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Enantio- and Diastereoselective Conjugate Borylation/Mannich Cyclization

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Table of Contents

1 General Practical Considerations

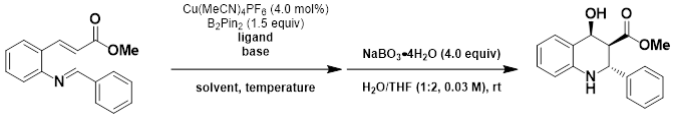
Unless otherwise stated, all catalytic reactions were run under an inert atmosphere of argon or nitrogen, with the use of glassware that was either oven (140 ^{o}C) or flame dried and cooled under the appropriate inert gas. Work-up and isolation was performed on the bench-top, open to air, utilizing standard techniques. Monitoring of reactions was done via thin-layer chromatography (TLC) on EMD Silica Gel 60 F254 plates. Developed plates were visualized with UV light (254 nm), $KMnO_4$ stain or by immersion into an iodine/silica stain. Reagents for catalytic reactions were used as follows: Tetrahydrofuran was distilled over sodium; toluene was distilled over calcium hydride; diethyl ether (ACS grade) and anhydrous methyl tert-butyl ether (MTBE) were purchased from Sigma-Aldrich and used as received; Ethanol (99%), methanol, isopropanol tert-butanol and tert-amyl alcohol were all used as received; tert-butoxide bases were sublimed under vacuum and high temperature and kept in a desiccator. Silica gel flash chromatography was performed using SiliaFlash® Irregular Silica Gel, P60, 40-63 µm, 60 Å silica gel purchased from Silicycle. Copper tetrakisacetonitrile hexafluorophosphate and Josiphos ligand (SL-J001-1) were purchased from Strem and stored in a desiccator under argon. Catalytic reactions were performed in 2 dram vials, equipped with a Teflon septum (ThermoScientific National B7995-15) and a stir bar (Fisher cat no. 14-513-57, 12 x 4.5 mm). All other reagents and organic building blocks were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar, TCI, Combi-Blocks, Oakwood Chemical, AK Scientific) and used as received.

NMR characterization data was collected at 296 K on a Varian Mercury 400 or an Agilent DD2 500 eqipped with a 5mm Xses Cold Probe. Assignment of dr for the catalytic reactions was determined by 1H NMR analysis of the crude mixture after oxidation and prior to isolation by flash column chromatography. Chromatography was performed with a high flow of air pressure to minimize product decomposition during isolation. Spectra were internally referenced to the residual solvent signal (^{1}H NMR: CDCl3 = 7.26 ppm, ^{13}C NMR: CDCl3 = 77.16 ppm). Data for ^{1}H NMR is reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. Coupling constants were rounded to the nearest 0.5 Hz. Infrared (IR) spectra were recorded on a PerkinElmer Spectrum 100 instrument equipped with a single-bounce diamond / ZnSe ATR accessory. Melting point ranges were determined on a Fisher-Johns Melting Point Apparatus and are reported uncorrected. High resolution mass spectra (HRMS) were obtained on a Micromass 70S-250 spectrometer (EI) or an ABI/Sciex QStar Mass Spectrometer (ESI) or a JEOL AccuTOF model JMS-T1000LC mass spectrometer equipped with and IONICS® Direct Analysis in Real Time (DART) ion source at Advanced Instrumentation for Molecular Structure (AIMS) in the Department of Chemistry at the University of Toronto.

2 Reaction Optimization

A 2-dram vial containing a stir bar was oven-dried and cooled under argon whereupon it was charged with copper salt, ligand, and base and reaction solvent (1 mL) was immediately added. The resulting suspension stirred for 15 min with noticeable darkening of color (see footnote [b] of table below). B_2Pin_2 (76 mg, 0.3 mmol, 1.5 equiv) was added as a solution in solvent (1 mL) and the resultant suspension was stirred for a further 15 min. Finally, substrate (0.2 mmol) and *t*AmOH (44 µL, 0.4 mmol, 2.0 equiv) were added as a solution in Et_2O (2 mL). The reaction was stirred for 4-18 h. Upon completion, it was filtered over a Celite pad and volatiles were removed. Subsequently, $NaBO_3•4H_2O$ (123.1 mg, 0.8 mmol, 4.0 equiv), water (2 mL) and THF (4 mL) were added and the reaction mixture was stirred for 4-18 hours. Upon completion, the reaction mixture was diluted with 50% NaCl solution, and extracted thrice with EtOAc. The combined organic fractions were washed five times with water to remove pinacol and once with brine and dried over $MgSO_4$. The dr was determined by ^{1}H NMR analysis of the crude mixture and the products were isolated by flash column chromatography.

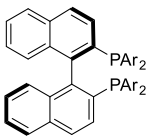
Table S1. Reaction Optimization



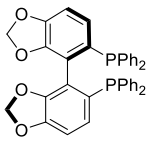
Entry[a]	Cu source (4 mol%)	Ligand (6 mol%)[b]	Base (eq)[c]	Alcohol (eq)	Solvent	% yield	d.r.	e.r.
1	$Cu(MeCN)_4PF_6$	**L5**	NaOtBu (1.05)	-	THF	75	>20:1	88:12
2	$Cu(MeCN)_4PF_6$	**L5**	NaOtBu (1.5)	-	THF	77	10:1	92:8
3	$Cu(MeCN)_4PF_6$	**L5**	LiOtBu (1.5)	-	THF	50	>20:1	85.5:14.5
4	$Cu(MeCN)_4PF_6$	**L5**	NaOMe (1.5)	-	PhMe	63	2.6:1	84.5:15.5
5	$Cu(MeCN)_4PF_6$	**L5**	NaOMe (1.5)	-	Et_2O	73	5:1	86.5:13.5
6	$Cu(MeCN)_4PF_6$	**L5**	NaOMe (1.5)	-	MTBE	68	5:1	86:14
7	$Cu(MeCN)_4PF_6$	**L5**	NaOMe (1.05)	-	THF	71	4:1	83:17
8	$Cu(MeCN)_4PF_6$	**L5**	NaOMe (0.3)	MeOH (2)	THF	55	8:1	88:12
9	$Cu(MeCN)_4PF_6$	**L5**	NaOtBu (0.3)	MeOH (2)	THF	69	>20:1	93.5:6.5
10	CuI	**L5**	NaOtBu (0.3)	MeOH (2)	THF	-	-	-
11	$Cu(OTf)_2$	**L5**	NaOtBu (0.3)	MeOH (2)	THF	60	>20:1	92:8
12	CuBr SMe_2	**L5**	NaOtBu (0.3)	MeOH (2)	THF	13	13:1	N/A

13	$Cu(MeCN)_4PF_6$	**L1**	NaOtBu (0.3)	MeOH (2)	THF	74	>20:1	12.5:87.5
14	$Cu(MeCN)_4PF_6$	**L2**	NaOtBu (0.3)	MeOH (2)	THF	47	>20:1	16.5:83.5
15	$Cu(MeCN)_4PF_6$	**L3**	NaOtBu (0.3)	MeOH (2)	THF	33	>20:1	19:81
16	$Cu(MeCN)_4PF_6$	**L4**	NaOtBu (0.3)	MeOH (2)	THF	13	1:1	48:52
17	$Cu(MeCN)_4PF_6$	**L6**	NaOtBu (0.3)	MeOH (2)	THF	19	1:3	53:47
18	$Cu(MeCN)_4PF_6$	**L7**	NaOtBu (0.3)	MeOH (2)	THF	26	1:1.3	72:28
19	$Cu(MeCN)_4PF_6$	**L5**	NaOtBu (0.3)	iPrOH (2)	Et_2O	54	>20:1	94:6
20	$Cu(MeCN)_4PF_6$	**L5**	NaOtBu (0.3)	tBuOH (2)	Et_2O	37	>20:1	88:12
21	$Cu(MeCN)_4PF_6$	**L5**	NaOtBu (0.3)	tAmOH (2)	Et_2O	74	19:1	93.5:6.5
22[b]	$Cu(MeCN)_4PF_6$	**L5**	NaOtBu (0.3)	tAmOH (2)	Et_2O	89(90)	>20:1	94.5:5.5

[a] Unless specified otherwise, reactions were carried out on 0.2 mmol scale of substrate. [b] The initial solution of copper, ligand and base was stirred for 30 minutes before the addition of B_2Pin_2 solution.



L1 Ar = C_6H_5
L2 Ar = 4-MeC_6H_4



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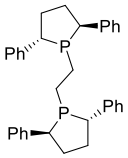

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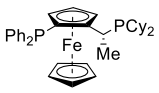

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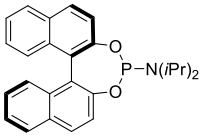

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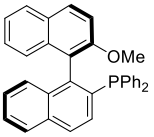
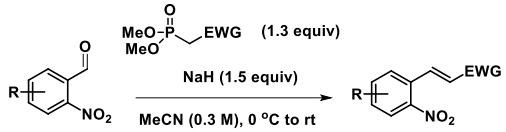
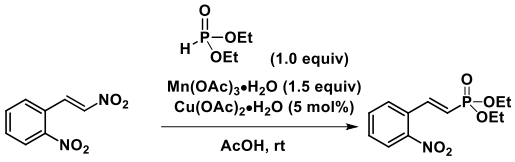


L7

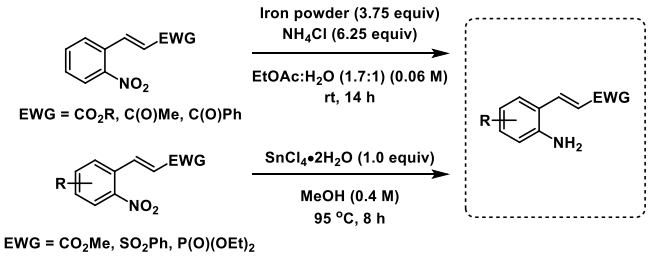
3 General Synthetic Remarks



Unless stated otherwise, substrates were synthesized starting from the corresponding 2-nitrobenzaldehydes. The corresponding phosphonate (1.3 equiv) was dissolved in MeCN (0.3 M) at 0 ^{o}C and sodium hydride (1.5 equiv) was added. After 25 minutes, the 2-nitrobenzaldehyde was added. The reaction was allowed to warm to room temperature overnight and the reaction was quenched with saturated aq. NH_4Cl. It was then extracted thrice with EtOAc, washed with brine, dried over $MgSO_4$ and concentrated. The resultant crude nitro compound was subjected to reduction without further purification.



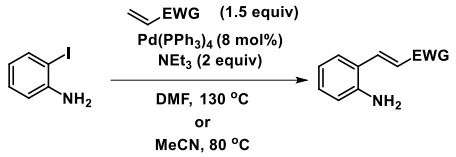
(E)-1-nitro-2-(2-nitrovinyl)benzene was dissolved in AcOH, (0.04 M) along with manganese triacetate hydrate (1.5 equiv) and copper acetate hydrate (5 mol%), and diethyl phoshpite (1.0 equiv) was added. The suspension was stirred vigorously overnight at room temperature. Upon reaction completion, volatiles were removed under reduced pressure and the residue was suspended in water and extracted thrice with EtOAc. The combined organic layers were washed thrice with saturated aq. NH_4Cl, saturated aq. $NaHCO_3$, and once with brine, and dried over $MgSO_4$. The resultant crude nitro compound was subjected to reduction without further purification.



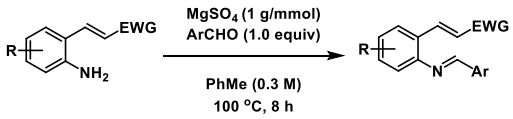
For substrates **1b**-**f**: The corresponding nitroaryl compound was suspended in EtOAc and water, iron powder (3.75 equiv) and NH_4Cl were added and the resulting suspension was stirred vigorously overnight. Afterwards, the mixture was filtered through a Celite pad and the mixture was extracted thrice with EtOAc, washed with brine, and dried over $MgSO_4$. The crude arylamine product was subjected to imine condensation without further purification.

For all other substrates: The corresponding nitroaryl compound, and tin tetrachloride (1.0 equiv) were dissolved in MeOH and the solution was refluxed. Upon reaction completion, volatiles were removed under reduced pressure and the concentrated crude was basified with 4M NaOH. The resulting

suspension was filtered through a Celite pad and the mixture was extracted thrice with EtOAc, washed with $NaHCO_3$, brine, and dried over $MgSO_4$. The crude arylamine product was subjected to imine condensation without further purification.

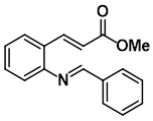


A Heck-Mizoroki reaction was employed towards substrates **1g** and **1h**: 2-iodoaniline, along with Pd(PPh3)4 (8 mol%0 were dissolved in DMF (0.5 M) (**1g**) or MeCN (0.5 M) (**1h**). The corresponding electron-deficient vinyl compound was added (1.5 equiv), followed by NEt_3, and the mixture was heated to reflux overnight. Upon reaction completion, the crude mixture was passed through a Celite plug, extracted thrice with EtOAc, washed with brine, and dried over $MgSO_4$. The crude amine product was subjected to subsequent imine condensation without further purification.

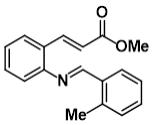


The arylamine was dissolved in toluene, and the corresponding aldehyde (1.0 equiv) and MgSO4 (1 gram/ mmol of arylamine) were added. The reaction mixture was heated to 100 °C and stirred overnight. The reaction was allowed to cool, and filtered, washing with DCM. The crude was then concentrated and purified via silica gel chromatography eluting with a gradient system of 1:5:94 to 1:10:89 NEt_3:EA:Pent.

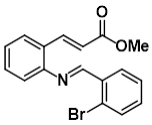
4 Characterization Data for Substrates



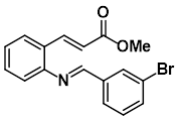
methyl (*E*)-3-(2-(((*E*)-benzylidene)amino)phenyl)acrylate (1a) – 0.911 g, 3.26 mmol (64% over 2 steps from methyl 3-(2-nitrophenyl)acrylate). White solid. All data corresponds to previously reported.[1]
MP = 62 – 64 °C.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.39 (s, 1H), 8.22 (d, J = 16.2 Hz, 1H), 7.96 (dd, J = 7.6, 2.1 Hz, 2H), 7.63 (dd, J = 8.0, 1.4 Hz, 1H), 7.55 – 7.46 (m, 3H), 7.40 (td, J = 7.6, 1.4 Hz, 1H), 7.31 – 7.18 (m, 1H), 7.01 (dd, J = 8.0, 1.2 Hz, 1H), 6.49 (d, J = 16.1 Hz, 1H), 3.79 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 167.7, 160.9, 151.5, 141.7, 136.1, 131.9, 131.3, 129.2, 129.0, 128.4, 127.6, 126.1, 119.0, 51.7.



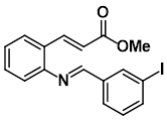
methyl (*E*)-3-(2-(((*E*)-2-methylbenzylidene)amino)phenyl)acrylate (1b) – 0.409 g, 1.46 mmol (59% over 2 steps from methyl 3-(2-nitrophenyl)acrylate). White solid.
MP = 68 - 70 °C.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.67 (s, 1H), 8.24 (d, J = 16.2 Hz, 1H), 8.13 (dd, J = 7.6, 1.6 Hz, 1H), 7.69 – 7.61 (m, 1H), 7.45 – 7.37 (m, 2H), 7.34 (tdt, J = 7.3, 1.3, 0.6 Hz, 1H), 7.25 (dddd, J = 7.9, 7.3, 1.3, 0.6 Hz, 2H), 6.99 (dd, J = 7.9, 1.3z Hz, 1H), 6.49 (d, J = 16.2 Hz, 1H), 3.79 (s, 3H), 2.64 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 167.7, 159.9, 152.1, 141.8, 139.0, 133.9, 131.4, 131.3, 131.3, 128.8, 128.3, 127.4, 126.5, 126.0, 119.1, 118.8, 51.7, 19.8.
IR (ATR, cm-1) 1713, 1634, 1621, 1488, 1438, 1375, 1314, 1266, 1167, 982, 862, 770.
HRMS (DART, M+H) Calc'd 280.1332 for $C_{18}H_{18}NO_2$, found 280.1340.



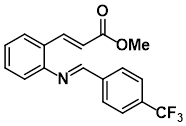
methyl (*E*)-3-(2-(((*E*)-2-bromobenzylidene)amino)phenyl)acrylate (1c) – 0.684 g, 1.99 mmol (79% over 2 steps from methyl 3-(2-nitrophenyl)acrylate). Yellow solid.
MP = 81 - 83 °C.
^{1}H NMR (400 MHz, Chloroform-d) δ 8.80 (s, 1H), 8.31 (dd, J = 7.9, 1.8 Hz, 1H), 8.22 (d, J = 16.2 Hz, 1H), 7.64 (ddd, J = 8.0, 4.6, 1.4 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.35 (ddd, J = 8.0, 7.3, 1.8 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.05 (dd, J = 7.9, 1.4 Hz, 1H), 6.47 (d, J = 16.2 Hz, 1H), 3.79 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 167.7, 159.9, 151.1, 141.6, 134.4, 133.4, 132.9, 131.4, 129.6, 128.7, 128.0, 127.5, 126.6, 126.4, 119.1 (two peaks), 51.8.
IR (ATR, cm-1) 1705, 1329, 1613, 1485, 1436, 1322, 1272, 1193, 1172, 1098, 999, 872, 752.
HRMS (DART, M+H) Calc'd 344.0281 for $C_{17}H_{15}NO_2Br$, found 344.0285.



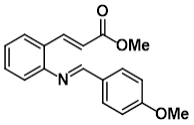
methyl (*E*)-3-(2-(((*E*)-3-bromobenzylidene)amino)phenyl)acrylate (1d) – 0.335 g, 0.97 mmol (39% over 2 steps from methyl 3-(2-nitrophenyl)acrylate). Pale orange solid.
MP = 73 - 75 °C.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.32 (s, 1H), 8.18 (dd, J = 16.1, 0.6 Hz, 1H), 8.09 (dd, J = 2.0, 1.6 Hz, 1H), 7.91 – 7.82 (m, 1H), 7.70 – 7.58 (m, 2H), 7.43 – 7.39 (m, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.29 – 7.20 (m, 1H), 7.04 – 6.92 (m, 1H), 6.46 (d, J = 16.1 Hz, 1H), 3.79 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 167.6, 159.3, 151.0, 141.4, 138.1, 134.7, 131.9, 131.3, 130.5, 128.6, 127.8, 127.6, 126.6, 123.2, 119.1, 118.8, 51.8.
IR (ATR, cm-1) 1707, 1629, 1437, 1382, 1320, 1266, 1167, 1119, 1065, 1017, 751.
HRMS (DART, M+H) Calc'd 344.0281 for $C_{17}H_{15}NO_2Br$, found 344.0282.



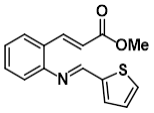
methyl (*E*)-3-(2-(((*E*)-3-iodobenzylidene)amino)phenyl)acrylate (1e) – 0.656 g, 1.68 mmol (67% over 2 steps from methyl 3-(2-nitrophenyl)acrylate). Pale yellow solid.
MP = 74 - 76 °C.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.28 (s, 1H), 8.27 (t, J = 1.7 Hz, 1H), 8.21 – 8.14 (m, 1H), 7.90 (dt, J = 7.8, 1.2 Hz, 1H), 7.83 (ddd, J = 7.8, 1.8, 1.1 Hz, 1H), 7.70 – 7.59 (m, 1H), 7.45 – 7.36 (m, 1H), 7.32 – 7.17 (m, 2H), 6.97 (dd, J = 7.8, 1.2 Hz, 1H), 6.46 (d, J = 16.1 Hz, 1H), 3.79 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 167.6, 159.2, 151.0, 141.4, 140.6, 138.1, 137.9, 131.3, 130.6, 128.5, 128.3, 127.6, 126.5, 119.1, 118.8, 94.7, 51.8.
IR (ATR, cm-1) 1698, 1616. 1587, 1568, 1433, 1314, 1260, 1155, 999, 995, 751.
HRMS (DART, M+H) Calc'd 392.0142 for $C_{17}H_{15}NO_2I$, found 392.0154.



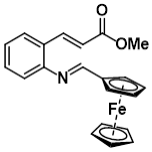
methyl (*E*)-3-(2-(((*E*)-4-(trifluoromethyl)benzylidene)amino)phenyl)acrylate (1f) – 0.596 g, 1.79 mmol (72% over 2 steps from methyl 3-(2-nitrophenyl)acrylate). White solid.
MP = 51 - 52 °C.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.44 (s, 1H), 8.28 – 8.14 (m, 1H), 8.06 (dt, J = 7.9, 0.9 Hz, 2H), 7.83 – 7.69 (m, 2H), 7.65 (dt, J = 7.8, 1.0 Hz, 1H), 7.42 (ddd, J = 7.9, 7.4, 1.4 Hz, 1H), 7.34 – 7.20 (m, 1H), 7.02 (dd, J = 7.9, 1.2 Hz, 1H), 6.47 (d, J = 16.2 Hz, 1H), 3.79 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 167.6, 159.3, 150.7, 141.4 (d, J = 1.4 Hz), 139.1 (t, J = 1.4 Hz), 133.2 (q, J = 32.5 Hz), 131.4, 129.4, 128.7, 127.7, 126.8, 126.0 (q, J = 3.8 Hz), 124.0 (q, J = 272.5 Hz), 119.3, 118.7, 51.8.
^{19}F NMR (375 MHz, Chloroform-d) δ -62.90.
IR (ATR, cm-1) 1720, 1629, 1437, 1416, 1316, 1269, 1168, 1136, 995, 835, 755.
HRMS (DART, M+H) Calc'd 334.1049 for $C_{18}H_{15}NO_2F_3$, found 334.1050.



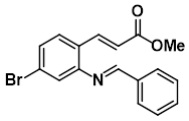
methyl (*E*)-3-(2-(((*E*)-4-methoxybenzylidene)amino)phenyl)acrylate (1g) – 0.350 g, 1.19 mmol (47% over 2 steps from methyl 3-(2-nitrophenyl)acrylate). Pale orange solid.
MP = 46 - 47 ºC.
^{1}H NMR (400 MHz, Chloroform-d) δ 8.31 (s, 1H), 8.20 (d, J = 16.2 Hz, 1H), 7.90 (d, J = 8.8 Hz, 2H), 7.61 (dd, J = 7.8, 1.5 Hz, 1H), 7.39 (td, J = 7.6, 1.5 Hz, 1H), 7.22 (td, J = 7.6, 1.4 Hz, 1H), 7.05 – 6.93 (m, 3H), 6.48 (d, J = 16.2 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 167.7, 162.5, 160.0, 151.8, 141.8, 131.2, 130.8, 129.1, 128.2, 127.5, 125.6, 118.9, 118.7, 114.3, 55.5, 51.6.
IR (ATR, cm-1) 2942, 1696, 1599, 1585, 1509, 1432, 1312, 1257, 1199, 1152, 1028, 831, 763.
HRMS (DART, M+H) Calc'd 296.1281 for $C_{18}H_{18}NO_3$, found 296.1284.



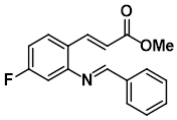
methyl (*E*)-3-(2-(((*E*)-thiophen-2-ylmethylene)amino)phenyl)acrylate (1h) – 0.578 g, 2.13 mmol (85% over 2 steps from methyl 3-(2-nitrophenyl)acrylate). Yellow solid.
MP = 46 - 47 ºC.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.46 (s, 1H), 8.18 (dd, J = 16.2, 1.8 Hz, 1H), 7.59 (dd, J = 7.9, 1.4 Hz, 1H), 7.53 (dd, J = 4.8, 1.1 Hz, 1H), 7.49 (dt, J = 3.7, 1.0 Hz, 1H), 7.36 (td, J = 7.9, 1.1 Hz, 1H), 7.22 (td, J = 7.6, 1.1 Hz, 1H), 7.13 (ddd, J = 4.8, 3.7, 0.8 Hz, 1H), 6.99 (dt, J = 7.6, 1.0 Hz, 1H), 6.50 (d, J = 16.1 Hz, 1H), 3.78 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 167.6, 153.4, 150.8, 142.8, 141.6, 132.6, 131.2, 131.1, 128.4, 127.9, 127.9, 126.1, 119.2, 118.9, 51.6.
IR (ATR, cm-1) 2946, 2846, 1695, 1585, 1509, 1432, 1312, 1273, 1257, 1199, 1153, 1043, 829.
HRMS (DART, M+H) Calc'd 272.0740 for $C_{15}H_{14}NO_2S$, found 272.0738.



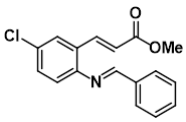
methyl 3-(2-((*E*)-ferrocenylideneamino)phenyl)acrylate (1i) – 0.338 g, 0.91 mmol (36% over 2 steps from methyl 3-(2-nitrophenyl)acrylate). Orange solid.
MP = 80 - 82 ºC.
^{1}H NMR (400 MHz, Chloroform-d) δ 8.24 (s, 1H), 8.09 (d, J = 16.2 Hz, 1H), 7.57 (dd, J = 7.9, 1.5 Hz, 1H), 7.37 (td, J = 7.5, 1.5 Hz, 1H), 7.20 (td, J = 7.5, 1.3 Hz, 1H), 6.90 (dd, J = 7.9, 1.3 Hz, 1H), 6.55 (d, J = 16.2 Hz, 1H), 4.85 (t, J = 1.9 Hz, 2H), 4.53 (t, J = 1.9 Hz, 2H), 4.27 (s, 5H), 3.80 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 167.8, 162.2, 153.0, 142.2, 131.3, 128.3, 127.6, 125.3, 119.3, 119.1, 80.3, 71.6, 69.6, 69.4, 51.7.
IR (ATR, cm-1) 3011, 1708, 1622, 1590, 1568, 1447, 1316, 1298, 1192, 1164, 1143, 980, 751.
HRMS (DART, M+H) Calc'd 374.0838 for $C_{21}H_{20}NO_2Fe$, found 374.0841.



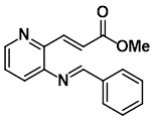
methyl (*E*)-3-(2-(((*E*)-benzylidene)amino)-4-bromophenyl)acrylate (1j) – 0.290 g, 0.843 mmol (8.4 % over 3 steps from the corresponding 2-nitrobenzaldehyde). White solid.
MP = 66 - 67 ºC.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.36 (s, 1H), 8.20 – 8.05 (d, J = 16.1 Hz, 1H), 7.98 – 7.90 (m, 2H), 7.56 – 7.43 (m, 4H), 7.36 (ddd, J = 8.4, 2.0, 0.6 Hz, 1H), 7.16 (d, J = 2.0 Hz, 1H), 6.46 (d, J = 16.1 Hz, 1H), 3.78 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 167.5, 161.8, 152.3, 140.6 (two peaks), 135.7, 132.2, 129.4, 129.0, 128.8, 127.5, 124.9, 122.0, 119.4, 51.8.
IR (ATR, cm-1) 3011, 2215, 211, 1615, 1454, 1375, 1310, 1290, 1207, 1173, 984, 881, 758, 737.
HRMS (DART, M+H) Calc'd 344.0281 for $C_{17}H_{15}NO_2Br$, found 344.0290.



methyl (*E*)-3-(2-(((*E*)-benzylidene)amino)-4-fluorophenyl)acrylate (1k) – 0.163 g, 0.575 mmol (6.6% over 3 steps from the corresponding 2-nitrobenzaldehyde). Orange solid.
MP = 60 - 62 ºC.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.36 (s, 1H), 8.13 (d, J = 16.2 Hz, 1H), 8.00 – 7.88 (m, 2H), 7.60 (dd, J = 8.6, 6.1 Hz, 1H), 7.55 – 7.46 (m, 3H), 6.95 (dddd, J = 8.6, 7.9, 2.6, 0.5 Hz, 1H), 6.74 (dd, J = 9.5, 2.6 Hz, 1H), 6.41 (dd, J = 16.2, 0.5 Hz, 1H), 3.78 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 167.6, 164.4 (d, J = 252.2 Hz), 161.8, 153.2 (d, J = 8.1 Hz), 140.6, 135.7, 132.2, 129.4, 129.0, 124.9 (d, J = 3.2 Hz), 118.5 (two peaks), 113.2 (d, J = 22.6 Hz), 106.1 (d, J = 22.6 Hz), 51.7.
^{19}F NMR (377 MHz, Chloroform-d) δ -108.68 (q, J = 7.9 Hz).
IR (ATR, cm-1) 3066, 2214, 1616, 1576, 1451, 1314, 1168, 1156, 966, 883, 748. 686.
HRMS (DART, M+H) Calc'd 284.1081 for $C_{17}H_{15}NO_2F$, found 284.1073.

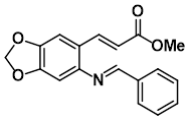


methyl (*E*)-3-(2-(((*E*)-benzylidene)amino)-5-chlorophenyl)acrylate (1l) – 0.719 g, 2.40 mmol (18 % over 3 steps from the corresponding 2-nitrobenzaldehyde). Light yellow solid.
MP = 80 - 82 ºC.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.36 (s, 1H), 8.13 (dd, J = 16.2, 0.5 Hz, 1H), 7.93 (dt, J = 6.6, 1.7 Hz, 2H), 7.59 (d, J = 2.4 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.35 (dd, J = 8.5, 2.4 Hz, 1H), 6.96 (d, J = 8.5 Hz, 1H), 6.46 (d, J = 16.2 Hz, 1H), 3.79 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 167.3, 161.3, 149.8, 140.3, 135.9, 132.1, 131.7, 131.0, 130.0, 129.3, 129.0, 127.2, 120.2, 120.1 (two peaks), 51.8.
IR (ATR, cm-1) 1702, 1624, 1581, 1471, 1432, 12822, 1180, 1119, 984, 860, 750, 688.
HRMS (METHOD, M+H) Calc'd 300.0786 for $C_{17}H_{15}NO_2Cl$, found 300.0794.

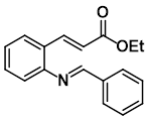


methyl (*E*)-3-(3-(((*E*)-benzylidene)amino)pyridin-2-yl)acrylate (1m) – 0.339 g, 1.27 mmol (9.1% over 3 steps from the corresponding 2-nitrobenzaldehyde). Yellow solid.
MP = 69 - 71 ºC.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.49 (ddd, J = 4.4, 1.8, 0.5 Hz, 1H), 8.38 (s, 1H), 8.22 (dd, J = 15.7, 0.4 Hz, 1H), 7.98 – 7.90 (m, 2H), 7.59 – 7.45 (m, 3H), 7.35 – 7.28 (m, 2H), 7.07 (d, J = 15.7 Hz, 1H), 3.79 (s, 3H).

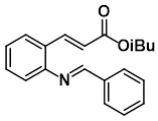
^{13}C NMR (126 MHz, Chloroform-d) δ 167.6, 162.6, 147.2, 147.1, 146.5, 139.7, 135.7, 132.3, 129.4, 129.0, 126.4, 125.4, 122.3 (two peaks, 51.8.
IR (ATR, cm-1) 2370, 1709, 1623, 1451, 1437, 1302, 1198, 1160, 1093, 995, 866, 774.
HRMS (DART, M+H) Calc'd 267.1128 for $C_{16}H_{15}N_2O_2$, found 267.1122.



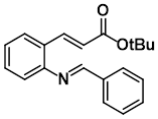
methyl (*E*)-3-(6-(((*E*)-benzylidene)amino)benzo[*d*][1,3]dioxol-5-yl)acrylate (1n) – 1.46 g, 4.72 mmol (47% over 3 steps from the corresponding 2-nitrobenzaldehyde). Brown-orange solid.
MP = 111 - 113 °C.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.37 (s, 1H), 8.33 (d, J = 16.5 Hz, 1H), 8.02 – 7.82 (m, 2H), 7.53 – 7.43 (m, 3H), 7.09 (s, 1H), 6.63 (s, 1H), 6.27 (d, J = 16.5 Hz, 1H), 6.01 (s, 2H), 3.78 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 167.9, 159.5, 150.5, 146.6 (two peaks), 141.2, 136.2, 131.7, 129.1, 128.9, 123.1, 116.1, 105.5, 101.9, 99.2, 51.6.
IR (ATR, cm-1) 2946, 1696, 1585, 1509, 1432, 1312, 1257, 1199, 1154, 1034, 830, 762.
HRMS (DART, M+H) Calc'd 310.1074 for $C_{18}H_{16}NO_4$, found 310.1081.



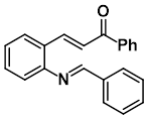
ethyl (*E*)-3-(2-(((*E*)-benzylidene)amino)phenyl)acrylate (1o) – 1.111 g, 3.978 mmol (79% from ethyl 3-(2-nitrophenyl)acrylate Yellowish solid. All data corresponds to previously reported.[2]
MP = 50 - 52 °C.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.39 (s, 1H), 8.23 (dt, J = 16.1, 0.5 Hz, 1H), 8.00 – 7.89 (m, 2H), 7.71 – 7.58 (m, 1H), 7.55 – 7.46 (m, 3H), 7.40 (ddd, J = 7.9, 7.3, 1.5 Hz, 1H), 7.31 – 7.19 (m, 1H), 7.01 (dd, J = 7.9, 1.2 Hz, 1H), 6.48 (d, J = 16.1 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 167.3, 160.9, 151.5, 141.4, 136.2, 131.8, 131.2, 129.2, 129.0, 128.6, 127.5, 126.1, 119.3, 118.9, 60.5, 14.4.



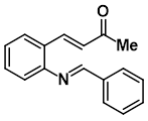
isobutyl (*E*)-3-(2-(((*E*)-benzylidene)amino)phenyl)acrylate (1p) – 0.321 g, 1.04 mmol (14% over 3 steps from the corresponding 2-nitrobenzaldehyde). Yellow oil.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.40 (s, 1H), 8.25 (d, J = 16.2 Hz, 1H), 8.01 – 7.85 (m, 2H), 7.65 (dd, J = 7.8, 1.5 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.40 (td, J = 7.6, 1.4 Hz, 1H), 7.30 – 7.17 (m, 1H), 7.03 (dd, J = 7.9, 1.2 Hz, 1H), 6.49 (d, J = 16.2 Hz, 1H), 3.98 (d, J = 6.7 Hz, 2H), 2.00 (hept, J = 6.7 Hz, 1H), 0.98 (d, J = 6.7 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-d) δ 167.3, 160.8, 151.3, 141.4, 136.2, 131.8, 131.2, 129.2, 128.9, 128.6, 127.4, 126.2, 119.3, 118.8, 70.6, 28.0 (two peaks), 19.3.
IR (ATR, cm-1) 2965, 1705, 1627, 1592, 1452, 1313, 1260, 1163, 1016, 984, 885, 862, 754, 689.
HRMS (DART, M+H) Calc'd 308.1645 for $C_{20}H_{22}NO_2$, found 308.1646.



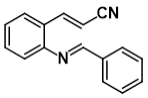
***tert*-butyl (*E*)-3-(2-(((*E*)-benzylidene)amino)phenyl)acrylate (1q)** – 0.471 g, 1.53 mmol (29% over 3 steps from the corresponding 2-nitrobenzaldehyde). Orange solid. All data corresponds to previously reported.[3]
MP = 38 - 40 °C.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.39 (s, 1H), 8.21 – 8.12 (m, 1H), 8.00 – 7.89 (m, 2H), 7.64 (dd, J = 7.8, 1.4 Hz, 1H), 7.56 – 7.44 (m, 3H), 7.41 – 7.35 (m, 1H), 7.23 (dddd, J = 7.8, 7.3, 1.2, 0.5 Hz, 1H), 7.01 (dd, J = 7.9, 1.2 Hz, 1H), 6.41 (d, J = 16.1 Hz, 1H), 1.52 (s, 9H).
^{13}C NMR (126 MHz, Chloroform-d) δ 166.6, 160.8, 151.3, 140.3, 136.2, 131.8, 131.0, 129.2, 128.9, 128.7, 127.2, 126.1, 121.0, 118.8, 80.3, 28.3.



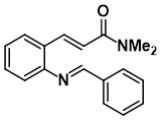
(*E*)-3-(2-(((*E*)-benzylidene)amino)phenyl)-1-phenylprop-2-en-1-one (1r) – 1.33 g, 4.27 mmol (57% over 3 steps from the corresponding 2-nitrobenzaldehyde). Yellow solid. All data corresponds to previously reported.[4]
MP = 86 - 87 °C.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.42 (s, 1H), 8.28 (d, J = 15.9 Hz, 1H), 7.98 (ddd, J = 8.2, 5.7, 1.6 Hz, 4H), 7.74 (dd, J = 7.8, 1.3 Hz, 1H), 7.62 (d, J = 15.9 Hz, 1H), 7.59 – 7.47 (m, 4H), 7.44 (ddt, J = 8.9, 7.6, 1.6 Hz, 3H), 7.29 (td, J = 7.6, 1.3 Hz, 1H), 7.04 (dd, J = 7.8, 1.2 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 191.1, 160.8, 152.0, 142.2, 138.5, 136.1, 132.6, 131.9, 131.4, 129.2, 129.0, 128.8, 128.7, 128.7, 128.6, 126.2, 124.2, 119.0.



(*E*)-4-(2-(((*E*)-benzylidene)amino)phenyl)but-3-en-2-one (1s) – 0.477 g, 0.191 mmol (24 % over 3 steps from the corresponding 2-nitrobenzaldehyde). Yellow-orange solid. All data corresponds to previously reported.[4]
MP = 44 - 45 °C.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.41 (s, 1H), 8.11 (d, J = 16.5 Hz, 1H), 7.95 (dd, J = 7.5, 2.1 Hz, 2H), 7.66 (dd, J = 7.9, 1.4 Hz, 1H), 7.53 – 7.48 (m, 3H), 7.42 (td, J = 7.6, 1.4 Hz, 1H), 7.26 (td, J = 7.7, 1.3 Hz, 1H), 7.03 (dd, J = 7.9, 1.2 Hz, 1H), 6.72 (d, J = 16.5 Hz, 1H), 2.38 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 199. 0, 161.0, 151.4, 140.4, 136.1, 131.9, 131.6, 129.1, 129.0, 128.6, 128.4, 127.2, 126.3, 118.9, 27.1.



(*E*)-3-(2-(((*E*)-benzylidene)amino)phenyl)acrylonitrile (1t) – 0.670 g, 2.88 mmol (39 % over 2 steps from 2-iodoaniline). Yellow solid.
MP = 37 - 39 °C.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.40 (s, 1H), 8.02 – 7.84 (m, 3H), 7.60 – 7.49 (m, 5H), 7.45 (td, J = 7.6, 1.4 Hz, 1H), 7.31 – 7.19 (m, 1H), 7.04 (dd, J = 7.9, 1.2 Hz, 1H), 5.99 (d, J = 16.8 Hz, 1H)
^{13}C NMR ((126 MHz, Chloroform-d) δ 161.3, 151.0, 147.8, 135.8, 132.2 (two peaks), 129.2, 129.1, 127.6, 127.3, 126.3, 119.0, 118.9, 97.4.
IR (ATR, cm-1) 3395, 2213, 2027, 2007, 1614, 1578, 1451, 1293, 1204, 967, 882, 749.
HRMS (DART, M+H) Calc'd 233.1073 for $C_{16}H_{13}N_2$, found 233.1079.



(*E*)-3-(2-(((*E*)-benzylidene)amino)phenyl)-N,N-dimethylacrylamide (1u) – 0.910 g, 3.27 mmol (65 % over 2 steps from 2-iodoaniline). Yellow solid.

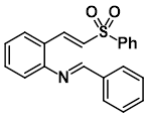
MP = 129 – 131 ºC.

^{1}H NMR (500 MHz, Chloroform-d) δ 8.37 (s, 1H), 8.03 (d, J = 15.6 Hz, 1H), 7.94 (dd, J = 7.8, 1.8 Hz, 2H), 7.61 – 7.56 (m, 1H), 7.52 – 7.41 (m, 3H), 7.35 (td, J = 7.6, 1.5 Hz, 1H), 7.22 (td, J = 7.5, 1.3 Hz, 1H), 7.01 – 6.87 (m, 2H), 3.07 (s, 3H), 3.03 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 167.2, 160.5, 151.5, 139.4, 136.2, 131.8, 130.3, 129.1, 128.9, 128.7, 125.9, 120.0 (two peaks), 118.9, 37.5, 35.9.

IR (ATR, cm-1) 1645, 1624, 1598, 1577, 1487, 1450, 1390, 1300, 1262, 1141, 998, 865, 750.

HRMS (METHOD, M+H) Calc'd 279.1492 for $C_{18}H_{19}N_2O$, found 279.1485.



(*E*)-1-phenyl-N-(2-((*E*)-2-(phenylsulfonyl)vinyl)phenyl)methanimine (1v) – 0.516 g, 1.49 mmol (30% over 3 steps from the corresponding 2-nitrobenzaldehyde). Pale yellow solid.

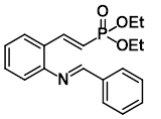
MP = 81 - 83 ºC.

^{1}H NMR (500 MHz, Chloroform-d) δ 8.10 (d, J = 15.6 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.92 – 7.84 (m, 2H), 7.63 – 7.56 (m, 1H), 7.56 – 7.45 (m, 7H), 7.43 (td, J = 7.6, 1.4 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.03 (dd, J = 8.0, 1.2 Hz, 1H), 6.98 (d, J = 15.5 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 161.2, 151.6, 141.1, 139.5, 135.9, 133.3, 132.13 (two peaks), 129.4, 129.2, 129.1 (three peaks), 127.8, 126.6, 126.3, 119.0.

IR (ATR, cm-1) 3066, 21991, 1715, 1608, 1591, 1488, 1447, 1298, 1160, 1139, 979, 748.

HRMS (DART, M+H) Calc'd 348.1053 for $C_{21}H_{18}NO_2S$, found 348.1059.



diethyl ((*E*)-2-(((*E*)-benzylidene)amino)styryl)phosphonate (1w) – 0.831 g, 2.42 mmol (32% over 3 steps from the corresponding 2-nitrobenzaldehyde). Yellowish oil.

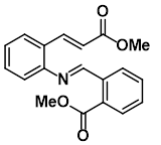
^{1}H NMR (500 MHz, Chloroform-d) δ 8.38 (s, 1H), 8.03 – 7.88 (m, 3H), 7.63 – 7.57 (m, 1H), 7.54 – 7.44 (m, 3H), 7.39 (td, J = 7.6, 1.4 Hz, 1H), 7.26 – 7.22 (m, 1H), 6.99 (dd, J = 7.8, 1.2 Hz, 1H), 6.32 (dd, J = 19.3, 17.7 Hz, 1H), 4.11 (dq, J = 7.8, 7.0 Hz, 4H), 1.32 (td, J = 7.0, 0.5 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-d) δ 160.9, 151.1, 145.5 – 144.7 (m), 136.1, 131.8, 131.2, 129.1, 128.9 (d, J = 1.0 Hz), 128.7, 127.4 (d, J = 1.3 Hz), 126.1, 118.9 (d, J = 1.4 Hz), 115.4 (dd, J = 190.0, 2.5 Hz), 61.9 (d, J = 5.4 Hz), 16.5 (d, J = 6.5 Hz).

^{31}P NMR (162 MHz, Chloroform-d) δ 19.55.

IR (ATR, cm-1) 2987, 1627, 1592, 1478, 1453, 1244, 1196, 1163, 1049, 1021, 951, 851, 760, 691.

HRMS (METHOD, M+H) Calc'd 344.1410 for $C_{19}H_{22}NO_3P$, found 344.1411.



methyl 2-((*E*)-((2-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)imino)methyl)benzoate (9) – 0.830 g, 2.57 mmol (60% over 2 steps from methyl 3-(2-nitrophenyl)acrylate). Pale yellow solid.

MP = 89 - 90 ºC.

^{1}H NMR (500 MHz, Chloroform-d) δ 9.17 (s, 1H), 8.37 – 8.32 (m, 1H), 8.25 (d, J = 16.1 Hz, 1H), 7.99 (ddd, J = 7.8, 1.3, 0.5 Hz, 1H), 7.67 (dddd, J = 7.9, 7.3, 1.4, 0.7 Hz, 1H), 7.63 (dd, J = 7.8, 1.4 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.44 – 7.37 (m, 1H), 7.25 (dddd, J = 7.8, 7.3, 1.2, 0.5 Hz, 1H), 7.11 (dd, J = 7.9, 1.2 Hz, 1H), 6.47 (d, J = 16.1 Hz, 1H), 3.94 (s, 3H), 3.79 (s, 3H).

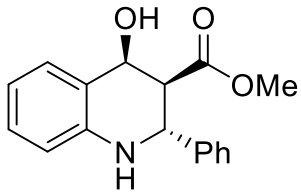
^{13}C NMR (126 MHz, Chloroform-d) δ 167.7, 167.3, 160.5, 151.5, 141.7, 137.0, 132.6, 131.4, 130.8 (two peaks), 130.6, 128.8, 128.6, 127.3, 126.4, 119.4, 118.8, 52.6, 51.7.

IR (ATR, cm-1) 3007, 1703, 1626, 1595, 1567, 1430, 1289, 1266, 1189, 1140, 1084, 1039, 748, 696.

HRMS (DART, M+H) Calc'd 324.1230 for $C_{19}H_{18}NO_4$, found 324.1237.

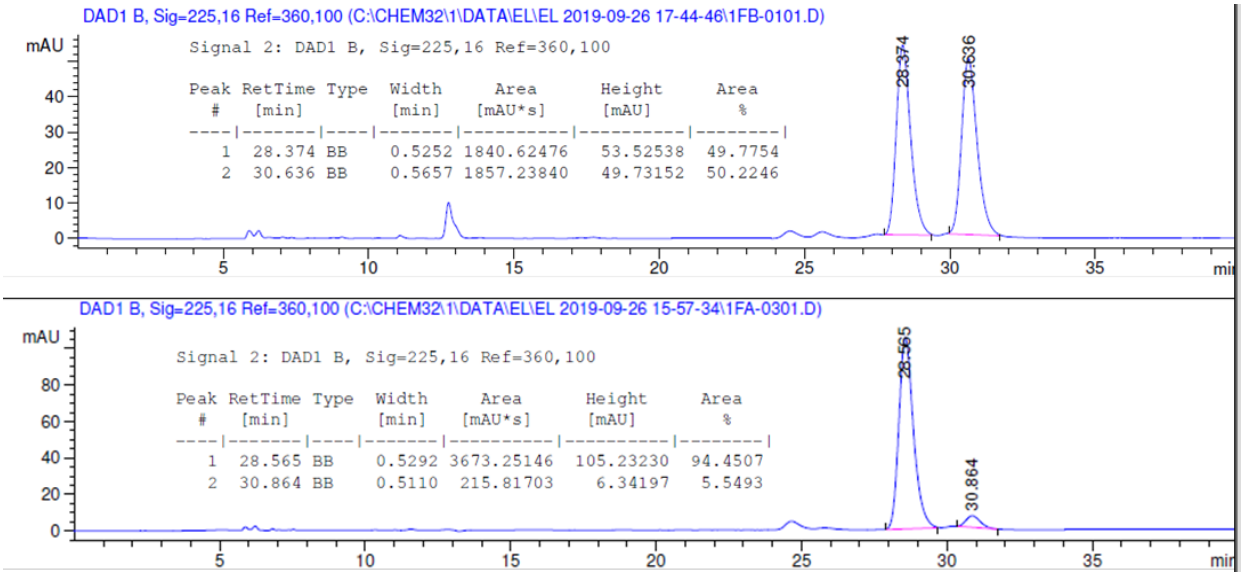
5 General Procedure for the Reported Catalytic Reaction

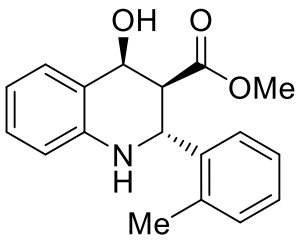
A 2-dram vial containing a stir bar was oven-dried and cooled under argon whereupon t was charged with $Cu(MeCN)_4PF_6$ (3.0 mg, 0.008 mmol, 4 mol%), Josiphos SL-J001-1 (7.7 mg, 0.012 mmol, 6 mol%) and NaO*t*Bu (5.77 mg, 0.06 mmol, 30 mol%), and Et_2O (1 mL) was immediately added. This was stirred for 30 min with noticeable darkening of color. B_2Pin_2 (76 mg, 0.3 mmol, 1.5 equiv) was added as a solution in Et_2O (1 mL) and the resultant suspension was stirred for a further 15 min. Finally, substrate (0.2 mmol) and *t*AmOH (44 µL, 0.4 mmol, 2.0 equiv) were added as a solution in Et_2O (2 mL). Reactions take 4-18 h (substrate dependent) but for comparison purposes all were stopped after 18 h except those noted. Upon completion, it was filtered over a Celite pad and volatiles were removed. Subsequently, $NaBO_3$•$4H_2O$ (123.1 mg, 0.8 mmol, 4.0 equiv), water (2 mL) and THF (4 mL) were added and the reaction mixture was stirred for 4 hours. Upon completion, the reaction mixture was diluted with 50% NaCl solution, and extracted thrice with EtOAc. The combined organic fractions were washed five times with water to remove pinacol and once with brine and dried over $MgSO_4$. The dr was determined by ^{5}H NMR analysis of the crude mixture and the products were isolated by flash column chromatography. Some decomposition of products occurs during chromatography; therefore, chromatography was performed with a high flow of air pressure.



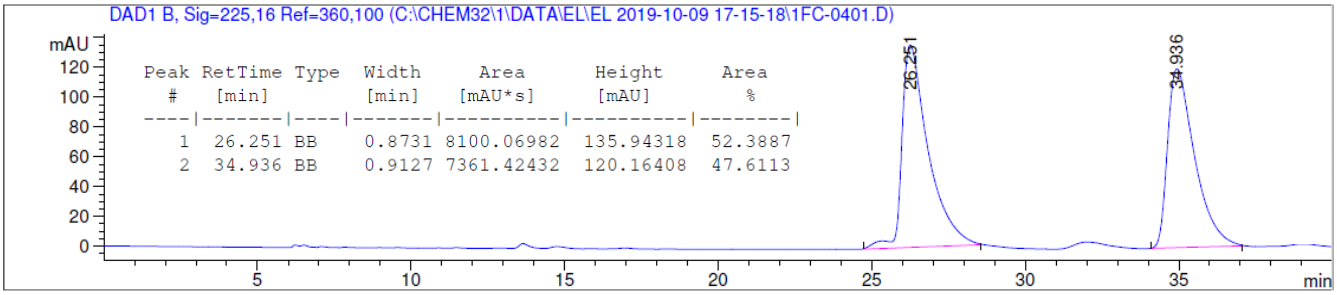
methyl (2*R*,3*S*,4*S*)-4-hydroxy-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3a) – 51.1 mg, 0.18 mmol (90%). White foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.48 – 7.42 (m, 2H), 7.39 – 7.30 (m, 3H), 7.28 (dd, J = 7.6, 1.6 Hz, 1H), 7.15 (ddd, J = 8.1, 7.3, 1.6 Hz, 1H), 6.74 (td, J = 7.4, 1.1 Hz, 1H), 6.57 (ddd, J = 8.0, 1.1, 0.5 Hz, 1H), 4.96 (t, J = 2.5 Hz, 1H), 4.84 (d, J = 10.8 Hz, 1H), 4.19 (s, 1H), 3.50 (s, 3H), 3.25 – 3.19 (m, 1H), 3.02 (dd, J = 10.8, 2.9 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 173.0, 143.4, 141.3, 130.0, 129.8, 128.6, 128.3, 127.9, 120.7, 117.5, 114.3, 67.0, 53.2, 51.9, 51.0.
IR (ATR, cm^{-1}) 3395, 2929, 1723, 1610, 1591, 1489, 1435, 1362, 1259, 1162, 1027, 892, 750, 699.
HRMS (DART, M+H) Calc'd 284.1281 for $C_{17}H_{18}NO_3$, found 284.1281.

