Supporting Information

Suzuki-Miyaura Cross-Coupling of Unprotected *ortho*-Bromoanilines with Benzyl, Alkyl, Aryl, Alkenyl and Heteroaromatic Boronic Esters

Alexandra E. Lubaev, Christopher C. Marvin, Amanda W. Dombrowski, Zafar Qureshi*

*Correspondence should be directed to: zafar.qureshi@abbvie.com

AbbVie, Inc., 1 N. Waukegan Road, North Chicago, Illinois, 60064, United States

1. General Experimental Methods

Unless otherwise noted, commercial solvents and reagents were purchased and used without additional purification, and reactions were carried out under an atmosphere of nitrogen. Proton and carbon magnetic resonance spectra (^{1}H and ^{13}C NMR) were recorded with a Varian 400 MHz NMR spectrometer. Chemical shifts are reported relative to internal $CDCl_3$ or d-DMSO solvent peaks, with respect to TMS (trimethylsilane): $CDCl_3$, ^{1}H, δ 7.26, ^{13}C, δ 77.16; DMSO-d_6, ^{1}H, δ 2.50, ^{13}C, δ 39.52. ^{19}F NMR spectra were recorded on a Varian 400 NMR spectrometer (at 376 MHz); chemical shifts are reported in parts per million and are referenced to $CFCl_3$ (δ 0.00). The NMR data is reported as chemical shift (δ) [multiplicity, coupling constant (hertz), integration]. Multiplicity and qualifier abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; hept, heptet; br, broad. HRMS was obtained from Proteomics and Mass Spectrometry at the University of Georgia, grant NIH S10 OD025118, Bruker Solarix XR 12 T FTICR MS. Reactions were monitored by thin layer chromatography (TLC) or LC-MS. Analytical LC-MS data was obtained on a Thermo MSQ-Plus mass spectrometer and Agilent 1100 HPLC system running XCalibur 2.0.7, Open-Access 1.4, and custom login software. Reaction conversion was monitored by TLC and accomplished with UV light (254 or 364 nm) and aqueous potassium permanganate stain for visualization. The crude products were purified on Biotage Selekt normal-phase chromatography system using silica gel cartridges purchased from Teledyne. The yields shown refer to isolated yields of analytically pure (>95%) material unless otherwise noted. The following common abbreviations are used: Mesylate[(di(1-adamantyl)-n-butylphosphine)-2-(2′-amino-1,1′-biphenyl)]palladium(II) (CataCXium A Pd G3), [1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride ($Pd(dppf)Cl_2$), potassium carbonate (K_2CO_3), cesium carbonate (Cs_2CO_3), ethyl acetate (EtOAc), toluene (PhMe) and 2-methyltetrahydrofuran (2-MeTHF).

2. General Procedures for the Preparation of Cross-Coupled Products

General Procedure A: Steroid Substrate

Into a 4 mL vial was weighed CataCXium A Pd G3 (10 mol%), *ortho*-bromoaniline steroid substrate (1.0 equiv, 0.5mmol), and Cs_2CO_3 (2.0 equiv). The reaction vial was capped with a Teflon sealed cap, and the vial was purged with nitrogen for 5 minutes. 2-MeTHF (0.25 mL) and deionized H_2O (0.063 mL) (0.32 M) were syringed into the vial followed by the respective boronate (1.5 equiv). The reactions were stirred at 400 rpm at 80 ºC for 14-17 h, as indicated for each substrate. Conversion was monitored by LC-MS, and after complete consumption of the *ortho*-bromoaniline, the reaction was cooled to room temperature. The aqueous and organic layers were separated, and the organic layer was concentrated under reduced pressure. The crude products were purified by flash column chromatography.

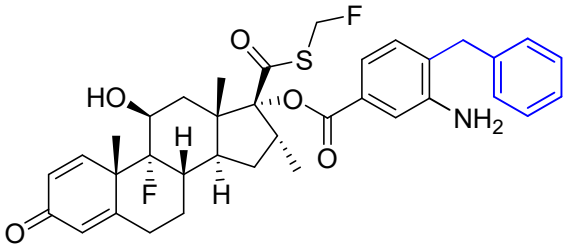
General Procedure B: Model Substrate - For solid boronic acid pinacol ester starting materials:

Into a 20 mL vial was weighed CataCXium A Pd G3 (5 mol%), *ortho*-bromoaniline substrate (1.0 equiv, 0.5mmol), Cs_2CO_3 (2.0 equiv), and the respective boronate (1.5 equiv). The reaction vial was capped with a Teflon sealed cap, and the vial was purged with nitrogen for 5 minutes. 2-MeTHF (4 mL) and deionized H_2O (1 mL) (0.01 M) was syringed into the vial. The reactions were stirred at 400 rpm at 70 ºC for 14-43 h, as indicated for each substrate. Conversion was monitored by TLC, and after complete consumption of the *ortho*-bromoaniline, the reaction was cooled to room temperature. The aqueous and organic layers were separated, and the organic layer was concentrated under reduced pressure. The crude products were purified by flash column chromatography.

General Procedure C: Model Substrate – For liquid boronic acid pinacol ester starting materials:

Into a 20 mL vial was weighed in CataCXium A Pd G3 (5 mol%), *ortho*-bromoaniline substrate (1.0 equiv, 0.5mmol), and Cs_2CO_3 (2.0 equiv). The reaction vial was capped with a Teflon sealed cap, and the vial was purged with nitrogen for 5 minutes. 2-MeTHF (4 mL) and deionized H_2O (1 mL) (0.01 M) were syringed into the vial followed by the respective boronate (1.5 equiv). The reactions were stirred at 400 rpm at 70 ºC for 14-43 h, as indicated for each substrate. Conversion was monitored by TLC, and after complete consumption of the *ortho*-bromoaniline, the reaction was cooled to room temperature. The aqueous and organic layers were separated, and the organic layer was concentrated under reduced pressure. The crude products were purified by flash column chromatography.

3. Characterization Data



(8*S*,9*R*,10*S*,11*S*,13*S*,14*S*,16*R*,17*R*)-9-fluoro-17-(((fluoromethyl)thio)carbonyl)-11-hydroxy-10,13,16-trimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3*H*-cyclopenta[*a*]phenanthren-17-yl 3-amino-4-benzylbenzoate (3a):

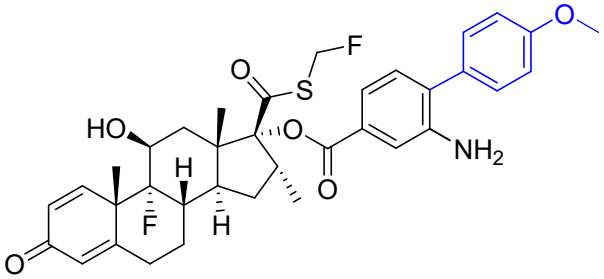
Following general procedure A, the reaction was run at 0.1 mmol for 17 h. The crude mixture was purified using flash column chromatography (4 g column, 30% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a beige solid (58 mg, 0.091 mmol, 91% yield).

^{1}H NMR (499 MHz, DMSO) δ 7.33 – 7.24 (m, 3H), 7.24 – 7.12 (m, 4H), 7.03 – 6.96 (m, 2H), 6.25 (dd, *J* = 10.1, 1.9 Hz, 1H), 6.06 – 6.01 (m, 1H), 5.99 (s, 1H), 5.89 (s, 1H), 5.53 (s, 1H), 5.24 (s, 2H), 4.28 – 4.23 (m, 1H), 3.82 (s, 2H), 2.64 (td, *J* = 13.6, 5.9 Hz, 1H), 2.45 – 2.38 (m, 1H), 2.39 – 2.31 (m, 1H), 2.27 – 2.10 (m, 2H), 1.96 – 1.78 (m, 3H), 1.50 (s, 3H), 1.48 – 1.36 (m, 1H), 1.33 – 1.19 (m, 1H), 1.05 (s, 3H), 0.89 (d, *J* = 7.2 Hz, 3H). (1H hidden under solvent peak)

^{13}C NMR (101 MHz, DMSO) δ 193.3, 185.3, 166.8, 165.1, 152.6, 146.6, 139.3, 130.3, 130.3, 129.1, 128.8, 128.3, 127.6, 126.0, 124.3, 116.5, 115.2, 101.0 (d, *J* = 175.3 Hz), 96.6, 81.1 (d, *J* = 212.3 Hz), 70.3 (d, *J* = 36.1 Hz), 48.7, 47.8 (d, *J* = 22.5 Hz), 43.5, 36.3, 36.1, 35.5, 33.7, 33.4 (d, *J* = 18.8 Hz), 30.2, 27.1, 22.9 (d, *J* = 5.4 Hz), 17.1, 16.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -166.7, -192.0.

HRMS: calc'd for $C_{36}H_{39}F_2NO_5S$ $(M + H)^+$ 636.25898; Found 636.25909.



(8*S*,9*R*,10*S*,11*S*,13*S*,14*S*,16*R*,17*R*)-9-fluoro-17-(((fluoromethyl)thio)carbonyl)-11-hydroxy-10,13,16-trimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3*H*-cyclopenta[*a*]phenanthren-17-yl 2-amino-4'-methoxy-[1,1'-biphenyl]-4-carboxylate (3b):

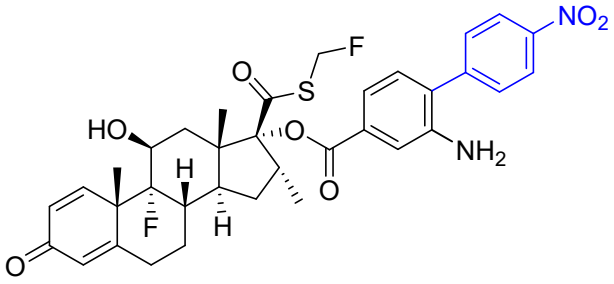
Following general procedure A, the reaction was run at 0.1 mmol for 14 h. The crude mixture was purified using flash column chromatography (4 g column, 25% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a white solid (58 mg, 0.091 mmol, 91% yield).

^{1}H NMR (400 MHz, DMSO) δ 7.42 – 7.24 (m, 4H), 7.15 – 7.08 (m, 2H), 7.05 – 7.00 (m, 2H), 6.29 – 6.21 (m, 1H), 6.07 – 6.00 (m, 2H), 5.90 (s, 1H), 5.58 – 5.52 (m, 1H), 5.06 (s, 2H), 4.31 – 4.24 (m, 1H), 3.79 (s, 3H), 2.66 (td, *J* = 13.4, 6.0 Hz, 1H), 2.48 – 2.13 (m, 4H), 1.99 – 1.81 (m, 3H), 1.51 (s, 3H), 1.48 – 1.38 (m, 1H), 1.32 – 1.21 (m, 1H), 1.07 (s, 3H), 0.93 (d, *J* = 7.1 Hz, 3H). (1H hidden under solvent peak)

^{13}C NMR (101 MHz, DMSO) δ 193.3, 185.3, 166.8, 165.1, 158.7, 152.6, 145.7, 130.7, 130.5, 130.5, 129.7, 129.2, 128.2, 124.3, 116.8, 115.8, 114.4, 101.1 (d, *J* = 175.1 Hz), 96.8, 81.1 (d, *J* = 212.1 Hz), 70.4 (d, *J* = 36.4 Hz), 55.2, 48.7, 47.8 (d, *J* = 22.6 Hz), 43.6, 36.2, 35.6, 33.8, 33.4 (d, *J* = 19.4 Hz), 30.2, 27.2, 22.9 (d, *J* = 5.6 Hz), 17.2, 16.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -166.7, -192.0.

HRMS: calc'd for $C_{36}H_{39}F_2NO_6S$ $(M + H)^+$ 652.25389; Found 652.25407.



(8*S*,9*R*,10*S*,11*S*,13*S*,14*S*,16*R*,17*R*)-9-fluoro-17-(((fluoromethyl)thio)carbonyl)-11-hydroxy-10,13,16-trimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3*H*-cyclopenta[*a*]phenanthren-17-yl 2-amino-4'-nitro-[1,1'-biphenyl]-4-carboxylate (3c):

Following general procedure A, the reaction was run at 0.1 mmol for 14 h. The crude mixture was purified using flash column chromatography (4 g column, 25% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a yellow solid (65 mg, 0.097 mmol, 97% yield).

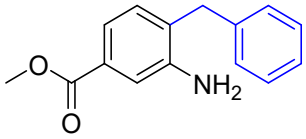
^{1}H NMR (400 MHz, DMSO) δ 8.29 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.9 Hz, 2H), 7.40 – 7.27 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.12 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.25 (dd, *J* = 10.1, 1.9 Hz, 1H), 6.06 – 6.00 (m, 2H), 5.90 (s, 1H), 5.55 (dd, J = 4.5, 1.7 Hz, 1H), 5.38 (s, 2H), 4.33 – 4.20 (m, 1H), 2.65 (td, *J* = 13.4,

12.3, 5.2 Hz, 1H), 2.45 – 2.30 (m, 1H), 2.31 – 2.08 (m, 2H), 2.04 – 1.77 (m, 3H), 1.51 (s, 3H), 1.48 – 1.40 (m, 1H), 1.33 – 1.18 (m, 2H), 1.08 (s, 3H), 0.94 (d, J = 7.1 Hz, 3H). (1H hidden under solvent peak)

^{13}C NMR (101 MHz, DMSO) δ 193.2, 185.3, 166.9, 164.9, 152.7, 146.5, 146.0, 145.6, 130.9, 130.0, 129.7, 129.2, 128.1, 124.3, 124.0, 116.5, 116.4, 101.1 (d, J = 175.3 Hz), 97.0, 81.1 (d, J = 212.1 Hz), 70.4 (d, J = 36.4 Hz), 48.8, 47.8 (d, J = 22.8 Hz), 43.6, 36.2, 35.5, 33.8, 33.4 (d, J = 19.2 Hz), 30.2, 27.2, 22.9 (d, J = 5.8 Hz), 17.2, 16.1.

^{19}F NMR (376 MHz, DMSO) δ -164.4, -191.0.

HRMS: calc'd for $C_{35}H_{36}F_2N_2O_7S$ $(M + H)^+$ 667.22841; Found 6667.22870.



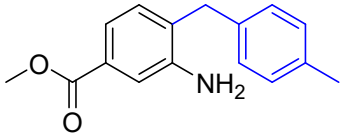
Methyl 3-amino-4-benzylbenzoate (3d):

Following general procedure C, the reaction was run on a 0.5 mmol scale for 18 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a yellow solid (109 mg, 0.453 mmol, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.29 (m, 4H), 7.25 – 7.11 (m, 4H), 3.94 (s, 2H), 3.89 (s, 3H), 3.63 (br s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 144.9, 138.5, 131.0, 130.2, 129.7, 128.9, 128.6, 126.8, 120.1, 116.8, 52.1, 38.2.

HRMS: calc'd for $C_{15}H_{15}NO_2$ $(M + H)^+$ 242.11756; Found 242.11756.



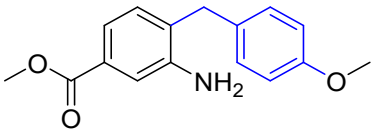
Methyl 3-amino-4-(4-methylbenzyl)benzoate (3e):

Following general procedure C, the reaction was run at 0.5 mmol for 21 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a light-yellow solid (63 mg, 0.248 mmol, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, J = 7.7, 1.8 Hz, 1H), 7.35 (d, J = 1.8 Hz, 1H), 7.14 – 7.03 (m, 5H), 3.89 (d, J = 3.7 Hz, 5H), 3.63 (br s, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 144.9, 136.3, 130.9, 130.5, 129.6, 129.3, 128.5, 127.2, 120.0, 116.8, 52.1, 37.8, 21.1.

HRMS: calc'd for $C_{16}H_{17}NO_2$ $(M + H)^+$ 256.13321; Found 256.13319.



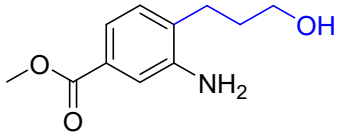
Methoxy 3-amino-4-(4-methoxybenzyl)benzoate (3f):

Following general procedure C, the reaction was run at 0.5 mmol for 21 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a yellow solid (73 mg, 0.268 mmol, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.34 (d, *J* = 1.8 Hz, 1H), 7.14 – 7.04 (m, 3H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.89 – 3.86 (m, 5H), 3.78 (s, 3H), 3.63 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 158.5, 144.9, 130.8, 130.7, 130.4, 129.6, 120.0, 116.8, 114.3, 55.4, 52.1, 37.4.

HRMS: calc'd for $C_{16}H_{17}NO_3$ $(M + H)^+$ 272.12812; Found 272.12813.



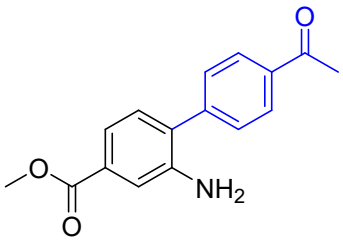
Methyl 3-amino-4-(3-hydroxypropyl)benzoate (3g):

Following general procedure C, the reaction was run at 0.5 mmol for 24 h. The crude mixture was purified using flash column chromatography (12 g column, 5% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a white solid (86 mg, 0.413 mmol, 82% yield).

^{1}H NMR (400 MHz, CD_3OD) δ 7.37 (d, J = 1.8 Hz, 1H), 7.28 (dd, J = 7.9, 1.8 Hz, 1H), 7.05 (d, J = 7.8 Hz, 1H), 4.81 (s, 2H), 3.82 (s, 3H), 3.59 (t, J = 6.3 Hz, 2H), 2.65 – 2.56 (m, 2H), 1.86 – 1.75 (m, 2H).

^{13}C NMR (101 MHz, CD_3OD) δ 169.2, 146.7, 133.1, 130.5, 129.7, 120.2, 117.3, 62.1, 52.3, 32.5, 28.2.

HRMS: calc'd for $C_{11}H_{15}NO_3$ $(M + H)^+$ 210.11247; Found 210.11246.



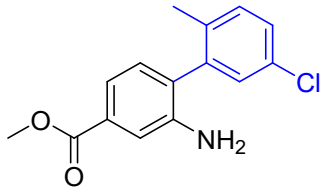
Methyl 4'-acetyl-2-amino-[1,1'-biphenyl]-4-carboxylate (3h):

Following general procedure B, the reaction was run at 0.5 mmol for 23 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a white solid (107 mg, 0.401 mmol, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.02 (m, 2H), 7.60 – 7.55 (m, 2H), 7.50 – 7.43 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 1H), 3.91 (s, 3H), 3.88 (br s, 2H), 2.64 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 167.1, 143.7, 136.5, 130.9, 130.4, 129.2, 129.1, 119.9, 116.8, 52.3, 26.8.

HRMS: calc'd for $C_{16}H_{15}NO_3$ $(M + H)^+$ 270.11247; Found 270.11250.



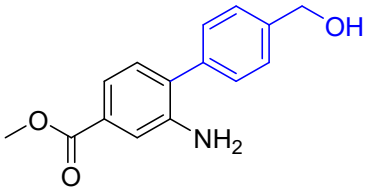
Methyl 2-amino-5'-chloro-2'-methyl-[1,1'-biphenyl]-4-carboxylate (3i)

Following general procedure B, the reaction was run at 0.5 mmol for 23 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a light-yellow viscous oil (74 mg, 0.269 mmol, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.28 – 7.16 (m, 3H), 7.02 (d, *J* = 7.7 Hz, 1H), 3.90 (s, 3H), 3.60 (br s, 2H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 143.8, 139.5, 135.4, 131.9, 130.8, 130.5, 130.1, 129.6, 128.3, 119.5, 116.1, 52.2, 19.1.

HRMS: calc'd for $C_{15}H_{14}ClNO_2$ $(M + H)^+$ 276.07858; Found 276.07857.



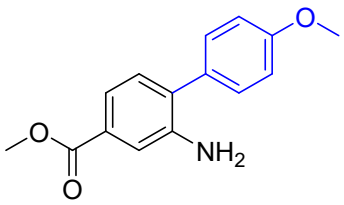
Methyl 2-amino-4'-(hydroxymethyl)-[1,1'-biphenyl]-4-carboxylate (z):

Following general procedure B, the reaction was run at 0.5 mmol for 23 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a white powder (75 mg, 0.292 mmol, 58% yield).

^{1}H NMR (400 MHz, CDCl3) δ 7.53 – 7.40 (m, 6H), 7.17 (d, J = 7.9 Hz, 1H), 4.76 (s, 2H), 3.91 (s, 3H), 3.86 (s, 2H), 1.75 (s, 1H).

^{13}C NMR (101 MHz, DMSO) δ 166.6, 145.4, 141.8, 137.0, 130.4, 130.1, 129.2, 128.2, 127.0, 117.3, 115.7, 62.7, 52.0.

HRMS: calc'd for $C_{15}H_{15}NO_3$ $(M + H)^+$ 258.11247; Found 258.11247.



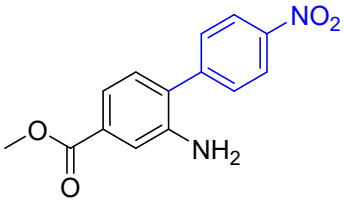
Methyl 2-amino-4'-methoxy-[1,1'-biphenyl]-4-carboxylate (3k):

Following general procedure B, the reaction was run at 0.5 mmol for 23 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a white solid (125 mg, 0.487 mmol, 97% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.37 (m, 4H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.01 – 6.97 (m, 2H), 3.90 (s, 3H), 3.86 (s, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 159.3, 143.9, 131.8, 130.9, 130.6, 130.1, 129.9, 119.8, 116.5, 114.5, 55.5, 52.2.

HRMS: calc'd for $C_{15}H_{15}NO_3$ $(M + H)^+$ 258.11247; Found 258.11249.



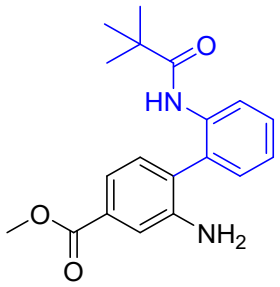
Methyl 2-amino-4'-nitro-[1,1'-biphenyl]-4-carboxylate (3l):

Following general procedure B, the reaction was run at 0.5 mmol for 21 h. The crude mixture was filtered through a fritted plug to collect the solid crashed out during the reaction. The title compound was afforded as an orange powder (107 mg, 0.396 mmol, 79% yield).

^{1}H NMR (400 MHz, DMSO) δ 7.38 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.53 (s, 1H), 6.37 – 6.21 (m, 2H), 4.43 (br s, 2H), 2.92 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 166.4, 146.5, 145.9, 145.8, 130.5, 130.5, 130.0, 127.5, 124.0, 117.2, 116.3, 52.1.

HRMS: calc'd for $C_{14}H_{12}N_2O_4$ $(M + H)^+$ 273.08698; Found 2273.08700.



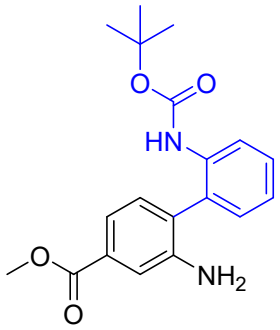
Methyl 2-amino-2'-pivalamido-[1,1'-biphenyl]-4-carboxylate (3m):

Following general procedure B, the reaction was run at 0.5 mmol for 19 h. The crude mixture was purified using flash column chromatography (12 g column, 20% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a hygroscopic yellow viscous oil/solid (146 mg, 0.449 mmol, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.69 (s, 1H), 7.54 – 7.48 (m, 2H), 7.44 – 7.38 (m, 1H), 7.25 – 7.13 (m, 3H), 3.92 (s, 3H), 3.78 (br s, 2H), 1.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 167.1, 143.8, 135.8, 131.3, 131.3, 130.3, 129.3, 128.9, 128.3, 124.9, 122.6, 120.2, 116.3, 52.3, 39.8, 27.4.

HRMS: calc'd for $C_{19}H_{22}N_2O_3$ $(M + H)^+$ 327.17032; Found 327.17033.



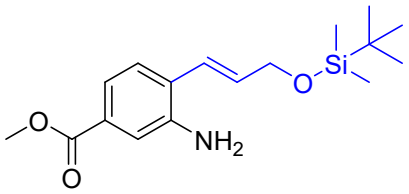
Methyl 2-amino-2'-((*tert*-butoxycarbonyl)amino-[1,1'-biphenyl]-4-carboxylate (3n):

Following general procedure B, the reaction was run at 0.5 mmol for 19 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a light-yellow solid (138 mg, 0.405 mmol, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.42 – 7.35 (m, 1H), 7.20 – 7.10 (m, 3H), 6.49 (s, 1H), 3.93 (s, 3H), 3.73 (br s, 2H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 144.2, 136.2, 131.3, 130.5, 129.3, 128.0, 127.5, 123.7, 120.8, 120.0, 116.6, 80.7, 52.3, 28.4.

HRMS: calc'd for $C_{19}H_{22}N_2O_4$ $(M + H)^+$ 343.16523; Found 343.16524.



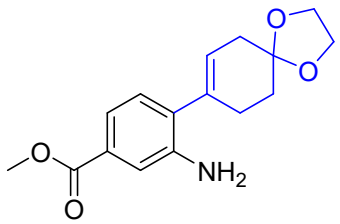
Methyl (*E*)-3-amino-4-(3-((*tert*-butyldimethylsilyl)oxy)prop-1-en-1-yl)benzoate (3o):

Following general procedure C, the reaction was run at 0.5 mmol for 17 h. The crude mixture was purified using column chromatography (12 g column, 10% EtOAc in hexanes with a flow rate of 30 mL/min) to afford the title compound as a yellow solid (140 mg, 0.438 mmol, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.15 (m, 3H), 6.57 (dt, *J* = 15.6, 2.0 Hz, 1H), 6.16 (dt, *J* = 15.6, 4.6 Hz, 1H), 4.28 (dd, *J* = 4.6, 2.0 Hz, 2H), 3.79 (s, 3H), 3.73 (br s, 2H), 0.85 (s, 9H), 0.03 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 143.7, 133.3, 129.8, 128.1, 127.5, 124.0, 120.1, 117.0, 63.9, 52.1, 26.1, 18.6, -5.0.

HRMS: calc'd for $C_{17}H_{27}NO_3Si$ $(M + H)^+$ 322.18330; Found 322.18334.



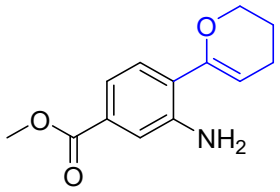
Methyl 3-amino-4-(1,4-dioxaspiro[4.5]dec-7-en-8-yl)benzoate (3p):

Following general procedure B, the reaction was run at 0.5 mmol for 22 h. The crude mixture was purified twice using flash column chromatography. First purification (12 g column, 20% EtOAc in heptanes with a flow rate of 30 mL/min). Second purification (12 g column, 20% EtOAc in heptanes at a flow rate of 30 mL/min) to afford the title compound as a white powder (108 mg, 0.375 mmol, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.05 (d, *J* = 7.8 Hz, 1H), 5.68 (hept, *J* = 1.6 Hz, 1H), 4.02 (s, 4H), 3.87 (s, 5H), 2.49 (ddt, *J* = 6.5, 4.4, 2.0 Hz, 2H), 2.45 – 2.41 (m, 2H), 1.90 (t, *J* = 6.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 143.5, 135.7, 133.7, 129.6, 128.7, 124.7, 119.5, 116.2, 107.7, 64.6, 52.1, 36.0, 31.5, 28.5.

HRMS: calc'd for $C_{16}H_{19}NO_4$ $(M + H)^+$ 290.13868; Found 290.13868.



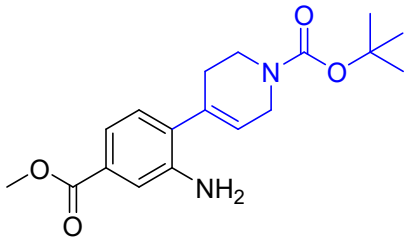
Methyl 3-amino-4-(3,4-dihydro-2*H*-pyran-6-yl)benzoate (3q):

Following general procedure C, the reaction was run at 0.5 mmol for 21 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a yellow solid (52 mg, 0.222 mmol, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 5.10 (t, *J* = 4.0 Hz, 1H), 4.38 (br s, 2H), 4.20 – 4.14 (m, 2H), 3.87 (s, 3H), 2.21 (td, *J* = 6.4, 4.0 Hz, 2H), 1.97 – 1.88 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 152.3, 144.6, 130.5, 129.0, 126.6, 119.1, 117.1, 101.9, 66.5, 52.1, 22.3, 20.8.

HRMS: calc'd for $C_{13}H_{15}NO_3$ $(M + H)^+$ 234.11247; Found 234.11246.



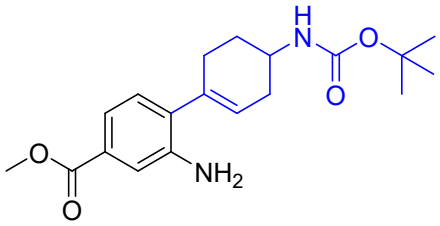
***Tert*-butyl-4-(2-amino-4-(methoxycarbonyl)phenyl)-3,6-dihydropyridine-1(2*H*)-carboxylate (3r):**

Following general procedure B, the reaction was run at 0.5 mmol for 21 h. The crude mixture was purified twice using flash column chromatography. First purification (12 g column, 10% EtOAc in heptanes with a flow rate of 30 mL/min). Second purification (12 g column, 20% EtOAc in heptanes at a flow rate of 30 mL/min) to afford the title compound as a white solid (139 mg, 0.420 mmol, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.02 (d, *J* = 7.8 Hz, 1H), 5.80 (s, 1H), 4.04 (s, 2H), 3.87 (s, 5H), 3.63 (t, *J* = 5.6 Hz, 2H), 2.38 (s, 2H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 155.0, 143.4, 134.7, 132.6, 129.8, 128.6, 124.4, 119.6, 116.5, 79.9, 52.1, 43.5, 29.1, 28.6.

HRMS: calc'd for $C_{18}H_{24}N_2O_4$ $(M + H)^+$ 333.18088; Found 333.18091.



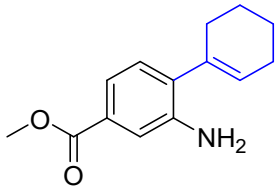
Methyl 2-amino-4'-((*tert*-butoxycarbonyl)amino)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]4-carboxylate (3s)

Following general procedure B, the reaction was run at 0.5 mmol for 20 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a white solid (149 mg, 0.431 mmol, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 2H), 7.01 (d, *J* = 7.8 Hz, 1H), 5.72 (s, 1H), 4.57 (s, 1H), 3.87 (s, 3H), 3.83 (s, 2H), 2.69 – 2.23 (m, 4H), 2.09 – 1.99 (m, 2H), 1.73 – 1.65 (m, 1H), 1.47 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 155.5, 143.3, 135.9, 133.6, 129.5, 128.6, 125.0, 119.5, 116.3, 79.4, 52.0, 45.8, 32.4, 29.2, 28.5, 28.0.

HRMS: calc'd for $C_{19}H_{26}N_2O_4$ $(M + H)^+$ 247.19653; Found 347.19654.



