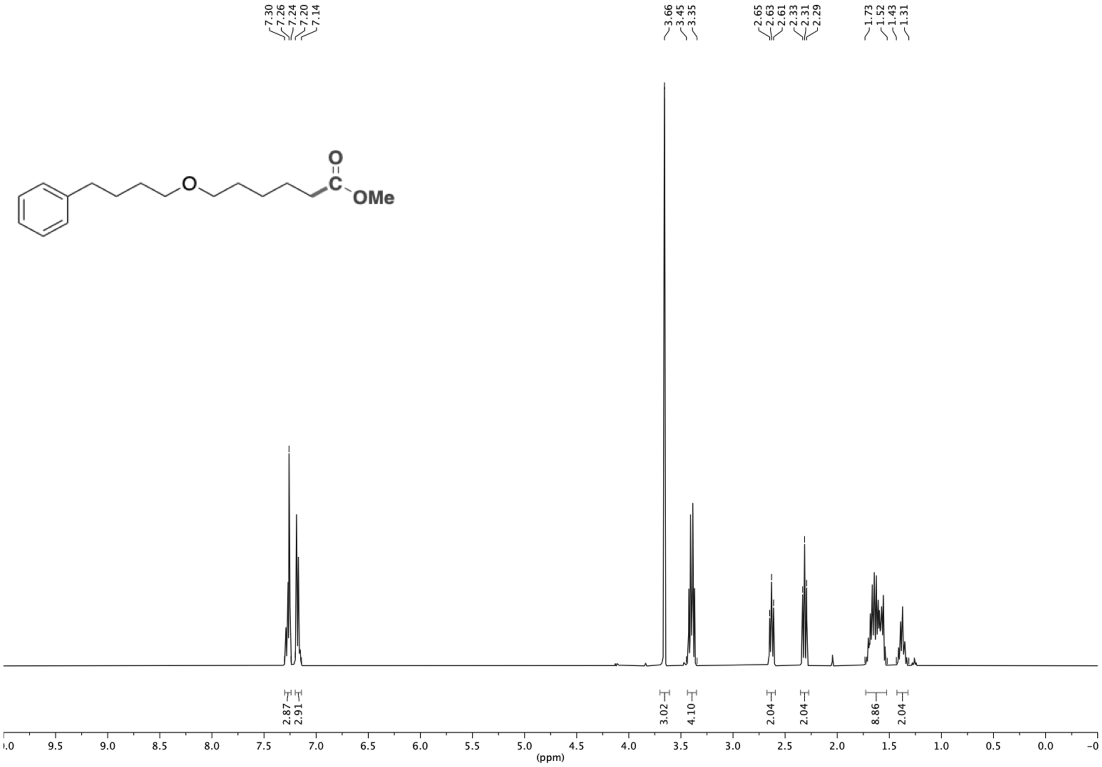
Methyl 6-(4-(2-butylbenzofuran-3-carbonyl)phenoxy)hexanoate (^{13}C-17) – ^{1}H NMR



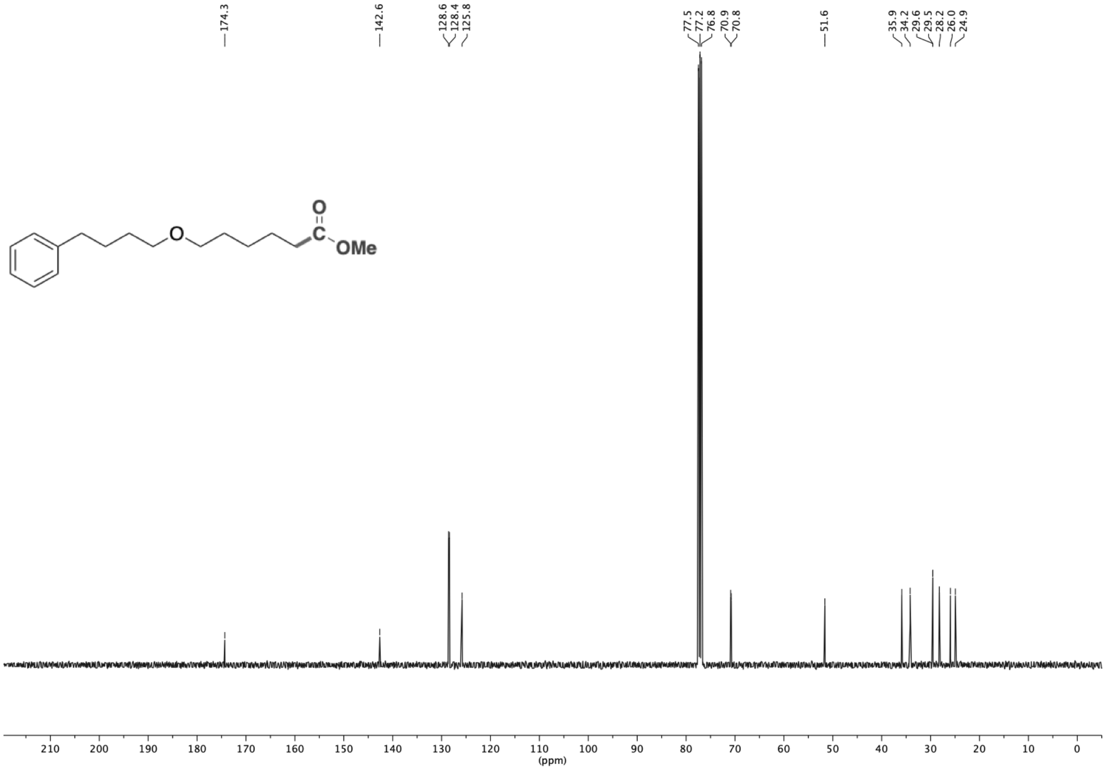
Methyl 6-(4-(2-butylbenzofuran-3-carbonyl)phenoxy)hexanoate (^{13}C-17) – ^{13}C NMR



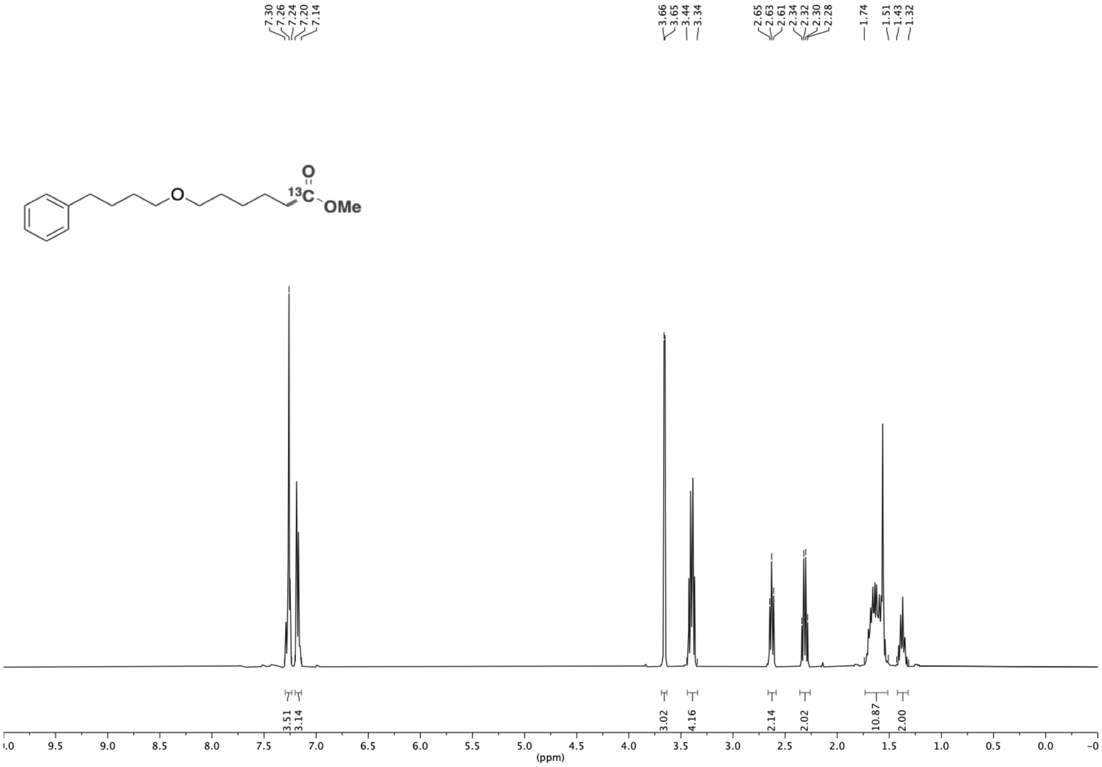
Methyl 5-(4-phenylbutoxy)pentanoate (18) – ^{1}H NMR



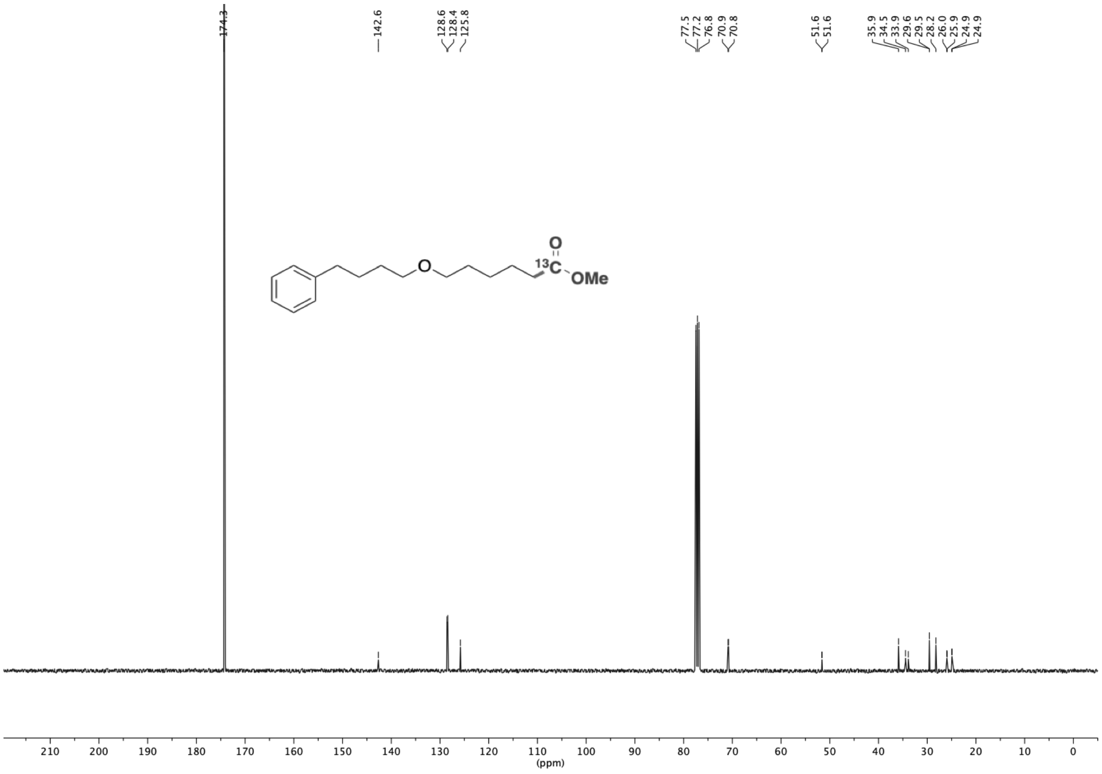
Methyl 5-(4-phenylbutoxy)pentanoate (18) – ^{13}C NMR



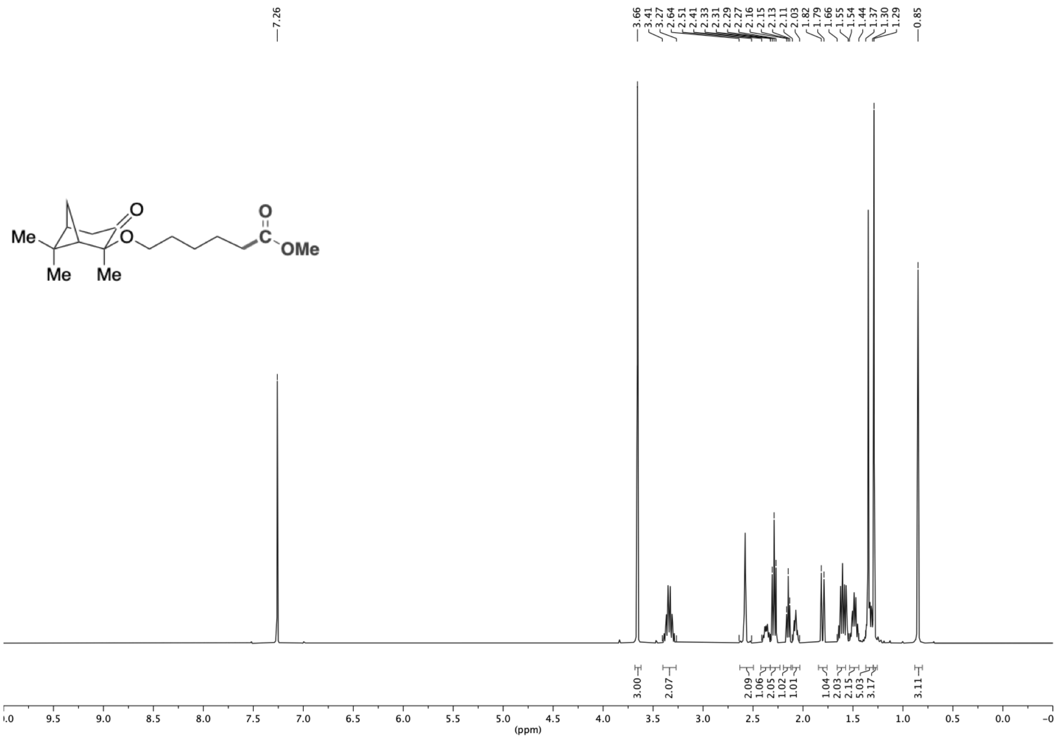
Methyl 5-(4-phenylbutoxy)pentanoate (^{13}C-18) – ^{1}H NMR



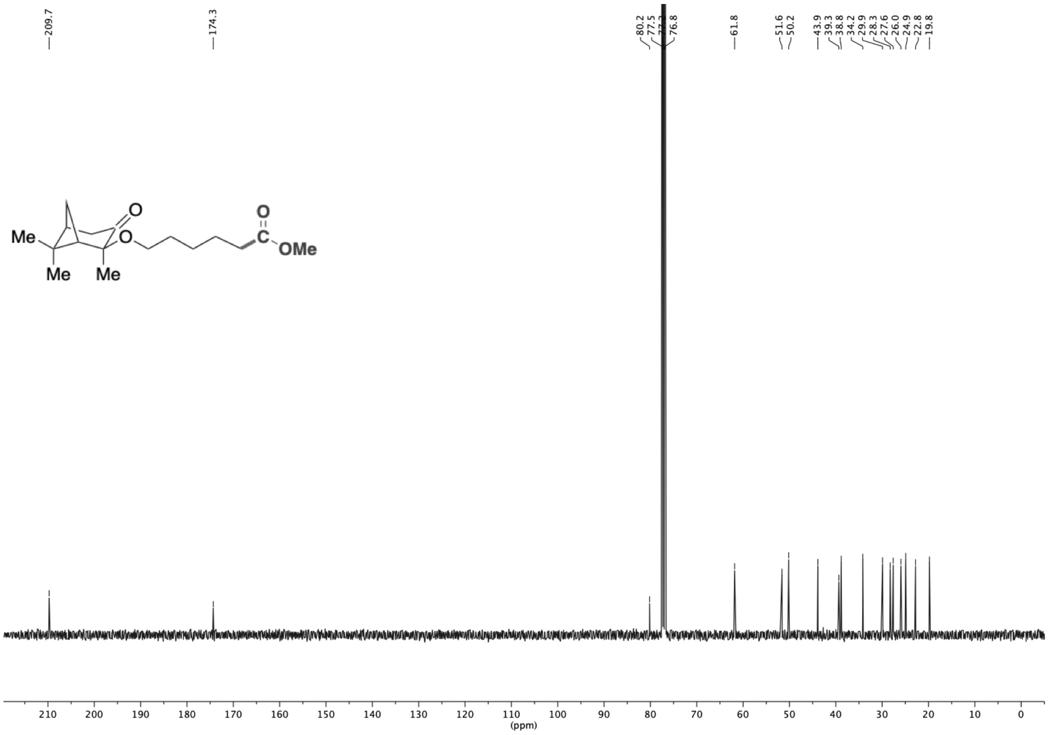
Methyl 5-(4-phenylbutoxy)pentanoate (^{13}C-18) – ^{13}C NMR



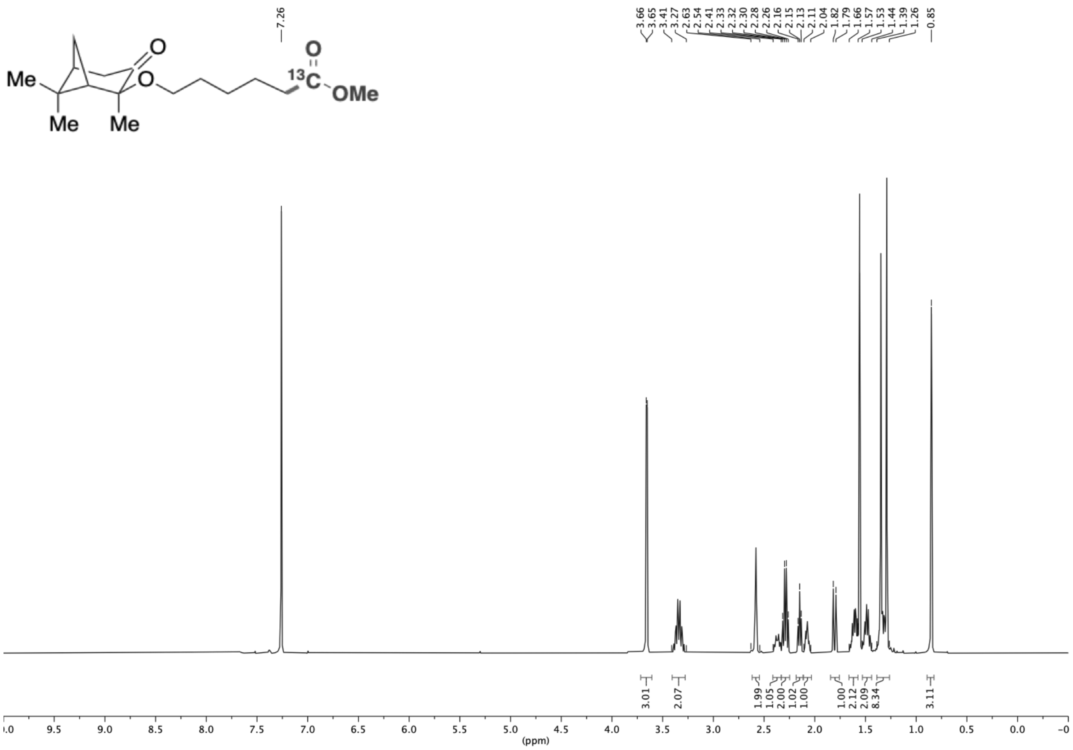
Methyl 6-(((*1S,2S,5S*)-2,6,6-trimethyl-3-oxobicyclo[3.1.1]heptan-2-yl)oxy)hexanoate (19) – ^{1}H NMR



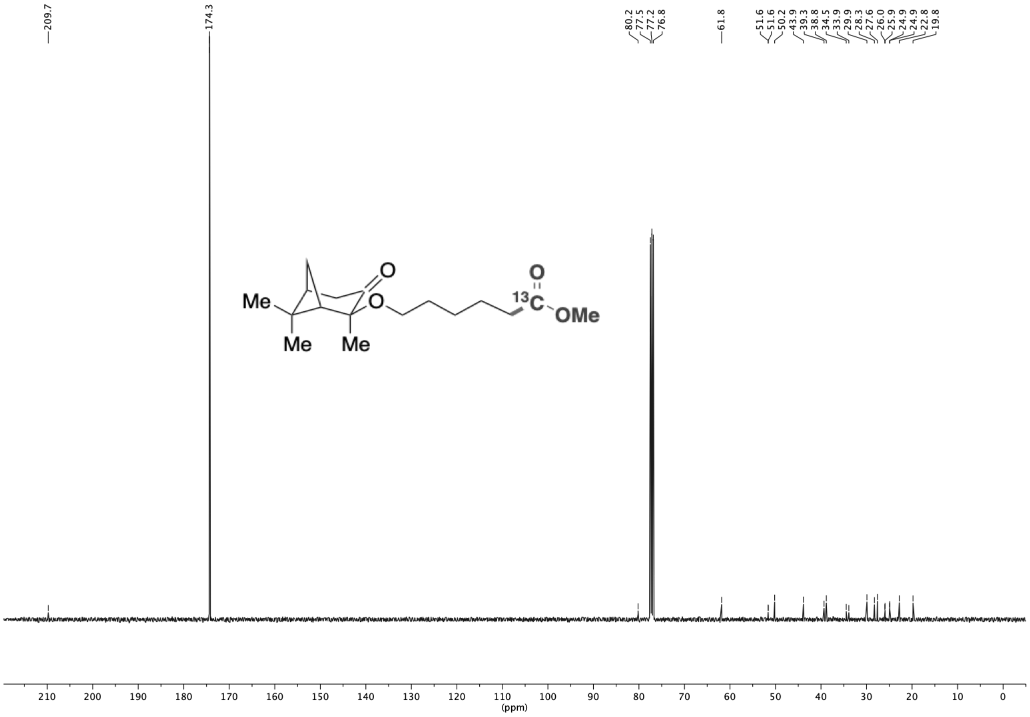
Methyl 6-(((*1S,2S,5S*)-2,6,6-trimethyl-3-oxobicyclo[3.1.1]heptan-2-yl)oxy)hexanoate (19) – ^{13}C NMR



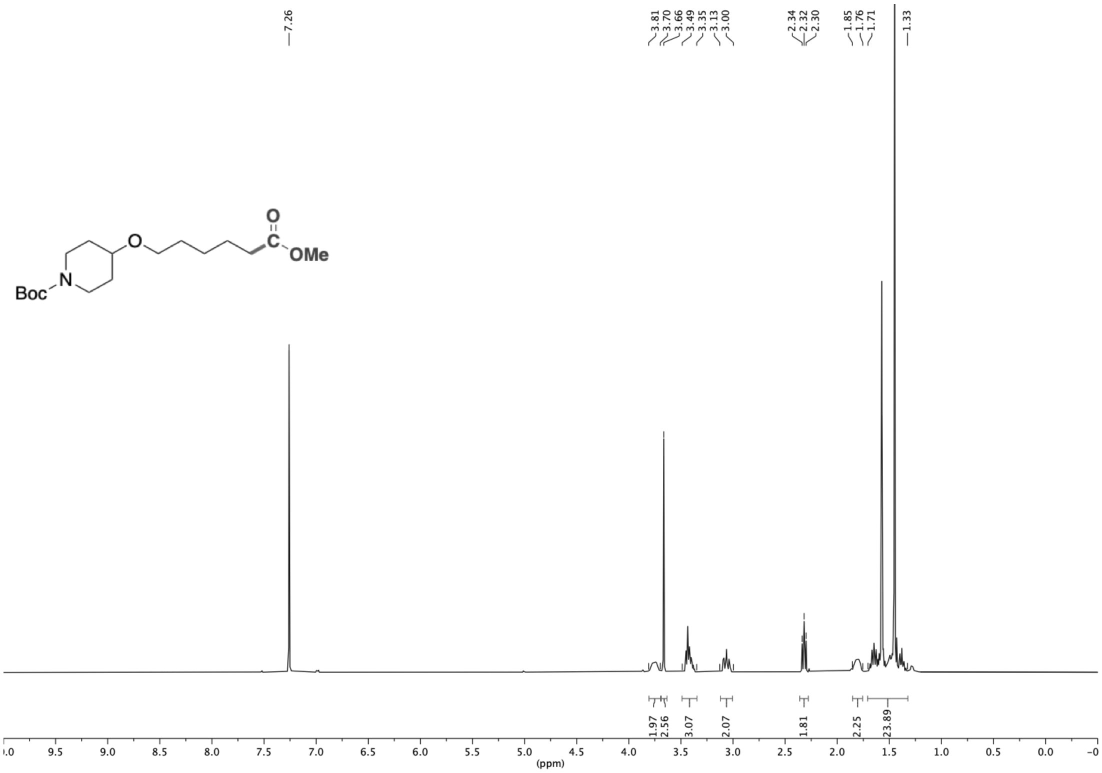
Methyl 6-(((*1S,2S,5S*)-2,6,6-trimethyl-3-oxobicyclo[3.1.1]heptan-2-yl)oxy)hexanoate (^{13}C-19) – ^{1}H NMR



