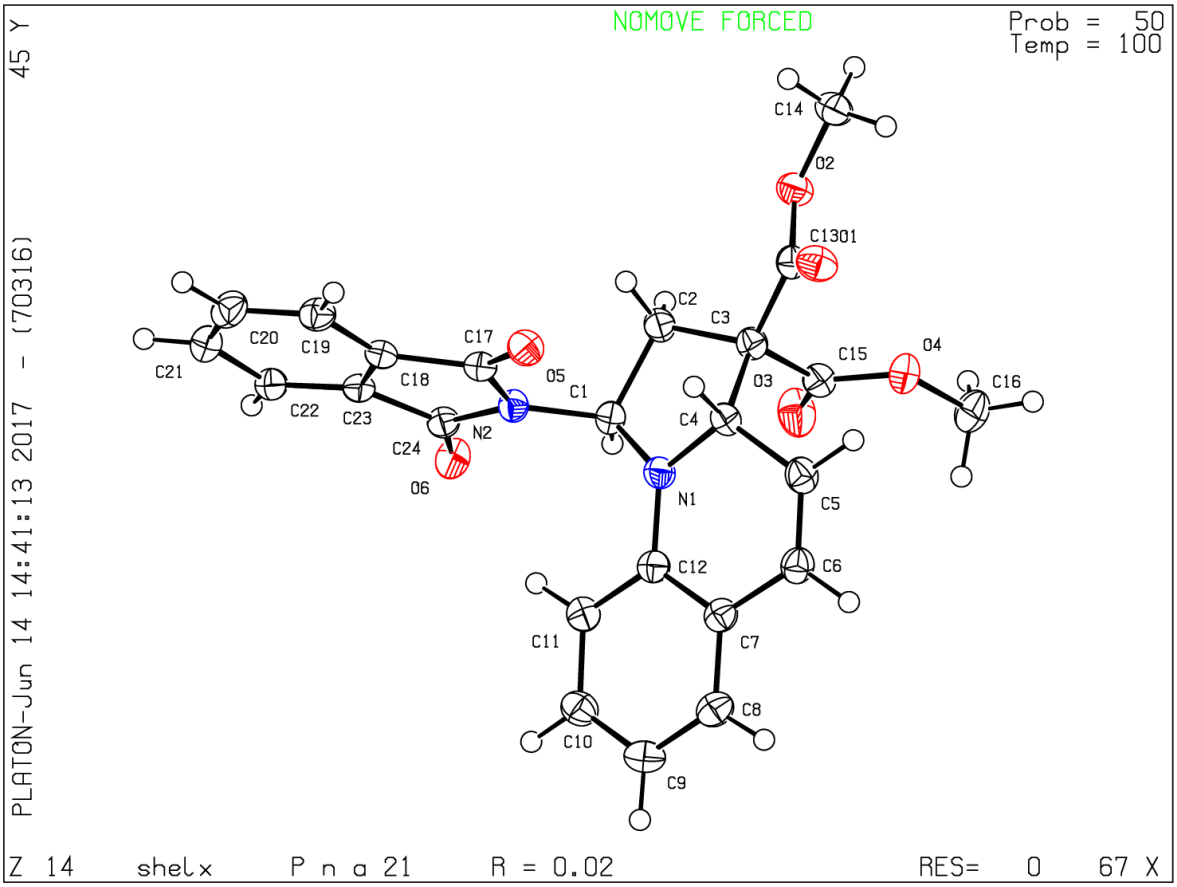
Content

1. X-ray diffraction analysis of compound 17



CCDC deposition number: 1556244

Table S1. Crystal data and structure refinement for compound **17**

Empirical formula	$C_{24}H_{20}N_2O_6$	
Formula weight	432.42	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	*Pna*2$_1$	
Unit cell dimensions	a = 28.9068(4) Å	α= 90°.
	b = 7.90250(10) Å	β= 90°.
	c = 8.98890(10) Å	γ = 90°.
Volume	2053.39(4) Å^3	
Z	4	
Density (calculated)	1.399 Mg/m^3	
Absorption coefficient	0.846 mm^{-1}	
F(000)	904	
Crystal size	0.509 x 0.409 x 0.265 mm^3	
Theta range for data collection	5.797 to 75.495°.	
Index ranges	$-36 \le h \le 36$, $-9 \le k \le 9$, $-11 \le l \le 11$	
Reflections collected	35518	
Independent reflections	4206 [R_{int} = 0.0326]	
Completeness to θ = 67.684°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.850 and 0.723	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4206 / 1 / 348	
Goodness-of-fit on F^2	1.059	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0236, wR_2 = 0.0639	
R indices (all data)	R_1 = 0.0243, wR_2 = 0.0645	
Absolute structure parameter	0.01(5)	
Extinction coefficient	0.0012(2)	
Largest diff. peak and hole	0.186 and -0.133 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **17**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	7071(1)	7430(2)	8003(1)	31(1)
O(2)	6456(1)	9031(2)	8589(1)	28(1)
O(3)	6155(1)	9739(2)	4455(2)	40(1)
O(4)	6861(1)	10163(1)	5425(2)	28(1)
O(5)	6107(1)	3180(2)	6928(1)	28(1)
O(6)	4927(1)	5102(2)	3972(1)	29(1)
N(1)	6306(1)	5697(2)	4369(2)	24(1)
N(2)	5585(1)	4517(2)	5362(2)	22(1)
C(1)	5855(1)	6043(2)	4984(2)	23(1)
C(2)	5951(1)	7102(2)	6398(2)	25(1)
C(3)	6453(1)	7729(2)	6229(2)	23(1)
C(4)	6677(1)	6213(2)	5381(2)	23(1)
C(5)	7124(1)	6551(2)	4597(2)	27(1)
C(6)	7193(1)	6080(2)	3193(2)	27(1)
C(7)	6828(1)	5288(2)	2309(2)	25(1)
C(8)	6908(1)	4733(2)	862(2)	29(1)
C(9)	6554(1)	4069(2)	-1(2)	31(1)
C(10)	6111(1)	3976(2)	596(2)	29(1)
C(11)	6021(1)	4511(2)	2044(2)	25(1)
C(12)	6379(1)	5161(2)	2917(2)	22(1)
C(13)	6702(1)	8019(2)	7697(2)	24(1)
C(14)	6674(1)	9411(2)	10007(2)	32(1)
C(15)	6464(1)	9325(2)	5267(2)	25(1)
C(16)	6908(1)	11653(2)	4490(2)	33(1)
C(17)	5726(1)	3275(2)	6378(2)	23(1)
C(18)	5320(1)	2151(2)	6596(2)	22(1)
C(19)	5265(1)	788(2)	7539(2)	27(1)
C(20)	4835(1)	7(2)	7551(2)	31(1)
C(21)	4476(1)	569(2)	6646(2)	29(1)
C(22)	4533(1)	1950(2)	5694(2)	25(1)
C(23)	4962(1)	2725(2)	5701(2)	21(1)
C(24)	5128(1)	4247(2)	4884(2)	23(1)

Table S3. Bond lengths [Å] and angles [°] for compound **17**. (Symmetry transform. used to gen. equiv. atoms)

O(1)-C(13)	1.195(2)	C(11)-H(11)	0.99(2)
O(2)-C(13)	1.339(2)	C(14)-H(14A)	0.9800
O(2)-C(14)	1.454(2)	C(14)-H(14B)	0.9800
O(3)-C(15)	1.199(2)	C(14)-H(14C)	0.9800
O(4)-C(15)	1.332(2)	C(16)-H(16A)	0.9800
O(4)-C(16)	1.453(2)	C(16)-H(16B)	0.9800
O(5)-C(17)	1.209(2)	C(16)-H(16C)	0.9800
O(6)-C(24)	1.211(2)	C(17)-C(18)	1.485(2)
N(1)-C(12)	1.389(2)	C(18)-C(19)	1.380(2)
N(1)-C(1)	1.442(2)	C(18)-C(23)	1.387(2)
N(1)-C(4)	1.464(2)	C(19)-C(20)	1.388(3)
N(2)-C(17)	1.401(2)	C(19)-H(19)	0.93(3)
N(2)-C(24)	1.405(2)	C(20)-C(21)	1.392(3)
N(2)-C(1)	1.476(2)	C(20)-H(20)	0.96(2)
C(1)-C(2)	1.547(2)	C(21)-C(22)	1.397(2)
C(1)-H(1)	0.94(2)	C(21)-H(21)	0.97(3)
C(2)-C(3)	1.542(2)	C(22)-C(23)	1.383(2)
C(2)-H(2A)	0.99(2)	C(22)-H(22)	1.03(2)
C(2)-H(2B)	0.98(2)	C(23)-C(24)	1.488(2)
C(3)-C(13)	1.520(2)	C(13)-O(2)-C(14)	114.64(13)
C(3)-C(15)	1.529(2)	C(15)-O(4)-C(16)	114.95(14)
C(3)-C(4)	1.561(2)	C(12)-N(1)-C(1)	123.82(14)
C(4)-C(5)	1.496(2)	C(12)-N(1)-C(4)	123.84(13)
C(4)-H(4)	1.02(2)	C(1)-N(1)-C(4)	111.78(13)
C(5)-C(6)	1.331(3)	C(17)-N(2)-C(24)	111.51(13)
C(5)-H(5)	1.00(2)	C(17)-N(2)-C(1)	124.65(13)
C(6)-C(7)	1.462(2)	C(24)-N(2)-C(1)	123.39(13)
C(6)-H(6)	1.00(2)	N(1)-C(1)-N(2)	114.27(13)
C(7)-C(8)	1.392(2)	N(1)-C(1)-C(2)	104.79(13)
C(7)-C(12)	1.411(2)	N(2)-C(1)-C(2)	110.32(13)
C(8)-C(9)	1.387(3)	N(1)-C(1)-H(1)	111.0(13)
C(8)-H(8)	0.98(2)	N(2)-C(1)-H(1)	106.2(12)
C(9)-C(10)	1.391(3)	C(2)-C(1)-H(1)	110.3(12)
C(9)-H(9)	0.94(3)	C(3)-C(2)-C(1)	105.19(13)
C(10)-C(11)	1.393(3)	C(3)-C(2)-H(2A)	113.3(13)
C(10)-H(10)	0.97(2)	C(1)-C(2)-H(2A)	109.5(14)
C(11)-C(12)	1.396(2)	C(3)-C(2)-H(2B)	108.8(13)

C(1)-C(2)-H(2B)	110.4(13)	O(1)-C(13)-O(2)	124.76(16)
H(2A)-C(2)-H(2B)	109.5(19)	O(1)-C(13)-C(3)	124.32(15)
C(13)-C(3)-C(15)	110.88(13)	O(2)-C(13)-C(3)	110.92(13)
C(13)-C(3)-C(2)	114.18(14)	O(2)-C(14)-H(14A)	109.5
C(15)-C(3)-C(2)	109.91(13)	O(2)-C(14)-H(14B)	109.5
C(13)-C(3)-C(4)	110.10(13)	H(14A)-C(14)-H(14B)	109.5
C(15)-C(3)-C(4)	110.35(13)	O(2)-C(14)-H(14C)	109.5
C(2)-C(3)-C(4)	101.01(12)	H(14A)-C(14)-H(14C)	109.5
N(1)-C(4)-C(5)	112.95(14)	H(14B)-C(14)-H(14C)	109.5
N(1)-C(4)-C(3)	102.39(12)	O(3)-C(15)-O(4)	124.76(17)
C(5)-C(4)-C(3)	116.76(13)	O(3)-C(15)-C(3)	123.63(15)
N(1)-C(4)-H(4)	109.5(11)	O(4)-C(15)-C(3)	111.60(14)
C(5)-C(4)-H(4)	109.1(11)	O(4)-C(16)-H(16A)	109.5
C(3)-C(4)-H(4)	105.7(12)	O(4)-C(16)-H(16B)	109.5
C(6)-C(5)-C(4)	121.74(16)	H(16A)-C(16)-H(16B)	109.5
C(6)-C(5)-H(5)	123.3(12)	O(4)-C(16)-H(16C)	109.5
C(4)-C(5)-H(5)	114.9(12)	H(16A)-C(16)-H(16C)	109.5
C(5)-C(6)-C(7)	121.79(16)	H(16B)-C(16)-H(16C)	109.5
C(5)-C(6)-H(6)	120.4(12)	O(5)-C(17)-N(2)	125.13(15)
C(7)-C(6)-H(6)	117.7(12)	O(5)-C(17)-C(18)	128.90(15)
C(8)-C(7)-C(12)	119.47(15)	N(2)-C(17)-C(18)	105.97(13)
C(8)-C(7)-C(6)	121.55(15)	C(19)-C(18)-C(23)	121.71(15)
C(12)-C(7)-C(6)	118.91(15)	C(19)-C(18)-C(17)	129.77(15)
C(9)-C(8)-C(7)	121.31(17)	C(23)-C(18)-C(17)	108.46(14)
C(9)-C(8)-H(8)	122.5(14)	C(18)-C(19)-C(20)	117.10(16)
C(7)-C(8)-H(8)	116.1(14)	C(18)-C(19)-H(19)	120.5(14)
C(8)-C(9)-C(10)	118.92(17)	C(20)-C(19)-H(19)	122.3(14)
C(8)-C(9)-H(9)	120.6(15)	C(19)-C(20)-C(21)	121.47(17)
C(10)-C(9)-H(9)	120.4(15)	C(19)-C(20)-H(20)	120.1(14)
C(9)-C(10)-C(11)	121.00(17)	C(21)-C(20)-H(20)	118.4(14)
C(9)-C(10)-H(10)	118.8(14)	C(20)-C(21)-C(22)	121.19(16)
C(11)-C(10)-H(10)	120.2(14)	C(20)-C(21)-H(21)	118.9(15)
C(10)-C(11)-C(12)	119.99(16)	C(22)-C(21)-H(21)	119.9(15)
C(10)-C(11)-H(11)	118.2(13)	C(23)-C(22)-C(21)	116.76(15)
C(12)-C(11)-H(11)	121.8(13)	C(23)-C(22)-H(22)	125.1(13)
N(1)-C(12)-C(11)	121.80(15)	C(21)-C(22)-H(22)	118.1(13)
N(1)-C(12)-C(7)	118.89(14)	C(22)-C(23)-C(18)	121.76(15)
C(11)-C(12)-C(7)	119.31(15)	C(22)-C(23)-C(24)	130.10(15)

C(18)-C(23)-C(24)	108.10(13)	O(6)-C(24)-C(23)	129.02(15)
O(6)-C(24)-N(2)	125.05(15)	N(2)-C(24)-C(23)	105.92(13)

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for compound **17**.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	29(1)	36(1)	29(1)	-2(1)	-5(1)	5(1)
O(2)	28(1)	31(1)	27(1)	-5(1)	0(1)	1(1)
O(3)	38(1)	38(1)	43(1)	12(1)	-17(1)	-7(1)
O(4)	24(1)	24(1)	35(1)	5(1)	0(1)	-2(1)
O(5)	24(1)	33(1)	27(1)	1(1)	-6(1)	1(1)
O(6)	23(1)	33(1)	32(1)	10(1)	-4(1)	0(1)
N(1)	20(1)	29(1)	24(1)	-4(1)	0(1)	-3(1)
N(2)	21(1)	23(1)	24(1)	1(1)	-1(1)	-2(1)
C(1)	22(1)	22(1)	25(1)	1(1)	1(1)	-2(1)
C(2)	23(1)	24(1)	29(1)	-4(1)	2(1)	-2(1)
C(3)	22(1)	23(1)	24(1)	-1(1)	-1(1)	-1(1)
C(4)	23(1)	22(1)	25(1)	-2(1)	-2(1)	-1(1)
C(5)	21(1)	27(1)	32(1)	-3(1)	0(1)	0(1)
C(6)	22(1)	27(1)	31(1)	0(1)	2(1)	0(1)
C(7)	26(1)	22(1)	25(1)	3(1)	1(1)	2(1)
C(8)	28(1)	30(1)	28(1)	2(1)	3(1)	3(1)
C(9)	35(1)	34(1)	23(1)	-2(1)	-2(1)	5(1)
C(10)	31(1)	30(1)	26(1)	-1(1)	-5(1)	1(1)
C(11)	26(1)	25(1)	26(1)	1(1)	-2(1)	1(1)
C(12)	26(1)	19(1)	23(1)	3(1)	-1(1)	2(1)
C(13)	26(1)	21(1)	25(1)	0(1)	0(1)	-3(1)
C(14)	33(1)	37(1)	27(1)	-8(1)	0(1)	-4(1)
C(15)	25(1)	24(1)	26(1)	-1(1)	-1(1)	0(1)
C(16)	33(1)	27(1)	39(1)	8(1)	5(1)	0(1)
C(17)	25(1)	24(1)	20(1)	-1(1)	0(1)	1(1)
C(18)	24(1)	22(1)	20(1)	-3(1)	1(1)	1(1)
C(19)	31(1)	26(1)	24(1)	2(1)	-1(1)	2(1)
C(20)	36(1)	28(1)	29(1)	7(1)	4(1)	-1(1)
C(21)	29(1)	29(1)	30(1)	2(1)	2(1)	-6(1)
C(22)	24(1)	27(1)	23(1)	-1(1)	0(1)	-2(1)
C(23)	23(1)	23(1)	19(1)	-2(1)	2(1)	1(1)
C(24)	23(1)	23(1)	22(1)	-1(1)	1(1)	1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for compound **17**.

	x	y	z	U(eq)
H(1)	5672(7)	6660(30)	4310(20)	23(5)
H(2A)	5722(8)	8030(30)	6470(30)	35(6)
H(2B)	5930(7)	6390(30)	7280(30)	33(6)
H(4)	6727(7)	5290(20)	6160(20)	21(5)
H(5)	7368(7)	7090(30)	5220(30)	30(5)
H(6)	7496(7)	6310(20)	2690(20)	25(5)
H(8)	7224(8)	4870(30)	490(30)	34(6)
H(9)	6615(8)	3650(30)	-960(30)	41(6)
H(10)	5861(8)	3540(30)	-20(30)	36(6)
H(11)	5700(7)	4440(30)	2410(20)	27(5)
H(14A)	7006	9584	9856	49
H(14B)	6626	8464	10694	49
H(14C)	6537	10440	10426	49
H(16A)	6898	11316	3441	49
H(16B)	7203	12211	4701	49
H(16C)	6653	12438	4697	49
H(19)	5510(8)	410(30)	8130(30)	34(6)
H(20)	4780(8)	-950(30)	8190(30)	33(6)
H(21)	4180(9)	-10(30)	6690(30)	42(6)
H(22)	4252(7)	2360(30)	5090(30)	30(5)

Table S6. Torsion angles [°] for compound **17**.

C(12)-N(1)-C(1)-N(2)	76.2(2)
C(4)-N(1)-C(1)-N(2)	-112.13(15)
C(12)-N(1)-C(1)-C(2)	-162.91(15)
C(4)-N(1)-C(1)-C(2)	8.74(17)
C(17)-N(2)-C(1)-N(1)	59.5(2)
C(24)-N(2)-C(1)-N(1)	-128.82(16)
C(17)-N(2)-C(1)-C(2)	-58.23(19)
C(24)-N(2)-C(1)-C(2)	113.43(16)
N(1)-C(1)-C(2)-C(3)	16.44(17)
N(2)-C(1)-C(2)-C(3)	139.89(14)
C(1)-C(2)-C(3)-C(13)	-151.30(13)
C(1)-C(2)-C(3)-C(15)	83.38(16)
C(1)-C(2)-C(3)-C(4)	-33.19(16)
C(12)-N(1)-C(4)-C(5)	15.4(2)
C(1)-N(1)-C(4)-C(5)	-156.26(14)
C(12)-N(1)-C(4)-C(3)	141.81(15)
C(1)-N(1)-C(4)-C(3)	-29.84(17)
C(13)-C(3)-C(4)-N(1)	158.69(13)
C(15)-C(3)-C(4)-N(1)	-78.59(15)
C(2)-C(3)-C(4)-N(1)	37.66(16)
C(13)-C(3)-C(4)-C(5)	-77.40(18)
C(15)-C(3)-C(4)-C(5)	45.33(19)
C(2)-C(3)-C(4)-C(5)	161.57(15)
N(1)-C(4)-C(5)-C(6)	-13.2(2)
C(3)-C(4)-C(5)-C(6)	-131.54(17)
C(4)-C(5)-C(6)-C(7)	3.4(3)
C(5)-C(6)-C(7)-C(8)	-177.23(16)
C(5)-C(6)-C(7)-C(12)	5.9(2)
C(12)-C(7)-C(8)-C(9)	0.6(2)
C(6)-C(7)-C(8)-C(9)	-176.30(17)
C(7)-C(8)-C(9)-C(10)	0.6(3)
C(8)-C(9)-C(10)-C(11)	-1.1(3)
C(9)-C(10)-C(11)-C(12)	0.4(3)
C(1)-N(1)-C(12)-C(11)	-16.3(2)
C(4)-N(1)-C(12)-C(11)	173.04(15)
C(1)-N(1)-C(12)-C(7)	163.36(14)
C(4)-N(1)-C(12)-C(7)	-7.3(2)

C(10)-C(11)-C(12)-N(1)	-179.55(15)
C(10)-C(11)-C(12)-C(7)	0.8(2)
C(8)-C(7)-C(12)-N(1)	179.08(15)
C(6)-C(7)-C(12)-N(1)	-4.0(2)
C(8)-C(7)-C(12)-C(11)	-1.3(2)
C(6)-C(7)-C(12)-C(11)	175.71(15)
C(14)-O(2)-C(13)-O(1)	1.0(2)
C(14)-O(2)-C(13)-C(3)	-178.56(13)
C(15)-C(3)-C(13)-O(1)	-107.51(18)
C(2)-C(3)-C(13)-O(1)	127.69(18)
C(4)-C(3)-C(13)-O(1)	14.9(2)
C(15)-C(3)-C(13)-O(2)	72.02(16)
C(2)-C(3)-C(13)-O(2)	-52.78(18)
C(4)-C(3)-C(13)-O(2)	-165.57(13)
C(16)-O(4)-C(15)-O(3)	-1.6(3)
C(16)-O(4)-C(15)-C(3)	177.12(14)
C(13)-C(3)-C(15)-O(3)	-145.69(18)
C(2)-C(3)-C(15)-O(3)	-18.5(2)
C(4)-C(3)-C(15)-O(3)	92.0(2)
C(13)-C(3)-C(15)-O(4)	35.57(19)
C(2)-C(3)-C(15)-O(4)	162.76(14)
C(4)-C(3)-C(15)-O(4)	-86.69(17)
C(24)-N(2)-C(17)-O(5)	177.73(15)
C(1)-N(2)-C(17)-O(5)	-9.8(3)
C(24)-N(2)-C(17)-C(18)	-1.79(17)
C(1)-N(2)-C(17)-C(18)	170.73(14)
O(5)-C(17)-C(18)-C(19)	4.4(3)
N(2)-C(17)-C(18)-C(19)	-176.13(16)
O(5)-C(17)-C(18)-C(23)	-178.23(16)
N(2)-C(17)-C(18)-C(23)	1.26(17)
C(23)-C(18)-C(19)-C(20)	0.3(3)
C(17)-C(18)-C(19)-C(20)	177.37(17)
C(18)-C(19)-C(20)-C(21)	0.2(3)
C(19)-C(20)-C(21)-C(22)	-0.3(3)
C(20)-C(21)-C(22)-C(23)	-0.1(3)
C(21)-C(22)-C(23)-C(18)	0.7(2)
C(21)-C(22)-C(23)-C(24)	-176.95(16)
C(19)-C(18)-C(23)-C(22)	-0.8(2)

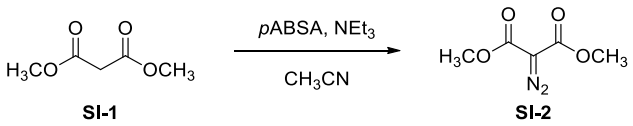
C(17)-C(18)-C(23)-C(22)	-178.39(15)
C(19)-C(18)-C(23)-C(24)	177.33(15)
C(17)-C(18)-C(23)-C(24)	-0.32(17)
C(17)-N(2)-C(24)-O(6)	-177.52(16)
C(1)-N(2)-C(24)-O(6)	9.9(3)
C(17)-N(2)-C(24)-C(23)	1.60(17)
C(1)-N(2)-C(24)-C(23)	-171.03(14)
C(22)-C(23)-C(24)-O(6)	-3.8(3)
C(18)-C(23)-C(24)-O(6)	178.32(17)
C(22)-C(23)-C(24)-N(2)	177.12(16)
C(18)-C(23)-C(24)-N(2)	-0.74(17)

2. General methods

All reactions were carried out in oven- or flame dried glassware under nitrogen atmosphere, unless stated otherwise. For quantitative flash chromatography, distilled technical grade solvents were used. THF, Et_2O, CH_3CN and CH_2Cl_2 were dried by passage over activated alumina under nitrogen atmosphere (H_2O content < 7 ppm, Karl-Fischer titration). NEt_3 was dried by distillation over CaH_2 under nitrogen atmosphere. All chemicals were purchased and used as received unless stated otherwise. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F254 TLC aluminium plates and visualized with UV-light, permanganate, CAM or *p*-anisaldehyde stains. ^{1}H-NMR spectra were recorded at room temperature on a Brucker DPX-400 400 MHz spectrometer in chloroform-d or D6-DMSO; all signals are reported in ppm with the internal chloroform signal at 7.26 ppm or the internal D6-DMSO signal at 2.50 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br = broad signal, integration, coupling constant(s) in Hz, interpretation). ^{13}C-NMR spectra were recorded with 1H-decoupling on a Bruker DPX-400 101 MHz spectrometer in chloroform-d or D6-DMSO; all signals are reported in ppm with the internal chloroform signal at 77.00 ppm or the internal DMSO signal at 39.51 ppm as standard. Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO4100-S and a ZnSe prism and are reported as cm^{-1} (w = weak, m = medium, s = strong). High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API. Melting points were measured on a Buechi B-540 melting point apparatus and were not corrected.

3. Synthesis of diazo compounds

Dimethyl 2-diazomalonate (**SI-2**).



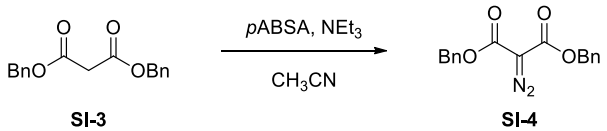
SI-1 **SI-2**

Following a modified procedure,[1] triethylamine (9.23 mL, 66.6 mmol, 2.4 equiv.) and dimethyl malonate **SI-1** (3.19 mL, 27.8 mmol, 1 equiv.) were added to a solution of *p*ABSA (10.0 g, 41.6 mmol, 1.5 equiv.) in CH_3CN (111 mL, 0.25 M) at room temperature and the resulting mixture was stirred for 18 hours at room temperature. Thereafter the mixture was filtered and the solvent was evaporated. The residue was triturated with CH_2Cl_2 (50 mL), the remaining solids were filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica, pentane:EtOAc 10:1 to 5:1) and 4.28 g (27.1 mmol, 98%) of the title compound **SI-2** were isolated as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 6H, C*H*$_3$).

^{1}H-NMR data match the literature report.[1]

Dibenzyl 2-diazomalonate (**SI-4**).



SI-3 **SI-4**

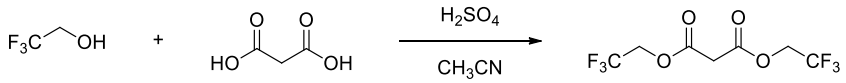
Following a modified procedure,[2] triethylamine (1.33 mL, 9.60 mmol, 2.4 equiv.) and dibenzyl malonate **SI-3** (1.00 mL, 4.00 mmol, 1 equiv.) were added to a solution of *p*ABSA (1.44 g, 6.00 mmol, 1.5 equiv.) in CH_3CN (16.0 mL, 0.25 M) at room temperature and the resulting mixture was stirred for 18 hours at room temperature. Thereafter the mixture was filtered and the solvent was evaporated. The residue was triturated with CH_2Cl_2 (20 mL), the remaining solids were filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica, pentane:EtOAc 10:1) and 1.19 g (3.83 mmol, 96%) of the title compound **SI-4** were isolated as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 – 7.28 (m, 10H, Ar*H*), 5.28 (s, 4H, C*H*$_2$).

^{1}H-NMR data match the literature report.[1]

[1] F. de Nanteuil, J. Waser, *Angew. Chem. Int. Ed.,* **2011**, *50*, 12075–12079.

Bis(2,2,2-trifluoroethyl) malonate (**SI-7**).



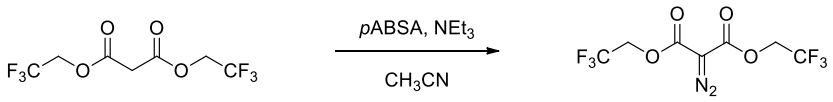
SI-5 **SI-6** **SI-7**

Following a modified procedure,[2] H_2SO_4 (1.00 mL, 18.8 mmol, 0.25 equiv.) was added to a solution of trifluoroethanol **SI-5** (29.9 mL, 415 mmol, 5.4 equiv.) and malonic acid **SI-6** (8.00 g, 77.0 mmol, 1 equiv.) in toluene (40.0 mL, 1.9 M) and the resulting mixture was heated to reflux for 8 hours. After cooling to room temperature, toluene (80.0 mL) was added and the mixture was washed with aq. NaOH (200 mL, 1 M), water (200 mL) and brine (200 mL). The organic layer was dried over $MgSO_4$ and the solvent was evaporated which afforded 6.80 g (25.4 mmol, 33%) of the title compound **SI-7** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.55 (q, *J* = 8.2 Hz, 4H, OC*H*$_2$), 3.61 (s, 2H, C*H*$_2$).

^{1}H-NMR data match the literature report.[2]

Bis(2,2,2-trifluoroethyl) 2-diazomalonate (**SI-8**).



SI-7 **SI-8**

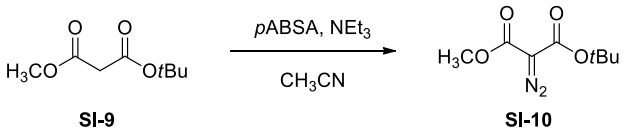
Following a modified procedure,[2] triethylamine (6.00 mL, 43.3 mmol, 2.4 equiv.) and bis(trifluorethyl)malonate **SI-7** (4.84 g, 18.0 mmol, 1 equiv.) were added to a solution of *p*ABSA (6.50 g, 27.1 mmol, 1.5 equiv.) in CH_3CN (72.0 mL, 0.25 M) at room temperature and the resulting mixture was stirred for 18 hours at room temperature. Thereafter the mixture was filtered and the solvent was evaporated. The residue was triturated with CH_2Cl_2 (50 mL), the solids were filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica, pentane:EtOAc 10:1 to 5:1) and 5.26 g (17.9 mmol, 99%) of the title compound **SI-8** were isolated as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.63 (q, *J* = 8.2 Hz, 4H, OC*H*$_2$).

^{1}H-NMR data match the literature report.[2]

[2] F. de Nanteuil, J. Loup, and J. Waser *Org. Lett.* **2013**, *15*, 3738-3741.

1-*tert*-Butyl 3-methyl 2-diazomalonate (**SI-10**).



SI-9 **SI-10**

Following a modified procedure,[3] triethylamine (1.97 mL, 14.2 mmol, 2.4 equiv.) and *tert*-butyl methyl malonate **SI-9** (1.00 mL, 5.91 mmol, 1 equiv.) were added to a solution of *p*ABSA (2.13 g, 8.87 mmol, 1.5 equiv.) in CH_3CN (23 mL, 0.25 M) at room temperature and the resulting mixture was stirred for 18 hours at room temperature. Thereafter the mixture was filtered and the solvent was evaporated. The residue was triturated with CH_2Cl_2 (25 mL), the remaining solids were filtered and the solvent was evaporated. The residue was purified by column chromatography (silica, pentane:EtOAc 20:1 to 10:1) and 1.05 g (5.24 mmol, 89%) of the title compound **SI-10** were isolated as a yellow oil.

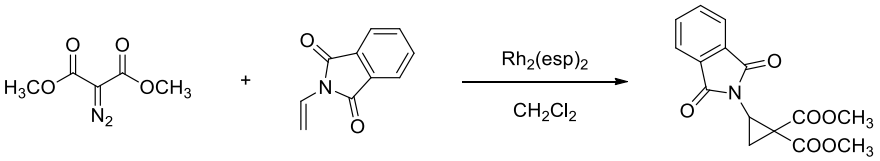
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3H, C*H*$_3$), 1.50 (s, 9H, C(C*H*$_3$)$_3$).

HRMS (ESI) calcd. for $C_8H_{13}N_2O_4^+$ $[M+H]^+$ 201.0870; found 201.0690.

^{1}H-NMR data match the literature report.[3]

4. Synthesis of aminocyclopropanes

Bimethyl 2-(1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (**14**).



SI-2 **SI-11** **14**

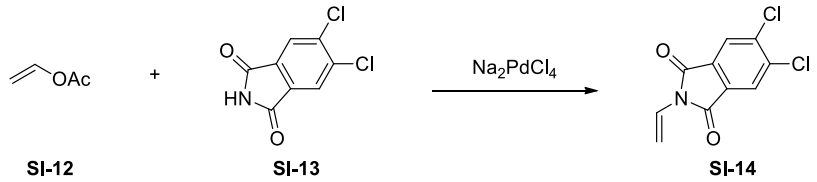
Following a modified procedure,[1] a solution of dimethyldiazomalonate **SI-2** (2.21 g, 14.0 mmol, 1.1 equiv.) in CH_2Cl_2 (10.0 mL) was added over 5 minutes at 0 °C to a solution of $Rh_2(esp)_2$ (19.0 mg, 25.0 µmol, 0.2 mol%) and *N*-vinyl-phtalimide **SI-11** (2.20 g, 12.7 mmol, 1 equiv.) in CH_2Cl_2 (40 mL). The reaction mixture was stirred for 16 hours while warming to room temperature. Thereafter the solvent was evaporated and the residue was purified by column chromatography (silica, pentane:EtOAc 10:1 to pentane:EtOAc 4:1) affording 3.23 g (10.7 mmol, 84%) of the title compound **14** as a colorless oil.

[3] F. de Simone, T. Saget, F. Benfatti, S. Almeida, J. Waser *Chem. Eur. J.* **2011**, *17,* 14527-14538.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 3.83 (s, 3H, OC*H*$_3$), 3.70 (dd, *J* = 8.5, 6.6 Hz, 1H, C*H*-Phth), 3.62 (s, 3H, OC*H*$_3$), 2.71 (t, *J* = 6.6 Hz, 1H, CH_2), 2.04 (dd, *J* = 8.5, 6.6 Hz, 1H, CH_2).

^{1}H-NMR data match the literature report.[1]

5,6-Dichloro-2-vinylisoindoline-1,3-dione (**SI-14**).



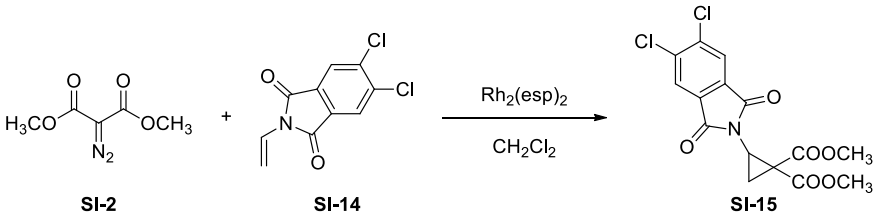
SI-12 **SI-13** **SI-14**

Following a modified procedure,[7] Na_2PdCl_4 (27.0 mg, 92 µmol, 2 mol%) was added to a stirred solution of 4,5-dichlorophthalimide (**SI-13**) (1.00 g, 4.63 mmol, 1.00 equiv.) in vinyl acetate (**SI-12**) (11.5 mL, 124 mmol, 26.8 equiv.), and the mixture was heated under reflux for 48 h. After solvent evaporation, the crude was purified by Biotage (SNAP Cartridge KP-Sil 25 g, 8:2 Hexane/EtOAc) to obtain 1.25 g (4.63 mmol, 46%) of the title compound **SI-14** as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (s, 2H, Ar*H*), 6.84 (dd, *J* = 16.4, 9.8 Hz, 1H, N-*CH*), 6.09 (dd, *J* = 16.4, 0.3 Hz, 1H, *=CH*), 5.10 (dd, *J* = 9.8, 0.3 Hz, 1H, *=CH*).

^{1}H-NMR data match the literature report.[7]

Dimethyl 2-(5,6-dichloro-1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (**SI-15**).



SI-2 **SI-14** **SI-15**

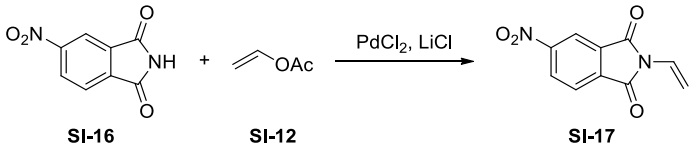
Following a modified procedure,[8] a solution of dimethyl diazomalonate (**SI-2**) (0.51 mL, 4.40 mmol, 1.5 equiv.) in CH_2Cl_2 (8.0 mL) was added dropwise over 5 minutes to a solution of 5,6-dichloro-2-vinylisoindoline- 1,3-dione (**SI-14**) (72.0 mg, 3.00 mmol, 1 equiv.) and $Rh_2(esp)_2$ (4.50 mg, 5.90 µmol, 0.2 mol%) in CH_2Cl_2 (4.0 mL) at 0 °C. After stirring the resulting mixture overnight at room temperature, the solution was concentrated under reduced pressure. Purification by Biotage (SNAP cartridge KP-Sil

25 g, hexane:EtOAc 95:5 to 6:4) afforded 810 mg (2.20 mmol, 74%) of the title compound **SI-15** as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (s, 2H, Ar*H*), 3.82 (s, 3H, OC*H*$_3$), 3.66 (dd, *J* = 8.5, 6.5 Hz, 1H, C*H*-Phth), 3.63 (s, 3H, OC*H*$_3$), 2.64 (dd, *J* = 6.5. 6.5 Hz, 1H, C*H*$_2$), 2.07-2.01 (m, 1H, C*H*$_2$).

^{1}H-NMR data match the literature report.[8]

5-Nitro-2-vinylisoindoline-1,3-dione (**SI-17**).

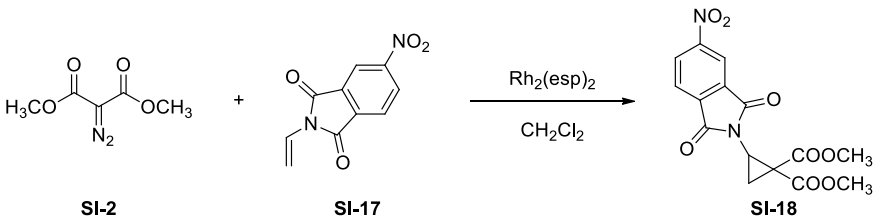


Following a modified procedure,[4] $PdCl_2$ (92 mg, 0.52 mmol, 10 mol%) and LiCl (221 mg, 5.20 mmol, 1 equiv.) were added to a solution of 5-nitrosoindoline-1,3-dione (**SI-16**) (1.00 g, 5.20 mmol, 1 equiv.) in vinyl acetate (**SI-12**) (12.9 mL, 139 mmol, 27 equiv.) and the mixture was heated to reflux for 20 hours. After cooling to room temperature the solvent was evaporated and the residue was purified by column chromatography (hexane:EtOAc 4:1 to 1:1) affording 1.14 g (5.23 mmol, quant.) of the title compound **SI-17** as a bright yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68 (dd, *J* = 2.0, 0.5 Hz, 1H, Ar*H*), 8.63 (dd, *J* = 8.1, 2.0 Hz, 1H, Ar*H*), 8.08 (m, 1H, Ar*H*), 6.88 (dd, *J* = 16.4, 9.8 Hz, 1H, *CH*-N), 6.14 (dd, *J* = 16.4, 0.5 Hz, 1H, =*CH*$_2$), 5.16 (dd, *J* = 9.8, 0.5 Hz, 1H, =*CH*$_2$) ppm.

^{1}H-NMR data match the literature report.[4]

Dimethyl 2-(5-nitro-1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (**SI-18**).



Following a modified procedure,[4] a solution of dimethyldiazomalonate (**SI-2**) (0.12 g 0.77 mmol, 1.2 equiv.) in CH_2Cl_2 (1.0 mL) was added over 5 minutes to a solution of 5-nitro-2-vinylisoindoline-1,3-

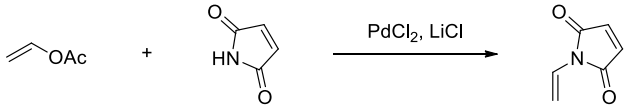
[4] F. de Nanteuil, E. Serrano, D. Perrotta, and J. Waser *J. Am. Chem. Soc.* **2014** *136*, 6239-6242.

dione (**SI-17**) (0.13 g, 0.64 mmol, 1 equiv.) and $Rh_2(esp)_2$ (1 mg, 1.2 µmol, 0.2 mol%) in CH_2Cl_2 (1.6 mL) at 0 °C and the resulting mixture was stirred for 16 hours while warming to room temperature. Thereafter the solvent was evaporated and the residue was purified by column chromatography (silica, hexane:EtOAc 6:4) affording 0.18 g (0.53 mmol, 83%) of the title compound **SI-18** as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.61 (m, 2H, Ar*H*), 8.03 (d, *J* = 8.1 Hz, 1H, Ar*H*), 3.83 (s, 3H, OCH_3), 3.70 (m, 1H, C*H*-N), 3.62 (s, 3H, OCH_3), 2.63 (m, 1H, CH_2), 2.07 (m, 1H, CH_2).

^{1}H-NMR data match the literature report.[4]

1-Vinyl-1H-pyrrole-2,5-dione (**SI-20**).



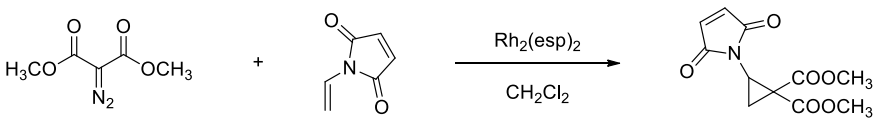
SI-12 **SI-19** **SI-20**

Following a modified procedure,[7] maleimide (**SI-19**) (1.30 g, 13.4 mmol, 1 equiv.), palladium(II) chloride (240 mg, 1.34 mmol, 0.1 equiv.), lithium chloride (57.0 mg, 1.34 mmol, 0.1 equiv.) and vinyl acetate (**SI-12**) (33.2 mL, 359 mmol, 27 equiv.) were added in a microwave tube sealed with a microwave cap. After stirring at 80 °C for 23 h, the resulting mixture was cooled down to room temperature. Purification by Biotage (SNAP cartridge KP-Sil 50 g, hexane:EtOAc 93:7 to 40:60) afforded 1.74 g (14.1 mmol, quant.) of the title compound **SI-20** as a bright yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.74 (s, 2H, *CH*-*C*=*O*), 6.67 (dd, *J* = 16.4, 9.8 Hz, 1H, C*H*-N), 5.87 (d, *J* = 16.4 Hz, 1H, =CH_2), 4.94 (d, *J* = 9.8 Hz, 1H, =CH_2).

^{1}H-NMR data match the literature report.[7]

Dimethyl 2-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)cyclopropane-1,1-dicarboxylate (**SI-21**).



SI-2 **SI-20** **SI-21**

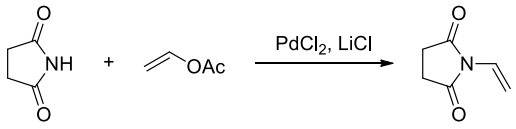
Following a modified procedure,[8] a solution of dimethyl diazomalonate (**SI-2**) (96 mg, 0.61 mmol, 1.5 equiv.) in CH_2Cl_2 (1.0 mL) was added dropwise over 5 minutes to a solution of 1-vinyl-1*H*-pyrrole-2,5-dione (**SI-20**) (50 mg, 0.41 mmol, 1 equiv.) and $Rh_2(esp)_2$ (0.7 mg, 0.9 µmol, 0.2 mol%) in CH_2Cl_2

(2.0 mL) at 0 °C. The resulting mixture was stirred for 5 hours at room temperature and thereafter concentrated under reduced pressure. Purification by Biotage (SNAP cartridge KP-Sil 10 g, hexane/EtOAc 95:5 to 70:30) afforded 66.9 mg (0.264 mmol, 65%) of the title compound **SI-21** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.67 (s, 2H, C*H*-C=O), 3.79 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.56-3.51 (m, 1H, C*H*-N), 2.56 (dd, *J* = 6.4, 6.5 Hz, 1H, CH_2), 1.96-1.91 (m, 1H, CH_2) ppm.

^{1}H-NMR data match the literature report.[8]

1-Vinylpyrrolidine-2,5-dione (**SI-23**).



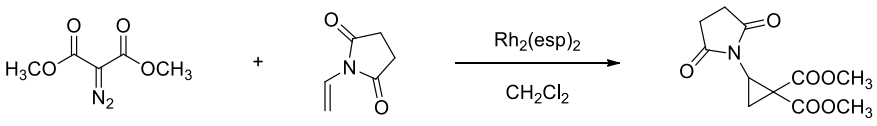
SI-22 **SI-12** **SI-23**

Following a modified procedure,[5] succinimide (**SI-22**) (1.00 g, 10.1 mmol, 1.00 equiv.), vinyl acetate (**SI-12**) (25.0 mL, 270 mmol, 26.8 eq) and Na_2PdCl_4 (59.0 mg, 0.202 mmol, 2.00 mol%) were heated under reflux for 72 hours. After solvent evaporation, the crude was purified by Biotage (SNAP Cartridge KP-Sil 50 g, 7:3 Hexane/EtOAc) to obtain the title compound **SI-23** (1.22 g, 9.78 mmol, 97%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.68 (dd, *J* = 16.4, 9.9 Hz, 1H, N-C*H*), 6.08 (d, *J* = 16.4 Hz, 1H, =C*H*), 5.06 (d, *J* = 9.9 Hz, 1H, =C*H*), 2.72 (s, 4H, CH_2) ppm.

^{1}H-NMR data match the literature report.[5]

Dimethyl 2-(2,5-dioxopyrrolidin-1-yl)cyclopropane-1,1-dicarboxylate (**SI-24**).



SI-2 **SI-23** **SI-24**

Following a modified procedure,[4] a solution of dimethyldiazomalonate (**SI-2**) (300 mg, 4.80 mmol, 1.2 equiv.) in CH_2Cl_2 (4 mL) was added over 5 minutes to a solution of *N*-vinyl-succinimide (**SI-23**) (500 mg, 4.00 mmol, 1.00 equiv.), and $Rh_2(esp)_2$ (3.0 mg, 4.0 µmol, 0.10 mol%) in CH_2Cl_2 (15 mL) at 0 °C

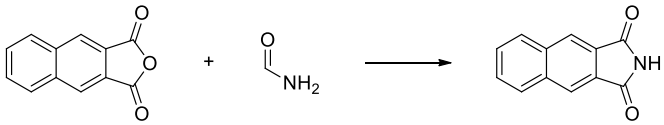
[5] E. Bayer, K. Geckeler, *Angew. Chem. Int. Ed.* **1979**, *18*, 533.

and the mixture was warmed to room temperature over 16 hours. Thereafter the solvent was evaporated and the residue was purified by Biotage (SNAP Cartridge KP-Sil 50 g, 1:1 hexane/EtOAc) affording the title compound **SI-24** as a yellow solid (801 mg, 3.14 mmol, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.78 (s, 3H, OC*H*$_3$), 3.68 (s, 3H, OC*H*$_3$), 3.45 (dd, *J* = 8.5, 6.5 Hz, 1H, N-C*H*), 2.73-2.58 (m, 4H, O=C-C*H*$_2$), 2.45 (dd, *J* = 6.5, 6.5 Hz, 1H, C*H*$_2$), 1.93 (dd, *J* = 8.5, 6.5 Hz, 1H, C*H*$_2$) ppm.

^{1}H-NMR data match the literature report.[4]

1H-Benzo[*f*]isoindole-1,3(2*H*)-dione (**SI-27**).



SI-25 **SI-26** **SI-27**

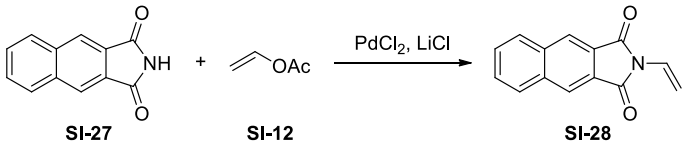
Following a modified procedure,[6] naphtho[2,3-*c*]furan-1,3-dione (**SI-25**) (500 mg, 2.52 mmol, 1 equiv.) and formamide **SI-26** (10.0 mL, 252 mmol, 100 equiv.) were added in a 20 mL microwave vial and sealed with a microwave cap. The mixture was stirred until the product was completely dissolved. The mixture was heated twice at 200 °C for 30 sec with 10 sec pre-stirring, using Biotage Initiator 2.0 microwave reactor. The mixture was cooled to 0 °C and cold water (10 mL) was added into the tube. The solid was filtrated over a filter paper, washed with water (15 mL) and hexane (20 mL) and dried under reduced pressure to afford 432 mg (2.19 mmol, 87%) of the title compound **SI-27** as a beige solid which was used without further purification.

^{1}H NMR (400 MHz, [D6]-DMSO) δ = 11.5 (s, 1H, *NH*), 8.45 (s, 2H, Ar*H*), 8.26 (dd, *J* = 6.6, 3.3 Hz, 2H, Ar*H*), 7.76 (dd, *J* = 6.6, 3.3 Hz, 2H, Ar*H*).

^{1}H-NMR data match the literature report.[6]

[6] K. Kacprzak, *Synth. Commun.* **2003**, *33*, 1499-1507.

2-Vinyl-1H-benzo[*f*]isoindole-1,3(2*H*)-dione (**SI-28**).



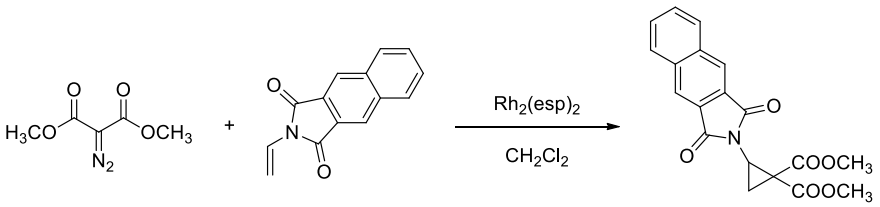
SI-27 **SI-12** **SI-28**

Following a modified procedure,[7] 1*H*-benzo[*f*]isoindole-1,3(2*H*)-dione (**SI-27**) (1.70 g, 8.62 mmol, 1 equiv.), palladium(II) chloride (0.15 g, 0.86 mmol, 0.1 equiv.), lithium chloride (40 mg, 0.86 mmol, 0.1 equiv.) and vinyl acetate (**SI-12**) (21.4 mL, 231 mmol, 27 equiv.) were added in a microwave tube sealed with a microwave cap. After stirring for 31 h at 80 °C, the resulting mixture was cooled down to room temperature. Purification by silica gel chromatography (hexane:EtOAc 17:1 to 10:1) afforded 1.26 g (5.66 mmol, 66%) the title compound **SI-28** as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.37 (s, 2H, Ar*H*), 8.07 (dd, *J* = 6.3, 3.4 Hz, 2H, Ar*H*), 7.72 (dd, *J* = 6.3, 3.4 Hz, 2H, Ar*H*), 6.97 (dd, *J* = 16.4, 9.8 Hz, 1H, Phth-*CH*), 6.20 (d, *J* = 16.4 Hz, 1H, =*CH*), 5.12 (d, *J* = 9.8 Hz, 1H, =*CH*).

^{1}H-NMR data match the literature report.[7]

Dimethyl 2-(1,3-dioxo-1H-benzo[f]isoindol-2(3*H*)-yl)cyclopropane-1,1-dicarboxylate (**SI-29**).



SI-2 **SI-28** **SI-29**

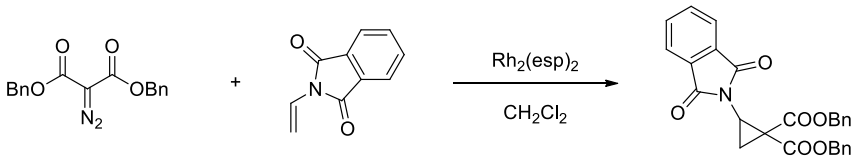
Following a modified procedure,[8] a solution of dimethyl 2-diazomalonate (**SI-2**) (20 mg, 1.30 mmol, 1.5 equiv.) in dichloromethane (2.00 mL) was added dropwise over 5 minutes to a solution of 2-vinyl-1*H*-benzo[*f*]isoindole- 1,3(2*H*)-dione (**SI-28**) (0.19 g, 0.85 mmol, 1 equiv.) and $Rh_2(esp)_2$ (1 mg, 1.70 µmol, 0.2 mol%) in CH_2Cl_2 (3.00 mL) at 0 °C. After stirring the resulting mixture for 26 hours at room temperature the solution was concentrated under reduced pressure. Purification by silica gel chromatography (hexane:EtOAc 8:2 to 6:4) afforded 0.28 g (0.80 mmol, 94%) the title compound **SI-29** as a colorless solid.

[7] N. Baret, J.-P. Dulcere, J. Rodriguez, J.-M. Pons, R. Faure, *Eur. J. Org. Chem.* **2000**, 1507-1516.
[8] F. Gonzalez-Bobes, M. D. B. Fenster, S. Kiau, L. Kolla, S. Kolotuchin, M. Soumeillant, *Adv. Synth. Catal.* **2008**, *350*, 813.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.34 (s, 2H, Ar*H*), 8.06 (dd, *J* = 6.2, 3.3 Hz, 2H, Ar*H*), 7.70 (dd, *J* = 6.2, 3.3 Hz, 2H, Ar*H*), 3.84 (s, 3H, OC*H*$_3$), 3.77 (dd, *J* = 8.5, 6.5 Hz, 1H C*H*-N), 3.60 (s, 3H, OC*H*$_3$), 2.78 (dd, *J* = 6.5, 6.5 Hz, 1H, C*H*$_2$), 2.08 (dd, *J* = 8.5, 6.5, 1H, C*H*$_2$).

^{1}H-NMR data match the literature report.[8]

Dibenzyl 2-(1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (**SI-30**).



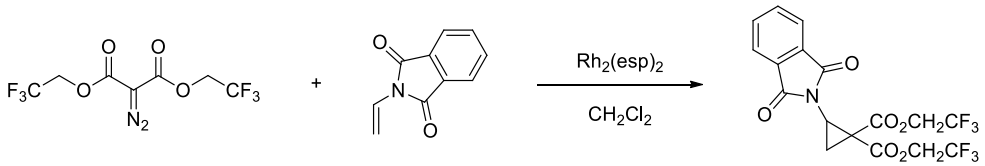
SI-4 **SI-11** **SI-30**

Following a modified procedure,[2] a solution of dibenzyl diazomalonate **SI-4** (1.19 g, 3.83 mmol, 1.1 equiv.) in CH_2Cl_2 (5 mL) was added over 5 minutes at 0 °C to a solution of $Rh_2(esp)_2$ (6 mg, 7 µmol, 0.2 mol%) and *N*-vinyl-phtalimide (**SI-11**) (604 mg, 3.49 mmol, 1 equiv.) in CH_2Cl_2 (9 mL). The reaction mixture was stirred for 16 hours while warming to room temperature. Thereafter the solvent was evaporated and the residue was purified by column chromatography (silica, pentane:EtOAc 10:1 to pentane:EtOAc 4:1) affording 625 mg (1.37 mmol, 39%) of the title compound **SI-30** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 5.5, 3.2 Hz, 2H, *Phth*), 7.73 – 7.66 (m, 2H, *Phth*), 7.35 – 7.30 (m, 5H, Ar*H*), 7.23 – 7.12 (m, 5H, Ar*H*), 5.29 – 5.17 (m, 2H, C*H*$_2$Ph), 5.04 – 4.95 (m, 2H, C*H*$_2$Ph), 3.78 – 3.70 (m, 1H, C*H*-Phth), 2.79 (dd, *J* = 6.5, 6.5 Hz, 1H, C*H*$_2$), 2.05 (dd, *J* = 8.5, 6.5 Hz, 1H, C*H*$_2$).

^{1}H-NMR data match the literature report.[2]

Bis(2,2,2-trifluoroethyl) 2-(1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (**SI-31**).



SI-8 **SI-11** **SI-31**

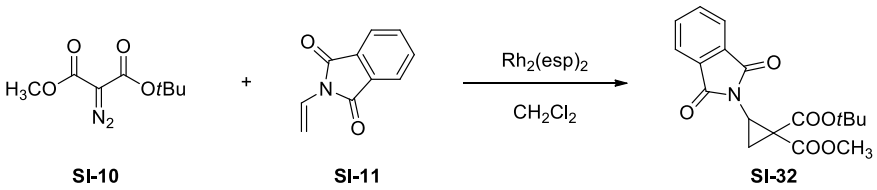
Following a modified procedure,[2] a solution of bis(trifluoroethyl)diazomalonate **SI-8** (5.26 g, 17.9 mmol, 1.1 equiv.) in CH_2Cl_2 (13 mL) was added over 5 minutes at 0 °C to a solution of $Rh_2(esp)_2$ (25 mg, 33 µmol, 0.2 mol%) and *N*-vinyl-phtalimide (**SI-11**) (2.82 g, 16.3 mmol, 1 equiv.) in CH_2Cl_2 (30 mL). The reaction mixture was stirred for 16 hours while warming to room temperature. Thereafter

the solvent was evaporated and the residue was purified by column chromatography (silica, pentane:EtOAc 10:1 to pentane:EtOAc 7:3) affording 5.18 g (11.8 mmol, 73%) of the title compound **SI-31** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 4.62 (q, *J* = 8.2 Hz, 2H, C*H*$_2$CF$_3$), 4.53 – 4.26 (m, 2H, C*H*$_2$CF$_3$), 3.84 (dd, *J* = 8.5, 6.9 Hz, 1H, C*H*-Phth), 2.91 (dd, *J* = 6.9, 6.9 Hz, 1H, C*H*$_2$), 2.20 (dd, *J* = 8.5, 6.9 Hz, 1H, C*H*$_2$).

^{1}H-NMR data match the literature report.[2]

1-*tert*-Butyl 1-methyl 2-(1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (**SI-32**).



SI-10 **SI-11** **SI-32**

A solution of *tert*-butyl methyl diazomalonate (**SI-10**) (1.05 g, 5.24 mmol, 1.1 equiv.) in CH_2Cl_2 (5 mL) was added over 5 minutes at 0 °C to a solution of $Rh_2(esp)_2$ (7.2 mg, 9.5 µmol, 0.2 mol%) and *N*-vinyl-phtalimide (**SI-11**) (826 mg, 4.77 mmol, 1 equiv.) in CH_2Cl_2 (12 mL). The reaction mixture was stirred for 16 hours while warming to room temperature. Thereafter the solvent was evaporated and the residue was purified by column chromatography (silica, pentane:EtOAc 10:1 to pentane:EtOAc 4:1) affording 1.26 g (3.65 mmol, 77%) of the title compound (**SI-32**) as a colorless oil.[9]

R_f: 0.5 (silica, pentane:EtOAc 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.67 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 6.61 – 6.52 (m, 1H, C*H*-Phth), 3.56 (s, 3H, OC*H*$_3$), 2.57 (dd, *J* = 6.4, 6.4 Hz, 1H, CH_2), 1.89 (dd, *J* = 8.5, 6.4 Hz, 1H, CH_2), 1.45 (s, 9H, C(C*H*$_3$)$_3$);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.9, 167.4, 166.9, 134.3, 131.4, 123.4, 82.5, 52.7, 34.3, 34.2, 27.9, 19.0 ppm;

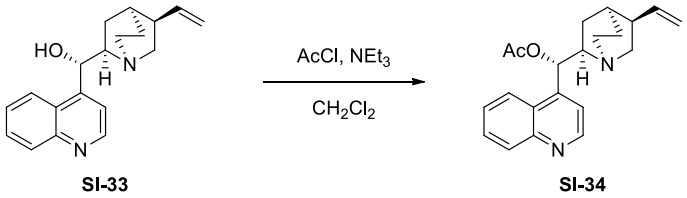
IR (film): $\tilde{\nu}$ = 2349 (w), 2139 (w), 1777 (m), 1764 (m), 1724 (s), 1438 (w), 1393 (w), 1331 (m), 1304 (m), 1275 (w), 1223 (w), 1201 (w), 1174 (w), 1132 (m), 1092 (w), 1058 (w), 982 (w), 957 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{18}H_{19}NNaO_6^+$ $[M+Na]^+$ 368.1105; found 368.1109.

[9] The compound was isolated as a single diastereoisomer of which the relative configuration was not assigned.

5. Substrate synthesis

(*S*)-Quinolin-4-yl((1*S*,2*R*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl acetate (**SI-34**).



SI-33 **SI-34**

Following a modified procedure,[10] NEt_3 (0.71 mL, 5.1 mmol, 1.5 equiv.) followed by acetyl chloride (0.32 mL, 4.4 mmol, 1.3 equiv.) were added to a suspension of cinchonine (**SI-33**) (1.00 g, 3.40 mmol, 1 equiv.) in CH_2Cl_2 (17 mL, 0.2 M) at room temperature and the resulting mixture was stirred for 16 hours. Thereafter water (20 mL) was added, the mixture was stirred for 30 minutes, then sat. aq. K_2CO_3 (20 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The comb. org. extracts were washed with brine (20 mL) and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica, EtOAc:MeOH 30:1) and 1.10 g (3.27 mmol, 96%) of the title compound **SI-34** were isolated as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 (d, *J* = 4.5 Hz, 1H, Ar*H*), 8.21 (d, *J* = 8.6 Hz, 1H, Ar*H*), 8.16 – 8.09 (m, 1H, Ar*H*), 7.72 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H, Ar*H*), 7.60 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H, Ar*H*), 7.38 (d, *J* = 4.5 Hz, 1H, Ar*H*), 6.58 (d, *J* = 6.9 Hz, 1H, C*H*), 6.02 (ddd, *J* = 17.4, 10.5, 7.3 Hz, 1H, C*H*=CH_2), 5.18 – 5.02 (m, 2H, CH=CH_2), 3.30 (q, *J* = 8.5 Hz, 1H, C*H*), 2.92 (d, *J* = 9.2 Hz, 2H, CH_2), 2.73 (ddd, *J* = 22.3, 14.6, 7.0 Hz, 2H, CH_2), 2.27 (q, *J* = 8.4 Hz, 1H, C*H*), 2.13 (s, 3H, C(O)CH_3), 1.85 (dd, *J* = 18.2, 7.6 Hz, 2H, C*H and* CH_2), 1.59 – 1.51 (m, 3H, CH_2 *and* CH_2) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.8, 149.9, 148.6, 145.4, 140.2, 130.4, 129.2, 126.8, 126.0, 123.4, 118.5, 114.9, 73.7, 59.5, 49.8, 49.0, 39.7, 27.8, 26.3, 23.6, 21.1;

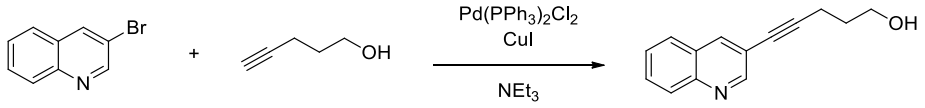
IR (film): $\tilde{\nu}$ = 2940 (w), 2874 (w), 2364 (w), 2320 (w), 1747 (m), 1594 (w), 1510 (w), 1457 (w), 1374 (w), 1276 (m), 1264 (s), 1231 (s), 1026 (m), 911 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{21}H_{25}N_2O_2^+$ $[M+H]^+$ 337.1911; found 337.1911.

The analytical data match the literature report.[10]

[10] J. Qi, A. B. Beeler, Q. Zhang, J. A. Porco *J. Am. Chem. Soc.* **2010**, *132*, 13642-13644.

5-(Quinolin-3-yl)pent-4-yn-1-ol (**SI-37**).



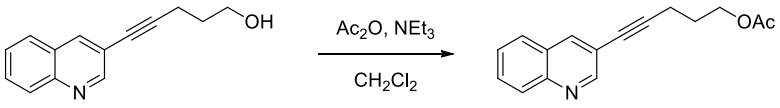
SI-35 **SI-36** **SI-37**

Following a modified procedure,[11] $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.20 mmol, 5 mol%) and pent-4-yn-1-ol (**SI-36**) (1.86 mL, 20.0 mmol, 5 equiv.) were added to a solution of 3-bromo-quinoline (**SI-35**) (0.54 mL, 4.00 mmol, 1 equiv.) and CuI (76 mg, 0.40 mmol, 10 mol%) in triethylamine (8.00 mL, 0.5 M) at room temperature and the resulting mixture was then refluxed for 18 hours. Thereafter the reaction mixture was cooled to room temperature and filtered through a plug of Celite®. The filtrate was washed with brine (15 mL) and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica, pentane:EtOAc 5:2) and 760 mg (3.60 mmol, 90%) of the title compound **SI-37** were isolated as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (s, 1H, Ar*H*), 8.19 (d, *J* = 1.6 Hz, 1H, Ar*H*), 8.12 (d, *J* = 8.3 Hz, 1H, Ar*H*), 7.77 (d, *J* = 8.3 Hz, 1H, Ar*H*), 7.71 (ddd, *J* = 8.3, 6.9, 1.6 Hz, 1H, Ar*H*), 7.56 (t, *J* = 6.9 Hz, 1H, Ar*H*), 3.86 (t, *J* = 6.1 Hz, 2H, C*H*$_2$-OH), 2.63 (t, *J* = 7.0 Hz, 2H, C≡C-C*H*$_2$), 1.92 (p, *J* = 6.6 Hz, 2H, CH_2-C*H*$_2$-CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.2, 146.3, 138.3, 129.9, 129.0, 127.4, 127.3, 127.2, 117.9, 93.2, 78.2, 61.5, 31.3, 16.1 ppm;
IR (film): $\tilde{\nu}$ = 3333 (w), 2946 (w), 2361 (w), 2231 (w), 1570 (w), 1490 (m), 1433 (w), 1350 (w), 1266 (m), 1126 (w), 1059 (s), 947 (w), 909 (s) cm^{-1};
HRMS (ESI) calcd. for $C_{14}H_{14}NO^+$ $[M+H]^+$ 212.1070; found 212.1075.

The analytical data match the literature report.[11]

5-(Quinolin-3-yl)pent-4-yn-1-yl acetate (**SI-38**).



SI-37 **SI-38**

Ac_2O was added to a solution of alcohol **SI-37** (200 mg, 0.947 mmol, 1 equiv.) and triethylamine (0.21 mL, 1.5 mmol, 1.6 equiv.) in CH_2Cl_2 (1.90 mL, 0.5 M) and the resulting mixture was stirred for 16 hours at room temperature. The reaction was quenched by the addition of sat. aq. $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The comb. org. extracts were washed with brine (20 mL) and

[11] A. Jean, J. Blanchet, J. Rouden, J. Maddalunob, M. de Paolis *Chem. Commun.* **2013**, *49*, 1651-1653.

dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 177 mg (0.70 mmol, 77%) of the title compound **SI-38** were isolated as a colorless oil.

R_f: 0.5 (silica, pentane:EtOAc 4:1);

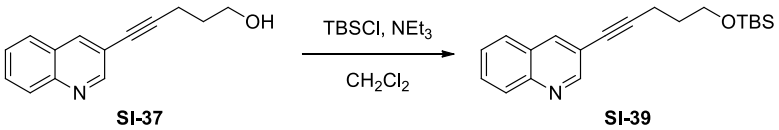
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 2.1 Hz, 1H, Ar*H*), 8.10 (d, *J* = 2.1 Hz, 1H, Ar*H*), 8.02 (dd, *J* = 8.3, 1.3 Hz, 1H, Ar*H*), 7.68 (dd, *J* = 8.3, 1.3 Hz, 1H, Ar*H*), 7.62 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H, Ar*H*), 7.47 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H, Ar*H*), 4.20 (t, *J* = 6.3 Hz, 2H, C*H*$_2$-OAc), 2.53 (t, *J* = 7.0 Hz, 2H, C≡C-C*H*$_2$), 2.02 (s, 3H, C(O)C*H*$_3$), 1.97 – 1.88 (m, 2H, CH_2-C*H*$_2$-CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.0, 152.2, 146.4, 138.2, 129.82, 129.1, 127.4, 127.3, 127.2, 117.8, 92.3, 78.5, 63.1, 27.65, 20.9, 16.3 ppm;

IR (film): $\tilde{\nu}$ = 2964 (w), 2901 (w), 2364 (w), 2327 (w), 2233 (w), 1736 (s), 1568 (w), 1490 (w), 1366 (m), 1238 (s), 1125 (w), 1043 (s) cm^{-1};

HRMS (ESI) calcd. for $C_{16}H_{16}NO_2^+$ $[M+H]^+$ 254.1176; found 254.1185.

3-(5-((*tert*-Butyldimethylsilyl)oxy)pent-1-yn-1-yl)quinoline (**SI-39**).



SI-37 **SI-39**

TBSCl (214 mg, 1.42 mmol, 1.5 equiv.) was added to a solution of alcohol **SI-37** (200 mg, 0.947 mmol, 1 equiv.) and triethylamine (0.21 mL, 1.5 mmol, 1.6 equiv.) in CH_2Cl_2 (1.60 mL, 0.5 M) and the resulting mixture was stirred for 16 hours at room temperature. The reaction was quenched by the addition of sat. aq. NH_4Cl (10 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The comb. org. extracts were washed with brine (20 mL) and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica, pentane:EtOAc 10:1) and 275 mg (0.85 mmol, 89%) of the title compound **SI-39** were isolated as a colorless oil.

R_f: 0.5 (silica, pentane:EtOAc 10:1);

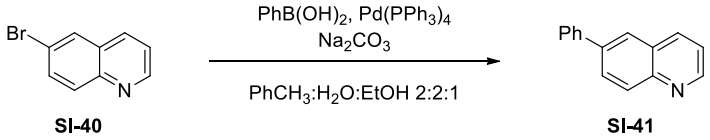
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (t, *J* = 1.6 Hz, 1H, Ar*H*), 8.16 (t, *J* = 2.6 Hz, 1H, Ar*H*), 8.11 – 8.04 (m, 1H, Ar*H*), 7.80 – 7.73 (m, 1H, Ar*H*), 7.69 (m, 1H, Ar*H*), 7.59 – 7.49 (m, 1H, Ar*H*), 3.85 – 3.71 (m, 2H, C*H*$_2$-OTBS), 2.57 (td, *J* = 7.0, 1.7 Hz, 2H, C≡C-C*H*$_2$), 1.92 – 1.78 (m, 2H, CH_2-C*H*$_2$-CH_2), 0.92 (s, 9H, Si-*tBu*), 0.09 (s, 6H, Si-*(CH$_3$)$_2$*);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.5, 146.5, 138.2, 129.9, 129.3, 127.6, 127.5, 127.3, 118.3, 93.8, 78.1, 61.6, 31.7, 26.1, 18.5, 16.1, -5.2 ppm.

IR (film): $\tilde{\nu}$ = 2953 (m), 2929 (m), 2856 (m), 2365 (w), 2233 (w), 1490 (w), 1472 (w), 1463 (w), 1276 (m), 1258 (s), 1103 (s), 1071 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{20}H_{28}NOSi^+$ $[M+H]^+$ 326.1935; found 326.1945.

6-Phenylquinoline (**SI-41**).



SI-40 **SI-41**

Following a modified procedure,[12] a mixture of 6-bromo-quinoline (**SI-40**) (0.70 mL, 5.00 mmol, 1 equiv.), sodium carbonate (2.12 g, 20.0 mmol, 4 equiv.), phenylboronic acid (732 mg, 6.00 mmol, 1.2 equiv.), water (4 mL), toluene (4 mL) and ethanol (2 mL) was degassed by nitrogen bubbling, then $Pd(PPh_3)_4$ (0.29 g, 0.25 mmol, 5 mol%) was added and the mixture was heated to 75 °C for 12 hours. Thereafter the mixture was filtered through a plug of celite®, the filtrate was diluted with water (20 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined org. extracts were washed with brine (20 mL) and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1 to 1:1) and 740 mg (3.61 mmol, 72%) of the title compound **SI-41** were isolated as a red-brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (dd, *J* = 4.3, 1.7 Hz, 1H, Ar*H*), 8.23 (dt, *J* = 7.4, 2.6 Hz, 2H, Ar*H*), 8.04 – 7.95 (m, 2H, Ar*H*), 7.77 – 7.67 (m, 2H, Ar*H*), 7.51 (dd, *J* = 8.4, 6.9 Hz, 2H, Ar*H*), 7.47 – 7.38 (m, 2H, Ar*H*) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.0, 147.2, 140.2, 139.5, 136.6, 129.6, 129.4, 129.0, 128.5, 127.8, 127.4, 125.4, 121.4 ppm.

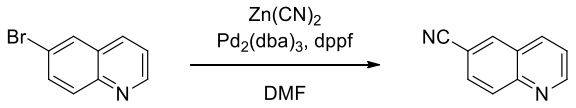
IR (film): $\tilde{\nu}$ = 3015 (w), 2326 (w), 1903 (w), 1775 (w), 1685 (w), 1591 (m), 1489 (s), 1444 (m), 1328 (m), 1276 (s), 1261 (s), 1188 (w), 1123 (m), 1040 (w), 891 (m), 845 (s) cm^{-1}.

HRMS (ESI) calcd. for $C_{15}H_{12}N^+$ $[M+H]^+$ 206.0964; found 206.0967.

The analytical data match the literature report.[12]

[12] L. Mengozzi, A. Gualandi, P.-G. Cozzi *Eur. J. Org. Chem*. **2016**, *19*, 3200-3207.

Quinoline-6-carbonitrile (**SI-42**).



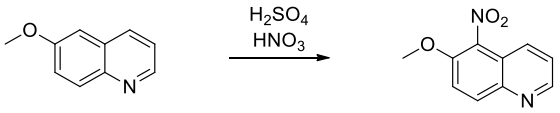
SI-40 **SI-42**

Following a modified procedure,[13] 6-bromoquinoline (**SI-40**) (0.70 mL, 5.00 mmol, 1 equiv.), $Zn(CN)_2$ (881 mg, 7.50 mmol, 1.5 equiv.) and dppf (0.28 mg, 0.50 mmol, 10 mol%) were dissolved in DMF (10 mL, 0.5 M), the mixture was degassed by N_2 bubbling for 10 minutes, then Pd_2dba_3 (0.23 g, 0.25 mmol, 5 mol%) was added and the mixture was heated to 130 °C for 14 hours. After cooling to room temperature the reaction was quenched with water (20 mL) and the mixture was extracted with EtOAc (3 x 20 mL). The comb. org. extracts were washed with brine (20 mL) and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by column chromatography (silica, pentane:EtOAc 5:1) and 581 mg (3.77 mmol, 75%) of the title compound **SI-42** were isolated as an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.07 (dd, *J* = 4.3, 1.7 Hz, 1H, Ar*H*), 8.30 – 8.16 (m, 3H, Ar*H*), 7.88 (dd, *J* = 8.7, 1.7 Hz, 1H, Ar*H*), 7.56 (dd, *J* = 8.4, 4.3 Hz, 1H, Ar*H*);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.1, 149.0, 136.5, 134.1, 131.0, 130.2, 127.6, 122.7, 118.5, 110.5 ppm.
IR (film): $\tilde{\nu}$ = 2987 (s), 2901 (m), 2328 (w), 1764 (w), 1699 (w), 1543 (w), 1509 (w), 1413 (m), 1339 (m), 1233 (s), 1059 (s) cm^{-1};
HRMS (ESI) calcd. for $C_{10}H_7N_2^+$ $[M+H]^+$ 155.0604; found 155.0603.

The analytical data match the literature report.[13]

6-Methoxy-5-nitroquinoline (**SI-44**).



SI-43 **SI-44**

Following a modified procedure,[14] 6-methoxy-quinoline (**SI-43**) (1.00 mL, 7.22 mmol) was added dropwise to a mixture of H_2SO_4 (4.00 mL) and HNO_3 (4.00 mL) at 0 °C and the resulting mixture was stirred for 1 hour. The reaction was basified with sat. aq. Na_2CO_3 and extracted with CH_2Cl_2 (3 x 50 mL). The comb. org. extracts were washed with brine (50 mL) and dried over $MgSO_4$. The drying agent was

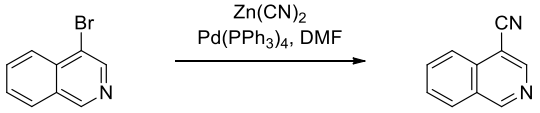
[13] F. Zhao, J. Zhang, L. Zhang, Y. Hao, C. Shi, G. Xia, J. Yu, , Y. Liu *Bioorg.Med. Chem.* **2016**, *24,* 4281-4290.
[14] H.-Y. Lee, J.-Y. Chang, C.-Y. Nien, C.-C. Kuo, K.-H. Shih, C.-H. Wu, C.-Y. Chang, W.-Y. Lai, J.-P. Liou *J. Med. Chem.* **2011**, *54*, 8517-8525.

filtered off and the solvent was evaporated. The crude product was purified by column chromatography (SiO_2, pentane:EtOAc 1:1) and 1.14 g (5.58 mmol, 77%) of the title compound **SI-44** were isolated as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 (dd, *J* = 4.1, 1.5 Hz, 1H, Ar*H*), 8.28 (d, *J* = 9.5 Hz, 1H, Ar*H*), 8.08 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.59 (d, *J* = 9.5Hz, 1H, Ar*H*), 7.53 (dd, *J* = 8.7, 4.1 Hz, 1H, Ar*H*), 4.08 (s, 3H, OCH_3).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.5, 149.2, 142.3, 134.6, 134.1, 129.2, 123.6, 121.4, 116.3, 57.2 ppm;
IR (film): $\tilde{\nu}$ = 2978 (s), 2909 (m), 2350 (w), 1648 (w), 1516 (w), 1389 (w), 1245 (w), 1068 (s), 878 (w) cm^{-1};
HRMS (ESI) calcd. for $C_{10}H_9N_2O_3^+$ $[M+H]^+$ 205.0608; found 205.0612.

The analytical data match the literature report.[14]

Isoquinoline-4-carbonitrile (**SI-46**).



SI-45 **SI-46**

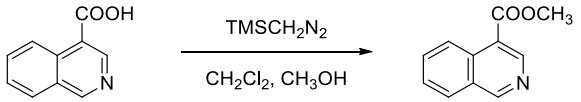
Following a modified procedure,[15] $Pd(PPh_3)_4$ (0.29 g, 0.25 mmol, 8 mol%) was added in one portion to a solution of 4-bromoisoquinoline (**SI-45**) (624 mg, 3.00 mmol, 1 equiv.) and $Zn(CN)_2$ (352 mmol, 3.00 mmol, 1 equiv.) in DMF (5 mL, 0.6 M) and the resulting mixture was heated to 80 °C for 16 hours. The reaction was quenched with sat. aq. Na_2CO_3 (10 mL) and the mixture was extracted 3 times with CH_2Cl_2 (10 mL). The combined org. extracts were washed with brine (15 mL) and the solvent was evaporated. The residue was purified by column chromatography (silica, pentane:EtOAc 4:1) and 412 mg (2.67 mmol, 89%) of the title compound **SI-46** were isolated as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.30 (s, 1H, Ar*H*), 8.76 (s, 1H, Ar*H*), 8.07 – 7.92 (m, 2H, Ar*H*), 7.81 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H, Ar*H*), 7.68 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H, Ar*H*);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.9, 147.9, 134.0, 132.7, 128.9, 128.2, 127.1, 123.6, 115.6, 105.5;
IR (film): $\tilde{\nu}$ = 3058 (w), 2230 (m), 1623 (m), 1578 (w), 1502 (m), 1390 (m), 1380 (m), 1268 (s), 1221 (w), 1149 (w), 909 (m) cm^{-1};
HRMS (ESI) calcd. for $C_{10}H_7N_2^+$ $[M+H]^+$ 155.0604; found 155.0602.

The analytical data match the literature report.[15]

[15] J. C. Barrow, B. D. Dorsey, H. G. Selnick, P. L. Ngo WO2001070229 A1.

Methyl isoquinoline-4-carboxylate (**SI-48**).



SI-47 **SI-48**

TMS diazomethane (1.08 mL, 2.17 mmol, 2 M in Et_2O) was added dropwise to a suspension of isoquinoline-4-carboxylic acid **SI-47** (250 mg, 1.44 mmol) in CH_2Cl_2 (10 mL) and CH_3OH (4 mL) at 0 °C. The resulting mixture was stirred for 16 hours while warming to room temperature, then the solvent was evaporated. The residue was purified by column chromatography (silica, pentane:EtOAc 3:1) affording 232 mg (1.24 mmol, 86%) of the title compound **SI-48** as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.38 (s, 1H), 9.19 (s, 1H), 8.96 (dq, *J* = 8.8, 0.9 Hz, 1H), 8.05 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.91 – 7.81 (m, 1H), 7.69 (m, 1H), 4.04 (s, 3H);

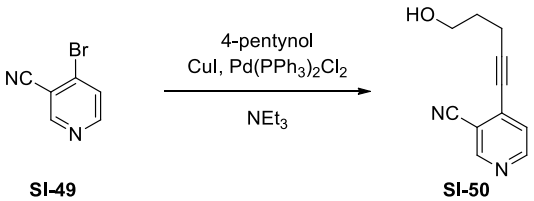
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.8, 156.9, 146.7, 133.9, 132.3, 128.4, 128.3, 127.7, 125.0, 120.5, 52.3;

IR (film): $\tilde{\nu}$ = 3014 (w), 2958 (w), 1722 (s), 1624 (w), 1572 (w), 1505 (m), 1436 (m), 1378 (w), 1294 (s), 1238 (w), 1208 (s), 1143 (m), 1045 (m), 1023 (w), 918 (w), 866 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{11}H_{10}NO_2^+$ $[M+H]^+$ 188.0706; found 188.0713.

The analytical data match the literature report.[16]

4-(5-Hydroxypent-1-yn-1-yl)nicotinonitrile (**SI-50**).



SI-49 **SI-50**

4-Pentynol (712 µL, 7.65 mmol, 4 equiv.) was added to a degassed (pump and freeze, 3 cycles) solution of 4-bromonicotinonitrile (**SI-49**) (350 mg, 1.91 mmol, 1 equiv.) $Pd(PPh_3)_2Cl_2$ (67 mg, 10 µmol, 5 mol%) and CuI (36 mg, 0.19 mmol, 10 mol%) in NEt_3 (3.8 mL, 0.5 M) and the resulting mixture was heated to 40 °C for 1.5 hours. After cooling to room temperature, sat. aq. NH_4Cl (15 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined org. extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica, pentane:EtOAc 1:1 to 1:2) and 332 mg (1.78 mmol, 93%) of the title compound **SI-50** were isolated as an orange oil.

[16] J. R. Martinelli, D. A. Watson, D. M. Freckmann, T. E. Barder, S. L. Buchwald *J. Org. Chem.* **2008**, *73*, 7102-7107.

R_f: 0.2 (silica, pentane:EtOAc 1:1);

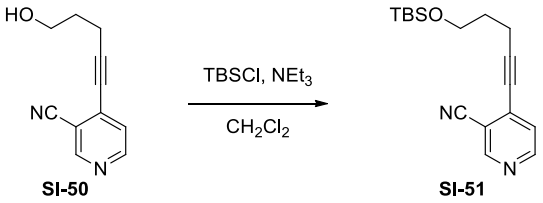
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (s, 1H, Ar*H*), 8.69 (d, *J* = 5.2 Hz, 1H, Ar*H*), 7.36 (d, *J* = 5.2 Hz, 1H, Ar*H*), 3.85 (t, *J* = 6.1 Hz, 2H, C*H*$_2$OH), 2.67 (t, *J* = 6.9 Hz, 2H, C≡C-C*H*$_2$), 1.91 (p, *J* = 6.5 Hz, 3H, C*H*$_2$ and O*H* underneath);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.5, 152.3, 135.6, 125.5, 115.8, 112.2, 103.4, 75.9, 61.0, 30.6, 16.2 ppm.

IR (film): $\tilde{\nu}$ = 3396 (w), 2932 (w), 2877 (w), 2235 (m), 1584 (s), 1537 (w), 1486 (w), 1409 (w), 1186 (w), 1058 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{11}H_{11}N_2O^+$ $[M+H]^+$ 187.0866; found 187.0865.

4-(5-((*tert*-Butyldimethylsilyl)oxy)pent-1-yn-1-yl)nicotinonitrile (**SI-51**).



TBSCl (389 mg, 2.58 mmol, 1.5 equiv.) was added to a solution of **SI-50** (320 mg, 1.78 mmol, 1 equiv.) and NEt_3 (480 µL, 3.44 mmol, 2 equiv.) in CH_2Cl_2 (3.4 mL) at room temperature and the mixture was stirred for 16 hours. The reaction was quenched with sat. aq. NH_4Cl (15 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined org. extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica, pentane:EtOAc 10:1 to 5:1) and 404 mg (1.35 mmol, 78%) of the title compound **SI-51** were isolated as an orange oil.

R_f: 0.7 (silica, pentane:EtOAc 2:1);

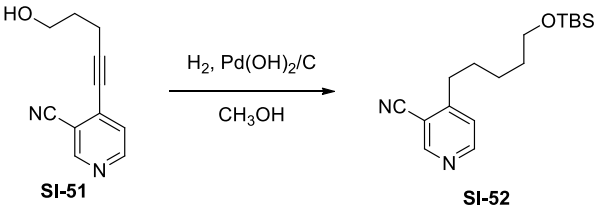
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 0.9 Hz, 1H, Ar*H*), 8.68 (d, *J* = 5.3 Hz, 1H, Ar*H*), 7.35 (dd, *J* = 5.3, 0.9 Hz, 1H, Ar*H*), 3.77 (t, *J* = 5.9 Hz, 2H, C*H*$_2$OTBS), 2.63 (t, *J* = 7.1 Hz, 2H, C≡C-C*H*$_2$), 1.86 (tt, *J* = 7.1, 5.9 Hz, 2H, C*H*$_2$), 0.90 (s, 9H, C(C*H*$_3$)$_3$), 0.07 (s, 6H, Si(C*H*$_3$)$_2$);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.6, 152.2, 135.7, 125.6, 115.7, 112.1, 104.0, 75.6, 61.2, 31.1, 25.9, 18.3, 16.2, -5.4 ppm;

IR (film): $\tilde{\nu}$ = 2956 (m), 2931 (w), 2855 (w), 2236 (w), 1583 (m), 1537 (w), 1485 (w), 1408 (w), 1107 (s), 838 (s) cm^{-1};

HRMS (ESI) calcd. for $C_{17}H_{25}N_2OSi^+$ $[M+H]^+$ 301.1731; found 301.1730.

