Supporting Information

One-pot C-N/C-C bond formation and oxidation of donor-acceptor cyclopropanes with tetrahydroisoquinolines: access to benzo-fused indolizines

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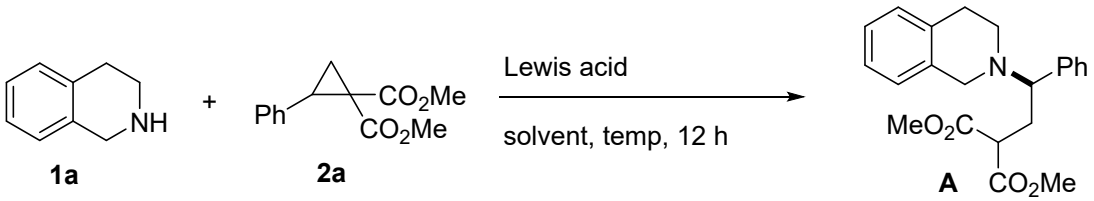
General Information. 1,2,3,4-Tetrahydroisoquinolines, MgI_2 (98%), $Mn(OAc)_3 \cdot 2H_2O$ (97%), MnO_2 (≥99%), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (98%) of Aldrich, TCI chemicals and BLD pharm were used as received. Solvents were dried prior as per the standard procedure. Cyclopropanes[1] and 2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepine[2] were prepared according to the reported procedure. Merck silica gel G/GF254 plates were used for analytical TLC and Rankem silica gel (60-120 mesh) was utilized for column chromatography. NMR spectra were recorded with Bruker Avance III 600, 500 and 400 MHz spectrometers using $CDCl_3$ as solvent and Me_4Si as an internal standard. Chemical shifts (δ) and spin-spin coupling constant (*J*) are reported in ppm and in Hz, respectively, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dd = doublet of doublets. Melting points were determined using a Büchi B-540 apparatus and are uncorrected. FT-IR spectra were collected on Perkin Elmer IR spectrometer. UHPLC-QTOF-ESI-MS instrument was used for recording mass spectra. Single crystal X-ray data was collected on a Bruker SMART APEX equipped with a CCD area detector using Mo/K*α* radiation and the structure was solved by direct method using *SHELXL-2014/7* (Göttingen, Germany).

Table S1 Optimization of Ring-Opening of Donor-Acceptor Cyclopropanes (DACs)[a]



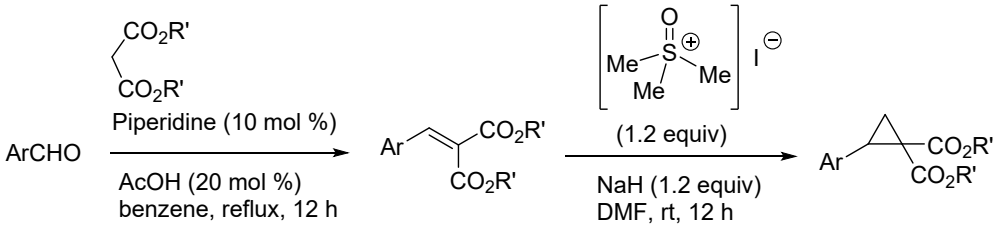
Entry	Lewis acid	Solvent	Temp. (ºC)	Yield(%)[b]
1	$InCl_3$	CH_2Cl_2	r.t.	n.d.
2	$FeCl_3$	CH_2Cl_2	r.t.	n.d.
3	$AlCl_3$	CH_2Cl_2	r.t.	12
4	$SnCl_2$	CH_2Cl_2	r.t.	trace
5	MgI_2	CH_2Cl_2	r.t.	15
6	MgI_2	$(CH_2Cl)_2$	r.t.	22
7	MgI_2	$(CH_2Cl)_2$	80	61

8	MgI_2	toluene	80	88
9	MgI_2	xylene	80	75
10	MgI_2	toluene	110	79

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), Lewis acid (20 mol %), solvent (2 mL), 12 h; [b]Isolated yield. r.t.= room temperature. n.d. = not detected.

General Procedure for the Preparation of DACs (GP-1).[1]

Cyclopropanes **2a-p** were synthesized from aromatic aldehydes through a standard synthetic sequence of Knoevenagel/Corey-Chaykovsky reactions.



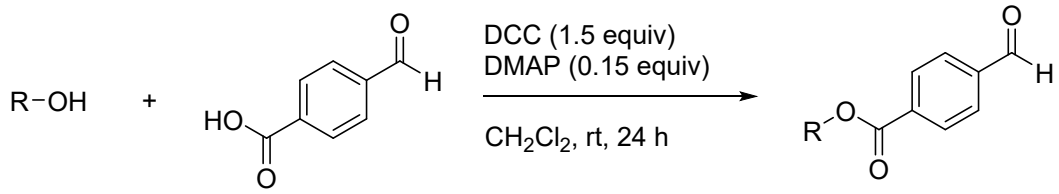
To a stirred solution of aldehyde (5 mmol) in benzene (10 mL), dimethyl malonate (5 mmol, 660 mg), piperidine (0.5 mmol, 50 μL) and acetic acid (0.5 mmol, 28 μL) were added. The flask was equipped with a Dean-Stark trap and condenser, and the solution was heated to reflux in an oil bath for 12 h. After completion, evaporation of the solvent gave a residue that was purified by silica gel column chromatography using ethyl acetate and hexane.

Sodium hydride (4 mmol, 60% dispersion in mineral oil, 96 mg) was suspended in dimethylformamide (DMF) (10 mL) under nitrogen. Trimethylsulfoxonium iodide (3.85 mmol, 847 mg) was added, and the solution was stirred for 1 h at room temperature. A solution of the appropriate benzylidene malonate (3.5 mmol) in DMF (1 mL) was added, and the reaction mixture was stirred for 12 h at room temperature. After completion, the solution was poured onto a mixture of ice and 2 M HCl (5 mL) and extracted with diethyl ether (25 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate as an eluent to give cyclopropanes.

Substrates **2k** and **2o-r** are new and their complete characterization data are provided, whereas **2a**,[1a] **2b**,[1c] **2c-d**,[1b] **2e**,[1c] **2f**,[1b] **2g-h**,[1a] **2i**,[1c] **2j-l**,[1b] **2m**[1a] and **2n**[1c] are known, synthesized according to the reported procedure and ^{1}H NMR are given to show the purity.

General Procedure for the Synthesis of 2o-q.

Step 1: Synthesis of Aldehydes[3]



First, carboxylic acid (1 mmol), dicyclohexylcarbodiimide (DCC) (1.5 mmol, 309 mg), 4-dimethylaminepyridine (DMAP) (0.15 mmol, 18 mg) and alcohol/phenol (1.2 mmol) were stirred in CH_2Cl_2 (10 mL) for 12 h at room temperature. The reaction mixture was then passed through as short pad of celite. The solvent was evaporated and the residue was purified on silica gel chromatography using ethyl acetate/hexane as an eluent.

Step 2: Synthesis of DA Cyclopropanes [1]

DA Cyclopropanes were made using GP-1.

General Procedure for the Synthesis of 3. Amine **1** (0.2 mmol), cyclopropane **2** (0.24 mmol) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC. The progress of the reaction was monitored by TLC using ethyl acetate and hexane. The reaction mixture was diluted with ethyl acetate (2 x 15 mL) and washed with water (2 x 5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave the residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford **3**.

General Procedure for the Synthesis of 4. Amine **1** (0.2 mmol), cyclopropane **2** (0.24 mmol) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (1.0 mmol, 268 mg) in MeOH (2 mL) for 12 h at 80 ºC. The progress of the reaction was monitored by TLC using ethyl acetate and hexane. The reaction mixture was diluted with ethyl acetate (2 x 15 mL) and washed with water (2 x 5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave the residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford **4**.

Scale-up Synthesis of 3aa. 1,2,3,4-Tetrahydroisoquinoline **1a** (2 mmol, 266 mg), dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **2a** (2.4 mmol, 561 mg) and MgI_2 (20 mol %, 111 mg) were stirred in toluene (10 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (6 mmol, 1.6 g) in MeOH (10 mL) for 12 h at 80 ºC. The progress of the reaction was monitored by TLC using ethyl acetate and hexane. The reaction mixture was diluted with ethyl acetate (2 x 30 mL) and washed with water (2 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave the residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford **3aa** in 41% yield (248 mg).

Sample Preparation for Crystal Growth. The compound **3ag** was dissolved in minimum volume of acetonitrile and kept at room temperature for slow evaporation (2 days). The block shaped crystal was then subjected to X-ray diffraction.

Crystal Data and Structure Refinement

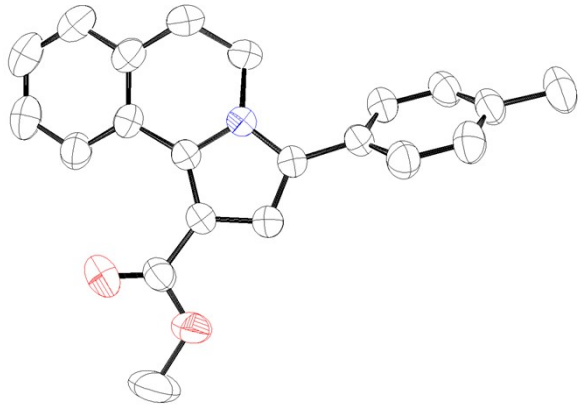
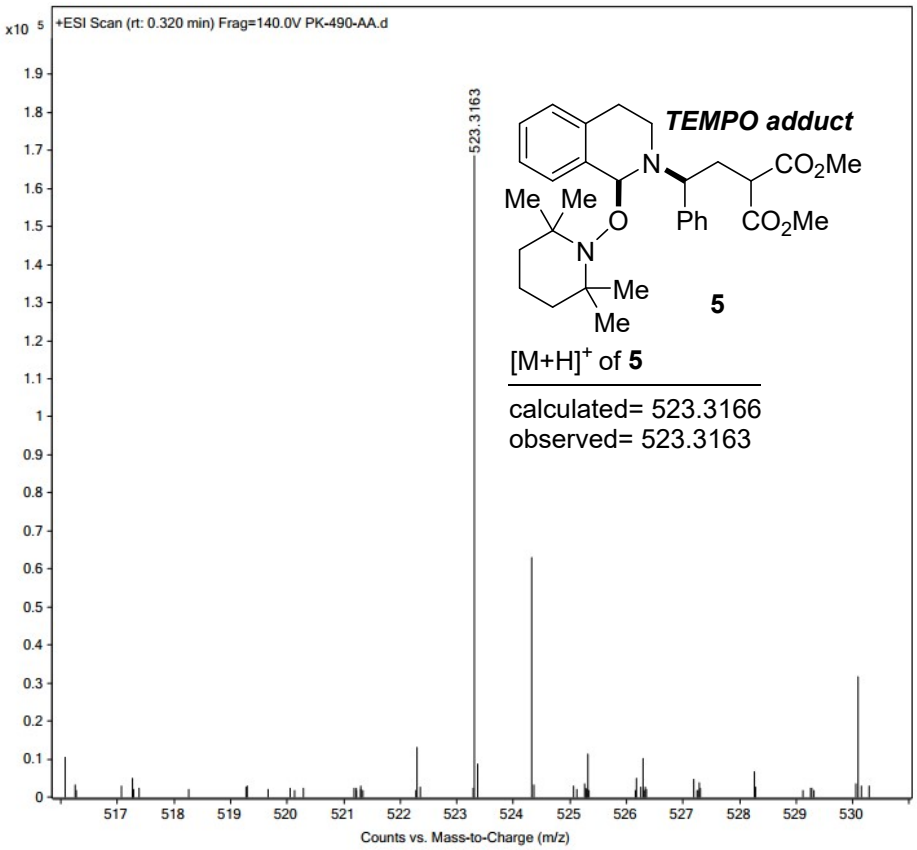


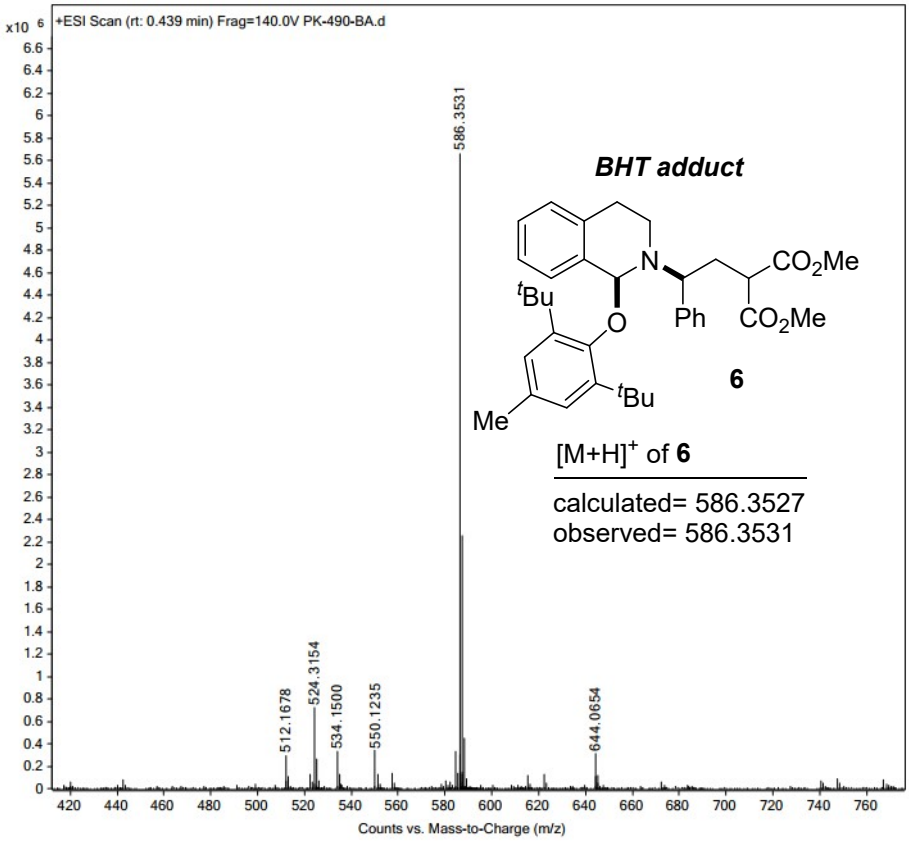
Figure S1. ORTEP diagram of Methyl 3-(*p*-tolyl)-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate **3ag** with 50% ellipsoid (CCDC 2290607). H-Atoms omitted for clarity.

Identification code	**3ag**
Empirical formula	'C21 H19 N1 O2'
Formula weight	317.37
Crystal habit, colour	Neddle /colourless
Crystal size, mm^3	0.32 x 0.29 x 0.27
Temperature, *T*/K	296 K
Wavelength, λ/Å	0.71073
Crystal system	' monoclinic '

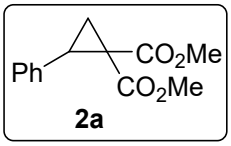
Space group	' P 21/c '
Unit cell dimensions	a = 10.0187(6) Å b = 15.8815(10) Å c = 10.6953(7) Å α = 90 β = 99.728 γ = 90
Volume, V/Å^3	1677.28(18)
Z	4
Calculated density, g cm^{-3}	1.257
Absorption coefficient, μ/mm^{-1}	0.081
F(000)	672
θ range for data collection	2.062 to 28.345°
Limiting indices	–13 ≤ h ≤ 12, –21≤ k ≤ 21, –14 ≤ l ≤ 14
Reflection collected / unique	4177/2685
Completeness to θ	99.6% (θ = 28.345°)
Absorption correction	None
Max. and min. transmission	0.974 and 0.978
Refinement method	'SHELXL-2014/7 (Sheldrick, 2014)'
Data / restraints / parameters	4177/0/219
Goodness–of–fit on F^2	0.853
Final R indices [I>2sigma(I)]	R1 = 0.0640, wR2 = 0.1850
R indices (all data)	R1 = 0.1009, wR2 = 0.2209

ESI-HRMS Spectra of Radical Trapping Experiments

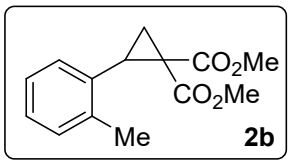




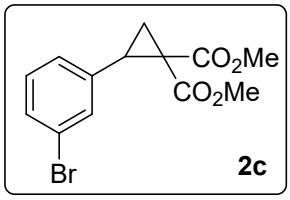
Characterization Data



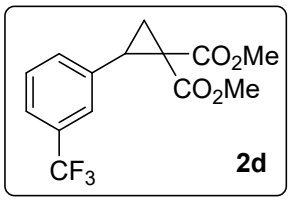
Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate 2a.[1a] Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21-7.14 (m, 3H), 7.12-7.10 (m, 2H), 3.72 (s, 3H), 3.28 (s, 3H), 3.15 (t, J = 9.0 Hz, 1H), 2.13 (dd, J = 8.0, 5.0 Hz, 1H), 1.67 (dd, J = 9.5, 5.5 Hz, 1H).



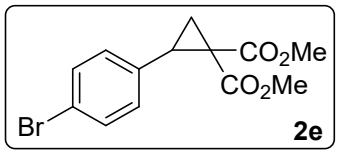
Dimethyl 2-(*o*-tolyl)cyclopropane-1,1-dicarboxylate 2b.[1c] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08-7.01 (m, 3H), 6.97 (d, J = 7.6 Hz, 1H), 3.74 (s, 3H), 3.21 (s, 3H), 3.11 (t, J = 8.4 Hz, 1H), 2.28 (s, 3H), 2.24 (dd, J = 8.4, 5.2 Hz, 1H), 1.65 (dd, J = 8.8, 4.8 Hz, 1H).



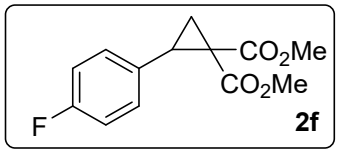
Dimethyl 2-(3-bromophenyl)cyclopropane-1,1-dicarboxylate 2c.[1b] Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.28 (m, 2H), 7.09-7.03 (m, 2H), 3.72 (s, 3H), 3.35 (s, 3H), 3.10 (t, *J* = 8.0 Hz, 1H), 2.08 (dd, *J* = 8.0, 5.5 Hz, 1H), 1.67 (dd, *J* = 9.5, 5.5 Hz, 1H).



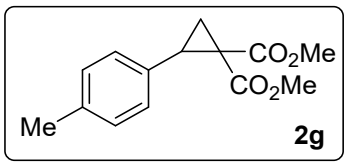
Dimethyl 2-(3-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate 2d.[1b] Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 1H), 7.38 (s, 1H), 7.34-7.30 (m, 2H), 3.73 (s, 3H), 3.31 (s, 3H), 3.19 (t, *J* = 8.5 Hz, 1H), 2.14 (dd, *J* = 8.0, 5.0 Hz, 1H), 1.72 (dd, *J* = 9.0, 5.5 Hz, 1H).



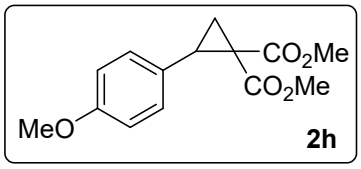
Dimethyl 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate 2e.[1c] Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 3.72 (s, 3H), 3.34 (s, 3H), 3.09 (t, *J* = 8.5 Hz, 1H), 2.07 (dd, *J* = 8.0, 5.0 Hz, 1H), 1.67 (dd, *J* = 9.0, 5.0 Hz, 1H).



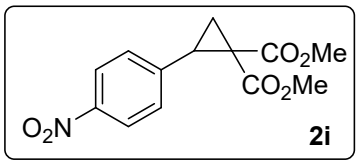
Dimethyl 2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate 2f.[1b] Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11-7.07 (m, 2H), 6.91-6.86 (m, 2H), 3.72 (s, 3H), 3.32 (s, 3H), 3.12 (t, *J* = 8.5 Hz, 1H), 2.08 (dd, *J* = 8.0, 5.5 Hz, 1H), 1.67 (dd, *J* = 9.0, 5.0 Hz, 1H).



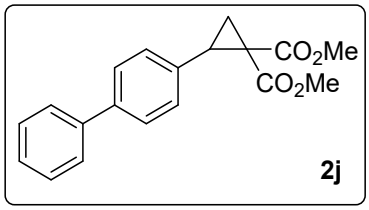
Dimethyl 2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate 2g.[1a] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 4H), 3.78 (s, 3H), 3.38 (s, 3H), 3.18 (t, *J* = 8.4 Hz, 1H), 2.29 (s, 3H), 2.17 (dd, *J* = 8.0, 5.2 Hz, 1H), 1.72 (dd, *J* = 9.2, 5.2 Hz, 1H).



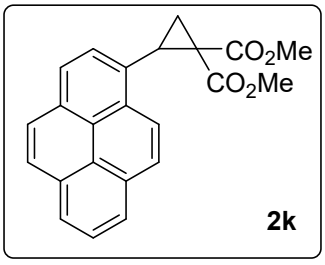
Dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxy-late 2h.[1a] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 3.38 (s, 3H), 3.18 (t, *J* = 8.4 Hz, 1H), 2.15 (dd, *J* = 8.0, 4.8 Hz, 1H), 1.72 (dd, *J* = 9.2, 5.2 Hz, 1H).



Dimethyl 2-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate 2i.[1c] Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 3.74 (s, 3H), 3.35 (s, 3H), 3.21 (t, *J* = 8.5 Hz, 1H), 2.16 (dd, *J* = 8.5, 6.0 Hz, 1H), 1.77 (dd, *J* = 9.5, 5.5 Hz, 1H).

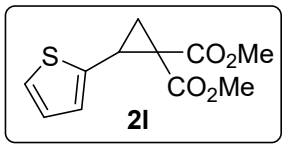


Dimethyl 2-([1,1'-biphenyl]-4-yl)cyclopropane-1,1-dicarboxyla-te 2j.[1b] Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.27-7.24 (m, 2H), 3.79 (s, 3H), 3.39 (s, 3H), 3.26 (t, *J* = 8.0 Hz, 1H), 2.25-2.21 (m, 1H), 1.78 (dd, *J* = 9.2, 5.2 Hz, 1H).

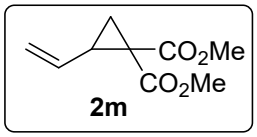


Dimethyl 2-(pyren-1-yl)cyclopropane-1,1-dicarboxylate 2k. The product **2k** was synthesized according to general procedure GP-1; Analytical TLC on silica gel, 1:19 ethyl acetate/hexane; R_f = 0.41; yellow solid; mp 138-139 ^{o}C; yield 76% (954 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 9.5 Hz, 1H), 8.14-8.07 (m, 3H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.99-7.92 (m, 3H), 7.77 (d, *J* = 8.0 Hz, 1H), 3.91 (t, *J* = 8.5 Hz, 1H), 3.86 (s, 3H), 2.88 (s, 3H), 2.57-2.55 (m, 1H), 1.93-1.91 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 167.2, 131.4, 131.06, 131.02, 130.8, 128.2, 127.9, 127.54, 127.53, 126.1, 126.0, 125.4, 125.3, 124.7, 124.6, 124.4, 123.7,

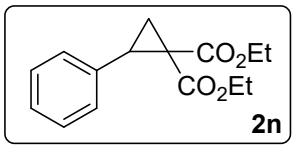
53.1, 52.1, 37.3, 31.1, 19.5; FT-IR (neat) 2952, 1726, 1602, 1435, 1323, 1283, 1206, 1130, 1094 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{19}H_{23}O_4$: 359.1278, found: 359.1284.



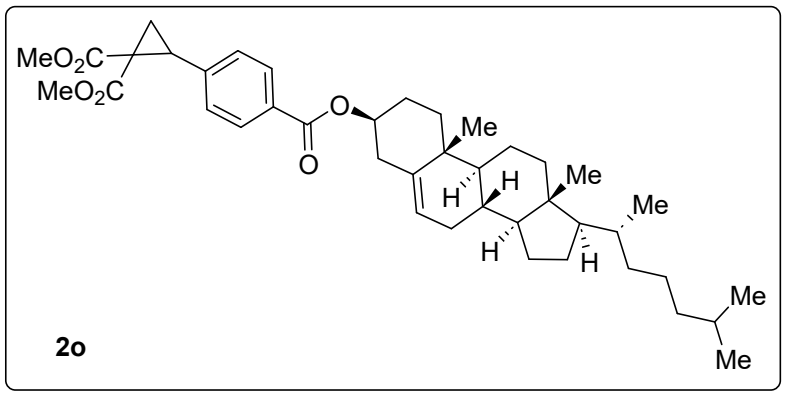
Dimethyl 2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate 2l.[1a] Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.89 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.84-6.82 (m, 1H), 3.78 (s, 3H), 3.48 (s, 3H), 3.28 (t, *J* = 8.8 Hz, 1H), 2.14 (dd, *J* = 7.6, 5.2 Hz, 1H), 1.83 (dd, *J* = 9.6, 5.2 Hz, 1H).



Dimethyl 2-vinylcyclopropane-1,1-dicarboxylate 2m.[1a] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48-5.39 (m, 1H), 5.31 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.15 (dd, J = 10.0, 1.6 Hz, 1H), 3.74 (s, 6H), 2.59 (q, *J* = 8.0 Hz, 1H), 1.72 (dd, *J* = 7.6, 4.8 Hz, 1H), 1.59-1.57 (m, 1H).

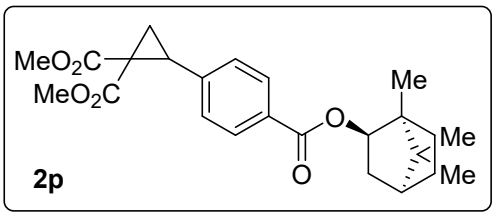


Diethyl 2-phenylcyclopropane-1,1-dicarboxylate 2n.[1c] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.19 (m, 5H), 4.29-4.18 (m, 2H), 3.84 (q, *J* = 7.2 Hz, 2H), 3.21 (t, *J* = 8.4 Hz, 1H), 2.17 (dd, *J* = 8.0, 5.2 Hz, 1H), 1.70 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H).

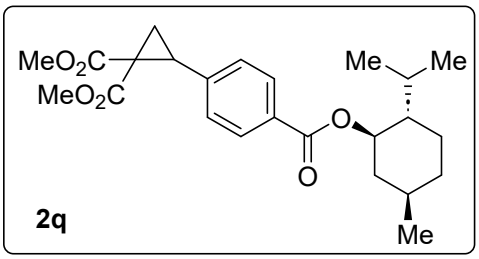


Dimethyl 2-(4-((((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)carbonyl)phenyl)cyclopropane-1,1-dicarboxylate 2o. The product **2o** was synthesized according to general procedure GP-1; Analytical TLC on silica gel, 1:19 ethyl acetate/hexane; R_f = 0.34; colorless solid; mp 97-

98 °C; yield 63% (1.42 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 5.41 (d, *J* = 4.0 Hz, 1H), 4.87-4.79 (m, 1H), 3.79 (s, 3H), 3.38 (s, 3H), 3.24 (t, *J* = 8.4 Hz, 1H), 2.46 (d, *J* = 7.6 Hz, 2H), 2.22 (dd, *J* = 8.0, 5.2 Hz, 1H), 2.03-1.96 (m, 3H), 1.93-1.88 (m, 1H), 1.86-1.81 (m, 1H), 1.79-1.76 (m, 1H), 1.74-1.68 (m, 1H), 1.62-1.45 (m, 7H), 1.40-1.31 (m, 3H), 1.27-1.23 (m, 2H), 1.21-1.20 (m, 1H), 1.18-1.17 (m, 1H), 1.13-1.11 (m, 2H), 1.10-1.09 (m, 1H), 1.06 (s, 3H), 1.03-0.96 (m, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.87 (dd, *J* = 6.8, 1.6 Hz, 6H), 0.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 166.9, 165.8, 139.9, 139.7, 130.0, 129.5, 128.4, 122.9, 74.8, 56.8, 56.2, 53.0, 52.5, 50.1, 42.4, 39.8, 39.6, 38.3, 37.6, 37.1, 36.7, 36.3, 35.9, 32.2, 32.07, 32.02, 28.3, 28.1, 28.0, 24.4, 23.9, 22.9, 22.7, 21.1, 19.5, 19.3, 18.8, 12.0; FT-IR (neat) 3420, 2934, 2867, 1714, 1612, 1438, 1333, 1274, 1115, 1020 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{41}H_{59}O_6$: 647.4306, found: 647.4308.

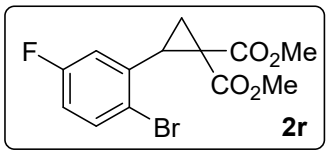


Dimethyl 2-(4-((((1*R*,2*S*,4*R*)-1,7,7-trimethylbicyclo [2.2.1]heptan-2-yl)oxy)carbonyl)phenyl)cyclopropane-1,1-dicarboxylate 2p. The product **2p** was synthesized according to general procedure **GP-1**; Analytical TLC on silica gel, 1:19 ethyl acetate/hexane; R_f = 0.33; thick liquid; yield 68% (987 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.27-7.25 (m, 2H), 5.10 (d, *J* = 9.6 Hz, 1H), 3.80 (s, 3H), 3.40 (s, 3H), 3.25 (t, *J* = 8.4 Hz, 1H), 2.50-2.42 (m, 1H), 2.22 (dd, *J* = 8.0, 5.6 Hz, 1H), 2.14-2.08 (m, 1H), 1.79 (dd, *J* = 9.2, 5.2 Hz, 2H), 1.73 (t, *J* = 4.4 Hz, 1H), 1.44-1.37 (m, 1H), 1.33-1.28 (m, 1H), 1.12 (d, *J* = 14.0 Hz, 1H), 0.96 (s, 3H), 0.91 (d, *J* = 4.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 166.9, 166.6, 139.9, 130.1, 129.5, 128.5, 80.7, 53.0, 52.5, 49.1, 47.9, 45.1, 37.6, 36.9, 32.2, 28.1, 27.5, 19.8, 19.3, 19.0, 13.7; FT-IR (neat) 2953, 2879, 1713, 1612, 1436, 1330, 1269, 1217, 1114, 1020 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{24}H_{31}O_6$: 415.2115, found: 415.2115.

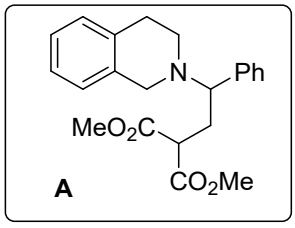


Dimethyl 2-(4-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methyl cyclo-hexyl)oxy)carbonyl)phenyl)cyclo propane-1,1-dicarboxylate 2q. The product **2q** was synthesized according to general procedure GP-1; Analytical TLC on silica gel, 1:19 ethyl

acetate/hexane; R_f = 0.37; thick liquid; yield 65% (948 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.27-7.24 (m, 2H), 4.94-4.88 (m, 1H), 3.80 (s, 3H), 3.40 (s, 3H), 3.25 (t, *J* = 8.4 Hz, 1H), 2.22 (dd, *J* = 7.6, 5.2 Hz, 1H), 2.12 (d, *J* = 11.6 Hz, 1H), 1.97-1.90 (m, 1H), 1.80-1.71 (m, 4H), 1.60-1.49 (m, 2H), 1.15-1.07 (m, 2H), 0.92 (dd, *J* = 6.4, 4.0 Hz, 6H), 0.79 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 166.8, 165.9, 139.8, 130.0, 129.5, 128.4, 75.0, 53.0, 52.5, 47.3, 41.0, 37.5, 34.4, 32.2, 31.5, 26.5, 23.7, 22.1, 20.8, 19.3, 16.6; FT-IR (neat) 2953, 2869, 1728, 1711, 1612, 1436, 1330, 1267, 1217, 1178, 1111, 1019 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{24}H_{33}O_6$: 417.2272, found: 417.2275.

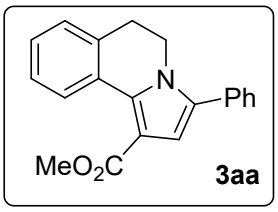


Dimethyl 2-(2-bromo-5-fluorophenyl)cyclopropane-1,1-dicarboxylate 2r. The product **2r** was synthesized according to general procedure GP-1; Analytical TLC on silica gel, 1:19 ethyl acetate/hexane; R_f = 0.42; colorless solid; mp 53-54 °C; yield 72% (831 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.8, 5.6 Hz, 1H), 6.88-6.81 (m, 2H), 3.82 (s, 3H), 3.42 (s, 3H), 3.29 (t, *J* = 8.8 Hz, 1H), 2.18 (dd, *J* = 8.4, 5.6 Hz, 1H), 1.81 (dd, *J* = 9.2, 5.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 166.8, 162.7 (J_{C-F} = 245.37 Hz), 136.9 (J_{C-F} = 7.87 Hz), 133.7 (J_{C-F} = 7.87 Hz), 121.0 (J_{C-F} = 3.25 Hz), 116.7 (J_{C-F} = 23.75 Hz), 116.3 (J_{C-F} = 22 Hz), 53.1, 52.5, 36.6, 33.5, 19.5; FT-IR (neat) 2952, 1727, 1582, 1470, 1437, 1328, 1287, 1271, 1212, 1130, 1038 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{13}H_{13}BrFO_4$: 330.9976, found: 330.9981.

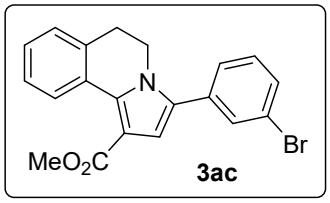


Synthesis of Dimethyl 2-(2-(3,4-dihydroisoquinolin-2(1H)-yl)-2-phenylethyl) malonate A. 1,2,3,4-Tetrahydroisoquinoline (THIQ) **1a** (0.2 mmol, 26 mg), dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **2a** (0.24 mmol, 47 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. The reaction mixture was cooled to room temperature and purified on silica gel column chromatography using ethyl acetate and hexane as an eluent. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane; R_f = 0.46; thick liquid; yield 88% (64 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7332 (m, 2H), 7.28-7.23 (m, 3H), 7.08-7.00 (m, 3H), 6.96-6.94 (m, 1H), 3.68-3.64 (m, 4H), 3.60-3.56 (m, 1H), 3.54 (s, 3H), 3.53-3.47 (m, 2H), 2.88-2.81 (m, 4H), 2.53-2.45 (m, 1H), 2.31-2.25 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.09,

170.03, 137.7, 135.3, 134.5, 128.7, 128.6, 128.2, 127.7, 126.6, 125.9, 125.4, 67.3, 52.5, 52.4, 52.3, 49.9, 47.5, 31.4, 29.4; FT-IR (Neat) 2951, 1749, 1731, 1495, 1434, 1346, 1196, 1150, 1099, 1029 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{22}H_{26}NO_4$: 368.1856, found: 368.1871.

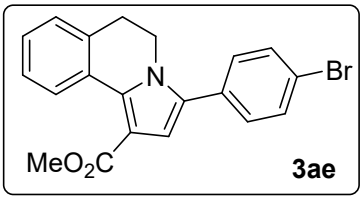


Methyl 3-phenyl-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3aa. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2a** (0.24 mmol, 56 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.42; thick liquid; yield 64% (38 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.0 Hz, 1H), 7.45-7.33 (m, 6H), 7.25-7.21 (m, 2H), 6.79 (s, 1H), 4.06 (t, *J* = 6.0 Hz, 2H), 3.86 (s, 3H), 2.95 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 133.8, 133.59, 133.55, 131.8, 129.1, 128.7, 128.6, 128.1, 127.75, 127.73, 127.3, 127.1, 112.2, 111.8, 51.3, 42.4, 30.3; FT-IR (neat) 2948, 1706, 1603, 1464, 1261, 1200, 1176, 1090, 1010 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{18}NO_2$: 304.1332, found: 304.1335.

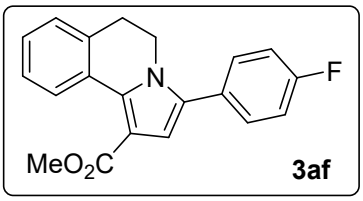


Methyl 3-(3-bromophenyl)-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3ac. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2c** (0.24 mmol, 74 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.39; colorless solid; mp 94-95 ºC; yield 53% (40 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.6 Hz, 1H), 7.49 (s, 1H), 7.43-7.39 (m, 1H), 7.30-7.23 (m, 3H), 7.21-7.14 (m, 2H), 6.74 (s, 1H), 3.98 (t, *J* = 6.4 Hz, 2H), 3.79 (s, 3H), 2.90 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 134.3, 133.9, 133.5, 131.9, 130.6, 130.1, 128.4, 128.2, 127.9, 127.5, 127.3, 127.2, 122.7, 112.9, 112.1, 51.3, 42.5, 30.2; FT-IR (neat) 2947,

1708, 1596, 1470, 1263, 1200, 1178, 1088, 1014 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{17}BrNO_2$: 382.0437, found: 382.0437.

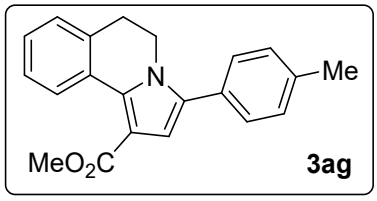


Methyl 3-(4-bromophenyl)-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3ae. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2e** (0.24 mmol, 74 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.40; colorless solid; mp 93-94 ºC; yield 63% (48 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.37-7.33 (m, 1H), 7.27-7.21 (m, 4H), 6.79 (s, 1H), 4.02 (t, *J* = 6.4 Hz, 2H), 3.85 (s, 3H), 2.96 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 134.1, 133.4, 132.2, 131.9, 130.7, 130.5, 128.4, 128.1, 127.9, 127.3, 127.2, 121.9, 112.5, 112.0, 51.4, 42.4, 30.2; FT-IR (neat) 2924, 1708, 1551, 1483, 1462, 1201, 1177, 1089, 1007 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{17}BrNO_2$: 382.0437, found: 382.0438.

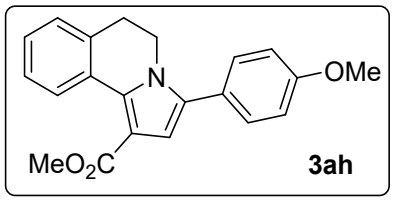


Methyl 3-(4-fluorophenyl)-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3af. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2f** (0.24 mmol, 60 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.37; orange solid; mp 122-123 ºC; yield 52% (33 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.0 Hz, 1H), 7.30-7.26 (m, 3H), 7.18-7.14 (m, 2H), 7.06 (t, *J* = 8.4 Hz, 2H), 6.68 (s, 1H), 3.94 (t, *J* = 6.4 Hz, 2H), 3.78 (s, 3H), 2.89 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 163.5 ($J_{C\text{-}F}$ = 246.3 Hz), 133.8, 133.4, 132.4, 130.9 ($J_{C\text{-}F}$ = 8.1 Hz), 128.6, 128.19, 128.11 ($J_{C\text{-}F}$ = 3.2 Hz), 127.8, 127.3, 127.2, 115.8 ($J_{C\text{-}F}$ = 21.3 Hz),

112.3, 111.9, 51.3, 42.4, 30.3; FT-IR (neat) 2949, 1707, 1560, 1492, 1464, 1262, 1201, 1178, 1088, 1011 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{17}FNO_2$: 322.1238, found: 322.1238.

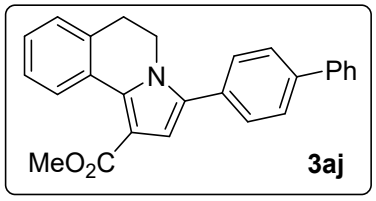


Methyl 3-(*p*-tolyl)-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3ag. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2g** (0.24 mmol, 59 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.43; colorless solid; mp 97-98 ºC; yield 65% (41 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.22-7.13 (m, 6H), 6.68 (s, 1H), 3.97 (t, *J* = 6.5 Hz, 2H), 3.78 (s, 3H), 2.87 (t, *J* = 6.5 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 137.6, 133.6, 133.5, 129.4, 129.08, 129.02, 128.7, 128.1, 127.6, 127.2, 127.1, 111.9, 111.8, 51.3, 42.4, 30.3, 21.3; FT-IR (neat) 2923, 1708, 1493, 1464, 1261, 1200, 1176, 1089, 1018 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{21}H_{20}NO_2$: 318.1489, found: 318.1491.

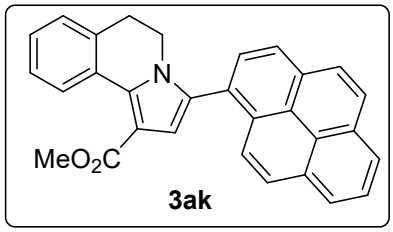


Methyl 3-(4-methoxyphenyl)-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3ah. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2h** (0.24 mmol, 63 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.38; colorless solid; mp 115-116 ºC; yield 68% (45 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.6 Hz, 1H), 7.29-7.23 (m, 3H), 7.18-7.13 (m, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.65 (s, 1H), 3.94 (t, *J* = 6.4 Hz, 2H), 3.78 (s, 6H), 2.87 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 159.4, 133.5, 133.38, 133.34, 130.4, 128.7, 128.0, 127.6, 127.3, 127.1, 124.3, 114.1, 111.7, 111.6, 55.5, 51.3, 42.2, 30.3; FT-IR (neat) 2947, 1704,

1558, 1493, 1463, 1249, 1200, 1175, 1088, 1036 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{21}H_{20}NO_3$: 334.1438, found: 334.1438.

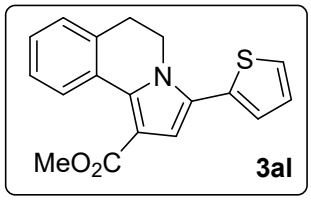


Methyl 3-([1,1'-biphenyl]-4-yl)-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3aj. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2j** (0.24 mmol, 74 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.39; colorless solid; mp 109-110 ºC; yield 59% (44 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.0 Hz, 1H), 7.59 (dd, *J* = 15.2, 8.0 Hz, 4H), 7.41-7.37 (m, 4H), 7.32-7.26 (m, 2H), 7.19-7.14 (m, 2H), 6.77 (s, 1H), 4.04 (t, *J* = 6.4 Hz, 2H), 3.79 (s, 3H), 2.90 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 163.5, 161.5, 133.8, 133.4, 132.4, 130.9, 130.8, 128.5, 128.1, 128.03, 128.00, 127.8, 127.3, 127.1, 115.8, 115.6, 112.2, 111.8, 51.3, 42.3, 30.2; FT-IR (neat) 2947, 1706, 1549, 1483, 1463, 1263, 1200, 1176, 1089, 1007 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{22}NO_2$: 380.1645, found: 380.1649.

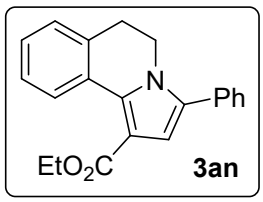


Methyl 3-(pyren-1-yl)-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3ak. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2k** (0.24 mmol, 85 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.41; yellow solid; mp 193-194 ºC; yield 67% (57 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.0 Hz, 1H), 8.17-8.12 (m, 3H), 8.08-8.03 (m, 2H), 8.01-7.95 (m, 2H), 7.91 (dd, *J* = 16.0, 8.0 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.20-7.16 (m, 1H), 7.14-7.12 (m, 1H), 6.90 (s, 1H), 3.84 (s, 3H), 3.74-3.69 (m, 1H), 3.66-3.59 (m, 1H), 2.86 (q,

J = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 133.5, 133.4, 131.7, 131.6, 131.4, 131.0, 130.7, 128.9, 128.6, 128.4, 128.2, 128.0, 127.8, 127.5, 127.4, 127.2, 126.6, 126.4, 125.7, 125.5, 124.99, 124.90, 124.7, 124.6, 114.1, 111.9, 51.4, 42.6, 30.1; FT-IR (neat) 2926, 1706, 1524, 1466, 1261, 1202, 1177, 1088, 1020 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{30}H_{22}NO_2$: 428.1645, found: 428.1646.

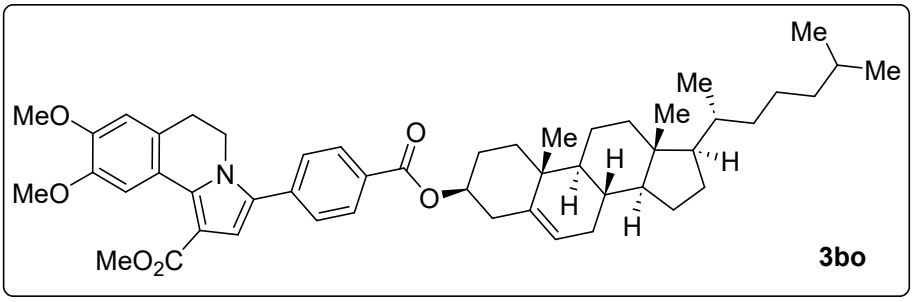


Methyl 3-(thiophen-2-yl)-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3al. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2l** (0.24 mmol, 57 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3{\cdot}2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.37; colorless solid; mp 109-110 ºC; yield 61% (37 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.0 Hz, 1H), 7.28-7.25 (m, 2H), 7.18-7.14 (m, 2H), 7.04-7.03 (m, 1H), 6.97-6.95 (m, 1H), 6.79 (s, 1H), 4.05 (t, *J* = 6.0 Hz, 2H), 3.78 (s, 3H), 2.92 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.6, 134.2, 133.4, 133.2, 128.3, 128.1, 127.9, 127.6, 127.3, 127.1, 126.8, 126.1, 126.0, 113.6, 111.9, 51.4, 41.9, 30.1; FT-IR (neat) 2924, 1708, 1465, 1333, 1262, 1201, 1176, 1088, 1018 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{16}NO_2S$: 310.0896, found: 310.0897.

