Synthesis of Benzannulated Medium-ring Lactams via a Tandem Oxidative Dearomatization–Ring Expansion Reaction

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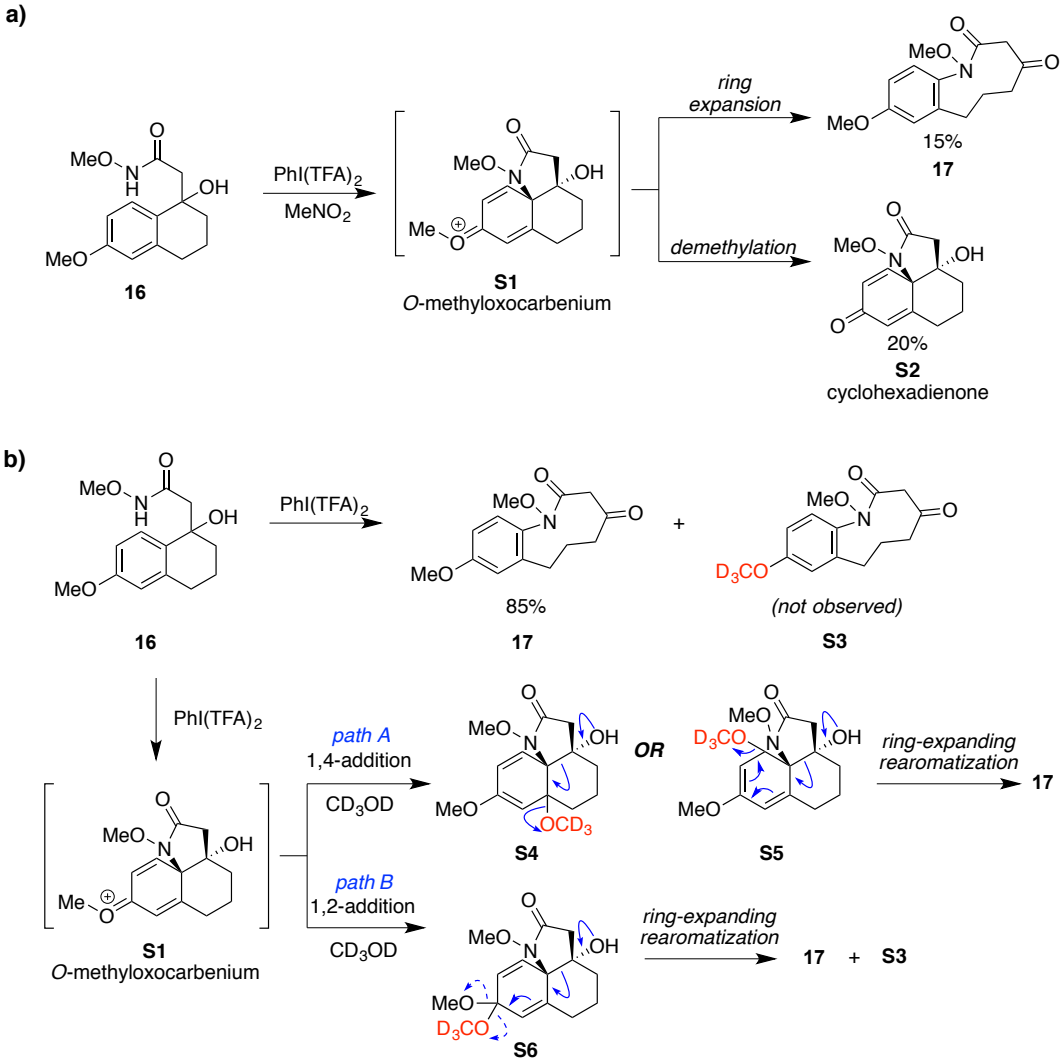
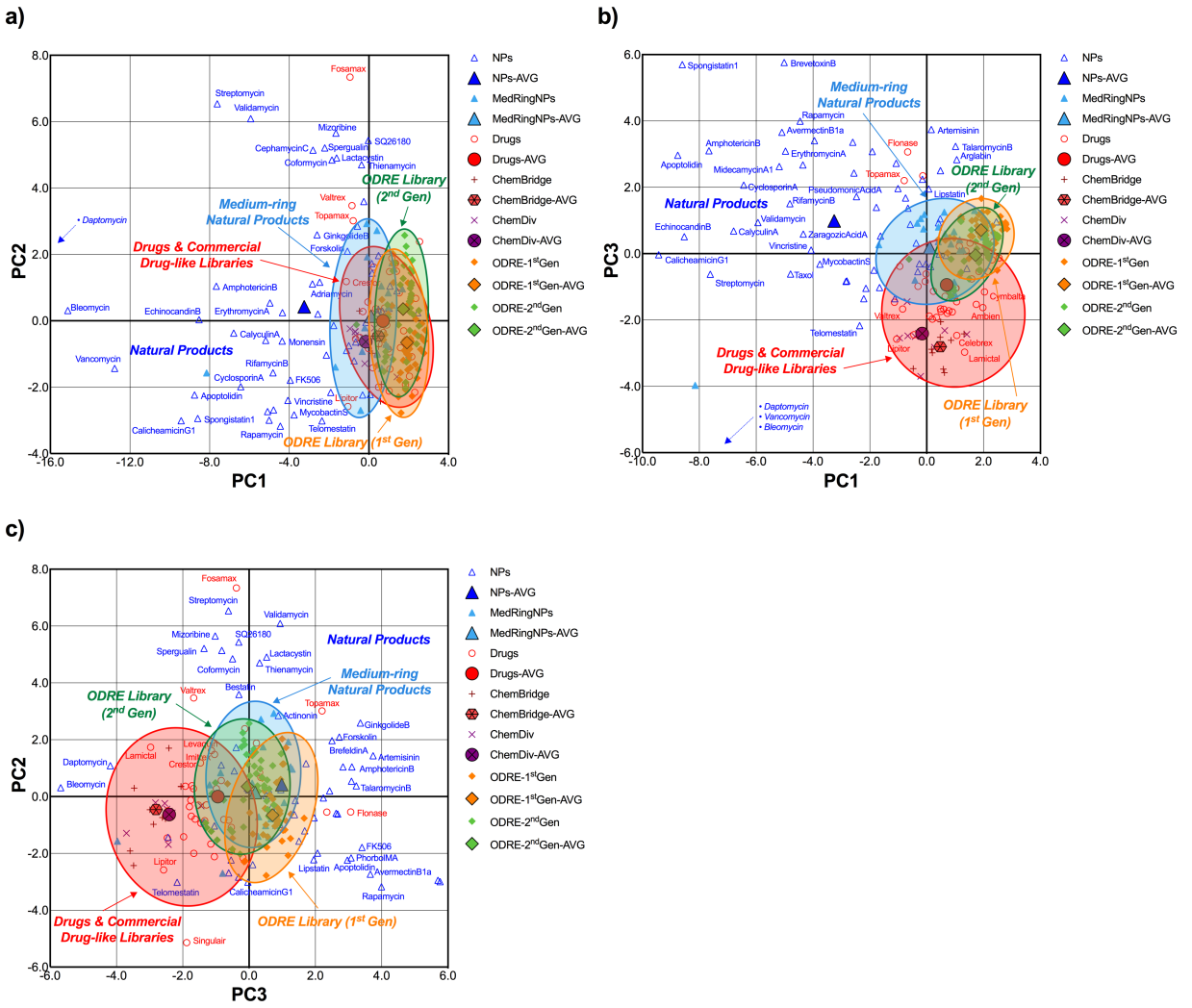
Supplementary Information

A. SUPPLEMENTARY FIGURES 1–10

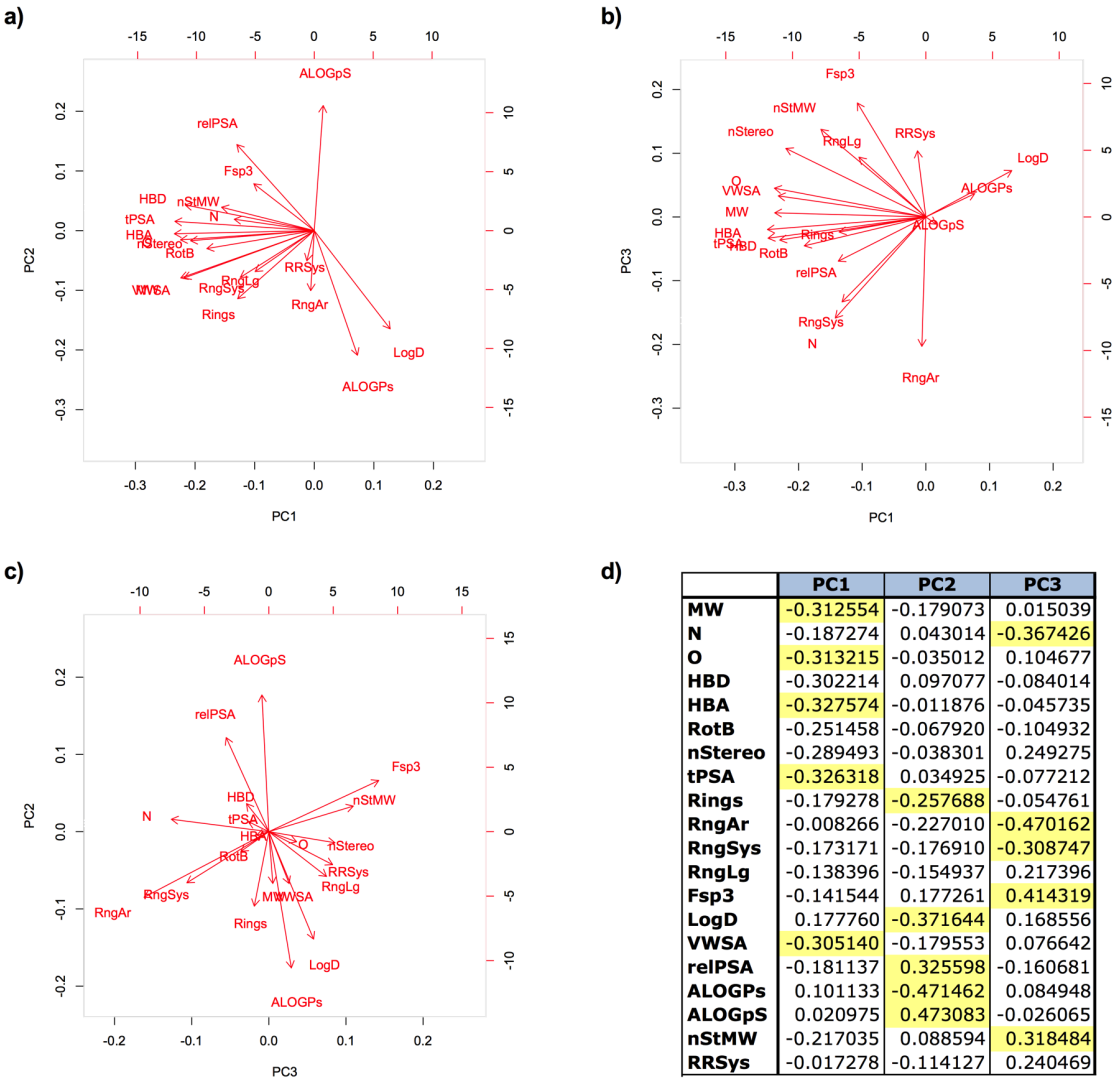


Supplementary Figure 1. (a) Treatment of 6-methoxytetralin **16** with PIFA in nitromethane results in a complex mixture from which 9-membered medium-ring lactam **17** and cyclohexadienone **S2** were recovered. The observation of **S2** in the crude mixture indicates the instability of intermediate **S1**, which hinders formation of desired product **17**. **(b)** Treatment of 6-methoxytetralin **16** with PIFA in methanol-d_4 affords lactam **17** in 85% yield. In the proposed mechanism of methanol-facilitated ODRE, treatment of **16** with PIFA generates the *O*-methyloxocarbenium intermediate **S1**, which can undergo either a 1,2- or 1,4-addition in the presence of the nucleophilic solvent methanol-d_4. Although either path A or path B can ultimately lead to the formation of lactam **17** through a nucleophilic addition/ring-expanding rearomatization sequence, conceivably only path A can circumvent deuterium incorporation in **17** as path B is more likely to generate a mixture of deuterated and non-deuterated medium-ring products **17** and **S3**, respectively. Notably, the crude ^{1}H-NMR spectrum of the overall reaction as shown above did not show the deuterium-incorporated product **S3**, suggesting that path A is favored over path B in the ODRE cascade. PIFA = (bis(trifluoroacetoxy)iodo)benzene.



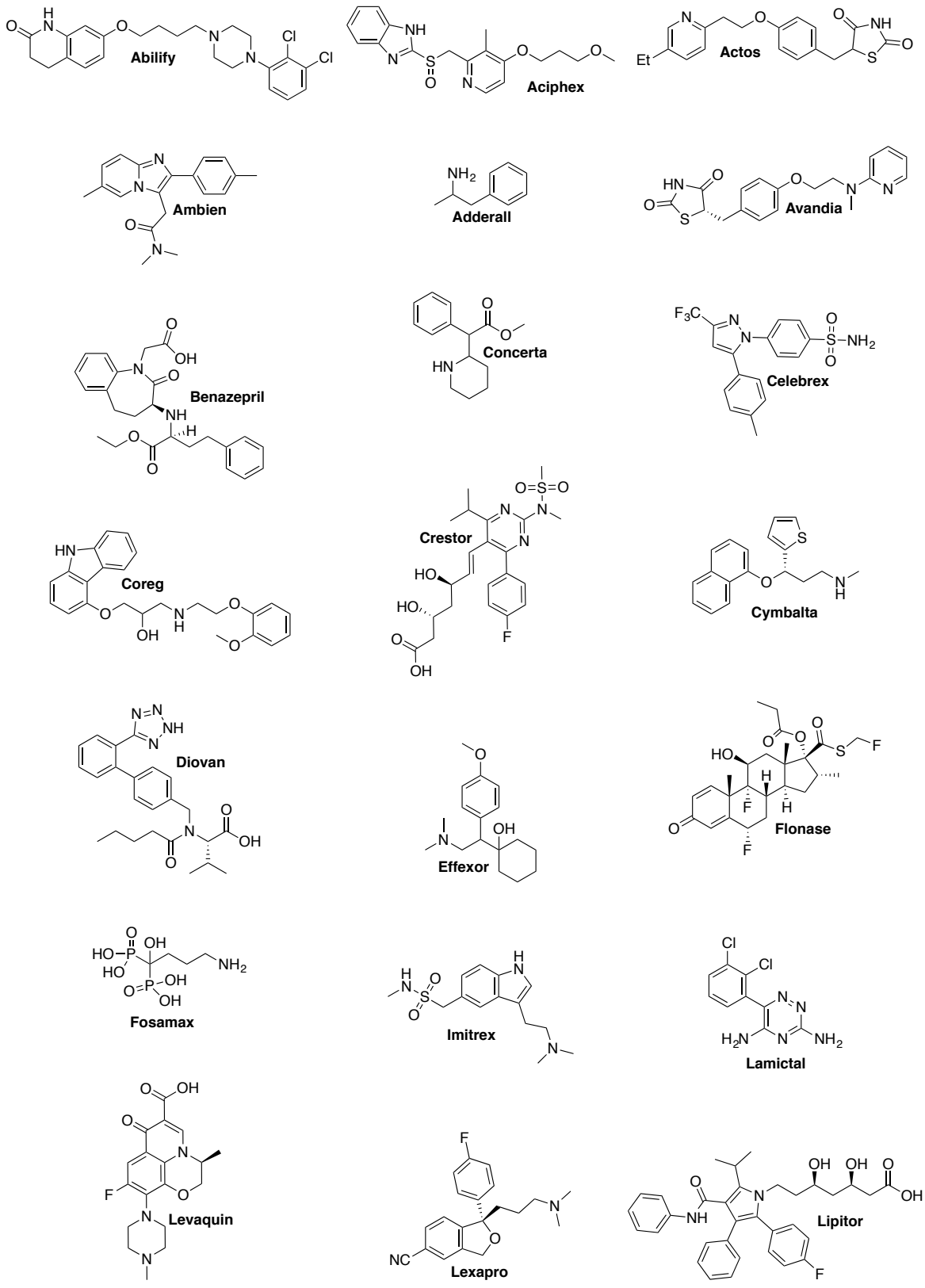
Supplementary Figure 2. Principal component analysis (PCA) of ODRE-derived libraries. **(a)** PCA plot of PC1 vs. PC2 **(b)** PCA plot of PC1 vs. PC3. **(c)** PCA plot of PC3 vs. PC2. PCA of 41 tandem ODRE benzannulated medium rings (ODRE-2nd Gen), 47 stepwise ODRE benzannulated medium rings[1] (ODRE-1st Gen), 20 benzannulated medium ring natural products (MedRingNPs), established reference sets of 40 top-selling brand-name drugs (Drugs), 60 diverse natural products (NPs), and 20 ChemBridge and ChemDiv commercial drug-like library compounds using 20 structural and physicochemical descriptors.[1,2] The hypothetical average structure for each series (-AVG) is also shown. The original 20-dimensional data set is plotted onto two dimensional unitless, orthogonal axes (principal components) that represent linear combinations of the original 20 parameters where PC1–PC3 represents 75% of the total variation. See **Supplementary Data Set 1** for complete data processing.

[1] Bauer, R. A.; Wenderski, T. A.; Tan, D. S. *Nat. Chem. Biol.* **2013**, *9*, 21–29.
[2] Wenderski, T. A.; Stratton, C. F.; Bauer, R. A.; Kopp, F.; Tan, D. S. *Methods Mol. Biol.* **2015**, *1263*, 225-242.

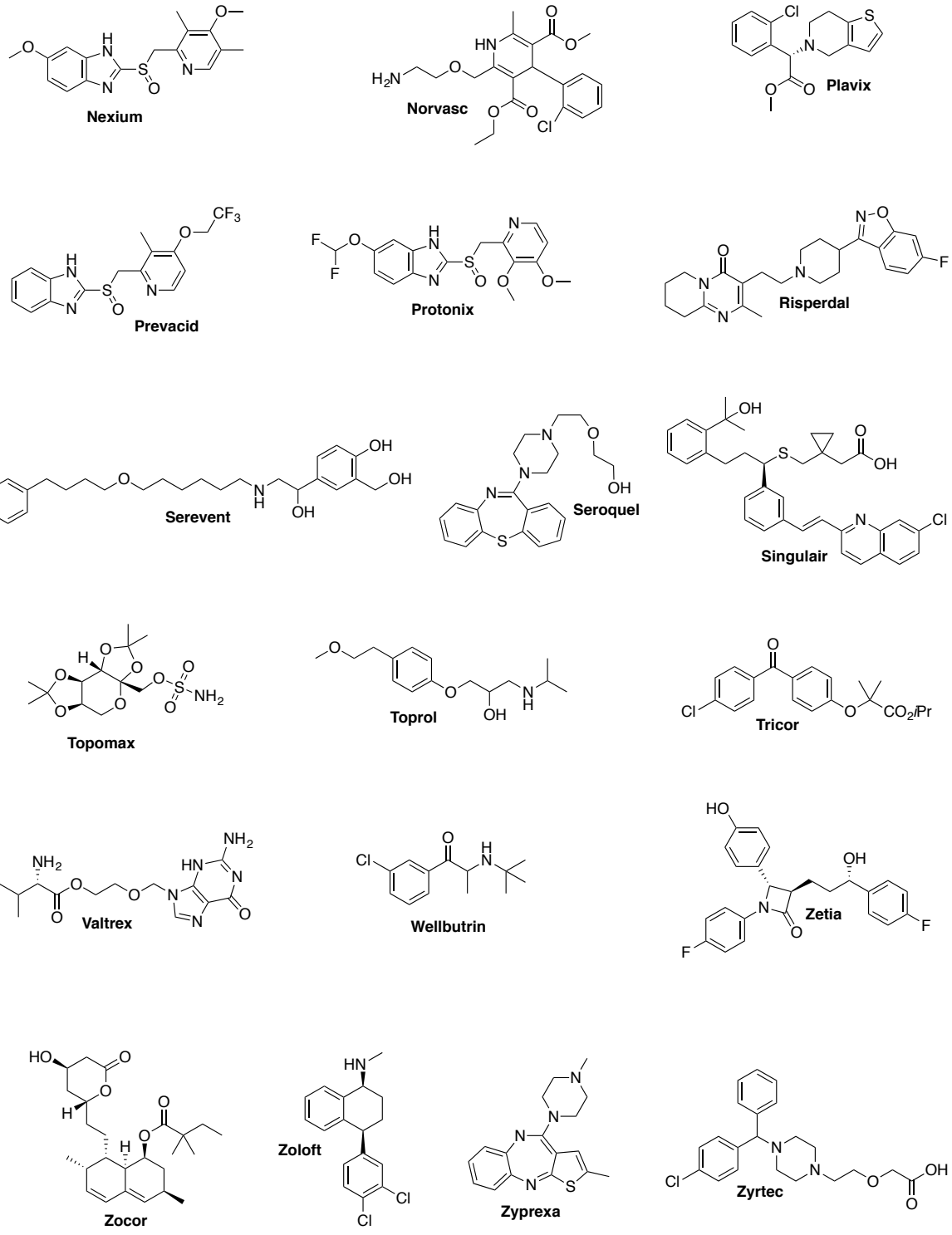


	PC1	PC2	PC3
MW	-0.312554	-0.179073	0.015039
N	-0.187274	0.043014	-0.367426
O	-0.313215	-0.035012	0.104677
HBD	-0.302214	0.097077	-0.084014
HBA	-0.327574	-0.011876	-0.045735
RotB	-0.251458	-0.067920	-0.104932
nStereo	-0.289493	-0.038301	0.249275
tPSA	-0.326318	0.034925	-0.077212
Rings	-0.179278	-0.257688	-0.054761
RngAr	-0.008266	-0.227010	-0.470162
RngSys	-0.173171	-0.176910	-0.308747
RngLg	-0.138396	-0.154937	0.217396
Fsp3	-0.141544	0.177261	0.414319
LogD	0.177760	-0.371644	0.168556
VWSA	-0.305140	-0.179553	0.076642
relPSA	-0.181137	0.325598	-0.160681
ALOGPs	0.101133	-0.471462	0.084948
ALOGpS	0.020975	0.473083	-0.026065
nStMW	-0.217035	0.088594	0.318484
RRSys	-0.017278	-0.114127	0.240469

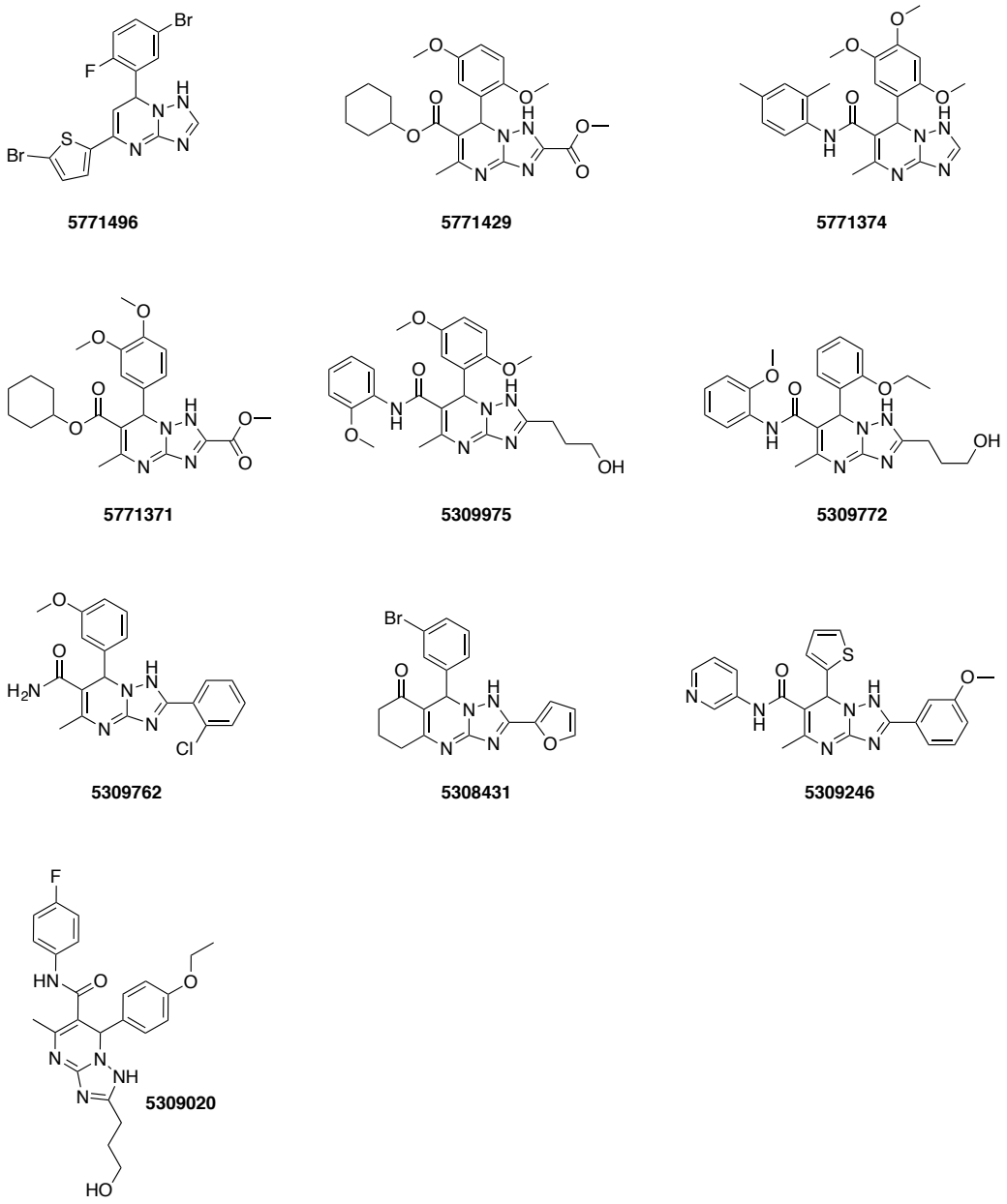
Supplementary Figure 3. Biplots and component loadings for PCA of tandem and stepwise ODRE libraries with benzannulated medium ring natural products and established reference sets. The biplots for **(a)** PC1 vs. PC2 **(b)** PC1 vs. PC3 **(c)** PC3 vs. PC2. **(d)** Component loadings of the 20 structural and physicochemical descriptors for the first three principal components that show the relative influence of each descriptor in the PCA plots. The top five most influential descriptors are highlighted in yellow.



Supplementary Figure 4. Structures of the 40 highest-selling brand-name drugs for PCA.

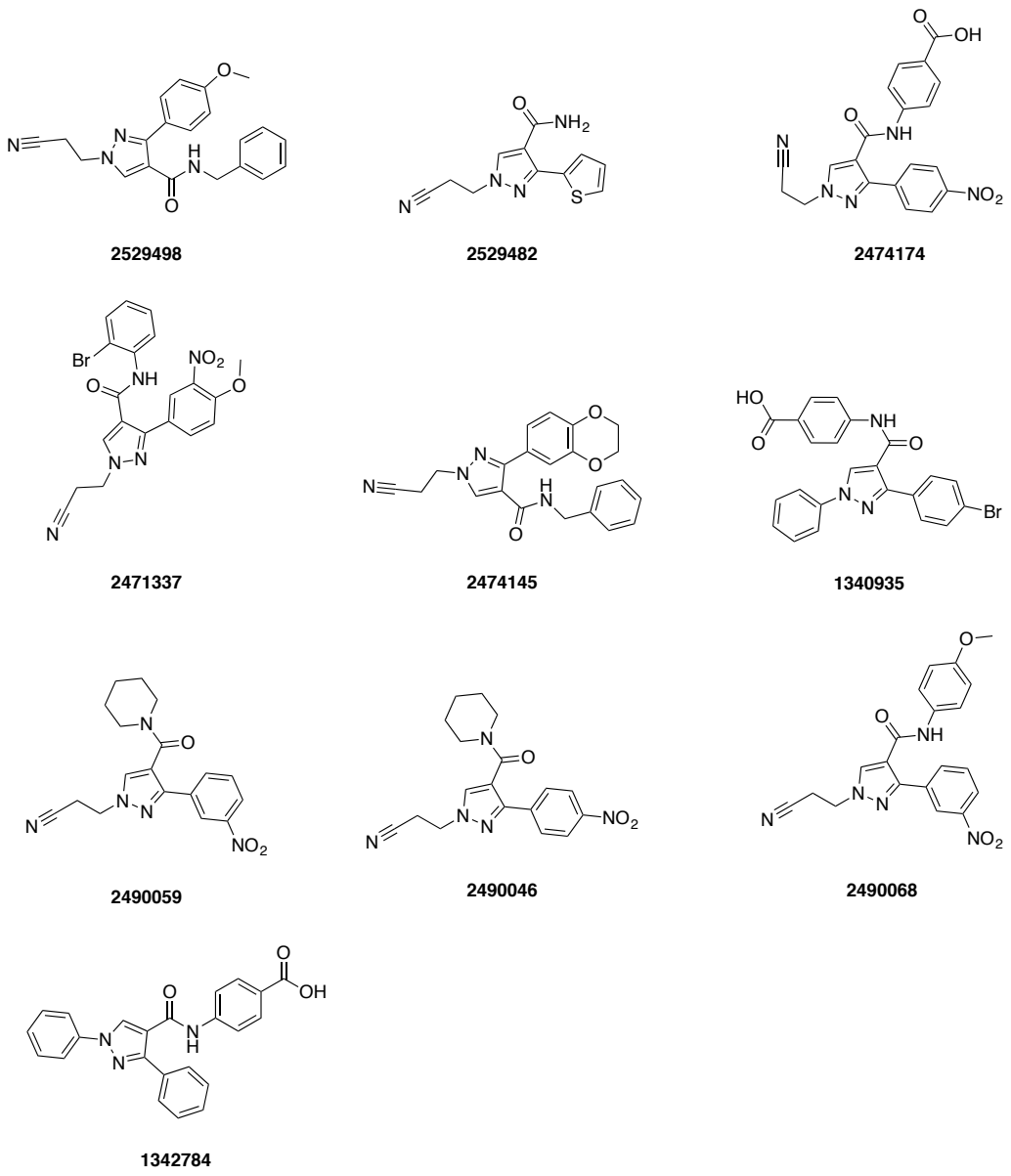


Supplementary Figure 4. Structures of the 40 highest-selling brand-name drugs for PCA (continued).

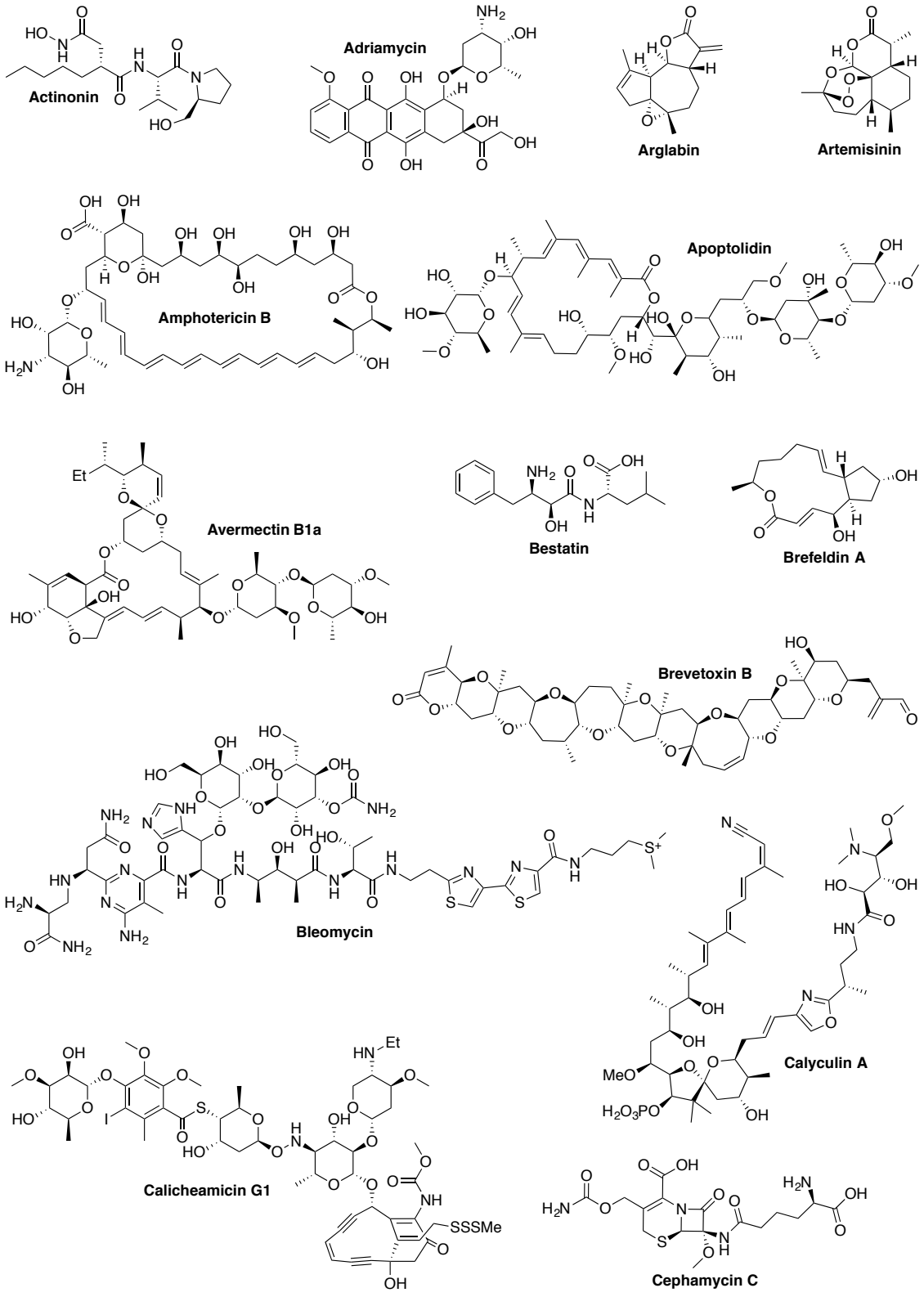


Supplementary Figure 5. Structures of 10 commercial drug-like library compounds from ChemBridge used in PCA. (PubChem[3] Compound ID numbers are indicated.)

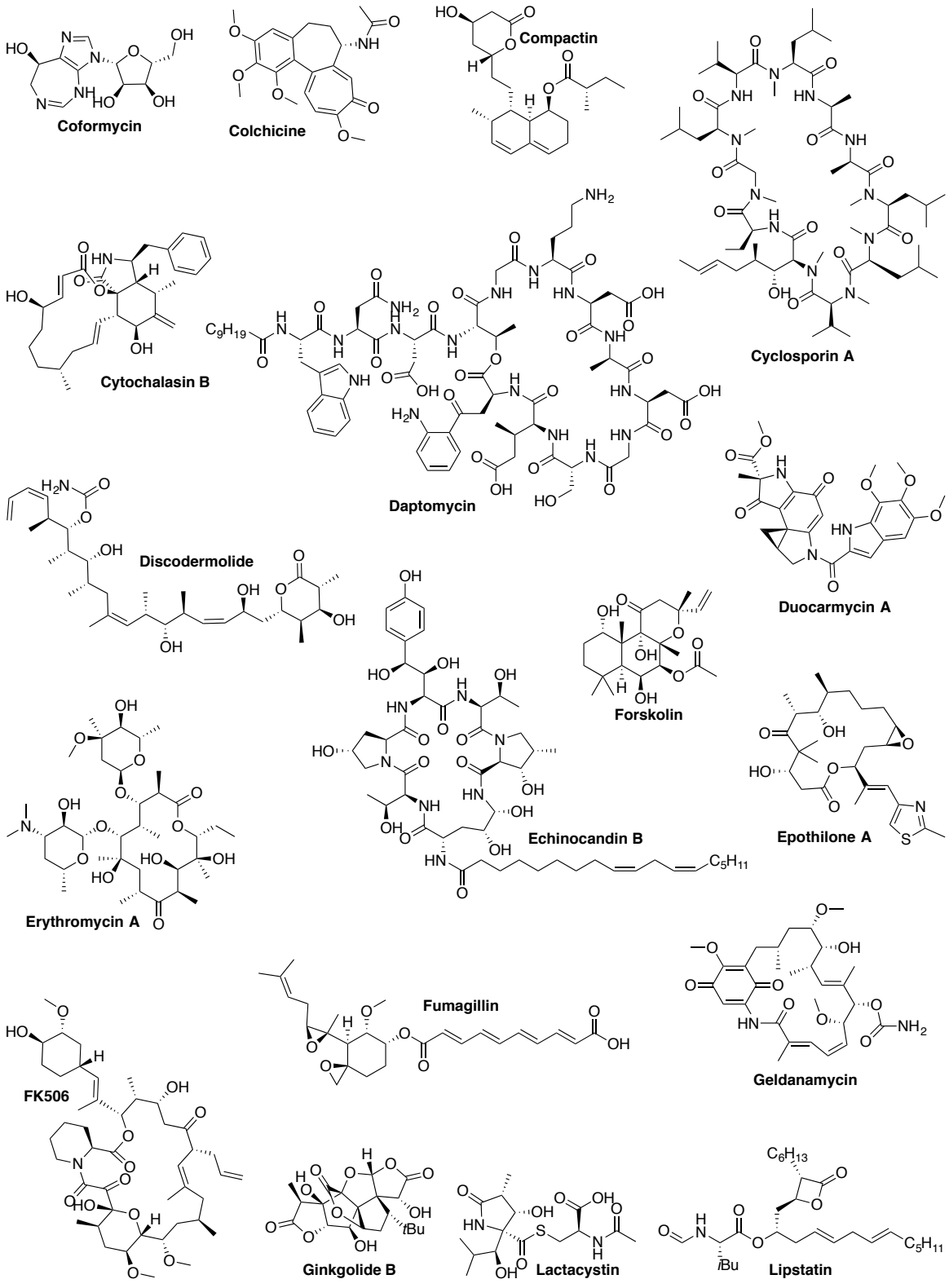
[3] For the PubChem database, see: https://pubchem.ncbi.nlm.nih.gov/search/



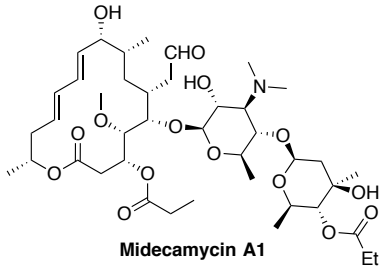
Supplementary Figure 6. Structures of 10 commercial drug-like library compounds from ChemDiv used in PCA. (PubChem[3] Compound ID numbers are indicated.)

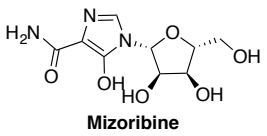


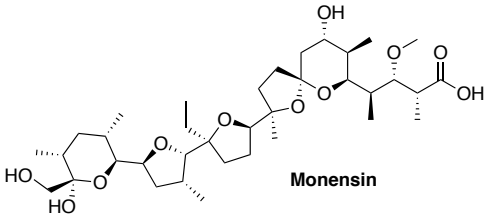
Supplementary Figure 7. Structures of 60 diverse natural products used in PCA.

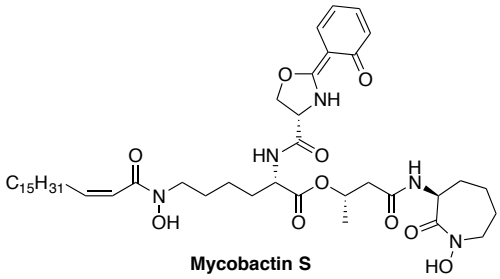


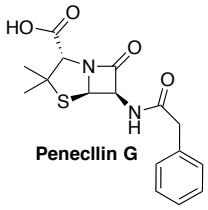
Supplementary Figure 7. Structures of 60 diverse natural products used in PCA (continued).

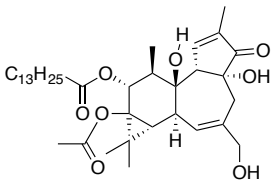


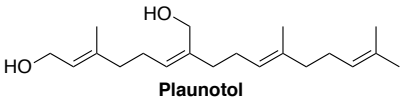


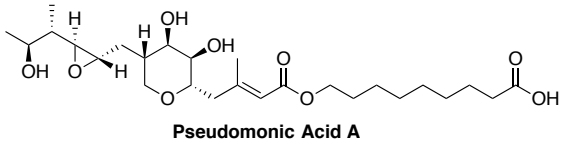


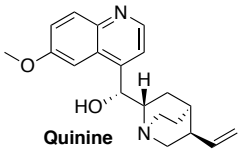


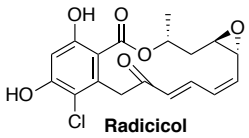


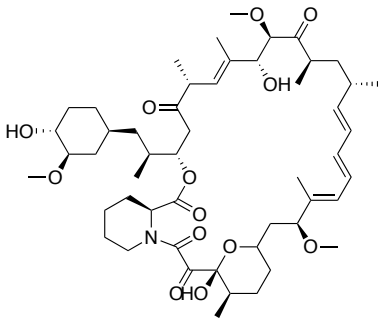


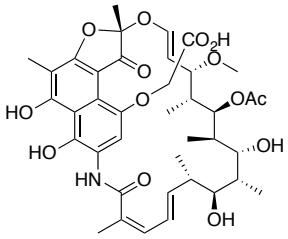


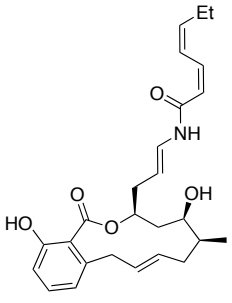


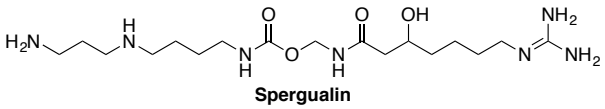


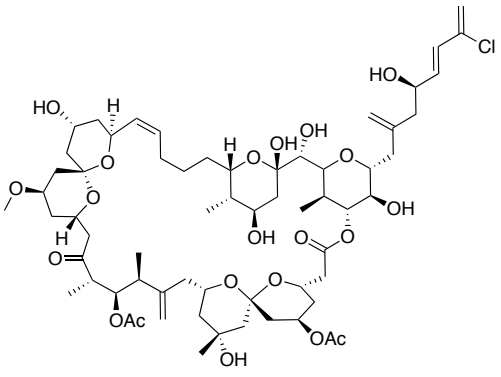




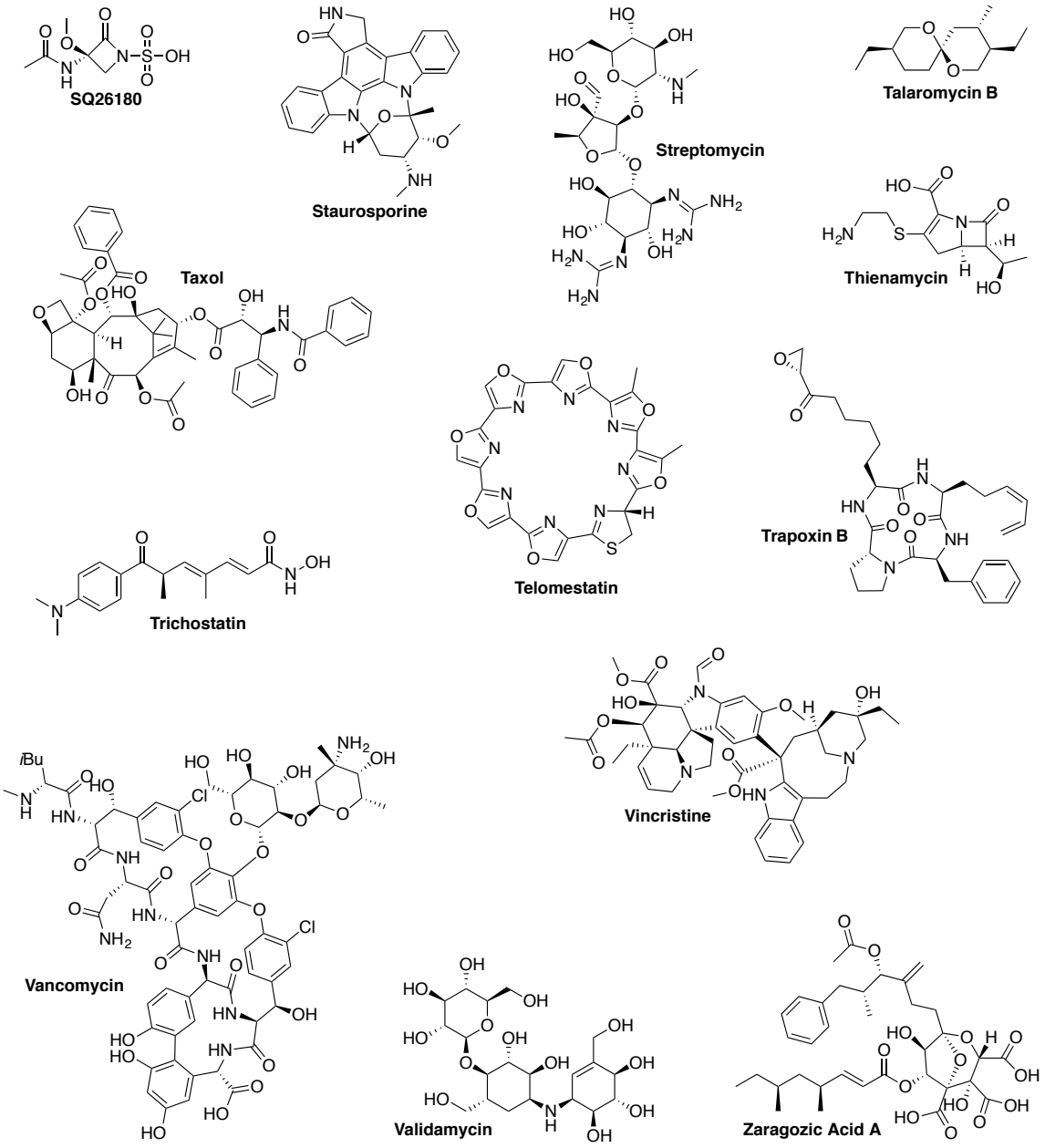




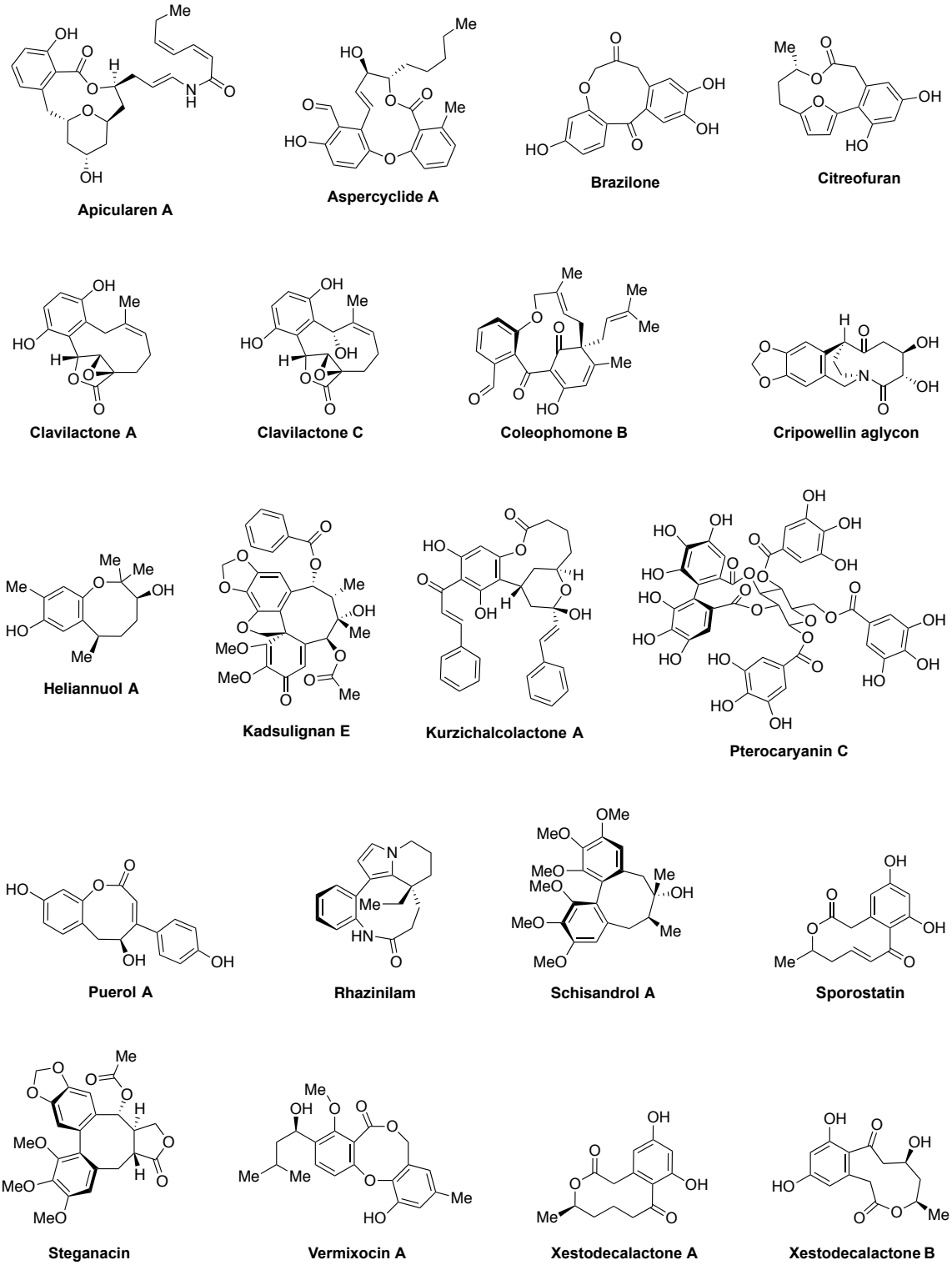




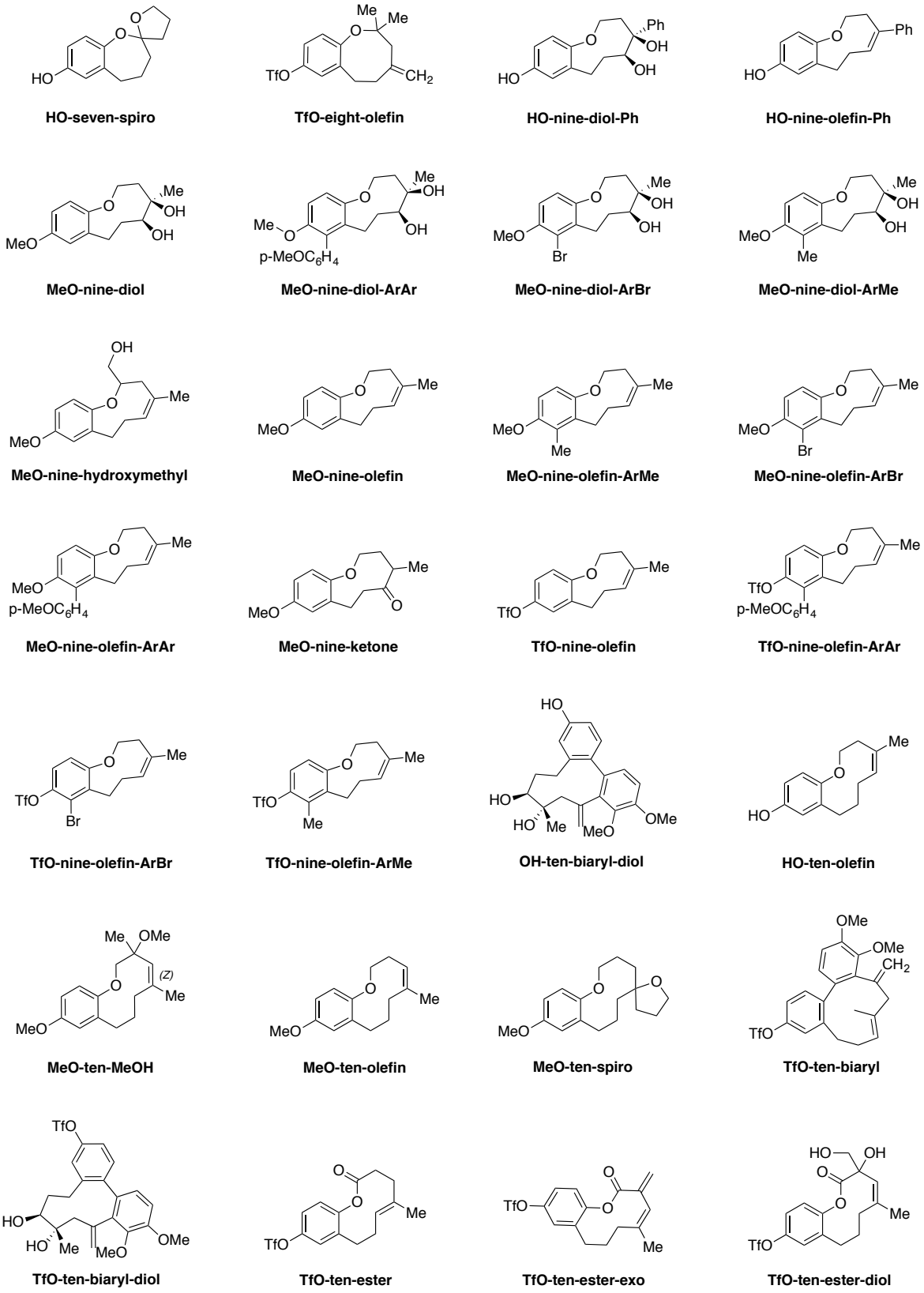
Supplementary Figure 7. Structures of 60 diverse natural products used in PCA (continued).



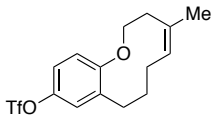
Supplementary Figure 7. Structures of 60 diverse natural products used in PCA (continued).



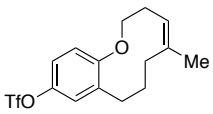
Supplementary Figure 8. Structures of 20 benzannulated medium ring natural products used in PCA.



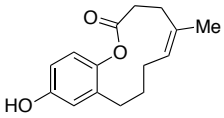
Supplementary Figure 9. Structures of 47 synthetic benzannulated medium rings derived from stepwise ODRE (1st Gen)[1] used in PCA.



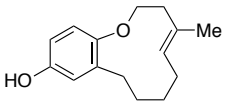
TfO-ten-olefin-5,7



TfO-ten-olefin-6,6



HO-eleven-ester



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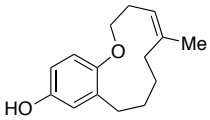

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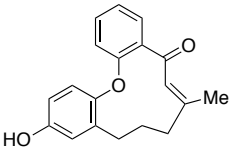

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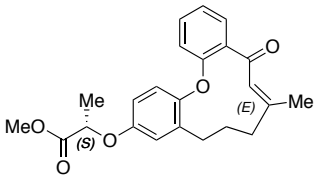

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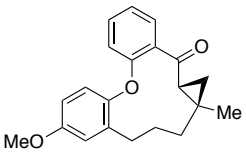

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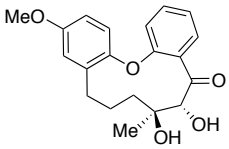

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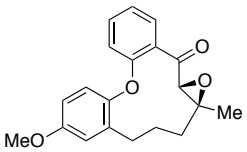
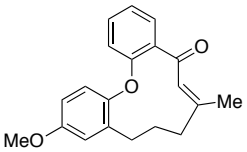


MeO-eleven-epoxidation



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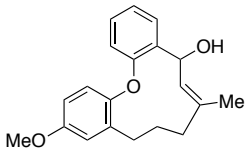

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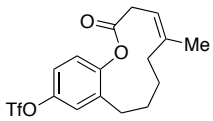

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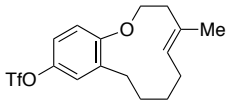
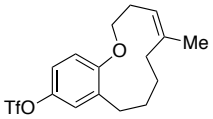


TfO-eleven-olefin-5,8



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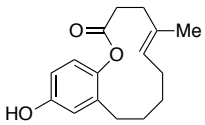

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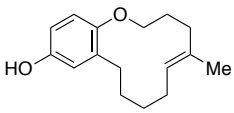

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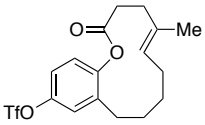

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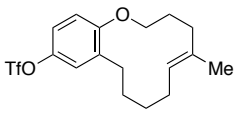

TfO-twelve-olefin

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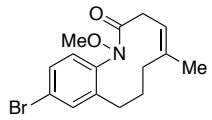
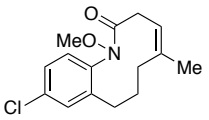
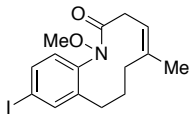


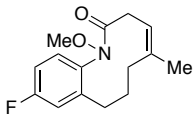
Br-ten-olefin-N(OMe)lactam
3a



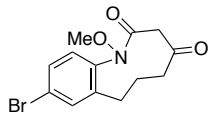
Cl-ten-olefin-N(OMe)lactam
3b



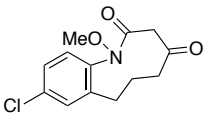
I-ten-olefin-N(OMe)lactam
3c



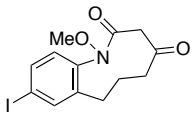
F-ten-olefin-N(OMe)lactam
3d



Br-nine-ketone-N(OMe)lactam
9a



Cl-nine-ketone-N(OMe)lactam
9b



I-nine-ketone-N(OMe)lactam
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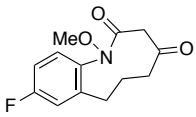
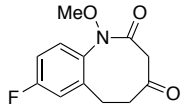
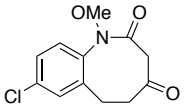


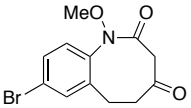
F-nine-ketone-N(OMe)lactam
9d



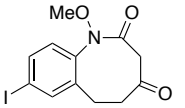
F-eight-ketone-N(OMe)lactam
11a



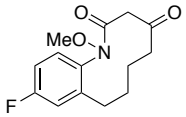
Cl-eight-ketone-N(OMe)lactam
11b



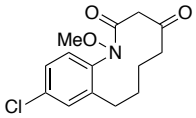
Br-eight-ketone-N(OMe)lactam
11c



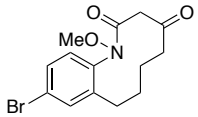
I-eight-ketone-N(OMe)lactam
11d



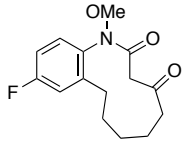
F-ten-ketone-N(OMe)lactam
13a



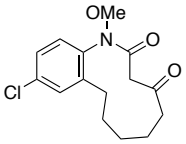
Cl-ten-ketone-N(OMe)lactam
13b



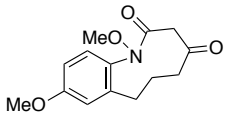
Br-ten-ketone-N(OMe)lactam
13c



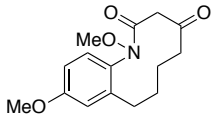
F-eleven-ketone-N(OMe)lactam
15a



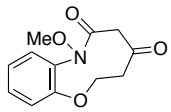
Cl-eleven-ketone-N(OMe)lactam
15b



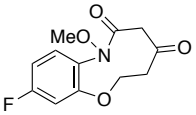
MeO-nine-ketone-N(OMe)lactam
17



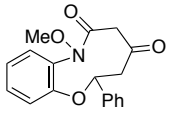
MeO-ten-ketone-N(OMe)lactam
19



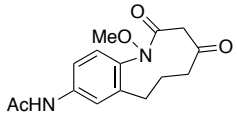
endo(O)-nine-ketone-N(OMe)lactam
21a



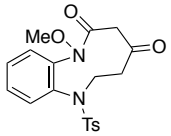
F-endo(O)-nine-ketone-N(OMe)lactam
21b



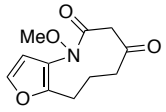
endo(O)-Ph-nine-ketone-N(OMe)lactam
23



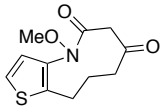
NHAc-nine-ketone-N(OMe)lactam
25



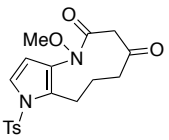
endo(NTs)-nine-ketone-N(OMe)lactam
27



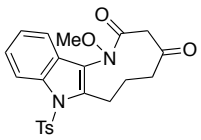
furan-nine-ketone-N(OMe)lactam
30



thiophene-nine-ketone-N(OMe)lactam
31

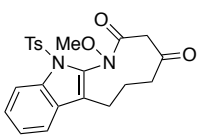


NTs-pyrrole-nine-ketone-N(OMe)lactam
33

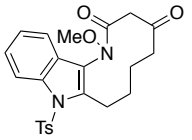


NTs-indole-C3-nine-ketone-N(OMe)lactam
35

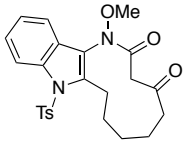
Supplementary Figure 10. Structures of 41 synthetic benzannulated medium rings derived from tandem ODRE (2nd Gen) used in PCA.



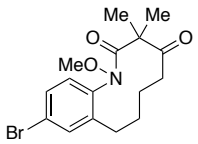
NTs-indole-C2-nine-ketone-N(OMe)lactam
37



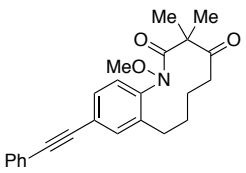
NTs-indole-C3-ten-ketone-N(OMe)lactam
39



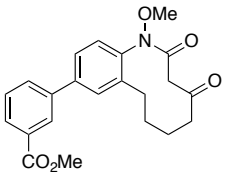
NTs-indole-C3-eleven-ketone-N(OMe)lactam
41



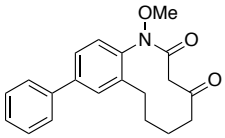
Br-ten-GemdiMe-ketone-N(OMe)lactam
47



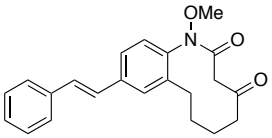
PhCC-ten-GemdiMe-ketone-N(OMe)lactam
48



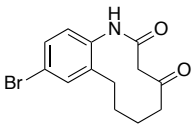
***m*-CO_2MePh-ten-ketone-N(OMe)lactam**
49



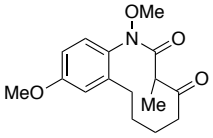
Ph-ten-ketone-N(OMe)lactam
50



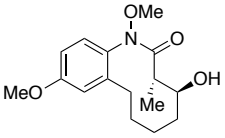
(*E*)-styrenyl-ten-ketone-N(OMe)lactam
51



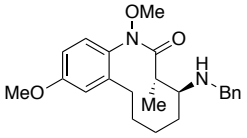
Br-ten-ketone-N(H)lactam
52



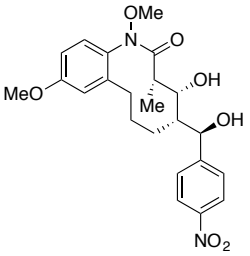
MeO-ten-αMe-ketone-N(OMe)lactam
53



MeO-ten-*anti*αMeβOH-N(OMe)lactam
54



MeO-ten-*anti*αMeβNHBn-N(OMe)lactam
55



MeO-ten-*anti*1,3diol-N(OMe)lactam
56

Supplementary Figure 10. Structures of 41 synthetic benzannulated medium rings derived from tandem ODRE (2nd Gen) used in PCA (continued).

B. PRINCIPAL COMPONENT ANALYSIS

Principal component analysis was conducted following the detailed protocols described in the literature.[1,2,4,5,6] The analysis compared the tandem ODRE library members to our original stepwise ODRE products as well as to our previously established reference set of drugs, commercial drug-like library memberes, and natural products.

1. PCA COMPOUND PROFILES

A total of 228 compounds were analyzed by PCA (**Supplementary Fig. 4-10**):

- 40 top-selling brand-name, small-molecule drugs by revenue in 2006[5]
- 10 drug-like pyrrazolecarboxamides in the MLSMR from ChemBridge
- 10 drug-like dihydrotriazolopyrimidines in the MLSMR from ChemDiv
- 60 natural products with diverse structures and biological activities
- 20 benzannulated medium ring natural products
- 47 synthetic benzannulated medium rings derived from stepwise ODRE[1]
- 41 synthetic benzannulated medium ring lactams derived from tandem ODRE (this work)

Average values for each parameter were calculated using Excel within each compound series. These seven hypothetical average molecules for each compound series were also included in the PCA.

Supplementary Table 1. Compounds analyzed by PCA.

Series	Compounds			
Top Selling Brand-Name Small-Molecule Drugs (40 entries)	abilify	crestor	lipitor	topamax
	aciphex	cymbalta	nexium	toprol
	actos	diovan	norvasc	tricor
	adderall	effexor	plavix	valtrex
	ambien	flonase	prevacid	wellbutrin
	avandia	fosamax	protonix	zetia
	benazepril	imitrex	risperdal	zocor
	celebrex	lamictal	serevent	zoloft
	concerta	levaquin	seroquel	zyprexa
	coreg	lexapro	singulair	zyrtec
ChemBridge Library (10 entries)	*PubChem CIDs:*	5771429	5309975	5308431
		5771374	5309772	5309246
	5771496	5771371	5309762	5309020
ChemDiv Library (10 entries)	*PubChem CIDs:*	2529482	2474145	2490046
		2474174	1340935	2490068
	2529498	2471337	2490059	1342784
Natural Products (60 entries)	actinonin	colchicine	lactacystin	spergualin
	adriamycin	compactin	lipstatin	spongistatin1
	amphotericinb	cyclosporina	midecamycina1	sq26180
	apoptolidin	cytochalasinb	mizoribine	staurosporine
	arglabin	daptomycin	monensin	streptomycin
	artemisinin	discodermolide	mycobactins	talaromycinb

[4] Kopp, F.; Stratton, C. F.; Akella, L. B.; Tan, D. S. *Nat. Chem. Biol.* **2012**, *8*, 358–365.
[5] Moura-Letts, G.; DiBlasi, C. M.; Bauer, R. A.; Tan, D. S. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 6745–6750.
[6] Bauer, R. A.; Wurst, J. M.; Tan, D. S. *Curr. Opin. Chem. Biol.* **2010**, *14*, 308–314.

	avermectinb1a	duocarmycina	penicilling	taxol
	bestatin	echinocandinb	phorbolma	telomestatin
	bleomycin	epothilonea	plaunotol	thienamycin
	brefeldina	erythromycina	pseudomonicacida	trapoxinb
	brevetoxinb	fk506	quinine	trichostatin
	calicheamicing1	forskolin	radicicol	validamycin
	calyculina	fumagillin	rapamycin	vancomycin
	cephamycinc	geldanamycin	rifamycinb	vincristine
	coformycin	ginkgolideb	salicylihalamidea	zaragozicacida
Benzannulated Medium Ring Natural Products (20 entries)	apicularenA	clavilactoneC	kurzichalcolactoneA	sporostatin
	aspercyclideA	coleophomoneB	pterocaryaninC	steganacin
	brazilone	cripowellinaglycon	puerolA	vermixocinA
	citreofuran	heliannuolA	rhazinilam	xestodecalactoneA
	clavilactoneA	kadsulignanE	schisandrolA	xestodecalactoneB
Benzannulated Medium Ring Library Derived from Stepwise ODRE (47 entries)[1]	HO-eleven-ester	MeO-eleven-cycloprop	MeO-nine-olefin-ArAr	TfO-nine-olefin-ArBr
	HO-eleven-olefin-58	MeO-eleven-diol	MeO-nine-olefin-ArBr	TfO-nine-olefin-ArMe
	HO-eleven-olefin-67	MeO-eleven-epoxidation	MeO-nine-olefin-ArMe	TfO-ten-biaryl
	HO-eleven-olefin-ArOAr	MeO-eleven-olefin	MeO-ten-MeOH	TfO-ten-biaryl-diol
	HO-nine-diol-Ph	MeO-eleven-reduction	MeO-ten-olefin	TfO-ten-ester
	HO-nine-olefin-Ph	MeO-nine-diol	MeO-ten-spiro	TfO-ten-ester-diol
	HO-seven-spiro	MeO-nine-diol-ArAr	TfO-eight-olefin	TfO-ten-ester-exo
	HO-ten-biaryl-diol	MeO-nine-diol-ArBr	TfO-eleven-ester	TfO-ten-olefin-57
	HO-ten-olefin	MeO-nine-diol-ArMe	TfO-eleven-olefin-58	TfO-ten-olefin-66
	HO-twelve-ester	MeO-nine-hydroxymethyl	TfO-eleven-olefin-67	TfO-twelve-ester
	HO-twelve-olefin	MeO-nine-ketone	TfO-nine-olefin	TfO-twelve-olefin
	lactate-eleven-olefin-S	MeO-nine-olefin	TfO-nine-olefin-ArAr	
Benzannulated Medium Ring Library Derived from Tandem ODRE (41 entries)	**3a**	**11d**	**25**	**49**
	3b	**13a**	**27**	**50**
	3c	**13b**	**30**	**51**
	3d	**13c**	**31**	**52**
	9a	**15a**	**33**	**53**
	9b	**15b**	**35**	**54**
	9c	**17**	**37**	**55**
	9d	**19**	**39**	**56**
	11a	**21a**	**41**	
	11b	**21b**	**47**	
	11c	**23**	**48**	

Supplementary Table 2. Average structural and physicochemical parameters by compound series.

AVGs	Drugs	NPs	ChemBridge	ChemDiv	MedRingNPs	ODRE_1st Gen	ODRE_2nd Gen
MW	361.0	629.0	381.5	446.5	385.7	319.6	319.7
N	2.2	2.6	4.3	4.7	0.2	0.0	1.2
O	2.9	9.7	3.1	3.4	6.8	3.7	3.5
HBD	1.5	4.9	1.1	1.9	2.7	0.7	0.1
HBA	5.4	10.8	5.9	7.7	6.8	3.0	3.5
RotB	6.3	9.7	5.3	6.1	2.7	1.9	1.7
nStereo	1.4	9.1	0.0	1.0	2.3	0.6	0.2
tPSA	68.9	183.2	102.9	93.6	106.7	49.7	55.9
Rings	2.9	3.8	3.2	4.2	3.6	2.4	2.4
RngAr	2.1	1.0	2.9	2.9	1.8	1.3	1.4
RngSys	2.1	2.0	3.1	3.1	1.5	1.1	1.3
RngLg	5.9	11.1	5.9	6.0	9.4	10.0	9.5
Fsp3	0.4	0.6	0.2	0.3	0.4	0.4	0.4
LogD	1.7	0.5	2.2	2.6	2.8	4.2	3.1
VWSA*	5.3	9.3	5.0	5.8	5.3	4.6	4.5
relPSA	0.1	0.2	0.2	0.2	0.2	0.1	0.1
ALOGPs	2.8	2.1	3.3	2.7	2.7	4.0	2.3
ALOGpS	-3.9	-3.8	-4.0	-3.8	-3.5	-4.3	-3.4
nStMW**	3.7	13.9	0.0	0.0	5.8	1.6	0.7
RRSys	1.4	2.3	1.0	1.4	2.9	2.2	1.9

Adjustments made for clarity:

* = VWSA ÷ 100

** = nStMW × 1000

2. PCA DESCRIPTORS

A set of 20 physicochemical descriptors (**Supplementary Table 3**) for all 228 compounds was obtained from PubChem and/or calculated using cheminformatics tools (Instant JChem[7] and VCCLab[8,9]) and ChemDraw. The resulting Excel spreadsheet (**Supplementary Data Set 1**) was used in the cheminformatic analysis of 228 compounds.

Supplementary Table 3. 20 structural and physicochemical descriptors.

Parameter	Description	Method of Determination
MW	molecular weight	Instant JChem
N	number of nitrogens	Instant JChem
O	number of oxygens	Instant JChem
HBD	number of hydrogen bond donors	Instant JChem
HBA	number of hydrogen bond acceptors	Instant JChem
RotB	number of rotatable bonds	Instant JChem
nStereo	number of stereocenters	Instant JChem
tPSA	topological polar surface area	Instant JChem
Rings	number of rings	Instant JChem
RngAr	number of aromatic rings	Instant JChem
RngSys	number of ring systems	Instant JChem
RngLg	number of atoms in largest ring outline	Instant JChem
Fsp3	fraction of sp^3-hybridized carbons	Instant JChem
LogD	calc n-octanol/water distribution coefficient	Instant JChem
VWSA	Van der Waals surface area	Instant JChem
relPSA	relative polar surface area	Instant JChem
ALOGPs	calc *n*-octanol/water partition coeff (alt)	http://www.vcclab.org
ALOGpS	calculated aqueous solubility	http://www.vcclab.org
nStMW	nStereo ÷ MW (stereochemical density)	Microsoft Excel
RRSys	Rings ÷ RngSys (ring complexity)	Microsoft Excel

[7] For Instant JChem; see: https://www.chemaxon.com/
[8] Tetko, I.V. Virtual Computational Chemistry Laboratory; http://www.vcclab.org/lab/alogps/
[9] Tetko, I.V.; Tanchuk, V.Y.; Kasheva, T.N.; Villa, A.E.P. *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 246–252.

3. PCA PLOTS

Following the computational protocol described in the literature,[1,2] the first three principal components (PC1–PC3) were obtained using R, an open source statistical computing package.[10] These top three principal components account for 74.6% of the cumulative variance in the complete data set (**Supplementary Table 4** and **Supplementary Data Set 1**). They were then plotted on newly generated, unitless, orthogonal axes (principal components) that are based on linear combinations of the original 20 parameters (**Supplementary Table 3**, and **Supplementary Data Set 1**). The PCA graphs shown in **Supplementary Fig. 2** were generated using an alternative data visualization software called Prism.[11]

Supplementary Table 4. Standard deviation and contribution for each principal component in PCA plot (summary information from R).

	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10
Standard deviation	2.957	1.828	1.681	1.289	1.013	0.827	0.689	0.533	0.488	0.420
Proportion of Variance	0.437	0.167	0.141	0.083	0.051	0.034	0.024	0.014	0.012	0.009
Cumulative Proportion	0.437	0.604	0.746	0.829	0.880	0.914	0.938	0.952	0.964	0.973
	PC11	**PC12**	**PC13**	**PC14**	**PC15**	**PC16**	**PC17**	**PC18**	**PC19**	**PC20**
Standard deviation	0.394	0.329	0.287	0.251	0.222	0.189	0.165	0.110	0.091	0.059
Proportion of Variance	0.008	0.005	0.004	0.003	0.002	0.002	0.001	0.001	0.000	0.000
Cumulative Proportion	0.981	0.986	0.990	0.993	0.996	0.997	0.999	0.999	1.000	1.000

[10] For the R project for statistical computing, see: https://www.r-project.org/
[11] For Prism, see: http://www.graphpad.com

C. MATERIALS AND METHODS

Reagents were obtained from Aldrich Chemical (www.sigma-aldrich.com) or Acros Organics (www.fishersci.com) and used without further purification. Lithium bis(trimethylsilyl)amide solution (1.0 M in THF) was obtained from Aldrich in SureSeal bottles. Optima grade solvents were obtained from Fisher Scientific (www.fishersci.com), degassed with Ar, and purified on a solvent drying system as described[12] unless otherwise indicated. Reactions were performed in flame-dried glassware under positive Ar pressure with magnetic stirring. Rubber septa and syringes were used for the transfer of liquid reagents and solutions. Cold baths were generated as follows: 0 °C, ice/water; –78 °C, dry ice/acetone.

TLC was performed on 0.25 mm E. Merck silica gel 60 F254 plates and visualized under UV light (254 nm) or by staining with potassium permanganate ($KMnO_4$) or cerium ammonium molybdenate (CAM). Flash chromatography was performed on E. Merck 230–400 mesh silica gel 60.

IR spectra were recorded on a Bruker Optics Tensor 27 FTIR spectrometer with the Pike technologies MIRacle ATR (attenuated total reflectance, ZnSe crystal) accessory and peaks reported in cm^{-1}. NMR spectra were recorded on a Bruker UltraShield Plus 500 MHz Avance III NMR or UltraShield Plus 600 MHz Avance III NMR with DCH CryoProbe at 24 °C in $CDCl_3$ unless otherwise indicated. Spectra were processed using Mnova (www.mestrelab.com/software/mnova-nmr) software, and chemical shifts are expressed in ppm relative to TMS (^1H, 0 ppm) or solvent signals: $CDCl_3$ (^{13}C, 77.0 ppm), C_6D_6 (^1H, 7.16 ppm; ^{13}C, 128.0 ppm), methanol-d_4 (^1H, 3.31 ppm; ^{13}C, 49.0 ppm), DMSO-d_6 (^1H, 2.50 ppm; ^{13}C, 39.50 ppm), or acetone-d_6 (^{13}C, 206.2 ppm); coupling constants are expressed in Hz. In the ^{13}C NMR data, reported signal multiplicities are related to C-F coupling unless noted otherwise. High resolution mass spectra were obtained at the MSKCC Analytical Core Facility on a Waters Acuity Premiere XE TOF LC-MS by electrospray ionization (ESI)

Compounds not cited in the paper are numbered herein from **S7**.

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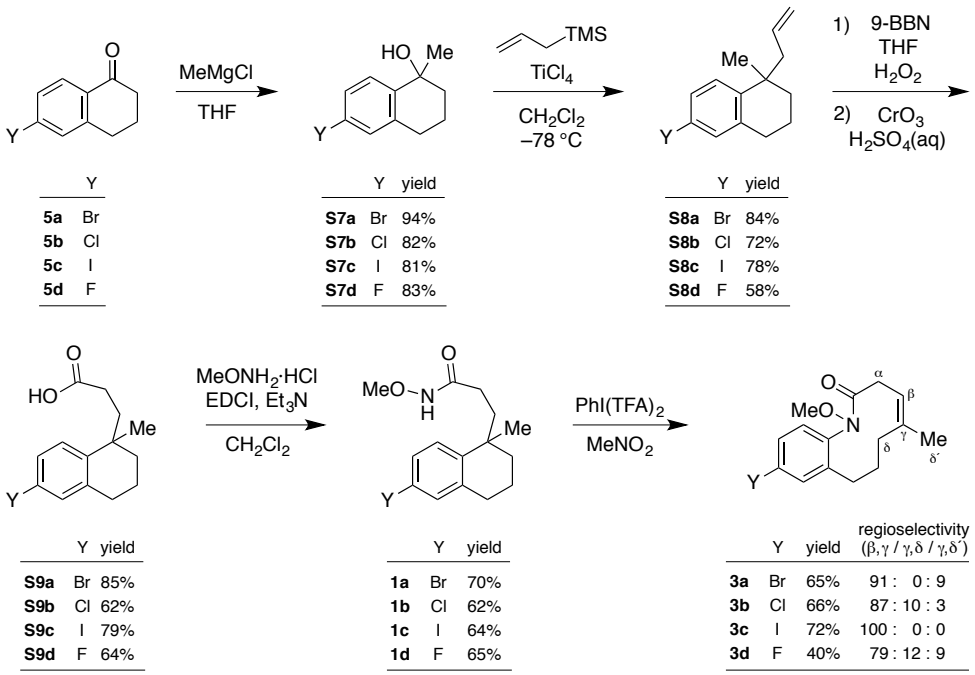
[12] Pangborn, A.B.; Giardello, M.A.; Grubbs, R.H.; Rosen, R.K; Timmers, F. *Organometallics* **1996**, *15*, 1518–1520.

D. SYNTHESIS OF OLEFIN-CONTAINING BENZANNULATED MEDIUM RING LACTAMS

1. SYNTHESIS OF LACTAMS 3A–3D



	Y
5a	Br
5b	Cl
5c	I
5d	F

	Y	yield
S7a	Br	94%
S7b	Cl	82%
S7c	I	81%
S7d	F	83%

	Y	yield
S8a	Br	84%
S8b	Cl	72%
S8c	I	78%
S8d	F	58%

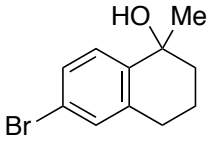
	Y	yield
S9a	Br	85%
S9b	Cl	62%
S9c	I	79%
S9d	F	64%

	Y	yield
1a	Br	70%
1b	Cl	62%
1c	I	64%
1d	F	65%

	Y	yield	regioselectivity (β,γ / γ,δ / γ,δ´)
3a	Br	65%	91 : 0 : 9
3b	Cl	66%	87 : 10 : 3
3c	I	72%	100 : 0 : 0
3d	F	40%	79 : 12 : 9

Supplementary Figure 11. Synthesis of 10-membered haloaromatics 3a–3d.

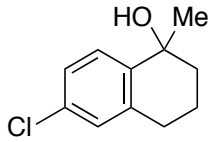
a. General procedure for nucleophilic addition of Grignard reagents to ketones 5a–5d



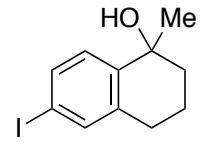
6-Bromo-1-methyl-1,2,3,4-tetrahydronaphthalen-1-ol (S7a). 6-bromo-1-tetralone **5a**[13] (296 mg, 1.31 mmol, 1.00 equiv) was dissolved in THF (15 mL) and cooled to 0 °C. A solution of MeMgCl (3.0 M in THF, 0.88 mL, 2.6 mmol, 2.0 equiv) was added by syringe and the reaction was stirred for 12 h or until complete conversion had occurred as judged by TLC. The reaction was then re-cooled to 0 °C and quenched with satd aq NH_4Cl, and diluted with EtOAc. The aqueous layer was extracted with EtOAc (4 × 20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (10% → 15% EtOAc in hexanes) yielded **S7a** as a colorless oil (298 mg, 94%). Compound **S7a** is known in the literature.[14]

[13] For preparation of 6-bromo-1-tetralone **5a**, see: Cui, L.-Q.; Dong, Z.-L.; Liu, K.; Zhang, C. *Org. Lett.*, **2011**, *13*, 6488–6491.

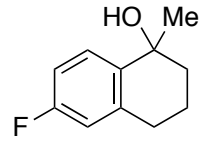
[14] Kumar, S., Sharma, R., Halder, S., Sawargave, S. P., Deore, V. B. PCT. Int. Appl. WO 2015125085 A1 Aug 27, 2015.



6-Chloro-1-methyl-1,2,3,4-tetrahydronaphthalen-1-ol (S7b).[15] Isolated as a colorless oil (311 mg, 82%). **TLC**: R_f 0.12 (9:1 hexanes/EtOAc). **IR** (NaCl, film): 3357 (O–H st), 2938, 1594, 1481, 1185, 1103, 931, 882, 821. **^{1}H-NMR** (600 MHz): δ 7.52 (d, 1H, J = 8.4 Hz), 7.17 (dd, 1H, J = 8.4, 2.0 Hz), 7.06 (dd, 1H, J = 2.2, 1.0 Hz), 2.86 – 2.68 (m, 2H), 1.99 – 1.85 (m, 3H), 1.85 – 1.77 (m, 1H), 1.53 (s, 3H). **^{13}C-NMR** (151 MHz): δ 141.3, 138.2, 132.6, 128.4, 127.9, 126.5, 70.3, 39.6, 30.8, 29.8, 20.3. **HRMS** (ESI) *m/z* calcd for $C_{11}H_{12}Cl$ ($[M–H_2O+H]^+$) 179.0628; found 179.0629.



6-Iodo-1-methyl-1,2,3,4-tetrahydronaphthalen-1-ol (S7c).[16] Isolated as a colorless oil (697 mg, 81%). **TLC**: R_f 0.21 (9:1 hexanes/EtOAc). **IR** (NaCl, film): 3362 (O–H st), 2935, 1583, 1477, 1400, 1103, 1048, 818. **^{1}H-NMR** (600 MHz): δ 7.52 (d, 1H, J = 1.8 Hz), 7.44 (d, 1H, J = 1.8 Hz), 7.32 (d, 1H, J = 8.3 Hz), 2.82 – 2.65 (m, 2H), 1.98 – 1.84 (m, 3H), 1.84 – 1.74 (m, 1H), 1.52 (s, 3H). **^{13}C-NMR** (151 MHz): δ 142.6, 138.8, 137.5, 135.4, 128.4, 92.8, 70.5, 39.5, 30.7, 29.5, 20.2. **HRMS** (ESI) *m/z* calcd for $C_{11}H_{12}I$ ($[M–H_2O+H]^+$) 270.9984; found 270.9992.



6-Fluoro-1-methyl-1,2,3,4-tetrahydronaphthalen-1-ol (S7d).[17] Isolated as a colorless oil (250 mg, 83%). Compound **S7d** is known in the literature.[18]

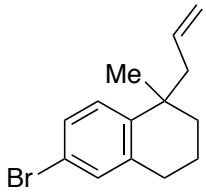
[15] For preparation of 6-chloro-1-tetralone **5b**, see: Cui, L.-Q.; Dong, Z.-L.; Liu, K.; Zhang, C. *Org. Lett.* **2011**, *13*, 6488–6491.

[16] For preparation of 6-iodo-1-tetralone **5c**, see: Murineddu, G.; Rulu, S.; Mussinu, J. M.; Loriga, G.; Grella, G. E.; Caral, M. A. M.; Lazzarl, P.; Pani, L.; Pinna, G. A. *Bioorg. Med. Chem.* **2005**, *13*, 3309–3320.

[17] For preparation of 6-fluoro-1-tetralone **5d**, see: Gavardinas, K.; Jadhav, P. K.; Wang, M. PCT Int. Appl. WO 2005/092854 A1, Feb 18, 2005.

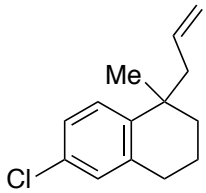
[18] a) Gavardinas, K., Jadhav, P. K., Wang, M. PCT Int. Appl. WO 2005/092854 A1, Feb 18, 2005; b) Adcock, W.; Cox, D. P. *J. Org. Chem.* **1979**, *44*, 3004–3017.

b. General procedure for Sakurai-type allylations of tetralols S7a–S7d

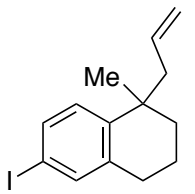


1-Allyl-6-bromo-1-methyl-1,2,3,4-tetrahydronaphthalene (S8a). Tertiary alcohol **S7a** (319 mg, 1.32 mmol, 1.00 equiv) and allyltrimethylsilane (1.1 mL, 6.9 mmol, 5.2 equiv) were dissolved in CH_2Cl_2 (15 mL) and cooled to –78 °C. A solution of $TiCl_4$ (1.0 M in toluene, 1.5 mL, 1.5 mmol, 1.1 equiv) was added by syringe and the reaction was stirred for 1 h. The reaction was quenched with satd aq $NaHCO_3$, diluted with CH_2Cl_2, allowed to warm to 24 °C and stirred for 30 min. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (100% hexanes) yielded **S8a** as a colorless oil (295 mg, 84%).

TLC: R_f 0.22 (100% hexanes). **IR** (NaCl, film): 3073, 2933, 1588, 1480, 1095, 1049, 996, 912, 815. **^{1}H-NMR** (600 MHz): δ 7.24 (dd, 1H, *J* = 8.4, 2.2 Hz), 7.20 – 7.18 (m, 1H), 7.15 (d, 1H, *J* = 8.5 Hz), 5.68 – 5.55 (m, 1H), 5.07 – 4.94 (m, 2H), 2.71 (t, 2H, *J* = 6.2 Hz), 2.46 (dd, 1H, *J* = 14.0, 6.8 Hz), 2.31 – 2.19 (m, 1H), 1.86 – 1.69 (m, 3H), 1.53 – 1.45 (m, 1H), 1.24 (s, 3H). **^{13}C-NMR** (151 MHz): δ 143.5, 139.2, 135.0, 131.7, 128.8, 128.7, 118.9, 117.5, 47.6, 36.7, 35.0, 30.4, 29.8, 19.1. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{19}Br$ ($[M+H]^+$) 265.0592; found 265.0599.

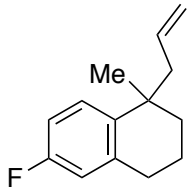


1-Allyl-6-chloro-1-methyl-1,2,3,4-tetrahydronaphthalene (S8b). Isolated as a colorless oil (249 mg, 72%). **TLC**: R_f 0.48 (100% hexanes). **IR** (NaCl, film): 3074, 2934, 1482, 1103, 913, 838, 817. **^{1}H-NMR** (600 MHz): δ = 7.21 (d, 1H, J = 8.5 Hz), 7.10 (dd, 1H, J = 8.4, 2.1 Hz), 7.03 (dt, 1H, J = 2.1, 1.0 Hz), 5.69 – 5.57 (m, 1H), 5.02 (d, 1H, J = 4.9 Hz), 5.00 (t, 1H, J = 1.2 Hz), 2.71 (t, 2H, J = 6.2 Hz), 2.46 (dd, 1H, J = 13.9, 6.9 Hz), 2.26 (dd, 1H, *J* = 13.9, 7.9 Hz), 1.85 – 1.65 (m, 3H), 1.54 – 1.46 (m, 1H), 1.24 (s, 3H). **^{13}C-NMR** (151 MHz): δ 143.0, 138.8, 135.1, 130.7, 128.7, 128.3, 125.9, 117.5, 47.6, 36.6, 35.1, 30.5, 29.8, 19.1. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{19}Cl$ ($[M+H]^+$) 221.1097; found 221.1100.



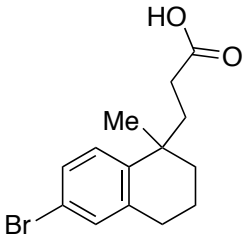
1-Allyl-6-iodo-1-methyl-1,2,3,4-tetrahydronaphthalene (S8c). Isolated as a colorless oil (585 mg, 78%). **TLC**: R_f 0.52 (100% hexanes). **IR** (NaCl, film): 3072, 2932, 1581, 1478, 1049, 913, 816. **^{1}H-NMR** (600 MHz): δ 7.44 (dd, 1H, *J* = 8.2, 1.8 Hz), 7.42 – 7.36 (m, 1H), 7.02 (d, 1H, *J* = 8.4 Hz), 5.69 – 5.55 (m, 1H), 5.02 (d, 1H, *J* = 4.2 Hz), 5.00 (s, 1H), 2.69 (t, 2H,

J = 6.3 Hz), 2.45 (dd, 1H, *J* = 13.9, 6.9 Hz), 2.25 (dd, 1H, *J* = 13.9, 7.8 Hz), 1.83 – 1.67 (m, 3H), 1.53 – 1.44 (m, 1H), 1.23 (s, 3H). **^{13}C-NMR** (151 MHz): δ 144.3, 139.6, 137.8, 135.0, 134.7, 128.9, 117.5, 90.7, 47.5, 36.7, 35.0, 30.3, 29.8, 19.0. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{19}I$ ($[M+H]^+$) 313.0453; found 313.0451.



1-Allyl-6-fluoro-1-methyl-1,2,3,4-tetrahydronaphthalene (S8d). Isolated as a yellow oil (166 mg, 58%). **TLC**: R_f 0.51 (100% hexanes). **IR** (NaCl, film): 3074, 2934, 1611, 1495, 1255, 1233, 914. **^{1}H-NMR** (600 MHz): δ 7.23 (dd, 1H, *J* = 8.7, 5.8 Hz), 6.83 (td, 1H, *J* = 8.6, 2.8 Hz), 6.73 (dd, 1H, *J* = 9.8, 2.3 Hz), 5.71 – 5.57 (m, 1H), 5.02 (d, 1H, *J* = 5.6 Hz), 5.00 (s, 1H), 2.72 (t, 2H, *J* = 6.2 Hz), 2.46 (dd, 1H, *J* = 14.0, 6.8 Hz), 2.26 (dd, 1H, *J* = 13.9, 7.8 Hz), 1.87 – 1.69 (m, 3H), 1.54 – 1.47 (m, 1H), 1.24 (s, 3H). **^{13}C-NMR** (151 MHz): δ 160.4 (d, *J* = 243.6 Hz), 140.1 (d, *J* = 3.0 Hz), 139.0 (d, *J* = 6.9 Hz), 135.2, 128.3 (d, H, *J* = 7.9 Hz), 117.3, 114.9 (d, *J* = 19.8 Hz), 112.8 (d, *J* = 20.9 Hz), 47.8, 36.5, 35.2, 30.8 (d, *J* = 1.5 Hz), 30.0, 19.1. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{19}F$ ($[M+H]^+$) 205.1393; found 205.1399.

c. General procedure for hydroboration–oxidations and Jones oxidations of allylated tetralones S8a–S8d

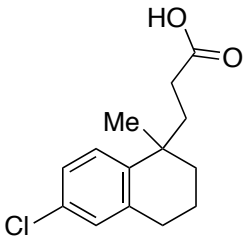


3-(6-Bromo-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)propanoic acid (S9a). Allylated intermediate **S8a** (295 mg, 1.12 mmol, 1.00 equiv) was dissolved in THF (12 mL) and cooled to 0 °C. A solution of 9-BBN (0.5 M in THF, 4.4 mL, 2.2 mmol, 2.0 equiv) was added by syringe and the reaction was stirred at 0 °C to 24 °C for 12 h. The reaction was cooled to 0 °C and aq H_2O_2 (30 wt%, 2.0 mL, 20 equiv), water (10 mL), aq NaOH (2.0 M, 2.0 mL), and EtOH (5 mL) were added sequentially. The reaction was warmed to 24 °C and stirred for 12 h. The volatile solvents were removed by rotary evaporation and EtOAc (10 mL) was added. The aqueous layer was extracted with EtOAc (4 × 20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Partial purification by silica flash chromatography (10% → 20% EtOAc in hexanes) afforded the intermediate (284 mg, 90%) containing about 15% 9-BBN byproducts that did not adversely affect the subsequent reaction. The intermediate alcohol (284 mg, 1.22 mmol, 1.00 equiv) was dissolved in acetone (12 mL) and cooled to 0 °C. A solution of Jones reagent, prepared by dissolving 670 mg CrO_3 in 1.25 mL H_2O followed by dropwise addition of 0.58 mL conc. H_2SO_4,[19] (0.60 mL) was added dropwise until an orange color persisted. The reaction was stirred at 0 °C for 1 h, then at 24 ºC for 15 min. The reaction was quenched with isopropanol and Celite

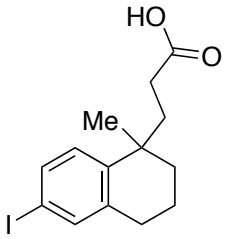
[19] Eisenbraun, E.J. *Org. Synth.* **1965,** *45*, 28.

was added. The mixture was stirred for 5 min, filtered through Celite and concentrated by rotary evaporation. In the event that water remained in the flask, the residue was redissolved in EtOAc and H_2O was added; the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (20% EtOAc in hexanes + 1% AcOH) yielded carboxylic acid **S10a** as a colorless oil (241 mg, 85% over 2 steps).

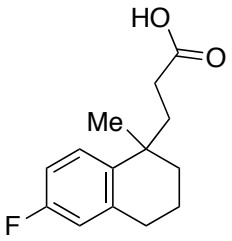
TLC: R_f 0.40 (7:3 hexanes/EtOAc + 1% AcOH). **IR** (NaCl, film): 2934, 1706 (C=O st), 1481, 1413, 1302, 1094, 818. **^{1}H-NMR** (600 MHz): δ 7.25 (dd, 1H, *J* = 8.4, 2.2 Hz), 7.21 – 7.18 (m, 1H), 7.11 (d, 1H, *J* = 8.4 Hz), 2.74 – 2.67 (t, 2H, *J* = 6.3 Hz), 2.27 (ddd, 1H, *J* = 17.1, 11.9, 5.1 Hz), 2.16 – 2.04 (m, 2H), 1.86 (ddd, 1H, *J* = 13.8, 11.7, 5.2 Hz), 1.82 – 1.74 (m, 2H), 1.73 – 1.66 (m, 1H), 1.55 (ddd, 1H, *J* = 13.4, 7.1, 2.9 Hz), 1.25 (s, 3H). **^{13}C-NMR** (151 MHz): δ 179.8, 142.3, 139.4, 131.9, 129.1, 128.4, 119.6, 37.3, 36.4, 34.8, 30.4, 30.4, 29.6, 19.2. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{16}BrO_2$ ($[M–H]^-$) 295.0334; found 295.0336.



3-(6-Chloro-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)propanoic acid (S9b). Isolated as a colorless oil (205 mg, 62% over 2 steps). **TLC**: R_f 0.43 (7:3 hexanes/EtOAc + 1% AcOH). **IR** (NaCl, film): 2935, 1706 (C=O st), 1484, 1457, 1302, 1102, 818. **^{1}H-NMR** (600 MHz): δ 7.17 (d, 1H, *J* = 8.4 Hz), 7.10 (dd, 1H, *J* = 8.4, 2.3 Hz), 7.04 (d, 1H, *J* = 2.4 Hz), 2.72 – 2.69 (m, 2H), 2.27 (ddd, 1H, *J* = 17.1, 11.8, 5.1 Hz), 2.17 – 2.03 (m, 2H), 1.87 (ddd, 1H, *J* = 13.9, 11.6, 5.1 Hz), 1.84 – 1.74 (m, 2H), 1.74 – 1.66 (m, 1H), 1.56 (ddd, 1H, *J* = 12.8, 7.0, 2.7 Hz), 1.26 (s, 3H). **^{13}C-NMR** (151 MHz): δ 179.8, 141.7, 139.0, 131.1, 128.9, 128.0, 126.2, 37.3, 36.3, 34.9, 30.5, 30.4, 29.6, 19.2. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{16}ClO_2$ ($[M–H]^-$) 251.0839; found 251.0845.

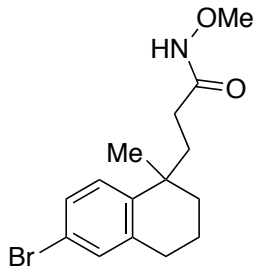


3-(6-Iodo-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)propanoic acid (S9c). Isolated as a colorless oil (508 mg, 79% over 2 steps). **TLC**: R_f 0.48 (7:3 hexanes/EtOAc + 1% AcOH). **IR** (NaCl, film): 2933, 1706 (C=O st), 1479, 1302, 815. **^{1}H-NMR** (600 MHz): δ 7.45 (dd, 1H, *J* = 8.3, 1.9 Hz), 7.41 (d, 1H, *J* = 1.6 Hz), 6.98 (d, 1H, *J* = 8.3 Hz), 2.70 (t, 2H, *J* = 6.0 Hz), 2.27 (ddd, 1H, *J* = 17.1, 11.9, 5.1 Hz), 2.16 – 2.02 (m, 2H), 1.86 (ddd, 1H, *J* = 13.9, 11.7, 5.1 Hz), 1.82 – 1.73 (m, 2H), 1.73 – 1.65 (m, 1H), 1.55 (ddd, 2H, *J* = 13.2, 7.1, 2.7 Hz), 1.25 (s, 3H). **^{13}C-NMR** (151 MHz): δ 179.0, 143.0, 139.7, 138.0, 135.0, 128.6, 91.0, 37.2, 36.5, 34.8, 30.4, 30.2, 29.4, 19.1. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{16}IO_2$ ($[M–H]^-$) 343.0195; found 343.0193.



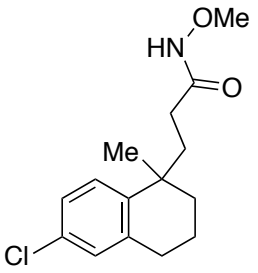
3-(6-Fluoro-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)propanoic acid (S9d). Isolated as a colorless oil (123 mg, 64% over 2 steps). **TLC**: R_f 0.48 (7:3 hexanes/EtOAc + 1% AcOH). **IR** (NaCl, film): 2935, 1707 (C=O st), 1496, 1418, 1242, 925. **^{1}H-NMR** (600 MHz): δ 7.19 (dd, 1H, *J* = 8.7, 5.8 Hz), 6.83 (td, 1H, *J* = 8.5, 2.8 Hz), 6.73 (dd, 1H, *J* = 9.7, 2.8 Hz), 2.72 (t, 2H, *J* = 6.3 Hz), 2.27 (ddd, 1H, *J* = 17.1, 11.9, 5.1 Hz), 2.16 – 2.03 (m, 2H), 1.87 (ddd, 1H, *J* = 14.4, 12.0, 5.6 Hz), 1.85 – 1.73 (m, 2H), 1.69 (td, 1H, *J* = 10.3, 3.7 Hz), 1.56 (ddd, 1H, *J* = 13.2, 7.0, 2.9 Hz), 1.26 (s, 3H). **^{13}C-NMR** (151 MHz): δ 180.0, 160.6 (d, *J* = 244.1 Hz), 139.2 (d, *J* = 7.0 Hz), 138.8 (d, *J* = 3.0 Hz), 128.1 (d, *J* = 8.0 Hz), 115.1 (d, *J* = 19.9 Hz), 113.1 (d, *J* = 21.0 Hz), 37.5, 36.2, 35.0, 30.7 (d, *J* = 1.5 Hz), 30.56, 29.6, 19.2. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{16}FO_2$ ($[M–H]^-$) 235.1134; found 235.1141.

d. General procedure for amidation of carboxylic acids S9a–S9d

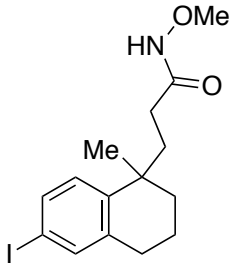


3-(6-Bromo-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methoxypropanamide (1a). Carboxylic acid **S9a** (205 mg, 0.691 mmol, 1.00 equiv) was dissolved in CH_2Cl_2 (7 mL) and methoxyamine hydrochloride (86.6 mg, 1.04 mmol, 1.50 equiv), *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (198 mg, 1.04 mmol, 1.50 equiv) and Et_3N (290 mL, 2.10 mmol, 3.00 equiv) were added sequentially. The reaction was stirred for at 24 ºC for 5 h, then quenched with satd aq NH_4Cl and diluted with CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (4 × 20 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (50% EtOAc in hexanes) yielded *N*-methoxyamide **1a** as a colorless oil (157 mg, 70%).

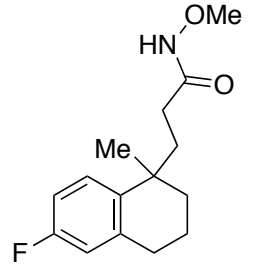
TLC: R_f 0.20 (1:1 hexanes/EtOAc). **IR** (NaCl, film): 3173, 2934, 1656 (C=O st), 1481, 1093, 820. **^{1}H-NMR** (600 MHz): δ 7.97 (s, 1H), 7.26 – 7.23 (m, 1H), 7.21 – 7.18 (m, 1H), 7.14 – 7.08 (m, 1H), 3.81 – 3.56 (m, 3H), 2.80 – 2.59 (m, 2H), 2.16 – 2.05 (m, 1H), 1.98 (s, 1H), 1.93 – 1.84 (m, 1H), 1.84 – 1.64 (m, 4H), 1.60 – 1.50 (m, 1H), 1.26 (s, 3H). **^{13}C-NMR** (151 MHz): δ 171.1, 142.3, 139.8, 131.9, 129.1, 128.5, 119.2, 64.6, 37.8, 36.6, 34.9, 30.7, 30.4, 28.7, 19.2. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{21}BrNO_2$ ($[M+H]^+$) 326.0756; found 326.0767.



3-(6-Chloro-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methoxypropanamide (1b). Isolated as a colorless oil (171 mg, 62%). **TLC**: R_f 0.24 (1:1 hexanes/EtOAc). **IR** (NaCl, film): 3173, 2935, 1654 (C=O st), 1438, 1459, 1102, 1075, 818. **^{1}H-NMR** (600 MHz): δ 8.05 (m, 1H), 7.17 (d, 1H, J = 8.6 Hz), 7.11 (dd, 1H, J = 8.4, 2.3 Hz), 7.04 (d, 1H, J = 2.2 Hz), 3.82 – 3.56 (m, 3H), 2.81 – 2.59 (m, 2H), 2.09 (t, 1H, J = 13.9 Hz), 1.98 (s, 1H), 1.90 (t, 1H, J = 13.5 Hz), 1.86 – 1.66 (m, 4H), 1.60 – 1.50 (m, 1H), 1.26 (s, 3H). **^{13}C-NMR** (151 MHz): δ 171.1, 141.7, 139.0, 131.0, 128.9, 128.1, 126.2, 64.5, 37.8, 36.5, 35.0, 30.7, 30.5, 28.7, 19.2. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{21}ClNO_2$ ($[M+H]^+$) 282.1261; found 282.1263.



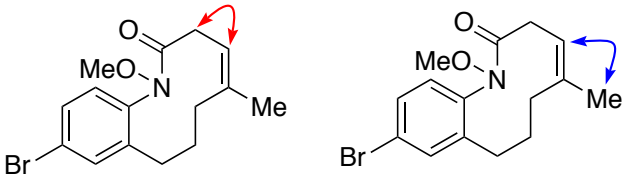
3-(6-Iodo-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methoxypropanamide (1c). Isolated as a colorless oil (353 mg, 64%). **TLC**: R_f 0.09 (6:4 hexanes/EtOAc). **IR** (NaCl, film): 2933, 1706 (C=O st), 1479, 1302, 815. **^{1}H-NMR** (600 MHz): δ 7.98 (s, 1H), 7.45 (dd, 1H, J = 8.3, 2.0 Hz), 7.43 – 7.38 (m, 1H), 6.98 (d, 1H, J = 7.6 Hz), 3.81 – 3.56 (m, 3H), 2.77 – 2.59 (m, 2H), 2.09 (t, 1H, J = 12.9, 4.3 Hz), 1.97 (s, 1H), 1.94 – 1.85 (m, 1H), 1.85 – 1.63 (m, 4H), 1.57 – 1.50 (m, 1H), 1.25 (s, 3H). **^{13}C-NMR** (151 MHz): δ 171.1, 143.0, 139.8, 137.9, 135.0, 128.7, 90.9, 64.6, 37.7, 36.7, 34.9, 30.6, 30.2, 28.7, 19.2. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{21}INO_2$ ($[M+H]^+$) 374.0617; found 374.0613.



3-(6-Fluoro-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methoxypropanamide (1d). Isolated as a colorless oil (89.5 mg, 65%). **TLC**: R_f 0.25 (1:1 hexanes/EtOAc). **IR** (NaCl, film): 3167, 2936, 1656 (C=O st), 1495, 1238, 1074. **^{1}H-NMR** (600 MHz): δ 7.96 (s, 1H), 7.24 – 7.14 (m, 1H), 6.84 (td, 1H, J = 8.5, 2.9 Hz), 6.74 (dd, 1H, J = 9.6, 2.6 Hz), 3.83 – 3.45 (m, 3H), 2.81 – 2.58 (m, 2H), 2.15 – 2.03 (m, 1H), 2.03 – 1.94 (m, 1H), 1.94 – 1.86 (m, 1H), 1.86 – 1.63 (m, 4H), 1.58 – 1.52 (m, 1H), 1.26 (s, 3H). **^{13}C-NMR** (151 MHz): δ 171.2, 160.5

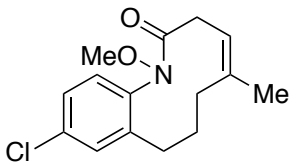
(d, J = 244.1 Hz), 139.2 (d, J = 7.0 Hz), 138.8, 128.2 (d, H, J = 8.0 Hz), 115.1 (d, J = 19.8 Hz), 113.1 (d, J = 21.1 Hz), 64.6, 38.0, 36.4, 35.1, 30.8, 30.7 (m, J = 1.5 Hz), 28.8, 19.3. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{21}FNO_2$ ($[M+H]^+$) 266.1556; found 266.1552.

e. General procedure for the oxidative dearomatization–ring expansion reaction of *N*-methoxyamides 1a–1d

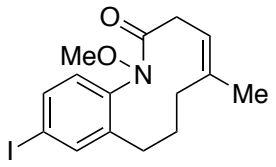


(*Z*)-10-Bromo-1-methoxy-5-methyl-3,6,7,8-tetrahydrobenzo[*b*]azecin-2(1*H*)-one (3a). *N*-methoxyamide **1a** (11.6 mg, 35.6 µmol, 1.00 equiv) was dissolved in nitromethane (0.5 mL) and cooled to 0 °C. [Bis(trifluoroacetoxy)iodo]benzene (PIFA) (2.8 mg, 71 µmol, 2.0 equiv) was added as a solid and the reaction was stirred at 0 °C to 24 ºC for 12 h. The reaction was quenched with satd aq $NaHCO_3$ and diluted with CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (4 × 20 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (30% EtOAc in hexanes) yielded 10-membered lactam **3a** as a colorless oil (7.5 mg, 65%).

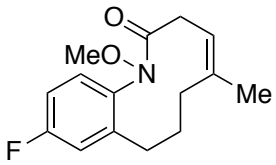
TLC: R_f 0.21 (7:3 hexanes/EtOAc). **IR** (NaCl, film): 2932, 1678 (C=O st), 1479, 1376, 1085, 1034, 984, 734. **^{1}H-NMR** (600 MHz): δ 7.59 (d, 1H, J = 2.2 Hz), 7.45 (dd, 1H, J = 8.4, 2.2 Hz), 7.21 (d, 1H, J = 8.4 Hz), 5.59 (dd, 1H, J = 11.4, 5.5 Hz), 3.69 (s, 3H), 2.87 – 2.75 (m, 2H), 2.67 – 2.52 (m, 2H), 2.02 – 1.81 (m, 2H), 1.73 (s, 3H). **^{13}C-NMR** (151 MHz): δ 168.1, 143.2, 137.9, 137.0, 132.3, 130.9, 130.5, 124.2, 119.6, 61.1, 34.1, 28.6, 26.1, 25.9, 23.2. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{19}BrNO_2$ ($[M+H]^+$) 324.0599; found 324.0609.



(*Z*)-10-Chloro-1-methoxy-5-methyl-3,6,7,8-tetrahydrobenzo[*b*]azecin-2(1*H*)-one (3b). Isolated as a colorless oil (12.8 mg, 66%). **TLC**: R_f 0.22 (7:3 hexanes/EtOAc). **IR** (NaCl, film): 2931, 1684 (C=O st), 1480, 1457, 1356, 1093, 1034, 812. **^{1}H-NMR** (600 MHz): δ 7.43 (d, 1H, J = 2.2 Hz), 7.33 – 7.26 (m, 2H), 5.59 (dd, 1H, J = 11.4, 5.4 Hz), 3.69 (s, 3H), 2.81 (t, 2H, J = 12.1 Hz), 2.65 – 2.53 (m, 2H), 2.02 – 1.92 (m, 2H), 1.89 (t, 2H, J = 11.4 Hz), 1.74 (s, 3H). **^{13}C-NMR** (151 MHz): δ 168.1, 142.9, 137.4, 137.0, 136.0, 130.3, 129.2, 127.9, 119.6, 61.6, 34.1, 28.6, 26.1, 26.0, 23.3. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{19}ClNO_2$ ($[M+H]^+$) 280.1104; found 280.1108.



(*Z*)-10-Iodo-1-methoxy-5-methyl-3,6,7,8-tetrahydrobenzo[*b*]azecin-2(1*H*)-one (3c). Isolated as a colorless oil (24.3 mg, 72%). **TLC**: R_f 0.23 (7:3 hexanes/EtOAc). **IR** (NaCl, film): 2929, 1680 (C=O st), 1477, 1354, 1034, 918. **^{1}H-NMR** (600 MHz): δ 7.79 (dd, 1H, *J* = 1.9, 0.9 Hz), 7.65 (dd, 1H, *J* = 8.4, 2.0 Hz), 7.06 (d, 1H, *J* = 8.3 Hz), 5.58 (ddd, 1H, *J* = 11.2, 5.3, 1.6 Hz), 3.68 (s, 3H), 2.81 (dd, 1H, *J* = 12.8, 11.3 Hz), 2.79 – 2.72 (m, 1H), 2.64 – 2.50 (m, 2H), 2.01 – 1.83 (m, 4H), 1.73 (s, 3H). **^{13}C-NMR** (151 MHz): δ 168.1, 143.3, 138.7, 138.4, 137.0, 136.8, 130.6, 119.6, 96.3, 61.1, 34.1, 28.6, 26.1, 25.7, 23.2. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{19}INO_2$ ($[M+H]^+$) 372.0461; found 372.0454.

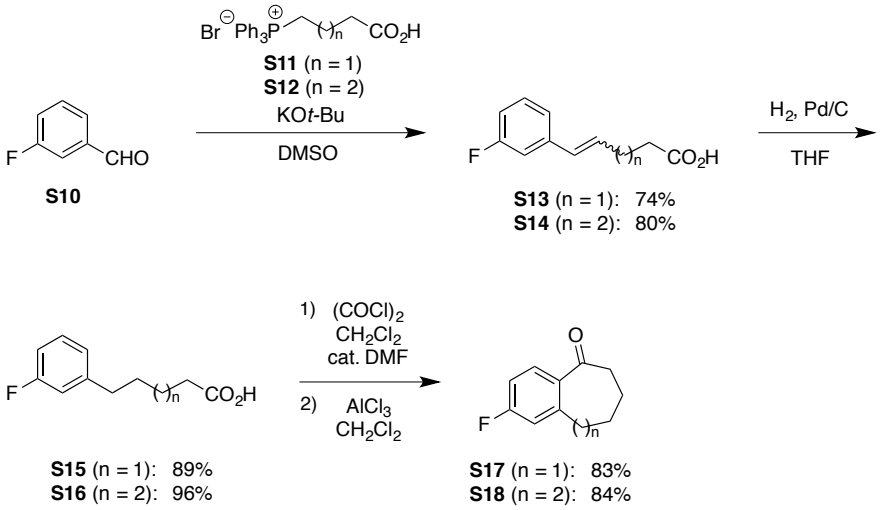


(*Z*)-10-Fluoro-1-methoxy-5-methyl-3,6,7,8-tetrahydrobenzo[*b*]azecin-2(1*H*)-one (3d). Isolated as a colorless oil (3.9 mg, 40%). **TLC**: R_f 0.22 (7:3 hexanes/EtOAc). **IR** (NaCl, film): 2932, 1681 (C=O st), 1662, 1494, 1219, 1148, 1034, 815. **^{1}H-NMR** (600 MHz): δ 7.32 (dd, 1H, *J* = 8.8, 5.5 Hz), 7.13 (dd, 1H, *J* = 9.6, 2.9 Hz), 7.03 (td, 1H, *J* = 8.8, 2.9 Hz), 5.59 (dd, 1H, *J* = 11.2, 5.5 Hz), 3.70 (s, 2H), 2.81 (dd, 2H, *J* = 12.9, 11.3 Hz), 2.67 – 2.51 (m, 2H), 2.00 – 1.89 (m, 2H), 1.91 – 1.79 (m, 2H), 1.73 (s, 3H). **^{13}C-NMR** (151 MHz): δ 168.3, 163.2 (d, *J* = 250.6 Hz), 143.8 (d, *J* = 8.1 Hz), 136.9, 134.9 (d, *J* = 3.0 Hz), 131.0 (d, *J* = 9.1 Hz), 119.7, 115.5 (d, *J* = 22.1 Hz), 115.0 (d, *J* = 22.8 Hz), 60.9, 34.1, 28.5, 26.2 (d, *J* = 1.9 Hz), 26.2, 23.3. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{19}FNO_2$ ($[M+H]^+$) 264.1400; found 264.1392.

E. SYNTHESIS OF BICYCLIC KETONE PRECURSORS

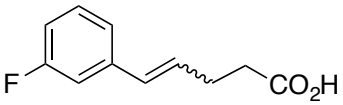
Herein we report the preparation of non-commercially available bicyclic ketones, the syntheses of which have not been reported in the literature unless otherwise indicated.

1. SYNTHESIS OF KETONES S17 AND S18



Supplementary Figure 12. Synthesis of fluorobenzosuberone and fluorobenzocyclooctanone.

a. General procedure for Wittig olefination of fluorobenzaldehyde S10

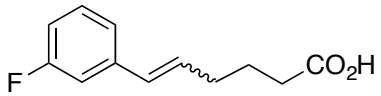


(*Z*,*E*)-5-(3-Fluorophenyl)pent-4-enoic acid S13.[20] To a suspension of (3-carboxypropyl)-triphenylphosphonium bromide **S11** (4.15 g, 9.67 mmol, 1.20 equiv) in anhydrous DMSO (10 mL) a solution of KO*t*-Bu (1.00 M in THF, 21.4 mL, 21.4 mmol, 2.65 equiv) was added by syringe over 10 min and the resulting mixture was stirred for 20 min at 24 ºC. A solution of 3-fluorobenzaldehyde **S10** (1.00 g, 8.06 mmol, 1.00 equiv) in DMSO (8 mL) was then added and the reaction was stirred for an additional 16 h at 24 ºC. The reaction was poured into 100 mL of ice water and extracted with $CHCl_3$ (3 × 20 mL). The aqueous layer was acidified with conc. HCl to a pH of 1 and extracted with $CHCl_3$ (3 × 20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 20% EtOAc in hexanes + 1% AcOH) yielded unsaturated carboxylic acid **S13** as white solid (1.16 g, 74%, *E*/*Z* 96:4).

TLC: R_f 0.43 (3:1 hexanes/EtOAc + 1% AcOH). **IR** (ATR, ZnSe): 2920, 1720 (C=O st), 1446, 1296, 1266, 1147, 973, 783, 770. **^{1}H-NMR** (600 MHz): δ 7.27 – 7.23 (m, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.04 (dt, *J* = 10.3, 1.9 Hz, 1H), 6.90 (td, *J* = 8.5, 2.7 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.26 – 6.20 (m, 1H), 2.57 – 2.54 (m, 4H). **^{13}C-NMR** (151 MHz): δ 178.9, 163.1 (d, *J* = 245.0 Hz), 139.6 (d, *J* = 7.7 Hz), 130.2 (d, *J* = 2.5 Hz), 129.9 (d, *J* = 8.4 Hz), 129.4,

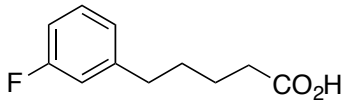
[20] Procedure was adapted from: Murineddu, G.; Ruiu, S.; Loriga, G.; Manca, I.; Lazzari, P.; Reali, R.; Pani, L.; Toma, L.; Pinna, G. A. *J. Med. Chem.* **2005**, *48*, 7351–7362.

122.0 (d, *J* = 2.7 Hz), 114.0 (d, *J* = 21.4 Hz), 112.5 (d, *J* = 21.7 Hz), 33.5, 27.8. **HRMS** (ESI) m/z calcd for $C_{11}H_{10}FO_2$ ([M–H]$^-$) 193.0665; found 193.0665.



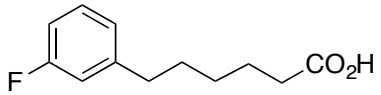
(*Z*,*E*)-6-(3-Fluorophenyl)hex-5-enoic acid (S14). Isolated as a white solid (1.35 g, 80%, *E*/*Z* 97:3). **TLC:** R_f 0.43 (3:1 hexanes/EtOAc + 1% AcOH). **IR** (ATR, ZnSe): 2935, 1707 (C=O st), 1489, 1269, 1143, 1143, 965, 777, 737. **^{1}H-NMR** (600 MHz): δ 7.28 – 7.21 (m, 1H), 7.09 (d, 1H, *J* = 7.7 Hz), 7.04 (d, 1H, *J* = 10.2 Hz), 6.89 (td, 1H, *J* = 8.4, 2.1 Hz), 6.38 (d, 1H, *J* = 15.8 Hz), 6.19 (dt, 1H, *J* = 15.7, 7.0 Hz), 2.41 (t, 2H, *J* = 7.4 Hz), 2.28 (q, 2H, *J* = 7.2 Hz), 1.83 (p, 2H, *J* = 7.4 Hz). **^{13}C-NMR** (151 MHz): δ 179.3, 163.1 (d, *J* = 244.9 Hz), 139.8 (d, *J* = 7.7 Hz), 130.8, 129.9, 129.9 (d, *J* = 11.0 Hz), 121.9 (d, *J* = 2.7 Hz), 113.8 (d, *J* = 21.4 Hz), 112.4 (d, *J* = 21.7 Hz), 33.2, 32.1, 24.0. **HRMS** (ESI) m/z calcd for $C_{12}H_{12}FO_2$ ([M–H]$^-$) 207.0821; found 207.0819.

b. General procedure for catalytic hydrogenation of olefins S13 and S14



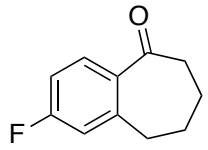
5-(3-Fluorophenyl)pentanoic acid (S15).[20] Olefinic carboxylic acid **S13** (1.00 g, 5.15 mmol, 1.00 equiv) was dissolved in EtOAc (13 mL). 5% Palladium on carbon (0.55 g) was added and the reaction was stirred for 16 h under at ambient hydrogen pressure at 24 ºC. The mixture was then filtered through a pad of Celite. The filtrate was concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 20% EtOAc in hexanes + 1% AcOH) yielded carboxylic acid **S15** as a white solid (0.90 g, 89%).

TLC: R_f 0.45 (3:1 hexanes/EtOAc + 1% AcOH). **IR** (ATR, ZnSe): 2947, 1695 (C=O st), 1487, 1408, 1260, 1201, 1147, 927. **^{1}H-NMR** (600 MHz): δ ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 – 7.21 (m, 1H), 6.94 (d, 1H, *J* = 7.6 Hz), 6.90 – 6.85 (m, 2H), 2.63 (t, 2H, *J* = 6.8 Hz), 2.39 (t, 2H, *J* = 6.7 Hz), 1.68 (p, 4H, *J* = 3.7 Hz). **^{13}C-NMR** (151 MHz): δ 179.3, 162.9 (d, *J* = 245.2 Hz), 144.5 (d, *J* = 7.1 Hz), 129.7 (d, *J* = 8.4 Hz), 124.0 (d, *J* = 2.8 Hz), 115.1 (d, *J* = 20.7 Hz), 112.7 (d, *J* = 21.0 Hz), 35.3, 33.7, 30.4, 24.1. **HRMS** (ESI) m/z calcd for $C_{11}H_{12}FO_2$ ([M–H]$^-$) 195.0821; found 195.0824.



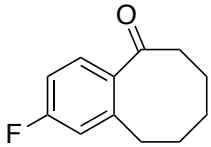
6-(3-Fluorophenyl)hexanoic acid (S16). Isolated as a white solid (1.26 g, 96%). **TLC:** R_f 0.48 (3:1 hexanes/EtOAc + 1% AcOH). **IR** (ATR, ZnSe): 2936, 1708 (C=O st), 1590, 1449, 1253, 1141, 941, 782. **^{1}H-NMR** (600 MHz): δ 7.25 – 7.20 (m, 1H), 6.94 (d, 1H, *J* = 7.6 Hz), 6.90 – 6.84 (m, 2H), 2.61 (d, 2H, *J* = 7.6 Hz), 2.36 (t, 2H, *J* = 7.5 Hz), 1.71 – 1.60 (m, 4H), 1.42 – 1.35 (m, 2H). **^{13}C-NMR** (151 MHz): δ 179.8, 162.9 (d, *J* = 245.1 Hz), 145.0 (d, *J* = 7.1 Hz), 129.6 (d, *J* = 8.3 Hz), 124.0 (d, *J* = 2.6 Hz), 115.1 (d, *J* = 20.7 Hz), 112.5 (d, *J* = 21.0 Hz), 35.4, 33.9, 30.8, 28.5, 24.4. **HRMS** (ESI) m/z calcd for $C_{12}H_{15}FO_2Na$ ([M+Na]$^+$) 233.0954; found 233.0955.

c. General procedure for intramolecular Friedel–Crafts annulation of carboxylic acids S15 and S16



2-Fluoro-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (S17).[21] Carboxylic acid **S15** (0.80 g, 4.1 mmol, 1.0 equiv) and oxalyl chloride (0.57 g, 4.5 mmol, 1.1 equiv) were dissolved in CH_2Cl_2 (8.2 mL) and cooled to 0 °C. DMF (0.1 mL) was then added and the reaction was stirred for 2 h at 24 ºC. The reaction mixture was then directly added to a suspension of $AlCl_3$ (2.72 g, 20.4 mmol, 5.00 equiv) in CH_2Cl_2 (20 mL) and stirred for 4 h at 24 ºC. The reaction was poured into 20 mL of ice water and extracted with CH_2Cl_2 (4 × 20 mL). The combined organic extracts were washed with 1 M solution of NaOH, brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 10% EtOAc in hexanes) yielded ketone **S17** as a yellow oil (0.60 g, 83%).

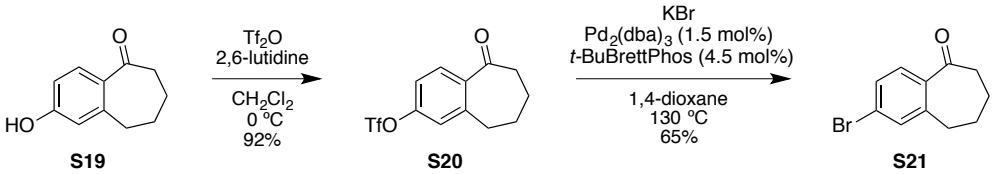
TLC: R_f 0.59 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 2943, 1677 (C=O st), 1606, 1584, 1264, 1091, 983, 870, 827. **^{1}H-NMR** (600 MHz): δ 7.77 (dd, 1H, *J* = 8.6, 6.1 Hz), 6.98 (td, 1H, *J* = 8.4, 2.5 Hz), 6.91 (dd, 1H, *J* = 9.3, 2.5 Hz), 2.95 – 2.90 (m, 2H), 2.76 – 2.71 (m, 2H), 1.92 – 1.86 (m, 2H), 1.84 – 1.79 (m, 2H). **^{13}C-NMR** (151 MHz): δ 204.4, 164.9 (d, *J* = 253.2 Hz), 144.5 (d, *J* = 8.4 Hz), 135.0 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 9.4 Hz), 116.4 (d, *J* = 21.4 Hz), 113.7 (d, *J* = 21.4 Hz), 40.7, 32.5, 24.9, 20.6. **HRMS** (ESI) m/z calcd for $C_{11}H_{11}FO$ ($[M+Na]^+$) 201.0692; found 201.0692.



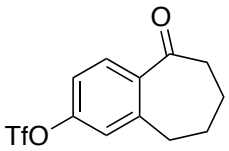
2-Fluoro-7,8,9,10-tetrahydrobenzo[8]annulen-5(6*H*)-one (S18). Isolated as a colorless oil (0.73 g, 84%). **TLC:** R_f 0.80 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 2933, 1667 (C=O st), 1603, 1582, 1253, 1233, 1104, 958, 735. **^{1}H-NMR** (600 MHz): δ 7.82 (dd, 1H, *J* = 8.7, 6.2 Hz), 6.97 (td, 1H, *J* = 8.4, 2.5 Hz), 6.89 (dd, 1H, *J* = 9.6, 2.5 Hz), 3.09 (d, 2H, *J* = 6.5 Hz), 2.96 (t, 2H, *J* = 7.0 Hz), 1.90 – 1.78 (m, 4H), 1.54 – 1.47 (m, 2H). **^{13}C-NMR** (151 MHz): δ 204.6, 164.7 (d, *J* = 252.5 Hz), 143.5 (d, *J* = 8.1 Hz), 135.8 (d, *J* = 3.0 Hz), 131.1 (d, *J* = 9.2 Hz), 117.7 (d, *J* = 21.1 Hz), 113.5 (d, *J* = 21.1 Hz), 43.5, 34.7, 27.5, 24.1 (2C). **HRMS** (ESI) m/z calcd for $C_{12}H_{14}FO$ ($[M+H]^+$) 193.1029; found 193.1036.

[21] Procedure was adapted from: Zhang, Y.; Burgess, J. P.; Brackeen, M.; Gilliam, A.; Mascarella, S. W.; Page, K.; Seltzman, H. H.; Thomas, B. F. *J. Med. Chem.* **2008**, *51*, 3526–3539.

2. SYNTHESIS OF KETONE S21

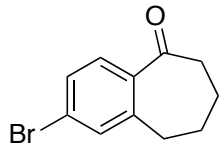


Supplementary Figure 13. Synthesis of bromobenzosuberone S21.



5-Oxo-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-2-yl trifluoromethanesulfonate (S20). 7-Hydroxy-1-benzosuberone **S19**[1] (1.25 g, 7.09 mmol, 1.00 equiv) was dissolved in CH_2Cl_2 (8 mL) and cooled to 0 °C. 2,6-Lutidine (0.860 mL, 7.45 mmol, 1.05 equiv) and a solution of trifluoromethanesulfonic anhydride (1.25 mL, 7.45 mmol, 1.05 equiv) in CH_2Cl_2 (8 mL) were then added sequentially and the reaction was stirred for 2 h at 0 ºC. The reaction was warmed to 24 ºC and diluted with CH_2Cl_2, and washed with 1 M HCl (2 × 10 mL). The combined organic extracts were then washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 10% EtOAc in hexanes) yielded triflate **S20** as an orange solid (2.0 g, 92%).

TLC: R_f 0.65 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 2944, 2870, 1683 (C=O st), 1603, 1426, 1211, 974, 844. **^{1}H-NMR** (600 MHz): δ 7.81 (d, *J* = 8.6 Hz, 1H), 7.21 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.14 (d, *J* = 2.3 Hz, 1H), 2.97 (t, *J* = 6.1 Hz, 2H), 2.76 (t, *J* = 6.2 Hz, 2H), 1.93 (p, *J* = 6.7 Hz, 2H), 1.85 (p, *J* = 6.7 Hz, 2H). **^{13}C-NMR** (151 MHz): δ 204.1, 151.4, 144.2, 138.7, 131.1, 122.3, 119.4, 118.7 (q, *J* = 320.8 Hz), 40.6, 32.5, 24.9, 20.7. **HRMS** (ESI) m/z calcd for $C_{12}H_{11}F_3O_4Na$ ($[M+Na]^+$) 331.0228; found 331.0223.



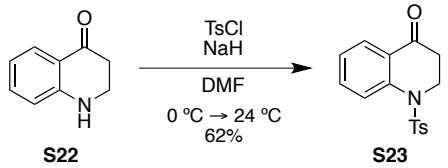
2-Bromo-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (S21).[22] To a 25-mL round-bottom flask was added potassium bromide (0.83 g, 7.0 mmol, 2.0 equiv), potassium fluoride (105 mg, 1.75 mmol, 0.500 equiv) and aryl triflate **S20** (1.1 g, 3.5 mmol, 1.0 equiv), which was evacuated and backfilled with argon three times. To a vial was added $Pd_2(dba)_3$ (48.0 mg, 52.5 µmol, 1.50 mol%) and *t*-BuBrettPhos (76.3 mg, 158 µmol, 4.50 mol%), which was evacuated and backfilled with argon three times. 1,4-Dioxane (3.5 mL) was added to the vial and the mixture was heated at 120 ºC in a preheated oil bath for 3 minutes. The catalyst solution was then cooled to 24 ºC, then it was added to the reaction mixture containing potassium bromide, potassium fluoride and aryl triflate **S20** followed by addition of 1,4-dioxane (10.5 mL). The resulting mixture was stirred at 130 ºC in a preheated oil bath for 16 h. The reaction mixture was then cooled to 24 ºC, filtered through a pad of Celite, and concentrated by rotary evaporation to afford

[22] Procedure was adapted from: Pan, J.; Wang, X. Y.; Zhang, Y.; Buchwald, S. L. *Org. Lett.* **2011**, *13*, 4974–4976.

the crude product. Purification by silica flash chromatography (0% → 20% EtOAc in hexanes) yielded ketone **S21** as an orange solid (0.54 g, 65%).

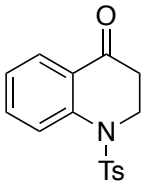
TLC: R_f 0.81 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 2941, 1676 (C=O st), 1585, 1261, 1105, 963, 824. **^{1}H-NMR** (600 MHz): δ 7.60 (d, 1H, *J* = 8.3 Hz), 7.44 (dd, 1H, *J* = 8.3, 1.8 Hz), 7.38 (d, 1H, *J* = 1.6 Hz), 2.90 (t, 2H, *J* = 6.5 Hz), 2.72 (d, 2H, *J* = 6.0 Hz), 1.89 (p, 2H, *J* = 6.7 Hz), 1.81 (p, 2H, *J* = 7.3, 6.6 Hz). **^{13}C-NMR** (151 MHz): δ 205.0, 143.2, 137.5, 132.5, 130.3, 129.9, 126.8, 40.7, 32.2, 25.0, 20.6. **HRMS** (ESI) m/z calcd for $C_{11}H_{12}BrO$ ($[M+H]^+$) 239.0072; found 239.0072.

3. SYNTHESIS OF KETONE S23



S22 **S23**

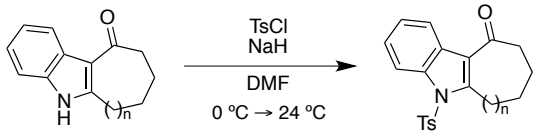
Supplementary Figure 14. Synthesis of 1-tosyl-2,3-dihydroquinolin-4(1*H*)-one S23.



1-Tosyl-2,3-dihydroquinolin-4(1*H*)-one (S23). 2,3-Dihydroquinolin-4(1*H*)-one **S22** (0.10 g, 0.68 mmol, 1.0 equiv) was dissolved in DMF (6.8 mL) and cooled to 0 ºC. NaH (27 mg, 60 % dispersion in mineral oil, 0.68 mmol, 1.0 equiv) was added and the reaction was stirred for 1 h at 0 ºC. *p*-Toluenesulfonyl chloride (0.13 g, 0.68 mmol, 1.0 equiv) was then added and the reaction was stirred for an additional 6 h at 24 ºC. The reaction was quenched slowly with satd aq NH_4Cl at 0 ºC, warmed to 24 ºC and diluted with EtOAc. The mixture was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 10% MeOH in CH_2Cl_2) yielded ketone S**23** as a yellow solid (127 mg, 62%).

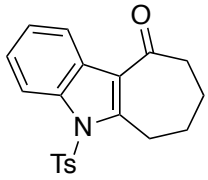
TLC: R_f 0.48 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 2941, 1687 (C=O st), 1598, 1475, 1458, 1353, 911, 736. **^{1}H-NMR** (600 MHz): δ 7.95 (dd, 1H, *J* = 7.8, 1.7 Hz), 7.87 (d, 1H, *J* = 8.3 Hz), 7.58 (td, 1H, *J* = 8.6, 8.1, 1.7 Hz), 7.55 (d, 2H, *J* = 8.3 Hz), 7.28 (d, 1H, *J* = 8.0 Hz), 7.23 (d, 2H, *J* = 8.2 Hz), 4.24 (t, 2H, *J* = 6.2 Hz), 2.40 – 2.37 (m, 5H). **^{13}C-NMR** (151 MHz): δ 192.7, 144.6, 142.3, 136.8, 134.7, 130.1, 127.7, 126.8, 125.7, 125.6, 124.6, 46.2, 36.5, 21.6. **HRMS** (ESI) m/z calcd for $C_{16}H_{16}NO_3S$ ($[M+H]^+$) 302.0851; found 302.0853.

4. SYNTHESIS OF KETONES S26 AND S27



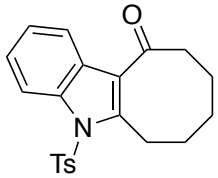
Supplementary Figure 15. Synthesis of tetrahydrocycloindolones S26 and S27.

a. General procedure for *N*-tosylation of tetrahydrocycloindolones S24 and S25



5-Tosyl-6,7,8,9-tetrahydrocyclohepta[*b*]indol-10(5*H*)-one (S26). 6,7,8,9-Tetrahydrocyclohepta[*b*]indol-10(5*H*)-one **S24**[23] (0.976 g, 4.91 mmol, 1.00 equiv) was dissolved in DMF (20 mL) and cooled to 0 ºC. NaH (0.14 g, 60% dispersion in mineral oil, 5.9 mmol, 1.2 equiv) was added and the reaction was stirred at 0 ºC for 30 min. *p*-Toluenesulfonyl chloride (1.40 g, 7.36 mmol, 1.50 equiv) was then added and the reaction was stirred at 0 ºC to 24 ºC over 12 h. The reaction was re-cooled to 0 ºC, and quenched with satd aq $NaHCO_3$ and diluted with Et_2O. The organic layer was extracted with Et_2O (4 × 20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (10% → 20% EtOAc in hexanes) yielded ketone **S26** as a light yellow solid (1.06 g, 61%).

TLC: R_f 0.28 (4:1 hexanes/EtOAc). **IR** (NaCl, film): 2941, 1655 (C=O st), 1450, 1378, 1173, 1089, 967, 751, 664 **^{1}H-NMR** (600 MHz): δ 8.25 (d, 2H, *J* = 7.8 Hz), 7.69 (d, 2H, *J* = 8.4 Hz), 7.39 – 7.30 (m, 2H), 7.28 – 7.23 (m, 2H), 3.44 (dd, 2H, *J* = 6.8, 5.0 Hz), 2.76 (dd, 2H, *J* = 7.1, 5.3 Hz), 2.38 (s, 3H), 1.95 – 1.82 (m, 4H). **^{13}C-NMR** (151 MHz): δ 199.3, 148.2, 145.6, 136.3, 136.0, 130.1, 127.3, 126.4, 125.3, 124.8, 121.7, 121.7, 114.4, 42.8, 26.1, 24.9, 21.7, 21.2. **HRMS** (ESI) *m/z* calcd for $C_{20}H_{20}NO_3S$ ($[M+H]^+$) 354.1164; found 354.1147.



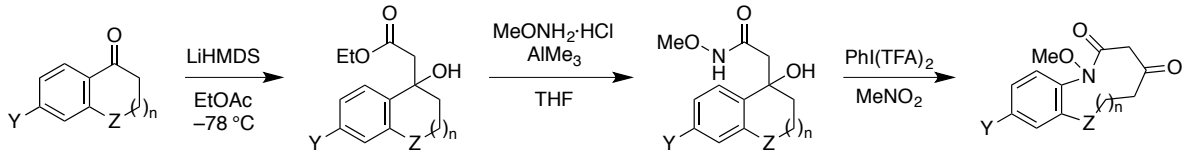
5-Tosyl-5,6,7,8,9,10-hexahydro-11*H*-cycloocta[*b*]indol-11-one (S27).[24] Isolated as a light yellow oil (681 mg, 46%). **TLC**: R_f 0.29 (4:1 hexanes/EtOAc). **IR** (NaCl, film): 2933, 1647 (C=O st), 1476, 1392, 1374, 1177, 1048, 751. **^{1}H-NMR** (500 MHz): δ 8.33 – 8.23 (m, 2H), 7.70

[23] For preparation of 6,7,8,9-tetrahydrocyclohepta[*b*]indol-10(5*H*)-one **S24**, see: Oikawa, Y.; Yonemitsu, O. *J. Org. Chem.* **1977**, *42*, 1213–1216.

[24] For preparation of 7,8,9,10-tetrahydro-5H-cycloocta[*b*]indol-11(6*H*)-one **S25**, see: Talez, O.; Saracoglu, N. *Tetrahedron*, **2010**, *66*, 1902–1910.

(d, 2H, J = 8.4 Hz), 7.37 – 7.29 (m, 2H), 7.26 – 7.23 (m, 2H), 3.55 (t, 2H, J =6.6 Hz), 2.89 (t, 2H, J = 7.1 Hz), 2.38 (s, 3H), 1.87 – 1.73 (m, 4H), 1.55 – 1.47 (m, 2H). **^{13}C-NMR** (126 MHz): δ 199.6, 145.5, 144.6, 136.4, 136.2, 130.2, 127.6, 126.4, 125.2, 124.7, 122.3, 121.9, 114.3, 43.1, 26.3, 24.5, 24.0, 23.2, 21.6. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{22}NO_3S$ ($[M+H]^+$) 368.1320; found 368.1314.

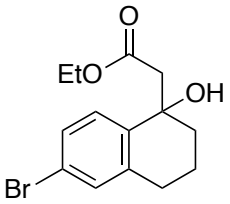
F. SYNTHESIS OF KETONE-CONTAINING BENZANNULATED MEDIUM-RING LACTAMS



Supplementary Figure 16. Three-step synthesis of medium-ring lactams from bicyclic ketones.

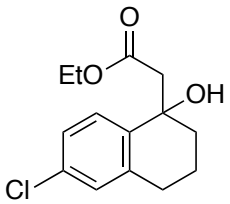
1. SYNTHESIS OF β-HYDROXYESTERS

a. General procedure for preparation of β-hydroxyesters



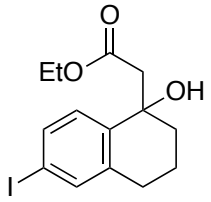
Ethyl 2-(6-bromo-1-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)acetate (6a). Ethyl acetate (0.65 mL, 6.7 mmol, 3.0 equiv) was dissolved in THF (13 mL) and cooled to –78 °C. A solution of LiHMDS (1.0 M in THF, 6.7 mL, 6.7 mmol, 3.0 equiv) was added by syringe over 5 min and the reaction was stirred for 1 h. A solution of 6-bromo-1-tetralone **5a**[13] (1.0 M in THF, 0.50 g, 2.2 mmol, 1.0 equiv) was then added by syringe over 5 min and the reaction was stirred for additional 4 h at –78 °C until complete conversion. The reaction was quenched slowly with satd aq NH_4Cl at –78 °C, warmed to 24 °C and diluted with EtOAc. The mixture was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 10% EtOAc in hexanes) yielded β-hydroxyester **6a** as a colorless oil (650 mg, 93%).

TLC: R_f 0.42 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3482 (O–H st), 2938, 1712 (C=O st), 1591, 1480, 1328, 1199, 1184, 1084, 1025, 823, 735. **^{1}H-NMR** (600 MHz): δ 7.44 (d, 1H, J = 8.4 Hz), 7.32 (dd, 1H, J = 8.5, 2.0 Hz), 7.24 – 7.22 (m, 1H), 4.19 (qd, 2H, J = 7.1, 2.0 Hz), 4.13 (s, 1H), 2.84 – 2.70 (m, 4H), 2.09 – 2.04 (m, 1H), 1.98 – 1.90 (m, 2H), 1.81 – 1.73 (m, 1H), 1.27 (t, 3H, J = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.4, 139.7, 138.8, 131.5, 129.4, 128.3, 121.3, 70.9, 60.9, 45.8, 36.0, 29.2, 19.8, 14.1. **HRMS** (ESI) m/z calcd for $C_{14}H_{17}BrO_3Na$ ($[M+Na]^+$) 335.0259; found 335.0247.

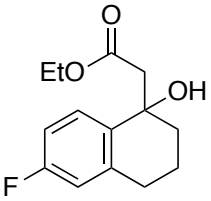


Ethyl 2-(6-chloro-1-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)acetate (S28).[15] Isolated as a yellow oil (350 mg, 94%). **TLC**: R_f 0.46 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3487 (O–H st), 2940, 1712 (C=O st), 1597, 1483, 1329, 1200, 1186, 1026, 884, 856. **^{1}H-NMR** (600 MHz): δ 7.49 (d, 1H, J = 8.5 Hz), 7.17 (dd, 1H, J = 8.5, 2.2 Hz), 7.08 – 7.05 (m, 1H), 4.19

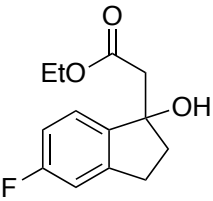
(qd, 2H, *J* = 7.2, 1.9 Hz), 4.12 (s, 1H), 2.83 – 2.70 (m, 4H), 2.10 – 2.04 (m, 1H), 1.98 – 1.91 (m, 2H), 1.81 – 1.74 (m, 1H), 1.27 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.4, 139.2, 138.4, 133.0, 128.5, 128.0, 126.5, 70.8, 60.9, 45.9, 36.1, 29.3, 19.8, 14.1. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{17}ClO_3Na$ ($[M+Na]^+$) 291.0764; found 291.0761.



Ethyl 2-(1-hydroxy-6-iodo-1,2,3,4-tetrahydronaphthalen-1-yl)acetate (S29).[16] Isolated as a colorless oil (588 mg, 89%). **TLC**: R_f 0.46 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3482 (O–H st), 2938, 1713 (C=O st), 1585, 1477, 1330, 1199, 1185, 978, 840, 735. **^{1}H-NMR** (600 MHz): δ 7.52 (d, 1H, *J* = 8.3 Hz), 7.45 (s, 1H), 7.30 (d, 1H, *J* = 8.3 Hz), 4.19 (q, 2H, *J* = 7.1 Hz), 4.12 (s, 1H), 2.83 – 2.69 (m, 4H), 2.09 – 2.03 (m, 1H), 1.98 – 1.89 (m, 2H), 1.81 – 1.72 (m, 1H), 1.27 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.4, 140.4, 139.0, 137.6, 135.3, 128.4, 93.3, 70.9, 60.9, 45.8, 36.0, 29.0, 19.8, 14.2. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{17}IO_3Na$ ($[M+Na]^+$) 383.0120; found 383.0114.