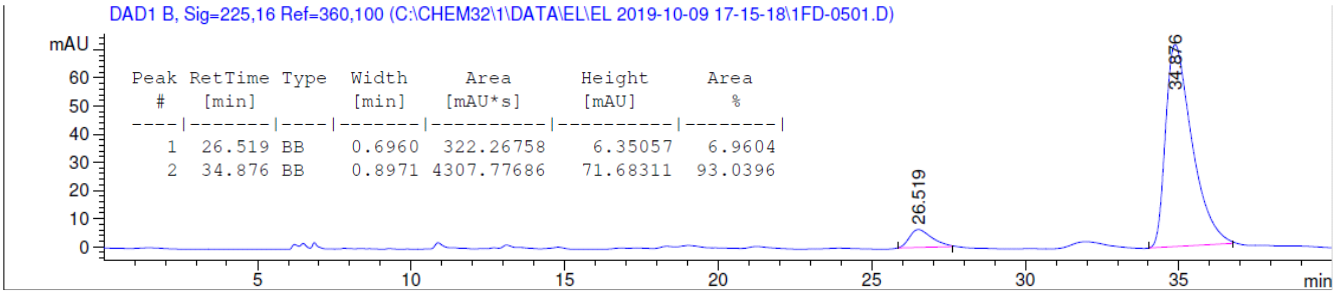
HPLC IA, 15% IPA/Hex, 0.5 mL/min

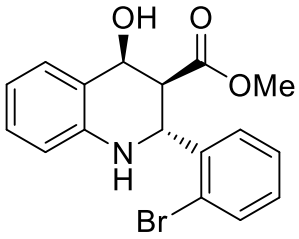




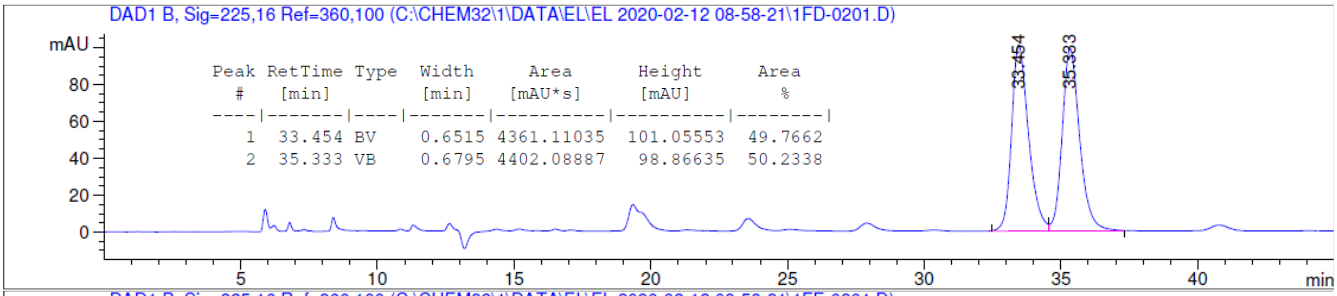
methyl (2*R*,3*S*,4*S*)-4-hydroxy-2-(*o*-tolyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3b) – 54.2 mg, 0.182 mmol (91%). Off-white foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.42 (dt, J = 5.7, 3.2 Hz, 1H), 7.31 (dd, J = 7.6, 1.6 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.15 (ddd, J = 8.1, 7.4, 1.6 Hz, 1H), 6.74 (td, J = 7.4, 1.1 Hz, 1H), 6.56 (dd, J = 8.1, 1.1 Hz, 1H), 5.18 (dd, J = 10.4, 1.1 Hz, 1H), 5.00 (t, J = 3.2 Hz, 1H), 4.05 (s, 1H), 3.53 (s, 3H), 3.17 – 3.06 (m, 2H), 2.50 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 173.2, 143.5, 139.2, 136.7, 130.8, 129.9, 129.8, 128.0, 127.3, 126.5, 120.8, 117.5, 114.2, 67.1, 52.0, 49.9, 48.8, 19.5.
IR (ATR, cm^{-1}) 3453, 3347, 3021, 2949, 1704, 1610, 1492, 1436, 1288, 1257, 1227, 1017, 742.
HRMS (DART, M+H) Calc'd 298.1438 for $C_{18}H_{20}NO_3$, found 298.1441.
HPLC IA, 15% IPA/Hex, 0.5 mL/min

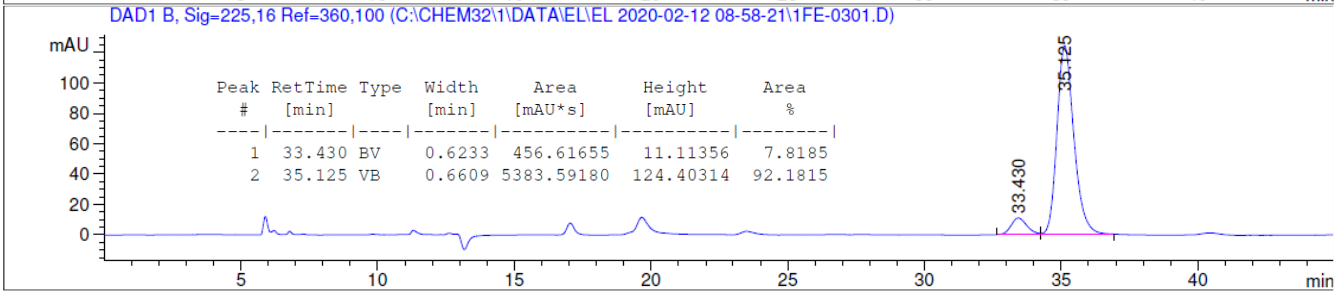


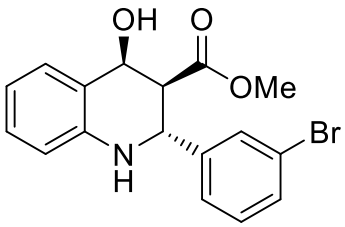




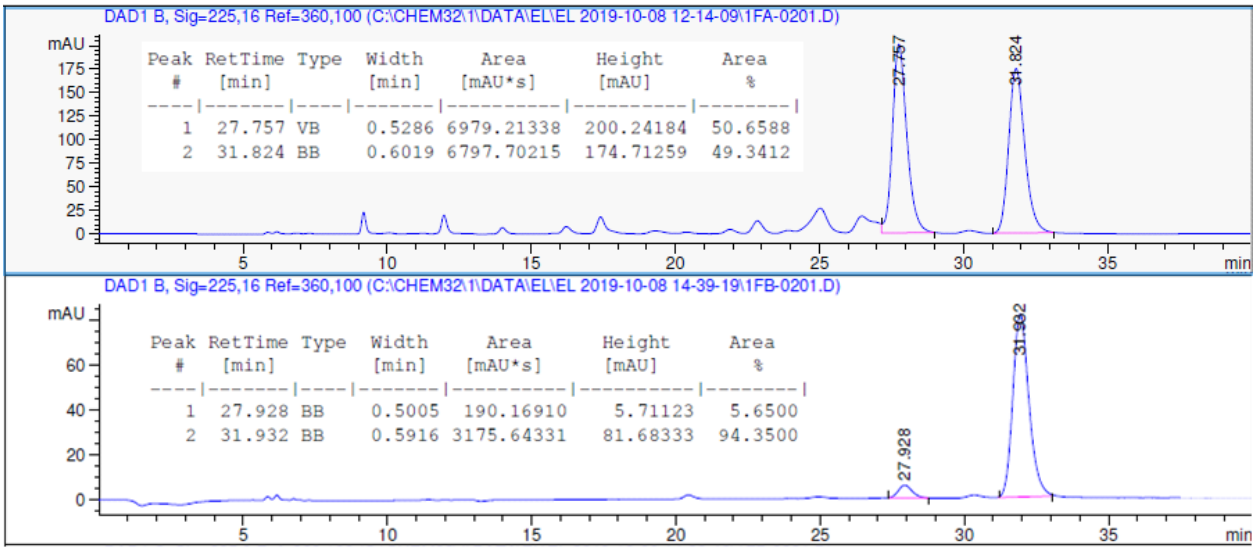
methyl (2*R*,3*S*,4*S*)-2-(2-bromophenyl)-4-hydroxy-1,2,3,4-tetrahydroquinoline-3-carboxylate (3c) – 48.3 mg, 0.133 mmol (67%). White foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.59 (dd, J = 8.0, 1.3 Hz, 1H), 7.45 (dd, J = 7.8, 1.6 Hz, 1H), 7.35 (ddd, J = 7.8, 1.6, 0.7 Hz, 1H), 7.30 (td, J = 7.6, 1.3 Hz, 1H), 7.22 – 7.09 (m, 2H), 6.76 (td, J = 7.4, 1.1 Hz, 1H), 6.57 (dd, J = 8.0, 1.1 Hz, 1H), 5.39 (dd, J = 8.4, 2.2 Hz, 1H), 4.89 (d, J = 3.6 Hz, 1H), 4.17 (d, J = 2.2 Hz, 1H), 3.61 (s, 3H), 3.34 (s, 1H), 3.26 (dd, J = 8.4, 3.6 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 172.5, 143.0, 140.5, 133.3, 129.5, 129.5, 129.0, 128.8, 127.9, 123.6, 121.6, 117.9, 114.0, 66.3, 53.0, 52.2, 48.6.
IR (ATR, cm^{-1}) 3433, 3347, 2953, 1703, 1609, 1492, 1438, 1288, 1274, 1256, 1228, 1083, 1020, 817, 752.
HRMS (ESI, M+Na) Calc'd 384.0206 for $C_{17}H_{16}BrNaNO_3$, found 384.0208.
HPLC IA, 15% IPA/Hex, 0.5 mL/min

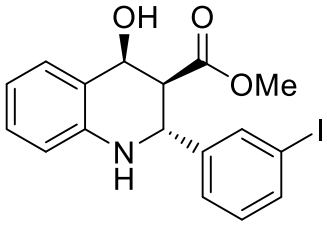




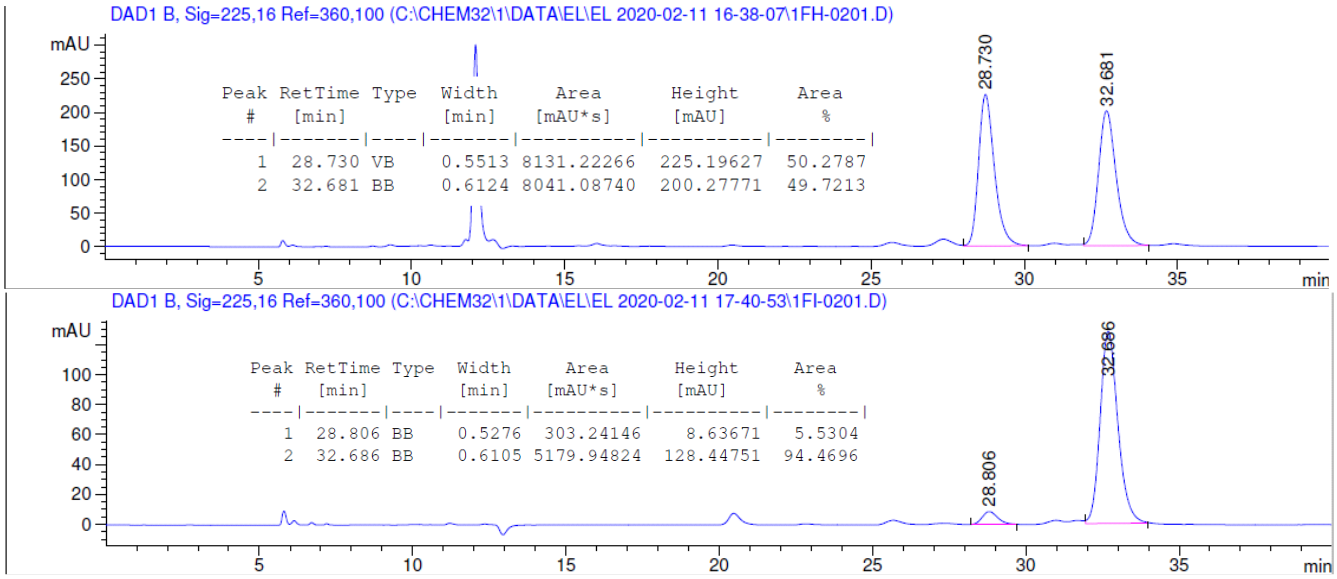


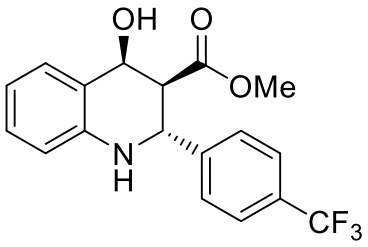
methyl (2*R*,3*S*,4*S*)-2-(3-bromophenyl)-4-hydroxy-1,2,3,4-tetrahydroquinoline-3-carboxylate (3d) – 42.8 mg, 0.118 mmol (59%). White foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.62 (t, J = 1.9 Hz, 1H), 7.44 (ddd, J = 8.0, 1.9, 1.1 Hz, 1H), 7.38 (dt, J = 8.0, 1.6 Hz, 1H), 7.26 (dd, J = 7.8, 1.6 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.15 (ddd, J = 8.1, 7.3, 1.6 Hz, 1H), 6.75 (td, J = 7.4, 1.1 Hz, 1H), 6.58 (dd, J = 8.1, 1.2 Hz, 1H), 4.95 (d, J = 2.9 Hz, 1H), 4.78 (d, J = 10.8 Hz, 1H), 4.16 (s, 1H), 3.54 (s, 3H), 3.11 (s, 1H), 2.96 (dd, J = 10.8, 2.9 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 172.6, 143.8, 143.1, 131.4, 130.9, 130.2, 129.9 (two peaks), 126.8, 122.6, 120.8, 117.9, 114.4, 66.9, 52.8, 52.0, 50.9.
IR (ATR, cm^{-1}) 3388, 2956, 1725, 1610, 1588, 1488, 1433, 1309, 1257, 1164, 1071, 1028, 999, 933, 749.
HRMS (ESI, M+Na) Calc'd 384.0206 for $C_{17}H_{16}BrNaNO_3$, found 384.0207.
HPLC IA, 15% IPA/Hex, 0.5 mL/min,



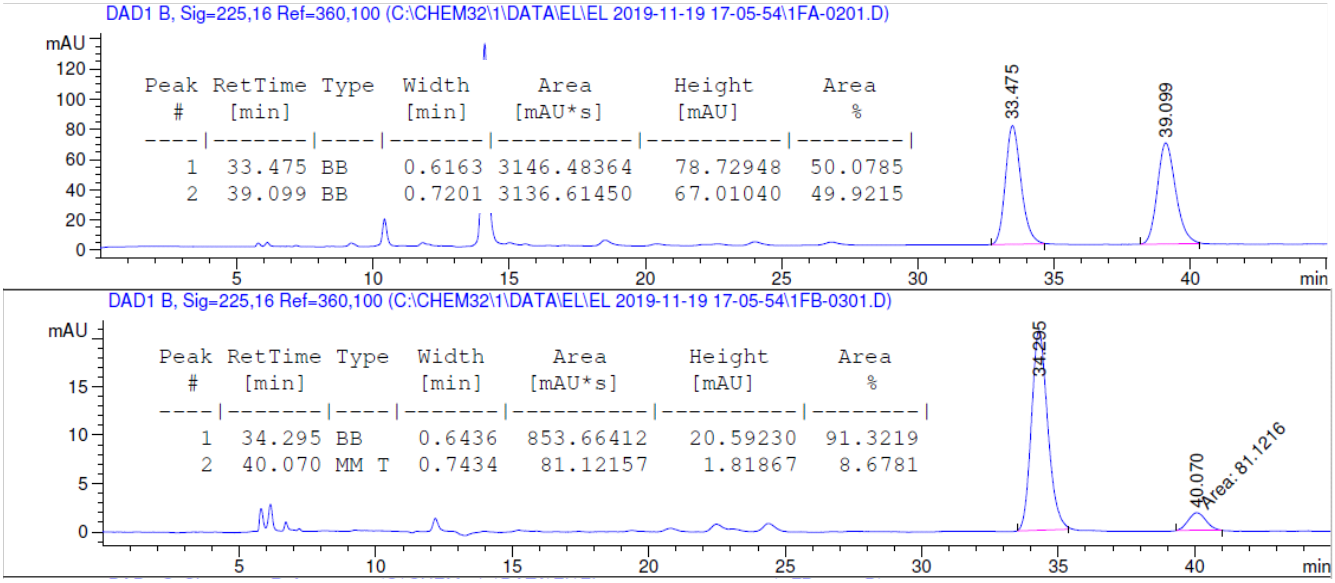


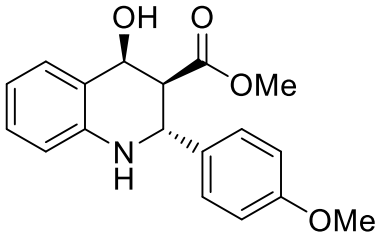
methyl (2*R*,3*S*,4*S*)-4-hydroxy-2-(3-iodophenyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3e) – 64.6 mg, 0.158 mmol (79%). Off-white foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.81 (t, J = 1.7 Hz, 1H), 7.65 (ddd, J = 7.9, 1.8, 1.0 Hz, 1H), 7.42 (dt, J = 7.7, 1.5 Hz, 1H), 7.28 – 7.21 (m, 1H), 7.15 (ddd, J = 8.1, 7.3, 1.6 Hz, 1H), 7.08 (t, J = 7.7 Hz, 1H), 6.75 (td, J = 7.4, 1.1 Hz, 1H), 6.59 (dd, J = 8.1, 1.1 Hz, 1H), 4.95 (t, J = 3.3 Hz, 1H), 4.77 (dd, J = 10.8, 0.9 Hz, 1H), 4.14 (s, 1H), 3.55 (s, 3H), 3.05 (d, J = 3.8 Hz, 1H), 2.96 (dd, J = 10.8, 2.9 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 172.5, 143.7, 143.0, 137.3, 136.7, 130.2, 129.9 (two peaks), 127.4, 120.7, 117.8, 114.3, 94.4, 66.8, 52.6, 51.9, 50.8.
IR (ATR, cm^{-1}) 3398, 2949, 1731, 1611, 1589, 1491, 1436, 1320, 1259, 1169, 1031, 909, 750, 732.
HRMS (ESI, M+H) Calc'd 410.0248 for $C_{17}H_{17}INO_3$, found 410.0255.
HPLC IA, 15% IPA/Hex, 0.5 mL/min



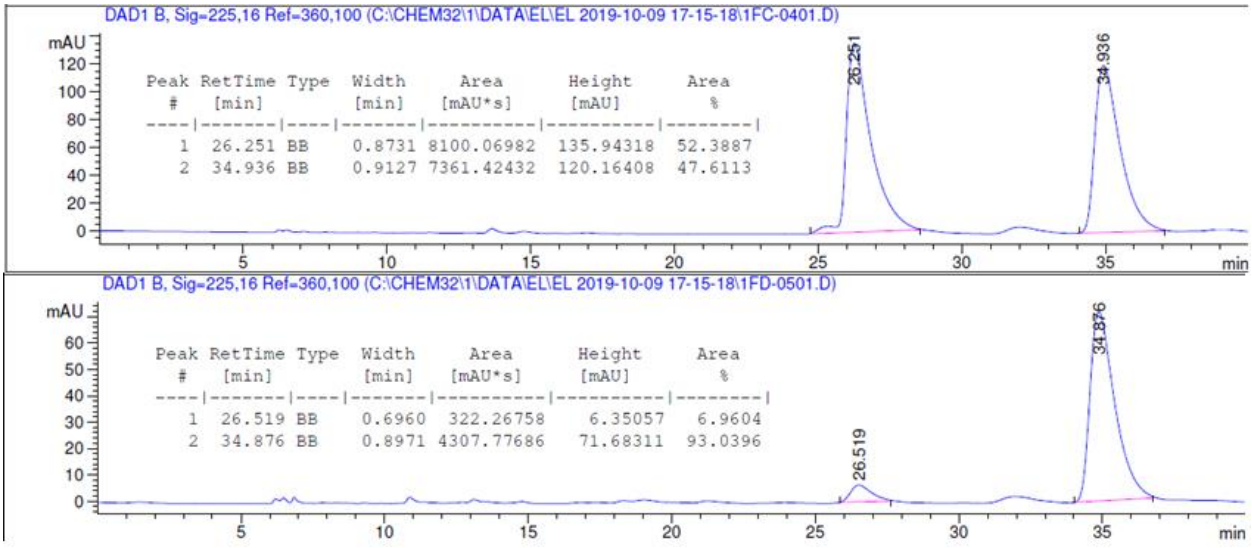


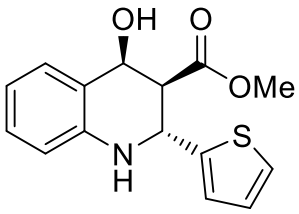
methyl (2*R*,3*S*,4*S*)-4-hydroxy-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3f) – 27.4 mg, 0.078 mmol (39%). Yellowish oil.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.66 – 7.55 (m, 5H), 7.29 (dd, J = 7.6, 1.5 Hz, 1H), 7.17 (ddd, J = 8.1, 7.3, 1.6 Hz, 1H), 6.77 (td, J = 7.4, 1.1 Hz, 1H), 6.60 (dd, J = 8.1, 1.1 Hz, 1H), 5.02 – 4.97 (m, 1H), 4.93 (d, J = 10.8 Hz, 1H), 4.15 (s, 1H), 3.53 (s, 3H), 3.03 (dd, J = 10.8, 2.9 Hz, 1H), 2.97 (s, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 172.3, 145.4 (q, J = 1.4 Hz), 142.9, 130.5 (q, J = 32.4 Hz), 129.9 (two peaks), 128.4, 125.5 (q, J = 3.8 Hz), 124.0 (q, J = 272.1 Hz), 120.7, 118.0, 114.3, 66.8, 52.8, 51.9, 50.8.
^{19}F NMR (376 MHz, Chloroform-d) δ -62.61.
IR (ATR, cm^{-1}) 3460, 3361, 2939, 2863, 1702, 1611, 1493, 1322, 1284, 1126, 1109, 1068, 1023, 850.
HRMS (DART, M+H) Calc'd 352.1155 for $C_{18}H_{17}NO_3F_3$, found 352.1164.
HPLC IA, 15% IPA/Hex, 0.5 mL/min



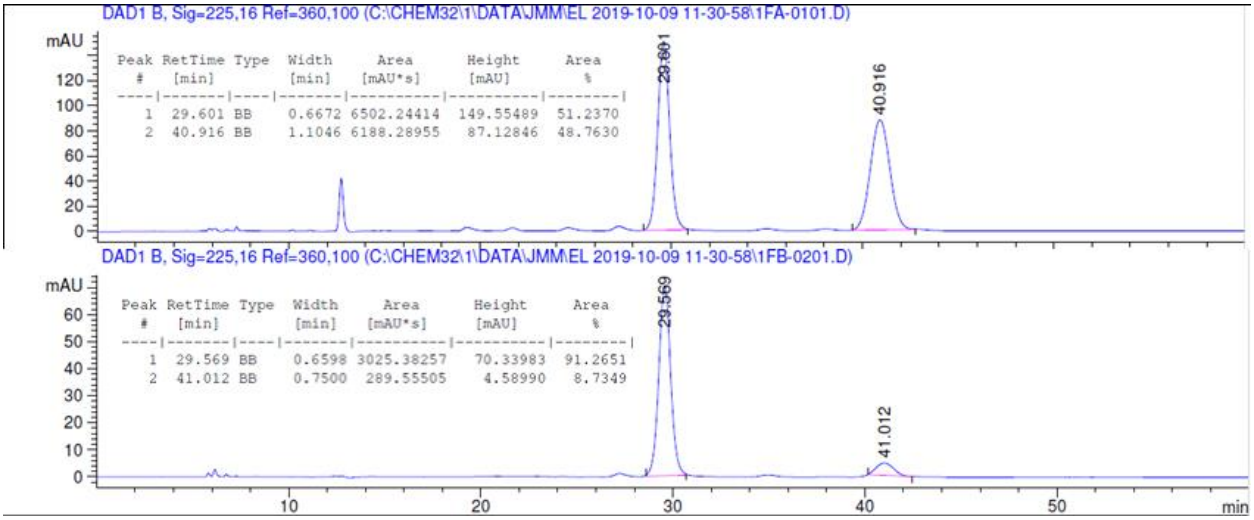


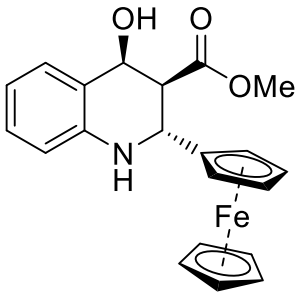
methyl (2*R*,3*S*,4*S*)-4-hydroxy-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3g) – 38.5 mg, 0.123 mmol (61%). Off-white foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.41 – 7.33 (m, 2H), 7.29 – 7.21 (m, 1H), 7.14 (ddd, J = 8.1, 7.3, 1.6 Hz, 1H), 6.91 – 6.83 (m, 2H), 6.73 (td, J = 7.4, 1.1 Hz, 1H), 6.56 (ddd, J = 8.1, 1.2, 0.6 Hz, 1H), 4.96 (d, J = 2.8 Hz, 1H), 4.80 (d, J = 11.0 Hz, 1H), 4.21 – 4.01 (broad s, 1H), 3.81 (s, 3H), 3.52 (s, 3H), 3.24 – 3.08 (broad s, 1H), 2.98 (dd, J = 11.0, 2.8 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 173.2, 159.6, 143.5, 133.2, 130.1, 129.9, 129.0, 120.7, 117.5, 114.3, 114.0, 67.1, 55.4, 52.6, 51.9, 51.1.
IR (ATR, cm^{-1}) 3385, 2983, 1729, 1609, 1491, 1437, 1367, 1303, 1245, 1171, 1073, 1025.
HRMS (DART, M+H) Calc'd 314.1387 for $C_{18}H_{20}INO_4$, found 314.1384.
HPLC IB, 15% IPA/Hex, 0.5 mL/min



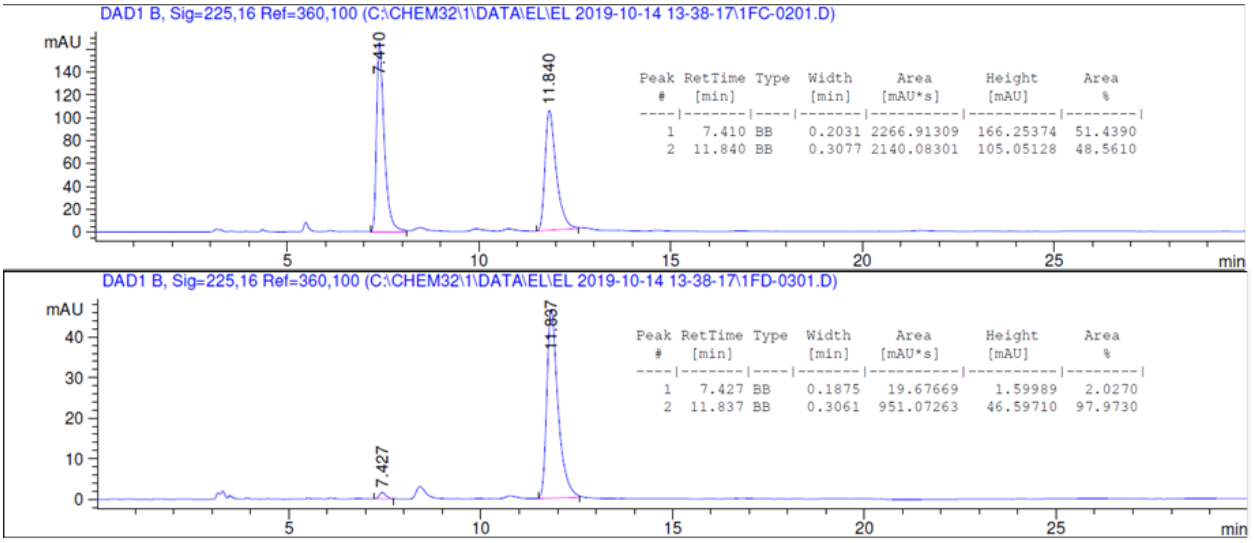


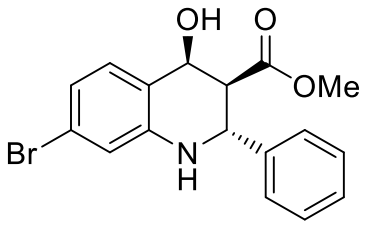
methyl (2*R*,3*S*,4*S*)-4-hydroxy-2-(thiophen-2-yl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (3h) – 21.3 mg, 0.074 mmol (37%). Off-white foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.30 – 7.23 (m, 2H), 7.15 (ddd, J = 8.1, 7.4z, 1.6 Hz, 1H), 7.11 (ddd, J = 3.5, 1.3, 0.6 Hz, 1H), 6.97 (dd, J = 5.1, 3.5 Hz, 1H), 6.75 (td, J = 7.4, 1.1 Hz, 1H), 6.59 (dd, J = 8.1, 1.1 Hz, 1H), 5.18 (d, J = 10.7 Hz, 1H), 4.95 (d, J = 2.9 Hz, 1H), 4.35 (s, 1H), 3.59 (s, 3H), 3.16 (s, 1H), 3.01 (dd, J = 10.7, 2.9 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 172.8, 145.1, 142.8, 129.9 (two peaks), 126.8, 126.0, 125.3, 120.9, 118.1, 114.5, 66.9, 52.2, 52.1, 49.2.
IR (ATR, cm^{-1}) 3439, 3335, 2956, 1709, 1607, 1591, 1486, 1435, 1399, 1260, 1073, 1022, 930, 757.
HRMS (DART, M+H) Calc'd 290.0845 for $C_{15}H_{15}NO_3S$, found 290.0839.
HPLC IA, 15% IPA/Hex, 0.5 mL/min



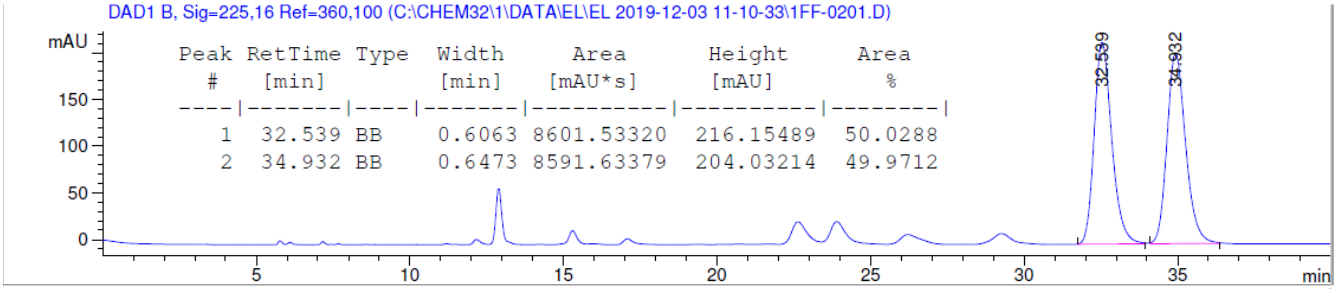


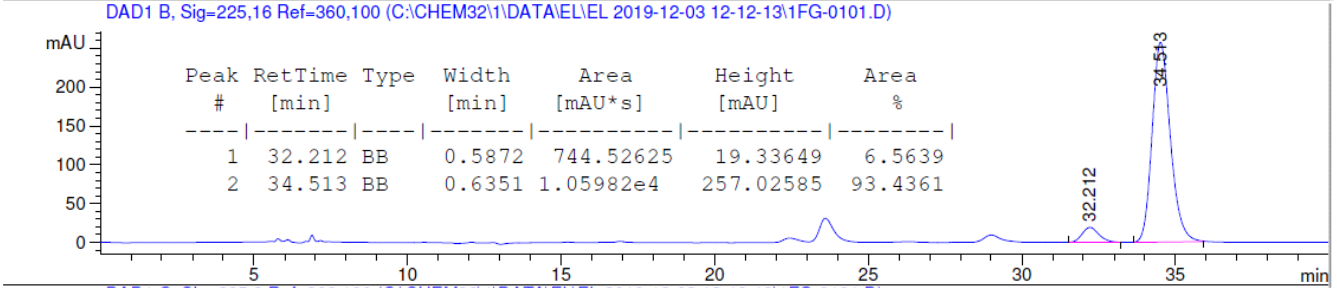
methyl (2*R*,3*S*,4*S*)-4-hydroxy-2-ferrocenyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3i) – 57.7 mg, 0.147 mmol (74%). Red solid.
MP = 99 - 101 °C.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.27 – 7.24 (m, 1H), 7.19 (ddd, J = 8.0, 7.4, 1.6 Hz, 1H), 6.72 (td, J = 7.4, 1.1 Hz, 1H), 6.71 – 6.65 (m, 1H), 4.89 (t, J = 2.5 Hz, 1H), 4.63 (s, 1H), 4.55 (d, J = 10.6 Hz, 1H), 4.29 (dt, J = 2.5, 1.3 Hz, 1H), 4.25 (m, 6H), 4.20 (td, J = 2.5, 1.3 Hz, 1H), 4.17 (tdd, J = 2.5, 1.3, 0.6 Hz, 1H), 3.57 (s, 3H), 3.36 (d, J = 2.7 Hz, 1H), 2.63 (dd, J = 10.6, 2.7 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 173.9, 143.4, 130.0, 129.9, 120.6, 117.3, 114.1, 89.9, 68.9, 68.5 (two peaks), 68.2, 67.2, 65.1, 52.0, 48.0.
IR (ATR, cm^{-1}) 3518, 3409, 1739, 1616, 1482, 1364, 1310, 1164, 1103, 1032, 940, 820, 753.
HRMS (DART, M+H) Calc'd 392.0944 for $C_{21}H_{22}NO_3Fe$, found 392.0950.
HPLC IB, 15% IPA/Hex, 1 mL/min

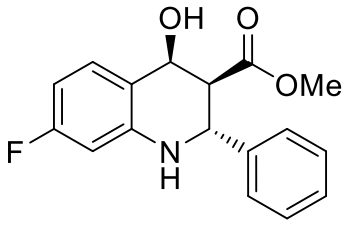




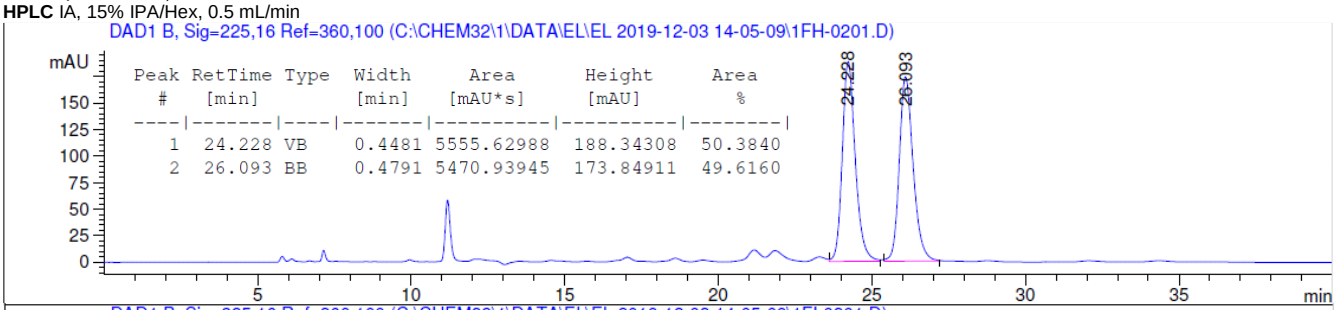
methyl (2*R*,3*S*,4*S*)-7-bromo-4-hydroxy-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3j) – 52.0 mg, 0.144 mmol (72%). Off-white foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.43 – 7.28 (m, 5H), 7.11 (d, J = 8.1 Hz, 1H), 6.83 (dd, J = 8.1, 1.9 Hz, 1H), 6.72 (d, J = 1.9 Hz, 1H), 4.87 (d, J = 2.1 Hz, 1H), 4.84 (dd, J = 10.4, 1.1 Hz, 1H), 4.25 (s, 1H), 3.50 (s, 3H), 3.31 (s, 1H), 2.97 (dd, J = 10.4, 2.9 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 173.0, 144.5, 140.7, 131.2, 128.8, 128.5, 127.7, 123.4, 120.4, 119.7, 116.7, 66.4, 53.3, 52.0, 50.6.
IR (ATR, cm^{-1}) 3453, 3347, 3028, 2953, 1704, 1605, 1490, 1436, 1396, 1273, 1257, 1159, 1019, 929, 742.
HRMS (ESI, M+Na) Calc'd 384.0206 for $C_{17}H_{16}BrNNaO_3$, found 384.0210.
HPLC IA, 15% IPA/Hex, 0.5 mL/min

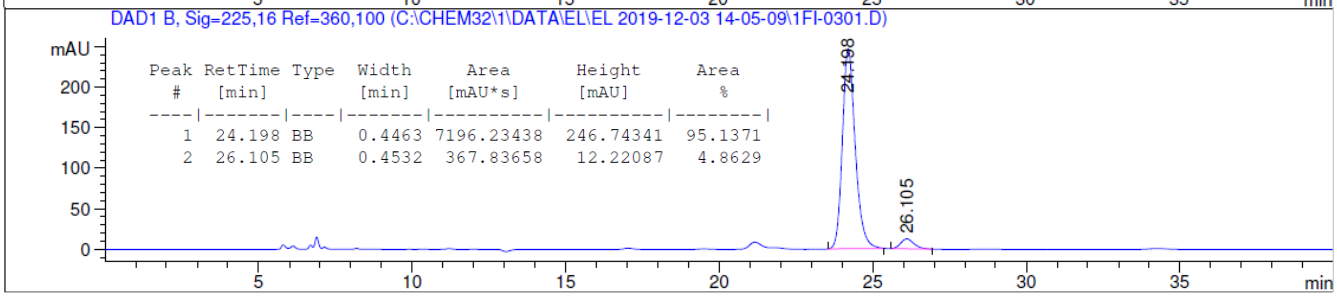


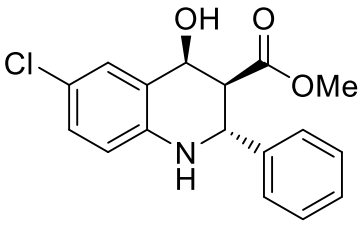




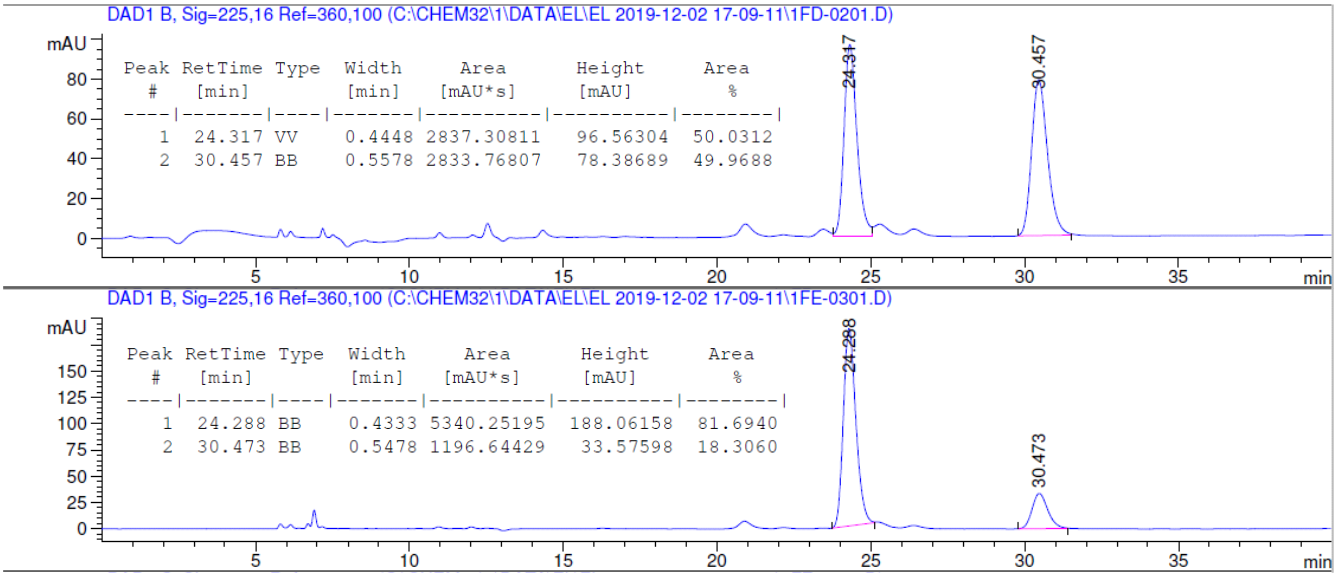
methyl (2*R*,3*S*,4*S*)-7-fluoro-4-hydroxy-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3k) – 42.1 mg, 0.140 mmol (70%). Yellowish oil.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.44 – 7.39 (m, 2H), 7.39 – 7.29 (m, 3H), 7.19 (dd, J = 8.5, 6.3 Hz, 1H), 6.41 (td, J = 8.5, 2.4 Hz, 1H), 6.24 (dd, J = 10.7, 2.5 Hz, 1H), 4.93 – 4.88 (m, 1H), 4.81 (d, J = 10.8 Hz, 1H), 4.31 (s, 1H), 3.49 (s, 3H), 3.31 (s, 1H), 2.97 (dd, J = 10.7, 2.8 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 173.0, 163.9 (d, J = 244.5 Hz), 144.8 (d, J = 11.4 Hz), 140.8, 131.4 (d, J = 10.4 Hz), 128.7, 128.5, 127.8, 116.7 (d, J = 2.3 Hz), 104.4 (dd, J = 22.1, 1.1 Hz), 100.4 (d, J = 25.1 Hz), 66.4, 53.1, 51.9, 50.8.
^{19}F NMR (470 MHz, Chloroform-d) δ -112.46 (td, J = 10.0, 6.4 Hz).
IR (ATR, cm^{-1}) 3419, 3333, 3042, 1701, 1620, 1598, 1499, 1495, 1279, 1231, 1163, 1022, 970, 846, 757, 698.
HRMS (DART, M-H) Calc'd 300.1031 for $C_{17}H_{15}NO_3F$, found 300.1029.
HPLC IA, 15% IPA/Hex, 0.5 mL/min

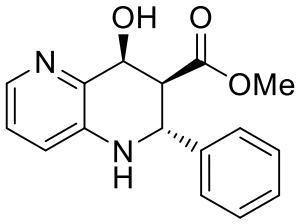




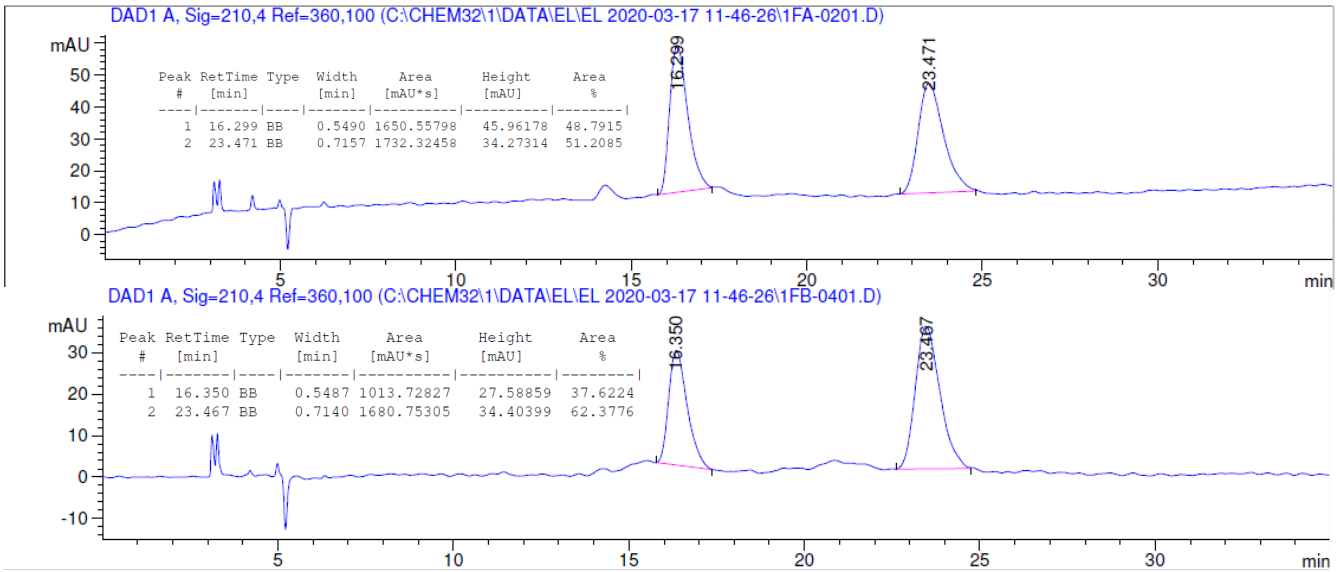


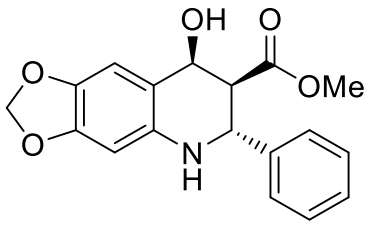
methyl (2*R*,3*S*,4*S*)-6-chloro-4-hydroxy-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3l) – 54.3 mg, 0.171 mmol (85%). Off-white foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.43 – 7.38 (m, 2H), 7.37 – 7.31 (m, 3H), 7.25 (d, J = 2.4 Hz, 1H), 7.08 (dd, J = 8.6, 2.4 Hz, 1H), 6.50 (d, J = 8.6 Hz, 1H), 4.91 – 4.75 (m, 2H), 4.23 (s, 1H), 3.50 (s, 3H), 3.39 (d, J = 4.2 Hz, 1H), 2.99 (dd, J = 10.2, 3.0 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 173.0, 141.9, 140.9, 129.6, 129.3, 128.8, 128.5, 127.6, 122.1, 122.0, 115.4, 66.3, 53.6, 52.0, 50.5.
IR (ATR, cm^{-1}) 3412, 3347, 2956, 1703, 1608, 1491, 1440, 1392, 1358, 1227, 1256, 1289, 1026, 943, 817, 752, 697.
HRMS (DART, M+H) Calc'd 318.0892 for $C_{17}H_{17}NO_3Cl$, found 318.0896.
HPLC IA, 15% IPA/Hex, 0.5 mL/min



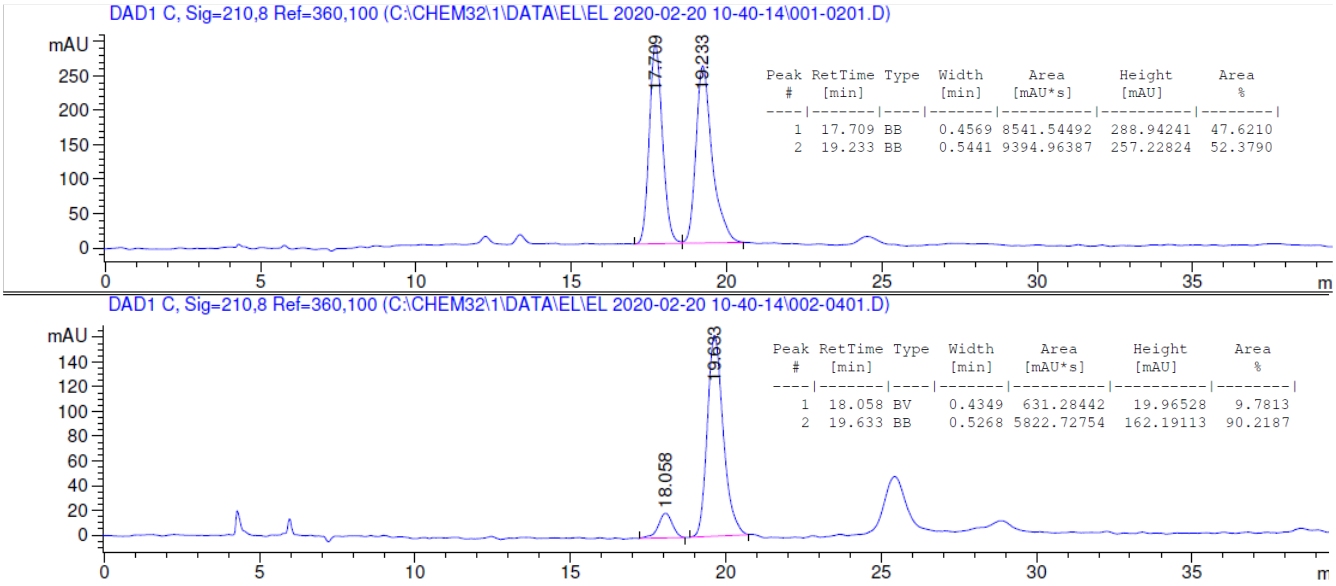


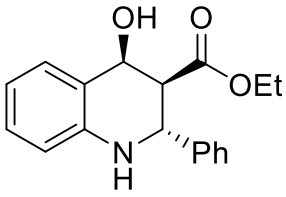
methyl (2*R*,3*S*,4*S*)-4-hydroxy-2-phenyl-1,2,3,4-tetrahydro-1,5-naphthyridine-3-carboxylate (3m) – 35.3 mg, 0.124 mmol (64%). Yellowish foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.94 (dd, J = 4.7, 1.4 Hz, 1H), 7.37 – 7.29 (m, 5H), 6.97 (ddt, J = 8.1, 4.8, 0.7 Hz, 1H), 6.83 (dd, J = 8.1, 1.5 Hz, 1H), 4.65 – 4.55 (m, 1H), 4.13 (s, 1H), 3.49 (s, 3H), 3.16 – 3.02 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-d) δ 173.5, 141.2, 140.6, 140.0, 138.6, 128.9, 128.6, 127.3, 122.6, 120.5, 57.9, 52.1, 45.9, 32.8.
IR (ATR, cm^{-1}) 2953, 1729, 1581, 1454, 1435, 1372, 1270, 1194, 1160, 1124, 1031, 914, 792, 728, 700.
HRMS (DART, M-H) Calc'd 283.1077 for $C_{16}H_{15}N_zO_3$, found 283.1098.
HPLC IC, 25% IPA/Hex, 1 mL/min





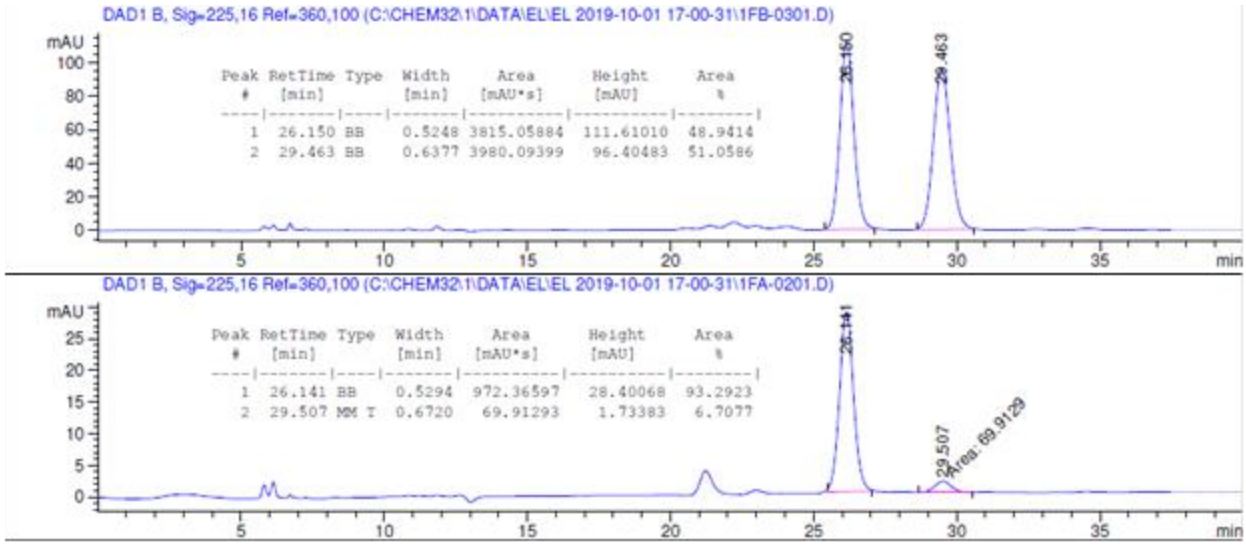
methyl (6*R*,7*S*,8*S*)-8-hydroxy-6-phenyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-*g*]quinoline-7-carboxylate (3n) – 28.3 mg, 0.086 mmol (43%). Yellow foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.50 – 7.38 (m, 2H), 7.38 – 7.30 (m, 3H), 6.75 (s, 1H), 6.13 (s, 1H), 5.85 (dd, J = 11.0, 1.4 Hz, 2H), 4.85 (t, J = 3.2 Hz, 1H), 4.77 (d, J = 10.8 Hz, 1H), 3.96 (m, 1H), 3.48 (s, 3H), 3.19 (d, J = 3.9 Hz, 1H), 3.00 (dd, J = 10.8, 3.0 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 173.2, 148.9, 141.2, 140.1, 138.9, 128.7, 128.4, 127.9, 112.8, 109.2, 100.8, 96.1, 66.9, 53.6, 51.9, 51.3.
IR (ATR, cm^{-1}) 3443, 3350, 2867, 1703, 1636, 1598, 1478, 1454, 1351, 1272, 1220, 1201, 1159, 1025, 930, 843, 756.
HRMS (DART, M+) Calc'd 327.1101 for $C_{18}H_{17}NO_5$, found 327.1103.
HPLC IC, 25% IPA/Hex, 0.75 mL/min

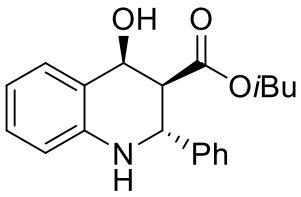




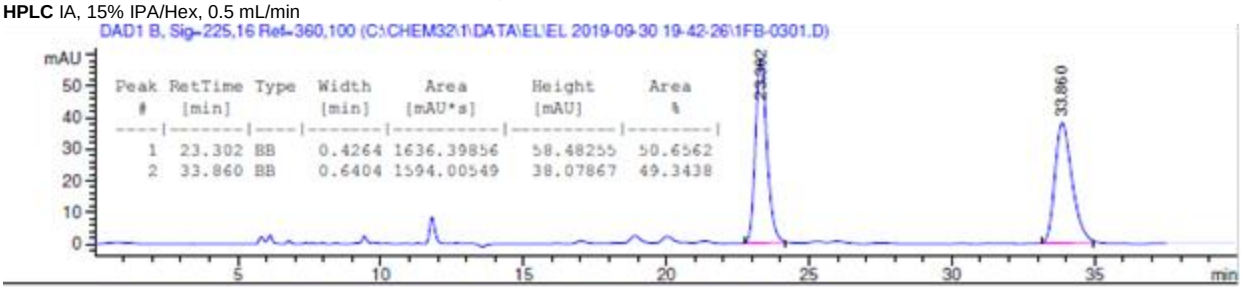
ethyl (2*R*,3*S*,4*S*)-4-hydroxy-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3o) – 49.7 mg, 0.167 mmol (84%). Off-white foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.48 – 7.42 (m, 2H), 7.39 – 7.30 (m, 3H), 7.28 (dd, J = 7.6, 1.6 Hz, 1H), 7.15 (ddd, J = 8.1, 7.4, 1.6 Hz, 1H), 6.74 (td, J = 7.4, 1.1 Hz, 1H), 6.57 (ddd, J = 8.1, 1.1, 0.5 Hz, 1H), 4.96 (t, J = 2.3 Hz, 1H), 4.85 (d, J = 10.8 Hz, 1H), 4.19 (s, 1H), 3.95 (qd, J = 7.1, 2.6 Hz, 2H), 3.46 (d, J = 3.1 Hz, 1H), 2.99 (dd, J = 10.8, 2.8 Hz, 1H), 0.96 (t, J = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 173.0, 143.5, 141.2, 130.1, 129.8, 128.6, 128.3, 128.0, 120.8, 117.6, 114.3, 66.9, 60.8, 53.5, 50.9, 13.8.
IR (ATR, cm^{-1}) 3344, 2927, 1701, 1610, 1588, 1493, 1297, 1270, 1256, 1230, 1021, 902, 760, 745, 697.
HRMS (DART, M+H) Calc'd 298.1438 for $C_{18}H_{19}NO_3$, found 298.1443.

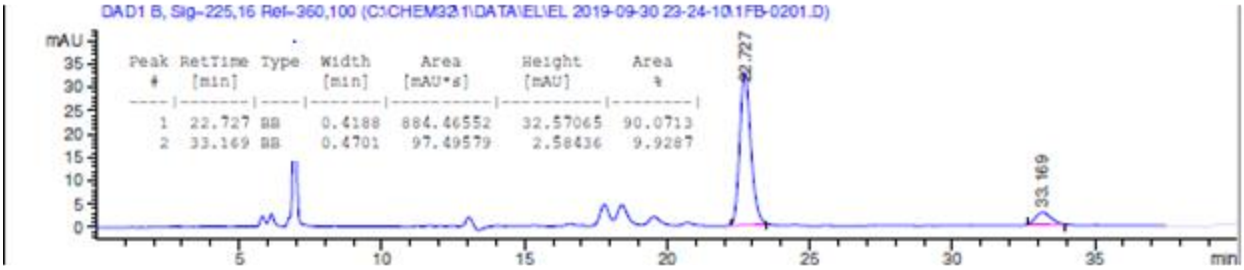
HPLC IA, 15% IPA/Hex, 0.5 mL/min

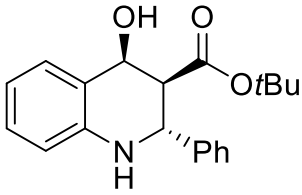




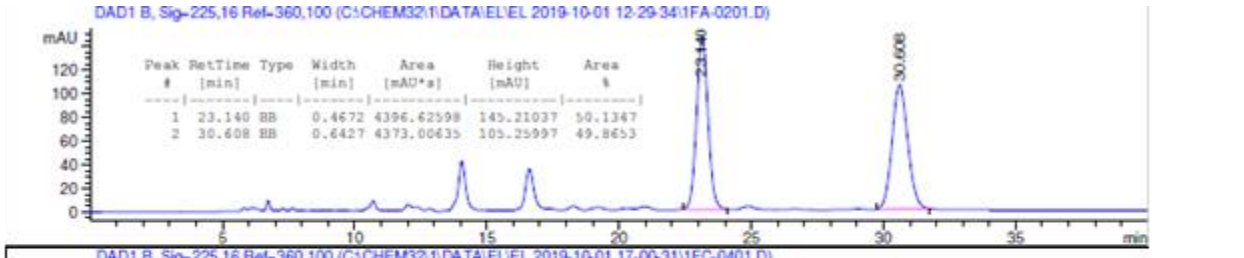
isobutyl (2R,3S,4S)-4-hydroxy-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3p) – 36.3 mg, 0.108 mmol (54%). Off-white oil.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.52 – 7.42 (m, 2H), 7.43 – 7.23 (m, 4H), 7.14 (ddd, J = 8.1, 7.3, 1.6 Hz, 1H), 6.73 (td, J = 7.4, 1.1 Hz, 1H), 6.57 (dd, J = 8.1, 1.1 Hz, 1H), 4.96 (s, 1H), 4.86 (d, J = 10.8 Hz, 1H), 4.19 (s, 1H), 3.84 – 3.60 (m, 2H), 3.48 – 3.38 (m, 1H), 3.03 (dd, J = 10.8, 2.8 Hz, 1H), 1.66 (dp, J = 13.4, 6.8 Hz, 1H), 0.72 (dd, J = 6.8, 1.5 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-d) δ 173.1, 143.4, 141.2, 130.0, 129.8, 128.7, 128.4, 127.9, 120.8, 117.5, 114.2, 71.0, 67.0, 53.4, 50.9, 27.5, 18.9 (two peaks).
IR (ATR, cm^{-1}) 3470, 3340, 2966, 1701, 1610, 1591, 1492, 1303, 1254, 1190, 1160, 1021, 919, 759.
HRMS (DART, M+H) Calc'd 326.1751 for $C_{20}H_{24}NO_3$, found 326.1749.
HPLC IA, 15% IPA/Hex, 0.5 mL/min

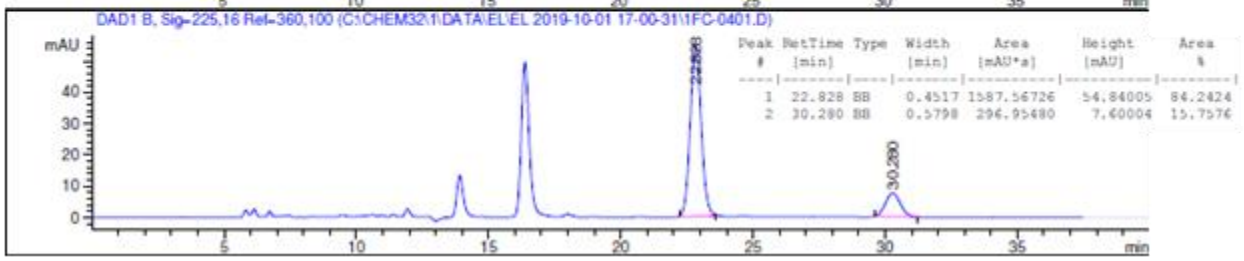


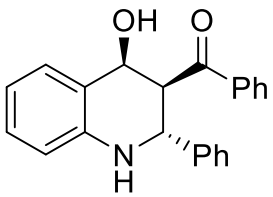




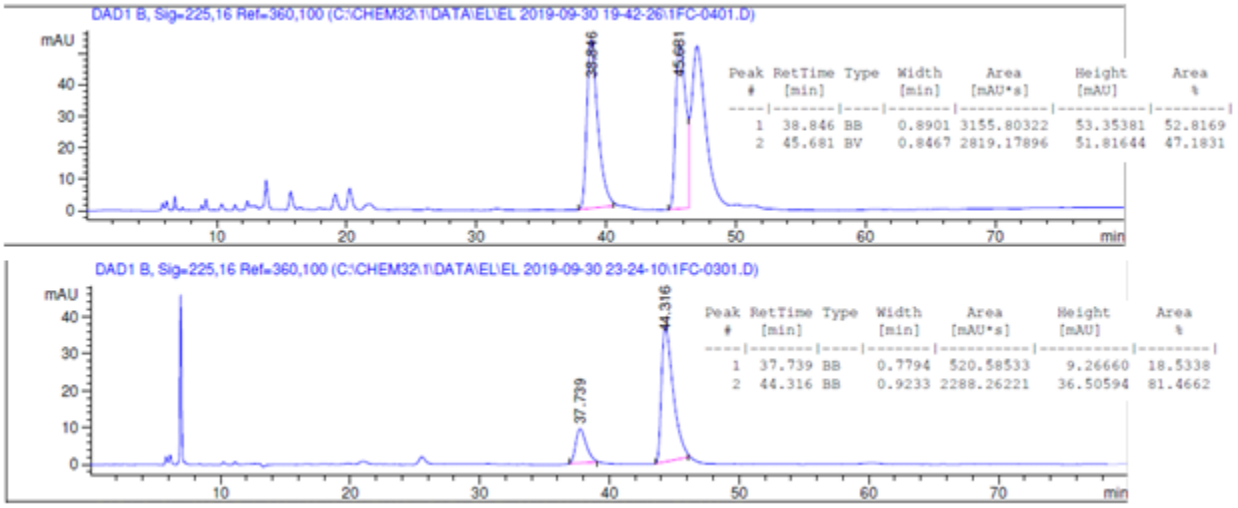
***tert*-butyl (2*R*,3*S*,4*S*)-4-hydroxy-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3q) –** 51.2 mg, 0.157 mmol (79%). Off-white oil.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.51 – 7.26 (both diastereomers overlapping, m, 9H), 7.13 (major, ddd, J = 8.1, 7.3, 1.6 Hz, 1H), 7.11 (minor, m, 0.45H), 6.82 (minor, td, J = 7.4, 1.2 Hz, 0.45H), 6.73 (major, td, J = 7.4, 1.1 Hz, 1H), 6.62 (minor, dd, J = 8.1, 1.2 Hz, 0.45H), 6.56 (major, dd, J = 8.0, 1.1 Hz, 1H), 5.17 (minor, dd, J = 9.6, 5.4 Hz, 0.45H), 4.95 (major, t, J = 2.2 Hz, 1H), 4.86 (minor, d, J = 3.6 Hz, 0.45H), 4.82 (major, d, J = 10.7 Hz, 1H), 4.16 (major, s, 1H), 4.13 (minor, s, 0.45H), 3.83 (major, d, J = 2.6 Hz, 1H), 3.31 (minor, dd, J = 5.4, 3.6 Hz, 0.45H), 2.95 (minor, d, J = 9.6 Hz, 0.45 H), 2.92 (major, dd, J = 10.7, 2.6 Hz, 1H), 1.23 (minor, s, 4.1H), 1.17 (major s, 9H).
^{13}C NMR (126 MHz, Chloroform-d) δ 172.9, 169.9, 143.9, 143.5, 141.0, 140.8, 130.1, 129.6, 128.5 (two peaks), 128.4, 128.3, 127.7, 127.5, 127.0, 123.9, 121.0, 118.7, 117.5, 114.3, 114.2, 81.9, 81.6, 68.2, 66.9, 57.2, 53.8, 51.7, 51.1, 27.9, 27.7.
IR (ATR, cm^{-1}) 3378, 2983, 2932, 1722, 1684, 1612, 1491, 1454, 1363, 1261, 1150, 1086, 1030, 897, 847.
HRMS (DART, M+H) Calc'd 326.1751 for $C_{20}H_{24}NO_3$, found 326.1756.
HPLC IA, 15% IPA/Hex, 0.5 mL/min

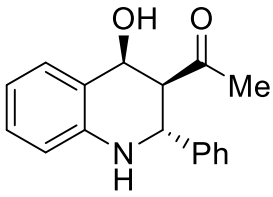




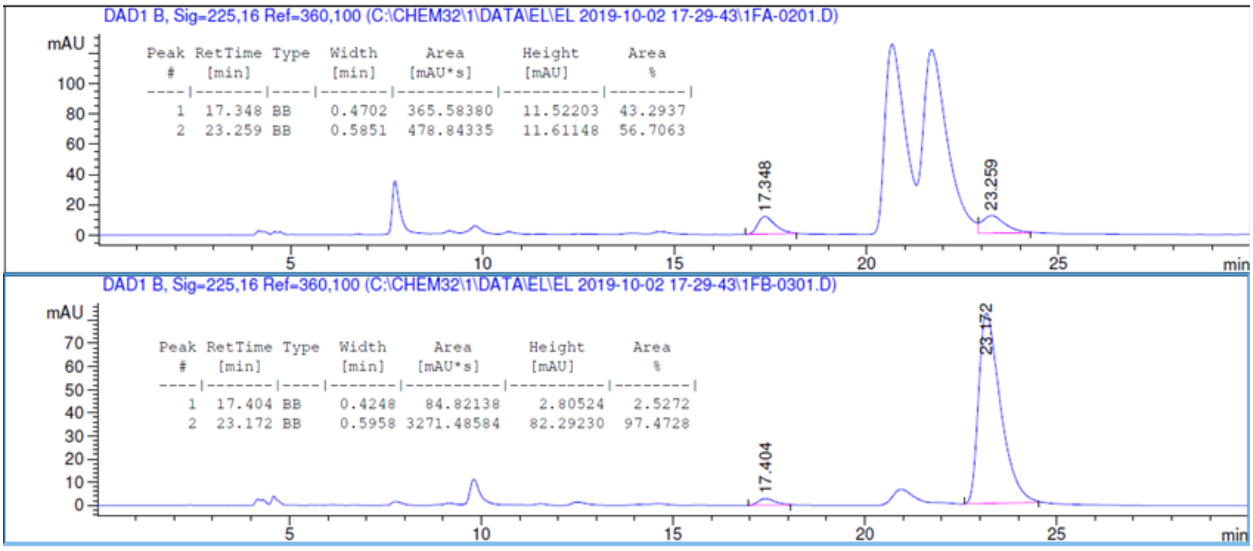


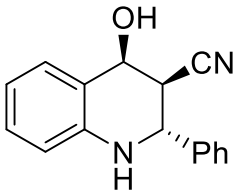
((2*R*,3*S*,4*S*)-4-hydroxy-2-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)(phenyl)methanone (3r) – 51.6 mg, 0.157 mmol (78%). Off-white foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.71 (dd, J = 8.4, 1.4 Hz, 2H), 7.51 – 7.42 (m, 2H), 7.34 (dd, J = 8.3, 7.3 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.19 – 7.15 (m, 2H), 6.74 (td, J = 7.4, 1.1 Hz, 1H), 6.63 (dd, J = 8.1, 1.1 Hz, 1H), 5.10 (d, J = 11.0 Hz, 1H), 4.98 (m, 1H), 4.25 (s, 1H), 4.09 (dd, J = 11.0, 2.5 Hz, 1H), 3.40 (d, J = 2.5 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 202.2, 143.6, 141.1, 136.8, 133.5, 130.2, 130.0, 128.7, 128.3 (two peaks), 128.2, 128.0, 120.9, 117.4, 114.4, 67.6, 53.7, 51.5.
IR (ATR, cm^{-1}) 3388, 3069, 3028, 1674, 1610, 1595, 1488, 1449, 1260, 1219, 1026, 1103, 905, 750, 698, 689.
HRMS (DART, M-H) Calc'd 328.1332 for $C_{22}H_{18}NO_2$, found 328.1339.
HPLC IA, 15% IPA/Hex, 0.5 mL/min





1-((2*R*,3*S*,4*S*)-4-hydroxy-2-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)ethan-1-one (3s) – 39.8 mg, 0.149 mmol (74%). White foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.49 – 7.43 (m, 2H), 7.40 – 7.31 (m, 3H), 7.27 – 7.22 (m, 1H), 7.14 (ddd, J = 8.1, 7.4, 1.6 Hz, 1H), 6.72 (td, J = 7.4, 1.1 Hz, 1H), 6.57 (dd, J = 8.1, 1.1 Hz, 1H), 4.94 (t, J = 2.6 Hz, 1H), 4.84 (d, J = 11.0 Hz, 1H), 4.18 (s, 1H), 3.56 (d, J = 2.6 Hz, 1H), 3.14 (dd, J = 11.0, 2.6 Hz, 1H), 1.83 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 211.7, 143.4, 141.2, 130.1, 129.9, 128.9, 128. 6, 127.9, 120.8, 117.5, 114.3, 67.0, 56.9, 53.4, 31.8.
IR (ATR, cm^{-1}) 3364, 2929, 1703, 1609, 1488, 1454, 1355, 1190, 1161, 1115, 1032, 1000, 912, 750, 700.
HRMS (DART, M+H) Calc'd 268.1332 for $C_{17}H_{18}NO_2$, found 268.1325.
HPLC IB, 15% IPA/Hex, 0.75 mL/min





(2*R*,3*R*,4*S*)-4-hydroxy-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carbonitrile (3t) – 28.2 mg, 0.113 mmol (56%). Off-white foam.