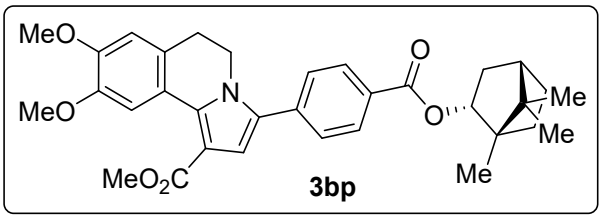


Ethyl 3-phenyl-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3an. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2n** (0.24 mmol, 62 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3{\cdot}2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.42; colorless solid; mp 68-69 ºC; yield 60% (38 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.0 Hz, 1H), 7.46-7.41 (m, 3H), 7.39-7.32 (m, 3H), 7.23-

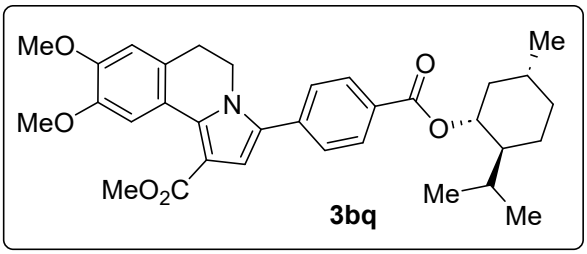
7.20 (m, 2H), 6.81 (s, 1H), 4.34 (q, J = 7.2 Hz, 2H), 4.06 (t, J = 6.4 Hz, 2H), 2.95 (t, J = 6.4 Hz, 2H), 1.38 (t, J = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 133.6, 133.5, 133.4, 131.9, 129.1, 128.7, 128.6, 128.2, 127.7, 127.6, 127.2, 127.0, 112.32, 112.30, 60.0, 42.4, 30.3, 14.6; FT-IR (neat) 2927, 1701, 1603, 1521, 1484, 1462, 1261, 1198, 1175, 1089, 1036 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{21}H_{20}NO_2$: 318.1489, found: 318.1492.



Methyl 3-(4-((((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)carbonyl)phenyl)-8,9-dimethoxy-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3bo. Amine **1b** (0.2 mmol, 38 mg), cyclopropane **2o** (0.24 mmol, 155 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 3:7 ethyl acetate/hexane; R_f = 0.47; colorless solid; mp 144-145 ºC; yield 42% (65 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.11 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 6.86 (s, 1H), 6.74 (s, 1H), 5.44 (d, J = 4.0 Hz, 1H), 4.92-4.84 (m, 1H), 4.08 (t, J = 6.0 Hz, 2H), 3.99 (s, 3H), 3.92 (s, 3H), 3.86 (s, 3H), 2.92 (t, J = 6.4 Hz, 2H), 2.49 (d, J = 7.6 Hz, 2H), 2.04-1.91 (m, 5H), 1.86-1.73 (m, 3H), 1.56-1.46 (m, 7H), 1.41-1.32 (m, 4H), 1.28-1.22 (m, 5H), 1.16-1.12 (m, 3H), 1.08 (s, 3H), 1.03-0.98 (m, 3H), 0.93 (d, J = 6.4 Hz, 3H), 0.88-0.86 (m, 6H), 0.69 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 165.7, 148.7, 147.7, 139.7, 136.1, 135.1, 132.1, 129.9, 129.6, 128.5, 126.4, 123.0, 121.2, 113.3, 112.0, 111.2, 110.4, 74.9, 60.5, 56.8, 56.2, 56.1, 51.4, 50.2, 42.8, 42.4, 39.8, 39.6, 38.3, 37.1, 36.8, 36.3, 35.9, 32.09, 32.04, 29.7, 28.3, 28.1, 28.0, 24.4, 23.9, 22.9, 22.7, 21.2, 19.5, 18.8, 12.0; FT-IR (neat) 2933, 2867, 1707, 1607, 1501, 1468, 1271, 1251, 1200, 1171, 1145, 1088, 1028 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{50}H_{66}NO_6$: 776.4885, found: 776.4877.

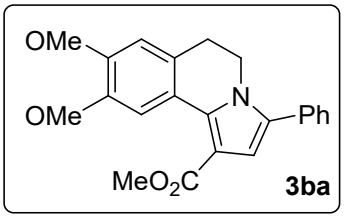


Methyl 8,9-dimethoxy-3-(4-((((1*R*,2*S*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)carbonyl)phenyl)-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3bp. Amine **1b** (0.2 mmol, 38 mg), cyclopropane **2p** (0.24 mmol, 99 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 3:7 ethyl acetate/hexane; R_f = 0.42; colorless solid; mp 84-85 ºC; yield 39% (42 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.87 (s, 1H), 6.74 (s, 1H), 5.16 (d, *J* = 10.0 Hz, 1H), 4.08 (t, *J* = 6.4 Hz, 2H), 3.99 (s, 3H), 3.92 (s, 3H), 3.86 (s, 3H), 2.92 (t, *J* = 6.4 Hz, 2H), 2.53-2.46 (m, 1H), 2.18-2.12 (m, 1H), 1.87-1.79 (m, 1H), 1.75 (t, *J* = 4.4 Hz, 1H), 1.36-1.29 (m, 2H), 1.15 (dd, *J* = 14.0, 3.6 Hz, 1H), 0.98 (s, 3H), 0.93 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.6, 165.7, 148.7, 147.8, 136.2, 135.1, 132.1, 129.9, 129.6, 128.5, 126.4, 121.2, 113.3, 112.0, 111.2, 110.4, 80.8, 56.3, 56.1, 51.4, 49.2, 48.0, 45.1, 42.8, 37.1, 28.2, 27.5, 19.8, 19.0, 13.7; FT-IR (neat) 2952, 1706, 1608, 1530, 1501, 1470, 1455, 1272, 1250, 1200, 1171, 1117, 1088, 1017 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{33}H_{38}NO_6$: 544.2694, found: 544.2693.

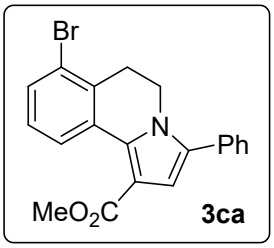


Methyl 3-(4-((((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)phenyl)-8,9-dimethoxy-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3bq. Amine **1b** (0.2 mmol, 26 mg), cyclopropane **2q** (0.24 mmol, 99 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 3:7 ethyl acetate/hexane; R_f = 0.44; thick liquid; yield 46% (50 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.86 (s, 1H), 6.74 (s, 1H), 4.99-4.92 (m,

1H), 4.08 (t, J = 6.4 Hz, 2H), 3.99 (s, 3H), 3.92 (s, 3H), 3.86 (s, 3H), 2.92 (t, J = 6.4 Hz, 2H), 2.16 (d, J = 12.0 Hz, 1H), 2.01-1.94 (m, 1H), 1.77-1.71 (m, 2H), 1.62-1.53 (m, 3H), 1.13 (q, J = 11.6 Hz, 2H), 0.94 (dd, J = 6.4, 3.2 Hz, 6H), 0.82 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 165.7, 148.7, 147.7, 136.1, 135.0, 132.1, 129.9, 129.6, 128.5, 126.4, 121.2, 113.3, 112.0, 111.2, 110.4, 75.1, 56.2, 56.0, 51.4, 47.4, 42.8, 41.1, 34.4, 31.6, 29.7, 26.7, 23.7, 22.1, 20.9, 16.6; FT-IR (neat) 2952, 2869, 1704, 1608, 1501, 1469, 1455, 1336, 1272, 1250, 1200, 1172, 1089, 1029 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{33}H_{40}NO_6$: 546.2850, found: 546.2851.

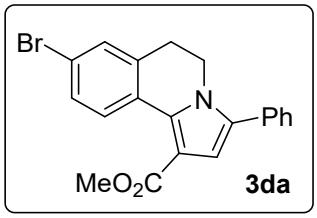


Methyl 8,9-dimethoxy-3-phenyl-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3ba. Amine **1b** (0.2 mmol, 38 mg), cyclopropane **2a** (0.24 mmol, 56 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 3:7 ethyl acetate/hexane; R_f = 0.45; orange solid; mp 125-126 ºC; yield 72% (52 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.45-7.33 (m, 5H), 6.77 (s, 1H), 6.72 (s, 1H), 4.04 (t, J = 6.4 Hz, 2H), 3.99 (s, 3H), 3.91 (s, 3H), 3.85 (s, 3H), 2.89 (t, J = 6.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 148.5, 147.7, 134.1, 133.0, 131.9, 129.0, 128.6, 127.6, 126.3, 121.5, 112.1, 111.9, 110.8, 110.4, 56.2, 56.0, 51.3, 42.5, 29.7; FT-IR (neat) 2947, 1701, 1528, 1496, 1472, 1288, 1248, 1202, 1171, 1090 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{22}H_{22}NO_4$: 364.1543, found: 364.1546.

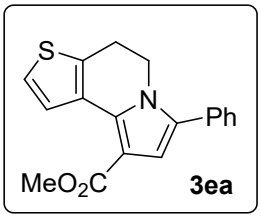


Methyl 7-bromo-3-phenyl-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3ca. Amine **1c** (0.2 mmol, 42 mg), cyclopropane **2a** (0.24 mmol, 56 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2

mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane; R_f = 0.44; colorless solid; mp 86-87 ºC; yield 52% (39 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.0 Hz, 1H), 7.47 (dd, *J* = 14.0, 8.0 Hz, 3H), 7.40-7.36 (m, 3H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.82 (s, 1H), 4.06 (t, *J* = 6.8 Hz, 2H), 3.85 (s, 3H), 3.13 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 133.6, 133.1, 132.7, 131.6, 131.5, 130.6, 129.0, 128.7, 128.2, 127.9, 127.3, 123.1, 112.6, 112.5, 51.4, 42.0, 29.8; FT-IR (neat) 2925, 1709, 1552, 1456, 1284, 1222, 1198, 1173, 1146, 1097 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{17}BrNO_2$: 382.0437, found: 382.0454.

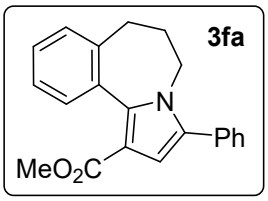


Methyl 8-bromo-3-phenyl-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 3da. Amine **1d** (0.2 mmol, 42 mg), cyclopropane **2a** (0.24 mmol, 56 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane; R_f = 0.43; thick liquid; yield 47% (35 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.4 Hz, 1H), 7.47-7.42 (m, 3H), 7.39-7.35 (m, 4H), 6.79 (s, 1H), 4.04 (t, *J* = 6.8 Hz, 2H), 3.85 (s, 3H), 2.93 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 135.5, 133.8, 132.8, 131.6, 130.25, 130.23, 129.7, 129.1, 128.7, 127.9, 127.6, 121.3, 112.4, 112.2, 51.4, 42.1, 30.0; FT-IR (neat) 2925, 1705, 1568, 1461, 1260, 1201, 1176, 1096, 1081, 1009 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{17}BrNO_2$: 382.0437, found: 382.0437.

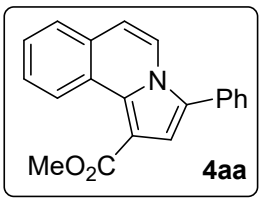


Methyl 7-phenyl-4,5-dihydrothieno[2,3-*g*]indolizine-9-carboxylate 3ea. Amine **1e** (0.2 mmol, 27 mg), cyclopropane **2a** (0.24 mmol, 56 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane; R_f = 0.41;

thick liquid; yield 54% (33 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 5.2 Hz, 1H), 7.46-7.34 (m, 5H), 7.17 (d, *J* = 5.6 Hz, 1H), 6.69 (s, 1H), 4.15 (t, *J* = 6.4 Hz, 2H), 3.85 (s, 3H), 3.09 (t, J = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 133.67, 133.60, 132.2, 132.1, 130.0, 129.1, 128.7, 127.88, 127.80, 122.1, 111.0, 110.1, 51.2, 43.0, 24.8; FT-IR (neat) 2948, 2925, 1704, 1571, 1469, 1436, 1265, 1196, 1090, 1061, 1042 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{16}NO_2S$: 310.0896, found: 310.0895.

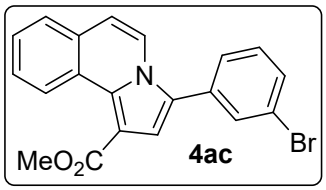


Methyl 3-phenyl-6,7-dihydro-5*H*-benzo[c]pyrrolo[1,2-*a*]azepine-1-carboxylate 3fa. Amine **1f** (0.2 mmol, 29 mg), cyclopropane **2a** (0.24 mmol, 56 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.6 mmol, 160 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane; R_f = 0.42; thick liquid; yield 51% (32 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71-7.69 (m, 1H), 7.44-7.42 (m, 4H), 7.37-7.35 (m, 1H), 7.34-7.29 (m, 2H), 7.26-7.25 (m, 1H), 6.77 (s, 1H), 4.12-4.00 (m, 1H), 3.75 (s, 3H), 3.55-3.34 (m, 1H), 2.79-2.74 (m, 2H), 2.63-2.28 (m, 1H), 2.23-1.89 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 139.1, 138.4, 134.1, 132.6, 131.9, 131.5, 128.8, 128.7, 128.5, 127.8, 126.2, 111.9, 110.9, 51.0, 42.6, 33.1, 30.7; FT-IR (neat) 2947, 2927, 1710, 1603, 1524, 1466, 1408, 1257, 1185, 1095, 1034 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{21}H_{20}NO_2$: 318.1489, found: 318.1492.

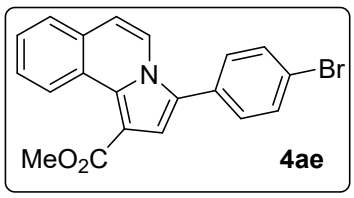


Methyl 3-phenylpyrrolo[2,1-*a*]isoquinoline-1-carboxylate 4aa. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2a** (0.24 mmol, 56 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (1.0 mmol, 268 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.43; colorless solid; mp 90-92 ºC; yield 48% (28 mg); ^{1}H NMR (400 MHz,

$CDCl_3$) δ 9.79 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.56-7.52 (m, 2H), 7.49-7.42 (m, 5H), 7.38-7.34 (m, 1H), 7.22 (s, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0, 132.8, 131.3, 129.4, 129.1, 129.0, 128.4, 128.2, 127.8, 127.7, 127.3, 126.7, 126.1, 122.0, 116.5, 113.6, 108.7, 51.6; FT-IR (neat) 2948, 2922, 1702, 1604, 1505, 1458, 1259, 1198, 1151, 1089, 1035 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{16}NO_2$: 302.1176, found: 302.1176.

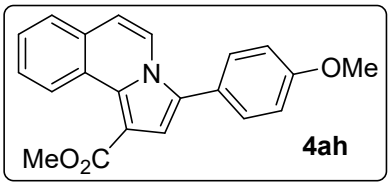


Methyl 3-(3-bromophenyl)pyrrolo[2,1-*a*]isoquinoline-1-carboxylate 4ac. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2c** (0.24 mmol, 74 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (1.0 mmol, 268 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.40; colorless solid; mp 105-106 ºC; yield 40% (30 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 2.0 Hz, 1H), 7.58-7.53 (m, 2H), 7.50-7.40 (m, 3H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 133.4, 133.1, 132.1, 131.3, 130.6, 129.0, 127.98, 127.94, 127.7, 127.4, 126.8, 126.5, 126.0, 123.2, 121.6, 117.2, 114.1, 108.9, 51.6; FT-IR (neat) 2947, 2924, 1702, 1596, 1504, 1458, 1336, 1259, 1199, 1152, 1088, 1030 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{15}BrNO_2$: 380.0281, found: 380.0282.

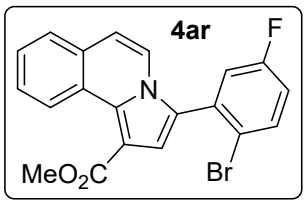


Methyl 3-(4-bromophenyl)pyrrolo[2,1-*a*]isoquinoline-1-carboxylate 4ae. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2e** (0.24 mmol, 74 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (1.0 mmol, 268 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.42; colorless solid; mp 132-133 ºC; yield 43% (32 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.66-7.59 (m, 4H),

7.54-7.50 (m, 1H), 7.43-7.40 (m, 2H), 7.29 (s, 1H), 6.96 (d, J = 7.6 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 133.0, 132.4, 130.8, 130.2, 128.9, 127.9, 127.8, 127.4, 126.9, 126.8, 126.1, 122.5, 121.6, 116.8, 114.0, 108.9, 51.6; FT-IR (neat) 2948, 2924, 1701, 1547, 1504, 1471, 1458, 1337, 1259, 1199, 1088, 1028 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{15}BrNO_2$: 380.0281, found: 380.0279.

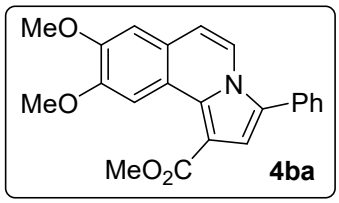


Methyl 3-(4-methoxyphenyl)pyrrolo[2,1-*a*]isoquinoline-1-carboxylate 4ah. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2h** (0.24 mmol, 63 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (1.0 mmol, 268 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.39; colorless solid; mp 99-100 ºC; yield 46% (30 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 7.2 Hz, 1H), 7.63-7.58 (m, 2H), 7.52-7.48 (m, 1H), 7.47-7.43 (m, 2H), 7.23 (s, 1H), 7.06-7.02 (m, 2H), 6.93 (d, J = 7.2 Hz, 1H), 3.94 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0, 159.8, 132.4, 130.8, 128.9, 128.0, 127.7, 127.6, 127.3, 126.7, 126.2, 123.6, 122.0, 116.1, 114.6, 113.5, 108.4, 55.5, 51.6; FT-IR (neat) 2949, 2924, 1700, 1564, 1511, 1496, 1458, 1336, 1250, 1200, 1088, 1035 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{21}H_{18}NO_3$: 332.1281, found: 332.1278.

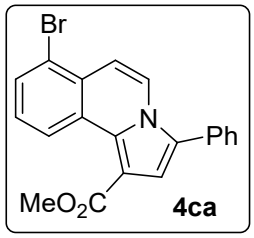


Methyl 3-(2-bromo-5-fluorophenyl)pyrrolo[2,1-*a*]isoquinoline-1-carboxylate 4ar. 1,2,3,4-Tetrahydroisoquinoline **1a** (0.2 mmol, 26 mg), cyclopropane **2r** (0.24 mmol, 79 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (1.0 mmol, 268 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.43; colorless solid; mp 106-107 ºC; yield 49% (39 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (d, J = 8.4 Hz, 1H), 7.64 (dd, J = 8.8, 5.2 Hz, 1H), 7.59-7.54 (m, 2H), 7.47 (t, J = 7.2 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.24 (s, 1H), 7.14 (dd, J = 8.4, 3.2

Hz, 1H), 7.05-7.00 (m, 1H), 6.92 (d, J = 7.6 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 163.2 ($J_{C\text{-}F}$ = 247.7 Hz), 134.7 ($J_{C\text{-}F}$ = 8.2 Hz), 134.2 ($J_{C\text{-}F}$ = 8.6 Hz), 132.6, 129.0, 127.98, 127.91, 127.5, 126.8, 125.9, 125.3, 122.3, 120.7 ($J_{C\text{-}F}$ = 22.4 Hz), 120.1 ($J_{C\text{-}F}$ = 3.5 Hz), 118.1 ($J_{C\text{-}F}$ = 22 Hz), 117.5, 113.8, 108.5, 51.6; FT-IR (neat) 2949, 2924, 1701, 1575, 1504, 1479, 1458, 1335, 1260, 1198, 1089, 1060, 1024 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{14}BrFNO_2$: 398.0186, found: 398.0198.

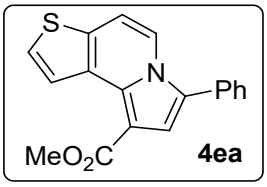


Methyl 8,9-dimethoxy-3-phenylpyrrolo[2,1-*a*]isoquinoline-1-carboxylate 4ba. Amine **1b** (0.2 mmol, 38 mg), cyclopropane **2a** (0.24 mmol, 56 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3{\cdot}2H_2O$ (1.0 mmol, 268 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 3:7 ethyl acetate/hexane; R_f = 0.46; orange solid; mp 111-112 ºC; yield 55% (39mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.56-7.48 (m, 4H), 7.44-7.40 (m, 1H), 7.28 (s, 1H), 7.02 (s, 1H), 6.88 (d, J = 7.6 Hz, 1H), 4.15 (s, 3H), 4.00 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.1, 149.6, 149.4, 133.3, 131.5, 129.3, 129.1, 128.2, 127.4, 124.0, 120.9, 120.5, 116.7, 113.0, 109.2, 107.0, 106.7, 56.5, 56.0, 51.5; FT-IR (neat) 2950, 2927, 1693, 1604, 1519, 1494, 1479, 1434, 1331, 1251, 1196, 1143, 1090, 1046 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{22}H_{20}NO_4$: 362.1387, found: 362.1387.

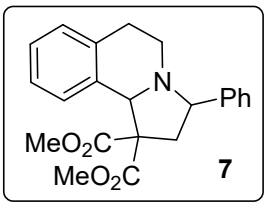


Methyl 7-bromo-3-phenylpyrrolo[2,1-*a*]isoquinoline-1-carboxylate 4ca. Amine **1c** (0.2 mmol, 42 mg), cyclopropane **2a** (0.24 mmol, 56 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3{\cdot}2H_2O$ (1.0 mmol, 268 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane; R_f = 0.45; colorless solid; mp 120-121 ºC; yield 38% (28 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (d, J =

8.4 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.55-7.50 (m, 4H), 7.47-7.41 (m, 3H), 7.34 (s, 1H), 3.95 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 131.7, 131.6, 130.9, 129.3, 129.2, 128.6, 128.4, 128.3, 127.9, 127.8, 126.8, 123.2, 121.5, 117.2, 112.1, 109.4, 51.7; FT-IR (neat) 2955, 2923, 1701, 1544, 1502, 1445, 1338, 1206, 1197, 1152, 1095, 1038 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{15}BrNO_2$: 380.0281, found: 380.0296.

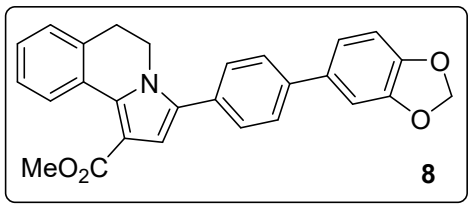


Methyl 7-phenylthieno[2,3-*g*]indolizine-9-carboxylate 4ea. Amine **1c** (0.2 mmol, 27 mg), cyclopropane **2a** (0.24 mmol, 56 mg) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (1.0 mmol, 268 mg) in MeOH (2 mL) for 12 h at 80 ºC according to general procedure. Analytical TLC on silica gel, 1:19 ethyl acetate/hexane; R_f = 0.42; thick liquid; yield 42% (25 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 5.6 Hz, 1H), 8.12 (d, *J* = 7.2 Hz, 1H), 7.55-7.48 (m, 5H), 7.44-7.39 (m, 1H), 7.26-7.25 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 134.9, 132.7, 131.5, 129.9, 129.22, 129.21, 128.3, 127.34, 127.32, 125.1, 120.4, 115.6, 108.0, 104.7, 51.2; FT-IR (neat) 2948, 2927, 1695, 1622, 1510, 1474, 1437, 1413, 1320, 1279, 1208, 1196, 1089, 1057, 1018 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{14}NO_2S$: 308.0740, found: 308.0737.



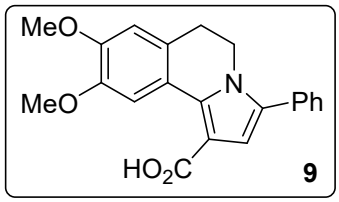
Synthesis of Dimethyl 3-phenyl-2,3,6,10b-tetrahydropyrrolo[2,1-a]isoquinoline-1,1(5*H*) dicarboxylate 7. Amine **1a** (0.2 mmol), cyclopropane **2a** (0.24 mmol) and MgI_2 (20 mol %, 11 mg) were stirred in toluene (2 mL) at 80 ºC for 12 h. The reaction was cooled to room temperature and passed through a short pad of celite using ethyl acetate. Evaporation of the solvent gave a residue that was reacted with $Mn(OAc)_3 \cdot 2H_2O$ (0.2 mmol, 53 mg) in MeOH (2 mL) for 12 h at 80 ºC. The progress of the reaction was monitored by TLC using ethyl acetate and hexane. The reaction mixture was diluted with ethyl acetate (2 x 15 mL) and washed with water (2 x 5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave the residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford **7**. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.36; thick liquid; yield 83%

(60 mg); 1.05:1 mixture of diastereomers; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.44 (m, 5H), 7.42-7.39 (m, 1H), 7.37-7.32 (m, 4H), 7.31 -7.26 (m, 2H), 7.14-7.04 (m, 6H), 5.60 (s, 1H), 4.66 (dd, *J* = 10.0, 6.0 Hz, 0.95H), 4.31 (s, 0.95H), 3.87 (s, 2.86H), 3.78 (s, 3H), 3.53 (t, *J* = 8.4 Hz, 1H), 3.44 (s, 2.85H), 3.11 (s, 3H), 3.07-3.00 (m, 1H), 2.93-2.86 (m, 3H), 2.82-2.71 (m, 4H), 2.65 (dd, *J* = 12.0, 3.2 Hz, 1H), 2.39-2.35 (m, 1H), 2.33-3.27 (m, 1H), 2.20 (dd, *J* = 13.2, 9.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 172.0, 171.0, 170.9, 142.9, 141.4, 137.3, 135.8, 135.5, 134.4, 128.7, 128.66, 128.62, 128.5, 128.25, 128.24, 127.7, 127.5, 127.4, 126.9, 126.5, 126.2, 125.5, 125.0, 70.1, 66.8, 65.8, 65.6, 65.5, 61.8, 52.9, 52.8, 52.2, 51.9, 46.2, 44.5, 43.7, 43.3, 30.2, 24.6; FT-IR (neat) 2953, 1730, 1652, 1604, 1493, 1437, 1266, 1214, 1156, 1065, 1030 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{22}H_{24}NO_4$: 366.1700, found: 366.1708.

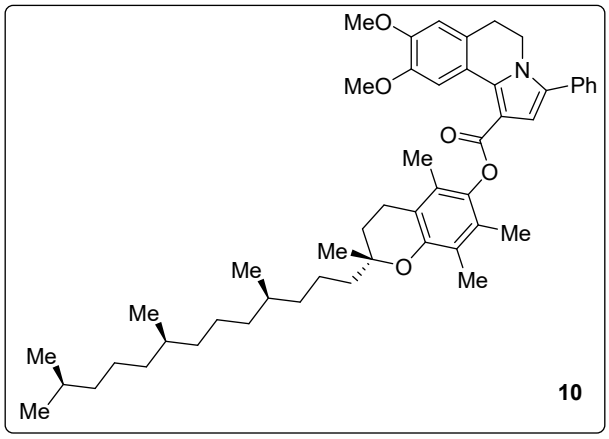


8

Synthesis of Methyl 3-(4-(benzo[*d*][1,3]dioxol-5-yl)phenyl)-5,6-dihydropyrrolo[2,1-*a*]isoquinoline-1-carboxylate 8.[3] Compound **3ae** (38 mg, 0.1 mmol), benzo[*d*][1,3]dioxol-5-ylboronic acid (0.1 mmol, 16 mg), $Pd(PPh_3)_4$ (0.002 mmol, 2.3 mg), Na_2CO_3 (0.2 mmol, 22 mg), H_2O (50 μL) and toluene:EtOH (1:1, 2 mL) were refluxed at 100 ºC for 6 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and passed through a short pad of celite using CH_2Cl_2 (10 ml). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography to give **8**. Analytical TLC on silica gel, 1:49 ethyl acetate/hexane; R_f = 0.40; colorless solid; mp 64-65 ºC; yield 73% (30 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.37-7.33 (m, 1H), 7.25-7.22 (m, 2H), 7.11-7.09 (m, 2H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.83 (s, 1H), 6.02 (s, 2H), 4.10 (t, *J* = 6.4 Hz, 2H), 3.86 (s, 3H), 2.97 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 148.4, 147.4, 140.2, 134.9, 133.9, 133.6, 133.2, 130.4, 129.4, 128.6, 128.1, 127.7, 127.3, 127.1, 127.0, 120.7, 112.3, 111.9, 108.8, 107.6, 101.3, 51.3, 42.5, 30.3; FT-IR (neat) 2950, 2924, 1705, 1504, 1479, 1463, 1337, 1263, 1225, 1201, 1177, 1089, 1038 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{27}H_{22}NO_4$: 424.1543, found: 424.1546.



Synthesis of 8,9-Dimethoxy-3-phenyl-5,6-dihydropyrrolo[2,1-*a*]isoquinoline -1-carboxylic acid 9.[4] Compound **3ba** (0.2 mmol, 69 mg), KOH (3.00 mmol, 168 mg), DMSO (3 mL) and H_2O (3 mL) were subjected to stir at 70 °C in an oil bath for 6 h. The progress of the reaction was monitored by TLC using ethyl acetate and hexane. After completion, 3 M HCl was added until the pH = 1. The mixture was then extracted with Et_2O (3 x 15 mL). The combined organic layer was washed with brine (5 mL) and dried (Na_2SO_4). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography to give **9** in 81% yield. Analytical TLC on silica gel, 1:1 ethyl acetate/hexane; R_f = 0.39; colorless solid; mp 203-204 ^oC; yield 81% (56 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.46-7.35 (m, 5H), 6.86 (s, 1H), 6.74 (s, 1H), 4.06 (t, *J* = 6.4 Hz, 2H), 3.97 (s, 3H), 3.92 (s, 3H), 2.92 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 148.7, 147.7, 135.3, 133.3, 131.8, 129.1, 128.7, 127.7, 126.5, 121.2, 112.9, 112.1, 110.4, 109.8, 56.19, 56.13, 42.6, 29.7; FT-IR (neat) 2931, 1675, 1555, 1528, 1494, 1474, 1336, 1292, 1267, 1240, 1212, 1146, 1094, 1055 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{21}H_{20}NO_4$: 350.1387, found: 350.1387.



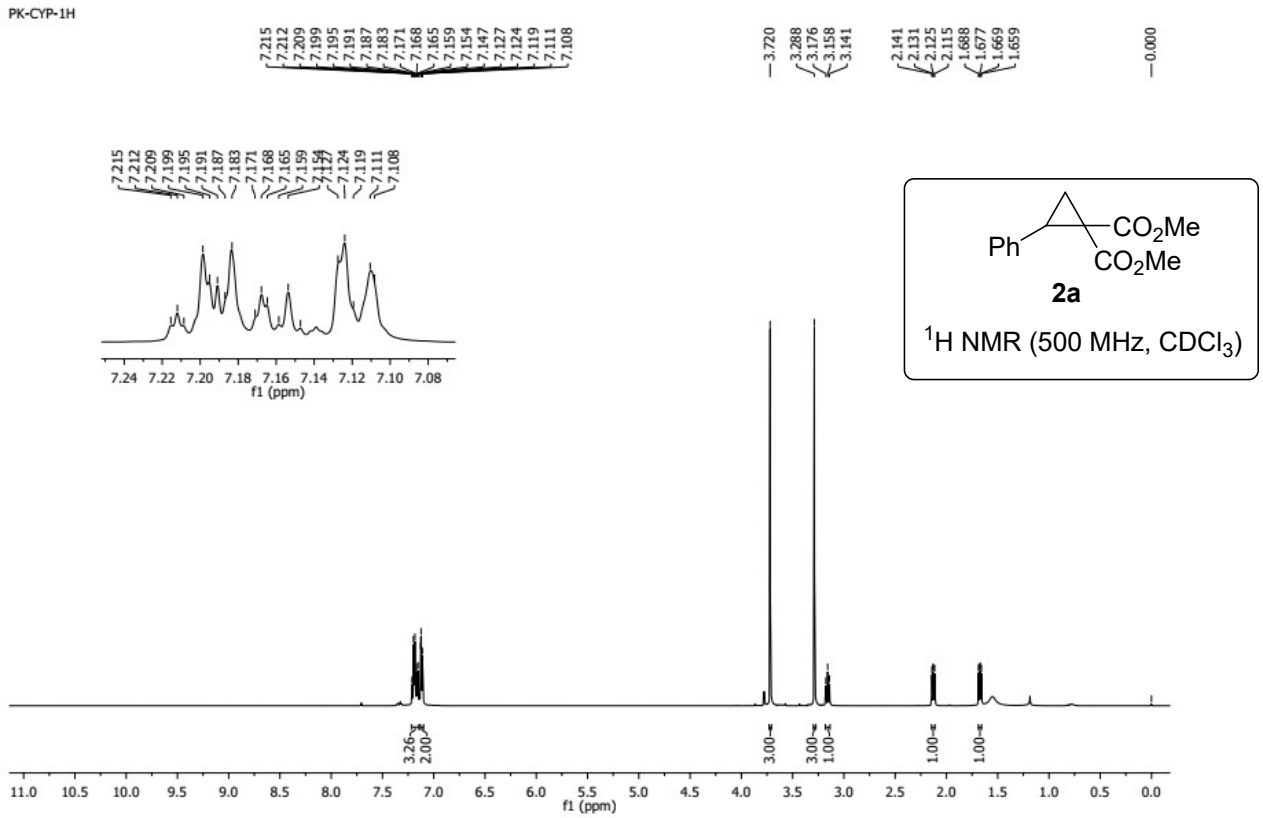
Synthesis of (R)-2,5,7,8-tetramethyl-2((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 8,9-dimethoxy-3-phenyl-5,6-dihydropy-rrolo[2,1-*a*]isoquinoline-1-carboxylate 10.[3] Compound **9** (0.1 mmol, 34 mg), dicyclohexylcarbodiimide (DCC) (0.15 mmol, 30 mg), 4-dimethylaminepyridine (DMAP) (0.015 mmol, 1.8 mg) and tocopherol (0.12 mmol, 43 mg) were stirred in CH_2Cl_2 (1 mL) for 12 h at room temperature. The reaction mixture was then passed through as short pad of celite. The solvent was evaporated and the residue was purified on silica gel chromatography using ethyl acetate/hexane as an eluent to get **10** in 52% yield. Analytical TLC on silica gel, 3:7 ethyl acetate/hexane; R_f = 0.40; thick liquid; yield 52% (39 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.48-7.44 (m, 3H), 7.41-7.36 (m,

1H), 7.03 (s, 1H), 6.73 (s, 1H), 4.10 (t, *J* = 6.4 Hz, 2H), 3.91 (d, *J* = 8.0 Hz, 6H), 2.95 (t, *J* = 6.8 Hz, 2H), 2.62 (t, *J* = 6.8 Hz, 2H), 2.12 (d, *J* = 3.6 Hz, 6H), 2.08 (s, 3H), 1.86-1.81 (m, 1H), 1.54-1.49 (m, 3H), 1.43-1.35 (m, 3H), 1.31-1.23 (m, 12H), 1.16-1.07 (m, 7H), 0.87-0.83 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 149.3, 148.6, 147.8, 140.8, 135.0, 133.1, 132.0, 129.2, 128.7, 127.7, 127.5, 126.3, 125.7, 123.0, 121.4, 117.4, 112.7, 112.0, 110.4, 110.3, 75.1, 56.4, 56.0, 42.7, 39.5, 37.7, 37.5, 37.4, 32.95, 32.93, 29.7, 28.1, 24.9, 24.6, 23.6, 22.8, 22.7, 21.2, 20.8, 19.9, 19.86, 19.84, 19.79, 19.75, 13.3, 12.4, 12.0; FT-IR (neat) 2947, 2926, 1714, 1527, 1496, 1464, 1377, 1288, 1239, 1193, 1157, 1083, 1050 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{50}H_{68}NO_5$: 762.5092, found: 762.5096.

References

1. (*a*) A. F. G. Goldberg, N. R. O'Connor, R. A. Craig II and B. M. Stoltz, *Org. Lett.* 2012, **14**, 5314; (*b*) M. Mishra, P. B. De, S. Pradhan and T. Punniyamurthy, *J. Org. Chem.*, 2019, **84**, 10901; (c) A. Jacob, P. Barkawitz, P. G. Jones, D. B. Werz, *Org. Lett.* 2022, **24**, 3028.
2. F. H. Darras, B. Kling, J. Heilmann and M. Decker, *ACS Med. Chem. Lett.,* 2012, **3**, 914.
3. P. Karjee, M. Mishra, B. Debnath and T. Punniyamurthy, *Chem. Commun*., 2022, **58**, 8670.
4. W. Xi, Y. Zhang, H. Wu, J. Li, Y. Wang, J. Yang, Z. Wang and W. Yao, *Org. Lett.*, 2023, **25**, 4908.

NMR (^{1}H and ^{13}C) Spectra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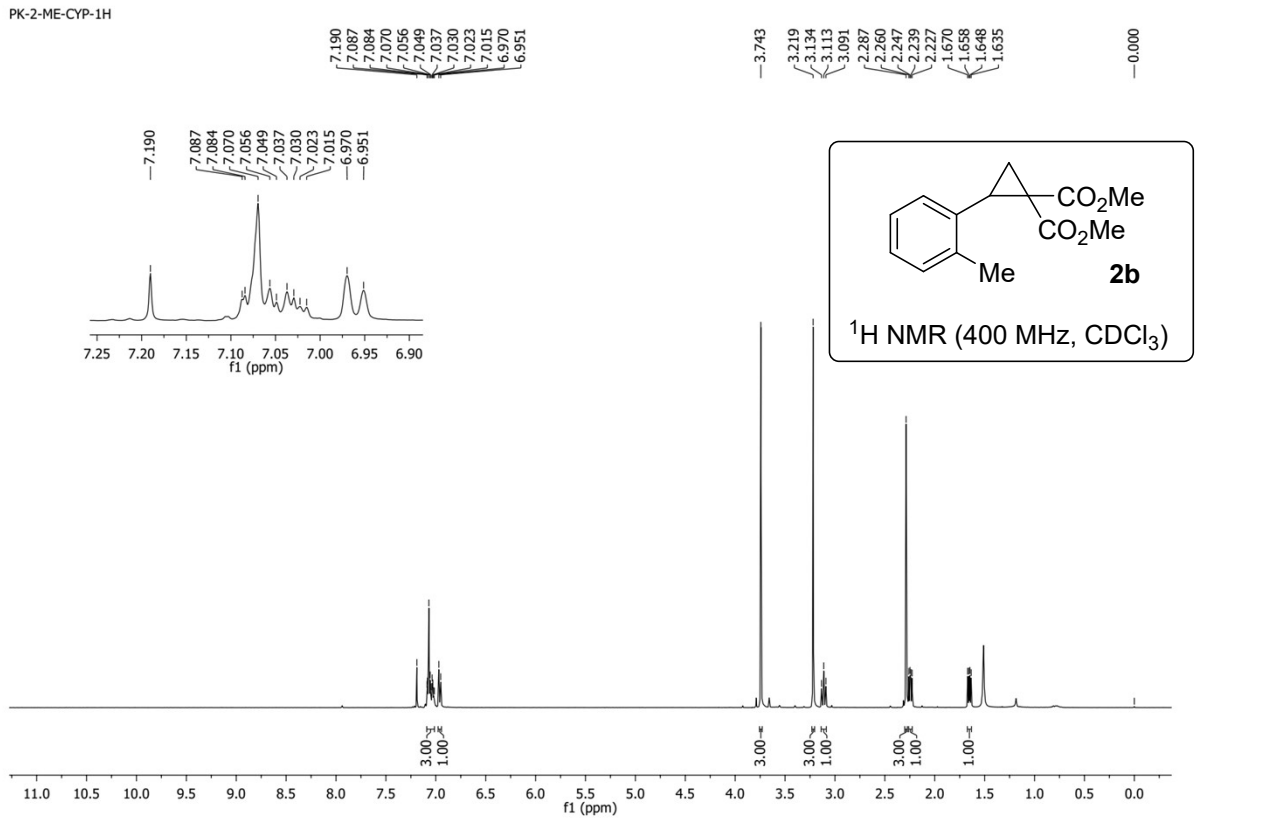
7.215
7.212
7.209
7.199
7.195
7.191
7.187
7.183
7.171
7.168
7.165
7.159
7.154
7.147
7.127
7.124
7.119
7.111
7.108
3.720
3.288
3.176
3.158
3.141
2.141
2.131
2.125
2.115
1.688
1.677
1.669
1.659
0.000
3.26
2.00
3.00
3.00
1.00
1.00
1.00
f1 (ppm)

Ph
CO2Me
CO2Me
2a
1H NMR (500 MHz, CDCl3)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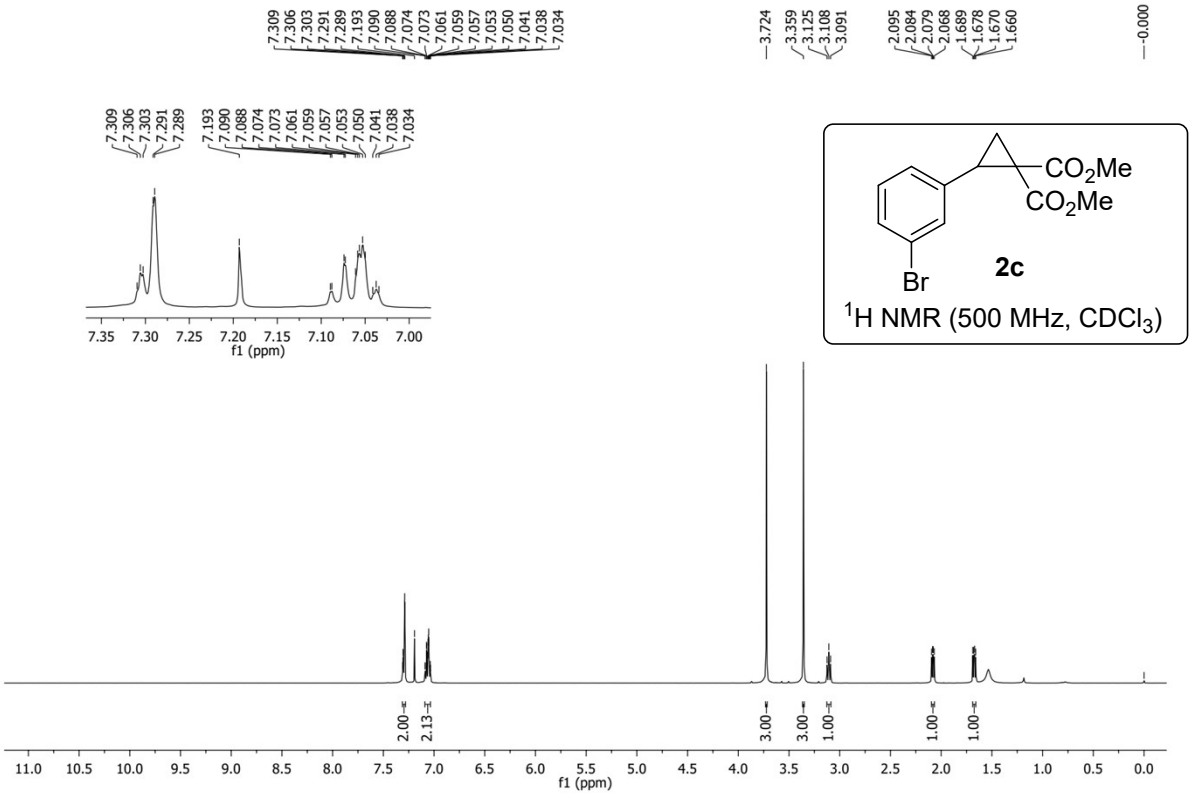
7.049
7.037
7.030
7.023
7.015
6.970
6.951
3.743
3.219
3.134
3.113
3.091
2.287
2.260
2.247
2.239
2.227
1.670
1.658
1.648
1.635
0.000
3.00
1.00
3.00
3.00
1.00
3.00
1.00
1.00
f1 (ppm)

CO2Me
CO2Me
Me
2b
1H NMR (400 MHz, CDCl3)