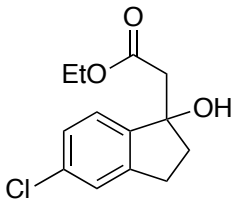


Ethyl 2-(6-fluoro-1-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)acetate (S30).[17] Isolated as a colorless oil (384 mg, 77%). **TLC**: R_f 0.51 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3436 (O–H st), 2938, 1716 (C=O st), 1613, 1589, 1496, 1329, 1235, 1195, 1029, 976, 914, 738. **^{1}H-NMR** (600 MHz): δ 7.53 (dd, 1H, *J* = 8.7, 5.8 Hz), 6.90 (td, 1H, *J* = 8.6, 2.7 Hz), 6.76 (dd, 1H, *J* = 9.6, 2.7 Hz), 4.20 (qd, 2H, *J* = 7.2, 1.6 Hz), 4.09 (s, 1H), 2.85 – 2.71 (m, 4H), 2.10 – 2.03 (m, 1H), 2.00 – 1.91 (m, 2H), 1.83 – 1.74 (m, 1H), 1.27 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.5, 161.8 (d, *J* = 244.6 Hz), 138.9 (d, *J* = 7.5 Hz), 136.4 (d, *J* = 3.0 Hz), 128.4 (d, *J* = 9.1 Hz), 114.8 (d, *J* = 20.0 Hz), 113.5 (d, *J* = 21.1 Hz), 70.8, 60.9, 46.1, 36.2, 29.6 (d, *J* = 1.5 Hz), 19.9, 14.2. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{17}FO_3Na$ ($[M+Na]^+$) 275.1059; found 275.1072.

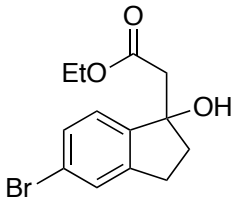


Ethyl 2-(5-fluoro-1-hydroxy-2,3-dihydro-1*H*-inden-1-yl)acetate (S31). Isolated as a colorless oil (450 mg, 95%). **TLC**: R_f 0.44 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3466 (O–H st), 2982, 1726 (C=O st), 1614, 1598, 1487, 1374, 1333, 1246, 1195, 1130, 1094, 1064, 963, 932, 864, 822, 735. **^{1}H-NMR** (600 MHz): δ 7.28 (dd, 1H, *J* = 9.0, 5.3 Hz), 6.93 – 6.89 (m, 2H), 4.21 (q, 2H, *J* = 7.1 Hz), 4.18 (s, 1H), 3.03 (dt, 1H, *J* = 16.1, 6.9 Hz), 2.86 (d, 1H, *J* = 16.0 Hz), 2.81

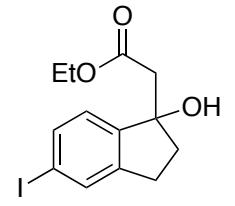
(dt, 1H, *J* = 15.7, 7.5 Hz), 2.69 (d, 1H, *J* = 16.0 Hz), 2.35 – 2.26 (m, 2H), 1.28 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.7, 163.2 (d, *J* = 244.6 Hz), 145.1 (d, *J* = 9.1 Hz), 141.6 (d, *J* = 3.0 Hz), 124.2 (d, *J* = 9.1 Hz), 113.9 (d, *J* = 22.7 Hz), 111.8 (d, *J* = 21.1 Hz), 80.3, 61.0, 43.9, 40.6, 29.3 (d, *J* = 3.0 Hz), 14.1. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{15}FO_3Na$ ($[M+Na]^+$) 261.0903; found 261.0895.



Ethyl 2-(5-chloro-1-hydroxy-2,3-dihydro-1*H*-inden-1-yl)acetate (S32). Isolated as a colorless oil (910 mg, 95%). **TLC**: R_f 0.44 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3469 (O–H st), 2980, 1727 (C=O st), 1601, 1581, 1474, 1373, 1191, 1071, 1029, 964, 912, 875, 823, 734. **^{1}H-NMR** (600 MHz): δ 7.27 – 7.25 (m, 1H), 7.22 – 7.18 (m, 2H), 4.23 (s, 1H), 4.21 (q, 2H, *J* = 7.1 Hz), 3.01 (dt, 1H, *J* = 16.2, 6.4 Hz), 2.84 (d, 1H, *J* = 15.9 Hz), 2.84 – 2.78 (m, 1H), 2.69 (d, 1H, *J* = 16.0 Hz), 2.32 – 2.24 (m, 2H), 1.28 (t, 3H, *J* = 7.2 Hz). **^{13}C-NMR** (151 MHz): δ 172.6, 144.6, 144.5, 134.2, 127.1, 125.1, 124.1, 80.5, 61.0, 43.7, 40.4, 29.2, 14.1. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{15}ClO_3Na$ ($[M+Na]^+$) 277.0607; found 277.0620.

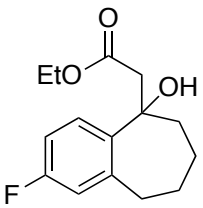


Ethyl 2-(5-bromo-1-hydroxy-2,3-dihydro-1*H*-inden-1-yl)acetate (S33). Isolated as a colorless oil (540 mg, 95%). **TLC**: R_f 0.46 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3466 (O–H st), 2981, 1725 (C=O st), 1597, 1472, 1373, 1333, 1192, 1063, 1028, 911, 866, 822, 735. **^{1}H-NMR** (600 MHz): δ 7.37 (s, 1H), 7.35 (d, 1H, *J* = 8.1 Hz), 7.21 (d, 1H, *J* = 8.1 Hz), 4.24 (s, 1H), 4.21 (q, 2H, *J* = 7.1 Hz), 3.02 (ddd, 1H, *J* = 16.2, 7.4, 5.6 Hz), 2.83 (d, 1H, *J* = 16.0 Hz), 2.83 – 2.79 (m, 1H), 2.68 (d, 1H, *J* = 16.0 Hz), 2.31 – 2.23 (m, 2H), 1.28 (t, 3H, *J* = 7.2 Hz). **^{13}C-NMR** (151 MHz): δ 172.6, 145.0, 145.0, 129.9, 128.1, 124.5, 122.4, 80.5, 61.0, 43.6, 40.3, 29.2, 14.1. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{15}BrO_3Na$ ($[M+Na]^+$) 321.0102; found 321.0111.

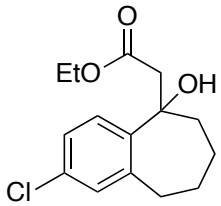


Ethyl 2-(1-hydroxy-5-iodo-2,3-dihydro-1*H*-inden-1-yl)acetate (S34). Isolated as a yellow oil (360 mg, 75%). **TLC**: R_f 0.62 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3448 (O–H st), 2980, 1718 (C=O st), 1591, 1470, 1401, 1372, 1196, 1028, 912, 821, 736. **^{1}H-NMR** (600 MHz): δ 7.59 (s, 1H), 7.56 (d, 1H, *J* = 8.0 Hz), 7.09 (d, 1H, *J* = 8.0 Hz), 4.23 (s, 1H), 4.21 (q, 2H, *J* = 7.1 Hz), 3.01 (ddd, 1H, *J* = 16.2, 7.7, 5.2 Hz), 2.82 (d, 1H, *J* = 16.0 Hz), 2.81 – 2.77 (m, 1H), 2.68 (d, 1H, *J* = 16.0 Hz), 2.30 – 2.21 (m, 2H), 1.28 (t, 3H, *J* = 7.2 Hz). **^{13}C-NMR** (151 MHz):

δ 172.6, 145.8, 145.2, 135.8, 134.2, 124.8, 94.2, 80.7, 61.0, 43.6, 40.2, 29.1, 14.1. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{15}IO_3Na$ ([M+Na]$^+$) 368.9964; found 368.9969.

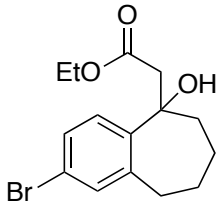


Ethyl 2-(2-fluoro-5-hydroxy-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-yl)acetate (S35). Isolated as a yellow oil (800 mg, 97%). **TLC**: R_f 0.63 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3495 (O–H st), 2932, 1711 (C=O st), 1611, 1590, 1493, 1447, 1371, 1329, 1240, 1190, 1097, 1048, 1025, 882, 862, 737. **^{1}H-NMR** (600 MHz): δ 7.62 (dd, 1H, *J* = 8.5, 6.2 Hz), 6.86 (td, 1H, *J* = 8.4, 2.8 Hz), 6.78 (dd, 1H, *J* = 9.6, 2.8 Hz), 4.56 (s, 1H), 4.11 (qd, 2H, *J* = 7.1, 2.7 Hz), 2.94 (d, 1H, *J* = 15.6 Hz), 2.90 – 2.84 (m, 3H), 2.04 (ddd, 1H, *J* = 13.4, 6.4, 2.3 Hz), 1.99 – 1.92 (m, 1H), 1.86 (ddd, 2H, *J* = 13.7, 11.7, 2.7 Hz), 1.82 – 1.74 (m, 1H), 1.56 – 1.48 (m, 1H), 1.18 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.8, 161.4 (d, *J* = 246.1 Hz), 142.0 (d, *J* = 6.0 Hz), 140.6 (d, *J* = 3.0 Hz), 127.7 (d, *J* = 7.5 Hz), 117.4 (d, *J* = 19.6 Hz), 112.2 (d, *J* = 19.6 Hz), 75.5, 60.9, 43.0, 40.4, 36.8, 27.6, 25.7, 14.0. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{19}FO_3Na$ ([M+Na]$^+$) 289.1216; found 289.1224.

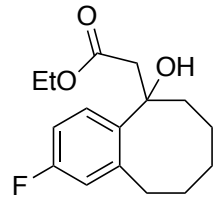


Ethyl 2-(2-chloro-5-hydroxy-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-yl)acetate (S36).[25] Isolated as a colorless oil (237 mg, 54%). **TLC**: R_f 0.65 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3486 (O–H st), 2933, 1715 (C=O st), 1479, 1447, 1330, 1192, 1047, 915, 828, 736. **^{1}H-NMR** (600 MHz): δ 7.59 (d, 1H, *J* = 8.5 Hz), 7.16 (dd, 1H, *J* = 8.5, 2.3 Hz), 7.07 (d, 1H, *J* = 2.3 Hz), 4.57 (s, 1H), 4.11 (qd, 2H, *J* = 7.1, 4.7 Hz), 2.93 (d, 1H, *J* = 15.7 Hz), 2.90 – 2.83 (m, 3H), 2.04 (ddd, 1H, *J* = 13.4, 6.2, 1.9 Hz), 1.95 (ddq, 1H, *J* = 12.9, 6.4, 3.3 Hz), 1.86 (dd, 2H, *J* = 11.9, 2.8 Hz), 1.81 – 1.73 (m, 1H), 1.51 (td, 1H, *J* = 10.2, 5.2 Hz), 1.19 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.8, 143.4, 141.5, 132.4, 130.6, 127.5, 126.0, 75.5, 60.9, 42.7, 40.4, 36.7, 27.6, 25.7, 14.0. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{19}ClO_3Na$ ([M+Na]$^+$) 305.0920; found 305.0922.

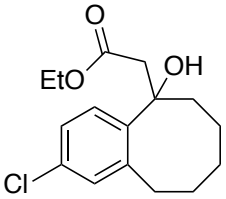
[25] For preparation of 7-chloro- and 7-bromo-2,3,4,5-tetrahydro-benzocycloheptan-1-one, see: Murineddu, G.; Ruiu, S.; Loriga, G.; Manca, I.; Lazzari, P.; Reali, R.; Pani, L.; Toma, L.; Pinna, G. A. *J. Med. Chem.* **2005**, *48*, 7351–7362.



Ethyl 2-(2-bromo-5-hydroxy-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-yl)acetate (S37).[25] Isolated as a white solid (916 mg, 89%). **TLC**: R_f 0.72 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3486 (O–H st), 2933, 1712 (C=O st), 1477, 1446, 1395, 1329, 1192, 1163, 1048, 1025, 910, 737. **^{1}H-NMR** (600 MHz): δ 7.53 (d, 1H, *J* = 8.5 Hz), 7.31 (dd, 1H, *J* = 8.5, 2.2 Hz), 7.23 (d, 1H, *J* = 2.1 Hz), 4.57 (s, 1H), 4.11 (qd, 3H, *J* = 7.3, 4.8 Hz), 2.92 (d, 1H, *J* = 15.7 Hz), 2.89 – 2.85 (m, 3H), 2.04 (ddd, 1H, *J* = 13.5, 6.5, 2.0 Hz), 1.95 (ddq, 1H, *J* = 12.8, 6.4, 3.1 Hz), 1.86 (td, 2H, *J* = 11.9, 2.9 Hz), 1.81 – 1.73 (m, 1H), 1.54 – 1.46 (m, 1H), 1.19 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.7, 144.0, 141.9, 133.4, 129.0, 127.8, 120.8, 75.5, 61.0, 42.7, 40.3, 36.7, 27.6, 25.7, 14.0. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{19}BrO_3Na$ ($[M+Na]^+$) 349.0415; found 349.0422.



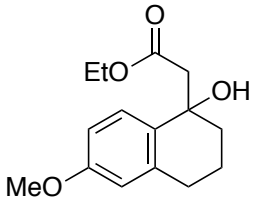
Ethyl 2-(2-fluoro-5-hydroxy-5,6,7,8,9,10-hexahydrobenzo[8]annulen-5-yl)acetate (S38). Isolated as a colorless oil (651 mg, 89%). **TLC**: R_f 0.67 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3487 (O–H st), 2928, 1712 (C=O st), 1608, 1589, 1490, 1445, 1393, 1331, 1230, 1199 1164, 1023, 965, 818, 737. **^{1}H-NMR** (600 MHz): δ 7.42 (br s, 1H), 6.82 (td, 1H, *J* = 8.5, 2.6 Hz), 6.77 (dd, 1H, *J* = 9.7, 2.7 Hz), 4.39 (s, 1H), 4.10 (qq, 2H, *J* = 7.3, 3.7 Hz), 3.02 (d, 1H, *J* = 12.3 Hz), 2.80 (br s, 1H), 2.68 (d, 1H, *J* = 15.8 Hz), 2.13 – 1.85 (m, 2H), 1.84 – 1.76 (m, 1H), 1.76 – 1.60 (m, 2H), 1.56 – 1.47 (m, 1H), 1.32 (br s, 1H), 1.19 (t, 3H, *J* = 7.1 Hz), 1.07 (br s, 1H). **^{13}C-NMR** (151 MHz): δ 172.8, 161.94 (d, *J* = 246.1 Hz), 139.6, 127.6 (2C), 117.64 (d, *J* = 19.6 Hz), 112.24 (d, *J* = 19.6 Hz), 76.1, 60.8, 48.1, 43.5, 32.2, 30.6, 23.5, 22.2, 14.1. **HRMS** (ESI) *m/z* calcd for $C_{16}H_{21}FO_3Na$ ($[M+Na]^+$) 303.1372; found 303.1371.



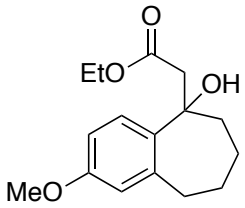
Ethyl 2-(2-chloro-5-hydroxy-5,6,7,8,9,10-hexahydrobenzo[8]annulen-5-yl)acetate (S39).[26] Isolated as a colorless oil (570 mg, 80%). **TLC**: R_f 0.70 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3486 (O–H st), 2928, 1712 (C=O st), 1478, 1445, 1204, 1158, 1023, 907, 832, 814, 736. **^{1}H-NMR** (600 MHz): δ 7.38 (s, 1H), 7.11 (d, 1H, *J* = 10.1 Hz), 7.05 (d, 1H, *J* = 2.1 Hz), 4.41 (s, 1H), 4.10 (qd, 2H, *J* = 7.1, 2.5 Hz), 3.01 (d, 1H, *J* = 12.7 Hz), 2.80 (s, 1H), 2.68 (d, 1H,

[26] For preparation of 2-chloro-7,8,9,10-tetrahydrobenzo[8]annulen-5(6*H*)-one, see: Zhang, Y.; Burgess, J. P.; Brackeen, M.; Gilliam, A.; Mascarella, S. W.; Page, K.; Seltzman, H. H.; Thomas, B. F. *J. Med. Chem.* **2008**, *51*, 3526–3539.

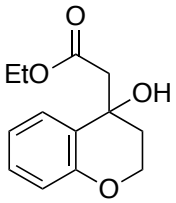
J = 15.9 Hz), 2.08 – 1.86 (m, 2H), 1.85 – 1.76 (m, 1H), 1.76 – 1.60 (m, 2H), 1.56 – 1.46 (m, 1H), 1.32 (s, 1H), 1.19 (t, 3H, *J* = 7.1 Hz), 1.07 (s, 1H). **^{13}C-NMR** (151 MHz): δ 172.8, 142.4, 132.9, 131.1, 127.6, 127.3, 125.7, 76.2, 60.9, 47.9, 43.2, 32.0, 30.5, 23.5, 22.1, 14.1. **HRMS** (ESI) *m/z* calcd for $C_{16}H_{21}ClO_3Na$ ([M+Na]$^+$) 319.1077; found 319.1080.



Ethyl 2-(1-hydroxy-6-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)acetate (S40). Isolated as a white solid (390 mg, 97%). **TLC**: R_f 0.43 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3498 (O–H st), 2937, 1723 (C=O st), 1609, 1502, 1323, 1252, 1197, 1039, 736. **^{1}H-NMR** (600 MHz): δ 7.47 (d, 1H, *J* = 8.7 Hz), 6.78 (dd, 1H, *J* = 8.7, 2.7 Hz), 6.59 (d, 1H, *J* = 2.5 Hz), 4.19 (qd, 2H, *J* = 7.1, 2.5 Hz), 3.93 (s, 1H), 3.78 (s, 3H), 2.87 (d, 1H, *J* = 15.5 Hz), 2.84 – 2.78 (m, 1H), 2.76 – 2.71 (m, 2H), 2.06 (ddd, 1H, *J* = 13.5, 8.0, 3.0 Hz), 1.99 – 1.91 (m, 2H), 1.81 – 1.74 (m, 1H), 1.27 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.6, 158.6, 138.1, 133.0, 127.8, 113.0, 112.7, 70.8, 60.8, 55.2, 46.2, 36.5, 29.9, 20.1, 14.2. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{20}O_4Na$ ([M+Na]$^+$) 287.1259; found 287.1258.

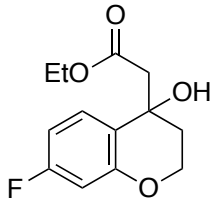


Ethyl 2-(5-hydroxy-2-methoxy-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-yl)acetate (S41). Isolated as a white solid (1.60 g, 74%). **TLC**: R_f 0.55 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3490 (O–H st), 2932, 1710 (C=O st), 1608, 1578, 1250, 1190, 1037, 912, 735. **^{1}H-NMR** (600 MHz, Methanol-d_4) δ 7.53 (d, 1H, *J* = 8.7 Hz), 6.70 (dd, 1H, *J* = 8.7, 2.8 Hz), 6.62 (d, 1H, *J* = 2.7 Hz), 4.02 (qd, 2H, *J* = 7.1, 1.8 Hz), 3.75 (s, 3H), 2.95 – 2.79 (m, 4H), 2.18 – 2.12 (m, 1H), 1.93 – 1.84 (m, 3H), 1.84 – 1.77 (m, 1H), 1.52 – 1.43 (m, 1H), 1.11 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 173.2, 159.8, 142.3, 138.9, 128.5, 117.5, 111.3, 77.1, 61.4, 55.5, 45.2, 42.0, 37.9, 29.2, 26.8, 14.4. **HRMS** (ESI) *m/z* calcd for $C_{16}H_{22}O_4Na$ ([M+Na]$^+$) 301.1416; found 301.1412.

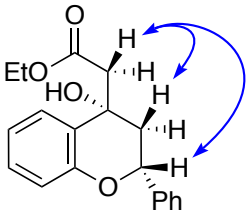


Ethyl 2-(4-hydroxychroman-4-yl)acetate (S42). Isolated as a colorless oil (436 mg, 91%). **TLC**: R_f 0.42 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3484 (O–H st), 2938, 1715 (C=O st), 1609, 1582, 1489, 1452, 1223, 1193, 1059, 757, 737. **^{1}H-NMR** (600 MHz): δ 7.4 (dd, 1H, *J* = 7.8, 1.6 Hz), 7.2 (ddd, 1H, *J* = 8.4, 7.3, 1.6 Hz), 6.9 (td, 1H, *J* = 7.9, 1.2 Hz), 6.8 (dd, 1H, *J* = 8.2, 1.1 Hz), 4.3 (ddd, 1H, *J* = 11.8, 7.9, 4.0 Hz), 4.2 – 4.2 (m, 3H), 4.1 (s, 1H), 3.1 (d, 1H,

J = 15.9 Hz), 2.7 (d, 1H, *J* = 15.9 Hz), 2.2 – 2.2 (m, 2H), 1.3 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.4, 154.1, 129.4, 126.7, 126.0, 120.8, 117.2, 66.9, 62.9, 61.1, 45.1, 35.5, 14.1. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{16}O_4Na$ ([M+Na]$^+$) 259.0946; found 259.0959.

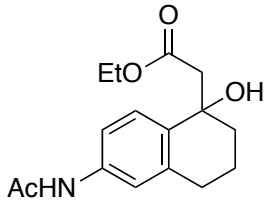


Ethyl 2-(7-fluoro-4-hydroxychroman-4-yl)acetate (S43). Isolated as a colorless oil (440mg, 96%). **TLC**: R_f 0.38 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3468 (O–H st), 2939, 1721(C=O st), 1616, 1595, 1501, 1432, 1335, 1312, 1194, 1127, 1056, 1028, 850, 806, 733. **^{1}H-NMR** (600 MHz): δ 7.39 (dd, 1H, *J* = 8.7, 6.5 Hz), 6.65 (td, 1H, *J* = 8.5, 2.6 Hz), 6.53 (dd, 1H, *J* = 10.2, 2.6 Hz), 4.31 (ddd, 1H, *J* = 11.8, 8.3, 3.7 Hz), 4.25 – 4.19 (m, 3H), 4.12 (s, 1H), 3.04 (d, 1H, *J* = 15.9 Hz), 2.69 (d, 1H, *J* = 15.9 Hz), 2.21 – 2.12 (m, 2H), 1.28 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.3, 162.96 (d, *J* = 246.1 Hz), 155.42 (d, *J* = 12.1 Hz), 128.14 (d, *J* = 10.6 Hz), 122.16 (d, *J* = 3.0 Hz), 108.17 (d, *J* = 22.7 Hz), 103.99 (d, *J* = 24.1 Hz), 66.6, 63.3, 61.1, 45.0, 35.2, 14.1. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{15}FO_4Na$ ([M+Na]$^+$) 277.0852; found 277.0858.

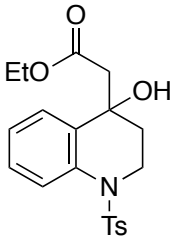


NOESY

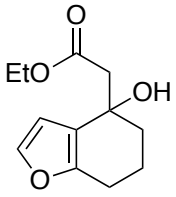
Ethyl 2-((2*R,4*S**)-4-hydroxy-2-phenylchroman-4-yl)acetate (S44).** Isolated as a colorless oil (385 mg, 92%). **TLC**: R_f 0.49 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3488 (O–H st), 2983, 1715 (C=O st), 1609, 1582, 1484, 1453, 1222, 1186, 1059, 1028, 914, 757. **^{1}H-NMR** (600 MHz): δ 7.54 (dd, 1H, *J* = 7.8, 1.6 Hz), 7.46 – 7.43 (m, 2H), 7.43 – 7.39 (m, 2H), 7.37 – 7.33 (m, 1H), 7.21 (ddd, 1H, *J* = 8.3, 7.3, 1.7 Hz), 6.98 (ddd, 1H, *J* = 7.9, 7.3, 1.2 Hz), 6.89 (dd, 1H, *J* = 8.2, 1.2 Hz), 5.18 (dd, 1H, *J* = 12.5, 2.2 Hz), 4.29 (s, 1H), 4.24 (qd, 2H, *J* = 7.1, 4.7 Hz), 3.03 (d, 1H, *J* = 15.8 Hz), 2.97 (dd, 1H, *J* = 15.8, 1.4 Hz), 2.45 (dd, 1H, *J* = 13.9, 2.4 Hz), 2.36 (ddd, 1H, *J* = 13.9, 12.6, 1.4 Hz), 1.30 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 171.9, 153.7, 140.5, 129.3, 128.7, 128.3, 127.0, 126.3, 126.0, 121.1, 116.9, 76.2, 68.9, 61.2, 46.1, 42.7, 14.2. **HRMS** (ESI) *m/z* calcd for $C_{19}H_{20}O_4Na$ ([M+Na]$^+$) 335.1259; found 335.1262.



Ethyl 2-(6-acetamido-1-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)acetate (S45).[27] Isolated as a colorless oil (87.0 mg, 72%). **TLC**: R_f 0.16 (1:1 benzene/EtOAc). **IR** (NaCl, film): 3313 (O–H st), 2937, 1718 (C=O st), 1670, 1613,1542, 1371. **^{1}H-NMR** (600 MHz): δ 7.49 (d, 1H, J = 8.5 Hz), 7.33 (s, 1H), 7.19 (d, 1H, J = 8.5 Hz), 7.17 (s, 1H), 4.19 (qd, 2H, J = 7.2, 2.8 Hz), 4.06 (s, 1H), 2.88 – 2.68 (m, 4H), 2.16 (s, 3H), 2.11 – 2.02 (m, 1H), 2.00 – 1.89 (m, 2H), 1.83 – 1.70 (m, 1H), 1.27 (t, 3H, J = 7.2 Hz). **^{13}C-NMR** (151 MHz): δ 172.6, 168.2, 137.6, 136.8, 136.7, 127.2, 119.7, 118.0, 70.9, 60.8, 46.0, 36.3, 29.6, 24.7, 20.0, 14.2. **HRMS** (ESI) *m/z* calcd for $C_{16}H_{21}NO_4Na$ ([M+Na]$^+$) 314.1368; found 314.1362.



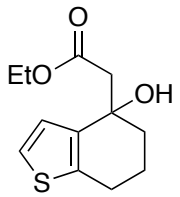
Ethyl 2-(4-hydroxy-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl)acetate (S46). Isolated as a yellow oil (53 mg, 68%). **TLC**: R_f 0.26 (3:1 hexanes/EtOAc). **IR** (ATR, ZnSe): 3478 (O–H st), 2926, 2360, 2341, 1731 (C=O st), 1345, 1307, 1166, 1092, 1072, 910, 737. **^{1}H-NMR** (600 MHz): δ 7.82 (d, 1H, J = 8.3 Hz), 7.52 (d, 2H, J = 8.2 Hz), 7.47 (d, 1H, J = 7.8 Hz), 7.29 (d, 1H, J = 8.5 Hz), 7.22 (d, 2H, J = 8.1 Hz), 7.18 (t, 1H, J = 7.5 Hz), 4.17 – 4.10 (m, 2H), 4.07 (s, 1H), 4.00 – 3.95 (m, 1H), 3.74 (ddd, 1H, J = 13.4, 8.1, 4.9 Hz), 2.63 (d, 1H, J = 15.9 Hz), 2.39 (s, 3H), 1.93 (d, 1H, J = 15.9 Hz), 1.90 – 1.83 (m, 2H), 1.25 (t, 3H, J = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.3, 143.9, 136.5, 135.7, 133.2, 129.7, 128.5, 127.1, 126.8, 125.3, 124.0, 68.3, 61.0, 45.0, 43.4, 35.0, 21.5, 14.1. **HRMS** (ESI) *m/z* calcd for $C_{20}H_{23}NO_5Na$ ([M+Na]$^+$) 412.1195; found 412.1198.



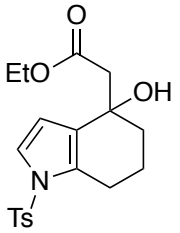
Ethyl 2-(4-hydroxy-4,5,6,7-tetrahydrobenzofuran-4-yl)acetate (S47). Isolated as a colorless oil (431 mg, 83%). **TLC**: R_f 0.37 (4:1 hexanes/EtOAc). **IR** (NaCl, film): 3493 (O–H st), 2940, 1713 (C=O st), 1372, 1327, 1196, 1035. **^{1}H-NMR** (400 MHz): δ 7.24 (d, 1H, J = 2.1 Hz), 6.37 (d, 1H, J = 2.0 Hz), 4.21 (q, 2H, J = 7.1 Hz), 4.00 (s, 1H), 2.87 (d, 1H, J = 15.7 Hz), 2.71 – 2.59 (m, 2H), 2.59 – 2.46 (m, 1H), 2.13 – 2.02 (m, 1H), 1.97 (ddd, 1H, J = 13.4, 7.5, 2.9 Hz), 1.85 (ddq, 1H, J = 10.9, 5.5, 2.8 Hz), 1.84 – 1.68 (m, 1H), 1.29 (t, 3H, J = 7.1 Hz). **^{13}C-NMR**

[27] For preparation of 6-acetamido-1-tetralone, see: Siqueira, F. A.; Ishikawa, E. E.; Fogaca, A.; Faccio, A. T.; Carneiro, V. M. T.; Soares, R. R. S.; Utaka, A.; Tebeka, I. R. M.; Bielawski, M.; Olofsson, B.; Silva, L. F. *J. Braz. Chem. Soc.* **2011**, *22*, 1795–1807.

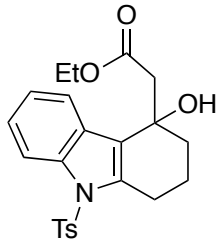
(151 MHz): δ 172.8, 152.0, 141.0, 121.6, 107.6, 68.5, 60.9, 45.1, 36.7, 23.0, 19.4, 14.2. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{16}O_4Na$ ($[M+Na]^+$) 247.0946; found 247.0938.



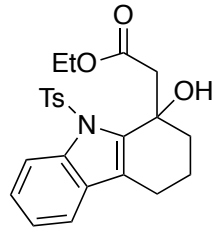
Ethyl 2-(4-hydroxy-4,5,6,7-tetrahydrobenzo[*b*]thiophen-4-yl)acetate (S48). Isolated as a colorless oil (260 mg, 82%). **TLC**: R_f 0.15 (9:1 hexanes/EtOAc). **IR** (NaCl, film): 3490 (O–H st), 2937, 1726 (C=O st), 1370, 1188, 1026, 709. **^{1}H-NMR** (600 MHz): δ 7.07 (d, 1H, *J* = 5.3 Hz), 7.03 (d, 1H, *J* = 5.2 Hz), 4.20 (q, 2H, *J* = 7.1 Hz), 3.96 (s, 1H), 2.95 (d, 1H, *J* = 15.5 Hz), 2.87 – 2.81 (m, 1H), 2.73 (ddd, 1H, *J* = 16.6, 7.5, 5.5 Hz), 2.68 (d, 1H, *J* = 15.5 Hz), 2.09 – 2.03 (m, 1H), 2.03 – 1.97 (m, 1H), 1.97 – 1.89 (m, 1H), 1.89 – 1.82 (m, 1H), 1.28 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.6, 139.1, 138.6, 124.9, 122.7, 69.6, 60.9, 45.4, 36.2, 25.1, 20.6, 14.2. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{16}O_3SNa$ ($[M+Na]^+$) 263.0718; found 263.0709.



Ethyl 2-(4-hydroxy-1-tosyl-4,5,6,7-tetrahydro-1*H*-indol-4-yl)acetate (S49). Isolated as a colorless oil (184 mg, 94%). **TLC**: R_f 0.28 (96:4 CH_2Cl_2/Et_2O). **IR** (NaCl, film): 3492 (O–H st), 2941, 1714 (C=O st), 1369, 1177, 1127, 1092, 665. **^{1}H-NMR** (400 MHz): δ 7.68 (d, 2H, *J* = 8.3 Hz), 7.30 (d, 2H, *J* = 8.2 Hz), 7.20 (d, 1H, *J* = 3.5 Hz), 6.28 (d, 1H, *J* = 3.5 Hz), 4.18 (q, 2H, *J* = 7.2 Hz), 4.02 (s, 1H), 2.85 (d, 1H, *J* = 15.7 Hz), 2.67 (t, 2H, *J* = 6.4 Hz), 2.56 (d, 1H, *J* = 15.8 Hz), 2.42 (s, 3H), 1.93 (ddd, 1H, *J* = 12.9, 6.4, 3.1 Hz), 1.86 (ddd, 1H, *J* = 13.2, 7.8, 2.9 Hz), 1.80 – 1.67 (m, 2H), 1.26 (t, 2H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.8, 145.0, 136.0, 130.2, 130.0, 127.0, 121.2, 108.9, 68.4, 60.9, 45.0, 35.9, 22.8, 21.6, 19.6, 14.1 (1 signal not resolved). **HRMS** (ESI) *m/z* calcd for $C_{19}H_{23}NO_5SNa$ ($[M+Na]^+$) 400.1195; found 400.1187.



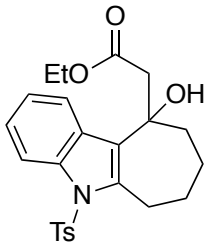
Ethyl 2-(4-hydroxy-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)acetate (S50).[28] Isolated as a yellow oil (393 mg, 86%). **TLC**: R_f 0.40 (7:3 hexanes/EtOAc). **IR** (NaCl, film): 3509 (O–H st), 2940, 1718 (C=O st), 1452, 1371, 1174, 1090, 669. **^{1}H-NMR** (600 MHz, C_6D_6): δ 8.54 (d, 1H, *J* = 8.5 Hz), 7.88 (d, 1H, *J* = 7.9 Hz), 7.57 (d, 2H, *J* = 8.3 Hz), 7.21 – 7.17 (m, 1H), 7.13 – 7.07 (m, 1H), 6.50 – 6.39 (m, 2H), 3.89 – 3.74 (m, 2H), 3.62 (s, 1H), 3.13 – 2.98 (m, 2H), 2.89 (ddd, 1H, *J* = 17.8, 8.6, 5.8 Hz), 2.42 (d, 1H, *J* = 15.6 Hz), 2.06 (ddd, 1H, *J* = 13.3, 7.3, 2.8 Hz), 1.79 – 1.69 (m, 1H), 1.63 (s, 4H), 1.46 – 1.40 (m, 1H), 0.82 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz, C_6D_6): δ 172.24, 144.27, 137.26, 137.05, 136.76, 129.84, 128.30, 126.40, 124.27, 123.61, 122.31, 121.51, 114.82, 70.44, 60.50, 43.39, 36.76, 24.92, 20.98, 20.69, 14.00. **HRMS** (ESI) *m/z* calcd for $C_{23}H_{25}NO_5SNa$ ($[M+Na]^+$) 450.1351; found 450.1359.



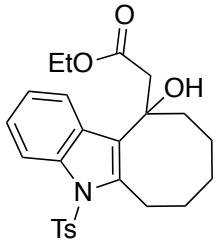
Ethyl 2-(1-hydroxy-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-yl)acetate (S51).[29] Isolated as a colorless oil (114 mg, 91%). **TLC**: R_f 0.30 (4:1 hexanes/EtOAc). **IR** (NaCl, film): 3528 (O–H st), 2939, 1731 (C=O st), 1453, 1346, 1171, 1089, 752. **^{1}H-NMR** (500 MHz): δ 8.01 (d, 1H *J* = 8.3 Hz), 7.66 (d, 2H, *J* = 8.2 Hz), 7.31 (d, 1H, *J* = 8.6 Hz), 7.30 – 7.23 (m, 1H), 7.18 (t, 1H, *J* = 7.4 Hz), 7.09 (d, 2H, *J* = 8.1 Hz), 4.92 (s, 1H), 4.05 (qd, 2H, *J* = 7.1, 1.7 Hz), 3.43 (d, 1H, *J* = 14.3 Hz), 3.15 (d, 1H, *J* = 14.3 Hz), 2.68 (dt, 1H, *J* = 16.9, 5.0 Hz), 2.56 (ddd, 1H, *J* = 16.9, 8.6, 5.3 Hz), 2.27 (s, 3H), 2.23 (ddd, 1H, *J* = 13.3, 7.1, 2.7 Hz), 2.16 (t, 1H, *J* = 13.1, 10.7 Hz), 2.13 – 2.00 (m, 1H), 1.97 – 1.84 (m, 1H), 1.12 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (126 MHz): δ 170.4, 144.6, 138.5, 137.8, 133.9, 130.3, 129.4, 126.8, 126.7, 125.7, 124.2, 119.3, 116.0, 69.3, 60.4, 46.3, 38.2, 22.6, 21.5, 19.1, 14.1. **HRMS** (ESI) *m/z* calcd for $C_{23}H_{25}NO_5SNa$ ($[M+Na]^+$) 450.1351; found 450.1334.

[28] For preparation of 9-tosyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one, see: Gartshore, C. J.; Lupton, D. W. *Aust. J. Chem.* **2013**, *66*, 882–890.

[29] For preparation of 9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-one, see: Wu, Z. J.; Li, Y.; Cai, Y.; Yuan, J. Y.; Yuan, C. Y. *Bioorg. Med. Chem. Lett.* **2013**, *23*, 4903–4906.



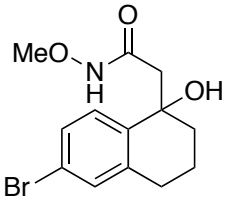
Ethyl 2-(10-hydroxy-5-tosyl-5,6,7,8,9,10-hexahydrocyclohepta[*b*]indol-10-yl)acetate (S52). Isolated as a light yellow oil (710 mg, 54%). **TLC**: R_f 0.18 (1:4 hexanes/CH_2Cl_2). **IR** (NaCl, film): 3492 (O–H st), 2937, 1711 (C=O st), 1451, 1368, 1171, 1090, 660. **^{1}H-NMR** (600 MHz): δ 8.23 (d, 1H, *J* = 8.4 Hz), 8.04 (d, 1H, *J* = 7.9 Hz), 7.57 (d, 2H, *J* = 8.4 Hz), 7.27 – 7.22 (m, 1H), 7.22 – 7.15 (m, 3H), 4.28 – 4.10 (m, 2H), 4.00 (s, 1H), 3.28 (ddd, 1H, *J* = 16.8, 9.0, 3.1 Hz), 3.20 (ddd, 1H, *J* = 16.6, 8.1, 2.7 Hz), 3.11 (d, 1H, *J* = 16.0 Hz), 2.69 (d, 1H, *J* = 15.9 Hz), 2.35 (s, 3H), 2.17 – 2.09 (m, 2H), 1.84 – 1.62 (m, 4H), 1.25 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.6, 144.7, 137.3, 137.0, 136.1, 129.8, 129.0, 126.3, 125.9, 124.1, 123.4, 121.8, 115.2, 74.1, 61.0, 42.7, 37.7, 25.5, 23.8, 22.0, 21.6, 14.1. **HRMS** (ESI) *m/z* calcd for $C_{24}H_{27}NO_5SNa$ ($[M+Na]^+$) 464.1508; found 464.1521.



Ethyl 2-(11-hydroxy-5-tosyl-6,7,8,9,10,11-hexahydro-5*H*-cycloocta[*b*]indol-11-yl)acetate (S53). Isolated as a colorless oil (654 mg, 77%). **TLC**: R_f 0.20 (1:4 hexanes/CH_2Cl_2). **IR** (NaCl, film): 3308 (O–H st), 2927, 1726 (C=O st), 1452, 1368, 1176, 1090, 658. **^{1}H-NMR** (600 MHz): δ 8.24 (d, 1H, *J* = 7.8 Hz), 8.08 (d, 1H, *J* = 7.8 Hz), 7.60 (d, 2H, *J* = 8.4 Hz), 7.28 – 7.19 (m, 2H), 7.19 (d, 2H, *J* = 8.1 Hz), 4.05 (q, 2H, *J* = 7.2 Hz), 3.78 (s, 1H), 3.68 (ddd, 1H, *J* = 15.6, 6.3, 3.9 Hz), 3.16 (d, 1H, *J* = 15.8 Hz), 3.13 – 2.99 (m, 1H), 2.64 (d, 1H, *J* = 15.9 Hz), 2.54 – 2.38 (m, 1H), 2.35 (s, 3H), 2.08 (dt, 1H, *J* = 15.5, 5.0 Hz), 1.99 – 1.89 (m, 1H), 1.78 – 1.64 (m, 2H), 1.64 – 1.57 (m, 1H), 1.44 – 1.27 (m, 2H), 1.14 (t, 3H, *J* = 7.1 Hz). **^{13}C-NMR** (151 MHz): δ 172.44, 144.58, 136.84, 136.77, 134.43, 129.75, 128.70, 126.23, 124.69, 123.89, 123.12, 122.07, 114.88, 74.07, 60.70, 46.11, 38.51, 26.75, 24.23, 23.61, 22.89, 21.56, 14.03. **HRMS** (ESI) *m/z* calcd for $C_{25}H_{29}NO_5SNa$ ($[M+Na]^+$) 478.1664; found 478.1669.

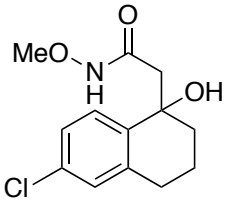
2. SYNTHESIS OF β-HYDROXY-*N*-METHOXYAMIDES

a. General procedure for preparation of β-hydroxy-*N*-methoxyamides

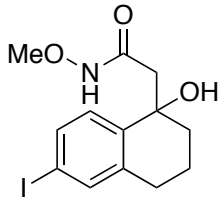


2-(6-Bromo-1-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methoxyacetamide (7a). Methoxyamine hydrochloride (0.48 g, 5.8 mmol, 3.0 equiv) was suspended in THF (11 mL) and cooled to 0 °C. A solution of $AlMe_3$ (2.0 M in hexanes, 2.9 mL, 5.8 mmol, 3.0 equiv) was added by syringe over 5 min and the mixture was stirred for 1 h. A solution of the ester **6a** (0.5 M in THF, 0.6 g, 1.9 mmol, 1.0 equiv) was then added by syringe over 5 min and the reaction was stirred at 0 °C to 24 °C for 16–24 h until complete conversion. The reaction was then cooled to 0 °C and quenched slowly with satd aq Rochelle salt. The mixture was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 10% MeOH in CH_2Cl_2) yielded β-hydroxyamide **7a** as a white solid (580 mg, 96%).

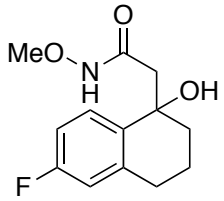
TLC: R_f 0.28 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3382 (O–H st), 2937, 2501, 1670 (C=O st), 1450, 1119, 1043, 975, 823, 751. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.47 (d, 1H, J = 8.5 Hz), 7.32 (dd, 1H, J = 8.4, 2.1 Hz), 7.27 – 7.23 (m, 1H), 3.64 (s, 3H), 2.83 – 2.72 (m, 2H), 2.58 (d, 1H, J = 14.2 Hz), 2.48 (d, 1H, J = 14.2 Hz), 2.27 – 2.20 (m, 1H), 1.95 – 1.79 (m, 3H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 169.8, 141.8, 140.6, 132.4, 130.2, 130.0, 122.0, 72.0, 64.3, 45.6, 37.2, 30.4, 20.8. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{16}BrNO_3Na$ ($[M+Na]^+$) 336.0211; found 336.0219.



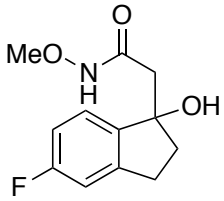
2-(6-Chloro-1-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methoxyacetamide (7b). Isolated as a white solid (340 mg, 97%). **TLC**: R_f 0.29 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3216 (O–H st), 2940, 1650 (C=O st), 1483, 1409, 1093, 1064, 856, 737, 701. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.53 (d, 1H, J = 8.5 Hz), 7.17 (dd, 1H, J = 8.5, 2.2 Hz), 7.09 (d, 1H, J = 2.0 Hz), 3.63 (s, 3H), 2.81 – 2.72 (m, 2H), 2.58 (d, 1H, J = 14.2 Hz), 2.48 (d, 1H, J = 14.2 Hz), 2.26 – 2.20 (m, 1H), 1.94 – 1.81 (m, 3H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 169.9, 141.3, 140.2, 133.9, 129.7, 129.3, 127.2, 72.0, 64.3, 45.7, 37.2, 30.4, 20.8. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{16}ClNO_3Na$ ($[M+Na]^+$) 292.0716; found 292.0705.



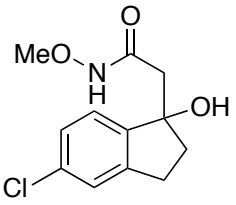
2-(1-Hydroxy-6-iodo-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methoxyacetamide (7c). Isolated as a white solid (420 mg, 93%). **TLC**: R_f 0.27 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3395 (O–H st), 2967, 2934, 2512, 1682 (C=O st), 1450, 1119, 1044, 976, 751. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.52 (dd, 1H, J = 8.3, 1.8 Hz), 7.46 (s, 1H), 7.32 (d, 1H, J = 8.3 Hz), 3.64 (s, 3H), 2.81 – 2.70 (m, 2H), 2.57 (d, 1H, J = 14.2 Hz), 2.48 (d, 1H, J = 14.2 Hz), 2.26 – 2.20 (m, 1H), 1.94 – 1.79 (m, 3H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 169.8, 142.4, 140.7, 138.6, 136.3, 130.1, 93.6, 72.1, 64.3, 45.6, 37.1, 30.2, 20.8. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{16}INO_3Na$ ($[M+Na]^+$) 384.0073; found 384.0067.



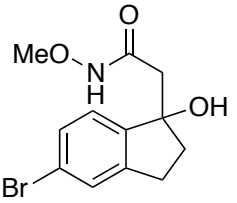
2-(6-Fluoro-1-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methoxyacetamide (7d). Isolated as a colorless oil (352 mg, 92%). **TLC**: R_f 0.34 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3389 (O–H st), 2939, 2502, 2071, 1649 (C=O st), 1496, 1439, 1241, 1117, 1067, 977, 946. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.56 (dd, 1H, J = 8.7, 5.8 Hz), 6.90 (td, 1H, J = 8.6, 2.8 Hz), 6.79 (dd, 1H, J = 9.7, 2.7 Hz), 3.63 (s, 3H), 2.82 – 2.73 (m, 2H), 2.60 (d, 1H, J = 14.2 Hz), 2.47 (d, 1H, J = 14.2 Hz), 2.26 – 2.19 (m, 1H), 1.96 – 1.80 (m, 3H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 170.0, 163.2 (d, J = 244.6 Hz), 140.7 (d, J = 7.5 Hz), 138.5 (d, J = 3.0 Hz), 130.1 (dd, J = 9.1, 4.5 Hz), 115.5 (dd, J = 21.1, 3.0 Hz), 114.0 (dd, J = 21.1, 3.0 Hz), 72.0, 64.3, 45.8, 37.4, 30.7 (d, J = 1.5 Hz), 20.9. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{16}FNO_3Na$ ($[M+Na]^+$) 276.1012; found 276.1021.



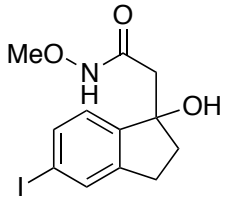
2-(5-Fluoro-1-hydroxy-2,3-dihydro-1*H*-inden-1-yl)-*N*-methoxyacetamide (10a). Isolated as a yellow oil (355 mg, 79%). **TLC**: R_f 0.31 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3400 (O–H st), 2942, 2510, 2073, 1656 (C=O st), 1487, 1441, 1247, 1121, 1084, 976, 865, 823. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.33 (dd, 1H, J = 9.0, 5.3 Hz), 6.96 – 6.91 (m, 2H), 3.62 (s, 3H), 2.98 (ddd, 1H, J = 16.1, 8.6, 4.3 Hz), 2.84 (dt, 1H, J = 15.8, 7.6 Hz), 2.61 (d, 1H, J = 14.0 Hz), 2.53 (ddd, 1H, J = 12.8, 8.2, 4.3 Hz), 2.45 (d, 1H, J = 14.0 Hz), 2.19 (ddd, 1H, J = 13.2, 8.6, 7.1 Hz). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 169.9, 164.7 (d, J = 244.6 Hz), 146.8 (d, J = 9.1 Hz), 143.5 (d, J = 3.0 Hz), 125.7 (d, J = 10.6 Hz), 114.5 (d, J = 24.2 Hz), 112.5 (d, J = 22.7 Hz), 82.0, 64.3, 43.9, 41.2, 30.1 (d, J = 3.0 Hz). **HRMS** (ESI) *m/z* calcd for $C_{12}H_{14}FNO_3Na$ ($[M+Na]^+$) 262.0855; found 262.0852.



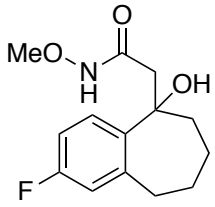
2-(5-Chloro-1-hydroxy-2,3-dihydro-1*H*-inden-1-yl)-*N*-methoxyacetamide (10b). Isolated as a colorless oil (473 mg, 94%). **TLC**: R_f 0.24 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3210 (O–H st), 2972, 1649 (C=O st), 1475, 1439, 1414, 1072, 975, 950, 874, 823, 737. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.31 (d, 1H, J = 8.0 Hz), 7.24 – 7.20 (m, 2H), 3.62 (s, 3H), 2.97 (ddd, 1H, J = 16.2, 8.7, 4.2 Hz), 2.84 (dt, 1H, J = 16.0, 7.7 Hz), 2.59 (d, 1H, J = 14.0 Hz), 2.52 (ddd, 1H, J = 12.7, 8.2, 4.2 Hz), 2.45 (d, 1H, J = 14.0 Hz), 2.17 (ddd, 1H, J = 13.2, 8.5, 7.4 Hz). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 169.7, 146.4, 146.4, 135.1, 127.8, 126.0, 125.6, 82.1, 64.3, 43.7, 40.9, 30.0. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{14}ClNO_3Na$ ($[M+Na]^+$) 278.0560; found 278.0568.



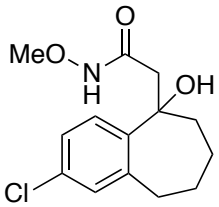
2-(5-bromo-1-hydroxy-2,3-dihydro-1*H*-inden-1-yl)-*N*-methoxyacetamide (10c). Isolated as a white solid (450 mg, 90%). **TLC**: R_f 0.28 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3305 (O–H st), 2939, 1649 (C=O st), 1472, 1439, 1439, 1409, 1200, 1062, 979, 864, 821. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.40 – 7.35 (m, 2H), 7.26 (d, 1H, J = 8.1 Hz), 3.62 (s, 3H), 2.98 (ddd, 1H, J = 16.2, 8.7, 4.1 Hz), 2.85 (dt, 1H, J = 16.0, 7.7 Hz), 2.59 (d, 1H, J = 14.0 Hz), 2.51 (ddd, 1H, J = 12.5, 8.1, 4.2 Hz), 2.45 (d, 1H, J = 14.0 Hz), 2.16 (ddd, 1H, J = 13.2, 8.6, 7.4 Hz). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 169.7, 146.9, 146.7, 130.7, 129.0, 126.0, 123.2, 82.2, 64.3, 43.7, 40.9, 30.0. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{14}BrNO_3Na$ ($[M+Na]^+$) 322.0055; found 322.0061.



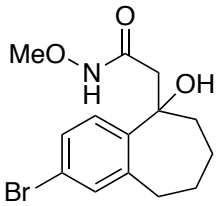
2-(1-Hydroxy-5-iodo-2,3-dihydro-1*H*-inden-1-yl)-*N*-methoxyacetamide (10d). Isolated as a yellow oil (280 mg, 80%). **TLC**: R_f 0.35 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3363 (O–H st), 2942, 1657 (C=O st), 1469, 1439, 1402, 1194, 1119, 978, 820, 735. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.60 (s, 1H), 7.57 (d, 1H, J = 8.0 Hz), 7.13 (d, 1H, J = 8.0 Hz), 3.61 (s, 3H), 2.96 (ddd, 1H, J = 16.1, 8.7, 4.1 Hz), 2.83 (dt, 1H, J = 16.0, 7.7 Hz), 2.58 (d, 1H, J = 14.0 Hz), 2.48 (ddd, 1H, J = 12.5, 8.1, 4.2 Hz), 2.44 (d, 1H, J = 14.0 Hz), 2.14 (ddd, 1H, J = 13.2, 8.5, 7.5 Hz). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 169.7, 147.6, 146.9, 136.8, 135.2, 126.3, 94.6, 82.3, 64.3, 43.7, 40.7, 29.9. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{14}INO_3Na$ ($[M+Na]^+$) 369.9916; found 369.9918.



2-(2-Fluoro-5-hydroxy-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-yl)-*N*-methoxyacetamide (12a). Isolated as a white solid (754 mg, 96%). **TLC**: R_f 0.35 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3385 (O–H st), 2935, 1648 (C=O st), 1491, 1446, 1241, 1093, 973, 820, 736. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.68 (dd, 1H, J = 8.8, 6.1 Hz), 6.87 (td, 1H, J = 8.5, 2.8 Hz), 6.82 (dd, 1H, J = 9.7, 2.8 Hz), 3.52 (s, 3H), 2.99 (t, 1H, J = 13.2 Hz), 2.81 (dd, 1H, J = 14.9, 6.0 Hz), 2.68 (d, 1H, J = 14.4 Hz), 2.62 (d, 1H, J = 14.4 Hz), 2.13 (dt, 1H, J = 12.8, 3.2 Hz), 1.96 – 1.87 (m, 3H), 1.84 – 1.78 (m, 1H), 1.49 – 1.41 (m, 1H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 170.3, 162.9 (d, J = 243.1 Hz), 143.4 (d, J = 7.5 Hz), 142.4 (d, J = 3.0 Hz), 129.7 (d, J = 7.5 Hz), 118.1 (d, J = 21.1 Hz), 113.0 (d, J = 19.6 Hz), 77.3, 64.3, 42.3, 41.9, 37.6, 28.9, 26.6. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{18}FNO_3Na$ ($[M+Na]^+$) 290.1168; found 290.1162.

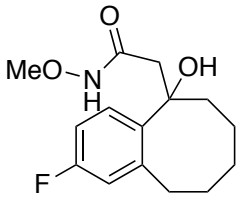


2-(2-Chloro-5-hydroxy-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-yl)-*N*-methoxyacetamide (12b). Isolated as a clear and colorless oil (137 mg, 85%). **TLC**: R_f 0.33 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3391 (O–H st), 2938, 1646 (C=O st), 1484, 1245, 1196, 1073, 932, 819, 739. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.66 (d, 1H, J = 8.5 Hz), 7.16 (d, 1H, J = 8.5 Hz), 7.10 (s, 1H), 3.52 (s, 3H), 2.98 (t, 1H, J = 13.7 Hz), 2.81 (dd, 1H, J = 15.3, 5.2 Hz), 2.67 (d, 1H, J = 14.4 Hz), 2.62 (d, 1H, J = 14.3 Hz), 2.17 – 2.10 (m, 1H), 1.96 – 1.87 (m, 3H), 1.84 – 1.78 (m, 1H), 1.48 – 1.39 (m, 1H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 170.2, 145.4, 142.9, 133.5, 131.4, 129.4, 126.8, 77.2, 64.3, 42.2, 41.8, 37.5, 28.9, 26.6. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{18}ClNO_3Na$ ($[M+Na]^+$) 306.0873; found 306.0874.

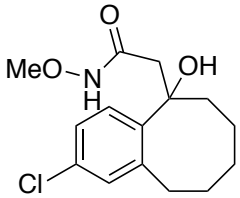


2-(2-Bromo-5-hydroxy-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-yl)-*N*-methoxyacetamide (12c). Isolated as a white solid (740 mg, 96%). **TLC**: R_f 0.33 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3391 (O–H st), 2936, 1642 (C=O st), 1477, 1445, 1267, 1075, 978, 738. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.60 (d, 1H, J = 8.5 Hz), 7.31 (dd, 1H, J = 8.5, 2.1 Hz), 7.25 (d, 1H, J = 2.1 Hz), 3.52 (s, 3H), 2.98 (t, 1H, J = 13.4 Hz), 2.80 (dd, 1H, J = 14.5, 5.6 Hz), 2.67 (d, 1H, J = 14.3 Hz), 2.62 (d, 1H, J = 14.3 Hz), 2.13 (dt, 1H, J = 12.9, 3.5 Hz), 1.96 – 1.87 (m, 3H), 1.85 – 1.78 (m, 1H), 1.48 – 1.40 (m, 1H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 170.2, 145.9, 143.2,

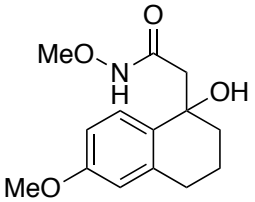
134.3, 129.9, 129.7, 121.6, 77.3, 64.3, 42.1, 41.7, 37.4, 28.9, 26.6. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{18}BrNO_3Na$ ($[M+Na]^+$) 350.0368; found 350.0367.



2-(2-Fluoro-5-hydroxy-5,6,7,8,9,10-hexahydrobenzo[8]annulen-5-yl)-*N*-methoxyacetamide (14a). Isolated as a white solid (555 mg, 92%). **TLC**: R_f 0.34 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3196 (O–H st), 2933, 1642 (C=O st), 1491, 1442, 1236, 1061, 961, 871, 821, 737. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.65 (br s, 1H), 6.89 (td, 1H, J = 8.5, 2.8 Hz), 6.77 (dd, 1H, J = 9.8, 2.8 Hz), 3.49 (s, 3H), 3.08 (br s, 2H), 2.69 – 2.32 (m, 3H), 1.99 (dq, 1H, J = 5.5, 4.0 Hz), 1.88 – 1.72 (m, 2H), 1.71 – 1.63 (m, 1H), 1.59 – 1.51 (m, 1H), 1.22 (br s, 2H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 170.0, 163.5 (d, J = 244.6 Hz), 141.6, 130.2 (2C), 118.1 (d, J = 21.1 Hz), 113.3 (d, J = 19.6 Hz), 77.3, 64.3, 49.6, 43.0, 34.2, 30.4, 23.9, 23.9. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{20}FNO_3Na$ ($[M+Na]^+$) 304.1325; found 304.1310.

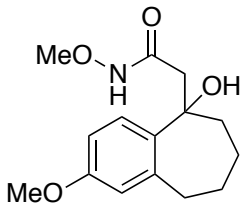


2-(2-Chloro-5-hydroxy-5,6,7,8,9,10-hexahydrobenzo[8]annulen-5-yl)-*N*-methoxyacetamide (14b). Isolated as a white solid (393 mg, 91%). **TLC**: R_f 0.34 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3194 (O–H st), 2932, 1643 (C=O st), 1484, 1441, 1268, 1087, 1061, 738. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.63 (br s, 1H), 7.17 (dd, 1H, J = 8.6, 2.3 Hz), 7.05 (d, 1H, J = 2.3 Hz), 3.49 (s, 3H), 3.07 (br s, 2H), 2.71 – 2.27 (m, 3H), 2.04 – 1.94 (m, 1H), 1.89 – 1.72 (m, 2H), 1.67 (q, 1H, J = 10.3, 7.7 Hz), 1.55 (ddq, 1H, J = 14.9, 9.6, 5.7 Hz), 1.20 (br s, 2H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 169.9, 144.5, 134.0, 131.6, 130.0, 128.7, 126.8, 77.3, 64.2, 49.6, 42.8, 34.0, 30.4, 23.9, 23.8. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{20}ClNO_3Na$ ($[M+Na]^+$) 320.1029; found 320.1030.

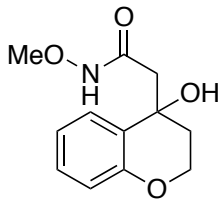


2-(1-Hydroxy-6-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methoxyacetamide (16). Isolated as a white solid (390 mg, 97%). **TLC**: R_f 0.40 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3206 (O–H st), 2938, 1646 (C=O st), 1608, 1501, 1245, 1039, 838, 738. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.45 (d, 1H, J = 8.7 Hz), 6.75 (dd, 1H, J = 8.7, 2.6 Hz), 6.60 (d, 1H, J = 2.5 Hz), 3.74 (s, 3H), 3.63 (s, 3H), 2.80 – 2.68 (m, 2H), 2.62 (d, 1H, J = 14.2 Hz), 2.45 (d, 1H, J = 14.2 Hz), 2.22 – 2.15 (m, 1H), 1.94 – 1.86 (m, 2H), 1.84 – 1.77 (m, 1H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 170.3, 160.2, 139.5, 134.5, 129.2, 113.8, 113.6, 72.2, 64.4, 55.6,

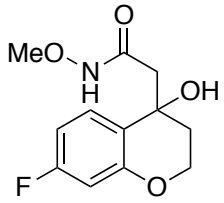
45.9, 37.7, 31.1, 21.1. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{19}NO_4Na$ ($[M+Na]^+$) 288.1212; found 288.1200.



2-(5-hydroxy-2-methoxy-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-yl)-*N*-methoxy-acetamide (18). Isolated as a white solid (1.10 g, 95%). **TLC**: R_f 0.35 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3401 (O–H st), 2932, 1647 (C=O st), 1495, 1266, 1251, 1066, 1032, 739.[1]**H-NMR** (600 MHz, Methanol-d_4): δ 7.56 (d, 1H, J = 8.7 Hz), 6.71 (dd, 1H, J = 8.7, 2.8 Hz), 6.64 (d, 1H, J = 2.7 Hz), 3.75 (s, 3H), 3.50 (s, 3H), 2.95 (t, 1H, J = 13.1 Hz), 2.79 (dd, 1H, J = 15.5, 5.2 Hz), 2.68 (d, 1H, J = 14.4 Hz), 2.59 (d, 1H, J = 14.4 Hz), 2.14 – 2.09 (m, 1H), 1.94 – 1.85 (m, 3H), 1.85 – 1.78 (m, 1H), 1.49 – 1.41 (m, 1H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 170.6, 159.9, 142.1, 138.4, 128.8, 117.6, 111.3, 77.4, 64.3, 55.5, 42.6, 42.1, 37.9, 29.1, 26.6. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{21}NO_4Na$ ($[M+Na]^+$) 302.1368; found 302.1361.

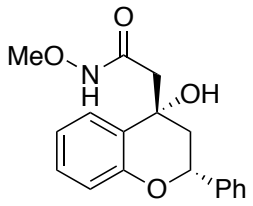


2-(4-Hydroxychroman-4-yl)-*N*-methoxyacetamide (20a). Isolated as a white solid (360 mg, 90%). **TLC**: R_f 0.28 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3230 (O–H st), 2932, 1650 (C=O st), 1489, 1453, 1266, 1224, 1059, 758, 740. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.47 (dd, 1H, J = 7.8, 1.6 Hz), 7.14 (ddd, 1H, J = 8.3, 7.2, 1.7 Hz), 6.90 (td, 1H, J = 7.9, 1.2 Hz), 6.76 (dd, 1H, J = 8.2, 1.1 Hz), 4.24 (t, 2H, J = 5.6 Hz), 3.63 (s, 3H), 2.77 (d, 1H, J = 14.2 Hz), 2.52 (d, 1H, J = 14.2 Hz), 2.44 – 2.38 (m, 1H), 2.11 – 2.06 (m, 1H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 169.6, 155.7, 130.1, 128.2, 128.2, 121.5, 118.0, 68.2, 64.3, 64.1, 45.0, 36.5. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{15}NO_4Na$ ($[M+Na]^+$) 260.0899; found 260.0900.

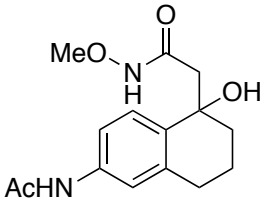


2-(7-Fluoro-4-hydroxychroman-4-yl)-*N*-methoxyacetamide (20b). Isolated as a white solid (440 mg, 96%). **TLC**: R_f 0.25 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3201 (O–H st), 1650 (C=O st), 1501, 1434, 1260, 1149, 1111, 1056, 977, 850, 737. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.48 (dd, 1H, J = 8.7, 6.6 Hz), 6.66 (td, 1H, J = 8.5, 2.6 Hz), 6.50 (dd, 1H, J = 10.4, 2.6 Hz), 4.26 (t, 2H, J = 5.6 Hz), 3.64 (s, 3H), 2.74 (d, 1H, J = 14.2 Hz), 2.52 (d, 1H, J = 14.2 Hz), 2.43 – 2.38 (m, 1H), 2.10 – 2.04 (m, 1H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 169.5, 164.3 (d, J = 244.6 Hz), 157.1 (d, J = 12.1 Hz), 130.0 (d, J = 10.6 Hz), 124.7

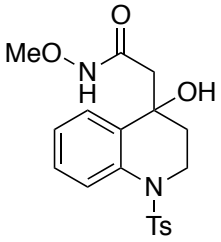
(d, *J* = 3.0 Hz), 108.6 (d, *J* = 21.1 Hz), 104.5 (d, *J* = 24.2 Hz), 68.0, 64.7, 64.4, 45.0, 36.2. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{14}FNO_4Na$ ($[M+Na]^+$) 278.0805; found 278.0813.



2-((2*R,4*S**)-4-Hydroxy-2-phenylchroman-4-yl)-*N*-methoxyacetamide (22).** Isolated as a white solid (330 mg, 91%). **TLC**: R_f 0.35 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3394 (O–H st), 3034, 1646 (C=O st), 1484, 1453, 1224, 1061, 756. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.54 (dd, 1H, *J* = 7.8, 1.6 Hz), 7.48 (d, 2H, *J* = 7.2 Hz), 7.39 (t, 2H, *J* = 7.6 Hz), 7.34 – 7.30 (m, 1H), 7.17 (ddd, 1H, *J* = 8.3, 7.3, 1.7 Hz), 6.95 (td, 1H, *J* = 7.8, 1.1 Hz), 6.84 (dd, 1H, *J* = 8.2, 1.0 Hz), 5.31 (dd, 1H, *J* = 12.5, 1.8 Hz), 3.69 (s, 3H), 2.75 (d, 1H, *J* = 14.2 Hz), 2.68 (dd, 1H, *J* = 14.2, 1.1 Hz), 2.61 (dd, 1H, *J* = 13.6, 2.1 Hz), 2.19 – 2.12 (m, 1H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 169.5, 155.2, 142.6, 130.1, 129.9, 129.5, 129.0, 127.7, 126.9, 121.8, 117.7, 77.5, 70.1, 64.4, 46.2, 44.0. **HRMS** (ESI) *m/z* calcd for $C_{18}H_{19}NO_4Na$ ($[M+Na]^+$) 336.1212; found 336.1212.

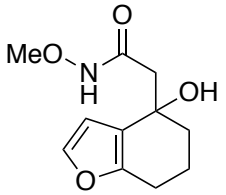


2-(6-Acetamido-1-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)-*N*-methoxyacetamide (24). Isolated as a white solid (50.2 mg, 58%). **TLC**: R_f 0.32 (90:10 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3307 (O–H st), 2941, 1665 (C=O st), 1544, 1416, 1025. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.49 (d, 1H, *J* = 8.5 Hz), 7.34 (dd, 1H, *J* = 8.5, 2.2 Hz), 7.29 (d, 1H, *J* = 2.1 Hz), 3.63 (s, 3H), 2.82 – 2.68 (m, 2H), 2.61 (d, 1H, *J* = 14.2 Hz), 2.46 (d, 1H, *J* = 14.2 Hz), 2.27 – 2.16 (m, 1H), 2.09 (s, 3H), 1.97 – 1.75 (m, 3H). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 171.7, 170.2, 138.9, 138.7, 138.1, 128.4, 120.8, 119.2, 72.2, 64.4, 45.8, 37.5, 31.0, 23.8, 21.1. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{20}N_2O_4Na$ ($[M+Na]^+$) 315.1321; found 315.1309.

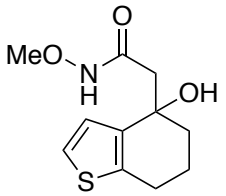


2-(4-Hydroxy-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl)-*N*-methoxyacetamide (26). Isolated as a white solid (15.2 mg, 76%). **TLC**: R_f 0.22 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3436 (O–H st), 1763 (C=O st), 1488, 1451, 1307, 1163, 1092, 814, 762, 729. **^{1}H-NMR** (600 MHz, Methanol-d_4): δ 7.75 (d, 1H, *J* = 8.3 Hz), 7.56 (d, 2H, *J* = 8.3 Hz), 7.52 (dd, 1H, *J* = 7.8, 1.5 Hz),

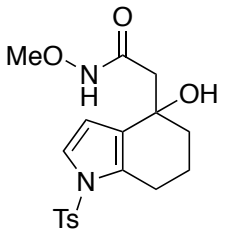
7.31 (d, 2H, J = 8.1 Hz), 7.23 (ddd, 1H, J = 8.5, 7.2, 1.6 Hz), 7.15 (td, 1H, J = 7.9, 1.1 Hz), 4.02 (ddd, 1H, J = 13.5, 7.9, 3.9 Hz), 3.79 (ddd, 1H, J = 13.4, 8.5, 3.7 Hz), 3.60 (s, 3H), 2.40 – 2.37 (m, 4H), 2.13 (ddd, 1H, J = 12.6, 8.5, 3.9 Hz), 1.85 (d, 1H, J = 14.2 Hz), 1.80 (ddd, 1H, J = 13.9, 7.9, 3.7 Hz). **^{13}C-NMR** (151 MHz, Methanol-d_4): δ 169.2, 145.7, 137.8, 137.1, 135.7, 131.0, 129.1, 128.4, 128.3, 125.9, 124.2, 69.6, 64.4, 45.0, 44.6, 35.5, 21.5. **HRMS** (ESI) *m/z* calcd for $C_{19}H_{20}N_2O_4Na$ ($[M+Na]^+$) 411.0991; found 411.0997.



2-(4-Hydroxy-4,5,6,7-tetrahydrobenzofuran-4-yl)-*N*-methoxyacetamide (28). Isolated as a colorless oil (381 mg, 88%). **TLC**: R_f 0.22 (1:3 hexanes/EtOAc). **IR** (NaCl, film): 3208 (O–H st), 2939, 1653 (C=O st), 1508, 1438, 1060, 942. **^{1}H-NMR** (600 MHz): δ 9.27 (s, 1H), 7.22 (d, 1H, J = 2.2 Hz), 6.36 (d, 1H, J = 2.1 Hz), 4.03 (s, 1H), 3.77 (s, 3H), 2.69 – 2.58 (m, 2H), 2.58 – 2.45 (m, 1H), 2.37 (d, 1H, J = 14.7 Hz), 2.07 – 1.94 (m, 1H), 1.91 (ddd, 1H, J = 13.2, 7.8, 2.9 Hz), 1.89 – 1.79 (m, 1H), 1.76 (ddd, 1H, J = 13.1, 10.1, 2.9 Hz). **^{13}C-NMR** (151 MHz): δ 169.6, 152.0, 141.2, 121.6, 107.5, 69.1, 64.4, 44.1, 36.6, 22.9, 19.5. **HRMS** (ESI) *m/z* calcd for $C_{11}H_{14}NO_4Na$ ($[M–H]^–$) 224.0923; found 224.0926.

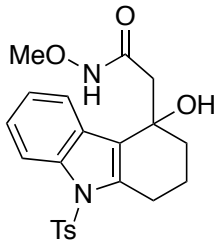


2-(4-Hydroxy-4,5,6,7-tetrahydrobenzo[*b*]thiophen-4-yl)-*N*-methoxyacetamide (29). Isolated as a colorless oil (251 mg, 96%). **TLC**: R_f 0.42 (1:3 hexanes/EtOAc). **IR** (NaCl, film): 3210 (O–H st), 2938, 1639 (C=O st), 1438, 1210, 1055. **^{1}H-NMR** (600 MHz): δ = 9.24 (s, 1H), 7.06 (d, 1H, J = 5.3 Hz), 7.00 (d, 1H, J = 5.3 Hz), 4.01 (s, 1H), 3.76 (s, 3H), 2.88 – 2.59 (m, 3H), 2.35 (d, 1H, J = 14.6 Hz), 2.12 – 1.77 (m, 4H) ppm **^{13}C-NMR** (151 MHz): δ 169.4, 139.2, 138.7, 124.8, 123.0, 70.0, 64.4, 44.4, 36.0, 25.0, 20.7. **HRMS** (ESI) *m/z* calcd for $C_{11}H_{15}NO_3SNa$ ($[M+Na]^+$) 264.0670; found 264.0669.

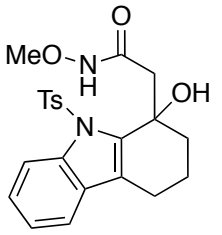


2-(4-Hydroxy-1-tosyl-4,5,6,7-tetrahydro-1*H*-indol-4-yl)-*N*-methoxyacetamide (32). Isolated as a colorless oil (136 mg, 81%). **TLC**: R_f 0.31 (95:5 CH_2Cl_2/MeOH). **IR** (NaCl, film): 3207 (O–H st), 2940, 1655 (C=O st), 1597, 1366, 1176, 814. **^{1}H-NMR** (600 MHz): δ 8.73 (s, 1H), 7.68 (d, 2H, J = 8.0 Hz), 7.30 (d, 2H, J = 8.1 Hz), 7.21 (d, 1H, J = 3.5 Hz), 6.28 (d, 1H, J = 3.5 Hz), 3.78 (s, 3H), 3.73 (s, 1H), 2.74 – 2.57 (m, 3H), 2.43 (s, 3H), 2.32 (d, 1H, J = 14.6 Hz), 1.92 – 1.85 (m, 1H), 1.85 – 1.67 (m, 3H). **^{13}C-NMR** (151 MHz): δ 169.5, 145.2,

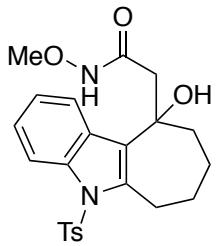
135.8, 130.1, 127.1, 121.5, 108.7, 68.9, 64.5, 44.4, 35.9, 22.7, 21.7, 19.6 (2 signals not resolved). **HRMS** (ESI) *m/z* calcd for $C_{18}H_{22}N_2O_5SNa$ ($[M+Na]^+$) 401.1147; found 401.1137.



2-(4-Hydroxy-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)-*N*-methoxyacetamide (34). Isolated as a colorless oil (388 mg, 86%). **TLC**: R_f 0.42 (1:3 hexanes/EtOAc). **IR** (NaCl, film): 3200 (O–H st), 2940, 1655 (C=O st), 1451, 1370, 1174, 1091, 661. **^{1}H-NMR** (600 MHz): δ 8.90 (s, 1H), 8.16 (d, 1H, *J* = 8.3 Hz), 7.75 (d, 1H, *J* = 7.8 Hz), 7.66 (d, 2H, *J* = 8.1 Hz), 7.26 (dd, 1H, *J* = 15.7, 1.4 Hz), 7.25 – 7.18 (m, 3H), 3.85 (s, 1H), 3.75 (s, 3H), 3.16 – 3.01 (m, 2H), 2.95 – 2.86 (m, 1H), 2.42 – 2.29 (m, 4H), 2.16 – 2.06 (m, 1H), 2.07 – 1.91 (m, 1H), 1.86 (t, 1H, *J* = 12.2 Hz), 1.83 – 1.69 (m, 1H) ppm. **^{13}C-NMR** (151 MHz): δ 169.4, 145.0, 136.5, 136.4, 135.9, 130.0, 127.2, 126.4, 124.1, 123.4, 121.2, 120.7, 114.3, 70.8, 64.4, 42.4, 36.2, 24.4, 21.6, 20.6. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{24}N_2O_5SNa$ ($[M+Na]^+$) 451.1304; found 451.1310.

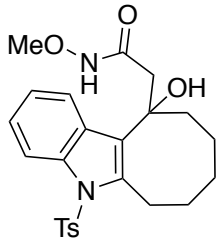


2-(1-Hydroxy-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-yl)-*N*-methoxyacetamide (36). Isolated as a white solid (124 mg, 91%). **TLC**: R_f 0.22 (1:1 hexanes/EtOAc). **IR** (NaCl, film): 3200 (O–H st), 2940, 1655 (C=O st), 1452, 1357, 1172, 1089, 704. **^{1}H-NMR** (600 MHz): δ 8.95 (s, 1H), 7.96 (d, 1H, *J* = 8.3 Hz), 7.58 (d, 2H, *J* = 8.0 Hz), 7.33 (d, 1H, *J* = 7.7 Hz), 7.29 (d, 1H, *J* = 8.5 Hz), 7.21 (t, 1H, *J* = 7.5 Hz), 7.12 (d, 2H, *J* = 8.1 Hz), 5.07 (s, 1H), 3.70 (s, 3H), 3.46 (d, 1H, *J* = 14.5 Hz), 2.75 – 2.64 (m, 2H), 2.58 (ddd, 1H, *J* = 17.0, 8.4, 5.4 Hz), 2.36 – 2.22 (m, 4H), 2.17 (t, 1H, *J* = 12.0, 10.8 Hz), 2.11 – 1.98 (m, 1H), 1.98 – 1.87 (m, 1H). **^{13}C-NMR** (151 MHz): δ 167.8, 145.1, 138.1, 137.7, 133.4, 130.2, 129.6, 127.3, 126.6, 126.1, 124.6, 119.6, 115.9, 69.4, 64.4, 46.0, 37.4, 22.5, 21.6, 19.0. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{24}N_2O_5SNa$ ($[M+Na]^+$) 451.1304; found 451.1307.



2-(10-hydroxy-5-tosyl-5,6,7,8,9,10-hexahydrocyclohepta[*b*]indol-10-yl)-*N*-methoxyacetamide (38). Isolated as a colorless oil (664 mg, 93%). **TLC**: R_f 0.20 (1:1 hexanes/EtOAc). **IR** (NaCl, film): 3204 (O–H st), 2935, 1658 (C=O st), 1642, 1451, 1367,

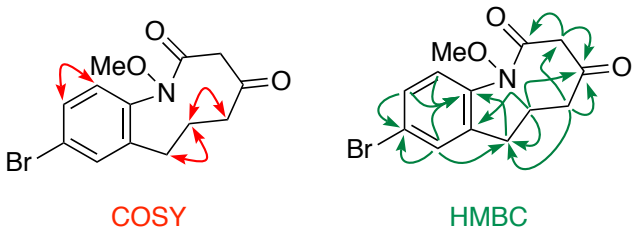
1171, 1089, 660. **^{1}H-NMR** (600 MHz): δ 8.69 (s, 1H), 8.25 (d, 1H, *J* = 8.4 Hz), 8.00 (d, 1H, *J* = 7.9 Hz), 7.58 (d, 2H, *J* = 8.3 Hz), 7.31 – 7.16 (m, 4H), 3.73 (s, 3H), 3.55 (s, 1H), 3.29 – 3.14 (m, 2H), 3.05 (d, 1H, *J* = 15.0 Hz), 2.41 (d, 1H, *J* = 14.9 Hz), 2.36 (s, 3H), 2.19 (dt, 1H, *J* = 14.2, 4.4 Hz), 2.07 (t, 1H, *J* = 13.1 Hz), 1.86 – 1.70 (m, 3H), 1.70 – 1.61 (m, 1H) ppm. **^{13}C-NMR** (151 MHz): δ 169.2, 144.9, 137.4, 136.9, 136.1, 129.8, 128.7, 126.3, 125.6, 124.3, 123.4, 121.5, 115.3, 74.6, 64.5, 42.4, 37.7, 25.3, 23.9, 21.8, 21.6. **HRMS** (ESI) *m/z* calcd for $C_{23}H_{26}N_2O_5SNa$ ([M+Na]$^+$) 465.1460; found 465.1464.



2-(11-hydroxy-5-tosyl-6,7,8,9,10,11-hexahydro-5*H*-cycloocta[*b*]indol-11-yl)-*N*-methoxy-acetamide (40). Isolated as a colorless oil (546 mg, 83%). **TLC**: R_f 0.17 (1:1 hexanes/EtOAc). **IR** (NaCl, film): 3208 (O–H st), 2933, 1655 (C=O st), 1452, 1366, 1176, 1090, 659. **^{1}H-NMR** (400 MHz): δ 8.48 (s, 1H), 8.26 (d, 1H, *J* = 8.3 Hz), 8.07 (d, 1H, *J* = 7.9 Hz), 7.61 (d, 2H, *J* = 8.0 Hz), 7.31 – 7.21 (m, 2H), 7.20 (d, 2H, *J* = 8.1 Hz), 3.63 (s, 3H), 3.56 (s, 1H), 3.06 (d, 1H, *J* = 14.8 Hz), 3.05 – 2.94 (m, 1H), 2.57 – 2.44 (m, 1H), 2.36 (s, 3H), 2.31 (d, 1H, *J* = 14.8 Hz), 2.10 (d, 1H, *J* = 15.6 Hz), 1.95 – 1.82 (m, 1H), 1.78 – 1.61 (m, 3H), 1.44 – 1.29 (m, 3H) ppm. **^{13}C-NMR** (151 MHz): δ 169.1, 144.8, 136.8, 136.7, 134.2, 129.9, 128.4, 126.2, 124.3, 124.1, 123.2, 121.8, 115.0, 74.5, 64.4, 45.7, 37.8, 26.3, 24.3, 23.5, 22.8, 21.6. **HRMS** (ESI) *m/z* calcd for $C_{24}H_{28}N_2O_5SNa$ ([M+Na]$^+$) 479.1617; found 479.1593.

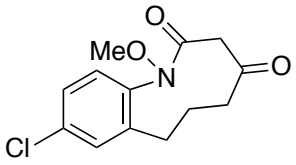
3. Synthesis of Medium Rings via Tandem ODRE

a. General procedure for tandem oxidative dearomatization–ring expanding rearomatization reactions

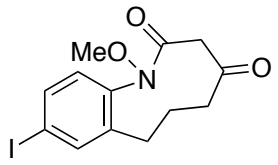


9-Bromo-1-methoxy-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (9a). *N*-Methoxyamide **7a** (0.10 g, 0.32 mmol, 1.0 equiv) was dissolved in nitromethane (3.2 mL) and cooled to 0 °C. [Bis(trifluoroacetoxy)iodo]benzene (PIFA) (0.21 g, 0.48 mmol, 1.5 equiv) was added as a solid and the reaction was stirred at 0 °C to 24 °C for 0.5–1 h until complete conversion. The reaction was then quenched with satd aq $NaHCO_3$. The mixture was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 5% MeOH in CH_2Cl_2) yielded 9-membered lactam **9a** as a colorless oil (72 mg, 73%).

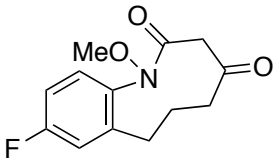
TLC: R_f 0.38 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2936, 1716 (C=O st), 1679 (C=O st), 1478, 1440, 1081, 1043, 984, 737. **^{1}H-NMR** (600 MHz) δ 7.47 – 7.44 (m, 2H), 7.10 (d, 1H, *J* = 8.9 Hz), 3.83 (s, 3H), 3.32 (d, 1H, *J* = 16.1 Hz), 3.13 (d, 1H, *J* = 16.1 Hz), 2.86 – 2.79 (m, 2H), 2.75 – 2.70 (m, 1H), 2.24 – 2.16 (m, 2H), 2.05 – 1.96 (m, 1H). **^{13}C-NMR** (151 MHz): δ 204.4, 163.9, 144.7, 135.1, 134.7, 131.3, 130.9, 126.0, 61.4, 54.5, 39.8, 31.1, 30.8. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{14}BrNO_3Na$ ($[M+Na]^+$) 334.0055; found 334.0056.



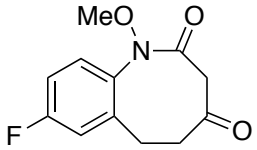
9-Chloro-1-methoxy-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (9b). Isolated as a yellow solid (48.5 mg, 72%). **TLC**: R_f 0.39 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2934, 1716 (C=O st), 1677 (C=O st), 1480, 1439, 1088, 1038, 734. **^{1}H-NMR** (600 MHz) δ 7.32 – 7.28 (m, 2H), 7.17 (d, 1H, *J* = 8.6 Hz), 3.83 (s, 3H), 3.32 (d, 1H, *J* = 16.1 Hz), 3.13 (d, 1H, *J* = 16.1 Hz), 2.87 – 2.80 (m, 2H), 2.75 – 2.70 (m, 1H), 2.24 – 2.16 (m, 2H), 2.05 – 1.96 (m, 1H). **^{13}C-NMR** (151 MHz): δ 204.4, 164.0, 144.5, 137.7, 134.7, 131.7, 130.7, 128.4, 61.4, 54.5, 39.8, 31.2, 30.8. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{14}ClNO_3Na$ ($[M+Na]^+$) 290.0560; found 290.0557.



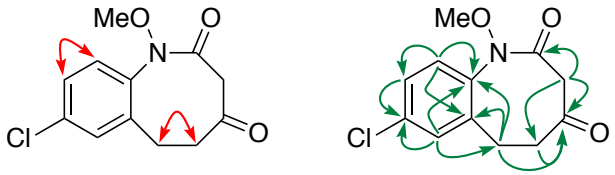
9-Iodo-1-methoxy-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (9c). Isolated as a colorless oil (75.1 mg, 75%). **TLC**: R_f 0.41 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2935, 1714 (C=O st), 1679 (C=O st), 1477, 1440, 1076, 1041, 984, 825, 737. **^{1}H-NMR** (600 MHz): δ 7.68 – 7.64 (m, 2H), 6.95 (d, 1H, *J* = 8.2 Hz), 3.82 (s, 3H), 3.31 (d, 1H, *J* = 16.1 Hz), 3.13 (d, 1H, *J* = 16.1 Hz), 2.85 – 2.76 (m, 2H), 2.73 – 2.68 (m, 1H), 2.24 – 2.14 (m, 2H), 2.05 – 1.95 (m, 1H). **^{13}C-NMR** (151 MHz): δ 204.4, 163.9, 144.7, 140.7, 137.3, 135.8, 130.9, 98.2, 61.4, 54.4, 39.8, 30.9, 30.8. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{14}INO_3Na$ ($[M+Na]^+$) 381.9916; found 381.9933.



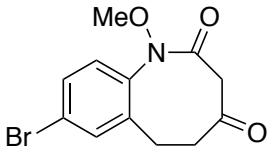
9-Fluoro-1-methoxy-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (9d). Isolated as a yellow solid (80.4 mg, 81%). **TLC**: R_f 0.38 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2937, 1716 (C=O st), 1680 (C=O st), 1493, 1270, 1044, 972, 738. **^{1}H-NMR** (600 MHz): δ 7.22 (dd, 1H, *J* = 8.5, 5.2 Hz), 7.04 – 6.98 (m, 2H), 3.84 (s, 3H), 3.32 (d, 1H, *J* = 16.0 Hz), 3.13 (d, 1H, *J* = 16.0 Hz), 2.88 – 2.81 (m, 2H), 2.77 – 2.71 (m, 1H), 2.24 – 2.16 (m, 2H), 2.06 – 1.97 (m, 1H). **^{13}C-NMR** (151 MHz): δ 204.4, 164.1, 164.0 (d, *J* = 253.7 Hz), 145.6 (d, *J* = 9.1 Hz), 132.2 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 9.1 Hz) , 118.2 (d, *J* = 22.7 Hz), 115.3 (d, *J* = 22.7 Hz), 61.3, 54.6, 39.8, 31.4 (d, *J* = 1.5 Hz), 30.8. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{14}FNO_3Na$ ($[M+Na]^+$) 274.0855; found 274.0850.



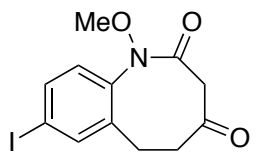
8-Fluoro-1-methoxy-5,6-dihydrobenzo[*b*]azocine-2,4(1*H*,3*H*)-dione (11a). Isolated as a red oil (45.8 mg, 46%). **TLC**: R_f 0.48 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2938, 1716 (C=O st), 1679 (C=O st), 1493, 1429, 1354, 1253, 1040, 912, 824, 736. **^{1}H-NMR** (600 MHz): δ 7.50 (dd, 1H, J = 8.8, 5.2 Hz), 7.13 (td, 1H, J = 8.3, 2.9 Hz), 7.10 (dd, 1H, J = 8.7, 2.8 Hz), 3.83 (s, 3H), 3.36 (d, 1H, J = 12.0 Hz), 3.25 (d, 1H, J = 12.0 Hz), 3.16 – 3.10 (m, 1H), 2.94 – 2.87 (m, 2H), 2.59 – 2.51 (m, 1H). **^{13}C-NMR** (151 MHz): δ 199.8, 162.9 (d, J = 252.2 Hz), 162.3 140.3 (d, J = 7.5 Hz), 134.5 (d, J = 3.0 Hz), 128.7 (d, J = 9.1 Hz), 116.9 (d, J = 22.7 Hz), 116.1 (d, J = 22.7 Hz), 61.8, 50.9, 43.5, 27.3 (d, J = 1.5 Hz). **HRMS** (ESI) *m/z* calcd for $C_{12}H_{12}FNO_3Na$ ($[M+Na]^+$) 260.0699; found 260.0701.



8-Chloro-1-methoxy-5,6-dihydrobenzo[*b*]azocine-2,4(1*H*,3*H*)-dione (11b). Isolated as a yellow solid (58.7 mg, 51%). **TLC**: R_f 0.40 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2937, 1715 (C=O st), 1679 (C=O st), 1482, 1418, 1343, 1269, 1185, 1095, 1072, 826, 737. **^{1}H-NMR** (600 MHz): δ 7.46 – 7.44 (m, 1H), 7.42 – 7.39 (m, 2H), 3.82 (s, 3H), 3.37 (d, 1H, J = 11.8 Hz), 3.25 (d, 1H, J = 11.7 Hz), 3.14 – 3.07 (m, 1H), 2.95 – 2.86 (m, 2H), 2.60 – 2.51 (m, 1H). **^{13}C-NMR** (151 MHz): δ 199.7, 162.0, 139.4, 137.0, 135.8, 130.4, 129.1, 127.8, 62.0, 50.8, 43.5, 27.2. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{12}ClNO_3Na$ ($[M+Na]^+$) 276.0403; found 276.0413.

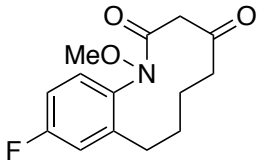


8-Bromo-1-methoxy-5,6-dihydrobenzo[*b*]azocine-2,4(1*H*,3*H*)-dione (11c). Isolated as a red solid (36.4 mg, 37%). **TLC**: R_f 0.50 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2937, 1716 (C=O st), 1680 (C=O st), 1480, 1342, 1271, 1183, 1039, 912, 821, 735. **^{1}H-NMR** (600 MHz): δ 7.58 – 7.53 (m, 2H), 7.38 (d, 1H, J = 8.1 Hz), 3.82 (s, 3H), 3.37 (d, 1H, J = 11.7 Hz), 3.25 (d, 1H, J = 11.6 Hz), 3.12 – 3.05 (m, 1H), 2.90 (t, 2H, J = 15.6 Hz), 2.55 (t, 1H, J = 13.1 Hz). **^{13}C-NMR** (151 MHz): δ 199.6, 161.9, 139.6, 137.5, 133.4, 132.1, 127.9, 123.9, 62.0, 50.8, 43.6, 27.2. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{12}BrNO_3Na$ ($[M+Na]^+$) 319.9898; found 319.9908.

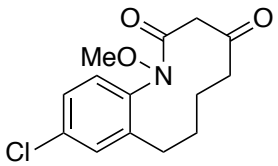


8-Iodo-1-methoxy-5,6-dihydrobenzo[*b*]azocine-2,4(1*H*,3*H*)-dione (11d). Isolated as a yellow solid (24.4 mg, 41%). **TLC**: R_f 0.64 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2933, 1715

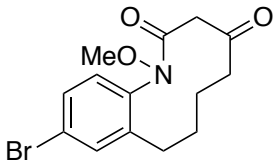
(C=O st), 1679 (C=O st), 1480, 1341, 1271, 1076, 1039, 913, 735. **^{1}H-NMR** (600 MHz): δ 7.77 (d, 1H, *J* = 1.9 Hz), 7.75 (dd, 1H, *J* = 8.3, 2.0 Hz), 7.23 (d, 1H, *J* = 8.3 Hz), 3.81 (s, 3H), 3.38 (d, 1H, *J* = 11.5 Hz), 3.24 (d, 1H, *J* = 11.5 Hz), 3.06 (t, 1H, *J* = 12.3 Hz), 2.89 (t, 2H, *J* = 12.8 Hz), 2.55 (t, 1H, *J* = 12.8 Hz). **^{13}C-NMR** (151 MHz): δ 199.6, 161.9, 139.7, 139.4, 138.2, 138.0, 127.9, 95.6, 62.0, 50.8, 43.6, 27.0. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{12}INO_3Na$ ($[M+Na]^+$) 367.9760; found 367.9770.



10-Fluoro-1-methoxy-5,6,7,8-tetrahydrobenzo[*b*]azecine-2,4(1*H*,3*H*)-dione (13a). Isolated as a yellow solid (89.0 mg, 90%). **TLC**: R_f 0.59 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2936, 1718 (C=O st), 1673 (C=O st), 1491, 1459, 1421, 1367, 1252, 1037, 915, 832, 734. **^{1}H-NMR** (600 MHz): δ 7.28 (dd, 1H, *J* = 8.6, 5.4 Hz), 7.07 (d, 1H, *J* = 9.1 Hz), 7.03 (t, 1H, *J* = 6.9 Hz), 3.75 (s, 3H), 3.53 (d, 1H, *J* = 15.2 Hz), 3.08 (d, 1H, *J* = 15.2 Hz), 2.99 (t, 1H, *J* = 15.7 Hz), 2.71 (d, 1H, *J* = 15.2 Hz), 2.57 (dt, 1H, *J* = 12.9, 6.2 Hz), 2.29 (ddd, 1H, *J* = 13.9, 8.6, 5.7 Hz), 2.01 – 1.93 (m, 1H), 1.91 – 1.83 (m, 1H), 1.80 – 1.73 (m, 1H), 1.30 – 1.21 (m, 1H). **^{13}C-NMR** (151 MHz): δ 203.2, 163.8, 163.5 (d, *J* = 252.2 Hz), 143.6 (d, *J* = 9.1 Hz), 133.8 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 9.1 Hz), 116.8 (d, *J* = 22.7 Hz), 114.8 (d, *J* = 22.7 Hz), 61.0, 47.5, 40.0, 27.9, 26.4, 20.9. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{16}FNO_3Na$ ($[M+Na]^+$) 288.1012; found 288.1015.

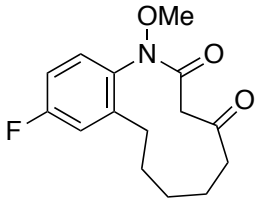


10-Chloro-1-methoxy-5,6,7,8-tetrahydrobenzo[*b*]azecine-2,4(1*H*,3*H*)-dione (13b). Isolated as a yellow oil (96.1 mg, 77%). **TLC**: R_f 0.42 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2935, 1718 (C=O st), 1674 (C=O st), 1480, 1361, 1115, 1092, 1039, 912, 830, 735. **^{1}H-NMR** (600 MHz): δ 7.37 (s, 1H), 7.31 (d, 1H, *J* = 8.3 Hz), 7.23 (d, 1H, *J* = 8.4 Hz), 3.74 (s, 3H), 3.54 (d, 1H, *J* = 15.2 Hz), 3.07 (d, 1H, *J* = 15.2 Hz), 2.97 (t, 1H, *J* = 16.0 Hz), 2.70 (d, 1H, *J* = 15.1 Hz), 2.56 (dt, 1H, *J* = 12.9, 6.1 Hz), 2.30 (dt, 1H, *J* = 13.8, 7.1 Hz), 1.99 (t, 1H, *J* = 11.9 Hz), 1.87 (t, 1H, *J* = 11.7 Hz), 1.80 – 1.74 (m, 1H), 1.29 – 1.21 (m, 1H). **^{13}C-NMR** (151 MHz): δ 203.3, 163.6, 142.6, 136.7, 136.4, 130.6, 130.3, 127.8, 61.1, 47.2, 40.3, 27.9, 26.2, 21.0. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{16}ClNO_3Na$ ($[M+Na]^+$) 304.0716; found 304.0717.

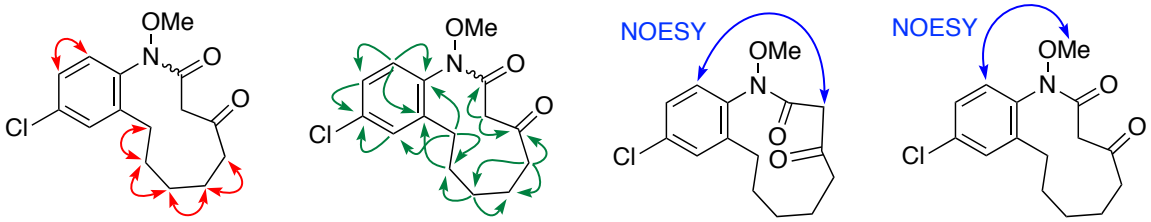


10-Bromo-1-methoxy-5,6,7,8-tetrahydrobenzo[*b*]azecine-2,4(1*H*,3*H*)-dione (13c). Isolated as a yellow oil (640 mg, 79%). **TLC**: R_f 0.47 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2934, 1719 (C=O st), 1673 (C=O st), 1479, 1358, 1083, 1038, 912, 832, 734. **^{1}H-NMR** (600 MHz): δ 7.53 (s, 1H), 7.47 (d, 1H, *J* = 7.5 Hz), 7.16 (d, 1H, *J* = 8.3 Hz), 3.74 (s, 3H), 3.54 (d, 1H, *J* = 15.2 Hz), 3.07 (d, 1H, *J* = 15.2 Hz), 2.97 (t, 1H, *J* = 13.9 Hz), 2.71 (d, 1H, *J* = 15.0 Hz), 2.56 (dt, 1H,

J = 12.9, 6.1 Hz), 2.31 (dt, 1H, *J* = 13.5, 7.9 Hz), 1.98 (t, 1H, *J* = 11.4 Hz), 1.87 (t, 1H, *J* = 11.9 Hz), 1.81 – 1.75 (m, 1H), 1.30 – 1.22 (m, 1H). **^{13}C-NMR** (151 MHz): δ 203.2, 163.6, 142.9, 136.9, 133.4, 130.8, 130.8, 124.9, 61.2, 47.1, 40.3, 28.0, 26.2, 21.1. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{16}BrNO_3Na$ ([M+Na]$^+$) 348.0211; found 348.0197.

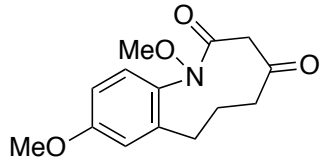


11-Fluoro-1-methoxy-1,5,6,7,8,9-hexahydro-2*H*-benzo[*b*][1]azacycloundecine-2,4(3*H*)-dione (15a). Isolated as a yellow oil (74.4 mg, 74%, mixture of rotamers (3:2 *E*/*Z*)). **TLC**: R_f 0.38 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2937, 1710 (C=O st), 1663 (C=O st), 1491, 1408, 1386, 1247, 1150, 966, 871, 826, 734. **^{1}H-NMR** (600 MHz, *E rotamer*): δ 7.22 (dd, 1H, *J* = 8.5, 5.4 Hz), 7.03 (dd, 1H, *J* = 9.0, 2.7 Hz), 7.01 – 6.95 (m, 1H), 4.03 (d, 1H, *J* = 15.0 Hz), 3.69 (s, 3H), 3.37 (d, 1H, *J* = 15.0 Hz), 2.94 (ddd, 1H, *J* = 12.7, 10.0, 2.9 Hz), 2.78 (ddd, 1H, *J* = 13.5, 7.5, 3.8 Hz), 2.38 (dt, 1H, *J* = 13.5, 8.6 Hz), 2.33 – 2.22 (m, 1H), 1.92 – 1.71 (m, 3H), 1.48 – 1.36 (m, 3H). **^{13}C-NMR** (151 MHz, *E rotamer*): δ 204.6, 167.1, 163.0 (d, *J* = 249.2 Hz), 144.9 (d, *J* = 7.5 Hz), 132.5 (d, *J* = 9.1 Hz), 130.2 (d, *J* = 3.0 Hz), 118.3 (d, *J* = 22.6 Hz), 113.3 (d, *J* = 22.6 Hz), 62.0, 48.7, 38.0, 29.4, 27.1, 26.6, 19.9. **^{1}H-NMR** (600 MHz, *Z rotamer*): δ 7.14 (dd, 1H, *J* = 8.4, 5.3 Hz), 7.08 (dd, 1H, *J* = 8.8, 1.9 Hz), 7.01 – 6.95 (m, 1H), 3.76 (s, 3H), 3.31 (d, 1H, *J* = 16.5 Hz), 3.22 (d, 1H, *J* = 16.5 Hz), 3.11 (dt, 1H, *J* = 15.3, 8.7 Hz), 3.02 – 2.97 (m, 1H), 2.64 (dt, 1H, *J* = 14.7, 4.3 Hz), 2.33 – 2.22 (m, 1H), 1.92 – 1.71 (m, 4H), 1.48 – 1.36 (m, 1H), 0.91 – 0.80 (m, 1H). **^{13}C-NMR** (151 MHz, *Z rotamer*): δ 203.8, 163.5, 163.4 (d, *J* = 252.2 Hz), 144.7 (d, *J* = 9.1 Hz), 132.7 (d, *J* = 1.5 Hz), 131.3 (d, *J* = 9.1 Hz), 118.1 (d, *J* = 21.1 Hz), 114.0 (d, *J* = 22.6 Hz), 60.7, 48.9, 41.2, 28.4, 28.0, 24.1, 21.8. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{18}FNO_3Na$ ([M+Na]$^+$) 302.1168; found 302.1173.

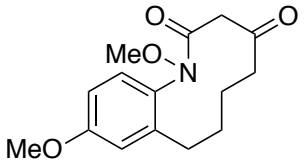


11-Chloro-1-methoxy-1,5,6,7,8,9-hexahydro-2*H*-benzo[*b*][1]azacycloundecine-2,4(3*H*) dione (15b). Isolated as a yellow oil (69.6 mg, 70%, mixture of rotamers (2:1 *E*/*Z*)). **TLC**: R_f 0.50 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2937, 1711 (C=O st), 1665 (C=O st), 1481, 1441, 1405, 1269, 1231, 1187, 981, 826, 738. **^{1}H-NMR** (600 MHz, *E rotamer*): δ 7.31 (d, 1H, *J* = 1.6 Hz), 7.29 – 7.25 (m, 1H), 7.18 (d, 1H, *J* = 8.3 Hz), 4.02 (d, 1H, *J* = 15.0 Hz), 3.69 (s, 3H), 3.37 (d, 1H, *J* = 15.0 Hz), 2.97 – 2.90 (m, 1H), 2.77 (ddd, 1H, *J* = 12.0, 7.3, 3.9 Hz), 2.38 (dt, 1H, *J* = 13.5, 8.6 Hz), 2.32 – 2.27 (m, 1H), 1.90 – 1.71 (m, 3H), 1.47 – 1.35 (m, 3H). **^{13}C-NMR** (151 MHz, *E rotamer*): δ 204.5, 167.0, 143.9, 135.6, 132.8, 131.9, 131.6, 126.6, 62.1, 48.7, 38.0, 29.2, 27.1, 26.6, 19.9. **^{1}H-NMR** (600 MHz, *Z rotamer*): δ 7.37 (s, 1H), 7.29 – 7.25 (m, 1H), 7.09 (d, 1H, *J* = 8.2 Hz), 3.75 (s, 3H), 3.31 (d, 1H, *J* = 16.5 Hz), 3.22 (d, 1H, *J* = 16.5 Hz), 3.11 (dt, 1H, *J* = 15.9, 8.3 Hz), 3.01 – 2.95 (m, 1H), 2.65 – 2.59 (m, 1H), 2.31 –

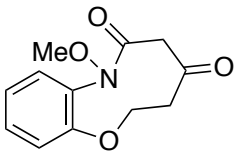
2.23 (m, 1H), 1.90 – 1.71 (m, 4H), 1.47 – 1.35 (m, 1H), 0.89 – 0.78 (m, 1H). **^{13}C-NMR** (151 MHz, *Z rotamer*): δ 203.7, 163.4, 143.7, 136.6, 135.1, 131.7, 130.7, 127.1, 60.9, 48.7, 41.2, 28.3, 27.9, 24.2, 21.8. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{18}ClNO_3Na$ ($[M+Na]^+$) 318.0873; found 318.0863.



1,9-Dimethoxy-1,5,6,7-tetrahydro-2*H*-benzo[*b*]azonine-2,4(3*H*)-dione (17). The general procedure was modified using methanol as the solvent at 0 ºC instead of nitromethane. Isolated as a white solid (85.5 mg, 86%). **TLC**: R_f 0.60 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2977, 2940 , 1723 (C=O st), 1679 (C=O st), 1501, 1446, 1280, 1239, 1050, 1030, 920. **^{1}H-NMR** (600 MHz): δ 7.13 (d, 1H, *J* = 8.6 Hz), 6.81 (dd, 1H, *J* = 8.6, 2.9 Hz), 6.76 (d, 1H, *J* = 2.9 Hz), 3.82 (s, 3H), 3.82 (s, 3H), 3.29 (d, 1H, *J* = 16.1 Hz), 3.16 (d, 1H, *J* = 16.1 Hz), 2.87 – 2.80 (m, 2H), 2.73 – 2.68 (m, 1H), 2.22 – 2.14 (m, 2H), 2.07 – 1.98 (m, 1H). **^{13}C-NMR** (151 MHz): δ 204.5, 164.4, 161.8, 144.3, 130.8, 128.6, 116.2, 113.5, 61.0, 55.5, 54.6, 39.9, 31.7, 31.1. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{17}NO_4Na$ ($[M+Na]^+$) 286.1055; found 286.1051

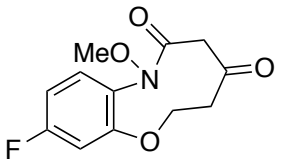


1,10-Dimethoxy-5,6,7,8-tetrahydrobenzo[*b*]azecine-2,4(1*H*,3*H*)-dione (19). The general procedure was modified using methanol as the solvent at 0 ºC instead of nitromethane. Isolated as a yellow oil (780 mg, 87%). **TLC**: R_f 0.55 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2937, 1717 (C=O st), 1675 (C=O st), 1604, 1495, 1424, 1248, 1214, 1035, 842, 703. **^{1}H-NMR** (600 MHz): δ 7.19 (d, 1H, *J* = 8.5 Hz), 6.86 (d, 1H, *J* = 2.3 Hz), 6.84 (dd, 1H, *J* = 8.6, 2.6 Hz), 3.85 (s, 3H), 3.73 (s, 3H), 3.58 (d, 1H, *J* = 15.1 Hz), 3.06 (d, 1H, *J* = 15.1 Hz), 2.97 (ddd, 1H, *J* = 14.9, 12.7, 4.7 Hz), 2.69 (dt, 1H, *J* = 14.8, 3.9 Hz), 2.59 (dt, 1H, *J* = 12.6, 6.0 Hz), 2.26 (ddd, 1H, *J* = 14.2, 9.1, 6.1 Hz), 2.00 – 1.92 (m, 1H), 1.83 (td, 1H, *J* = 13.9, 3.7 Hz), 1.76 – 1.69 (m, 1H), 1.27 – 1.19 (m, 1H). **^{13}C-NMR** (151 MHz): δ 203.5, 164.0, 161.1, 142.4, 130.7, 130.2, 115.3, 112.6, 60.6, 55.5, 47.6, 39.6, 28.2, 26.3, 20.8. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{19}NO_4Na$ ($[M+Na]^+$) 300.1212; found 300.1206.

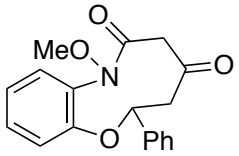


7-Methoxy-2,3-dihydrobenzo[*b*][1,4]oxazonine-4,6(5*H*,7*H*)-dione (21a). Isolated as a yellow oil (88.7 mg, 89%). **TLC**: R_f 0.30 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2936, 1718 (C=O st), 1678 (C=O st), 1491, 1346, 1237, 1118, 1034, 1015, 898, 767, 738. **^{1}H-NMR** (600 MHz): δ 7.48 (ddd, 1H, *J* = 8.1, 7.6, 1.7 Hz), 7.42 (dd, 1H, *J* = 7.9, 1.6 Hz), 7.25 – 7.20 (m, 2H), 4.64 (br s, 1H), 4.37 (br s, 1H), 3.83 (s, 3H), 3.29 (s, 2H), 3.18 (br s, 1H), 2.47 (br s, 1H). **^{13}C-NMR** (151 MHz): δ 202.2, 164.6, 155.8, 132.3, 131.2, 129.6, 125.0, 120.8, 72.8,

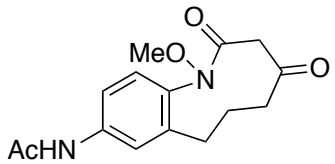
61.5, 51.8, 42.9. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{13}NO_4Na$ ($[M+Na]^+$) 258.0742; found 258.0735.



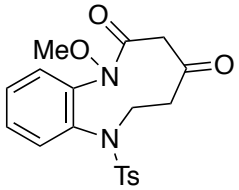
10-Fluoro-7-methoxy-2,3-dihydrobenzo[*b*][1,4]oxazonine-4,6(5*H*,7*H*)-dione (21b). Isolated as a yellow oil (85.0 mg, 86%). **TLC**: R_f 0.30 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2938, 1721 (C=O st), 1682 (C=O st), 1498, 1359, 1274, 1248, 1151, 1109, 1034, 1015, 739. **^{1}H-NMR** (600 MHz): δ 7.42 (dd, 1H, *J* = 8.7, 6.0 Hz), 6.97 – 6.92 (m, 2H), 4.67 (br s, 1H), 4.35 (br s, 1H), 3.82 (s, 3H), 3.29 (s, 2H), 3.18 (br s, 1H), 2.48 (br s, 1H). **^{13}C-NMR** (151 MHz): δ 201.9, 164.6, 164.3 (d, *J* = 253.7 Hz), 157.0 (d, *J* = 10.6 Hz), 131.0 (d, *J* = 10.6 Hz), 127.6 (d, *J* = 4.5 Hz), 112.5 (d, *J* = 22.7 Hz), 108.6 (d, *J* = 24.2 Hz), 73.3, 61.5, 52.0, 42.7. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{12}FNO_4Na$ ($[M+Na]^+$) 276.0648; found 276.0643.



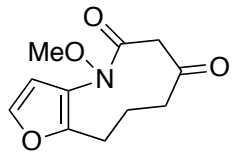
7-Methoxy-2-phenyl-2,3-dihydrobenzo[*b*][1,4]oxazonine-4,6(5*H*,7*H*)-dione (23). Isolated as a yellow oil (81.6 mg, 82%). **TLC**: R_f 0.41 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2932, 1713 (C=O st), 1684 (C=O st), 1489, 1354, 1259, 1216, 1160, 1121, 1032, 911, 812, 756, 737. **^{1}H-NMR** (600 MHz): δ 7.48 – 7.36 (m, 7H), 7.23 (td, 1H, *J* = 7.7, 1.2 Hz), 7.09 (d, 1H, *J* = 8.2 Hz), 5.31 (d, 1H, *J* = 11.6 Hz), 3.92 (s, 3H), 3.46 (dd, 1H, *J* = 14.4, 11.1 Hz), 3.38 (s, 2H), 2.61 (dd, 1H, *J* = 14.4, 1.9 Hz). **^{13}C-NMR** (151 MHz): δ 201.2, 165.3, 155.6, 139.7, 132.3, 131.2, 129.3, 128.9, 128.6, 125.4, 125.2, 120.7, 86.1, 61.7, 51.9, 50.4. **HRMS** (ESI) *m/z* calcd for $C_{18}H_{17}NO_4Na$ ($[M+Na]^+$) 334.1055; found 334.1055.



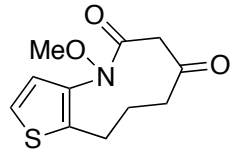
***N*-(1-Methoxy-2,4-dioxo-2,3,4,5,6,7-hexahydro-1*H*-benzo[*b*]azonin-9-yl)acetamide (25).** Isolated as a light yellow oil (11.0 mg, 57%). **TLC**: R_f 0.28 (95:5 EtOAc/MeOH). **IR** (NaCl, film): 2935, 1710 (C=O st), 1671 (C=O st), 1543, 1499, 729. **^{1}H-NMR** (600 MHz): 7.52 (dd, 1H, *J* = 8.4, 2.5 Hz), 7.47 (d, 1H, *J* = 2.5 Hz), 7.32 (s, 1H), 7.16 (d, 1H, *J* = 8.5 Hz), 3.83 (s, 3H), 3.30 (d, 1H, *J* = 16.1 Hz), 3.15 (d, 1H, *J* = 16.0), 2.84 (td, 2H, *J* = 13.2, 2.4 Hz), 2.76 – 2.67 (m, 1H), 2.27 – 2.12 (m, 5H), 2.08 – 1.95 (m, 1H). **^{13}C-NMR** (151 MHz): δ 204.8, 168.3, 164.2, 143.9, 140.8, 131.5, 130.4, 121.5, 118.7, 61.2, 54.6, 39.9, 31.5, 31.1, 24.8. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{18}N_2O_4Na$ ($[M+Na]^+$) 313.1164; found 313.1157.



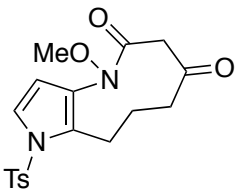
1-Methoxy-7-tosyl-1,5,6,7-tetrahydro-2*H*-benzo[*b*][1,4]diazonine-2,4(3*H*)-dione (27). Isolated as a yellow oil (8.7 mg, 88%). **TLC**: R_f 0.38 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2934, 2359, 2341, 1719 (C=O st), 1681 (C=O st), 1492, 1356, 1164, 912, 771, 734. **^{1}H-NMR** (600 MHz): δ 7.88 (d, 2H, *J* = 8.2 Hz), 7.55 – 7.47 (m, 3H), 7.38 (d, 2H, *J* = 8.1 Hz), 7.22 (dd, 1H, *J* = 7.5, 1.7 Hz), 4.05 (d, 1H, *J* = 13.6 Hz), 4.01 (s, 3H), 3.46 (t, 1H, *J* = 11.9 Hz), 3.30 (d, 1H, *J* = 15.8 Hz), 3.16 (d, 1H, *J* = 15.8 Hz), 3.01 (t, 1H, *J* = 10.9 Hz), 2.47 (s, 3H), 2.20 (dd, 1H, *J* = 13.3, 4.0 Hz). **^{13}C-NMR** (151 MHz): δ 202.1, 163.5, 144.6, 139.0, 138.5, 135.1, 132.5, 130.9, 130.6, 130.2, 129.9, 128.7, 62.6, 53.2, 51.6, 41.3, 21.7. **HRMS** (ESI) *m/z* calcd for $C_{19}H_{22}N_2O_5SNa$ ($[M+Na]^+$) 413.1147; found 413.1133.



4-Methoxy-4,8,9,10-tetrahydro-5*H*-furo[3,2-*b*]azonine-5,7(6*H*)-dione (30). Isolated as a light yellow oil (22.6 mg, 57%). **TLC**: R_f 0.31 (1:3 hexanes/EtOAc). **IR** (NaCl, film): 2937, 1682 (C=O st), 1438, 1358, 1130, 1038. **^{1}H-NMR** (400 MHz): δ 7.39 (d, 1H, *J* = 2.1 Hz), 6.31 (d, 1H, *J* = 2.0 Hz), 3.83 (s, 3H), 3.42 – 3.14 (m, 2H), 2.83 – 2.70 (m, 2H), 2.35 – 2.01 (m, 4H). **^{13}C-NMR** (151 MHz): δ 202.1, 164.7, 155.5, 142.8, 120.9, 109.5, 61.6, 54.2, 39.8, 28.4, 26.0. **HRMS** (ESI) *m/z* calcd for $C_{11}H_{13}NO_4Na$ ($[M+Na]^+$) 246.0742; found 246.0740.

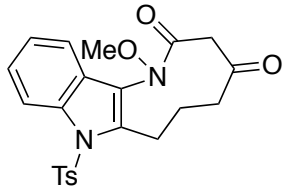


4-Methoxy-4,8,9,10-tetrahydro-5*H*-thieno[3,2-*b*]azonine-5,7(6*H*)-dione (31). Isolated as a yellow oil (19.8 mg, 61%). **TLC**: R_f 0.16 (1:1 hexanes/EtOAc). **IR** (NaCl, film): 2933, 1711 (C=O st), 1678 (C=O st), 1441, 1402, 1349, 1042. **^{1}H-NMR** (600 MHz): δ 7.29 – 7.26 (m, 1H), 6.85 (d, 1H, *J* = 5.3 Hz), 3.85 (s, 3H), 3.34 (d, 1H, *J* = 16.1 Hz), 3.17 (d, 1H, *J* = 16.1 Hz), 3.06 – 2.87 (m, 3H), 2.83 – 2.70 (m, 1H), 2.23 (dt, 1H, *J* = 13.5, 4.6 Hz), 2.20 – 2.10 (m, 2H). **^{13}C-NMR** (151 MHz): δ 203.0, 164.6, 146.4, 132.8, 125.7, 125.2, 61.7, 54.3, 39.7, 31.9, 27.4. **HRMS** (ESI) *m/z* calcd for $C_{11}H_{13}NO_3Na$ ($[M+Na]^+$) 262.0514; found 262.0525.

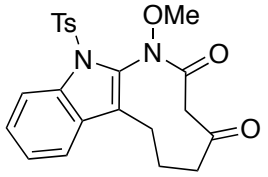


4-Methoxy-1-tosyl-4,8,9,10-tetrahydropyrrolo[3,2-*b*]azonine-5,7(1*H*,6*H*)-dione (33). Isolated as a light yellow oil (15.0 mg, 55%). **TLC**: R_f 0.15 (1:1 hexanes/EtOAc). **IR** (NaCl,

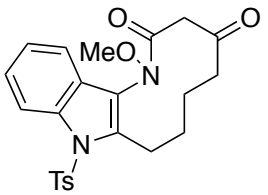
film): 2934, 1712 (C=O st), 1681 (C=O st), 1370, 1177, 1125, 702. **^{1}H-NMR** (600 MHz): δ 7.76 (d, 2H, *J* = 8.2 Hz), 7.38 (d, 2H, *J* = 8.0 Hz), 7.34 (d, 1H, *J* = 3.6 Hz), 6.19 (d, 1H, *J* = 3.6 Hz), 3.76 (s, 3H), 3.29 (d, 1H, *J* = 16.3 Hz), 3.11 (d, 1H, *J* = 16.2 Hz), 2.65 (t, 2H, *J* = 13.8 Hz), 2.50 – 2.39 (m, 3H), 2.13 – 1.99 (m, 2H), 1.96 – 1.86 (m, 1H). **^{13}C-NMR** (151 MHz): δ 202.9, 164.8, 146.0, 135.3, 135.0, 130.3, 127.4, 124.1, 122.5, 109.9, 61.5, 54.2, 39.6, 29.1, 24.6, 21.8. **HRMS** (ESI) *m/z* calcd for $C_{18}H_{21}N_2O_5S$ ($[M+H]^+$) 377.1171; found 377.1187.



1-Methoxy-8-tosyl-5,6,7,8-tetrahydroazonino[3,2-*b*]indole-2,4(1*H*,3*H*)-dione (35). Isolated as a light yellow oil (25.6 mg, 68%). **TLC**: R_f 0.25 (1:1 hexanes/EtOAc). **IR** (NaCl, film): 2935, 1714 (C=O st), 1686 (C=O st), 1450, 1374, 1175, 1039, 660. **^{1}H-NMR** (600 MHz): δ 8.08 (d, 1H, *J* = 8.4 Hz), 7.78 (d, 2H, *J* = 8.4 Hz), 7.41 (d, 1H, *J* = 8.0 Hz), 7.36 (t, 1H, *J* = 7.1 Hz), 7.32 – 7.29 (m, 3H), 3.84 (s, 3H), 3.60 – 3.53 (m, 1H), 3.31 (d, 1H, *J* = 16.2 Hz), 3.00 (d, 1H, *J* = 16.2 Hz), 2.98 – 2.90 (m, 1H), 2.82 – 2.72 (m, 1H), 2.52 (q, 1H, *J* = 12.9 Hz), 2.39 (s, 3H), 2.28 – 2.12 (m, 2H). **^{13}C-NMR** (151 MHz): δ 202.9, 165.3, 145.7, 142.3, 135.6, 135.2, 130.1, 126.8, 125.9, 125.1, 124.7, 119.8, 117.3, 115.1, 62.5, 53.4, 40.0, 29.8, 26.0, 21.7. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{22}N_2O_5SNa$ ($[M+Na]^+$) 449.1147; found 449.1156.

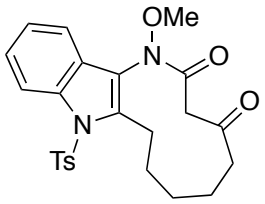


1-Methoxy-12-tosyl-5,6,7,12-tetrahydroazonino[2,3-*b*]indole-2,4(1*H*,3*H*)-dione (37). Isolated as a yellow oil (25.3 mg, 67%). **TLC**: R_f 0.23 (4:1 benzene/EtOAc). **IR** (ATR, ZnSe): 2923, 1721 (C=O st), 1697 (C=O st), 1368, 1170, 1140, 748. **^{1}H-NMR** (600 MHz): δ 8.20 (d, 1H, *J* = 8.5 Hz), 7.95 (d, 2H, *J* = 8.1 Hz), 7.54 (d, 1H, *J* = 7.9 Hz), 7.51 (t, 1H, *J* = 7.9 Hz), 7.33 (t, 1H, *J* = 7.6 Hz), 7.21 (d, 2H, *J* = 8.1 Hz), 3.81 (s, 3H), 3.53 (d, 1H, *J* = 16.4 Hz), 3.46 (d, 1H, *J* = 16.4 Hz), 3.01 (dt, 1H, *J* = 14.2, 3.4 Hz), 2.75 (td, 1H, *J* = 13.7, 3.5 Hz), 2.66 (t, 1H, *J* = 11.9 Hz), 2.35 (s, 3H), 2.34 – 2.21 (m, 2H), 2.23 – 2.14 (m, 1H). **^{13}C-NMR** (151 MHz): δ 202.1, 165.7, 145.2, 135.5, 135.3, 129.5, 128.0, 127.7, 127.4, 126.6, 125.5, 123.8, 120.2, 114.8, 61.7, 53.7, 40.5, 29.2, 24.2, 21.6. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{23}N_2O_5S$ ($[M+H]^+$) 427.1328; found 427.1334.



1-Methoxy-9-tosyl-1,5,6,7,8,9-hexahydro-2*H*-azecino[3,2-*b*]indole-2,4(3*H*)-dione (39). Isolated as a light yellow oil (46.3 mg, 66%). **TLC**: R_f 0.25 (1:1 hexanes/EtOAc). **IR** (NaCl, film): 2933, 1721 (C=O st), 1688 (C=O st), 1452, 1373, 1174, 1031, 733, 659. **^{1}H-NMR**

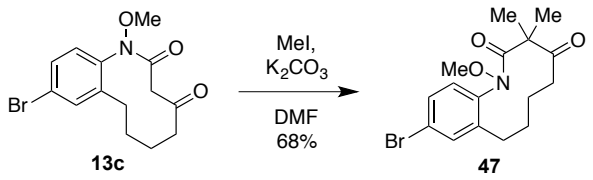
(600 MHz): δ 8.19 (d, 1H, *J* = 8.4 Hz), 7.59 (d, 2H, *J* = 8.0 Hz), 7.43 – 7.34 (m, 2H), 7.35 – 7.28 (m, 1H), 7.20 (d, 2H, *J* = 8.1 Hz), 3.62 (s, 3H), 3.52 (d, 1H, *J* = 15.4 Hz), 3.32 (dt, 1H, *J* = 15.3, 4.6 Hz), 3.12 (ddd, 1H, *J* = 15.6, 11.6, 5.0 Hz), 3.06 (d, 1H, *J* = 15.4 Hz), 2.58 (ddd, 1H, *J* = 13.8, 8.8, 5.5 Hz), 2.54 – 2.42 (m, 1H), 2.40 – 2.31 (m, 4H), 1.92 (td, 1H, *J* = 12.0, 11.2, 4.8 Hz), 1.78 (dq, 1H, *J* = 12.6, 6.6, 5.2 Hz), 1.25 (dd, 1H, *J* = 16.1, 9.3 Hz). **^{13}C-NMR** (151 MHz): δ 203.7, 164.7, 145.6, 141.2, 136.0, 134.6, 130.0, 129.9, 126.4, 126.0, 125.2, 122.6, 117.6, 115.9, 61.3, 47.1, 41.4, 27.6, 23.3, 21.9, 21.6. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{25}N_2O_5S$ ($[M+H]^+$) 441.1484; found 441.1484.



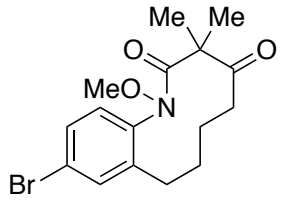
1-Methoxy-10-tosyl-5,6,7,8,9,10-hexahydro-[1]azacycloundecino[3,2-*b*]indole-2,4(1*H*,3*H*) dione (41). Isolated as a light yellow oil (53.7 mg, 60%). **TLC**: R_f 0.30 (1:1 hexanes/EtOAc). **IR** (NaCl, film): 2936, 1712 (C=O st), 1677 (C=O st), 1450, 1373, 1174, 1089, 729. **^{1}H-NMR** (600 MHz): δ 8.21 (d, 1H, *J* = 8.5 Hz), 7.64 (d, 2H, *J* = 8.0 Hz), 7.38 (t, 1H, *J* = 7.9 Hz), 7.34 (t, 1H, *J* = 7.5 Hz), 7.31 – 7.18 (m, 3H), 3.68 (s, 3H), 3.43 – 3.33 (m, 1H), 3.32 – 3.21 (m, 2H), 3.17 (d, 1H, *J* = 16.6 Hz), 2.88 (dt, 1H, *J* = 15.5, 5.0 Hz), 2.37 (s, 3H), 2.35 – 2.24 (m, 1H), 2.25 – 2.16 (m, 1H), 2.04 – 1.94 (m, 1H), 1.85 – 1.76 (m, 1H), 1.52 – 1.29 (m, 2H), 0.88 (q, 1H, *J* = 12.9 Hz). **^{13}C-NMR** (151 MHz): δ 203.8, 164.4, 145.5, 140.6, 135.2, 135.1, 130.1, 126.7, 126.4, 125.6, 125.1, 121.4, 116.5, 115.7, 61.9, 47.1, 42.4, 27.0, 25.7, 23.9, 22.0, 21.6. **HRMS** (ESI) *m/z* calcd for $C_{24}H_{27}N_2O_5S$ ($[M+H]^+$) 455.1641; found 455.1638.

G. DOWNSTREAM MODIFICATIONS OF ODRE SCAFFOLDS

1. α-GEMINAL DIMETHYLATION OF β-KETOLACTAM 13C



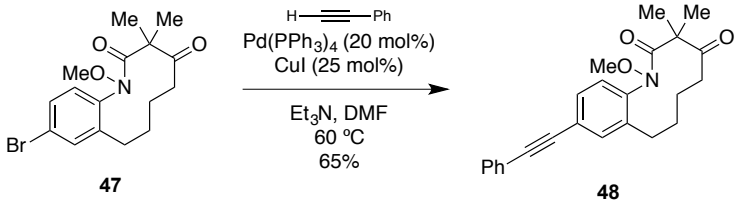
Supplementary Figure 17. α-Geminal dimethylation of β-ketolactam 13c to form lactam 47.



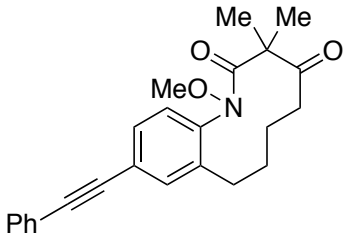
10-Bromo-1-methoxy-3,3-dimethyl-5,6,7,8-tetrahydrobenzo[*b*]azecine-2,4(1*H*,3*H*)-dione (47). β-Ketolactam **13c** (20.0 mg, 61.3 μmol, 1.00 equiv) was dissolved in DMF (1.0 mL) at 24 ºC. Potassium carbonate (34.0 mg, 245 μmol, 4.00 equiv) was added followed by methyl iodide (35.0 mg, 245 μmol, 4.00 equiv). The reaction was stirred at 24 ºC for 48 h and monitored by TLC. The mixture was then filtered through a pad of Celite. The filtrate was diluted with EtOAc and washed with H_2O (4 × 10 mL) and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 50% EtOAc in hexanes) yielded α,α-dimethyl lactam **47** as a colorless oil (15 mg, 68%).

TLC: R_f 0.55 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2973, 2935, 1715 (C=O st), 1666 (C=O st), 1477, 1020, 910, 734. **^{1}H-NMR** (600 MHz): δ 7.45 (d, 1H, *J* = 2.1 Hz), 7.39 (dd, 1H, *J* = 8.3, 2.2 Hz), 7.11 (d, 1H, *J* = 8.3 Hz), 3.69 (s, 3H), 2.75 (t, 1H, *J* = 13.6 Hz), 2.62 (dd, 1H, *J* = 15.3, 5.7 Hz), 2.56 (d, 1H, *J* = 10.7 Hz), 2.19 (br s, 1H), 1.94 (br s, 1H), 1.82 – 1.71 (m, 2H), 1.70 – 1.62 (m, 1H), 1.42 (s, 3H), 1.30 (s, 3H). **^{13}C-NMR** (151 MHz): δ 207.4, 170.7, 143.3, 135.4, 133.4, 131.9, 129.8, 125.6, 60.5, 56.5, 34.8, 25.3, 25.0, 23.2, 18.9. **HRMS** (ESI) m/z calcd for $C_{16}H_{20}BrNO_3Na$ ($[M+Na]^+$) 376.0524; found 376.0542.

2. SONOGASHIRA COUPLING OF BROMO β-KETOLACTAM 47



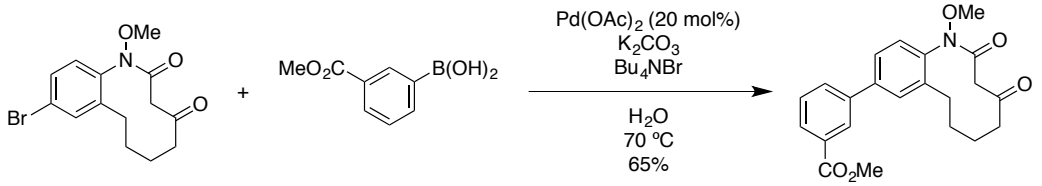
Supplementary Figure 18. Sonogashira coupling of bromo β-ketolactam 47 to form lactam 48.



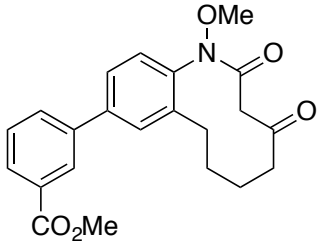
1-Methoxy-3,3-dimethyl-10-(phenylethynyl)-5,6,7,8-tetrahydrobenzo[*b*]azecine-2,4(1*H*,3*H*)-dione (48). To a vial containing bromo β-ketolactam **47** (8.00 mg, 22.5 μmol, 1.00 equiv) was added tetrakis(triphenylphosphine palladium(0) (5.3 mg, 4.4 μmol, 0.20 equiv) and copper (I) iodide (1.0 mg, 5.6 μmol, 0.25 equiv). The vial was then flushed with argon. Phenylacetylene (25.0 μL, 0.225 mmol, 10.0 equiv), triethylamine (1.0 mL) and DMF (0.1 mL) were then added at 24 ºC. The reaction was heated at 60 ºC for 16 h. The mixture was then allowed to cool, diluted with CH_2Cl_2 and then washed with H_2O (4 × 5 mL) and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 30% EtOAc in hexanes) yielded lactam **48** as a white solid (5.5 mg, 65%).

TLC: R_f 0.64 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2934, 2250, 1713 (C=O st), 1667 (C=O st), 1497, 1020, 912, 735. **^{1}H-NMR** (600 MHz): δ 7.54 (dd, 2H, *J* = 6.6, 3.0 Hz), 7.46 (s, 1H), 7.41 (dd, 1H, *J* = 8.1, 1.7 Hz), 7.39 – 7.36 (m, 3H), 7.23 (d, 1H, *J* = 8.1 Hz), 3.74 (s, 3H), 2.78 (t, 1H, *J* = 13.6 Hz), 2.64 (dd, 1H, *J* = 15.5, 5.5 Hz), 2.58 (d, 1H, *J* = 10.7 Hz), 2.17 (br s, 1H), 2.00 (br s, 1H), 1.83 – 1.65 (m, 3H), 1.43 (s, 3H), 1.32 (s, 3H). **^{13}C-NMR** (151 MHz): δ 207.4, 170.7, 141.2, 135.8, 133.3, 131.7 (2C), 130.6, 129.6, 128.7, 128.4 (2C), 126.4, 122.7, 91.5, 88.3, 60.5, 56.5, 34.8, 25.3, 24.8, 23.3, 18.8. **HRMS** (ESI) m/z calcd for $C_{24}H_{25}NO_3Na$ ($[M+Na]^+$) 398.1716; found 398.1732.

3. SUZUKI-MIYAURA COUPLING OF BROMO β-KETOLACTAM 13C



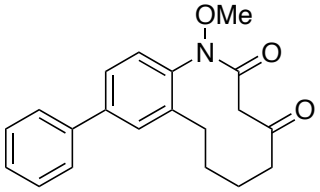
Supplementary Figure 19. Suzuki-Miyaura coupling of bromo β-ketolactam 13c to form β-ketolactam 49.



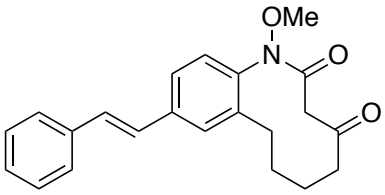
Methyl 3-(1-methoxy-2,4-dioxo-1,2,3,4,5,6,7,8-octahydrobenzo[*b*]azecin-10-yl)benzoate (49). To a vial containing bromo β-ketolactam **13c** (13.0 mg, 40.0 μmol, 1.00 equiv) was added

3-methoxycarbonylphenylboronic acid (7.50 mg, 44.0 µmol, 1.10 equiv), potassium carbonate (13.8 mg, 100 µmol, 2.50 equiv) and tetra-*N*-butylammonium bromide (12.8 mg, 40.0 µmol, 1.10 equiv). The vial was then flushed with argon. Water (1.0 mL) was added and the resulting suspension was heated at 70 ºC for 2 h. The mixture was then allowed to cool, diluted with water and then extracted with EtOAc (4 × 10 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 20% EtOAc in hexanes) yielded biaryl lactam **49** as a colorless oil (10 mg, 65%).

TLC: R_f 0.53 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2935, 1720 (C=O st), 1673 (C=O st), 1250, 913, 736. **^{1}H-NMR** (600 MHz): δ 8.29 (s, 1H), 8.08 (d, 1H, *J* = 7.7 Hz), 7.80 (d, 1H, *J* = 7.6 Hz), 7.61 (s, 1H), 7.57 (t, 2H, *J* = 7.9 Hz), 7.37 (d, 1H, *J* = 8.1 Hz), 3.97 (s, 3H), 3.79 (s, 3H), 3.64 (d, 1H, *J* = 15.2 Hz), 3.13 – 3.04 (m, 2H), 2.84 – 2.79 (m, 1H), 2.61 (dt, 1H, *J* = 12.8, 6.1 Hz), 2.31 (dt, 1H, *J* = 13.9, 7.3 Hz), 2.07 (t, 1H, *J* = 12.0 Hz), 1.90 (t, 1H, *J* = 12.0 Hz), 1.80 – 1.72 (m, 1H), 1.31 – 1.22 (m, 1H). **^{13}C-NMR** (151 MHz): δ 203.5, 166.8, 163.7, 142.6, 141.3, 139.9, 137.2, 131.6, 130.9, 129.9, 129.2, 129.1, 129.0, 128.3, 126.2, 61.1, 52.4, 47.3, 40.1, 28.2, 26.4, 21.1. **HRMS** (ESI) m/z calcd for $C_{22}H_{23}NO_5Na$ ($[M+Na]^+$) 404.1474; found 404.1490.



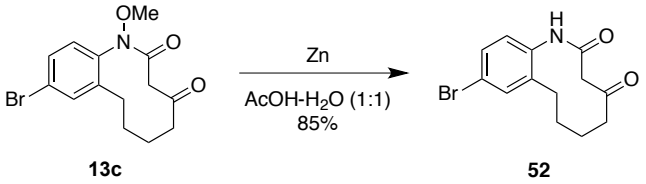
1-Methoxy-10-phenyl-5,6,7,8-tetrahydrobenzo[*b*]azecine-2,4(1*H*,3*H*)-dione (50). Isolated as a colorless oil (9.7 mg, 75%). **TLC:** R_f 0.50 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2934, 1718 (C=O st), 1672 (C=O st), 1484, 1366, 912, 735. **^{1}H-NMR** (600 MHz): δ 7.62 – 7.57 (m, 3H), 7.54 (d, 1H, *J* = 8.1 Hz), 7.49 (t, 2H, *J* = 7.5 Hz), 7.42 (t, 1H, *J* = 7.3 Hz), 7.35 (d, 1H, *J* = 8.1 Hz), 3.79 (s, 3H), 3.65 (d, 1H, *J* = 15.2 Hz), 3.12 – 3.03 (m, 2H), 2.80 (dt, 1H, *J* = 15.0, 4.4 Hz), 2.60 (dt, 1H, *J* = 12.8, 6.1 Hz), 2.34 – 2.27 (m, 1H), 2.10 – 2.02 (m, 1H), 1.89 (dd, 1H, *J* = 14.0, 2.7 Hz), 1.78 – 1.71 (m, 1H), 1.29 – 1.22 (m, 1H). **^{13}C-NMR** (151 MHz): δ 203.6, 163.8, 143.7, 141.0, 139.6, 136.8, 129.7, 129.0 (3C), 128.2 (2C), 127.2, 126.2, 61.1, 47.2, 40.1, 28.3, 26.3, 21.1. **HRMS** (ESI) m/z calcd for $C_{20}H_{21}NO_3Na$ ($[M+Na]^+$) 346.1419; found 346.1426.



(*E*)-1-methoxy-10-styryl-5,6,7,8-tetrahydrobenzo[*b*]azecine-2,4(1*H*,3*H*)-dione (51). Isolated as a colorless oil (10.8 mg, 77%). **TLC:** R_f 0.50 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2933, 1717 (C=O st), 1761 (C=O st), 1497, 1366, 912, 733. **^{1}H-NMR** (600 MHz): δ 7.54 (d, 2H, *J* = 7.6 Hz), 7.50 – 7.46 (m, 2H), 7.39 (t, 2H, *J* = 7.6 Hz), 7.31 (t, 1H, *J* = 7.3 Hz), 7.26 (d, 1H, *J* = 7.4 Hz), 7.18 (d, 1H, *J* = 16.3 Hz), 7.10 (d, 1H, *J* = 16.3 Hz), 3.77 (s, 3H), 3.62 (d, 1H, *J* = 15.1 Hz), 3.08 (d, 1H, *J* = 15.1 Hz), 3.02 (td, 1H, *J* = 15.1, 4.5 Hz), 2.75 (dt, 1H, *J* = 15.1, 4.5 Hz), 2.59 (dt, 1H, *J* = 12.9, 6.2 Hz), 2.29 (ddd, 1H, *J* = 14.1, 8.9, 5.9 Hz), 2.10 – 2.01 (m,

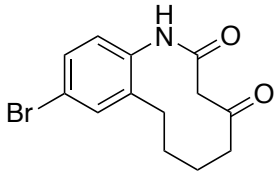
1H), 1.92 – 1.85 (m, 1H), 1.80 – 1.72 (m, 1H), 1.30 – 1.23 (m, 1H). **^{13}C-NMR** (151 MHz): δ 203.5, 163.7, 140.9, 139.8, 136.6, 136.5, 131.1, 129.7, 128.8 (2C), 128.3, 128.3, 127.0 (2C), 126.7, 125.1, 61.0, 47.4, 40.1, 28.2, 26.2, 21.1. **HRMS** (ESI) m/z calcd for $C_{22}H_{23}NO_3Na$ ($[M+Na]^+$) 372.1576; found 372.1565.

4. Reductive cleavage of the N–O bond in 13c



13c **52**

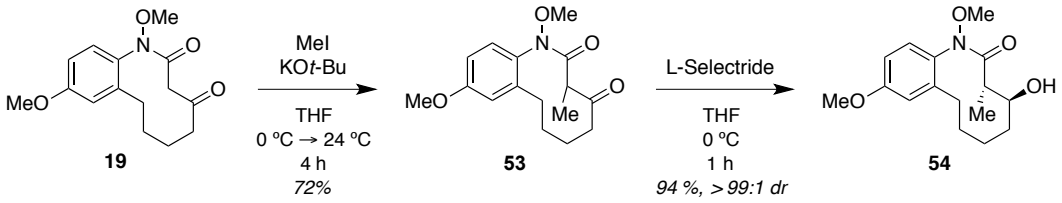
Supplementary Figure 20. Reductive cleavage of the N–O bond in 13c to form secondary lactam 52.



10-Bromo-5,6,7,8-tetrahydrobenzo[*b*]azecine-2,4(1*H*,3*H*)-dione (52). β-Ketolactam **13c** (5.00 mg, 15.3 μmol, 1.00 equiv) was dissolved in an acetic acid and water mixture (1.0 mL, 1:1) at 24 ºC. Zinc powder (40.1 mg, 612 μmol, 40.0 equiv) was added and the resulting suspension was stirred at 24 ºC for 24 h. The mixture was then diluted with CH_2Cl_2 and then filtered through a pad of Celite. The filtrate was washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 10% MeOH in CH_2Cl_2) yielded secondary lactam **52** as a white solid (3.9 mg, 85%).

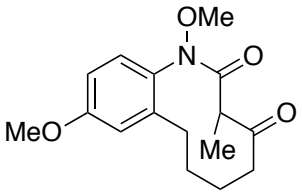
TLC: R_f 0.42 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3274, 2916, 2849, 1707 (C=O st), 1647 (C=O st), 1524, 1463, 738. **^{1}H-NMR** (600 MHz, DMSO-d_6): δ 10.15 (s, 1H), 7.49 (d, 1H, J = 2.0 Hz), 7.42 (dd, 1H, J = 8.4, 2.2 Hz), 7.14 (d, 1H, J = 8.3 Hz), 3.42 (s, 2H), 2.78 (t, 2H, J = 6.6 Hz), 2.71 (t, 2H, J = 6.5 Hz), 1.45 – 1.36 (m, 4H). **^{13}C-NMR** (151 MHz, DMSO-d_6): δ 204.4, 164.4, 141.2, 135.1, 132.8, 130.3, 129.3, 119.2, 56.1, 39.9, 39.8, 39.6, 39.5, 39.4, 39.2, 39.1, 37.5, 28.2, 27.7, 23.7. **HRMS** (ESI) m/z calcd for $C_{13}H_{14}NO_2Na$ ($[M+Na]^+$) 318.0106; found 318.0106.

5. Reduction of the ketone in α-methyl-β-ketolactam 53



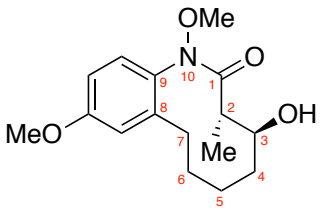
19 **53** **54**

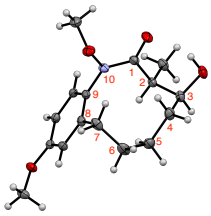
Supplementary Figure 21. Synthesis of α-methyl-β-hydroxylactam 52.