4-(5-((*tert*-Butyldimethylsilyl)oxy)pentyl)nicotinonitrile (**SI-52**).



$Pd(OH)_2/C$ (34 mg, 20% Pd, 10%$_{w/w}$) was added to a solution of **SI-51** (340 mg, 1.13 mmol) in CH_3OH (2.3 mL, 0.5 M) and the resulting mixture was purged with hydrogen and thereafter stirred for 18 hours under H_2-atmosphere (1 atm). Then the mixture was filtered through a plug of Celite® and concentrated. The residue was purified by column chromatography (silica, pentane:EtOAc 10:1 to 5:1) affording 243 mg (0.80 mmol, 71%) of the title compound **SI-52** as a colorless oil.

R_f: 0.7 (silica, pentane:EtOAc 2:1);

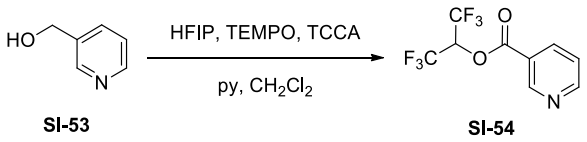
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, *J* = 0.8 Hz, 1H, Ar*H*), 8.65 (d, *J* = 5.2 Hz, 1H, Ar*H*), 7.26 (dd, *J* = 5.2, 0.8 Hz, 1H, Ar*H*), 3.60 (t, *J* = 6.3 Hz, 2H, CH_2OTBS), 2.90 – 2.77 (m, 2H, Ar-CH_2), 1.76 – 1.65 (m, 2H CH_2), 1.60 – 1.50 (m, 2H CH_2), 1.47 – 1.36 (m, 2H CH_2), 0.86 (s, 9H, C(CH_3)$_3$), 0.02 (s, 6H Si(CH_3)$_2$) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.3, 152.9, 152.5, 123.9, 115.9, 110.4, 62.7, 34.0, 32.3, 29.6, 25.9, 25.4, 18.3, -5.3 ppm.

IR (film): $\tilde{\nu}$ = 2931 (w), 2857 (w), 2229 (w), 1590 (w), 1556 (w), 1472 (w), 1463 (w), 1407 (w), 1255 (m), 834 (s) cm^{-1};

HRMS (ESI) calcd. for $C_{17}H_{25}N_2OSi^+$ $[M+H]^+$ 301.1731; found 301.1730.

1,1,1,3,3,3-Hexafluoropropan-2-yl nicotinate (**SI-54**).



Following a modified procedure,[17] TEMPO (161 mg, 1.03 mmol, 5 mol%) followed by trichloroisocyanuric acid (5.75 g, 24.7 mmol, 1.2 equiv.) were added to a solution of pyridine-3-ylmethanol (**SI-53**) (2.00 mL, 20.6 mmol, 1 equiv.) in CH_2Cl_2 (41.2 mL, 0.5 M) at 0 °C and the resulting mixture was stirred for 2 hours. Thereafter pyridine (6.70 mL, 82.0 mmol, 4 equiv.) followed by 1,1,1,3,3,3-hexafluoropropan-2-ol (4.40 mL, 41.2 mmol, 2 equiv.) were added and stirring was continued for 16 hours at room temperature. The reaction mixture was filtered through a plug of

[17] J.-M. Vatéle *Synlett* **2015**, *26*, 2280-2284.

Celite® and concentrated. The residue was purified by column chromatography (silica, pentane:EtOAc 5:1) affording 4.53 g (16.6 mmol, 81%) of the title compound **SI-54** as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.28 (dd, *J* = 2.2, 0.8 Hz, 1H, Ar*H*), 8.86 (dd, *J* = 4.9, 1.7 Hz, 1H, Ar*H*), 8.42 (ddd, *J* = 8.0, 2.2, 1.7 Hz, 1H, Ar*H*), 7.54 (ddd, *J* = 8.0, 4.9, 0.8 Hz, 1H, Ar*H*), 6.02 (p, *J* = 6.0 Hz, 1H, C*H*$(CF_3)_2$);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.9, 154.5, 151.0, 138.3, 124.0, 123.4, 120.7 (q, *J* = 282.6 Hz), 67.1 (p, *J* = 67.2 Hz);

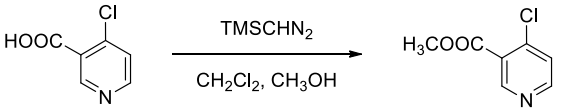
^{19}F NMR (376 MHz, $CDCl_3$): δ = -75.60 (d, *J* = 5.8 Hz);

IR (film): $\tilde{\nu}$ = 1764 (m), 1595 (w), 1426 (w), 1386 (w), 1361 (w), 1297 (m), 1266 (m), 1197 (s), 1101 (s), 1017 (w), 912 (m) cm^{-1};

HRMS (ESI) calcd for $C_9H_6F_6NO_2^+$ $[M+H]^+$ 274.0297; found 274.0300.

The analytical data match the literature report.[18]

Methyl 4-chloronicotinate (**SI-56**).



SI-55 **SI-56**

Following a modified procedure,[19] trimethylsilyldiazomethane (4.76 mL, 9.52 mmol, 1.5 equiv.) was added dropwise to a suspension of chloronicotinic acid (**SI-55**) (1.00 g, 6.35 mmol, 1 equiv.) in a mixture of CH_2Cl_2 (5.5 mL) and methanol (2.2 mL) at 0 °C. The resulting mixture was warmed to room temperature and stirred for 1 hour, then concentrated and the residue was purified by column chromatography (silica, pentane:EtOAc 10:1 to 5:1) affording 1.02 g (5.92 mmol, 93%) of the title compound **SI-56** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.03 (t, *J* = 0.6 Hz, 1H), 8.58 (dd, *J* = 5.4, 0.6 Hz, 1H), 7.49 – 7.28 (m, 1H), 3.97 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.2, 152.6, 152.2, 144.2, 125.9, 125.8, 52.7 ppm;

IR (film): $\tilde{\nu}$ = 3003 (w), 2953 (w), 1725 (s), 1627 (w), 1573 (m), 1436 (m), 1292 (s), 1275 (s), 1130 (m), 1082 (s), 1046 (w), 955 (w), 832 (m) cm^{-1};

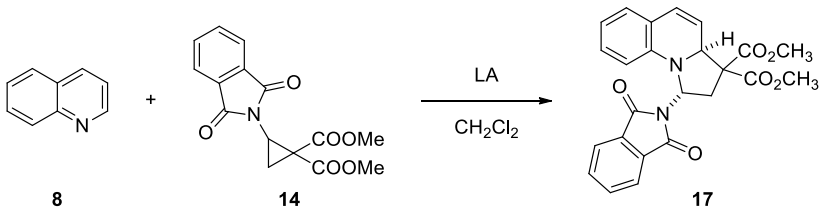
HRMS (ESI) calcd. for $C_7H_7ClNO_2^+$ $[M+H]^+$ 172.0160; found 172.0161.

The analytical data match the literature report.[19]

[18] C. B. Kelly, M. A. Mercadante, R. J. Wiles, N. E. Leadbeater *Org. Lett.* **2013**, *15*, 2222-2225.
[19] D. Norton, D. Andreotti, S. E. Ward, R. Profeta, S. Spada, H. S. Price WO 2012098400 A1.

6. Optimization of the reaction

Table S7 Optimization of the annulation of quinoline (**8**) and cyclopropane **14**.



8 **14** **17**

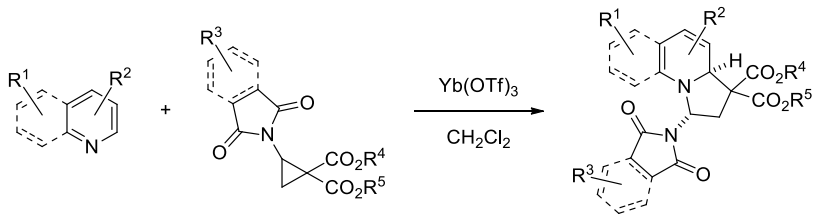
Entry	14	Lewis Acid (mol%)	Conc.	Result[a]	Comment[b]
1	1.0 equiv.	$Sc(OTf)_3$ (20 mol%)	0.1 M	30% of **17**	full conversion of cyclopropane
2	1.0 equiv.	$Sc(OTf)_3$ (20 mol%)	0.05 M	62% of **17**	full conversion of cyclopropane
3	1.5 equiv.	$Sc(OTf)_3$ (20 mol%)	0.1 M	69% of **17**	full conversion of cyclopropane
4	1.5 equiv.	$Sc(OTf)_3$ (20 mol%)	0.05 M	80% of **17**	full conversion of cyclopropane
5	1.5 equiv.	$Sn(OTf)_2$ (20 mol%)	0.05 M	no conversion	
6	1.5 equiv.	$In(OTf)_3$ (20 mol%)	0.05 M	no conversion	
7	1.5 equiv.	$Cu(OTf)_2$ (20 mol%)	0.05 M	no conversion	
8	1.5 equiv.	$Hf(OTf)_4$ (20 mol%)	0.05 M	decomposition	
9	1.5 equiv.	$FeCl_3$ (20 mol%)	0.05 M	no conversion	
10	1.5 equiv.	$FeCl_2$ (20 mol%)	0.05 M	no conversion	
11	1.5 equiv.	$InCl_3$ (20 mol%)	0.05 M	no conversion	
12	1.5 equiv.	$MgCl_2$ (20 mol%)	0.05 M	no conversion	
13	1.5 equiv.	$Yb(OTf)_3$ (20 mol%)	0.05 M	90% of **17**	remaining cyclopropane
14	1.1 equiv.	$Yb(OTf)_3$ (20 mol%)	0.05 M	88% of **17**	
15	1.05 equiv.	$Yb(OTf)_3$ (10 mol%)	0.05 M	89% of **17**	reaction time: 2 days
16	1.05 equiv.	$Yb(OTf)_3$ (5 mol%)	0.05 M	96% of **17**	reaction time: 4 days
17	1.05 equiv.	$Yb(OTf)_3$ (5 mol%)	0.5 M	96% of **17**	reaction time: 16 hours
18	1.05 equiv.	HOTf (20 mol%)	0.2 M	no conversion	

[a] Yields determined by isolation; [b] remaining cyclopropane was detected by TLC.

Experimental procedure for optimization

A vial was charged with cyclopropane **14**, the Lewis acid and quinoline **8** (0.10 mmol, 1.00 equiv.) in the glovebox, then capped, removed from the glovebox and CH_2Cl_2 was added. The mixture was stirred, if not stated otherwise in the table, for 16 hours, then concentrated and the residue was purified by column chromatography.

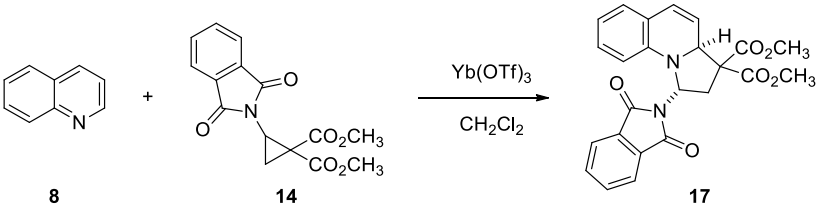
7. General procedure



A vial was charged with cyclopropane (0.21 mmol, 1.05 equiv.), $Yb(OTf)_3$ (0.01 mmol, 5 mol% or 0.02 mmol, 10 mol%) and the *N*-heterocyclic compound (0.20 mmol, 1.00 equiv.) in the glovebox, then capped, removed from the glovebox and CH_2Cl_2 was added. The mixture was stirred for the indicated time, then concentrated and the residue was purified by column chromatography to afford the title compound.

8. Scope of the reaction with quinolines

***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**17**).



8 **14** **17**

Following the general procedure quinoline (**8**) (260 mg, 2.00 mmol, 1.00 equiv.), cyclopropane **14** (640 mg, 2.10 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (62 mg, 0.10 mmol, 5 mol%) were stirred in CH_2Cl_2 (4.0 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 820 mg (1.90 mmol, 95%) of the title compound **17** were isolated as a yellow oil which was crystallized from EtOAc by overlaying it with pentane.

Performing the reaction with quinoline **8** (26 mg, 0.20 mmol), **14** (64 mg, 0.21 mmol) and $Yb(OTf)_3$ (6 mg, 0.01 mmol) afforded 83 mg (0.19 mmol, 96%) of the title compound **17**.

mp: 127-129 °C;

R_f: 0.3 (silica, pentane:EtOAc 4:1);

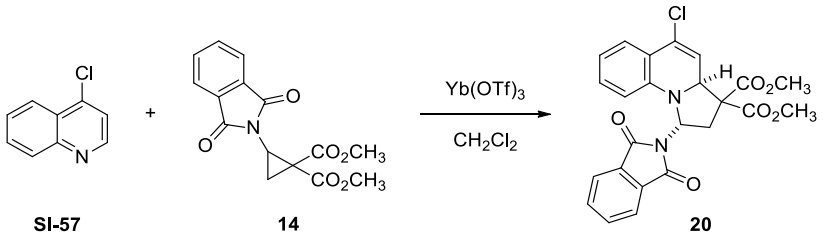
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 6.95 (td, *J* = 7.9, 1.6 Hz, 1H, Ar*H*), 6.78 (dd, *J* = 7.4, 1.6 Hz, 1H, Ar*H*), 6.55 (td, *J* = 7.4, 1.0 Hz, 1H, Ar*H*), 6.42 (d, *J* = 7.9 Hz, 1H, Ar*H*), 6.30 (dd, *J* = 10.2, 2.0 Hz, 1H, C=C*H*), 6.21 (dd, *J* = 8.6, 5.9 Hz, 1H, N-C*H*-Phth), 5.94 (t, *J* = 2.5 Hz, 1H, C*H*-N), 5.85 (dd, *J* = 10.2, 2.9 Hz, 1H, CH=C*H*), 3.82 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 2.98 (dd, *J* = 13.7, 8.6 Hz, 1H, CH_2), 2.53 (dd, *J* = 13.7, 5.9 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.0, 169.1, 167.7, 141.6, 134.3, 131.7, 129.5, 127.2, 126.2, 123.4, 120.4, 119.4, 118.0, 109.7, 67.3, 65.3, 64.4, 52.7, 52.6, 35.3 ppm;

IR (film): $\tilde{\nu}$ = 3050 (w), 2996 (w), 2953 (w), 1721 (s), 1604 (w), 1497 (w), 1458 (w), 1442 (w), 1390 (w), 1357 (m), 1321 (m), 1273 (s), 1222 (w), 1141 (w), 1078 (w), 969 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{24}H_{20}N_2NaO_6^+$ $[M+Na]^+$ 455.1214; found 455.1223.

***anti*-Dimethyl 5-chloro-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**20**).



SI-57 **14** **20**

Following the general procedure 4-chloroquinoline (**SI-57**) (33 mg, 0.20 mmol, 1.00 equiv.), cyclopropane **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 84 mg (0.18 mmol, 90%) of the title compound **20** were isolated as a yellow oil.

R_f: 0.3 (silica, pentane:EtOAc 4:1);

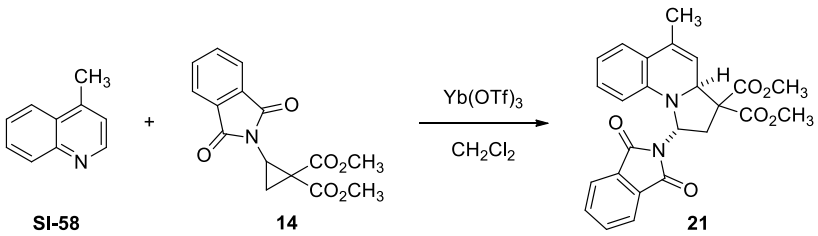
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.73 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.32 (dd, *J* = 7.8, 1.6 Hz, 1H, Ar*H*), 7.03 (td, *J* = 7.8, 1.6 Hz, 1H, Ar*H*), 6.63 (td, *J* = 7.5, 1.0 Hz, 1H, Ar*H*), 6.44 (d, *J* = 8.2 Hz, 1H, Ar*H*), 6.20 (dd, *J* = 8.6, 5.9 Hz, 1H, C*H*-Phth), 6.06 (d, *J* = 3.3 Hz, 1H, C*H*=CCl), 5.97 (d, *J* = 3.3 Hz, 1H, C*H*-N), 3.83 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.00 (dd, *J* = 13.8, 8.6 Hz, 1H, CH_2), 2.51 (dd, *J* = 13.8, 5.9 Hz, 1H, CH_2) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.6, 168.7, 167.6, 142.1, 134.4, 131.5, 130.8, 129.6, 125.2, 123.5, 118.2, 118.1, 117.1, 109.9, 67.1, 65.1, 65.0, 52.9, 52.8, 35.0 ppm;

IR (film): $\tilde{\nu}$ = 2955 (w), 2925 (w), 2852 (w), 1772 (w), 1732 (s), 1710 (s), 1647 (w), 1598 (w), 1491 (m), 1458 (w), 1436 (w), 1396 (w), 1354 (w), 1276 (m), 1266 (s) cm^{-1};

HRMS (ESI) calcd. for $C_{24}H_{20}ClN_2O_6^+$ $[M+H]^+$ 467.1004; found 467.0997.

***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-5-methyl-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**21**).



SI-58 **14** **21**

Following the general procedure lepidine (**SI-58**) (29 mg, 0.20 mmol, 1.00 equiv.), cyclopropane **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 83 mg (0.19 mmol, 93%) of the title compound **21** were isolated as a yellow oil.

R_f: 0.3 (silica, pentane:EtOAc 4:1);

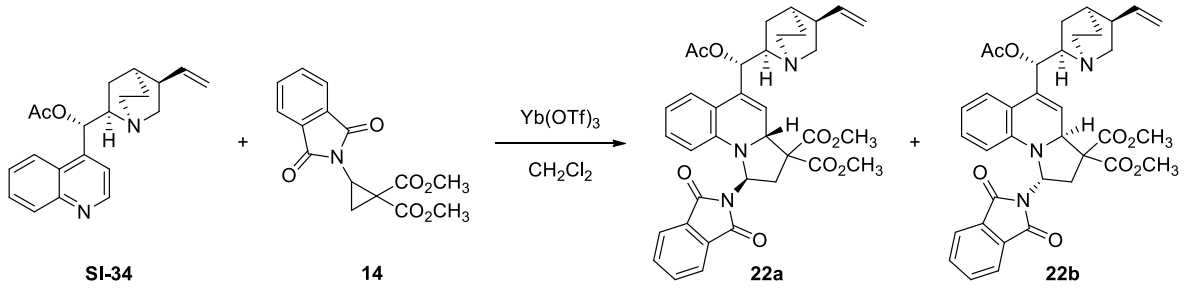
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 6.98 (td, *J* = 7.3, 1.3 Hz, 2H, Ar*H*), 6.60 (td, *J* = 7.3, 1.3 Hz, 1H, Ar*H*), 6.44 (d, *J* = 8.2 Hz, 1H, Ar*H*), 6.22 (dd, *J* = 8.6, 5.9 Hz, 1H, C*H*-Phth), 5.87 (dd, *J* = 3.1, 1.6 Hz, 1H, C*H*-N), 5.73 (dd, *J* = 3.1, 1.6 Hz, 1H, C*H*=CCH$_3$), 3.82 (s, 3H, OC*H$_3$*), 3.59 (s, 3H, OC*H$_3$*), 2.98 (dd, *J* = 13.7, 8.6 Hz, 1H, C*H$_2$*), 2.51 (dd, *J* = 13.7, 5.9 Hz, 1H, C*H$_2$*), 1.98 (t, *J* = 1.6 Hz, 3H, C*H$_3$*);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.0, 169.3, 167.7, 141.8, 134.3, 131.7, 130.7, 129.3, 123.8, 123.4, 120.6, 117.8, 117.8, 109.7, 67.6, 65.2, 64.1, 52.7, 52.5, 35.3, 19.0;

IR (film): $\tilde{\nu}$ 2987 (s), 2972 (s), 2902 (m), 2362 (w), 1717 (w), 1406 (w), 1395 (w), 1384 (w), 1276 (w), 1258 (w), 1231 (w), 1076 (s), 1066 (s), 1057 (s) cm^{-1};

HRMS (ESI) calcd for $C_{25}H_{23}N_2O_6^+$ $[M+H]^+$ 447.1551; found 447.1548.

(1*R*,3a*R*)-Dimethyl 5-((*S*)-acetoxy((1*S*,2*R*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl)-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (**22a**) and **(1*S*,3a*S*)-dimethyl 5-((*S*)-acetoxy((1*S*,2*R*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl)-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**22b**)



SI-34 **14** **22a** **22b**

Following the general procedure **SI-34** (67 mg, 0.20 mmol, 1.00 equiv.), cyclopropane **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, EtOAc:CH_3OH 30:1 to 20:1) and 97 mg (0.15 mmol, 76%) of the title compounds **22a** and **22b** were isolated as a yellow oil and 1:1 mixture of diastereoisomers.[20]

R_f: 0.1 (silica, EtOAc: CH_3OH 30:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 5.7 Hz, 4H), 7.78 – 7.69 (m, 4H), 7.18 (m, 2H, Ar*H*), 7.00 (m, 2H, Ar*H*), 6.63 (m, 2H, Ar*H*), 6.44 (m, 2H, Ar*H*), 6.17 (m, 2H, C*H*-Phth), 6.06 – 5.87 (m, 6H, =C*H*-N, C*H*-O and C*H*=CH_2), 5.84 (d, *J* = 8.1 Hz, 2H, C=C*H*), 5.29 – 4.96 (m, 4H, =CH_2), 3.82 (m, 6H, OCH_3), 3.62 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 3.23 – 2.86 (m, 12H, 3 x CH_2), 2.63 – 2.27 (m, 4H, CH_2), 2.14 (s, 6H, C(O)CH_3), 1.97 – 1.43 (m, 10H, CH_2, 3 x CH);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.0, 169.6, 169.2, 169.1, 168.7, 167.8, 167.7, 142.0, 141.6, 139.1, 138.7, 134.4, 132.7, 132.2, 131.6, 130.0, 129.7, 123.5, 123.1, 118.5, 118.1, 117.4, 116.8, 115.9, 115.6, 110.4, 67.9, 66.5, 65.3, 64.7, 64.0, 63.7, 57.4, 57.3, 53.1, 52.9, 52.8, 52.7, 50.0, 49.8, 49.2, 49.0, 38.8, 38.5, 35.7, 34.9, 27.8, 27.7, 25.4, 25.1, 21.2, 21.2;[21]

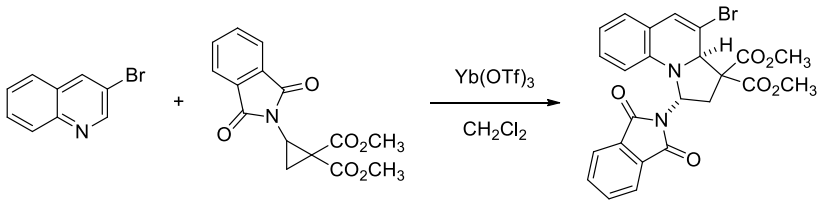
IR (film): $\tilde{\nu}$ 2987 (w), 2958 (w), 2902 (w), 1732 (s), 1714 (s), 1599 (w), 1498 (w), 1458 (w), 1437 (w), 1396 (w), 1363 (w), 1328 (w), 1268 (m), 1231 (s), 1211 (m), 1126 (w), 1105 (w), 1078 (m), 1031 (m), 967 (w), 919 (w), 879 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{36}H_{38}N_3O_8^+$ $[M+H]^+$ 640.2653; found 640.2647.

[20] The diastereomeric ratio was determined by integration of the methyl esters in the ^{1}H-NMR. Both the diastereoisomers were not individually assigned due to overlapping signals in ^{1}H-NMR.

[21] Some olefinic carbons are overlapping.

***anti*-Dimethyl 4-bromo-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**23**).



SI-35 **14** **23**

Following the general procedure 6-bromoquinoline (**SI-35**) (41 mg, 0.20 mmol, 1.00 equiv.), cyclopropane **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 94 mg (0.18 mmol, 92%) of the title compound **23** were isolated as an orange oil.

R_f: 0.4 (silica, pentane:EtOAc 4:1);

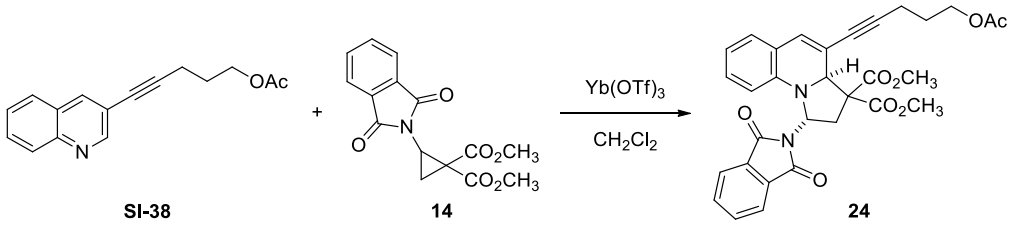
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.74 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.05 – 6.90 (m, 1H, Ar*H*), 6.76 (dd, *J* = 7.5, 1.5 Hz, 1H, Ar*H*), 6.74 – 6.65 (m, 1H, C*H*=CBr), 6.58 (td, *J* = 7.5, 1.5 Hz, 1H, Ar*H*), 6.42 (d, *J* = 8.2 Hz, 1H, Ar*H*), 6.28 (d, *J* = 1.4 Hz, 1H, C*H*-N), 6.15 (dd, *J* = 8.4, 7.0 Hz, 1H, C*H*-Phth), 3.84 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.11 (dd, *J* = 13.0, 8.4 Hz, 1H, CH_2), 2.72 (dd, *J* = 13.0, 7.0 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.6, 168.4, 167.5, 140.2, 134.4, 131.6, 130.0, 129.5, 126.8, 123.6, 118.9, 118.6, 115.4, 109.7, 70.5, 66.8, 65.5, 52.9, 52.7, 37.1 ppm;

IR (film): $\tilde{\nu}$ = 2955 (w), 2901 (w), 1772 (w), 1731 (m), 1714 (s), 1598 (w), 1495 (m), 1398 (w), 1365 (w), 1352 (w), 1264 (s), 1229 (w), 1134 (m), 1079 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{24}H_{18}BrN_2O_6$ [M+] 509.0343; found 509.0359.

***anti*-Dimethyl 4-(5-acetoxypent-1-yn-1-yl)-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**24**).



SI-38 **14** **24**

Following the general procedure **SI-38** (51 mg, 0.20 mmol, 1.00 equiv.), cyclopropane **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M)

for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 88 mg (0.16 mmol, 79%) of the title compound **24** were isolated as a yellow oil.

R_f: 0.2 (silica, pentane:EtOAc 4:1);

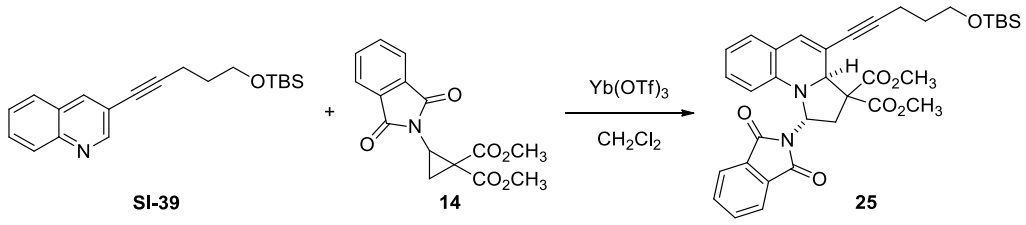
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 6.93 (td, *J* = 8.0, 1.5 Hz, 1H, Ar*H*), 6.75 (dd, *J* = 7.4, 1.5 Hz, 1H, Ar*H*), 6.54 (t, *J* = 7.4 Hz, 1H, Ar*H*), 6.50 (d, *J* = 1.5 Hz, 1H, C*H*=C), 6.38 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.17 – 6.08 (m, 2H, C*H*-N and C*H*-Phth), 4.19 (t, *J* = 6.3 Hz, 2H, CH_2-O), 3.80 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 3.04 (dd, *J* = 13.1, 8.4 Hz, 1H, CH_2), 2.63 (dd, *J* = 13.1, 6.5 Hz, 1H, CH_2), 2.45 (t, *J* = 7.0 Hz, 2H, C≡C-CH_2), 2.06 (s, 3H, COCH_3), 1.88 (p, *J* = 6.7 Hz, 2H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.9, 169.3, 168.7, 167.5, 140.9, 134.3, 131.6, 131.4, 130.0, 127.2, 123.5, 123.4, 119.2, 118.3, 114.5, 109.5, 91.9, 79.1, 67.0, 66.6, 65.1, 63.1, 52.6, 52.5, 37.3, 27.6, 20.9, 16.4 ppm;

IR (film): $\tilde{\nu}$ 2954 (w), 2851 (w), 1773 (w), 1731 (s), 1711 (s), 1597 (w), 1495 (w), 1459 (w), 1436 (w), 1397 (w), 1365 (w), 1353 (w), 1259 (s), 1242 (s), 1134 (w), 1075 (w), 1044 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{23}H_{24}NO_6$ [M+] 410.1598; found 410.1605.

***anti*-Dimethyl 4-(5-((*tert*-butyldimethylsilyl)oxy)pent-1-yn-1-yl)-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**25**).



Following the general procedure **SI-39** (65 mg, 0.20 mmol, 1.00 equiv.), cyclopropane **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 6:1) and 88 mg (0.16 mmol, 81%) of the title compound **25** were isolated as a yellow oil.

R_f: 0.5 (silica, pentane:EtOAc 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 6.93 (td, *J* = 7.6, 1.5 Hz, 1H, Ar*H*), 6.76 (dd, *J* = 7.6, 1.5 Hz, 1H, Ar*H*), 6.60 – 6.51 (m, 1H, Ar*H*), 6.49 (d, *J* = 1.5 Hz, 1H, C*H*=C), 6.38 (d, *J* = 8.1 Hz, 1H, Ar*H*), 6.17 – 6.08 (m, 2H, C*H*-N and C*H*-Phth), 3.81 (s, 3H, OCH_3), 3.72 (t, *J* = 6.0 Hz, 2H, CH_2O), 3.65 (s, 3H, OCH_3), 3.05 (dd, *J* = 13.1, 8.4 Hz, 1H, CH_2), 2.67 (dd, *J*

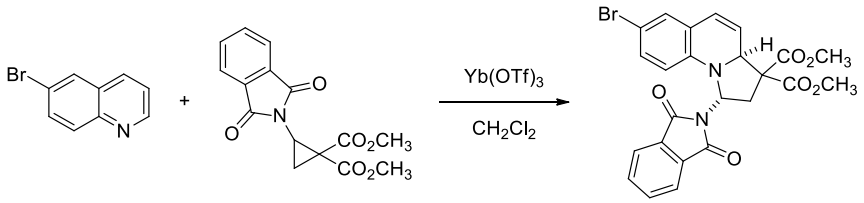
= 13.1, 6.6 Hz, 1H, CH_2), 2.43 (t, *J* = 7.2 Hz, 2H, C≡CCH_2), 1.81 – 1.72 (m, 2H, CH_2), 0.90 (s, 9H, SiC$(CH_3)_3$), 0.07 (s, 6H, Si$(CH_3)_2$);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.3, 168.7, 167.5, 140.9, 134.3, 131.7, 130.9, 129.9, 127.2, 123.5, 119.4, 118.3, 114.9, 109.5, 93.3, 78.5, 67.2, 66.6, 65.2, 61.7, 52.6, 52.5, 37.4, 31.8, 25.9, 18.3, 16.1, -5.4;

IR (film): $\tilde{\nu}$ 2953 (w), 2946 (w), 2856 (w), 1773 (w), 1731 (s), 1714 (s), 1598 (w), 1495 (w), 1460 (w), 1354 (w), 1289 (w), 1259 (m), 1134 (w), 1099 (m), 1076 (m), 836 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{27}H_{36}NO_5Si$ [M+] 482.2357; found 482.2363.

***anti*-Dimethyl 7-bromo-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**26**).



SI-40 **14** **26**

Following the general procedure 6-bromoquinoline (**SI-40**) (42 mg, 0.20 mmol, 1.00 equiv.), cyclopropane **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 98 mg (0.19 mmol, 96%) of the title compound **26** were isolated as an orange oil.

R_f: 0.4 (silica, pentane:EtOAc 4:1);

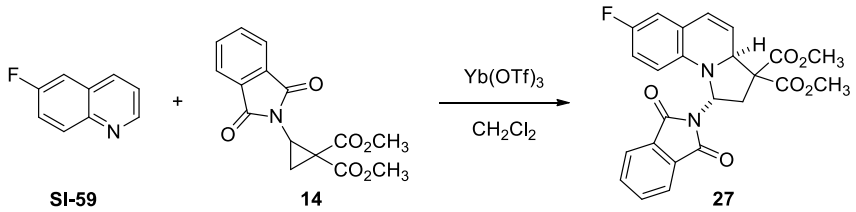
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.00 (dd, *J* = 8.6, 2.4 Hz, 1H, Ar*H*), 6.86 (d, *J* = 2.4 Hz, 1H, Ar*H*), 6.30 (d, *J* = 8.6 Hz, 1H, Ar*H*), 6.24 – 6.19 (m, 1H, CH=C*H*), 6.14 (dd, *J* = 8.7, 5.9 Hz, 1H, C*H*-Phth), 5.93 – 5.86 (m, 2H, CH=C*H* and C*H*-N), 3.81 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 2.96 (dd, *J* = 13.7, 8.7 Hz, 1H, CH_2), 2.52 (dd, *J* = 13.7, 5.9 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.8, 168.9, 167.6, 140.7, 134.4, 131.8, 131.5, 129.4, 125.1, 123.5, 121.8, 121.3, 111.4, 109.9, 67.1, 65.1, 64.3, 52.7, 52.7, 35.1;

IR (film): $\tilde{\nu}$ = 3466 (w), 3058 (w), 2956 (w), 2851 (w), 1772 (w), 1733 (s), 1709 (s), 1490 (m), 1436 (w), 1396 (w), 1352 (w), 1327 (w), 1266 (s), 1214 (m), 1179 (w), 1156 (w), 1130 (m), 1112 (m), 1087 (m), 970 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{24}H_{18}BrN_2O_6$ [M+] 509.0343; found 509.0343.

***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-7-fluoro-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**27**).



Following the general procedure 6-fluoroquinoline (**SI-59**) (29 mg, 0.20 mmol, 1.00 equiv.), cyclopropane **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 87 mg (0.19 mmol, 97%) of the title compound **27** were isolated as a yellow oil.

R_f: 0.3 (silica, pentane:EtOAc 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.73 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 6.64 (td, *J* = 8.6, 3.0 Hz, 1H, Ar*H*), 6.51 (dd, *J* = 8.6, 3.0 Hz, 1H, Ar*H*), 6.34 (dd, *J* = 8.9, 4.3 Hz, 1H, Ar*H*), 6.23 (dd, *J* = 10.0, 2.1 Hz, 1H, CH=C*H*), 6.16 (dd, *J* = 8.6, 5.9 Hz, 1H, C*H*-Phth), 5.97 – 5.86 (m, 2H, C*H*-N and C*H*=CH), 3.81 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 2.96 (dd, *J* = 13.7, 8.6 Hz, 1H, CH_2), 2.52 (dd, *J* = 13.7, 5.9 Hz, 1H, CH_2);

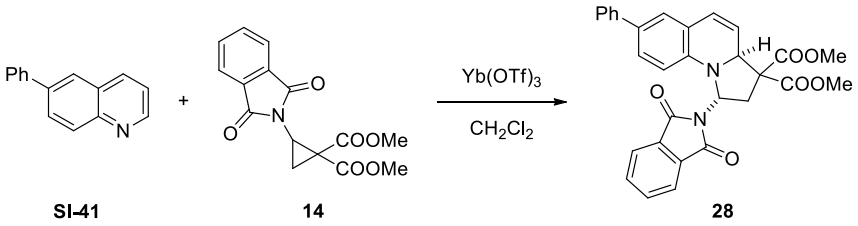
^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.0, 169.0, 167.7, 155.9 (d, *J* = 235.5 Hz), 138.1 (d, *J* = 1.9 Hz), 134.4, 131.6, 125.4 (d, *J* = 2.0 Hz), 123.5, 122.3, 120.4 (d, *J* = 7.5 Hz), 115.1 (d, *J* = 22.2 Hz), 113.7 (d, *J* = 23.9 Hz), 110.3 (d, *J* = 7.4 Hz), 67.8, 65.4, 64.4, 52.7, 52.7, 35.1;

^{19}F NMR (376 MHz, $CDCl_3$) δ = -127.77 (td, *J* = 8.6, 4.3 Hz) ppm.

IR (film): $\tilde{\nu}$ = 2958 (w), 2849 (w), 1773 (w), 1732 (s), 1709 (s), 1498 (s), 1436 (w), 1396 (w), 1352 (w), 1276 (s), 1246 (s), 1219 (m), 1160 (m), 1111 (m), 1078 (m), 952 (w), 873 (m) cm^{-1};

HRMS (ESI) calcd for $C_{24}H_{20}FN_2O_6^+$ $[M+H]^+$ 451.1300; found 451.1205.

***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-7-phenyl-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**28**).



SI-41 **14** **28**

Following the general procedure 6-phenylquinoline (**SI-41**) (41 mg, 0.20 mmol, 1.00 equiv.), cycloproane **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 98 mg (0.19 mmol, 96%) of the title compound **28** were isolated as a yellow oil.

R_f: 0.3 (silica, pentane:EtOAc 4:1);

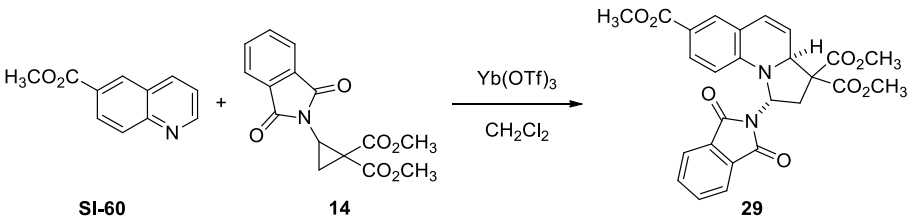
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.50 – 7.42 (m, 2H, Ar*H*), 7.35 (t, *J* = 7.7 Hz, 2H, Ar*H*), 7.25 – 7.19 (m, 2H, Ar*H*), 7.06 (d, *J* = 2.2 Hz, 1H, Ar*H*), 6.52 (d, *J* = 8.4 Hz, 1H, Ar*H*), 6.39 (dd, *J* = 10.2, 2.9 Hz, 1H, C*H*=CH), 6.27 (dd, *J* = 8.6, 5.9 Hz, 1H, C*H*-Phth), 5.97 (dd, *J* = 2.9, 1.9 Hz, 1H, C*H*-N), 5.92 (dd, *J* = 10.2, 2.9 Hz, 1H, CH=C*H*), 3.84 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.02 (dd, *J* = 13.7, 8.6 Hz, 1H, CH_2), 2.57 (dd, *J* = 13.7, 5.9 Hz, 1H,CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.0, 169.1, 167.8, 141.1, 140.7, 134.4, 131.7, 131.0, 128.6, 128.1, 126.3, 126.2, 126.1, 125.9, 123.5, 120.9, 119.8, 110.1, 67.2, 65.3, 64.5, 52.8, 52.8, 35.4 ppm;

IR (film): $\tilde{\nu}$ 1774 (w), 1732 (s), 1711 (s), 1651 (w), 1609 (w), 1488 (m), 1436 (w), 1395 (w), 1352 (m), 1327 (m), 1265 (s), 1219 (w), 1180 (w), 1131 (w), 1113 (w), 1077 (m), 1019 (w), 970 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{30}H_{25}N_2O_6^+$ $[M+H]^+$ 509.1707; found 509.1711.

***anti*-Trimethyl 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3,7(3a*H*)-tricarboxylate** (**29**).



SI-60 **14** **29**

Following the general procedure methyl quinoline-6-carboxylate (**SI-60**) (37 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography

(silica, pentane:EtOAc 10:1 to 4:1) and 93 mg (0.19 mmol, 95%) of the title compound **29** were isolated as a yellow oil.

R_f: 0.3 (silica, pentane:EtOAc 4:1);

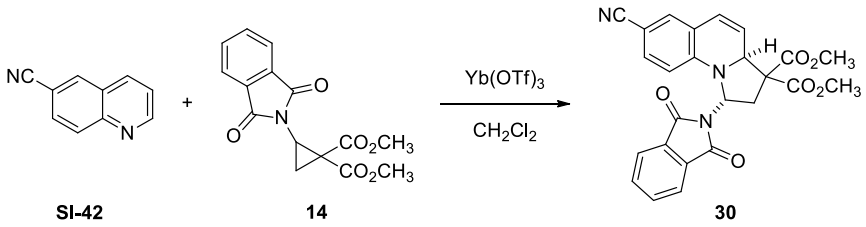
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.73 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.64 (dd, *J* = 8.6, 2.0 Hz, 1H, Ar*H*), 7.44 (d, *J* = 2.0 Hz, 1H, Ar*H*), 6.43 (d, *J* = 8.6 Hz, 1H, Ar*H*), 6.33 (dd, *J* = 10.2, 2.0 Hz, 1H, CH=C*H*), 6.22 (dd, *J* = 8.7, 6.0 Hz, 1H, C*H*-Phth), 5.97 – 5.93 (m, 1H, C*H*-N), 5.89 (dd, *J* = 10.2, 2.9 Hz, 1H, C*H*=CH), 3.81 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 2.98 (dd, *J* = 13.7, 8.7 Hz, 1H, CH_2), 2.53 (dd, *J* = 13.7, 6.0 Hz, 1H, CH_2) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.7, 168.7, 167.5, 166.8, 145.4, 134.5, 131.8, 131.5, 128.5, 125.8, 123.6, 120.8, 119.5, 119.0, 109.2, 66.5, 64.9, 64.3, 52.8, 52.7, 51.5, 35.1;

IR (film): $\tilde{\nu}$ 2988 (w), 2956 (w), 2902 (w), 1773 (w), 1733 (m), 1708 (s), 1603 (w), 1506 (w), 1432 (w), 1393 (w), 1353 (w), 1276 (s), 1201 (m), 1151 (w), 1111 (m), 1078 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{26}H_{23}N_2O_8^+$ $[M+H]^+$ 491.1449; found 491.1446.

***anti*-Dimethyl 7-cyano-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**30**).



SI-42 **14** **30**

Following the general procedure methyl quinoline-6-carboxylate (**SI-42**) (31 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 85 mg (0.19 mmol, 93%) of the title compound **30** were isolated as a yellow oil.

R_f: 0.2 (silica, pentane:EtOAc 4:1);

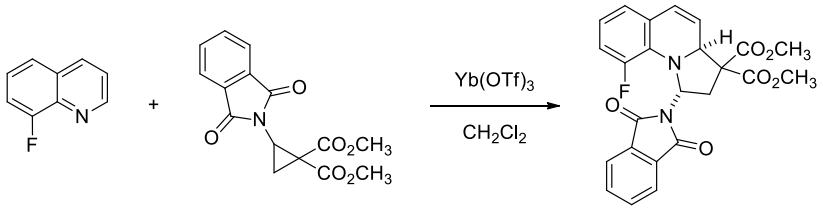
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.19 (dd, *J* = 8.5, 2.0 Hz, 1H, Ar*H*), 6.99 (d, *J* = 2.0 Hz, 1H, Ar*H*), 6.44 (d, *J* = 8.5 Hz, 1H, CH=C*H*), 6.30 – 6.23 (m, 1H, Ar*H*), 6.17 (dd, *J* = 8.8, 6.0 Hz, 1H, C*H*-Phth), 5.97 – 5.89 (m, 2H, C*H*-N and C*H*=CH), 3.80 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 2.97 (dd, *J* = 13.8, 8.8 Hz, 1H, CH_2), 2.54 (dd, *J* = 13.8, 6.0 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.5, 168.5, 167.4, 144.8, 134.5, 134.0, 131.3, 130.2, 124.8, 123.6, 122.0, 119.9, 119.6, 109.9, 100.2, 66.1, 64.7, 64.2, 52.8, 52.8, 34.8;

IR (film): $\tilde{\nu}$ 2956 (w), 2925 (w), 2853 (w), 2215 (m), 1773 (m), 1749 (m), 1731 (s), 1713 (s), 1602 (m), 1505 (s), 1462 (w), 1393 (w), 1354 (w), 1277 (s), 1240 (m), 1215 (m), 1176 (m), 1146 (m), 1107 (w), 1089 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{26}H_{23}N_2O_8^+$ $[M+H]^+$ 491.1449; found 491.1446.

***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-9-fluoro-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**31**).



SI-61 **14** **31**

Following the general procedure 8-fluoroquinoline (**SI-61**) (29 mg, 0.20 mmol, 1.00 equiv.), cyclopropane **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 81 mg (0.18 mmol, 90%) of the title compound **31** were isolated as a yellow oil.

R_f: 0.3 (silica, pentane:EtOAc 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H, *Phth*), 7.71 (dd, *J* = 5.4, 3.1 Hz, 2H, *Phth*), 6.70 (ddd, *J* = 13.8, 8.1, 1.6 Hz, 1H, Ar*H*), 6.59 (dd, *J* = 7.5, 1.6 Hz, 1H, Ar*H*), 6.51 (td, *J* = 7.5, 4.4 Hz, 1H, Ar*H*), 6.39 – 6.24 (m, 2H, C*H*-Phth and C*H*=CH), 5.96 (dd, *J* = 10.1, 3.1 Hz, 1H, CH=C*H*), 5.91 (dd, *J* = 3.1, 1.6 Hz, 1H, C*H*-N), 3.79 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 2.98 (dd, *J* = 13.8, 8.6 Hz, 1H, CH_2), 2.27 (dd, *J* = 13.8, 6.2 Hz, 1H, CH_2);

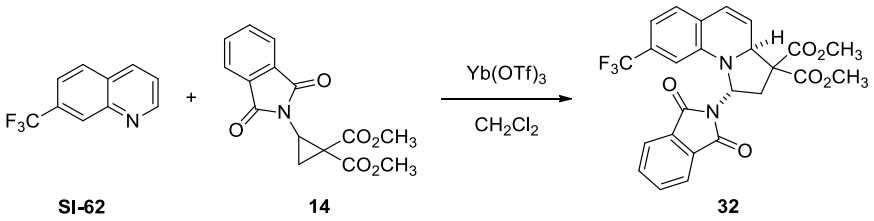
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.9, 168.9, 167.5, 150.1 (d, *J* = 238.3 Hz), 134.0, 131.9, 130.4 (d, *J* = 8.7 Hz), 125.5 (d, *J* = 4.0 Hz), 123.21, 123.15, 123.1 (d, *J* = 2.2 Hz), 122.5, 119.0 (d, *J* = 8.1 Hz), 117.1 (d, *J* = 22.9 Hz), 70.5 (s, *J* = 5.1 Hz), 65.7, 64.8, 52.7, 52.7, 36.2;

^{19}F NMR (376 MHz, $CDCl_3$) δ = -131.20 (dt, *J* = 13.8, 3.2 Hz);

IR (film): $\tilde{\nu}$ = 3003 (w), 2955 (w), 2845 (w), 1773 (w), 1732 (s), 1710 (s), 1611 (w), 1475 (m), 1397 (w), 1353 (m), 1267 (s), 1246 (m), 1219 (m), 1114 (m), 1077 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{24}H_{19}FN_2NaO_6^+$ $[M+Na]^+$ 473.1119; found 473.1124.

***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-8-(trifluoromethyl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**32**).



SI-62 **14** **32**

Following the general procedure 7-(trifluormethyl)quinoline (**SI-62**) (39 mg, 0.20 mmol, 1.00 equiv.), cyclopropane **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 98 mg (0.20 mmol, 98%) of the title compound **32** were isolated as a yellow oil.

R_f: 0.4 (silica, pentane:EtOAc 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.74 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 6.85 (d, *J* = 7.6 Hz, 1H, Ar*H*), 6.79 (dd, *J* = 7.6, 1.5 Hz, 1H, Ar*H*), 6.72 (s, 1H, Ar*H*), 6.33 (dd, *J* = 10.0, 1.5 Hz, 1H, CH=C*H*), 6.22 (dd, *J* = 8.7, 5.8 Hz, 1H, C*H*-Phth), 6.01 – 5.92 (m, 2H, C*H*-N and C*H*=CH), 3.83 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 2.99 (dd, *J* = 13.8, 8.7 Hz, 1H, CH_2), 2.58 (dd, *J* = 13.8, 5.8 Hz, 1H, CH_2) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.9, 168.9, 167.7, 141.8, 134.5, 131.5, 131.2 (q, *J* = 31.9 Hz), 127.2, 125.3, 123.6, 122.9, 122.3, 114.9 (q, *J* = 3.6 Hz), 106.4 (q, *J* = 3.5 Hz), 66.9, 65.2, 64.3, 52.8, 52.8, 34.9;[22]

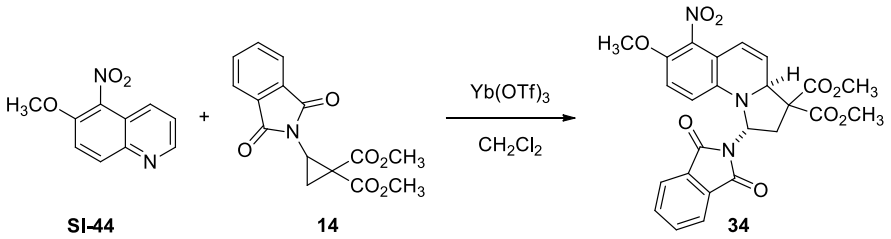
^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.1 (s) ppm.

IR (film): $\tilde{\nu}$ = 2959 (w), 2924 (w), 2365 (w), 1772 (w), 1732 (s), 1709 (s), 1509 (w), 1453 (m), 1436 (w), 1396 (w), 1355 (w), 1327 (w), 1270 (m), 1224 (w), 1143 (w), 1111 (m), 1078 (s), 1046 (w), 1002 (w) cm^{-1};

HRMS (ESI) calcd for $C_{25}H_{18}F_3N_2O_6^+$ $[M+H]^+$ 499.1111; found 499.1109.

[22] The CF_3 carbon was not observed.

***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-7-methoxy-6-nitro-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**34**).



SI-44 **14** **34**

Following the general procedure 6-methoxy-5-nitroquinoline (**SI-44**) (41 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 4:1) and 98 mg (0.19 mmol, 97%) of the title compound **34** were isolated as a yellow oil.

R_f: 0.1 (silica, pentane:EtOAc 4:1);

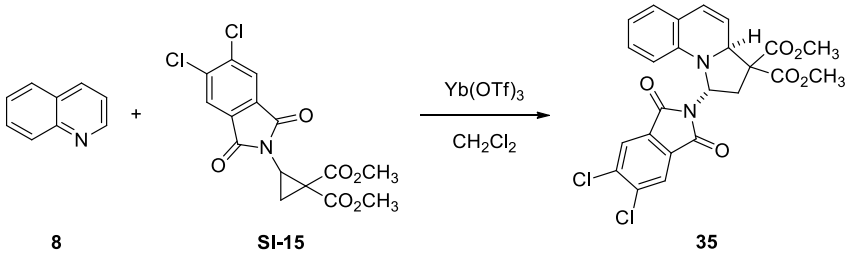
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 6.66 (d, *J* = 9.0 Hz, 1H, C*H*=CH), 6.47 (d, *J* = 9.0 Hz, 1H, CH=C*H*), 6.22 – 6.11 (m, 2H, C*H*-Phth and Ar*H*), 6.08 (dd, *J* = 10.5, 3.0 Hz, 1H, Ar*H*), 5.88 (dd, *J* = 2.9, 2.0 Hz, 1H, C*H*-N), 3.81 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 2.97 (dd, *J* = 13.7, 8.6 Hz, 1H, CH_2), 2.53 (dd, *J* = 13.7, 5.9 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.7, 168.7, 167.7, 142.7, 139.2, 135.9, 134.5, 131.5, 125.7, 123.6, 118.7, 113.5, 112.3, 111.5, 67.6, 65.1, 63.9, 56.8, 52.9, 35.0;

IR (film): $\tilde{\nu}$ 2957 (w), 2923 (w), 2849 (w), 1771 (w), 1733 (s), 1713 (s), 1532 (m), 1494 (m), 1437 (w), 1395 (w), 1355 (m), 1329 (w), 1277 (s), 1243 (w), 1222 (w), 1133 (w), 1114 (w), 1077 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{25}H_{22}N_3O_9^+$ $[M+H]^+$ 508.1351; found 508.1367.

***anti*-Dimethyl 1-(5,6-dichloro-1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**35**).



8 **SI-15** **35**

Following the general procedure quinoline (**8**) (26 mg, 0.20 mmol, 1.00 equiv.), **SI-15** (78 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M)

for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 87 mg (0.17 mmol, 87%) of the title compound **35** were isolated as a red oil.

R_f: 0.2 (silica, pentane:EtOAc 4:1);

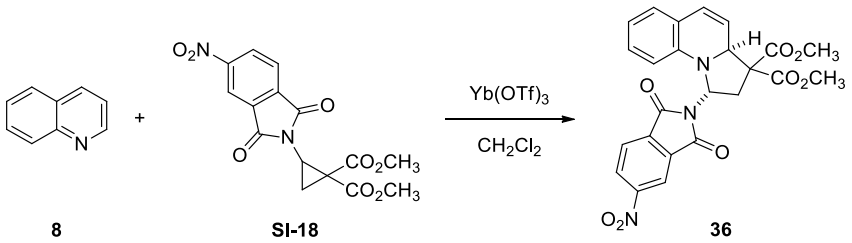
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 2H, *Phth*), 6.94 (t, *J* = 7.7 Hz, 1H, Ar*H*), 6.78 (d, *J* = 7.1 Hz, 1H, Ar*H*), 6.57 (t, *J* = 7.1 Hz, 1H, Ar*H*), 6.32 (dd, *J* = 12.6, 9.0 Hz, 2H, C*H*=CH and Ar*H*), 6.18 (dd, *J* = 8.4, 5.8 Hz, 1H, C*H*-Phth), 5.93 – 5.78 (m, 2H, C*H*-N and C*H*=CH), 3.83 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 3.00 (dd, *J* = 13.7, 8.4 Hz, 1H, CH_2), 2.48 (dd, *J* = 13.7, 5.8 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.8, 168.9, 165.7, 141.3, 139.2, 130.7, 129.5, 127.2, 126.2, 125.5, 120.3, 119.4, 118.3, 109.5, 67.8, 65.2, 64.3, 52.8, 52.7, 35.3 ppm;

IR (film): $\tilde{\nu}$ 2955 (w), 1773 (w), 1732 (s), 1708 (s), 1596 (w), 1492 (w), 1437 (w), 1386 (w), 1345 (s), 1264 (s), 1221 (m), 1134 (w), 1110 (m), 1083 (w), 955 (w), 908 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{24}H_{19}Cl_2N_2O_6^+$ $[M+H]^+$ 501.0615; found 501.0615.

***anti*-Dimethyl 1-(5-nitro-1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**36**).



Following the general procedure quinoline (**8**) (26 mg, 0.20 mmol, 1.00 equiv.), **SI-18** (73 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 2:1) and 85 mg (0.18 mmol, 89%) of the title compound **36** were isolated as a red oil.

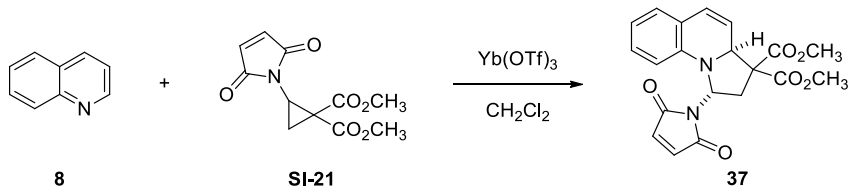
R_f: 0.1 (silica, pentane:EtOAc 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, *J* = 20.3 Hz, 2H, *Phth*), 8.04 (d, *J* = 6.2 Hz, 1H, *Phth*), 6.92 (t, *J* = 7.6 Hz, 1H, Ar*H*), 6.76 (d, *J* = 7.0 Hz, 1H, Ar*H*), 6.55 (t, *J* = 7.0 Hz, 1H, Ar*H*), 6.30 (dd, *J* = 13.6, 8.8 Hz, 2H, Ar*H* and C*H*=CH), 6.26 – 6.16 (m, 1H, C*H*-Phth), 5.92 – 5.79 (m, 2H, C*H*-N and CH=C*H*), 3.84 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 3.03 (dd, *J* = 13.0, 8.1 Hz, 1H, CH_2), 2.50 (dd, *J* = 13.0, 5.8 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.7, 168.8, 165.6, 165.3, 151.7, 141.2, 135.9, 133.0, 129.5, 129.4, 127.2, 126.1, 124.7, 120.2, 119.4, 118.8, 118.4, 109.5, 68.1, 65.1, 64.3, 52.8, 52.7, 35.3 ppm;

IR (film): $\tilde{\nu}$ 3007 (w), 2989 (w), 2957 (w), 1780 (w), 1730 (s), 1719 (s), 1599 (w), 1542 (m), 1494 (w), 1436 (w), 1397 (w), 1340 (m), 1276 (s), 1263 (s), 1221 (w), 1137 (w), 1109 (w), 1079 (w) cm^{-1};
HRMS (ESI) calcd. for $C_{24}H_{20}N_3O_8^+$ $[M+H]^+$ 478.1245; found 478.1242.

***anti*-Dimethyl 1-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**37**).

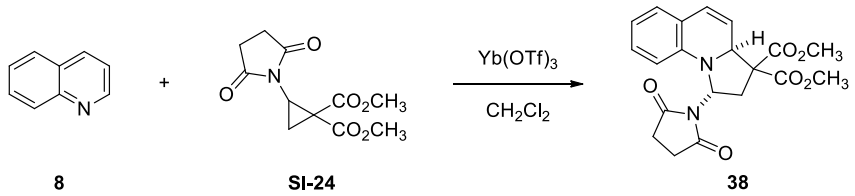


8 **SI-21** **37**

Following the general procedure quinoline (**8**) (26 mg, 0.20 mmol, 1.00 equiv.), **SI-21** (53 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 71 mg (0.19 mmol, 93%) of the title compound **37** were isolated as a colorless oil.

R_f: 0.4 (silica, pentane:EtOAc 4:1);
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.96 (td, *J* = 7.8, 1.6 Hz, 1H, Ar*H*), 6.78 (dd, *J* = 7.4, 1.6 Hz, 1H, Ar*H*), 6.69 (s, 2H, *Mal*), 6.57 (td, *J* = 7.4, 1.0 Hz, 1H, Ar*H*), 6.39 – 6.22 (m, 2H, C*H*=CH and Ar*H*), 6.01 (dd, *J* = 8.6, 5.9 Hz, 1H, C*H*-Mal), 5.82 (dd, *J* = 10.1, 2.9 Hz, 1H, CH=C*H*), 5.78 (dd, *J* = 2.9, 1.9 Hz, 1H, C*H*-N), 3.80 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 2.92 (dd, *J* = 13.7, 8.6 Hz, 1H, CH_2), 2.38 (dd, *J* = 13.7, 5.9 Hz, 1H, CH_2);
^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.1, 169.8, 169.0, 141.5, 134.3, 129.5, 127.2, 126.3, 120.3, 119.4, 118.2, 109.5, 67.0, 65.2, 64.2, 52.7, 52.6, 35.3;
IR (film): $\tilde{\nu}$ 2959 (w), 2901 (w), 1731 (s), 1704 (s), 1651 (w), 1599 (w), 1495 (w), 1460 (w), 1436 (w), 1406 (w), 1355 (m), 1265 (s), 1221 (w), 1159 (m), 1101 (w), 1081 (m), 1054 (w), 911 (w) cm^{-1};
HRMS (ESI) calcd for $C_{20}H_{17}N_2O_6$ [M+] 381.1081; found 381.1079.

***anti*-Dimethyl 1-(2,5-dioxopyrrolidin-1-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**38**).



8 **SI-24** **38**

Following the general procedure quinoline (**8**) (26 mg, 0.20 mmol, 1.00 equiv.), **SI-24** (26 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 61 mg (0.16 mmol, 79%) of the title compound **38** were isolated as a colorless oil.

R_f: 0.4 (silica, pentane:EtOAc 4:1);

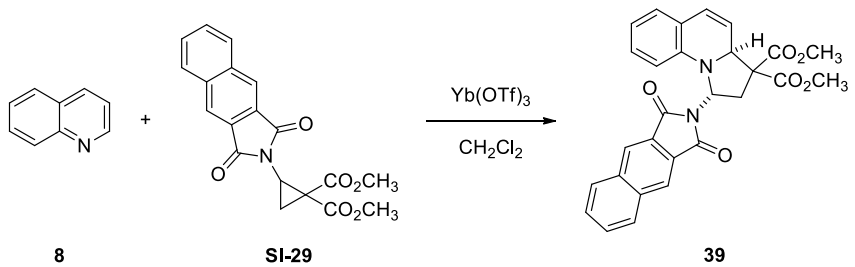
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.97 (td, *J* = 7.8, 1.5 Hz, 1H, Ar*H*), 6.78 (dd, *J* = 7.4, 1.5 Hz, 1H, Ar*H*), 6.57 (td, *J* = 7.4, 0.9 Hz, 1H, Ar*H*), 6.34 – 6.24 (m, 2H, Ar*H* and C*H*=CH), 6.04 (dd, *J* = 8.6, 5.9 Hz, 1H, C*H*-Succ), 5.84 – 5.76 (m, 2H, CH=C*H* and C*H*-N), 3.79 (s, 3H, OCH_3), 3.58 (s, 3H, OCH_3), 2.84 (dd, *J* = 13.6, 8.6 Hz, 1H, CH_2), 2.69 (s, 4H*, Succ*), 2.40 (dd, *J* = 13.6, 5.9 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.7, 169.9, 169.0, 141.6, 129.5, 127.2, 126.1, 120.4, 119.4, 118.1, 109.7, 68.2, 65.4, 64.6, 52.7, 52.6, 34.2, 28.1;

IR (film): $\tilde{\nu}$ 2954 (w), 2127 (w), 1732 (s), 1702 (s), 1599 (w), 1496 (w), 1459 (w), 1436 (w), 1398 (w), 1353 (m), 1310 (w), 1266 (s), 1222 (m), 1176 (s), 1150 (w), 1100 (w), 1085 (m), 1053 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{20}H_{20}N_2NaO_6^+$ $[M+Na]^+$ 407.1214; found 407.1208.

***anti*-Dimethyl 1-(1,3-dioxo-1H-benzo[f]isoindol-2(3H)-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**39**).



8 **SI-29** **39**

Following the general procedure quinoline (**8**) (26 mg, 0.20 mmol, 1.00 equiv.), **SI-29** (74 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 78 mg (0.16 mmol, 81%) of the title compound **39** were isolated as a yellow oil.

R_f: 0.5 (silica, pentane:EtOAc 4:1);

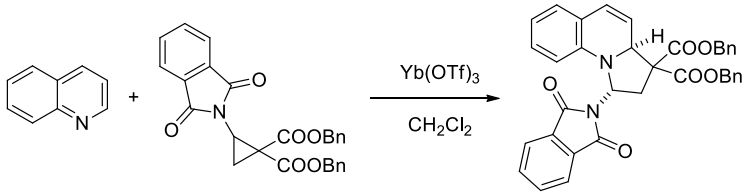
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 2H, *Naphth*), 8.05 (dd, *J* = 6.3, 3.3 Hz, 2H, *Naphth*), 7.69 (dd, *J* = 6.3, 3.3 Hz, 2H, *Naphth*), 6.96 (td, *J* = 8.0, 1.6 Hz, 1H, Ar*H*), 6.79 (dd, *J* = 7.3, 1.6 Hz, 1H, Ar*H*), 6.60 – 6.51 (m, 1H, Ar*H*), 6.48 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.37 – 6.22 (m, 2H, C*H*-Phth and CH=C*H*), 6.01 (dd, *J* = 2.5 Hz, 1H, C*H*-N), 5.88 (dd, *J* = 10.2, 2.5 Hz, 1H, C*H*=CH), 3.84 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.02 (dd, *J* = 13.7, 8.7 Hz, 1H, CH_2), 2.60 (dd, *J* = 13.7, 5.9 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.0, 169.2, 167.4, 141.7, 135.5, 130.3, 129.6, 129.3, 127.3, 127.2, 126.3, 125.0, 120.5, 119.5, 118.1, 109.9, 67.6, 65.4, 64.5, 52.7, 52.7, 35.2;

IR (film): $\tilde{\nu}$ 2955 (w), 1765 (m), 1731 (s), 1704 (s), 1650 (w), 1600 (w), 1496 (w), 1459 (w), 1339 (s), 1310 (w), 1265 (s), 1220 (m), 1149 (m), 1136 (m), 1112 (m), 1083 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{28}H_{22}N_2NaO_6^+$ $[M+Na]^+$ 505.1370; found 505.1370.

***anti*-Dibenzyl 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**40**).



Following the general procedure quinoline (**8**) (26 mg, 0.20 mmol, 1.00 equiv.), **SI-30** (96 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 107 mg (0.18 mmol, 92%) of the title compound **40** were isolated as a yellow oil.

R_f: 0.4 (silica, pentane:EtOAc 4:1);

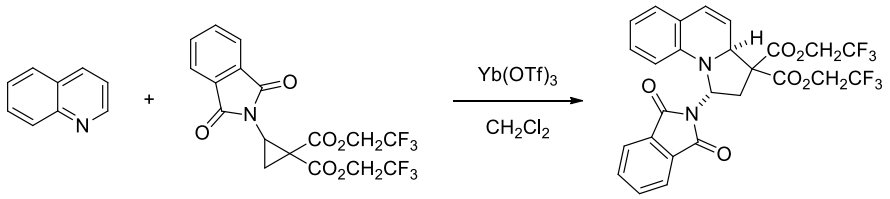
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (dd, *J* = 5.4, 3.0 Hz, 2H, *Phth*), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H, *Phth*), 7.35 – 7.16 (m, 8H, Ar*H*), 7.10 – 7.01 (m, 2H, Ar*H*), 6.94 (td, *J* = 7.8, 1.5 Hz, 1H, Ar*H*), 6.72 (dd, *J* = 7.3, 1.5 Hz, 1H, Ar*H*), 6.55 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.38 (d, *J* = 10.0 Hz, 1H, C*H*=CH), 6.19 – 6.10 (m, 2H, C*H*-Phth and Ar*H*), 5.99 (t, *J* = 2.4 Hz, 1H, C*H*-N), 5.79 (dd, *J* = 10.0, 2.4 Hz, 1H, CH=C*H*), 5.22 (m, 2H, CH_2Ph), 5.02 (m, 2H, CH_2Ph), 3.00 (dd, *J* = 13.7, 8.6 Hz, 1H, CH_2), 2.54 (dd, *J* = 13.7, 5.8 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.4, 168.4, 167.7, 141.5, 135.1, 134.7, 134.3, 131.6, 129.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 127.3, 126.3, 123.4, 120.2, 119.4, 118.0, 109.7, 67.6, 67.3, 67.2, 65.4, 64.5, 35.3 ppm;

IR (film): $\tilde{\nu}$ 3033 (w), 2960 (w), 1772 (w), 1730 (s), 1712 (s), 1599 (w), 1497 (w), 1459 (w), 1351 (m), 1265 (s), 1203 (m), 1134 (m), 1072 (m), 909 (s) cm^{-1};

HRMS (ESI) calcd. for $C_{36}H_{29}N_2O_6^+$ $[M+H]^+$ 585.2020; found 585.2018.

***anti-bis*(2,2,2-Trifluoroethyl) 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**41**).



Following the general procedure quinoline (**8**) (26 mg, 0.20 mmol, 1.00 equiv.), **SI-31** (92 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 106 mg (0.186 mmol, 93%) of the title compound **41** were isolated as a yellow oil.

R_f: 0.4 (silica, pentane:EtOAc 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.74 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 6.99 (td, *J* = 7.9, 1.5 Hz, 1H, Ar*H*), 6.80 (dd, *J* = 7.4, 1.5 Hz, 1H, Ar*H*), 6.59 (td, *J* = 7.4, 0.9 Hz, 1H, Ar*H*), 6.49 (d, *J* = 7.9 Hz, 1H, Ar*H*), 6.35 (dd, *J* = 10.2, 2.0 Hz, 1H, C*H*=CH), 6.27 (dd, *J* = 8.7, 5.7 Hz, 1H, C*H*-Phth), 6.06 (dd, *J* = 2.9, 2.0 Hz, 1H, C*H*-N), 5.82 (dd, *J* = 10.2, 2.9 Hz, 1H, CH=C*H*), 4.70 – 4.55 (m, 2H, C$H_2$$CF_3$), 4.52 – 4.36 (m, 2H, C$H_2$$CF_3$), 3.07 (dd, *J* = 13.9, 8.7 Hz, 1H, CH_2), 2.63 (dd, *J* = 13.9, 5.7 Hz, 1H, CH_2);

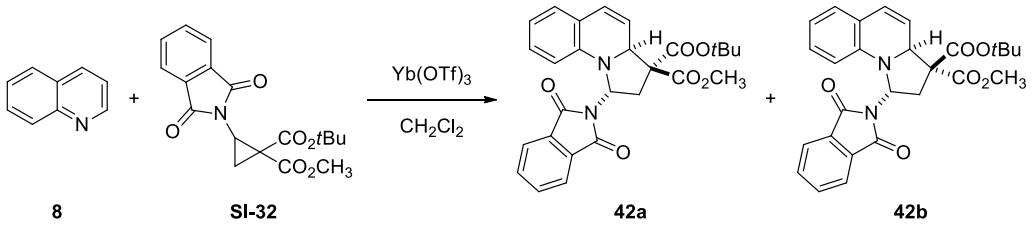
^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.7, 167.5, 166.4, 141.1, 134.4, 131.6, 129.8, 127.5, 127.3, 123.6, 122.5 (q, *J* = 276.4 Hz), 122.3 (q, *J* = 277.2 Hz), 119.1, 118.9, 118.5, 109.9, 66.7, 65.0, 64.8, (d, *J* = 24.9 Hz), 61.3 (q, *J* = 37.8 Hz), 61.2 (*J* = 37.0 Hz), 35.2;

^{19}F NMR (376 MHz, $CDCl_3$) δ = -73.68 (t, *J* = 8.4 Hz), -73.74 (t, *J* = 8.4 Hz);

IR (film): $\tilde{\nu}$ 2976 (w), 2901 (w), 1753 (m), 1712 (s), 1600 (w), 1497 (w), 1461 (w), 1405 (w), 1352 (w), 1310 (w), 1276 (m), 1236 (w), 1166 (s), 1132 (m), 1110 (m), 1087 (m), 977 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{26}H_{18}F_6N_2NaO_6^+$ $[M+Na]^+$ 591.0961; found 591.0962.

***rac*-(1*R*,3*S*,3a*R*)-3-*tert*-Butyl 3-methyl 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**42a**) and ***rac*-(1*R*,3*R*,3a*R*)-3-*tert*-Butyl 3-methyl 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**42b**)



8 **SI-32** **42a** **42b**

Following the general procedure quinoline (**8**) (26 mg, 0.20 mmol, 1.00 equiv.), **SI-32** (73 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) affording **42a** (53 mg, 0.11 mmol, 56%) and **42b** (15 mg, 0.05 mmol, 16%) as yellow oils.[23]

42a

R_f: 0.51 (silica, pentane:EtOAc 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 6.95 (td, *J* =8.0, 1.6 Hz, 1H, Ar*H*), 6.78 (dd, *J* = 7.3, 1.6 Hz, 1H, Ar*H*), 6.55 (td, *J* = 7.3, 1.0 Hz, 1H, Ar*H*), 6.41 (d, *J* = 8.1 Hz, 1H, Ar*H*), 6.33 – 6.26 (m, 1H, C*H*=CH), 6.11 (dd, *J* = 8.6, 6.1 Hz, 1H, C*H*-Phth), 5.98 – 5.82 (m, 2H, C*H*-N and CH=C*H*), 3.81 (s, 3H, OCH_3), 2.88 (dd, *J* = 13.7, 8.6 Hz, 1H, CH_2), 2.51 (dd, *J* = 13.7, 6.1 Hz, 1H, CH_2), 1.25 (s, 9H, C(CH_3)$_3$);

^{13}C NMR (101 MHz, $CDCl_3$): 169.4, 168.6, 167.7, 142.2, 134.3, 131.7, 129.5, 127.1, 126.4, 123.4, 120.5, 119.6, 118.0, 109.7, 83.0, 68.1, 66.1, 64.2, 52.5, 35.2, 27.6;

IR (film): $\tilde{\nu}$ 2981 (w), 1772 (w), 1710 (s), 1600 (w), 1496 (w), 1459 (w), 1394 (w), 1367 (w), 1263 (s), 1227 (w), 1151 (m), 1134 (m), 1078 (m), 1050 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{27}H_{27}N_2O_6^+$ $[M+H]^+$ 475.1864; found 475.1872.

[23] The minor diasteroisomer **30b** slowly converts into the major diastereoisomer **30a** in $CDCl_3$.

42b

R_f: 0.49 (silica, pentane:EtOAc 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (dd, *J* = 5.6, 3.3 Hz, 2H, *Phth*), 7.73 (dd, *J* = 5.6, 3.3 Hz, 2H, *Phth*), 6.95 (t, *J* = 7.9 Hz, 1H, Ar*H*), 6.77 (d, *J* = 7.2 Hz, 1H, Ar*H*), 6.54 (t, *J* = 7.2 Hz, 1H, Ar*H*), 6.40 (d, *J* = 7.9 Hz, 1H, Ar*H*), 6.28 (d, *J* = 10.1 Hz, 1H, C*H*=CH), 6.19 (dd, *J* = 8.2, 6.5 Hz, 1H, C*H*-Phth), 5.95 – 5.79 (m, 2H, C*H*-N and CH=C*H*), 3.64 (s, 3H, OCH_3), 2.94 (dd, *J* = 13.7, 8.2 Hz, 1H, CH_2), 2.50 (dd, *J* = 13.7, 6.5 Hz, 1H, CH_2), 1.51 (s, 9H, C(CH_3)$_3$);

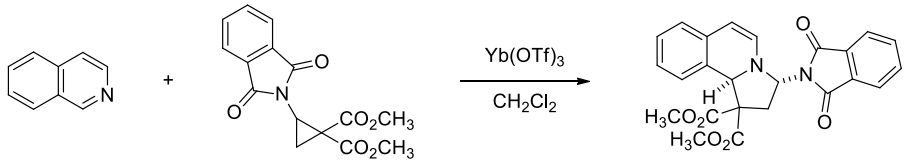
^{13}C NMR (101 MHz, $CDCl_3$): 170.5, 167.7, 167.7, 141.8, 134.3, 131.8, 129.5, 127.1, 126.1, 123.5, 120.9, 119.5, 117.9, 109.7, 82.4, 67.3, 66.1, 64.3, 52.4, 35.5, 27.9 ppm;

IR (film): $\tilde{\nu}$ 2981 (w), 1777 (w), 1726 (s), 1714 (s), 1600 (w), 1497 (w), 1459 (w), 1395 (w), 1354 (w), 1276 (m), 1262 (m), 1219 (w), 1149 (w), 1135 (m), 1112 (w), 1050 (w), 844 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{27}H_{27}N_2O_6^+$ $[M+H]^+$ 475.1864; found 475.1868.

9. Scope of the reaction with isoquinolines

***anti*-Dimethyl 3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydropyrrolo[2,1-a]isoquinoline-1,1(10b*H*)-dicarboxylate** (**43**).



SI-63 **14** **43**

Following the general procedure isoquinoline (**SI-63**) (26 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 72 mg (0.17 mmol, 83%) of the title compound **43** were isolated as a yellow oil.

R_f: 0.2 (silica, pentane:EtOAc 4:1);

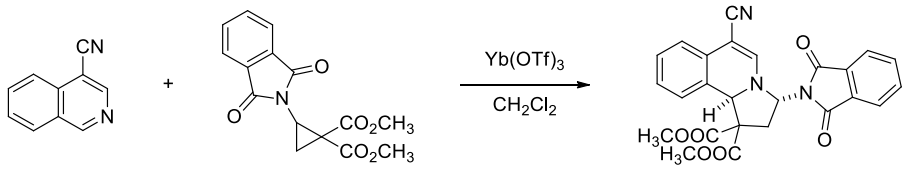
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.73 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.55 – 7.50 (m, 1H, Ar*H*), 7.09 (td, *J* = 7.5, 1.5 Hz, 1H, Ar*H*), 7.01 (td, *J* = 7.5, 1.5 Hz, 1H, Ar*H*), 6.80 (dd, *J* = 7.5, 1.5 Hz, 1H, Ar*H*), 6.16 (d, *J* = 7.6 Hz, 1H, CH=C*H*-N), 6.10 (s, 1H, C*H*-N), 6.07 (dd, *J* = 9.0, 5.3 Hz, 1H, C*H*-Phth), 5.12 (d, *J* = 7.6 Hz, 1H, N-CH=C*H*), 3.86 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 3.02 (dd, *J* = 13.7, 9.0 Hz, 1H, CH_2), 2.85 (dd, *J* = 13.7, 5.3 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.6, 170.0, 168.1, 134.4, 134.3, 131.9, 131.8, 128.1, 127.8, 127.0, 125.3, 123.9, 123.6, 98.4, 69.6, 67.7, 64.9, 52.8, 52.5, 34.2;

IR (film): $\tilde{\nu}$ 2960 (w), 2358 (w), 1774 (w), 1731 (s), 1714 (s), 1635 (w), 1462 (w), 1436 (w), 1371 (w), 1356 (w), 1329 (w), 1271 (w), 1214 (w), 1141 (w), 1093 (w), 1062 (w), 914 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{24}H_{21}N_2O_6^+$ $[M+H]^+$ 433.1394; found 433.1404.

***anti*-Dimethyl 6-cyano-3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydropyrrolo[2,1-a]isoquinoline-1,1(10b*H*)-dicarboxylate** (**44**).



SI-46 **14** **44**

Following the general procedure isoquinoline-4-carbonitrile (**SI-46**) (31 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2

(0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 3:1) and 83 mg (0.18 mmol, 91%) of the title compound **44** were isolated as a yellow oil.

R_f: 0.1 (silica, pentane:EtOAc 3:1);

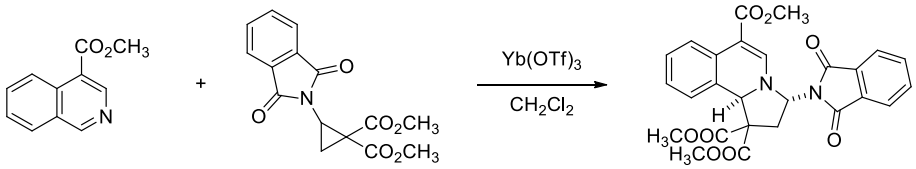
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.77 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.56 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.25 – 7.15 (m, 2H, Ar*H*), 7.15 – 7.07 (m, 1H, Ar*H*), 6.98 (s, 1H, C=C*H*-N), 6.16 (s, 1H, C*H*-N), 6.11 (dd, *J* = 8.9, 5.2 Hz, 1H, C*H*-Phth), 3.89 (s, 3H, OCH_3), 3.37 (s, 3H, OCH_3), 3.03 (dd, *J* = 14.1, 8.9 Hz, 1H, CH_2), 2.93 (dd, *J* = 14.1, 5.2 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.7, 169.5, 167.6, 143.7, 134.7, 131.3, 128.8, 127.6, 126.9, 126.8, 124.7, 123.8, 122.4, 118.2, 82.3, 67.4, 67.0, 63.9, 53.1, 52.7, 34.0;

IR (film): $\tilde{\nu}$ 2956 (w), 2251 (w), 2207 (m), 1835 (w), 1776 (w), 1730 (s), 1730 (s), 1713 (s), 1623 (s), 1571 (w), 1497 (w), 1457 (m), 1436 (w), 1366 (m), 1353 (m), 1327 (m), 1272 (m), 1206 (m), 1117 (m), 1092 (m), 1064 (m), 910 (s) cm^{-1};

HRMS (ESI) calcd. for $C_{25}H_{20}N_3O_6^+$ $[M+H]^+$ 458.1347; found 458.1346.

***anti*-Trimethyl 3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydropyrrolo[2,1-a]isoquinoline-1,1,6(10b*H*)-tricarboxylate** (**45**).



SI-48 **14** **45**

Following the general procedure methyl isoquinoline-4-carboxylate (**SI-48**) (37 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 4:1 to 2:1) and 87 mg (0.18 mmol, 89%) of the title compound **45** were isolated as a yellow oil.

R_f: 0.3 (silica, pentane:EtOAc 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (dd, *J* = 8.1, 1.4 Hz, 1H, Ar*H*), 7.85 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.73 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.54 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.50 (s, 1H, C*H*=C($COOCH_3$)), 7.17 (td, *J* = 7.7, 1.4 Hz, 1H, Ar*H*), 7.05 (td, *J* = 7.7, 1.4 Hz, 1H, Ar*H*), 6.19 – 6.11 (m, 2H, Ar-C*H*-N and C*H*-Phth), 3.87 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 3.03 (dd, *J* = 13.9, 9.0 Hz, 1H, CH_2), 2.87 (dd, *J* = 13.9, 5.3 Hz, 1H, CH_2);

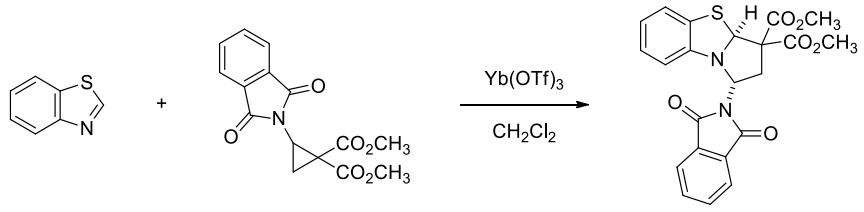
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.9, 169.5, 167.6, 166.2, 144.4, 134.6, 131.4, 128.7, 128.2, 127.2, 125.5, 125.4, 123.8, 123.7, 98.5, 68.0, 67.0, 64.3, 52.9, 52.6, 50.7, 34.3;

IR (film): $\tilde{\nu}$ 3499 (w), 2938 (w), 2830 (w), 1738 (s), 1636 (s), 1417 (m), 1298 (m), 1246 (m), 1176 (m), 1157 (m), 940 (s) cm^{-1};

HRMS (ESI) calcd. for $C_{26}H_{23}N_2O_8^+$ $[M+H]^+$ 491.1449; found 491.1449.

10. Scope of the reaction with benzo- thia/oxa-zole

***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydrobenzo[d]pyrrolo[2,1-b]thiazole-3,3(3a*H*)-dicarboxylate** (**46**).



SI-64 **14** **46**

Following the general procedure benzothiazole (**SI-64**) (27 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 83 mg (0.19 mmol, 95%) of the title compound **46** were isolated as a colorless oil.

R_f: 0.6 (silica, pentane:EtOAc 4:1);

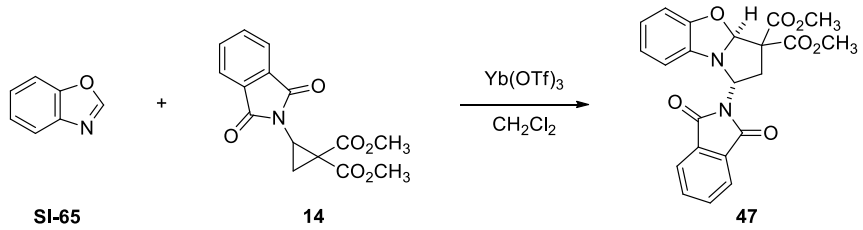
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 5.4, 3.1 Hz, 2H, *Phth*), 7.75 (dd, *J* = 5.4, 3.1 Hz, 2H, *Phth*), 6.94 (ddd, *J* = 9.0, 7.9, 1.2 Hz, 2H, Ar*H*), 6.71 (td, *J* = 7.5, 1.2 Hz, 1H, Ar*H*), 6.65 (d, *J* = 7.8 Hz, 1H, C*H*-Phth), 6.30 (s, 1H, S-C*H*-N), 6.20 (t, *J* = 7.9 Hz, 1H, Ar*H*), 3.85 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 2.95 (d, *J* = 7.8 Hz, 2H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.4, 168.8, 167.6, 147.1, 134.4, 131.6 (3C overlapping, two of them symmetric), 125.6, 123.5, 121.2, 120.9, 109.2, 74.1, 69.9, 66.7, 53.0, 52.5, 35.0;

IR (film): $\tilde{\nu}$ 2956 (w), 2364 (w), 2257 (w), 1773 (w), 1748 (m), 1724 (m), 1716 (s), 1583 (w), 1472 (m), 1393 (w), 1364 (m), 1350 (m), 1333 (m), 1297 (m), 1273 (m), 1220 (w), 1131 (m), 1070 (w), 1036 (w), 971 (w), 907 (s) cm^{-1};

HRMS (ESI) calcd. for $C_{22}H_{18}N_2NaO_6S^+$ $[M+Na]^+$ 461.0778; found 461.0773.

***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydrobenzo[d]pyrrolo[2,1-b]oxazole-3,3(3a*H*)-dicarboxylate** (**47**).



SI-65 **14** **47**

Following the general procedure benzoxazole (**SI-65**) (24 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (6 mg, 0.01 mmol, 5 mol%) were stirred in CH_2Cl_2 (0.4 mL, 0.5 M) for 16 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1) and 62 mg (0.15 mmol, 73%) of the title compound **47** were isolated as a colorless oil.

R_f: 0.5 (silica, pentane:EtOAc 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (dd, *J* = 5.3, 3.0 Hz, 2H, *Phth*), 7.77 (dd, *J* = 5.3, 3.0 Hz, 2H, *Phth*), 6.79 (pd, *J* = 7.5, 1.4 Hz, 2H, Ar*H*), 6.75 – 6.67 (m, 3H, O-C*H*-N and Ar*H*), 6.09 (dd, *J* = 8.4, 6.8 Hz, 1H, C*H*-Phth), 3.92 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.12 – 2.95 (m, 2H, CH_2);

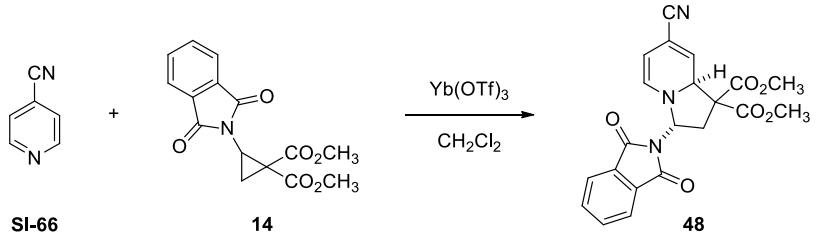
^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.8, 168.3, 167.5, 149.8, 138.4, 134.4, 131.7, 123.6, 122.2, 121.9, 110.5, 108.0, 101.7, 70.5, 65.8, 53.3, 53.1, 34.3 ppm;

IR (film): $\tilde{\nu}$ 2957 (w), 1737 (s), 1720 (s), 1487 (m), 1437 (w), 1363 (m), 1279 (m), 1252 (s), 1127 (m), 1054 (w), 898 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{22}H_{19}N_2O_7^+$ $[M+H]^+$ 423.1187; found 423.1179.