PK-3-BR-CYP-1H



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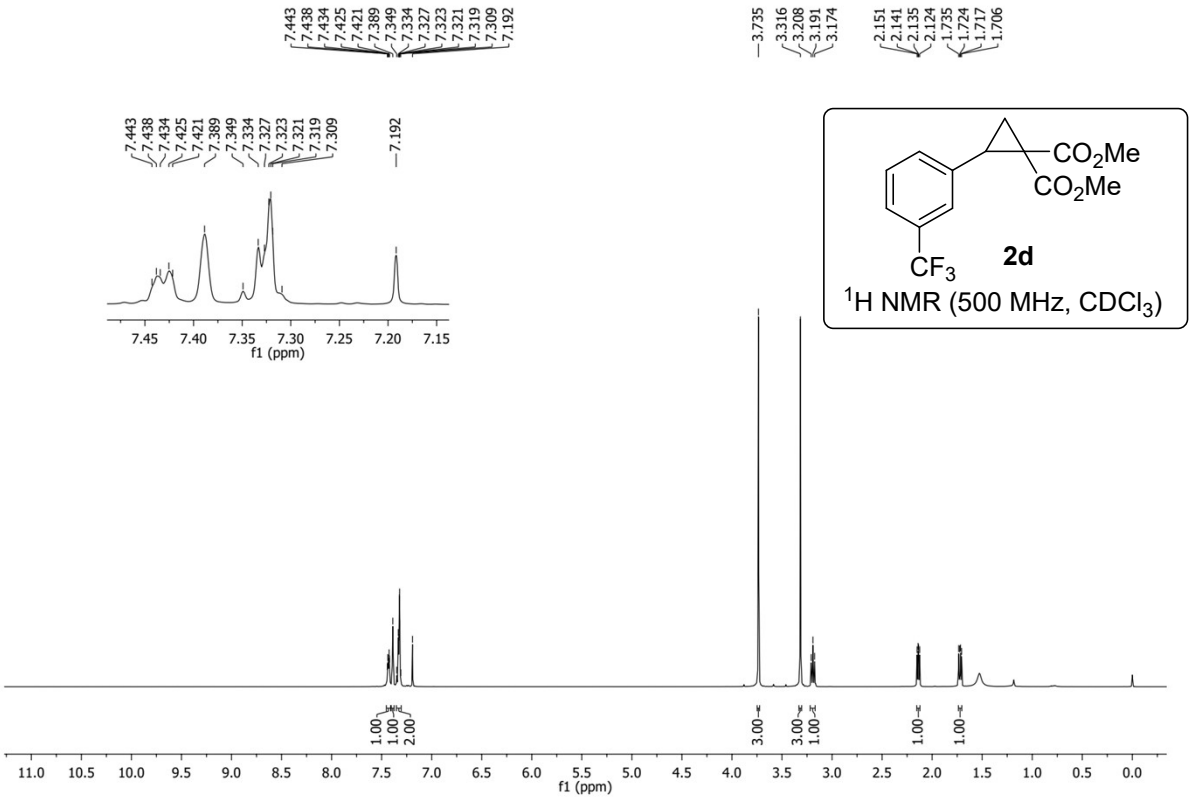
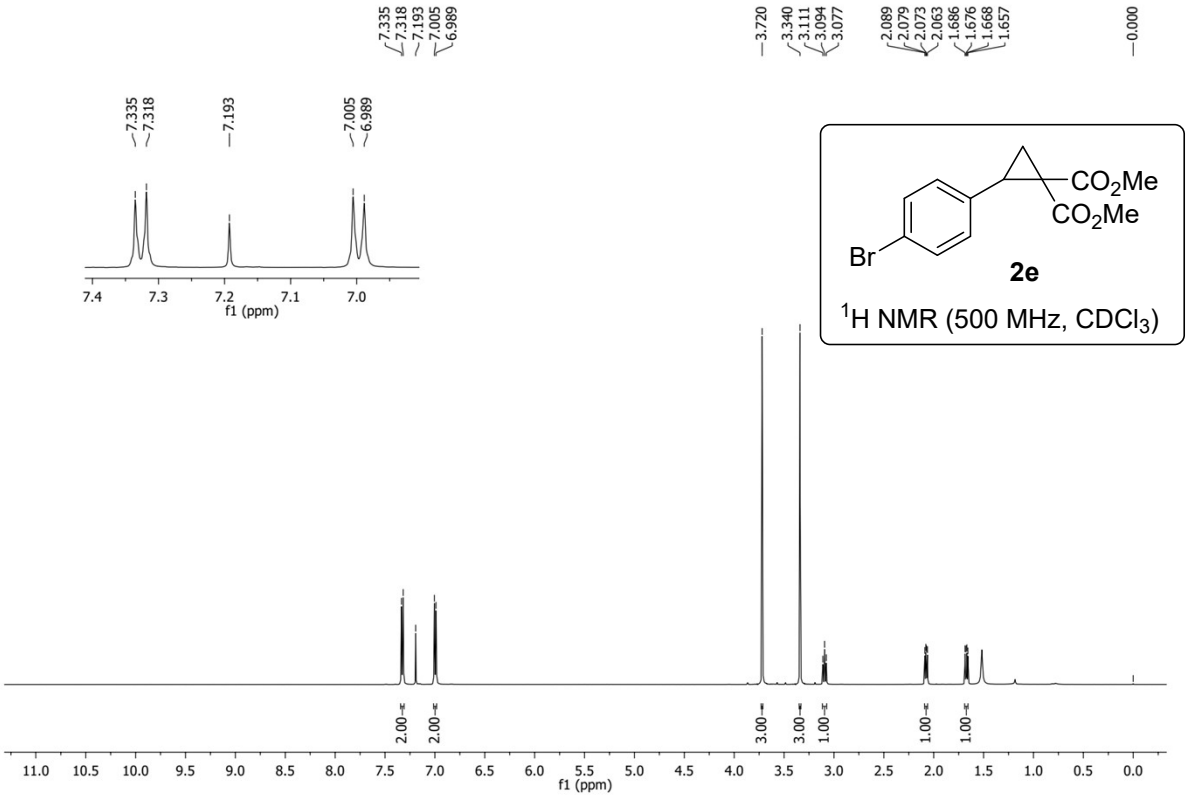


^{1}H NMR (500 MHz, $CDCl_3$)

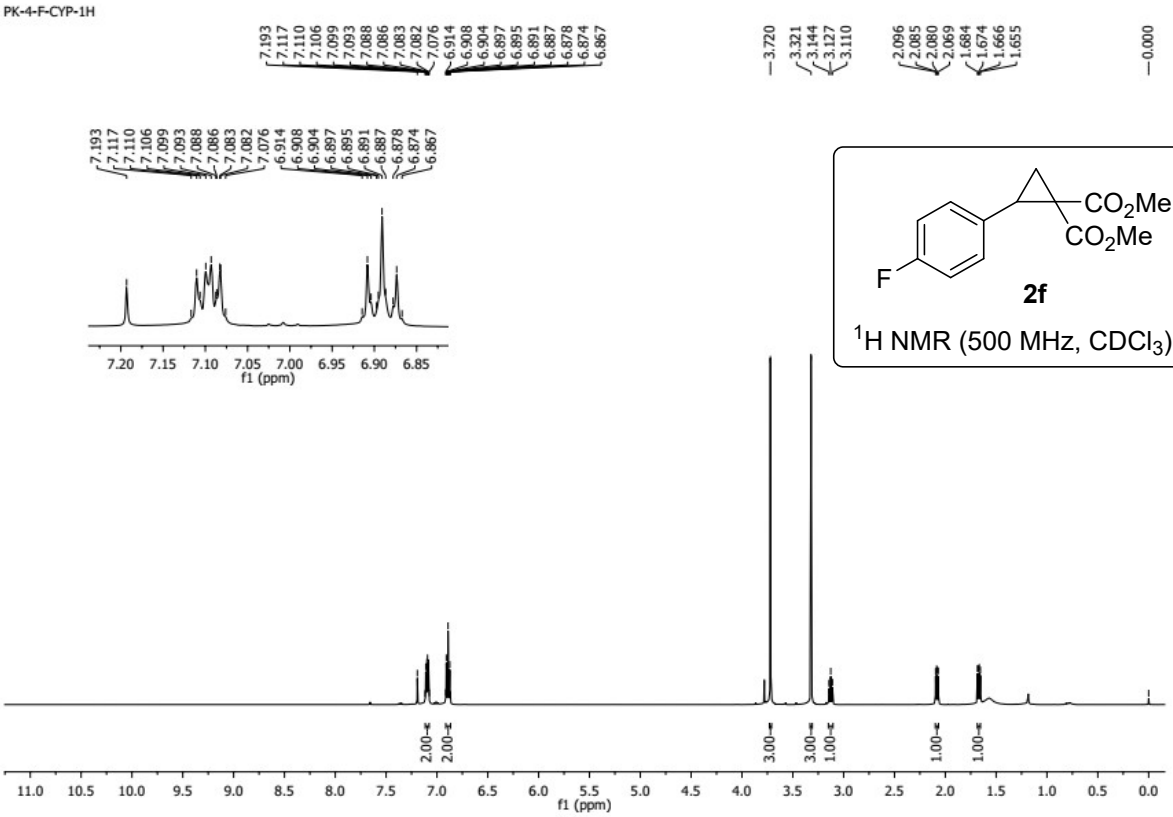
PK-4-BR-CYP-1H



2e

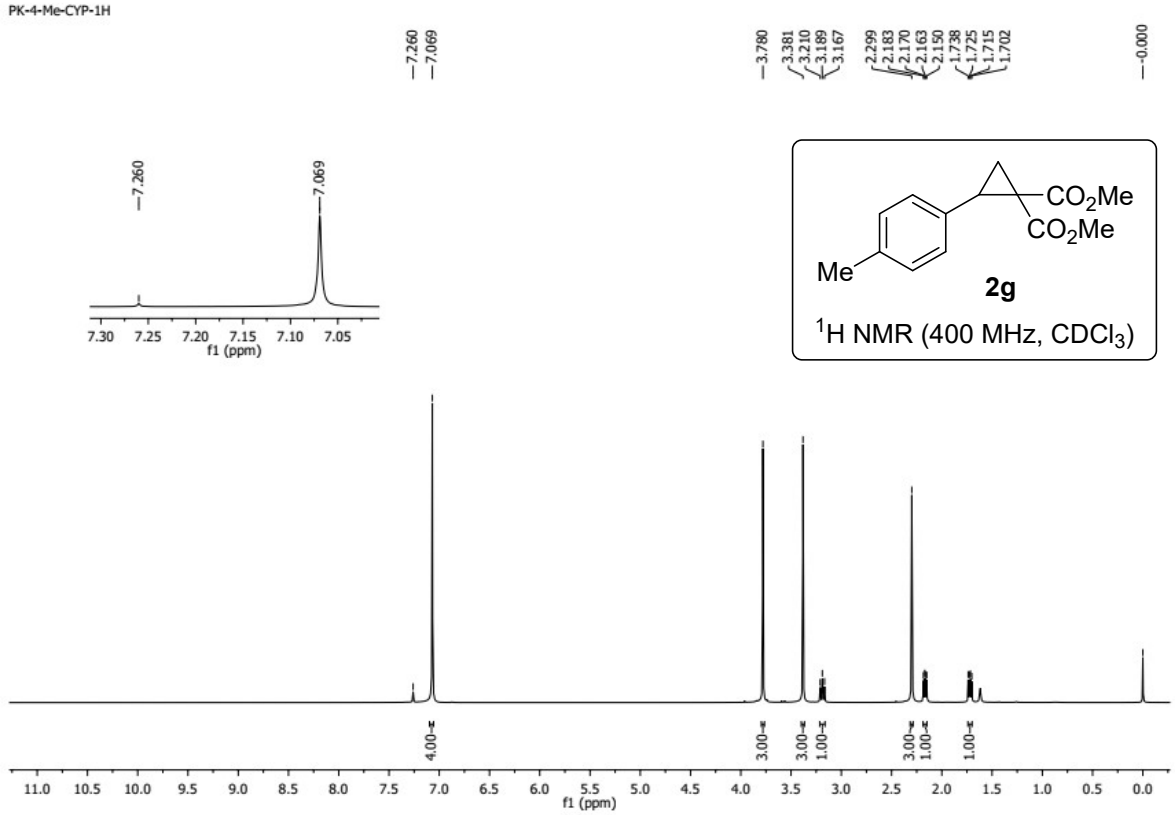
^{1}H NMR (500 MHz, $CDCl_3$)

PK-4-F-CYP-1H



2f

^{1}H NMR (500 MHz, $CDCl_3$)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3.780
3.381
3.210
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3.167
2.299
2.183
2.170
2.163
2.150
1.738
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1.702
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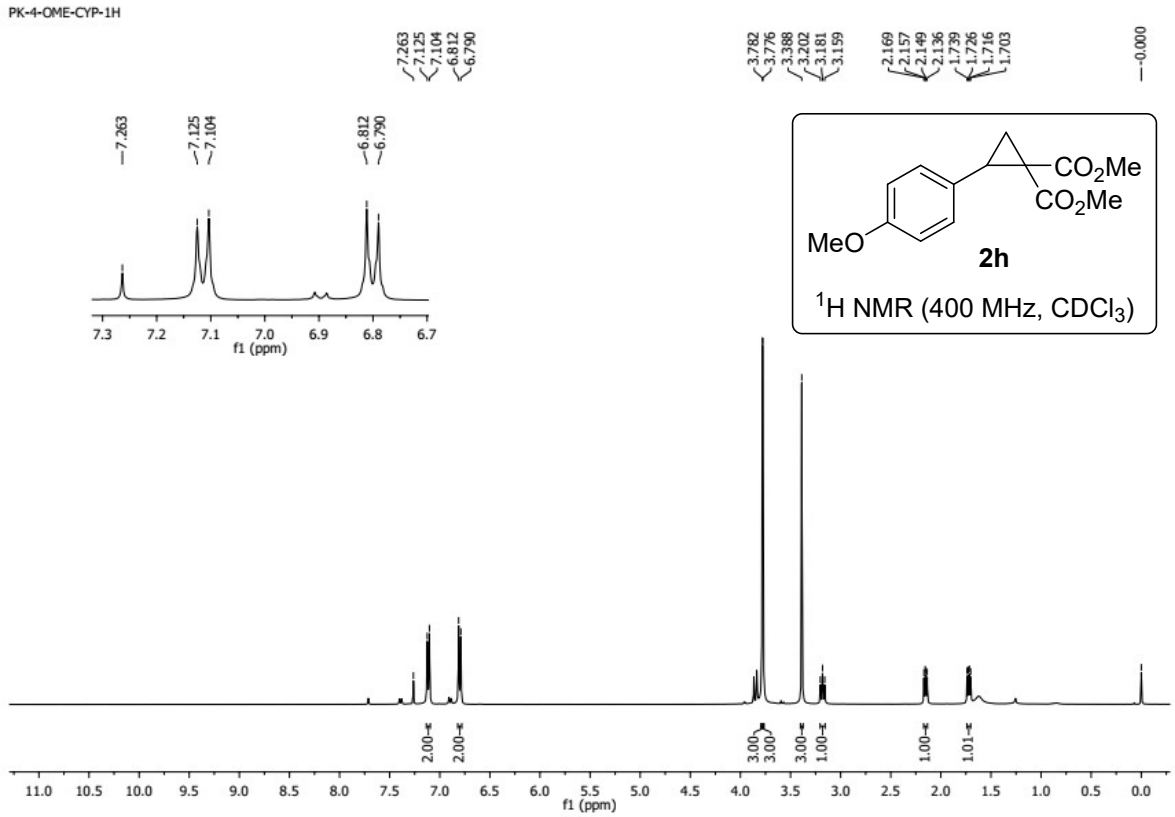
CO2Me
CO2Me
Me
2g
1H NMR (400 MHz, CDCl3)
f1 (ppm)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7.104
6.812
6.790
3.782
3.776
3.388
3.202
3.181
3.159
2.169
2.157
2.149
2.136
1.739
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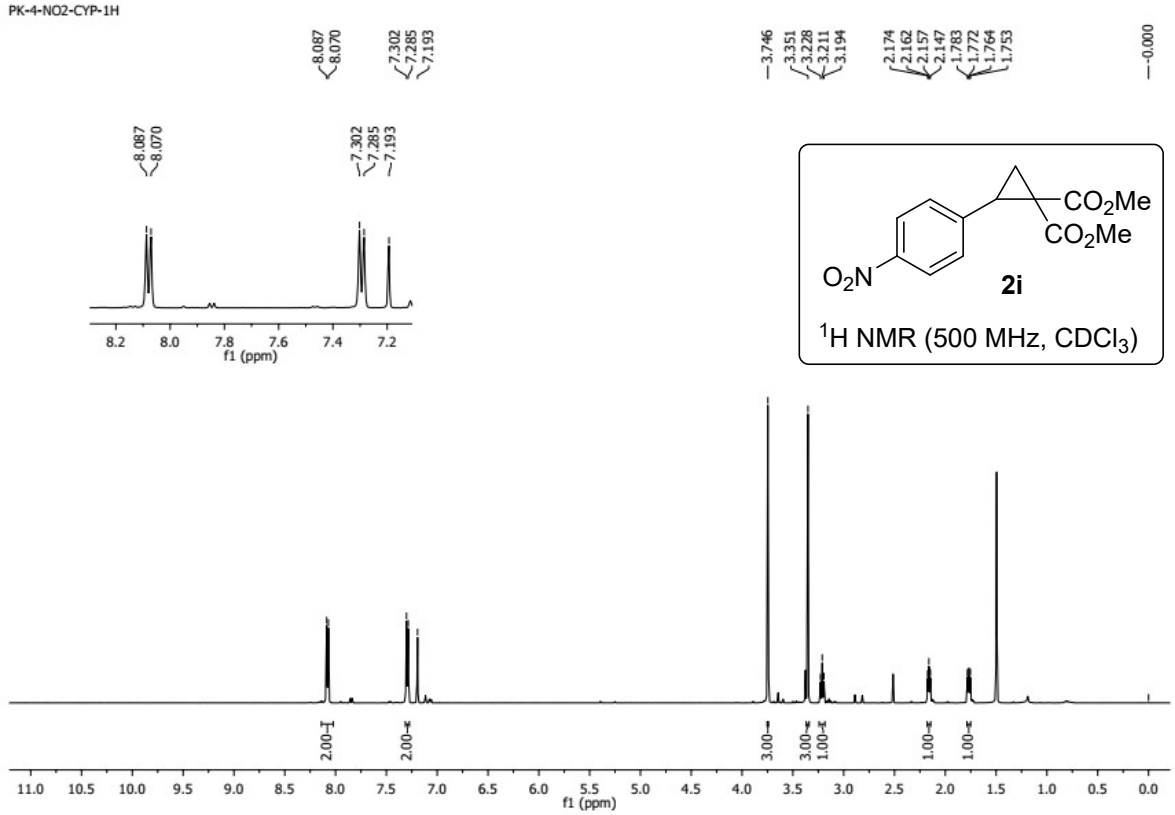
1.703
0.000
CO2Me
CO2Me
MeO
2h
1H NMR (400 MHz, CDCl3)
f1 (ppm)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7.302
7.285
7.193
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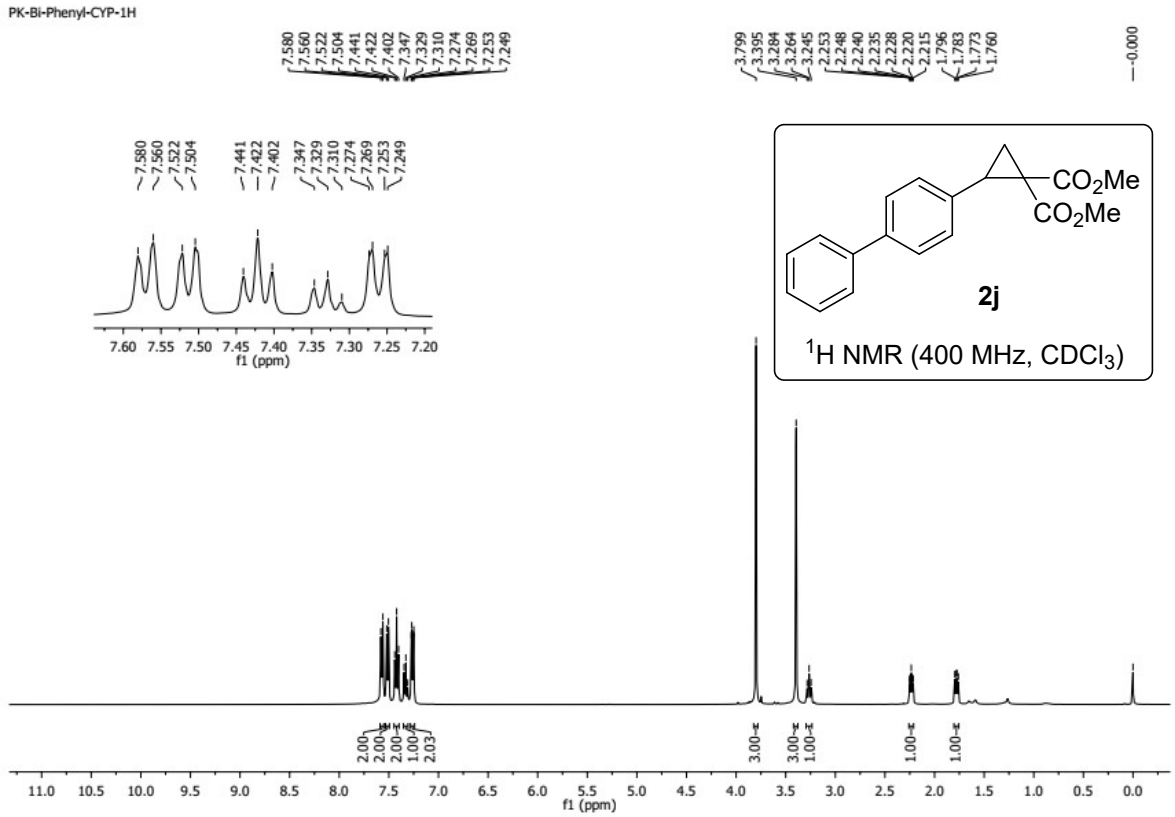
3.228
3.211
3.194
2.174
2.162
2.157
2.147
1.783
1.772
1.764
1.753
0.000
f1 (ppm)
CO2Me
CO2Me
O2N
2i
1H NMR (500 MHz, CDCl3)
2.00
2.00
3.00
3.00
1.00
1.00
1.00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7.310
7.274
7.269
7.253
7.249
3.799
3.395
3.284
3.264
3.245
2.253
2.248
2.240
2.235
2.228
2.220
2.215
1.796
1.783
1.773
1.760
0.000
f1 (ppm)
CO2Me
CO2Me
2j
1H NMR (400 MHz, CDCl3)
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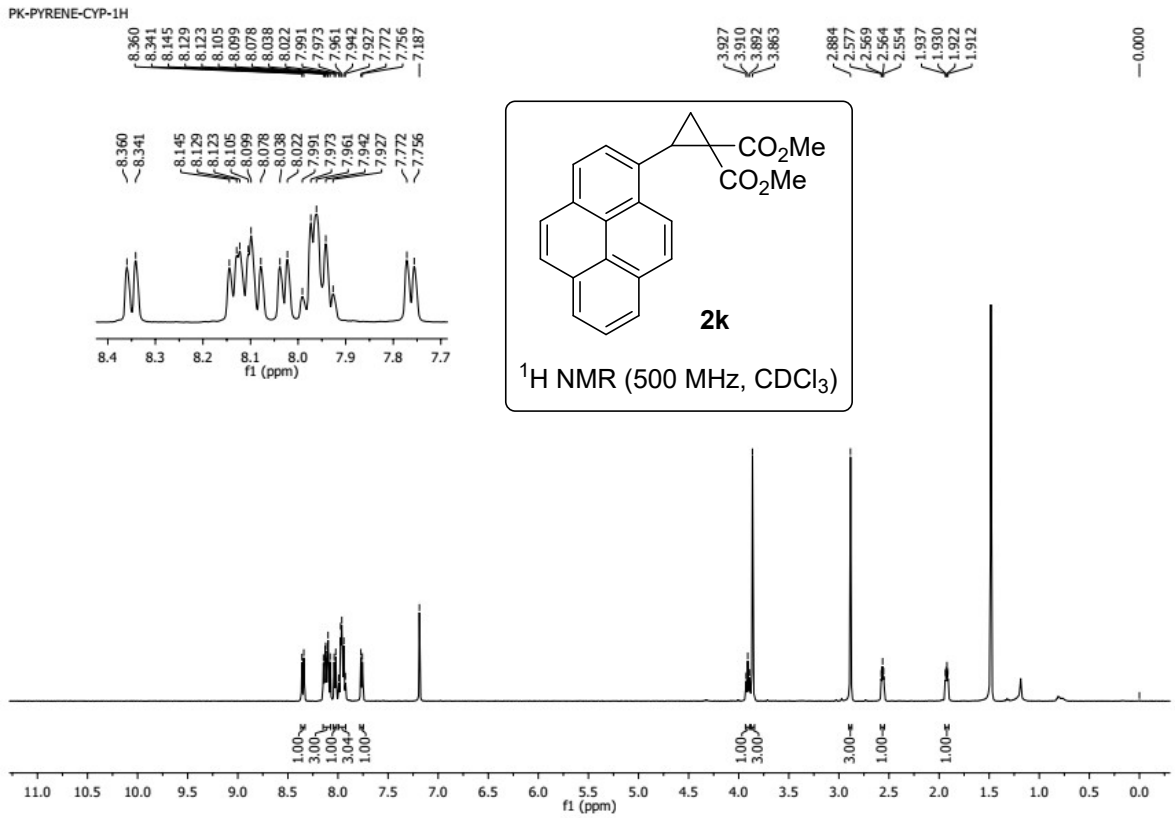
2.00
2.00
1.00
2.03
3.00
3.00
1.00
1.00
1.00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8.145
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8.123
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8.078
8.038
8.022
7.991
7.973
7.961
7.942
7.927
7.772
7.756
7.187
3.927
3.910
3.892
3.863
2.884
2.577
2.569
2.564
2.554
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f1 (ppm)
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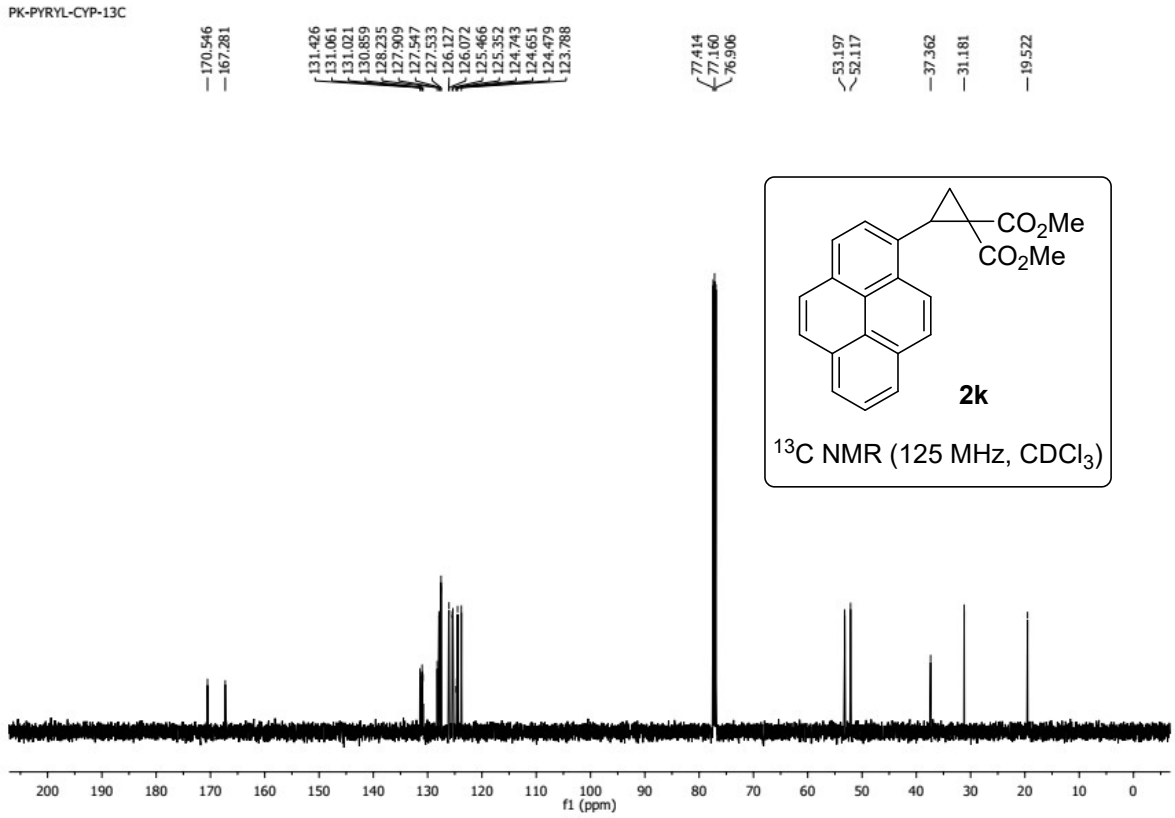
CO2Me
2k
1H NMR (500 MHz, CDCl3)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167.281
131.426
131.061
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130.859
128.235
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127.547
127.533
126.127
126.072
125.466
125.352
124.743
124.651
124.479
123.788
77.414
77.160
76.906
53.197
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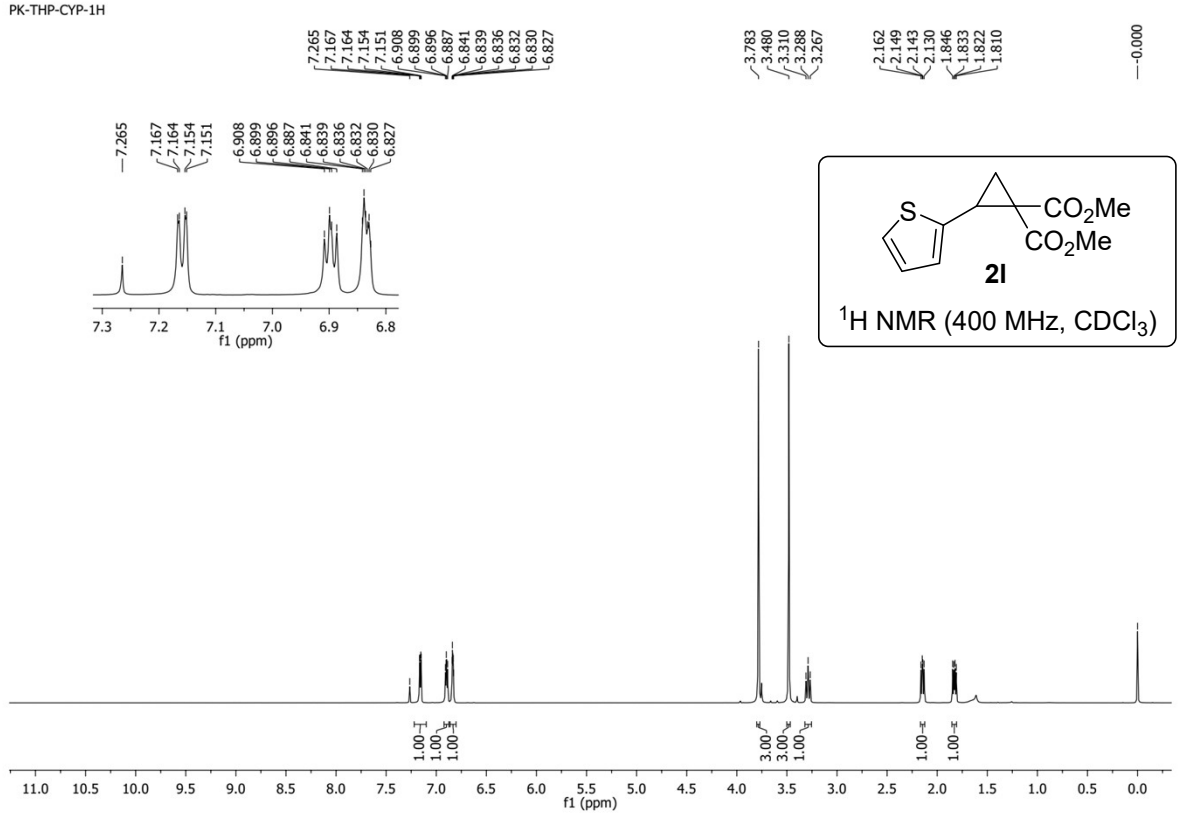
37.362
31.181
19.522
f1 (ppm)
CO2Me
CO2Me
2k
13C NMR (125 MHz, CDCl3)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7.167
7.164
7.154
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6.841
6.839
6.836
6.832
6.830
6.827
3.783
3.480
3.310
3.288
3.267
2.162
2.149
2.143
2.130
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0.000
f1 (ppm)
S
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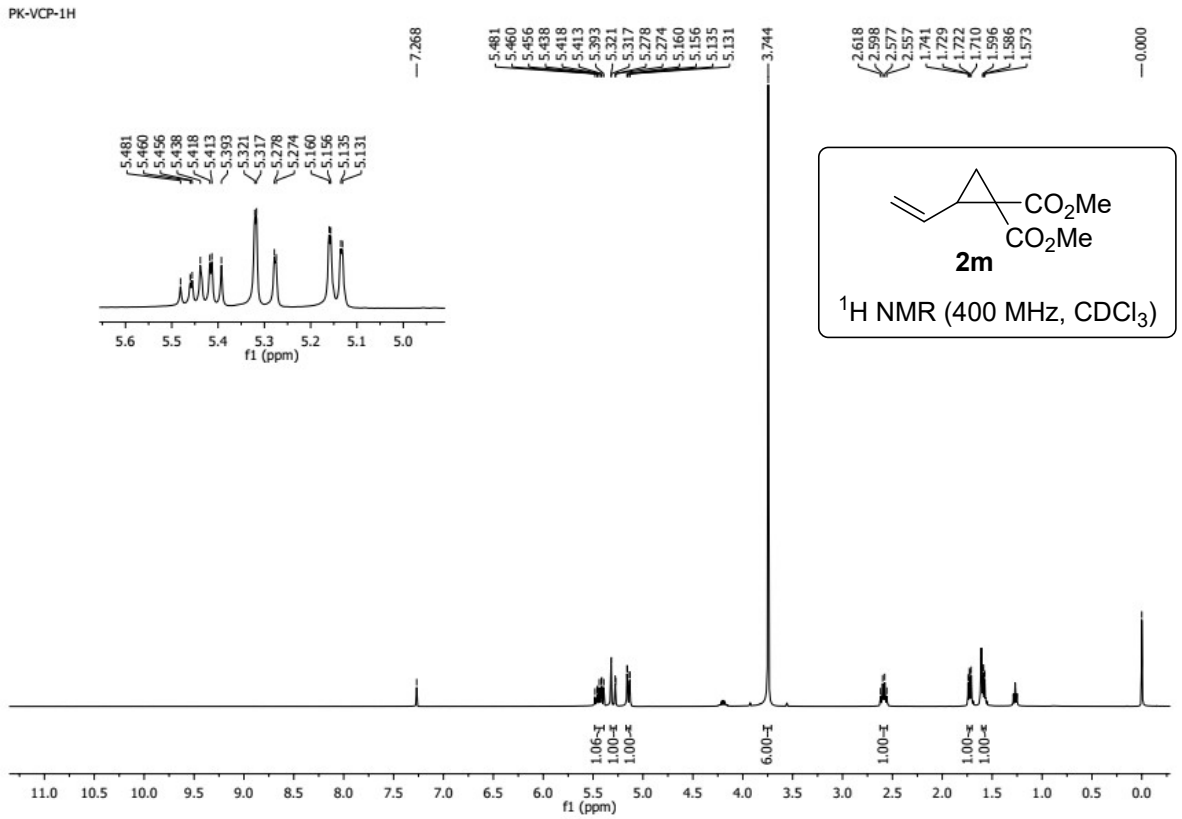
CO2Me
2l
1H NMR (400 MHz, CDCl3)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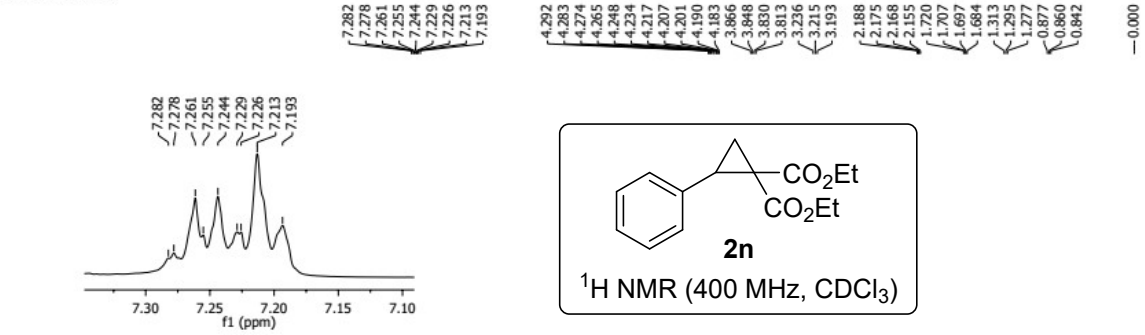
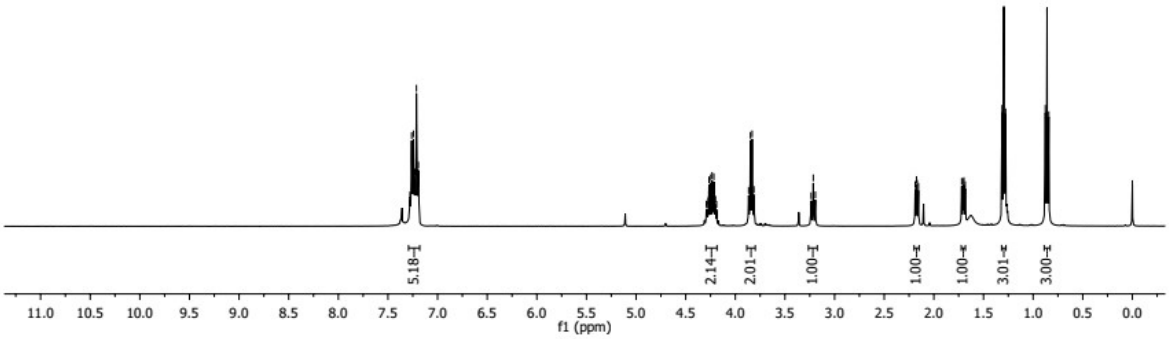
5.393
5.321
5.317
5.278
5.274
5.160
5.156
5.135
5.131
3.744
2.618
2.598
2.577
2.557
1.741
1.729
1.722
1.710
1.596
1.586
1.573
0.000
f1 (ppm)
CO2Me
CO2Me
2m
1H NMR (400 MHz, CDCl3)

PK-CO2ET-CYP-1H

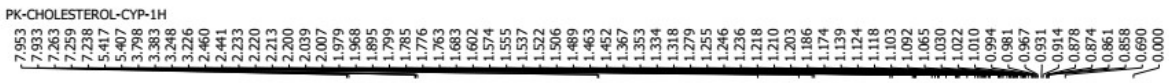


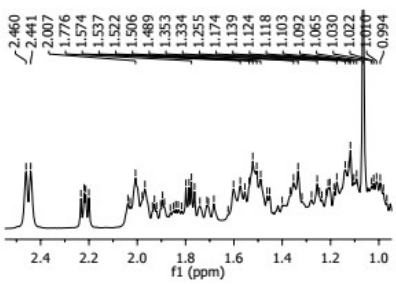
2n

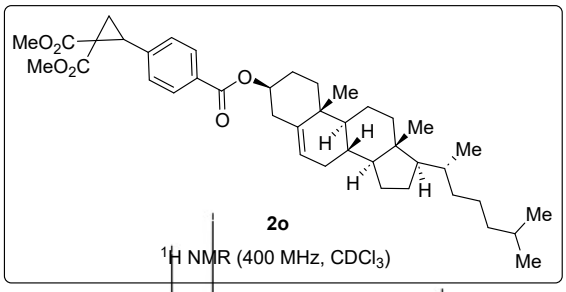
^{1}H NMR (400 MHz, $CDCl_3$)



PK-CHOLESTEROL-CYP-1H

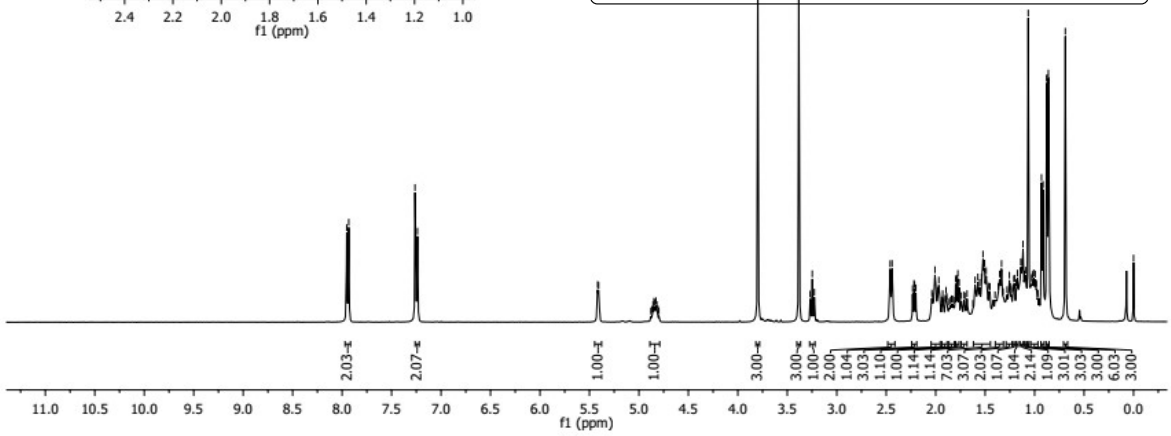


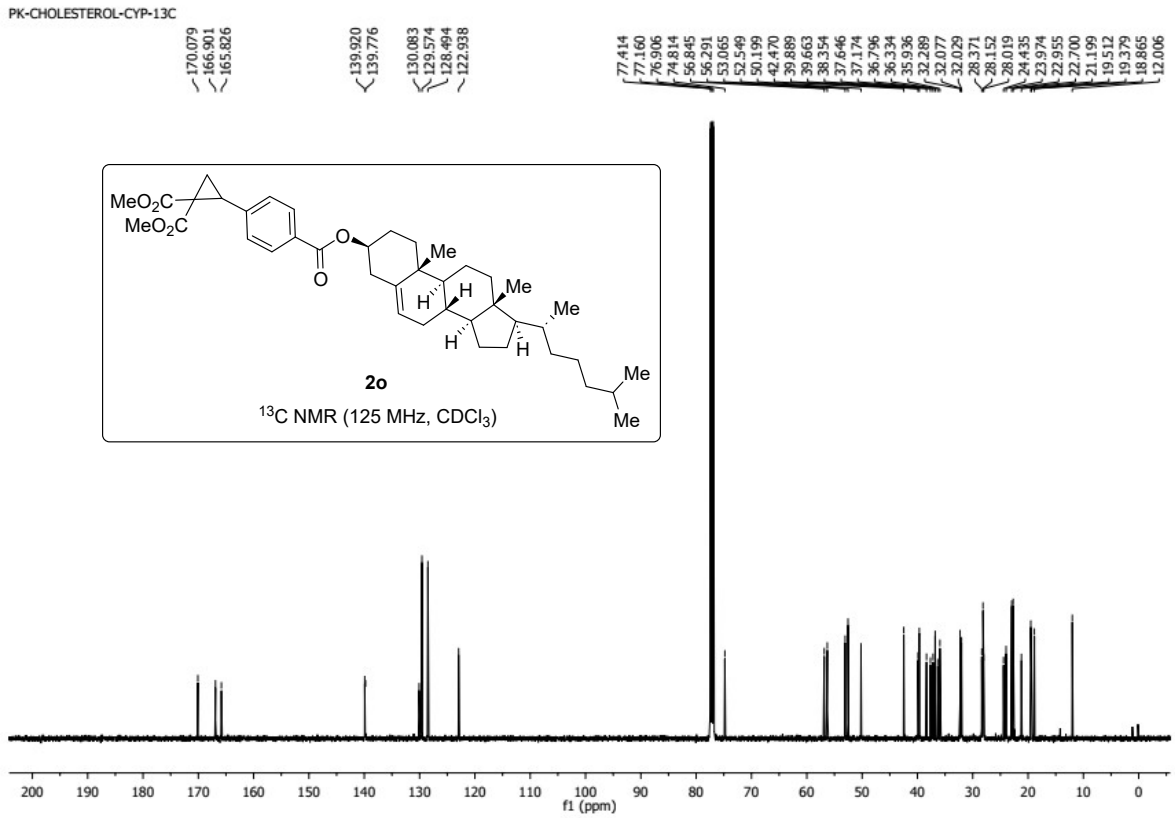




2o

^{1}H NMR (400 MHz, $CDCl_3$)