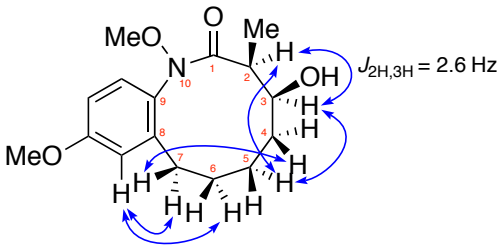
1,10-Dimethoxy-3-methyl-5,6,7,8-tetrahydrobenzo[*b*]azecine-2,4(1*H*,3*H*)-dione (53). Methoxyaryl lactam **19** (0.20 g, 0.72 mmol, 1.0 equiv) was dissolved in THF (6.5 mL) and cooled to 0 °C. A solution of KO*t*-Bu (1.0 M in THF, 0.75 mL, 0.75 mmol, 1.05 equiv) was added by syringe over 5 min and the reaction was stirred for 1 h. Methyl iodide (135 µL, 2.16 mmol, 3.00 equiv) was then added and the reaction was stirred for an additional 3 h at 24 ºC. The reaction was quenched slowly with satd aq NH_4Cl at 0 °C, warmed to 24 °C and diluted with CH_2Cl_2. The mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 10% MeOH in CH_2Cl_2) yielded α-methyl-β-hydroxylactam **53** as a yellow oil (152 mg, 72%).

TLC: R_f 0.51 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2935, 1719 (C=O st), 1672 (C=O st), 1496, 1245, 1016, 915, 733. **^{1}H-NMR** (600 MHz): δ 7.15 (d, 1H, *J* = 8.6 Hz), 6.89 (d, 1H, *J* = 2.8 Hz), 6.83 (dd, 1H, *J* = 8.6, 2.9 Hz), 3.86 (s, 3H), 3.75 (s, 3H), 3.56 (q, 1H, *J* = 6.8 Hz), 3.06 (td, 1H, *J* = 14.4, 4.5 Hz), 2.70 (dt, 1H, *J* = 14.7, 4.2 Hz), 2.56 (ddd, 1H, *J* = 13.5, 7.0, 4.2 Hz), 2.30 (ddd, 1H, *J* = 13.5, 9.9, 7.3 Hz), 1.93 (ddq, 1H, *J* = 17.8, 7.9, 4.6 Hz), 1.81 (ddq, 1H, *J* = 13.8, 10.4, 3.6 Hz), 1.74 – 1.66 (m, 1H), 1.26 (d, 3H, *J* = 6.8 Hz), 1.14 – 1.06 (m, 1H). **^{13}C-NMR** (151 MHz): δ 205.7, 168.0, 161.1, 142.9, 130.7, 130.2, 115.8, 112.4, 60.6, 55.5, 47.5, 38.2, 29.0, 26.5, 21.1, 12.3. **HRMS** (ESI) m/z calcd for $C_{16}H_{21}NO_4Na$ ([M+Na]$^+$) 314.1368; found 314.1353.





X-ray structure

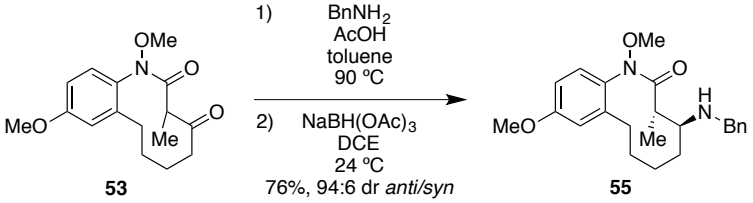


NOESY

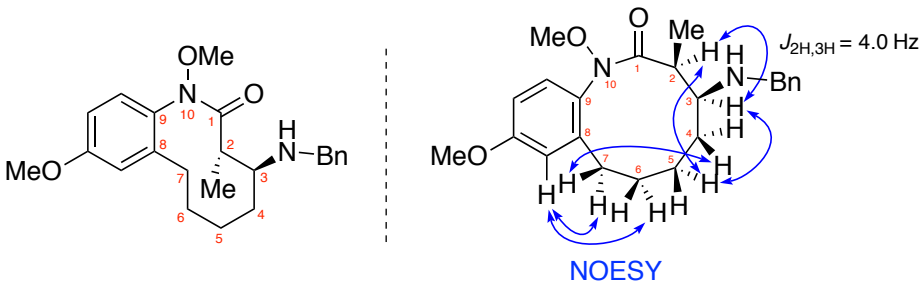
(3*S,4*S**)-4-hydroxy-1,10-dimethoxy-3-methyl-3,4,5,6,7,8-hexahydrobenzo[*b*]azecin-2(1*H*)-one (54).** α-Methyl methoxyaryl lactam **53** (10.0 mg, 34.0 µmol, 1.00 equiv) was dissolved in THF (0.5 mL) and cooled to 0 °C. A solution of L-Selectride (1.00 M in THF, 70.0 µL, 68.0 µmol, 2.00 equiv) was added and the reaction was stirred for 1 h. The reaction was quenched with satd aq NH_4Cl at 0 °C, warmed to 24 °C and diluted with CH_2Cl_2. The mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 10% MeOH in CH_2Cl_2) yielded hydroxylactam **54** as a white solid (9.5 mg, 94%). The relative stereochemistry of **54** was assigned as *anti*-α-methyl-β-hydroxylactam based on X-ray crystal structure analysis (see Section F below). Key diagnostic NOESY correlations were entirely consistent with the ring conformation assignment.

TLC: R_f 0.35 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3464 (O–H st), 2936, 2874, 1651 (C=O st), 1495, 1425, 1242, 1217, 984, 738. **^{1}H-NMR** (600 MHz): δ 7.09 (d, 1H, *J* = 8.6 Hz), 6.89 (d, 1H, *J* = 2.6 Hz), 6.80 (dd, 1H, *J* = 8.5, 2.7 Hz), 3.85 (s, 3H), 3.74 (s, 3H), 3.73 (br s, 1H), 3.26 (tt, 1H, *J* = 11.5, 2.7 Hz), 2.96 (td, 1H, *J* = 13.8, 4.3 Hz), 2.60 (dt, 1H, *J* = 13.8, 4.0 Hz), 2.56 (qd, 1H, *J* = 6.9, 2.6 Hz), 1.89 (dtd, 1H, *J* = 13.8, 10.0, 3.6 Hz), 1.79 (ddt, 1H, *J* = 17.6, 13.1, 4.0 Hz), 1.69 (tq, 1H, *J* = 13.8, 3.4 Hz), 1.46 (tdd, 1H, *J* = 13.6, 8.1, 3.4 Hz), 1.35 (td, 1H, *J* = 13.1, 9.3 Hz), 1.28 (d, 1H, *J* = 6.9 Hz), 0.38 (tdd, 1H, *J* = 13.6, 9.4, 2.8 Hz). **^{13}C-NMR** (151 MHz): δ 173.0, 161.2, 143.4, 130.2, 130.1, 115.7, 112.0, 73.9, 60.5, 55.5, 37.3, 32.3, 29.2, 26.2, 19.5, 14.7. **HRMS** (ESI) m/z calcd for $C_{16}H_{23}NO_4Na$ ([M+Na]$^+$) 316.1525; found 316.1520.

6. Reductive amination of α-methyl-β-ketolactam 53



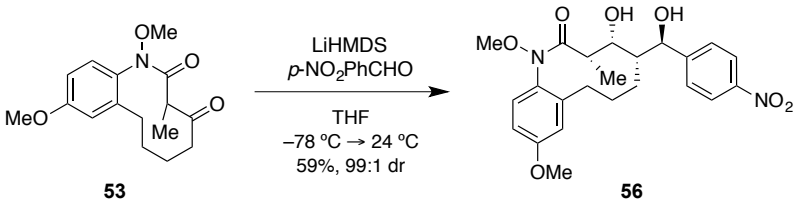
Supplementary Figure 22. Synthesis of α-methyl-β-hydroxylactam 55.



(3*S,4*S**)-4-(benzylamino)-1,10-dimethoxy-3-methyl-3,4,5,6,7,8-hexahydrobenzo[b]azecin-2(1H)-one (55).** α-Methyl methoxyaryl lactam **53** (50.0 mg, 0.170 mmol, 1.00 equiv) was dissolved in toluene (1.7 mL) and benzyl amine (20.6 µL, 0.190 mmol, 1.10 equiv), acetic acid (17.0 M, 10.0 µL, 0.170 mmol, 1.00 equiv) and crushed molecular sieves (≈50 mg) were added and the reaction was stirred at 90 ºC for 2 h. The reaction mixture was then cooled to 24 ºC and filtered through a pad of Celite. The filtrate was concentrated by rotary evaporation to afford the crude imine, which was used directly in the following step. The imine was dissolved in dichloroethane (1.7 mL) and sodium triacetoxyborohydride (145 mg, 0.690 mmol, 4.00 equiv) was added. The resulting reaction mixture was stirred at 24 ºC for 16 h. The reaction was quenched with satd aq $NaHCO_3$ and diluted with CH_2Cl_2. The mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (30% → 80% EtOAc in hexanes) yielded amine **55** as a colorless oil (51 mg, 76%). The relative stereochemistry of **55** was assigned as *anti*-α-methyl-β-aminolactam based on extensive NMR studies. The key diognostic NOESY correlations of **55** showed perfect alignment with the NOESY correlations of *anti*-α-methyl-β-hydroxylactam **54**. Additionally, the $J_{2H,3H}$ coupling constants of both **54** and **55** support *anti* configuration.

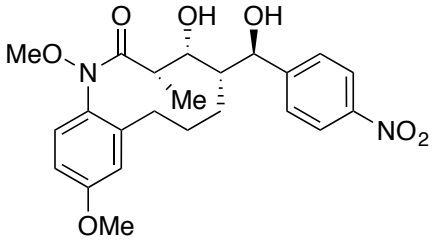
TLC: R_f 0.32 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2933, 2869, 1664 (C=O st), 1494, 1463, 1246, 1027, 912, 736. **^{1}H-NMR** (600 MHz): δ 7.36 (d, 2H, *J* = 7.5 Hz), 7.29 – 7.27 (m, 2H), 7.18 (t, 1H, *J* = 7.3 Hz), 7.06 (d, 1H, *J* = 8.6 Hz), 6.86 (d, 1H, *J* = 2.8 Hz), 6.77 (dd, 1H, *J* = 8.6, 2.9 Hz), 3.97 (d, 1H, *J* = 13.8 Hz), 3.84 (s, 3H), 3.73 (s, 3H), 3.65 (d, 1H, *J* = 13.8 Hz), 3.01 (td, 1H, *J* = 13.7, 4.4 Hz), 2.63 (qd, 1H, *J* = 6.9, 4.0 Hz), 2.58 (dt, 1H, *J* = 13.9, 3.7 Hz), 2.19 (dt, 1H, *J* = 12.1, 3.2 Hz), 2.01 (dtd, 1H, *J* = 12.7, 9.9, 2.2 Hz), 1.76 (tq, 1H, *J* = 13.3, 4.5 Hz), 1.68 (dtd, 1H, *J* = 13.7, 6.8, 2.9 Hz), 1.34 (dddt, 1H, *J* = 13.5, 9.9, 6.9, 3.4 Hz), 1.25 (d, 3H, *J* = 6.9 Hz), 1.09 (td, 1H, *J* = 12.6, 9.5 Hz), 0.43 (tdd, 1H, *J* = 13.4, 9.8, 2.5 Hz). **^{13}C-NMR** (151 MHz): ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 160.9, 143.6, 141.5, 130.9, 130.2, 128.0, 128.0, 126.4, 115.6, 111.9, 60.2, 59.3, 55.5, 50.7, 37.4, 29.3, 27.8, 26.5, 20.9, 15.2. **HRMS** (ESI) m/z calcd for $C_{23}H_{31}N_2O_3$ ($[M+H]^+$) 383.2335; found 383.2339.

7. ALDOL-TISHCHENKO REACTION OF α-METHYL-β-KETOLACTAM 53



53 56

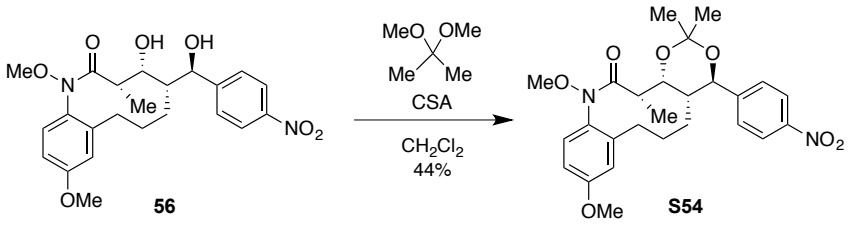
Supplementary Figure 23. Synthesis of 1,3-diol 56.



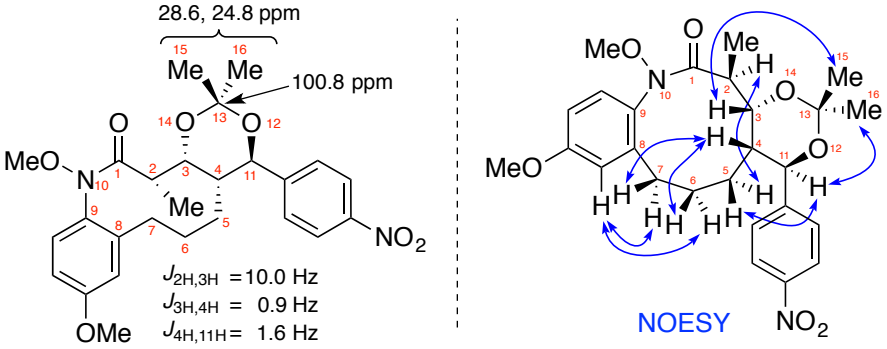
(3*S,4*R**,5*R**)-4-hydroxy-5-((*R**)-hydroxy(4-nitrophenyl)methyl)-1,10-dimethoxy-3-methyl-3,4,5,6,7,8-hexahydrobenzo[*b*]azecin-2(1*H*)-one (56).** α-Methyl methoxyaryl lactam **53** (20.0 mg, 68.0 μmol, 1.00 equiv) was dissolved in THF (0.7 mL) and cooled to –78 °C. A solution of LiHMDS (1.00 M in THF, 2.00 mL, 2.04 mmol, 3.00 equiv) was added and the reaction was stirred for 1 h. A solution of *p*-nitrobenzaldehyde (0.100 M in THF, 26.0 mg, 0.170 mmol, 2.50 equiv) was added and the reaction was stirred for an additional 15 h while the reaction slowly warmed to 24 ºC. The reaction was quenched with satd aq NH_4Cl and diluted with EtOAc. The mixture was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 10% MeOH in CH_2Cl_2) yielded 1,3-diol **56** as a yellow oil (18 mg, 59%, 99:1 dr).

TLC: R_f 0.33 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 3425 (O–H st), 2931, 2874, 1650 (C=O st), 1347, 1243, 911, 736. **^{1}H-NMR** (600 MHz): δ 8.24 (d, 2H, *J* = 8.6 Hz), 7.56 (d, 2H, *J* = 8.6 Hz), 7.08 (d, 1H, *J* = 8.4 Hz), 6.91 (d, 1H, *J* = 2.7 Hz), 6.80 (dd, 1H, *J* = 8.6, 2.8 Hz), 4.91 (d, 1H, *J* = 3.6 Hz), 3.85 (s, 3H), 3.82 (d, 1H, *J* = 9.7 Hz), 3.67 (s, 3H), 2.78 (td, 1H, *J* = 14.0, 3.9 Hz), 2.64 (dt, 1H, *J* = 14.5, 3.9 Hz), 2.40 (dq, 1H, *J* = 9.5, 6.5 Hz), 1.85 – 1.78 (m, 2H), 1.72 – 1.67 (m, 1H), 1.55 (t, 1H, *J* = 13.9 Hz), 1.14 (d, 3H, *J* = 6.6 Hz), 1.01 (t, 1H, *J* = 14.4 Hz). **^{13}C-NMR** (151 MHz): δ 170.9, 161.3, 150.6, 147.1, 142.9, 130.3, 128.6, 126.7

(2C), 123.8 (2C), 115.6, 112.2, 75.2, 73.7, 60.5, 55.6, 43.2, 41.3, 27.3, 26.5, 20.4, 14.5. **HRMS** (ESI) m/z calcd for $C_{23}H_{27}N_2O_7$ ([M–H]$^-$) 443.1818; found 443.1830.



Supplementary Figure 24. Synthesis of acetonide S54.

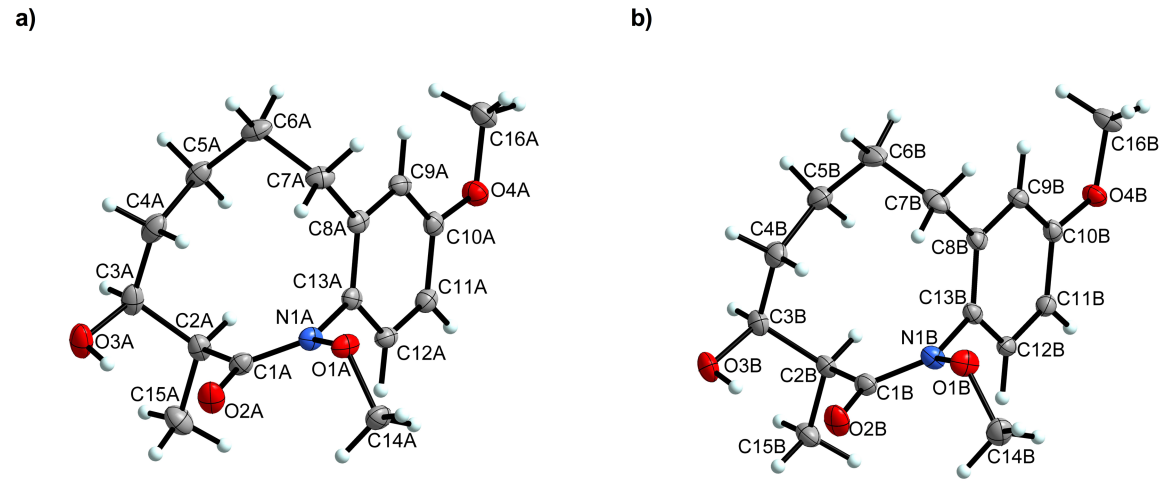


(4*R,4a*R**,14*S**,14a*R**)-9,12-dimethoxy-2,2,14-trimethyl-4-(4-nitrophenyl)-4,4a,5,6,7,12,14,14a-octahydro-13*H*-benzo[*b*][1,3]dioxino[5,4-*g*]azecin-13-one (S54).** Diol **56** (4.3 mg, 10 µmol, 1.0 equiv) was dissolved in CH_2Cl_2 (1.0 mL). Dimethoxypropane (6.0 µL, 50 µmol, 5.0 equiv) and camphorsulfonic acid (10 mM in CH_2Cl_2, 0.10 mL, 1.0 µmol 0.10 equiv) were added. The resultant reaction mixture was stirred at 24 ºC for 16 h. The mixture was concentrated by rotary evaporation to afford the crude product. Purification by silica flash chromatography (0% → 10% EtOAc in hexanes) yielded acetonide **S54** as a yellow oil (2.1 mg, 44%). Upon extensive NMR analysis of **S54**, the relative stereochemistry of the acetoinde was assigned as *anti*-1,3-diol acetonide. Characteristic ^{13}C NMR resonances reported in the literature[30] for the ketal carbon as well as the geminal dimethyl groups were in agreement with the observed NMR data of **S54**. The assigned stereochemistry was also supported by NOESY correlations analogous to the observed NOESY correlations in **54** and **55**.

TLC: R_f 0.77 (95:5 CH_2Cl_2/MeOH). **IR** (ATR, ZnSe): 2933, 1670 (C=O st), 1522, 1350, 1244, 741, 669. **^{1}H-NMR** (600 MHz): δ 8.24 (d, 2H, *J* = 8.6 Hz), 7.68 (d, 2H, *J* = 8.7 Hz), 7.15 (d, 1H, *J* = 8.5 Hz), 6.92 (d, 1H, *J* = 2.8 Hz), 6.80 (dd, 1H, *J* = 8.5, 2.8 Hz), 4.74 (d, 1H, *J* = 1.6 Hz), 4.18 (dd, 1H, *J* = 10.1, 0.9 Hz), 3.86 (s, 3H), 3.75 (s, 3H), 2.76 (td, 1H, *J* = 13.9, 3.8 Hz), 2.64 (dt, 1H, *J* = 14.4, 3.9 Hz), 2.54 (dq, 1H, *J* = 10.0, 6.6 Hz), 2.04 (d, 1H, *J* = 6.4 Hz), 1.87 (t, 1H, *J* = 13.8 Hz), 1.69 – 1.60 (m, 2H), 1.33 (s, 3H), 1.20 (d, 3H, *J* = 6.5 Hz), 1.03 (s, 3H), 0.87 – 0.80 (m, 1H). **^{13}C-NMR** (151 MHz): δ 171.6, 161.3, 149.6, 147.1, 143.0, 130.4, 130.3, 128.0 (2C), 123.8 (2C), 115.8, 112.0, 100.8, 76.5, 71.0, 60.6, 55.6, 39.2, 35.4, 28.6, 28.2, 26.9, 24.8, 24.4, 14.5. **HRMS** (ESI) m/z calcd for $C_{26}H_{32}N_2O_7Na$ ([M+Na]$^+$) 507.2107; found 507.2090.

[30] Evans, D. A.; Rieger, D. L.; Gage, J. R. *Tetrahedron Lett.* **1990**, *31* ,7099–7100.

H. X-RAY CRYSTALLOGRAPHIC ANALYSIS OF *ANTI*-α-METHYL-β-HYDROXYLACTAM 54



Supplementary Figure 25. X-ray crystal structures of anti α-methyl-β-hydroxylactam 54. The two cocrystallized conformers A (a) and B (b) are shown.

Lactam **54** (10 mg) was placed in a 15 mL conical flask and dissolved in 1.5 mL EtOAc/pentane (3:1) upon heating. After 3 days at 24 ºC, clear needle shaped crystals were obtained for X-ray crystallographic analysis.

A colorless irregular prism-like specimen of $C_{16}H_{23}NO_4$, approximate dimensions 0.116 mm × 0.227 mm × 0.246 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 27.54 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 52524 reflections to a maximum θ angle of 71.17° (0.81 Å resolution), of which 5853 were independent (average redundancy 8.974, completeness = 98.2%, R_{int} = 2.32%, R_{sig} = 1.16%) and 5679 (97.03%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.2770(5) Å, b = 32.3108(18) Å, c = 11.1622(6) Å, β = 113.1263(17)°, volume = 3077.0(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9001 reflections above 20 σ(I) with 9.039° < 2θ < 141.7°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.914.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 8 for the formula unit, $C_{16}H_{23}NO_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 563 variables converged at R1 = 3.41%, for the observed data and wR2 = 8.42% for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was 0.228 $e^-/Å^3$ and the largest hole was -0.245 $e^-/Å^3$ with an RMS deviation of 0.041 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.267 g/cm^3 and F(000), 1264 e^-.

CCDC 1534702 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Supplementary Table 5. Sample and crystal data for α-methyl-β-hydroxylactam 54.

Identification code	α-methyl-β-hydroxylactam **54**	
Chemical formula	$C_{16}H_{23}NO_4$	
Formula weight	293.36 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.116 × 0.227 × 0.246 mm	
Crystal habit	colorless irregular prism	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 9.2770(5) Å	α = 90°
	b = 32.3108(18) Å	β = 113.1263(17)°
	c = 11.1622(6) Å	γ = 90°
Volume	3077.0(3) $Å^3$	
Z	8	
Density (calculated)	1.267 g/cm^3	
Absorption coefficient	0.739 mm^{-1}	
F(000)	1264	

Supplementary Table 6. Data collection and structure refinement for for α-methyl-β-hydroxylactam 54.

Theta range for data collection	2.73 to 71.17°	
Index ranges	-11≤h≤11, -39≤k≤39, -13≤l≤13	
Reflections collected	52524	
Independent reflections	5853 [R(int) = 0.0232]	
Coverage of independent reflections	98.2%	
Absorption correction	multi-scan	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/4	
Refinement method	full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5853 / 0 / 563	
Goodness-of-fit on F^2	1.044	
Δ/σ_{max}	0.001	
Final R indices	5679 data; I>2σ(I)	R1 = 0.0341, wR2 = 0.0836
	all data	R1 = 0.0348, wR2 = 0.0842
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0406P)^2+1.2059P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.228 and -0.245 eÅ^{-3}	
R.M.S. deviation from mean	0.041 eÅ^{-3}	

Supplementary Table 7. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for α-methyl-β-hydroxylactam 54. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O1A	0.41488(9)	0.57762(2)	0.43376(7)	0.02165(17)
O2A	0.43762(9)	0.60291(3)	0.21674(8)	0.02852(19)
O3A	0.38570(10)	0.56748(3)	0.97629(9)	0.0311(2)
O4A	0.76172(9)	0.49479(2)	0.32652(8)	0.02435(18)
N1A	0.28955(10)	0.57250(3)	0.31166(8)	0.01818(19)
C1A	0.31634(12)	0.58468(3)	0.20678(10)	0.0194(2)
C2A	0.19181(13)	0.57426(3)	0.07397(10)	0.0202(2)
C3A	0.26872(13)	0.54564(4)	0.00492(11)	0.0243(2)
C4A	0.33760(13)	0.50631(4)	0.08235(12)	0.0255(2)
C5A	0.21540(13)	0.47714(4)	0.09868(11)	0.0228(2)
C6A	0.27237(13)	0.45405(3)	0.22862(12)	0.0238(2)
C7A	0.30375(13)	0.48240(3)	0.34759(11)	0.0223(2)
C8A	0.16213(12)	0.50812(3)	0.33487(10)	0.0179(2)
C9A	0.02966(13)	0.48857(3)	0.33947(10)	0.0189(2)
C10A	0.89515(12)	0.51103(3)	0.32328(10)	0.0189(2)
C11A	0.89140(13)	0.55377(3)	0.30307(10)	0.0200(2)
C12A	0.02201(13)	0.57352(3)	0.30012(10)	0.0192(2)
C13A	0.15615(12)	0.55095(3)	0.31503(10)	0.0171(2)
C14A	0.41124(15)	0.61869(4)	0.48182(11)	0.0244(2)
C15A	0.12557(15)	0.61429(4)	0.99930(12)	0.0296(3)
C16A	0.75788(15)	0.45111(4)	0.34510(12)	0.0258(2)
O1B	0.77179(9)	0.83300(3)	0.58778(8)	0.02488(18)
O2B	0.52013(10)	0.78503(3)	0.52102(8)	0.0287(2)
O3B	0.46121(10)	0.70684(3)	0.59967(8)	0.02595(18)
O4B	0.10494(9)	0.85875(2)	0.19138(7)	0.02165(17)
N1B	0.71956(10)	0.81713(3)	0.68201(8)	0.01899(19)
C1B	0.59642(12)	0.79086(3)	0.63818(10)	0.0190(2)
C2B	0.55919(12)	0.76759(3)	0.74082(10)	0.0177(2)
C3B	0.57819(13)	0.72085(3)	0.72101(11)	0.0212(2)
C4B	0.74179(14)	0.70999(4)	0.72833(12)	0.0251(2)
C5B	0.87494(14)	0.71762(4)	0.86206(12)	0.0262(3)
C6B	0.02825(14)	0.73172(4)	0.85469(13)	0.0287(3)
C7B	0.02233(13)	0.77538(4)	0.79737(12)	0.0245(2)
C8B	0.96929(12)	0.80771(3)	0.86898(10)	0.0183(2)
C9B	0.06719(12)	0.81850(3)	0.99659(10)	0.0185(2)
C10B	0.01676(12)	0.84623(3)	0.06728(10)	0.0174(2)
C11B	0.86671(12)	0.86349(3)	0.01178(10)	0.0182(2)

	x/a	y/b	z/c	U(eq)
C12B	0.77032(12)	0.85379(3)	0.88523(10)	0.0176(2)
C13B	0.82146(12)	0.82625(3)	0.81413(10)	0.0169(2)
C14B	0.68351(15)	0.86921(4)	0.52767(12)	0.0277(3)
C15B	0.39505(13)	0.77825(4)	0.73198(12)	0.0241(2)
C16B	0.26343(13)	0.84427(4)	0.25018(11)	0.0244(2)

Supplementary Table 8. Bond lengths (Å) for α-methyl-β-hydroxylactam 54.

O1A-N1A	1.4114(11)	O1A-C14A	1.4368(13)
O2A-C1A	1.2357(13)	O3A-C3A	1.4319(14)
O3A-H3OA	0.86(2)	O4A-C10A	1.3579(13)
O4A-C16A	1.4290(14)	N1A-C1A	1.3475(14)
N1A-C13A	1.4333(14)	C1A-C2A	1.5167(14)
C2A-C15A	1.5308(16)	C2A-C3A	1.5459(16)
C2A-H2A	0.965(13)	C3A-C4A	1.5287(18)
C3A-H3A	0.969(13)	C4A-C5A	1.5391(16)
C4A-H4A	0.998(15)	C4A-H4B	0.959(15)
C5A-C6A	1.5287(17)	C5A-H5A	0.992(14)
C5A-H5B	0.996(14)	C6A-C7A	1.5438(16)
C6A-H6A	1.007(14)	C6A-H6B	0.987(14)
C7A-C8A	1.5134(15)	C7A-H7A	0.996(15)
C7A-H7B	0.976(14)	C8A-C13A	1.3990(15)
C8A-C9A	1.4005(15)	C9A-C10A	1.3924(15)
C9A-H9A	0.965(14)	C10A-C11A	1.3975(16)
C11A-C12A	1.3812(16)	C11A-H11A	0.958(14)
C12A-C13A	1.3948(15)	C12A-H12A	0.960(14)
C14A-H14A	0.957(16)	C14A-H14B	0.974(14)
C14A-H14C	0.975(16)	C15A-H15A	0.974(16)
C15A-H15B	1.009(17)	C15A-H15C	0.958(17)
C16A-H16A	0.996(15)	C16A-H16B	0.983(16)
C16A-H16C	0.983(15)	O1B-N1B	1.4157(11)
O1B-C14B	1.4345(15)	O2B-C1B	1.2327(13)
O3B-C3B	1.4361(13)	O3B-H3OB	0.90(2)
O4B-C10B	1.3644(13)	O4B-C16B	1.4330(13)
N1B-C1B	1.3514(14)	N1B-C13B	1.4354(13)
C1B-C2B	1.5191(15)	C2B-C15B	1.5261(15)
C2B-C3B	1.5463(15)	C2B-H2B	0.963(13)
C3B-C4B	1.5283(16)	C3B-H3B	0.984(14)
C4B-C5B	1.5384(16)	C4B-H4C	1.018(15)
C4B-H4D	0.952(16)	C5B-C6B	1.5260(18)
C5B-H5C	1.001(14)	C5B-H5D	0.990(16)
C6B-C7B	1.5410(18)	C6B-H6C	0.969(16)
C6B-H6D	0.979(15)	C7B-C8B	1.5105(15)
C7B-H7C	0.987(15)	C7B-H7D	0.972(15)
C8B-C13B	1.3981(15)	C8B-C9B	1.3997(15)
C9B-C10B	1.3907(15)	C9B-H9B	0.961(14)
C10B-C11B	1.3983(15)	C11B-C12B	1.3787(15)

C11B-H11B	0.977(14)	C12B-C13B	1.3937(15)
C12B-H12B	0.965(14)	C14B-H14D	0.961(17)
C14B-H14E	0.954(16)	C14B-H14F	0.995(16)
C15B-H15D	1.015(16)	C15B-H15E	0.964(16)
C15B-H15F	1.007(16)	C16B-H16D	0.987(16)
C16B-H16E	0.965(15)	C16B-H16F	0.999(16)

Supplementary Table 9. Bond angles (°) for α-methyl-β-hydroxylactam 54.

N1A-O1A-C14A	109.72(8)	C3A-O3A-H3OA	105.9(14)
C10A-O4A-C16A	117.41(9)	C1A-N1A-O1A	116.21(8)
C1A-N1A-C13A	128.35(9)	O1A-N1A-C13A	115.08(8)
O2A-C1A-N1A	122.22(10)	O2A-C1A-C2A	120.72(10)
N1A-C1A-C2A	117.05(9)	C1A-C2A-C15A	109.47(9)
C1A-C2A-C3A	107.25(9)	C15A-C2A-C3A	113.52(10)
C1A-C2A-H2A	110.5(7)	C15A-C2A-H2A	108.9(7)
C3A-C2A-H2A	107.1(7)	O3A-C3A-C4A	110.54(9)
O3A-C3A-C2A	110.81(9)	C4A-C3A-C2A	112.81(9)
O3A-C3A-H3A	105.4(8)	C4A-C3A-H3A	109.3(8)
C2A-C3A-H3A	107.6(8)	C3A-C4A-C5A	114.35(9)
C3A-C4A-H4A	108.2(8)	C5A-C4A-H4A	110.1(8)
C3A-C4A-H4B	107.3(9)	C5A-C4A-H4B	109.3(9)
H4A-C4A-H4B	107.5(12)	C6A-C5A-C4A	114.51(10)
C6A-C5A-H5A	107.0(8)	C4A-C5A-H5A	110.1(8)
C6A-C5A-H5B	108.8(8)	C4A-C5A-H5B	108.4(8)
H5A-C5A-H5B	107.8(11)	C5A-C6A-C7A	113.88(9)
C5A-C6A-H6A	107.4(8)	C7A-C6A-H6A	109.7(8)
C5A-C6A-H6B	109.0(8)	C7A-C6A-H6B	109.4(8)
H6A-C6A-H6B	107.3(11)	C8A-C7A-C6A	112.44(9)
C8A-C7A-H7A	108.9(8)	C6A-C7A-H7A	109.2(8)
C8A-C7A-H7B	109.3(8)	C6A-C7A-H7B	109.6(8)
H7A-C7A-H7B	107.3(11)	C13A-C8A-C9A	118.10(10)
C13A-C8A-C7A	122.49(10)	C9A-C8A-C7A	119.39(10)
C10A-C9A-C8A	120.99(10)	C10A-C9A-H9A	121.5(8)
C8A-C9A-H9A	117.5(8)	O4A-C10A-C9A	125.11(10)
O4A-C10A-C11A	114.89(10)	C9A-C10A-C11A	120.00(10)
C12A-C11A-C10A	119.60(10)	C12A-C11A-H11A	121.2(8)
C10A-C11A-H11A	119.2(8)	C11A-C12A-C13A	120.37(10)
C11A-C12A-H12A	121.2(8)	C13A-C12A-H12A	118.4(8)
C12A-C13A-C8A	120.93(10)	C12A-C13A-N1A	118.81(9)
C8A-C13A-N1A	120.25(9)	O1A-C14A-H14A	111.5(9)
O1A-C14A-H14B	102.1(8)	H14A-C14A-H14B	108.9(11)
O1A-C14A-H14C	109.9(9)	H14A-C14A-H14C	111.7(13)
H14B-C14A-H14C	112.3(12)	C2A-C15A-H15A	110.9(9)
C2A-C15A-H15B	110.5(9)	H15A-C15A-H15B	107.9(12)
C2A-C15A-H15C	111.3(10)	H15A-C15A-H15C	107.6(13)
H15B-C15A-H15C	108.5(13)	O4A-C16A-H16A	110.4(8)
O4A-C16A-H16B	105.2(9)	H16A-C16A-H16B	110.7(12)

O4A-C16A-H16C	110.5(8)	H16A-C16A-H16C	110.9(12)
H16B-C16A-H16C	108.9(12)	N1B-O1B-C14B	110.10(8)
C3B-O3B-H3OB	103.5(12)	C10B-O4B-C16B	117.80(9)
C1B-N1B-O1B	116.48(8)	C1B-N1B-C13B	128.52(9)
O1B-N1B-C13B	114.18(8)	O2B-C1B-N1B	122.10(10)
O2B-C1B-C2B	121.25(10)	N1B-C1B-C2B	116.63(9)
C1B-C2B-C15B	110.87(9)	C1B-C2B-C3B	107.63(9)
C15B-C2B-C3B	112.21(9)	C1B-C2B-H2B	110.7(7)
C15B-C2B-H2B	108.4(7)	C3B-C2B-H2B	107.0(7)
O3B-C3B-C4B	110.17(9)	O3B-C3B-C2B	110.88(9)
C4B-C3B-C2B	112.53(9)	O3B-C3B-H3B	106.7(8)
C4B-C3B-H3B	108.7(8)	C2B-C3B-H3B	107.7(8)
C3B-C4B-C5B	114.66(10)	C3B-C4B-H4C	108.3(8)
C5B-C4B-H4C	110.8(8)	C3B-C4B-H4D	108.9(9)
C5B-C4B-H4D	108.6(9)	H4C-C4B-H4D	105.0(12)
C6B-C5B-C4B	113.93(11)	C6B-C5B-H5C	107.3(8)
C4B-C5B-H5C	111.2(8)	C6B-C5B-H5D	108.1(9)
C4B-C5B-H5D	109.3(9)	H5C-C5B-H5D	106.8(12)
C5B-C6B-C7B	114.43(9)	C5B-C6B-H6C	109.5(9)
C7B-C6B-H6C	108.6(9)	C5B-C6B-H6D	110.7(9)
C7B-C6B-H6D	106.5(9)	H6C-C6B-H6D	106.8(12)
C8B-C7B-C6B	112.30(10)	C8B-C7B-H7C	111.1(8)
C6B-C7B-H7C	109.4(8)	C8B-C7B-H7D	108.9(8)
C6B-C7B-H7D	108.4(9)	H7C-C7B-H7D	106.6(12)
C13B-C8B-C9B	118.15(10)	C13B-C8B-C7B	122.14(10)
C9B-C8B-C7B	119.65(10)	C10B-C9B-C8B	120.63(10)
C10B-C9B-H9B	120.4(8)	C8B-C9B-H9B	119.0(8)
O4B-C10B-C9B	124.47(10)	O4B-C10B-C11B	115.28(9)
C9B-C10B-C11B	120.25(10)	C12B-C11B-C10B	119.70(10)
C12B-C11B-H11B	121.2(8)	C10B-C11B-H11B	119.1(8)
C11B-C12B-C13B	119.98(10)	C11B-C12B-H12B	120.9(8)
C13B-C12B-H12B	119.1(8)	C12B-C13B-C8B	121.26(10)
C12B-C13B-N1B	118.82(9)	C8B-C13B-N1B	119.93(9)
O1B-C14B-H14D	111.1(9)	O1B-C14B-H14E	102.6(9)
H14D-C14B-H14E	109.7(13)	O1B-C14B-H14F	110.0(9)
H14D-C14B-H14F	109.6(13)	H14E-C14B-H14F	113.8(13)
C2B-C15B-H15D	109.1(9)	C2B-C15B-H15E	110.5(9)
H15D-C15B-H15E	106.8(12)	C2B-C15B-H15F	109.4(9)
H15D-C15B-H15F	111.5(12)	H15E-C15B-H15F	109.6(13)
O4B-C16B-H16D	105.3(9)	O4B-C16B-H16E	110.7(8)

H16D-C16B-H16E	109.4(12)	O4B-C16B-H16F	111.7(8)
H16D-C16B-H16F	110.7(12)	H16E-C16B-H16F	109.1(12)

Supplementary Table 10. Torsion angles (°) for α-methyl-β-hydroxylactam 54.

C9A-C10A-O4A-C16A	-1.47(15)	C9B-C10B-O4B-C16B	3.84(15)
C11A-C10A-O4A-C16A	179.15(9)	C11B-C10B-O4B-C16B	-175.90(9)
C1A-N1A-O1A-C14A	86.27(11)	C1B-N1B-O1B-C14B	86.16(11)
C13A-N1A-O1A-C14A	-100.05(10)	C13B-N1B-O1B-C14B	-103.30(10)
O2A-C1A-C2A-C15A	-63.04(14)	O2B-C1B-C2B-C15B	-63.10(13)
N1A-C1A-C2A-C15A	118.19(11)	N1B-C1B-C2B-C15B	118.78(10)
H3OA-O3A-C3A-C4A	-80.6(15)	H3OB-O3B-C3B-C4B	-75.4(12)
H3OA-O3A-C3A-C2A	45.2(15)	H3OB-O3B-C3B-C2B	49.8(12)

Supplementary Table 11. Anisotropic atomic displacement parameters (Å^2) for α-methyl-β-hydroxylactam 54. The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1A	0.0213(4)	0.0199(4)	0.0159(4)	-0.0030(3)	-0.0012(3)	-0.0005(3)
O2A	0.0245(4)	0.0356(5)	0.0253(4)	-0.0076(4)	0.0096(3)	-0.0136(4)
O3A	0.0290(5)	0.0425(5)	0.0272(4)	-0.0066(4)	0.0167(4)	-0.0118(4)
O4A	0.0229(4)	0.0235(4)	0.0280(4)	0.0008(3)	0.0114(3)	-0.0027(3)
N1A	0.0172(4)	0.0190(4)	0.0136(4)	-0.0015(3)	0.0010(3)	-0.0016(3)
C1A	0.0186(5)	0.0185(5)	0.0198(5)	-0.0039(4)	0.0060(4)	-0.0025(4)
C2A	0.0176(5)	0.0251(6)	0.0165(5)	-0.0008(4)	0.0052(4)	-0.0048(4)
C3A	0.0209(5)	0.0339(6)	0.0191(5)	-0.0065(5)	0.0087(5)	-0.0081(5)
C4A	0.0197(5)	0.0300(6)	0.0292(6)	-0.0088(5)	0.0119(5)	-0.0022(5)
C5A	0.0188(5)	0.0230(6)	0.0255(6)	-0.0084(5)	0.0074(4)	-0.0014(4)
C6A	0.0188(5)	0.0178(5)	0.0322(6)	-0.0046(5)	0.0071(5)	0.0024(4)
C7A	0.0197(5)	0.0189(5)	0.0228(6)	0.0007(4)	0.0025(4)	0.0024(4)
C8A	0.0204(5)	0.0183(5)	0.0114(4)	-0.0005(4)	0.0022(4)	0.0022(4)
C9A	0.0240(5)	0.0158(5)	0.0146(5)	0.0004(4)	0.0051(4)	0.0001(4)
C10A	0.0210(5)	0.0214(5)	0.0135(5)	-0.0012(4)	0.0058(4)	-0.0019(4)
C11A	0.0207(5)	0.0204(5)	0.0182(5)	-0.0010(4)	0.0069(4)	0.0032(4)
C12A	0.0242(5)	0.0154(5)	0.0165(5)	-0.0005(4)	0.0061(4)	0.0016(4)
C13A	0.0194(5)	0.0180(5)	0.0119(5)	-0.0011(4)	0.0041(4)	-0.0011(4)
C14A	0.0303(6)	0.0203(6)	0.0206(6)	-0.0050(4)	0.0079(5)	-0.0032(5)
C15A	0.0298(6)	0.0322(7)	0.0242(6)	0.0065(5)	0.0077(5)	-0.0014(5)
C16A	0.0291(6)	0.0246(6)	0.0231(6)	0.0031(5)	0.0094(5)	-0.0064(5)
O1B	0.0254(4)	0.0312(4)	0.0214(4)	0.0057(3)	0.0129(3)	0.0009(3)
O2B	0.0329(5)	0.0322(5)	0.0152(4)	-0.0026(3)	0.0031(3)	-0.0087(4)
O3B	0.0254(4)	0.0261(4)	0.0241(4)	-0.0085(3)	0.0072(3)	-0.0090(3)
O4B	0.0179(4)	0.0256(4)	0.0172(4)	-0.0031(3)	0.0023(3)	0.0002(3)
N1B	0.0172(4)	0.0253(5)	0.0147(4)	0.0020(4)	0.0065(4)	-0.0021(4)
C1B	0.0179(5)	0.0199(5)	0.0168(5)	-0.0016(4)	0.0043(4)	0.0005(4)
C2B	0.0154(5)	0.0202(5)	0.0155(5)	-0.0026(4)	0.0039(4)	-0.0029(4)
C3B	0.0212(5)	0.0203(5)	0.0209(5)	-0.0041(4)	0.0070(4)	-0.0041(4)
C4B	0.0244(6)	0.0207(6)	0.0294(6)	-0.0072(5)	0.0096(5)	-0.0006(4)
C5B	0.0255(6)	0.0207(6)	0.0289(6)	0.0000(5)	0.0071(5)	0.0048(5)
C6B	0.0204(6)	0.0275(6)	0.0333(7)	-0.0086(5)	0.0052(5)	0.0082(5)
C7B	0.0154(5)	0.0329(6)	0.0260(6)	-0.0075(5)	0.0089(5)	-0.0001(4)
C8B	0.0150(5)	0.0195(5)	0.0213(5)	-0.0007(4)	0.0081(4)	-0.0026(4)
C9B	0.0128(5)	0.0193(5)	0.0215(5)	0.0016(4)	0.0048(4)	-0.0002(4)
C10B	0.0173(5)	0.0168(5)	0.0165(5)	0.0013(4)	0.0049(4)	-0.0035(4)
C11B	0.0190(5)	0.0151(5)	0.0210(5)	-0.0006(4)	0.0084(4)	-0.0003(4)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C12B	0.0140(5)	0.0158(5)	0.0219(5)	0.0035(4)	0.0058(4)	0.0001(4)
C13B	0.0150(5)	0.0182(5)	0.0163(5)	0.0010(4)	0.0047(4)	-0.0034(4)
C14B	0.0314(7)	0.0257(6)	0.0228(6)	0.0034(5)	0.0071(5)	-0.0021(5)
C15B	0.0168(5)	0.0281(6)	0.0260(6)	-0.0052(5)	0.0069(5)	-0.0018(4)
C16B	0.0161(5)	0.0359(7)	0.0181(5)	0.0011(5)	0.0035(4)	-0.0005(5)

Supplementary Table 12. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for α-methyl-β-hydroxylactam 54.

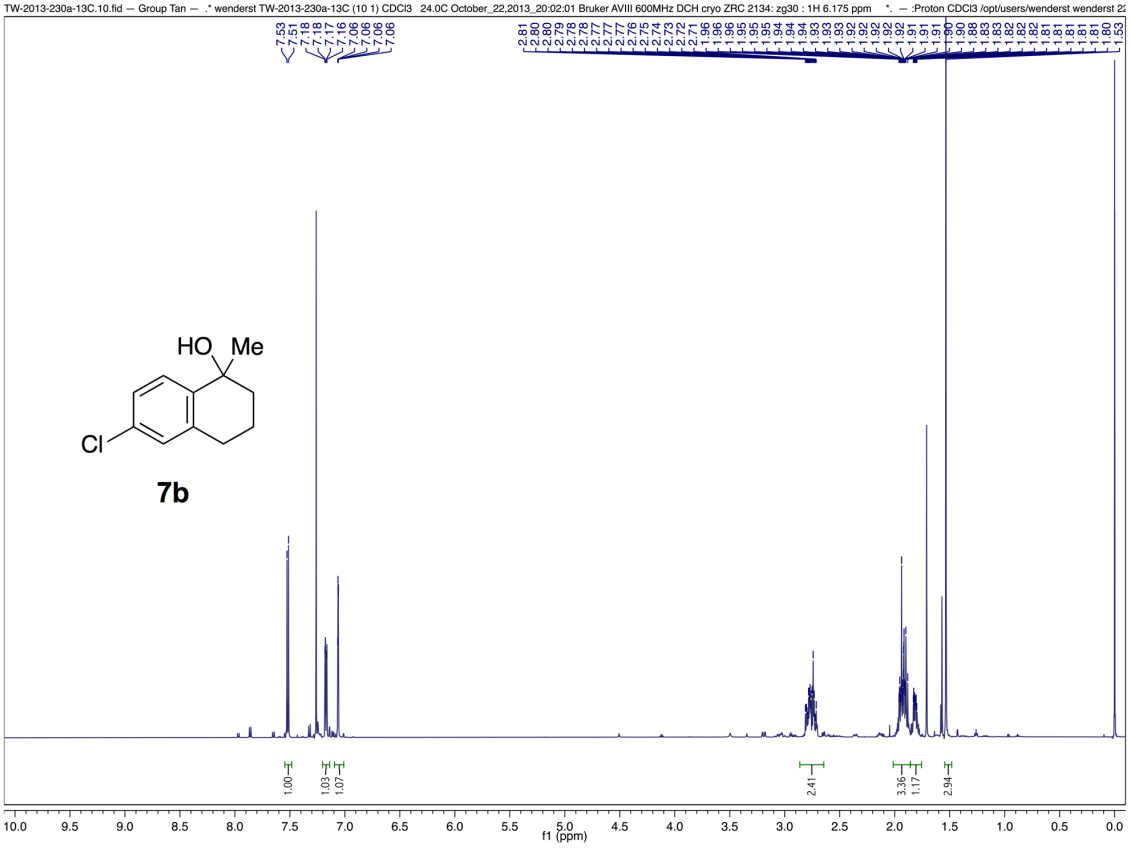
	x/a	y/b	z/c	U(eq)
H3OA	0.440(2)	0.5812(7)	0.046(2)	0.066(6)
H2A	0.1075(15)	0.5588(4)	0.0829(12)	0.015(3)
H3A	0.1888(15)	0.5382(4)	-0.0790(13)	0.018(3)
H4A	0.4167(17)	0.5146(4)	0.1695(14)	0.028(4)
H4B	0.3922(16)	0.4920(5)	0.0376(14)	0.029(4)
H5A	0.1209(16)	0.4930(4)	0.0918(13)	0.025(3)
H5B	0.1831(16)	0.4565(4)	0.0267(14)	0.025(3)
H6A	0.1898(16)	0.4330(4)	0.2229(13)	0.026(3)
H6B	0.3688(17)	0.4387(4)	0.2401(14)	0.027(3)
H7A	0.3343(17)	0.4651(5)	0.4276(15)	0.030(4)
H7B	0.3918(16)	0.5007(4)	0.3588(13)	0.022(3)
H9A	0.0352(16)	0.4591(5)	0.3540(13)	0.025(3)
H11A	-0.2013(16)	0.5689(4)	0.2932(13)	0.024(3)
H12A	0.0228(15)	0.6029(4)	0.2872(13)	0.022(3)
H14A	0.4317(17)	0.6392(5)	0.4286(15)	0.032(4)
H14B	0.4986(15)	0.6181(4)	0.5665(13)	0.018(3)
H14C	0.3112(19)	0.6235(5)	0.4890(15)	0.036(4)
H15A	0.2096(18)	0.6326(5)	0.0008(14)	0.032(4)
H15B	0.0610(18)	0.6295(5)	0.0398(16)	0.040(4)
H15C	0.0607(18)	0.6088(5)	-0.0901(16)	0.038(4)
H16A	-0.2359(16)	0.4360(5)	0.2696(15)	0.030(4)
H16B	-0.3429(18)	0.4458(5)	0.3520(15)	0.034(4)
H16C	-0.1567(17)	0.4427(4)	0.4269(14)	0.026(3)
H3OB	0.467(2)	0.7253(6)	0.5418(19)	0.056(5)
H2B	0.6333(15)	0.7745(4)	0.8269(13)	0.015(3)
H3B	0.5597(15)	0.7059(4)	0.7904(13)	0.020(3)
H4C	0.7608(16)	0.7260(4)	0.6573(14)	0.026(3)
H4D	0.7434(17)	0.6816(5)	0.7060(14)	0.032(4)
H5C	0.8446(16)	0.7391(4)	0.9125(14)	0.027(3)
H5D	0.8958(17)	0.6918(5)	0.9139(15)	0.033(4)
H6C	1.0587(17)	0.7122(5)	0.8029(15)	0.033(4)
H6D	1.1130(17)	0.7321(4)	0.9415(15)	0.030(4)
H7C	0.9538(17)	0.7750(4)	0.7037(14)	0.028(4)
H7D	1.1268(17)	0.7825(4)	0.8034(14)	0.029(4)
H9B	1.1710(16)	0.8071(4)	1.0339(13)	0.020(3)

	x/a	y/b	z/c	U(eq)
H11B	0.8327(15)	0.8826(4)	1.0634(13)	0.023(3)
H12B	0.6672(16)	0.8658(4)	0.8446(13)	0.023(3)
H14D	0.6991(18)	0.8909(5)	0.5904(16)	0.037(4)
H14E	0.7286(18)	0.8770(5)	0.4676(15)	0.035(4)
H14F	0.5700(18)	0.8623(5)	0.4857(15)	0.035(4)
H15D	0.3714(18)	0.7612(5)	0.7984(15)	0.034(4)
H15E	0.3175(18)	0.7710(5)	0.6474(16)	0.035(4)
H15F	0.3888(18)	0.8088(5)	0.7473(15)	0.036(4)
H16D	1.3101(18)	0.8592(5)	1.3338(16)	0.035(4)
H16E	1.3202(17)	0.8511(4)	1.1966(14)	0.028(4)
H16F	1.2682(16)	0.8137(5)	1.2648(14)	0.030(4)

Supplementary Table 13. Hydrogen bond distances (Å) and angles (°) for α-methyl-β-hydroxylactam 54.

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
O3A-H3OA···O2A	0.86(2)	2.04(2)	2.7804(12)	143.4(19)
C16A-H16A···O3A	0.996(15)	2.546(15)	3.3543(15)	138.2(11)
O3B-H3OB···O2B	0.90(2)	2.03(2)	2.7979(12)	143.3(17)
C9B-H9B···O3B	0.961(14)	2.537(14)	3.4717(13)	164.4(11)
C12B-H12B···O2A	0.965(14)	2.282(14)	3.2344(13)	169.1(11)
C14B-H14F···O2B	0.995(16)	2.598(16)	3.1003(15)	111.2(11)

I. ^{1}H-NMR AND ^{13}C-NMR SPECTRA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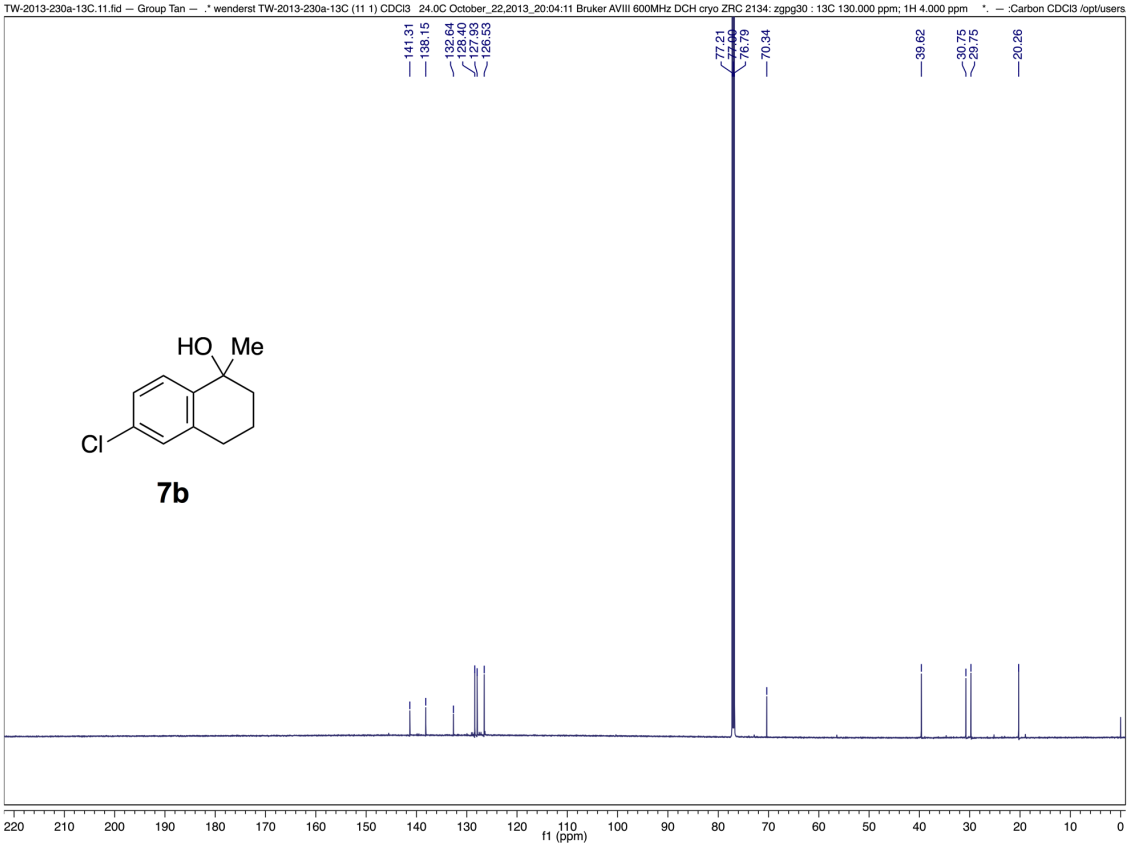
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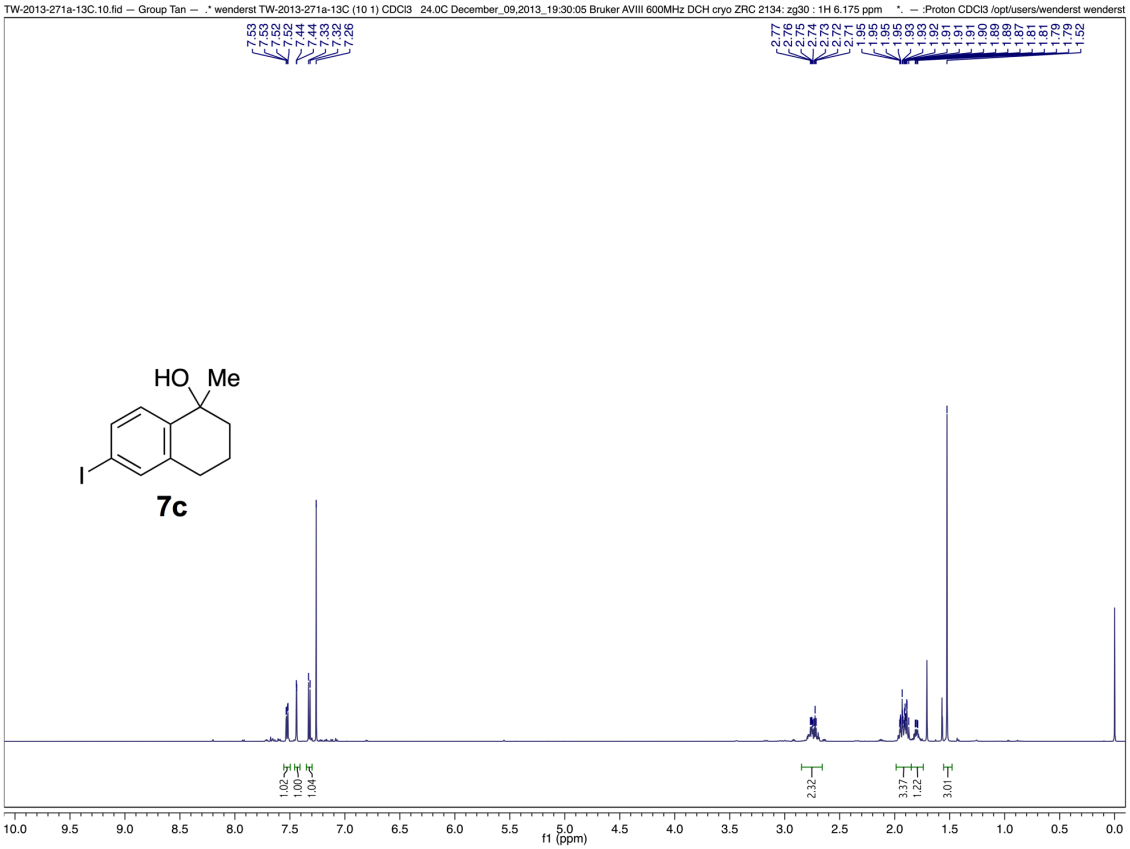
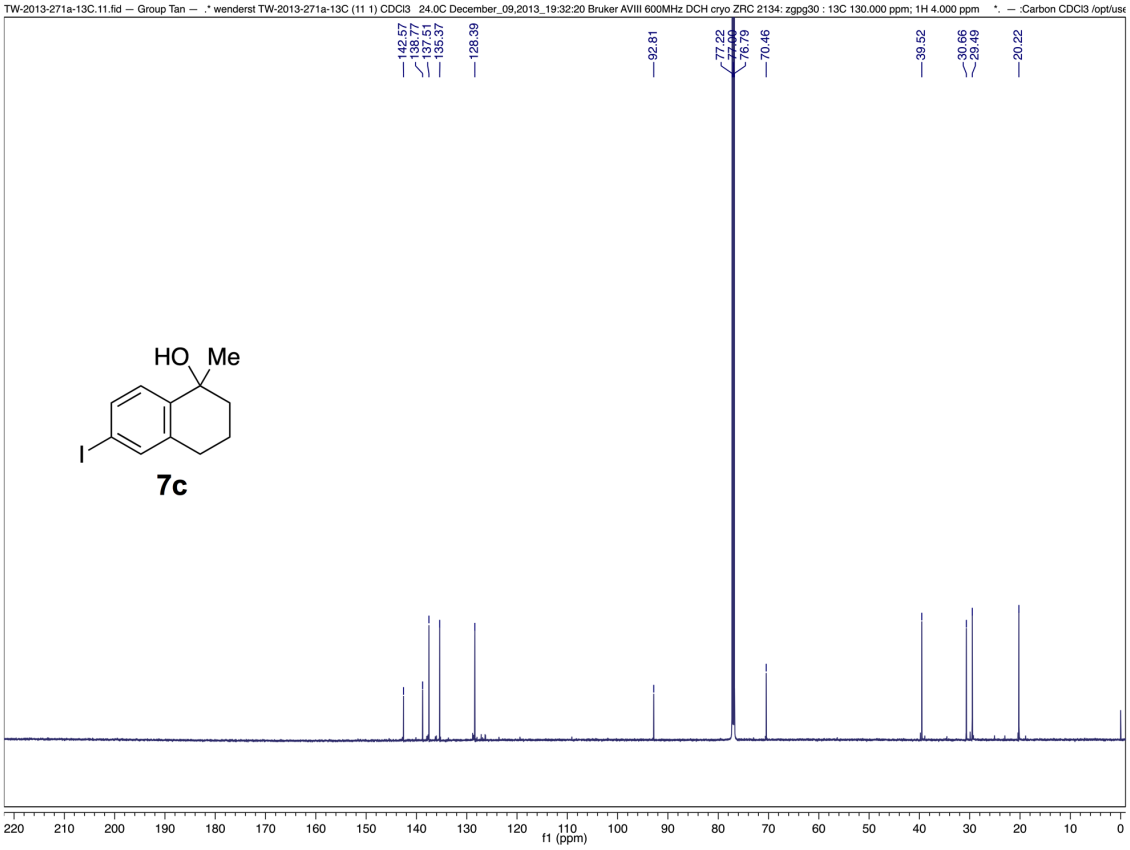
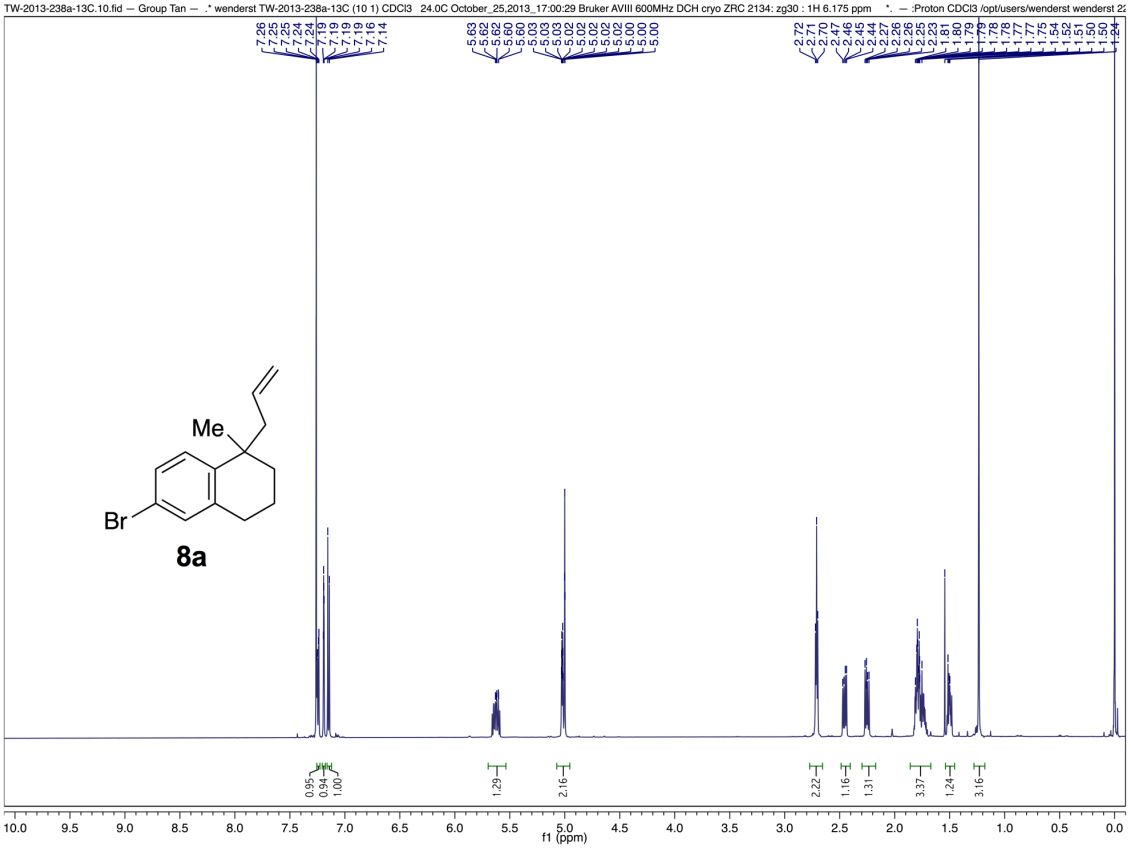
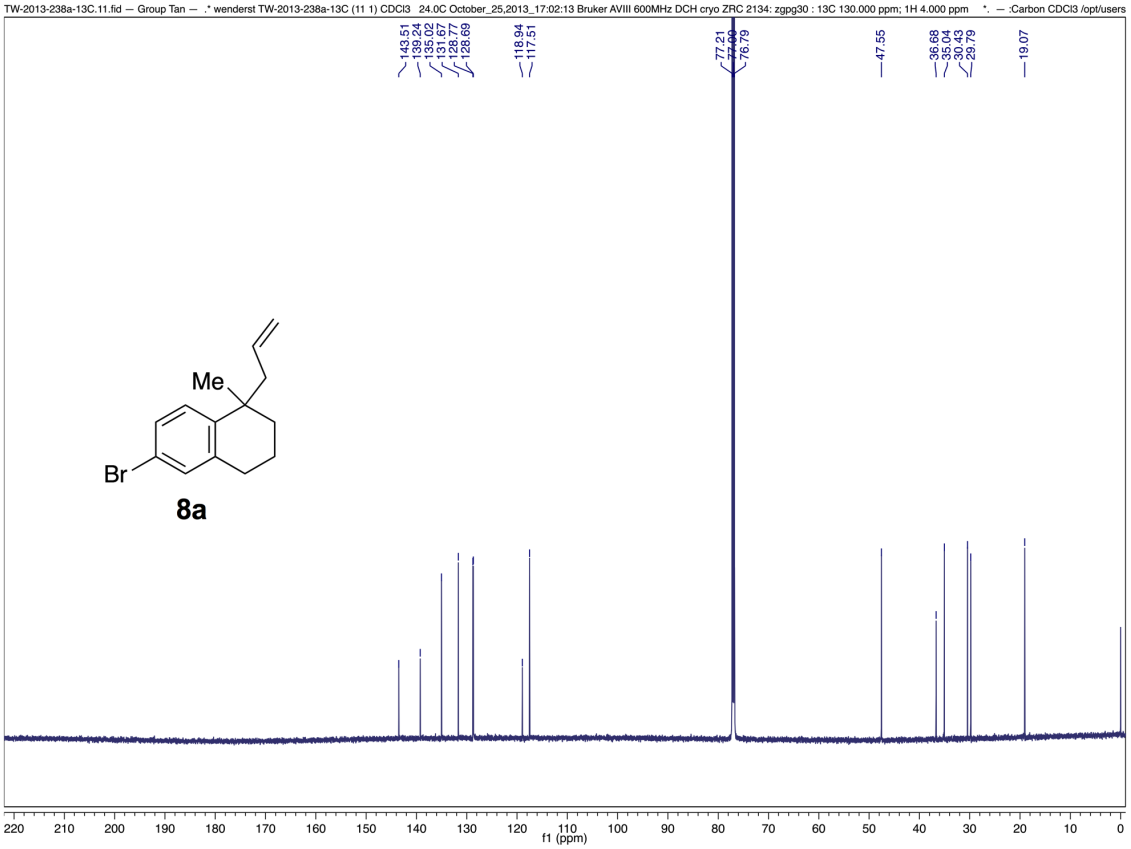
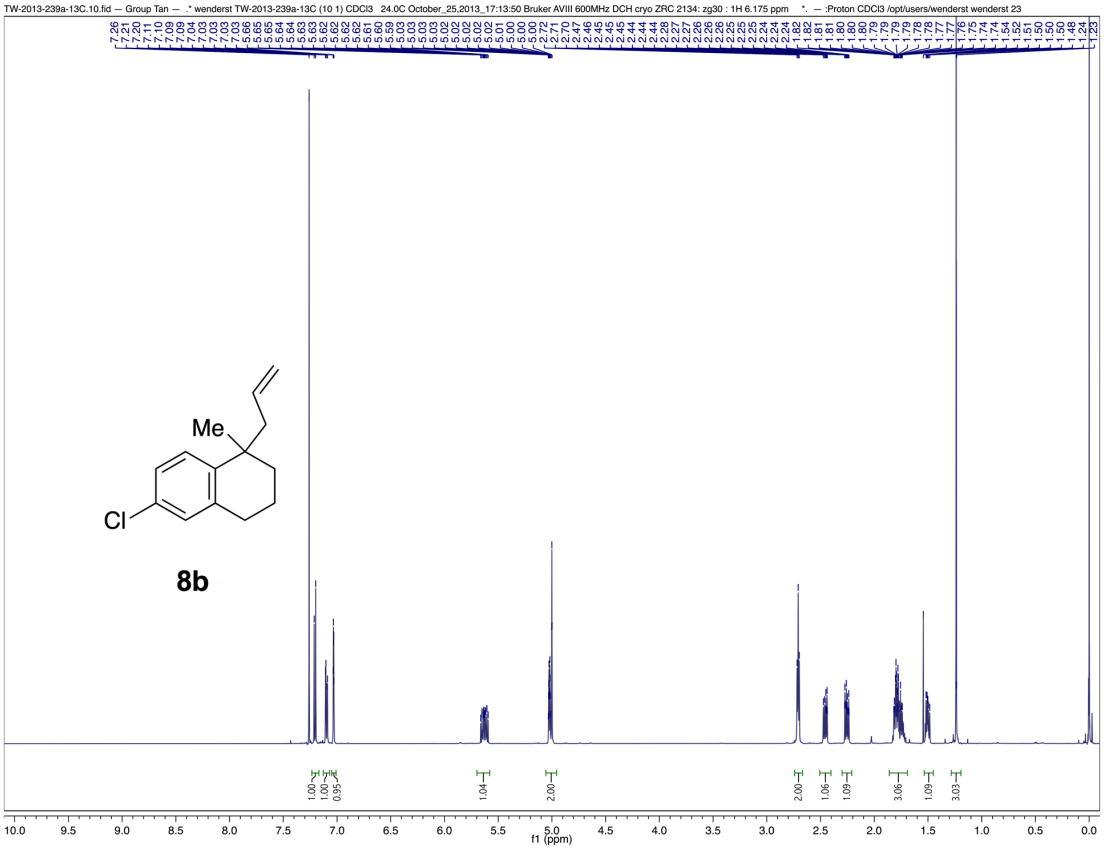

TW-2013-271a-13C.10.fid — Group Tan — .* wenderst TW-2013-271a-13C (10 1) CDCl3 24.0C December_09,2013_19:30:05 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm :Proton CDCl3 /opt/users/wenderst wenderst
HO Me
I
7c
f1 (ppm)

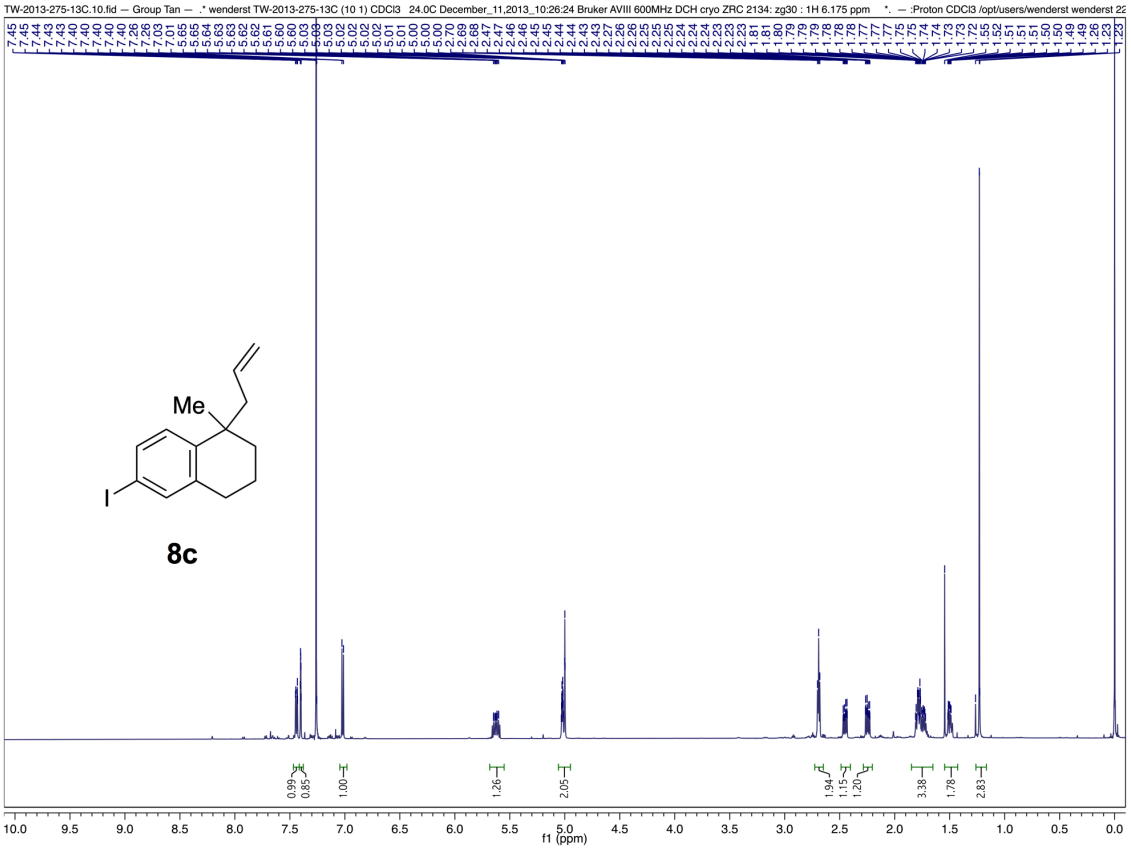

TW-2013-271a-13C.11.fid — Group Tan — .* wenderst TW-2013-271a-13C (11 1) CDCl3 24.0C December_09,2013_19:32:20 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm :Carbon CDCl3 /opt/use
HO Me
I
7c
f1 (ppm)

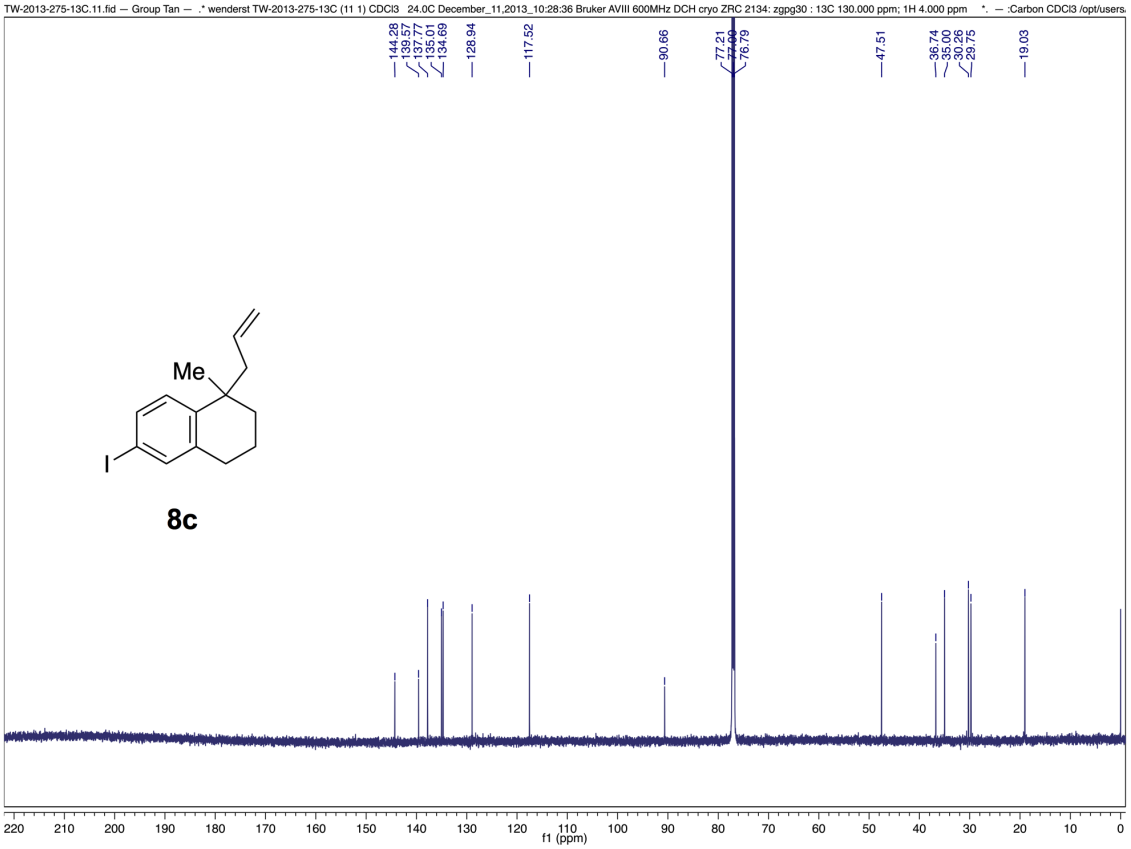

Me
Br
8a
f1 (ppm)

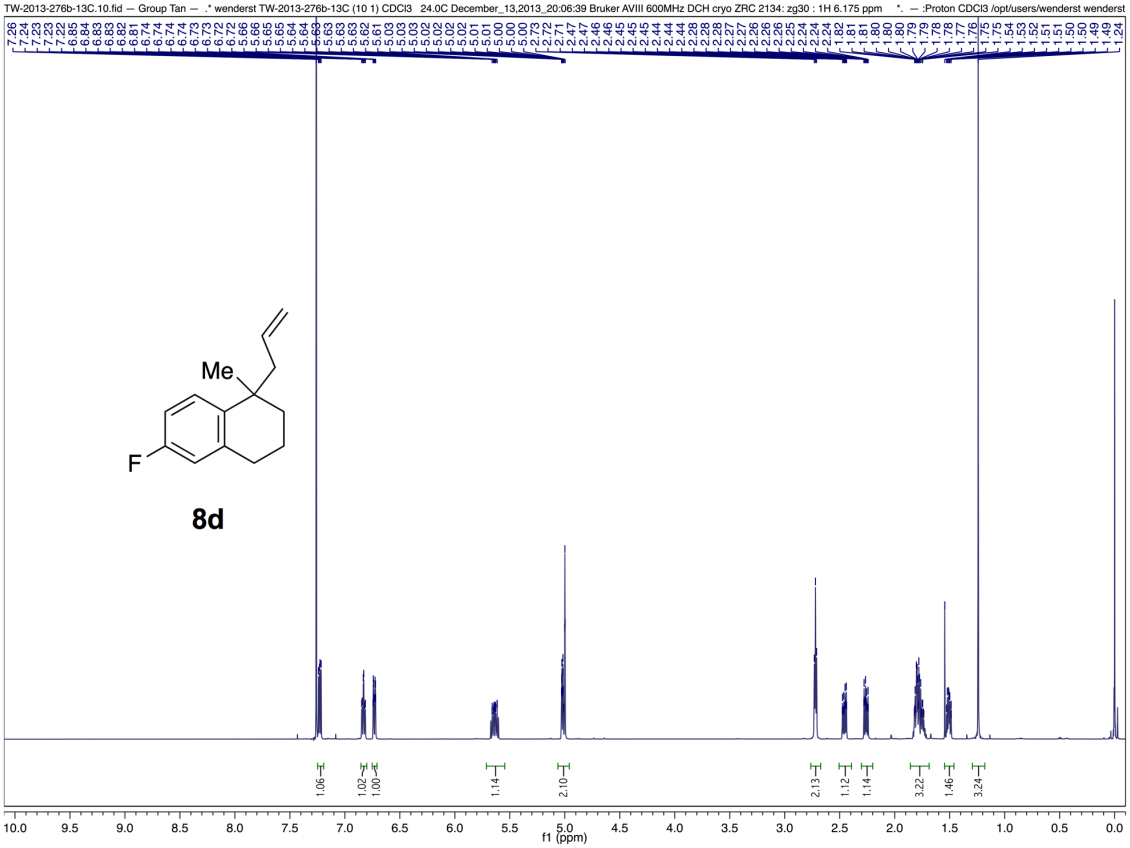

Me
Br
8a
f1 (ppm)

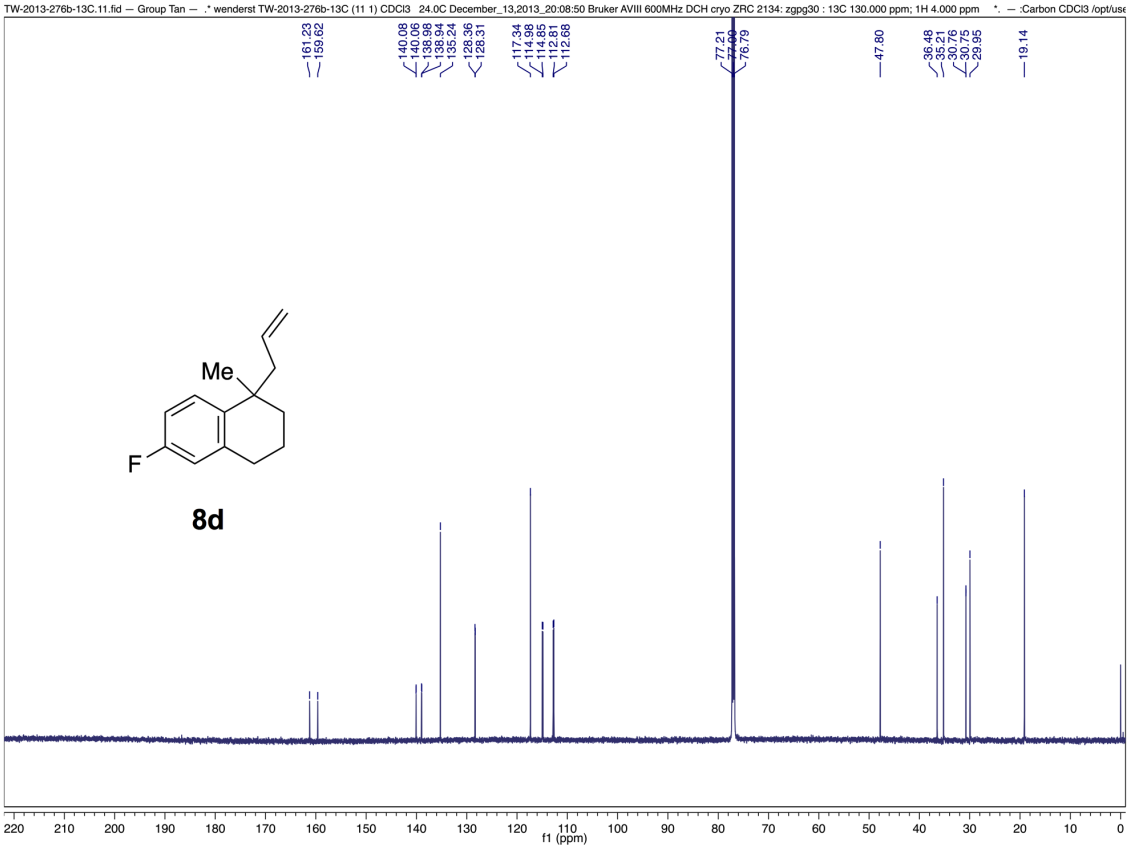

TW-2013-239a-13C.10.fid — Group Tan — .* wenderst TW-2013-239a-13C (10 1) CDCl3 24.0C October_25,2013_17:13:50 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 23
Me
Cl
8b
f1 (ppm)

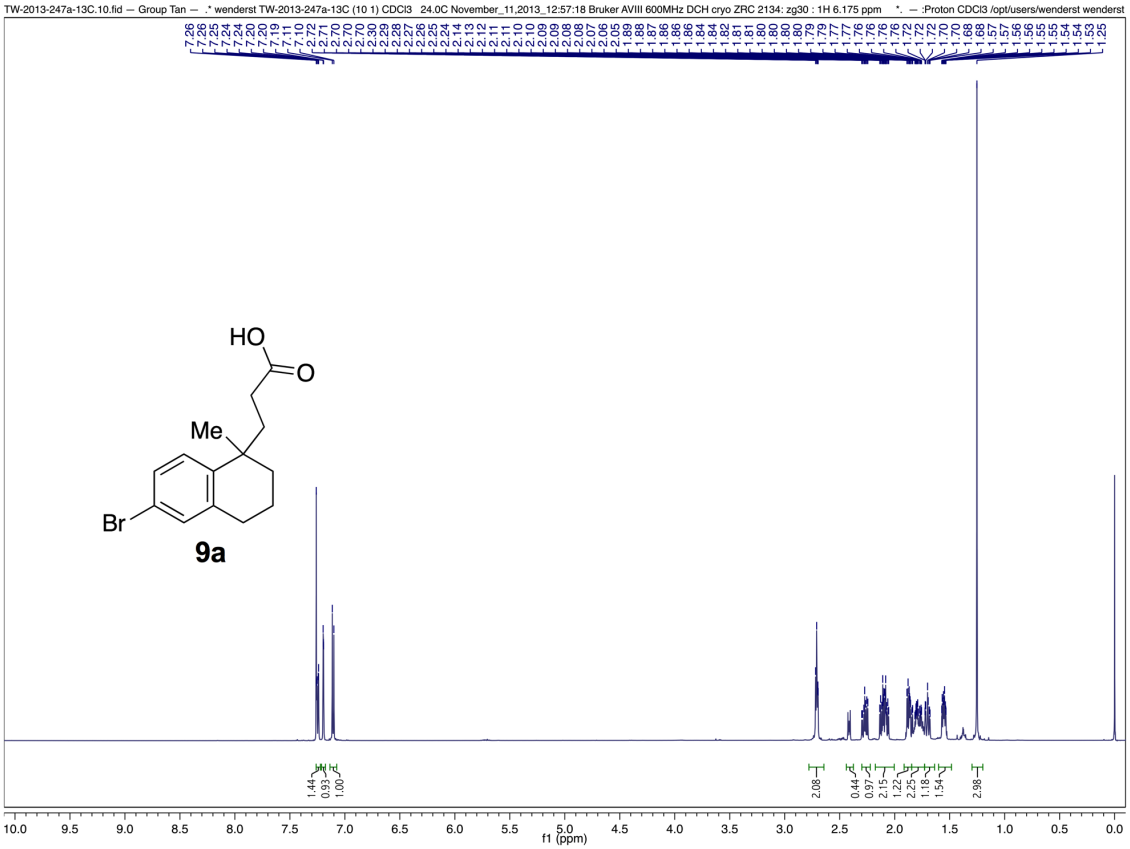

TW-2013-239a-13C.11.fid — Group Tan — .* wenderst TW-2013-239a-13C (11 1) CDCl3 24.0C October_25,2013_17:15:37 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/wenderst wenderst
Me
Cl
8b
f1 (ppm)

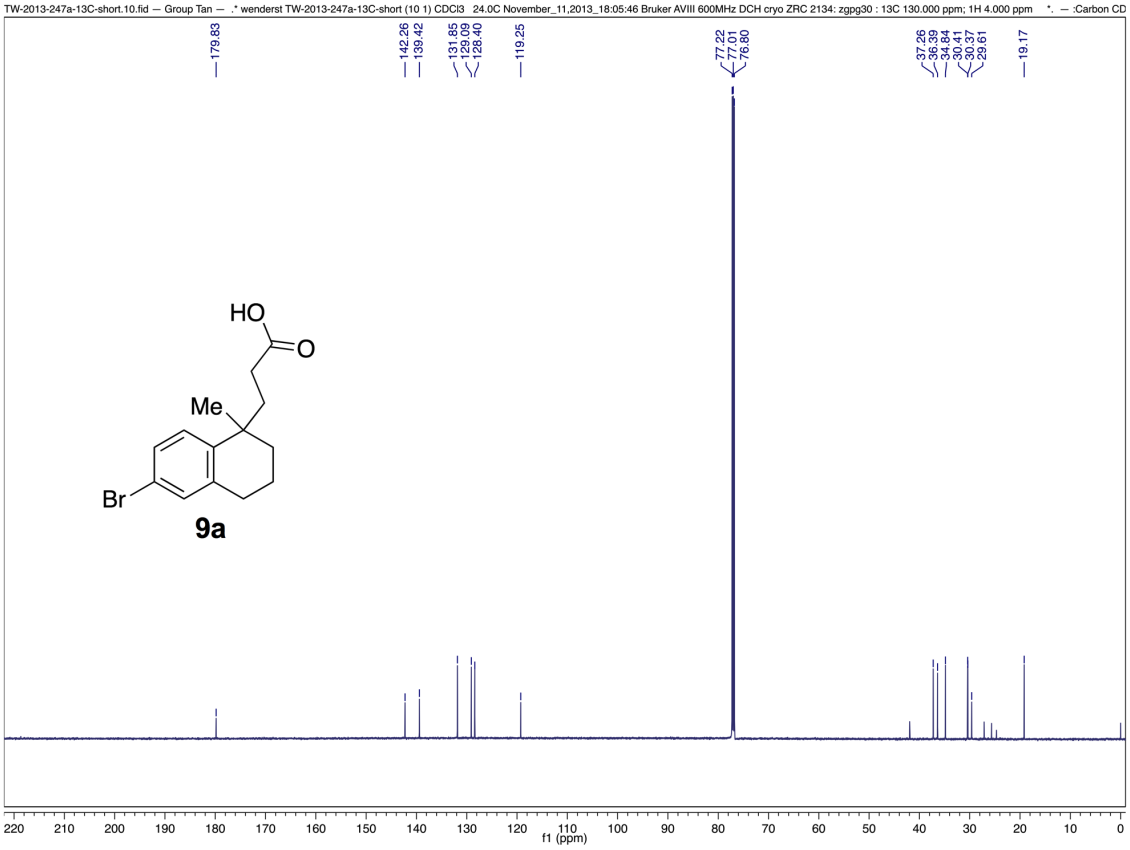

TW-2013-275-13C.10.fid — Group Tan — .* wenderst TW-2013-275-13C (10 1) CDCl3 24.0C December_11,2013_10:26:24 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
Me
I
8c
f1 (ppm)

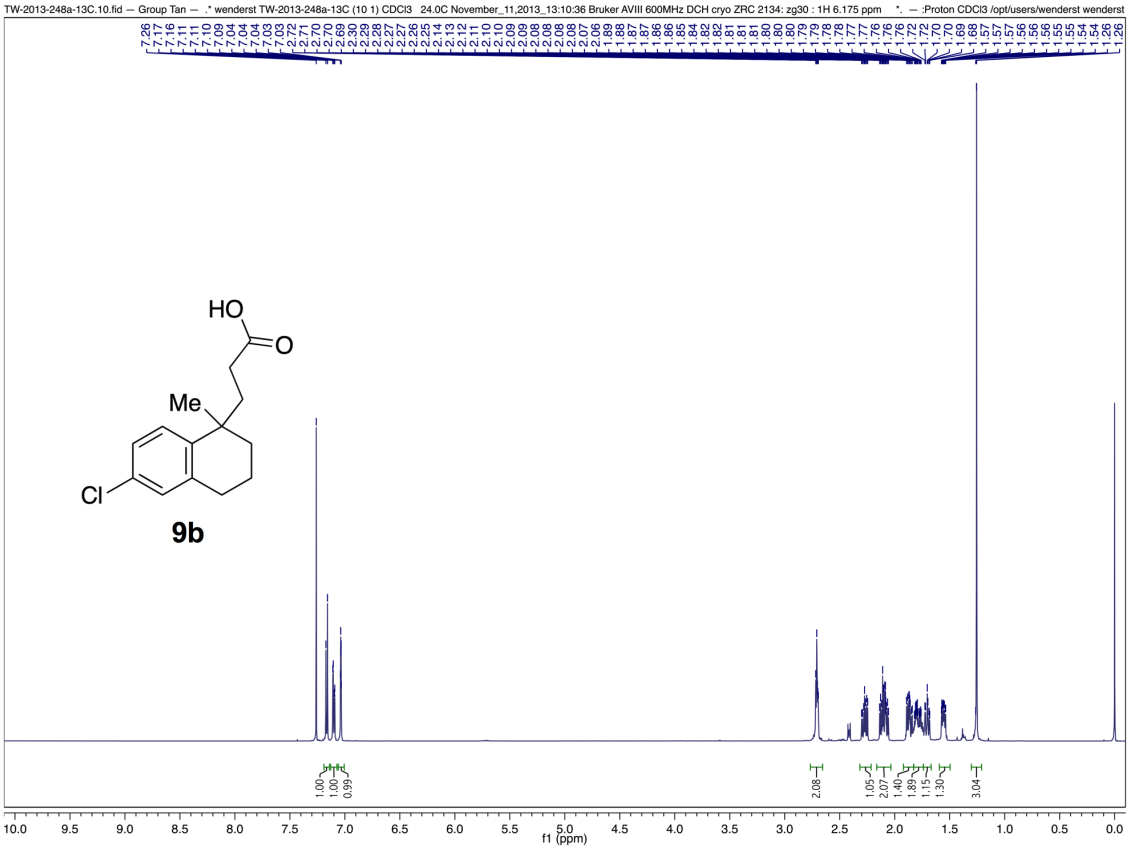

TW-2013-275-13C.11.fid — Group Tan — .* wenderst TW-2013-275-13C (11 1) CDCl3 24.0C December_11,2013_10:28:36 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm
144.28
139.57
137.77
135.01
134.69
128.94
117.52
90.66
77.21
77.00
76.79
47.51
36.74
35.00
30.26
29.75
19.03
Me
I
8c
f1 (ppm)

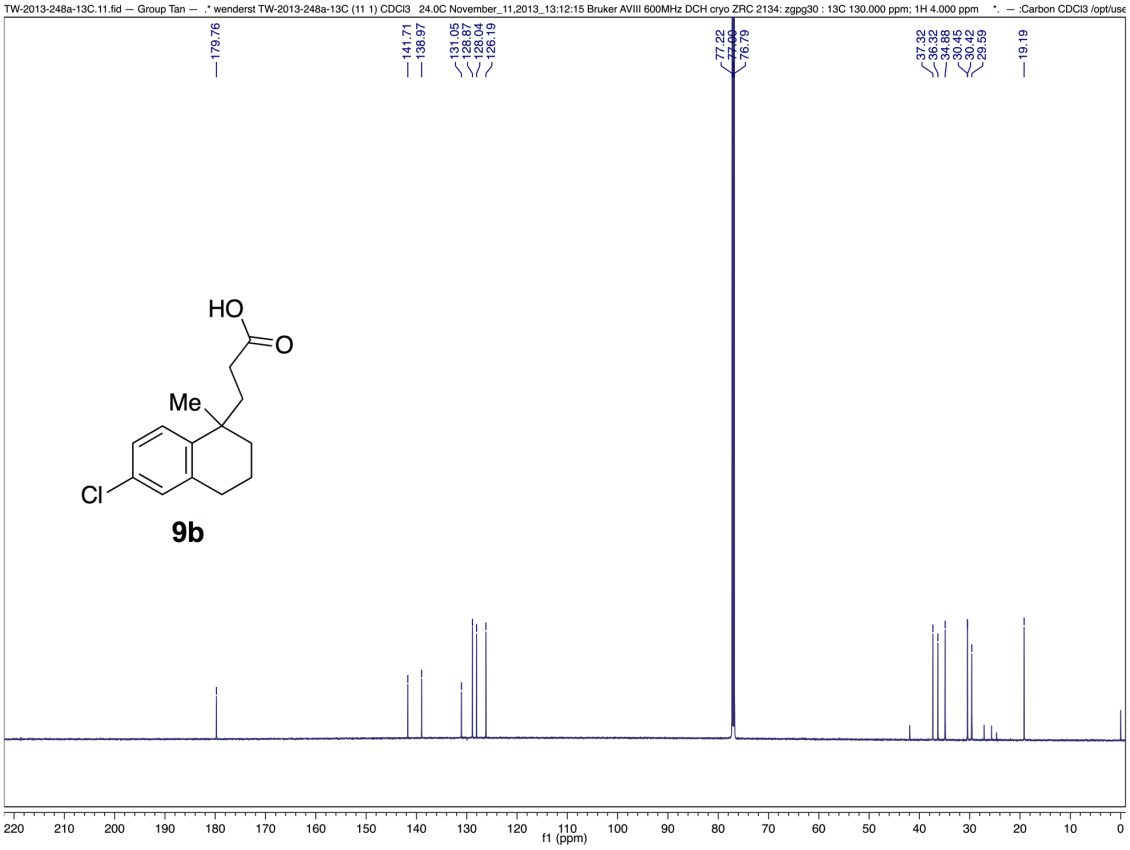

TW-2013-276b-13C.10.fid — Group Tan — .* wenderst TW-2013-276b-13C (10 1) CDCl3 24.0C December_13,2013_20:06:39 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst
Me
F
8d
f1 (ppm)

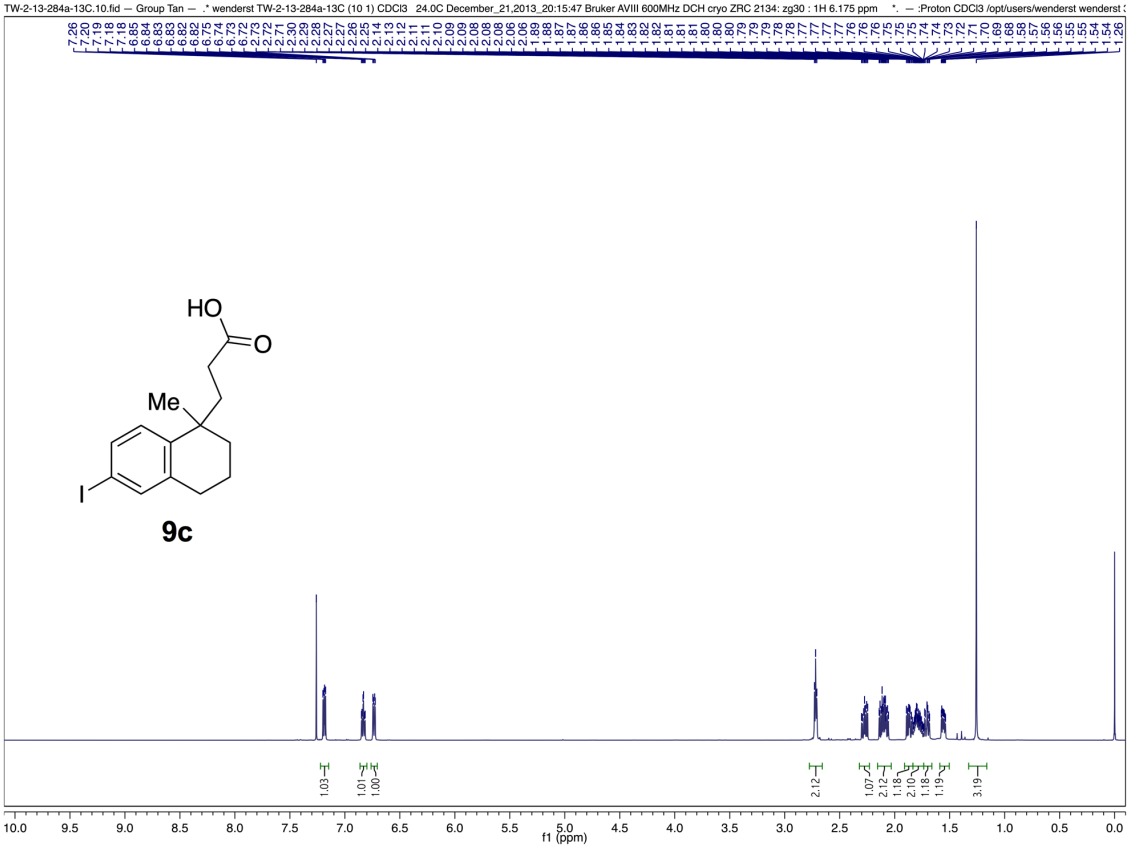

TW-2013-276b-13C.11.fid — Group Tan — .* wenderst TW-2013-276b-13C (11 1) CDCl3 24.0C December_13,2013_20:08:50 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
Me
F
8d
f1 (ppm)

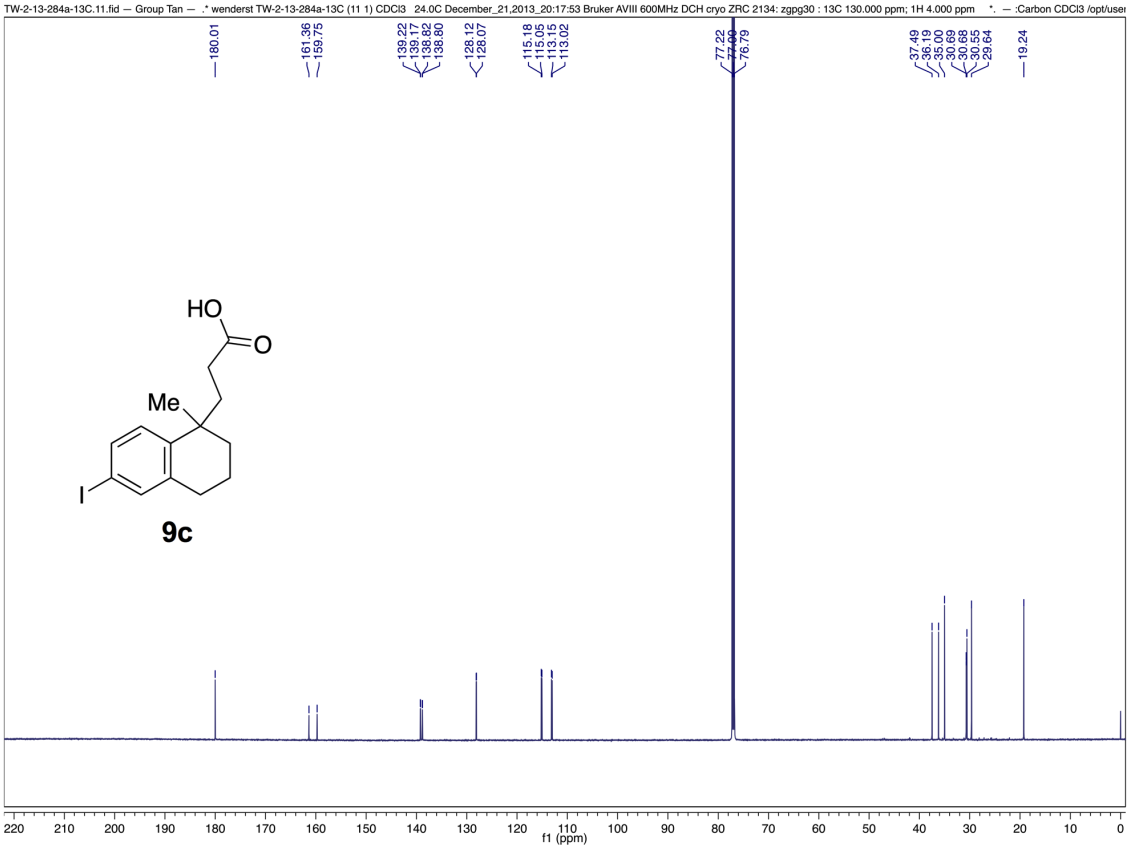

TW-2013-247a-13C.10.fid — Group Tan — .* wenderst TW-2013-247a-13C (10 1) CDCl3 24.0C November_11,2013_12:57:18 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst
HO
O
Me
Br
9a
f1 (ppm)

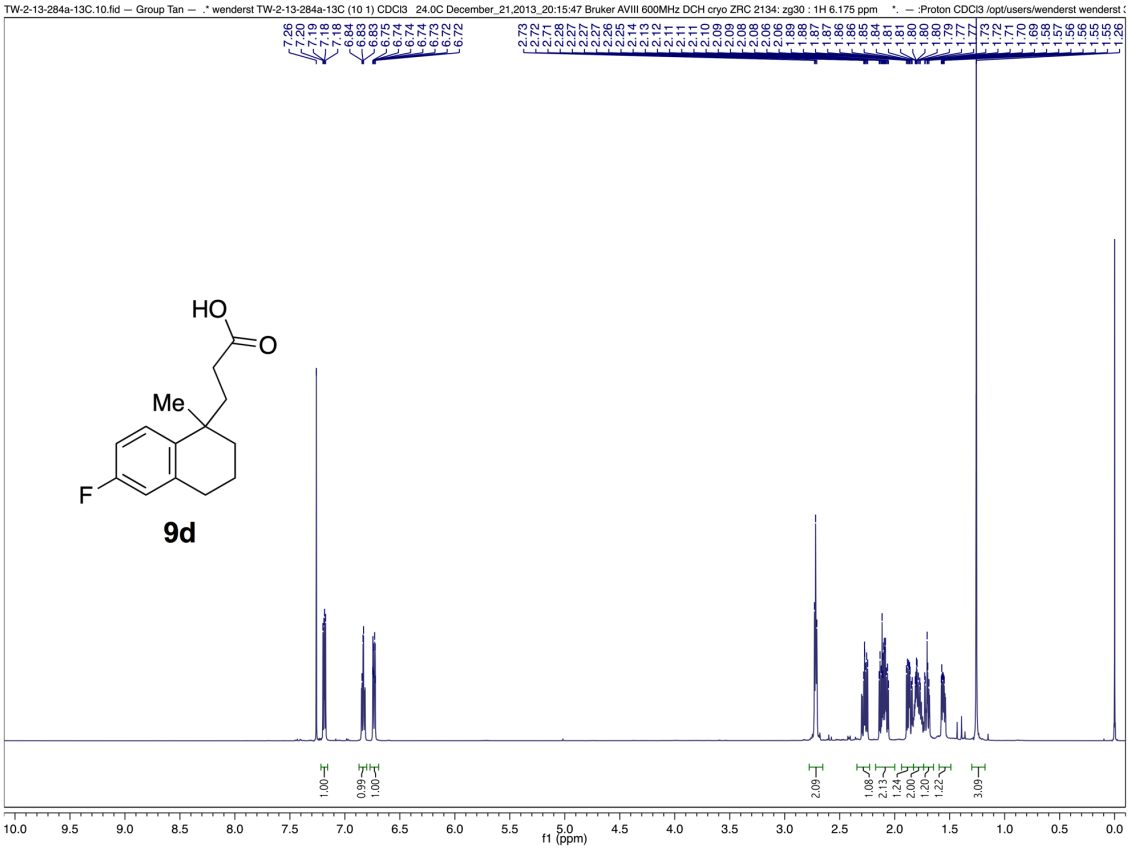

TW-2013-247a-13C-short.10.fid — Group Tan — .* wenderst TW-2013-247a-13C-short (10 1) CDCl3 24.0C November_11,2013_18:05:46 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CD
179.83
142.26
139.42
131.85
129.09
128.40
119.25
77.22
77.01
76.80
37.26
36.39
34.84
30.41
30.37
29.61
19.17
HO
O
Me
Br
9a
f1 (ppm)

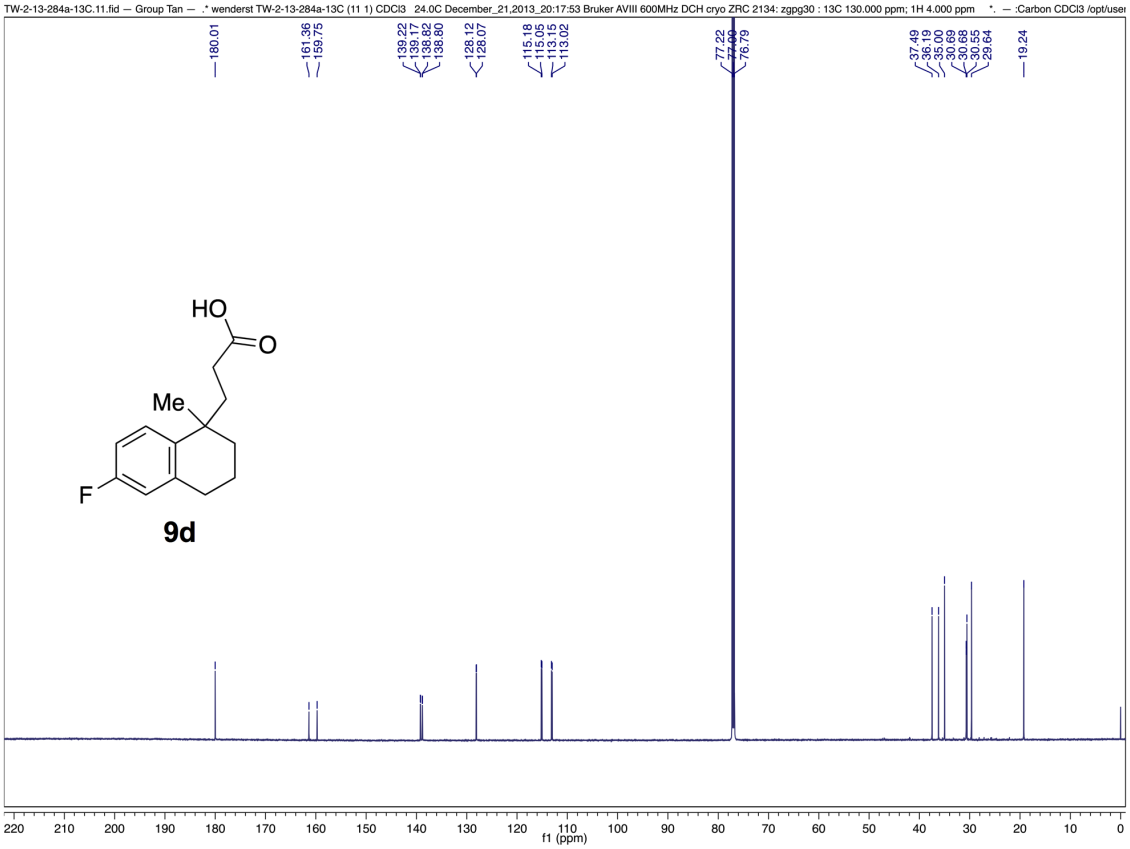

TW-2013-248a-13C.10.fid — Group Tan — .* wenderst TW-2013-248a-13C (10 1) CDCl3 24.0C November_11,2013_13:10:36 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst
HO
O
Me
Cl
9b
f1 (ppm)

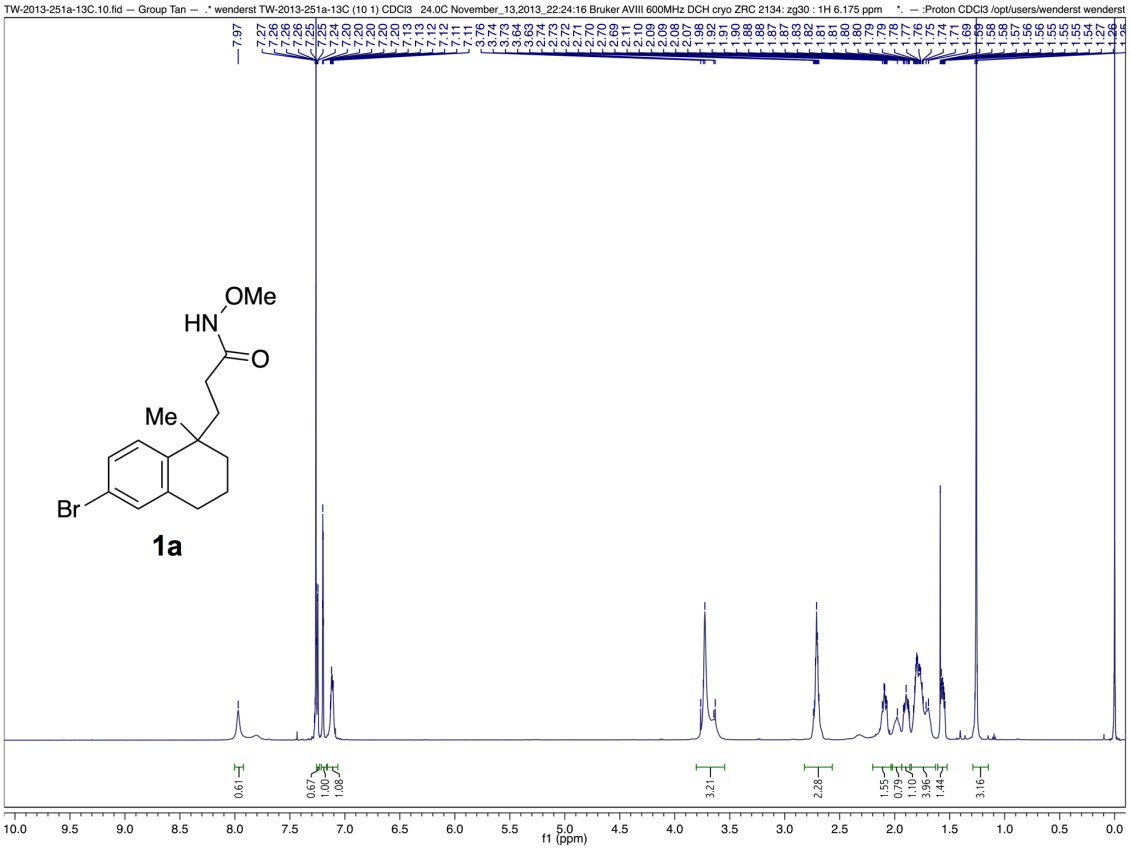

TW-2013-248a-13C.11.fid — Group Tan — .* wenderst TW-2013-248a-13C (11 1) CDCl3 24.0C November_11,2013_13:12:15 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
179.76
141.71
138.97
131.05
128.87
128.04
126.19
77.22
77.00
76.79
37.32
36.32
34.88
30.45
30.42
29.59
19.19
HO
O
Me
Cl
9b
f1 (ppm)

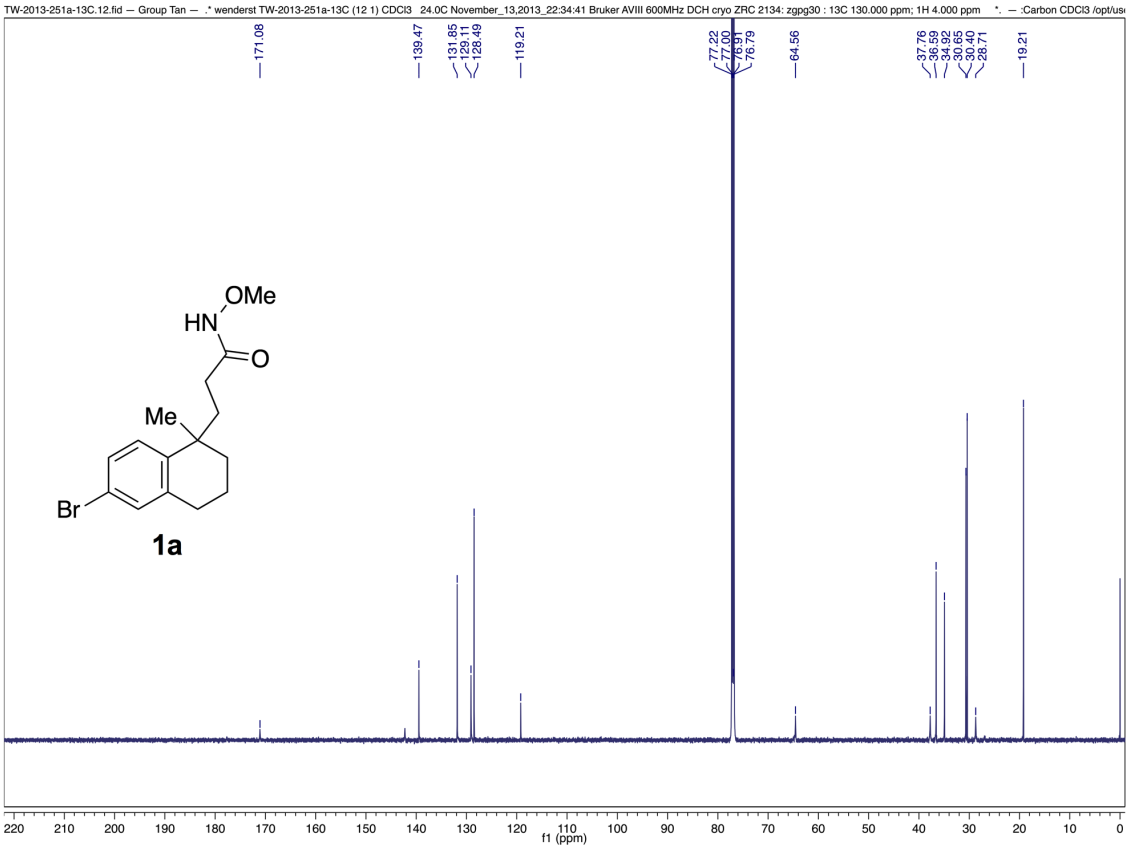

HO
O
Me
I
9c
f1 (ppm)

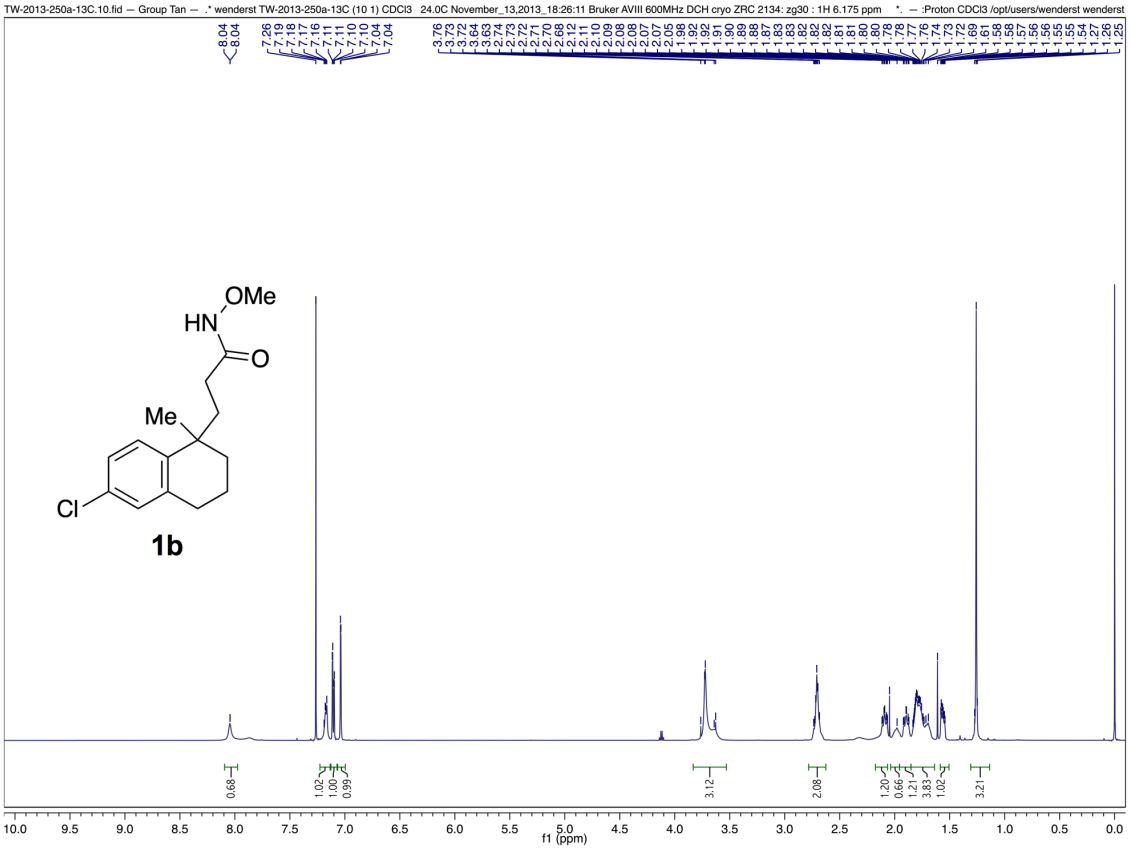

HO
O
Me
I
9c
f1 (ppm)

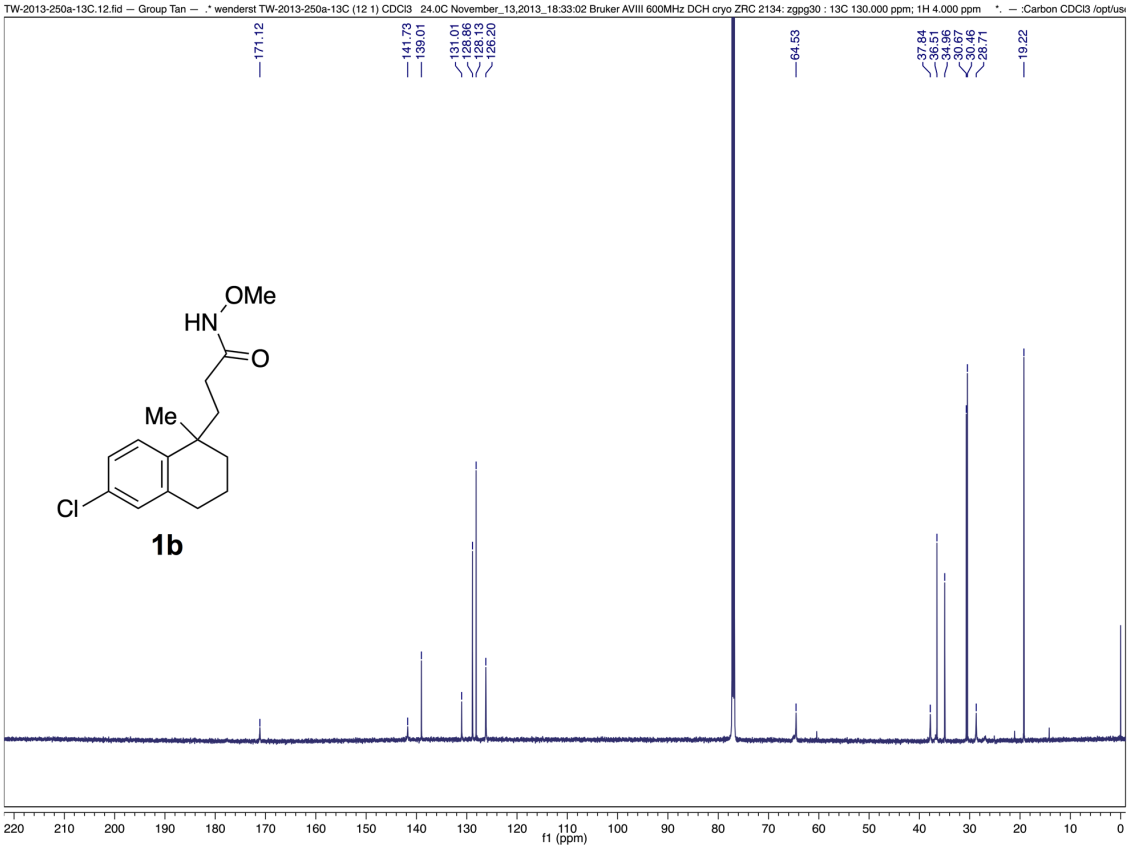

HO
O
Me
F
9d
f1 (ppm)

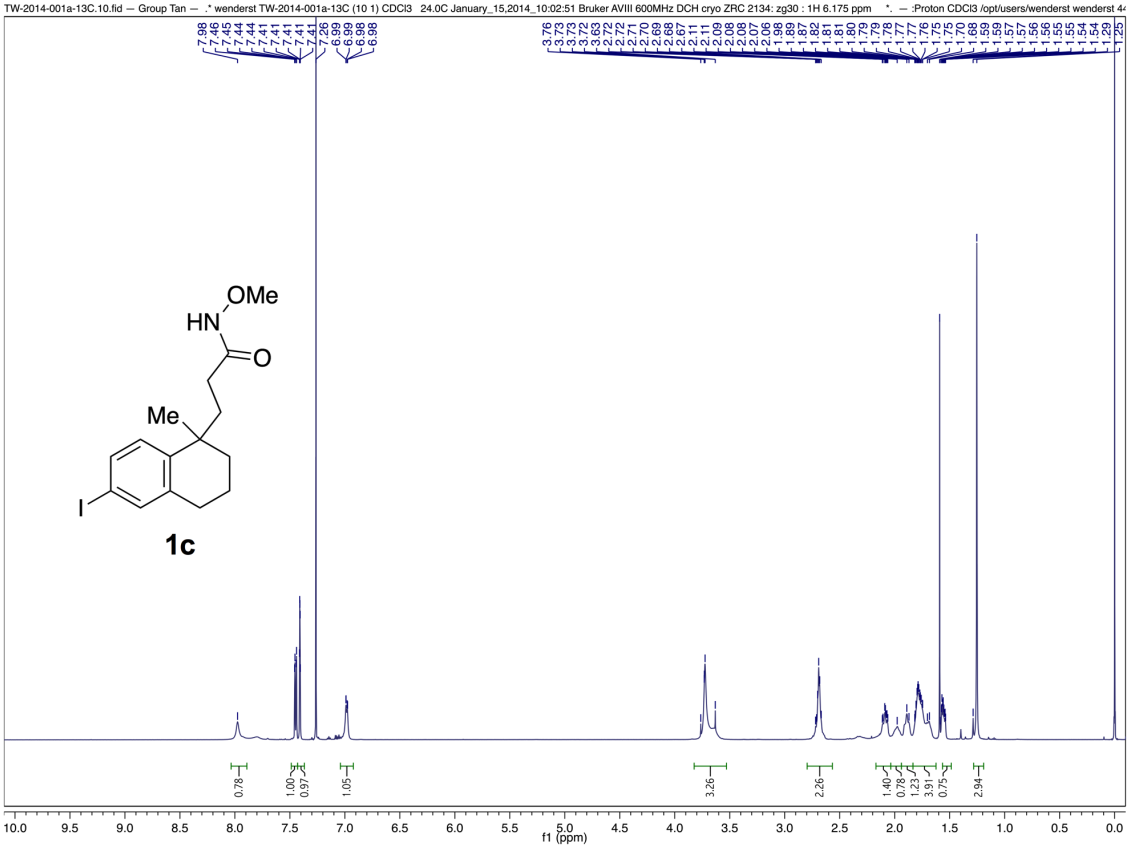

HO
O
Me
F
9d
f1 (ppm)

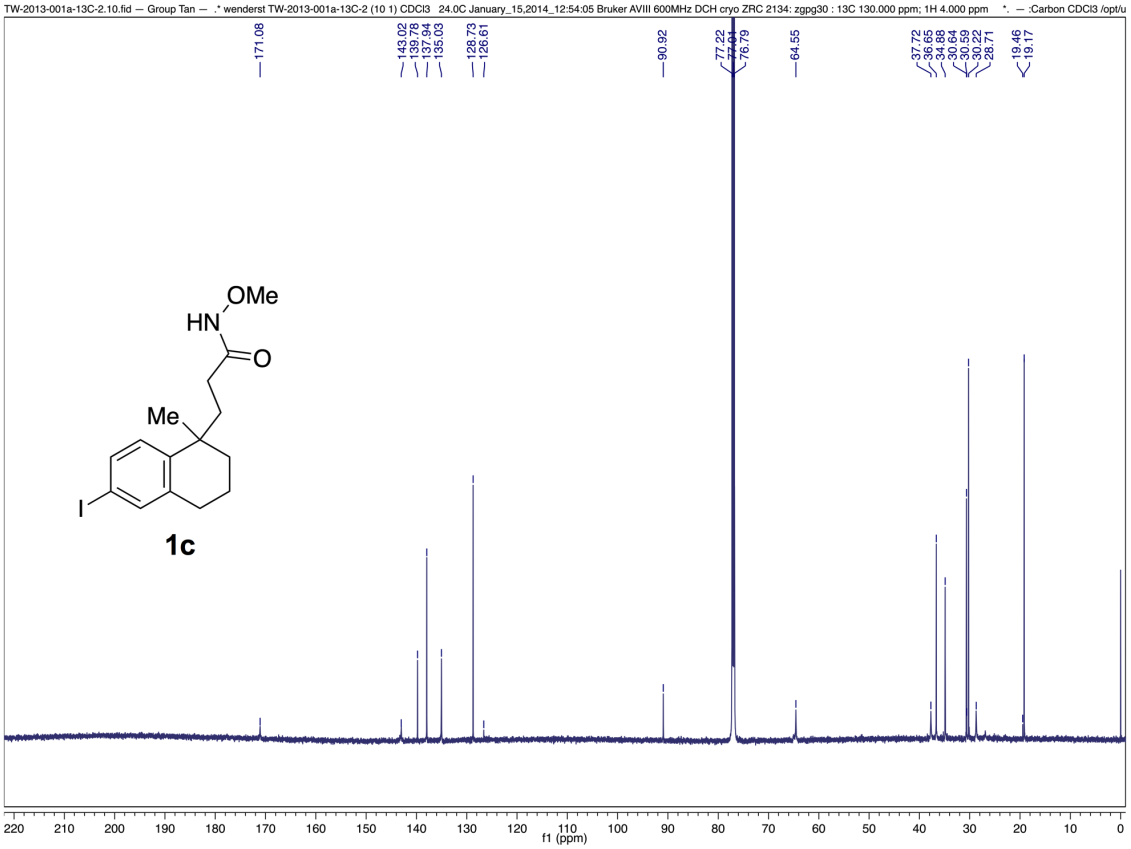

TW-2013-251a-13C.10.fid — Group Tan — .* wenderst TW-2013-251a-13C (10 1) CDCl3 24.0C November_13,2013_22:24:16 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst
OMe
HN
O
Me
Br
1a
f1 (ppm)

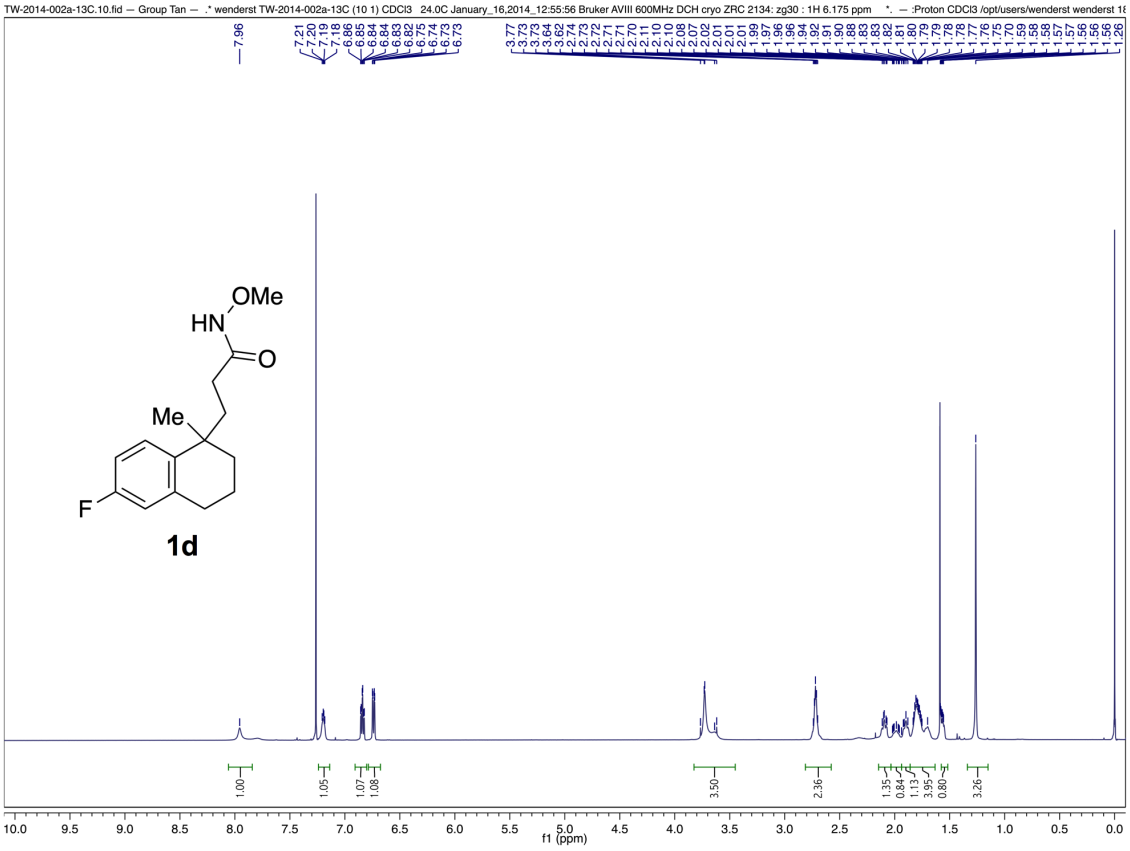

TW-2013-251a-13C.12.fid — Group Tan — .* wenderst TW-2013-251a-13C (12 1) CDCl3 24.0C November_13,2013_22:34:41 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/us
OMe
HN
O
Me
Br
1a
f1 (ppm)

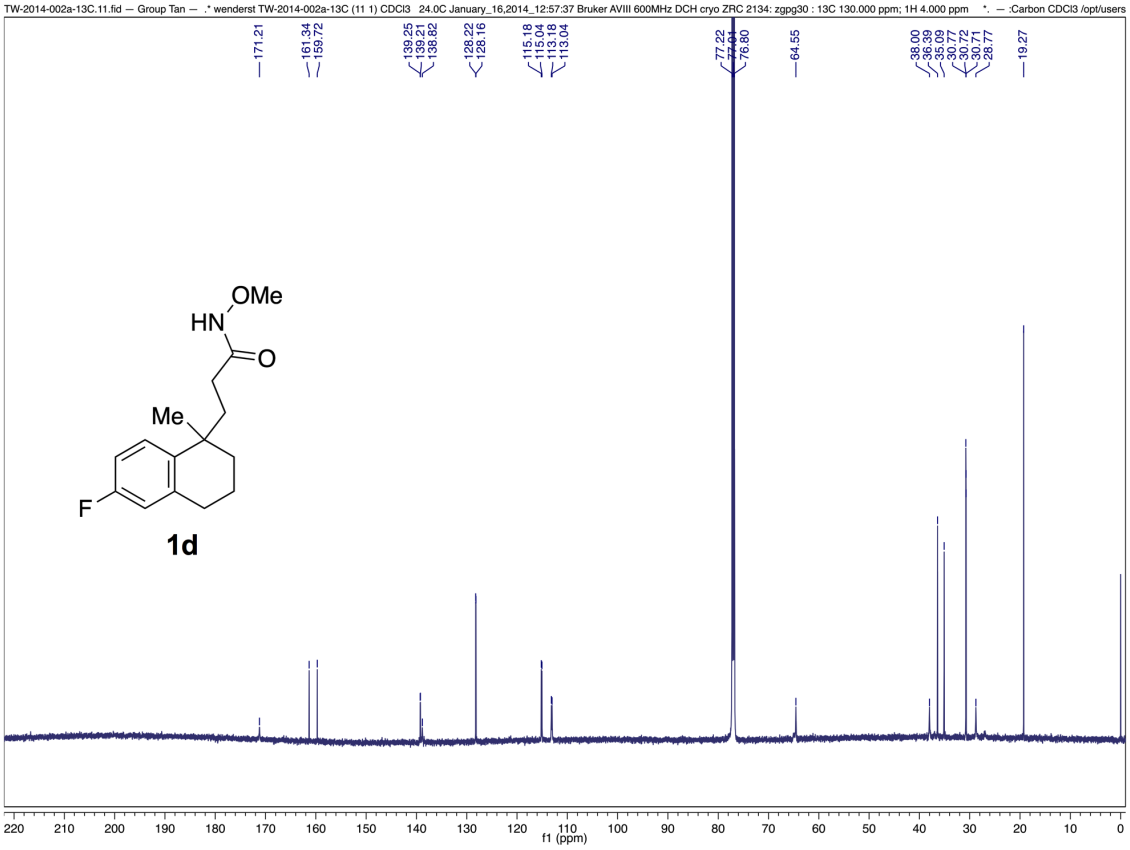

TW-2013-250a-13C.10.fid — Group Tan — .* wenderst TW-2013-250a-13C (10 1) CDCl3 24.0C November_13,2013_18:26:11 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst
OMe
HN
O
Me
Cl
1b
f1 (ppm)

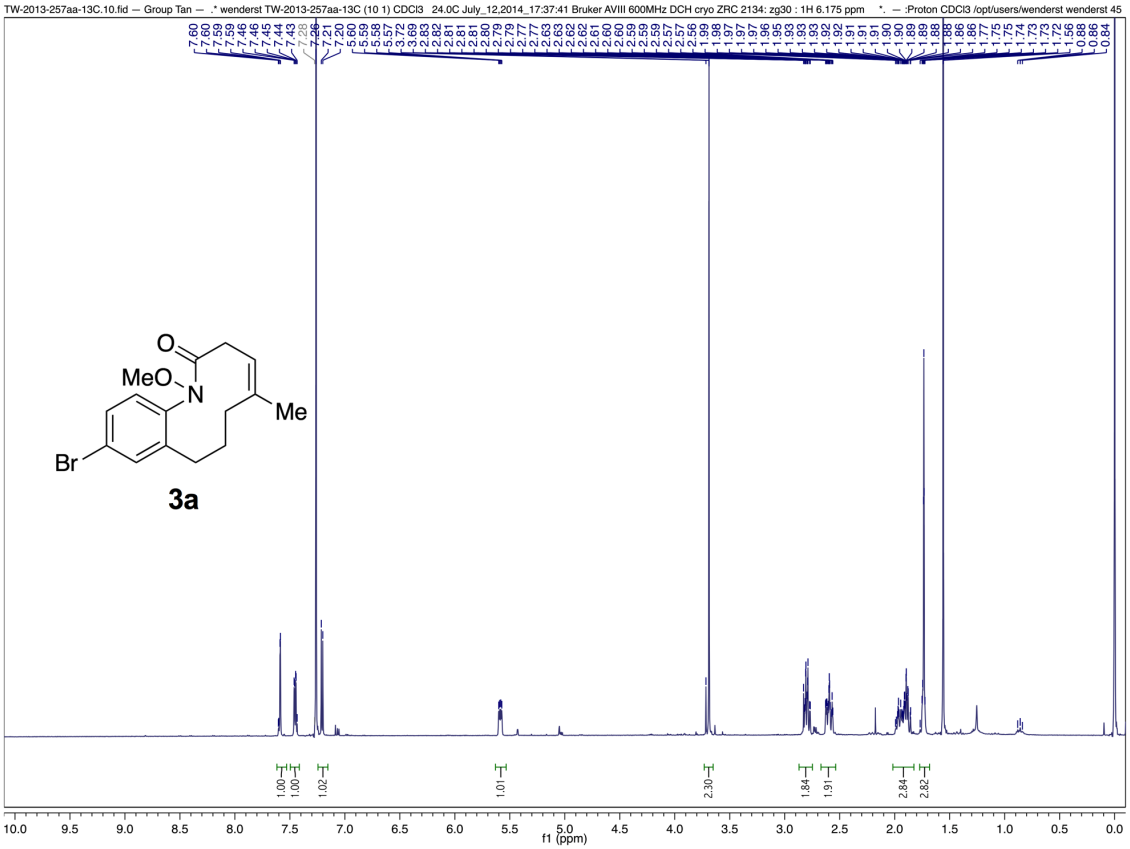

TW-2013-250a-13C.12.fid — Group Tan — .* wenderst TW-2013-250a-13C (12 1) CDCl3 24.0C November_13,2013_18:33:02 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/us
171.12
141.73
139.01
131.01
128.86
128.13
126.20
64.53
37.84
36.51
34.96
30.67
30.46
28.71
19.22
OMe
HN
O
Me
Cl
1b
f1 (ppm)

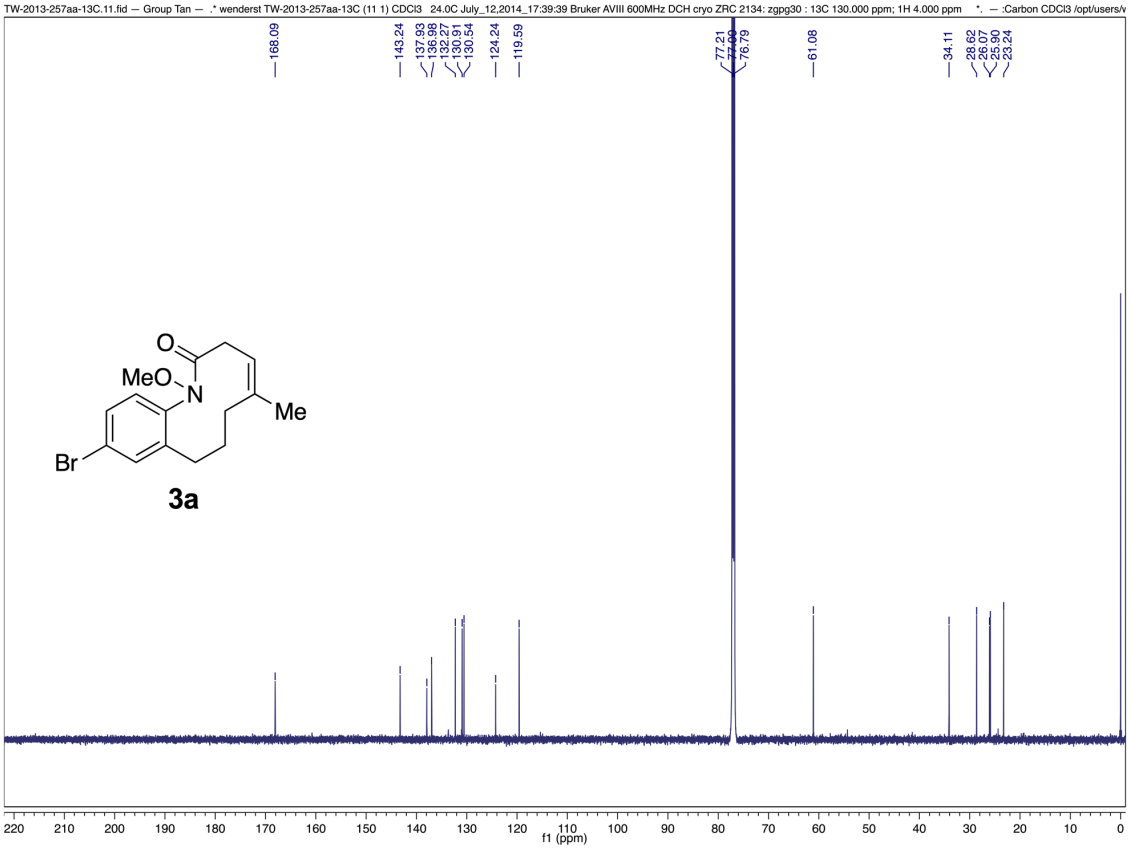

TW-2014-001a-13C.10.fid — Group Tan — .* wenderst TW-2014-001a-13C (10 1) CDCl3 24.0C January_15,2014_10:02:51 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
OMe
HN
O
Me
I
1c
f1 (ppm)