11. Scope of the reaction with pyridines

***anti*-Dimethyl 7-cyano-3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate** (**48**).



SI-66 **14** **48**

Following the general procedure isonicotinonitrile (**SI-66**) (21 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (12 mg, 20 µmol, 10 mol%) were stirred in CH_2Cl_2 (0.2 mL, 1 M) for 3 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 10:1 to 3:1) and 61 mg (0.15 mmol, 75%) of the title compound **48** were isolated as a yellow oil.

R_f: 0.3 (silica, pentane:EtOAc 3:1);

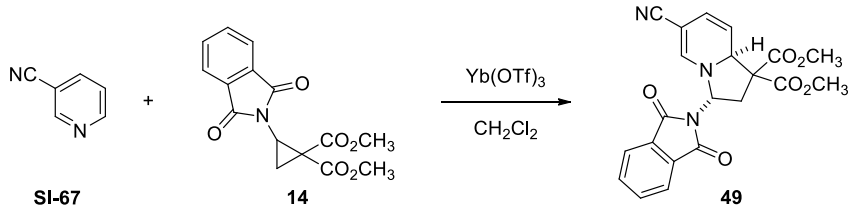
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 6.08 (dt, *J* = 7.5, 0.7 Hz, 1H, CH=C*H*N), 6.04 – 5.92 (m, 2H, N-C*H*-Phth and C=C*H*-CHN), 5.64 (d, *J* = 3.4 Hz, 1H, C*H*-N), 4.52 (dd, *J* = 7.4, 1.6 Hz, 1H, C*H*=CHN), 3.82 (s, 6H, 2 OCH_3), 2.80 (dd, *J* = 13.8, 8.5 Hz, 1H, CH_2), 2.64 (dd, *J* = 13.9, 6.1 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.8, 168.4, 167.8, 134.6, 134.6, 131.5, 125.8, 123.7, 117.5, 111.6, 91.7, 68.0, 66.7, 63.3, 53.2, 53.0, 32.1 ppm;

IR (film): $\tilde{\nu}$ 2958 (w), 2226 (w), 1775 (w), 1732 (s), 1712 (s), 1633 (w), 1572 (w), 1436 (w), 1354 (w), 1328 (w), 1271 (m), 1218 (w), 1130 (w), 1088 (w), 972 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{21}H_{16}N_3O_6$ [M+] 406.1034; found 406.1036.

***anti*-Dimethyl 6-cyano-3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate** (**49**).



Following the general procedure nicotinonitrile (**SI-67**) (104 mg, 1.00 mmol, 1.00 equiv.), **14** (318 mg, 1.05 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (62 mg, 0.10 mmol, 10 mol%) were stirred in CH_2Cl_2 (1.0 mL, 1 M) for 3 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 4:1 to 2:1) and 280 mg (0.69 mmol, 69%) of the title compound **49** were isolated as a yellow oil.

Performing the reaction with **SI-67** (21 mg, 0.20 mmol), **14** (64 mg, 0.21 mmol) and $Yb(OTf)_3$ (12 mg, 20 µmol) afforded 58 mg (0.14 mmol, 71%) of the title compound **49**.

R_f: 0.3 (silica, pentane:EtOAc 2:1);

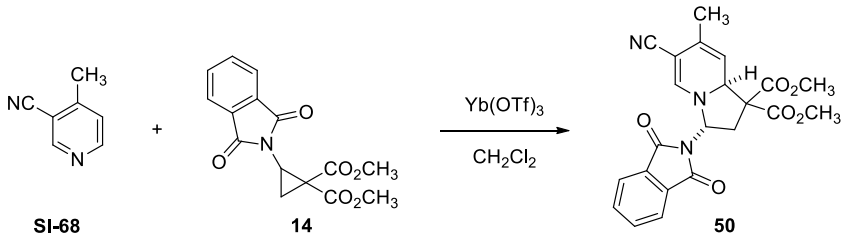
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 6.76 (t, *J* = 1.2 Hz, 1H, C=C*H*-N), 6.07 (dd, *J* = 8.6, 6.3 Hz, 1H, C*H*-NPhth), 5.81 (dt, *J* = 10.3, 1.7 Hz, 1H, C*H*=CH-CHN), 5.57 (t, *J* = 2.2 Hz, 1H, N-C*H*-CH=CH), 5.37 (ddd, *J* = 10.2, 2.4, 1.0 Hz, 1H, CH=C*H*-CHN), 3.82 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 2.82 (dd, *J* = 14.0, 8.6 Hz, 1H, CH_2), 2.72 (dd, *J* = 13.9, 6.3 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.7, 168.4, 167.5, 143.8, 134.8, 131.3, 123.9, 121.4, 119.7, 113.9, 79.4, 67.2, 66.0, 62.7, 53.1, 53.0, 32.1 ppm;

IR (film): $\tilde{\nu}$ 3007 (w), 2956 (w), 2257 (w), 2203 (m), 1776 (w), 1713 (s), 1644 (m), 1577 (m), 1435 (w), 1394 (w), 1353 (m), 1332 (m), 1273 (s), 1226 (m), 1128 (m), 1100 (m), 981 (w), 910 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{21}H_{18}N_3O_6^+$ $[M+H]^+$ 408.1190; found 408.1186.

***anti*-Dimethyl 6-cyano-3-(1,3-dioxoisoindolin-2-yl)-7-methyl-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate** (**50**).



SI-68 **14** **50**

Following the general procedure 3-cyano-4-methylpyridine (**SI-68**) (24 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (12 mg, 20 µmol, 10 mol%) were stirred in CH_2Cl_2 (0.2 mL, 1 M) for 3 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 3:1 to 2:1) and 63 mg (0.15 mmol, 75%) of the title compound **50** were isolated as a yellow oil.

R_f: 0.3 (silica, pentane:EtOAc 2:1);

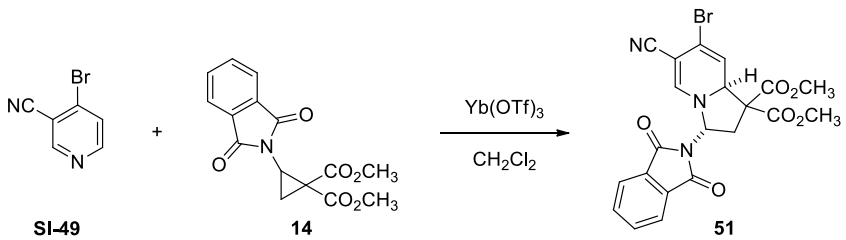
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 6.78 (s, 1H, C*H*=C(CN)), 6.06 (dd, *J* = 8.6, 6.2 Hz, 1H, N-C*H*-Phth), 5.51 (t, *J* = 2.0 Hz, 1H, N-C*H*-CH=C(CH_3)), 5.18 – 5.11 (m, 1H, C*H*=C(CH_3)), 3.81 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 2.81 (dd, *J* = 14.0, 8.6 Hz, 1H, CH_2), 2.71 (dd, *J* = 14.0, 6.2 Hz, 1H, CH_2), 1.80 (t, *J* = 1.6 Hz, 3H, CH_3);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.8, 168.6, 167.5, 144.0, 134.7, 131.4, 128.4, 123.8, 119.1, 109.4, 82.4, 67.1, 66.0, 63.5, 53.0, 52.9, 32.2, 19.4;

IR (film): $\tilde{\nu}$ 3056 (w), 2956 (w), 2202 (w), 1777 (w), 1718 (s), 1660 (w), 1585 (w), 1436 (w), 1351 (w), 1329 (w), 1266 (s), 1130 (w), 1092 (m), 909 (s) cm^{-1};

HRMS (ESI) calcd. for $C_{22}H_{19}N_3NaO_6^+$ $[M+Na]^+$ 444.1166; found 444.1165.

***anti*-Dimethyl 7-bromo-6-cyano-3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate** (**51**).



SI-49 **14** **51**

Following the general procedure 4-bromopyridine-3-carbonitrile (**SI-49**) (37 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (12 mg, 20 µmol, 10 mol%) were stirred in CH_2Cl_2 (0.2 mL, 1 M) for 3 hours. The crude product was purified by column chromatography (silica,

pentane:EtOAc 4:1 to 2:1) and 68 mg (0.14 mmol, 70%) of the title compound **51** were isolated as a yellow oil.

R_f: 0.3 (silica, pentane:EtOAc 2:1);

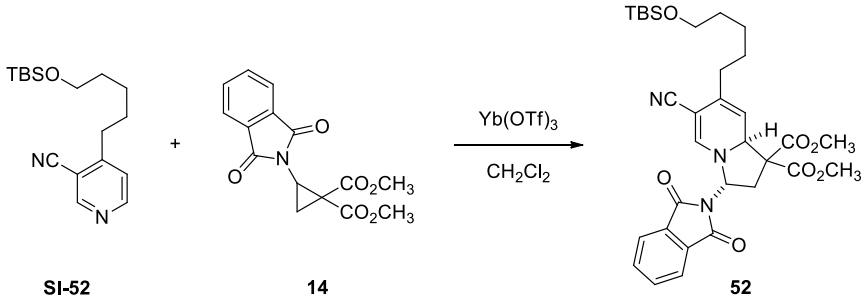
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.79 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 6.81 (s, 1H, N-C*H*=C(CN)), 6.08 (dd, *J* = 8.6, 6.3 Hz, 1H, N-C*H*-Phth), 5.70 (d, *J* = 2.5 Hz, 1H, C(Br)=C*H*), 5.58 (d, *J* = 2.5 Hz, 1H, N-C*H*-CH=C(Br)), 3.83 (s, 6H, OCH_3), 2.84 (dd, *J* = 14.0, 8.6 Hz, 1H, CH_2), 2.73 (dd, *J* = 13.9, 6.3 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.3, 168.0, 167.3, 144.8, 134.9, 131.2, 124.0, 117.9, 114.3, 113.1, 83.5, 66.8, 65.7, 65.1, 53.4, 53.2, 32.1 ppm;

IR (film): $\tilde{\nu}$ 2956 (w), 2208 (w), 1730 (s), 1712 (s), 1626 (m), 1577 (m), 1434 (w), 1351 (m), 1273 (s), 1133 (m), 1103 (m), 1001 (m), 912 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{21}H_{15}BrN_3O_6^+$ $[M+H]^+$ 484.0139; found 484.0130.

***anti*-Dimethyl 7-(5-((*tert*-butyldimethylsilyl)oxy)pentyl)-6-cyano-3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate** (**52**).



SI-52 **14** **52**

Following the general procedure **SI-52** (61 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (12 mg, 20 µmol, 10 mol%) were stirred in CH_2Cl_2 (0.2 mL, 1 M) for 3 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 3:1 to 2:1) and 88 mg (0.15 mmol, 72%) of the title compound **52** were isolated as a yellow oil containing minor impurities which could not be removed.

R_f: 0.5 (silica, pentane:EtOAc 2:1);

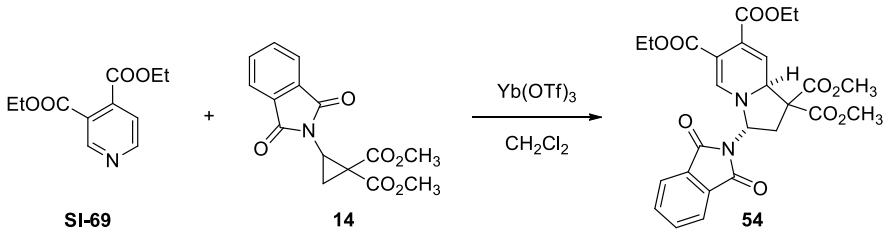
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 6.79 (s, 1H, N-C*H*=C(CN)), 6.07 (dd, *J* = 8.6, 6.3 Hz, 1H, C*H*Pthth), 5.55 (dt, *J* = 2.4, 1.3 Hz, 1H, C*H*-CH-N), 5.12 (dd, *J* = 2.4, 1.3 Hz, 1H, N-C*H*-CH), 3.83 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.59 (t, *J* = 6.6 Hz, 2H, CH_2-OTBS), 2.82 (dd, *J* = 14.1, 8.6 Hz, 1H, CH_2-CHPhth), 2.73 (dd, *J* = 14.1, 6.3 Hz, 1H, CH_2-CHPhth), 2.09 (t, *J* = 7.6 Hz, 2H, C-CH_2), 1.56 – 1.40 (m, 4H, 2x CH_2), 1.34 (m, 2H, CH_2), 0.87 (s, 9H, C(CH_3)$_3$), 0.03 (s, 6H, Si(CH_3)$_2$);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.8, 168.6, 167.5, 144.4, 134.8, 132.8, 131.4, 123.9, 119.1, 109.0, 82.1, 67.2, 66.1, 63.5, 63.1, 53.0 (2 C), 33.3, 32.6, 32.3, 28.2, 26.0, 25.3, 18.3, -5.3;

IR (film): $\tilde{\nu}$ 2953 (w), 2931 (w), 2857 (w), 2202 (w), 1777 (w), 1716 (s), 1602 (w), 1470 (w), 1436 (w), 1394 (w), 1351 (w), 1327 (w), 1273 (w), 1217 (w), 1099 (m), 912 (m), 836 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{32}H_{42}N_3O_7Si^+$ $[M+H]^+$ 608.2787; found 608.2767.

***anti*-6,7-Diethyl 1,1-dimethyl 3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1,6,7(8a*H*)-tetracarboxylate** (**54**).



Following the general procedure dietyl pyridine-3,4-dicarboxylate (**SI-69**) (45 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (12 mg, 20 µmol, 10 mol%) were stirred in CH_2Cl_2 (0.2 mL, 1 M) for 3 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 4:1 to 2:1) and 78 mg (0.15 mmol, 74%) of the title compound **54** were isolated as a yellow oil.

R_f: 0.2 (silica, pentane:EtOAc 2:1);

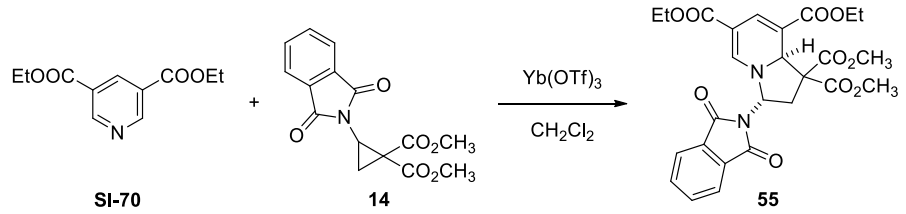
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.77 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.19 (s, 1H, N-C*H*=C(COOEt)), 6.12 (dd, *J* = 8.6, 6.3 Hz, 1H, C*H*-Phth), 5.67 – 5.54 (m, 2H, N-C*H*-CH and N-CH-C*H*=C(COOEt)), 4.20 (qd, *J* = 7.1, 4.0 Hz, 2H, OCH_2), 4.06 (qd, *J* = 7.1, 2.5 Hz, 2H, OCH_2), 3.81 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 2.86 (dd, *J* = 13.9, 8.6 Hz, 1H, CH_2), 2.65 (dd, *J* = 13.9, 6.3 Hz, 1H, CH_2), 1.26 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.17 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.5, 168.3, 168.0, 167.4, 164.6, 142.9, 134.7, 131.4, 130.6, 123.8, 114.6, 97.9, 67.1, 65.6, 63.0, 61.0, 59.7, 53.1, 53.0, 32.6, 14.3, 14.0 ppm;

IR (film): $\tilde{\nu}$ 2999 (w), 2968 (w), 2238 (w), 1786 (w), 1742 (s), 1702 (s), 1653 (w), 1557 (m), 1459 (m), 1342 (m), 1283 (s), 1166 (s), 1082 (s), 1043 (m), 982 (w), 934 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{26}H_{27}N_2O_{10}^+$ $[M+H]^+$ 527.1660; found 527.1669.

***anti*-6,8-Diethyl 1,1-dimethyl 3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1,6,8(8a*H*)-tetracarboxylate** (**55**).



Following the general procedure dietyl pyridine-3,5-dicarboxylate (**SI-70**) (45 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (12 mg, 20 µmol, 10 mol%) were stirred in CH_2Cl_2 (0.2 mL, 1 M) for 3 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 4:1 to 2:1) and 82 mg (0.16 mmol, 78%) of the title compound **55** were isolated as a yellow oil.

R_f: 0.3 (silica, pentane:EtOAc 2:1);

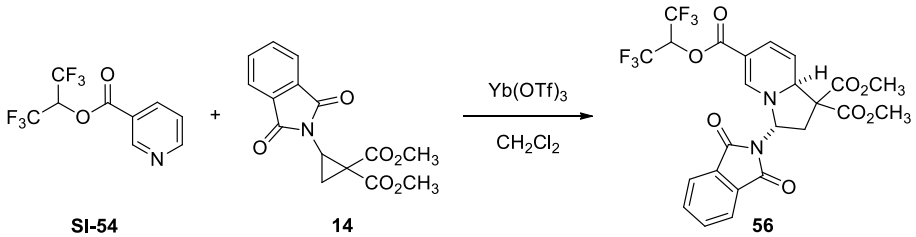
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.42 (t, *J* = 1.4 Hz, 1H, N-C*H*=C(COOEt)), 7.30 (d, *J* = 1.4 Hz, 1H, (COOEt)C-C*H*=C(COOEt)), 6.09 (d, *J* = 1.4 Hz, 1H, N-C*H*-C(COOEt)), 5.98 (dd, *J* = 8.1 Hz, 1H, C*H*-Phth), 4.28 – 4.00 (m, 4H, 2xOCH_2), 3.83 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 2.97 (m, 2H, CH_2), 1.27 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.20 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.8, 167.9, 167.0, 165.2, 165.0, 145.6, 134.7, 131.7, 131.4, 123.8, 114.4, 99.0, 66.4, 65.7, 65.4, 60.2, 59.8, 52.9, 35.0, 14.4, 14.2

IR (film): $\tilde{\nu}$ 2983 (w), 2956 (w), 2261 (w), 1779 (w), 1718 (s), 1687 (s), 1634 (m), 1557 (m), 1435 (w), 1368 (w), 1330 (m), 1270 (m), 1225 (s), 1131 (s), 1089 (m), 1023 (w), 910 (s) cm^{-1};

HRMS (ESI) calcd. for $C_{26}H_{27}N_2O_{10}^+$ $[M+H]^+$ 527.1660; found 527.1642.

***anti*-6-(1,1,1,3,3,3-Hexafluoropropan-2-yl) 1,1-dimethyl 3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1,6(8a*H*)-tricarboxylate** (**56**).



Following the general procedure 1,1,1,3,3,3-hexafluoropropan-2-yl nicotinate (**SI-54**) (55 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (12 mg, 20 µmol, 10 mol%) were stirred in CH_2Cl_2 (0.2 mL, 1 M) for 3 hours. The crude product was purified by column

chromatography (silica, pentane:EtOAc 5:1 to 4:1) and 84 mg (0.15 mmol, 73%) of the title compound **56** were isolated as a yellow oil.

R_f: 0.5 (silica, pentane:EtOAc 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.78 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.38 (s, 1H, (COOR)C=C*H*-N), 6.32 (dt, *J* = 10.5, 1.8 Hz, 1H, CH=C*H*-C(COOR)), 6.17 (dd, *J* = 8.7, 6.2 Hz, 1H, N-C*H*-Phth), 5.81 (quint, *J* = 6.3 Hz, 1H, C*H*(CCF_3)$_2$), 5.65 (t, *J* = 2.2 Hz, 1H, N-C*H*), 5.39 (dd, *J* = 10.5, 2.2 Hz, 1H, N-CH-C*H*=CH), 3.84 (s, 3H, OC*H*$_3$), 3.78 (s, 3H, OC*H*$_3$), 2.88 (dd, *J* = 14.0, 8.7 Hz, 1H, CH_2), 2.72 (dd, *J* = 14.0, 6.2 Hz, 1H, CH_2);

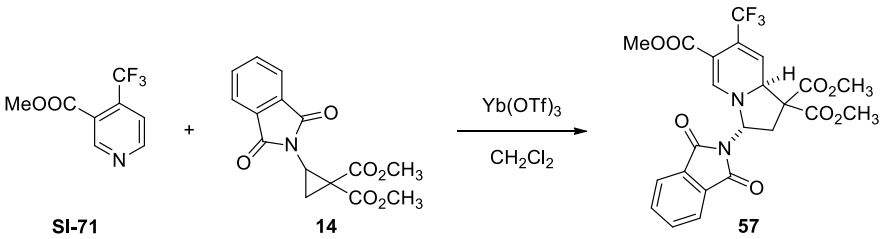
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.6, 168.4, 167.4, 161.9, 145.3, 134.8, 131.4, 123.9, 121.5, 120.7 (q, *J* = 282.9 Hz), 112.3, 95.8, 67.1, 65.6, 65.5 (quint, *J* = 34.5 Hz), 63.4, 53.1, 53.0, 32.6;

^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.3 – –73.4 (m);

IR (film): $\tilde{\nu}$ 2958 (w), 2259 (w), 1715 (s), 1638 (w), 1574 (m), 1436 (w), 1352 (m), 1274 (m), 1195 (m), 1099 (s), 982 (w), 907 (s) cm^{-1};

HRMS (ESI) calcd. for $C_{24}H_{18}F_6N_2NaO_8^+$ $[M+Na]^+$ 599.0860; found 599.0850.

***anti*-Trimethyl 3-(1,3-dioxoisoindolin-2-yl)-7-(trifluoromethyl)-2,3-dihydroindolizine-1,1,6(8a*H*)-tricarboxylate** (**57**).



SI-71 **14** **57**

Following the general procedure methyl 4-(trifluormethyl)nicotinate (**SI-71**) (41 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and Yb(OTf)$_3$ (12 mg, 20 µmol, 10 mol%) were stirred in CH_2Cl_2 (0.2 mL, 1 M) for 3 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 4:1 to 2:1) and 75 mg (0.15 mmol, 74%) of the title compound **57** were isolated as a yellow oil.

R_f: 0.4 (silica, pentane:EtOAc 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.79 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.36 (s, 1H, N-C*H*=C(COOMe)), 6.14 (dd, *J* = 8.6, 6.3 Hz, 1H, N-C*H*-Phth), 5.97 (s, 1H, C*H*=C(CF_3)), 5.67 (dd, *J* = 2.7 Hz, 1H, N-C*H*-CH=C(CF_3)), 3.84 (s, 3H, OC*H*$_3$), 3.77 (s, 3H, OC*H*$_3$), 3.62 (s, 3H, OC*H*$_3$), 2.89 (dd, *J* = 13.9, 8.6 Hz, 1H, C*H*$_2$), 2.68 (dd, *J* = 13.9, 6.3 Hz, 1H, C*H*$_2$);

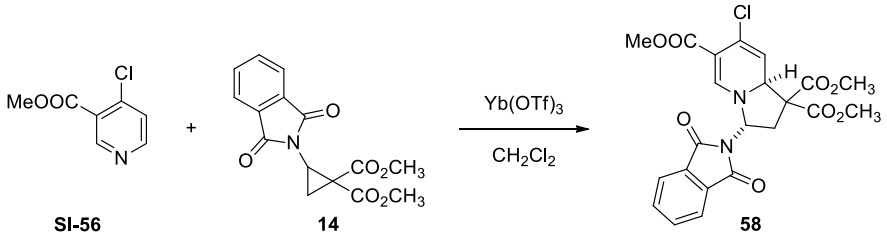
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.2, 168.1, 167.4, 163.9, 145.1, 134.8, 131.4, 126.0 (q, *J* = 32.2 Hz), 123.9, 116.6 (q, *J* = 7.8 Hz), 95.2, 67.1, 65.7, 62.6, 53.2, 53.1, 51.0, 32.6; [24]

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.3 (s);

IR (film): $\tilde{\nu}$ 2956 (w), 2372 (w), 2350 (m), 1713 (s), 1642 (w), 1572 (m), 1436 (m), 1354 (m), 1326 (m), 1289 (m), 1222 (w), 1142 (s), 1089 (m), 1013 (m), 916 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{23}H_{20}F_3N_2O_8^+$ $[M+H]^+$ 509.1166; found 509.1136.

***anti*-Trimethyl 7-chloro-3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1,6(8a*H*)-tricarboxylate** (**58**).



SI-56 **14** **58**

Following the general procedure methyl 4-chloronicotinate (**SI-56**) (34 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (12 mg, 20 μmol, 10 mol%) were stirred in CH_2Cl_2 (0.2 mL, 1 M) for 3 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 4:1 to 2:1) and 72 mg (0.15 mmol, 76%) of the title compound **58** were isolated as a yellow oil.

R_f: 0.3 (silica, pentane:EtOAc 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.33 (s, 1H, N-C*H*=C($COOCH_3$)), 6.13 (dd, *J* = 8.7, 6.3 Hz, 1H, C*H*-Phth), 5.63 (d, *J* = 2.7 Hz, 1H, C*H*=CCl), 5.46 (d, *J* = 2.7 Hz, 1H, N-C*H*-CH), 3.83 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 2.86 (dd, *J* = 13.9, 8.7 Hz, 1H, CH_2), 2.68 (dd, *J* = 13.9, 6.3 Hz, 1H, CH_2);

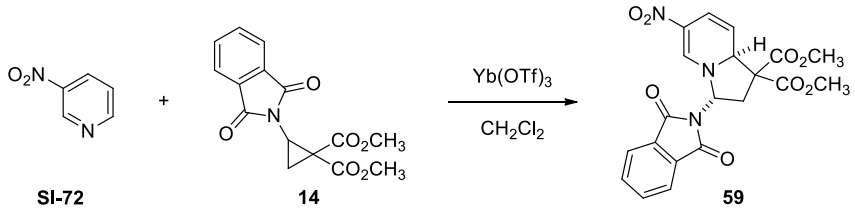
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.6, 168.3, 167.4, 164.1, 144.8, 134.8, 131.4, 127.6, 123.9, 111.3, 97.3, 67.1, 65.8, 64.8, 53.3, 53.1, 50.9, 32.7;

IR (film): $\tilde{\nu}$ 2955 (w), 1777 (w), 1732 (s), 1715 (s), 1626 (w), 1566 (w), 1435 (w), 1354 (m), 1327 (m), 1263 (m), 1149 (m), 1016 (w), 917 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{22}H_{20}ClN_2O_8^+$ $[M+H]^+$ 475.0903; found 475.0900.

[24] The CF_3 carbon was not observed.

***anti*-Dimethyl 3-(1,3-dioxoisoindolin-2-yl)-6-nitro-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate** (**59**).



Following the general procedure 3-nitropyridine (**SI-72**) (25 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (12 mg, 20 µmol, 10 mol%) were stirred in CH_2Cl_2 (0.2 mL, 1 M) for 3 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 4:1 to 2:1) and 65 mg (0.15 mmol, 76%) of the title compound **59** were isolated as a red oil.

R_f: 0.2 (silica, pentane:EtOAc 2:1);

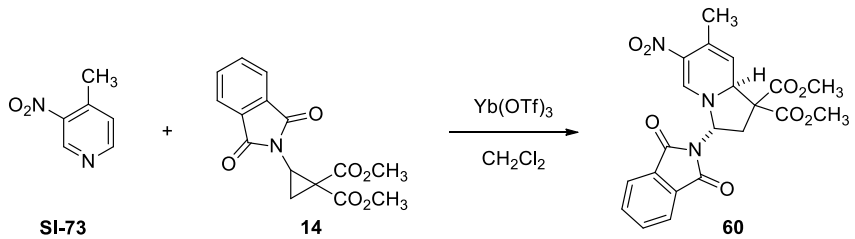
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.87 (d, *J* = 1.7 Hz, 1H, C=C*H*N), 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 6.72 (dt, *J* = 10.8, 2.1 Hz, 1H, NCH=CH=C*H*), 6.22 (dd, *J* = 8.6, 6.7 Hz, 1H, C*H*-NPhth), 5.67 (t, *J* = 2.1 Hz, 1H, NC*H*-CH=CH), 5.43 (dd, *J* = 10.8, 2.1 Hz, 1H, NCH-C*H*=CH), 3.85 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 2.91 (dd, *J* = 13.9, 8.6 Hz, 1H, CH_2), 2.79 (dd, *J* = 13.9, 6.7 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.2, 168.0, 167.2, 141.6, 135.0, 131.2, 124.4, 124.0, 119.3, 112.5, 66.8, 65.0, 63.9, 53.3, 53.2, 32.7 ppm;

IR (film): $\tilde{\nu}$ 2958 (w), 1780 (w), 1715 (s), 1635 (m), 1577 (m), 1549 (w), 1490 (w), 1435 (w), 1361 (w), 1267 (m), 1223 (m), 1181 (s), 1131 (w), 1085 (s), 982 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{20}H_{18}N_3O_8^+$ $[M+H]^+$ 428.1088; found 428.1092.

***anti*-Dimethyl 3-(1,3-dioxoisoindolin-2-yl)-7-methyl-6-nitro-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate** (**60**).



Following the general procedure 4-methyl-3-nitropyridine (**SI-73**) (28 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (12 mg, 20 µmol, 10 mol%) were stirred in CH_2Cl_2 (0.2 mL, 1 M) for 3 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 3:1 to 2:1) and 65 mg (0.15 mmol, 74%) of the title compound **60** were isolated as a red oil.

R_f: 0.2 (silica, pentane:EtOAc 2:1);

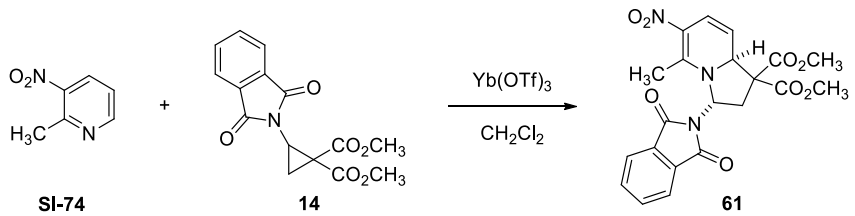
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (s, 1H, C=C*H*-N), 7.89 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.80 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 6.21 (dd, *J* = 8.5, 6.8 Hz, 1H, N-C*H*-Phth), 5.58 (t, *J* = 2.0 Hz, 1H, N-C*H*-CH), 5.12 (t, *J* = 1.7 Hz, 1H, (CH_3)C=C*H*), 3.84 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 2.88 (dd, *J* = 13.9, 8.5 Hz, 1H, CH_2), 2.75 (dd, *J* = 13.9, 6.8 Hz, 1H, CH_2), 2.15 (t, *J* = 1.7 Hz, 3H, CH_3);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.3, 168.2, 167.1, 143.2, 134.9, 131.3, 129.2, 125.9, 124.0, 110.5, 66.8, 65.1, 64.1, 53.2, 53.1, 32.8, 21.5;

IR (film): $\tilde{\nu}$ 2957 (w), 1778 (w), 1715 (s), 1671 (m), 1640 (m), 1571 (m), 1497 (w), 1434 (w), 1359 (w), 1265 (s), 1234 (m), 1169 (s), 1079 (s), 1041 (m), 942 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{21}H_{20}N_3O_8^+$ $[M+H]^+$ 442.1245; found 442.1241.

***anti*-Dimethyl 3-(1,3-dioxoisoindolin-2-yl)-5-methyl-6-nitro-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate** (**61**).



Following the general procedure 2-methyl-3-nitropyridine (**SI-74**) (28 mg, 0.20 mmol, 1.00 equiv.), **14** (64 mg, 0.21 mmol, 1.05 equiv.) and $Yb(OTf)_3$ (12 mg, 20 µmol, 10 mol%) were stirred in CH_2Cl_2 (0.2 mL, 1 M) for 3 hours. The crude product was purified by column chromatography (silica, pentane:EtOAc 3:1 to 2:1) and 71 mg (0.15 mmol, 80%) of the title compound **61** were isolated as a yellow oil.

R_f: 0.3 (silica, pentane:EtOAc 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.79 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 6.84 (dd, *J* = 10.7, 2.3 Hz, 1H, C*H*-C(NO_2)), 6.42 (dd, *J* = 8.5, 6.8 Hz, 1H, C*H*-Phth), 5.77 (t, *J* = 2.3 Hz, 1H, N-C*H*-CH), 5.40 (dd, *J* = 10.7, 2.3 Hz, 1H, n-CH-C*H*=CH), 3.80 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 2.95 (dd, *J* = 13.7, 8.5 Hz, 1H, CH_2), 2.50 (dd, *J* = 13.7, 6.8 Hz, 1H, CH_2), 2.40 (s, 3H, CH_3);

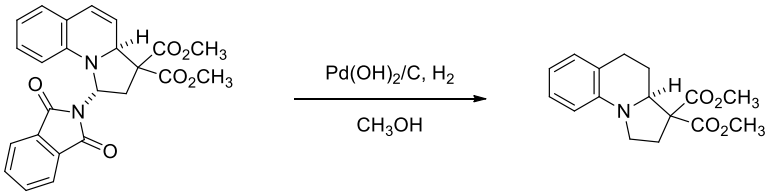
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.1, 167.8, 166.6, 154.7, 135.0, 130.9, 125.1, 124.0, 121.3, 110.7, 65.1, 64.9, 63.8, 53.2, 53.1, 34.9, 18.0;

IR (film): $\tilde{\nu}$ 2977 (w), 2277 (w), 1788 (w), 1748 (s), 1557 (m), 1487 (w), 1282 (s), 1254 (s), 1216 (s), 1175 (s), 1105 (m), 1024 (m), 930 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{21}H_{20}N_3O_8^+$ $[M+H]^+$ 442.1245; found 442.1251.

12. Product modification

Dimethyl 1,2,4,5-tetrahydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (**SI-75**).



17 **SI-75**

$Pd(OH)_2$/C (3 mg, 20% Pd, 10%$_{w/w}$) was added to a solution of **17** (30 mg, 70 µmol) in CH_3OH (0.4 mL, 0.17 M), the mixture was purged with H_2 and stirred for 18 hours. Thereafter the mixture was filtered through a plug of celite® and concentrated. The residue product was purified by column chromatograohy (SiO_2, pentane:EtOAc 50:1) and 14 mg (50 µmol, 70%) of the title compound **SI-75** were isolated as a yellow oil.

R_f: 0.8 (silica, pentane:EtOAc 4:1);

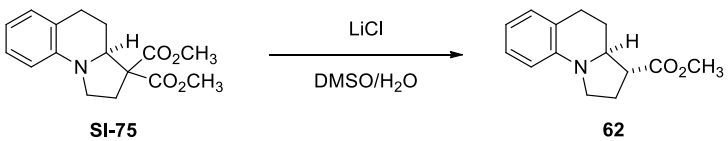
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 – 7.04 (m, 1H, Ar*H*), 6.98 (d, *J* = 7.4 Hz, 1H, Ar*H*), 6.59 (td, *J* = 7.3, 1.1 Hz, 1H, Ar*H*), 6.39 (dd, *J* = 8.1, 1.1 Hz, 1H, Ar*H*), 4.03 (dd, *J* = 11.5, 2.9 Hz, 1H, C*H*), 3.79 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.62 (q, *J* = 8.4 Hz, 1H, CH_2), 3.32 (td, *J* = 9.3, 2.4 Hz, 1H, CH_2), 2.99 – 2.87 (m, 1H, CH_2), 2.80 (ddd, *J* = 16.2, 4.7, 2.4 Hz, 1H, CH_2), 2.73 (ddd, *J* = 13.1, 7.8, 2.4 Hz, 1H, CH_2), 2.34 (ddt, *J* = 12.3, 5.1, 2.7 Hz, 1H, CH_2), 2.22 (ddd, *J* = 13.1, 9.6, 8.8 Hz, 1H, CH_2), 1.37 (tdd, *J* = 12.7, 11.6, 4.7 Hz, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.6, 169.8, 144.1, 128.3, 127.2, 121.0, 115.7, 110.2, 62.1, 61.9, 52.6, 52.4, 45.7, 31.8, 27.8, 23.9;

IR (film): $\tilde{\nu}$ = 2954 (w), 2925 (w), 2854 (w), 1732 (s), 1605 (m), 1576 (w), 1506 (m), 1480 (w), 1460 (m), 1436 (m), 1365 (w), 1314 (m), 1270 (s), 1221 (m), 1199 (m), 1172 (m), 1090 (s) cm^{-1};

HRMS (ESI) calcd. for $C_{16}H_{19}NNaO_4^+$ $[M+Na]^+$ 312.1206; found 312.1205.

(3*S*,3a*R*)-methyl 1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinoline-3-carboxylate (**62**).



SI-75 **62**

LiCl (37 mg, 0.86 mmol) was added to a solution of **SI-75** (50 mg, 0.17 mmol) in DMSO:H_2O 10:1 (0.88 mL, 0.2 M) at room temperature and the resulting mixture was then heated for 5 hours to 140 °C.

The mixture was cooled to room temperature, quenched with sat. aq. NH_4Cl (5 mL) and extracted with DCM (3x15 mL). The combined org. extracts were washed with brine (10 mL) and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The residue was purified by column chromatograohy (SiO_2, pentane:EtOAc 50:1) and 34 mg (0.15 mmol, 85%) of the title compound **62** were isolated as a yellow oil.

R_f: 0.5 (silica, pentane:EtOAc 20:1);

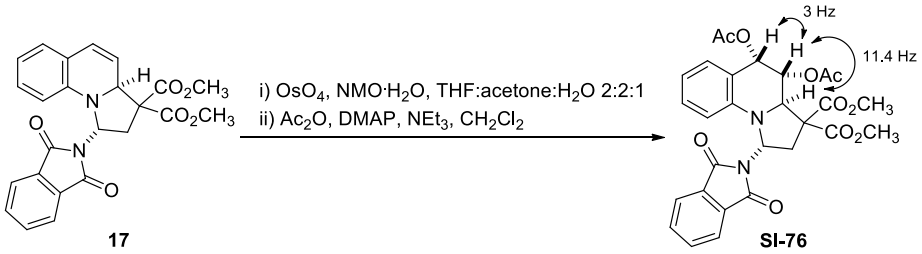
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 – 7.04 (m, 1H, Ar*H*), 7.00 (d, *J* = 7.3 Hz, 1H, Ar*H*), 6.60 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.41 (d, *J* = 8.1 Hz, 1H, Ar*H*), 3.75 (s, 3H, OCH_3), 3.65 – 3.53 (m, 1H, N-C*H*), 3.43 (td, *J* = 9.1, 2.3 Hz, 1H, N-CH_2), 3.31 (td, *J* = 9.3, 7.5 Hz, 1H, N-CH_2), 2.86 (m, 1H, Ar-CH_2), 2.78 (m, 1H, Ar-CH_2), 2.67 (m, 1H, C*H*-COOMe), 2.41 – 2.19 (m, 3H, CH_2), 1.56 – 1.41 (m, 1H, CH_2) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.4, 144.1, 128.5, 127.2, 121.3, 115.8, 110.2, 60.5, 51.9, 50.0, 46.4, 27.8, 27.6, 26.4 ppm;

IR (film): $\tilde{\nu}$ = 2952 (w), 2849 (w), 1737 (s), 1605 (m), 1506 (m), 1460 (w), 1352 (m), 1312 (w), 1279 (w), 1204 (w), 1054 (w), 1021 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{14}H_{18}NO_2^+$ $[M+H]^+$ 232.1332; found 232.1339.

***rac*-(1*R*,3a*S*,4*S*,5*R*)-Dimethyl 4,5-diacetoxy-1-(1,3-dioxoisoindolin-2-yl)-1,2,4,5-tetrahydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**SI-76**).



OsO_4 (0.38 mL, 60 µmol, 4% in water, 5 mol%) was added to a solution of **17** (510 mg, 1.18 mmol, 1 equiv.) and NMO·H_2O (261 mg, 1.93 mmol, 1.2 equiv.) in THF:acetone:water (2:2:1, 5.0 mL, 0.23 M) at room temperature and the resulting mixture was stirred for 18 hours. The reaction was diluted with water (10 mL) and extracted with EtOAc (3 x 15 mL). The combined org. extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solution was concentrated. The crude product was dissolved in CH_2Cl_2 (2.0 mL, 0.58 M), DMAP (14 mg, 0.12 mmol, 0.1 equiv.), NEt_3 (0.66 mL, 4.7 mmol, 4 equiv.) and Ac_2O (0.33 mL, 3.5 mmol, 3 equiv.) were added and the resulting mixture was stirred for 16 hours. The reaction was quenched with sat. aq. NH_4Cl (10 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined org. extracts were washed with brine (15 mL) and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The residue was purified by

column chromatography (silica, pentane:EtOAc 2:1) and 0.46 g (0.84 mmol, 71%) of the title compound **SI-76** were isolated as a colorless oil.

R_f: 0.3 (silica, pentane:EtOAc 1:1);

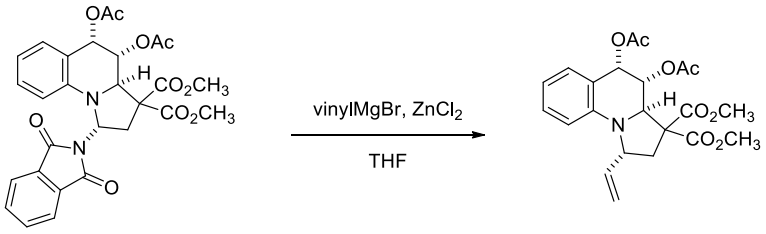
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.71 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.22 (dd, *J* = 7.5, 1.6 Hz, 1H, Ar*H*), 7.14 (ddd, *J* = 8.7, 7.5, 1.6 Hz, 1H, Ar*H*), 6.67 (td, *J* = 7.4, 1.0 Hz, 1H, Ar*H*), 6.55 (d, *J* = 8.2 Hz, 1H, Ar*H*), 6.32 (dd, *J* = 8.4, 6.0 Hz, 1H, C*H*-Phth), 6.14 (d, *J* = 3.0 Hz, 1H, Ar-C*H*-OAc), 5.41 (d, *J* = 11.4 Hz, 1H, C*H*-N), 5.05 (dd, *J* = 11.4, 3.0 Hz, 1H, C*H*-OAc), 3.82 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.29 (dd, *J* = 13.5, 8.3 Hz, 1H, CH_2), 2.79 (dd, *J* = 13.5, 6.0 Hz, 1H, CH_2), 2.14 (s, 3H, O*Ac*), 2.06 (s, 3H, O*Ac*);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.6, 169.8, 169.2, 168.8, 167.6, 140.3, 134.3, 131.8, 131.5, 131.1, 123.6, 117.9, 117.5, 110.8, 69.3, 68.8, 62.9, 61.3, 60.0, 53.3, 52.8, 38.2, 21.3, 20.7;

IR (film): $\tilde{\nu}$ = 3016 (w), 2951 (w), 1742 (s), 1716 (s), 1610 (w), 1500 (w), 1374 (m), 1266 (s), 1243 (m), 1222 (m), 1188 (w), 1139 (w), 1053 (s), 1025 (m), 968 (w), 913 (w) cm^{-1};

HRMS (ESI) calcd. for $C_{28}H_{26}N_2NaO_{10}^+$ $[M+Na]^+$ 573.1480; found 573.1490.

***rac*-(1*S*,3a*S*,4*S*,5*R*)-Dimethyl 4,5-diacetoxy-1-vinyl-1,2,4,5-tetrahydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**63**).



SI-76 **63**

Vinylmagnesium bromide (0.47 mL, 0.33 mmol, 0.7 M in THF, 4 equiv.) was added dropwise to a solution of dry $ZnCl_2$ (0.11 g, 0.82 mmol, 10 equiv.) in THF (1 mL) and the resulting mixture was stirred for 10 minutes at room temperature. Thereafter a solution of **SI-76** (45 mg, 82 µmol, 1 equiv.) in THF (3.5 mL) was added dropwise and the resulting mixture was heated to 50 °C for 18 hours. Thereafter, the reaction was cooled to room temperature and quenched with sat. aq. NH_4Cl (10 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL), the combined org. extracts were washed with brine (20 mL) and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica, pentane:EtOAc 3:1) and 24 mg (0.056 mmol, 68%) of the title compound **63** were isolated as a colorless oil.

R_f: 0.6 (silica, pentane:EtOAc 1:1);

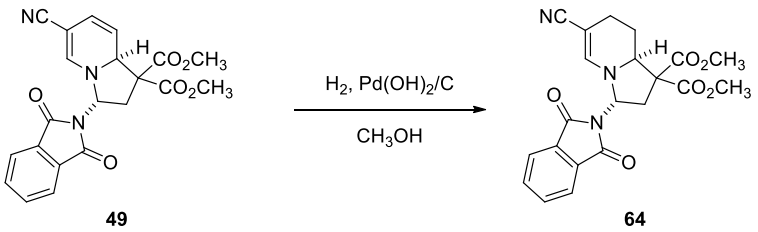
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 – 7.11 (m, 2H, Ar*H*), 6.65 (td, *J* = 7.4, 1.0 Hz, 1H, Ar*H*), 6.56 (d, *J* = 8.2 Hz, 1H, Ar*H*), 6.15 (d, *J* = 3.0 Hz, 1H, Ar-C*H*-OAc), 5.77 (ddd, *J* = 17.1, 10.2, 7.0 Hz, 1H, C*H*=CH_2), 5.31 (dt, *J* = 17.2, 1.1 Hz, 1H, CH=CH_2), 5.24 (dt, *J* = 10.2, 1.1 Hz, 1H, CH=CH_2), 5.13 (dd, *J* = 11.3, 3.0 Hz, 1H, CH-C*H*-OAc), 4.76 (d, *J* = 11.3 Hz, 1H, N-C*H*-CHOAc), 4.47 (q, *J* = 7.6 Hz, 1H, N-C*H*-CH=CH_2), 3.78 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.07 (dd, *J* = 13.1, 7.7 Hz, 1H, CH_2), 2.15 (dd, *J* = 13.1, 8.0 Hz, 1H, CH_2), 2.10 (s, 3H, O*Ac*), 2.01 (s, 3H, O*Ac*).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.4, 169.8, 169.6, 169.0, 142.7, 138.5, 131.3, 130.5, 116.9, 116.8, 116.5, 111.9, 69.4, 69.1, 60.4, 60.2, 60.1, 53.1, 52.8, 41.1, 21.3, 20.7;

IR (film): $\tilde{\nu}$ = 2675 (w), 2350 (w), 1739 (s), 1610 (w), 1498 (w), 1372 (w), 1261 (m), 1242 (m), 1224 (m), 1179 (w), 1060 (s), 1026 (m), 954 (w), 912 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{22}H_{26}NO_8^+$ $[M+H]^+$ 432.1653; found 432.1652.

***anti*-Dimethyl 6-cyano-3-(1,3-dioxoisoindolin-2-yl)-2,3,8,8a-tetrahydroindolizine-1,1(7*H*)-dicarboxylate** (**64**).



49 **64**

$Pd(OH)_2$/C (12 mg, 10%$_{w/w}$, 20% Pd) was added to a solution of **49** (0.12 mg, 0.30 mmol) in methanol (3 mL), the mixture was purged with hydrogen and then stirred for 8 hours under hydrogen atmosphere. The mixture was filtered through a plug of Celite®, concentrated and the residue was purified by column chromatography (silica, pentane:EtOAc 2:1) affording 88 mg (0.22 mmol, 73%) of the title compound **64**.

R_f: 0.2 (silica, pentane:EtOAc 2:1);

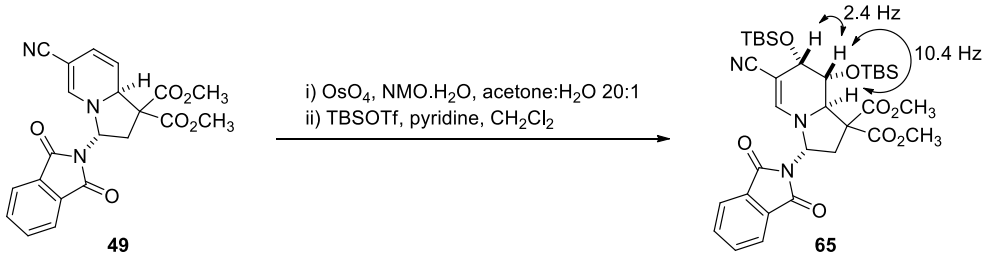
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 5.5, 3.1 Hz, 2H, *Phth*), 7.77 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 6.74 (d, *J* = 1.6 Hz, 1H, N-C*H*=C(CN)), 6.02 (dd, *J* = 8.2, 6.6 Hz, 1H, C*H*-Phth), 4.35 (dd, *J* = 11.4, 3.3 Hz, 1H, N-C*H*-CH_2), 3.81 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 2.89 (qd, *J* = 14.0, 7.4 Hz, 2H, CH_2), 2.42 – 2.29 (m, 2H, CH_2), 2.27 – 2.18 (m, 1H, CH_2), 1.24 – 1.13 (m, 1H, CH_2);

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.5, 168.9, 167.5, 141.2, 134.7, 131.3, 123.7, 121.6, 77.6, 65.0, 62.2, 59.8, 53.0, 52.9, 34.7, 23.4, 22.5;

IR (film): $\tilde{\nu}$ = 2955 (w), 2854 (w), 2193 (m), 1776 (w), 1733 (s), 1714 (s), 1623 (s), 1438 (w), 1397 (w), 1353 (m), 1324 (m), 1272 (m), 1219 (w), 1151 (m), 1106 (m), 972 (w), 913 (m) cm^{-1};

HRMS (ESI) calcd. for $C_{21}H_{20}N_3O_6^+$ [M+H]$^+$ 410.1347; found 410.1348.

***rac*-(3*R*,7*R*,8*S*,8a*S*)-Dimethyl 7,8-bis((*tert*-butyldimethylsilyl)oxy)-6-cyano-3-(1,3-dioxoisoindolin-2-yl)-2,3,8,8a-tetrahydroindolizine-1,1(7*H*)-dicarboxylate** (**65**).



OsO_4 (0.21 mL, 0.026 mmol, 4% in water, 5 mol%) was added to a solution of **49** (214 mg, 0.525 mmol, 1 equiv.) and NMO·H_2O (85 mg, 0.63 mmol, 1.2 equiv.) in acetone:water 20:1 (5.25 mL, 0.1 M) at 0 °C. The resulting mixture was stirred for 16 hours, while warming to room temperature, then the solvent was evaporated and the residue was dried in high vacuo. The residue was suspended in CH_2Cl_2 (2.5 mL) and pyridine (0.21 mL, 2.6 mmol, 5 equiv.) followed by TBSOTf (0.48 mL, 2.1 mmol, 4 equiv.) were added. The resulting mixture was stirred for 18 hours at room temperature and thereafter quenched with sat. aq. NH_4Cl (10 mL). The mixture was extracted with Et_2O (3 x 15 mL), the combined org. extracts were washed with brine (10 mL) and then dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica, pentane:EtOAc 4:1) affording 231 mg (0.345 mmol, 66%) of the title compound **65** as a colorless oil.

R_f: 0.2 (silica, pentane:EtOAc 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 7.78 (dd, *J* = 5.5, 3.0 Hz, 2H, *Phth*), 6.75 (s, 1H, N-C*H*=C(CN)), 6.03 (t, *J* = 7.8 Hz, 1H, C*H*-Phth), 5.09 (d, *J* = 10.4 Hz, 1H, N-C*H*-CH(OTBS)), 4.27 (d, *J* = 2.4 Hz, 1H, C(CN)-C*H*(OTBS)), 3.82 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.72 (dd, *J* = 10.4, 2.4 Hz, 1H, (CN)C-CH-C*H*-CHN), 3.06 (dd, *J* = 13.2, 7.8 Hz, 1H, CH_2), 2.96 (dd, *J* = 13.2, 7.8 Hz, 1H, CH_2), 0.92 (s, 9H, C(CH_3)$_3$), 0.89 (s, 9H, C(CH_3)$_3$), 0.15 (s, 3H, SiCH_3), 0.13 (s, 3H, SiCH_3), 0.04 (s, 3H, SiCH_3), -0.06 (s, 3H, SiCH_3) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.0, 168.2, 167.0, 143.6, 134.8, 131.3, 123.8, 121.1, 80.2, 70.7, 67.8, 64.9, 61.2, 61.0, 53.0, 52.9, 36.5, 25.9, 25.5, 18.1, 17.9, -3.2, -3.5, -4.8, -5.5 ppm;

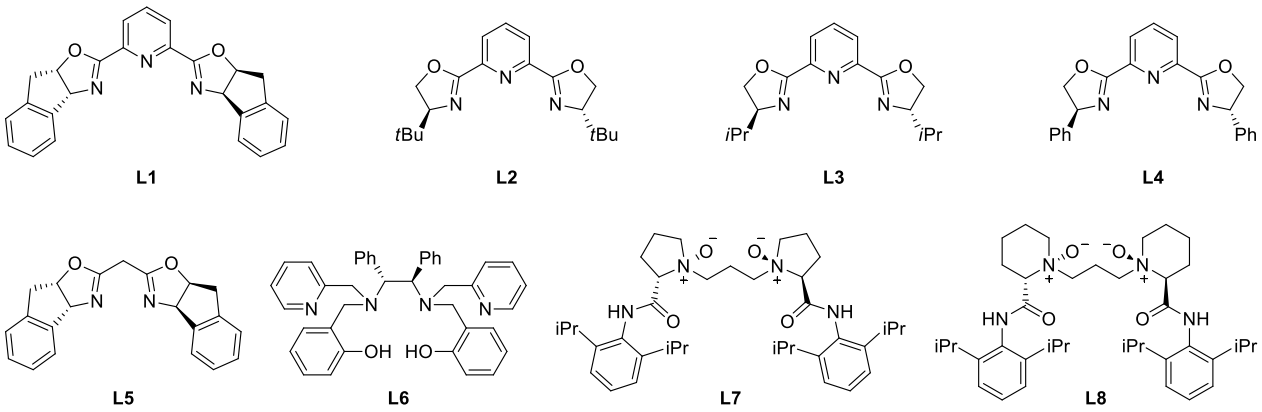
IR (film): $\tilde{\nu}$ = 2954 (w), 2930 (w), 2894 (w), 2857 (w), 2195 (w), 1720 (s), 1618 (s), 1472 (w), 1360 (w), 1255 (m), 1133 (m), 1109 (m), 958 (m), 913 (m), 840 (s) cm^{-1};

HRMS (ESI) calcd. for $C_{33}H_{47}N_3NaO_8Si_2^+$ [M+Na]$^+$ 692.2794; found 692.2797.

13. Attempts towards the Enantioselective Dearomatization

Table S8 Screening of chiral ligands for the annulation reaction.

8 1 equiv. | **14** 1.05 equiv. | 5 mol% | 6 mol% | **17**



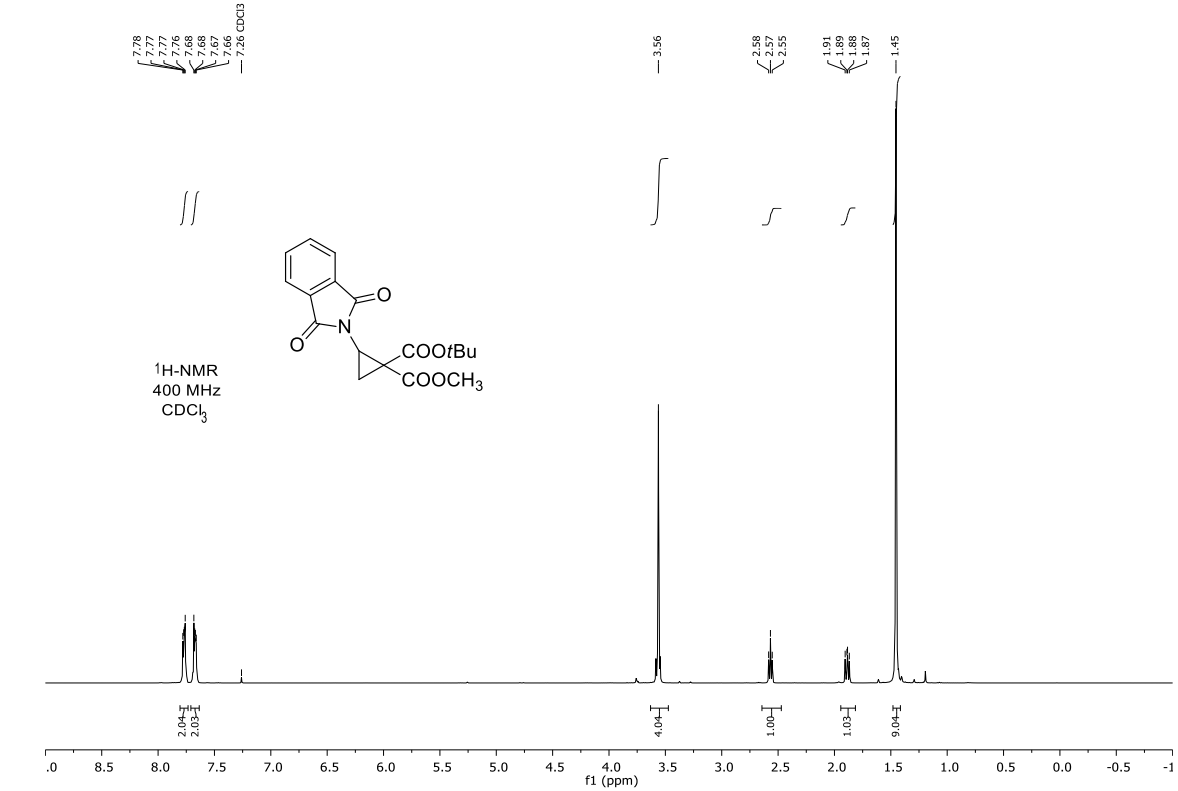
Entry	Lewis Acid	Ligand	Solvent	Yield	ee
1	$Yb(OTf)_3$	**L1**	CH_2Cl_2	88%	0%
2	$Sc(OTf)_3$	**L1**	CH_2Cl_2	90%	12%
3	$Sc(OTf)_3$	**L1**	PhCl	56%	9%
4	MgI_2	**L1**	CH_2Cl_2	81%	6%
5	$La(OTf)_3$	**L1**	CH_2Cl_2	91%	10%
6	$La(OTf)_3$	**L1**	THF	84%	10%
7	$Zn(OTf)_2$	**L1**	CH_2Cl_2	no conversion	-
8	$Zn(NTf_2)_2$	**L1**	CH_2Cl_2	9%	18%
9	$Sc(OTf)_3$	**L2**	CH_2Cl_2	55%	1%
10	$Sc(OTf)_3$	**L3**	CH_2Cl_2	35%	1%
11	$Sc(OTf)_3$	**L4**	CH_2Cl_2	44%	2%
12	$Cu(OTf)_2$	**L5**	CH_2Cl_2	no conversion	-
13	$Ni(OTf)_2$	**L5**	CH_2Cl_2	93%	6%
14	$Zn(OTf)_2$	**L5**	CH_2Cl_2	83%	10%
15	$Yb(OTf)_3$	**L6**	CH_2Cl_2	93%	0%
16	$Yb(OTf)_3$	**L7**	CH_2Cl_2	87%	0%
17	$Sc(OTf)_3$	**L7**	CH_2Cl_2	85%	0%
18	$Yb(OTf)_3$	**L8**	CH_2Cl_2	83%	0%
19	$Sc(OTf)_3$	**L8**	CH_2Cl_2	88%	0%

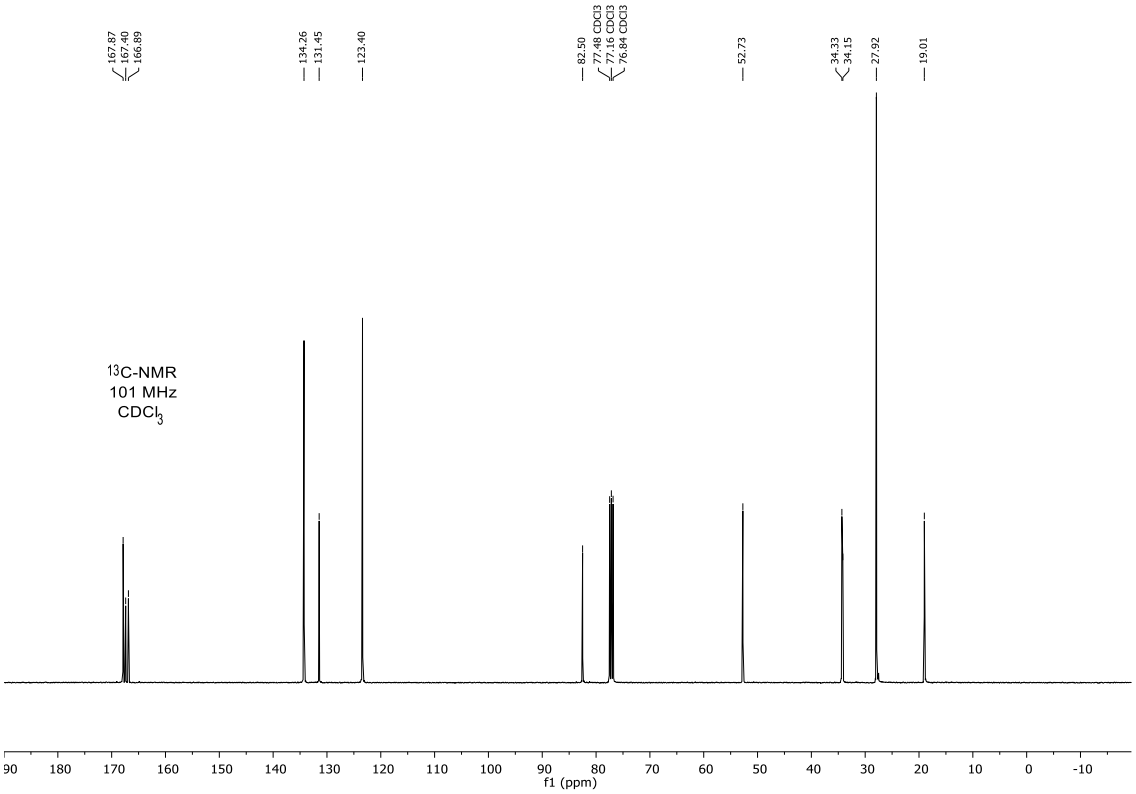
General procedure for the attempted enantioselective dearomatization

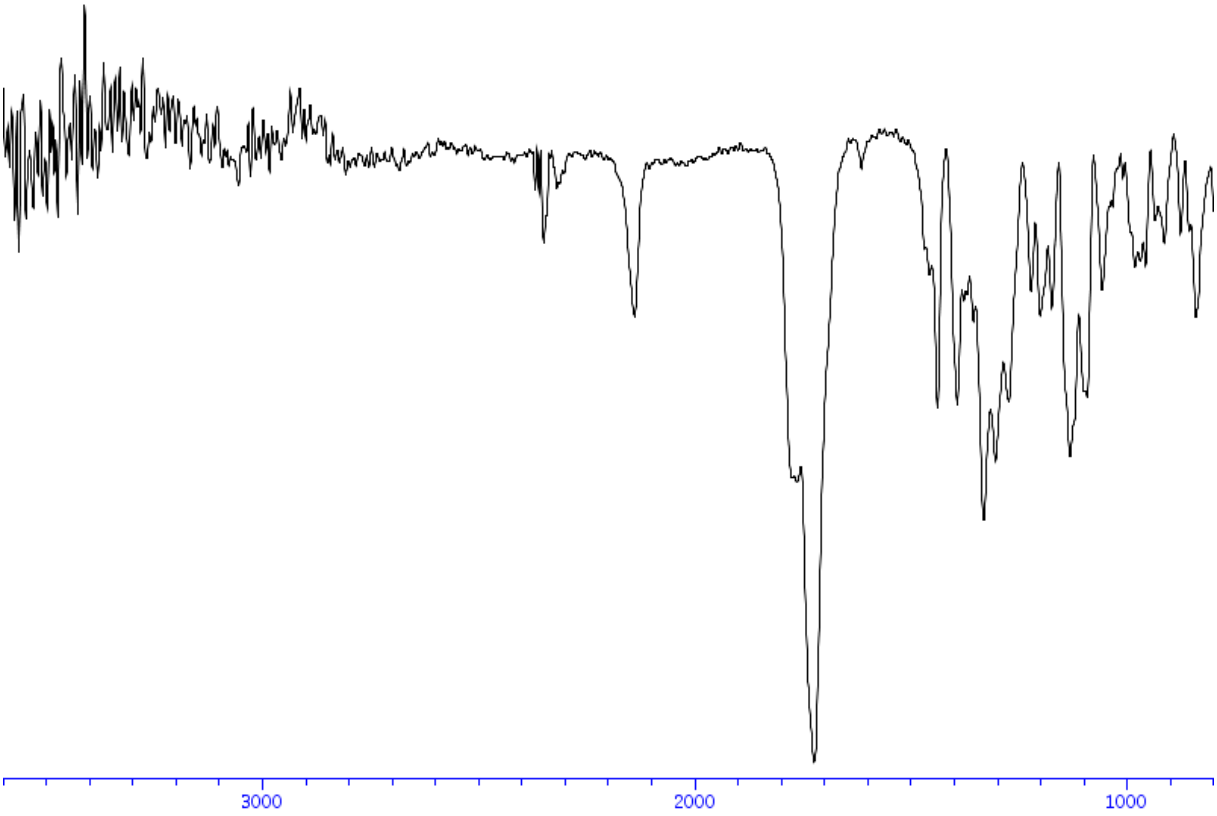
A vial was charged with the ligand (0.06 mmol, 6 mol%) and the Lewis acid (0.05 mmol, 5 mol%) in the glovebox, then CH_2Cl_2 (0.1 mL) was added and the resulting mixture was stirred for 3 hours at room temperature. Thereafter a solution of the cyclopropane **14** in CH_2Cl_2 (0.1 mL) was added, followed by quinoline **8** (0.10 mmol, 1.00 equiv.) and stirring of the mixture was continued for 16 hours at room temperature. The solvent was then evaporated and the residue was purified by column chromatography (silica, pentane:EtOAc 10:1 to 4:1). The enantiomeric excess was determined by chiral HPLC. Chiralcel IA, hexane:*i*PrOH 60:40, 1 mL/min, 31 min, t_{R1} = 10.2 min, t_{R2} 14.4 min, λ = 254 nm.

14. Spectra of new compounds

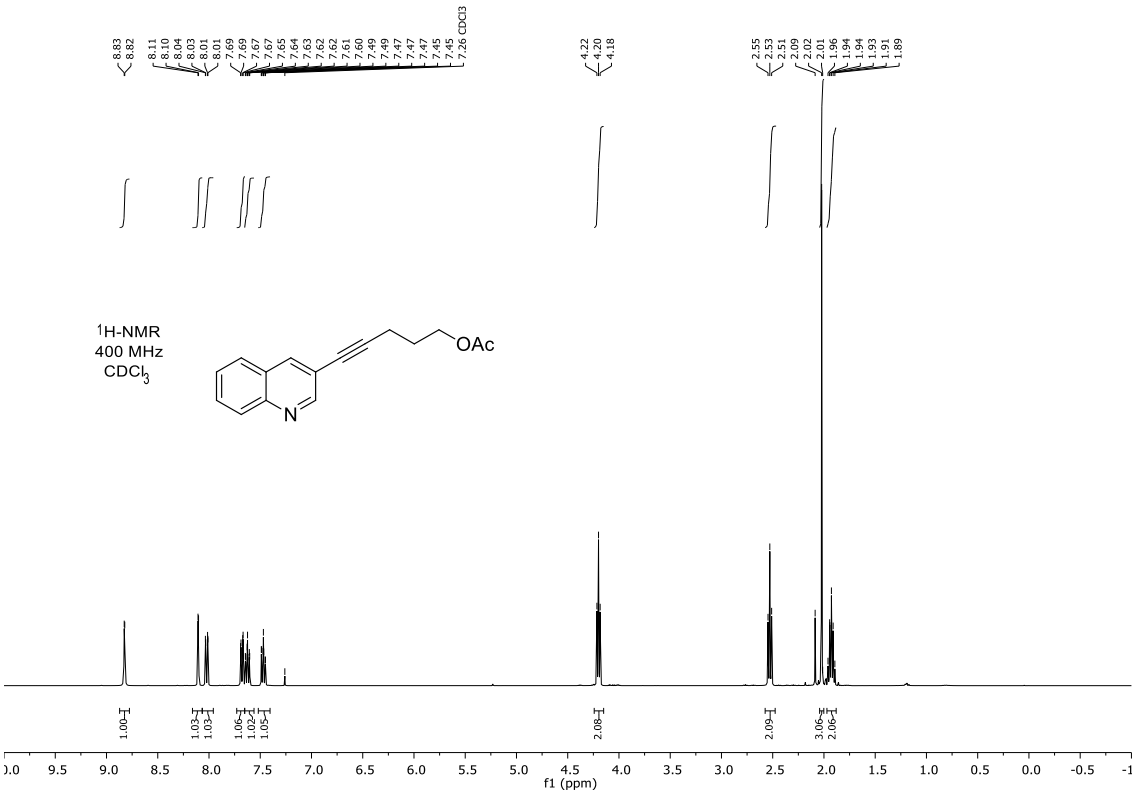
1-*tert*-Butyl 1-methyl 2-(1,3-dioxoisoindolin-2-yl)cyclopropane-1,1-dicarboxylate (SI-32).

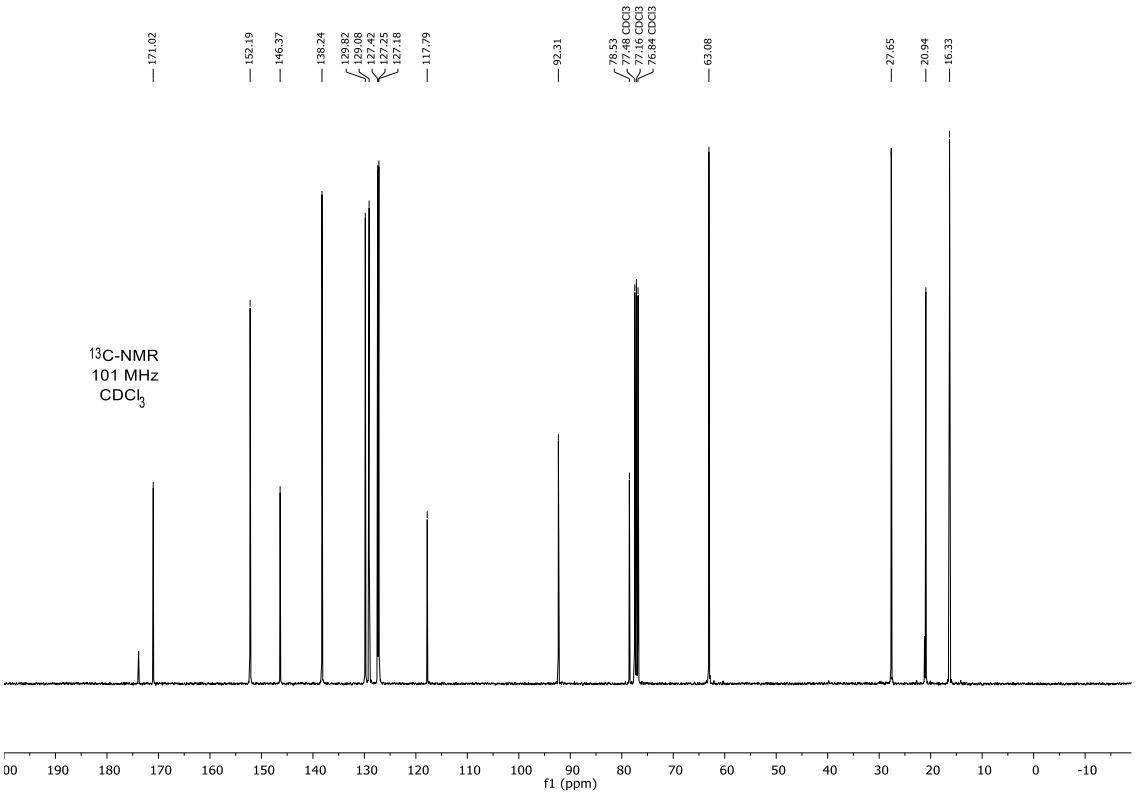


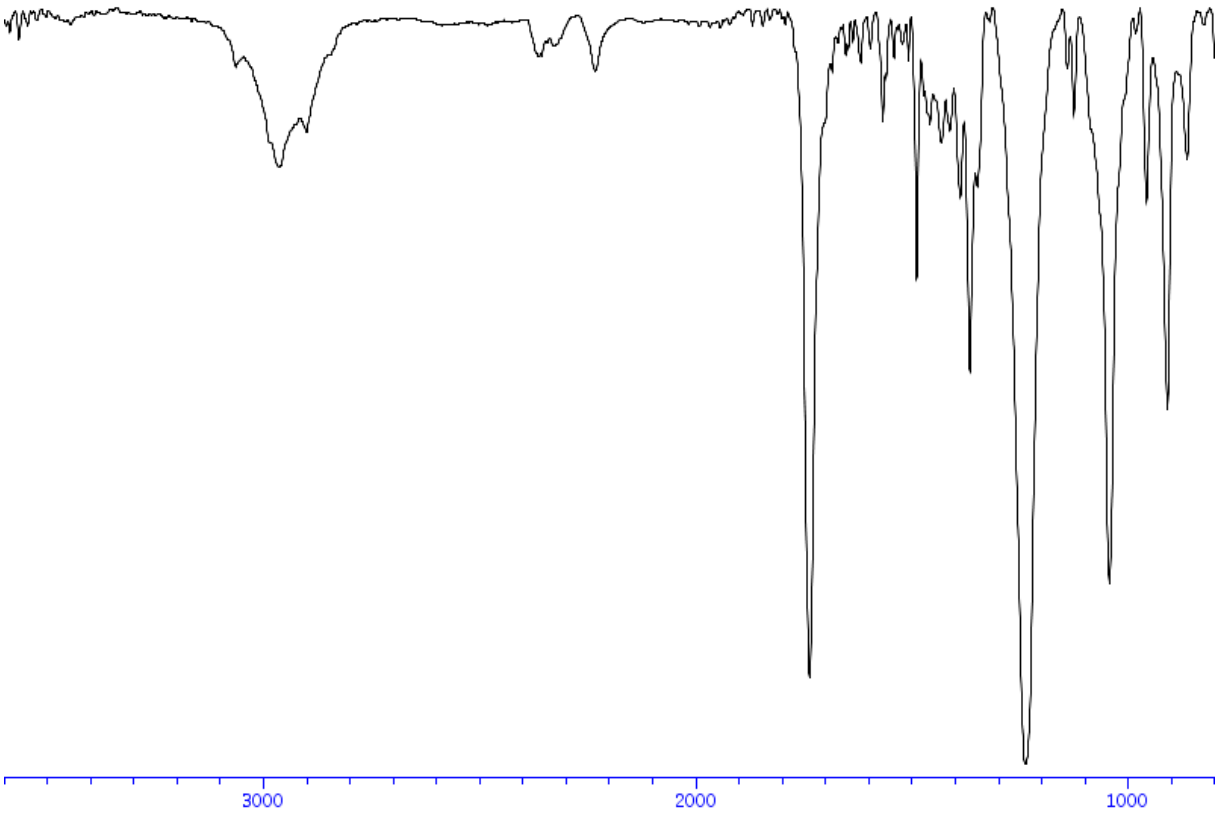




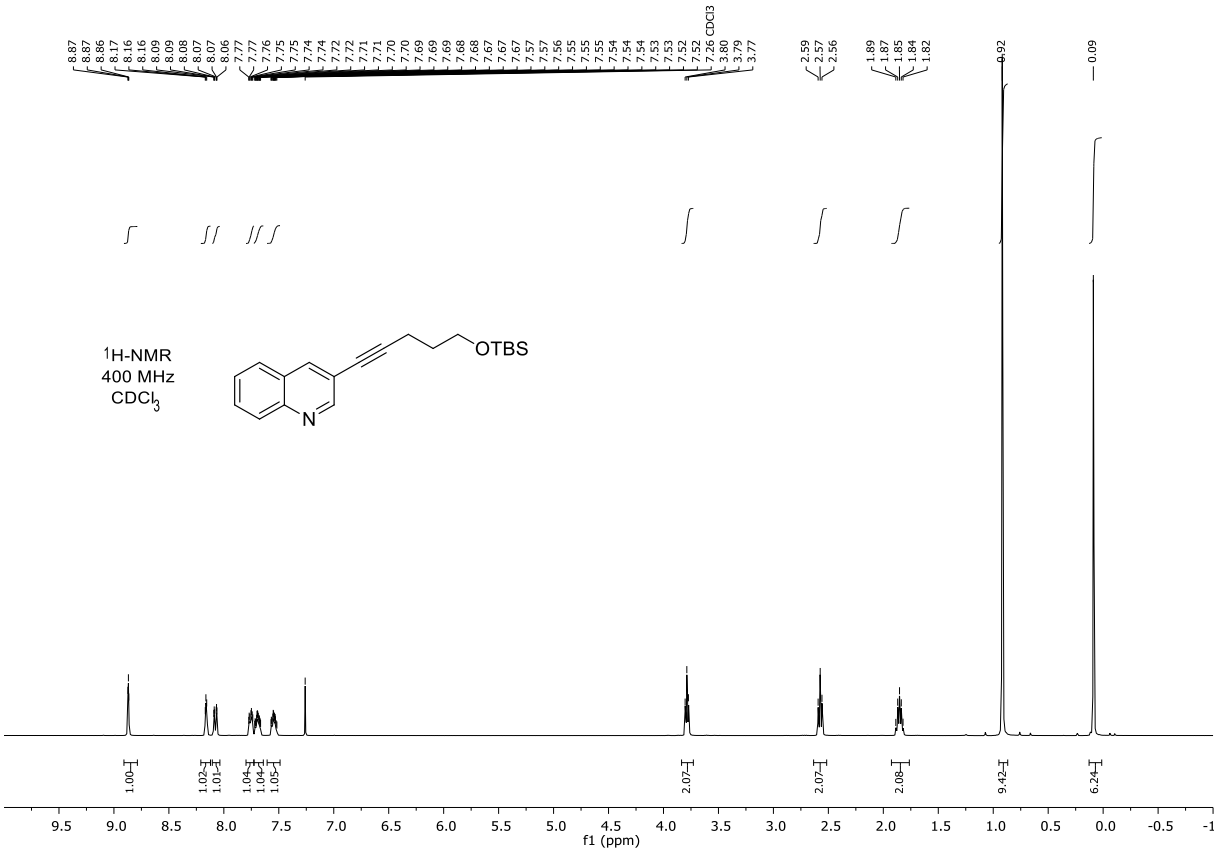
5-(Quinolin-3-yl)pent-4-yn-1-yl acetate (**SI-38**).

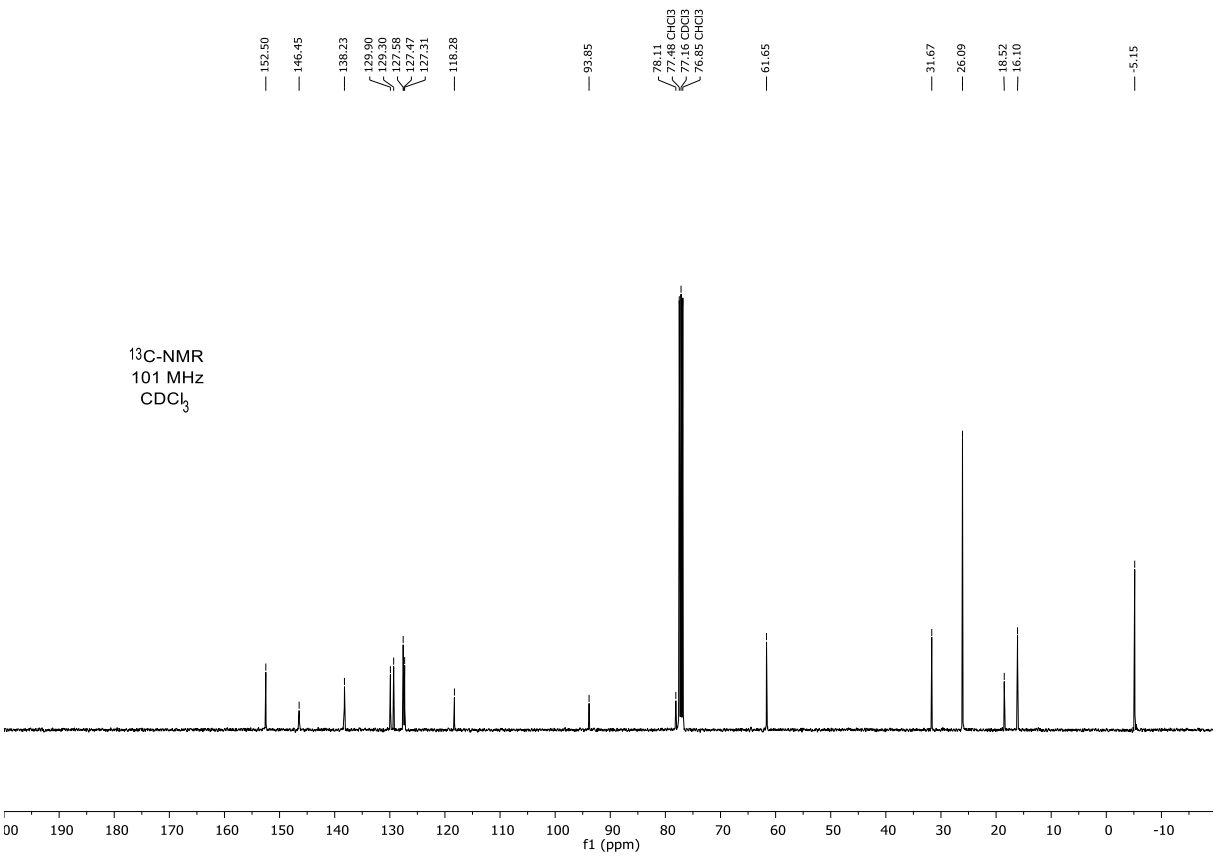


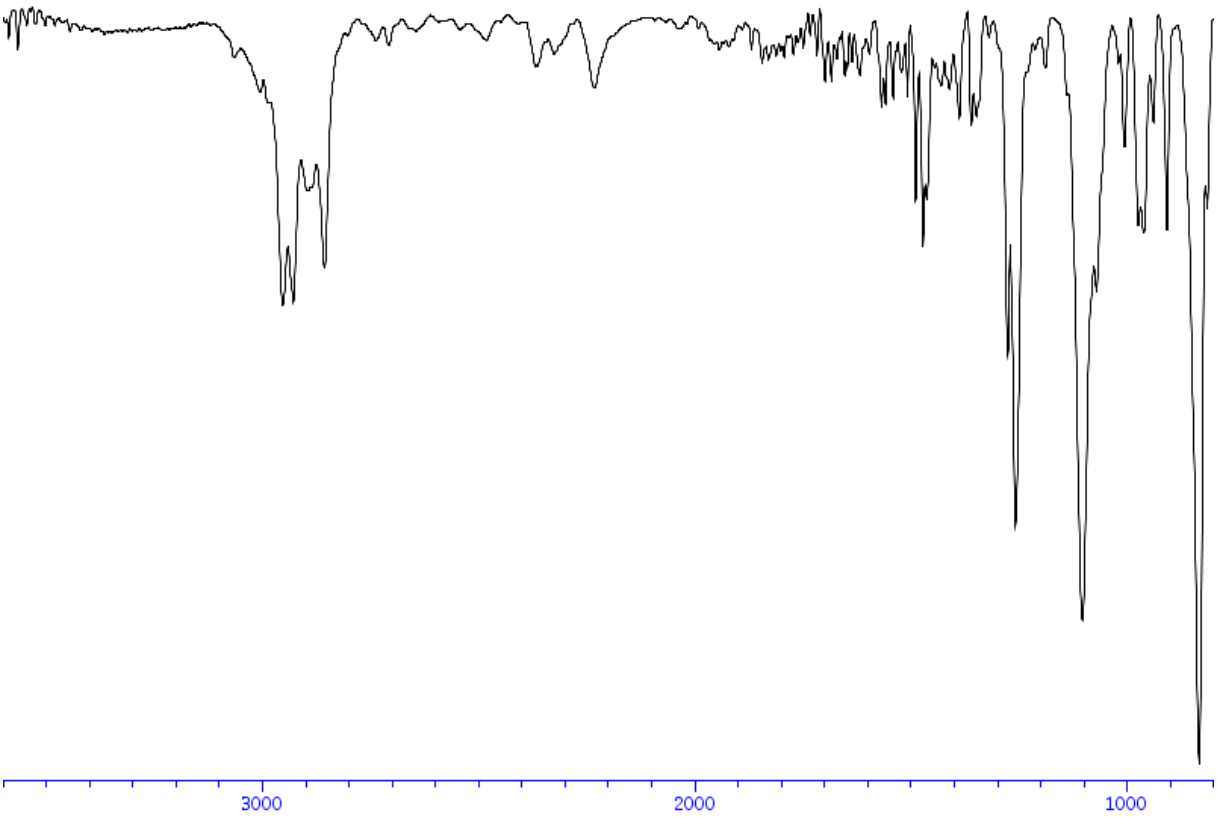

171.02
152.19
146.37
138.24
129.82
129.08
127.42
127.25
127.18
117.79
92.31
78.53
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.08
27.65
20.94
16.33
13C-NMR
101 MHz
CDCl3
f1 (ppm)


3000
2000
1000

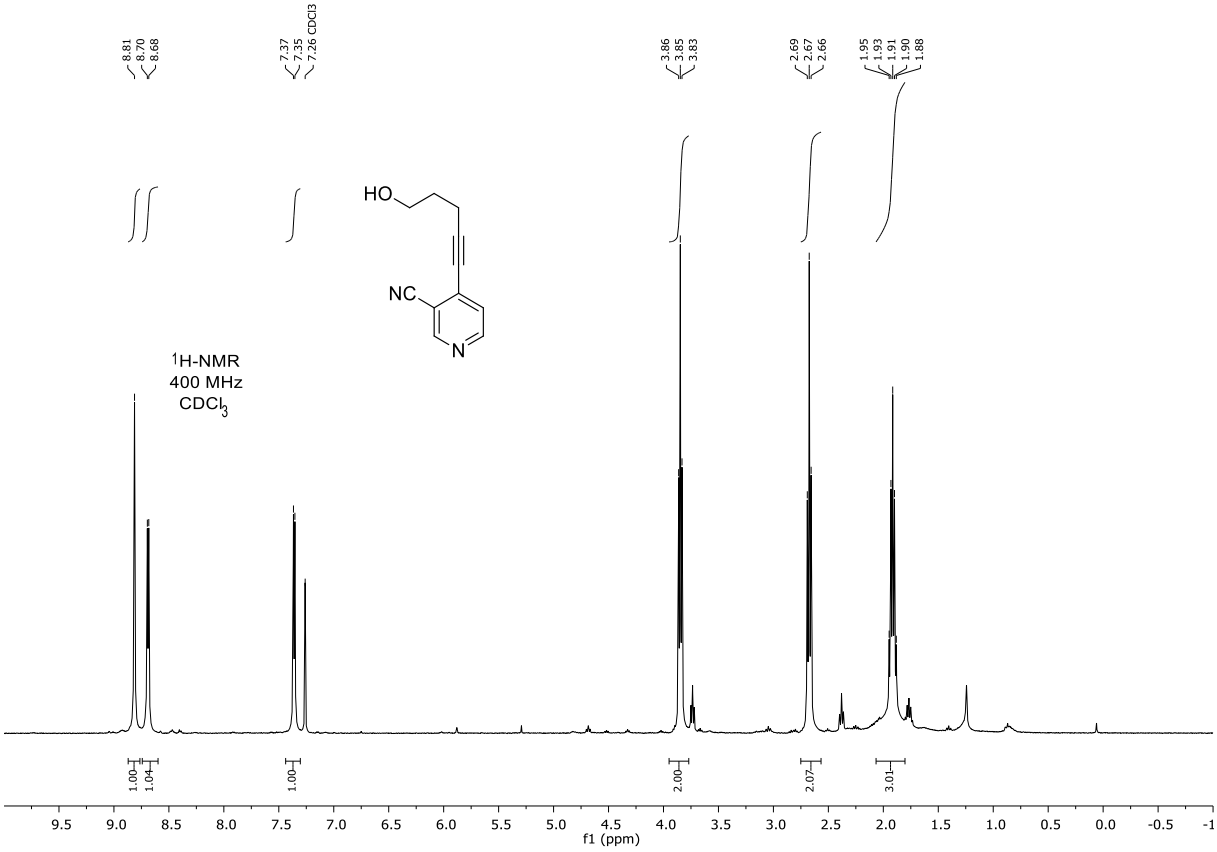
3-(5-((*tert*-Butyldimethylsilyl)oxy)pent-1-yn-1-yl)quinoline (SI-39).