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139.776
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77.160
76.906
74.814
56.845
56.291
53.065
52.549
50.199
42.470
39.889
39.663
38.354
37.646
37.174
36.796
36.334
35.936
32.289
32.077
32.029
28.371
28.152
28.019
24.435
23.974
22.955
22.700
21.199
19.512
19.379
18.865
12.006
MeO2C
MeO2C
O
O
Me
H
H
Me
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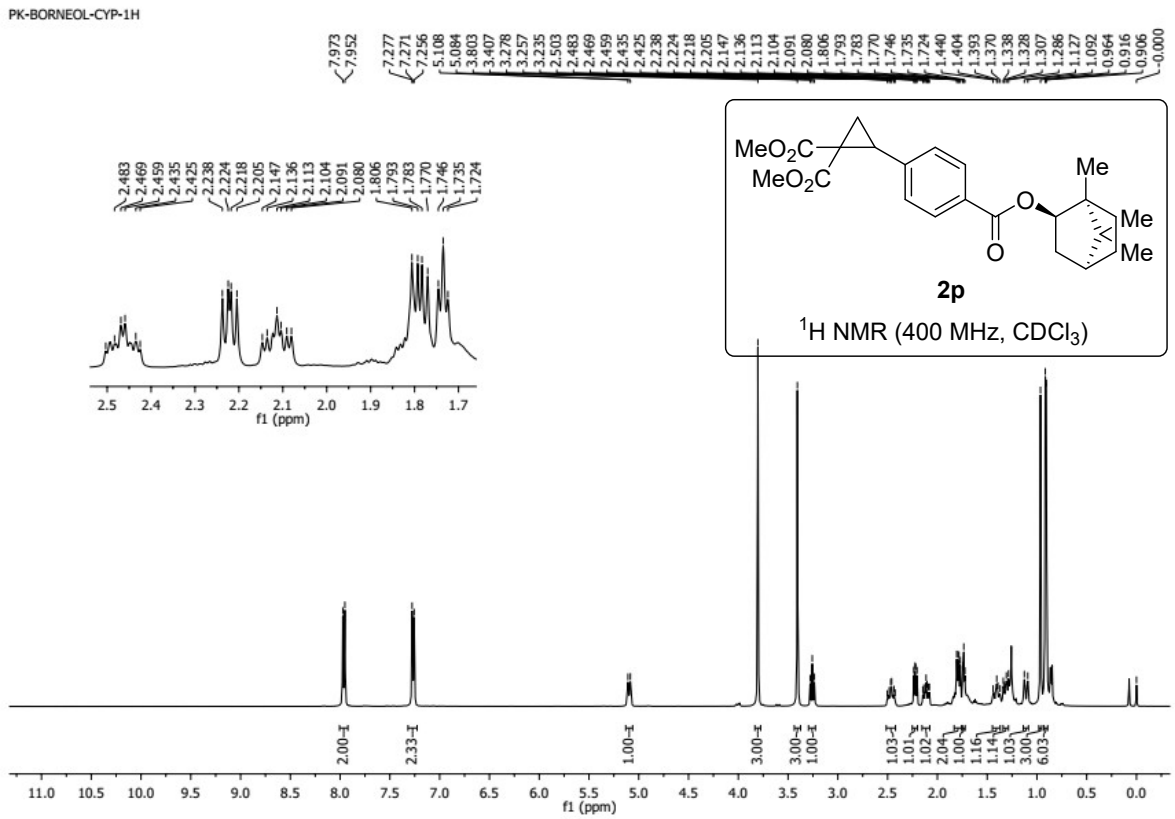
f1 (ppm)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5.084
3.803
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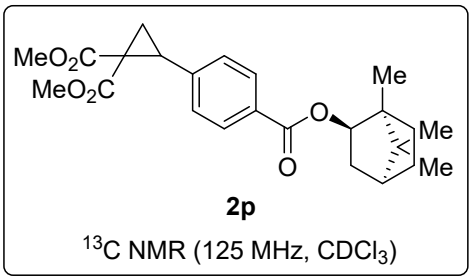
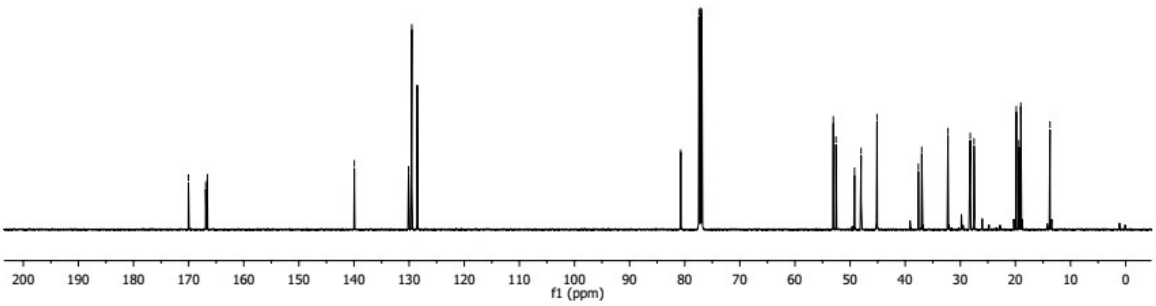
3.278
3.257
3.235
2.503
2.483
2.469
2.459
2.435
2.425
2.238
2.224
2.218
2.205
2.147
2.136
2.113
2.104
2.091
2.080
1.806
1.793
1.783
1.770
1.746
1.735
1.724
1.440
1.404
1.393
1.370
1.338
1.328
1.307
1.286
1.127
1.092
0.964
0.916
0.906
-0.000
MeO2C
MeO2C
O
O
Me
Me
Me
2p
1H NMR (400 MHz, CDCl3)
2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7
f1 (ppm)
2.00
2.33
1.00
3.00
3.00
1.00
1.03
1.01
1.02
2.04
1.00
1.16
1.14
1.03
3.00
6.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

PK-BORNEOL-CYP-13c

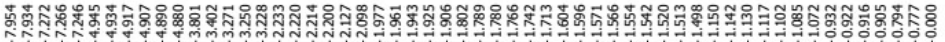


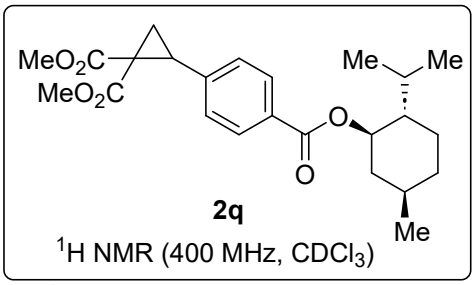
2p

^{13}C NMR (125 MHz, $CDCl_3$)



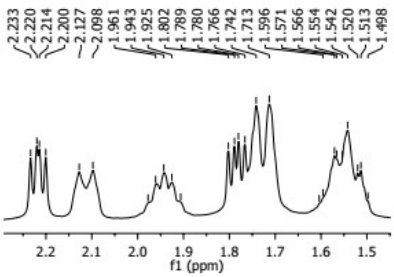
PK-MENTHOL-CYP-1H

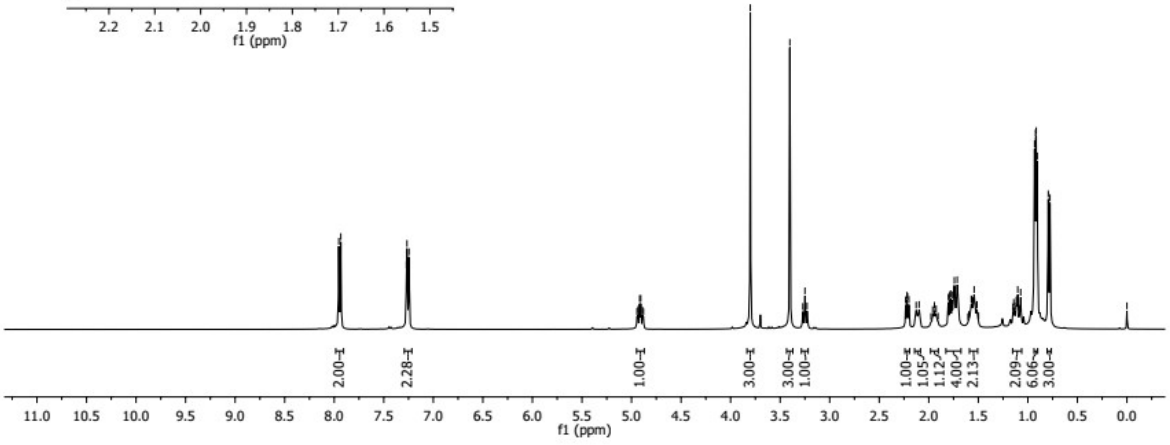


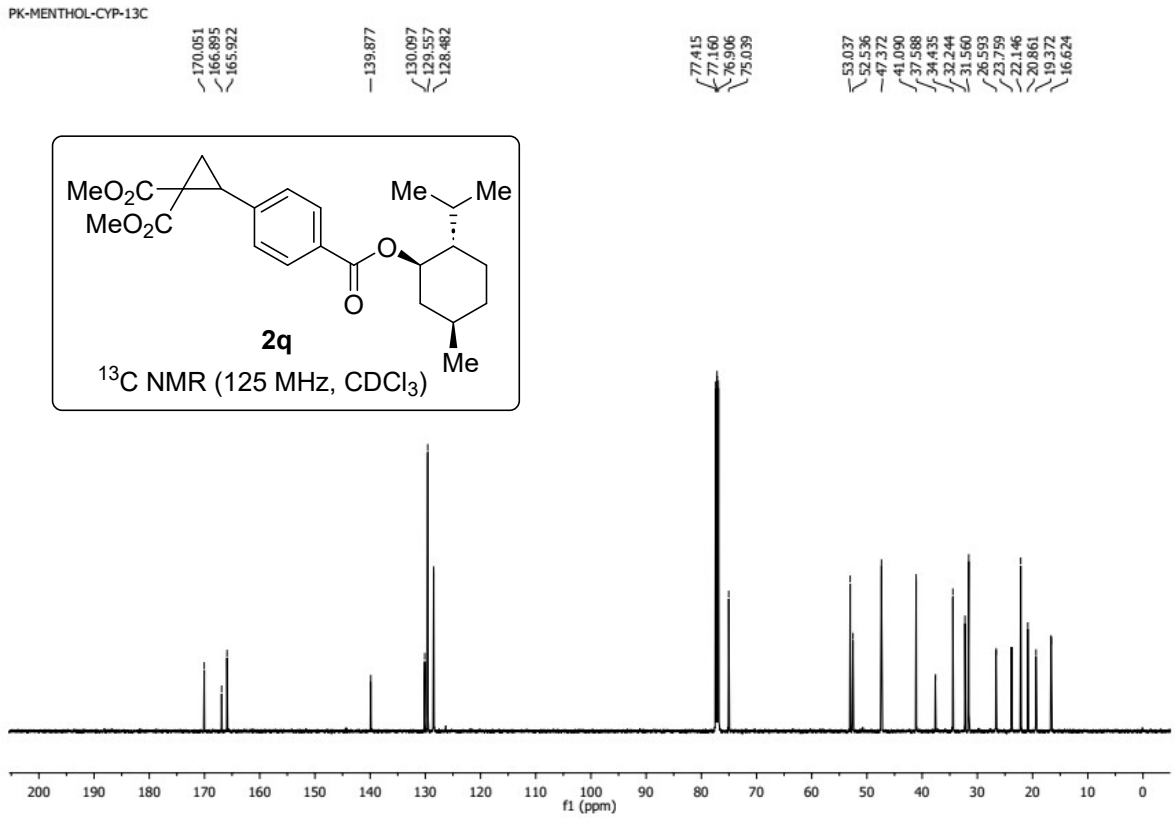


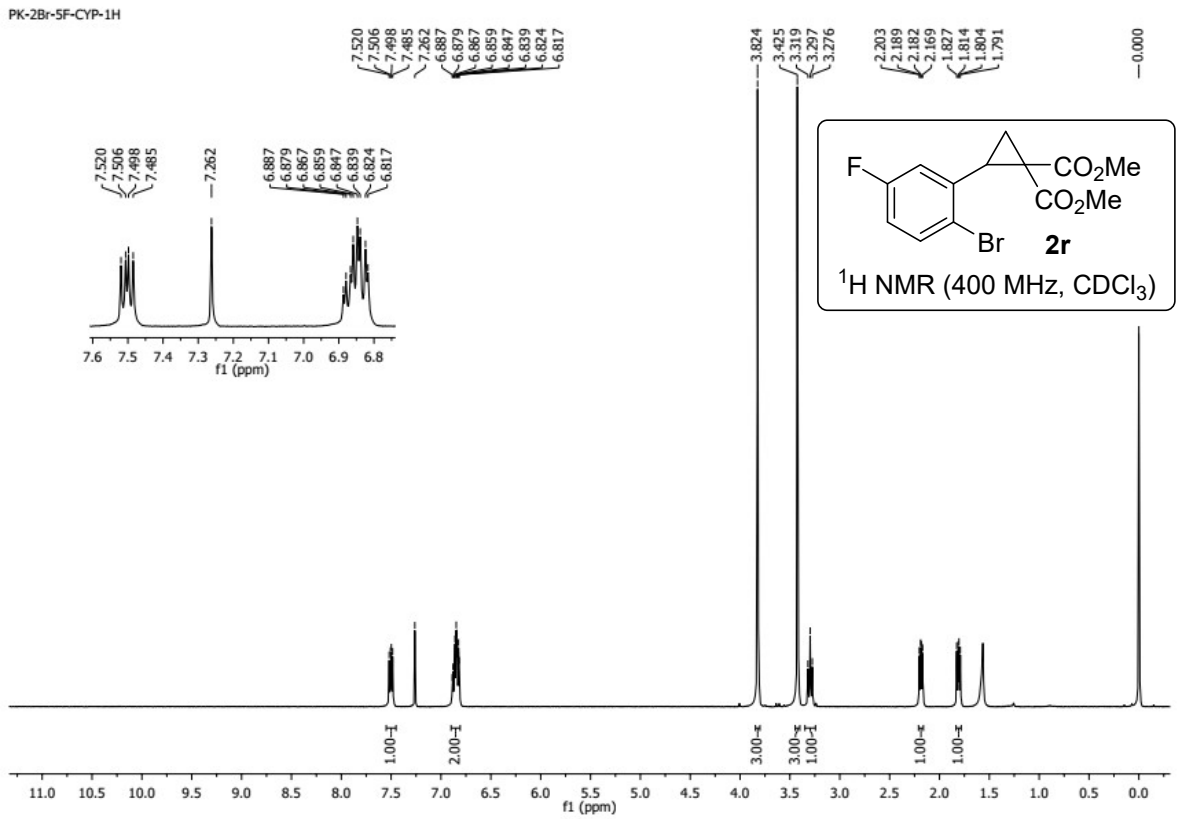
2q

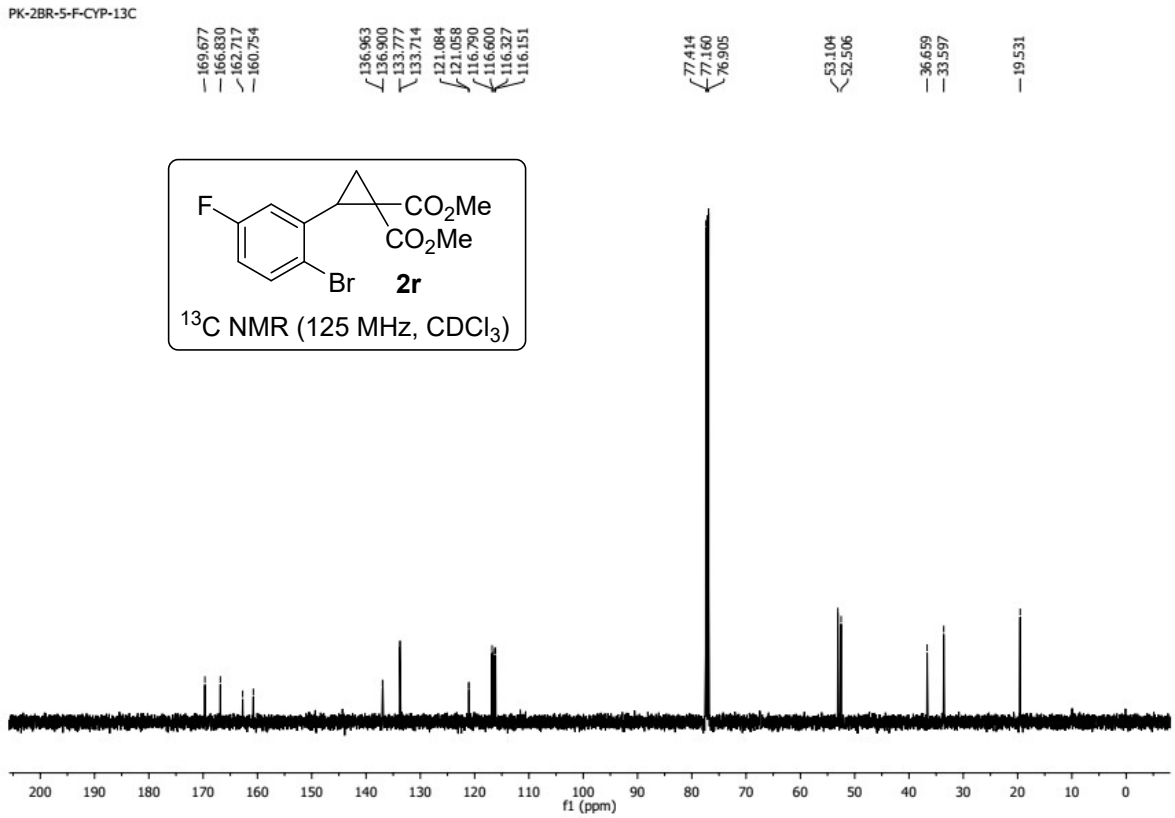
^{1}H NMR (400 MHz, $CDCl_3$)

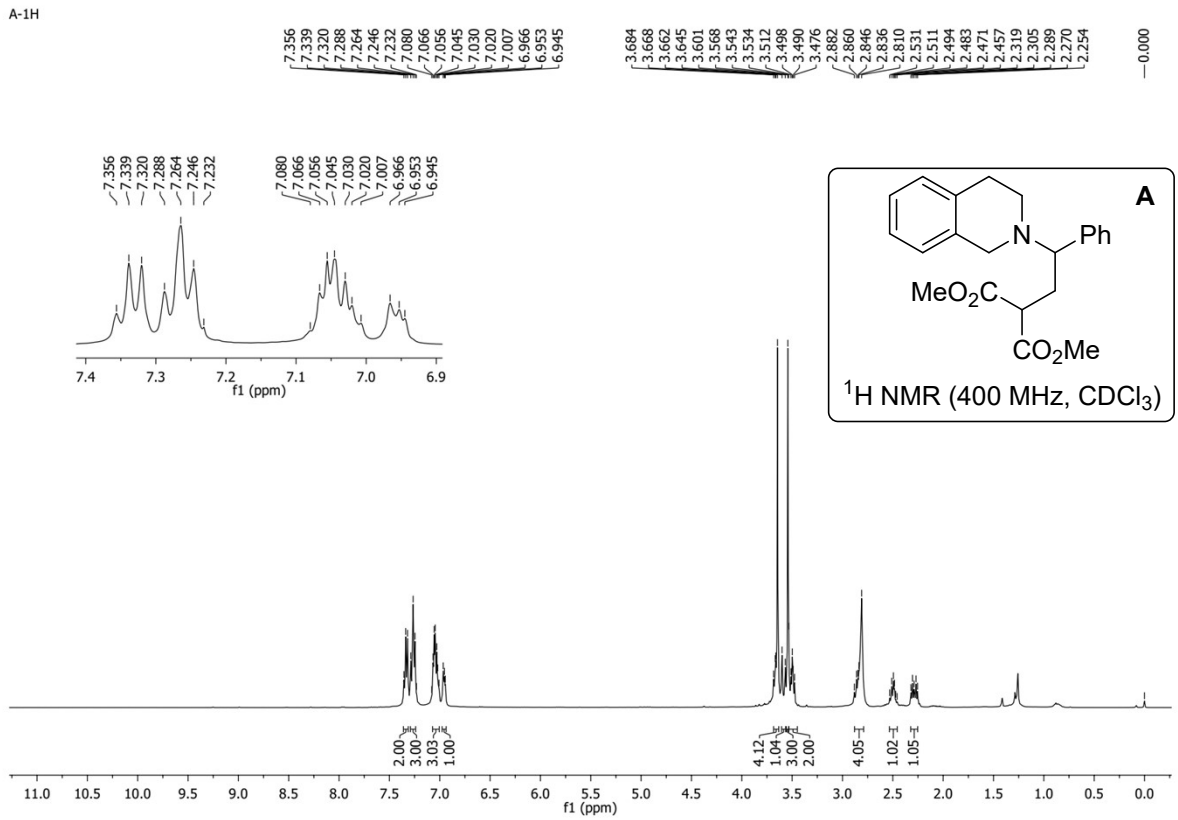




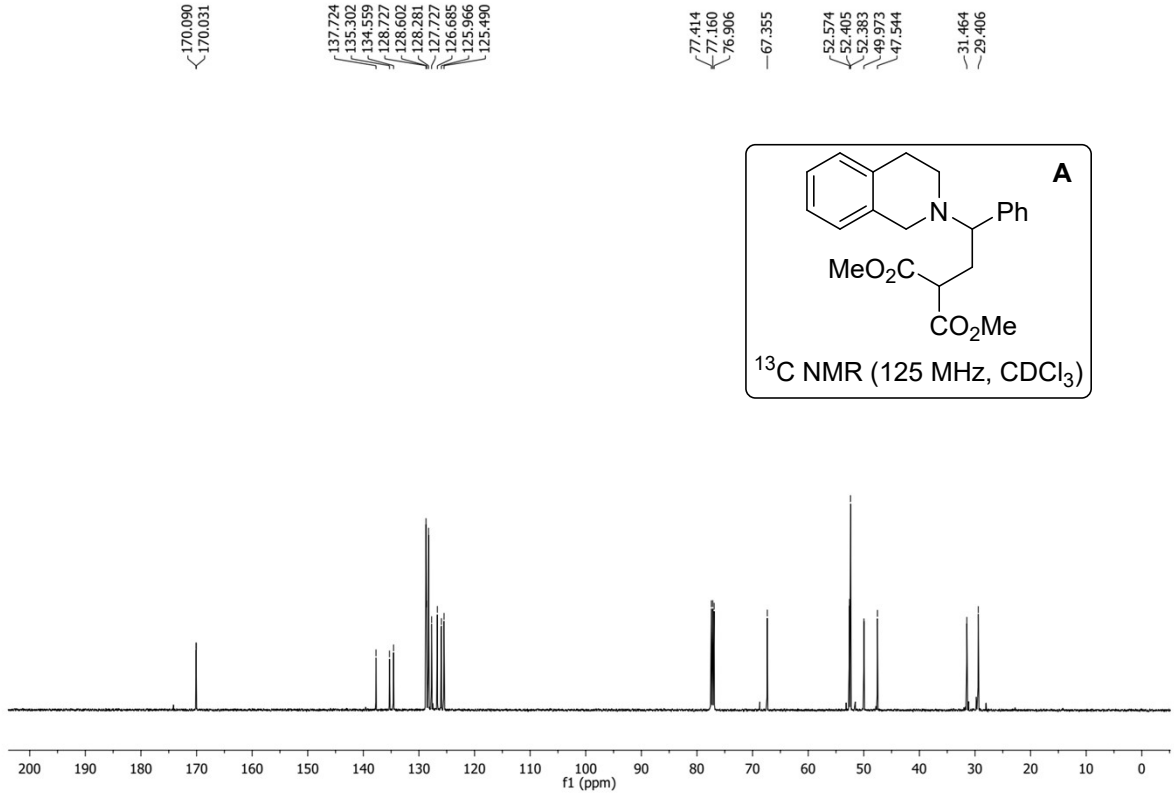

PK-MENTHOL-CYP-13C
170.051
166.895
165.922
139.877
130.097
129.557
128.482
77.415
77.160
76.906
75.039
53.037
52.536
47.372
41.090
37.588
34.435
32.244
31.560
26.593
23.759
22.146
20.861
19.372
16.624
MeO2C
MeO2C
Me
Me
O
O
Me
2q
13C NMR (125 MHz, CDCl3)
f1 (ppm)


PK-2Br-5F-CYP-1H
7.520
7.506
7.498
7.485
7.262
6.887
6.879
6.867
6.859
6.847
6.839
6.824
6.817
3.824
3.425
3.319
3.297
3.276
2.203
2.189
2.182
2.169
1.827
1.814
1.804
1.791
0.000
F
CO2Me
CO2Me
Br
2r
1H NMR (400 MHz, CDCl3)
1.00
2.00
3.00
3.00
1.00
1.00
1.00
f1 (ppm)

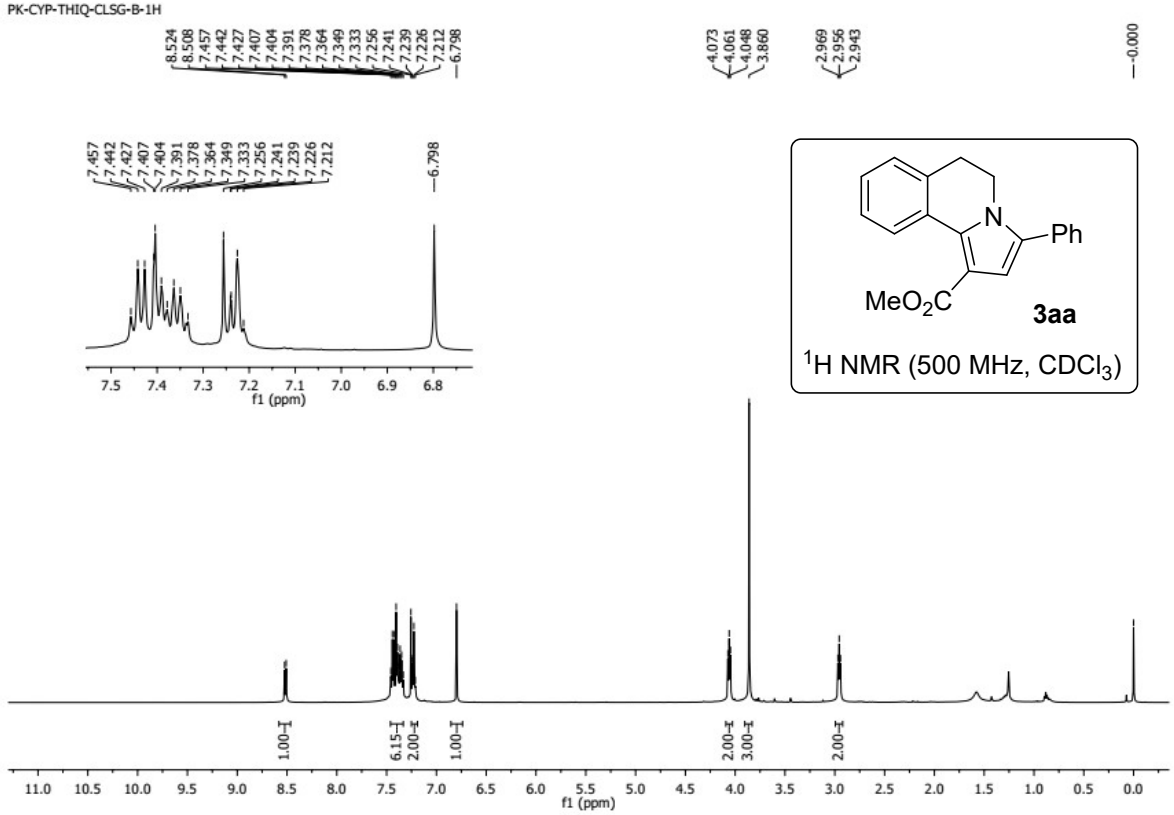

PK-2BR-5-F-CYP-13C
169.677
166.830
162.717
160.754
136.963
136.900
133.777
133.714
121.084
121.058
116.790
116.600
116.327
116.151
77.414
77.160
76.905
53.104
52.506
36.659
33.597
19.531
F
CO2Me
CO2Me
Br
2r
13C NMR (125 MHz, CDCl3)
f1 (ppm)

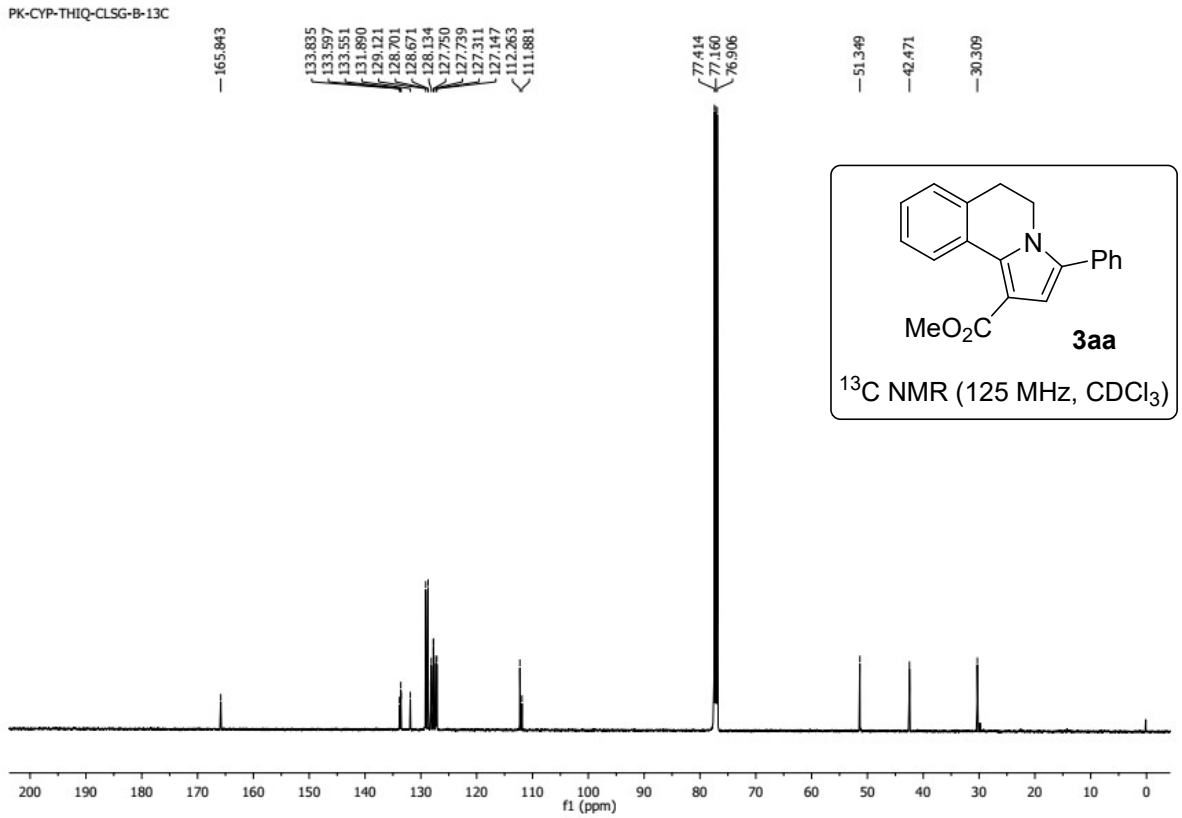

A-1H
7.356
7.339
7.320
7.288
7.264
7.246
7.232
7.080
7.066
7.056
7.045
7.030
7.020
7.007
6.966
6.953
6.945
3.684
3.668
3.662
3.645
3.601
3.568
3.543
3.534
3.512
3.498
3.490
3.476
2.882
2.860
2.846
2.836
2.810
2.531
2.511
2.494
2.483
2.471
2.457
2.319
2.305
2.289
2.270
2.254
0.000
A
N
Ph
MeO2C
CO2Me
1H NMR (400 MHz, CDCl3)
f1 (ppm)

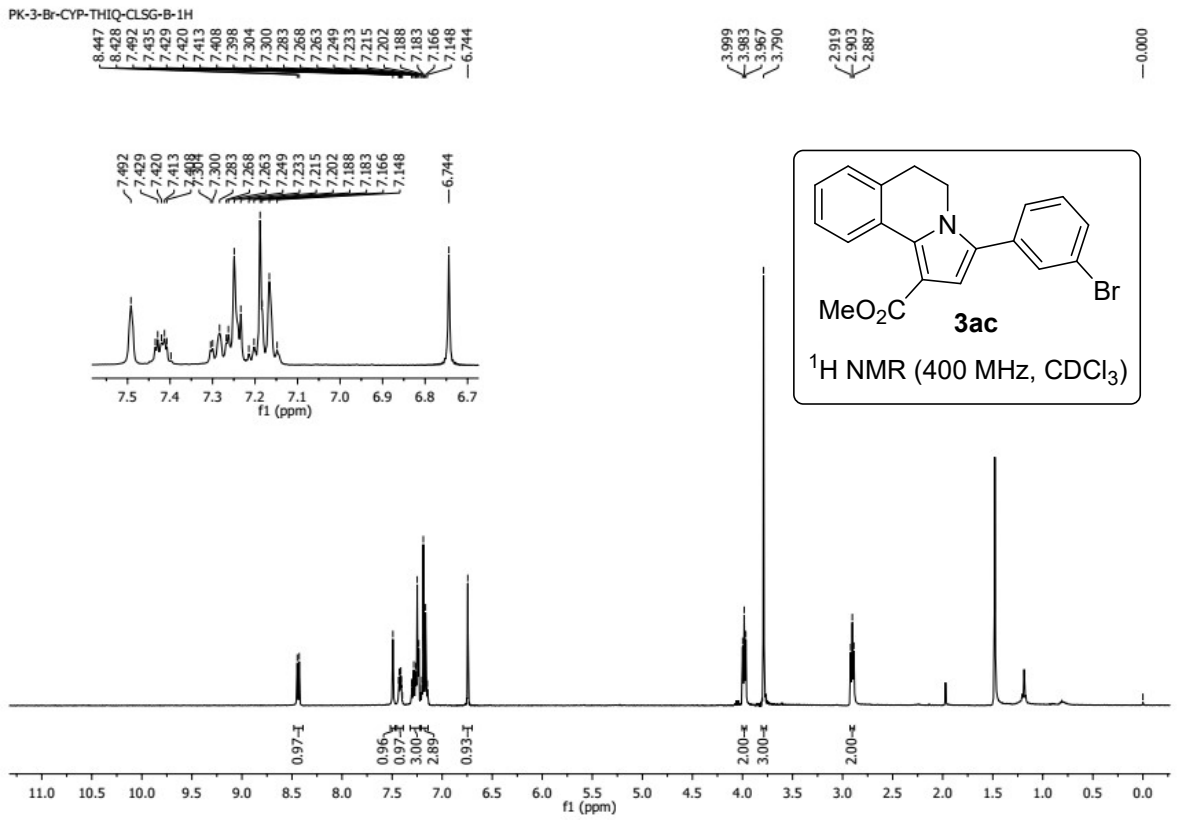
A-13C

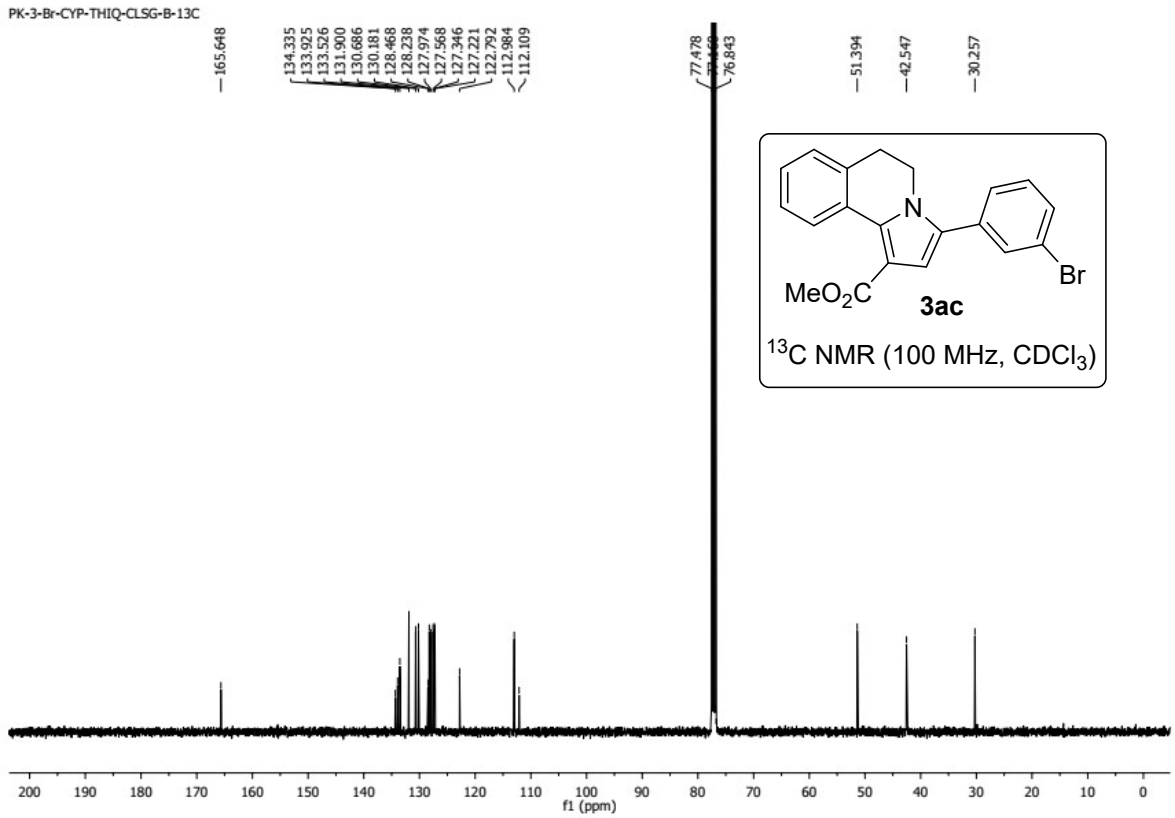


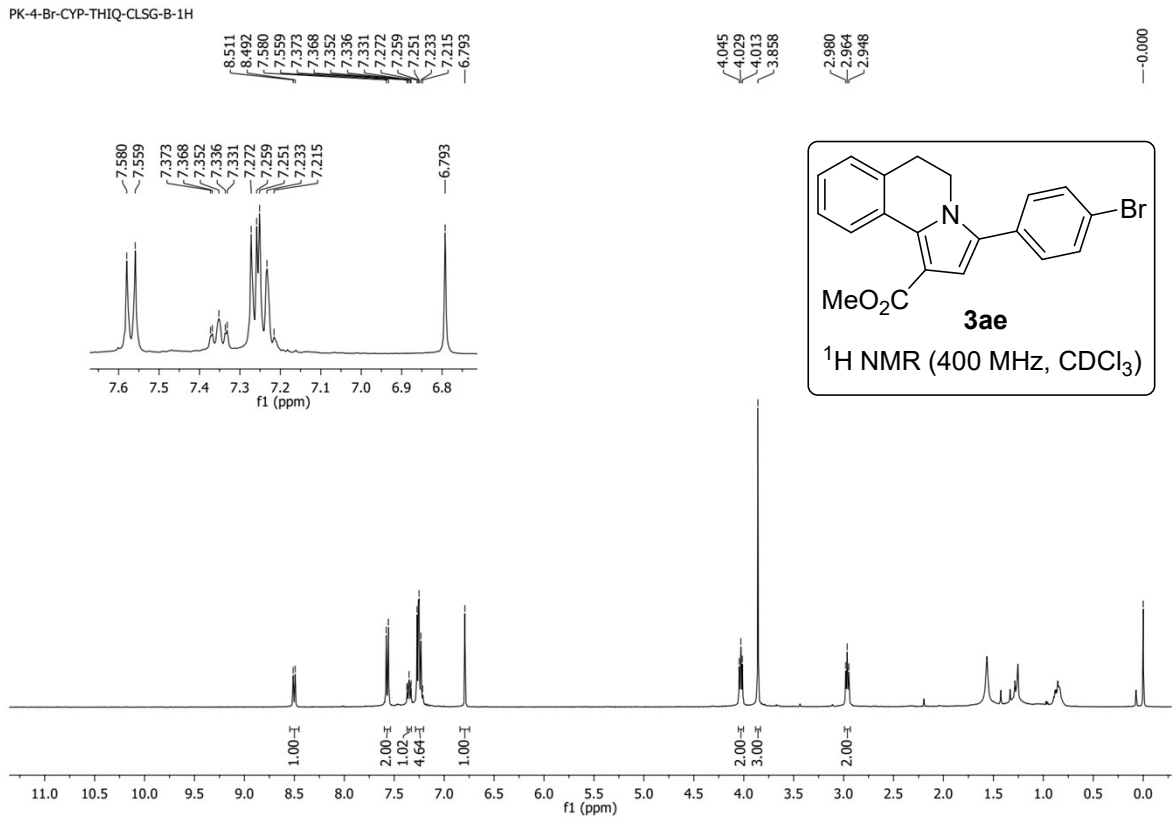
PK-CYP-THIQ-CLSG-B-1H

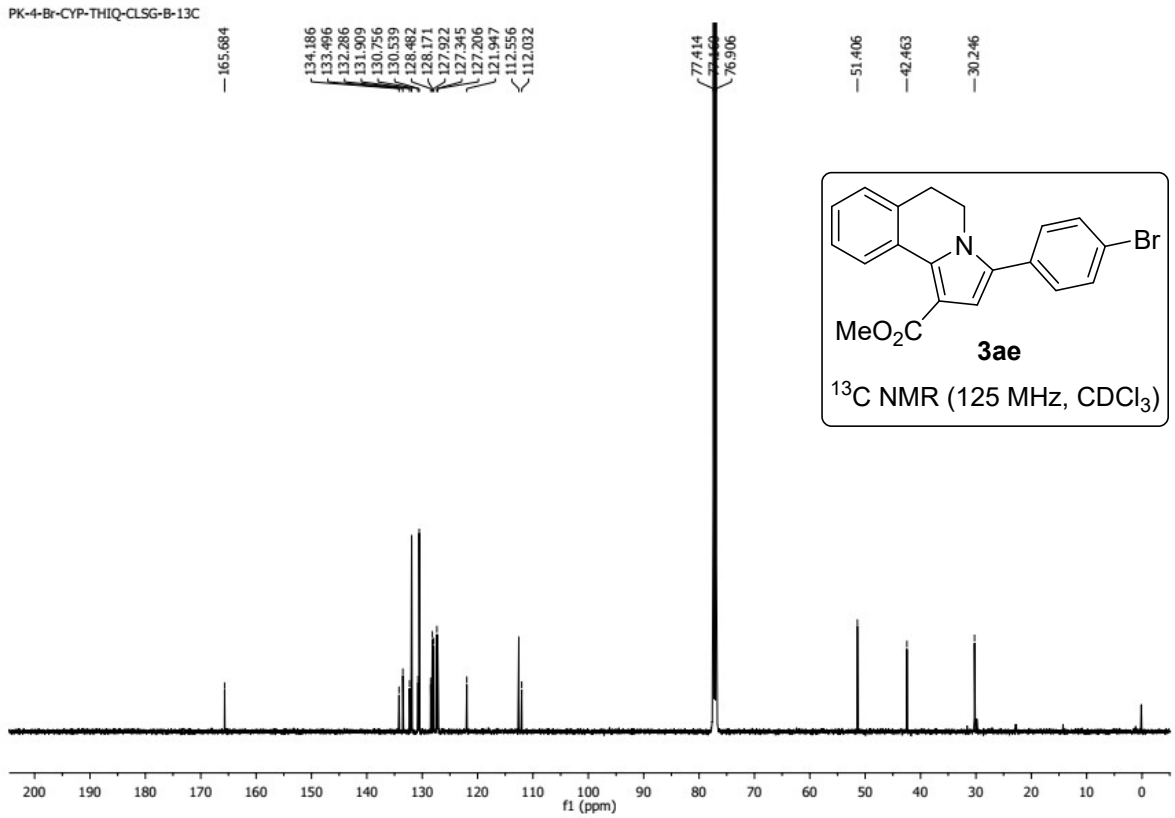


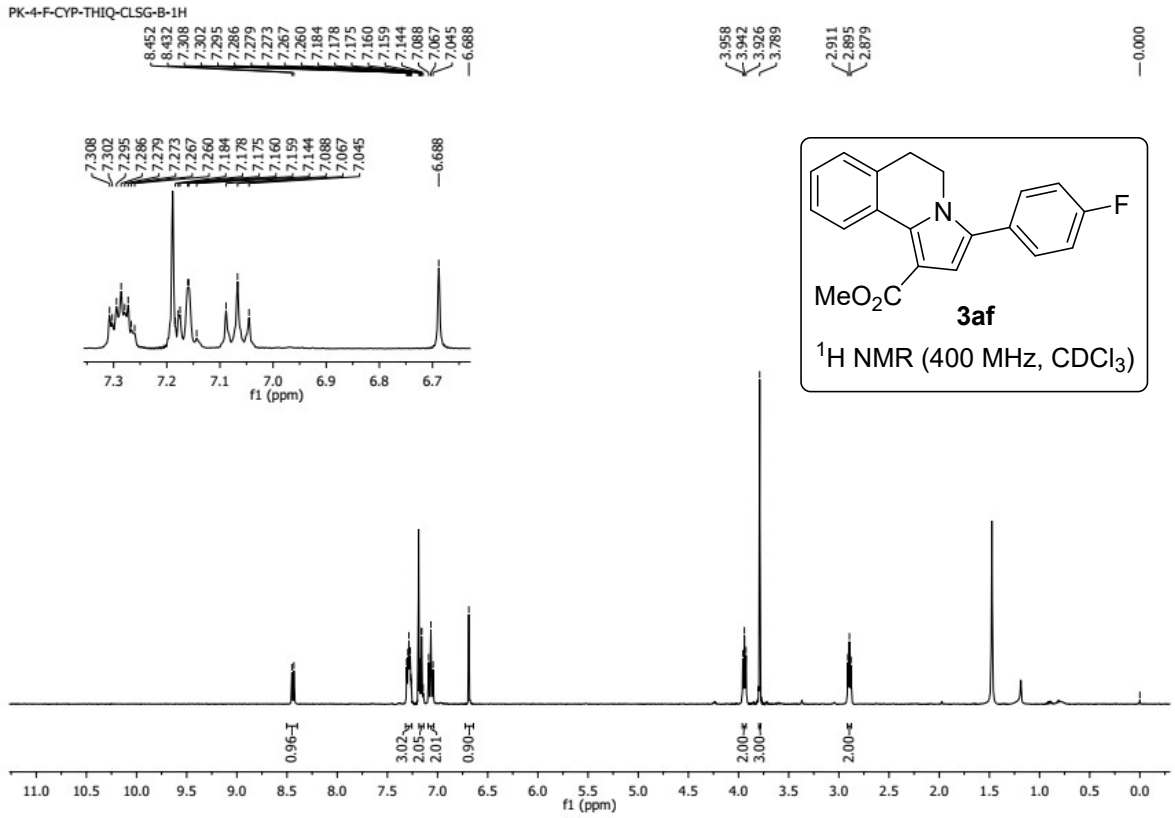

PK-CYP-THIQ-CLSG-B-13C
165.843
133.835
133.597
133.551
131.890
129.121
128.701
128.671
128.134
127.750
127.739
127.311
127.147
112.263
111.881
77.414
77.160
76.906
51.349
42.471
30.309
N
Ph
MeO2C
3aa
13C NMR (125 MHz, CDCl3)
f1 (ppm)