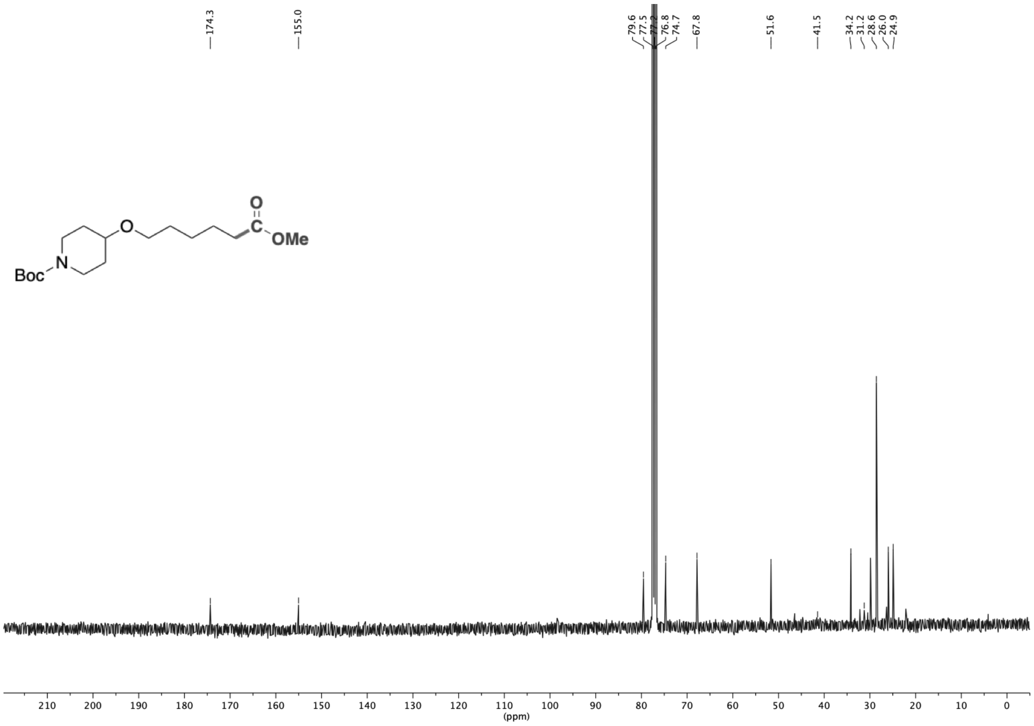
Methyl 6-(((*1S,2S,5S*)-2,6,6-trimethyl-3-oxobicyclo[3.1.1]heptan-2-yl)oxy)hexanoate (^{13}C-19) – ^{13}C NMR



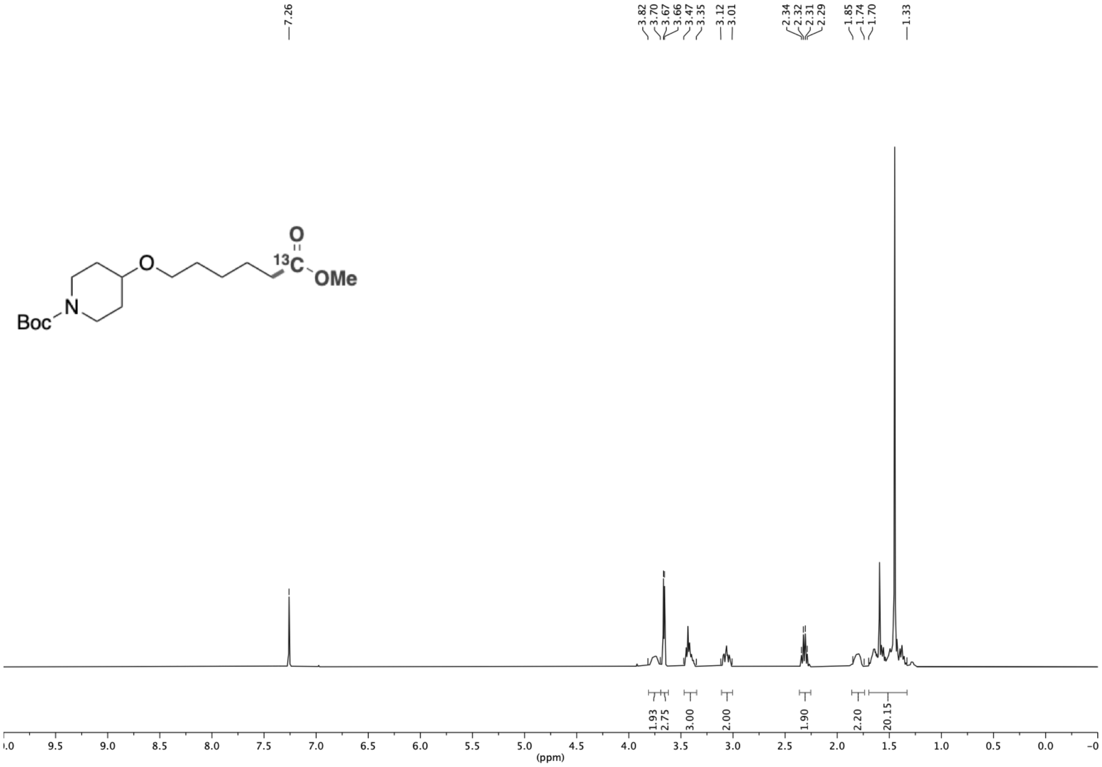
tert-Butyl 4-((6-methoxy-6-oxohexyl)oxy)piperidine-1-carboxylate (20) – ^{1}H NMR



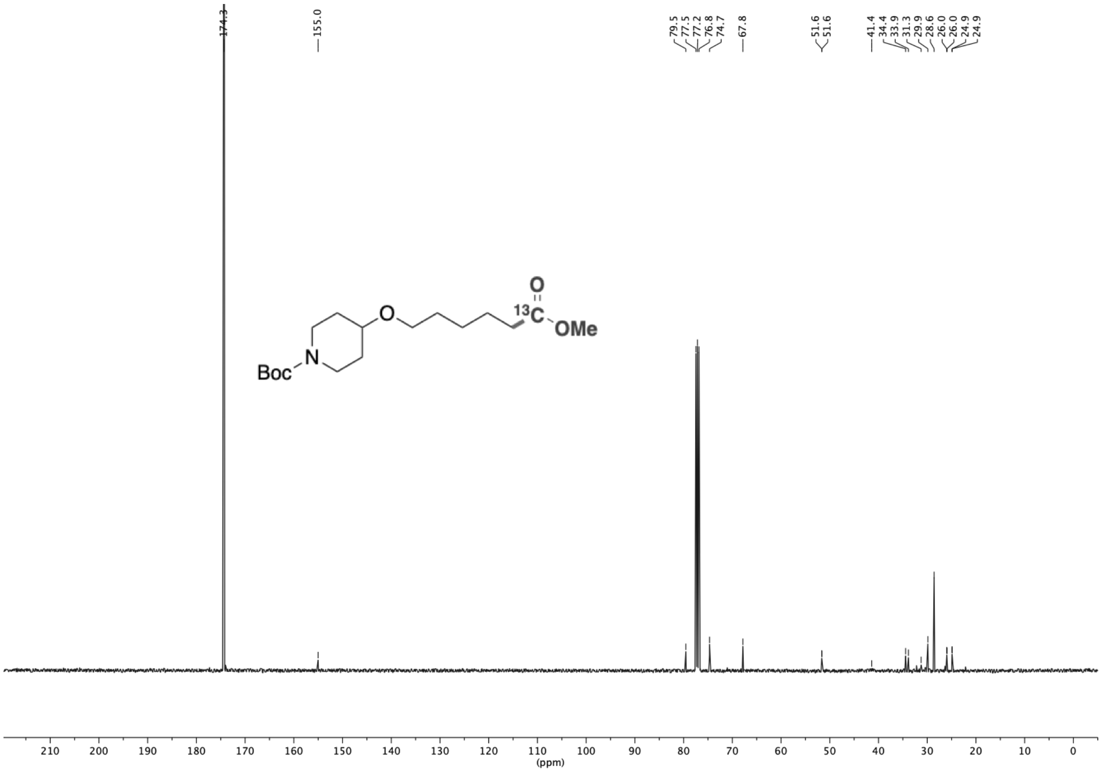
tert-Butyl 4-((6-methoxy-6-oxohexyl)oxy)piperidine-1-carboxylate (20) – ^{13}C NMR



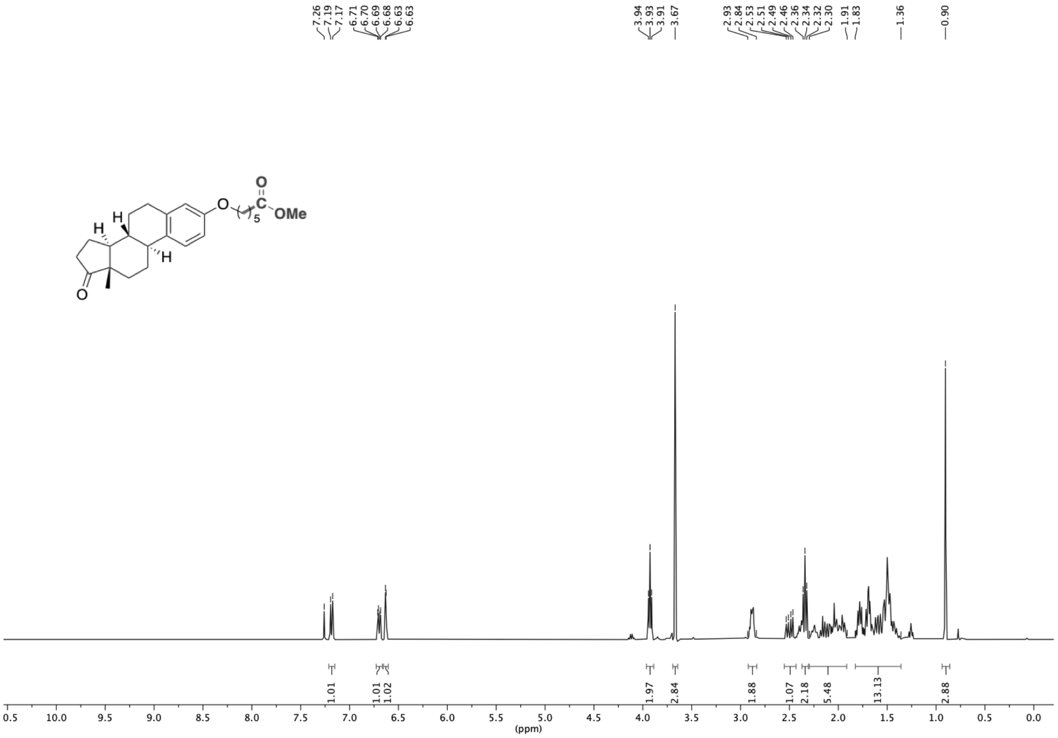
[^{13}C]-*tert*-Butyl 4-((6-methoxy-6-oxohexyl)oxy)piperidine-1-carboxylate (^{13}C-20)



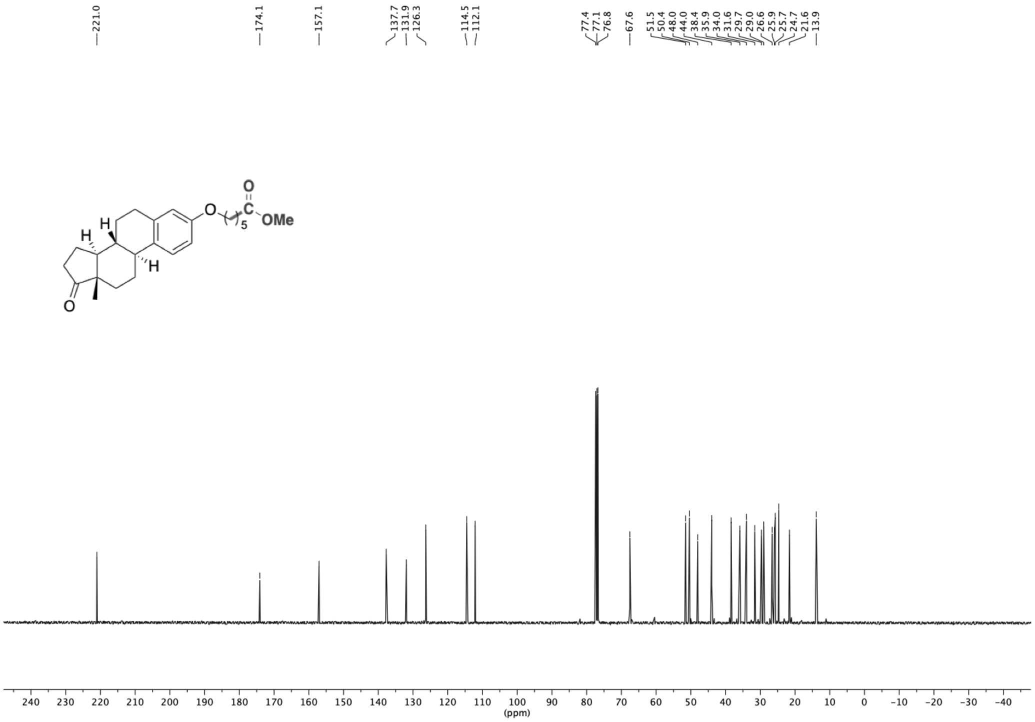
[^{13}C]-*tert*-Butyl 4-((6-methoxy-6-oxohexyl)oxy)piperidine-1-carboxylate (^{13}C-20)



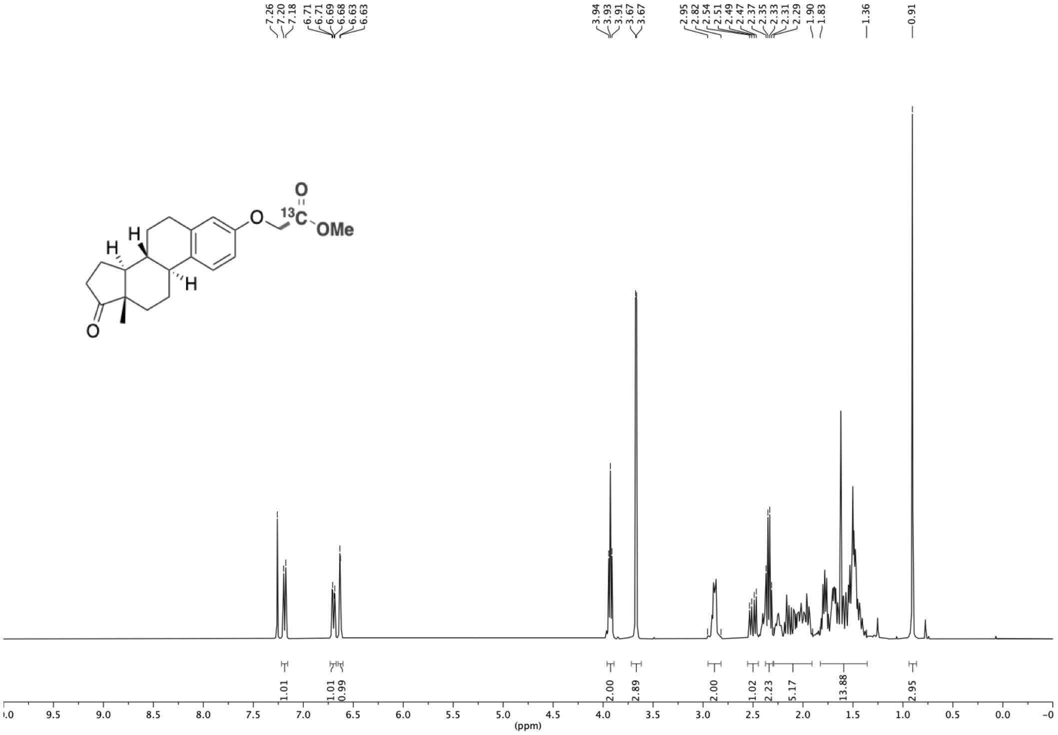
Methyl 6-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)hexanoate (21) – ^{1}H NMR



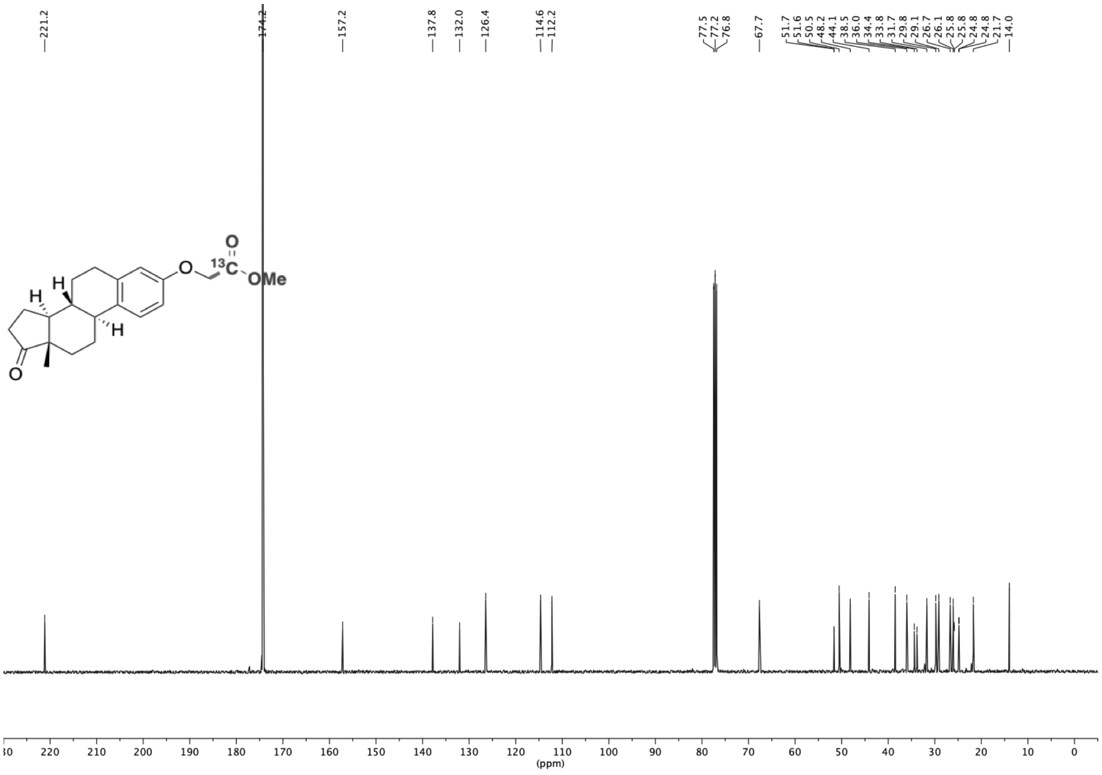
Methyl 6-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)hexanoate (21) – ^{13}C NMR



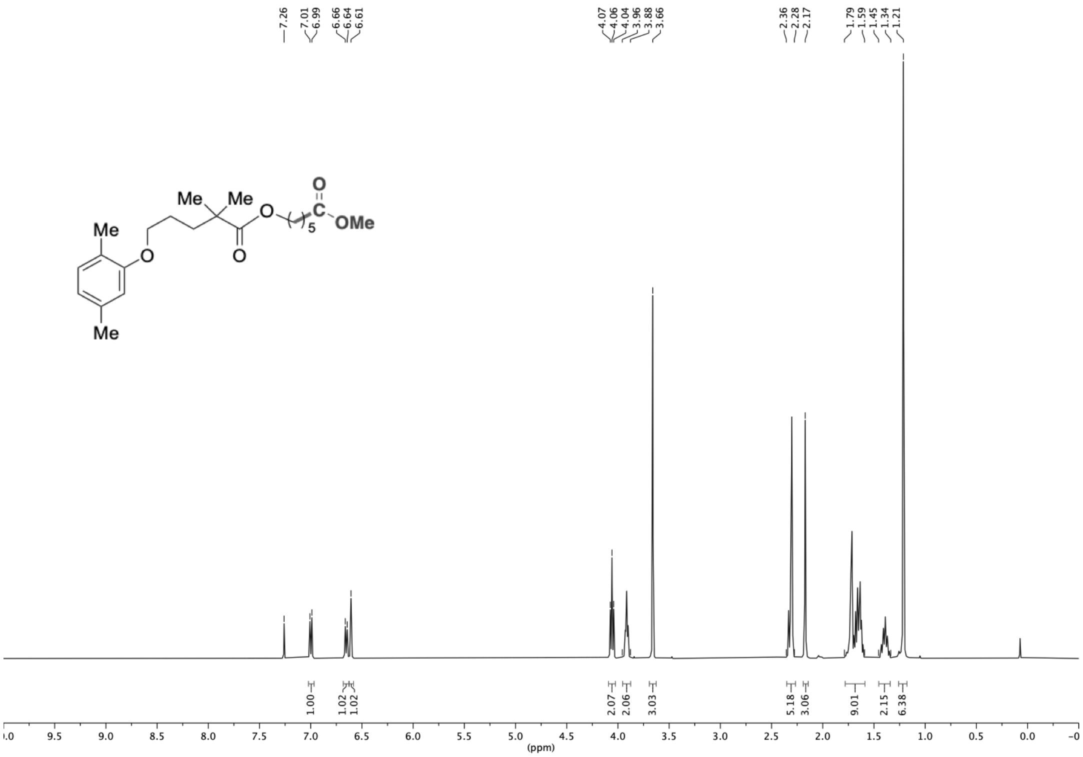
Methyl 6-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)hexanoate (21) – ^{1}H NMR



