Supporting Information

1,4-Dihydropyridines as Alkyl Radical Precursors: Introducing the Aldehyde Feedstock to Nickel/Photoredox Dual Catalysis

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1. General considerations.

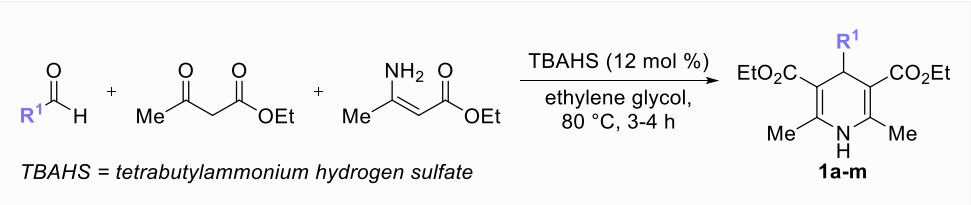
1.1 Reagents.

All reactions were carried out under an inert atmosphere of nitrogen or argon unless otherwise noted. Standard Schlenk techniques were used for the manipulation of solvents and reagents. Reactions were monitored by GC/MS, HPLC, ^{1}H NMR, and/or by TLC on silica gel plates (60 Å porosity, 250 µm thickness). TLC analysis was performed using hexanes/EtOAc as the eluant and visualized using permanganate stain and/or UV light. Silica plugs utilized flash silica gel (60 Å porosity, 32-63 µm). Flash chromatography was accomplished using an automated system (visualizing at 254 nm, monitoring at 280 nm) with silica cartridges (60 Å porosity, 20-40 µm). Solvents were purified either by distillation over sodium or CaH_2 or by use of drying cartridges through a solvent delivery system. Irradiation of reaction vessels was accomplished using blue LEDs (Light-emitting diode) at a distance of ~3 cm. A fan was employed to ensure reactions remained at or near rt when using LEDs.

1.2 Analytical Methods.

Melting points (°C) are uncorrected. NMR Spectra (^{1}H, ^{13}C {^{1}H}) were recorded on a 500 or 400 MHz spectrometer at 298 K. All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for $CHCl_3$ (7.26 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.2 ppm) and were obtained with ^{1}H decoupling. Coupling constants, *J*, are reported in Hertz (*Hz*). In the case of diastereisomeric mixtures, a crude NMR was recorded to determine the ratio. HRMS was obtained by either ESI or CI with a TOF spectrometer in MeCN or CH_2Cl_2. IR spectra were obtained on neat samples. The yields reported in Table 2 and Table 3 refer to isolated yields and represent an average of at least two independent runs. The procedures described in this section are representative. Thus, the yields may differ slightly from those given in Tables 2 and 3.

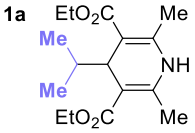
2. Synthesis of 1,4-Dihydropyridines:



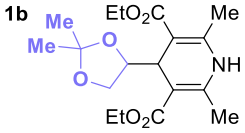
Scheme S1. Synthesis of 1,4-DHP derivatives.

General Procedure I: Synthesis of 1,4-dihydropyridnes: 1,4-Dihydropyridnes were prepared following a modified literature protocol.[1] Into a round-bottom flask charged with ethyl 3-aminocrotonate (1.0 equiv) was added ethylene glycol (2.5 M). Next, ethyl acetoacetate (1.0 equiv) was added followed by the aldehyde (1.0 equiv).[2] Finally, Bu_4NHSO_4 (12 mol %) was added in one portion. The flask was closed with a septum and heated at 80 ºC for 3-4 h. At this time, the reaction was cooled to rt and diluted with EtOAc. The solution was poured into a separatory funnel containing brine and extracted three times with EtOAc. After drying over $MgSO_4$, it was filtered and taken to dryness. The crude reaction mixture was purified using an automated system (visualizing at 254 nm, monitoring at 280 nm) with silica cartridges (60 Å porosity, 20-40 µm) using hexanes/EtOAc (0 to 40%) as eluent.

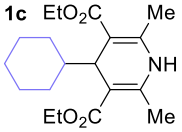
2.1 Characterization Data: 1,4-Dihydropyridines.



Diethyl 4-isopropyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1a): Following General Procedure I using isobutyraldehyde (793.2 mg, 11.0 mmol, 1.0 equiv). The product was isolated as a white solid (2.01 g, 62% yield). Mp = 95-97 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51 (s, 1H), 4.27 – 4.08 (m, 4H), 3.92 (d, *J* = 5.4 Hz, 1H), 2.30 (s, 6H), 1.63 – 1.57 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 6H), 0.75 (d, *J* = 6.9 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 144.7, 101.9, 59.7, 38.9, 35.7, 19.5, 18.6, 14.5 ppm. The spectral data were in agreement with those previously reported.[3]

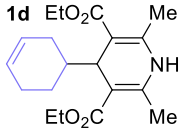


Diethyl 4-(2,2-dimethyl-1,3-dioxolan-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1b): Following General Procedure I using (*R*)-2,2-dimethyl-1,3-dioxolane-4-carboxaldehyde (1.0 g, 7.7 mmol, 1.0 equiv). The product was isolated as a white solid (1.85 g, 68% yield). Mp = 106-109 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.61 (br s, 1H), 4.32 (d, *J* = 4.9 Hz, 1H), 4.26 – 4.13 (m, 4H), 4.04 – 3.96 (m, 1H), 3.83 (td, *J* = 8.1, 1.9 Hz, 1H), 3.79 – 3.69 (m, 1H), 2.31 (dd, *J* = 5.0, 2.0 Hz, 6H), 1.36 – 1.24 (m, 12H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 168.1, 146.1, 145.5, 108.7, 99.8, 99.4, 79.6, 66.3, 59.9, 36.2, 26.3, 25.8, 19.6, 19.5, 14.5 ppm. IR (neat, cm^{-1}): 3327, 2984, 1693, 1664, 1206, 1095, 1046, 775. HRMS *calcd for* ($C_{18}H_{27}NO_6$+H) 354.1917, *found* 354.1903.

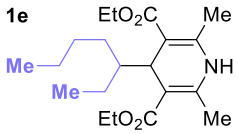


Diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1c): Following General Procedure I using cyclohexanecarboxaldehyde (1.1 g, 10.0 mmol, 1.0 equiv). The product was isolated as a white solid (1.88 g, 56% yield). Mp = 111-114 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51 (s, 1H), 4.27 – 4.09 (m, 4H), 3.92 (d, *J* = 5.6 Hz, 1H), 2.30 (s, 6H), 1.70 – 1.62 (m, 2H), 1.58 – 1.51 (m, 3H), 1.30 (t, *J* = 7.1 Hz, 6H), 1.25 – 1.17 (m, 1H), 1.13 – 1.03 (m, 3H), 0.99 – 0.86 (m, 2H) ppm. ^{13}C NMR (126 MHz,

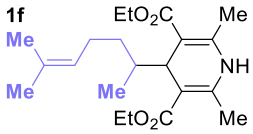
$CDCl_3$) δ 168.9, 145.0, 101.5, 59.6, 45.8, 38.4, 28.8, 26.7, 26.6, 19.2, 14.4 ppm. The spectroscopical data were in agreement with those previously reported.[4]



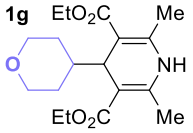
Diethyl 4-(cyclohex-3-en-1-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1d): Following General Procedure I using 3-cyclohexene-1-carboxaldehyde (1.4 g, 12.8 mmol, 1.0 equiv) The product was isolated as a white solid (2.26 g, 53% yield). Mp = 127-130 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.64 – 5.56 (m, 2H), 5.55 (s, 1H), 4.30 – 4.08 (m, 4H), 4.02 (d, *J* = 5.9 Hz, 1H), 2.31 (s, 6H), 2.11 – 1.84 (m, 3H), 1.82 – 1.72 (m, 1H), 1.68 – 1.59 (m, 1H), 1.58 – 1.50 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 6H), 1.26 – 1.13 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 168.6, 144.9, 144.8, 127.2, 126.8, 101.8, 59.8, 41.7, 37.9, 27.6, 26.2, 25.1, 19.7, 19.6, 14.5 ppm. IR (neat, cm^{-1}): 3350, 1644, 1485, 1215, 1098, 1049, 661. HRMS *calcd for* ($C_{19}H_{27}NO_4$+Na) 356.1838, *found* 358.1827.



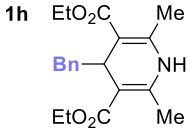
Diethyl 4-(heptan-3-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1e): Following General Procedure I using 2-ethylhexanal (1.3 g, 10.3 mmol, 1.0 equiv). The product was isolated as a yellow solid (2.20 g, 61% yield). Mp = 63-65 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.89 – 5.45 (m, 1H), 4.22 – 4.10 (m, 5H), 2.28 (d, *J* = 2.6 Hz, 6H), 1.30 (t, *J* = 7.1 Hz, 6H), 1.27 – 1.17 (m, 5H), 1.15 – 1.07 (m, 4H), 0.86 (t, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 169.0, 144.9, 144.8, 102.1, 102.0, 59.7, 48.2, 35.0, 29.6, 28.4, 23.3, 21.8, 19.3, 19.3, 14.4, 14.2, 11.9 ppm. IR (neat, cm^{-1}): 3361, 1618, 1486, 1268, 1200, 1110, 1096, 1017, 741. HRMS *calcd for* ($C_{20}H_{33}NO_4$+Na) 374.2307, *found* 374.2320.



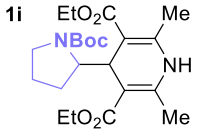
Diethyl 2,6-dimethyl-4-(7-methyloct-6-en-3-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1f): Following General Procedure I using 2,6-dimethyl-5-heptenal (1.7 g, 12.1 mmol, 1.0 equiv). The product was isolated as a yellow oil (2.47 g, 54% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46 (s, 1H), 5.03 (t, *J* = 7.0 Hz, 1H), 4.25 – 4.09 (m, 4H), 4.01 (d, *J* = 4.4 Hz, 1H), 2.29 (d, *J* = 3.6 Hz, 6H), 2.03 – 1.93 (m, 1H), 1.92 – 1.82 (m, 1H), 1.66 (s, 3H), 1.58 (s, 3H), 1.48 – 1.40 (m, 1H), 1.38 – 1.32 (m, 1H), 1.29 (td, *J* = 7.1, 2.7 Hz, 6H), 1.05 – 0.94 (m, 1H), 0.73 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 168.6, 144.8, 144.6, 130.9, 125.3, 102.2, 101.4, 59.7, 59.7, 41.0, 38.1, 32.8, 26.2, 25.8, 19.5, 19.4, 17.8, 15.1, 14.5, 14.5 ppm. The spectral data were in agreement with those previously reported.[5]



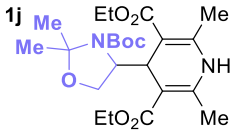
Diethyl 2,6-dimethyl-4-(tetrahydro-2H-pyran-4-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1g): Following General Procedure I using 4-formyltetrahydropyran (2.0 g, 17.8 mmol, 1.0 equiv). The product was isolated as a yellowish solid (4.09 g, 68% yield). Mp = 113-117 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60 (s, 1H), 4.25 – 4.12 (m, 4H), 3.99 (d, *J* = 5.9 Hz, 1H), 3.95 – 3.87 (m, 2H), 3.30 – 3.14 (m, 2H), 2.32 (s, 6H), 1.50 – 1.32 (m, 5H), 1.30 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 145.2, 101.3, 68.5, 59.8, 42.7, 37.8, 29.0, 19.6, 14.5 ppm. IR (neat, cm^{-1}): 3342, 1698, 1646, 1223, 1205, 1139, 1087, 772. HRMS *calcd for* ($C_{18}H_{27}NO_5$+H) 338.1967, *found* 338.1970.



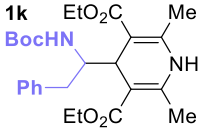
Diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1h): Following General Procedure I using phenylacetaldehyde (1.4 g, 11.5 mmol, 1.0 equiv). The product was isolated as a white solid (2.06 g, 52% yield). Mp = 102-106 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.11 (m, 3H), 7.02 (d, *J* = 7.8 Hz, 2H), 5.17 (s, 1H), 4.20 (t, *J* = 5.4 Hz, 1H), 4.13 – 3.98 (m, 4H), 2.58 (d, *J* = 5.5 Hz, 2H), 2.18 (s, 6H), 1.23 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 145.5, 139.4, 130.2, 127.4, 125.7, 102.0, 59.7, 42.4, 35.6, 19.4, 14.5 ppm. The spectral data were in agreement with those previously reported.[4]



Diethyl 4-(1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1i): Following General Procedure I using Boc-L-prolinal (1.0 g, 5.0 mmol, 1.0 equiv). The product was isolated as a yellow semisolid (1.31 g, 62% yield). Mixture of rotamers, major is reported: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (br s, 1H), 4.23–4.06 (m, 4H), 3.93 (d, *J* = 9.6 Hz, 1H), 3.63 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.26–3.22 (m, 2H), 2.32 (s, 3H), 2.20 (s, 3H), 2.01–1.78 (m, 4H), 1.38 (s, 9H), 1.30 (t, *J* = 7.0 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.2, 154.9, 147.9, 100.2, 78.6, 59.3, 45.6, 34.9, 28.4, 27.7, 24.9, 22.6, 19.0, 14.3 ppm; IR (neat, cm^{-1}): 2977, 2934, 1690, 1671, 1481, 1446, 1390, 1366, 1341, 1302, 1286, 1250, 1210, 1165, 1121, 1098, 1050, 1019. HRMS *calcd for* ($C_{22}H_{34}N_2O_6$+H) 423.2495, *found* 423.2485.



Diethyl 4-(3-(*tert*-butoxycarbonyl)-2,2-dimethyloxazolidin-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1j): Following General Procedure I using (*S*)-(-)-3-Boc-2,2-dimethyloxazolidine-4-carboxaldehyde (424.1 mg, 1.85 mmol, 1.0 equiv). The product was isolated as a white semisolid (524.0 mg, 63% yield). Mixture of rotamers, major is reported: ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.97 (s, 1H), 4.29 (d, *J* = 9.0 Hz, 1H), 4.23–4.16 (m, 4H), 3.90 (m, 1H), 3.76–3.73 (m, 1H), 3.67–3.65 (m, 1H), 2.32 (s, 3H), 2.24 (s, 3H), 1.48 (s, 3H), 1.43 (s, 9H), 1.39 (s, 3H), 1.27 (t, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.8, 153.6, 146.8, 100.0, 64.0, 79.6, 65.6, 60.3, 59.6, 36.1, 28.4, 26.6 (gem dimethyl), 24.5 (gem dimethyl), 19.3, 14.4 ppm; IR (neat, cm^{-1}): 3333, 2979, 2937, 1692, 1551, 1480, 1366, 1285, 1252, 1213, 1170, 1096, 1049, 951. HRMS *calcd for* ($C_{23}H_{36}N_2O_7$+Na) 475.2420, *found* 475.2417.



Diethyl 4-(1-((*tert*-butoxycarbonyl)amino)-2-phenylethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1k): Following General Procedure I using *N*-Boc-L-phenylalaninal (1.0 g, 4.0 mmol, 1.0 equiv). The product was isolated as a white solid (701.2 mg, 37% yield). Mp = 146–147 °C; Mixture of rotamers, major is reported (Coalescence was observed at 330 K): ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.92 (s, 1H), 7.15–7.12 (m, 2H), 7.11–7.06 (m, 3H), 5.95 (d, *J* = 6.0 Hz, 1H), 4.11–3.96 (m, 4H), 3.90 (d, *J* = 7.2 Hz, 1H), 3.37–3.35 (m, 1H), 3.59–2.54 (m, 2H), 2.23 (s, 3H), 2.18 (s, 3H), 1.04 (br s, 15H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 167.4, 155.0, 146.6, 140.2, 128.7, 127.7, 125.4, 98.6, 76.7, 58.9, 55.5, 37.7, 30.6, 28.1, 18.4, 14.4 ppm. IR (neat, cm^{-1}): 1693, 1659, 1632, 1528, 1474, 1368, 1303, 1252, 1236, 1206, 1166, 1122, 1097, 1053, 1038, 1010, 776.

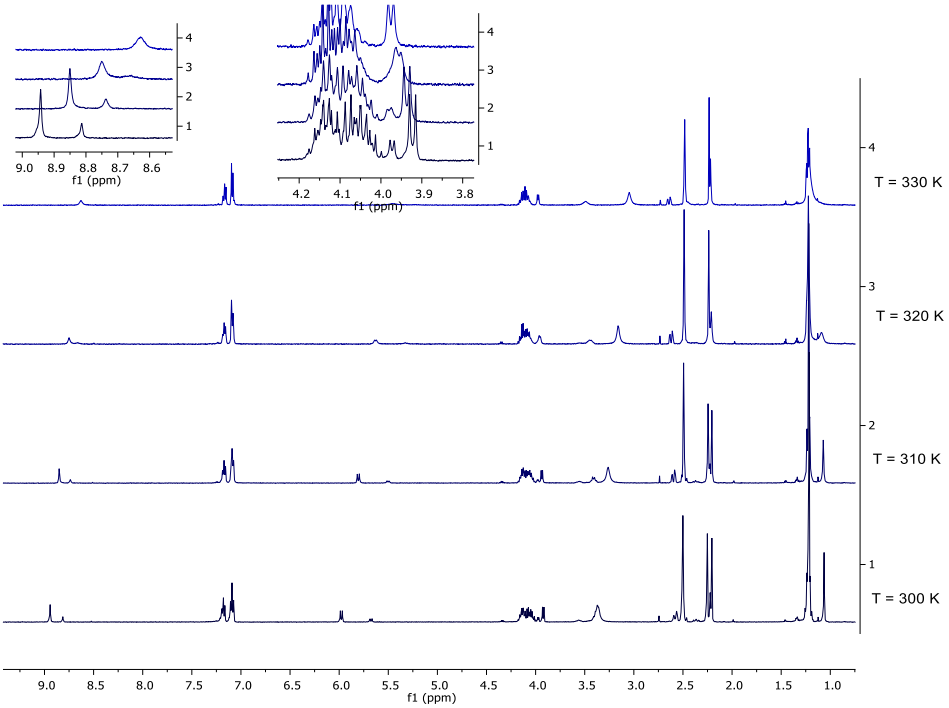
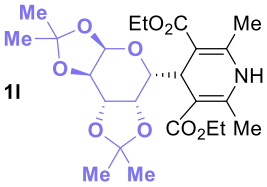


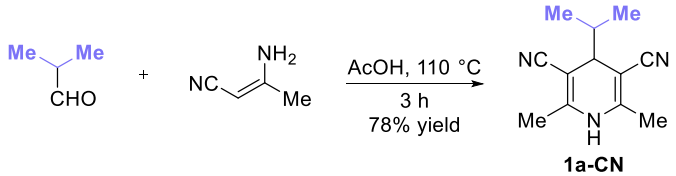
Figure S1. Coalescence Studies for Substrate **1k**



1l

Diethyl 2,6-dimethyl-4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1l): Following General Procedure using (3a*R*,5*S*,5a*R*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-carbaldehyde[6] (1.24 g, 4.94 mmol, 1.0 equiv). The product was isolated as a white solid (1.27 g, 53% yield). Mp = 154-159 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 (d, *J* = 4.9 Hz, 1H), 4.49 (d, *J* = 7.3 Hz, 1H), 4.46 (d, *J* = 7.9 Hz, 1H), 4.26 – 4.08 (m, 6H), 3.46 (d, *J* = 7.5 Hz, 1H), 2.31 (s, 3H), 2.29 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.33 – 1.23 (m, 12H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 168.3, 145.7, 144.0, 109.2, 108.2, 101.1, 99.4, 96.8, 71.7, 71.3, 70.1, 59.9, 59.5, 35.0, 26.1, 26.0, 25.2, 24.9, 19.2, 14.4, 14.4 ppm. The spectroscopical data were in agreement with those previously reported.[1]

2.1 Synthesis and Characterization of compound 4-isopropyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile (1a-CN)



1a-CN

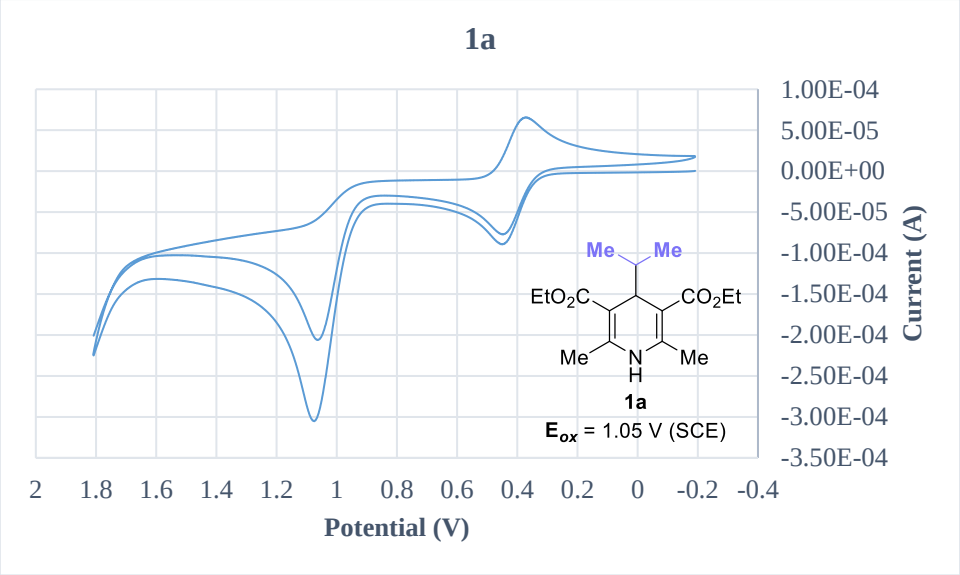
A round bottom flask was charged with 3-aminocrotononitrile (1.6 g, 20 mmol), butyraldehyde (721.2 mg, 10 mmol) and glacial AcOH (10 mL). The reaction was heated at 110 ºC with stirring for 3 h. Then it was allowed to cool to rt, diluted with H_2O and extracted with EtOAc three times. The combined organic layers were neutralized with a saturated solution of $NaHCO_3$ until a netural pH was reached, washed with brine, dried ($MgSO_4$), and filtered. The crude reaction mixture was purified using an automated system using hexanes/EtOAc (0 to 40%) as eluent, obtaining the product as a white solid (1.56 g, 78% yield). Mp = 118-120 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (s, 1H), 3.16 (d, *J* = 3.3 Hz, 1H), 2.13 (s, 6H), 1.95 – 1.86 (m, 1H), 1.00 (d, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 120.0, 81.9, 42.2, 35.9, 18.3, 18.3

ppm. IR (neat, cm-1): 3277, 3234, 3118, 2197, 1655, 1507, 1435, 1287, 1012, 622. HRMS *calcd for* ($C_{12}H_{15}N_3$+H) 202.1344, *found* 202.1350.

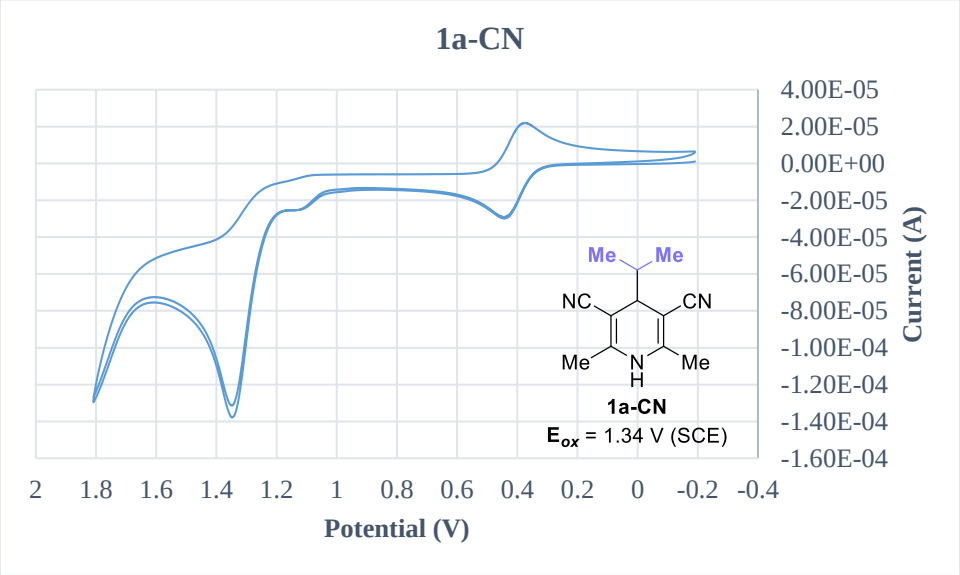
3. Cyclic Voltammetry Measurements

Voltammetric measurements were recorded on a CH Instruments: Model 600E Series Electrochemical Analyzer using a standard three electrode setup in dry and degassed MeCN (10 mL), with ferrocene as internal reference ($E^0_{1/2}$ = + 0.41 V vs SCE) and tetrabutylammonium hexafluorophosphate as electrolyte (0.10 mmol). Cyclic voltammograms were recorded with a step potential of 0.002 V at a scan rate of 0.1 V/s. Voltammetric measurements were repeated at different scan rate to ensure the accuracy of the measurement.

3.1 Cyclic Voltammetry of Compound 1a



3.2 Cyclic Voltammetry of Compound 1a-C



4. Synthesis of [Ni(dtbbpy)(H_2O)$_4$]Cl_2

4.1 Experimental Procedure: Into a Schlenk flask charged with $NiCl_2{\cdot}(H_2O)_6$ (885.6 mg, 3.725 mmol, 1.0 equiv) and 4 4'-di-*tert*-butyl-2 2'-bipyridine (dtbbpy) (1.0 g, 3.7 mmol, 1.0 equiv) was added EtOH

(37.0 mL, 0.1 M, reagent grade). The reaction was heated at 80 ºC for 14-16 h. The resuting green solution was taken to dryness, and the green solid obtained was washed with cold THF and filtered. The green solid was collected and dried under vacuum, allowing isolation of $[Ni(dtbbpy)(H_2O)_4]Cl_2$ in 78% yield. Mp > 250 ºC. Suitable crystals for X-Ray analysis were obtained by slow evaporation of a THF solution of the nickel(II) complex. IR (neat, cm^{-1}): 3297, 2963, 1614, 1551, 1409, 1366, 1250, 862, 607.

5. Optimization of Reaction Conditions.

5.1 General Procedure for Screening Reactions and Control Experiments: A 5.0 mL test tube was charged with Ni precatalyst ($5x10^{-3}$ mmol, 5 mol %), ligand (if necessary) ($5x10^{-3}$ mmol, 5 mol %), photocatalyst ($3x10^{-3}$ mmol, 3 mol %), 1,4-dihydropyridine **1a** (35.4 mg, 0.12 mmol, 1.2 equiv) and 4-bromobenzonitrile **2a** (18.2 mg, 0.1 mmol, 1.0 equiv). The vial was capped, and three cycles of vacuum/argon were made. Next, degassed solvent[7] was added (2.0 mL, 0.05 M). The reaction was placed under blue LED irradiation and stirred for 24 h at rt. After this time, 4,4′-di-*tert*-butylbiphenyl (2.7 mg, 0.01 mmol, 0.1 equiv) was added as internal standard followed by 1.0 mL of MeCN. An aliquot was filtered through a plug of silica and Celite® and analyzed by HPLC.

5.2 Control Experiments.

Entry	$[Ni(dtbbpy)(H_2O)_4]Cl_2$	4-CzlPN	Light	3aa yield (%)
1	×	✓	✓	0
2	✓	×	✓	0
3	✓	✓	×	0

6. Scope.

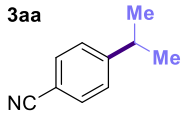
6.1 General Procedures

General Procedure A (GP-A): A 20.0 mL sealable screw cap vial was charged with **1** (0.6 mmol, 1.2 equiv) and **2** (0.5 mmol, 1.0 equiv) if solids followed by addition of $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (11.8 mg, 0.025 mmol, 5 mol %) and 4CzlPN (11.8 mg, 0.015 mmol, 3 mol %). The vial was sealed and three vacuum/argon cycles were made. Next, dry, degassed acetone[7] was added (10.0 mL, 0.05 M). If the (hetero)aryl bromide **2** or **1** were oils, they were added at this point as a solution in acetone or directly via microsyringe. The reaction was placed under blue LED irradiation and stirred for 24 h at rt. Next, the reaction was taken to dryness and purified on an automated liquid chromatographic system, obtaining the pure product.

General Procedure B (GP-B): A 20.0 mL sealable screw cap vial was charged with **1** (0.75 mmol, 1.5 equiv) and **2** (0.5 mmol, 1.0 equiv) if solids followed by addition of $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (23.6 mg, 0.025 mmol, 10 mol %) and 4CzlPN (11.8 mg, 0.015 mmol, 3 mol %). The vial was sealed and three vacuum/argon cycles were made. Next, dry, degassed acetone[7] was added (10.0 mL, 0.05 M). If the (hetero)aryl bromide **2** or **1** were oils, they were added at this point as a solution in acetone or directly via microsyringe. The reaction was placed under blue LED irradiation and stirred for 24 h at rt. Next, the reaction was taken to dryness and purified on an automated liquid chromatographic system, obtaining the pure product.

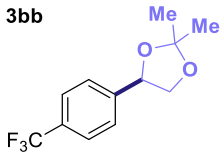
6.2 Characterization Data: (Hetero)aryl bromide scope (Table 2):

3aa

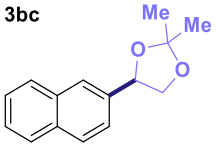


4-Isopropylbenzonitrile (3aa): Prepared following GP-A using **1a** (177.2 mg, 0.6 mmol) and **2a** (91.0 mg, 0.5 mmol). The product was purified using hexanes/EtOAc (0 to 5%) on an automated system and was obtained as a colorless oil (43.8 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 7.1 Hz, 2H),

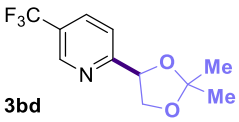
7.32 (d, J = 7.7 Hz, 2H), 3.00 – 2.90 (m, 1H), 1.26 (d, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 132.4, 127.4, 119.3, 109.7, 34.5, 23.7 ppm. The spectral data were in agreement with those previously reported.[8]



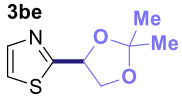
2,2-Dimethyl-4-(4-(trifluoromethyl)phenyl)-1,3-dioxolane (3bb): Prepared following GP-B using **1b** (265.1 mg, 0.75 mmol) and **2b** (112.5 mg, 0.5 mmol). The product was purified using pentane/Et_2O (0 to 15%) on an automated system and was obtained as a colorless oil (42.5 mg, 35% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 7.9 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 5.13 (t, J = 7.1 Hz, 1H), 4.35 (t, J = 7.6 Hz, 1H), 3.69 (t, J = 8.2 Hz, 1H), 1.55 (s, 3H), 1.50 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 130.3 (q, J = 32.8 Hz), 126.5, 125.6 (q, J = 3.6 Hz), 124.2 (q, J = 272.0 Hz), 110.3, 77.3, 71.6, 26.6, 26.0 ppm. IR (neat, cm^{-1}): 2989, 1621, 1323, 1160, 1122, 1112, 1063, 833.



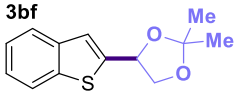
2,2-Dimethyl-4-(naphthalen-2-yl)-1,3-dioxolane (3bc): Prepared following GP-B using **1b** (265.1 mg, 0.75 mmol) and **2c** (103.5 mg, 0.5 mmol). The product was purified using hexanes/Et_2O (3:1) and obtained as a colorless oil (47.0 mg, 46% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 6.6 Hz, 4H), 7.49 (d, J = 7.7 Hz, 3H), 5.26 (s, 1H), 4.39 (s, 1H), 3.81 (t, J = 8.4 Hz, 1H), 1.63 (s, 3H), 1.55 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7, 133.4, 133.3, 128.6, 128.1, 127.9, 126.4, 126.1, 125.4, 124.0, 110.0, 78.2, 71.7, 26.8, 26.1 ppm. IR (neat, cm^{-1}): 2985, 1379, 1370, 1212, 1154, 1060, 855. HRMS *calcd for* ($C_{15}H_{16}O_2$+H) 229.1229, *found* 229.1226.



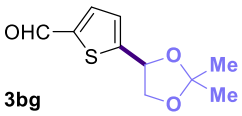
2-(2,2-Dimethyl-1,3-dioxolan-4-yl)-5-(trifluoromethyl)pyridine (3bd): Prepared following GP-A using **1b** (212.1 mg, 0.6 mmol) and **2d** (113.0 mg, 0.5 mmol). The product was purified using pentane/Et_2O (0 to 40%) on an automated system and obtained as a colorless oil (74.1 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.94 (dd, J = 8.3, 2.3 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 5.25 (t, J = 6.7 Hz, 1H), 4.50 (dd, J = 8.5, 7.0 Hz, 1H), 3.98 (dd, J = 8.5, 6.3 Hz, 1H), 1.53 (s, 3H), 1.51 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 146.1 (q, J = 3.4 Hz), 134.0 (q, J = 3.4 Hz), 126.9 – 124.7 (m), 122.6, 119.9, 110.8, 77.9, 70.2, 26.6, 25.6 ppm. IR (neat, cm^{-1}): 2990, 1607, 1373, 1325, 1213, 1159, 1124, 1077, 844. HRMS *calcd for* ($C_{11}H_{12}F_3NO_2$+H) 248.0898, *found* 248.0891.



2-(2,2-Dimethyl-1,3-dioxolan-4-yl)thiazole (3be): Prepared following GP-B using **1b** (265.1 mg, 0.75 mmol) and **2e** (82.0 mg, 0.5 mmol). The product was purified using pentane/Et_2O (0 to 40%) on an automated system and obtained as a yellow oil (48.4 mg, 52% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 3.3 Hz, 1H), 7.30 (d, J = 3.3 Hz, 1H), 5.40 (t, J = 6.1 Hz, 1H), 4.44 (dd, J = 8.6, 6.6 Hz, 1H), 4.08 (dd, J = 8.6, 5.6 Hz, 1H), 1.57 (s, 3H), 1.47 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 143.1, 119.3, 111.1, 75.7, 70.5, 26.6, 25.5 ppm. IR (neat, cm^{-1}): 2987, 2936, 1721, 1210, 1142, 842, 724, 510. HRMS *calcd for* ($C_8H_{11}NO_2S$+H) 186.0589, *found* 186.0589.

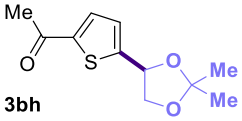


4-(Benzo[b]thiophen-2-yl)-2,2-dimethyl-1,3-dioxolane (3bf): Prepared following GP-B using **1b** (265.1 mg, 0.75 mmol) and **2f** (106.5 mg, 0.5 mmol). The product was purified using hexanes/Et_2O (5:1) and obtained as a colorless oil (34.0 mg, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.17 (m, 2H), 7.16 (s, 1H), 5.32 (t, *J* = 6.7 Hz, 1H), 4.34 – 4.19 (m, 1H), 3.89 (t, *J* = 7.8 Hz, 1H), 1.50 (s, 3H), 1.41 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 139.8, 139.6, 124.5, 124.5, 123.6, 122.6, 121.5, 110.5, 74.6, 71.4, 26.7, 26.0 ppm. IR (neat, cm^{-1}): 3056, 2986, 2935, 1208, 1061, 837, 583. HRMS *calcd for* ($C_{13}H_{14}O_2S$) 234.0711, *found* 234.0715. HRMS *calcd for* ($C_{13}H_{14}O_2S$+H) 235.0793, *found* 235.0782.



3bg

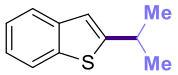
5-(2,2-Dimethyl-1,3-dioxolan-4-yl)thiophene-2-carbaldehyde (3bg): Prepared following GP-A using **1b** (212.1 mg, 0.6 mmol) and **2g** (95.5 mg, 0.5 mmol). The product was purified using hexanes/EtOAc (0 to 20%) on an automated system and was obtained as a yellow oil (71.4 mg, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.65 (d, *J* = 3.1 Hz, 1H), 7.09 (d, *J* = 3.3 Hz, 1H), 5.32 (t, *J* = 6.5 Hz, 1H), 4.36 (t, *J* = 7.3 Hz, 1H), 3.86 (t, *J* = 7.6 Hz, 1H), 1.55 (s, 3H), 1.46 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.0, 154.8, 143.2, 136.4, 125.4, 110.9, 74.1, 71.6, 26.6, 25.8 ppm. IR (neat, cm^{-1}): 3073, 1418, 1231, 1212, 1044, 726, 663.



3bh

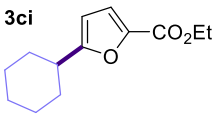
1-(5-(2,2-Dimethyl-1,3-dioxolan-4-yl)thiophen-2-yl)ethan-1-one (3bh): Prepared following GP-B using **1b** (265.1 mg, 0.75 mmol) and **2h** (102.5 mg, 0.5 mmol). The product was purified using hexanes/Et_2O (5:1) and obtained as a yellow oil (39.0 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.01 (s, 1H), 5.28 (d, *J* = 6.7 Hz, 1H), 4.34 (t, *J* = 7.5 Hz, 1H), 3.85 (t, *J* = 7.8 Hz, 1H), 2.53 (s, 3H), 1.54 (s, 3H), 1.46 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 190.7, 152.8, 143.9, 132.4, 125.4, 110.8, 74.1, 71.6, 26.8, 26.6, 25.9 ppm. IR (neat, cm^{-1}): 2987, 1662, 1276, 1061. HRMS *calcd for* ($C_{11}H_{14}O_3S$+H) 227.0742, *found* 227.0743.

6.3 Characterization Data: (Hetero)aryl bromide scope (Table 3):



3af

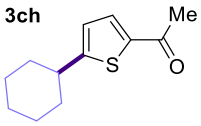
2-Isopropylbenzo[b]thiophene (3af): Prepared following GP-B using **1a** (221.4 mg, 0.75 mmol) and **2f** (106.5 mg, 0.5 mmol). The product was purified using hexanes/Et_2O (5:1) and obtained as a clear oil (61.2, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.03 (s, 1H), 3.26 (hept, *J* = 7.0 Hz, 1H), 1.42 (d, *J* = 6.8 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 140.2, 139.0, 124.1, 123.5, 122.9, 122.3, 118.4, 30.7, 24.5 ppm. IR (neat, cm^{-1}): 2962, 2930, 1457, 1436, 1071, 1001, 855. HRMS *calcd for* ($C_{11}H_{12}S$+H) 177.0738, *found* 177.0745.



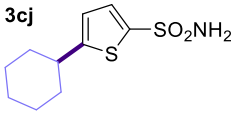
3ci

Ethyl 5-cyclohexylfuran-2-carboxylate (3ci): Prepared following GP-A using **1c** (203.1 mg, 0.6 mmol) and **2i** (109.5 mg, 0.5 mmol). The product was purified using hexanes/EtOAc (0 to 20%) on an automated system and was obtained as a colorless oil (73.5 mg, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 3.5 Hz, 1H), 6.08 (d, *J* = 3.4 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.73 – 2.66 (m, 1H), 2.05 (d, *J* = 10.8 Hz, 2H), 1.80 (d, *J* = 12.6 Hz, 2H), 1.71 (d, *J* = 12.8 Hz, 1H), 1.46 – 1.30 (m, 7H), 1.30 – 1.19 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 159.1, 142.9, 118.9, 105.5, 60.7, 37.6, 31.4, 26.0, 25.9, 14.5 ppm.

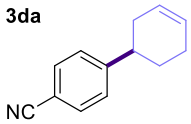
IR (neat, cm^{-1}): 2929, 2855, 1517, 1294, 1213, 1174, 1138, 1120, 799. HRMS *calcd for* ($C_{13}H_{18}O_3$+H) 223.1334, *found* 223.1344.



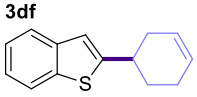
1-(5-Cyclohexylthiophen-2-yl)ethan-1-one (3ch): Prepared following GP-A using **1c** (203.1 mg, 0.6 mmol) and **2h** (102.5 mg, 0.5 mmol). The product was purified using hexanes/EtOAc (0 to 15%) on an automated system and was obtained as a white solid (47.2 mg, 45% yield). Mp = 48-52 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 3.6 Hz, 1H), 6.83 (d, *J* = 3.7 Hz, 1H), 2.87 – 2.77 (m, 1H), 2.51 (s, 3H), 2.04 (d, *J* = 11.3 Hz, 2H), 1.83 (d, *J* = 11.7 Hz, 2H), 1.73 (d, *J* = 11.3 Hz, 1H), 1.52 – 1.33 (m, 4H), 1.32 – 1.19 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.7, 162.4, 141.4, 132.8, 123.6, 40.2, 35.2, 26.6, 26.4, 25.9 ppm. IR (neat, cm^{-1}): 2927, 2854, 1645, 1447, 1354, 1030, 927, 807, 595. HRMS *calcd for* ($C_{12}H_{16}O_S$+H) 209.1000, *found* 209.0991.