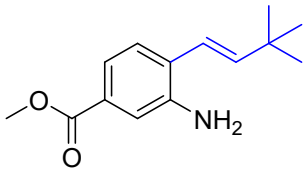
Methyl 2-amino-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carboxylate (3t):

Following general procedure C, the reaction was run at 0.5 mmol for 21 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in hexanes with a flow rate of 30 mL/min) to afford the title compound as a tan solid (72 mg, 0.310 mmol, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.02 (d, *J* = 7.9 Hz, 1H), 5.79 (dq, *J* = 3.8, 1.8 Hz, 1H), 3.87 (s, 5H), 2.26 – 2.20 (m, 2H), 2.20 – 2.15 (m, 2H), 1.81 – 1.74 (m, 2H), 1.73 – 1.66 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 143.4, 136.0, 135.0, 129.3, 128.7, 127.6, 119.6, 116.3, 52.1, 29.1, 25.5, 23.2, 22.2.

HRMS: calc'd for $C_{14}H_{17}NO_2$ $(M + H)^+$ 232.13321; Found 232.13321.



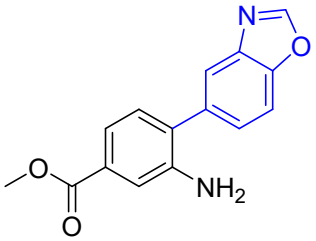
Methyl (*E*)-3-amino-4-(3,3-dimethylbut-1-en-1-yl)benzoate (3u):

Following general procedure C, the reaction was run at 0.5 mmol for 21 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in hexanes with a flow rate of 30 mL/min) to afford the title compound as a tan powder (72 mg, 0.310 mmol, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.38 (m, 2H), 7.27 – 7.24 (m, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.22 (d, *J* = 16.0 Hz, 1H), 3.88 (s, 3H), 3.79 (br s, 2H), 1.14 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 143.4, 132.8, 129.2, 127.3, 120.2, 119.5, 116.9, 116.4, 52.1, 34.0, 29.7.

HRMS: calc'd for $C_{14}H_{19}NO_2$ $(M + H)^+$ 234.14886; Found 234.14886.



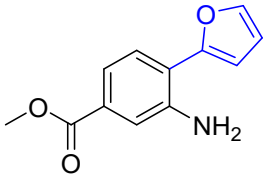
Methyl 3-amino-4-(benzo[*d*]oxazol-5-yl)benzoate (3v):

Following general procedure B, the reaction was run at 0.5 mmol for 22 h. The crude mixture was purified twice using flash column chromatography. First purification (12 g column, 30% EtOAc in heptanes with a flow rate of 30 mL/min). Second purification (12 g column, 20% EtOAc in heptanes at a flow rate of 30 mL/min) to afford the title compound as a white solid (108 mg, 0.403 mmol, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.87 (d, *J* = 1.7 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.51 – 7.45 (m, 3H), 7.19 (d, *J* = 7.8 Hz, 1H), 3.91 (s, 3H), 3.88 (br s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 153.4, 149.6, 143.9, 140.8, 135.5, 131.3, 130.9, 130.5, 126.8, 121.0, 119.8, 116.6, 111.5, 52.2.

HRMS: calc'd for $C_{15}H_{12}N_2O_3$ $(M + H)^+$ 269.09207; Found 269.09208.



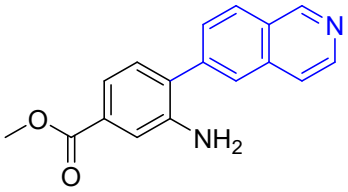
Methyl 3-amino-4-(furan-2-yl)benzoate (3w):

Following general procedure B, the reaction was run at 0.5 mmol for 23 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a beige powder (61 mg, 0.282 mmol, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.45 – 7.41 (m, 2H), 6.70 (dd, *J* = 3.4, 0.7 Hz, 1H), 6.53 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.50 (br s, 2H), 3.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 143.1, 142.1, 130.0, 127.4, 120.0, 119.5, 118.0, 111.8, 108.1, 52.2.

HRMS: calc'd for $C_{12}H_{11}NO_3$ $(M + H)^+$ 218.08117; Found 218.08117.



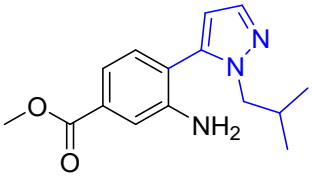
Methyl 3-amino-4-(isoquinolin-6-yl)benzoate (3x):

Following general procedure B, the reaction was run at 0.5 mmol for 21 h. The crude mixture was purified using flash column chromatography (12 g column, 30% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a light pink powder (56 mg, 0.200 mmol, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.57 (d, *J* = 5.9 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.92 (s, 1H), 7.74 – 7.65 (m, 2H), 7.54 – 7.47 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 1H), 3.93 (s, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 152.5, 143.8, 141.0, 136.2, 131.0, 130.7, 128.5, 128.0, 126.5, 120.6, 120.0, 116.9, 52.3.

HRMS: calc'd for $C_{17}H_{14}N_2O_2$ $(M + H)^+$ 279.11280; Found 279.11280.



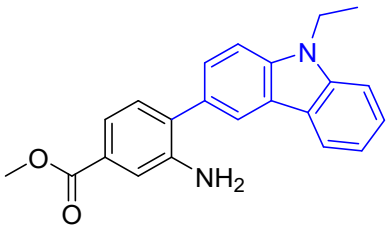
Methyl 3-amino-4-(1-isobutyl-1*H*-pyrazol-5-yl)benzoate (3y):

Following general procedure B, the reaction was run at 0.5 mmol for 21 h. The crude mixture was purified using flash column chromatography (12 g column, 30% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a viscous yellow oil (56 mg, 0.201 mmol, 34% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.8 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.15 – 7.11 (m, 1H), 6.29 (d, *J* = 2.0 Hz, 1H), 3.91 (s, 3H), 3.85 (br s, 2H), 3.79 (d, *J* = 7.4 Hz, 2H), 2.19 – 2.05 (m, 1H), 0.73 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 145.2, 139.2, 131.8, 131.3, 120.3, 119.0, 116.3, 106.4, 57.0, 52.3, 29.7, 19.9.

HRMS: calc'd for $C_{15}H_{19}N_3O_2$ $(M + H)^+$ 274.15550; Found 274.15498.



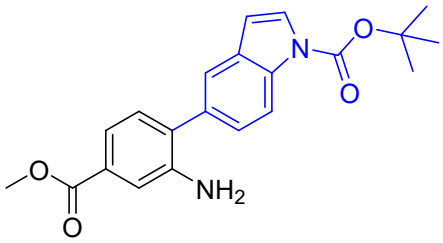
Methyl 3-amino-4-(9-ethyl-9*H*-carbazol-3-yl)benzoate (3z):

Following general procedure B, the reaction was run at 0.5 mmol for 19 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as white crystalline flakes (96 mg, 0.278 mmol, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.4 Hz, 1H), 8.07 (d, *J* = 9.8 Hz, 1H), 7.55 – 7.39 (m, 6H), 7.28 – 7.19 (m, 2H), 4.37 (q, *J* = 7.3 Hz, 2H), 3.91 (d, *J* = 7.1 Hz, 5H), 1.44 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 144.1, 140.4, 139.5, 133.1, 131.0, 129.7, 129.1, 126.5, 126.1, 123.4, 122.8, 120.8, 120.6, 119.8, 119.2, 116.4, 108.9, 108.8, 52.1, 37.7, 13.9.

HRMS: calc'd for $C_{22}H_{20}N_2O_2$ $(M + H)^+$ 245.15975; Found 245.15978.



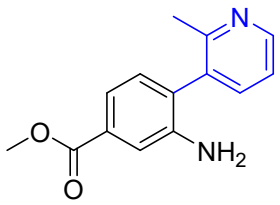
***Tert*-butyl 5-(2-amino-4-(methoxycarbonyl)phenyl)-1*H*-indole-1-carboxylate (3aa):**

Following general procedure B, the reaction was run at 0.5 mmol for 18 h. The crude mixture was purified using flash column chromatography (12 g column, 10% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a hygroscopic yellow solid (161 mg, 0.438 mmol, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.51 – 7.44 (m, 2H), 7.39 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 6.60 (d, *J* = 3.0 Hz, 1H), 3.91 (d, *J* = 6.5 Hz, 5H), 1.69 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 149.8, 144.0, 141.0, 134.7, 133.1, 132.5, 131.2, 130.9, 130.0, 126.8, 125.1, 121.3, 119.8, 116.5, 115.7, 107.4, 84.1, 52.2, 28.3.

HRMS: calc'd for $C_{21}H_{22}N_2O_4$ $(M + H)^+$ 367.16523; Found 367.16525.



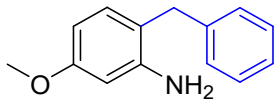
Methyl 3-amino-4-(2-methylpyridin-3-yl)benzoate (3ab):

Following general procedure B, weighed in methyl 3-amino-4-bromobenzoate (69 mg, 0.3 mmol, 1.0 equiv), CataCXium A Pd G3 (21.85 mg, 0.03 mmol, 0.10 equiv), Cs_2CO_3 (195 mg, 0.60 mmol, 2.0 equiv), and 2-methylpyridine-3-boronic acid pinacol ester (131 mg, 0.60 mmol, 2.0 equiv). The solution was stirred at 80 ºC overnight for 16 h. The crude mixture was purified using flash column chromatography (12 g column, 40% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a white solid (71 mg, 0.291 mmol, 97% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.53 – 7.43 (m, 3H), 7.26 – 7.19 (m, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 3.91 (s, 3H), 3.62 (br s, 2H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 157.2, 149.1, 143.9, 137.8, 133.0, 131.0, 130.3, 129.5, 121.5, 119.6, 116.3, 52.3, 22.8.

HRMS: calc'd for $C_{14}H_{14}N_2O_2$ $(M + H)^+$ 243.11280; Found 343.11280.



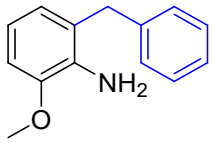
2-benzyl-5-methoxyaniline (3ac):

Following general procedure C, the reaction was run at 0.5 mmol for 16 h. The crude mixture was purified using flash column chromatography (12 g column, 5% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a clear oil (53 mg, 0.248 mmol, 50% yield).

^{1}H NMR (400 MHz, CDCl3) δ 7.31 – 7.21 (m, 2H), 7.21 – 7.11 (m, 3H), 6.94 (d, J = 8.2 Hz, 1H), 6.32 (dd, J = 8.2, 2.5 Hz, 1H), 6.22 (d, J = 2.5 Hz, 1H), 3.82 (s, 2H), 3.72 (s, 3H), 3.47 (s, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 159.6, 145.8, 139.9, 131.7, 128.7, 128.5, 126.4, 117.8, 103.9, 101.8, 55.2, 37.4.

HRMS: calc'd for $C_{14}H_{15}NO$ $(M + H)^+$ 214.12264; Found 214.12262.



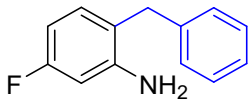
2-benzyl-6-methoxyaniline (3ad):

Following general procedure C, the reaction was run at 0.5 mmol for 43 h. The crude mixture was purified using flash column chromatography (12 g column, 5% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a yellow solid (70 mg, 0.327 mmol, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.23 – 7.16 (m, 3H), 6.77 – 6.70 (m, 3H), 3.92 (s, 2H), 3.83 (s, 3H), 3.69 (br s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 139.5, 134.5, 128.7, 128.6, 126.4, 125.5, 123.1, 117.8, 108.8, 55.7, 38.0.

HRMS: calc'd for $C_{14}H_{15}NO$ $(M + H)^+$ 214.12264; Found 214.12262.



2-benzyl-5-fluoroaniline (3ae):

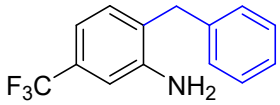
Following general procedure C, the reaction was run at 0.5 mmol for 16 h. The crude mixture was purified using flash column chromatography (12 g column, 5% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a clear oil (66 mg, 0.330 mmol, 66% yield).

^{1}H NMR (400 MHz, CDCL3) δ 7.31 – 7.23 (m, 2H), 7.23 – 7.15 (m, 1H), 7.14 (dd, J = 7.2, 1.7 Hz, 2H), 6.94 (dd, J = 8.3, 6.4 Hz, 1H), 6.42 (td, J = 8.4, 2.6 Hz, 1H), 6.32 (dd, J = 10.5, 2.6 Hz, 1H), 3.80 (s, 2H), 3.53 (s, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 164.0, 161.6, 146.3 (d, J = 10.7 Hz), 139.2, 131.9 (d, J = 9.6 Hz), 128.65 (d, J = 34.3 Hz), 126.6, 120.7 (d, J = 2.7 Hz), 105.0 (d, J = 21.1 Hz), 102.6 (d, J = 24.5 Hz), 37.4.

^{19}F NMR (376 MHz, CDCl3) δ -116.44 – -116.56 (m).

HRMS: calc'd for $C_{13}H_{12}NF$ $(M + H)^+$ 202.10265; Found 202.10265.



2-benzyl-5-(trifluoromethyl)aniline (3af):

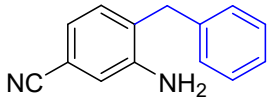
Following general procedure C, the reaction was run at 0.5 mmol for 16 h. The crude mixture was purified using flash column chromatography (12 g column, 5% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a clear oil (97 mg, 0.386 mmol, 77% yield).

^{1}H NMR (400 MHz, CDCl3) δ 7.49 – 7.37 (m, 2H), 7.37 – 7.30 (m, 1H), 7.30 – 7.19 (m, 3H), 7.10 (d, J = 7.8 Hz, 1H), 6.97 (s, 1H), 4.00 (s, 2H), 3.74 (s, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 145.2, 138.4, 131.2, 130.05 (q, J = 32.0 Hz), 129.0, 128.6, 126.84, 124.5 (q, J = 272.2 Hz), 115.2 (q, J = 3.9 Hz), 112.2 (q, J = 3.8 Hz), 37.95.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9.

HRMS: calc'd for $C_{14}H_{12}NF_3$ $(M + H)^+$ 252.09946; Found 252.09945.



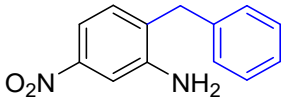
3-amino-4-benzylbenzonitrile (3ag):

Following general procedure C, the reaction was run at 0.5 mmol for 38 h. The crude mixture was purified using flash column chromatography (12 g column, 5% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a white solid (54 mg, 0.258 mmol, 52% yield).

^{1}H NMR (400 MHz, CDCl3) δ 7.42 – 7.31 (m, 2H), 7.31 – 7.24 (m, 1H), 7.23 – 7.16 (m, 2H), 7.13 (d, J = 7.7 Hz, 1H), 7.04 (dd, J = 7.7, 1.5 Hz, 1H), 6.92 (d, J = 1.5 Hz, 1H), 3.94 (s, 2H), 3.78 (s, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 145.5, 137.7, 131.4, 130.2, 129.0, 128.5, 126.9, 122.1, 119.4, 118.3, 111.1, 38.1.

HRMS: calc'd for $C_{13}H_{12}NF$ $(M + H)^+$ 209.10732; Found 209.10733.



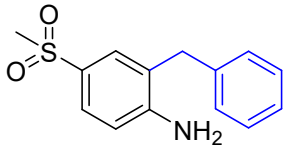
2-benzyl-5-nitroaniline (3ah):

Following general procedure C, the reaction was run at 0.5 mmol for 24 h. The crude mixture was purified using flash column chromatography (12 g column, 5% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a yellow solid (82 mg, 0.361 mmol, 72% yield).

^{1}H NMR (400 MHz, CDCl3) δ 7.55 (dd, J = 8.3, 2.3 Hz, 1H), 7.47 (d, J = 2.3 Hz, 1H), 7.40 – 7.27 (m, 2H), 7.27 – 7.21 (m, 1H), 7.18 – 7.10 (m, 3H), 3.92 (s, 2H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 147.8, 145.7, 137.6, 132.0, 131.2, 129.1, 128.6, 127.1, 113.3, 109.9, 38.0.

HRMS: calc'd for $C_{13}H_{12}N_2O_2$ $(M + H)^+$ 229.09715; Found 229.09716.



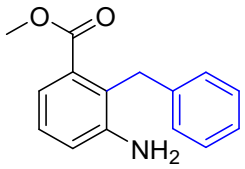
2-benzyl-4-(methylsulfonyl)aniline (3ai):

Following general procedure C, the reaction was run at 0.5 mmol for 38 h. The crude mixture was purified using flash column chromatography (12 g column, 5% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a white solid (74 mg, 0.282 mmol, 56% yield).

^{1}H NMR (400 MHz, CDCl3) δ 7.65 – 7.52 (m, 2H), 7.33 – 7.25 (m, 2H), 7.26 – 7.18 (m, 1H), 7.18 – 7.11 (m, 2H), 6.73 – 6.66 (m, 1H), 4.17 (s, 2H), 3.89 (s, 2H), 2.98 (s, 3H).

^{13}C NMR i(101 MHz, CDCl3) δ 150.1, 137.7, 130.2, 128.9, 128.5, 128.4, 127.7, 126.9, 124.3, 115.0, 45.0, 37.9.

HRMS: calc'd for $C_{14}H_{15}NO_2S$ $(M + H)^+$ 262.08963; Found 2622.08964.



methyl 3-amino-2-benzylbenzoate (3aj):

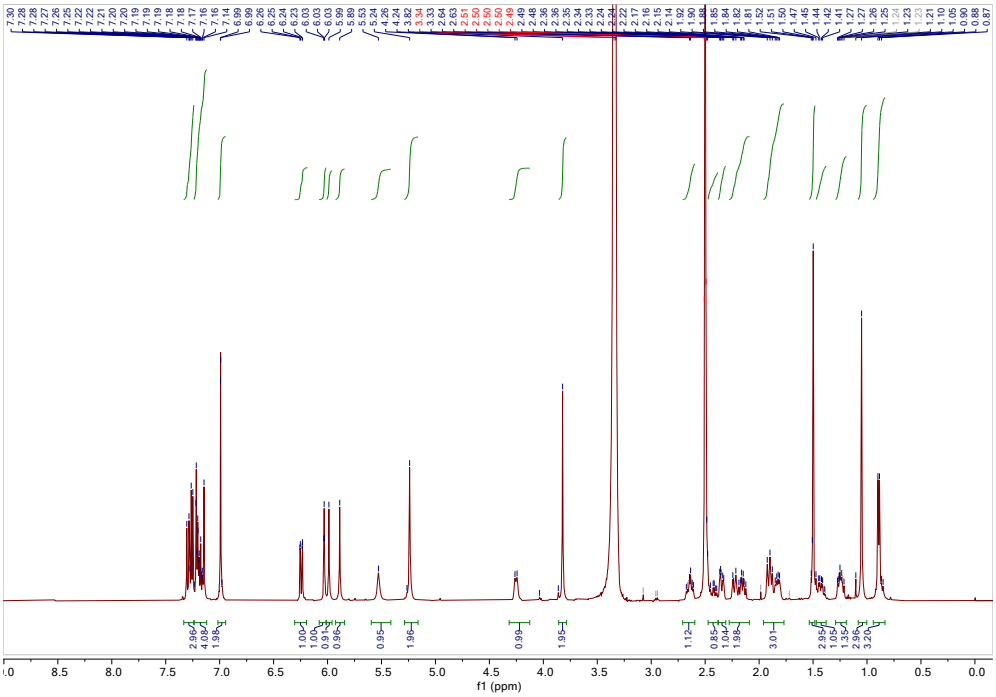
Following general procedure C, the reaction was run at 0.5 mmol for 24 h. The crude mixture was purified using flash column chromatography (12 g column, 5% EtOAc in heptanes with a flow rate of 30 mL/min) to afford the title compound as a clear oil (49 mg, 0.203 mmol, 40% yield).

^{1}H NMR (400 MHz, CDCl3) δ 7.33 – 7.20 (m, 3H), 7.20 – 7.04 (m, 4H), 6.77 (dd, J = 7.9, 1.3 Hz, 1H), 4.24 (s, 2H), 3.80 (s, 3H), 3.43 (s, 2H).

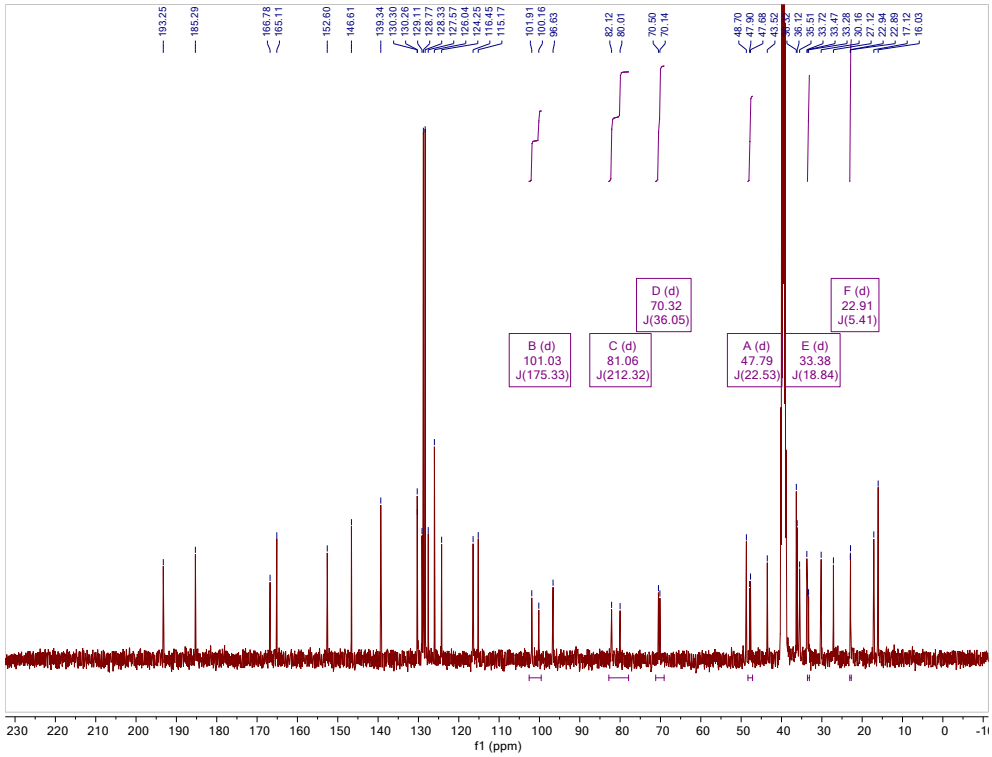
^{13}C NMR (101 MHz, CDCl3) δ 169.1, 146.2, 139.3, 132.4, 128.7, 128.2, 127.2, 126.3, 125.1, 120.5, 119.4, 52.1, 34.1.

HRMS: calc'd for $C_{15}H_{15}NO_2$ $(M + H)^+$ 242.11756; Found 242.11756.

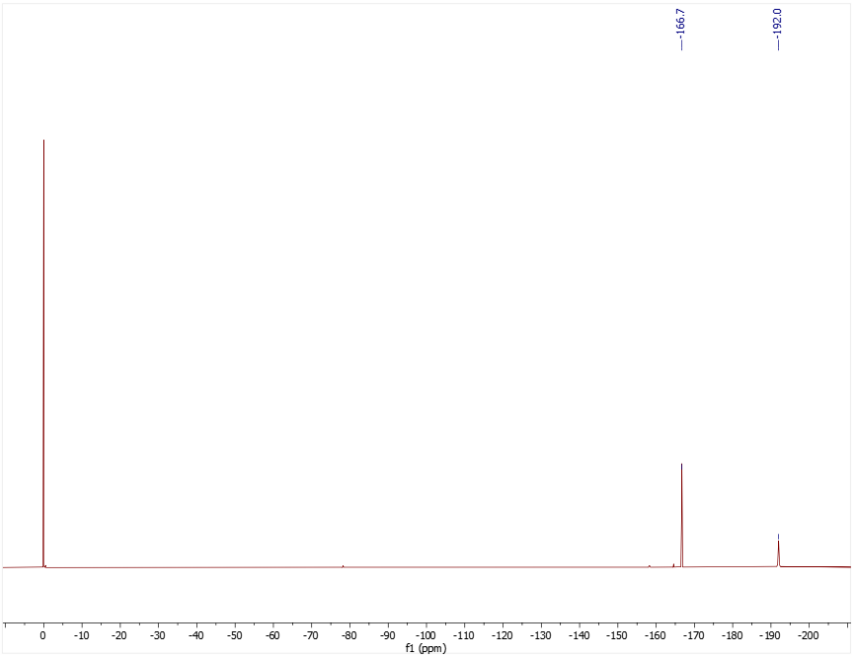
(8*S*,9*R*,10*S*,11*S*,13*S*,14*S*,16*R*,17*R*)-9-fluoro-17-(((fluoromethyl)thio)carbonyl)-11-hydroxy-10,13,16-trimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3*H*-cyclopenta[*a*]phenanthren-17-yl 3-amino-4-benzylbenzoate (3a): ^{1}H NMR, DMSO-d_6, 400 MHz



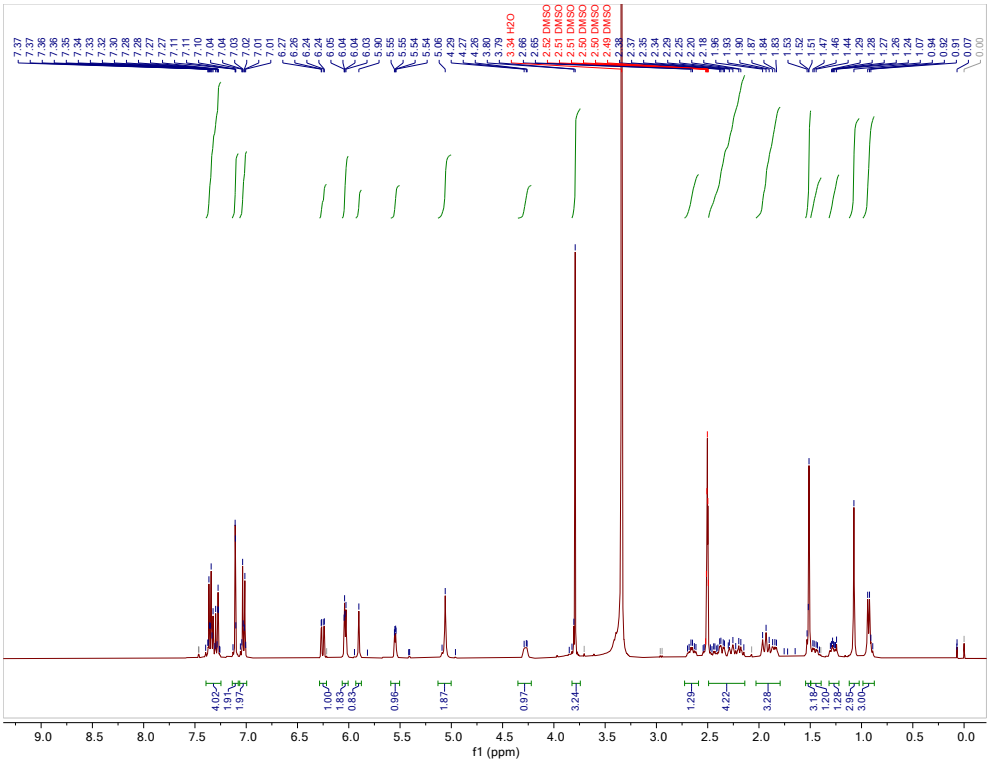
(8*S*,9*R*,10*S*,11*S*,13*S*,14*S*,16*R*,17*R*)-9-fluoro-17-(((fluoromethyl)thio)carbonyl)-11-hydroxy-10,13,16-trimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3*H*-cyclopenta[*a*]phenanthren-17-yl 3-amino-4-benzylbenzoate (3a): ^{13}C NMR, DMSO-d_6, 101 MHz



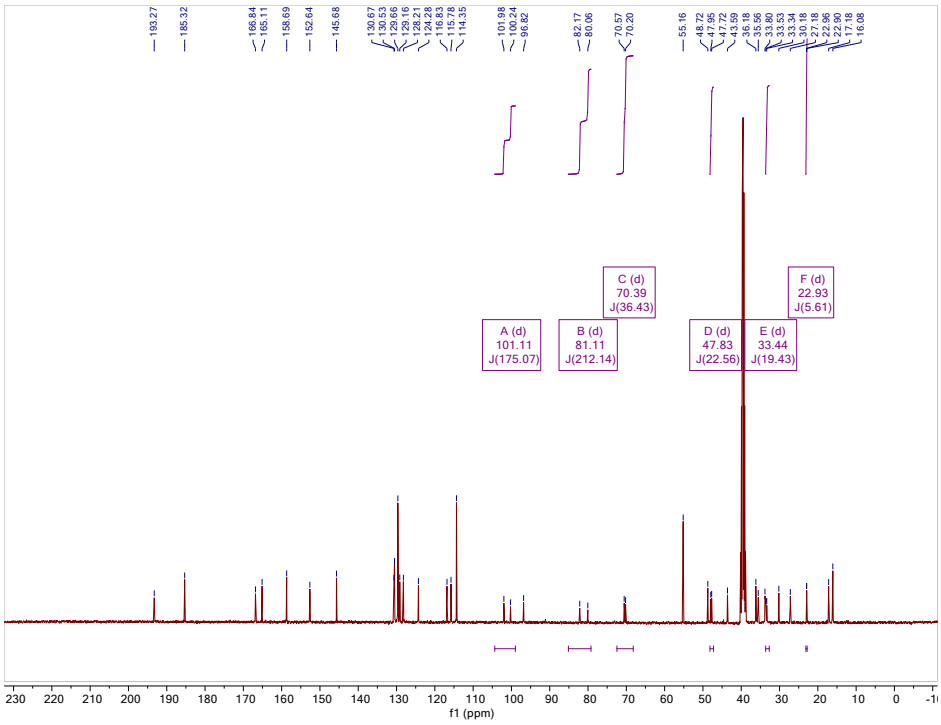
(8*S*,9*R*,10*S*,11*S*,13*S*,14*S*,16*R*,17*R*)-9-fluoro-17-(((fluoromethyl)thio)carbonyl)-11-hydroxy-10,13,16-trimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3*H*-cyclopenta[*a*]phenanthren-17-yl 3-amino-4-benzylbenzoate (3a): ^{19}F NMR, $CDCl_3$, 565 MHz



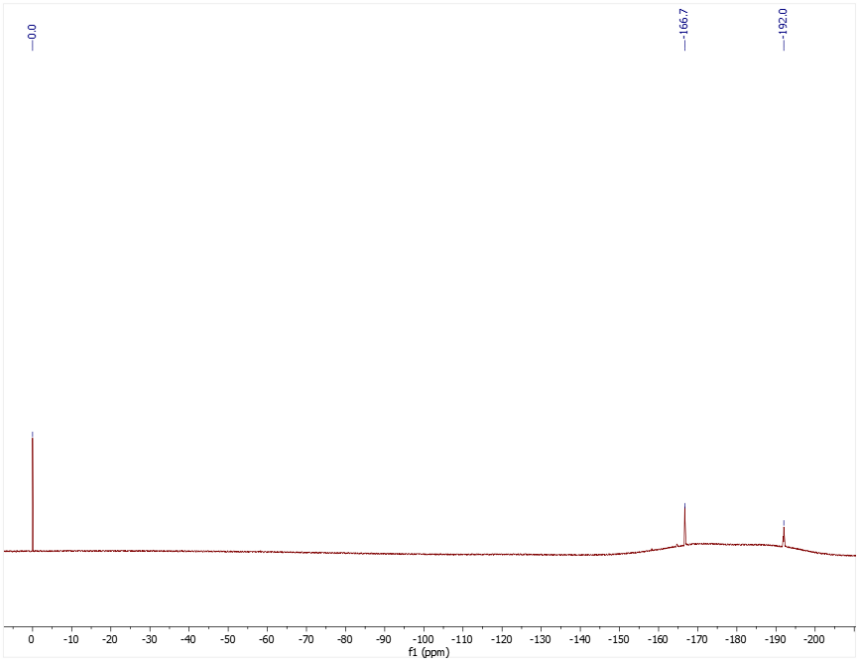
(8*S*,9*R*,10*S*,11*S*,13*S*,14*S*,16*R*,17*R*)-9-fluoro-17-(((fluoromethyl)thio)carbonyl)-11-hydroxy-10,13,16-trimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3*H*-cyclopenta[*a*]phenanthren-17-yl 2-amino-4'-methoxy-[1,1'-biphenyl]-4-carboxylate (3b): ^{1}H NMR, DMSO-d_6, 400 MHz