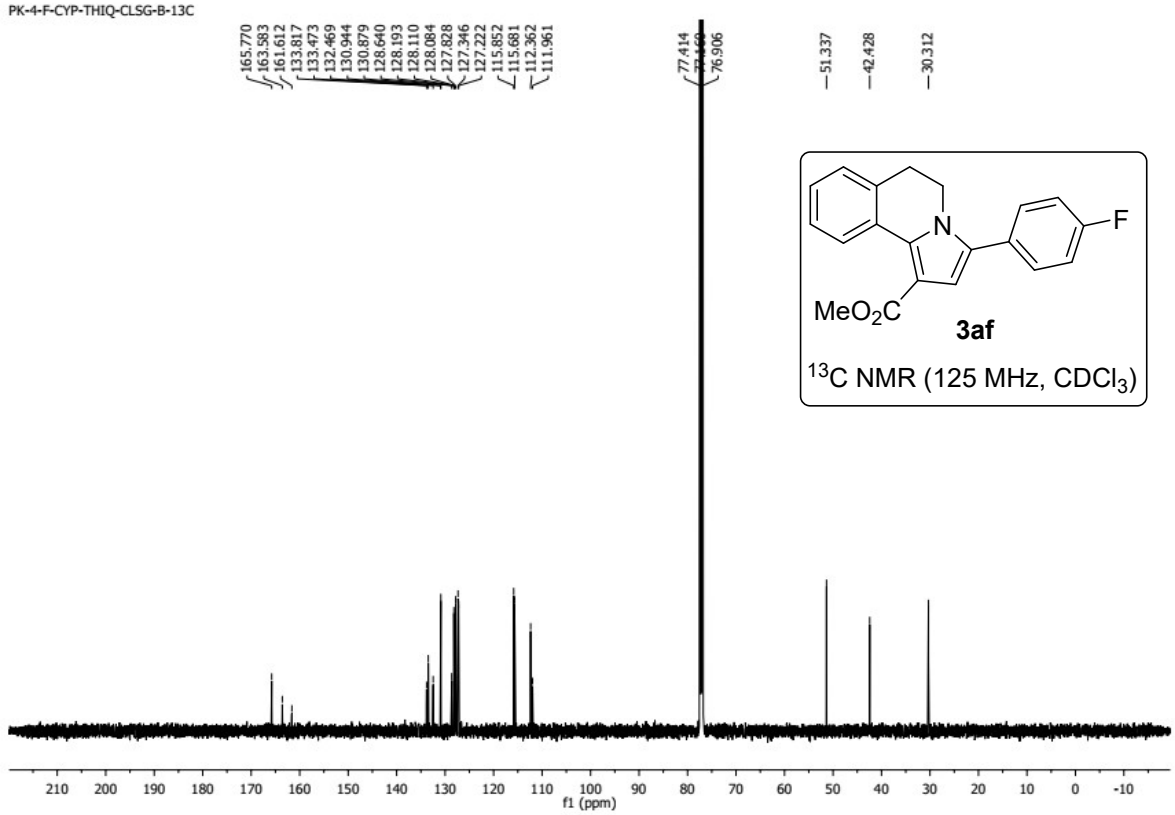

PK-3-Br-CYP-THIQ-CLSG-B-1H
8.447
8.428
7.492
7.435
7.429
7.420
7.413
7.408
7.398
7.304
7.300
7.283
7.268
7.263
7.249
7.233
7.215
7.202
7.188
7.183
7.166
7.148
6.744
3.999
3.983
3.967
3.790
2.919
2.903
2.887
0.000
N
Br
MeO2C
3ac
1H NMR (400 MHz, CDCl3)
0.97
0.96
0.97
3.00
2.89
0.93
2.00
3.00
2.00
f1 (ppm)


PK-3-Br-CYP-THIQ-CLSG-B-13C
165.648
134.335
133.925
133.526
131.900
130.686
130.181
128.468
128.238
127.974
127.568
127.346
127.221
122.792
112.984
112.109
77.478
76.843
51.394
42.547
30.257
N
Br
MeO2C
3ac
13C NMR (100 MHz, CDCl3)
f1 (ppm)


PK-4-Br-CYP-THIQ-CLSG-B-1H
8.511
8.492
7.580
7.559
7.373
7.368
7.352
7.336
7.331
7.272
7.259
7.251
7.233
7.215
6.793
4.045
4.029
4.013
3.858
2.980
2.964
2.948
0.000
N
Br
MeO2C
3ae
1H NMR (400 MHz, CDCl3)
1.00
2.00
1.02
4.64
1.00
2.00
3.00
2.00
f1 (ppm)

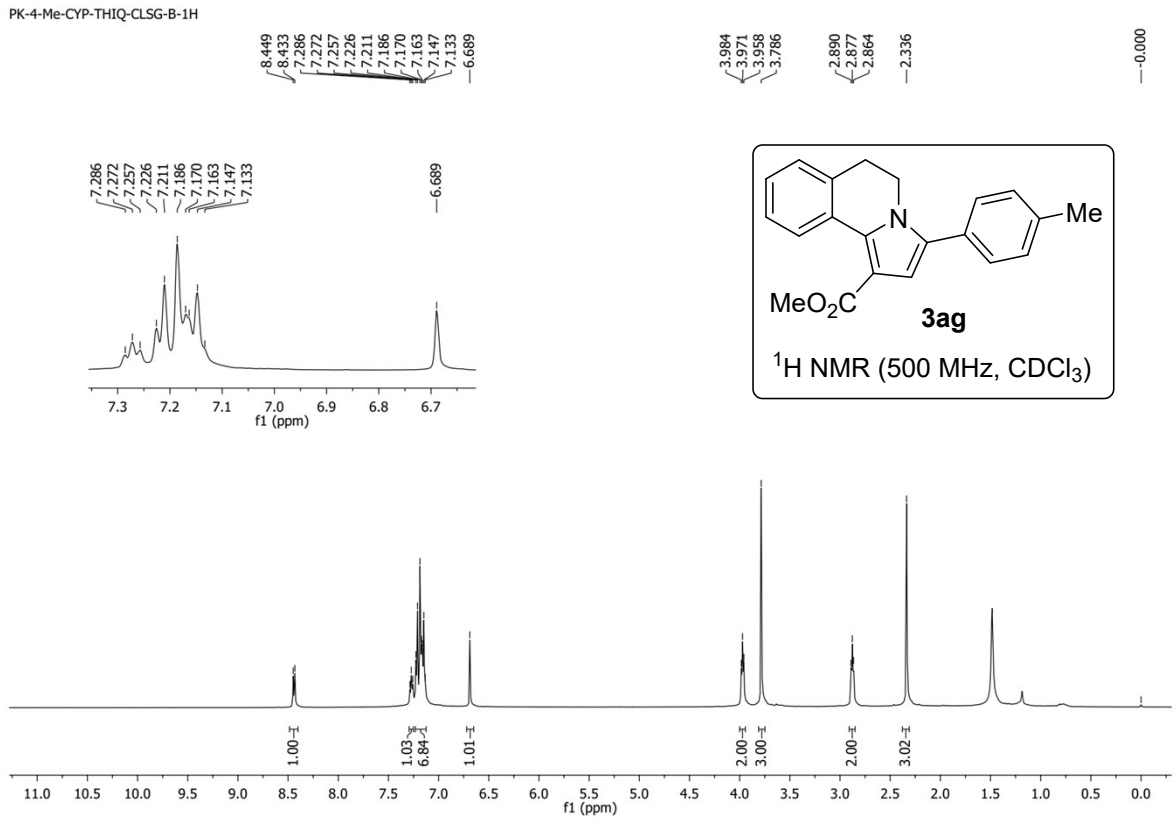

PK-4-Br-CYP-THIQ-CLSG-B-13C
165.684
134.186
133.496
132.286
131.909
130.756
130.539
128.482
128.171
127.922
127.345
127.206
121.947
112.556
112.032
77.414
76.906
51.406
42.463
30.246
Br
N
MeO2C
3ae
13C NMR (125 MHz, CDCl3)
f1 (ppm)


PK-4-F-CYP-THIQ-CLSG-B-1H
8.452
8.432
7.308
7.302
7.295
7.286
7.279
7.273
7.267
7.260
7.184
7.178
7.175
7.160
7.159
7.144
7.088
7.067
7.045
6.688
3.958
3.942
3.926
3.789
2.911
2.895
2.879
0.000
F
N
MeO2C
3af
1H NMR (400 MHz, CDCl3)
0.96
3.02
2.05
2.01
0.90
2.00
3.00
2.00
f1 (ppm)



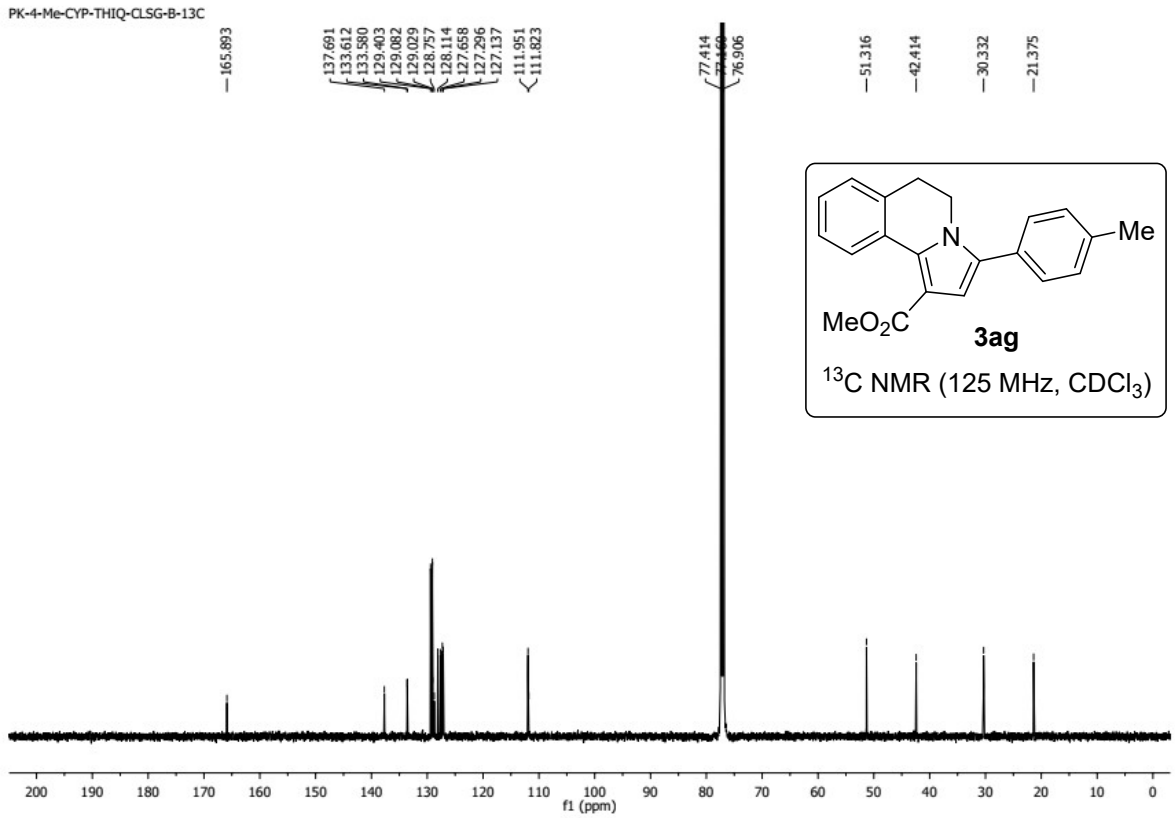
3af

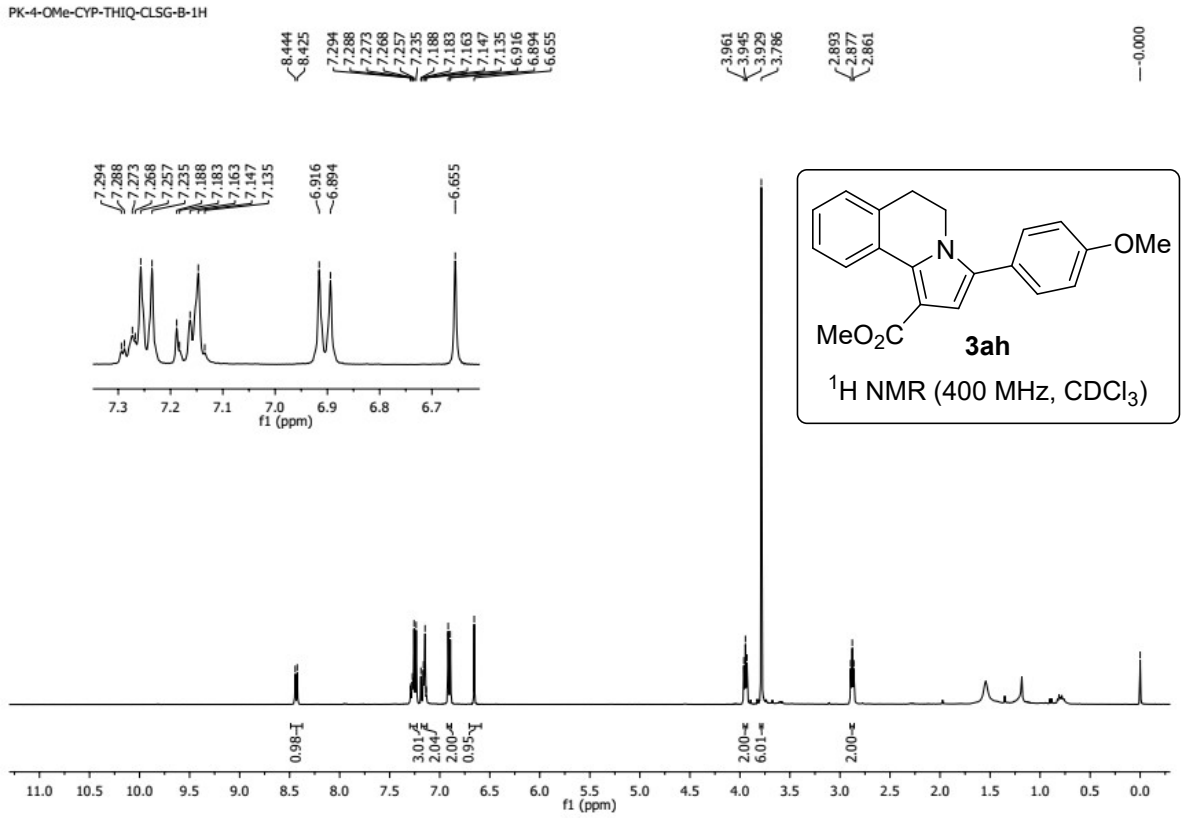
^{13}C NMR (125 MHz, $CDCl_3$)

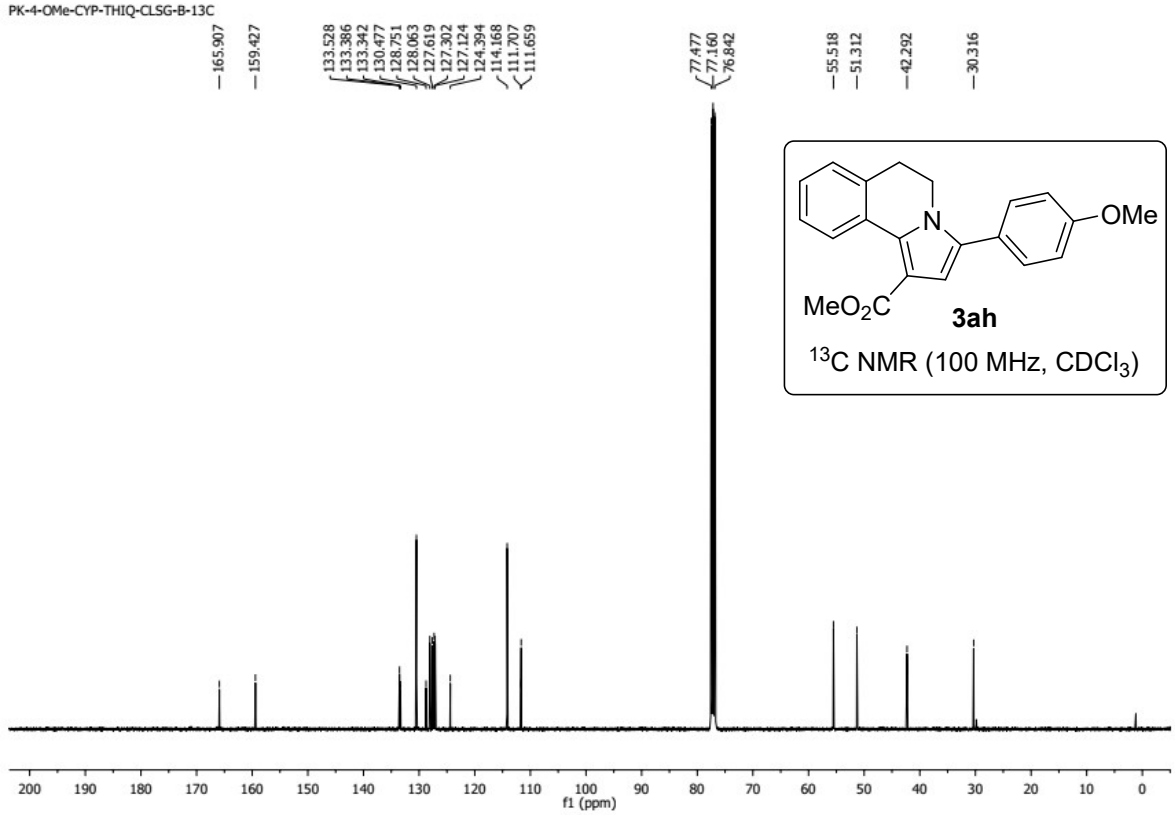


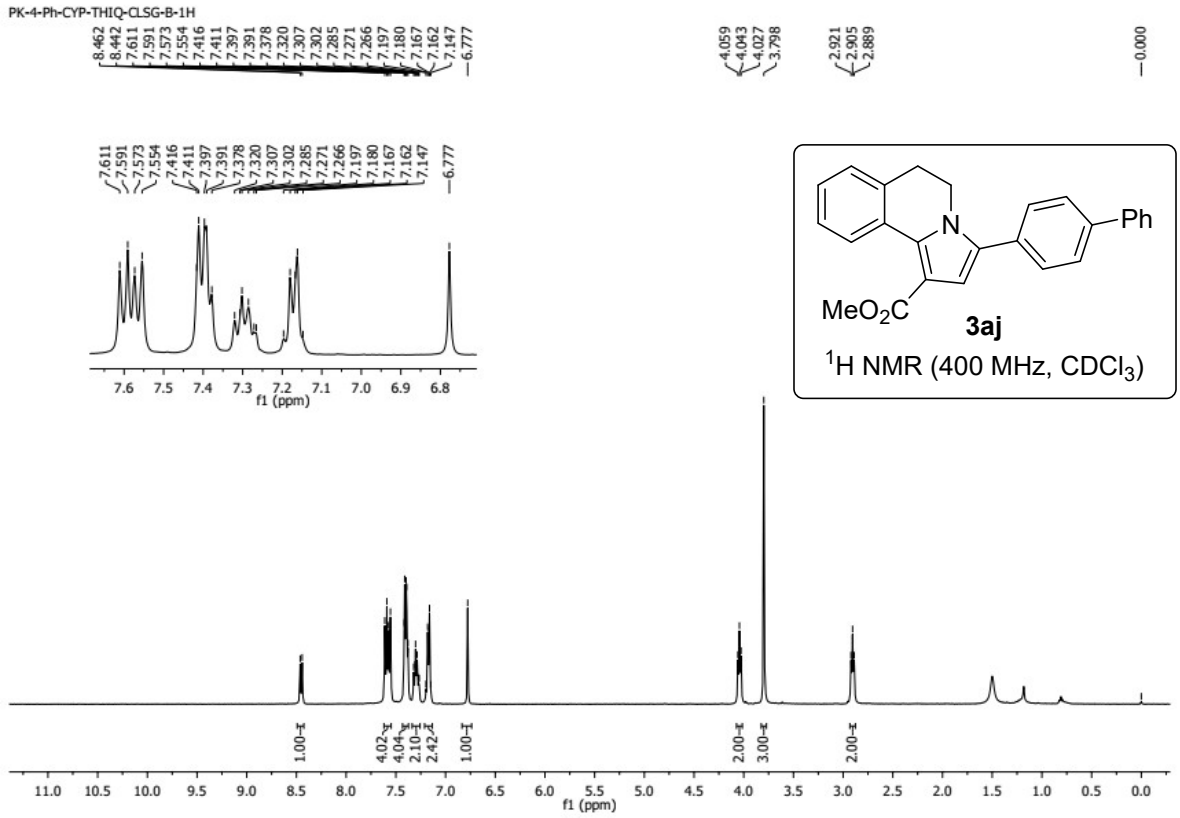
3ag

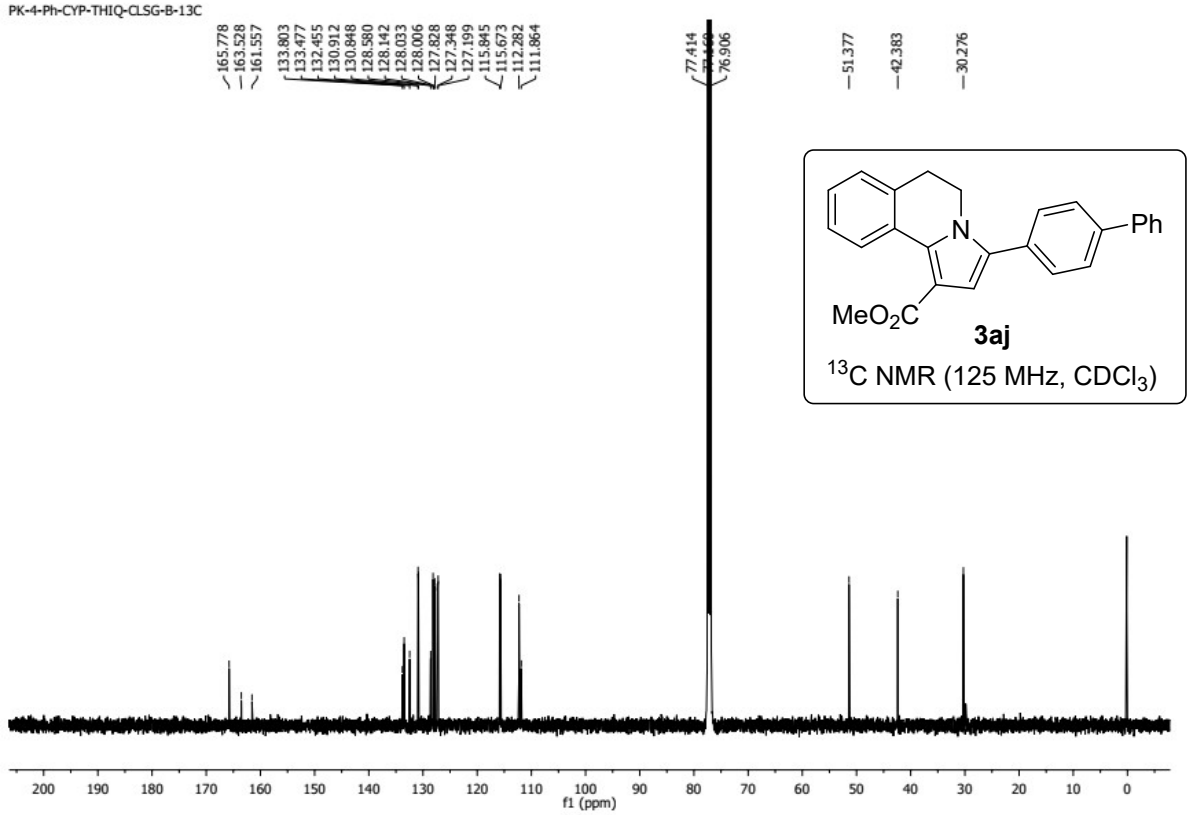
^{1}H NMR (500 MHz, $CDCl_3$)


PK-4-Me-CYP-THIQ-CLSG-B-13C
165.893
137.691
133.612
133.580
129.403
129.082
129.029
128.757
128.114
127.658
127.296
127.137
111.951
111.823
77.414
77.160
76.906
51.316
42.414
30.332
21.375
N
Me
MeO2C
3ag
13C NMR (125 MHz, CDCl3)
f1 (ppm)


PK-4-OMe-CYP-THIQ-CLSG-B-1H
8.444
8.425
7.294
7.288
7.273
7.268
7.257
7.235
7.188
7.183
7.163
7.147
7.135
6.916
6.894
6.655
3.961
3.945
3.929
3.786
2.893
2.877
2.861
0.000
0.98
3.01
2.04
2.00
0.95
2.00
6.01
2.00
N
OMe
MeO2C
3ah
1H NMR (400 MHz, CDCl3)
f1 (ppm)

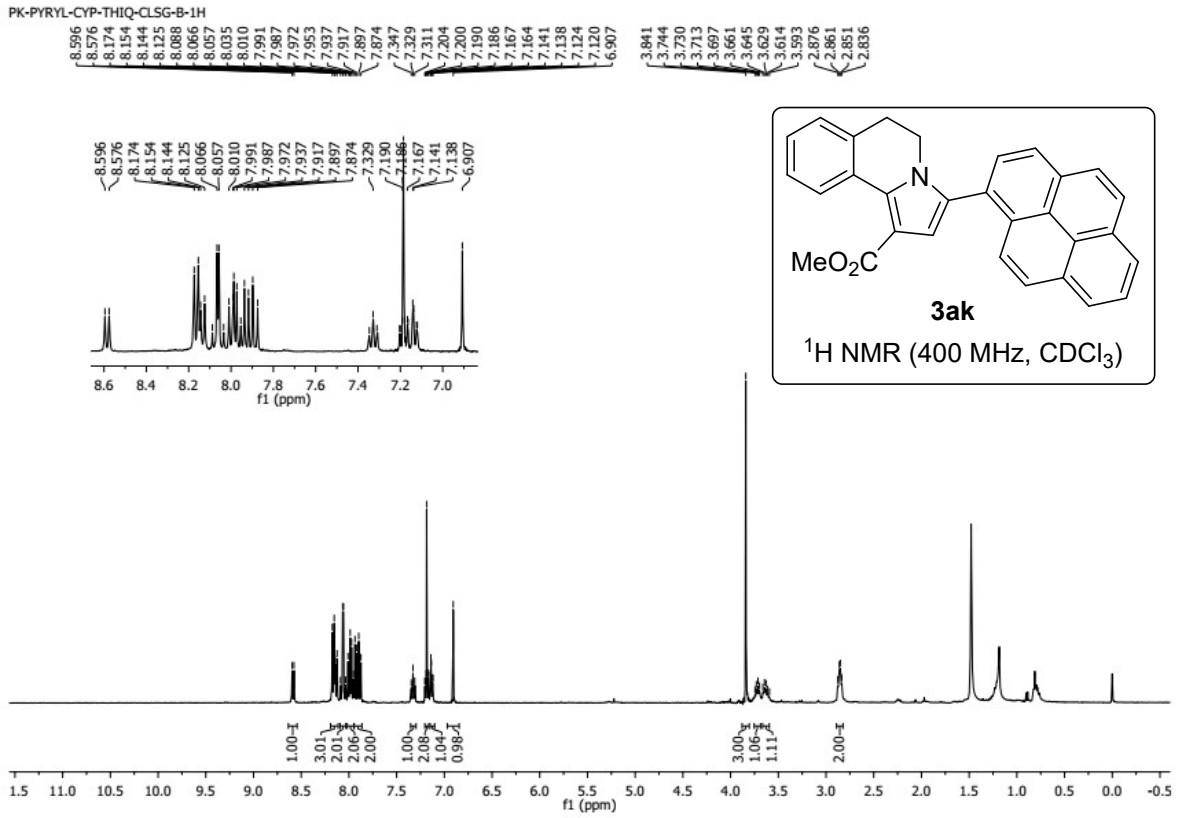

PK-4-OMe-CYP-THIQ-CLSG-B-13C
165.907
159.427
133.528
133.386
133.342
130.477
128.751
128.063
127.619
127.302
127.124
124.394
114.168
111.707
111.659
77.477
77.160
76.842
55.518
51.312
42.292
30.316
OMe
N
MeO2C
3ah
13C NMR (100 MHz, CDCl3)
f1 (ppm)


PK-4-Ph-CYP-THIQ-CLSG-B-1H
8.462
8.442
7.611
7.591
7.573
7.554
7.416
7.411
7.397
7.391
7.378
7.320
7.307
7.302
7.285
7.271
7.266
7.197
7.180
7.167
7.162
7.147
6.777
4.059
4.043
4.027
3.798
2.921
2.905
2.889
0.000
Ph
N
MeO2C
3aj
1H NMR (400 MHz, CDCl3)
1.00
4.02
4.04
2.10
2.42
1.00
2.00
3.00
2.00
f1 (ppm)



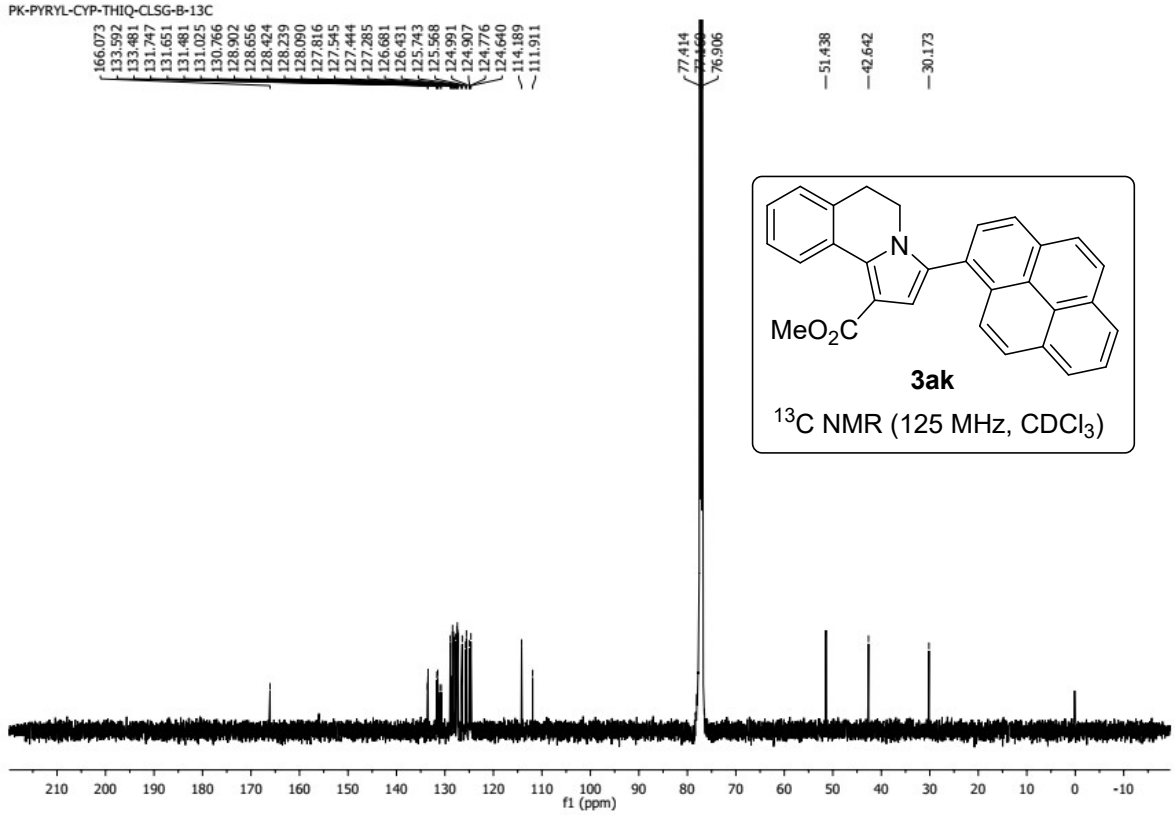
3aj

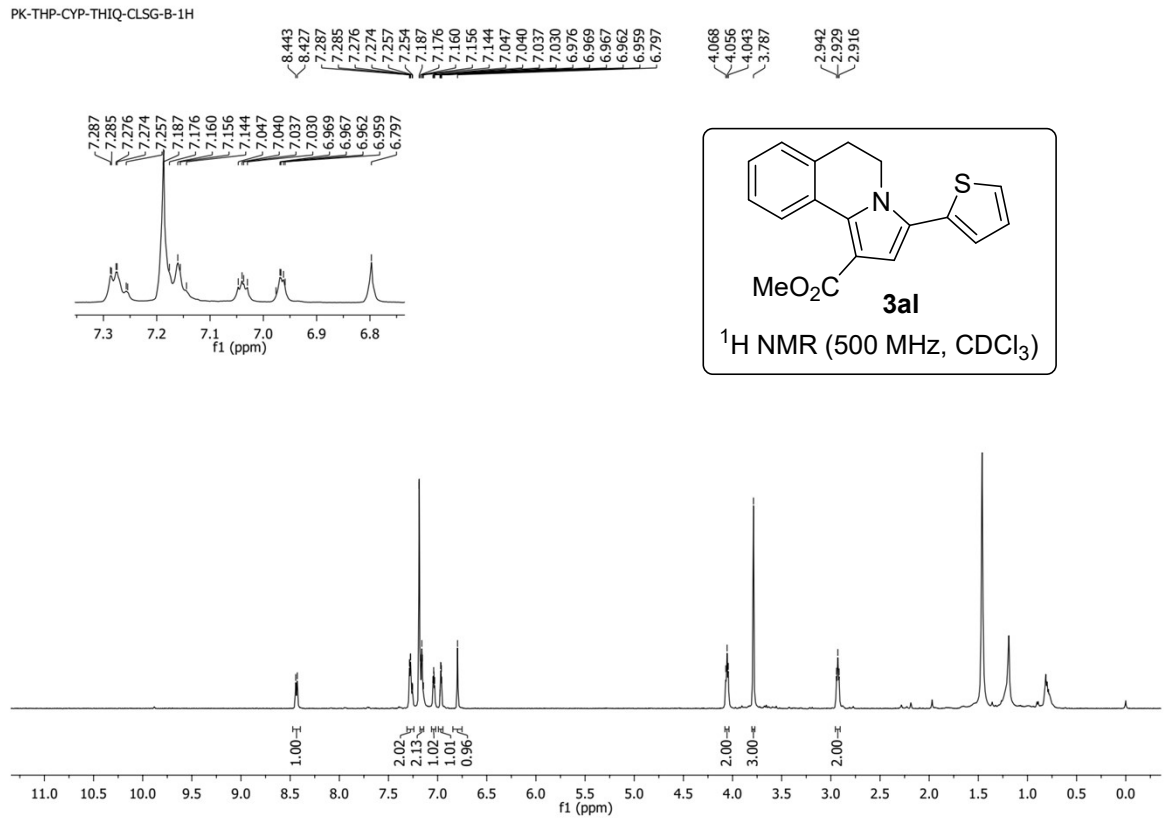
^{13}C NMR (125 MHz, $CDCl_3$)

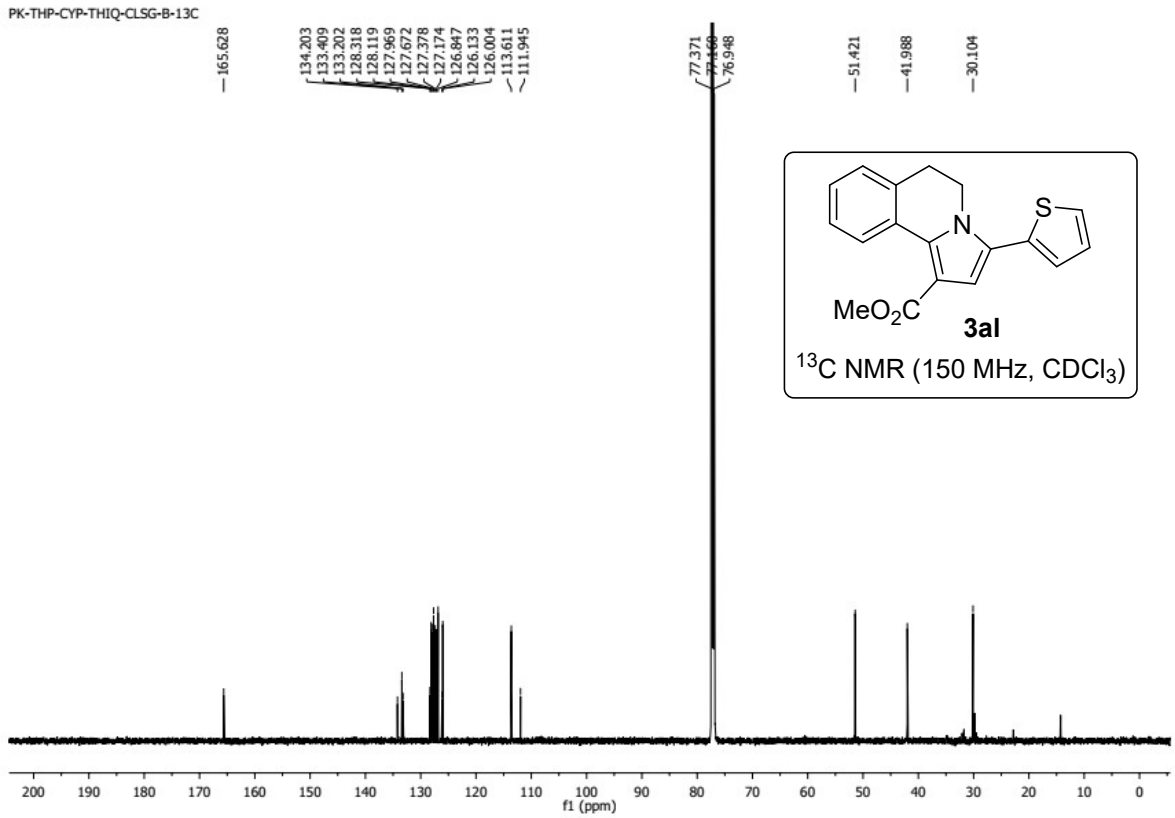


3ak

^{1}H NMR (400 MHz, $CDCl_3$)

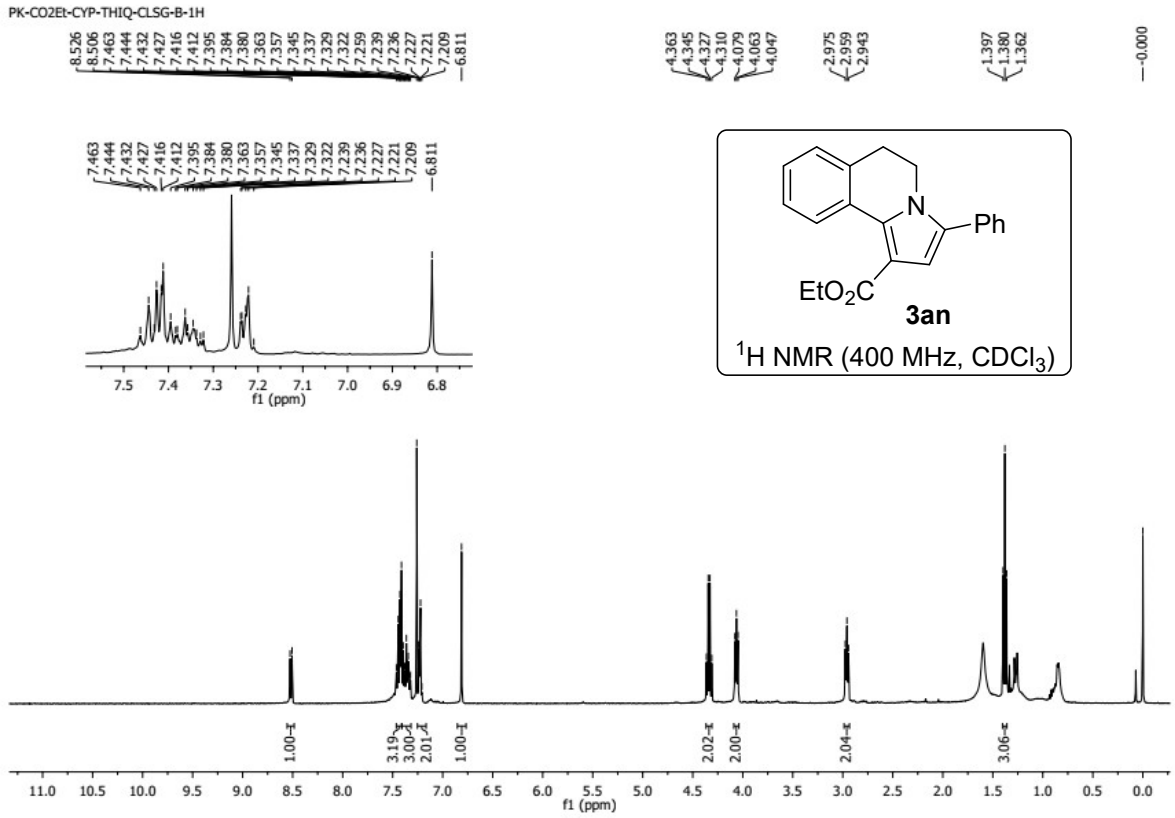

PK-PYRYL-CYP-THIQ-CLSG-B-13C
166.073
133.592
133.481
131.747
131.651
131.481
131.025
130.766
128.902
128.656
128.424
128.239
128.090
127.816
127.545
127.444
127.285
126.681
126.431
125.743
125.568
124.991
124.907
124.776
124.640
114.189
111.911
77.414
76.906
51.438
42.642
30.173
N
MeO2C
3ak
13C NMR (125 MHz, CDCl3)
f1 (ppm)


PK-THP-CYP-THIQ-CLSG-B-1H
8.443
8.427
7.287
7.285
7.276
7.274
7.257
7.254
7.187
7.176
7.160
7.156
7.144
7.047
7.040
7.037
7.030
6.976
6.969
6.967
6.962
6.959
6.797
4.068
4.056
4.043
3.787
2.942
2.929
2.916
N
S
MeO2C
3al
1H NMR (500 MHz, CDCl3)
1.00
2.02
2.13
1.02
1.01
0.96
2.00
3.00
2.00
f1 (ppm)



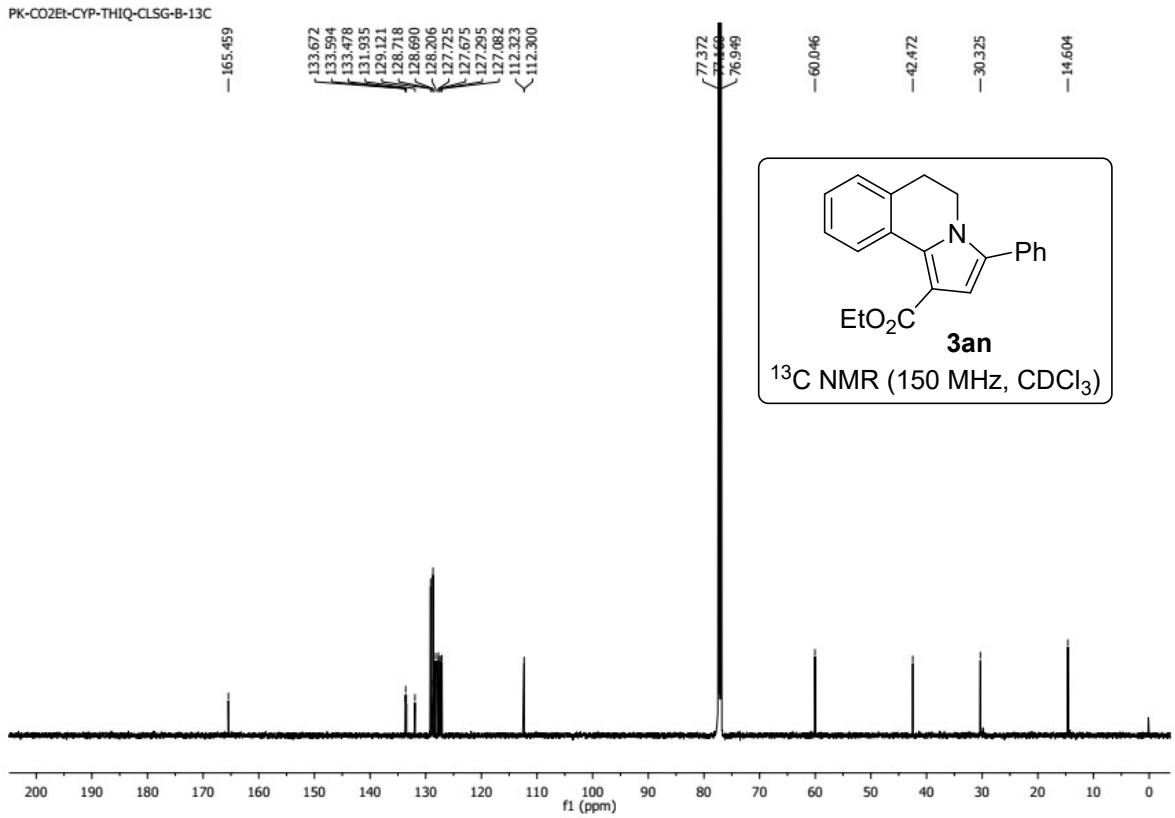
3al

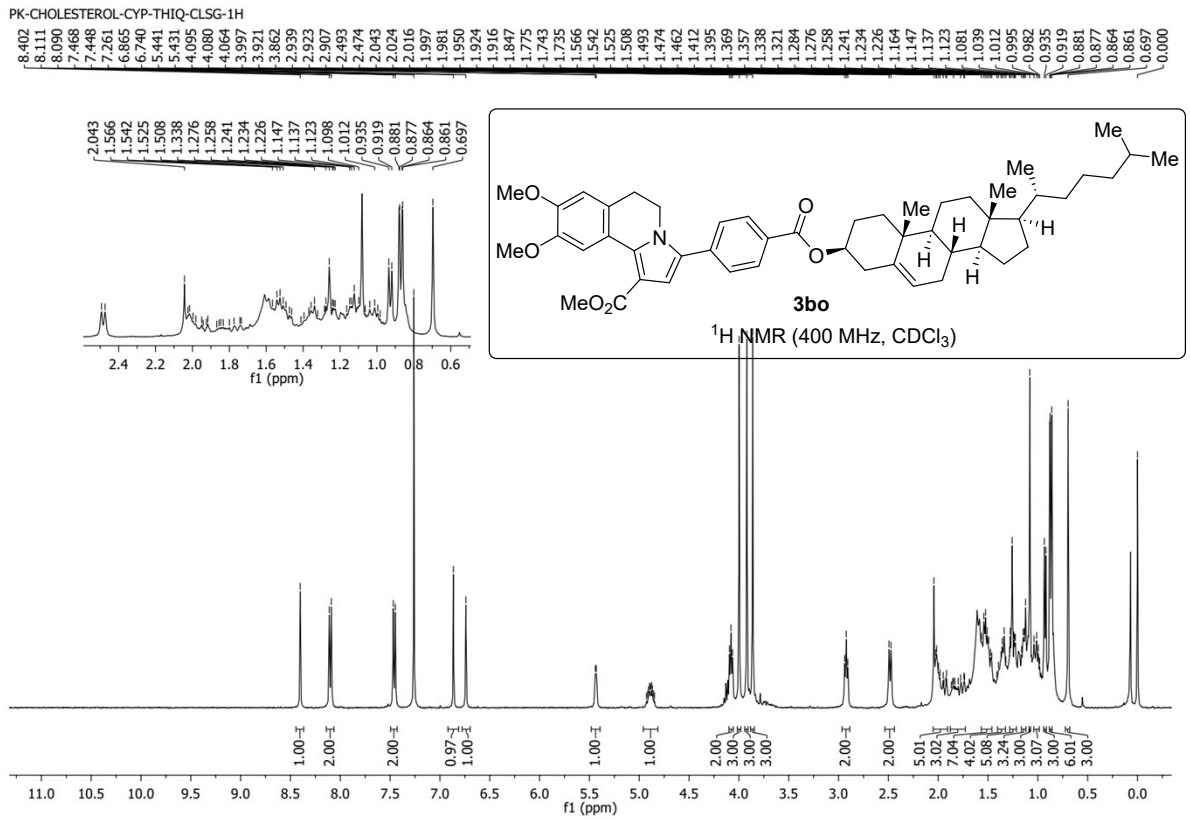
^{13}C NMR (150 MHz, $CDCl_3$)