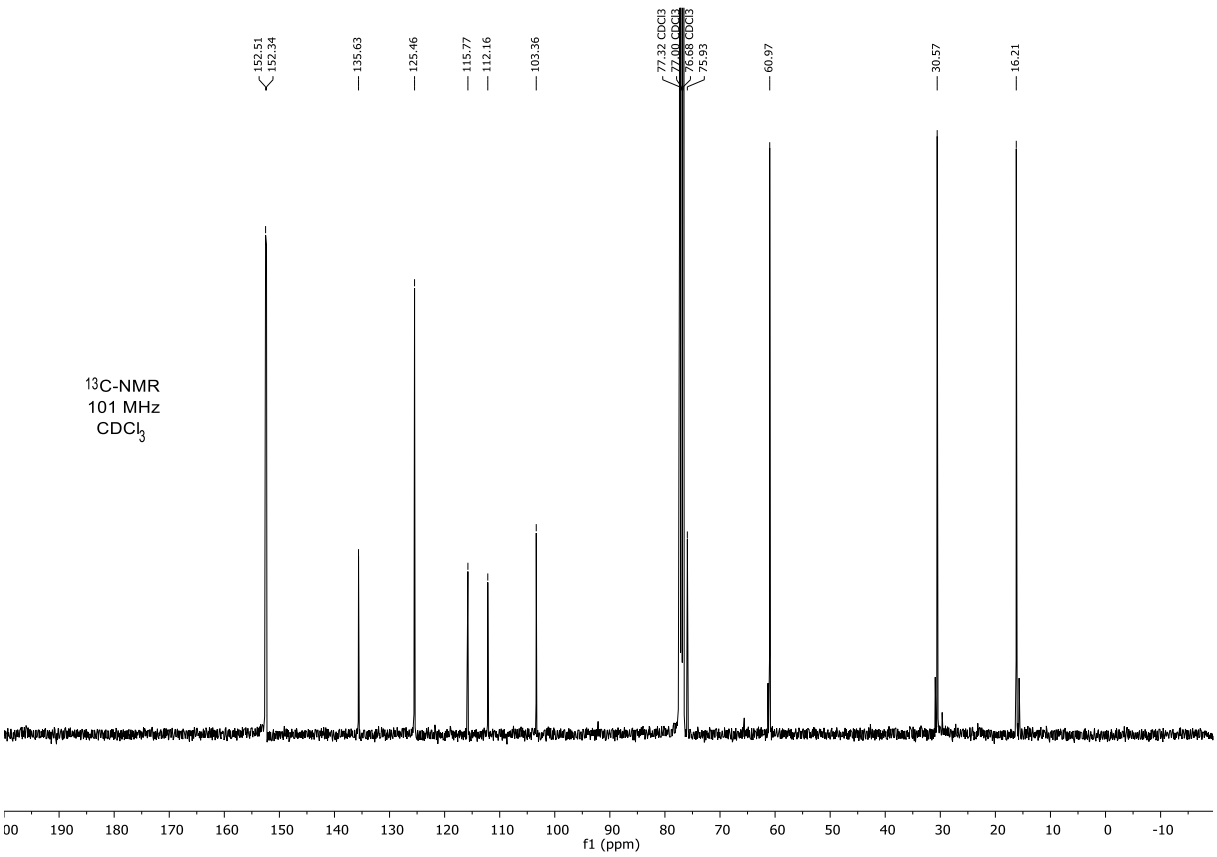


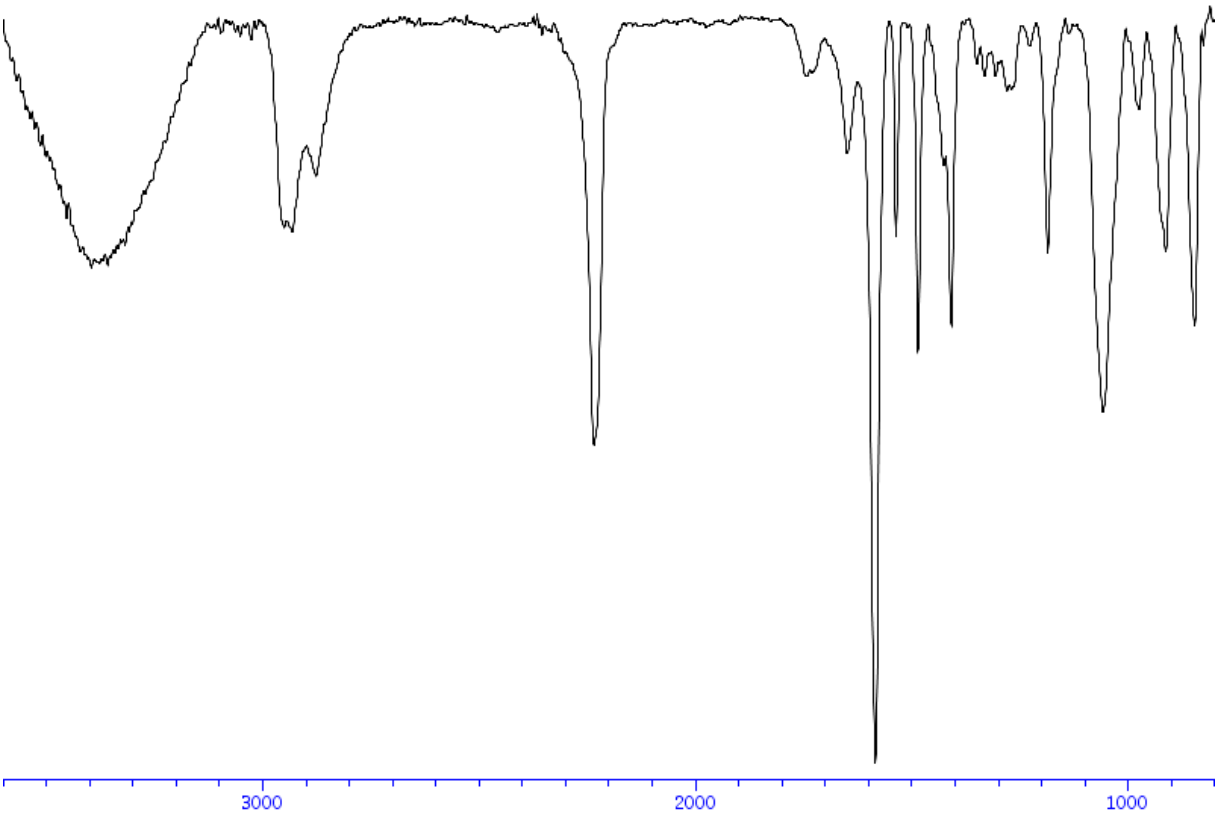




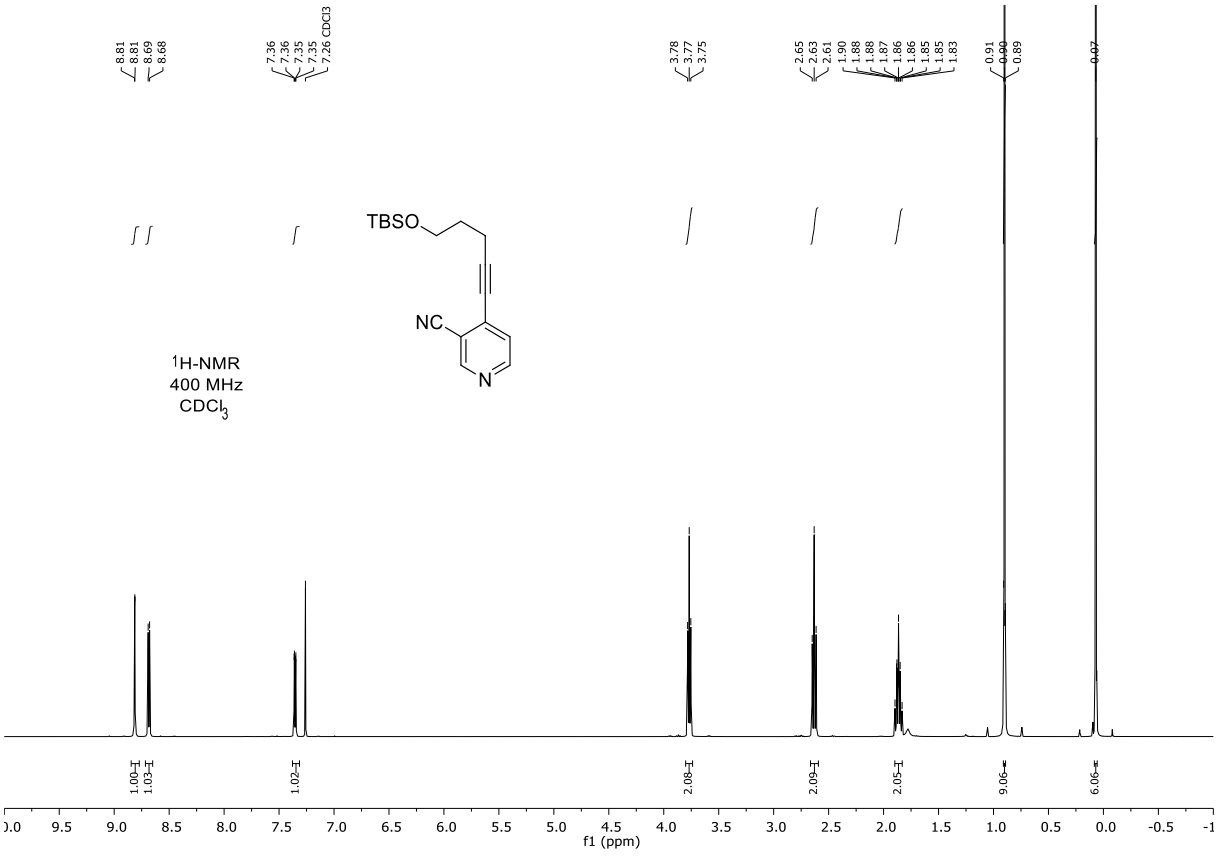
4-(5-Hydroxypent-1-yn-1-yl)nicotinonitrile (SI-50).

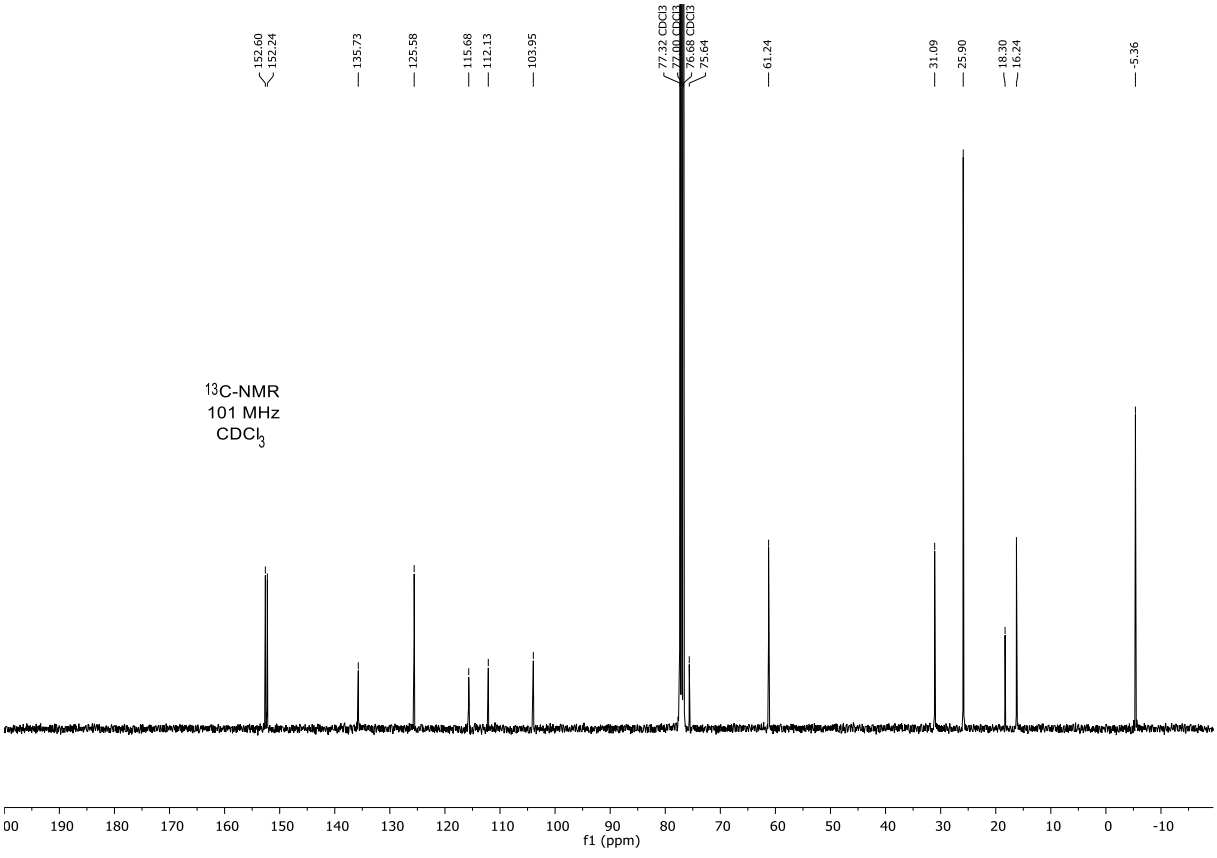


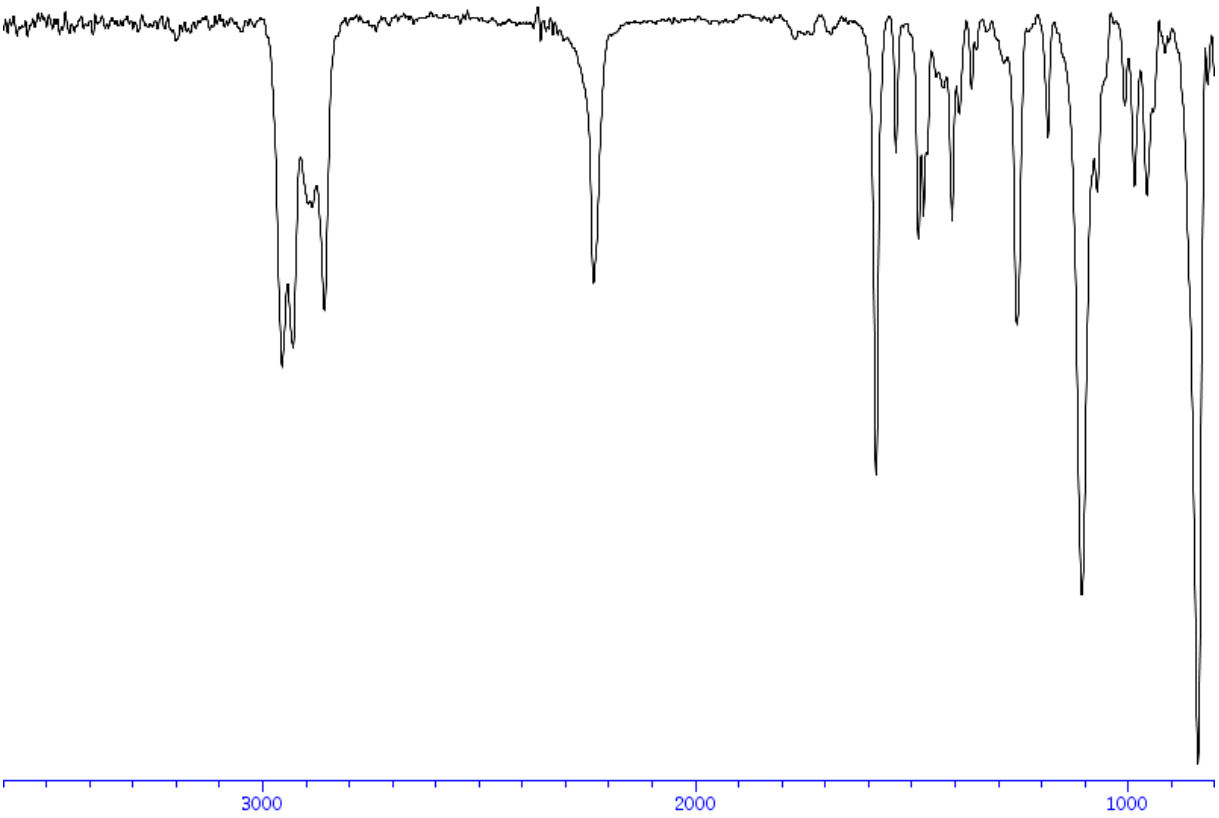

152.51
152.34
135.63
125.46
115.77
112.16
103.36
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
75.93
60.97
30.57
16.21
13C-NMR
101 MHz
CDCl3
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3000
2000
1000

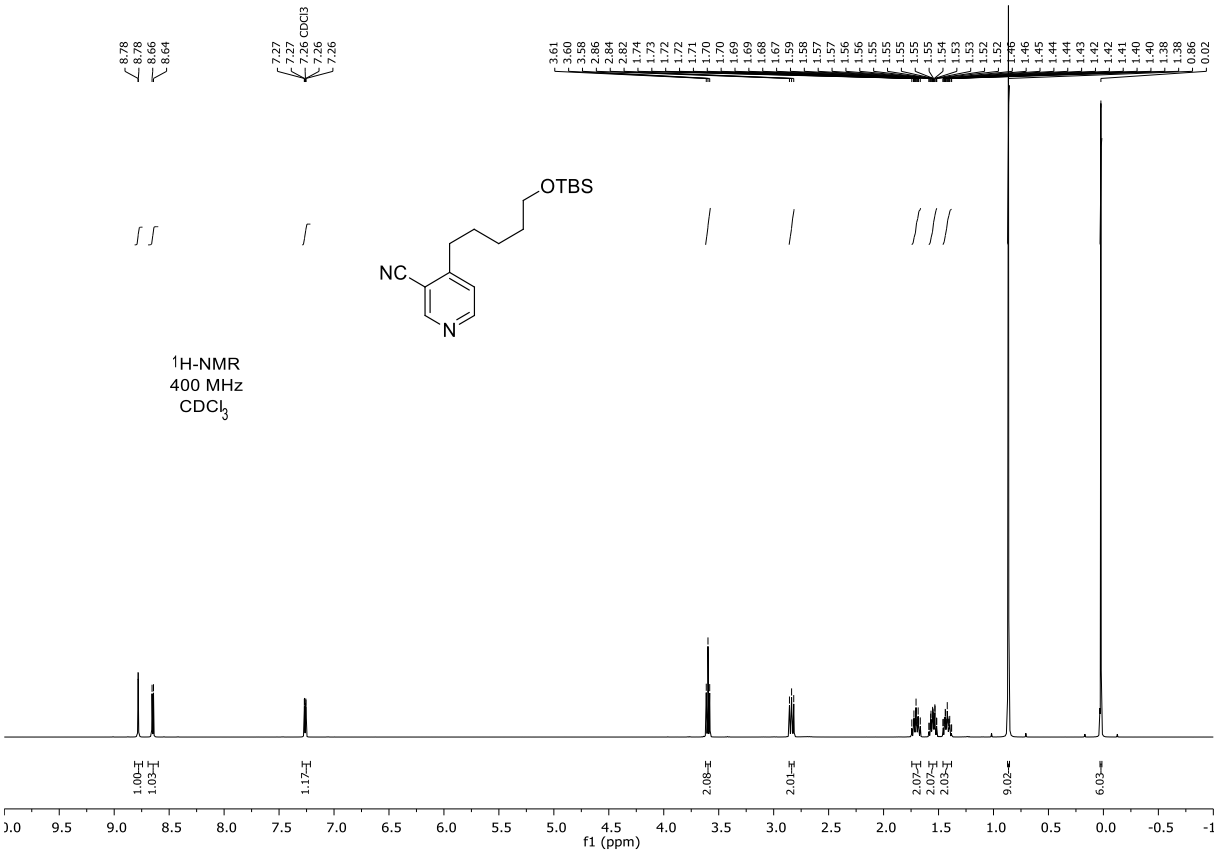
4-(5-((*tert*-Butyldimethylsilyl)oxy)pent-1-yn-1-yl)nicotinonitrile (**SI-51**).

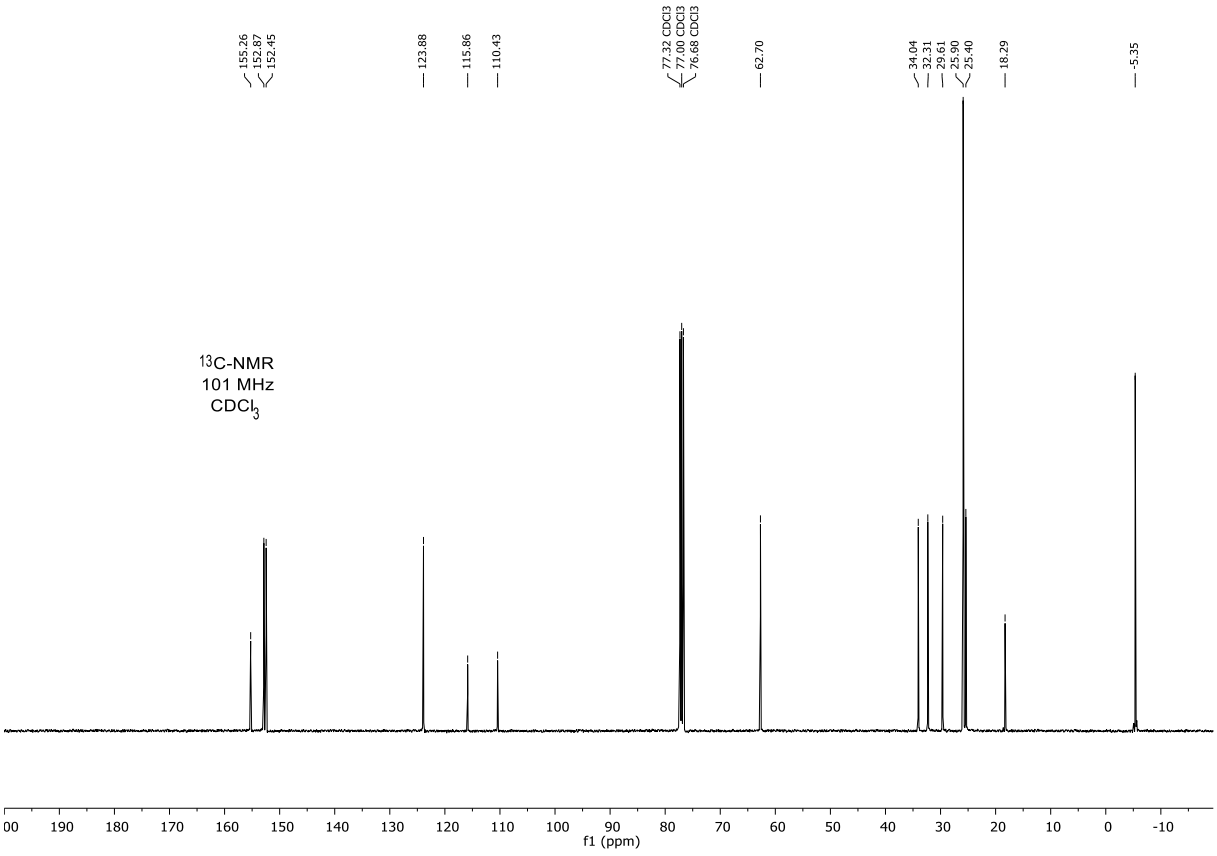


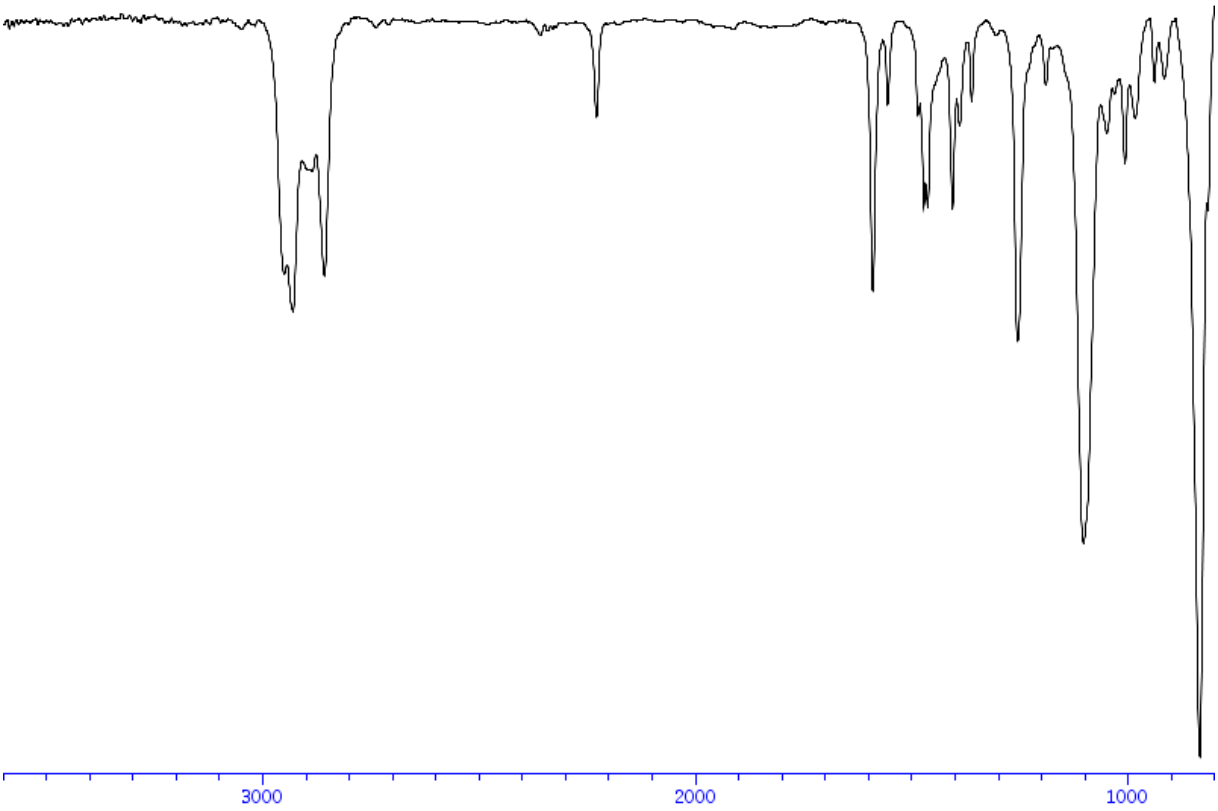




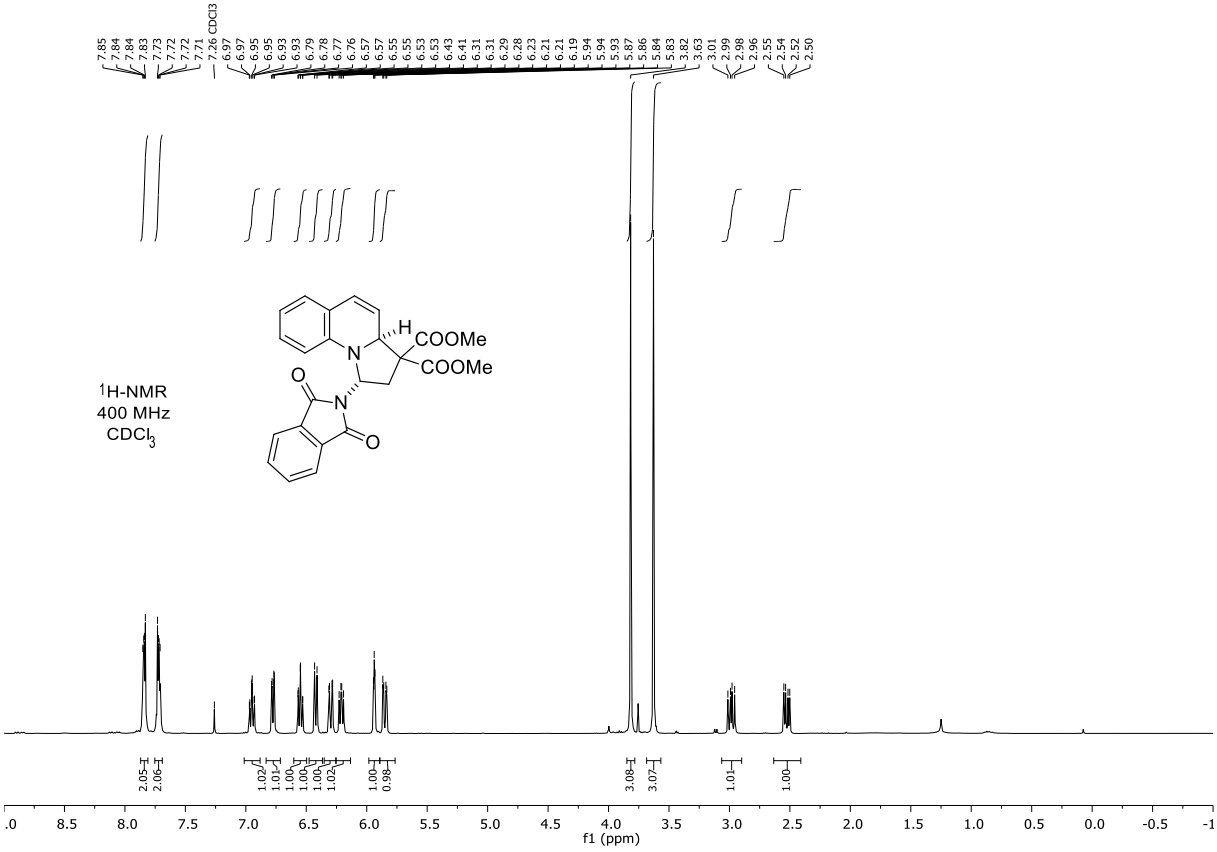
4-(5-((*tert*-Butyldimethylsilyl)oxy)pentyl)nicotinonitrile (SI-52).

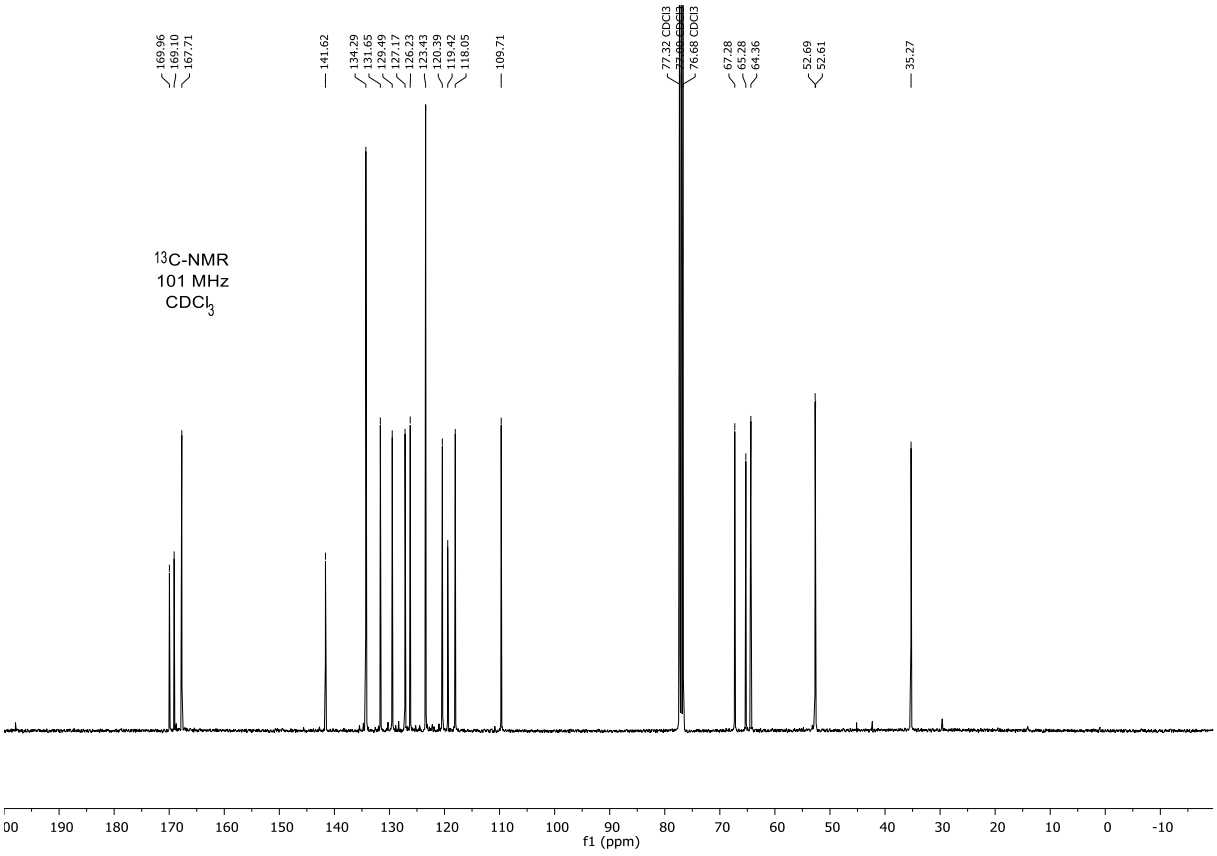


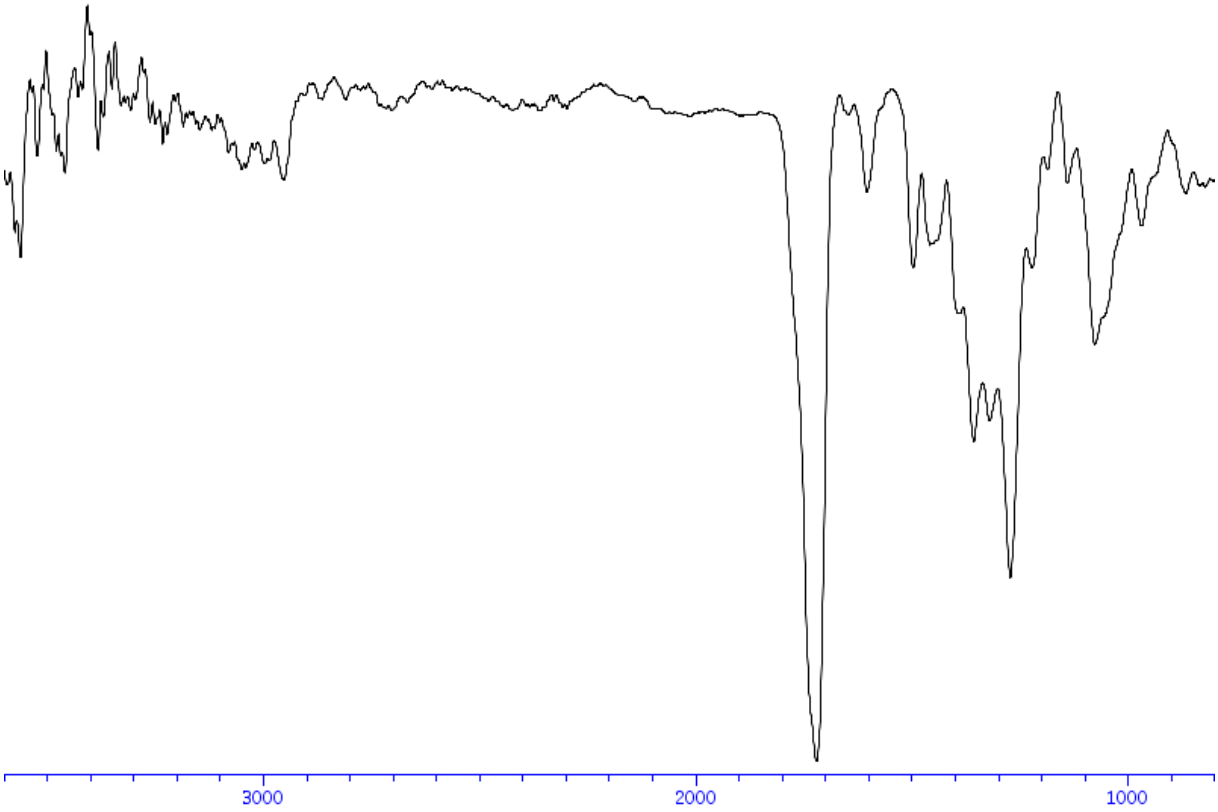

155.26
152.87
152.45
123.88
115.86
110.43
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
62.70
34.04
32.31
29.61
25.90
25.40
18.29
-5.35
13C-NMR
101 MHz
CDCl3
f1 (ppm)


3000
2000
1000

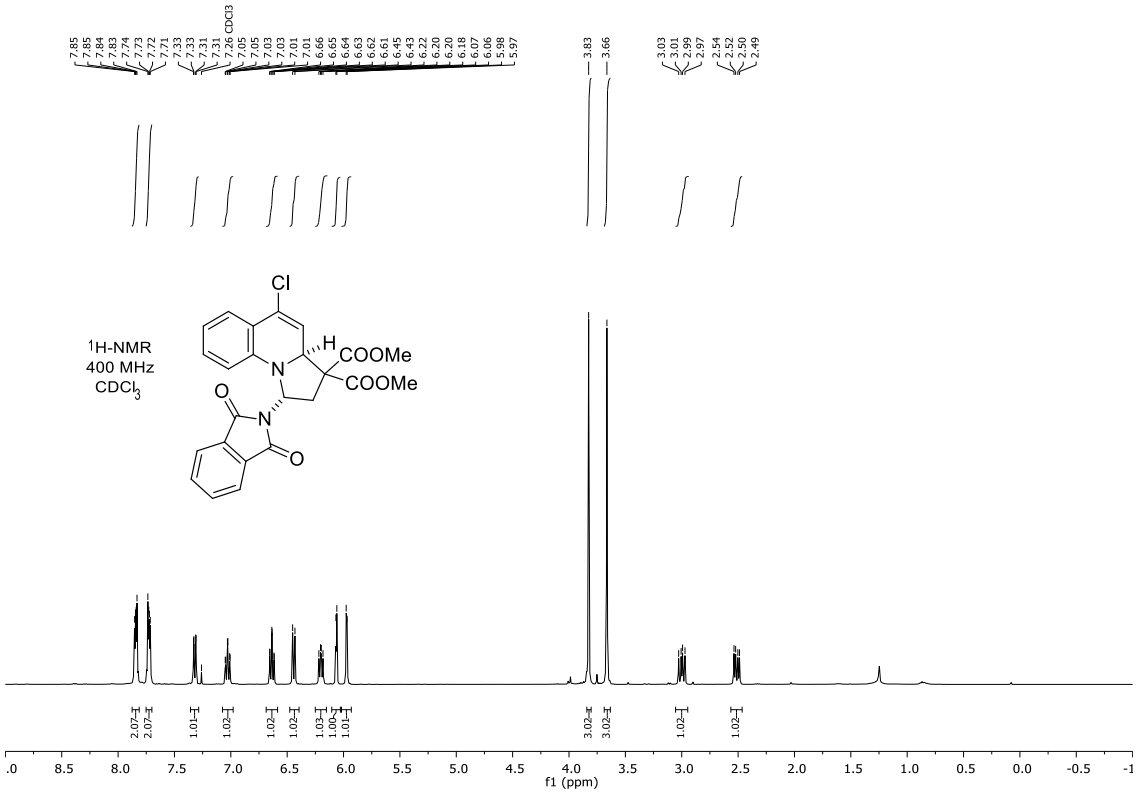
***anti*-Dimethyl 1,2,4,5-tetrahydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (17).**

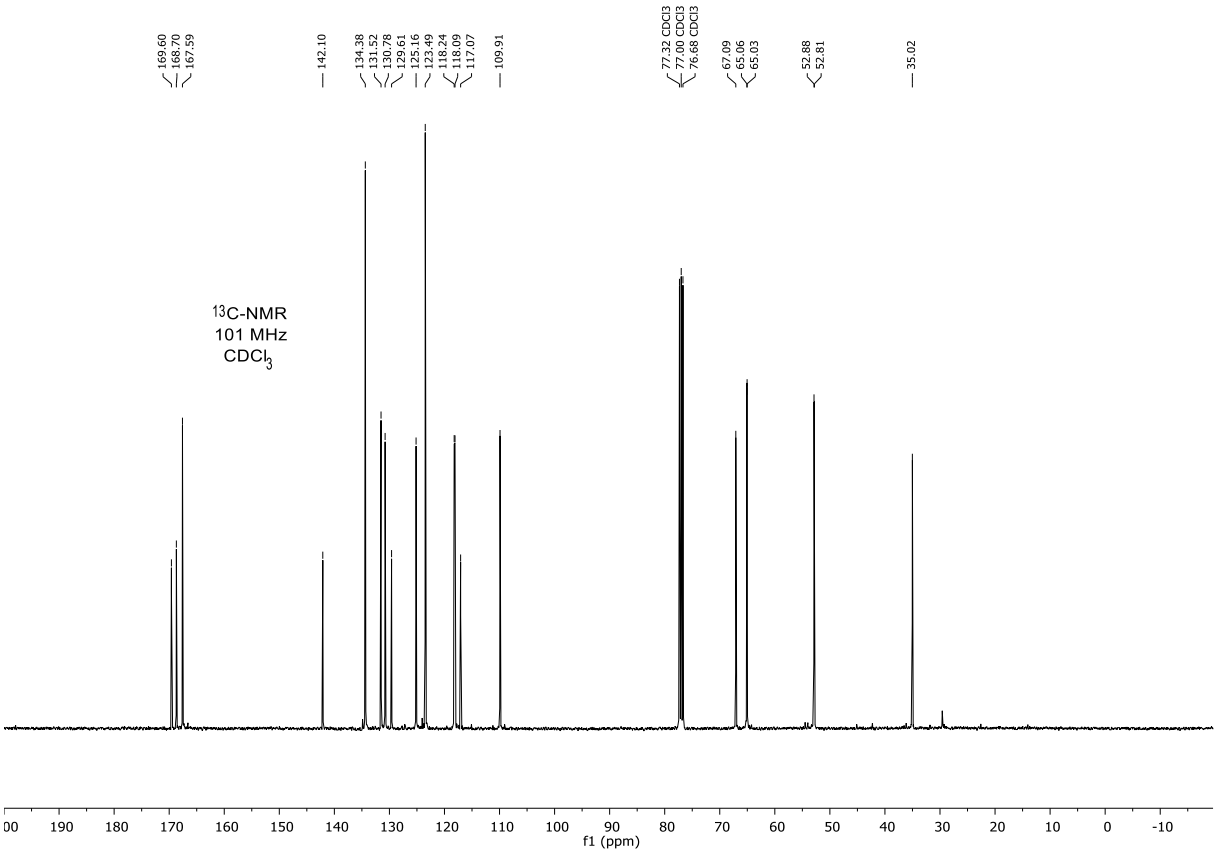


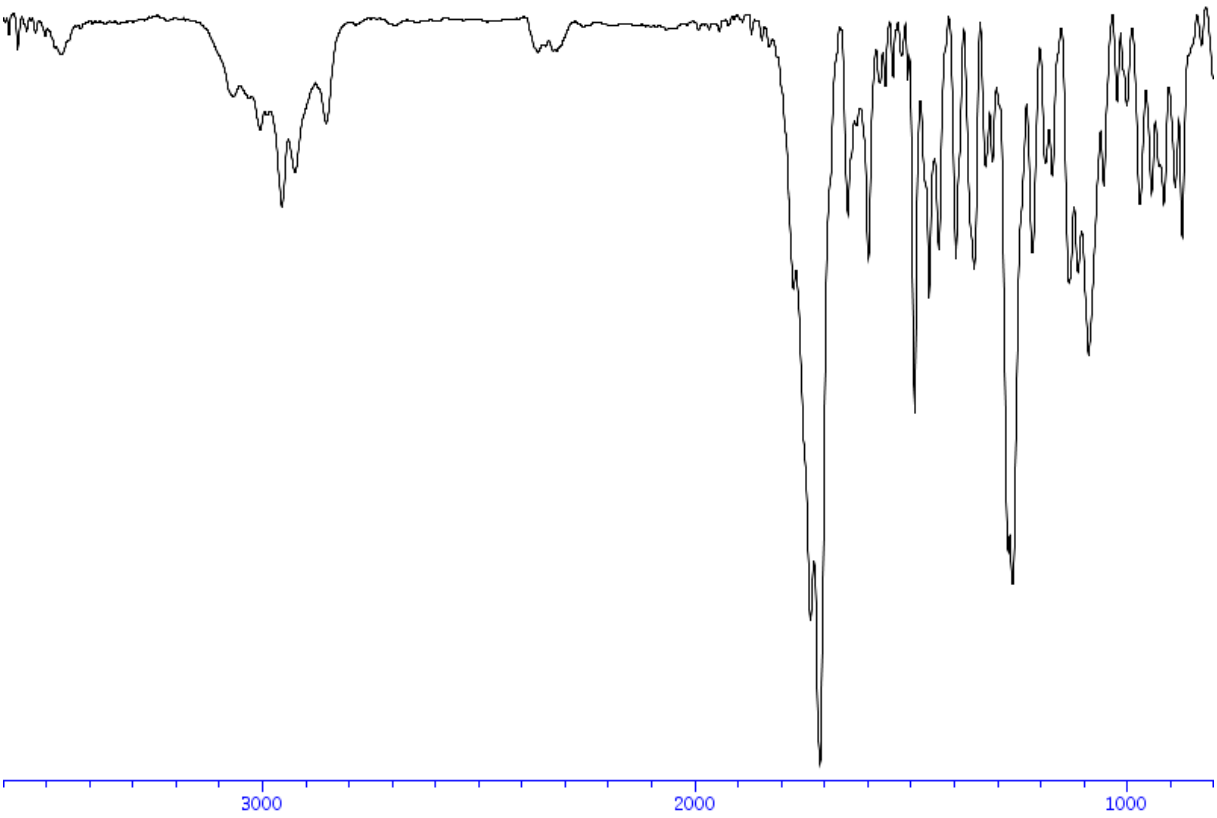




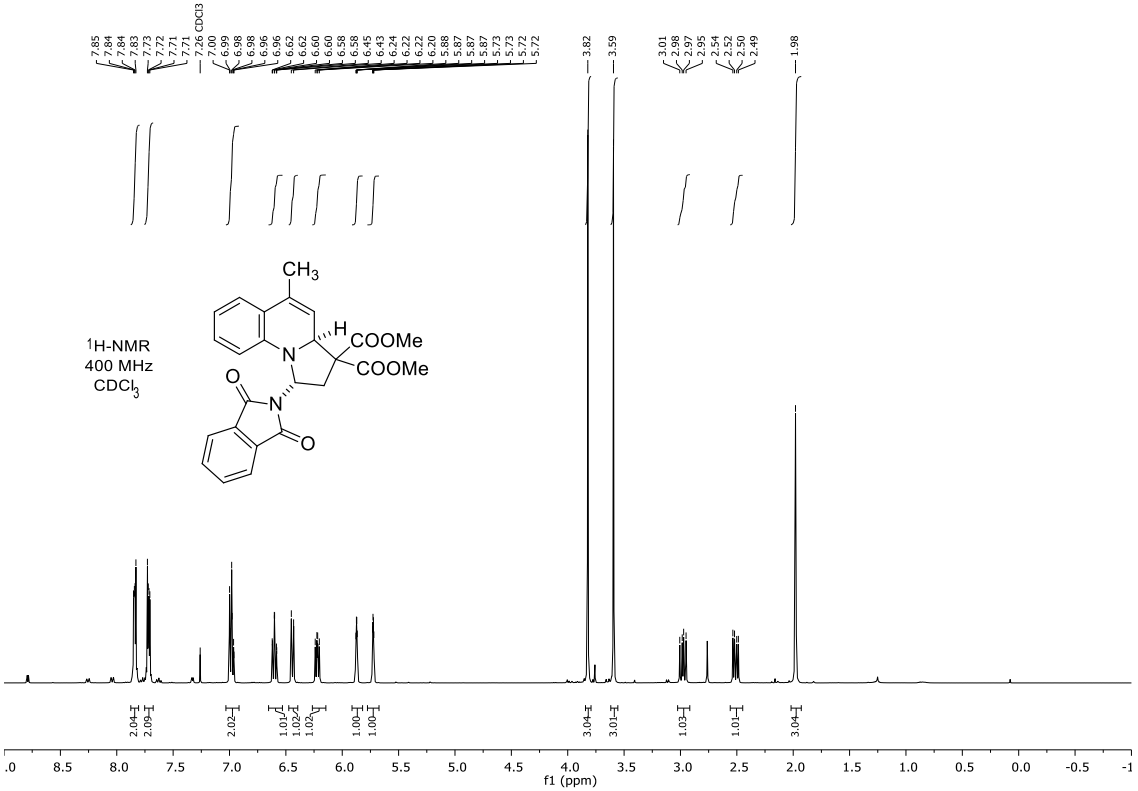
***anti*-Dimethyl 5-chloro-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (20).**

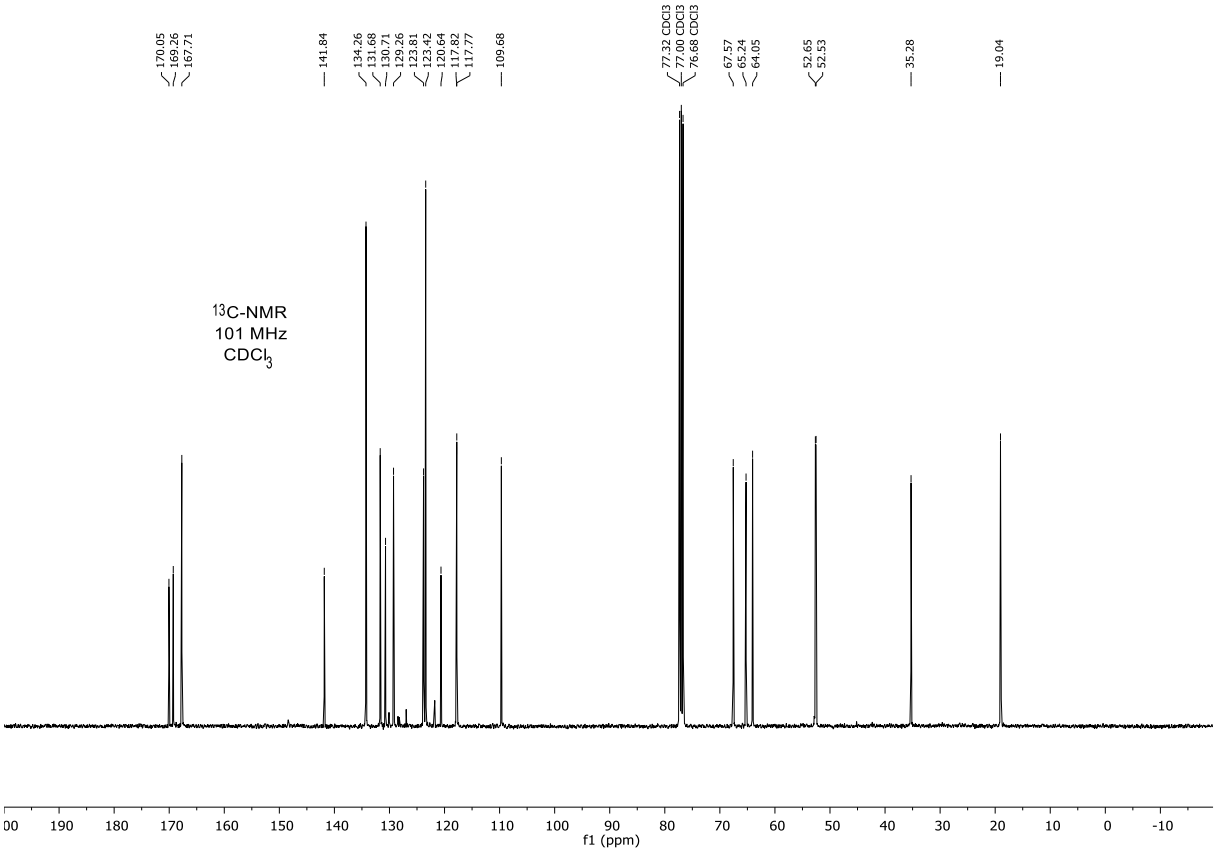


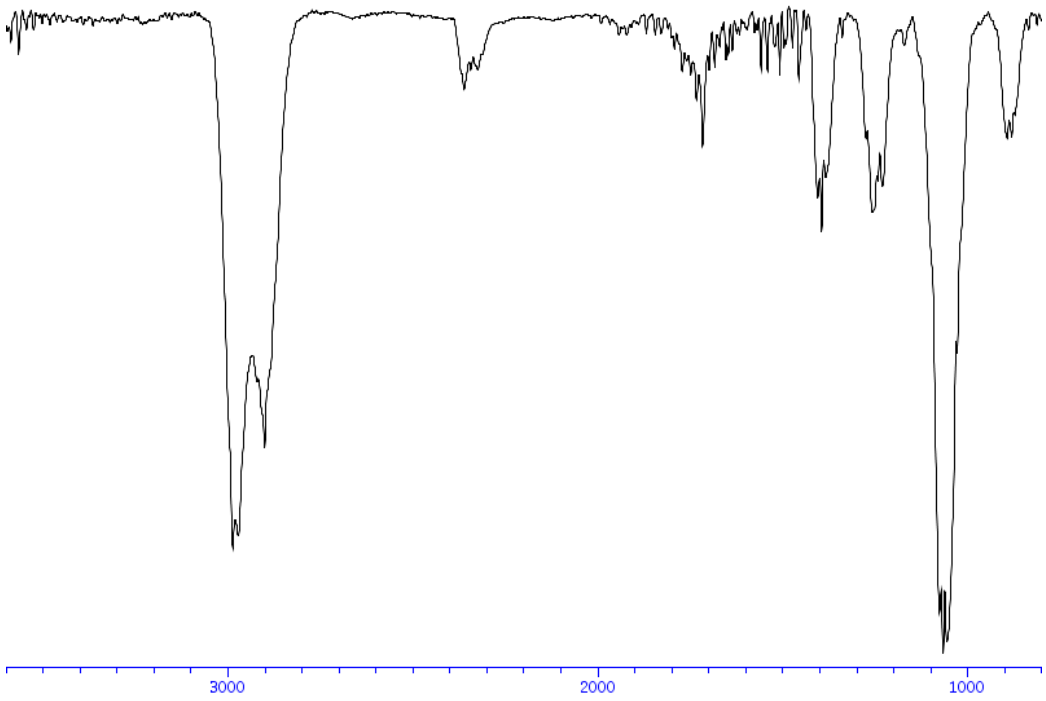

169.60
168.70
167.59
142.10
134.38
131.52
130.78
129.61
125.16
123.49
118.24
118.09
117.07
109.91
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.09
65.06
65.03
52.88
52.81
35.02
13C-NMR
101 MHz
CDCl3
f1 (ppm)


3000
2000
1000

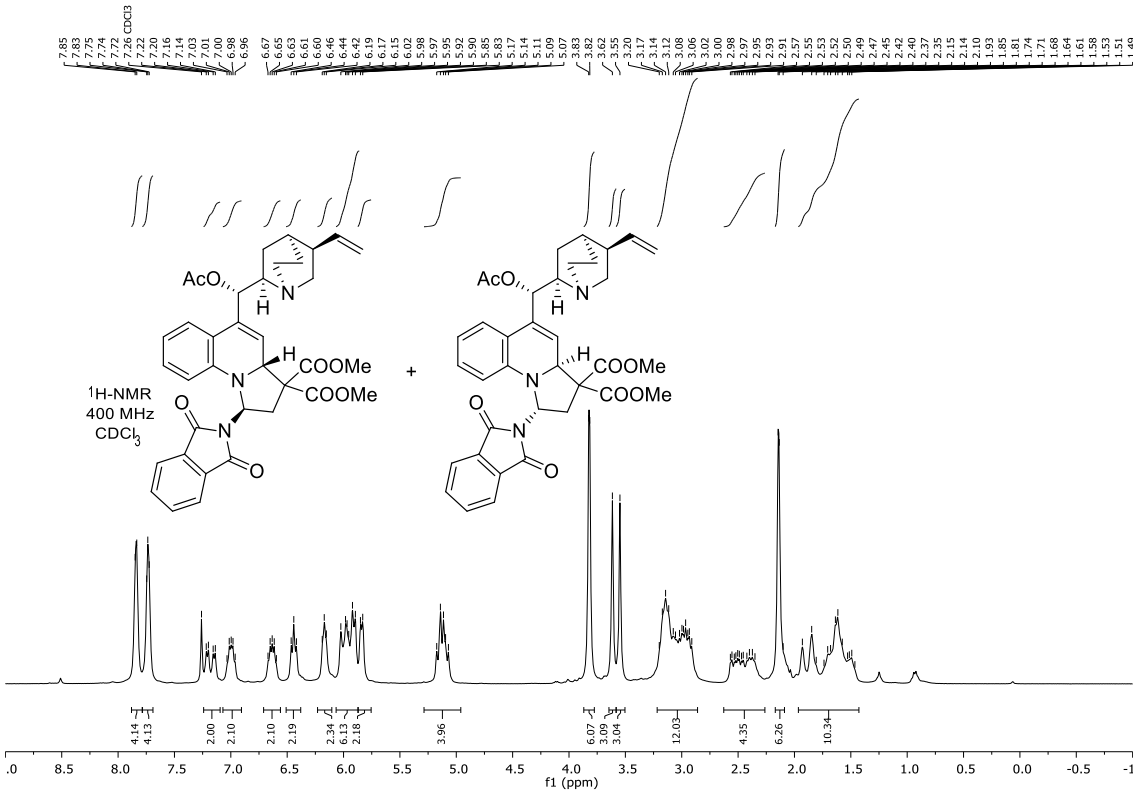
***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-5-methyl-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**21**).

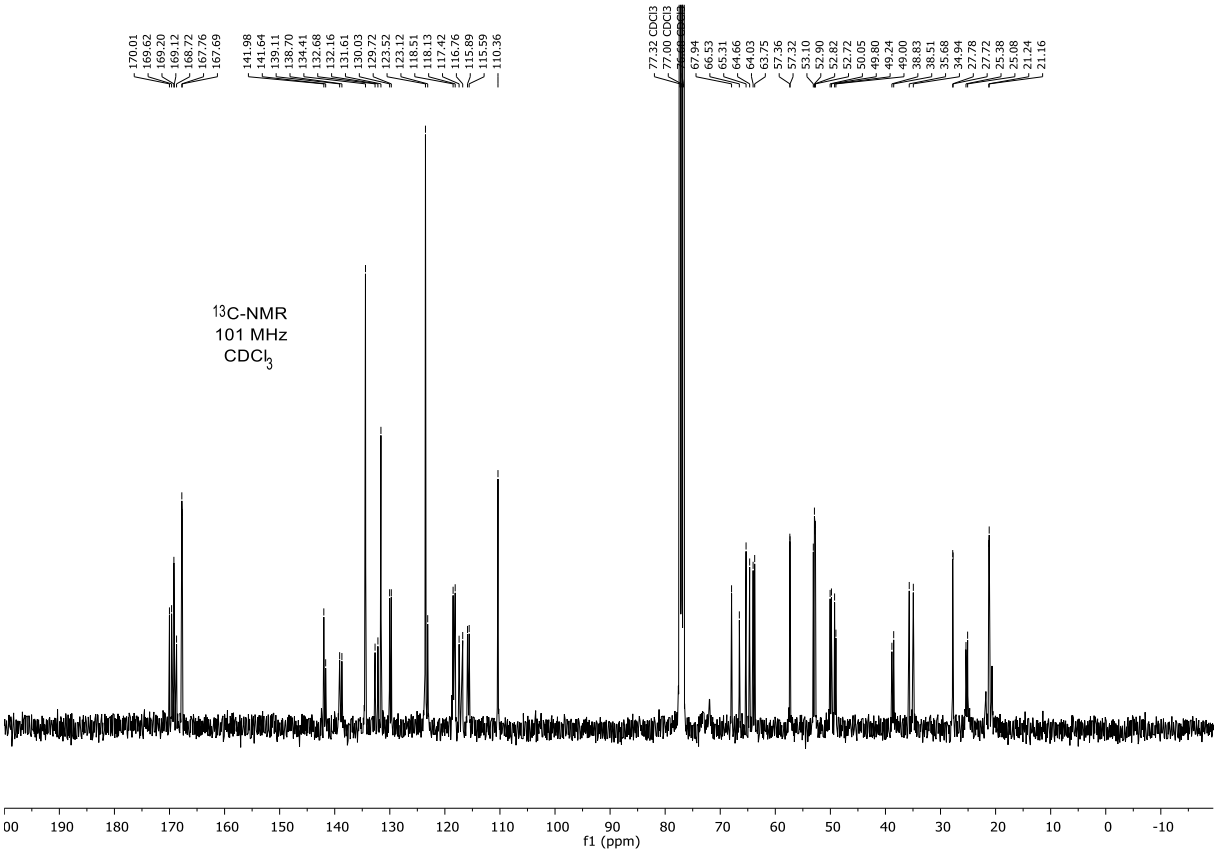


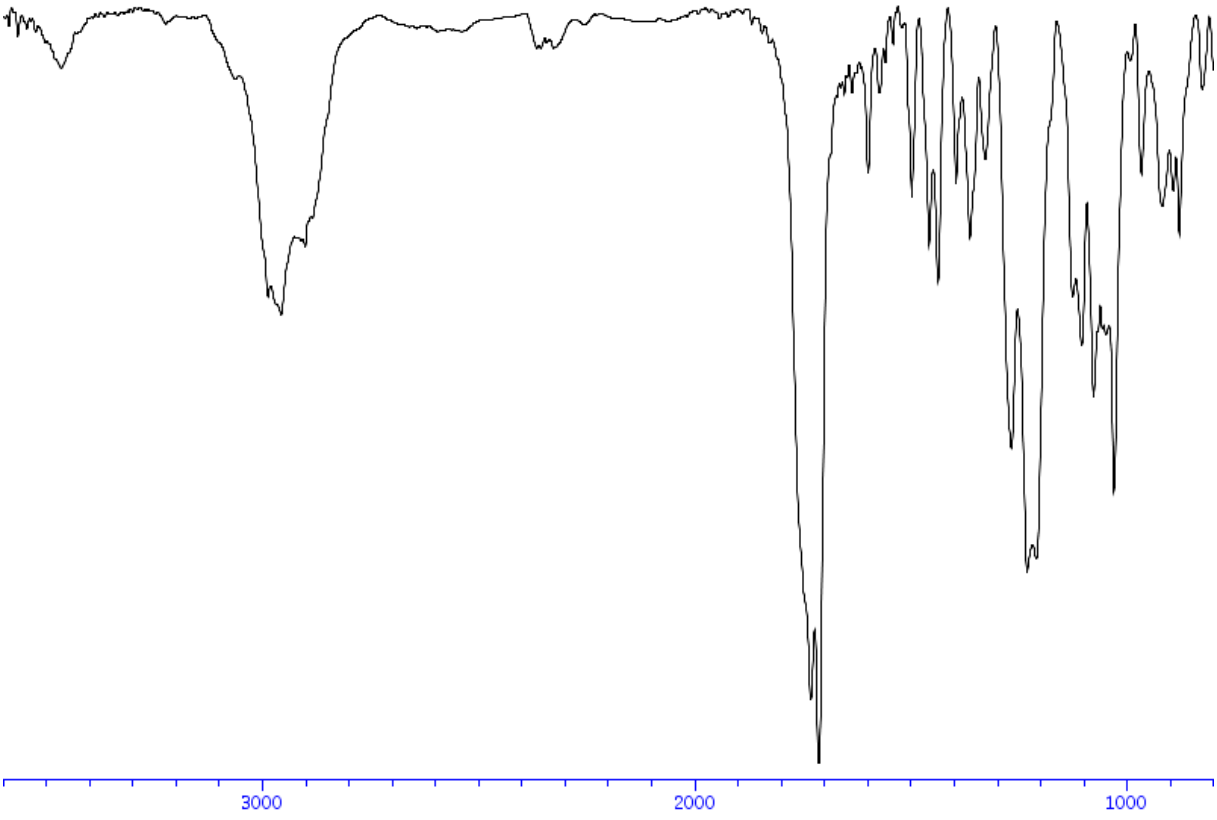




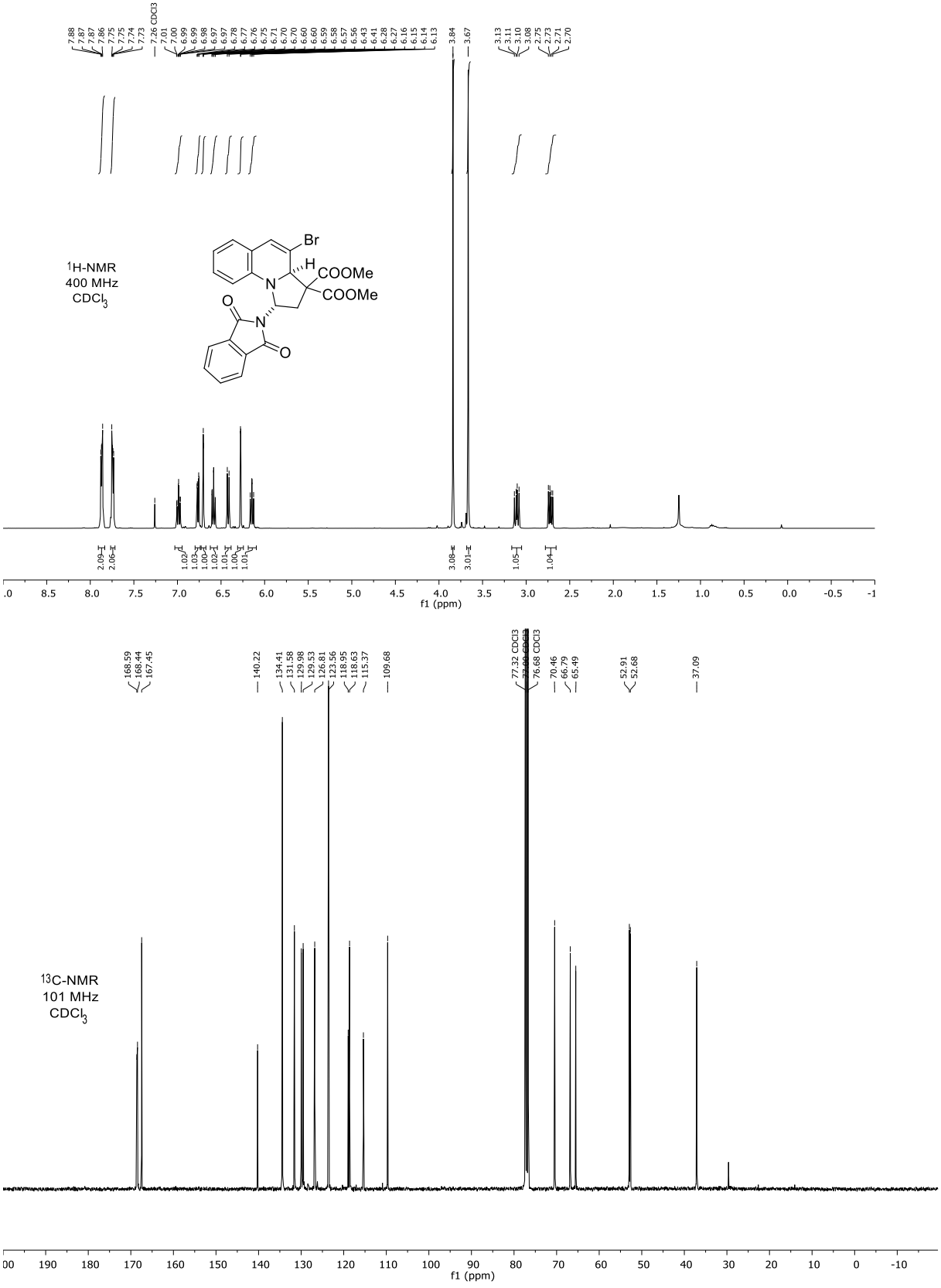
(1*R*,3a*R*)-Dimethyl 5-((*S*)-acetoxy((1*S*,2*R*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl)-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (**22a**) and **(1*S*,3a*S*)-dimethyl 5-((*S*)-acetoxy((1*S*,2*R*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methyl)-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**22b**).

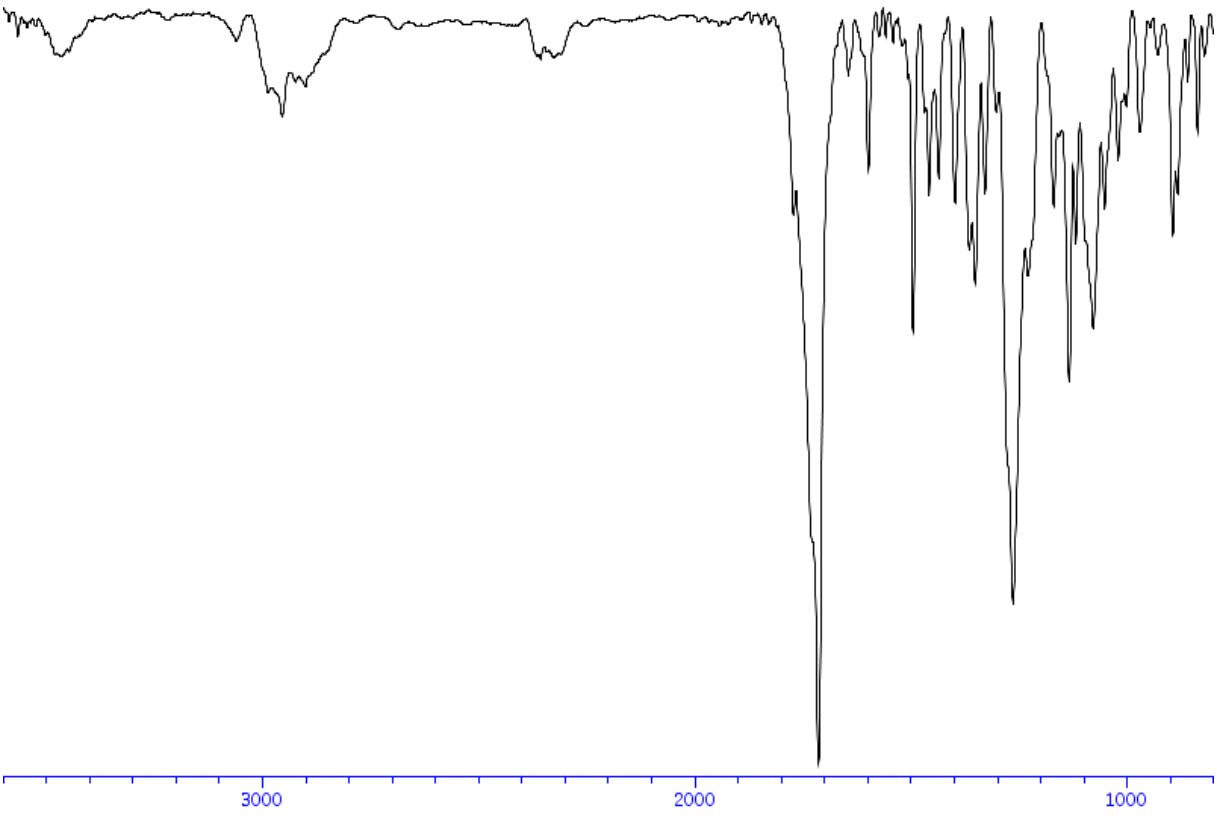



170.01
169.62
169.20
169.12
168.72
167.76
167.69
141.98
141.64
139.11
138.70
134.41
132.68
132.16
131.61
130.03
129.72
123.52
123.12
118.51
118.13
117.42
116.76
115.89
115.59
110.36
77.32 CDCl3
77.00 CDCl3
67.94
66.53
65.31
64.66
64.03
63.75
57.36
57.32
53.10
52.90
52.82
52.72
50.05
49.80
49.24
49.00
38.83
38.51
35.68
34.94
27.78
27.72
25.38
25.08
21.24
21.16
13C-NMR
101 MHz
CDCl3
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

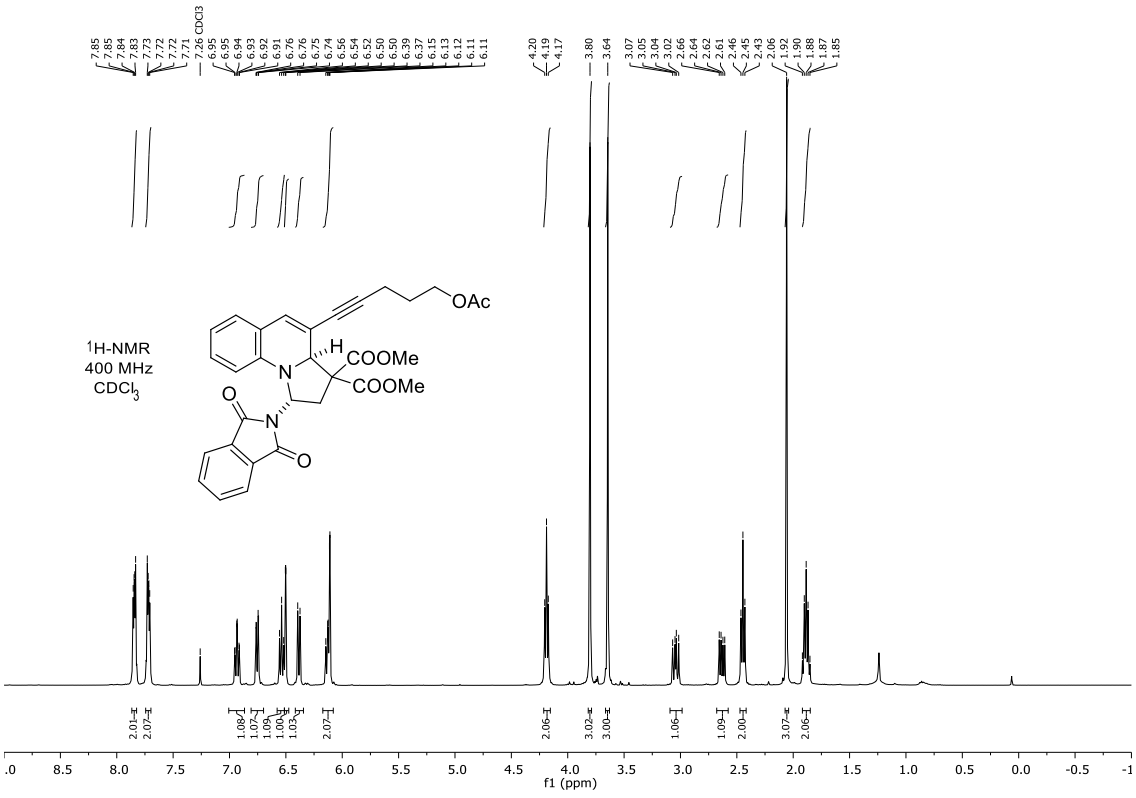

3000
2000
1000

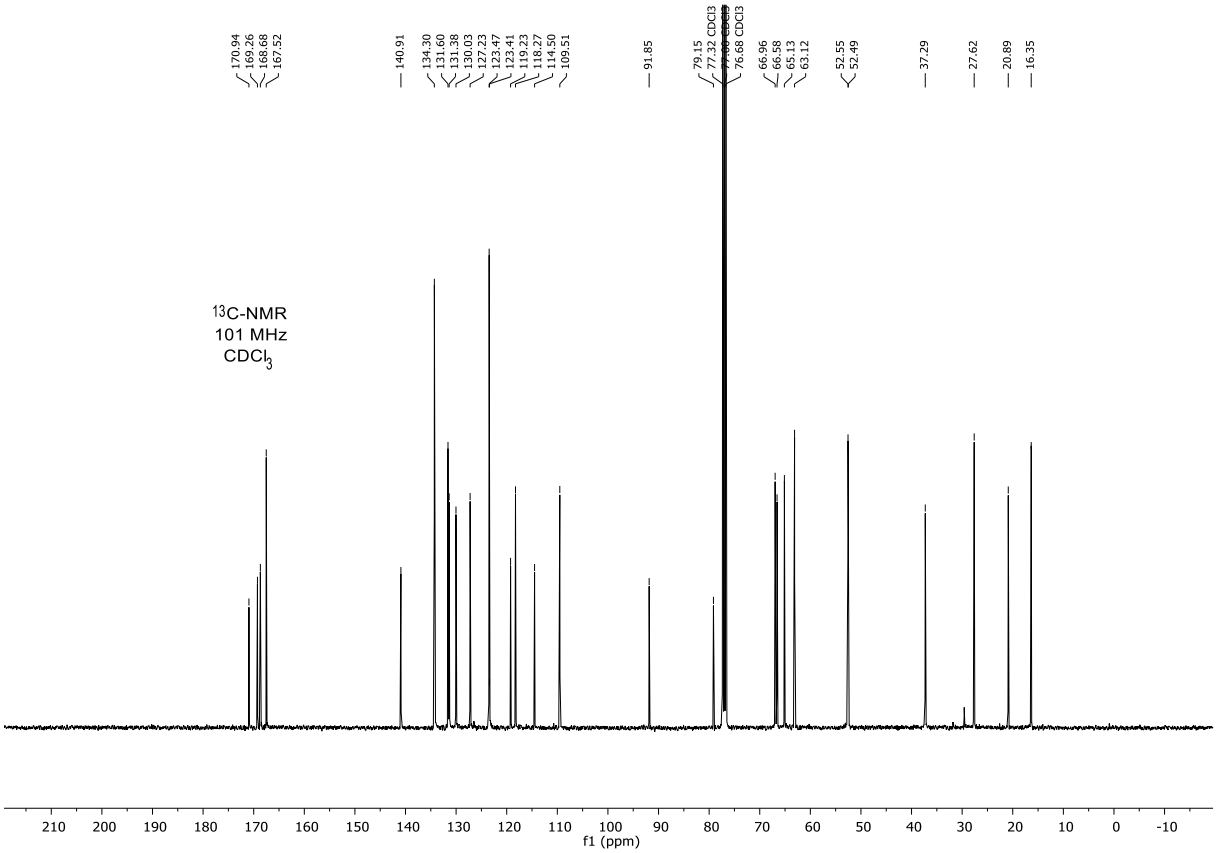
***anti*-Dimethyl 4-bromo-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**23**).

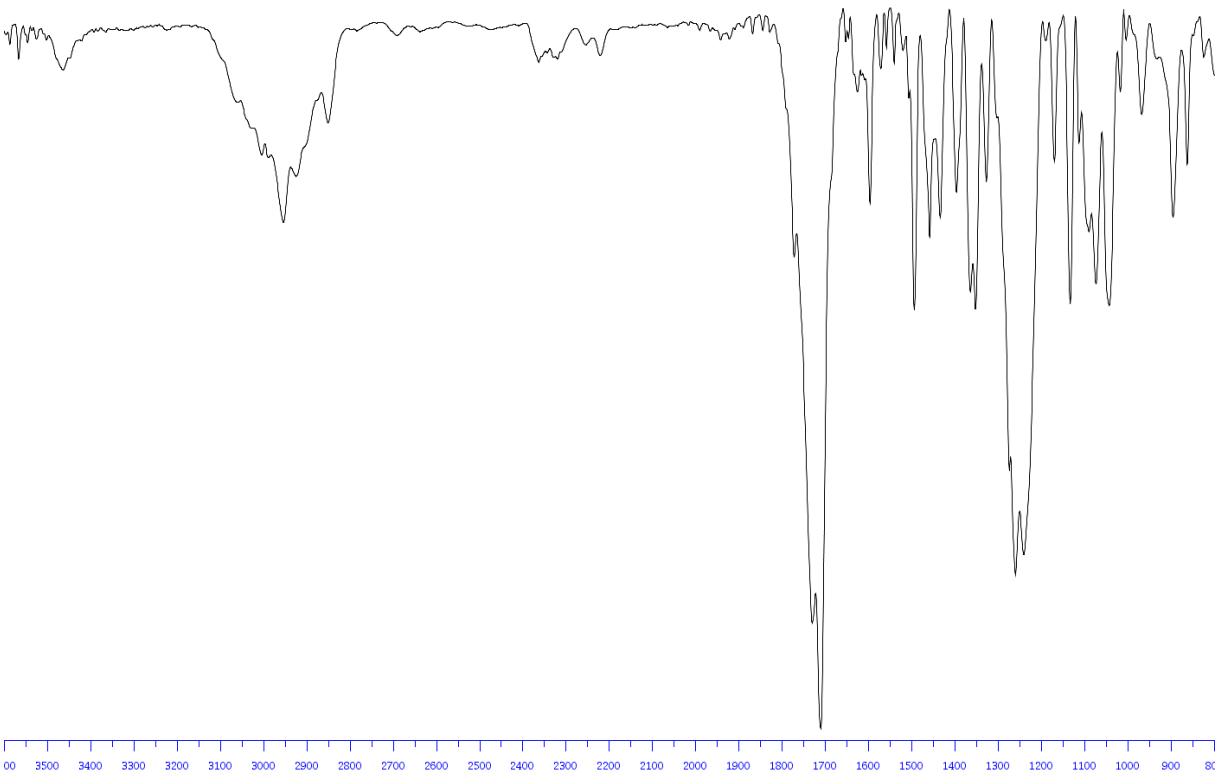




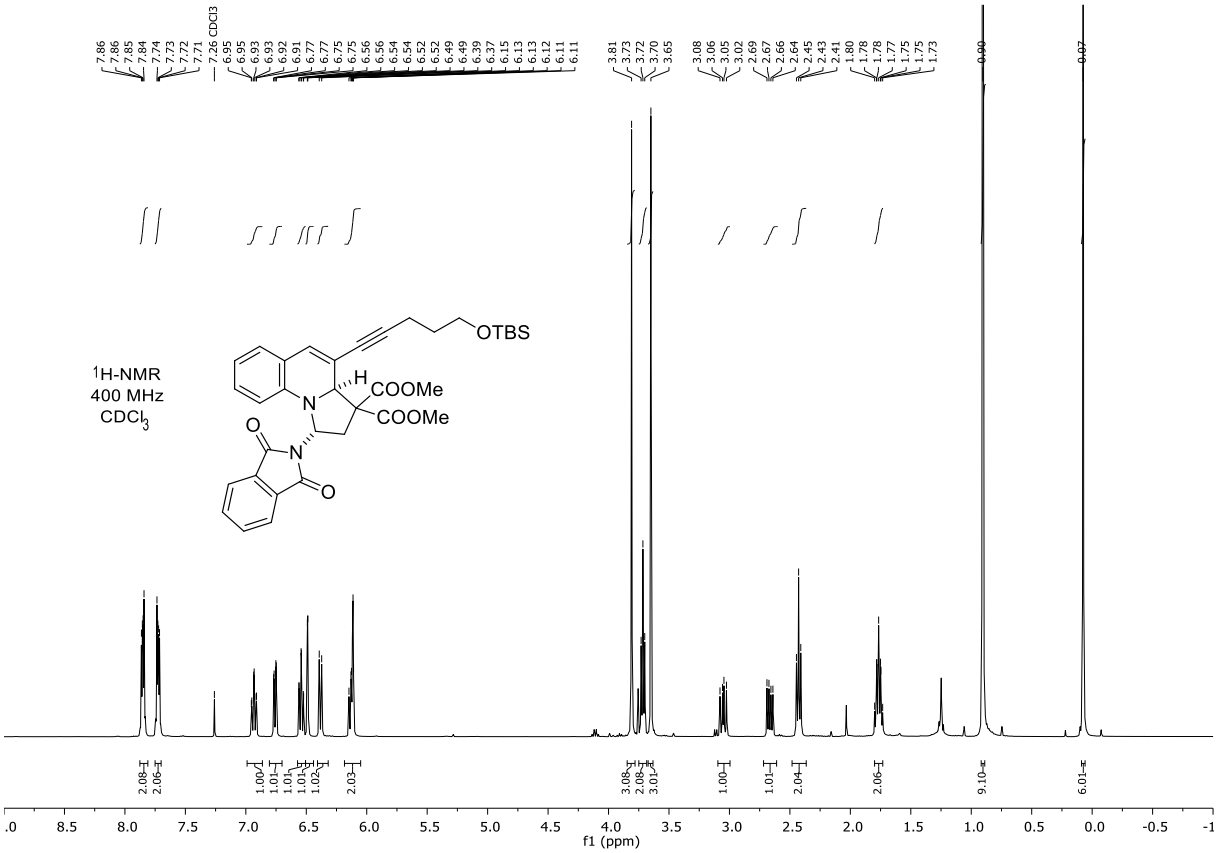
***anti*-Dimethyl 4-(5-acetoxypent-1-yn-1-yl)-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**24**).