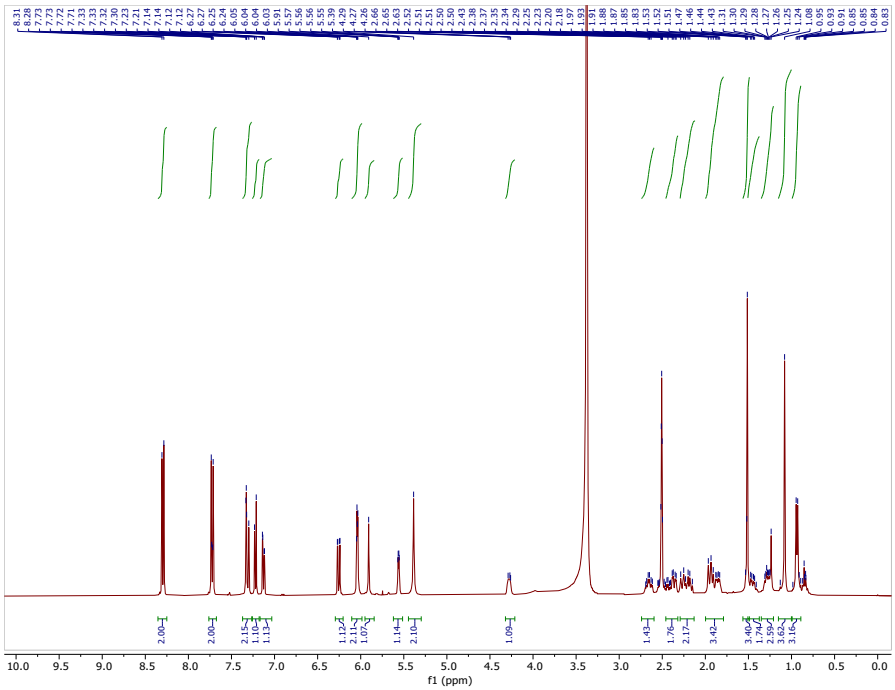
(8*S*,9*R*,10*S*,11*S*,13*S*,14*S*,16*R*,17*R*)-9-fluoro-17-(((fluoromethyl)thio)carbonyl)-11-hydroxy-10,13,16-trimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3*H*-cyclopenta[*a*]phenanthren-17-yl 2-amino-4'-methoxy-[1,1'-biphenyl]-4-carboxylate (3b): ^{13}C NMR, DMSO-d_6, 101 MHz



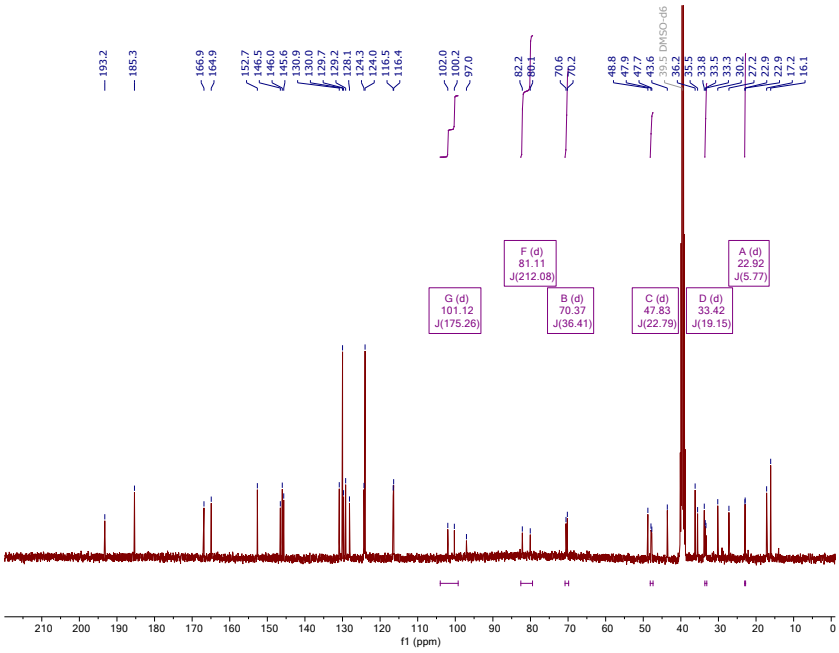
(8*S*,9*R*,10*S*,11*S*,13*S*,14*S*,16*R*,17*R*)-9-fluoro-17-(((fluoromethyl)thio)carbonyl)-11-hydroxy-10,13,16-trimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3*H*-cyclopenta[*a*]phenanthren-17-yl 2-amino-4'-methoxy-[1,1'-biphenyl]-4-carboxylate (3b): ^{19}F NMR, $CDCl_3$, 565 MHz



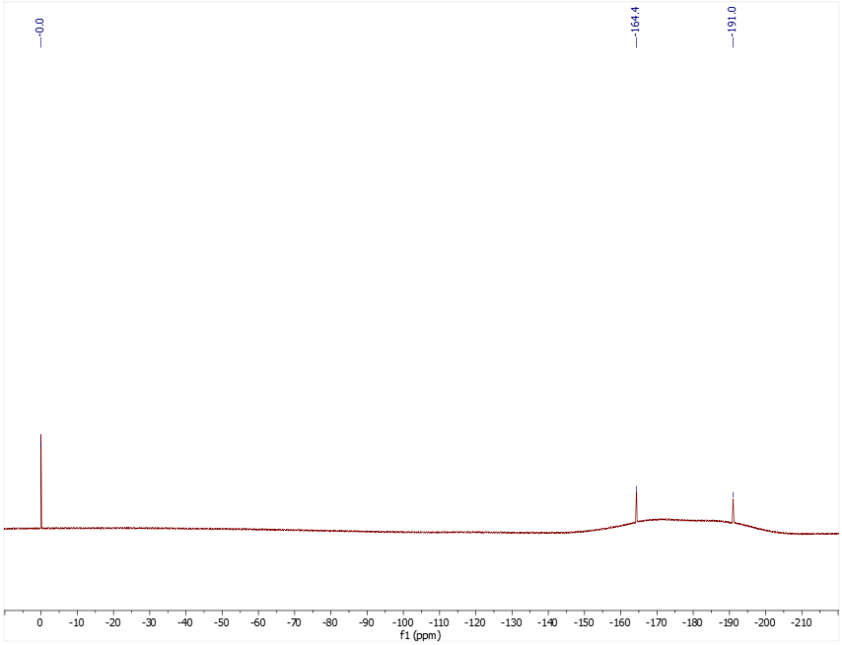
(8*S*,9*R*,10*S*,11*S*,13*S*,14*S*,16*R*,17*R*)-9-fluoro-17-(((fluoromethyl)thio)carbonyl)-11-hydroxy-10,13,16-trimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3*H*-cyclopenta[*a*]phenanthren-17-yl 2-amino-4'-nitro-[1,1'-biphenyl]-4-carboxylate (3c): ^{1}H NMR, DMSO-d_6, 400 MHz



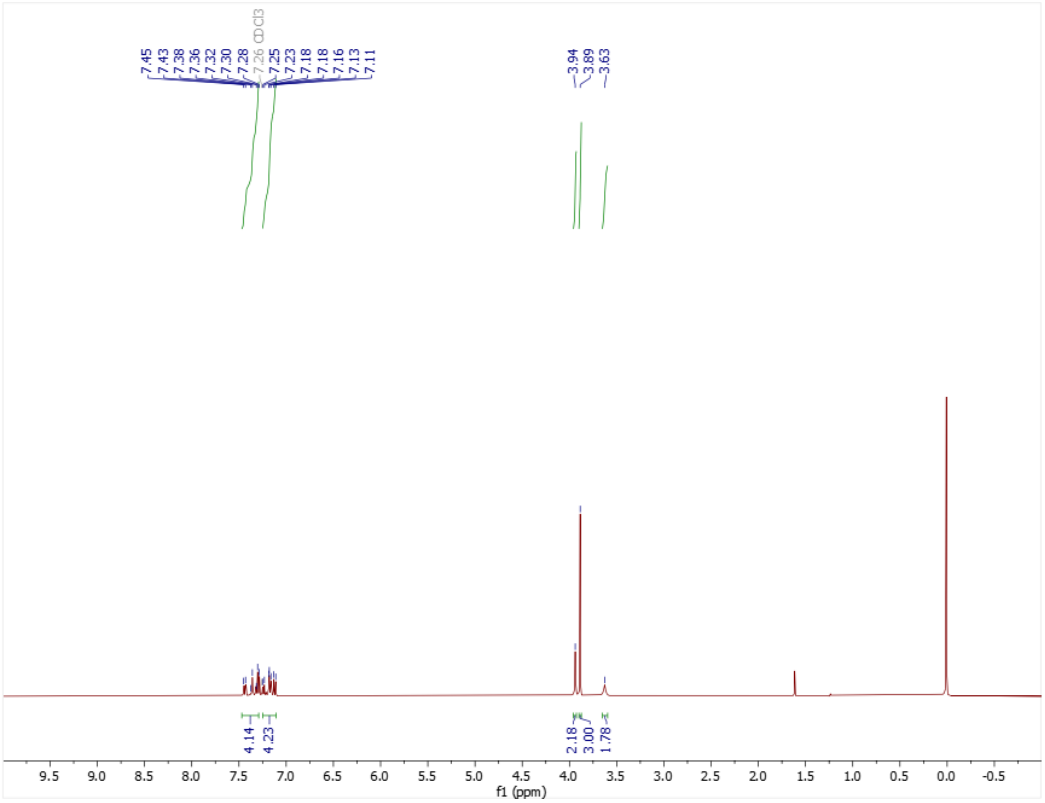
(8*S*,9*R*,10*S*,11*S*,13*S*,14*S*,16*R*,17*R*)-9-fluoro-17-(((fluoromethyl)thio)carbonyl)-11-hydroxy-10,13,16-trimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3*H*-cyclopenta[*a*]phenanthren-17-yl 2-amino-4'-nitro-[1,1'-biphenyl]-4-carboxylate (3c): ^{13}C NMR, DMSO-d_6, 101 MHz



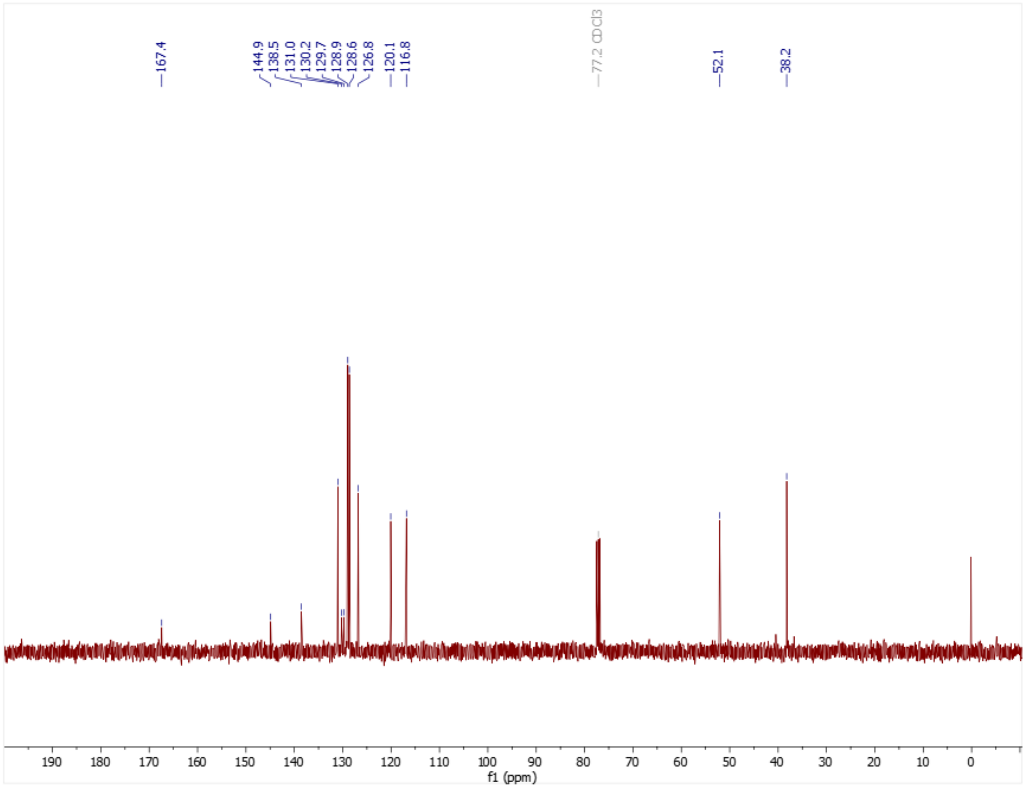
(8*S*,9*R*,10*S*,11*S*,13*S*,14*S*,16*R*,17*R*)-9-fluoro-17-(((fluoromethyl)thio)carbonyl)-11-hydroxy-10,13,16-trimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3*H*-cyclopenta[*a*]phenanthren-17-yl 2-amino-4'-nitro-[1,1'-biphenyl]-4-carboxylate (3c): ^{19}F NMR, DMSO-d_6, 565 MHz



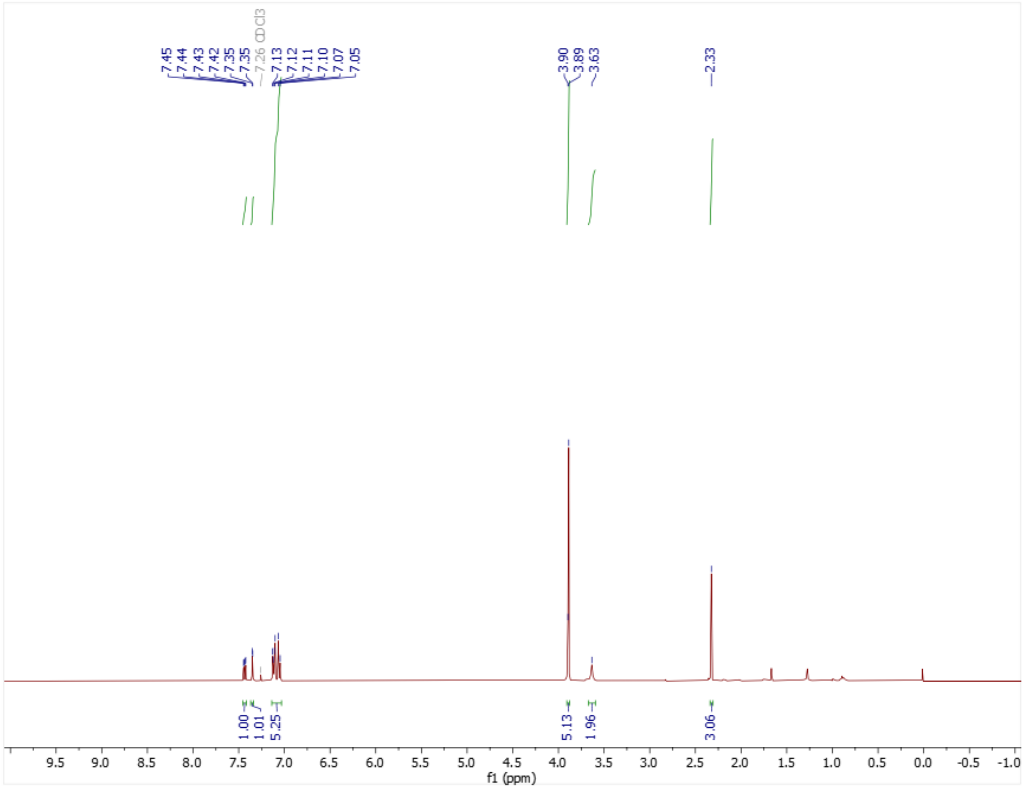
Methyl 3-amino-4-benzylbenzoate (3d): ^{1}H NMR, $CDCl_3$, 400 MHz



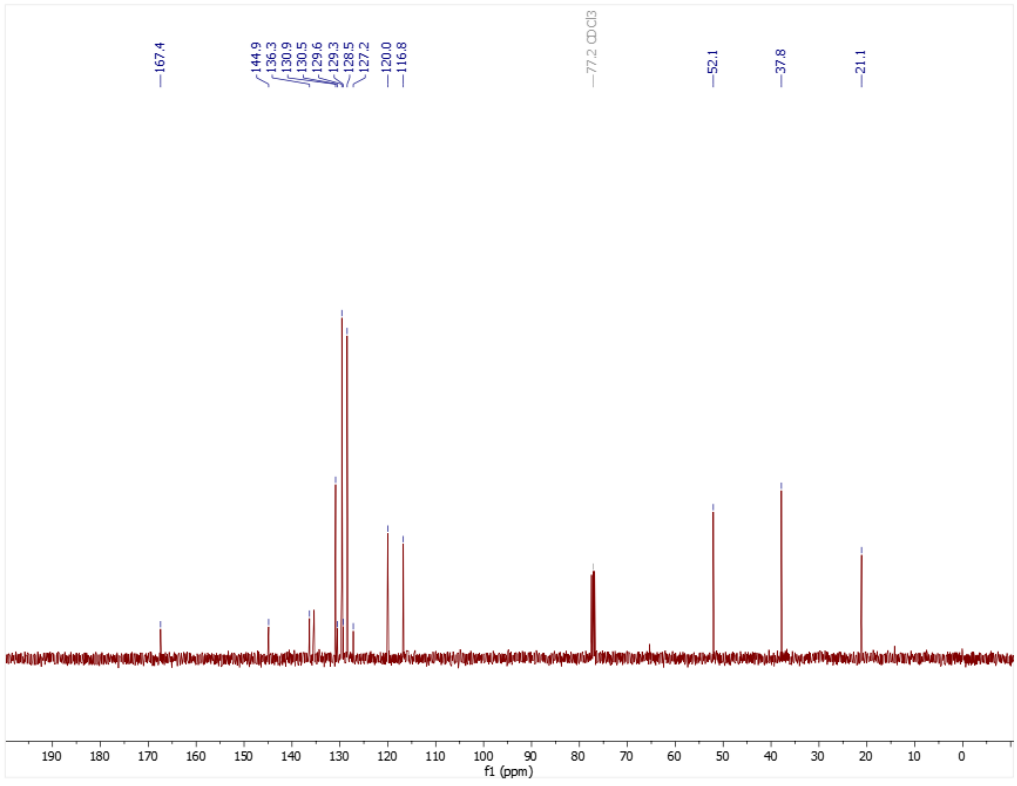
Methyl 3-amino-4-benzylbenzoate (3d): ^{13}C NMR, $CDCl_3$, 101 MHz



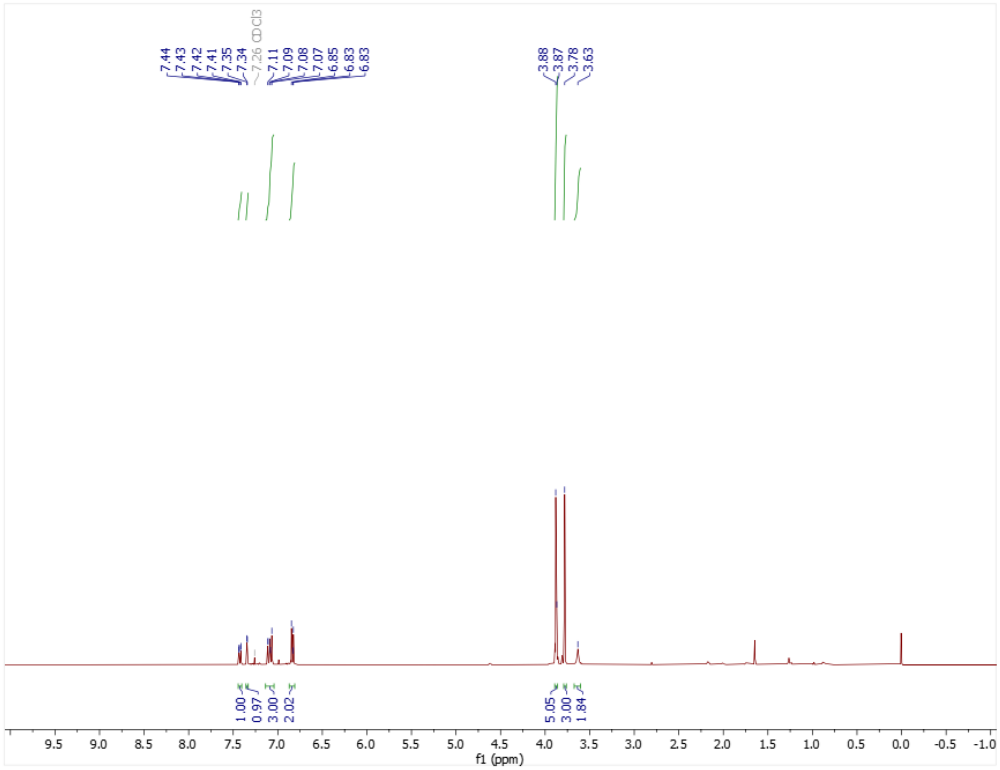
Methyl 3-amino-4-(4-methylbenzyl)benzoate (3e): ^{1}H NMR, $CDCl_3$, 400 MHz



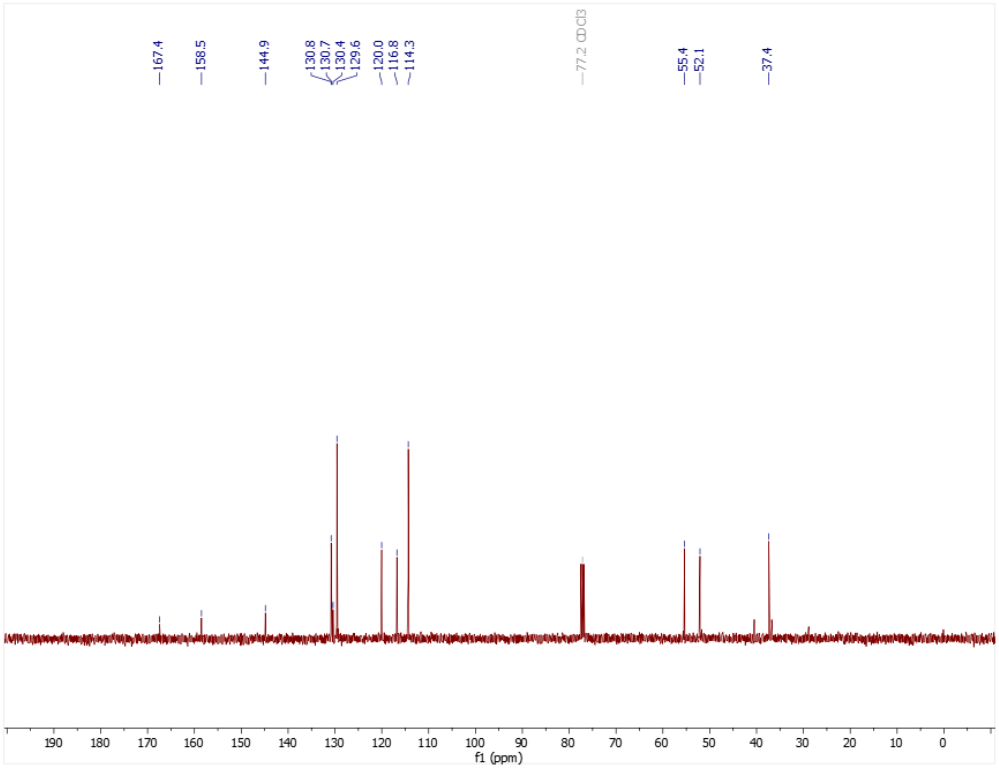
Methyl 3-amino-4-(4-methylbenzyl)benzoate (3e): ^{13}C NMR, $CDCl_3$, 101 MHz



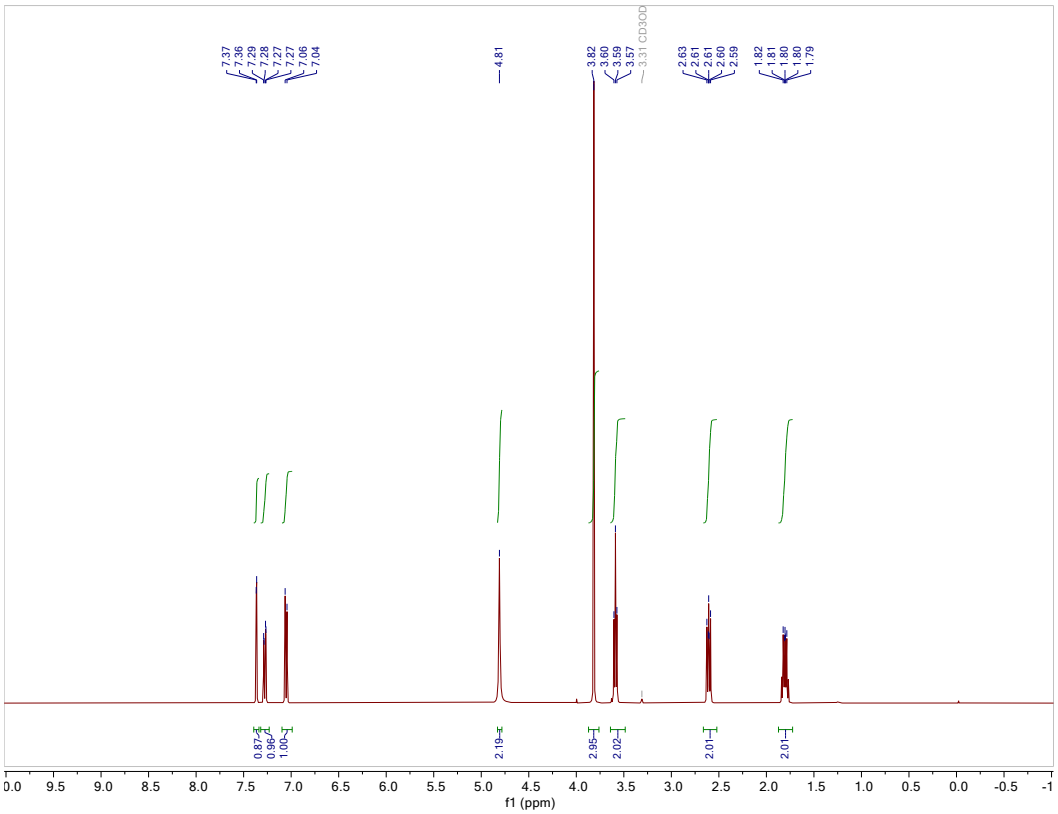
Methoxy 3-amino-4-(4-methoxybenzyl)benzoate (3f): ^{1}H NMR, $CDCl_3$, 400 MHz



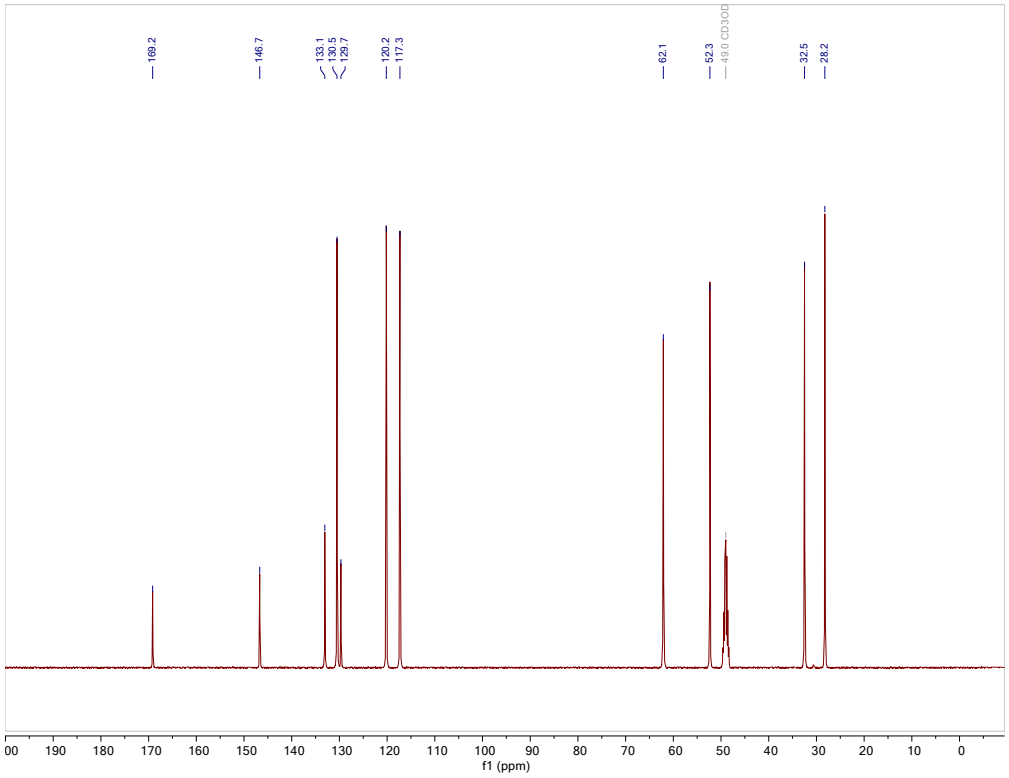
Methoxy 3-amino-4-(4-methoxybenzyl)benzoate (3f): ^{13}C NMR, $CDCl_3$, 101 MHz