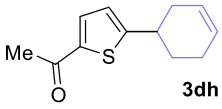
5-Cyclohexylthiophene-2-sulfonamide (3cj): Prepared according to GP-B using **1c** (251.6 mg, 0.75 mmol) and **2j** (121.0 mg, 0.5 mmol). The product was purified using hexanes/EtOAc (9:1) and obtained as a yellow oil (12.0 mg, 24% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 3.8 Hz, 1H), 6.76 (d, *J* = 3.8 Hz, 1H), 4.87 (s, 2H), 2.82 (s, 1H), 2.05 (d, *J* = 10.0 Hz, 2H), 1.84 (d, *J* = 10.6 Hz, 2H), 1.41 (h, *J* = 12.3 Hz, 4H), 1.26 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 139.0, 132.1, 122.4, 40,0, 35.3, 26.4, 25.8 ppm. IR (neat, cm^{-1}): 2931, 1447, 1334, 1157. HRMS *calcd for* ($C_{10}H_{15}NO_2S_2$+H) 246.0622, *found* 246.0630.



1',2',3',6'-Tetrahydro-[1,1'-biphenyl]-4-carbonitrile (3da): Prepared following GP-A using **1d** (200.1 mg, 0.6 mmol) and **2a** (91.0 mg, 0.5 mmol). The product was purified using hexanes/EtOAc (0 to 5%) on an automated system and was obtained as a white solid (39.0 mg, 43% yield). Mp = 53-55 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.77 (s, 2H), 2.93 – 2.80 (m, 1H), 2.33 – 2.25 (m, 1H), 2.24 – 2.08 (m, 3H), 1.97 – 1.89 (m, 1H), 1.79 – 1.71 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 132.4, 127.9, 127.2, 126.2, 119.2, 109.9, 40.4, 32.9, 29.4, 25.5 ppm. IR (neat, cm^{-1}): 3024, 2917, 2836, 226, 1607, 830, 690, 651, 561. HRMS *calcd for* ($C_{13}H_{13}N$+H) 184.1126, *found* 184.1123.

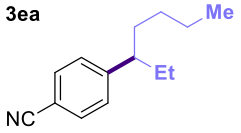


2-(Cyclohex-3-en-1-yl)benzo[b]thiophene (3df): Prepared following GP-B using **1d** (249.9 mg, 0.75 mmol) and **2f** (106.5 mg, 0.5 mmol). The product was purified using hexanes/Et_2O (5:1) and obtained as a clear oil (40.3 mg, 38% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.3 Hz, 1H), 7.06 (s, 1H), 5.78 (s, 2H), 3.20 (s, 1H), 2.57 – 2.40 (m, 1H), 2.27 – 2.18 (m, 1H), 2.16 – 2.04 (m, 3H), 2.00 – 1.86 (m, 1H), 1.79 – 1.59 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 140.2, 139.0, 127.2, 126.0, 124.2, 123.6, 123.0, 122.3, 118.8, 36.2, 33.6, 30.7, 25.5 ppm. IR (neat, cm^{-1}): 3023, 2916, 1436, 1068, 854, 734. HRMS *calcd for* ($C_{14}H_{14}S$+H) 215.0894, *found* 215.0891.

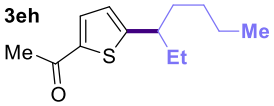


1-(5-(Cyclohex-3-en-1-yl)thiophen-2-yl)ethan-1-one (3dh): Prepared following GP-B using **1d** (249.9 mg, 0.75 mmol) and **2h** (102.5 mg, 0.5 mmol). The product was purified using hexanes/Et_2O (5:1) and was

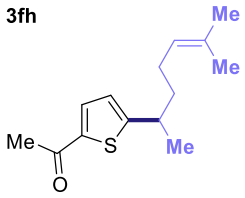
obtained as a clear oil (67.3 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 3.8 Hz, 1H), 6.87 (d, *J* = 3.7 Hz, 1H), 5.75 (s, 2H), 3.14 (tt, *J* = 9.5, 4.1 Hz, 1H), 2.52 (s, 3H), 2.49 – 2.37 (m, 1H), 2.28 – 2.13 (m, 3H), 2.13 – 2.04 (m, 1H), 1.76 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.7, 190.7, 161.3, 141.8, 132.8, 127.2, 125.7, 124.0, 36.2, 33.6, 30.7, 26.6, 25.3 ppm. IR (neat, cm^{-1}): 3025, 2913, 2837, 1659, 1455, 1278, 670. HRMS *calcd for* ($C_{12}H_{14}OS$+H) 207.0844, *found* 207.0847.



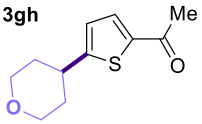
4-(Heptan-3-yl)benzonitrile (3ea): Prepared following GP-A using **1e** (210.7 mg, 0.6 mmol) and **2a** (91.0 mg, 0.5 mmol). The product was purified using hexanes/EtOAc (0 to 5%) on an automated system and was obtained as a colorless oil (56.2 mg, 56% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 6.8 Hz, 2H), 7.23 (d, *J* = 6.9 Hz, 2H), 2.52 – 2.41 (m, 1H), 1.75 – 1.61 (m, 2H), 1.59 – 1.46 (m, 2H), 1.34 – 1.16 (m, 2H), 1.20 – 1.08 (m, 1H), 1.10 – 0.98 (m, 1H), 0.82 (t, *J* = 7.3 Hz, 3H), 0.74 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 132.2, 128.7, 119.3, 109.7, 48.3, 36.0, 29.8, 29.5, 22.8, 14.1, 12.2 ppm. IR (neat, cm^{-1}): 2959, 2927, 2873, 2858, 2227, 1607, 1460, 834, 570. HRMS *calcd for* ($C_{14}H_{19}N$+H) 202.1596, *found* 202.1595.



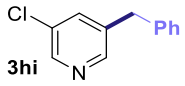
1-(5-(Heptan-3-yl)thiophen-2-yl)ethan-1-one (3eh): Prepared following GP-B using **1e** (0.75 mmol, 252.9 mg) and **2h** (102.5 mg, 0.5 mmol). The product was purified using hexanes/Et_2O (5:1) and was obtained as a clear oil (51.3 mg, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 3.8 Hz, 1H), 6.80 (d, *J* = 3.8 Hz, 1H), 2.74 (tt, *J* = 9.4, 5.2 Hz, 1H), 2.52 (s, 3H), 1.71 (m, 2H), 1.64 – 1.50 (m, 2H), 1.37 – 1.11 (m, 4H), 0.84 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.6, 160.9, 141.9, 132.7, 125.3, 44.1, 37.2, 30.8, 29.7, 26.6, 22.7, 14.1, 12.0 ppm. IR (neat, cm^{-1}): 2960, 2929, 1661, 1457, 1278, 809. HRMS *calcd for* ($C_{14}H_{22}OS$+H) 239.1470, *found* 239.1470.



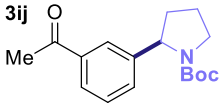
1-(5-(6-Methylhept-5-en-2-yl)thiophen-2-yl)ethan-1-one (3fh): Prepared following GP-B using **1f** (261.9 mg, 0.75 mmol) and **2h** (102.5 mg, 0.5 mmol). The product was purified using hexanes/Et_2O (5:1) and was obtained as a yellow oil (92.0 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 6.81 (s, 1H), 5.06 (s, 1H), 3.05 – 3.01 (m, 1H), 2.50 (s, 3H), 1.95 (m, 2H), 1.65 (m, 5H), 1.53 (s, 3H), 1.31 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.6, 162.2, 141.7, 132.7, 132.2, 124.3, 123.7, 39.2, 35.8, 26.6, 25.9, 25.8, 23.0, 17.8 ppm. IR (neat, cm^{-1}): 2965, 2918, 1600, 1447, 1276, 807. HRMS *calcd for* ($C_{14}H_{20}OS$+H) 237.1313, *found* 237.1296.



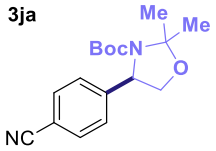
1-(5-(Tetrahydro-2H-pyran-4-yl)thiophen-2-yl)ethan-1-one (3gh): Prepared following GP-A using **1g** (253.1 mg, 0.75 mmol) and **2h** (102.5 mg, 0.5 mmol). The product was purified using hexanes/EtOAc (0 to 30%) on an automated system and was obtained as a white solid (80.1 mg, 77% yield). Mp = 58-61 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 3.8 Hz, 1H), 6.87 (d, *J* = 3.8 Hz, 1H), 4.26 – 3.91 (m, 2H), 3.52 (td, *J* = 11.8, 2.1 Hz, 2H), 3.11 – 3.00 (m, 1H), 2.52 (s, 3H), 2.01 – 1.89 (m, 2H), 1.82 (ddd, *J* = 24.7, 11.9, 4.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5, 159.6, 141.9, 132.8, 123.8, 67.8, 37.3, 34.5, 26.6 ppm. IR (neat, cm^{-1}): 1650, 1448, 1271, 1087, 1015, 877, 818, 600. HRMS *calcd for* ($C_{11}H_{14}O_2S$+H) 211.0793, *found* 211.0780.



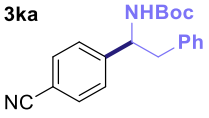
3-Benzyl-5-chloropyridine (3hi): Prepared following GP-A using **1h** (253.1 mg, 0.75 mmol), **2i** (102.5 mg, 0.5 mmol) and [Ni(dme)(dtbbpy)]Br_2 (14.0 mg, 0.025 mmol, 5 mol %). The product was purified using pentane/Et_2O (0 to 40%) on an automated system and was obtained as a colorless oil (42.9 mg, 42% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.38 (s, 1H), 7.45 (s, 1H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.21 (m, 1H), 7.17 (d, *J* = 7.4 Hz, 2H), 3.97 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0, 146.7, 138.9, 138.0, 136.1, 132.1, 129.0 (2C), 126.9, 38.7 ppm. IR (neat, cm^{-1}): 3029, 1579, 1419, 1104, 1025, 708, 696, 682. HRMS *calcd for* ($C_{12}H_{10}ClN$+H) 204.0580, *found* 204.0587.



***tert*-Butyl 2-(3-acetylphenyl)pyrrolidine-1-carboxylate (3ij):** Prepared following GP-B using **1i** (316.9 mg, 0.75 mmol) and **2j** (99.5 mg, 0.5 mmol). The product was purified using hexanes/EtOAc (0 to 20%) on an automated system to afford a light yellow oil (55.0 mg, 38% yield); Mixture of rotamers, major is reported: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (m, 1H), 7.75 (s, 1H), 7.40–7.35 (m, 2H), 4.79 (br s, 1H), 3.63 (br, 2H), 2.57 (s, 3H), 2.34 (br, 1H), 1.87–1.82 (m, 3H), 1.43 (s, 4H, Boc), 1.14 (s, 5H, Boc) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ 198.0, 154.4, 145.7, 137.1, 130.1, 128.4, 126.7, 125.3, 79.3, 61.1, 47.1, 35.9, 34.8, 28.4, 26.6, 23.2 ppm; IR (neat, cm^{-1}): 2974, 2931, 2899, 1684, 1602, 1587, 1478, 1390, 1364, 1256, 1159, 1115, 1080, 957, 905, 876. HRMS *calcd for* ($C_{17}H_{23}NO_3$+Na) 312.1576, *found* 312.1561.

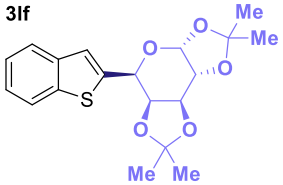


***tert*-Butyl 4-(4-cyanophenyl)-2,2-dimethyloxazolidine-3-carboxylate (3ja):** Prepared following GP-B using **1j** (135.8 mg, 0.3 mmol) and **2a** (36.4 mg, 0.2 mmol). The product was purified using hexanes/EtOAc (0 to 10%) on an automated system to afford a light yellow oil (22.0 mg, 37% yield); Mixture of rotamers, major is reported: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.42 (m, 2H), 4.83 (br s, 1H), 4.30 (dd, *J* = 9.0, 7.0 Hz, 1H), 3.83 (m, 1H), 1.60 (s, 3H), 1.58 (s, 3H), 1.45 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.6, 140.9, 132.4, 127.1, 118.7, 111.2, 95.0, 80.3, 70.2, 60.8, 28.3, 26.0 (gem dimethyl), 24.9 (gem dimethyl) ppm; IR (neat, cm^{-1}): 2980, 2929, 2229, 1695, 1609, 1505, 1478, 1457, 1376, 1365, 1255, 1206, 1171, 1146, 1088, 1057. HRMS *calcd for* ($C_{17}H_{22}N_2O_3$+H) 303.1709, *found* 303.1712.

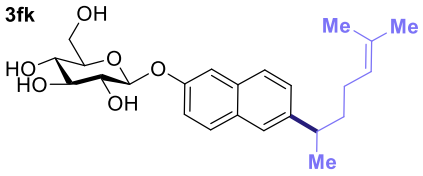


***tert*-Butyl (1-(4-cyanophenyl)-2-phenylethyl)carbamate (3ka):** Prepared following GP-B using **1k** (141.8 mg, 0.3 mmol) and **2a** (36.4 mg, 0.2 mmol). The product was purified using hexanes/EtOAc (0 to 20%) on an automated system to afford a light yellow oil (28.1 mg, 47%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.36–7.21 (m, 5H), 7.01 (d, *J* = 6.5 Hz, 2H), 4.97 (br s, 2H), 3.02 (br s, 2H), 1.40 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ 155.1, 136.3, 132.4, 129.4 (2C), 128.7, 127.3, 127.1, 118.9, 111.1, 80.2, 55.8, 43.1, 28.4 ppm; IR (neat, cm^{-1}) 2978, 2229, 1695, 1608, 1495, 1455, 1391, 1366, 1289, 1247, 1163, 1108, 1045, 1018, 911. HRMS *calcd for* ($C_{20}H_{22}N_2O_2$+H) 323.1760, *found* 323.1772.

6.4 Characterization Data: Synthesis of aryl-containing saccharides (Figure 1):



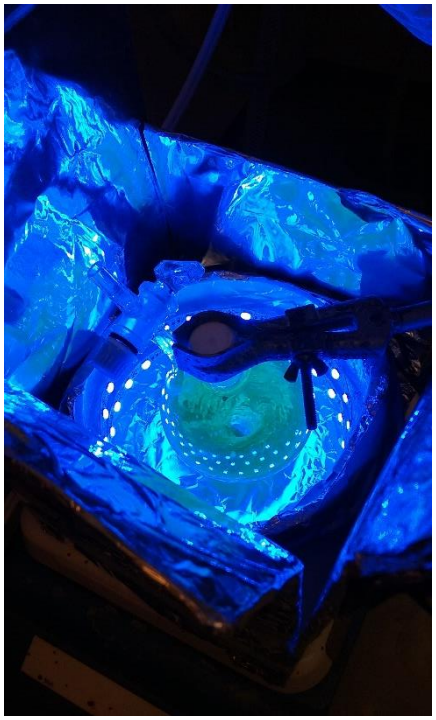
(3a*R*,5*S*,5a*R*,8a*S*,8b*R*)-5-(Benzo[b]thiophen-2-yl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (3lf): Prepared following GP-B using **1l** (0.525 mmol 252.8 mg) and **2f** (0.35 mmol, 74.6 mg). The product was purified using hexanes/EtOAc (0 to 30%) on an automated system and was obtained as a white solid with a >20:1 dr (89.3 mg, 70% yield). Mp = 118-120 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.41 (s, 1H), 7.38 – 7.28 (m, 2H), 5.63 (d, *J* = 5.0 Hz, 1H), 5.15 (s, 1H), 4.74 (dd, *J* = 7.8, 2.3 Hz, 1H), 4.54 (dd, *J* = 7.8, 2.0 Hz, 1H), 4.47 (dd, *J* = 4.7, 1.9 Hz, 2H), 1.53 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6) δ 141.8, 139.2, 138.7, 124.1, 124.0, 123.3, 122.1, 121.3, 108.6, 108.2, 96.2, 72.8, 70.4, 69.9, 66.7, 25.9 (2C), 24.7, 24.2 ppm. The absolute configuration was determined by NOE NMR experiments in combination with HSQC and HMBC experiments. IR (neat, cm^{-1}): 2927, 1377, 1163, 1142, 1065, 1040, 996, 895, 746. HRMS *calcd for* ($C_{19}H_{22}O_5S$+H) 363.1266, *found* 363.1248. Crystals suitable for X-Ray difraction were achieved by slow evaporation of an acetonitrile solution of compound **3lf.**



(2*R*,3*S*,4*S*,5*R*,6*S*)-2-(Hydroxymethyl)-6-((6-(6-methylhept-5-en-2-yl)naphthalen-2-yl)oxy)tetrahydro-2H-pyran-3,4,5-triol (3fk): Prepared following GP-B using **1f** (261.9 mg, 0.75 mmol) and **2k** (192.6 mg, 0.5 mmol). The product was purified using EtOAc/MeOH (9:1) and obtained as a light yellow oil (262.0 mg, 31% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.78 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.61 (s, 1H), 7.42 (s, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.22 (d, *J* = 9.1 Hz, 1H), 5.33 (d, *J* = 4.5 Hz, 1H), 5.12 – 5.05 (m, 2H), 5.00 (dd, *J* = 11.8, 6.1 Hz, 2H), 4.56 (t, *J* = 5.8 Hz, 1H), 3.73 (dd, *J* = 12.1, 5.2 Hz, 1H), 3.50 (dt, *J* = 11.9, 6.1 Hz, 1H), 3.40 (t, *J* = 7.8 Hz, 1H), 3.32 – 3.27 (m, 2H), 3.21 (dt, *J* = 14.2, 6.8 Hz, 1H), 2.81 (h, *J* = 7.1 Hz, 1H), 1.83 (tt, *J* = 14.5, 7.3 Hz, 2H), 1.73 – 1.54 (m, 5H), 1.44 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.3, 143.2, 133.2, 131.4, 129.8, 129.3, 127.6, 126.7, 126.7, 125.3, 125.3, 124.9, 119.3, 111.0, 111.0, 101.3, 101.3, 77.7, 77.3, 73.9, 70.4, 61.3, 39.3, 38.4, 26.3, 26.1, 22.8, 18.1 ppm. IR (neat, cm^{-1}): 3413, 2254, 2128, 1659, 1208, 1023, 823.

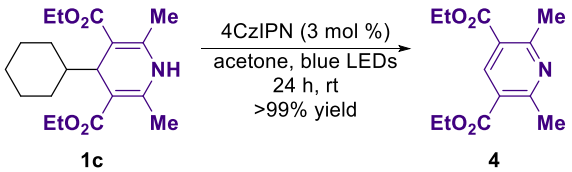
7. Gram Scale Reaction.

The reaction was done following procedure A: A 250.0 mL Schlenk flask was charged with **1g** (2.47 g, 7.31 mmol, 1.5 equiv), **2h** (1.0 g, 4.88 mmol, 1.0 equiv), [Ni(dtbbpy)(H_2O)$_4$]Cl_2 (114.7 mg, 0.24 mmol, 5 mol %) and 4CzlPN (118.3 mg, 0.15 mmol, 3 mol %). Next, three vacuum/argon cycles were made and dry, degassed acetone was added via cannula (100.0 mL, 0.05 M). The reaction was placed under blue LED irradiation and stirred for 24 h at rt. Next, the reaction was taken to dryness and purified on an automated system using hexanes/EtOAc obtaining the pure product **3gh**. The obtained product presented no differences with the 0.5 mmol scale reaction.



8. Mechanistic Studies.

8.1 1,4-DHP decomposition studies: Stability under photocatalytic conditions



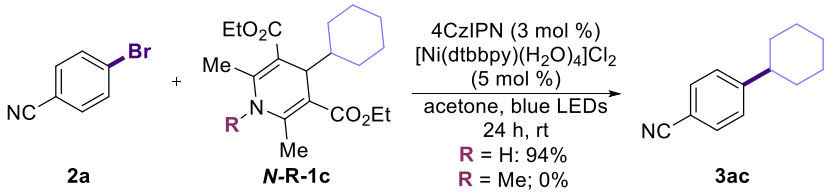
1c 4

A 5.0 mL sealable screw cap vial was charged with **1c** (40.3 mg, 0.12 mmol, 1.2 equiv) and 4CzlPN (2.4 mg, 0.003 mmol, 2.5 mol %). The vial was sealed and three vacuum/argon cycles were made. Next, dry, degassed acetone was added (2.0 mL, 0.05 M). The reaction was placed under blue LED irradiation and

stirred for 24 h at rt. Next, the reaction was taken to dryness and $MeNO_2$ (14.6 mg, 0.24 mmol, 2.0 equiv) was added as internal standard. The crude was diluted with $CDCl_3$ (0.5 mL) and analyzed by ^1H NMR, showing quantitative yield (>99%) for the formation of pyridine **4**. GC-MS analysis showed formation of cyclohexane and bicyclohexyl. Such behavior has been already reported.[9]

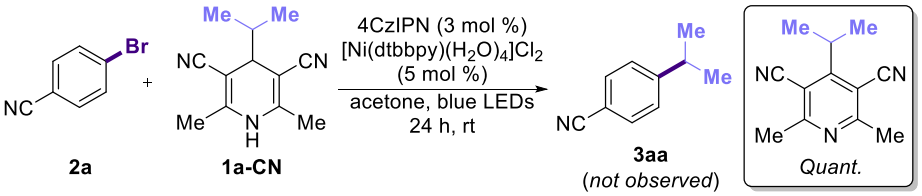
Based on the previous experiment, in cases were low yields of cross-coupled product were obtained, the reaction was attempted using General Procedure B in which the amount of Ni-precatalyst and 1,4-DHP are increased to achieve higher yields of the expected product.

8.2 1,4-DHP decomposition studies: Deprotonative pathway.



A 5.0 mL sealable screw cap vial was charged with ***N*-R-1c** (0.12 mmol, 1.2 equiv), **2a** (18.2 mg, 0.1 mmol, 1.0 equiv), $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (2.4 mg, 0.005 mmol, 5 mol %) and 4CzlPN (2.4 mg, 0.003 mmol, 2.5 mol %). The vial was sealed and three vacuum/argon cycles were made. Next, dry, degassed acetone was added (2.0 mL, 0.05 M). The reaction was placed under blue LED irradiation and stirred for 24 h at rt. Next, the reaction was taken to dryness and $MeNO_2$ (14.6 mg, 0.24 mmol, 2.0 equiv) was added as internal standard. The crude was diluted with $CDCl_3$ (0.5 mL) and analyzed by ^1H NMR, showing 94% yield of **3ac** when starting from ***N*-H-1c**, and no product formation when using ***N*-Me-1c**, thus suggesting that after SET and formation of a radical cation a proton needs to be released to ensure the C-C cleavage event.[9a]

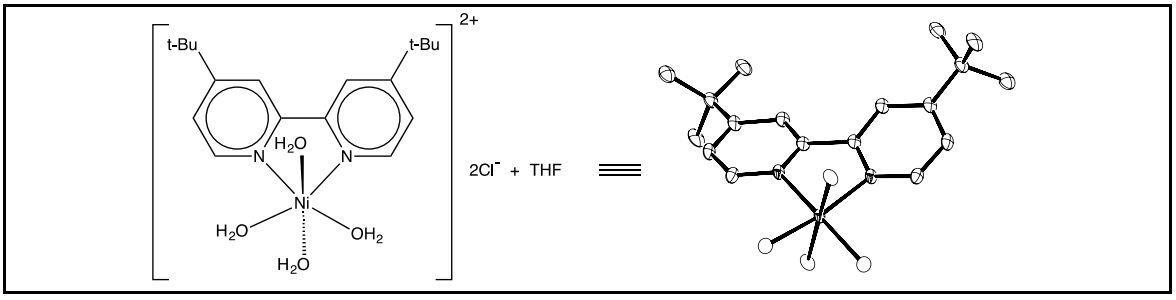
8.3 1,4-DHP: Backbone Influence.



A 5.0 mL sealable screw cap vial was charged with **1c-CN** (24.1 mg, 0.12 mmol, 1.2 equiv), **2a** (18.2 mg, 0.1 mmol, 1.0 equiv), $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (2.4 mg, 0.005 mmol, 5 mol %) and 4CzlPN (2.4 mg, 0.003 mmol, 2.5 mol %). The vial was sealed and three vacuum/argon cycles were made. Next, dry, degassed acetone was added (2.0 mL, 0.05 M). The reaction was placed under blue LED irradiation and stirred for 24 h at rt. After this time, 4,4′-di-*tert*-butylbiphenyl (2.7 mg, 0.01 mmol, 0.1 equiv) was added as internal standard followed by 1.0 mL of MeCN. An aliquot was filtered through a plug of silica and Celite® and analyzed by HPLC and GC-MS, showing no product formation.

9. X-Ray Crystallographic data

9.1 X-Ray Crystallograpic data for [Ni(dtbbpy)(H₂O)₄]Cl₂:



Compound $[Ni(dtbbpy)(H_2O)_4]Cl_2$, $C_{22}H_{40}Cl_2N_2NiO_5$, crystallizes in the monoclinic space group C2/c (systematic absences hkl: h+k=odd, h0l: l=odd) with a=13.0843(9)Å, b=30.400(2)Å, c=6.6223(5)Å, β=92.470(2)°, V=2631.7(3)Å^3, Z=4, and d_{calc}=1.368 g/cm$_3$. X-ray intensity data were collected on a Bruker D8QUEST [1] CMOS area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073Å) at a temperature of 100K. Preliminary indexing was performed from a series of twenty-four 0.5° rotation frames with exposures of 10 seconds. A total of 1614 frames were collected with a crystal to detector distance of 34.1 mm, rotation widths of 0.5° and exposures of 15 seconds:

scan type	2θ	ω	φ	χ	Frames
ω	0.00	195.50	0.00	54.72	298
ϕ	-1.00	345.19	0.00	54.72	720
ω	0.00	195.50	90.00	54.72	298
ω	0.00	195.50	180.00	54.72	298

Rotation frames were integrated using SAINT [2], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 36013 reflections were measured over the ranges $6.234 \leq 2\theta \leq 50.876°$, $-15 \leq h \leq 15$, $-36 \leq k \leq 36$, $-7 \leq l \leq 7$ yielding 2417 unique reflections (R_{int} = 0.0650). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS [3] (minimum and maximum transmission 0.5113, 0.7456). The structure was solved by direct methods - SHELXT [4]. Refinement was by full-matrix least squares based on F^2 using SHELXL-2014 [5]. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.1083P)^2 + 11.2889P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model, except for the water hydrogens, which were located on a difference map, but were not refined. Refinement converged to R1=0.0571 and wR2=0.1568 for 2217 observed reflections for which $F > 4\sigma(F)$ and R1=0.0617 and wR2=0.1639 and GOF =1.083 for all 2417 unique, non-zero reflections and 149 variables. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +2.33 and -1.28 e/Å^3.

Table S1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables S2. and S3. Anisotropic thermal parameters are in Table S4. Tables S5. and S6. list bond distances and bond angles. Figure S2. is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

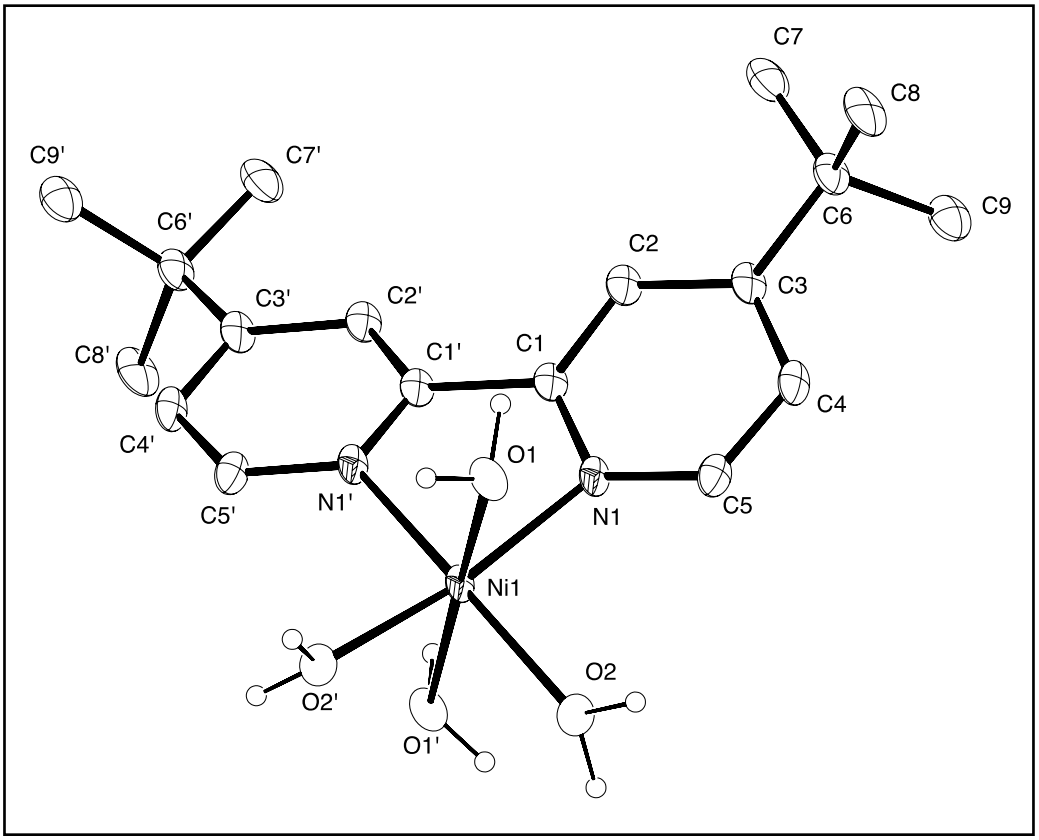


Figure S2. ORTEP drawing of the title compound with 50% thermal ellipsoids.

Table S1. Summary of Structure Determination of Compound $[Ni(dtbbpy)(H_2O)_4]Cl_2$

Empirical formula	$C_{22}H_{40}Cl_2N_2NiO_5$
Formula weight	542.17
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a	13.0843(9)Å
b	30.400(2)Å
c	6.6223(5)Å
β	92.470(2)°
Volume	2631.7(3)$Å^3$
Z	4
d_{calc}	1.368 g/cm^3
μ	0.974 mm^{-1}
F(000)	1152.0
Crystal size, mm	0.28 × 0.18 × 0.03
2θ range for data collection	6.234 - 50.876°
Index ranges	$-15 \leq h \leq 15$, $-36 \leq k \leq 36$, $-7 \leq l \leq 7$
Reflections collected	36013
Independent reflections	2417[R(int) = 0.0650]
Data/restraints/parameters	2417/0/149
Goodness-of-fit on F^2	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0571, wR_2 = 0.1568
Final R indexes [all data]	R_1 = 0.0617, wR_2 = 0.1639
Largest diff. peak/hole	2.33/-1.28 $eÅ^{-3}$

Table S2. Refined Positional Parameters for Compound [Ni(dtbbpy)(H_2O)$_4$]Cl_2

Atom	*x*	*y*	*z*	U(eq)
Ni1	0.5	0.75601(2)	0.75	0.0138(2)
O1	0.34718(18)	0.76087(8)	0.8088(4)	0.0195(5)
O2	0.47754(17)	0.80527(8)	0.5361(4)	0.0200(5)
N1	0.45760(19)	0.70343(9)	0.5649(4)	0.0152(6)
C1	0.4691(2)	0.66373(11)	0.6532(5)	0.0157(7)
C2	0.4241(2)	0.62601(11)	0.5727(5)	0.0171(7)
C3	0.3651(2)	0.62789(11)	0.3920(5)	0.0172(7)
C4	0.3560(2)	0.66888(12)	0.2989(5)	0.0180(7)
C5	0.4021(2)	0.70527(12)	0.3898(5)	0.0181(7)
C6	0.3068(2)	0.58811(11)	0.3054(5)	0.0194(7)
C7	0.3345(3)	0.54563(12)	0.4189(6)	0.0269(8)
C8	0.1919(2)	0.59735(14)	0.3260(6)	0.0256(8)
C9	0.3289(3)	0.58191(12)	0.0807(6)	0.0242(8)
Cl1	0.69206(6)	0.81637(3)	0.31042(12)	0.0181(3)
O3	0	0.50320(12)	0.75	0.0273(8)
C10	0.0828(3)	0.53080(13)	0.8217(6)	0.0265(8)
C11	0.0407(3)	0.57674(13)	0.8358(6)	0.0281(8)

Table S3. Positional Parameters for Hydrogens in Compound [Ni(dtbbpy)(H_2O)$_4$]Cl_2

Atom	*x*	*y*	*z*	U(eq)
H1a	0.3391	0.7728	0.9211	0.05
H1b	0.334	0.7305	0.8116	0.05
H2a	0.4259	0.8094	0.4652	0.05
H2b	0.5279	0.8162	0.4574	0.05
H2	0.4331	0.5993	0.6394	0.023
H4	0.3191	0.6718	0.1764	0.024
H5	0.3943	0.7324	0.3262	0.024
H7a	0.4067	0.5404	0.413	0.04
H7b	0.2976	0.5215	0.3575	0.04
H7c	0.3167	0.5484	0.5575	0.04
H8a	0.153	0.5722	0.2809	0.038
H8b	0.1723	0.6224	0.245	0.038
H8c	0.1789	0.6032	0.465	0.038
H9a	0.4002	0.5756	0.0679	0.036
H9b	0.3114	0.6083	0.0078	0.036
H9c	0.2888	0.5579	0.0263	0.036
H10a	0.138	0.53	0.7287	0.035
H10b	0.1089	0.5209	0.9533	0.035
H11a	0.093	0.5987	0.8144	0.037
H11b	0.011	0.5819	0.9654	0.037

Table S4. Refined Thermal Parameters (U's) for Compound $[Ni(dtbbpy)(H_2O)_4]Cl_2$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni1	0.0037(3)	0.0250(4)	0.0126(4)	0	-0.0016(2)	0
O1	0.0078(12)	0.0304(13)	0.0204(13)	-0.005(1)	0.0008(9)	-0.0016(9)
O2	0.0088(11)	0.0308(13)	0.0202(12)	0.0051(10)	-0.0029(9)	0.0005(9)
N1	0.0056(12)	0.0267(14)	0.0133(13)	-0.0002(11)	-0.0011(10)	0.0008(10)
C1	0.0049(14)	0.0271(17)	0.0152(16)	-0.0004(13)	0.0014(12)	-0.0006(12)
C2	0.0083(15)	0.0259(17)	0.0172(16)	-0.0006(13)	0.0004(12)	0.0009(12)
C3	0.0042(15)	0.0302(18)	0.0171(16)	-0.0016(13)	0.0003(12)	0.0000(12)
C4	0.0078(15)	0.0313(18)	0.0147(16)	0.0000(13)	-0.0020(12)	0.0025(13)
C5	0.0110(15)	0.0282(18)	0.0151(16)	0.0025(13)	-0.0003(12)	0.0026(13)
C6	0.0102(16)	0.0274(18)	0.0202(18)	-0.0015(13)	-0.0026(13)	-0.0014(13)
C7	0.0210(18)	0.0289(19)	0.030(2)	-0.0005(15)	-0.0080(15)	-0.0072(15)
C8	0.0074(17)	0.041(2)	0.028(2)	-0.0068(16)	-0.0015(14)	-0.0036(14)
C9	0.0151(17)	0.0320(19)	0.0254(19)	-0.0046(15)	0.0008(14)	-0.0027(14)
Cl1	0.0078(4)	0.0288(5)	0.0174(5)	0.0010(3)	-0.0018(3)	0.0004(3)
O3	0.0175(18)	0.031(2)	0.033(2)	0	-0.0010(15)	0
C10	0.0127(17)	0.037(2)	0.030(2)	0.0014(16)	-0.0021(14)	-0.0001(14)
C11	0.0157(17)	0.036(2)	0.033(2)	-0.0028(16)	-0.0012(16)	-0.0037(15)

Table S5. Bond Distances in Compound [Ni(dtbbpy)(H_2O)$_4$]Cl_2, Å

Ni1-O1	2.059(2)	Ni1-O1	2.059(2)	Ni1-O2	2.073(2)
Ni1-O2	2.073(2)	Ni1-N1	2.075(3)	Ni1-N1	2.075(3)
N1-C1	1.347(4)	N1-C5	1.343(4)	C1-C1	1.486(6)
C1-C2	1.385(5)	C2-C3	1.397(5)	C3-C4	1.393(5)
C3-C6	1.529(5)	C4-C5	1.386(5)	C6-C7	1.530(5)
C6-C8	1.540(4)	C6-C9	1.540(5)	O3-C10	1.435(4)
O3-C10	1.435(4)	C10-C11	1.505(5)	C11-C11	1.524(7)

[1]1-X,+Y,3/2-Z; [2]-X,+Y,3/2-Z

Table S6. Bond Angles in Compound [Ni(dtbbpy)(H_2O)$_4$]Cl_2, °

O1-Ni1-O1[1]	171.76(14)	O1-Ni1-O2[1]	85.93(9)	O1-Ni1-O2[1]	88.12(10)
O1-Ni1-O2	88.12(10)	O1-Ni1-O2	85.93(9)	O1-Ni1-N1[1]	100.41(10)
O1-Ni1-N1	100.41(10)	O1-Ni1-N1[1]	85.99(10)	O1-Ni1-N1	85.98(10)
O2-Ni1-O2[1]	87.53(14)	O2-Ni1-N1[1]	170.46(10)	O2-Ni1-N1	170.46(10)
O2-Ni1-N1	97.26(10)	O2-Ni1-N1[1]	97.26(10)	N1-Ni1-N1	79.24(15)
C1-N1-Ni1	114.3(2)	C5-N1-Ni1	126.8(2)	C5-N1-C1	117.3(3)
N1-C1-C1	114.91(18)	N1-C1-C2	122.5(3)	C2-C1-C1	122.6(2)
C1-C2-C3	120.4(3)	C2-C3-C6	122.5(3)	C4-C3-C2	116.7(3)
C4-C3-C6	120.6(3)	C5-C4-C3	119.6(3)	N1-C5-C4	123.5(3)
C3-C6-C7	112.3(3)	C3-C6-C8	107.2(3)	C3-C6-C9	110.3(3)
C7-C6-C8	108.8(3)	C7-C6-C9	108.7(3)	C9-C6-C8	109.4(3)
C10-O3-C10	108.4(4)	O3-C10-C11	106.9(3)	C10-C11-C11	101.5(2)

[1]1-X,+Y,3/2-Z; [2]-X,+Y,3/2-Z

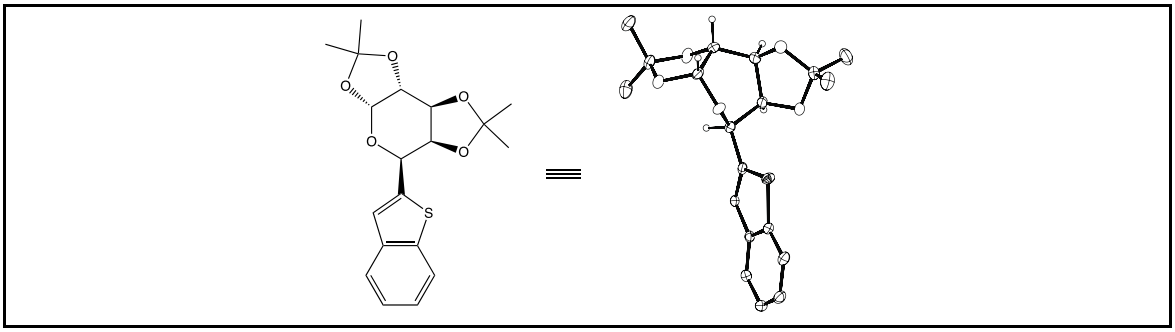
Table S7. Hydrogen Bonds for [Ni(dtbbpy)(H_2O)$_4$]Cl_2.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1a	Cl1[1]	0.838(2)	2.2683(8)	3.095(2)	169.09(17)
O1	H1b	Cl1[2]	0.940(2)	2.3404(8)	3.104(2)	138.10(14)
O2	H2a	Cl1[3]	0.816(2)	2.3486(8)	3.141(2)	164.06(17)
O2	H2b	Cl1	0.920(2)	2.3960(8)	3.254(2)	155.18(15)

[1]1-X,+Y,3/2-Z; [2]-1/2+X,3/2-Y,1/2+Z; [3]1-X,+Y,1/2-Z

This report has been created with Olex2 [6], compiled on 2016.05.11 svn.r3296 for OlexSys.