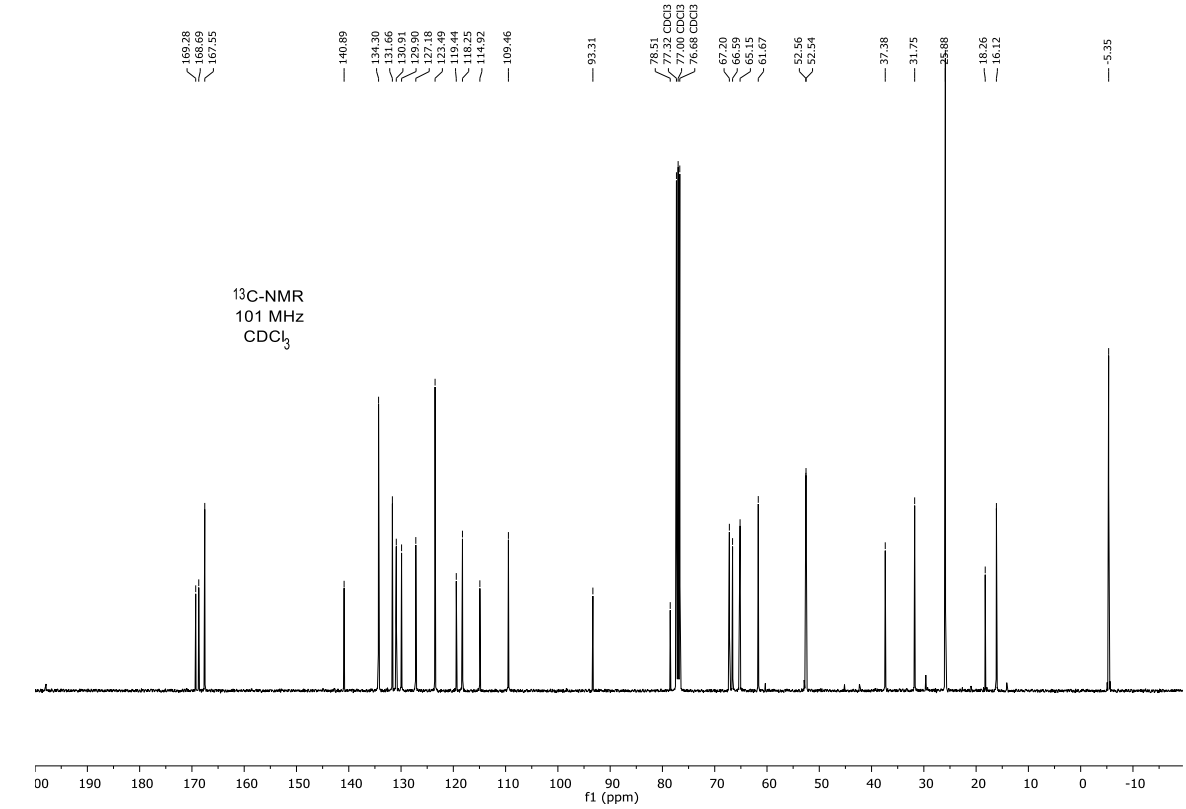


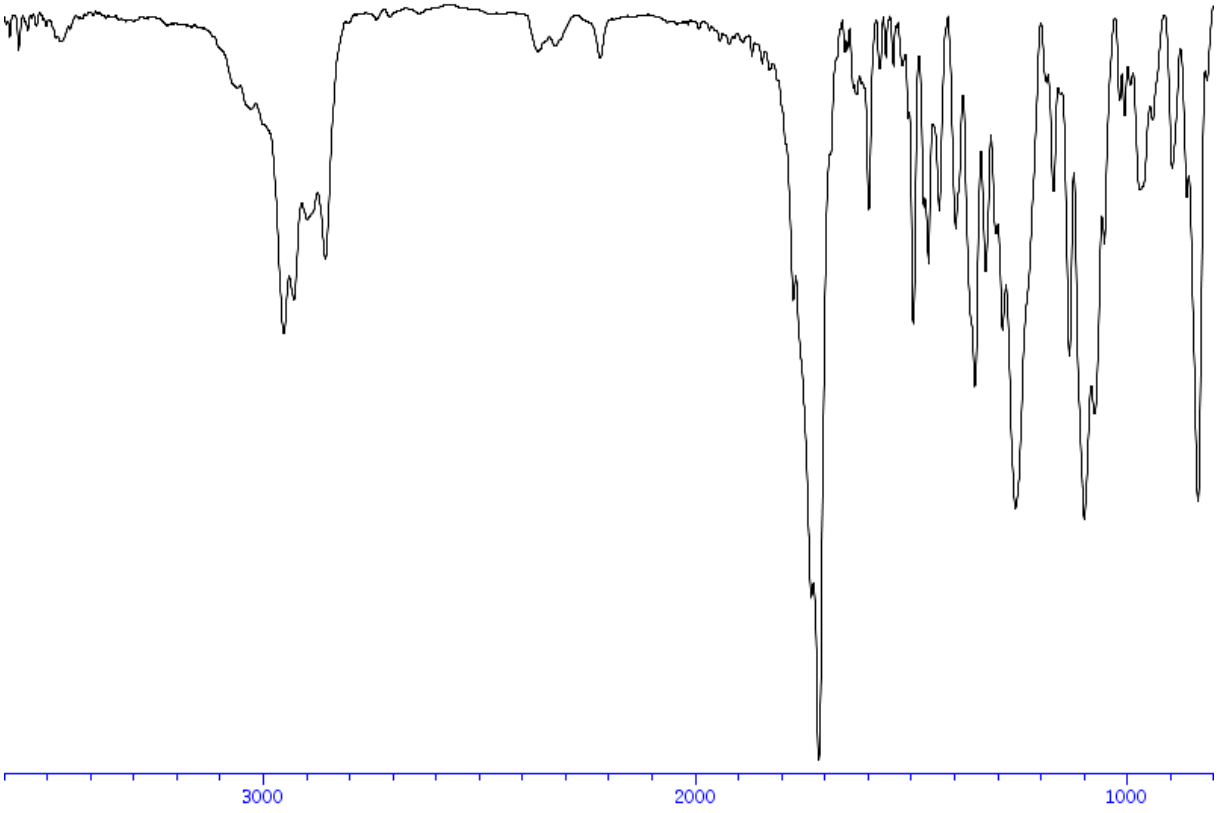

170.94
169.26
168.68
167.52
140.91
134.30
131.60
131.38
130.03
127.23
123.47
123.41
119.23
118.27
114.50
109.51
91.85
79.15
77.32 CDCl3
76.68 CDCl3
66.96
66.58
65.13
63.12
52.55
52.49
37.29
27.62
20.89
16.35
13C-NMR
101 MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



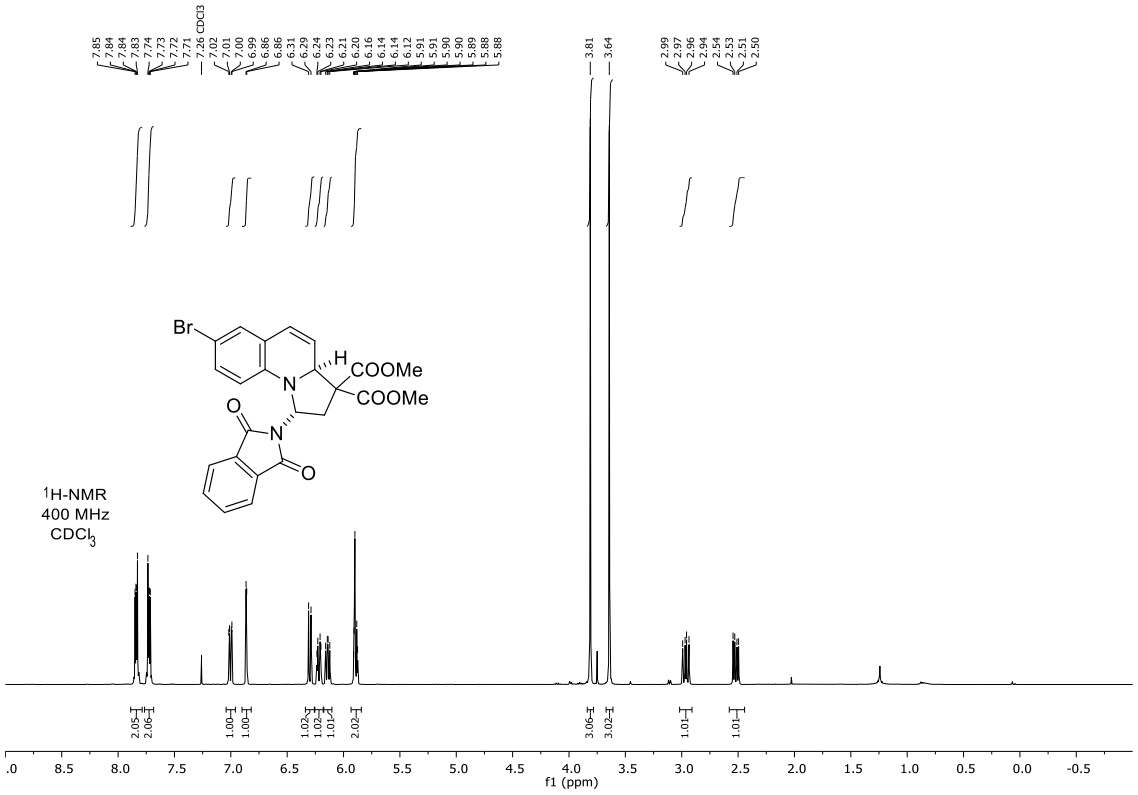
***anti*-Dimethyl 4-(5-((*tert*-butyldimethylsilyl)oxy)pent-1-yn-1-yl)-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**25**).

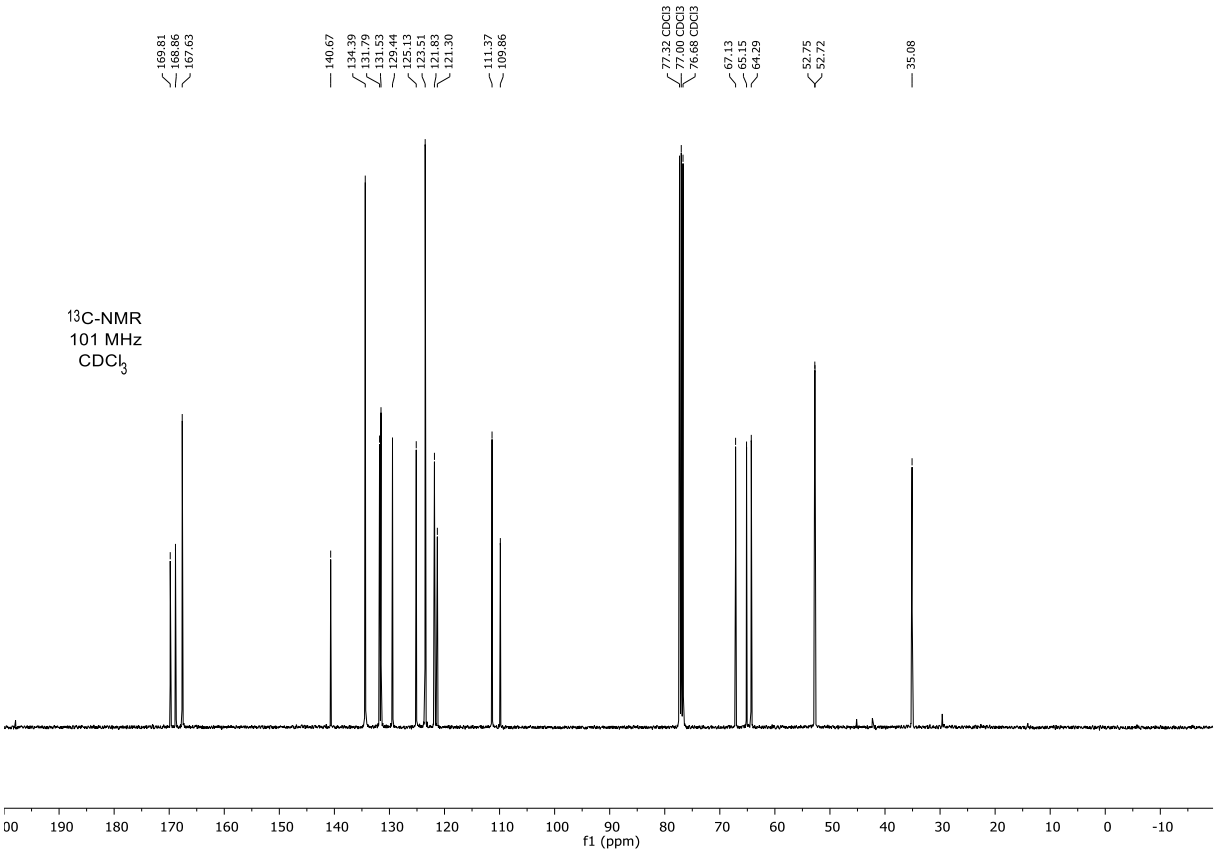


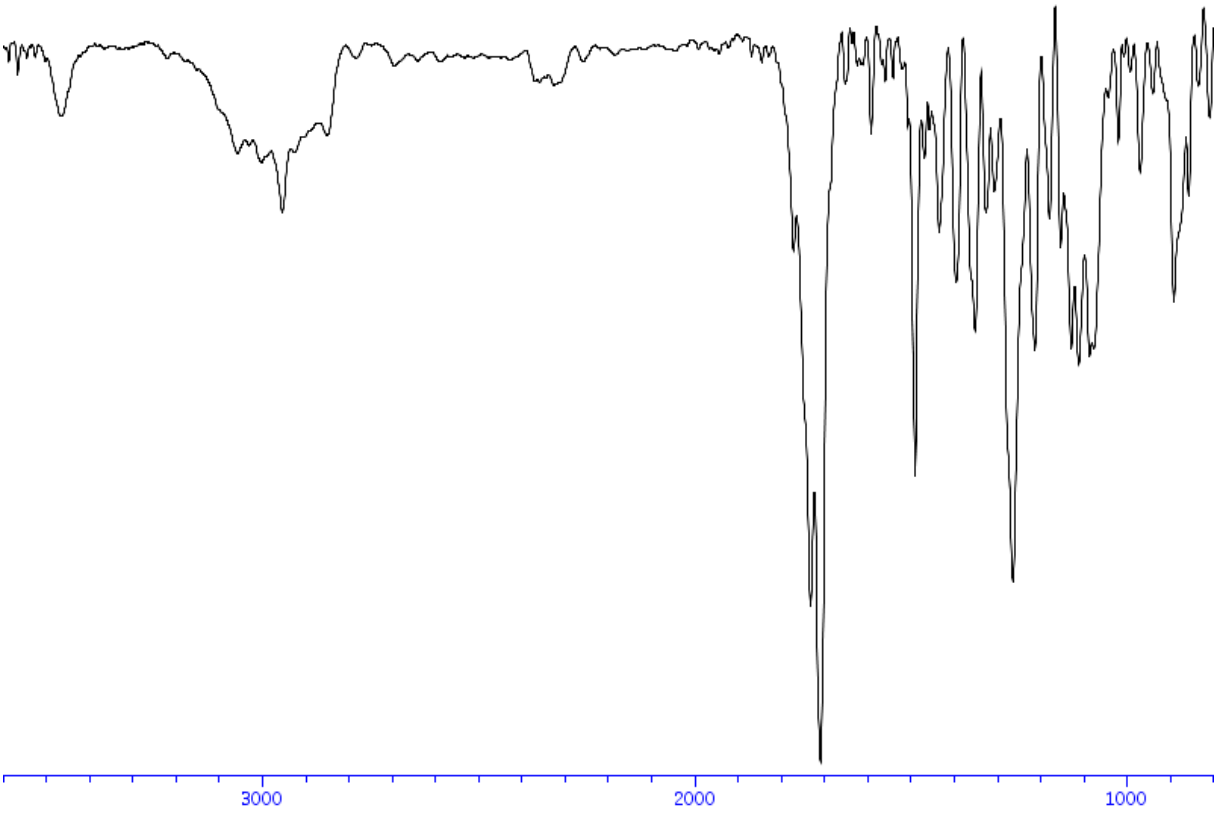




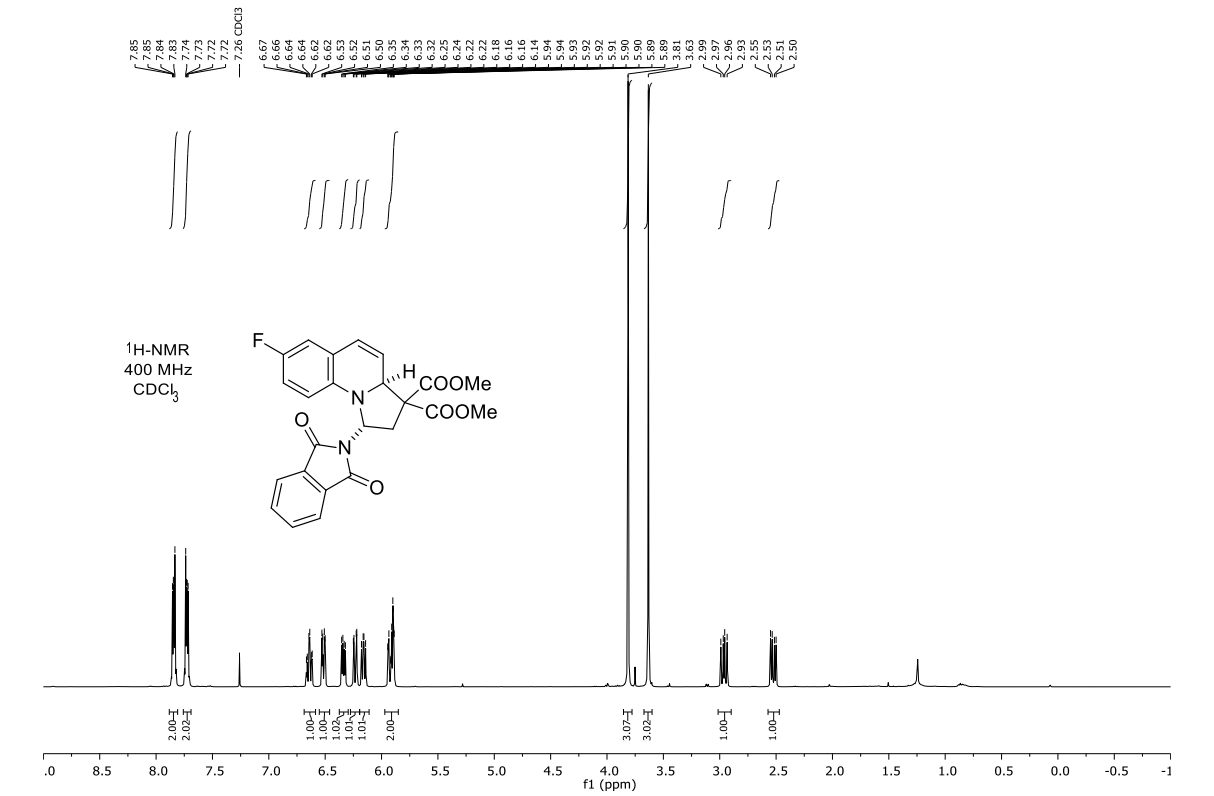
***anti*-Dimethyl 7-bromo-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (26).**

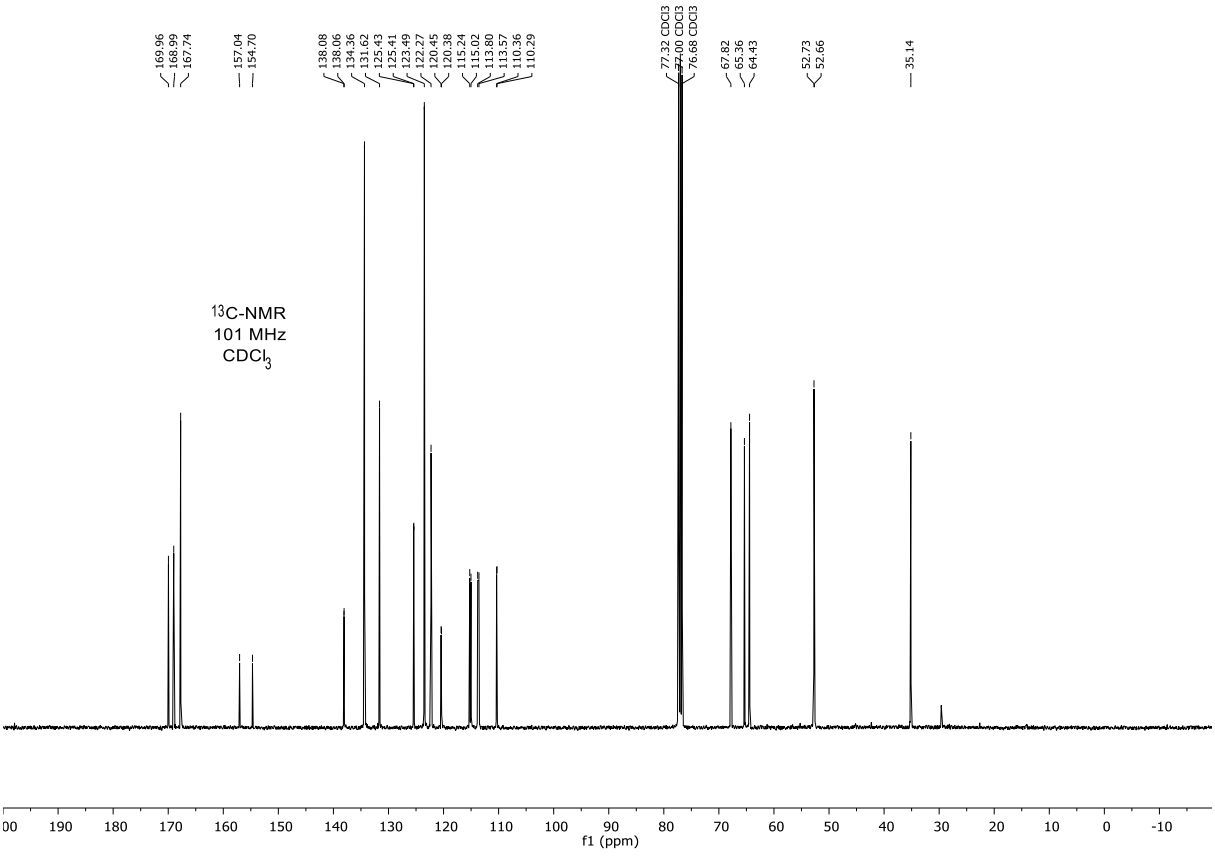


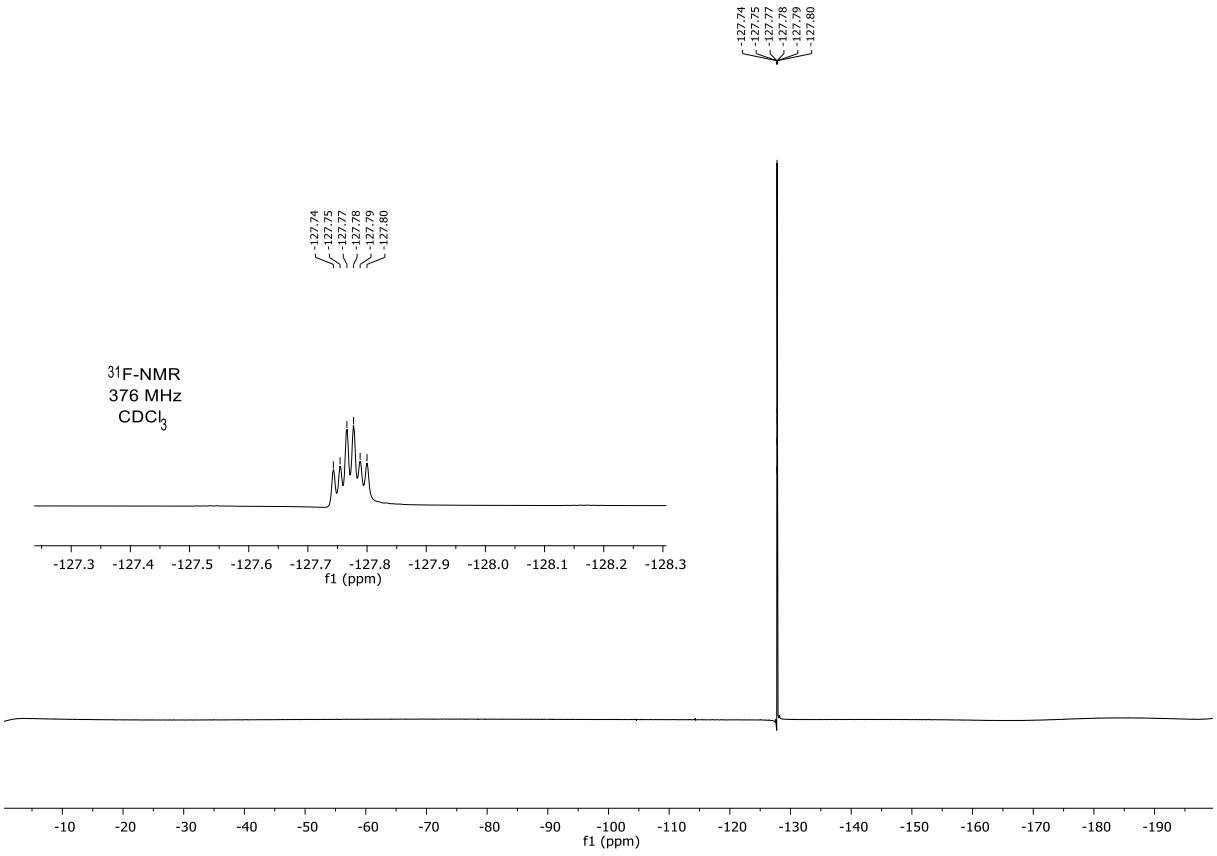

169.81
168.86
167.63
140.67
134.39
131.79
131.53
129.44
125.13
123.51
121.83
121.30
111.37
109.86
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.13
65.15
64.29
52.75
52.72
35.08
13C-NMR
101 MHz
CDCl3
f1 (ppm)

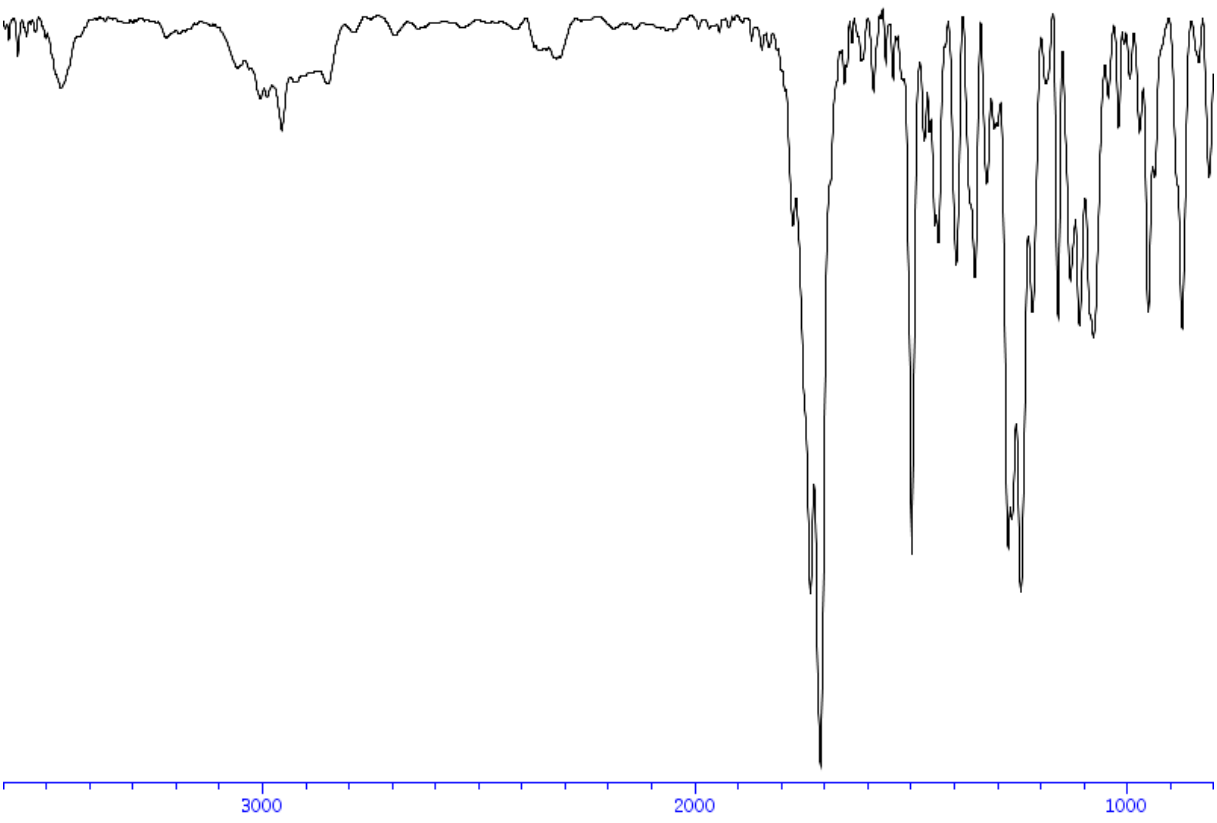

3000
2000
1000

***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-7-fluoro-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (27).**

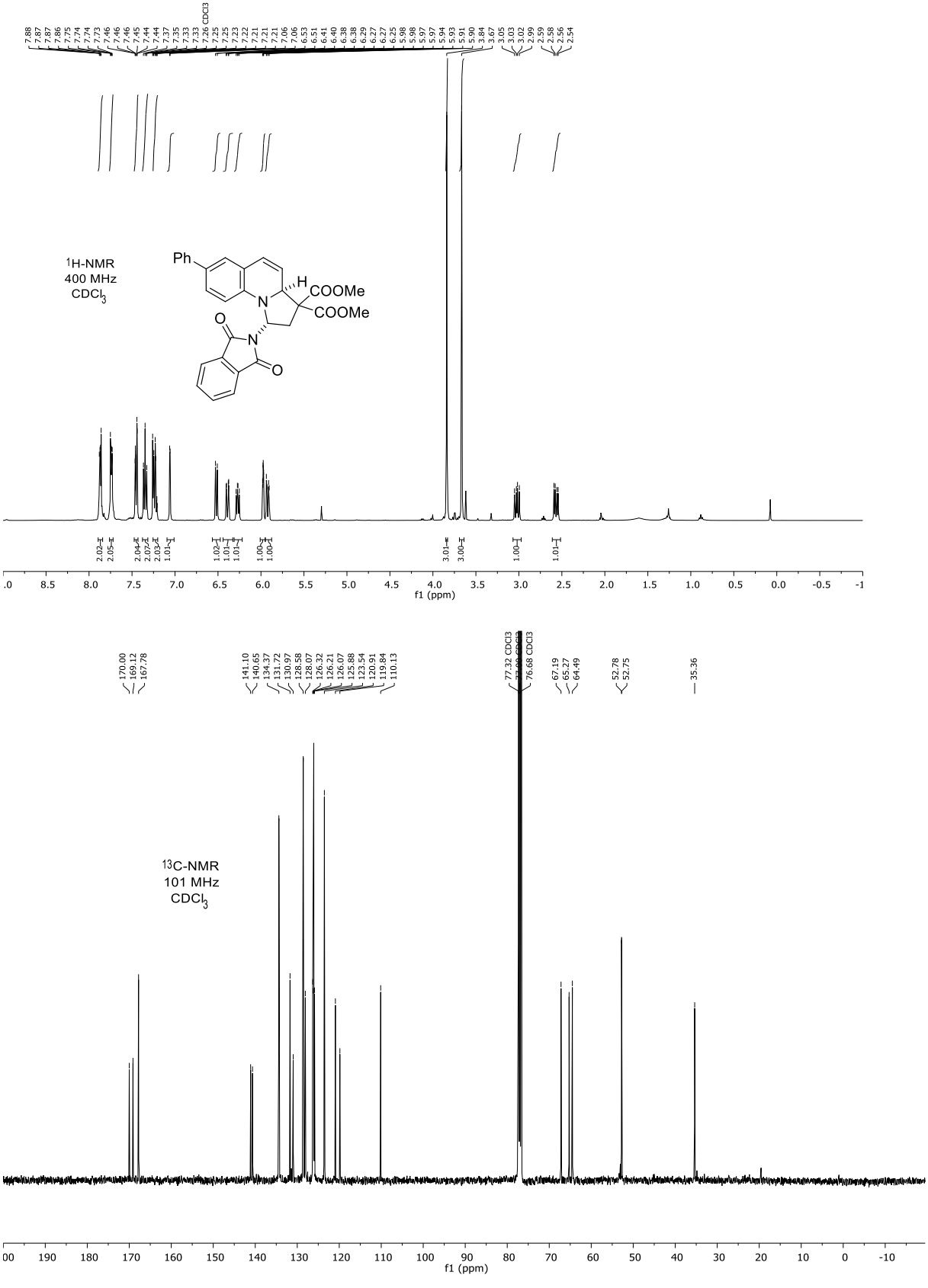


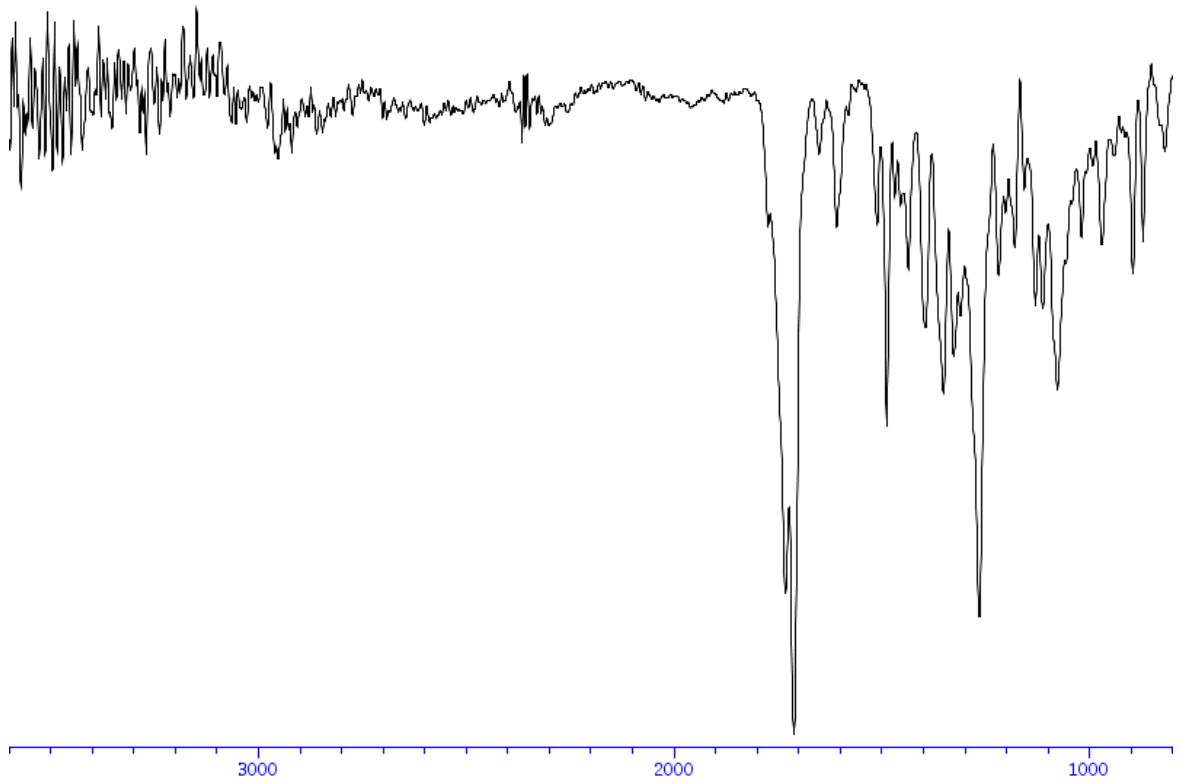



-127.74
-127.75
-127.77
-127.78
-127.79
-127.80
31F-NMR
376 MHz
CDCl3
-127.3 -127.4 -127.5 -127.6 -127.7 -127.8 -127.9 -128.0 -128.1 -128.2 -128.3
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

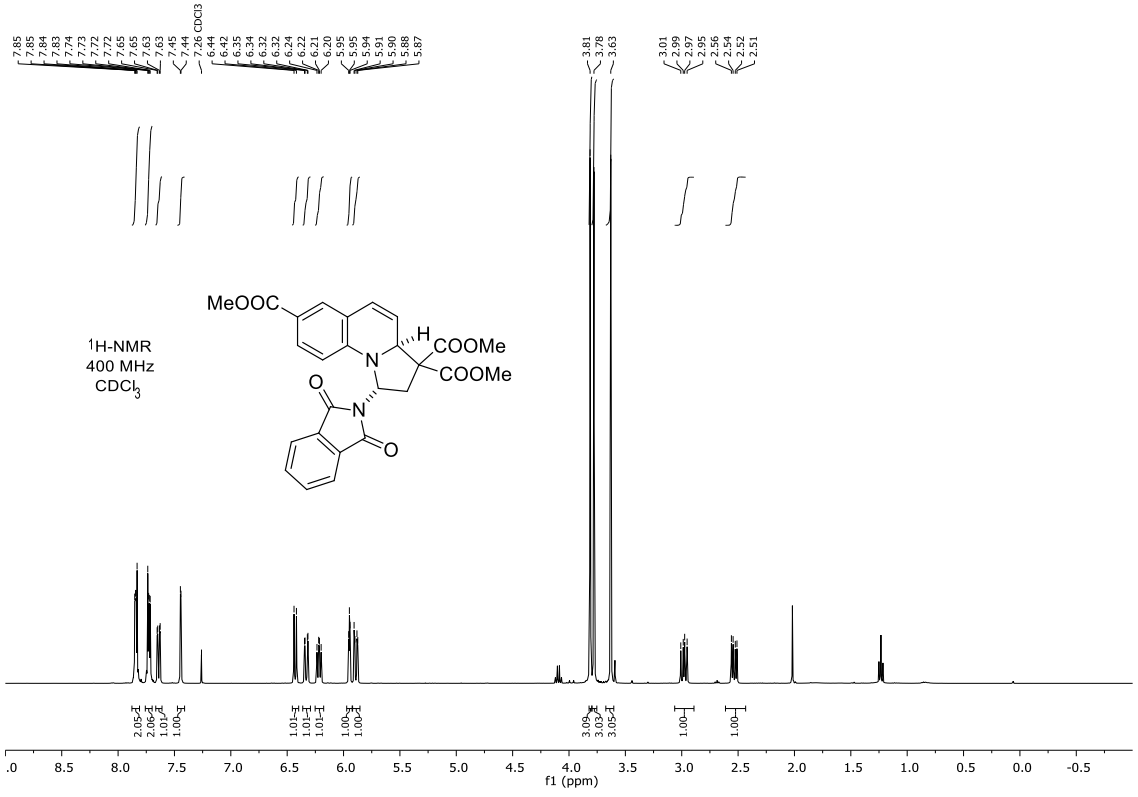

3000
2000
1000

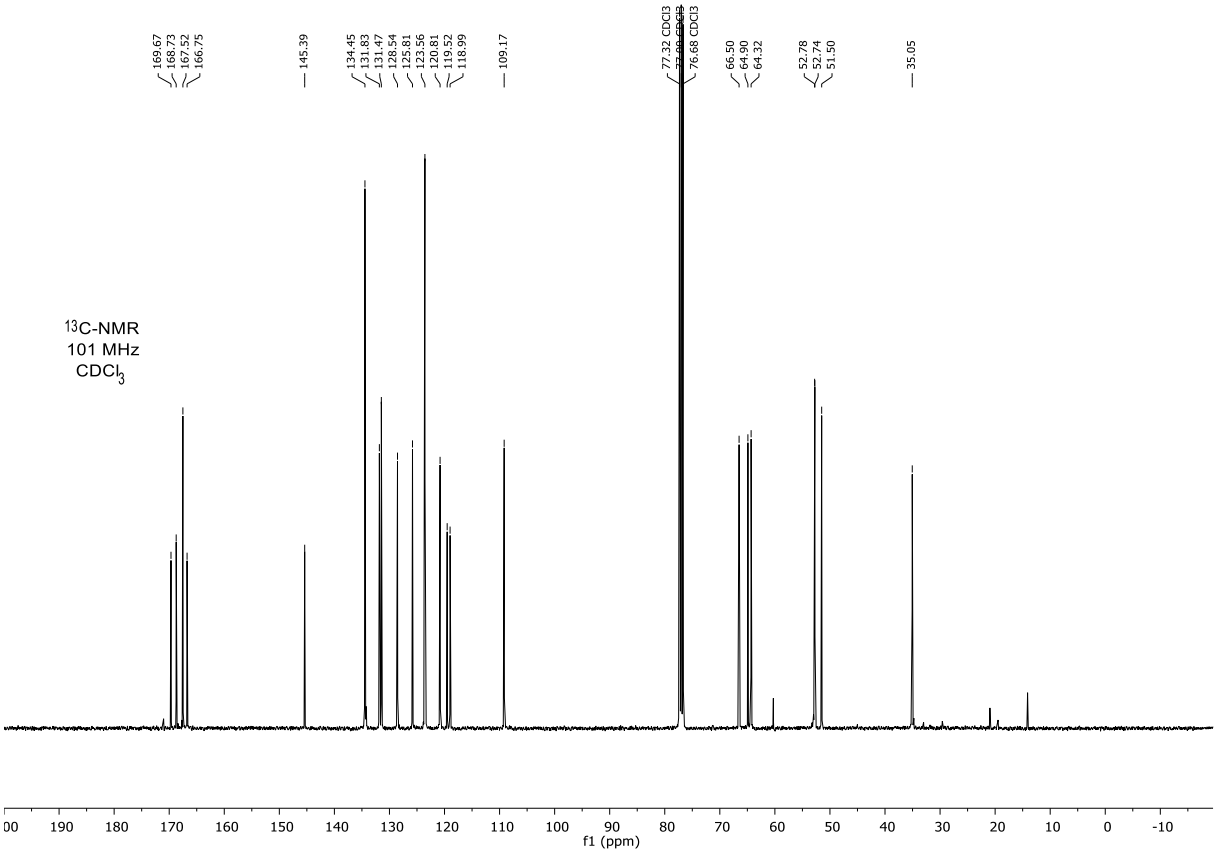
***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-7-phenyl-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**28**).

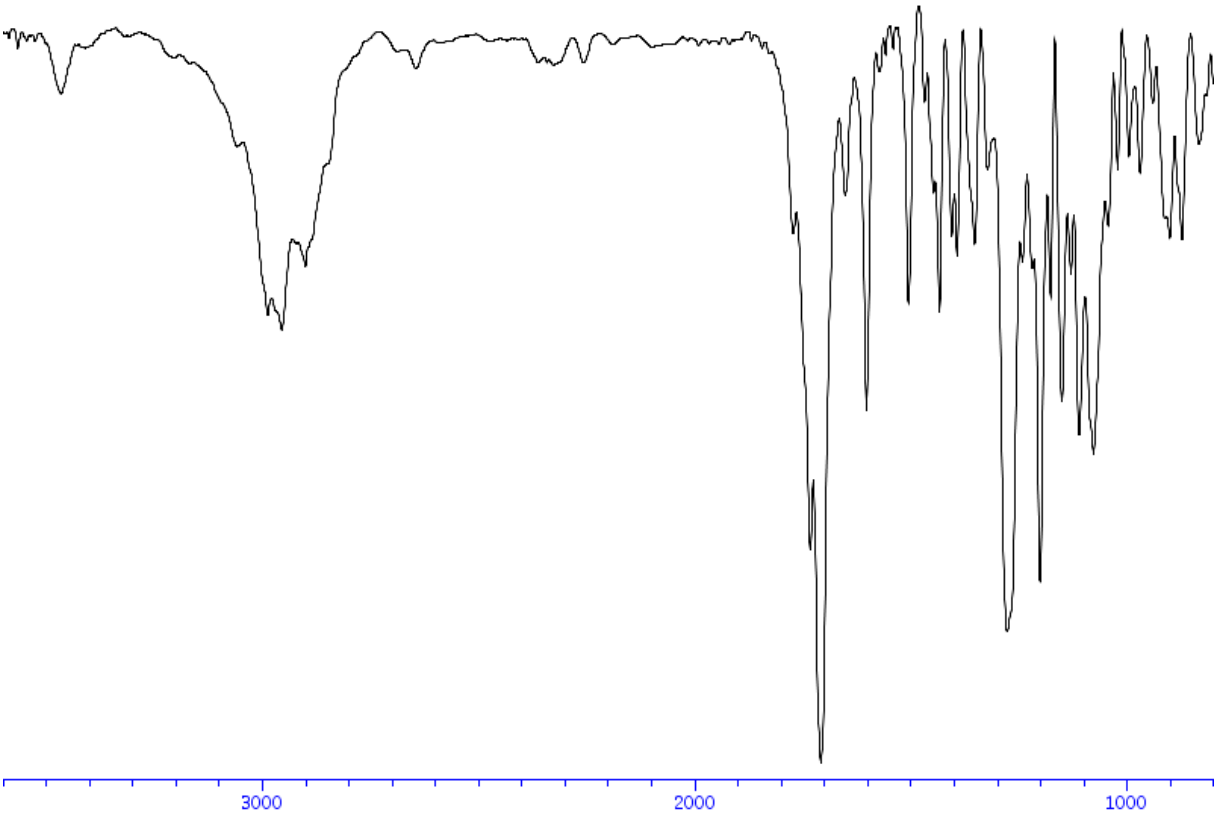




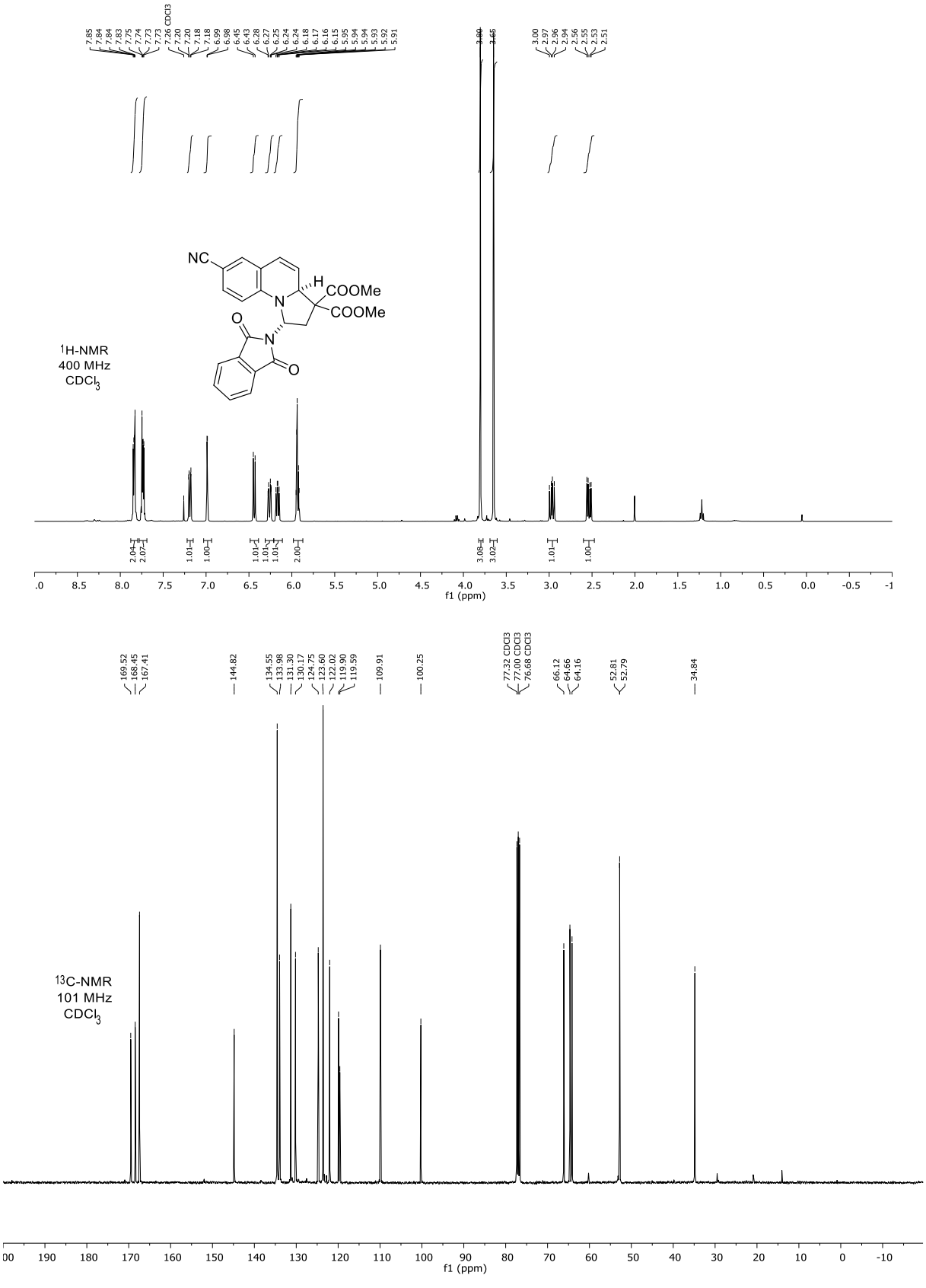
***anti*-Trimethyl 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3,7(3a*H*)-tricarboxylate** (**29**).

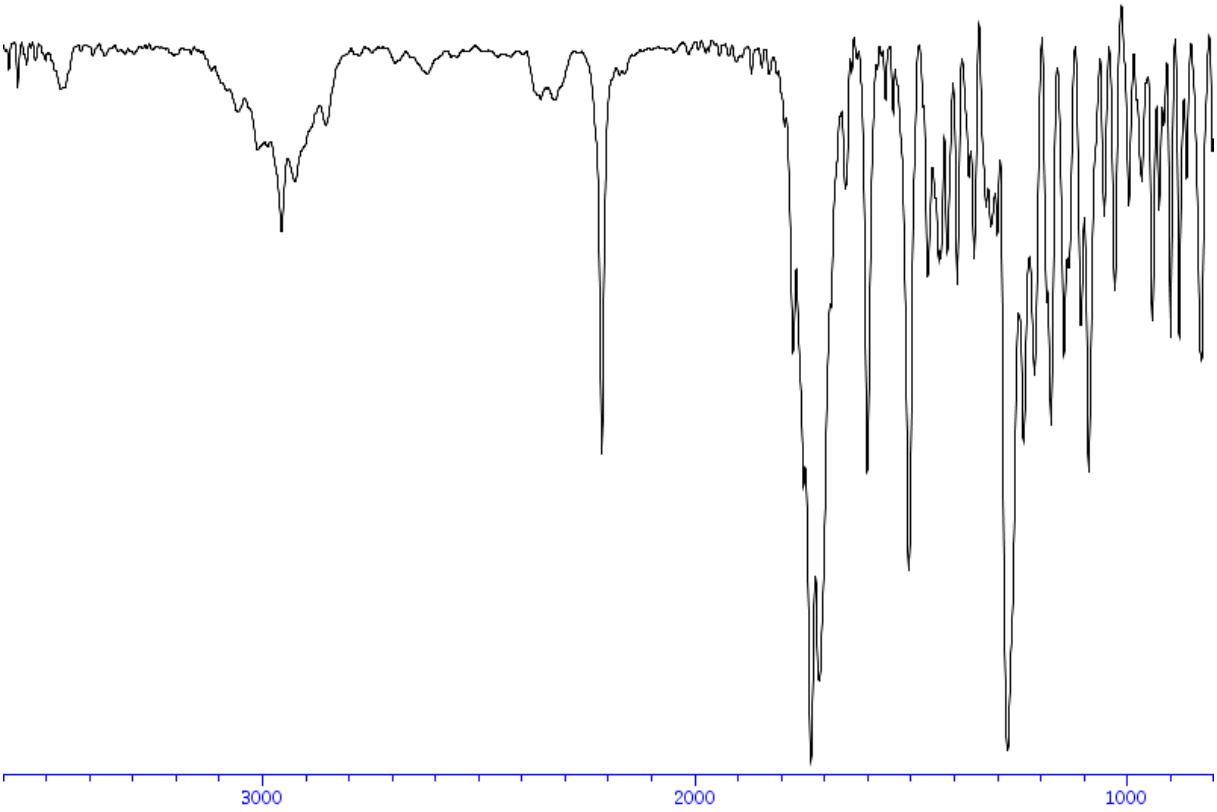



169.67
168.73
167.52
166.75
145.39
134.45
131.83
131.47
128.54
125.81
123.56
120.81
119.52
118.99
109.17
77.32 CDCl3
76.68 CDCl3
66.50
64.90
64.32
52.78
52.74
51.50
35.05
13C-NMR
101 MHz
CDCl3
f1 (ppm)

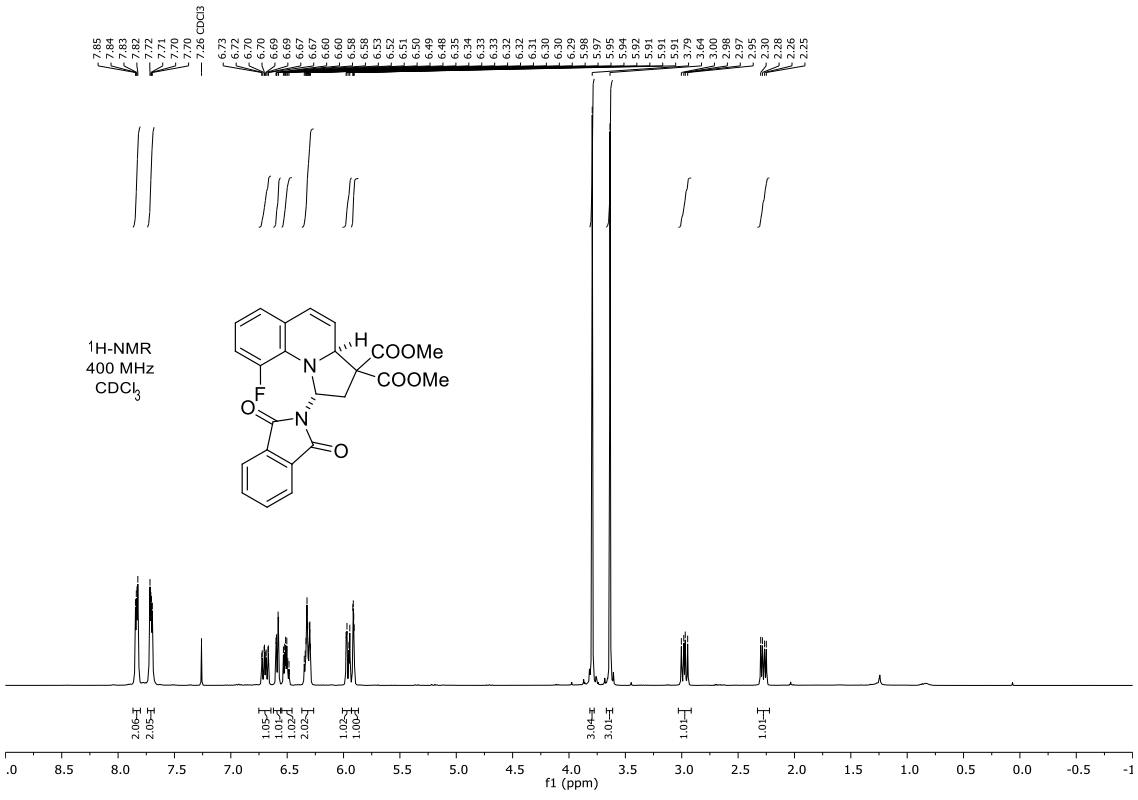

3000
2000
1000

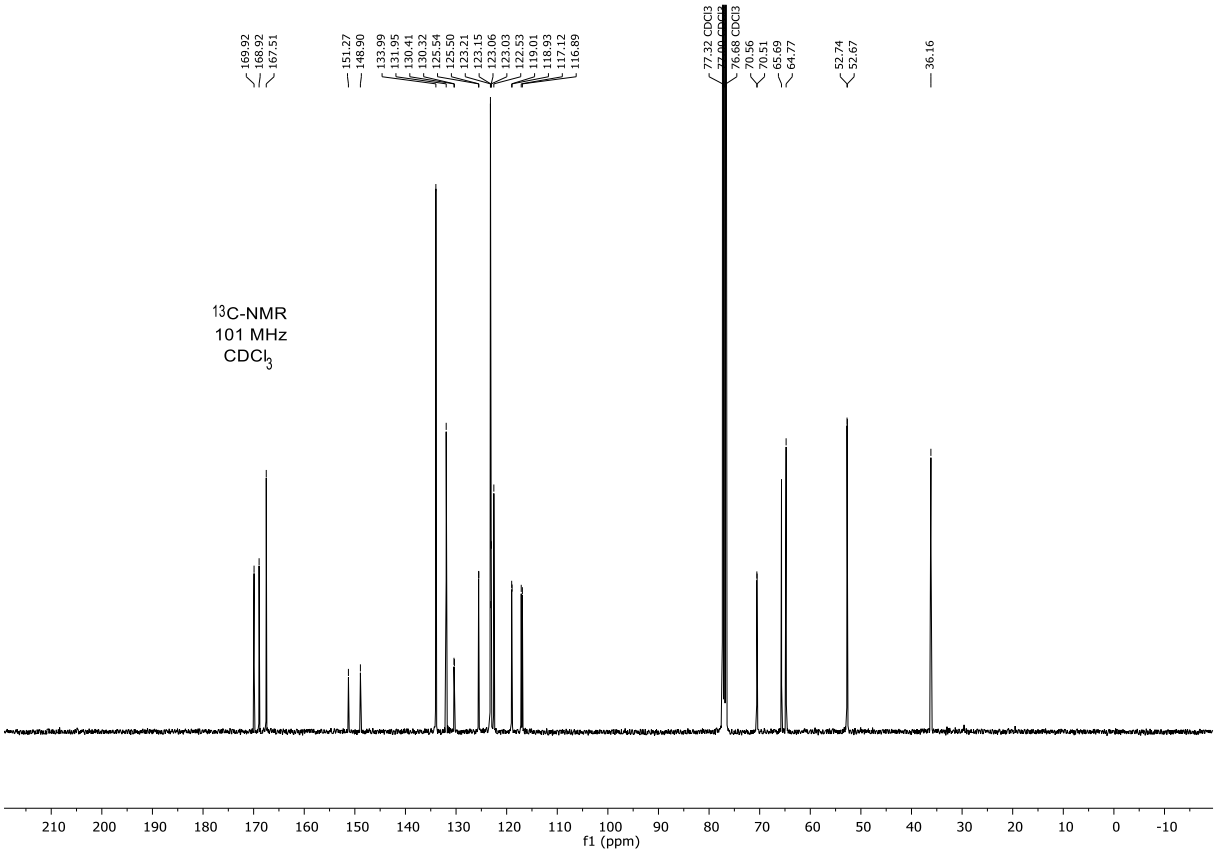
***anti*-Dimethyl 7-cyano-1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate** (**30**).

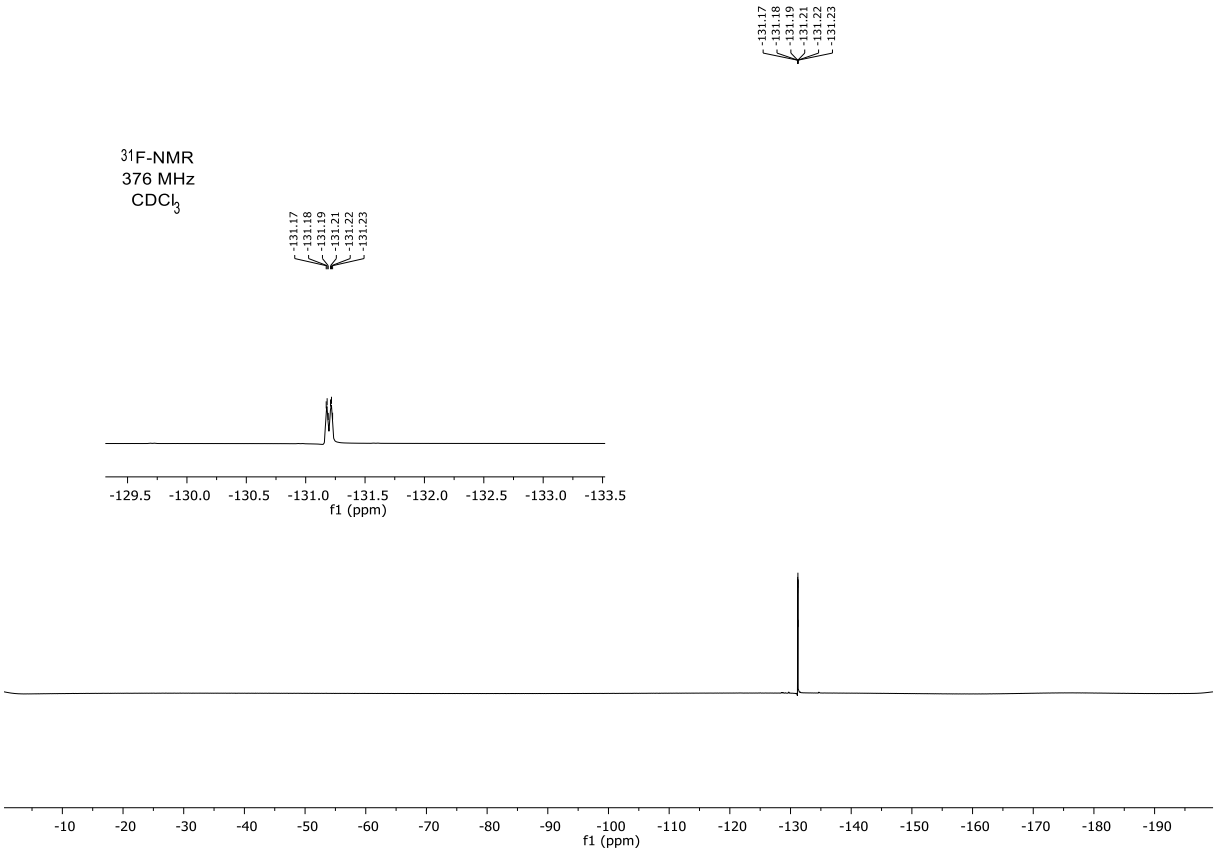


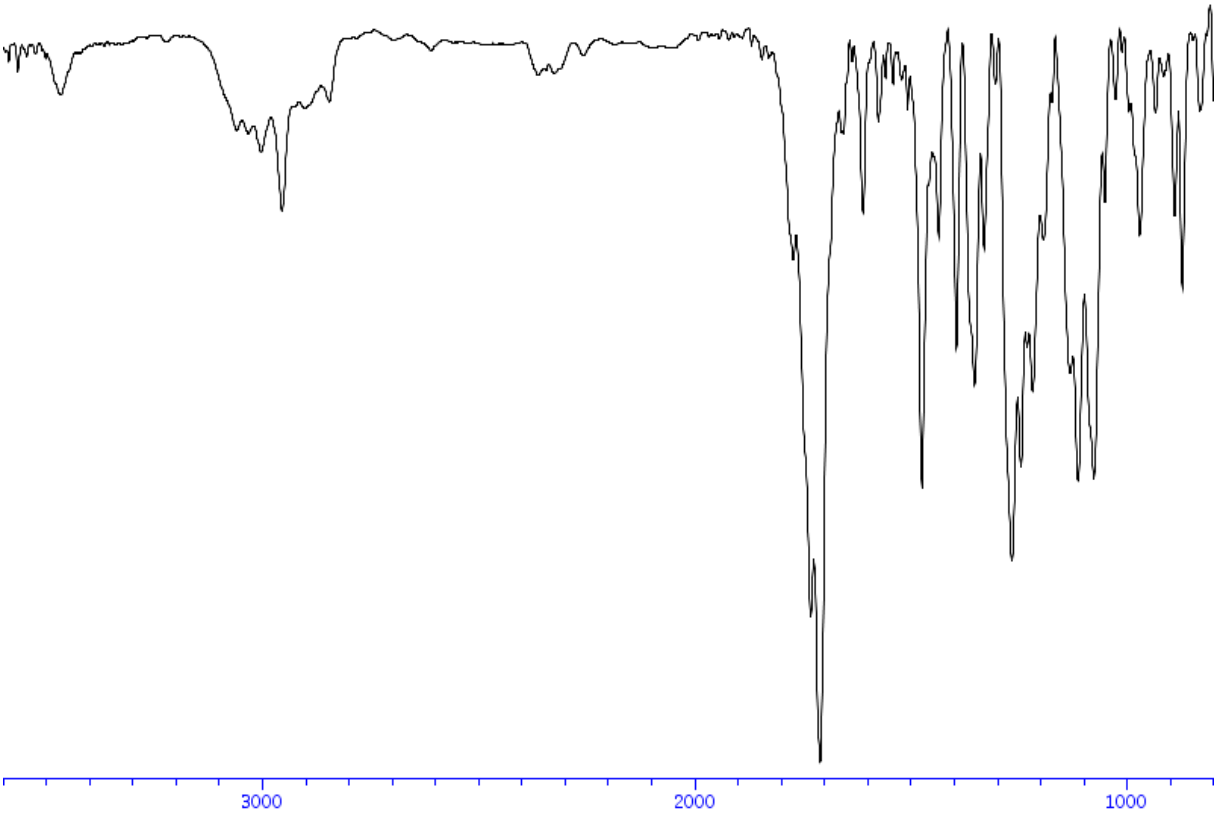


***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-9-fluoro-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (31).**

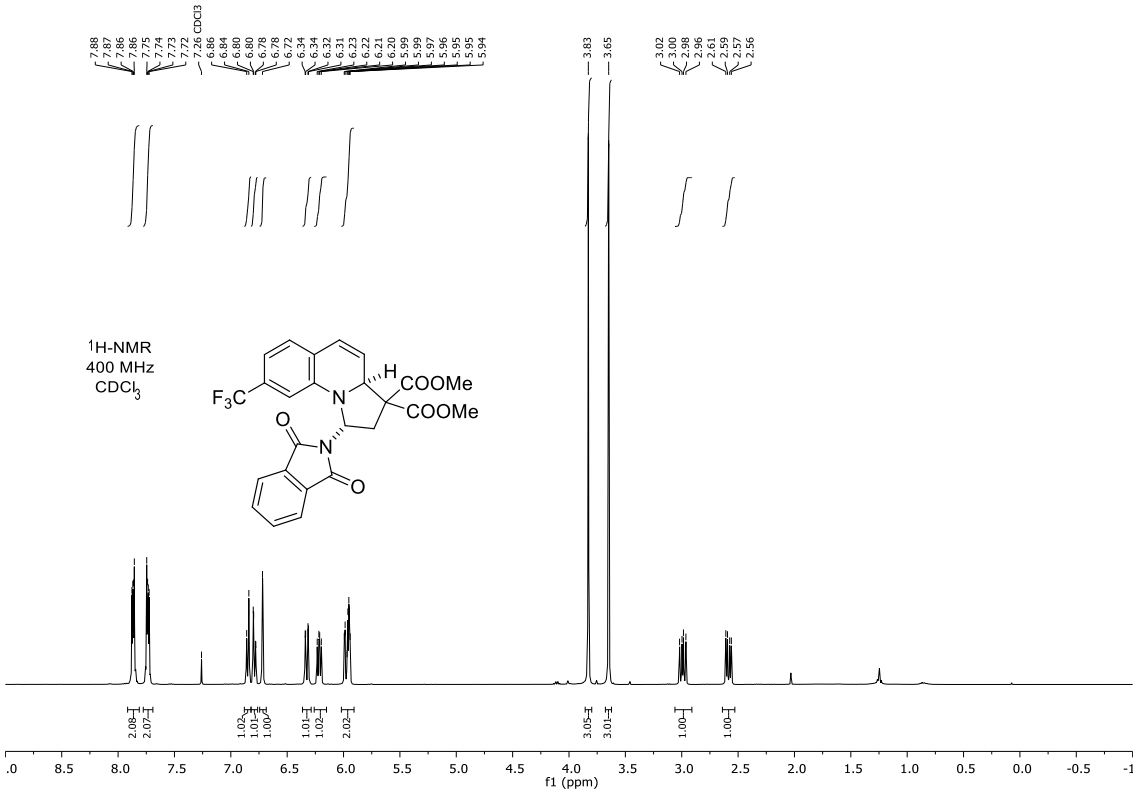


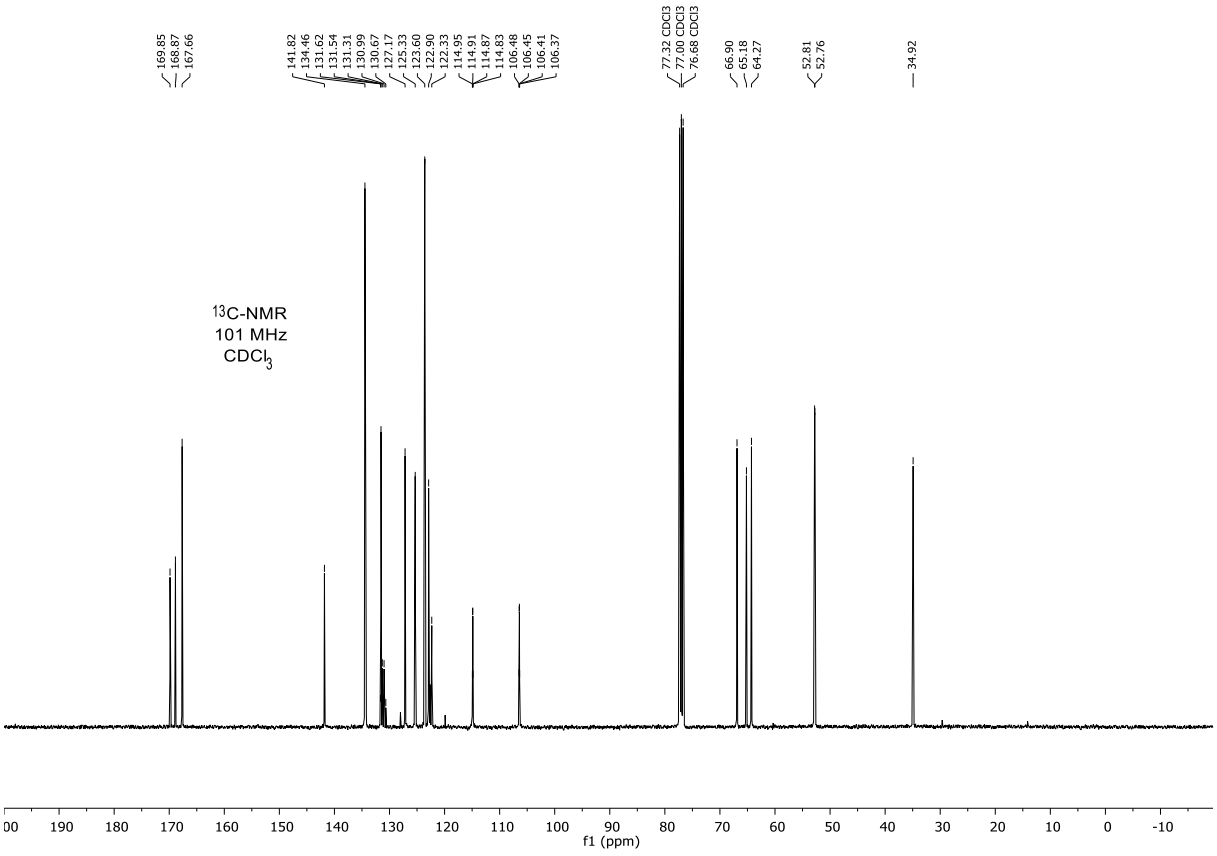

169.92
168.92
167.51
151.27
148.90
133.99
131.95
130.41
130.32
125.54
125.50
123.21
123.15
123.06
123.03
122.53
119.01
118.93
117.12
116.89
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
70.56
70.51
65.69
64.77
52.74
52.67
36.16
13C-NMR
101 MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

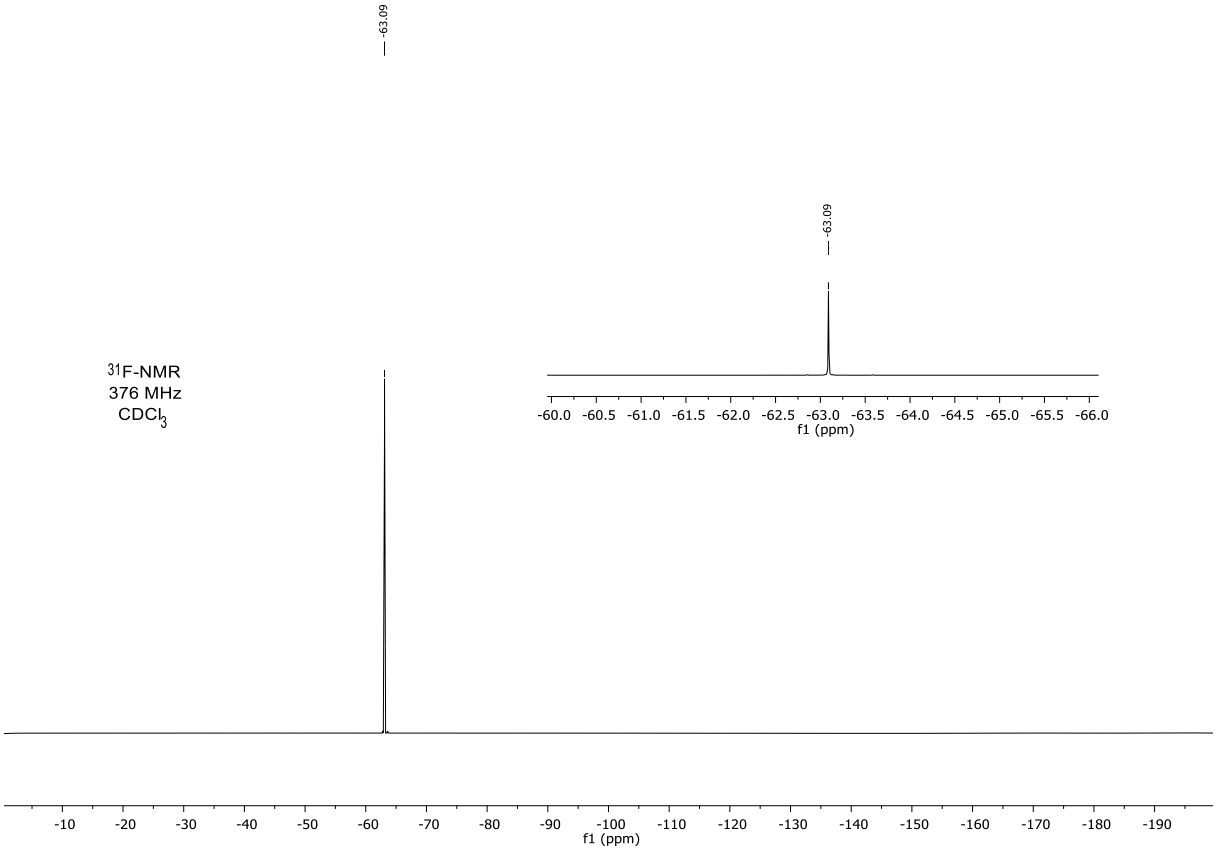

-131.17
-131.18
-131.19
-131.21
-131.22
-131.23
31F-NMR
376 MHz
CDCl3
-129.5 -130.0 -130.5 -131.0 -131.5 -132.0 -132.5 -133.0 -133.5
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

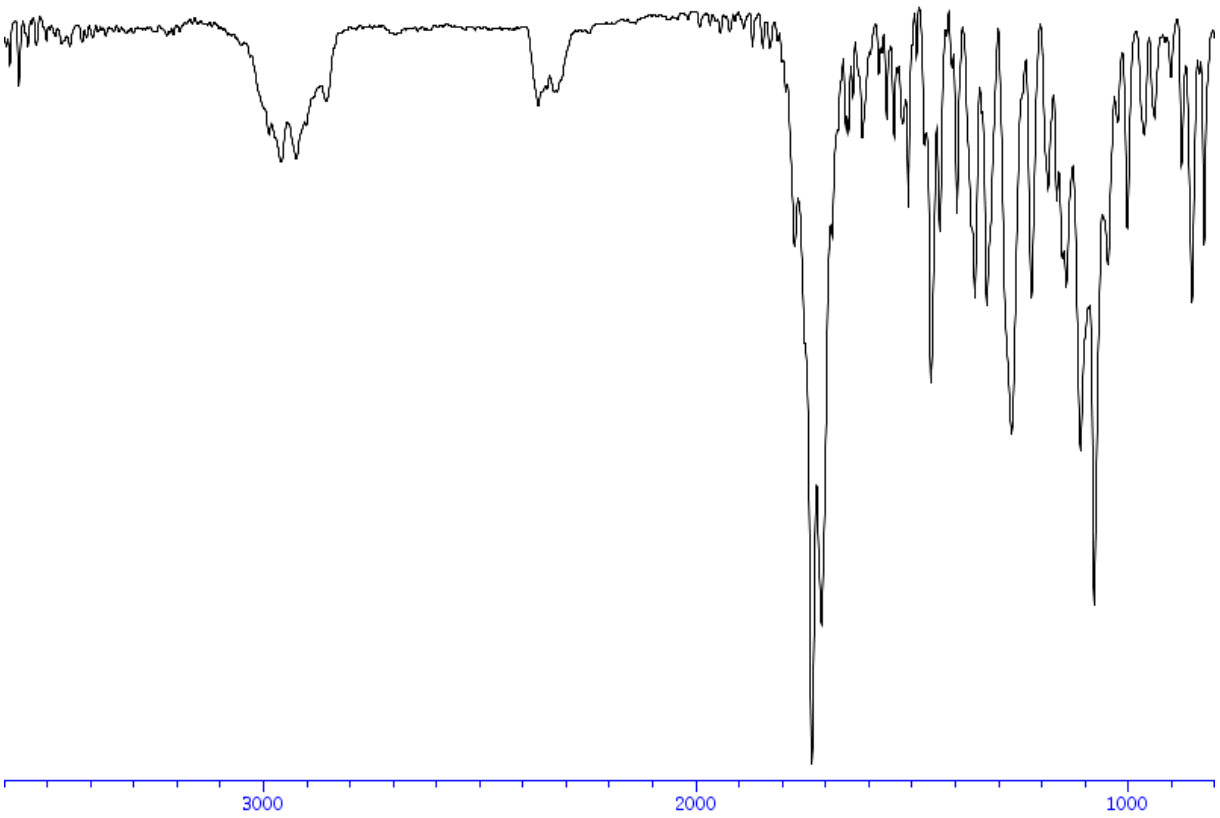


***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-8-(trifluoromethyl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (32).**

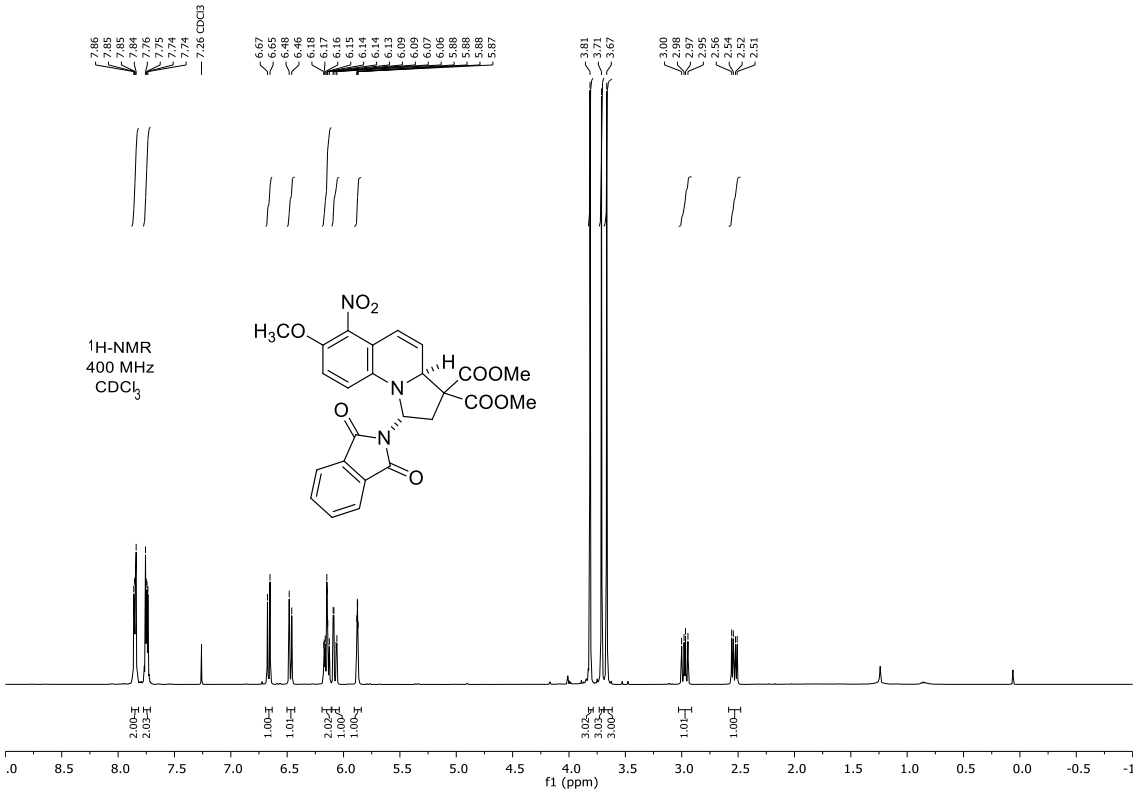


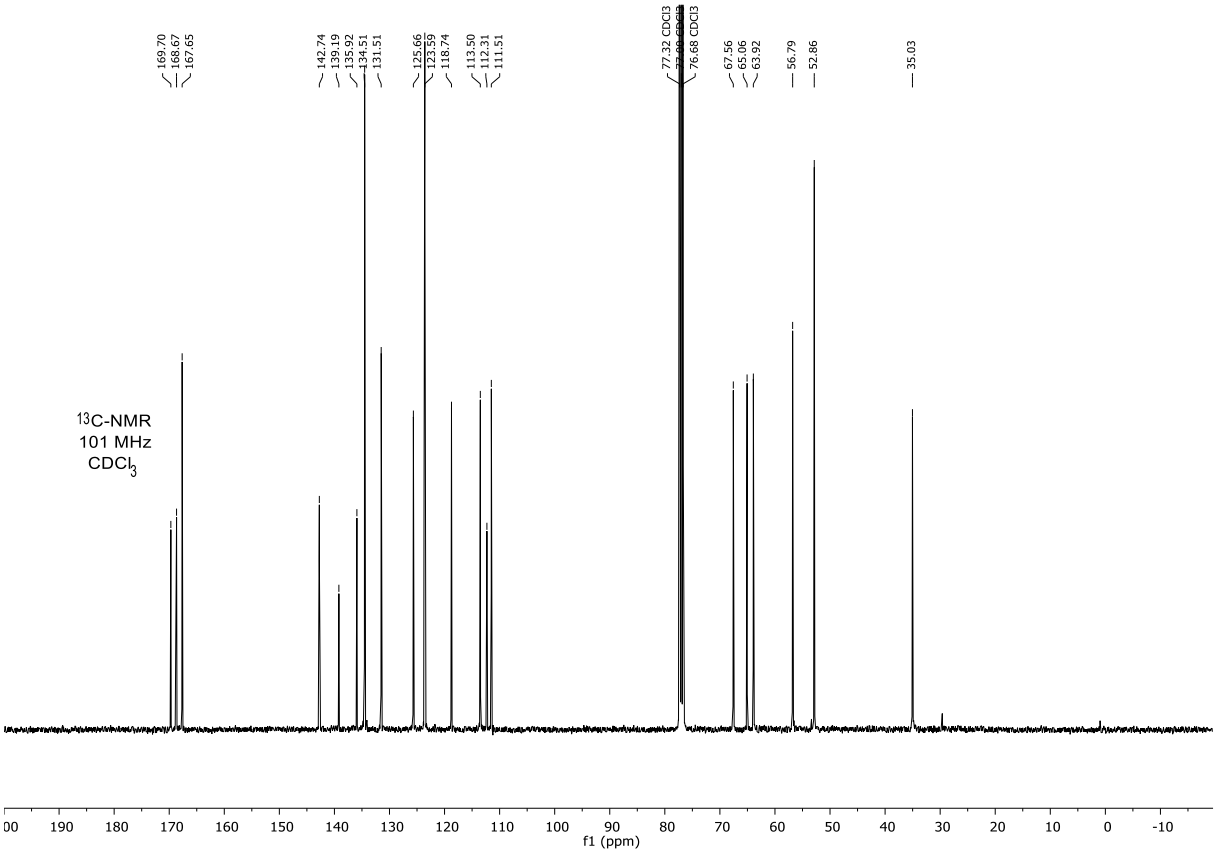

169.85
168.87
167.66
141.82
134.46
131.62
131.54
131.31
130.99
130.67
127.17
125.33
123.60
122.90
122.33
114.95
114.91
114.87
114.83
106.48
106.45
106.41
106.37
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
66.90
65.18
64.27
52.81
52.76
34.92
13C-NMR
101 MHz
CDCl3
f1 (ppm)

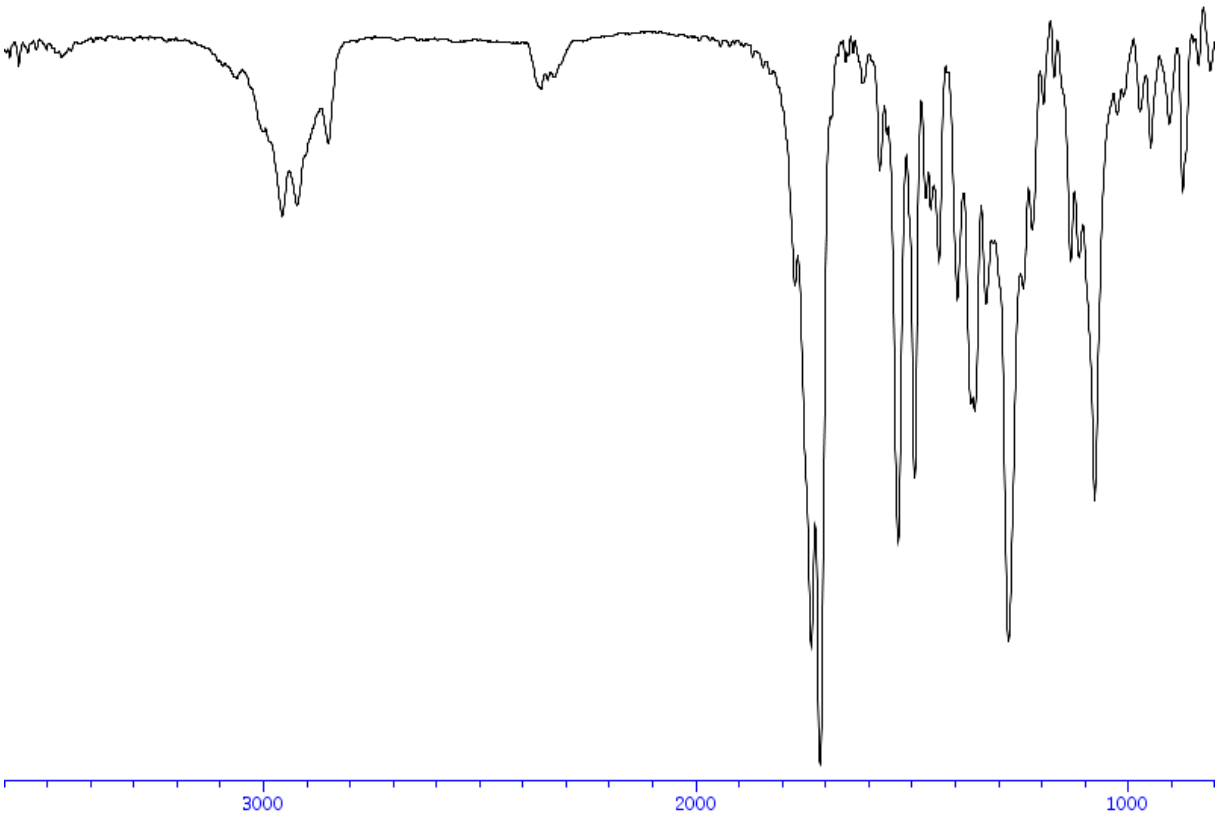

-63.09
-63.09
31F-NMR
376 MHz
CDCl3
f1 (ppm)
f1 (ppm)