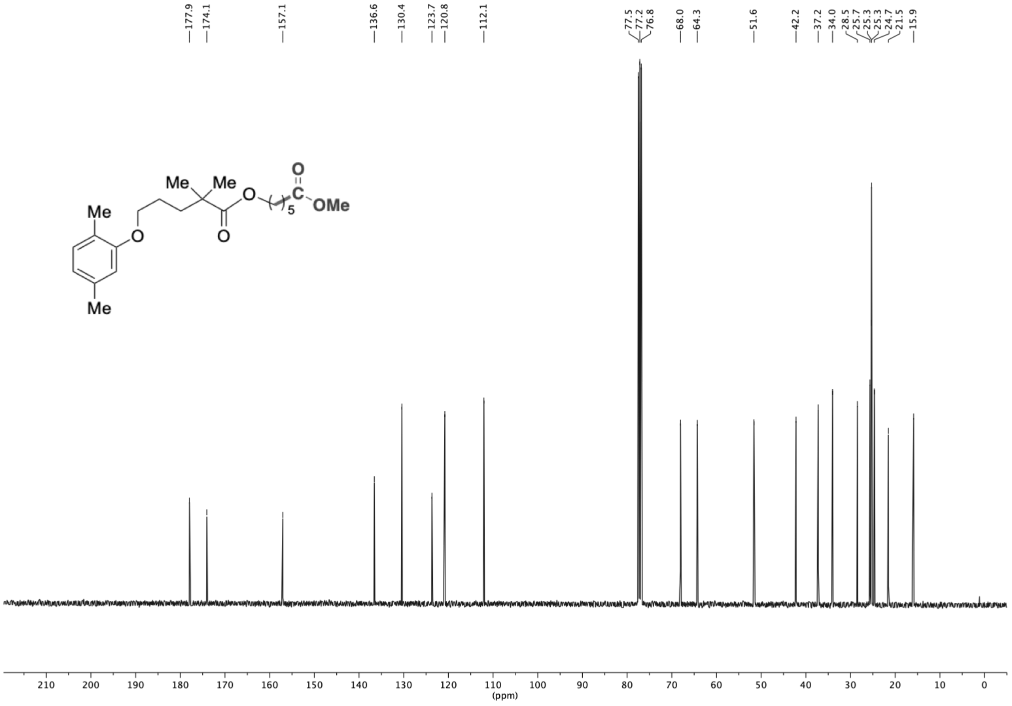
Methyl 6-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)hexanoate (21) – ^{13}C NMR



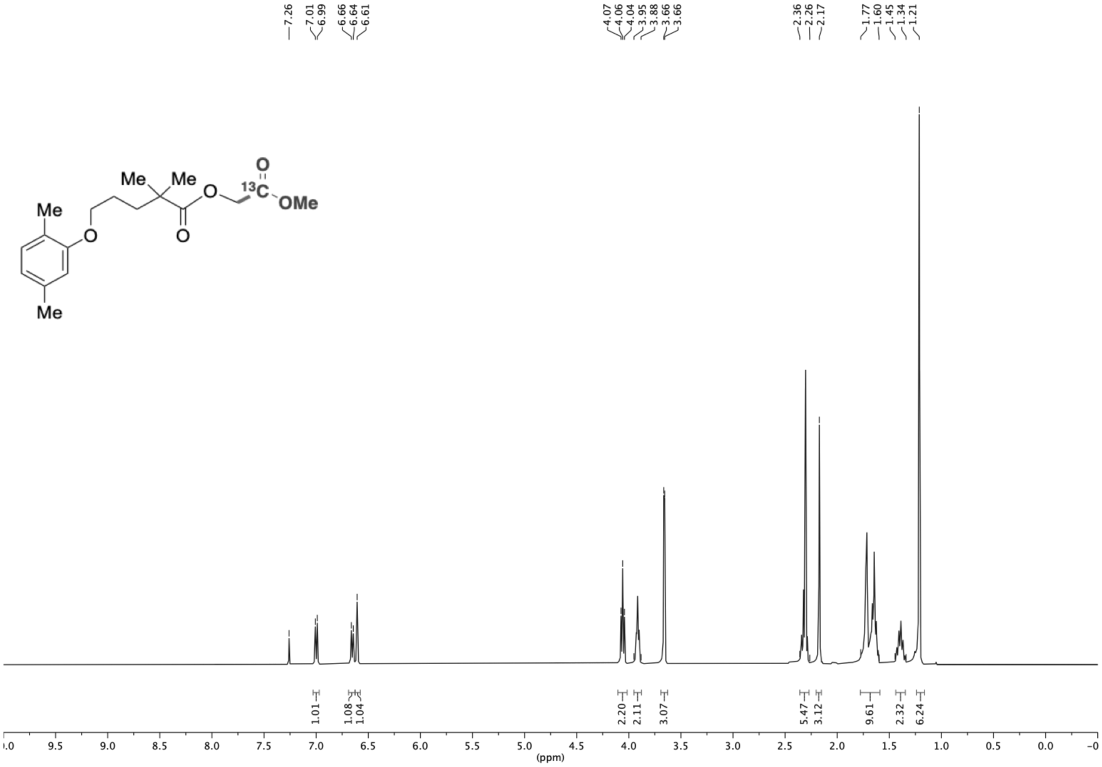
Methyl 6-((5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl)oxy)hexanoate (22) – ^{1}H NMR



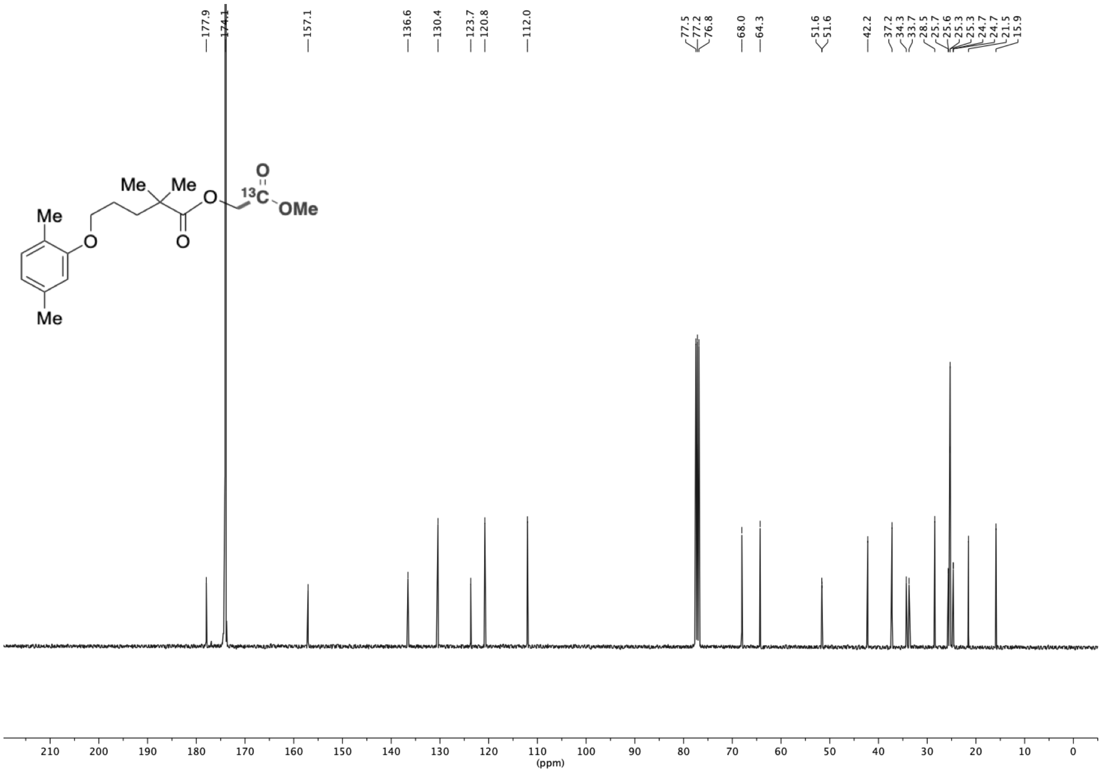
Methyl 6-((5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl)oxy)hexanoate (22) – ^{13}C NMR



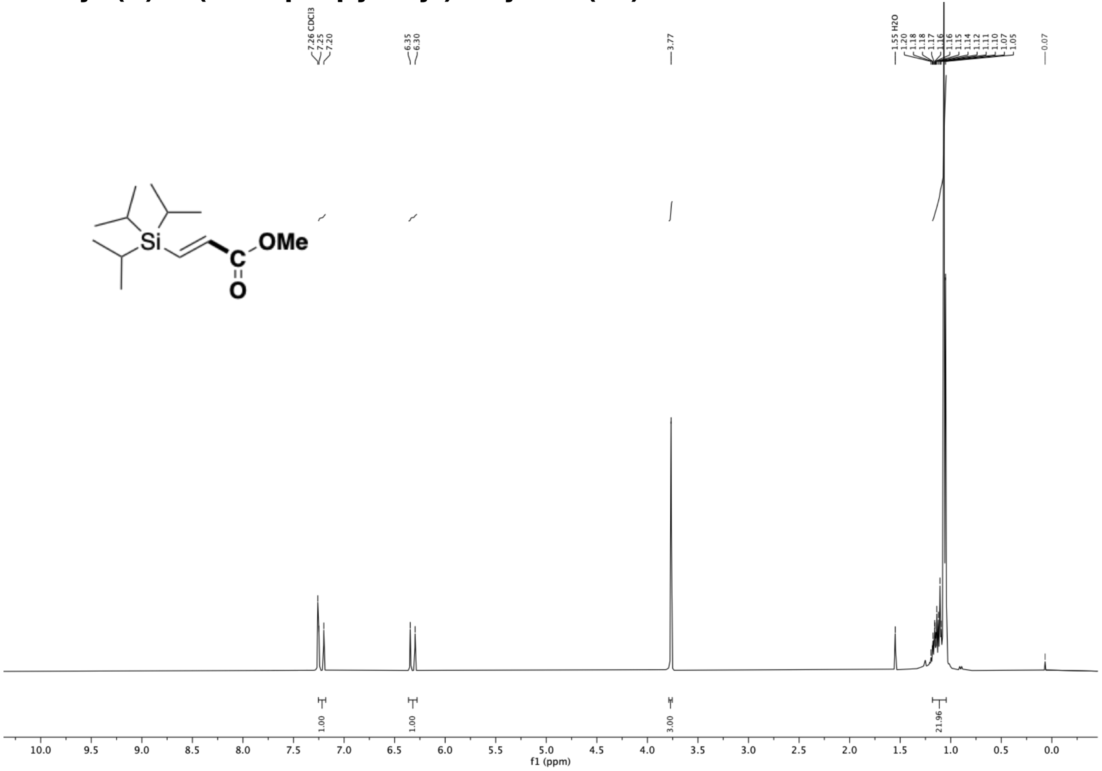
Methyl 6-((5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl)oxy)hexanoate (^{13}C-22) – ^{1}H NMR



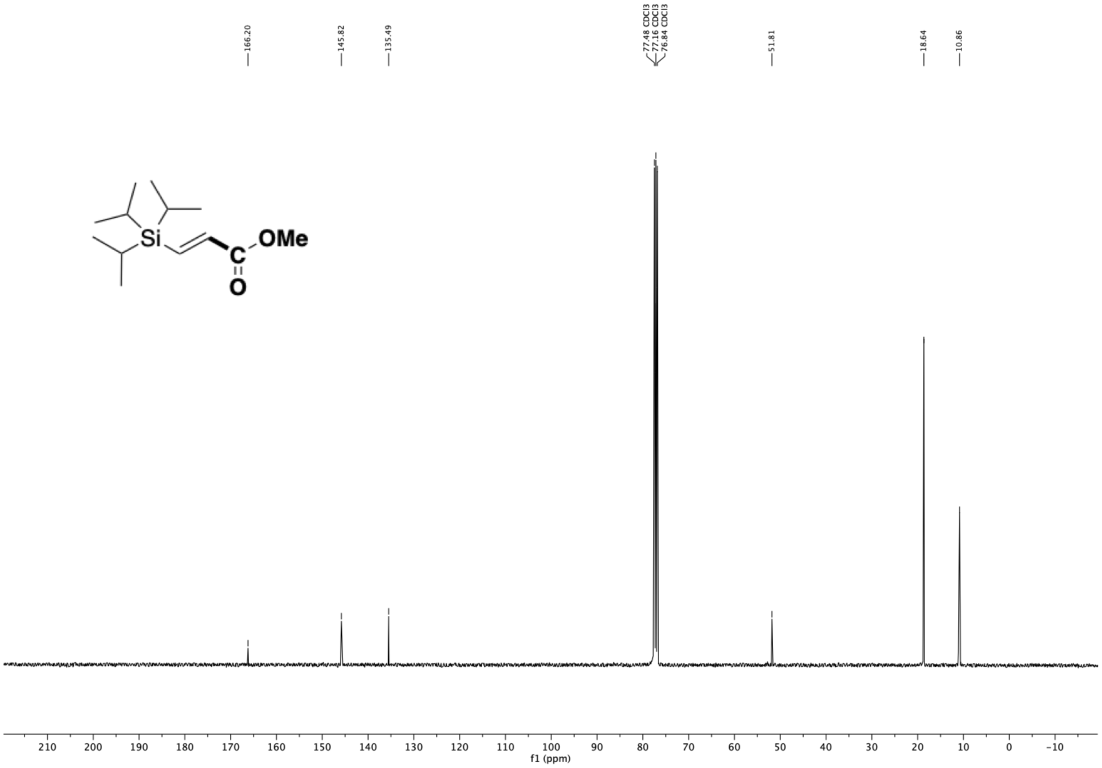
Methyl 6-((5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl)oxy)hexanoate (^{13}C-22) – ^{13}C NMR



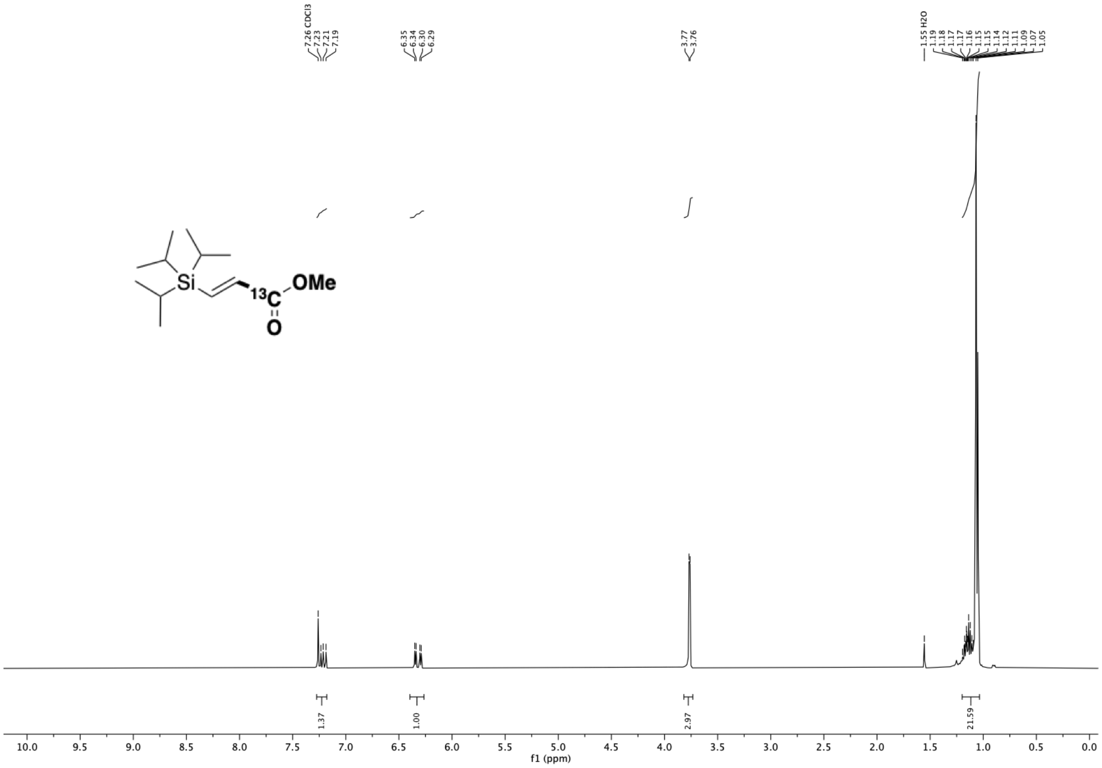
Methyl (E)-3-(triisopropylsilyl)acrylate (23) – ^{1}H NMR



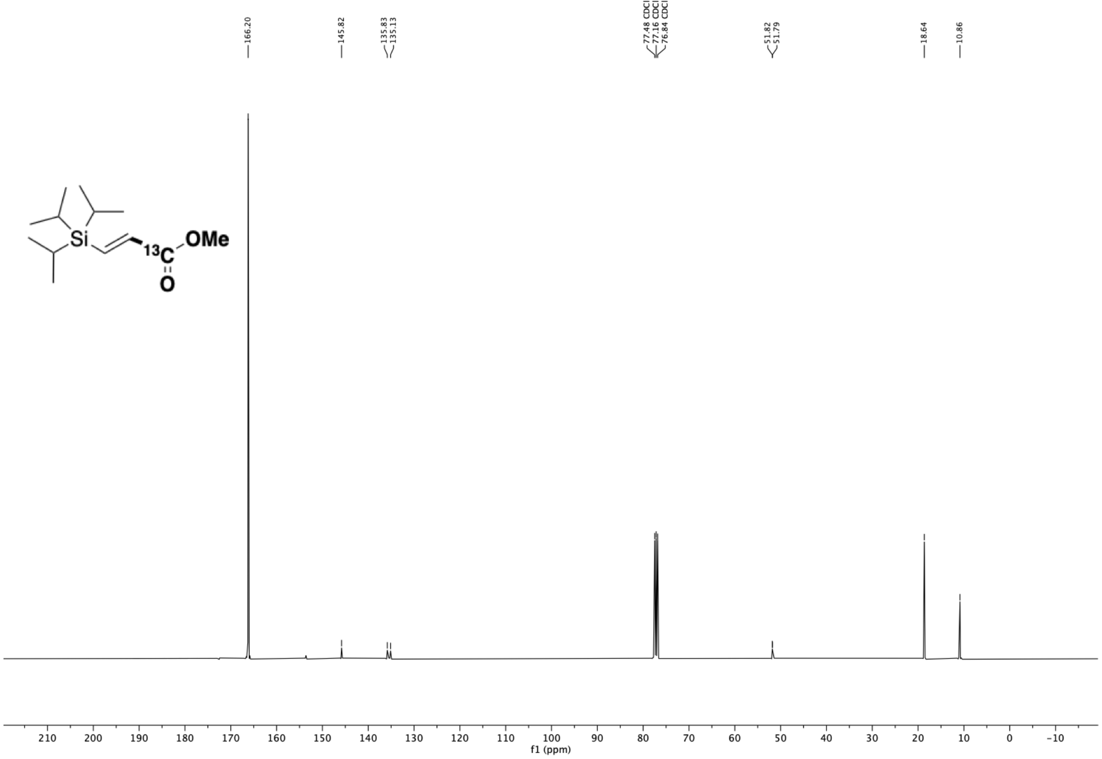
Methyl (E)-3-(triisopropylsilyl)acrylate (23) – ^{13}C NMR



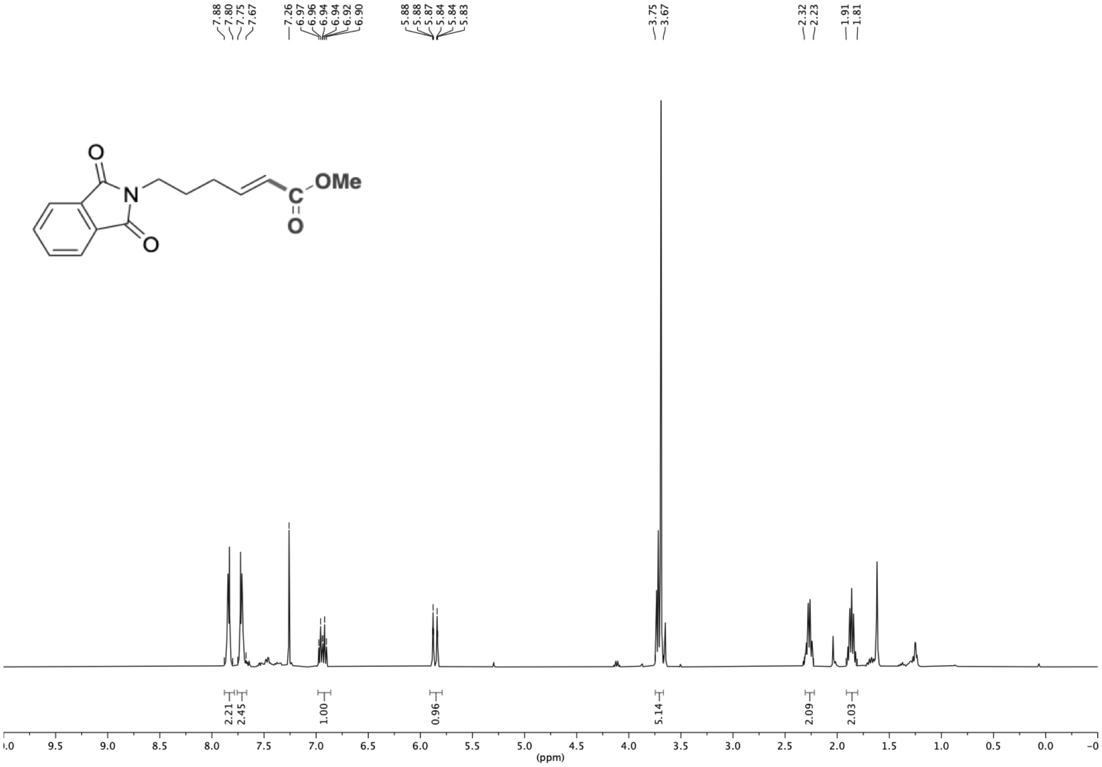
Methyl (E)-3-(triisopropylsilyl)acrylate (^{13}C-23) – ^{1}H NMR



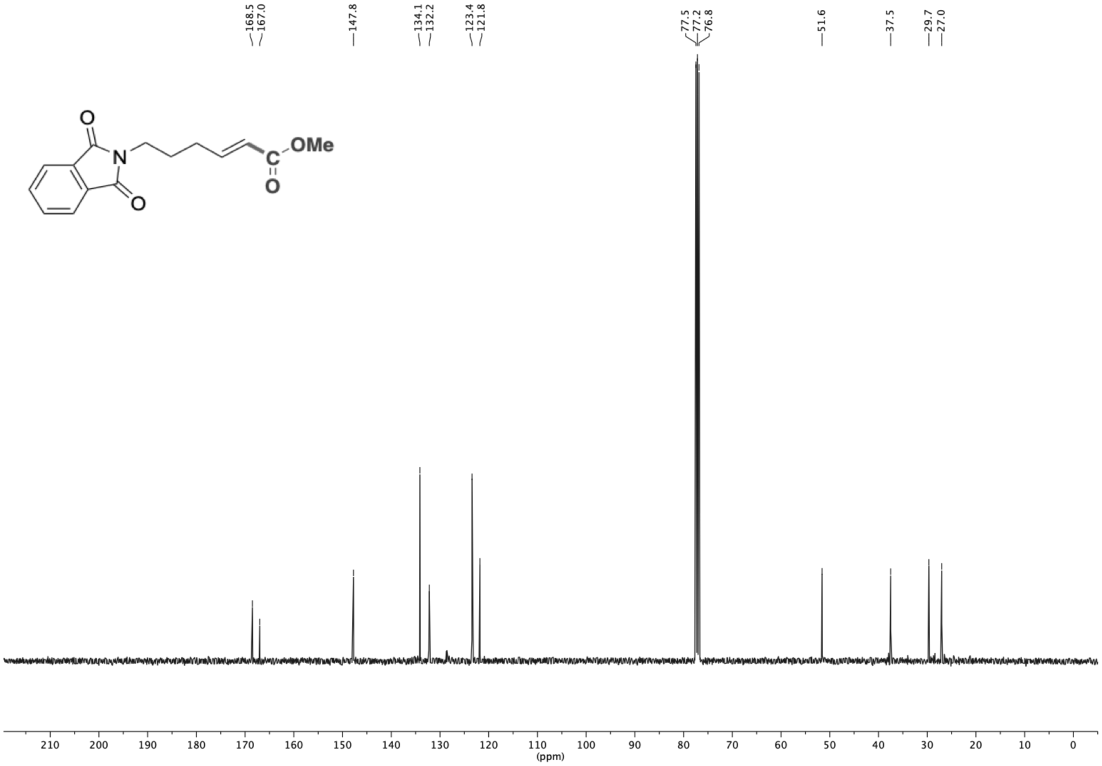
Methyl (E)-3-(triisopropylsilyl)acrylate (^{13}C-23) – ^{13}C NMR