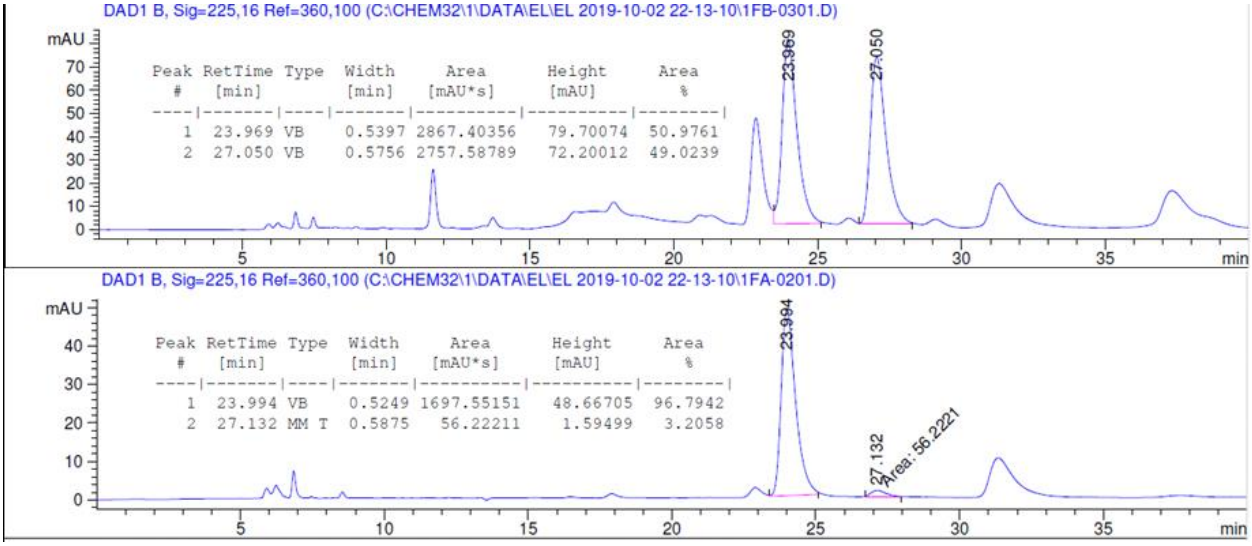
^{1}H NMR (mixture of isomers) (500 MHz, Chloroform-d) δ 7.67 – 7.52 (m, 2H), 7.52 – 7.37 (m, 3H), 7.30 (dd, J = 7.7, 1.5 Hz, 1H), 7.24 – 7.10 (m, 1H), 6.89 – 6.77 (m, 1H), 6.74 – 6.52 (m, 1H), 5.44 – 4.84 (m, 1H), 4.76 – 4.63 (m, 1H), 4.22 – 4.05 (m, 1H), 3.53 – 3.10 (m, 1H), 2.34 (s, 1H).

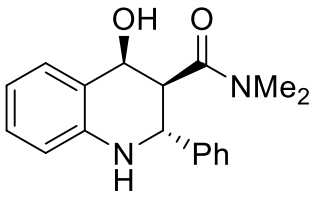
^{13}C NMR (major isomer) (126 MHz, Chloroform-d) δ 143.7, 138.8, 130.8, 130.5, 129.3, 129.2 (two peaks), 127.3, 126.9, 119.0, 115.7, 67.6, 51.8, 40.6.

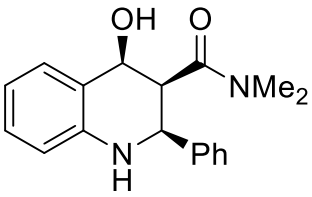
IR (ATR, cm^{-1}) 3360, 2925, 2250, 1611, 1591, 1485, 1455, 1324, 1253, 1156, 1116, 1030, 992.

HRMS (DART, M-H) Calc'd 249.1022 for $C_{16}H_{13}N_2O$, found 249.1026.

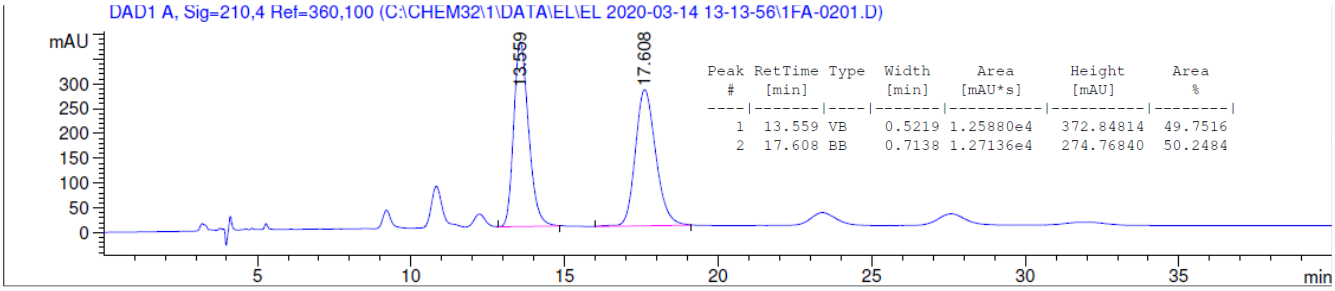
HPLC IA, 15% IPA/Hex, 0.5 mL/min

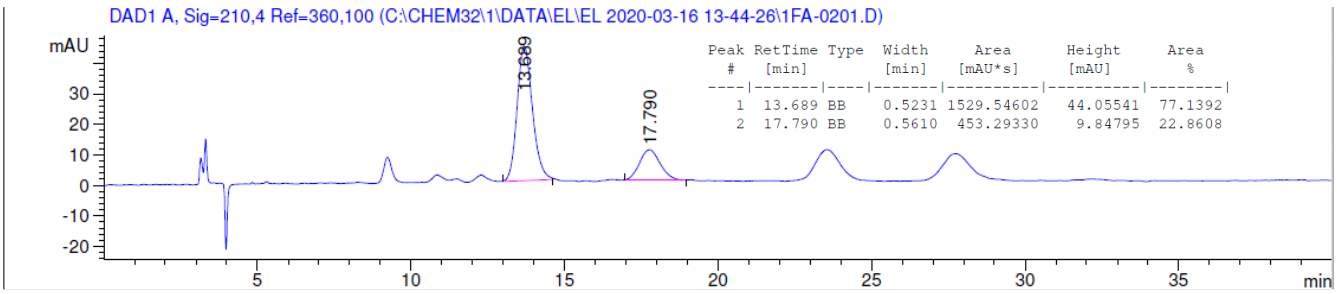


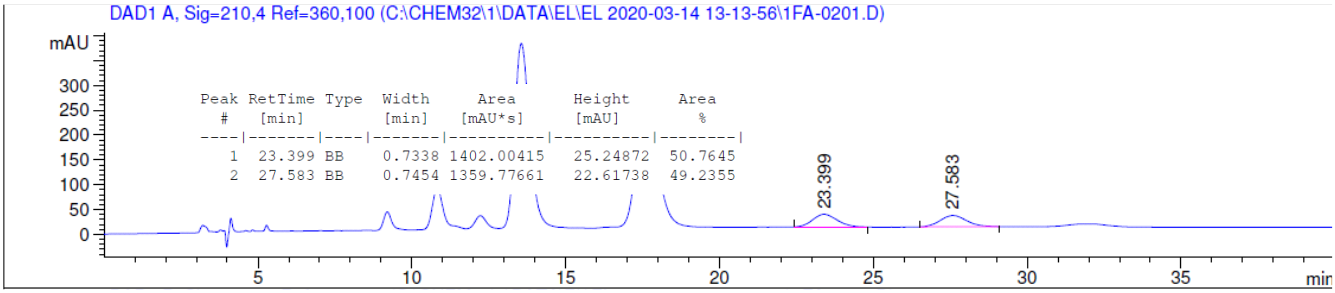


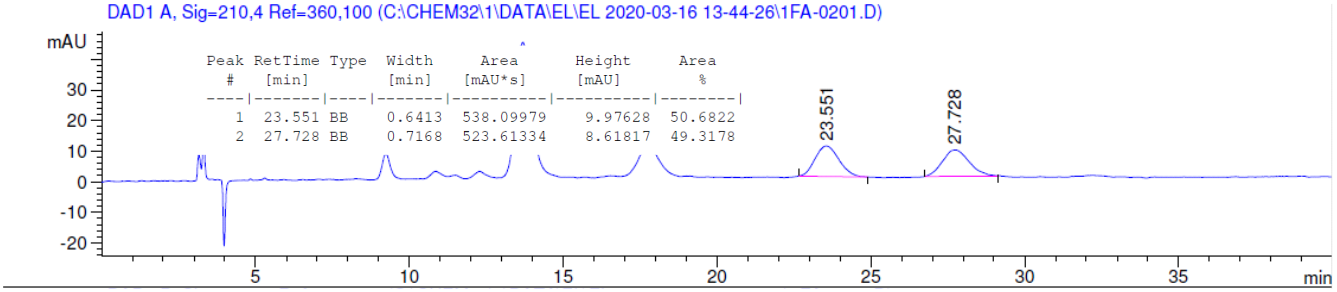


(2R,3S,4S)-4-hydroxy-N,N-dimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxamide (minor, 3u) & (2S,3S,4S)-4-hydroxy-N,N-dimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxamide (major, 3u') – 28.2 mg, 0.113 mmol (56%, combined yield) Yield was determined through the use of an internal standard in the ^{1}H NMR analysis of the crude mixture. Off-white foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.56 – 7.28 (both diastereomers overlapping, m, 11H), 7.15 (minor, td, J = 7.7, 1.6 Hz, 0.7H), 7.07 (major, td, J = 7.7, 1.6 Hz, 1H), 6.82 – 6.75 (major, m, 1H), 6.74 – 6.70 (minor, m, 0.7H), 6.64 (minor, d, J = 8.1 Hz, 0.7H), 6.58 (d, J = 8.0 Hz, 1H), 5.99 (minor, s, 0.8H), 5.14 (major, d, J = 5.7 Hz, 1H), 5.02 (minor, d, J = 11.0 Hz, 0.8H), 4.83 (major, d, J = 3.1 Hz, 2H), 4.26 (major, s, 1H), 4.18 – 3.99 (minor, m, 0.8H), 3.62 (major, dd, J = 5.6, 3.8 Hz, 1H), 3.33 (minor, s, 0.8H), 3.16 (minor, dd, J = 11.0, 2.1 Hz, 0.8H), 2.81 (major, s, 3H), 2.70 (minor, s, 2H), 2.38 (minor, s, 2H), 2.28 (major, s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 174.1, 170.0, 143.8, 143.5, 141.1, 140.8, 130.2, 129.7, 128.6, 128.6, 128.5, 128.4, 128.2, 127.5, 127.4, 127.3, 126.6, 124.9, 121.1, 120.0, 118.7, 117.4, 117.1, 114.5, 114.1, 68.5, 67.3, 58.0, 54.1, 46.4, 45.7, 37.1, 36.8, 35.4, 35.3.
IR (ATR, cm^{-1}) 3294, 2933, 1611, 1489, 1454, 1418, 1399, 1256, 1148, 1004, 914, 748, 730, 724, 698
HRMS (DART, M+H) Calc'd 249.1022 for $C_{16}H_{13}N_2O$, found 249.1026.
HPLC IC, 45% IPA/Hex, 1.0 mL/min

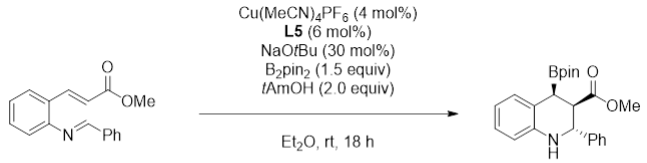








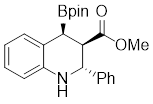
6 Reaction Scale-up and Test Oxidation



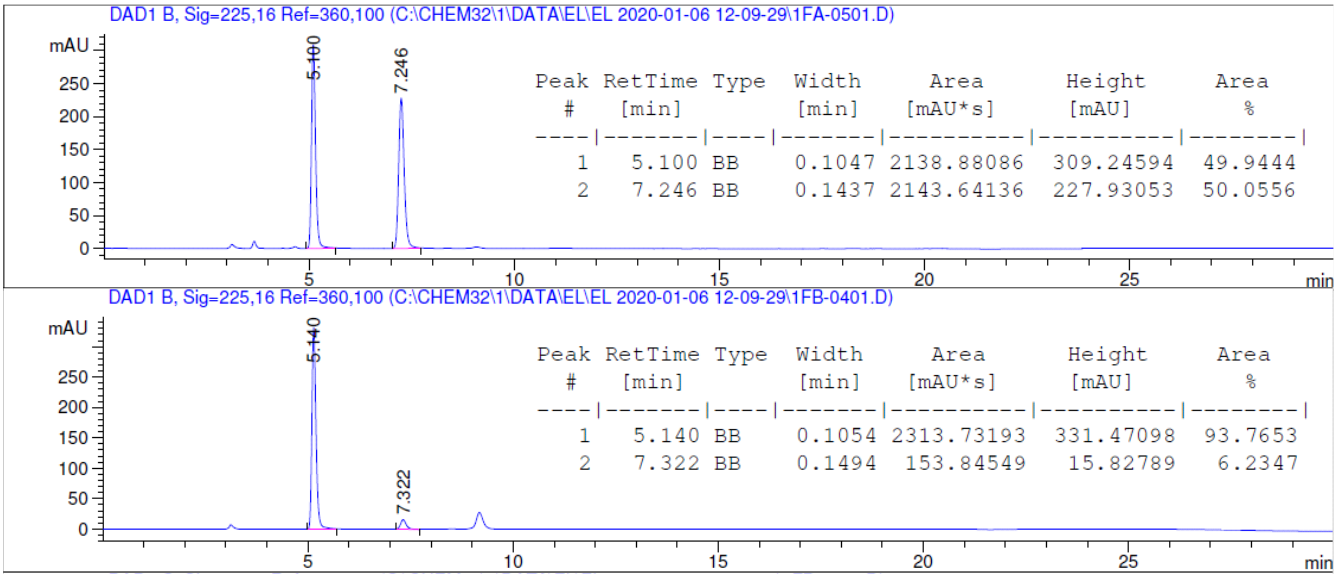
1a
3 mmol
0.795 gram

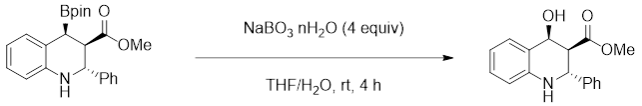
2a
0.734 gram (62%) isolated
>20:1 dr, 93.5:6.5 er

A 150 mL round bottom flask was fitted with a Teflon stir bar and was flame-dried and kept under argon throughout. Into this flask, $Cu(MeCN)_4PF_6$ (44.73 mg, 0.12 mmol, 4 mol%), **L5** (112.08 mg, 0.18 mmol, 6 mol%) and NaO*t*Bu (86.49 mg, 0.9 mmol, 30 mol%) were charged and Et_2O (15 mL) was added. The catalyst mixture was stirred for 30 minutes. A solution of B_2pin_2 (1142.73 mg, 4.5 mmol, 1.5 equiv) in Et_2O (15 mL) were added and the mixture was stirred for a further 15 minutes. A separate flame-dried and argon-cooled 20 mL scintillation vial was loaded with substrate **1a** (795.93 mg, 3.0 mmol) and *t*AmOH (0.46 mL, 6 mmol, 2.0 equiv). This was then dissolved in 15 mL of Et_2O and added to the catalyst mixture. The scintillation vial was rinsed with a further 15 mL of Et_2O and this rinse was also added to the reaction (for a total reaction solvent volume of 60 mL). The reaction was stirred vigorously for 18 hours. Upon completion, the reaction mixture was filtered through a plug of Celite and concentrated. The borylated product was then purified via column chromatography utilizing basic alumina (a gradient of 5:95 to 10:90 EtOAc:pentanes v:v was used). **NOTE 1**: **Due to the instability of the relted Bpin-containing compounds, purification by column chromatography was performed as quickly as possible with a high air flow to minimize decomposition.**



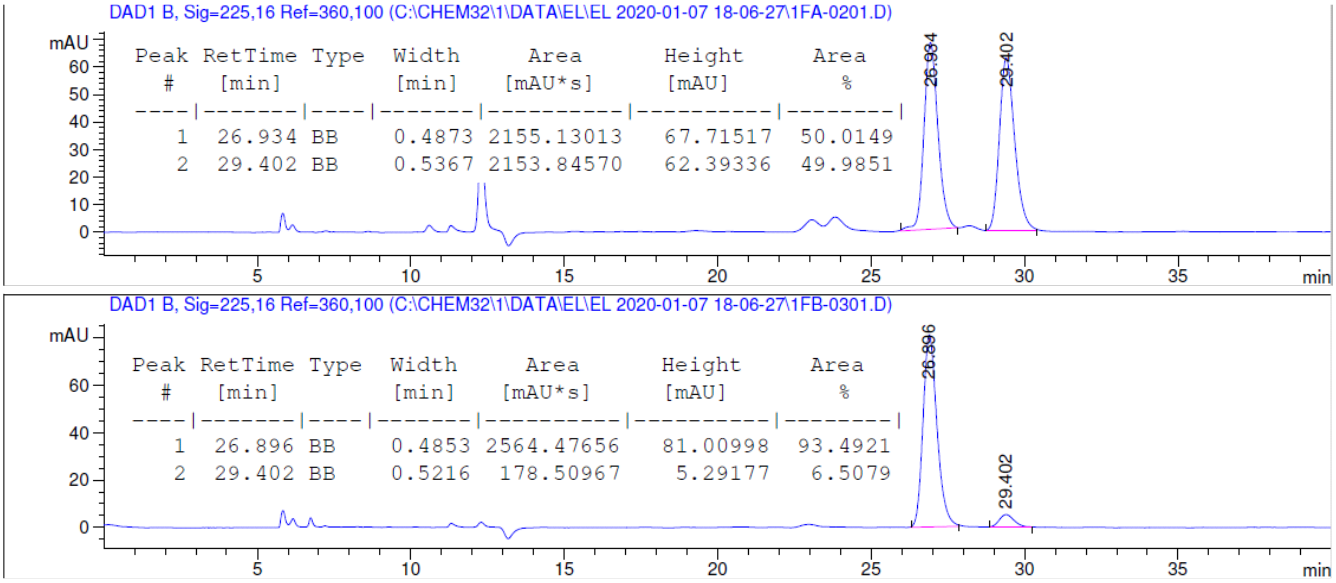
methyl (2*R*,3*R*,4)-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (2a) – 0.734 g, 1.87 mmol (62 %). Off white paste.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.40 – 7.36 (m, 2H), 7.36 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 7.10 (dt, J = 7.4, 1.2 Hz, 1H), 6.98 (tdd, J = 7.2, 1.5, 0.5 Hz, 1H), 6.64 (td, J = 7.4, 1.2 Hz, 1H), 6.54 (dd, J = 7.9, 1.2 Hz, 1H), 4.90 (d, J = 9.0 Hz, 1H), 4.07 (s, 1H), 3.40 (s, 3H), 2.99 (dd, J = 9.0, 5.2 Hz, 1H), 2.79 (d, J = 5.2 Hz, 1H), 1.27 (s, 6H), 1.22 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-d) δ 174.4, 143.3, 142.4, 128.7, 128.6, 128.0, 127.5, 126.5, 120.6, 117.3, 114.0, 83.5, 56.6, 51.7, 48.2, 24.9, 24.6.
IR (ATR, cm^{-1}). 3347, 2971, 1730, 1605, 1494, 1442, 1356, 1322, 1297, 1253, 1220, 1171, 1141, 1107, 1025, 840, 742, 701.
HRMS (DART, M+H) Calc'd 394.2184 for $C_{23}H_{29}BNO_4$, found 394.2189.
HPLC IA, 5% IPA/Hex, 1 mL/min



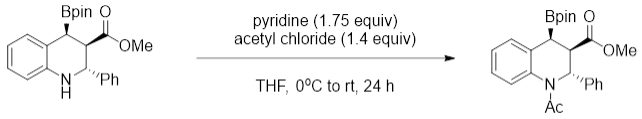


2a **3a**

2a (39.3 mg, 0.1 mmol) and sodium perborate (61.55 mg, 0.4 mmol, 4 equiv) were loaded in a 1 dram vial. THF (4 mL) and distilled water (2 mL) were subsequently added and the mixture was stirred at room temperature for 4 hours. Upon completion, the solution was poured into water, and extracted thrice with EtOAc. The combined organic layers were combined and washed five times with water to remove pinacol and once with brine, then dried over $MgSO_4$ and concentrated *in vacuo*. The product **3a** was purified via silica gel column chromatography using a gradient of 10:90 to 20:80 EtOAc:pentanes to isolate the product in quantitative yield (28.2 mg, 0.1 mmol). The characterization data was entirely consistent to that reported in Section 5 of this document

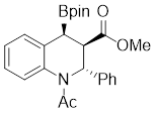


7 Further Product Elaborations

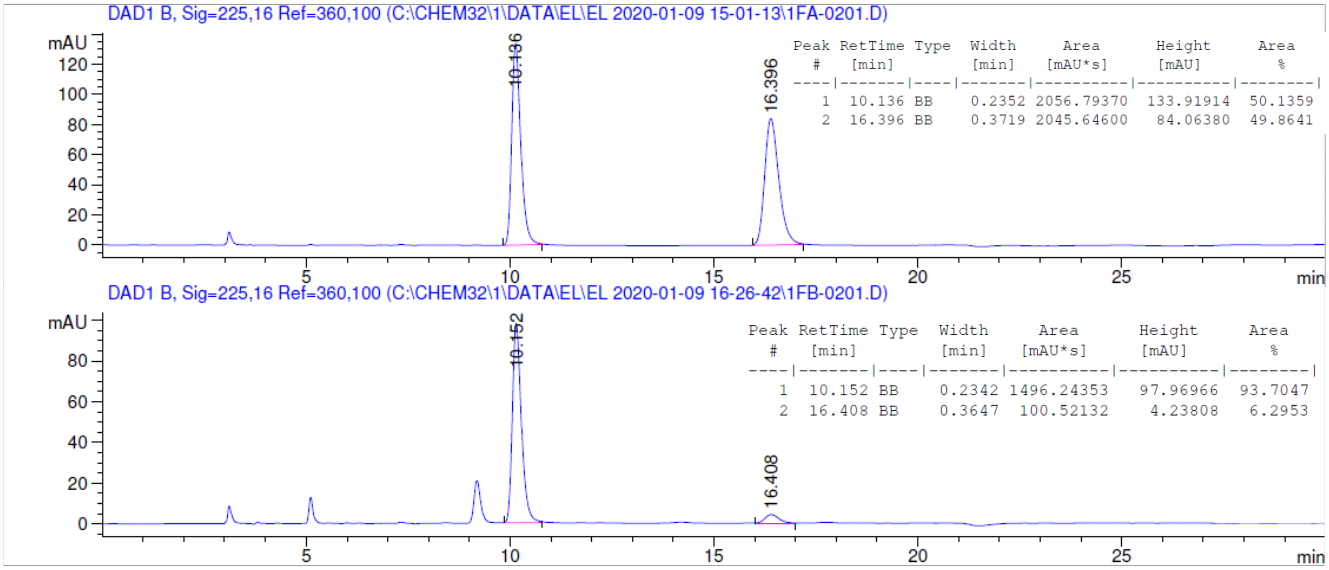


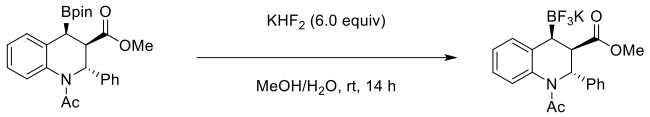
2a **4**

2a (542 mg, 1.38 mmol) was dissolved in THF (20 mL) and cooled to 0 ºC. Pyridine (0.195 mL, 2.4 mmol, 1.75 equiv) were added, and then acetyl chloride (0.138 mL, 1.95 mmol, 1.4 equiv) was added dropwise. The reaction was left to slowly warm to room temperature. Upon reaction completion, it was quenched with a saturated aqueous solution of $NaHCO_3$ and extracted thrice with EtOAc. The combined organic layers were washed thrice with $NaHCO_3$, then thrice with NH_4Cl, then once with brine. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo* to obtain **4** of sufficient purity.



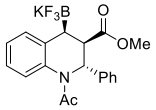
methyl (2*R*,3*R*,4*S*)-1-acetyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydroquinoline-3-carboxylate (4) – 584.7 mg, 1.34 mmol (97%). White paste.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.38 – 6.90 (m, 8H), 6.14 (s, 1H), 3.69 (s, 3H), 3.08 (dd, J = 9.3, 5.0 Hz, 1H), 2.91 (d, J = 5.0 Hz, 1H), 2.09 (s, 3H), 1.19 (s, 6H), 1.18 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-d) δ 172.8, 167.0, 143.0, 128.4, 127.7, 127.4, 127.2, 126.6, 126.2, 84.1, 57.9, 53.8, 52.2, 24.8, 23.3.
IR (ATR, cm-1) 2994, 1733, 1657, 1495, 1269, 1362, 1324, 1247, 1146, 1053, 969, 844, 770, 700.
HRMS (DART, M+H) Calc'd 436.2290 for $C_{25}H_{31}BNO_5$, found 436.2293
HPLC IA, 5% IPA/Hex, 1 mL/min





4 **5**

To a solution of **4** (87.1 mg, 0.2 mmol) in MeOH (1 mL) was added a solution of KHF_2 (91.32 mg, 1.2 mmol, 6 equiv) in H_2O. The reaction was left to stir for 14 hours. Upon reaction completion, it was concentrated *in vacuo*. The residue was then mobilized in acetone and passed through a glass wool filter in order to remove insoluble salts. The acetone solution was then concentrated to roughly 0.5 mL and the product salt was precipitated via the addition of a 1:1 Et_2O:pentane solution. The precipitated salt was then isolated via filtration, washing with pentane.



((2R,3R,4S)-1-acetyl-3-(methoxycarbonyl)-2-phenyl-1,2,3,4-tetrahydroquinolin-4-yl)trifluoroborate, potassium salt (5) – 73.1 mg, 0.176 mmol (88%). White powder.

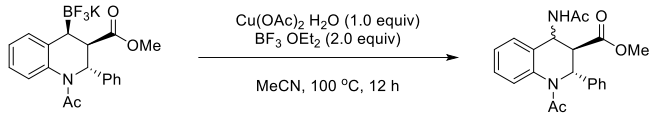
MP = 144-147 ºC.

^{1}H NMR (500 MHz, Acetonitrile-d3) δ 7.27 – 7.08 (m, 7H), 6.13 (s, 1H), 3.64 (s, 3H), 2.83 (dd, J = 9.9, 5.3 Hz, 1H), 2.31 (m, 4H).

^{13}C NMR (126 MHz, Acetonitrile-d3) δ 176.0, 171.9, 146.3, 143.7, 139.5, 129.2, 128.9, 127.8, 127.6, 126.8, 126.3, 125.3, 75.3, 58.9, 55.2, 52.4, 25.2, 23.3.

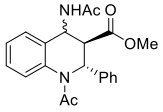
IR (ATR, cm-1) 2267, 1723, 1632, 1490, 1311, 1261, 1193, 1053, 969, 760, 700.

HRMS (ESI-, M-) Calc'd 376.1341 for $C_{19}H_{18}BF_3NO_3$, found 376.1345.



5 **6**

5 (73.1 mg, 0.175 mmol) and $Cu(OAc)_2$ monohydrate (35 mg, 0.175 mmol, 1 equiv) were loaded in a flame-dried and argon-cooled vial and were then dissolved in 1.75 mL of acetonitrile. BF_3 OEt_2 (0.043 mL, 0.35 mmol, 2 equiv) was added dropwise and the reaction was then placed in an oil bath preheated to 100 ºC. Upon, reaction completion, it was quenched with water and extracted thrice with EtOAc and the combined organic layers were once washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified via column chromatography eluting with a gradient of 25:75 to 50:50 to 100:0 (EtOAc:pentanes) to 60:40 (EtOAc:acetone).



6

methyl (2*R*,3*R*,4*S*)-1-acetyl-4-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (6) – 36.3 mg, 0.1 mmol (57%). Off white foam.

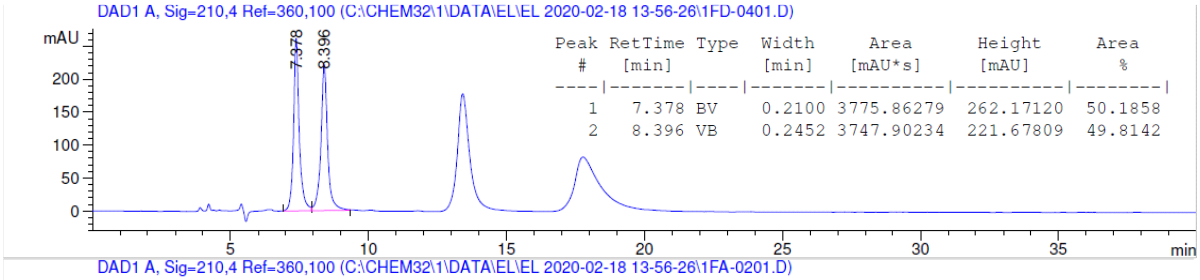
^{1}H NMR (500 MHz, Chloroform-d) δ 7.70 – 6.72 (m, 10H), 6.79 – 5.07 (m, 3H), 3.75 – 3.69 (m, 3H), 3.35 – 3.95 (m, 1H), 2.22 – 2.08 (m, 3H), 2.01 – 1.92 (m, 3H).

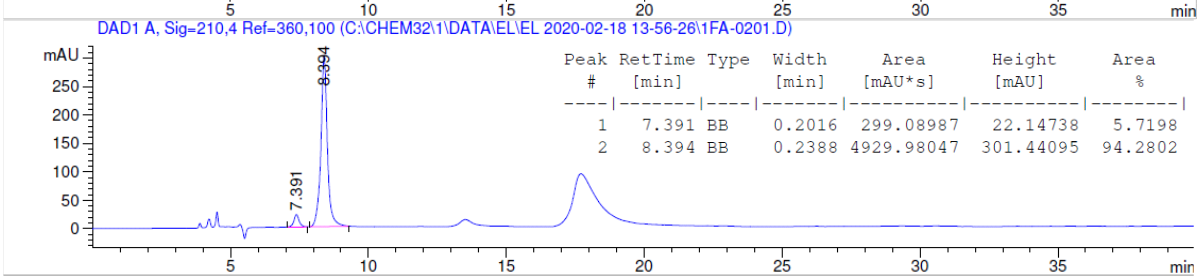
^{13}C NMR (126 MHz, Chloroform-d) δ 171.2, 170.7, 169.8, 129.1, 129.0, 128.8, 128.4, 127.8, 127.8, 126.7, 126.5, 126.2, 125.8, 57.2, 52.9, 52.8, 47.9, 23.4, 23.2.

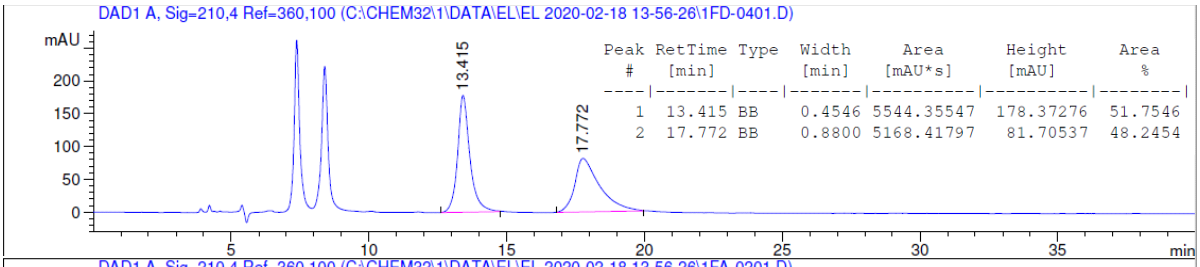
IR (ATR, cm-1) 3259, 1739, 1654, 1531, 1489, 1390, 1369, 1343, 1281, 1194, 1171, 1121, 106, 952, 760, 698

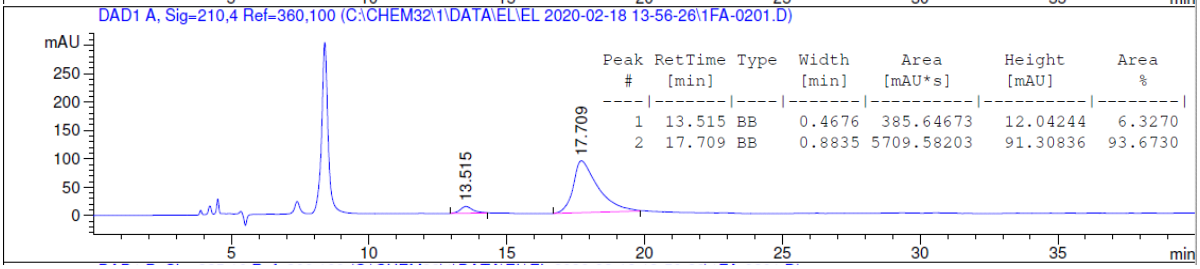
HRMS (DART, M+H) Calc'd 367.1652 for $C_{21}H_{23}N_2O_4$, found 367.1654

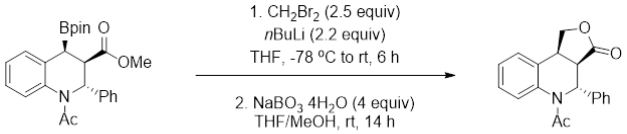
HPLC IA, 30% IPA/Hex, 0.75 mL/min.





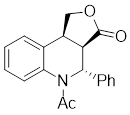




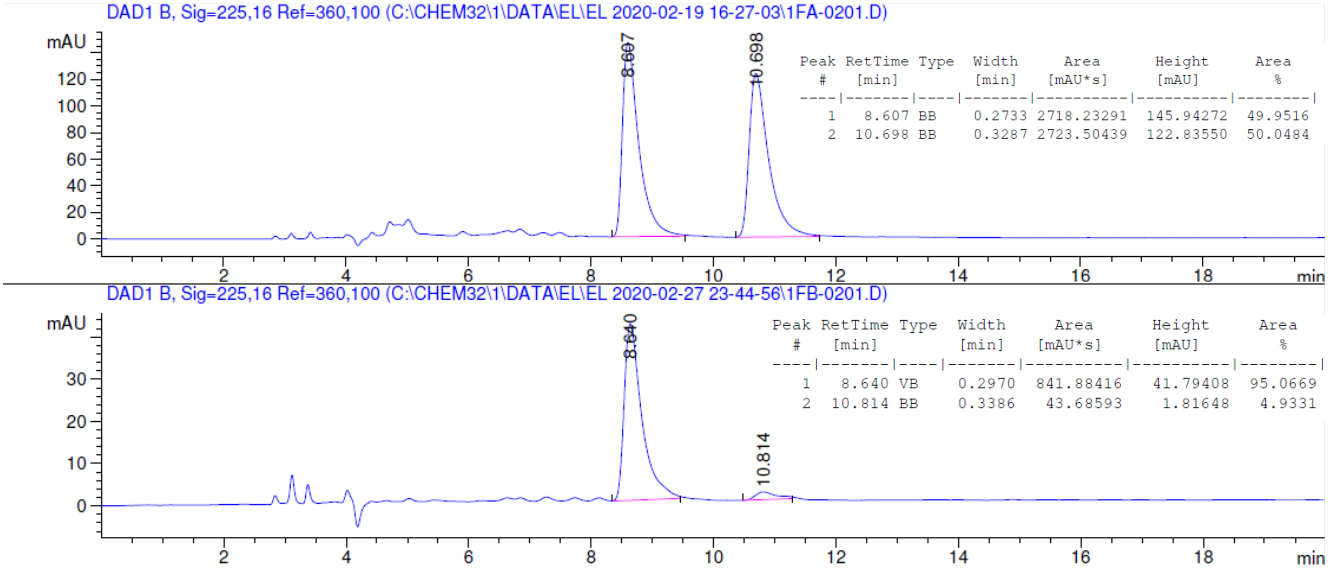


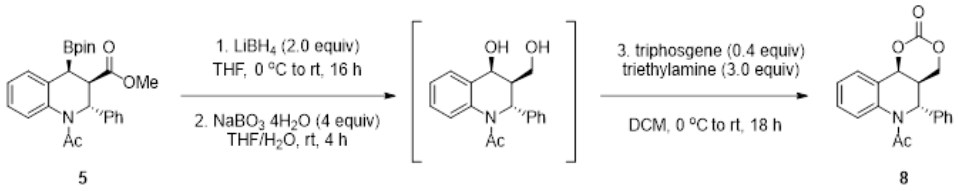
5 **7**

A solution of **5** (87.1 mg, 0.2 mmol) and CH_2Br_2 (0.035 mL, 0.5 mmol, 2.5 equiv) under argon in THF (2 mL) was cooled to -78 ºC and *n*BuLi (0.180 mL (2.5 M hexanes solution), 0.44 mmol, 2.2 equiv) was added dropwise and the reaction was stirred at -78 ºC for 20 minute and then at room temperature for 6 hours. The reaction was then cooled to 0 ºC and methanol (2 mL) was added slowly. The reaction was warmed to room temperature and sodium perborate (123 mg, 0.8 mmol, 4 equiv) was added. The reaction was left to stir vigorously for 14 hours. Upon completion, it was poured into saturated aqueous NH_4Cl and extracted thrice with EtOAc. The combined organic layers were washed twice with water and once with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified via column chromatography eluting with a gradient of 75:25 to 50:50 EtOAc:pentanes.



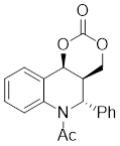
(3a*R*,4*R*,9b*S*)-5-acetyl-4-phenyl-3a,4,5,9b-tetrahydrofuro[3,4-*c*]quinolin-3(1H)-one (7) – 10.5 mg, 0.034 mmol (17%). White foam.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.27 – 6.90 (m, 9H), 4.74 (dd, J = 9.1, 7.0 Hz, 1H), 4.31 (d, J = 9.1 Hz, 1H), 3.86 – 3.66 (m, 2H), 2.39 (d, J = 8.7 Hz, 2H), 1.26 – 1.24 (m, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 176.5, 170.3, 128.9, 128.8, 127.9, 127.7, 126.3, 125.8, 74.4, 45.7, 29.7, 24.8, 23.1.
IR (ATR, cm-1) 2003, 1768, 1656, 1582, 1494, 1374, 1315, 1204, 1156, 1020, 910, 821, 768, 725, 696.
HRMS (DART, M+) Calc'd 308.1281 for $C_{19}H_{18}NO_3$, found 308.1290
HPLC IA, 30% IPA/Hex, 1 mL/min





5 **8**

$LiBH_4$ (0.35 mL (2 M THF solution), 0.7 mmol, 1.75 equiv) was slowly added to a solution of **5** (174 mg, 0.4 mmol) under argon in THF (4 mL) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 16 hours. The reaction mixture was cooled to 0 °C, and water (2 mL) was very carefully added, followed by sodium perborate (246.2 mg, 1.6 mmol, 4 equiv) and vigorously stirred at room temperature for 4 hours. The reaction mixture was then poured into saturated aqueous $NaHCO_3$ and extracted thrice with EtOAc. The combined organic layers were then washed 4 times with water, once with saturated aqueous NH_4Cl and once with brine, and dried over $MgSO_4$. This solution was then concentrated *in vacuo.* The diol was used directly in the next step, where it was dissolved in DCM (15 mL), triethylamine (0.17 mL, 1.2 mmol, 3 equiv) was added and the reaction solution was cooled to 0 °C. Triphosgene (47.5 mg, 0.16 mmol, 0.4 equiv) was then added neat and the reaction was allowed to stir for 18 hours. The reaction was quenched with aqueous NH_4Cl and extracted thrice with DCM. The combined organic layers were washed once with brine and dried over $MgSO_4$. The product was isolated using column chromatography, eluting with a gradient of 30:70 to 50:50 to 70:30 EtOAc:pentane.



(4a*R*,5*R*,10b*S*)-6-acetyl-5-phenyl-4a,5,6,10b-tetrahydro-4*H*-[1,3]dioxino[5,4-*c*]quinolin-2-one (8) – 56.7 mg, 0.175 mmol (44%). White paste.

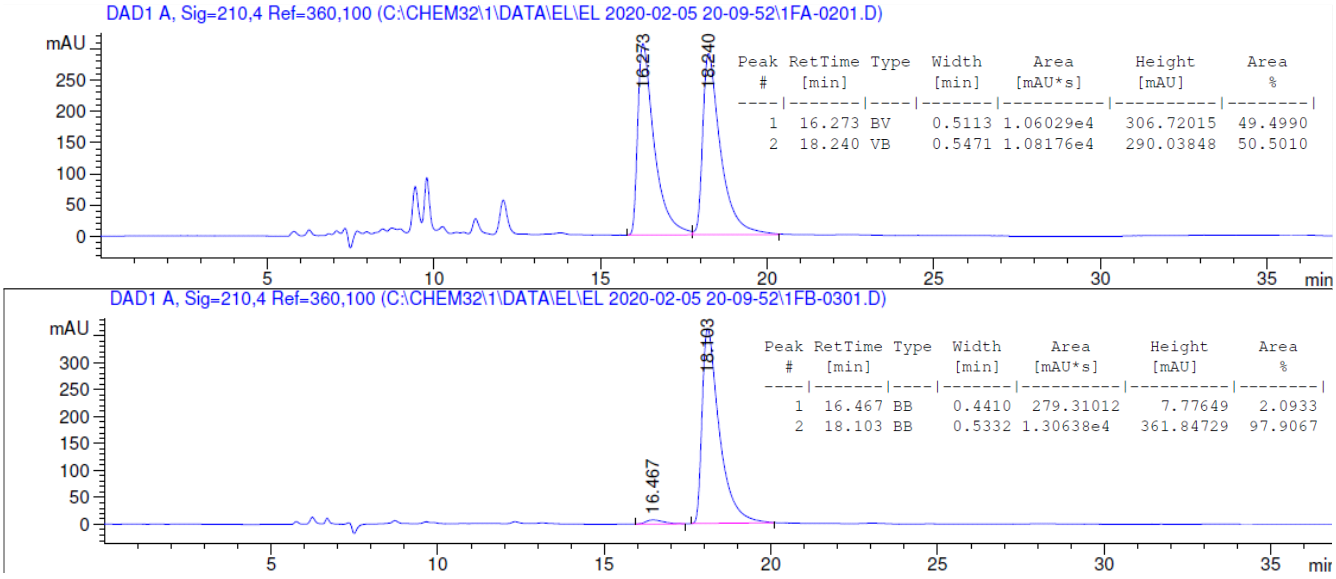
^{1}H NMR (500 MHz, Chloroform-d) δ 7.47 (ddd, J = 15.8, 7.9, 1.6 Hz, 2H), 7.30 (td, J = 7.6, 1.1 Hz, 1H), 7.27 – 7.21 (m, 4H), 7.13 – 7.09 (m, 2H), 5.87 (d, J = 6.0 Hz, 1H), 5.53 (d, J = 4.4 Hz, 1H), 4.64 (dd, J = 11.4, 3.6 Hz, 1H), 4.45 (dd, J = 11.4, 3.5 Hz, 1H), 2.82 (ddt, J = 6.0, 4.5, 3.6 Hz, 1H), 2.18 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 169.9, 148.2, 140.3, 138.2, 130.9, 129.2, 129.0, 128.0, 127.8, 126.7, 126.4, 126.1, 76.3, 69.8, 54.8, 39.9, 22.8.

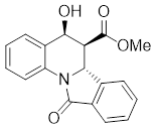
IR (ATR, cm-1) 2994, 1732, 1657, 1582, 1490, 1363, 1322, 1250, 1199, 1142, 972, 859, 847, 771, 757, 699

HRMS (DART, M+H) Calc'd 324.1230 for $C_{19}H_{18}NO_4$, found 324.1227.

HPLC IA, 40% IPA/Hex, 0.5 mL/min



A 2-dram vial containing a stir bar was oven-dried and cooled under argon whereupon it was charged with $Cu(MeCN)_4PF_6$ (3.0 mg, 0.008 mmol, 4 mol%), Josiphos SL-J001-1 (7.7 mg, 0.012 mmol, 6 mol%) and NaOtBu (5.77 mg, 0.06 mmol, 30 mol%), and Et_2O (1 mL) was immediately added. This was stirred for 30 min with noticeable darkening of color. B_2Pin_2 (76 mg, 0.3 mmol, 1.5 equiv) was added as a solution in Et_2O (1 mL) and the resultant suspension was stirred for a further 15 min. Finally, **9** (0.2 mmol), *t*AmOH (44 µL, 0.4 mmol, 2.0 equiv) and Et2O (2 mL) were subsequently added into the reaction vial. The reaction was stirred for the indicated period of time. Upon completion, it was filtered over a Celite pad and volatiles were removed. Subsequently, $NaBO_3 \cdot 4H_2O$ (123.1 mg, 0.8 mmol, 4.0 equiv), MeOH (2 mL) and THF (4 mL) were added and the reaction mixture was stirred for 14 hours at 70 °C. Upon completion, the reaction mixture was diluted with 50% NaCl solution, and extracted thrice with EtOAc. The combined organic fractions were washed five times with water to remove pinacol and once with brine and dried over $MgSO_4$. The dr was determined by 1H NMR analysis of the crude mixture and the products were isolated by flash column chromatography



methyl (5*S*,6*S*,6a*R*)-5-hydroxy-11-oxo-5,6,6a,11-tetrahydroisoindolo[2,1-*a*]quinoline-6-carboxylate (10) – 29.2 mg, 0.0944 mmol (47 %). White foam.

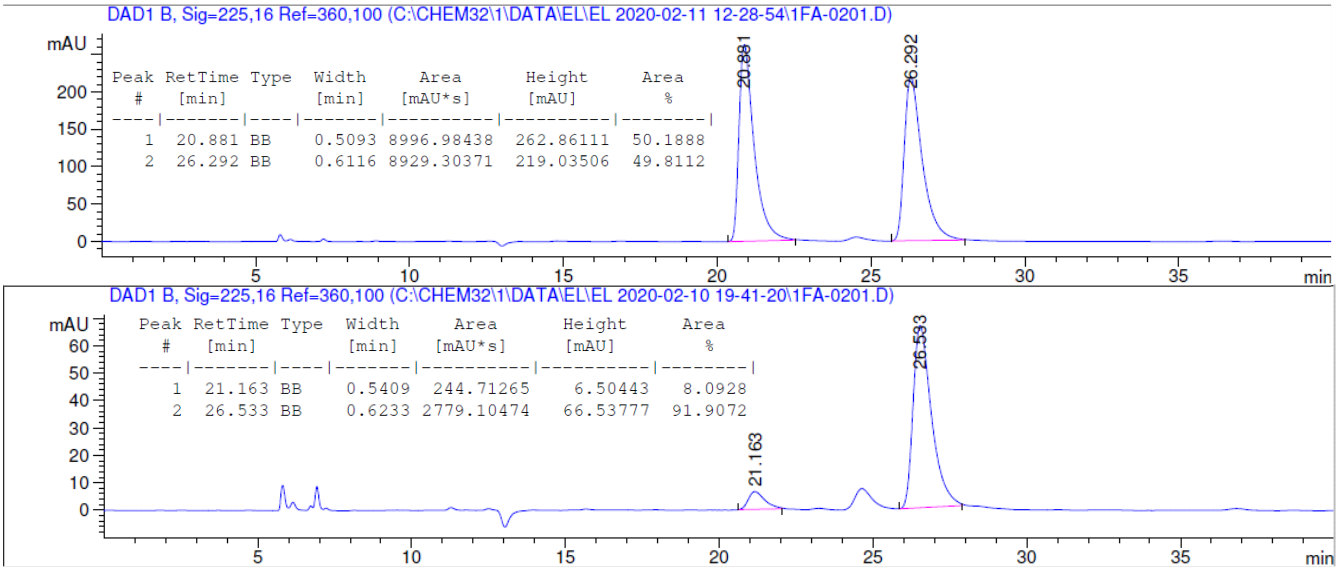
^{1}H NMR (500 MHz, Chloroform-d) δ 8.47 (dt, J = 8.4, 1.9 Hz, 1H), 7.88 (dd, J = 7.5, 0.9 Hz, 1H), 7.68 (dd, J = 7.7, 1.0 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.51 (tt, J = 7.3, 0.8 Hz, 1H), 7.47 – 7.38 (m, 1H), 7.34 (tdd, J = 8.4, 7.3, 3.2, 1.3 Hz, 1H), 7.11 (tdd, J = 7.5, 2.2, 1.2 Hz, 1H), 5.32 (dd, J = 11.8, 1.6 Hz, 1H), 5.16 (t, J = 3.3 Hz, 1H), 3.87 (s, 3H), 3.13 (d, J = 14.2 Hz, 1H), 2.79 (ddd, J = 11.7, 3.3, 1.1 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 171.7, 166.5, 142.7, 135.1, 132.7, 132.6 (two peaks), 129.8, 129.1, 126.4, 124.6, 124.5, 124.4, 120.6, 67.5, 54.8, 52.4, 50.8.

IR (ATR, cm^{-1}) 3356, 1737, 1667, 1489, 1381, 1366, 1312, 1293, 1200, 1161, 1052, 940, 750, 693.

HRMS (DART, M+H) Calc'd 310.1074 for $C_{18}H_{16}NO_4$, found 310.1073.

HPLC IA, 15% IPA/Hex, 0.5 mL/min



8 X-Ray Structures and Corresponding Data

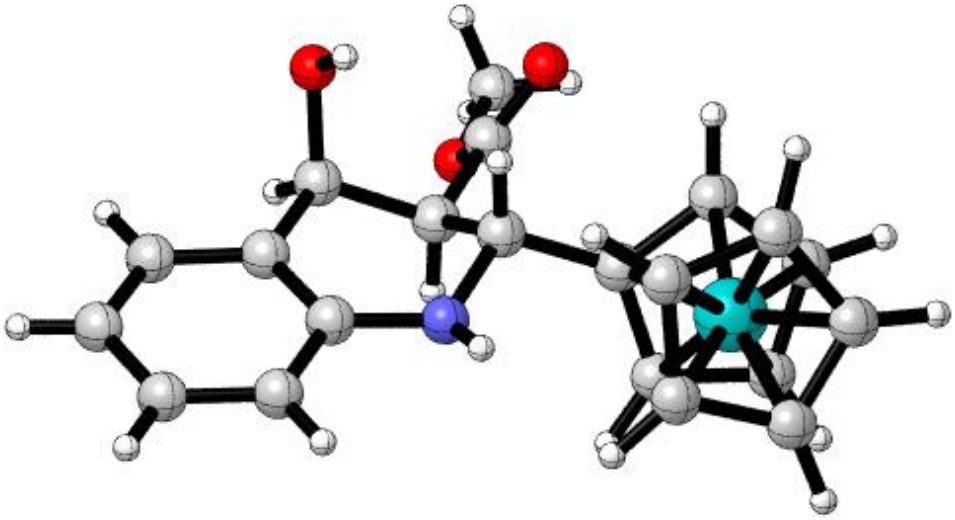


Table 2. Crystal data and structure refinement for d19205_a.

Identification code	d19205_a	
Empirical formula	C21 H21 Fe N O3	
Formula weight	391.24	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.9439(4) Å	α= 90°.
	b = 8.6162(4) Å	β= 90°.
	c = 25.8718(12) Å	γ = 90°.
Volume	1770.83(15) $Å^3$	
Z	4	

Density (calculated)	1.467 Mg/m^3
Absorption coefficient	0.872 mm^{-1}
F(000)	816
Crystal size	0.170 x 0.140 x 0.060 mm^3
Theta range for data collection	1.574 to 27.599°.
Index ranges	-10<=h<=10, -11<=k<=11, -33<=l<=33
Reflections collected	53341
Independent reflections	4097 [R(int) = 0.0378]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.7072
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4097 / 0 / 244
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0213, wR2 = 0.0519
R indices (all data)	R1 = 0.0249, wR2 = 0.0536
Absolute structure parameter	0.007(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.251 and -0.175 $e.Å^{-3}$

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d19205_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	2644(1)	8821(1)	6947(1)	18(1)
O(1)	6418(2)	5831(2)	5120(1)	27(1)
O(2)	7768(2)	6412(2)	6241(1)	32(1)
O(3)	7550(2)	3819(2)	6255(1)	23(1)
N(1)	2478(2)	6372(2)	5888(1)	24(1)
C(1)	4182(2)	6665(2)	6073(1)	18(1)
C(2)	5184(2)	5180(2)	5966(1)	18(1)
C(3)	5246(2)	4842(2)	5379(1)	20(1)
C(4)	3501(2)	4928(2)	5149(1)	18(1)
C(5)	3160(3)	4229(2)	4674(1)	24(1)
C(6)	1568(3)	4261(3)	4460(1)	26(1)
C(7)	268(3)	4968(2)	4731(1)	24(1)
C(8)	570(3)	5679(2)	5201(1)	22(1)
C(9)	2200(2)	5685(2)	5412(1)	19(1)
C(10)	6963(2)	5257(2)	6172(1)	19(1)
C(11)	9288(2)	3714(3)	6416(1)	28(1)
C(12)	4095(2)	7098(2)	6636(1)	18(1)
C(13)	2947(2)	6465(2)	7004(1)	21(1)
C(14)	3266(3)	7182(3)	7490(1)	26(1)
C(15)	4601(3)	8256(3)	7423(1)	26(1)
C(16)	5122(2)	8208(2)	6898(1)	24(1)
C(17)	2494(3)	11095(2)	6731(1)	33(1)
C(18)	1694(3)	10871(3)	7216(1)	32(1)
C(19)	378(3)	9792(3)	7145(1)	28(1)
C(20)	349(3)	9337(3)	6616(1)	24(1)
C(21)	1662(3)	10144(3)	6361(1)	27(1)

Table 4. Bond lengths [Å] and angles [°] for d19205_a.