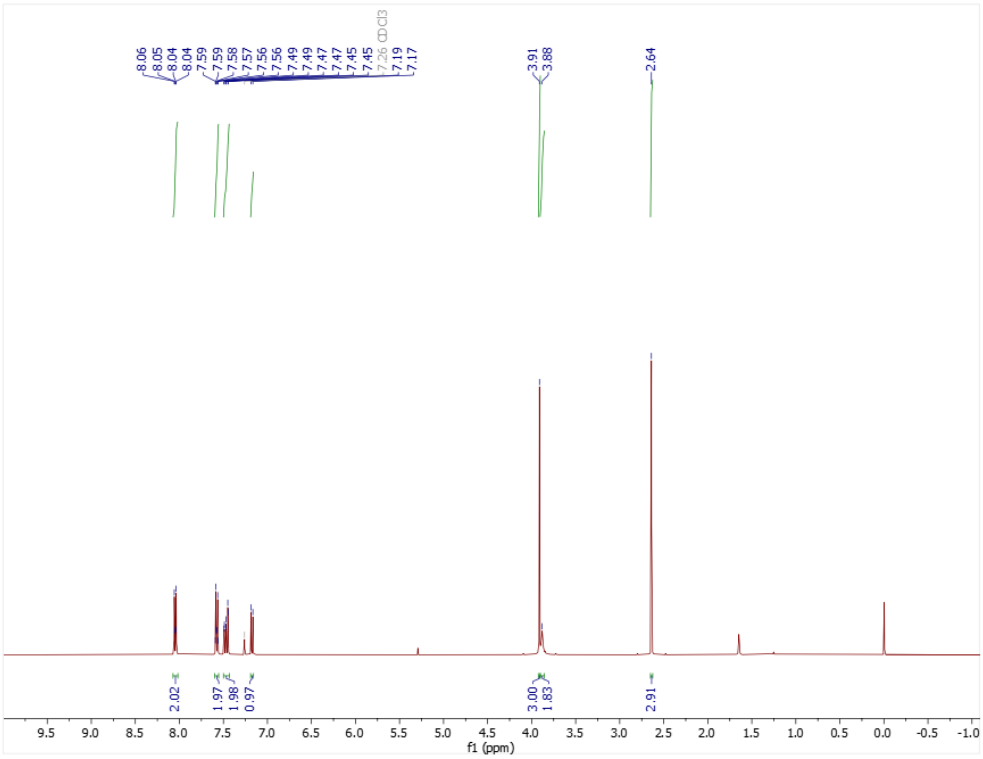
Methyl 3-amino-4-(3-hydroxypropyl)benzoate (3g): ^{1}H NMR, CD_3OD, 400 MHz



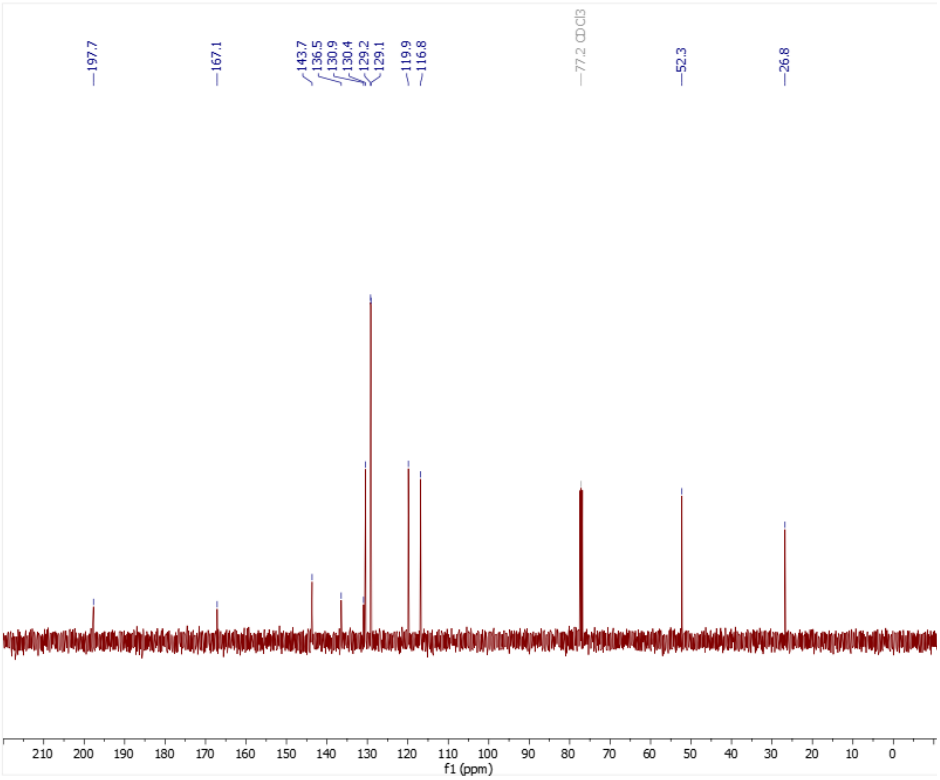
Methyl 3-amino-4-(3-hydroxypropyl)benzoate (3g): ^{13}C NMR, CD_3OD, 400 MHz



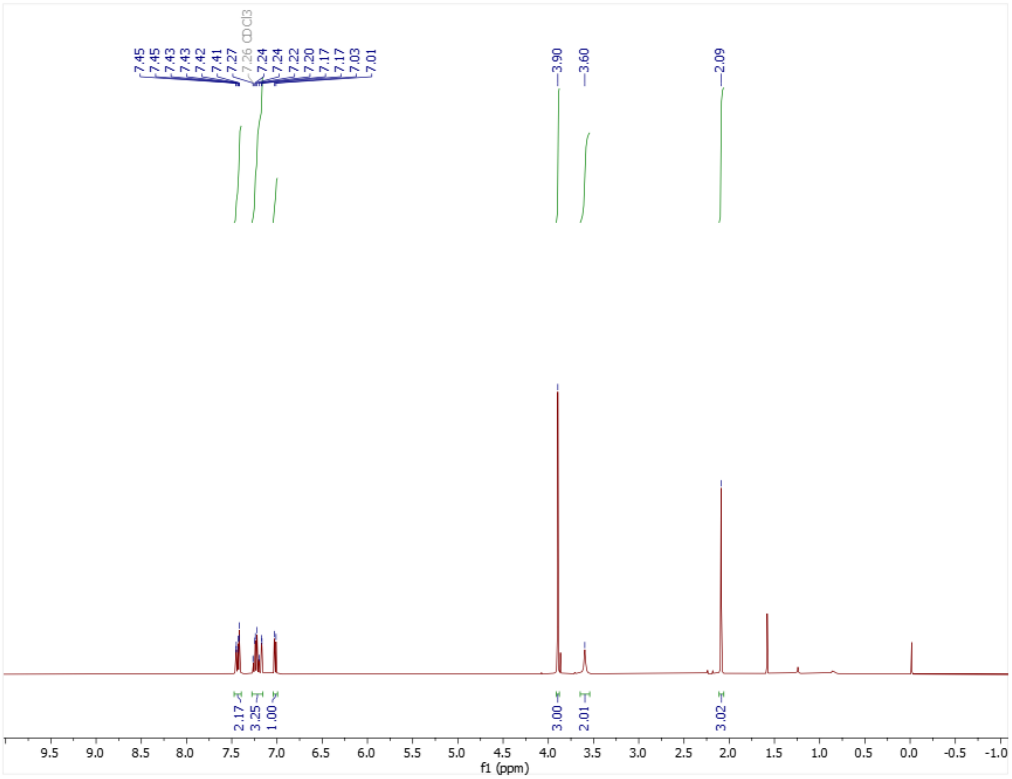
Methyl 4'-acetyl-2-amino-[1,1'-biphenyl]-4-carboxylate (3h): ^{1}H NMR, $CDCl_3$, 400 MHz



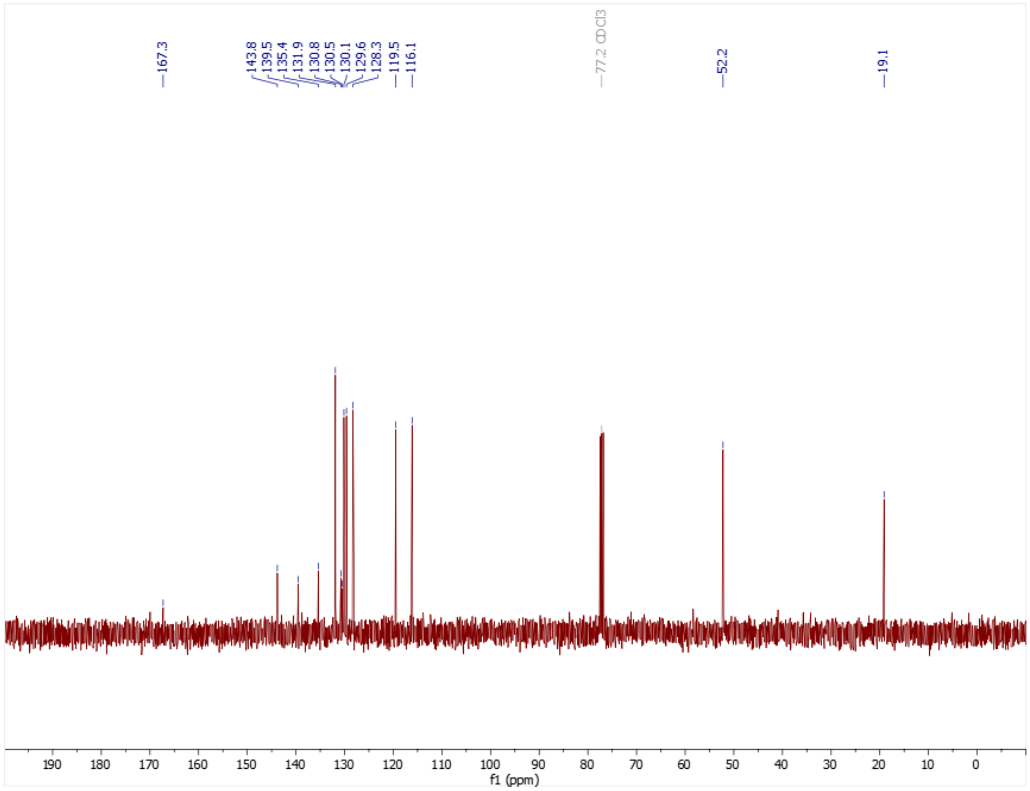
Methyl 4'-acetyl-2-amino-[1,1'-biphenyl]-4-carboxylate (3h): ^{13}C NMR, $CDCl_3$, 101 MHz



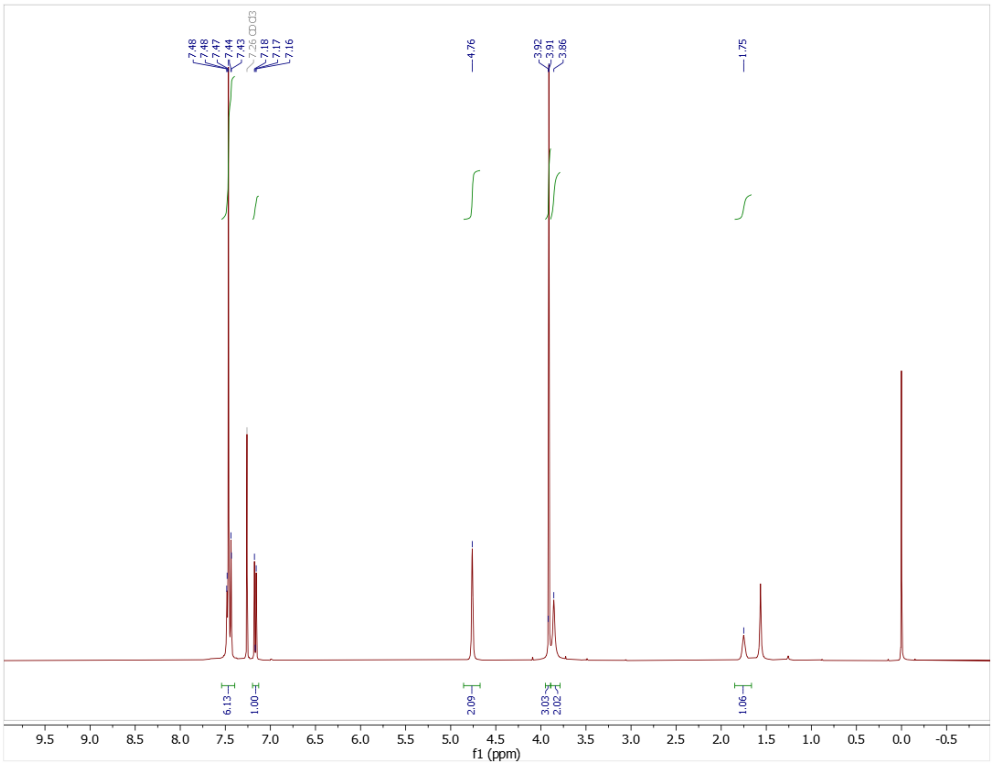
Methyl 2-amino-5'-chloro-2'-methyl-[1,1'-biphenyl]-4-carboxylate (3i): ^{1}H NMR, $CDCl_3$, 400 MHz



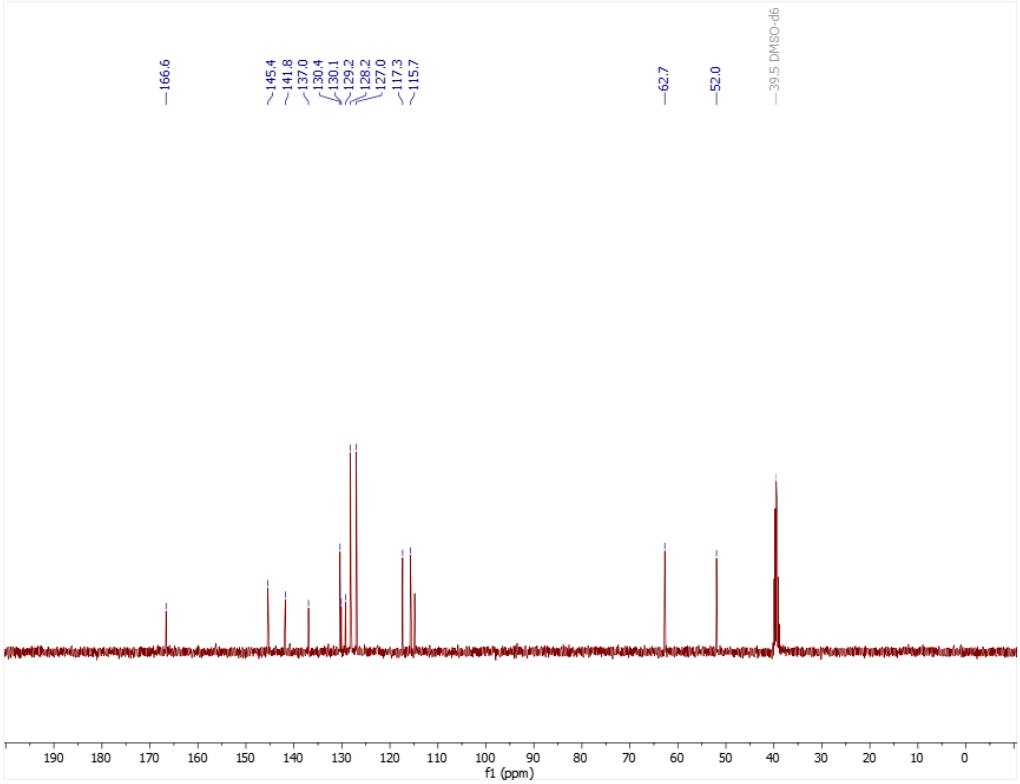
Methyl 2-amino-5'-chloro-2'-methyl-[1,1'-biphenyl]-4-carboxylate (3i): ^{13}C NMR, $CDCl_3$, 101 MHz



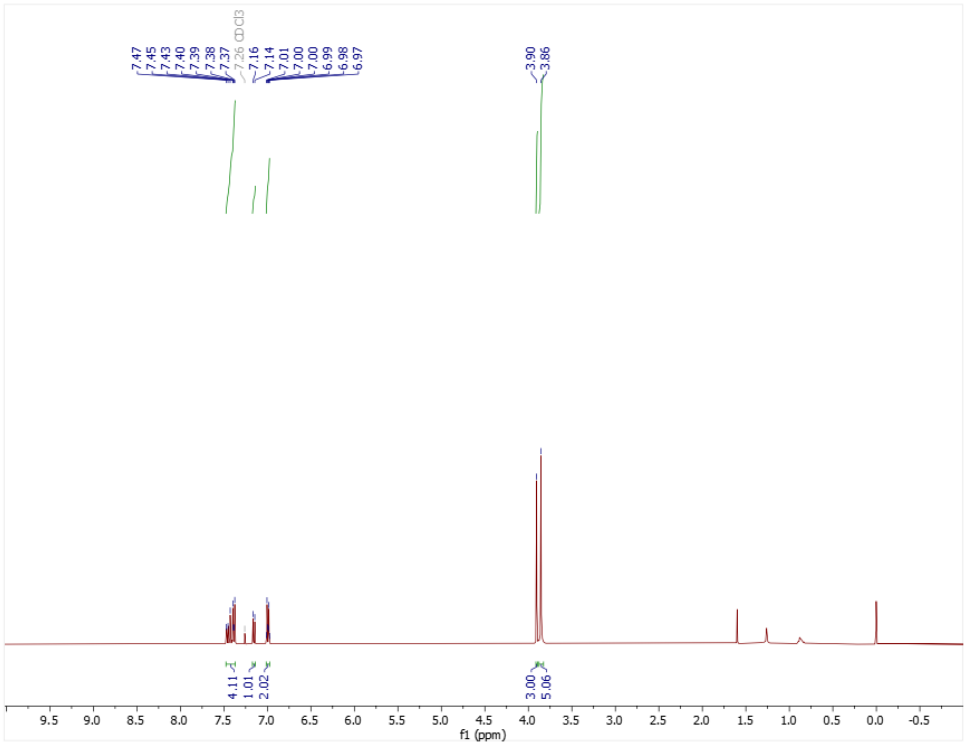
Methyl 2-amino-4'-(hydroxymethyl)-[1,1'-biphenyl]-4-carboxylate (3j): ^{1}H NMR, $CDCl_3$, 400 MHz



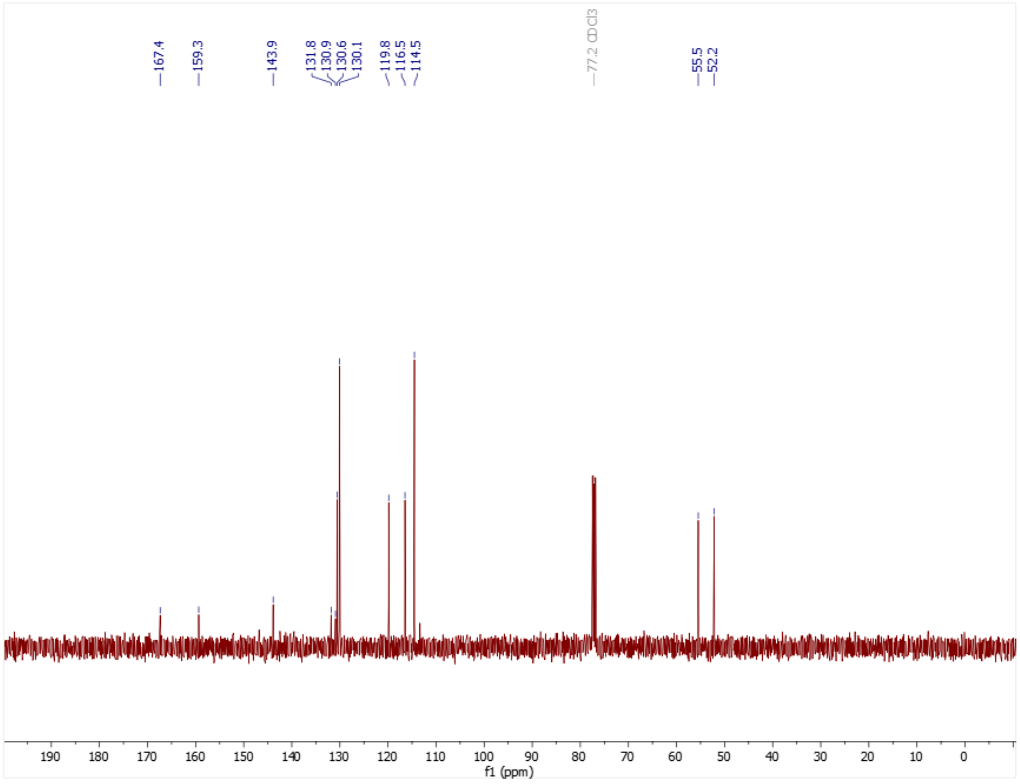
Methyl 2-amino-4'-(hydroxymethyl)-[1,1'-biphenyl]-4-carboxylate (3j): ^{13}C NMR, DMSO-d_6, 101 MHz



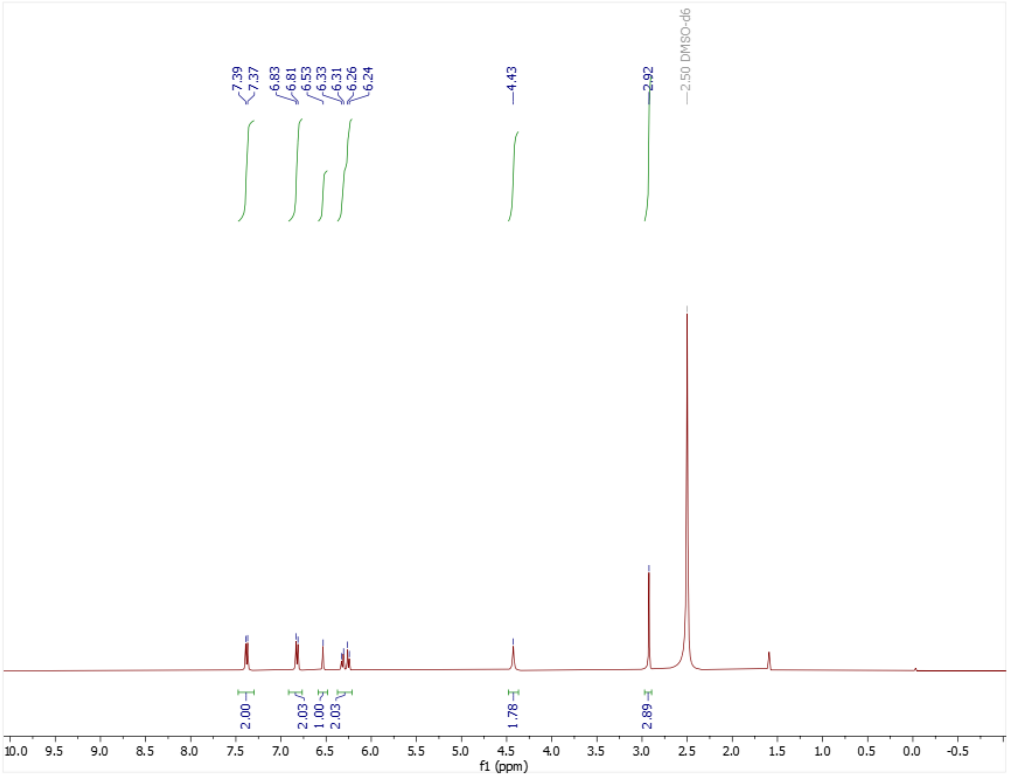
Methyl 2-amino-4'-methoxy-[1,1'-biphenyl]-4-carboxylate (3k): ^{1}H NMR, $CDCl_3$, 400 MHz



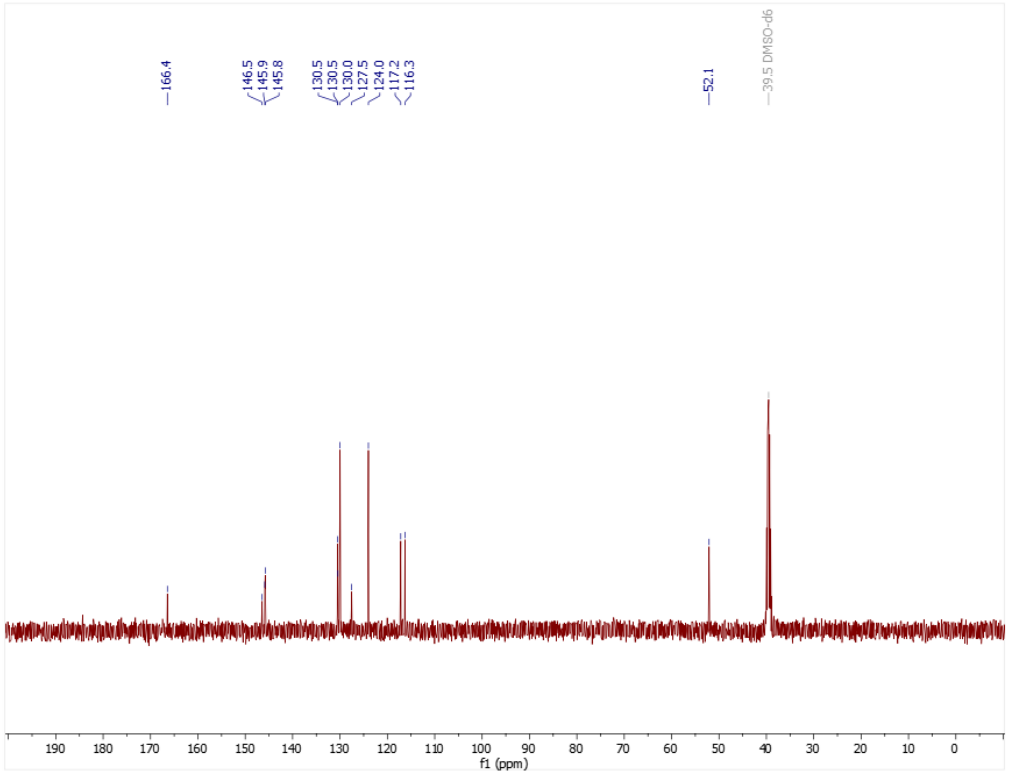
Methyl 2-amino-4'-methoxy-[1,1'-biphenyl]-4-carboxylate (3k): ^{13}C NMR, $CDCl_3$, 101 MHz



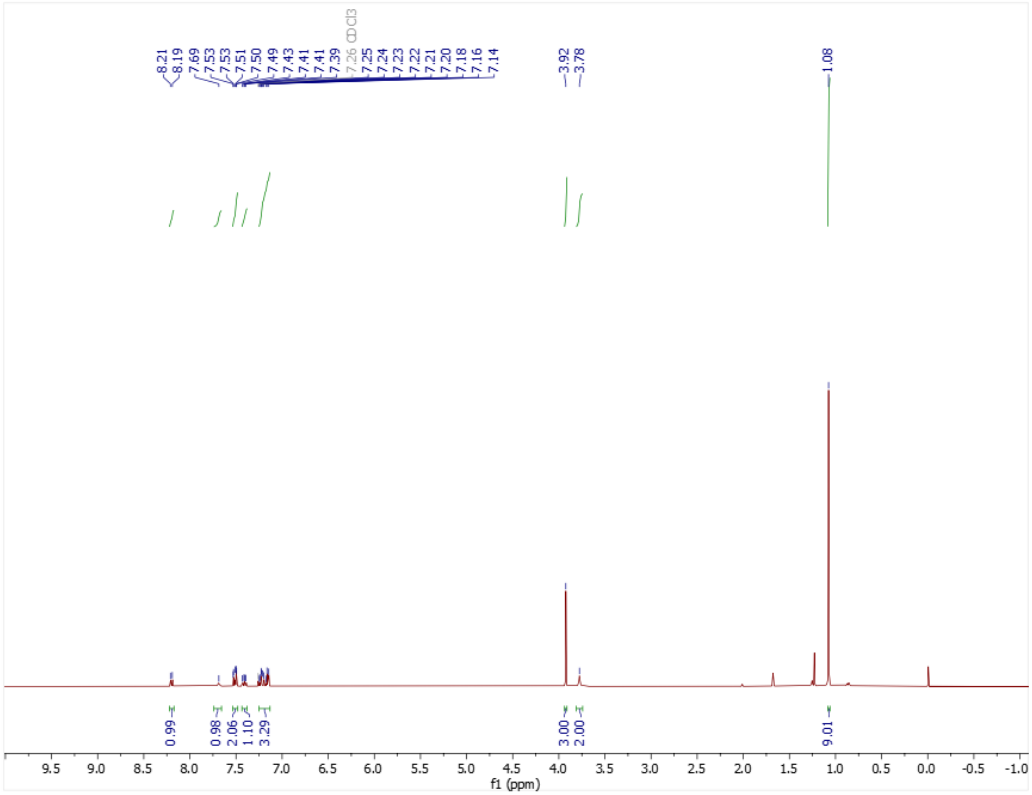
Methyl 2-amino-4'-nitro-[1,1'-biphenyl]-4-carboxylate (3l): ^{1}H NMR, DMSO-d_6, 400 MHz



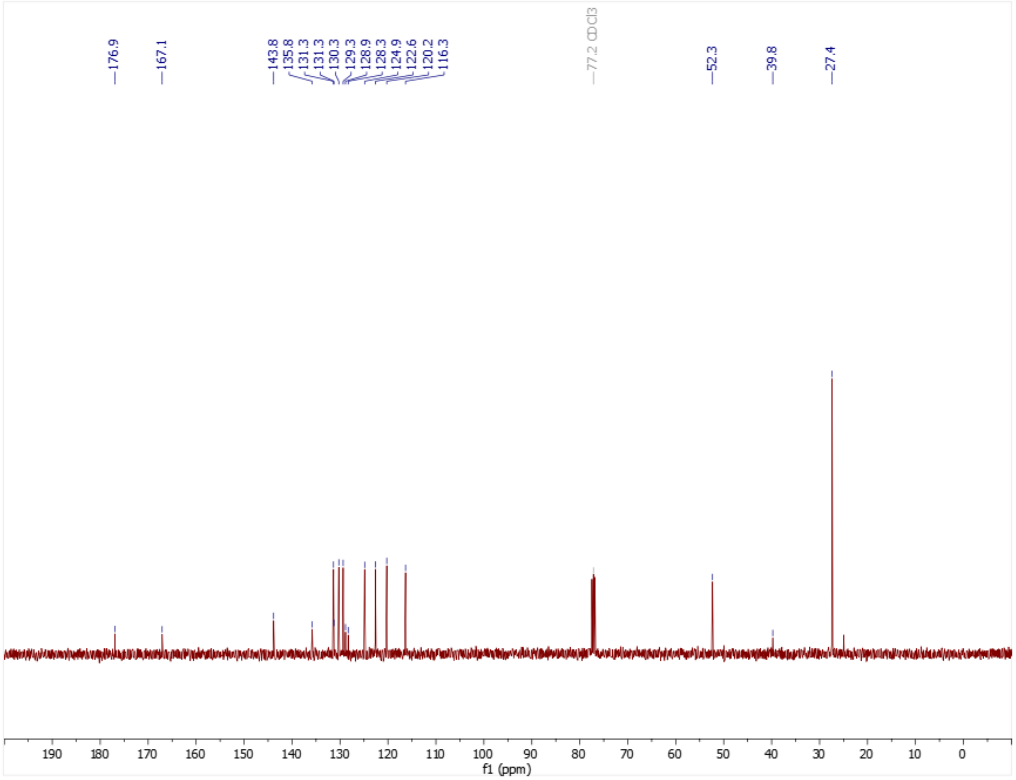
Methyl 2-amino-4'-nitro-[1,1'-biphenyl]-4-carboxylate (3l): ^{13}C NMR, DMSO-d_6, 101 MHz