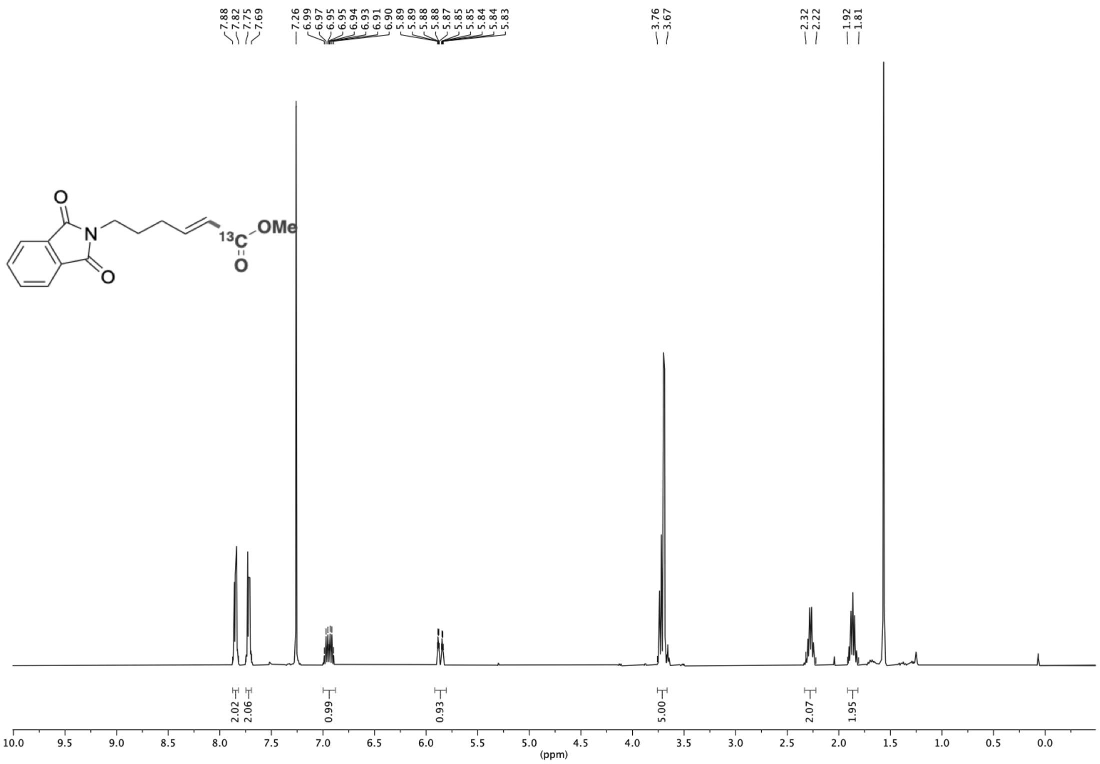
Methyl (*E*)-6-(1,3-dioxoisoindolin-2-yl)hex-2-enoate (24) – ^{1}H NMR



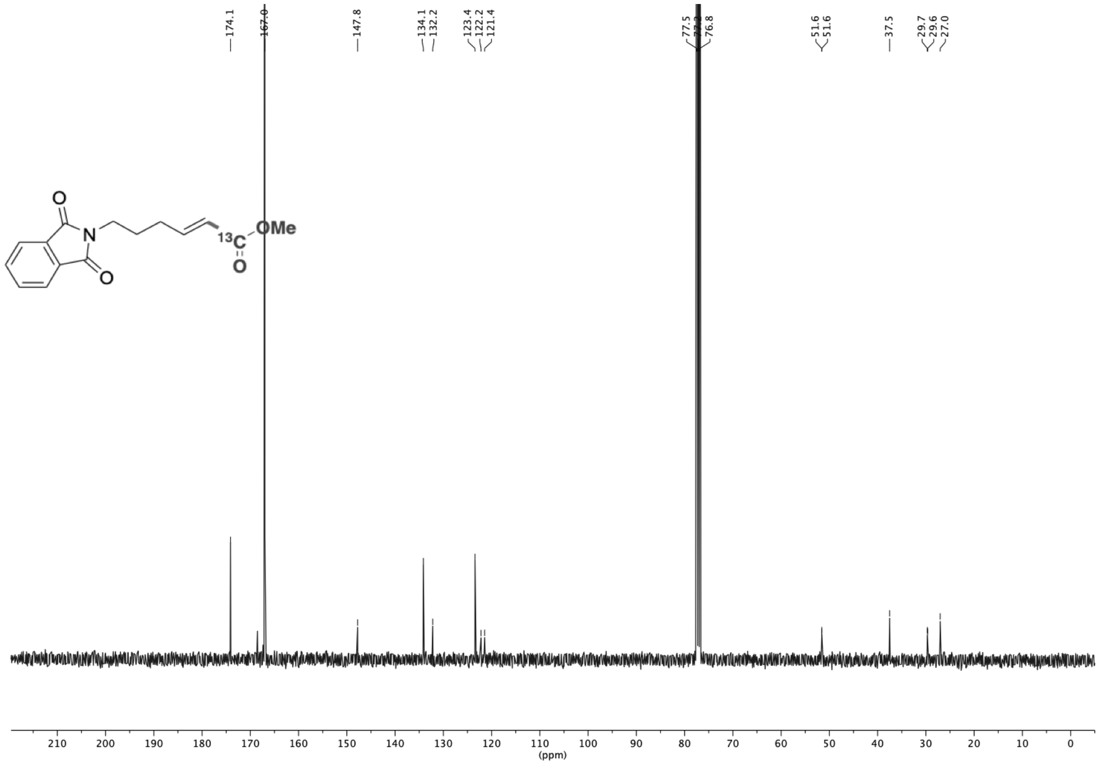
Methyl (*E*)-6-(1,3-dioxoisoindolin-2-yl)hex-2-enoate (24) – ^{13}C NMR



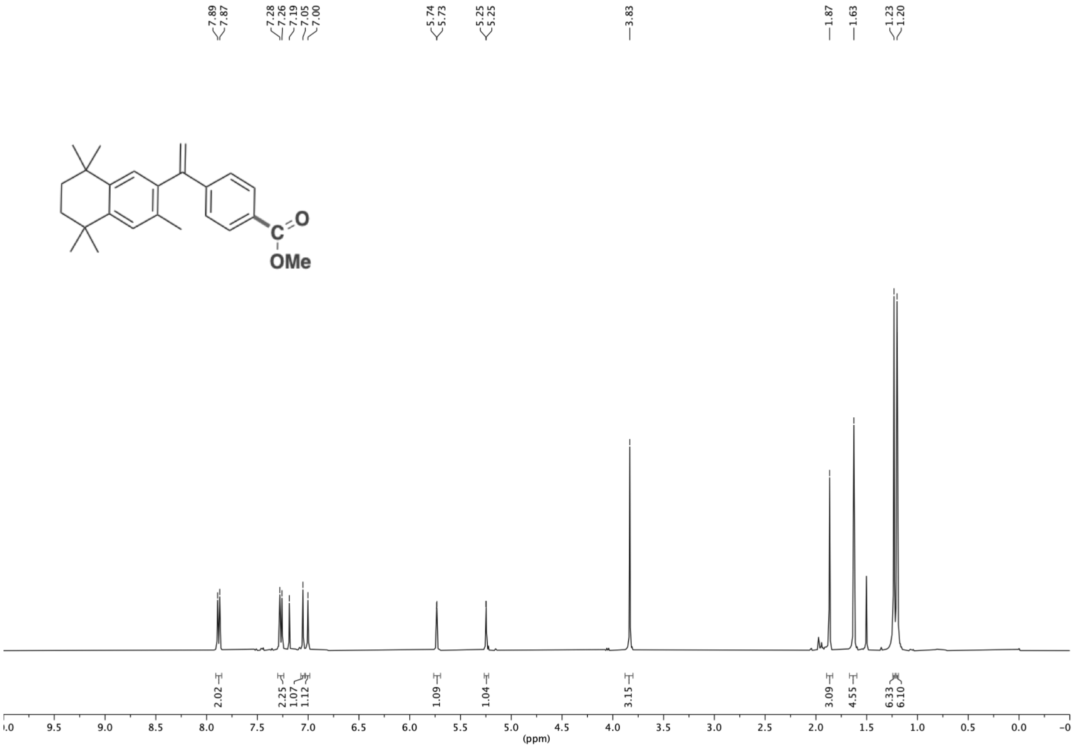
Methyl (*E*)-6-(1,3-dioxoisoindolin-2-yl)hex-2-enoate (^{13}C-24) – ^{1}H NMR



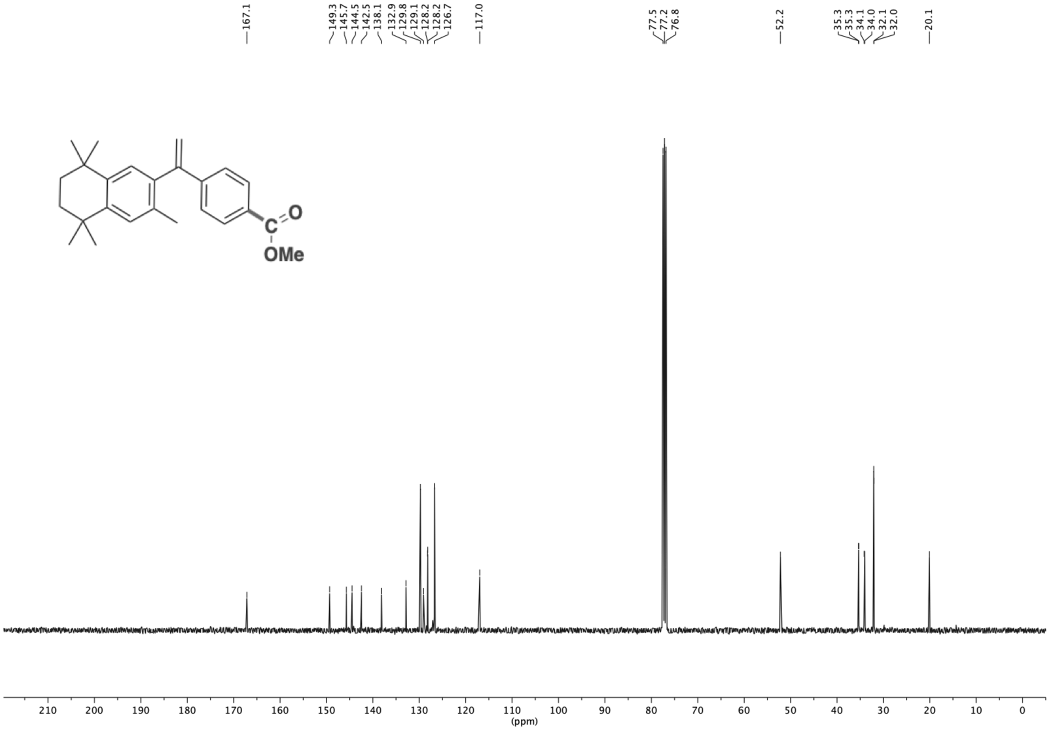
Methyl (*E*)-6-(1,3-dioxoisoindolin-2-yl)hex-2-enoate (^{13}C-24) – ^{13}C NMR



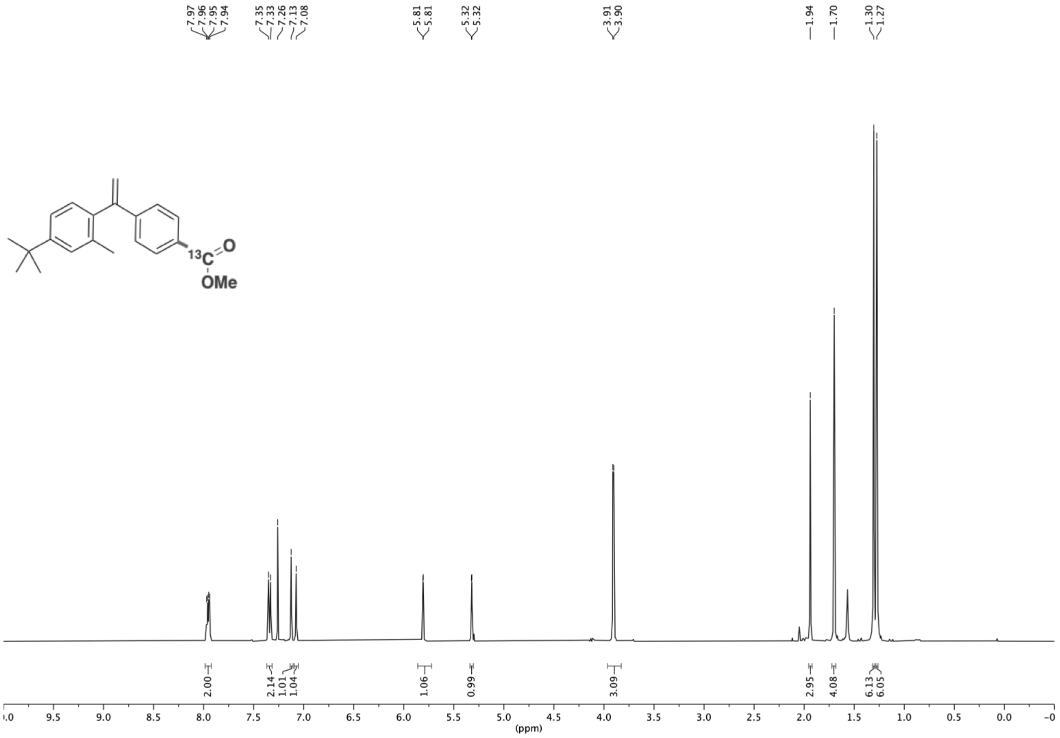
Methyl 4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoate (25) – ^{1}H NMR



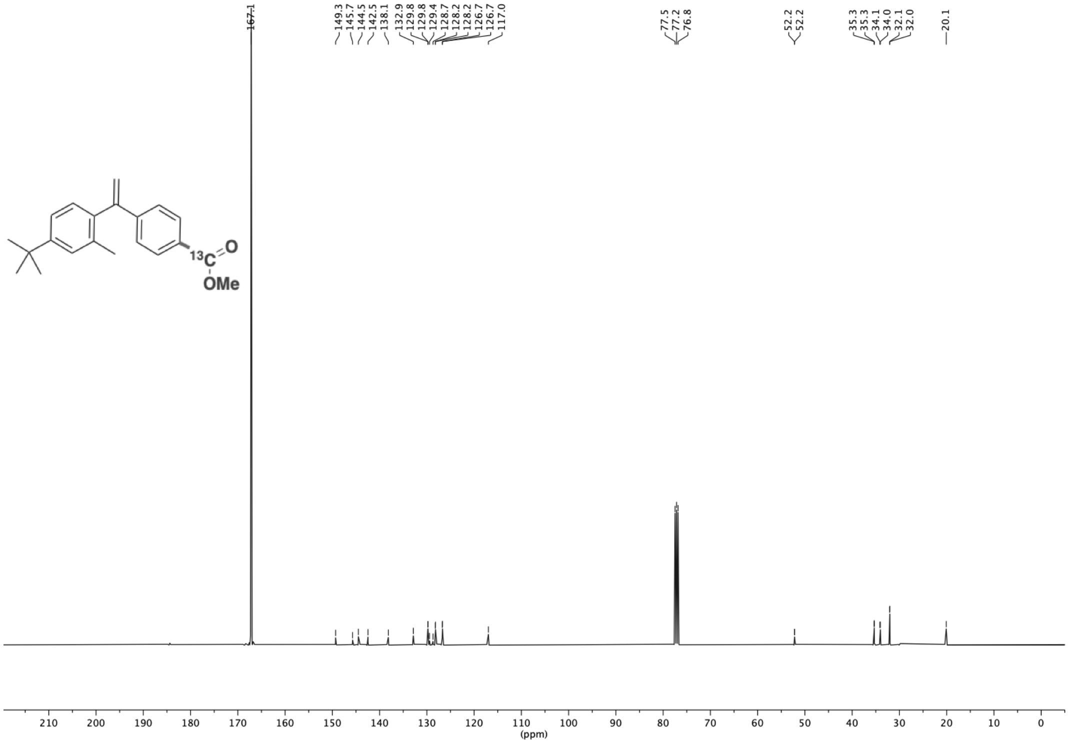
Methyl 4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoate (25) – ^{13}C NMR



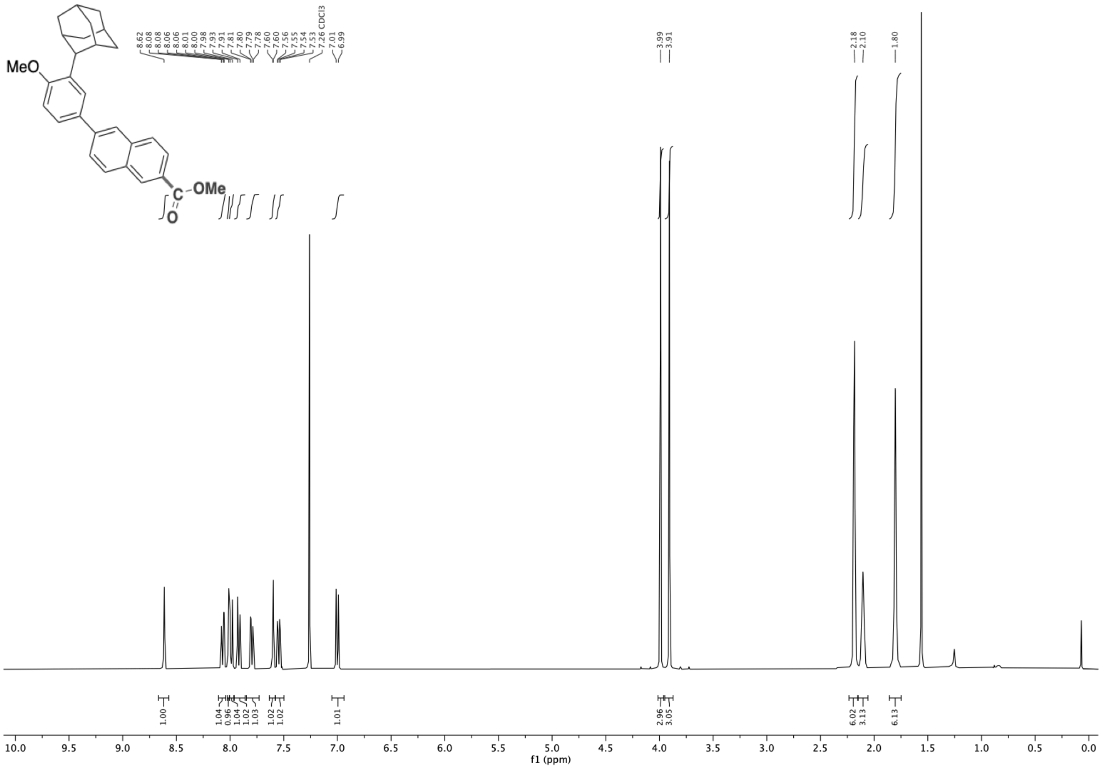
Methyl 4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoate (^{13}C-25) – ^{1}H NMR



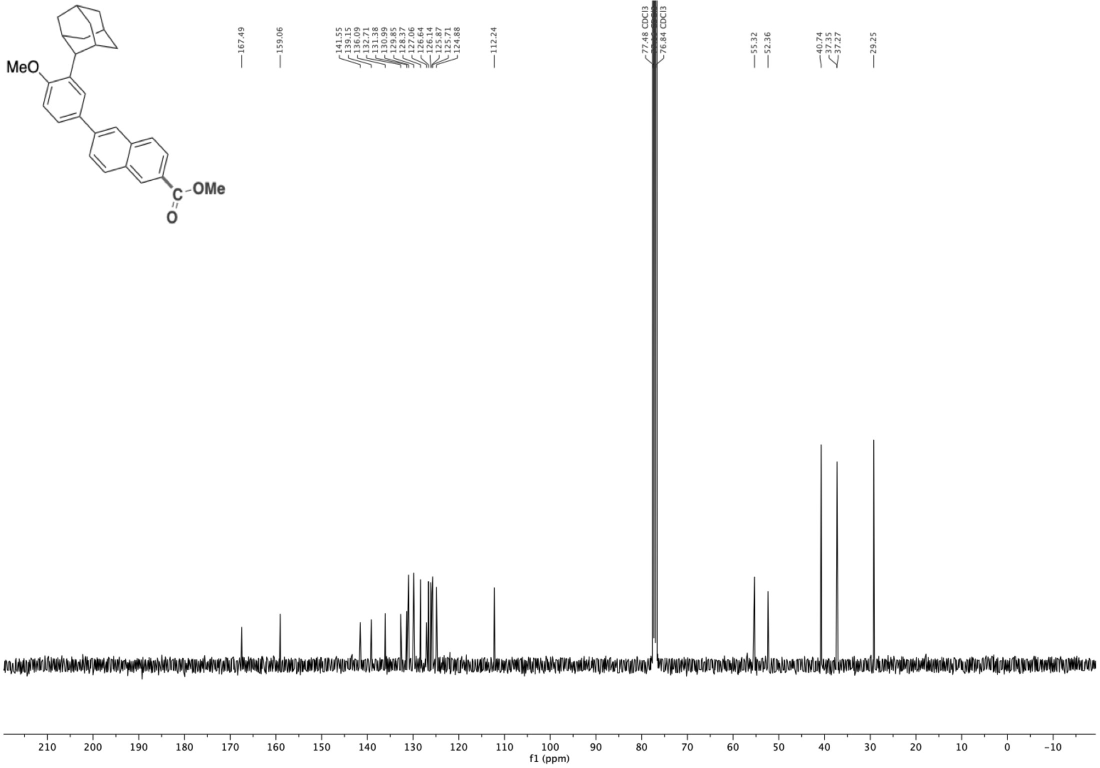
Methyl 4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoate (^{13}C-25) – ^{13}C NMR