Fe(1)-C(17)	2.041(2)
Fe(1)-C(15)	2.042(2)
Fe(1)-C(16)	2.042(2)
Fe(1)-C(18)	2.042(2)
Fe(1)-C(12)	2.0452(19)
Fe(1)-C(19)	2.049(2)
Fe(1)-C(13)	2.0494(19)
Fe(1)-C(14)	2.051(2)
Fe(1)-C(21)	2.051(2)
Fe(1)-C(20)	2.062(2)
O(1)-C(3)	1.428(3)
O(1)-H(1O)	0.82(3)
O(2)-C(10)	1.196(2)
O(3)-C(10)	1.341(2)
O(3)-C(11)	1.444(2)
N(1)-C(9)	1.384(2)
N(1)-C(1)	1.458(2)
N(1)-H(1N)	0.83(3)
C(1)-C(12)	1.505(3)
C(1)-C(2)	1.533(3)
C(1)-H(1A)	1.0000
C(2)-C(10)	1.512(3)
C(2)-C(3)	1.547(3)
C(2)-H(2A)	1.0000
C(3)-C(4)	1.511(3)
C(3)-H(3A)	1.0000
C(4)-C(5)	1.394(3)
C(4)-C(9)	1.398(3)
C(5)-C(6)	1.381(3)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.389(3)
C(6)-H(6A)	0.9500
C(7)-C(8)	1.382(3)
C(7)-H(7A)	0.9500

C(8)-C(9)	1.405(3)
C(8)-H(8A)	0.9500
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(13)	1.426(3)
C(12)-C(16)	1.428(3)
C(13)-C(14)	1.424(3)
C(13)-H(13A)	1.0000
C(14)-C(15)	1.418(3)
C(14)-H(14A)	1.0000
C(15)-C(16)	1.420(3)
C(15)-H(15A)	1.0000
C(16)-H(16A)	1.0000
C(17)-C(18)	1.419(4)
C(17)-C(21)	1.423(3)
C(17)-H(17A)	1.0000
C(18)-C(19)	1.410(3)
C(18)-H(18A)	1.0000
C(19)-C(20)	1.422(3)
C(19)-H(19A)	1.0000
C(20)-C(21)	1.417(3)
C(20)-H(20A)	1.0000
C(21)-H(21A)	1.0000

C(17)-Fe(1)-C(15)	116.00(9)
C(17)-Fe(1)-C(16)	106.70(9)
C(15)-Fe(1)-C(16)	40.68(10)
C(17)-Fe(1)-C(18)	40.67(10)
C(15)-Fe(1)-C(18)	106.42(9)
C(16)-Fe(1)-C(18)	126.95(9)
C(17)-Fe(1)-C(12)	128.43(9)
C(15)-Fe(1)-C(12)	68.60(8)
C(16)-Fe(1)-C(12)	40.91(8)
C(18)-Fe(1)-C(12)	165.93(10)
C(17)-Fe(1)-C(19)	68.00(9)

C(15)-Fe(1)-C(19)	128.01(9)
C(16)-Fe(1)-C(19)	165.38(9)
C(18)-Fe(1)-C(19)	40.33(10)
C(12)-Fe(1)-C(19)	152.83(9)
C(17)-Fe(1)-C(13)	167.73(9)
C(15)-Fe(1)-C(13)	68.36(9)
C(16)-Fe(1)-C(13)	68.56(8)
C(18)-Fe(1)-C(13)	151.16(9)
C(12)-Fe(1)-C(13)	40.77(8)
C(19)-Fe(1)-C(13)	119.35(9)
C(17)-Fe(1)-C(14)	149.59(9)
C(15)-Fe(1)-C(14)	40.53(9)
C(16)-Fe(1)-C(14)	68.40(9)
C(18)-Fe(1)-C(14)	116.87(9)
C(12)-Fe(1)-C(14)	68.52(8)
C(19)-Fe(1)-C(14)	108.81(9)
C(13)-Fe(1)-C(14)	40.62(8)
C(17)-Fe(1)-C(21)	40.69(9)
C(15)-Fe(1)-C(21)	150.19(10)
C(16)-Fe(1)-C(21)	117.68(9)
C(18)-Fe(1)-C(21)	68.30(9)
C(12)-Fe(1)-C(21)	109.05(8)
C(19)-Fe(1)-C(21)	67.88(9)
C(13)-Fe(1)-C(21)	130.38(9)
C(14)-Fe(1)-C(21)	168.52(9)
C(17)-Fe(1)-C(20)	68.17(9)
C(15)-Fe(1)-C(20)	167.07(9)
C(16)-Fe(1)-C(20)	151.89(9)
C(18)-Fe(1)-C(20)	68.17(9)
C(12)-Fe(1)-C(20)	119.41(8)
C(19)-Fe(1)-C(20)	40.47(9)
C(13)-Fe(1)-C(20)	110.30(9)
C(14)-Fe(1)-C(20)	130.19(9)
C(21)-Fe(1)-C(20)	40.30(9)
C(3)-O(1)-H(1O)	109(2)
C(10)-O(3)-C(11)	115.88(17)

C(9)-N(1)-C(1)	120.94(17)
C(9)-N(1)-H(1N)	116.4(18)
C(1)-N(1)-H(1N)	115.7(18)
N(1)-C(1)-C(12)	108.53(16)
N(1)-C(1)-C(2)	106.16(16)
C(12)-C(1)-C(2)	113.89(16)
N(1)-C(1)-H(1A)	109.4
C(12)-C(1)-H(1A)	109.4
C(2)-C(1)-H(1A)	109.4
C(10)-C(2)-C(1)	112.66(16)
C(10)-C(2)-C(3)	108.93(16)
C(1)-C(2)-C(3)	110.50(16)
C(10)-C(2)-H(2A)	108.2
C(1)-C(2)-H(2A)	108.2
C(3)-C(2)-H(2A)	108.2
O(1)-C(3)-C(4)	112.62(17)
O(1)-C(3)-C(2)	111.63(17)
C(4)-C(3)-C(2)	110.39(16)
O(1)-C(3)-H(3A)	107.3
C(4)-C(3)-H(3A)	107.3
C(2)-C(3)-H(3A)	107.3
C(5)-C(4)-C(9)	119.08(18)
C(5)-C(4)-C(3)	120.28(18)
C(9)-C(4)-C(3)	120.63(18)
C(6)-C(5)-C(4)	121.52(19)
C(6)-C(5)-H(5A)	119.2
C(4)-C(5)-H(5A)	119.2
C(5)-C(6)-C(7)	119.17(19)
C(5)-C(6)-H(6A)	120.4
C(7)-C(6)-H(6A)	120.4
C(8)-C(7)-C(6)	120.56(19)
C(8)-C(7)-H(7A)	119.7
C(6)-C(7)-H(7A)	119.7
C(7)-C(8)-C(9)	120.23(19)
C(7)-C(8)-H(8A)	119.9
C(9)-C(8)-H(8A)	119.9

N(1)-C(9)-C(4)	120.94(18)
N(1)-C(9)-C(8)	119.61(18)
C(4)-C(9)-C(8)	119.37(18)
O(2)-C(10)-O(3)	123.97(18)
O(2)-C(10)-C(2)	126.09(19)
O(3)-C(10)-C(2)	109.92(17)
O(3)-C(11)-H(11A)	109.5
O(3)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
O(3)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(13)-C(12)-C(16)	107.67(18)
C(13)-C(12)-C(1)	125.50(18)
C(16)-C(12)-C(1)	126.83(19)
C(13)-C(12)-Fe(1)	69.77(11)
C(16)-C(12)-Fe(1)	69.44(11)
C(1)-C(12)-Fe(1)	125.94(13)
C(14)-C(13)-C(12)	108.05(18)
C(14)-C(13)-Fe(1)	69.76(12)
C(12)-C(13)-Fe(1)	69.46(11)
C(14)-C(13)-H(13A)	126.0
C(12)-C(13)-H(13A)	126.0
Fe(1)-C(13)-H(13A)	126.0
C(15)-C(14)-C(13)	107.99(19)
C(15)-C(14)-Fe(1)	69.39(12)
C(13)-C(14)-Fe(1)	69.61(11)
C(15)-C(14)-H(14A)	126.0
C(13)-C(14)-H(14A)	126.0
Fe(1)-C(14)-H(14A)	126.0
C(14)-C(15)-C(16)	108.36(19)
C(14)-C(15)-Fe(1)	70.08(12)
C(16)-C(15)-Fe(1)	69.67(12)
C(14)-C(15)-H(15A)	125.8
C(16)-C(15)-H(15A)	125.8
Fe(1)-C(15)-H(15A)	125.8

C(15)-C(16)-C(12)	107.94(19)
C(15)-C(16)-Fe(1)	69.66(12)
C(12)-C(16)-Fe(1)	69.65(11)
C(15)-C(16)-H(16A)	126.0
C(12)-C(16)-H(16A)	126.0
Fe(1)-C(16)-H(16A)	126.0
C(18)-C(17)-C(21)	107.9(2)
C(18)-C(17)-Fe(1)	69.71(12)
C(21)-C(17)-Fe(1)	70.04(12)
C(18)-C(17)-H(17A)	126.0
C(21)-C(17)-H(17A)	126.0
Fe(1)-C(17)-H(17A)	126.0
C(19)-C(18)-C(17)	107.9(2)
C(19)-C(18)-Fe(1)	70.10(13)
C(17)-C(18)-Fe(1)	69.62(12)
C(19)-C(18)-H(18A)	126.1
C(17)-C(18)-H(18A)	126.1
Fe(1)-C(18)-H(18A)	126.1
C(18)-C(19)-C(20)	108.6(2)
C(18)-C(19)-Fe(1)	69.57(13)
C(20)-C(19)-Fe(1)	70.26(13)
C(18)-C(19)-H(19A)	125.7
C(20)-C(19)-H(19A)	125.7
Fe(1)-C(19)-H(19A)	125.7
C(21)-C(20)-C(19)	107.5(2)
C(21)-C(20)-Fe(1)	69.43(12)
C(19)-C(20)-Fe(1)	69.26(13)
C(21)-C(20)-H(20A)	126.3
C(19)-C(20)-H(20A)	126.3
Fe(1)-C(20)-H(20A)	126.3
C(20)-C(21)-C(17)	108.1(2)
C(20)-C(21)-Fe(1)	70.26(12)
C(17)-C(21)-Fe(1)	69.27(12)
C(20)-C(21)-H(21A)	125.9
C(17)-C(21)-H(21A)	125.9
Fe(1)-C(21)-H(21A)	125.9

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for d19205_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	16(1)	18(1)	20(1)	-2(1)	-2(1)	3(1)
O(1)	19(1)	31(1)	31(1)	3(1)	6(1)	2(1)
O(2)	19(1)	22(1)	54(1)	-6(1)	-1(1)	-2(1)
O(3)	19(1)	21(1)	28(1)	1(1)	-7(1)	5(1)
N(1)	16(1)	34(1)	21(1)	-7(1)	-2(1)	10(1)
C(1)	15(1)	18(1)	20(1)	1(1)	0(1)	4(1)
C(2)	14(1)	15(1)	23(1)	1(1)	-1(1)	2(1)
C(3)	16(1)	20(1)	24(1)	-1(1)	2(1)	4(1)
C(4)	18(1)	18(1)	20(1)	3(1)	1(1)	1(1)
C(5)	26(1)	22(1)	23(1)	-3(1)	3(1)	2(1)
C(6)	32(1)	24(1)	23(1)	-2(1)	-4(1)	-2(1)
C(7)	21(1)	25(1)	26(1)	5(1)	-6(1)	-2(1)
C(8)	18(1)	26(1)	21(1)	4(1)	2(1)	3(1)
C(9)	18(1)	21(1)	18(1)	3(1)	1(1)	2(1)
C(10)	16(1)	20(1)	21(1)	-1(1)	2(1)	3(1)
C(11)	19(1)	37(1)	28(1)	3(1)	-6(1)	9(1)
C(12)	15(1)	17(1)	23(1)	1(1)	-1(1)	4(1)
C(13)	24(1)	18(1)	22(1)	1(1)	-1(1)	3(1)
C(14)	31(1)	26(1)	20(1)	2(1)	-3(1)	6(1)
C(15)	26(1)	26(1)	26(1)	-4(1)	-10(1)	8(1)
C(16)	16(1)	21(1)	34(1)	0(1)	-4(1)	4(1)
C(17)	25(1)	19(1)	55(1)	7(1)	-7(1)	4(1)
C(18)	34(1)	27(1)	36(1)	-12(1)	-11(1)	14(1)
C(19)	24(1)	35(1)	27(1)	-3(1)	3(1)	13(1)
C(20)	19(1)	26(1)	26(1)	-4(1)	-4(1)	8(1)
C(21)	25(1)	28(1)	27(1)	5(1)	0(1)	12(1)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for d19205_a.

	x	y	z	U(eq)
H(1O)	6080(40)	6730(40)	5137(12)	53(10)
H(1N)	1750(30)	6990(30)	5989(9)	29(7)
H(1A)	4684	7544	5873	22
H(2A)	4596	4296	6140	21
H(3A)	5653	3752	5335	24
H(5A)	4043	3720	4494	28
H(6A)	1365	3805	4132	32
H(7A)	-839	4963	4592	29
H(8A)	-327	6165	5382	26
H(11A)	9569	2628	6488	42
H(11B)	9457	4337	6728	42
H(11C)	10017	4104	6139	42
H(13A)	2066	5665	6932	25
H(14A)	2648	6975	7819	31
H(15A)	5090	8935	7698	32
H(16A)	6041	8842	6740	28
H(17A)	3468	11801	6661	40
H(18A)	2003	11391	7548	39
H(19A)	-398	9406	7421	34
H(20A)	-447	8579	6455	28
H(21A)	1955	10057	5986	32

Table 7. Torsion angles [°] for d19205_a.

C(9)-N(1)-C(1)-C(12)	-168.28(17)
C(9)-N(1)-C(1)-C(2)	-45.5(2)
N(1)-C(1)-C(2)-C(10)	-175.92(16)
C(12)-C(1)-C(2)-C(10)	-56.6(2)
N(1)-C(1)-C(2)-C(3)	62.0(2)
C(12)-C(1)-C(2)-C(3)	-178.66(17)
C(10)-C(2)-C(3)-O(1)	-47.8(2)
C(1)-C(2)-C(3)-O(1)	76.4(2)
C(10)-C(2)-C(3)-C(4)	-173.92(16)
C(1)-C(2)-C(3)-C(4)	-49.7(2)
O(1)-C(3)-C(4)-C(5)	73.8(2)
C(2)-C(3)-C(4)-C(5)	-160.70(18)
O(1)-C(3)-C(4)-C(9)	-107.2(2)
C(2)-C(3)-C(4)-C(9)	18.3(3)
C(9)-C(4)-C(5)-C(6)	-0.4(3)
C(3)-C(4)-C(5)-C(6)	178.62(19)
C(4)-C(5)-C(6)-C(7)	-1.8(3)
C(5)-C(6)-C(7)-C(8)	2.2(3)
C(6)-C(7)-C(8)-C(9)	-0.4(3)
C(1)-N(1)-C(9)-C(4)	15.1(3)
C(1)-N(1)-C(9)-C(8)	-168.13(18)
C(5)-C(4)-C(9)-N(1)	178.94(19)
C(3)-C(4)-C(9)-N(1)	-0.1(3)
C(5)-C(4)-C(9)-C(8)	2.2(3)
C(3)-C(4)-C(9)-C(8)	-176.82(18)
C(7)-C(8)-C(9)-N(1)	-178.60(19)
C(7)-C(8)-C(9)-C(4)	-1.8(3)
C(11)-O(3)-C(10)-O(2)	-2.8(3)
C(11)-O(3)-C(10)-C(2)	175.45(15)
C(1)-C(2)-C(10)-O(2)	-25.9(3)
C(3)-C(2)-C(10)-O(2)	97.1(2)
C(1)-C(2)-C(10)-O(3)	155.92(16)
C(3)-C(2)-C(10)-O(3)	-81.1(2)
N(1)-C(1)-C(12)-C(13)	35.9(3)

C(2)-C(1)-C(12)-C(13)	-82.1(2)
N(1)-C(1)-C(12)-C(16)	-143.72(19)
C(2)-C(1)-C(12)-C(16)	98.3(2)
N(1)-C(1)-C(12)-Fe(1)	-53.7(2)
C(2)-C(1)-C(12)-Fe(1)	-171.68(14)
C(16)-C(12)-C(13)-C(14)	0.0(2)
C(1)-C(12)-C(13)-C(14)	-179.66(18)
Fe(1)-C(12)-C(13)-C(14)	-59.29(14)
C(16)-C(12)-C(13)-Fe(1)	59.32(13)
C(1)-C(12)-C(13)-Fe(1)	-120.36(19)
C(12)-C(13)-C(14)-C(15)	0.1(2)
Fe(1)-C(13)-C(14)-C(15)	-58.96(15)
C(12)-C(13)-C(14)-Fe(1)	59.10(13)
C(13)-C(14)-C(15)-C(16)	-0.3(2)
Fe(1)-C(14)-C(15)-C(16)	-59.36(14)
C(13)-C(14)-C(15)-Fe(1)	59.11(14)
C(14)-C(15)-C(16)-C(12)	0.3(2)
Fe(1)-C(15)-C(16)-C(12)	-59.35(13)
C(14)-C(15)-C(16)-Fe(1)	59.62(15)
C(13)-C(12)-C(16)-C(15)	-0.2(2)
C(1)-C(12)-C(16)-C(15)	179.50(18)
Fe(1)-C(12)-C(16)-C(15)	59.35(14)
C(13)-C(12)-C(16)-Fe(1)	-59.53(13)
C(1)-C(12)-C(16)-Fe(1)	120.15(19)
C(21)-C(17)-C(18)-C(19)	0.0(2)
Fe(1)-C(17)-C(18)-C(19)	-59.91(15)
C(21)-C(17)-C(18)-Fe(1)	59.87(14)
C(17)-C(18)-C(19)-C(20)	0.0(2)
Fe(1)-C(18)-C(19)-C(20)	-59.62(16)
C(17)-C(18)-C(19)-Fe(1)	59.61(14)
C(18)-C(19)-C(20)-C(21)	0.1(2)
Fe(1)-C(19)-C(20)-C(21)	-59.14(15)
C(18)-C(19)-C(20)-Fe(1)	59.20(16)
C(19)-C(20)-C(21)-C(17)	-0.1(2)
Fe(1)-C(20)-C(21)-C(17)	-59.12(14)
C(19)-C(20)-C(21)-Fe(1)	59.03(15)

C(18)-C(17)-C(21)-C(20)	0.1(2)
Fe(1)-C(17)-C(21)-C(20)	59.74(15)
C(18)-C(17)-C(21)-Fe(1)	-59.66(14)

Symmetry transformations used to generate equivalent atoms:

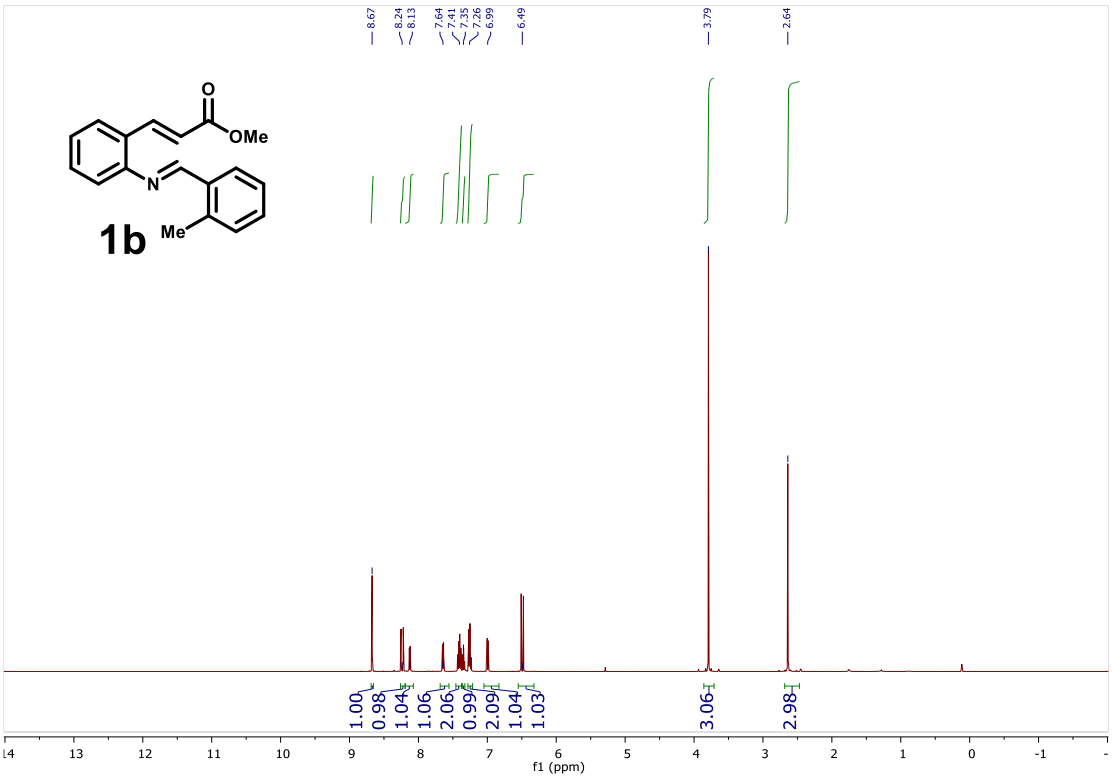
Table 8. Hydrogen bonds for d19205_a [Å and °].

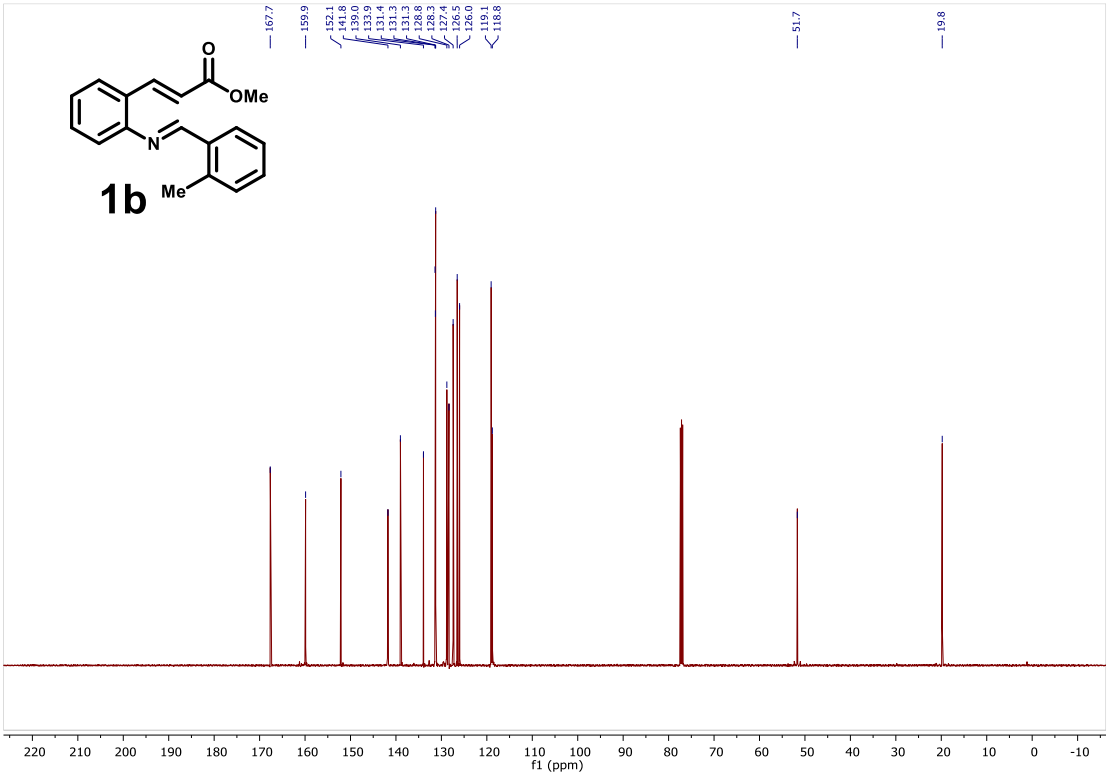
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...Cg#1	0.82(3)	2.93(3)	3.6495(12)	14893)

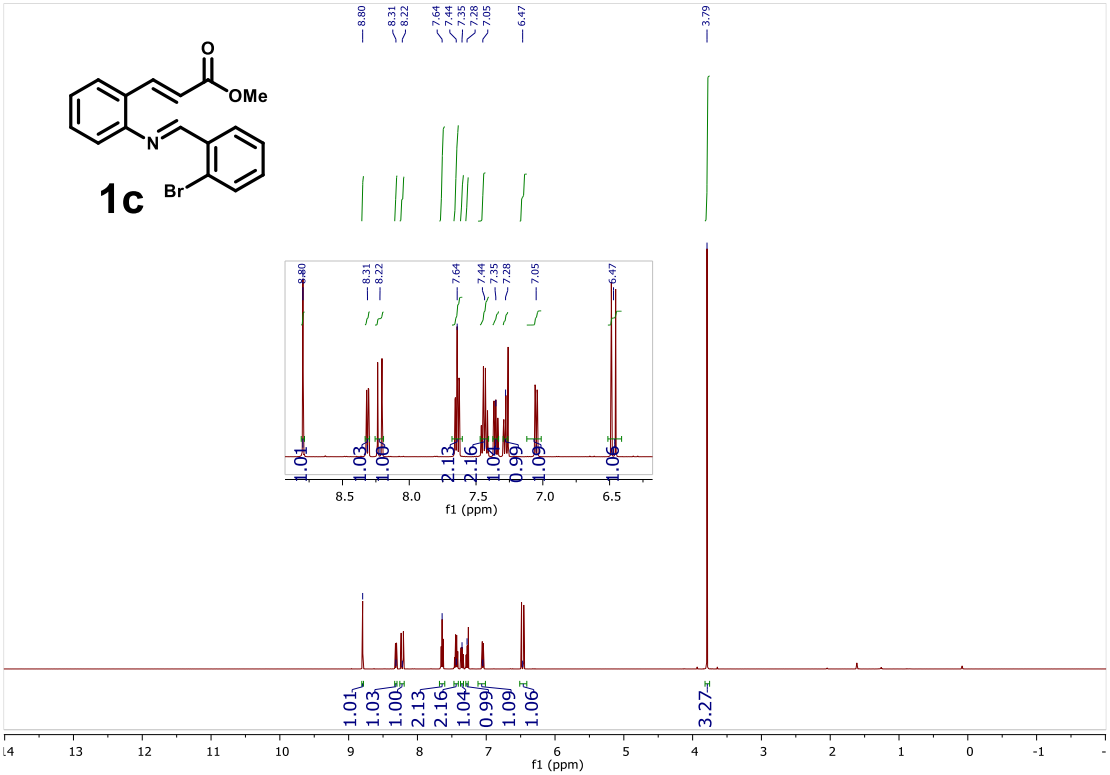
Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+3/2,-z+1

9 Spectra of New Compounds



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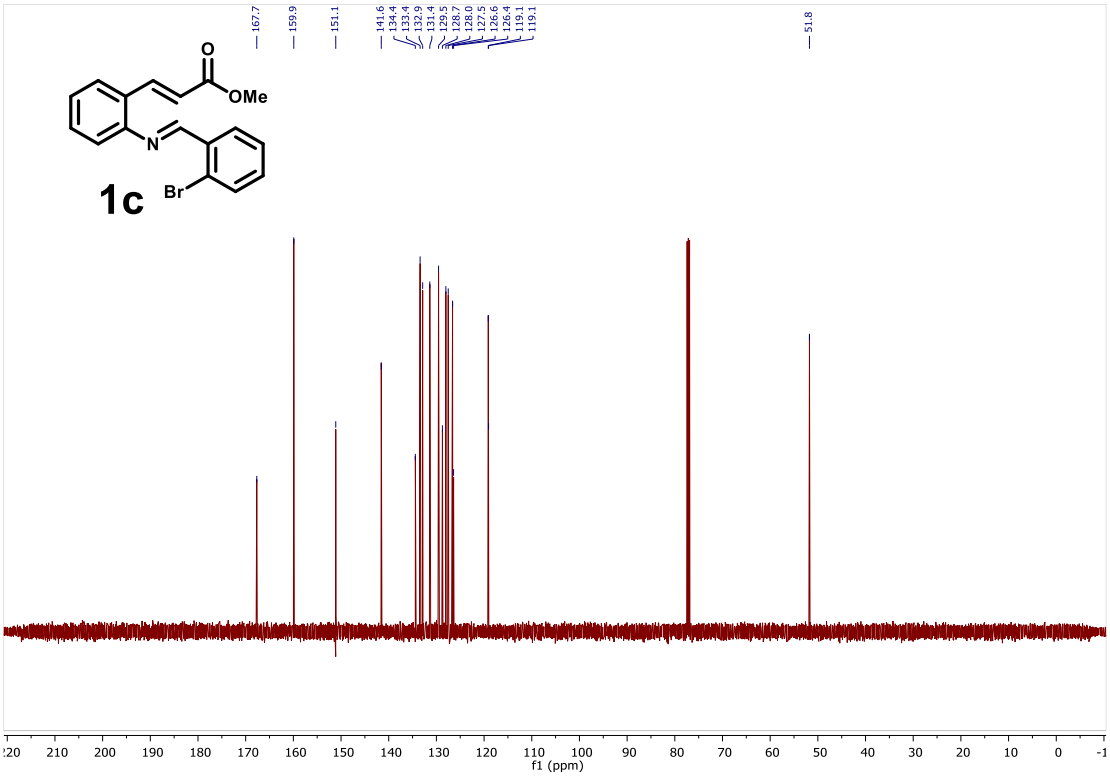
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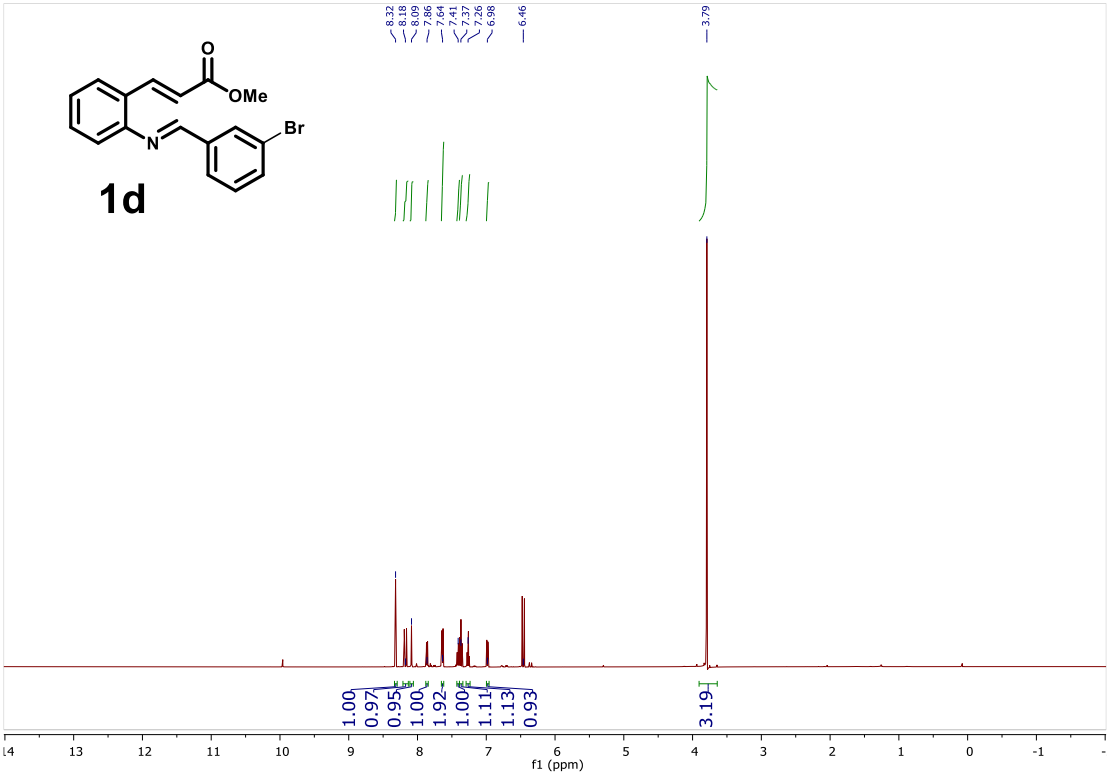
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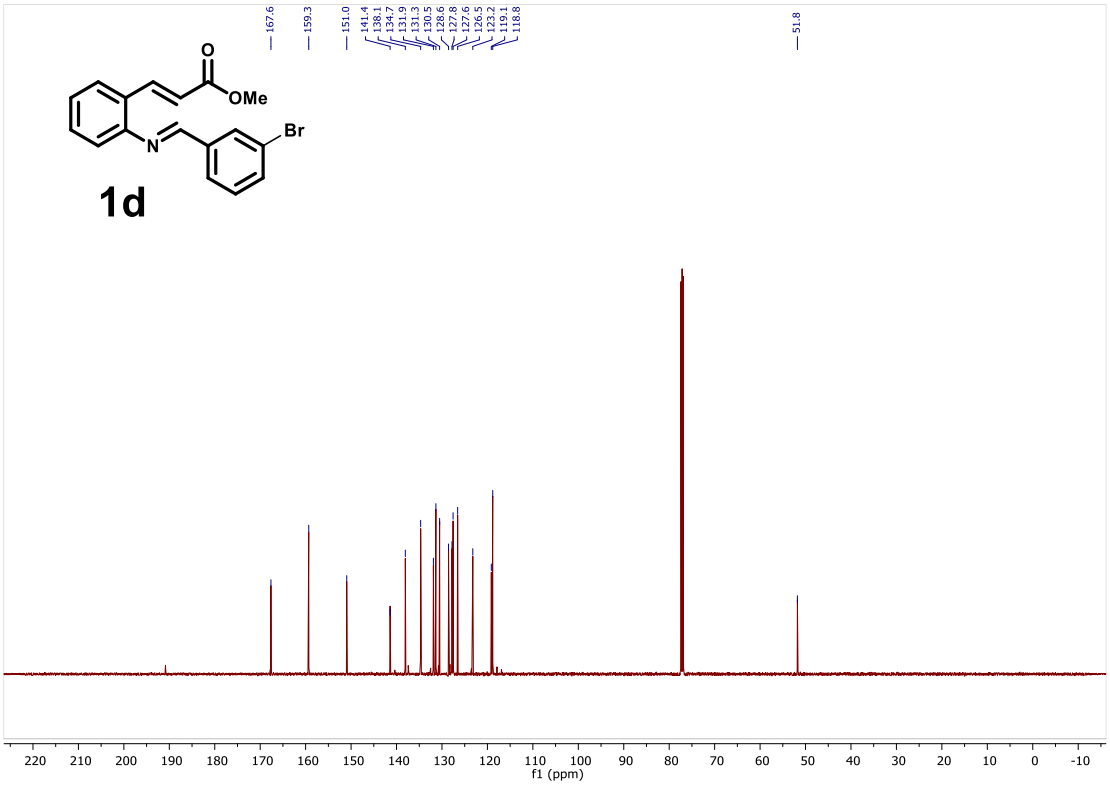
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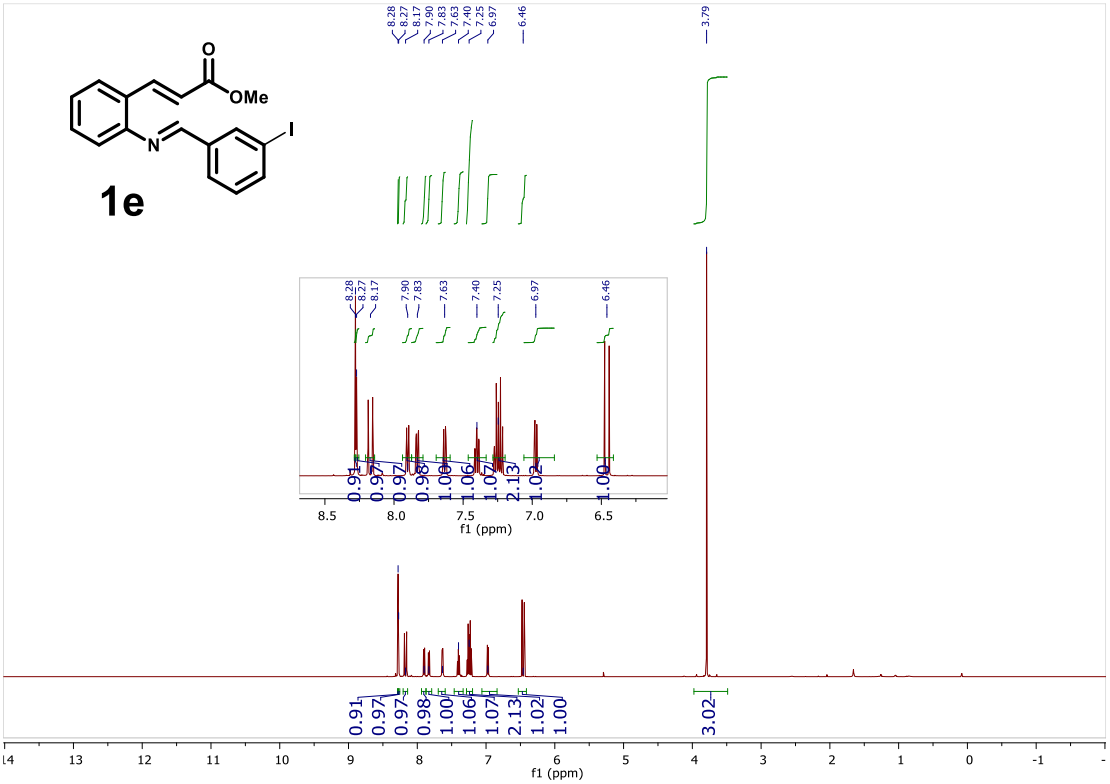
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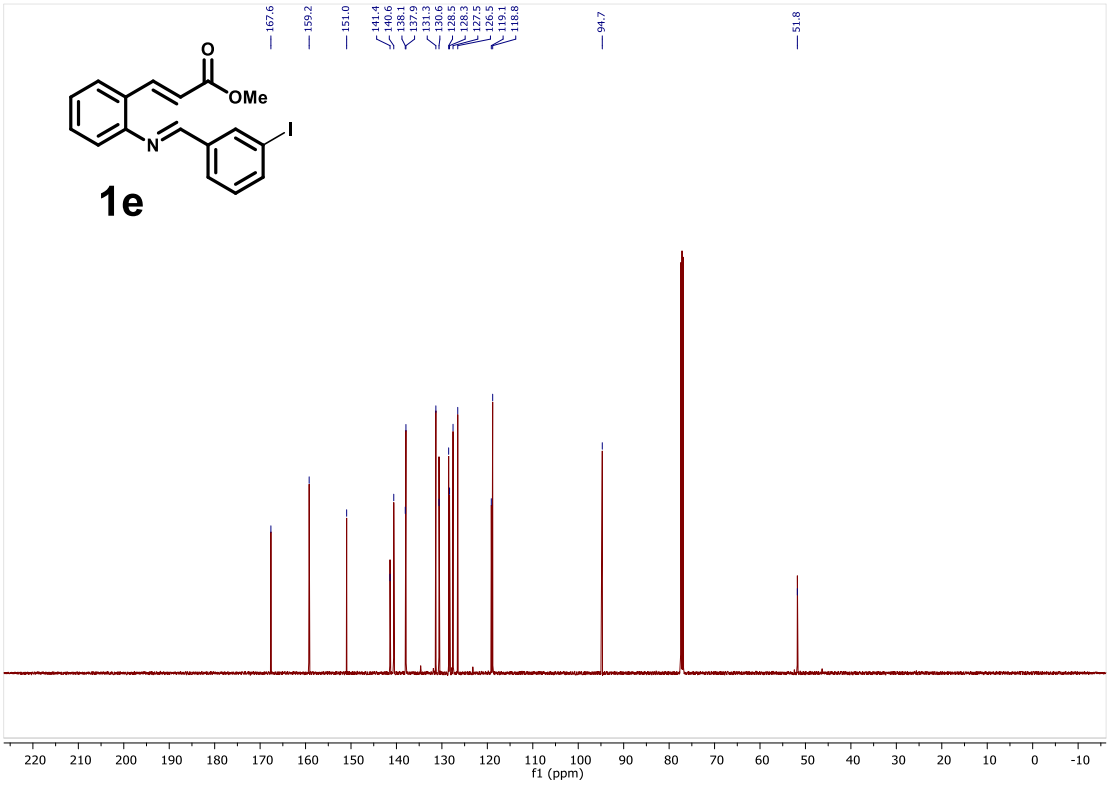
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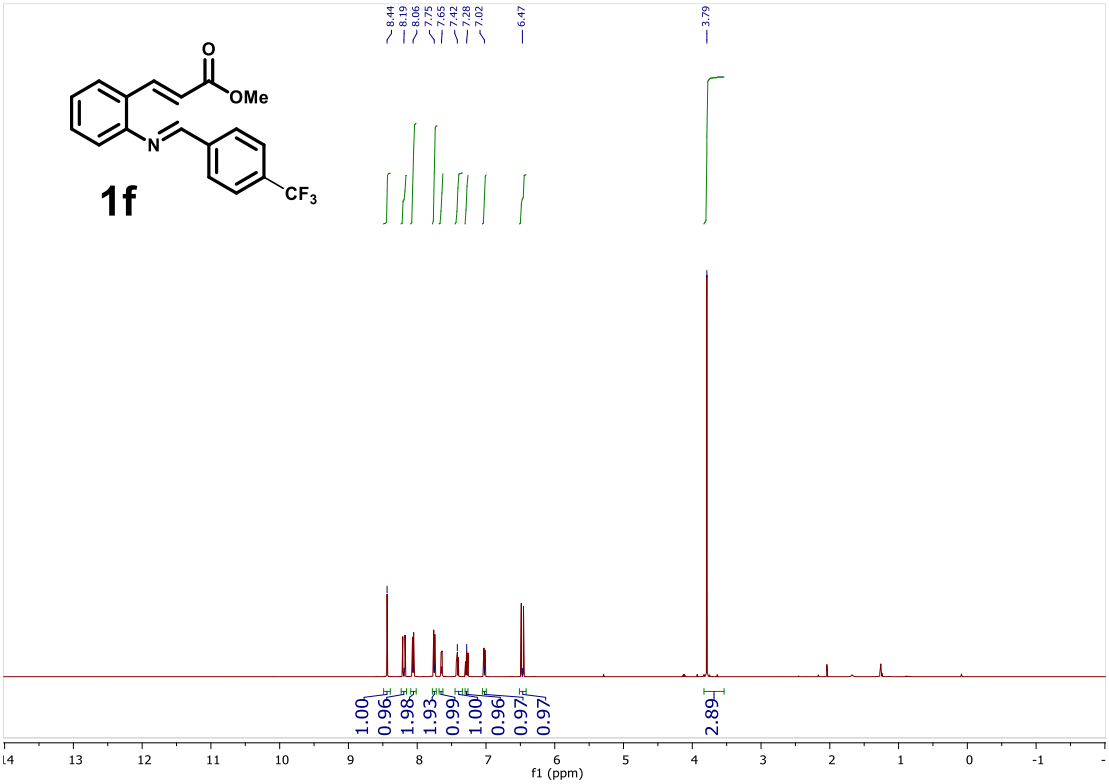
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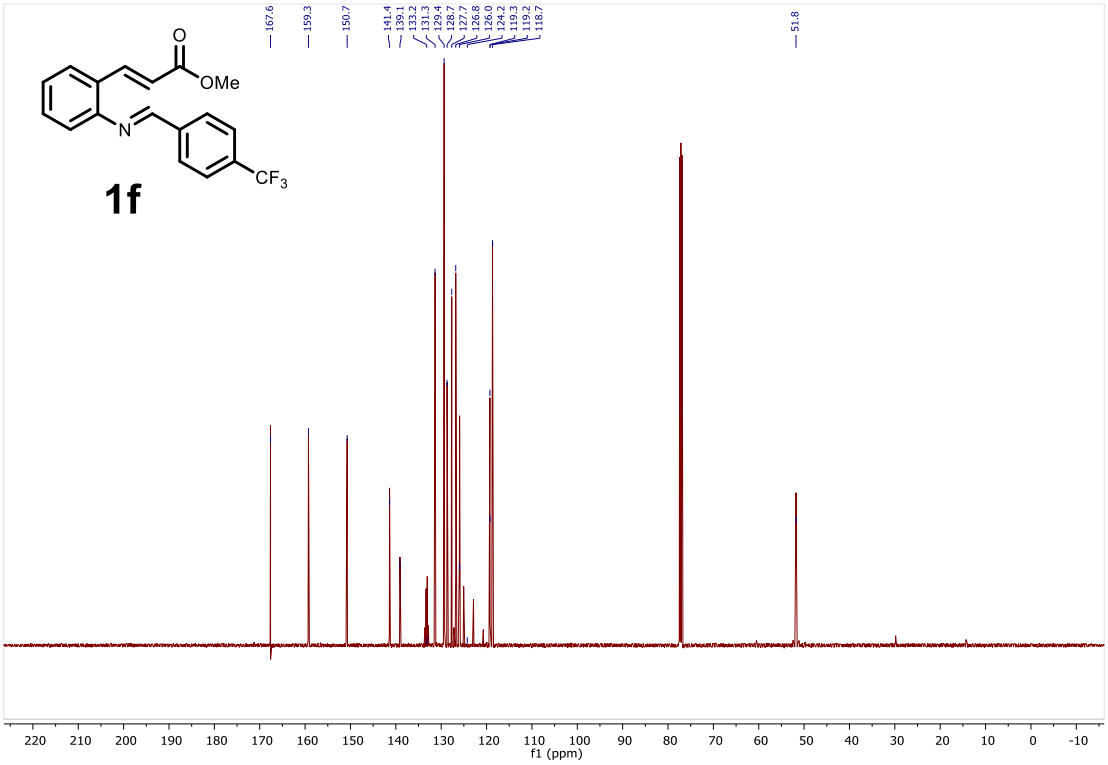
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O
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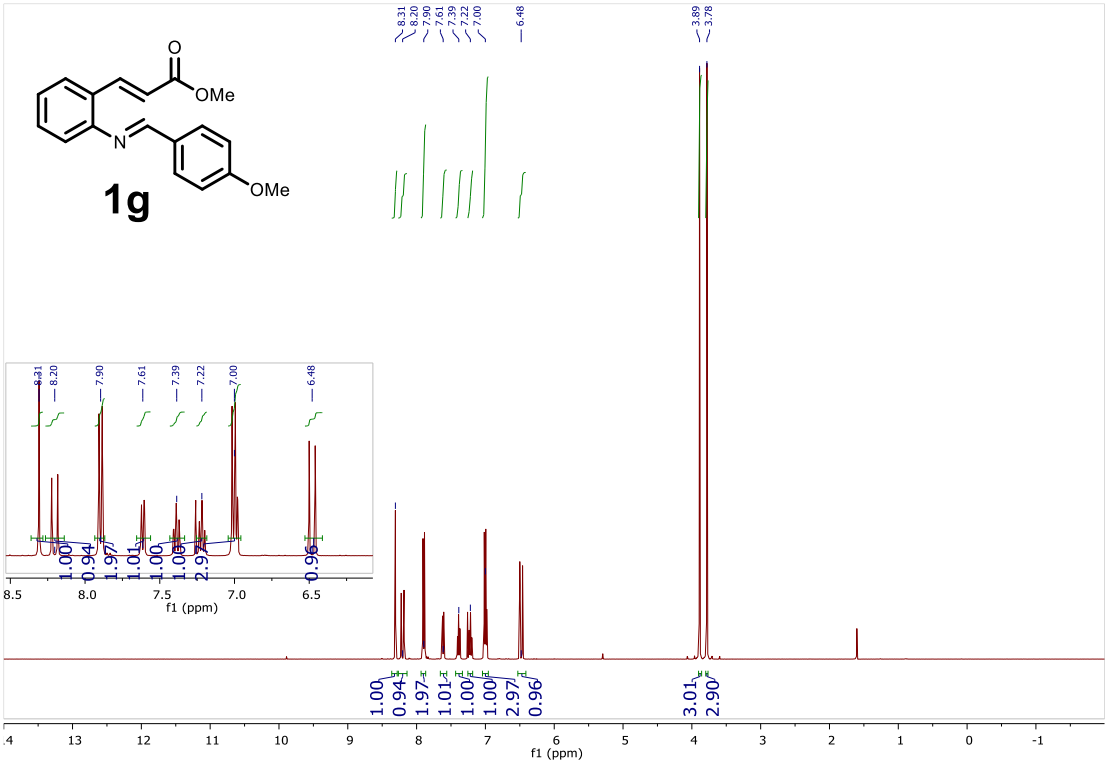
N
CF3
1f
f1 (ppm)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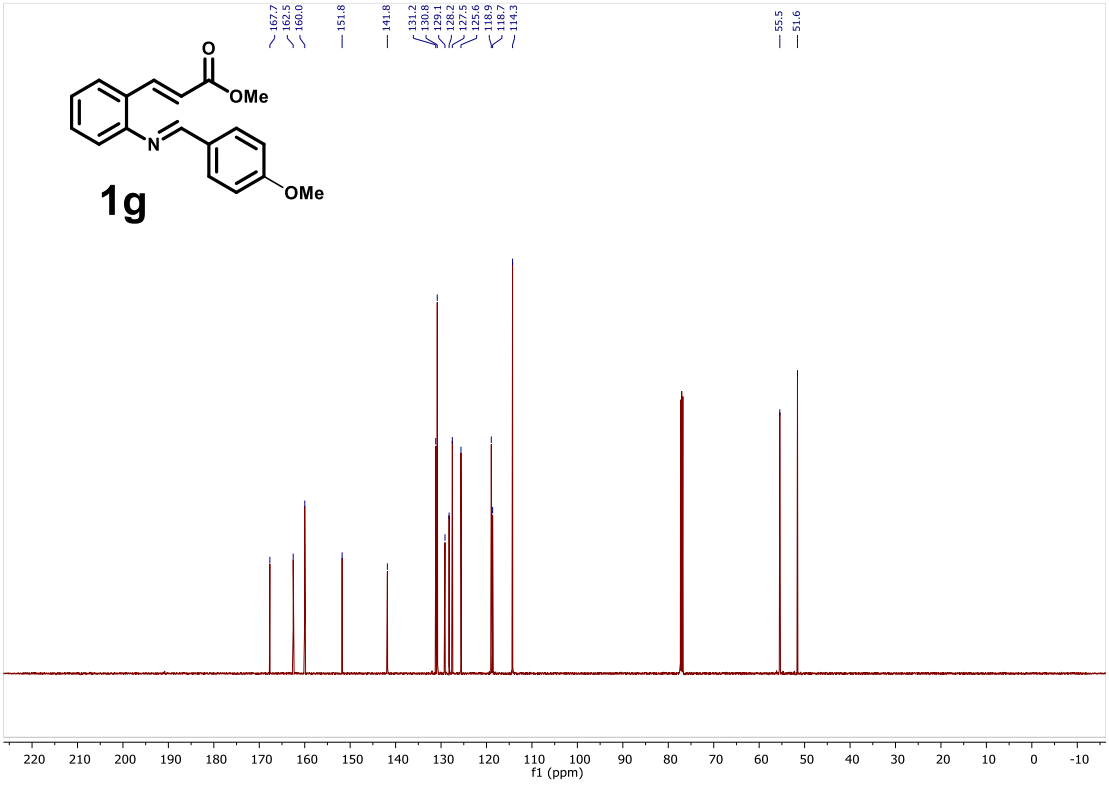
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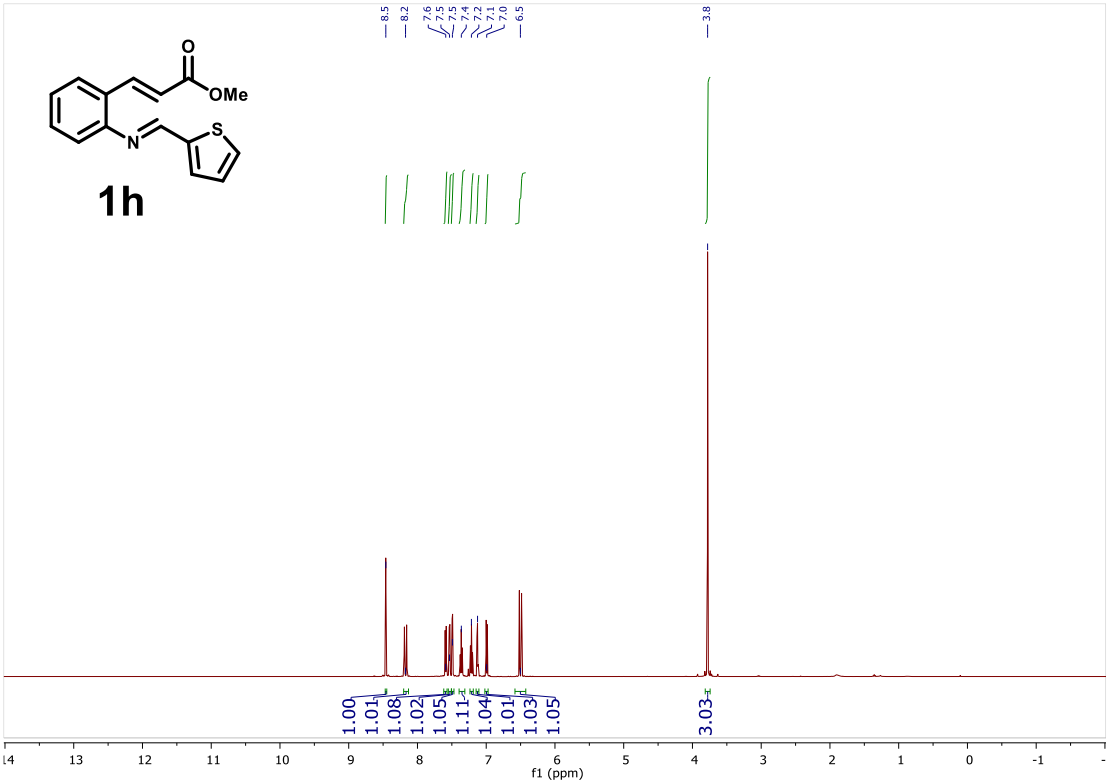
51.6
f1 (ppm)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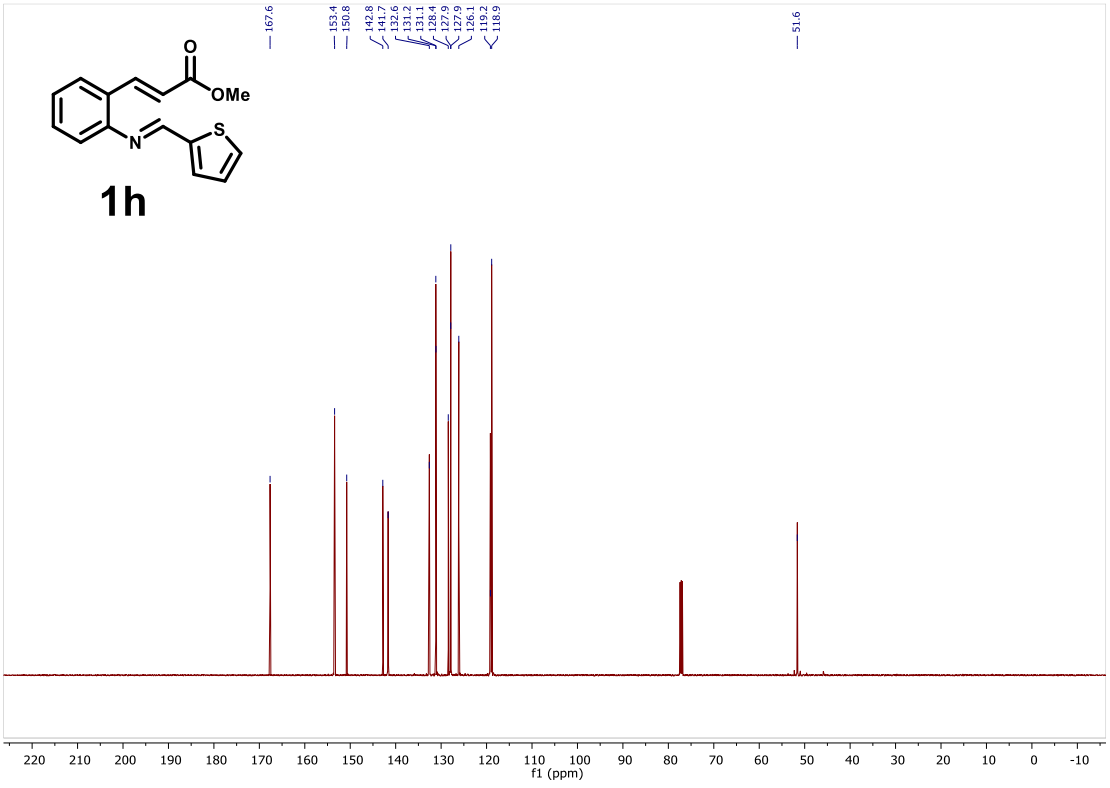
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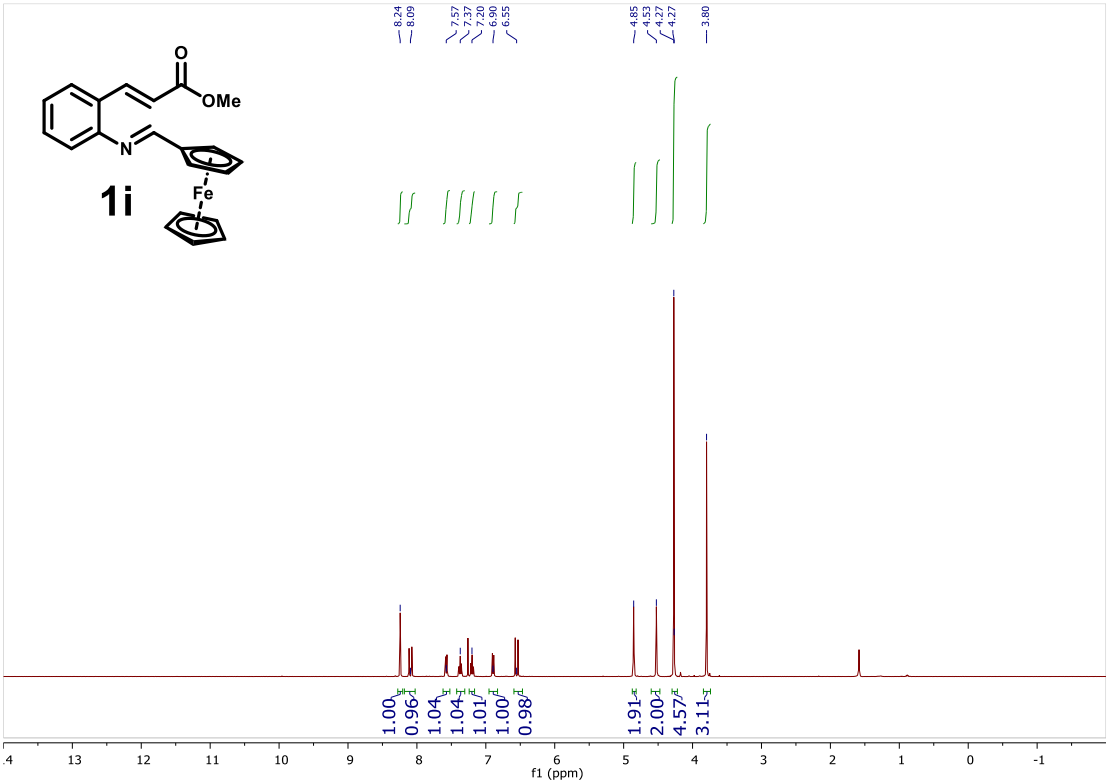
119.2
118.9
51.6
f1 (ppm)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8.09
7.57
7.37
7.20
6.90
6.55
4.85
4.53
4.37
4.27
3.80
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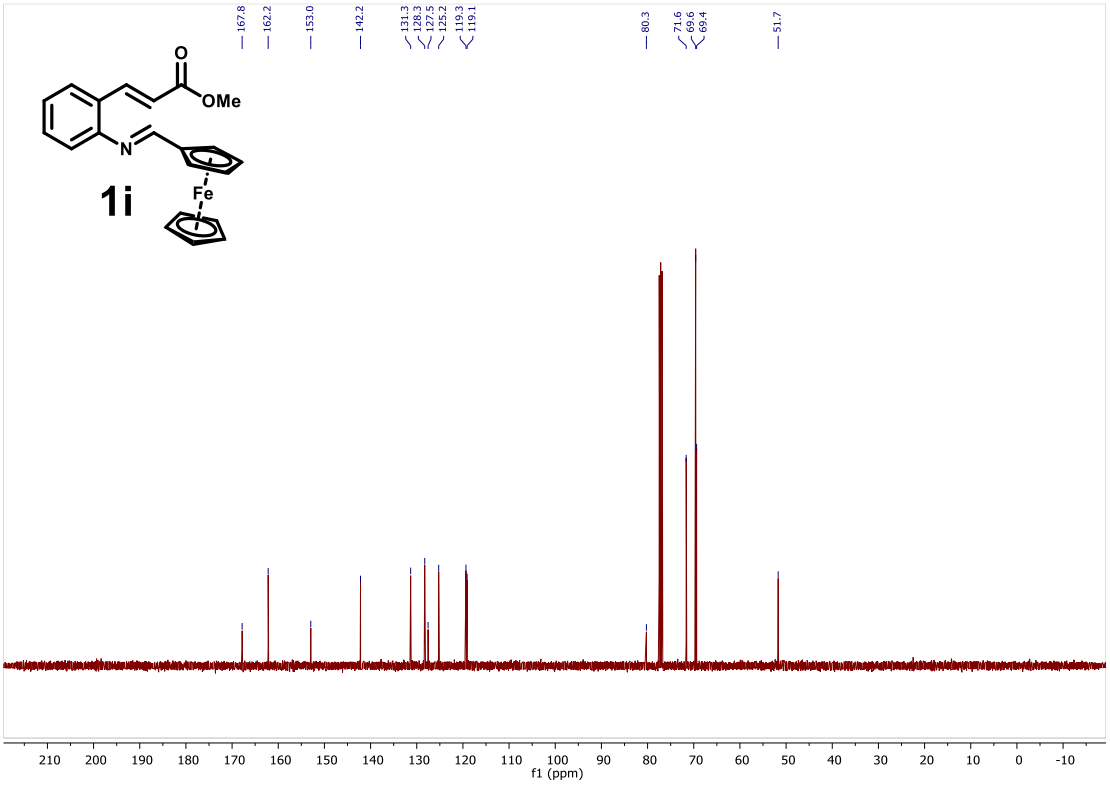
0.96
1.04
1.04
1.01
1.00
0.98
1.91
2.00
4.57
3.11
f1 (ppm)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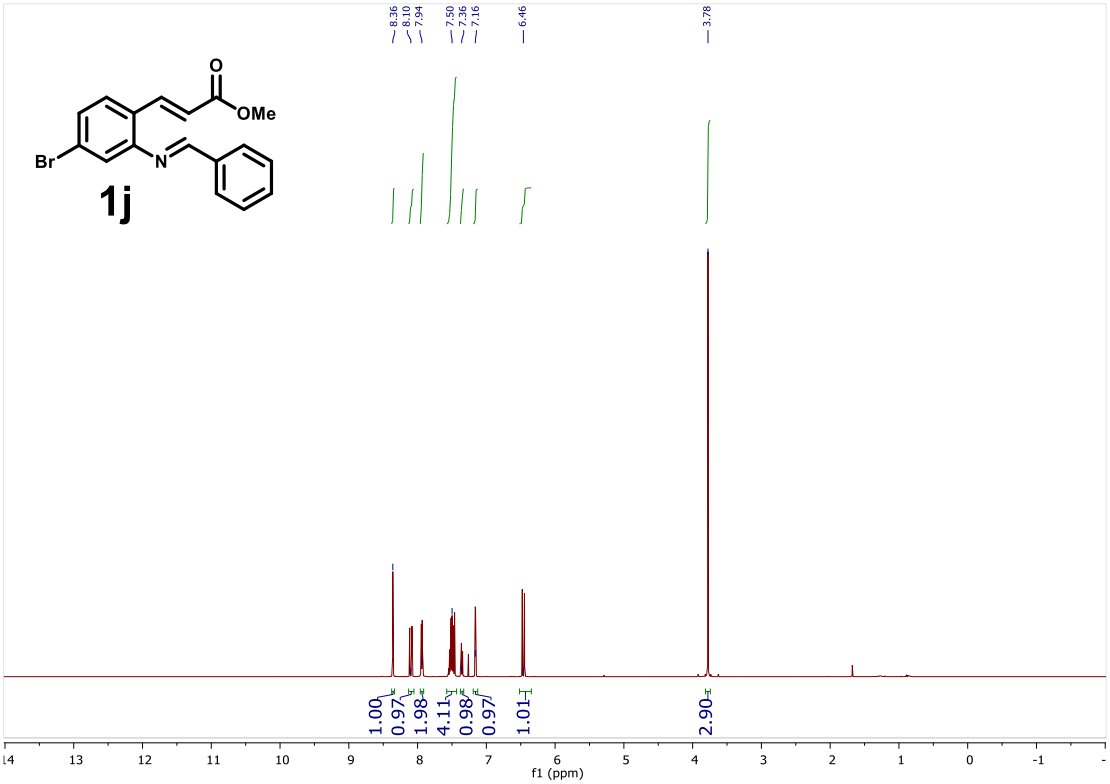
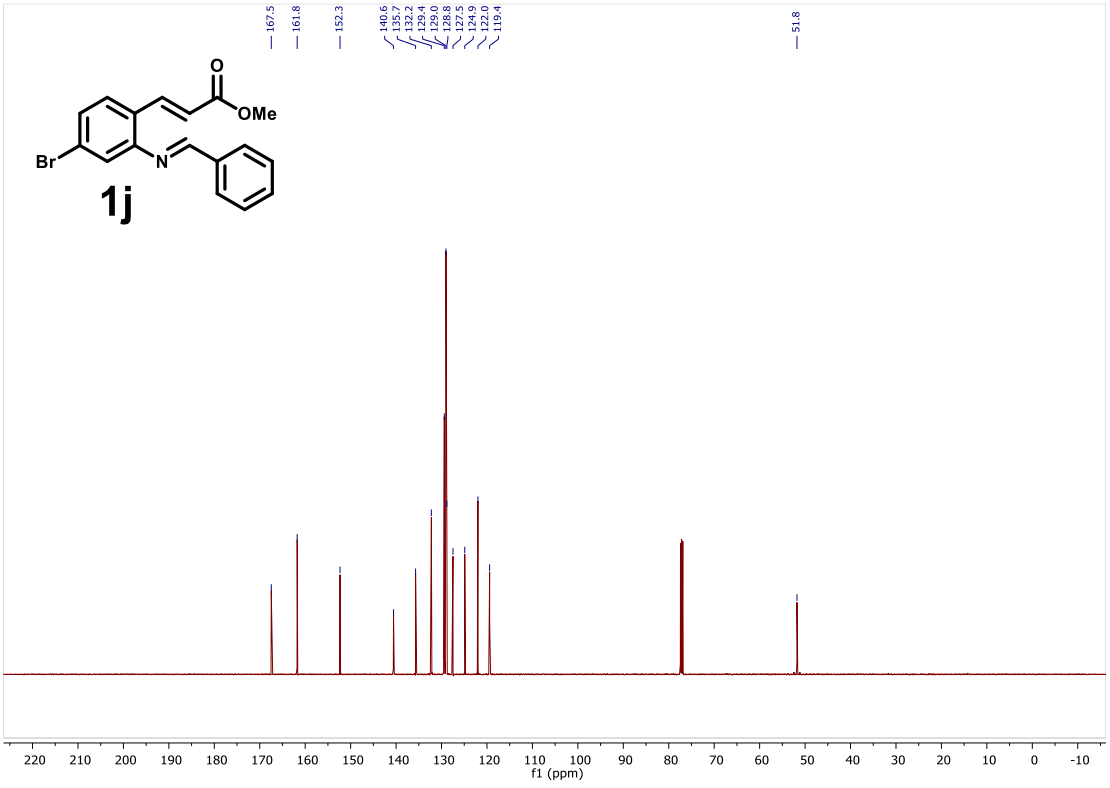
162.2
153.0
142.2
131.3
128.3
127.5
125.2
119.3
119.1
80.3
71.6
69.6
69.4
51.7
f1 (ppm)