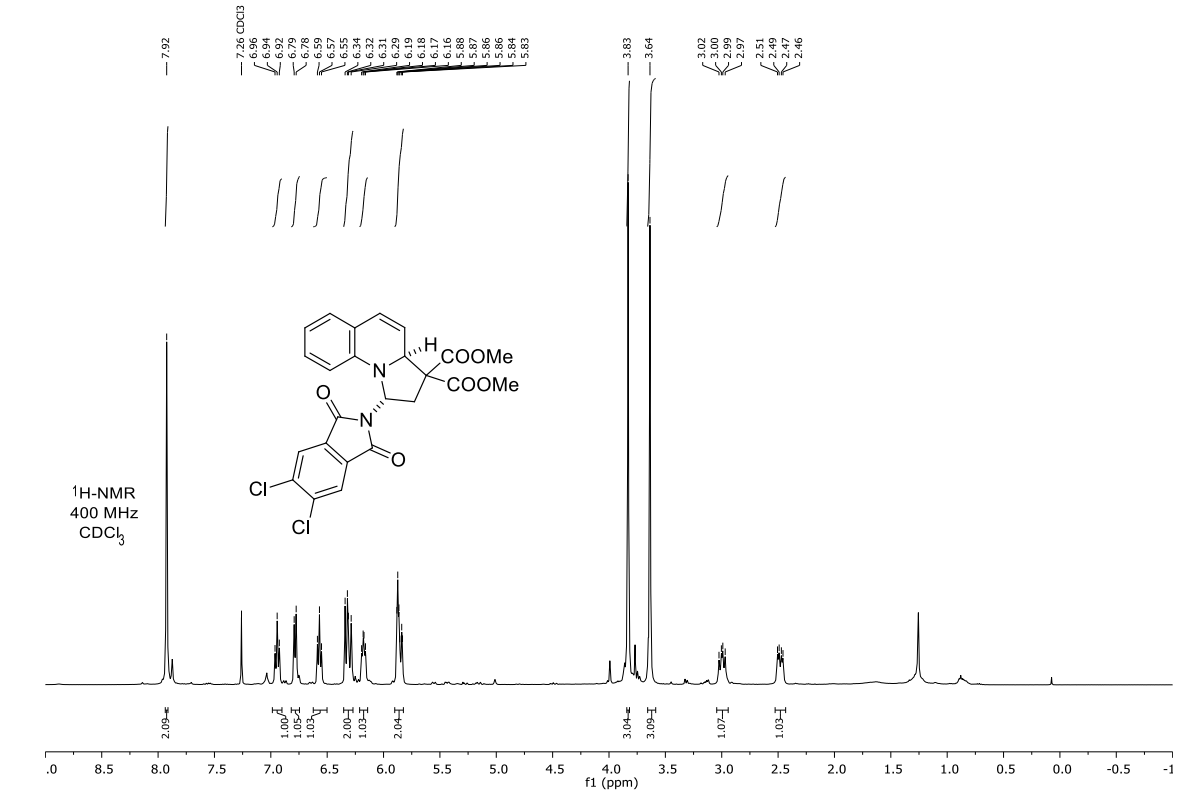
***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-7-methoxy-6-nitro-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (34).**

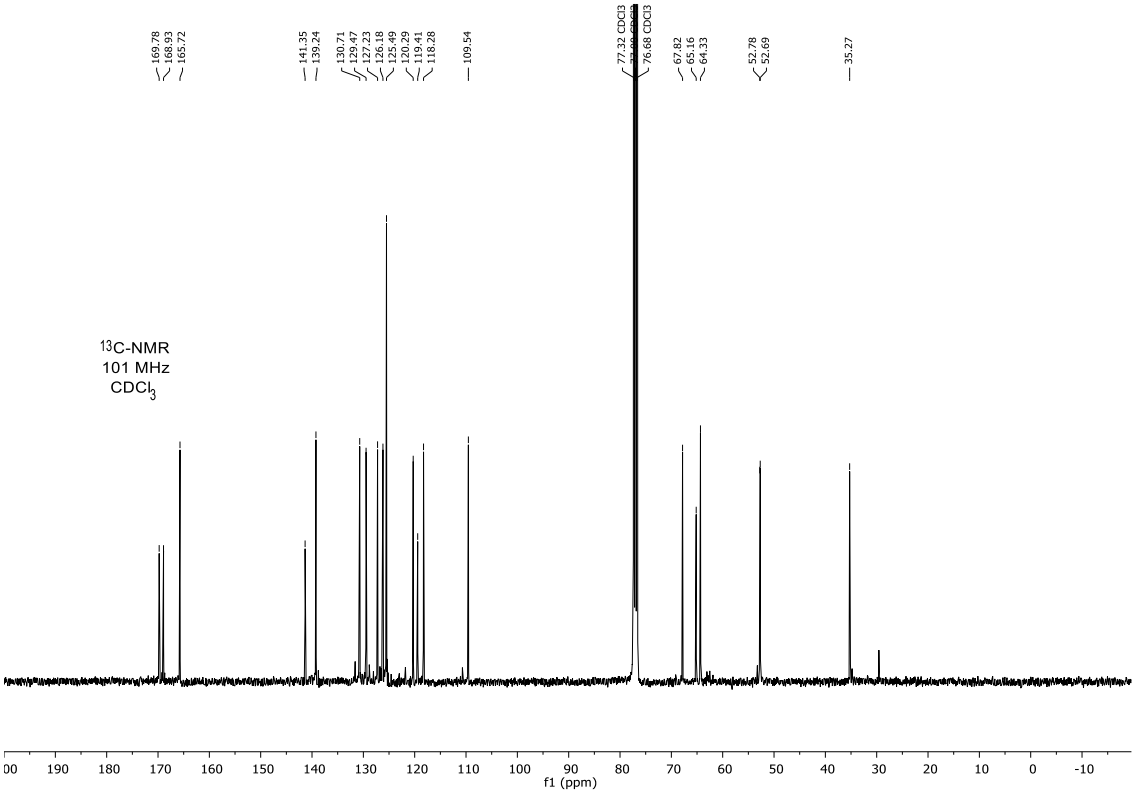


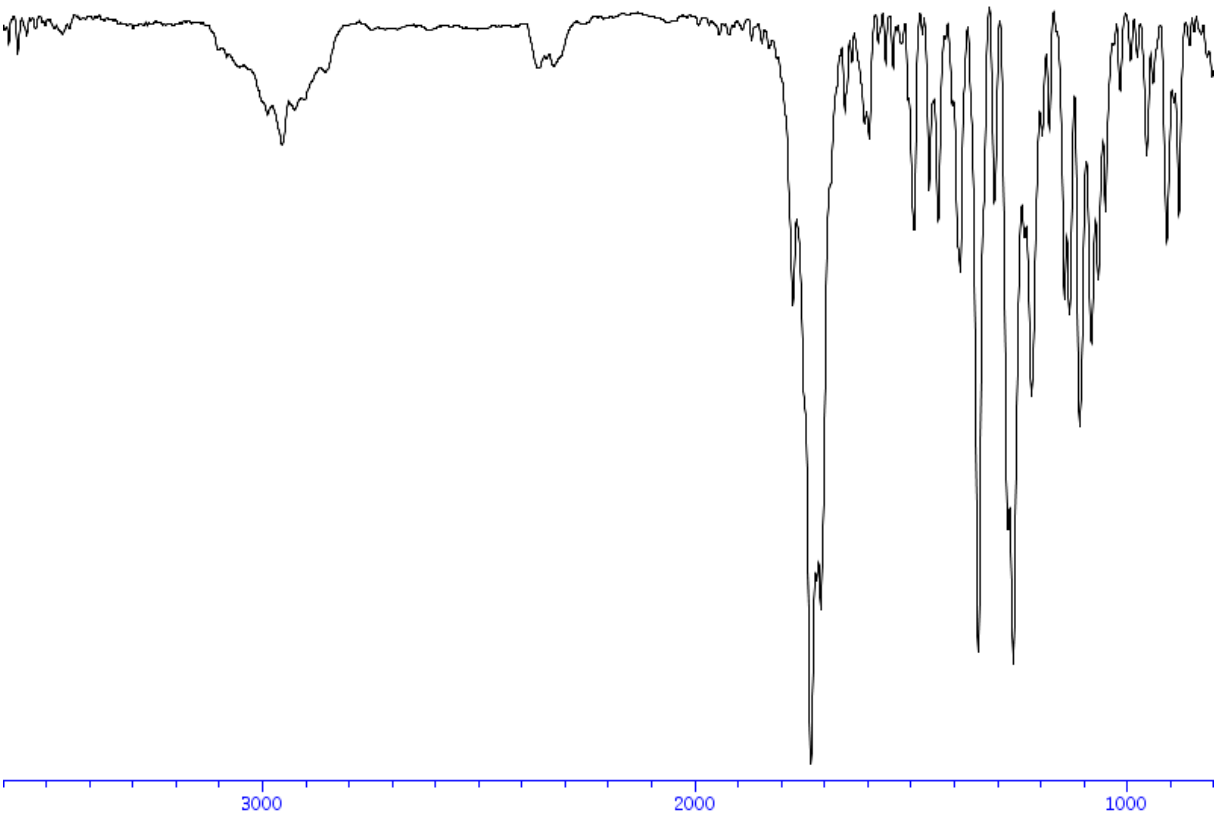

169.70
168.67
167.65
142.74
139.19
135.92
134.51
131.51
125.66
123.59
118.74
113.50
112.31
111.51
77.32 CDCl3
76.68 CDCl3
67.56
65.06
63.92
56.79
52.86
35.03
13C-NMR
101 MHz
CDCl3
f1 (ppm)


3000
2000
1000

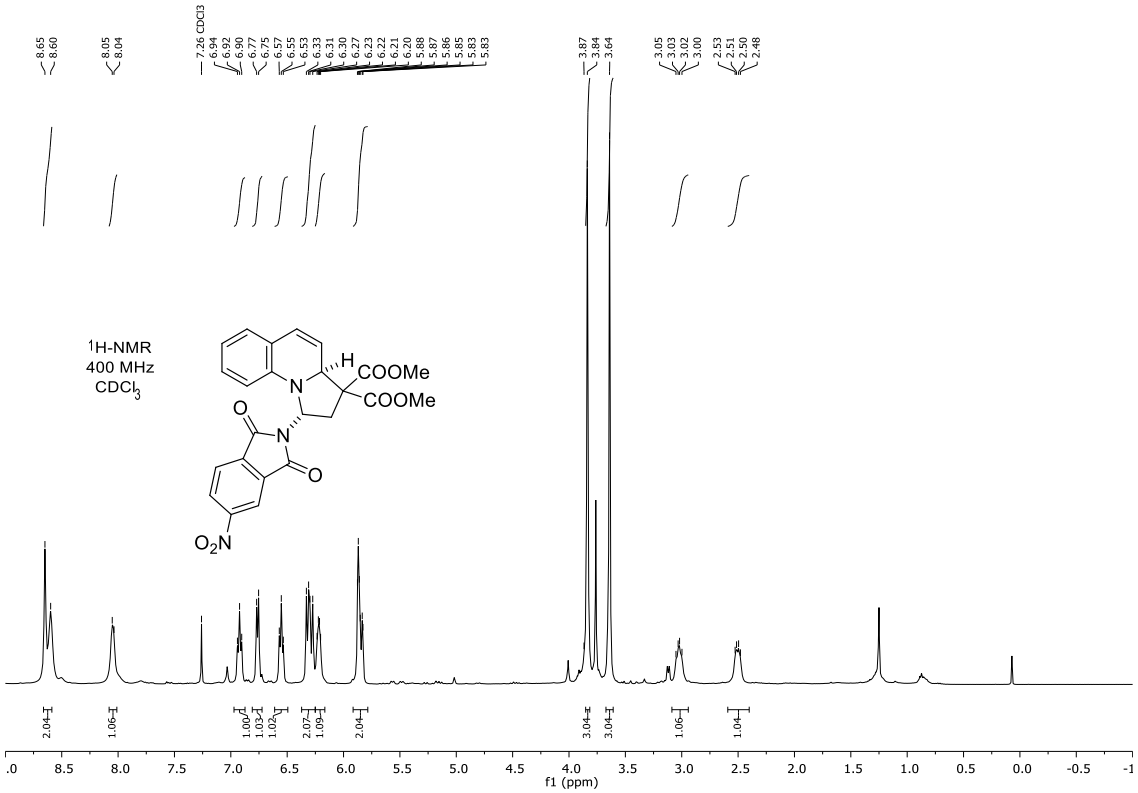
***anti*-Dimethyl 1-(5,6-dichloro-1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (35).**

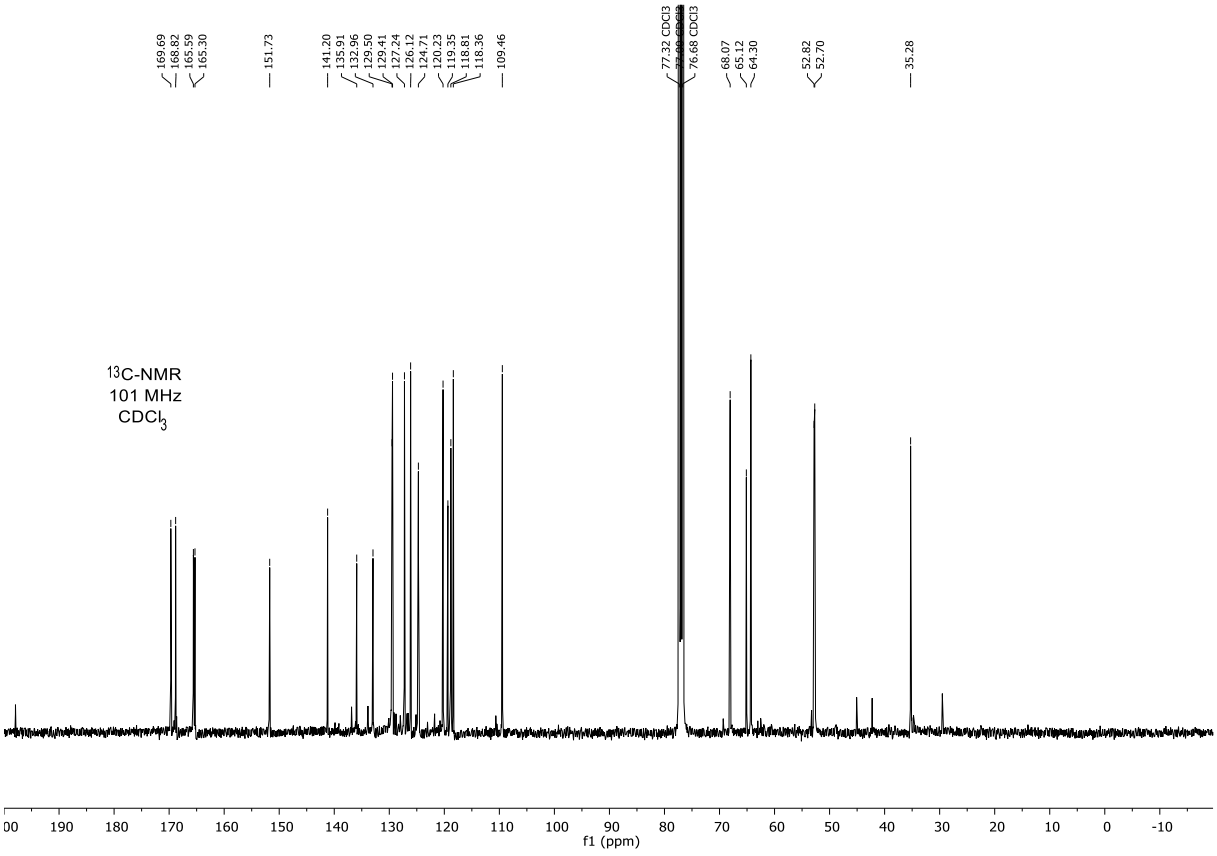


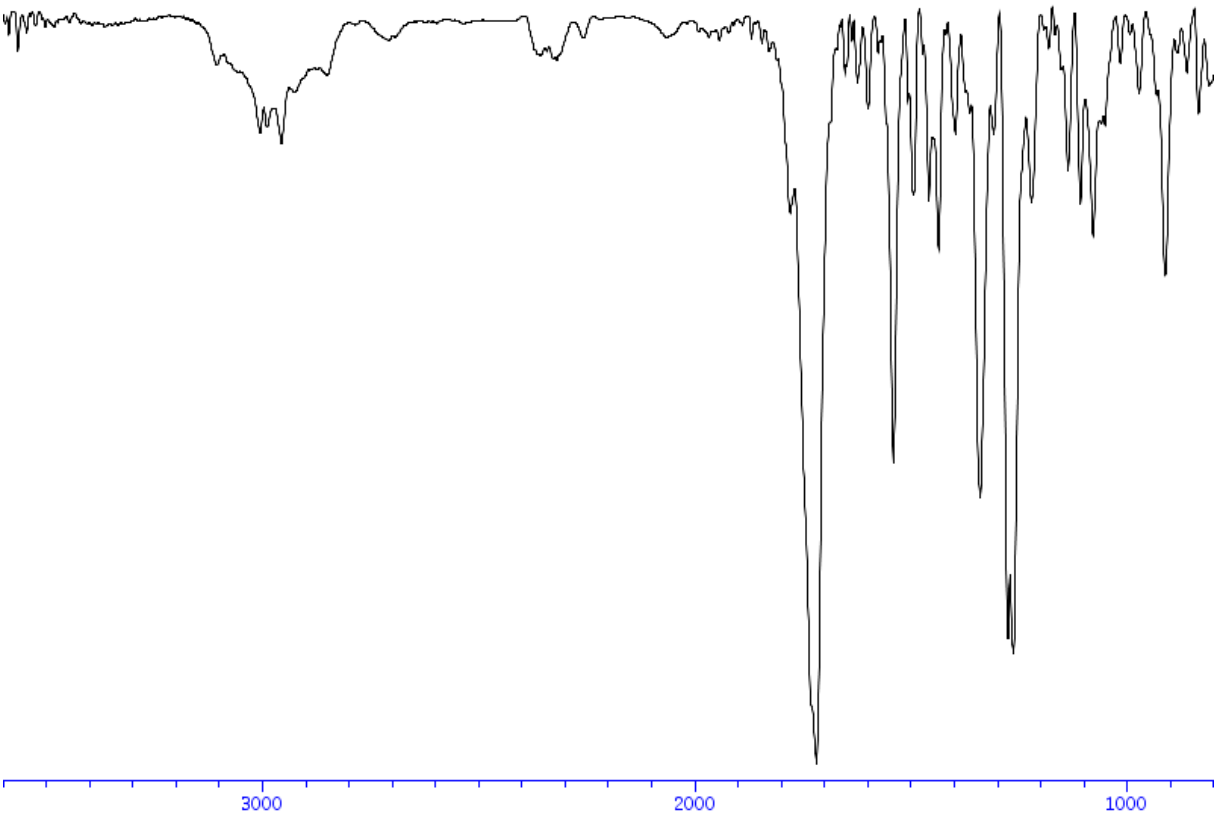




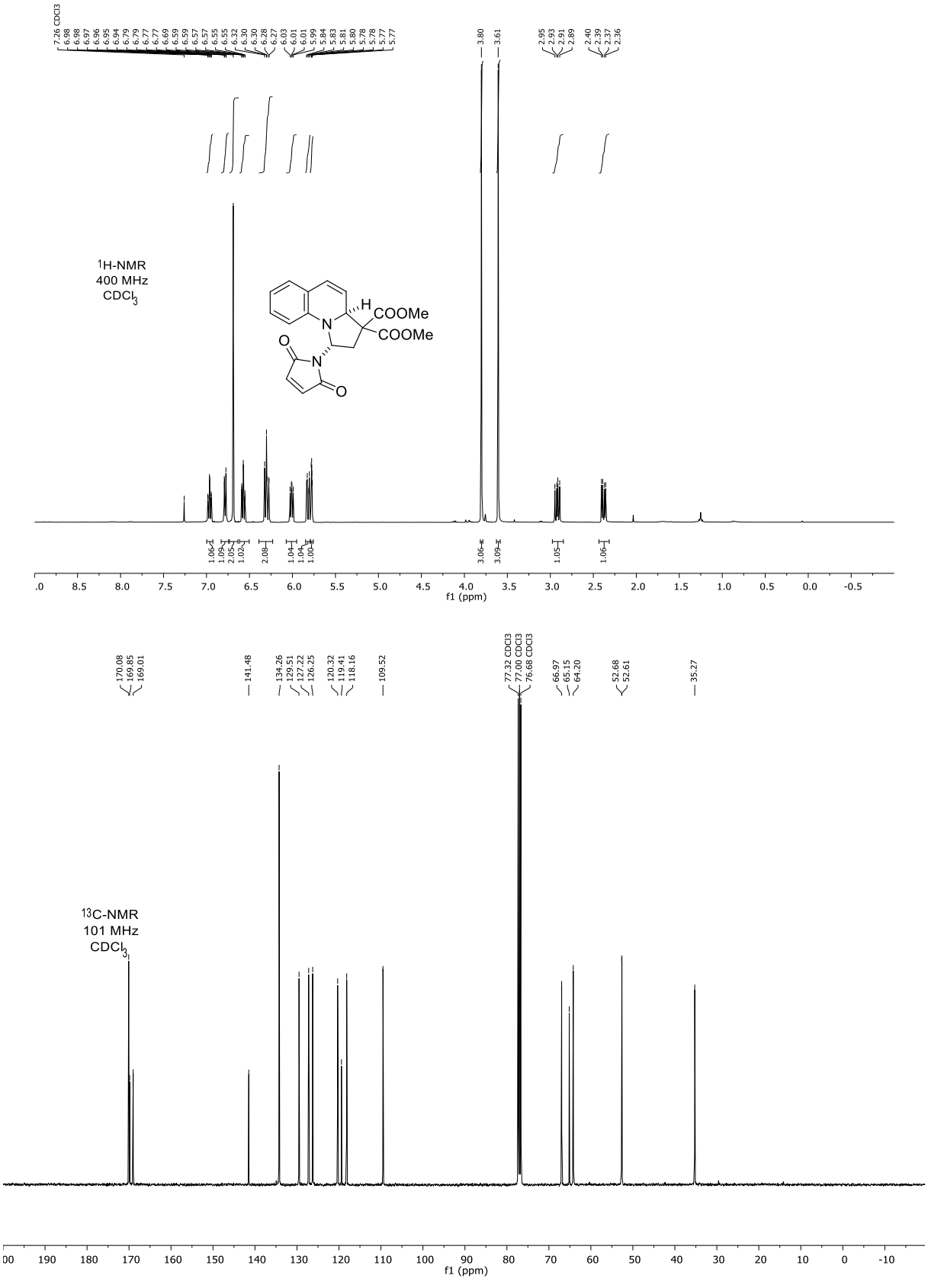
***anti*-Dimethyl 1-(5-nitro-1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (36).**

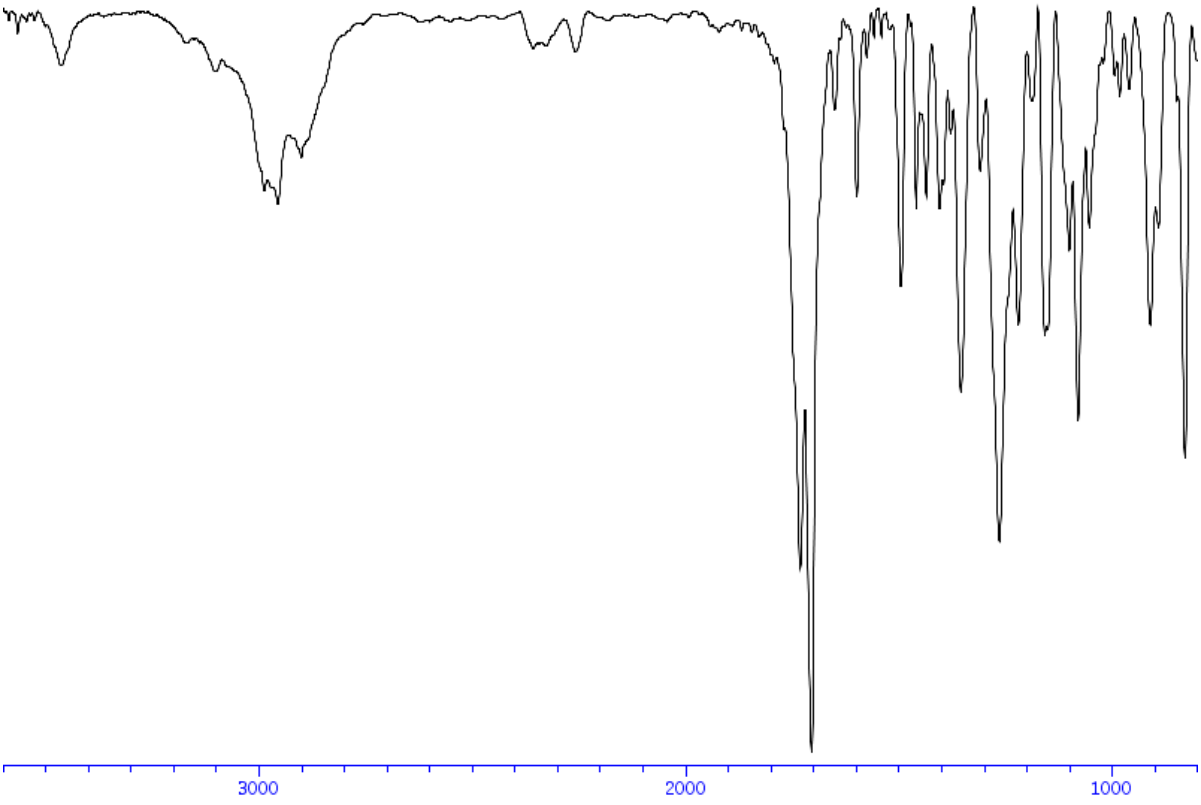



169.69
168.82
165.59
165.30
151.73
141.20
135.91
132.96
129.50
129.41
127.24
126.12
124.71
120.23
119.35
118.81
118.36
109.46
77.32 CDCl3
76.68 CDCl3
68.07
65.12
64.30
52.82
52.70
35.28
13C-NMR
101 MHz
CDCl3
f1 (ppm)

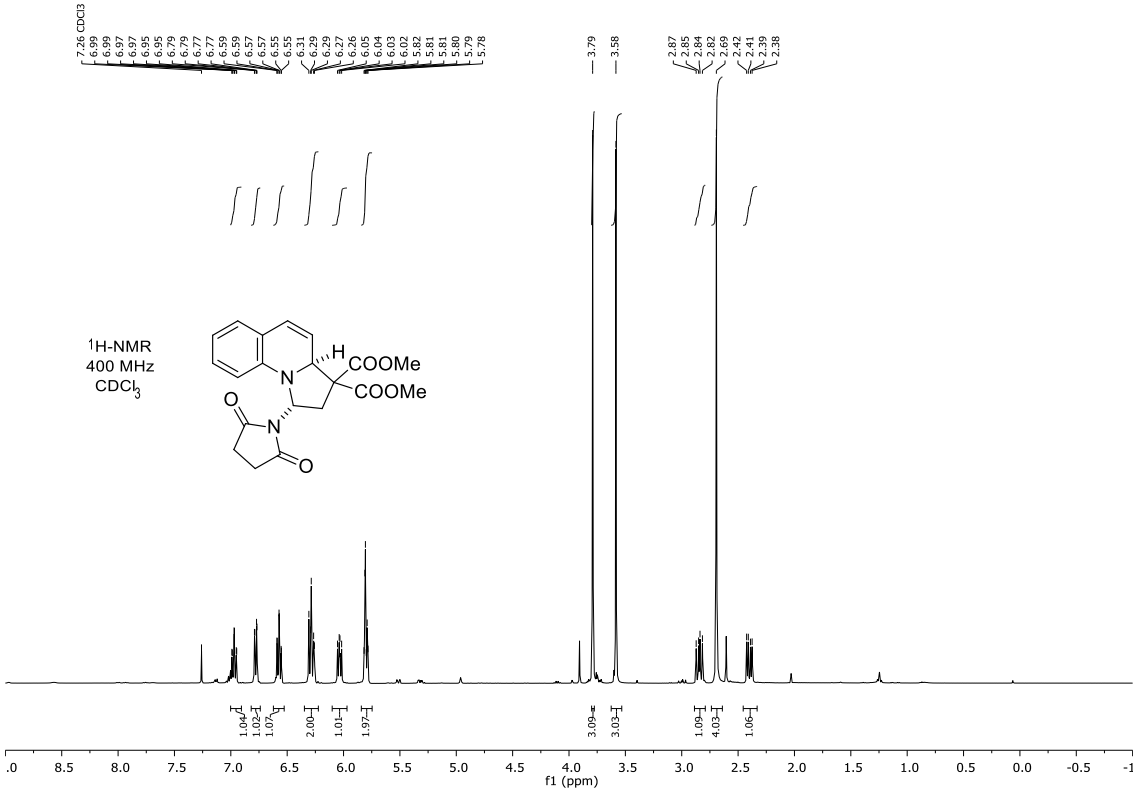

3000
2000
1000

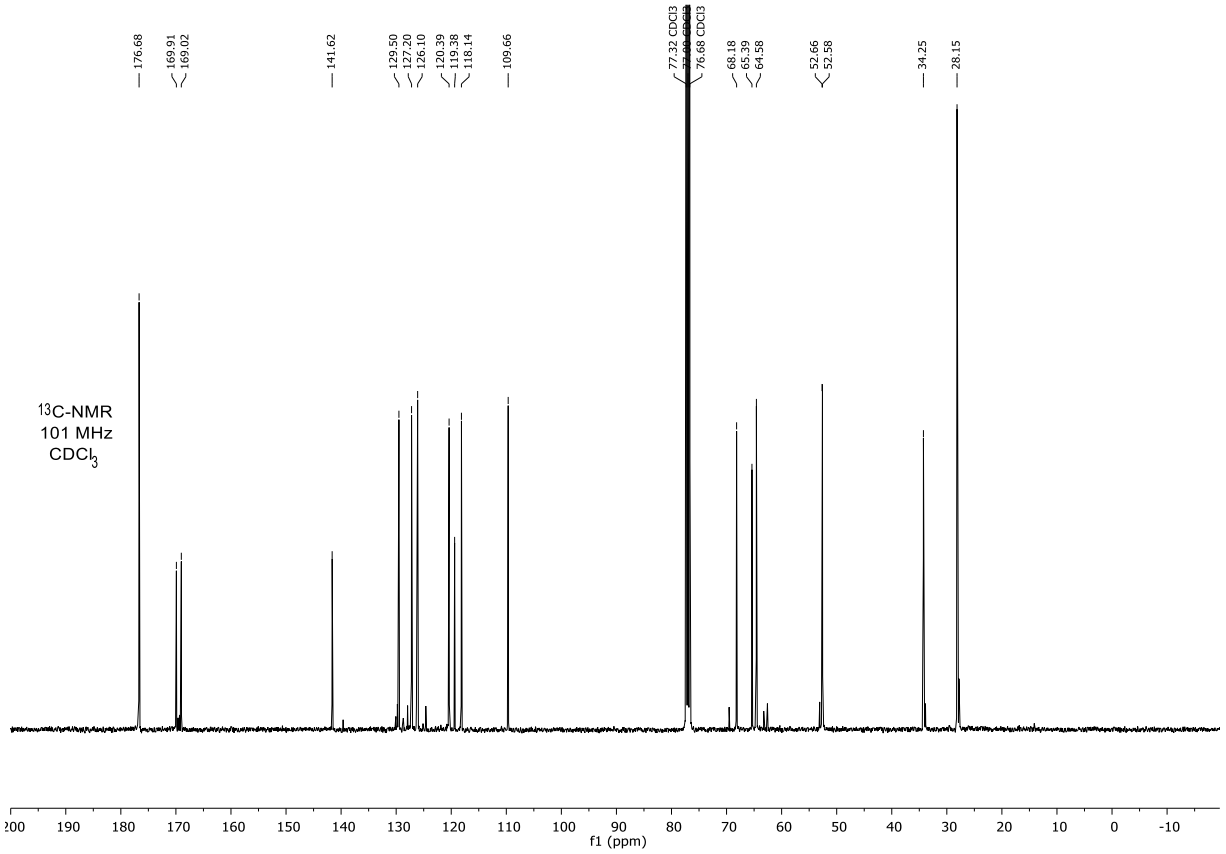
***anti*-Dimethyl 1-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (37).**

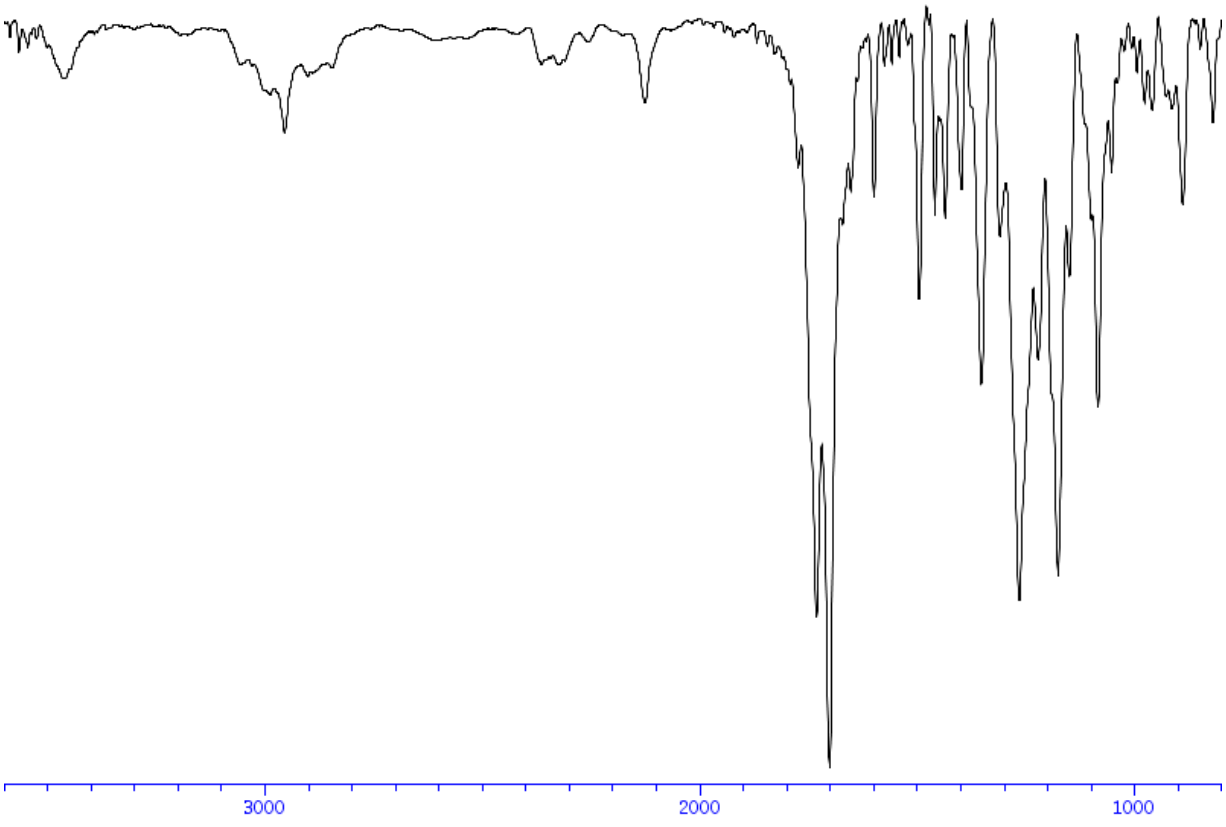




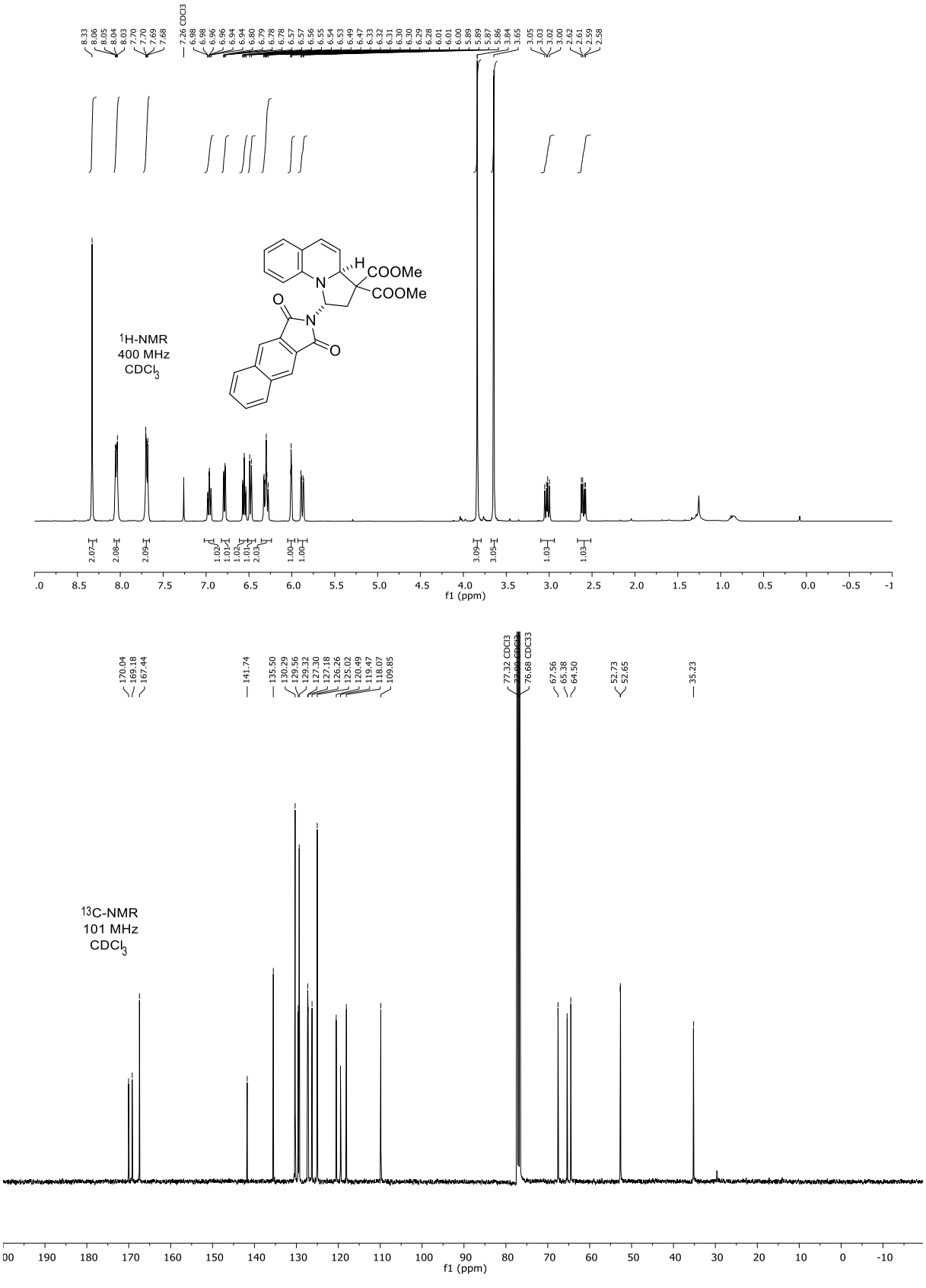
***anti*-Dimethyl 1-(2,5-dioxopyrrolidin-1-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (38).**

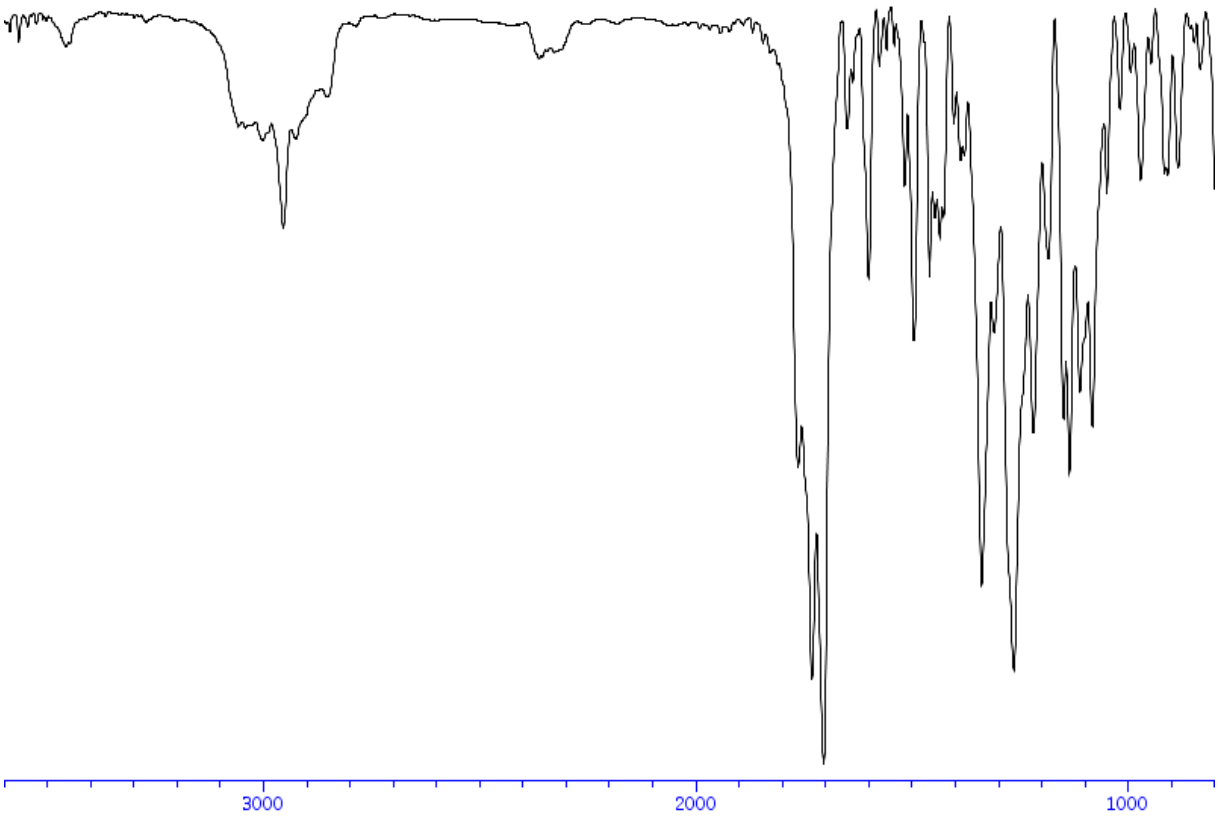



176.68
169.91
169.02
141.62
129.50
127.20
126.10
120.39
119.38
118.14
109.66
77.32 CDCl3
76.68 CDCl3
68.18
65.39
64.58
52.66
52.58
34.25
28.15
13C-NMR
101 MHz
CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

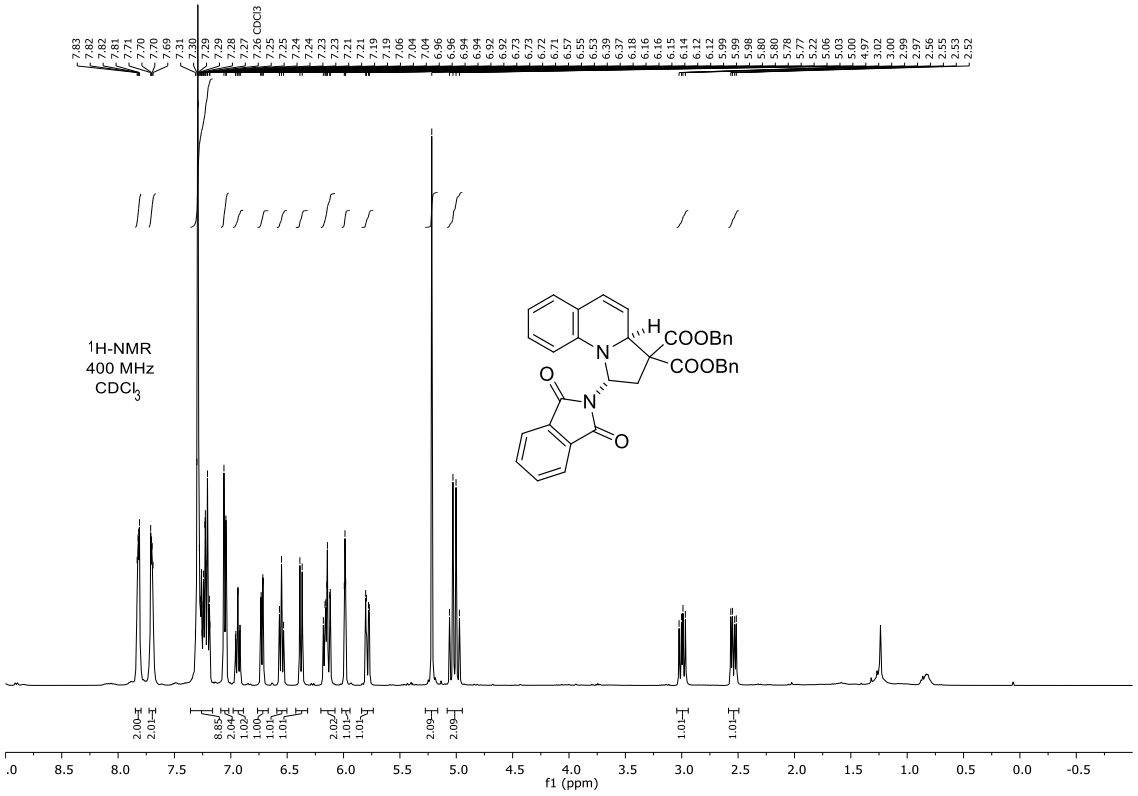

3000
2000
1000

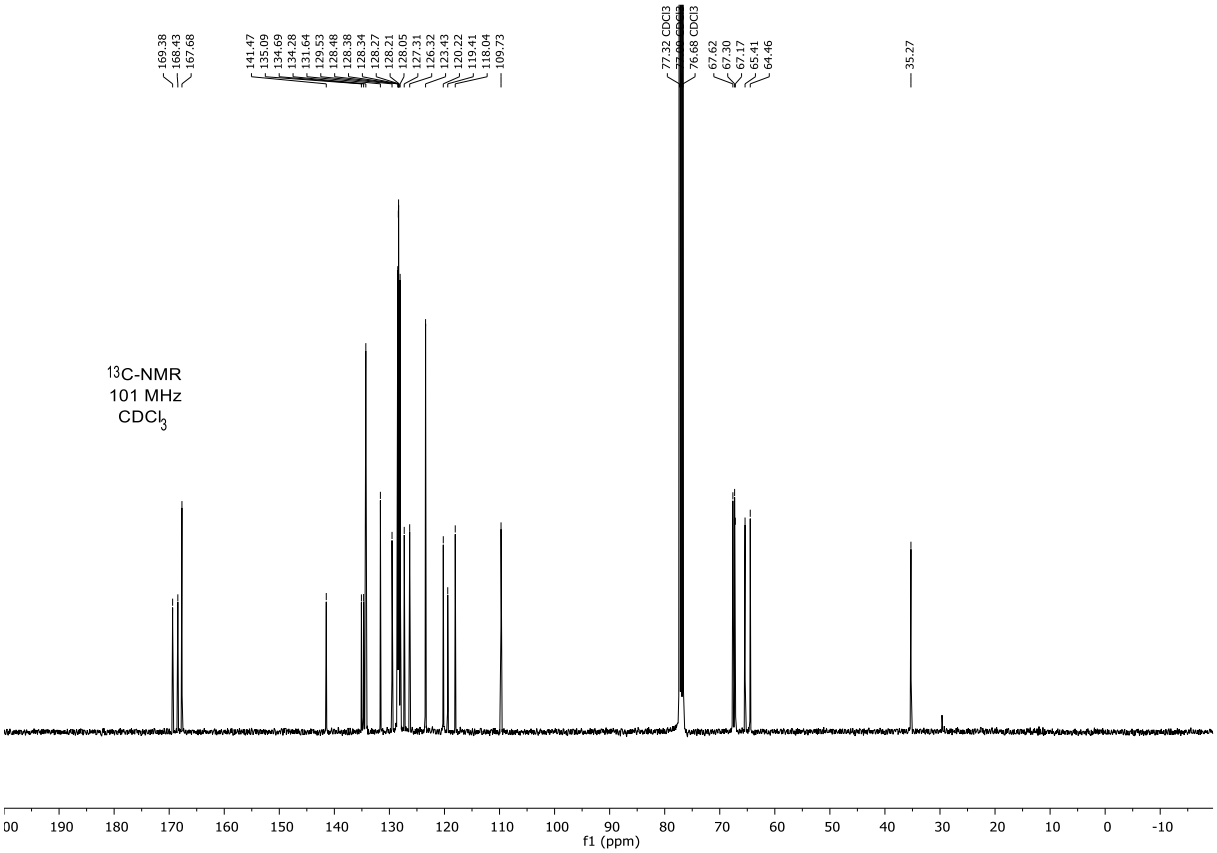
***anti*-Dimethyl 1-(1,3-dioxo-1H-benzo[f]isoindol-2(3H)-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (39).**

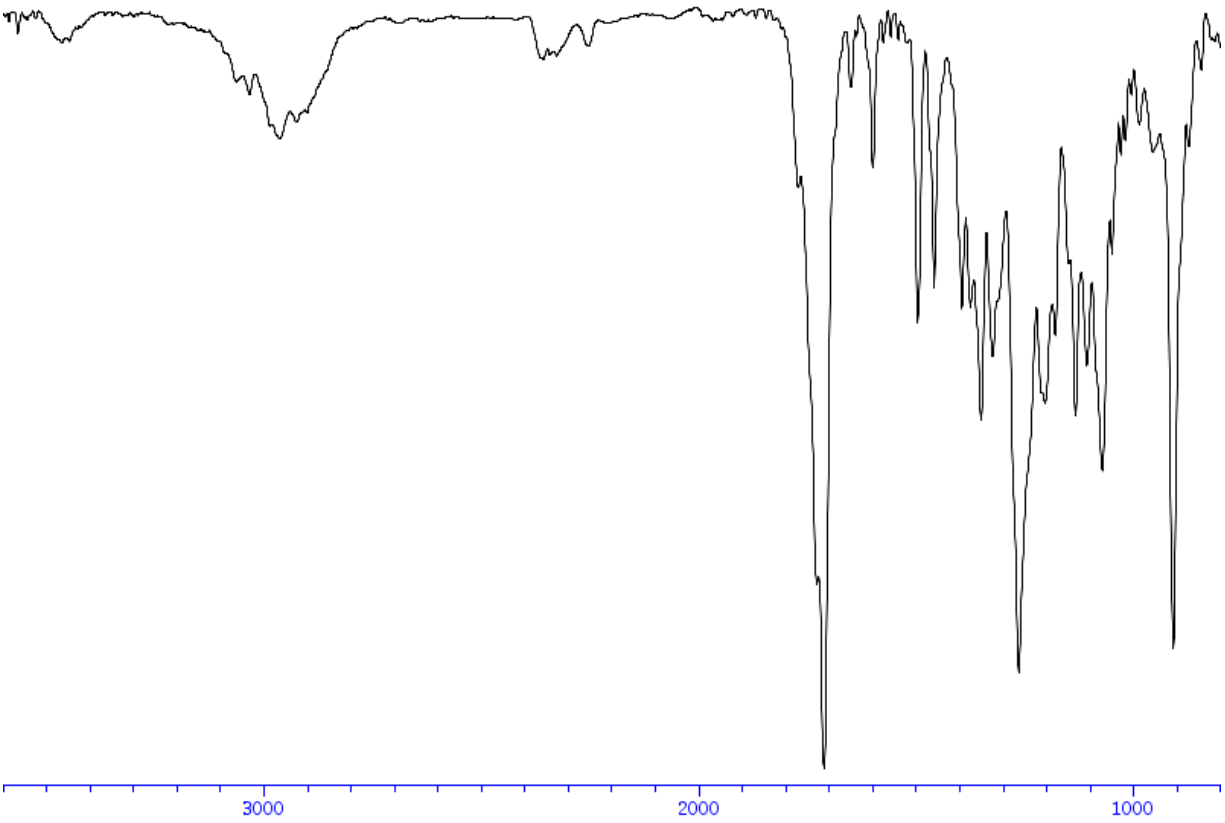




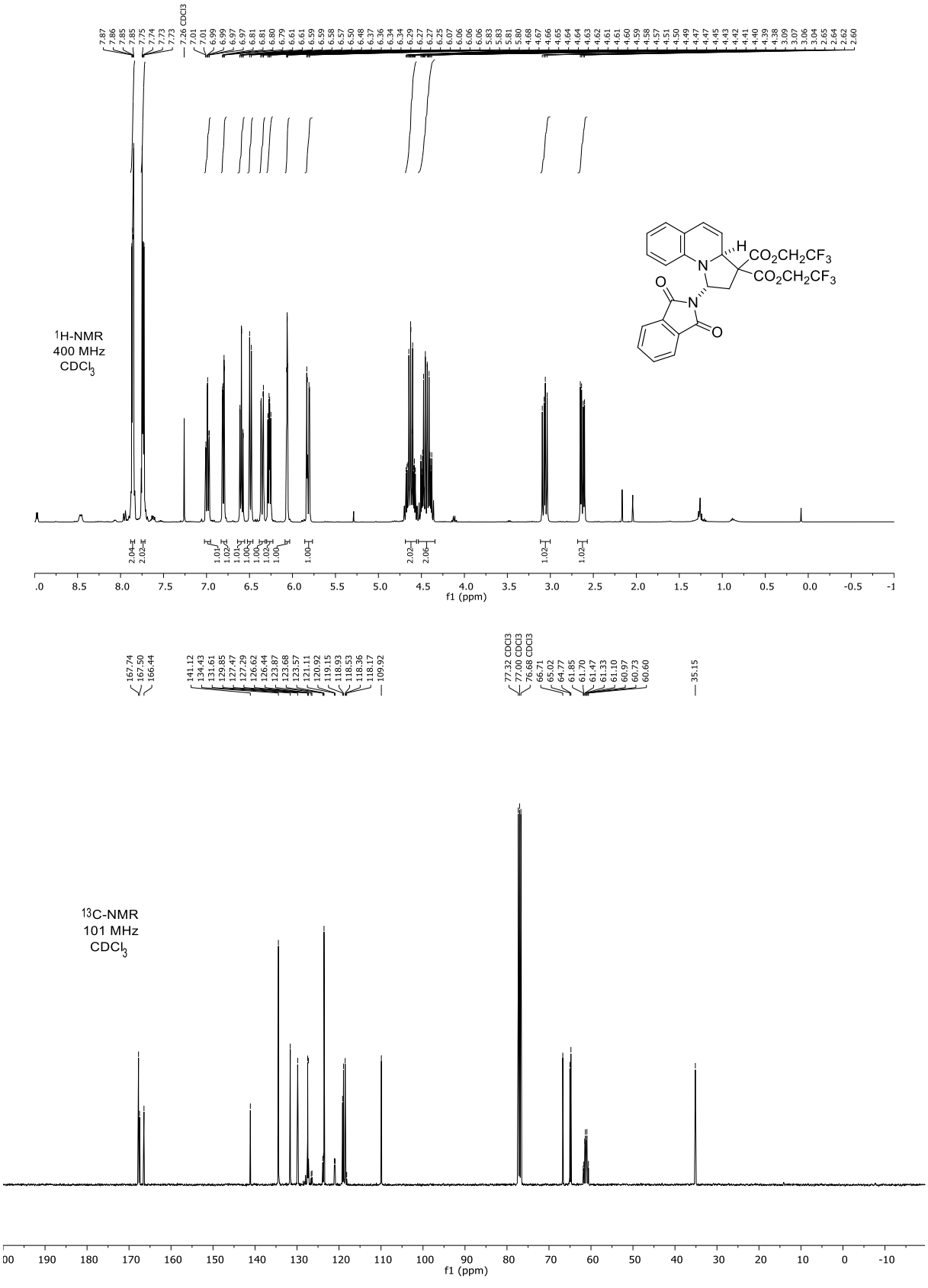
***anti*-Dibenzyl 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (40).**

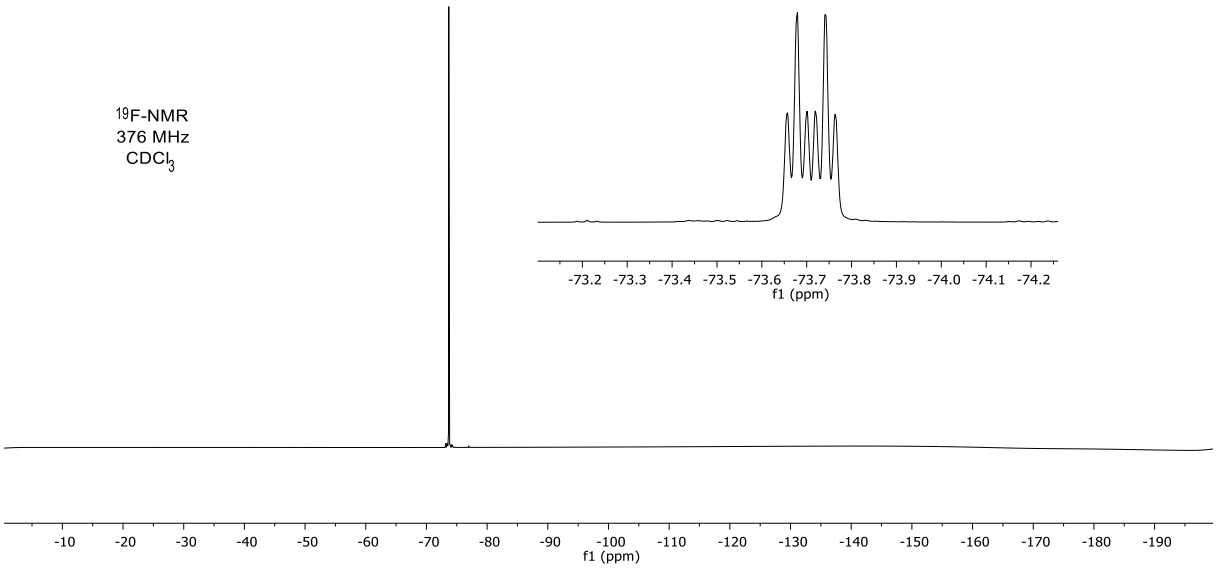


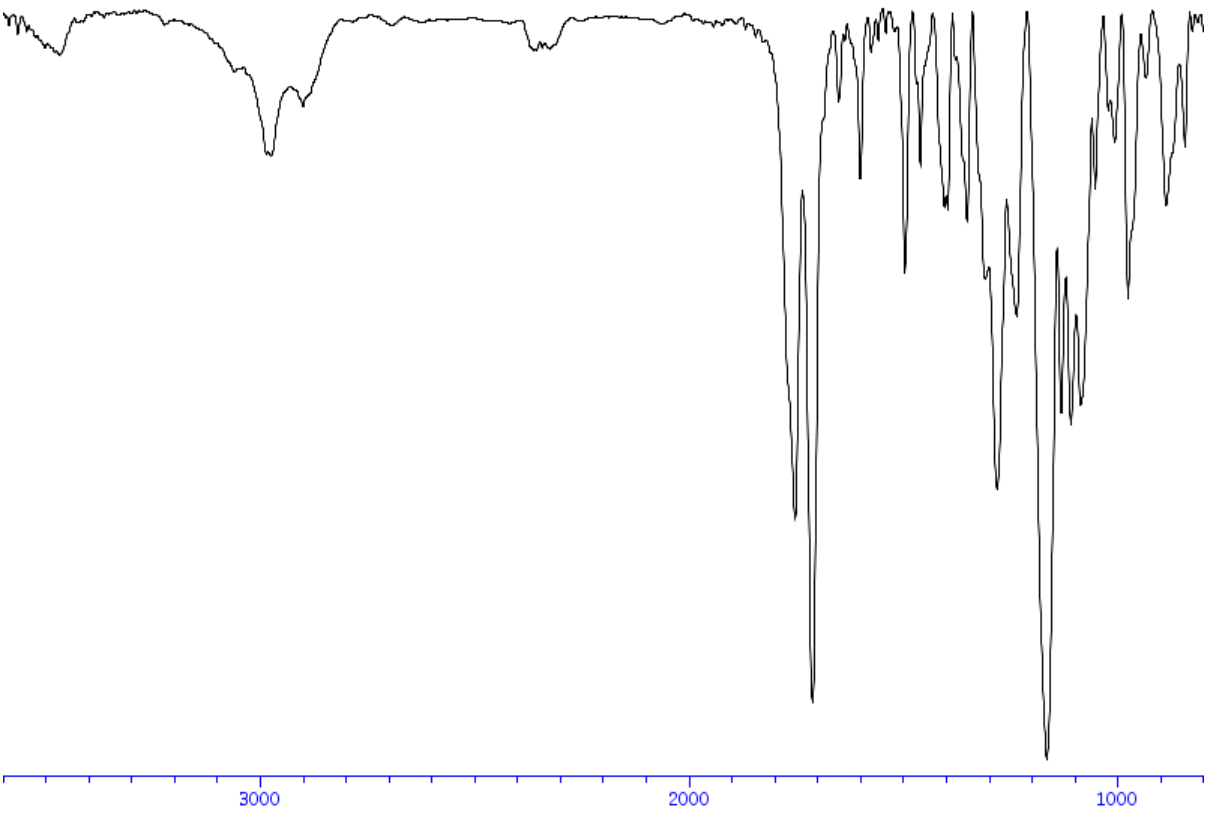

169.38
168.43
167.68
141.47
135.09
134.69
134.28
131.64
129.53
128.48
128.38
128.34
128.27
128.21
127.05
127.31
126.32
123.43
120.22
119.41
118.04
109.73
77.32 CDCl3
76.68 CDCl3
67.62
67.30
67.17
65.41
64.46
35.27
13C-NMR
101 MHz
CDCl3
f1 (ppm)


3000
2000
1000

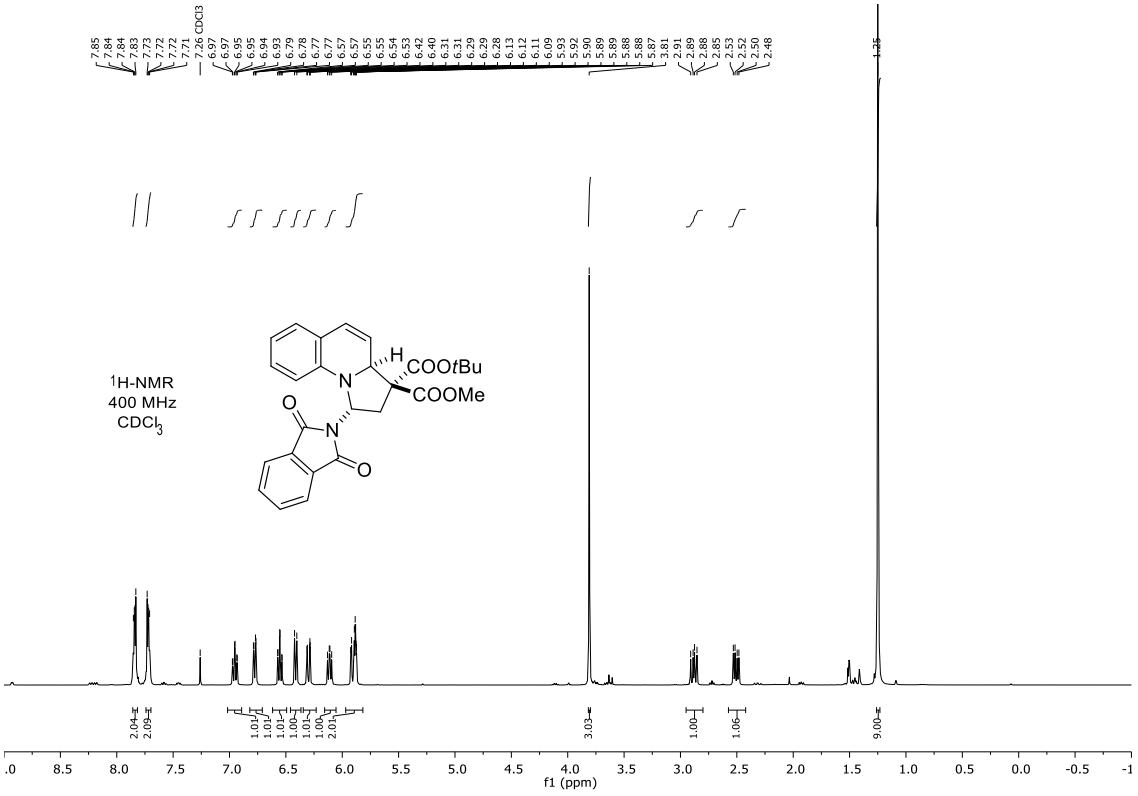
***anti-bis*(2,2,2-Trifluoroethyl) 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (41).**

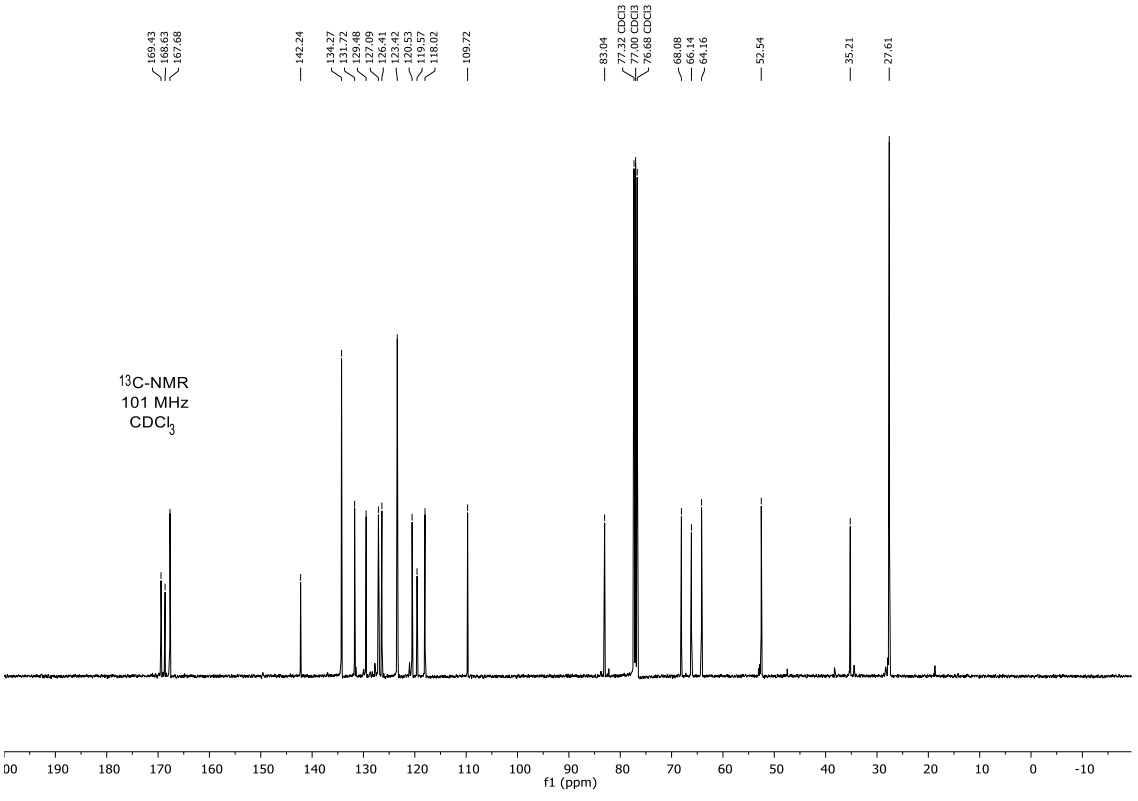


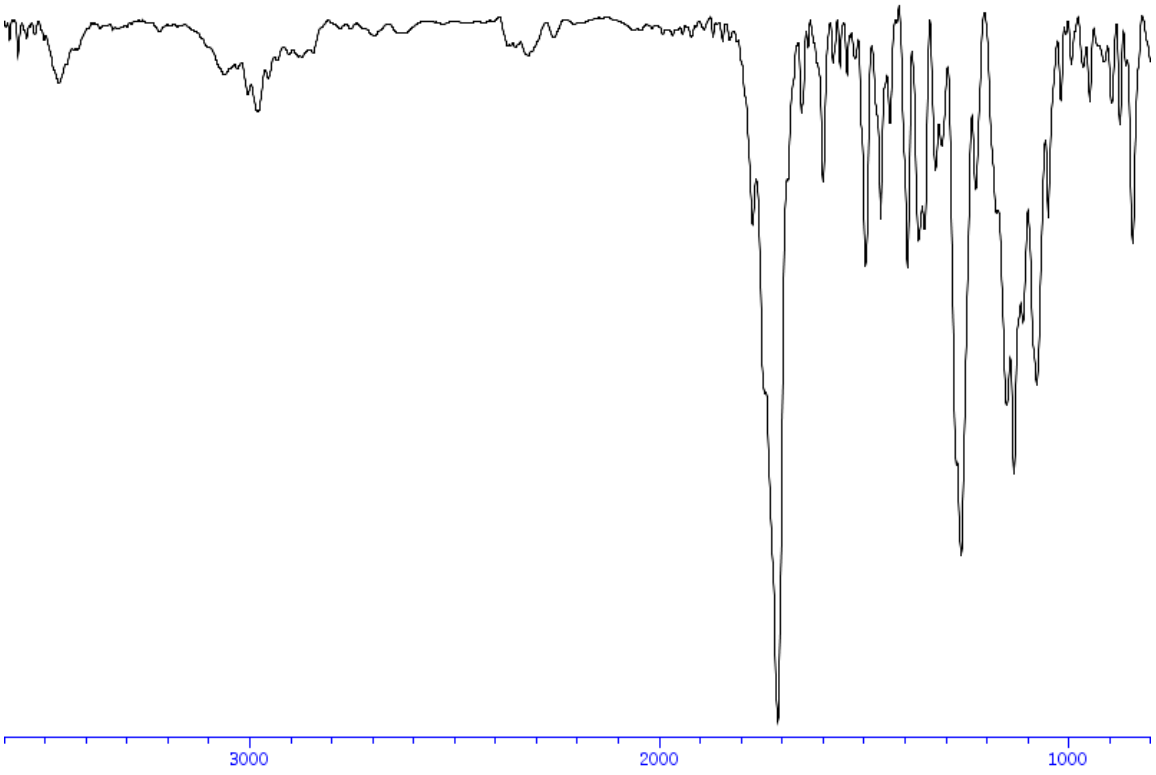

19F-NMR
376 MHz
CDCl3
-73.2 -73.3 -73.4 -73.5 -73.6 -73.7 -73.8 -73.9 -74.0 -74.1 -74.2
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


3000
2000
1000

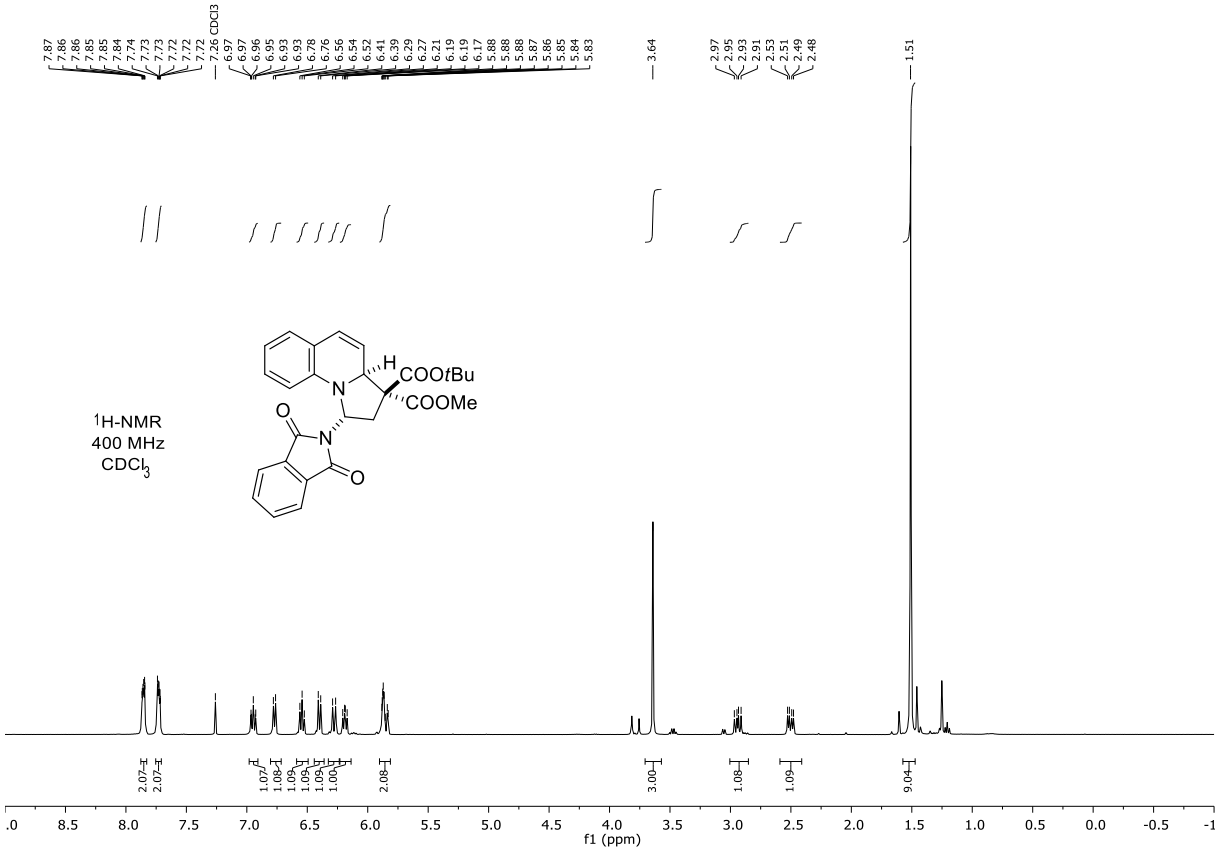
***(1R,3S,3aR)*-3-*tert*-Butyl 3-methyl 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (42a).**

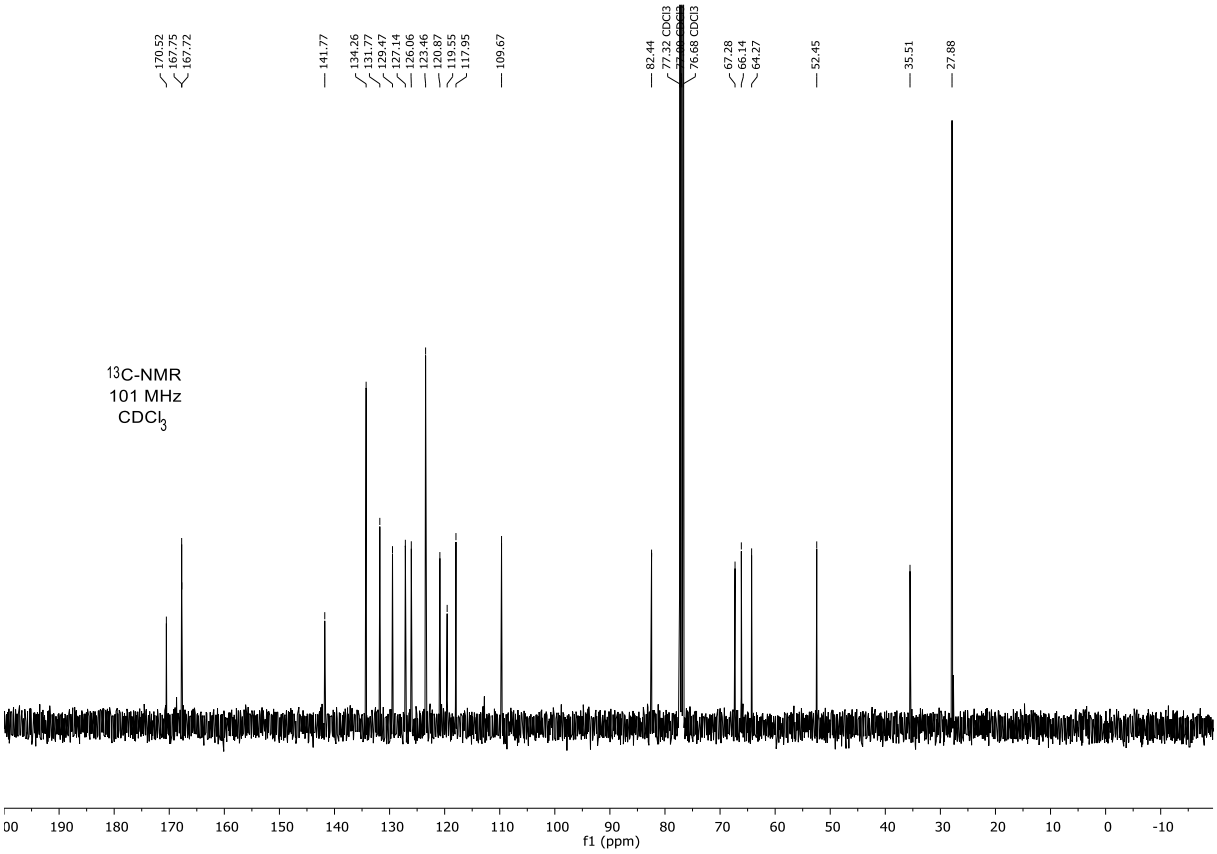


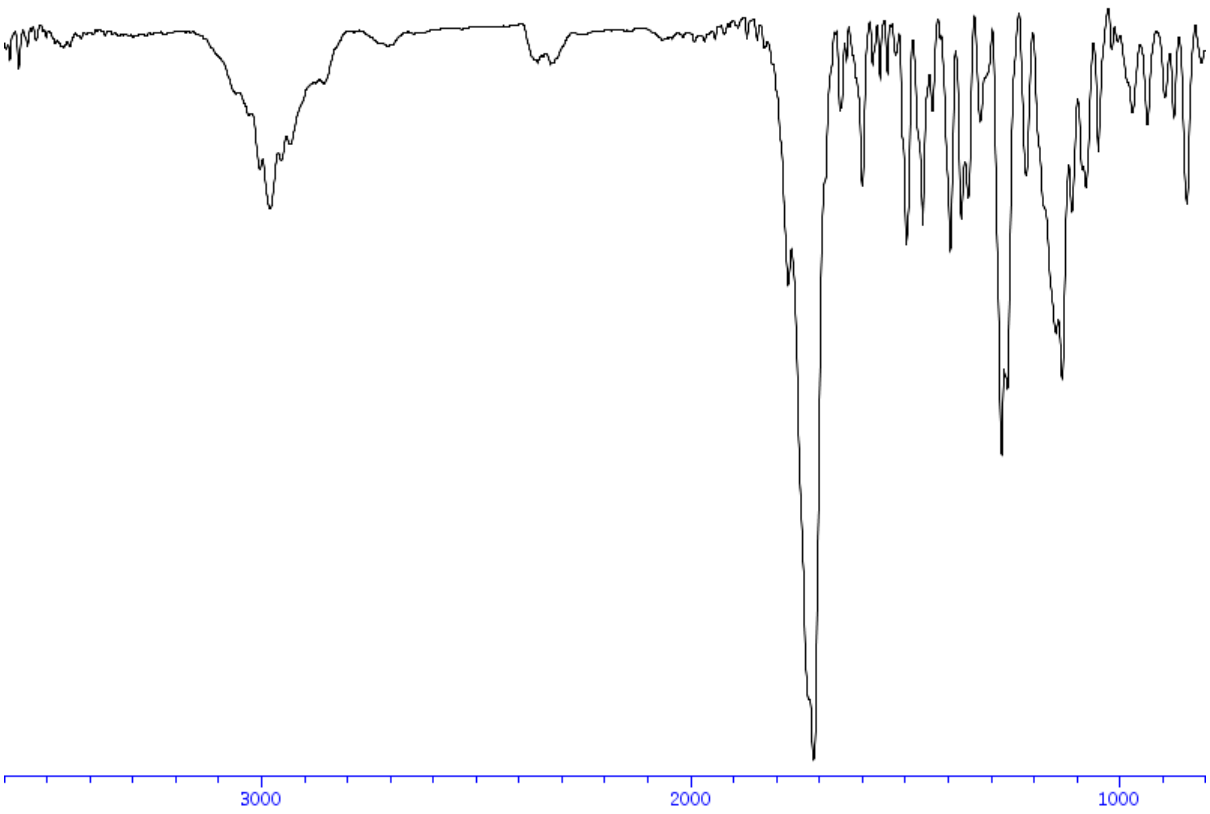




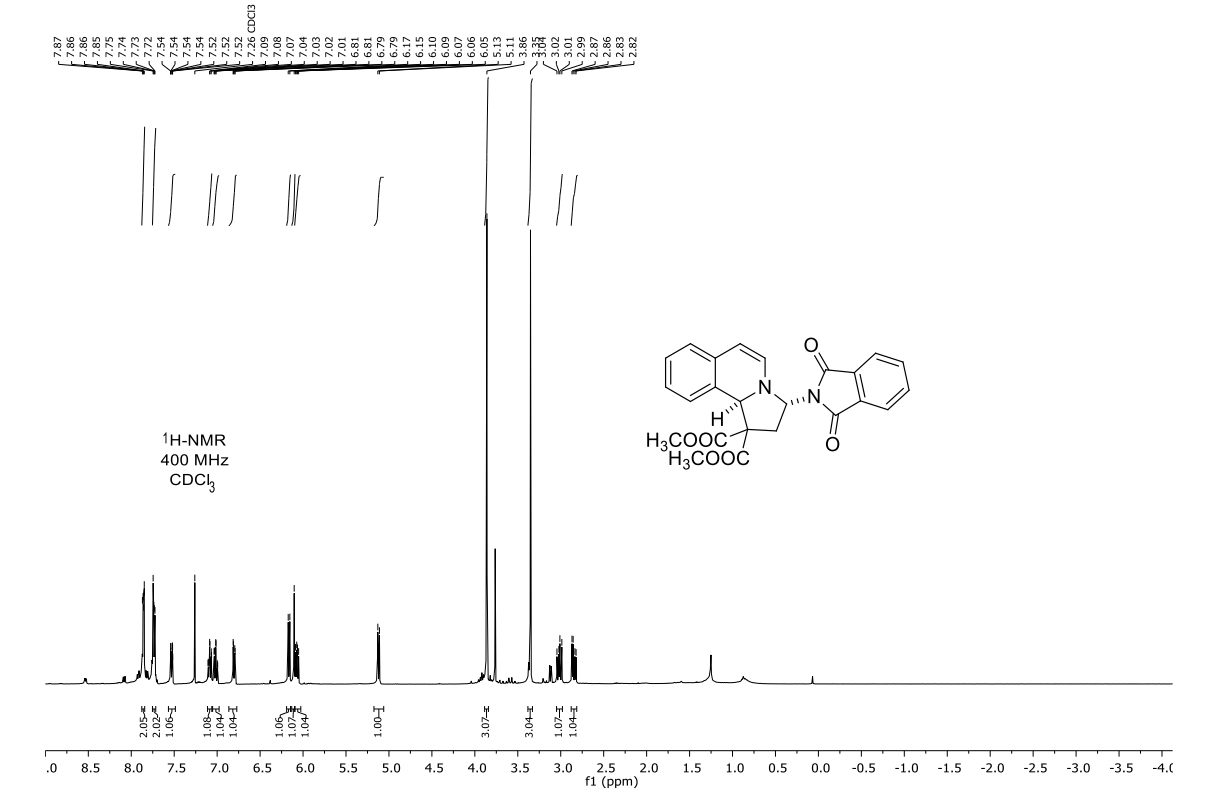
(1*R*,3*R*,3a*R*)-3-*tert*-Butyl 3-methyl 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (**42b**).