9.2 X-Ray crystallographic data for compound (3a*R*,5*S*,5a*R*,8a*S*,8b*R*)-5-(Benzo[b]thiophen-2-yl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (3lf)



Compound **3lf**, $C_{19}H_{22}O_5S$, crystallizes in the orthorhombic space group $P2_12_12_1$ (systematic absences h00: h=odd, 0k0: k=odd and 00l: l=odd) with a=5.63430(10)Å, b=17.0439(4)Å, c=18.3976(4)Å, V=1766.73(6)Å^3, Z=4, and d_{calc}=1.363 g/cm$_3$. X-ray intensity data were collected on a Bruker APEXII [1] CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073Å) at a temperature of 100K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. A total of 4232 frames were collected with a crystal to detector distance of 37.4 mm, rotation widths of 0.5° and exposures of 10 seconds:

scan type	2θ	ω	φ	χ	Frames
ϕ	24.50	7.41	12.48	28.88	739
ϕ	-23.00	334.21	44.72	73.66	727
ϕ	-20.50	342.55	321.55	-73.06	542
ω	-23.00	333.49	158.99	-70.01	69
ω	-25.50	330.51	47.91	-56.95	137
ω	27.00	276.67	5.00	57.63	227
ϕ	-23.00	315.83	12.48	28.88	739
ϕ	19.50	59.55	348.71	-26.26	739
ω	17.00	321.50	184.44	82.07	116
ω	-10.50	306.95	272.07	99.72	80
ω	17.00	321.08	318.36	83.36	117

Rotation frames were integrated using SAINT [2], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 76138 reflections were measured over the ranges $3.258 \leq 2\theta \leq 55.2°$, $-7 \leq h \leq 7$, $-22 \leq k \leq 22$, $-23 \leq l \leq 23$ yielding 4098 unique reflections ($R_{int} = 0.0244$). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS [3] (minimum and maximum transmission 0.7252, 0.7456). The structure was solved by direct methods - SHELXS-97 [4]. Refinement was by full-matrix least squares based on F^2 using SHELXL-2014 [5]. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0372P)^2 + 0.4474P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0236 and wR2=0.0627 for 3997 observed reflections for which $F > 4\sigma(F)$ and R1=0.0244 and wR2=0.0636 and GOF =1.032 for all 4098 unique, non-zero reflections and 230 variables. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.26 and -0.20 e/Å^3. The Flack absolute structure parameter refined to a value of 0.000(8) thus corroborating the assigned stereochemistry.

Table S8 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables S9 and S10. Anisotropic thermal

parameters are in Table S11 Tables S12 and S13 list bond distances and bond angles. Figure S3 is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

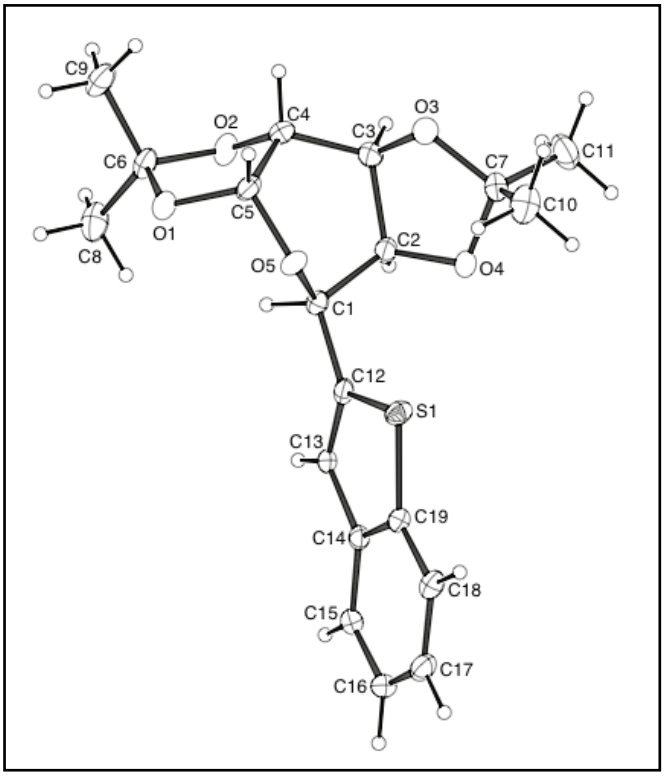


Figure S3. ORTEP drawing of the compound **3lf** with 50% thermal ellipsoids.

Table S8. Summary of Structure Determination of Compound 3lf

Empirical formula	$C_{19}H_{22}O_5S$
Formula weight	362.42
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a	5.63430(10)Å
b	17.0439(4)Å
c	18.3976(4)Å
Volume	1766.73(6)$Å^3$
Z	4
d_{calc}	1.363 g/cm^3
μ	0.210 mm^{-1}
F(000)	768.0
Crystal size, mm	0.27 × 0.22 × 0.07
2θ range for data collection	3.258 - 55.2°
Index ranges	$-7 \leq h \leq 7$, $-22 \leq k \leq 22$, $-23 \leq l \leq 23$
Reflections collected	76138
Independent reflections	4098[R(int) = 0.0244]
Data/restraints/parameters	4098/0/230
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0236, wR_2 = 0.0627
Final R indexes [all data]	R_1 = 0.0244, wR_2 = 0.0636
Largest diff. peak/hole	0.26/-0.20 $eÅ^{-3}$
Flack parameter	0.000(8)

Table S9. Refined Positional Parameters for Compound 3lf

Atom	*x*	*y*	*z*	U(eq)
C1	0.6373(3)	0.50568(9)	0.51875(8)	0.0145(3)
C2	0.7001(3)	0.42985(9)	0.47838(8)	0.0172(3)
C3	0.5746(3)	0.35804(9)	0.51175(9)	0.0222(3)
C4	0.4763(3)	0.37244(9)	0.58716(8)	0.0207(3)
C5	0.3429(3)	0.45049(9)	0.59475(8)	0.0178(3)
C6	0.5803(3)	0.4253(1)	0.69607(8)	0.0195(3)
C7	0.4446(3)	0.37174(10)	0.39391(9)	0.0225(3)
C8	0.7835(3)	0.46938(13)	0.73007(10)	0.0286(4)
C9	0.4471(4)	0.37383(11)	0.74995(9)	0.0274(4)
C10	0.2302(3)	0.40696(13)	0.35715(10)	0.0306(4)
C11	0.5599(4)	0.30581(11)	0.35112(10)	0.0304(4)
C12	0.6783(3)	0.57838(9)	0.47468(8)	0.0144(3)
C13	0.8724(3)	0.62536(8)	0.47743(8)	0.0137(3)
C14	0.8484(3)	0.69286(9)	0.42958(8)	0.0144(3)
C15	1.0044(3)	0.75587(9)	0.41932(8)	0.0175(3)
C16	0.9400(3)	0.81664(9)	0.37318(9)	0.0206(3)
C17	0.7226(3)	0.81538(10)	0.33700(9)	0.0211(3)
C18	0.5653(3)	0.75346(9)	0.34553(8)	0.0191(3)
C19	0.6295(3)	0.69260(9)	0.39259(8)	0.0153(3)
O1	0.4194(2)	0.48015(7)	0.66282(6)	0.0193(2)
O2	0.6695(2)	0.37960(7)	0.63673(6)	0.0219(3)
O3	0.3764(3)	0.34537(7)	0.46493(7)	0.0282(3)
O4	0.6157(2)	0.43222(7)	0.40557(6)	0.0217(3)
O5	0.39104(19)	0.50437(6)	0.53894(6)	0.0162(2)
S1	0.46110(7)	0.61115(2)	0.41498(2)	0.01748(9)

Table S10. Positional Parameters for Hydrogens in Compound 3lf

Atom	*x*	*y*	*z*	U(eq)
H1	0.7355	0.5088	0.5639	0.019
H2	0.8759	0.4218	0.4788	0.023
H3	0.6822	0.3114	0.5116	0.03
H4	0.3712	0.3279	0.602	0.028
H5	0.1684	0.4401	0.5966	0.024
H8a	0.8601	0.5023	0.6932	0.043
H8b	0.8991	0.432	0.7496	0.043
H8c	0.7234	0.5026	0.7695	0.043
H9a	0.3871	0.4063	0.7899	0.041
H9b	0.5547	0.3338	0.7693	0.041
H9c	0.3137	0.3483	0.7253	0.041
H10a	0.1675	0.4498	0.387	0.046
H10b	0.108	0.3666	0.3512	0.046
H10c	0.2759	0.4274	0.3094	0.046
H11a	0.6138	0.3259	0.304	0.046
H11b	0.4443	0.2637	0.3434	0.046
H11c	0.6961	0.2854	0.3783	0.046
H13	1.0074	0.6154	0.507	0.018
H15	1.153	0.757	0.4437	0.023
H16	1.0451	0.8596	0.3662	0.027
H17	0.6814	0.8577	0.3059	0.028
H18	0.4184	0.7524	0.3202	0.025

Table S11. Refined Thermal Parameters (U's) for Compound 3lf

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0155(7)	0.0154(7)	0.0127(6)	0.0013(5)	-0.0005(6)	0.0007(6)
C2	0.0235(8)	0.0155(7)	0.0126(7)	0.0002(5)	0.0006(6)	0.0022(6)
C3	0.0363(10)	0.0141(7)	0.0163(7)	-0.0002(6)	0.0001(7)	-0.0014(7)
C4	0.0313(8)	0.0157(7)	0.0150(7)	0.0041(6)	-0.0004(7)	-0.0036(6)
C5	0.0187(7)	0.0211(7)	0.0136(7)	0.0041(6)	0.0011(6)	-0.0029(6)
C6	0.0225(8)	0.0236(8)	0.0124(7)	0.0028(6)	0.0005(6)	0.0044(7)
C7	0.0314(9)	0.0208(8)	0.0152(7)	-0.0028(6)	0.0003(7)	-0.0021(7)
C8	0.0239(8)	0.0431(11)	0.0187(8)	-0.0027(8)	-0.0016(7)	-0.0001(8)
C9	0.0338(9)	0.0306(9)	0.0176(7)	0.0084(6)	0.0027(8)	0.0037(8)
C10	0.0280(9)	0.0404(11)	0.0234(9)	-0.0018(8)	0.0012(7)	0.0029(8)
C11	0.0425(11)	0.0230(8)	0.0257(8)	-0.0083(7)	-0.0042(8)	0.0033(8)
C12	0.0179(7)	0.0155(7)	0.0097(6)	-0.0001(5)	0.0000(5)	0.0030(6)
C13	0.0169(6)	0.0136(7)	0.0106(6)	-0.0020(5)	0.0024(5)	-0.0001(5)
C14	0.0170(7)	0.0145(6)	0.0115(6)	-0.0013(5)	0.0011(5)	0.0011(6)
C15	0.0211(7)	0.0172(7)	0.0142(7)	-0.0022(5)	0.0000(6)	-0.0027(6)
C16	0.0288(8)	0.0154(7)	0.0177(7)	-0.0001(6)	0.0036(7)	-0.0041(6)
C17	0.0287(8)	0.0186(7)	0.0159(7)	0.0038(6)	0.0030(6)	0.0024(7)
C18	0.0208(7)	0.0219(7)	0.0147(7)	0.0031(6)	0.0001(6)	0.0023(6)
C19	0.0171(7)	0.0160(7)	0.0128(6)	-0.0002(5)	0.0024(5)	-0.0008(6)
O1	0.0247(6)	0.0200(5)	0.0133(5)	0.0018(4)	-0.0007(4)	0.0031(4)
O2	0.0295(6)	0.0231(6)	0.0131(5)	0.0016(4)	0.0001(5)	0.0073(5)
O3	0.0422(8)	0.0251(6)	0.0171(6)	0.0000(5)	-0.0006(5)	-0.0124(6)
O4	0.0346(6)	0.0190(5)	0.0115(5)	-0.0002(4)	-0.0007(5)	-0.0034(5)
O5	0.0150(5)	0.0184(5)	0.0153(5)	0.0052(4)	0.0011(4)	0.0005(4)
S1	0.01670(17)	0.01913(17)	0.01660(17)	0.00510(14)	-0.00268(14)	-0.00218(14)

Table S12. Bond Distances in Compound 3lf, Å

C1-C2	1.532(2)	C1-C12	1.499(2)	C1-O5	1.4363(19)
C2-C3	1.541(2)	C2-O4	1.4221(18)	C3-C4	1.514(2)
C3-O3	1.427(2)	C4-C5	1.534(2)	C4-O2	1.425(2)
C5-O1	1.4176(19)	C5-O5	1.4038(18)	C6-C8	1.505(3)
C6-C9	1.522(2)	C6-O1	1.4387(19)	C6-O2	1.4323(19)
C7-C10	1.509(3)	C7-C11	1.518(2)	C7-O3	1.434(2)
C7-O4	1.428(2)	C12-C13	1.356(2)	C12-S1	1.7368(15)
C13-C14	1.455(2)	C14-C15	1.401(2)	C14-C19	1.409(2)
C15-C16	1.388(2)	C16-C17	1.394(3)	C17-C18	1.387(2)
C18-C19	1.399(2)	C19-S1	1.7310(16)		

Table S13. Bond Angles in Compound 3lf. °

C12-C1-C2	113.55(12)	O5-C1-C2	109.61(13)	O5-C1-C12	107.57(12)
C1-C2-C3	111.77(13)	O4-C2-C1	110.82(13)	O4-C2-C3	104.15(13)
C4-C3-C2	113.83(13)	O3-C3-C2	103.82(12)	O3-C3-C4	106.93(15)
C3-C4-C5	113.78(13)	O2-C4-C3	108.70(14)	O2-C4-C5	103.99(12)
O1-C5-C4	103.93(12)	O5-C5-C4	113.96(13)	O5-C5-O1	110.74(12)
C8-C6-C9	113.09(14)	O1-C6-C8	109.36(14)	O1-C6-C9	109.92(14)
O2-C6-C8	108.75(14)	O2-C6-C9	110.86(14)	O2-C6-O1	104.50(12)
C10-C7-C11	113.86(15)	O3-C7-C10	108.58(15)	O3-C7-C11	110.80(14)
O4-C7-C10	108.71(14)	O4-C7-C11	108.86(15)	O4-C7-O3	105.70(12)
C1-C12-S1	119.95(12)	C13-C12-C1	126.34(14)	C13-C12-S1	113.69(11)
C12-C13-C14	111.69(14)	C15-C14-C13	129.01(14)	C15-C14-C19	119.14(14)
C19-C14-C13	111.78(14)	C16-C15-C14	119.38(15)	C15-C16-C17	120.69(15)
C18-C17-C16	121.27(15)	C17-C18-C19	117.99(15)	C14-C19-S1	111.56(11)
C18-C19-C14	121.53(15)	C18-C19-S1	126.90(13)	C5-O1-C6	109.60(12)
C4-O2-C6	105.44(12)	C3-O3-C7	107.02(13)	C2-O4-C7	110.29(12)
C5-O5-C1	112.69(11)	C19-S1-C12	91.27(8)		

This report has been created with Olex2 [6], compiled on 2016.08.25 svn.r3337 for OlexSys.

References

[1] APEX2 2014.11-0
[2] SAINT v8.34A
[3] SADABS v2014/5
[4] SHELXS-97
[5] SHELXL-2014/7
[6] Olex2 (Dolomanov et al., 2009)

10. References

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(2) In cases where the aldehyde was too thick it could be dissolved in dichloromethane and added to the reaction mixture with any noticeable effect.

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(7) The solvent was purged with argon for 30 minutes prior to use.

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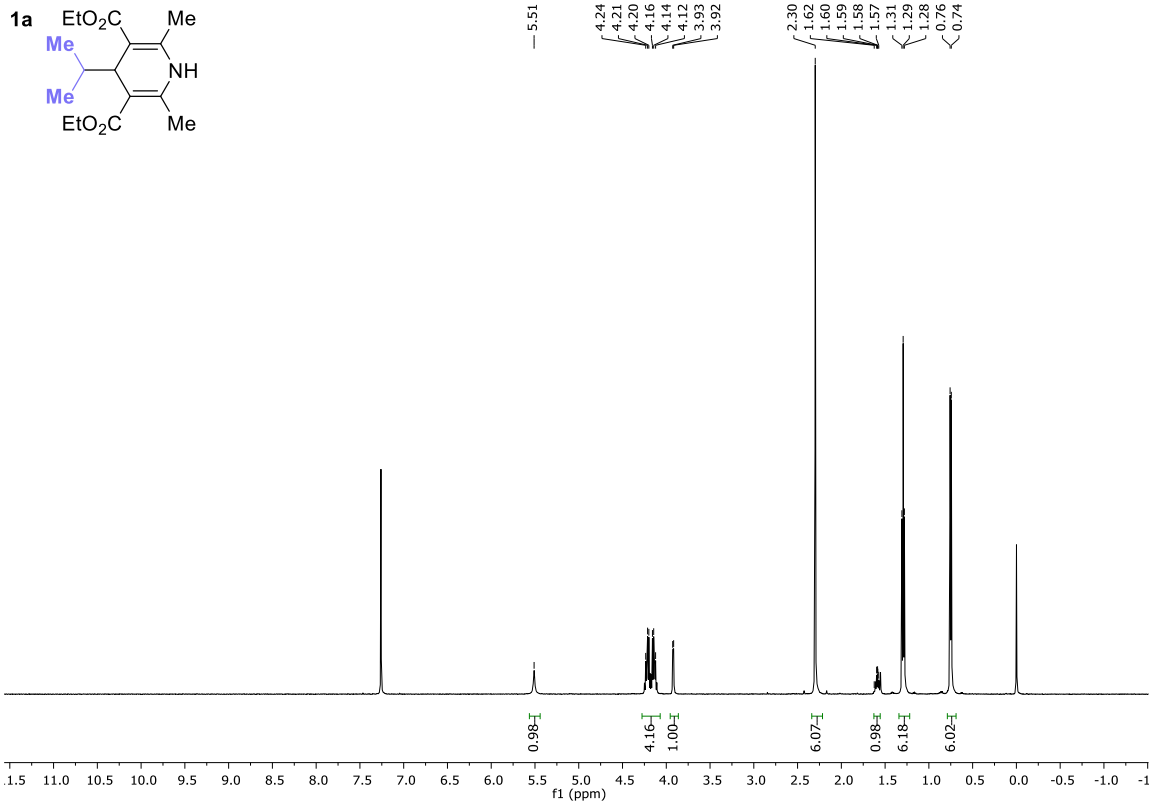
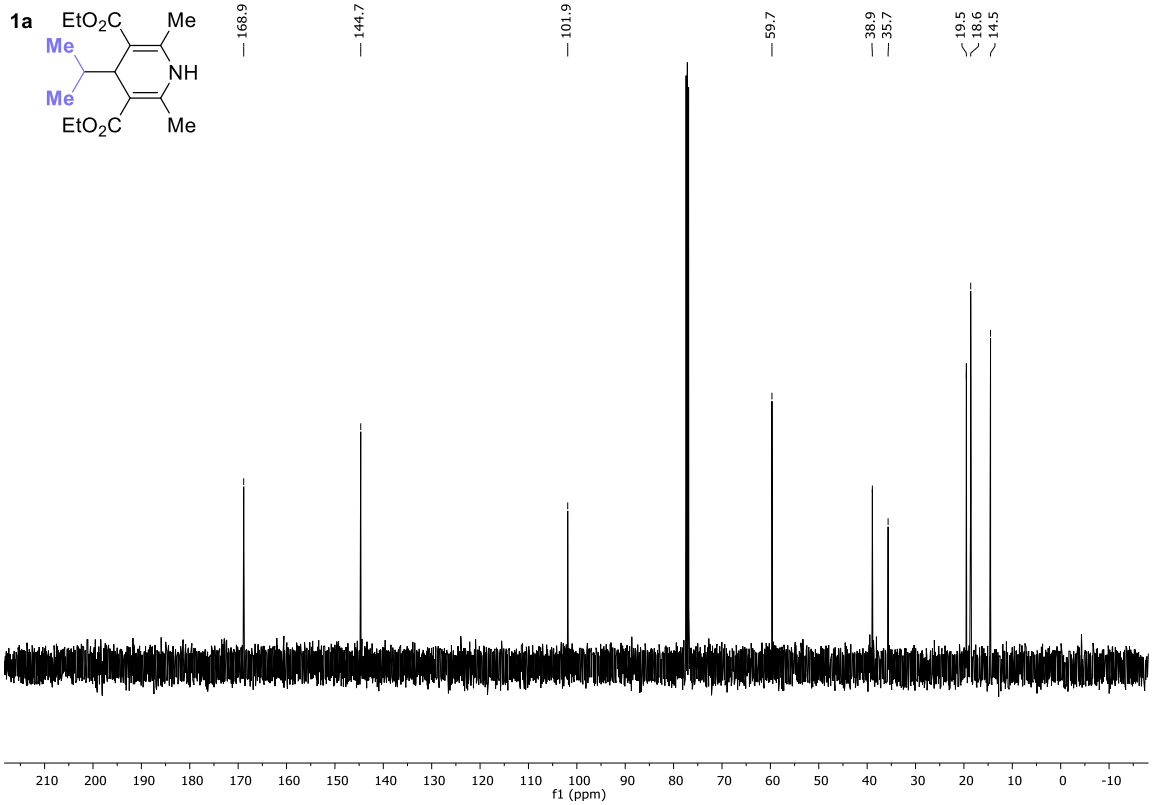
11. ^{1}H and ^{13}C NMR Spectra: 1,4-Dihydropyridines

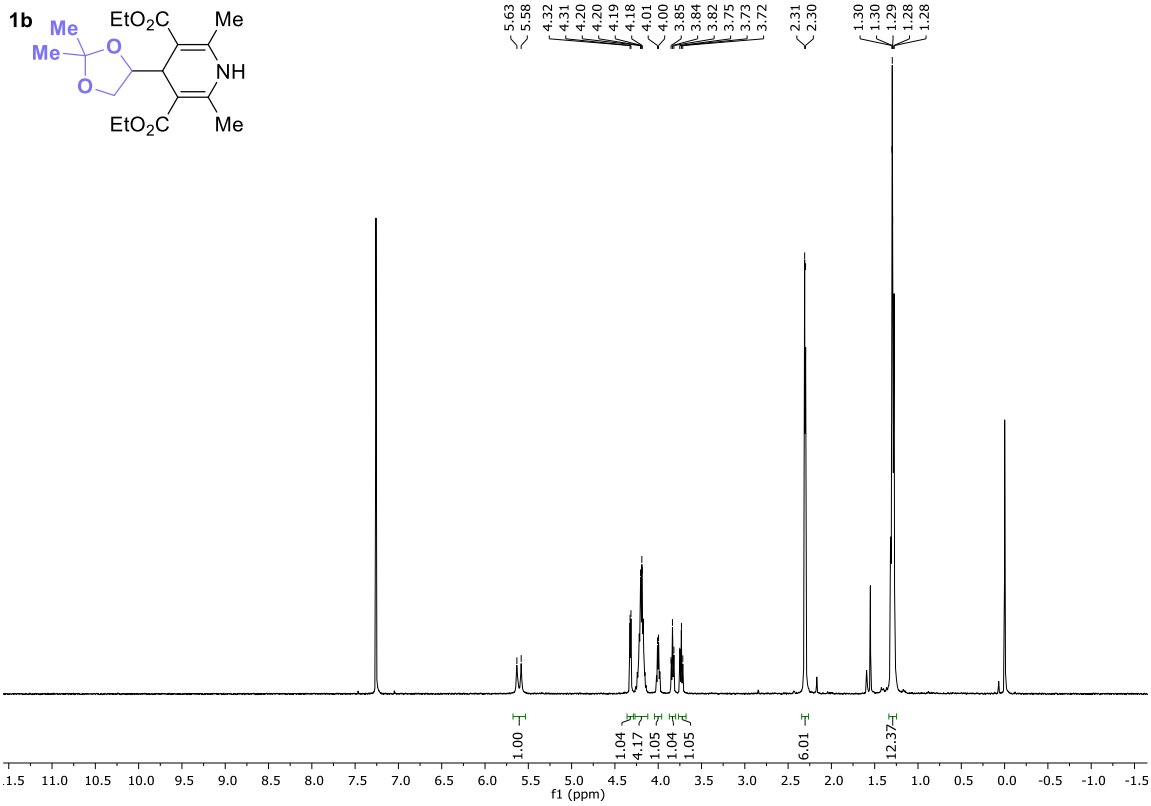
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 4-isopropyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1a**)



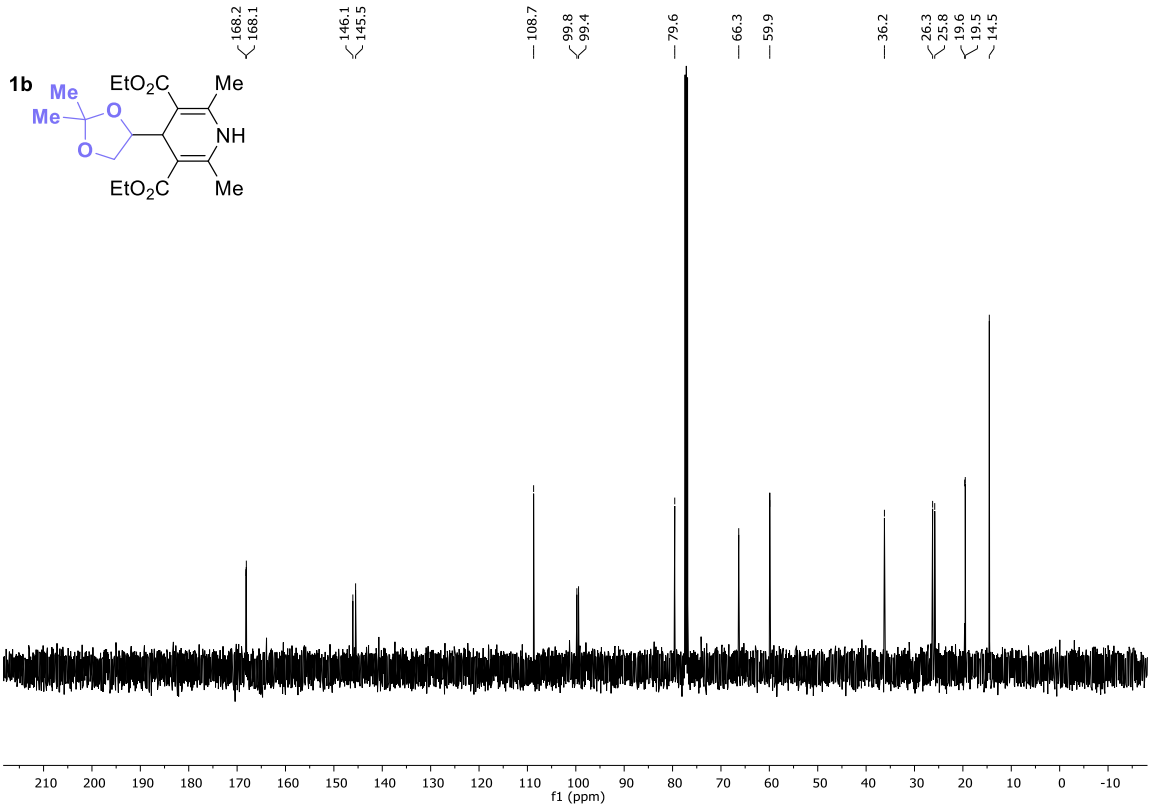
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 4-isopropyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1a**)



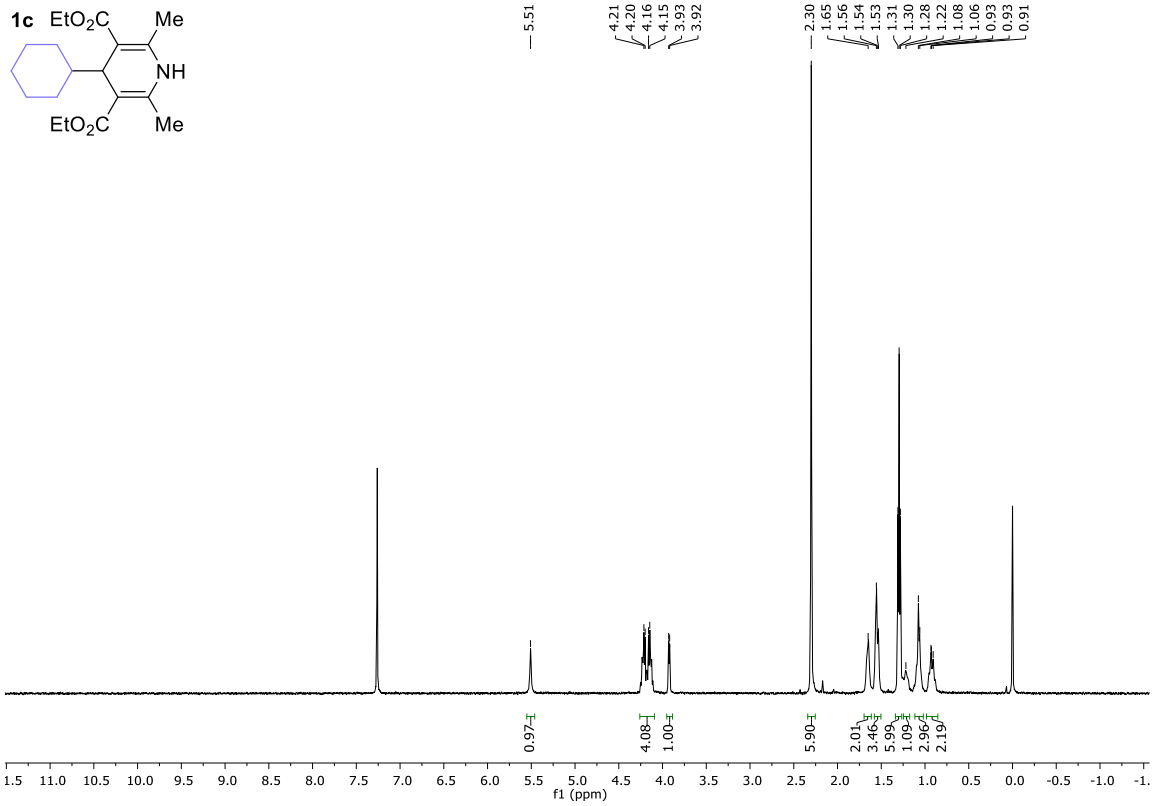
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 4-(2,2-dimethyl-1,3-dioxolan-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1b**)



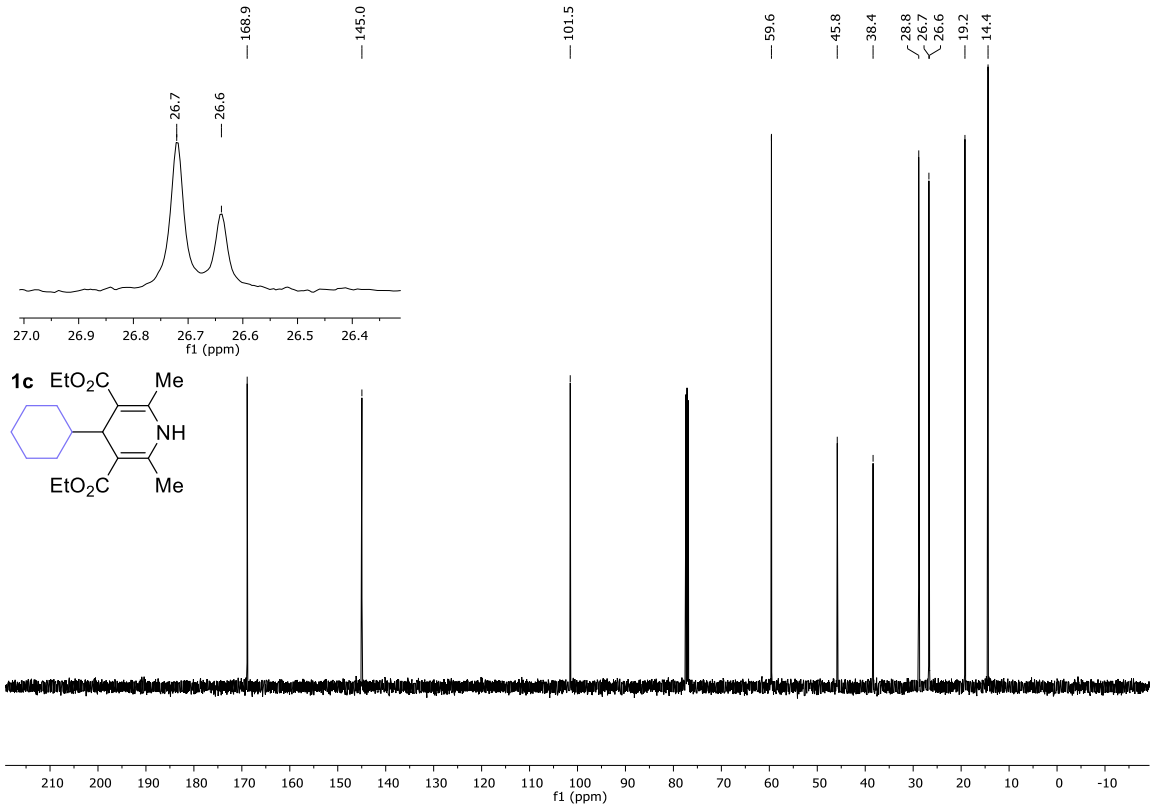
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 4-(2,2-dimethyl-1,3-dioxolan-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1b**)



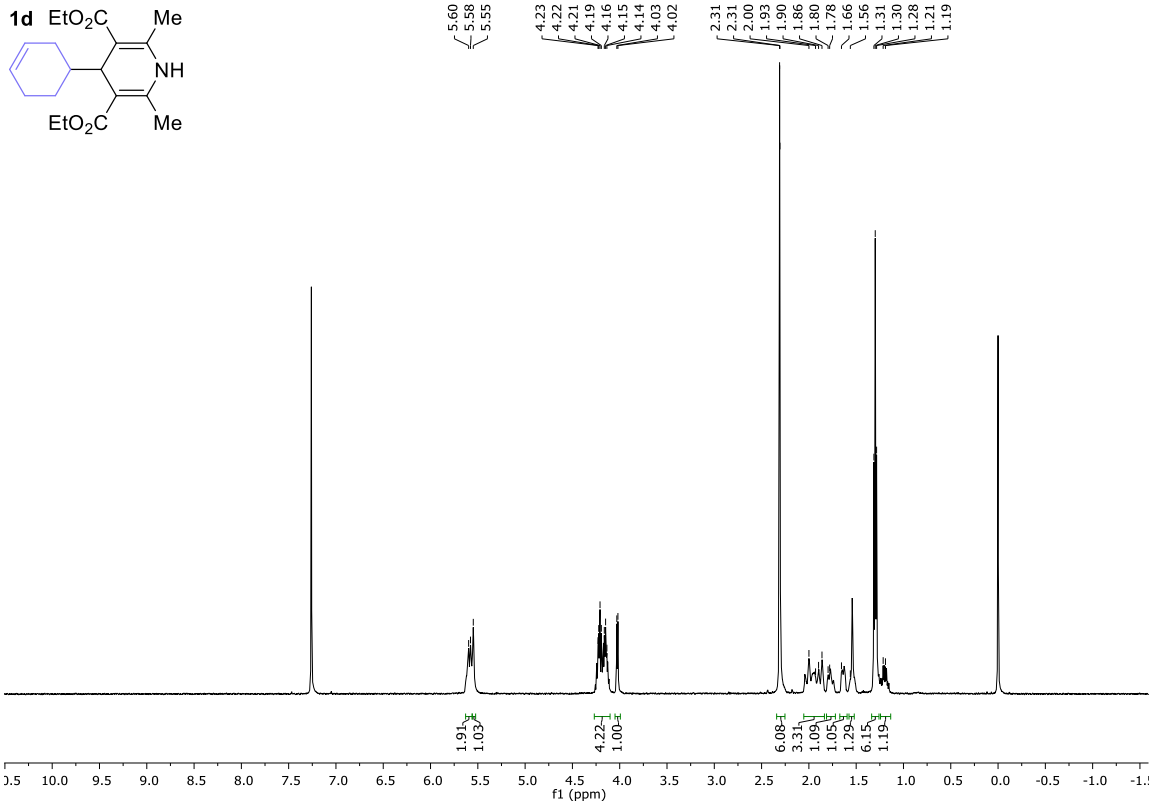
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1c**)



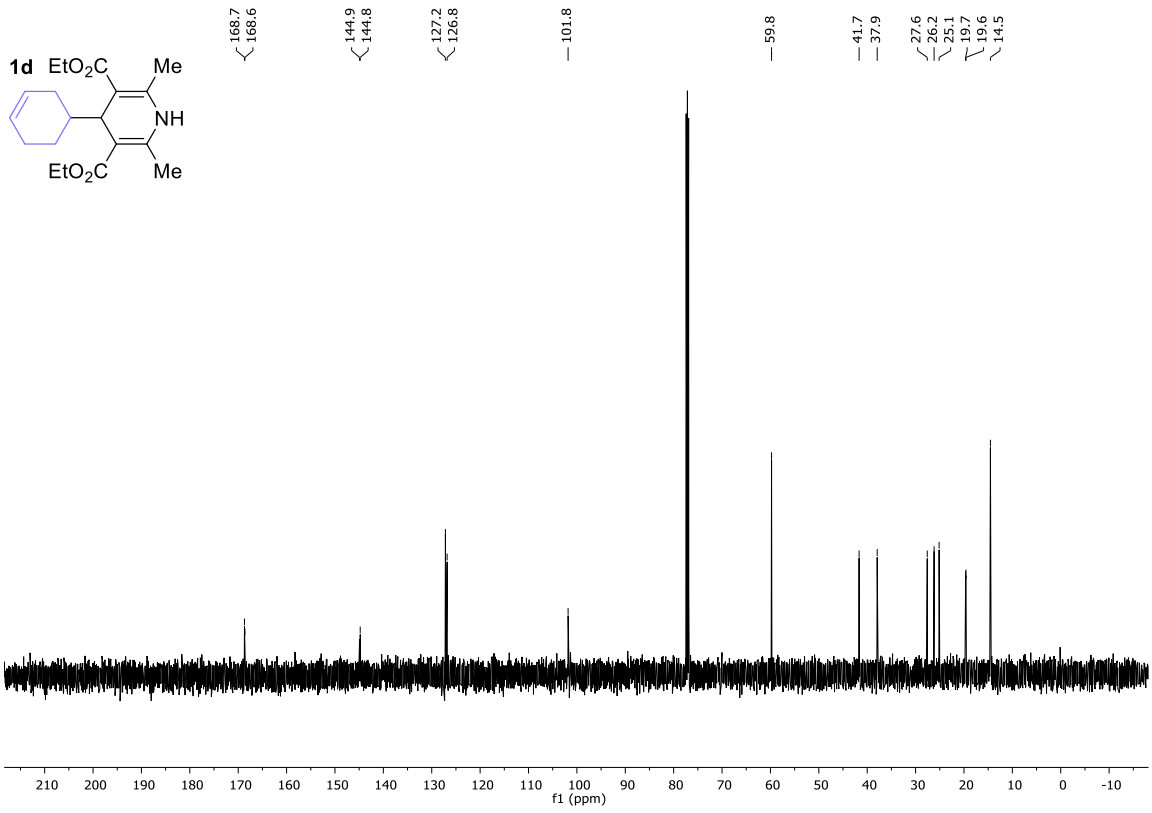
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1c**)



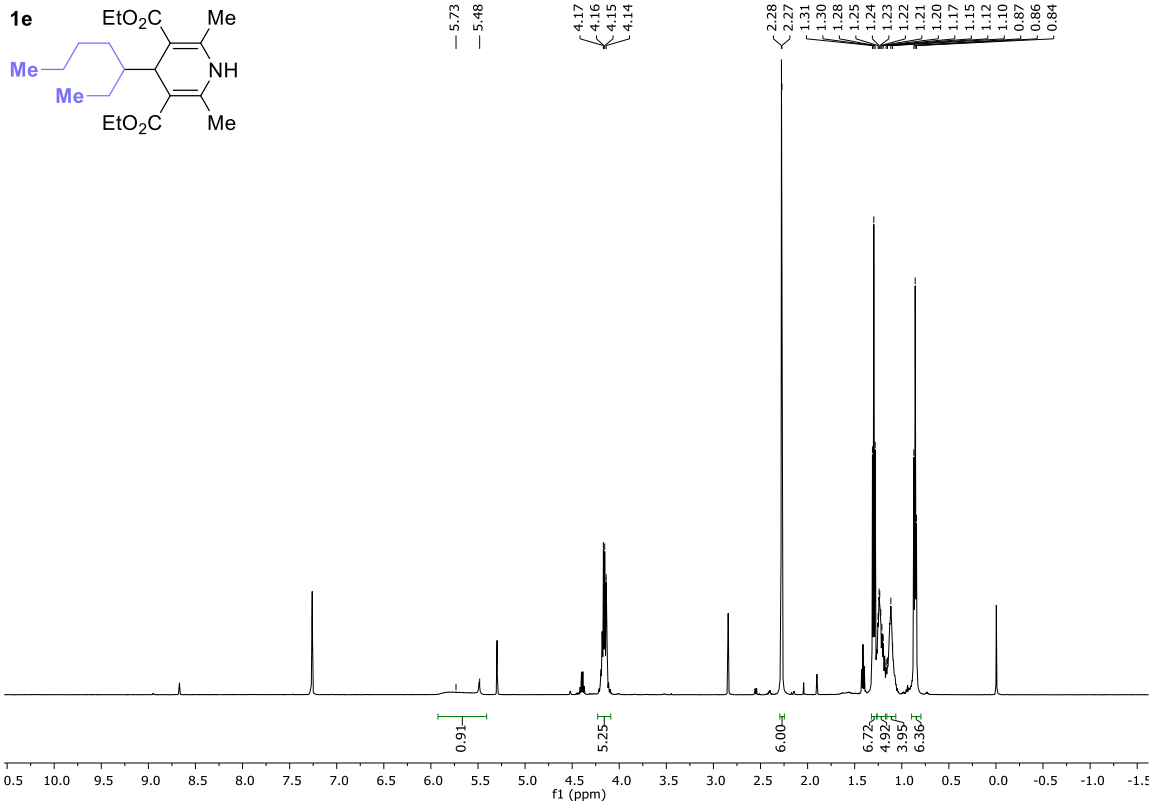
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 4-(cyclohex-3-en-1-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1d**)