8.36
8.10
7.94
7.50
7.36
7.16
6.46
3.78
O
OMe
Br
N
1j
1.00
0.97
1.98
4.11
0.98
0.97
1.01
2.90
f1 (ppm)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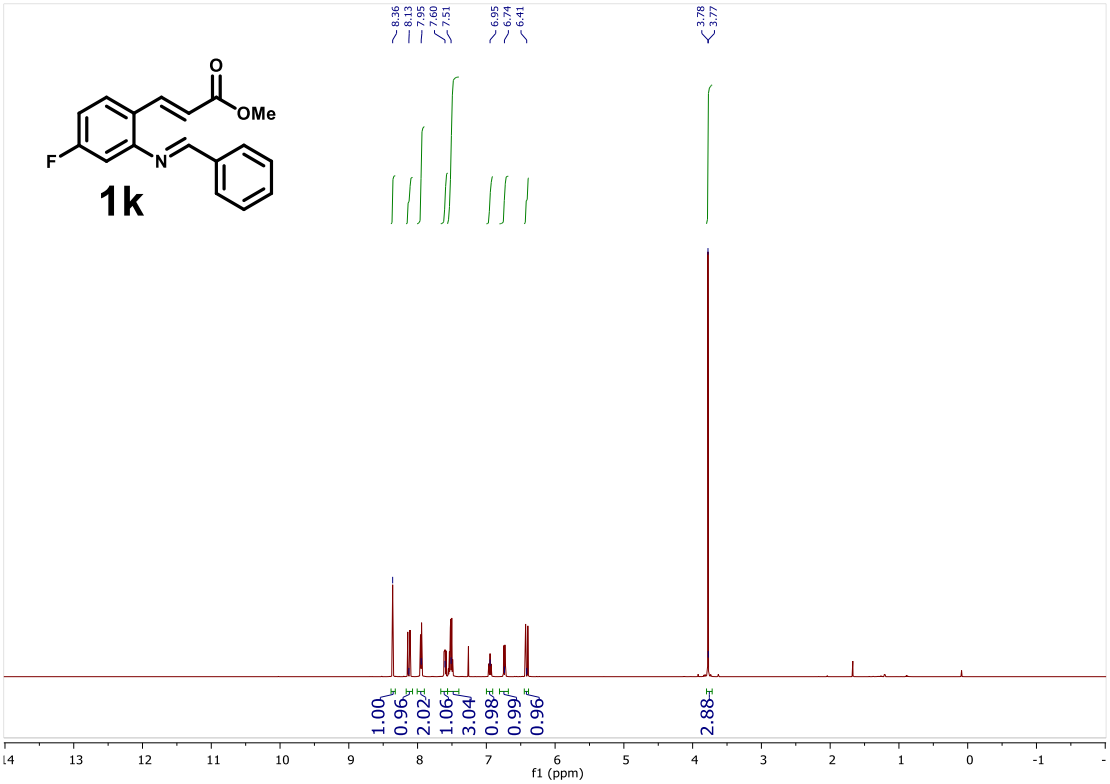
161.8
152.3
140.6
135.7
132.2
130.4
129.0
128.8
127.5
124.9
122.0
119.4
51.8
O
OMe
Br
N
1j
f1 (ppm)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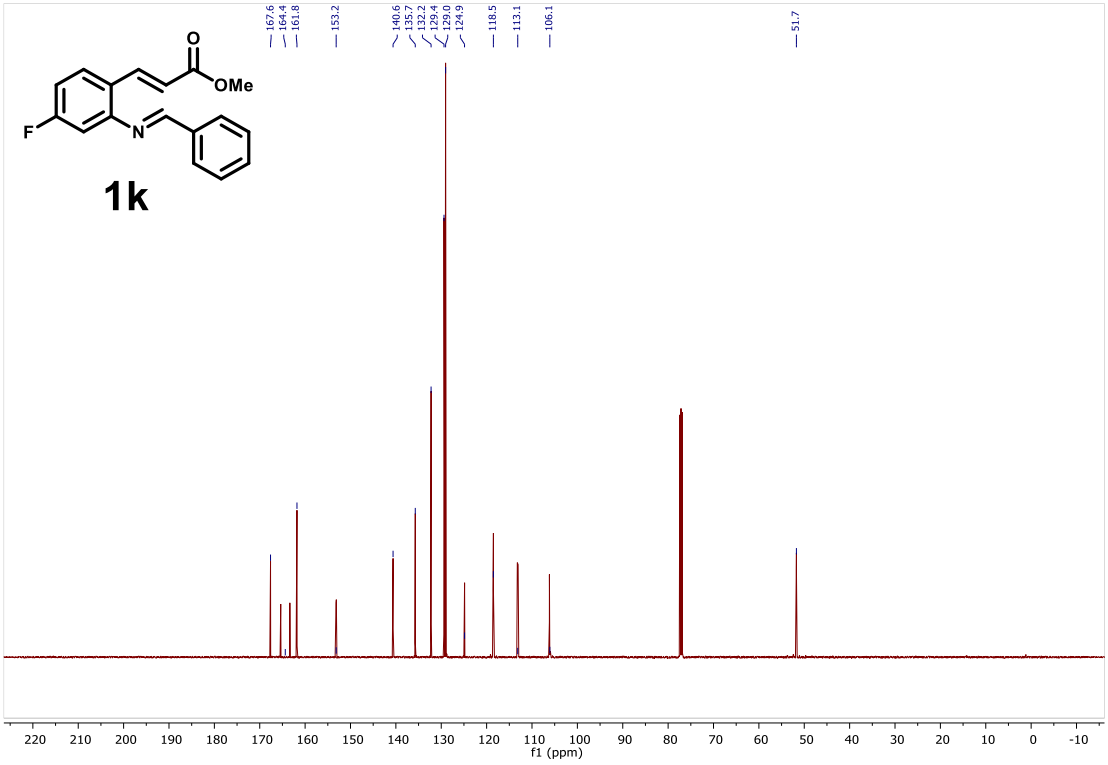
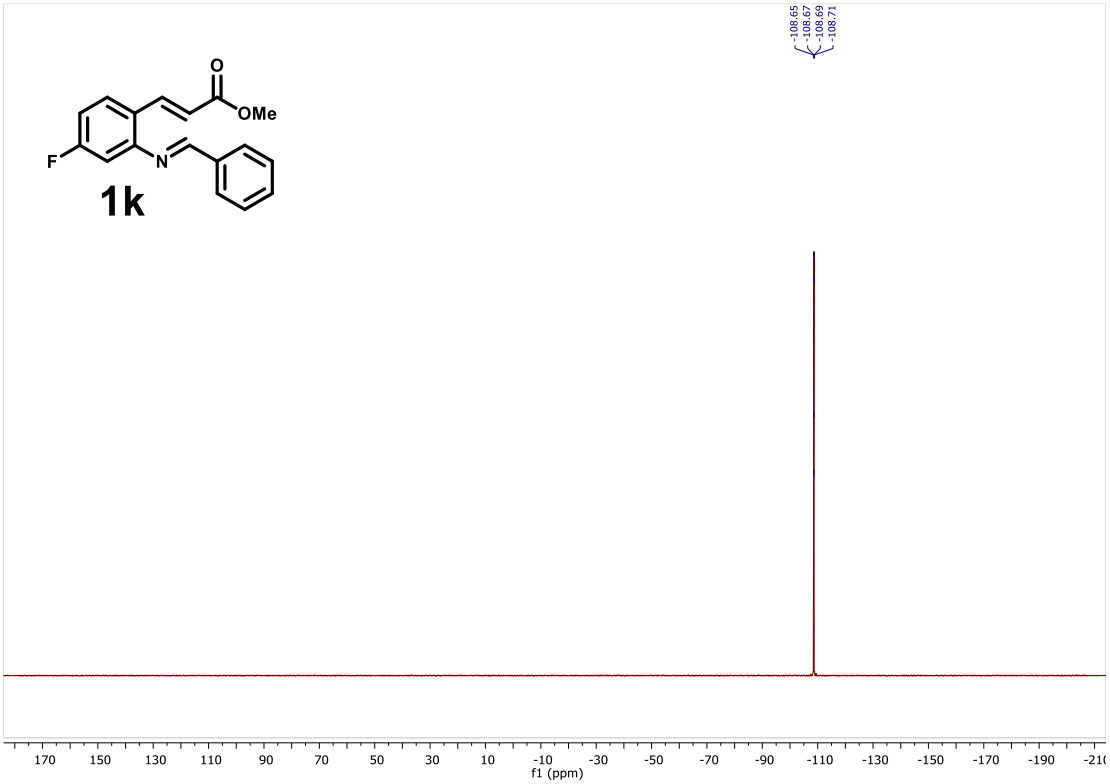
8.13
7.95
7.60
7.51
6.95
6.74
6.41
3.78
3.77
O
OMe
F
N
1k
1.00
0.96
2.02
1.06
3.04
0.98
0.99
0.96
2.88
f1 (ppm)


167.6
164.4
161.8
153.2
140.6
135.7
132.2
129.4
129.0
124.9
118.5
113.1
106.1
51.7
O
OMe
F
N
1k
f1 (ppm)


O
OMe
F
N
1k
-108.65
-108.67
-108.69
-108.71
170
150
130
110
90
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-10
-30
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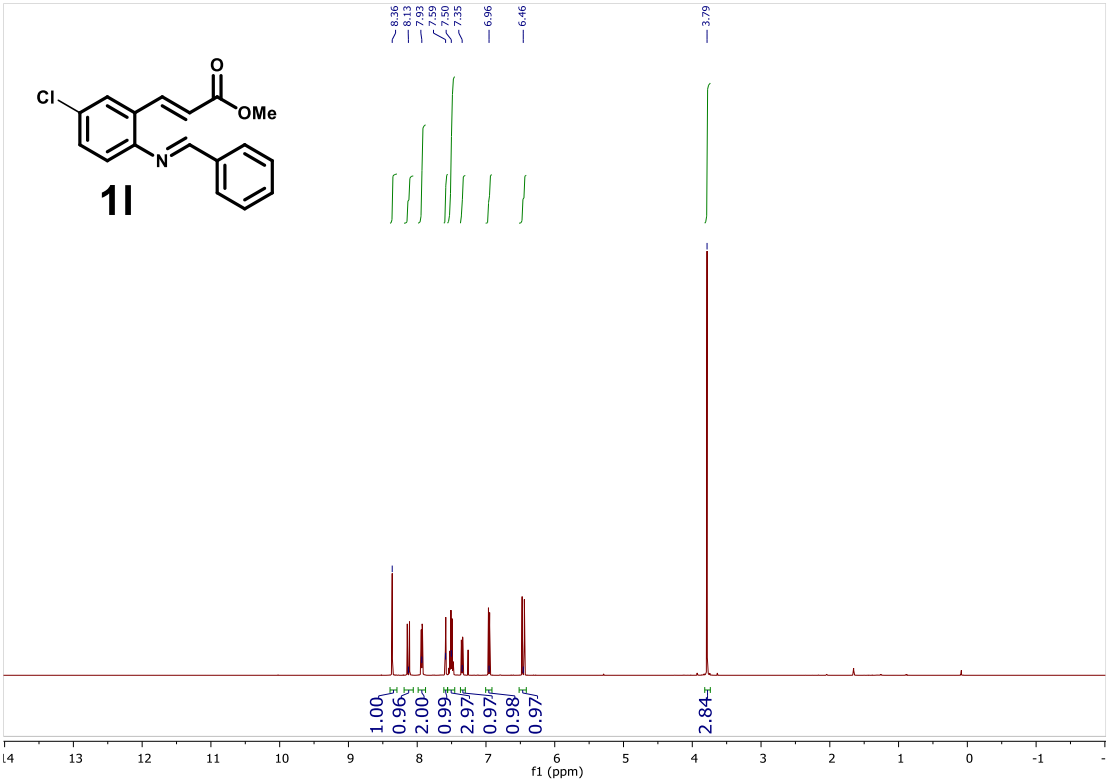
-90
-110
-130
-150
-170
-190
f1 (ppm)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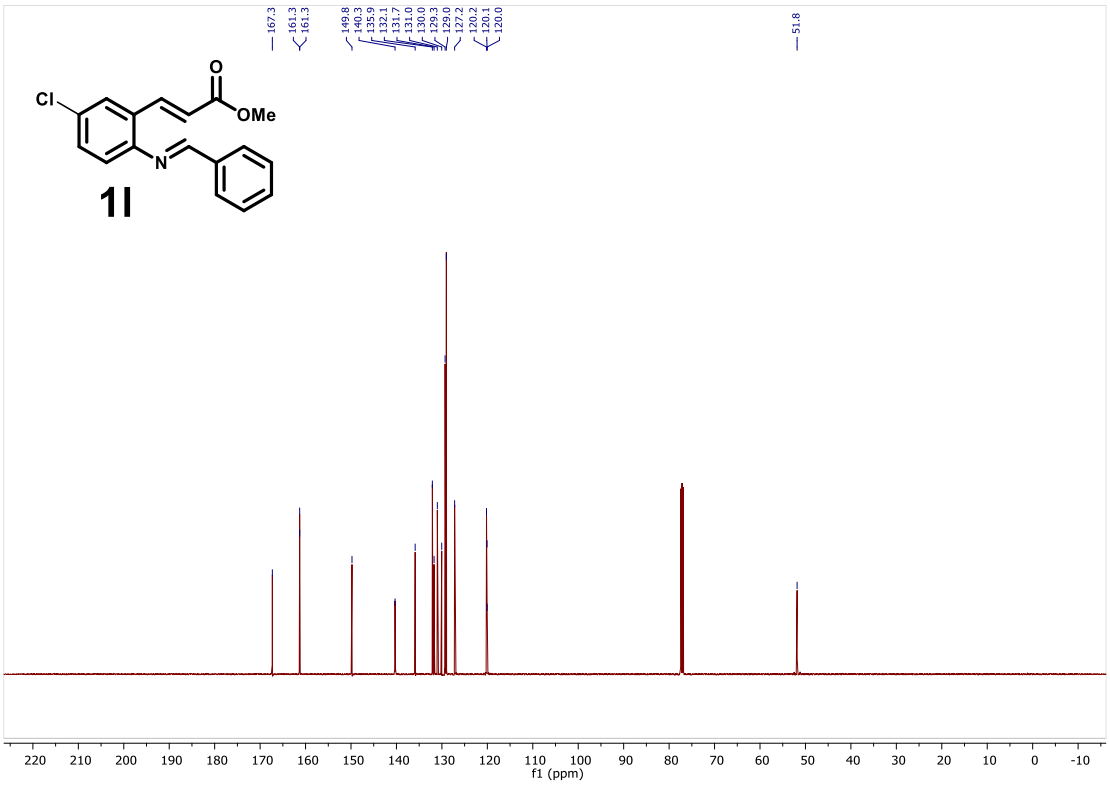
8.33
7.93
7.59
7.50
7.35
6.96
6.46
3.79
Cl
O
OMe
N
1l
1.00
0.96
2.00
0.99
2.97
0.97
0.98
0.97
2.84
f1 (ppm)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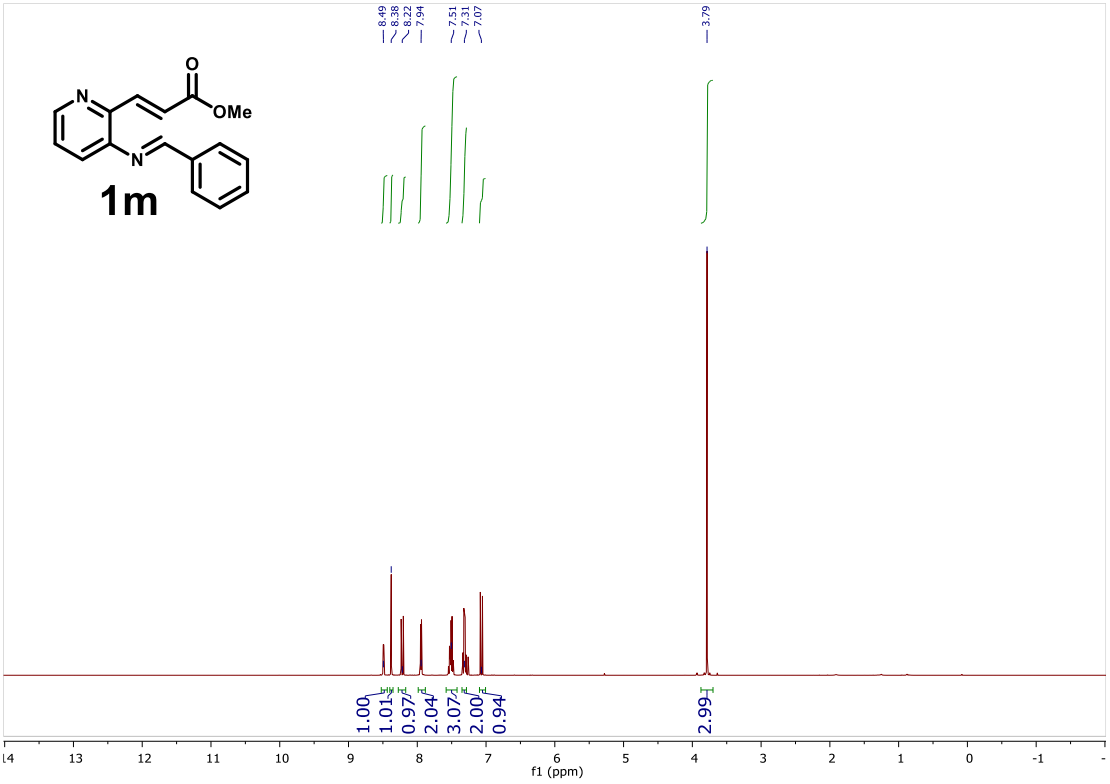
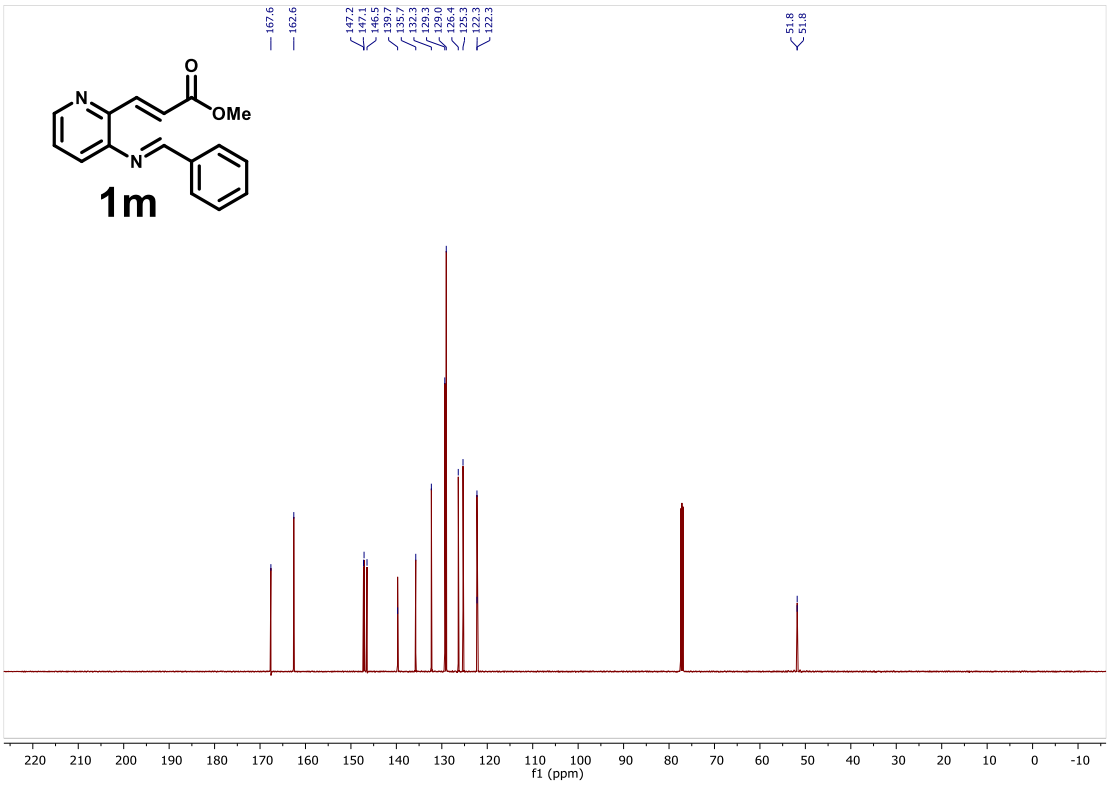
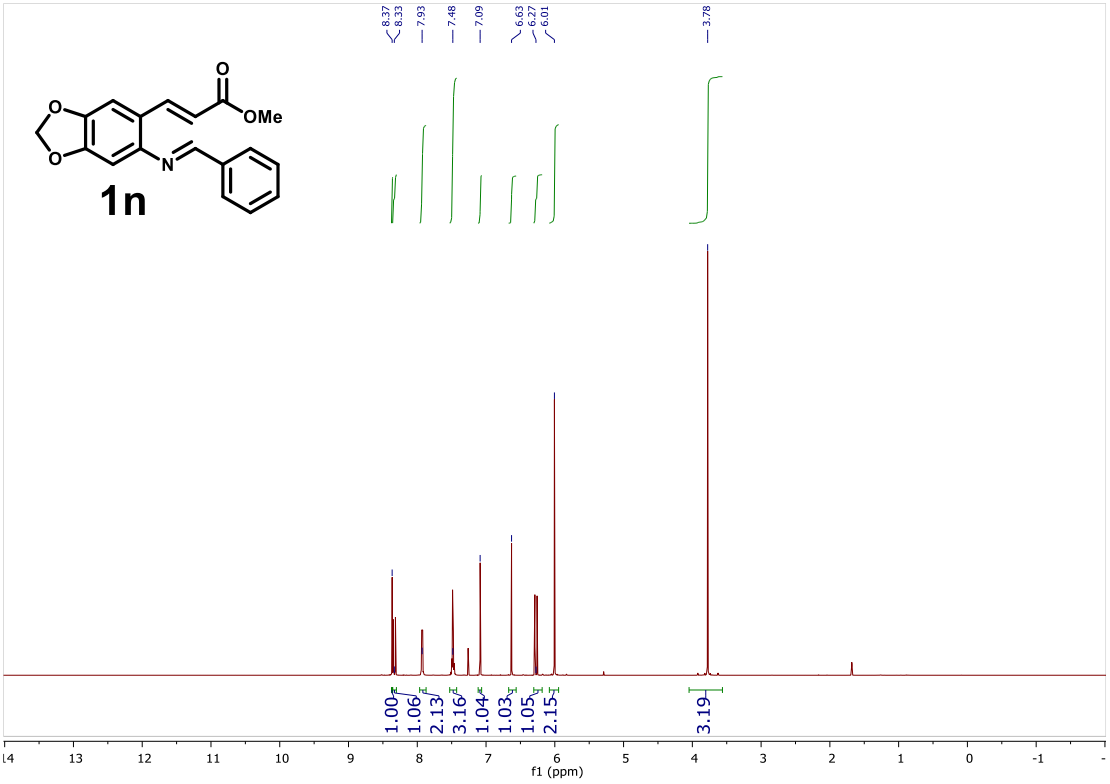
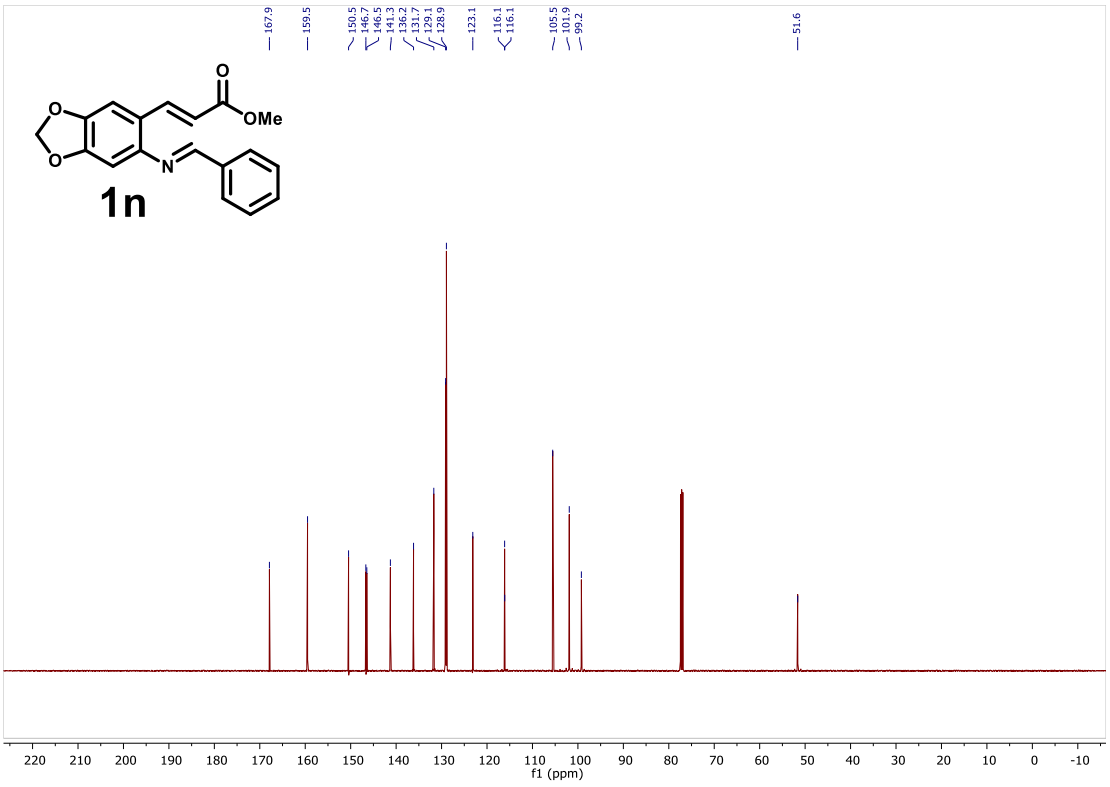
161.3
161.3
149.8
140.3
135.9
132.1
131.7
131.0
130.0
129.3
129.0
127.2
120.2
120.1
120.0
51.8
Cl
O
OMe
N
1l
f1 (ppm)


8.49
8.38
8.23
7.94
7.51
7.31
7.07
3.79
1.00
1.01
0.97
2.04
3.07
2.00
0.94
2.99
f1 (ppm)
1m


167.6
162.6
147.2
147.1
146.5
139.7
135.7
132.3
129.3
129.0
126.4
125.3
122.3
122.3
51.8
51.8
f1 (ppm)
1m


8.37
8.33
7.93
7.48
7.09
6.63
6.27
6.01
3.78
O
OMe
O
O
N
1n
1.00
1.06
2.13
3.16
1.04
1.03
1.05
2.15
3.19
f1 (ppm)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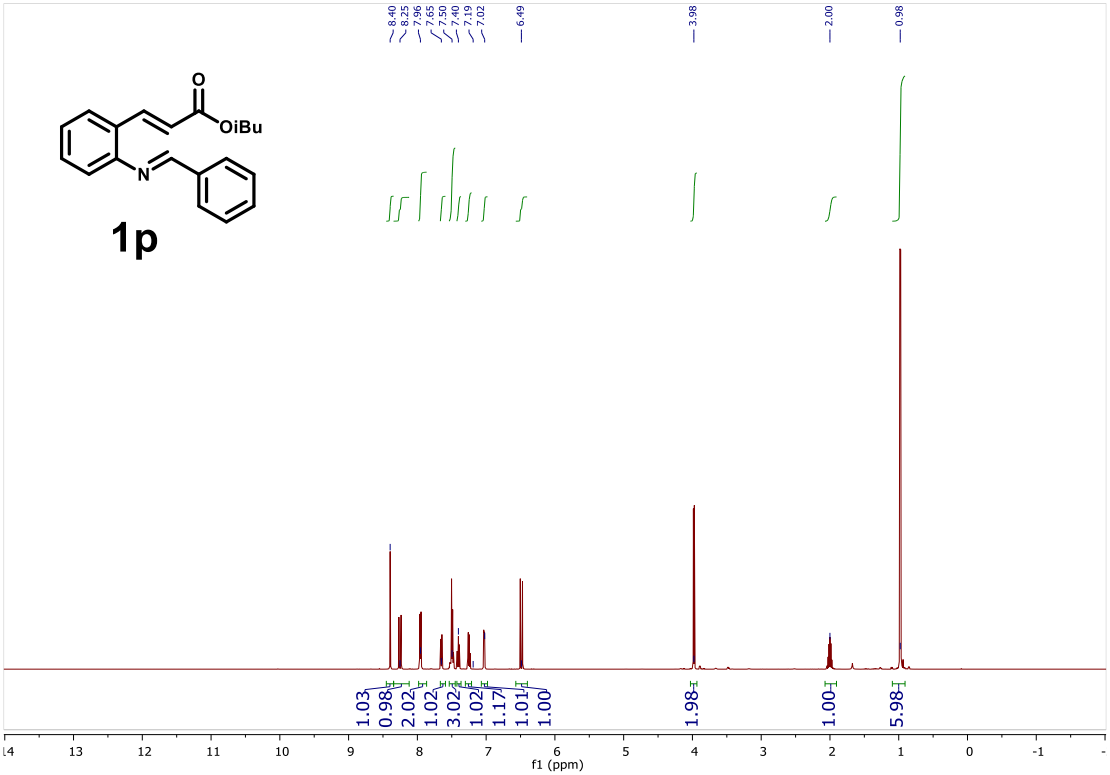
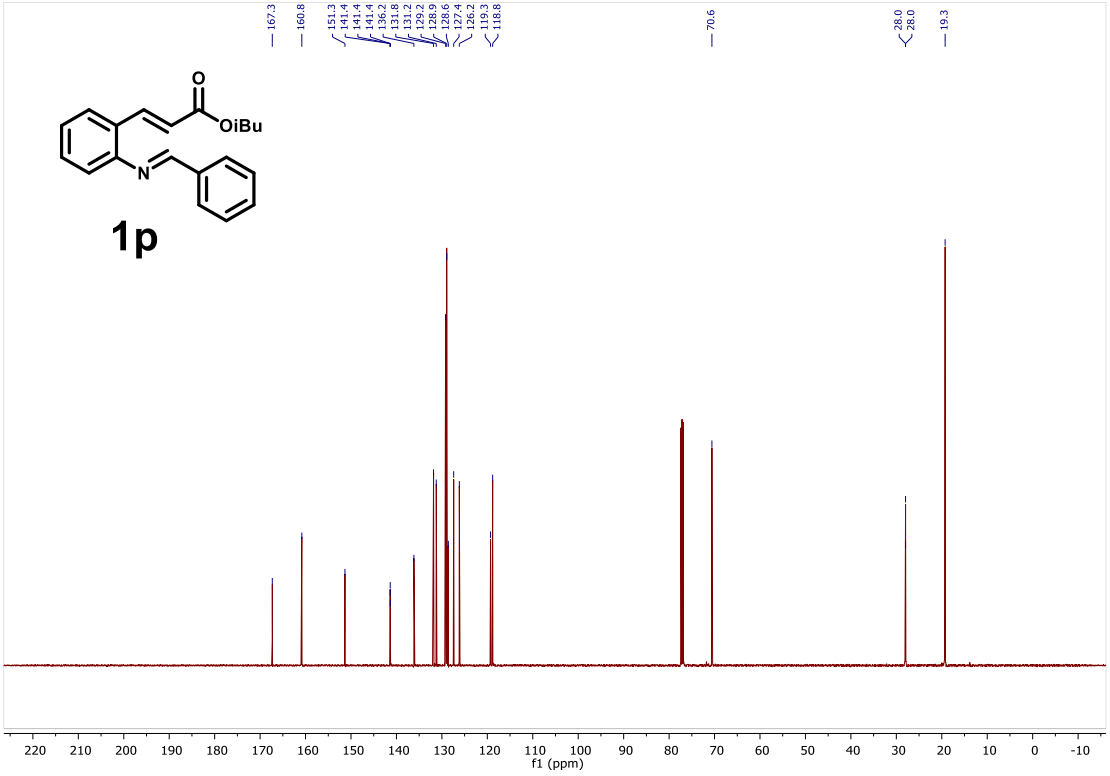
159.5
150.5
146.7
146.5
141.3
136.2
131.7
129.1
128.9
123.1
116.1
116.1
105.5
101.9
99.2
51.6
O
OMe
O
O
N
1n
f1 (ppm)


8.40
8.25
7.96
7.65
7.50
7.40
7.19
7.02
6.49
3.98
2.00
0.98
O
OiBu
N
1p
1.03
0.98
2.02
1.02
3.02
1.02
1.17
1.01
1.00
1.98
1.00
5.98
f1 (ppm)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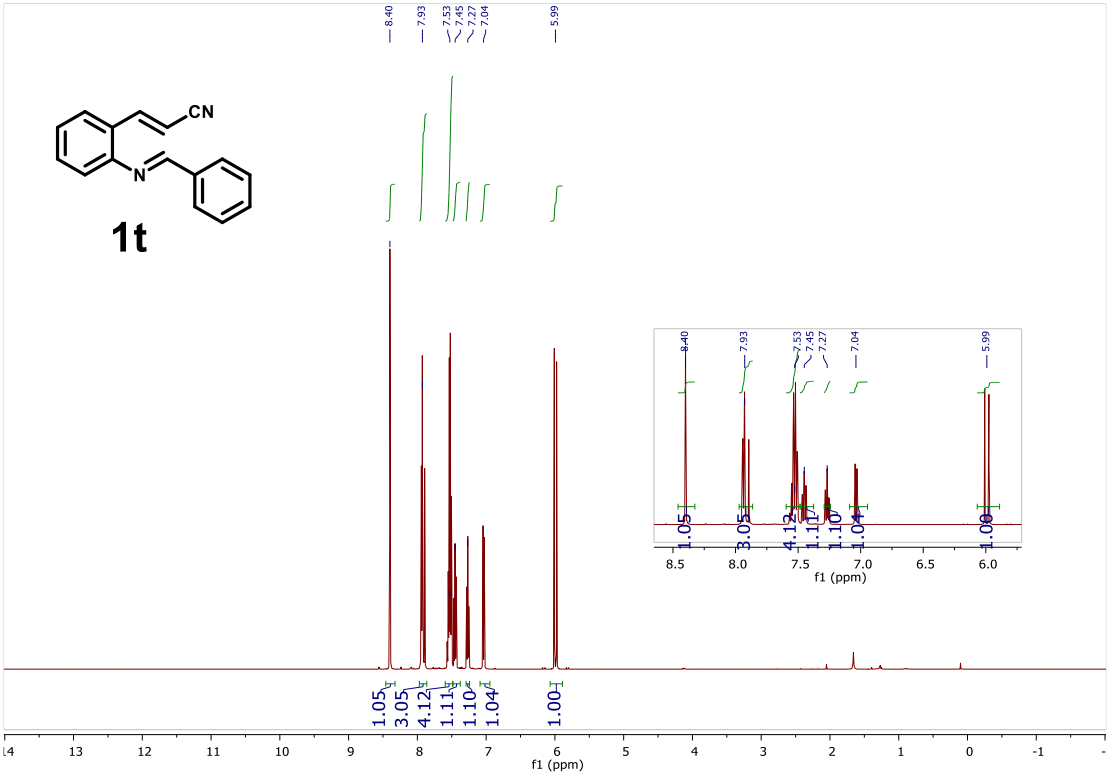
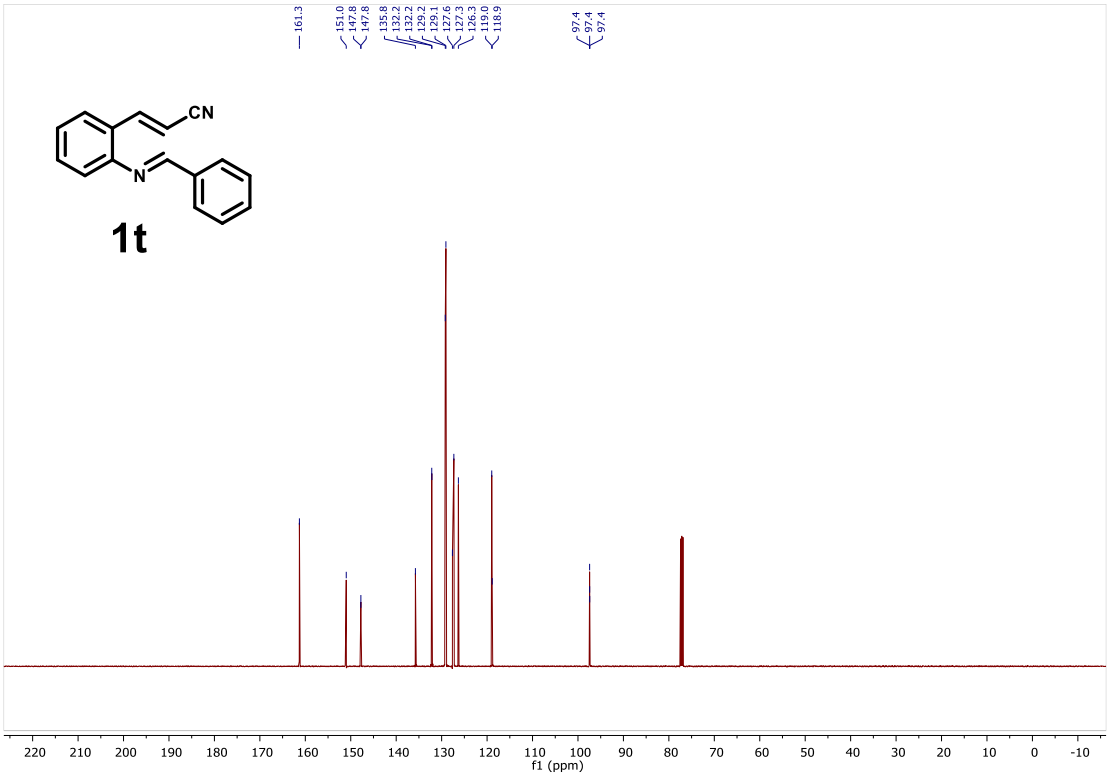
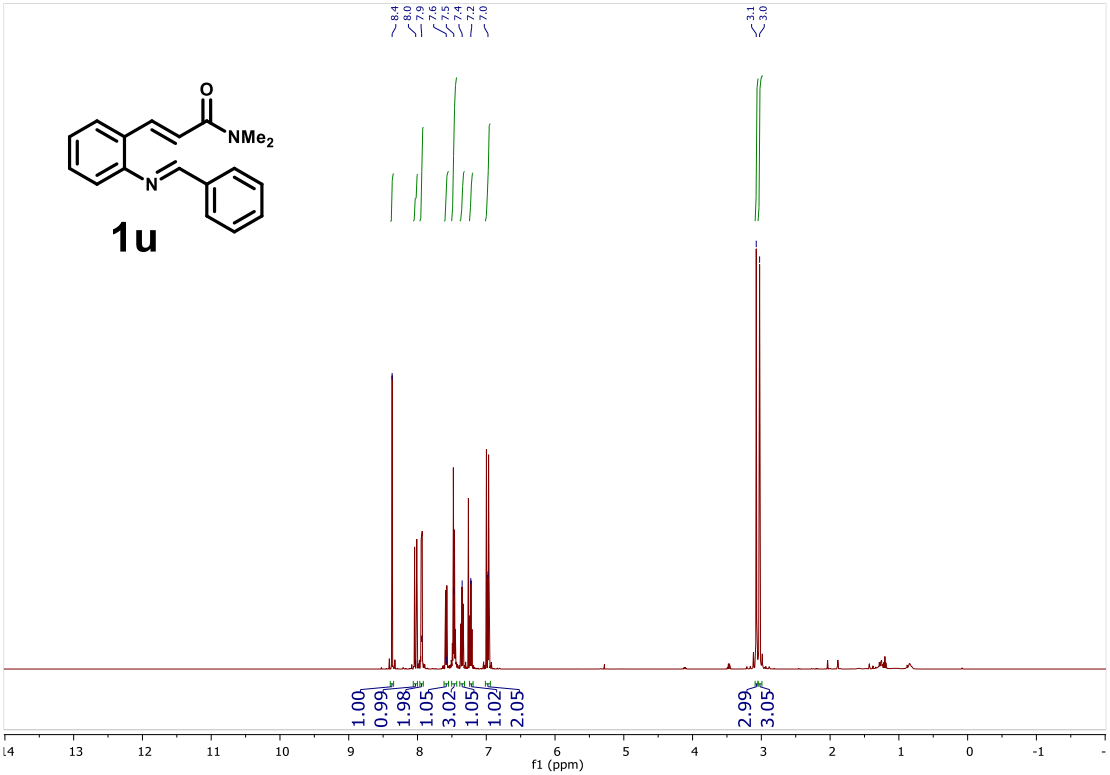
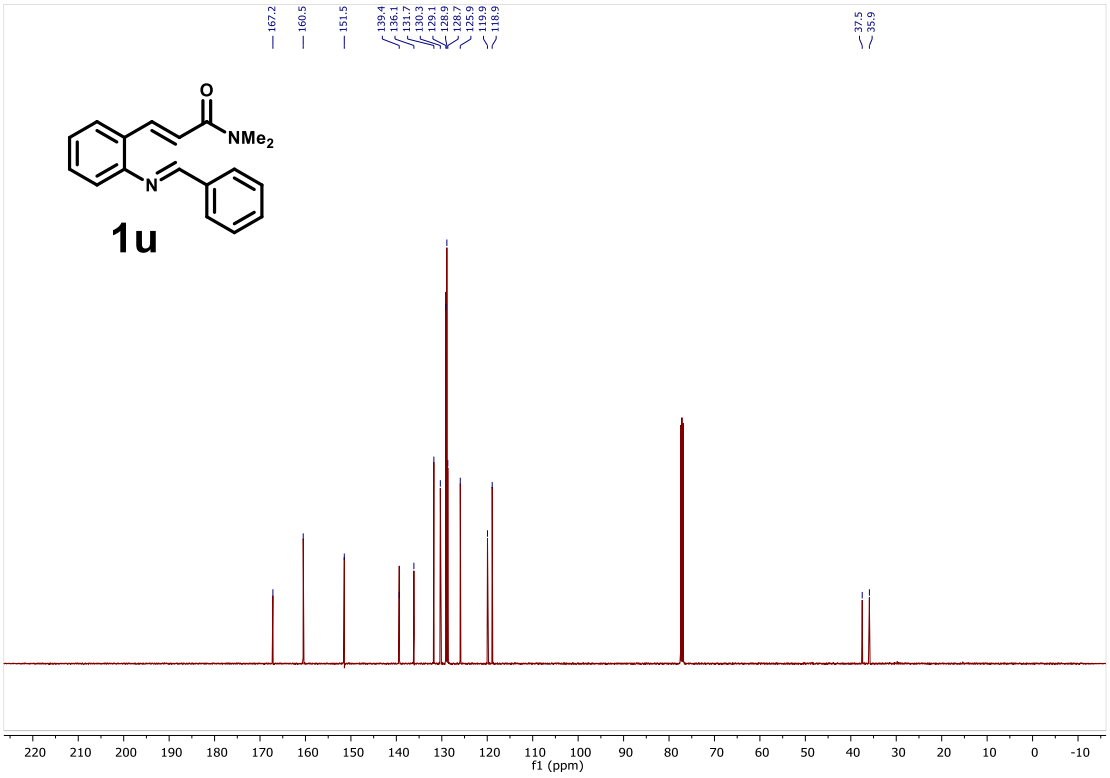
160.8
151.3
141.4
141.4
141.4
136.2
131.8
131.2
129.2
128.9
128.6
127.4
126.2
119.3
118.8
70.6
28.0
28.0
19.3
O
OiBu
N
1p
f1 (ppm)


8.40
7.93
7.53
7.45
7.27
7.04
5.99
CN
N
1t
1.05
3.05
4.12
1.11
1.10
1.04
1.00
f1 (ppm)


161.3
151.0
147.8
147.8
135.8
132.2
132.2
129.2
129.1
127.6
127.3
126.3
119.0
118.9
97.4
97.4
97.4
CN
N
1t
f1 (ppm)


8.4
8.0
7.9
7.6
7.5
7.4
7.2
7.0
3.1
3.0
O
NMe2
N
1u
1.00
0.99
1.98
1.05
3.02
1.05
1.02
2.05
2.99
3.05
f1 (ppm)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160.5
151.5
139.4
136.1
131.7
130.3
129.1
128.9
128.7
125.9
119.9
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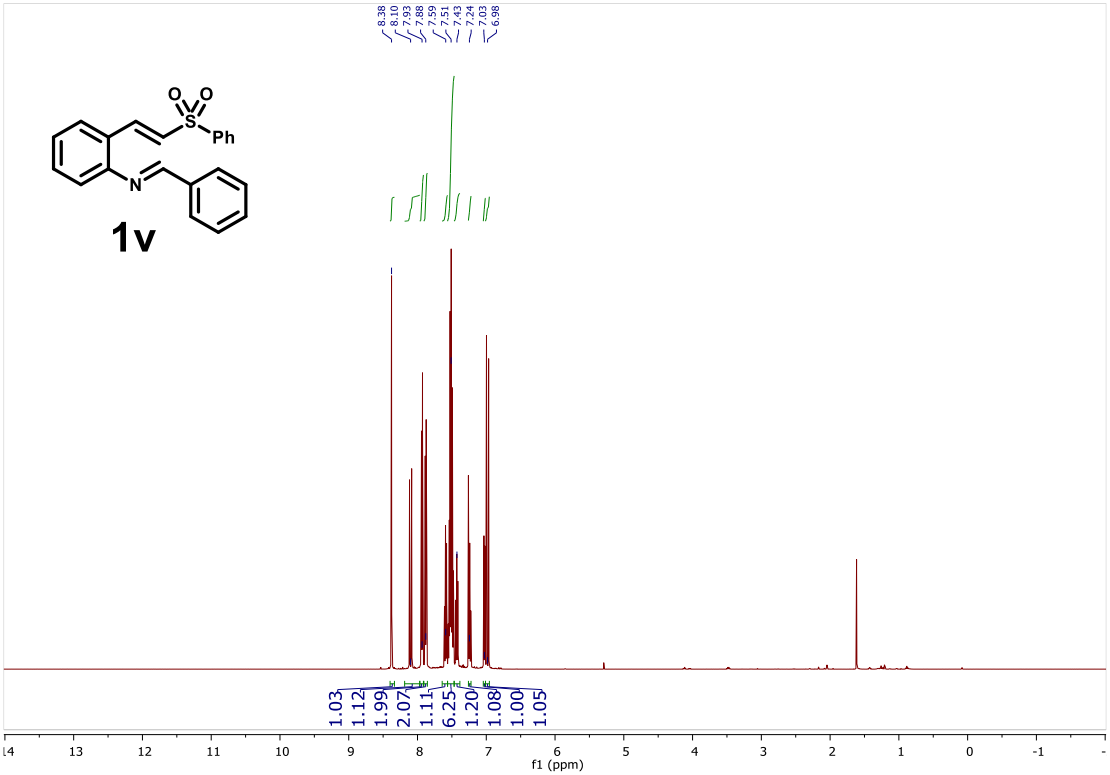
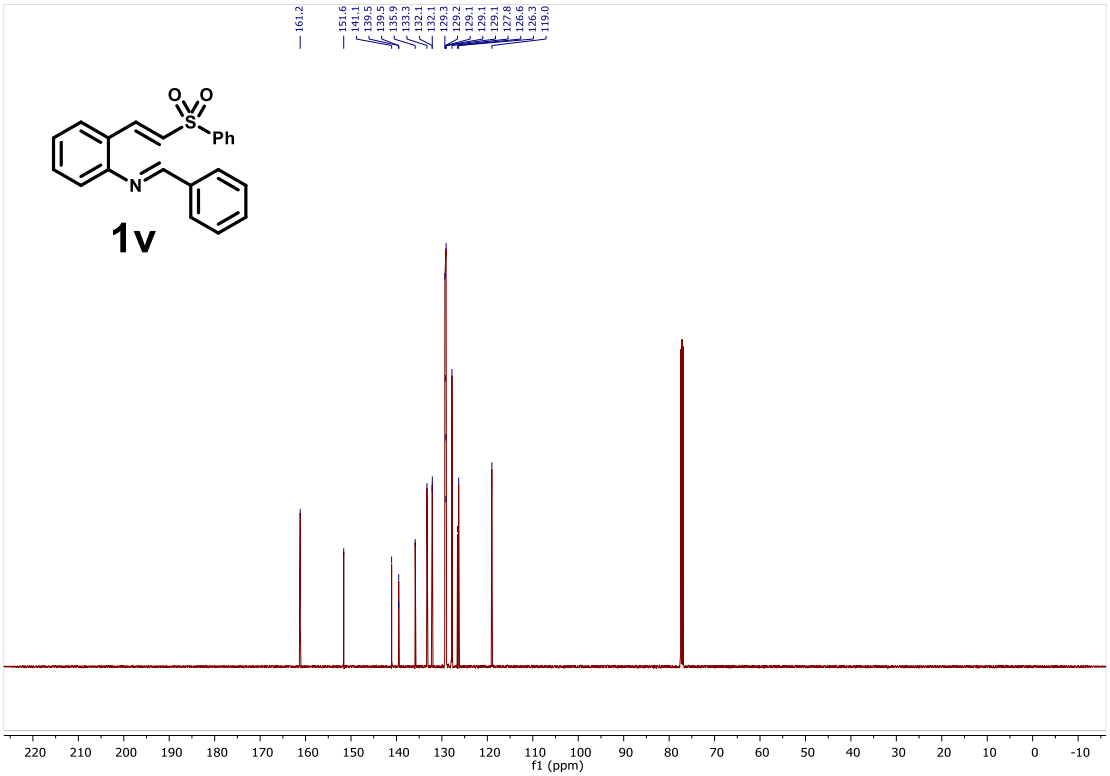
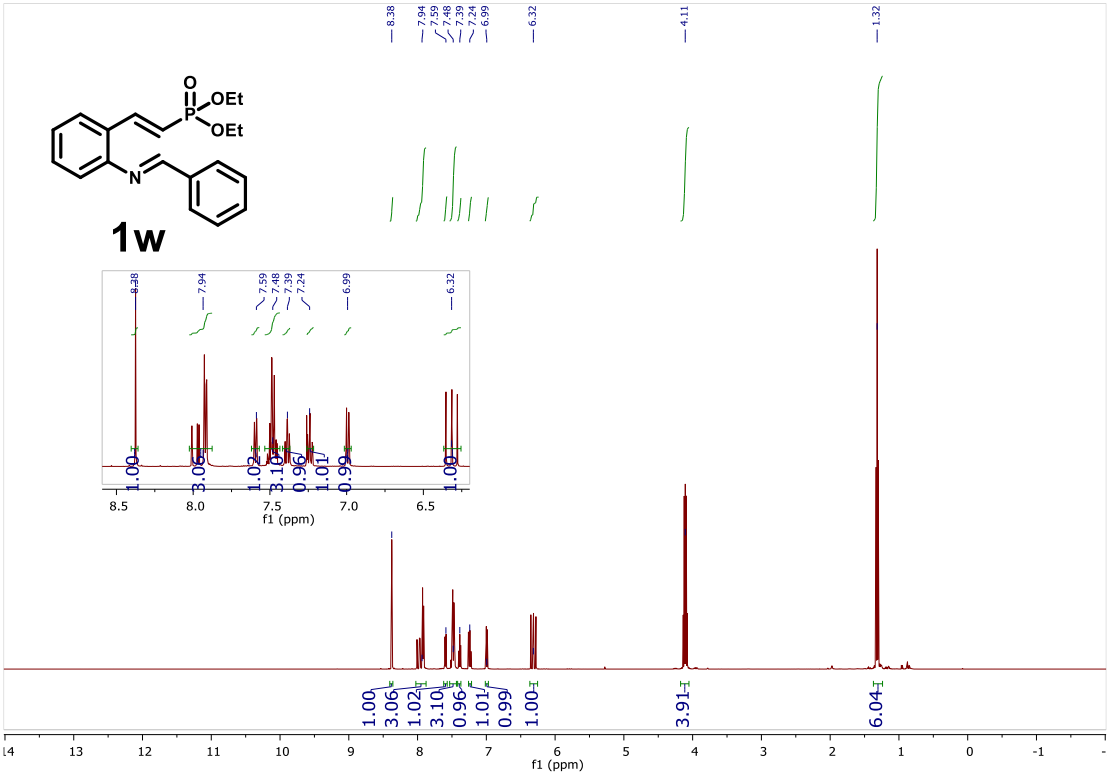
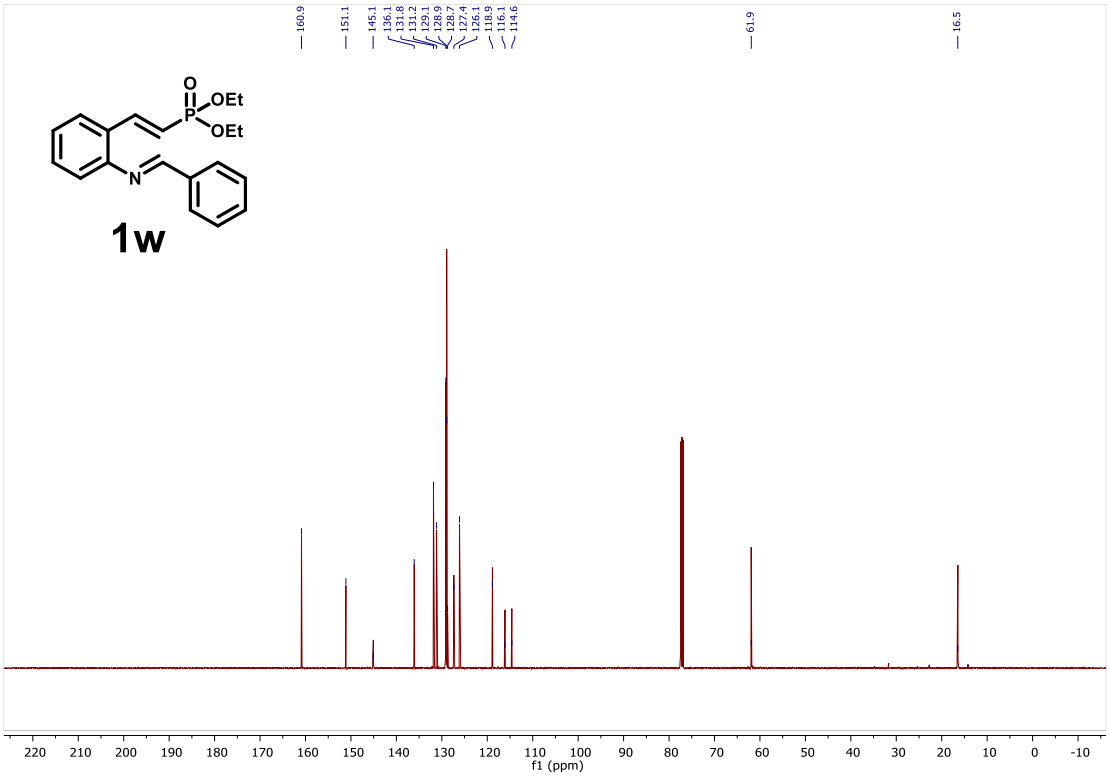
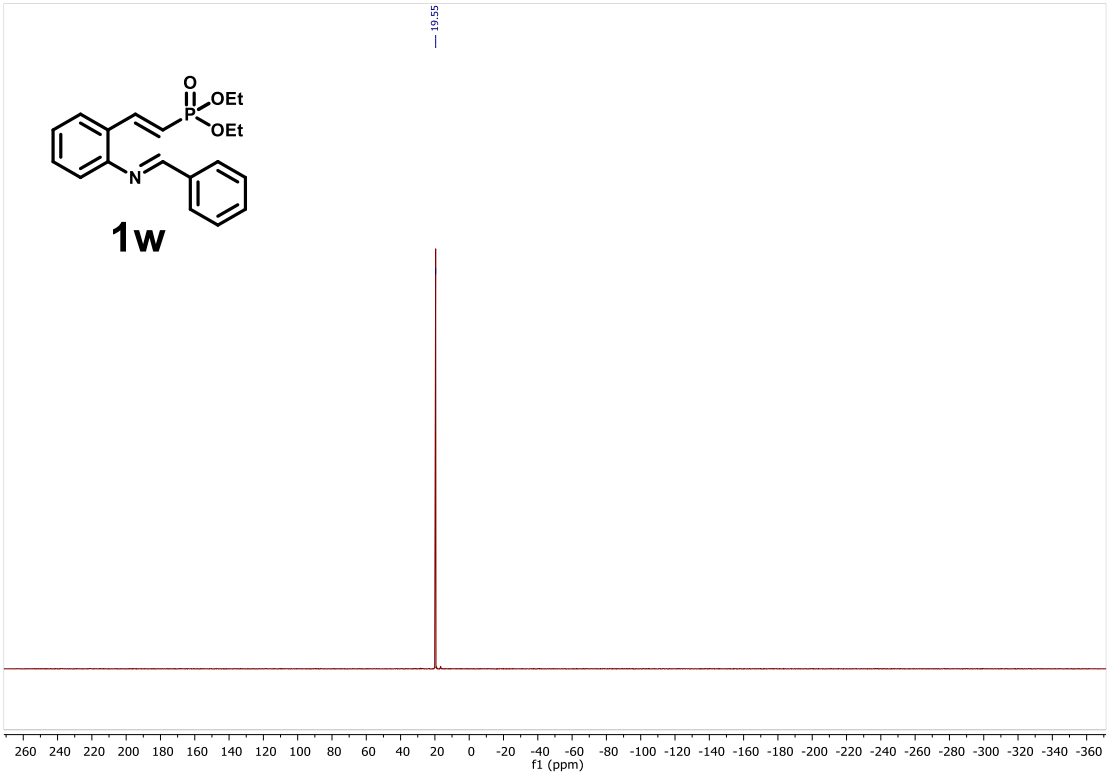
35.9
O
NMe2
N
1u
f1 (ppm)