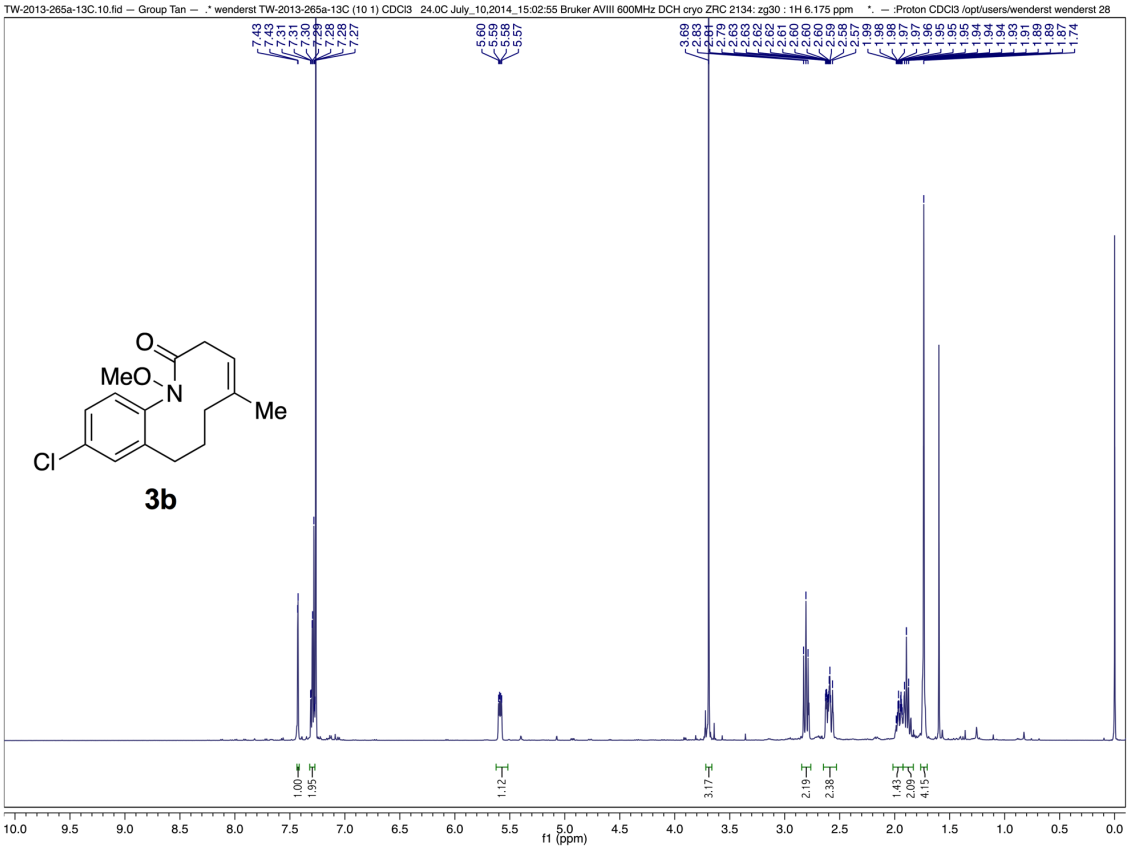

TW-2013-001a-13C-2.10.fid — Group Tan — .* wenderst TW-2013-001a-13C-2 (10 1) CDCl3 24.0C January_15,2014_12:54:05 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm
OMe
HN
O
Me
I
1c
f1 (ppm)

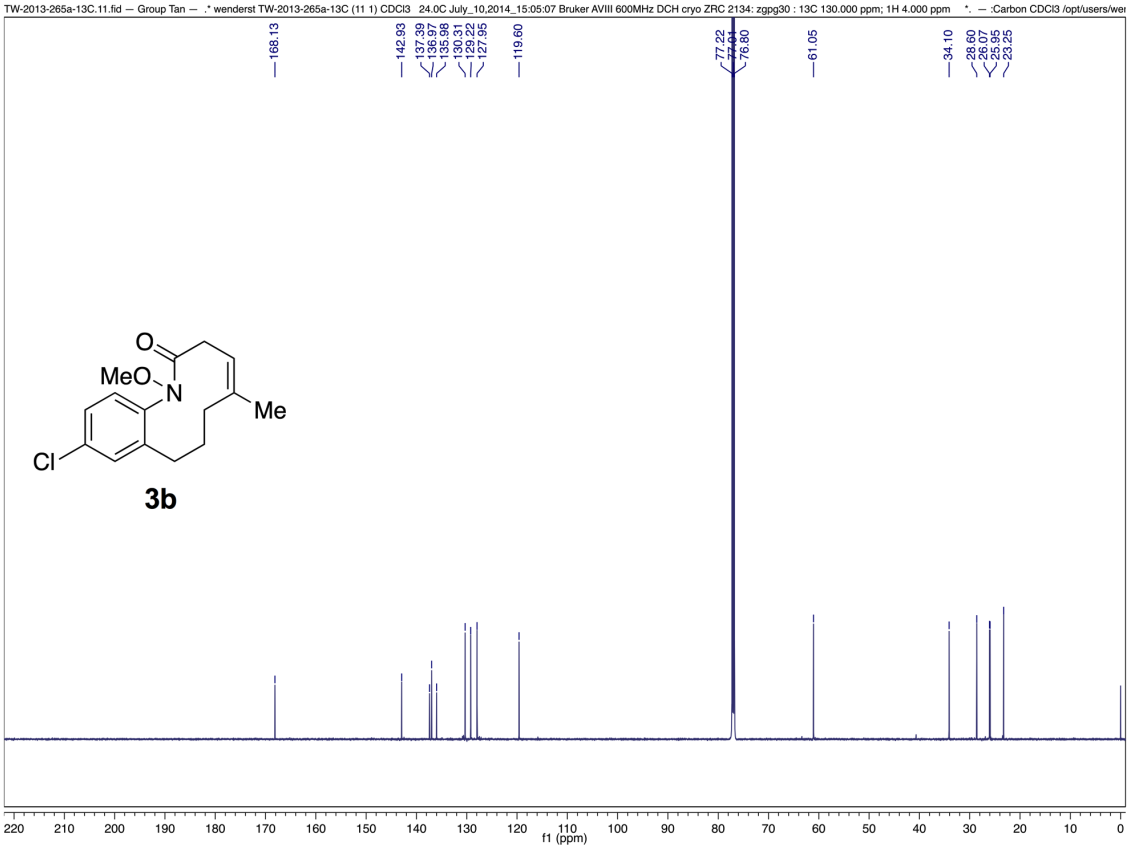

TW-2014-002a-13C.10.fid — Group Tan — .* wenderst TW-2014-002a-13C (10 1) CDCl3 24.0C January_16,2014_12:55:56 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 18
OMe
HN
O
Me
F
1d
f1 (ppm)

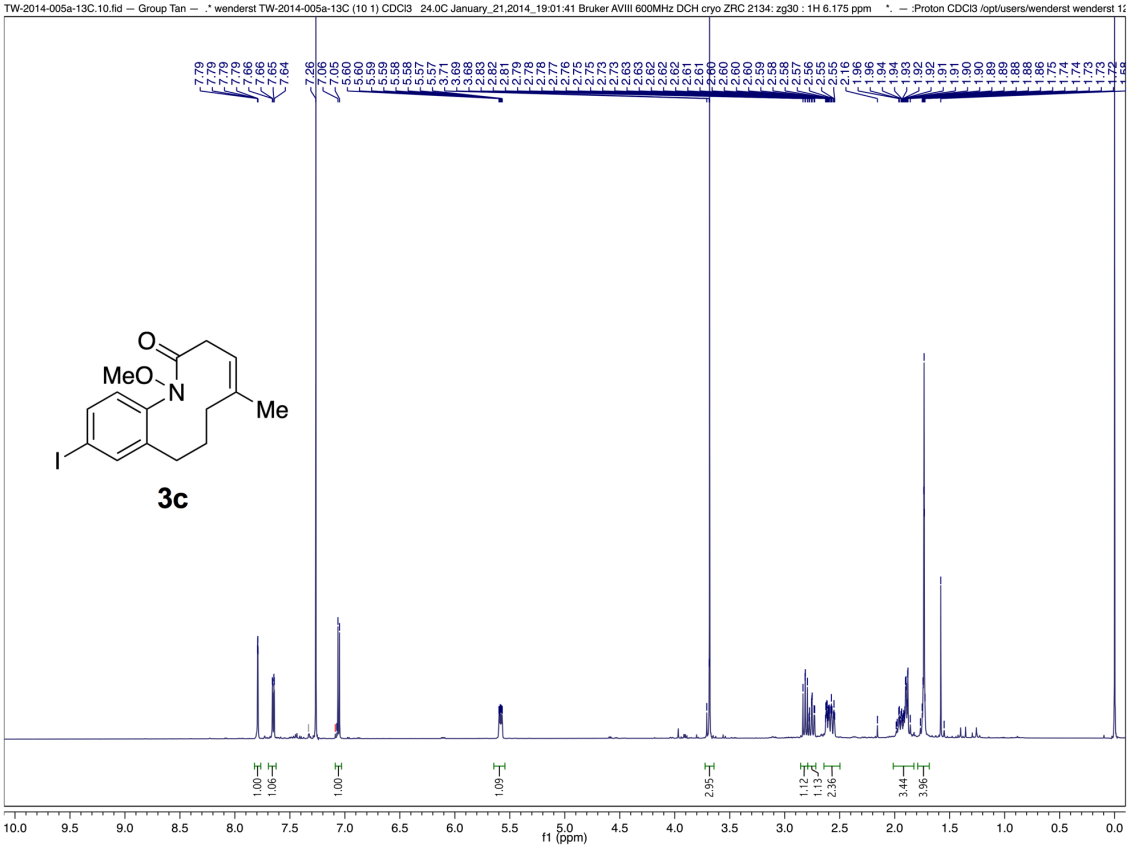

TW-2014-002a-13C.11.fid — Group Tan — .* wenderst TW-2014-002a-13C (11 1) CDCl3 24.0C January_16,2014_12:57:37 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users
OMe
HN
O
Me
F
1d
f1 (ppm)

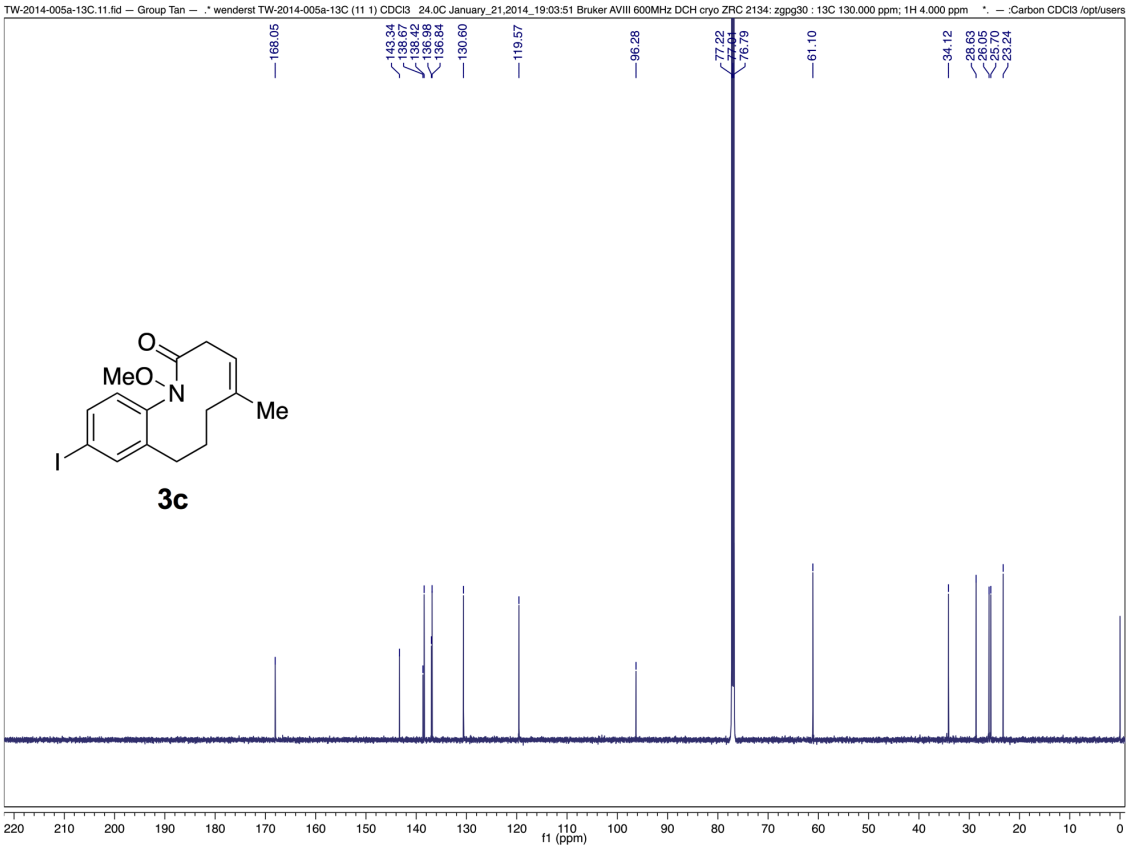

TW-2013-257aa-13C.10.fid — Group Tan — .* wenderst TW-2013-257aa-13C (10 1) CDCl3 24.0C July_12,2014_17:37:41 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 45
O
MeO
N
Me
Br
3a
1.00
1.00
1.02
1.01
2.30
1.84
1.91
2.84
2.82
f1 (ppm)

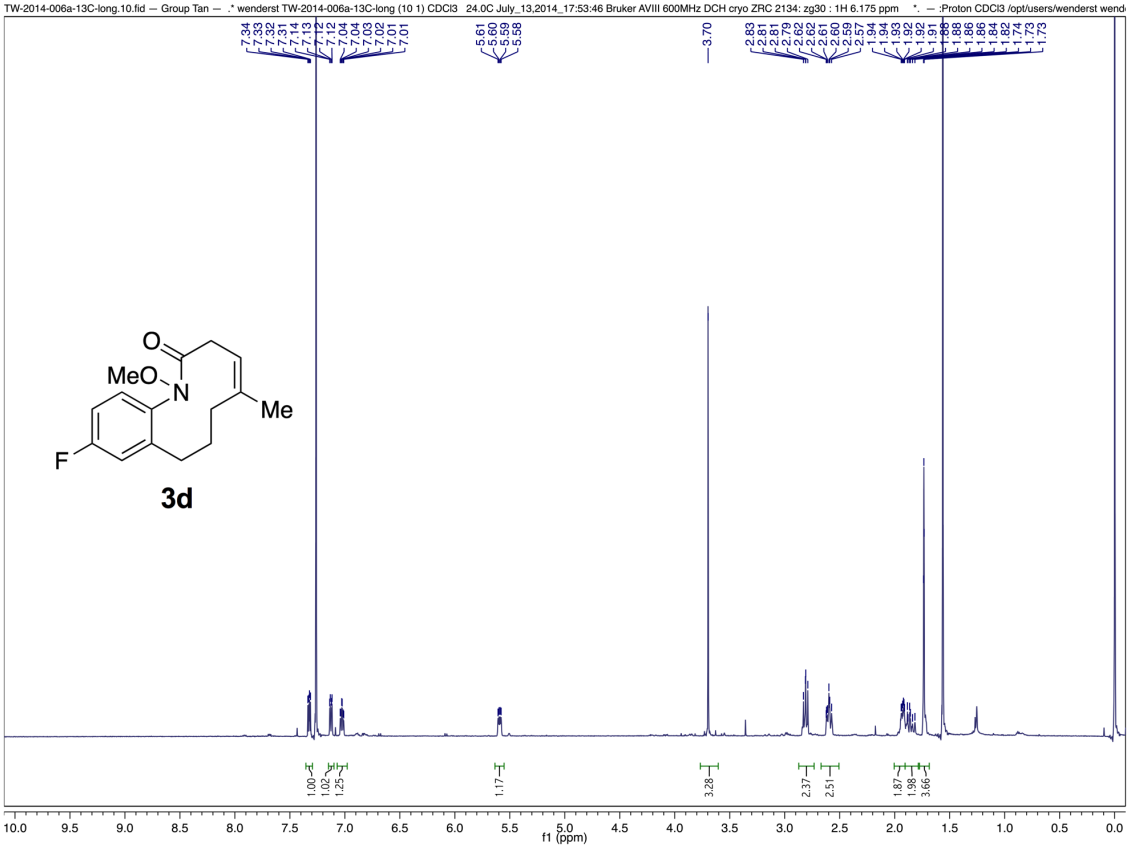

TW-2013-257aa-13C.11.fid — Group Tan — .* wenderst TW-2013-257aa-13C (11 1) CDCl3 24.0C July_12,2014_17:39:39 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/v
168.09
143.24
137.93
136.98
132.27
130.91
130.54
124.24
119.59
77.21
77.00
76.79
61.08
34.11
28.62
26.07
23.90
23.24
O
MeO
N
Me
Br
3a
f1 (ppm)

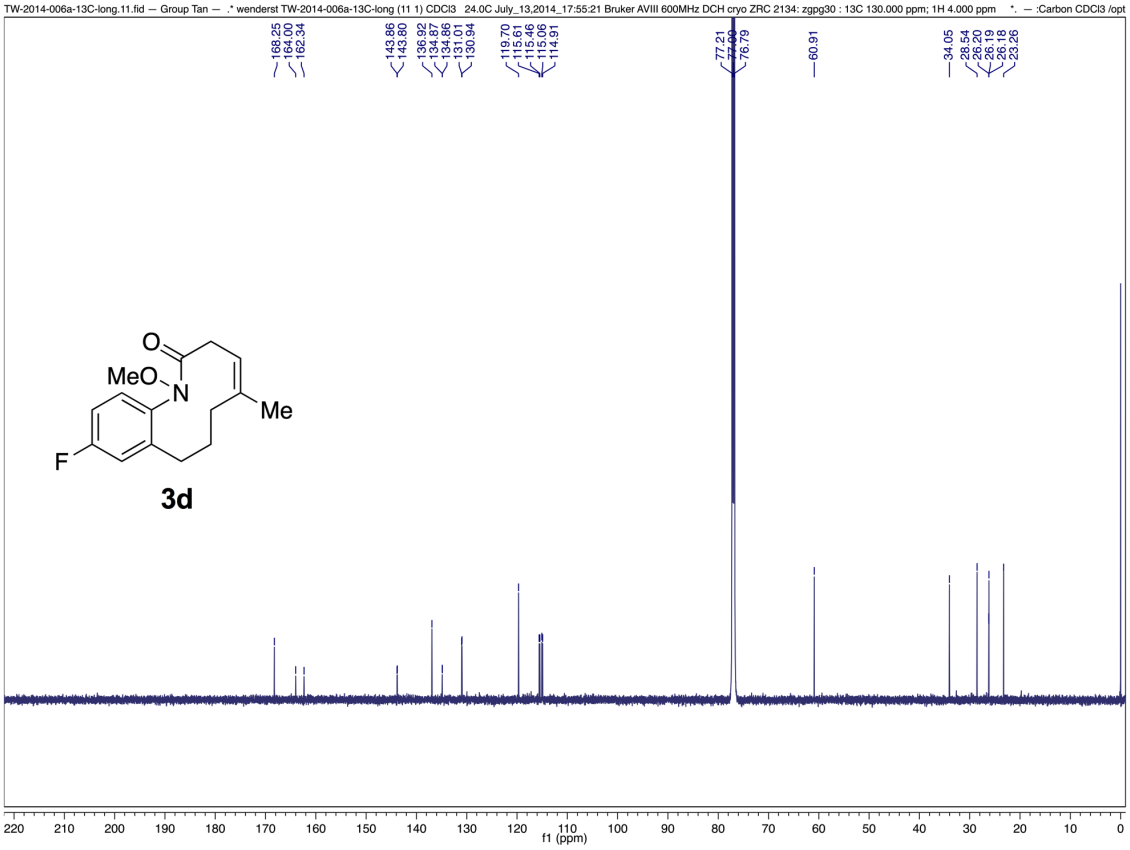

TW-2013-265a-13C.10.fid — Group Tan — .* wenderst TW-2013-265a-13C (10 1) CDCl3 24.0C July_10,2014_15:02:55 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 28
7.43 7.43 7.31 7.31 7.30 7.29 7.28 7.28 7.27
5.60 5.59 5.58 5.57
3.69 2.83 2.81 2.79 2.63 2.63 2.62 2.62 2.61 2.60 2.60 2.60 2.59 2.58 2.57 1.97 1.98 1.98 1.97 1.97 1.96 1.95 1.95 1.94 1.94 1.94 1.93 1.91 1.89 1.89 1.87 1.74
O
MeO
N
Me
Cl
3b
1.00 1.95 1.12 3.17 2.19 2.38 1.43 2.09 4.15
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)

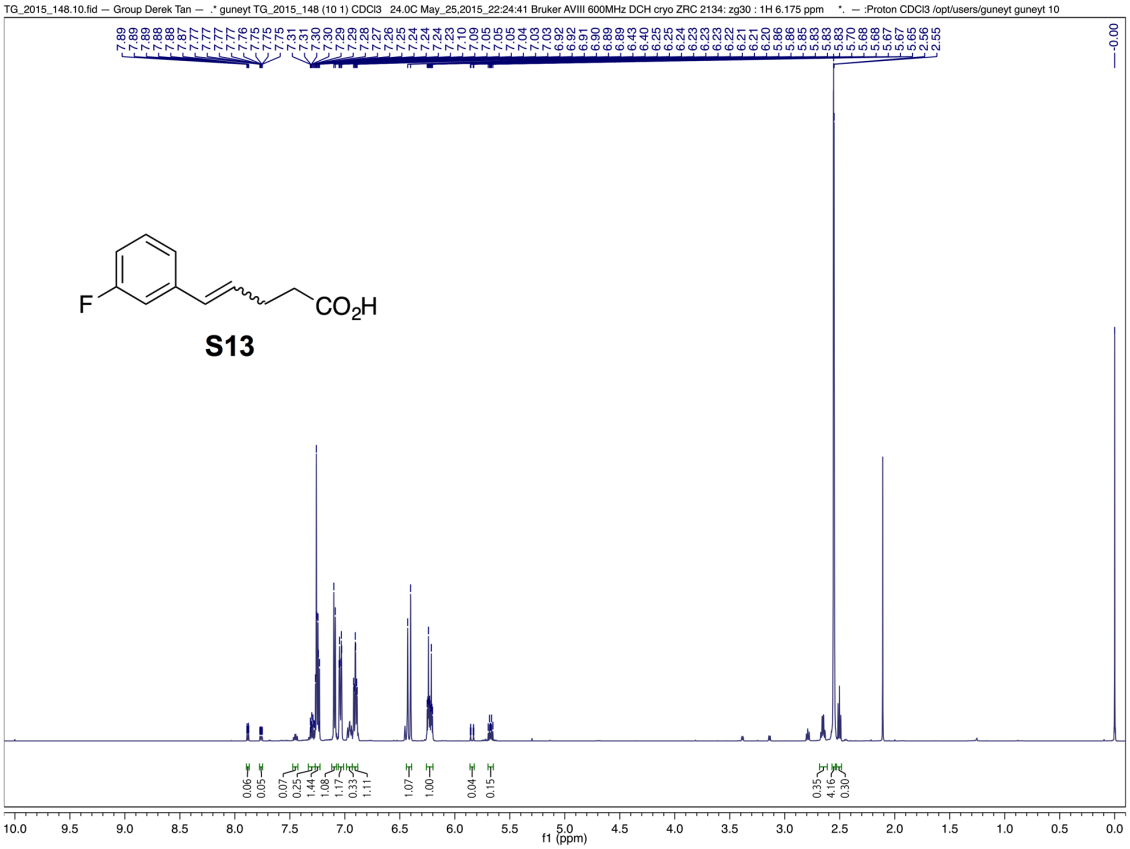

TW-2013-265a-13C.11.fid — Group Tan — .* wenderst TW-2013-265a-13C (11 1) CDCl3 24.0C July_10,2014_15:05:07 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/we
168.13
142.93 137.39 136.97 135.98 130.31 129.22 127.95
119.60
77.22 77.01 76.80
61.05
34.10 28.60 26.07 23.95 23.25
O
MeO
N
Me
Cl
3b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

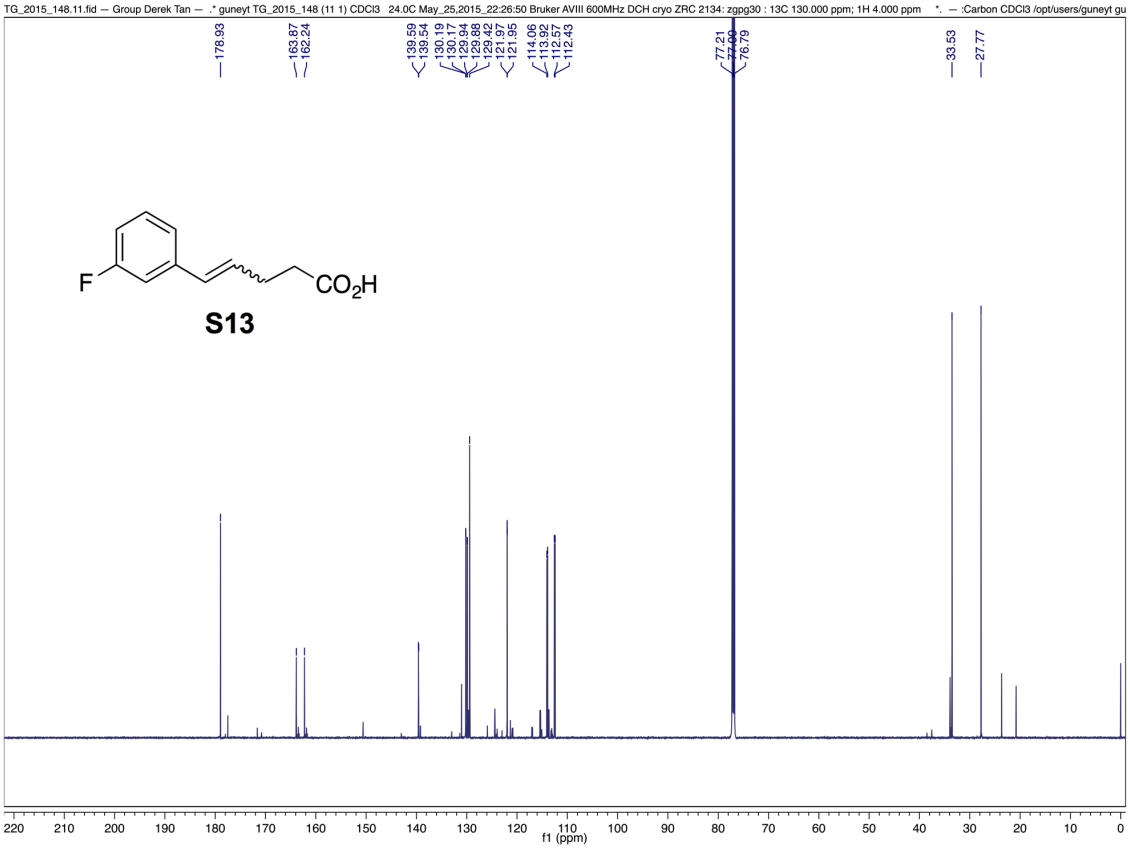

TW-2014-005a-13C.10.fid — Group Tan — .* wenderst TW-2014-005a-13C (10 1) CDCl3 24.0C January_21,2014_19:01:41 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 12
O
MeO
N
Me
I
3c
1.00
1.06
1.00
1.09
2.95
1.12
1.13
2.36
3.44
3.96
f1 (ppm)

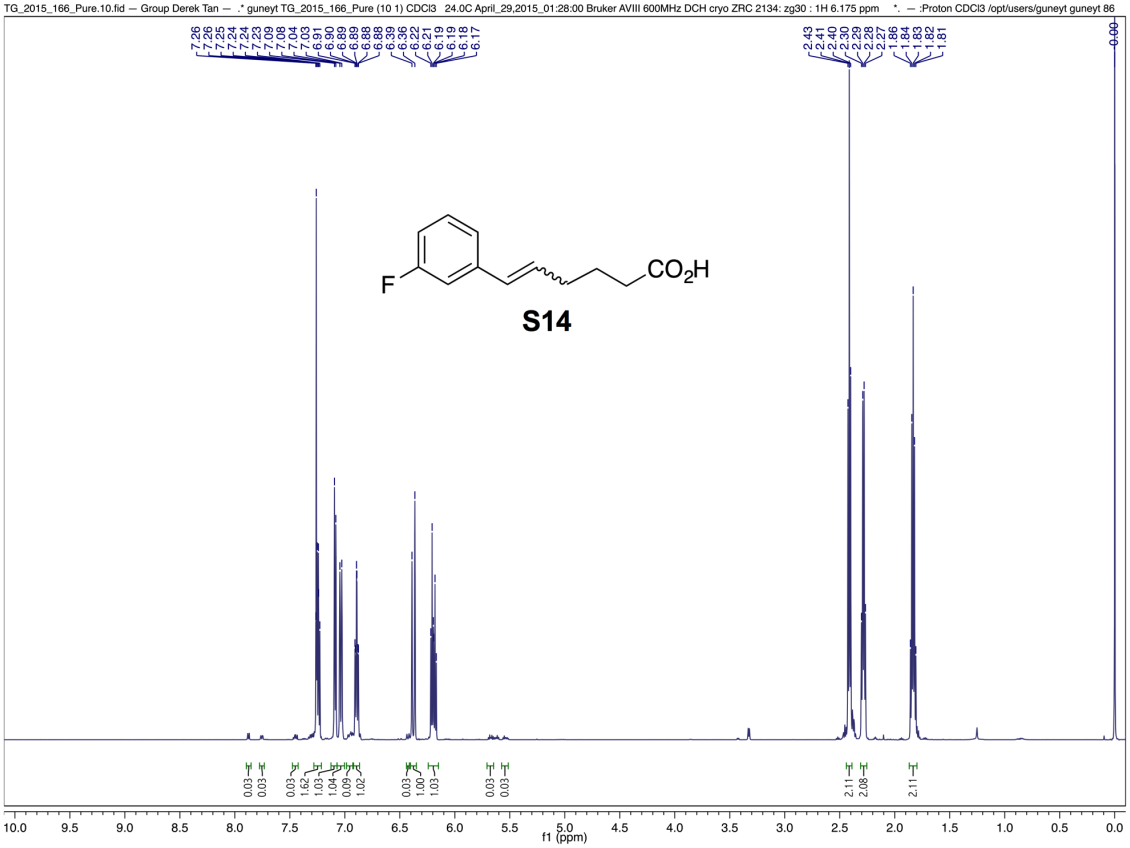

TW-2014-005a-13C.11.fid — Group Tan — .* wenderst TW-2014-005a-13C (11 1) CDCl3 24.0C January_21,2014_19:03:51 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users
168.05
143.34
138.67
138.42
136.98
136.84
130.60
119.57
96.28
77.22
77.01
76.79
61.10
34.12
28.63
26.05
25.70
23.24
O
MeO
N
Me
I
3c
f1 (ppm)

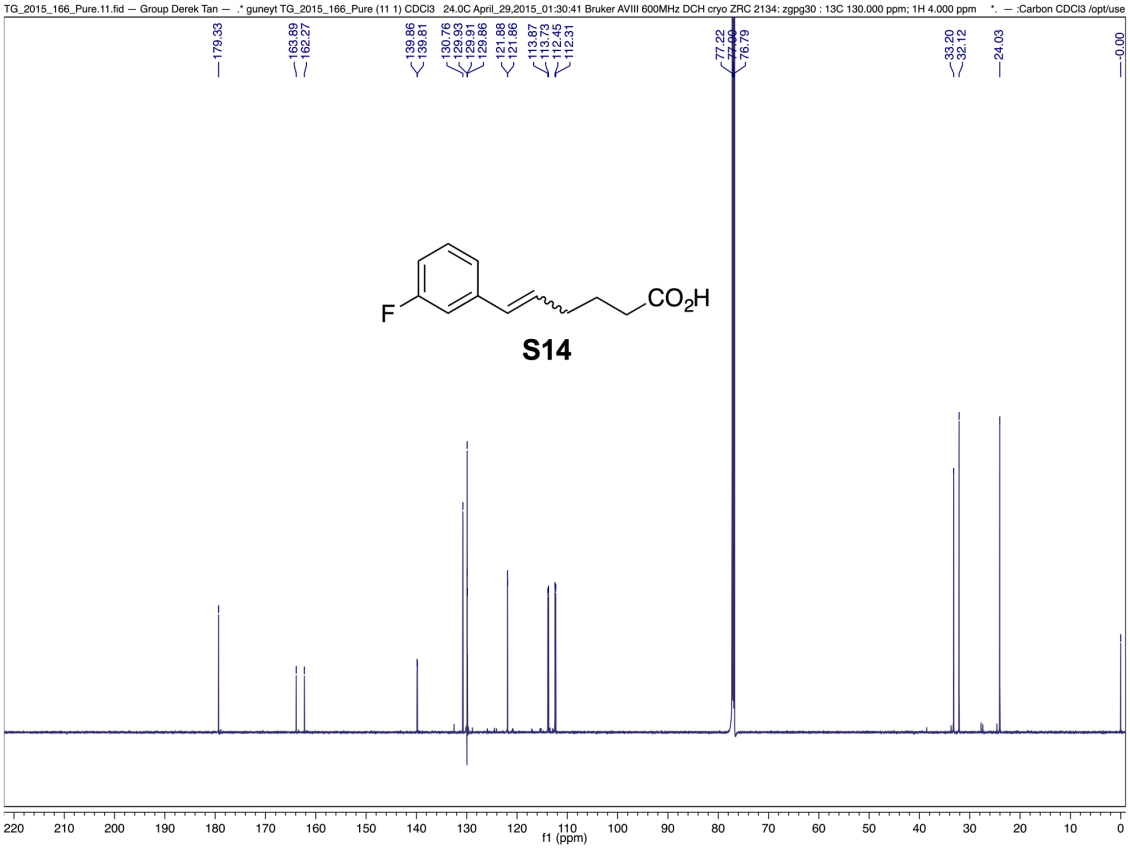

TW-2014-006a-13C-long.10.fid — Group Tan — .* wenderst TW-2014-006a-13C-long (10 1) CDCl3 24.0C July_13,2014_17:53:46 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wend
7.34
7.33
7.32
7.31
7.14
7.13
7.12
7.12
7.04
7.04
7.03
7.02
7.01
7.01
5.61
5.60
5.59
5.58
3.70
2.83
2.81
2.81
2.79
2.62
2.61
2.60
2.59
2.57
1.94
1.94
1.93
1.92
1.91
1.88
1.88
1.86
1.86
1.84
1.82
1.74
1.73
1.73
O
MeO
N
Me
F
3d
1.00
1.02
1.25
1.17
3.28
2.37
2.51
1.87
1.98
3.66
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)

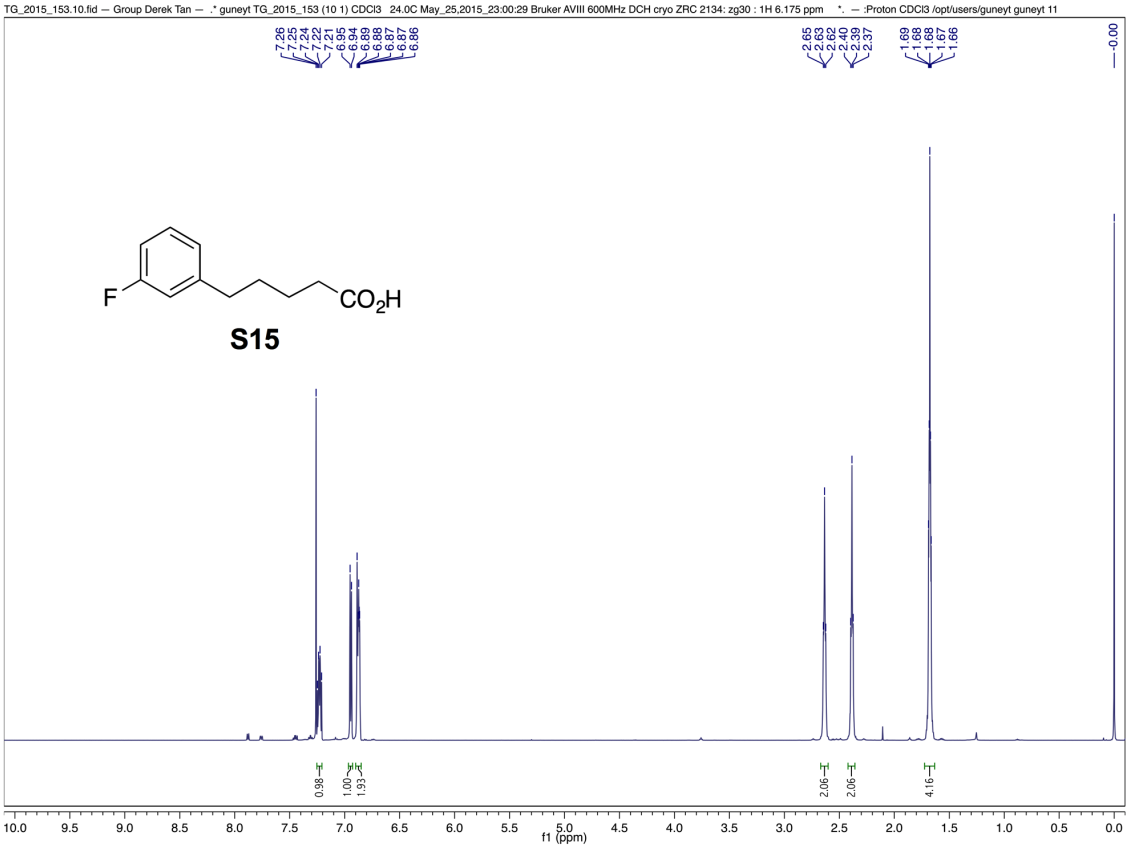

TW-2014-006a-13C-long.11.fid — Group Tan — .* wenderst TW-2014-006a-13C-long (11 1) CDCl3 24.0C July_13,2014_17:55:21 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt
168.25
164.00
162.34
143.86
143.80
136.92
134.87
134.86
131.01
130.94
119.70
115.61
115.46
115.06
114.91
77.21
77.00
76.79
60.91
34.05
28.54
26.20
26.19
26.18
23.26
O
MeO
N
Me
F
3d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

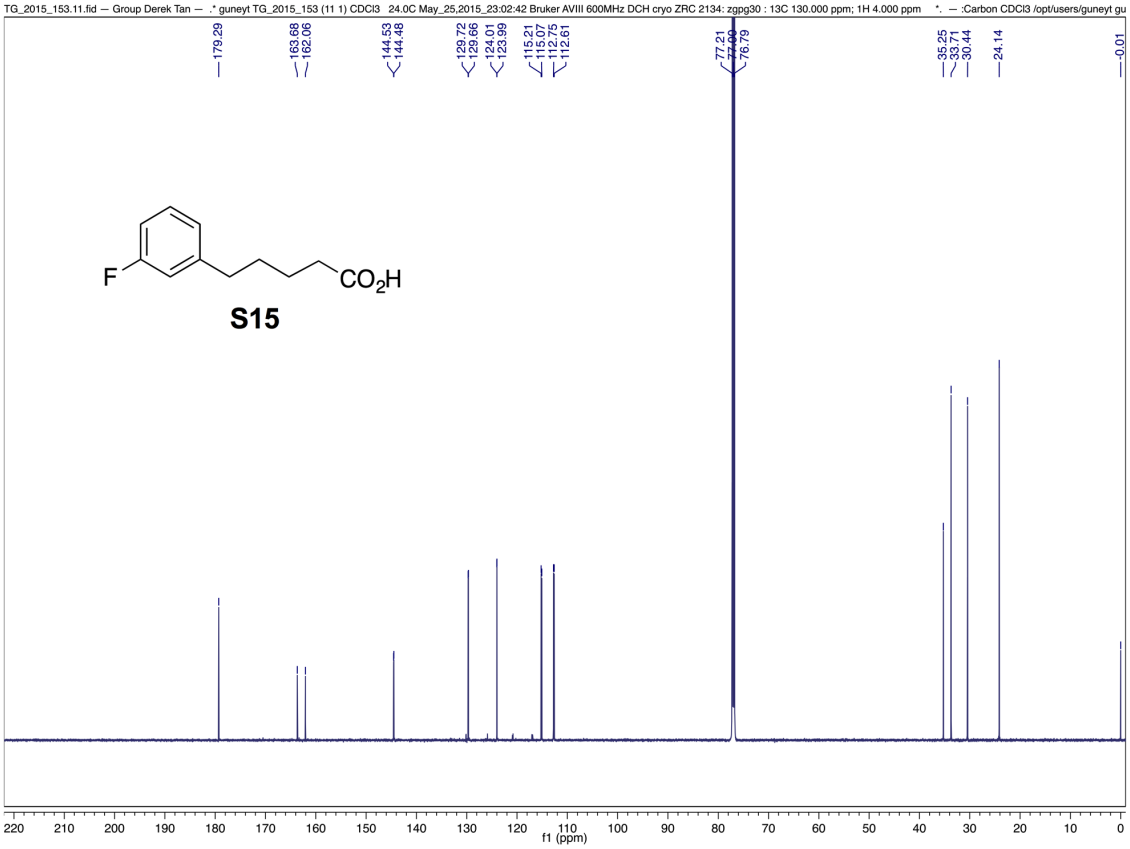

TG_2015_148.10.fid — Group Derek Tan — .* guneyt TG_2015_148 (10 1) CDCl3 24.0C May_25,2015_22:24:41 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 10
F
CO2H
S13
f1 (ppm)

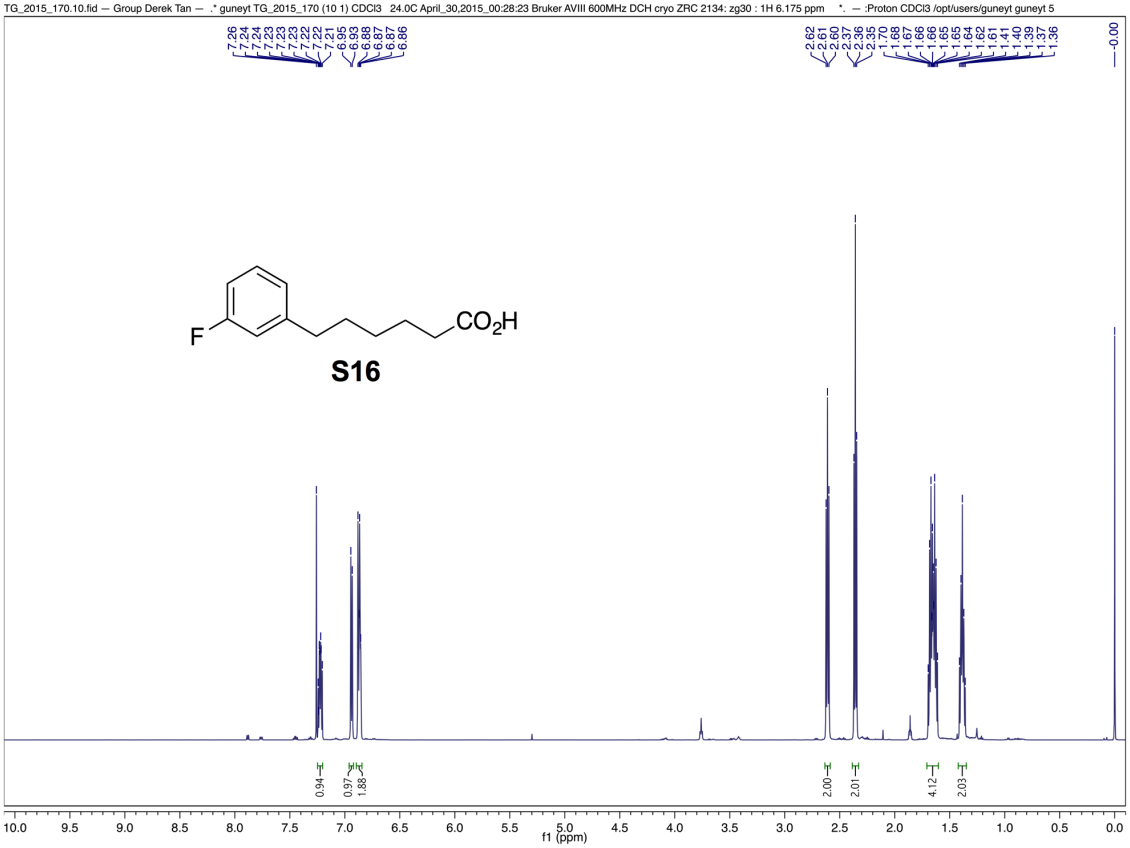

TG_2015_148.11.fid — Group Derek Tan — .* guneyt TG_2015_148 (11 1) CDCl3 24.0C May_25,2015_22:26:50 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/guneyt gu
F
CO2H
S13
f1 (ppm)

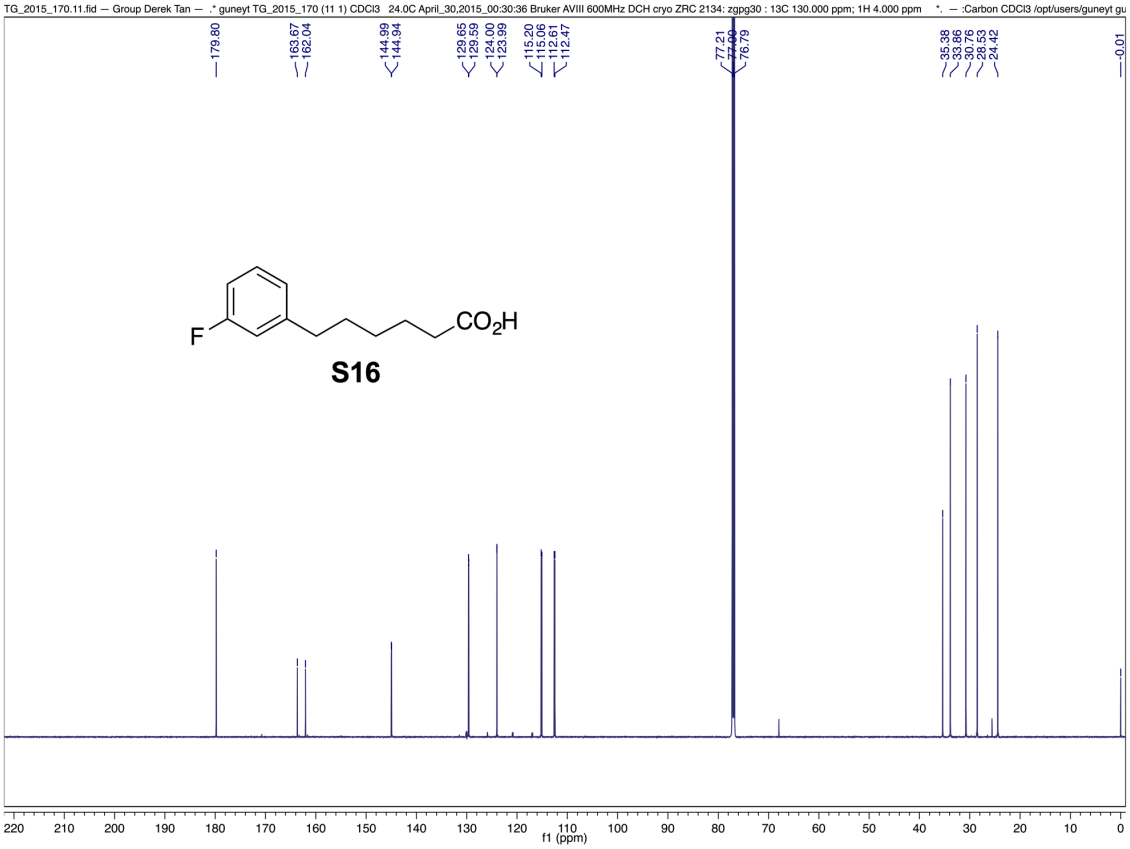

TG_2015_166_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_166_Pure (10 1) CDCl3 24.0C April_29,2015_01:28:00 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 86
7.26
7.26
7.25
7.24
7.24
7.23
7.09
7.08
7.04
7.03
6.91
6.90
6.89
6.89
6.88
6.88
6.39
6.36
6.22
6.21
6.19
6.19
6.18
6.17
2.43
2.41
2.40
2.30
2.29
2.29
2.27
1.86
1.84
1.83
1.82
1.81
0.00
F
CO2H
S14
0.03
0.03
0.03
1.62
1.03
1.04
0.09
1.02
0.03
1.00
1.03
0.03
0.03
2.11
2.08
2.11
f1 (ppm)

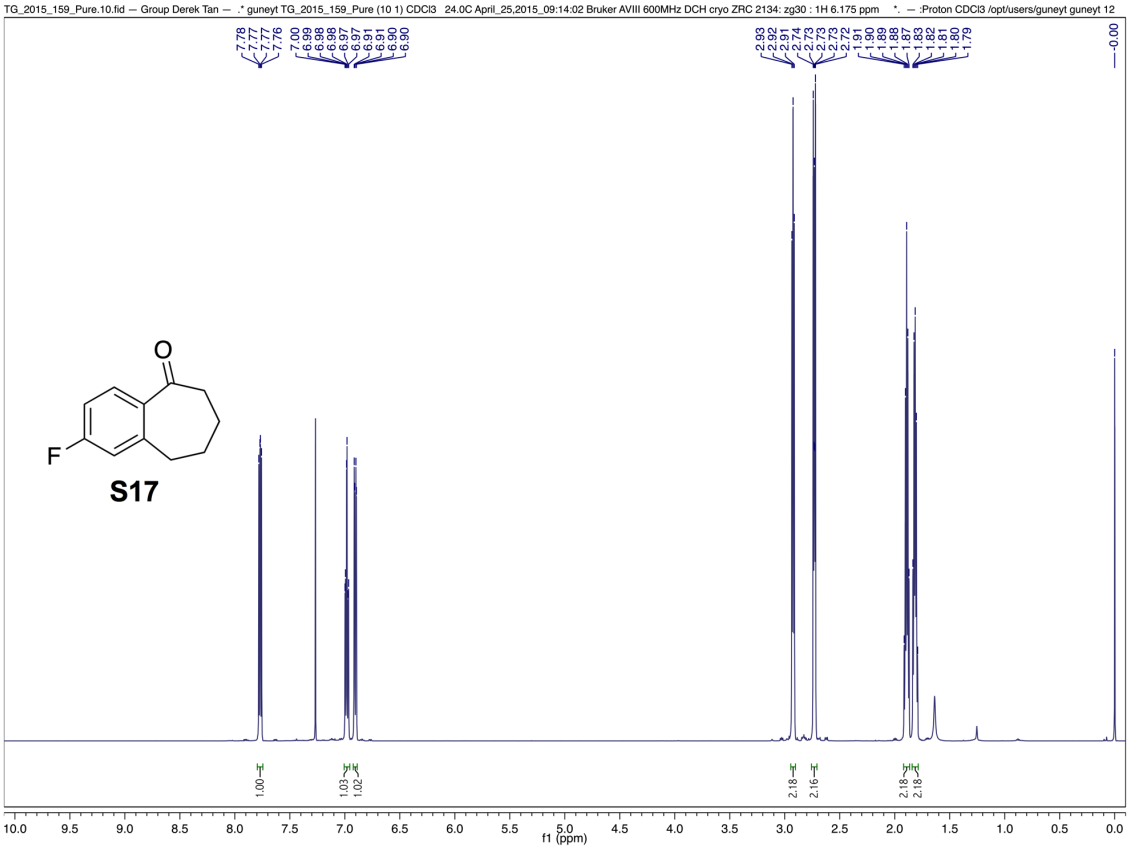

TG_2015_166_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_166_Pure (11 1) CDCl3 24.0C April_29,2015_01:30:41 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
179.33
163.89
162.27
139.86
139.81
130.76
129.93
129.91
129.86
121.88
121.86
113.97
113.73
112.45
112.31
77.22
77.00
76.79
33.20
32.12
24.03
0.00
F
CO2H
S14
f1 (ppm)

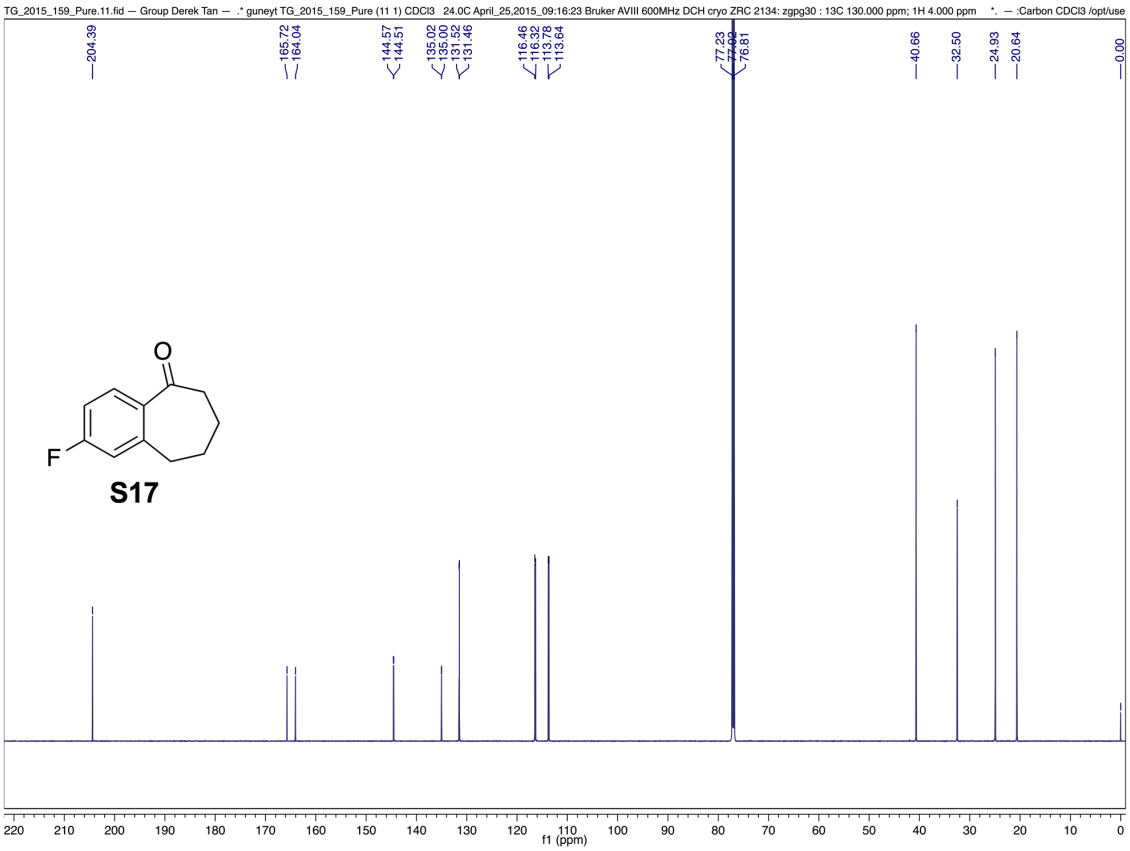

TG_2015_153.10.fid — Group Derek Tan — .* guneyt TG_2015_153 (10 1) CDCl3 24.0C May_25,2015_23:00:29 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 11
7.26
7.25
7.24
7.22
7.21
6.95
6.94
6.89
6.88
6.87
6.87
6.86
2.65
2.63
2.62
2.40
2.39
2.37
1.69
1.68
1.68
1.67
1.66
-0.00
F
CO2H
S15
0.98
1.00
1.93
2.06
2.06
4.16
f1 (ppm)

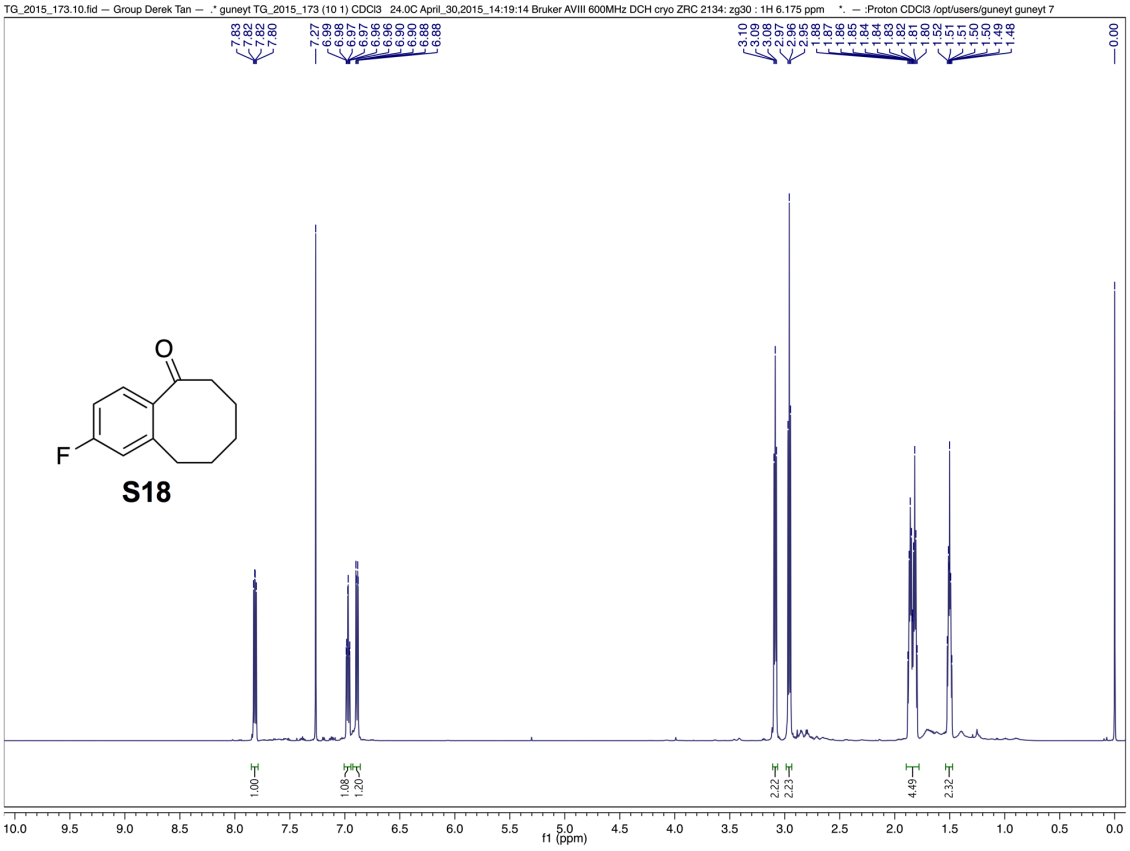

TG_2015_153.11.fid — Group Derek Tan — .* guneyt TG_2015_153 (11 1) CDCl3 24.0C May_25,2015_23:02:42 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/guneyt gu
179.29
163.68
162.06
144.53
144.48
129.72
129.66
124.01
123.99
115.21
115.07
112.75
112.61
77.21
77.00
76.79
35.25
33.71
30.44
24.14
-0.01
F
CO2H
S15
f1 (ppm)

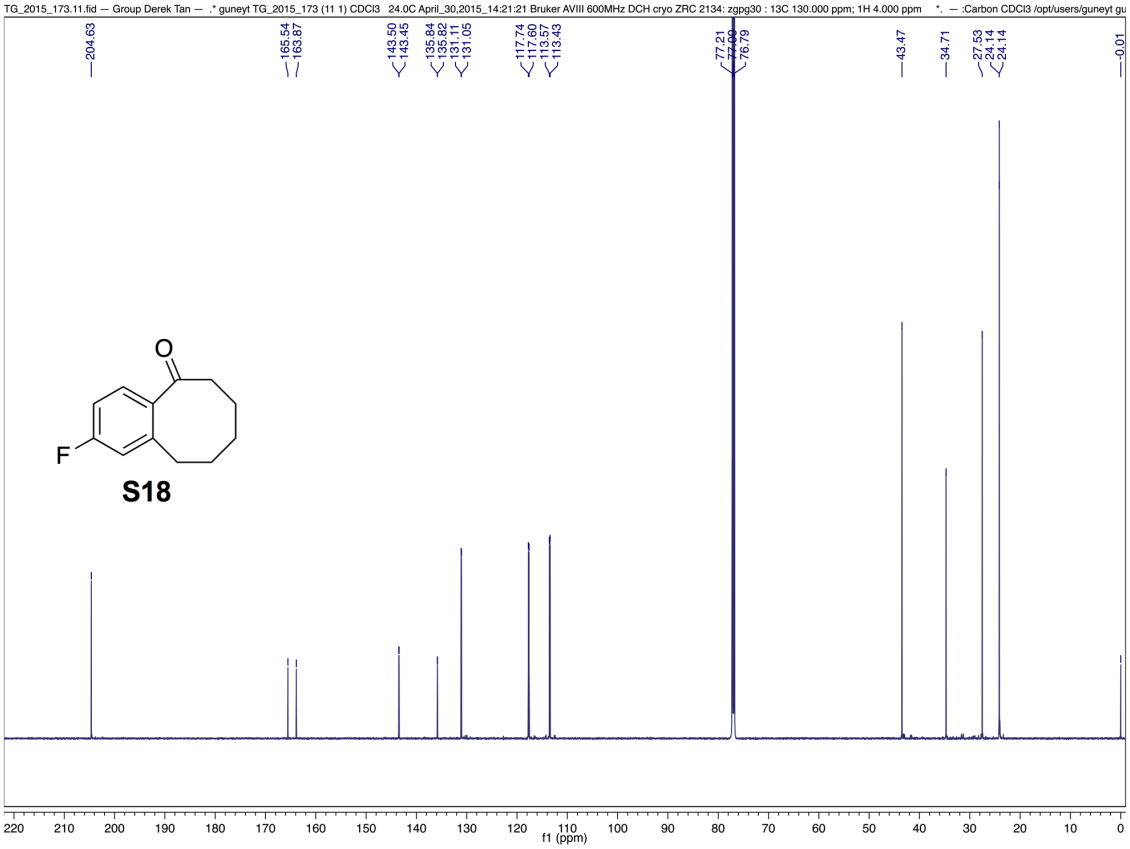

TG_2015_170.10.fid — Group Derek Tan — .* guneyt TG_2015_170 (10 1) CDCl3 24.0C April_30,2015_00:28:23 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 5
7.26
7.24
7.24
7.23
7.23
7.22
7.22
7.21
6.95
6.93
6.88
6.87
6.87
6.86
2.62
2.61
2.60
2.37
2.36
2.35
1.70
1.67
1.67
1.66
1.66
1.65
1.65
1.64
1.62
1.61
1.41
1.40
1.39
1.37
1.36
0.00
F
CO2H
S16
0.94
0.97
1.88
2.00
2.01
4.12
2.03
f1 (ppm)

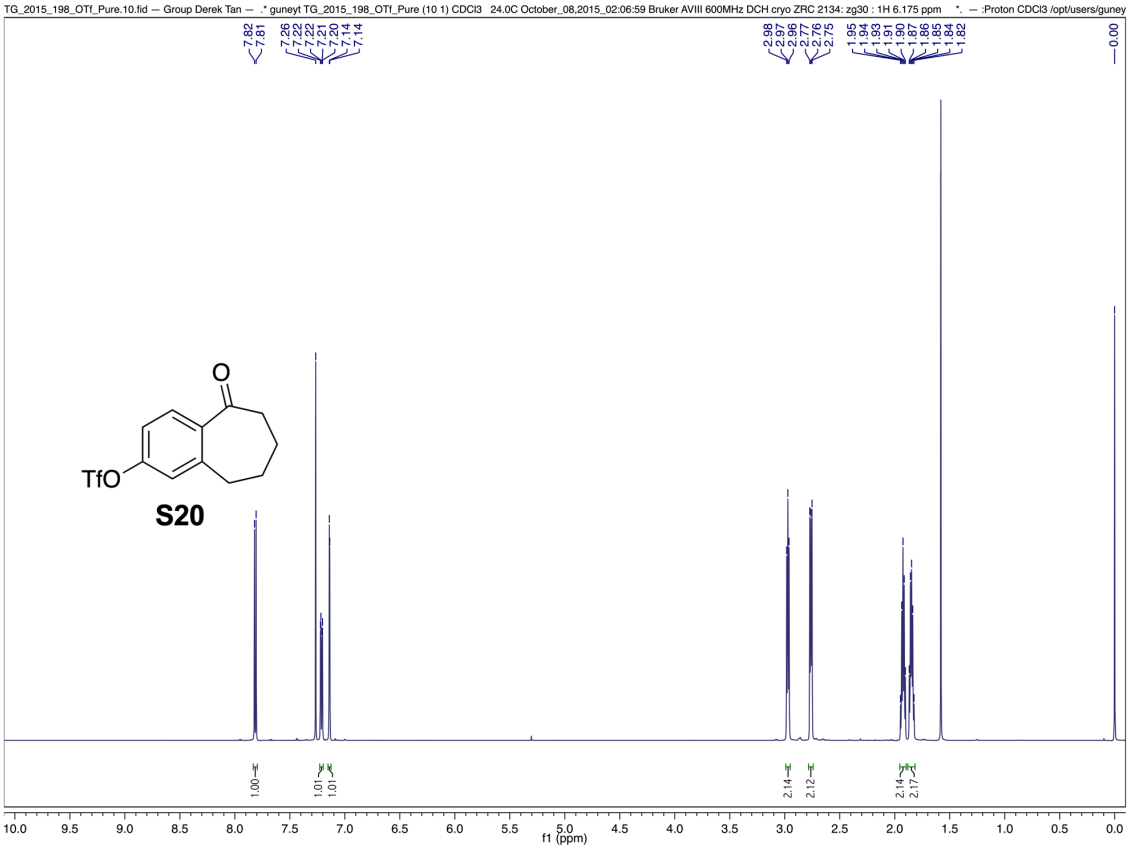

TG_2015_170.11.fid — Group Derek Tan — .* guneyt TG_2015_170 (11 1) CDCl3 24.0C April_30,2015_00:30:36 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/guneyt gu
179.80
163.67
162.04
144.99
144.94
129.65
129.59
124.00
123.99
115.20
115.06
112.61
112.47
77.21
77.00
76.79
35.38
33.86
30.76
28.53
24.42
0.01
F
CO2H
S16
f1 (ppm)

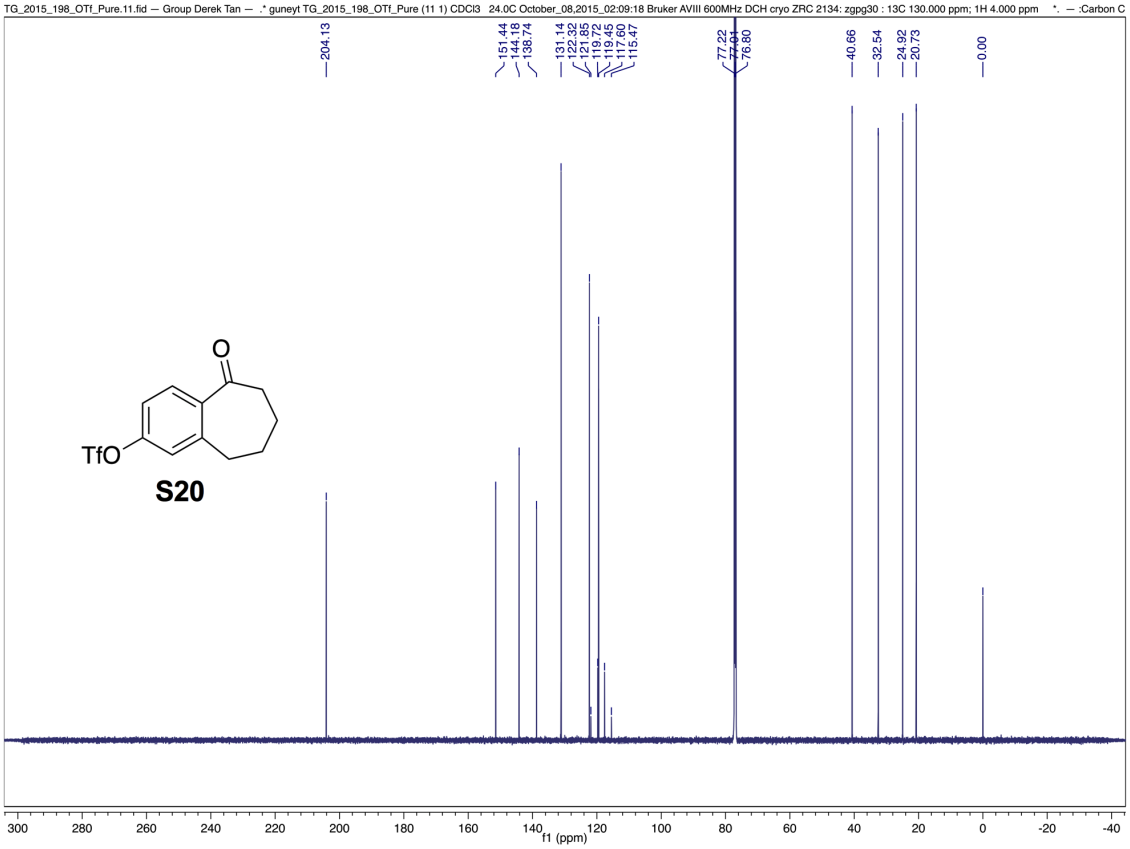

TG_2015_159_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_159_Pure (10 1) CDCl3 24.0C April_25,2015_09:14:02 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 12
7.78
7.77
7.77
7.76
7.00
6.99
6.98
6.98
6.97
6.97
6.91
6.91
6.90
6.90
2.93
2.92
2.91
2.74
2.73
2.73
2.73
2.72
1.91
1.90
1.89
1.88
1.87
1.83
1.82
1.81
1.80
1.79
0.00
O
F
S17
1.00
1.03
1.02
2.18
2.16
2.18
2.18
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)

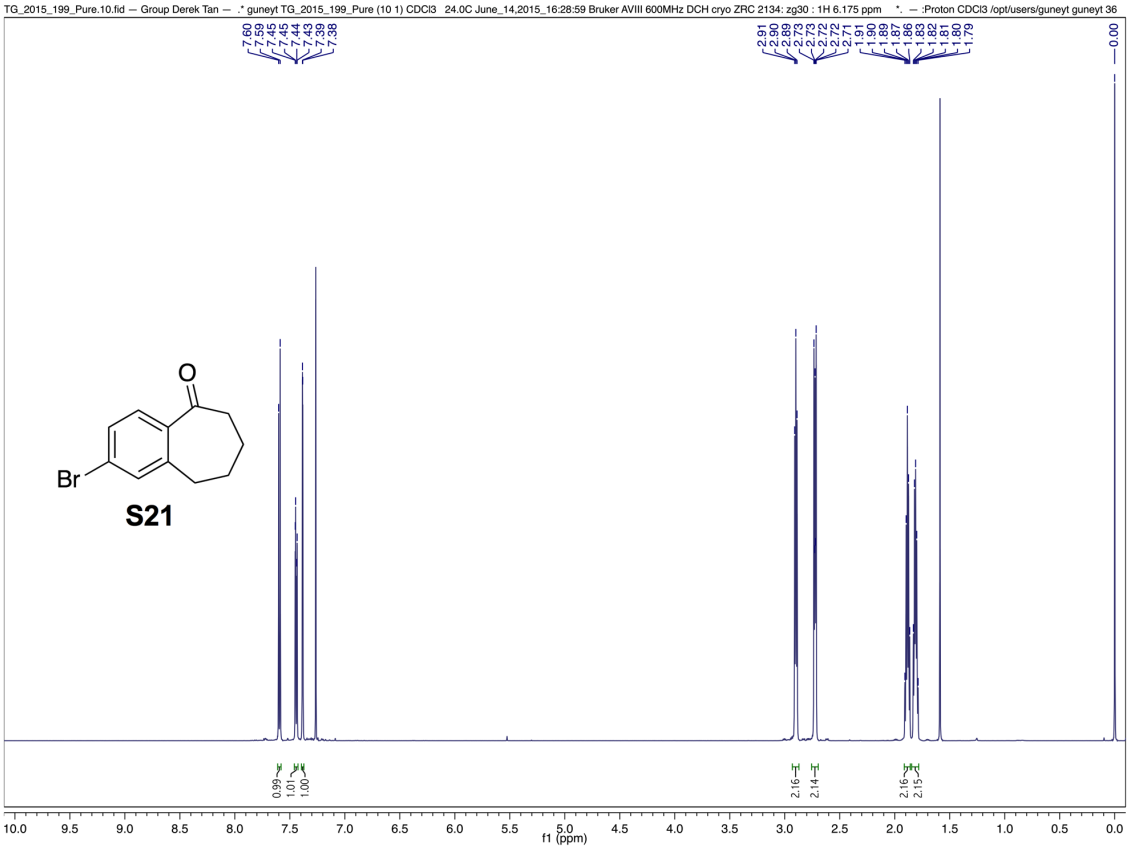

TG_2015_159_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_159_Pure (11 1) CDCl3 24.0C April_25,2015_09:16:23 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
204.39
165.72
164.04
144.57
144.51
135.02
135.00
131.52
131.46
116.46
116.32
113.78
113.64
77.23
77.02
76.81
40.66
32.50
24.93
20.64
0.00
O
F
S17
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

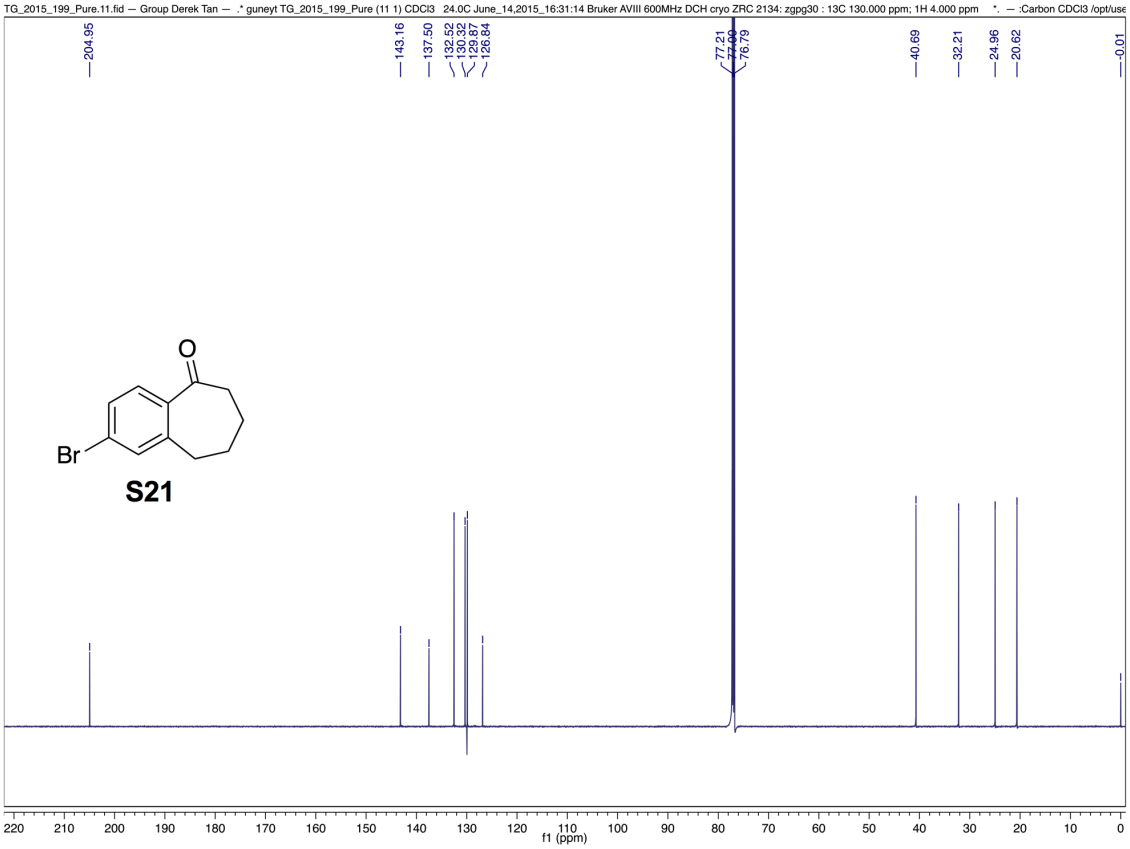

TG_2015_173.10.fid — Group Derek Tan — .* guneyt TG_2015_173 (10 1) CDCl3 24.0C April_30,2015_14:19:14 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 7
7.83 7.82 7.82 7.80
7.27
6.99 6.98 6.97 6.97 6.96 6.96 6.90 6.90 6.88 6.88
3.10 3.09 3.08 2.97 2.96 2.95
1.88 1.87 1.86 1.85 1.84 1.84 1.83 1.82 1.81 1.80 1.52 1.51 1.51 1.50 1.50 1.49 1.48
0.00
O
F
S18
1.00 1.08 1.20 2.22 2.23 4.49 2.32
f1 (ppm)

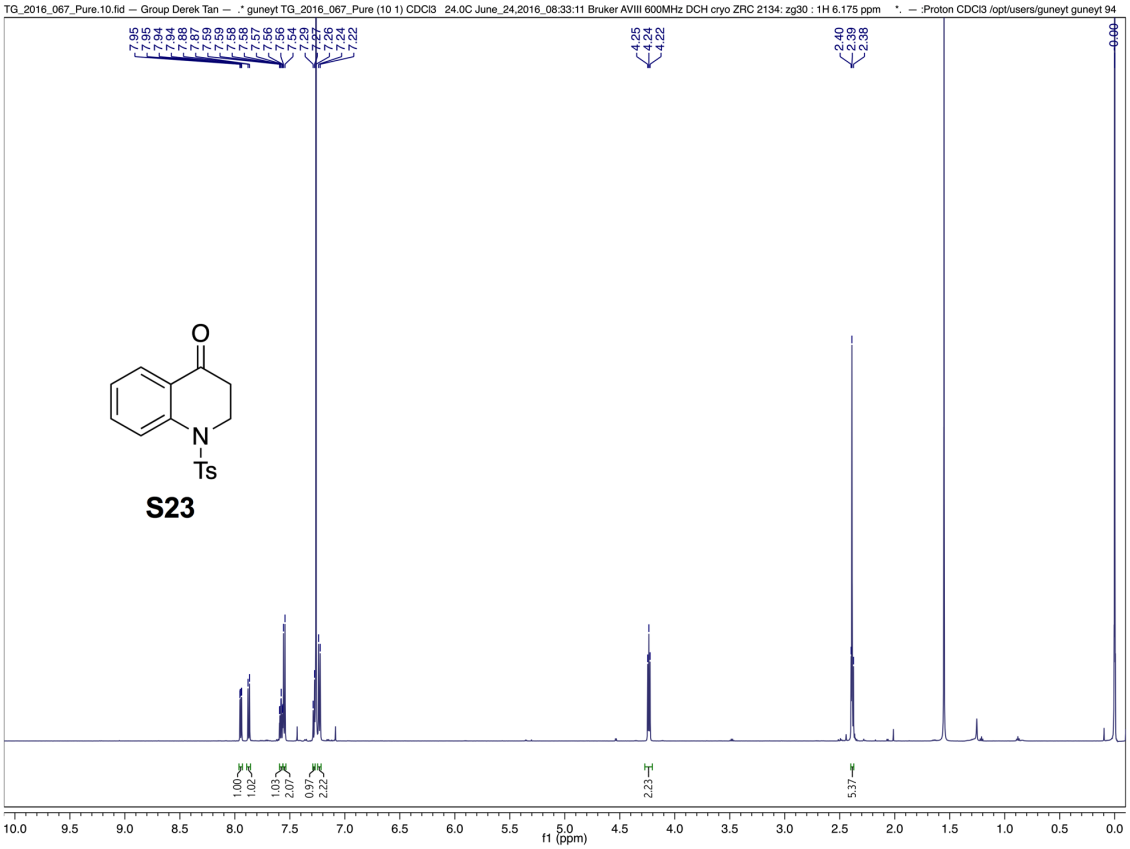

TG_2015_173.11.fid — Group Derek Tan — .* guneyt TG_2015_173 (11 1) CDCl3 24.0C April_30,2015_14:21:21 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/guneyt gu
204.63
165.54 163.87
143.50 143.45
135.84 135.82 131.11 131.05
117.74 117.60 113.57 113.43
77.21 77.00 76.79
43.47
34.71
27.53 24.14 24.14
0.01
O
F
S18
f1 (ppm)

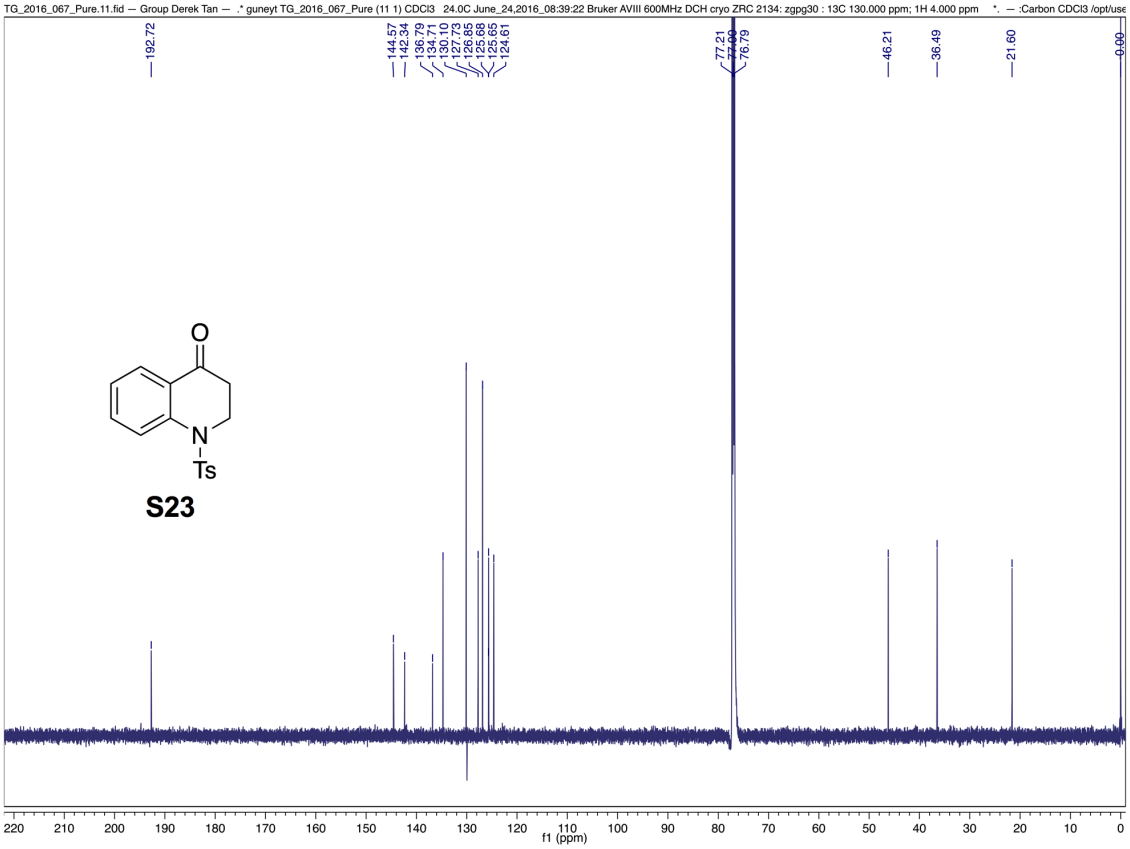

TG_2015_198_OTf_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_198_OTf_Pure (10 1) CDCl3 24.0C October_08,2015_02:06:59 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guney
7.82
7.81
7.26
7.22
7.21
7.20
7.14
2.98
2.97
2.96
2.77
2.76
2.75
1.95
1.94
1.93
1.91
1.90
1.87
1.85
1.84
1.82
0.00
1.00
1.01
1.01
2.14
2.12
2.14
2.17
O
TfO
S20
f1 (ppm)

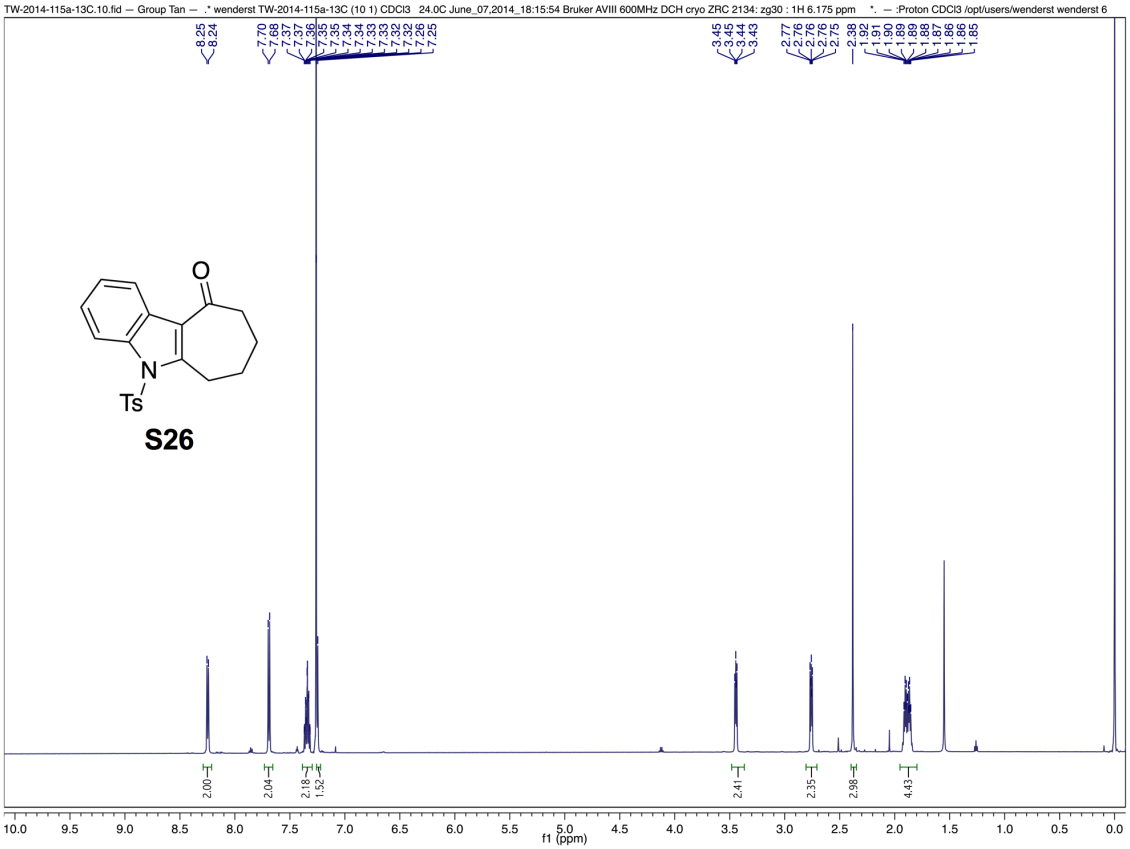

TG_2015_198_OTf_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_198_OTf_Pure (11 1) CDCl3 24.0C October_08,2015_02:09:18 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon C
204.13
151.44
144.18
138.74
131.14
122.32
121.85
119.72
119.45
117.60
115.47
77.22
77.01
76.80
40.66
32.54
24.92
20.73
0.00
O
TfO
S20
f1 (ppm)

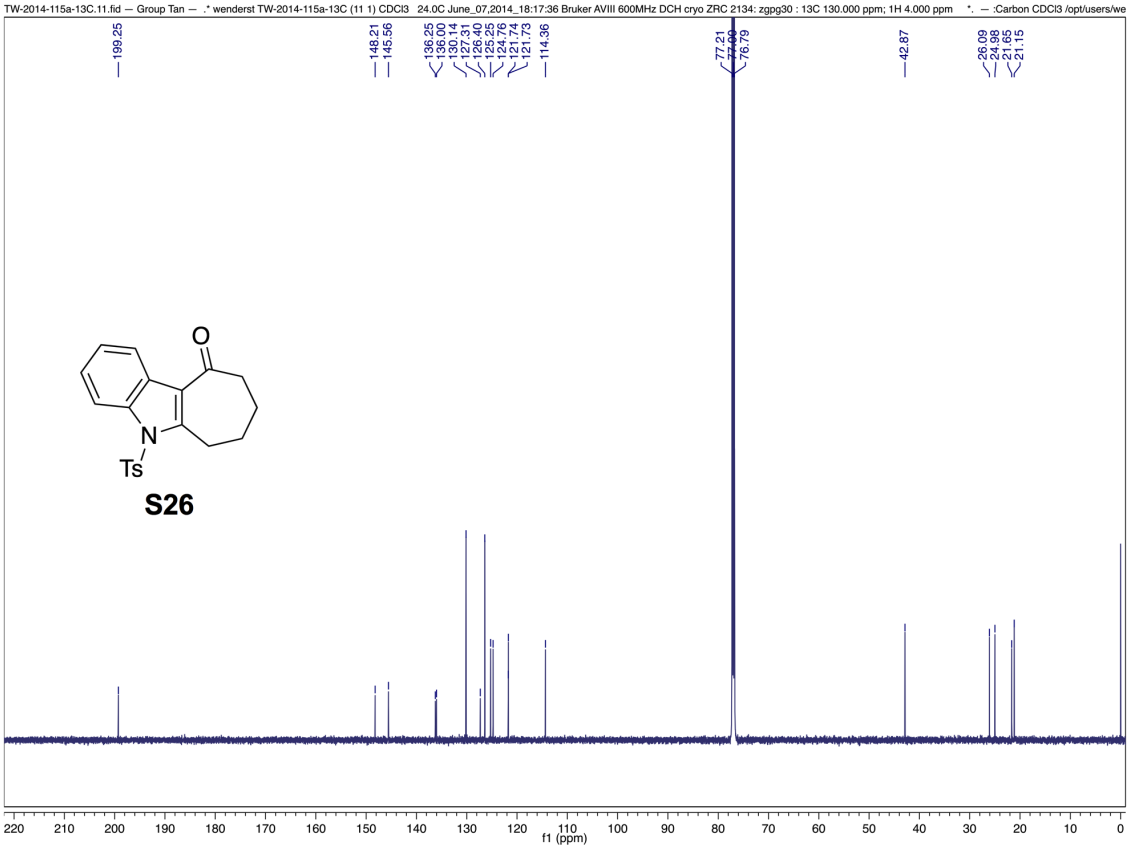

TG_2015_199_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_199_Pure (10 1) CDCl3 24.0C June_14,2015_16:28:59 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 36
7.60
7.59
7.45
7.45
7.44
7.43
7.39
7.38
2.91
2.90
2.89
2.73
2.72
2.72
2.71
1.91
1.90
1.89
1.87
1.86
1.83
1.82
1.81
1.80
1.79
0.00
0.99
1.01
1.00
2.16
2.14
2.16
2.15
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)
O
Br
S21

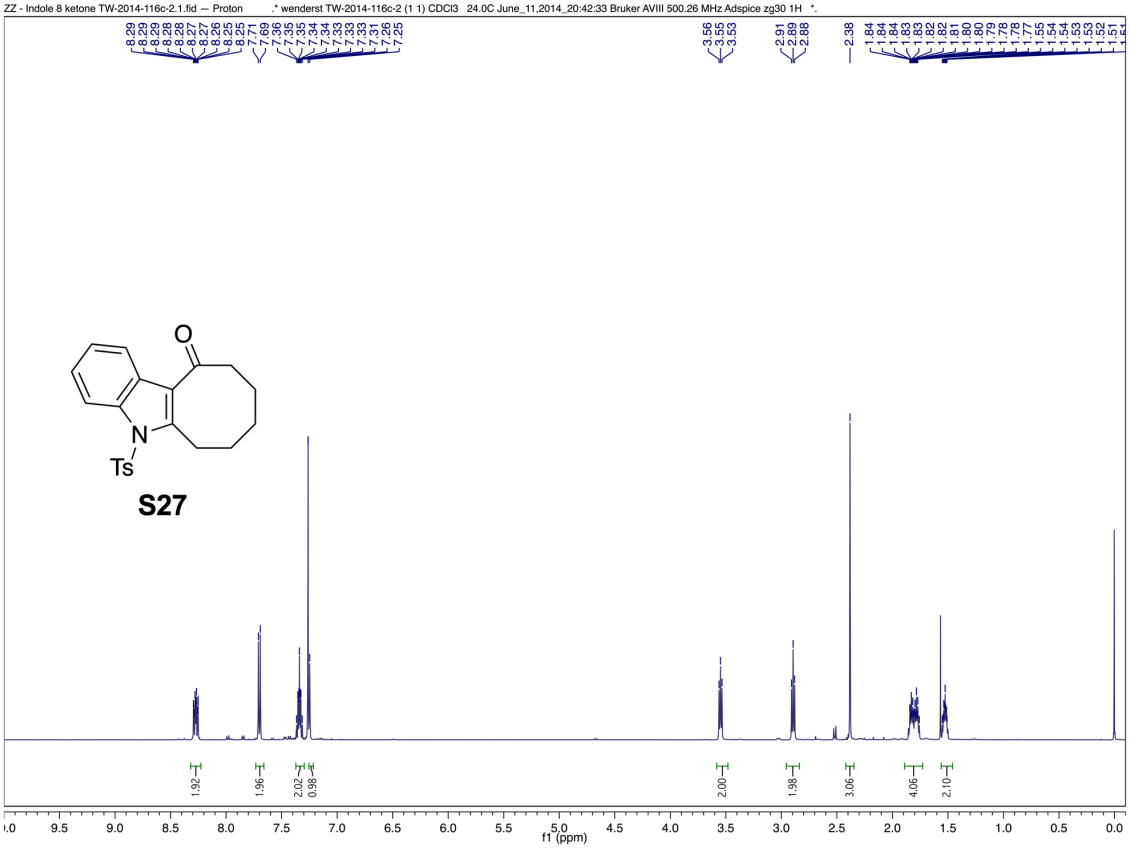

TG_2015_199_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_199_Pure (11 1) CDCl3 24.0C June_14,2015_16:31:14 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
204.95
143.16
137.50
132.52
130.32
129.87
126.84
77.21
77.00
76.79
40.69
32.21
24.96
20.62
0.01
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
Br
S21

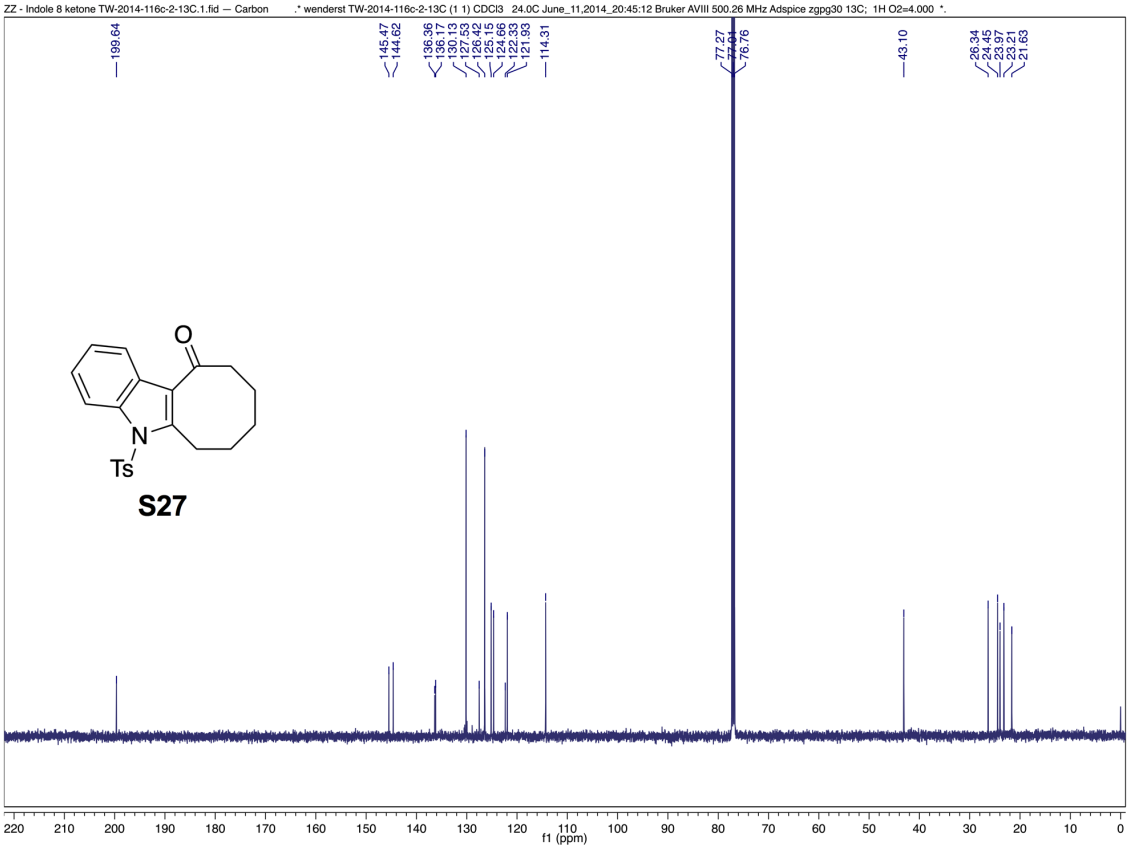

TG_2016_067_Pure.10.fid — Group Derek Tan — .* guneyt TG_2016_067_Pure (10 1) CDCl3 24.0C June_24,2016_08:33:11 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 94
7.95
7.95
7.94
7.94
7.89
7.87
7.59
7.59
7.58
7.58
7.57
7.56
7.54
7.29
7.27
7.26
7.24
7.22
4.25
4.24
4.22
2.40
2.39
2.38
0.00
O
N
Ts
S23
1.00
1.02
1.03
2.07
0.97
2.22
2.23
5.37
f1 (ppm)

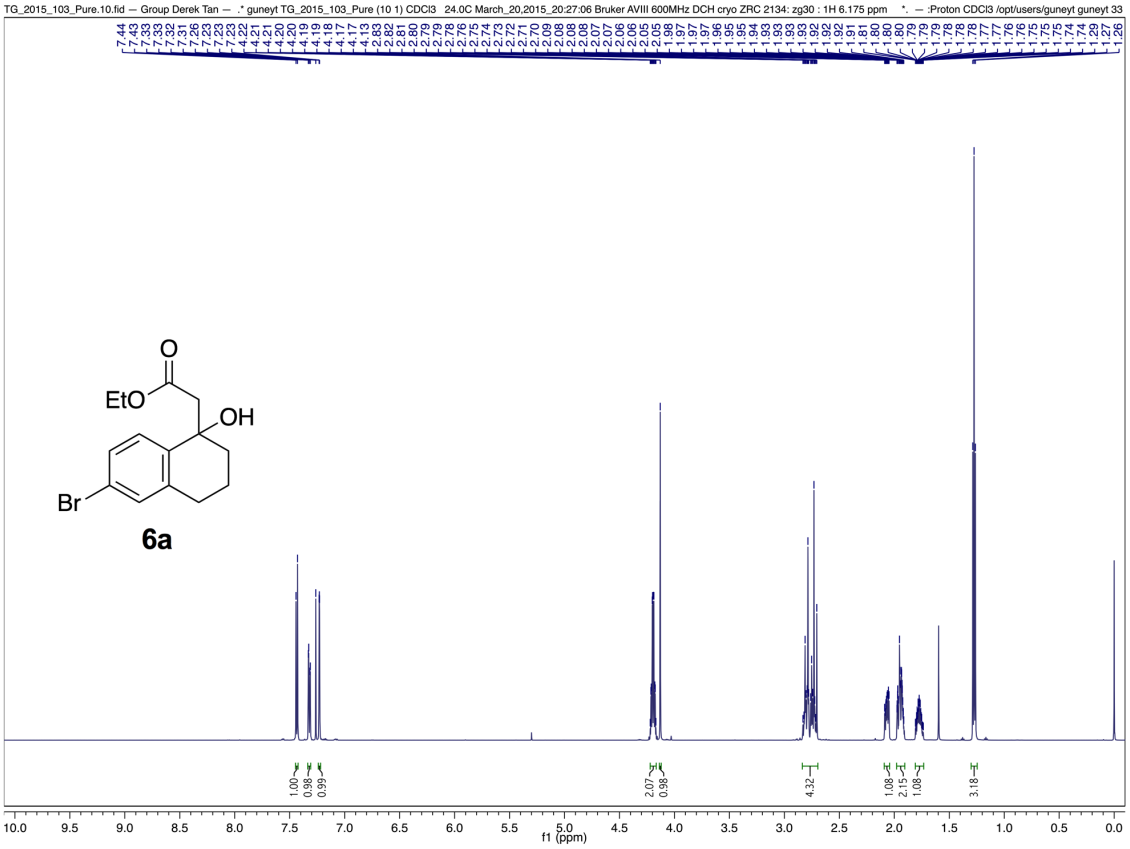

TG_2016_067_Pure.11.fid — Group Derek Tan — .* guneyt TG_2016_067_Pure (11 1) CDCl3 24.0C June_24,2016_08:39:22 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
192.72
144.57
142.34
136.79
134.71
130.10
127.73
126.85
125.88
125.65
124.61
77.21
77.00
76.79
46.21
36.49
21.60
0.00
O
N
Ts
S23
f1 (ppm)

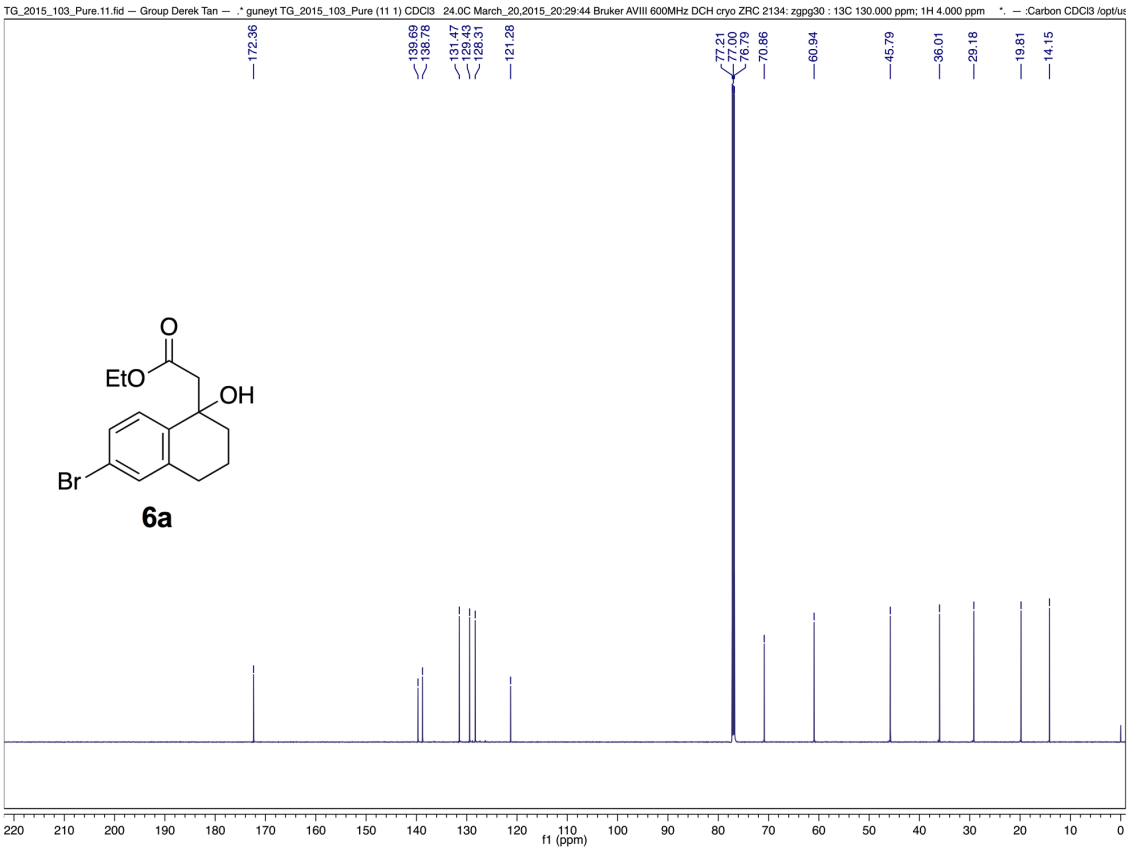

TW-2014-115a-13C.10.fid — Group Tan — .* wenderst TW-2014-115a-13C (10 1) CDCl3 24.0C June_07,2014_18:15:54 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 6
8.25
8.24
7.70
7.68
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.26
7.25
3.45
3.44
3.44
3.43
3.43
2.77
2.76
2.76
2.76
2.75
2.38
1.92
1.91
1.90
1.89
1.89
1.87
1.87
1.86
1.86
1.85
O
N
Ts
S26
2.00
2.04
2.18
1.52
2.41
2.35
2.98
4.43
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)

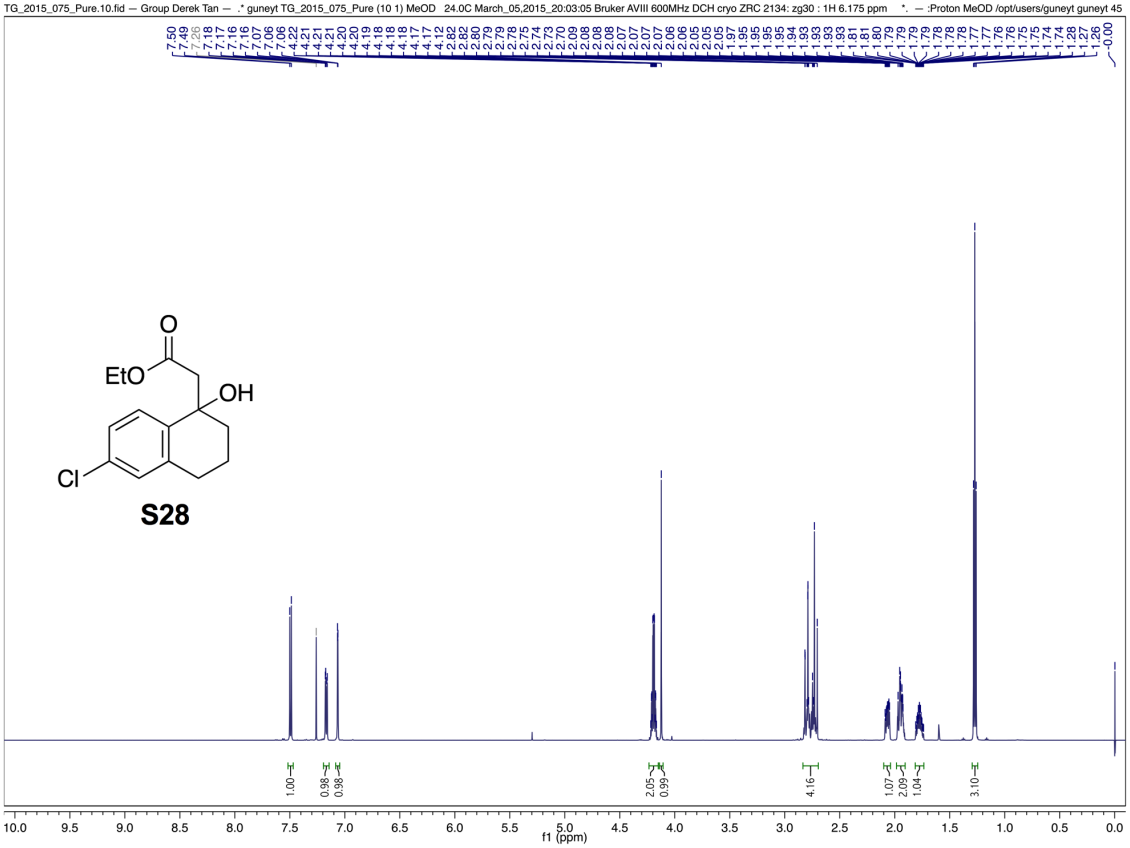

TW-2014-115a-13C.11.fid — Group Tan — .* wenderst TW-2014-115a-13C (11 1) CDCl3 24.0C June_07,2014_18:17:36 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/we
199.25
148.21
145.56
136.25
136.00
130.14
127.31
126.40
125.20
124.76
121.74
121.73
114.36
77.21
77.00
76.79
42.87
26.09
24.98
21.65
21.15
O
N
Ts
S26
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

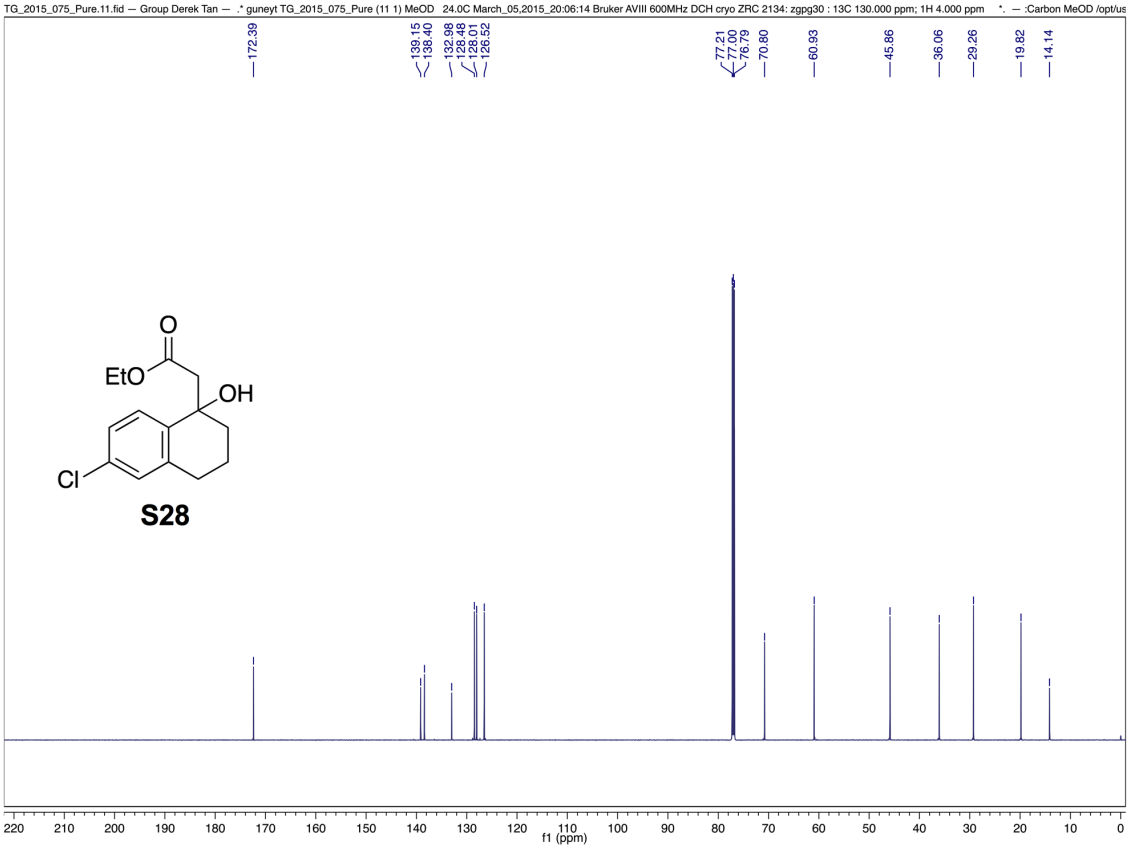

ZZ - Indole 8 ketone TW-2014-116c-2.1.fid — Proton .* wenderst TW-2014-116c-2 (1 1) CDCl3 24.0C June_11,2014_20:42:33 Bruker AVIII 500.26 MHz Adspice zg30 1H *.
8.29
8.29
8.28
8.28
8.28
8.27
8.27
8.26
8.25
7.71
7.69
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.31
7.26
7.25
3.56
3.55
3.53
2.91
2.89
2.88
2.38
1.84
1.84
1.84
1.83
1.83
1.82
1.82
1.81
1.80
1.80
1.79
1.78
1.78
1.77
1.55
1.54
1.54
1.53
1.53
1.52
1.51
O
N
Ts
S27
1.92
1.96
2.02
0.98
2.00
1.98
3.06
4.06
2.10
f1 (ppm)

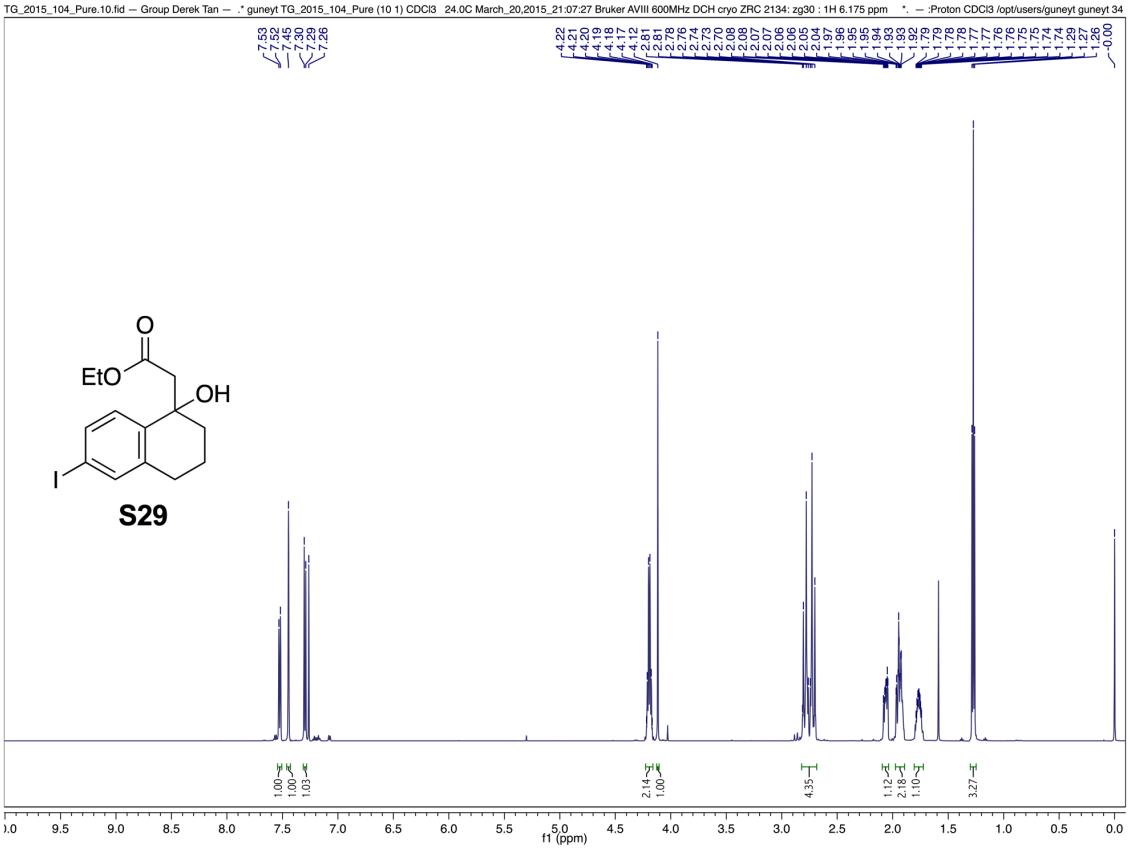

ZZ - Indole 8 ketone TW-2014-116c-2-13C.1.fid — Carbon .* wenderst TW-2014-116c-2-13C (1 1) CDCl3 24.0C June_11,2014_20:45:12 Bruker AVIII 500.26 MHz Adspice zgpg30 13C; 1H O2=4.000 *.
199.64
145.47
144.62
136.36
136.17
130.13
127.53
126.42
125.15
124.66
122.33
121.93
114.31
77.27
77.01
76.76
43.10
26.34
24.45
23.97
23.21
21.63
O
N
Ts
S27
f1 (ppm)

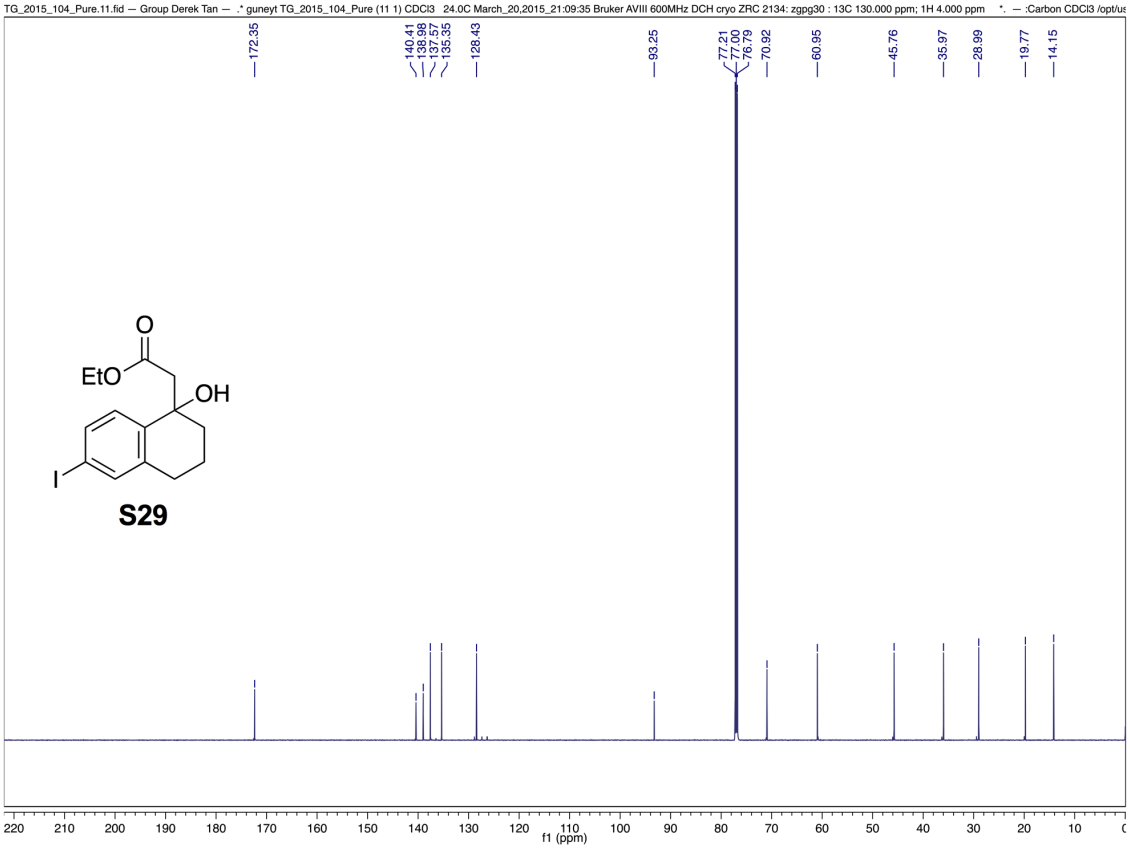

TG_2015_103_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_103_Pure (10 1) CDCl3 24.0C March_20,2015_20:27:06 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 33
O
EtO
OH
Br
6a
1.00
0.98
0.99
2.07
0.98
4.32
1.08
2.15
1.08
3.18
f1 (ppm)

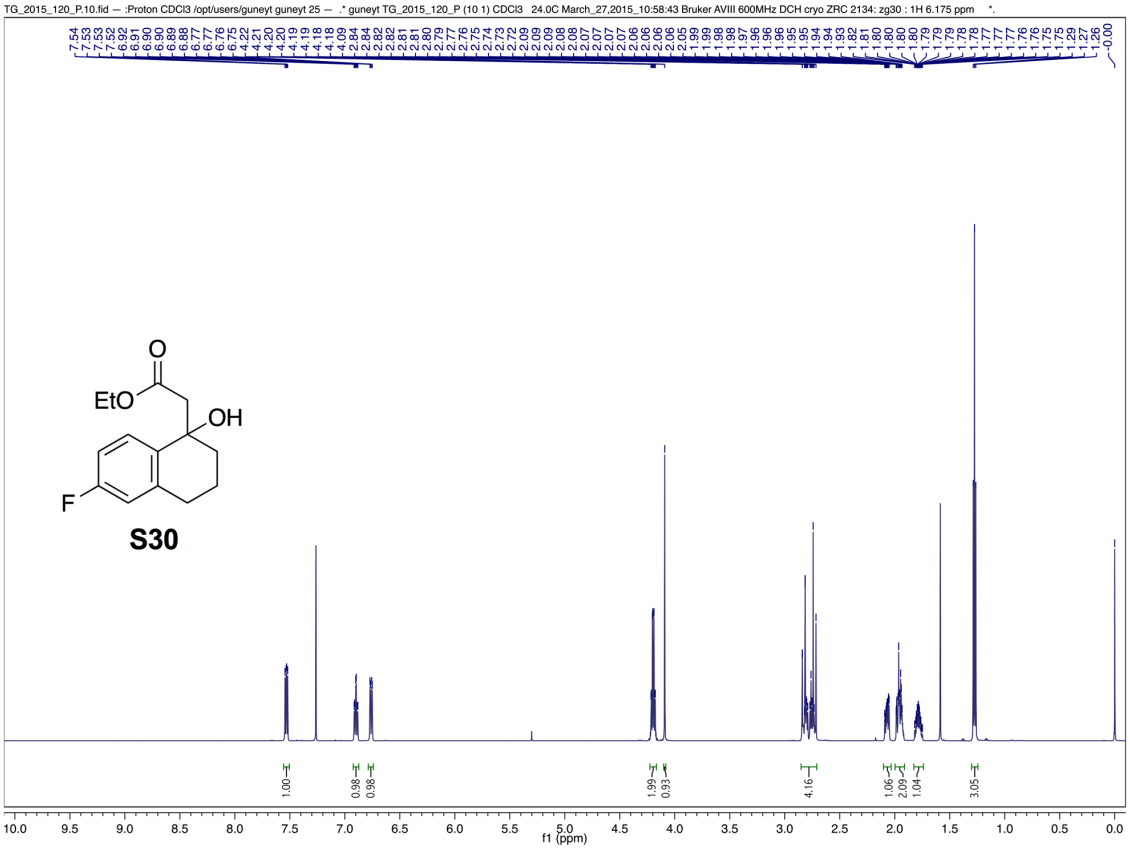

TG_2015_103_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_103_Pure (11 1) CDCl3 24.0C March_20,2015_20:29:44 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/us
172.36
139.69
138.78
131.47
129.43
128.31
121.28
77.21
77.00
76.79
70.86
60.94
45.79
36.01
29.18
19.81
14.15
O
EtO
OH
Br
6a
f1 (ppm)

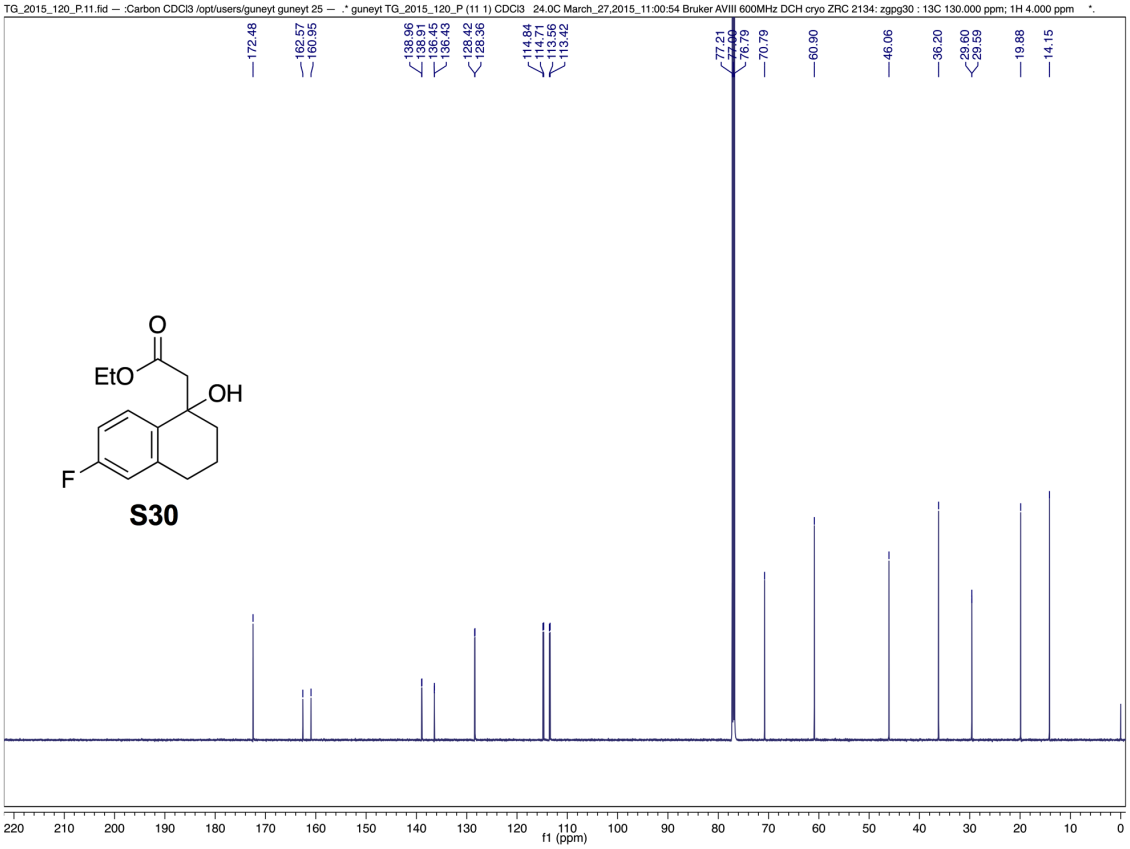

TG_2015_075_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_075_Pure (10 1) MeOD 24.0C March_05,2015_20:03:05 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guneyt guneyt 45
O
EtO
OH
Cl
S28
f1 (ppm)

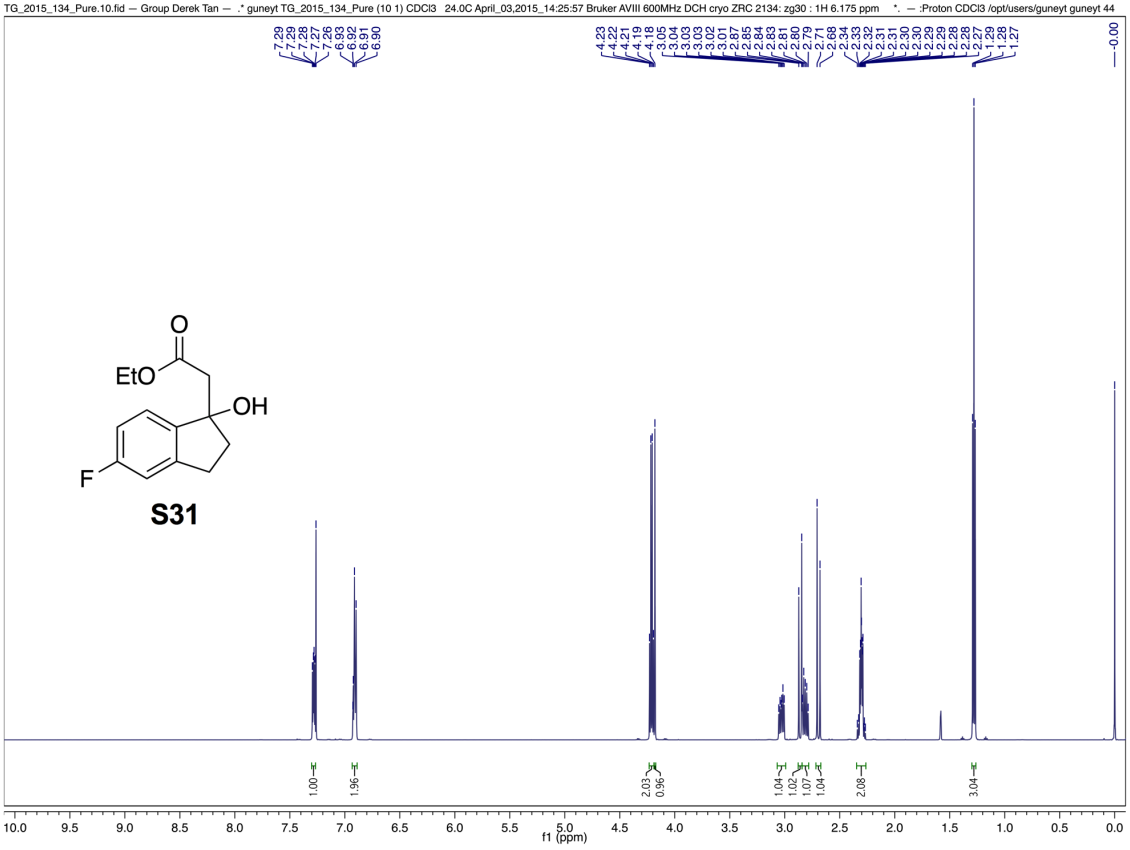

TG_2015_075_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_075_Pure (11 1) MeOD 24.0C March_05,2015_20:06:14 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon MeOD /opt/us
O
EtO
OH
Cl
S28
f1 (ppm)

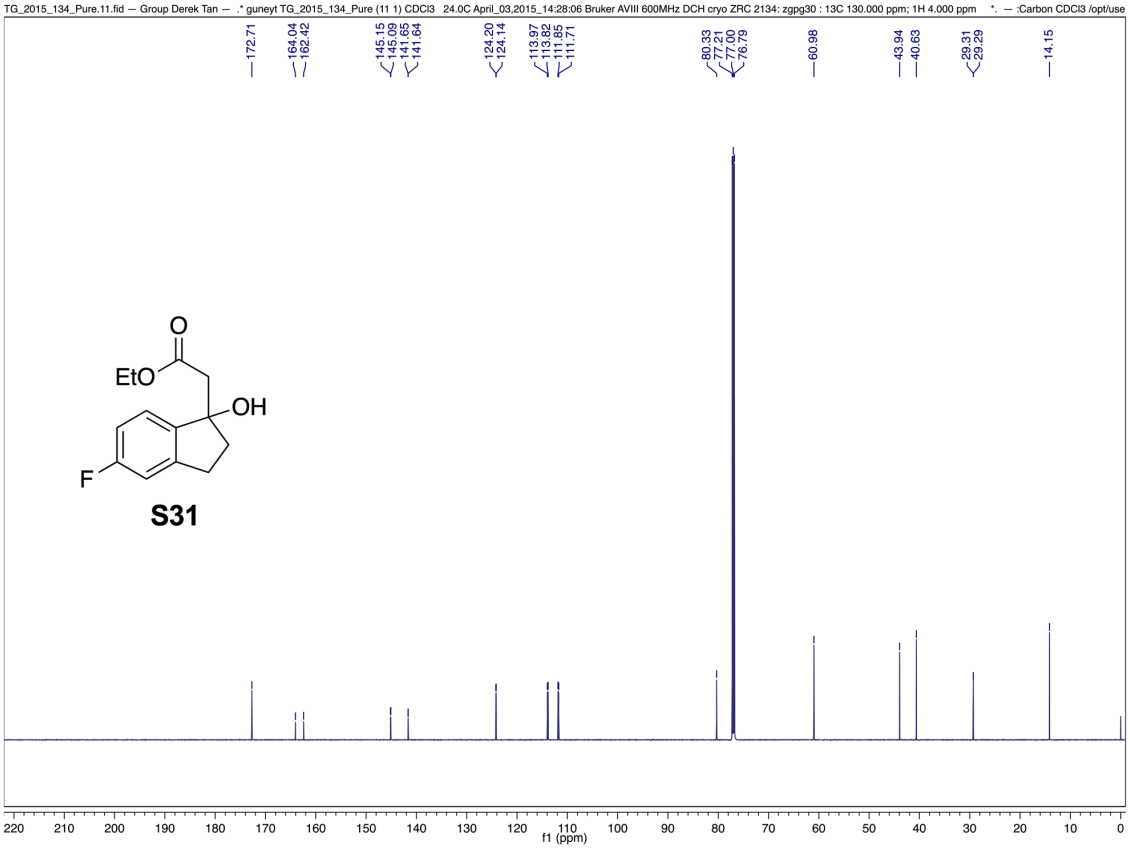

TG_2015_104_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_104_Pure (10 1) CDCl3 24.0C March_20,2015_21:07:27 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 34
7.53
7.52
7.45
7.30
7.29
7.26
4.22
4.21
4.20
4.19
4.18
4.17
4.12
2.81
2.78
2.76
2.74
2.73
2.70
2.08
2.08
2.07
2.06
2.06
2.05
2.04
1.97
1.96
1.95
1.94
1.93
1.93
1.92
1.79
1.78
1.78
1.77
1.77
1.76
1.76
1.75
1.75
1.74
1.74
1.29
1.27
1.26
0.00
1.00
1.00
1.03
2.14
1.00
4.35
1.12
2.18
1.10
3.27
f1 (ppm)
O
EtO
OH
I
S29

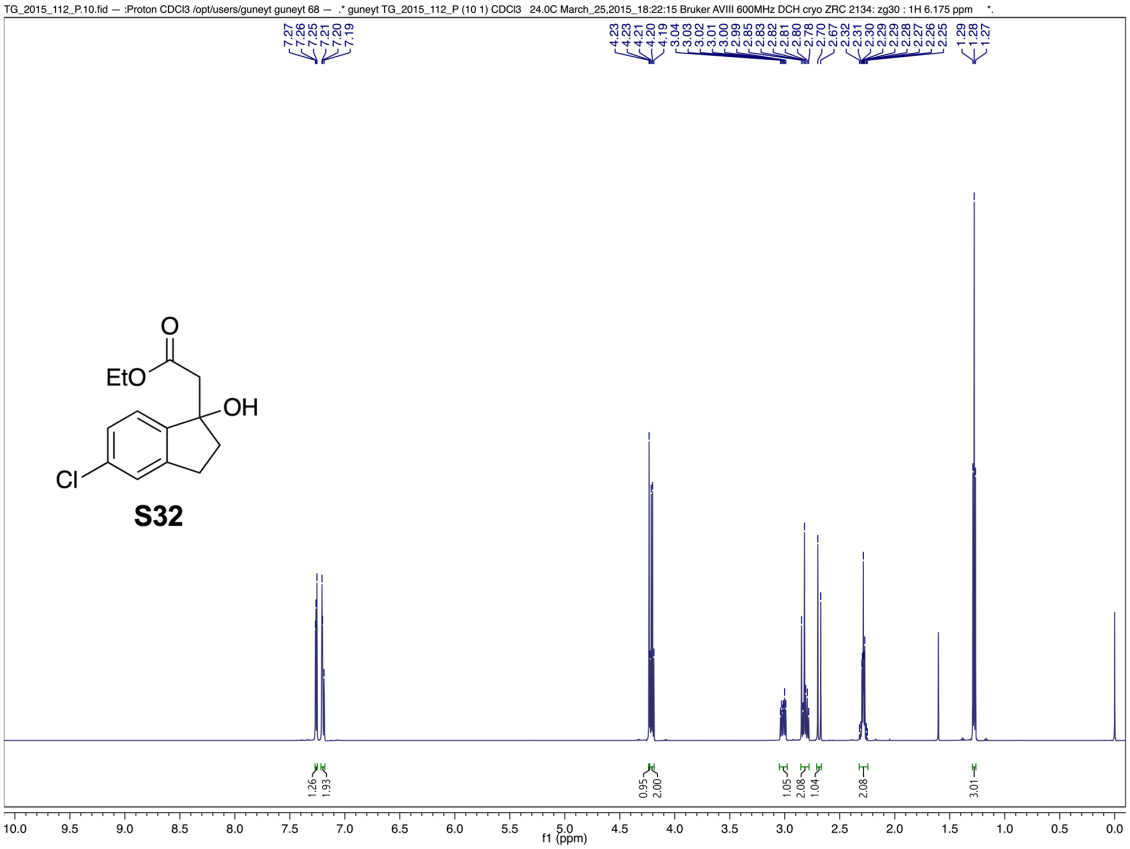

TG_2015_104_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_104_Pure (11 1) CDCl3 24.0C March_20,2015_21:09:35 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/us
172.35
140.41
138.89
137.77
135.35
128.43
93.25
77.21
77.00
76.79
70.92
60.95
45.76
35.97
28.99
19.77
14.15
f1 (ppm)
O
EtO
OH
I
S29

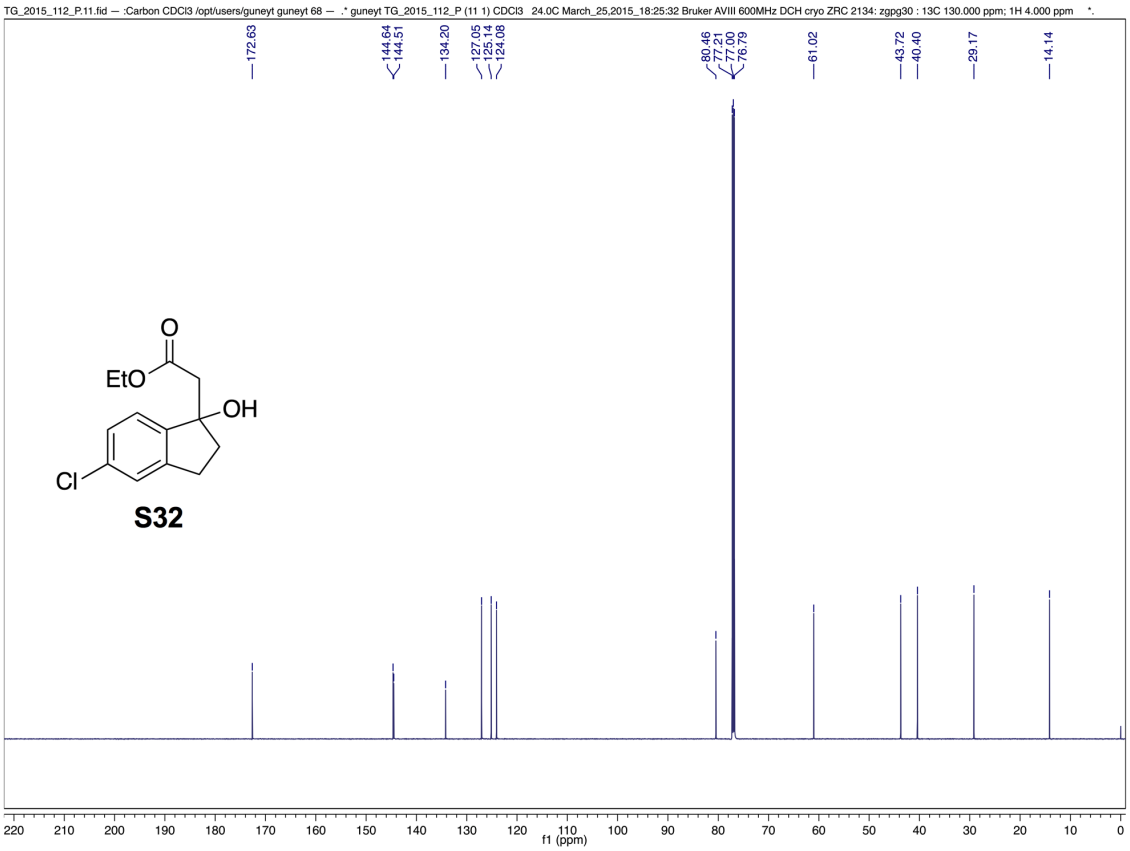

TG_2015_120_P.10.fid — :Proton CDCl3 /opt/users/guneyt guneyt 25 — .* guneyt TG_2015_120_P (10 1) CDCl3 24.0C March_27,2015_10:58:43 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
O
EtO
OH
F
S30
f1 (ppm)

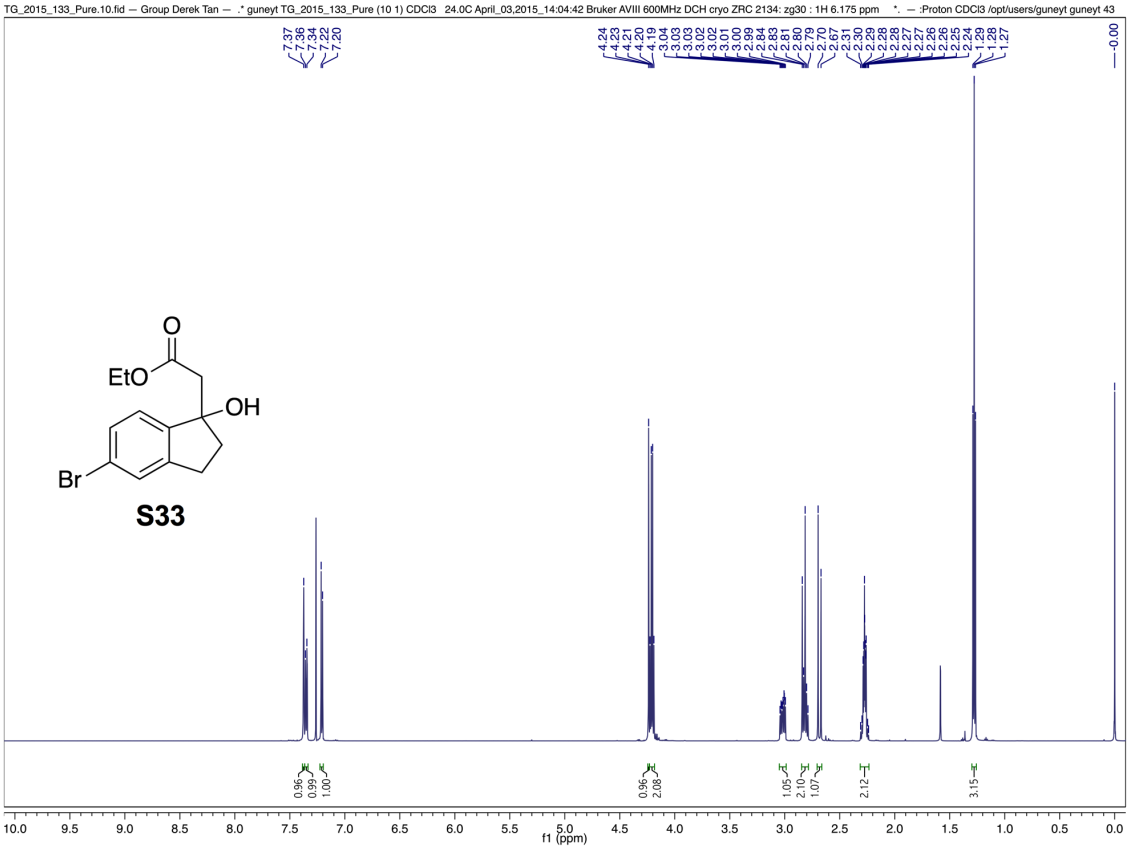

TG_2015_120_P.11.fid — :Carbon CDCl3 /opt/users/guneyt guneyt 25 — .* guneyt TG_2015_120_P (11 1) CDCl3 24.0C March_27,2015_11:00:54 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *.
O
EtO
OH
F
S30
f1 (ppm)

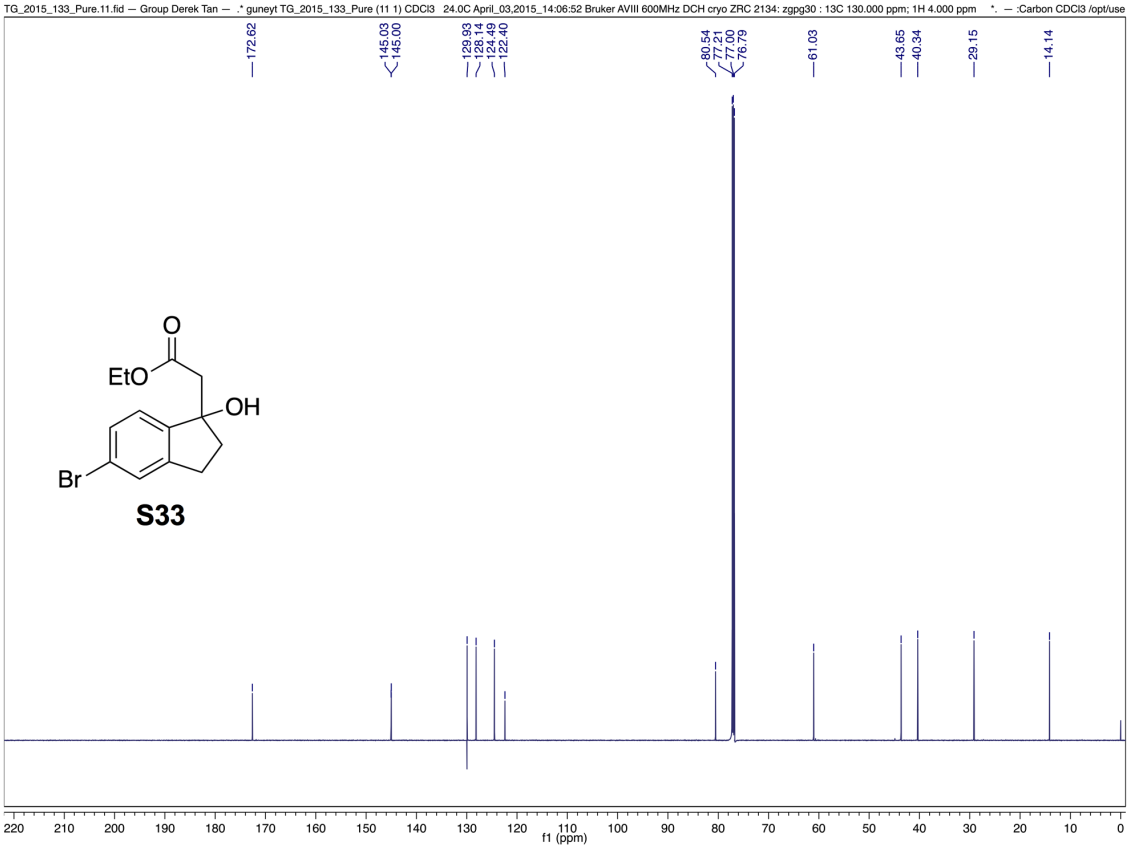

TG_2015_134_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_134_Pure (10 1) CDCl3 24.0C April_03,2015_14:25:57 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 44
7.29
7.29
7.28
7.27
7.26
6.93
6.92
6.91
6.90
4.23
4.22
4.21
4.19
4.18
3.05
3.04
3.03
3.02
3.01
2.87
2.85
2.84
2.83
2.81
2.80
2.79
2.71
2.68
2.34
2.33
2.32
2.31
2.31
2.30
2.30
2.29
2.29
2.28
2.28
2.27
1.29
1.28
1.27
0.00
1.00
1.96
2.03
0.96
1.04
1.02
1.07
1.04
2.08
3.04
f1 (ppm)
O
EtO
OH
F
S31