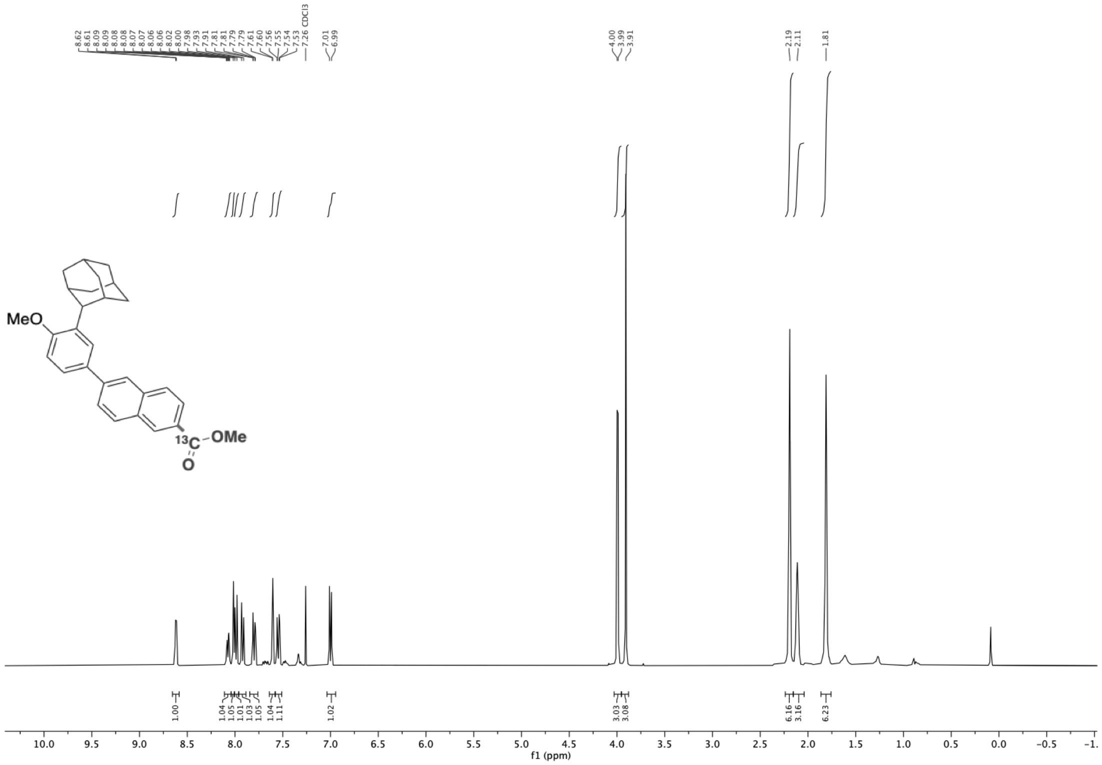
Methyl 6-(3-(1-adamantyl)-4-methoxyphenyl)-2-naphthoate (26) – ^{1}H NMR



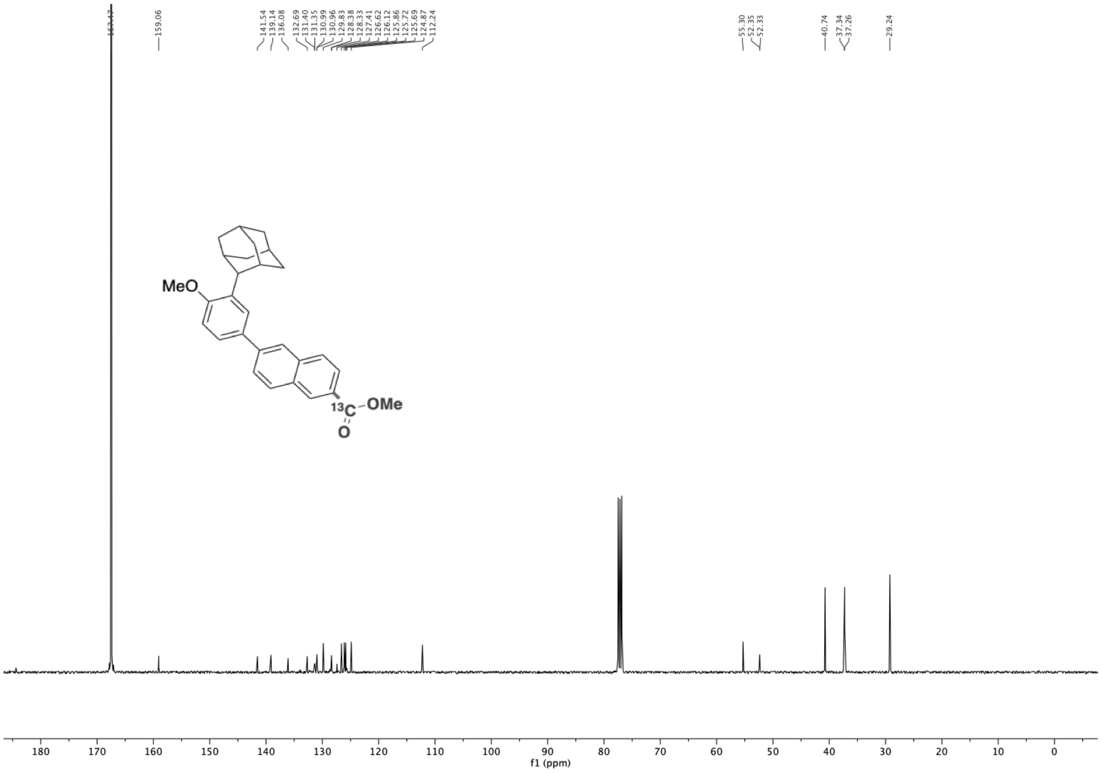
Methyl 6-(3-(1-adamantyl)-4-methoxyphenyl)-2-naphthoate (26) – ^{13}C NMR



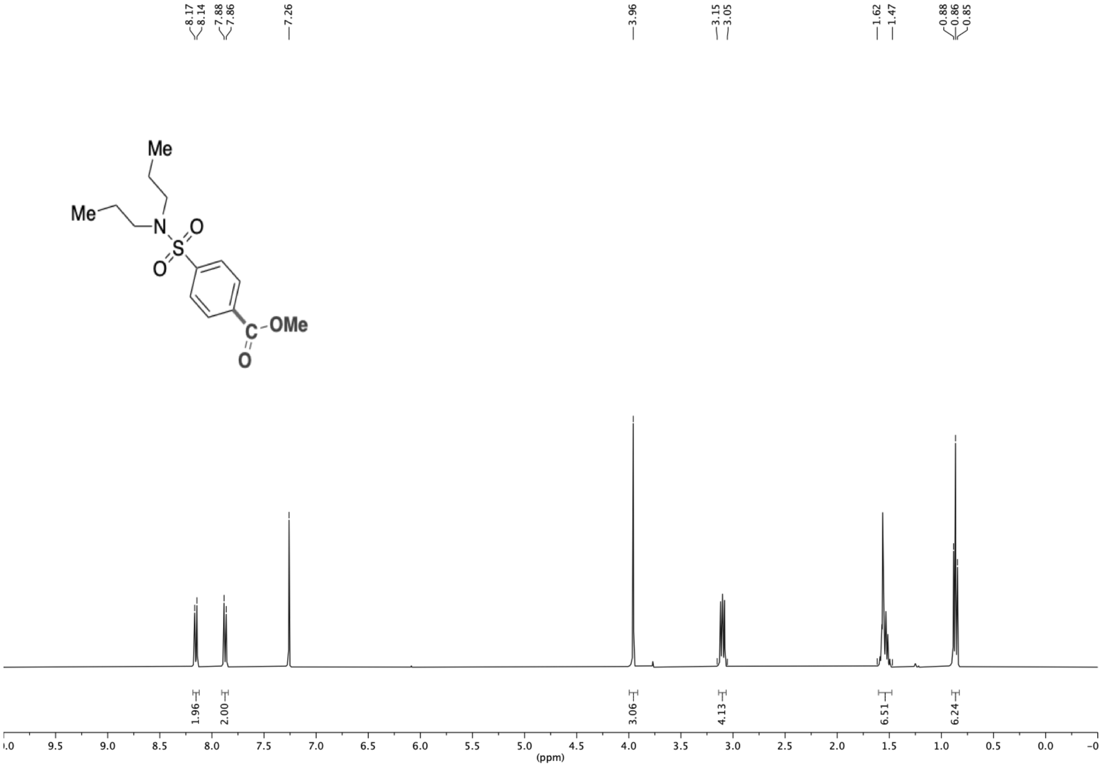
Methyl 6-(3-(1-adamantyl)-4-methoxyphenyl)-2-naphthoate (^{13}C-26) – ^{1}H NMR



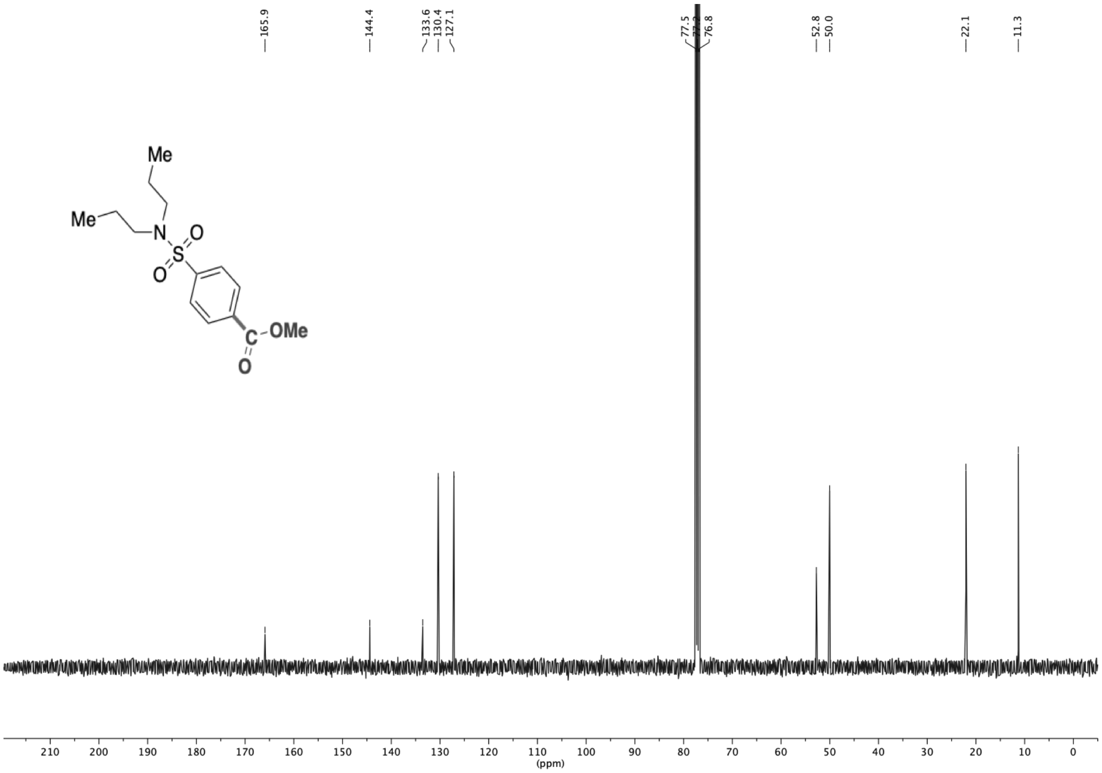
Methyl 6-(3-(1-adamantyl)-4-methoxyphenyl)-2-naphthoate (^{13}C-26) – ^{13}C NMR



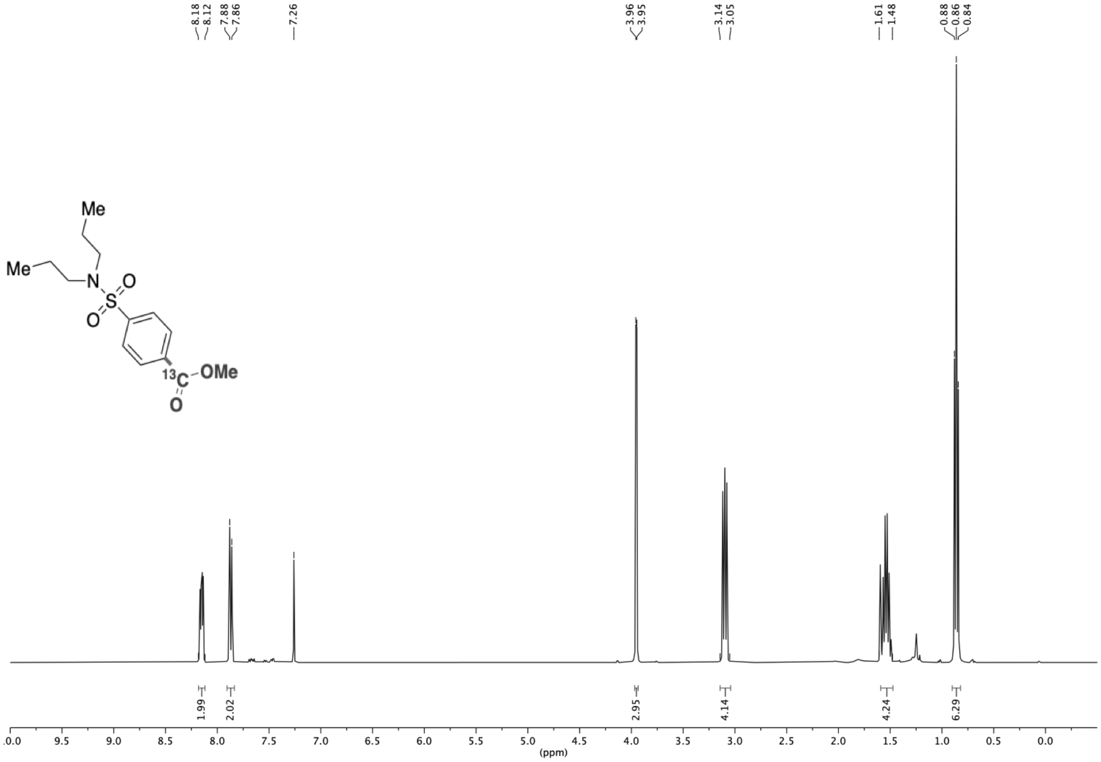
Methyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (27) – ^{1}H NMR



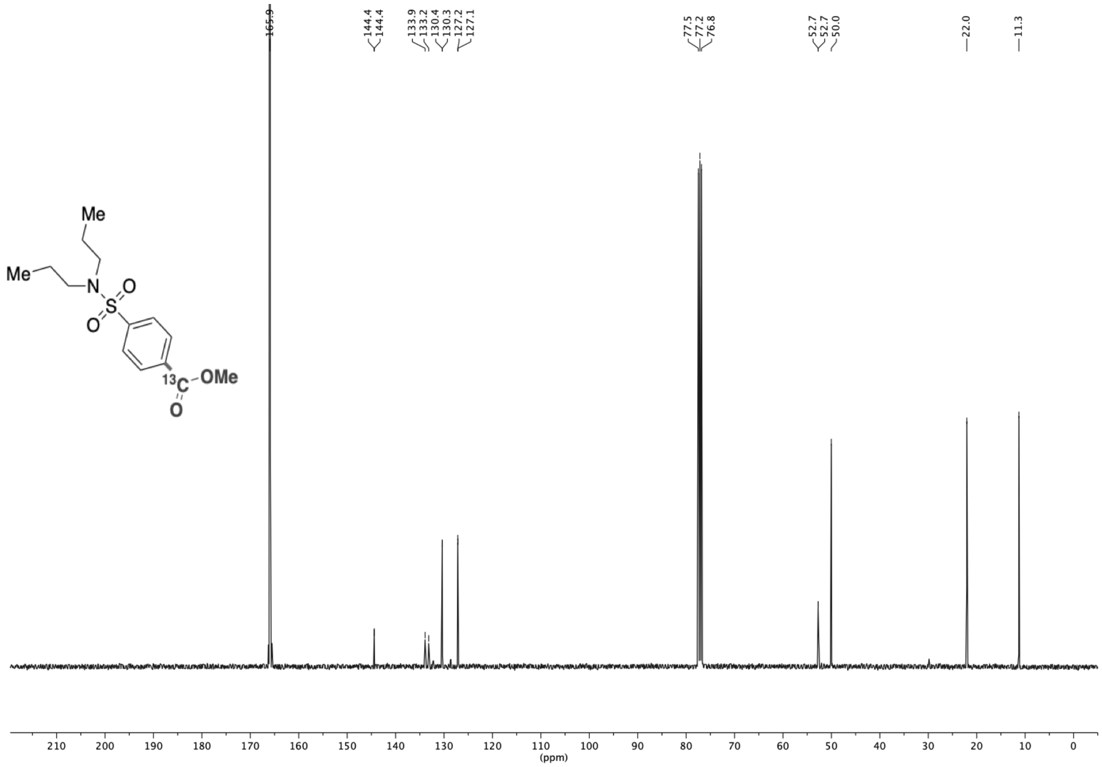
Methyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (27) – ^{13}C NMR



Methyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (^{13}C-27) – ^{1}H NMR

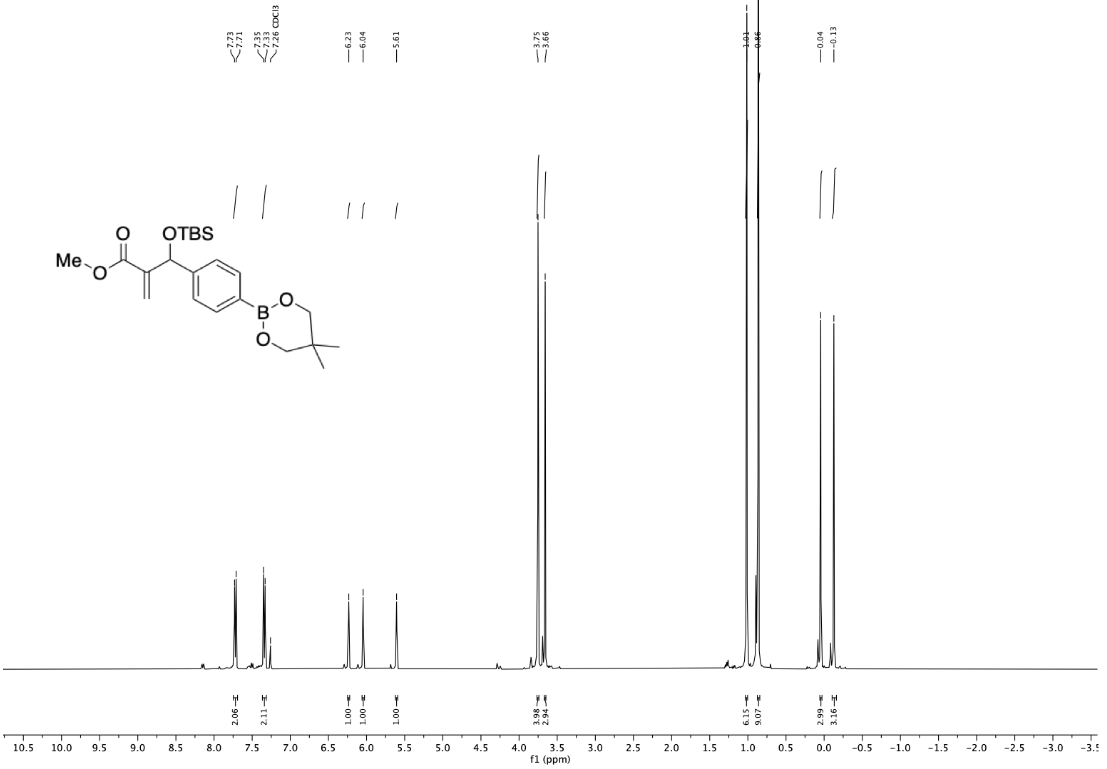


Methyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (^{13}C-27) – ^{13}C NMR

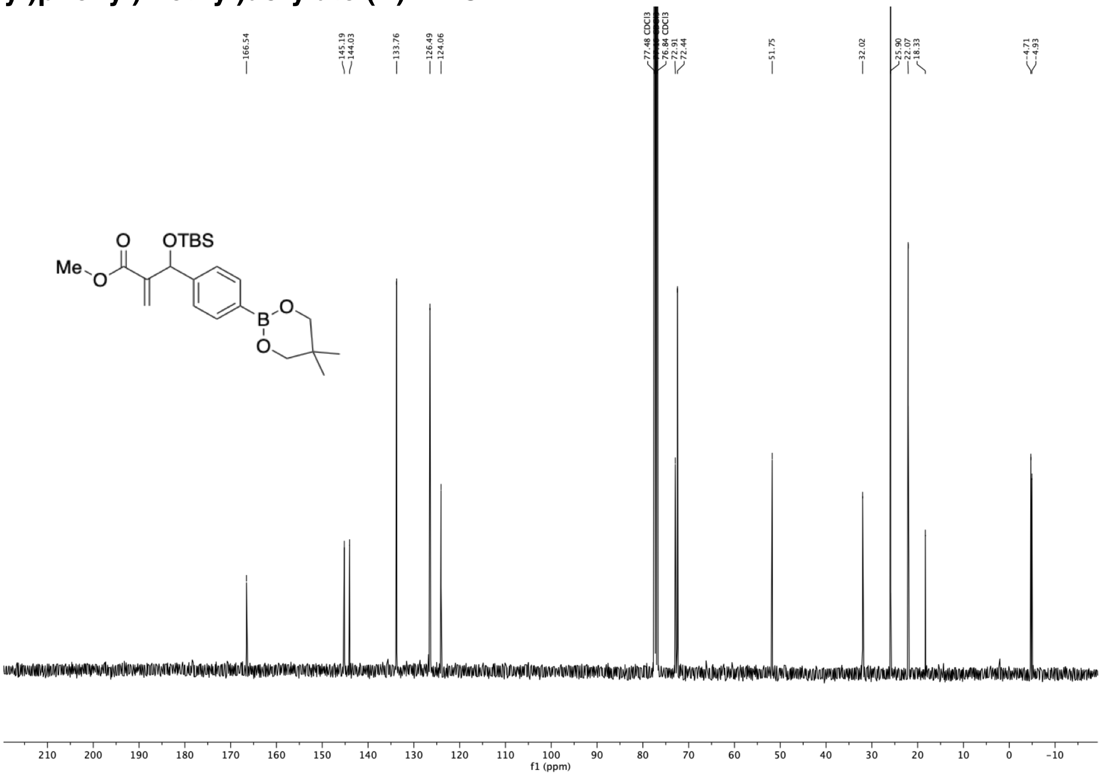


NMR Spectra (Boronic Esters, A - H)

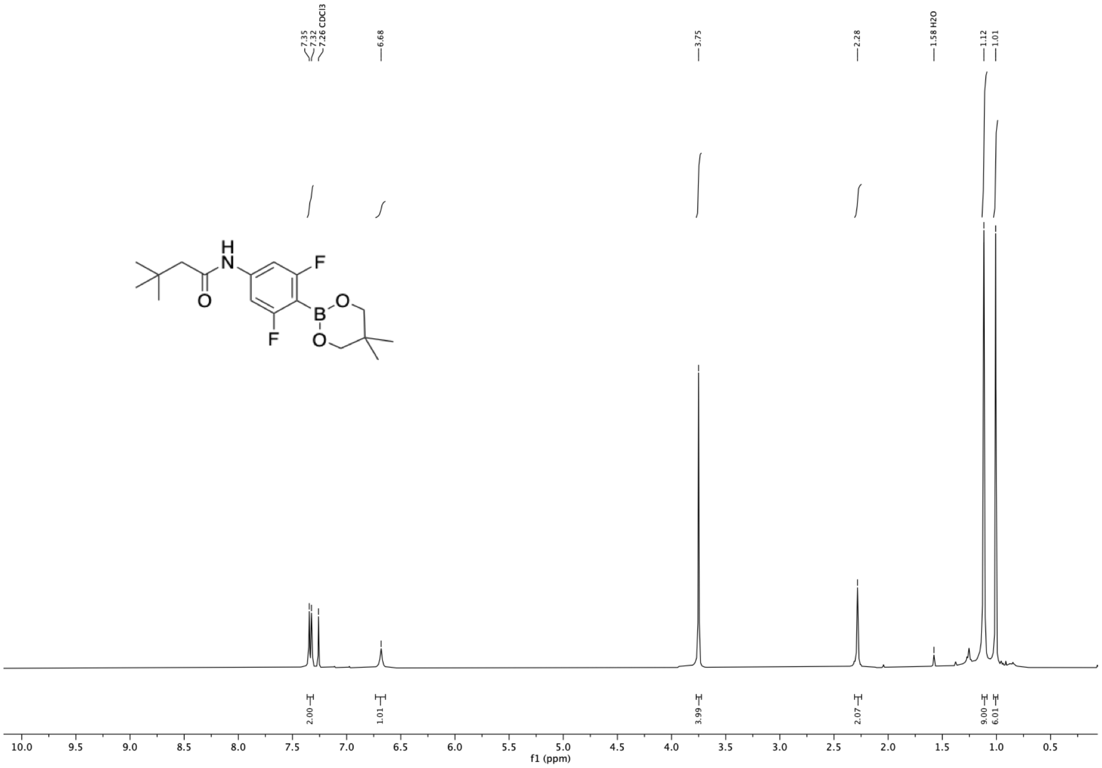
Methyl 2-(((tert-butyldimethylsilyl)oxy)(4-(5,5-dimethyl-1,3,2-dioxaborinan-2 yl)phenyl)methyl)acrylate (A) – ^{1}H NMR