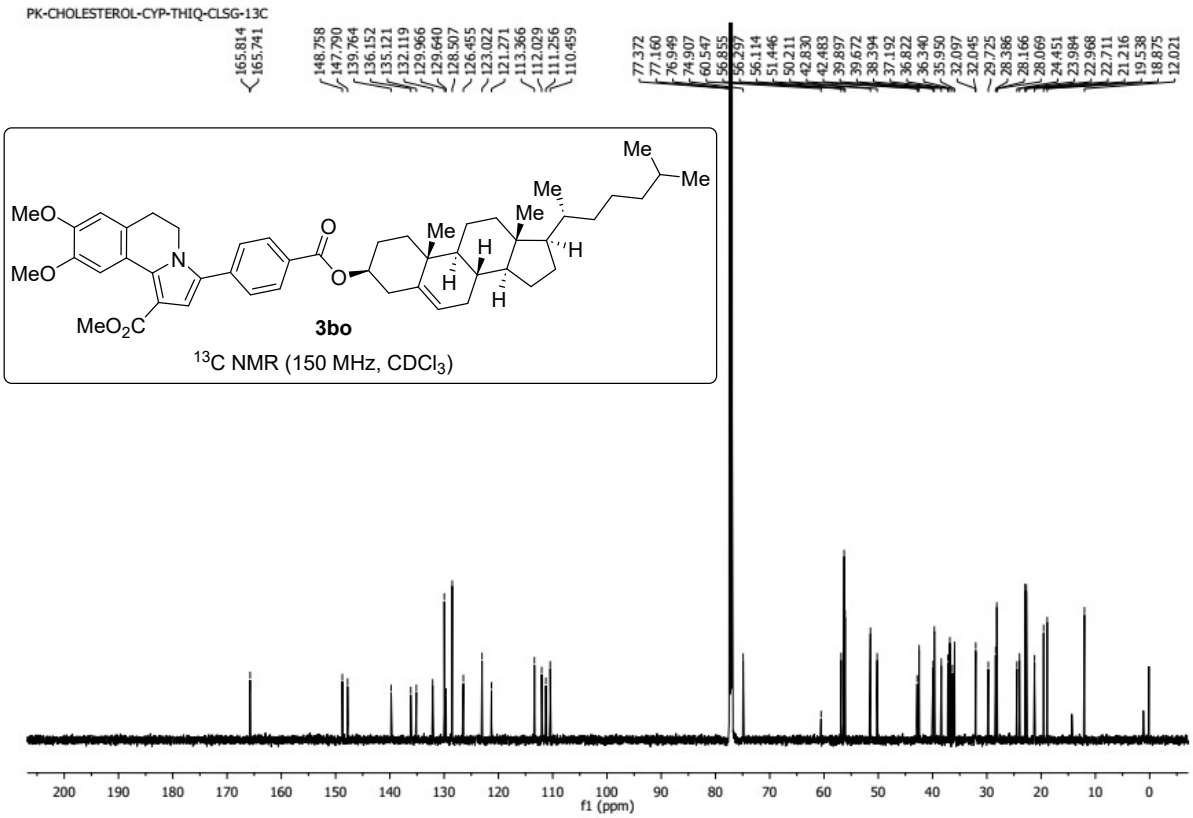


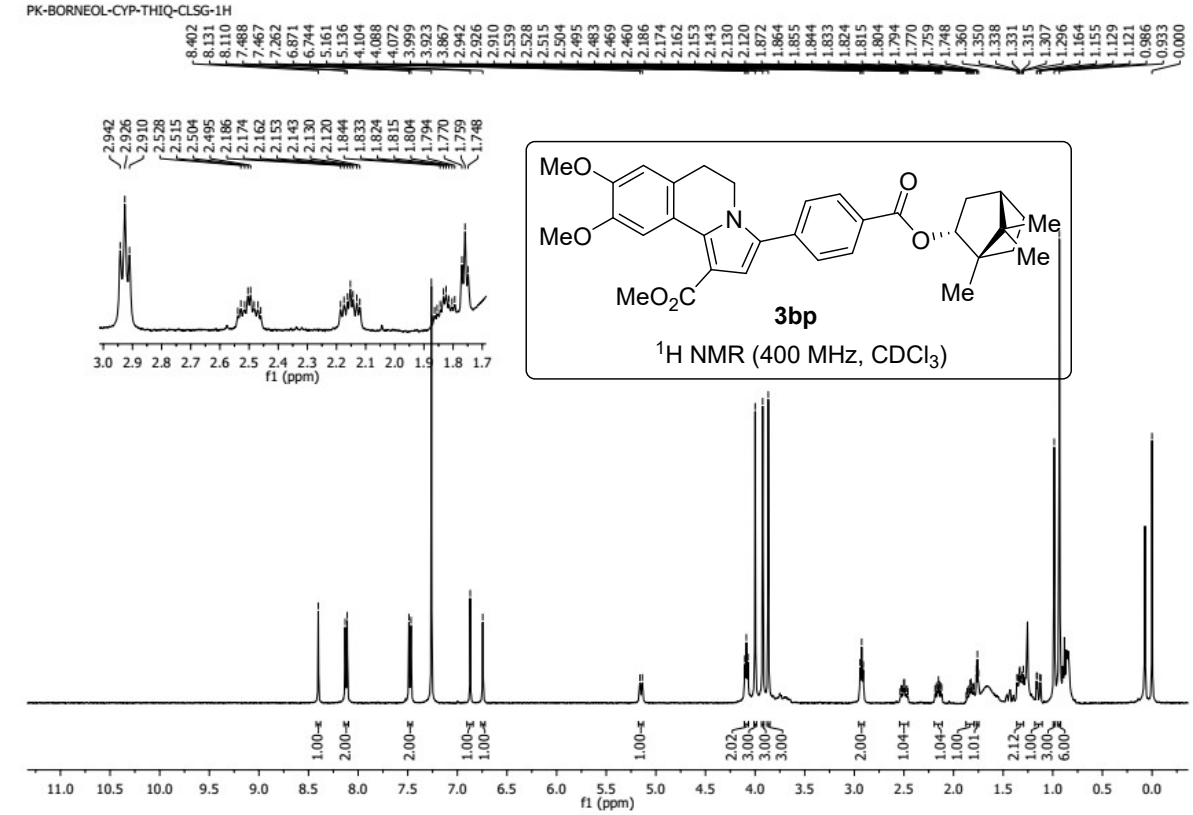
3an

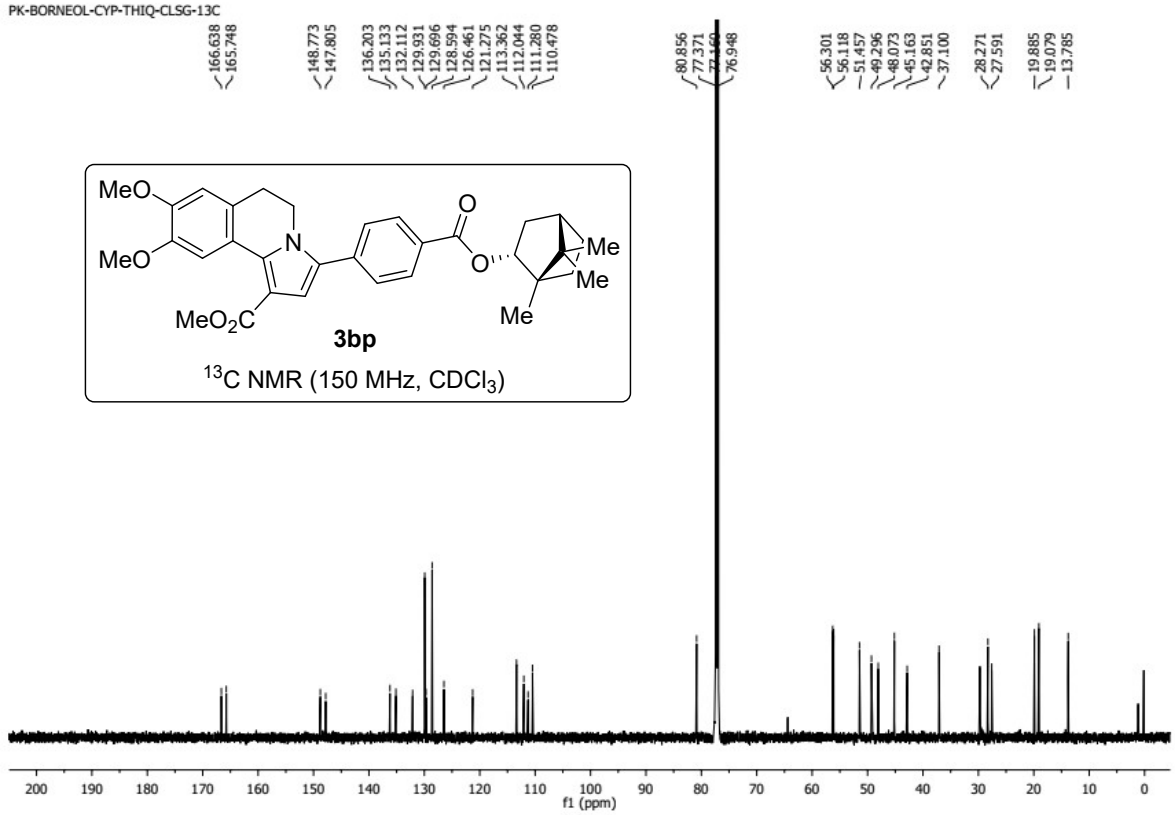
^{1}H NMR (400 MHz, $CDCl_3$)

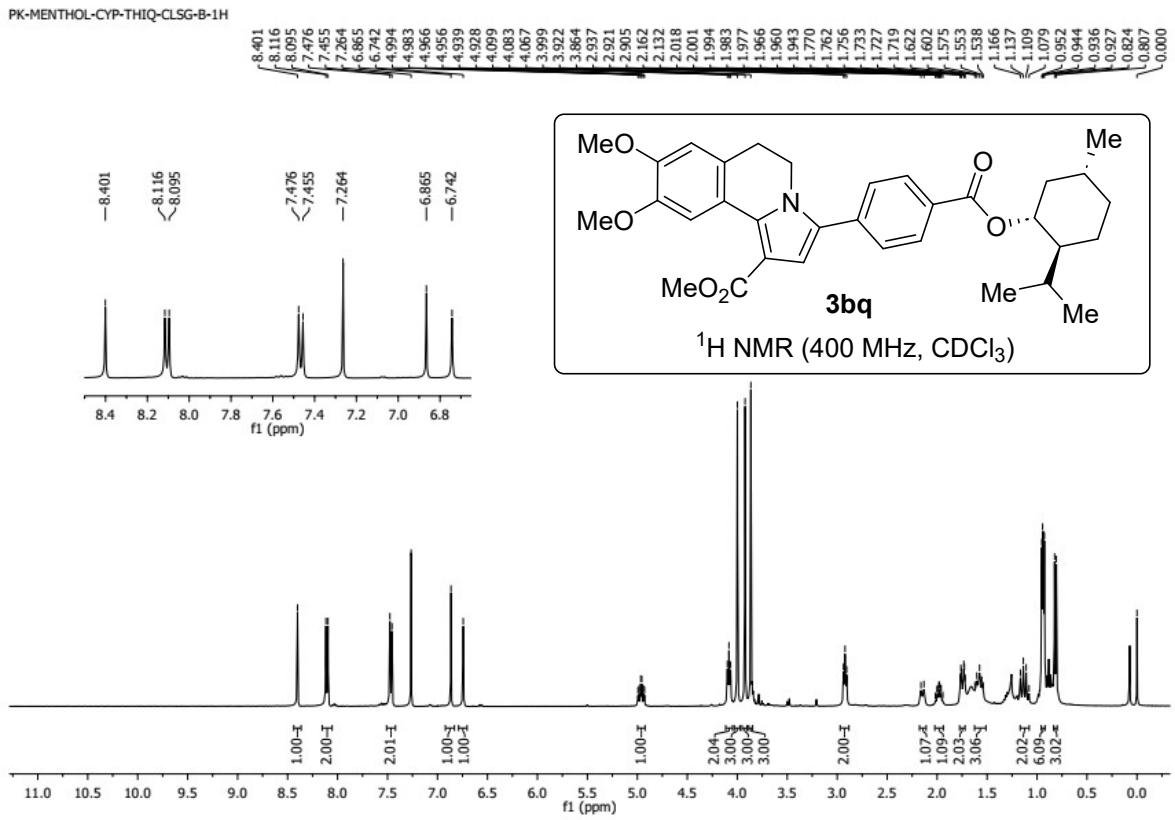

PK-CO2Et-CYP-THIQ-CLSG-B-13C
165.459
133.672
133.594
133.478
131.935
129.121
128.718
128.690
128.206
127.725
127.675
127.295
127.082
112.323
112.300
77.372
76.949
60.046
42.472
30.325
14.604
N
Ph
EtO2C
3an
13C NMR (150 MHz, CDCl3)
f1 (ppm)

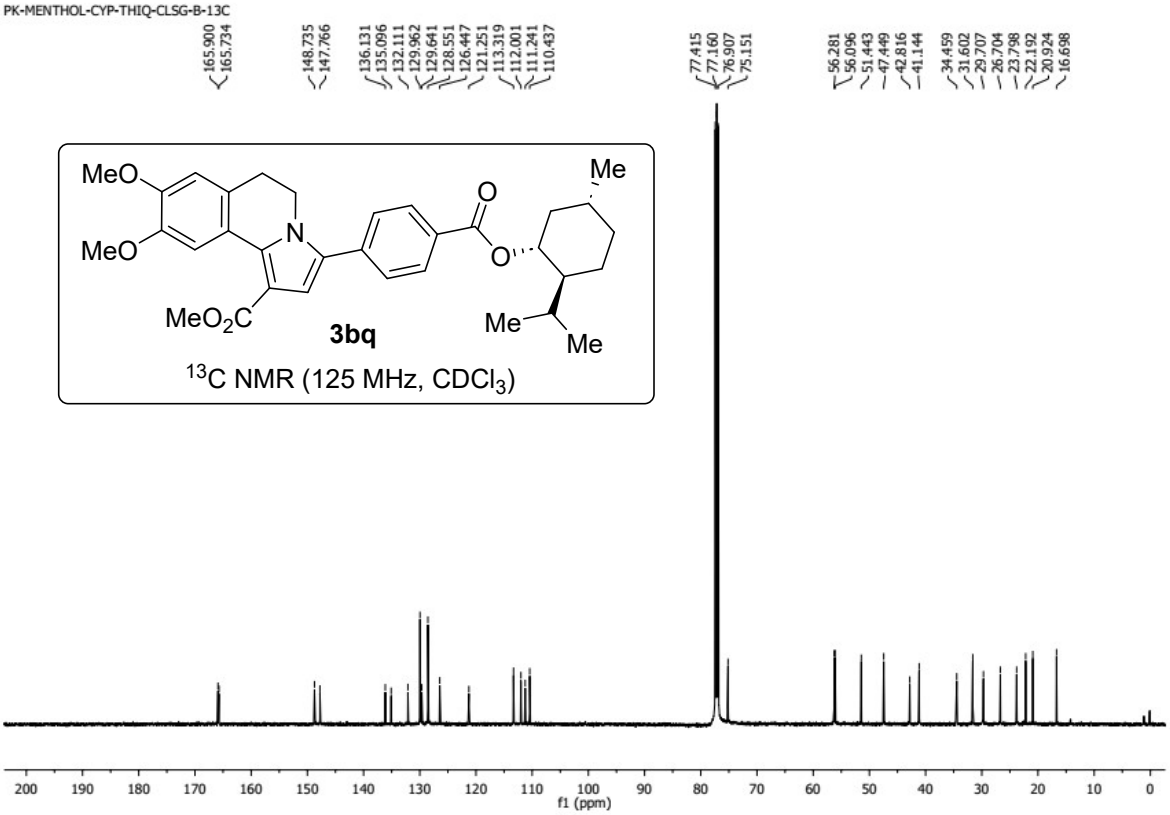

PK-CHOLESTEROL-CYP-THIQ-CLSG-1H
MeO
MeO
MeO2C
N
O
Me
H
3bo
1H NMR (400 MHz, CDCl3)
f1 (ppm)

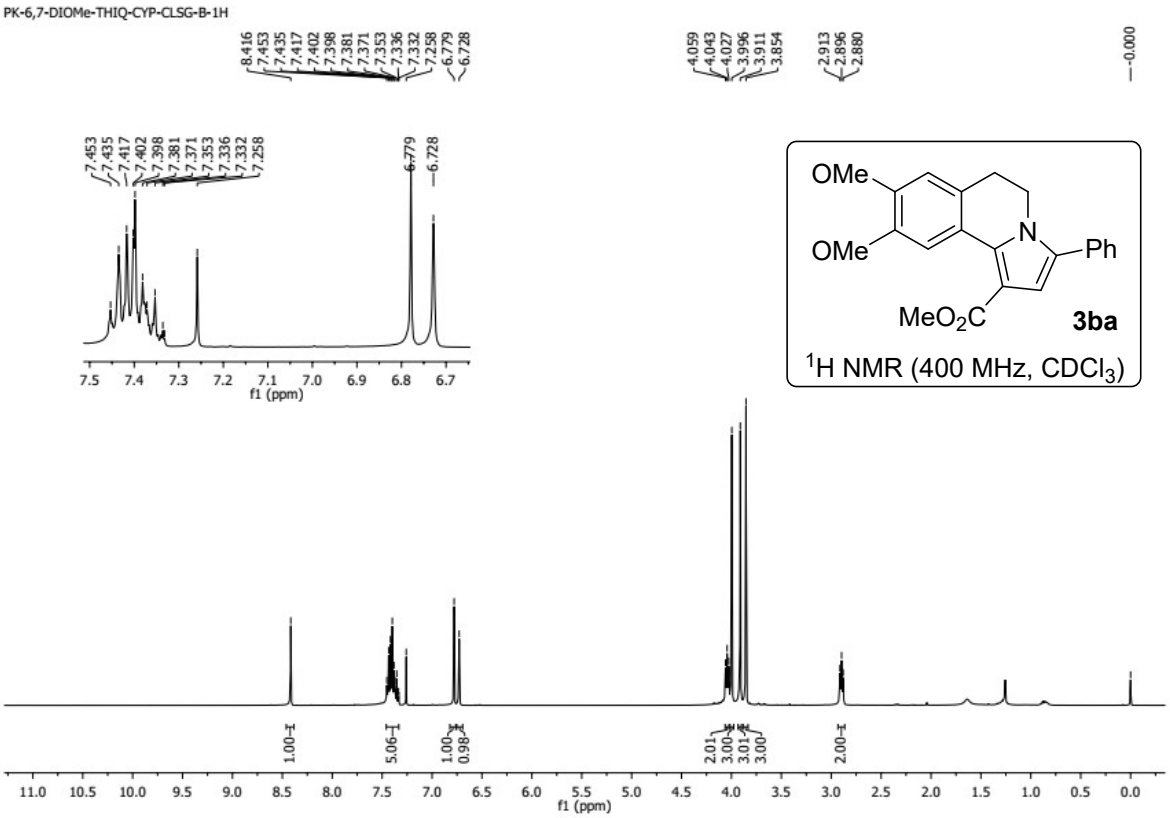

PK-CHOLESTEROL-CYP-THIQ-CLSG-13C
MeO
MeO
MeO2C
3bo
13C NMR (150 MHz, CDCl3)
f1 (ppm)


PK-BORNEOL-CYP-THIQ-CLSG-1H
MeO
MeO
MeO2C
3bp
1H NMR (400 MHz, CDCl3)
f1 (ppm)

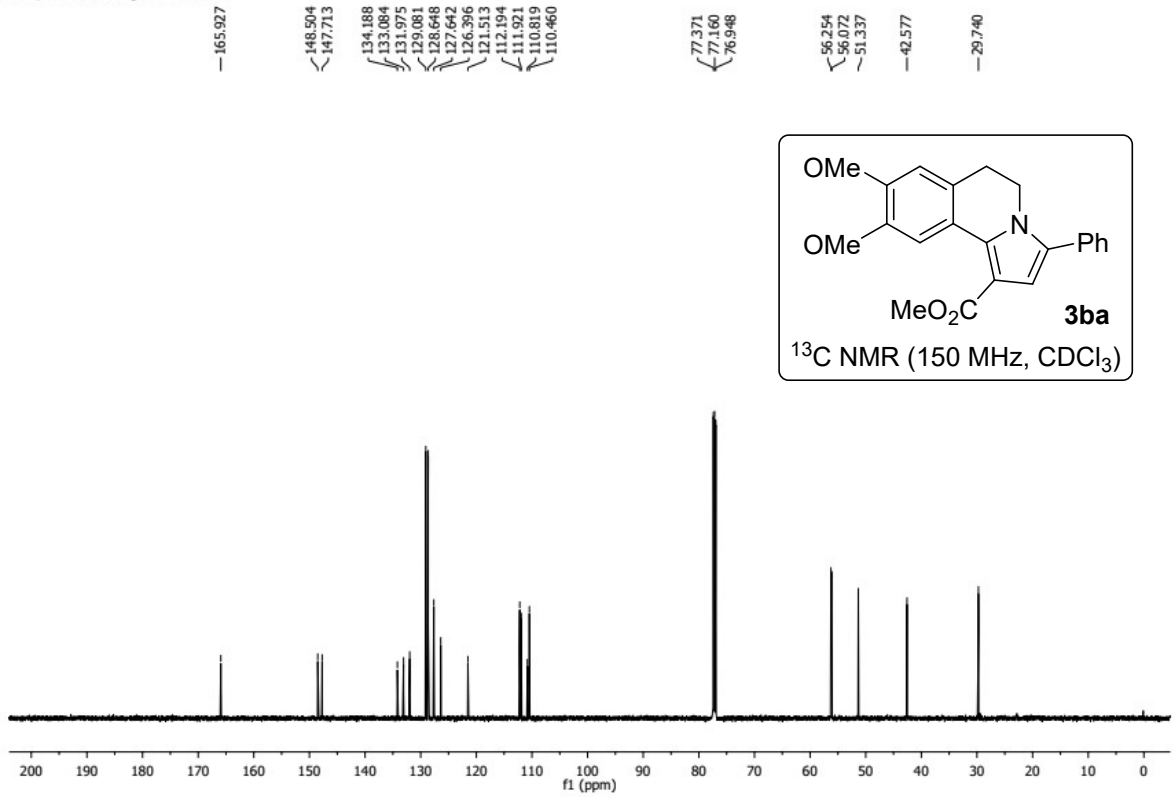

PK-BORNEOL-CYP-THIQ-CLSG-13C
MeO
MeO
N
O
O
Me
Me
Me
MeO2C
3bp
13C NMR (150 MHz, CDCl3)
f1 (ppm)


PK-MENTHOL-CYP-THIQ-CLSG-B-1H
MeO
MeO
N
O
O
Me
MeO2C
Me
Me
3bq
1H NMR (400 MHz, CDCl3)
f1 (ppm)

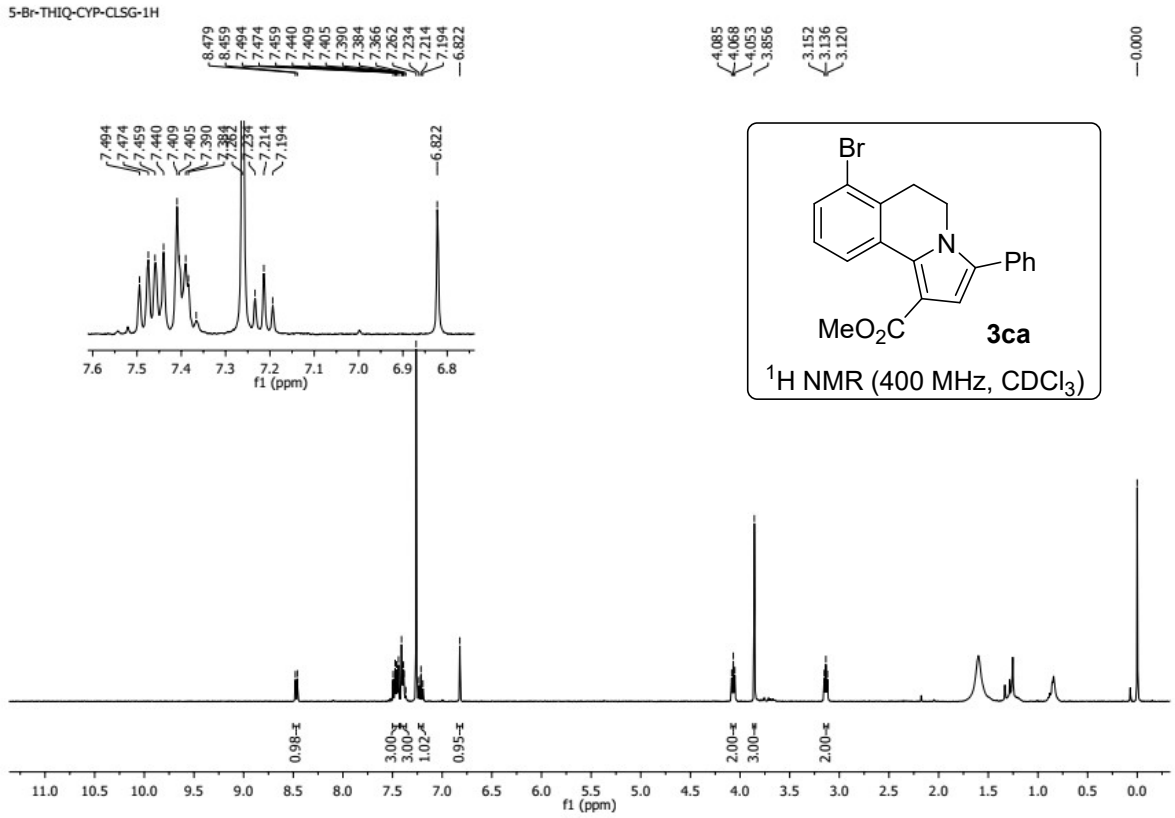

PK-MENTHOL-CYP-THIQ-CLSG-B-13C
MeO
MeO
MeO2C
N
O
O
Me
Me
Me
3bq
13C NMR (125 MHz, CDCl3)
f1 (ppm)

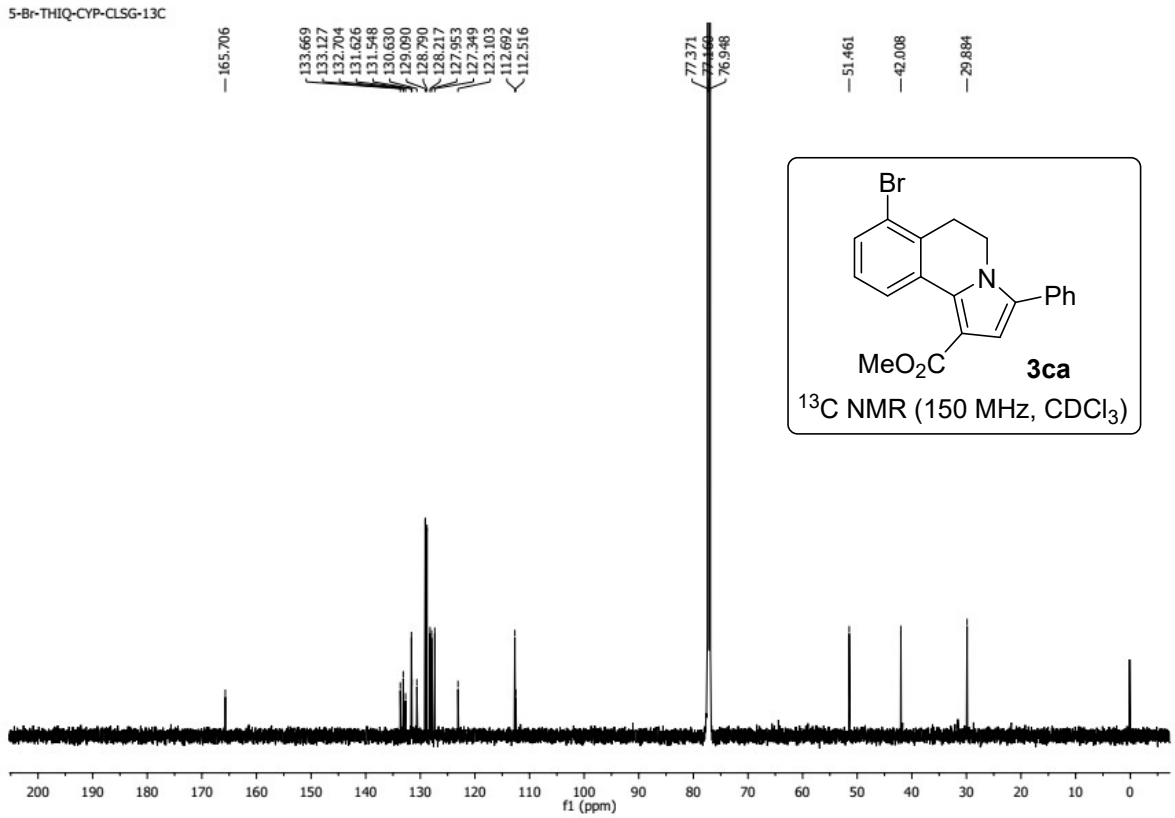

PK-6,7-DIOMe-THIQ-CYP-CLSG-B-1H
OMe
OMe
MeO2C
N
Ph
3ba
1H NMR (400 MHz, CDCl3)
f1 (ppm)

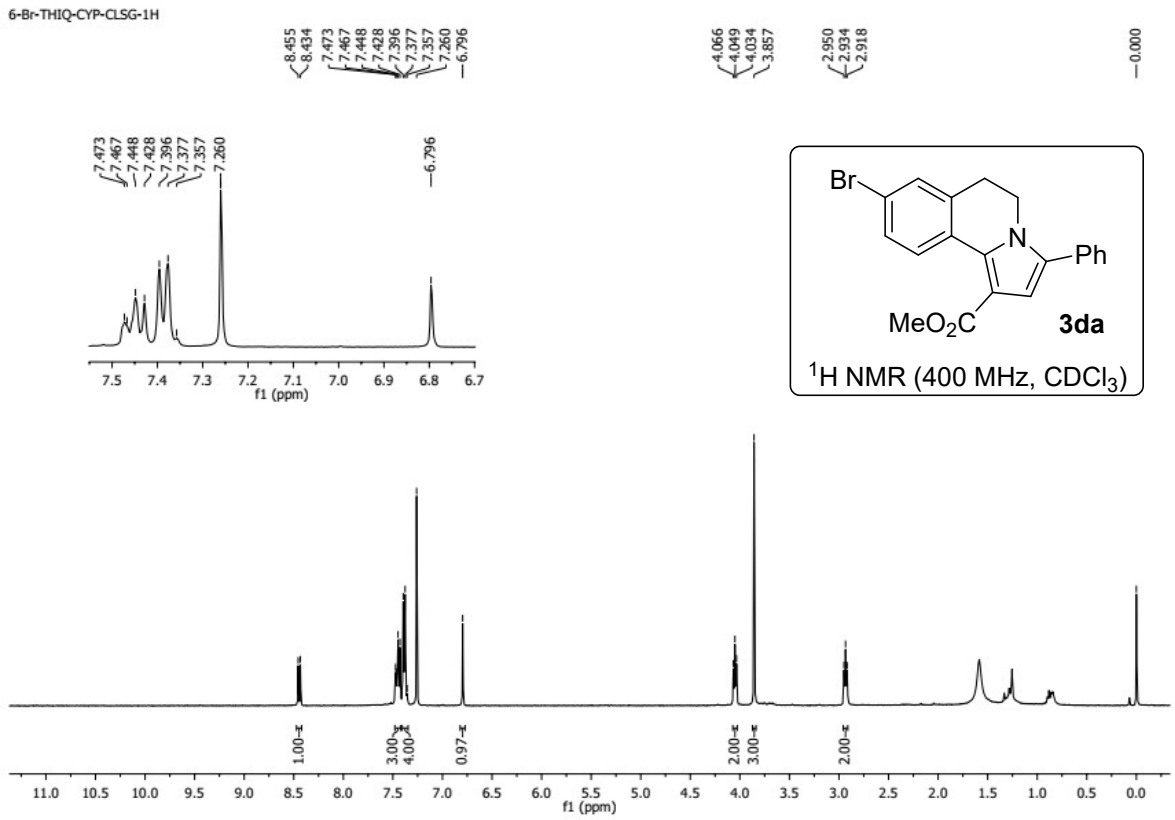
PK-6,7-Di-OMe-THIQ-CYP-CLSG-13C

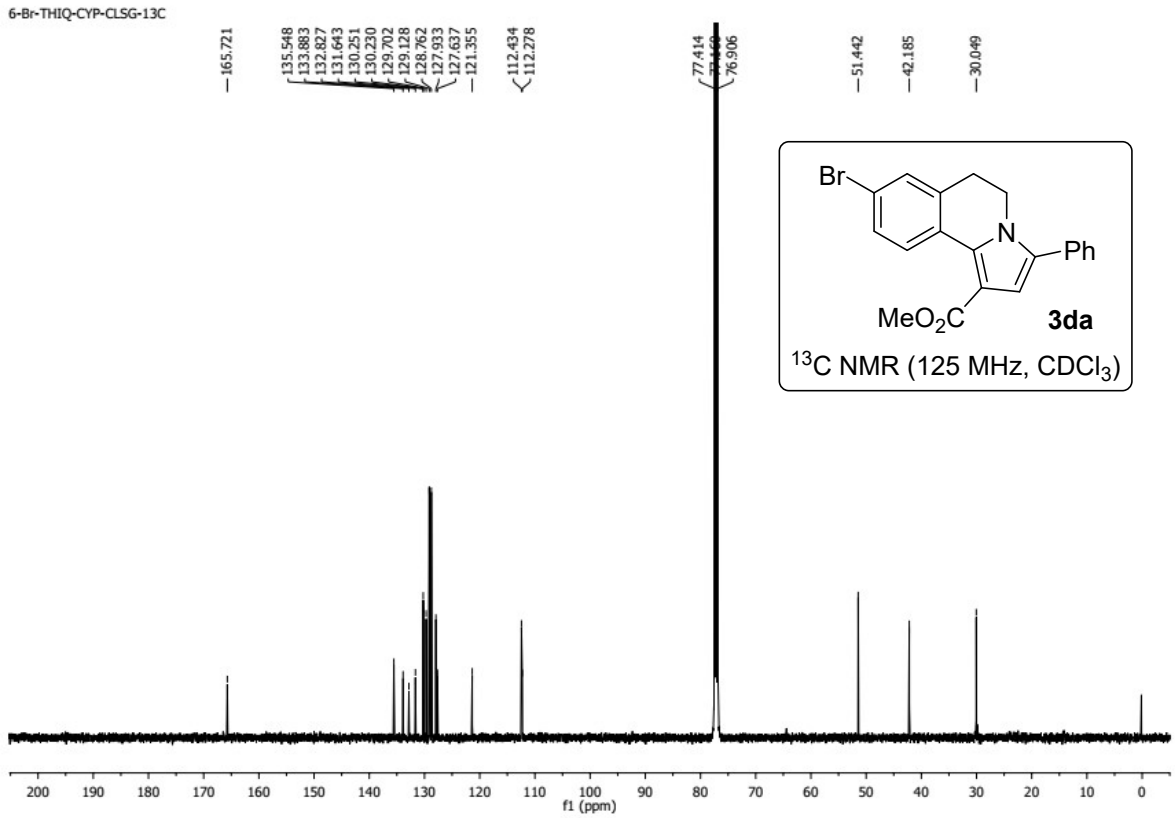


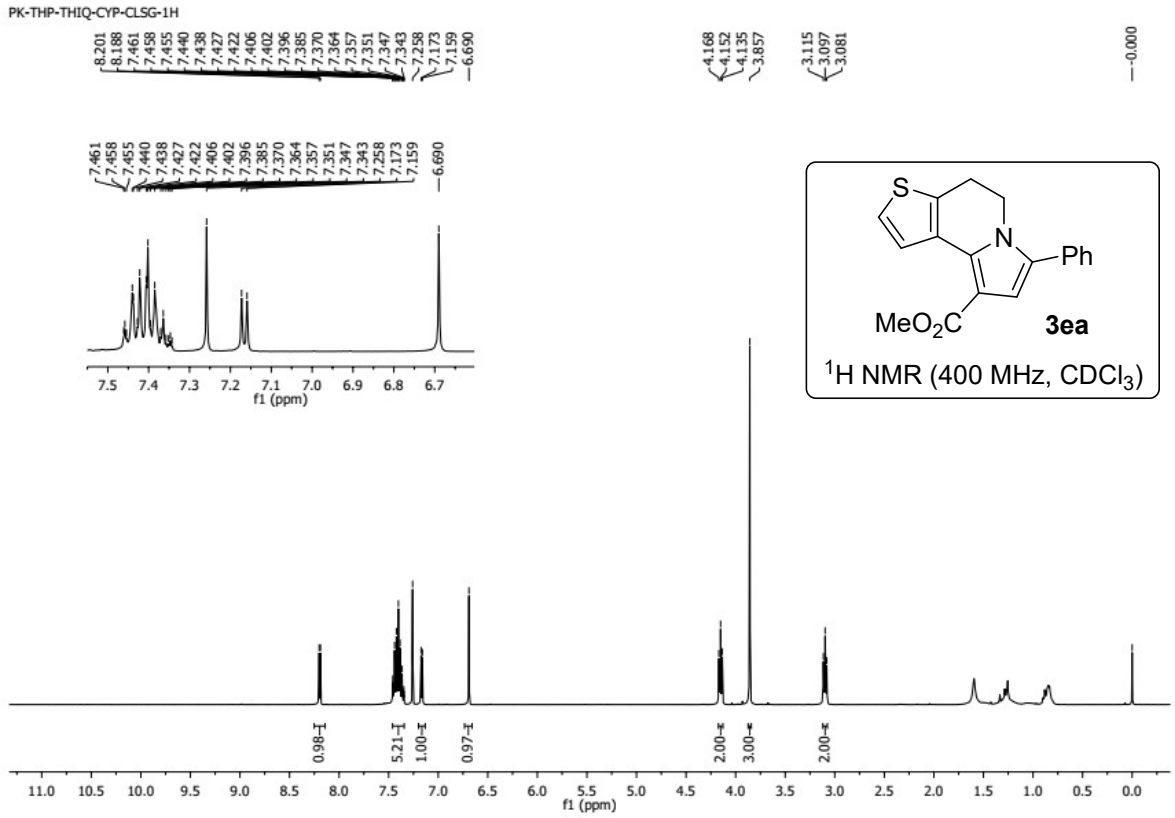
5-Br-THIQ-CYP-CLSG-1H

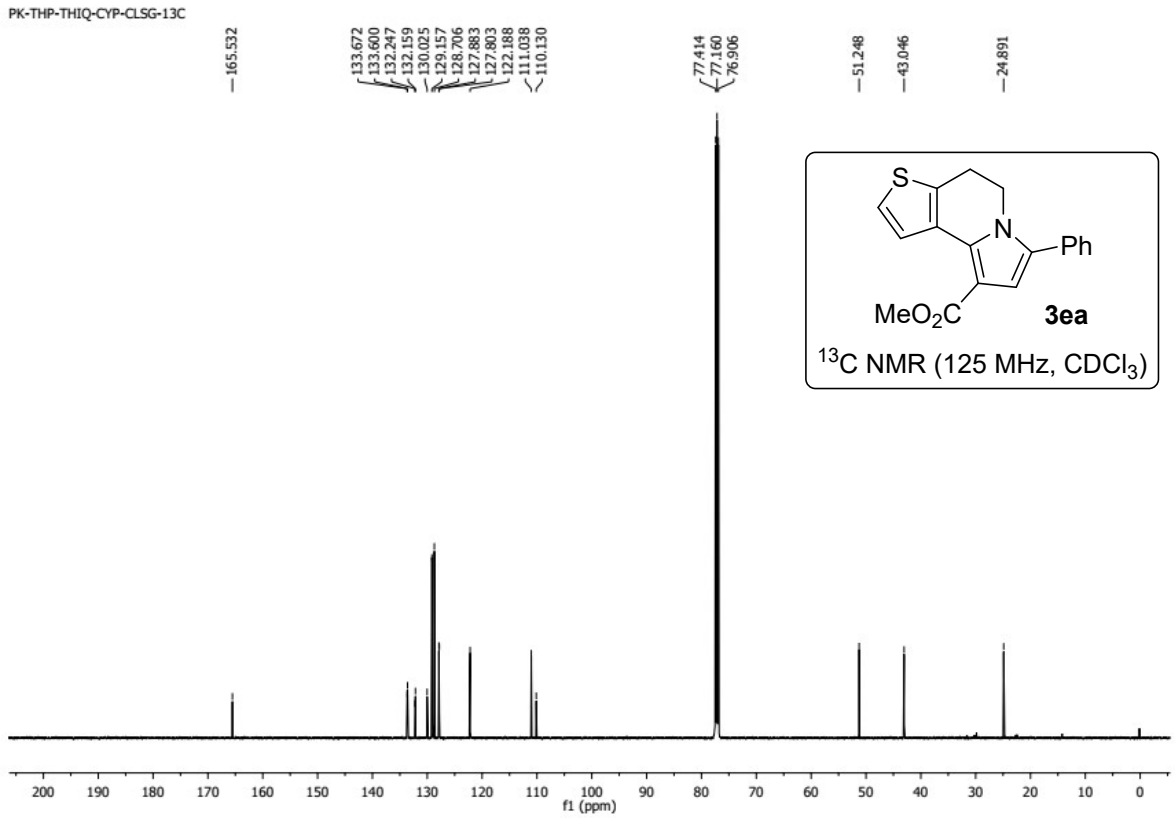


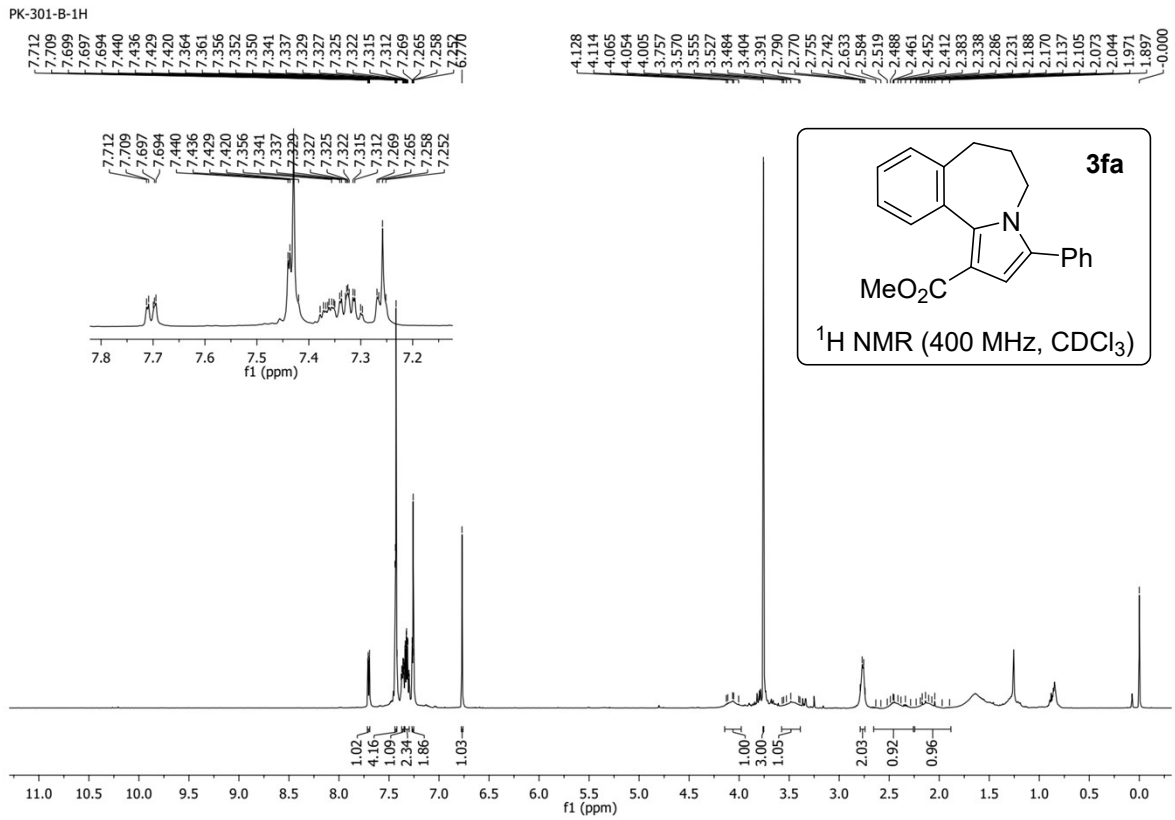

5-Br-THIQ-CYP-CLSG-13C
165.706
133.669
133.127
132.704
131.626
131.548
130.630
129.090
128.790
128.217
127.953
127.349
123.103
112.692
112.516
77.371
77.160
76.948
51.461
42.008
29.884
Br
N
Ph
MeO2C
3ca
13C NMR (150 MHz, CDCl3)
f1 (ppm)