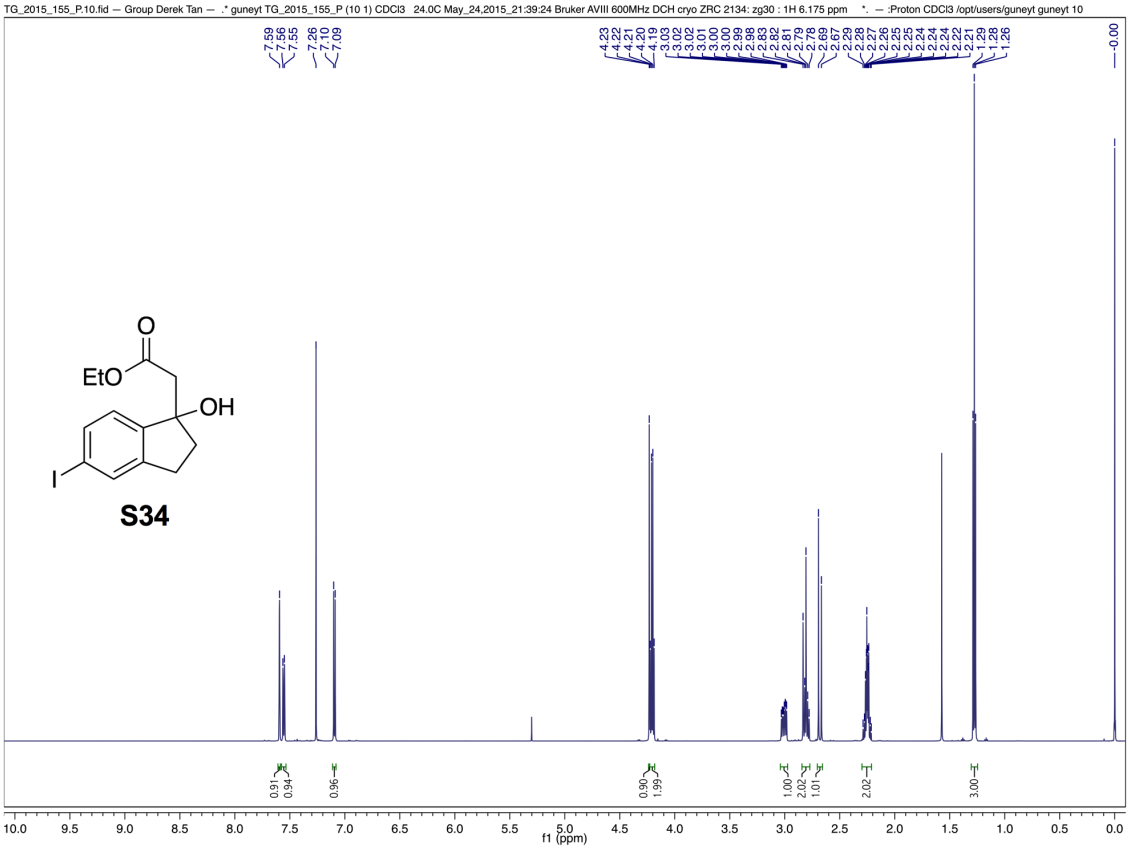

TG_2015_134_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_134_Pure (11 1) CDCl3 24.0C April_03,2015_14:28:06 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
172.71
164.04
162.42
145.15
145.09
141.65
141.64
124.20
124.14
113.97
113.92
111.85
111.71
80.33
77.21
77.00
76.79
60.98
43.94
40.63
29.31
29.29
14.15
f1 (ppm)
O
EtO
OH
F
S31

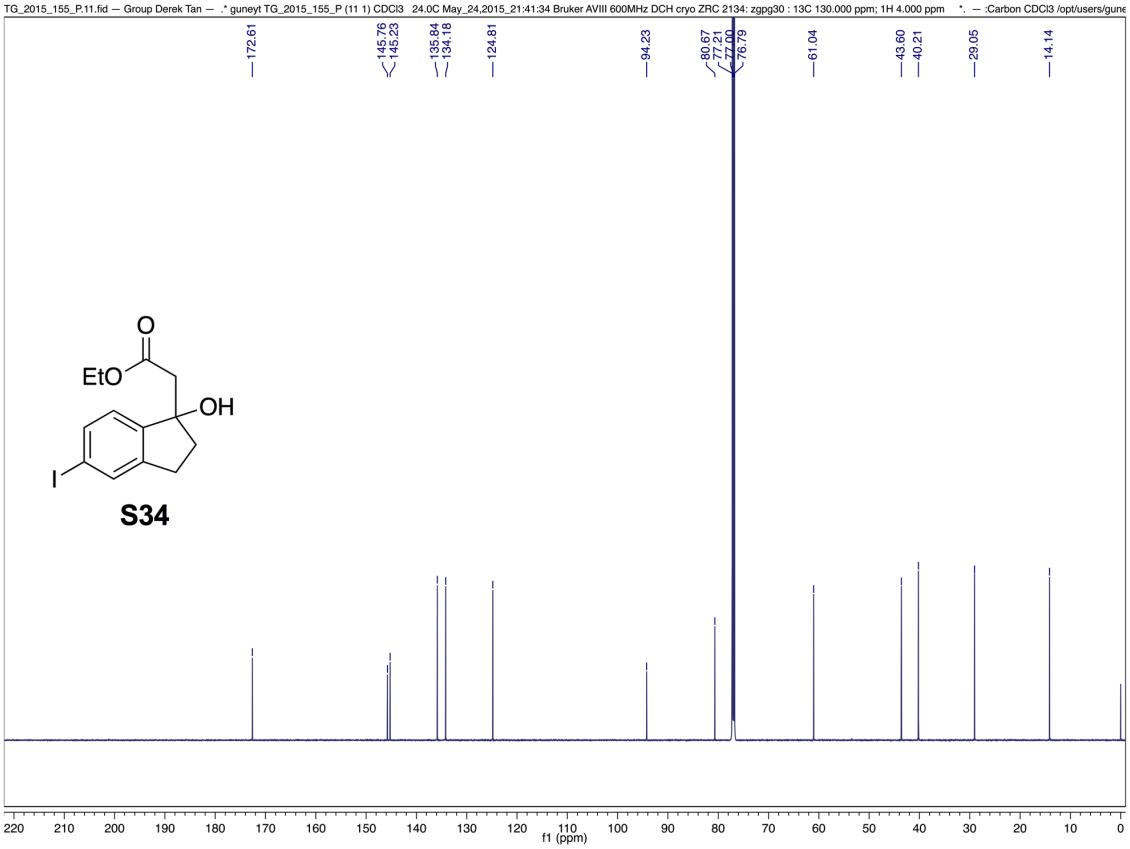

TG_2015_112_P.10.fid — :Proton CDCl3 /opt/users/guneyt guneyt 68 — .* guneyt TG_2015_112_P (10 1) CDCl3 24.0C March_25,2015_18:22:15 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
7.27
7.26
7.25
7.21
7.20
7.19
4.23
4.23
4.21
4.20
4.19
3.04
3.03
3.01
3.00
2.99
2.85
2.83
2.82
2.81
2.80
2.78
2.70
2.67
2.32
2.31
2.30
2.29
2.28
2.27
2.26
2.25
1.29
1.28
1.27
O
EtO
OH
Cl
S32
1.26
1.93
0.95
2.00
1.05
2.08
1.04
2.08
3.01
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)

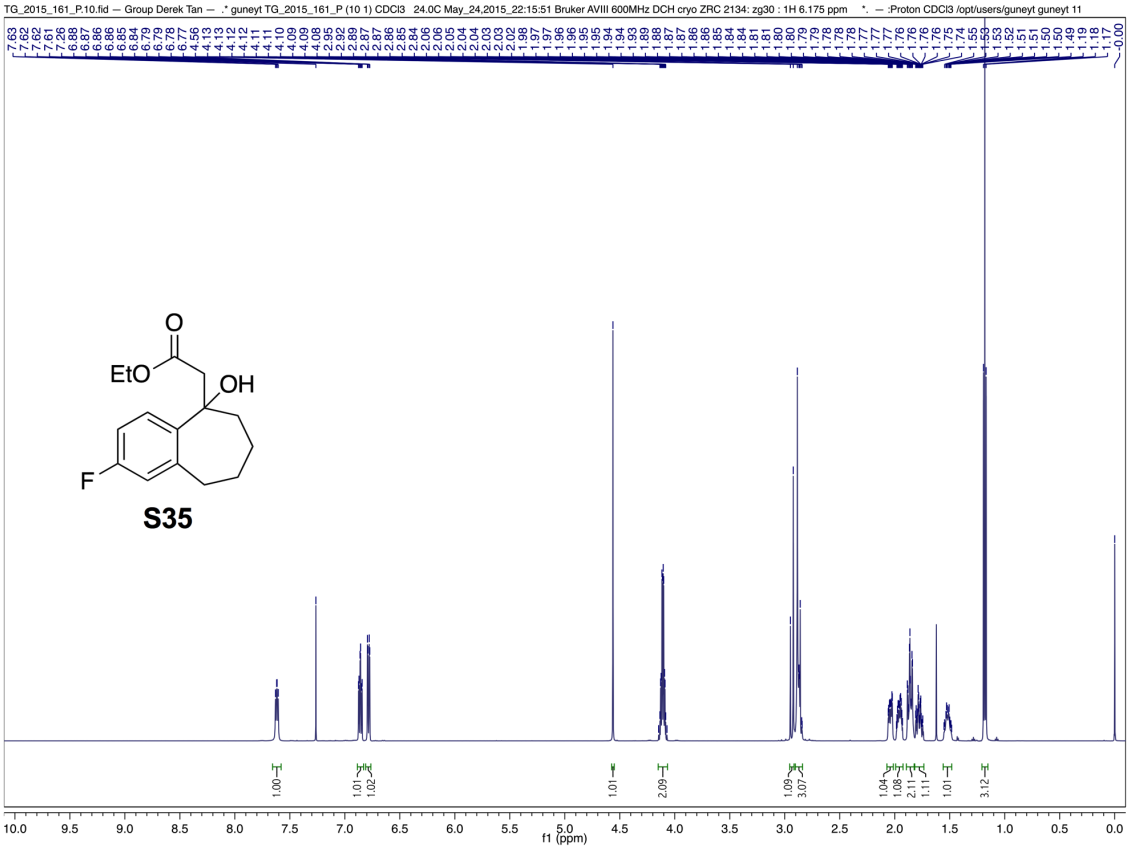

TG_2015_112_P.11.fid — :Carbon CDCl3 /opt/users/guneyt guneyt 68 — .* guneyt TG_2015_112_P (11 1) CDCl3 24.0C March_25,2015_18:25:32 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *.
172.63
144.64
144.51
134.20
127.05
125.14
124.08
80.46
77.21
77.00
76.79
61.02
43.72
40.40
29.17
14.14
O
EtO
OH
Cl
S32
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

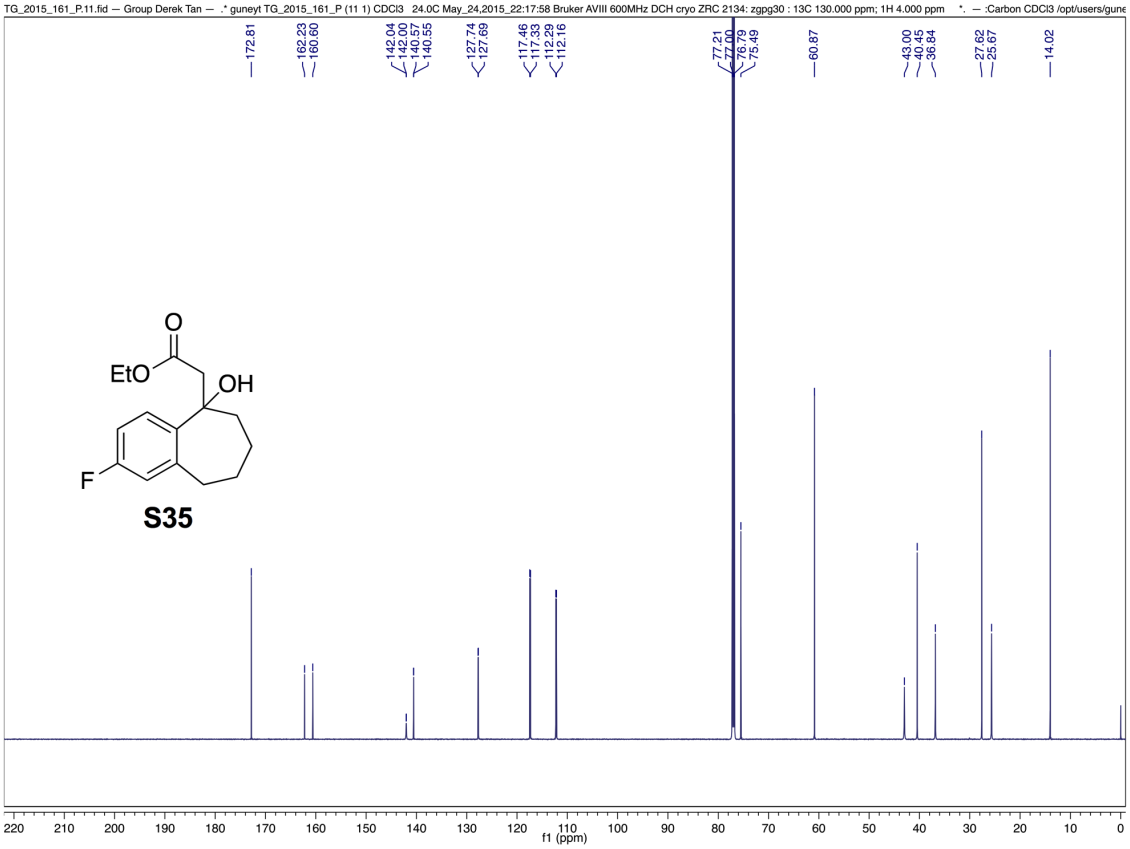

TG_2015_133_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_133_Pure (10 1) CDCl3 24.0C April_03,2015_14:04:42 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 43
7.37
7.36
7.34
7.22
7.20
4.24
4.23
4.21
4.20
4.19
3.04
3.03
3.03
3.02
3.02
3.01
3.00
2.99
2.84
2.83
2.81
2.80
2.79
2.70
2.67
2.31
2.30
2.29
2.28
2.27
2.27
2.26
2.26
2.25
2.24
1.28
1.27
-0.00
O
EtO
OH
Br
S33
0.96
0.99
1.00
0.96
2.08
1.05
2.10
1.07
2.12
3.15
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)

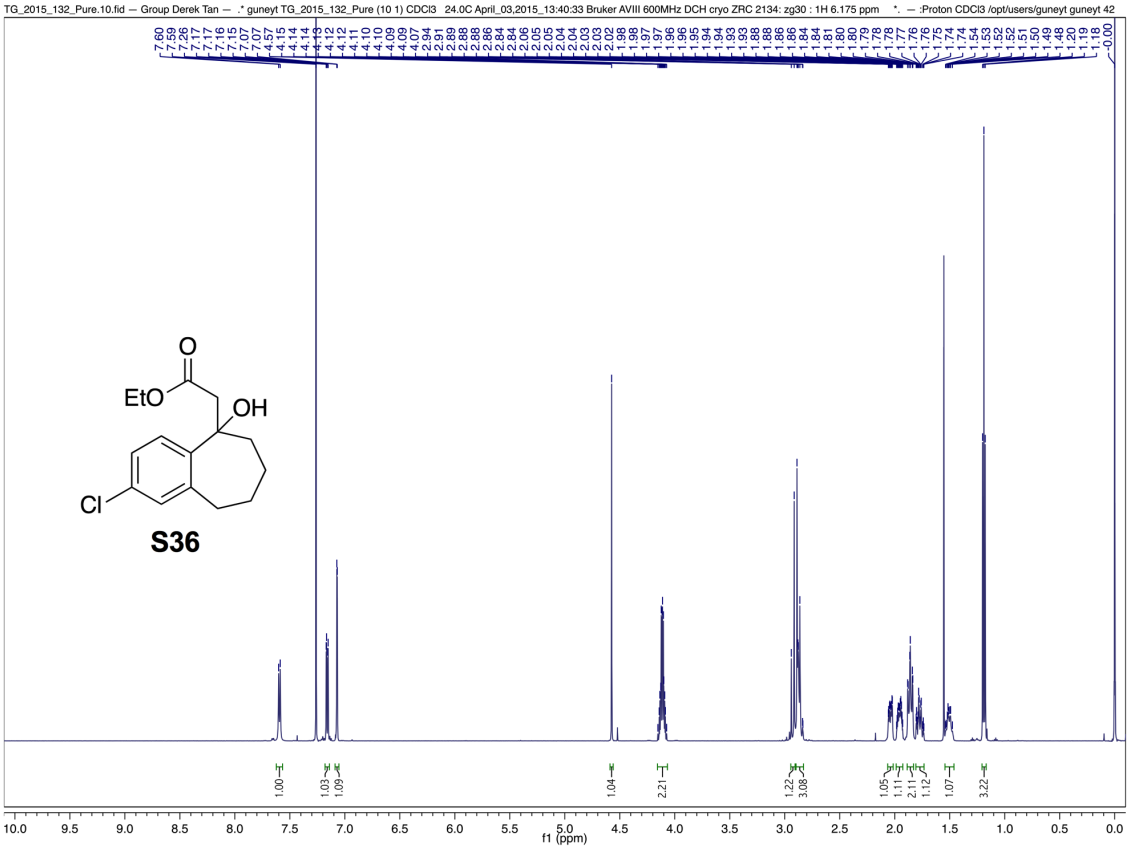

TG_2015_133_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_133_Pure (11 1) CDCl3 24.0C April_03,2015_14:06:52 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
172.62
145.03
145.00
129.93
128.14
124.49
122.40
80.54
77.21
77.00
76.79
61.03
43.65
40.34
29.15
14.14
O
EtO
OH
Br
S33
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

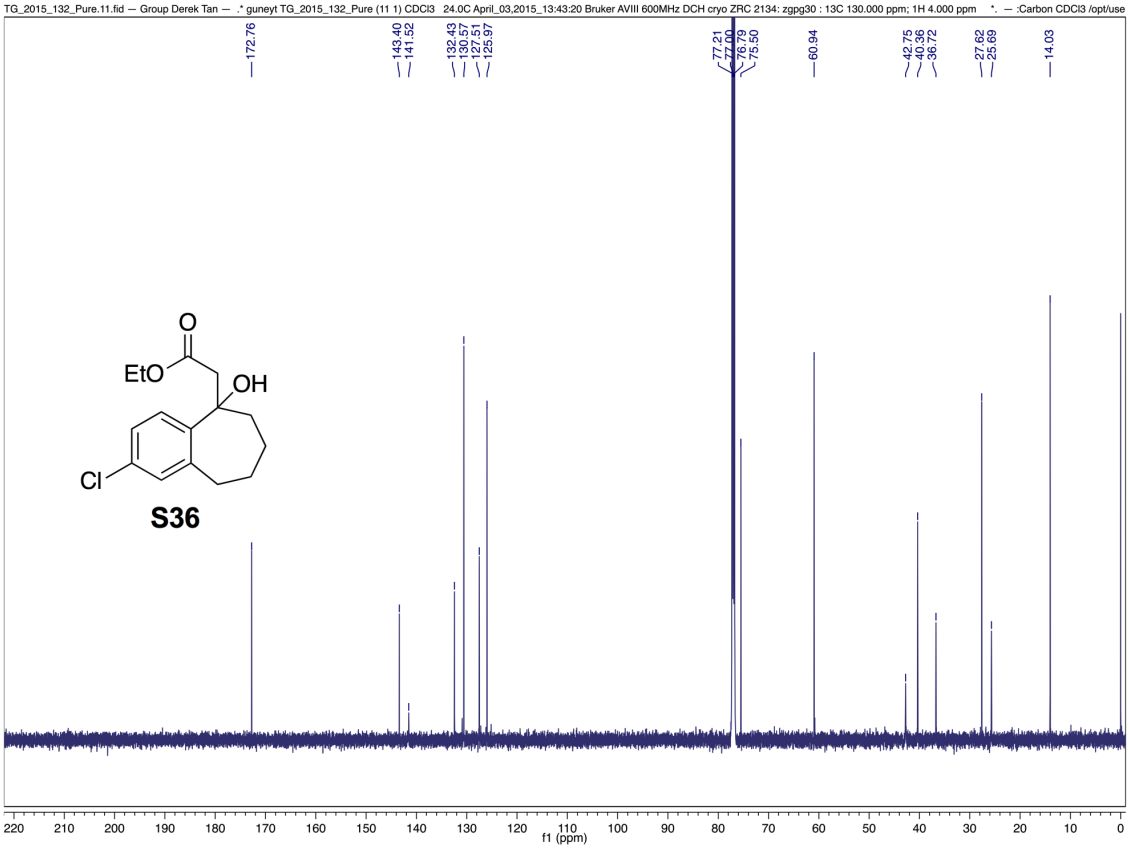

TG_2015_155_P.10.fid — Group Derek Tan — .* guneyt TG_2015_155_P (10 1) CDCl3 24.0C May_24,2015_21:39:24 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 10
7.59
7.56
7.55
7.26
7.10
7.09
4.23
4.22
4.21
4.20
4.19
3.03
3.02
3.02
3.01
3.01
3.00
2.99
2.98
2.83
2.82
2.81
2.79
2.69
2.67
2.29
2.28
2.27
2.26
2.25
2.24
2.24
2.24
2.22
2.21
1.29
1.26
-0.00
0.91
0.94
0.96
0.90
1.99
1.00
2.02
1.01
2.02
3.00
f1 (ppm)
EtO
O
OH
I
S34

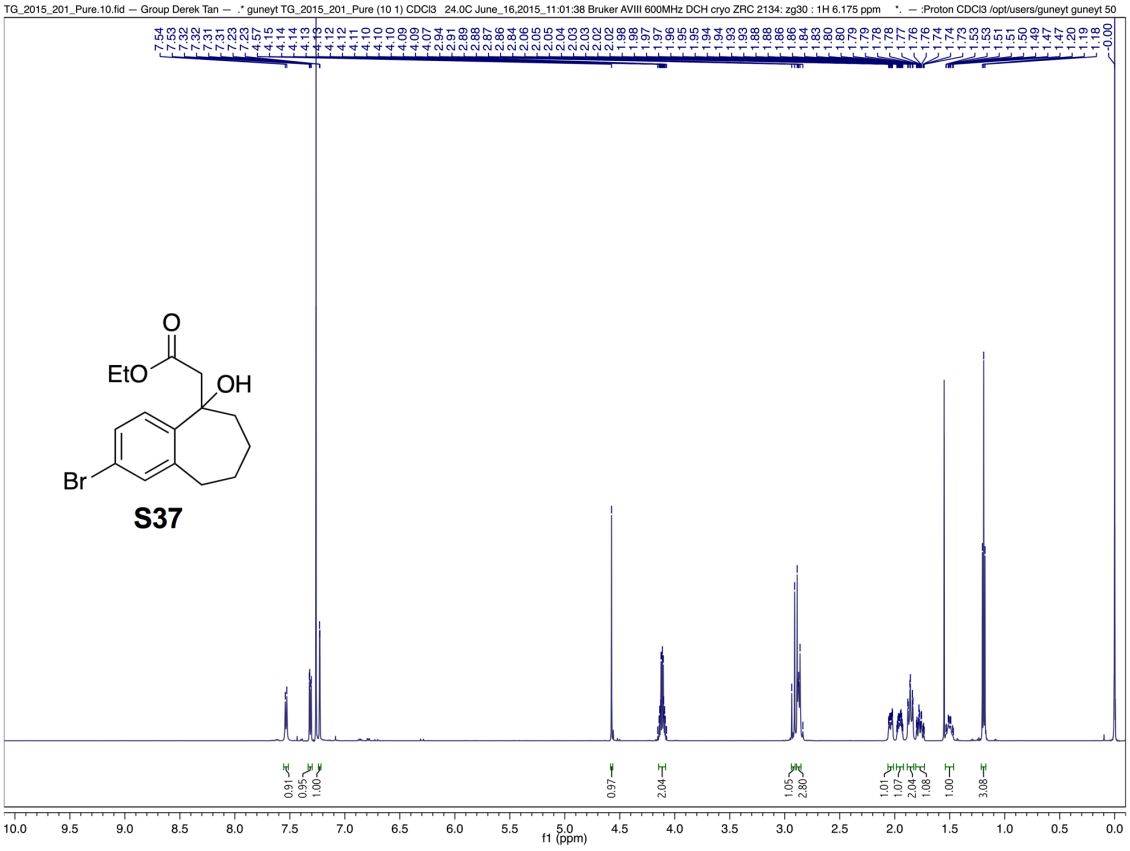

TG_2015_155_P.11.fid — Group Derek Tan — .* guneyt TG_2015_155_P (11 1) CDCl3 24.0C May_24,2015_21:41:34 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/gune
172.61
145.76
145.23
135.84
134.18
124.81
94.23
80.67
77.21
77.00
76.79
61.04
43.60
40.21
29.05
14.14
f1 (ppm)
EtO
O
OH
I
S34

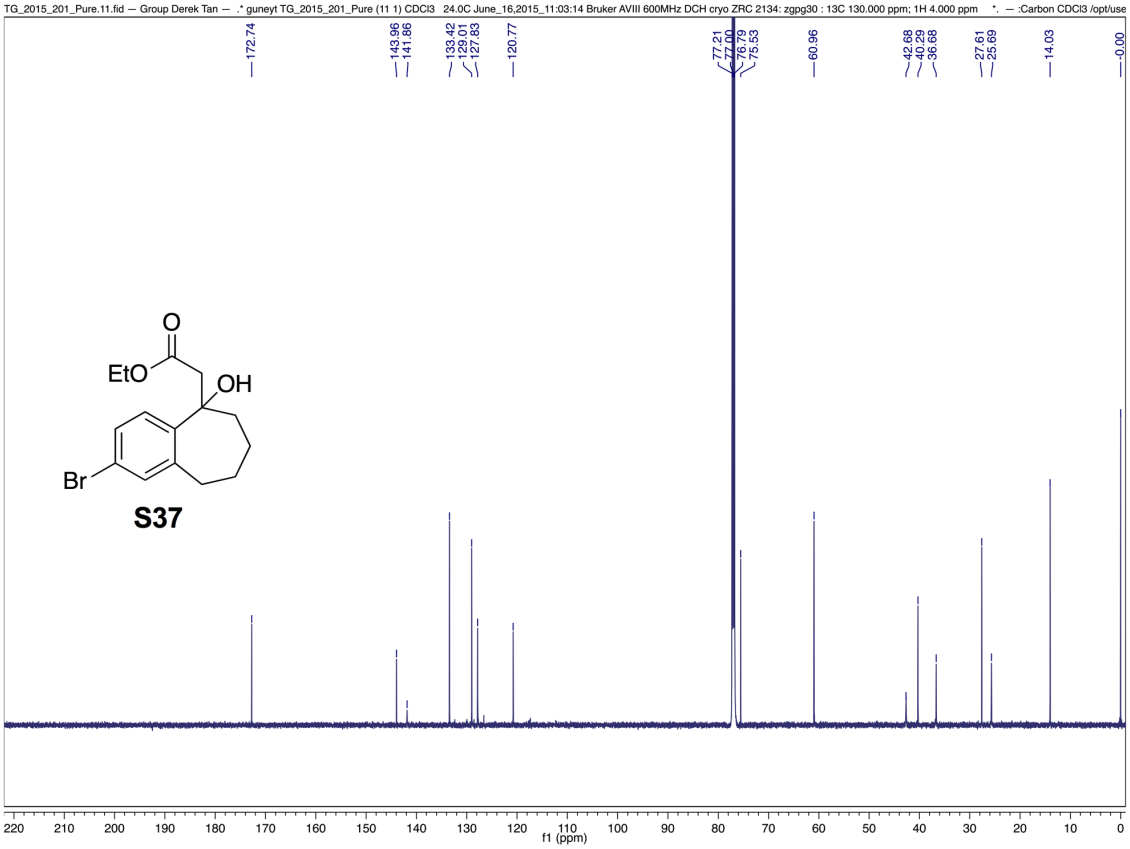

TG_2015_161_P.10.fid — Group Derek Tan — .* guneyt TG_2015_161_P (10 1) CDCl3 24.0C May_24,2015_22:15:51 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 11
O
EtO
OH
F
S35
f1 (ppm)

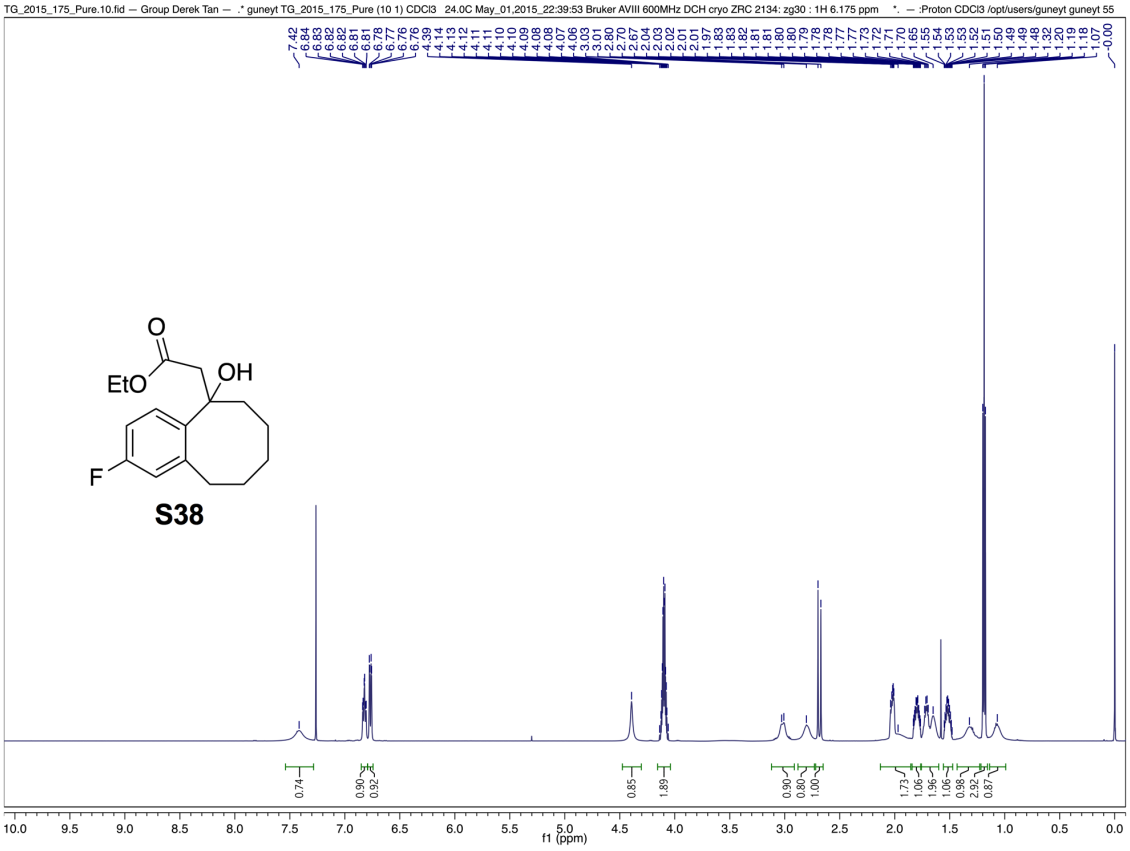

TG_2015_161_P.11.fid — Group Derek Tan — .* guneyt TG_2015_161_P (11 1) CDCl3 24.0C May_24,2015_22:17:58 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/gune
O
EtO
OH
F
S35
f1 (ppm)

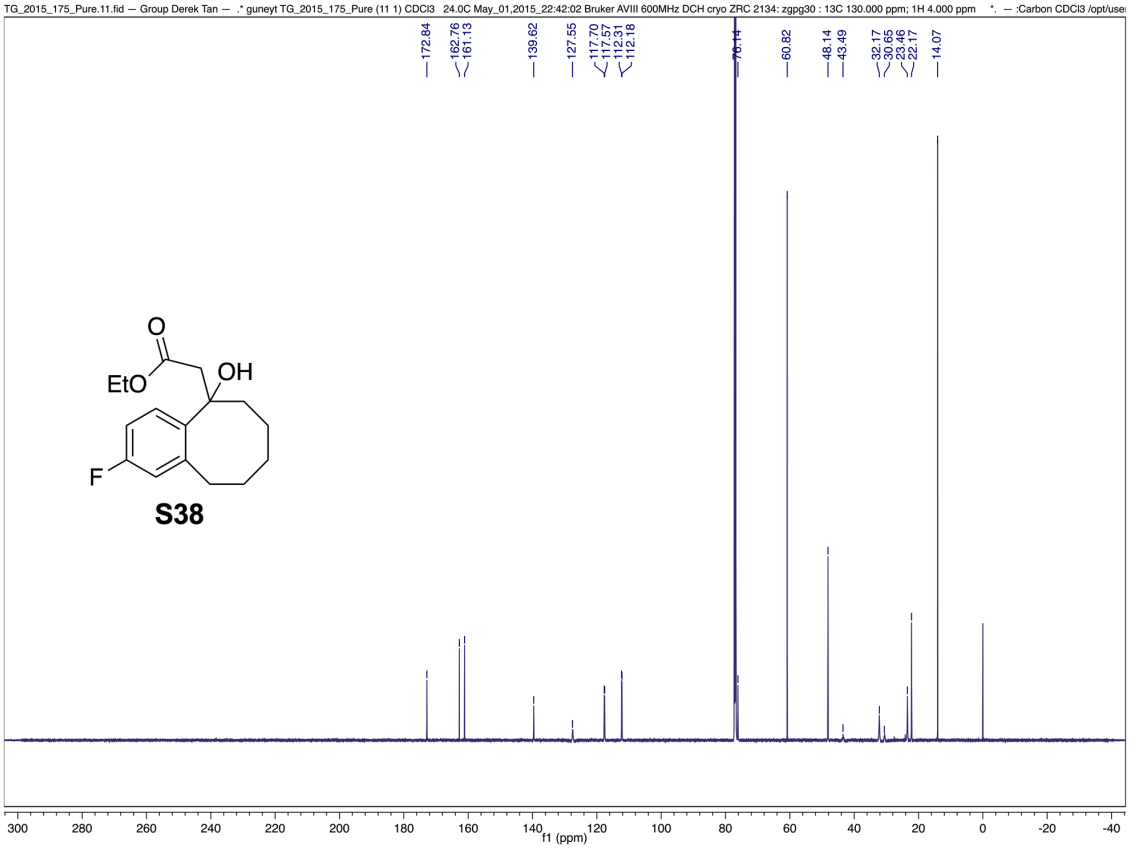

TG_2015_132_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_132_Pure (10 1) CDCl3 24.0C April_03,2015_13:40:33 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 42
O
EtO
OH
Cl
S36
f1 (ppm)

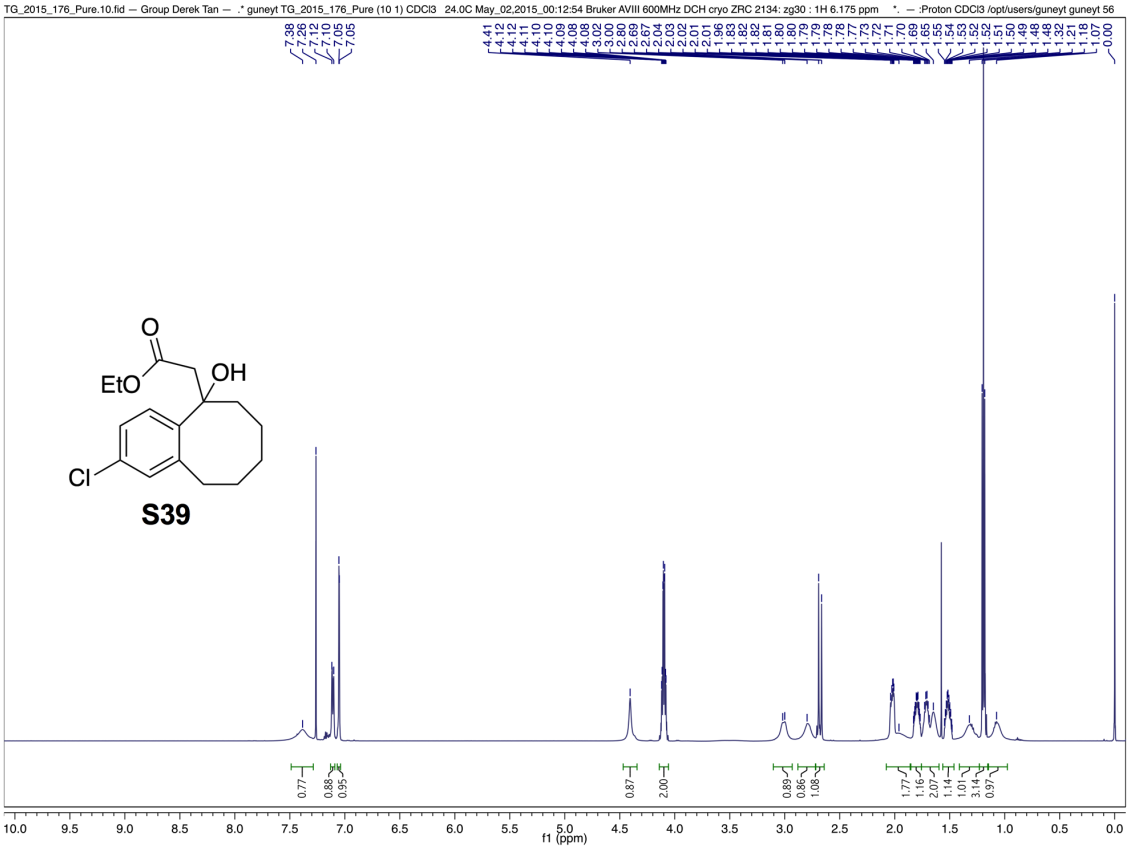

TG_2015_132_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_132_Pure (11 1) CDCl3 24.0C April_03,2015_13:43:20 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
O
EtO
OH
Cl
S36
f1 (ppm)

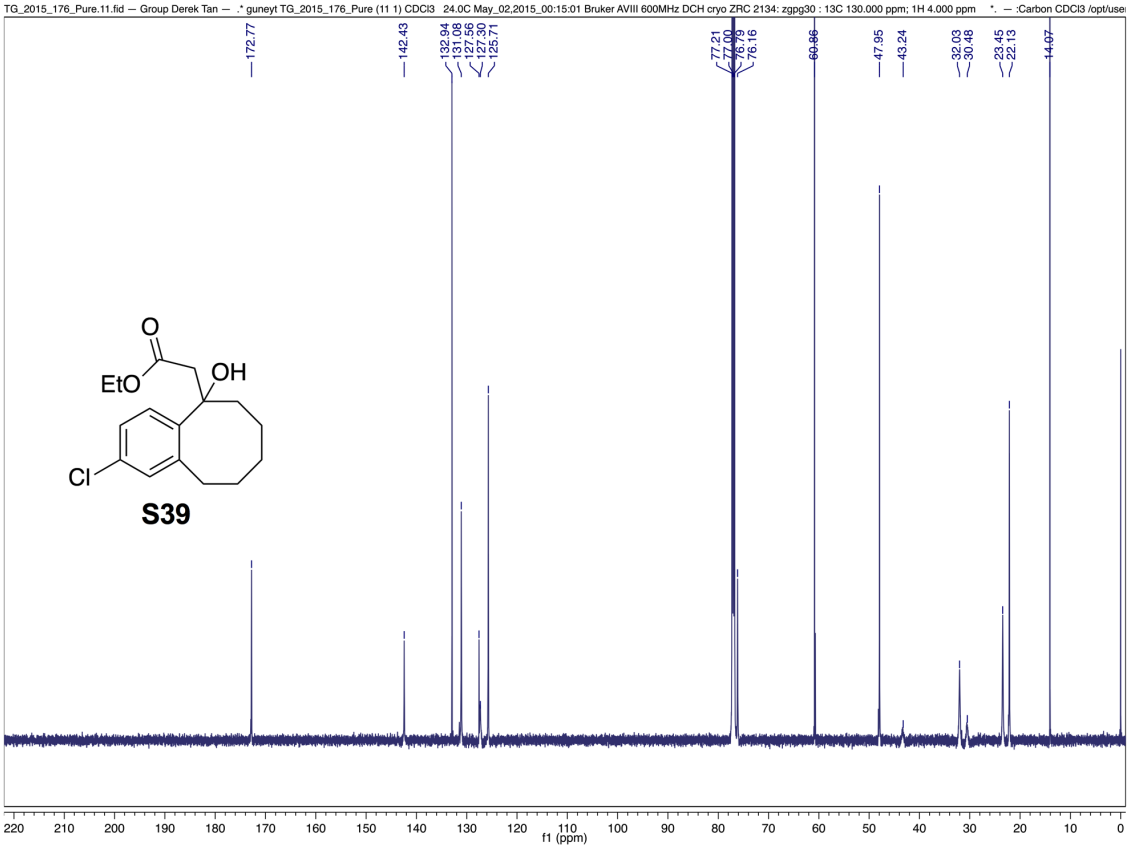

TG_2015_201_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_201_Pure (10 1) CDCl3 24.0C June_16,2015_11:01:38 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 50
O
EtO
OH
Br
S37
f1 (ppm)

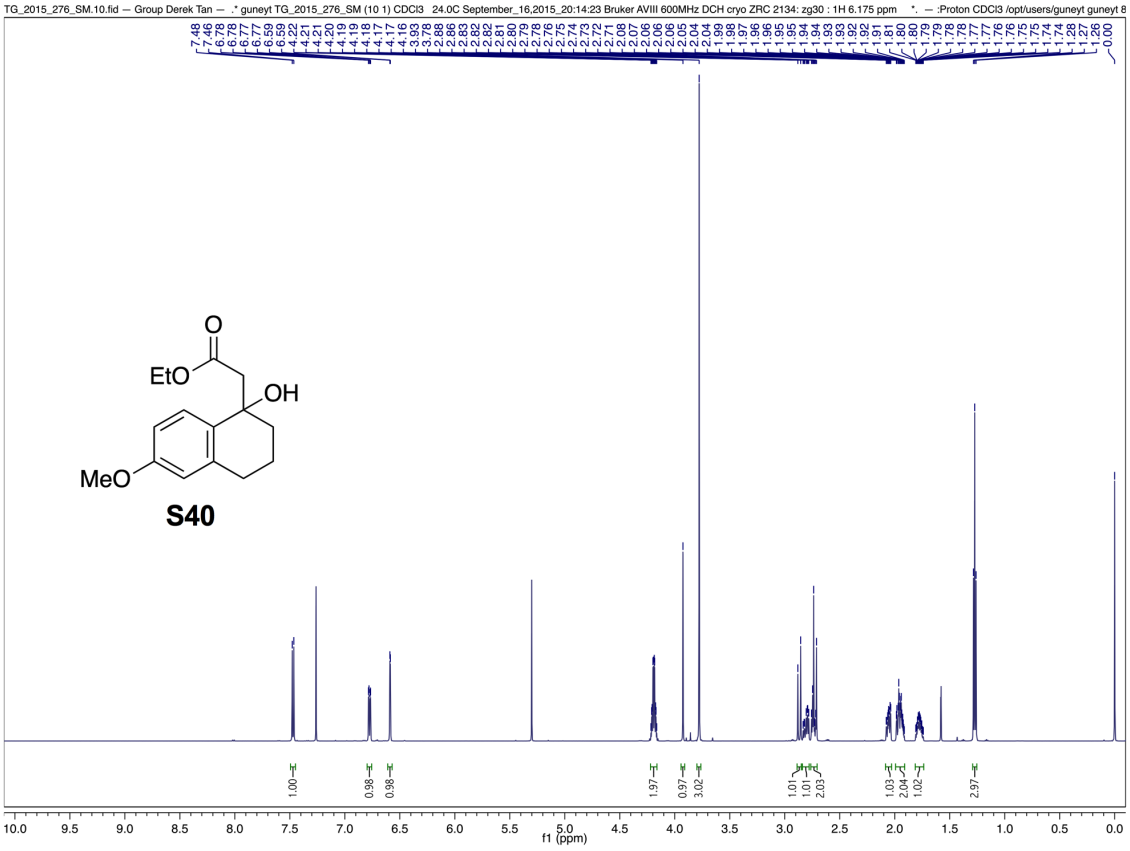

TG_2015_201_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_201_Pure (11 1) CDCl3 24.0C June_16,2015_11:03:14 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
O
EtO
OH
Br
S37
f1 (ppm)

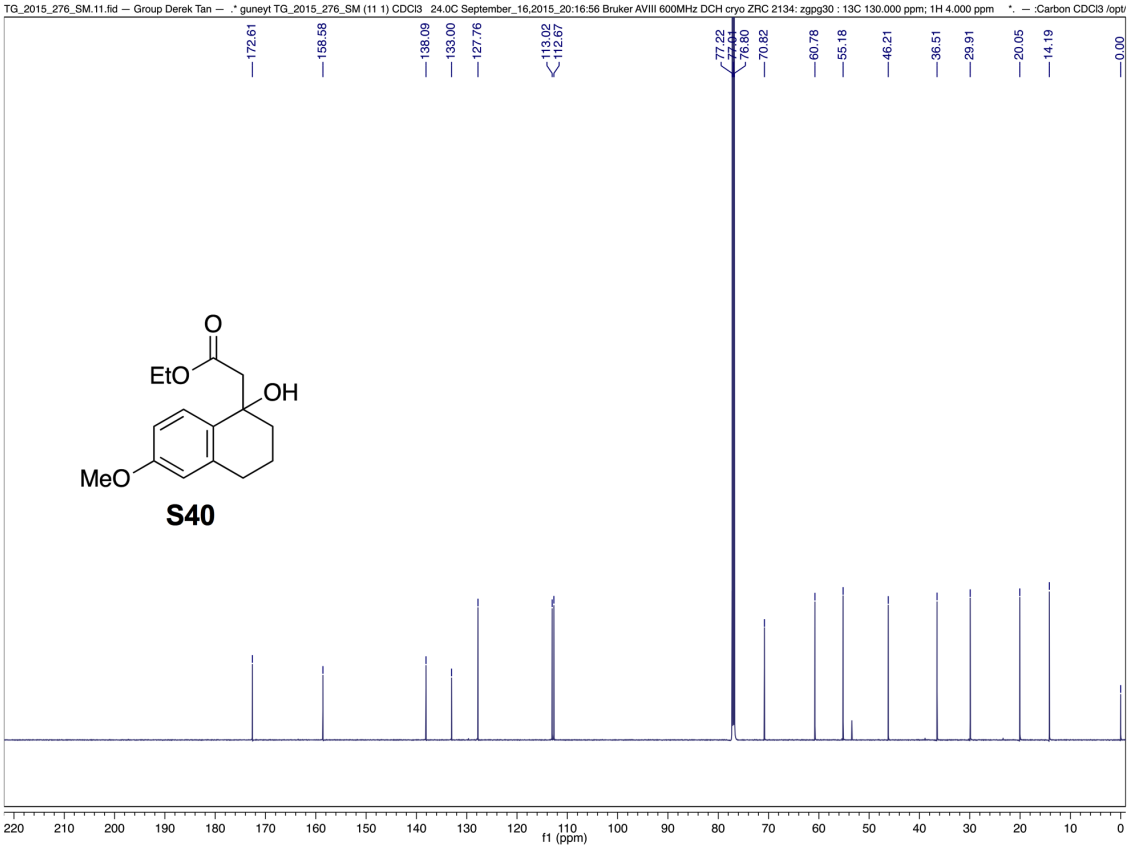

TG_2015_175_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_175_Pure (10 1) CDCl3 24.0C May_01,2015_22:39:53 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 55
O
EtO
OH
F
S38
f1 (ppm)

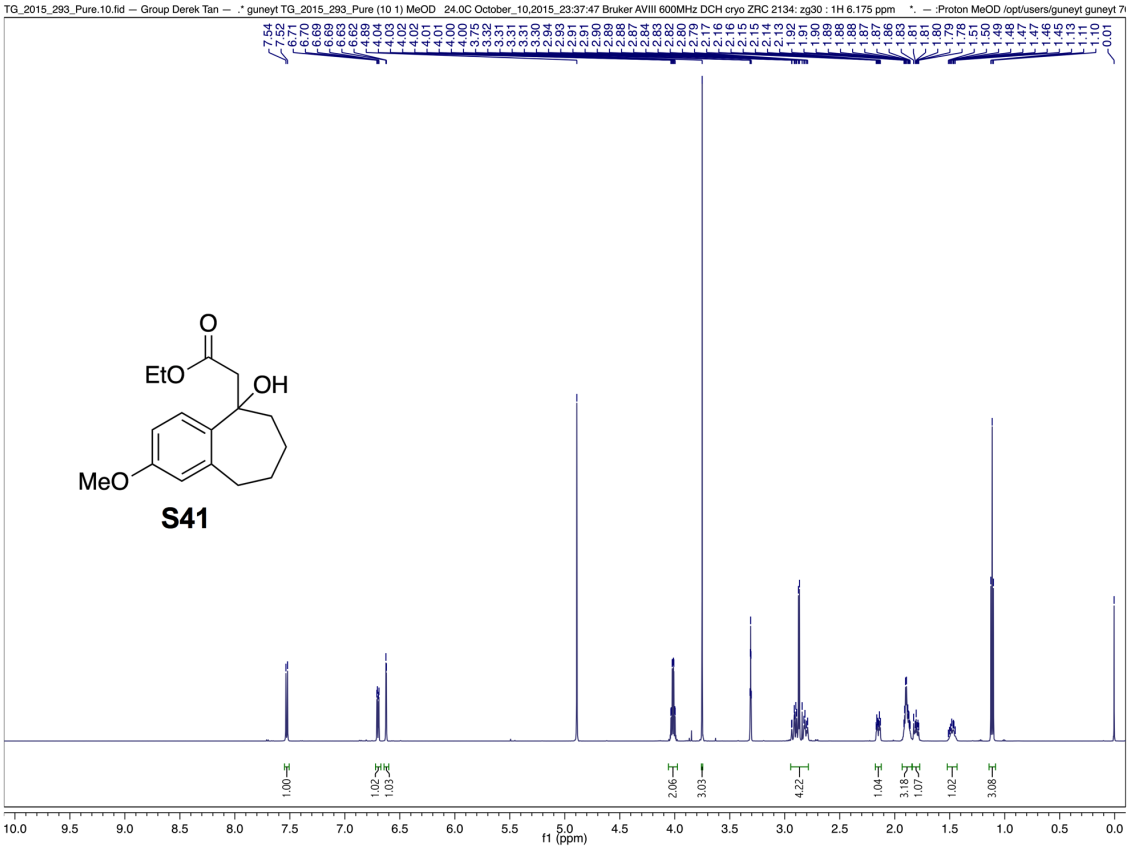

TG_2015_175_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_175_Pure (11 1) CDCl3 24.0C May_01,2015_22:42:02 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
O
EtO
OH
F
S38
f1 (ppm)

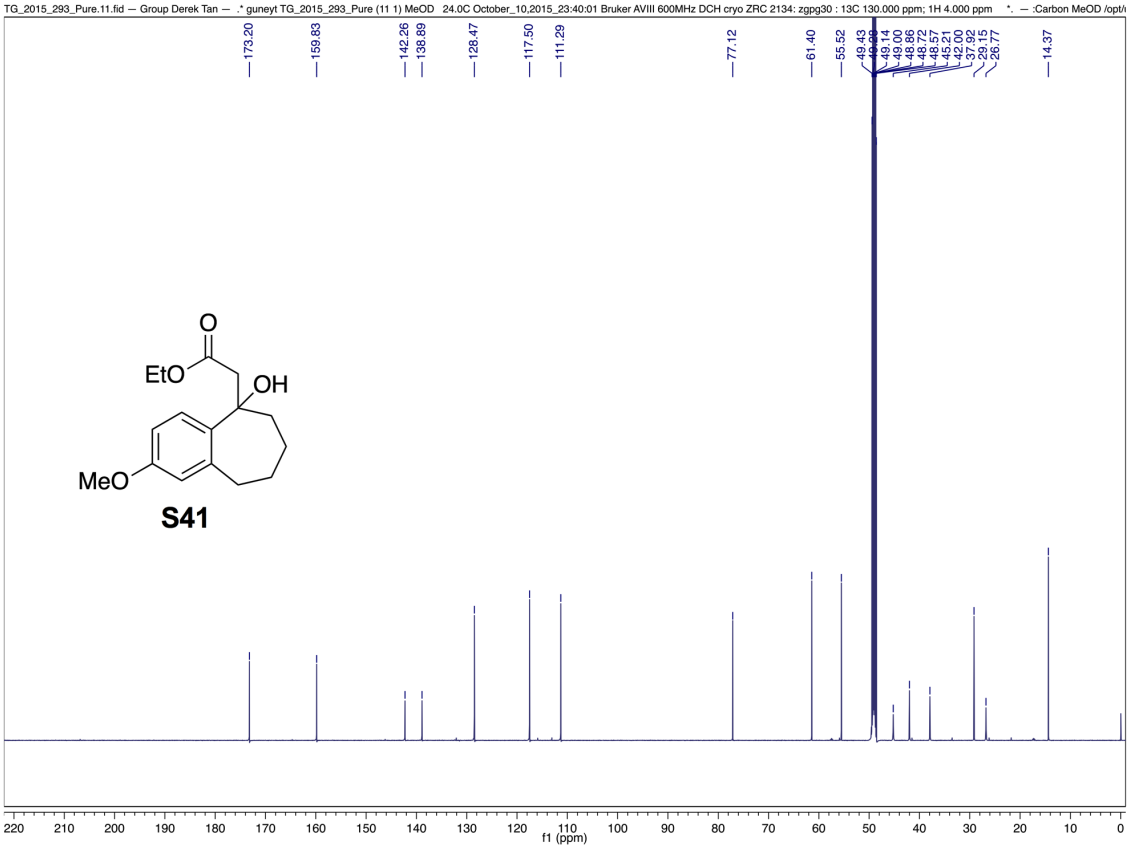

TG_2015_176_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_176_Pure (10 1) CDCl3 24.0C May_02,2015_00:12:54 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 56
O
EtO
OH
Cl
S39
f1 (ppm)

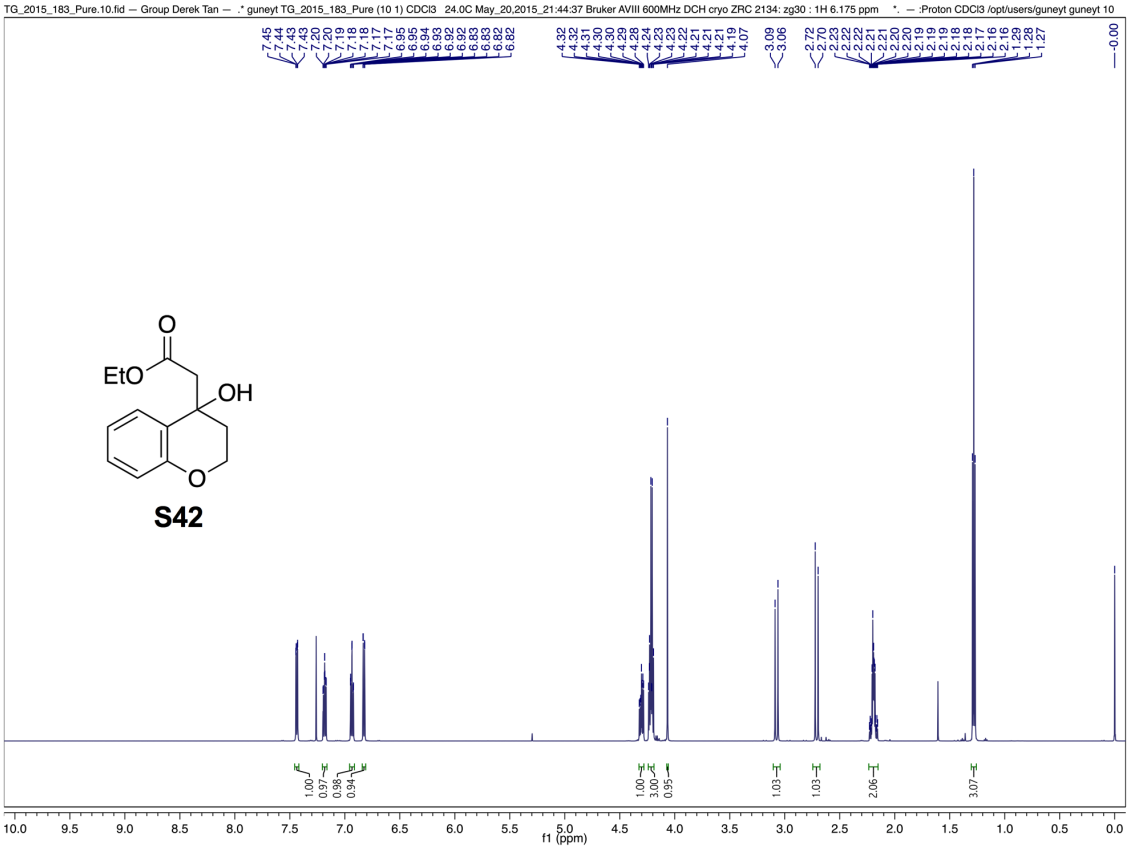

TG_2015_176_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_176_Pure (11 1) CDCl3 24.0C May_02,2015_00:15:01 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/user
O
EtO
OH
Cl
S39
f1 (ppm)

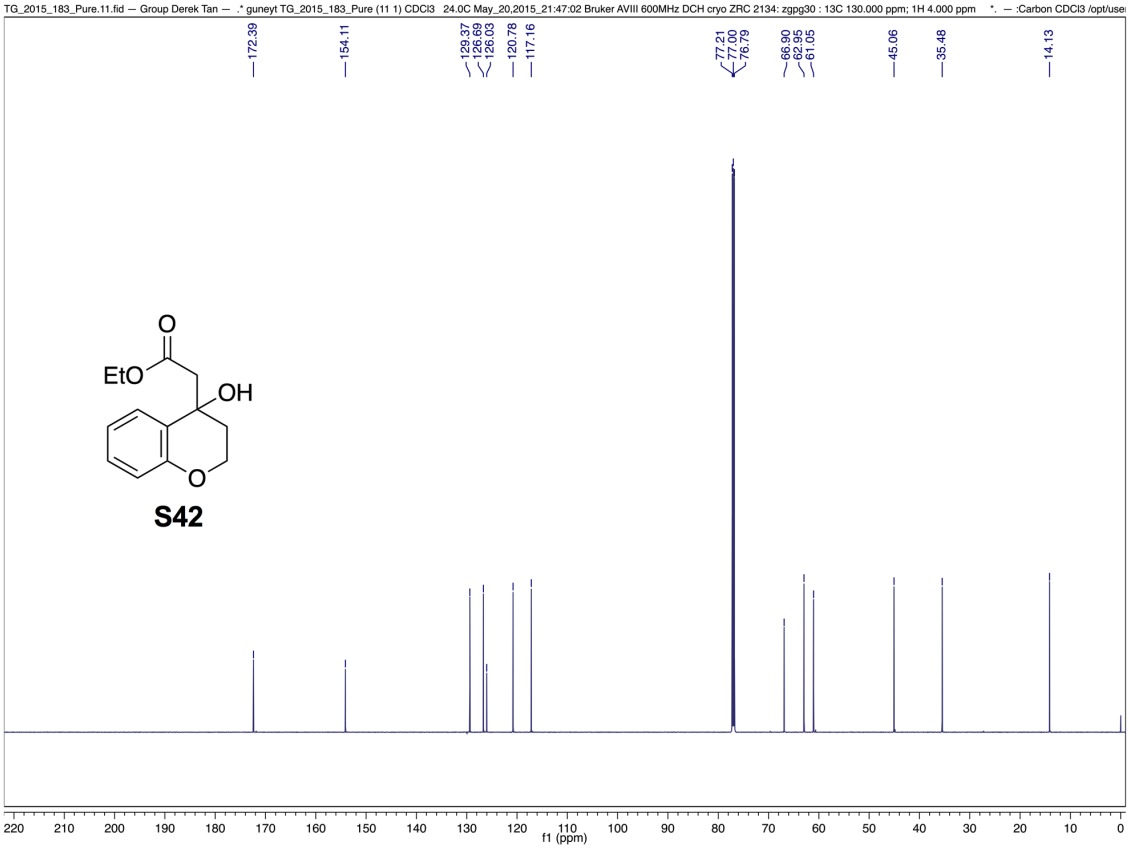

TG_2015_276_SM.10.fid — Group Derek Tan — .* guneyt TG_2015_276_SM (10 1) CDCl3 24.0C September_16,2015_20:14:23 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 8
O
EtO
OH
MeO
S40
f1 (ppm)

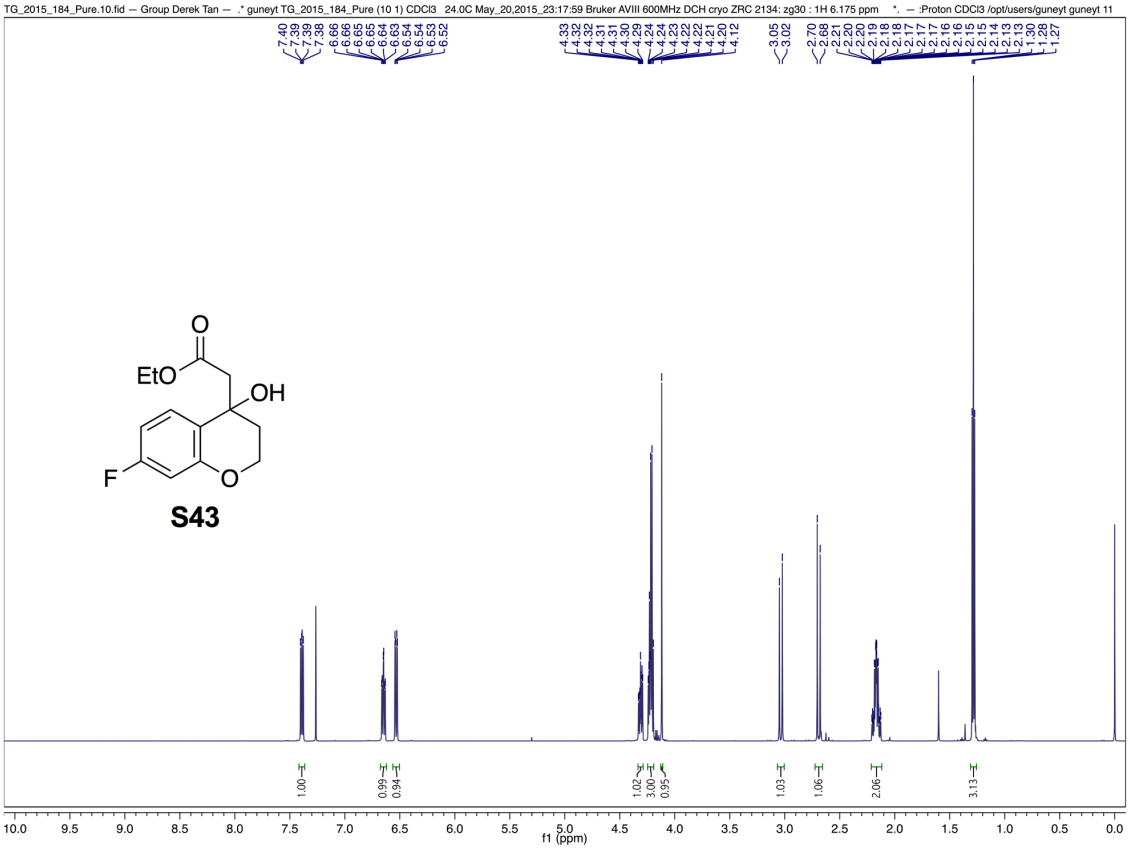

TG_2015_276_SM.11.fid — Group Derek Tan — .* guneyt TG_2015_276_SM (11 1) CDCl3 24.0C September_16,2015_20:16:56 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/
O
EtO
OH
MeO
S40
f1 (ppm)

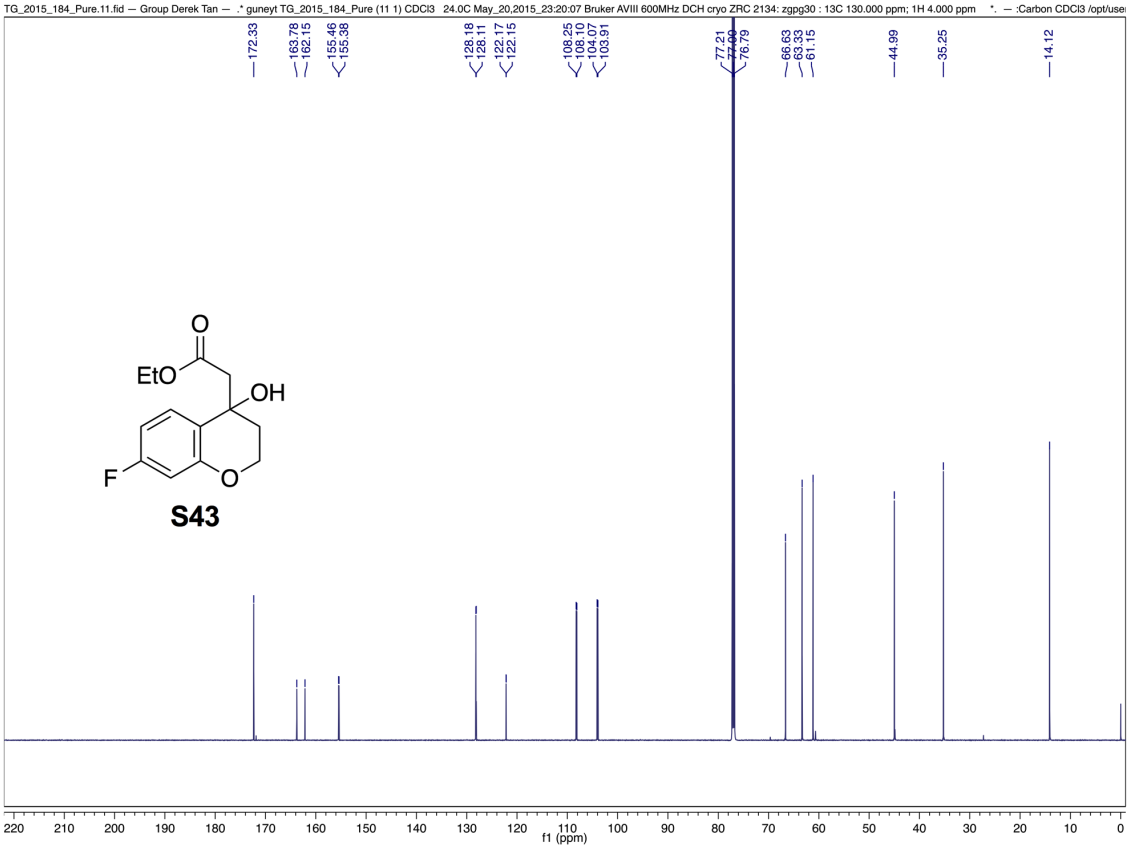

TG_2015_293_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_293_Pure (10 1) MeOD 24.0C October_10,2015_23:37:47 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
O
EtO
OH
MeO
S41
f1 (ppm)

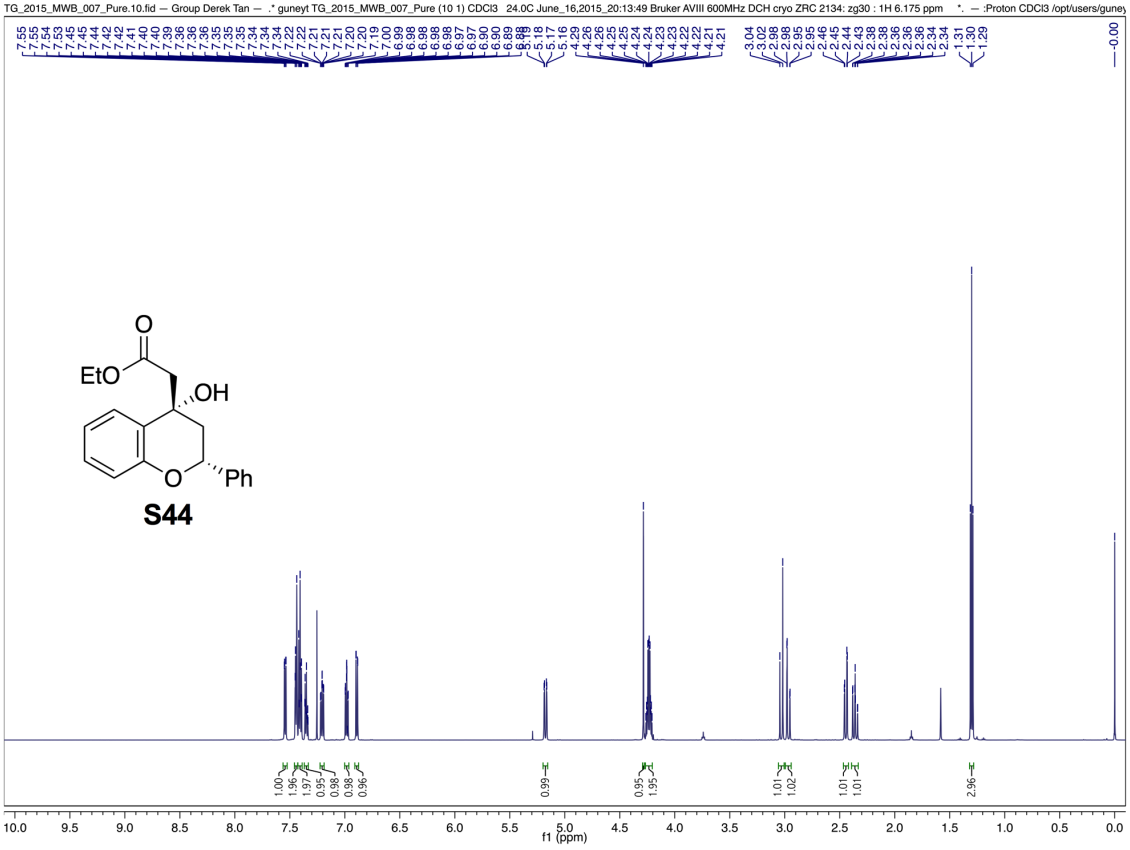

TG_2015_293_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_293_Pure (11 1) MeOD 24.0C October_10,2015_23:40:01 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm
O
EtO
OH
MeO
S41
f1 (ppm)

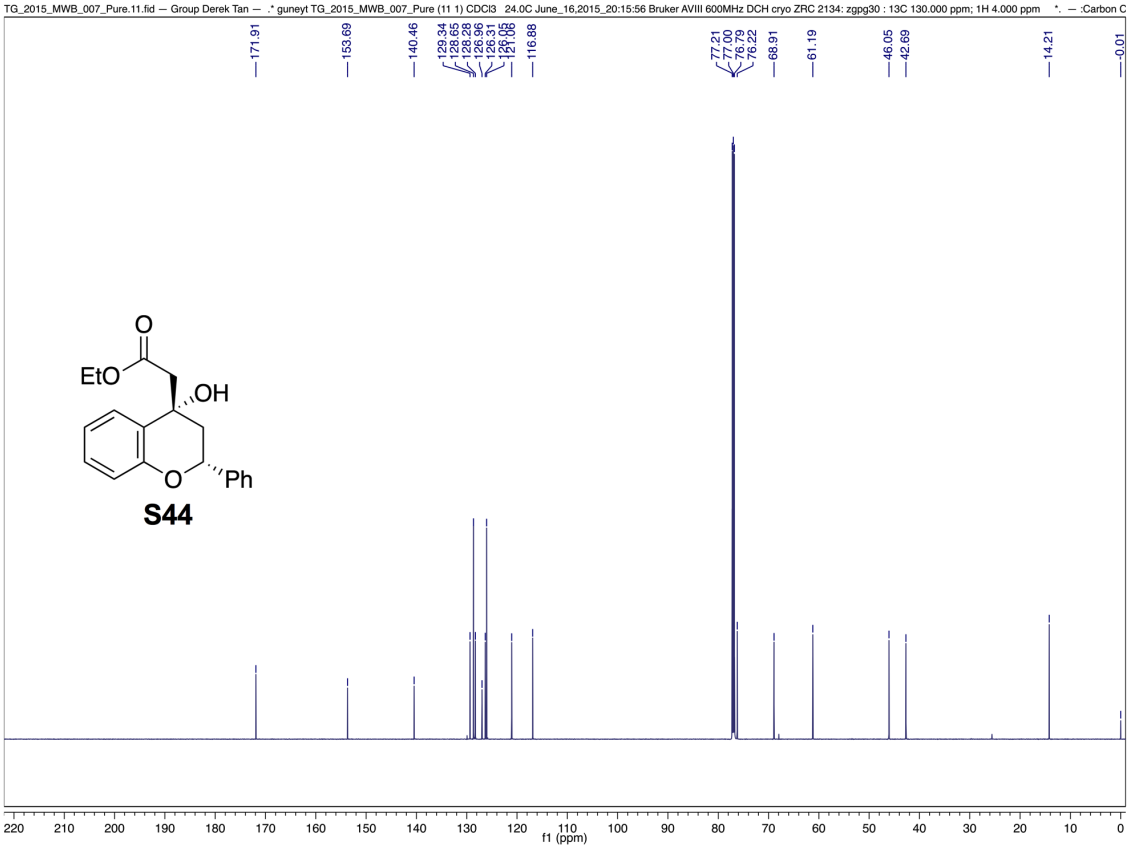

TG_2015_183_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_183_Pure (10 1) CDCl3 24.0C May_20,2015_21:44:37 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 10
7.45 7.44 7.43 7.43 7.20 7.20 7.19 7.18 7.17 7.17 7.17 6.95 6.94 6.93 6.92 6.83 6.83 6.82 6.82
4.32 4.31 4.31 4.30 4.30 4.29 4.28 4.24 4.23 4.22 4.21 4.21 4.21 4.19 4.07
3.09 3.06
2.72 2.70 2.23 2.22 2.22 2.21 2.21 2.20 2.19 2.19 2.19 2.18 2.17 2.16 2.16 1.29 1.28 1.27
-0.00
1.00 0.97 0.98 0.94 1.00 3.00 0.95 1.03 1.03 2.06 3.07
f1 (ppm)
EtO
O
OH
O
S42

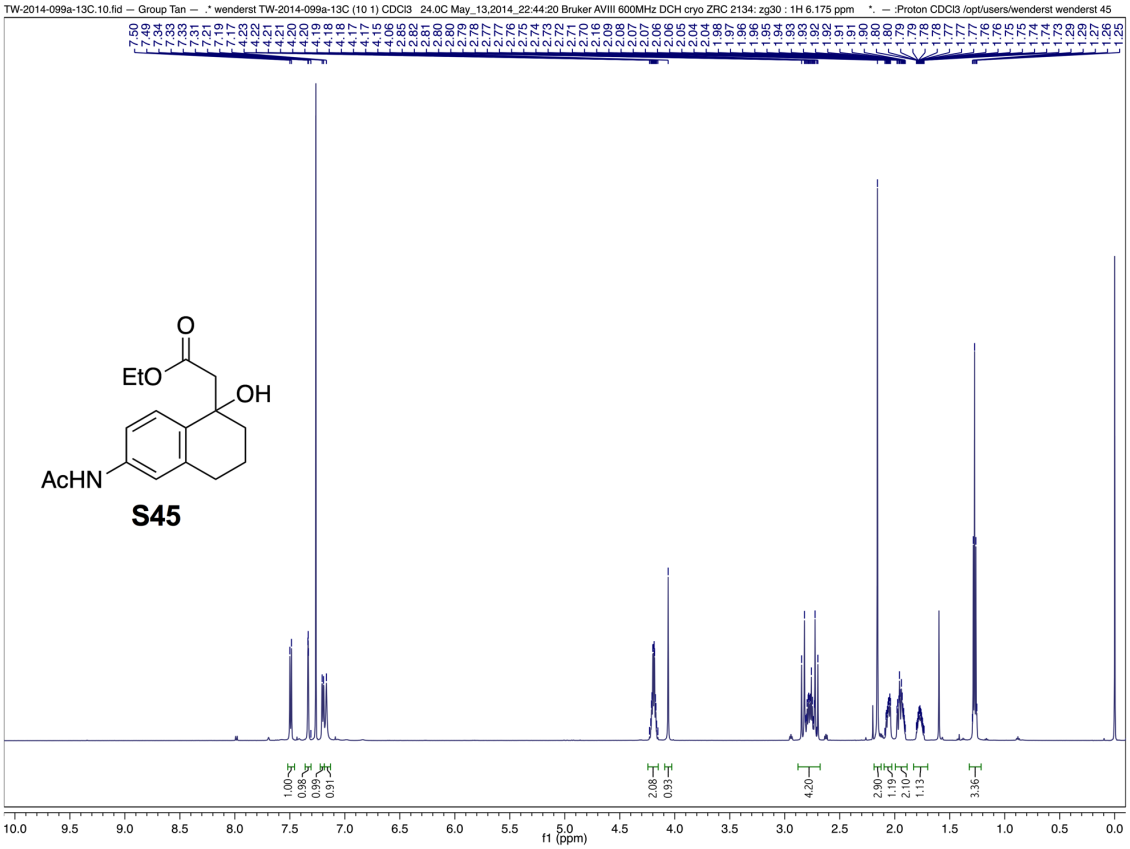

TG_2015_183_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_183_Pure (11 1) CDCl3 24.0C May_20,2015_21:47:02 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
172.39
154.11
129.37 128.69 128.03
120.78
117.16
77.21 77.00 76.79
66.90 62.95 61.05
45.06
35.48
14.13
f1 (ppm)
EtO
O
OH
O
S42

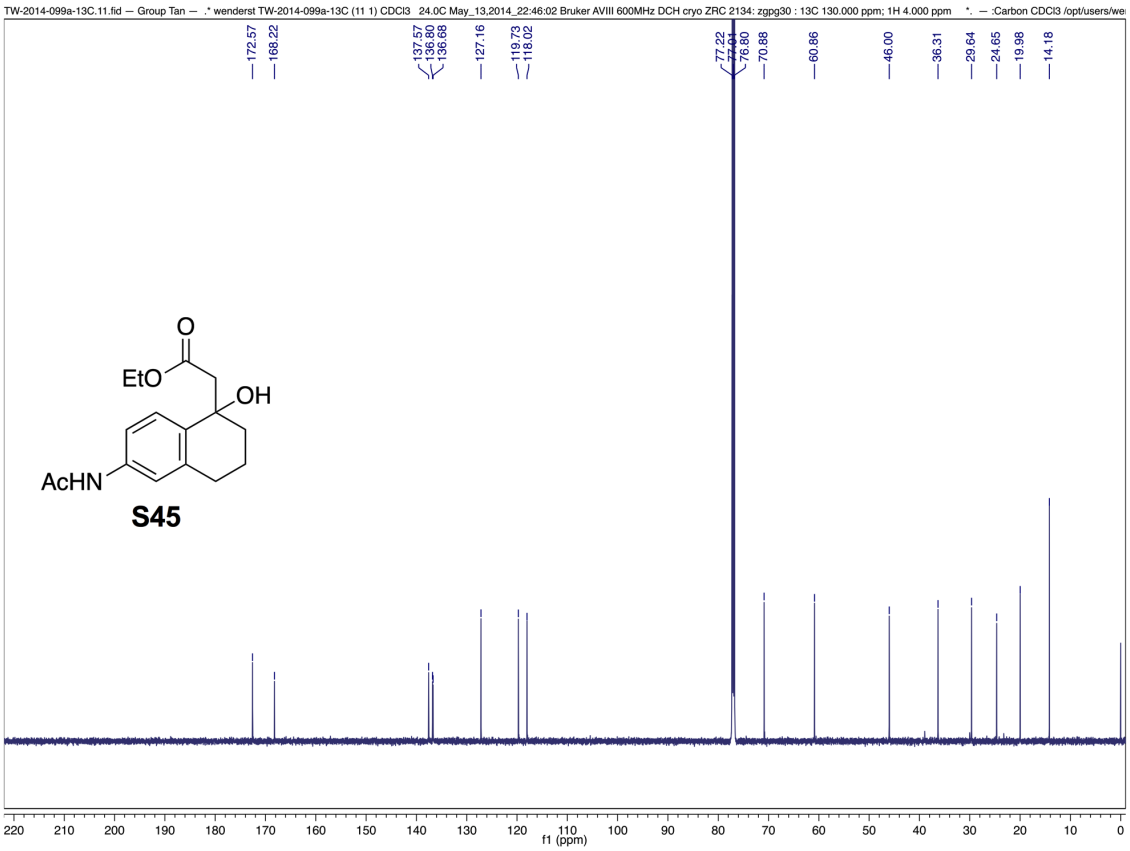

TG_2015_184_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_184_Pure (10 1) CDCl3 24.0C May_20,2015_23:17:59 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 11
7.40
7.39
7.39
7.38
6.66
6.66
6.65
6.65
6.64
6.63
6.54
6.53
6.52
4.33
4.32
4.32
4.31
4.30
4.29
4.24
4.24
4.23
4.22
4.21
4.20
4.12
3.05
3.02
2.70
2.68
2.21
2.20
2.20
2.19
2.18
2.17
2.17
2.17
2.16
2.16
2.15
2.15
2.14
2.13
2.13
1.30
1.28
1.27
1.00
0.99
0.94
1.02
3.00
0.95
1.03
1.06
2.06
3.13
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)
O
EtO
OH
F
O
S43

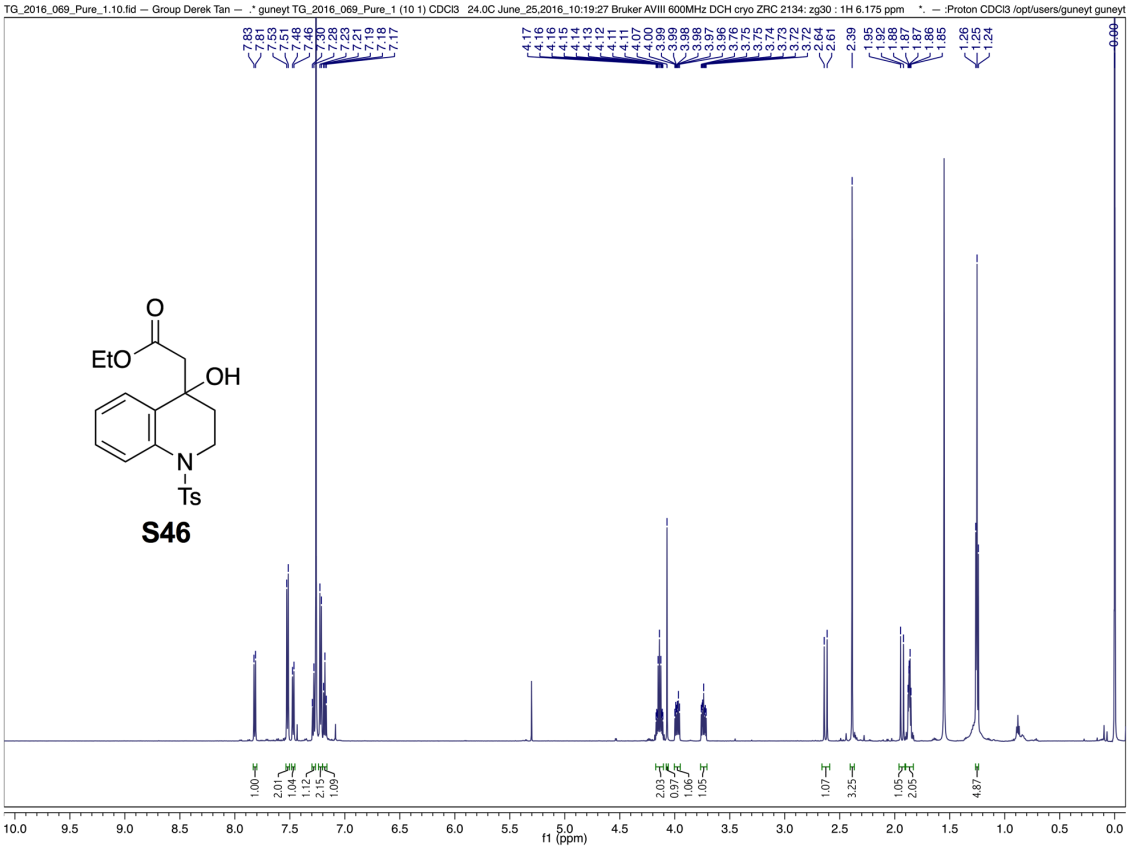

TG_2015_184_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_184_Pure (11 1) CDCl3 24.0C May_20,2015_23:20:07 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
172.33
163.78
162.15
155.46
155.38
128.18
128.11
122.17
122.15
108.25
108.10
104.07
103.91
77.21
77.00
76.79
66.63
66.33
61.15
44.99
35.25
14.12
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
EtO
OH
F
O
S43

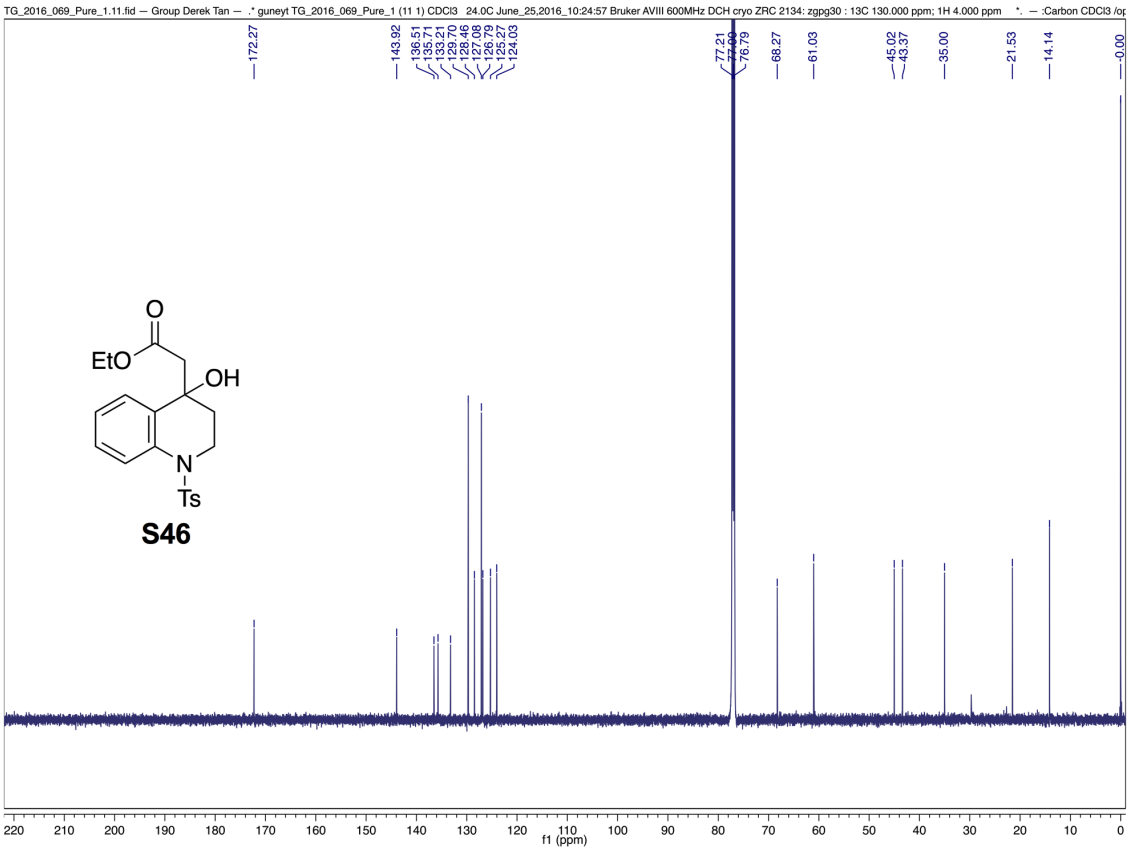

TG_2015_MWB_007_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_MWB_007_Pure (10 1) CDCl3 24.0C June_16,2015_20:13:49 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
EtO
OH
O
Ph
S44
f1 (ppm)

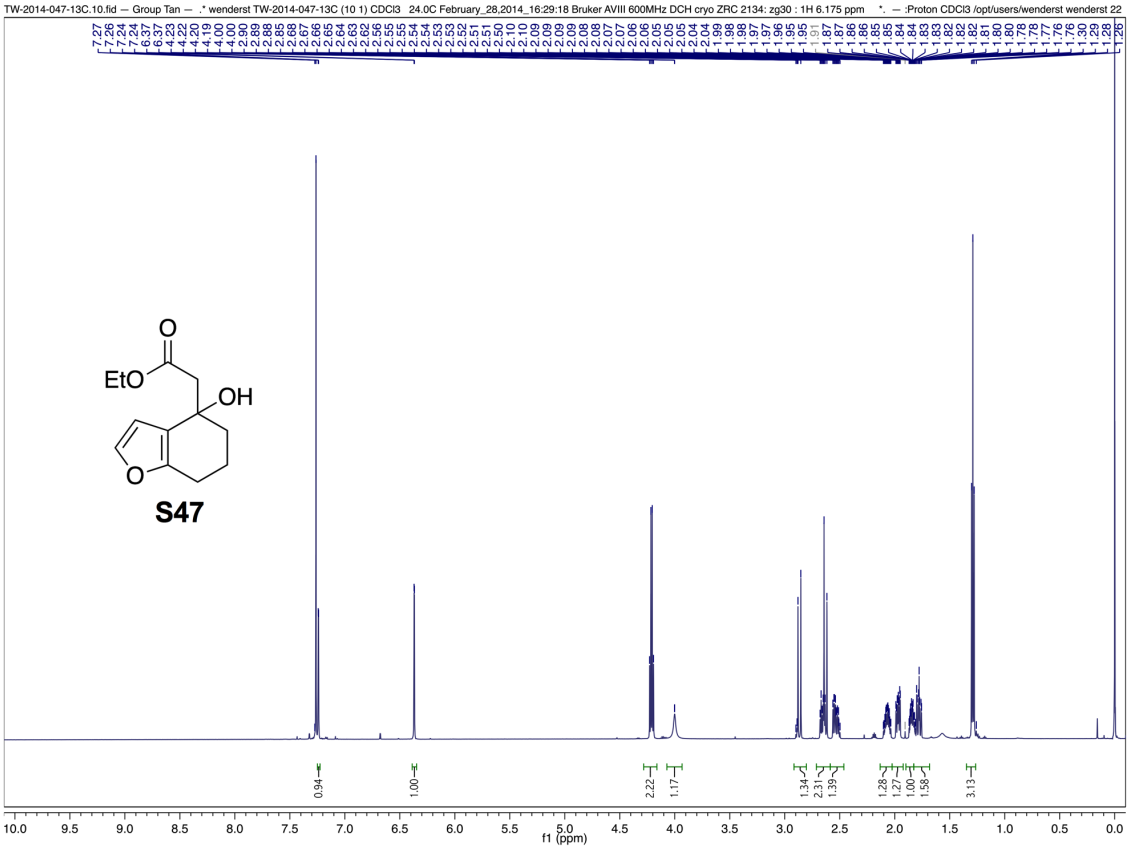

TG_2015_MWB_007_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_MWB_007_Pure (11 1) CDCl3 24.0C June_16,2015_20:15:56 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm
EtO
OH
O
Ph
S44
f1 (ppm)

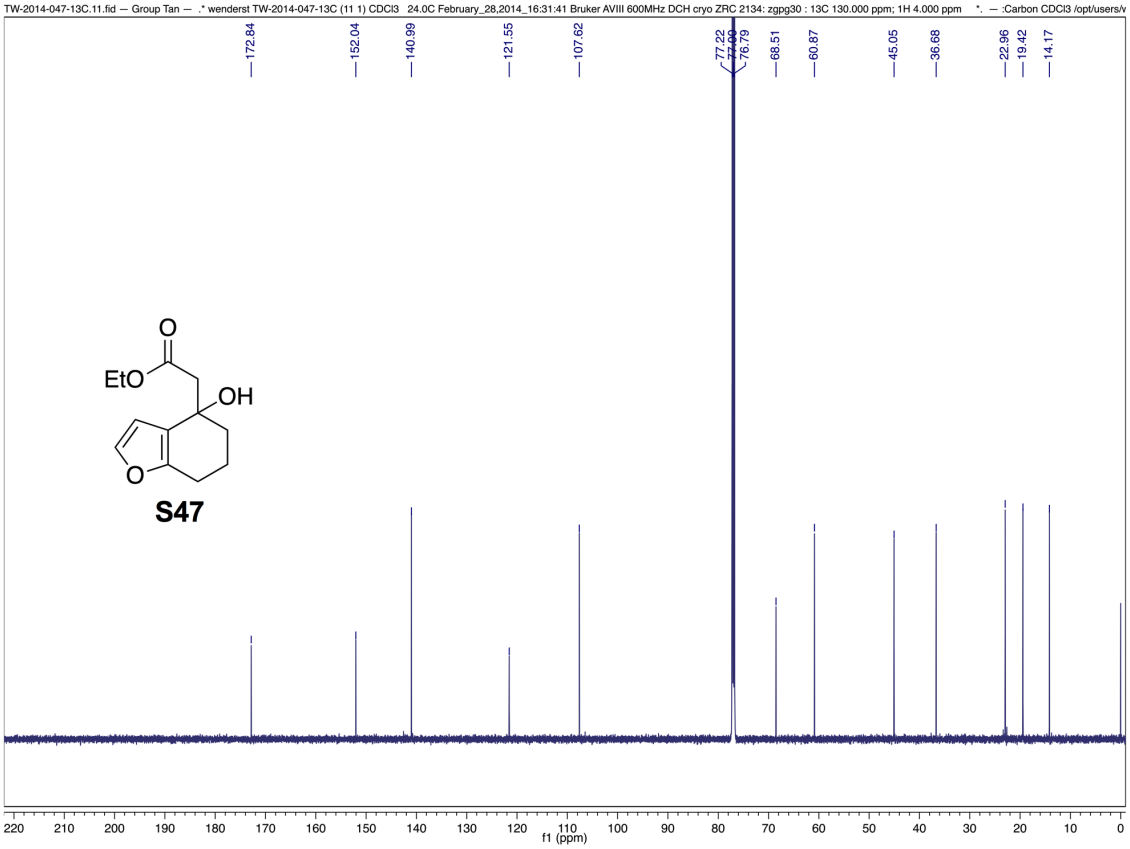

TW-2014-099a-13C.10.fid — Group Tan — .* wenderst TW-2014-099a-13C (10 1) CDCl3 24.0C May_13,2014_22:44:20 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm :Proton CDCl3 /opt/users/wenderst wenderst 45
O
EtO
OH
AcHN
S45
1.00
0.98
0.99
0.91
2.08
0.93
4.20
2.90
1.19
2.10
1.13
3.36
f1 (ppm)

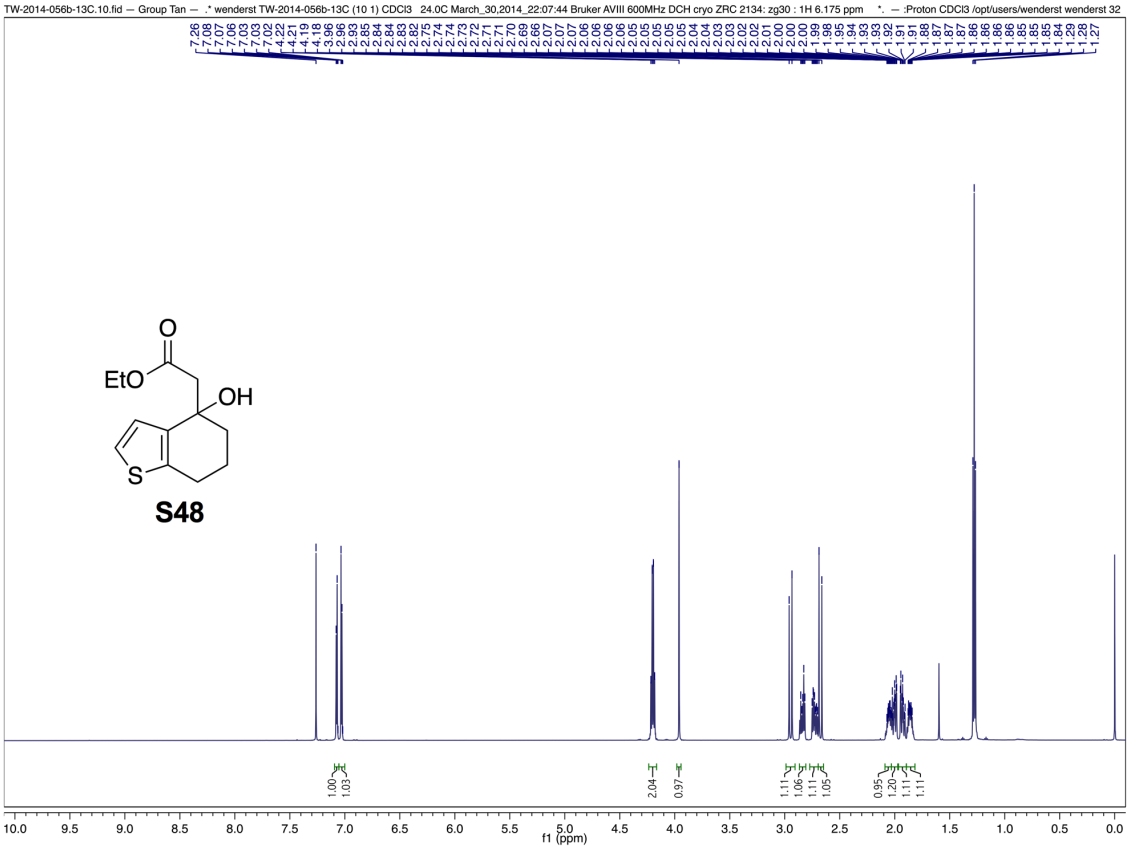

TW-2014-099a-13C.11.fid — Group Tan — .* wenderst TW-2014-099a-13C (11 1) CDCl3 24.0C May_13,2014_22:46:02 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm :Carbon CDCl3 /opt/users/we
172.57
168.22
137.57
136.80
136.68
127.16
119.73
118.02
77.22
77.01
76.80
70.88
60.86
46.00
36.31
29.64
24.65
19.98
14.18
O
EtO
OH
AcHN
S45
f1 (ppm)

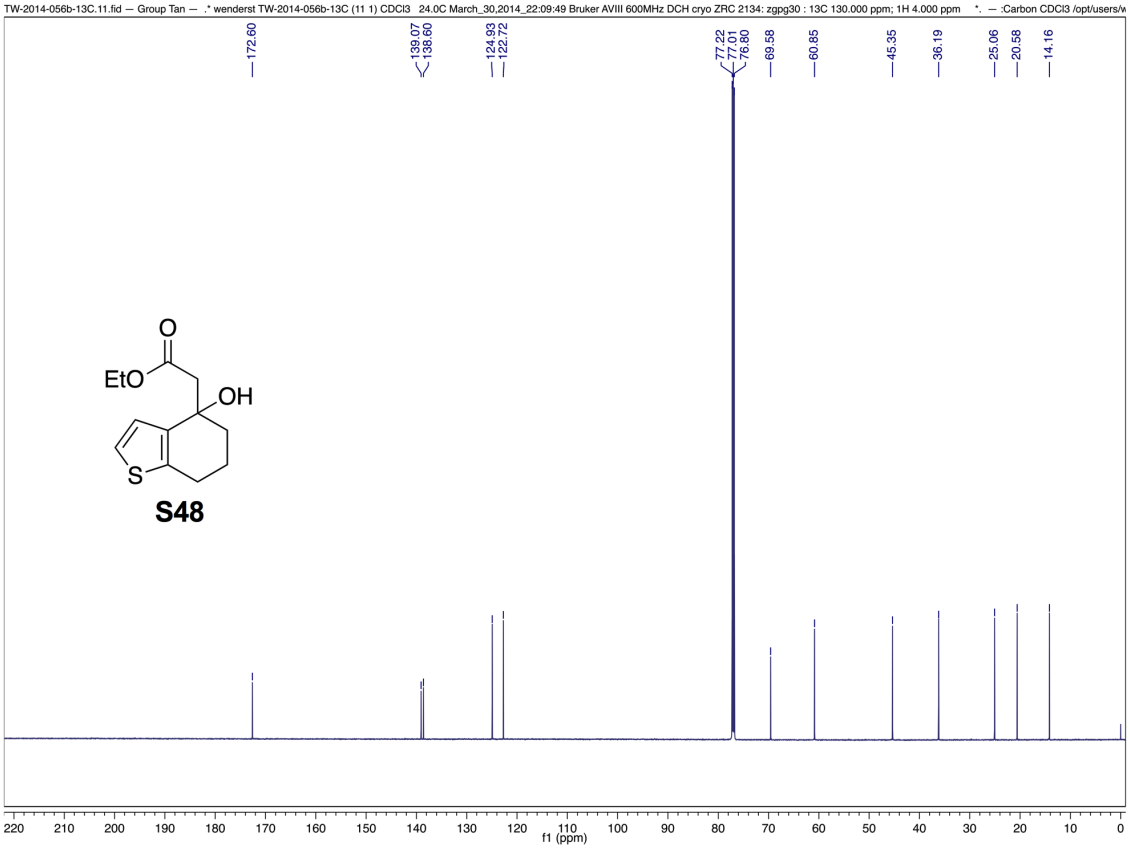

TG_2016_069_Pure_1.10.fid — Group Derek Tan — .* guneyt TG_2016_069_Pure_1 (10 1) CDCl3 24.0C June_25,2016_10:19:27 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt
EtO
O
OH
N
Ts
S46
f1 (ppm)

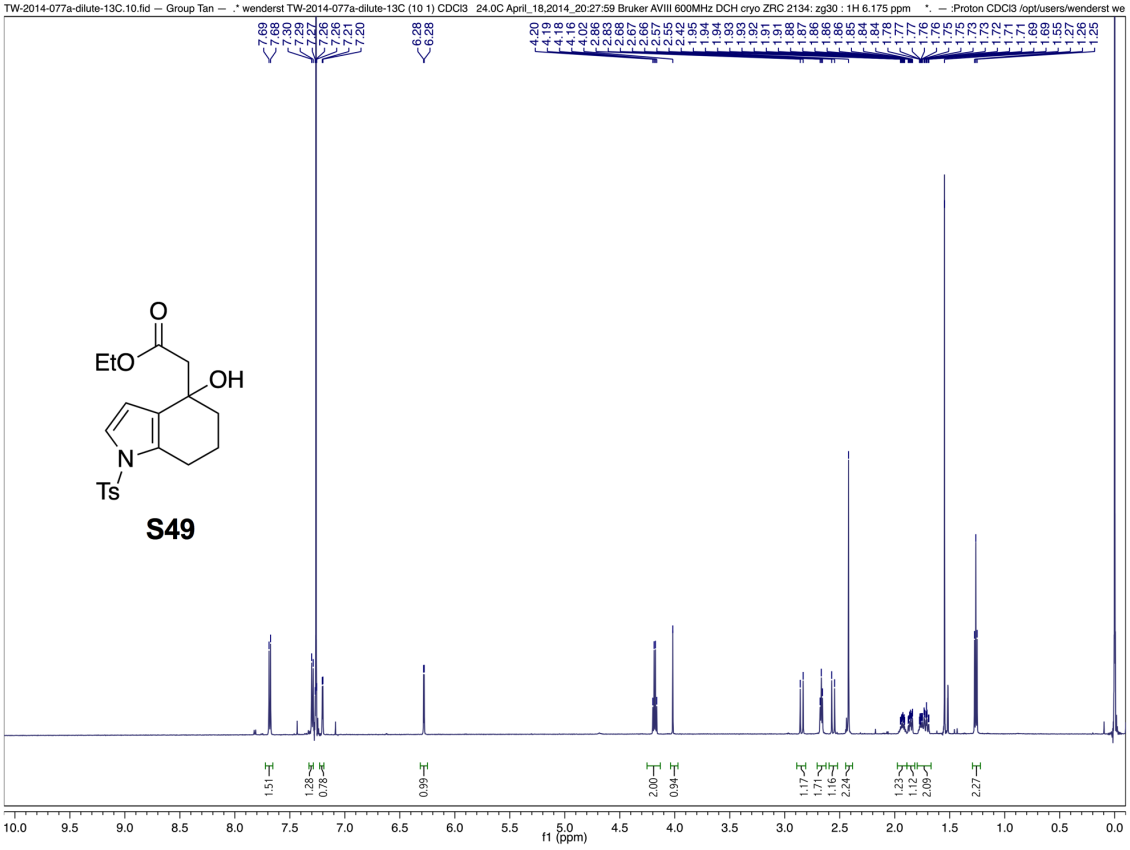

TG_2016_069_Pure_1.11.fid — Group Derek Tan — .* guneyt TG_2016_069_Pure_1 (11 1) CDCl3 24.0C June_25,2016_10:24:57 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /op
EtO
O
OH
N
Ts
S46
f1 (ppm)

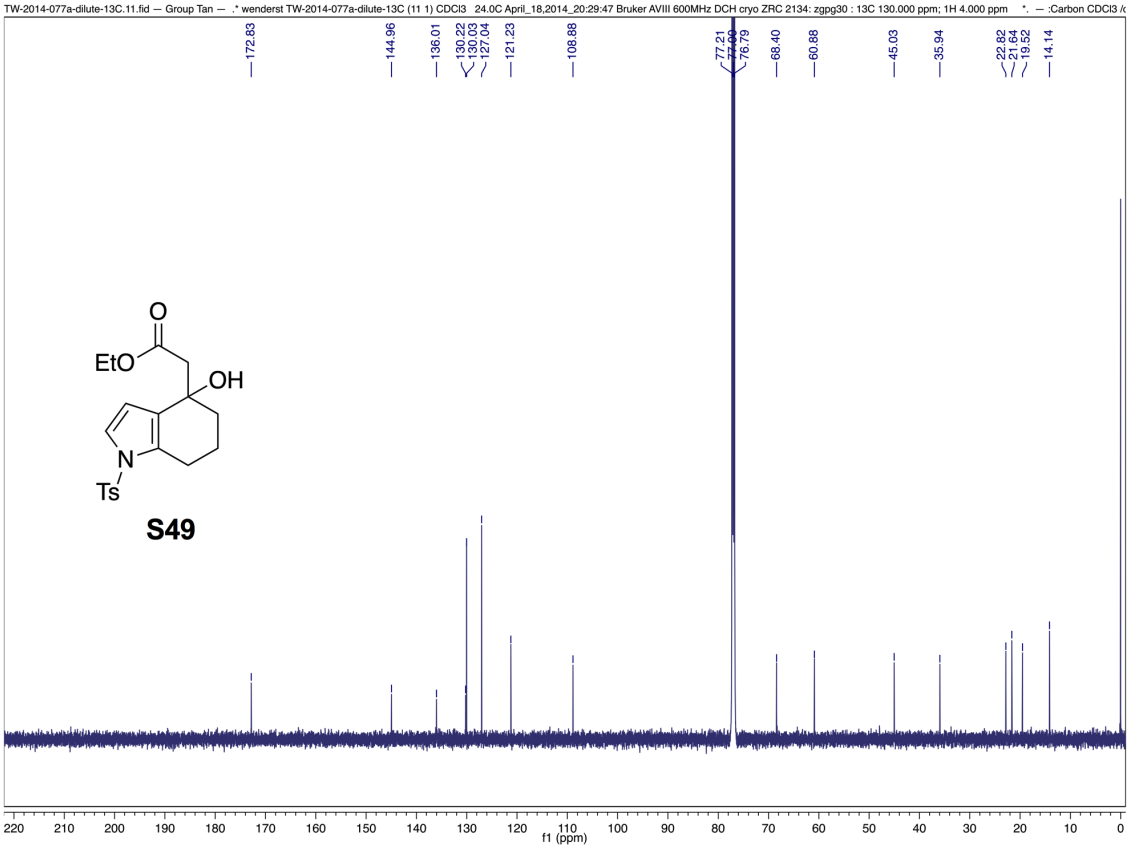

TW-2014-047-13C.10.fid — Group Tan — .* wenderst TW-2014-047-13C (10 1) CDCl3 24.0C February_28,2014_16:29:18 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 22
EtO
O
OH
O
S47
0.94
1.00
2.22
1.17
1.34
2.31
1.39
1.28
1.27
1.00
1.58
3.13
f1 (ppm)

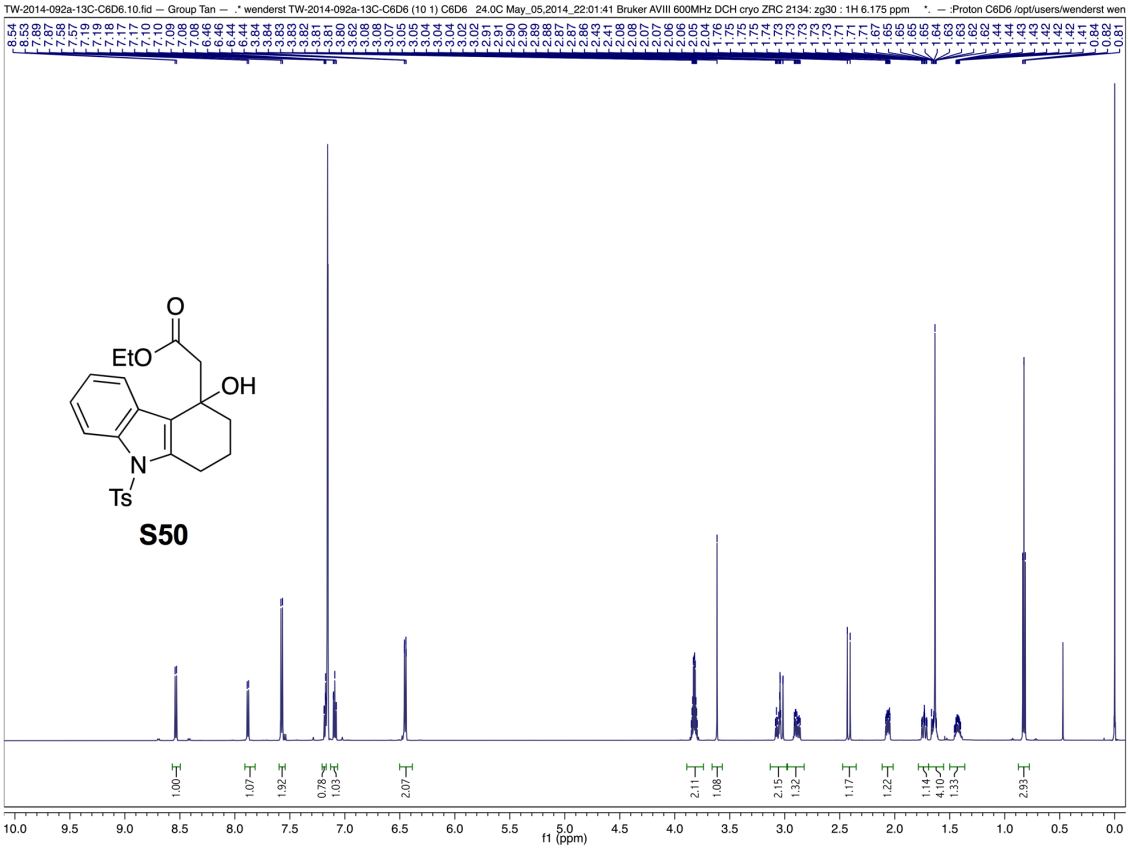

TW-2014-047-13C.11.fid — Group Tan — .* wenderst TW-2014-047-13C (11 1) CDCl3 24.0C February_28,2014_16:31:41 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/v
172.84
152.04
140.99
121.55
107.62
77.22
77.00
76.79
68.51
60.87
45.05
36.68
22.96
19.42
14.17
EtO
O
OH
O
S47
f1 (ppm)

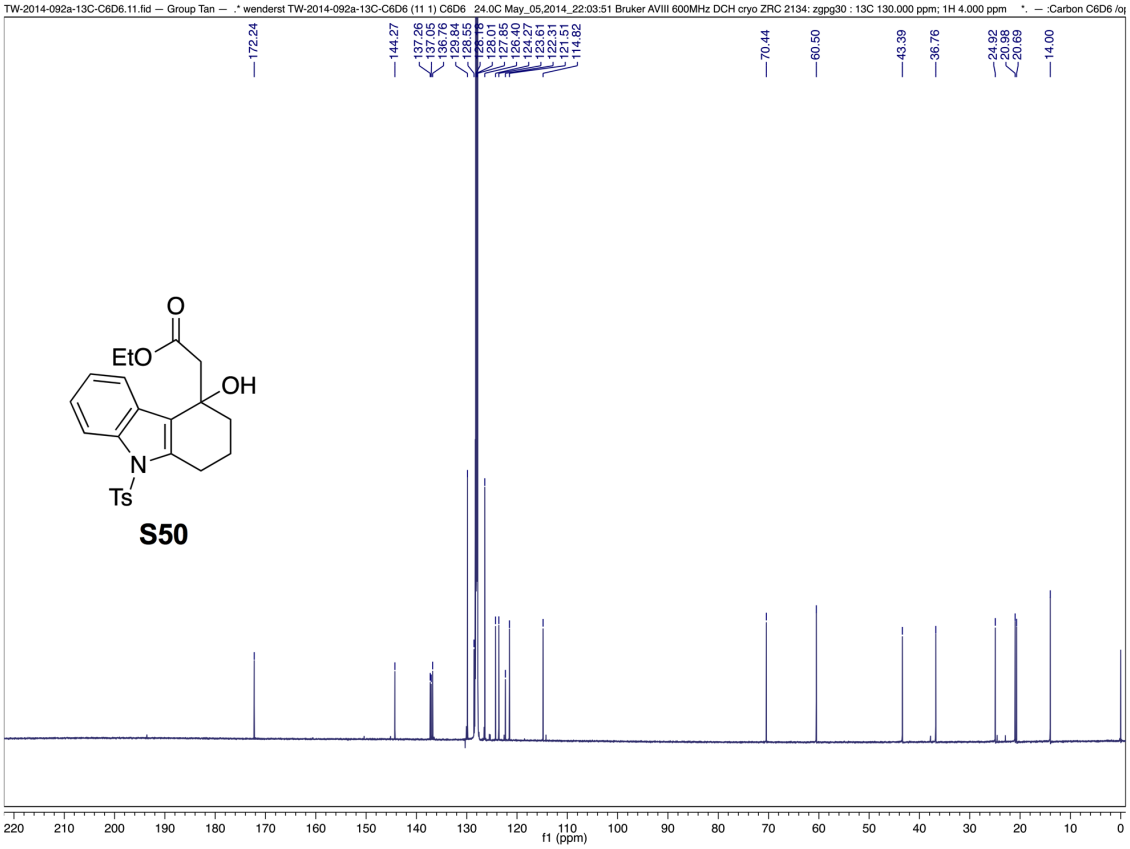

TW-2014-056b-13C.10.fid — Group Tan — .* wenderst TW-2014-056b-13C (10 1) CDCl3 24.0C March_30,2014_22:07:44 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 32
O
EtO
OH
S
S48
f1 (ppm)

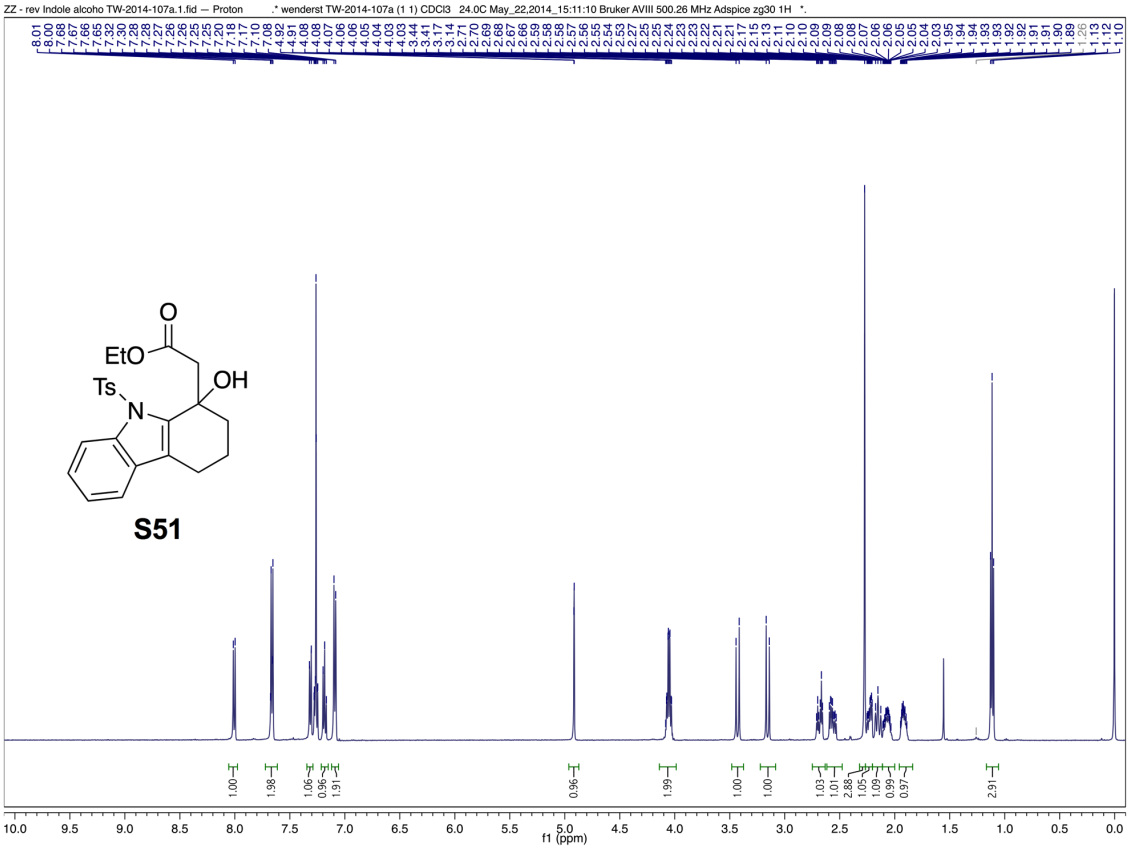

TW-2014-056b-13C.11.fid — Group Tan — .* wenderst TW-2014-056b-13C (11 1) CDCl3 24.0C March_30,2014_22:09:49 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/w
172.60
139.07
138.60
124.93
122.72
77.22
77.01
76.80
69.58
60.85
45.35
36.19
25.06
20.58
14.16
O
EtO
OH
S
S48
f1 (ppm)

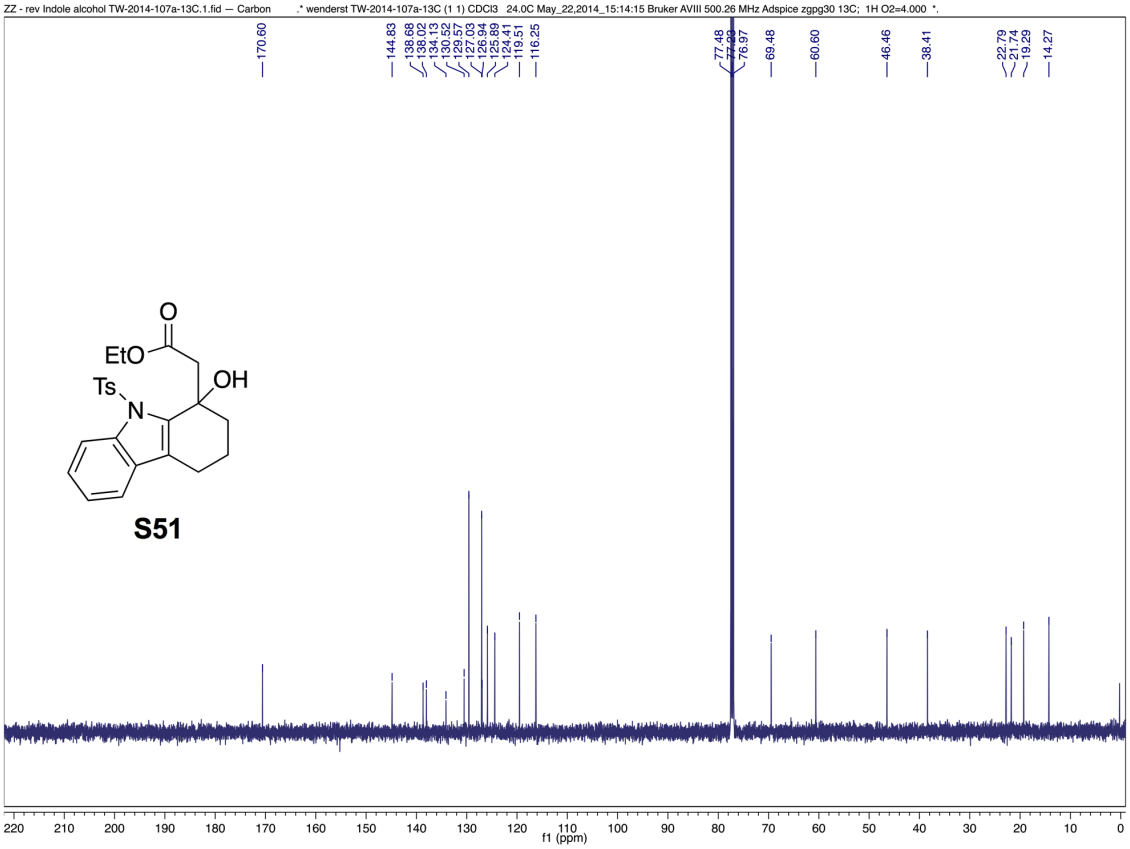

TW-2014-077a-dilute-13C.10.fid — Group Tan — .* wenderst TW-2014-077a-dilute-13C (10 1) CDCl3 24.0C April_18,2014_20:27:59 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
f1 (ppm)
EtO
OH
N
Ts
S49

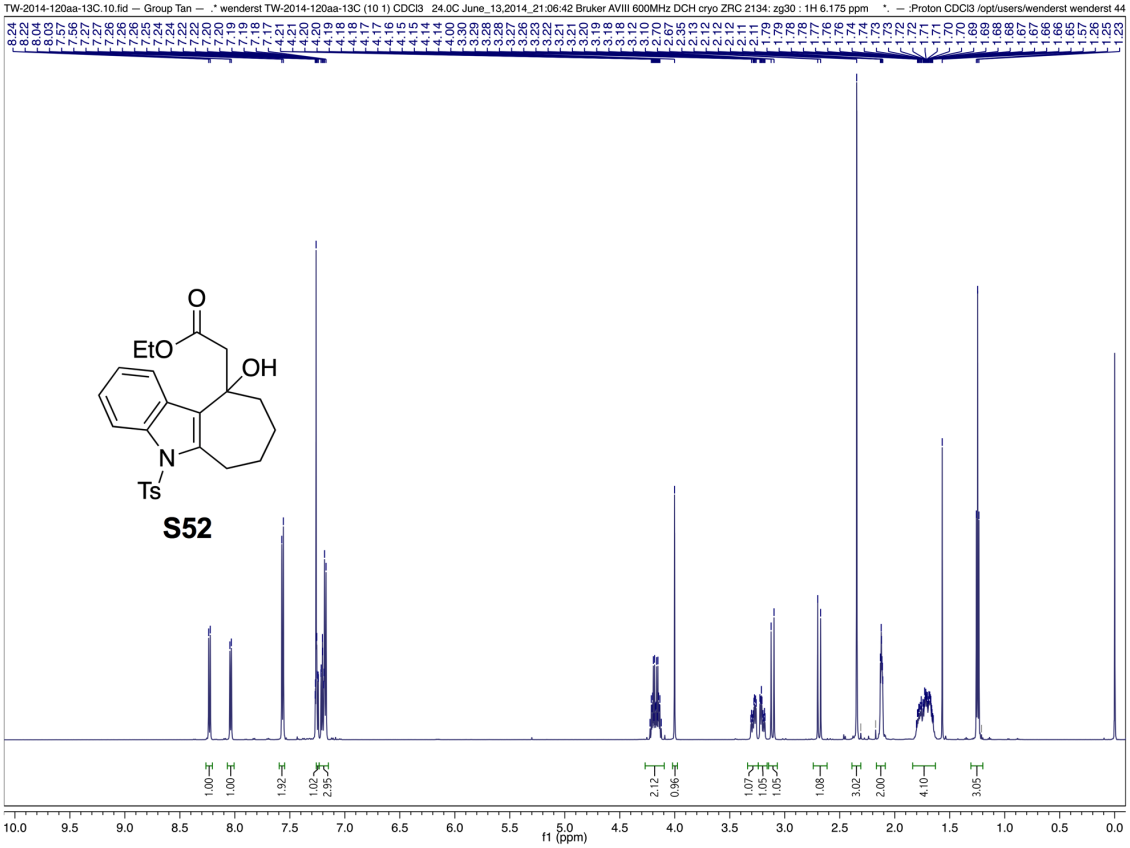

TW-2014-077a-dilute-13C.11.fid — Group Tan — .* wenderst TW-2014-077a-dilute-13C (11 1) CDCl3 24.0C April_18,2014_20:29:47 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm
f1 (ppm)
EtO
OH
N
Ts
S49

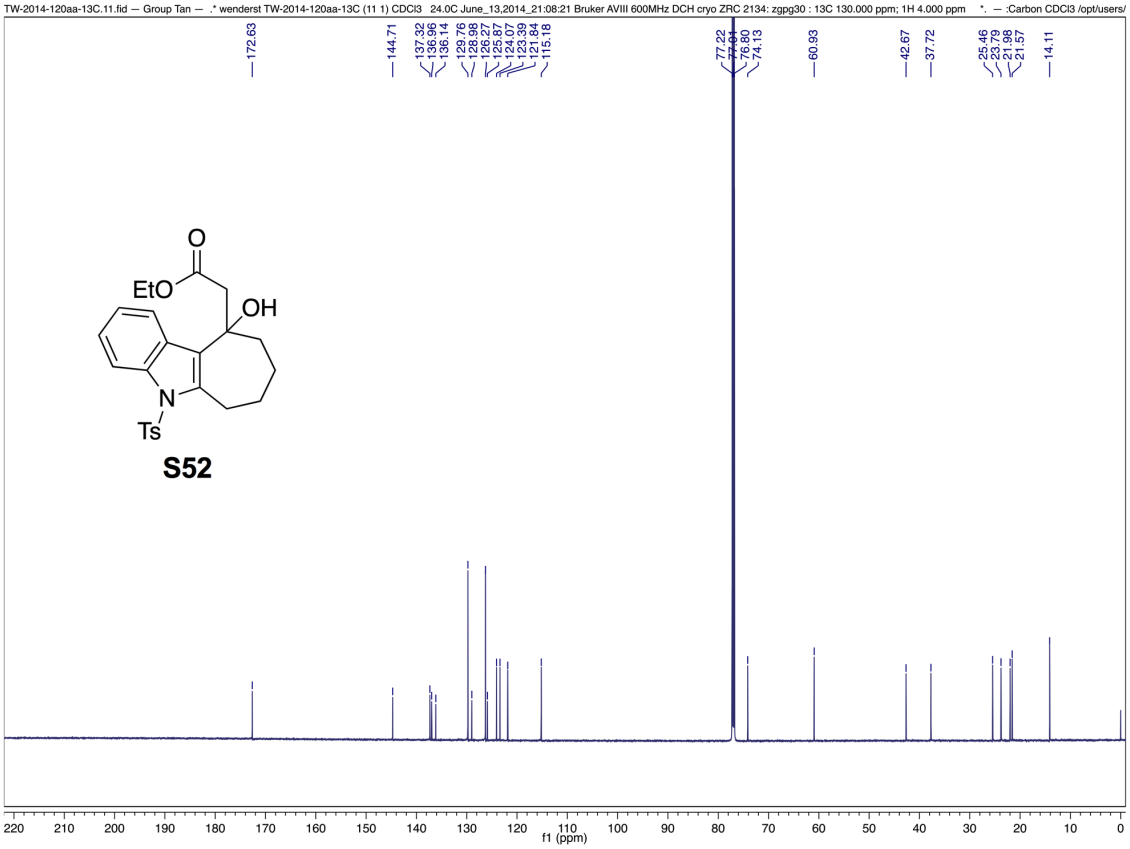

TW-2014-092a-13C-C6D6.10.fid — Group Tan — .* wenderst TW-2014-092a-13C-C6D6 (10 1) C6D6 24.0C May_05,2014_22:01:41 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm :Proton C6D6 /opt/users/wenderst wen
O
EtO
OH
N
Ts
S50
f1 (ppm)

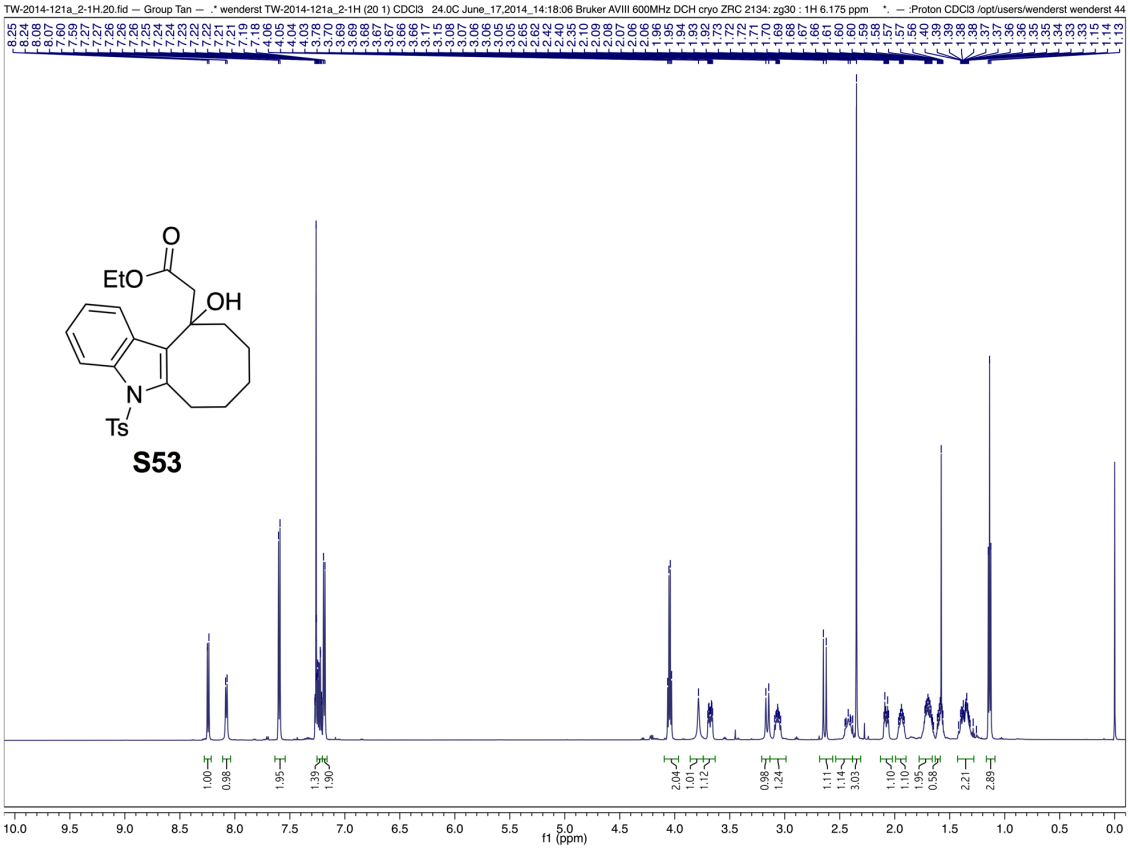

TW-2014-092a-13C-C6D6.11.fid — Group Tan — .* wenderst TW-2014-092a-13C-C6D6 (11 1) C6D6 24.0C May_05,2014_22:03:51 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm :Carbon C6D6
172.24
144.27
137.26
137.05
136.76
129.84
128.55
70.44
60.50
43.39
36.76
24.92
20.98
20.69
14.00
O
EtO
OH
N
Ts
S50
f1 (ppm)

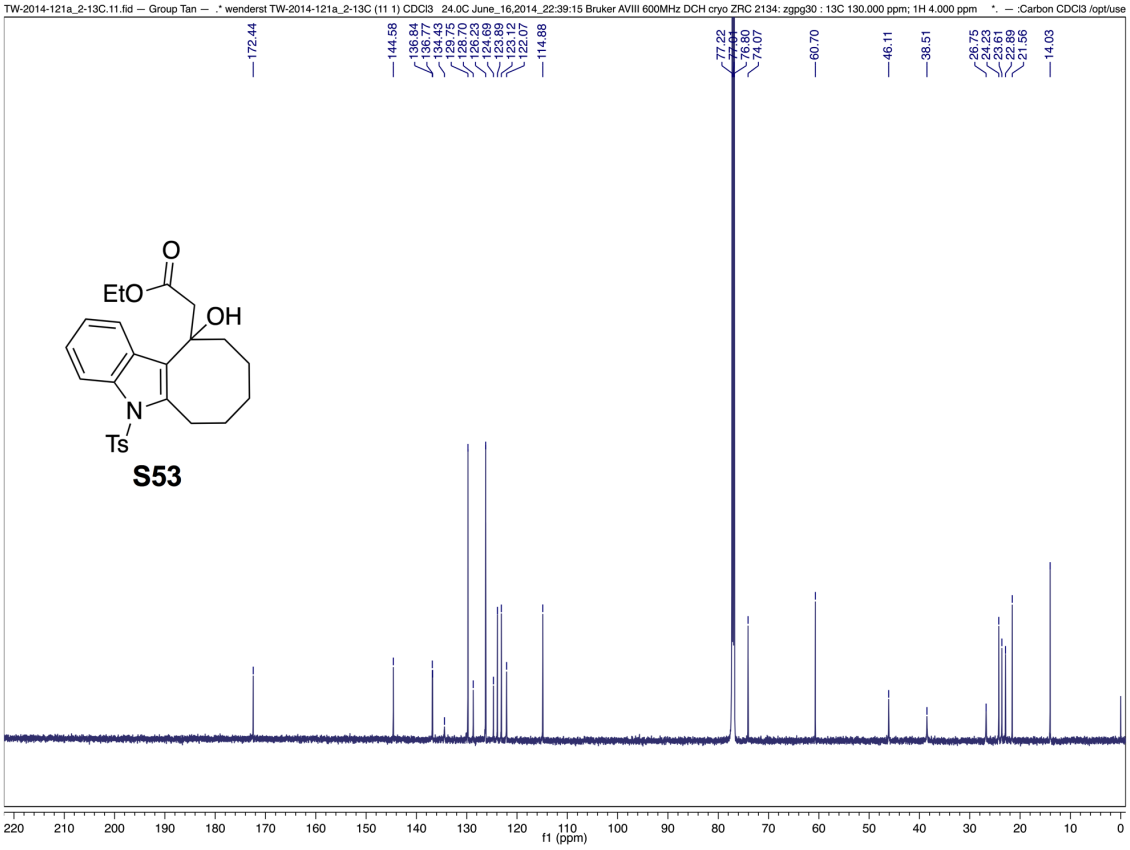

ZZ - rev Indole alcoho TW-2014-107a.1.fid — Proton .* wenderst TW-2014-107a (1 1) CDCl3 24.0C May_22,2014_15:11:10 Bruker AVIII 500.26 MHz Adspice zg30 1H *.
EtO
O
Ts
N
OH
S51
f1 (ppm)

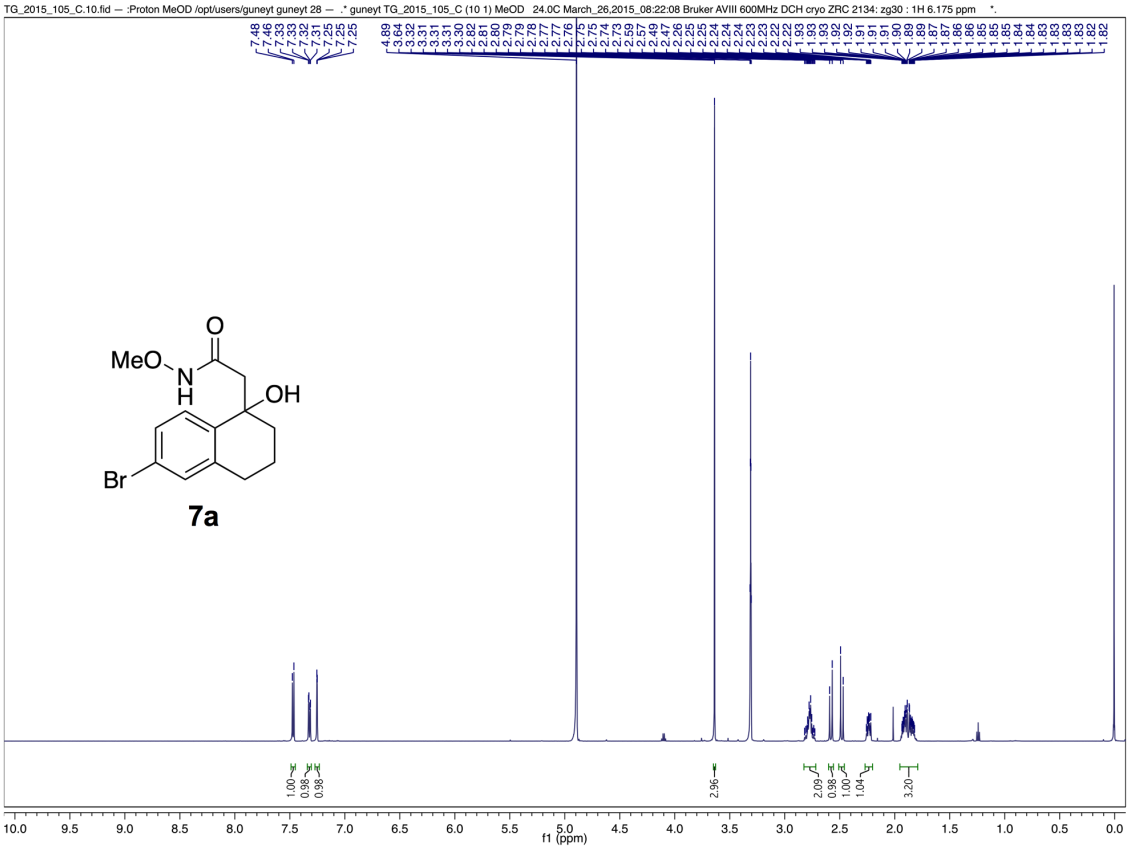

ZZ - rev Indole alcohol TW-2014-107a-13C.1.fid — Carbon .* wenderst TW-2014-107a-13C (1 1) CDCl3 24.0C May_22,2014_15:14:15 Bruker AVIII 500.26 MHz Adspice zgpg30 13C; 1H O2=4.000 *.
EtO
O
Ts
N
OH
S51
f1 (ppm)

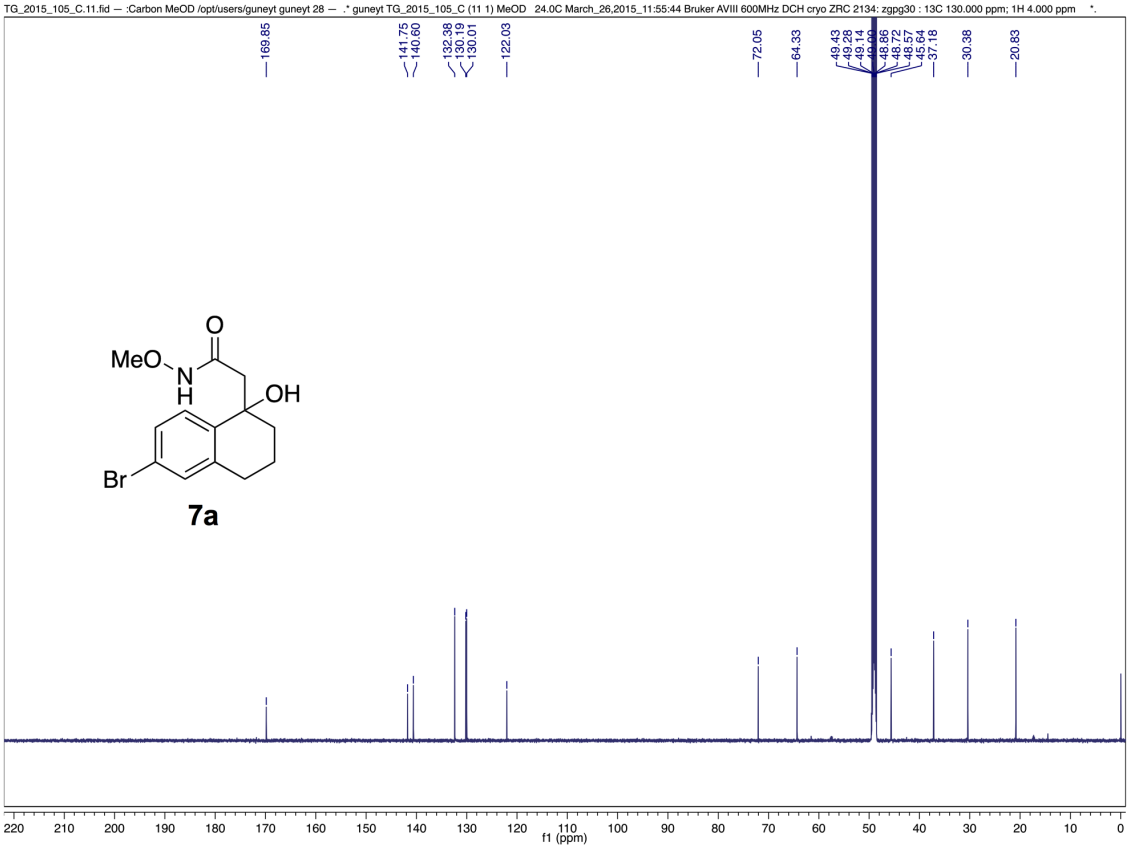

TW-2014-120aa-13C.10.fid — Group Tan — .* wenderst TW-2014-120aa-13C (10 1) CDCl3 24.0C June_13,2014_21:06:42 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 44
O
EtO
OH
N
Ts
S52
f1 (ppm)

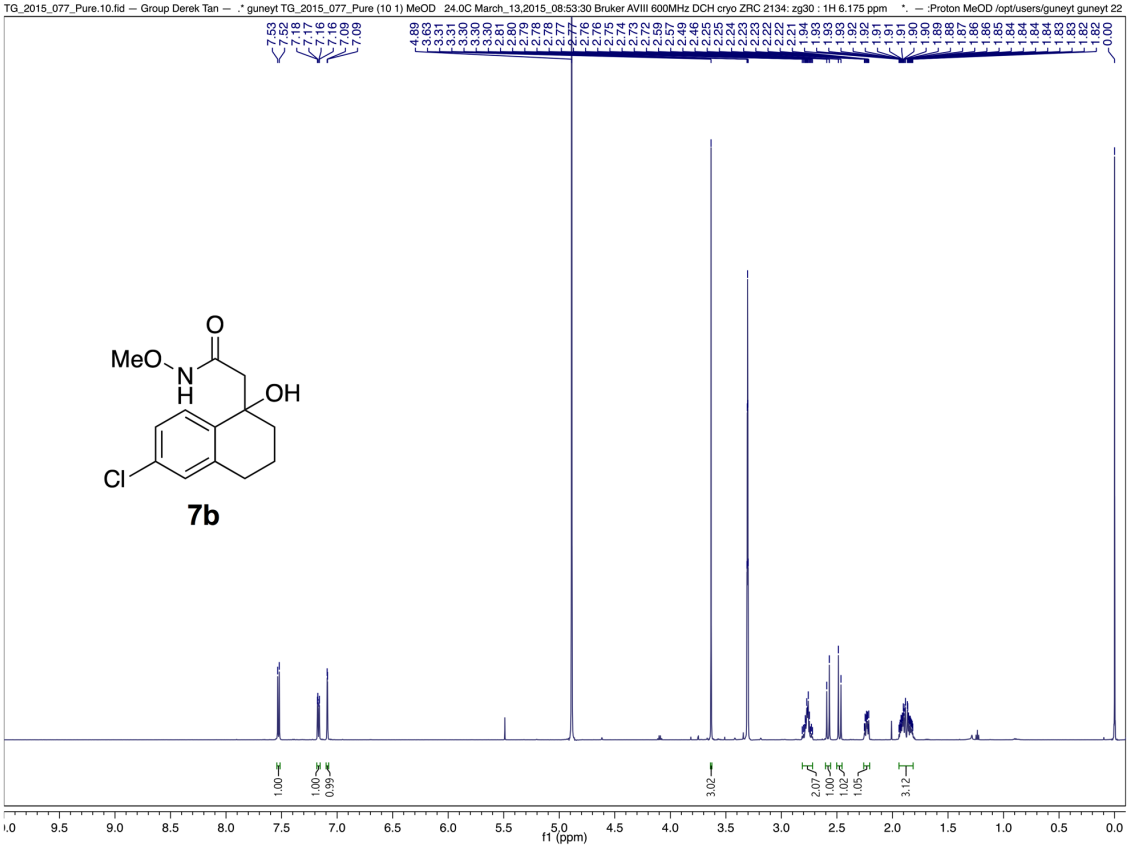

TW-2014-120aa-13C.11.fid — Group Tan — .* wenderst TW-2014-120aa-13C (11 1) CDCl3 24.0C June_13,2014_21:08:21 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/
O
EtO
OH
N
Ts
S52
f1 (ppm)