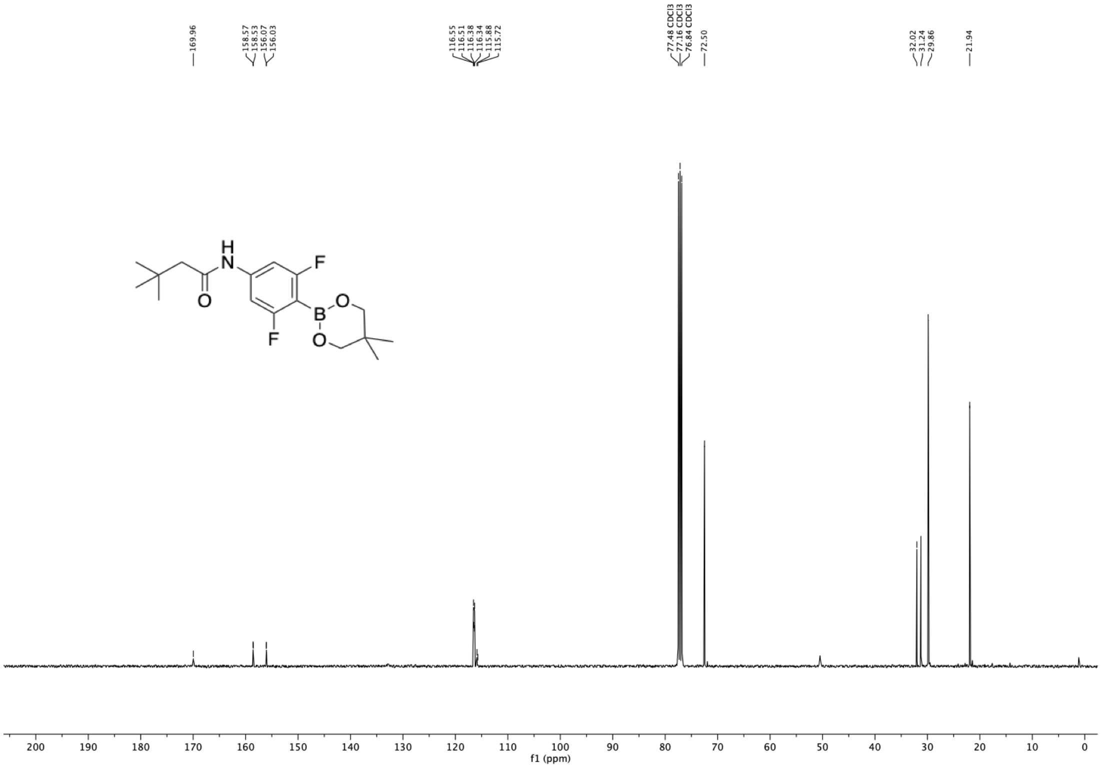
Methyl 2-(((tert-butyldimethylsilyl)oxy)(4-(5,5-dimethyl-1,3,2-dioxaborinan-2 yl)phenyl)methyl)acrylate (A) – ^{13}C NMR



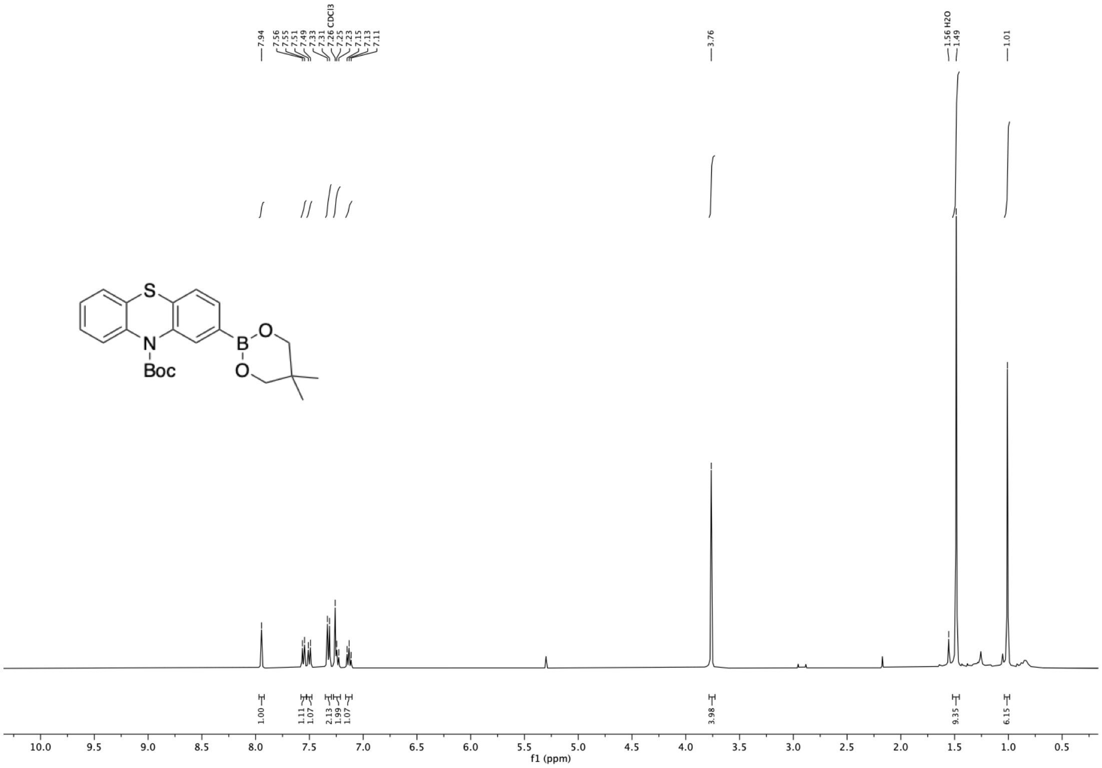
N-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-2,6-difluorophenyl)-3,3-dimethylbutanamide (B) – ^{1}H NMR



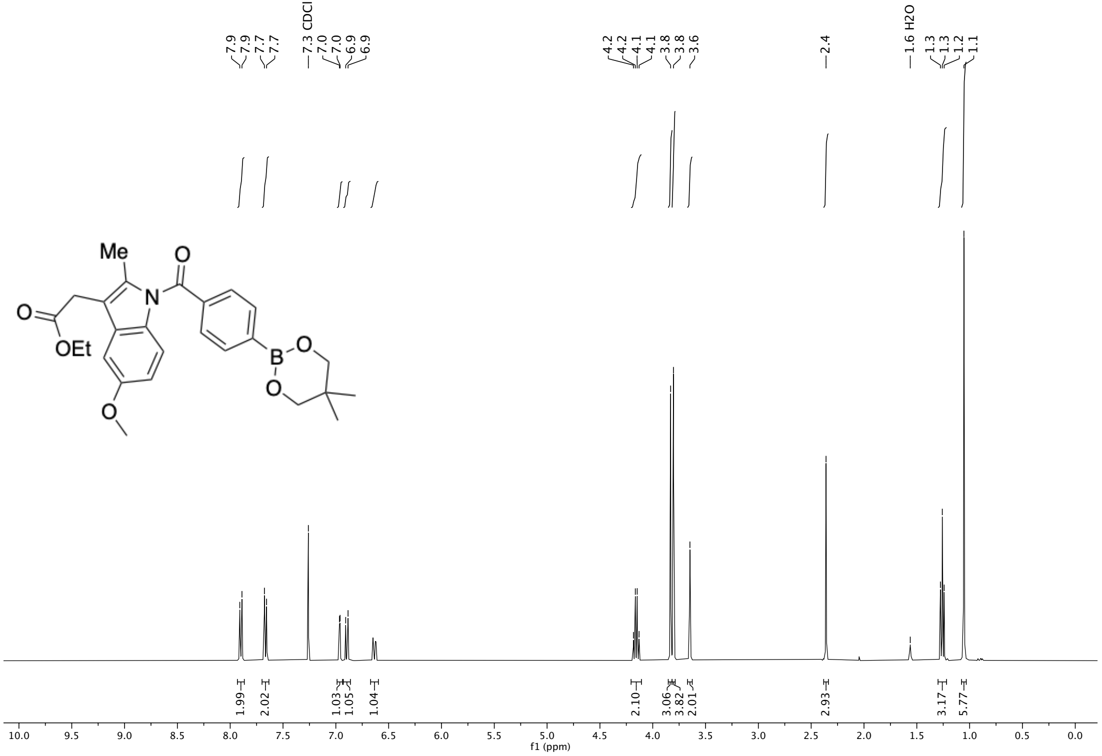
N-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-2,6-difluorophenyl)-3,3-dimethylbutanamide (B) – ^{13}C NMR



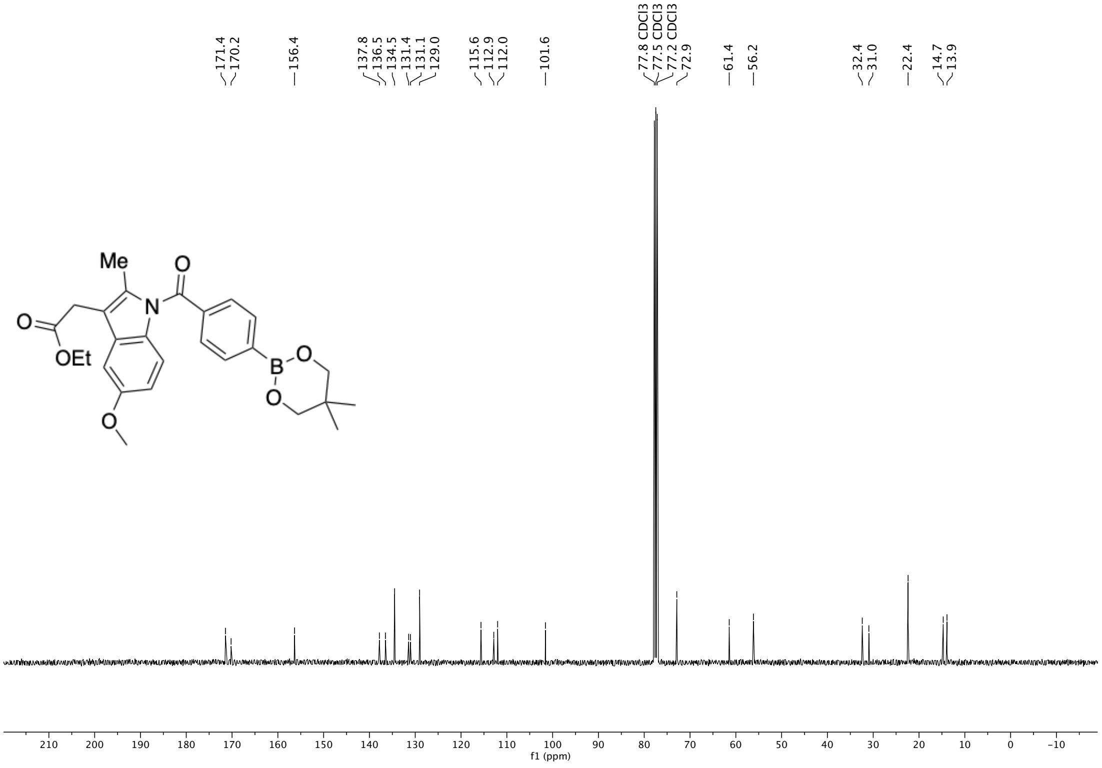
N-Boc-2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-10H-phenothiazine (C) – ^{1}H NMR



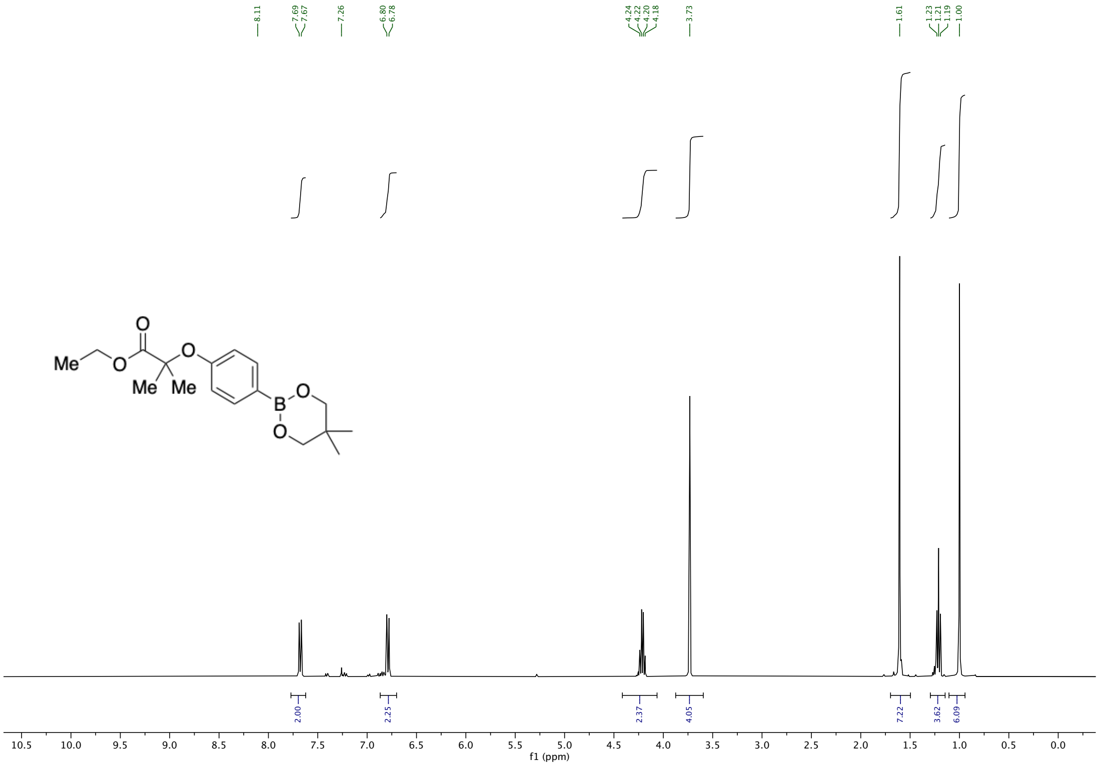
Methyl 2-(1-(4-(difluoromethyl)benzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (D) – ^{1}H NMR



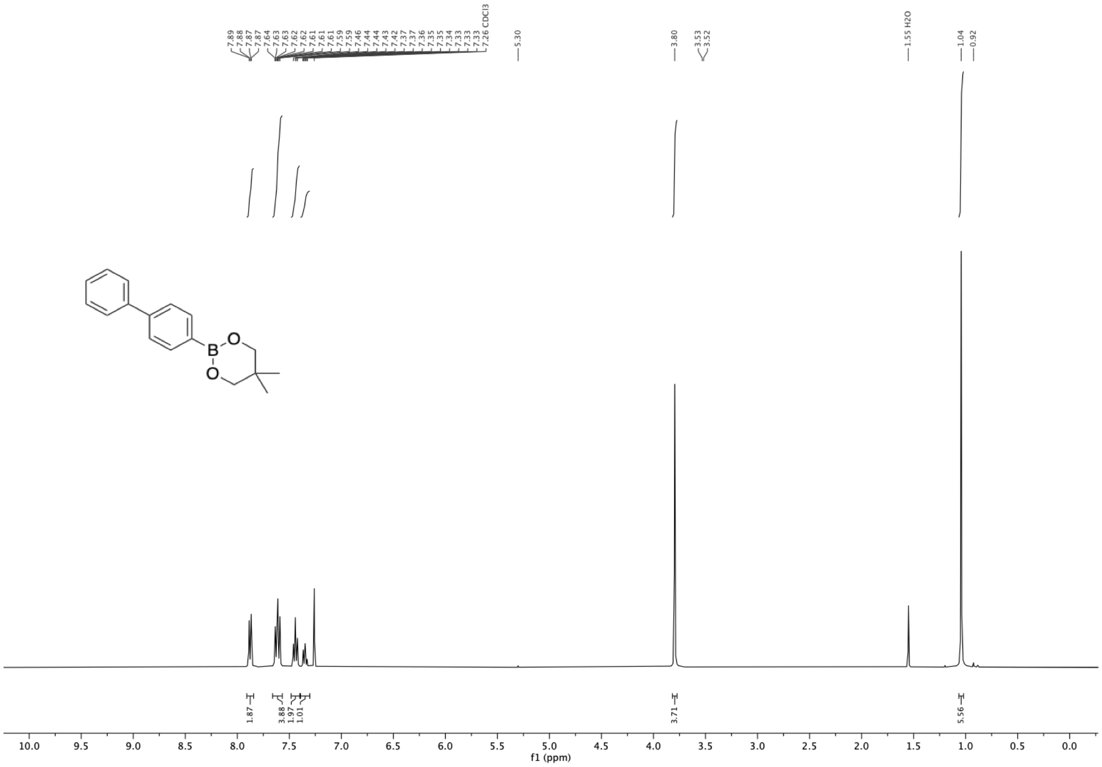
Methyl 2-(1-(4-(difluoromethyl)benzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (D) – ^{13}C NMR



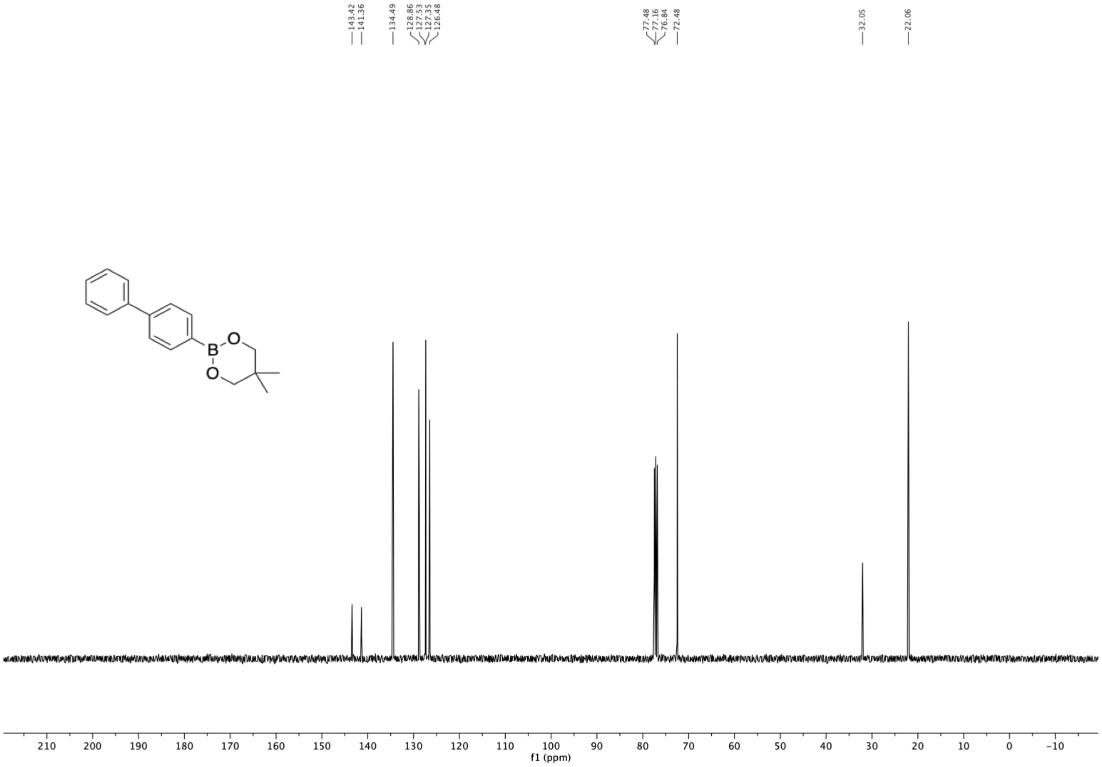
Ethyl 2-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenoxy)-2-methylpropanoate (E) – ^{1}H NMR



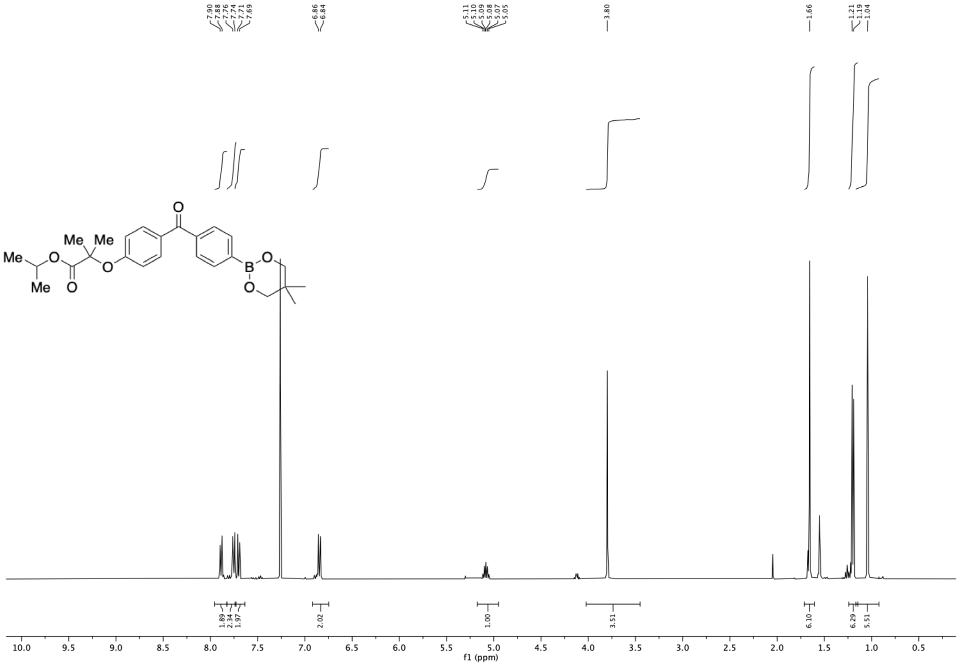
2-(biphenyl-4-yl)-5,5-dimethyl-1,3,2-dioxaborinane (F) – ^{1}H NMR