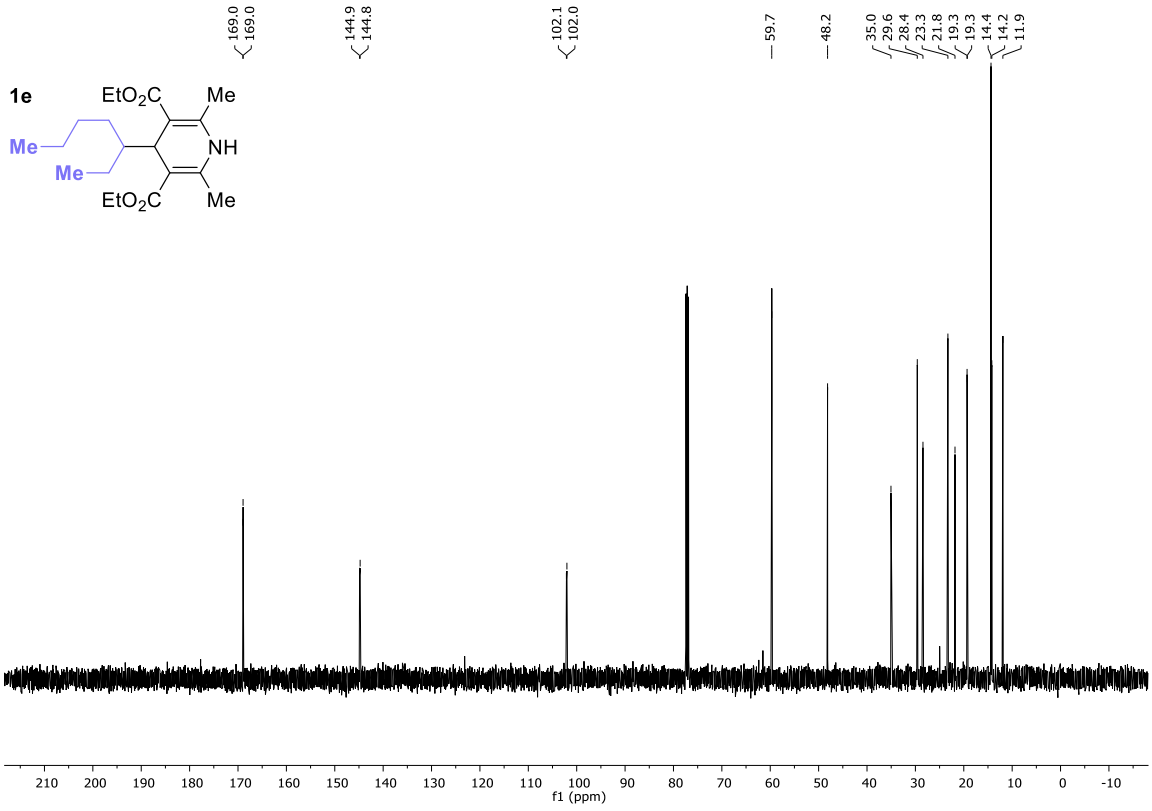
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 4-(cyclohex-3-en-1-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1d**)



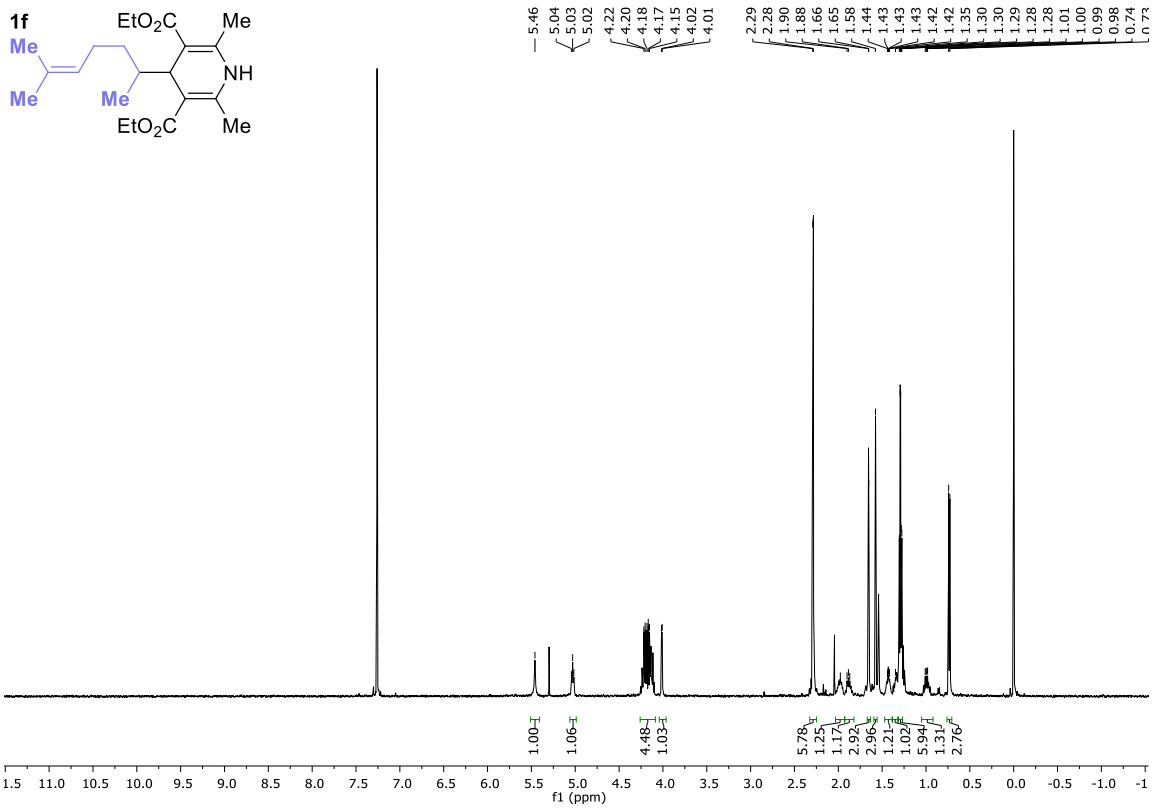
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 4-(heptan-3-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1e**)



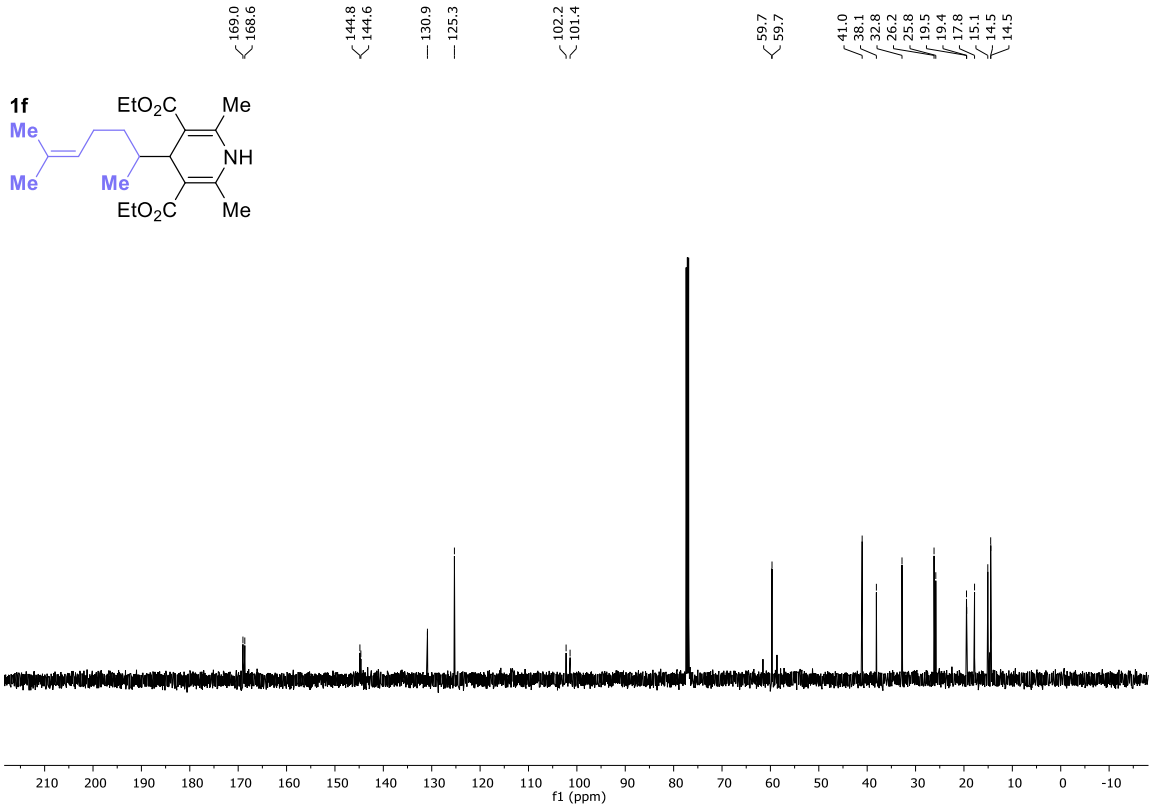
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 4-(heptan-3-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1e**)



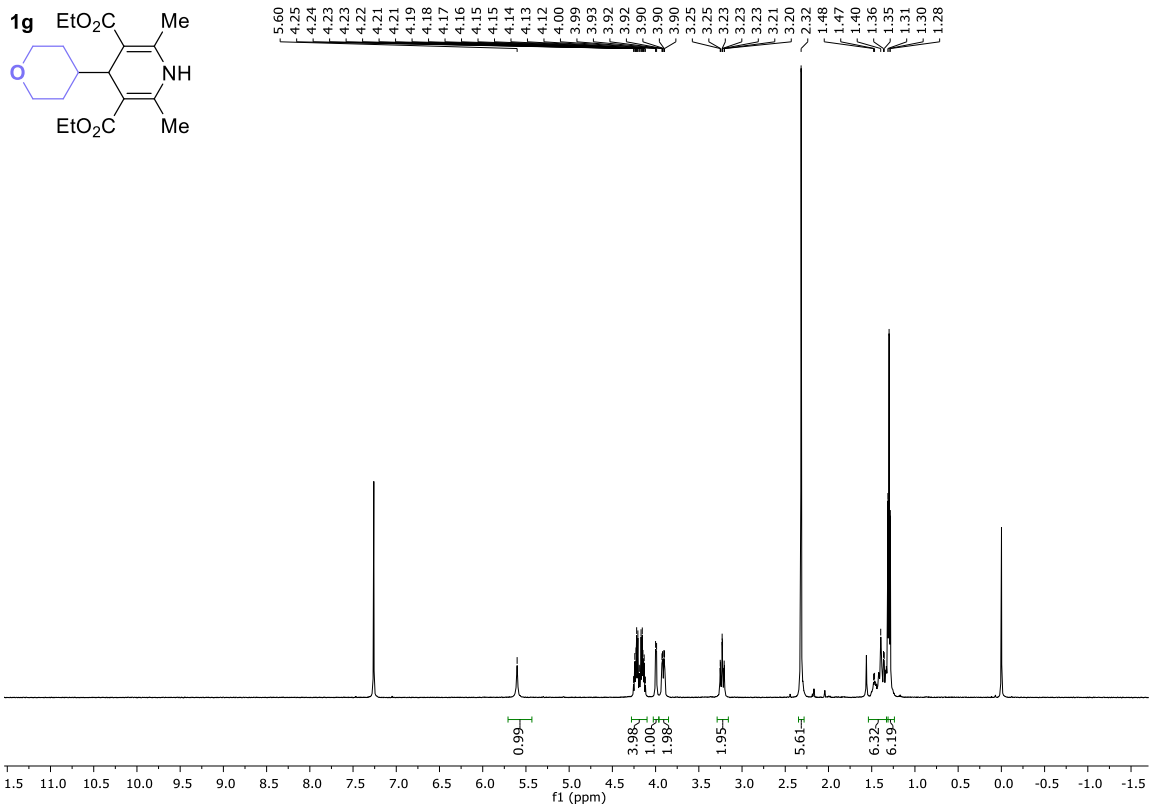
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 2,6-dimethyl-4-(7-methyloct-6-en-3-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**1f**)



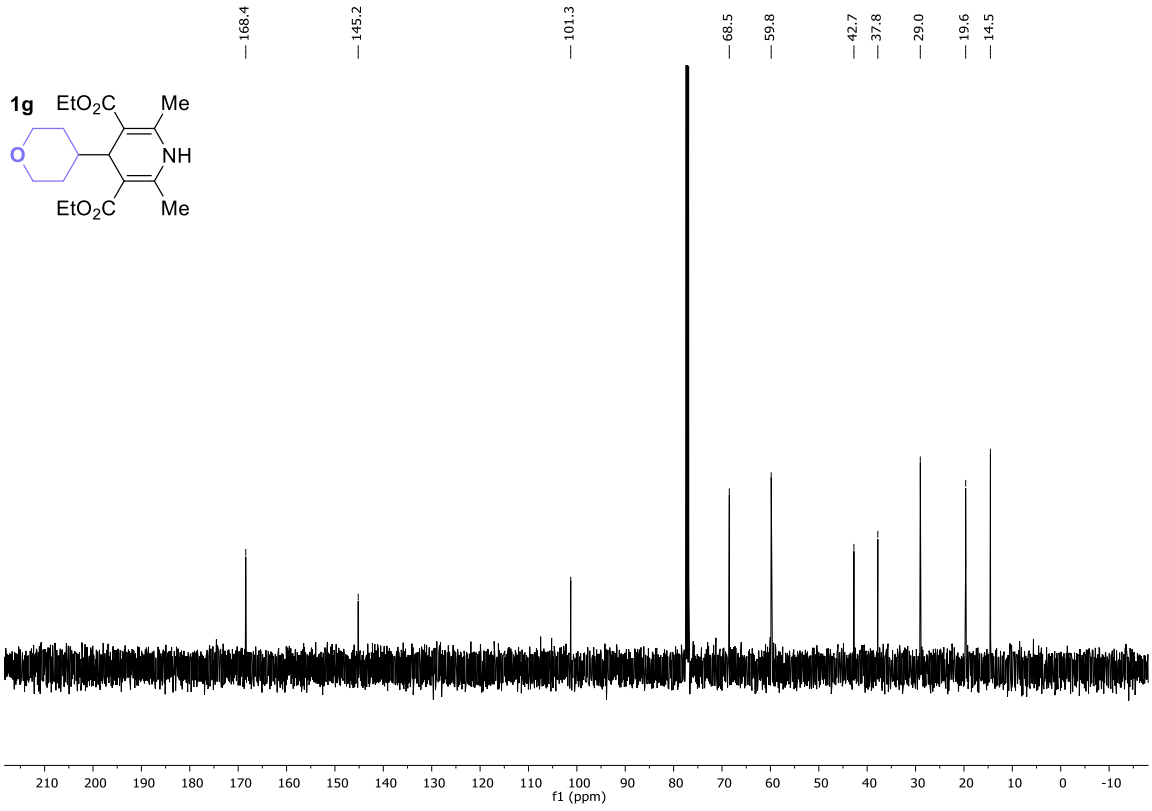
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 2,6-dimethyl-4-(7-methyloct-6-en-3-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**1f**)



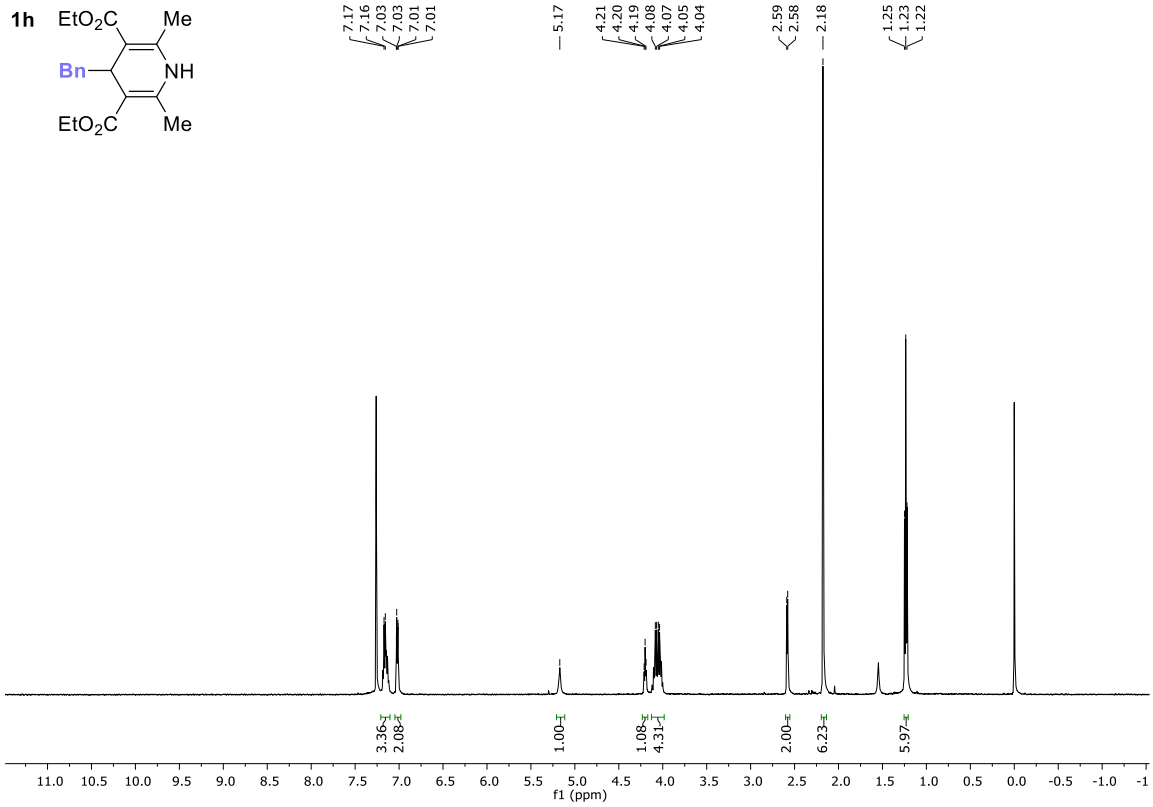
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 2,6-dimethyl-4-(tetrahydro-2H-pyran-4-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**1g**)



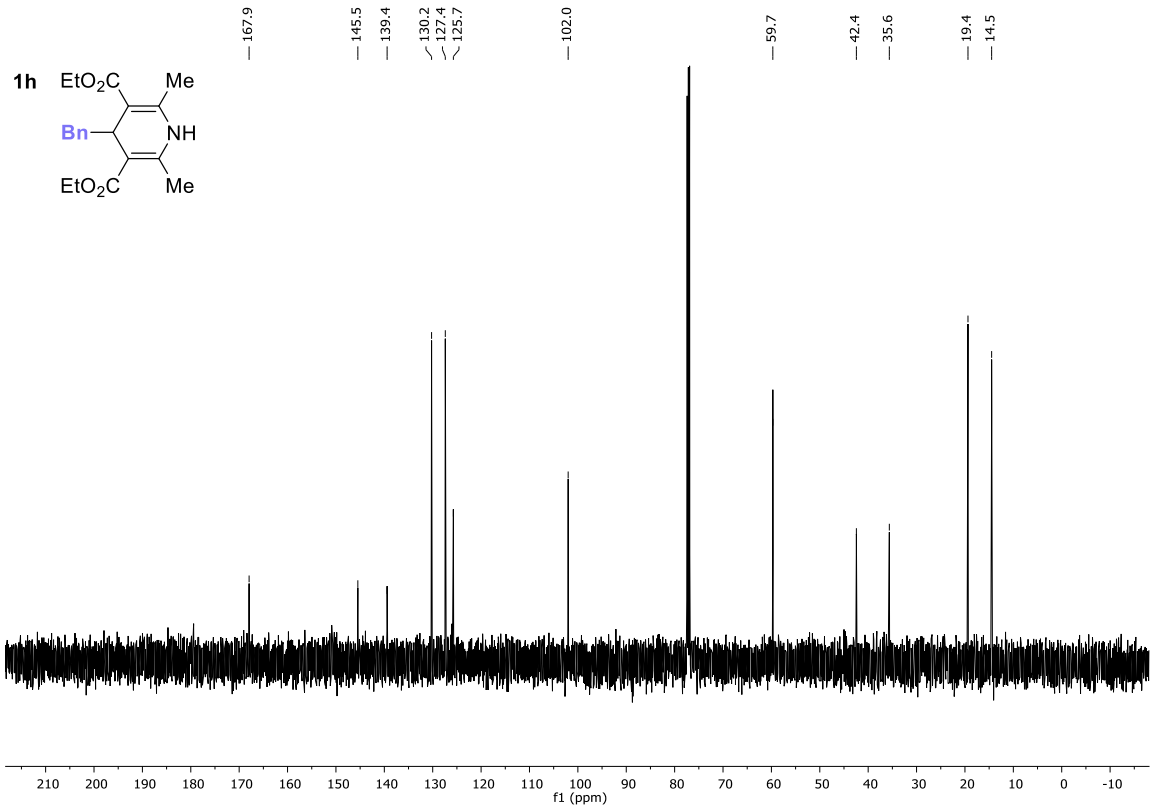
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 2,6-dimethyl-4-(tetrahydro-2H-pyran-4-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**1g**)



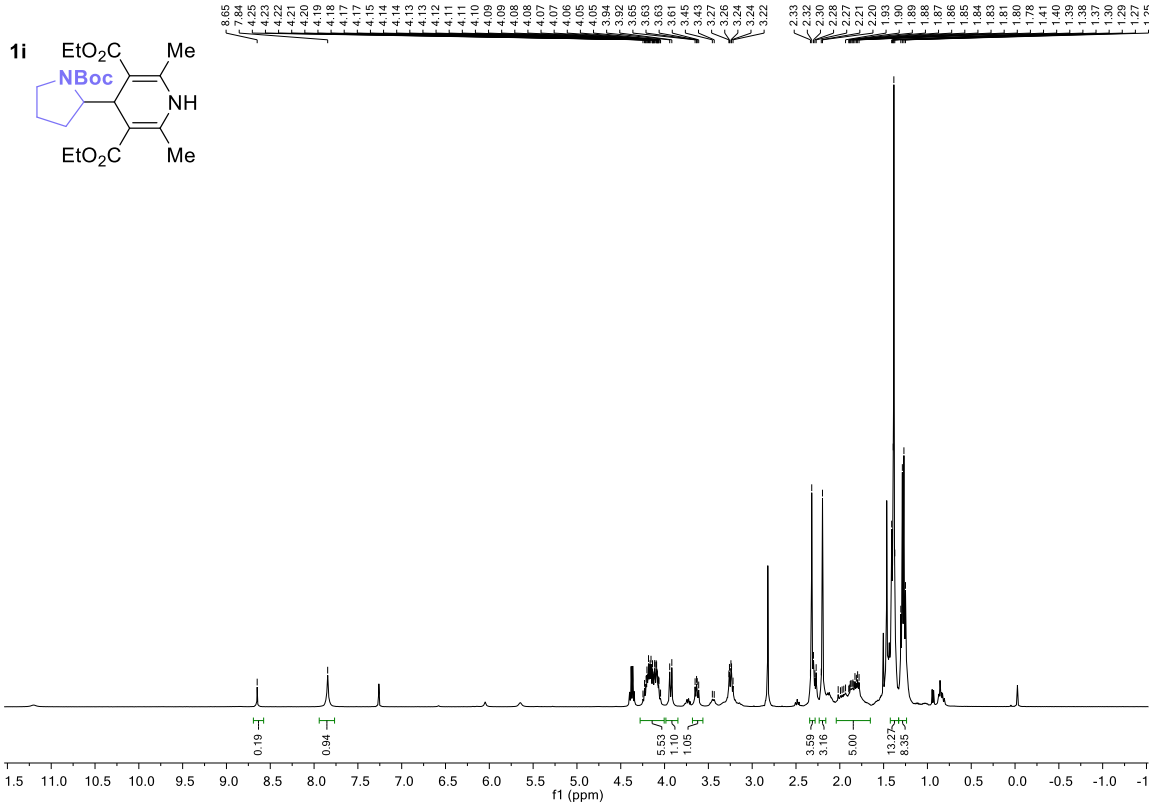
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1h**)



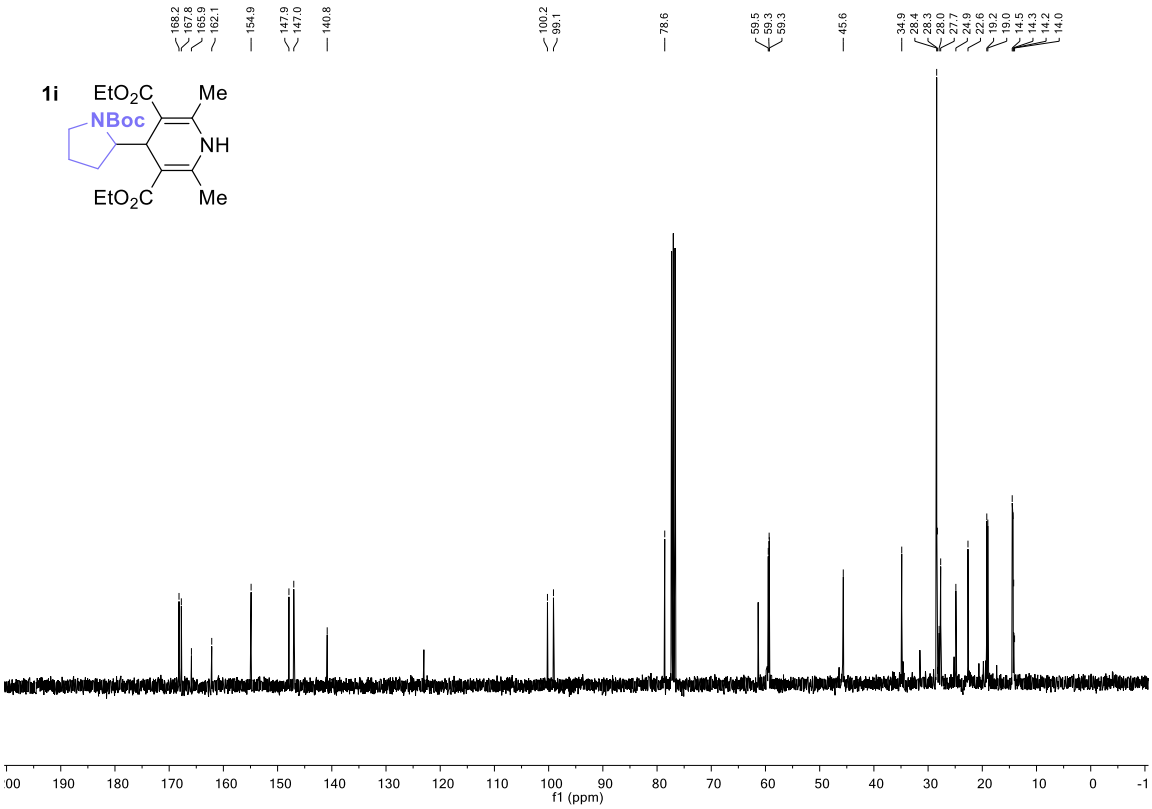
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1h**)



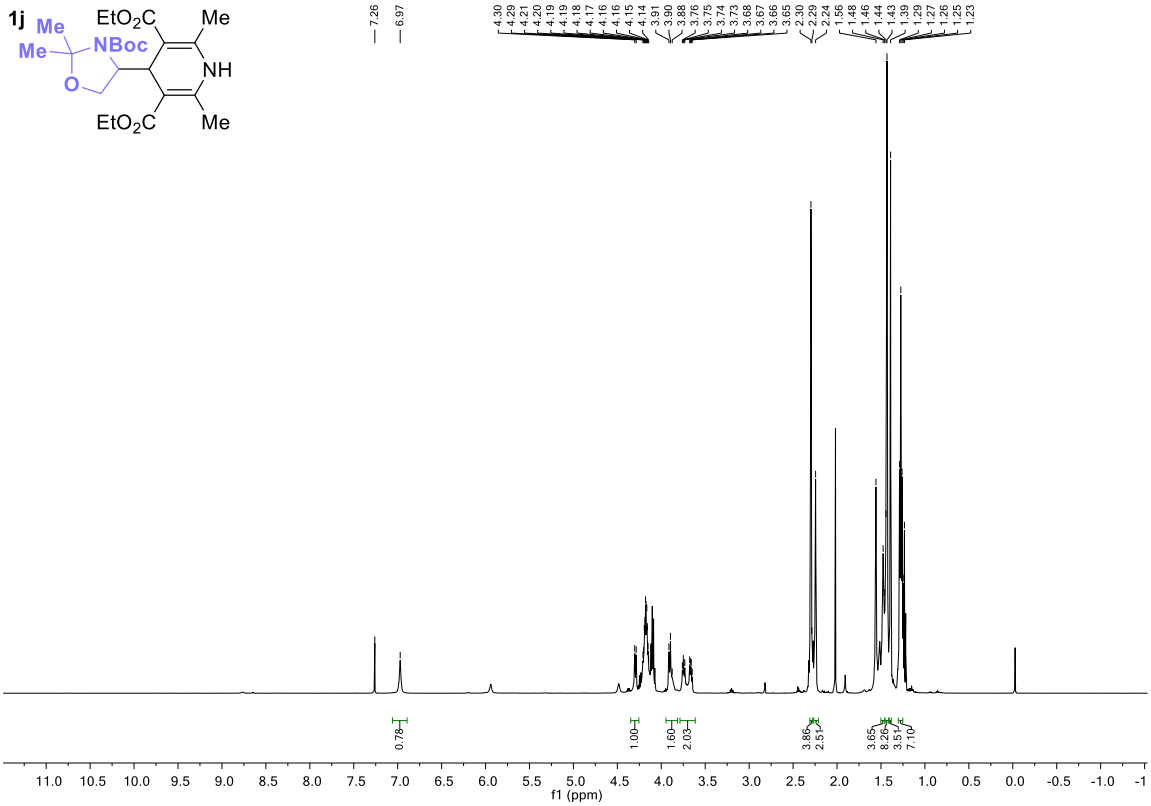
^{1}H NMR ($CDCl_3$, 400 MHz) of diethyl 4-(1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1i**)



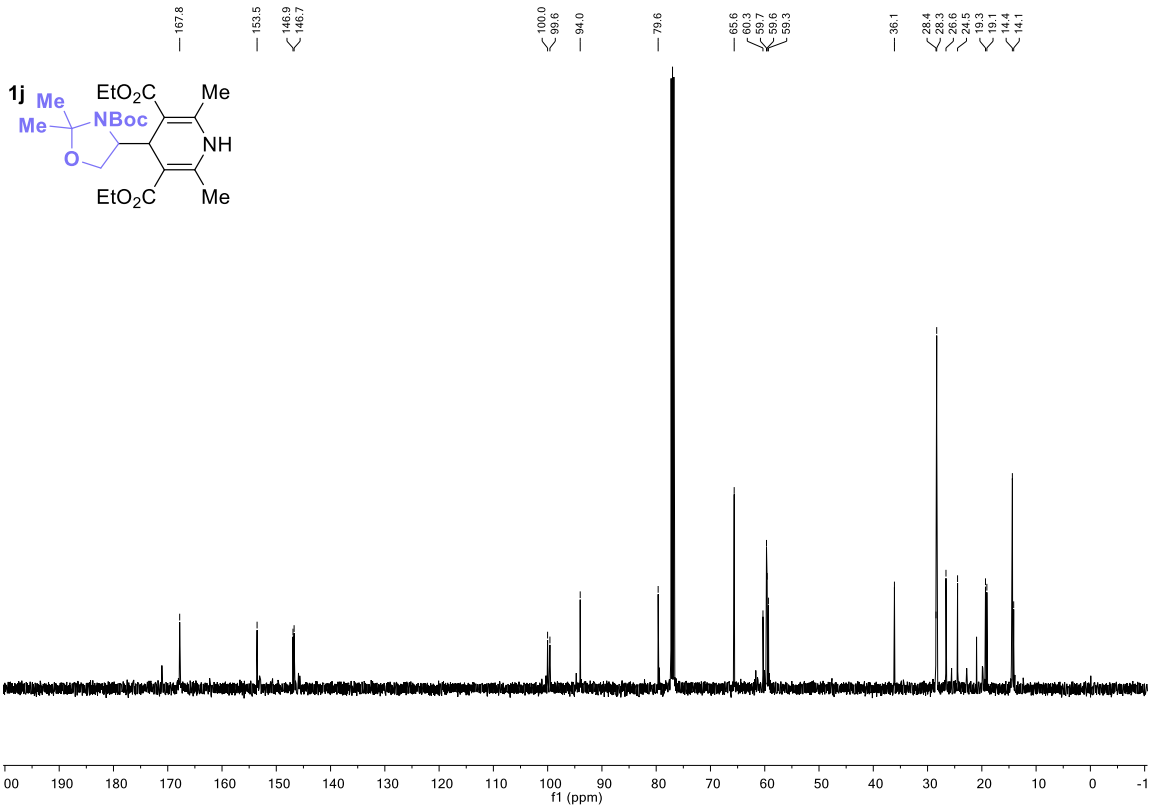
^{13}C NMR ($CDCl_3$, 101 MHz) of diethyl 4-(1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1i**)



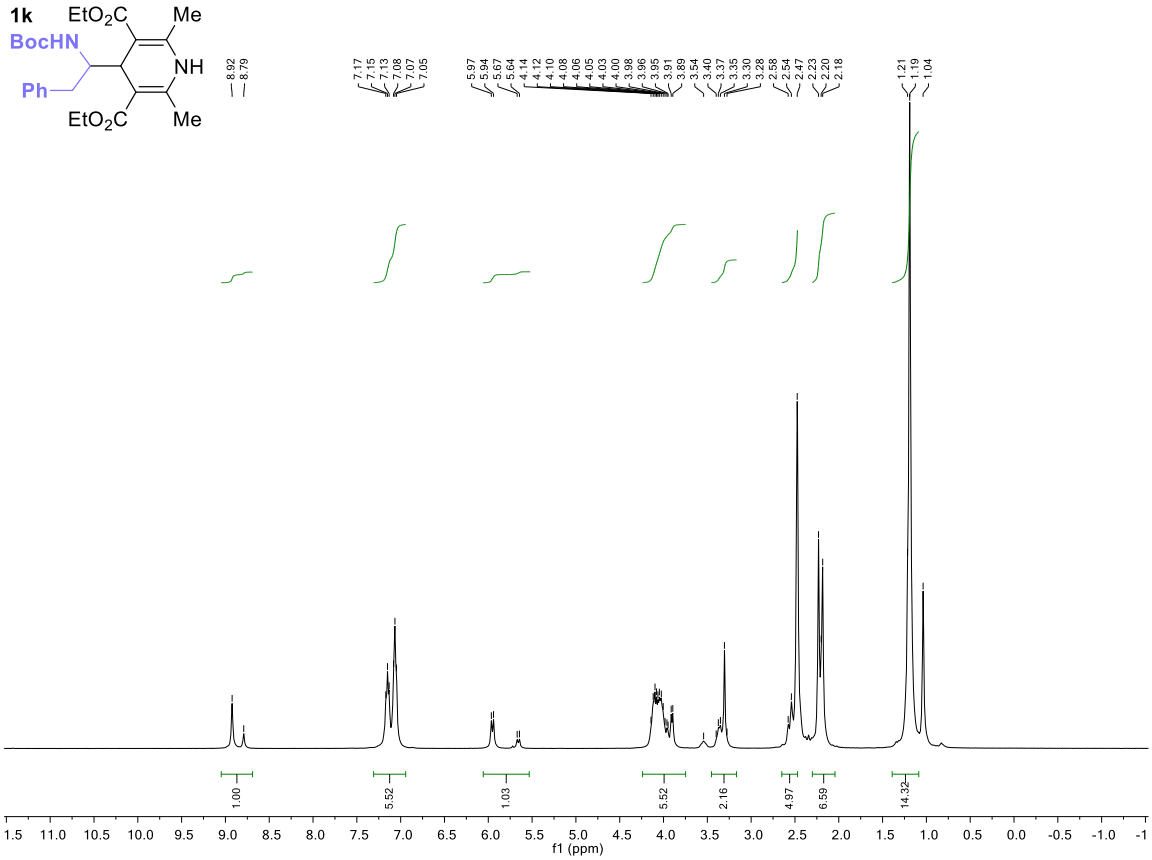
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 4-(3-(*tert*-butoxycarbonyl)-2,2-dimethyloxazolidin-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1j**)



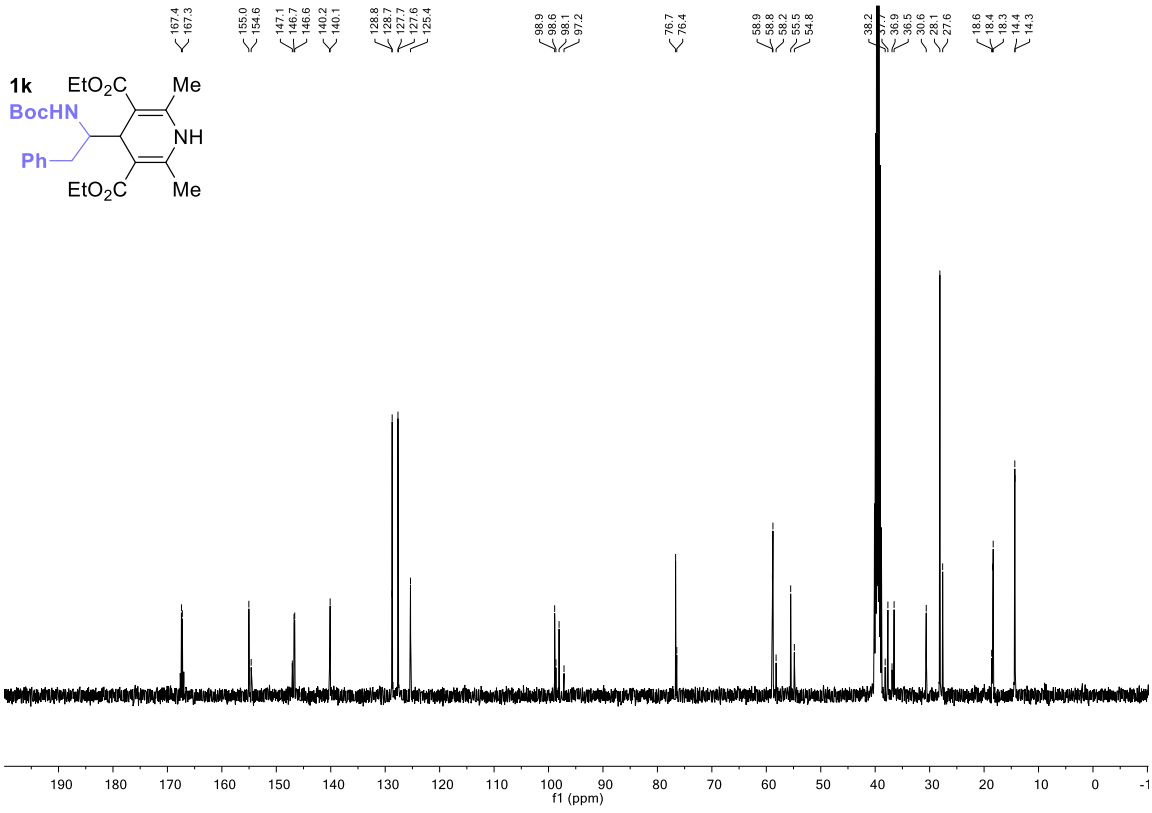
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 4-(3-(*tert*-butoxycarbonyl)-2,2-dimethyloxazolidin-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1j**)