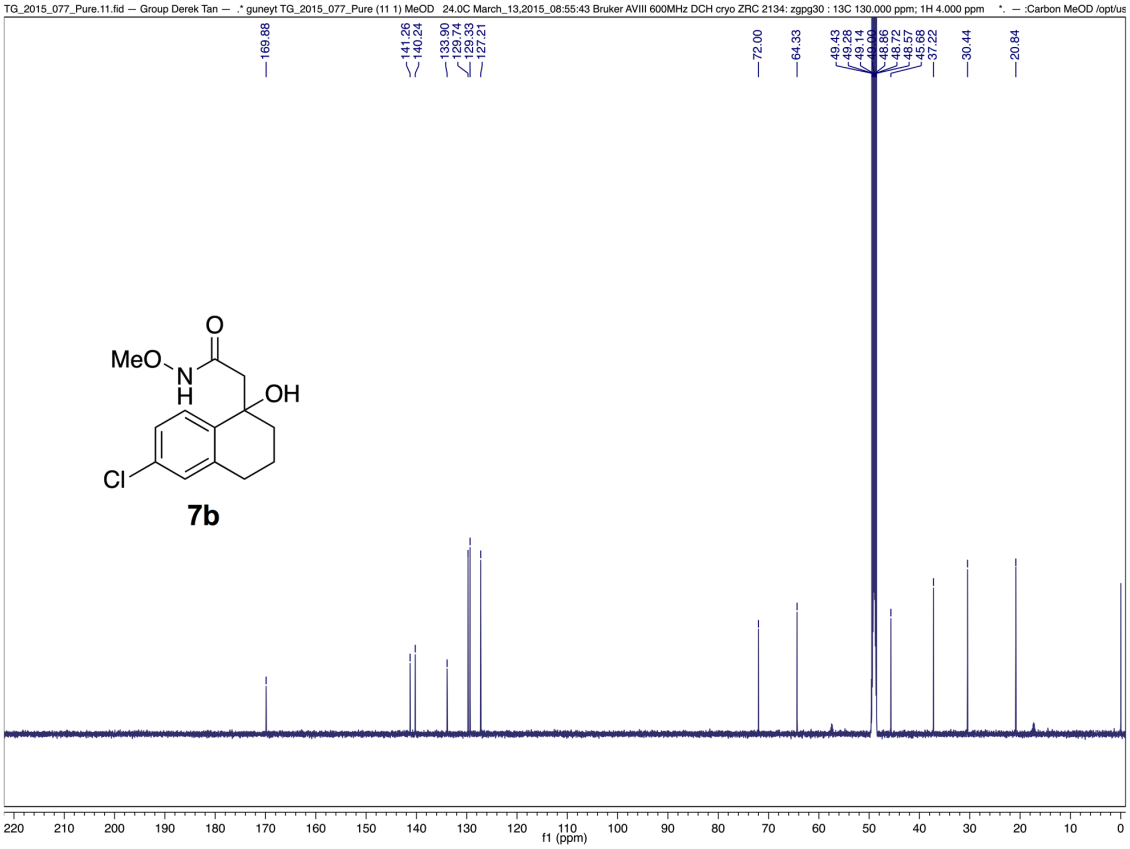

TW-2014-121a_2-1H.20.fid — Group Tan — .* wenderst TW-2014-121a_2-1H (20 1) CDCl3 24.0C June_17,2014_14:18:06 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 44
O
EtO
OH
N
Ts
S53
f1 (ppm)

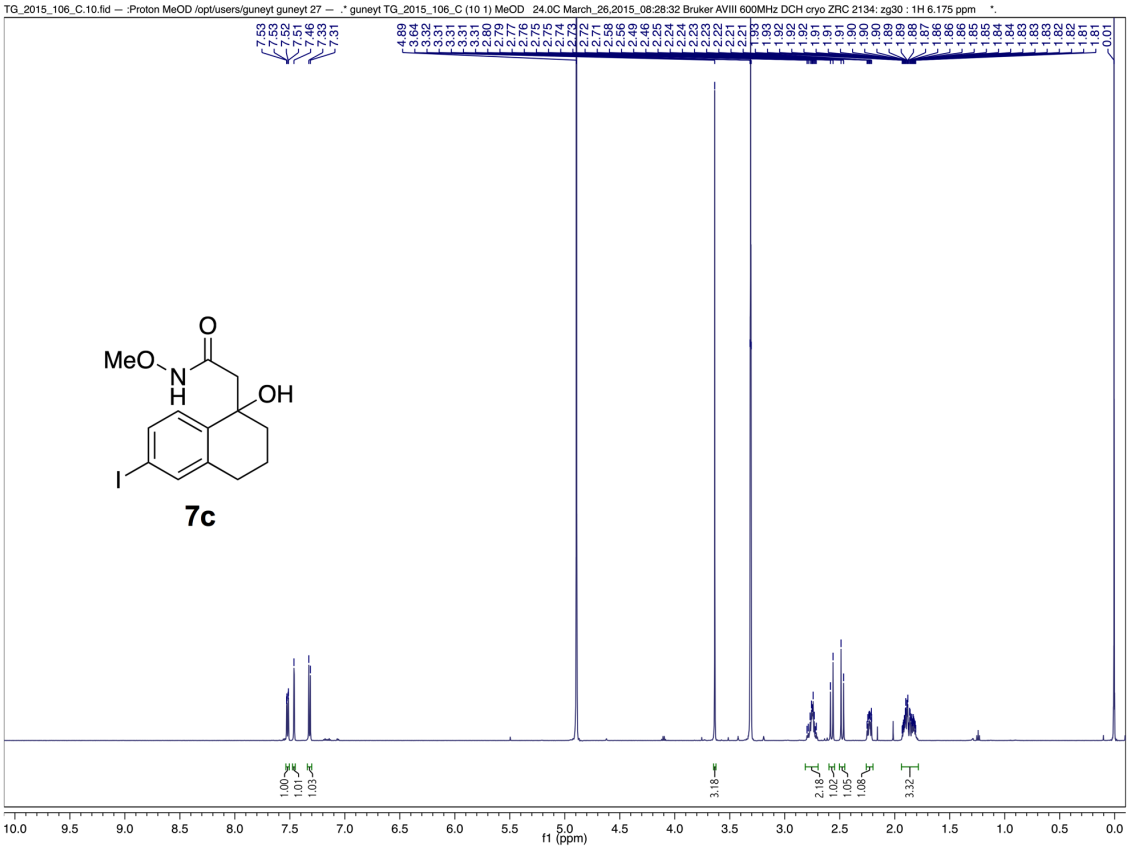

TW-2014-121a_2-13C.11.fid — Group Tan — .* wenderst TW-2014-121a_2-13C (11 1) CDCl3 24.0C June_16,2014_22:39:15 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
172.44
144.58
136.84
136.77
134.43
129.75
128.70
126.23
124.69
123.89
123.12
122.07
114.88
77.22
77.01
76.80
74.07
60.70
46.11
38.51
26.75
24.23
23.61
22.89
21.56
14.03
O
EtO
OH
N
Ts
S53
f1 (ppm)

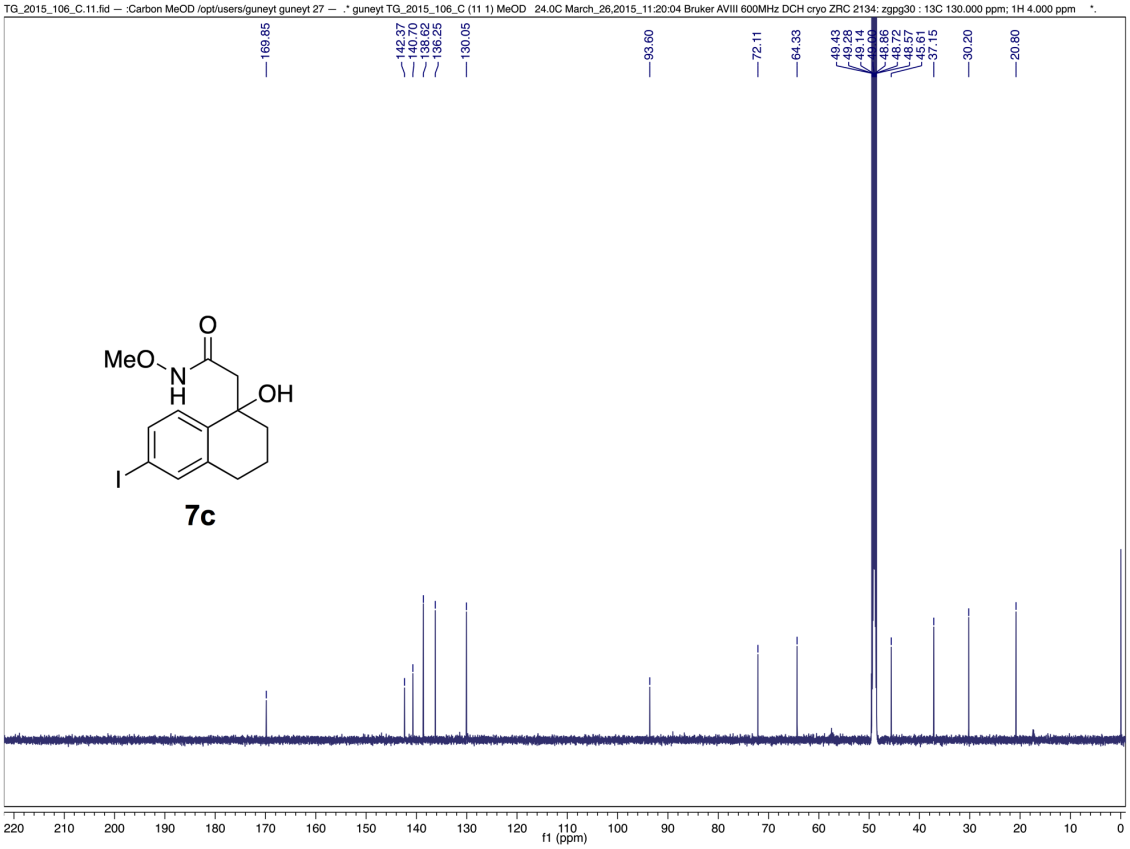

TG_2015_105_C.10.fid — :Proton MeOD /opt/users/guneyt guneyt 28 — .* guneyt TG_2015_105_C (10 1) MeOD 24.0C March_26,2015_08:22:08 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
MeO
N
H
O
OH
Br
7a
f1 (ppm)

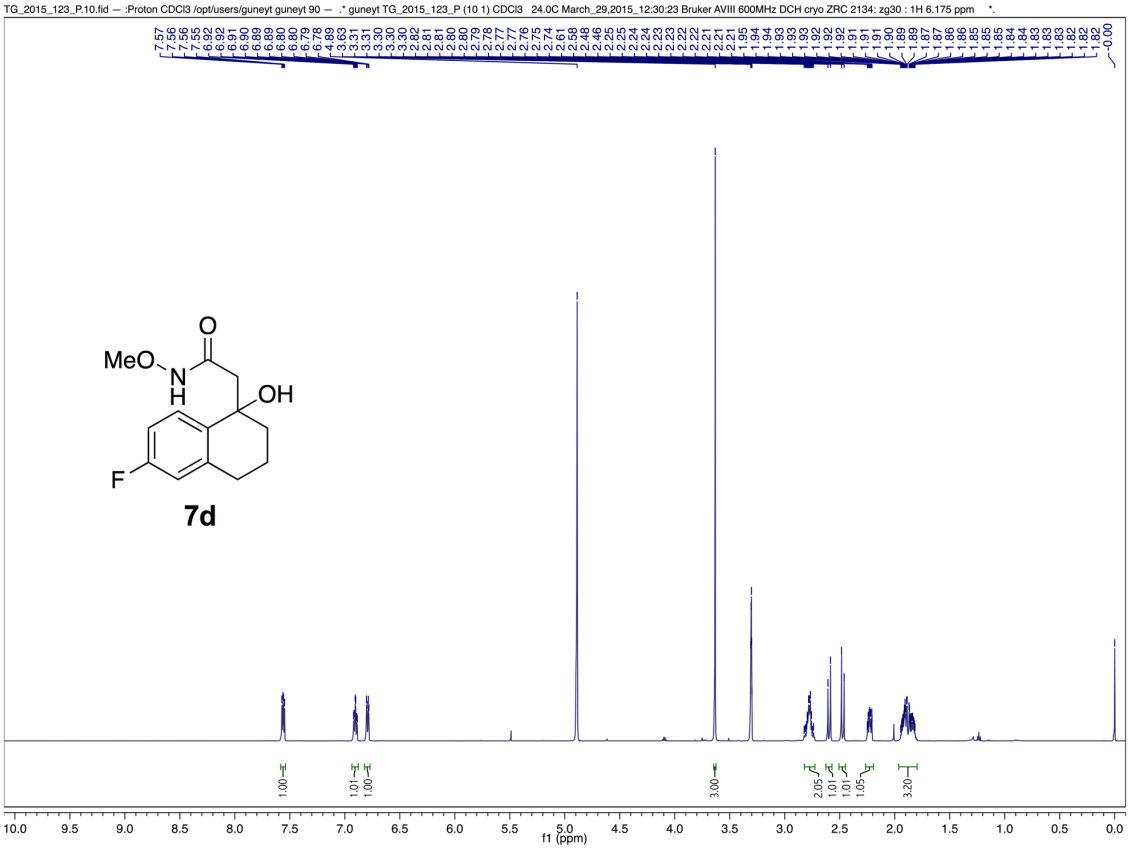

TG_2015_105_C.11.fid — :Carbon MeOD /opt/users/guneyt guneyt 28 — .* guneyt TG_2015_105_C (11 1) MeOD 24.0C March_26,2015_11:55:44 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *.
MeO
N
H
O
OH
Br
7a
f1 (ppm)

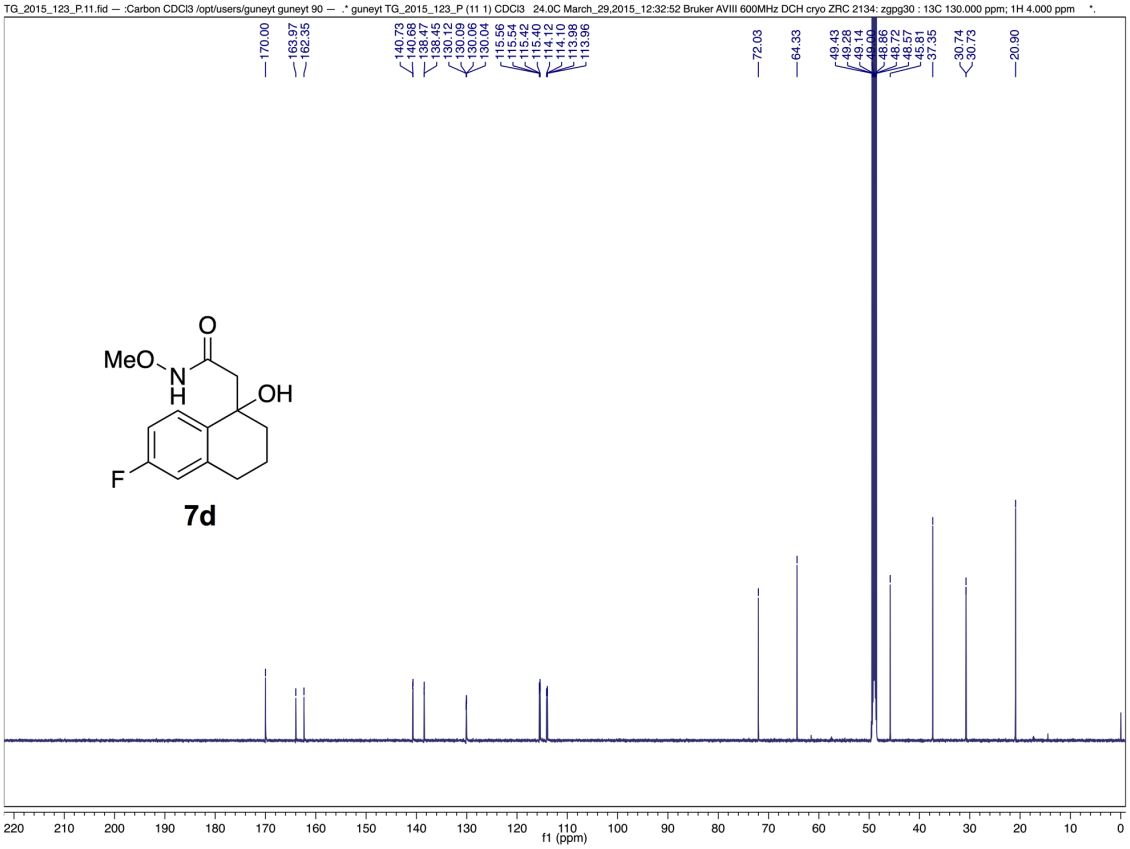

TG_2015_077_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_077_Pure (10 1) MeOD 24.0C March_13,2015_08:53:30 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guneyt guneyt 22
MeO
N
H
O
OH
Cl
7b
f1 (ppm)

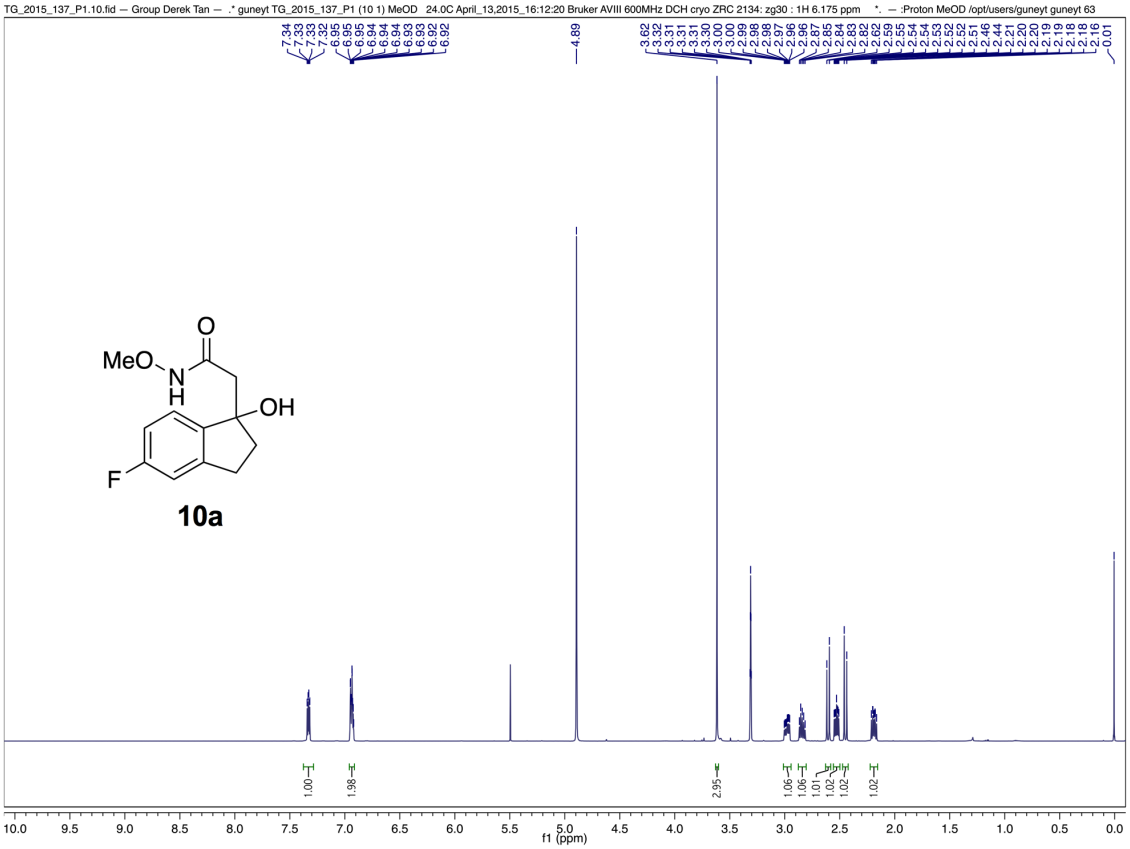

TG_2015_077_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_077_Pure (11 1) MeOD 24.0C March_13,2015_08:55:43 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon MeOD /opt/us
MeO
N
H
O
OH
Cl
7b
f1 (ppm)

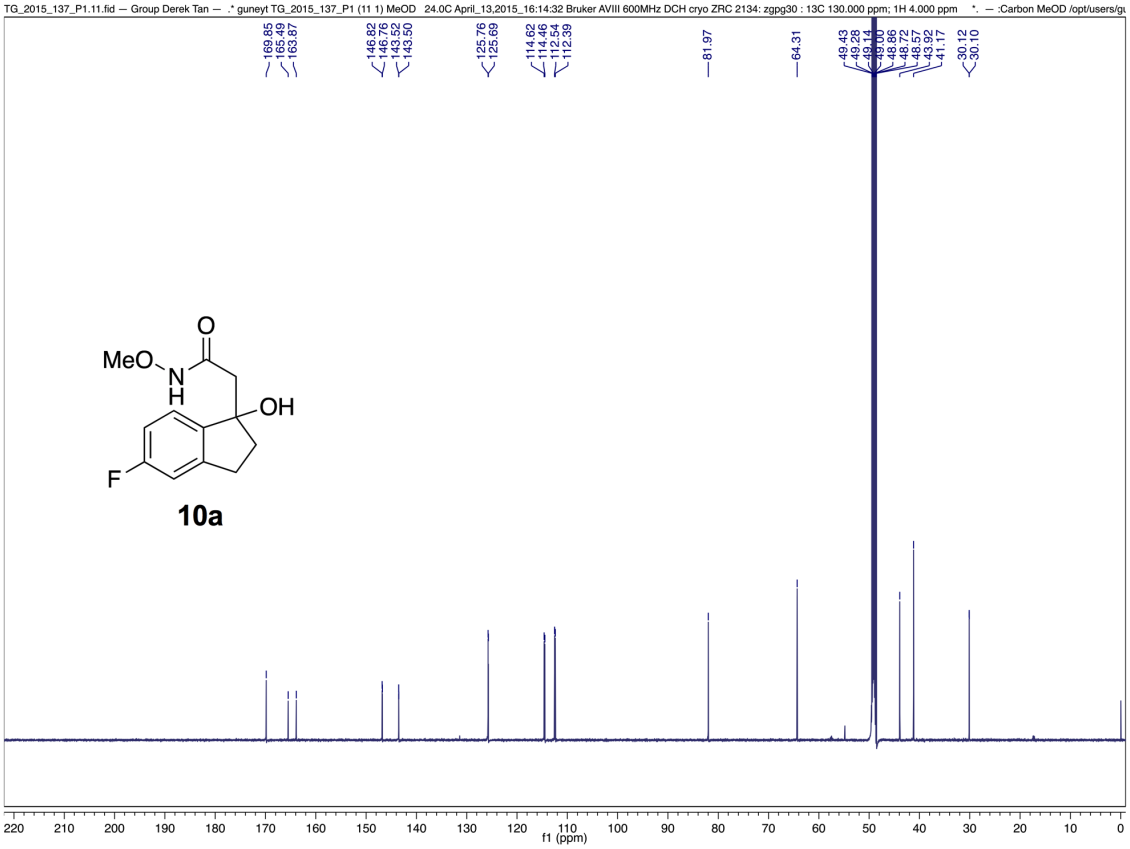

TG_2015_106_C.10.fid — :Proton MeOD /opt/users/guneyt guneyt 27 — .* guneyt TG_2015_106_C (10 1) MeOD 24.0C March_26,2015_08:28:32 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
MeO
N
H
O
OH
I
7c
f1 (ppm)

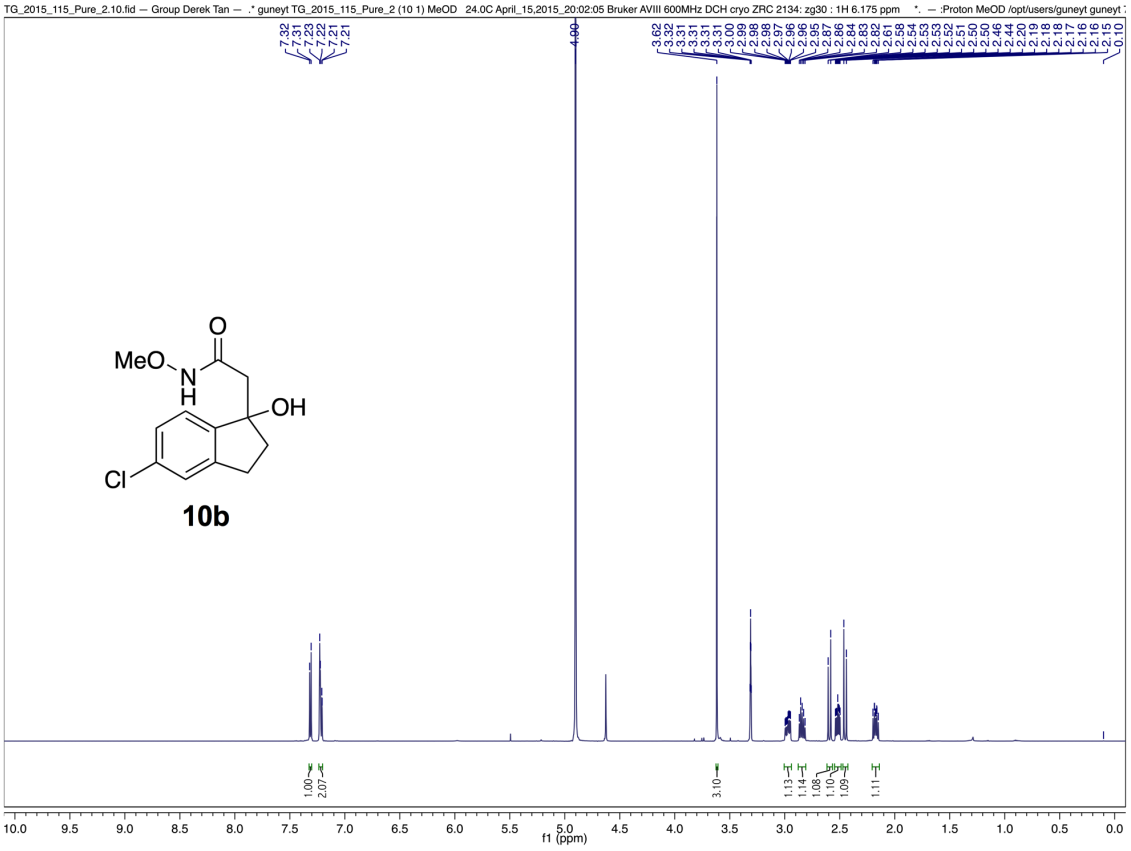

TG_2015_106_C.11.fid — :Carbon MeOD /opt/users/guneyt guneyt 27 — .* guneyt TG_2015_106_C (11 1) MeOD 24.0C March_26,2015_11:20:04 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *.
MeO
N
H
O
OH
I
7c
f1 (ppm)

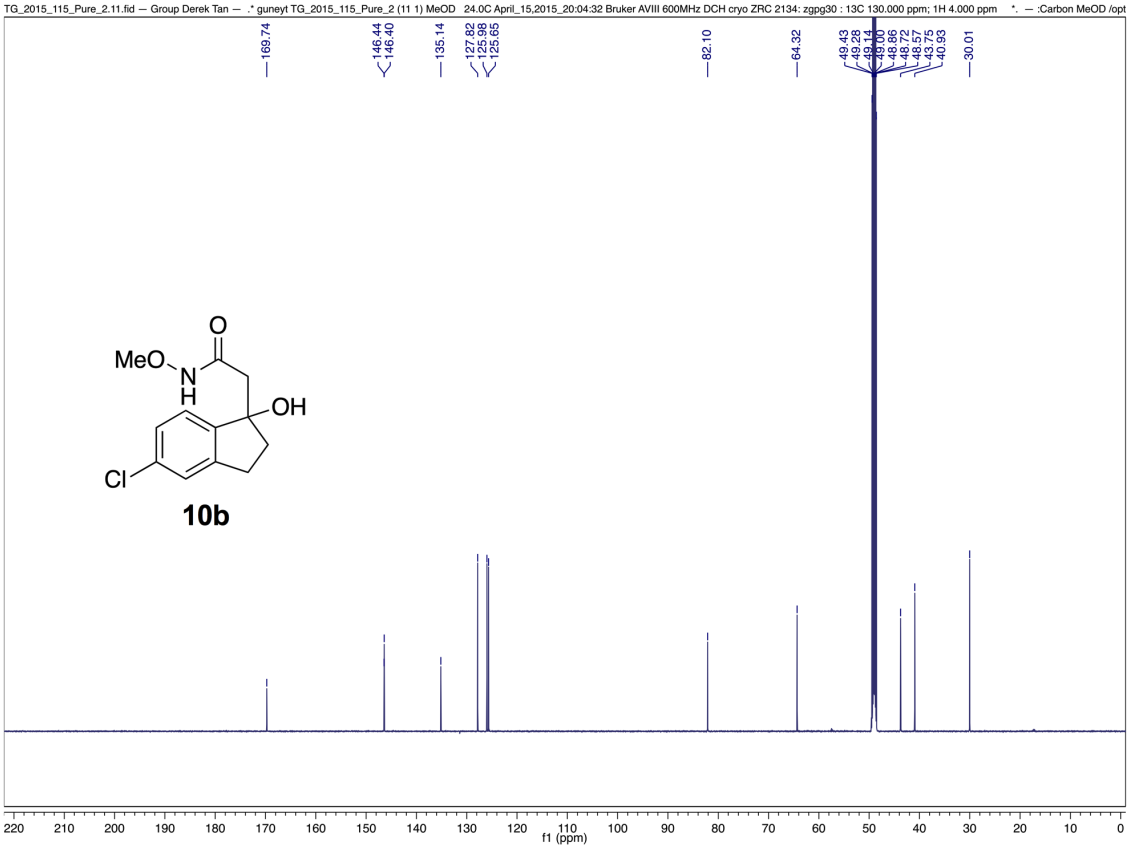

TG_2015_123_P.10.fid — :Proton CDCl3 /opt/users/guneyt guneyt 90 — .* guneyt TG_2015_123_P (10 1) CDCl3 24.0C March_29,2015_12:30:23 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
MeO
N
H
O
OH
F
7d
1.00
1.01
1.00
3.00
2.05
1.01
1.01
1.05
3.20
f1 (ppm)

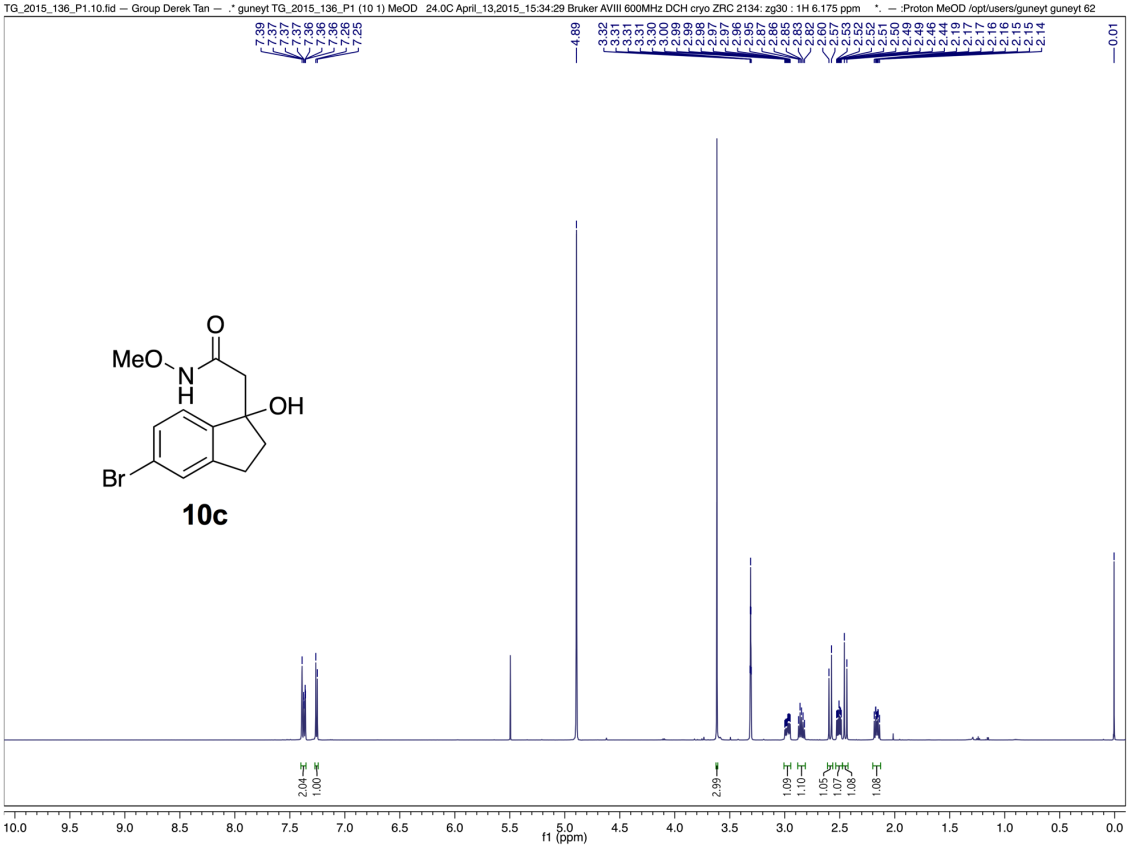

TG_2015_123_P.11.fid — :Carbon CDCl3 /opt/users/guneyt guneyt 90 — .* guneyt TG_2015_123_P (11 1) CDCl3 24.0C March_29,2015_12:32:52 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *.
MeO
N
H
O
OH
F
7d
f1 (ppm)

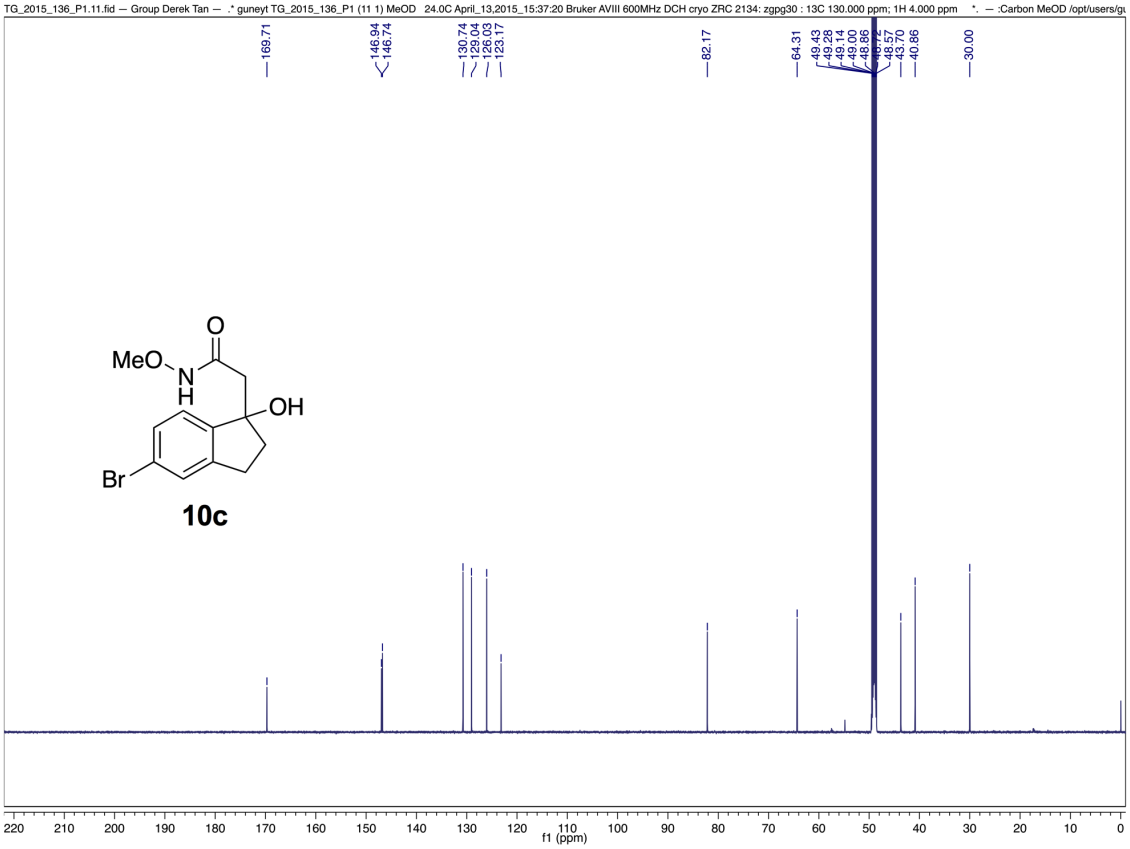

TG_2015_137_P1.10.fid — Group Derek Tan — .* guneyt TG_2015_137_P1 (10 1) MeOD 24.0C April_13,2015_16:12:20 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guneyt guneyt 63
MeO
N
H
O
OH
F
10a
f1 (ppm)

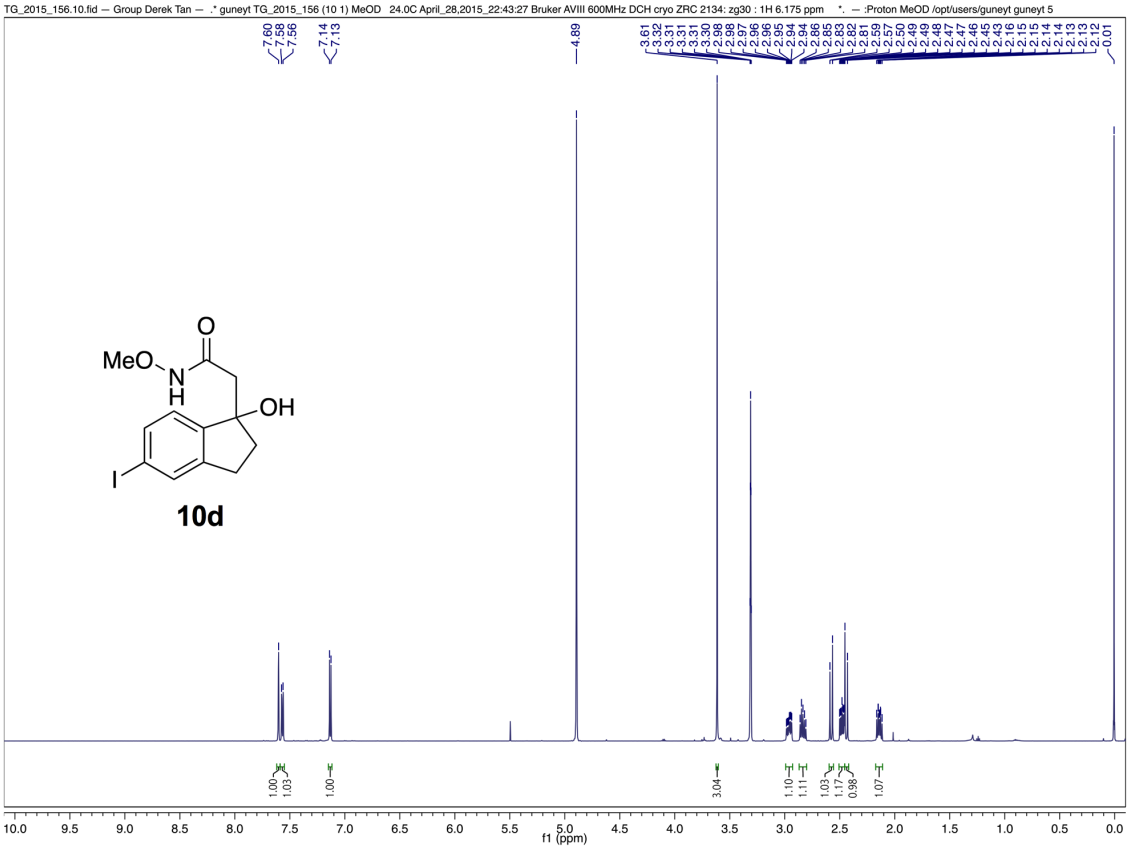

TG_2015_137_P1.11.fid — Group Derek Tan — .* guneyt TG_2015_137_P1 (11 1) MeOD 24.0C April_13,2015_16:14:32 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon MeOD /opt/users/gu
MeO
N
H
O
OH
F
10a
f1 (ppm)

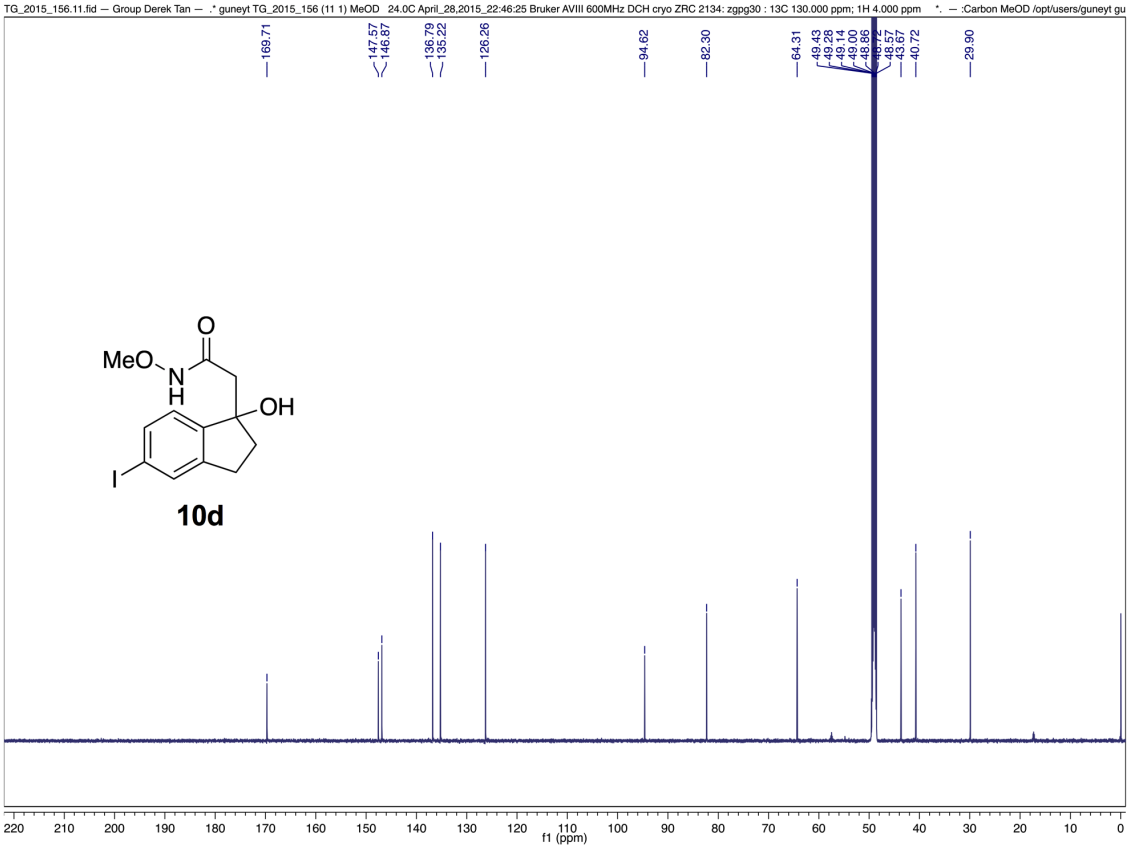

TG_2015_115_Pure_2.10.fid — Group Derek Tan — .* guneyt TG_2015_115_Pure_2 (10 1) MeOD 24.0C April_15,2015_20:02:05 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
MeO
N
H
O
OH
Cl
10b
f1 (ppm)

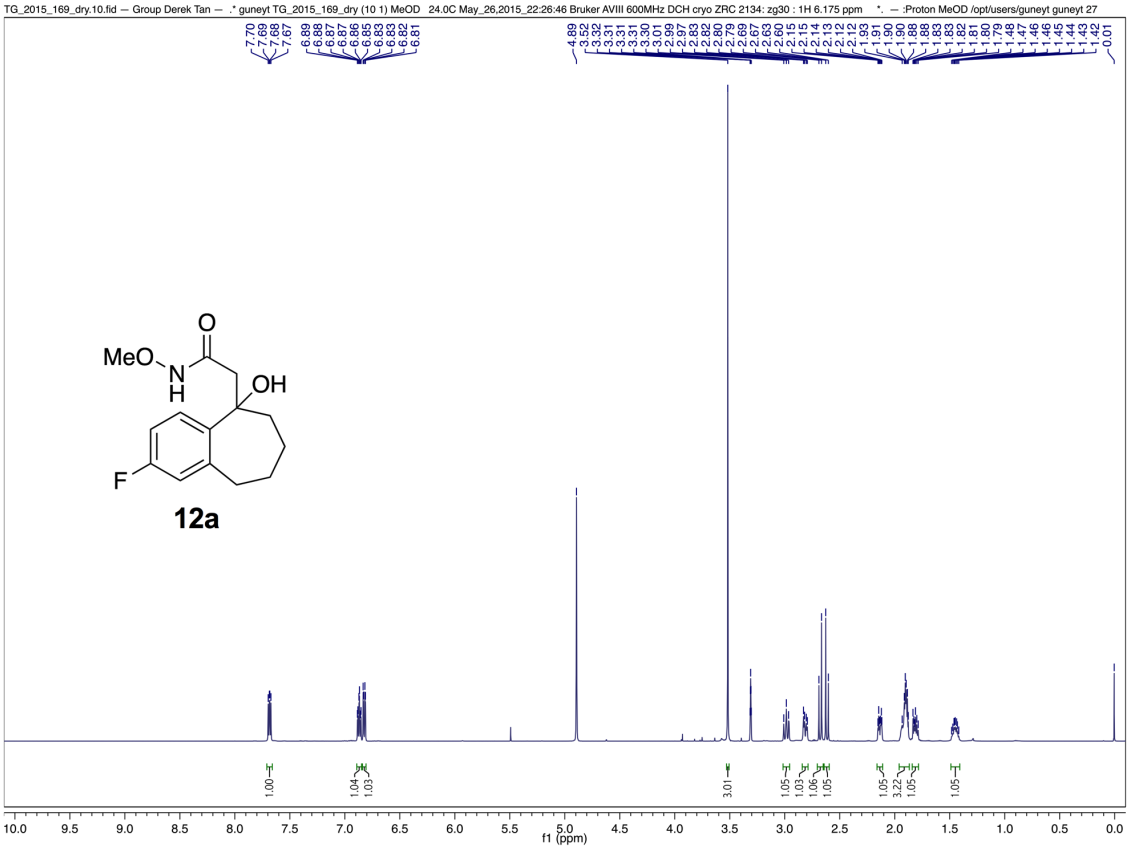

TG_2015_115_Pure_2.11.fid — Group Derek Tan — .* guneyt TG_2015_115_Pure_2 (11 1) MeOD 24.0C April_15,2015_20:04:32 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm
MeO
N
H
O
OH
Cl
10b
f1 (ppm)

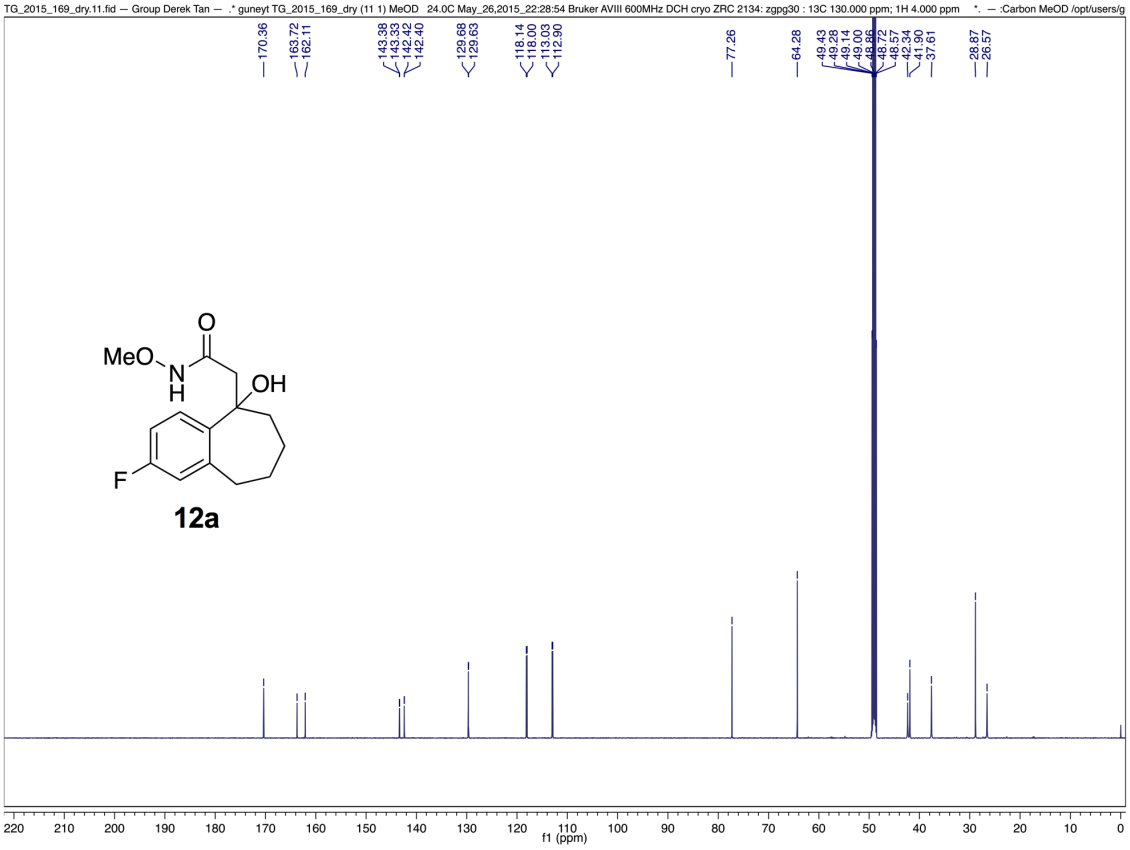

TG_2015_136_P1.10.fid — Group Derek Tan — .* guneyt TG_2015_136_P1 (10 1) MeOD 24.0C April_13,2015_15:34:29 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guneyt guneyt 62
MeO
N
H
O
OH
Br
10c
f1 (ppm)

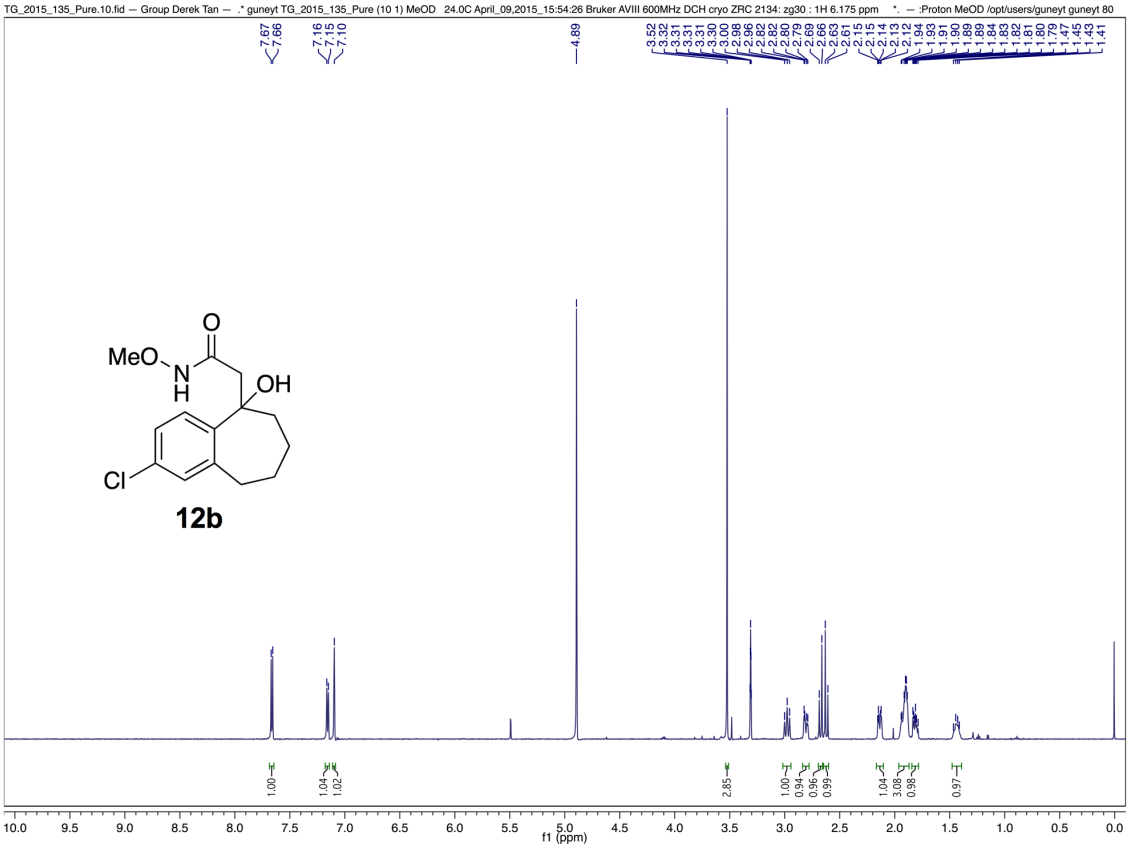

TG_2015_136_P1.11.fid — Group Derek Tan — .* guneyt TG_2015_136_P1 (11 1) MeOD 24.0C April_13,2015_15:37:20 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon MeOD /opt/users/gu
MeO
N
H
O
OH
Br
10c
f1 (ppm)

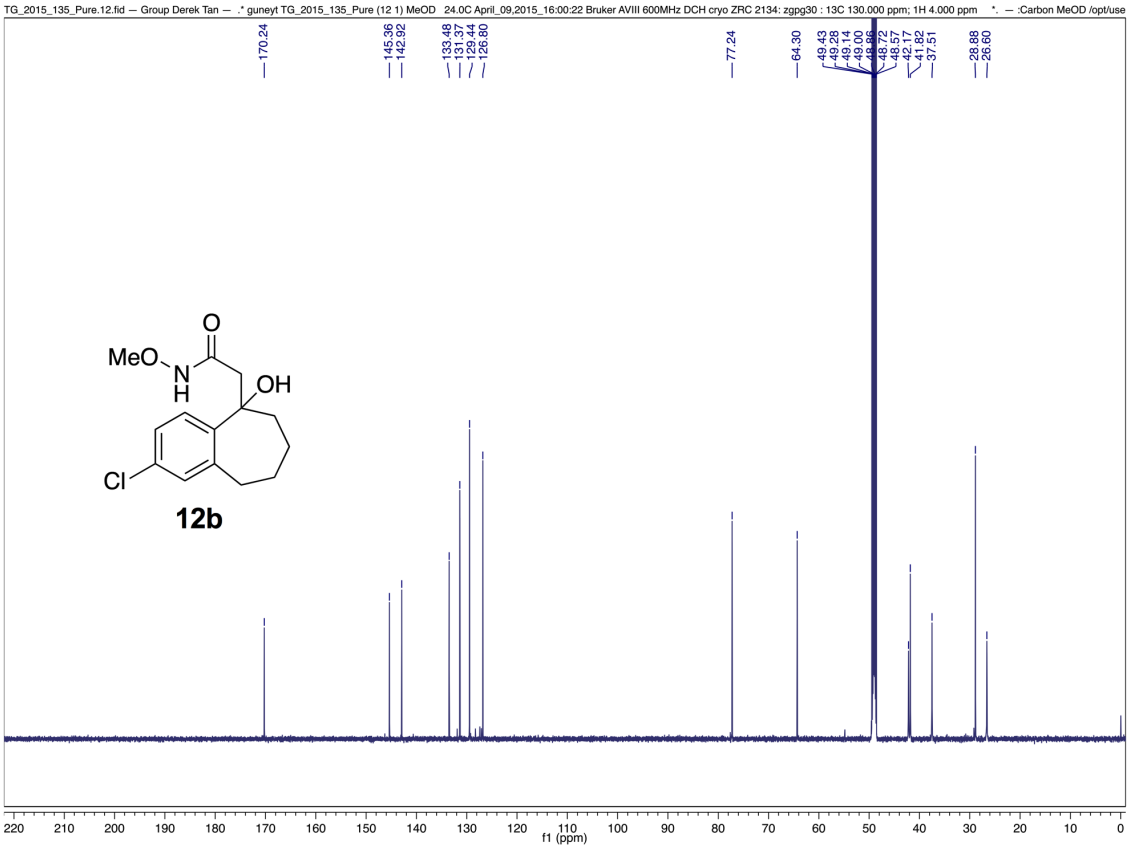

TG_2015_156.10.fid — Group Derek Tan — .* guneyt TG_2015_156 (10 1) MeOD 24.0C April_28,2015_22:43:27 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guneyt guneyt 5
MeO
N
H
O
OH
I
10d
f1 (ppm)

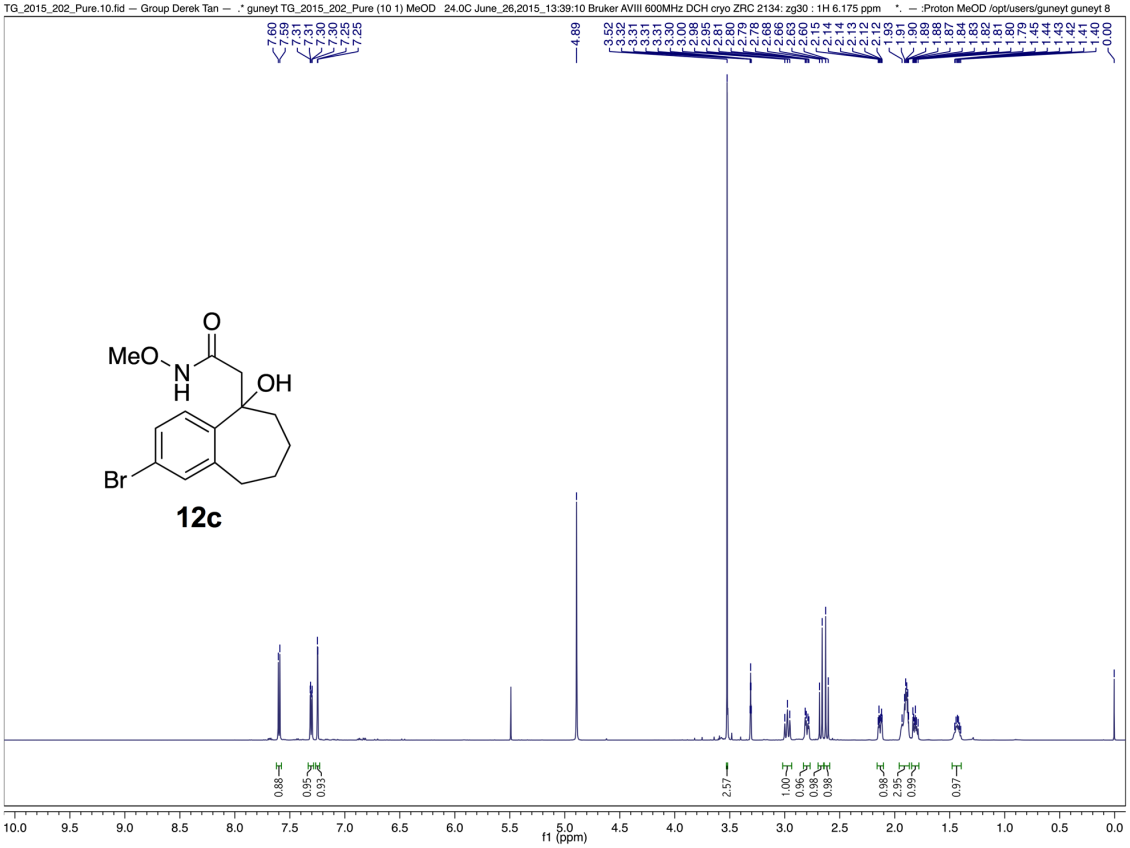

TG_2015_156.11.fid — Group Derek Tan — .* guneyt TG_2015_156 (11 1) MeOD 24.0C April_28,2015_22:46:25 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon MeOD /opt/users/guneyt gu
MeO
N
H
O
OH
I
10d
f1 (ppm)

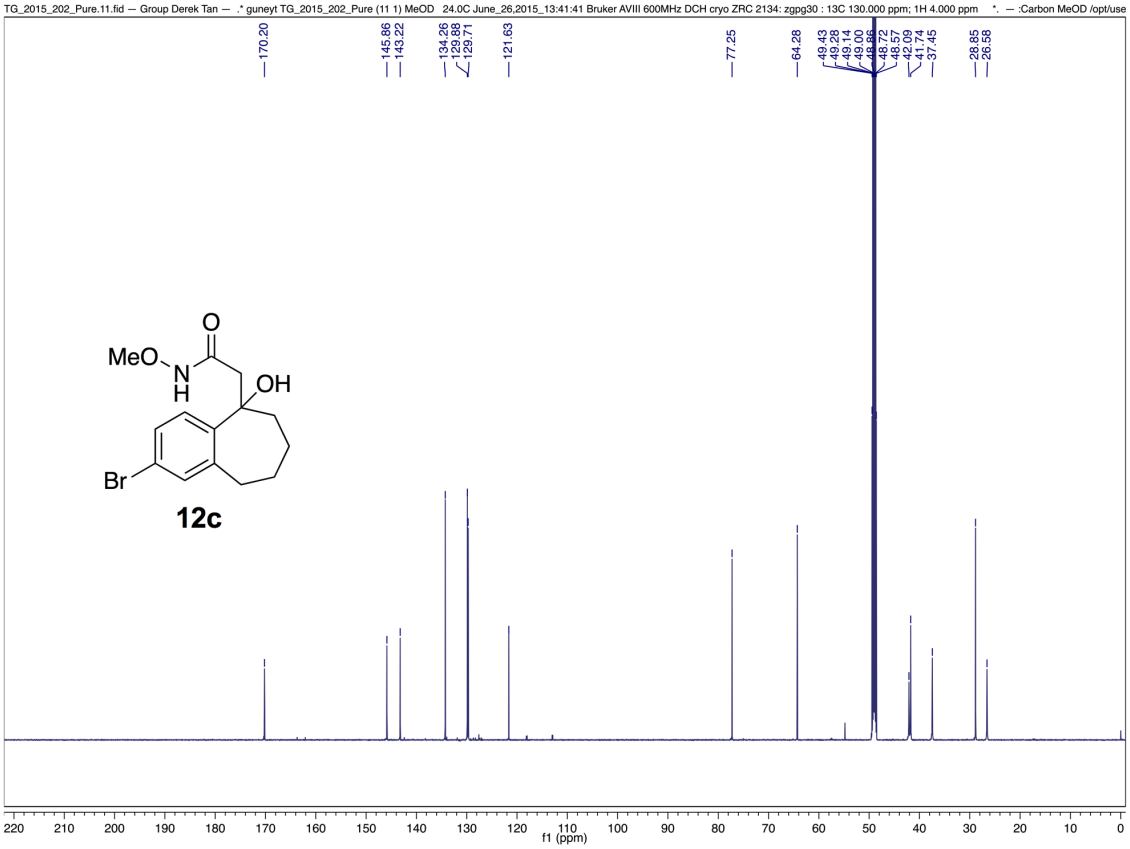

TG_2015_169_dry.10.fid — Group Derek Tan — .* guneyt TG_2015_169_dry (10 1) MeOD 24.0C May_26,2015_22:26:46 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guneyt guneyt 27
MeO
N
H
O
OH
F
12a
f1 (ppm)

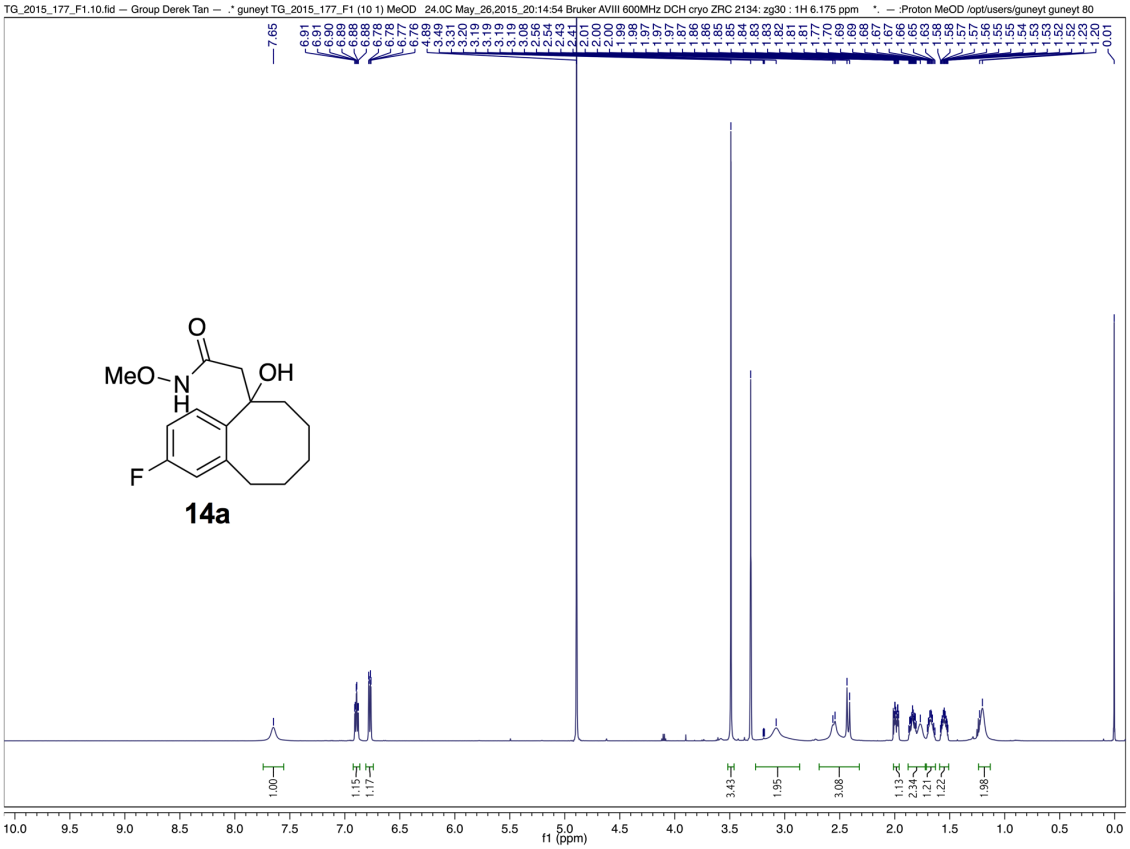

TG_2015_169_dry.11.fid — Group Derek Tan — .* guneyt TG_2015_169_dry (11 1) MeOD 24.0C May_26,2015_22:28:54 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon MeOD /opt/users/g
MeO
N
H
O
OH
F
12a
f1 (ppm)

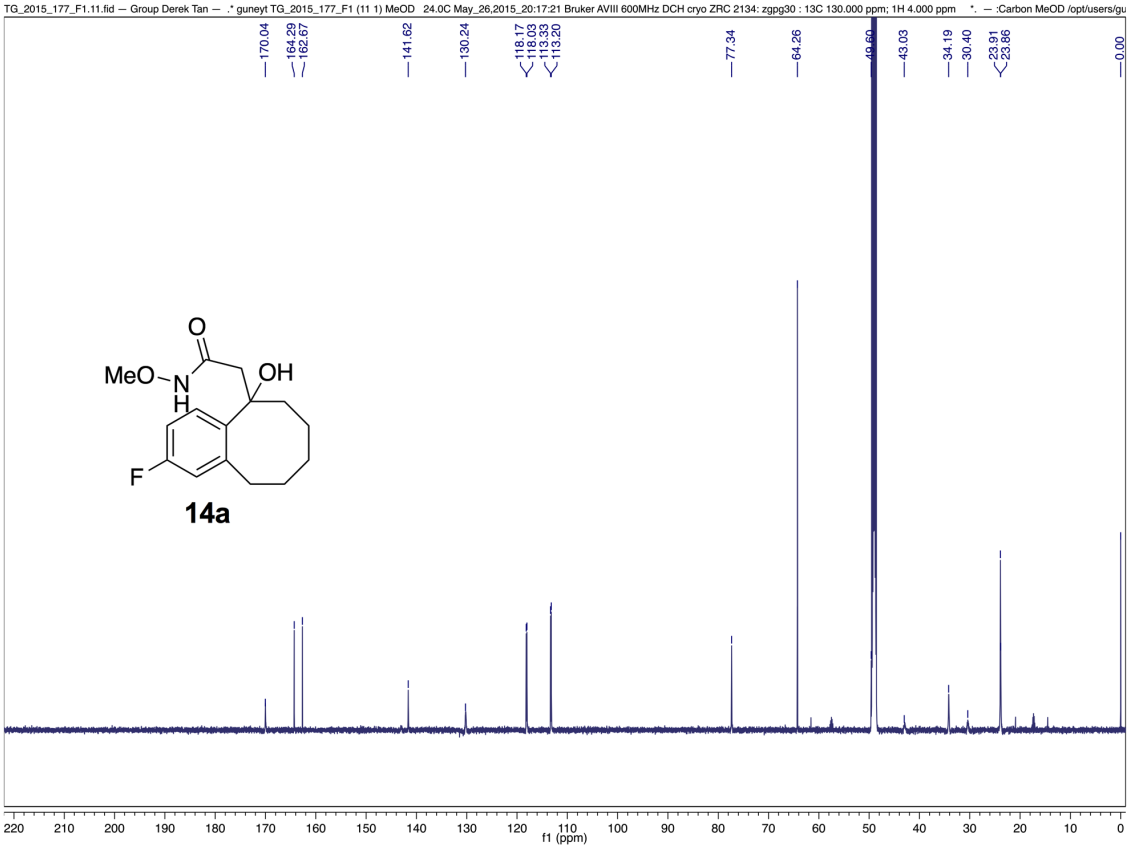

TG_2015_135_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_135_Pure (10 1) MeOD 24.0C April_09,2015_15:54:26 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guneyt guneyt 80
MeO
N
H
O
OH
Cl
12b
f1 (ppm)

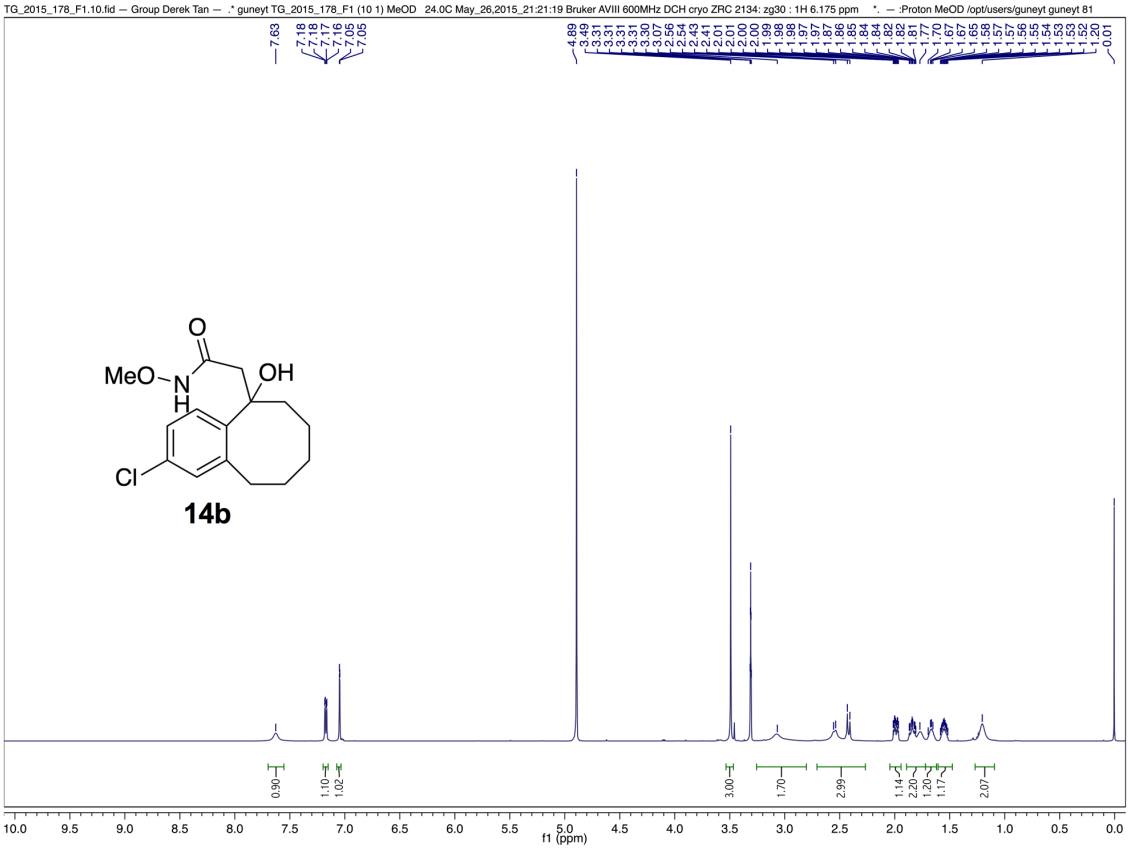

TG_2015_135_Pure.12.fid — Group Derek Tan — .* guneyt TG_2015_135_Pure (12 1) MeOD 24.0C April_09,2015_16:00:22 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon MeOD /opt/use
MeO
N
H
O
OH
Cl
12b
f1 (ppm)

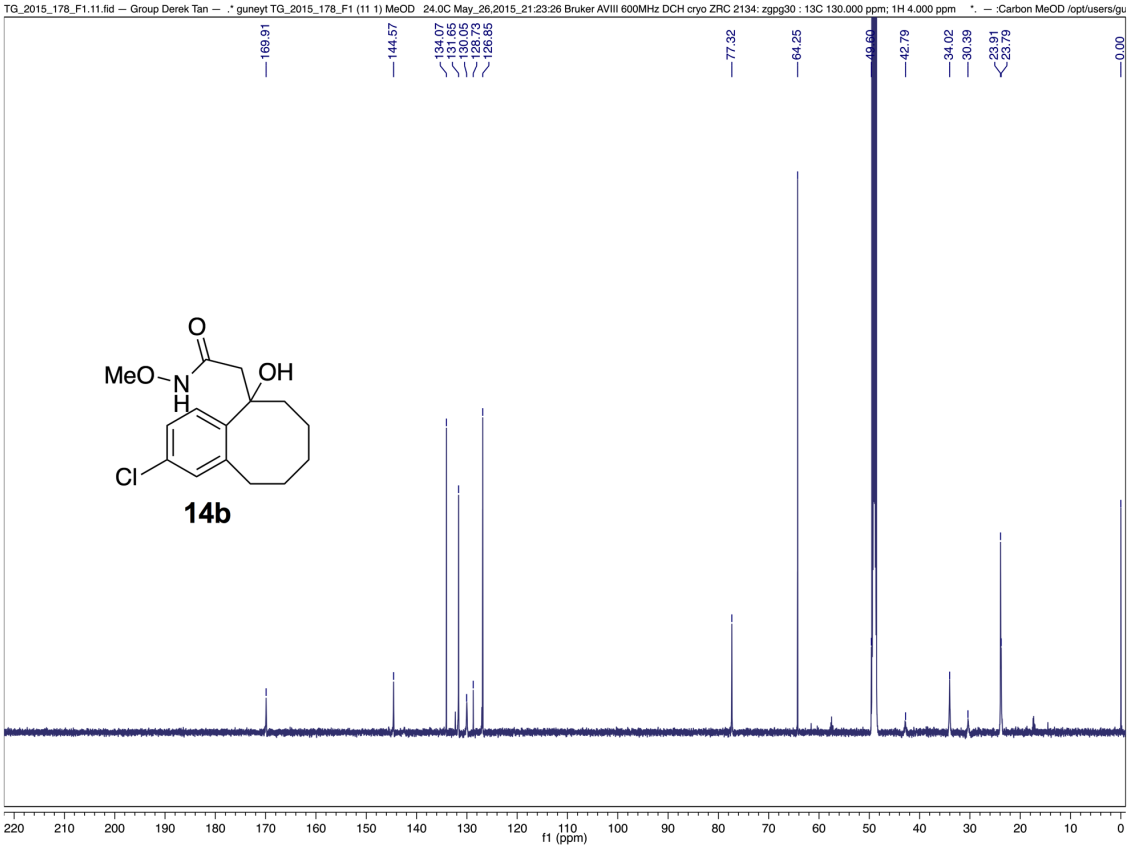

TG_2015_202_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_202_Pure (10 1) MeOD 24.0C June_26,2015_13:39:10 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guneyt guneyt 8
MeO
N
H
O
OH
Br
12c
f1 (ppm)

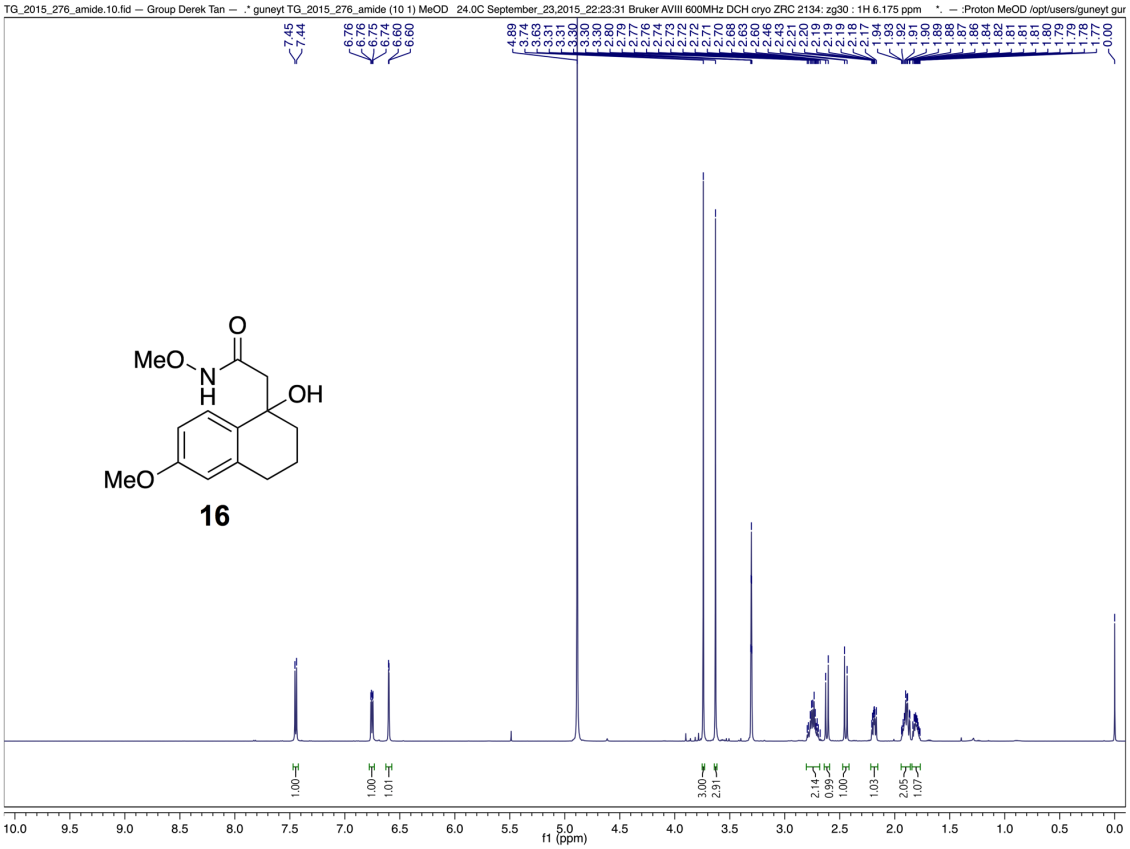

TG_2015_202_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_202_Pure (11 1) MeOD 24.0C June_26,2015_13:41:41 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon MeOD /opt/use
MeO
N
H
O
OH
Br
12c
f1 (ppm)

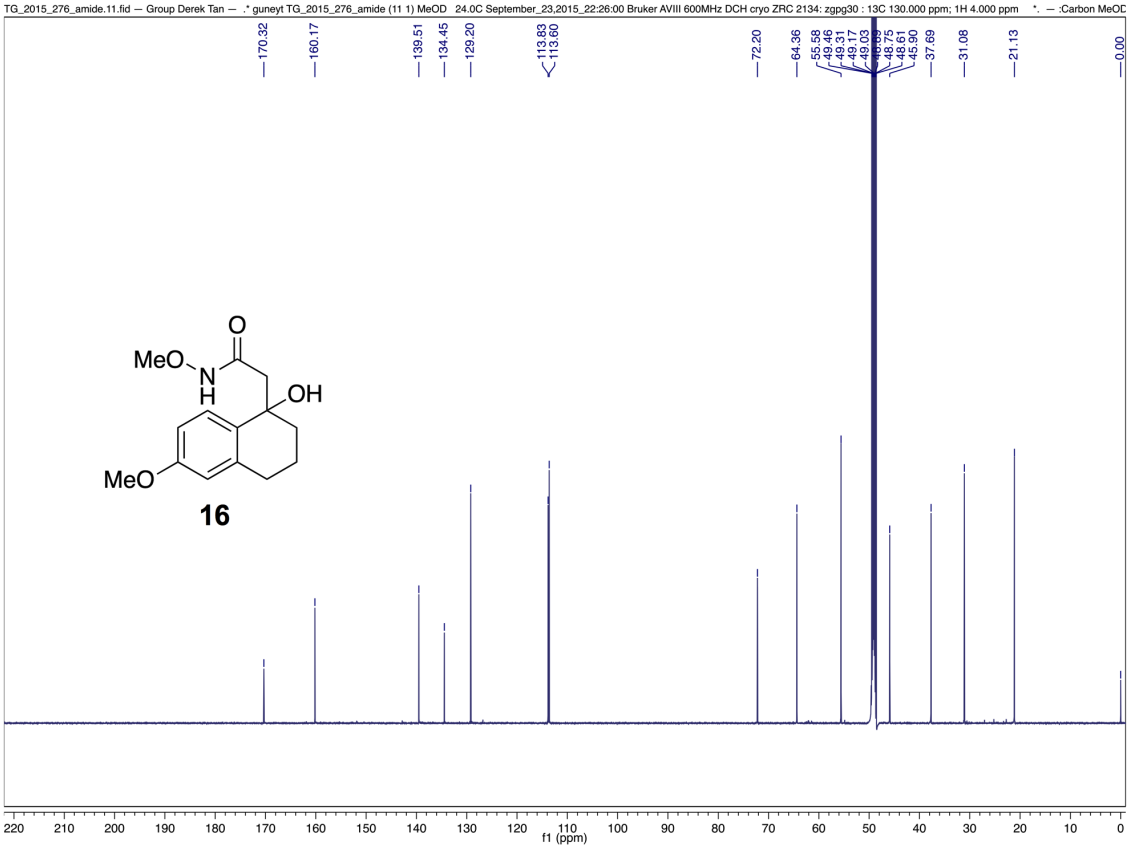

TG_2015_177_F1.10.fid — Group Derek Tan — .* guneyt TG_2015_177_F1 (10 1) MeOD 24.0C May_26,2015_20:14:54 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guneyt guneyt 80
MeO
N
H
O
OH
F
14a
f1 (ppm)

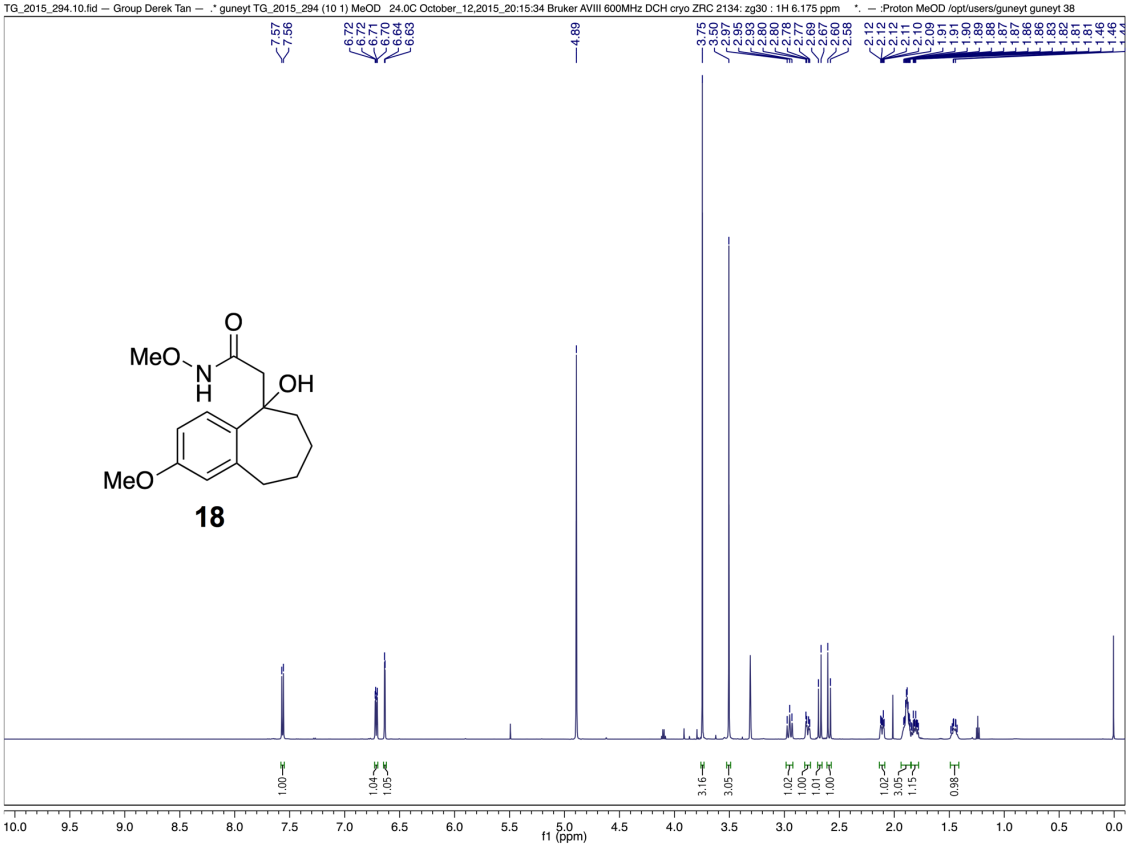

TG_2015_177_F1.11.fid — Group Derek Tan — .* guneyt TG_2015_177_F1 (11 1) MeOD 24.0C May_26,2015_20:17:21 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon MeOD /opt/users/gu
MeO
N
H
O
OH
F
14a
f1 (ppm)

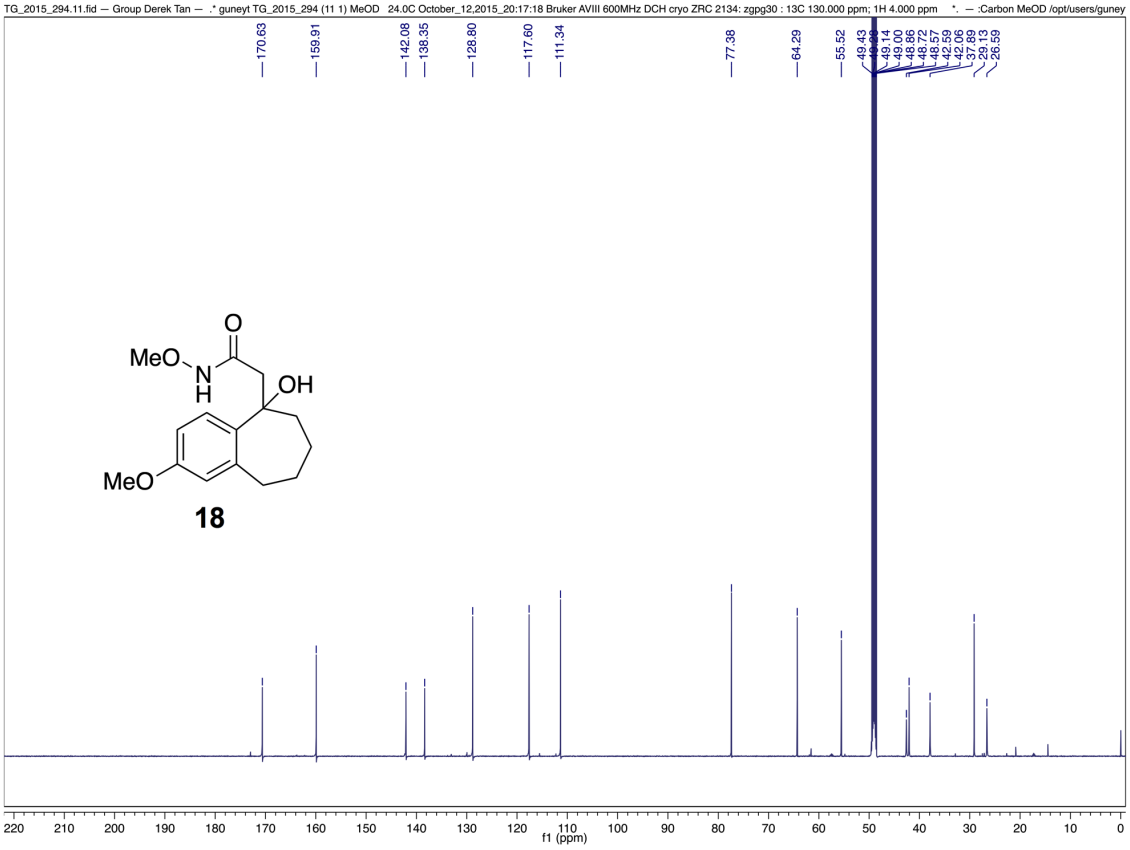

TG_2015_178_F1.10.fid — Group Derek Tan — .* guneyt TG_2015_178_F1 (10 1) MeOD 24.0C May_26,2015_21:21:19 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guneyt guneyt 81
7.63
7.18
7.18
7.17
7.17
7.16
7.05
7.05
4.89
3.49
3.31
3.31
3.31
3.31
3.30
3.07
2.56
2.54
2.43
2.41
2.01
2.01
2.00
2.00
1.99
1.98
1.98
1.97
1.97
1.87
1.86
1.85
1.84
1.84
1.82
1.82
1.81
1.77
1.70
1.67
1.67
1.65
1.58
1.57
1.57
1.56
1.55
1.54
1.53
1.53
1.52
1.20
0.01
O
MeO
N
H
OH
Cl
14b
0.90
1.10
1.02
3.00
1.70
2.99
1.14
2.20
1.20
1.17
2.07
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)

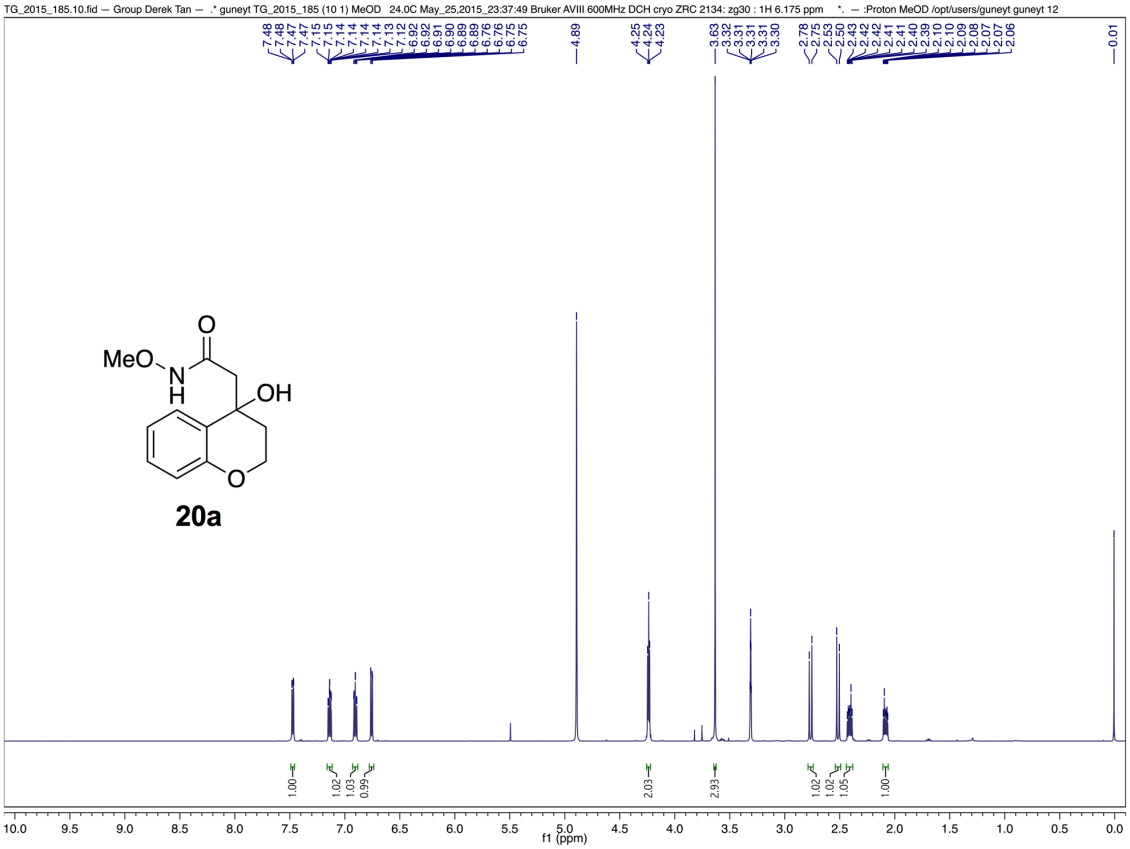

TG_2015_178_F1.11.fid — Group Derek Tan — .* guneyt TG_2015_178_F1 (11 1) MeOD 24.0C May_26,2015_21:23:26 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon MeOD /opt/users/gu
169.91
144.57
134.07
131.65
130.95
128.73
126.85
77.32
64.25
49.60
42.79
34.02
30.39
23.91
23.79
0.00
O
MeO
N
H
OH
Cl
14b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

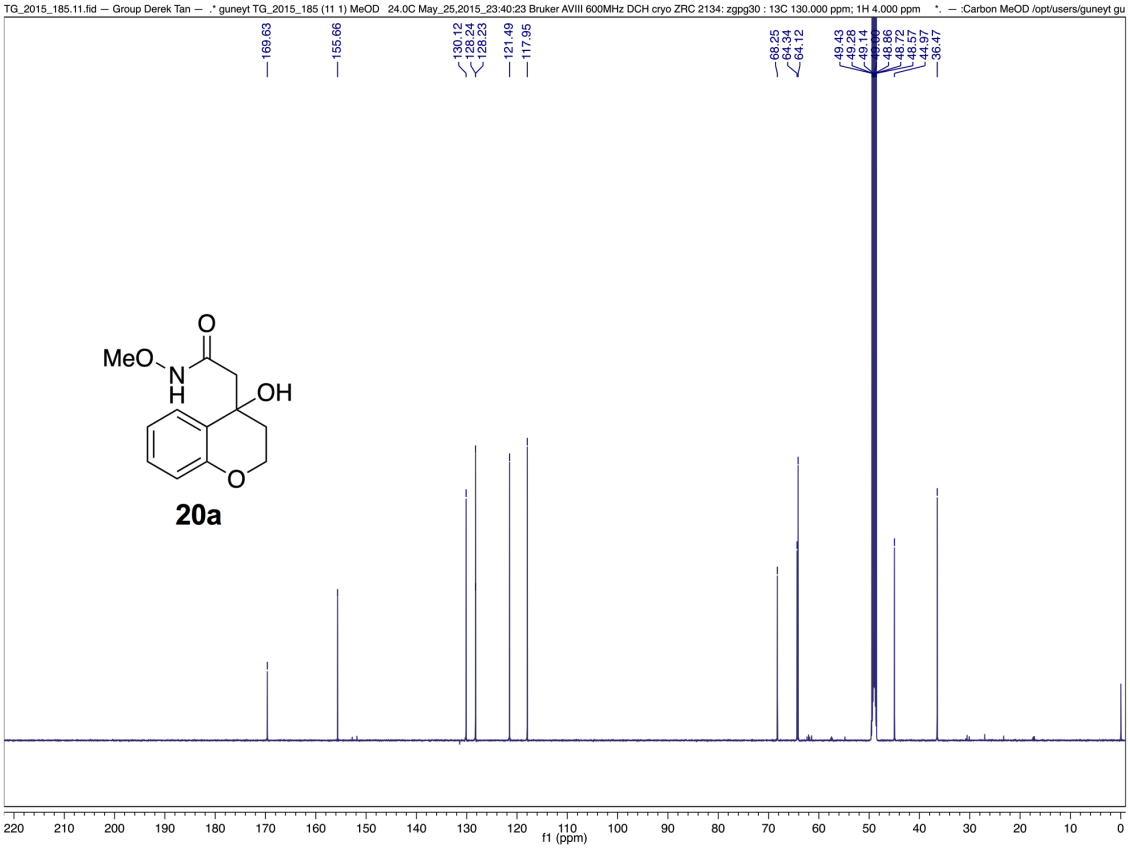

TG_2015_276_amide.10.fid — Group Derek Tan — .* guneyt TG_2015_276_amide (10 1) MeOD 24.0C September_23,2015_22:23:31 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guneyt gur
MeO
N
H
O
OH
MeO
16
f1 (ppm)

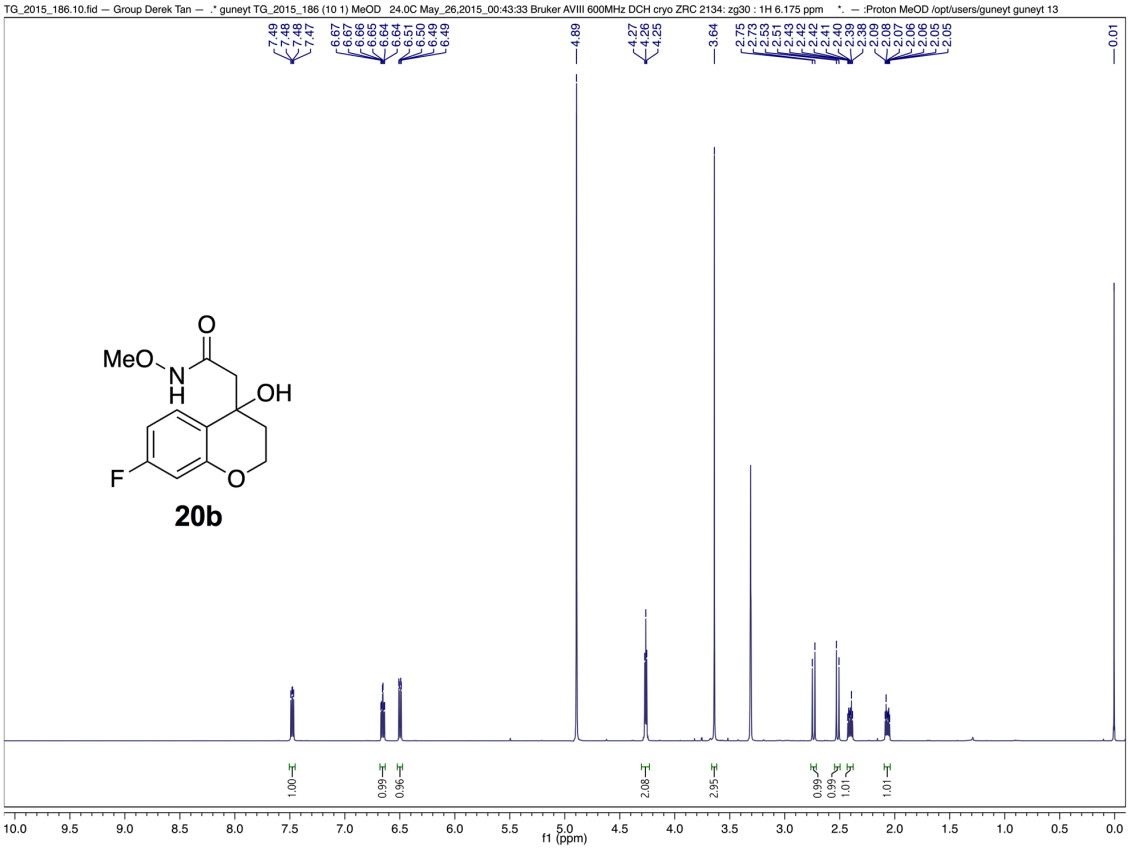

TG_2015_276_amide.11.fid — Group Derek Tan — .* guneyt TG_2015_276_amide (11 1) MeOD 24.0C September_23,2015_22:26:00 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon MeOD
MeO
N
H
O
OH
MeO
16
f1 (ppm)

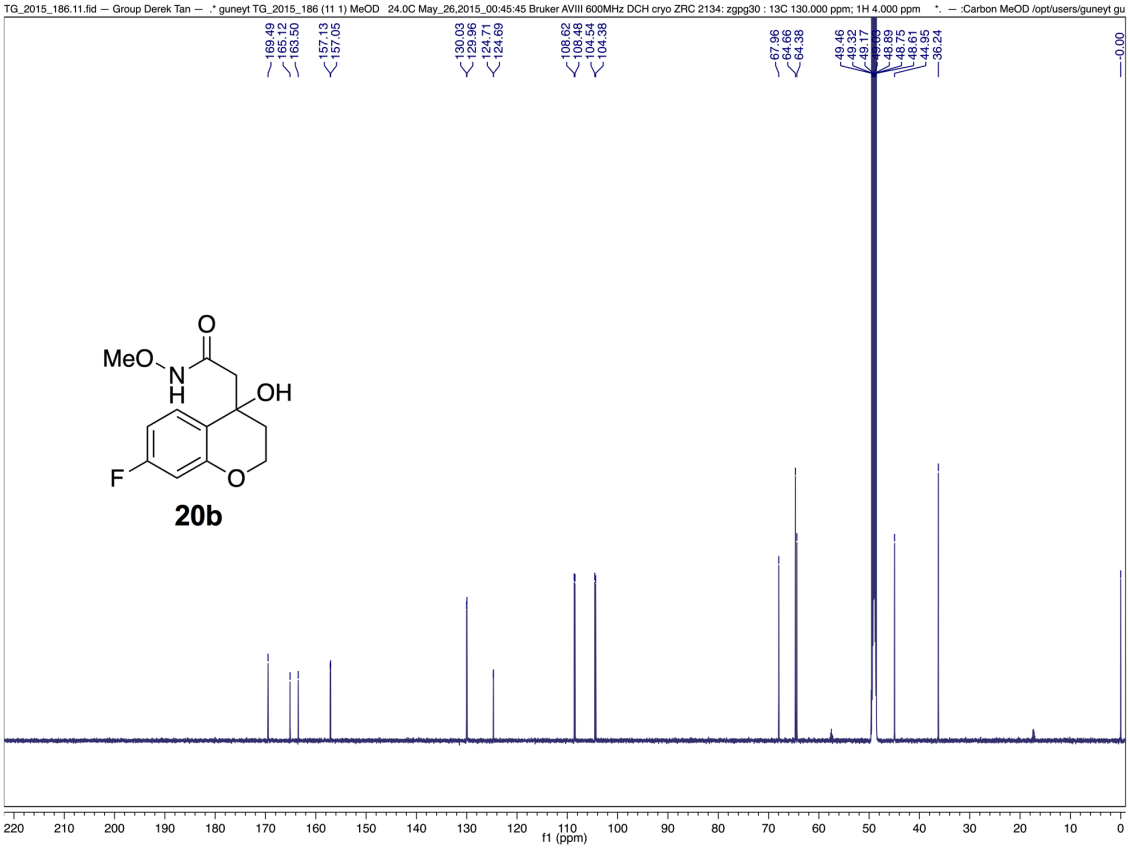

TG_2015_294.10.fid — Group Derek Tan — .* guneyt TG_2015_294 (10 1) MeOD 24.0C October_12,2015_20:15:34 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guneyt guneyt 38
7.57
7.56
6.72
6.72
6.71
6.70
6.64
6.63
4.89
3.75
3.50
2.97
2.95
2.93
2.80
2.80
2.78
2.77
2.69
2.67
2.60
2.58
2.12
2.12
2.12
2.11
2.10
2.09
1.91
1.91
1.90
1.89
1.88
1.87
1.87
1.86
1.86
1.83
1.83
1.81
1.81
1.46
1.46
1.44
1.00
1.04
1.05
3.16
3.05
1.02
1.00
1.01
1.00
1.02
3.05
1.15
0.98
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)
MeO
N
H
O
OH
MeO
18

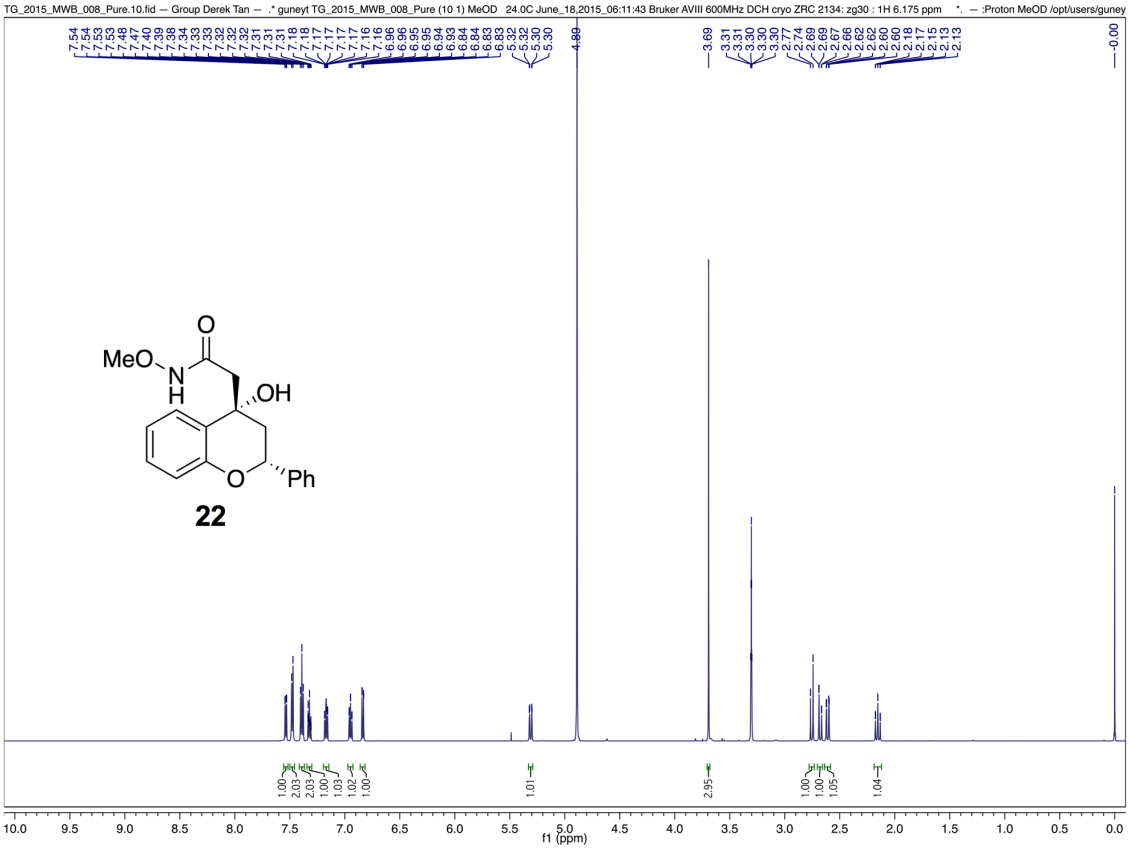

TG_2015_294.11.fid — Group Derek Tan — .* guneyt TG_2015_294 (11 1) MeOD 24.0C October_12,2015_20:17:18 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon MeOD /opt/users/guney
170.63
159.91
142.08
138.35
128.80
117.60
111.34
77.38
64.29
55.52
49.43
49.29
49.14
49.00
48.86
48.72
48.57
42.59
42.06
37.89
29.13
26.59
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
MeO
N
H
O
OH
MeO
18

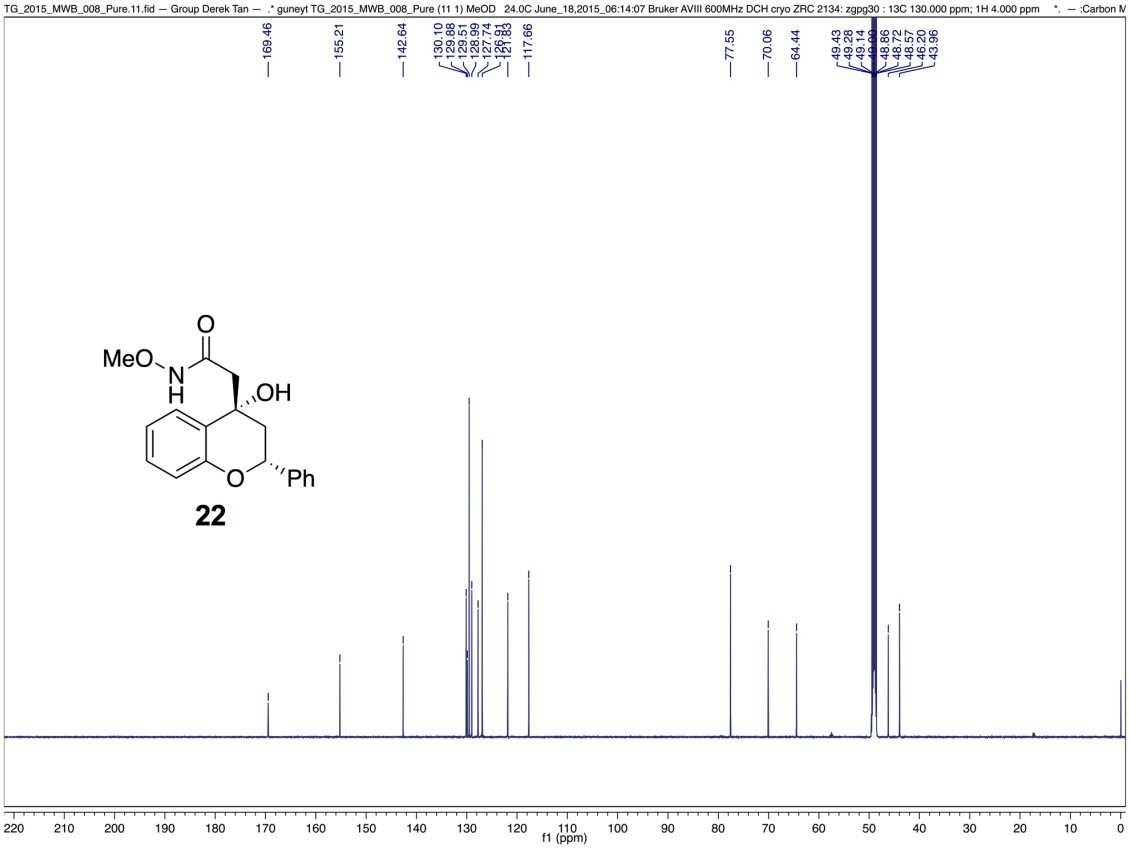

TG_2015_185.10.fid — Group Derek Tan — .* guneyt TG_2015_185 (10 1) MeOD 24.0C May_25,2015_23:37:49 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guneyt guneyt 12
MeO
N
H
O
OH
O
20a
f1 (ppm)

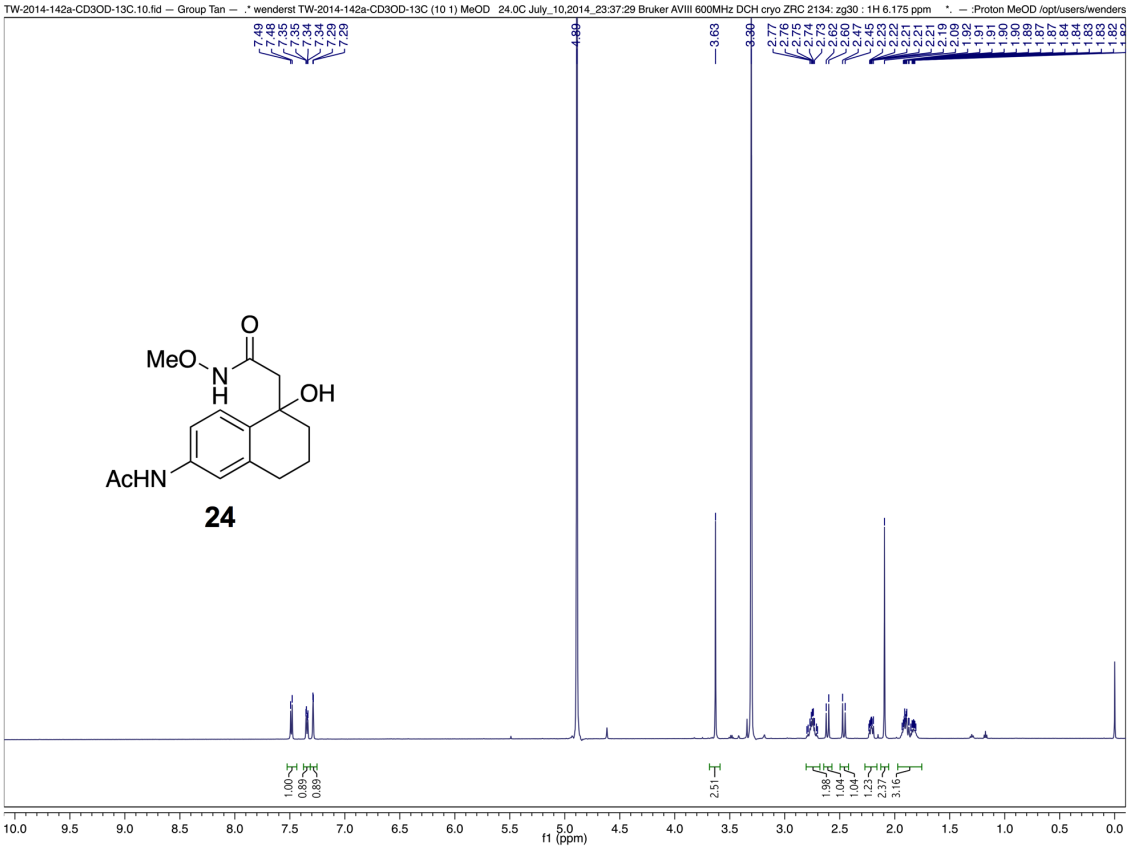

TG_2015_185.11.fid — Group Derek Tan — .* guneyt TG_2015_185 (11 1) MeOD 24.0C May_25,2015_23:40:23 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon MeOD /opt/users/guneyt gu
MeO
N
H
O
OH
O
20a
f1 (ppm)

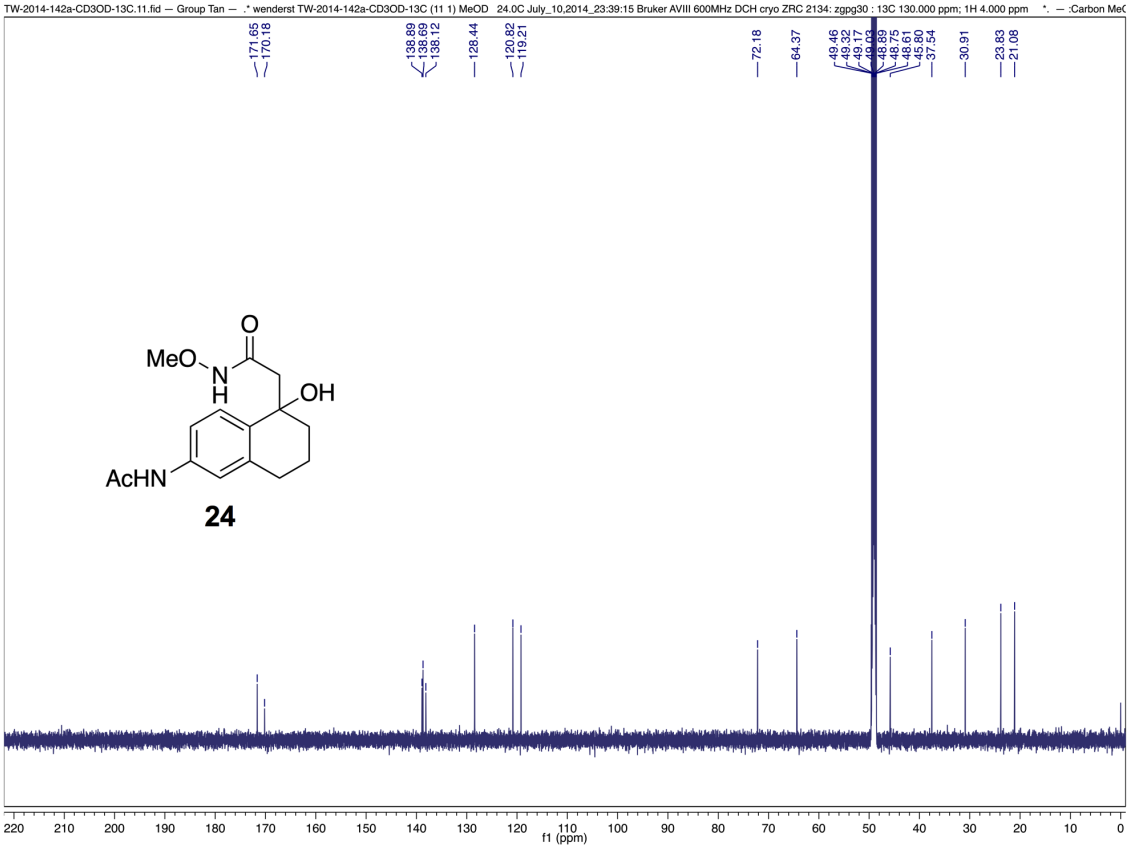

TG_2015_186.10.fid — Group Derek Tan — .* guneyt TG_2015_186 (10 1) MeOD 24.0C May_26,2015_00:43:33 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guneyt guneyt 13
7.49
7.48
7.48
7.47
6.67
6.67
6.66
6.65
6.64
6.64
6.51
6.50
6.49
6.49
4.89
4.27
4.26
4.25
3.64
2.75
2.73
2.53
2.51
2.43
2.42
2.41
2.40
2.39
2.38
2.09
2.08
2.07
2.06
2.05
2.05
0.01
1.00
0.99
0.96
2.08
2.95
0.99
0.99
1.01
1.01
MeO
N
H
O
OH
F
O
20b
f1 (ppm)

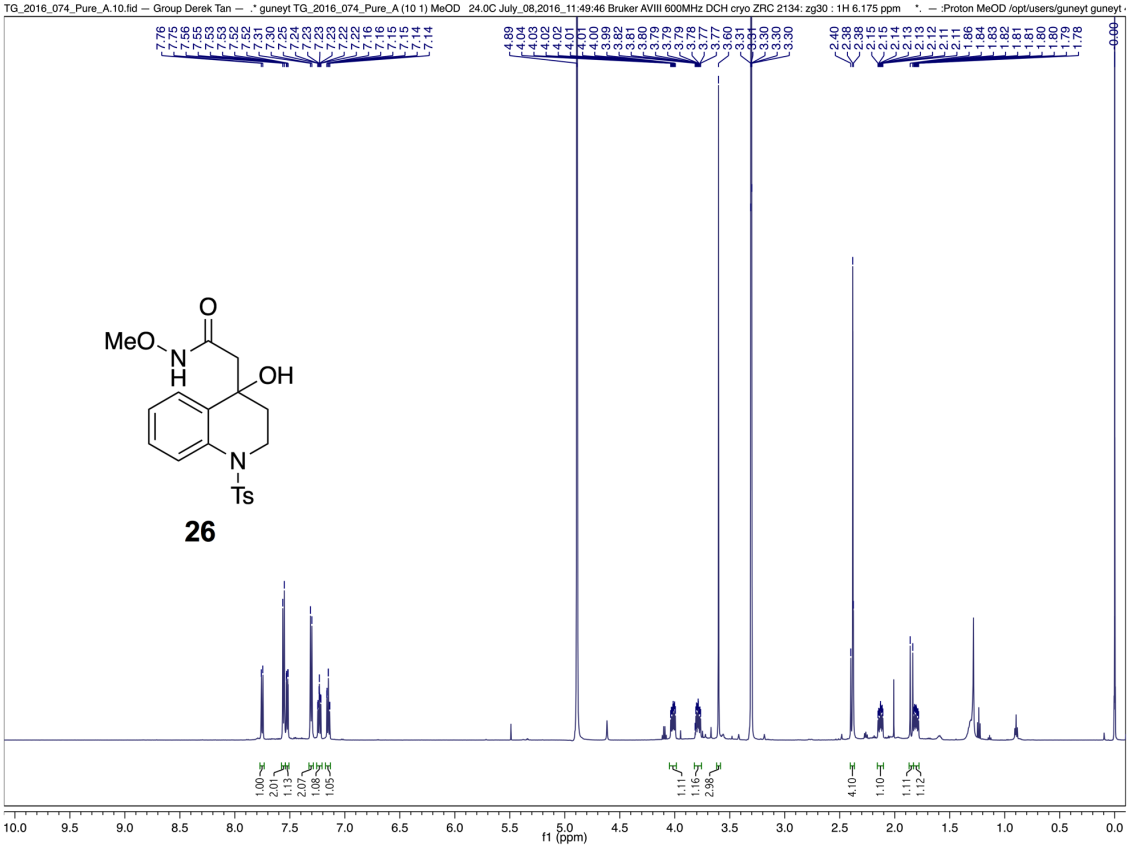

TG_2015_186.11.fid — Group Derek Tan — .* guneyt TG_2015_186 (11 1) MeOD 24.0C May_26,2015_00:45:45 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon MeOD /opt/users/guneyt gu
169.49
165.12
163.50
157.13
157.05
130.03
129.96
124.71
124.69
108.62
108.48
104.54
104.38
67.96
64.66
64.38
49.46
49.32
49.17
48.89
48.75
48.61
44.65
36.24
0.00
MeO
N
H
O
OH
F
O
20b
f1 (ppm)

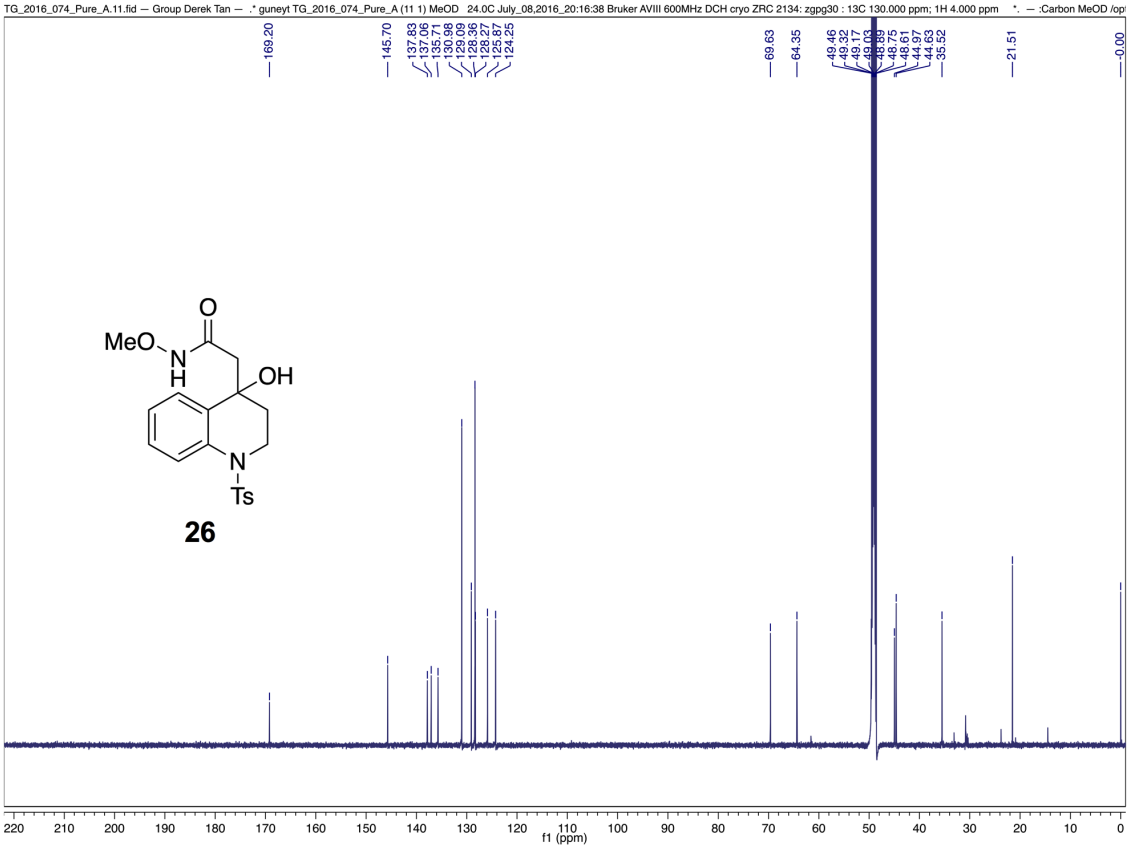

TG_2015_MWB_008_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_MWB_008_Pure (10 1) MeOD 24.0C June_18,2015_06:11:43 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton MeOD /opt/users/guney
MeO
N
H
O
OH
O
Ph
22
f1 (ppm)

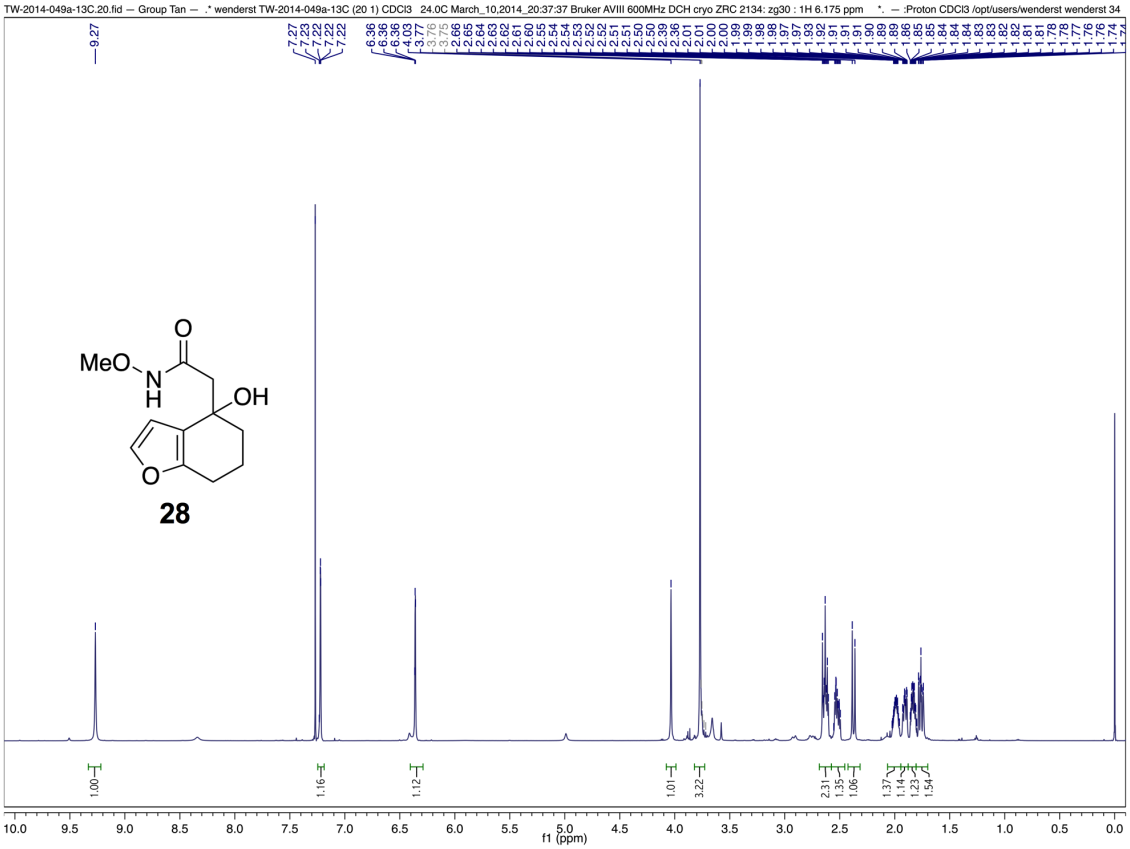

TG_2015_MWB_008_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_MWB_008_Pure (11 1) MeOD 24.0C June_18,2015_06:14:07 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon M
MeO
N
H
O
OH
O
Ph
22
f1 (ppm)

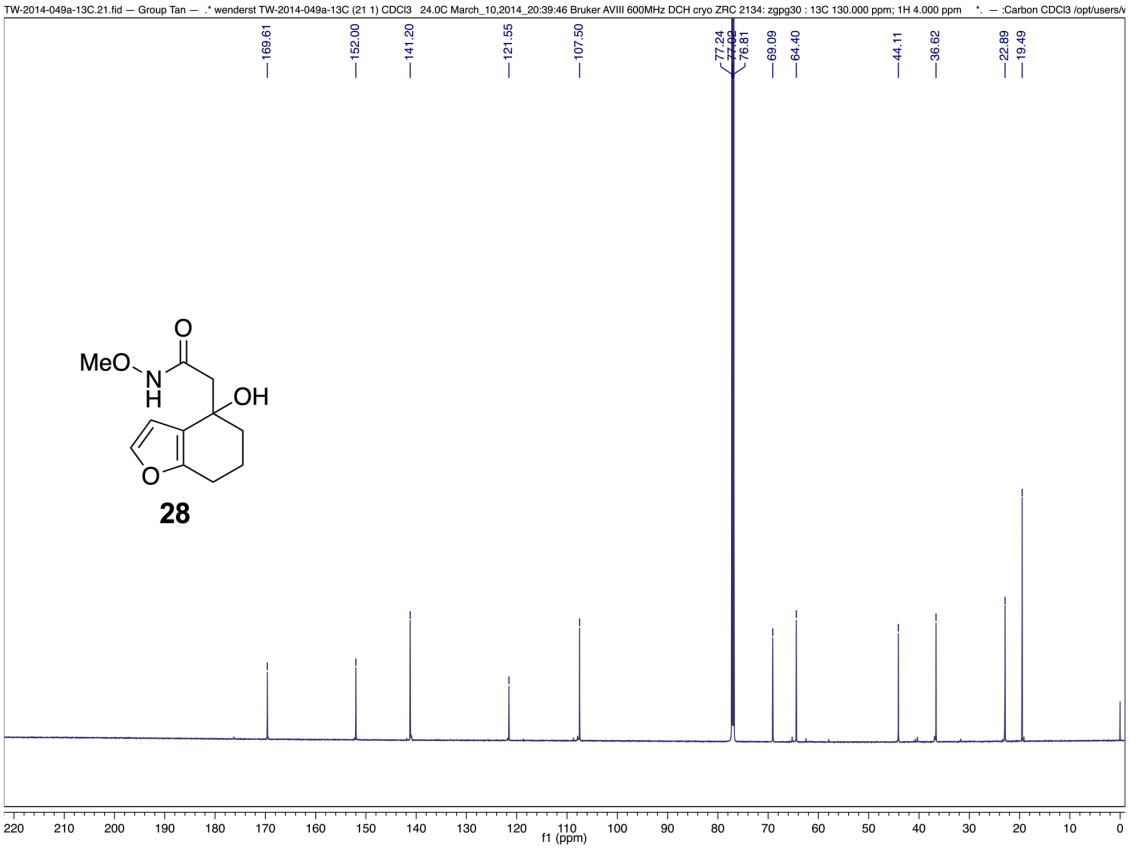

TW-2014-142a-CD3OD-13C.10.fid — Group Tan — .* wenderst TW-2014-142a-CD3OD-13C (10 1) MeOD 24.0C July_10,2014_23:37:29 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
MeO
N
H
O
OH
AcHN
24
f1 (ppm)

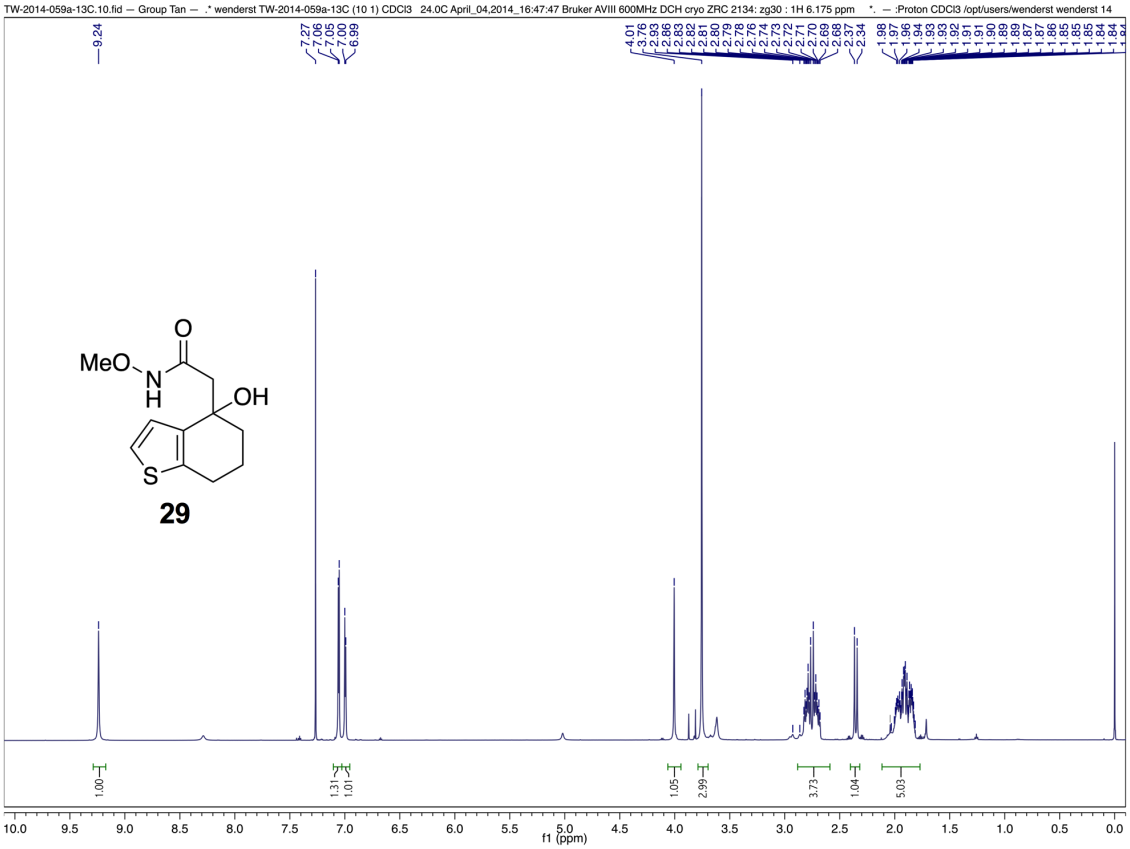

TW-2014-142a-CD3OD-13C.11.fid — Group Tan — .* wenderst TW-2014-142a-CD3OD-13C (11 1) MeOD 24.0C July_10,2014_23:39:15 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm
MeO
N
H
O
OH
AcHN
24
f1 (ppm)

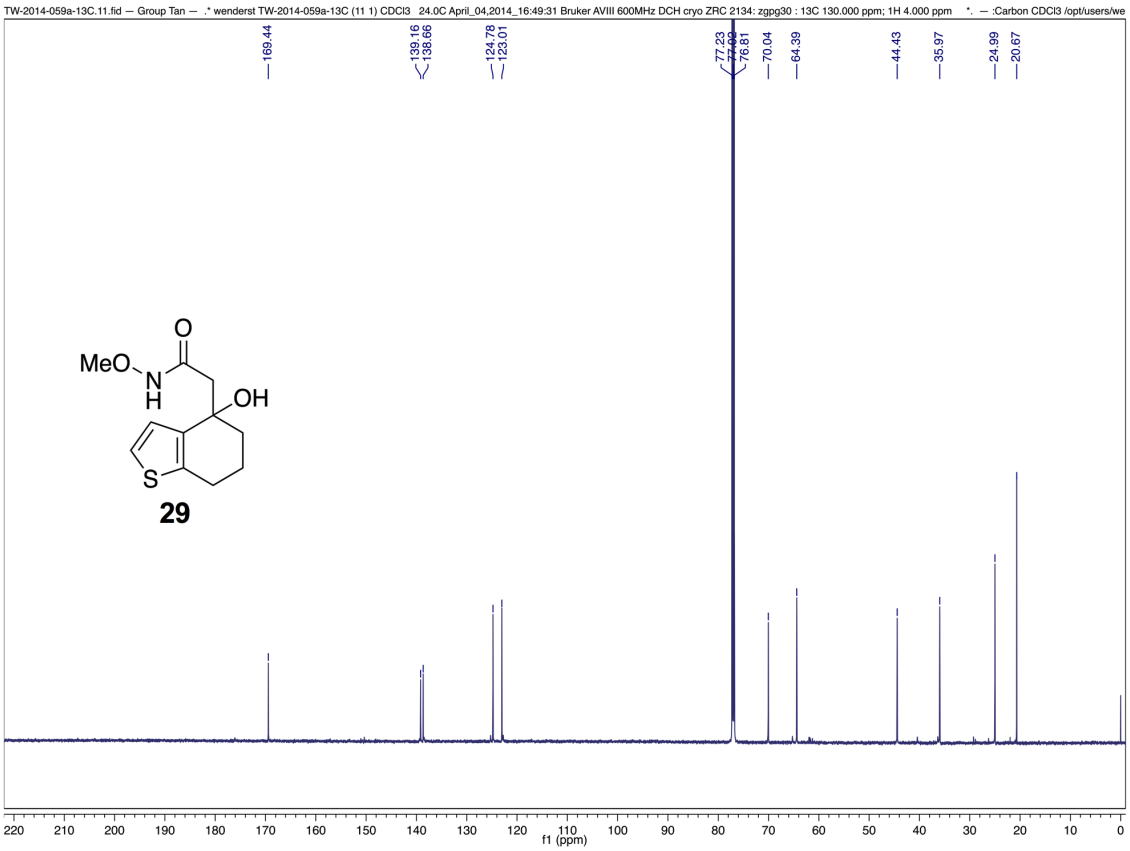

MeO
N
H
O
OH
N
Ts
26

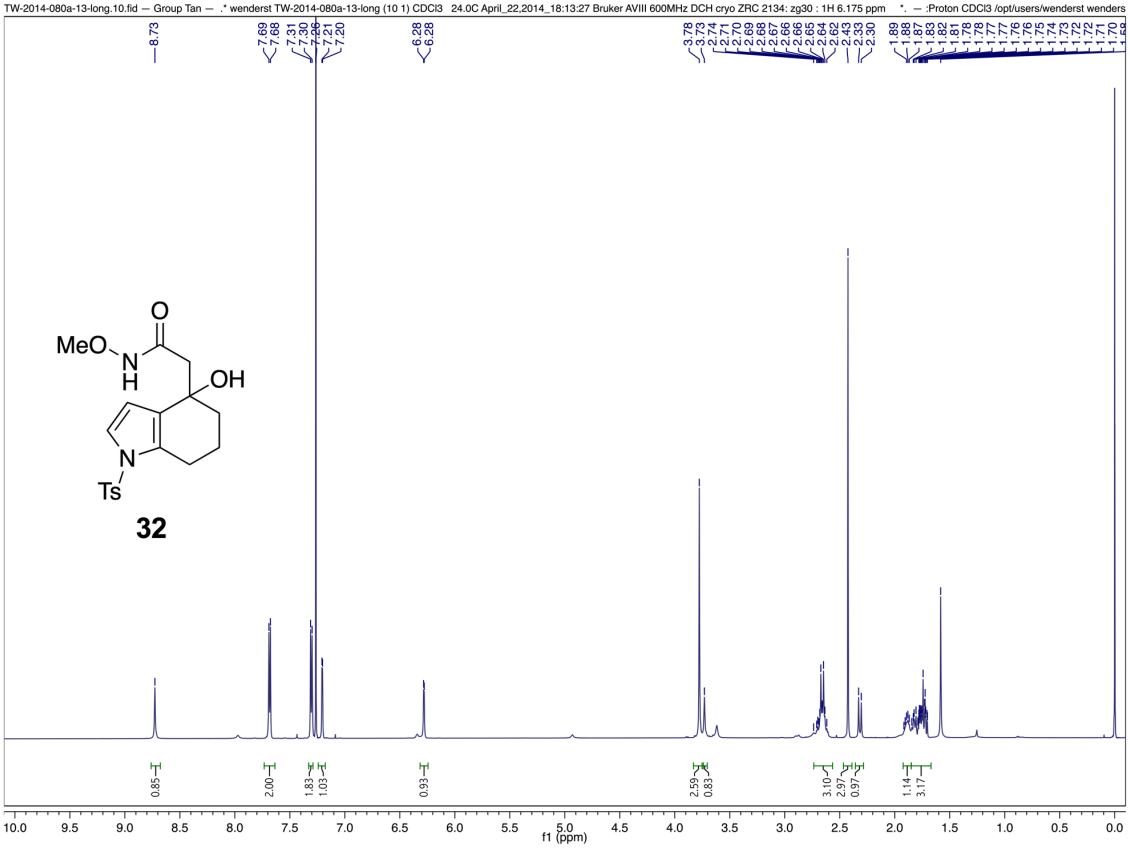

MeO
N
H
O
OH
N
Ts
26

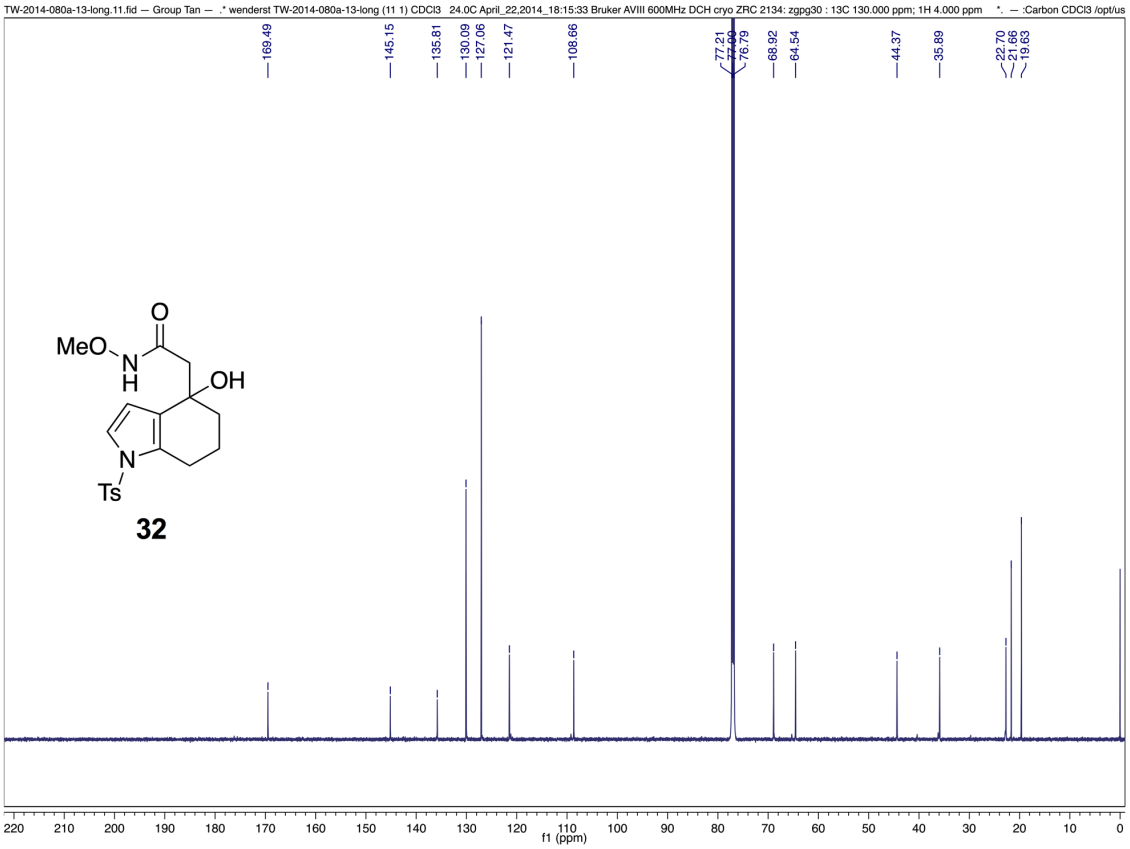

TW-2014-049a-13C.20.fid — Group Tan — .* wenderst TW-2014-049a-13C (20 1) CDCl3 24.0C March_10,2014_20:37:37 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 34
MeO
N
H
O
OH
O
28
f1 (ppm)