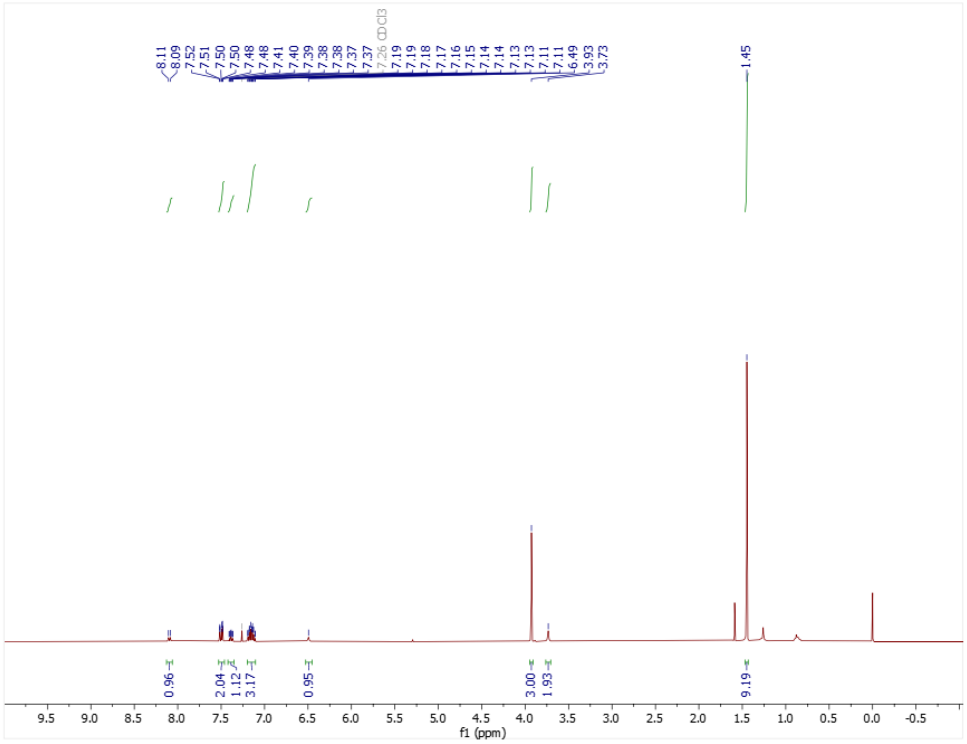
Methyl 2-amino-2'-pivalamido-[1,1'-biphenyl]-4-carboxylate (3m): ^{1}H NMR, $CDCl_3$, 400 MHz



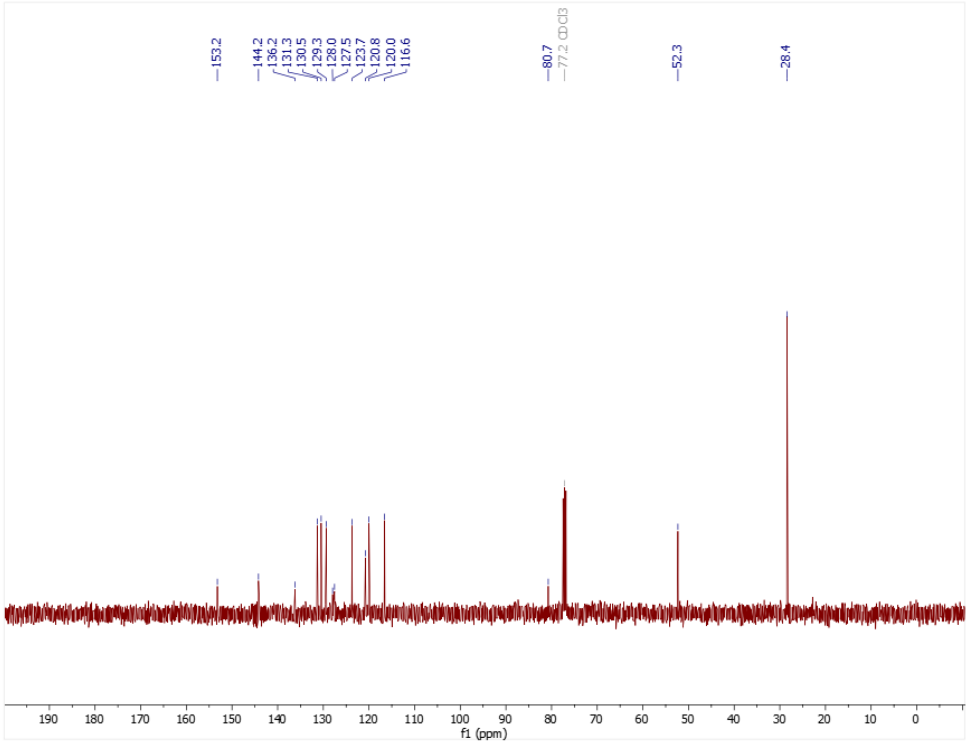
Methyl 2-amino-2'-pivalamido-[1,1'-biphenyl]-4-carboxylate (3m): ^{13}C NMR, $CDCl_3$, 101 MHz



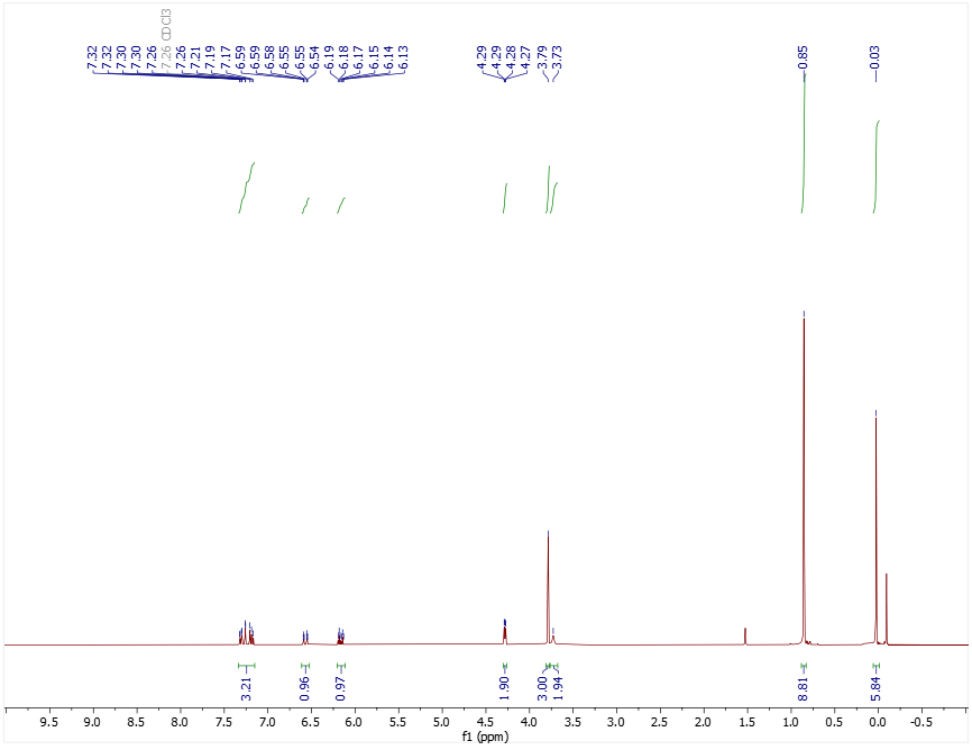
Methyl 2-amino-2'-((*tert*-butoxycarbonyl)amino-[1,1'-biphenyl]-4-carboxylate (3n): ^{1}H NMR, $CDCl_3$, 400 MHz



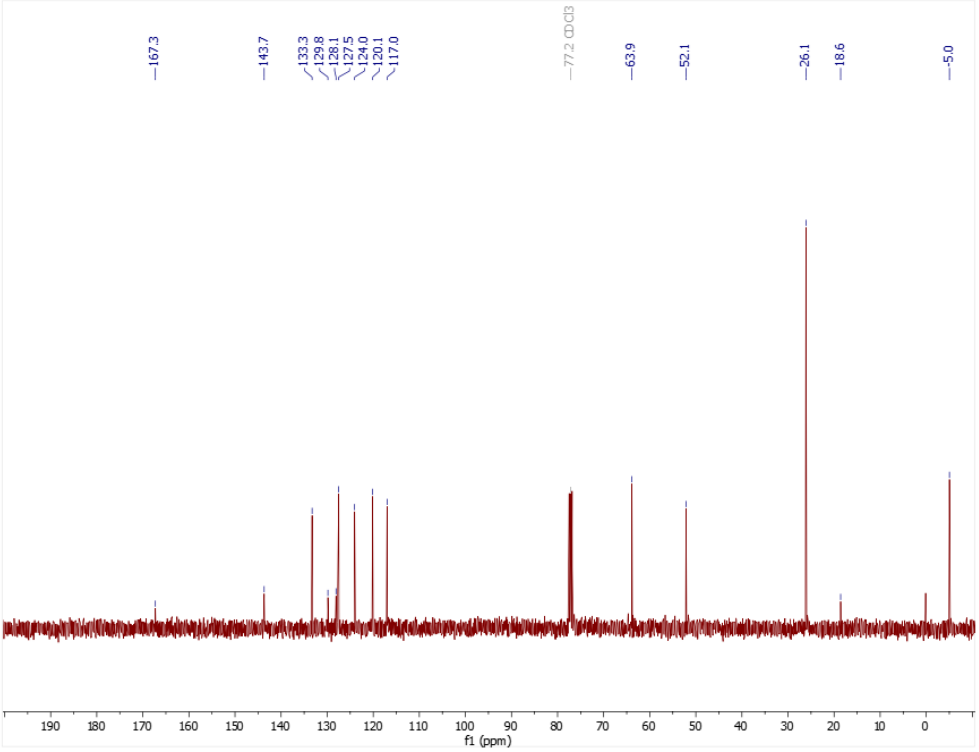
Methyl 2-amino-2'-((*tert*-butoxycarbonyl)amino-[1,1'-biphenyl]-4-carboxylate (3n): ^{13}C NMR, $CDCl_3$, 101 MHz



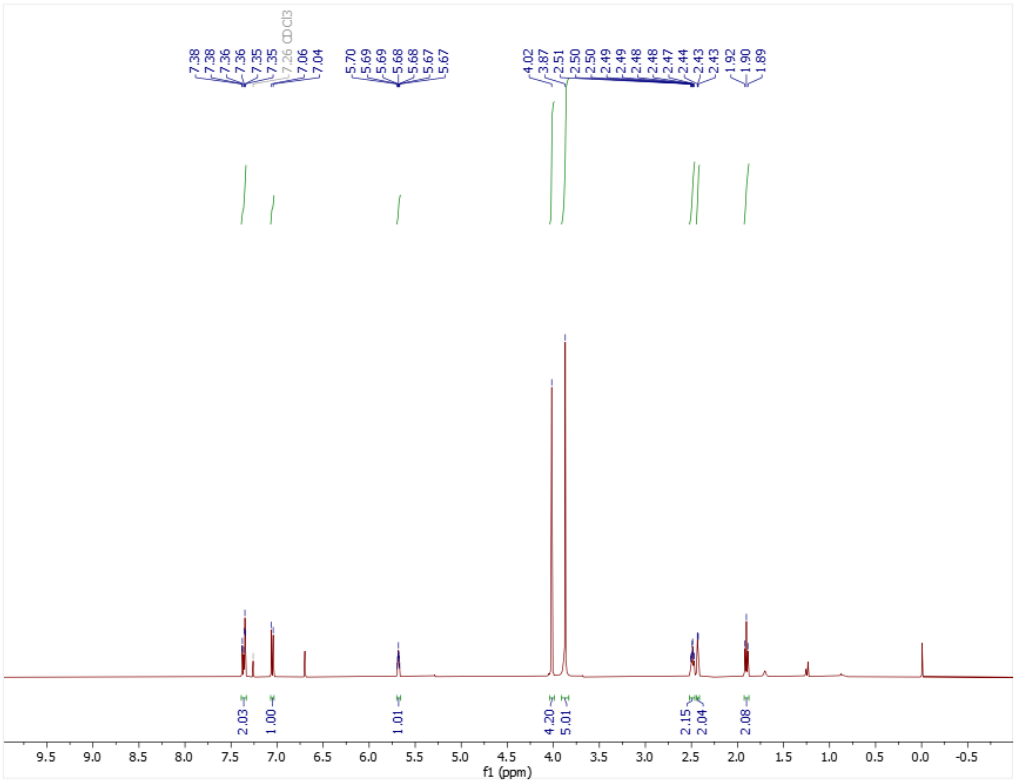
Methyl (*E*)-3-amino-4-(3-((*tert*-butyldimethylsilyl)oxy)prop-1-en-1-yl)benzoate (3o): ^{1}H NMR, $CDCl_3$, 400 MHz



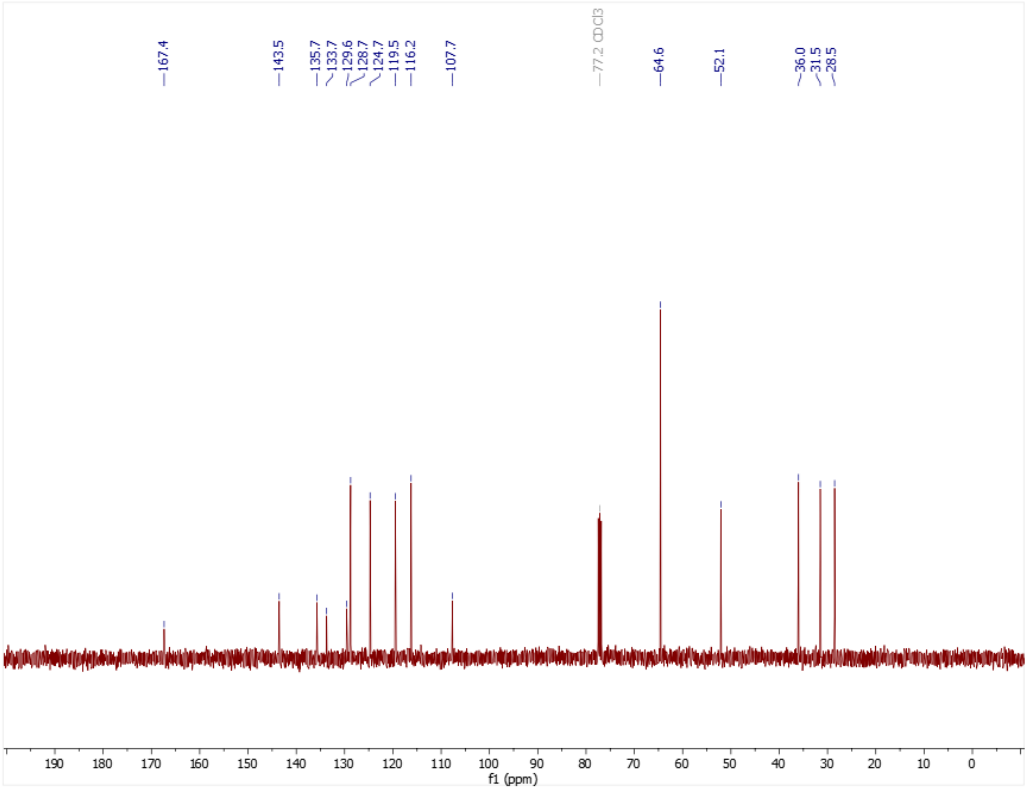
Methyl (*E*)-3-amino-4-(3-((*tert*-butyldimethylsilyl)oxy)prop-1-en-1-yl)benzoate (3o): ^{13}C NMR, $CDCl_3$, 101 MHz



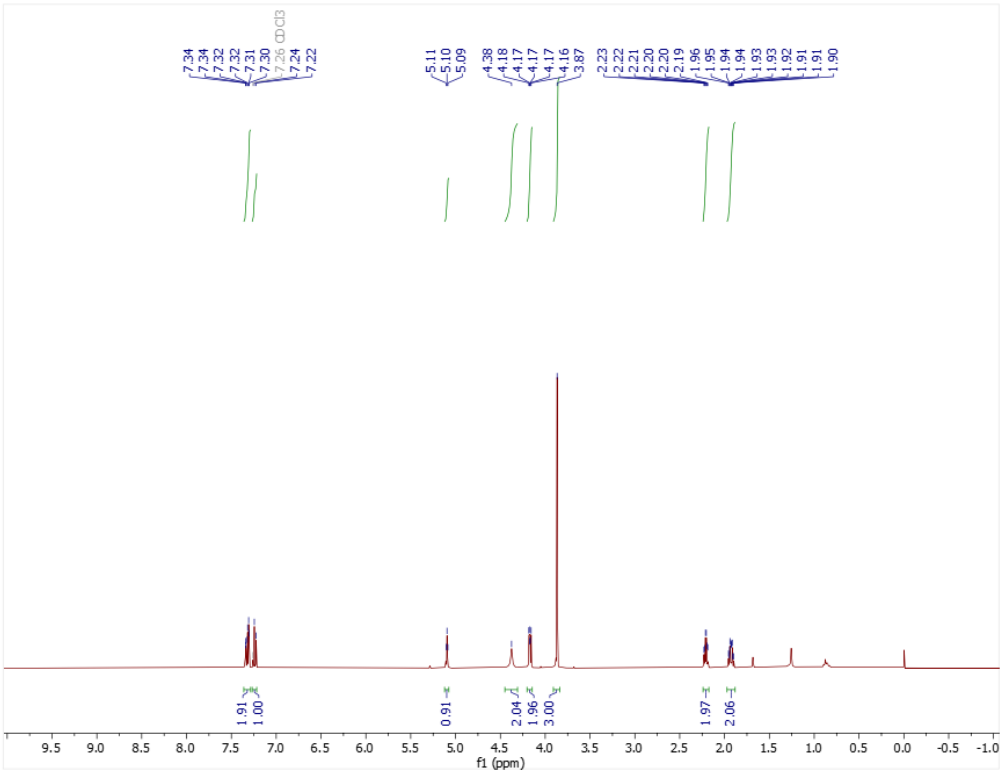
Methyl 3-amino-4-(1,4-dioxaspiro[4.5]dec-7-en-8-yl)benzoate (3p): ^{1}H NMR, $CDCl_3$, 400 MHz



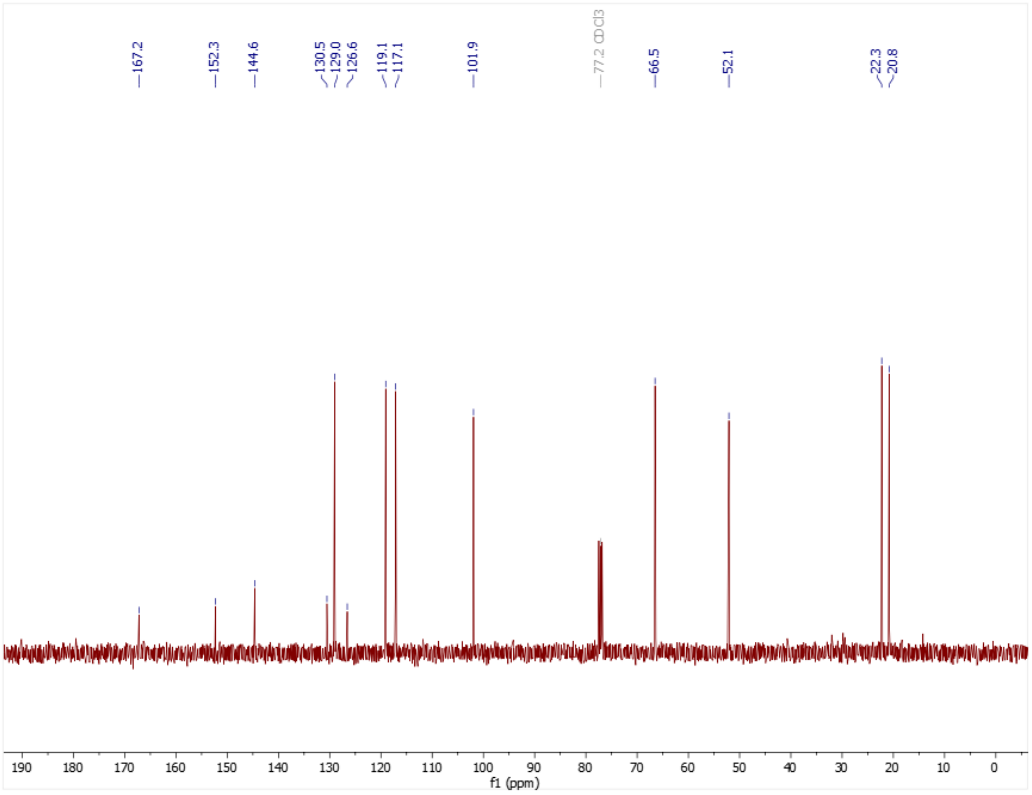
Methyl 3-amino-4-(1,4-dioxaspiro[4.5]dec-7-en-8-yl)benzoate (3p): ^{13}C NMR, $CDCl_3$, 101 MHz



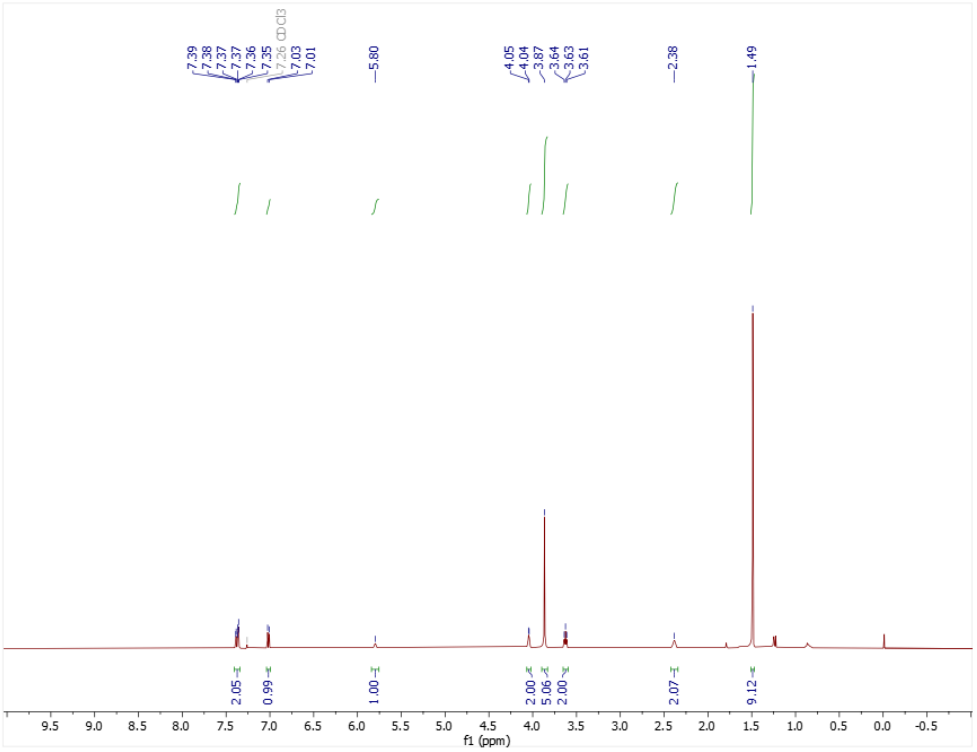
Methyl 3-amino-4-(3,4-dihydro-2*H*-pyran-6-yl)benzoate (3q): ^{1}H NMR, $CDCl_3$, 400 MHz



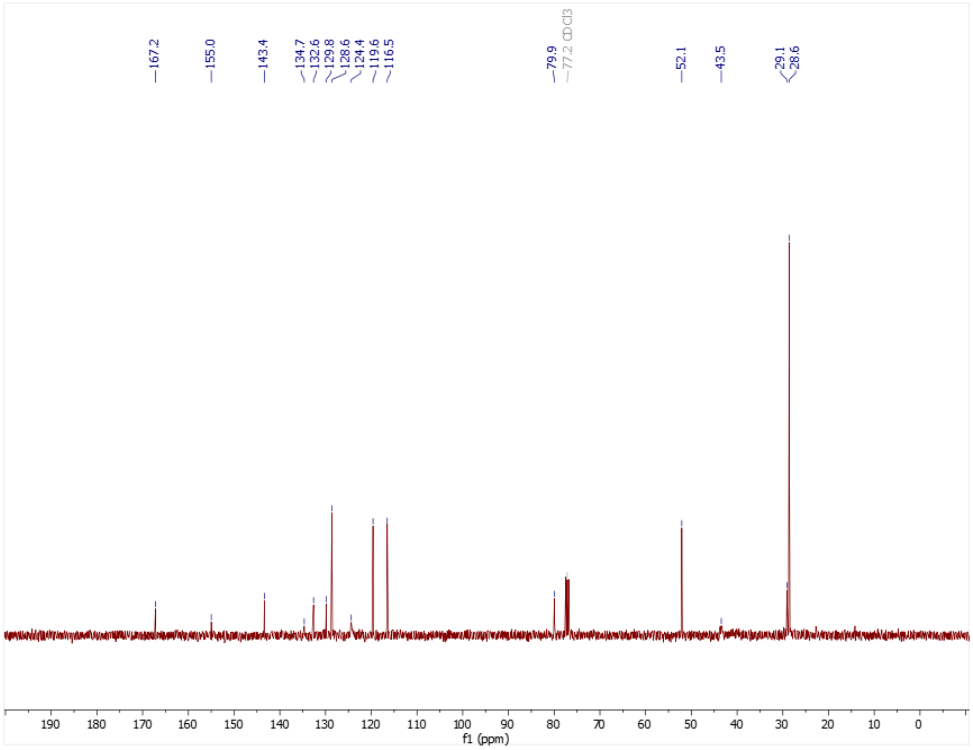
Methyl 3-amino-4-(3,4-dihydro-2*H*-pyran-6-yl)benzoate (3q): ^{13}C NMR, $CDCl_3$, 101 MHz



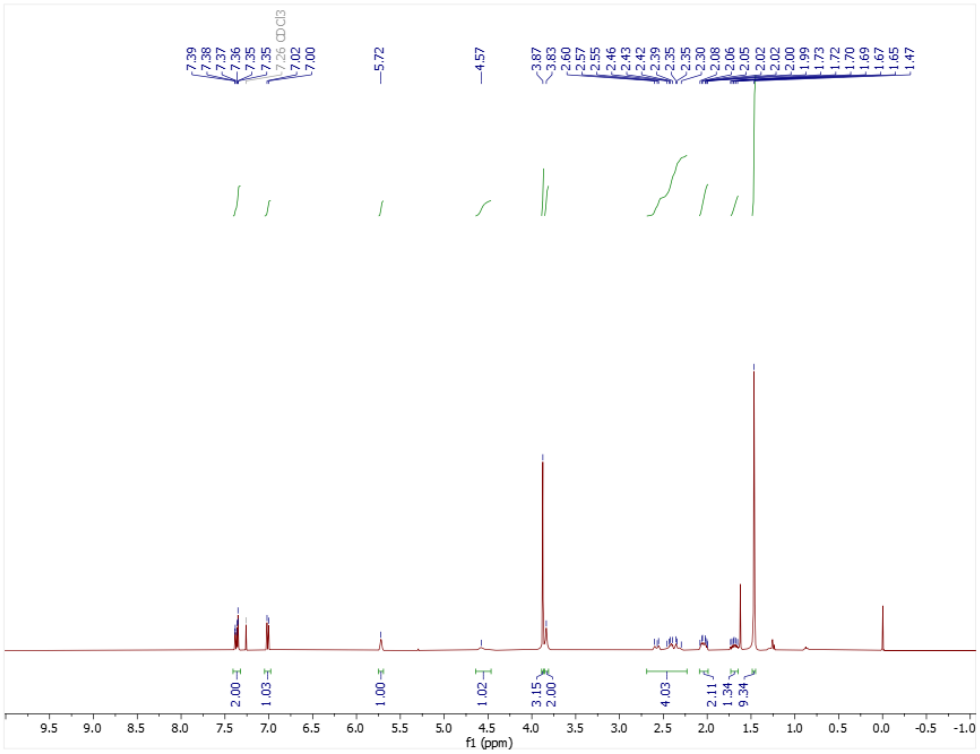
Tert-butyl-4-(2-amino-4-(methoxycarbonyl)phenyl)-3,6-dihydropyridine-1(2_H_)-carboxylate (3r): ^{1}H NMR, $CDCl_3$, 400 MHz



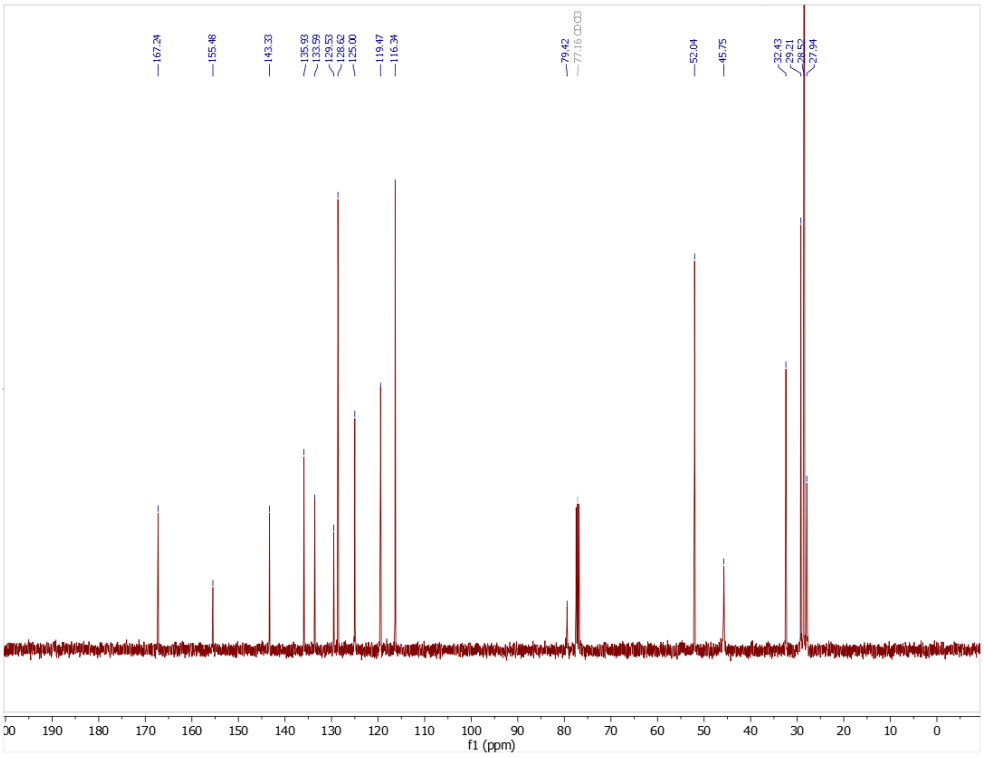
Tert-butyl-4-(2-amino-4-(methoxycarbonyl)phenyl)-3,6-dihydropyridine-1(2_H_)-carboxylate (3r): ^{13}C NMR, $CDCl_3$, 101 MHz