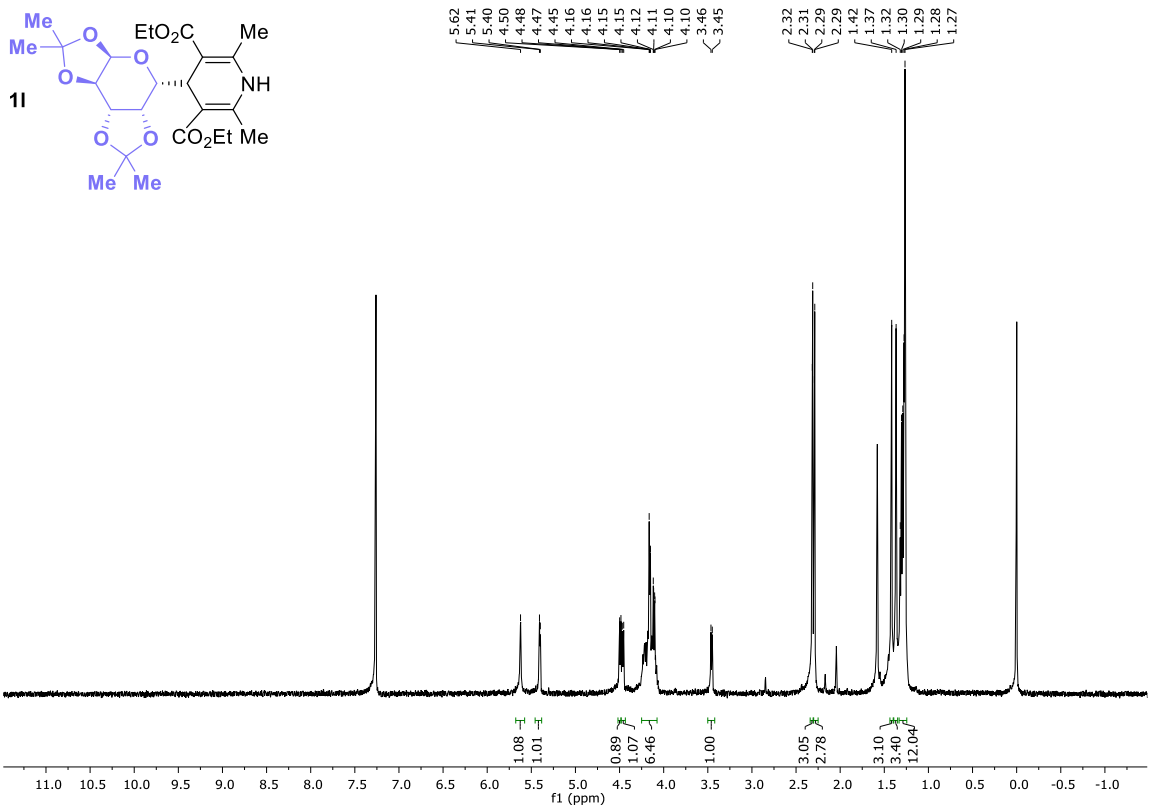
^{1}H NMR (DMSO-d_6, 400 MHz) of diethyl 4-(1-((*tert*-butoxycarbonyl)amino)-2-phenylethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1k**)



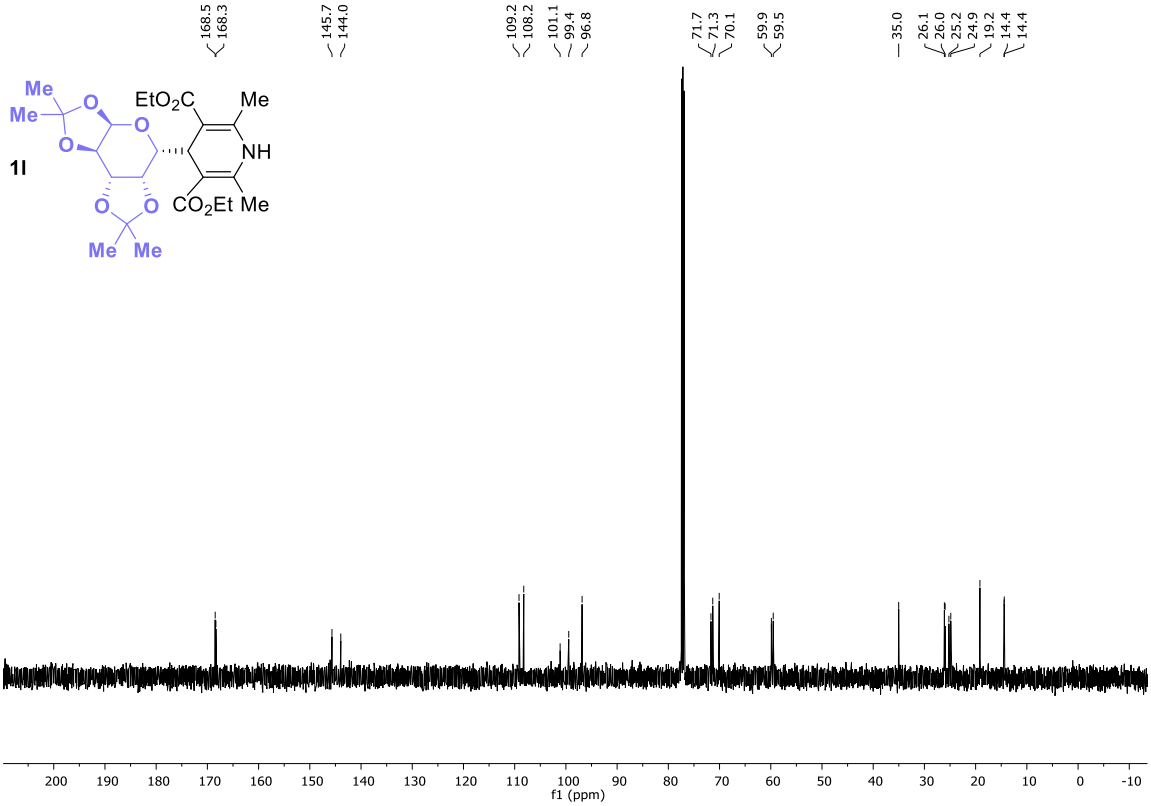
^{13}C NMR (DMSO-d_6, 101 MHz) of diethyl 4-(1-((*tert*-butoxycarbonyl)amino)-2-phenylethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1k**)



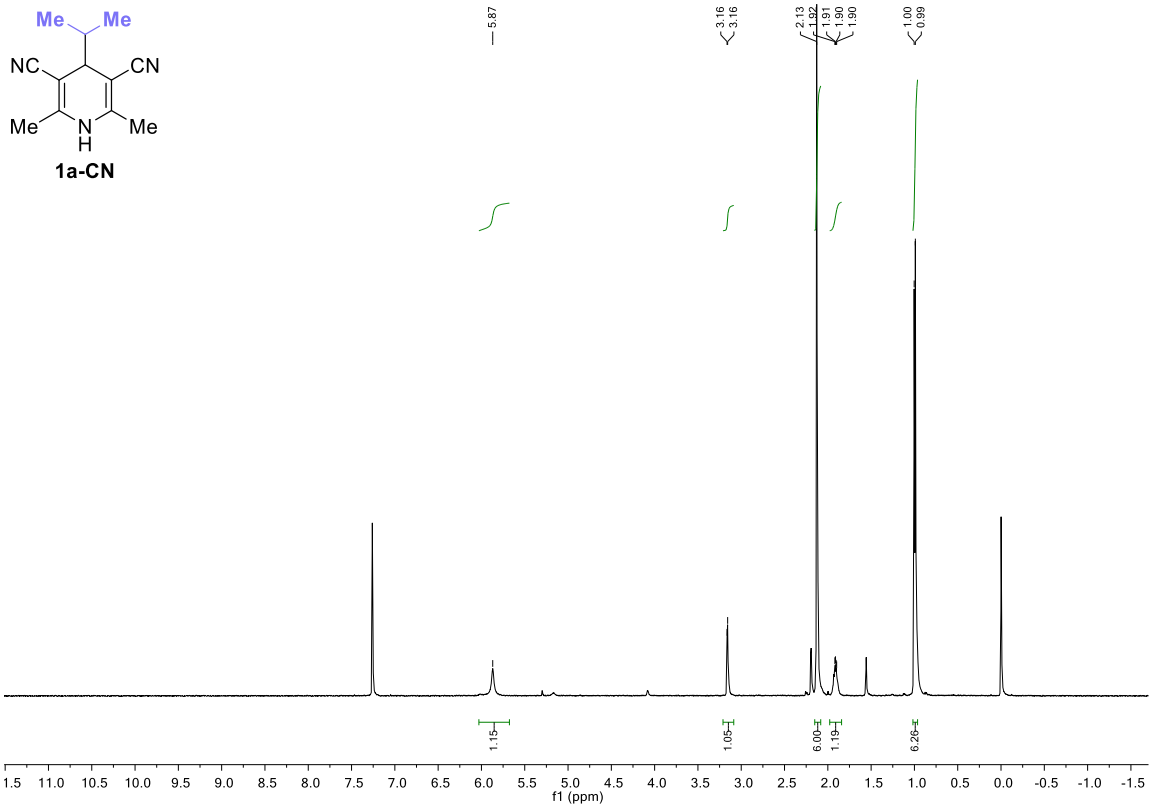
^{1}H NMR ($CDCl_3$, 500 MHz) of diethyl 2,6-dimethyl-4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**1l**)



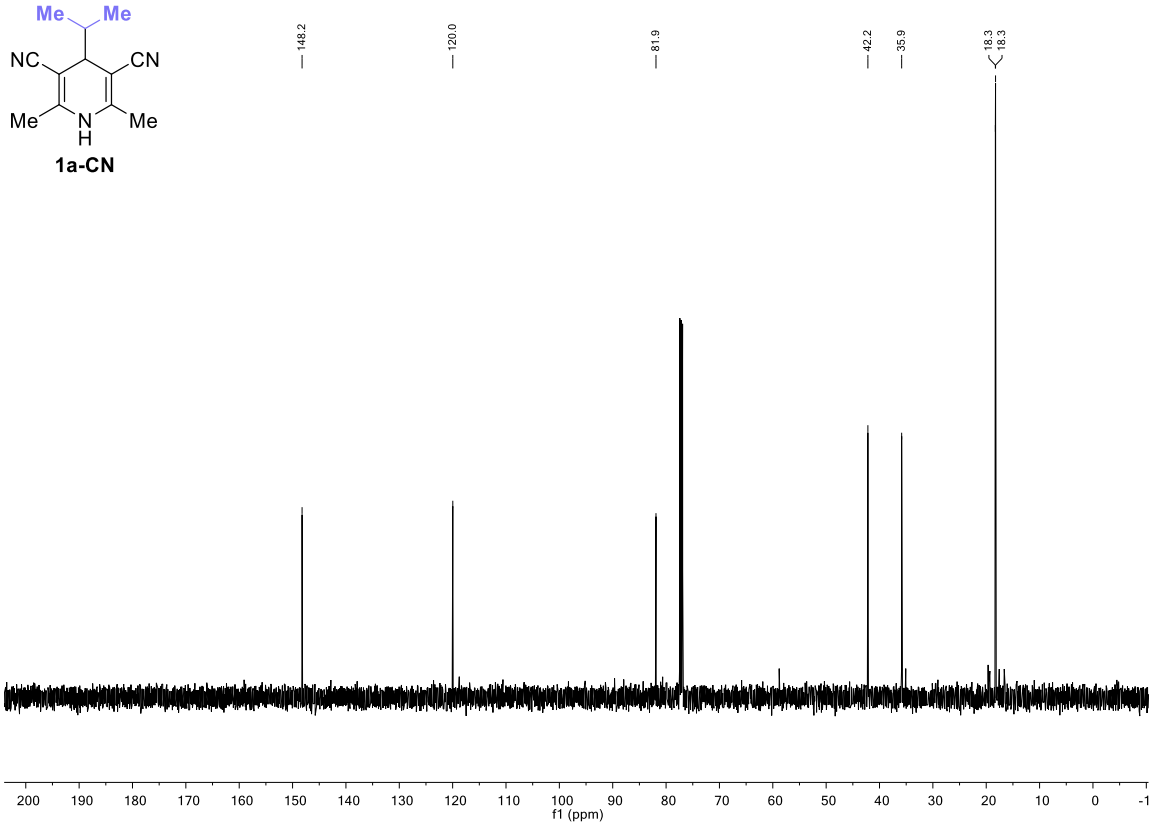
^{13}C NMR ($CDCl_3$, 126 MHz) of diethyl 2,6-dimethyl-4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**1l**)



^{1}H NMR ($CDCl_3$, 500 MHz) of 4-isopropyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile (**1a-CN**)

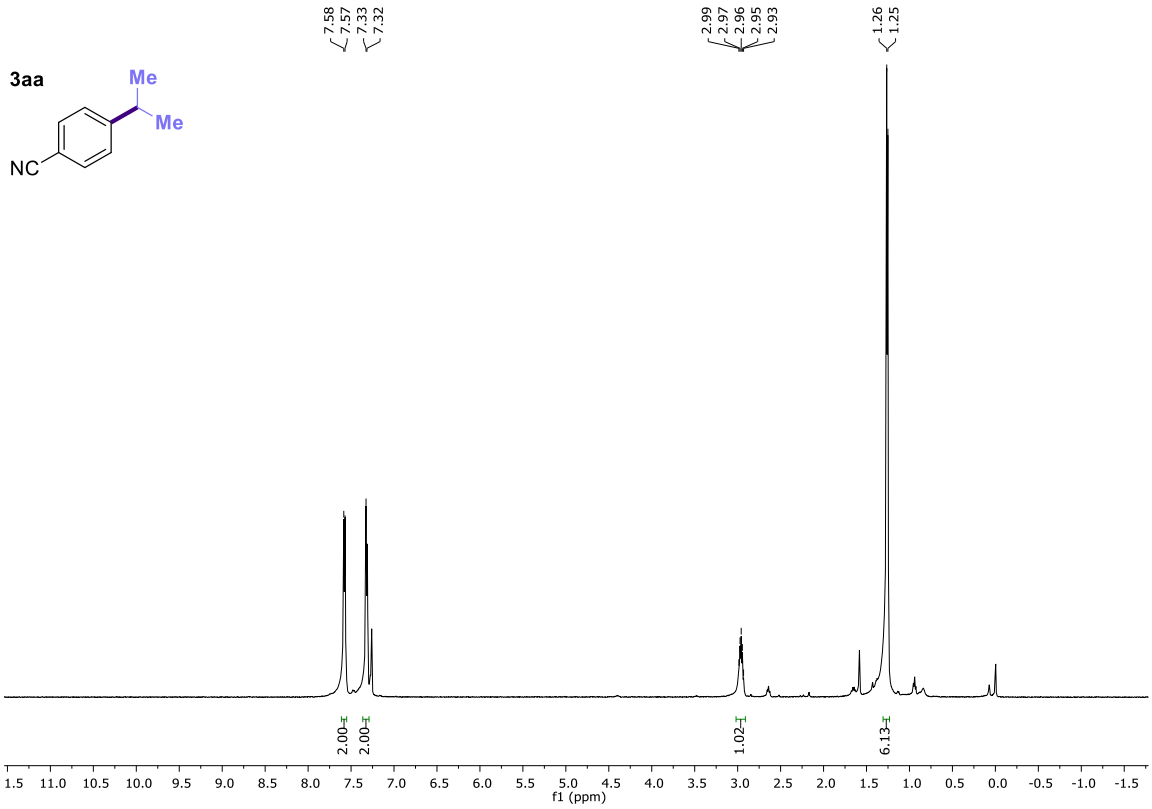


^{13}C NMR ($CDCl_3$, 126 MHz) of 4-isopropyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile (**1a-CN**)

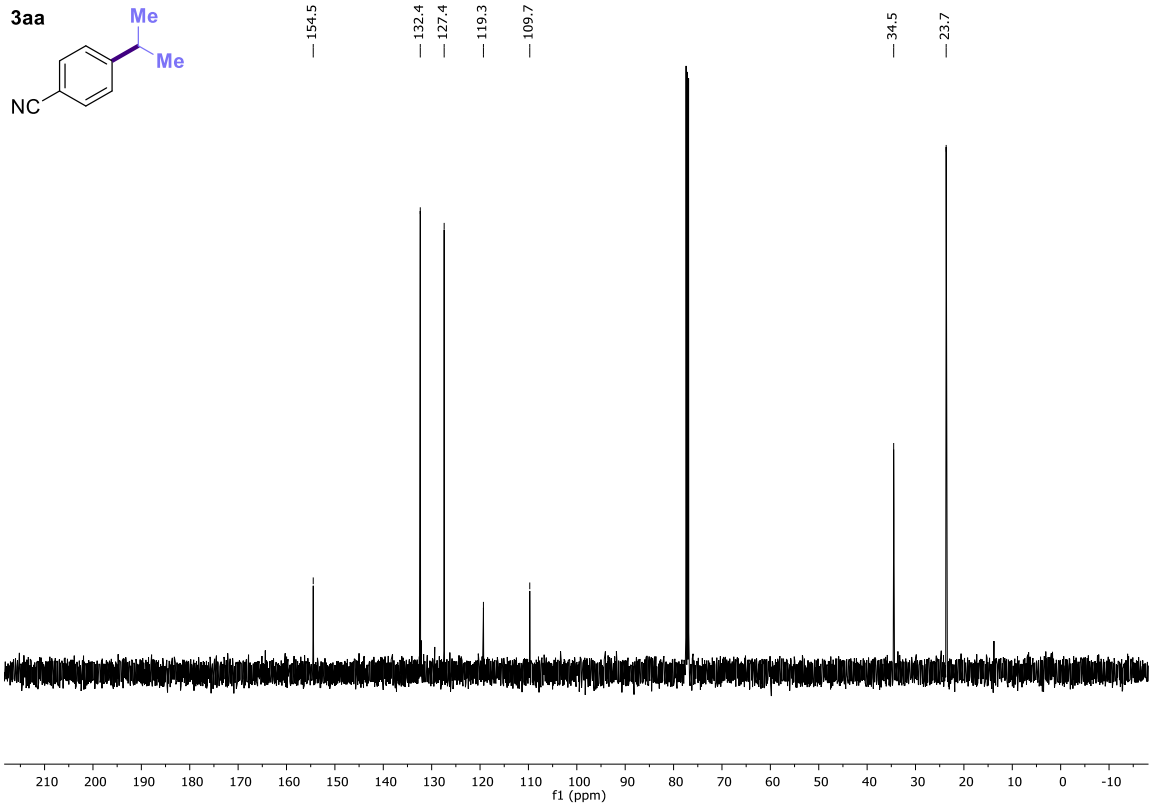


12. ^{1}H and ^{13}C NMR Spectra: Scope of (Hetero)Aryl Bromides

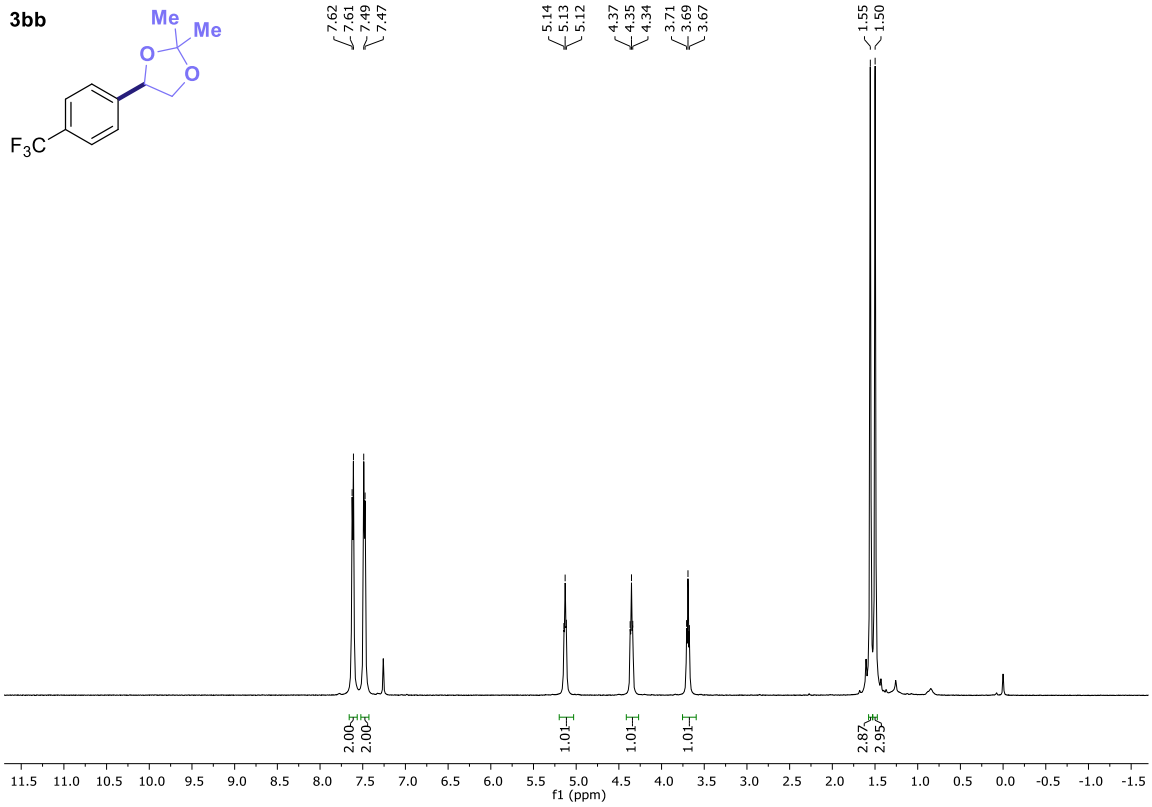
^{1}H NMR ($CDCl_3$, 500 MHz) of 4-isopropylbenzonitrile (**3aa**)



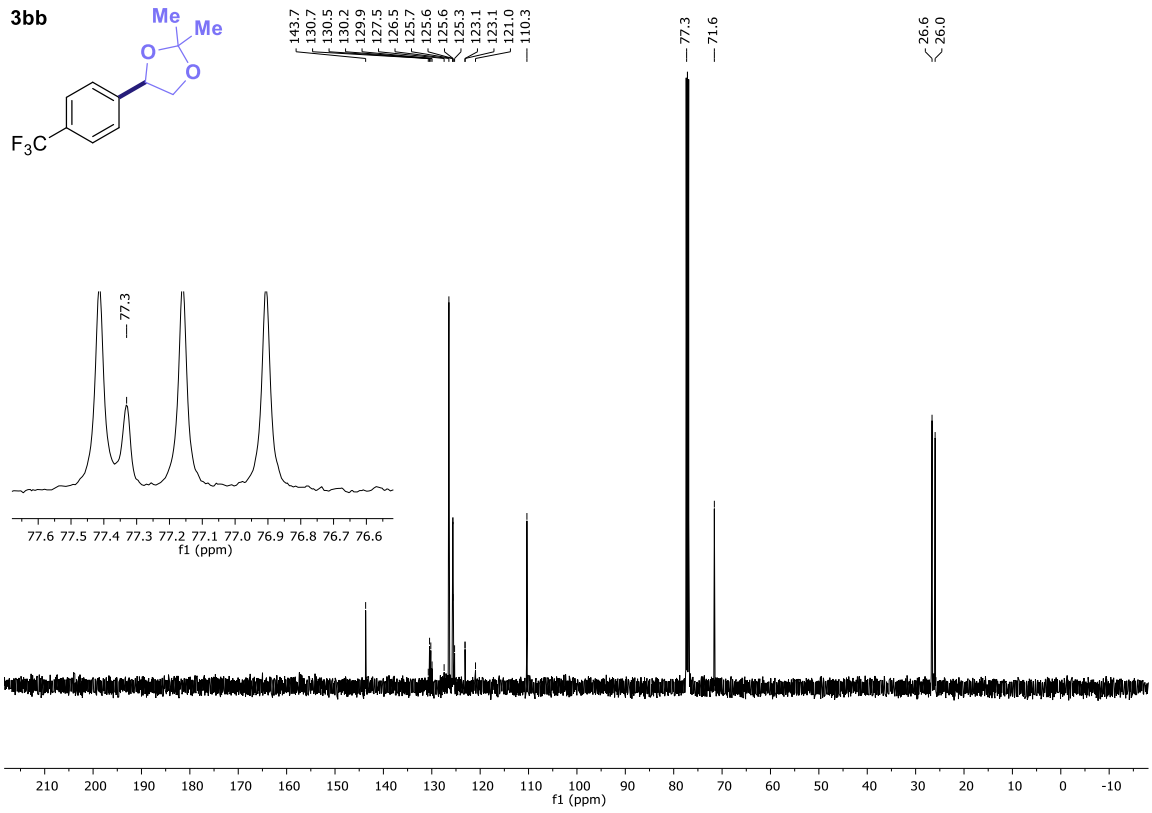
^{13}C NMR ($CDCl_3$, 126 MHz) of 4-isopropylbenzonitrile (**3aa**)



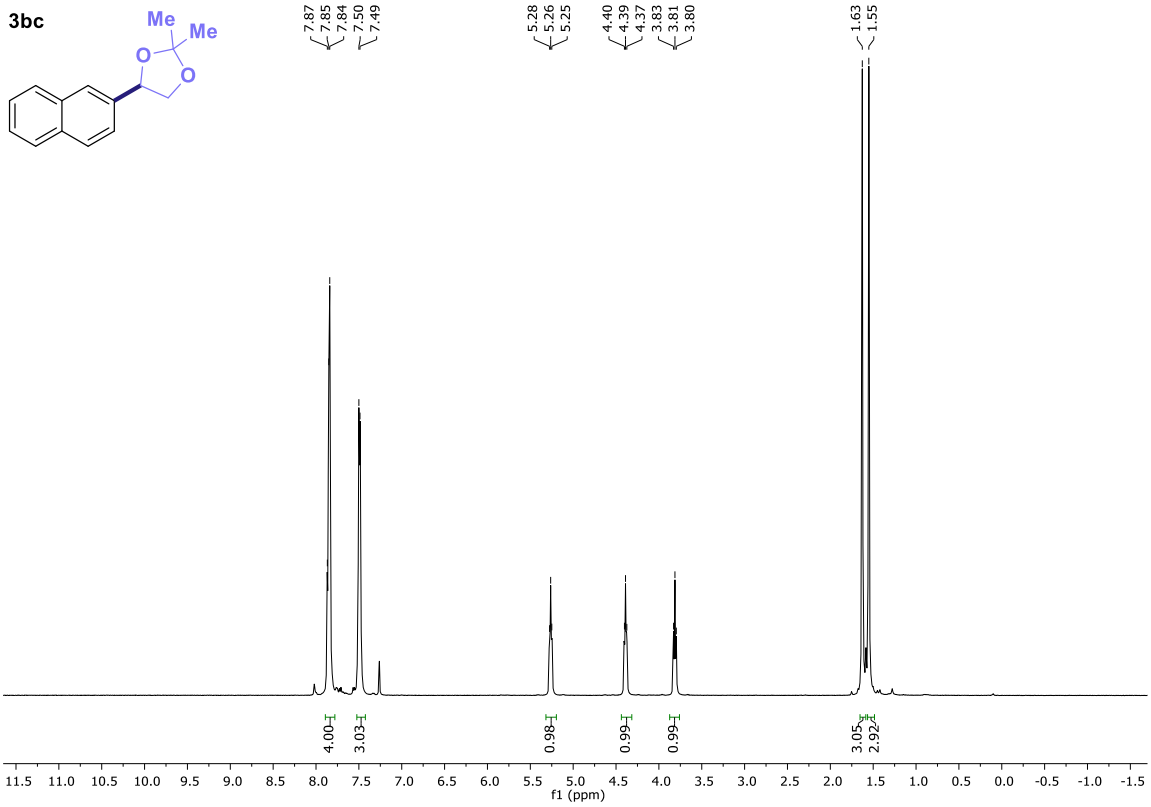
^{1}H NMR ($CDCl_3$, 500 MHz) of 2,2-dimethyl-4-(4-(trifluoromethyl)phenyl)-1,3-dioxolane (**3bb**)



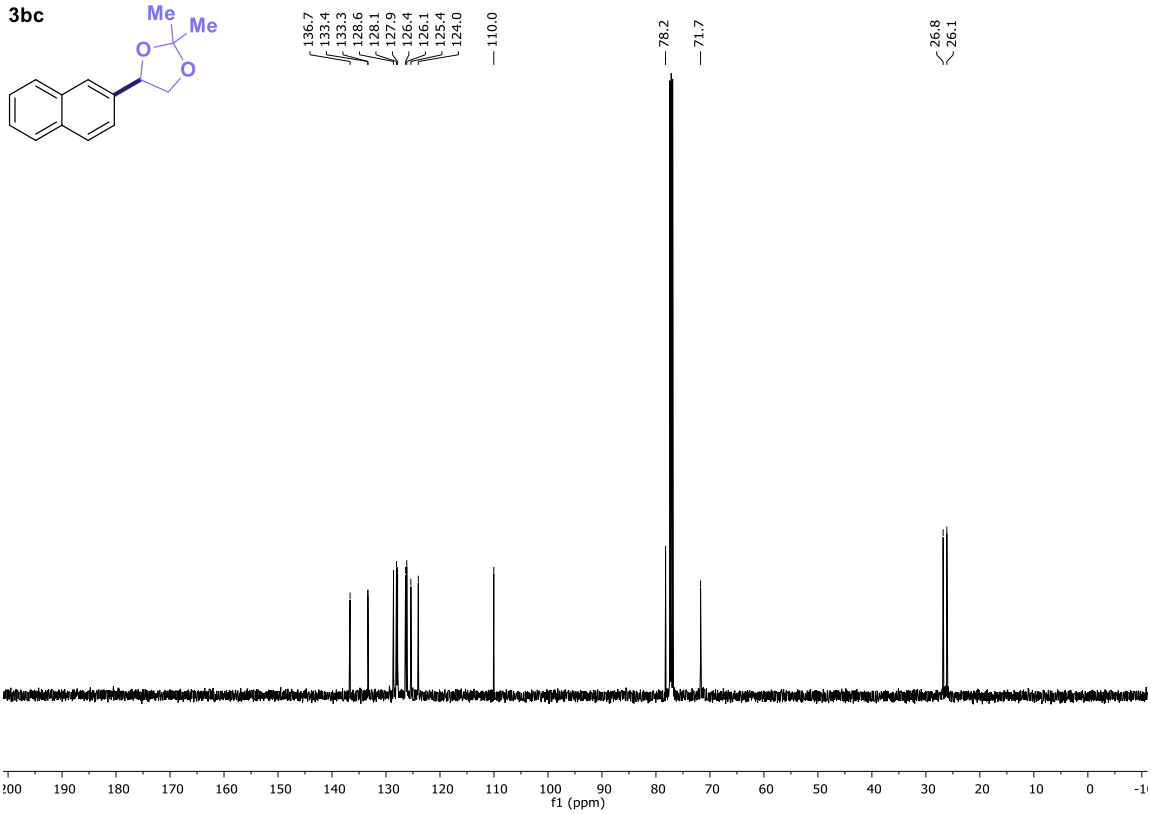
^{13}C NMR ($CDCl_3$, 126 MHz) of 2,2-dimethyl-4-(4-(trifluoromethyl)phenyl)-1,3-dioxolane (**3bb**)



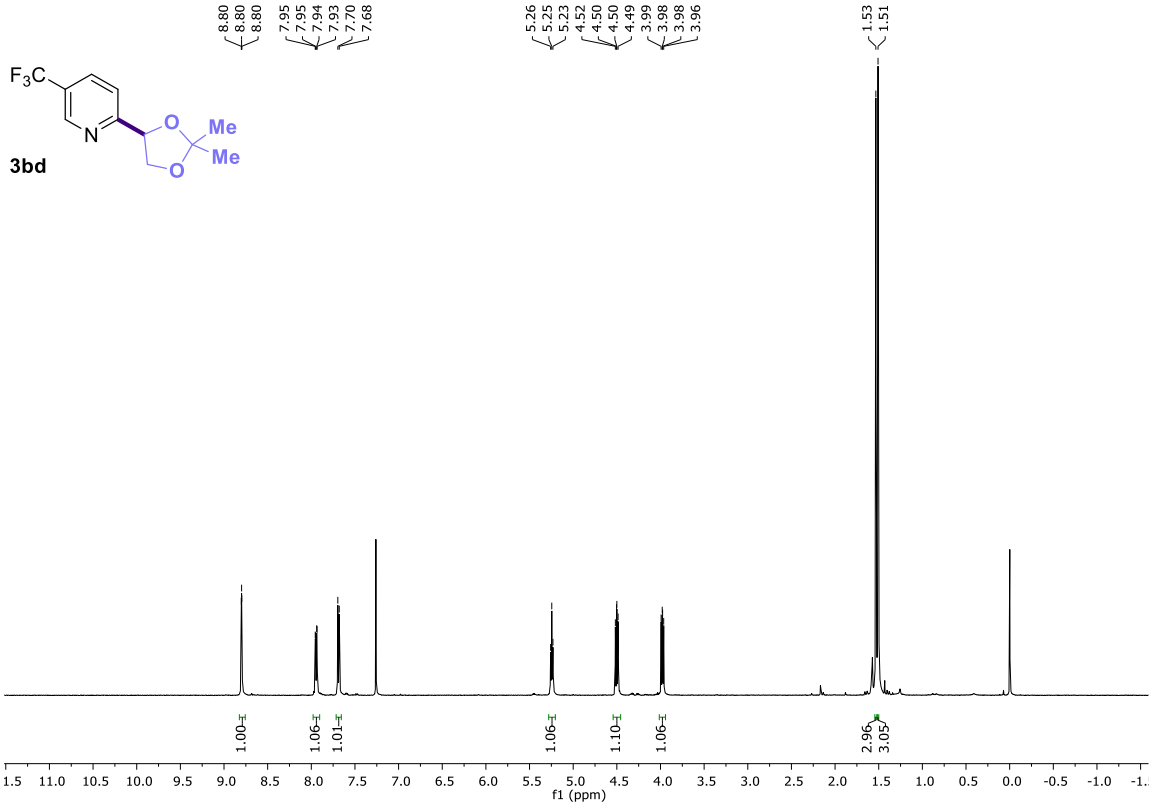
^{1}H NMR ($CDCl_3$, 500 MHz) of 2,2-dimethyl-4-(naphthalen-2-yl)-1,3-dioxolane (**3bc**)



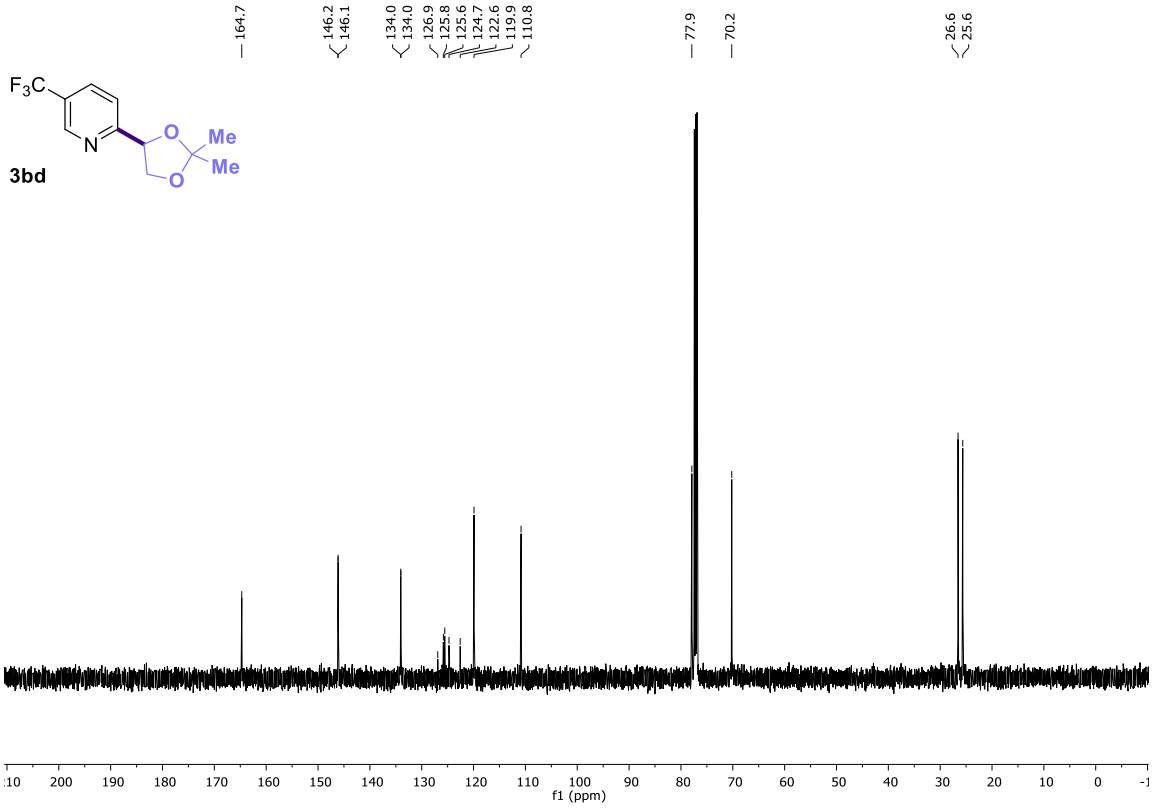
^{13}C NMR ($CDCl_3$, 126 MHz) of 2,2-dimethyl-4-(naphthalen-2-yl)-1,3-dioxolane (**3bc**)



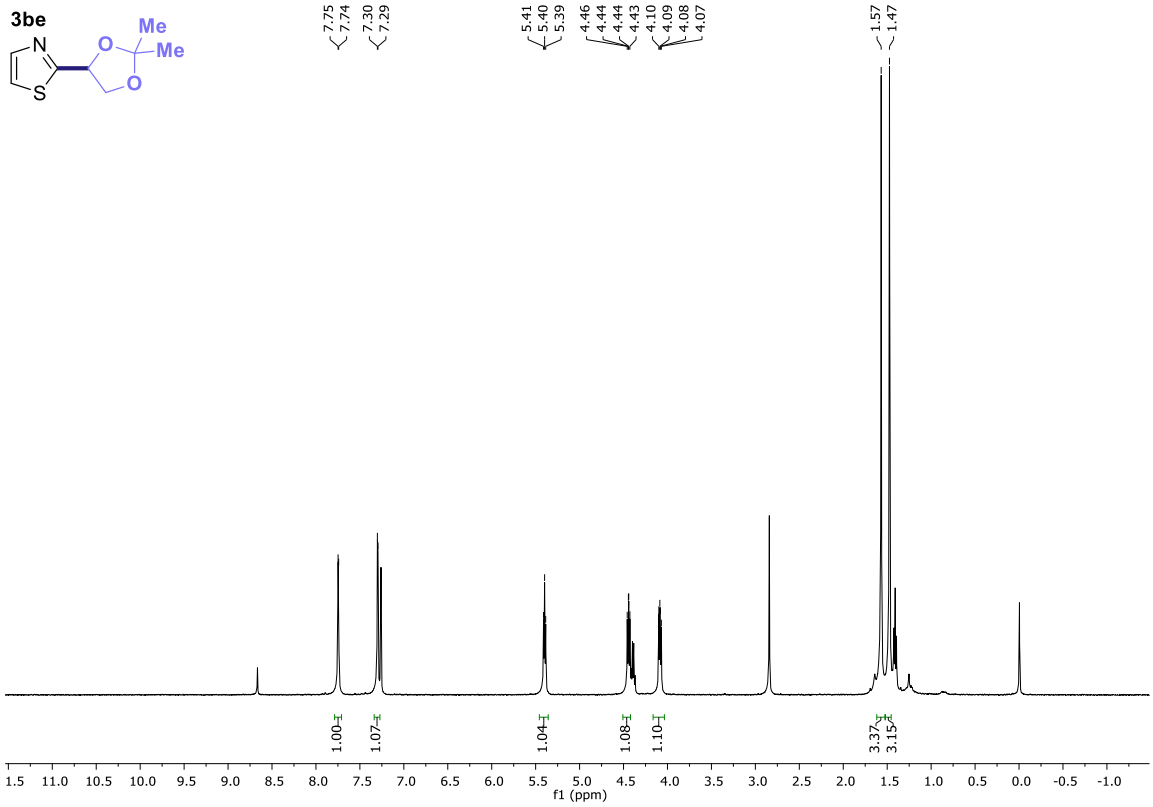
^{1}H NMR ($CDCl_3$, 500 MHz) of 2-(2,2-dimethyl-1,3-dioxolan-4-yl)-5-(trifluoromethyl)pyridine (**3bd**)



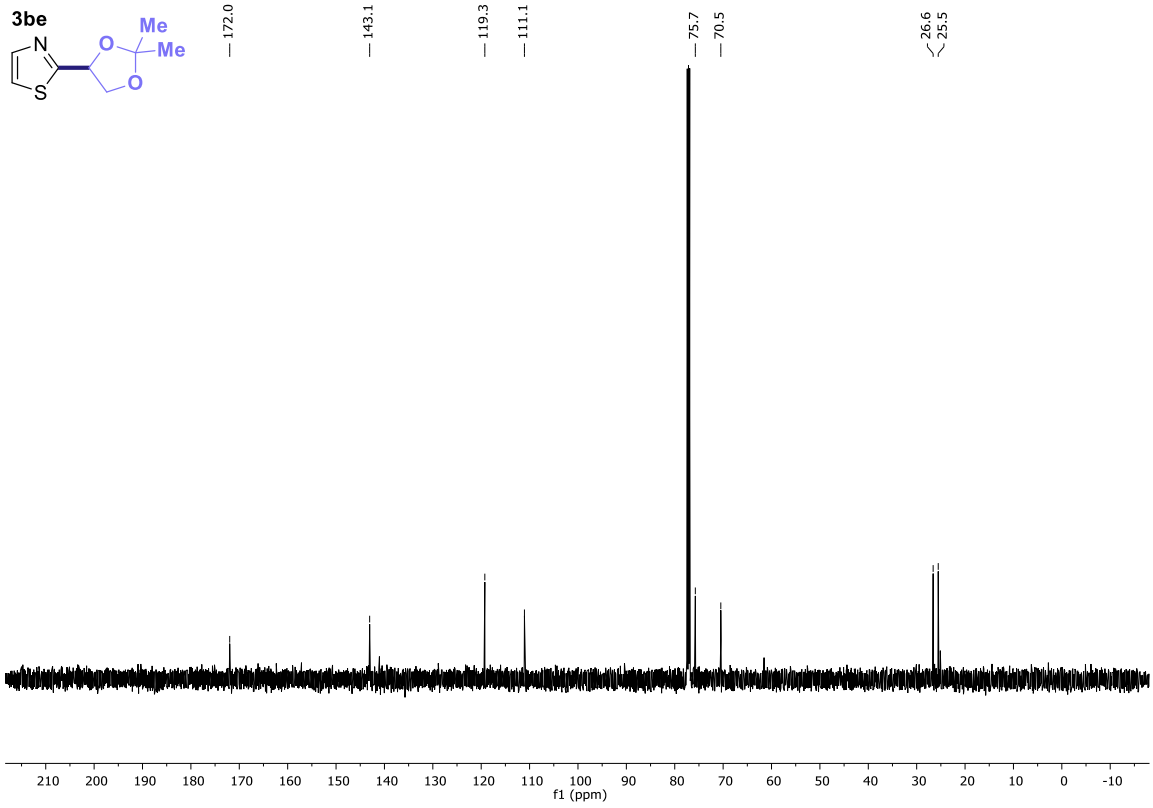
^{13}C NMR ($CDCl_3$, 126 MHz) of 2-(2,2-dimethyl-1,3-dioxolan-4-yl)-5-(trifluoromethyl)pyridine (**3bd**)