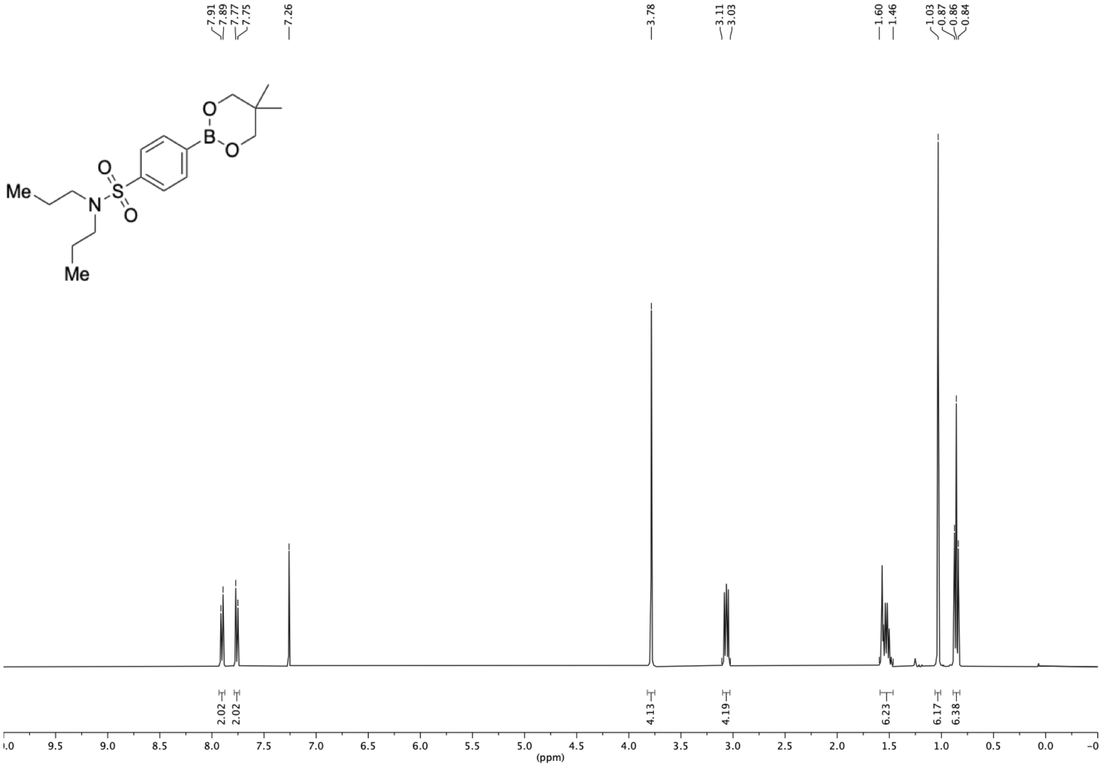
2-(biphenyl-4-yl)-5,5-dimethyl-1,3,2-dioxaborinane (F) – ^{13}C NMR



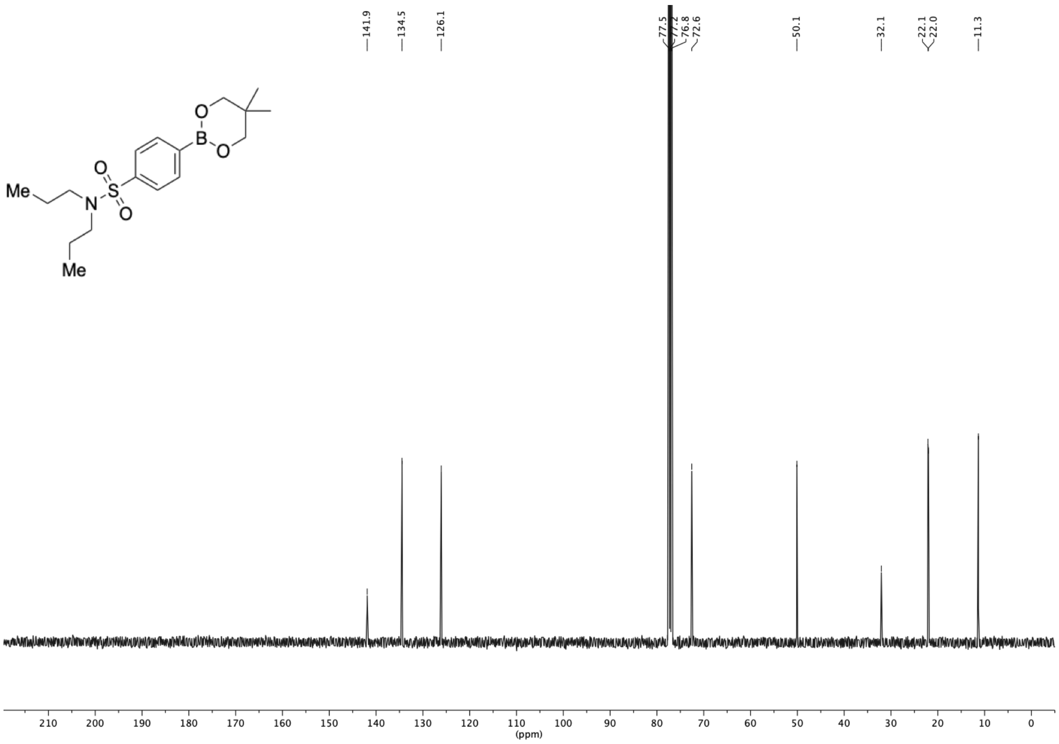
Isopropyl 2-(4-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoyl)phenoxy)-2-methylpropanoate (G) – ^{1}H NMR



4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)-N,N-dipropylbenzenesulfonamide (H) – ^{1}H NMR

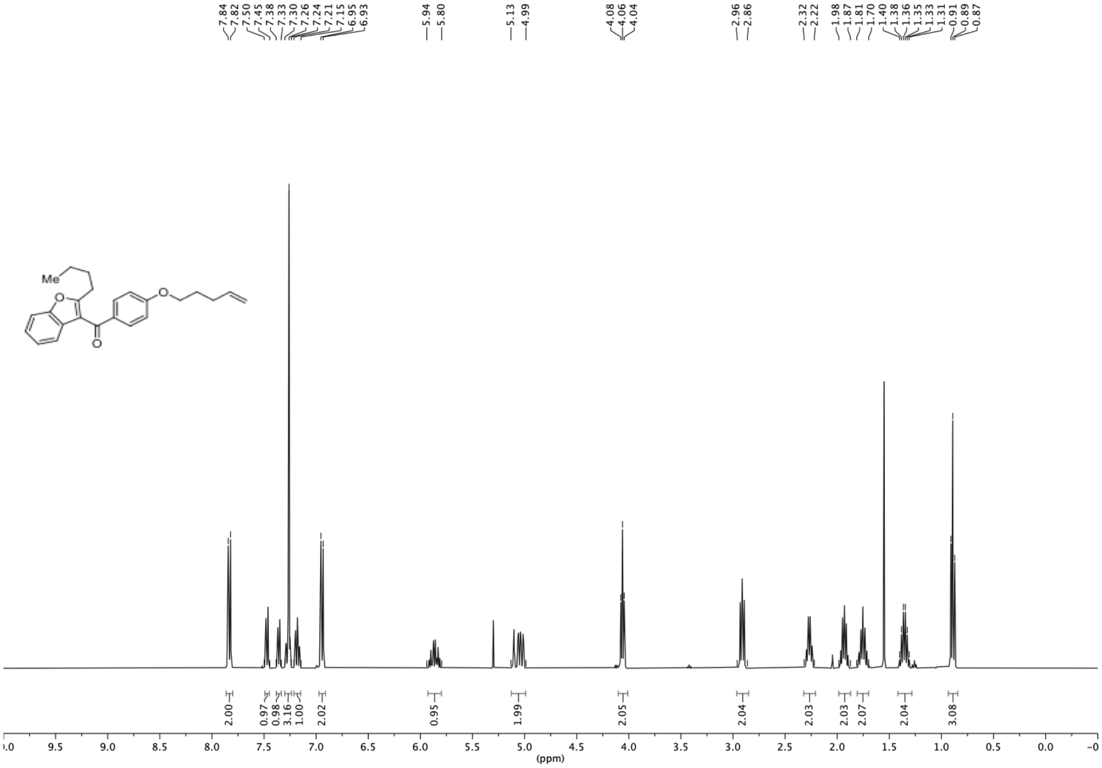


4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)-N,N-dipropylbenzenesulfonamide (H) – ^{13}C NMR

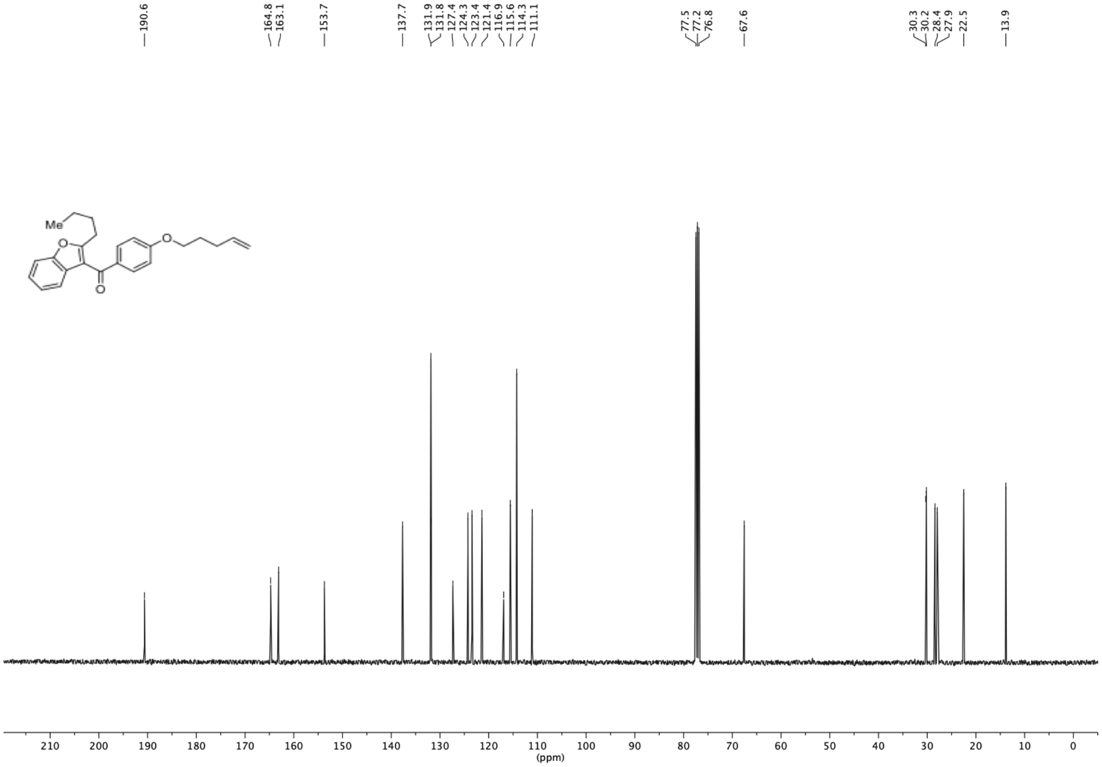


NMR Spectra (Alkenes and Alkynes, I - O)

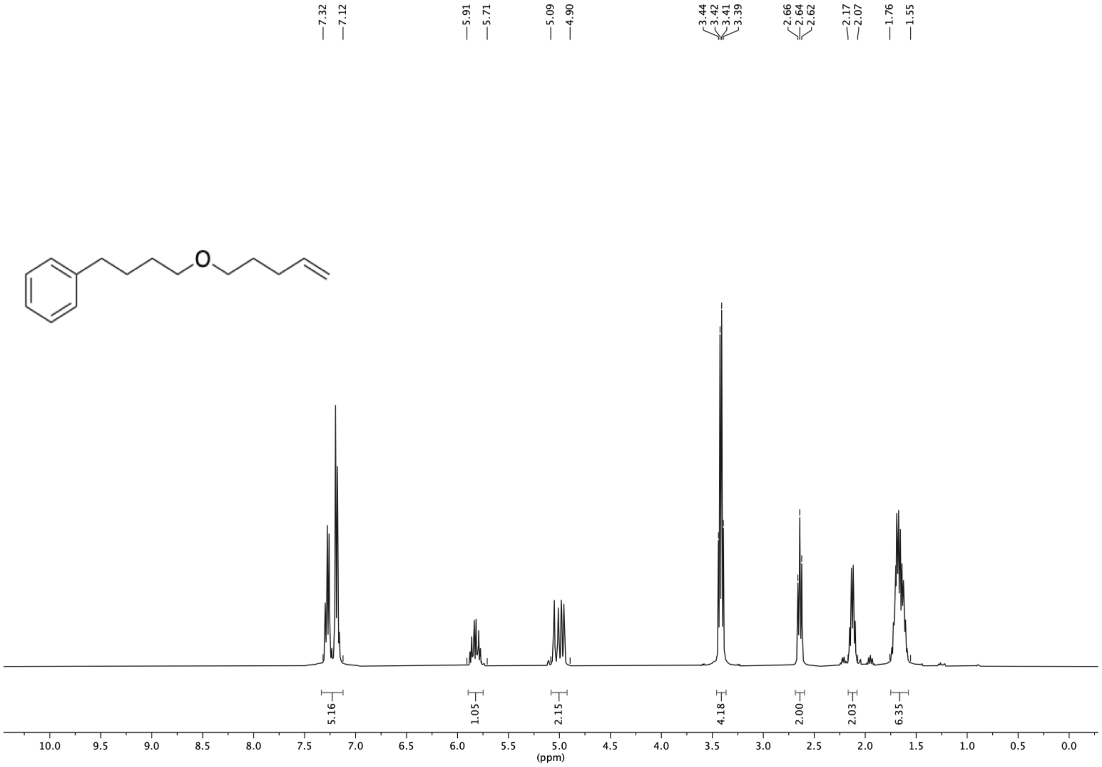
(2-butylbenzofuran-3-yl)(4-(pent-4-en-1-yloxy)phenyl)methanone (I) – ^{1}H NMR



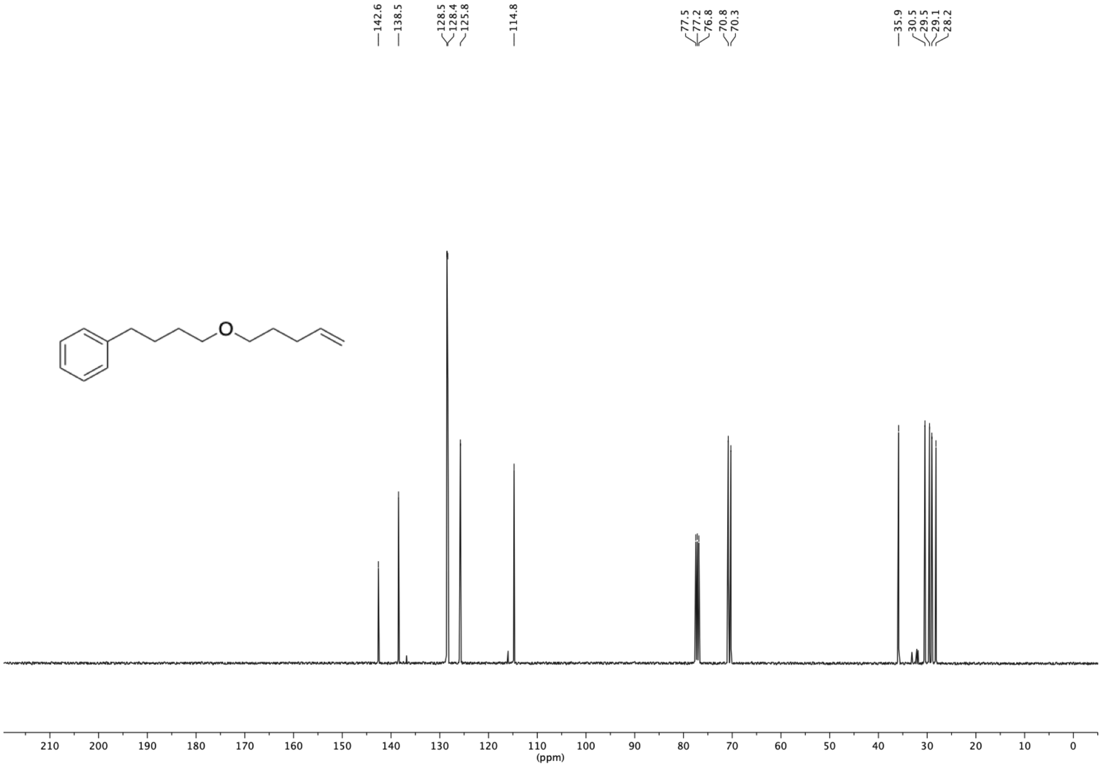
(2-butylbenzofuran-3-yl)(4-(pent-4-en-1-yloxy)phenyl)methanone (I) – ^{13}C NMR



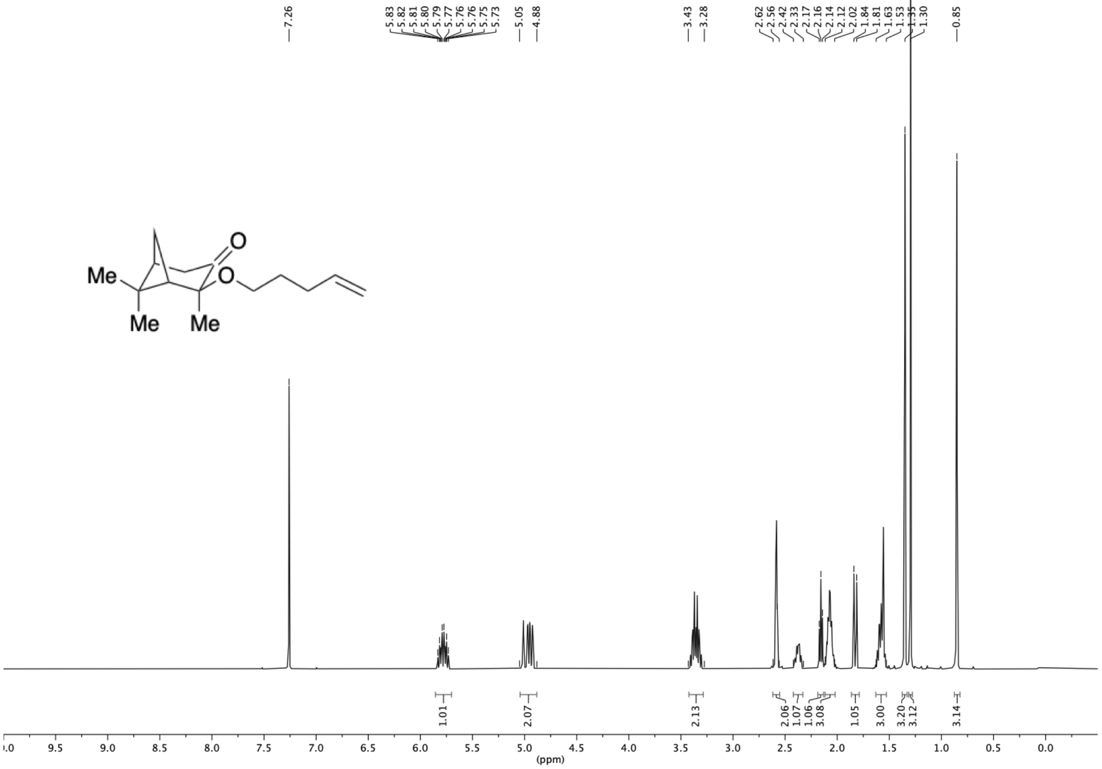
(4-(But-3-en-1-yloxy)butyl)benzene (J) – ^{1}H NMR



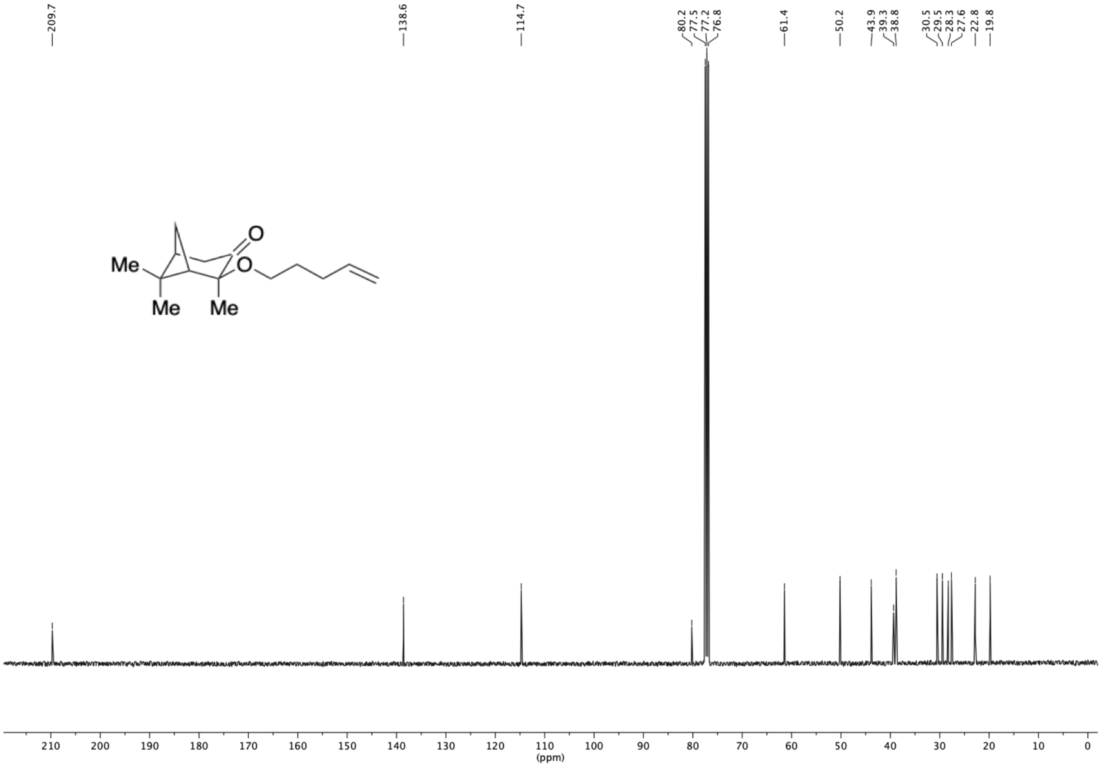
(4-(But-3-en-1-yloxy)butyl)benzene (J) – ^{13}C NMR



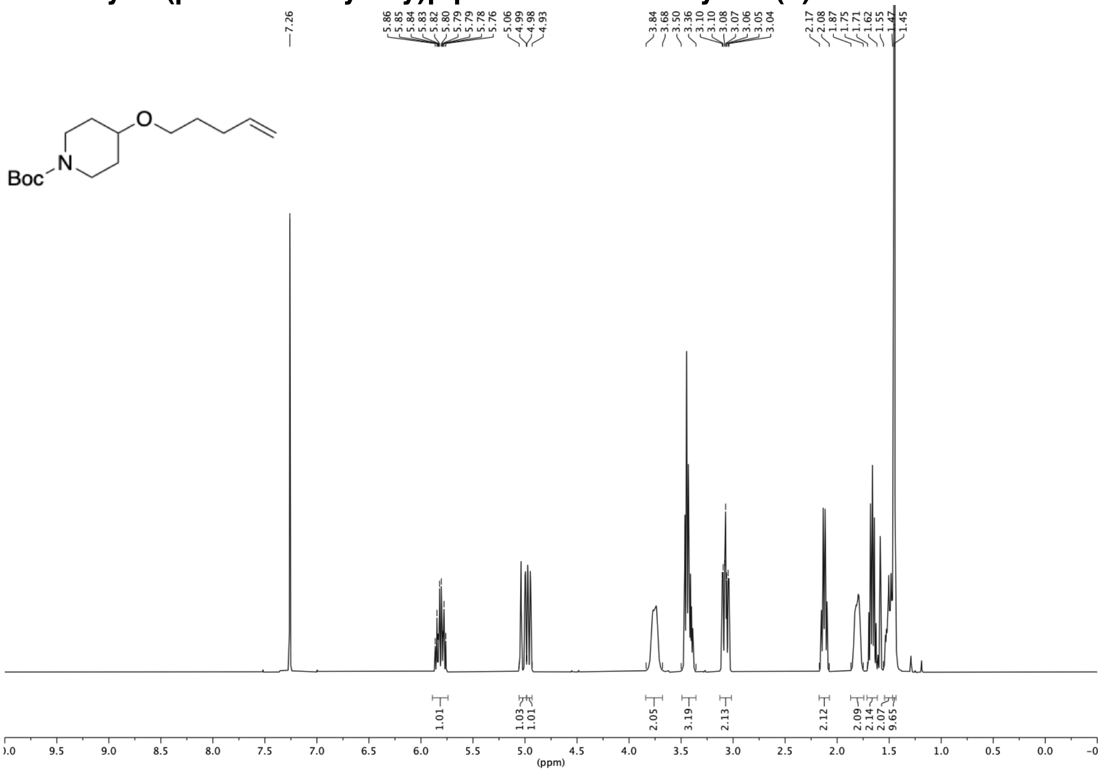
(*1S,2S,5S*)-2,6,6-trimethyl-2-(pent-4-en-1-yloxy)bicyclo[3.1.1]heptan-3-one (K) – ^{1}H NMR