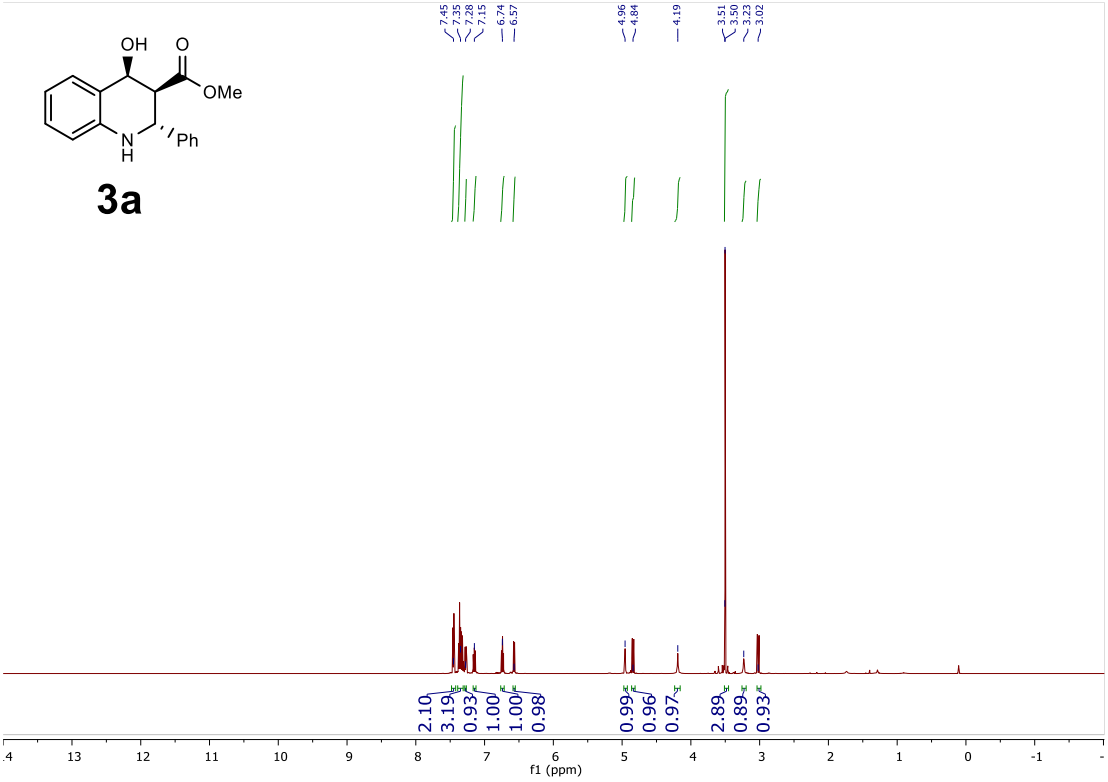

8.38
8.10
8.03
7.88
7.59
7.51
7.43
7.24
7.03
6.98
O
O
S
Ph
N
1v
1.03
1.12
1.99
2.07
1.11
6.25
1.20
1.08
1.00
1.05
f1 (ppm)

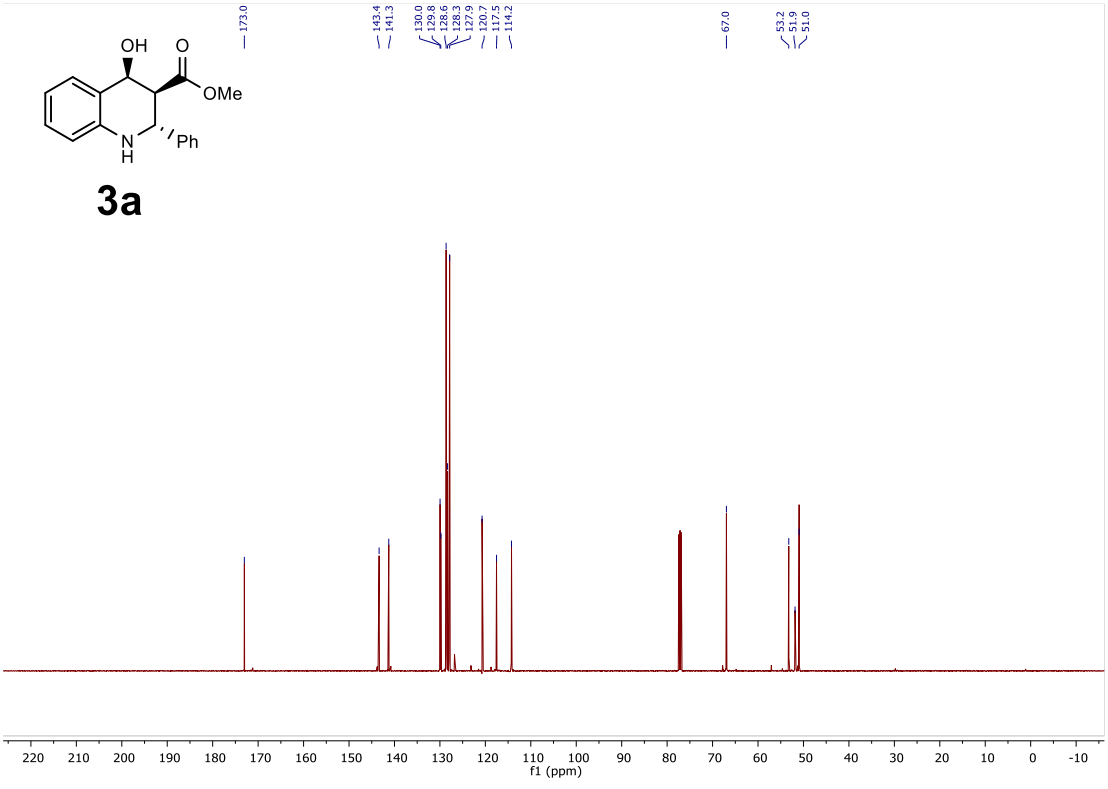

161.2
151.6
141.1
139.5
139.5
135.9
133.3
132.1
129.3
129.2
129.1
129.1
129.1
127.8
126.6
126.3
119.0
O
O
S
Ph
N
1v
f1 (ppm)

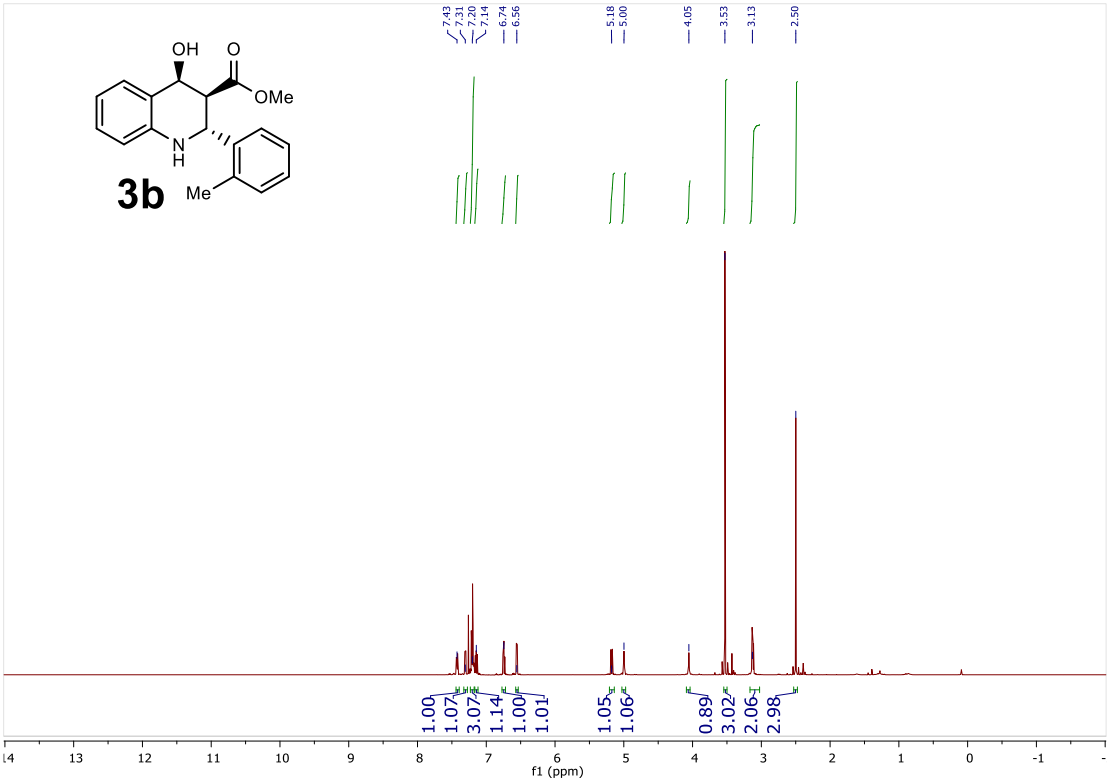

1w
8.38
7.94
7.59
7.48
7.39
7.24
6.99
6.32
4.11
1.32
1.00
3.06
1.02
3.10
0.96
1.01
0.99
1.00
3.91
6.04
f1 (ppm)

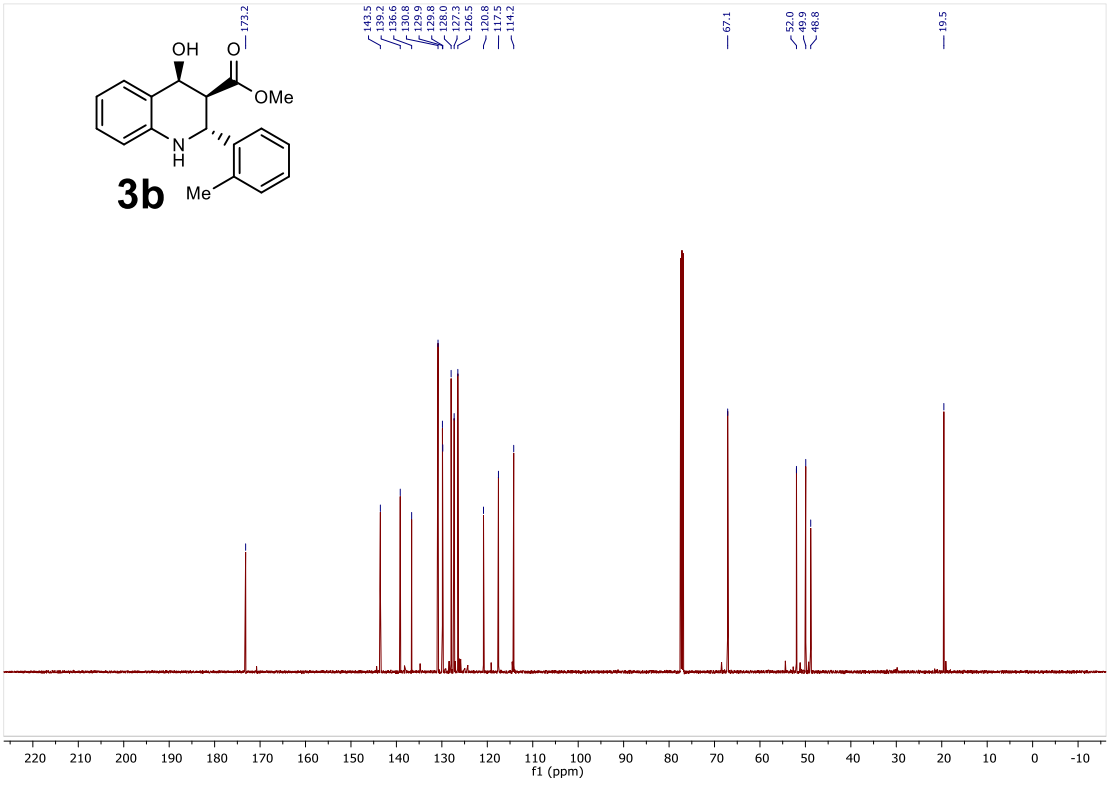

1w
160.9
151.1
145.1
136.1
131.8
131.2
129.1
128.9
128.7
127.4
126.1
118.9
116.1
114.6
61.9
16.5
f1 (ppm)

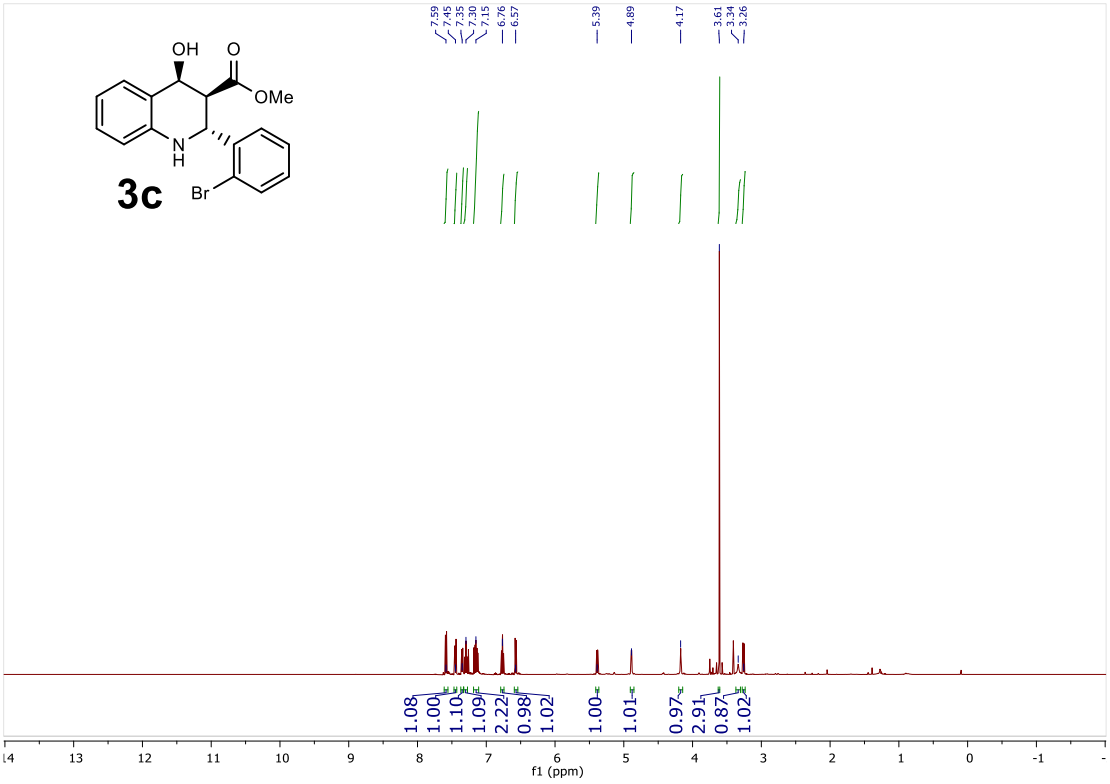

19.55
O
OEt
P
OEt
N
1w
260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300 -320 -340 -360
f1 (ppm)

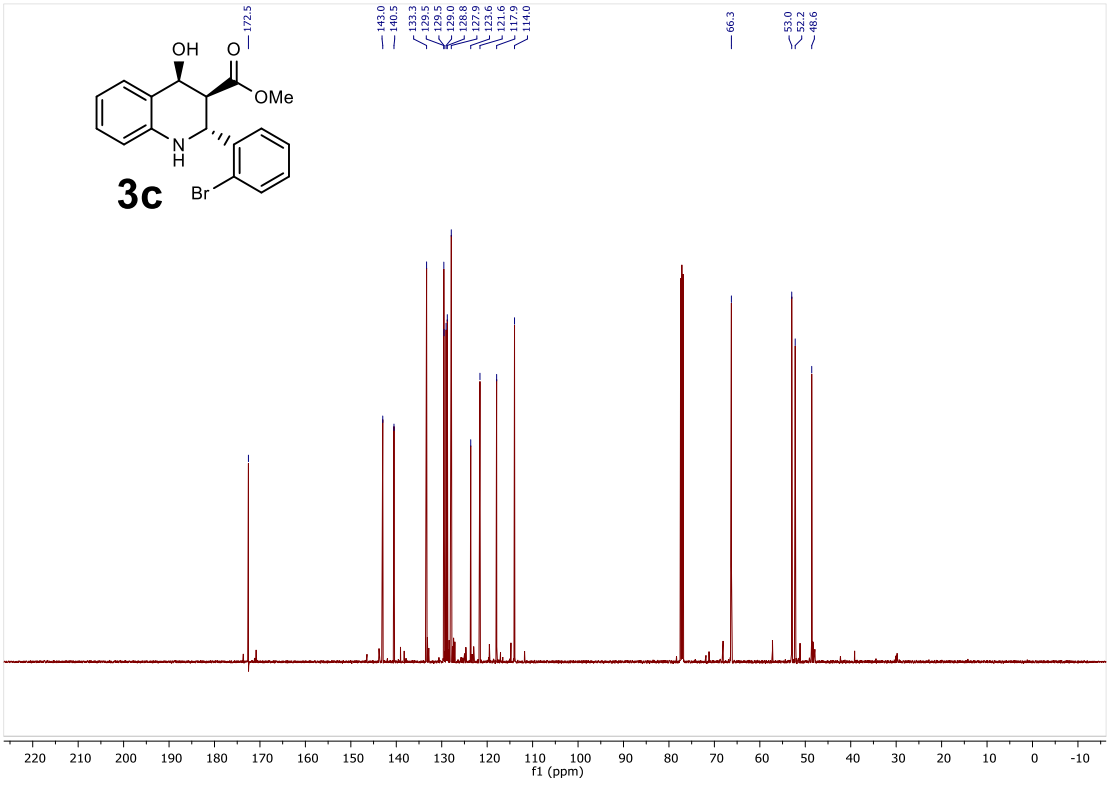

OH
O
OMe
N
H
Ph
3a
7.45
7.35
7.28
7.15
6.74
6.57
4.96
4.84
4.19
3.51
3.50
3.23
3.02
2.10
3.19
0.93
1.00
1.00
0.98
0.99
0.96
0.97
2.89
0.89
0.93
f1 (ppm)

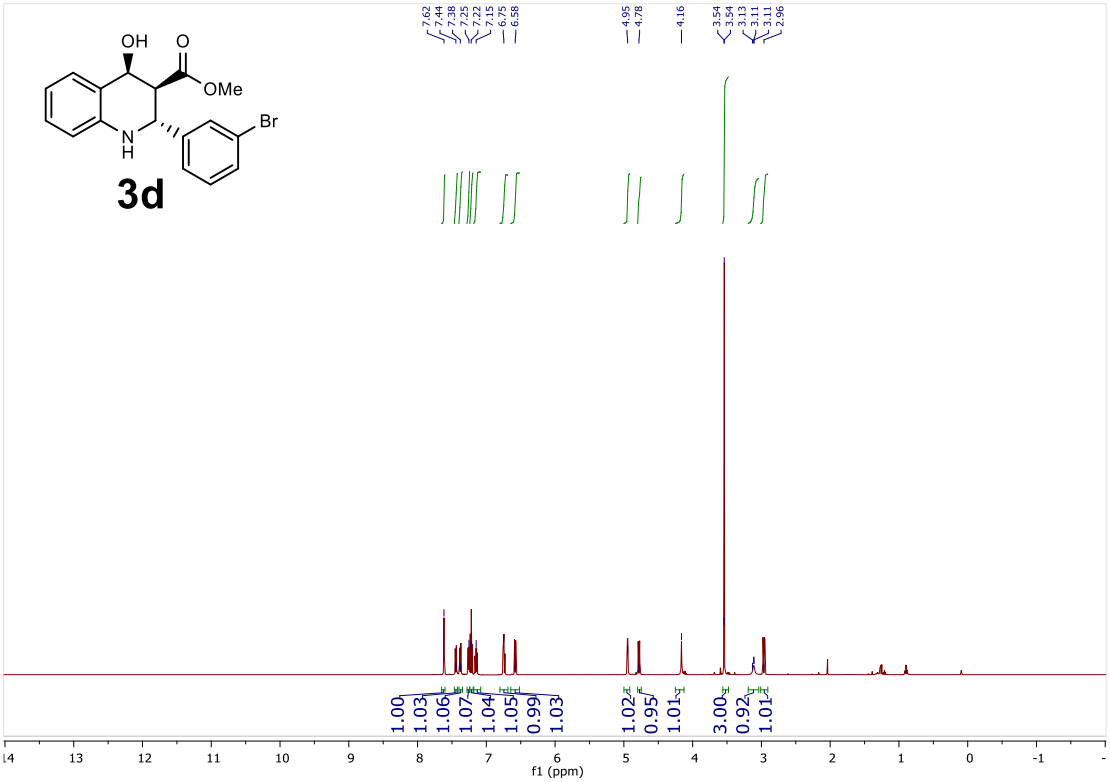

OH
O
OMe
N
H
Ph
3a
173.0
143.4
141.3
130.0
129.8
128.6
128.3
127.9
127.7
117.5
114.2
67.0
53.2
51.9
51.0
f1 (ppm)

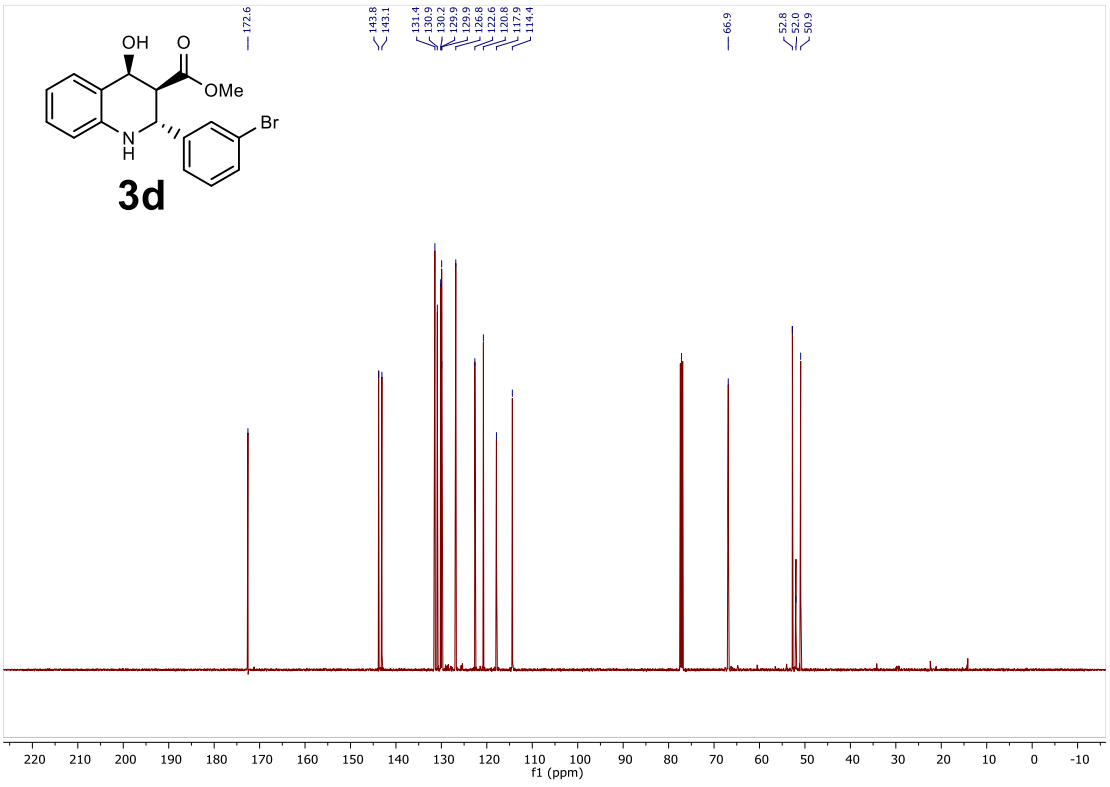

OH
O
OMe
N
H
Me
3b
7.43
7.31
7.20
7.14
6.74
6.56
5.18
5.00
4.05
3.53
3.13
2.50
1.00
1.07
3.07
1.14
1.00
1.01
1.05
1.06
0.89
3.02
2.06
2.98
f1 (ppm)

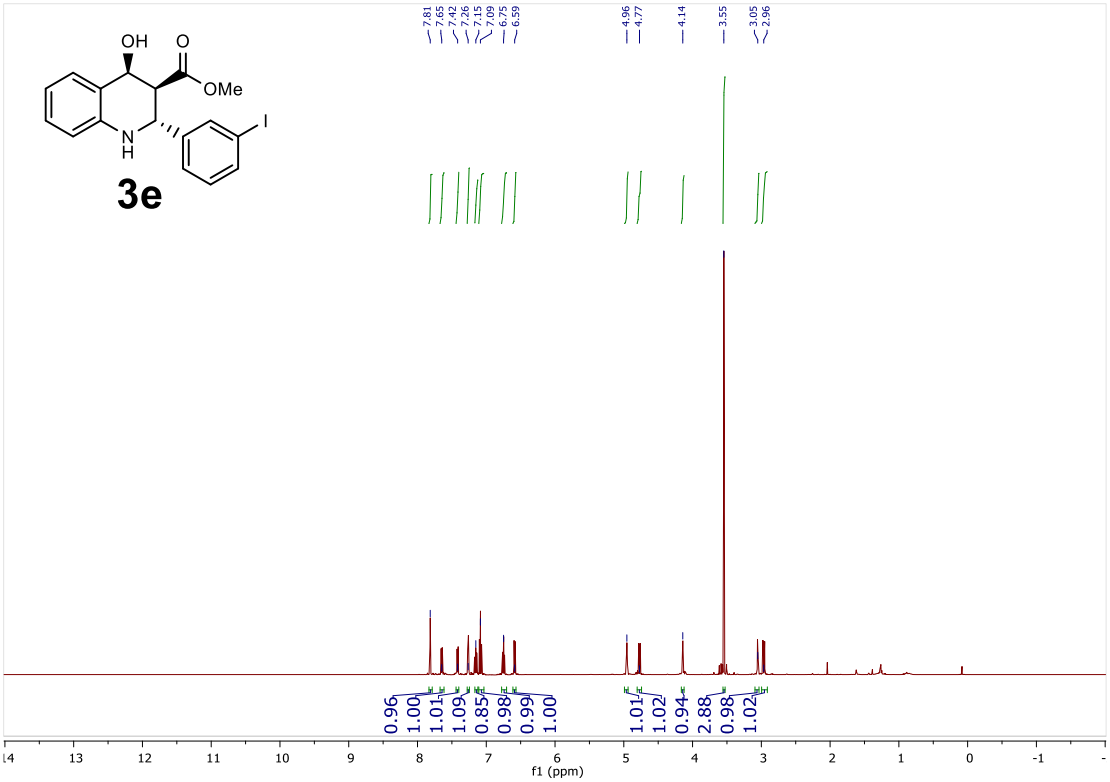

OH
O
OMe
N
H
Me
3b
173.2
143.5
139.2
136.6
130.8
129.9
129.8
128.0
127.3
126.5
120.8
117.5
114.2
67.1
52.0
49.9
48.8
19.5
f1 (ppm)

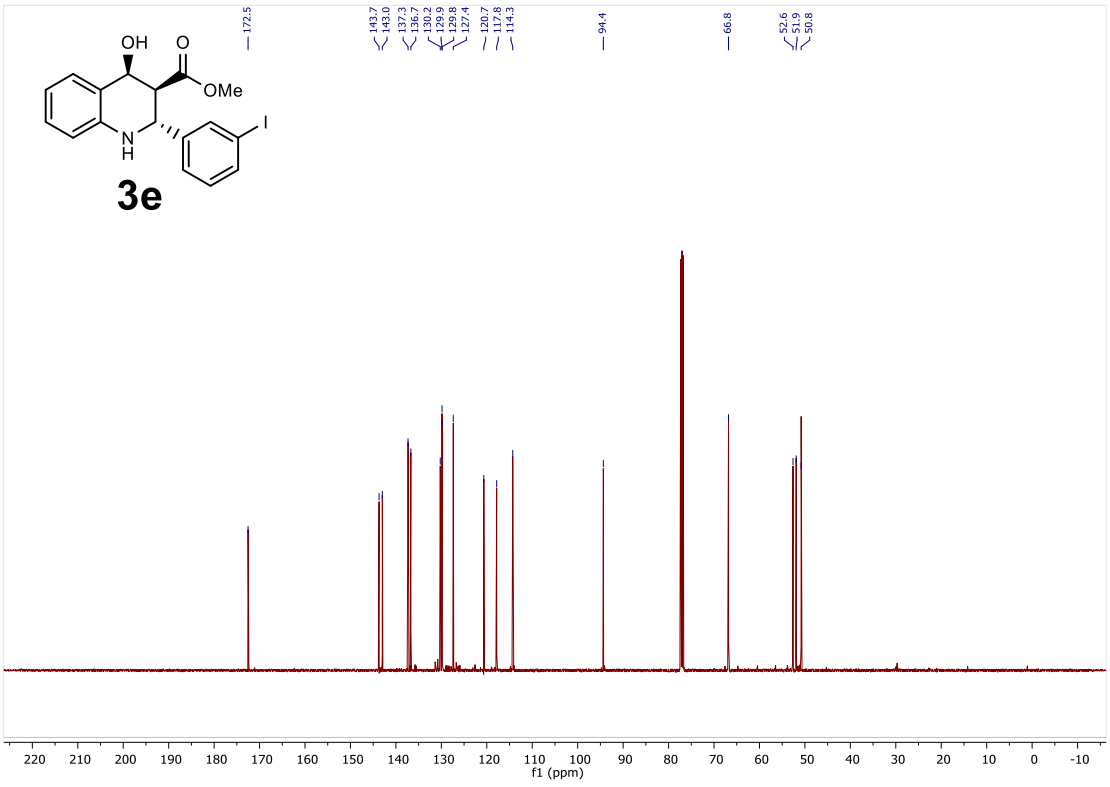

OH
O
OMe
N
H
Br
3c
7.59
7.45
7.35
7.30
7.15
6.76
6.57
5.39
4.89
4.17
3.61
3.34
3.26
1.08
1.00
1.10
1.09
2.22
0.98
1.02
1.00
1.01
0.97
2.91
0.87
1.02
f1 (ppm)

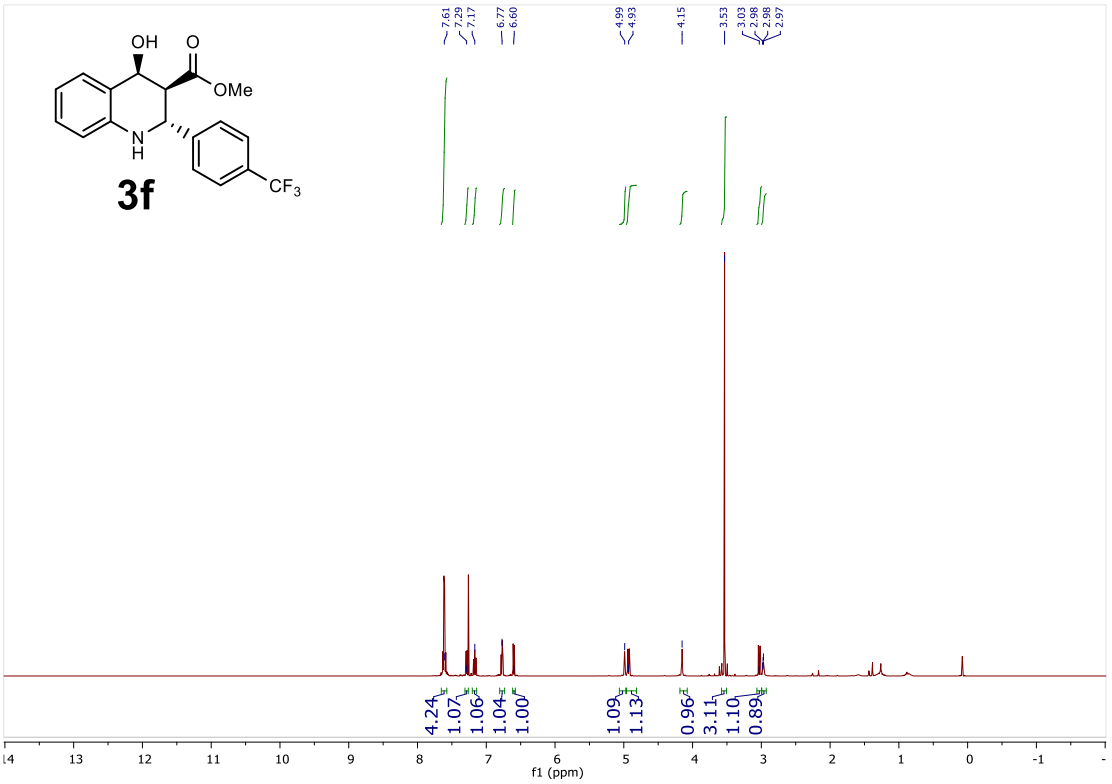

OH
O
OMe
N
H
Br
3c
172.5
143.0
140.5
133.3
129.5
129.5
129.0
128.8
127.9
123.6
121.6
117.9
114.0
66.3
53.0
52.2
48.6
f1 (ppm)

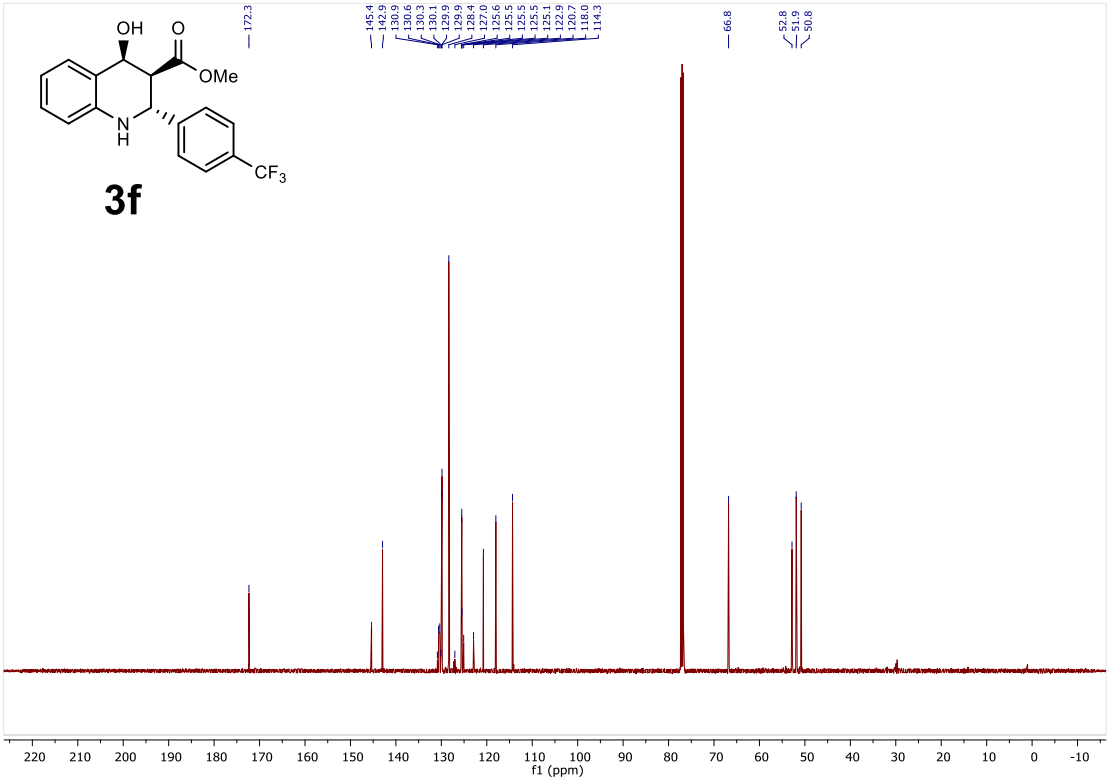

OH
O
OMe
N
H
Br
3d
7.62
7.44
7.38
7.25
7.22
7.15
6.75
6.58
4.95
4.78
4.16
3.54
3.54
3.13
3.11
3.11
2.96
1.00
1.03
1.06
1.07
1.04
1.05
0.99
1.03
1.02
0.95
1.01
3.00
0.92
1.01
f1 (ppm)

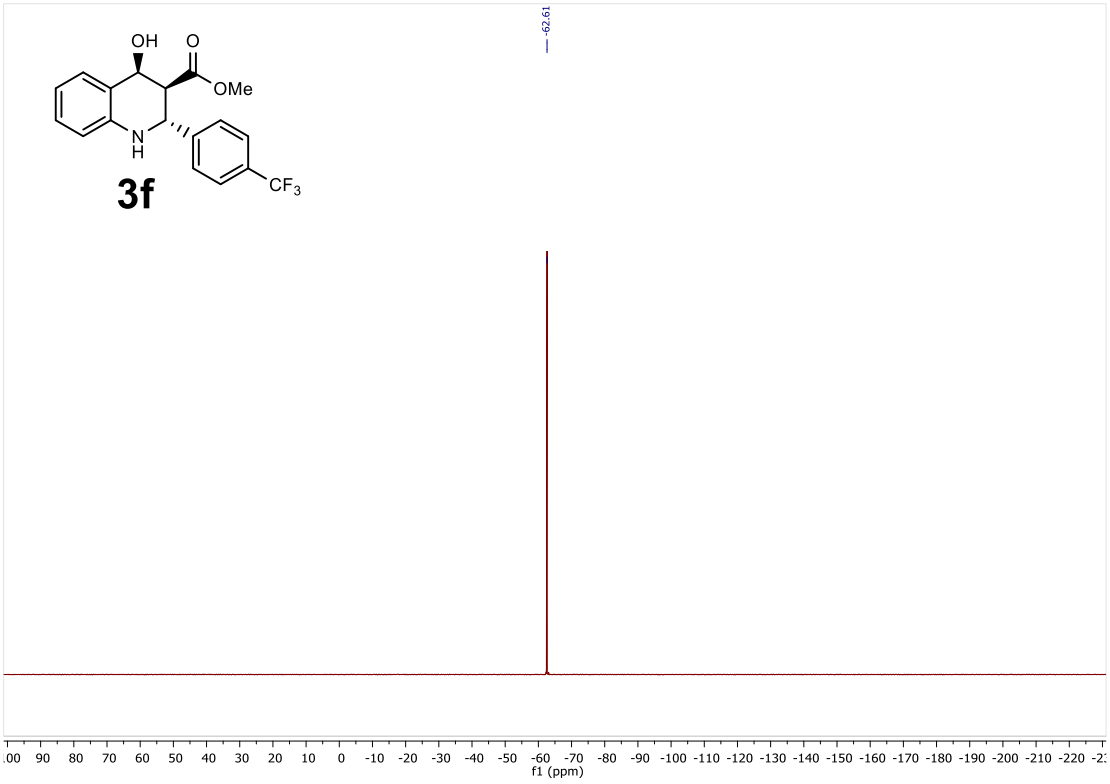

OH
O
OMe
N
H
Br
3d
172.6
143.8
143.1
131.4
130.9
130.2
129.9
129.9
126.8
123.6
120.8
117.9
114.4
66.9
52.8
52.0
50.9
f1 (ppm)

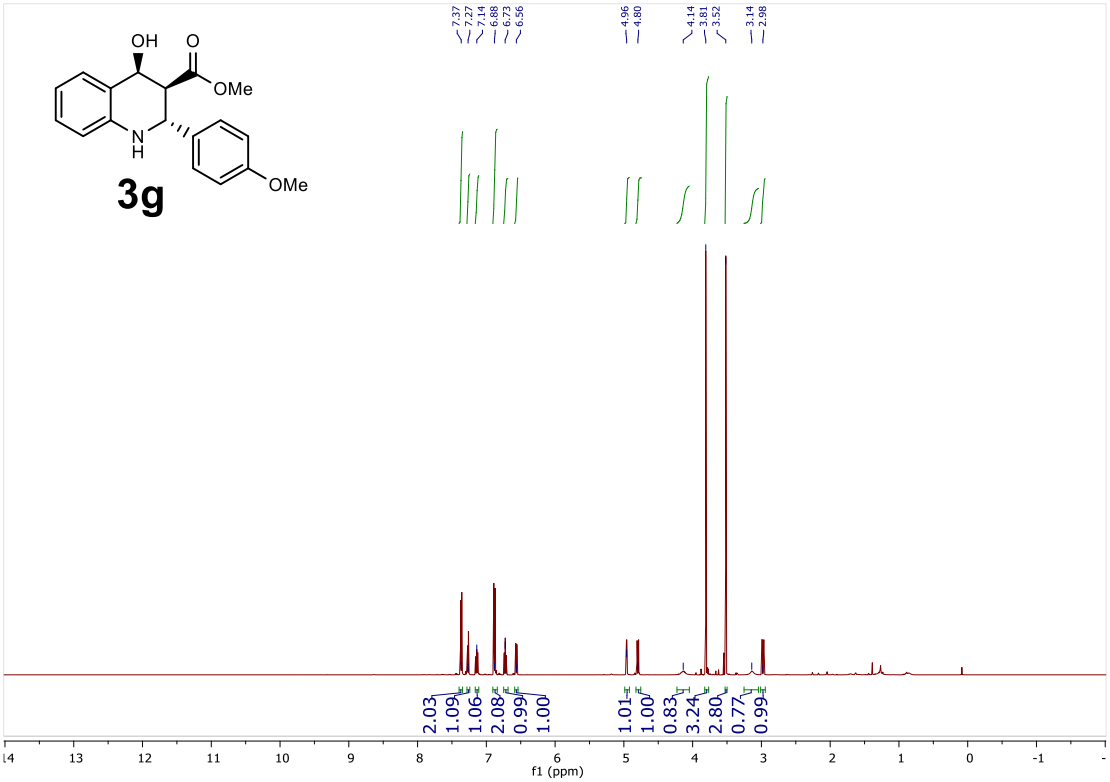

OH
O
OMe
N
H
I
3e
7.81
7.65
7.42
7.26
7.15
7.09
6.75
6.59
4.96
4.77
4.14
3.55
3.05
2.96
0.96
1.00
1.01
1.09
0.85
0.98
0.99
1.00
1.01
1.02
0.94
2.88
0.98
1.02
f1 (ppm)

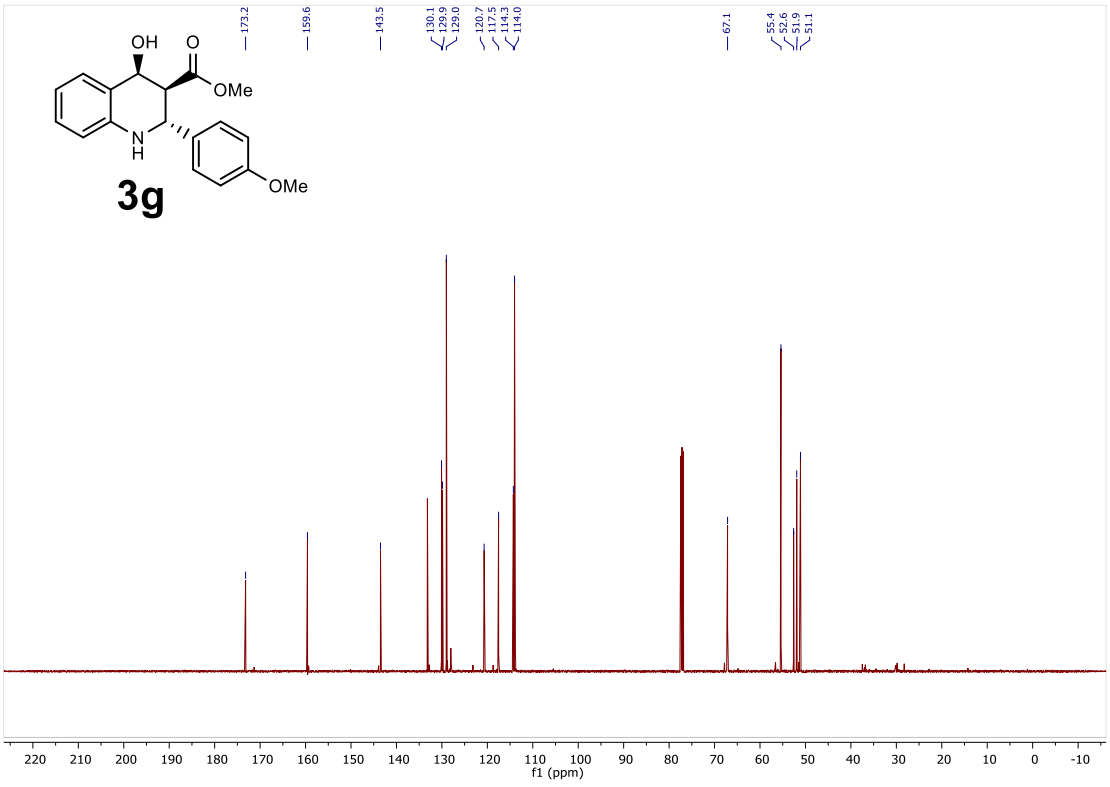

OH
O
OMe
N
H
I
3e
172.5
143.7
143.0
137.3
136.7
130.2
129.9
129.8
127.4
120.7
117.8
114.3
94.4
66.8
52.6
51.9
50.8
f1 (ppm)

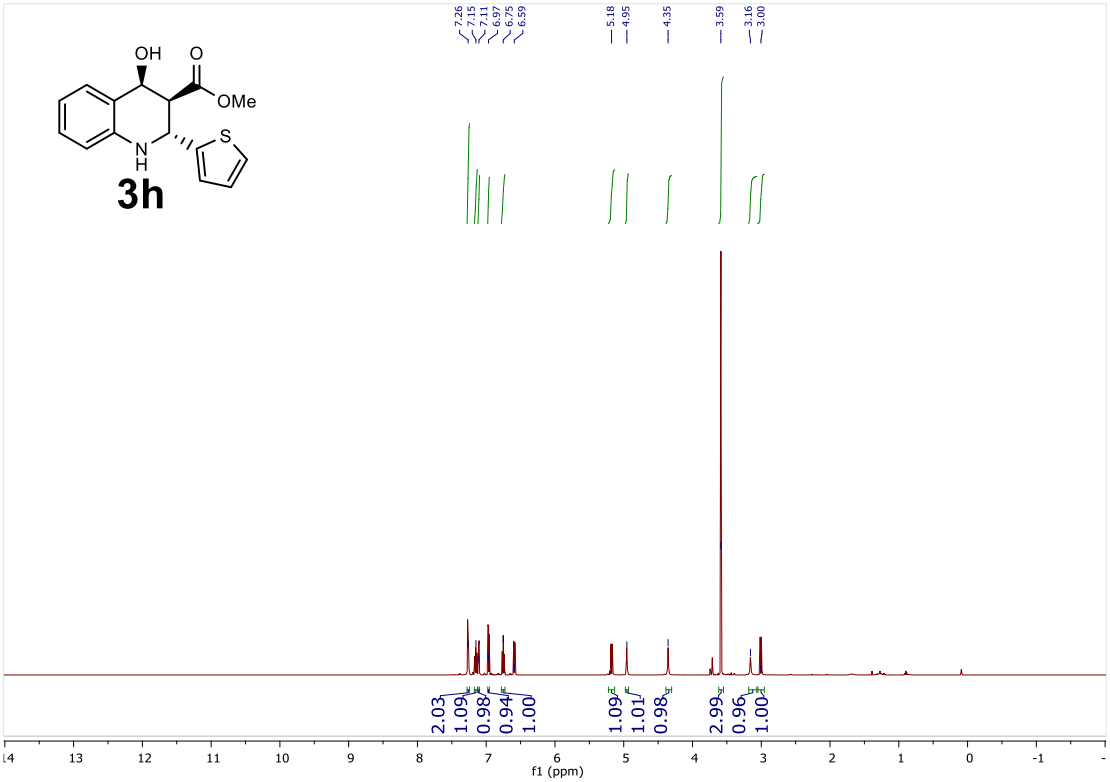

OH
O
OMe
N
H
CF3
3f
7.61
7.29
7.17
6.77
6.60
4.99
4.93
4.15
3.53
3.03
2.98
2.98
2.97
4.24
1.07
1.06
1.04
1.00
1.09
1.13
0.96
3.11
1.10
0.89
f1 (ppm)

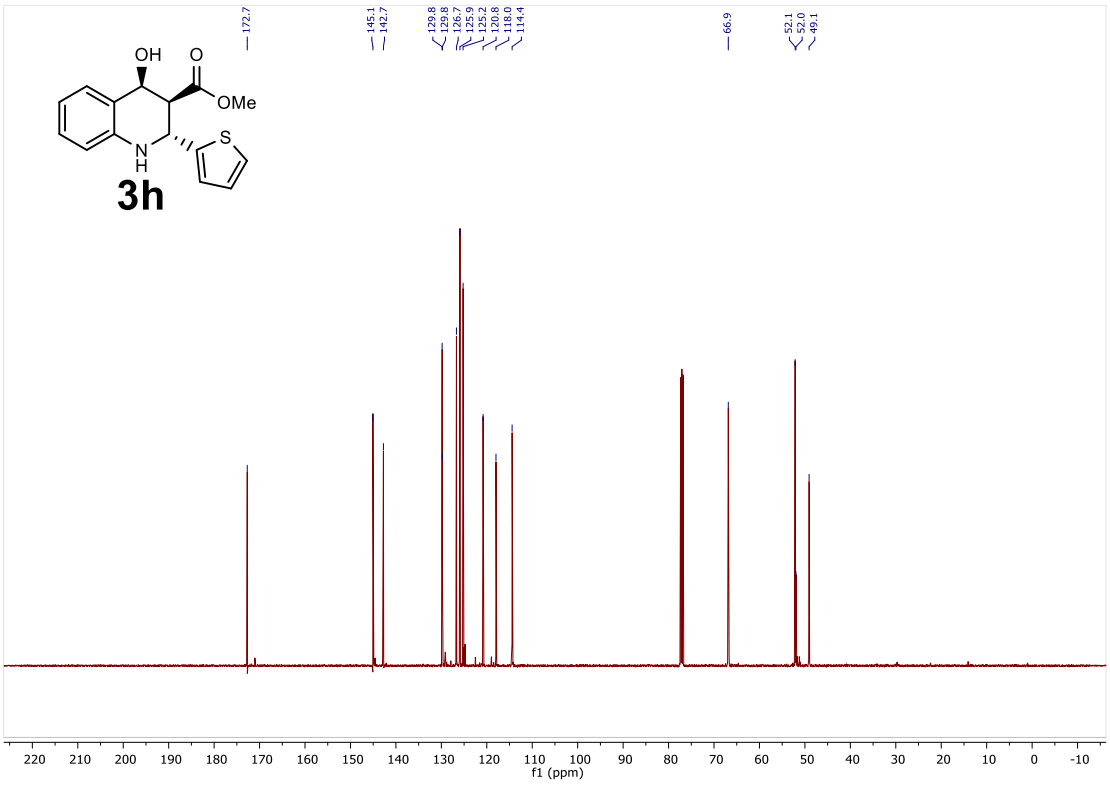

OH
O
OMe
N
H
CF3
3f
172.3
145.4
142.9
130.9
130.6
130.3
130.1
129.9
129.9
128.4
127.0
125.6
125.5
125.5
125.5
125.1
122.9
120.7
118.0
114.3
66.8
52.8
51.9
50.8
f1 (ppm)

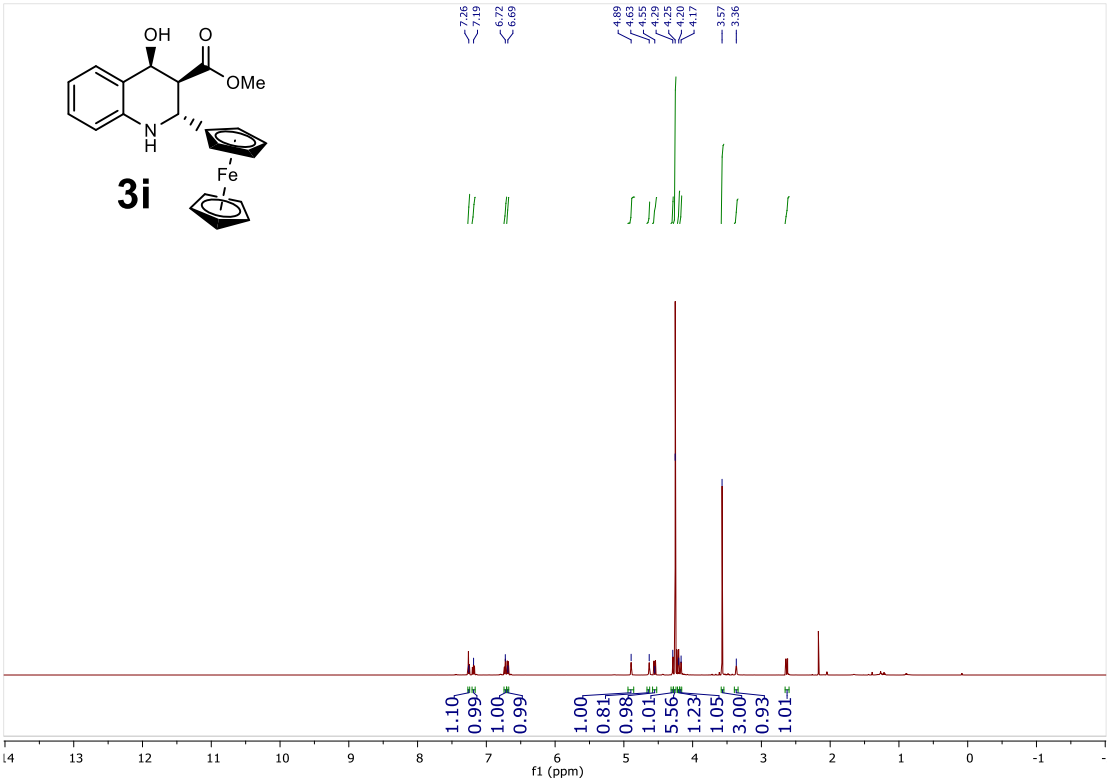

OH
O
OMe
N
H
CF3
3f
-62.61
.00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

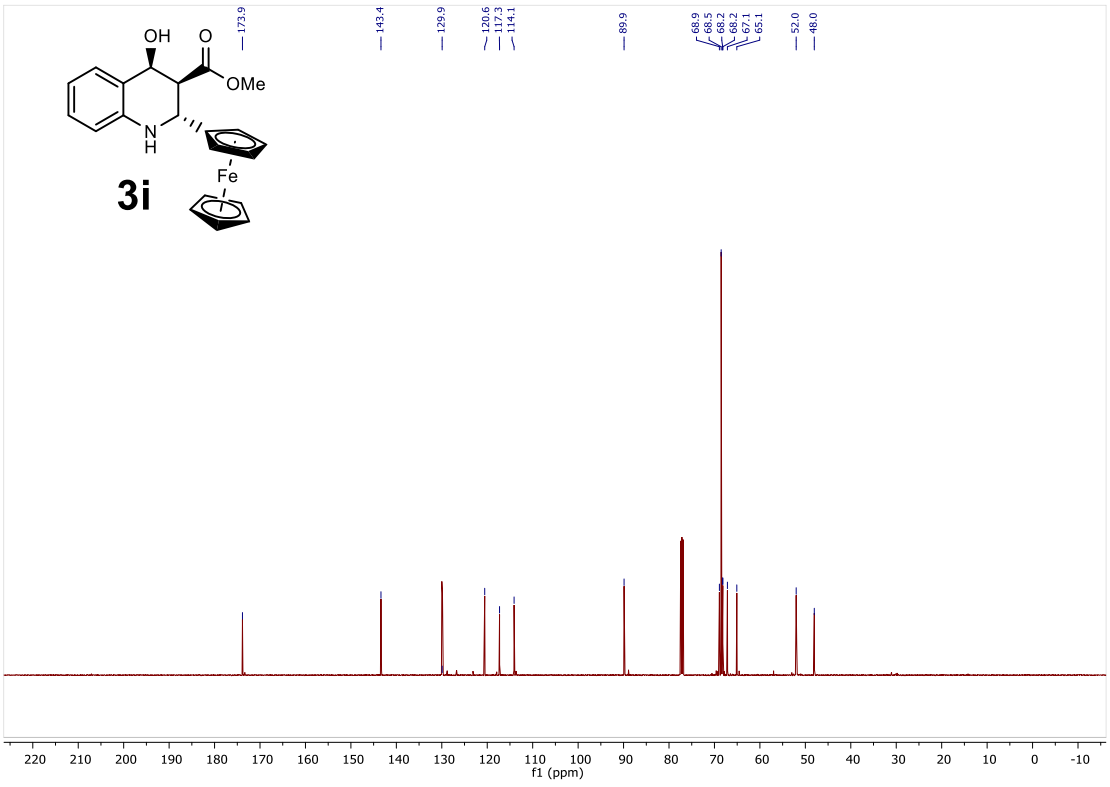

OH
O
OMe
N
H
OMe
3g
7.37
7.27
7.14
6.88
6.73
6.56
4.96
4.80
4.14
3.61
3.52
3.14
2.98
2.03
1.09
1.06
2.08
0.99
1.00
1.01
1.00
0.83
3.24
2.80
0.77
0.99
f1 (ppm)

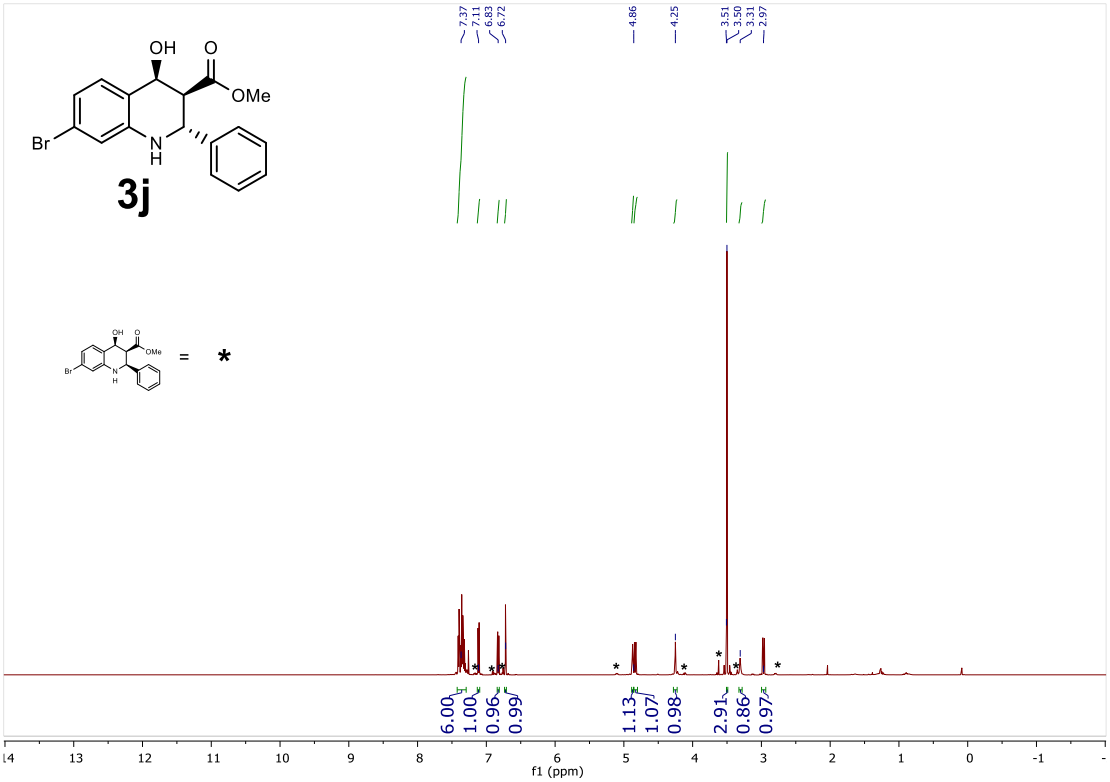

OH
O
OMe
N
H
OMe
3g
173.2
159.6
143.5
130.1
129.9
129.0
120.7
117.5
114.3
114.0
67.1
55.4
52.6
51.9
51.1
f1 (ppm)

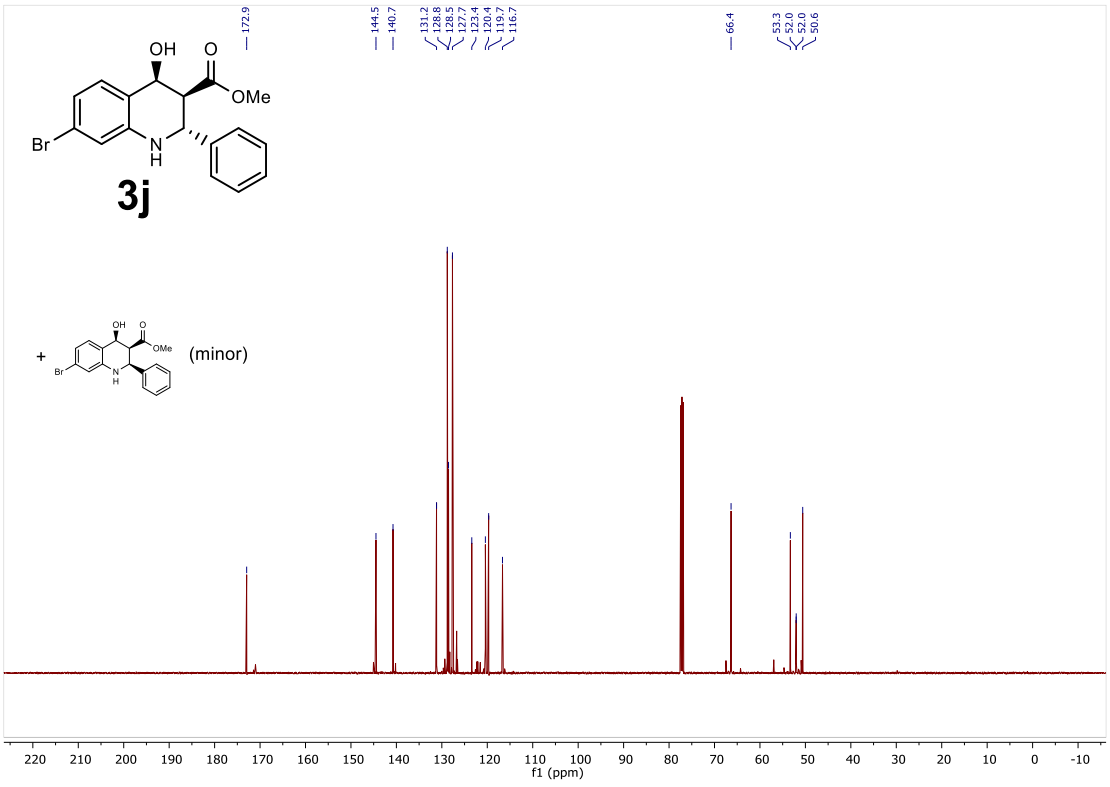

OH
O
OMe
N
H
S
3h
7.26
7.15
7.11
6.97
6.75
6.59
5.18
4.95
4.35
3.59
3.16
3.00
2.03
1.09
0.98
0.94
1.00
1.09
1.01
0.98
2.99
0.96
1.00
f1 (ppm)