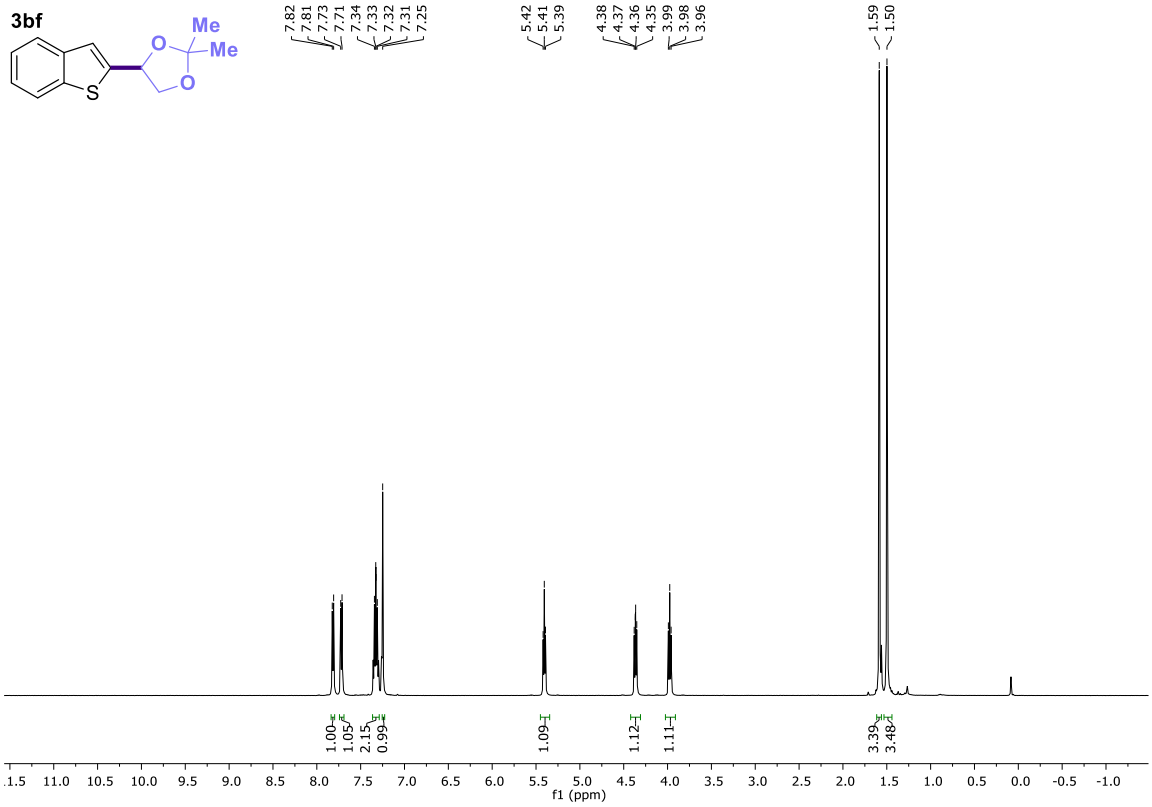
^{1}H NMR ($CDCl_3$, 500 MHz) of 2-(2,2-dimethyl-1,3-dioxolan-4-yl)thiazole (**3be**)



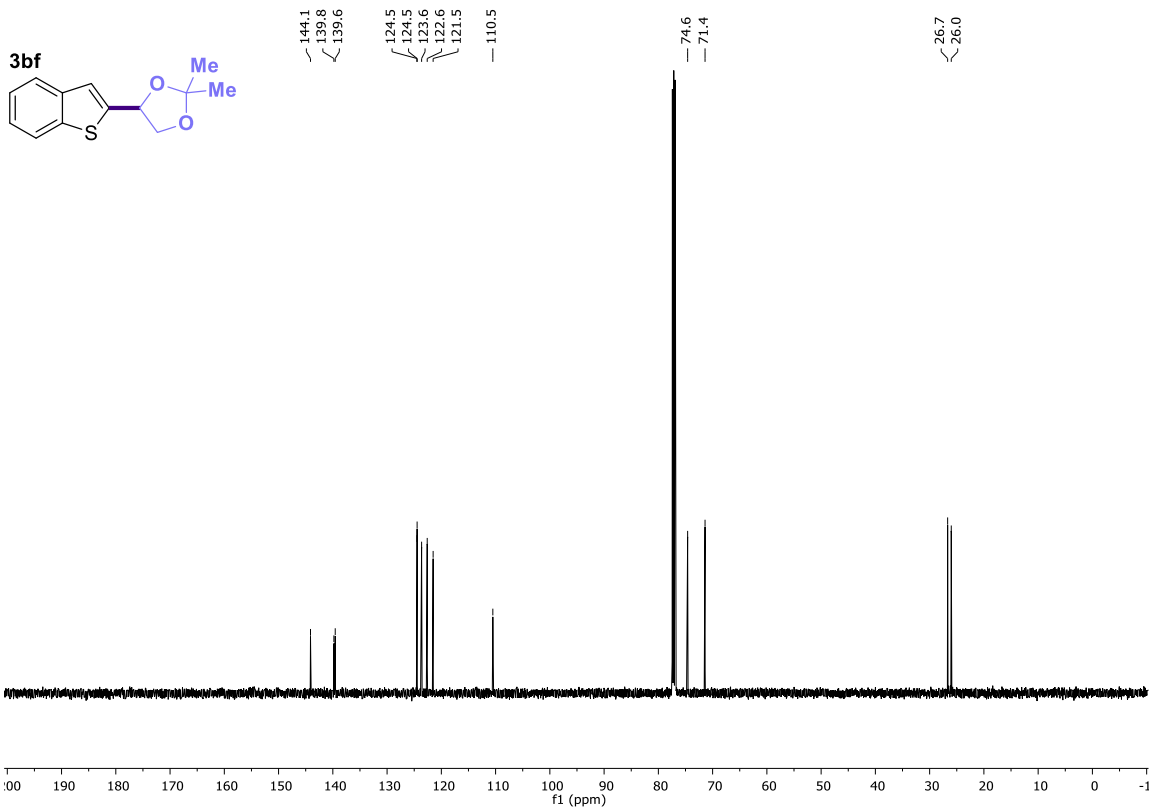
^{13}C NMR ($CDCl_3$, 126 MHz) of 2-(2,2-dimethyl-1,3-dioxolan-4-yl)thiazole (**3be**)



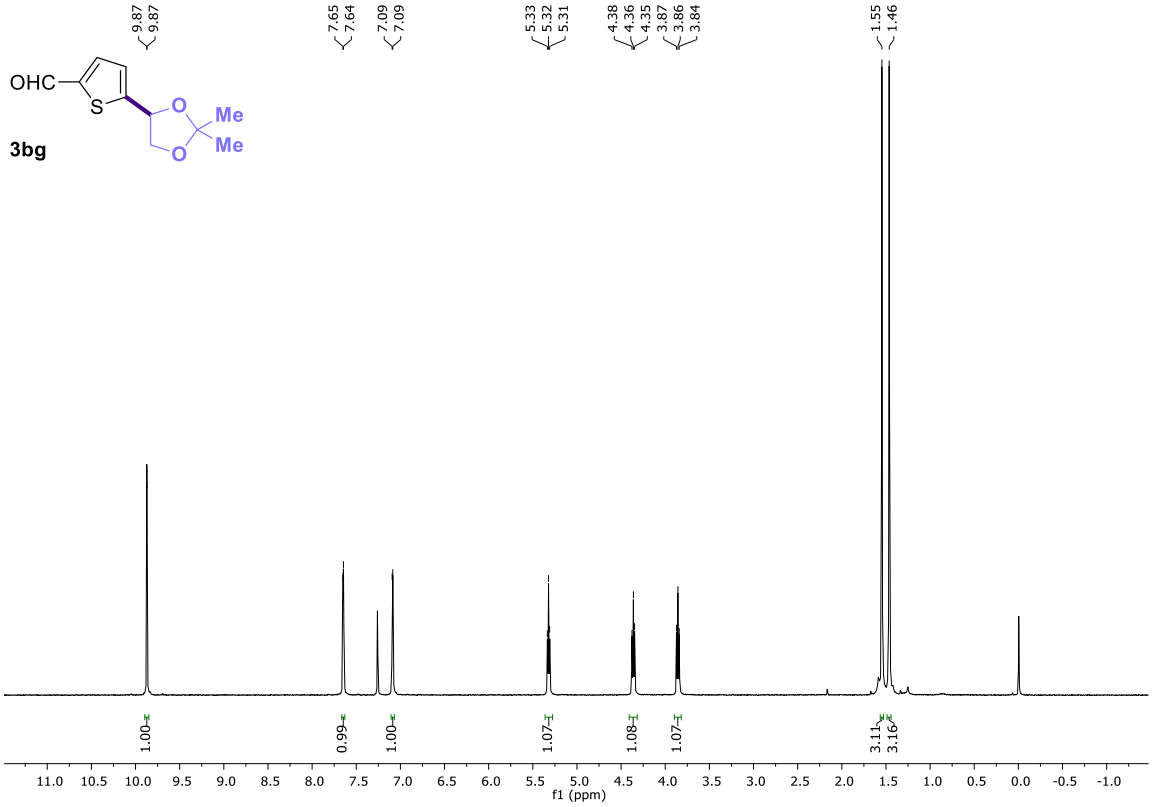
^{1}H NMR ($CDCl_3$, 500 MHz) of 4-(benzo[b]thiophen-2-yl)-2,2-dimethyl-1,3-dioxolane (**3bf**)



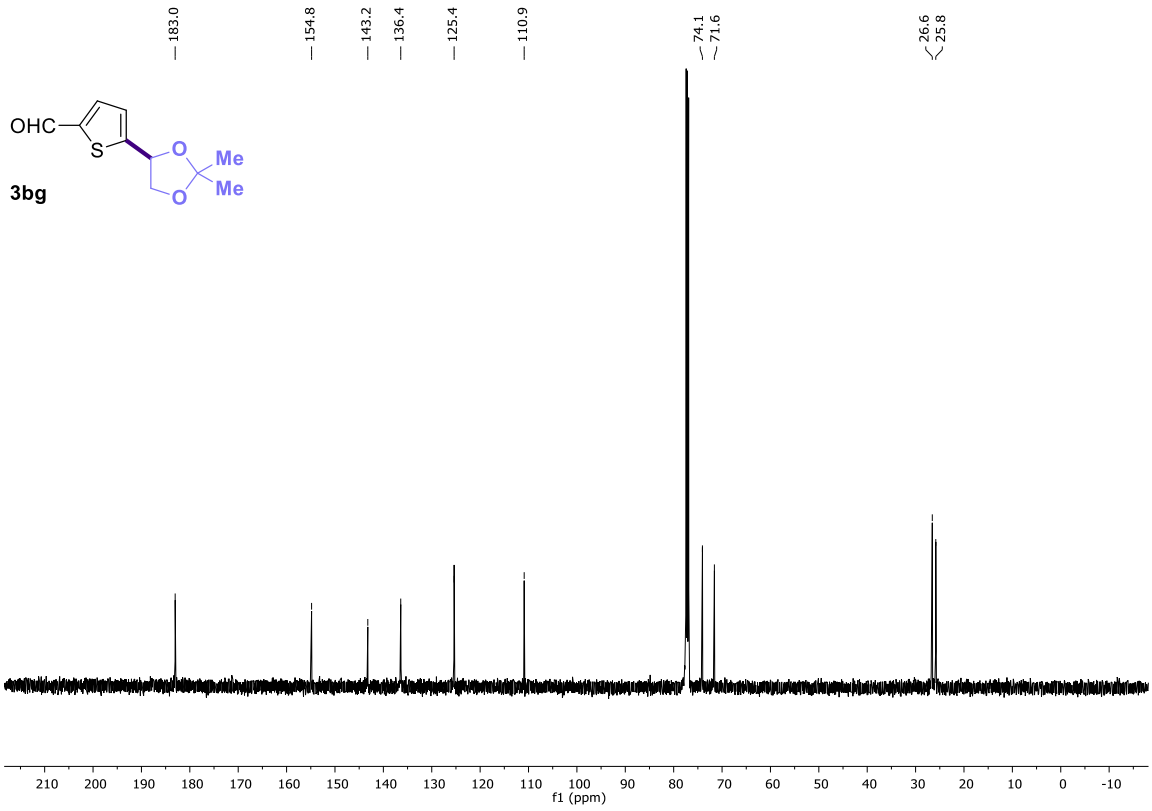
^{13}C NMR ($CDCl_3$, 126 MHz) of 4-(benzo[b]thiophen-2-yl)-2,2-dimethyl-1,3-dioxolane (**3bf**)



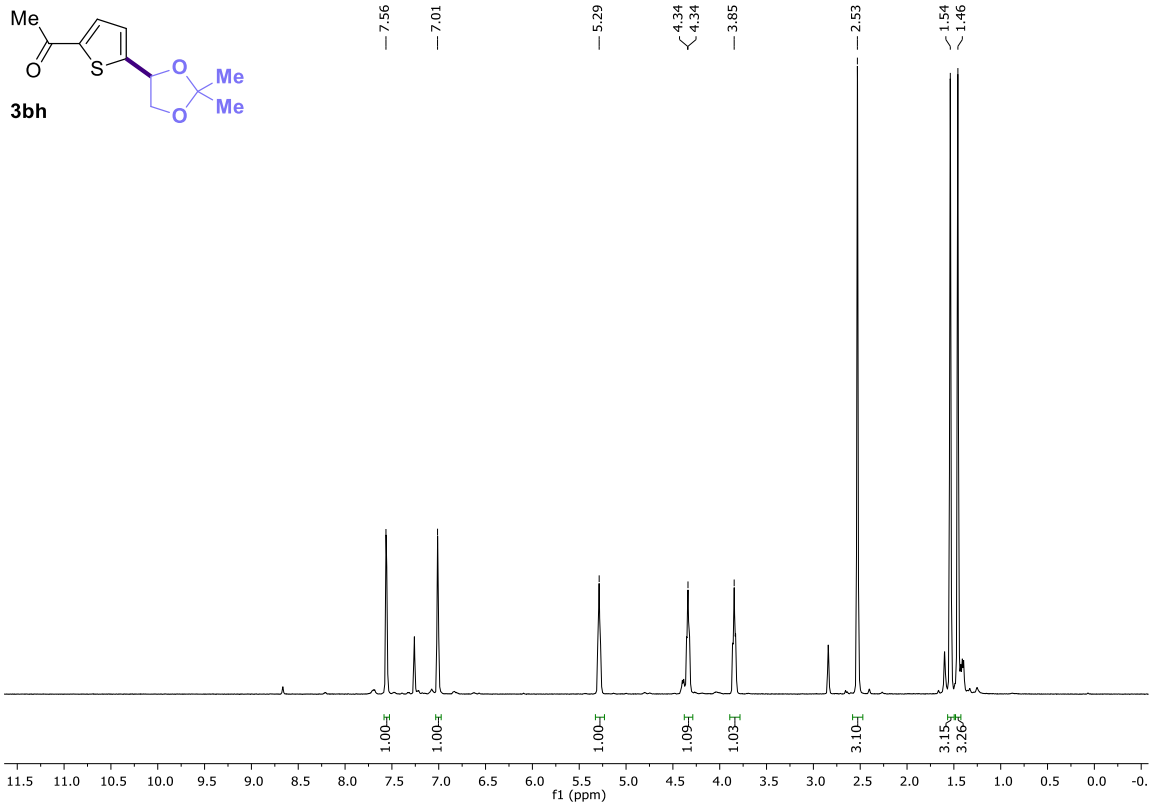
^{1}H NMR ($CDCl_3$, 500 MHz) of 5-(2,2-dimethyl-1,3-dioxolan-4-yl)thiophene-2-carbaldehyde (**3bg**)



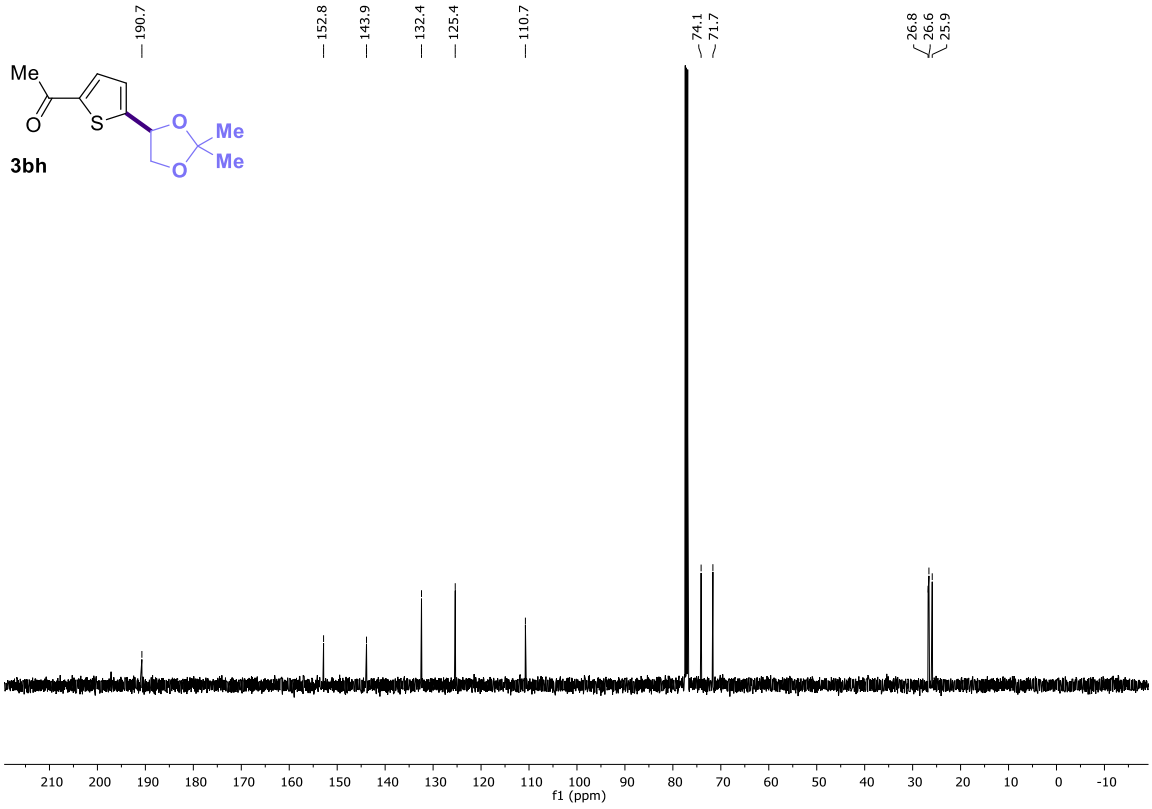
^{13}C NMR ($CDCl_3$, 126 MHz) of 5-(2,2-dimethyl-1,3-dioxolan-4-yl)thiophene-2-carbaldehyde (**3bg**)



^{1}H NMR ($CDCl_3$, 500 MHz) of 1-(5-(2,2-dimethyl-1,3-dioxolan-4-yl)thiophen-2-yl)ethan-1-one (**3bh**)

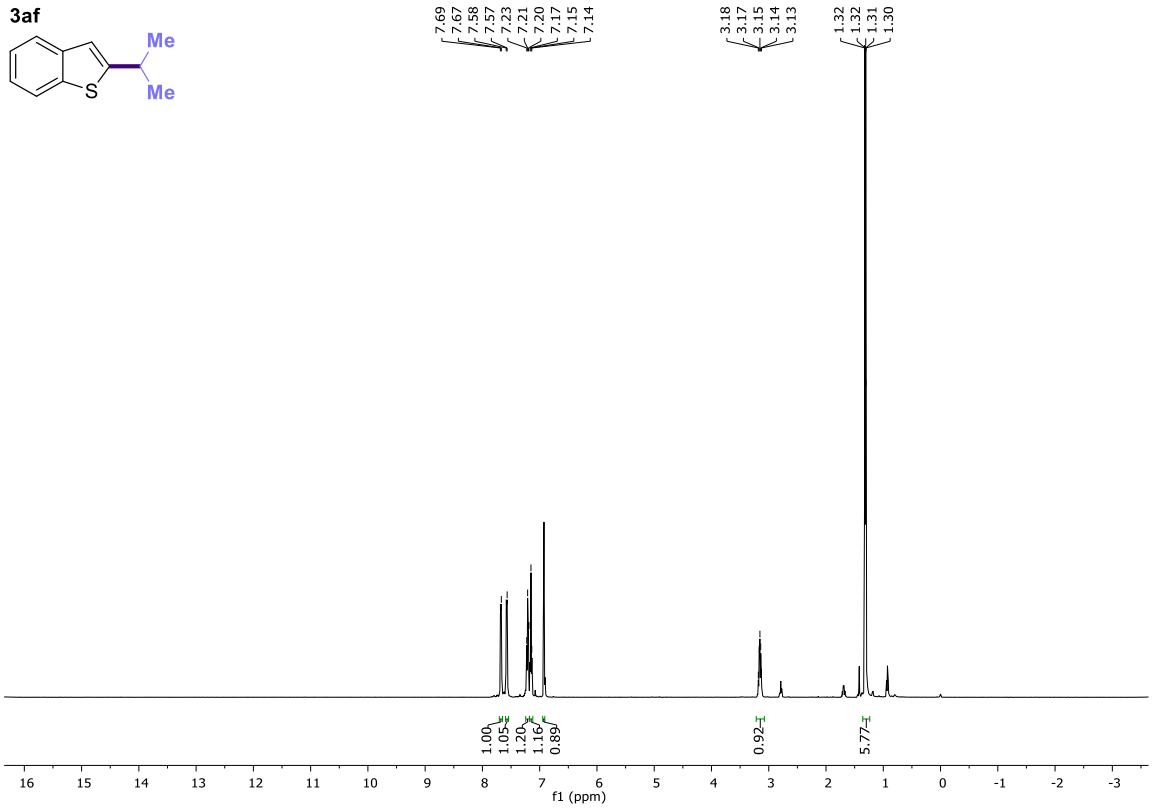


^{13}C NMR ($CDCl_3$, 126 MHz) of 1-(5-(2,2-dimethyl-1,3-dioxolan-4-yl)thiophen-2-yl)ethan-1-one (**3bh**)

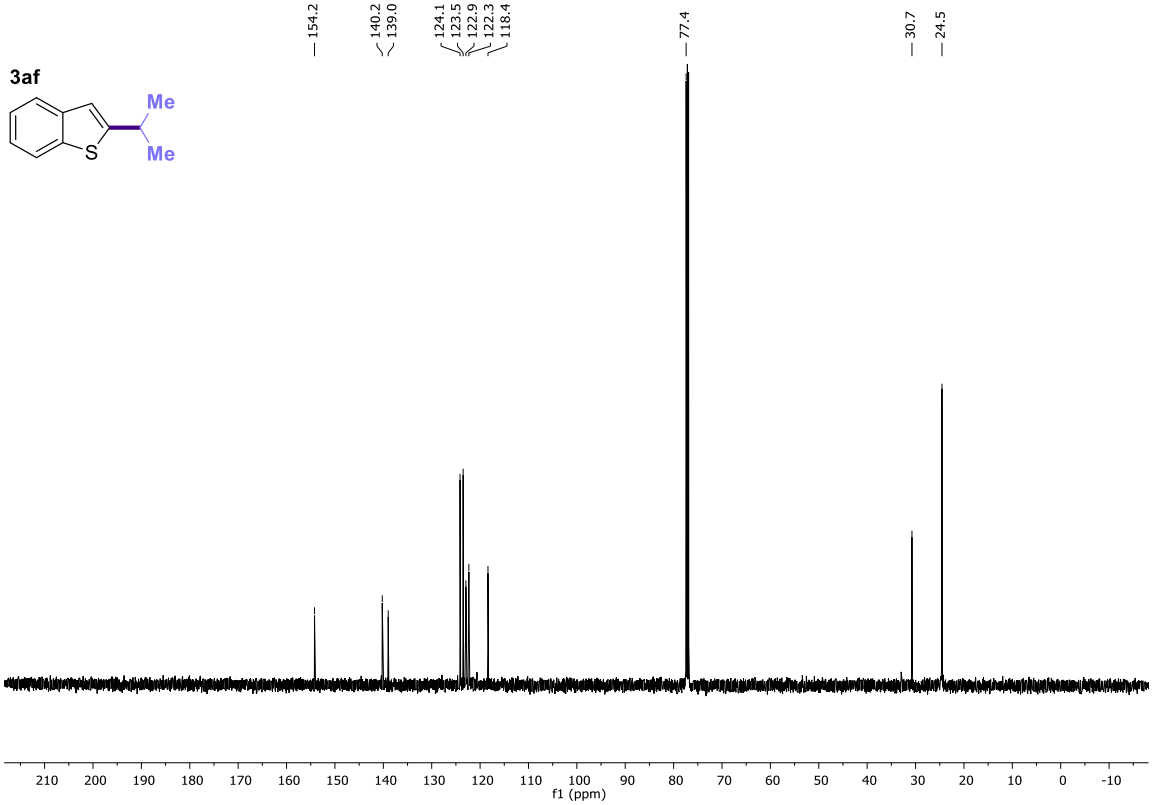


13. ^{1}H and ^{13}C NMR Spectra: Scope of (Hetero)Aryl Bromides and Dihydropyridines

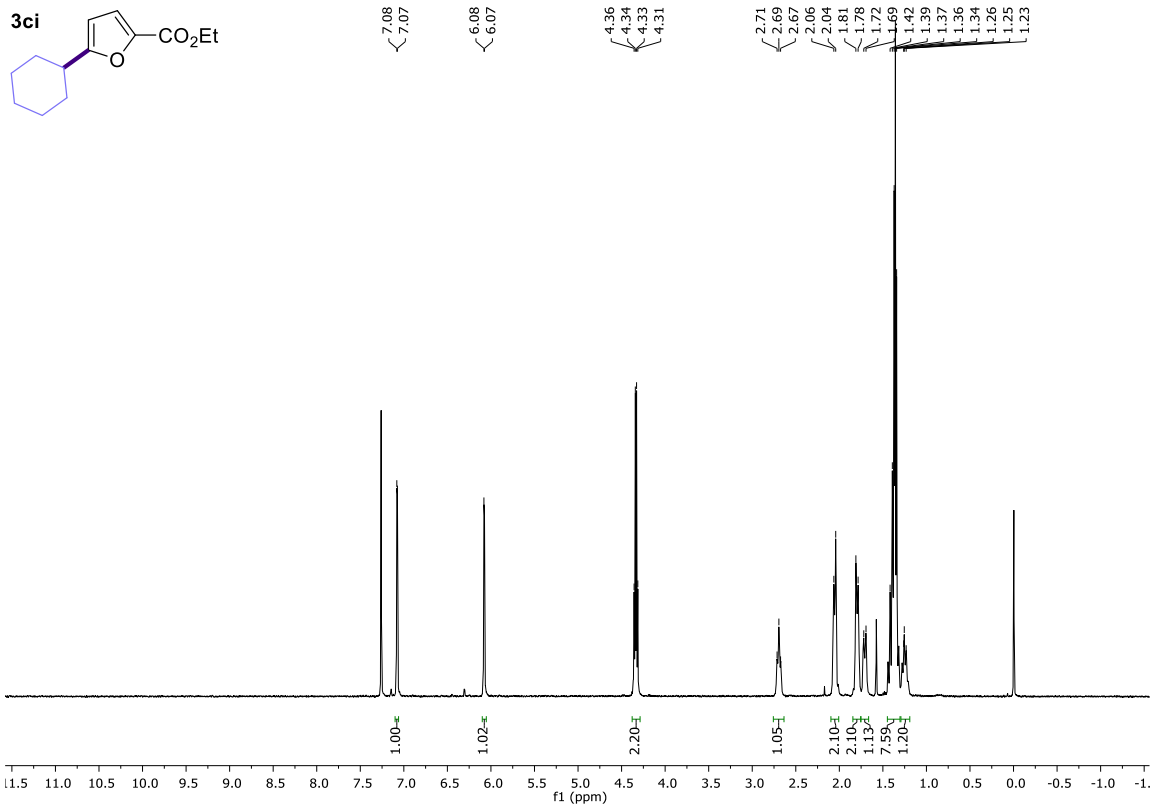
^{1}H NMR ($CDCl_3$, 500 MHz) of 2-isopropylbenzo[b]thiophene (**3af**)



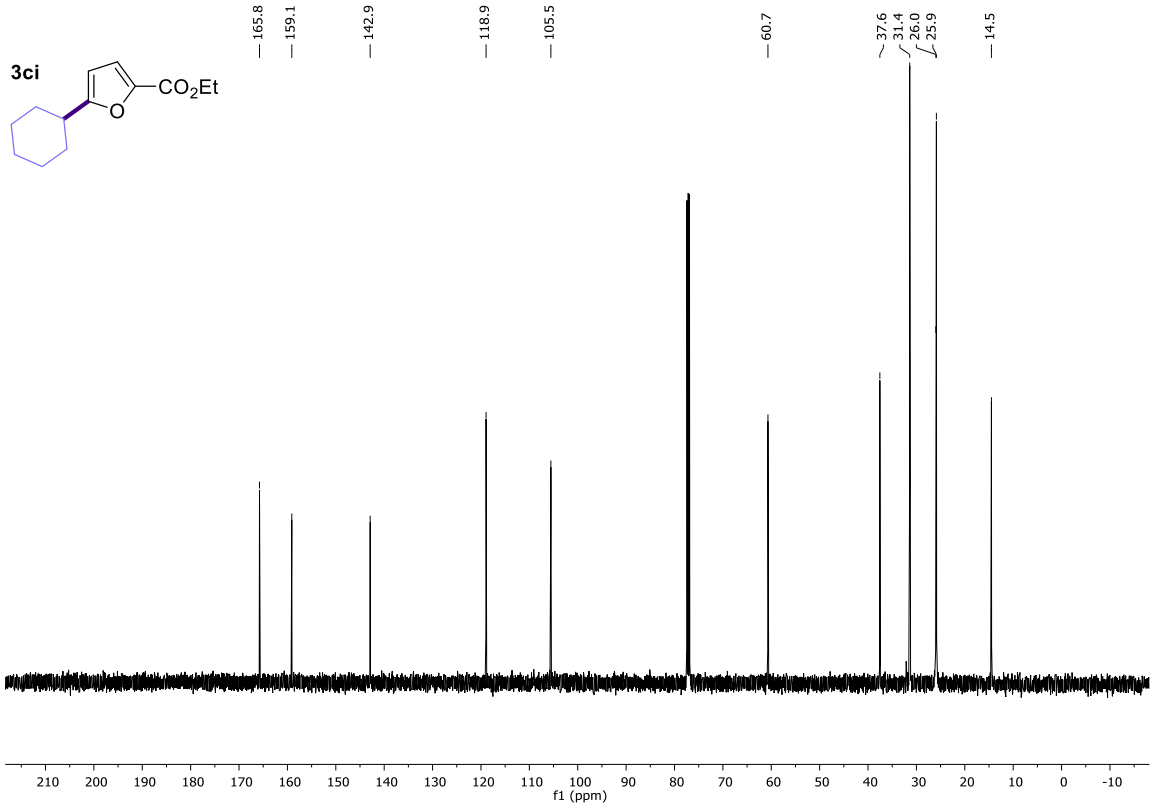
^{13}C NMR ($CDCl_3$, 126 MHz) of 2-isopropylbenzo[b]thiophene (**3af**)



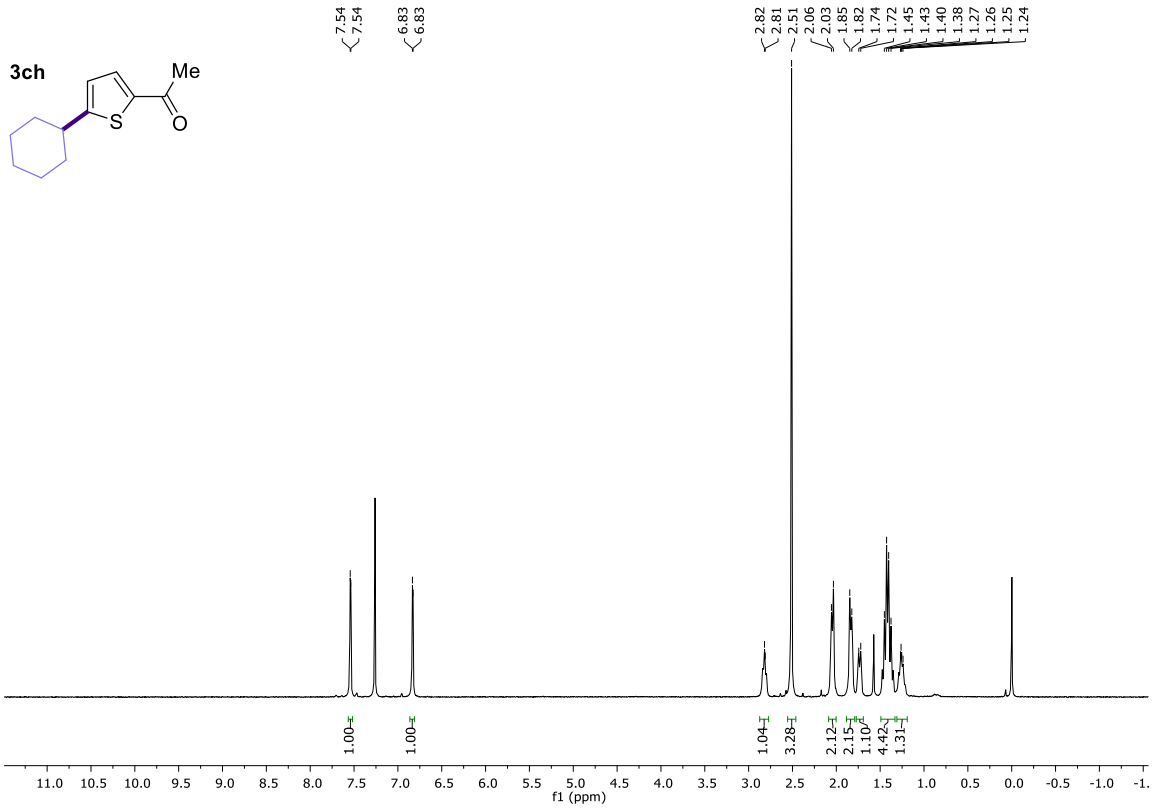
^{1}H NMR ($CDCl_3$, 500 MHz) of ethyl 5-cyclohexylfuran-2-carboxylate (**3ci**)



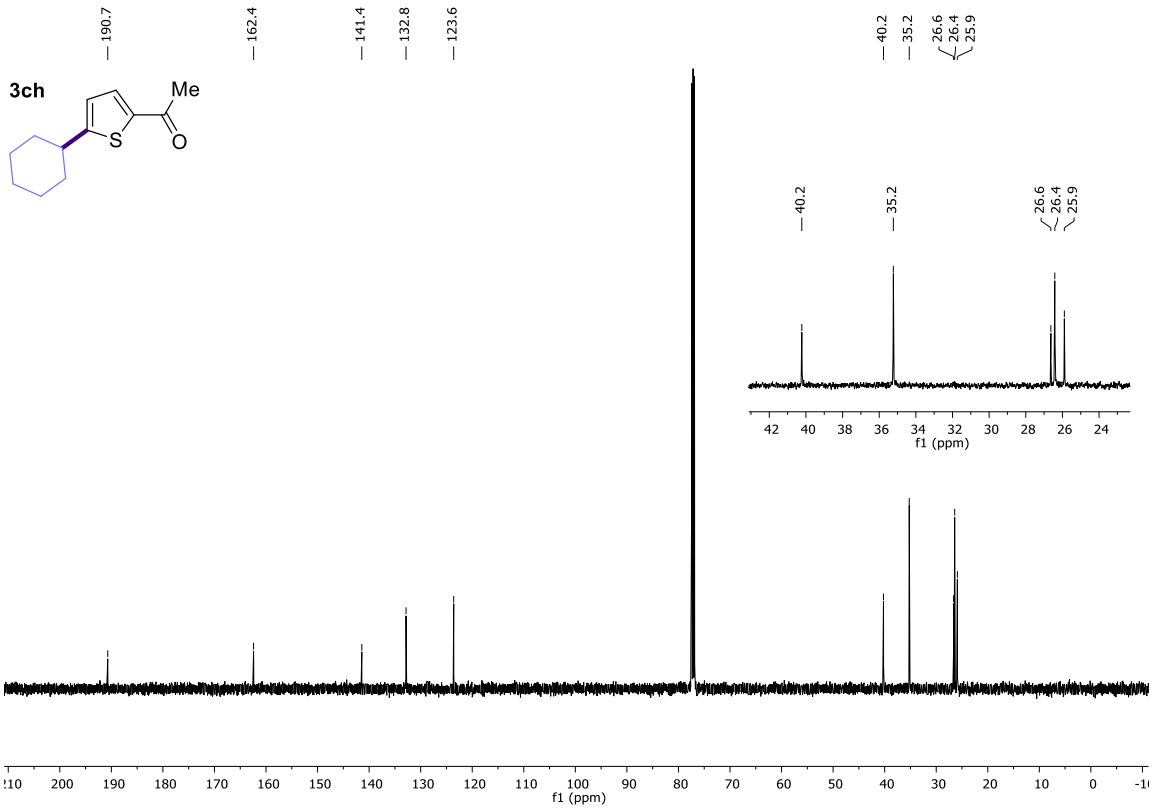
^{13}C NMR ($CDCl_3$, 126 MHz) of ethyl 5-cyclohexylfuran-2-carboxylate (**3ci**)



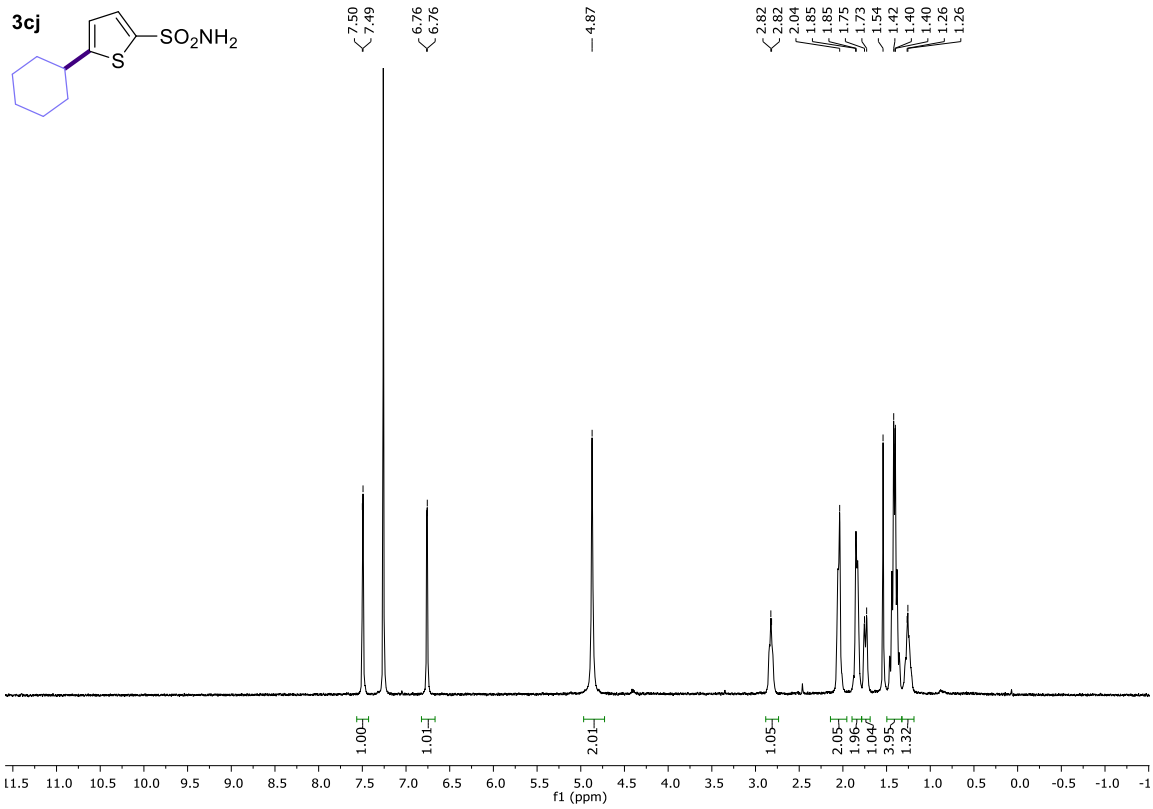
^{1}H NMR ($CDCl_3$, 500 MHz) of 1-(5-cyclohexylthiophen-2-yl)ethan-1-one (**3ch**)