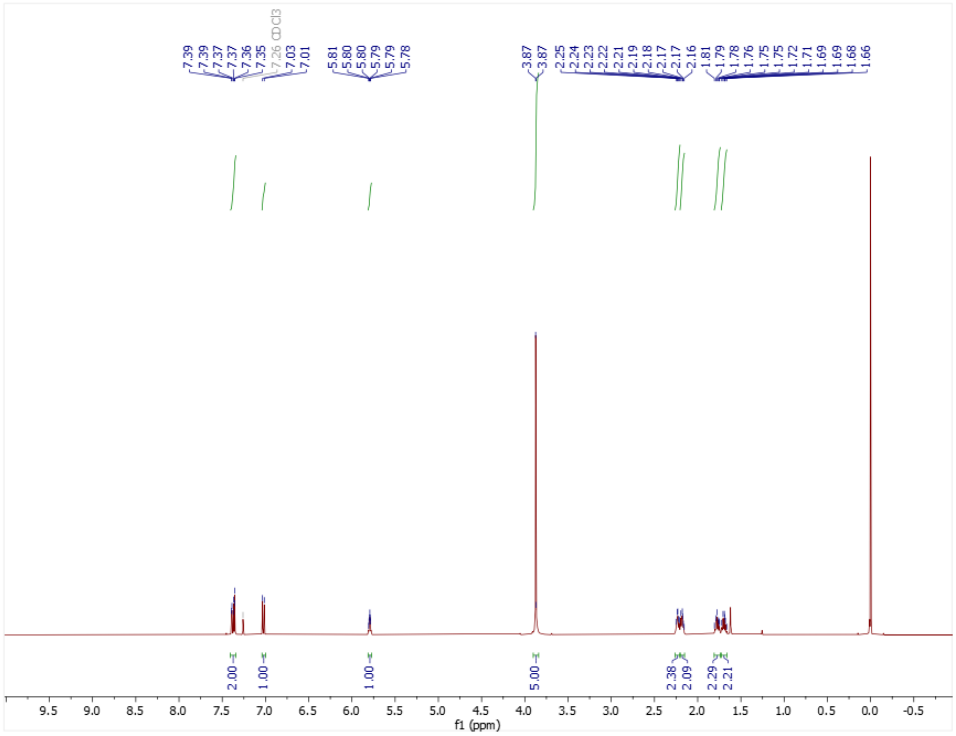
Methyl 2-amino-4'-((*tert*-butoxycarbonyl)amino)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]4-carboxylate (3s): ^{1}H NMR, $CDCl_3$, 400 MHz



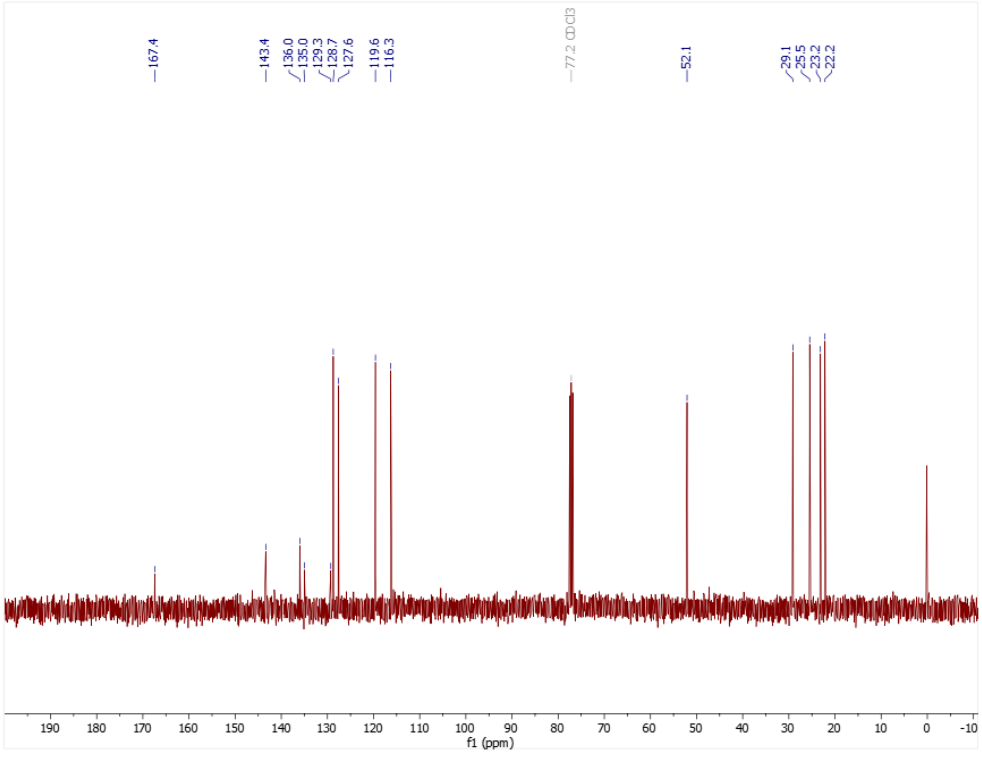
Methyl 2-amino-4'-((*tert*-butoxycarbonyl)amino)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]4-carboxylate (3s): ^{13}C NMR, $CDCl_3$, 101 MHz



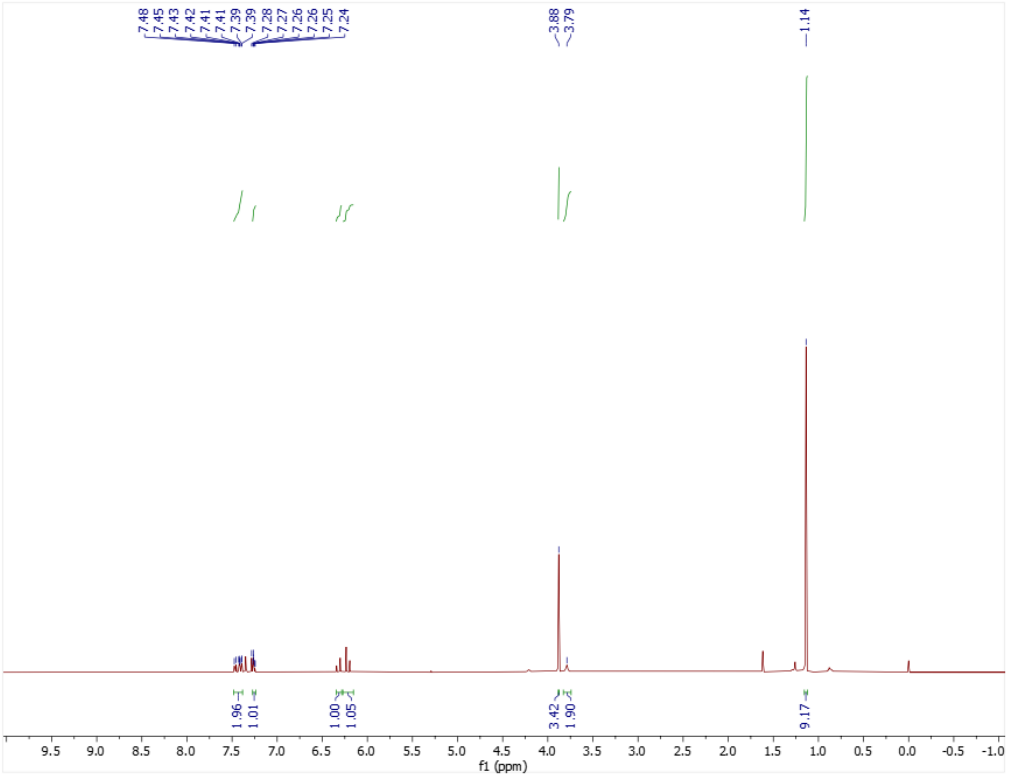
Methyl 2-amino-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carboxylate (3t): ^{1}H NMR, $CDCl_3$, 400 MHz



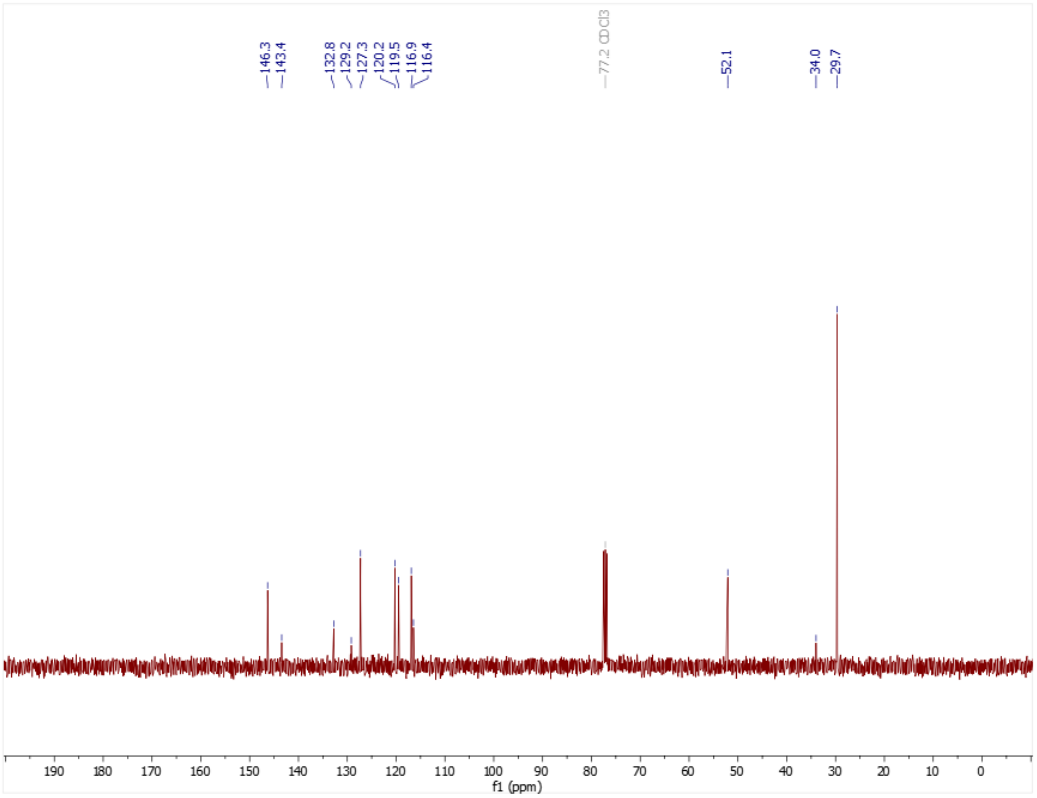
Methyl 2-amino-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carboxylate (3t): ^{13}C NMR, $CDCl_3$, 101 MHz



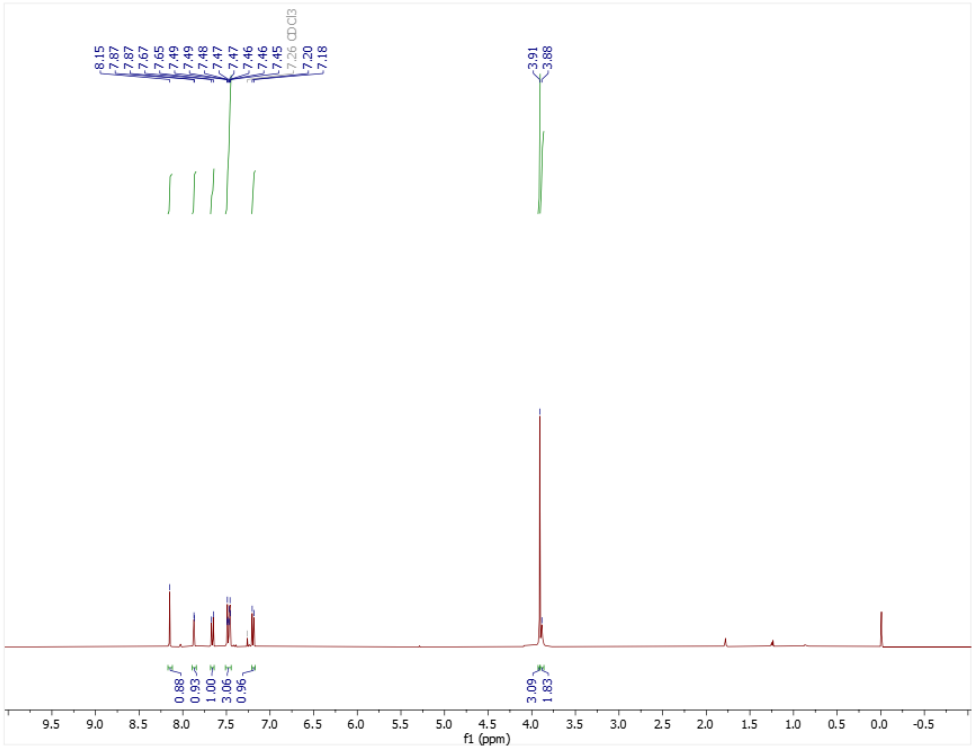
Methyl (*E*)-3-amino-4-(3,3-dimethylbut-1-en-1-yl)benzoate (3u): ^{1}H NMR, $CDCl_3$, 400 MHz



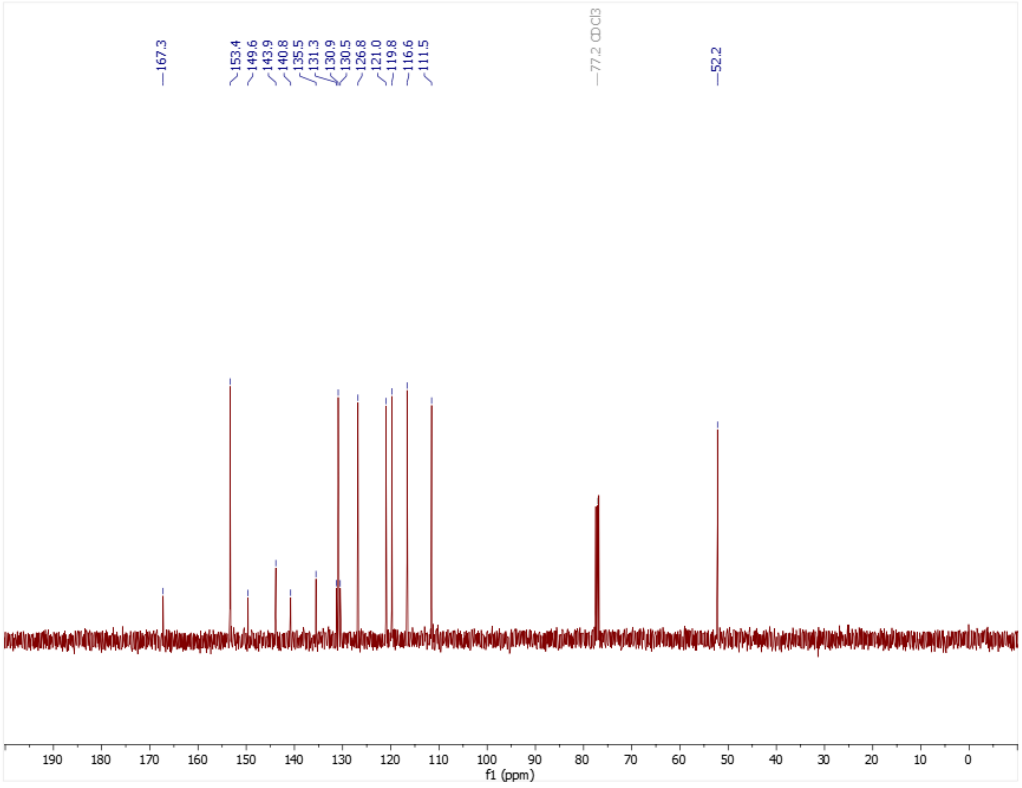
Methyl (*E*)-3-amino-4-(3,3-dimethylbut-1-en-1-yl)benzoate (3u): ^{13}C NMR, $CDCl_3$, 101 MHz



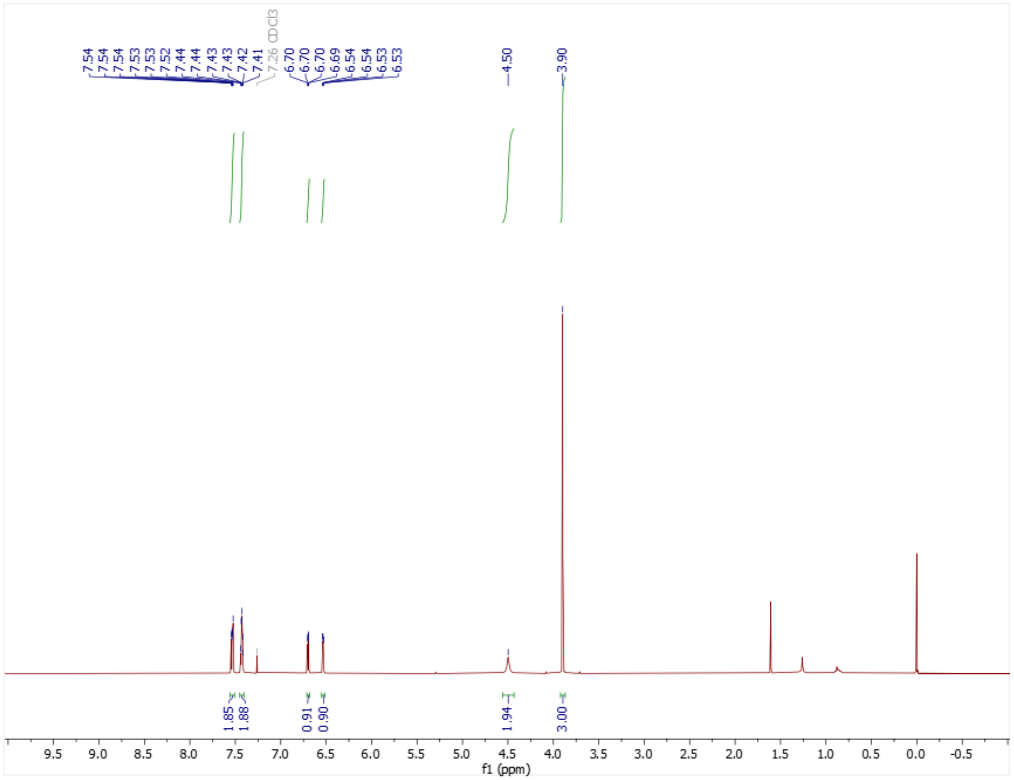
Methyl 3-amino-4-(benzo[*d*]oxazol-5-yl)benzoate (3v): ^{1}H NMR, $CDCl_3$, 400 MHz



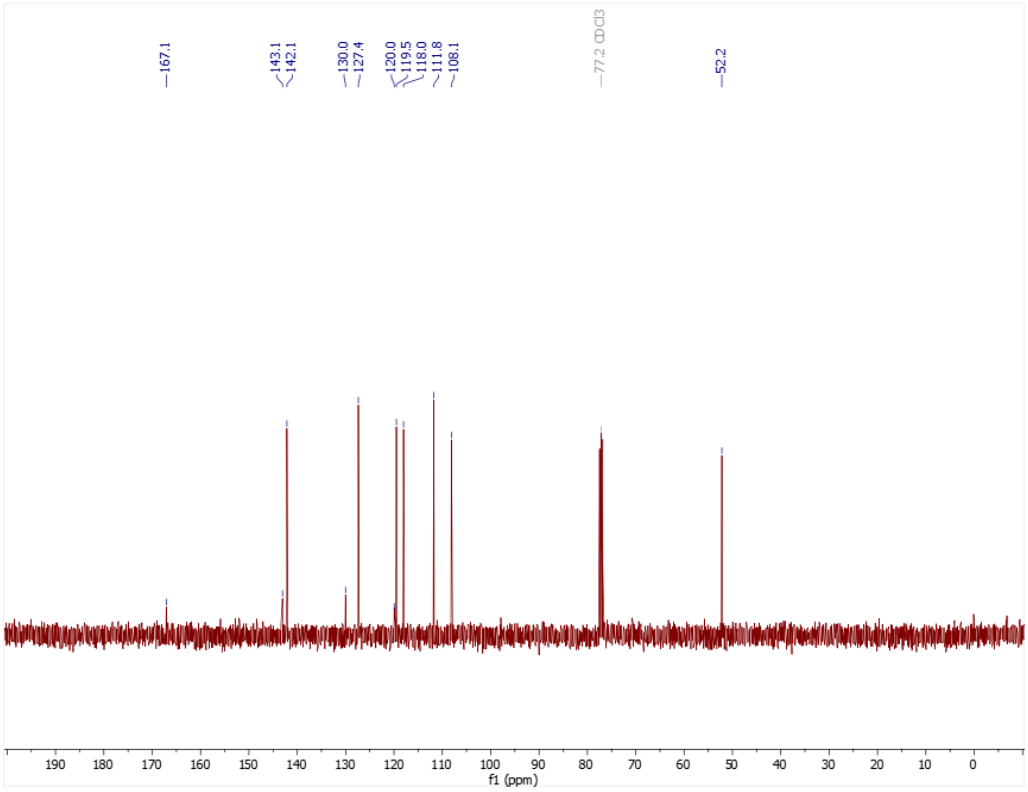
Methyl 3-amino-4-(benzo[*d*]oxazol-5-yl)benzoate (3v): ^{13}C NMR, $CDCl_3$, 101 MHz



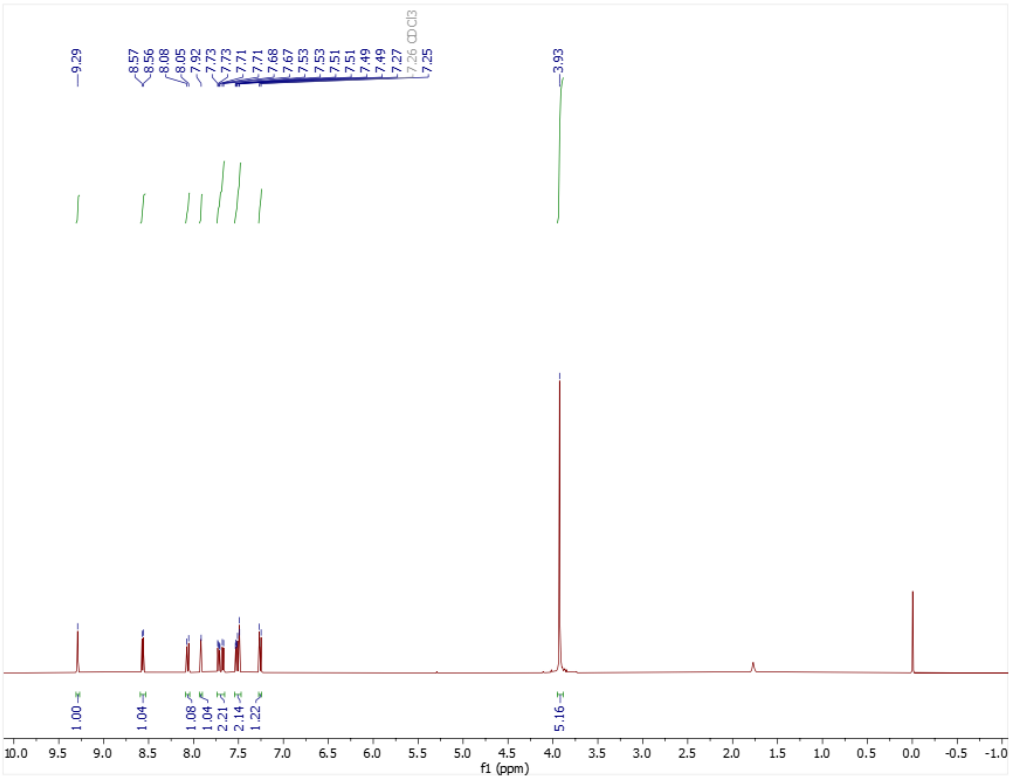
Methyl 3-amino-4-(furan-2-yl)benzoate (3w): ^{1}H NMR, $CDCl_3$, 400 MHz



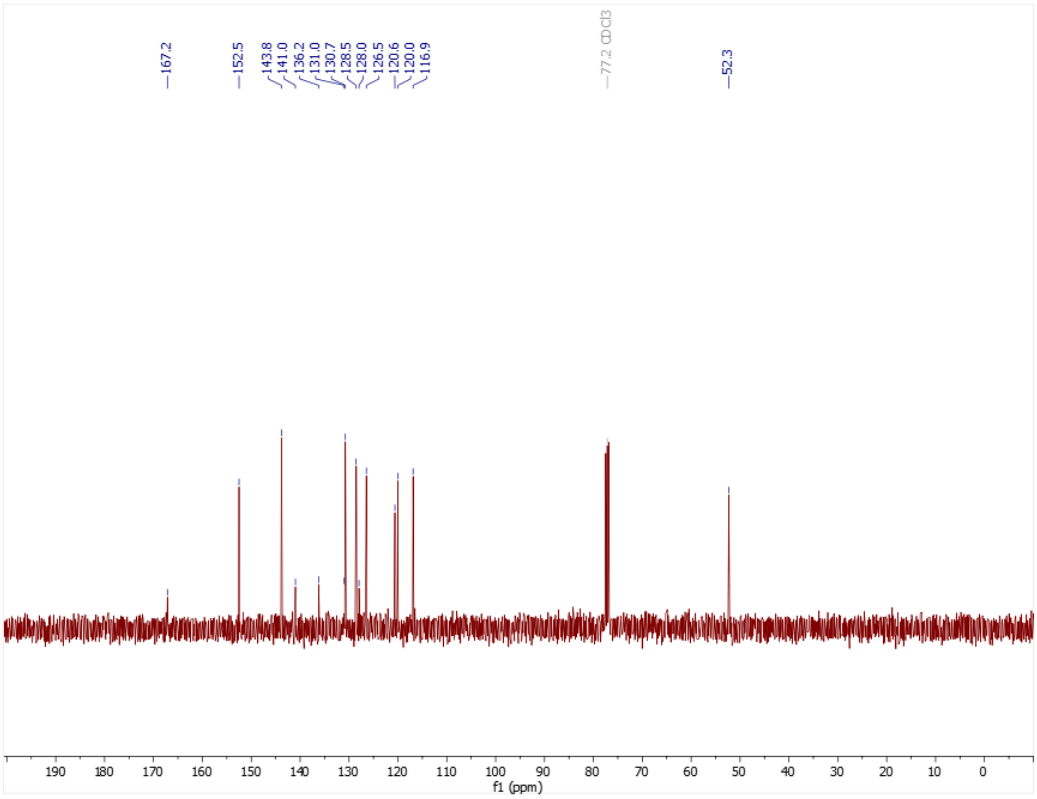
Methyl 3-amino-4-(furan-2-yl)benzoate (3w): ^{13}C NMR, $CDCl_3$, 101 MHz



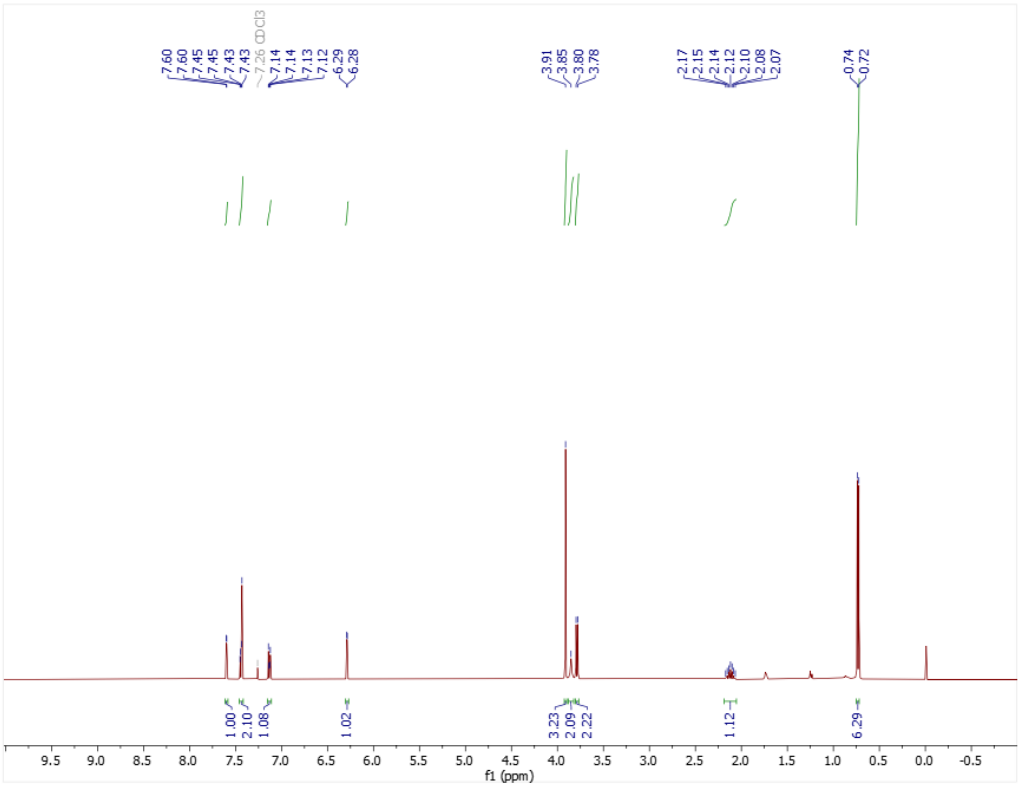
Methyl 3-amino-4-(isoquinolin-6-yl)benzoate (3x): ^{1}H NMR, $CDCl_3$, 400 MHz



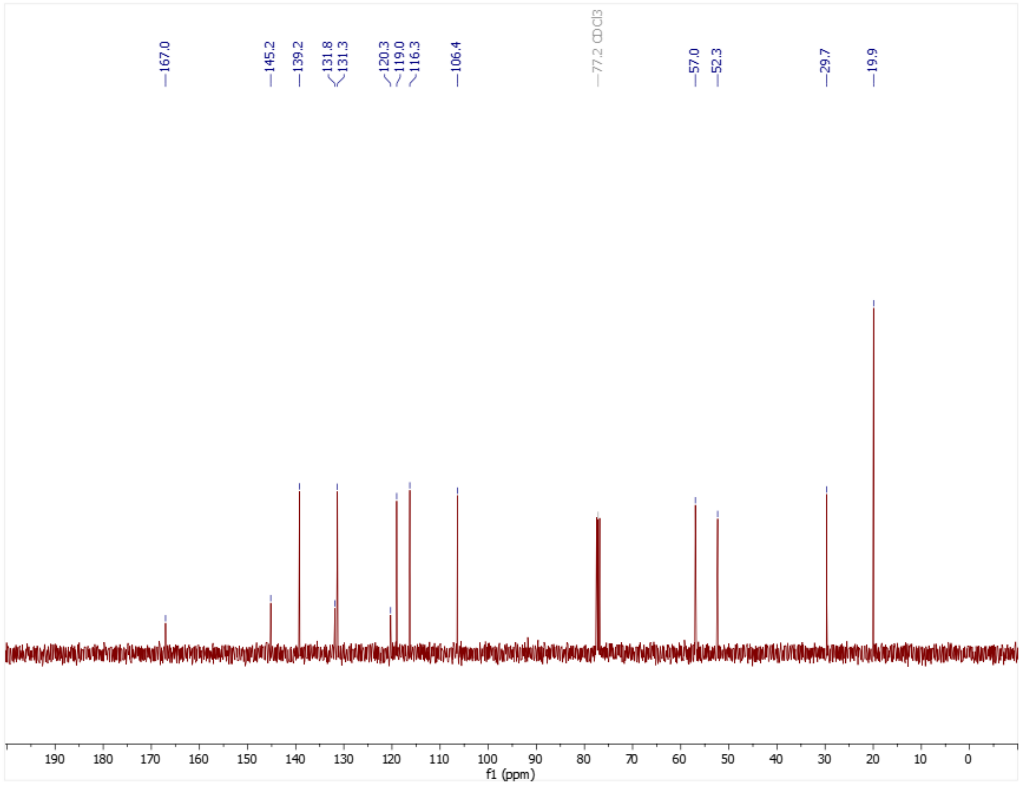
Methyl 3-amino-4-(isoquinolin-6-yl)benzoate (3x): ^{13}C NMR, $CDCl_3$, 101 MHz