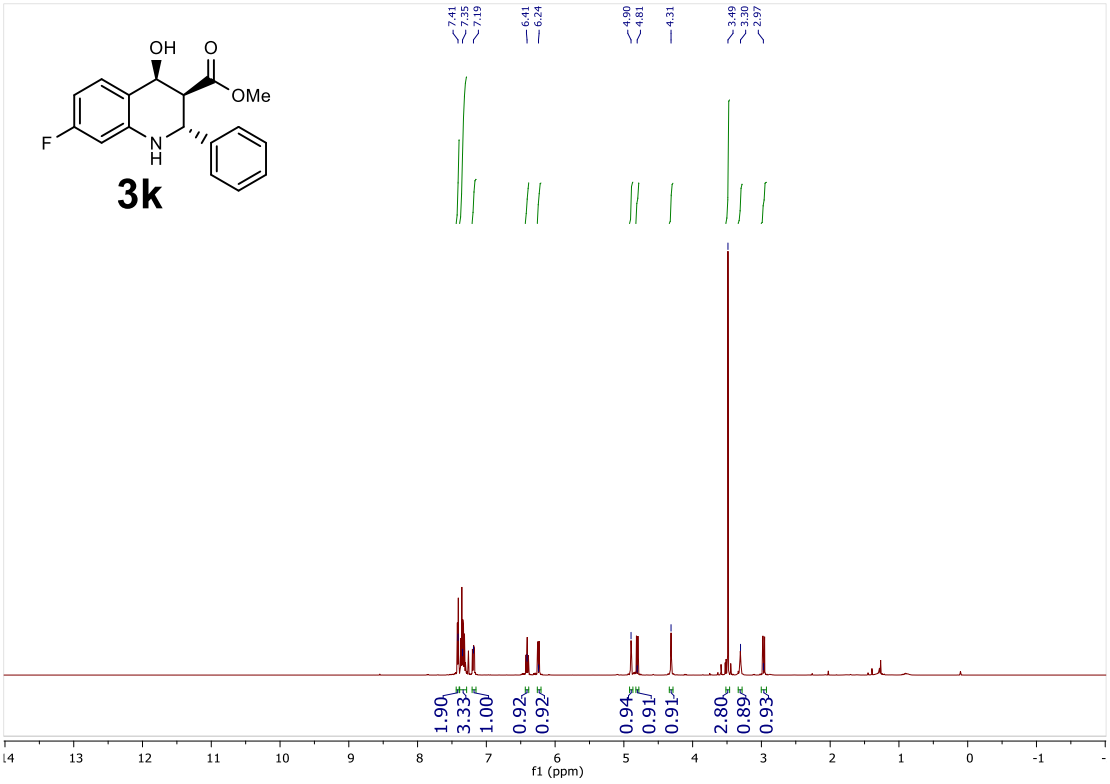

OH
O
OMe
N
H
S
3h
172.7
145.1
142.7
129.8
129.8
126.7
125.9
125.2
120.8
118.0
114.4
66.9
52.1
52.0
49.1
f1 (ppm)

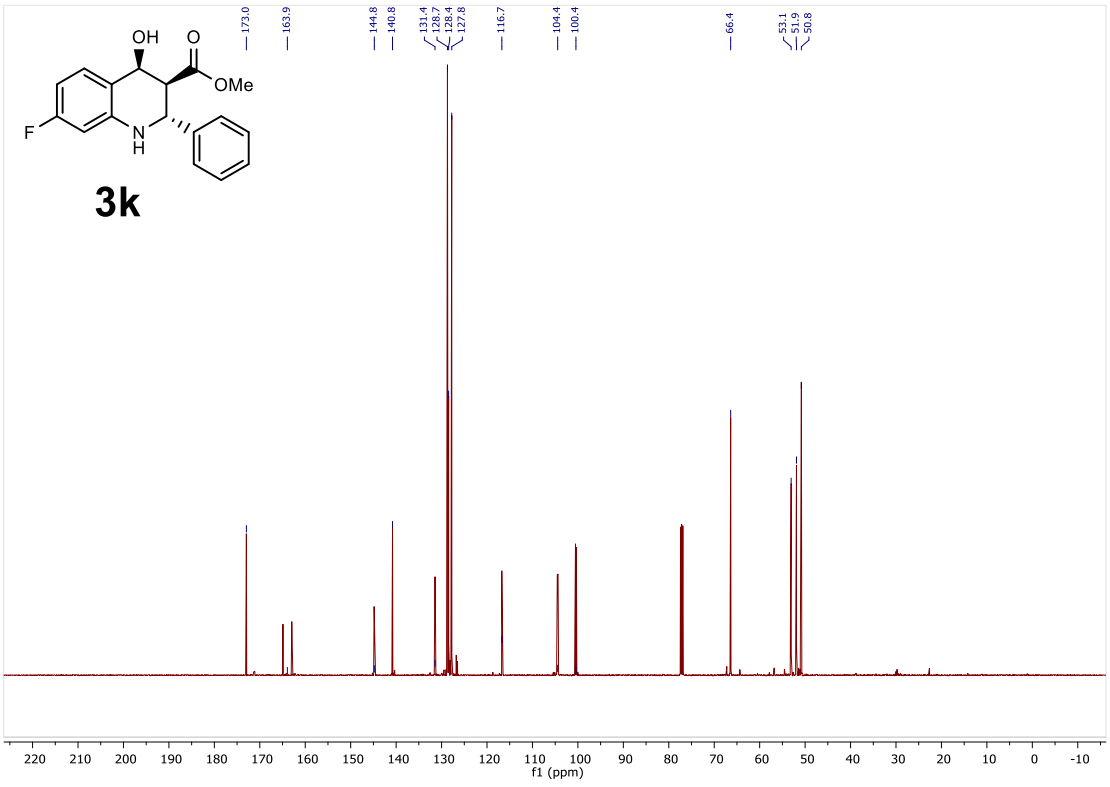

OH
O
OMe
N
H
Fe
3i
7.26
7.19
6.72
6.69
4.89
4.63
4.55
4.29
4.25
4.20
4.17
3.57
3.36
1.10
0.99
1.00
0.99
1.00
0.81
0.98
1.01
5.56
1.23
1.05
3.00
0.93
1.01
f1 (ppm)

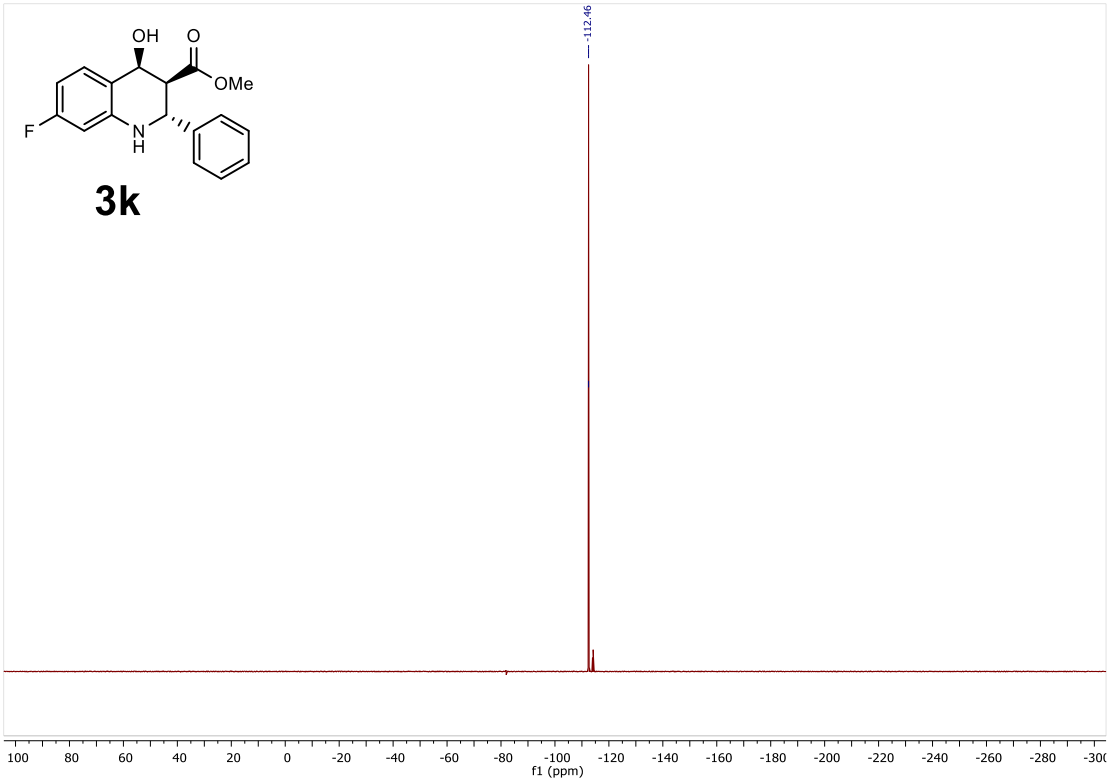

OH
O
OMe
N
H
Fe
3i
173.9
143.4
129.9
120.6
117.3
114.1
89.9
68.9
68.5
68.2
68.2
67.1
65.1
52.0
48.0
f1 (ppm)


OH
O
OMe
Br
N
H
3j
7.37
7.11
6.83
6.72
4.86
4.25
3.51
3.50
3.31
2.97
= *
6.00
1.00
0.96
0.99
1.13
1.07
0.98
2.91
0.86
0.97
f1 (ppm)

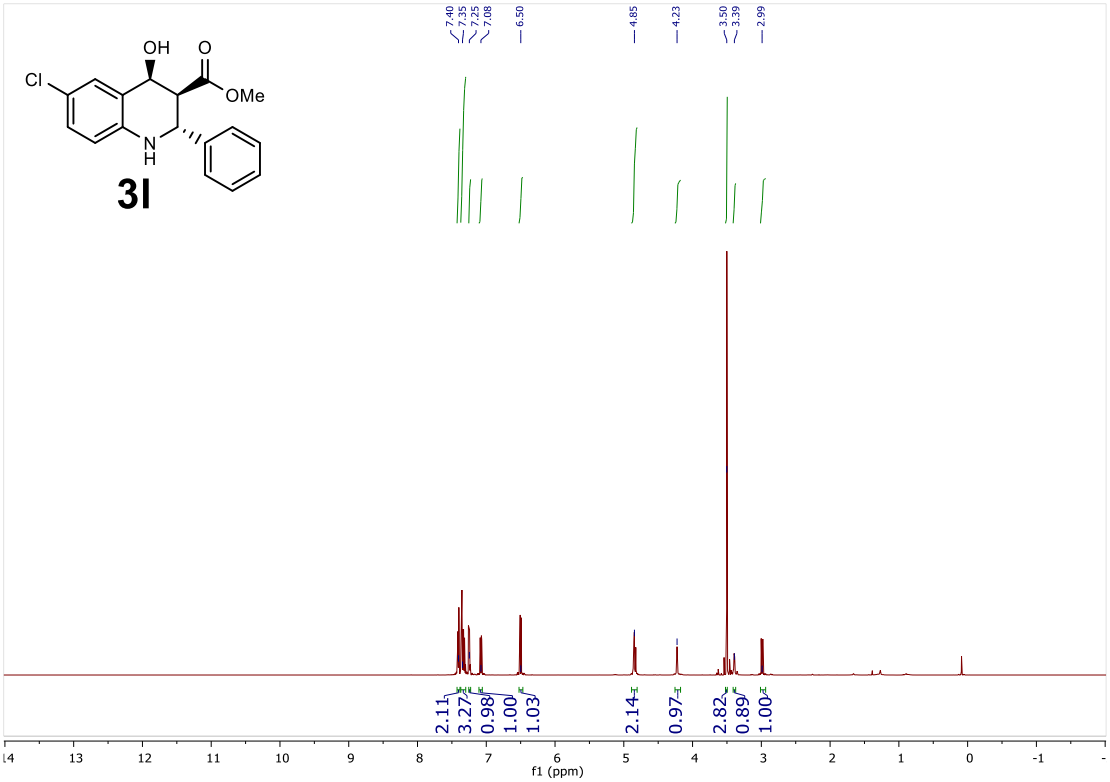

OH
O
OMe
Br
N
H
3j
172.9
144.5
140.7
131.2
128.8
128.5
127.7
123.4
120.4
119.7
116.7
66.4
53.3
52.0
52.0
50.6
+ (minor)
f1 (ppm)

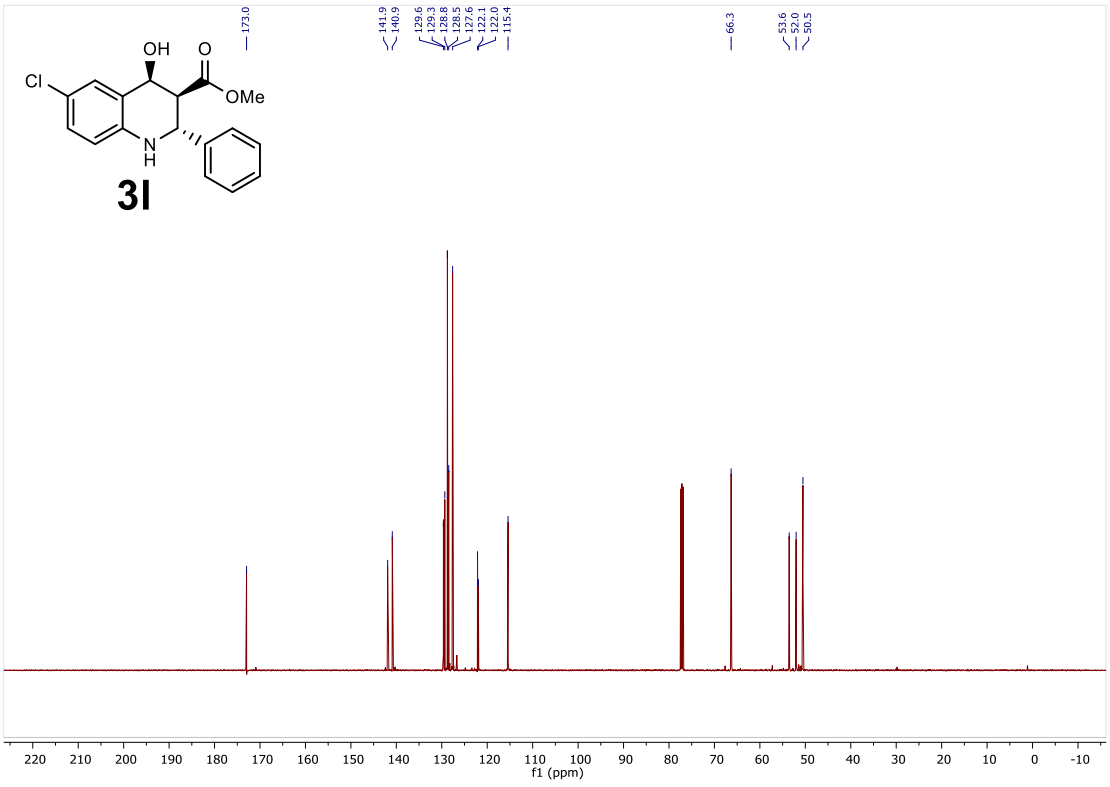

OH
O
OMe
F
N
H
3k
7.41
7.35
7.19
6.41
6.24
4.90
4.81
4.31
3.49
3.30
2.97
1.90
3.33
1.00
0.92
0.92
0.94
0.91
0.91
2.80
0.89
0.93
f1 (ppm)

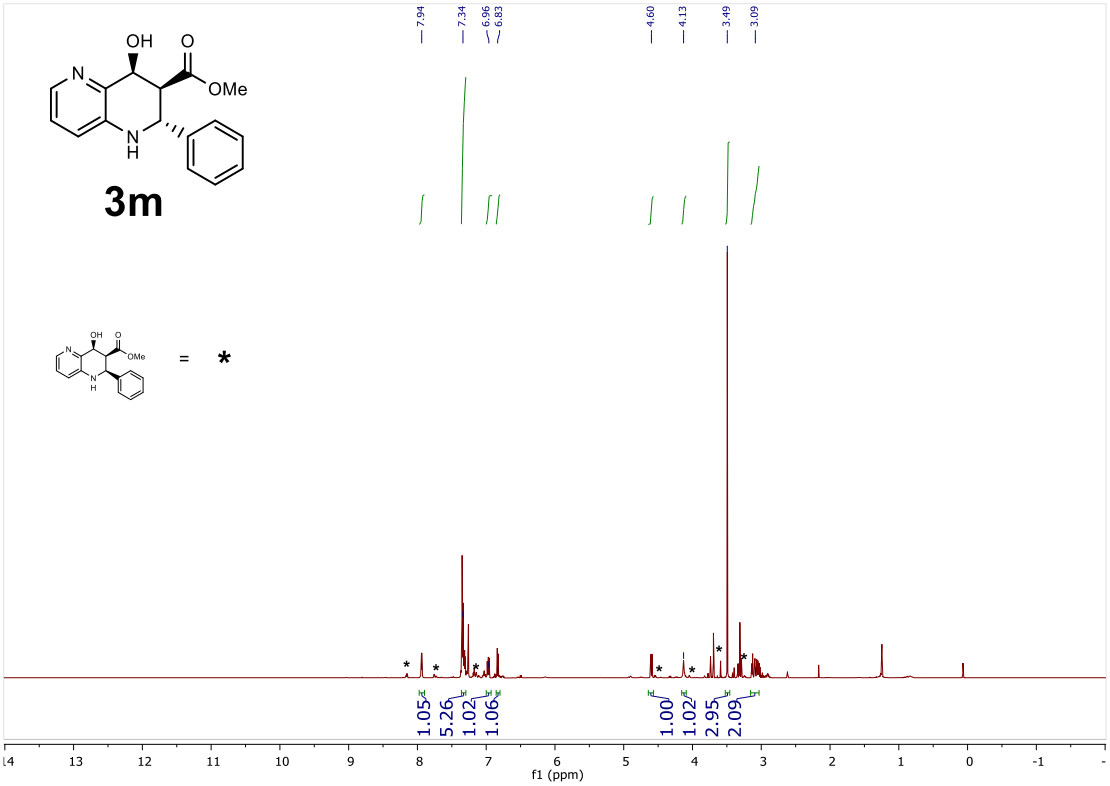

OH
O
OMe
F
N
H
3k
173.0
163.9
144.8
140.8
131.4
128.7
128.4
127.8
116.7
104.4
100.4
66.4
53.1
51.9
50.8
f1 (ppm)

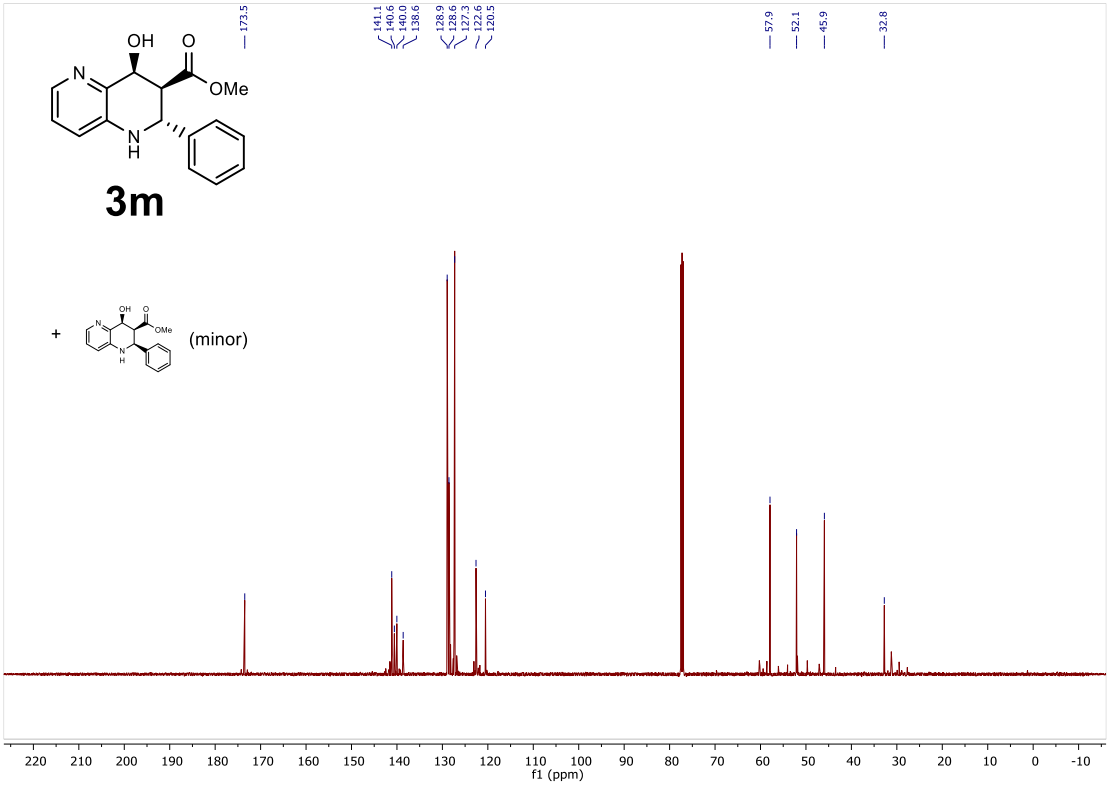

OH
O
OMe
F
N
H
-112.46
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)

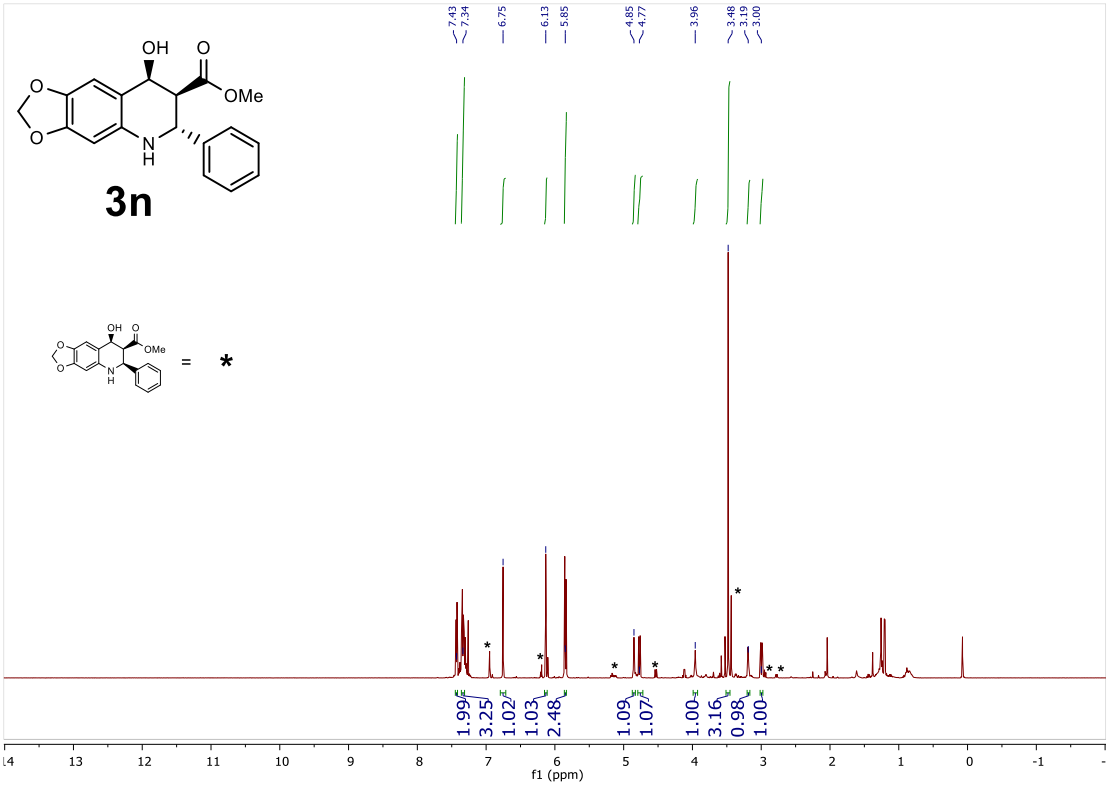
3k

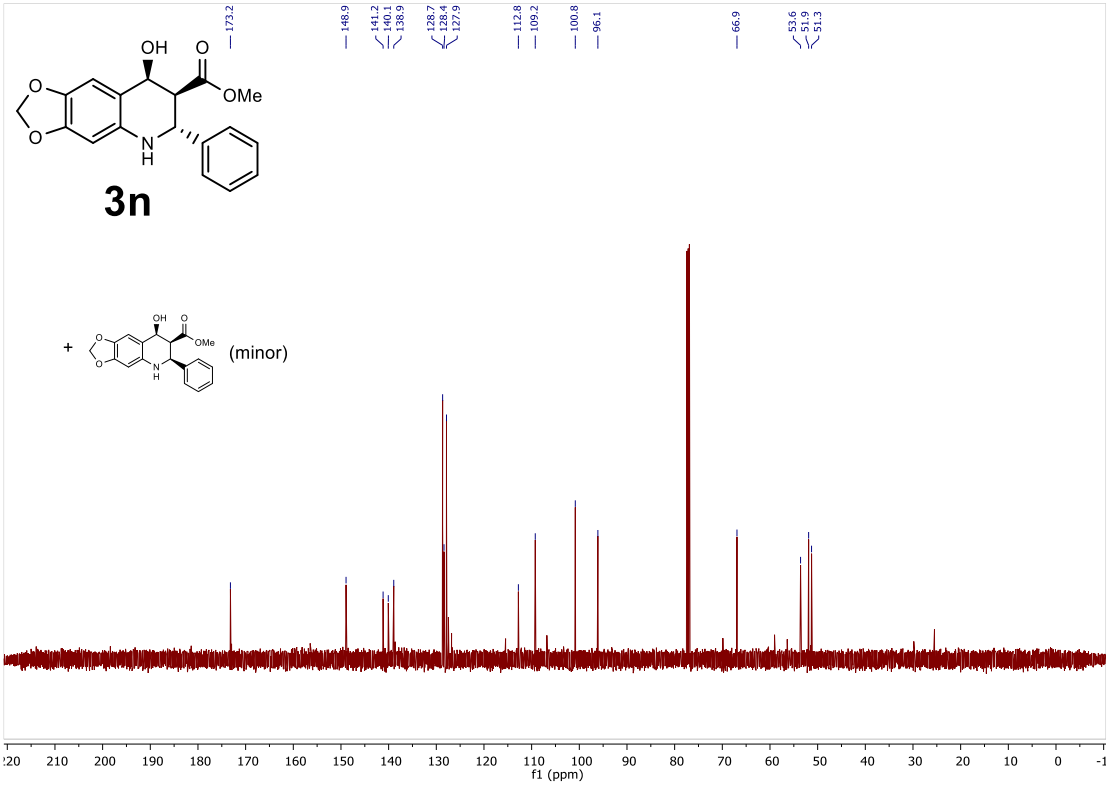

OH
O
Cl
OMe
N
H
3l
7.40
7.35
7.25
7.08
6.50
4.85
4.23
3.50
3.39
2.99
2.11
3.27
0.98
1.00
1.03
2.14
0.97
2.82
0.89
1.00
f1 (ppm)

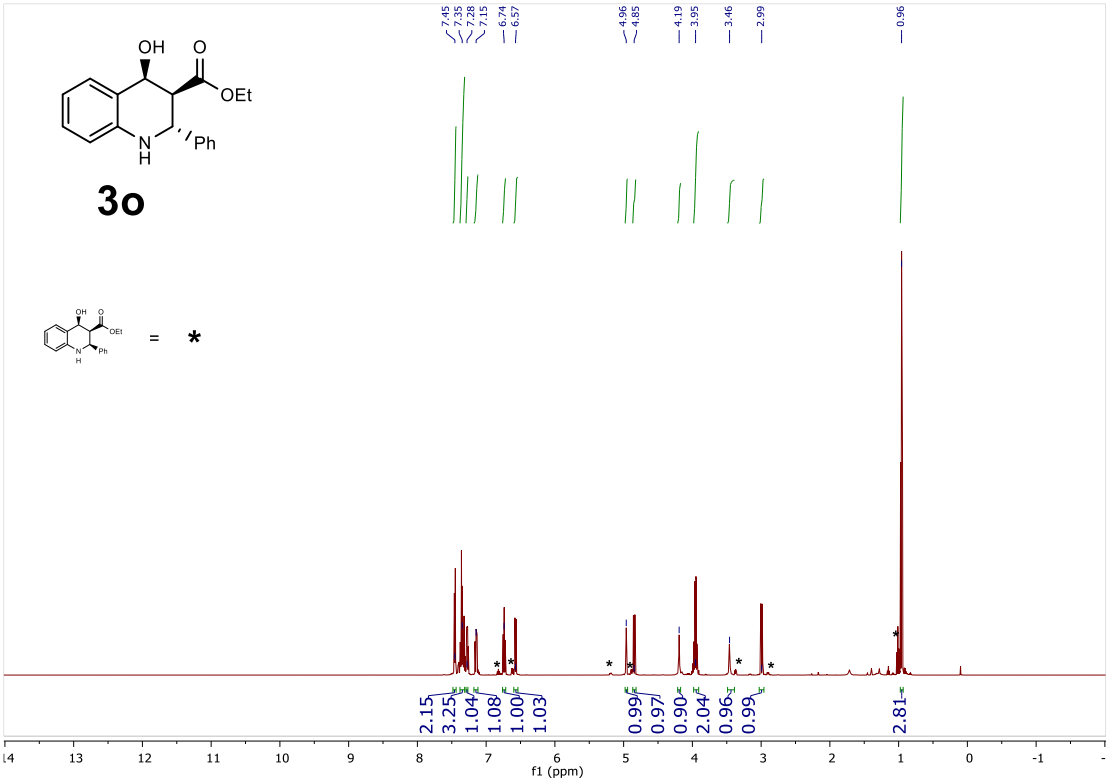

OH
O
Cl
OMe
N
H
3l
173.0
141.9
140.9
129.6
129.3
128.8
128.5
127.6
122.1
122.0
115.4
66.3
53.6
52.0
50.5
f1 (ppm)

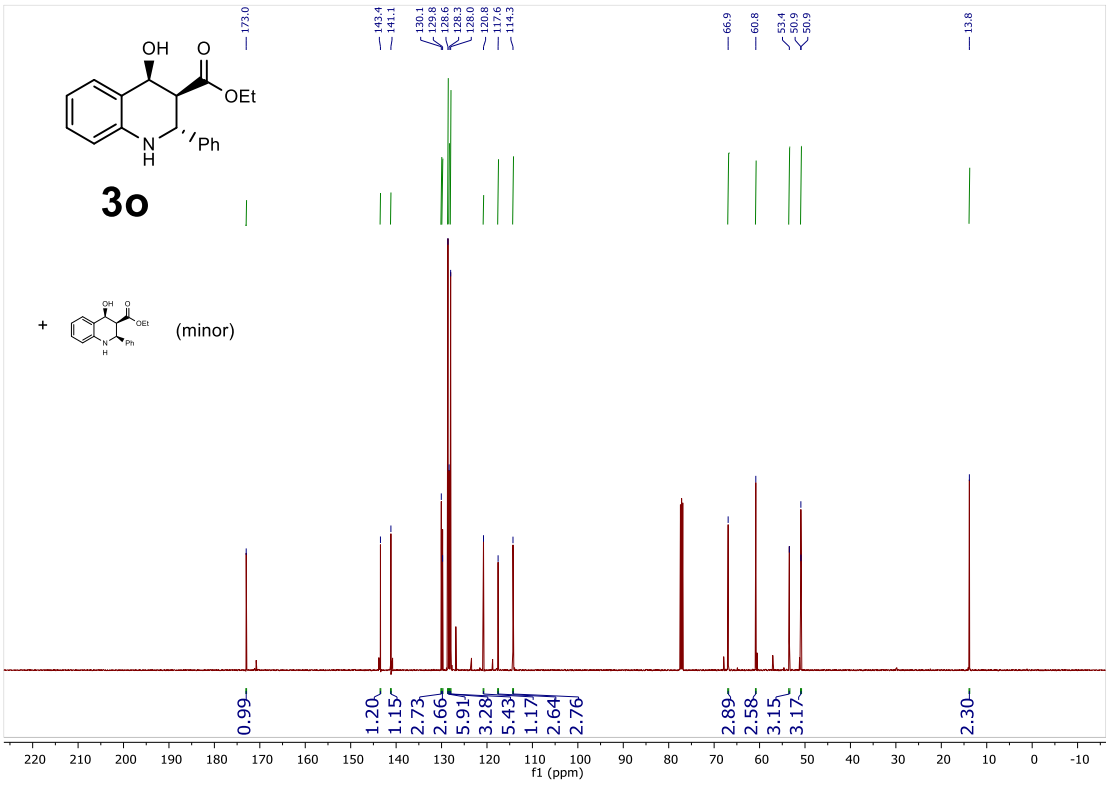

OH
O
N
OMe
N
H
3m
7.94
7.34
6.96
6.83
4.60
4.13
3.49
3.09
= *
1.05
5.26
1.02
1.06
1.00
1.02
2.95
2.09
f1 (ppm)

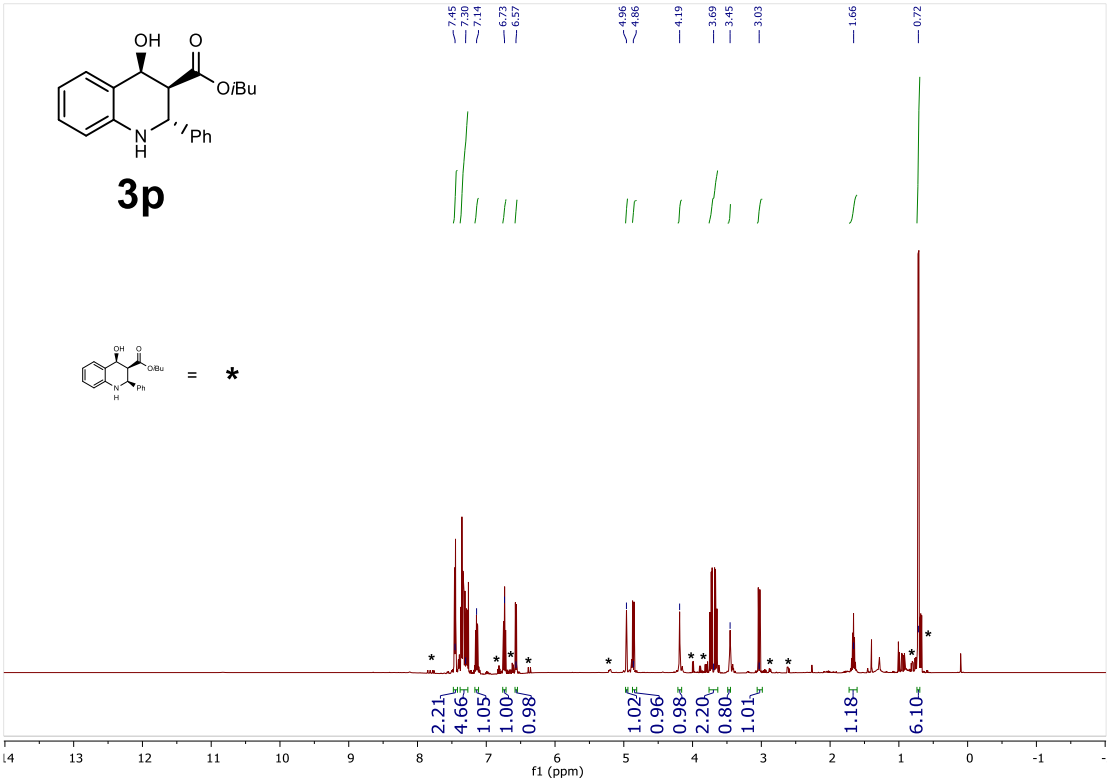

OH
O
N
OMe
N
H
3m
173.5
141.1
140.6
140.0
138.6
128.9
128.6
127.3
122.6
120.5
57.9
52.1
45.9
32.8
+ (minor)
f1 (ppm)

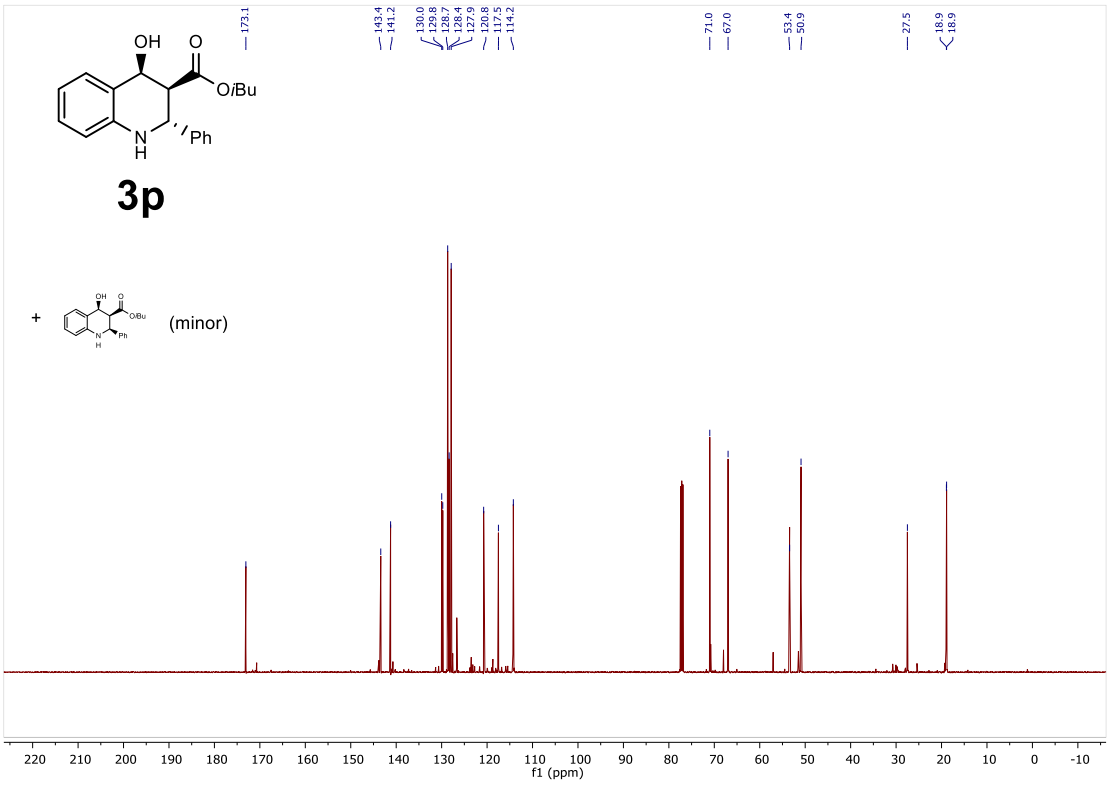

7.43
7.34
6.75
6.13
5.85
4.85
4.77
3.96
3.48
3.19
3.00
OH
O
OMe
O
O
N
H
3n
OH
O
OMe
N
H
=
*
1.99
3.25
1.02
1.03
2.48
1.09
1.07
1.00
3.16
0.98
1.00
f1 (ppm)

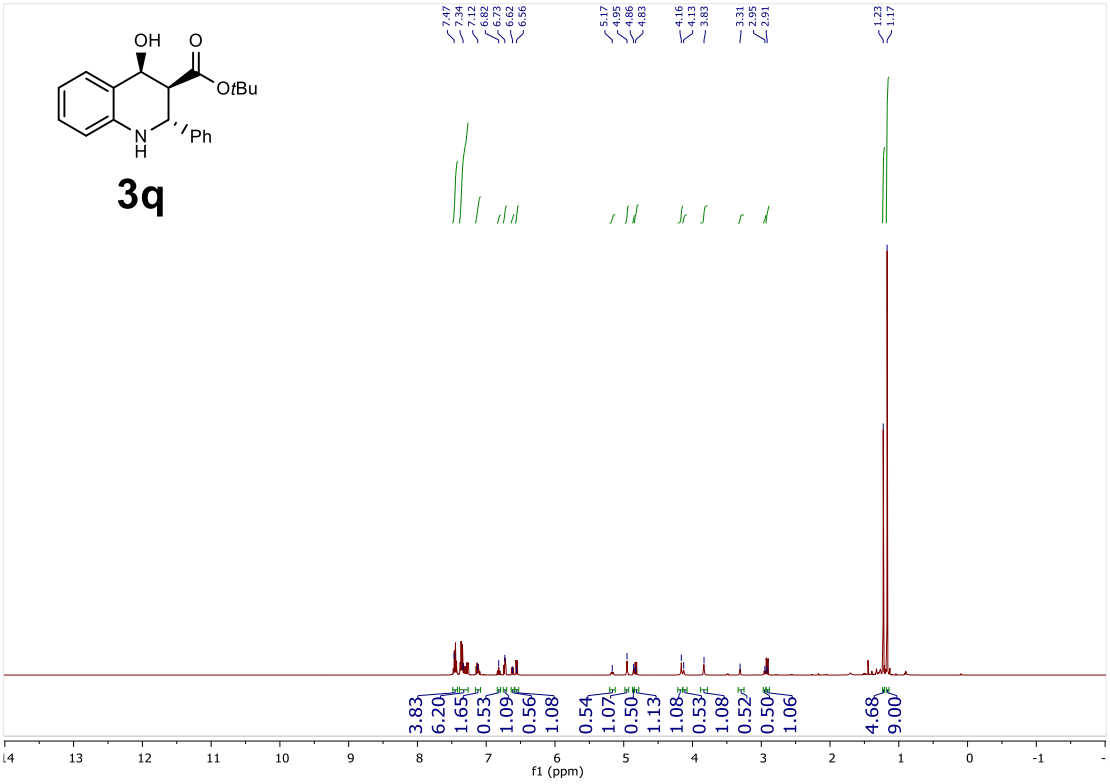

173.2
148.9
141.2
140.1
138.9
128.7
128.4
127.9
112.8
109.2
100.8
96.1
66.9
53.6
51.9
51.3
OH
O
OMe
O
O
N
H
3n
+
OH
O
OMe
N
H
(minor)
f1 (ppm)

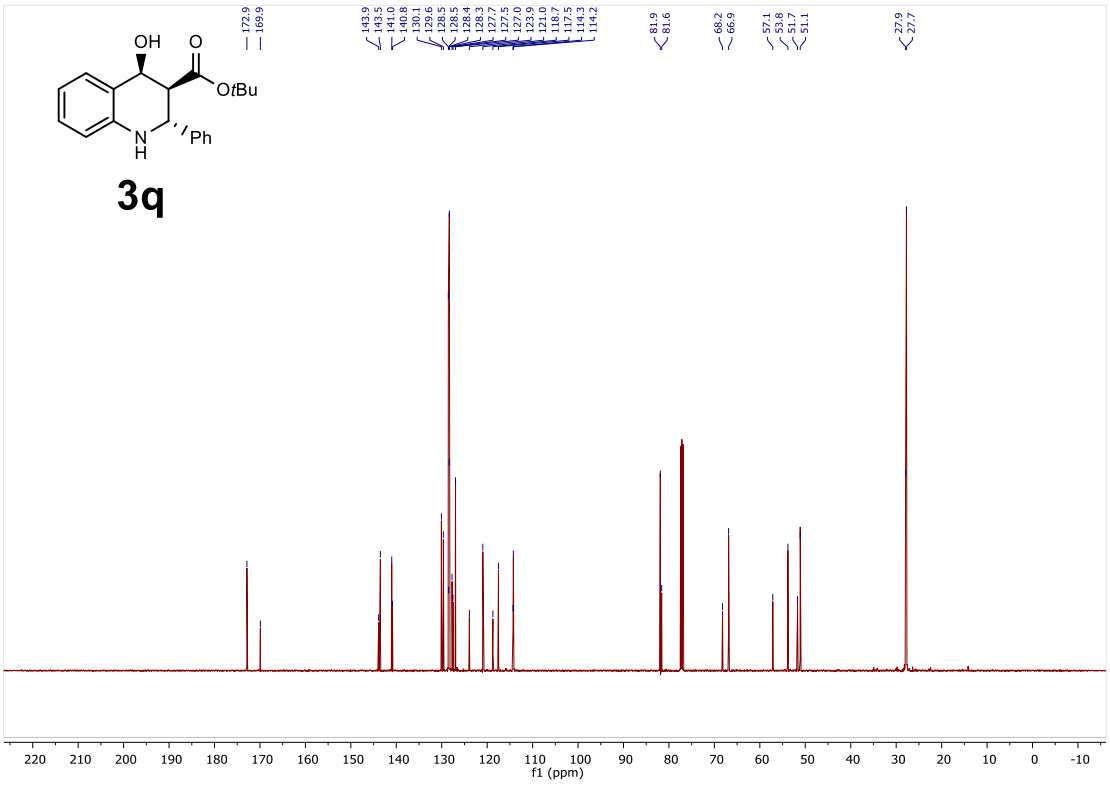

OH
O
OEt
N
H
Ph
3o
= *
7.45
7.35
7.28
7.15
6.74
6.57
4.96
4.85
4.19
3.95
3.46
2.99
0.96
2.15
3.25
1.04
1.08
1.00
1.03
0.99
0.97
0.90
2.04
0.96
0.99
2.81
f1 (ppm)

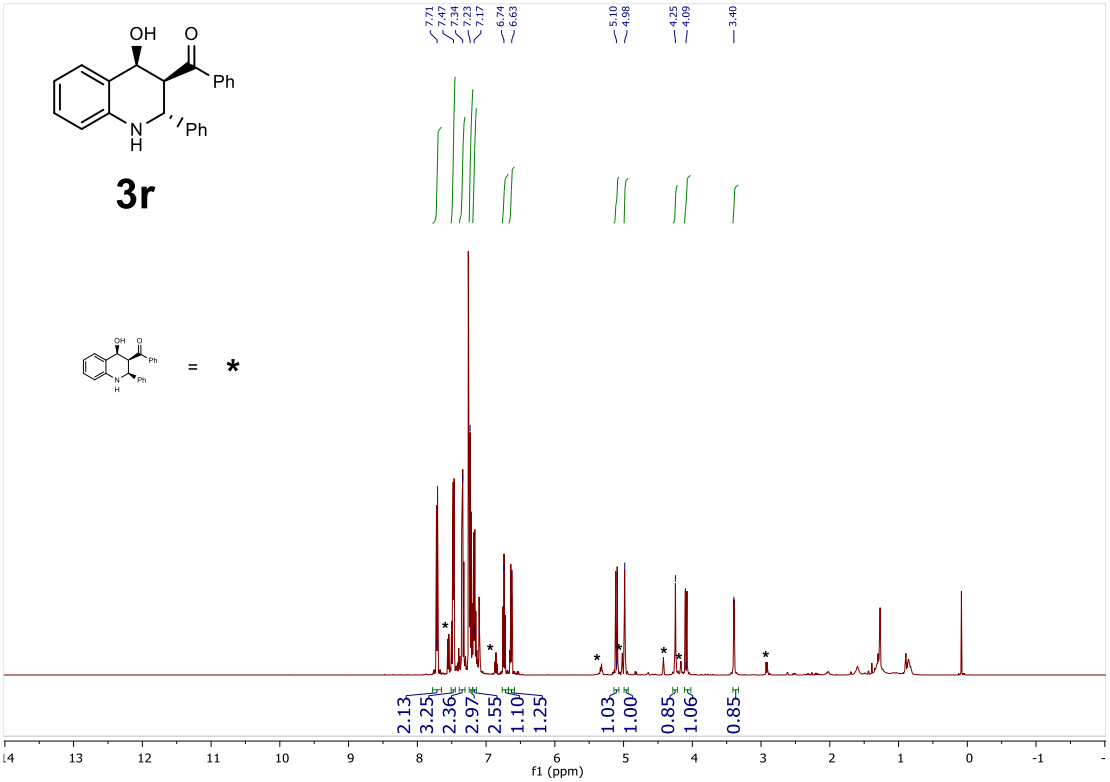

OH
O
OEt
N
H
Ph
3o
+
(minor)
173.0
143.4
141.1
130.1
129.8
128.6
128.3
128.0
120.8
117.6
114.3
66.9
60.8
53.4
50.9
50.9
13.8
0.99
1.20
1.15
2.73
2.66
5.91
3.28
5.43
1.17
2.64
2.76
2.89
2.58
3.15
3.17
2.30
f1 (ppm)

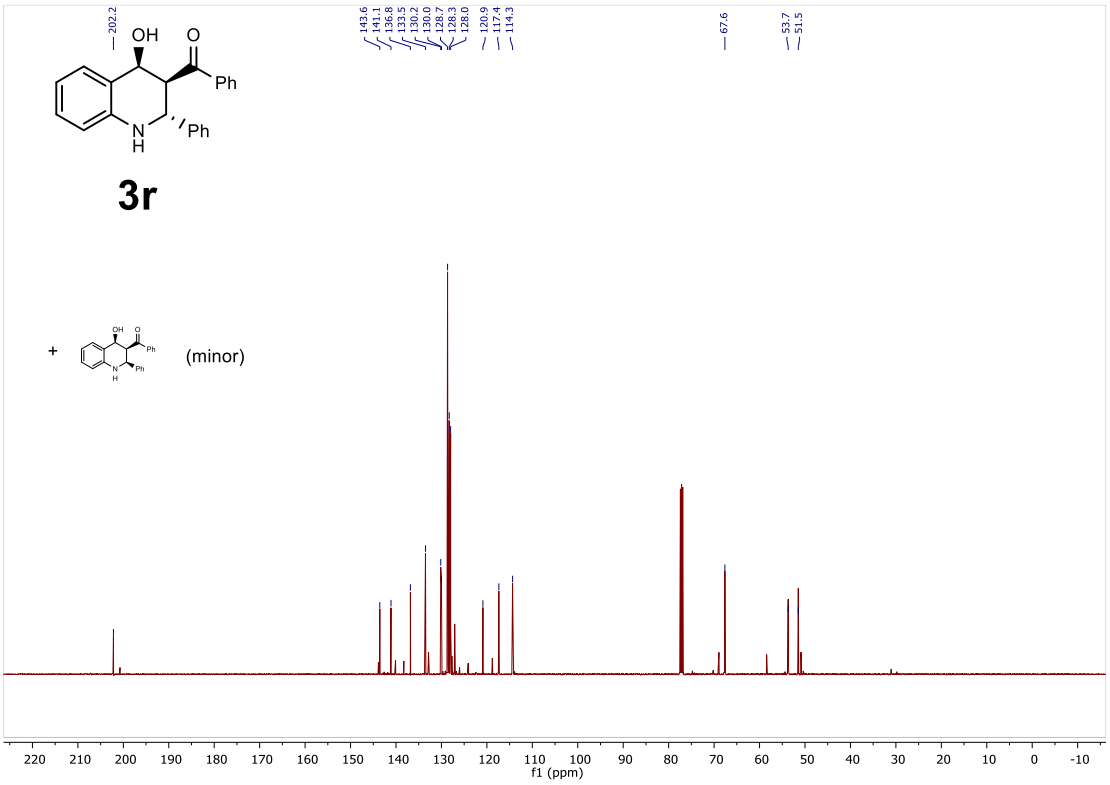

OH
O
O*i*Bu
N
H
Ph
3p
= *
7.45
7.30
7.14
6.73
6.57
4.96
4.86
4.19
3.69
3.45
3.03
1.66
0.72
2.21
4.66
1.05
1.00
0.98
1.02
0.96
0.98
2.20
0.80
1.01
1.18
6.10
f1 (ppm)

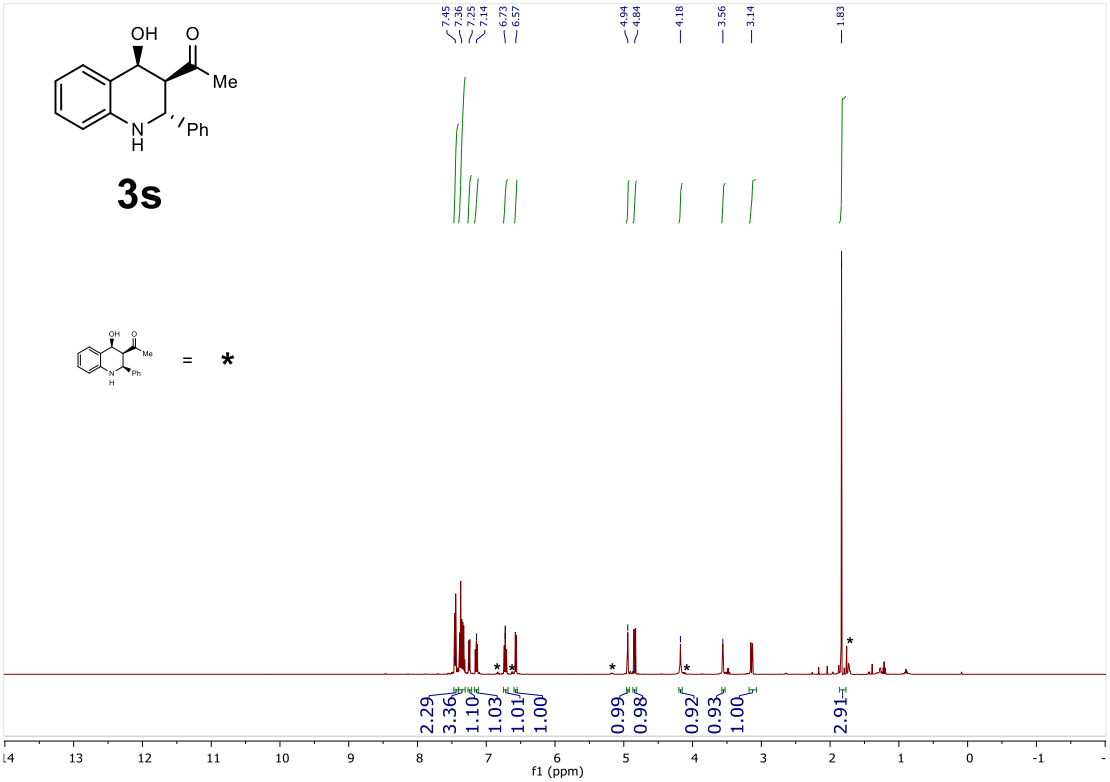

OH
O
O*i*Bu
N
H
Ph
3p
+
(minor)
173.1
143.4
141.2
130.0
129.8
128.7
128.4
127.9
120.8
117.5
114.2
71.0
67.0
53.4
50.9
27.5
18.9
18.9
f1 (ppm)

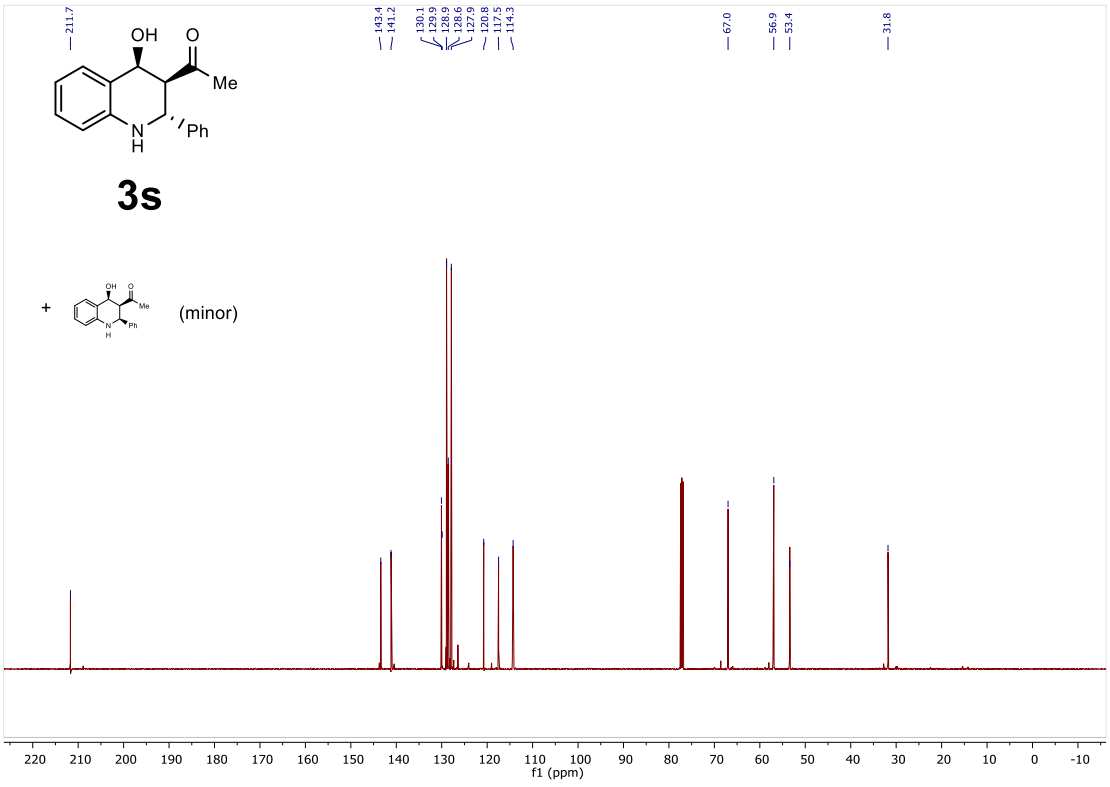

OH
O
OtBu
N
H
Ph
3q
7.47
7.34
7.12
6.82
6.73
6.62
6.56
5.17
4.95
4.86
4.83
4.16
4.13
3.83
3.31
2.95
2.91
1.23
1.17
3.83
6.20
1.65
0.53
1.09
0.56
1.08
0.54
1.07
0.50
1.13
1.08
0.53
1.08
0.52
0.50
1.06
4.68
9.00
f1 (ppm)

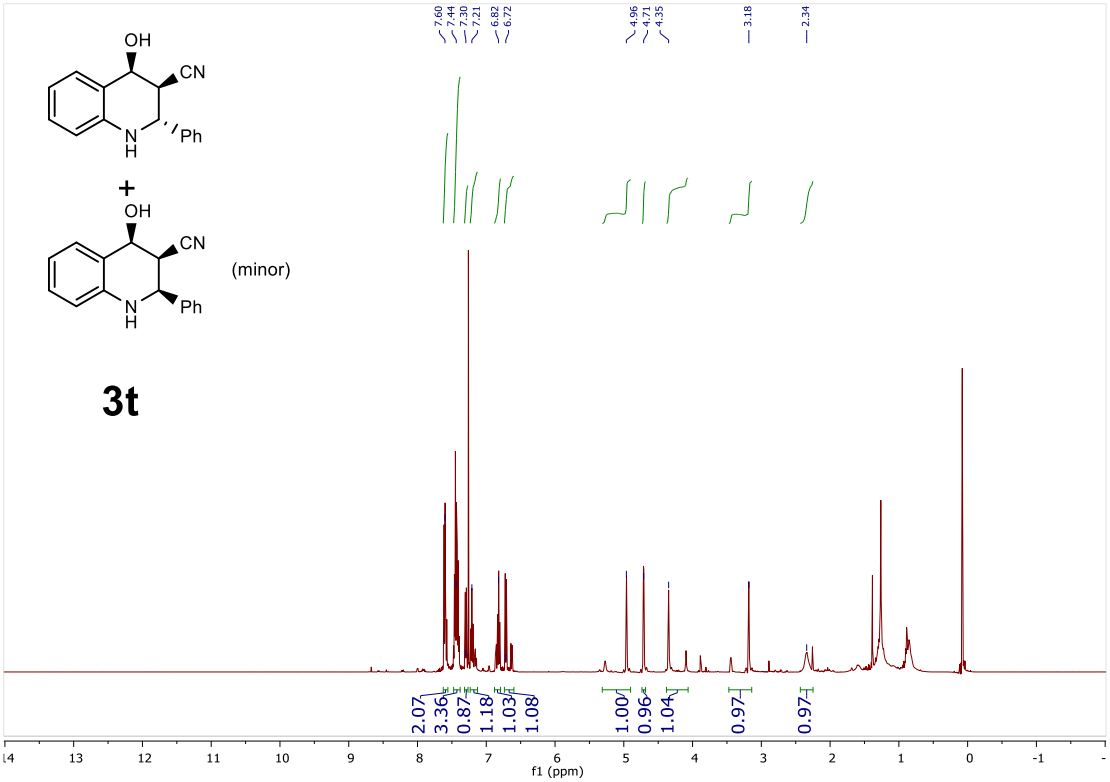

OH
O
OtBu
N
H
Ph
3q
172.9
169.9
143.9
143.5
141.0
140.8
130.1
129.6
128.5
128.5
128.4
128.3
127.7
127.5
127.0
123.9
121.0
118.7
117.5
114.3
114.2
81.9
81.6
68.2
66.9
57.1
53.8
51.7
51.1
27.9
27.7
f1 (ppm)