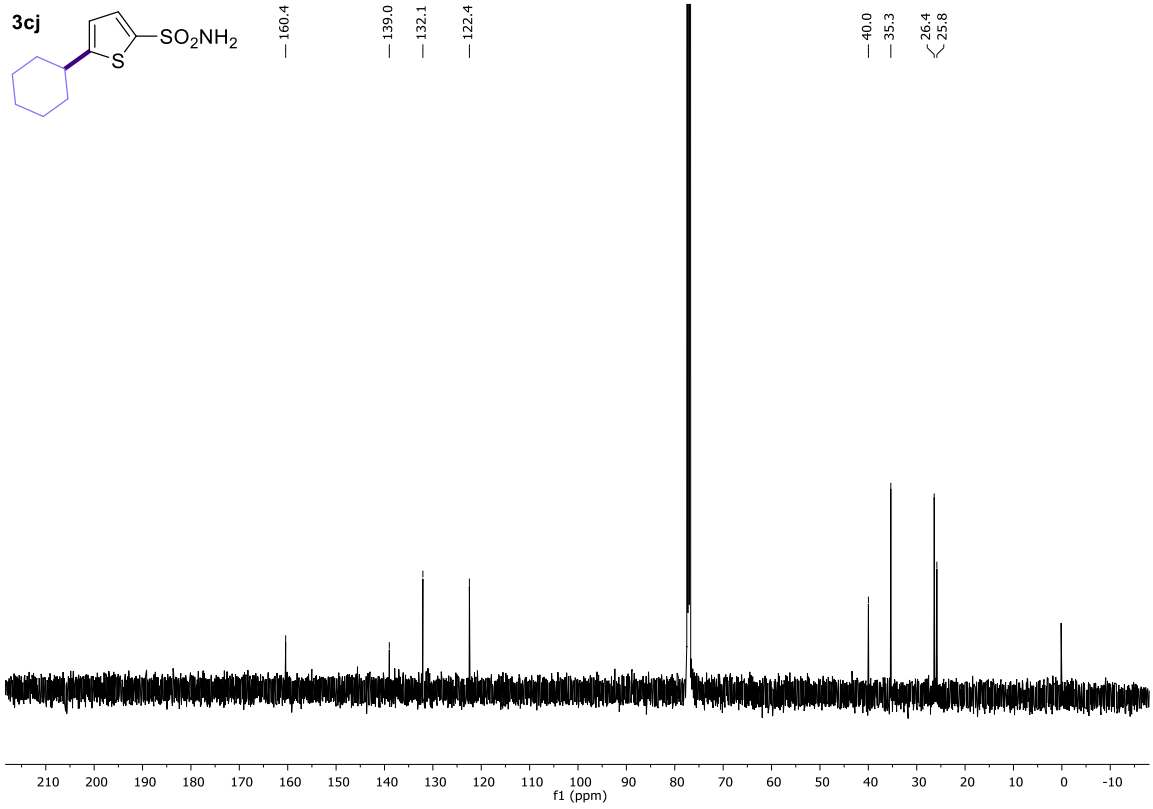
^{13}C NMR ($CDCl_3$, 126 MHz) of 1-(5-cyclohexylthiophen-2-yl)ethan-1-one (**3ch**)



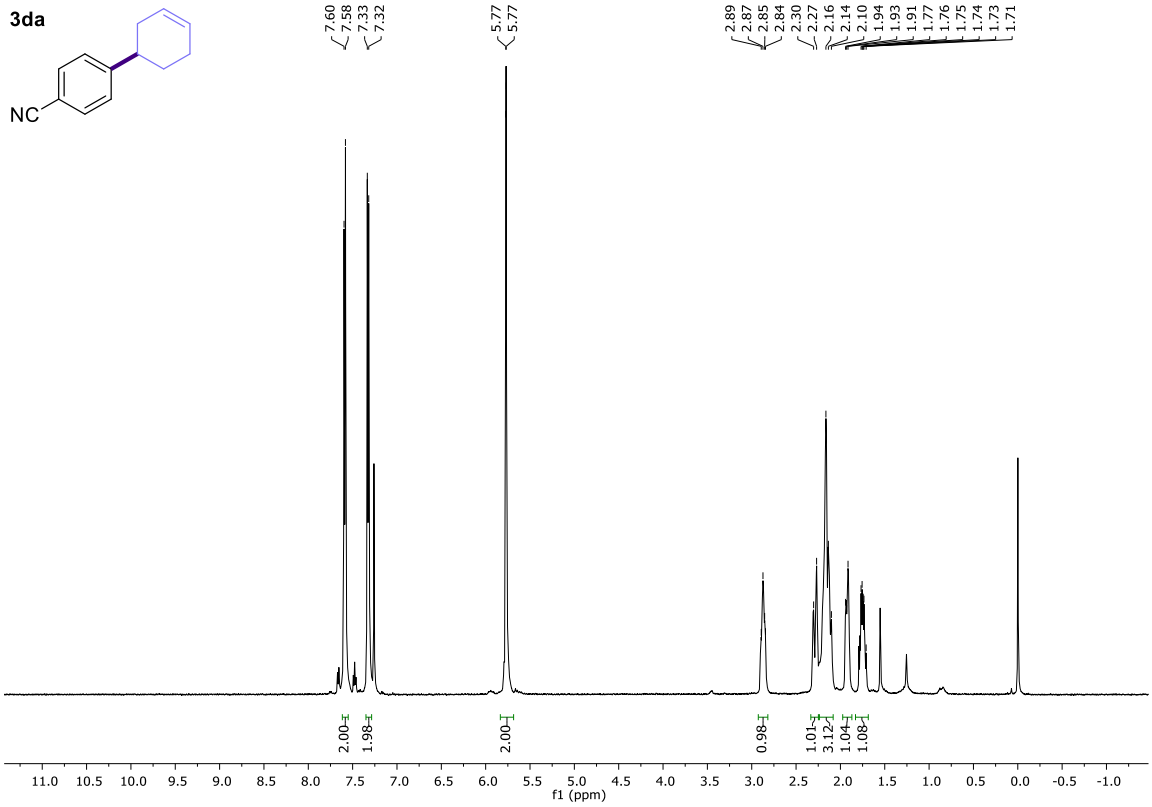
^{1}H NMR ($CDCl_3$, 500 MHz) of 5-cyclohexylthiophene-2-sulfonamide (**3cj**)



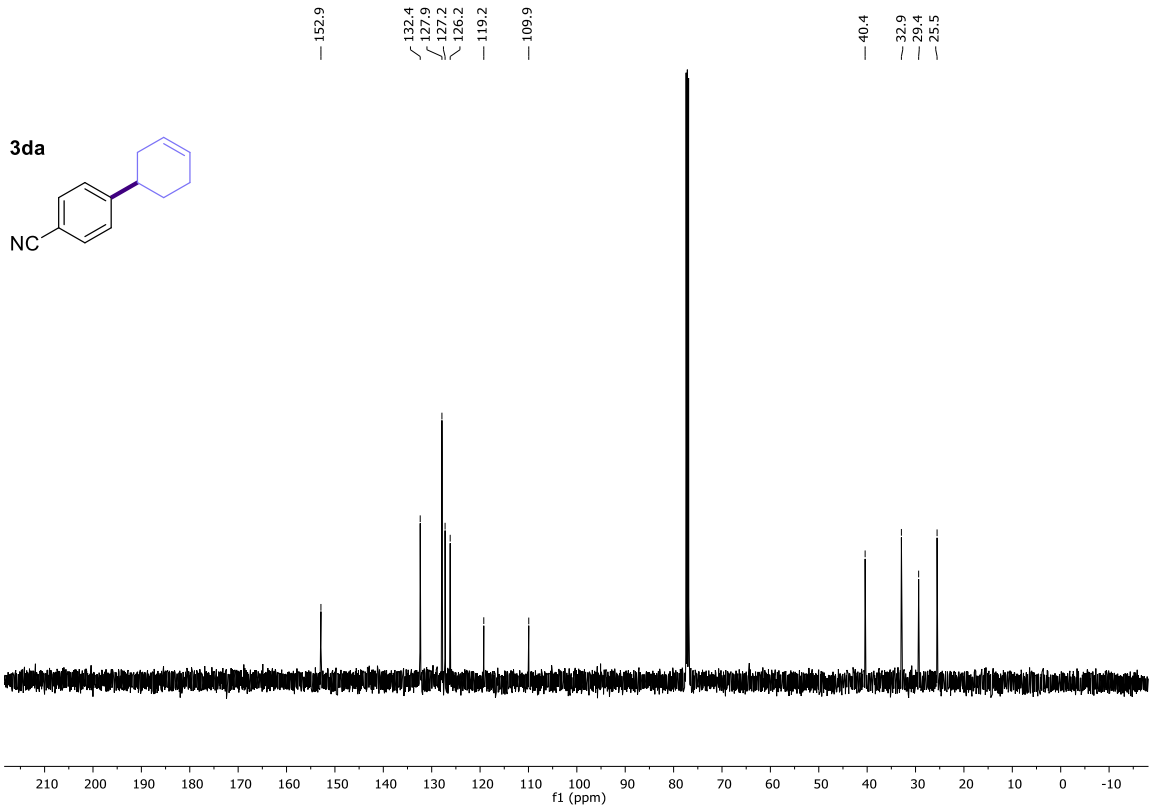
^{13}C NMR ($CDCl_3$, 126 MHz) of 5-cyclohexylthiophene-2-sulfonamide (**3cj**)



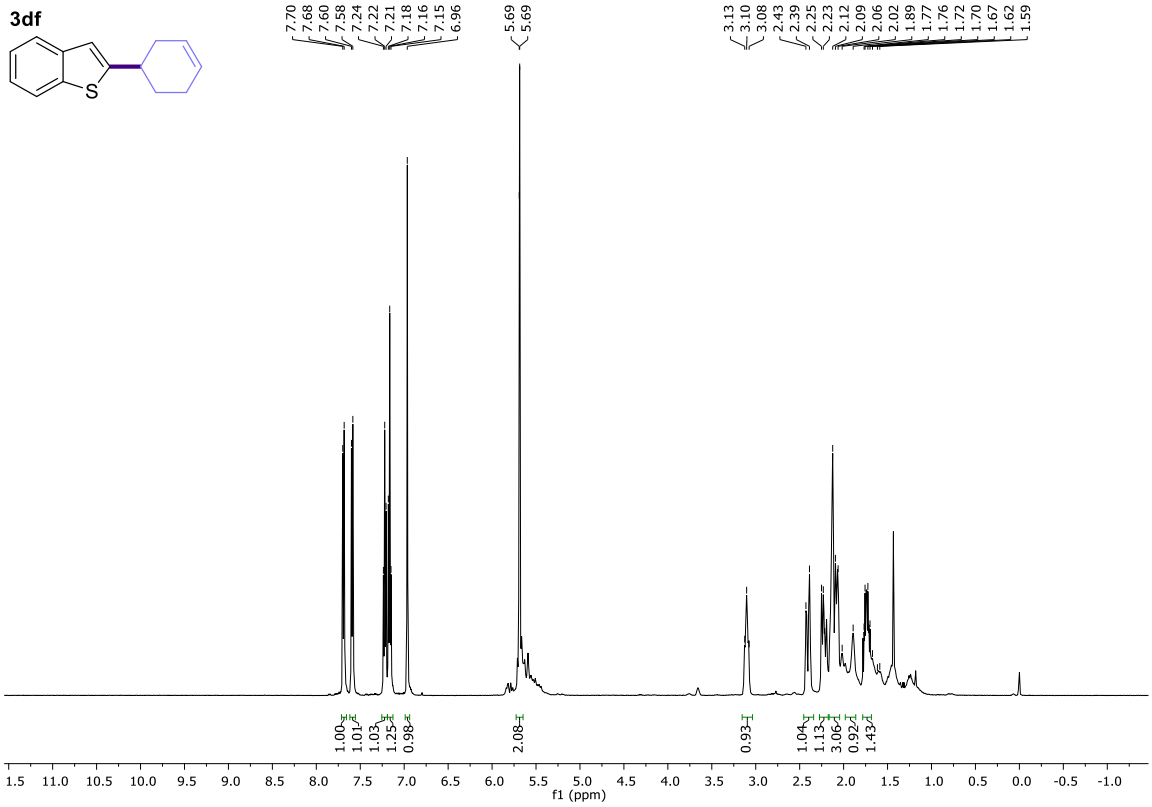
^{1}H NMR ($CDCl_3$, 500 MHz) of 1',2',3',6'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (**3da**)



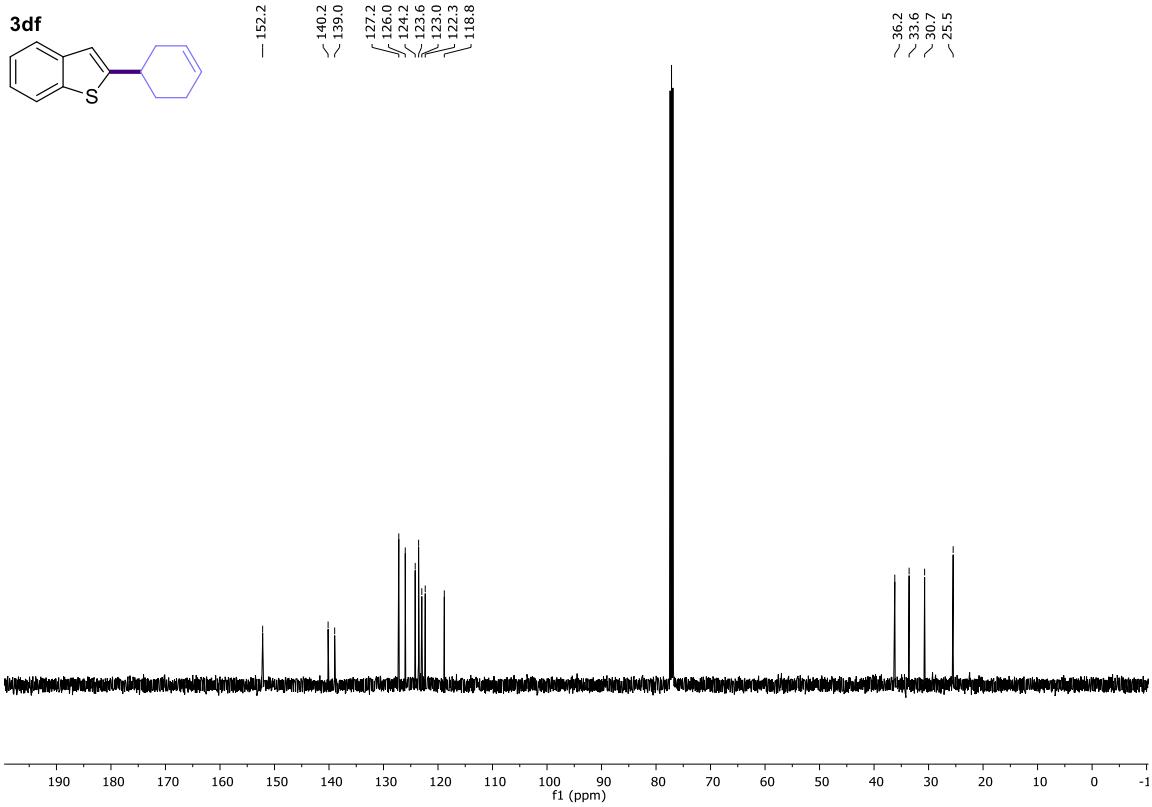
^{13}C NMR ($CDCl_3$, 126 MHz) of 1',2',3',6'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (**3da**)



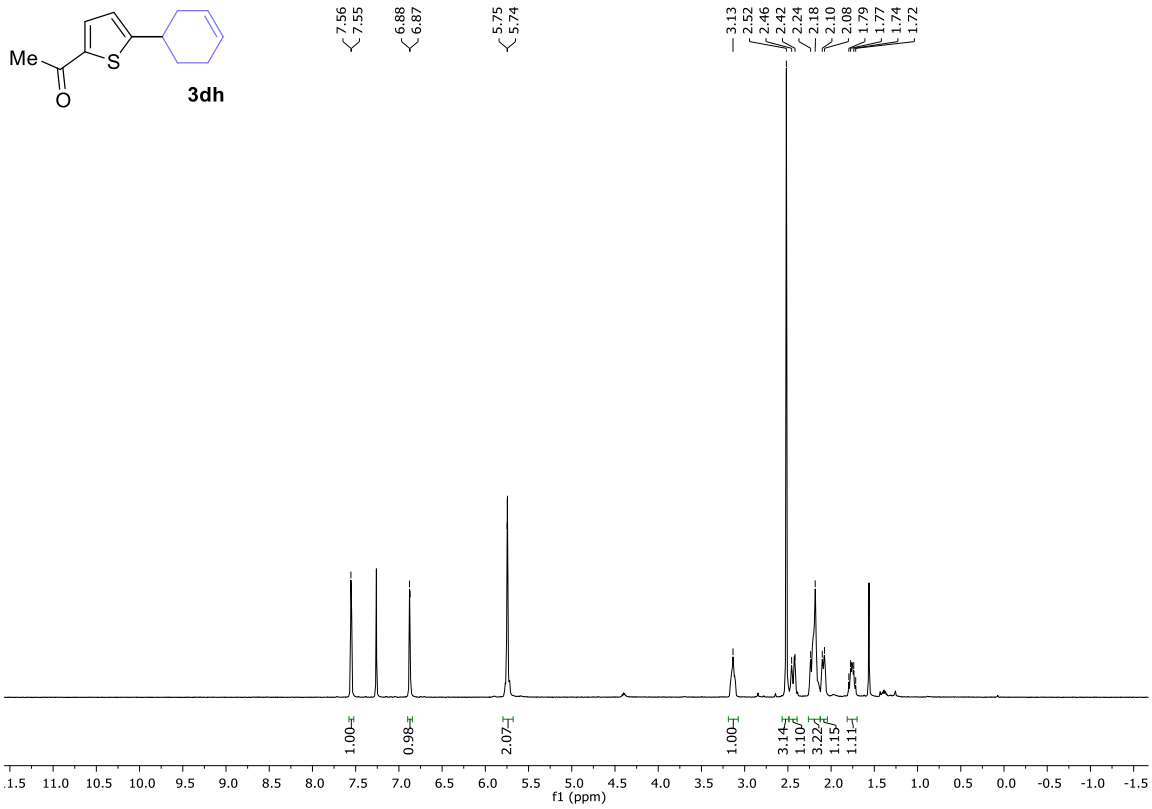
^{1}H NMR ($CDCl_3$, 500 MHz) of 2-(cyclohex-3-en-1-yl)benzo[b]thiophene (**3df**)



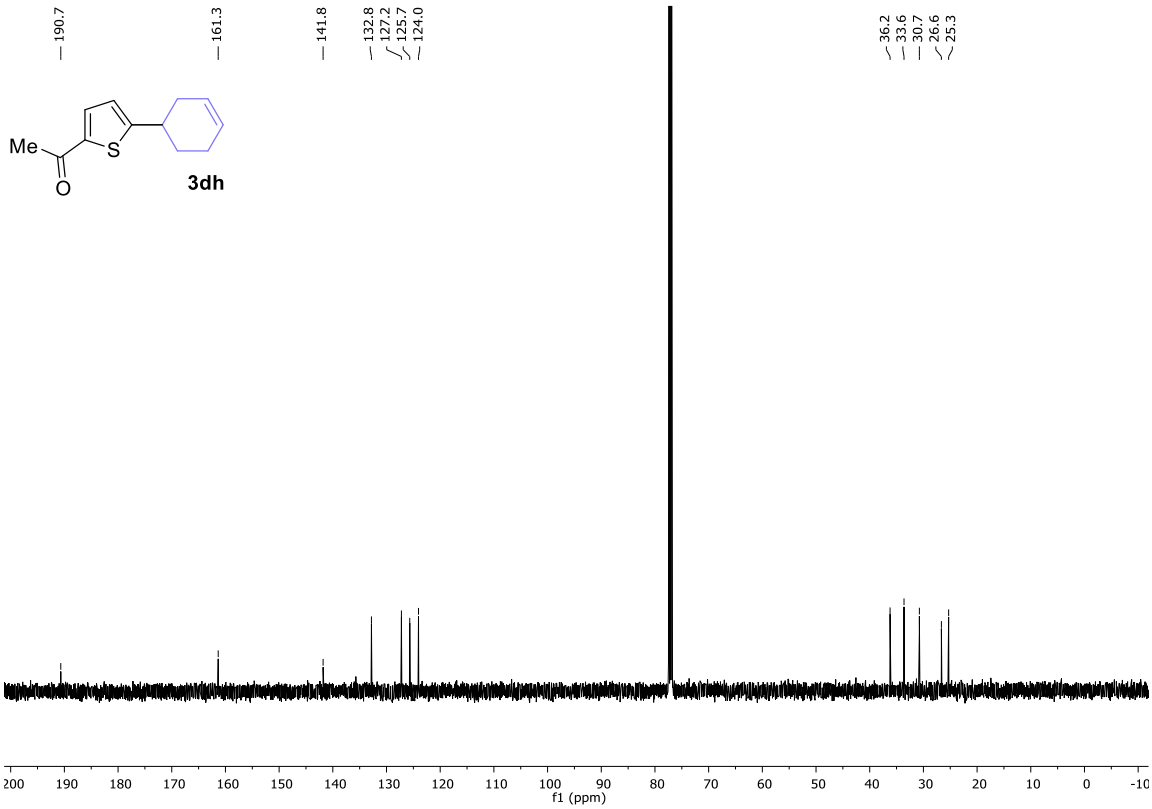
^{13}C NMR ($CDCl_3$, 126 MHz) of 2-(cyclohex-3-en-1-yl)benzo[b]thiophene (**3df**)



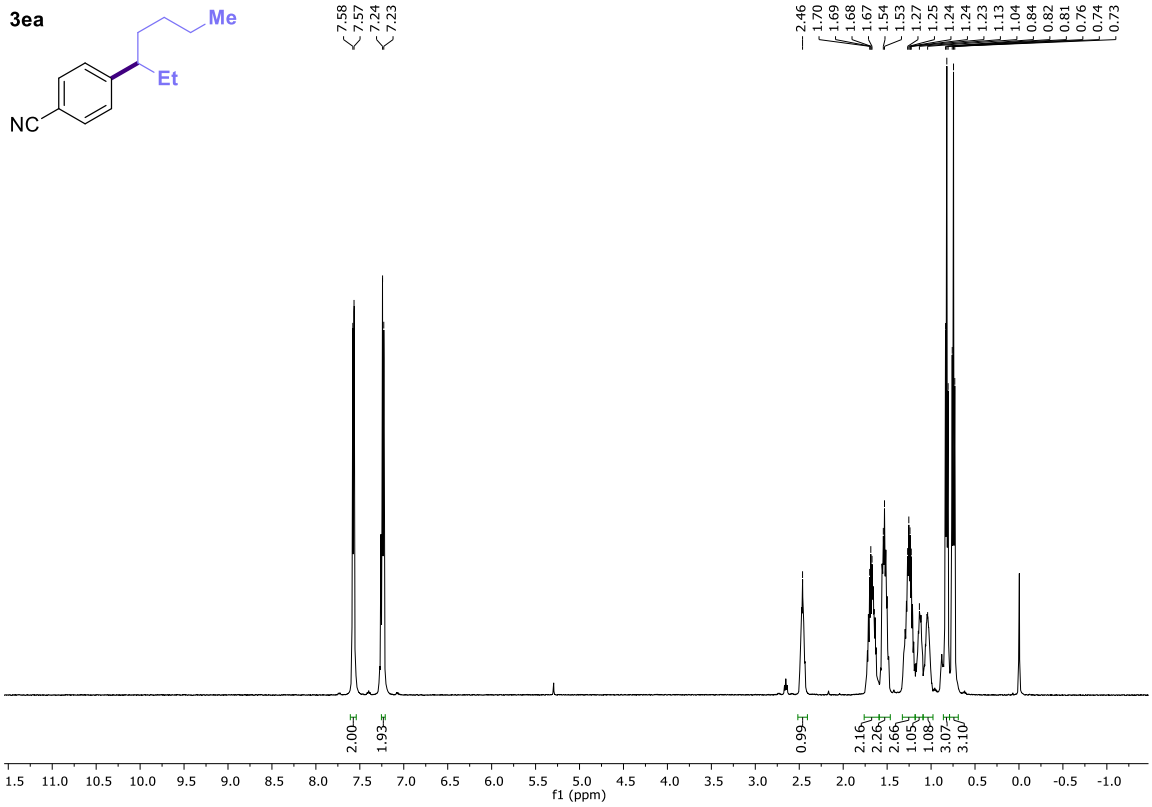
^{1}H NMR ($CDCl_3$, 500 MHz) of 1-(5-(cyclohex-3-en-1-yl)thiophen-2-yl)ethan-1-one (**3dh**)



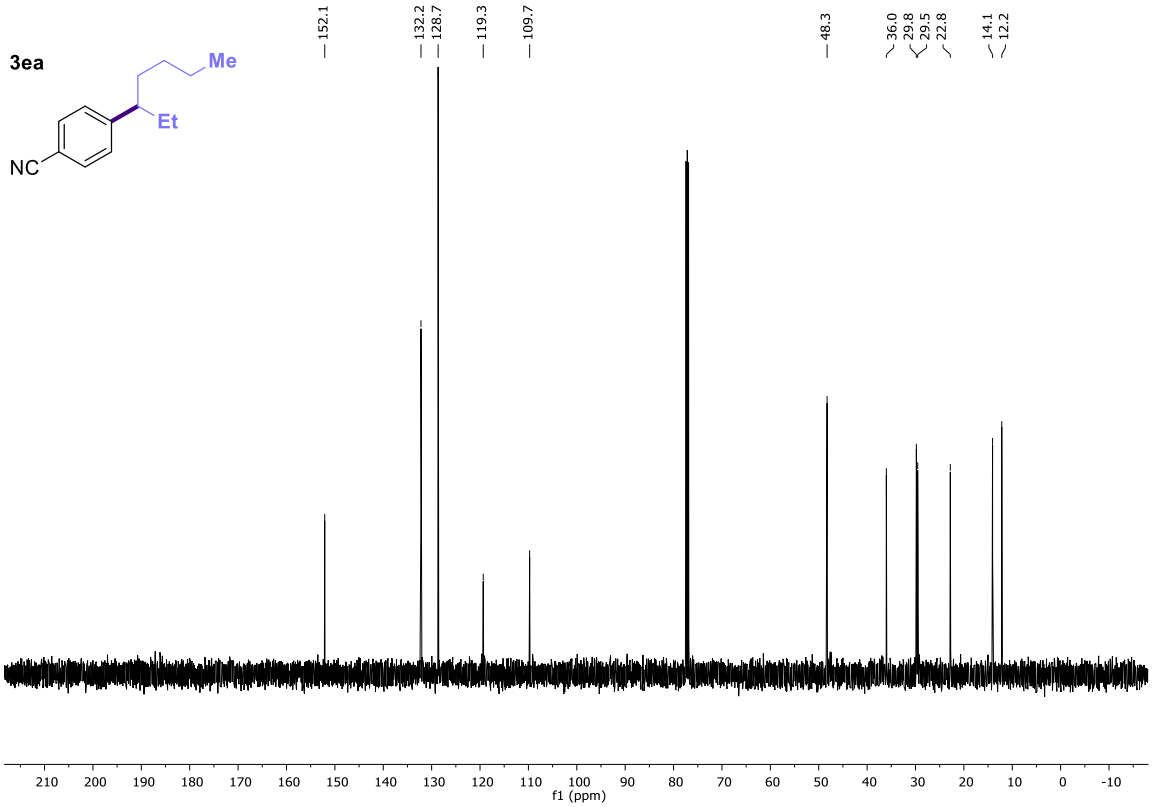
^{13}C NMR ($CDCl_3$, 126 MHz) of 1-(5-(cyclohex-3-en-1-yl)thiophen-2-yl)ethan-1-one (**3dh**)



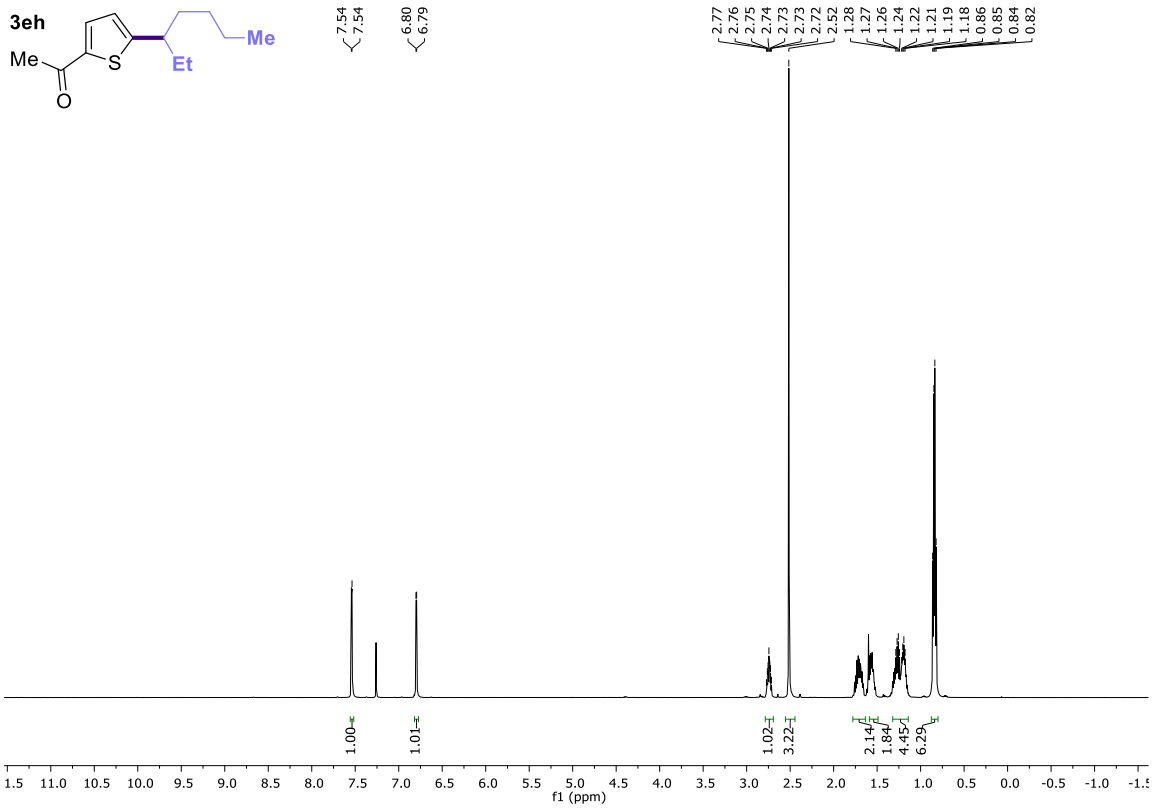
^{1}H NMR ($CDCl_3$, 500 MHz) of 4-(heptan-3-yl)benzonitrile (**3ea**)



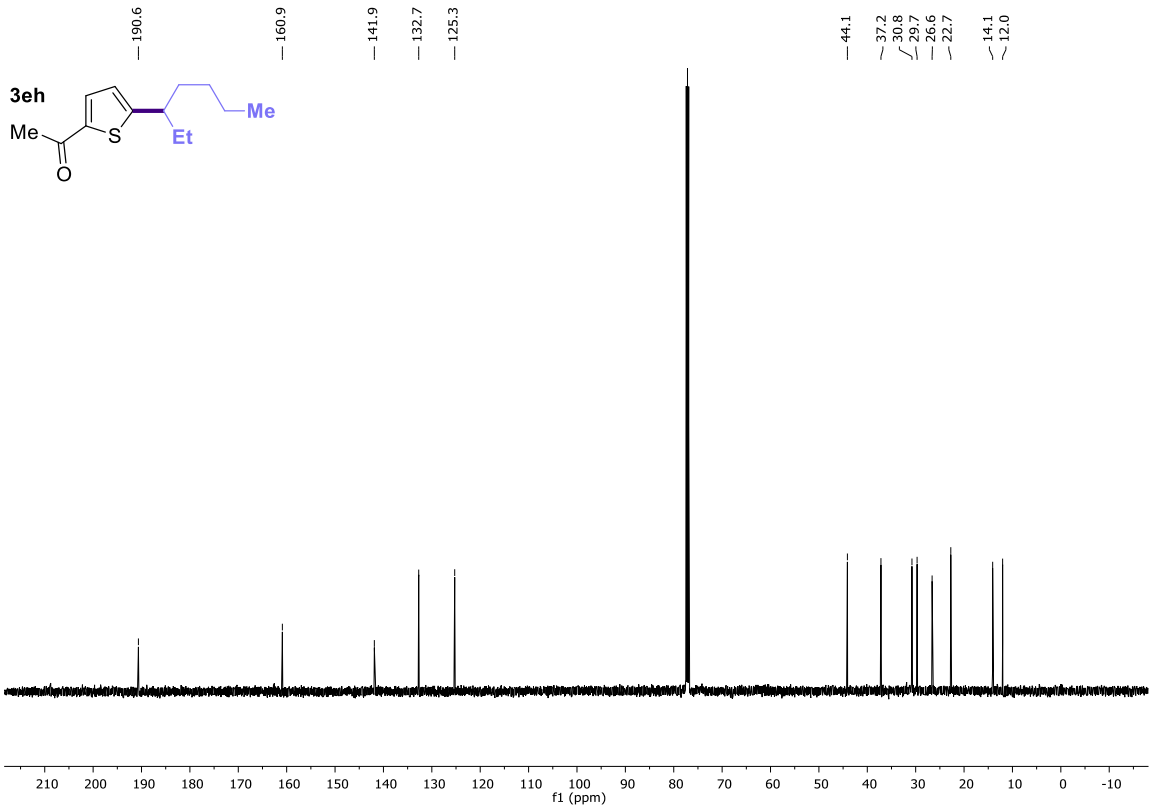
^{13}C NMR ($CDCl_3$, 126 MHz) of 4-(heptan-3-yl)benzonitrile (**3ea**)



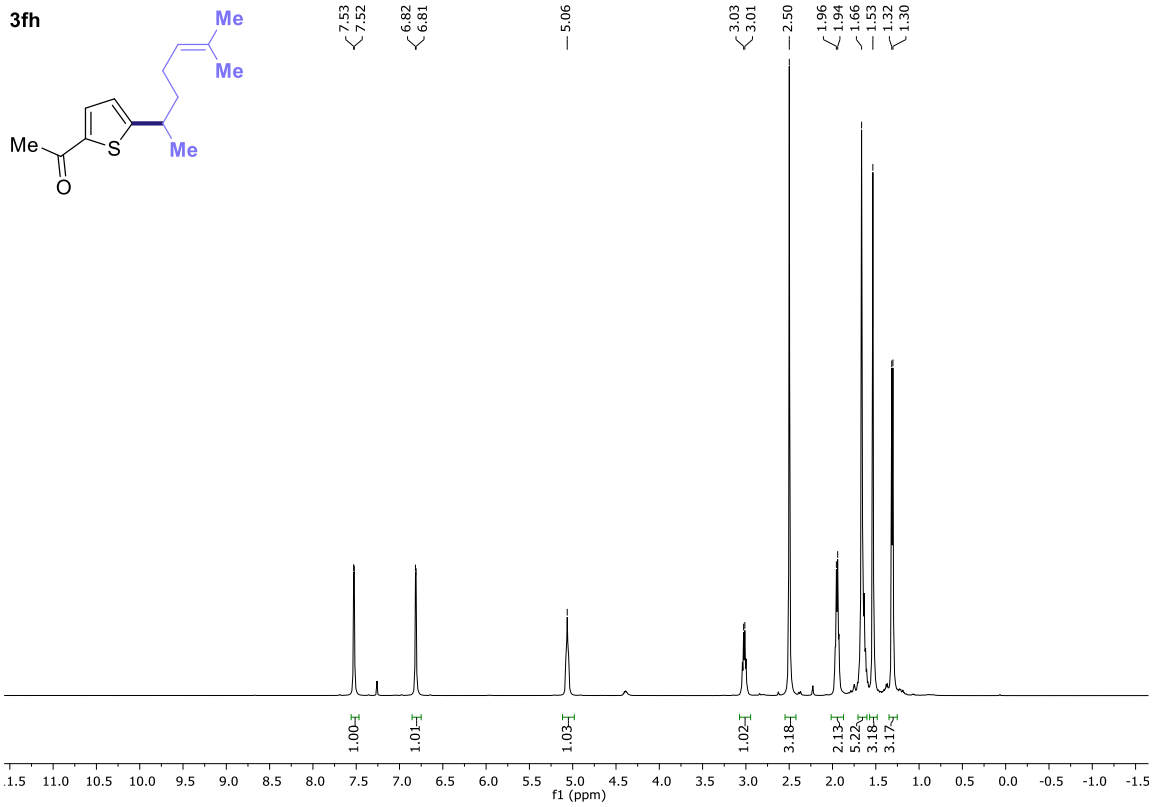
^{1}H NMR ($CDCl_3$, 500 MHz) of 1-(5-(heptan-3-yl)thiophen-2-yl)ethan-1-one (**3eh**)



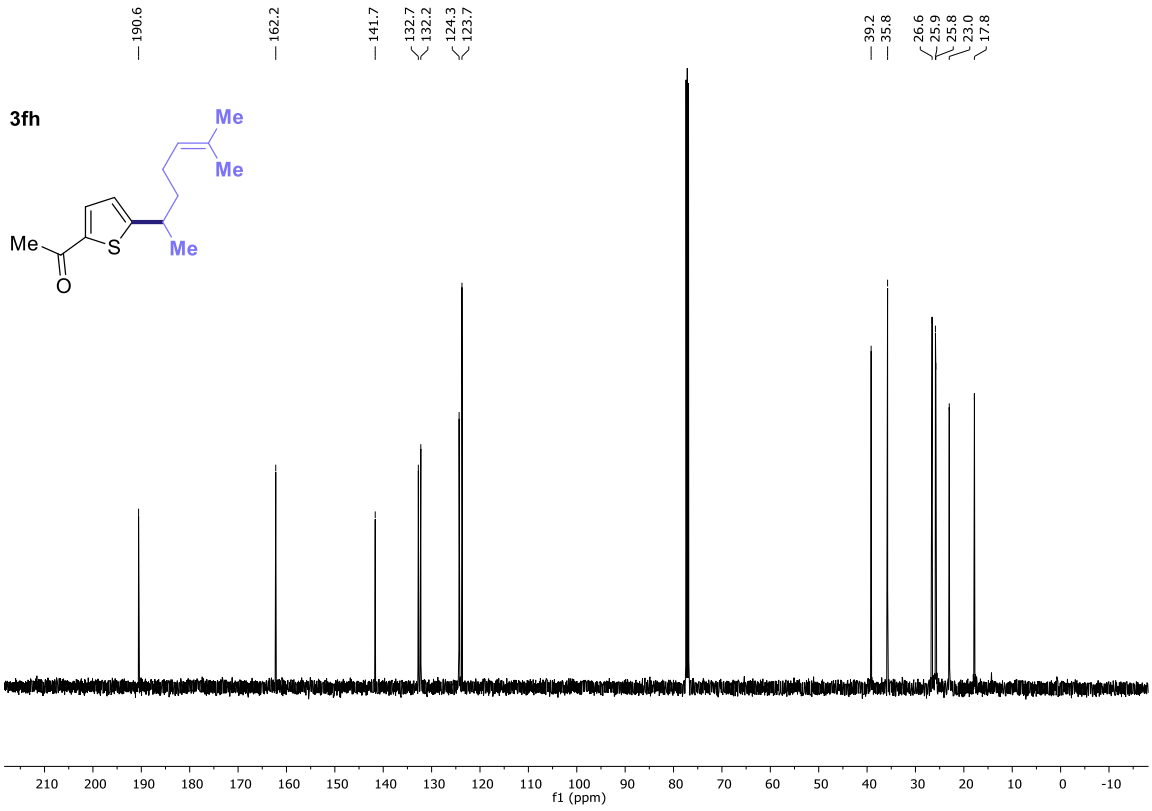
^{13}C NMR ($CDCl_3$, 126 MHz) of 1-(5-(heptan-3-yl)thiophen-2-yl)ethan-1-one (**3eh**)