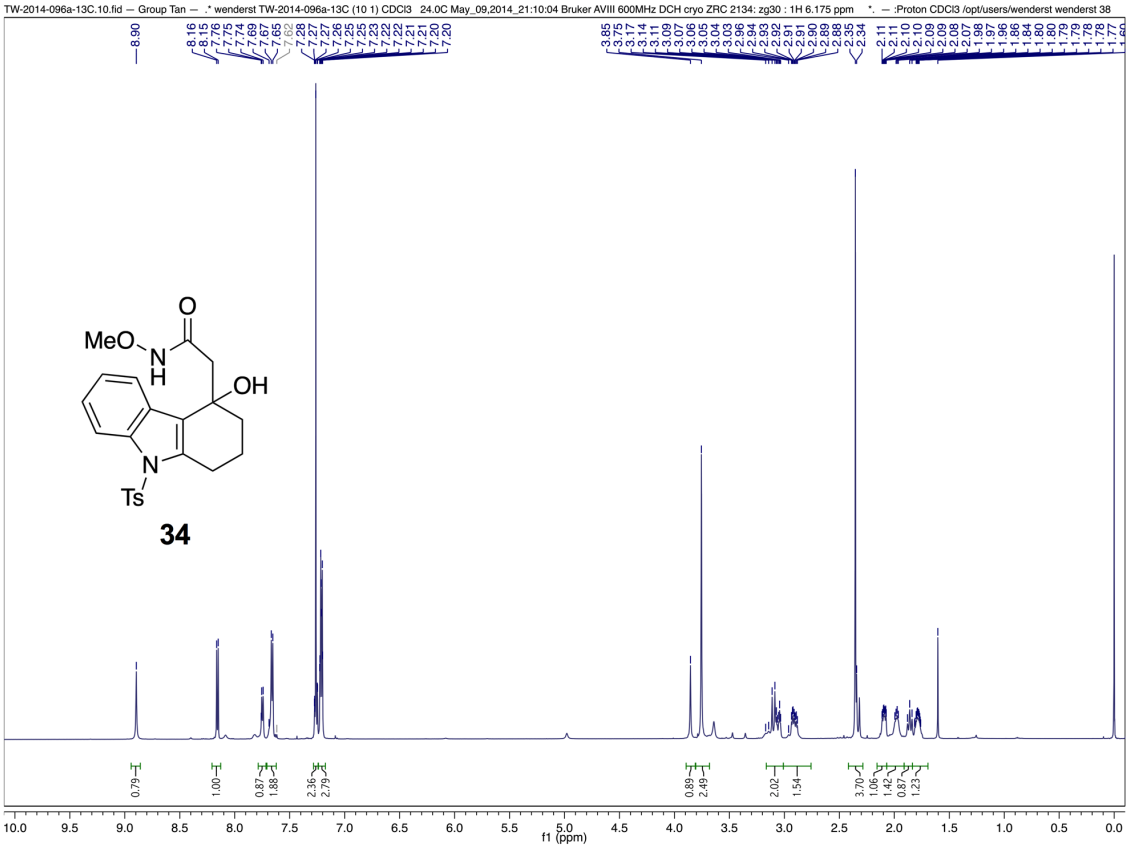

TW-2014-049a-13C.21.fid — Group Tan — .* wenderst TW-2014-049a-13C (21 1) CDCl3 24.0C March_10,2014_20:39:46 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/
169.61
152.00
141.20
121.55
107.50
77.24
77.02
76.81
69.09
64.40
44.11
36.62
22.89
19.49
MeO
N
H
O
OH
O
28
f1 (ppm)

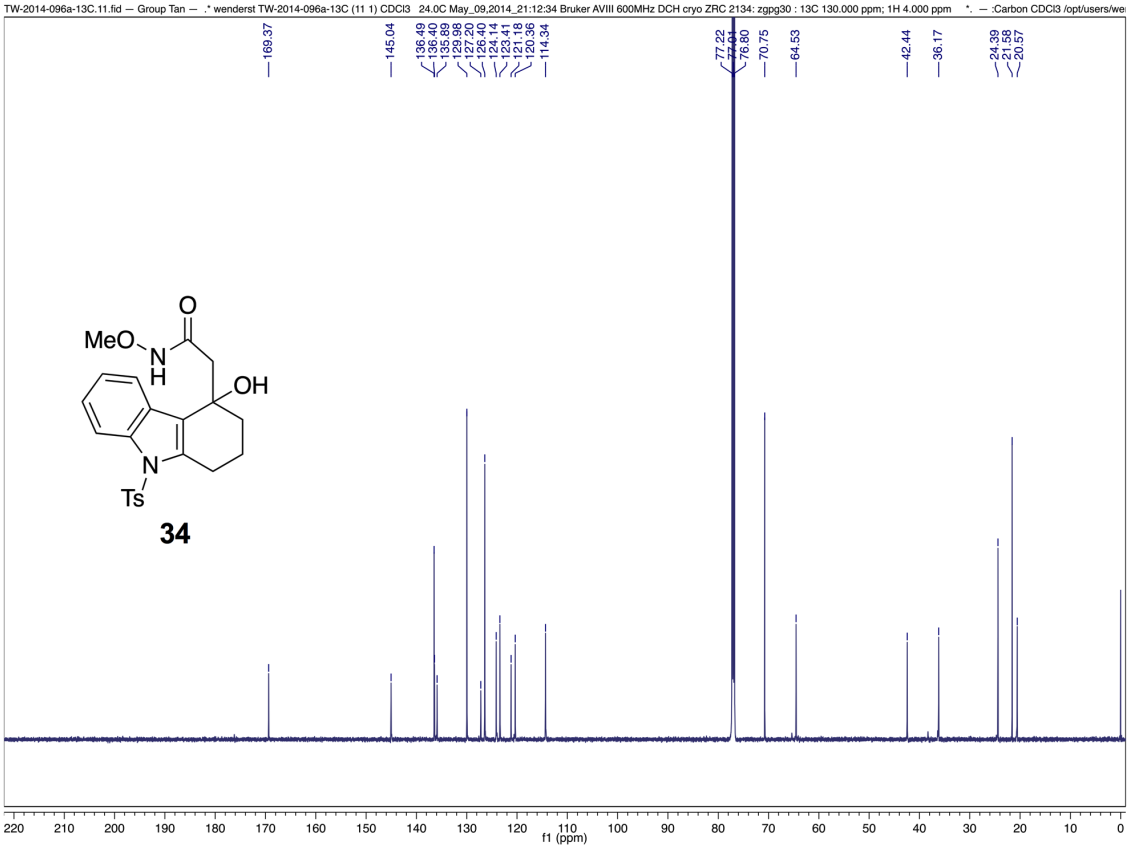

TW-2014-059a-13C.10.fid — Group Tan — .* wenderst TW-2014-059a-13C (10 1) CDCl3 24.0C April_04,2014_16:47:47 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm :Proton CDCl3 /opt/users/wenderst wenderst 14
9.24
7.27
7.06
7.05
7.00
6.99
4.01
3.76
2.93
2.86
2.83
2.82
2.81
2.80
2.78
2.76
2.74
2.73
2.72
2.71
2.70
2.69
2.68
2.37
2.34
1.98
1.97
1.96
1.94
1.93
1.92
1.91
1.90
1.89
1.87
1.86
1.85
1.84
MeO
N
H
O
OH
S
29
1.00
1.31
1.01
1.05
2.99
3.73
1.04
5.03
f1 (ppm)

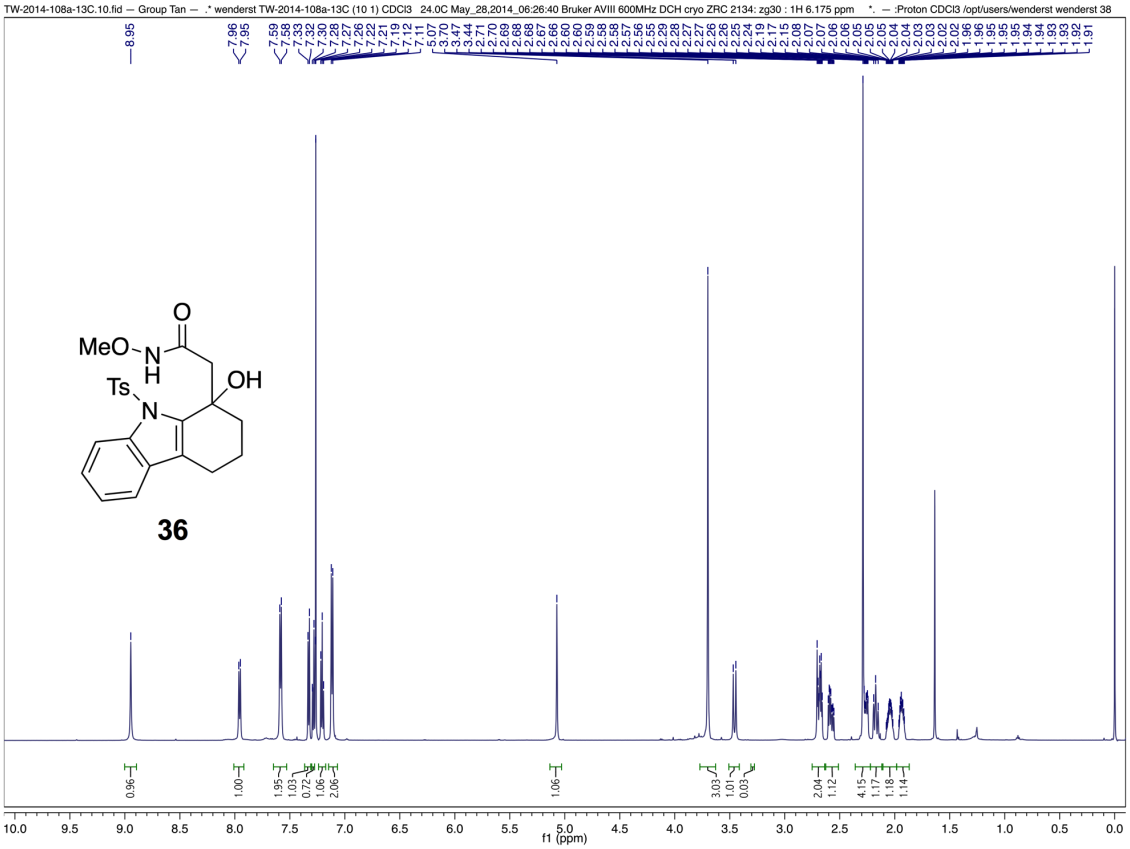

TW-2014-059a-13C.11.fid — Group Tan — .* wenderst TW-2014-059a-13C (11 1) CDCl3 24.0C April_04,2014_16:49:31 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm :Carbon CDCl3 /opt/users/we
169.44
139.16
138.66
124.78
123.01
77.23
77.02
76.81
70.04
64.39
44.43
35.97
24.99
20.67
MeO
N
H
O
OH
S
29
f1 (ppm)

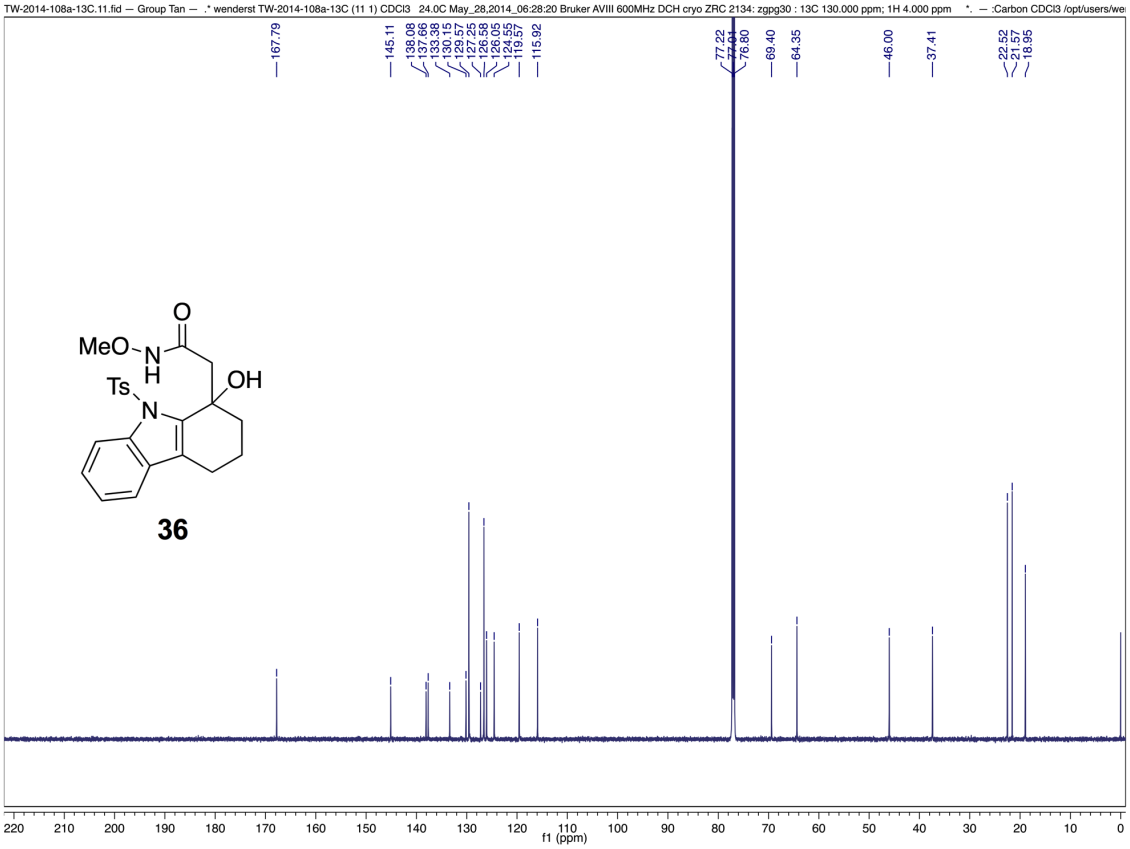

TW-2014-080a-13-long.10.fid — Group Tan — .* wenderst TW-2014-080a-13-long (10 1) CDCl3 24.0C April_22,2014_18:13:27 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenders
8.73
7.69
7.68
7.31
7.30
7.26
7.21
7.20
6.28
6.28
3.78
3.73
3.74
2.71
2.70
2.69
2.68
2.67
2.66
2.65
2.64
2.62
2.43
2.33
2.30
1.89
1.88
1.87
1.83
1.82
1.81
1.78
1.77
1.77
1.76
1.76
1.75
1.74
1.73
1.72
1.72
1.71
1.70
0.85
2.00
1.83
1.03
0.93
2.59
0.83
3.10
2.97
0.97
1.14
3.17
MeO
N
H
O
OH
N
Ts
32
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)

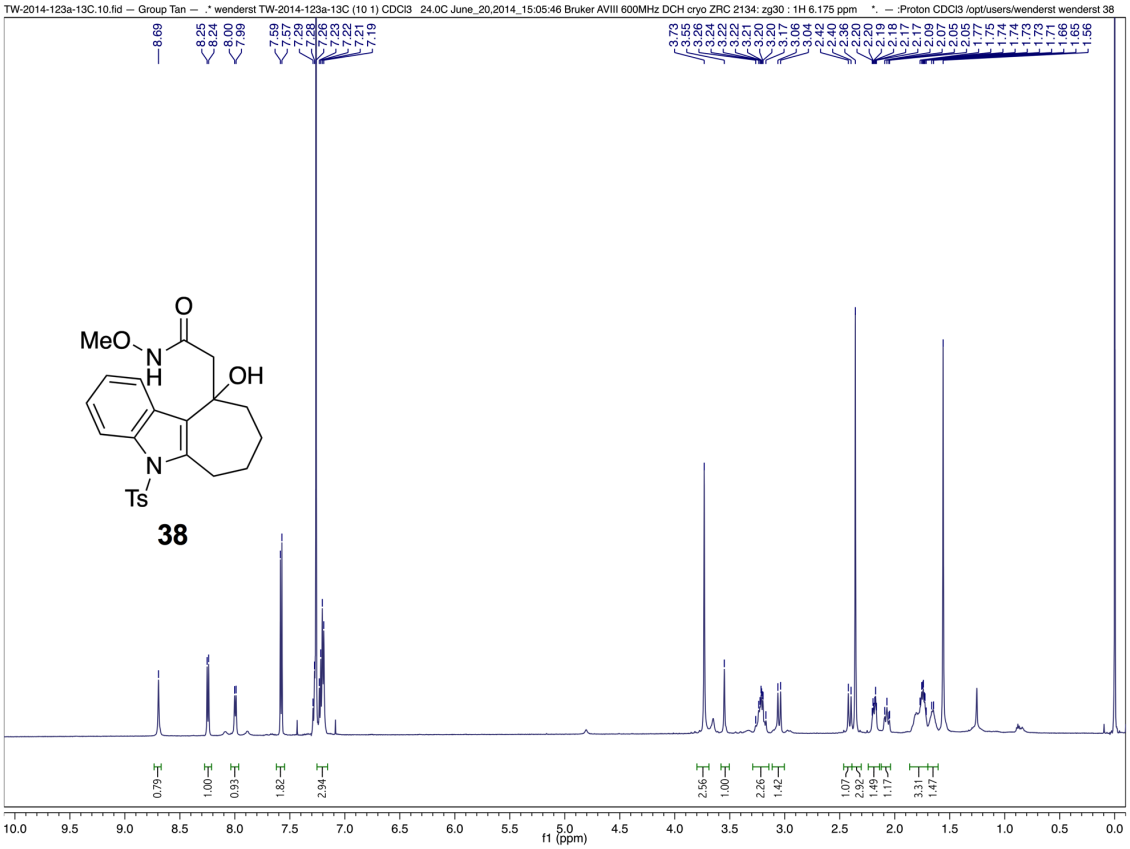

TW-2014-080a-13-long.11.fid — Group Tan — .* wenderst TW-2014-080a-13-long (11 1) CDCl3 24.0C April_22,2014_18:15:33 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/us
169.49
145.15
135.81
130.09
127.06
121.47
108.66
77.21
77.00
76.79
68.92
64.54
44.37
35.89
22.70
21.66
19.63
MeO
N
H
O
OH
N
Ts
32
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

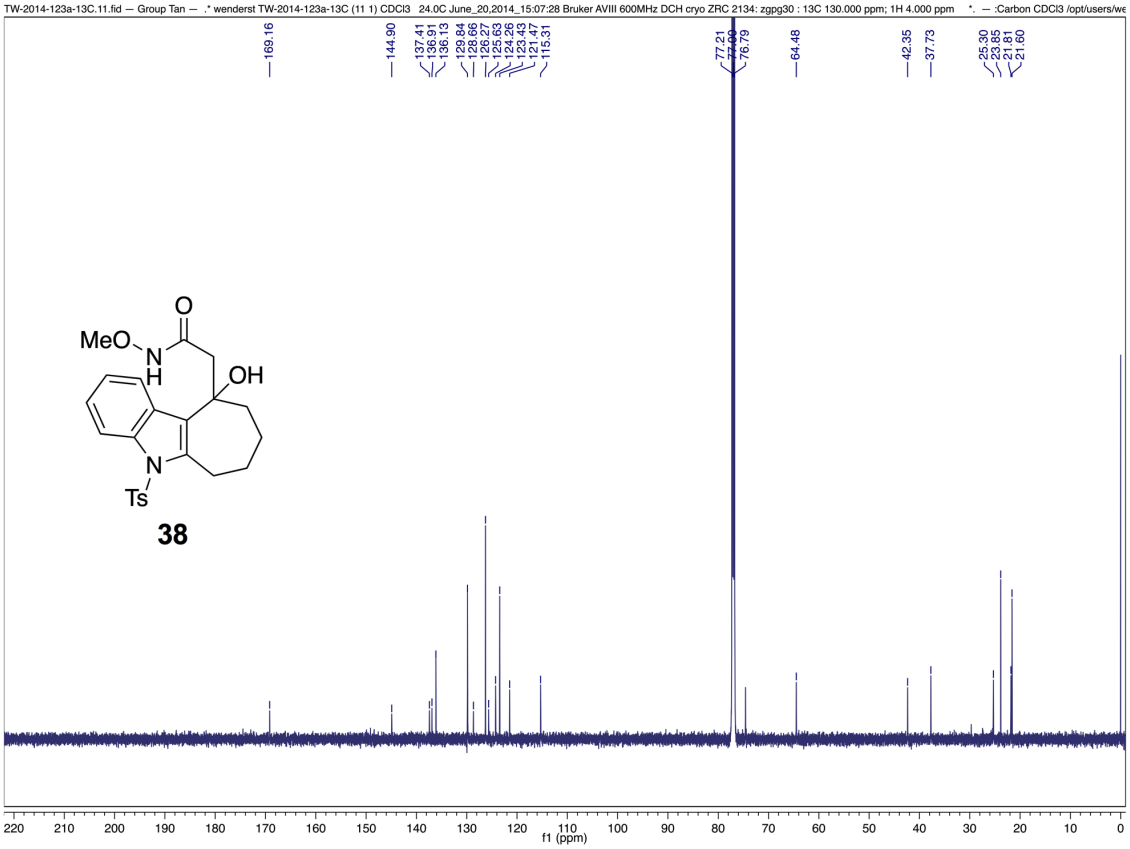

TW-2014-096a-13C.10.fid — Group Tan — .* wenderst TW-2014-096a-13C (10 1) CDCl3 24.0C May_09,2014_21:10:04 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm :Proton CDCl3 /opt/users/wenderst wenderst 38
MeO
N
H
O
OH
N
Ts
34
f1 (ppm)

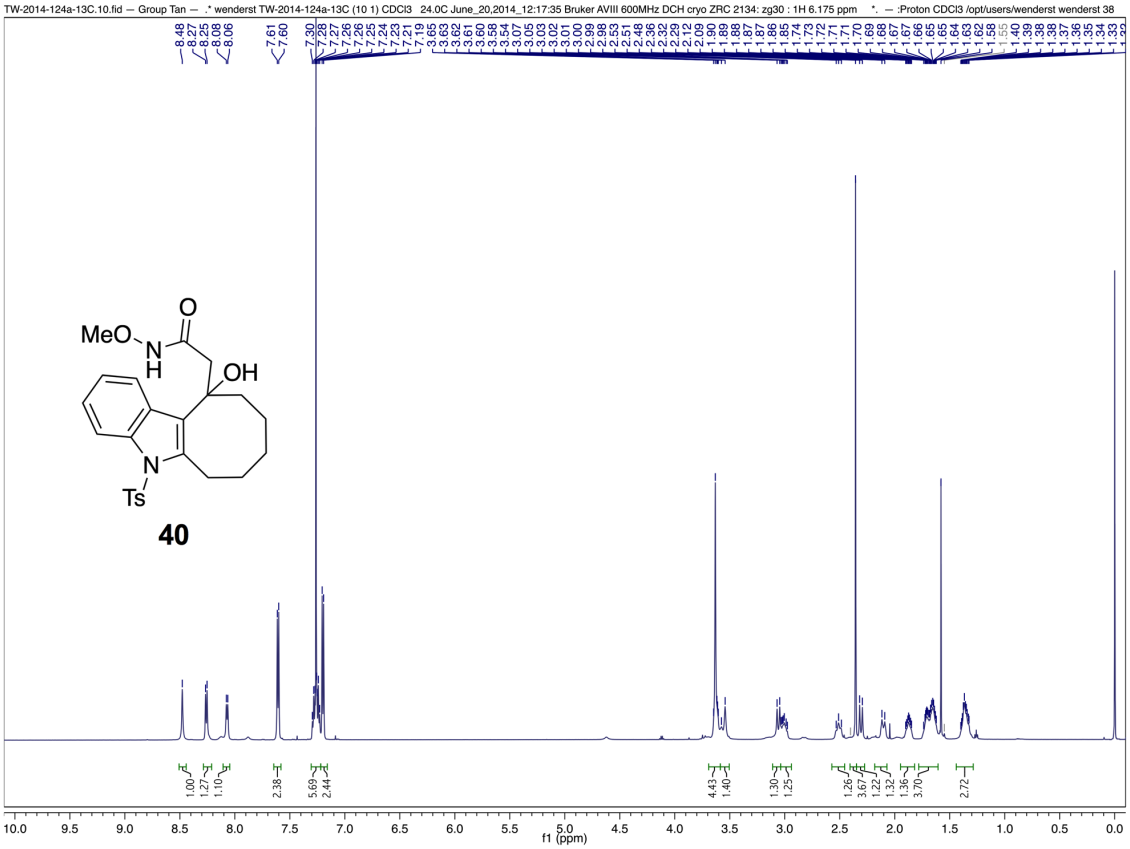

TW-2014-096a-13C.11.fid — Group Tan — .* wenderst TW-2014-096a-13C (11 1) CDCl3 24.0C May_09,2014_21:12:34 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm :Carbon CDCl3 /opt/users/we
MeO
N
H
O
OH
N
Ts
34
f1 (ppm)

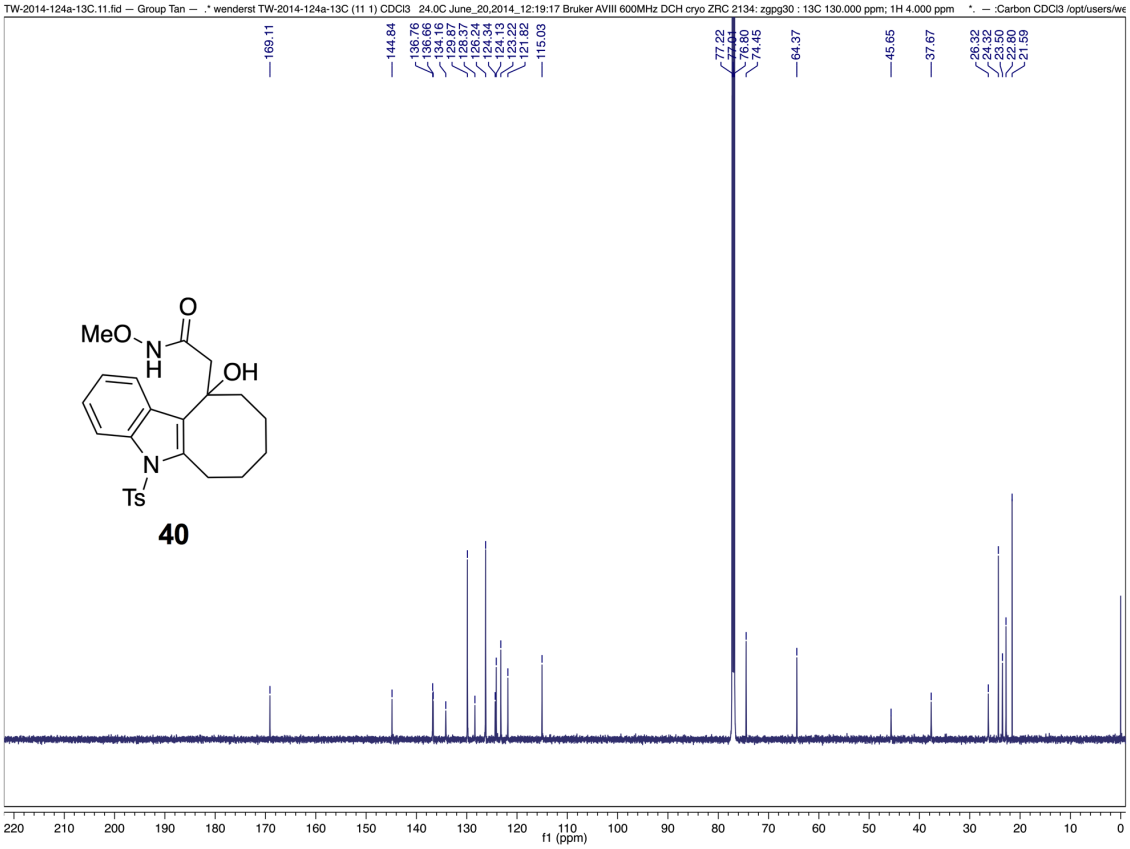

TW-2014-108a-13C.10.fid — Group Tan — .* wenderst TW-2014-108a-13C (10 1) CDCl3 24.0C May_28,2014_06:26:40 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 38
MeO
N
H
O
Ts
N
OH
36
f1 (ppm)

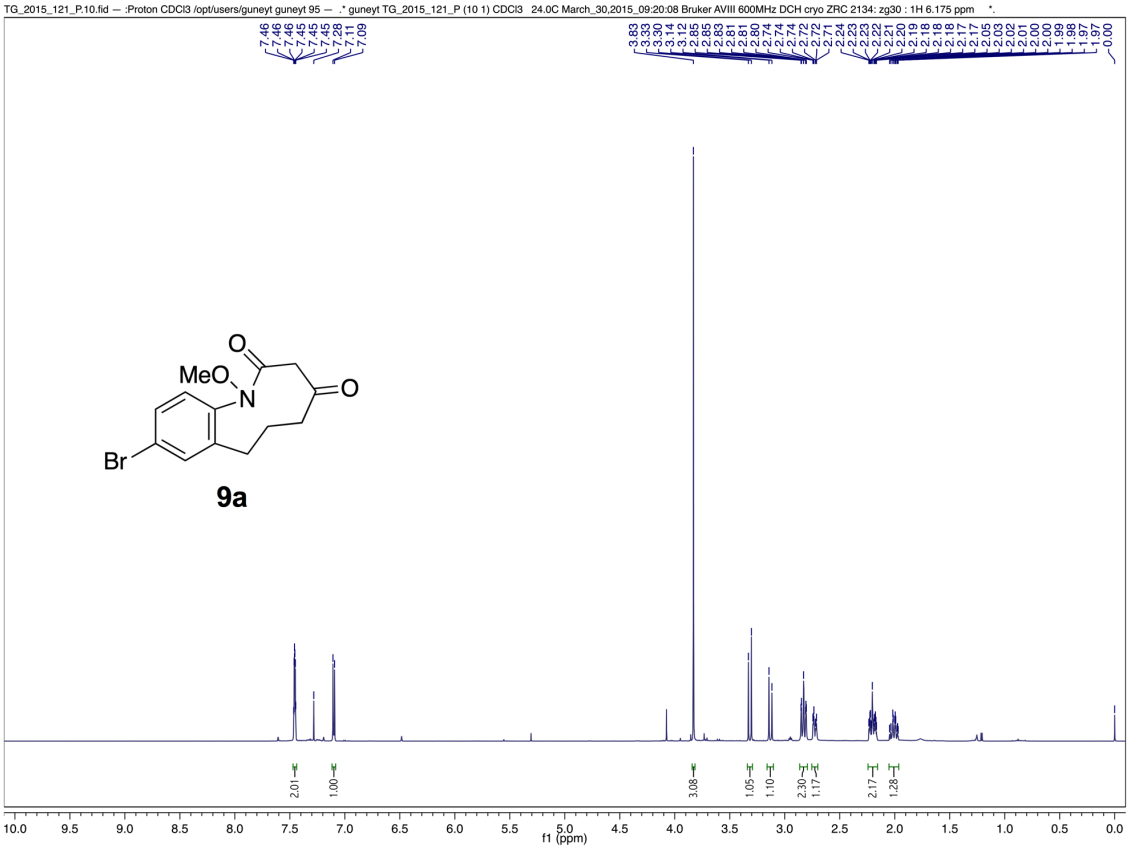

TW-2014-108a-13C.11.fid — Group Tan — .* wenderst TW-2014-108a-13C (11 1) CDCl3 24.0C May_28,2014_06:28:20 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/we
MeO
N
H
O
Ts
N
OH
36
f1 (ppm)

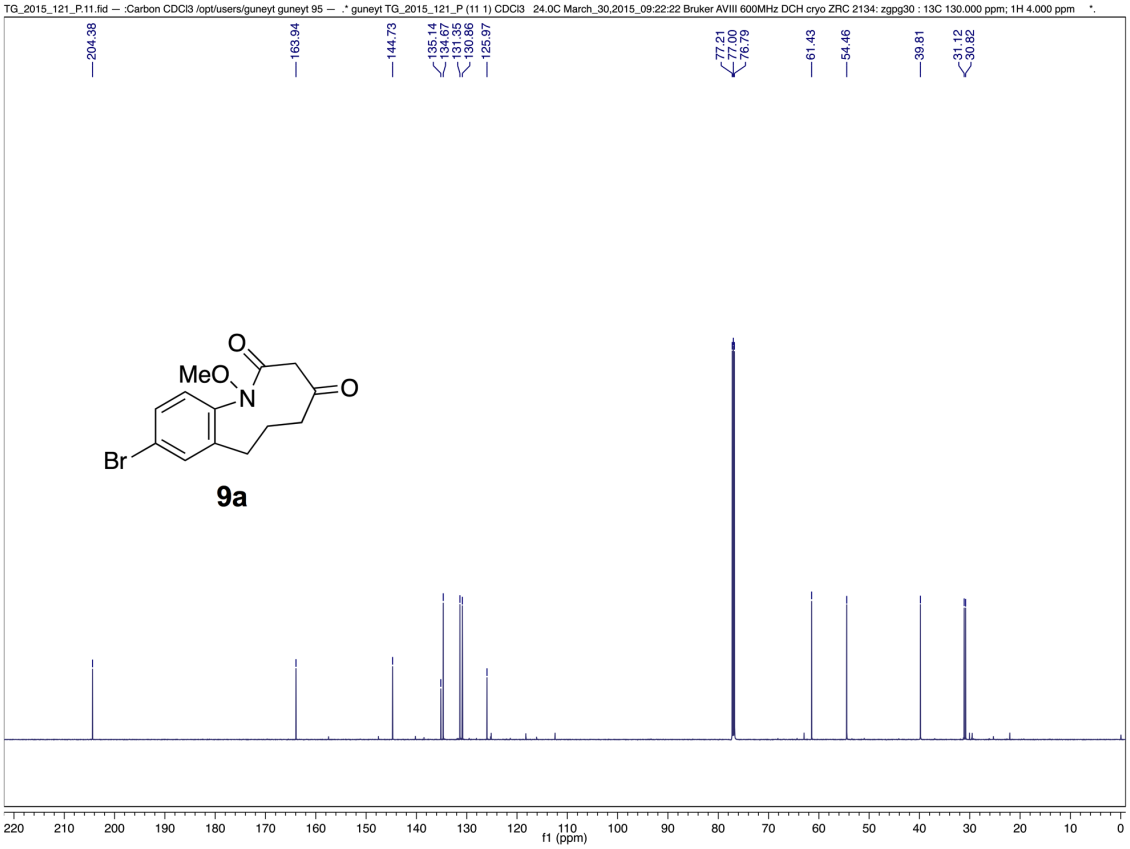

TW-2014-123a-13C.10.fid — Group Tan — .* wenderst TW-2014-123a-13C (10 1) CDCl3 24.0C June_20,2014_15:05:46 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 38
8.69
8.25
8.24
8.00
7.99
7.59
7.57
7.29
7.28
7.28
7.22
7.21
7.19
3.73
3.15
3.26
3.24
3.22
3.21
3.20
3.17
3.06
3.04
2.42
2.40
2.36
2.20
2.19
2.18
2.17
2.17
2.09
2.07
2.05
1.77
1.75
1.74
1.73
1.73
1.71
1.66
1.65
1.56
MeO
N
H
O
OH
N
Ts
38
0.79
1.00
0.93
1.82
2.94
2.56
1.00
2.26
1.42
1.07
2.92
1.49
1.17
3.31
1.47
f1 (ppm)

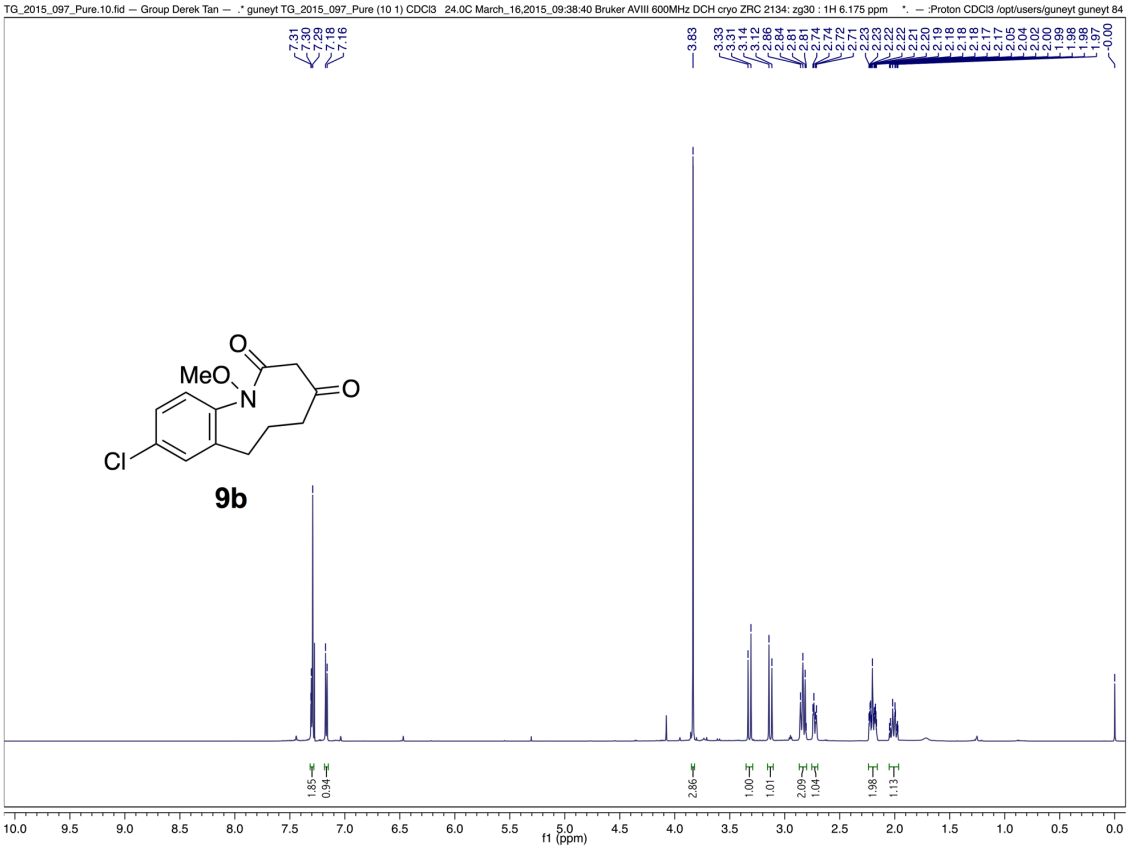

TW-2014-123a-13C.11.fid — Group Tan — .* wenderst TW-2014-123a-13C (11 1) CDCl3 24.0C June_20,2014_15:07:28 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/we
169.16
144.90
137.41
136.91
136.13
129.84
128.66
126.27
125.63
124.26
123.43
121.47
115.31
77.21
77.00
76.79
64.48
42.35
37.73
25.30
23.85
21.81
21.60
MeO
N
H
O
OH
N
Ts
38
f1 (ppm)

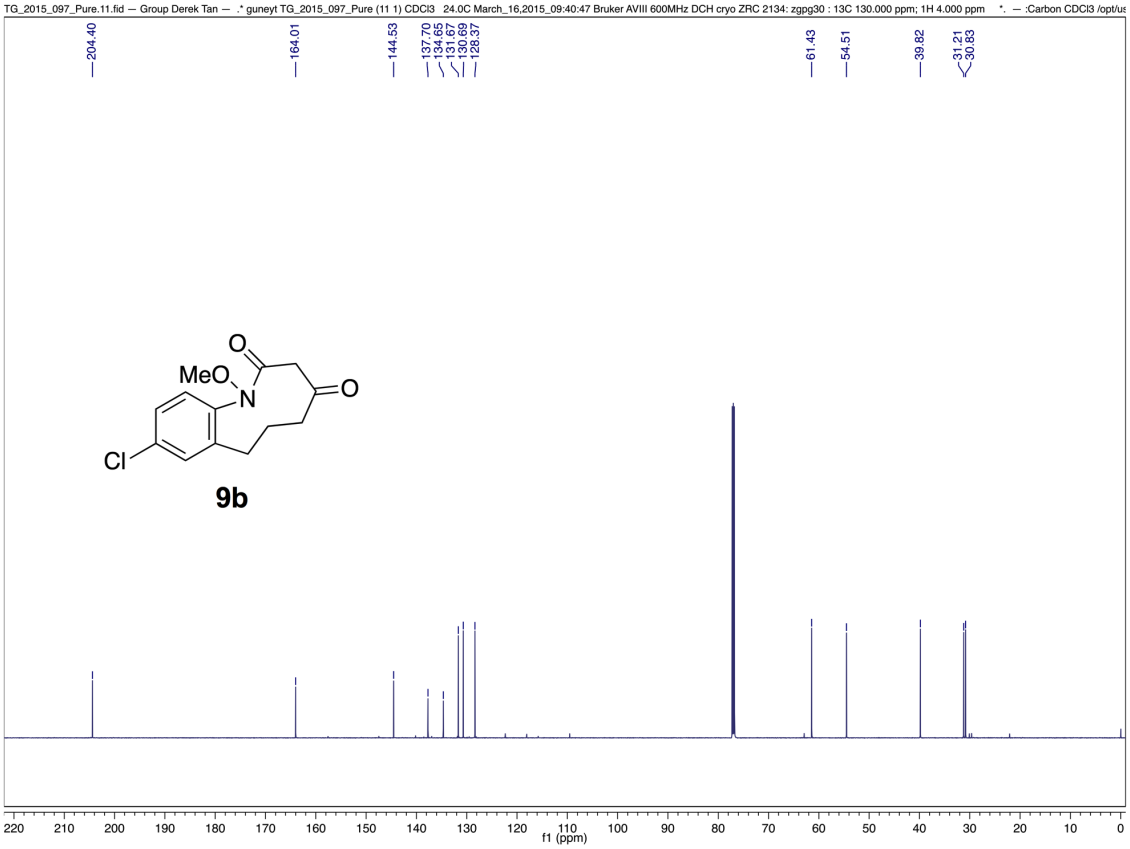

TW-2014-124a-13C.10.fid — Group Tan — .* wenderst TW-2014-124a-13C (10 1) CDCl3 24.0C June_20,2014_12:17:35 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 38
MeO
N
H
O
OH
N
Ts
40
f1 (ppm)

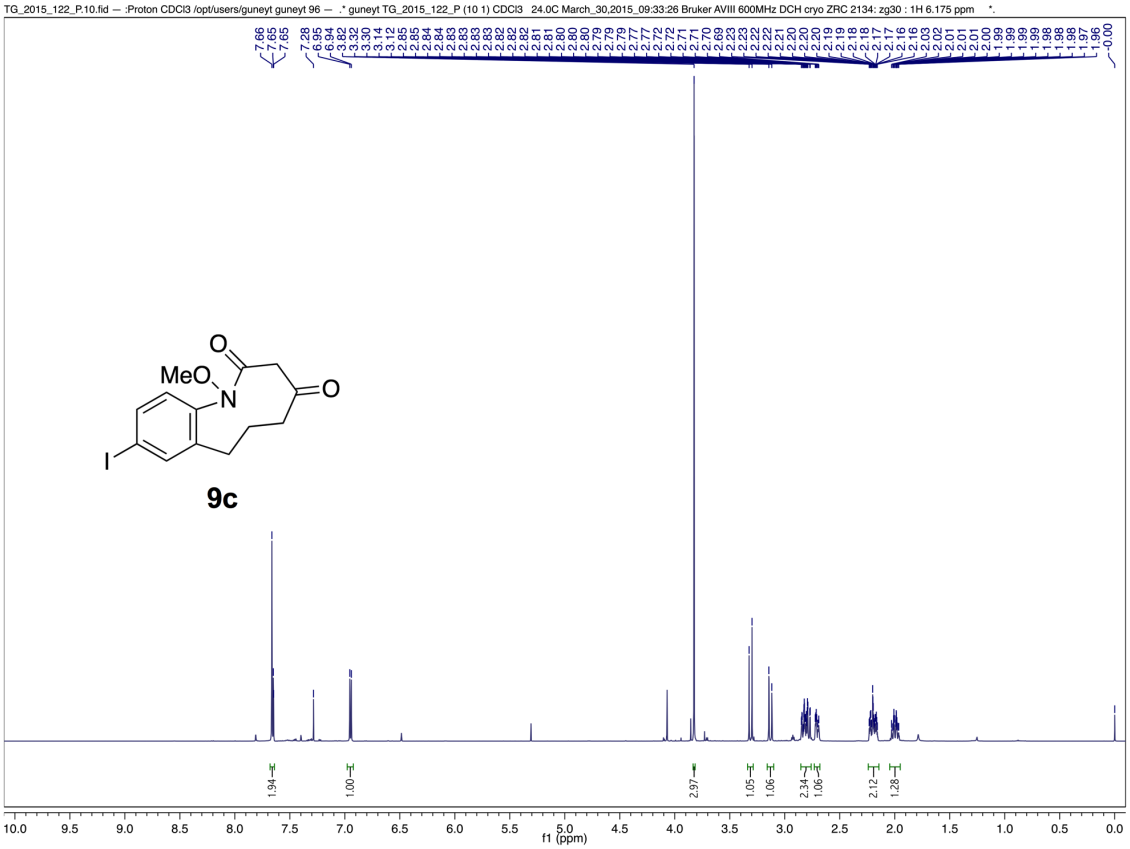

TW-2014-124a-13C.11.fid — Group Tan — .* wenderst TW-2014-124a-13C (11 1) CDCl3 24.0C June_20,2014_12:19:17 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/we
MeO
N
H
O
OH
N
Ts
40
f1 (ppm)

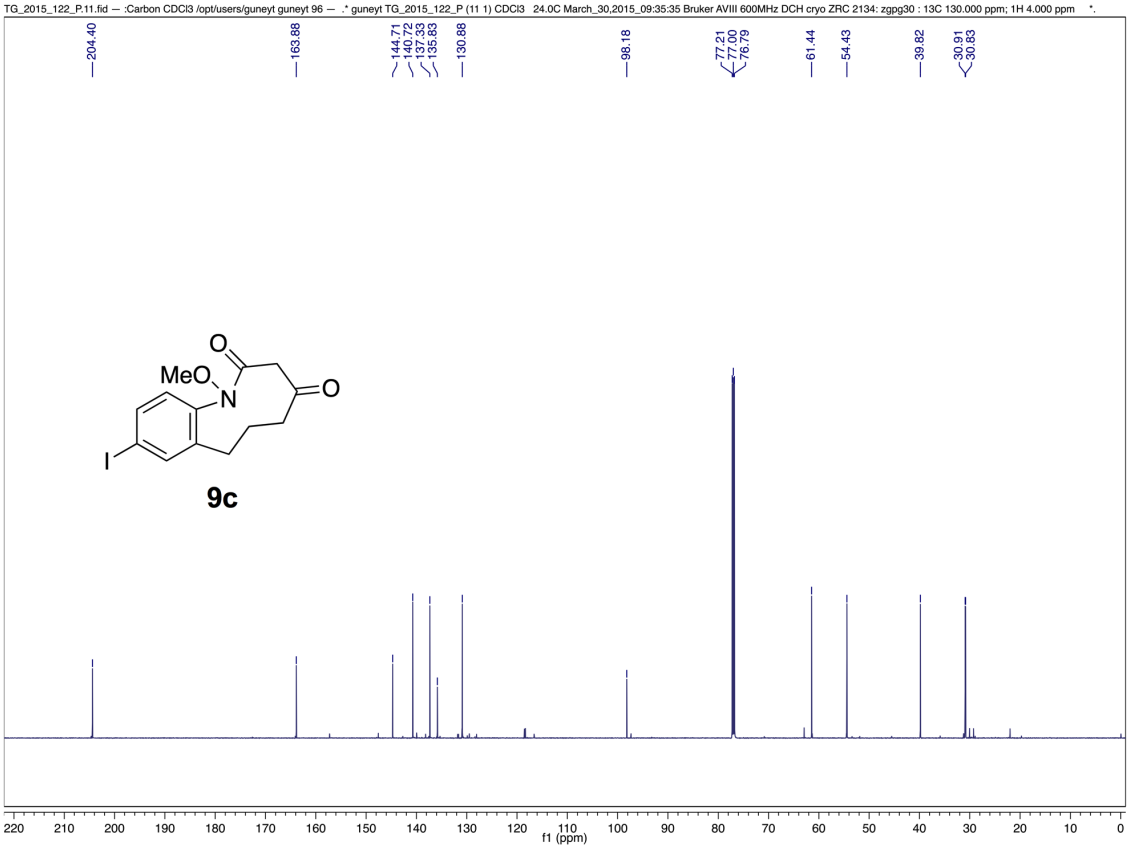

TG_2015_121_P.10.fid — :Proton CDCl3 /opt/users/guneyt guneyt 95 — .* guneyt TG_2015_121_P (10 1) CDCl3 24.0C March_30,2015_09:20:08 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
MeO
N
O
O
Br
9a
f1 (ppm)

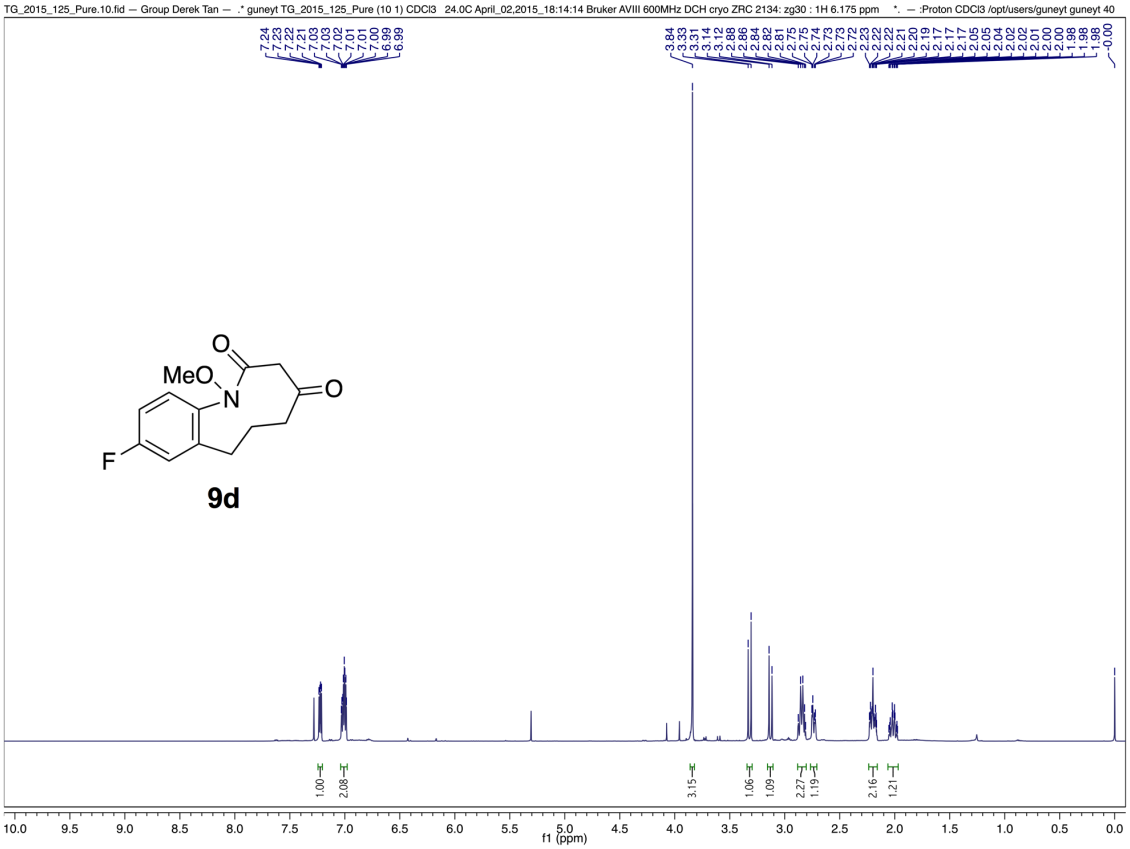

TG_2015_121_P.11.fid — :Carbon CDCl3 /opt/users/guneyt guneyt 95 — .* guneyt TG_2015_121_P (11 1) CDCl3 24.0C March_30,2015_09:22:22 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *.
MeO
N
O
O
Br
9a
f1 (ppm)


TG_2015_097_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_097_Pure (10 1) CDCl3 24.0C March_16,2015_09:38:40 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 84
7.31
7.30
7.29
7.18
7.16
3.83
3.33
3.31
3.14
3.12
2.86
2.84
2.81
2.81
2.74
2.74
2.72
2.71
2.23
2.23
2.22
2.22
2.21
2.20
2.19
2.18
2.18
2.18
2.17
2.17
2.05
2.04
2.02
2.00
1.99
1.98
1.98
1.97
0.00
MeO
N
O
O
Cl
9b
1.85
0.94
2.86
1.00
1.01
2.09
1.04
1.98
1.13
f1 (ppm)


TG_2015_097_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_097_Pure (11 1) CDCl3 24.0C March_16,2015_09:40:47 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/us
204.40
164.01
144.53
137.70
134.65
131.67
130.69
128.37
61.43
54.51
39.82
31.21
30.83
MeO
N
O
O
Cl
9b
f1 (ppm)

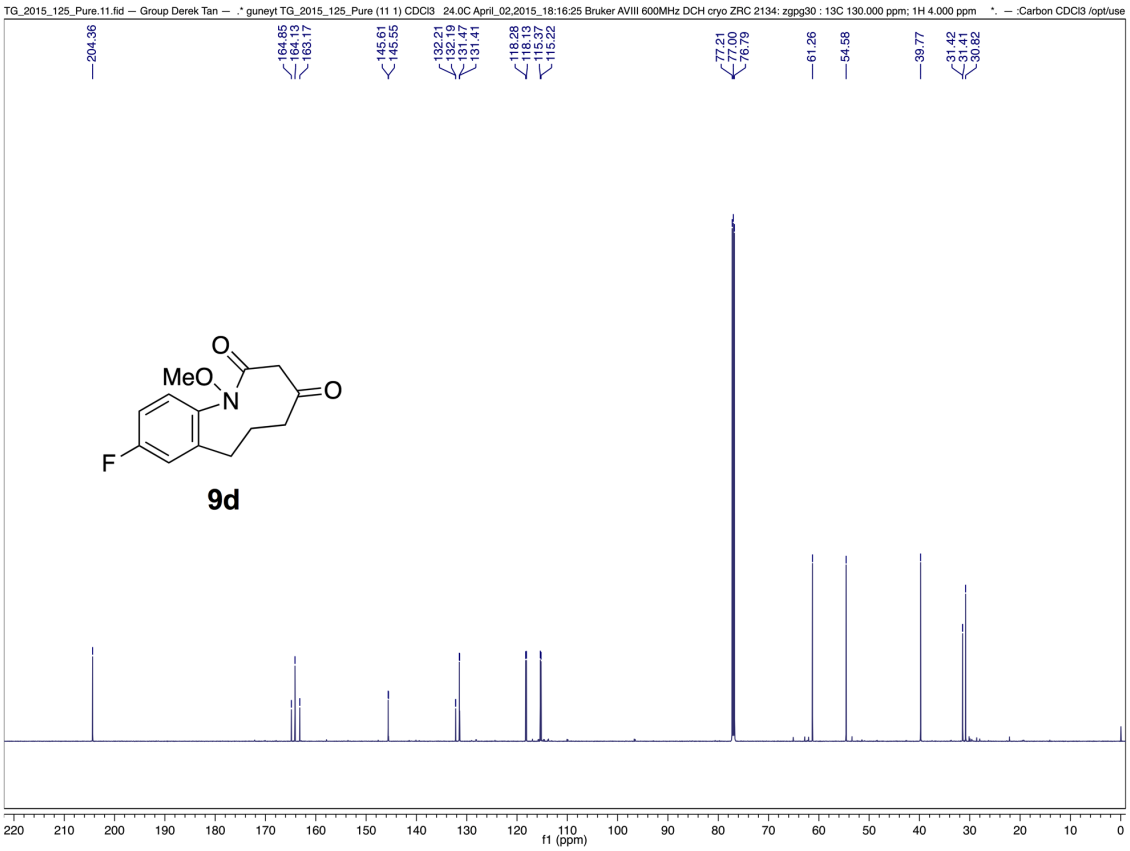

TG_2015_122_P.10.fid — :Proton CDCl3 /opt/users/guneyt guneyt 96 — .* guneyt TG_2015_122_P (10 1) CDCl3 24.0C March_30,2015_09:33:26 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
MeO
N
O
O
I
9c
f1 (ppm)


TG_2015_122_P.11.fid — :Carbon CDCl3 /opt/users/guneyt guneyt 96 — .* guneyt TG_2015_122_P (11 1) CDCl3 24.0C March_30,2015_09:35:35 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *.
MeO
N
O
O
I
9c
f1 (ppm)


TG_2015_125_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_125_Pure (10 1) CDCl3 24.0C April_02,2015_18:14:14 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 40
7.24 7.23 7.22 7.21 7.03 7.03 7.02 7.02 7.01 7.01 7.00 6.99 6.99
3.84 3.33 3.31 3.14 3.12 2.88 2.86 2.82 2.82 2.81 2.75 2.75 2.74 2.73 2.73 2.23 2.22 2.22 2.21 2.20 2.19 2.19 2.17 2.17 2.05 2.05 2.04 2.02 2.02 2.01 2.01 2.00 2.00 1.98 1.98 1.98 0.00
1.00 2.08 3.15 1.06 1.09 2.27 1.19 2.16 1.21
f1 (ppm)

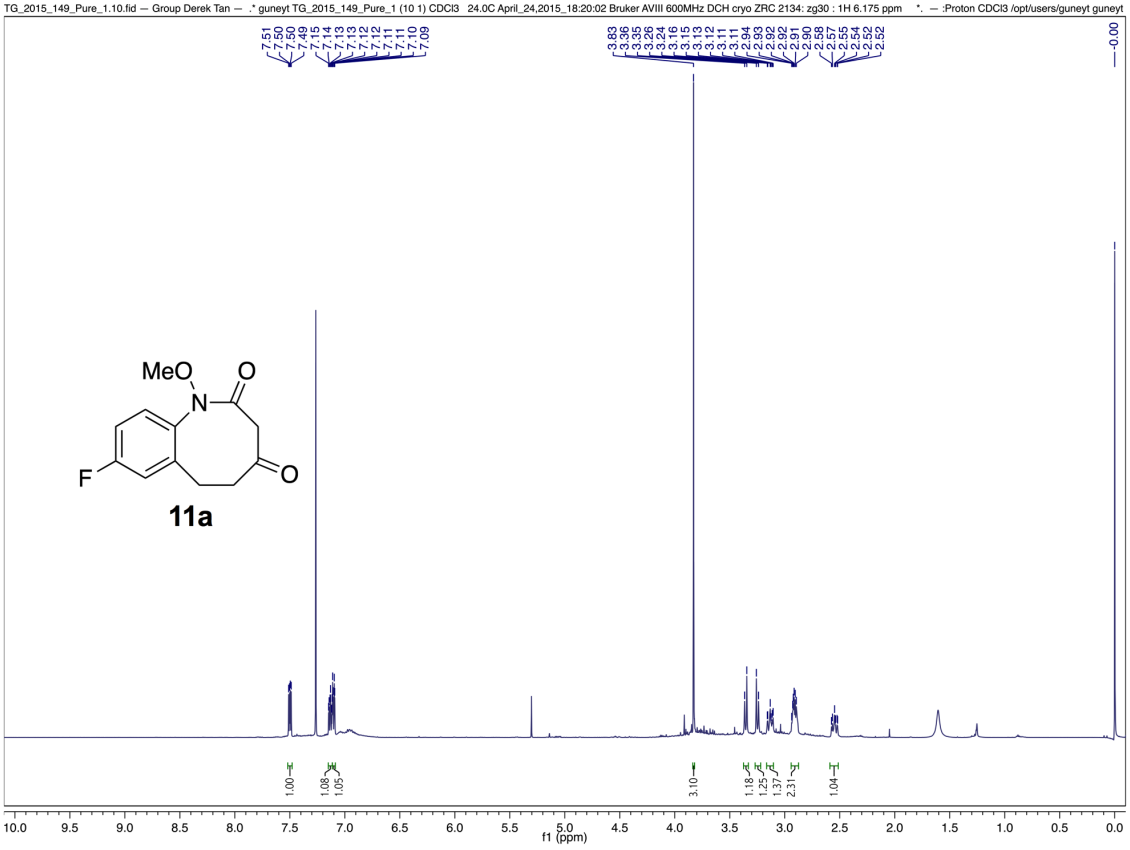
O
MeO
N
O
F

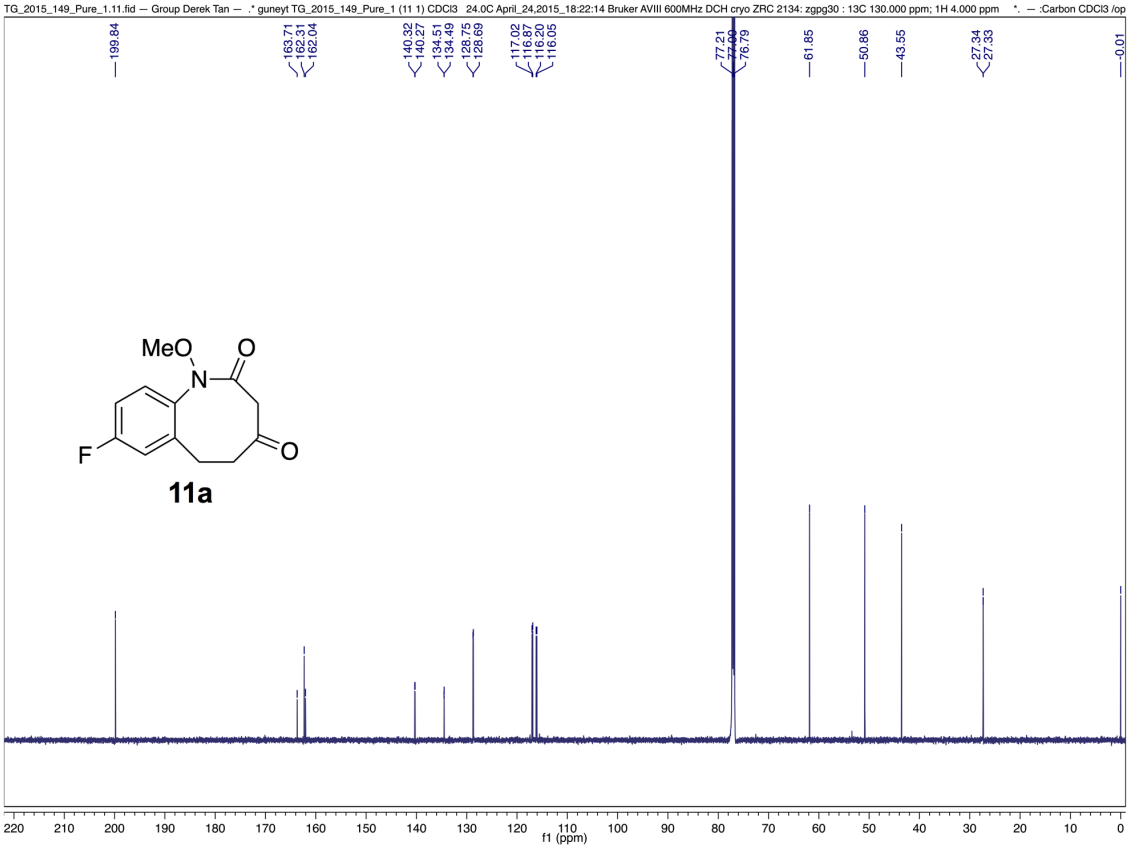
9d

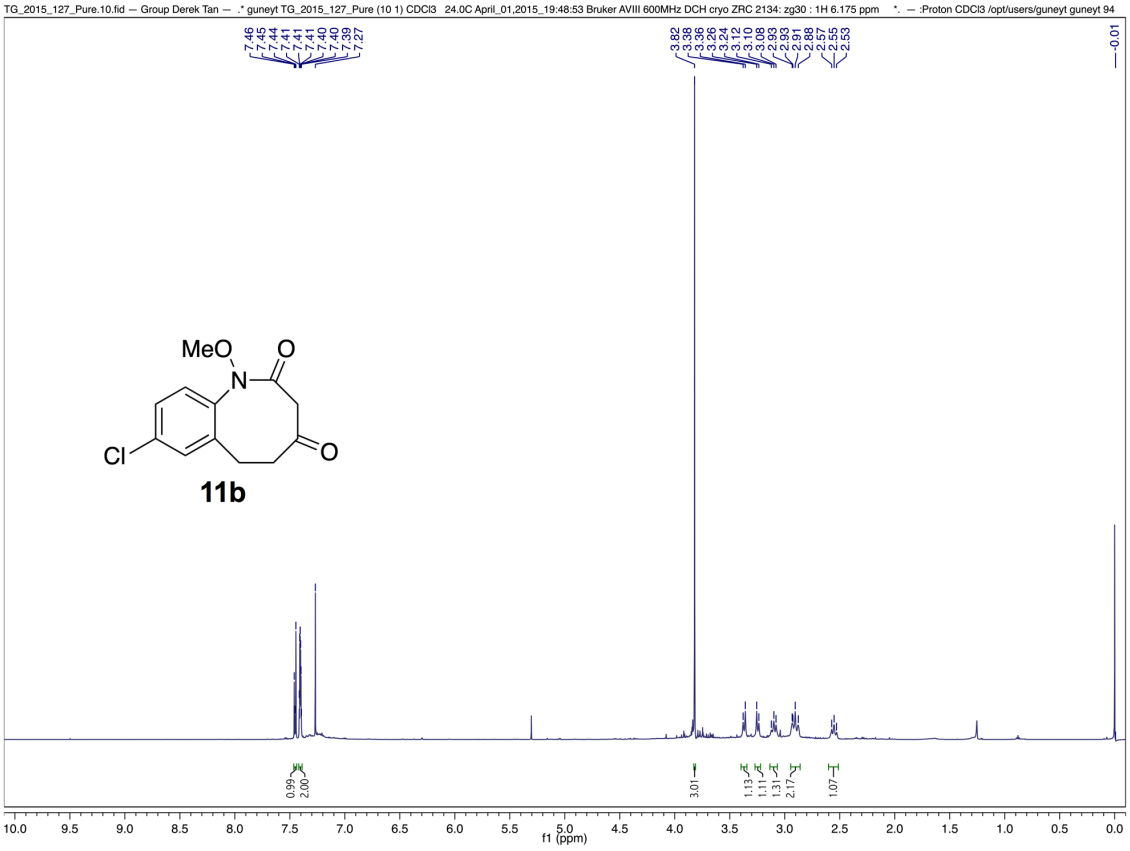

TG_2015_125_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_125_Pure (11 1) CDCl3 24.0C April_02,2015_18:16:25 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
204.36
164.85 164.13 163.17
145.61 145.55
132.21 132.19 131.47 131.41
118.28 118.13 115.37 115.22
77.21 77.00 76.79
61.26
54.58
39.77
31.42 31.41 30.82
f1 (ppm)

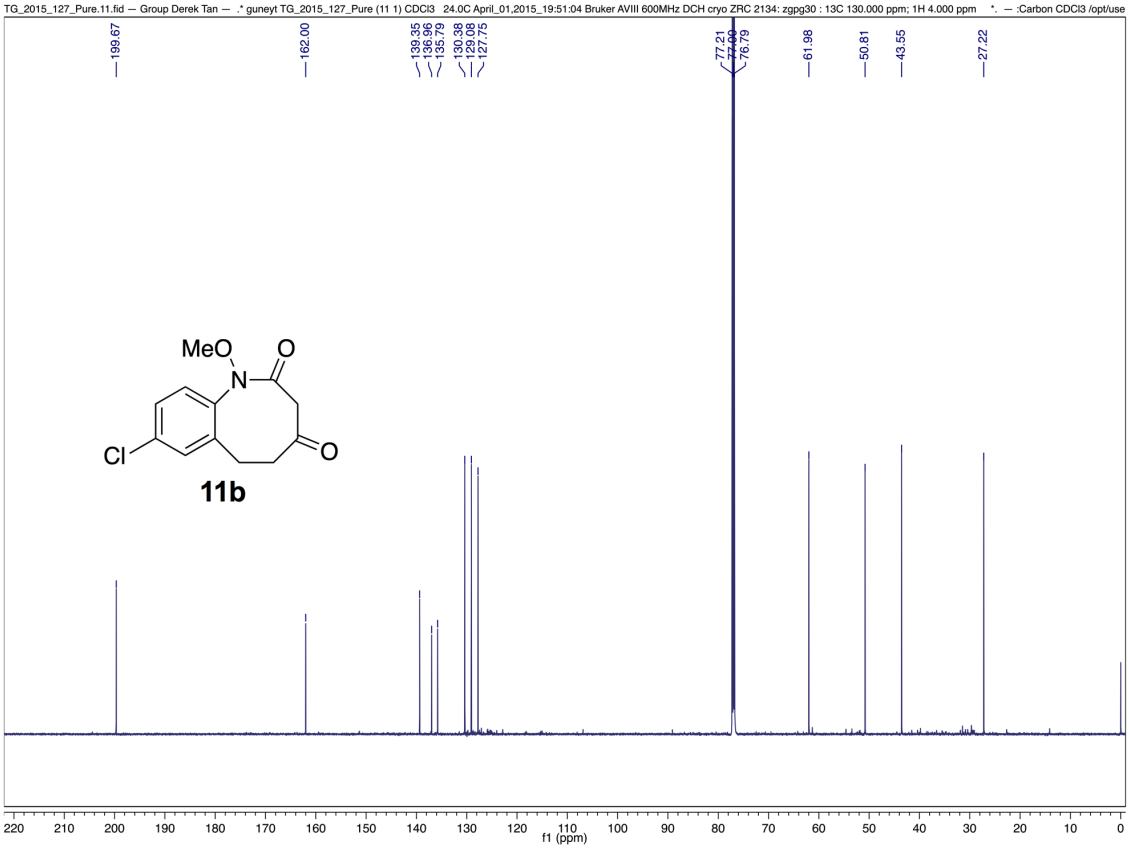
O
MeO
N
O
F

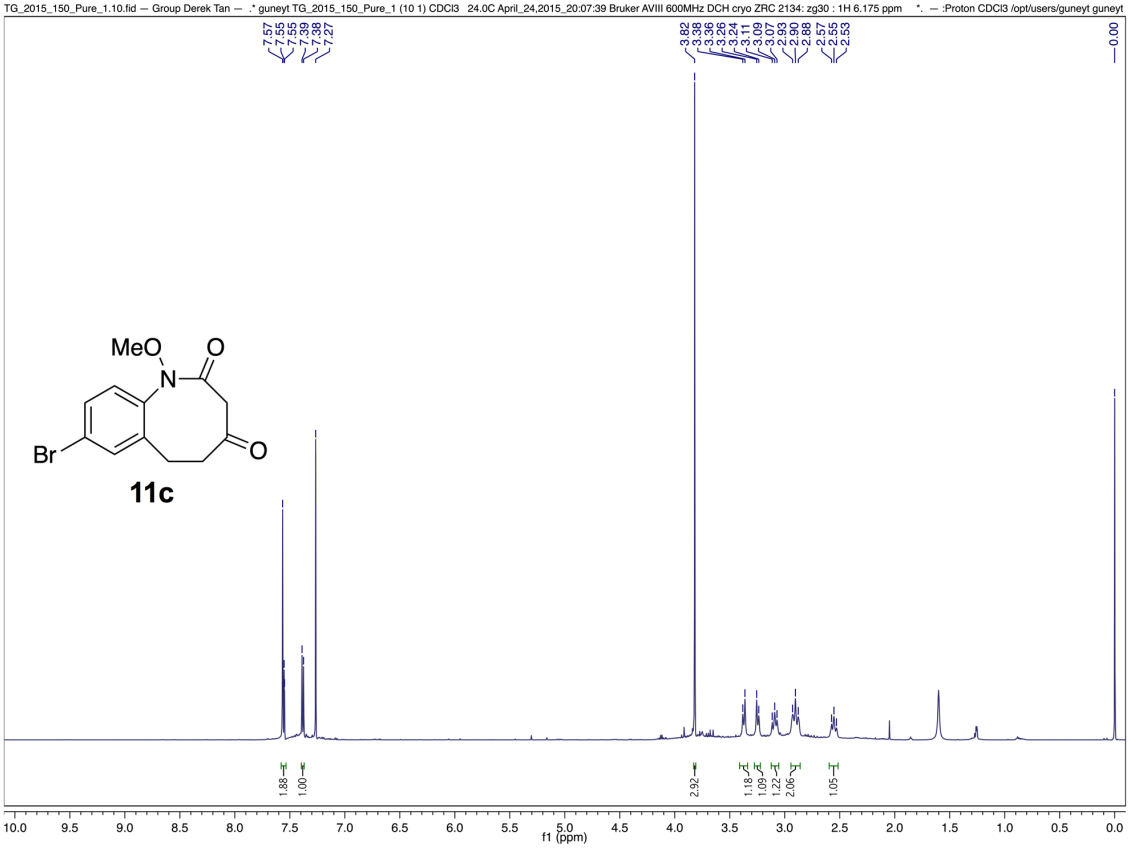
9d

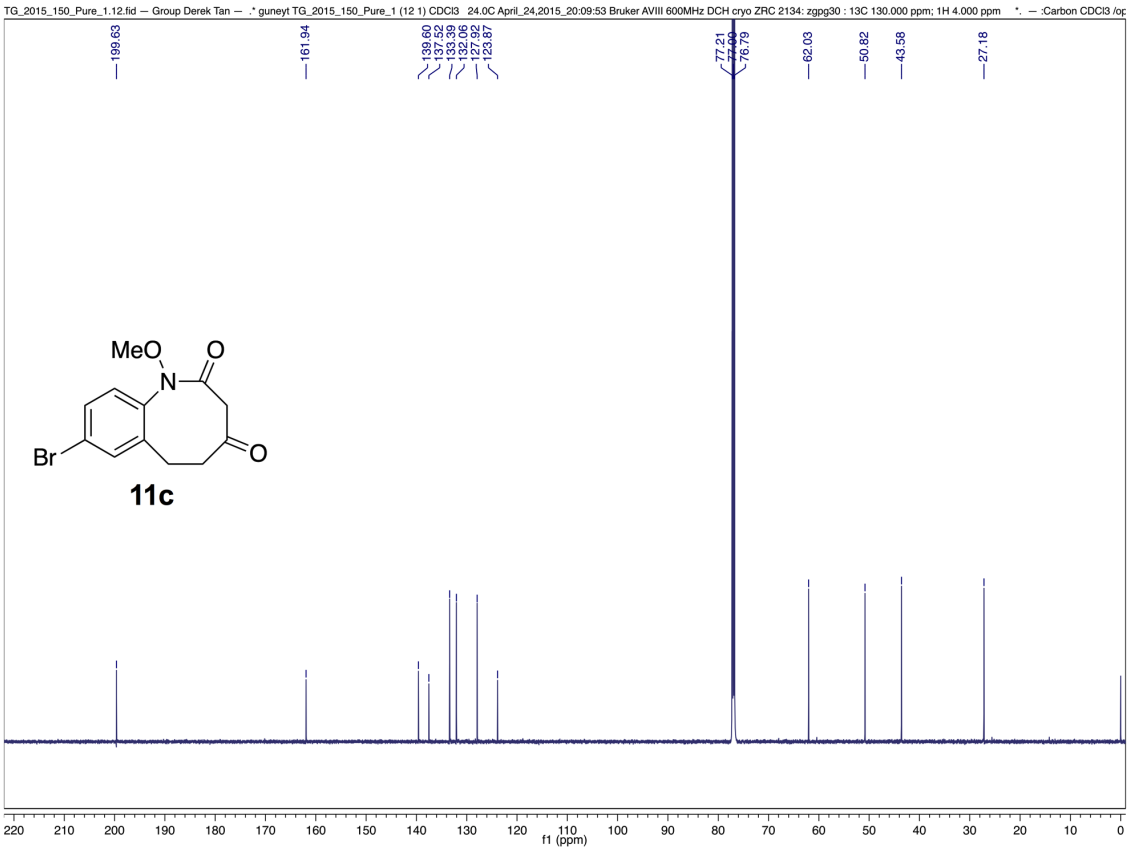

TG_2015_149_Pure_1.10.fid — Group Derek Tan — .* guneyt TG_2015_149_Pure_1 (10 1) CDCl3 24.0C April_24,2015_18:20:02 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt
MeO
N
O
O
F
11a
f1 (ppm)

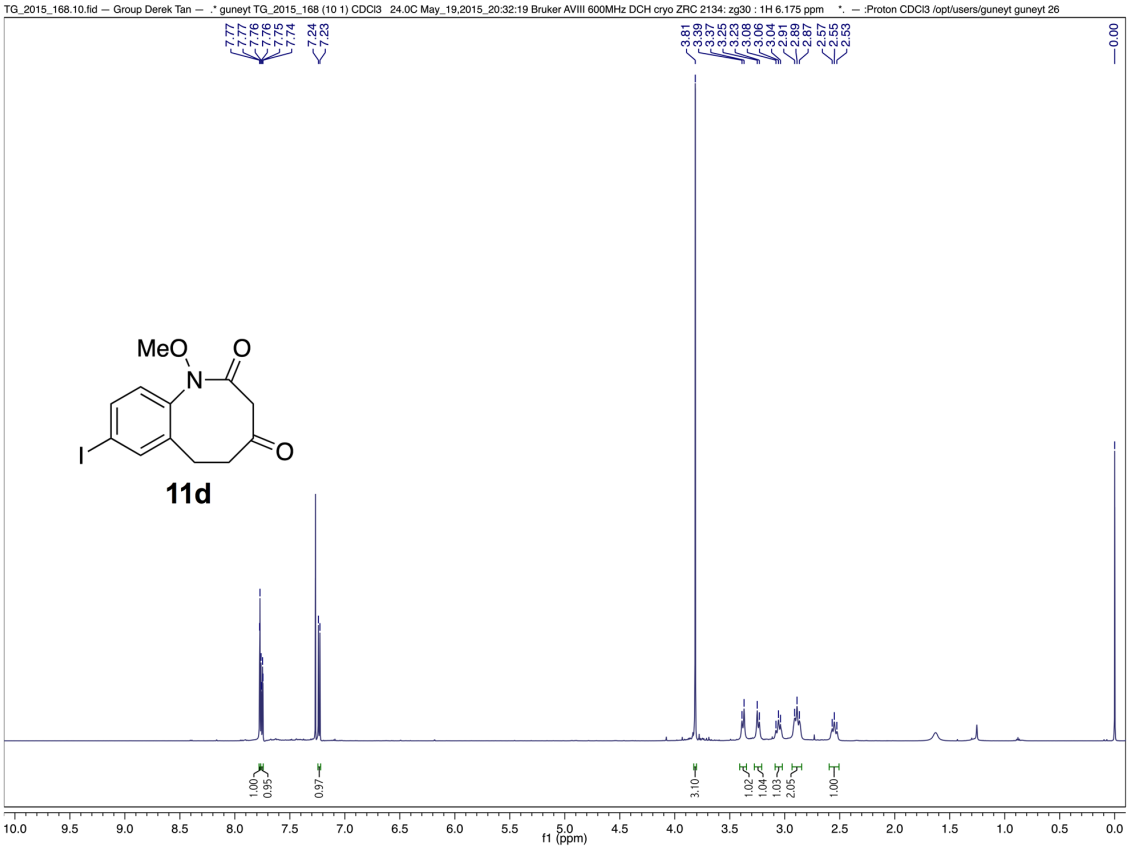

TG_2015_149_Pure_1.11.fid — Group Derek Tan — .* guneyt TG_2015_149_Pure_1 (11 1) CDCl3 24.0C April_24,2015_18:22:14 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /op
MeO
N
O
O
F
11a
f1 (ppm)

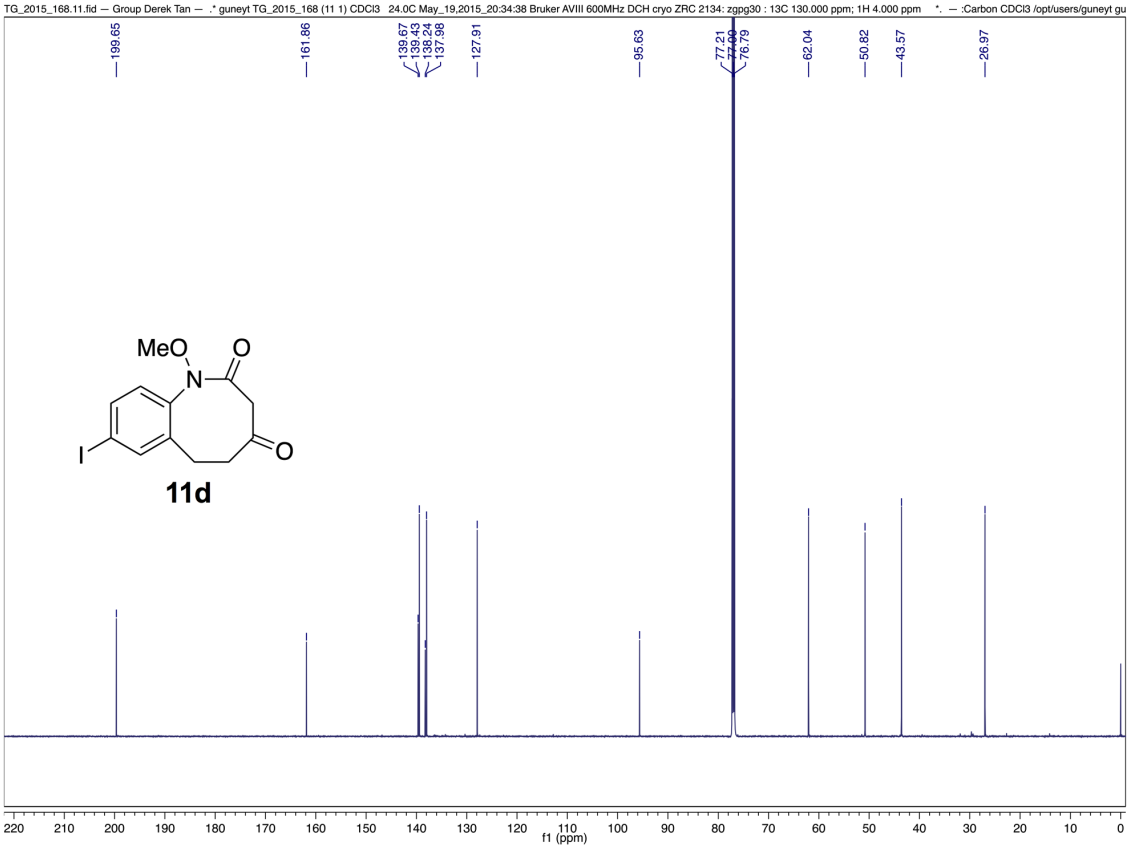

TG_2015_127_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_127_Pure (10 1) CDCl3 24.0C April_01,2015_19:48:53 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 94
7.46
7.45
7.44
7.41
7.41
7.41
7.40
7.40
7.39
7.27
3.82
3.38
3.36
3.26
3.24
3.12
3.10
3.08
2.93
2.93
2.91
2.88
2.57
2.55
2.53
-0.01
MeO
N
O
O
Cl
11b
0.99
2.00
3.01
1.13
1.11
1.31
2.17
1.07
f1 (ppm)

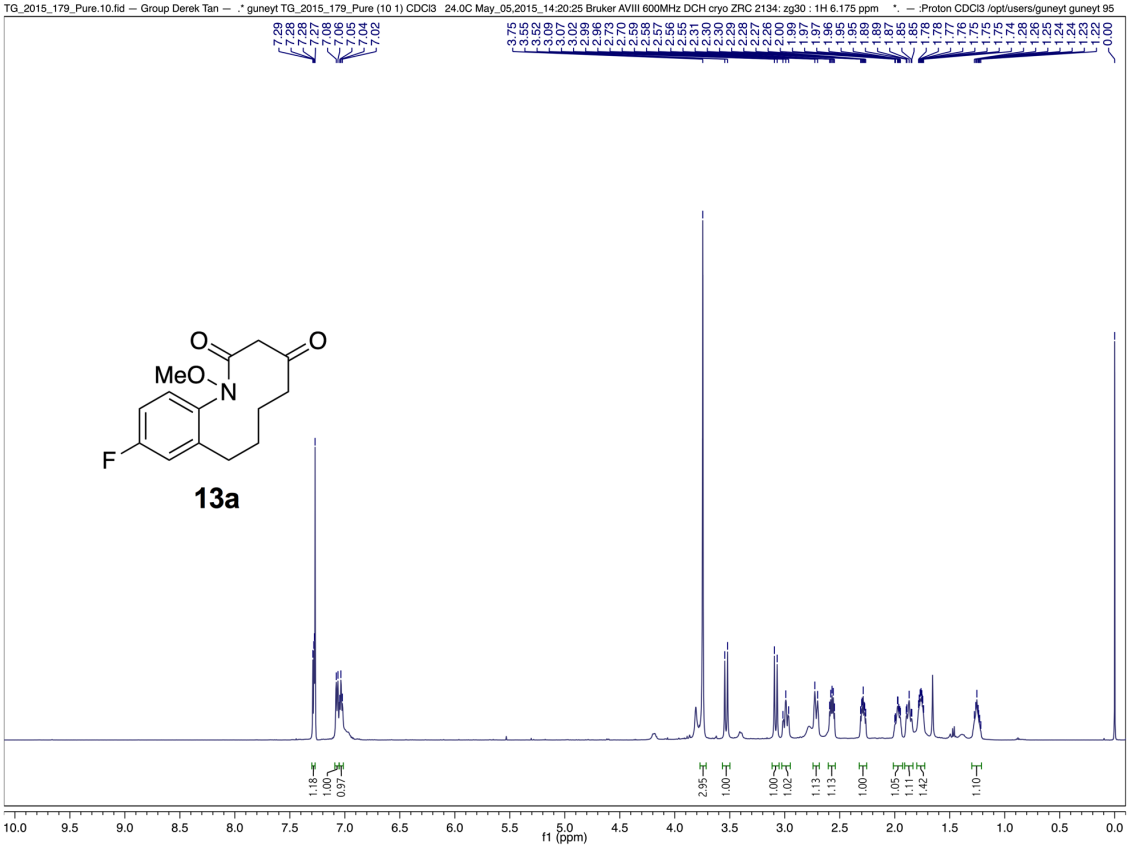

TG_2015_127_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_127_Pure (11 1) CDCl3 24.0C April_01,2015_19:51:04 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
199.67
162.00
139.35
136.96
135.79
130.38
129.08
127.75
77.21
77.00
76.79
61.98
50.81
43.55
27.22
MeO
N
O
O
Cl
11b
f1 (ppm)

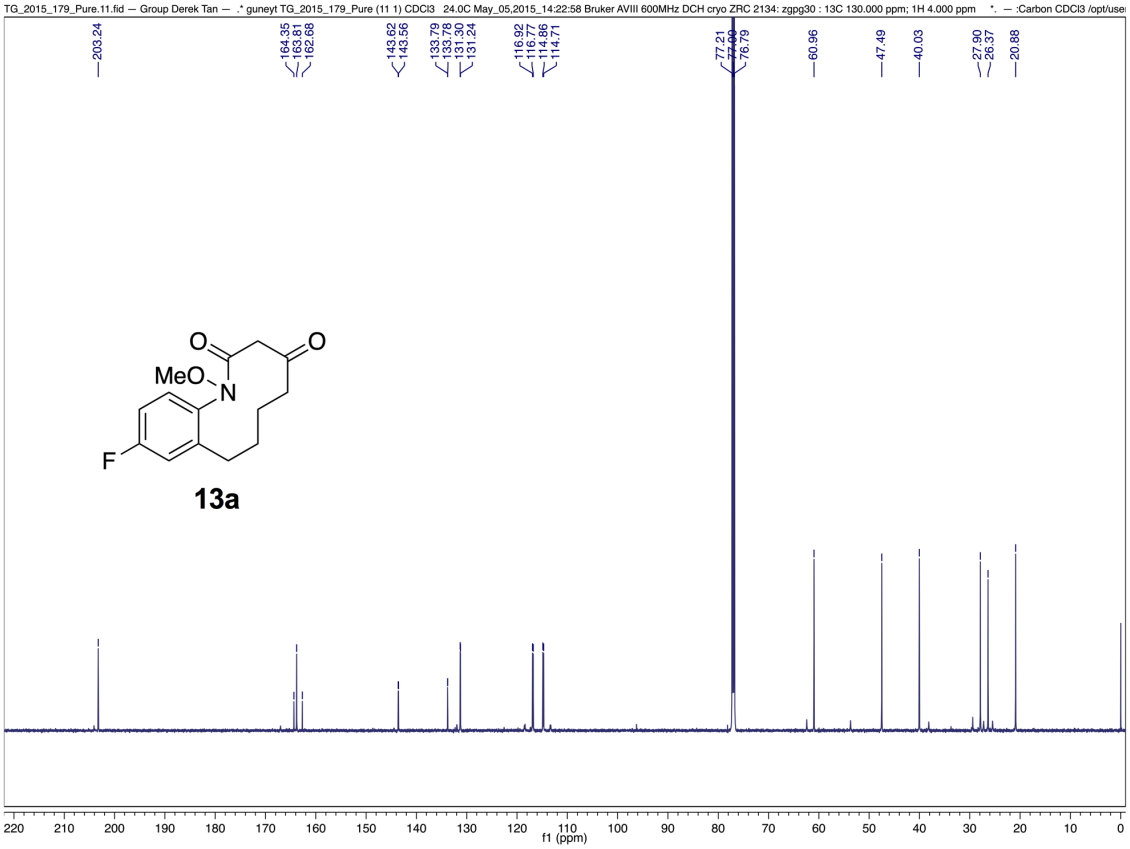

TG_2015_150_Pure_1.10.fid — Group Derek Tan — .* guneyt TG_2015_150_Pure_1 (10 1) CDCl3 24.0C April_24,2015_20:07:39 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt
7.57
7.55
7.55
7.39
7.38
7.27
3.82
3.38
3.36
3.26
3.24
3.11
3.09
3.07
2.93
2.90
2.88
2.57
2.55
2.53
0.00
MeO
N
O
O
Br
11c
1.88
1.00
2.92
1.18
1.09
1.22
2.06
1.05
f1 (ppm)

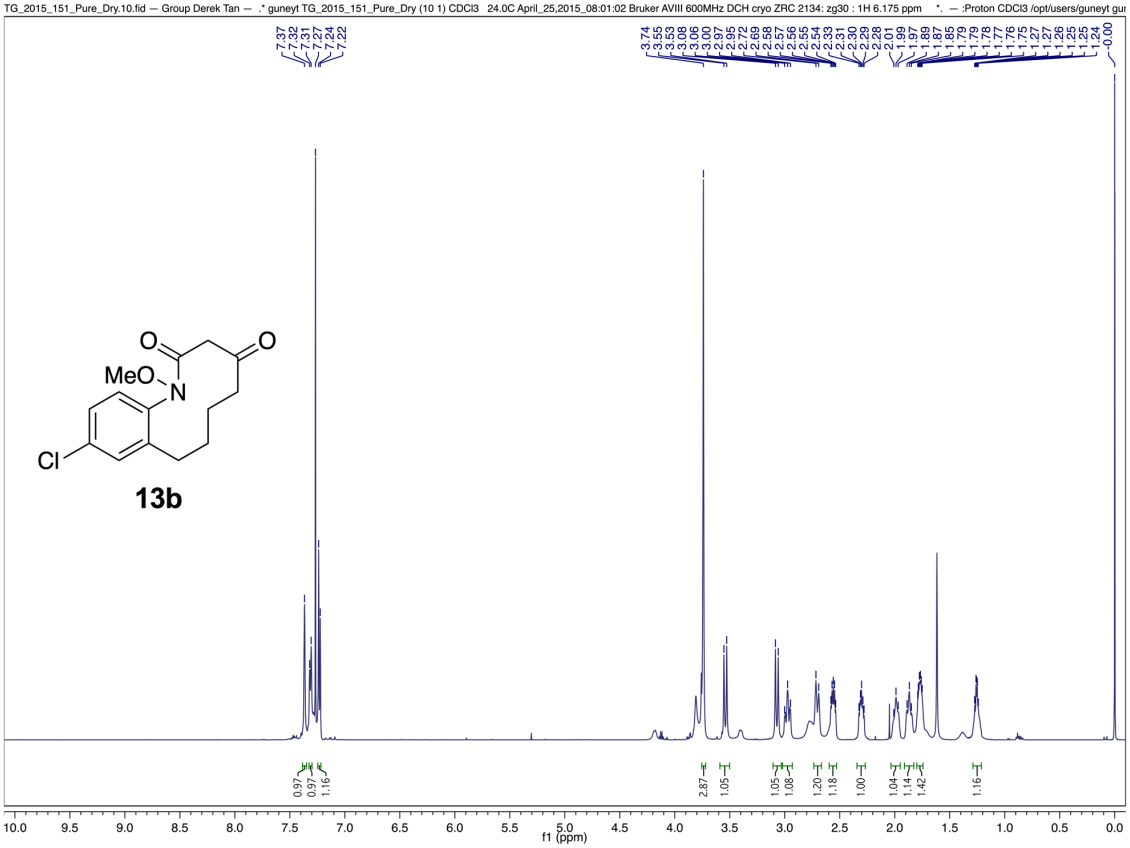

TG_2015_150_Pure_1.12.fid — Group Derek Tan — .* guneyt TG_2015_150_Pure_1 (12 1) CDCl3 24.0C April_24,2015_20:09:53 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /op
199.63
161.94
139.60
137.52
133.39
132.06
127.95
123.87
77.21
77.00
76.79
62.03
50.82
43.58
27.18
MeO
N
O
O
Br
11c
f1 (ppm)

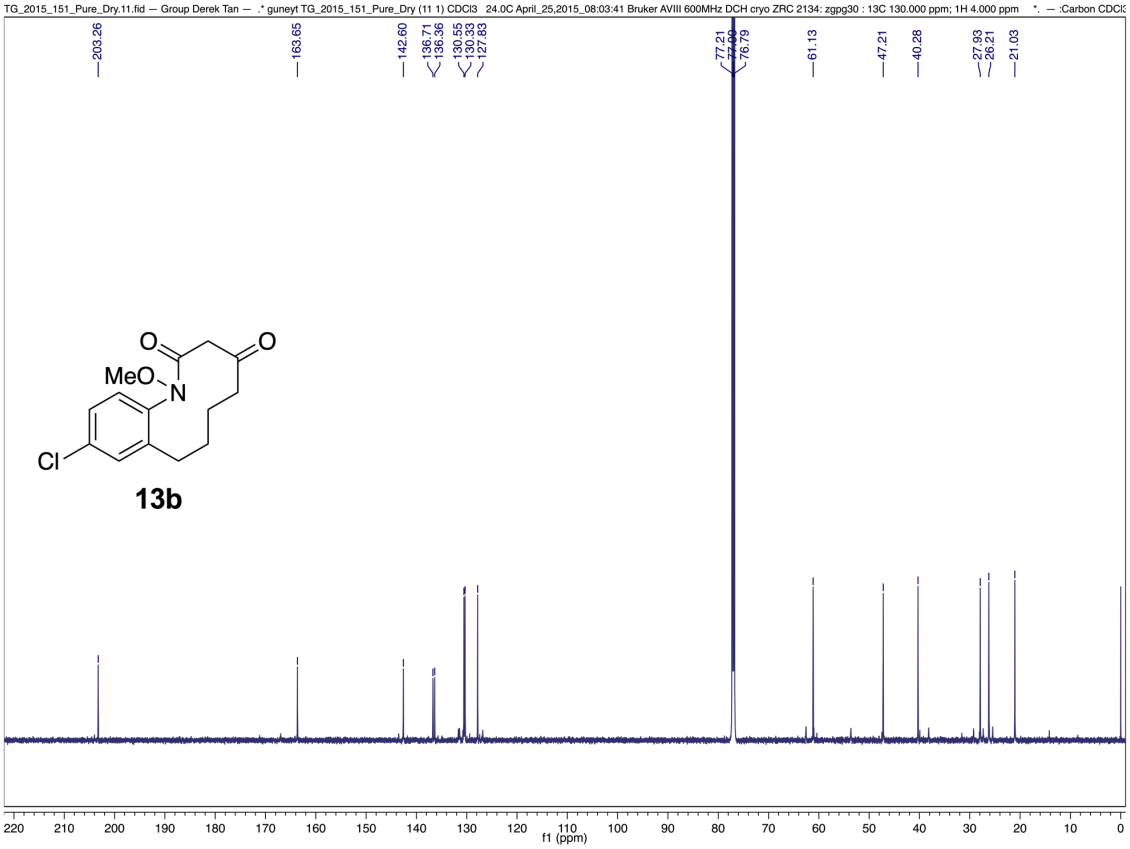

TG_2015_168.10.fid — Group Derek Tan — .* guneyt TG_2015_168 (10 1) CDCl3 24.0C May_19,2015_20:32:19 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 26
7.77
7.77
7.76
7.76
7.75
7.74
7.24
7.23
3.81
3.39
3.37
3.25
3.23
3.08
3.06
3.04
2.91
2.89
2.87
2.57
2.55
2.53
0.00
MeO
N
O
O
I
11d
1.00
0.95
0.97
3.10
1.02
1.04
1.03
2.05
1.00
f1 (ppm)

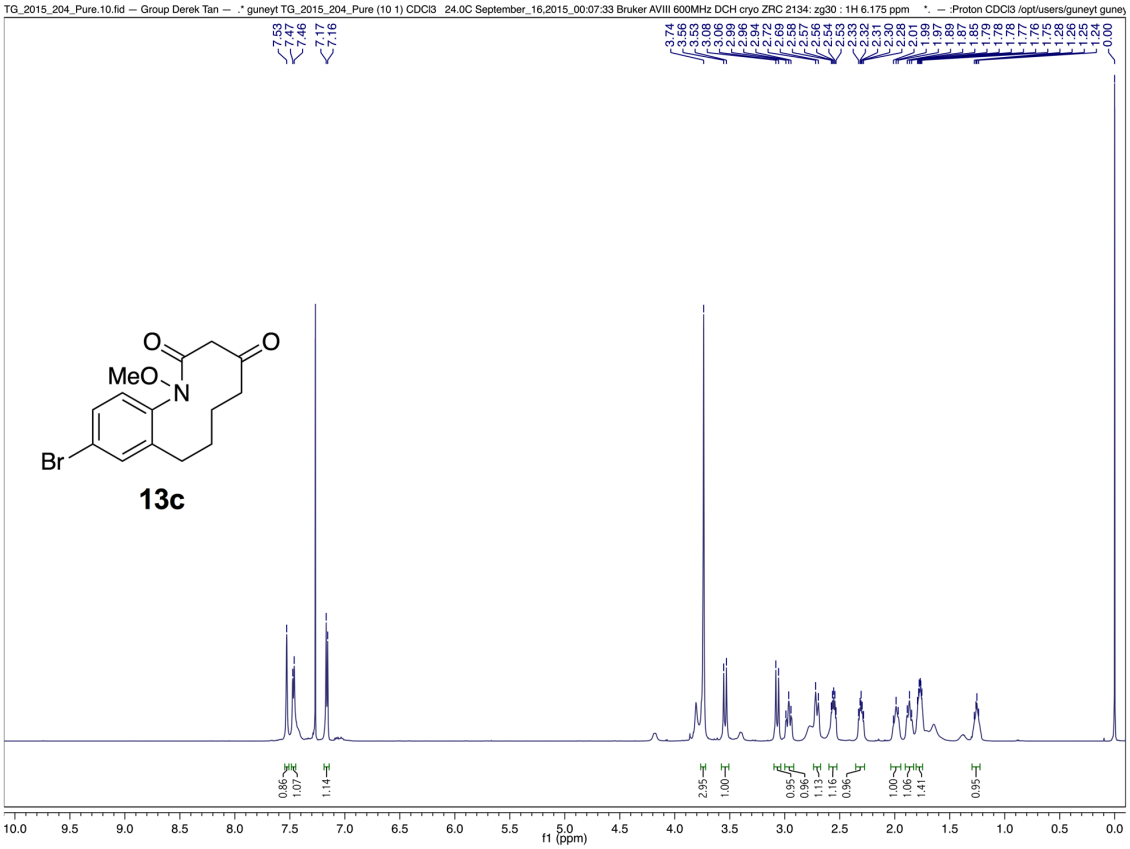

TG_2015_168.11.fid — Group Derek Tan — .* guneyt TG_2015_168 (11 1) CDCl3 24.0C May_19,2015_20:34:38 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/guneyt gu
199.65
161.86
139.67
139.43
138.24
137.98
127.91
95.63
77.21
77.00
76.79
62.04
50.82
43.57
26.97
MeO
N
O
O
I
11d
f1 (ppm)

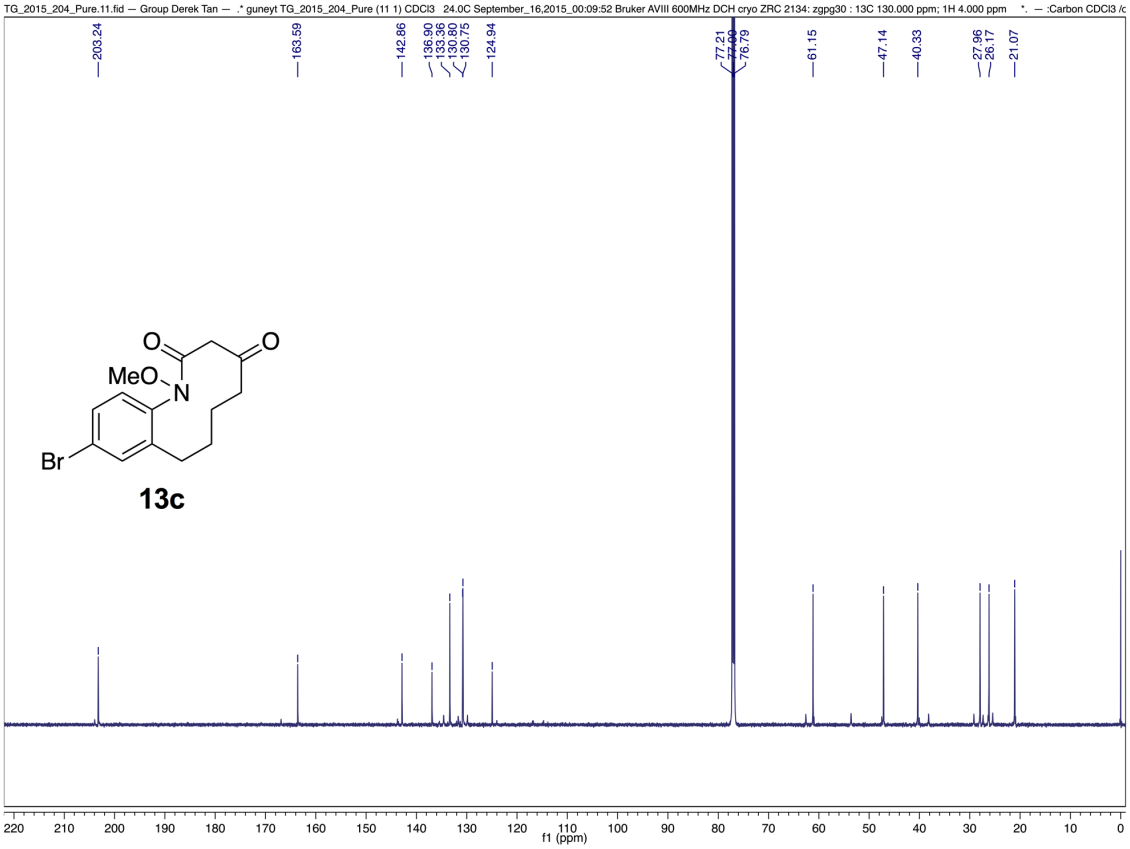

TG_2015_179_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_179_Pure (10 1) CDCl3 24.0C May_05,2015_14:20:25 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 95
MeO
N
O
O
F
13a
f1 (ppm)

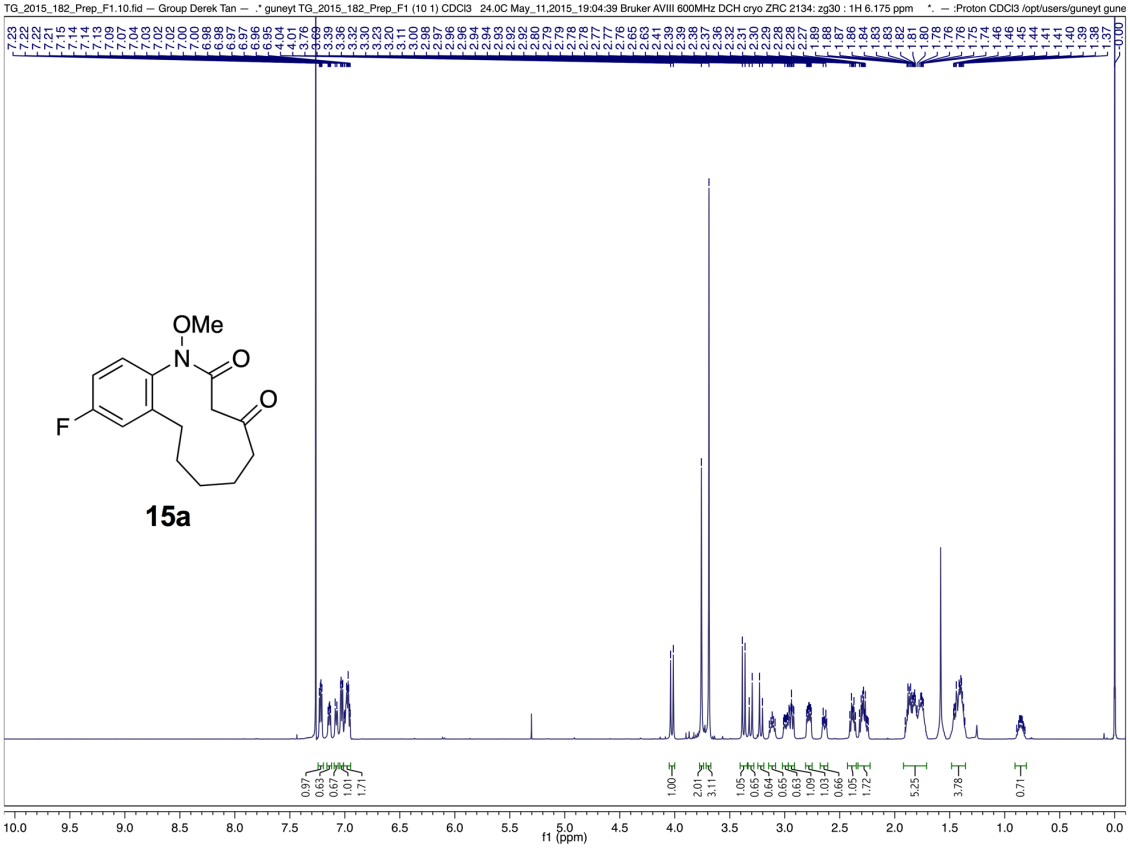

TG_2015_179_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_179_Pure (11 1) CDCl3 24.0C May_05,2015_14:22:58 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/user
MeO
N
O
O
F
13a
f1 (ppm)

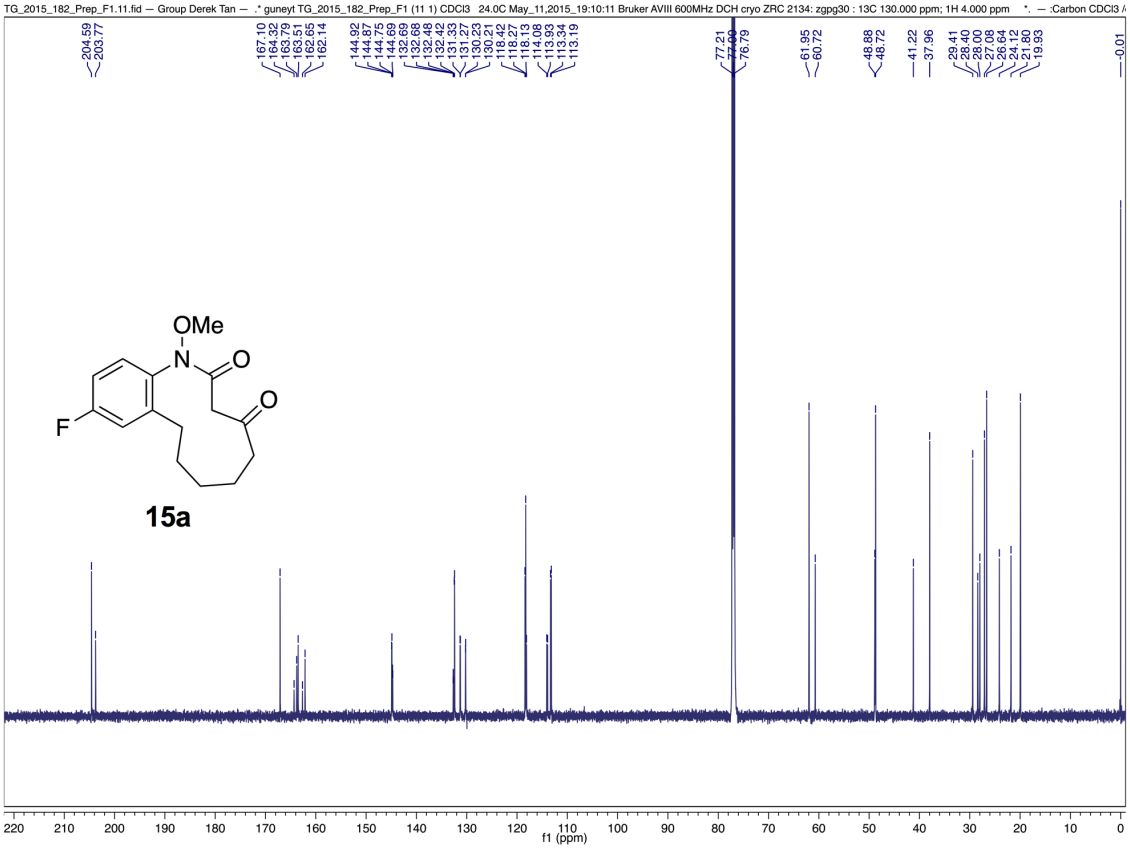

TG_2015_151_Pure_Dry.10.fid — Group Derek Tan — .* guneyt TG_2015_151_Pure_Dry (10 1) CDCl3 24.0C April_25,2015_08:01:02 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
MeO
N
O
O
Cl
13b
f1 (ppm)

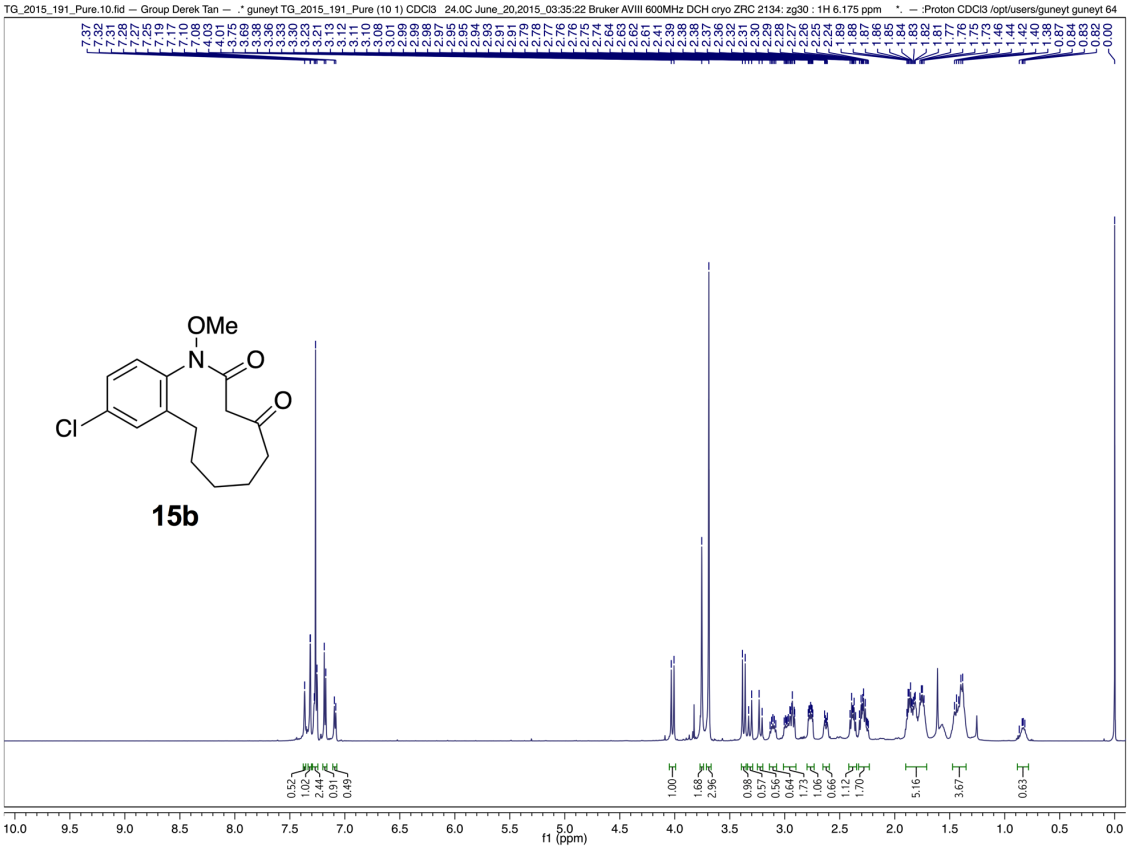

TG_2015_151_Pure_Dry.11.fid — Group Derek Tan — .* guneyt TG_2015_151_Pure_Dry (11 1) CDCl3 24.0C April_25,2015_08:03:41 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm
MeO
N
O
O
Cl
13b
f1 (ppm)

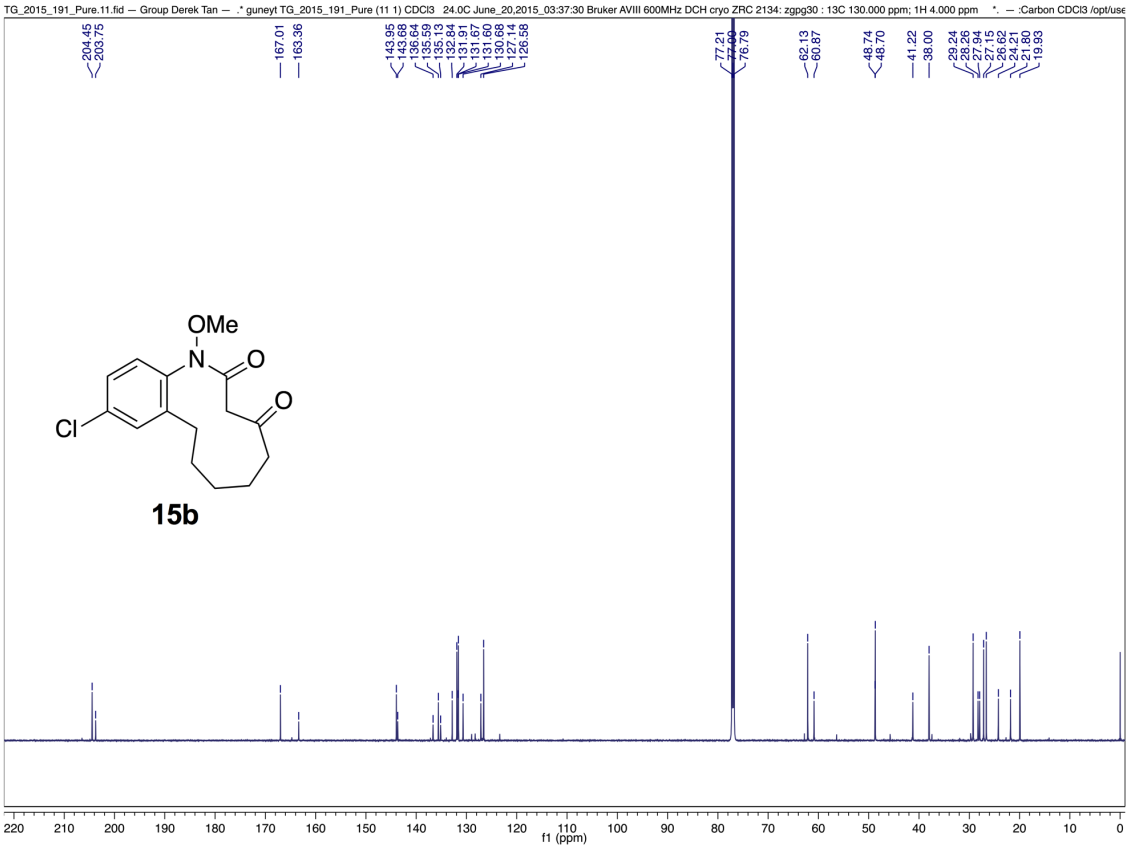

TG_2015_204_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_204_Pure (10 1) CDCl3 24.0C September_16,2015_00:07:33 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
7.53
7.47
7.46
7.17
7.16
3.74
3.56
3.53
3.08
3.06
2.99
2.96
2.94
2.72
2.69
2.58
2.57
2.56
2.54
2.53
2.33
2.32
2.31
2.30
2.28
2.01
1.99
1.97
1.89
1.87
1.85
1.79
1.78
1.77
1.76
1.75
1.28
1.26
1.25
1.24
0.00
0.86
1.07
1.14
2.95
1.00
0.95
0.96
1.13
1.16
0.96
1.00
1.06
1.41
0.95
f1 (ppm)
MeO
N
O
O
Br
13c

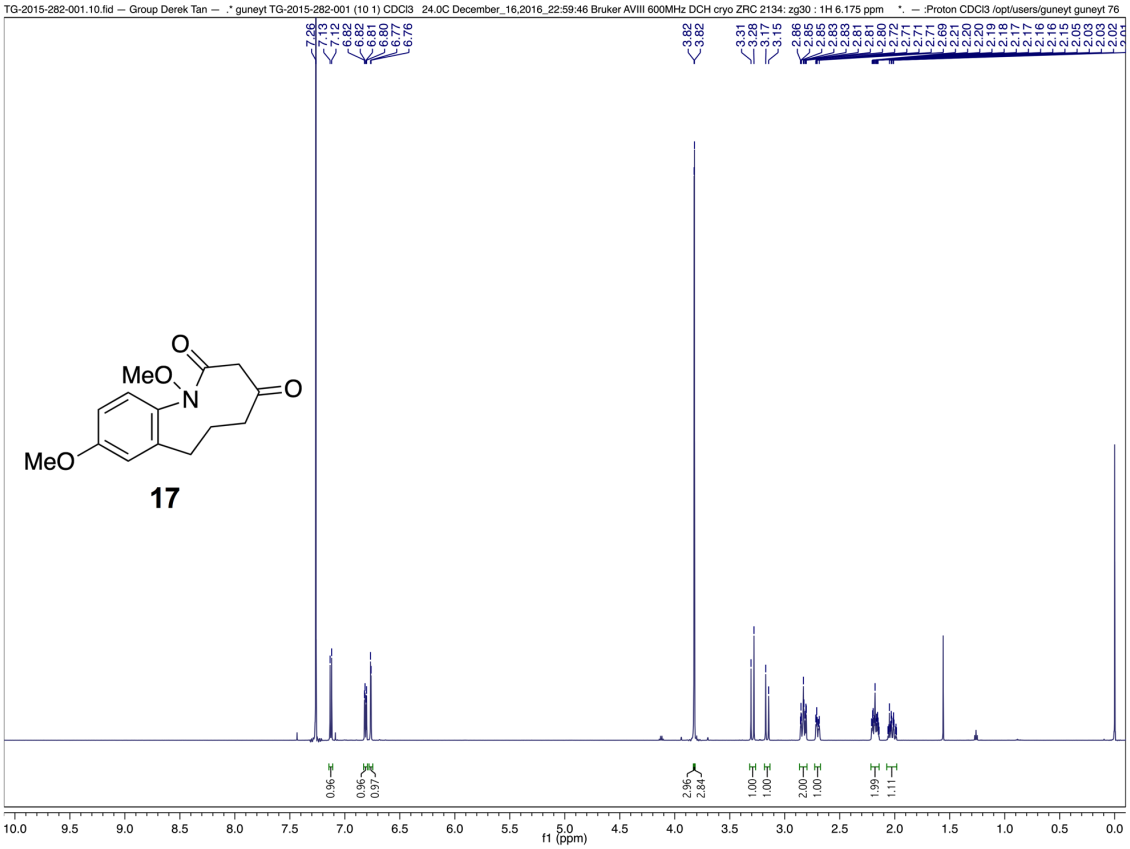

TG_2015_204_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_204_Pure (11 1) CDCl3 24.0C September_16,2015_00:09:52 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm
203.24
163.59
142.86
136.90
133.36
130.80
130.75
124.94
77.21
77.00
76.79
61.15
47.14
40.33
27.96
26.17
21.07
f1 (ppm)
MeO
N
O
O
Br
13c

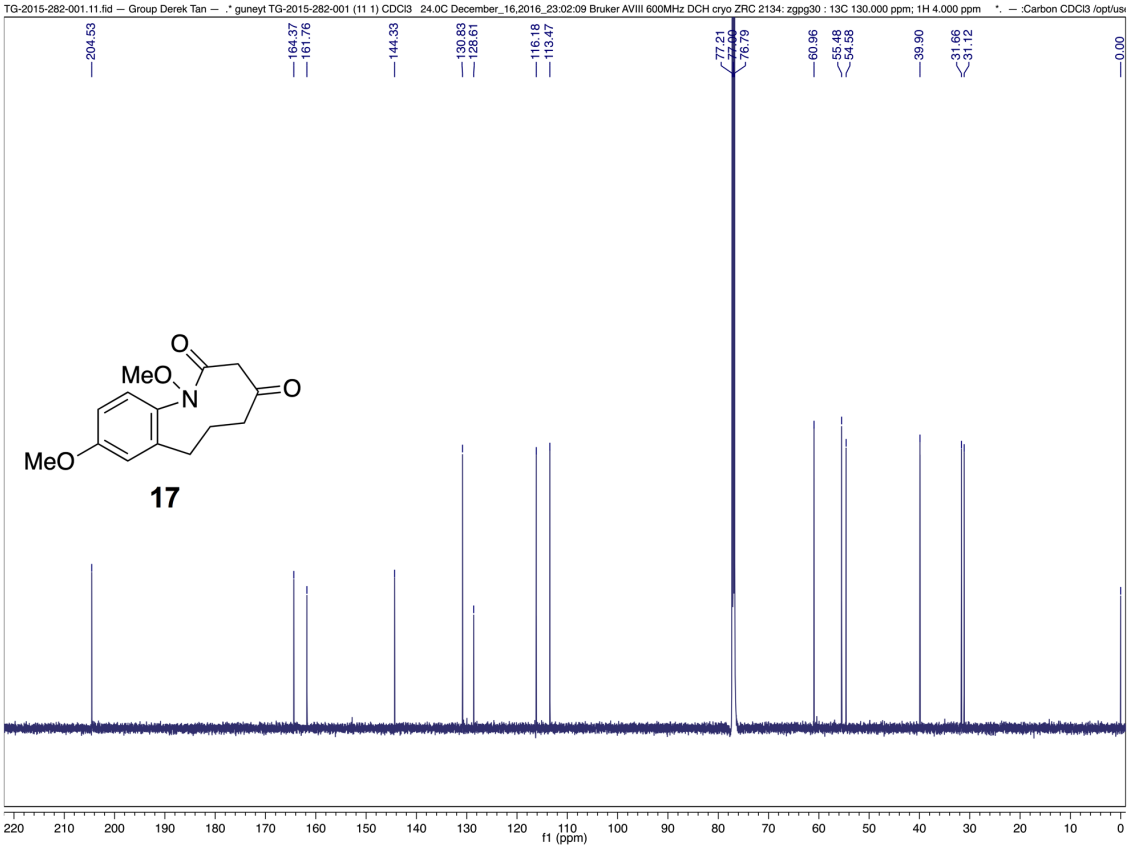

TG_2015_182_Prep_F1.10.fid — Group Derek Tan — .* guneyt TG_2015_182_Prep_F1 (10 1) CDCl3 24.0C May_11,2015_19:04:39 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm :Proton CDCl3 /opt/users/guneyt gune
OMe
N
O
O
F
15a
f1 (ppm)

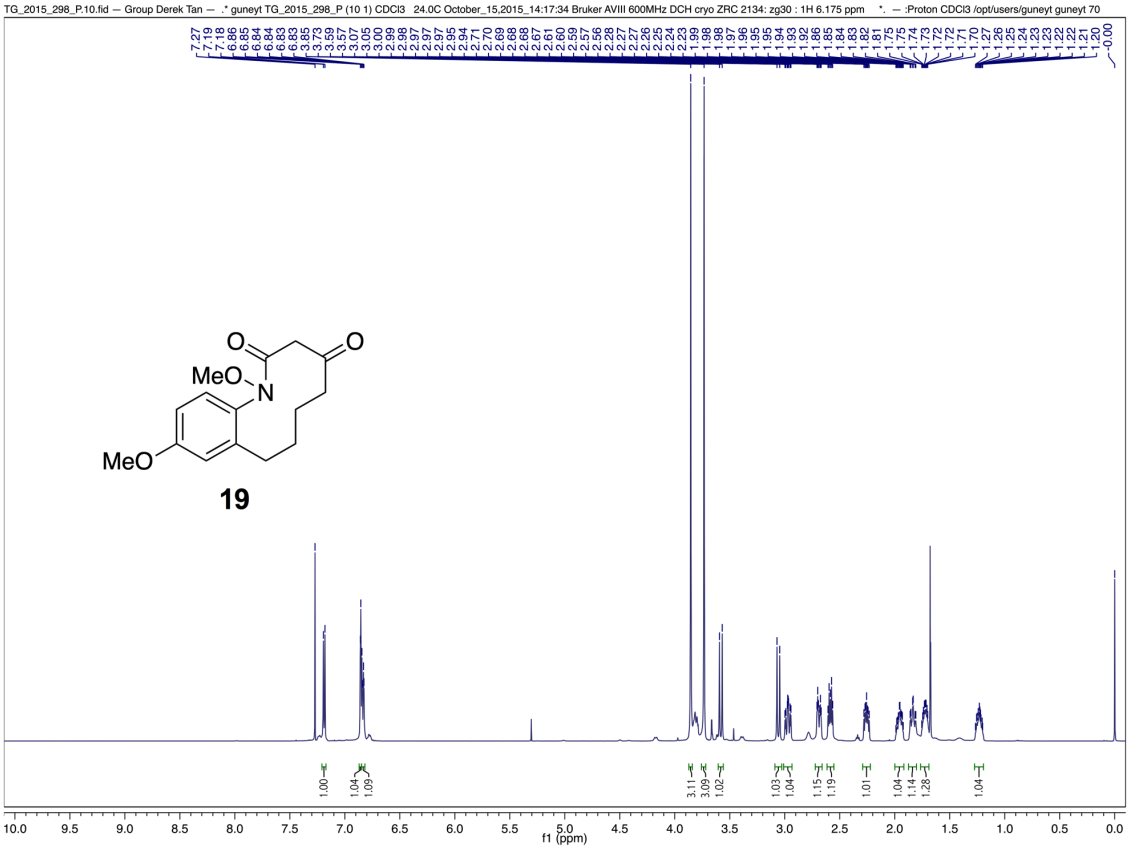

TG_2015_182_Prep_F1.11.fid — Group Derek Tan — .* guneyt TG_2015_182_Prep_F1 (11 1) CDCl3 24.0C May_11,2015_19:10:11 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm :Carbon CDCl3
OMe
N
O
O
F
15a
f1 (ppm)

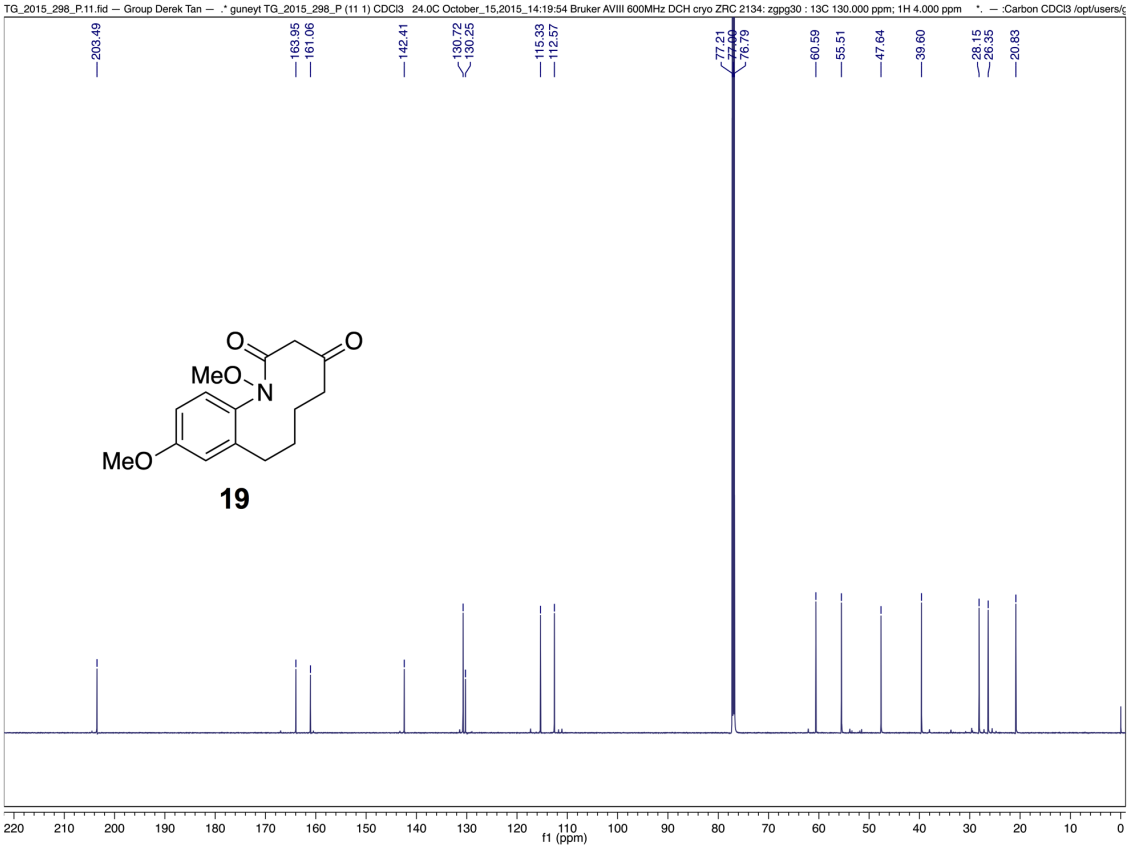

TG_2015_191_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_191_Pure (10 1) CDCl3 24.0C June_20,2015_03:35:22 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 64
OMe
N
O
O
Cl
15b
f1 (ppm)

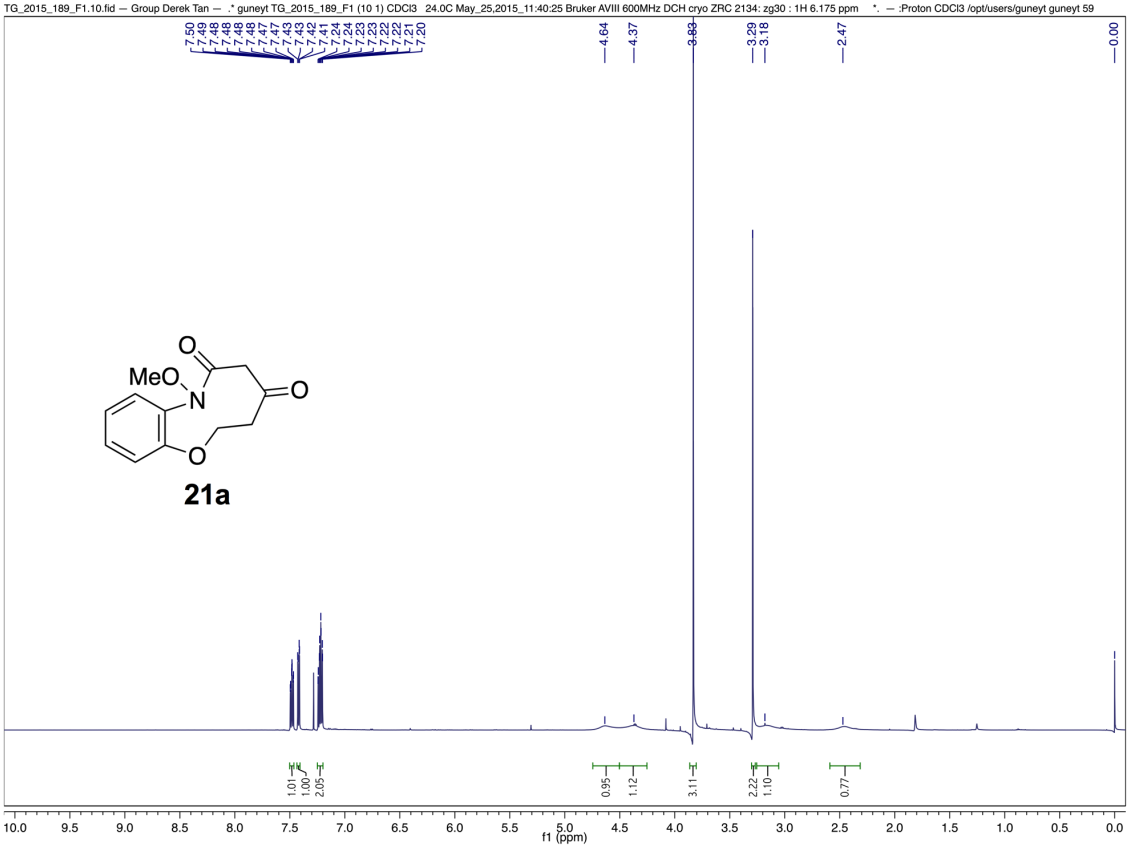

TG_2015_191_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_191_Pure (11 1) CDCl3 24.0C June_20,2015_03:37:30 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/use
OMe
N
O
O
Cl
15b
f1 (ppm)

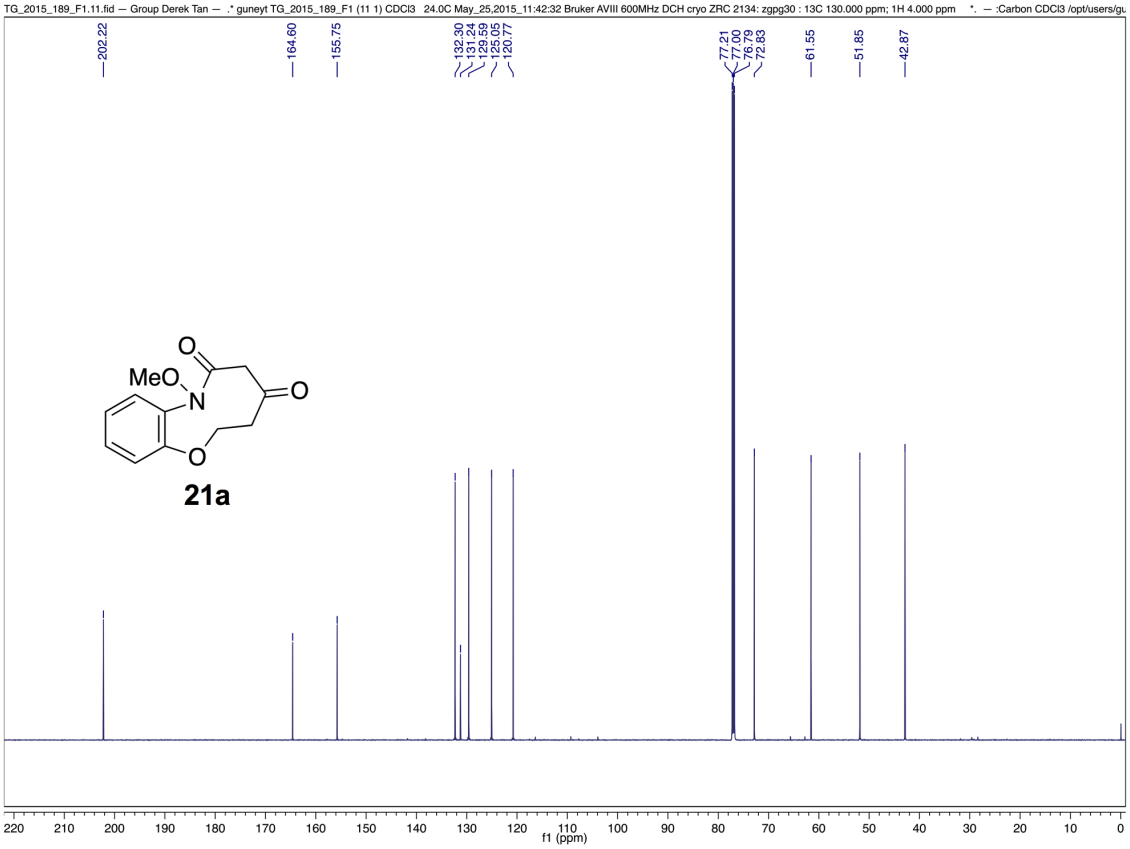

TG-2015-282-001.10.fid — Group Derek Tan — .* guneyt TG-2015-282-001 (10 1) CDCl3 24.0C December_16,2016_22:59:46 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm :Proton CDCl3 /opt/users/guneyt guneyt 76
MeO
N
O
O
MeO
17
f1 (ppm)

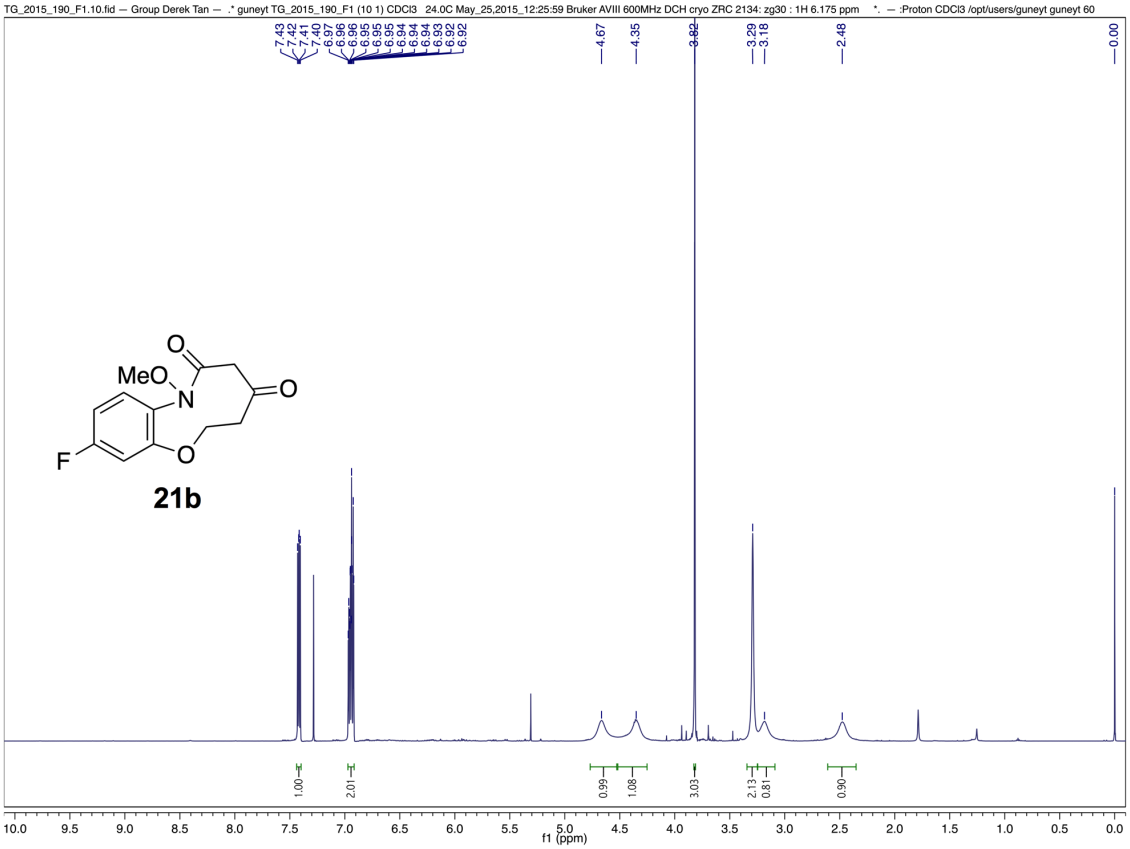

TG-2015-282-001.11.fid — Group Derek Tan — .* guneyt TG-2015-282-001 (11 1) CDCl3 24.0C December_16,2016_23:02:09 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm :Carbon CDCl3 /opt/us
MeO
N
O
O
MeO
17
f1 (ppm)

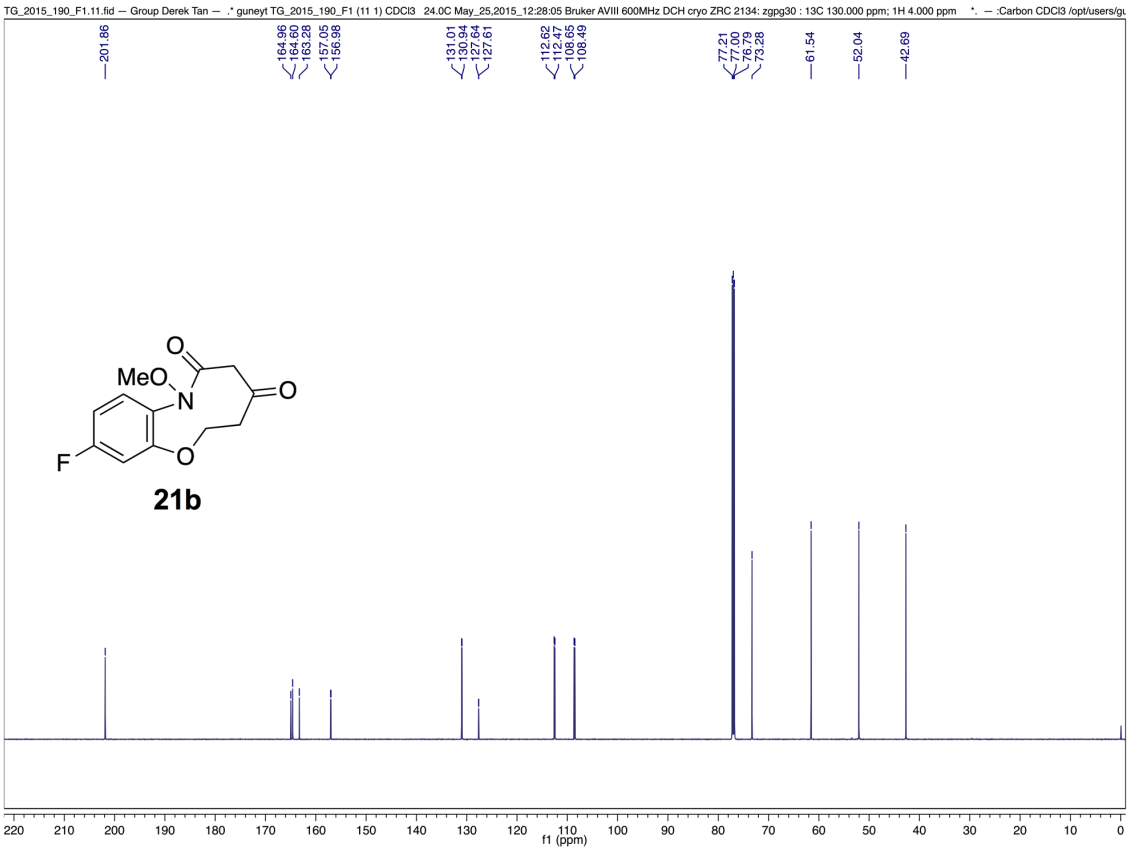

TG_2015_298_P.10.fid — Group Derek Tan — .* guneyt TG_2015_298_P (10 1) CDCl3 24.0C October_15,2015_14:17:34 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 70
MeO
N
O
O
MeO
19
f1 (ppm)