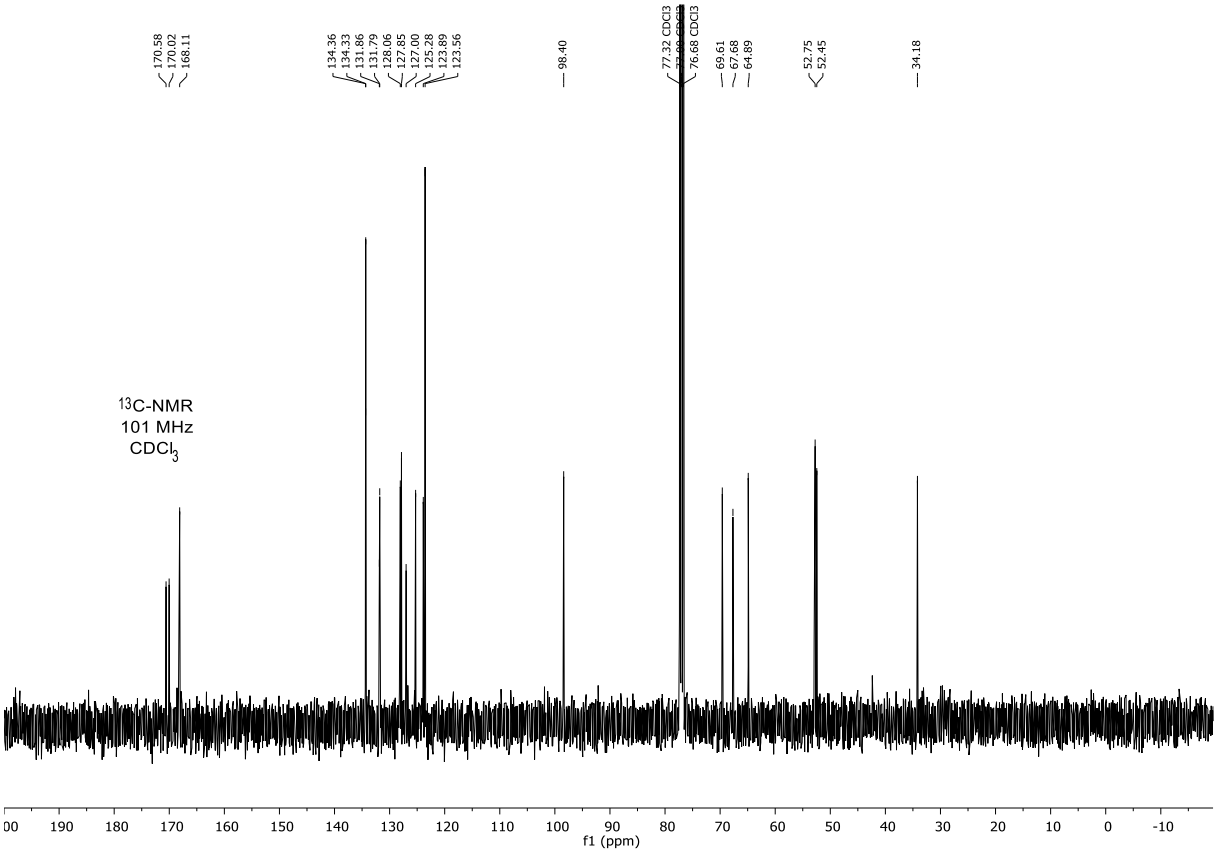


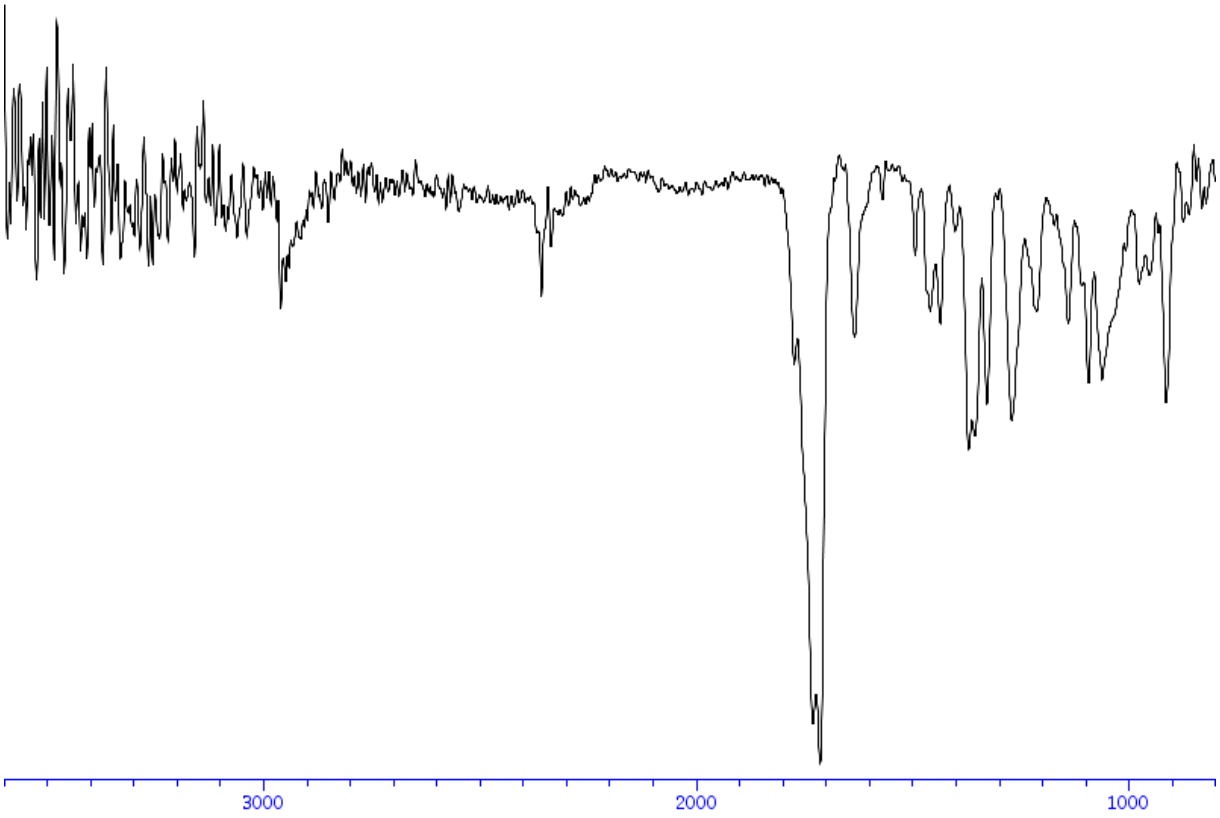

170.52
167.75
167.72
141.77
134.26
131.77
129.47
127.14
126.06
123.46
120.87
119.55
117.95
109.67
82.44
77.32 CDCl3
76.68 CDCl3
67.28
66.14
64.27
52.45
35.51
27.88
13C-NMR
101 MHz
CDCl3
f1 (ppm)


3000
2000
1000

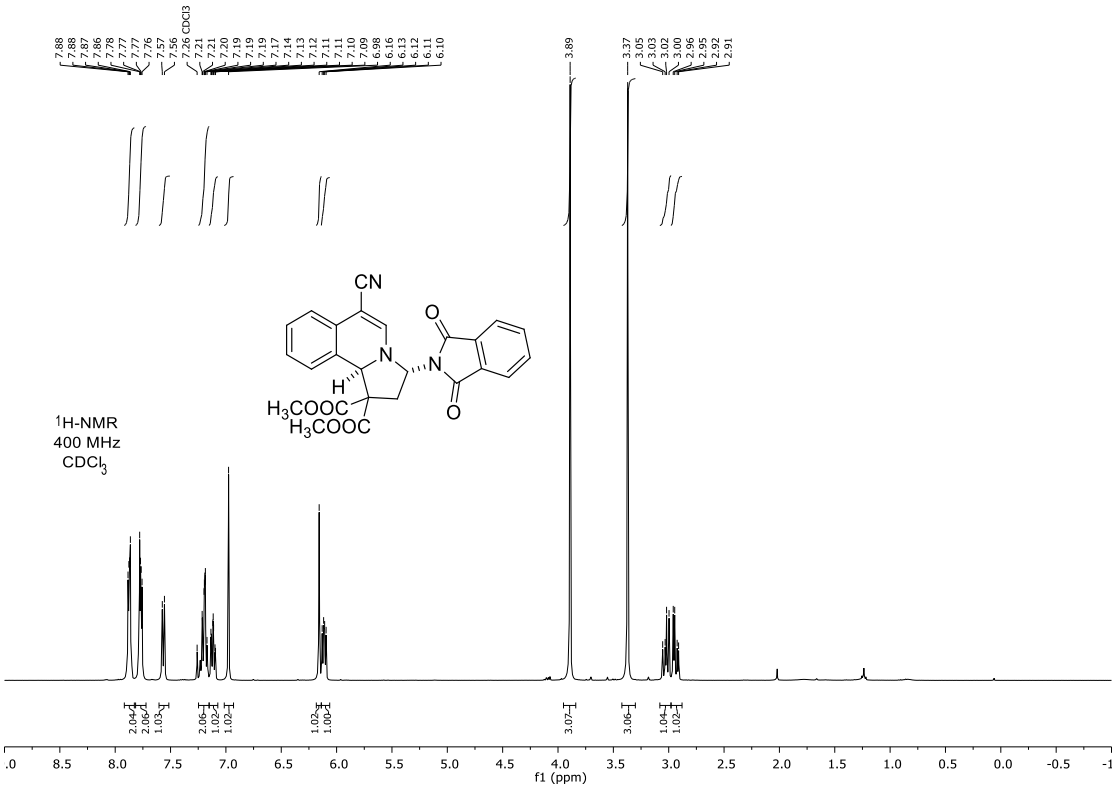
***anti*-Dimethyl 3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydropyrrolo[2,1-a]isoquinoline-1,1(10b*H*)-dicarboxylate (43).**

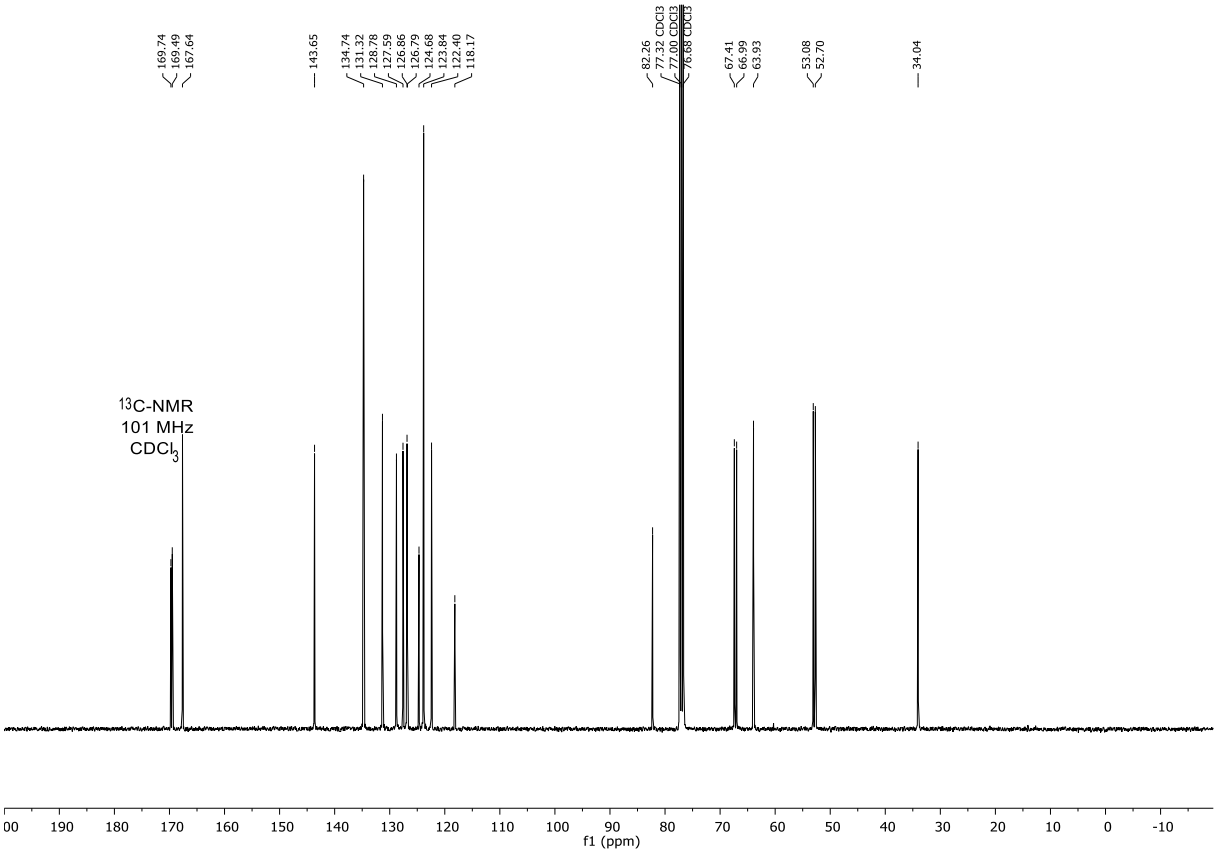


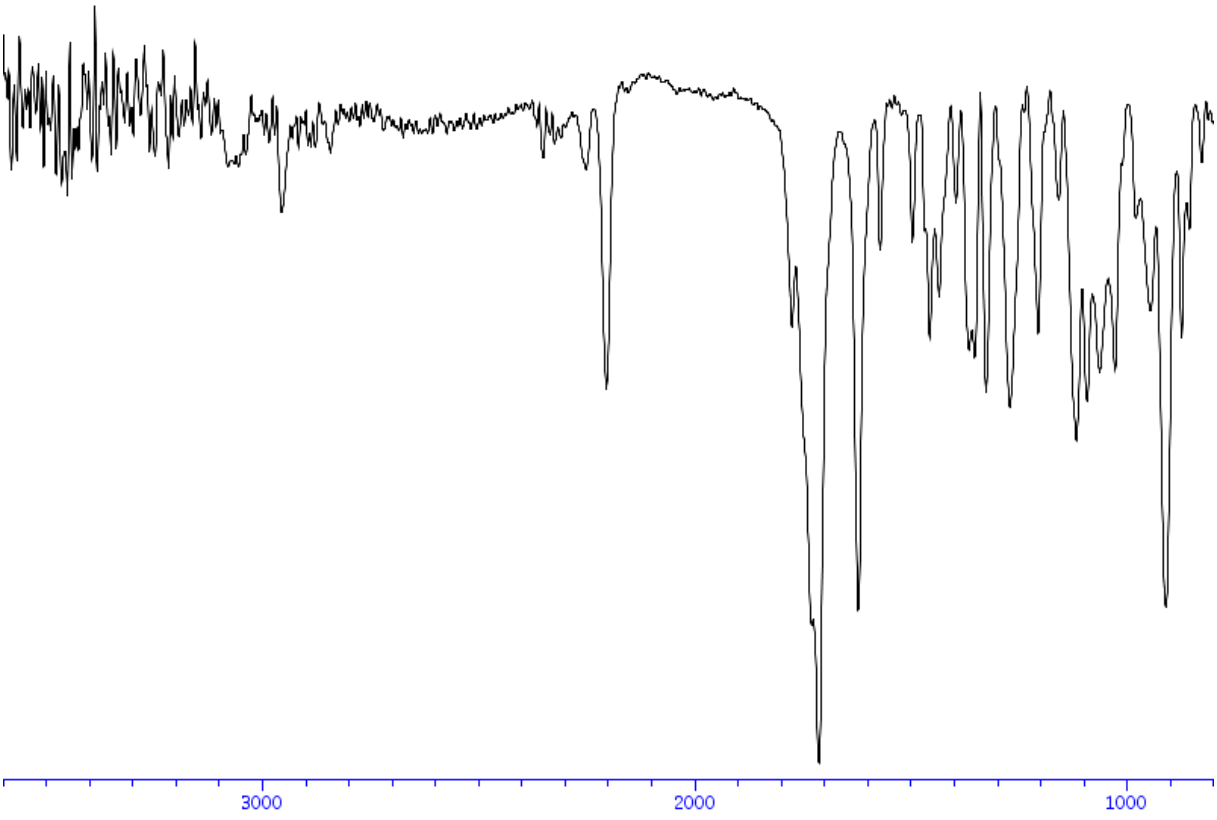




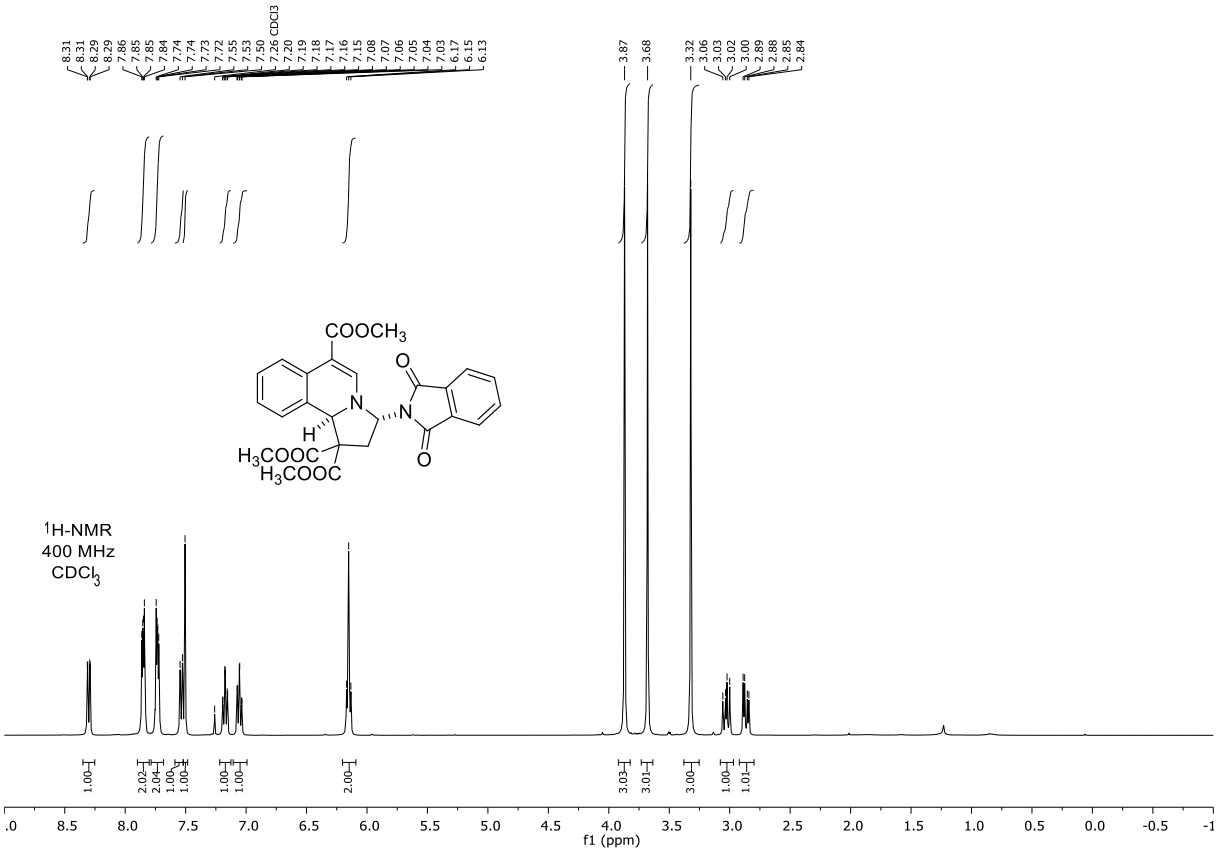
***anti*-Dimethyl 6-cyano-3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydropyrrolo[2,1-a]isoquinoline-1,1(10b*H*)-dicarboxylate (44).**

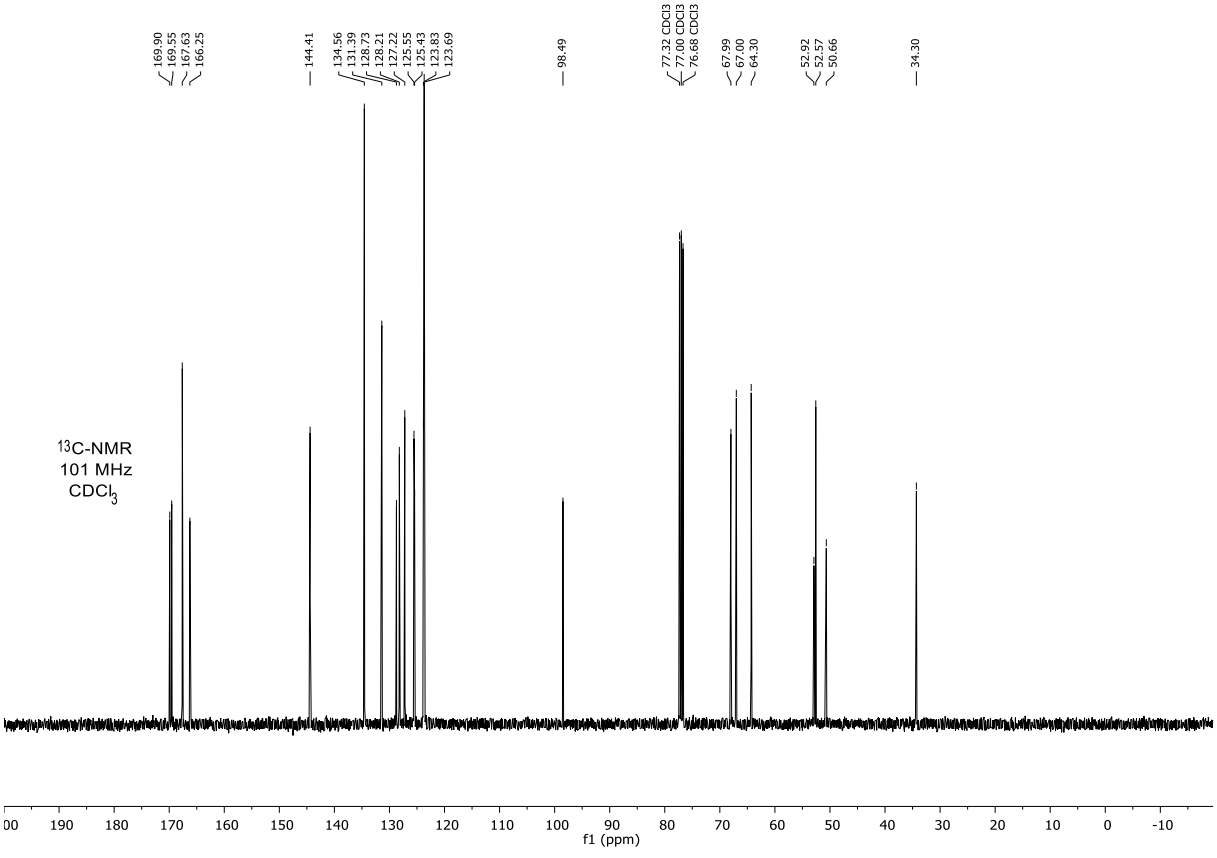


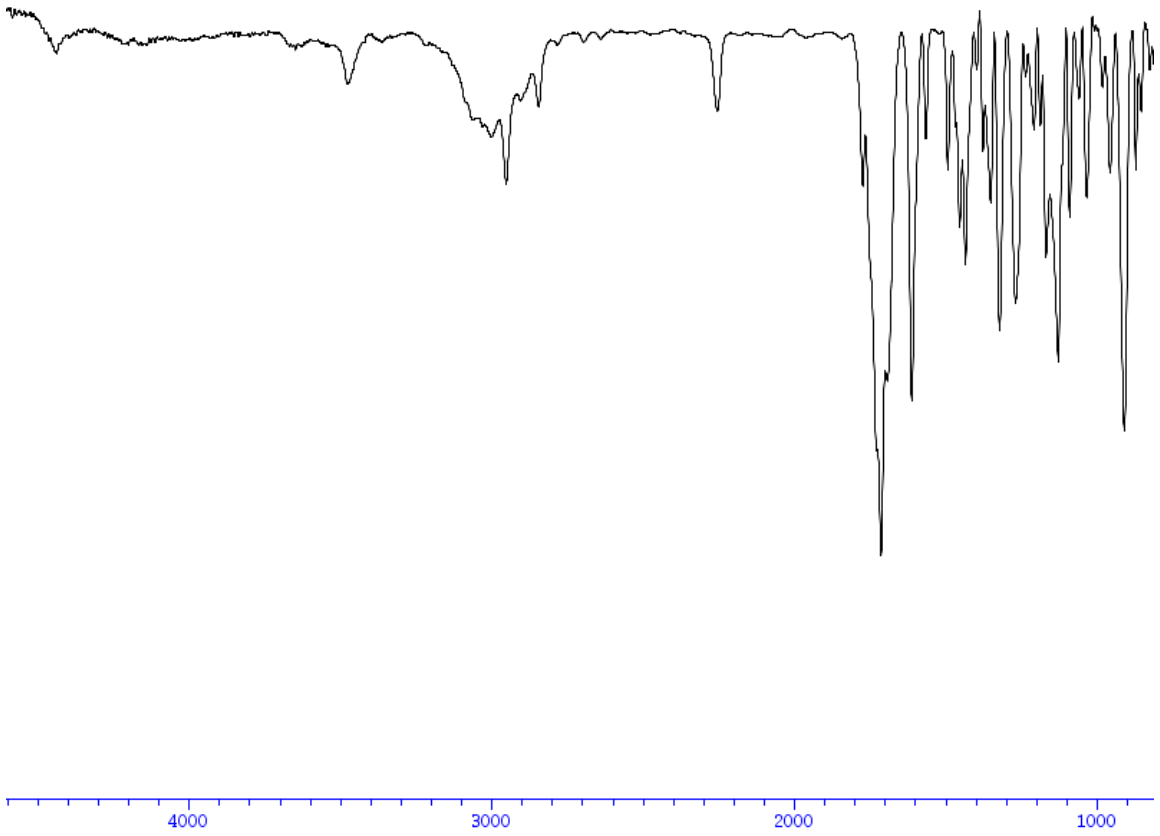

169.74
169.49
167.64
143.65
134.74
131.32
128.78
127.59
126.86
126.79
124.68
123.84
122.40
118.17
82.26
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.41
66.99
63.93
53.08
52.70
34.04
13C-NMR
101 MHz
CDCl3
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3000
2000
1000

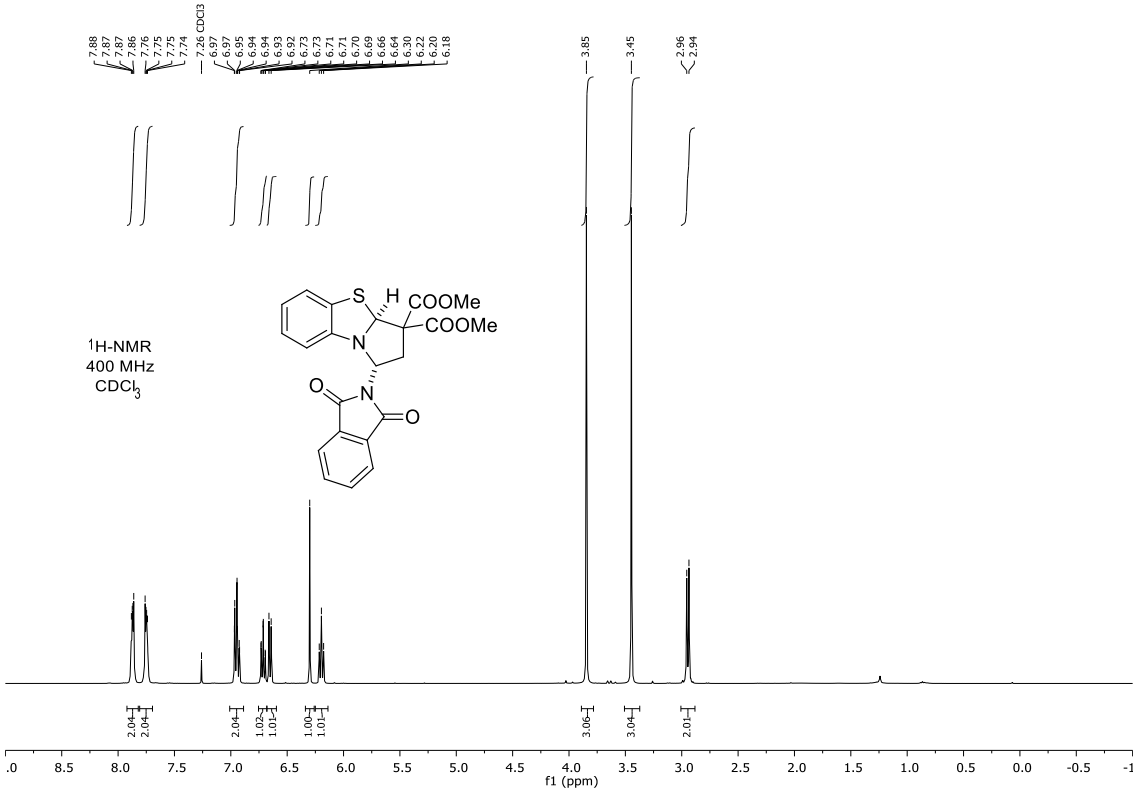
***anti*-Trimethyl 3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydropyrrolo[2,1-a]isoquinoline-1,1,6(10b*H*)-tricarboxylate** (**45**).

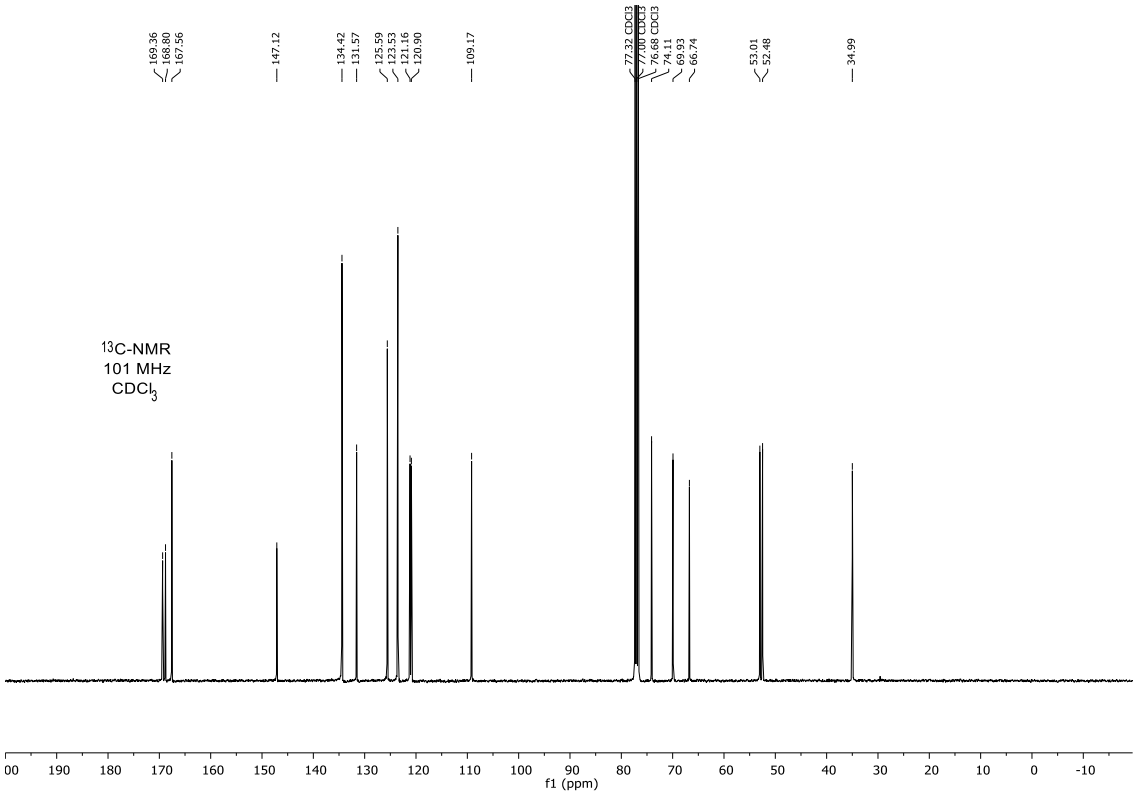


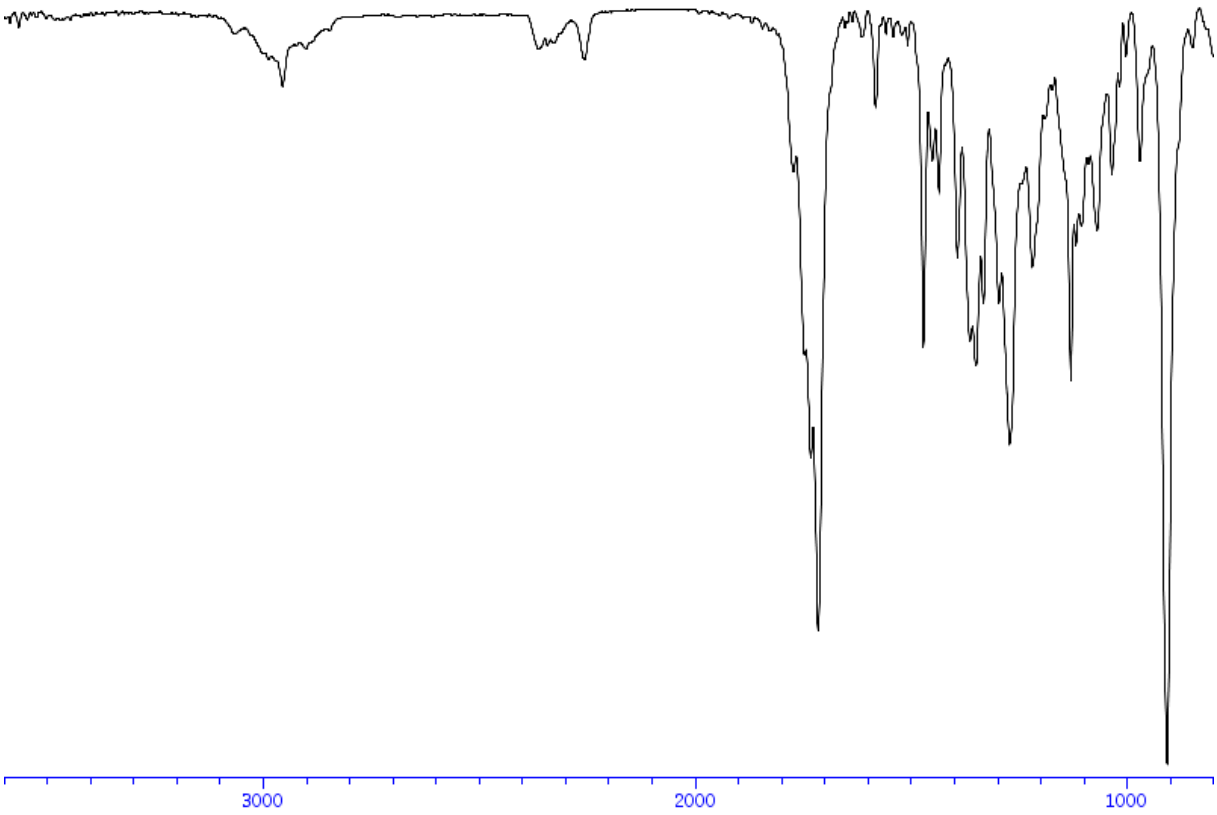




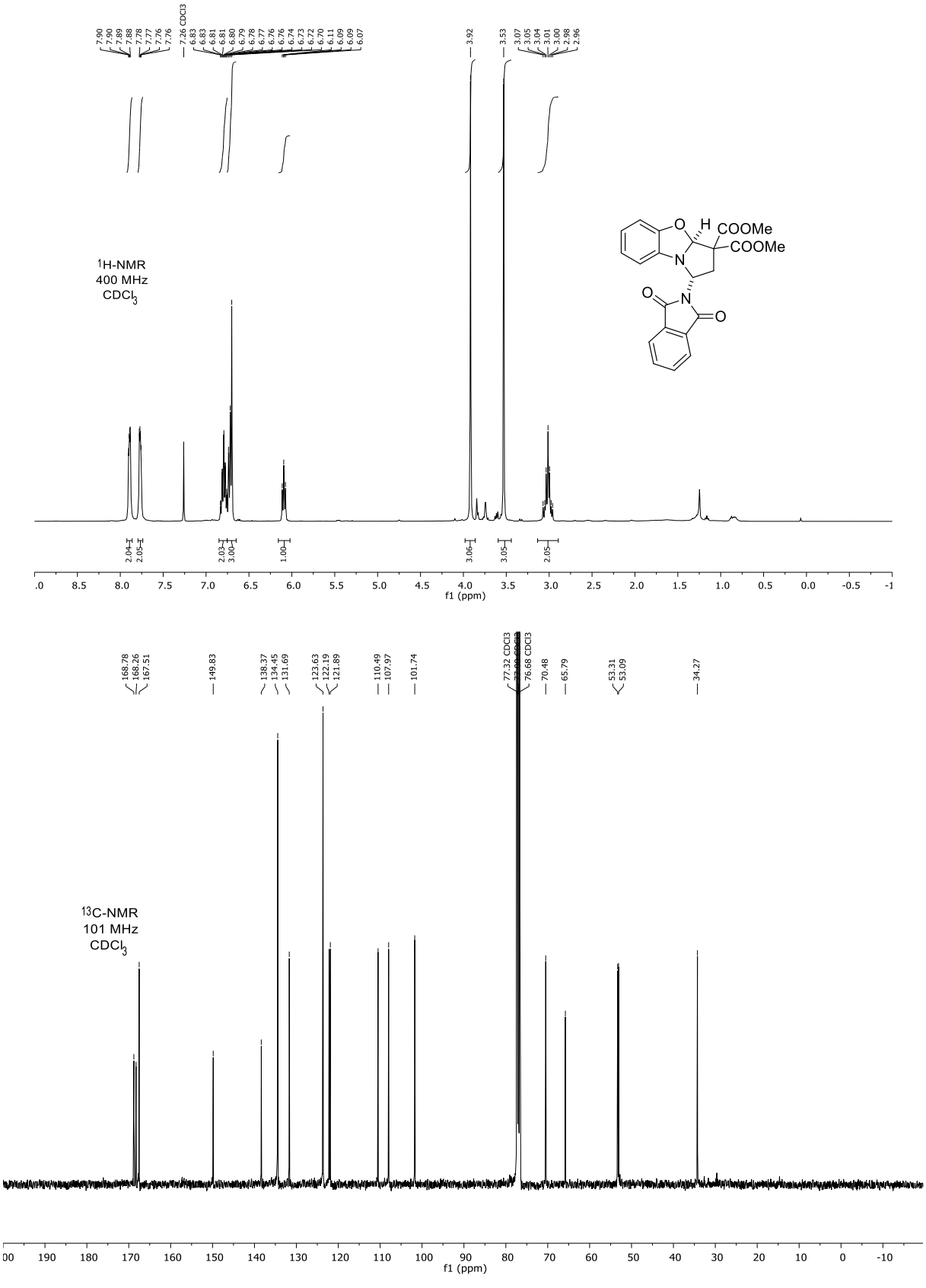
***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydrobenzo[d]pyrrolo[2,1-b]thiazole-3,3(3a*H*)-dicarboxylate** (**46**).

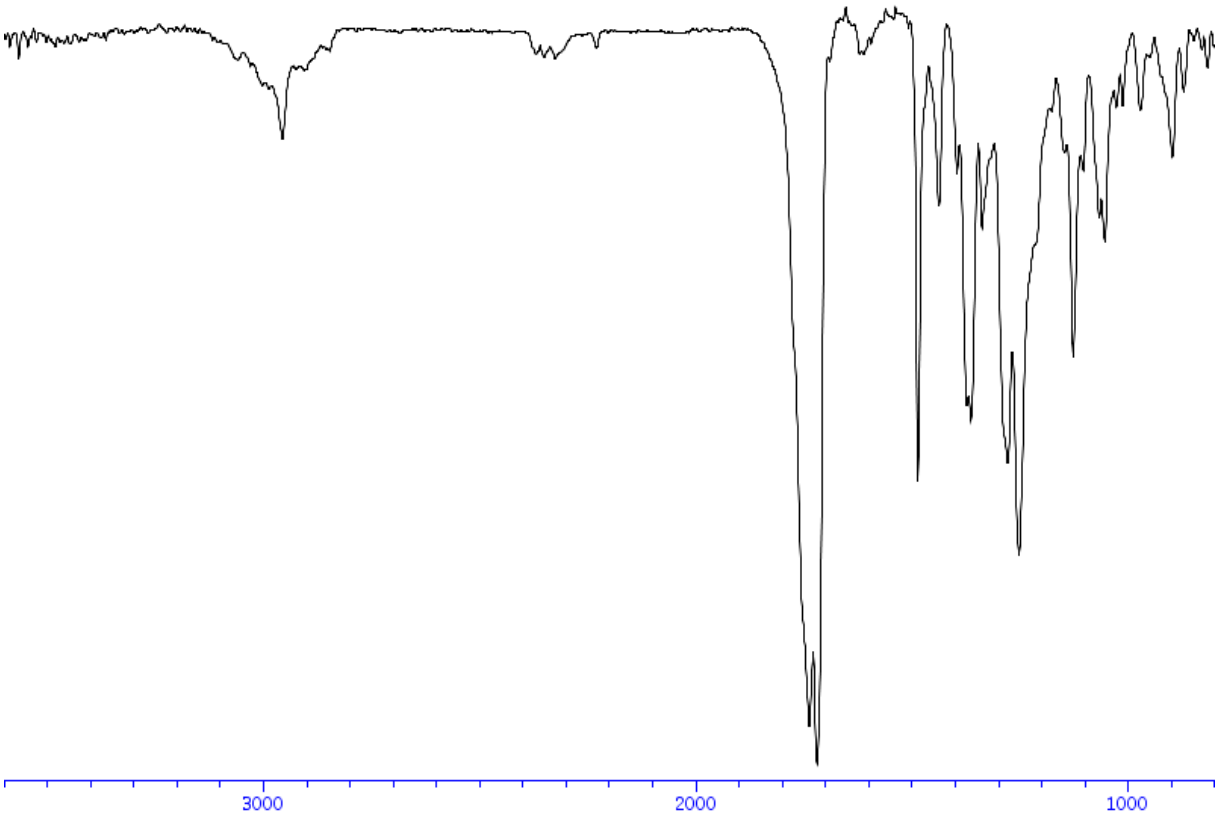



169.36
168.80
167.56
147.12
134.42
131.57
125.59
123.53
121.16
120.90
109.17
77.23 CDCl3
77.00 CDCl3
76.68 CDCl3
74.11
69.93
66.74
53.01
52.48
34.99
13C-NMR
101 MHz
CDCl3
f1 (ppm)

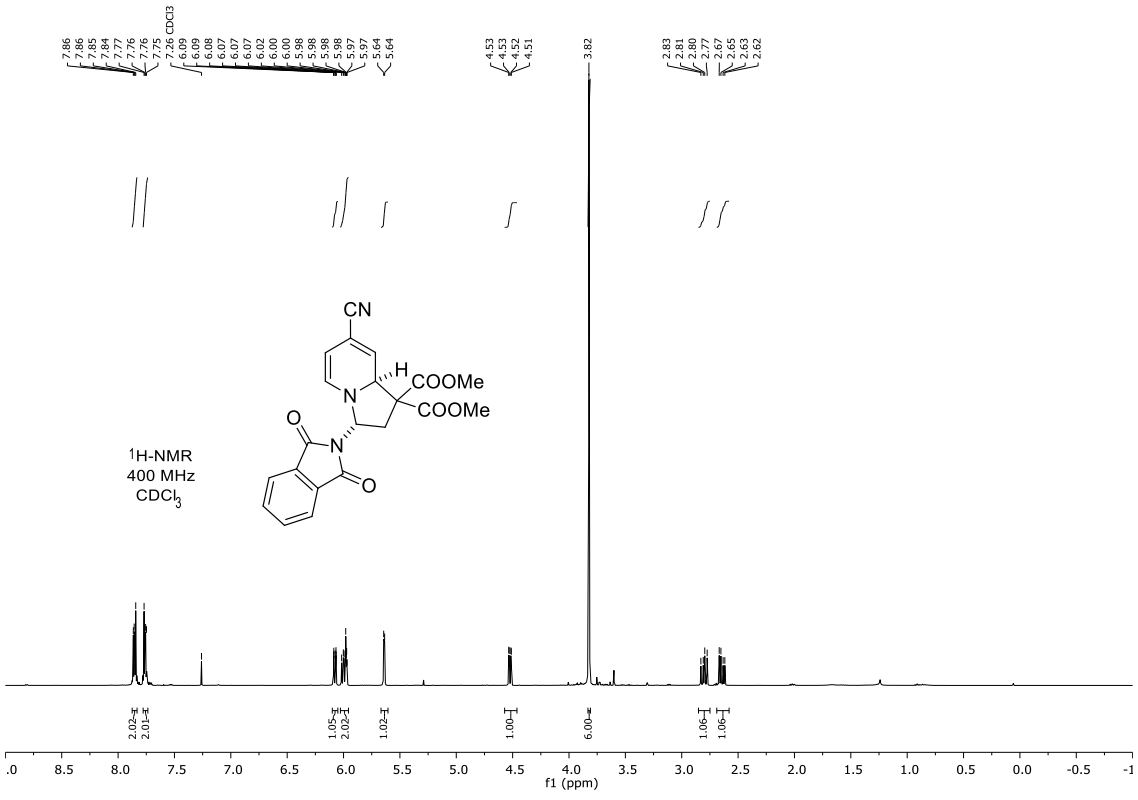

3000
2000
1000

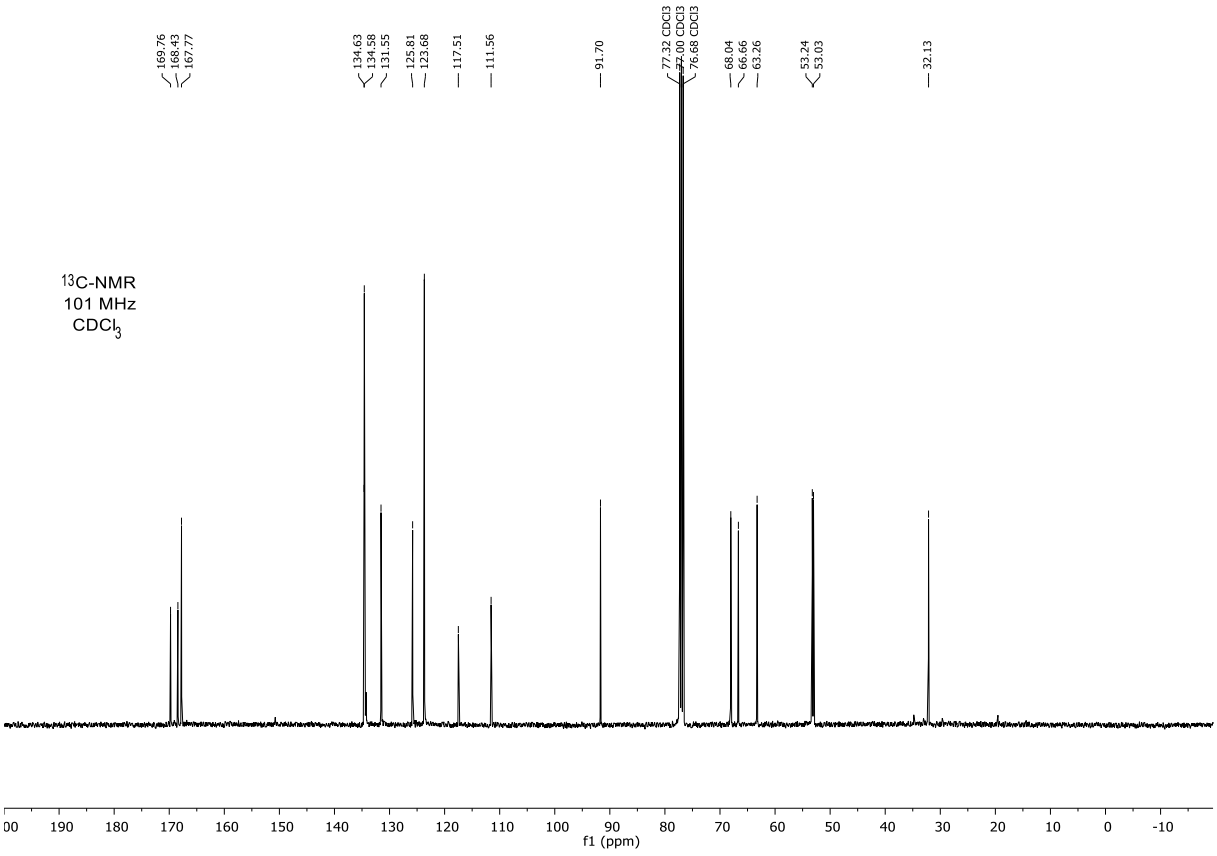
***anti*-Dimethyl 1-(1,3-dioxoisoindolin-2-yl)-1,2-dihydrobenzo[d]pyrrolo[2,1-b]oxazole-3,3(3a*H*)-dicarboxylate** (**47**).

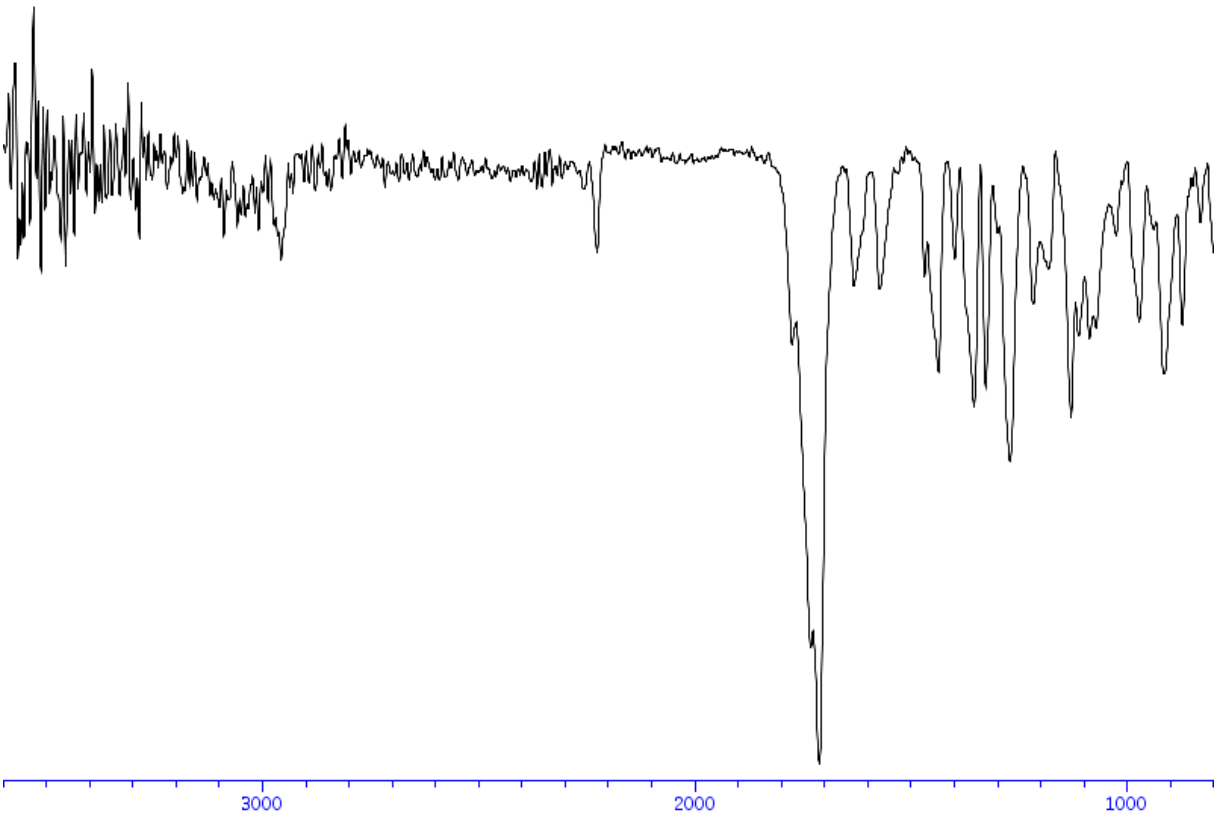




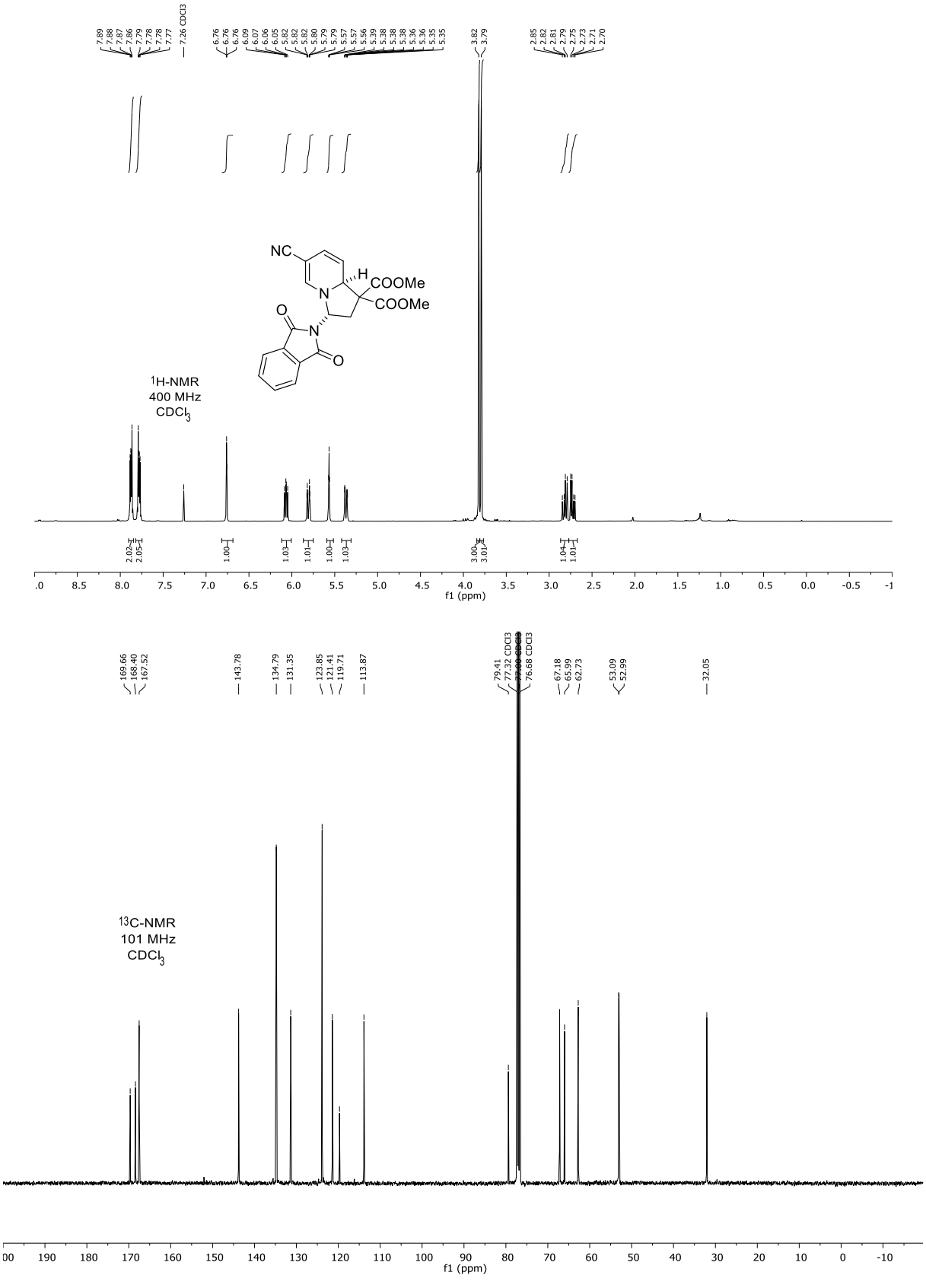
***anti*-Dimethyl 7-cyano-3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate (48).**

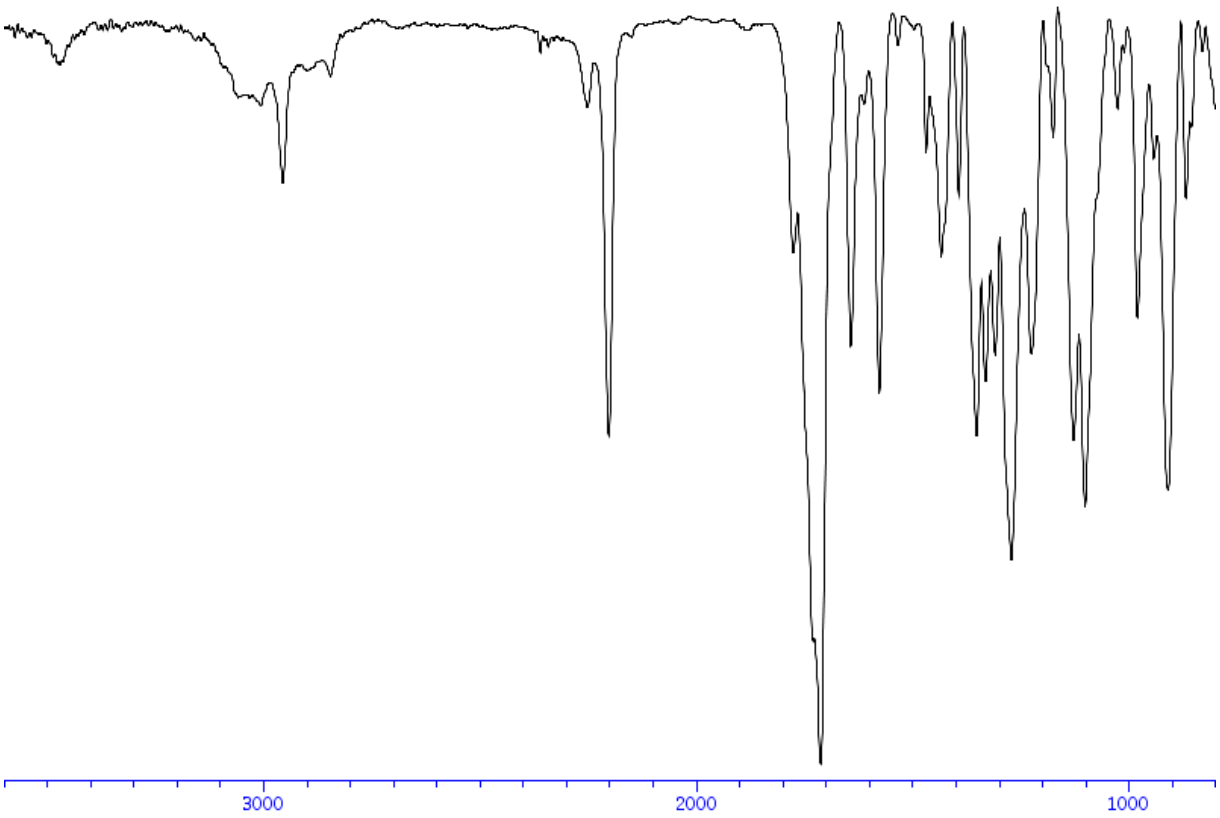



169.76
168.43
167.77
134.63
134.58
131.55
125.81
123.68
117.51
111.56
91.70
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
68.04
66.66
63.26
53.24
53.03
32.13
13C-NMR
101 MHz
CDCl3
f1 (ppm)

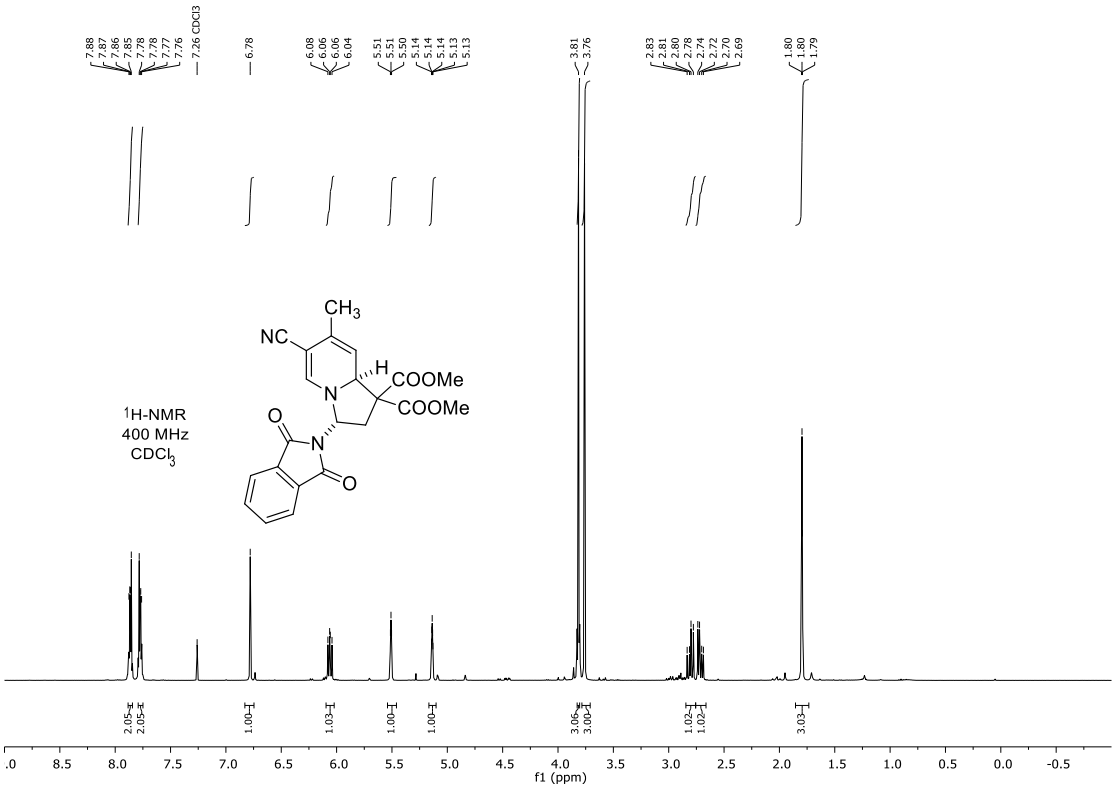

3000
2000
1000

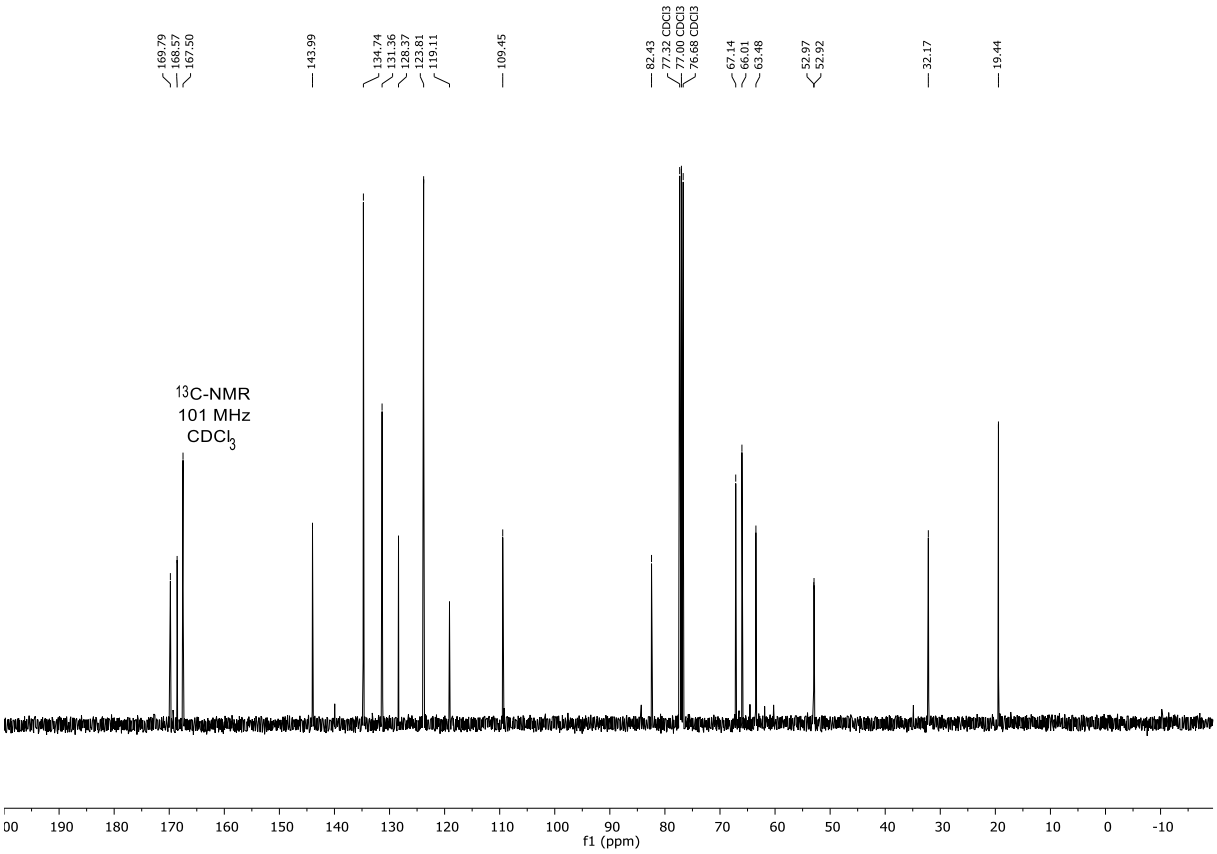
***anti*-Dimethyl 6-cyano-3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate (49).**

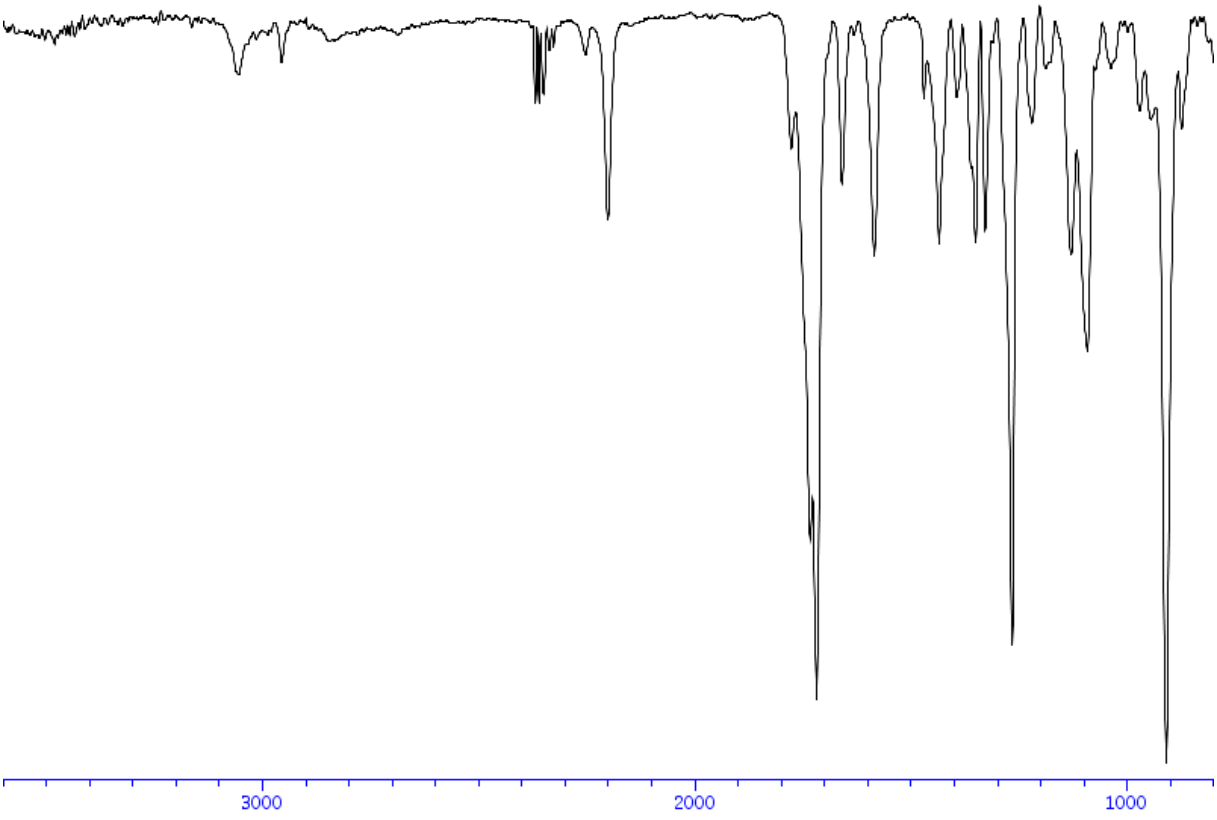




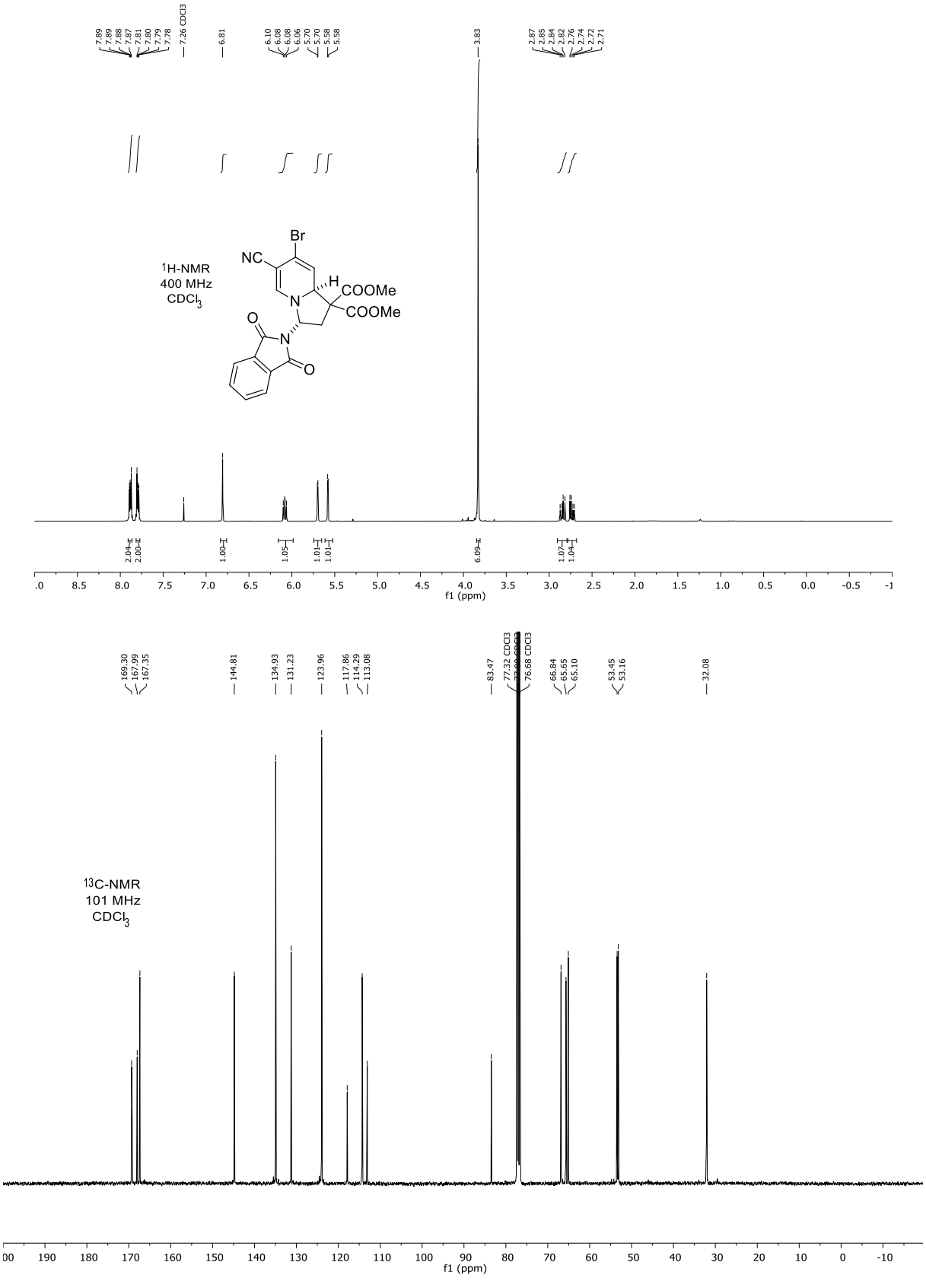
***anti*-Dimethyl 6-cyano-3-(1,3-dioxoisoindolin-2-yl)-7-methyl-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate (50).**

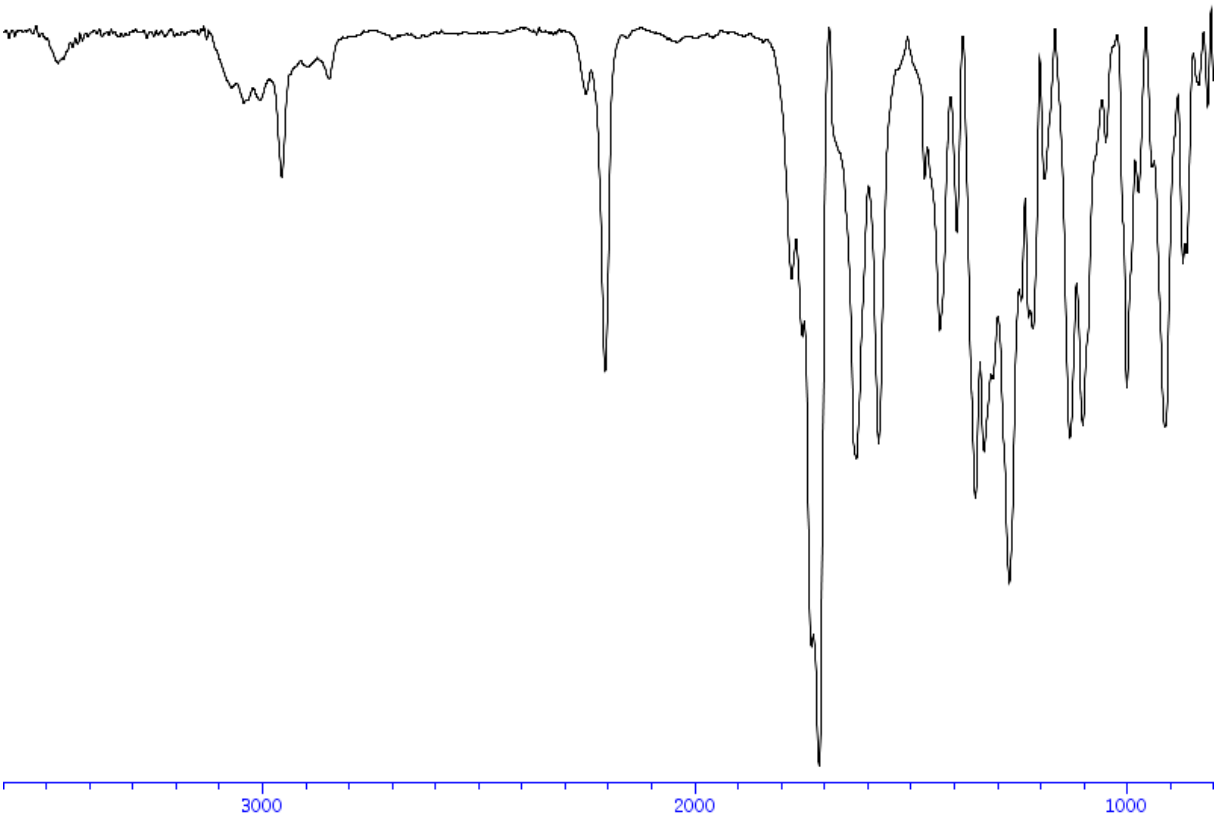



169.79
168.57
167.50
143.99
134.74
131.36
128.37
123.81
119.11
109.45
82.43
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.14
66.01
63.48
52.97
52.92
32.17
19.44
13C-NMR
101 MHz
CDCl3
f1 (ppm)

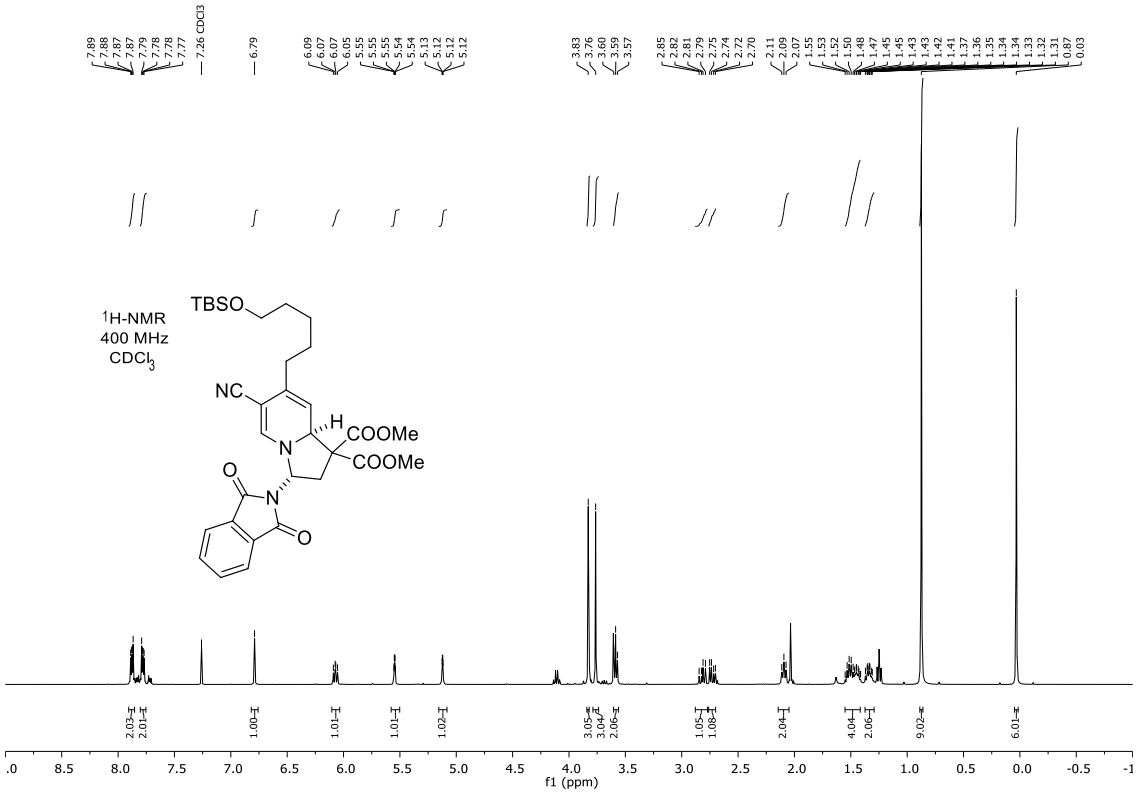

3000
2000
1000

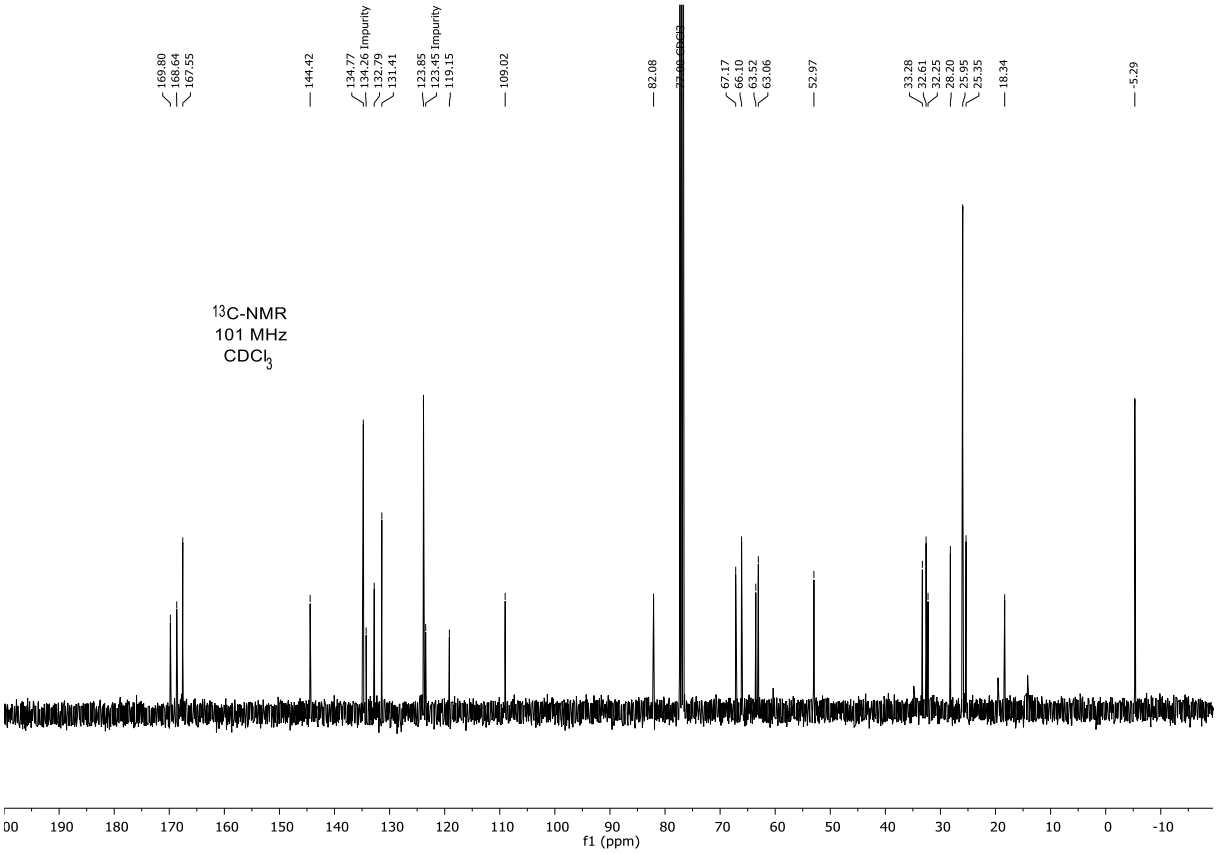
***anti*-Dimethyl 7-bromo-6-cyano-3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate (51).**

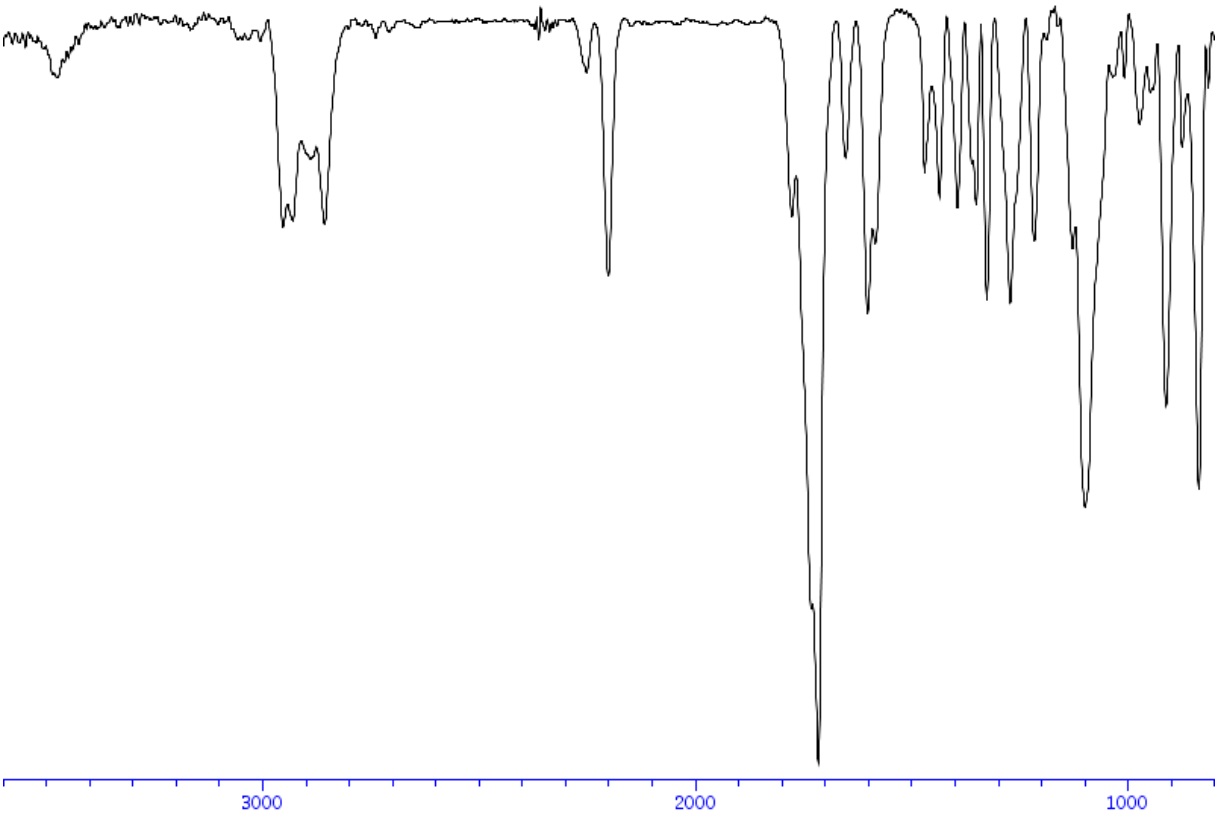




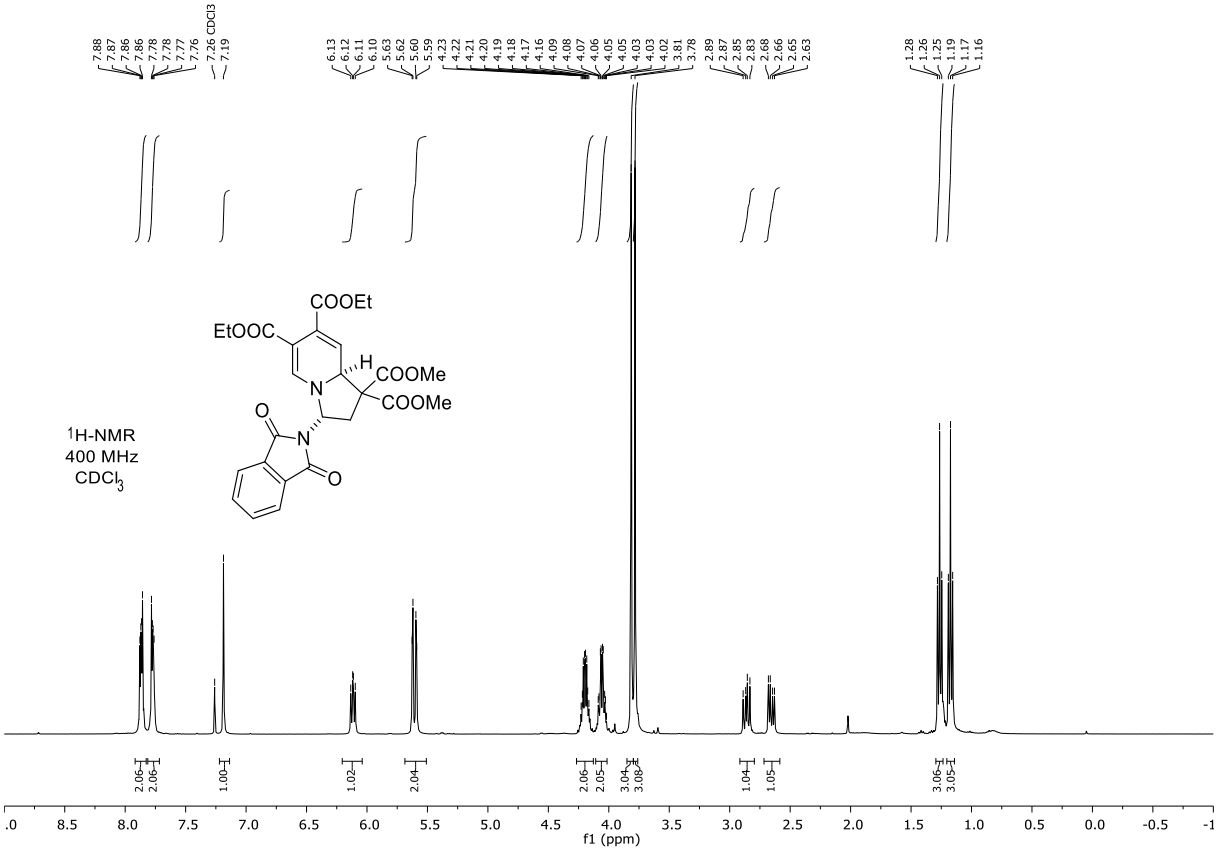
***anti*-Dimethyl 7-(5-((*tert*-butyldimethylsilyl)oxy)pentyl)-6-cyano-3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate (52).**

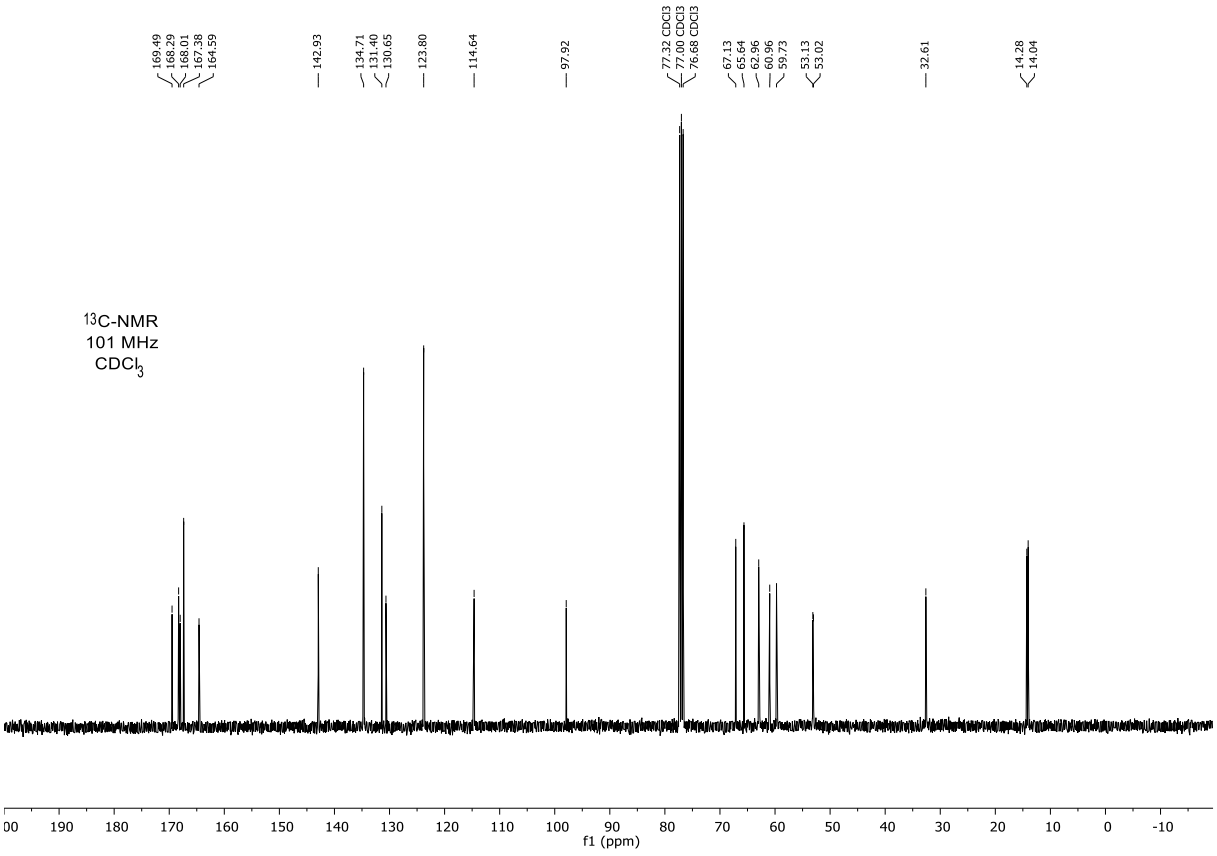


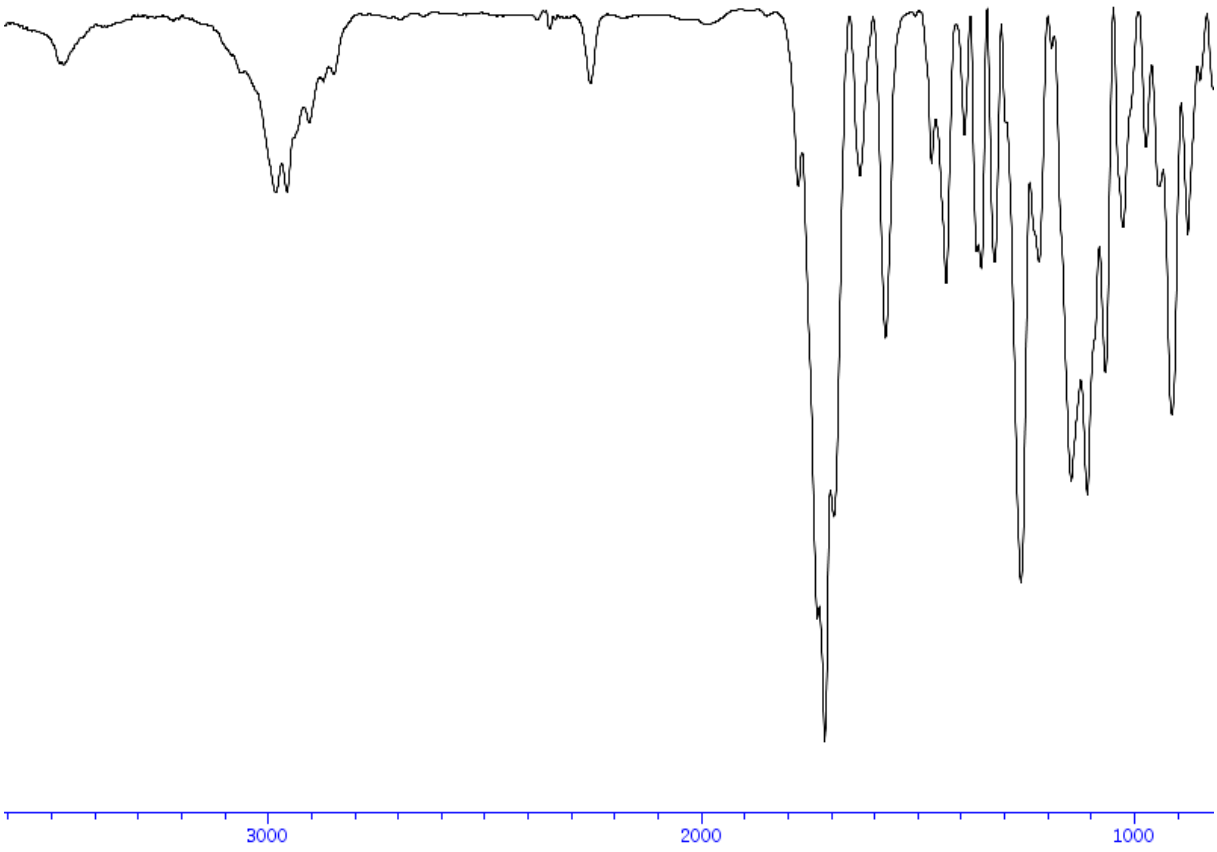

169.80
168.64
167.55
144.42
134.77
134.26 Impurity
132.79
131.41
123.85
123.45 Impurity
119.15
109.02
82.08
77.00 CDCl3
67.17
66.10
63.52
63.06
52.97
33.28
32.61
32.25
28.20
25.95
25.35
18.34
-5.29
13C-NMR
101 MHz
CDCl3
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3000
2000
1000

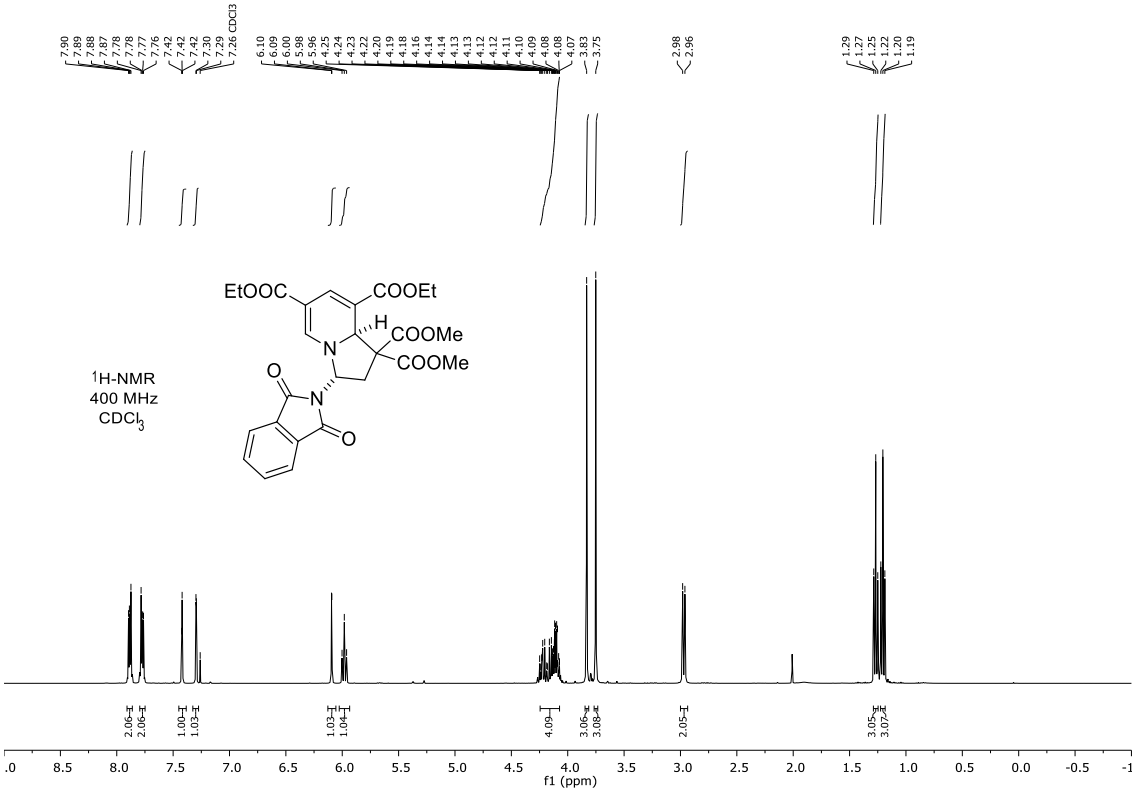
***anti*-6,7-Diethyl 1,1-dimethyl 3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1,6,7(8a*H*)-tetracarboxylate** (**54**).