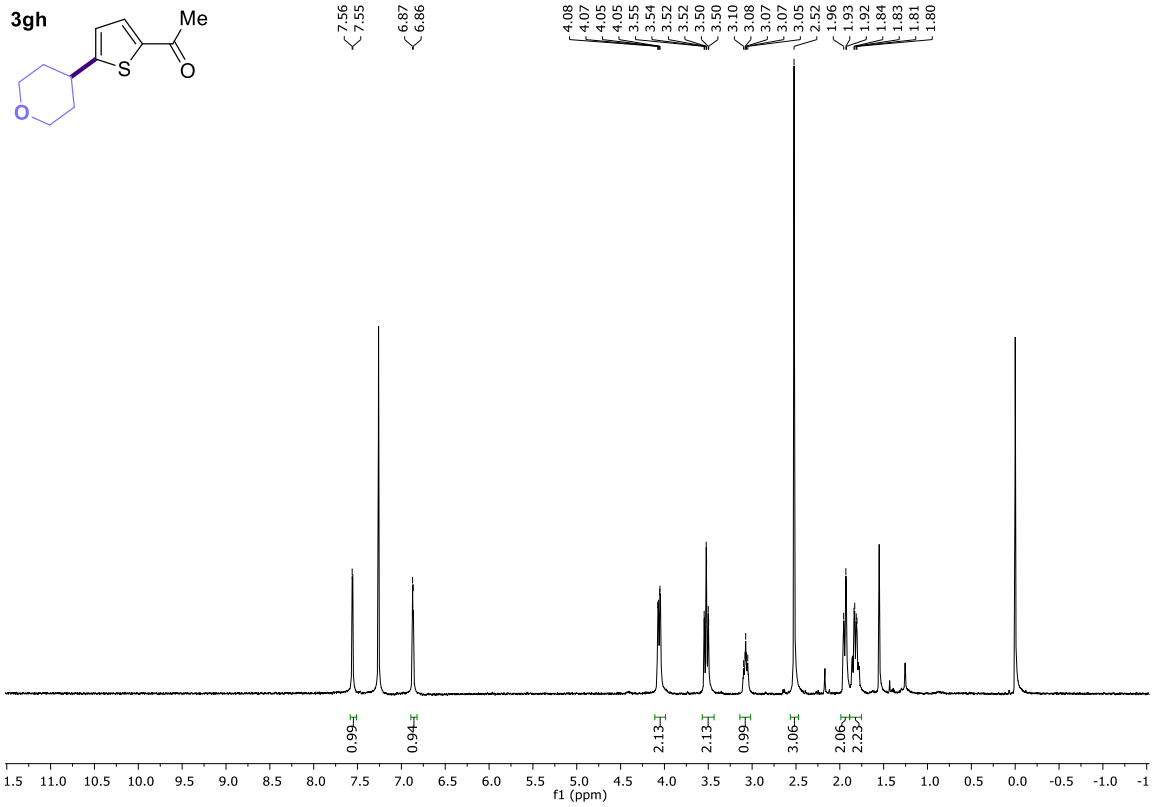
^{1}H NMR ($CDCl_3$, 500 MHz) of 1-(5-(6-methylhept-5-en-2-yl)thiophen-2-yl)ethan-1-one (**3fh**)



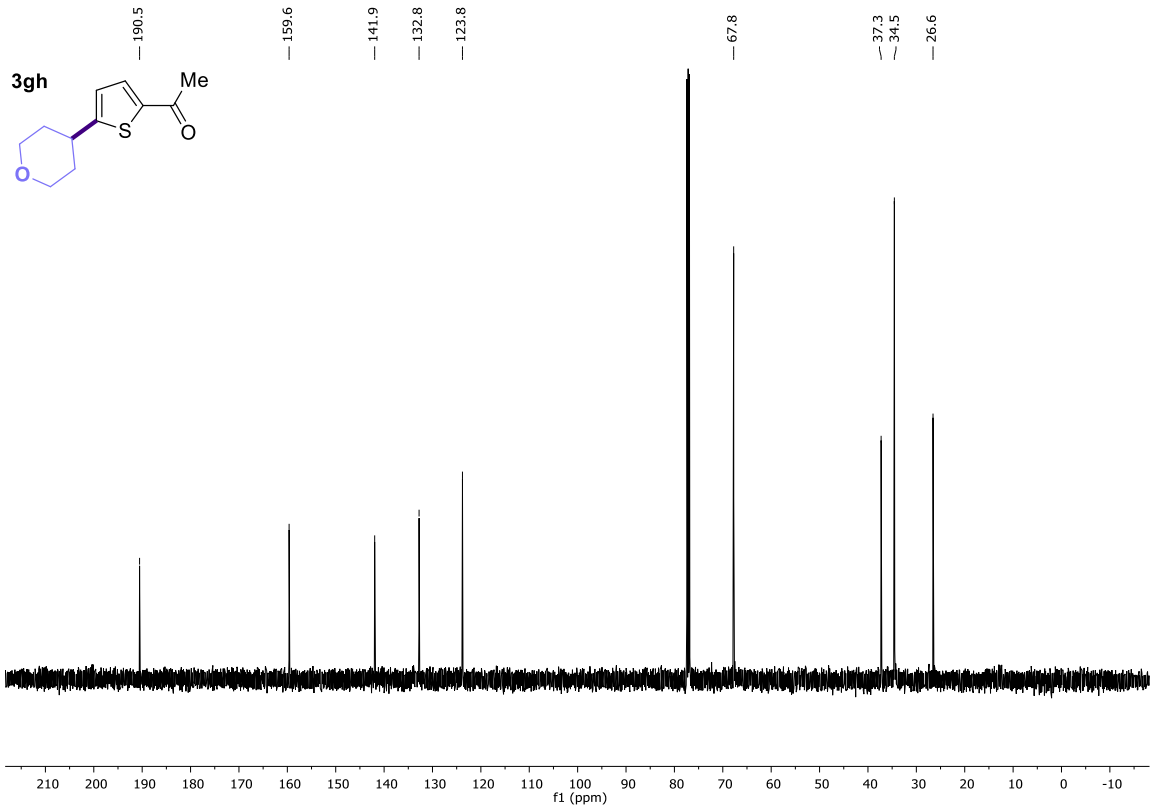
^{13}C NMR ($CDCl_3$, 126 MHz) of 1-(5-(6-methylhept-5-en-2-yl)thiophen-2-yl)ethan-1-one (**3fh**)



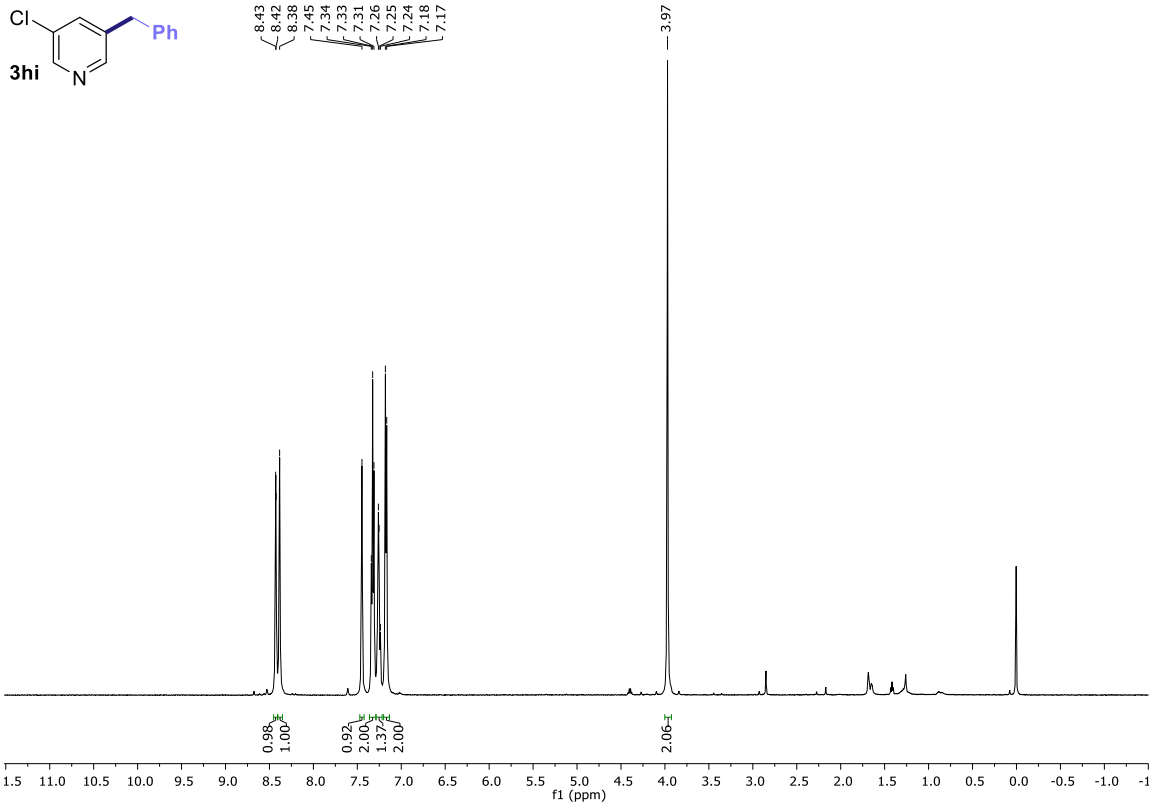
^{1}H NMR ($CDCl_3$, 500 MHz) of 1-(5-(tetrahydro-2H-pyran-4-yl)thiophen-2-yl)ethan-1-one (**3gh**)



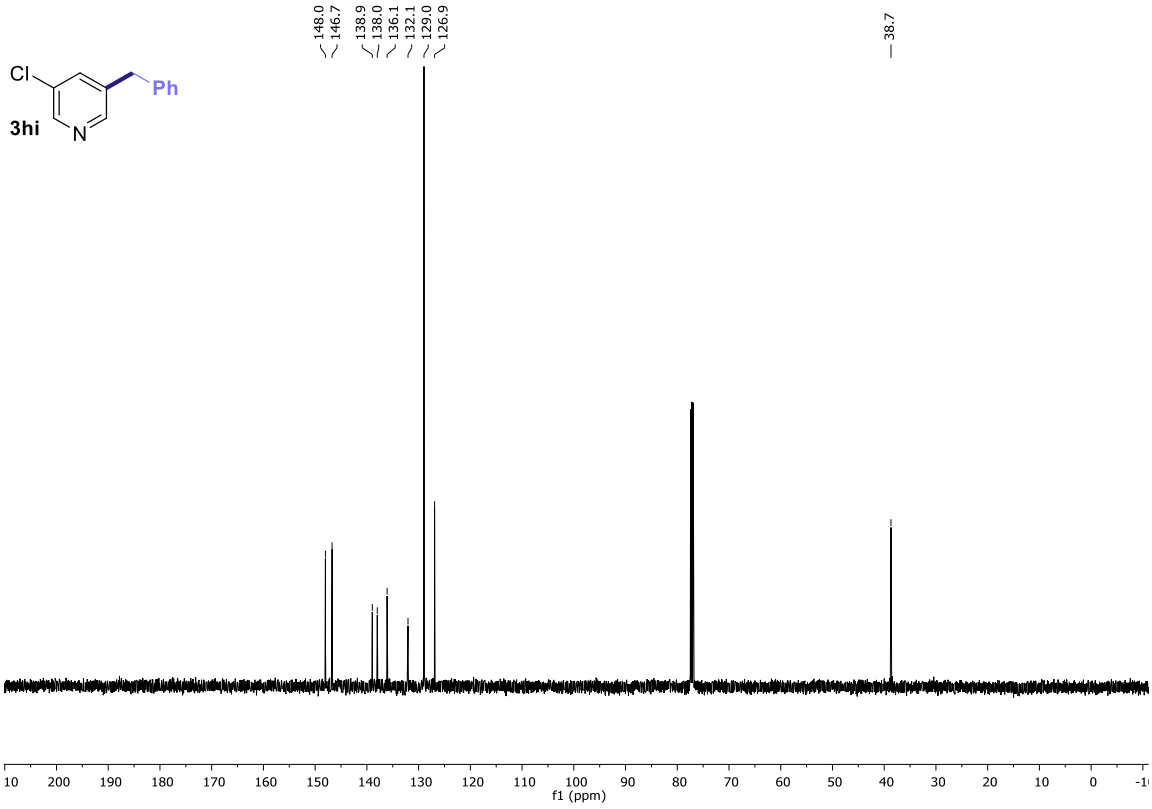
^{13}C NMR ($CDCl_3$, 126 MHz) of 1-(5-(tetrahydro-2H-pyran-4-yl)thiophen-2-yl)ethan-1-one (**3gh**)



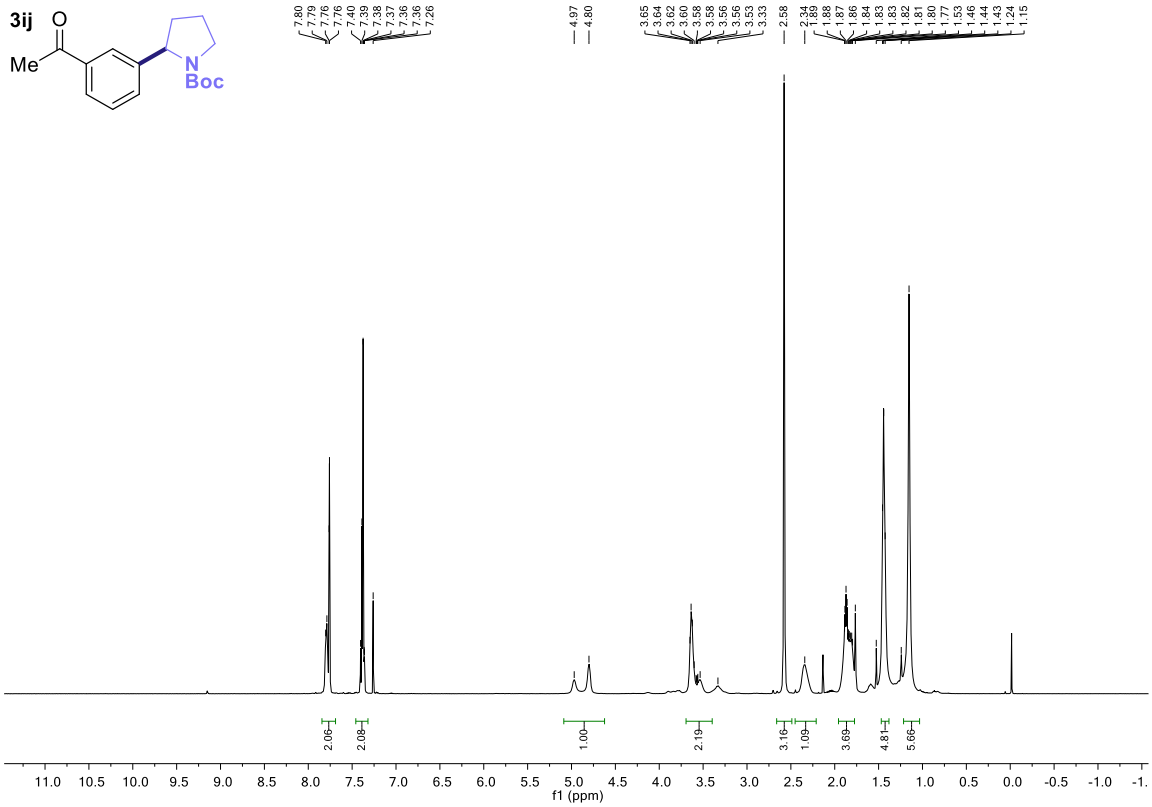
^{1}H NMR ($CDCl_3$, 500 MHz) of 3-benzyl-5-chloropyridine (**3hi**)



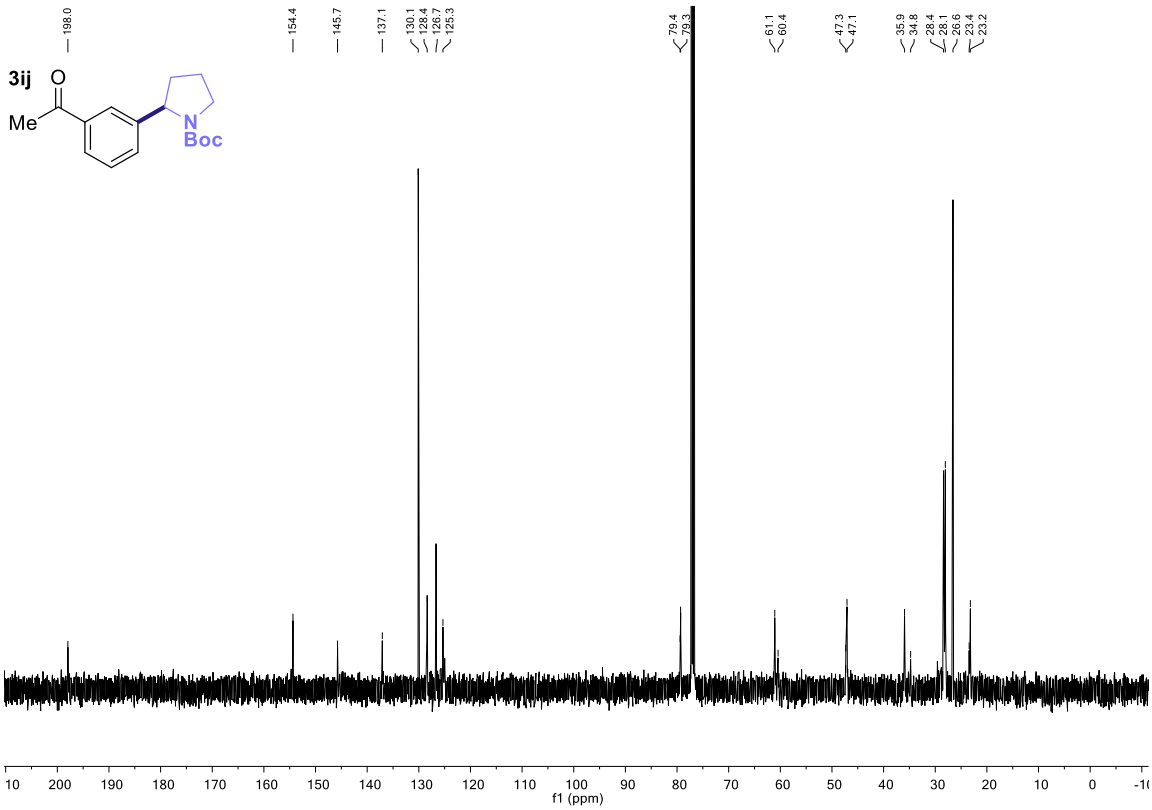
^{13}C NMR ($CDCl_3$, 126 MHz) of 3-benzyl-5-chloropyridine (**3hi**)



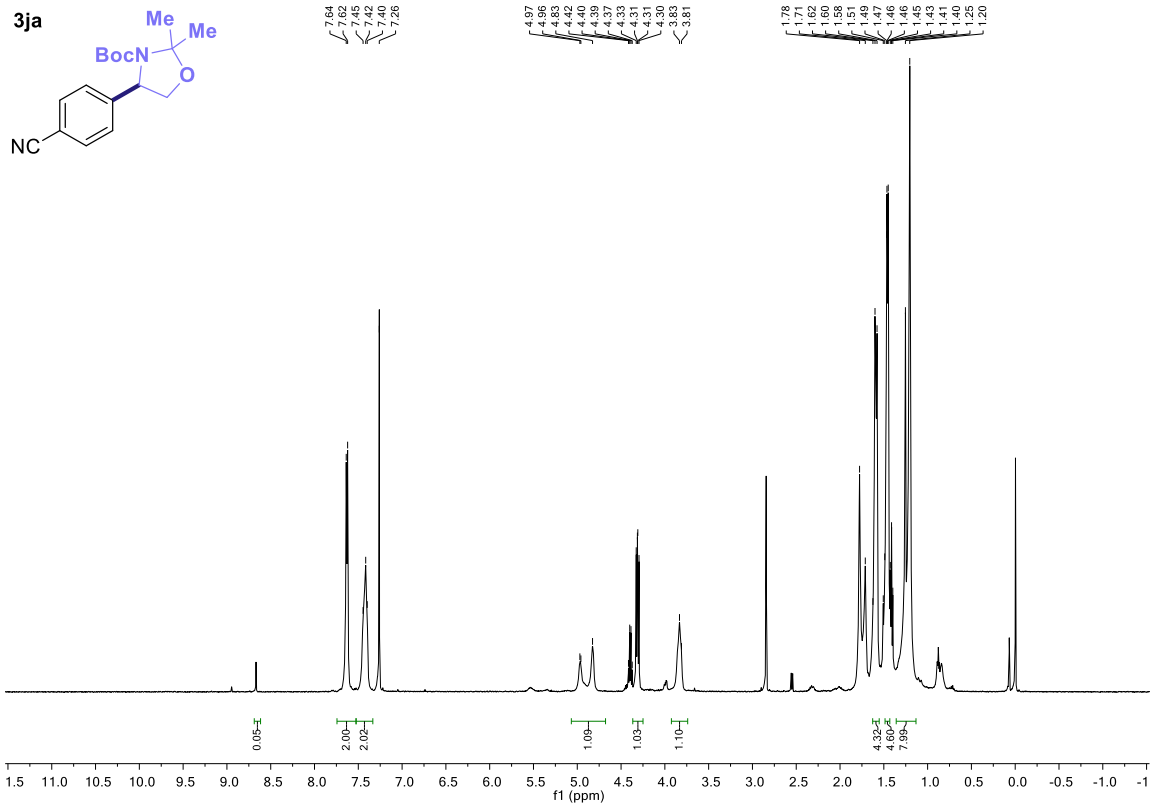
^{1}H NMR ($CDCl_3$, 500 MHz) of *tert*-butyl 2-(3-acetylphenyl)pyrrolidine-1-carboxylate (**3ij**)



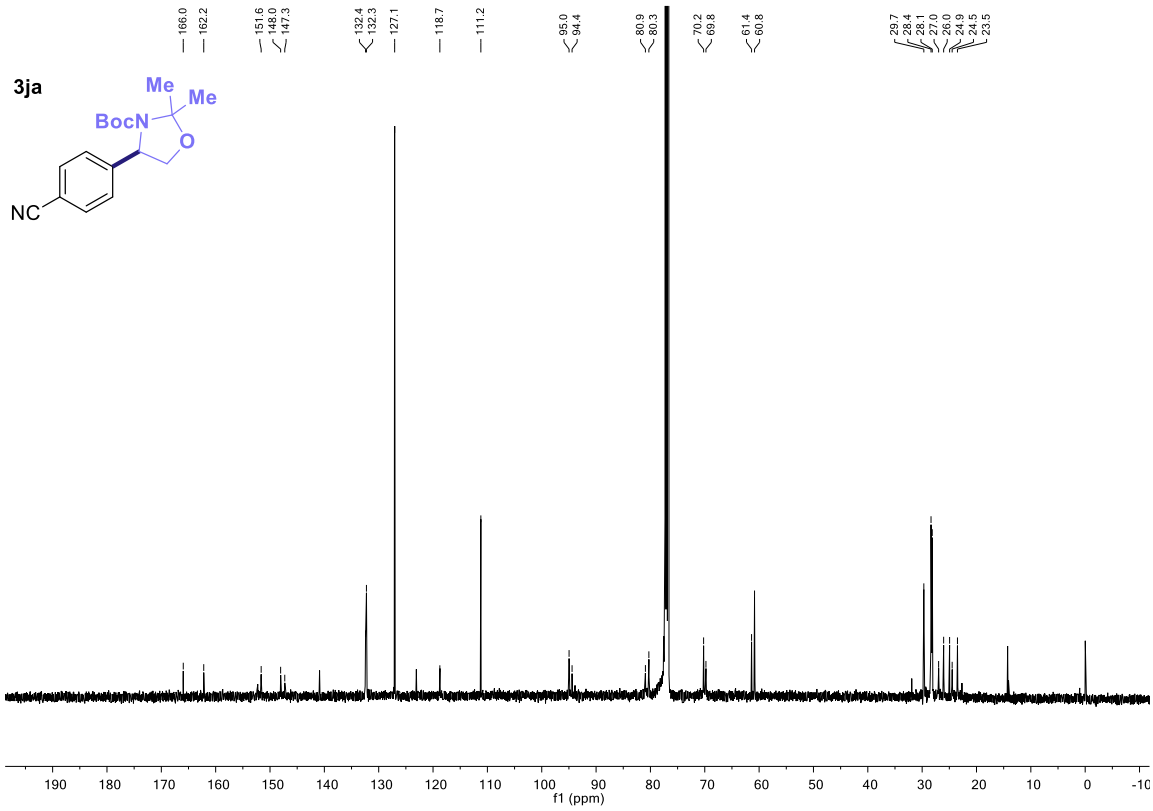
^{13}C NMR ($CDCl_3$, 126 MHz) of *tert*-butyl 2-(3-acetylphenyl)pyrrolidine-1-carboxylate (**3ij**)



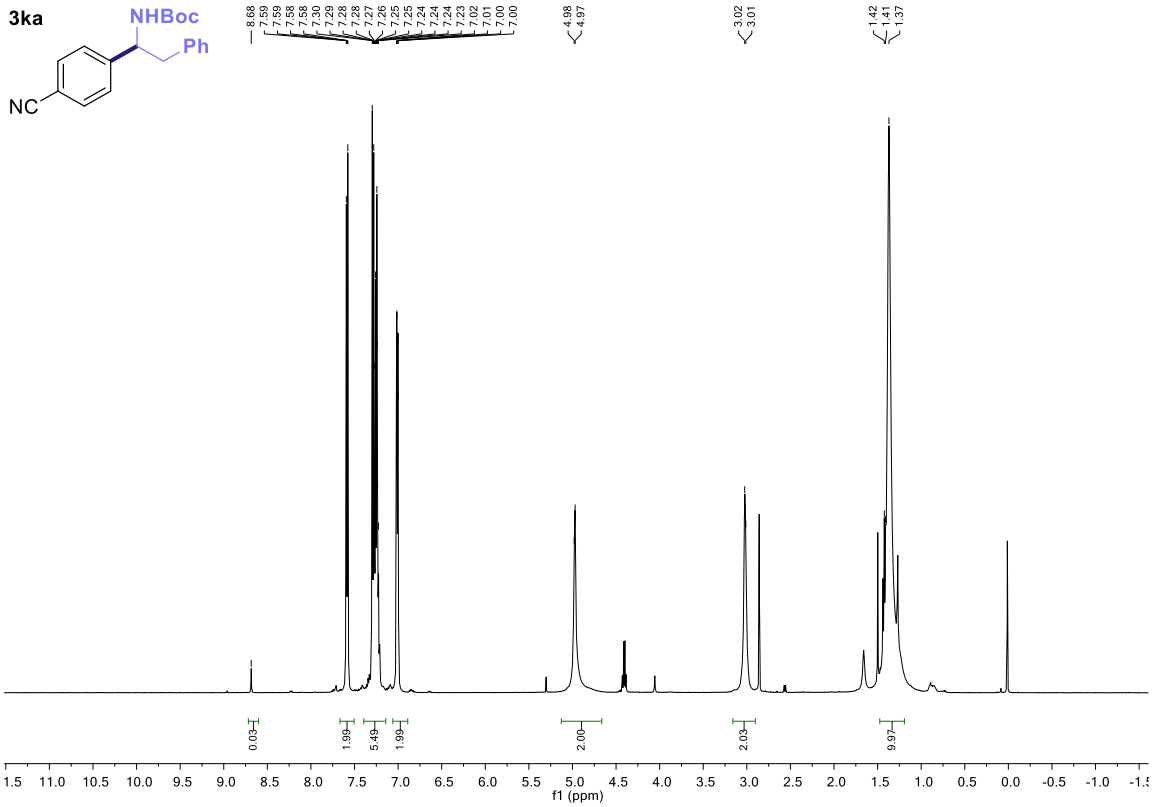
^{1}H NMR ($CDCl_3$, 500 MHz) of *tert*-butyl 4-(4-cyanophenyl)-2,2-dimethyloxazolidine-3-carboxylate (**3ja**)



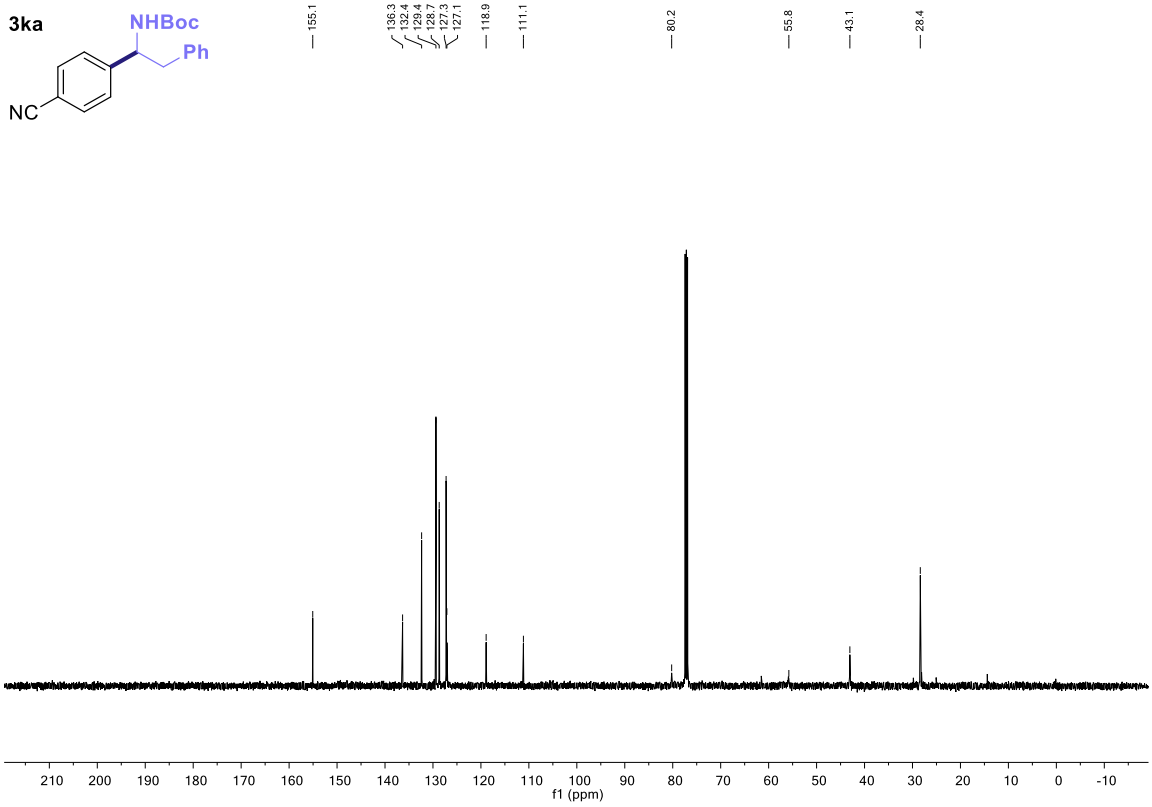
^{13}C NMR ($CDCl_3$, 126 MHz) of *tert*-butyl 4-(4-cyanophenyl)-2,2-dimethyloxazolidine-3-carboxylate (**3ja**)



^{1}H NMR ($CDCl_3$, 500 MHz) of *tert*-butyl (1-(4-cyanophenyl)-2-phenylethyl)carbamate (**3ka**)

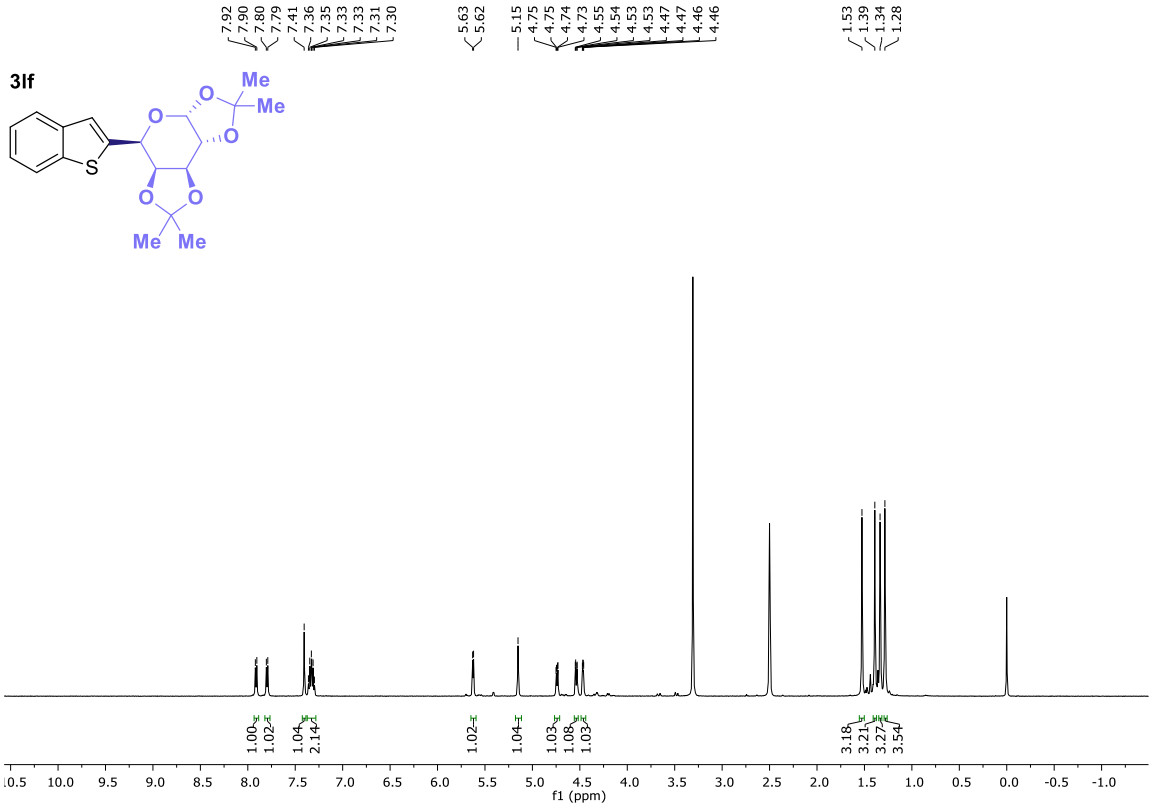


^{13}C NMR ($CDCl_3$, 126 MHz) of *tert*-butyl (1-(4-cyanophenyl)-2-phenylethyl)carbamate (**3ka**)

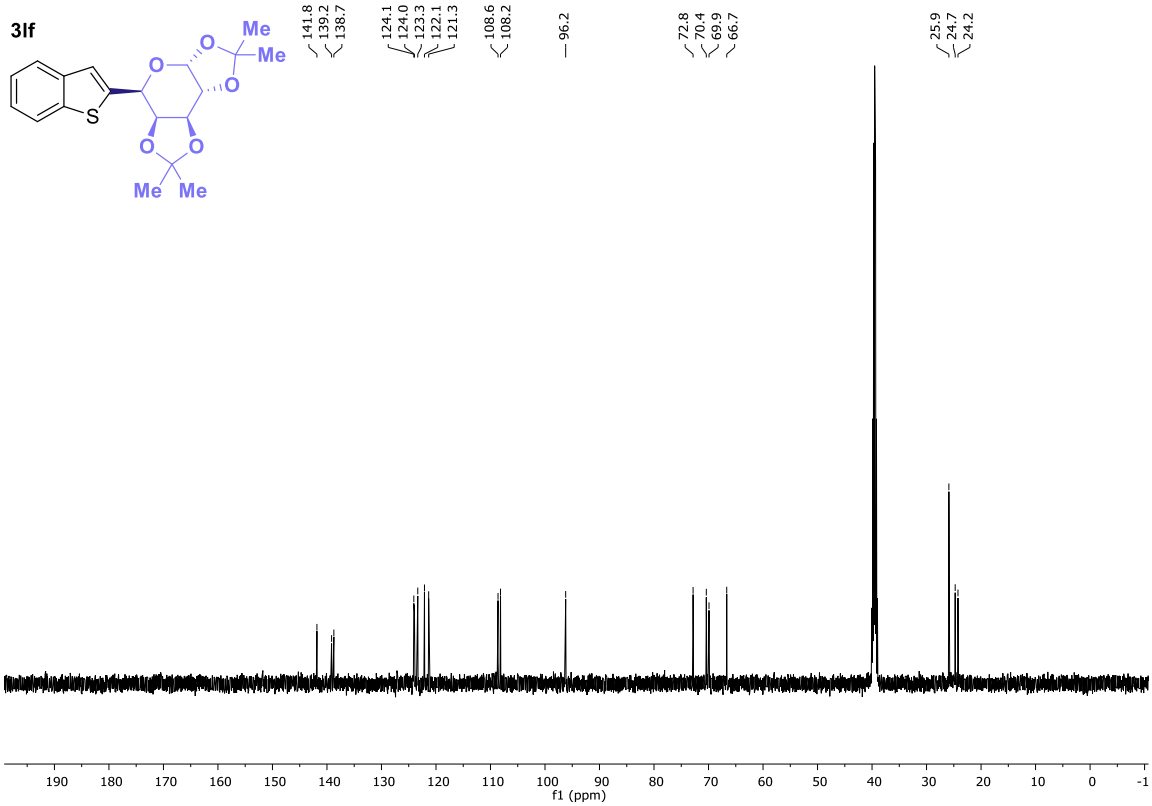


14. ^{1}H and ^{13}C NMR Spectra: Synthesis of Aryl-Containing Saccharides

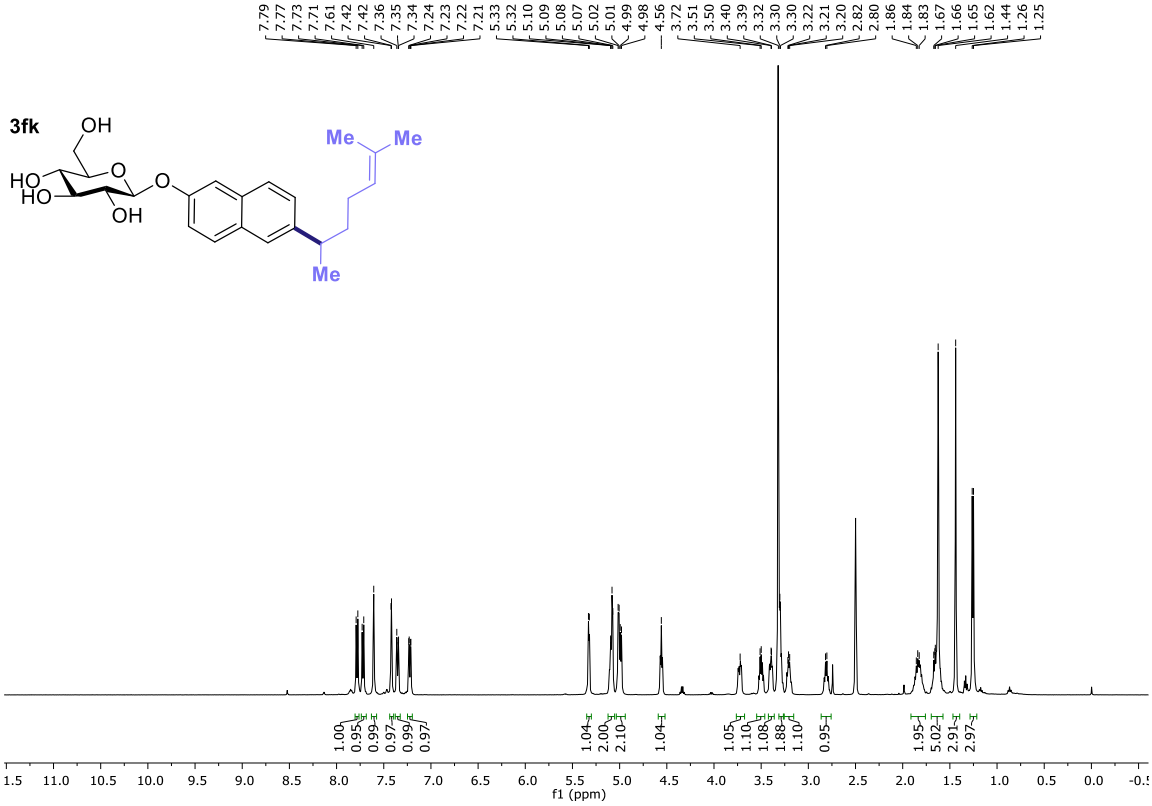
^{1}H NMR (DMSO-d_6, 500 MHz) of (3a*R*,5*S*,5a*R*,8a*S*,8b*R*)-5-(benzo[b]thiophen-2-yl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (**3lf**)



^{13}C NMR (DMSO-d_6, 126 MHz) of (3a*R*,5*S*,5a*R*,8a*S*,8b*R*)-5-(benzo[b]thiophen-2-yl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (**3lf**)



^{1}H NMR (DMSO-d_6, 500 MHz) of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(hydroxymethyl)-6-((6-(6-methylhept-5-en-2-yl)naphthalen-2-yl)oxy)tetrahydro-2H-pyran-3,4,5-triol (**3fk**)



^{13}C NMR (DMSO-d_6, 126 MHz) of (2*R*,3*S*,4*S*,5*R*,6*S*)-2-(hydroxymethyl)-6-((6-(6-methylhept-5-en-2-yl)naphthalen-2-yl)oxy)tetrahydro-2H-pyran-3,4,5-triol (**3fk**)