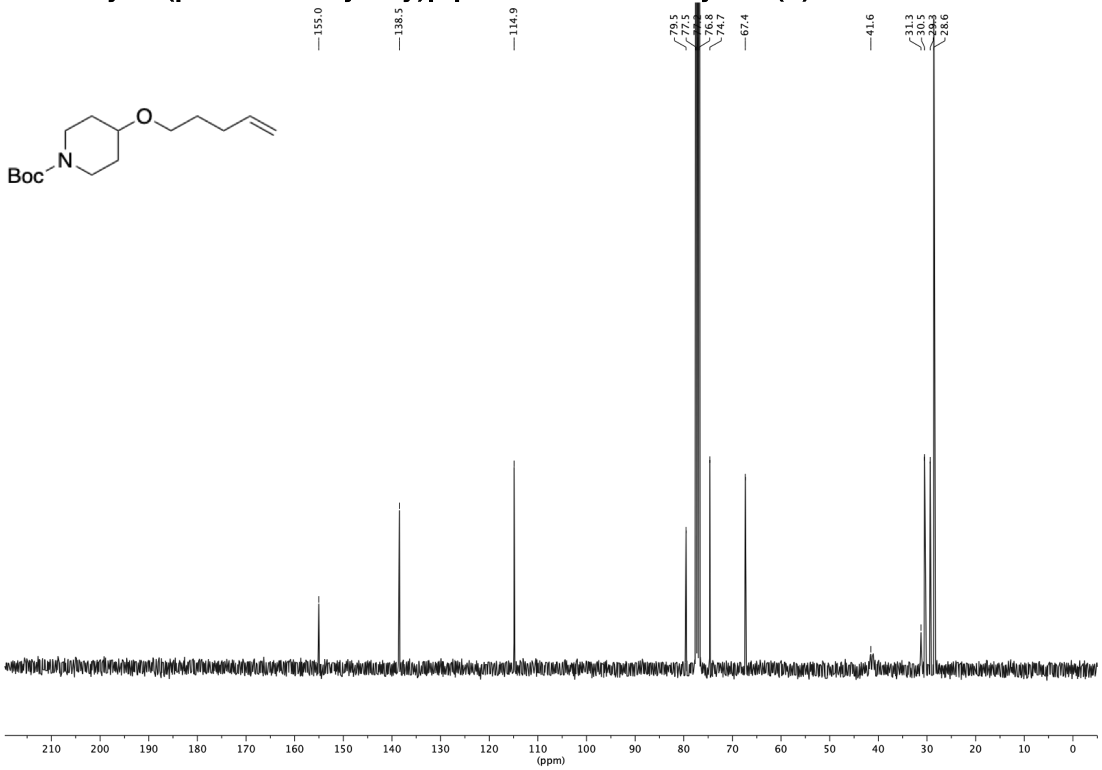
(*1S,2S,5S*)-2,6,6-trimethyl-2-(pent-4-en-1-yloxy)bicyclo[3.1.1]heptan-3-one (K) – ^{13}C NMR



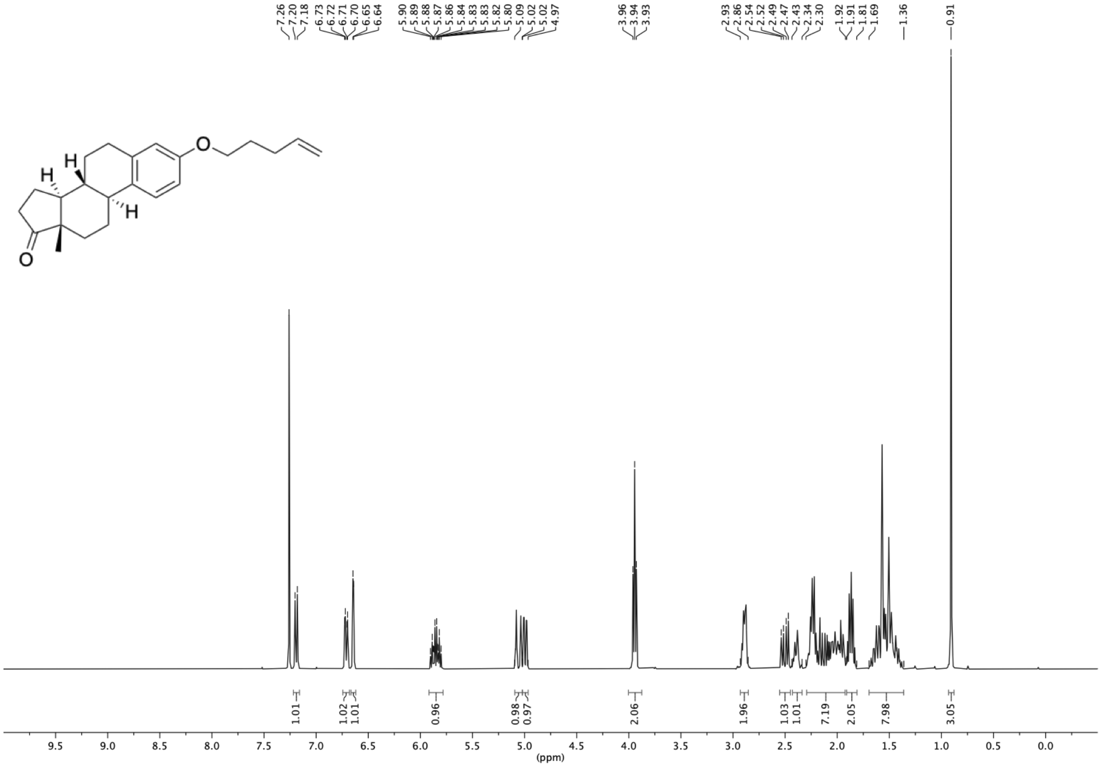
tert-butyl 4-(pent-4-en-1-yloxy)piperidine-1-carboxylate (L) – ^{1}H NMR



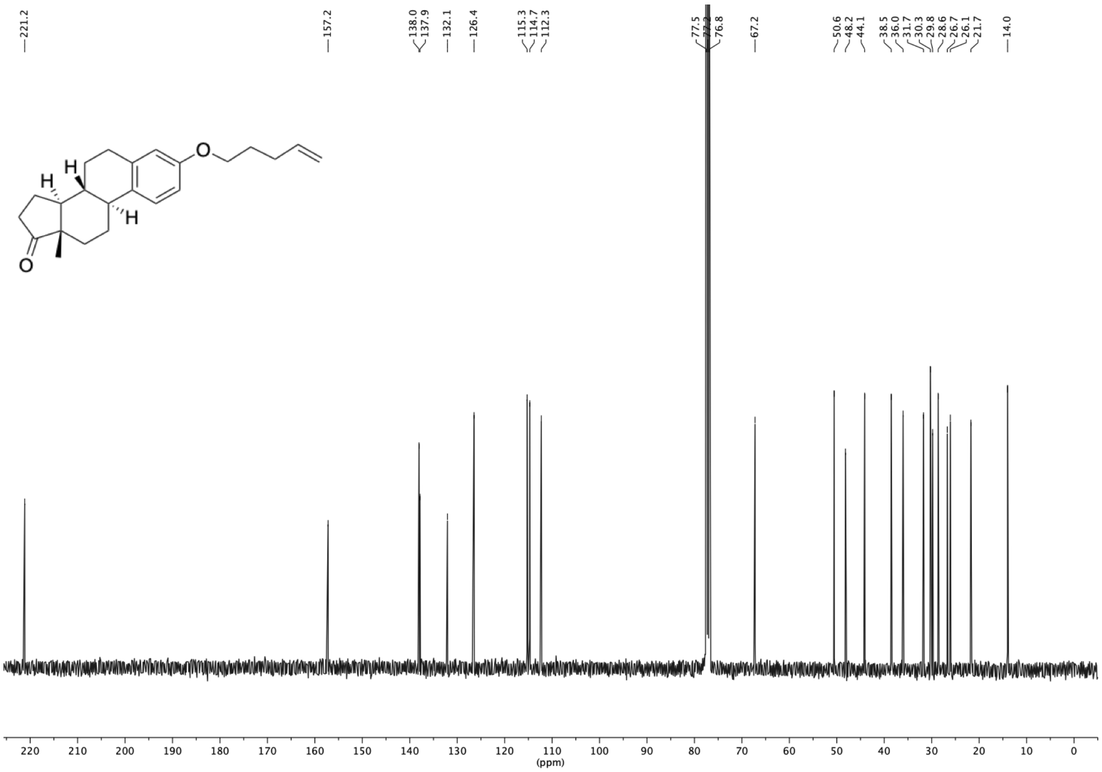
tert-butyl 4-(pent-4-en-1-yloxy)piperidine-1-carboxylate (L) – ^{13}C NMR



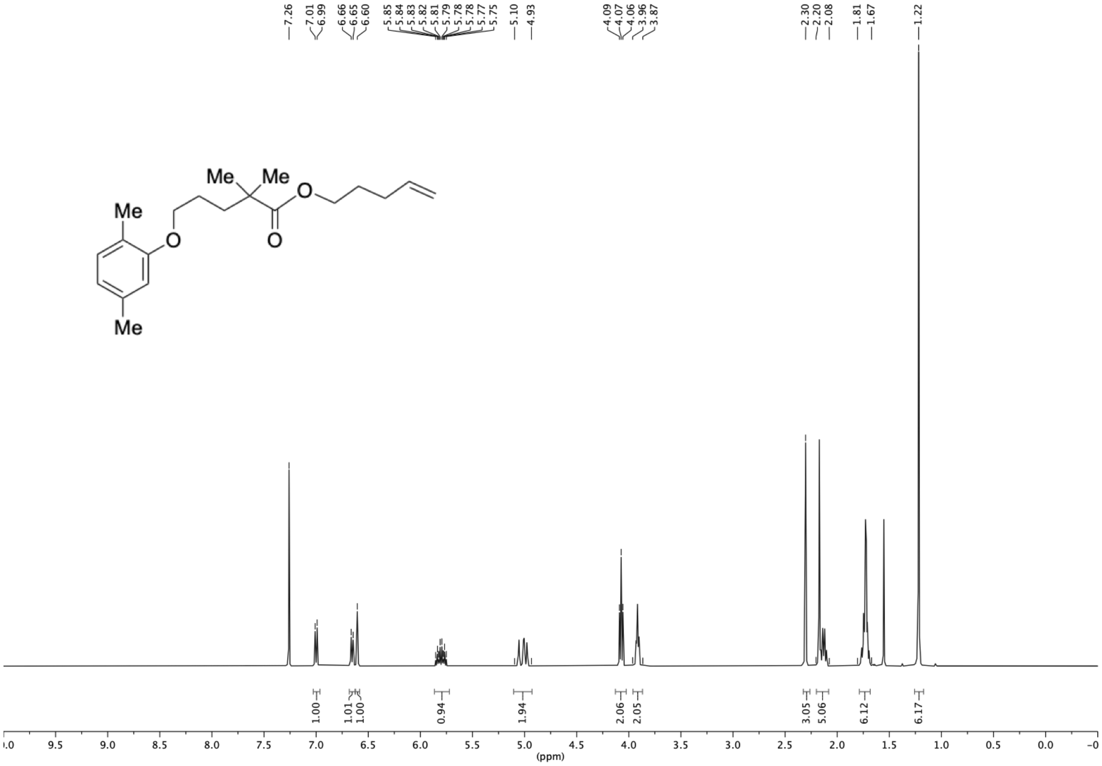
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(pent-4-en-1-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H* cyclopenta[*a*]phenanthren-17-one (M) – ^{1}H NMR



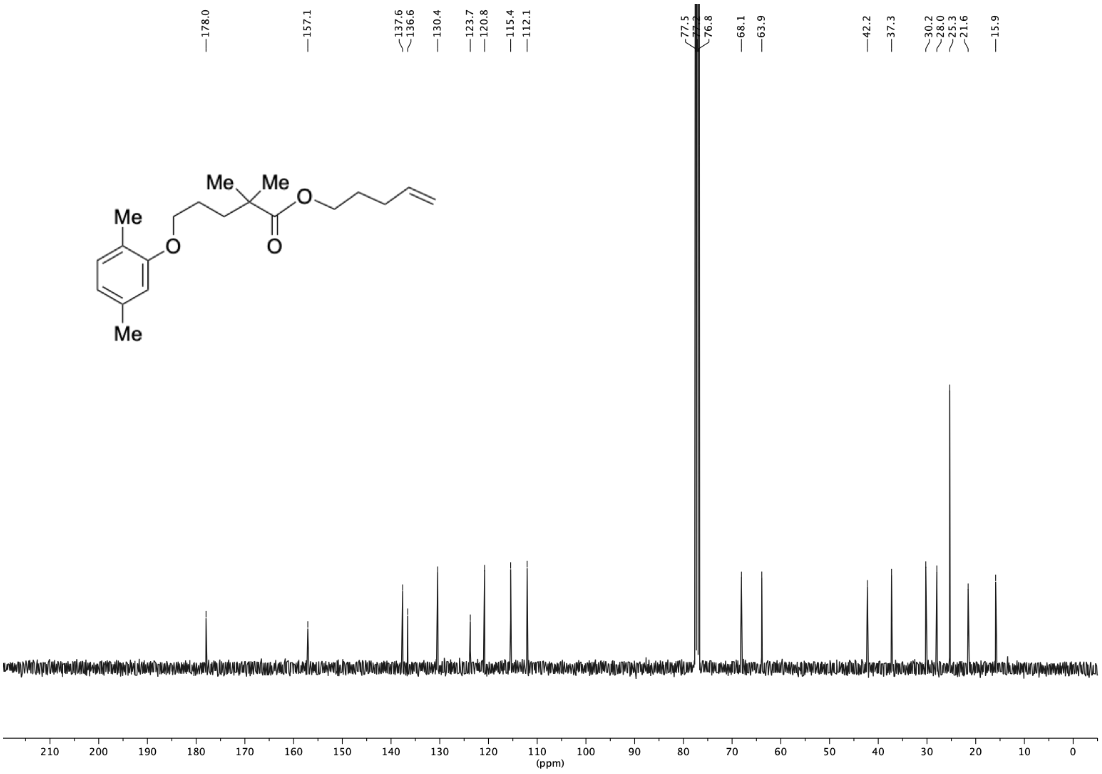
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(pent-4-en-1-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H* cyclopenta[*a*]phenanthren-17-one (M) – ^{13}C NMR



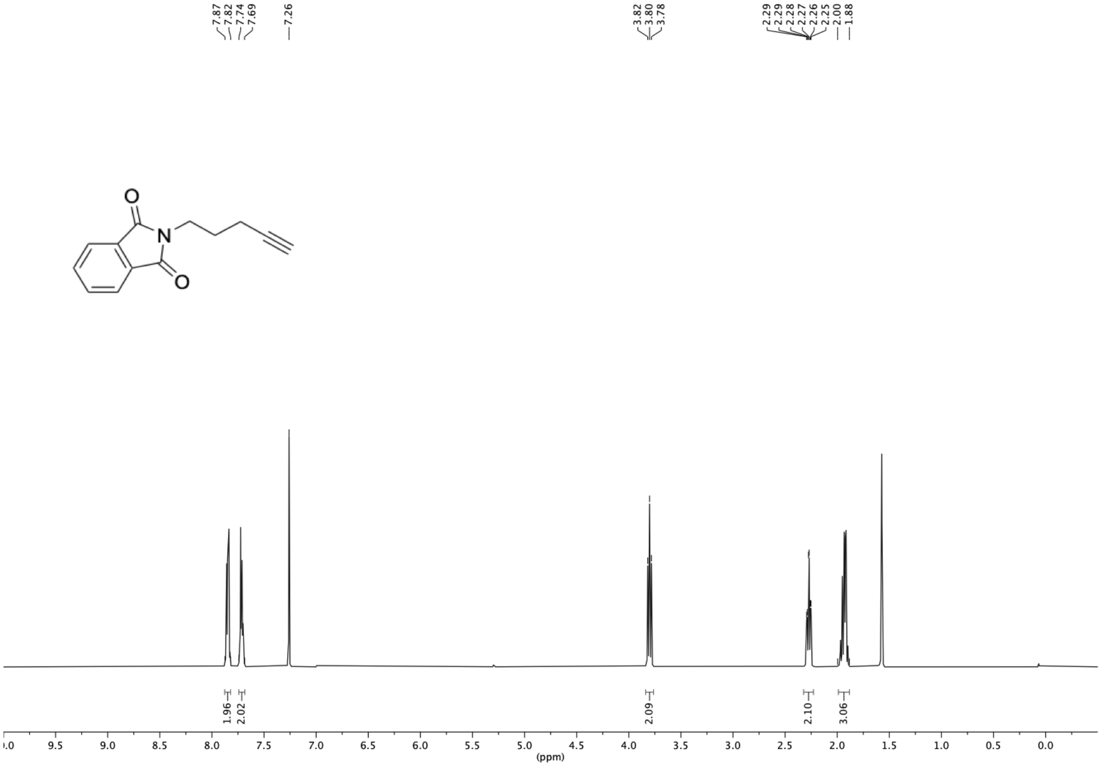
Pent-4-en-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (N) – ^{1}H NMR



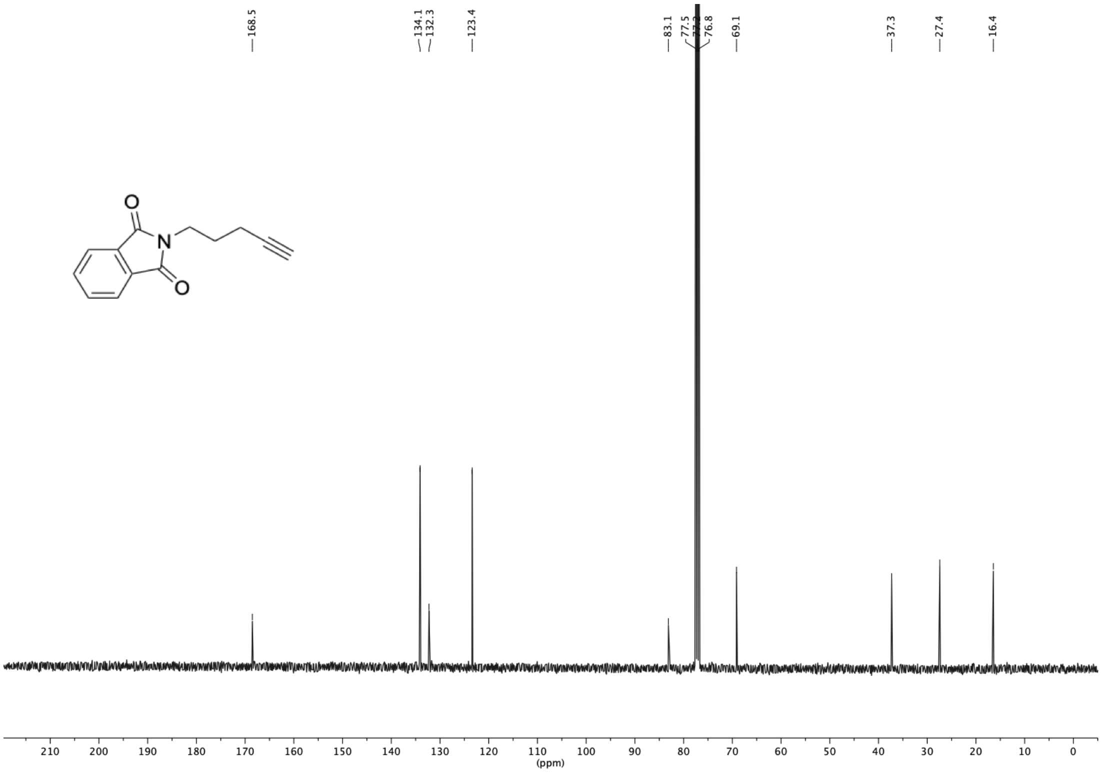
Pent-4-en-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (N) – ^{13}C NMR



2-(Pent-4-yn-1-yl)isoindoline-1,3-dione (O) – ^{1}H NMR



2-(Pent-4-yn-1-yl)isoindoline-1,3-dione (O) – ^{13}C NMR



References

1. Feng, Z.; Min, Q.-Q.; Fu, X.-P.; An, L.; Zhang, X., Chlorodifluoromethane-triggered formation of difluoromethylated arenes catalysed by palladium. *Nat. Chem* **2017,** *9* (9), 918-923.
2. Moon, P. J.; Yin, S.; Lundgren, R. J., Ambient Decarboxylative Arylation of Malonate Half-Esters via Oxidative Catalysis. *J. Am. Chem. Soc.* **2016,** *138* (42), 13826-13829.
3. Malapit, C. A.; Bour, J. R.; Laursen, S. R.; Sanford, M. S., Mechanism and Scope of Nickel-Catalyzed Decarbonylative Borylation of Carboxylic Acid Fluorides. *J. Am. Chem. Soc.* **2019,** *141* (43), 17322-17330.
4. Qin, T.; Cornella, J.; Li, C.; Malins, L. R.; Edwards, J. T.; Kawamura, S.; Maxwell, B. D.; Eastgate, M. D.; Baran, P. S., A general alkyl-alkyl cross-coupling enabled by redox-active esters and alkylzinc reagents. *Science* **2016,** *352* (6287), 801-805.
5. Wang, X.; Wu, Y., Direct oxidative isoperfluoropropylation of terminal alkenes via hexafluoropropylene (HFP) and silver fluoride. *ChemComm* **2018,** *54* (15), 1877-1880.
6. Falk, E.; Makai, S.; Delcaillau, T.; Gürtler, L.; Morandi, B., Design and Scalable Synthesis of N-Alkylhydroxylamine Reagents for the Direct Iron-Catalyzed Installation of Medicinally Relevant Amines. *Angew. Chem. Int. Ed.* **2020,** *59* (47), 21064-21071.
7. Yu, T.-B.; Bai, J. Z.; Guan, Z., Cycloaddition-Promoted Self-Assembly of a Polymer into Well-Defined β Sheets and Hierarchical Nanofibrils. *Angew. Chem. Int. Ed.* **2009,** *48* (6), 1097-1101.
8. Nayal, O. S.; Hong, J.; Yang, Y.; Mo, F., Cu-Catalysed carboxylation of aryl boronic acids with CO_2. *Org. Chem. Front.* **2019,** *6* (21), 3673-3677.
9. Yamamoto, Y., The First General and Selective Palladium(II)-Catalyzed Alkoxycarbonylation of Arylboronates: Interplay among Benzoquinone-Ligated Palladium(0) Complex, Organoboron, and Alcohol Solvent. *Adv. Synth. Catal.* **2010,** *352* (2-3), 478-492.