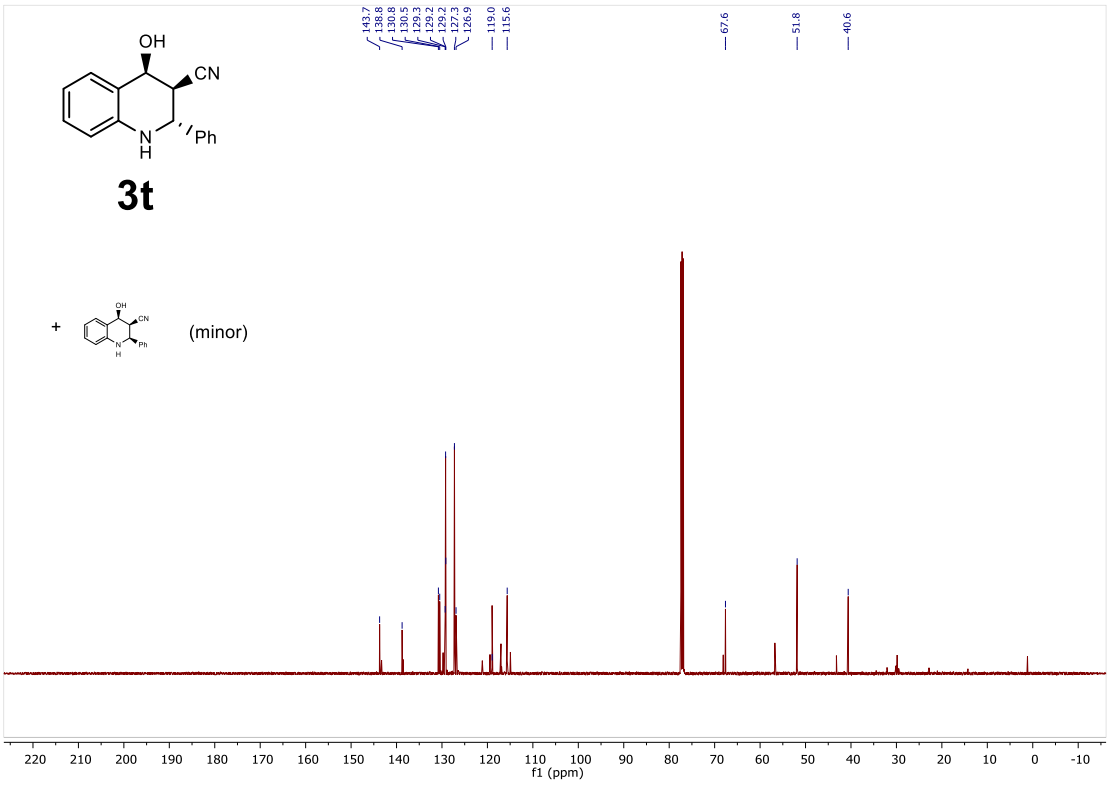

OH
O
Ph
N
H
Ph
3r
= *
7.71
7.47
7.34
7.23
7.17
6.74
6.63
5.10
4.98
4.25
4.09
3.40
2.13
3.25
2.36
2.97
2.55
1.10
1.25
1.03
1.00
0.85
1.06
0.85
f1 (ppm)

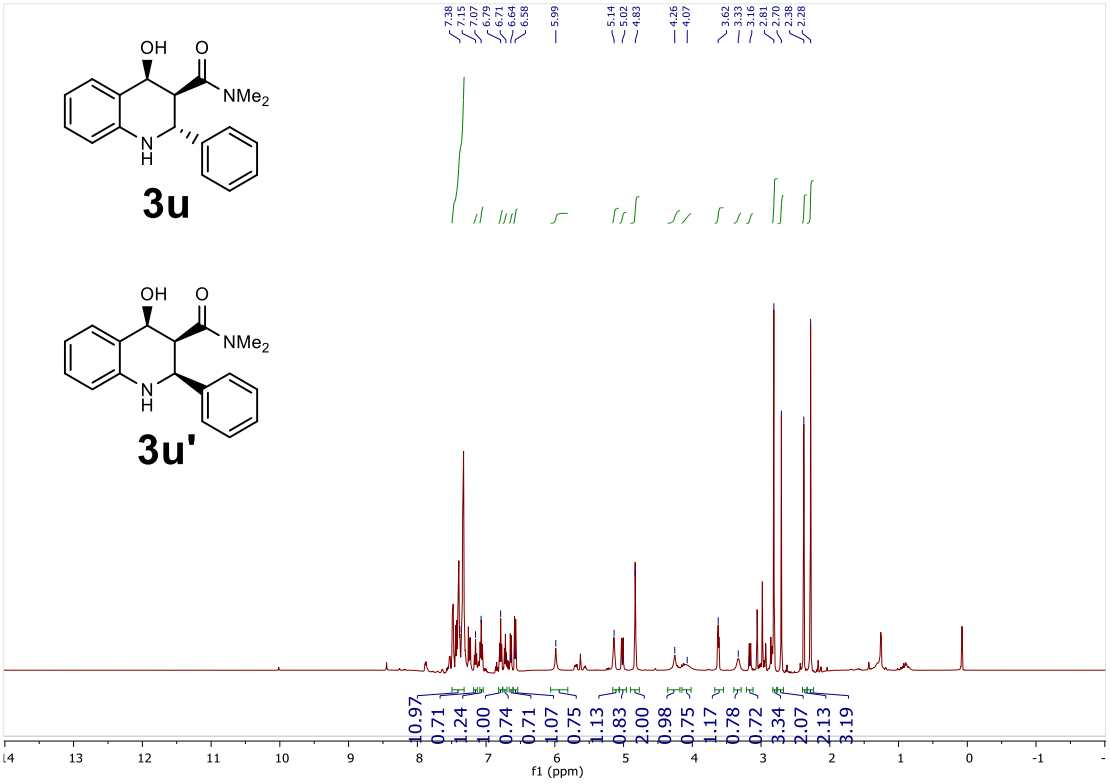

OH
O
Ph
N
H
Ph
3r
+
(minor)
202.2
143.6
141.1
136.8
133.5
130.2
130.0
128.7
128.3
128.0
120.9
117.4
114.3
67.6
53.7
51.5
f1 (ppm)

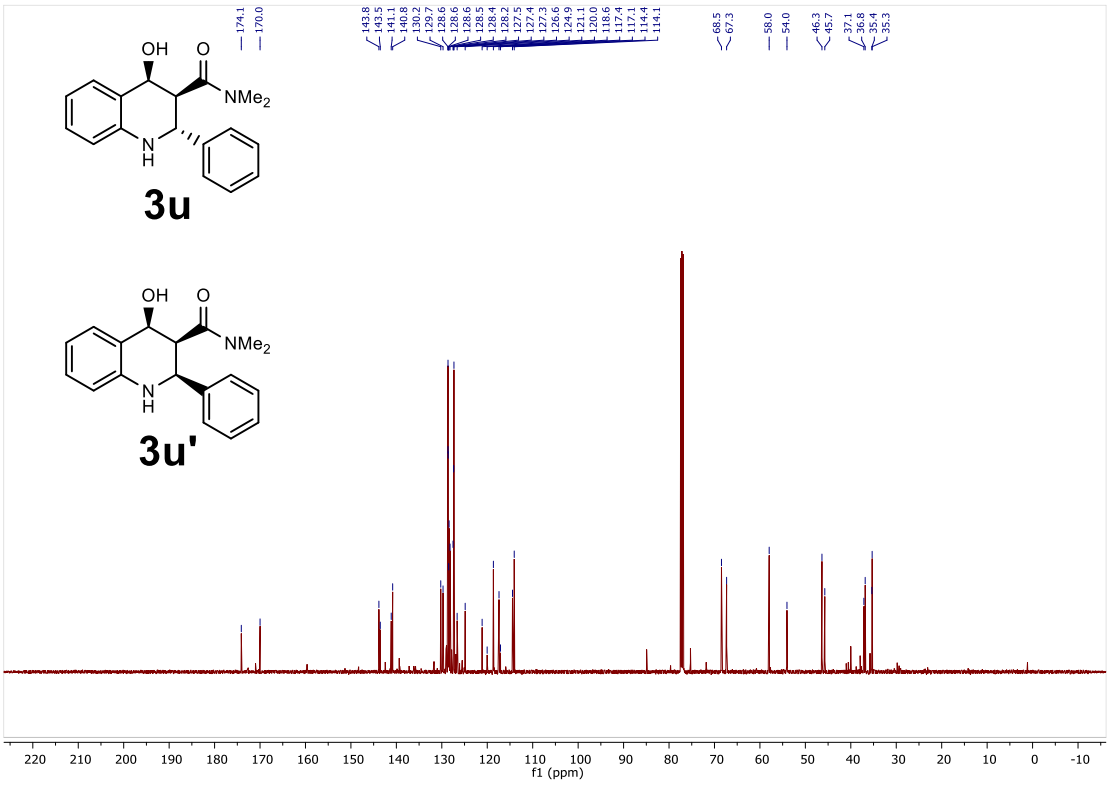

OH
O
Me
N
H
Ph
3s
= *
7.45
7.36
7.25
7.14
6.73
6.57
4.94
4.84
4.18
3.56
3.14
1.83
2.29
3.36
1.10
1.03
1.01
1.00
0.99
0.98
0.92
0.93
1.00
2.91
f1 (ppm)

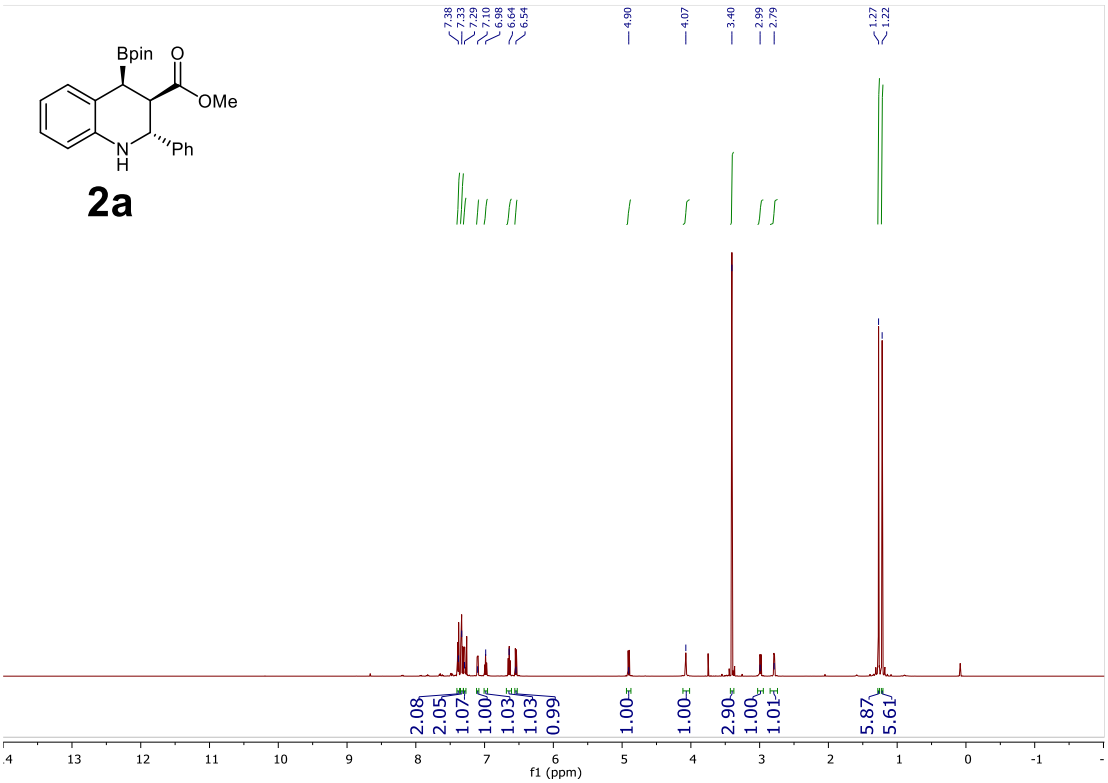

211.7
OH
O
Me
N
H
Ph
3s
+ (minor)
143.4
141.2
130.1
129.9
128.9
128.6
127.9
120.8
117.5
114.3
67.0
56.9
53.4
31.8
f1 (ppm)

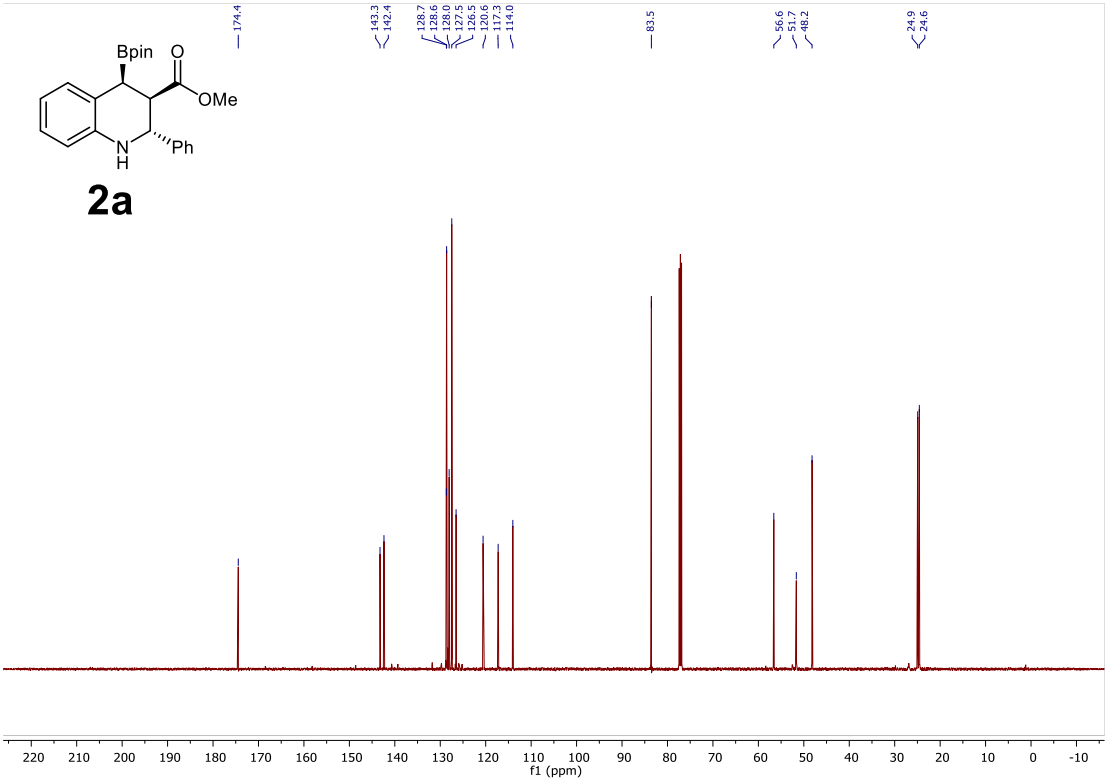

OH
CN
N
H
Ph
+
OH
CN
N
H
Ph
(minor)
3t
7.60
7.44
7.30
7.21
6.82
6.72
4.96
4.71
4.35
3.18
2.34
2.07
3.36
0.87
1.18
1.03
1.08
1.00
0.96
1.04
0.97
0.97
f1 (ppm)

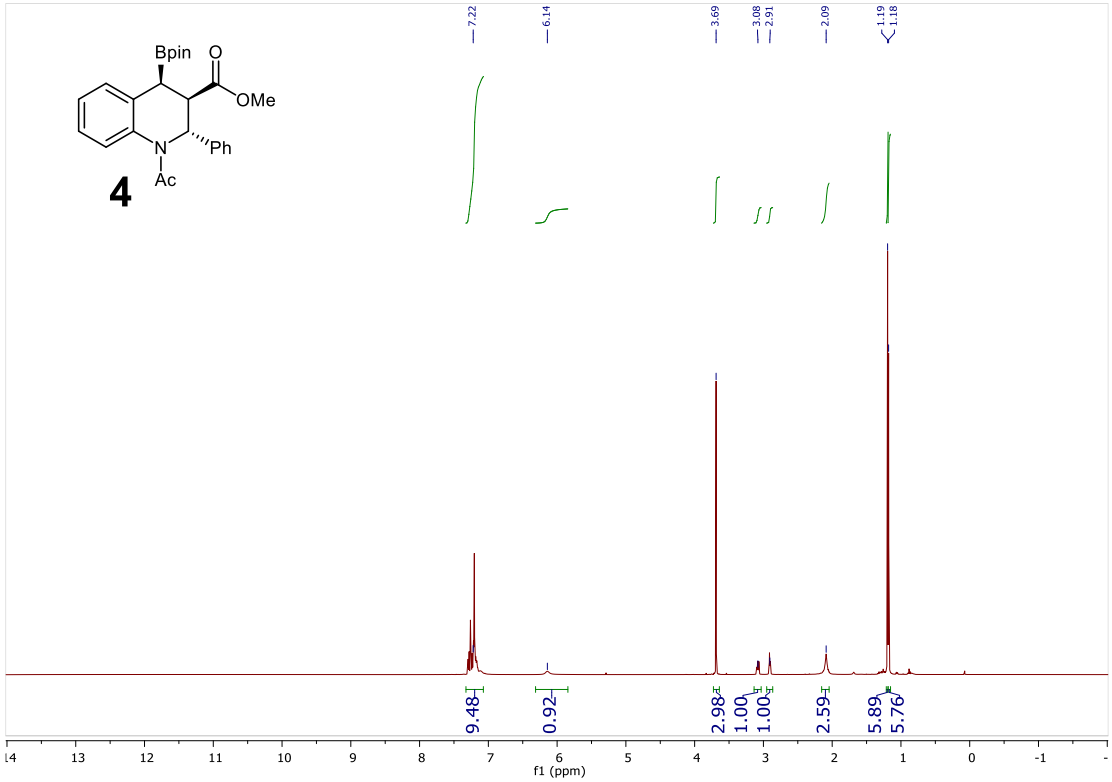

OH
CN
N
H
Ph
3t
+
(minor)
143.7
138.8
130.8
130.5
129.3
129.2
129.2
127.3
126.9
119.0
115.6
67.6
51.8
40.6
f1 (ppm)

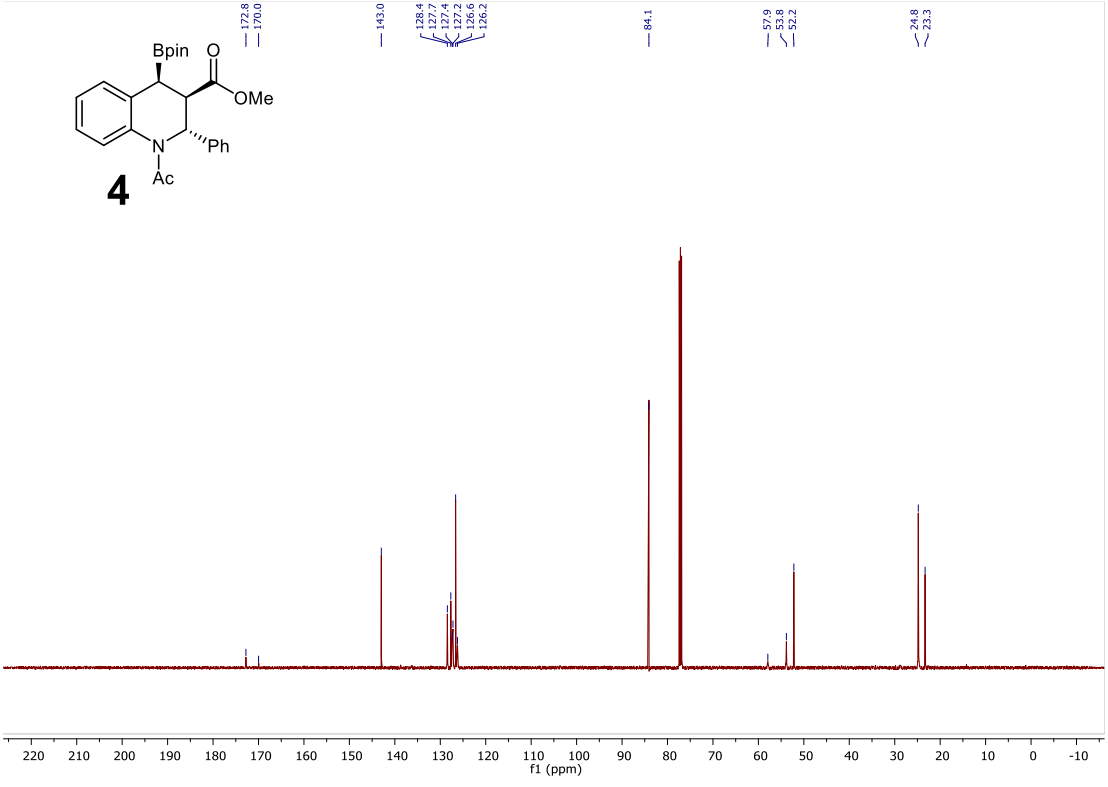

OH
O
NMe2
N
H
3u
OH
O
NMe2
N
H
3u'
7.38
7.15
7.07
6.79
6.71
6.64
6.58
5.99
5.14
5.02
4.83
4.26
4.07
3.62
3.33
3.16
2.81
2.70
2.38
2.28
10.97
0.71
1.24
1.00
0.74
0.71
1.07
0.75
1.13
0.83
2.00
0.98
0.75
1.17
0.78
0.72
3.34
2.07
2.13
3.19
f1 (ppm)

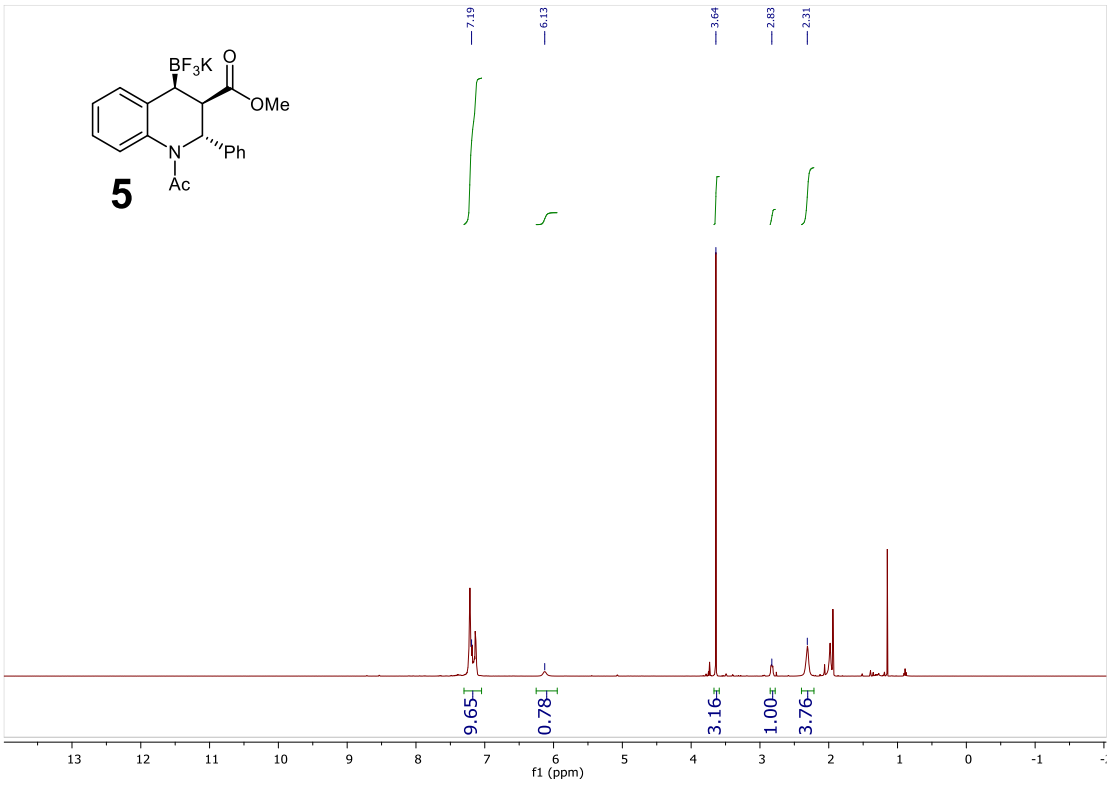

OH
O
NMe2
N
H
3u
OH
O
NMe2
N
H
3u'
174.1
170.0
143.8
143.5
141.1
140.8
130.2
129.7
128.6
128.6
128.6
128.5
128.4
128.2
127.5
127.4
127.3
126.6
124.9
121.1
120.0
118.6
117.4
117.1
114.4
114.1
68.5
67.3
58.0
54.0
46.3
45.7
37.1
36.8
35.4
35.3
f1 (ppm)

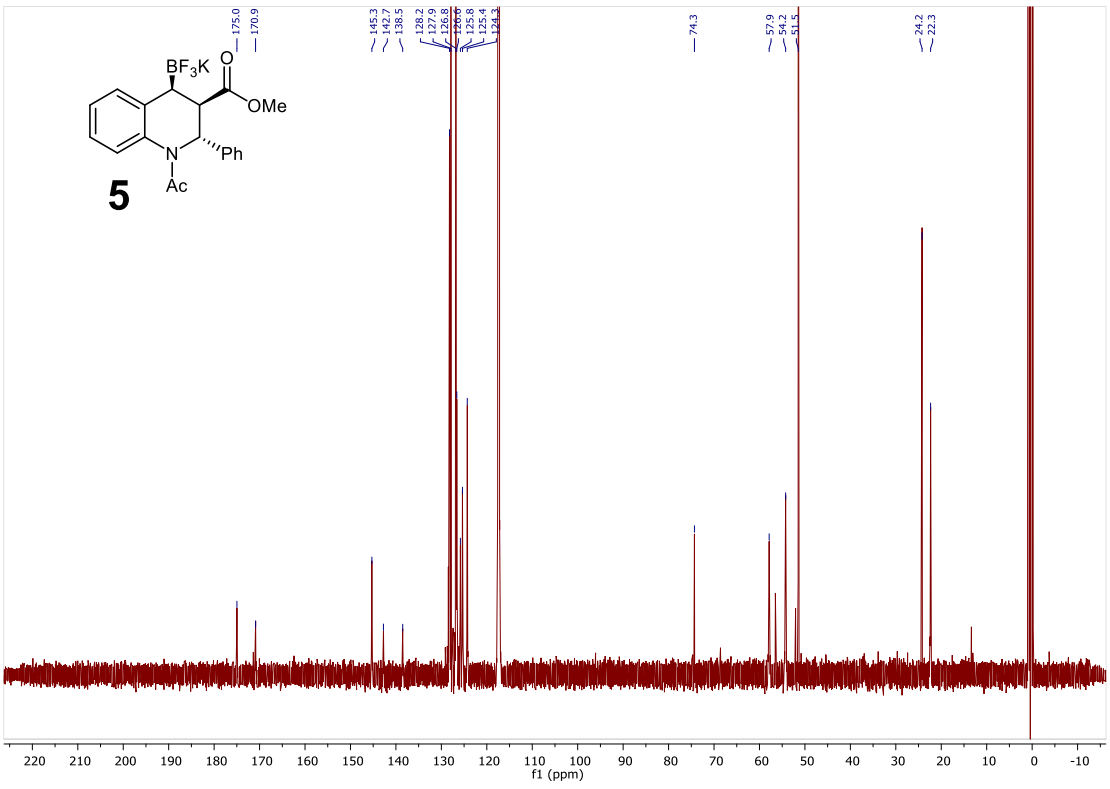

Bpin
O
OMe
N
H
Ph
2a
7.38
7.33
7.29
7.10
6.98
6.64
6.54
4.90
4.07
3.40
2.99
2.79
1.27
1.22
2.08
2.05
1.07
1.00
1.03
1.03
0.99
1.00
1.00
2.90
1.00
1.01
5.87
5.61
f1 (ppm)

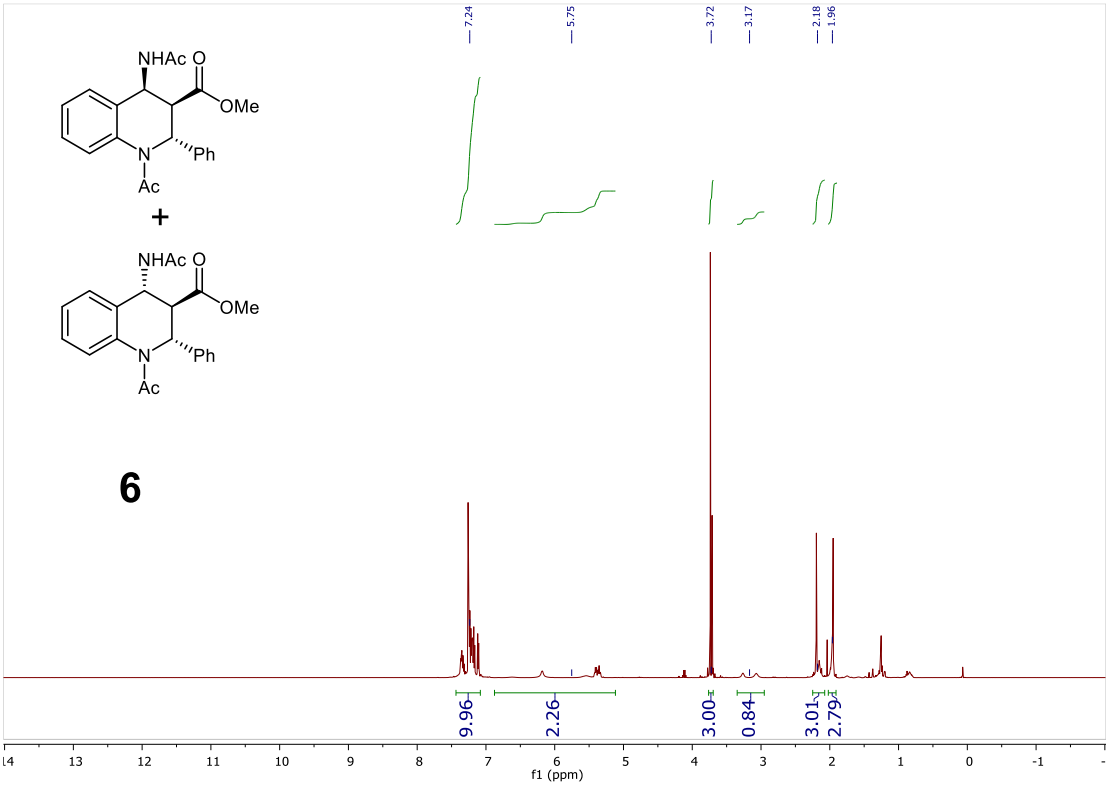

Bpin
O
OMe
N
H
Ph
2a
174.4
143.3
142.4
128.7
128.6
128.0
127.5
126.5
120.6
117.3
114.0
83.5
56.6
51.7
48.2
24.9
24.6
f1 (ppm)

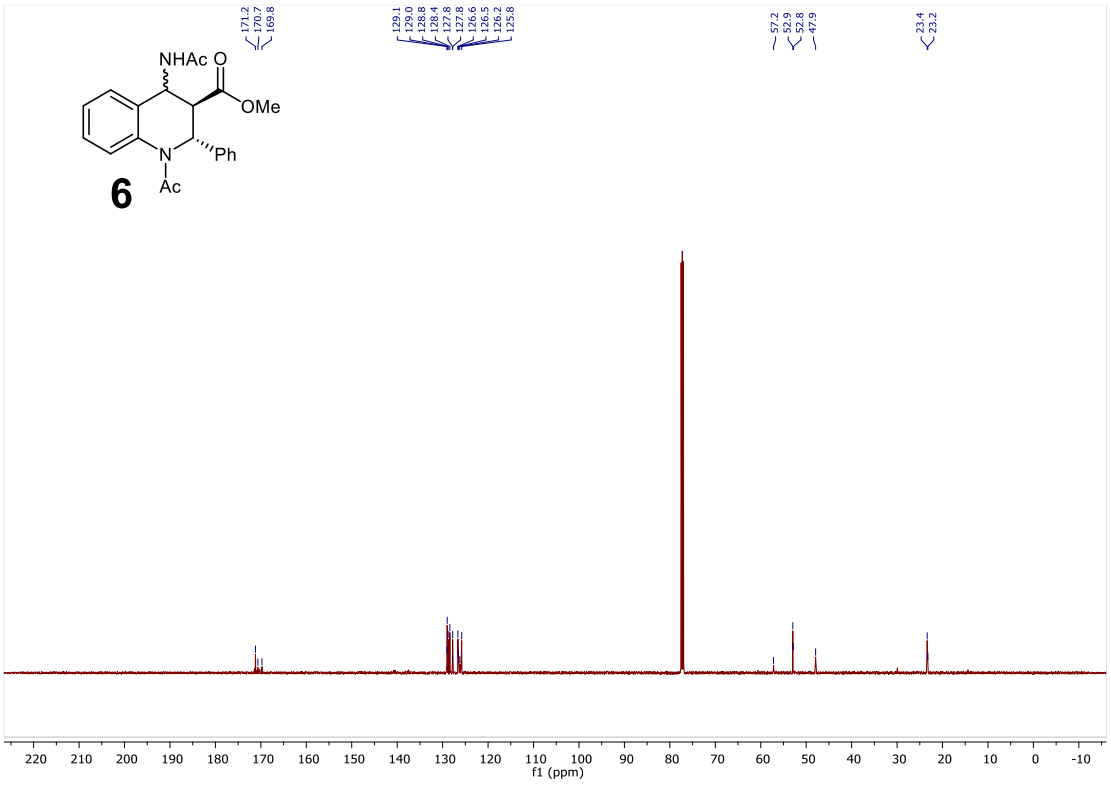

Bpin
O
OMe
N
Ph
Ac
4
7.22
6.14
3.69
3.08
2.91
2.09
1.19
1.18
9.48
0.92
2.98
1.00
1.00
2.59
5.89
5.76
f1 (ppm)

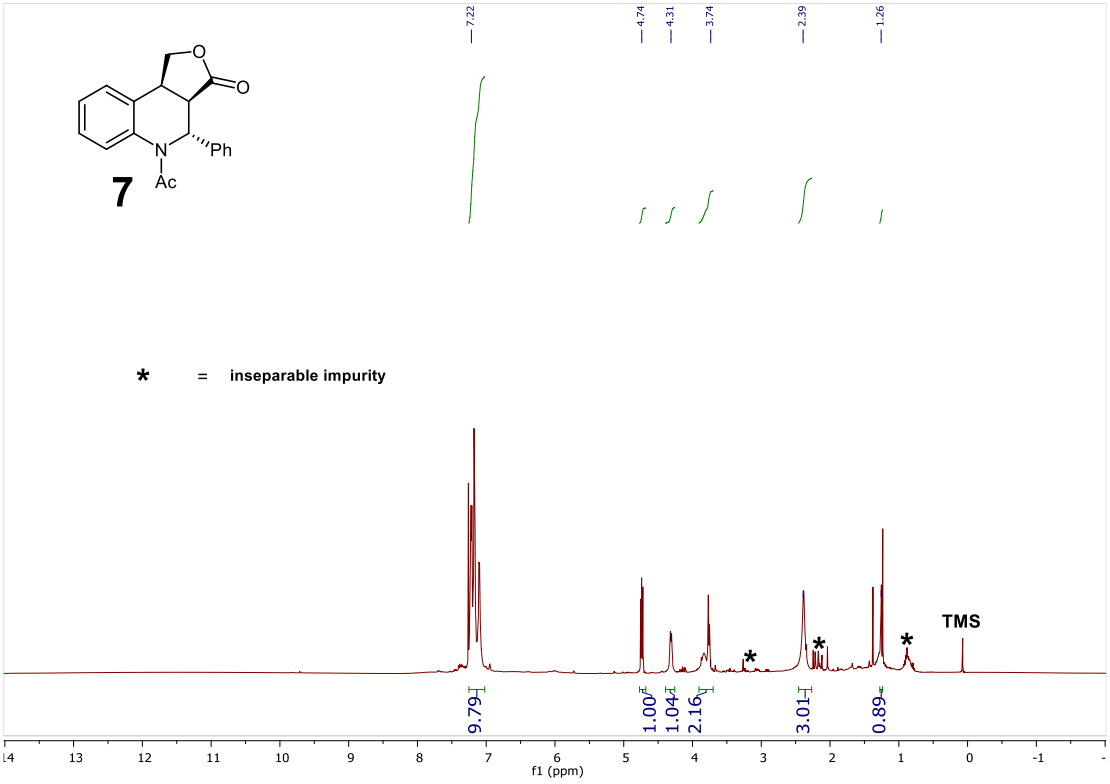

Bpin
O
OMe
N
Ph
Ac
4
172.8
170.0
143.0
128.4
127.7
127.4
127.2
126.6
126.2
84.1
57.9
53.8
52.2
24.8
23.3
f1 (ppm)

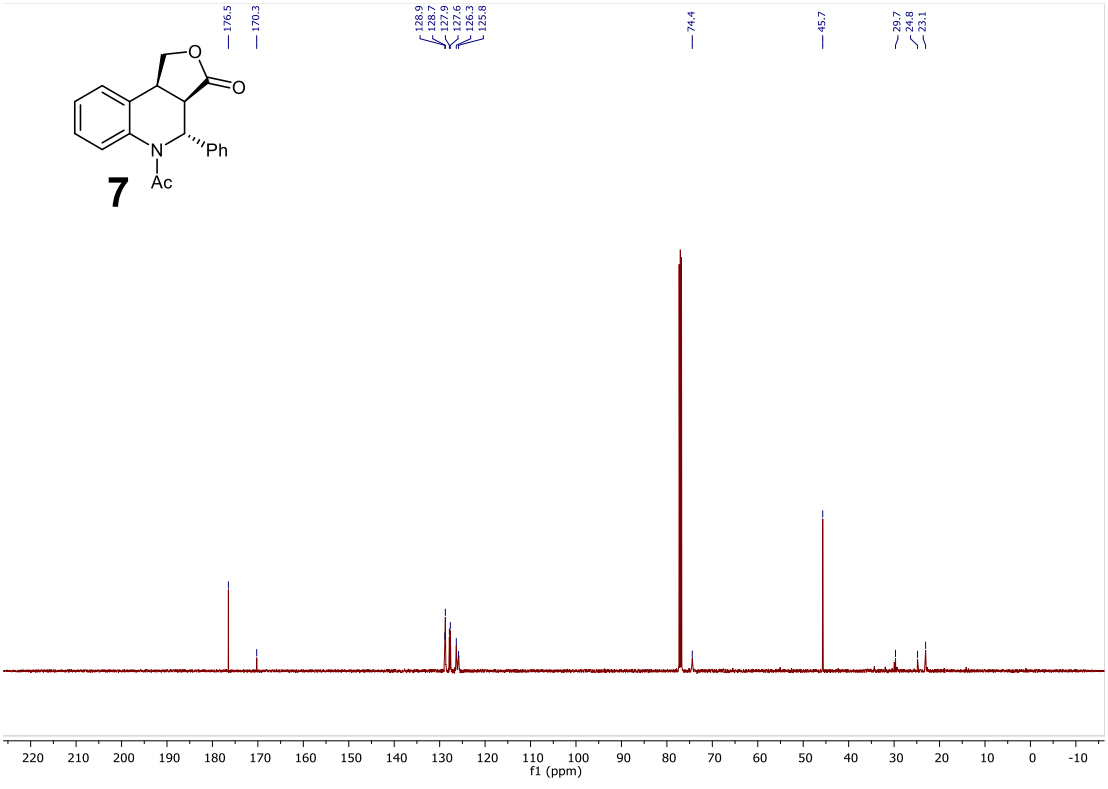

BF3K
O
OMe
N
Ac
Ph
5
7.19
6.13
3.64
2.83
2.31
9.65
0.78
3.16
1.00
3.76
f1 (ppm)

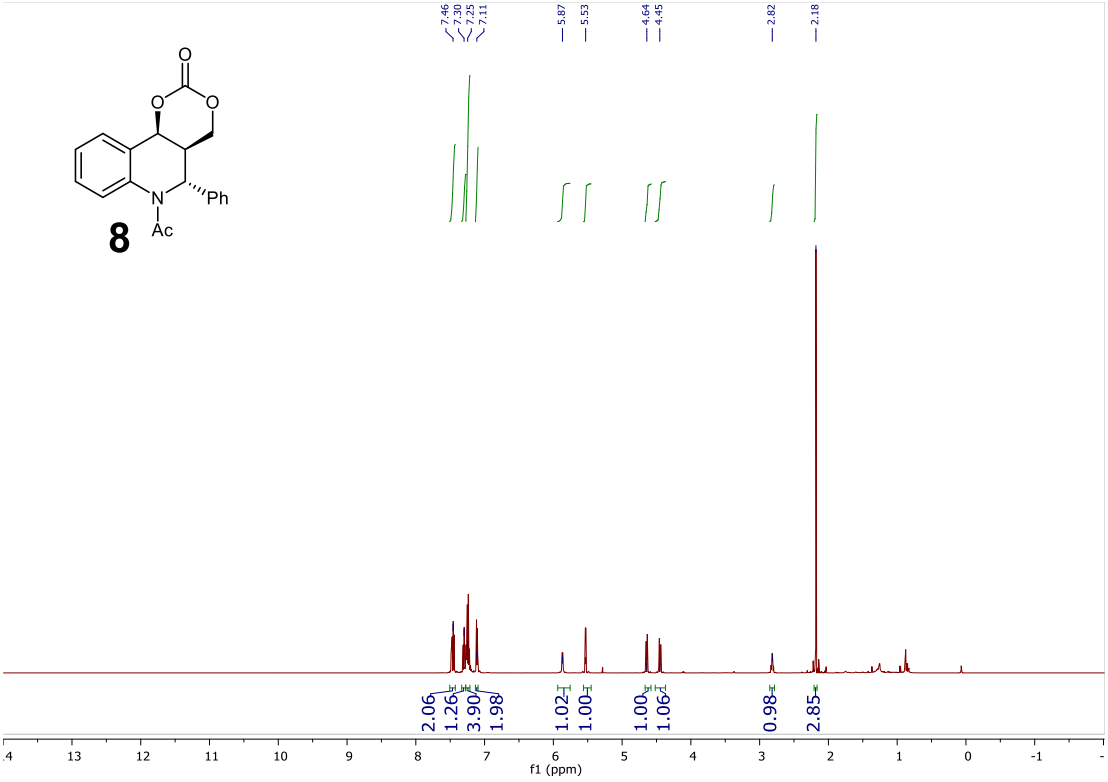

BF3K
O
OMe
N
Ac
Ph
5
175.0
170.9
145.3
142.7
138.5
128.2
127.9
126.8
126.6
125.8
125.4
124.3
74.3
57.9
54.2
51.5
24.2
22.3
f1 (ppm)

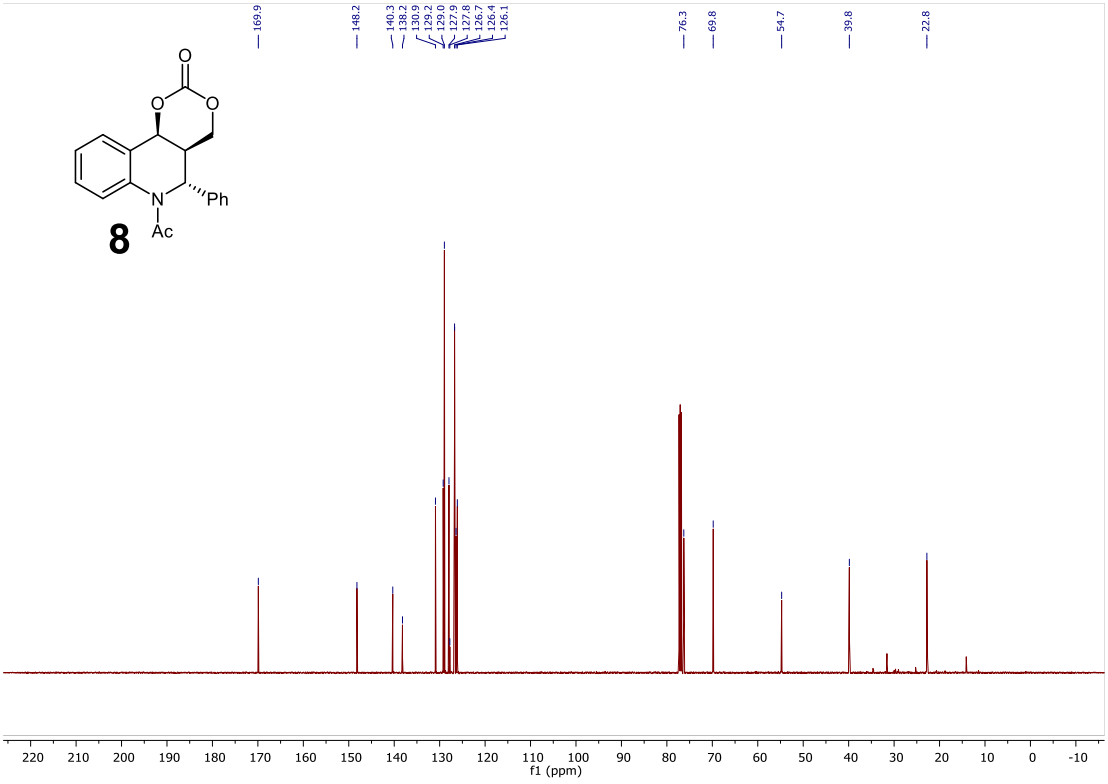

NHAc O
OMe
N
Ph
Ac
+
NHAc O
OMe
N
Ph
Ac
6
7.24
5.75
3.72
3.17
2.18
1.96
9.96
2.26
3.00
0.84
3.01
2.79
f1 (ppm)

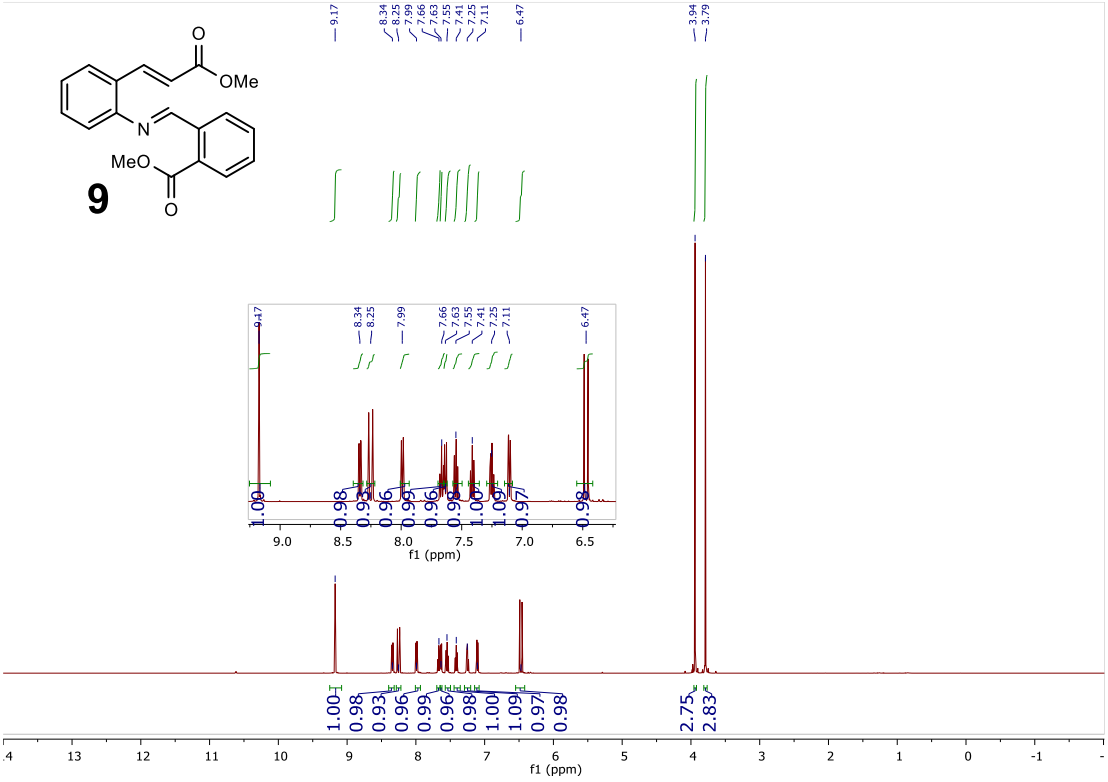

NHAc O
OMe
N
Ph
Ac
6
171.2
170.7
169.8
129.1
129.0
128.8
128.4
127.8
127.8
126.6
126.5
126.2
125.8
57.2
52.9
52.8
47.9
23.4
23.2
f1 (ppm)

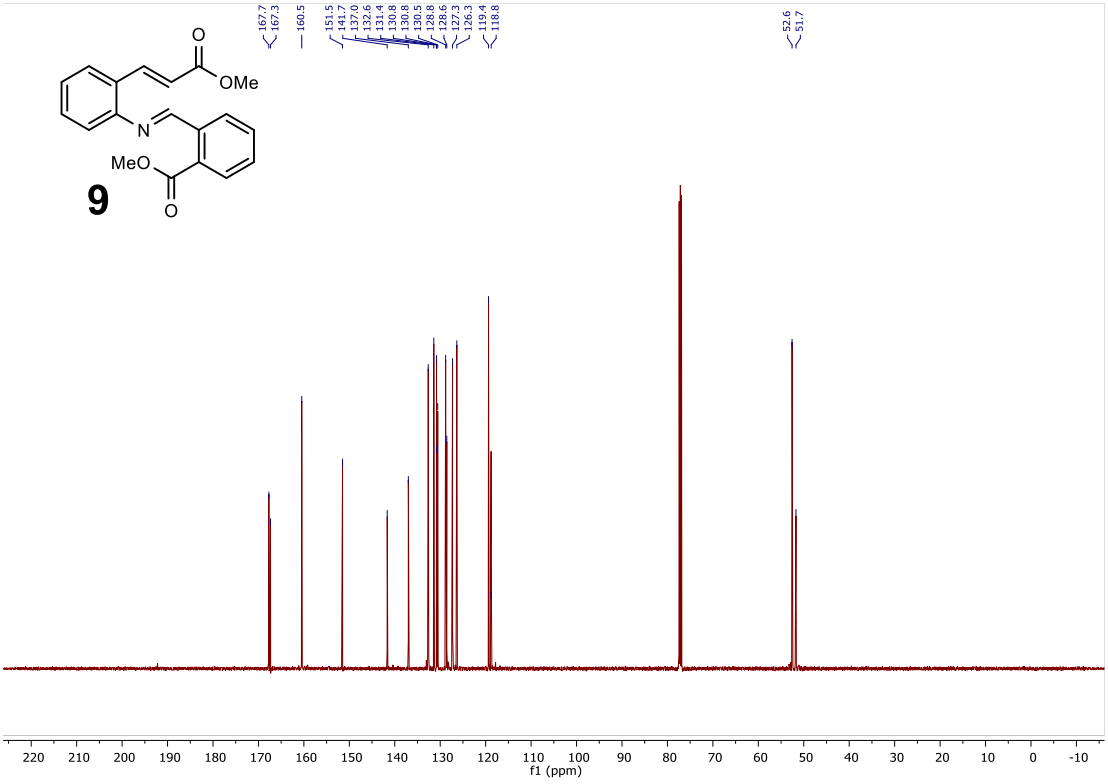

7.22
4.74
4.31
3.74
2.39
1.26
O
O
N
Ph
Ac
7
* = inseparable impurity
TMS
9.79
1.00
1.04
2.16
3.01
0.89
f1 (ppm)

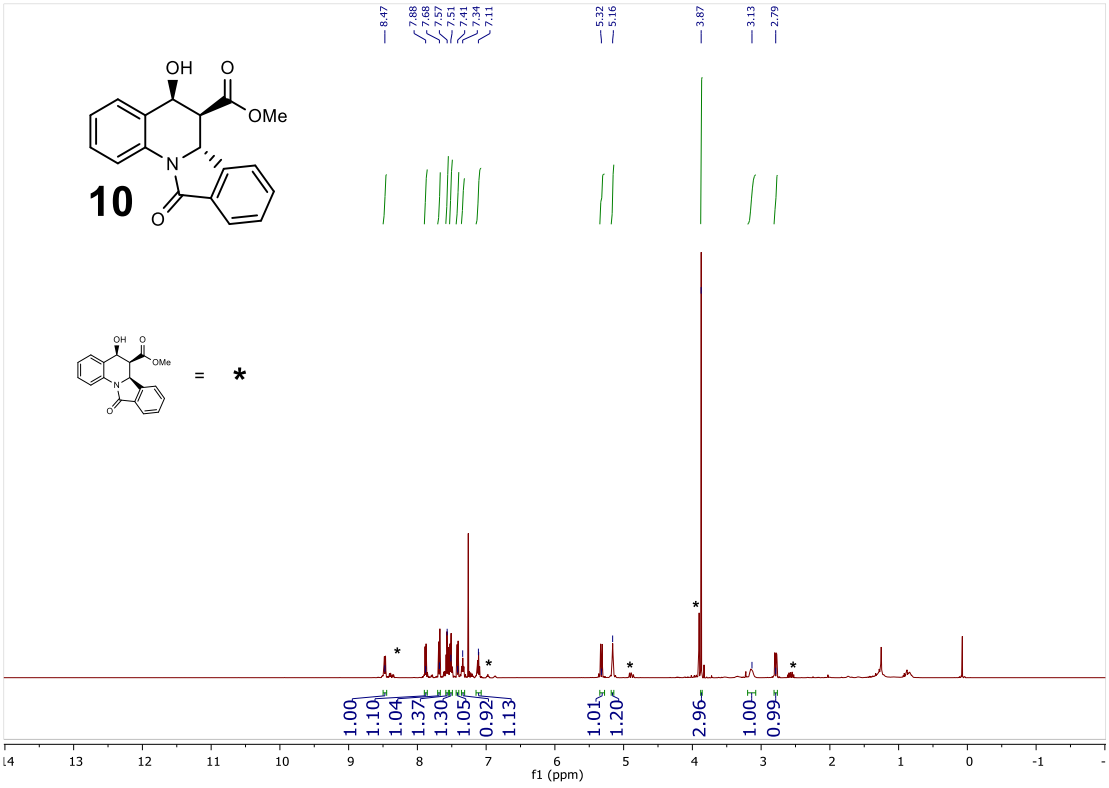

176.5
170.3
128.9
128.7
127.9
127.6
126.3
125.8
74.4
45.7
29.7
24.8
23.1
O
O
N
Ph
Ac
7
f1 (ppm)

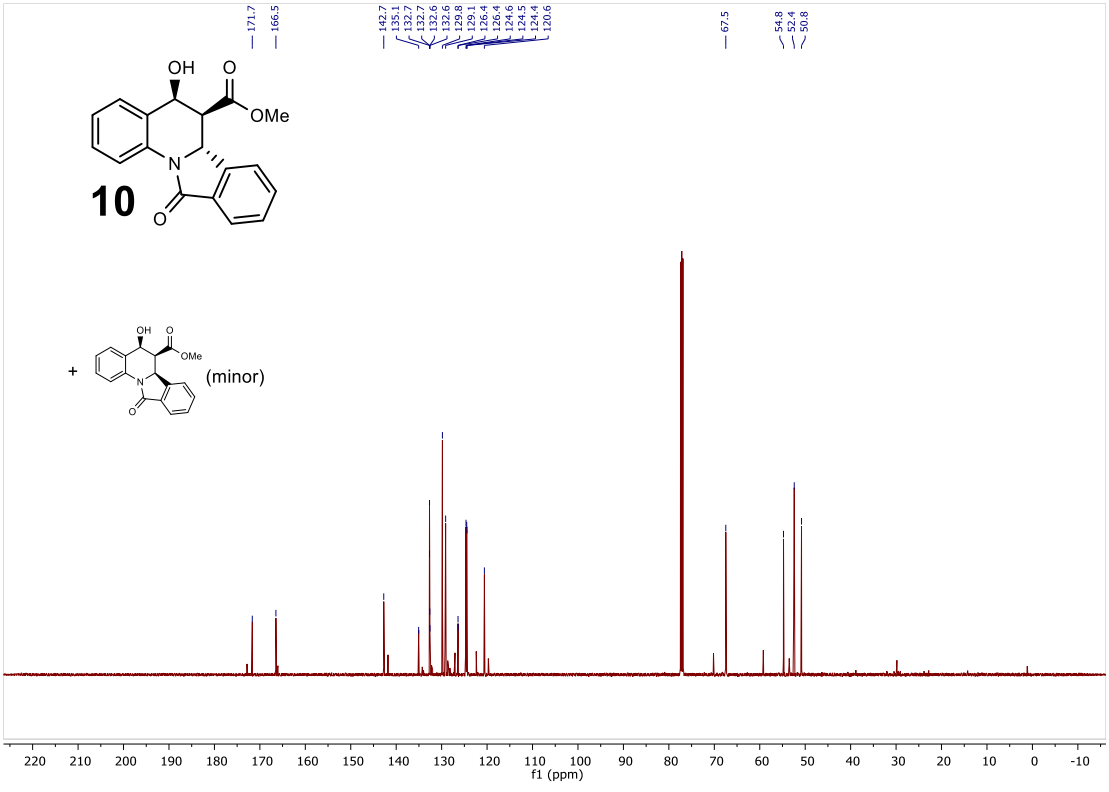

7.46
7.30
7.25
7.11
5.87
5.53
4.64
4.45
2.82
2.18
O
O
O
N
Ph
Ac
8
2.06
1.26
3.90
1.98
1.02
1.00
1.00
1.06
0.98
2.85
f1 (ppm)


169.9
148.2
140.3
138.2
130.9
129.2
129.0
127.9
127.8
126.7
126.4
126.1
76.3
69.8
54.7
39.8
22.8
O
O
O
N
Ph
Ac
8
f1 (ppm)


9.17
8.34
8.25
7.99
7.66
7.63
7.55
7.41
7.25
7.11
6.47
3.94
3.79
1.00
0.98
0.93
0.96
0.99
0.96
0.98
1.00
1.09
0.97
0.98
2.75
2.83
f1 (ppm)
O
OMe
N
MeO
O
9


167.7
167.3
160.5
151.5
141.7
137.0
132.6
131.4
130.8
130.5
128.8
128.6
127.3
126.5
119.4
116.8
52.6
51.7
f1 (ppm)
O
OMe
N
MeO
O
9


8.47
7.88
7.68
7.57
7.51
7.41
7.34
7.11
5.32
5.16
3.87
3.13
2.79
OH
O
OMe
N
O
10
= *
1.00
1.10
1.04
1.37
1.30
1.05
0.92
1.13
1.01
1.20
2.96
1.00
0.99
f1 (ppm)


171.7
166.5
142.7
135.1
133.7
132.7
132.6
132.6
129.8
129.1
126.4
126.4
124.6
124.5
124.4
120.6
67.5
54.8
52.4
50.8
OH
O
OMe
N
O
10
+
(minor)
f1 (ppm)

10 References

[1] X, Ji, H. Huang, Y. Li, H. Chen, H. Jiang, *Angew. Chem. Int. Ed.* **2012**, *51*, 7292-7296

[2] Y.-P. Bi, H.-M. Wang, H.-Y. Qu, X.-C. Liang, Y. Zhou, X.-Y. Li, D. Xu, M.-H. Shen, H.-D. Xu, *Org. Biomol. Chem.* **2019**, *17*, 1542-1546

[3] A. Patra, S. Mukherjee, T.K. Das, S. Jain, R.G. Gonnade, A.T. Biju, *Angew. Chem. Int. Ed*. **2017**, *56*, 2730-2734

[4] Z.-X. Jia, Y.-C. Luo, P.-F. Xu *Org. Lett.* **2011**, *13*, 832-835