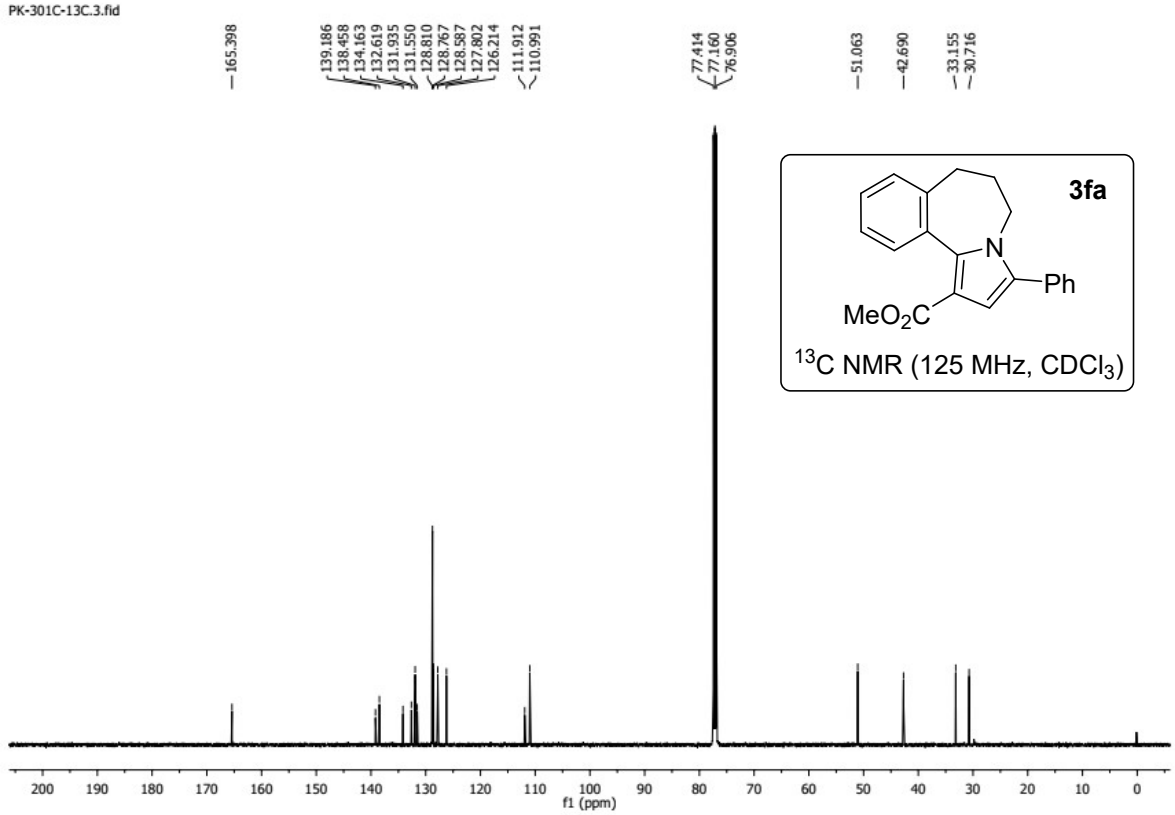

6-Br-THIQ-CYP-CLSG-1H
8.455
8.434
7.473
7.467
7.448
7.428
7.396
7.377
7.357
7.260
6.796
4.066
4.049
4.034
3.857
2.950
2.934
2.918
0.000
Br
N
Ph
MeO2C
3da
1H NMR (400 MHz, CDCl3)
1.00
3.00
4.00
0.97
2.00
3.00
2.00
f1 (ppm)

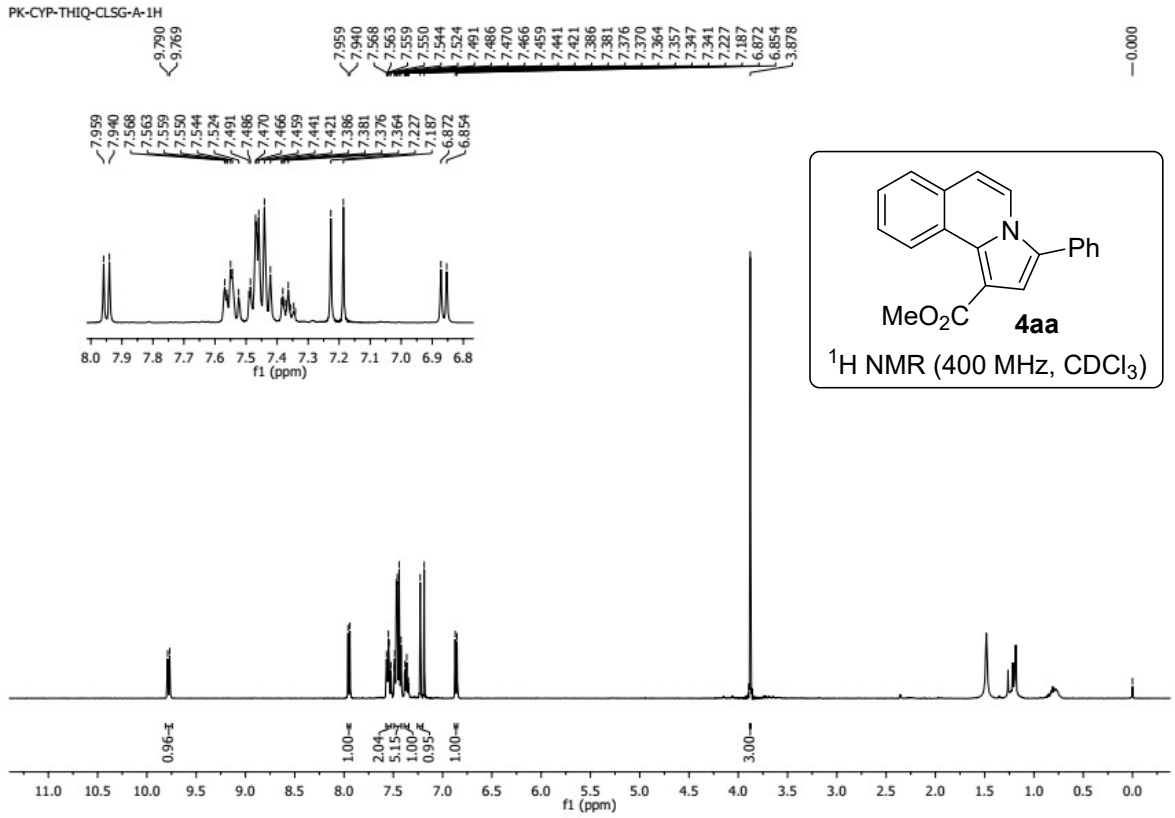

6-Br-THIQ-CYP-CLSG-13C
Br
N
Ph
MeO2C
3da
13C NMR (125 MHz, CDCl3)
f1 (ppm)

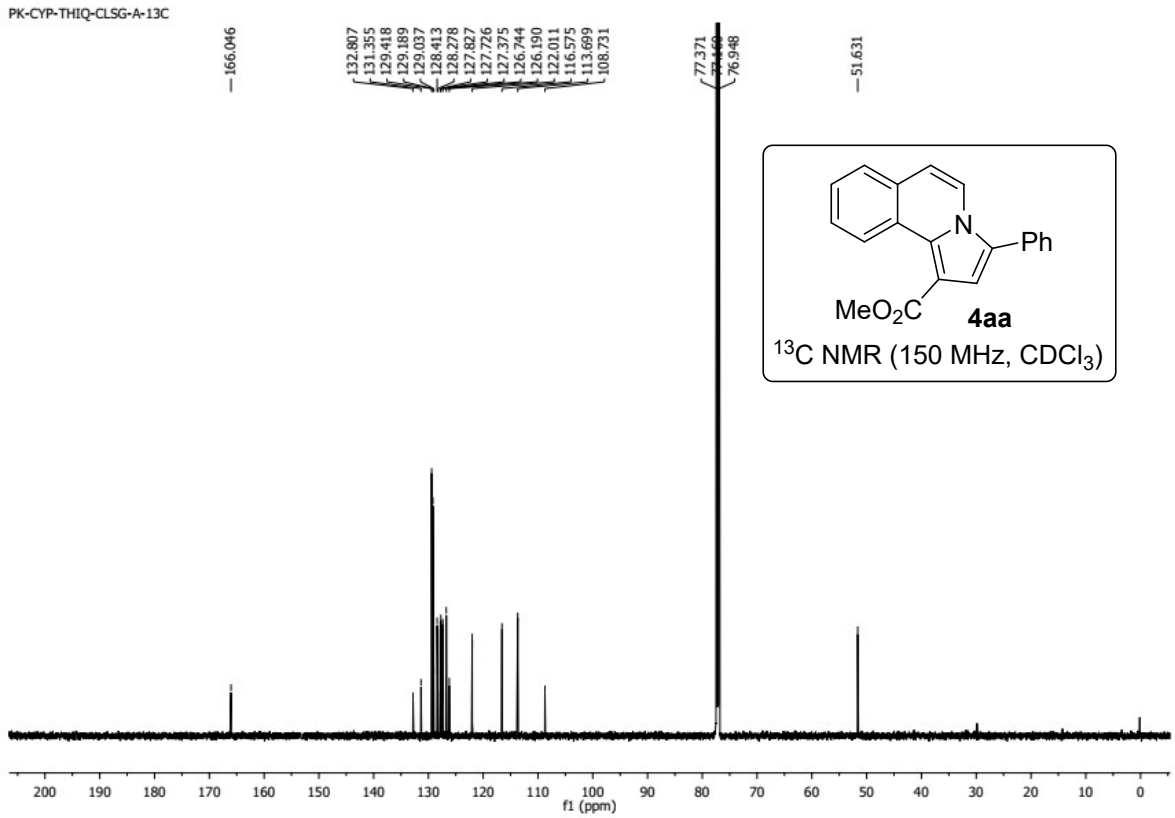

PK-THP-THIQ-CYP-CLSG-1H
S
N
Ph
MeO2C
3ea
1H NMR (400 MHz, CDCl3)
f1 (ppm)

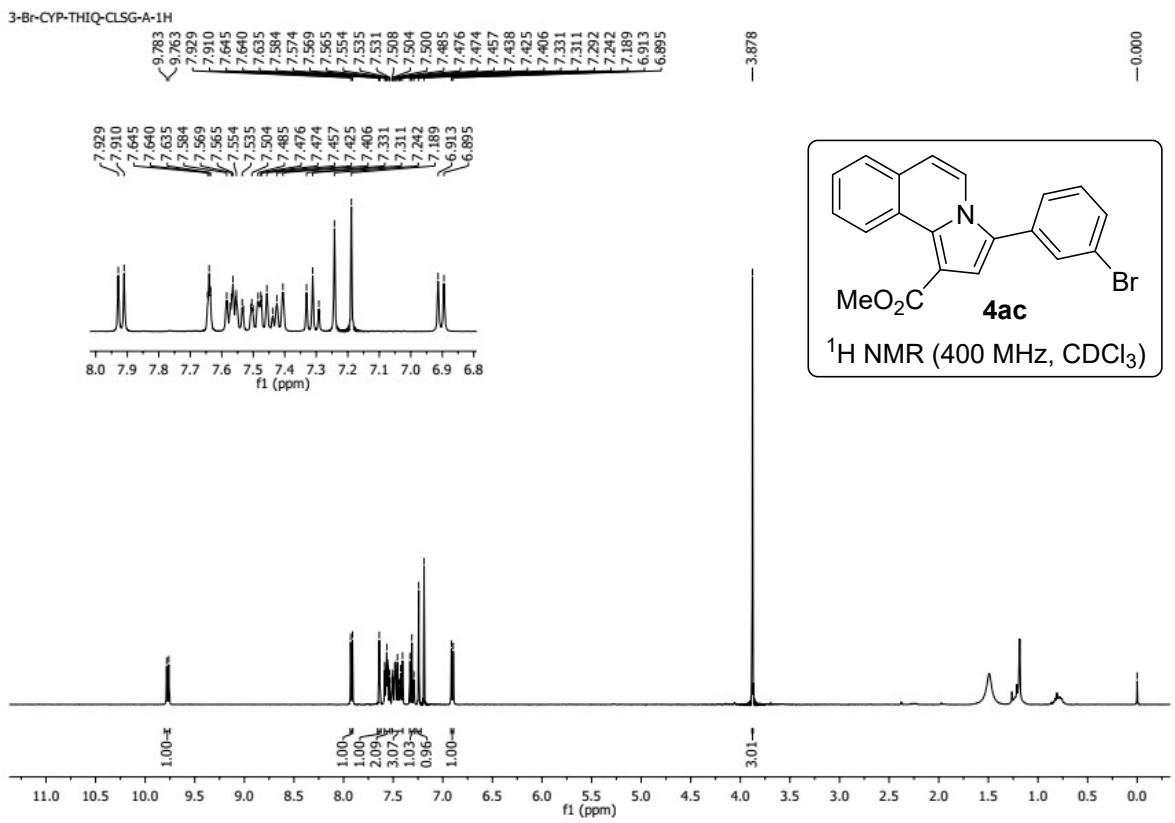

PK-THP-THIQ-CYP-CLSG-13C
165.532
133.672
133.600
132.247
132.159
130.025
129.157
128.706
127.883
127.803
122.188
111.038
110.130
77.414
77.160
76.906
51.248
43.046
24.891
S
N
Ph
MeO2C
3ea
13C NMR (125 MHz, CDCl3)
f1 (ppm)

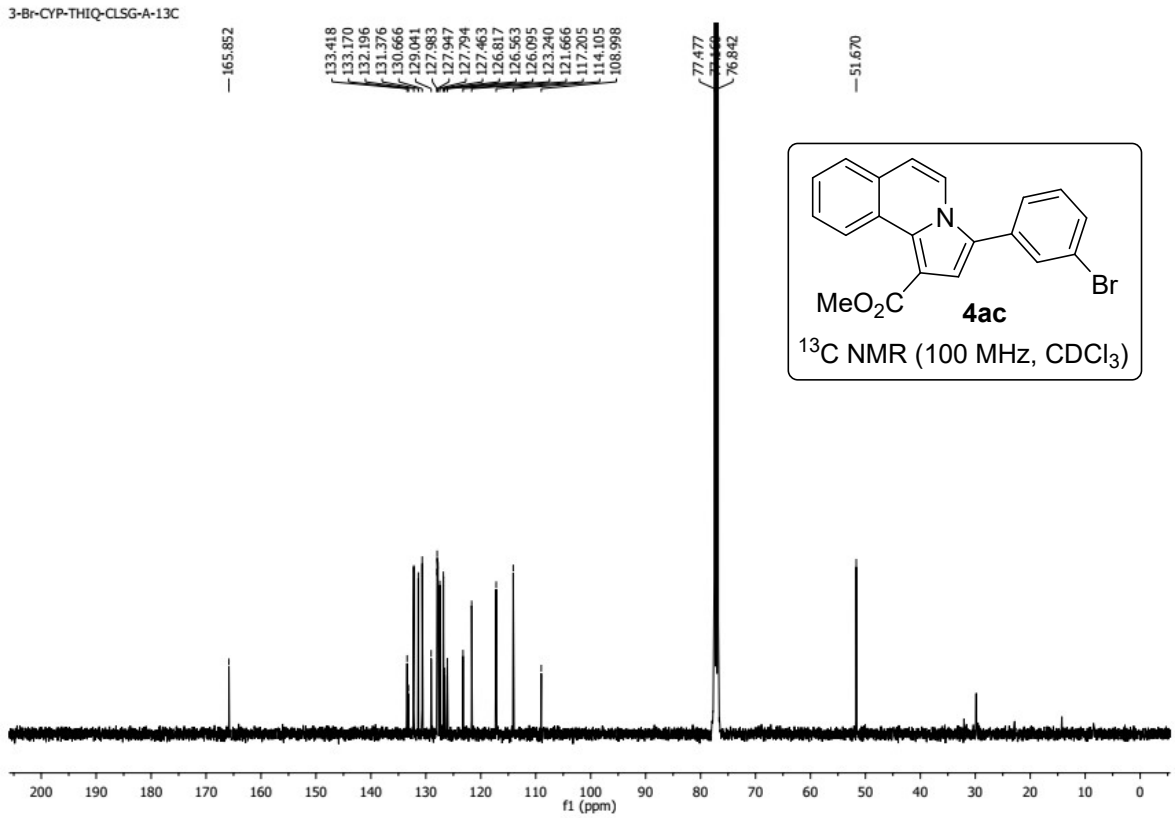

PK-301-B-1H
7.712
7.709
7.699
7.697
7.694
7.440
7.436
7.429
7.420
7.364
7.361
7.356
7.352
7.350
7.341
7.337
7.329
7.327
7.325
7.322
7.315
7.312
7.269
7.265
7.258
7.252
6.770
4.128
4.114
4.065
4.054
4.005
3.757
3.570
3.555
3.527
3.484
3.404
3.391
2.790
2.770
2.755
2.742
2.633
2.584
2.519
2.488
2.461
2.452
2.412
2.383
2.338
2.286
2.231
2.188
2.170
2.137
2.105
2.073
2.044
1.971
1.897
0.000
3fa
N
Ph
MeO2C
1H NMR (400 MHz, CDCl3)
1.02
4.16
1.09
2.34
1.86
1.03
1.00
3.00
1.05
2.03
0.92
0.96
f1 (ppm)

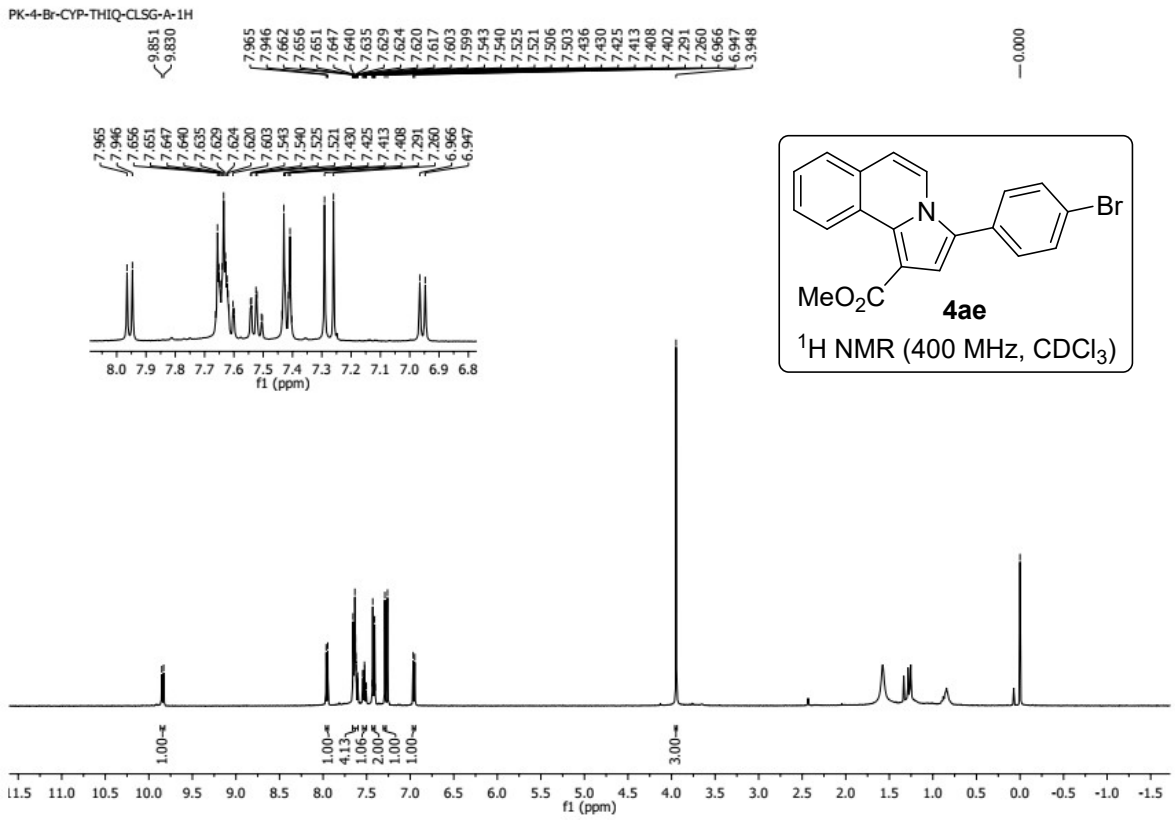

PK-301C-13C.3.fid
165.398
139.186
138.458
134.163
132.619
131.935
131.550
128.810
128.767
128.587
127.802
126.214
111.912
110.991
77.414
77.160
76.906
51.063
42.690
33.155
30.716
3fa
N
Ph
MeO2C
13C NMR (125 MHz, CDCl3)
f1 (ppm)

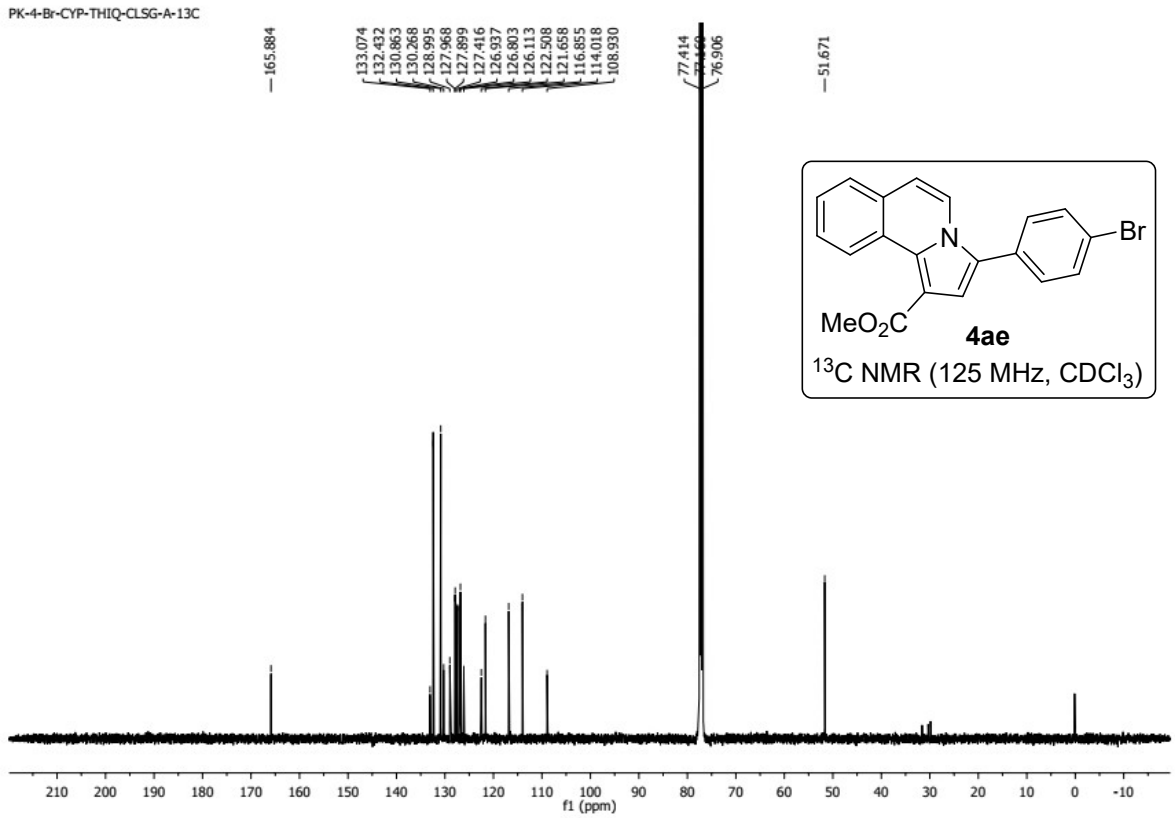

PK-CYP-THIQ-CLSG-A-1H
9.790
9.769
7.959
7.940
7.568
7.563
7.559
7.550
7.544
7.524
7.491
7.486
7.470
7.466
7.459
7.441
7.421
7.386
7.381
7.376
7.364
7.357
7.347
7.341
7.227
7.187
6.872
6.854
3.878
0.000
N
Ph
MeO2C
4aa
1H NMR (400 MHz, CDCl3)
0.96
1.00
2.04
5.15
1.00
0.95
1.00
3.00
f1 (ppm)

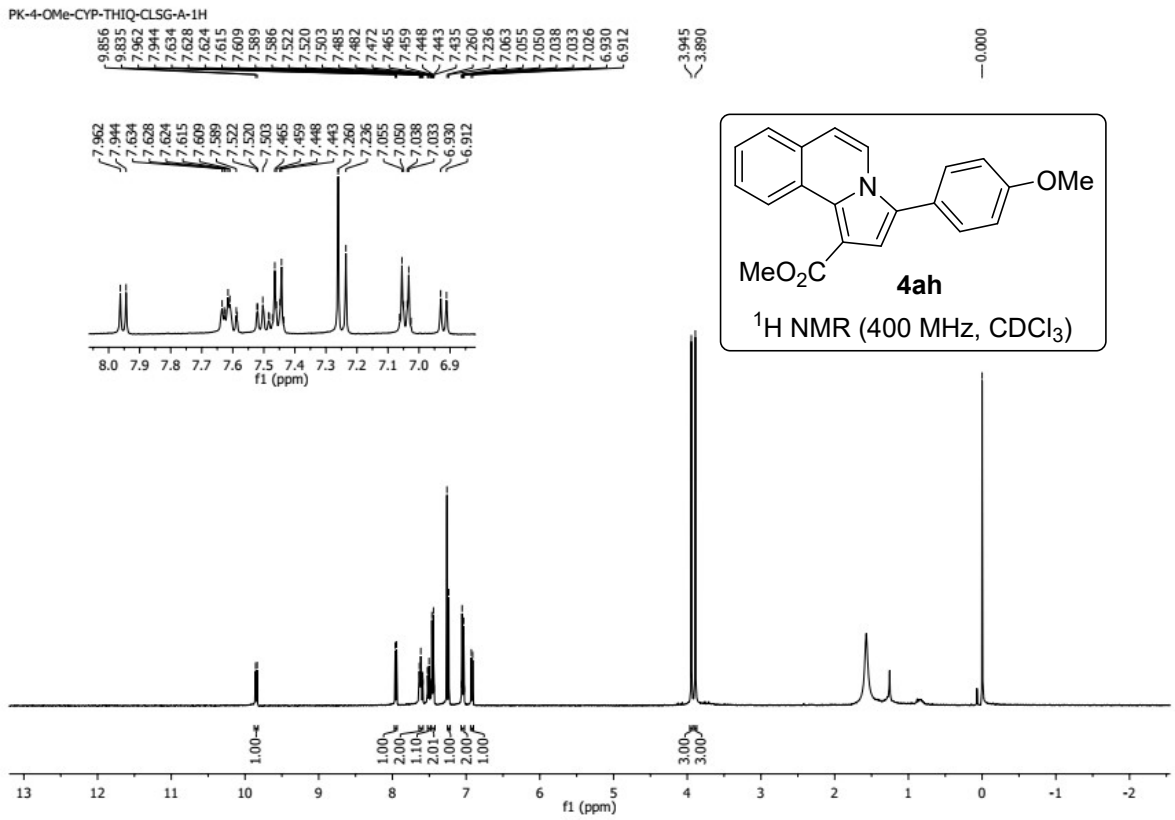

PK-CYP-THIQ-CLSG-A-13C
166.046
132.807
131.355
129.418
129.189
129.037
128.413
128.278
127.827
127.726
127.375
126.744
126.190
122.011
116.575
113.699
108.731
77.371
76.948
51.631
N
Ph
MeO2C
4aa
13C NMR (150 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

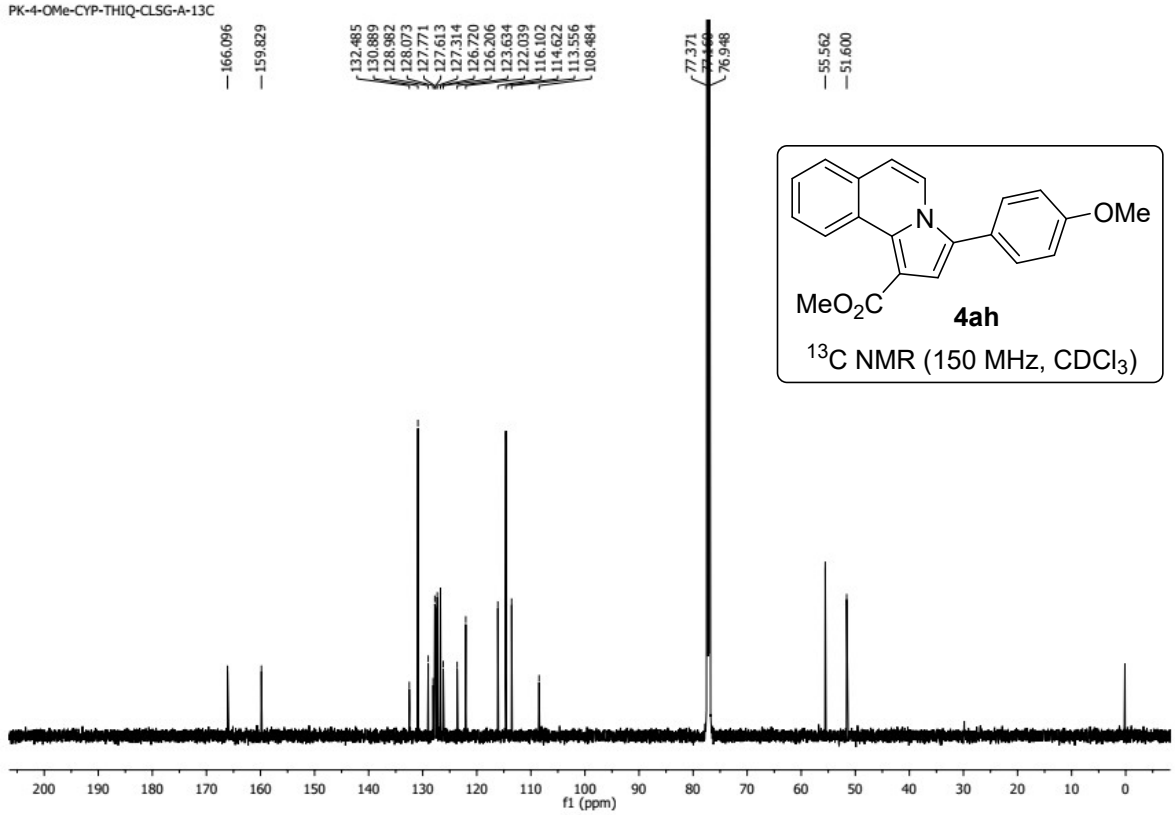

3-Br-CYP-THIQ-CLSG-A-1H
9.783
9.763
7.929
7.910
7.645
7.640
7.635
7.584
7.574
7.569
7.565
7.554
7.535
7.531
7.508
7.504
7.500
7.485
7.476
7.474
7.457
7.438
7.425
7.406
7.331
7.311
7.292
7.242
7.189
6.913
6.895
3.878
0.000
N
Br
MeO2C
4ac
1H NMR (400 MHz, CDCl3)
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.00
1.00
2.09
3.07
1.03
0.96
1.00
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

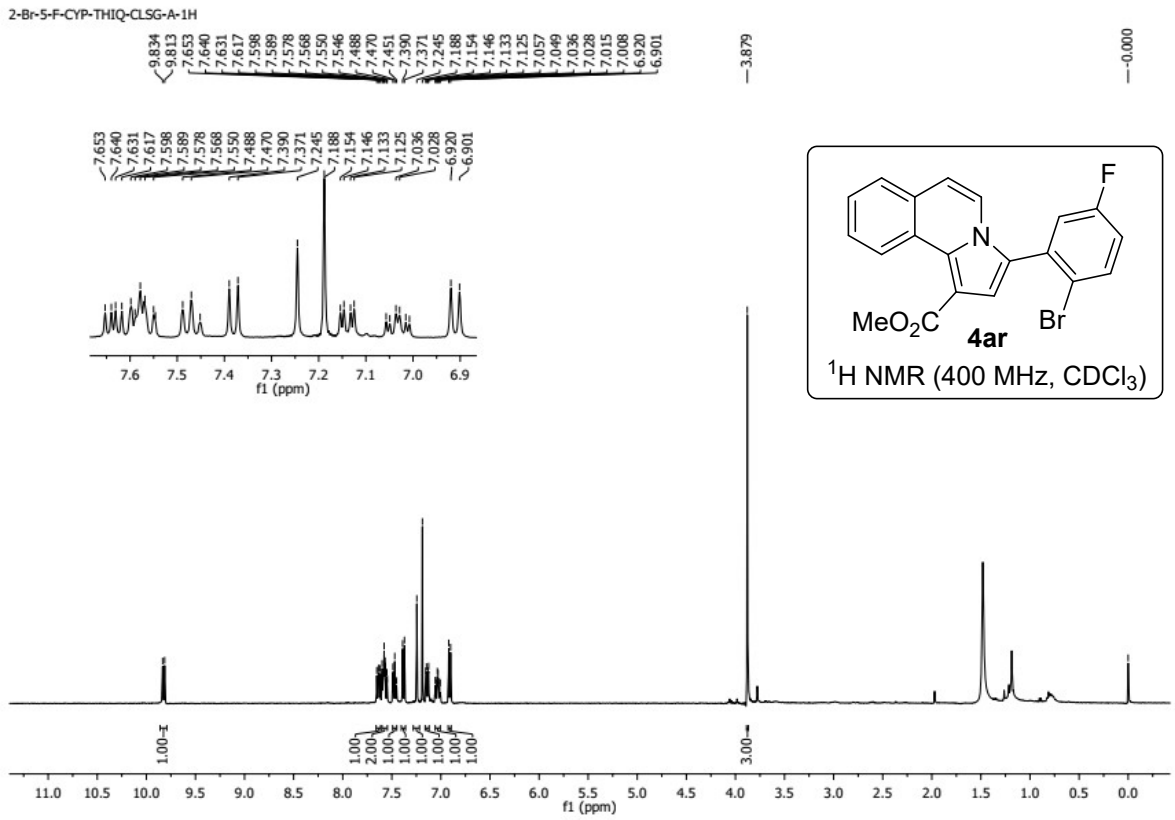

3-Br-CYP-THIQ-CLSG-A-13C
165.852
133.418
133.170
132.196
131.376
130.666
129.041
127.983
127.947
127.794
127.463
126.817
126.563
126.095
123.240
121.666
117.205
114.105
108.998
77.477
76.842
51.670
N
Br
MeO2C
4ac
13C NMR (100 MHz, CDCl3)
f1 (ppm)

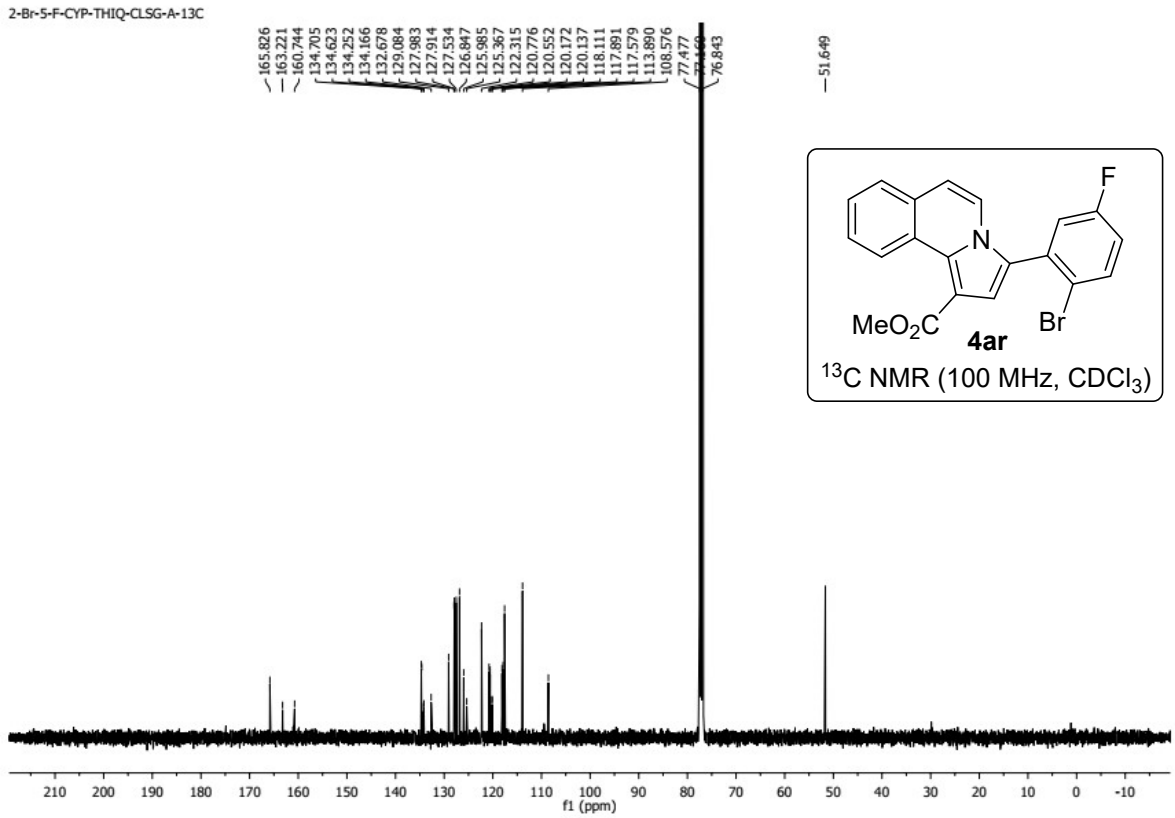

PK-4-Br-CYP-THIQ-CLSG-A-1H
9.851
9.830
7.965
7.946
7.662
7.656
7.651
7.647
7.640
7.635
7.629
7.624
7.620
7.617
7.603
7.599
7.543
7.540
7.525
7.521
7.506
7.503
7.436
7.430
7.425
7.413
7.408
7.402
7.291
7.260
6.966
6.947
3.948
0.000
N
Br
MeO2C
4ae
1H NMR (400 MHz, CDCl3)
f1 (ppm)

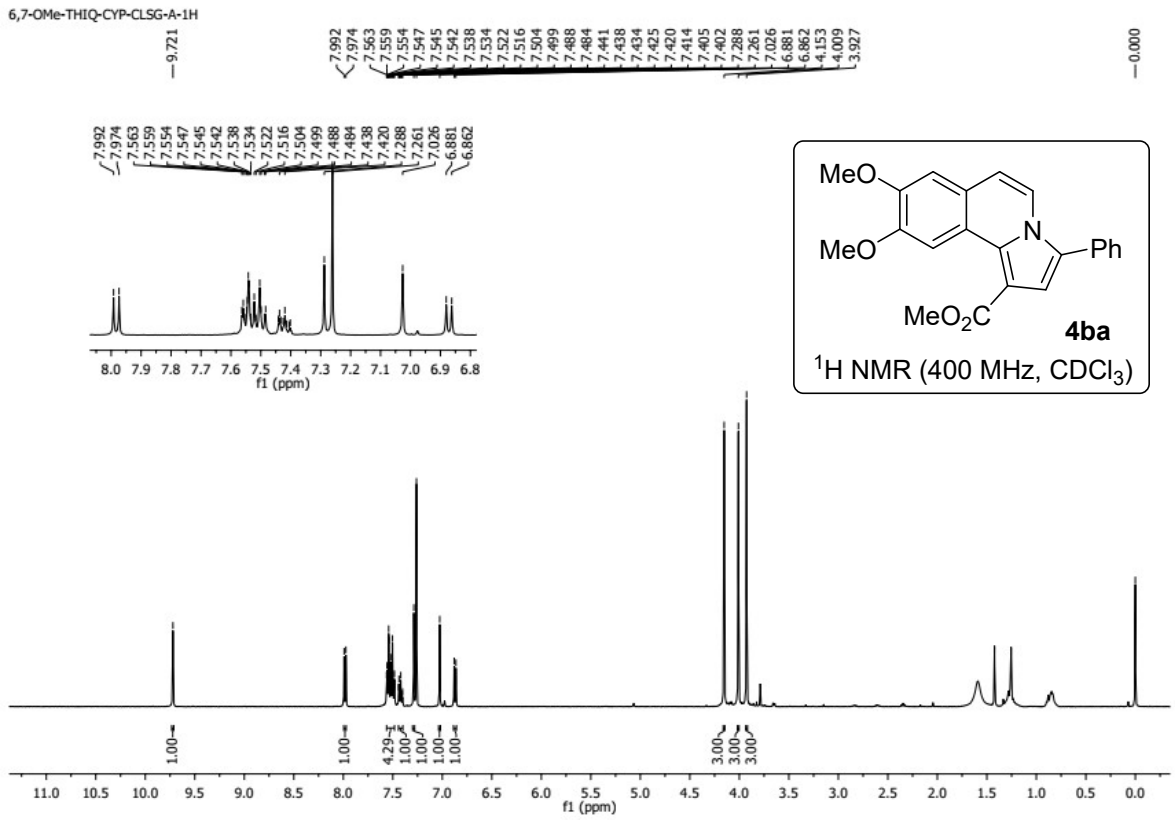

PK-4-Br-CYP-THIQ-CLSG-A-13C
165.884
133.074
132.432
130.863
130.268
128.995
127.968
127.899
127.416
126.937
126.803
126.113
122.508
121.658
116.855
114.018
108.930
77.414
76.906
51.671
Br
N
MeO2C
4ae
13C NMR (125 MHz, CDCl3)
f1 (ppm)

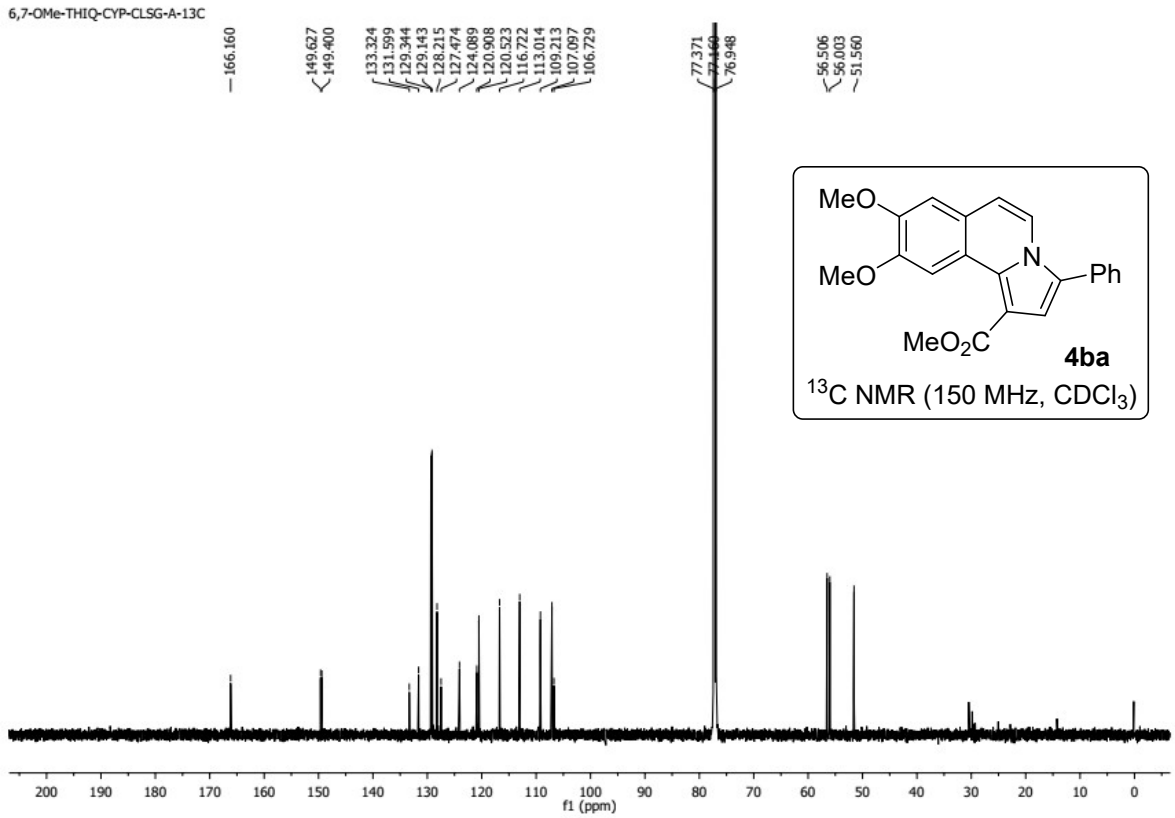

PK-4-OMe-CYP-THIQ-CLSG-A-1H
9.856
9.835
7.962
7.944
7.634
7.628
7.624
7.615
7.609
7.589
7.586
7.522
7.520
7.503
7.485
7.482
7.472
7.465
7.459
7.448
7.443
7.435
7.260
7.236
7.063
7.055
7.050
7.038
7.033
7.026
6.930
6.912
3.945
3.890
0.000
OMe
N
MeO2C
4ah
1H NMR (400 MHz, CDCl3)
f1 (ppm)