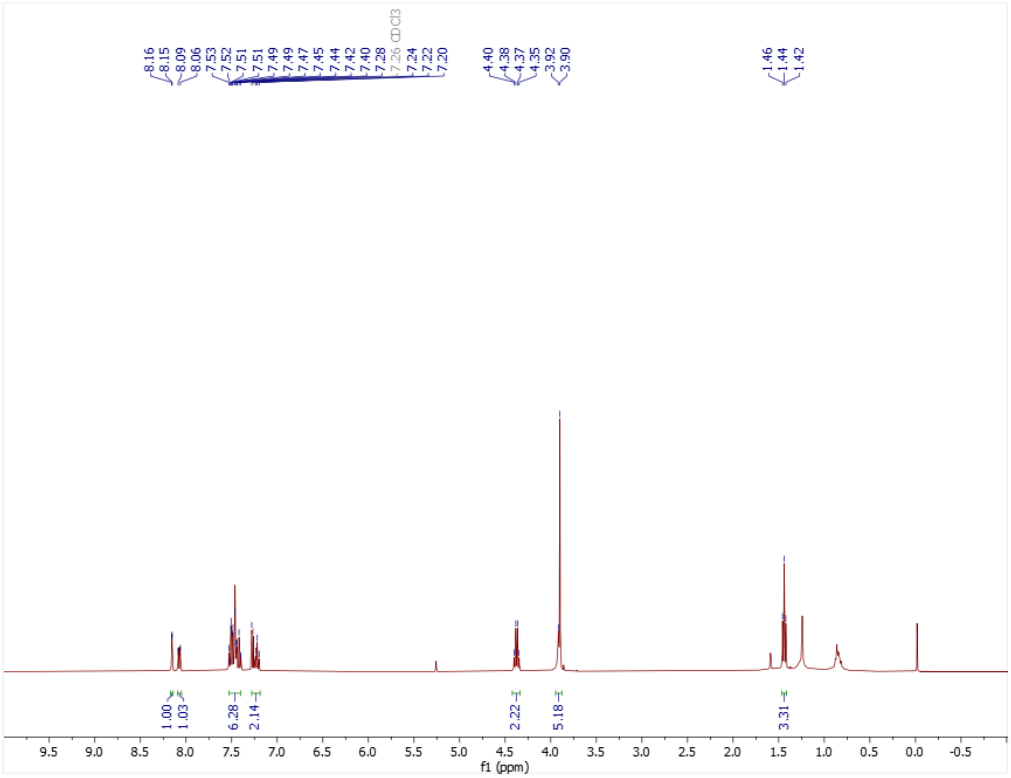
Methyl 3-amino-4-(1-isobutyl-1*H*-pyrazol-5-yl)benzoate (3y): ^{1}H NMR, $CDCl_3$, 400 MHz



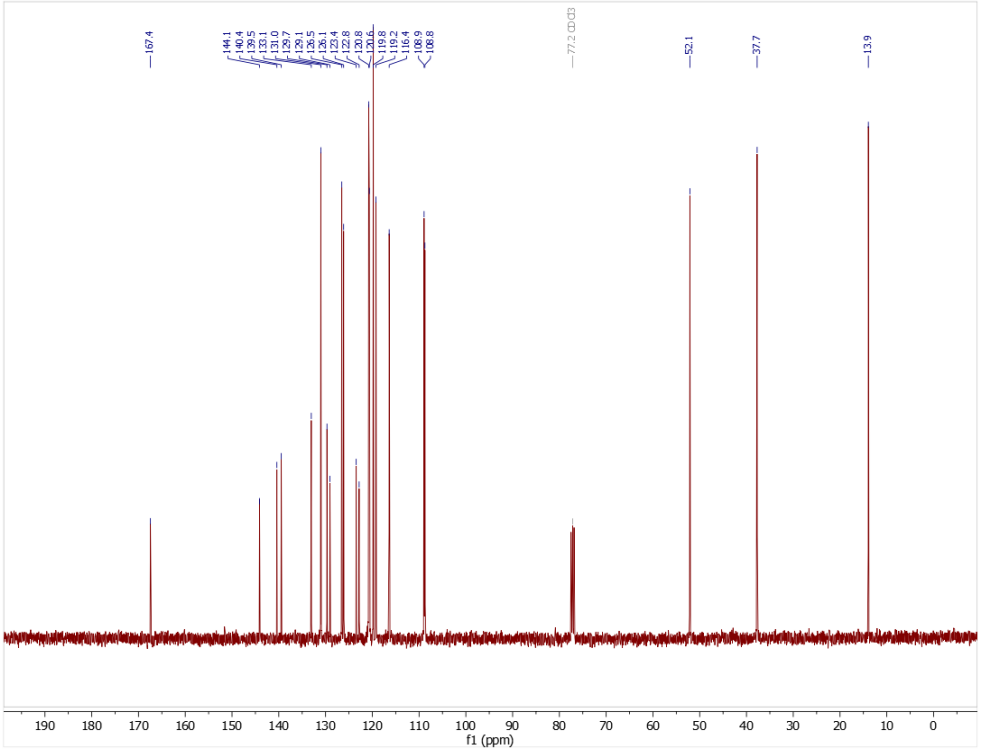
Methyl 3-amino-4-(1-isobutyl-1*H*-pyrazol-5-yl)benzoate (3y): ^{13}C NMR, $CDCl_3$, 101 MHz



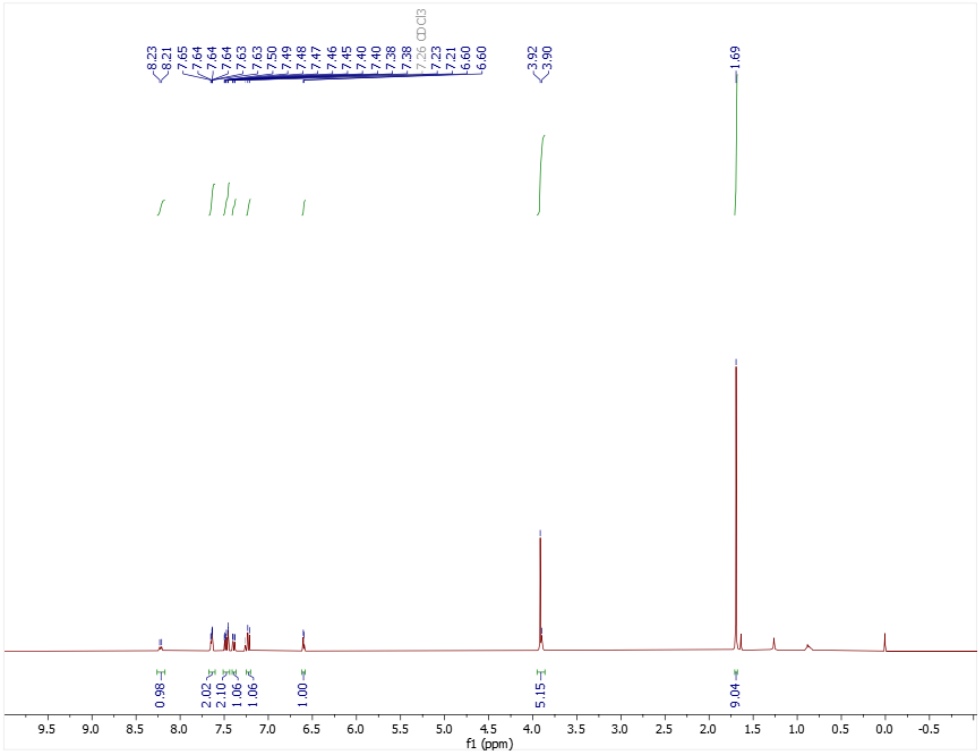
Methyl 3-amino-4-(9-ethyl-9*H*-carbazol-3-yl)benzoate (3z): ^{1}H NMR, $CDCl_3$, 400 MHz



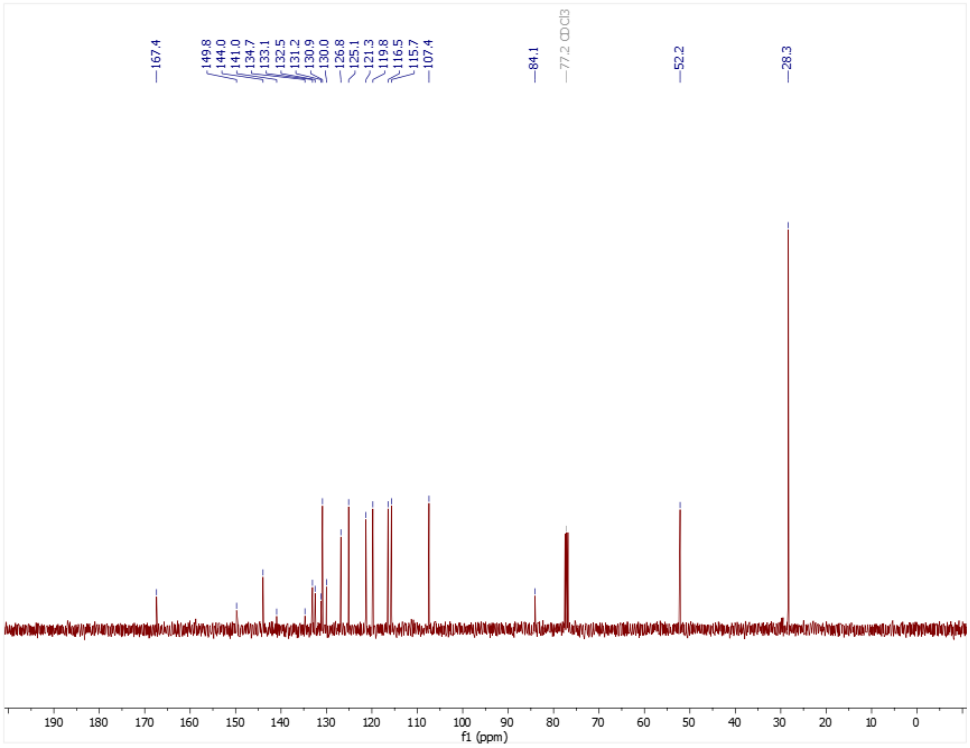
Methyl 3-amino-4-(9-ethyl-9*H*-carbazol-3-yl)benzoate (3z): ^{13}C NMR, $CDCl_3$, 101 MHz



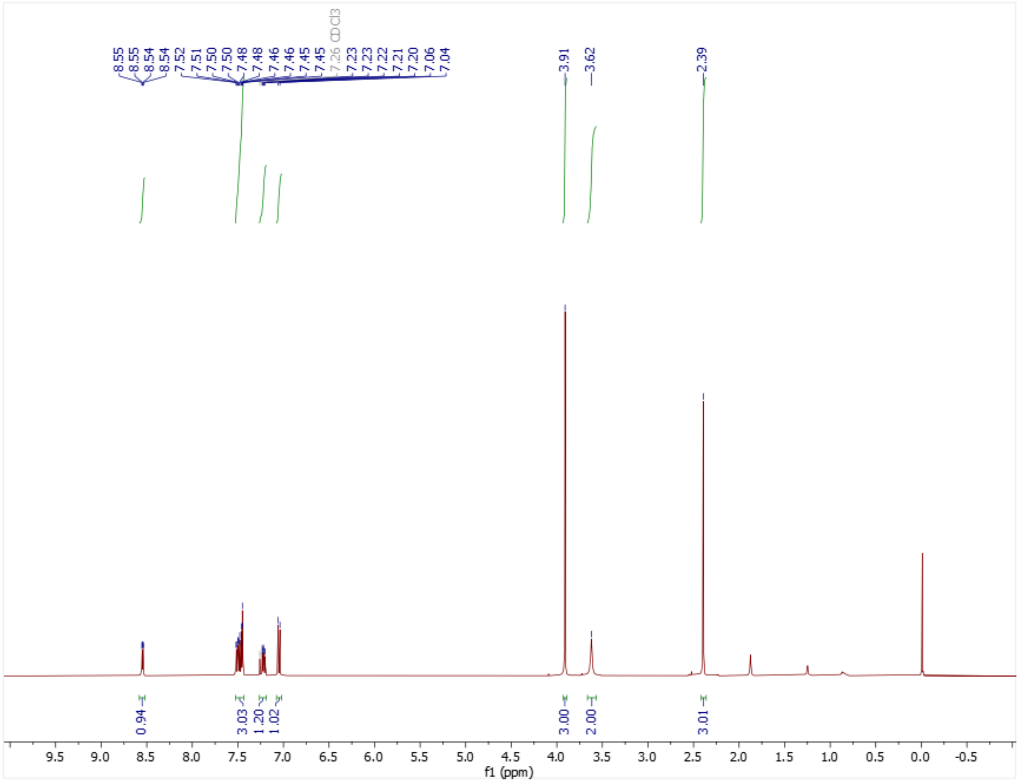
Tert-butyl 5-(2-amino-4-(methoxycarbonyl)phenyl)-1_H_-indole-1-carboxylate (3aa): ^{1}H NMR, $CDCl_3$, 400 MHz



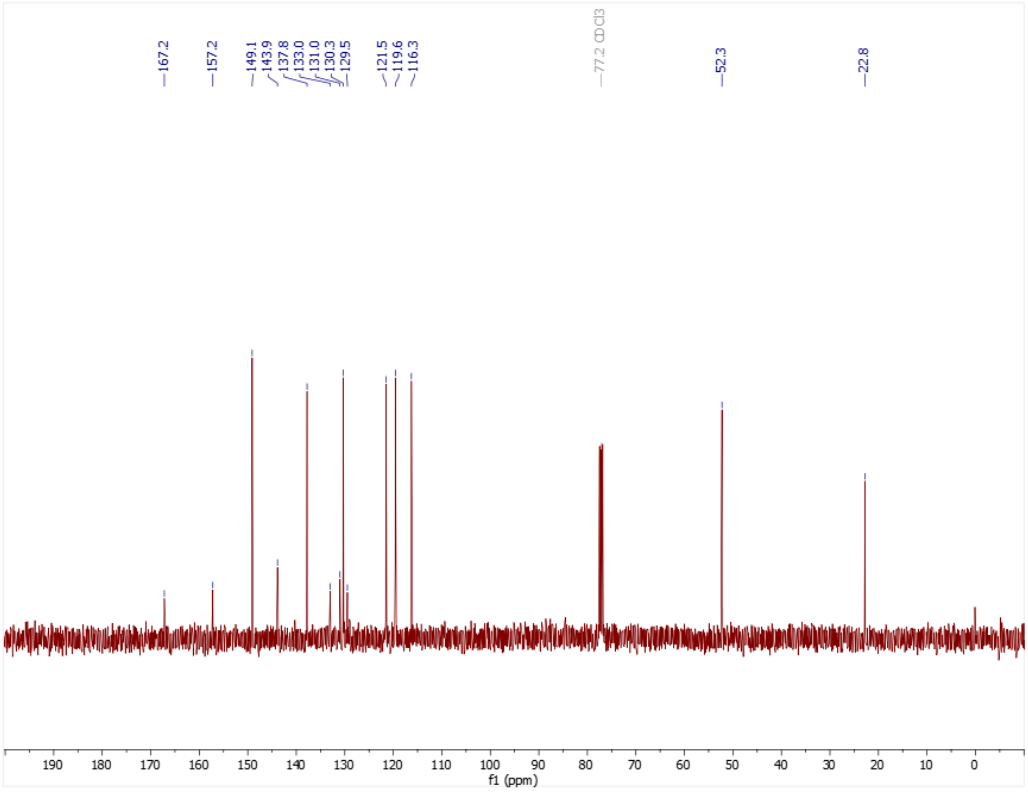
Tert-butyl 5-(2-amino-4-(methoxycarbonyl)phenyl)-1_H_-indole-1-carboxylate (3aa): ^{13}C NMR, $CDCl_3$, 101 MHz



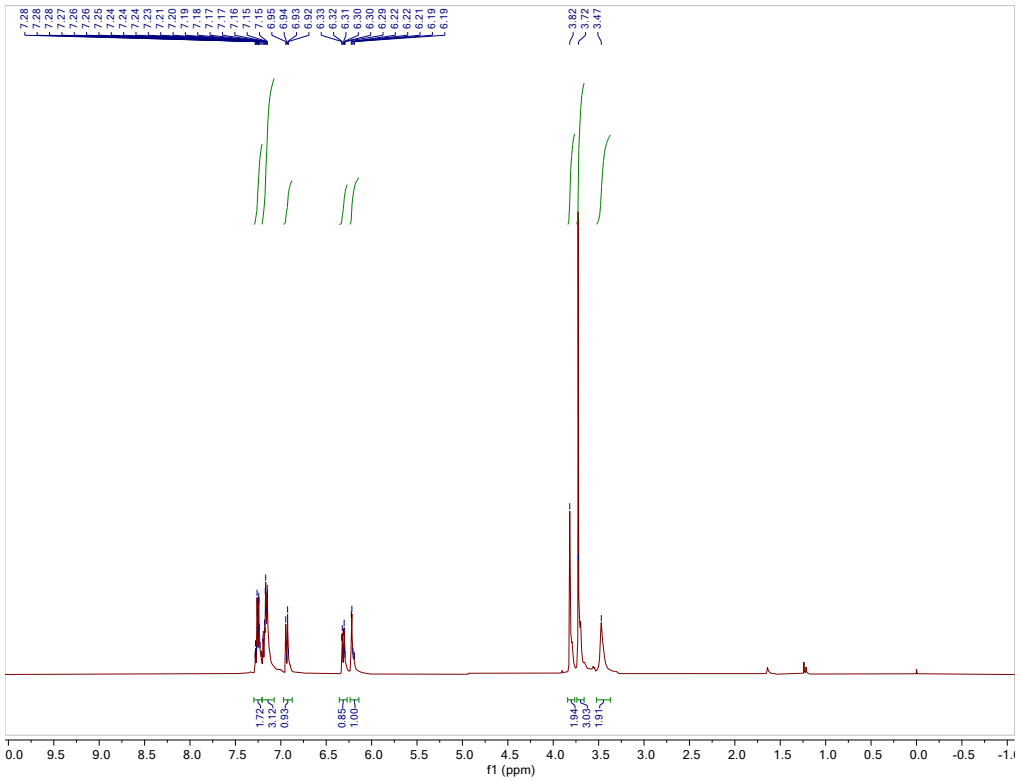
Methyl 3-amino-4-(2-methylpyridin-3-yl)benzoate (3ab): ^{1}H NMR, $CDCl_3$, 400 MHz



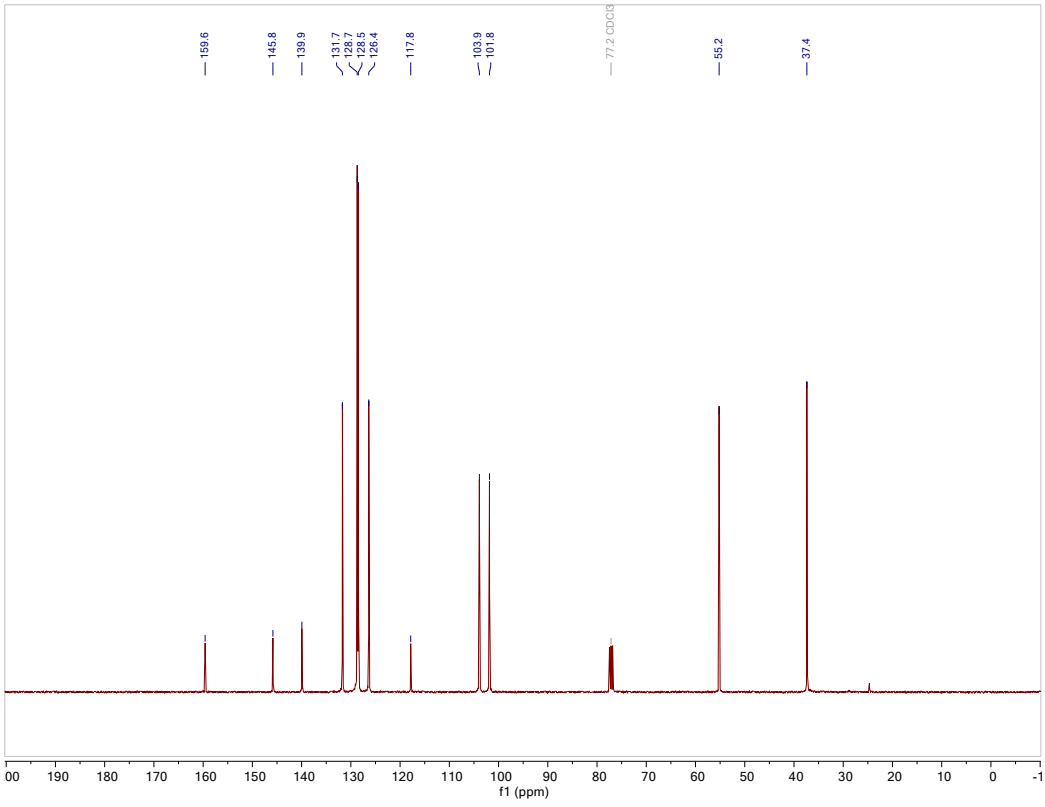
Methyl 3-amino-4-(2-methylpyridin-3-yl)benzoate (3ab): ^{13}C NMR, $CDCl_3$, 101 MHz



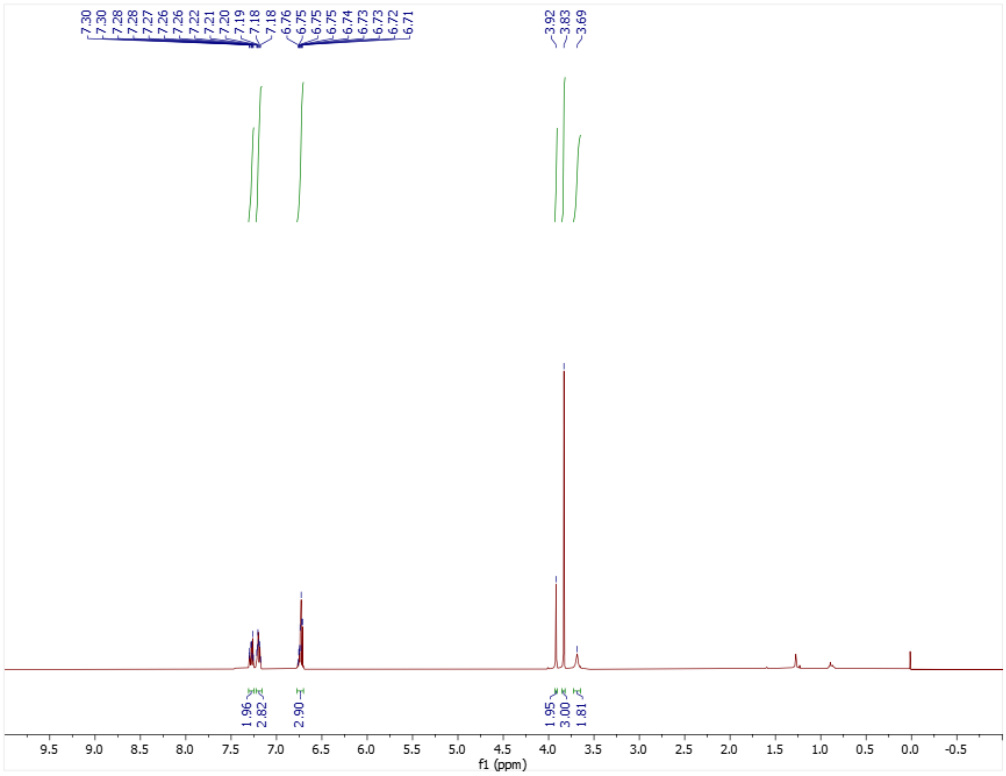
2-benzyl-5-methoxyaniline (3ac): ^{1}H NMR, $CDCl_3$, 400 MHz



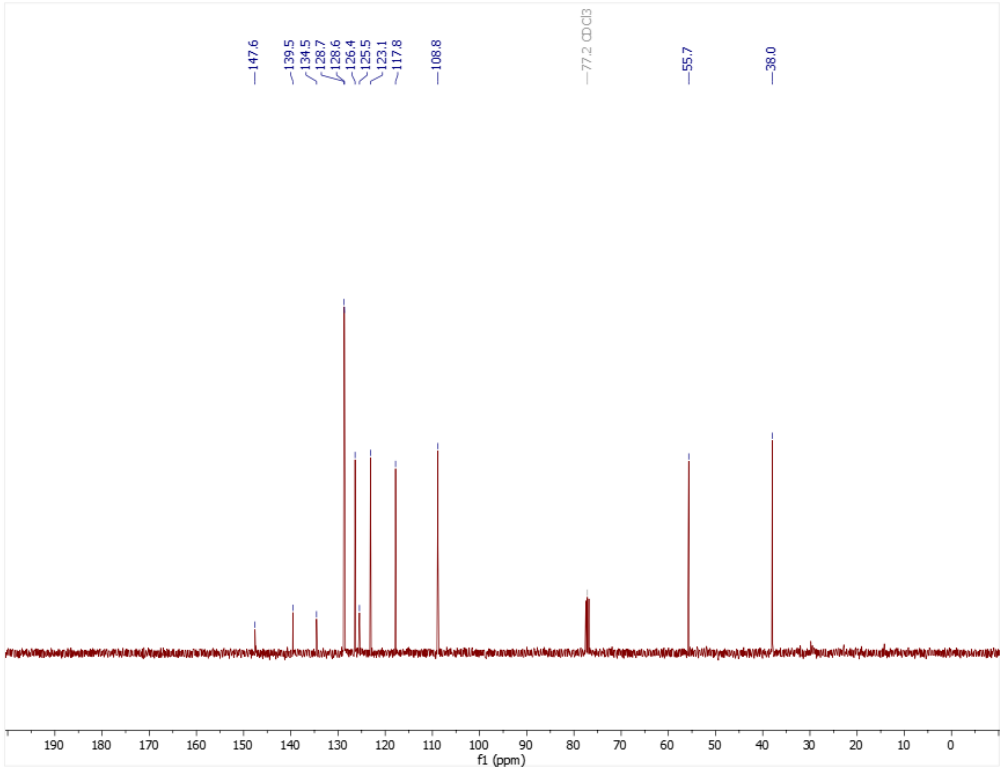
2-benzyl-5-methoxyaniline (3ac): ^{13}C NMR, $CDCl_3$, 101 MHz



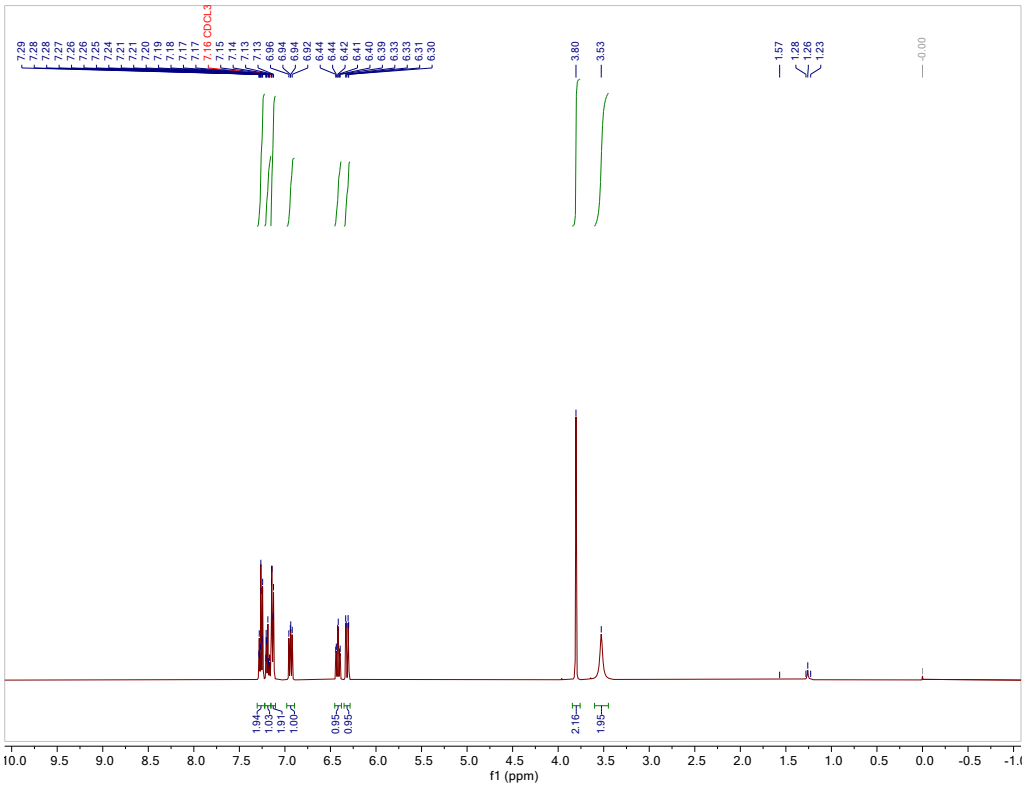
2-benzyl-6-methoxyaniline (3ad): ^{1}H NMR, $CDCl_3$, 400 MHz



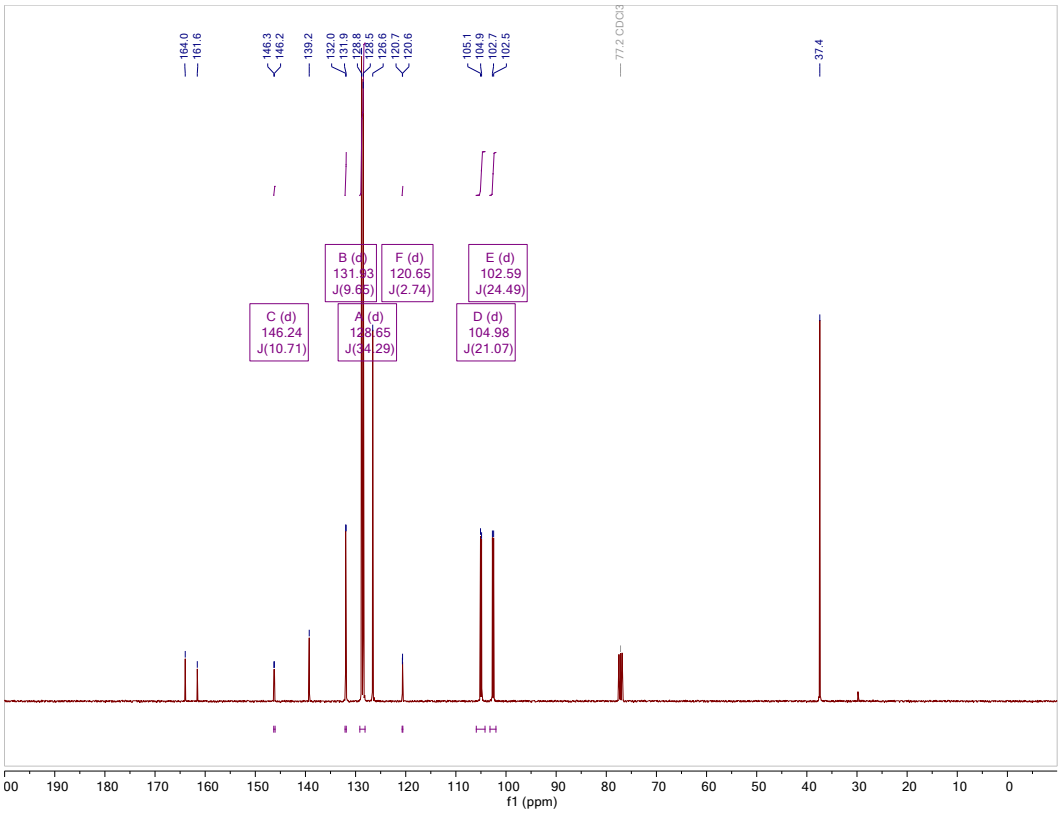
2-benzyl-6-methoxyaniline (3ad): ^{13}C NMR, $CDCl_3$, 101 MHz