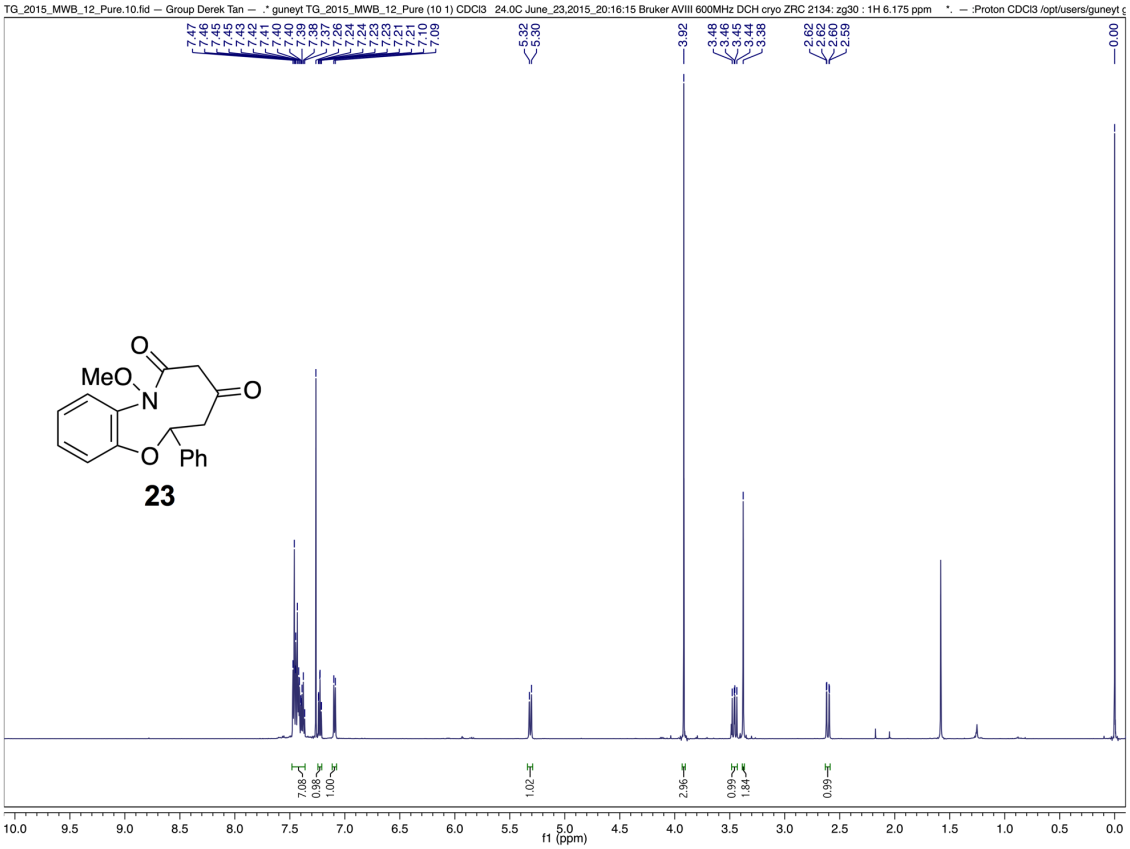

TG_2015_298_P.11.fid — Group Derek Tan — .* guneyt TG_2015_298_P (11 1) CDCl3 24.0C October_15,2015_14:19:54 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/g
MeO
N
O
O
MeO
19
f1 (ppm)

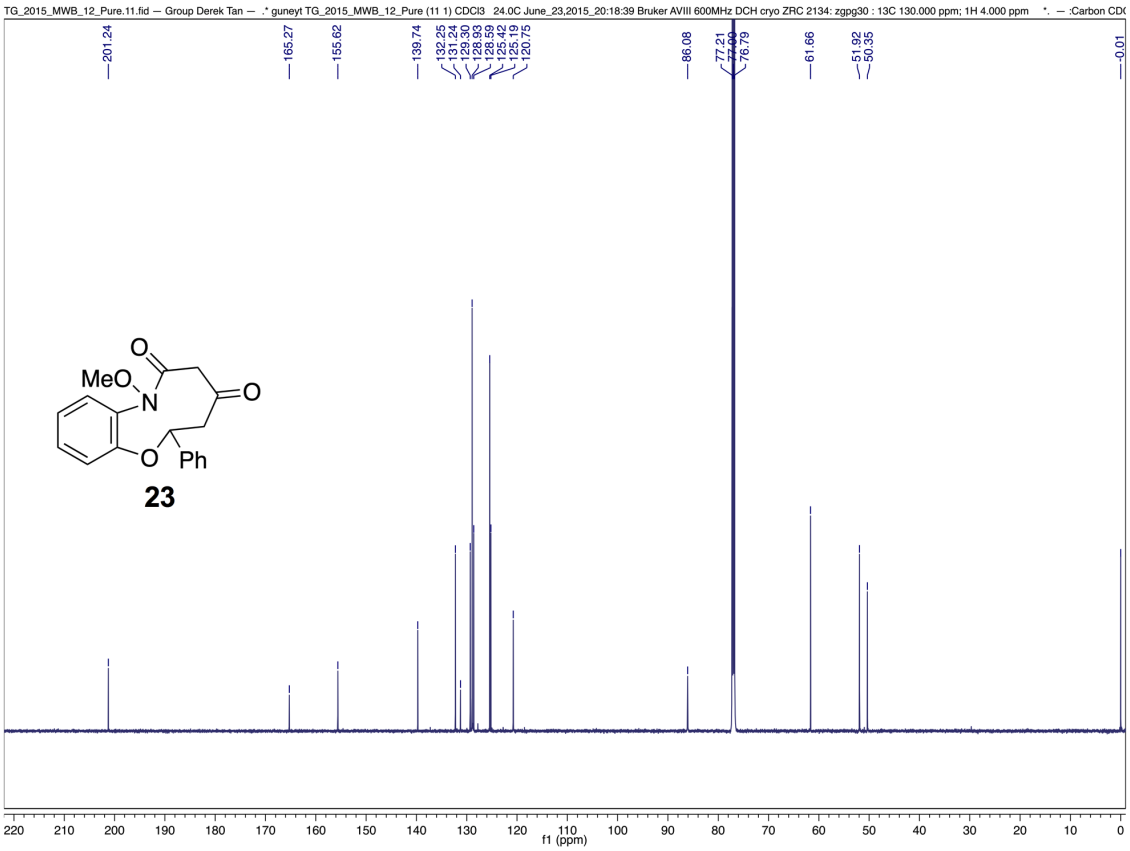

TG_2015_189_F1.10.fid — Group Derek Tan — .* guneyt TG_2015_189_F1 (10 1) CDCl3 24.0C May_25,2015_11:40:25 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 59
7.50
7.49
7.48
7.48
7.48
7.48
7.47
7.47
7.43
7.43
7.42
7.41
7.24
7.23
7.23
7.22
7.22
7.21
7.20
4.64
4.37
3.83
3.29
3.18
2.47
0.00
MeO
N
O
O
O
21a
1.01
1.00
2.05
0.95
1.12
3.11
2.22
1.10
0.77
f1 (ppm)

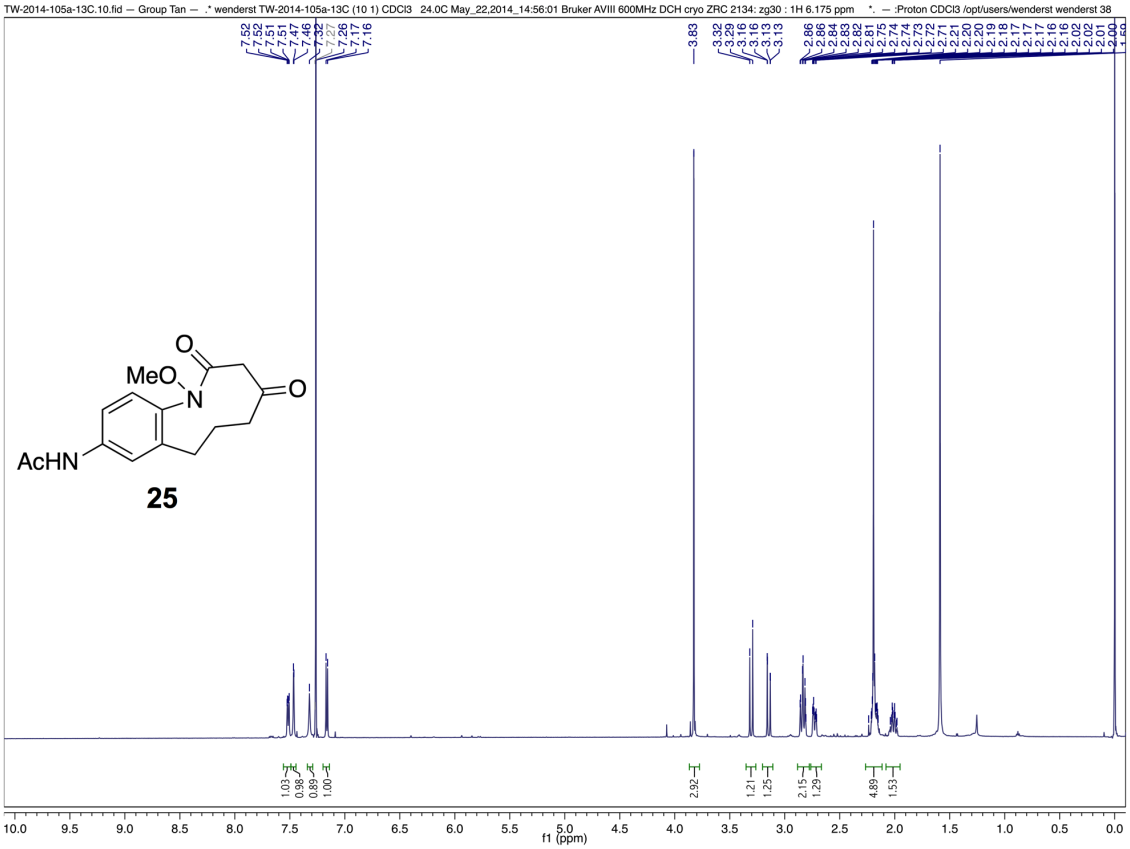

TG_2015_189_F1.11.fid — Group Derek Tan — .* guneyt TG_2015_189_F1 (11 1) CDCl3 24.0C May_25,2015_11:42:32 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/gu
202.22
164.60
155.75
132.30
131.24
129.59
125.05
120.77
77.21
77.00
76.79
72.83
61.55
51.85
42.87
MeO
N
O
O
O
21a
f1 (ppm)

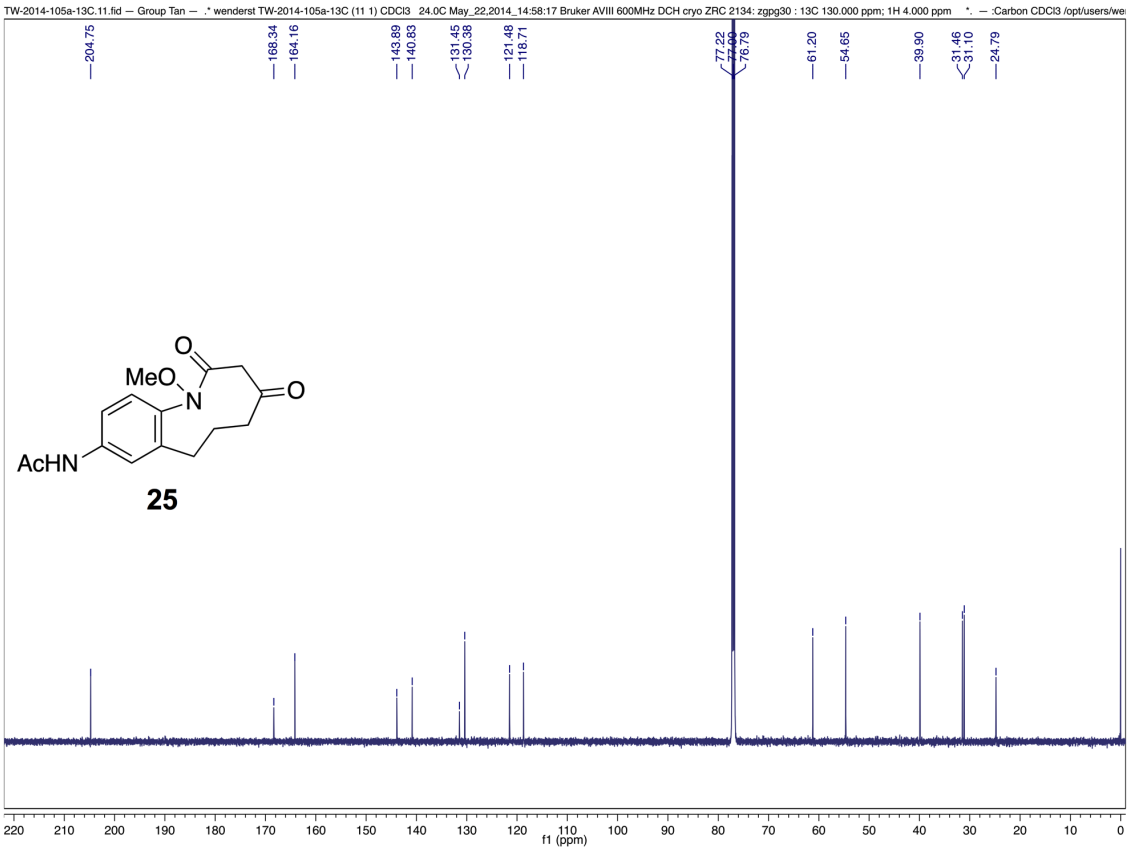

TG_2015_190_F1.10.fid — Group Derek Tan — .* guneyt TG_2015_190_F1 (10 1) CDCl3 24.0C May_25,2015_12:25:59 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 60
7.43
7.42
7.41
7.40
6.97
6.96
6.96
6.95
6.95
6.95
6.94
6.94
6.94
6.93
6.92
6.92
4.67
4.35
3.82
3.29
3.18
2.48
0.00
MeO
N
O
O
F
O
21b
1.00
2.01
0.99
1.08
3.03
2.13
0.81
0.90
f1 (ppm)

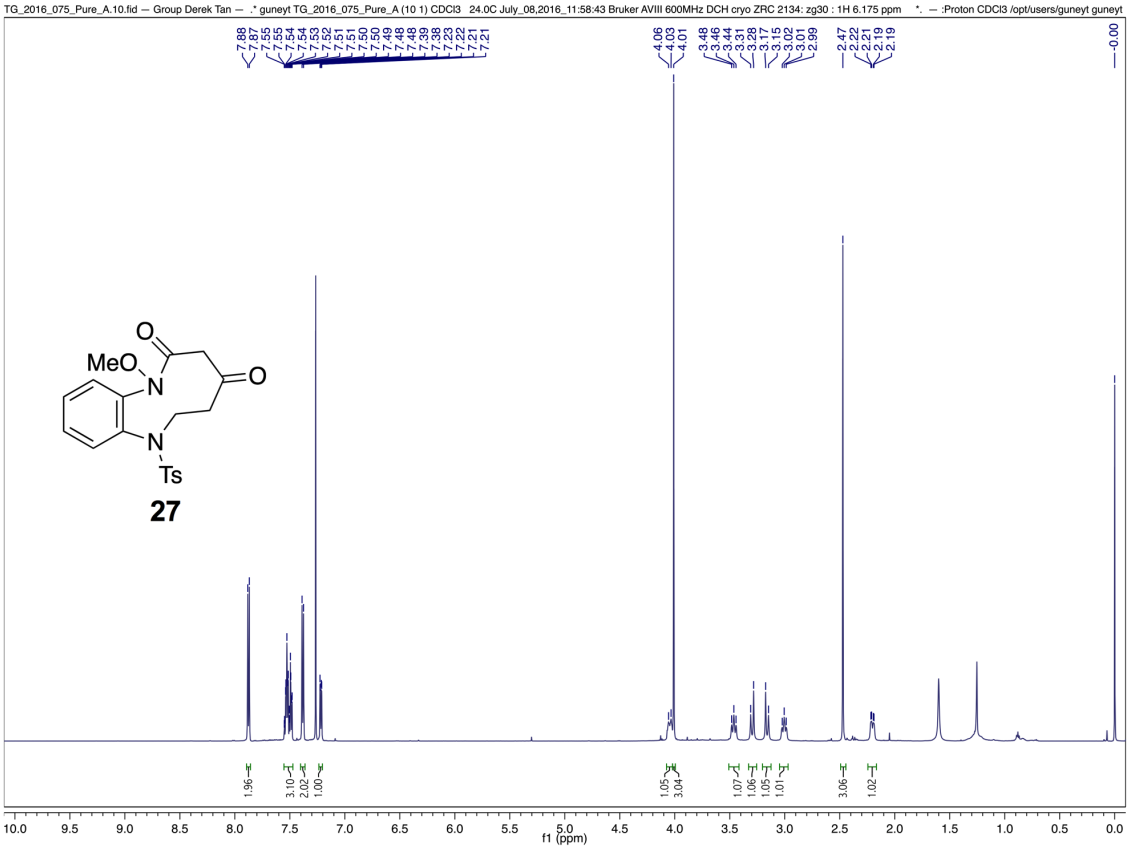

TG_2015_190_F1.11.fid — Group Derek Tan — .* guneyt TG_2015_190_F1 (11 1) CDCl3 24.0C May_25,2015_12:28:05 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/gu
201.86
164.96
164.60
163.28
157.05
156.98
131.01
130.84
127.64
127.61
112.62
112.47
108.65
108.49
77.21
77.00
76.79
73.28
61.54
52.04
42.69
MeO
N
O
O
F
O
21b
f1 (ppm)

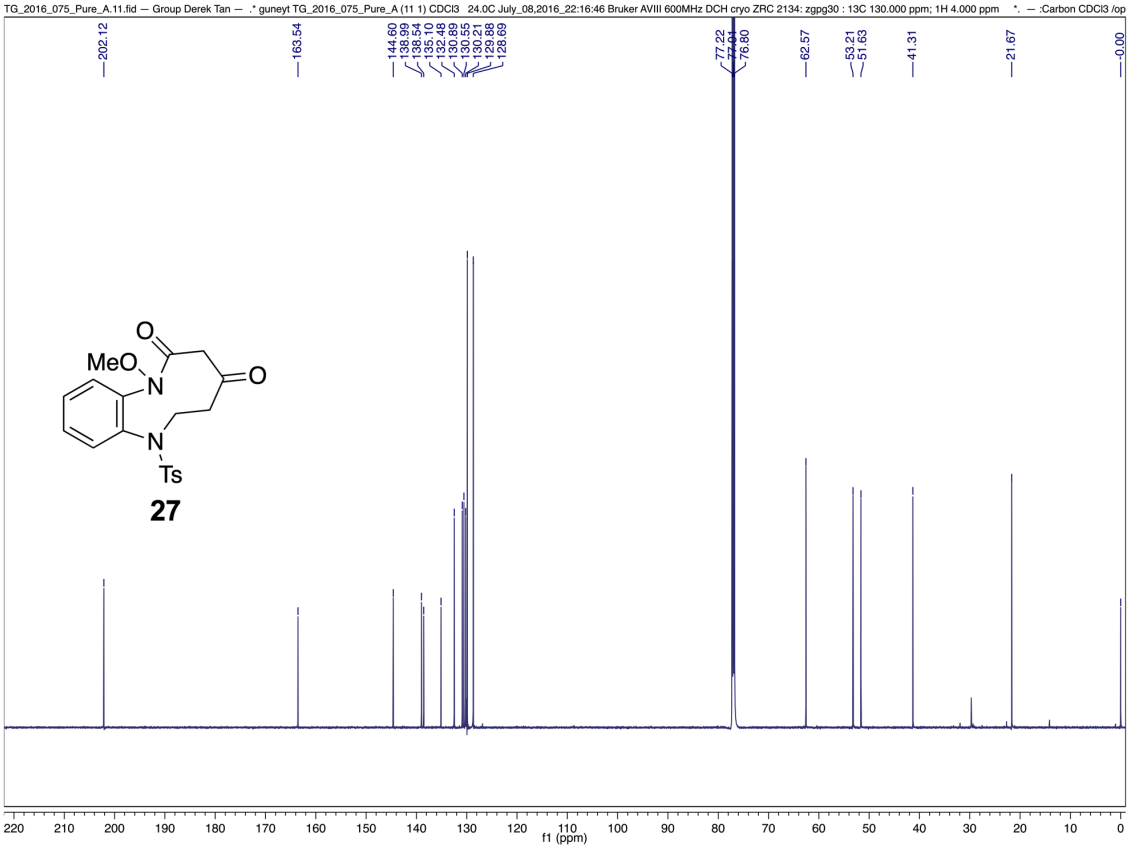

TG_2015_MWB_12_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_MWB_12_Pure (10 1) CDCl3 24.0C June_23,2015_20:16:15 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
7.47 7.46 7.45 7.45 7.43 7.42 7.41 7.40 7.40 7.39 7.38 7.37 7.26 7.24 7.23 7.23 7.21 7.21 7.10 7.09
5.32 5.30
3.92
3.48 3.46 3.45 3.44 3.38
2.62 2.62 2.60 2.59
0.00
7.08 0.98 1.00 1.02 2.96 0.99 1.84 0.99
f1 (ppm)
MeO
N
O
O
Ph
23

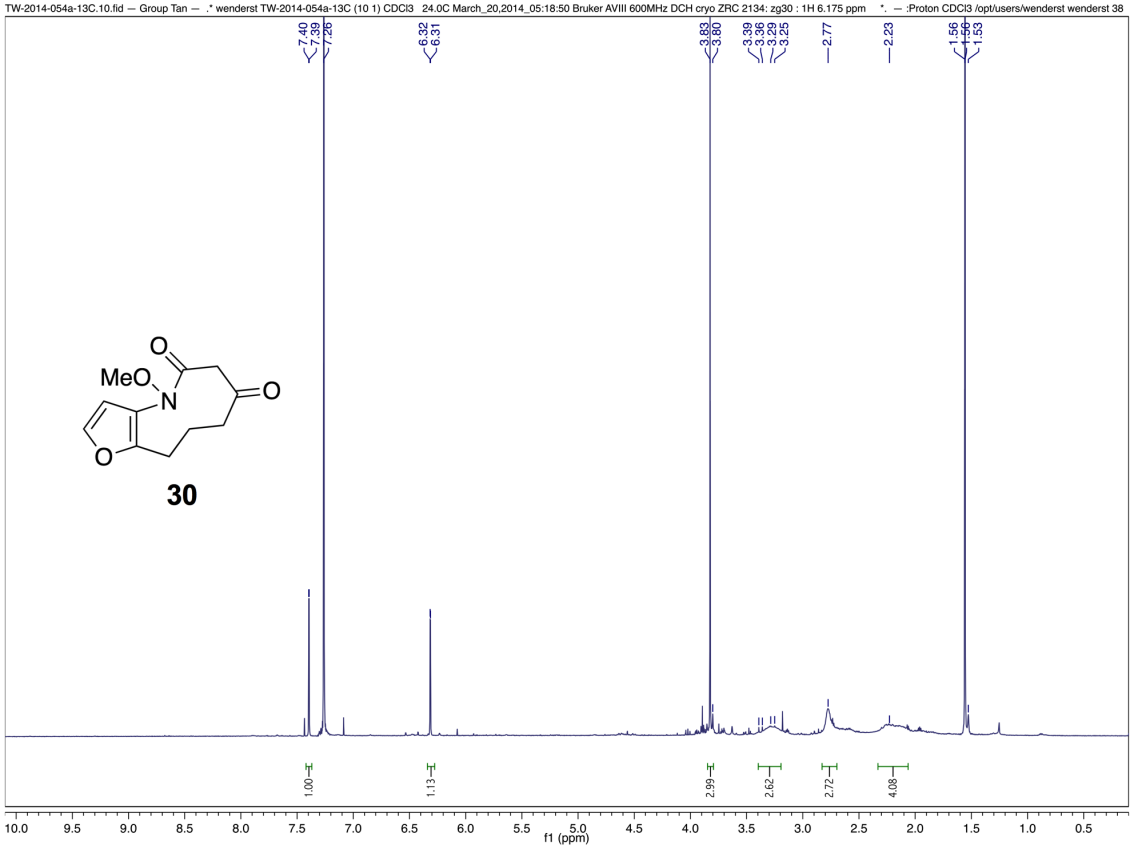

TG_2015_MWB_12_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_MWB_12_Pure (11 1) CDCl3 24.0C June_23,2015_20:18:39 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm
201.24
165.27
155.62
139.74
132.25 131.24 129.30 128.93 128.59 125.42 125.19 120.75
86.08
77.21 77.00 76.79
61.66
51.92 50.35
0.01
f1 (ppm)
MeO
N
O
O
Ph
23

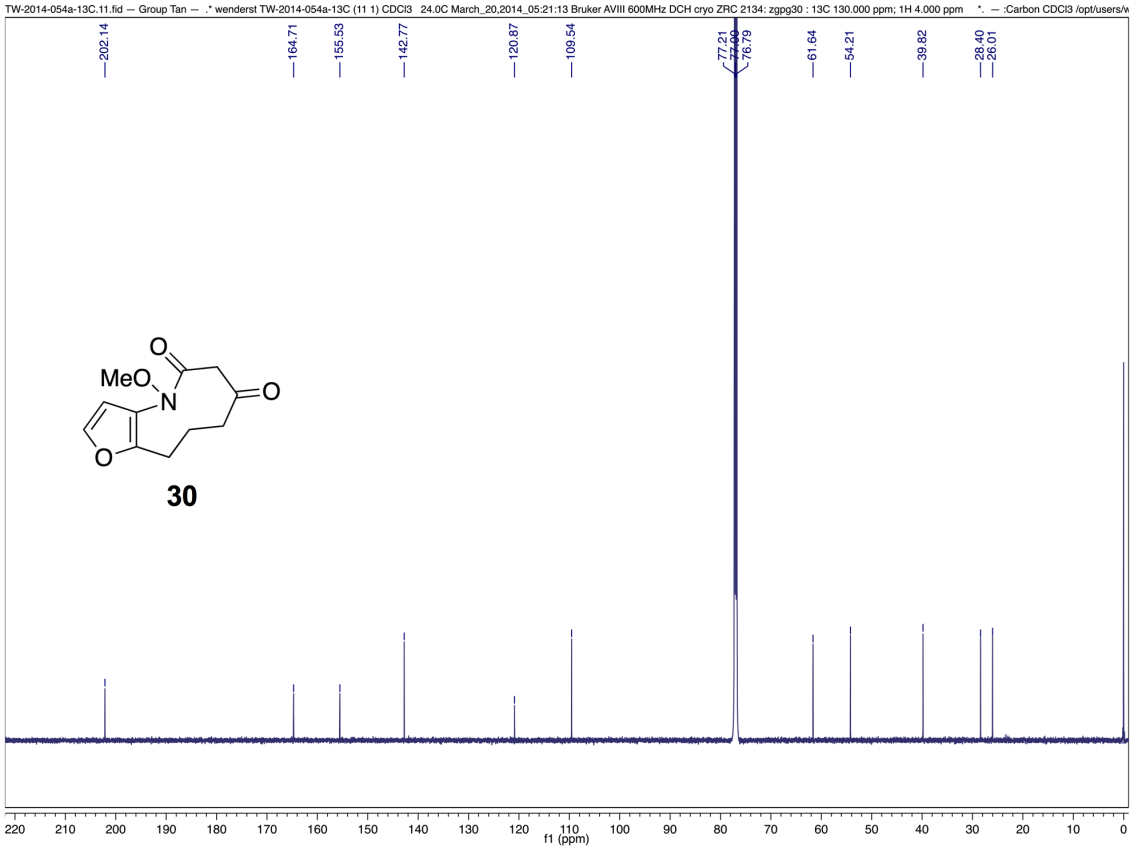

TW-2014-105a-13C.10.fid — Group Tan — .* wenderst TW-2014-105a-13C (10 1) CDCl3 24.0C May_22,2014_14:56:01 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 38
7.52
7.52
7.51
7.51
7.47
7.46
7.32
7.27
7.26
7.17
7.16
3.83
3.32
3.29
3.16
3.13
3.13
2.86
2.86
2.84
2.83
2.82
2.81
2.75
2.74
2.73
2.72
2.71
2.21
2.20
2.19
2.18
2.17
2.17
2.16
2.02
2.02
2.01
2.00
1.03
0.98
0.89
1.00
2.92
1.21
1.25
2.15
1.29
4.89
1.53
MeO
N
O
O
AcHN
25
f1 (ppm)

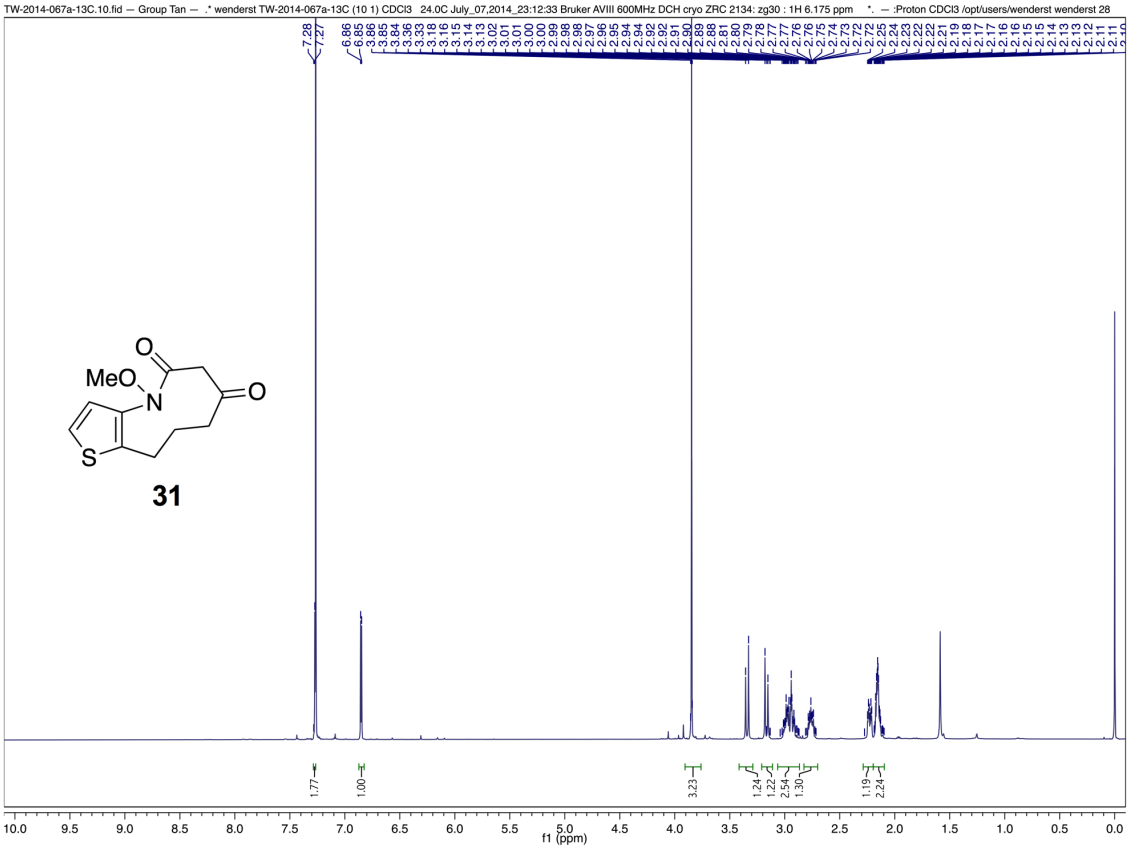

TW-2014-105a-13C.11.fid — Group Tan — .* wenderst TW-2014-105a-13C (11 1) CDCl3 24.0C May_22,2014_14:58:17 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/we
204.75
168.34
164.16
143.89
140.83
131.45
130.38
121.48
118.71
77.22
77.00
76.79
61.20
54.65
39.90
31.46
31.10
24.79
MeO
N
O
O
AcHN
25
f1 (ppm)

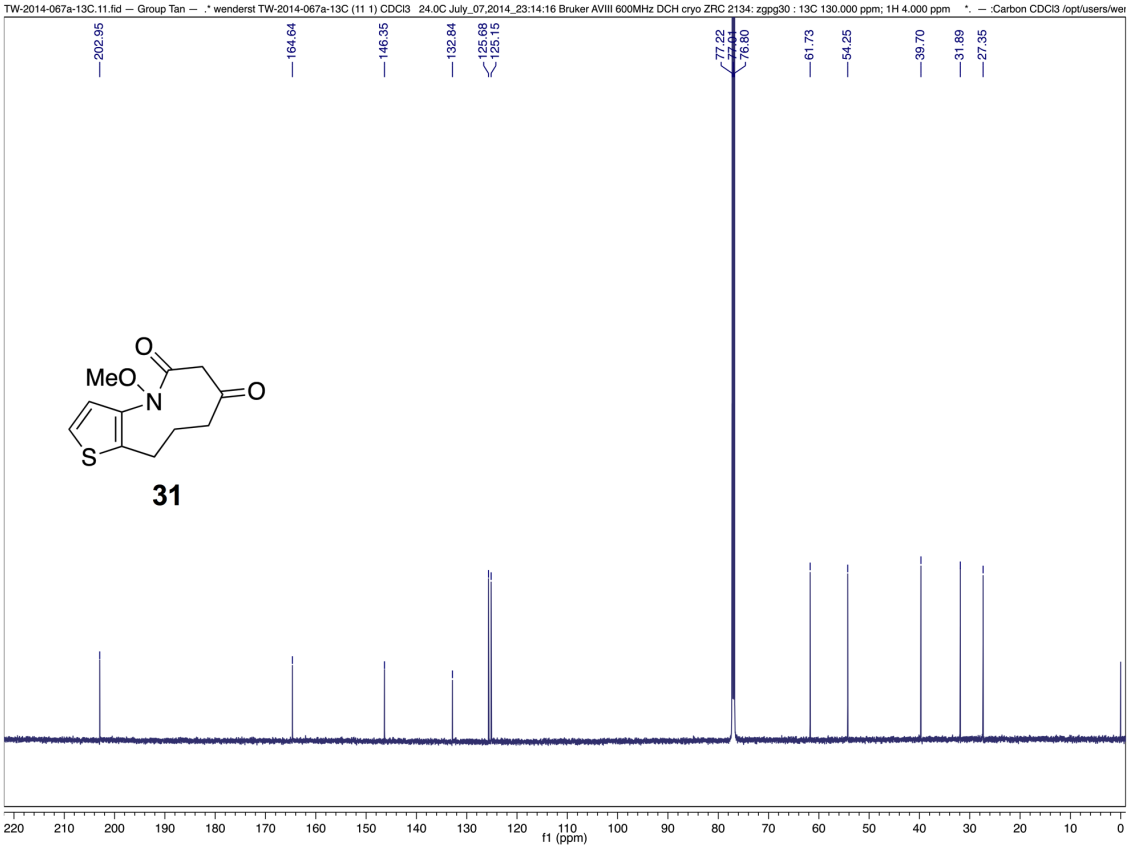

TG_2016_075_Pure_A.10.fid — Group Derek Tan — .* guneyt TG_2016_075_Pure_A (10 1) CDCl3 24.0C July_08,2016_11:58:43 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt
MeO
N
O
O
N
Ts
27
f1 (ppm)

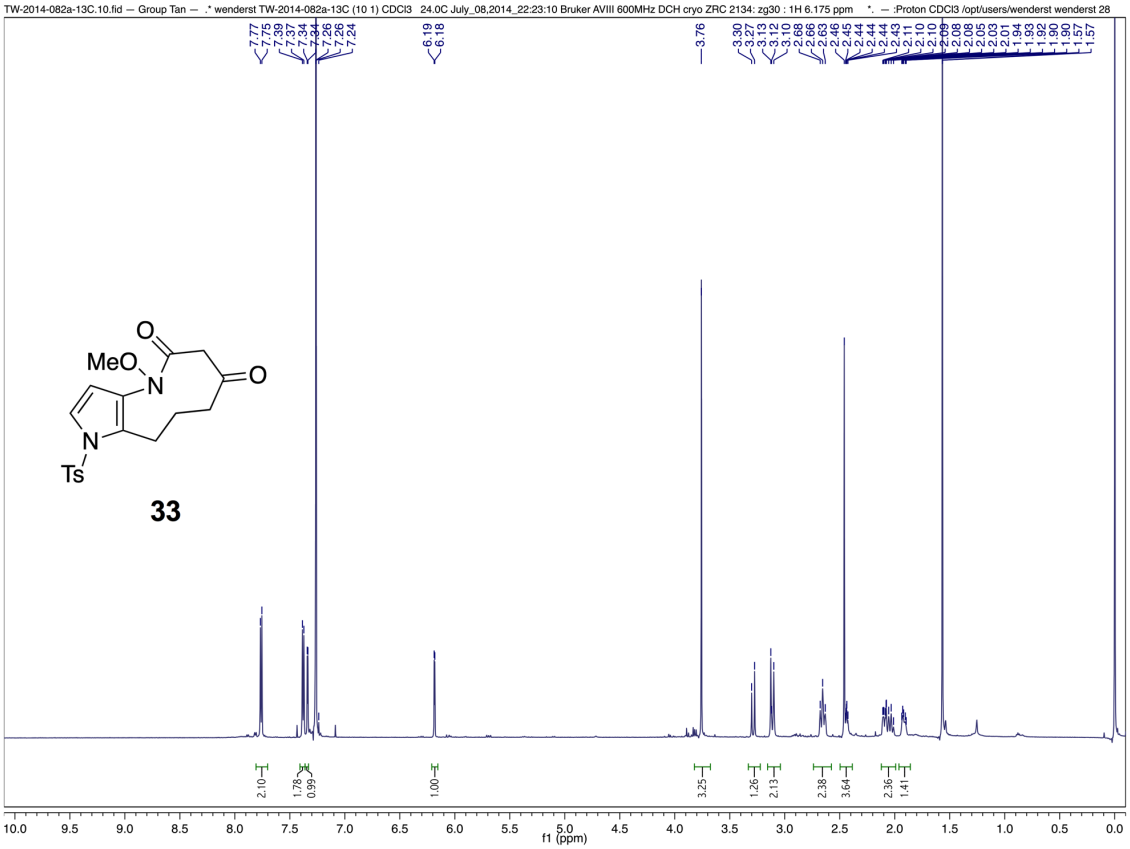

TG_2016_075_Pure_A.11.fid — Group Derek Tan — .* guneyt TG_2016_075_Pure_A (11 1) CDCl3 24.0C July_08,2016_22:16:46 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /op
MeO
N
O
O
N
Ts
27
f1 (ppm)

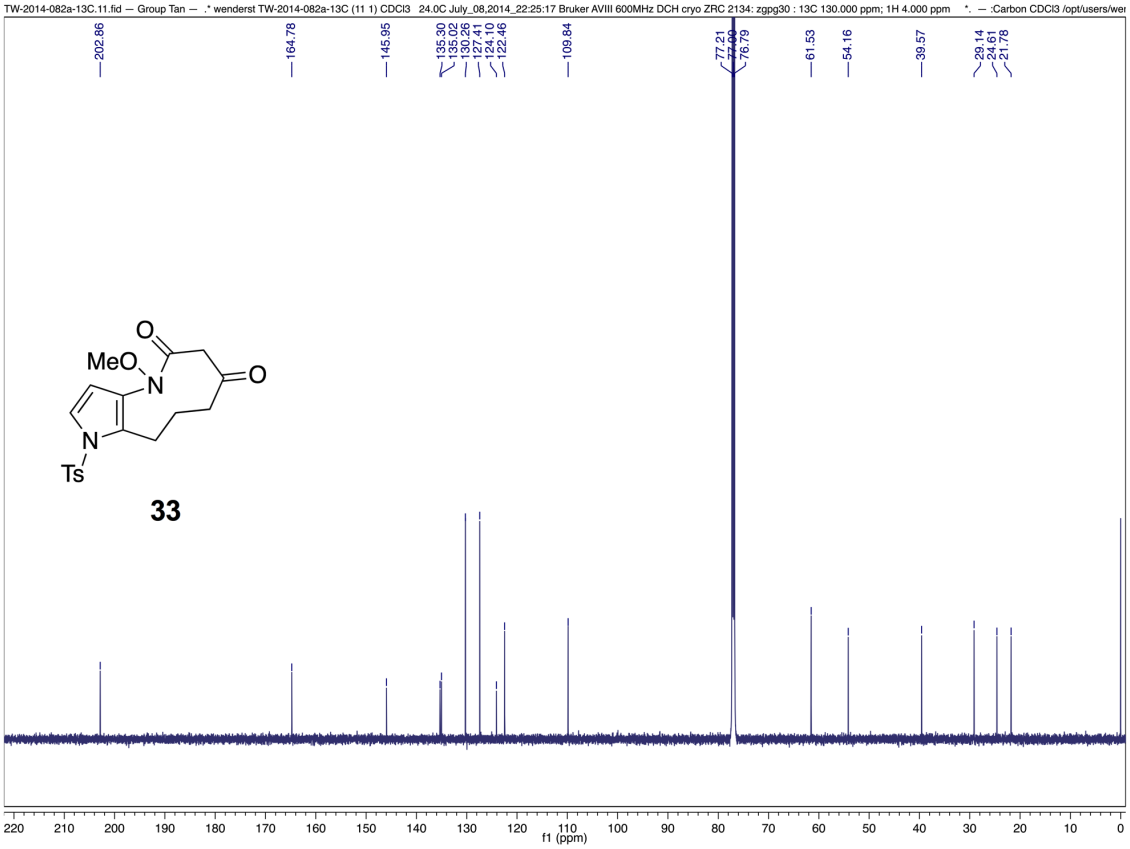

TW-2014-054a-13C.10.fid — Group Tan — .* wenderst TW-2014-054a-13C (10 1) CDCl3 24.0C March_20,2014_05:18:50 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 38
7.40
7.39
7.26
6.32
6.31
3.83
3.80
3.39
3.36
3.32
3.25
2.77
2.23
1.56
1.56
1.53
MeO
N
O
O
O
30
1.00
1.13
2.99
2.62
2.72
4.08
f1 (ppm)

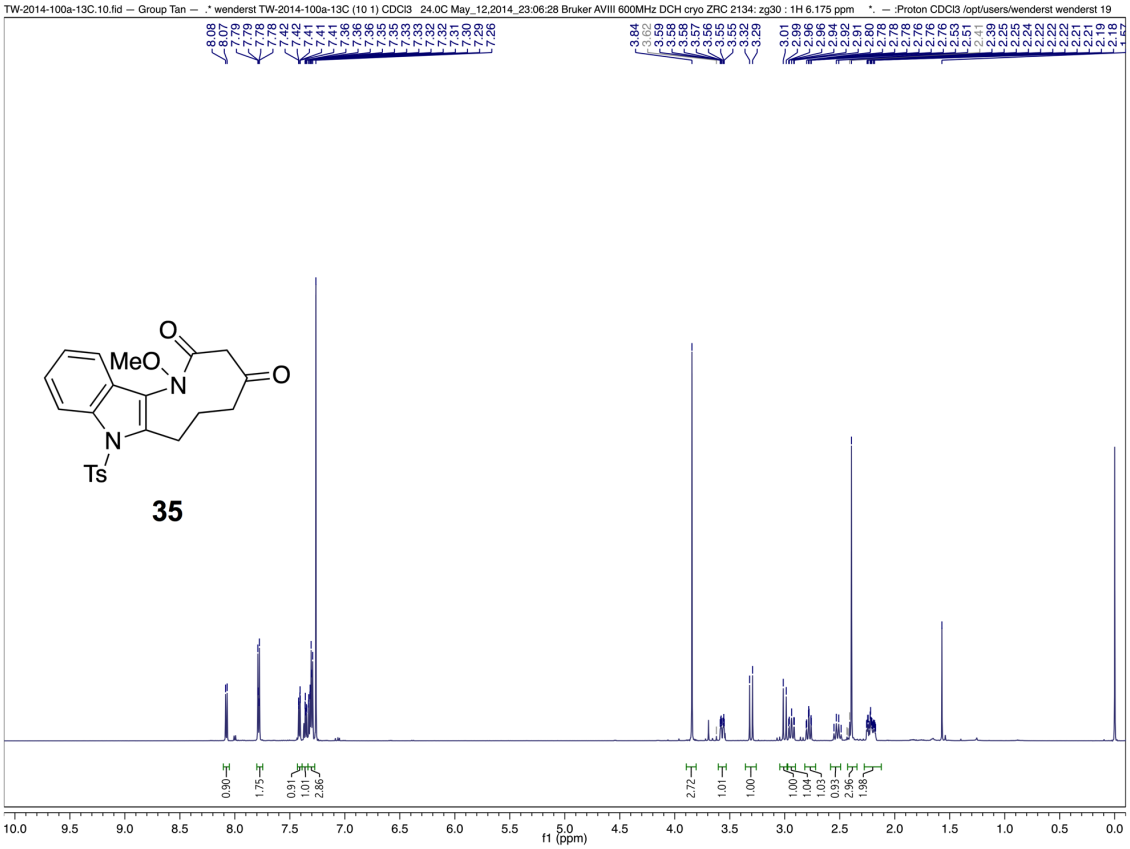

TW-2014-054a-13C.11.fid — Group Tan — .* wenderst TW-2014-054a-13C (11 1) CDCl3 24.0C March_20,2014_05:21:13 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/w
202.14
164.71
155.53
142.77
120.87
109.54
77.21
77.00
76.79
61.64
54.21
39.82
28.40
26.01
MeO
N
O
O
O
30
f1 (ppm)

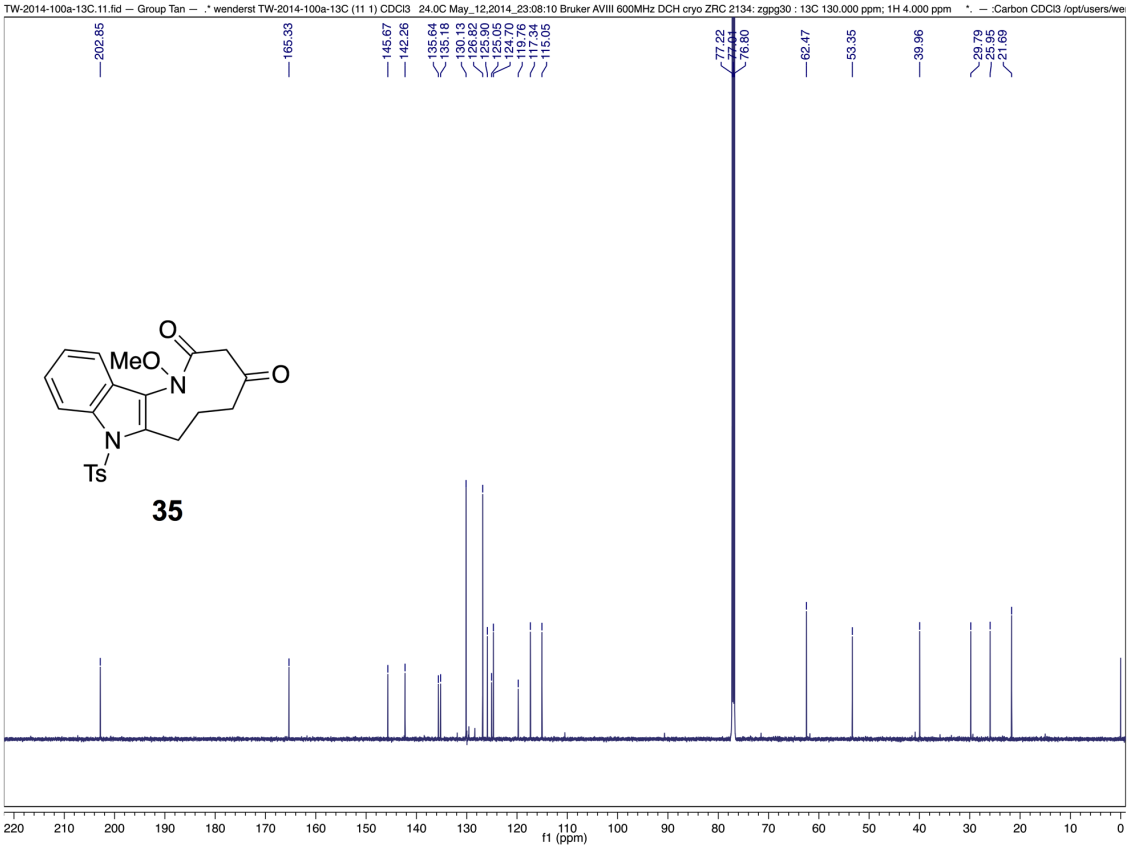

TW-2014-067a-13C.10.fid — Group Tan — .* wenderst TW-2014-067a-13C (10 1) CDCl3 24.0C July_07,2014_23:12:33 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 28
MeO
N
O
O
S
31
f1 (ppm)

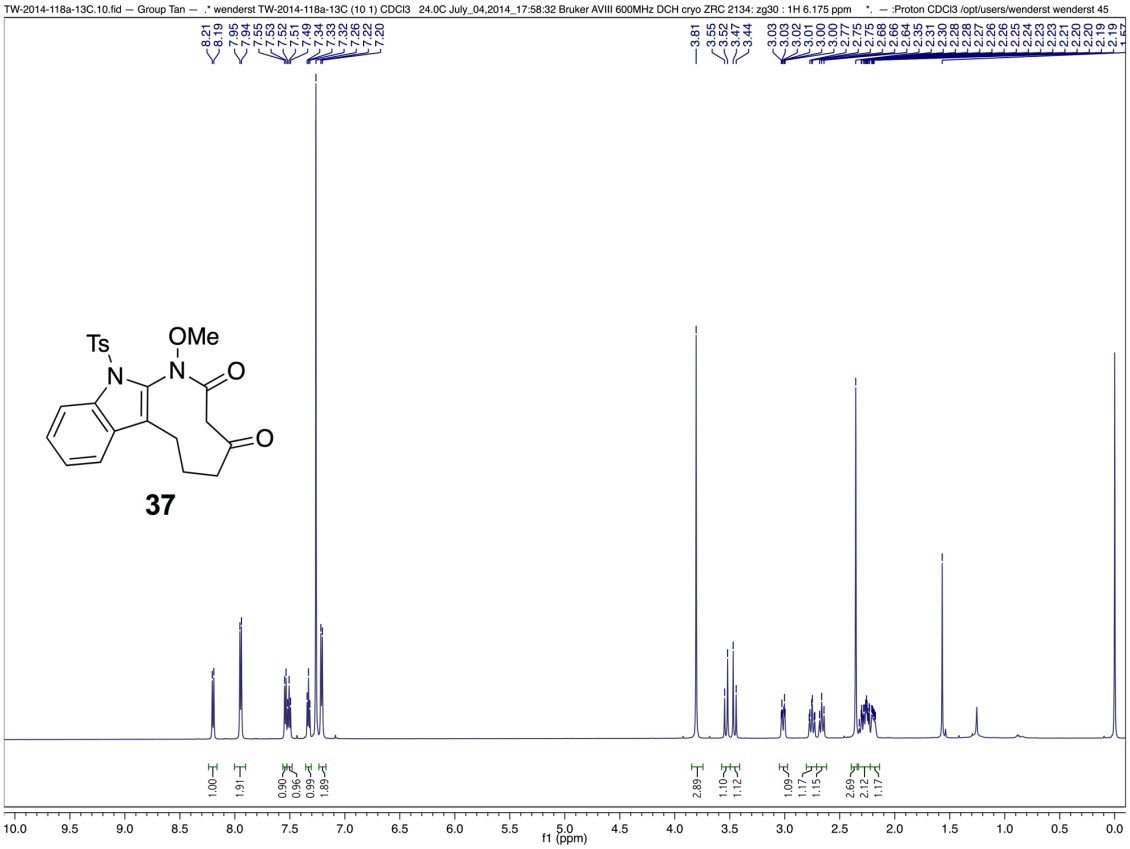

TW-2014-067a-13C.11.fid — Group Tan — .* wenderst TW-2014-067a-13C (11 1) CDCl3 24.0C July_07,2014_23:14:16 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/wer
202.95
164.64
146.35
132.84
125.68
125.15
77.22
77.01
76.80
61.73
54.25
39.70
31.89
27.35
MeO
N
O
O
S
31
f1 (ppm)

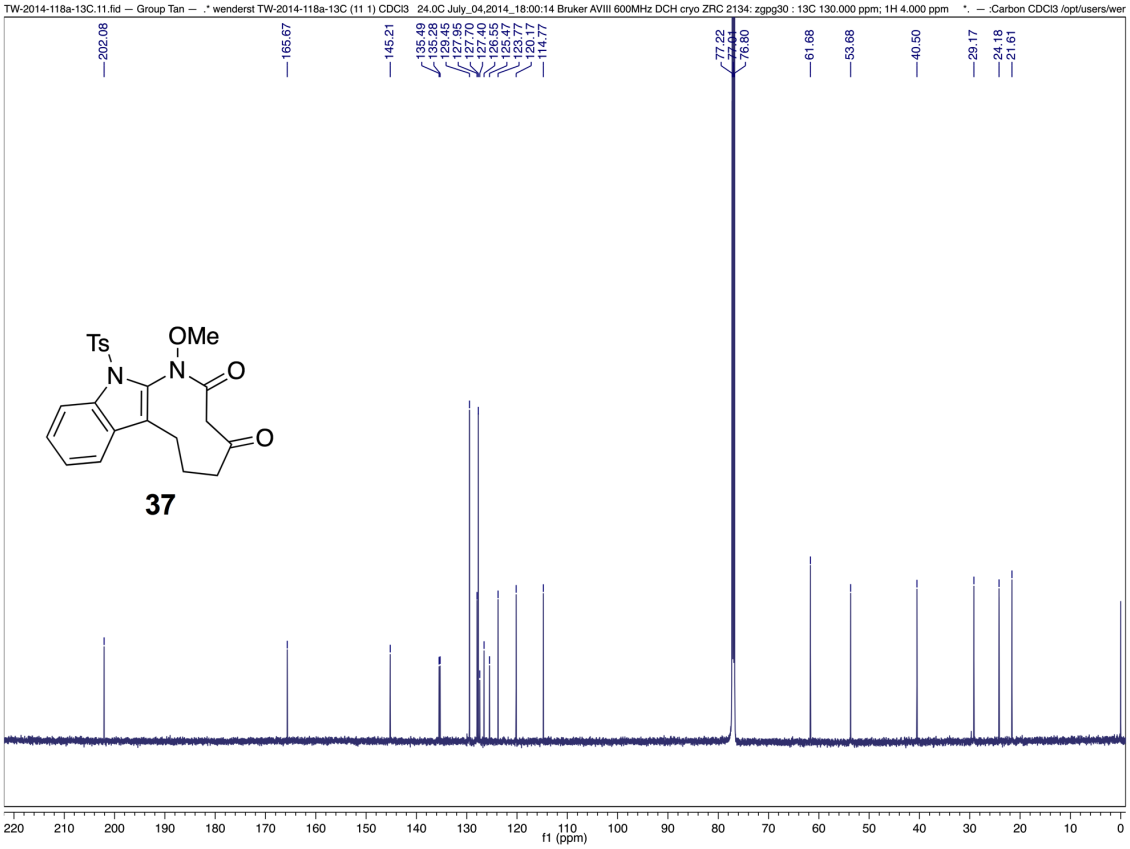

TW-2014-082a-13C.10.fid — Group Tan — .* wenderst TW-2014-082a-13C (10 1) CDCl3 24.0C July_08,2014_22:23:10 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 28
MeO
N
O
O
N
Ts
33
f1 (ppm)

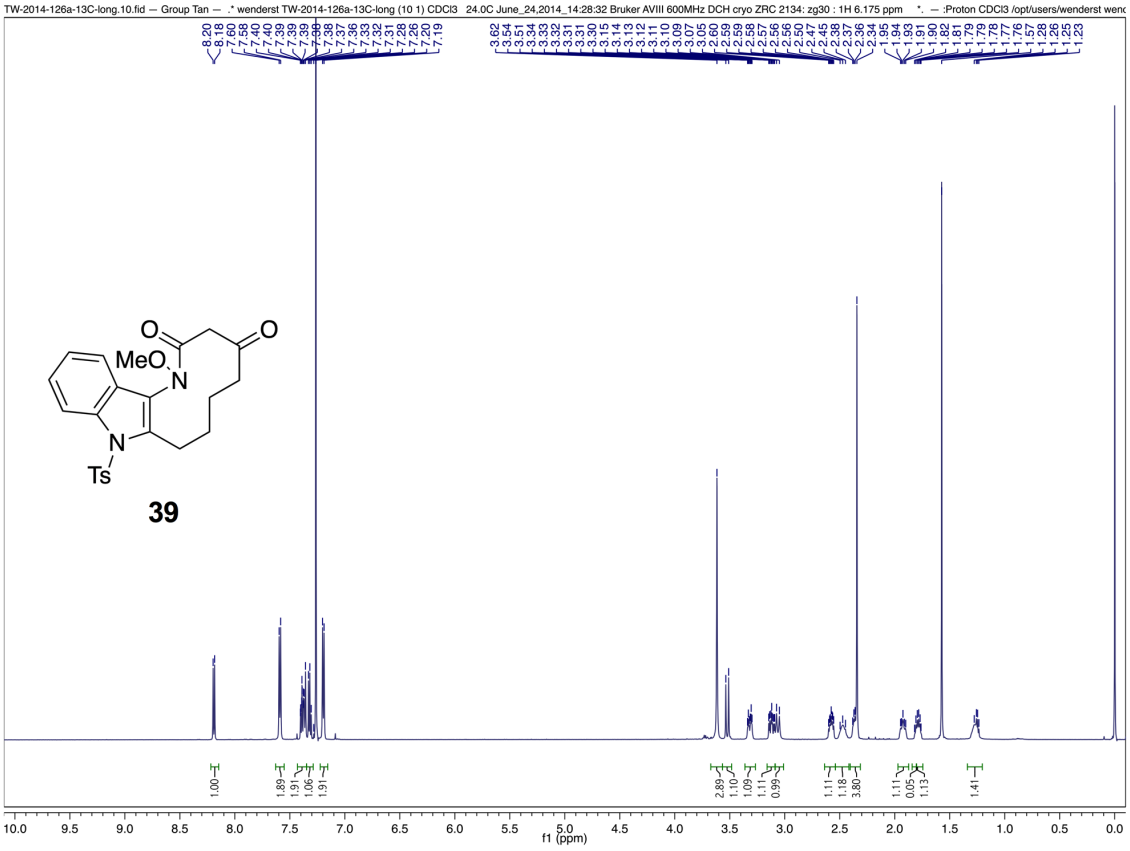

TW-2014-082a-13C.11.fid — Group Tan — .* wenderst TW-2014-082a-13C (11 1) CDCl3 24.0C July_08,2014_22:25:17 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/wer
MeO
N
O
O
N
Ts
33
f1 (ppm)

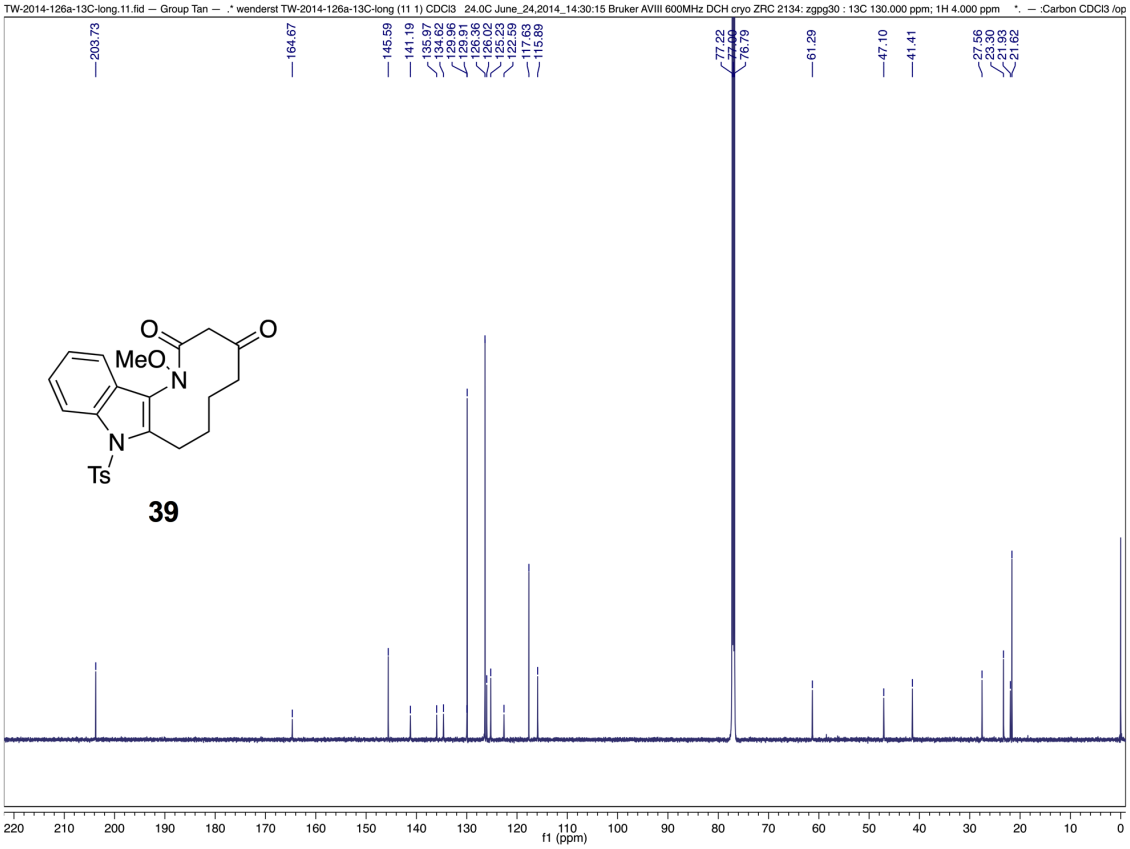

TW-2014-100a-13C.10.fid — Group Tan — .* wenderst TW-2014-100a-13C (10 1) CDCl3 24.0C May_12,2014_23:06:28 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 19
MeO
N
O
O
N
Ts
35
f1 (ppm)

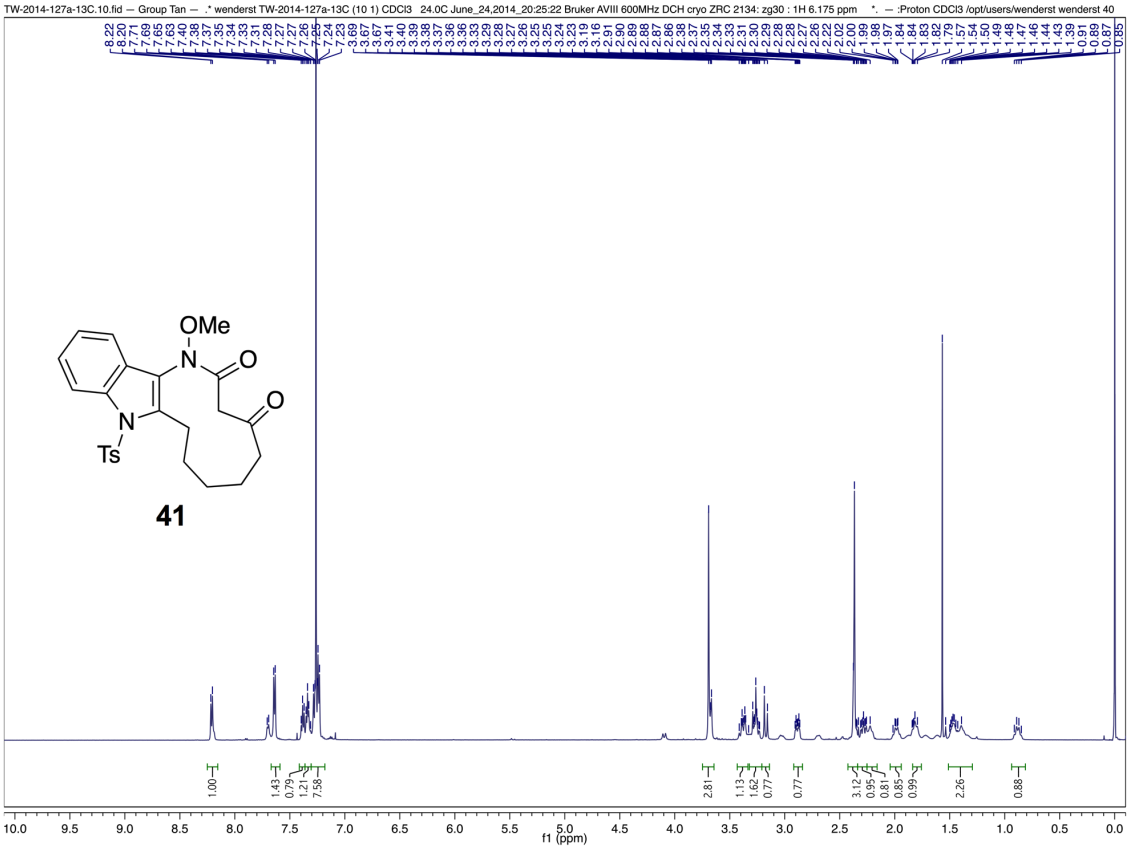

TW-2014-100a-13C.11.fid — Group Tan — .* wenderst TW-2014-100a-13C (11 1) CDCl3 24.0C May_12,2014_23:08:10 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/we
MeO
N
O
O
N
Ts
35
f1 (ppm)

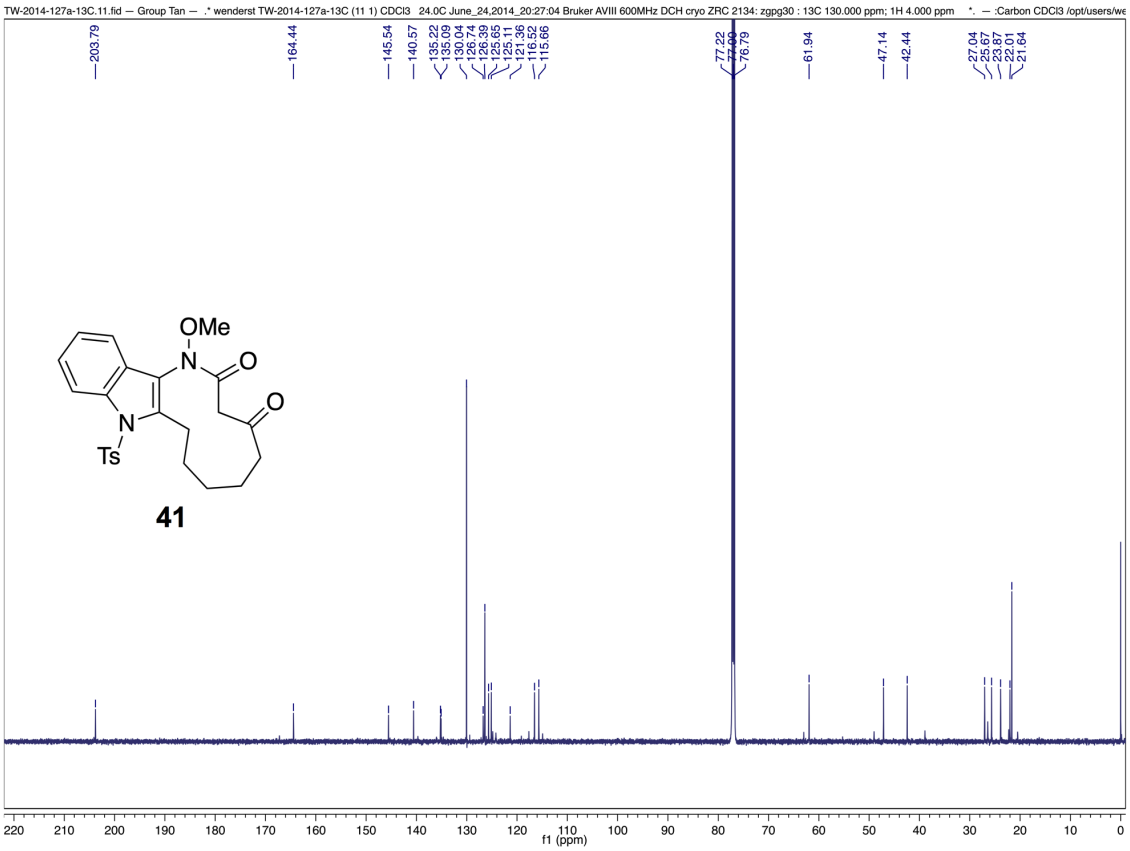

TW-2014-118a-13C.10.fid — Group Tan — .* wenderst TW-2014-118a-13C (10 1) CDCl3 24.0C July_04,2014_17:58:32 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 45
Ts
N
OMe
N
O
O
37
f1 (ppm)

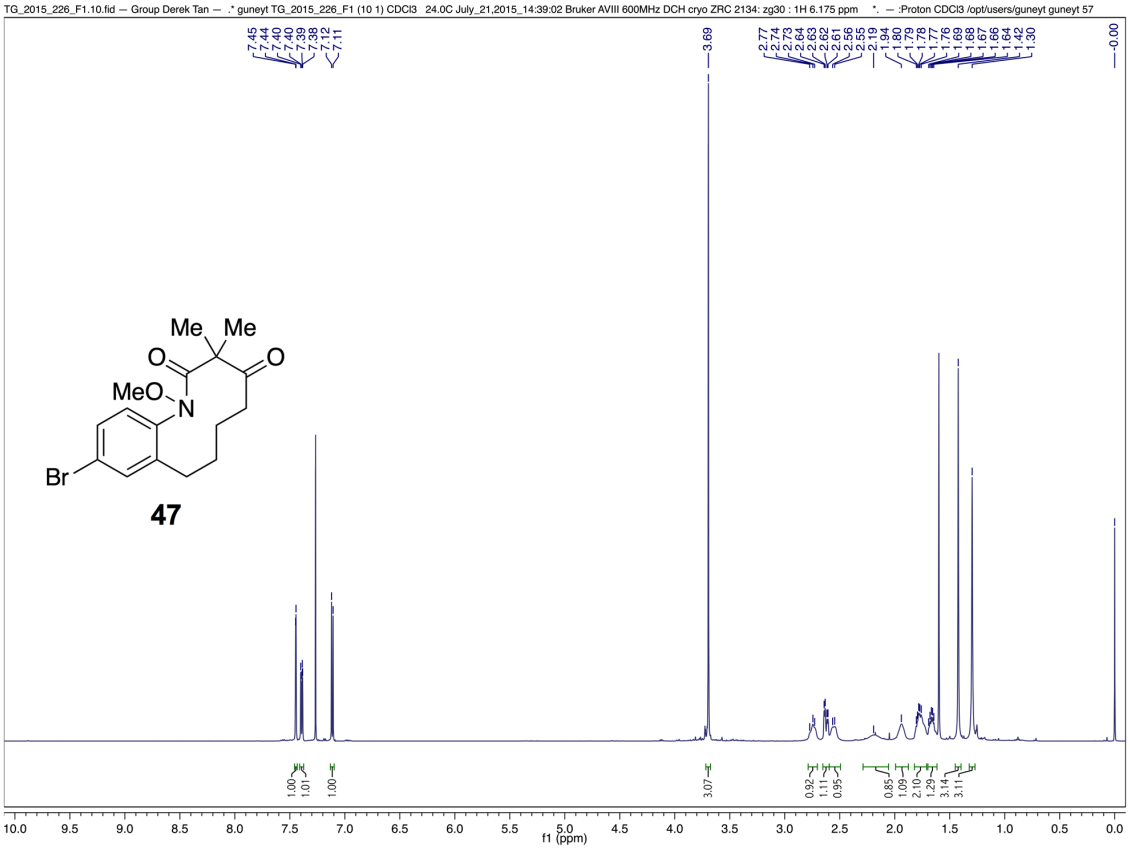

TW-2014-118a-13C.11.fid — Group Tan — .* wenderst TW-2014-118a-13C (11 1) CDCl3 24.0C July_04,2014_18:00:14 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/wer
Ts
N
OMe
N
O
O
37
f1 (ppm)

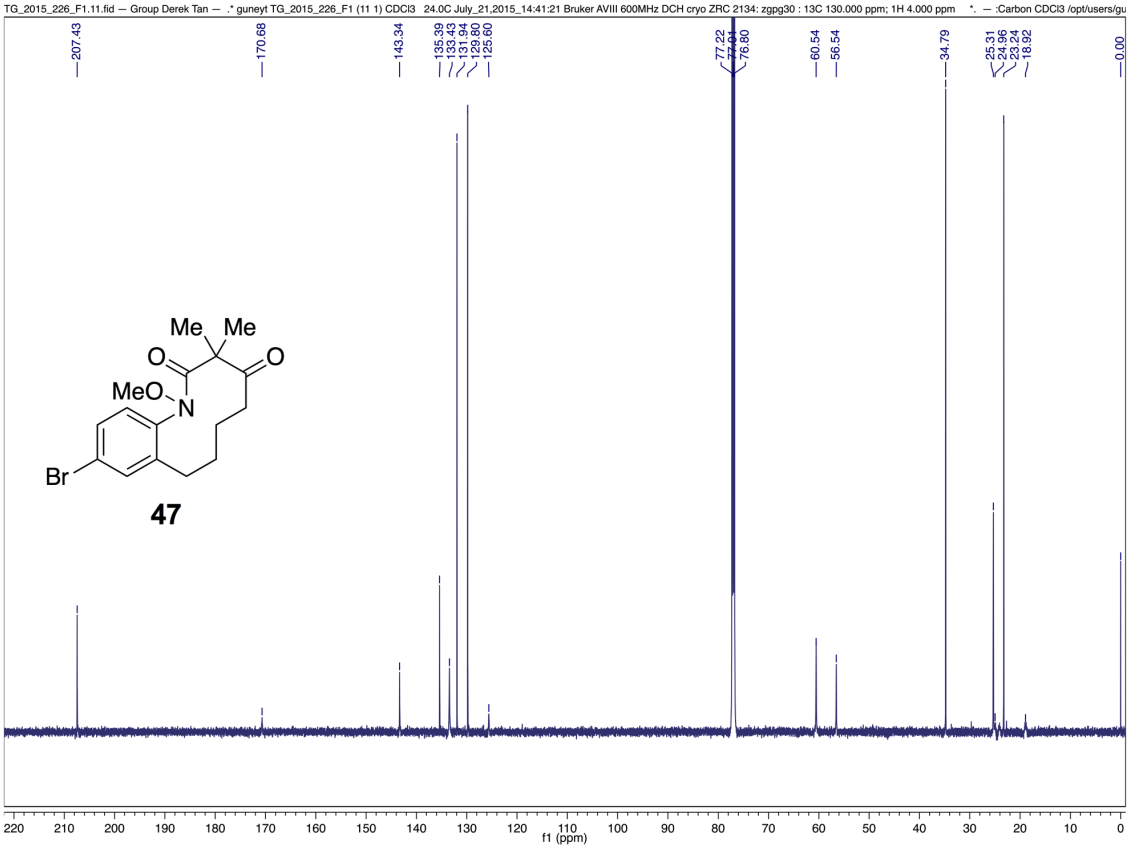

TW-2014-126a-13C-long.10.fid — Group Tan — .* wenderst TW-2014-126a-13C-long (10 1) CDCl3 24.0C June_24,2014_14:28:32 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wend
MeO
N
O
O
N
Ts
39
f1 (ppm)

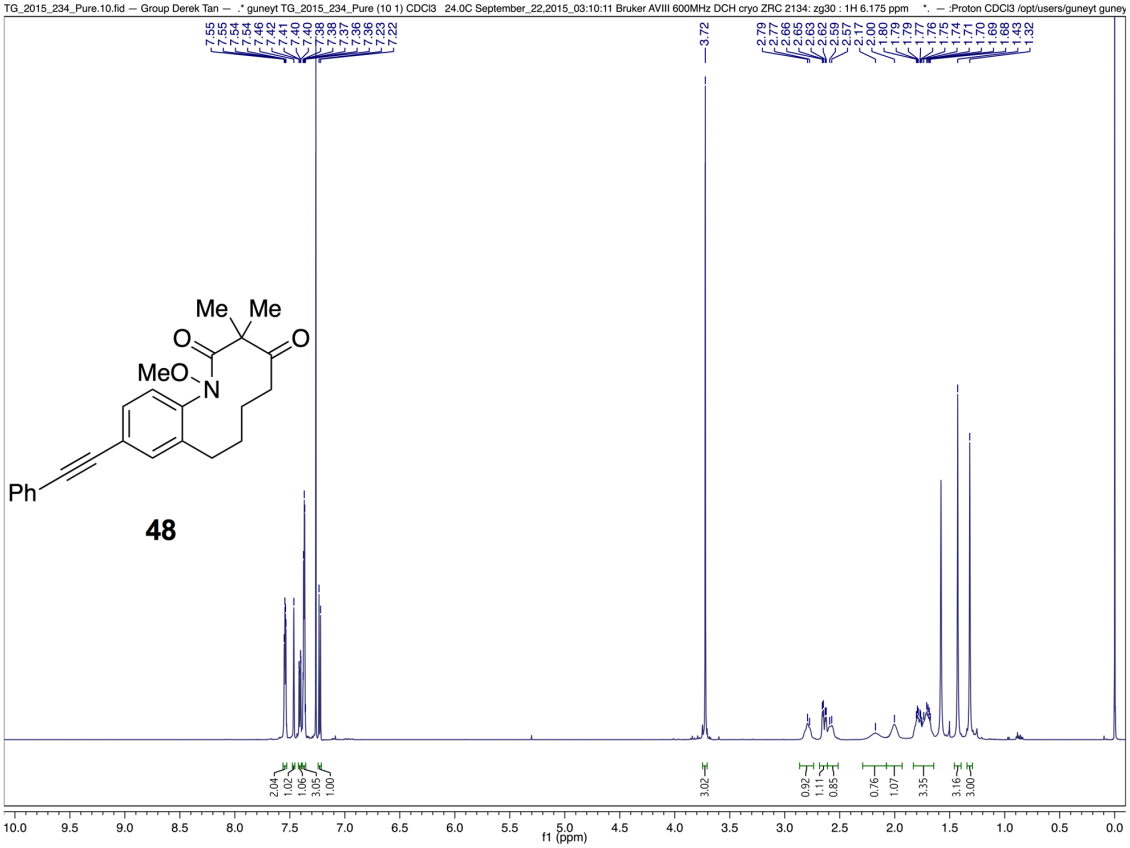

TW-2014-126a-13C-long.11.fid — Group Tan — .* wenderst TW-2014-126a-13C-long (11 1) CDCl3 24.0C June_24,2014_14:30:15 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /op
MeO
N
O
O
N
Ts
39
f1 (ppm)

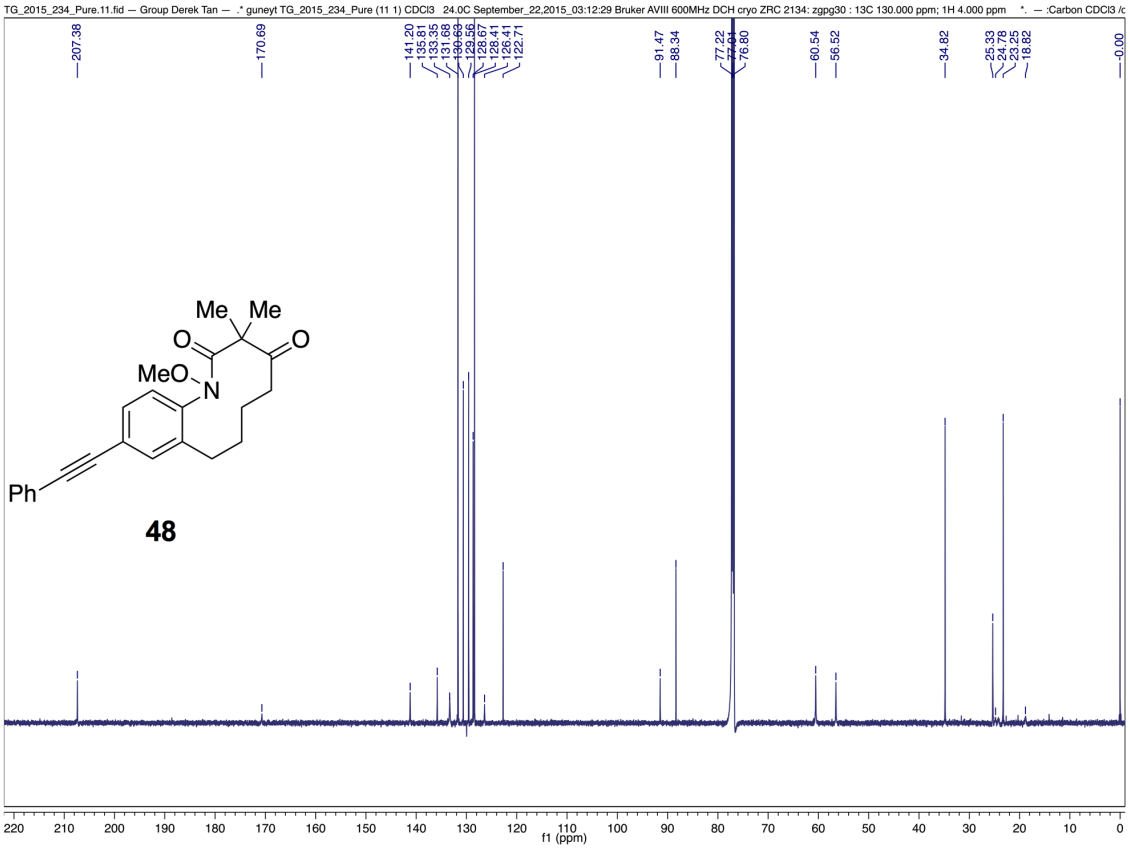

TW-2014-127a-13C.10.fid — Group Tan — .* wenderst TW-2014-127a-13C (10 1) CDCl3 24.0C June_24,2014_20:25:22 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/wenderst wenderst 40
OMe
N
O
O
N
Ts
41
f1 (ppm)

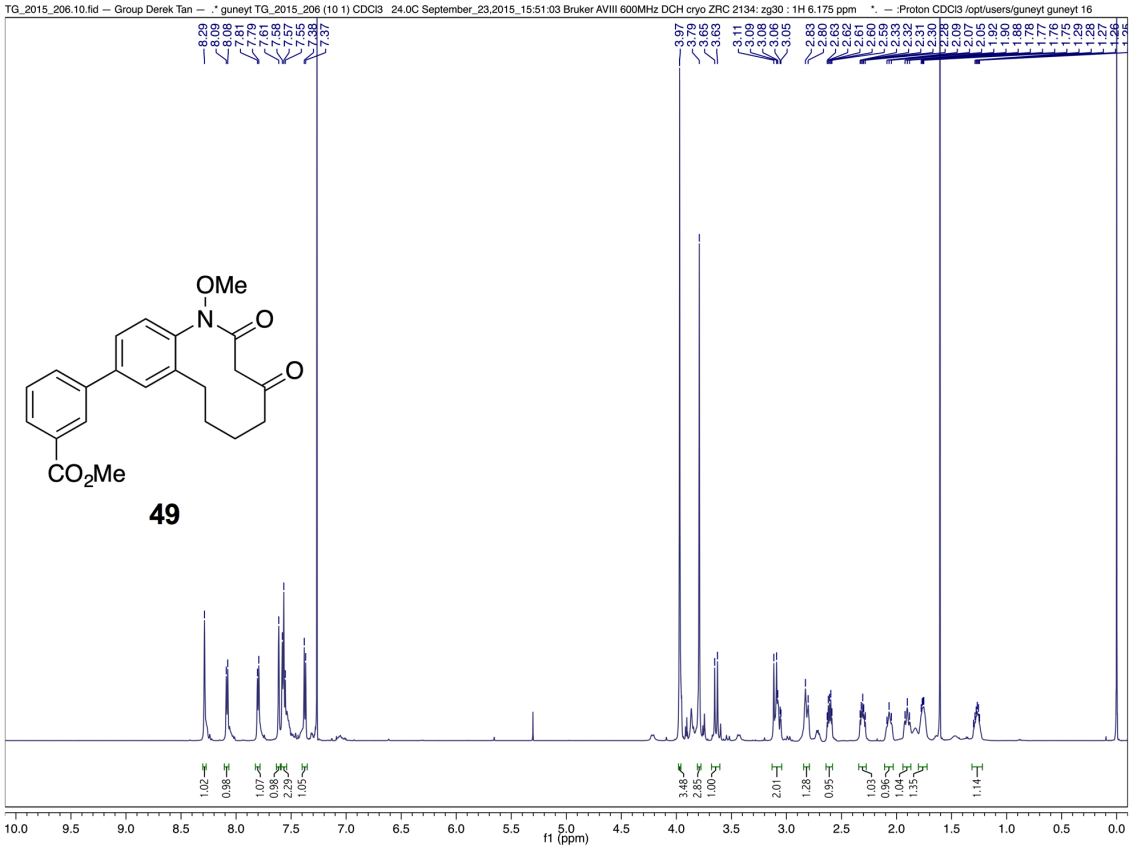

TW-2014-127a-13C.11.fid — Group Tan — .* wenderst TW-2014-127a-13C (11 1) CDCl3 24.0C June_24,2014_20:27:04 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/we
OMe
N
O
O
N
Ts
41
f1 (ppm)

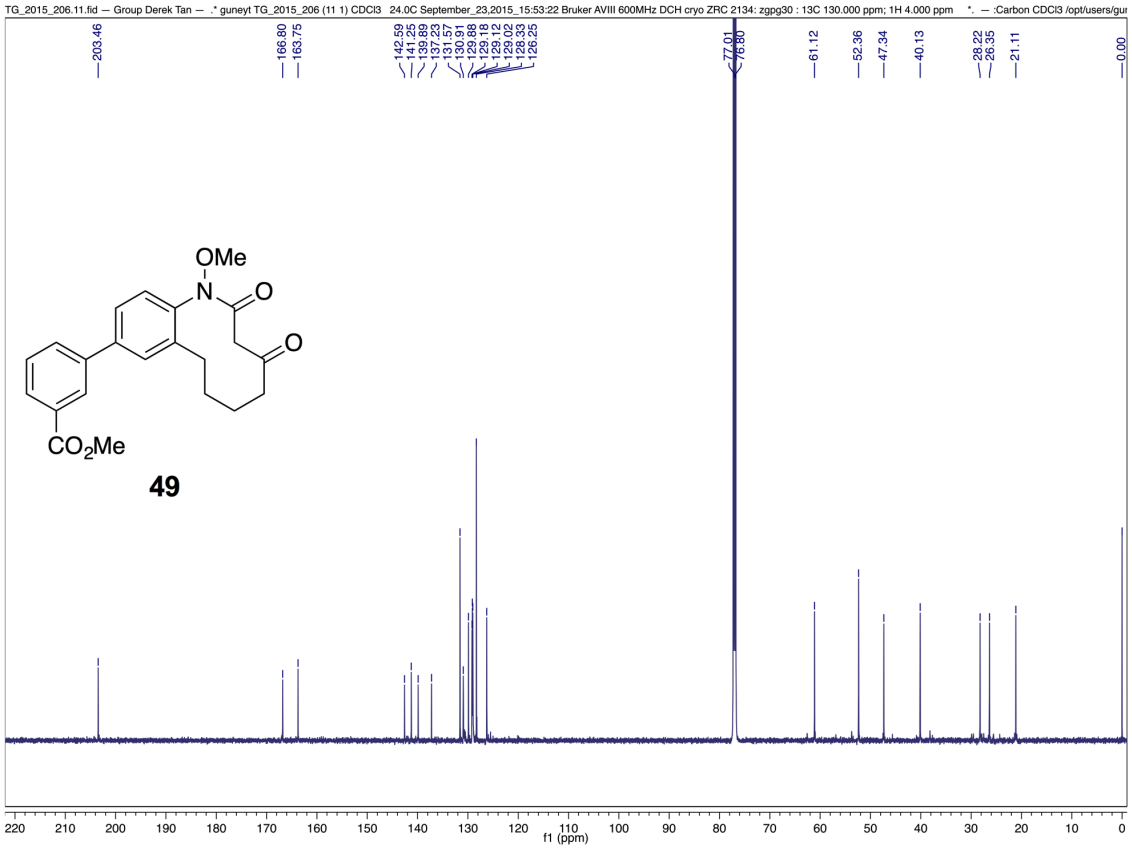

TG_2015_226_F1.10.fid — Group Derek Tan — .* guneyt TG_2015_226_F1 (10 1) CDCl3 24.0C July_21,2015_14:39:02 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 57
Me Me
O
O
MeO
N
Br
47
f1 (ppm)

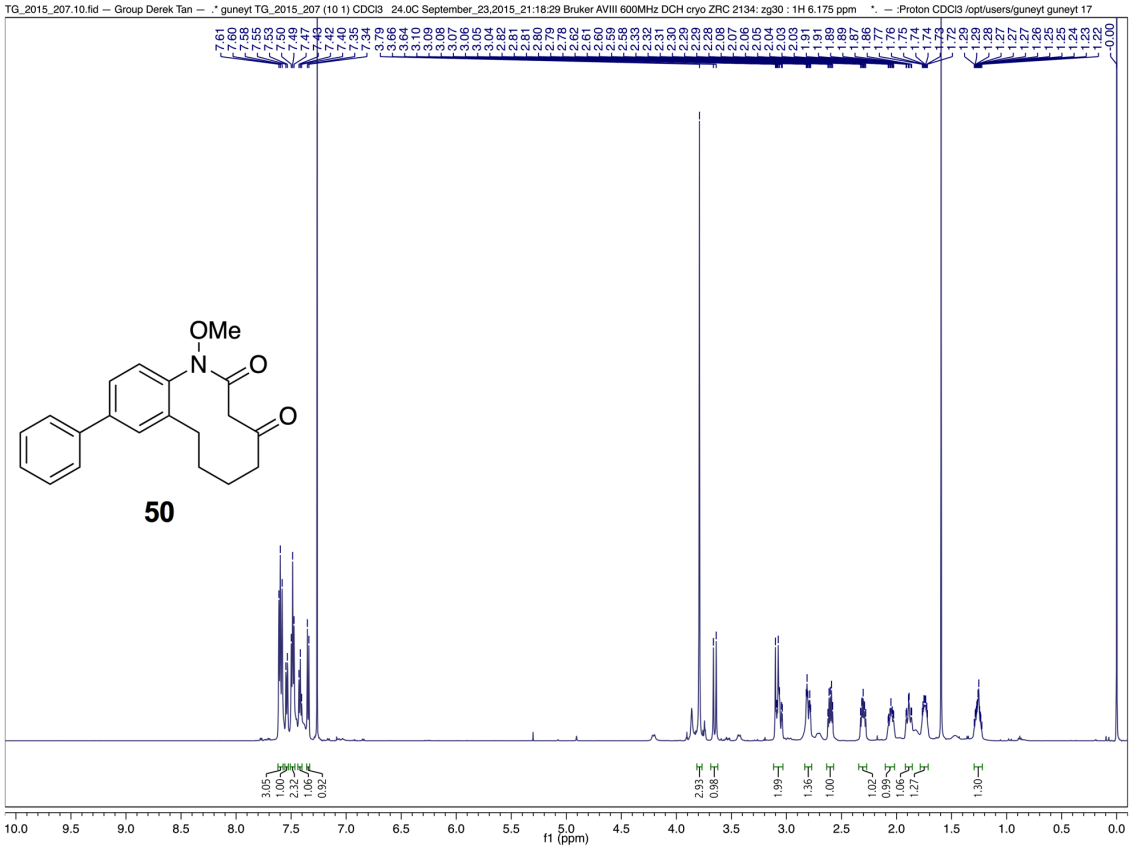

TG_2015_226_F1.11.fid — Group Derek Tan — .* guneyt TG_2015_226_F1 (11 1) CDCl3 24.0C July_21,2015_14:41:21 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/gu
Me Me
O
O
MeO
N
Br
47
f1 (ppm)

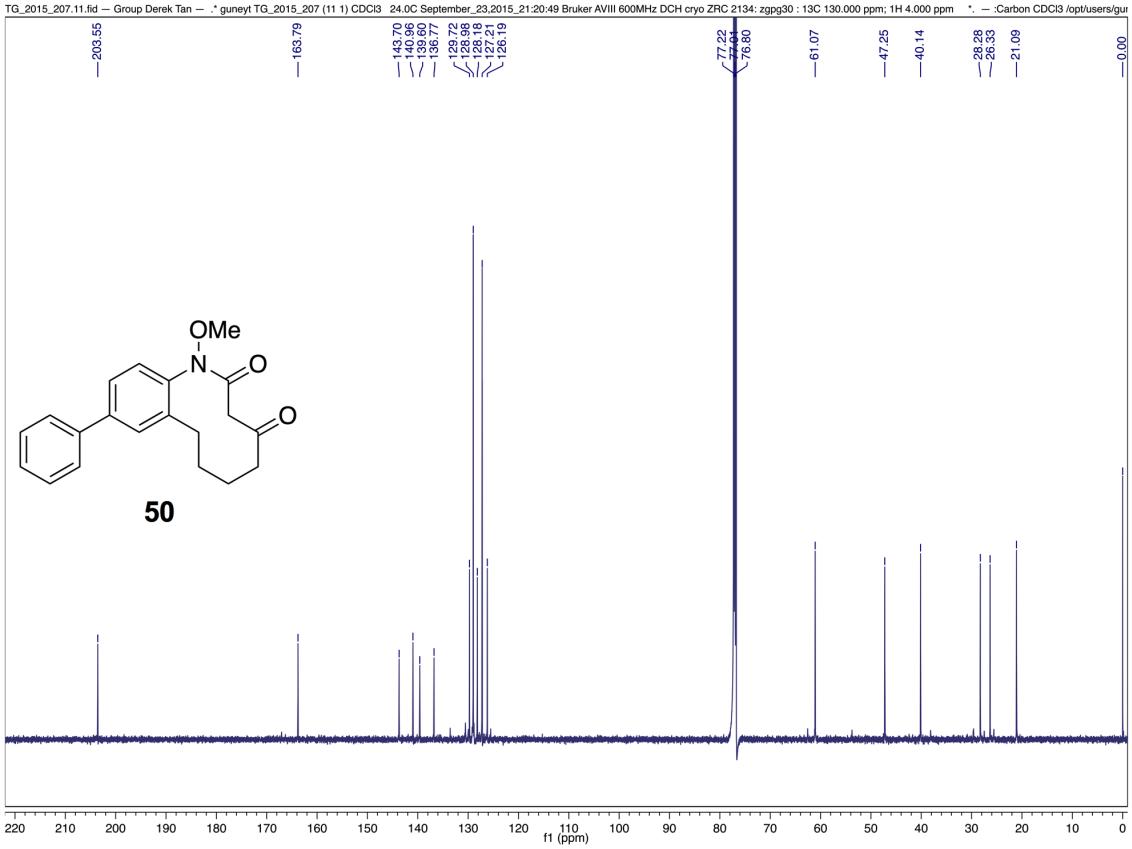

TG_2015_234_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_234_Pure (10 1) CDCl3 24.0C September_22,2015_03:10:11 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
Me Me
O
O
MeO
N
Ph
48
f1 (ppm)

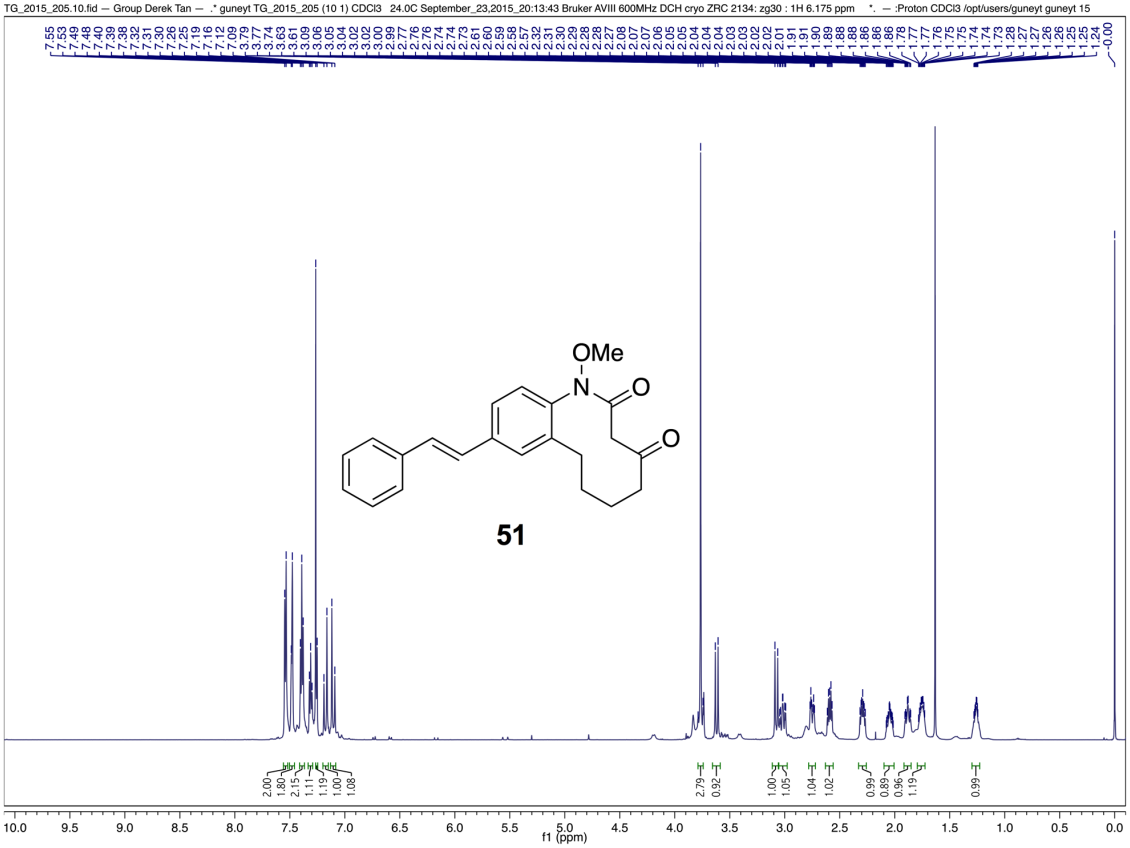

TG_2015_234_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_234_Pure (11 1) CDCl3 24.0C September_22,2015_03:12:29 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm
Me Me
O
O
MeO
N
Ph
48
f1 (ppm)

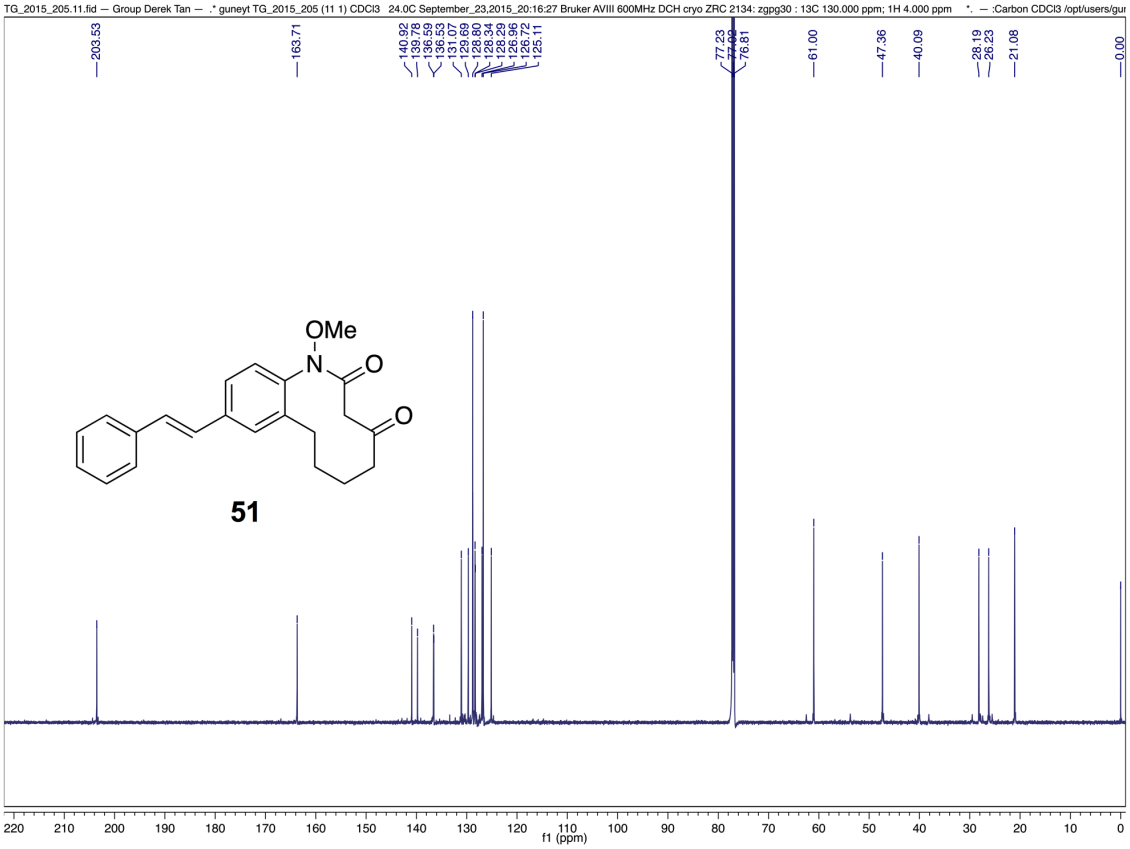

TG_2015_206.10.fid — Group Derek Tan — .* guneyt TG_2015_206 (10 1) CDCl3 24.0C September_23,2015_15:51:03 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm :Proton CDCl3 /opt/users/guneyt guneyt 16
OMe
N
O
O
O
CO2Me
49
f1 (ppm)

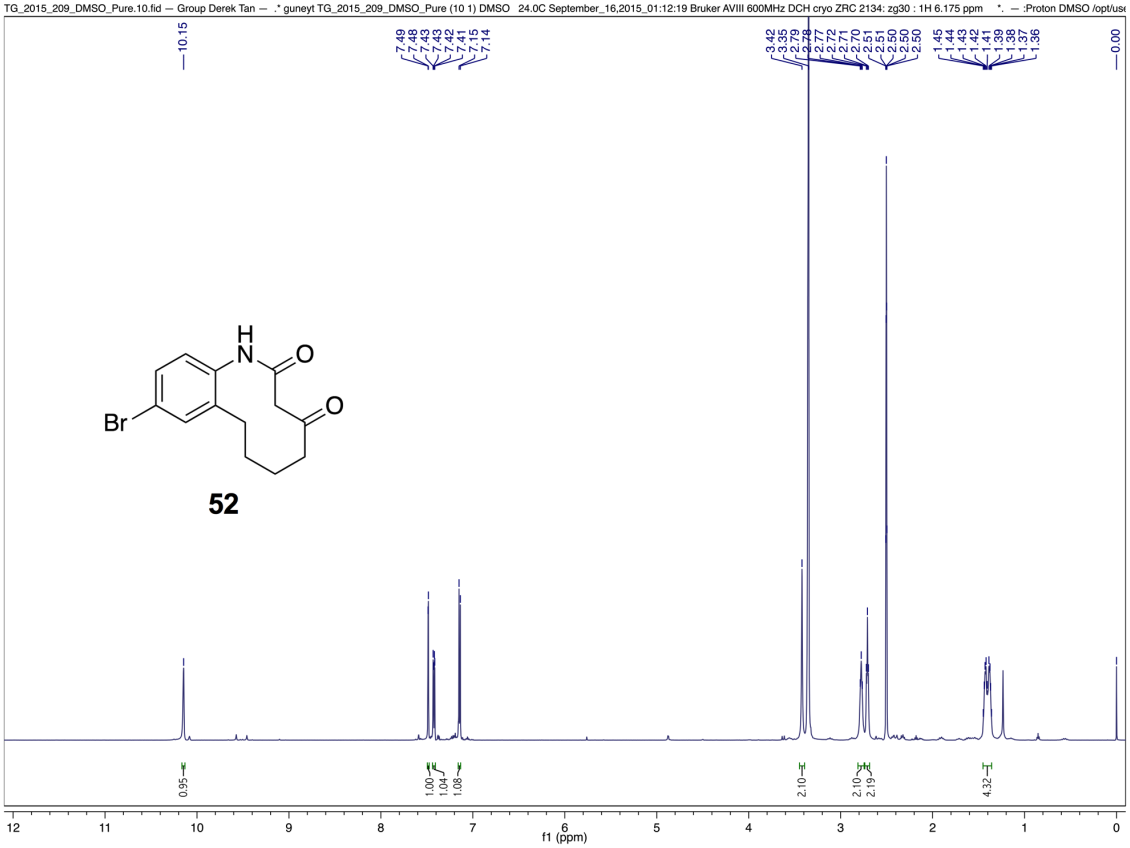

TG_2015_206.11.fid — Group Derek Tan — .* guneyt TG_2015_206 (11 1) CDCl3 24.0C September_23,2015_15:53:22 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm :Carbon CDCl3 /opt/users/gu
OMe
N
O
O
O
CO2Me
49
f1 (ppm)

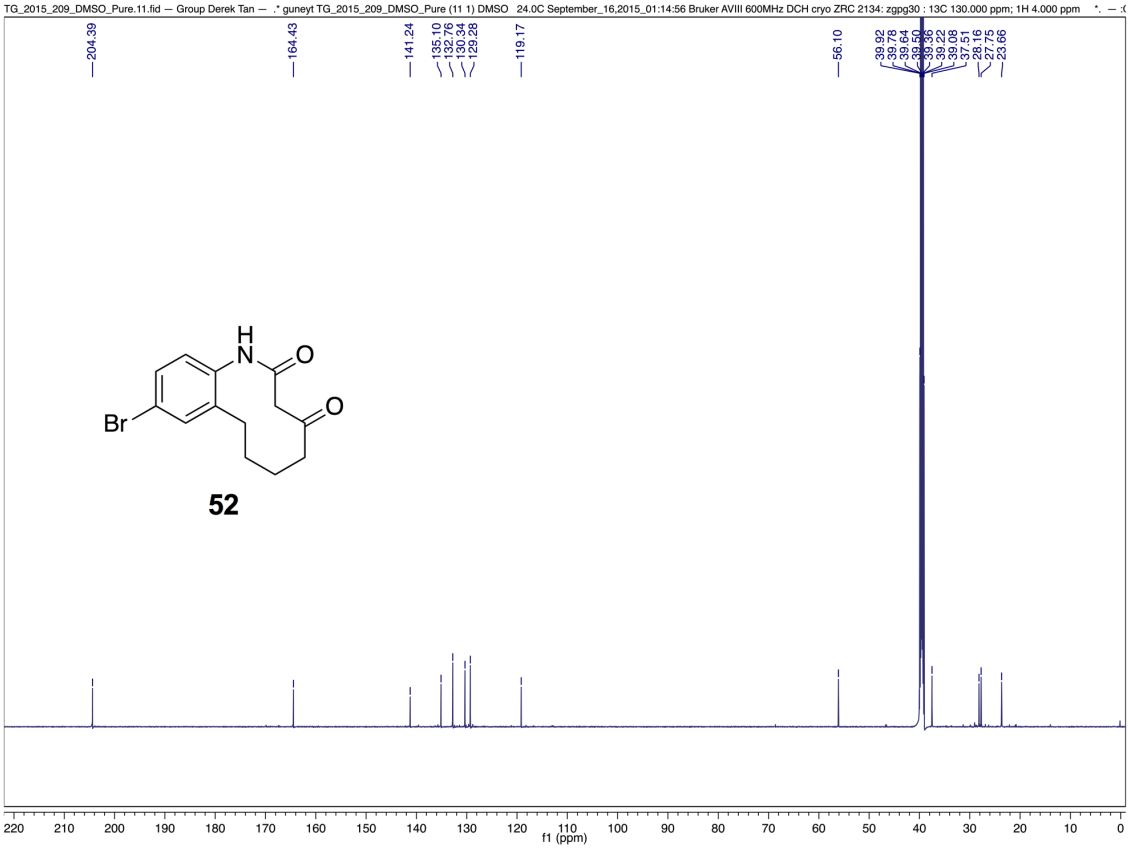

TG_2015_207.10.fid — Group Derek Tan — .* guneyt TG_2015_207 (10 1) CDCl3 24.0C September_23,2015_21:18:29 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 17
OMe
N
O
O
50
f1 (ppm)

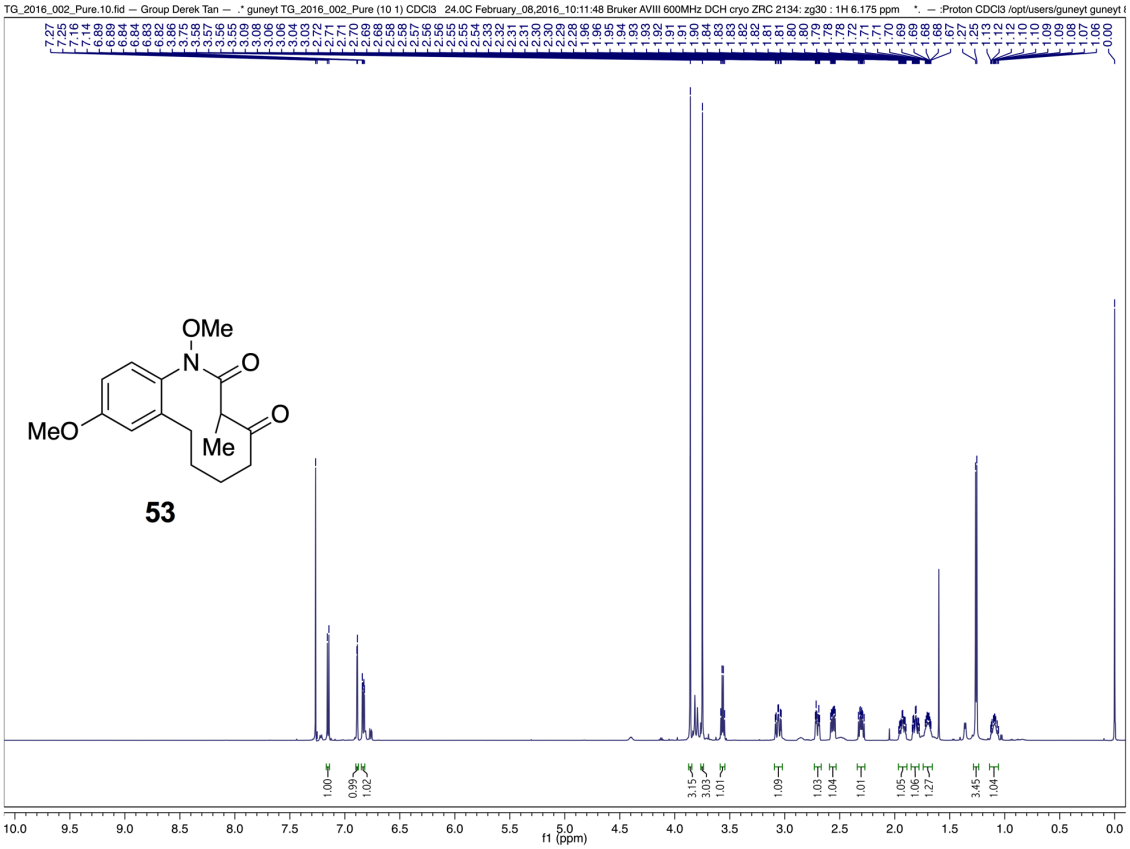

TG_2015_207.11.fid — Group Derek Tan — .* guneyt TG_2015_207 (11 1) CDCl3 24.0C September_23,2015_21:20:49 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/gur
OMe
N
O
O
50
f1 (ppm)

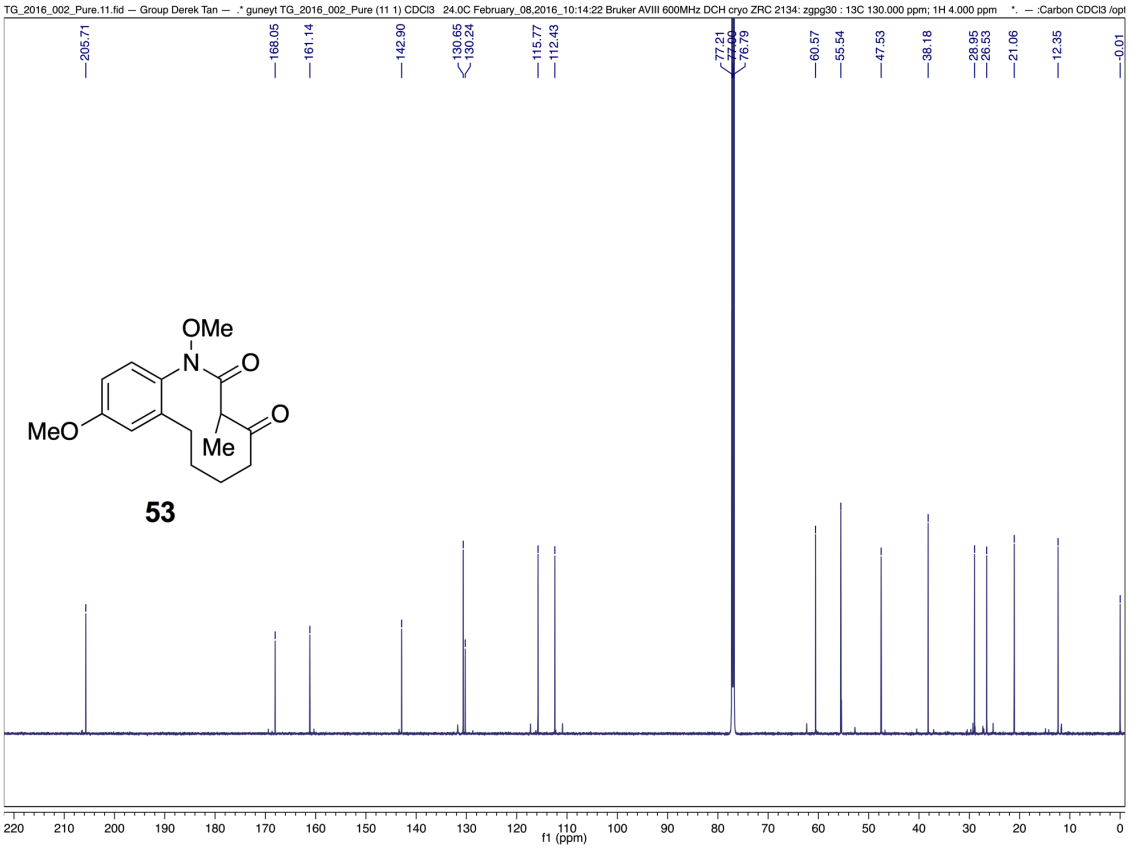

TG_2015_205.10.fid — Group Derek Tan — .* guneyt TG_2015_205 (10 1) CDCl3 24.0C September_23,2015_20:13:43 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 15
OMe
N
O
O
51
f1 (ppm)

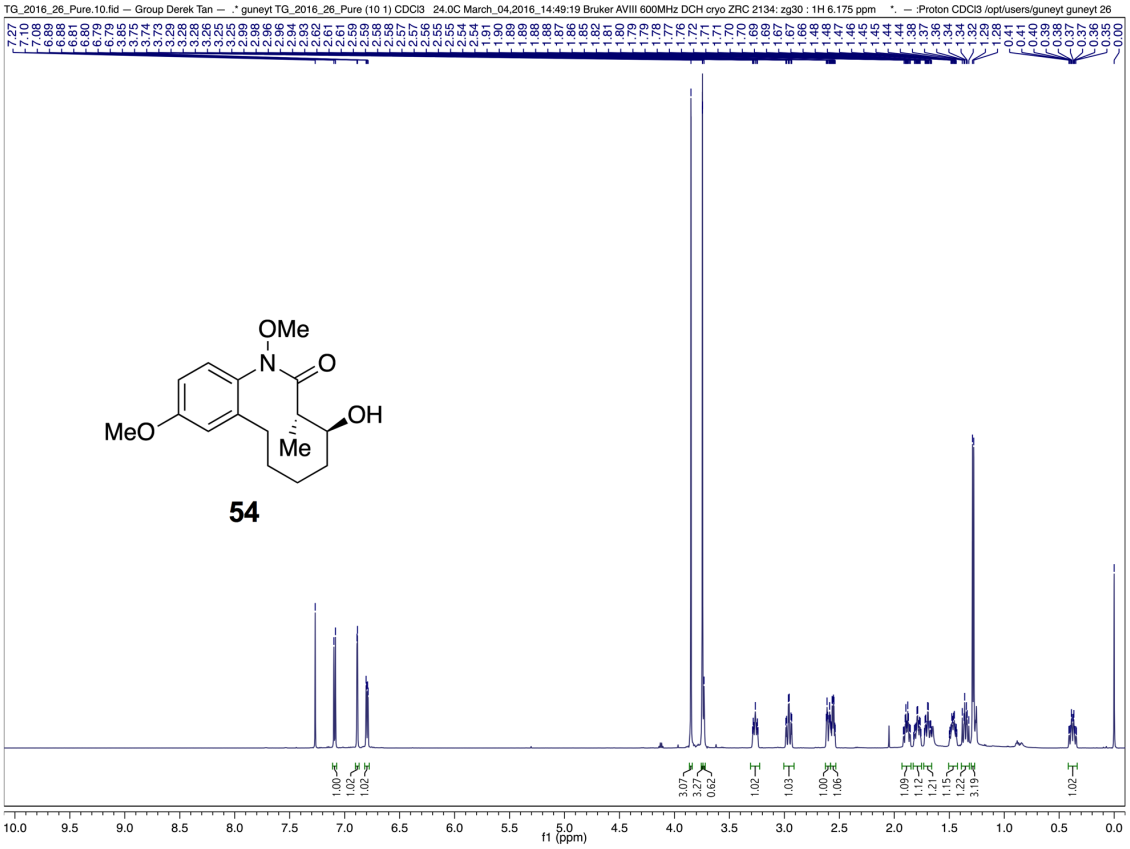

TG_2015_205.11.fid — Group Derek Tan — .* guneyt TG_2015_205 (11 1) CDCl3 24.0C September_23,2015_20:16:27 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/users/gu
OMe
N
O
O
51
f1 (ppm)

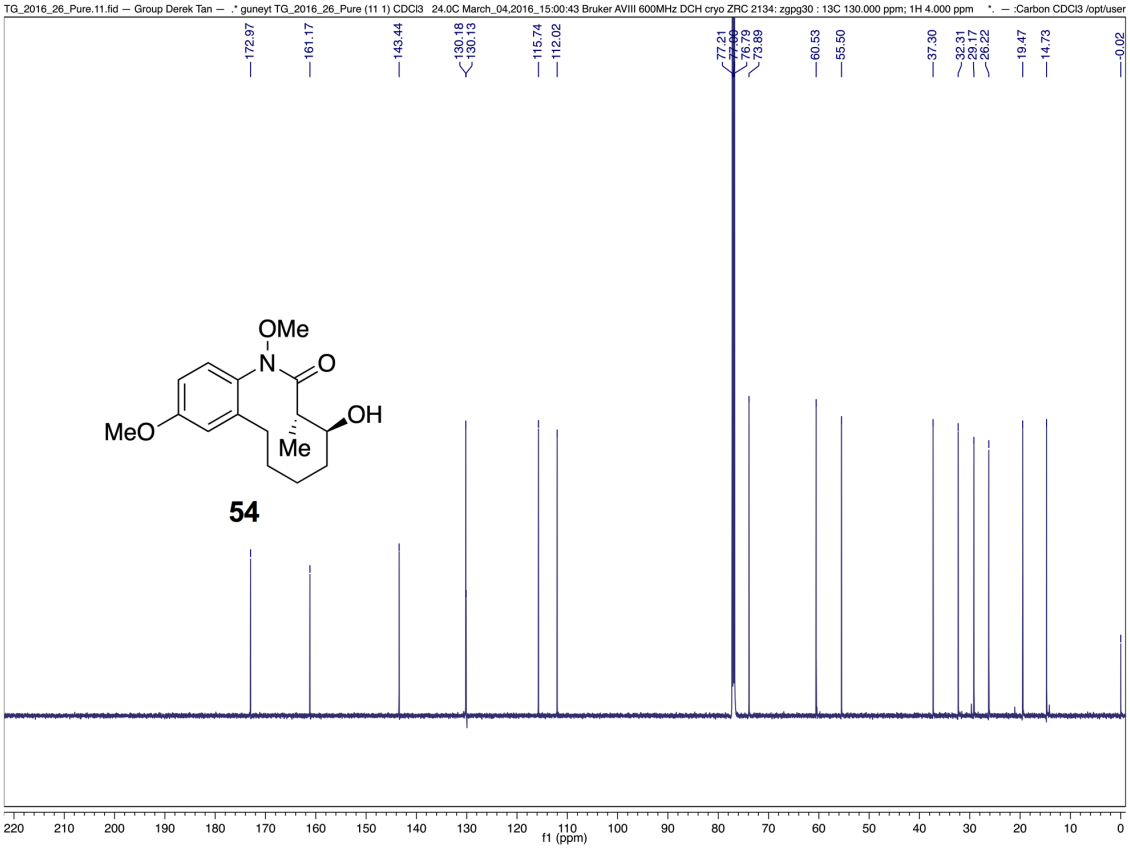

TG_2015_209_DMSO_Pure.10.fid — Group Derek Tan — .* guneyt TG_2015_209_DMSO_Pure (10 1) DMSO 24.0C September_16,2015_01:12:19 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
10.15
7.49
7.48
7.43
7.43
7.42
7.41
7.15
7.14
3.42
3.35
2.79
2.78
2.77
2.72
2.71
2.70
2.51
2.50
2.50
2.50
1.45
1.44
1.43
1.42
1.41
1.39
1.38
1.37
1.35
0.00
0.95
1.00
1.04
1.08
2.10
2.10
2.19
4.32
f1 (ppm)
52

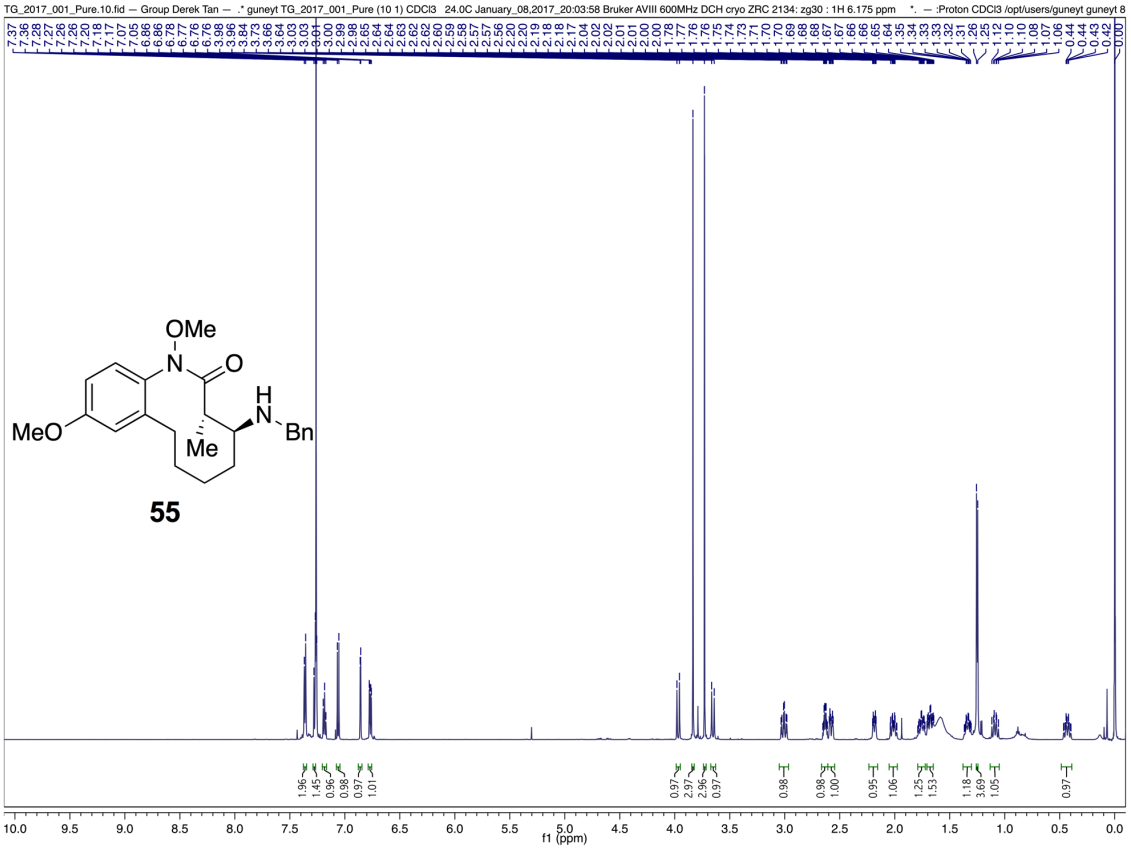

TG_2015_209_DMSO_Pure.11.fid — Group Derek Tan — .* guneyt TG_2015_209_DMSO_Pure (11 1) DMSO 24.0C September_16,2015_01:14:56 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 ; 13C 130.000 ppm; 1H 4.000 ppm
204.39
164.43
141.24
135.10
132.76
130.34
129.28
119.17
56.10
39.92
39.78
39.64
39.50
39.36
39.22
39.08
37.51
28.16
27.75
23.66
f1 (ppm)
52

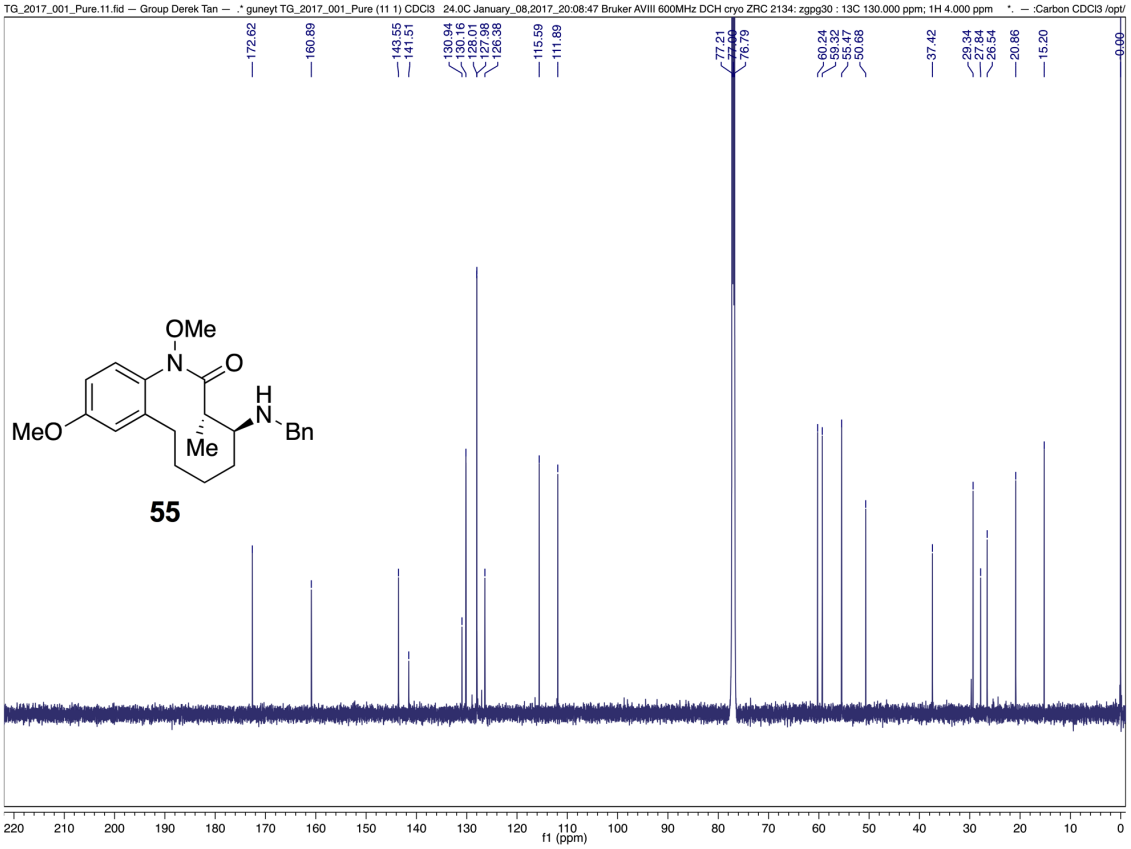

TG_2016_002_Pure.10.fid — Group Derek Tan — .* guneyt TG_2016_002_Pure (10 1) CDCl3 24.0C February_08,2016_10:11:48 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt
OMe
N
O
O
MeO
Me
53
f1 (ppm)

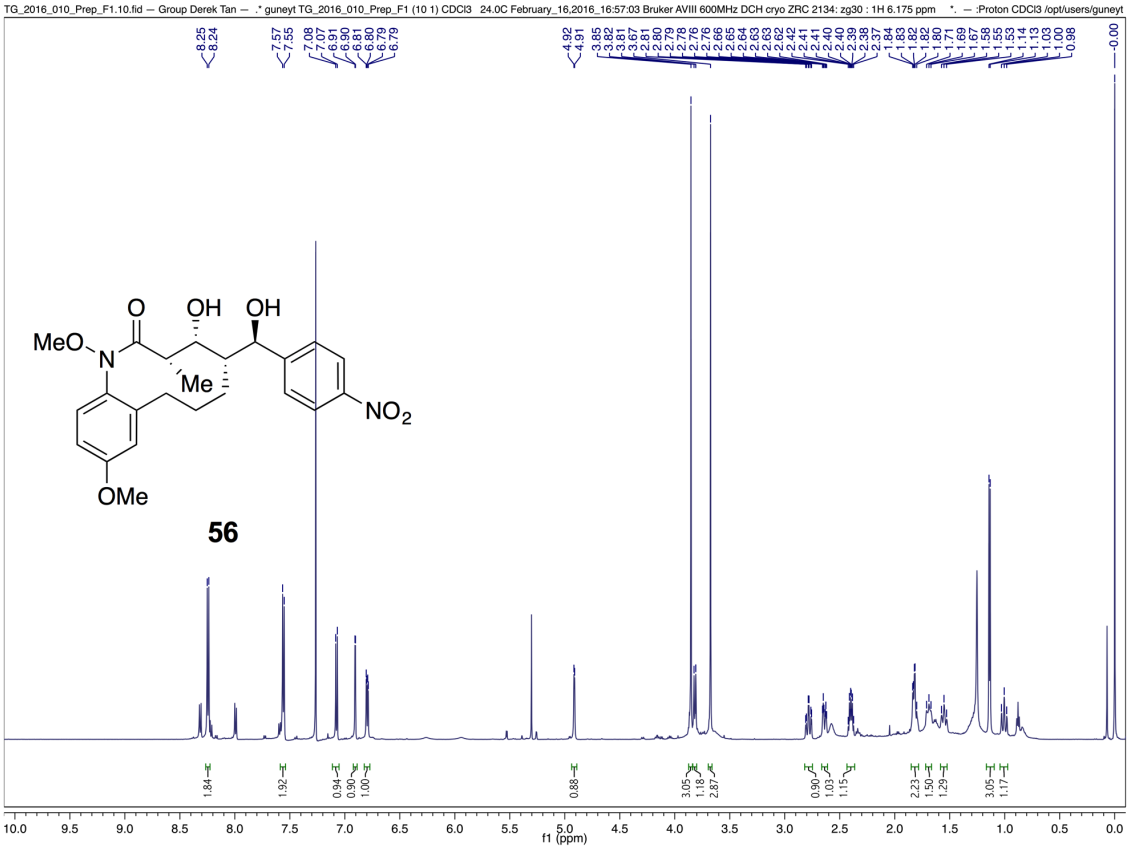

TG_2016_002_Pure.11.fid — Group Derek Tan — .* guneyt TG_2016_002_Pure (11 1) CDCl3 24.0C February_08,2016_10:14:22 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt
205.71
168.05
161.14
142.90
130.65
130.24
115.77
112.43
77.21
77.00
76.79
60.57
55.54
47.53
38.18
28.95
26.53
21.06
12.35
-0.01
OMe
N
O
O
MeO
Me
53
f1 (ppm)

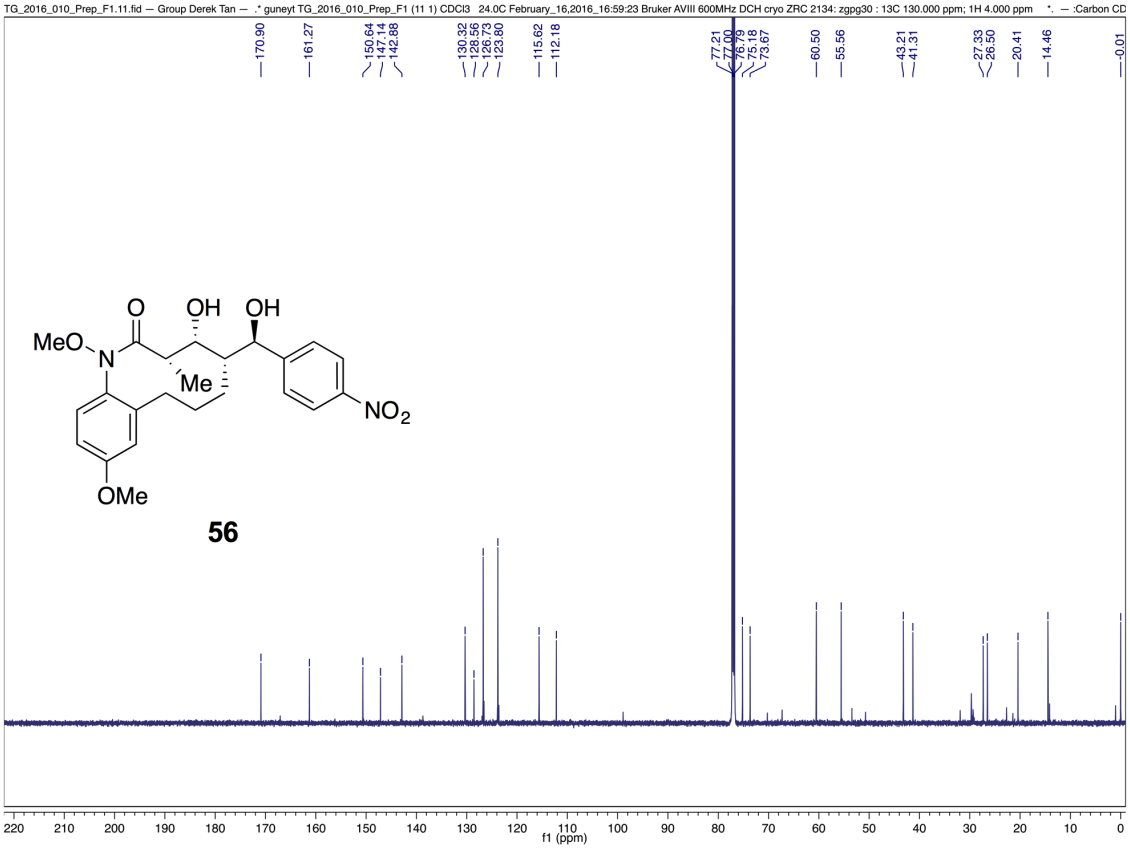

TG_2016_26_Pure.10.fid — Group Derek Tan — .* guneyt TG_2016_26_Pure (10 1) CDCl3 24.0C March_04,2016_14:49:19 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 26
OMe
N
O
MeO
OH
Me
54
f1 (ppm)

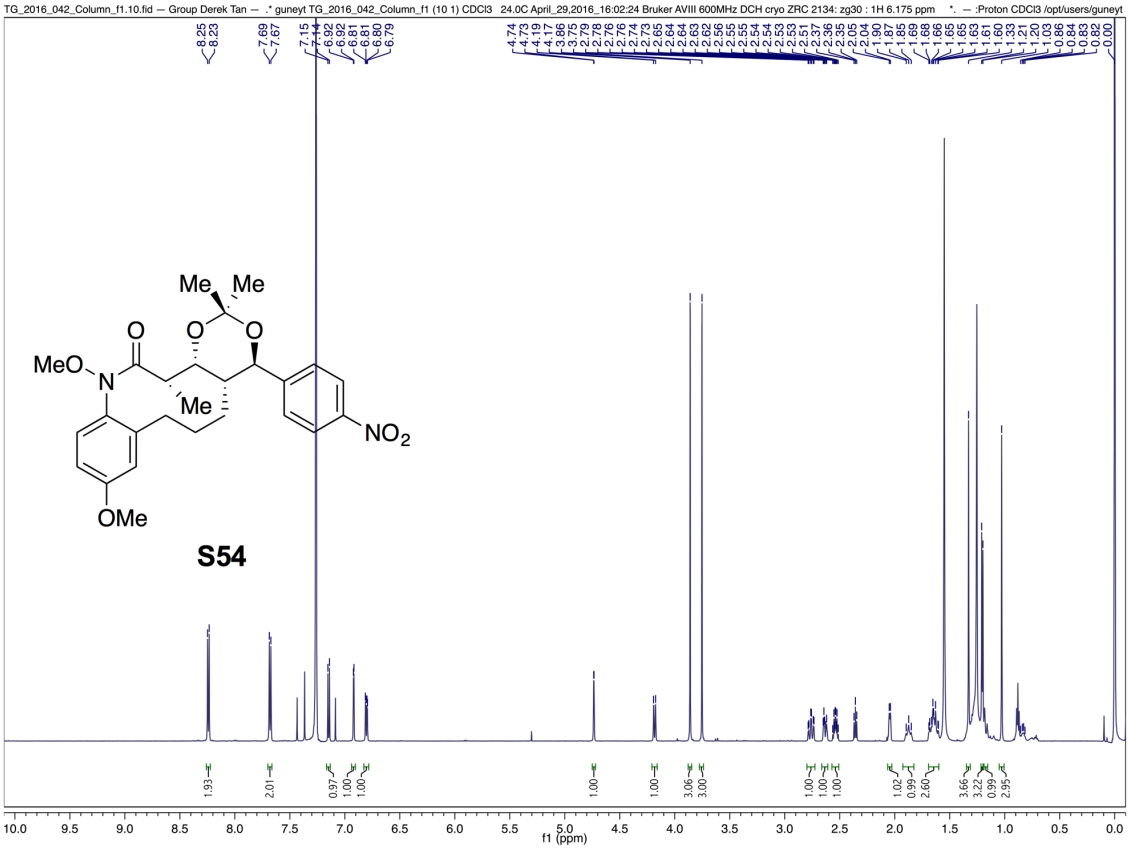

TG_2016_26_Pure.11.fid — Group Derek Tan — .* guneyt TG_2016_26_Pure (11 1) CDCl3 24.0C March_04,2016_15:00:43 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/user
172.97
161.17
143.44
130.18
130.13
115.74
112.02
77.21
77.00
76.79
73.89
60.53
55.50
37.30
32.31
29.17
26.22
19.47
14.73
-0.02
OMe
N
O
MeO
OH
Me
54
f1 (ppm)

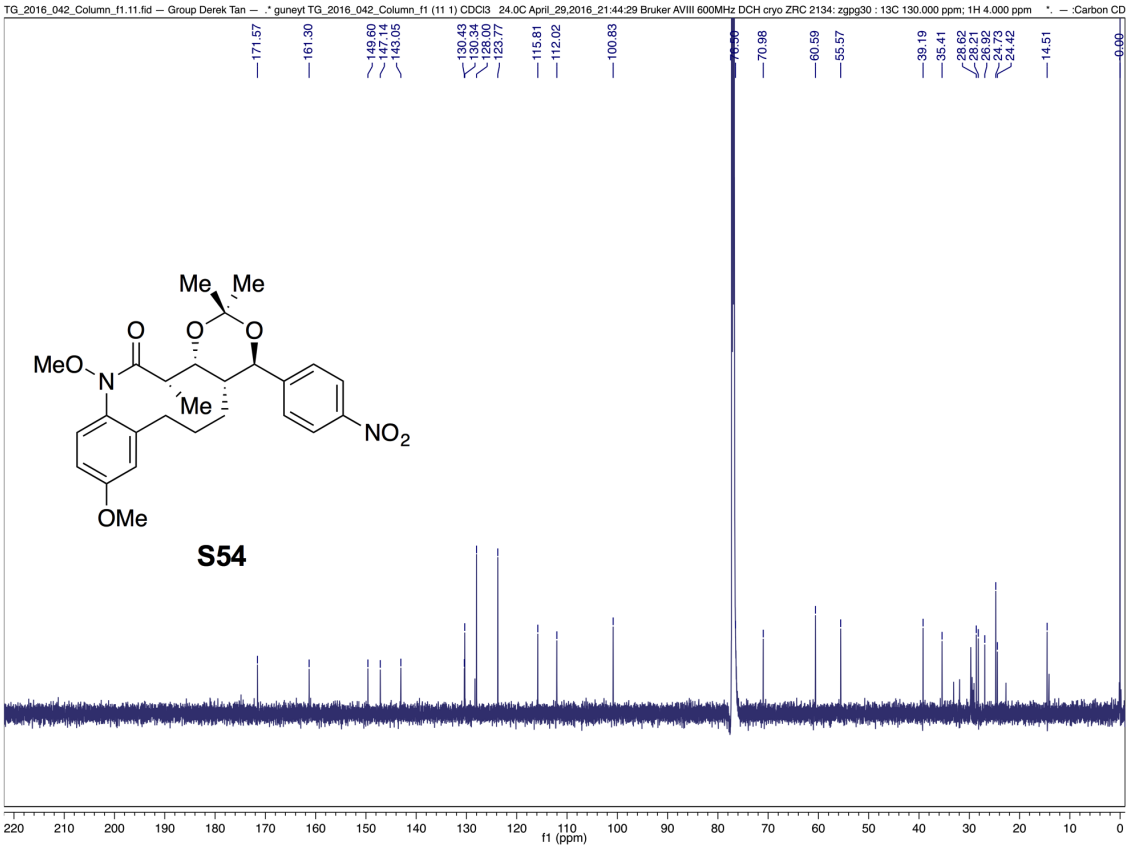

TG_2017_001_Pure.10.fid — Group Derek Tan — .* guneyt TG_2017_001_Pure (10 1) CDCl3 24.0C January_08,2017_20:03:58 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt guneyt 8
OMe
N
O
H
N
Bn
MeO
Me
55
f1 (ppm)


TG_2017_001_Pure.11.fid — Group Derek Tan — .* guneyt TG_2017_001_Pure (11 1) CDCl3 24.0C January_08,2017_20:08:47 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CDCl3 /opt/
OMe
N
O
H
N
Bn
MeO
Me
55
f1 (ppm)


TG_2016_010_Prep_F1.10.fid — Group Derek Tan — .* guneyt TG_2016_010_Prep_F1 (10 1) CDCl3 24.0C February_16,2016_16:57:03 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt
8.25
8.24
7.57
7.55
7.08
7.07
6.91
6.90
6.81
6.80
6.79
6.79
4.92
4.91
3.85
3.82
3.81
3.67
2.81
2.79
2.78
2.76
2.66
2.65
2.64
2.63
2.62
2.42
2.41
2.40
2.39
2.38
2.37
1.84
1.83
1.82
1.82
1.81
1.71
1.69
1.67
1.58
1.55
1.53
1.14
1.13
1.03
1.00
0.98
-0.00
O
OH
OH
MeO
N
Me
NO2
OMe
56
1.84
1.92
0.94
0.90
1.00
0.88
3.05
1.18
2.87
0.90
1.03
1.15
2.23
1.50
1.29
3.05
1.17
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)


TG_2016_010_Prep_F1.11.fid — Group Derek Tan — .* guneyt TG_2016_010_Prep_F1 (11 1) CDCl3 24.0C February_16,2016_16:59:23 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CD
170.90
161.27
150.64
147.14
142.88
130.32
128.56
126.73
123.80
115.62
112.18
77.21
77.00
76.79
75.18
73.67
60.50
55.56
43.21
41.31
27.33
26.50
20.41
14.46
-0.01
O
OH
OH
MeO
N
Me
NO2
OMe
56
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TG_2016_042_Column_f1.10.fid — Group Derek Tan — .* guneyt TG_2016_042_Column_f1 (10 1) CDCl3 24.0C April_29,2016_16:02:24 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *. — :Proton CDCl3 /opt/users/guneyt
Me
Me
O
O
O
MeO
N
Me
NO2
OMe
S54
f1 (ppm)


TG_2016_042_Column_f1.11.fid — Group Derek Tan — .* guneyt TG_2016_042_Column_f1 (11 1) CDCl3 24.0C April_29,2016_21:44:29 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *. — :Carbon CD
Me
Me
O
O
O
MeO
N
Me
NO2
OMe
S54
f1 (ppm)