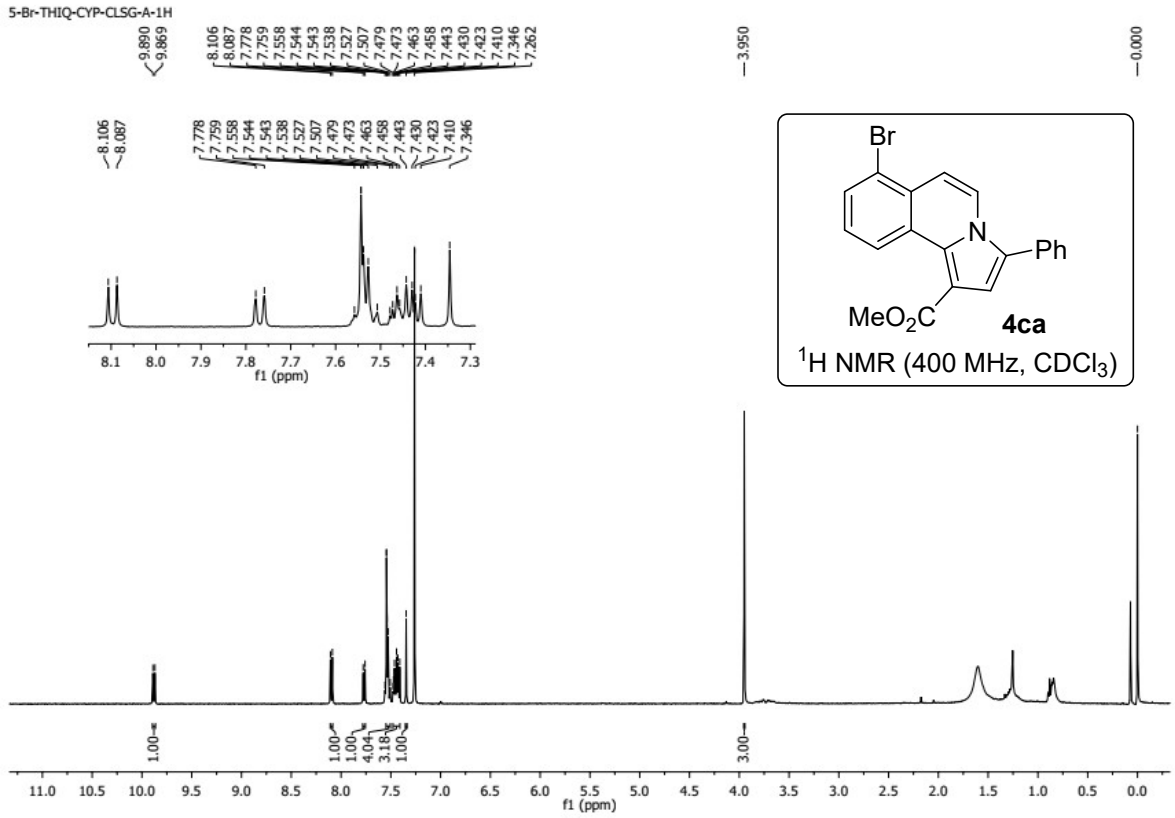

PK-4-OMe-CYP-THIQ-CLSG-A-13C
166.096
159.829
132.485
130.889
128.982
128.073
127.771
127.613
127.314
126.720
126.206
123.634
122.039
116.102
114.622
113.556
108.484
77.371
76.948
55.562
51.600
OMe
N
MeO2C
4ah
13C NMR (150 MHz, CDCl3)
f1 (ppm)

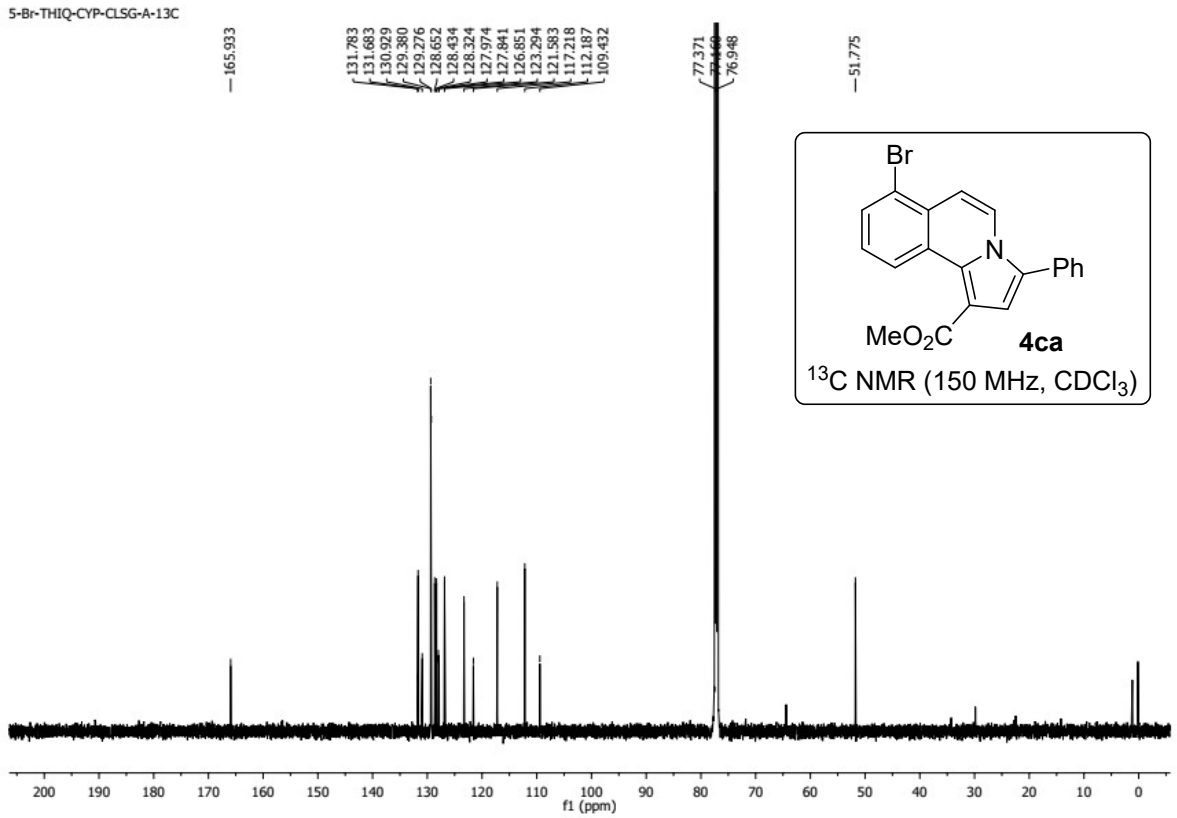

2-Br-5-F-CYP-THIQ-CLSG-A-1H
9.834
9.813
7.653
7.640
7.631
7.617
7.598
7.589
7.578
7.568
7.550
7.546
7.488
7.470
7.451
7.390
7.371
7.245
7.188
7.154
7.146
7.133
7.125
7.057
7.049
7.036
7.028
7.015
7.008
6.920
6.901
3.879
0.000
F
N
MeO2C
Br
4ar
1H NMR (400 MHz, CDCl3)
f1 (ppm)

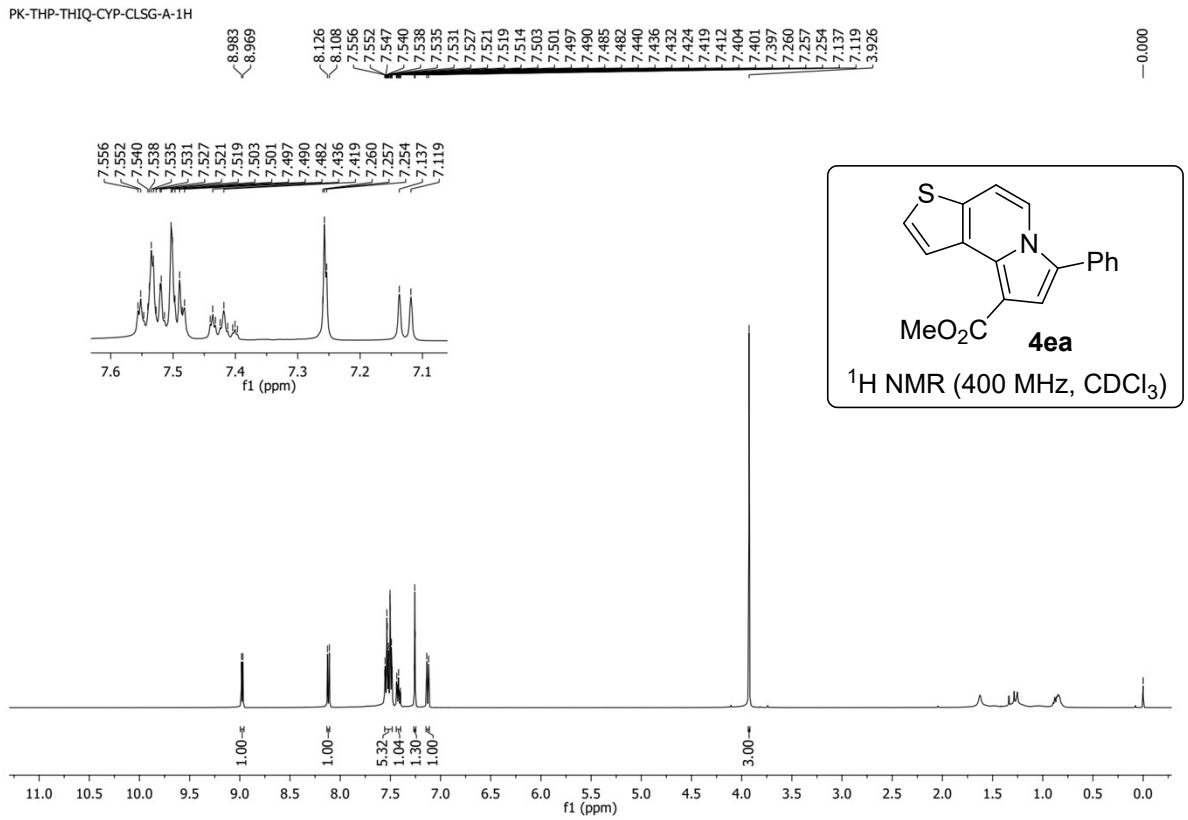

2-Br-5-F-CYP-THIQ-CLSG-A-13C
165.826
163.221
160.744
134.705
134.623
134.252
134.166
132.678
129.084
127.983
127.914
127.534
126.847
125.985
125.367
122.315
120.776
120.552
120.172
120.137
118.111
117.891
117.579
113.890
108.576
77.477
76.843
51.649
F
N
MeO2C
Br
4ar
13C NMR (100 MHz, CDCl3)
f1 (ppm)

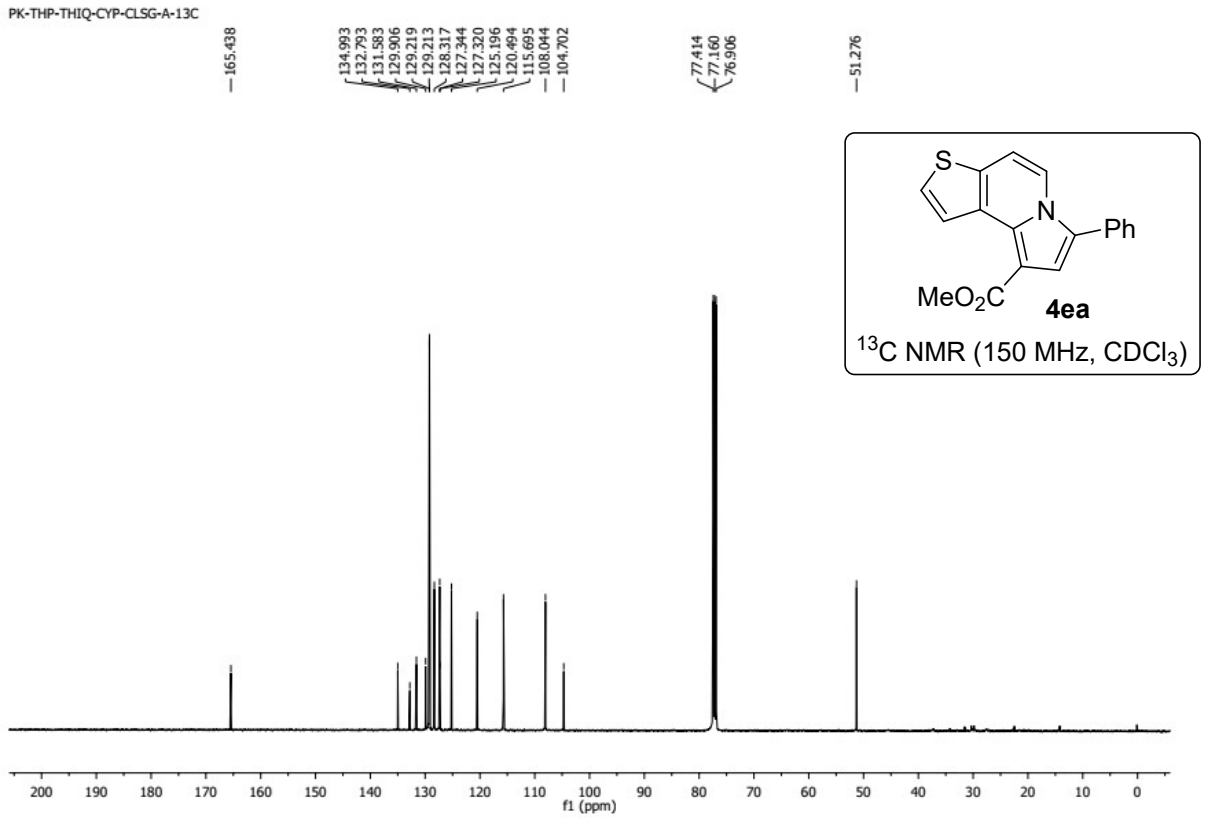

6,7-OMe-THIQ-CYP-CLSG-A-1H
9.721
7.992
7.974
7.563
7.559
7.554
7.547
7.545
7.542
7.538
7.534
7.522
7.516
7.504
7.499
7.488
7.484
7.441
7.438
7.434
7.425
7.420
7.414
7.405
7.402
7.288
7.261
7.026
6.881
6.862
4.153
4.009
3.927
0.000
MeO
MeO
N
Ph
MeO2C
4ba
1H NMR (400 MHz, CDCl3)
1.00
1.00
4.29
1.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)

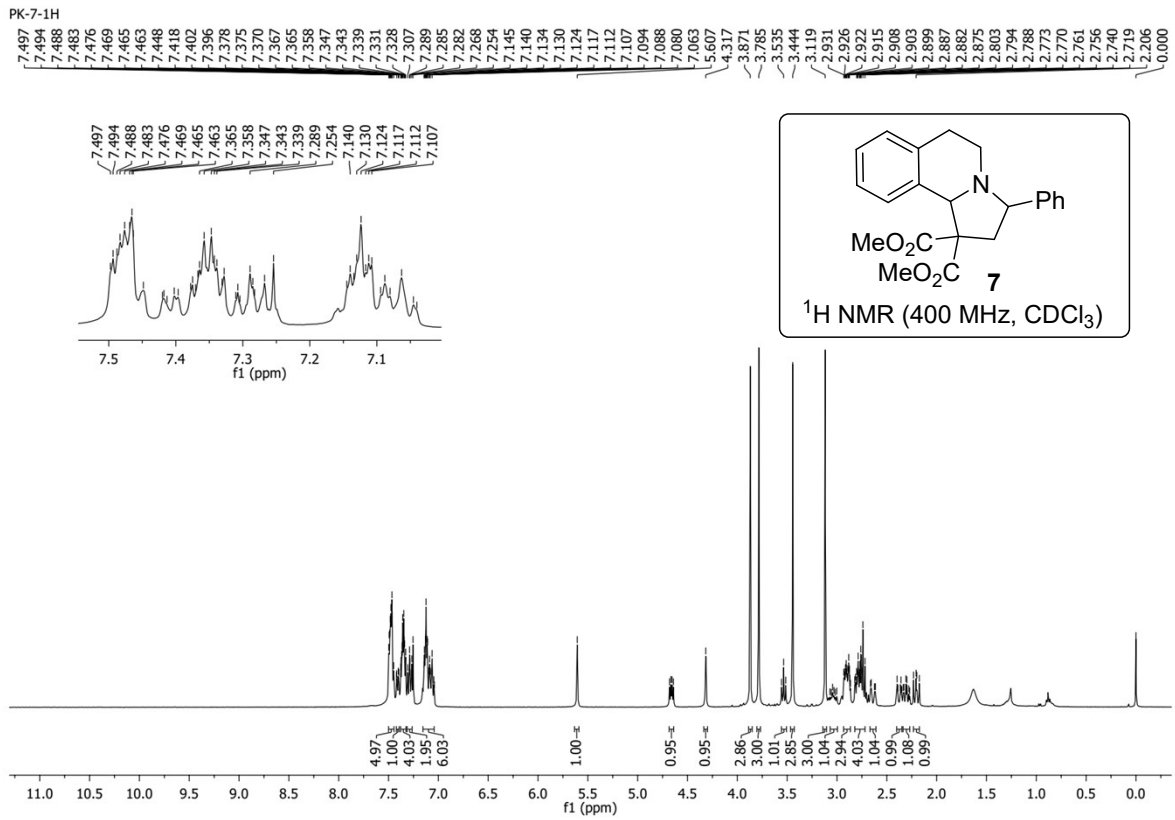

6,7-OMe-THIQ-CYP-CLSG-A-13C
166.160
149.627
149.400
133.324
131.599
129.344
129.143
128.215
127.474
124.089
120.908
120.523
116.722
113.014
109.213
107.097
106.729
77.371
77.160
76.948
56.506
56.003
51.560
MeO
MeO
N
Ph
MeO2C
4ba
13C NMR (150 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

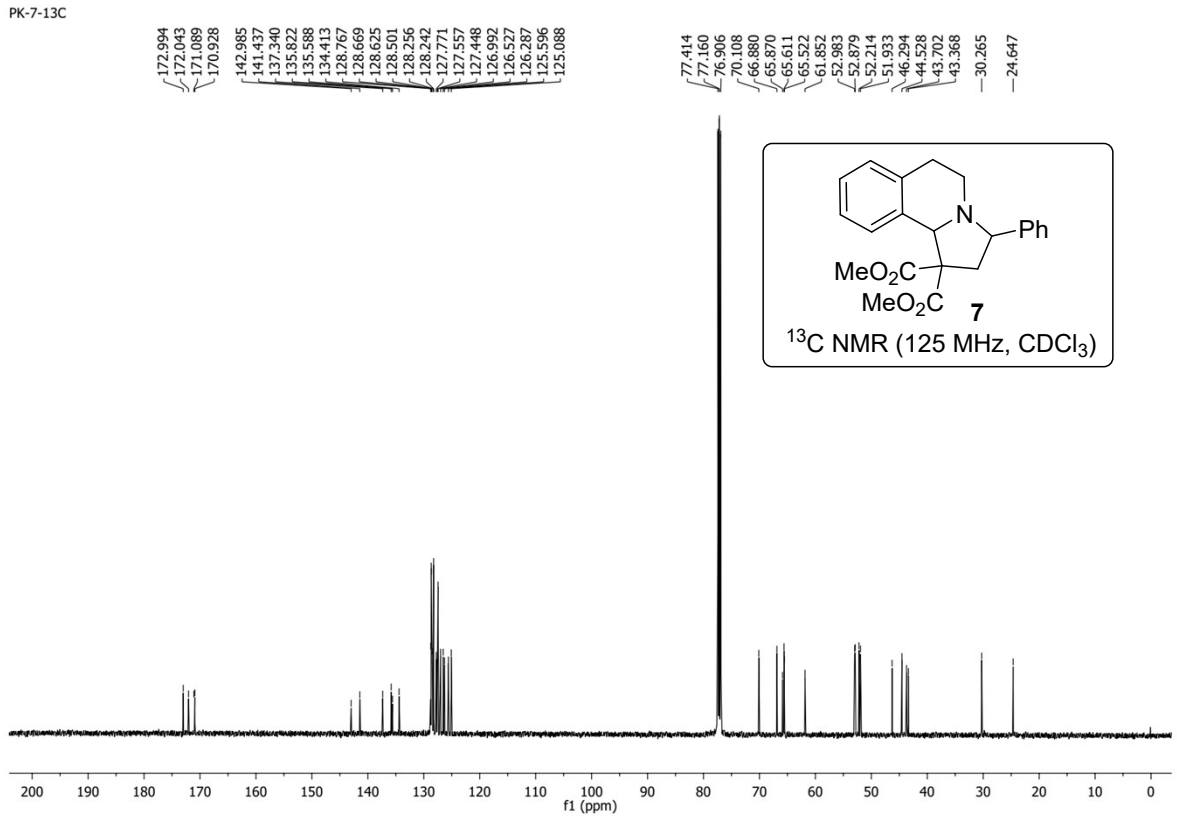

5-Br-THIQ-CYP-CLSG-A-1H
9.890
9.869
8.106
8.087
7.778
7.759
7.558
7.544
7.543
7.538
7.527
7.507
7.479
7.473
7.463
7.458
7.443
7.430
7.423
7.410
7.346
7.262
3.950
0.000
Br
N
Ph
MeO2C
4ca
1H NMR (400 MHz, CDCl3)
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
1.00
1.00
1.00
4.04
3.18
1.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

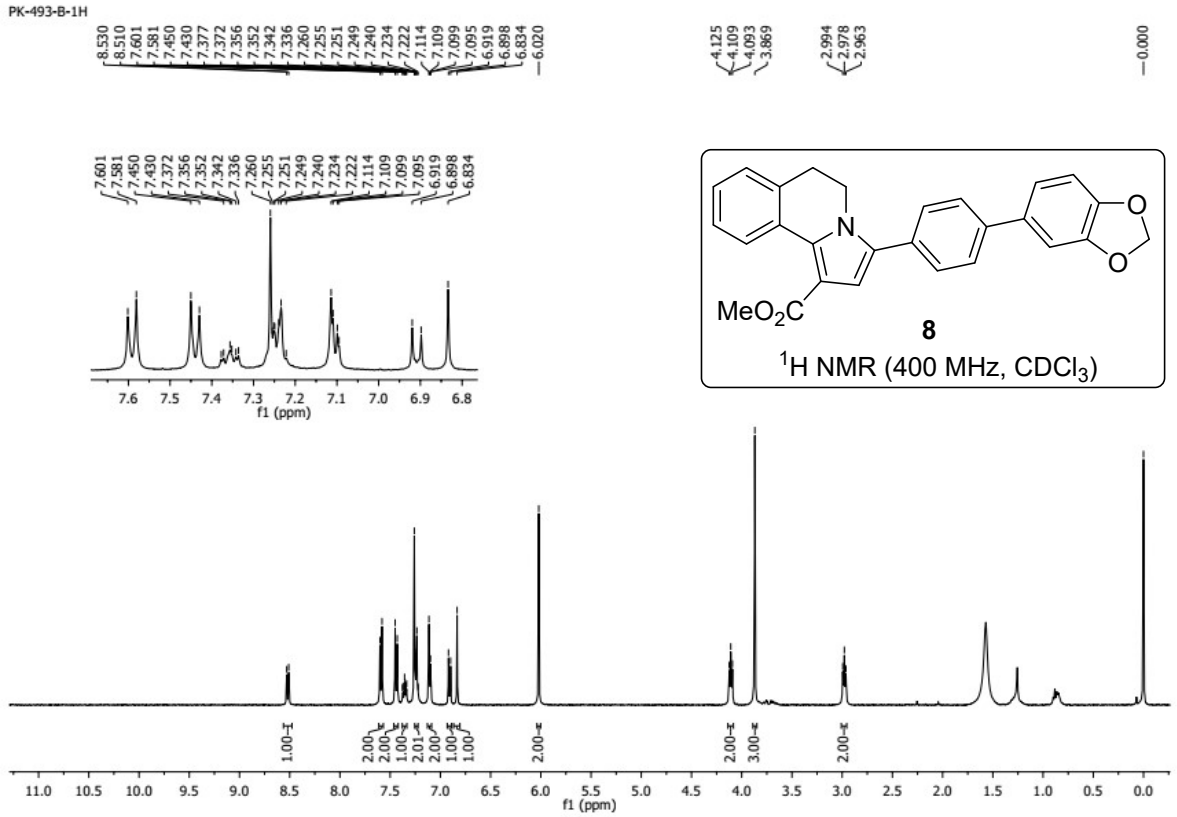

5-Br-THIQ-CYP-CLSG-A-13C
165.933
131.783
131.683
130.929
129.380
129.276
128.652
128.434
128.324
127.974
127.841
126.851
123.294
121.583
117.218
112.187
109.432
77.371
77.160
76.948
51.775
Br
N
Ph
MeO2C
4ca
13C NMR (150 MHz, CDCl3)
f1 (ppm)

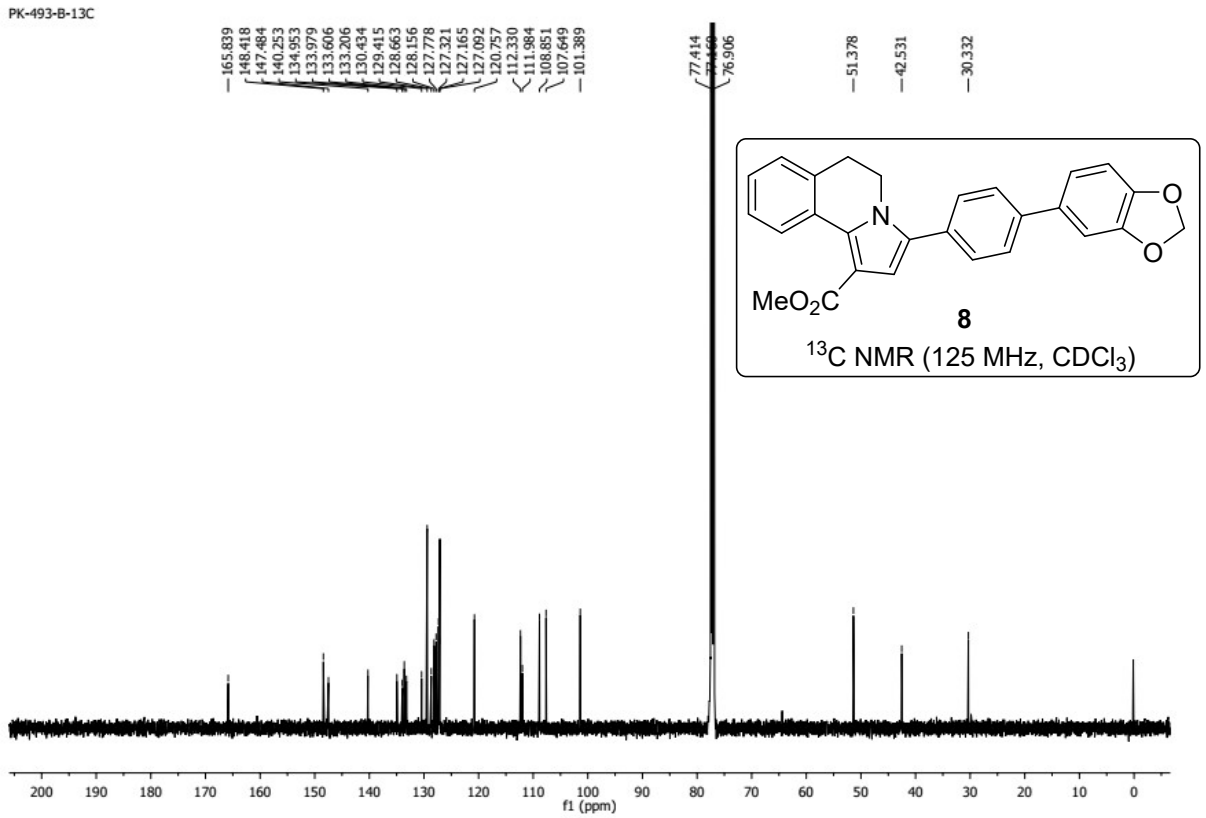

PK-THP-THIQ-CYP-CLSG-A-1H
8.983
8.969
8.126
8.108
7.556
7.552
7.547
7.540
7.538
7.535
7.531
7.527
7.521
7.519
7.514
7.503
7.501
7.497
7.490
7.485
7.482
7.440
7.436
7.432
7.424
7.419
7.412
7.404
7.401
7.397
7.260
7.257
7.254
7.137
7.119
3.926
0.000
S
N
Ph
MeO2C
4ea
1H NMR (400 MHz, CDCl3)
1.00
1.00
5.32
1.04
1.30
1.00
3.00
f1 (ppm)

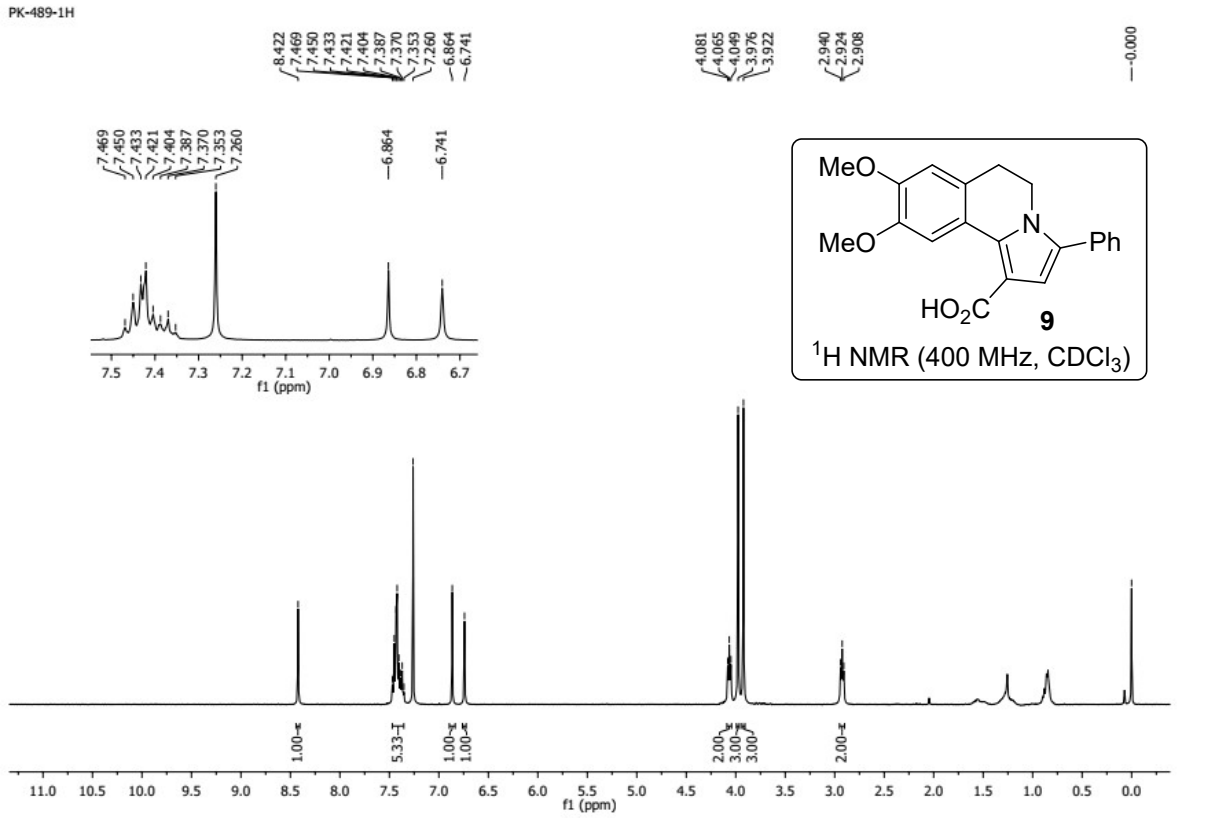

PK-THP-THIQ-CYP-CLSG-A-13C
165.438
134.993
132.793
131.583
129.906
129.219
129.213
128.317
127.344
127.320
125.196
120.494
115.695
108.044
104.702
77.414
77.160
76.906
51.276
S
N
Ph
MeO2C
4ea
13C NMR (150 MHz, CDCl3)
f1 (ppm)

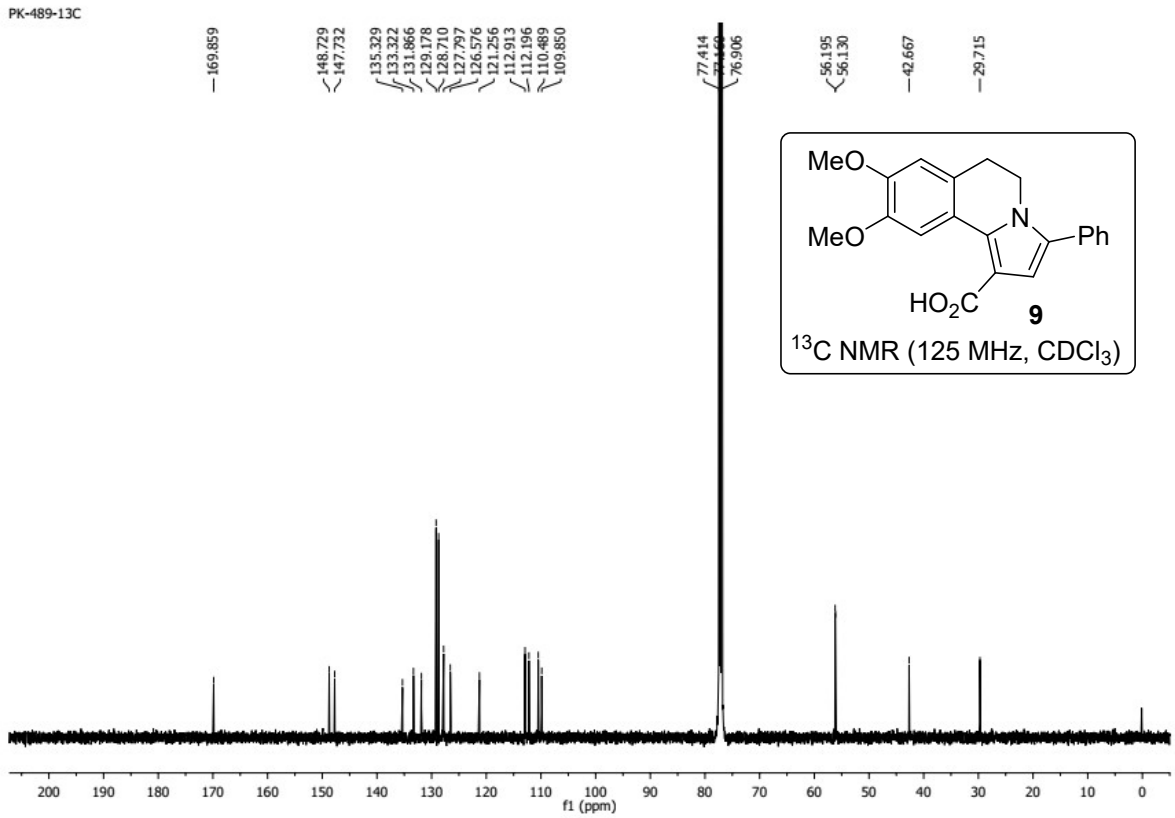

PK-7-1H
N
Ph
MeO2C
MeO2C
7
1H NMR (400 MHz, CDCl3)
f1 (ppm)

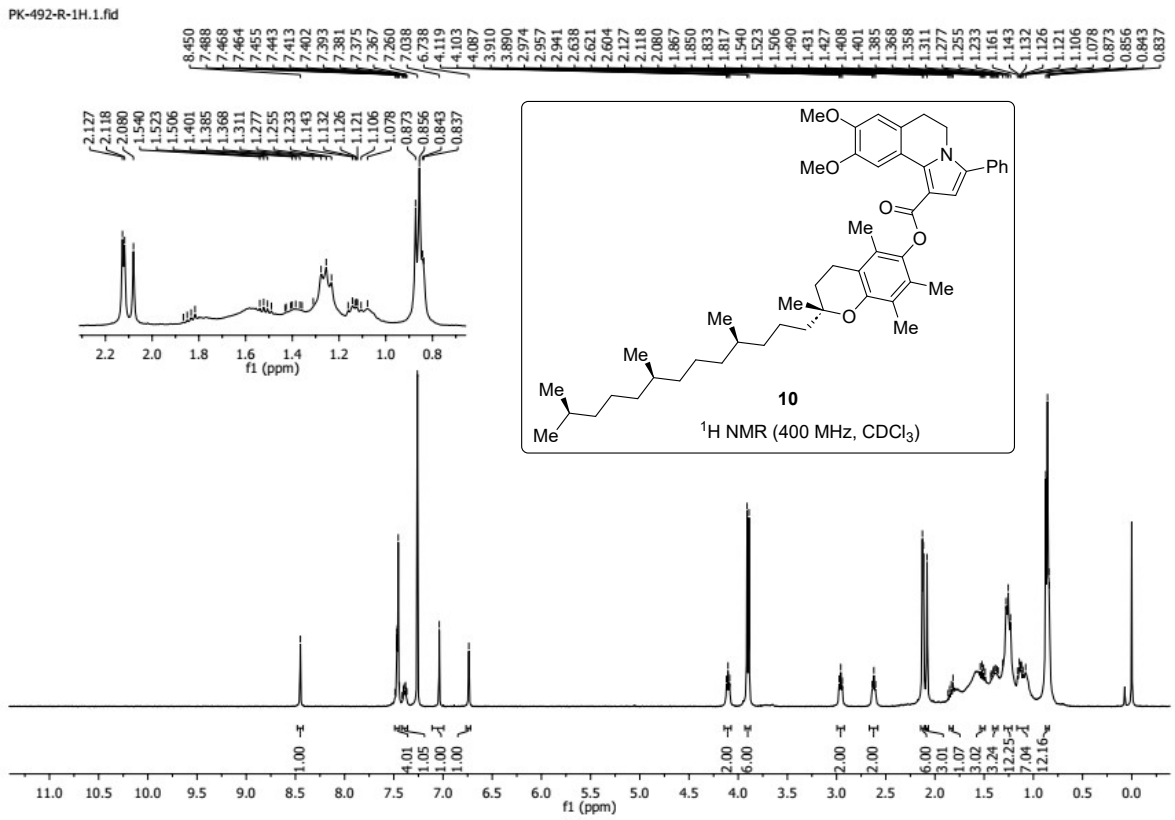

PK-7-13C
172.994
172.043
171.089
170.928
142.985
141.437
137.340
135.822
135.588
134.413
128.767
128.669
128.625
128.501
128.256
128.242
127.771
127.557
127.448
126.992
126.527
126.287
125.596
125.088
77.414
77.160
76.906
70.108
66.880
65.870
65.611
65.522
61.852
52.983
52.879
52.214
51.933
46.294
44.528
43.702
43.368
30.265
24.647
N
Ph
MeO2C
MeO2C
7
13C NMR (125 MHz, CDCl3)
f1 (ppm)

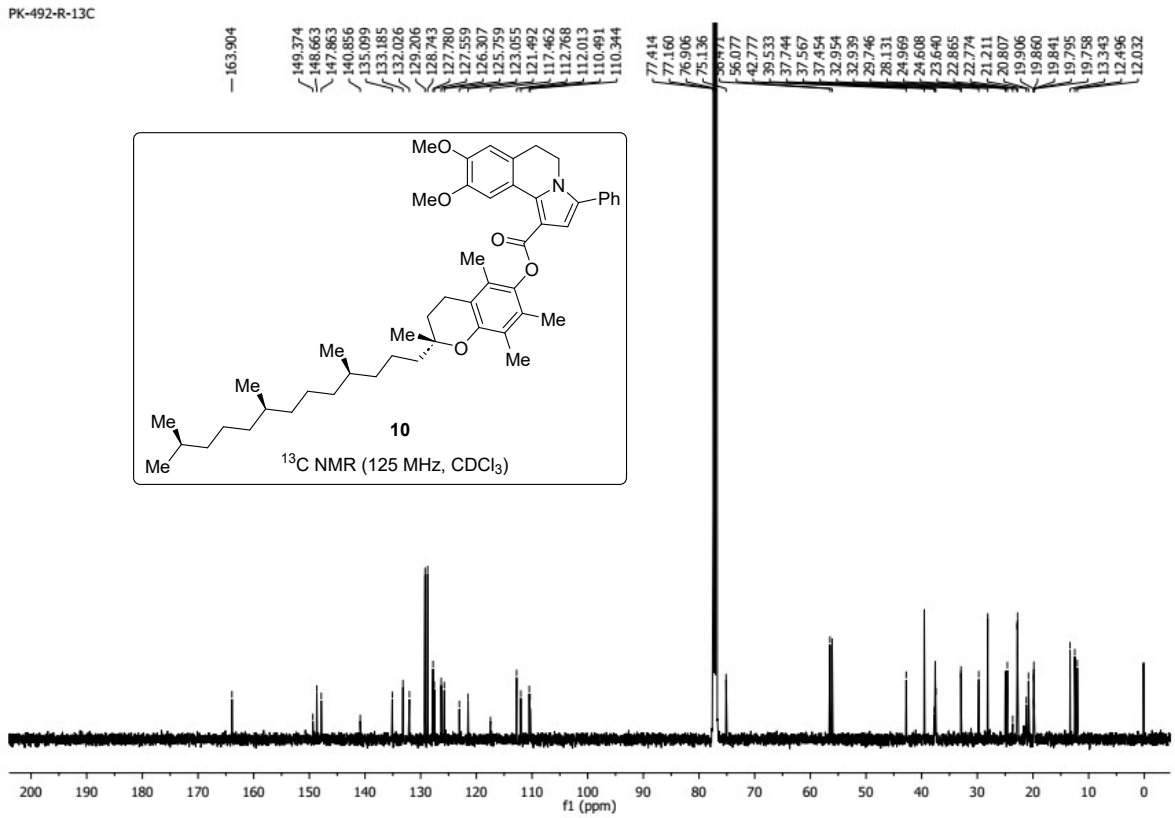

PK-493-B-1H
8.530
8.510
7.601
7.581
7.450
7.430
7.377
7.372
7.356
7.352
7.342
7.336
7.260
7.255
7.251
7.249
7.240
7.234
7.222
7.114
7.109
7.099
7.095
6.919
6.898
6.834
6.020
4.125
4.109
4.093
3.869
2.994
2.978
2.963
0.000
N
O
O
MeO2C
8
1H NMR (400 MHz, CDCl3)
1.00
2.00
2.00
1.00
2.01
2.00
1.00
1.00
2.00
2.00
3.00
2.00
f1 (ppm)


PK-493-B-13C
165.839
148.418
147.484
140.253
134.953
133.979
133.606
133.206
130.434
129.415
128.663
128.156
127.778
127.321
127.165
127.092
120.757
112.330
111.984
108.851
107.649
101.389
77.414
76.906
51.378
42.531
30.332
MeO2C
8
13C NMR (125 MHz, CDCl3)
f1 (ppm)


PK-489-1H
8.422
7.469
7.450
7.433
7.421
7.404
7.387
7.370
7.353
7.260
6.864
6.741
4.081
4.065
4.049
3.976
3.922
2.940
2.924
2.908
0.000
MeO
MeO
N
Ph
HO2C
9
1H NMR (400 MHz, CDCl3)
1.00
5.33
1.00
1.00
2.00
3.00
3.00
2.00
f1 (ppm)


PK-489-13C
169.859
148.729
147.732
135.329
133.322
131.866
129.178
128.710
127.797
126.576
121.256
112.913
112.196
110.489
109.850
77.414
76.906
56.195
56.130
42.667
29.715
MeO
MeO
N
Ph
HO2C
9
13C NMR (125 MHz, CDCl3)
f1 (ppm)


PK-492-R-1H.1.fid
MeO
MeO
N
Ph
O
O
Me
Me
Me
Me
Me
Me
Me
Me
10
1H NMR (400 MHz, CDCl3)
f1 (ppm)


PK-492-R-13C
163.904
149.374
148.663
147.863
140.856
135.099
133.185
132.026
129.206
128.743
127.780
127.559
126.307
125.759
123.055
121.492
117.462
112.768
112.013
110.491
110.344
77.414
77.160
76.906
75.136
56.077
42.777
39.533
37.744
37.567
37.454
32.954
32.939
29.746
28.131
24.969
24.608
23.640
22.865
22.774
21.211
20.807
19.906
19.860
19.841
19.795
19.758
13.343
12.496
12.032
MeO
MeO
N
Ph
O
O
Me
Me
Me
Me
Me
Me
Me
Me
10
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)