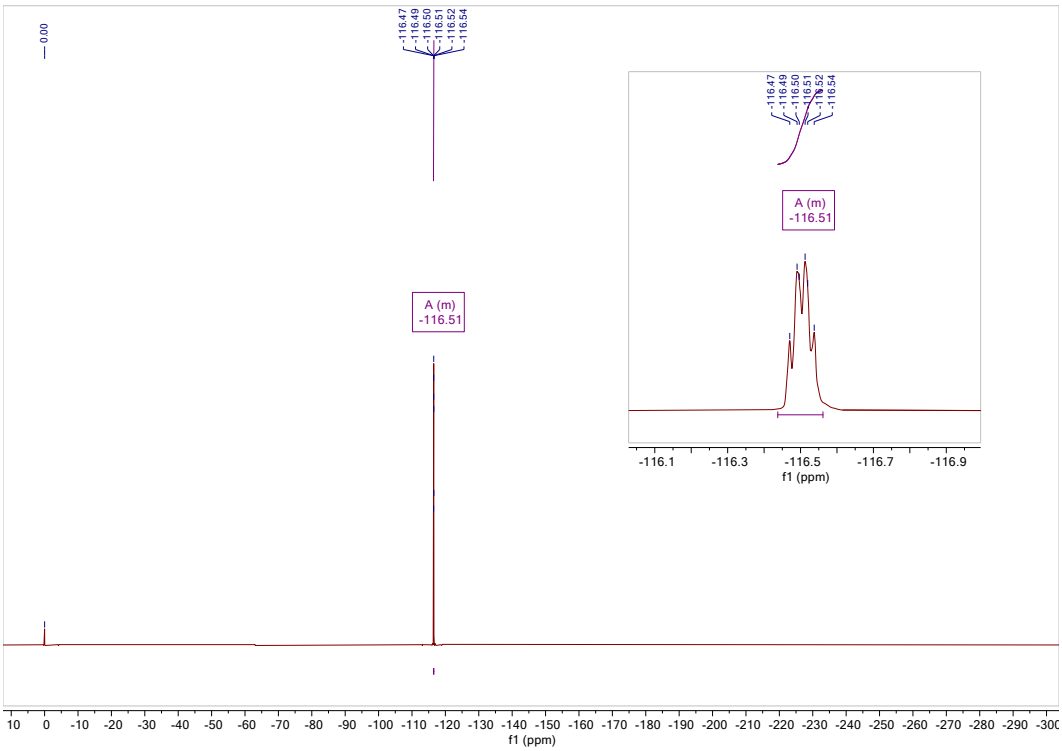
2-benzyl-5-fluoroaniline (3ae): ^{1}H NMR, $CDCl_3$, 400 MHz



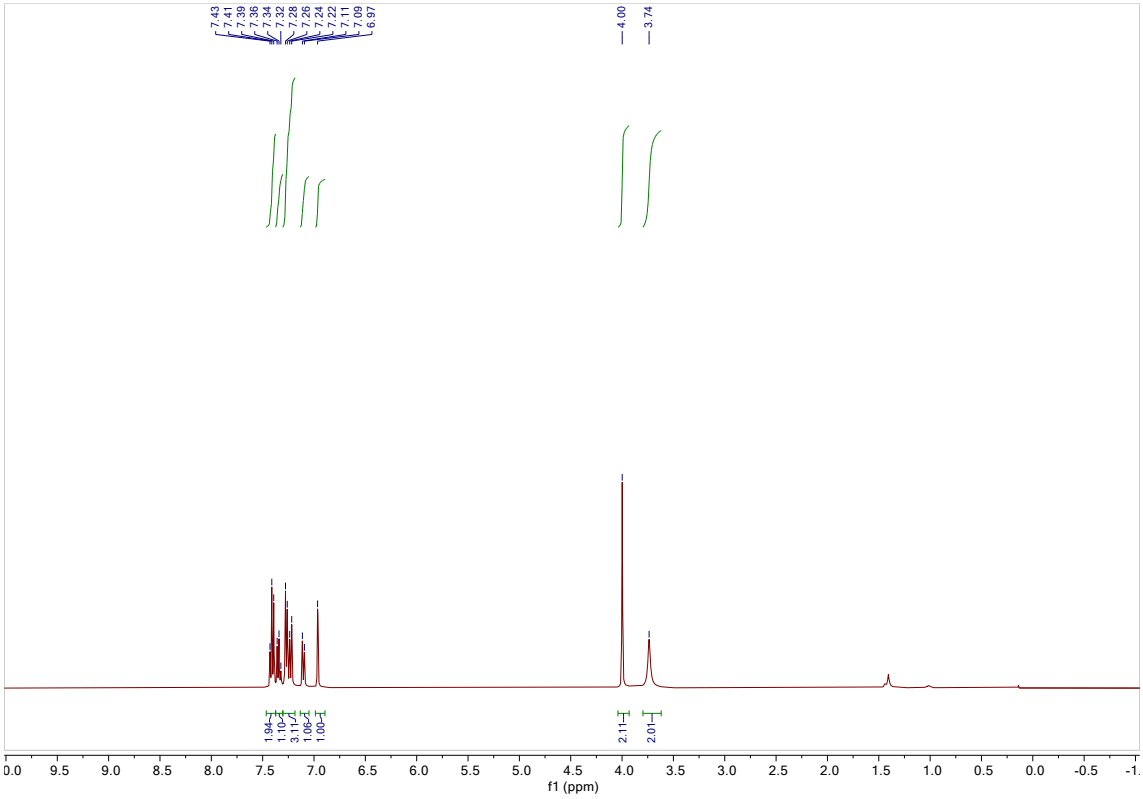
2-benzyl-5-fluoroaniline (3ae): ^{13}C NMR, $CDCl_3$, 101 MHz



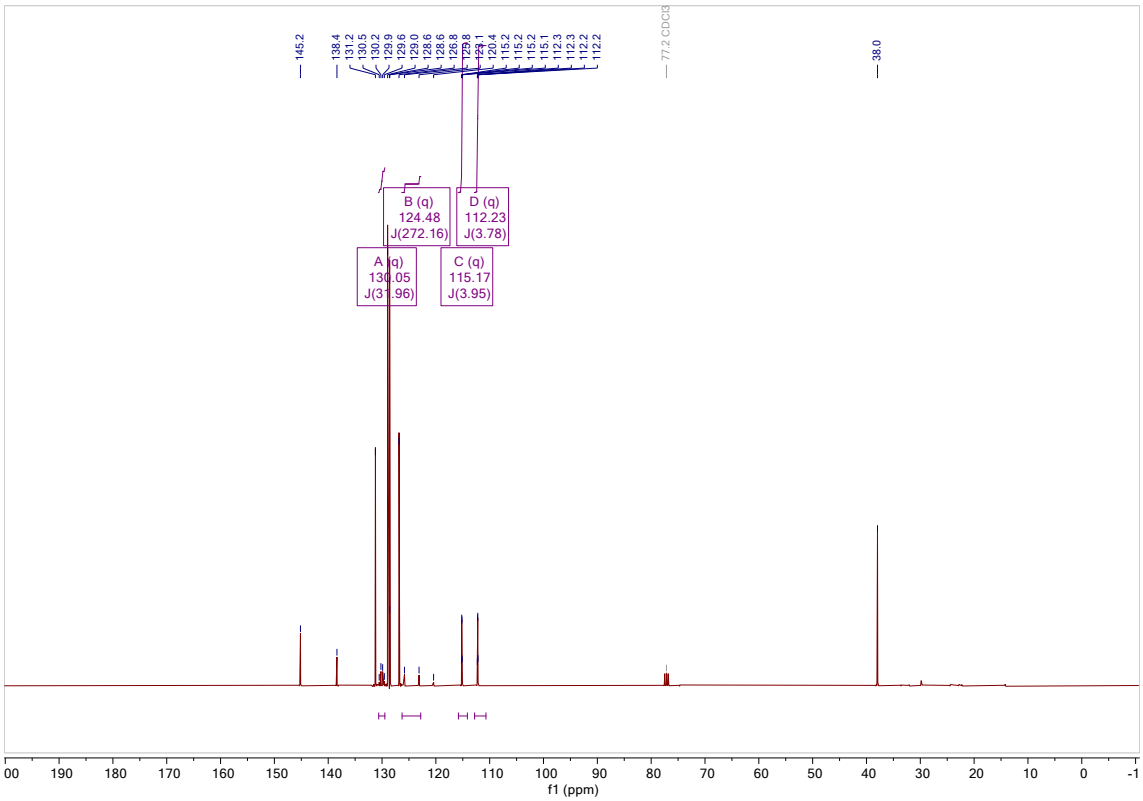
2-benzyl-5-fluoroaniline (3ae): ^{19}F NMR, $CDCl_3$, 376 MHz



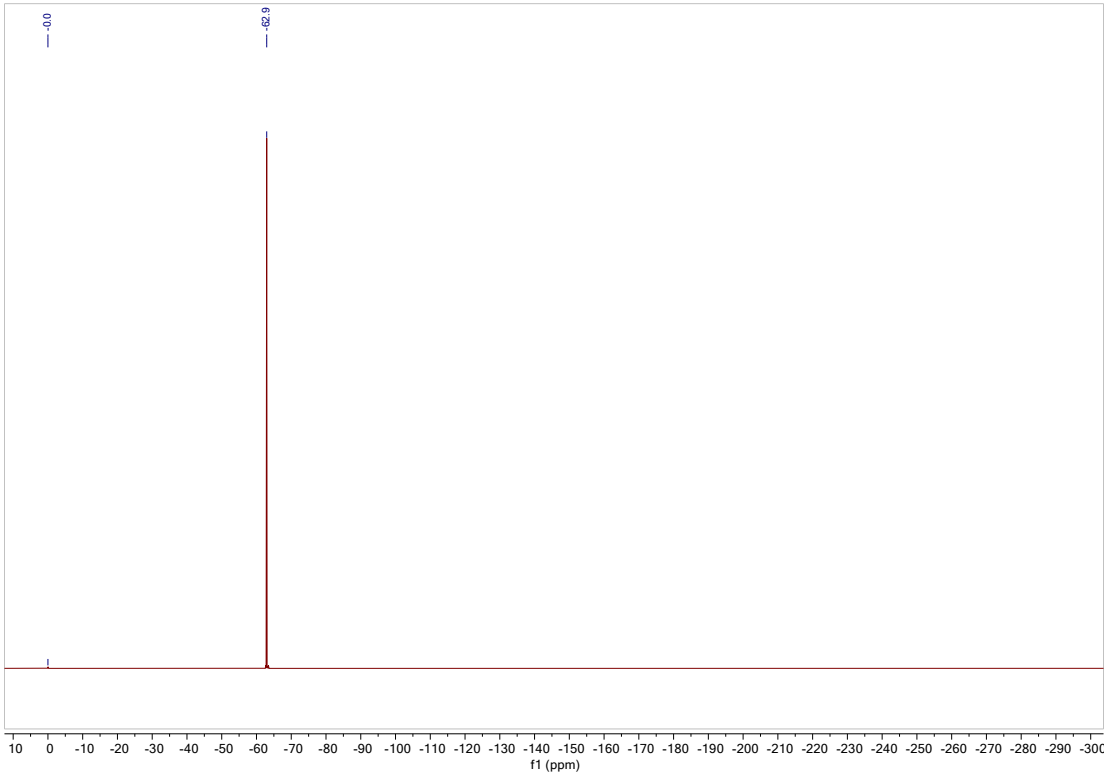
2-benzyl-5-(trifluoromethyl)aniline (3af): ^{1}H NMR, $CDCl_3$, 400 MHz



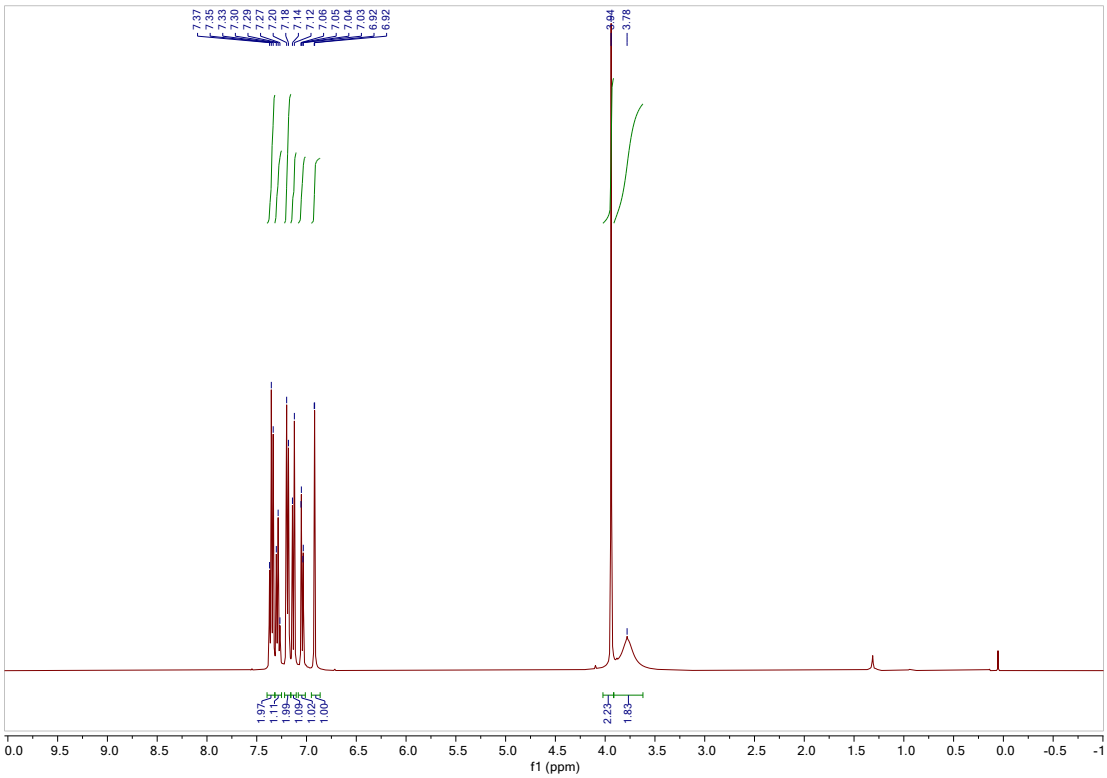
2-benzyl-5-(trifluoromethyl)aniline (3af): ^{13}C NMR, $CDCl_3$, 101 MHz



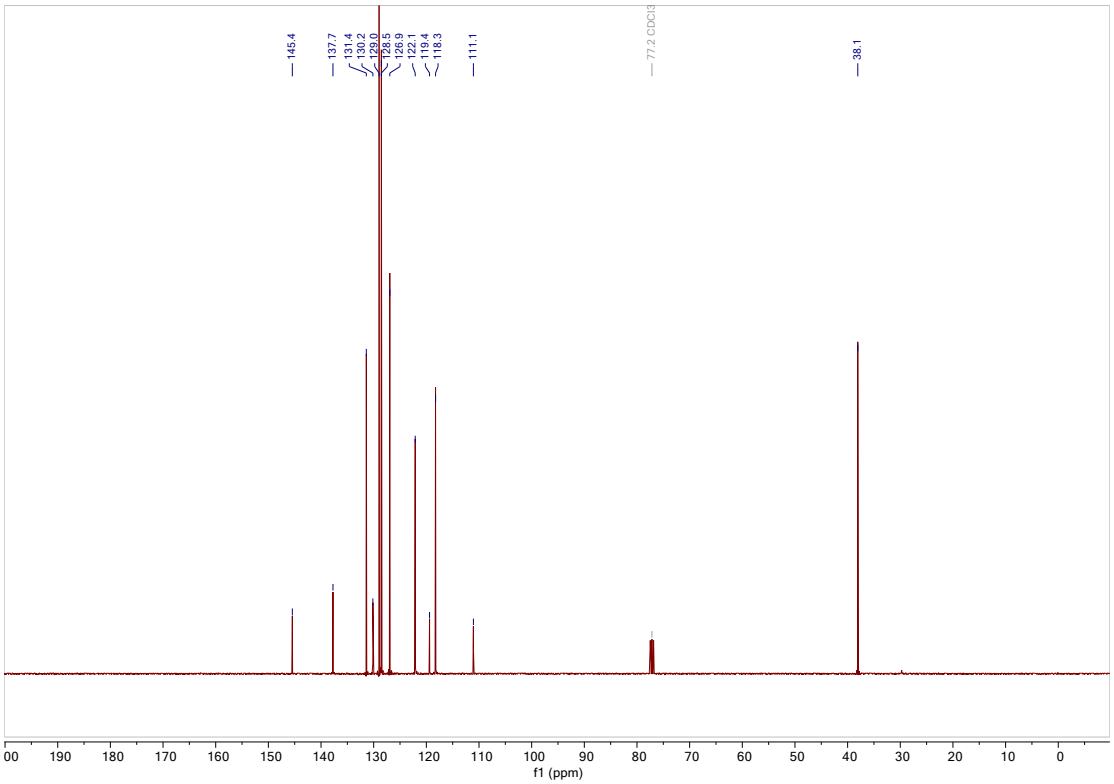
2-benzyl-5-(trifluoromethyl)aniline (3af): ^{19}F NMR, $CDCl_3$, 376 MHz



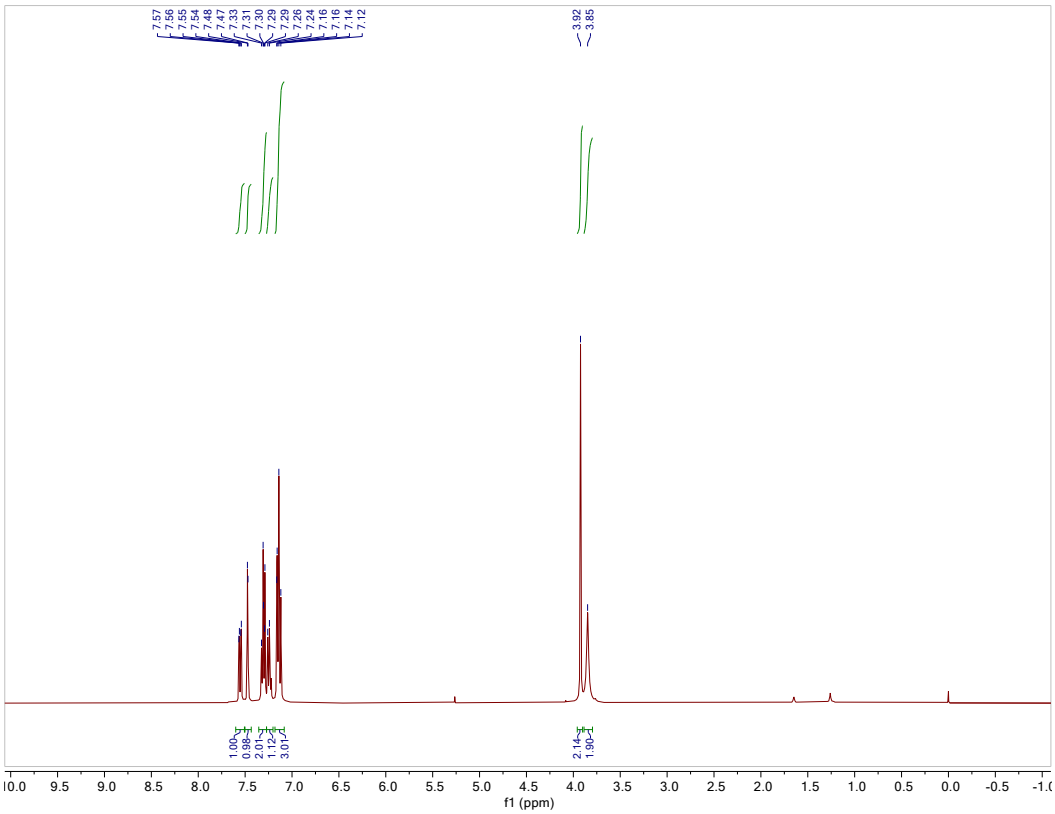
3-amino-4-benzylbenzonitrile (3ag): ^{1}H NMR, $CDCl_3$, 400 MHz



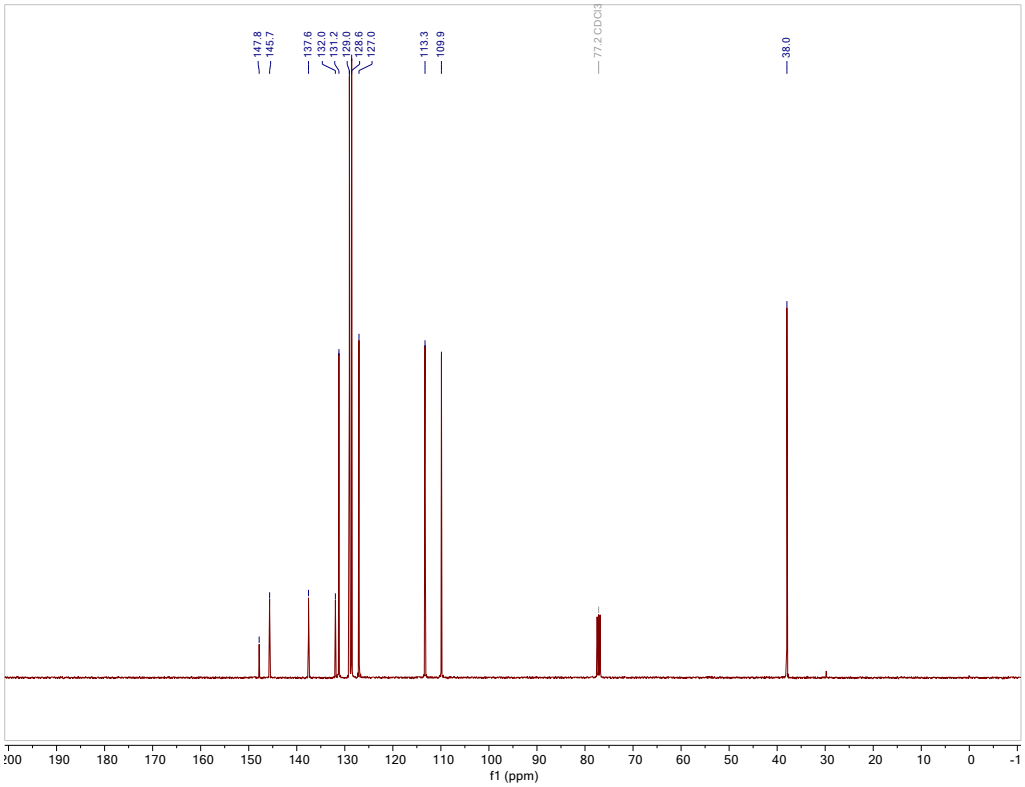
3-amino-4-benzylbenzonitrile (3ag): ^{13}C NMR, $CDCl_3$, 101 MHz



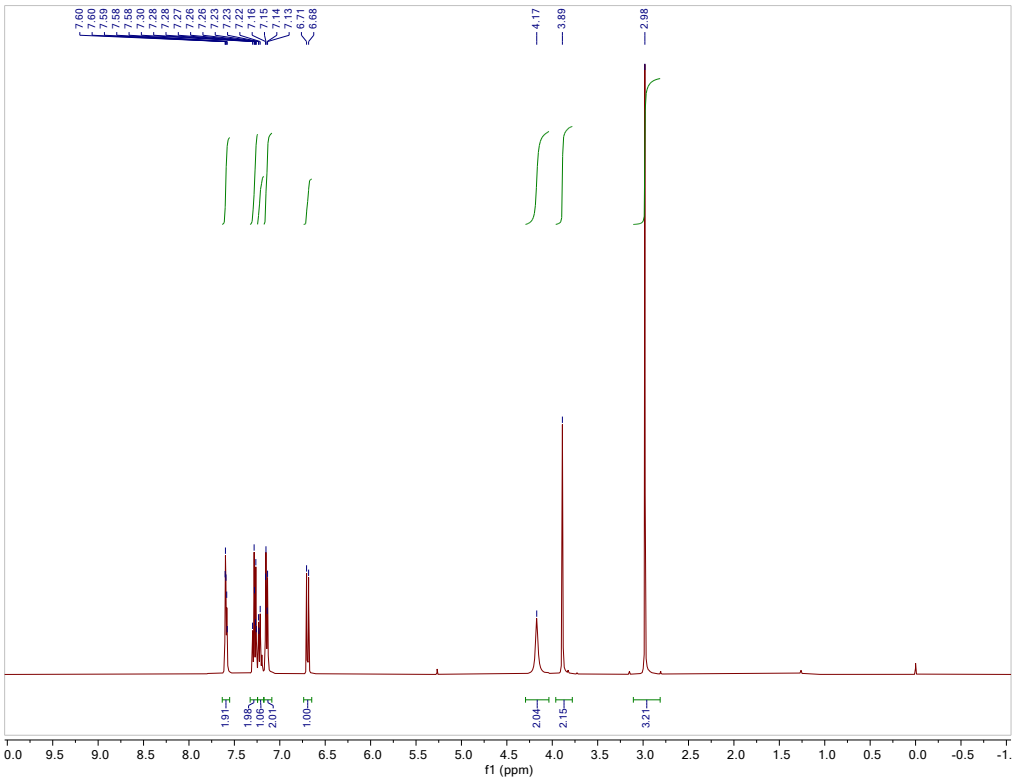
2-benzyl-5-nitroaniline (3ah): ^{1}H NMR, $CDCl_3$, 400 MHz



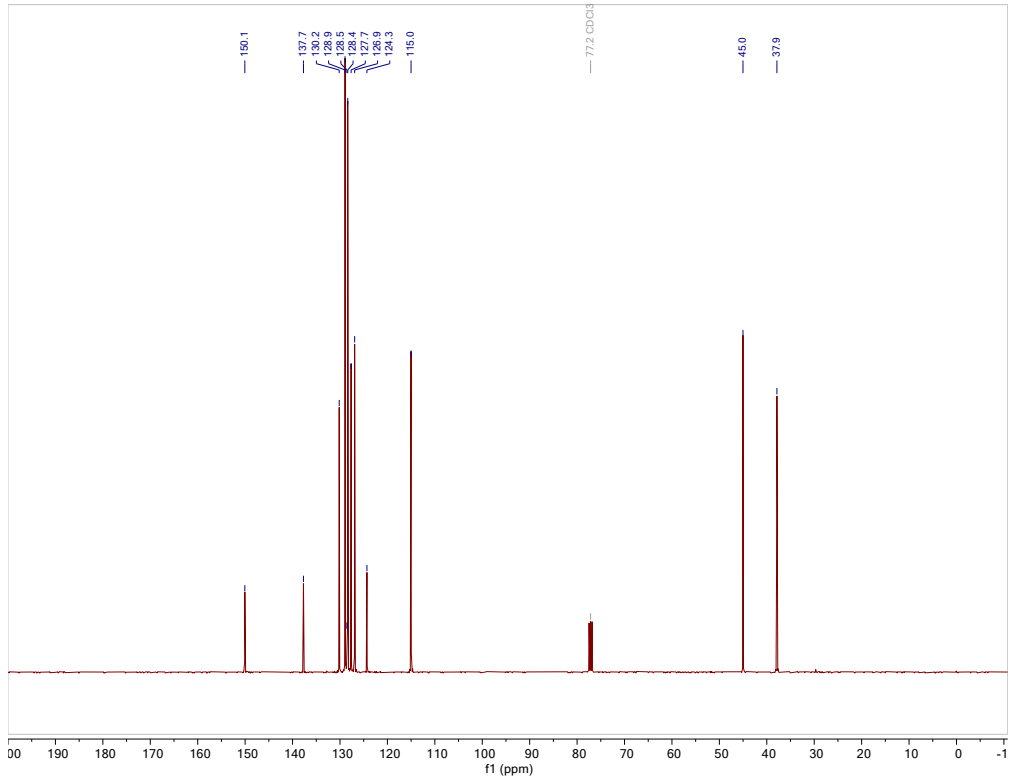
2-benzyl-5-nitroaniline (3ah): ^{13}C NMR, $CDCl_3$, 101 MHz



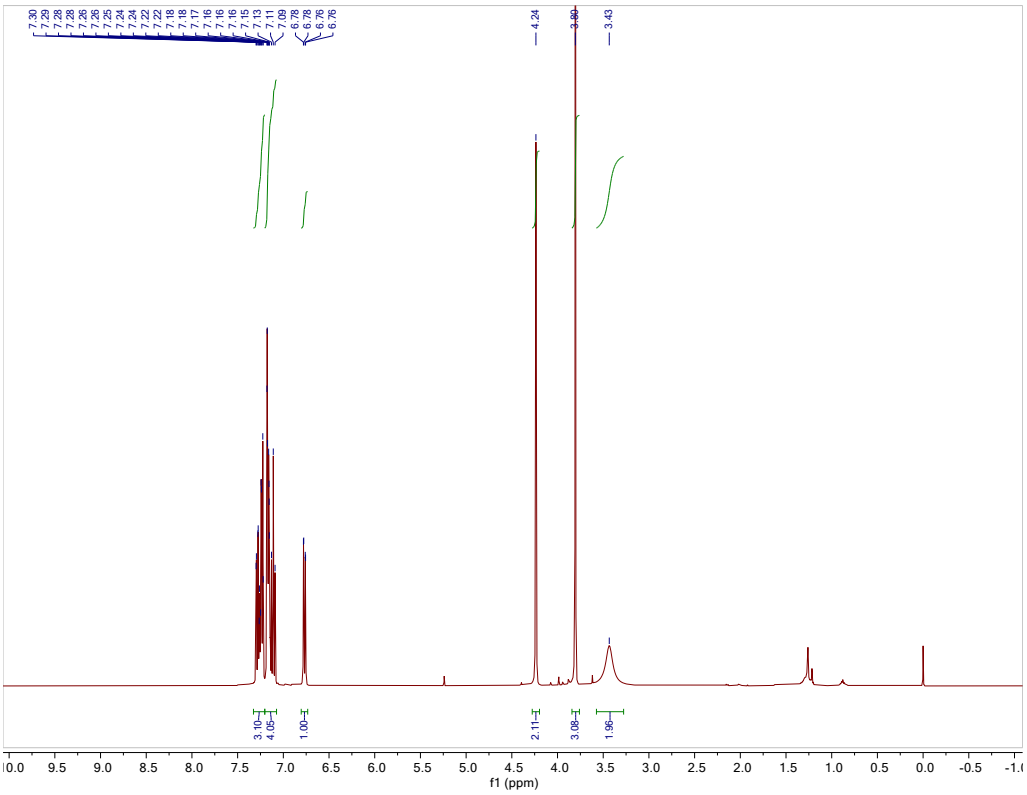
2-benzyl-4-(methylsulfonyl)aniline (3ai): ^{1}H NMR, $CDCl_3$, 400 MHz



2-benzyl-4-(methylsulfonyl)aniline (3ai): ^{13}C NMR, $CDCl_3$, 101 MHz



Methyl 3-amino-2-benzylbenzoate (3aj): ^{1}H NMR, $CDCl_3$, 400 MHz



Methyl 3-amino-2-benzylbenzoate (3aj): ^{13}C NMR, $CDCl_3$, 101 MHz