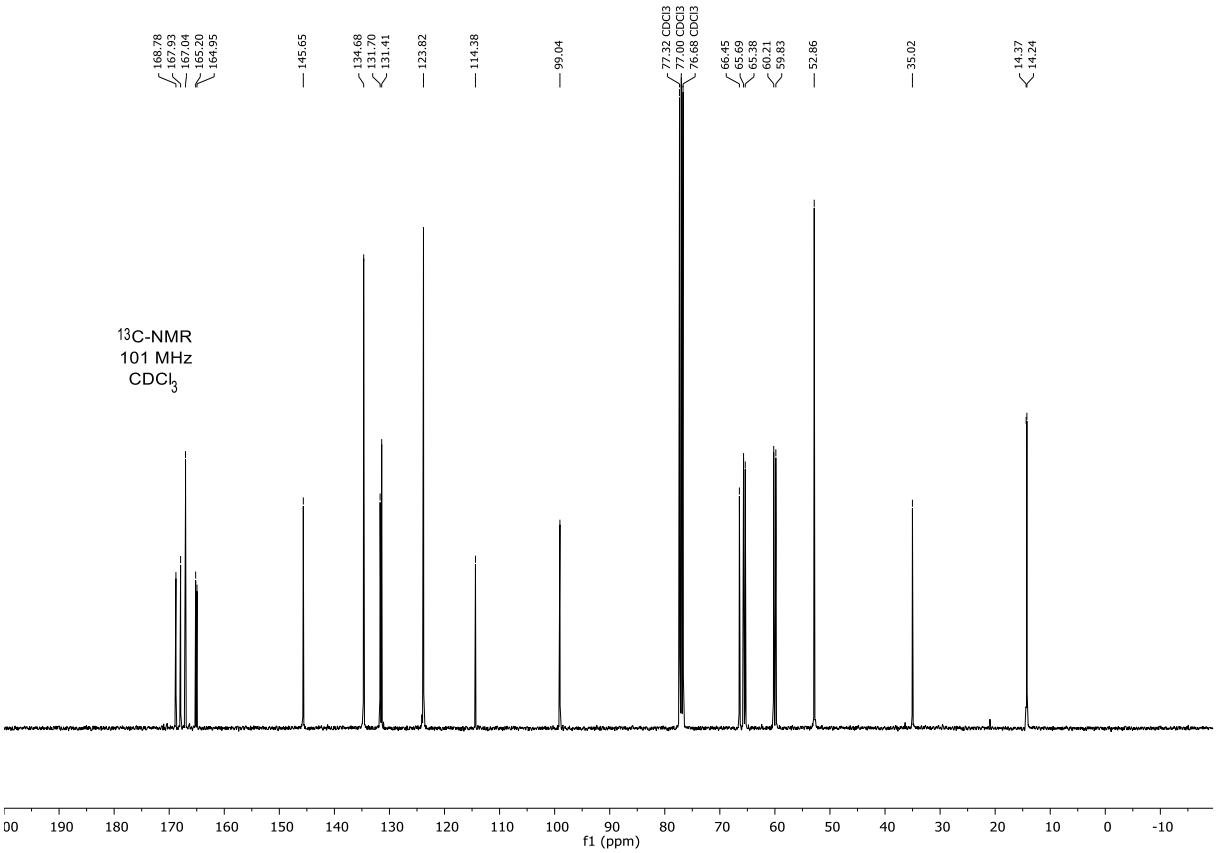


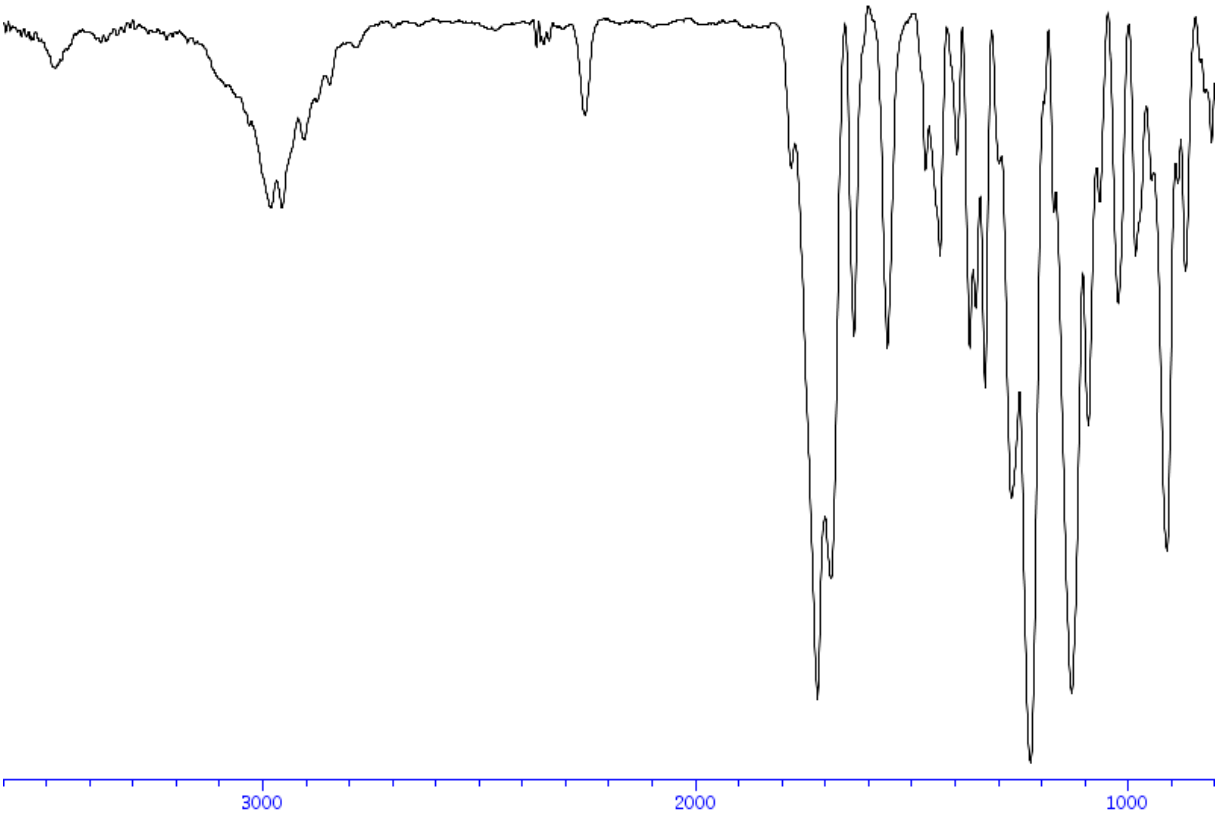




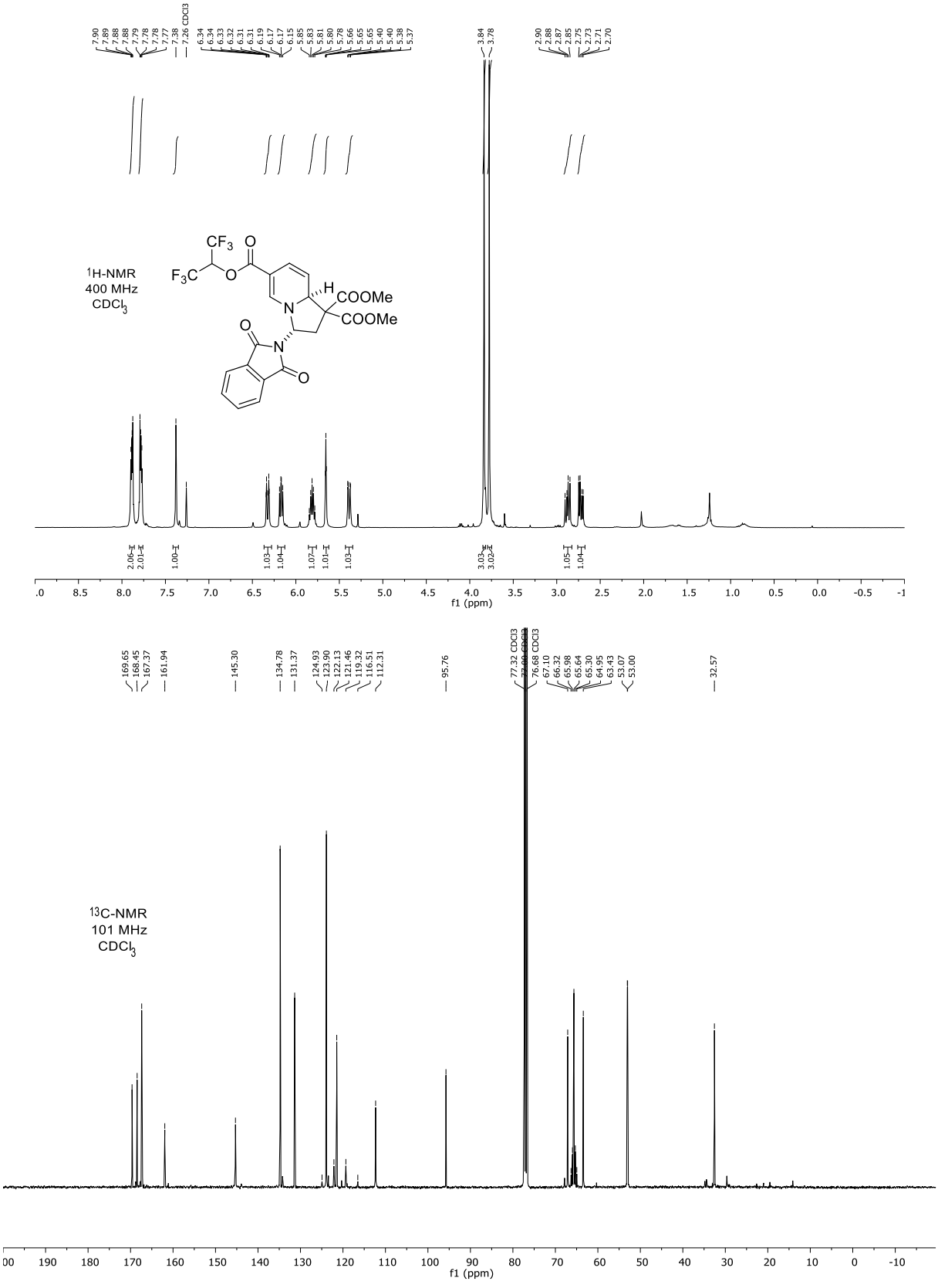
***anti*-6,8-Diethyl 1,1-dimethyl 3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1,6,8(8a*H*)-tetracarboxylate** (**55**).

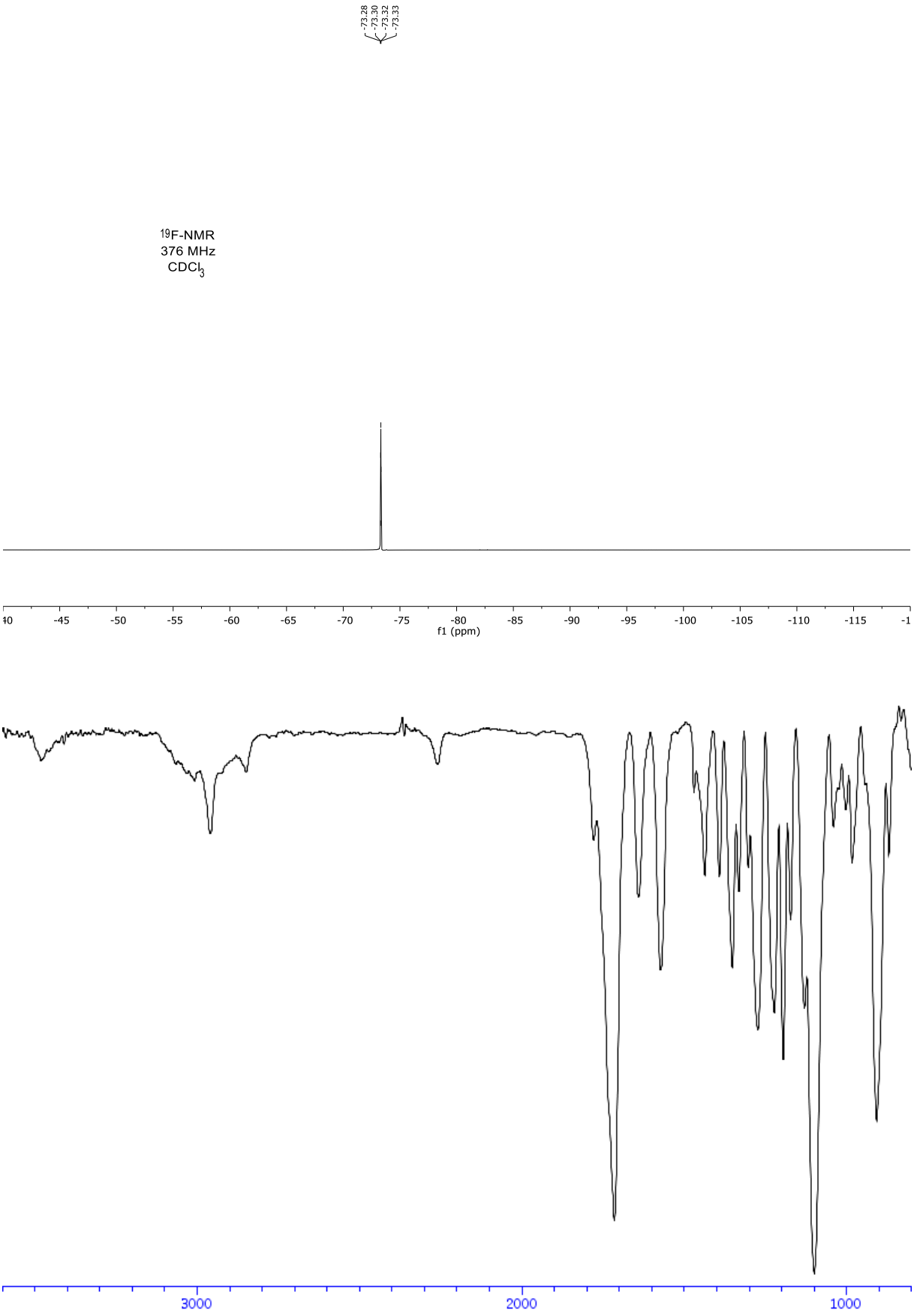



168.78
167.93
167.04
165.20
164.95
145.65
134.68
131.70
131.41
123.82
114.38
99.04
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
66.45
65.98
65.38
60.21
59.83
52.86
35.02
14.37
14.24
13C-NMR
101 MHz
CDCl3
f1 (ppm)

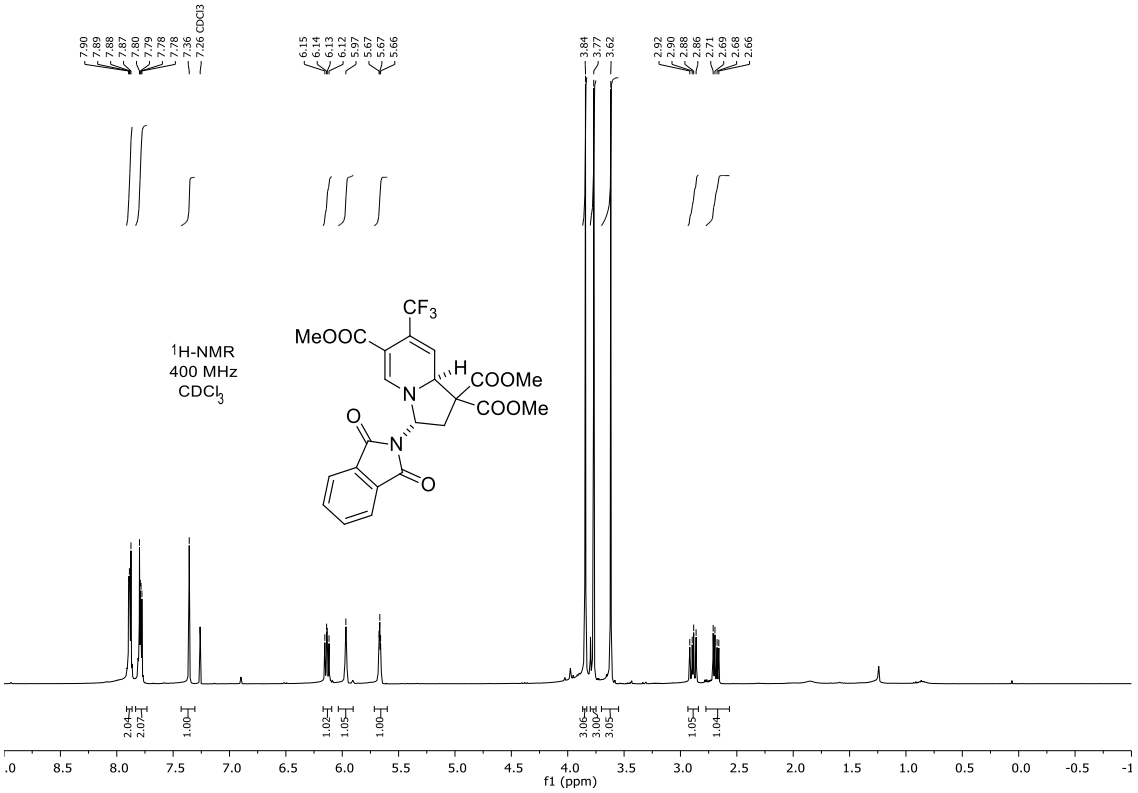

3000
2000
1000

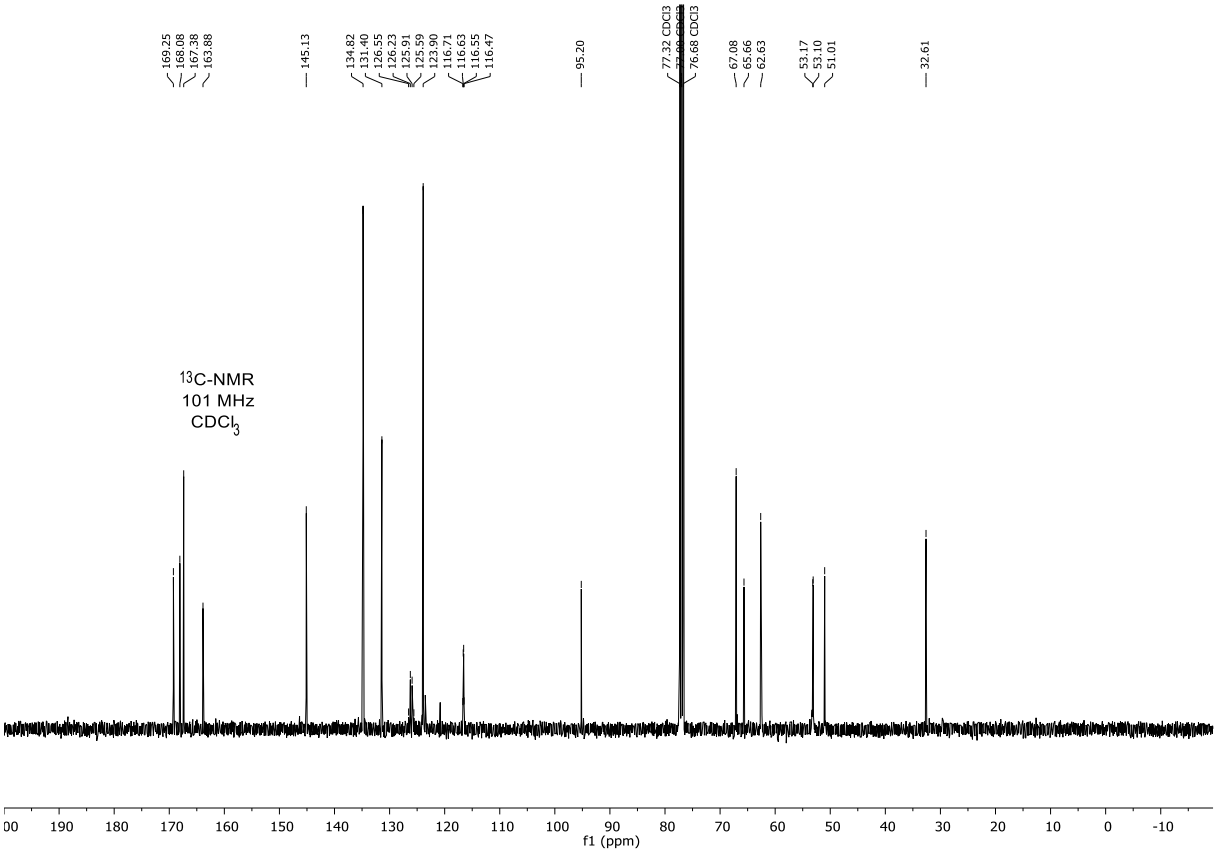
***anti*-6-(1,1,1,3,3,3-Hexafluoropropan-2-yl) 1,1-dimethyl 3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1,6(8a*H*)-tricarboxylate** (**56**).

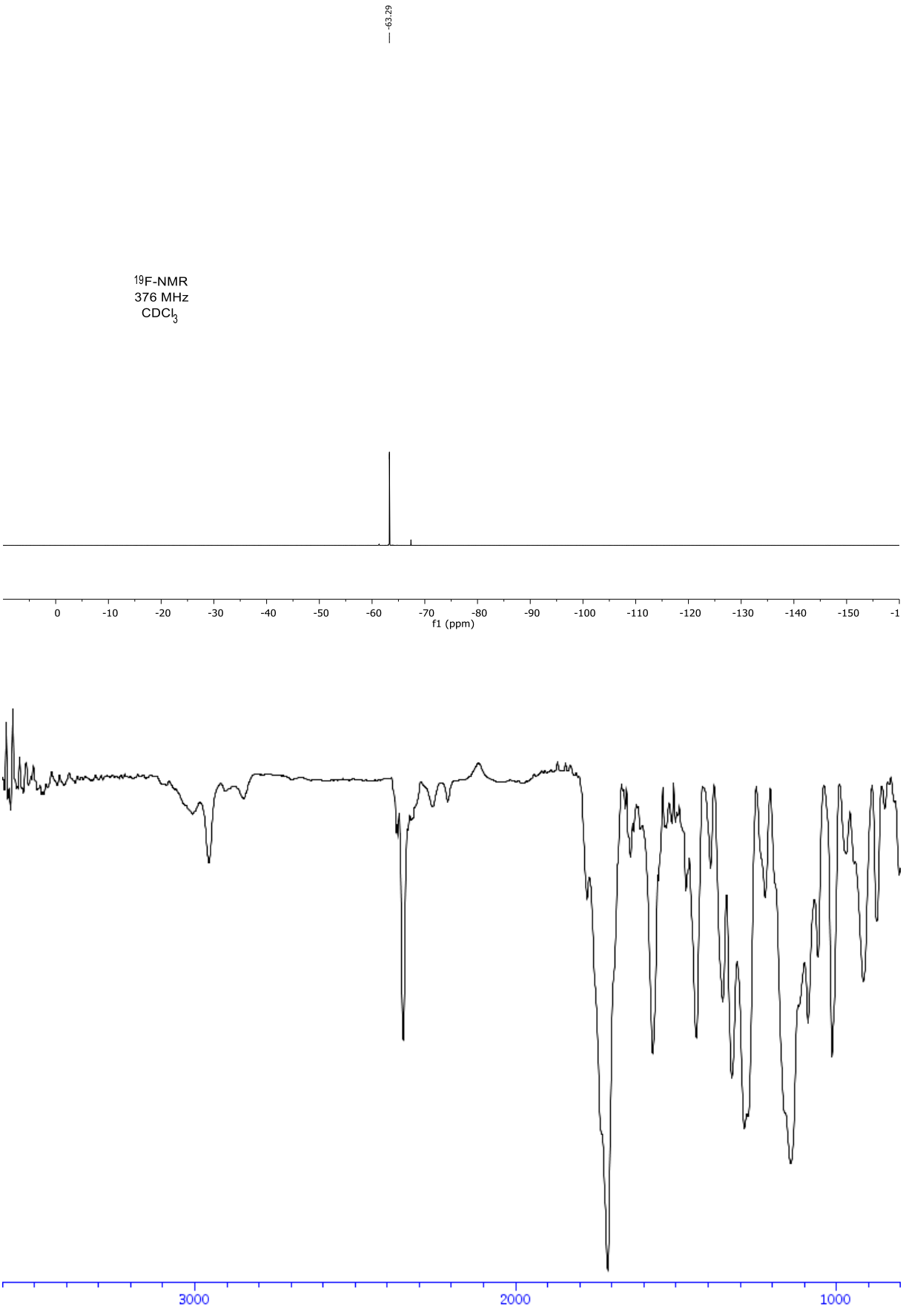



-73.28
-73.30
-73.32
-73.33
19F-NMR
376 MHz
CDCl3
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
f1 (ppm)
3000
2000
1000

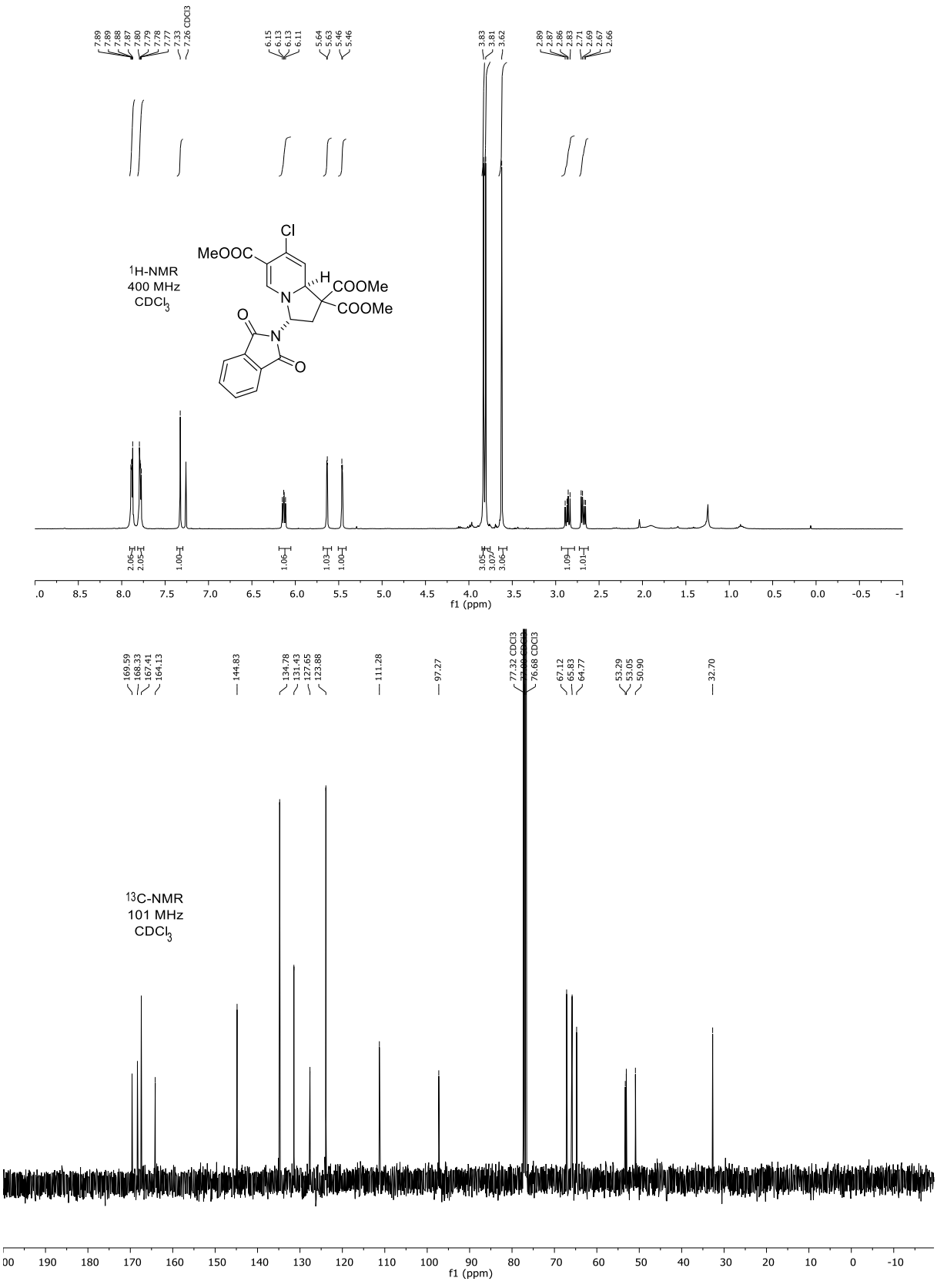
***anti*-Trimethyl 3-(1,3-dioxoisoindolin-2-yl)-7-(trifluoromethyl)-2,3-dihydroindolizine-1,1,6(8a*H*)-tricarboxylate (57).**

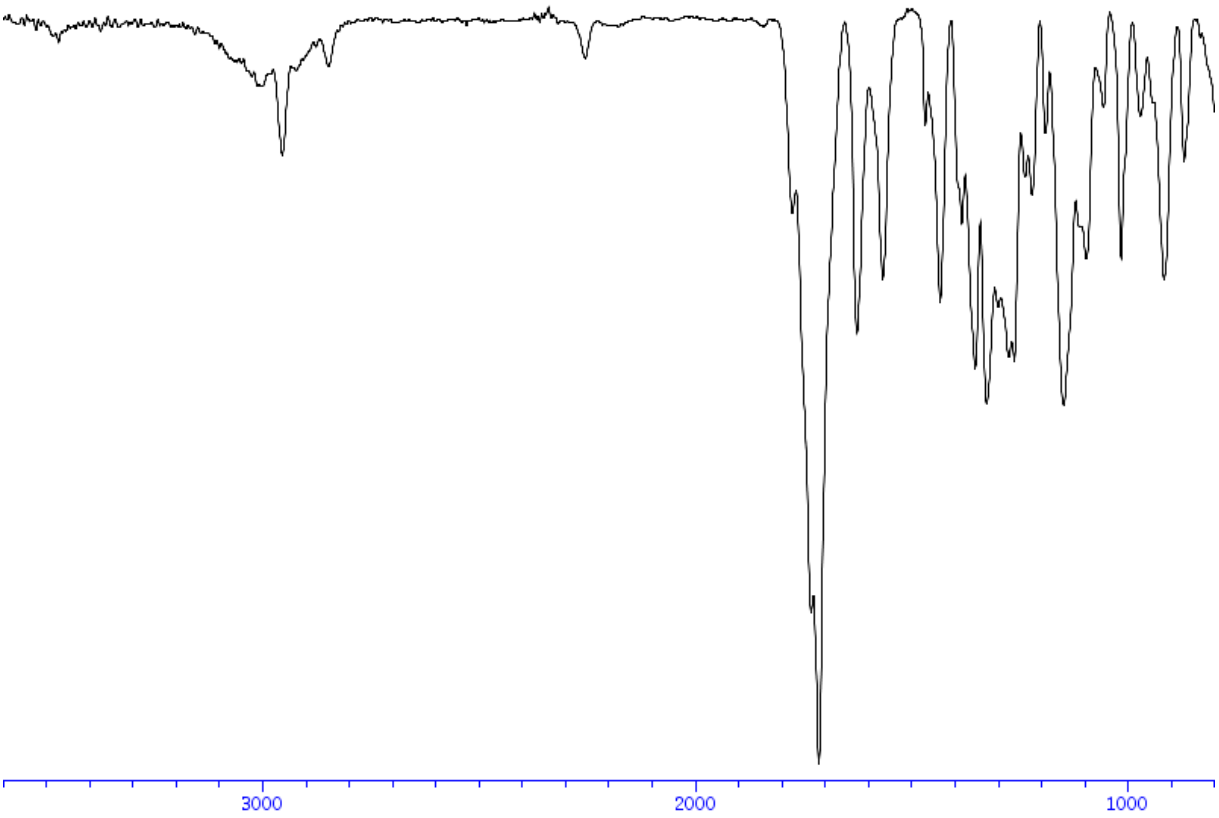




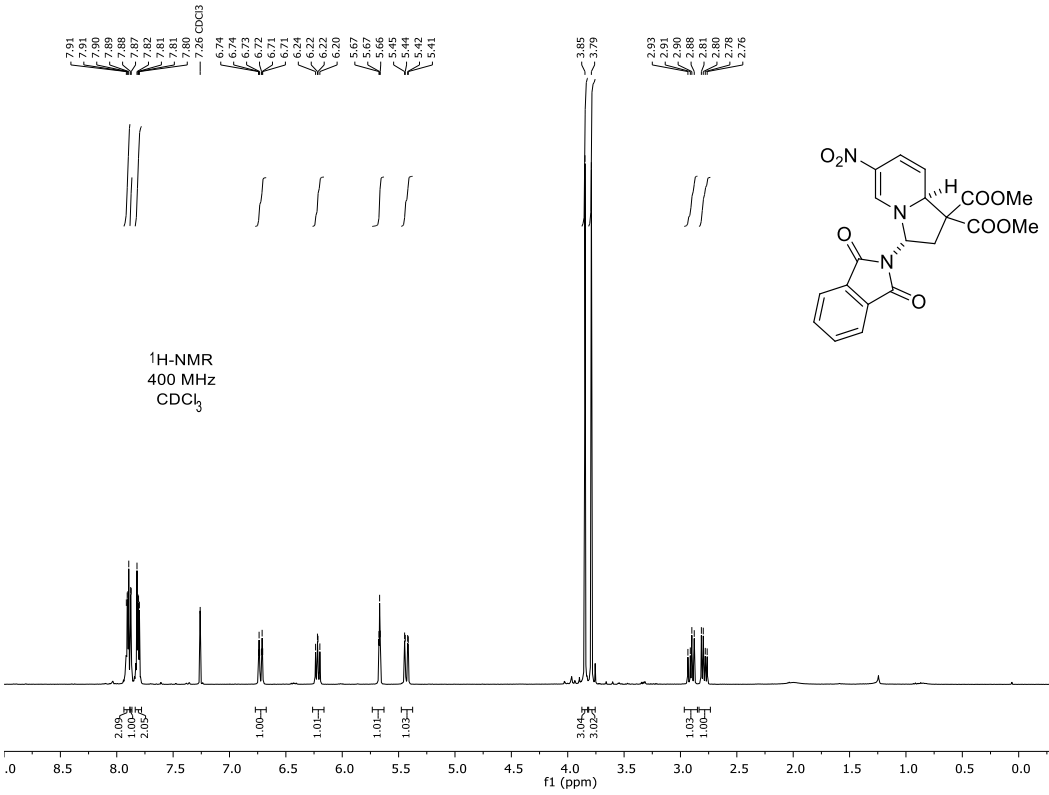

— -63.29
19F-NMR
376 MHz
CDCl3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)
3000
2000
1000

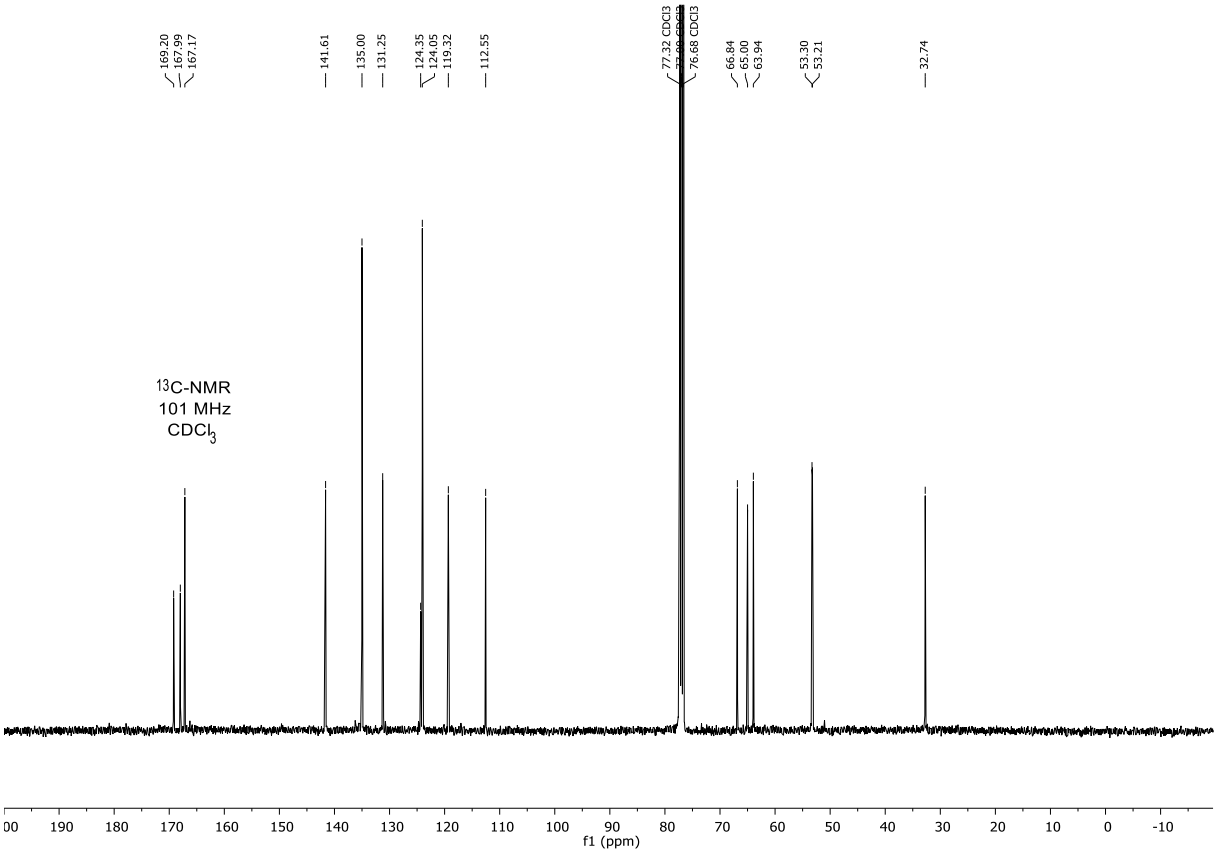
***anti*-Trimethyl 7-chloro-3-(1,3-dioxoisoindolin-2-yl)-2,3-dihydroindolizine-1,1,6(8a*H*)-tricarboxylate (58).**

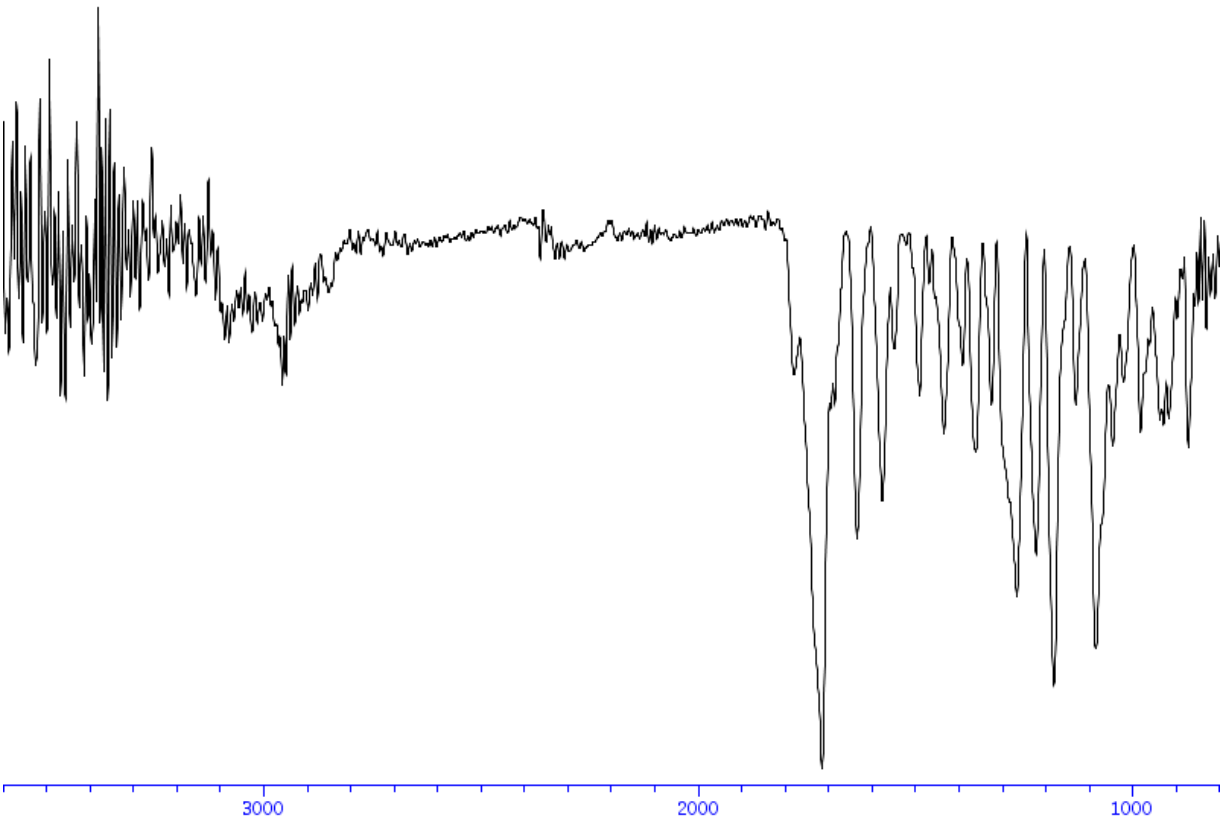




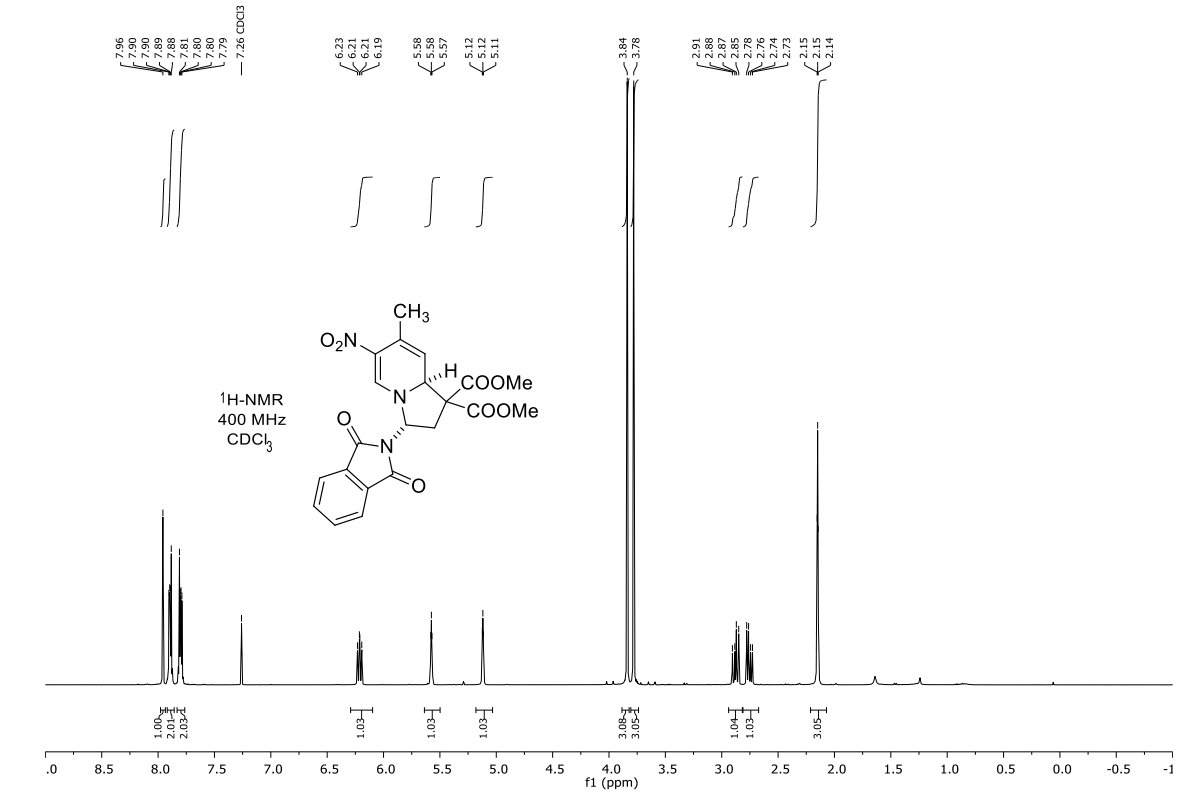
***anti*-Dimethyl 3-(1,3-dioxoisoindolin-2-yl)-6-nitro-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate (59).**

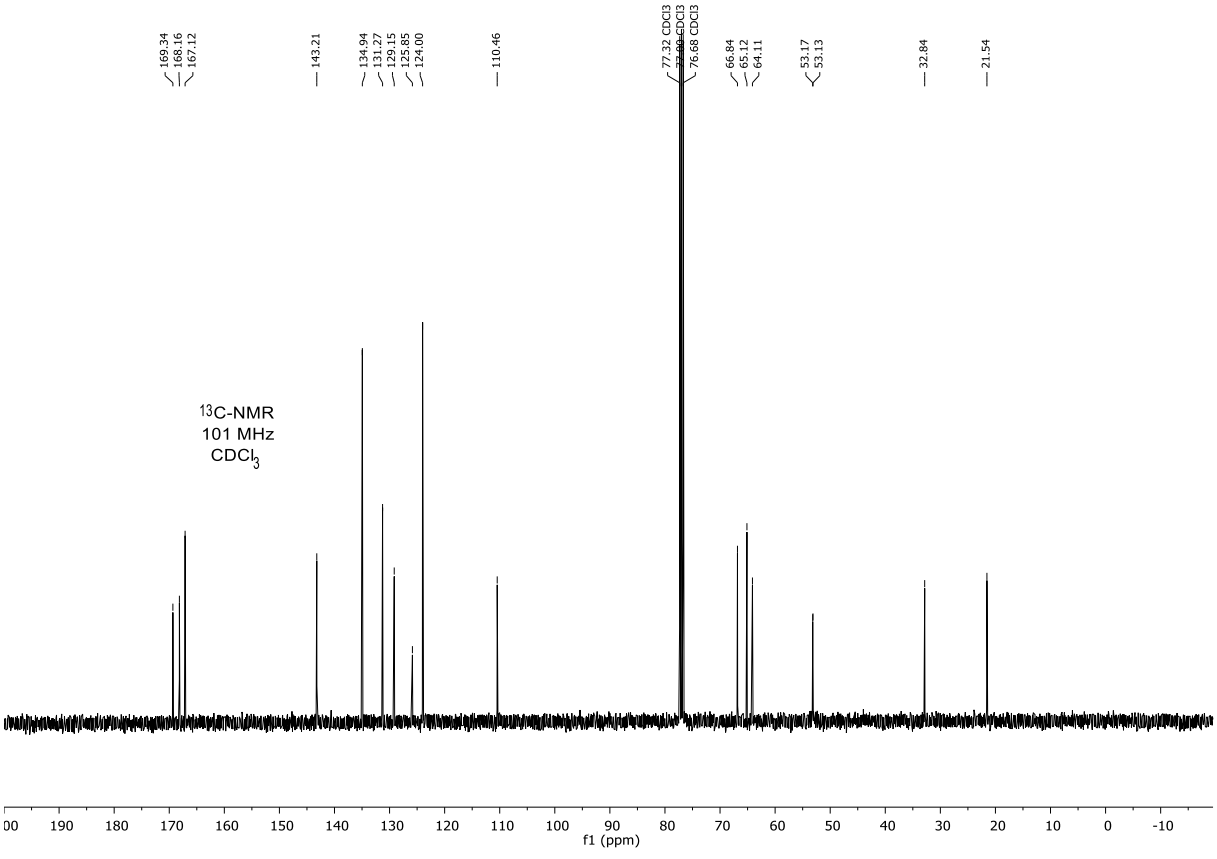


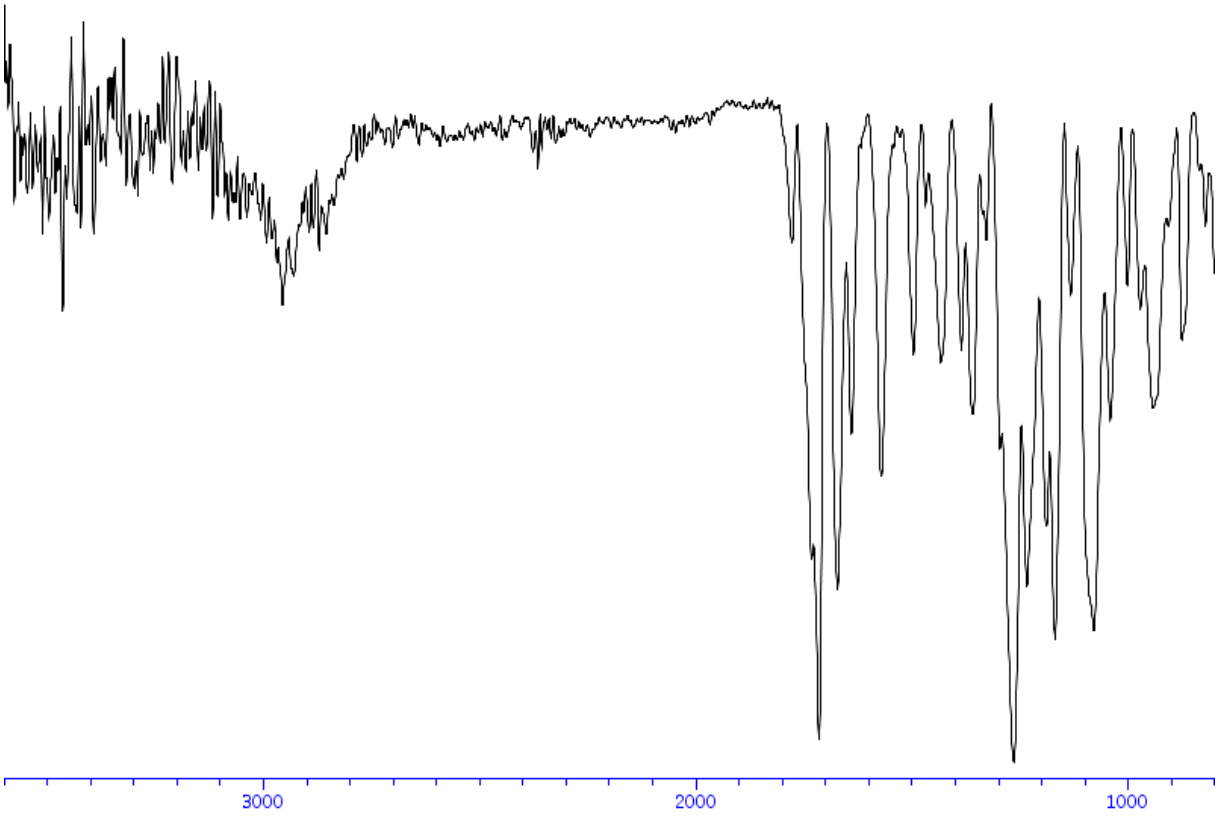

169.20
167.99
167.17
141.61
135.00
131.25
124.35
124.05
119.32
112.55
77.32 CDCl3
76.68 CDCl3
66.84
65.00
63.94
53.30
53.21
32.74
13C-NMR
101 MHz
CDCl3
f1 (ppm)


3000
2000
1000

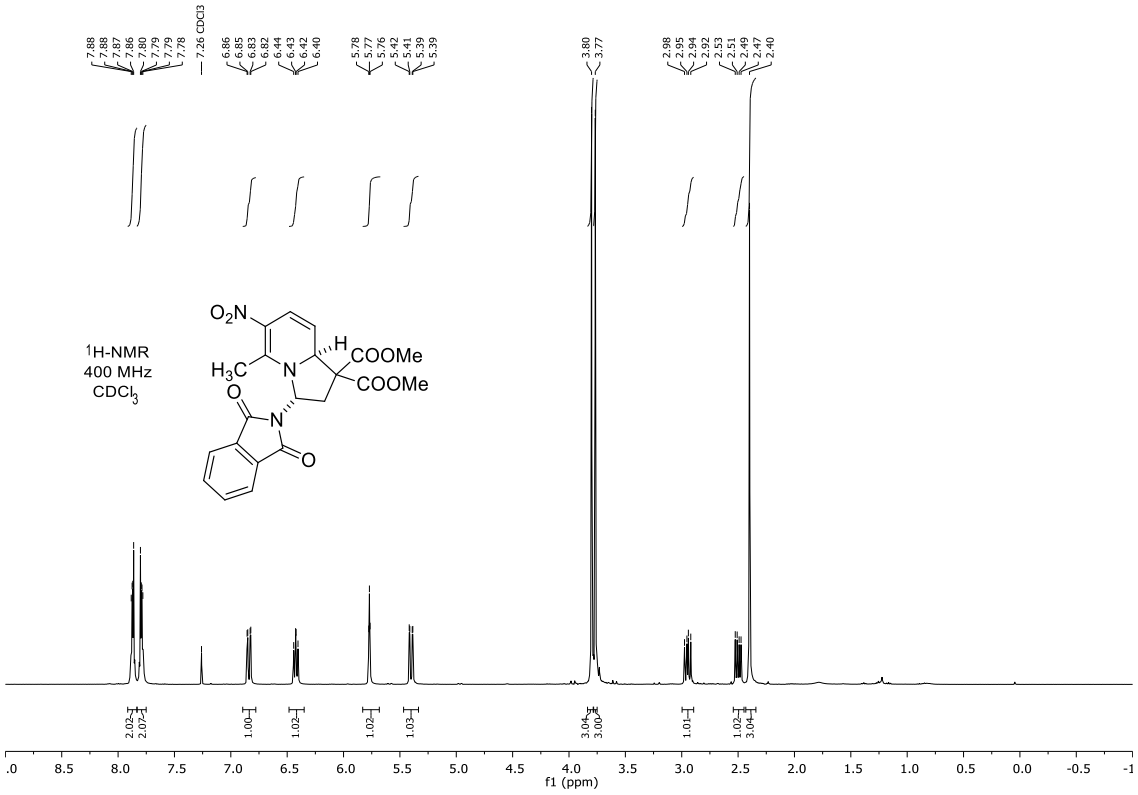
***anti*-Dimethyl 3-(1,3-dioxoisoindolin-2-yl)-7-methyl-6-nitro-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate (60).**

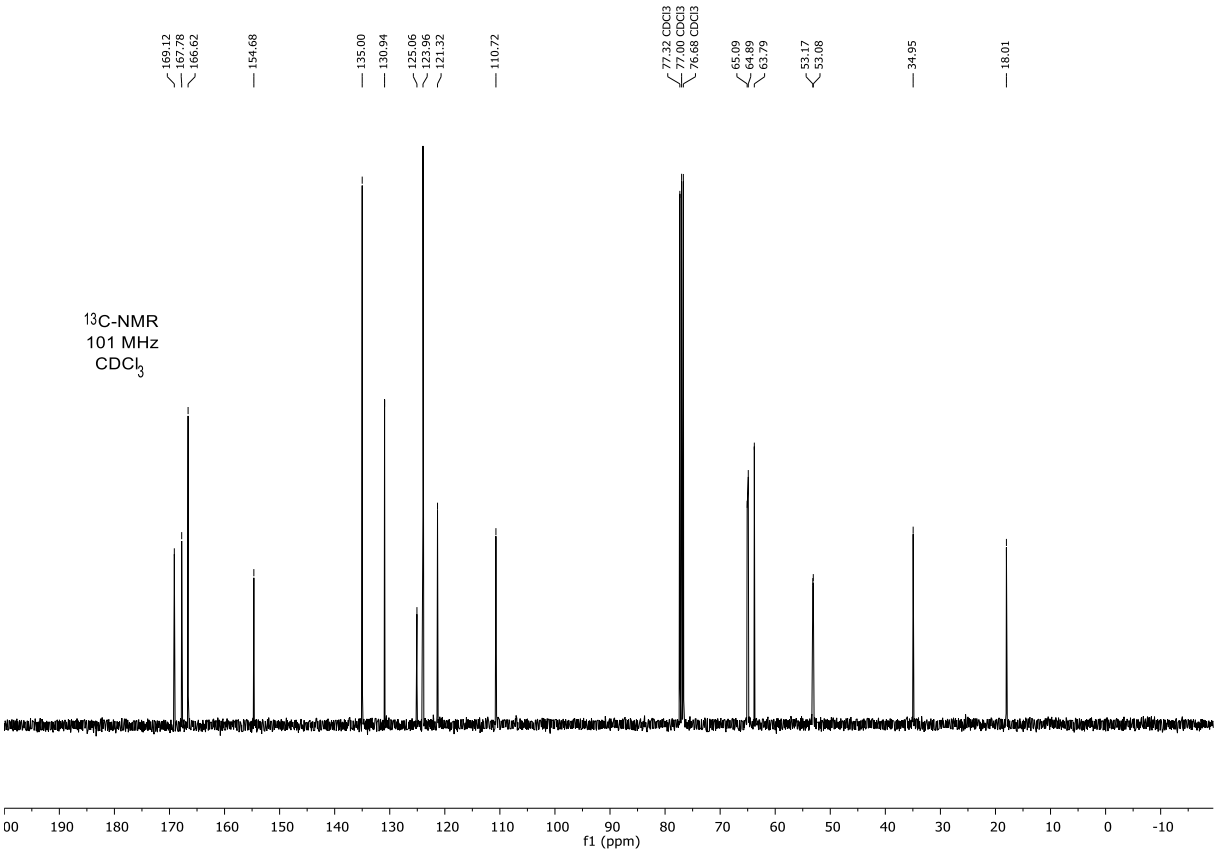


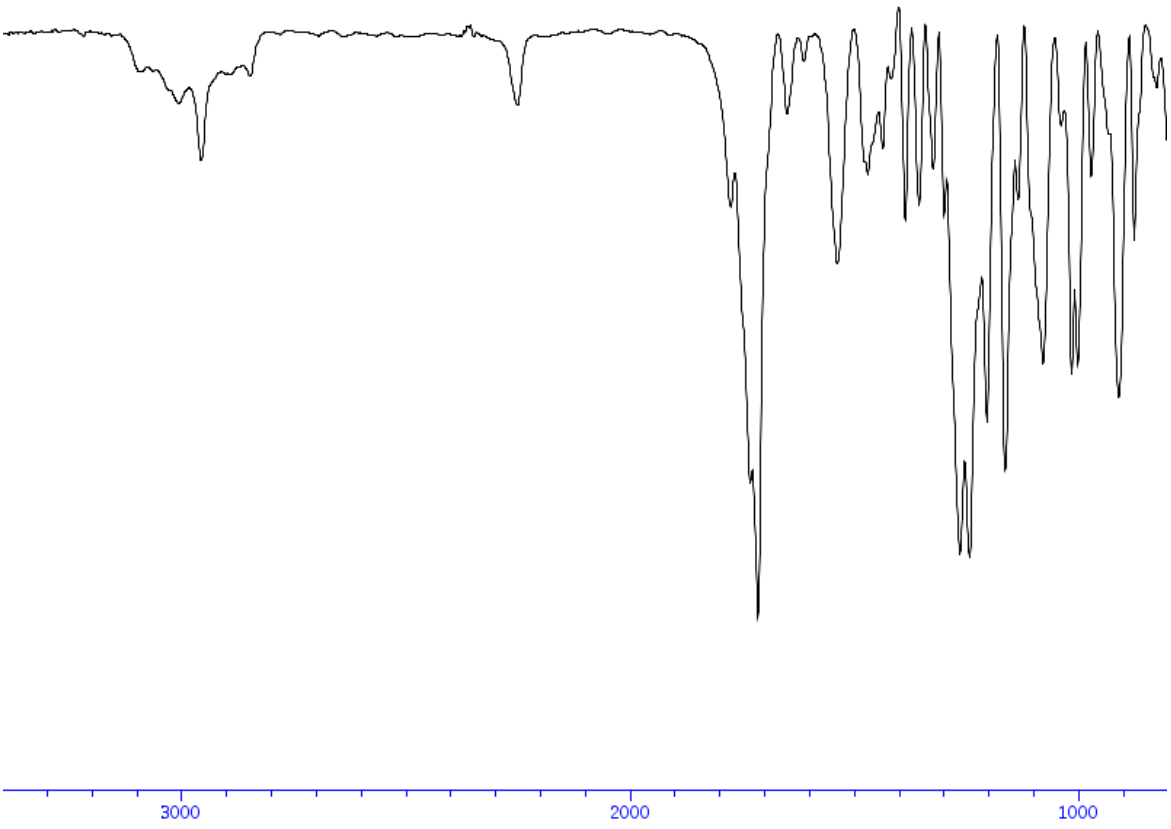




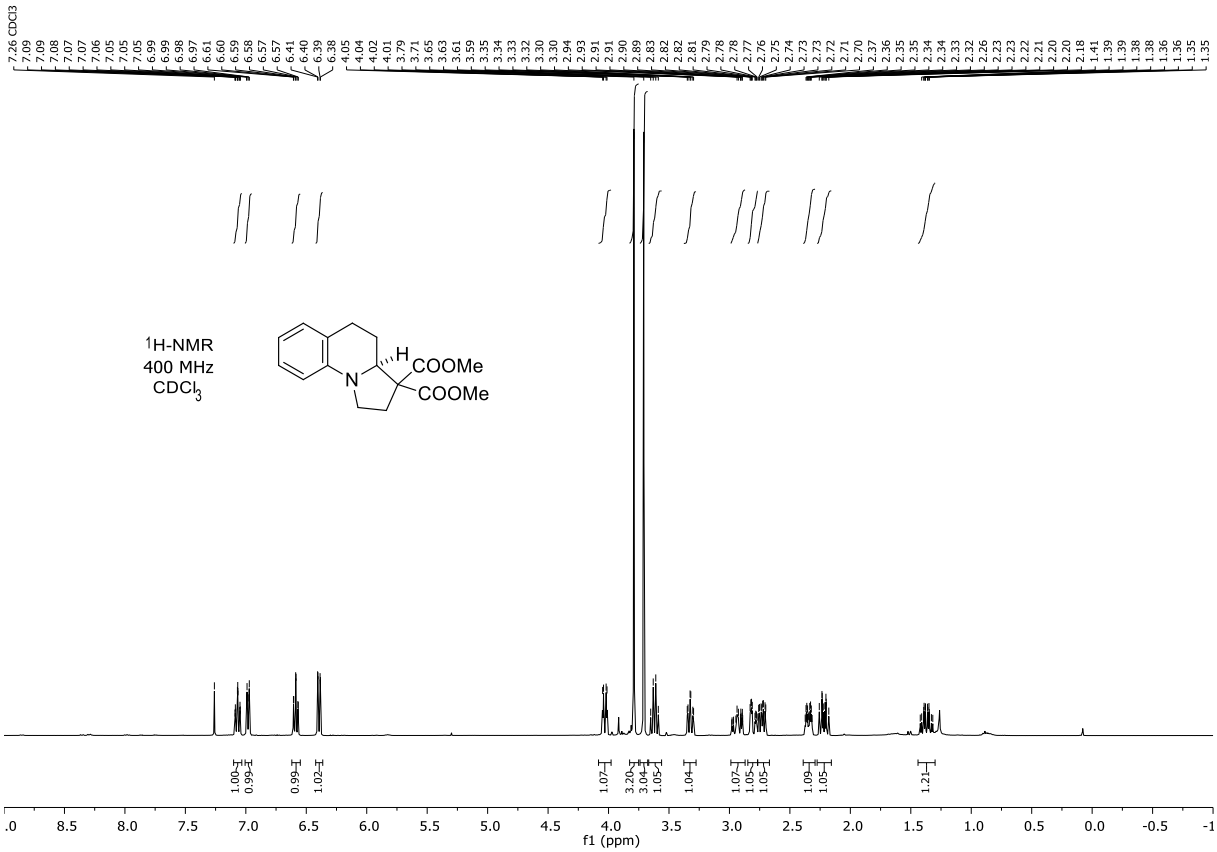
***anti*-Dimethyl 3-(1,3-dioxoisoindolin-2-yl)-5-methyl-6-nitro-2,3-dihydroindolizine-1,1(8a*H*)-dicarboxylate (61).**

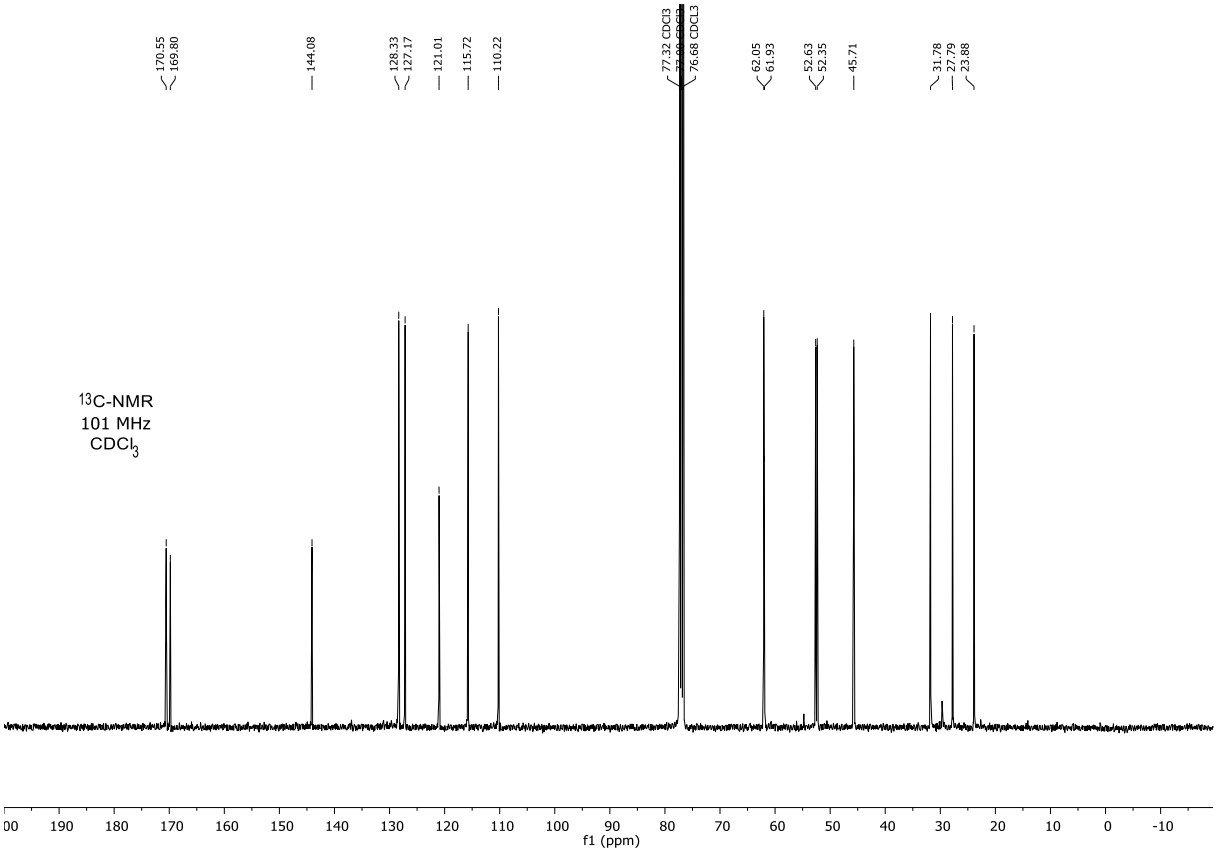


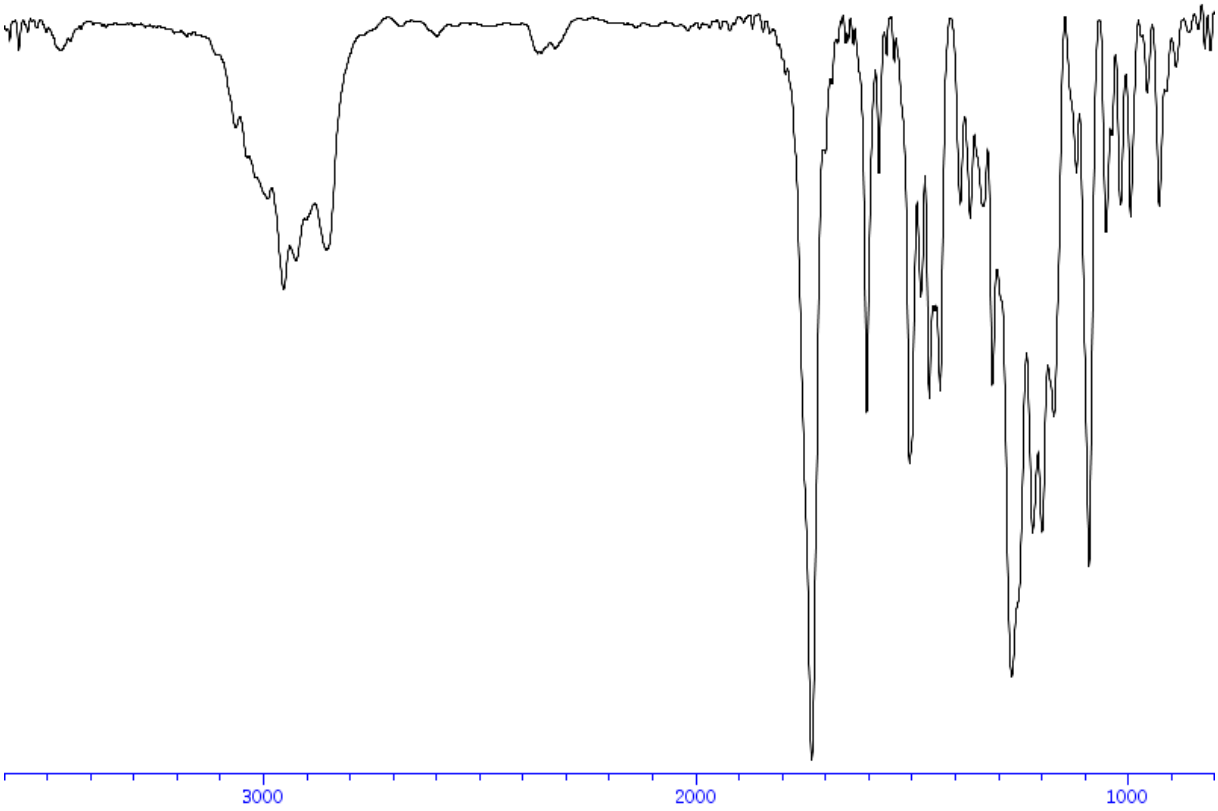

169.12
167.78
166.62
154.68
135.00
130.94
125.06
123.96
121.32
110.72
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
65.09
64.89
63.79
53.17
53.08
34.95
18.01
13C-NMR
101 MHz
CDCl3
f1 (ppm)


3000
2000
1000

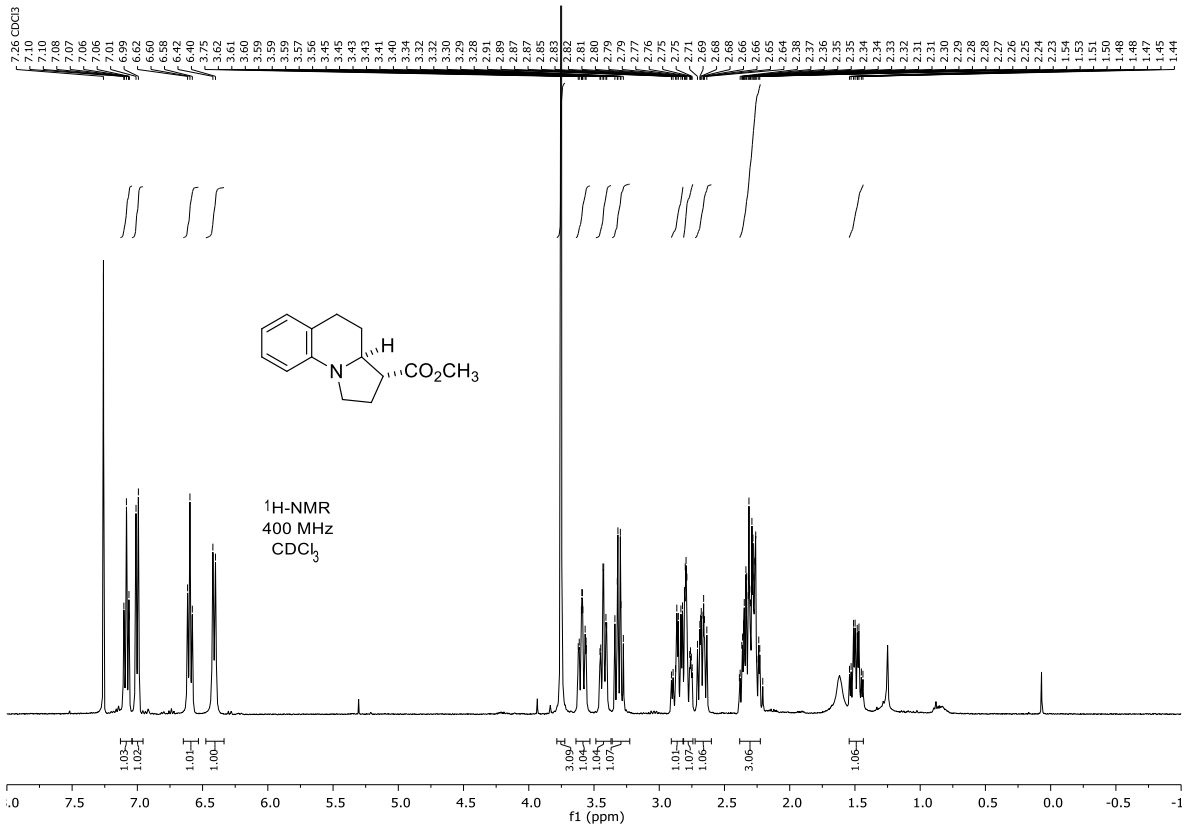
Dimethyl 1,2,4,5-tetrahydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (**SI-75**).

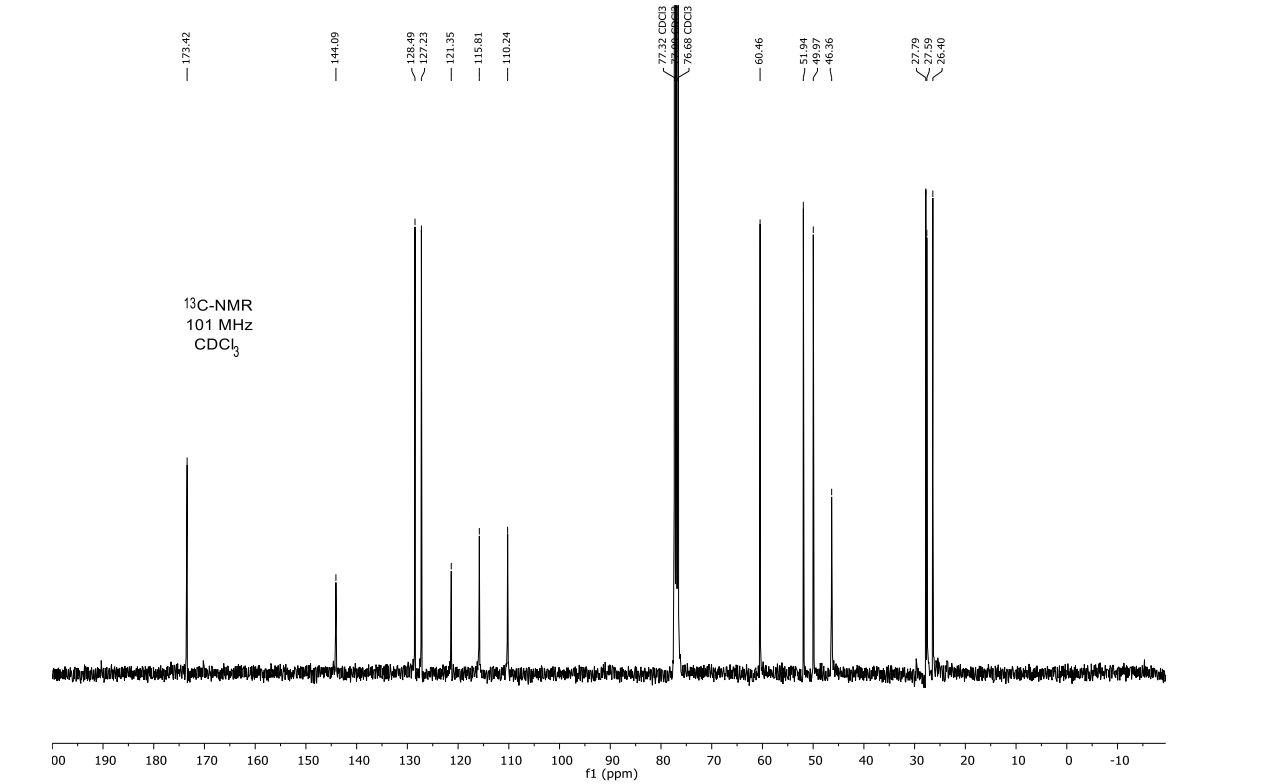


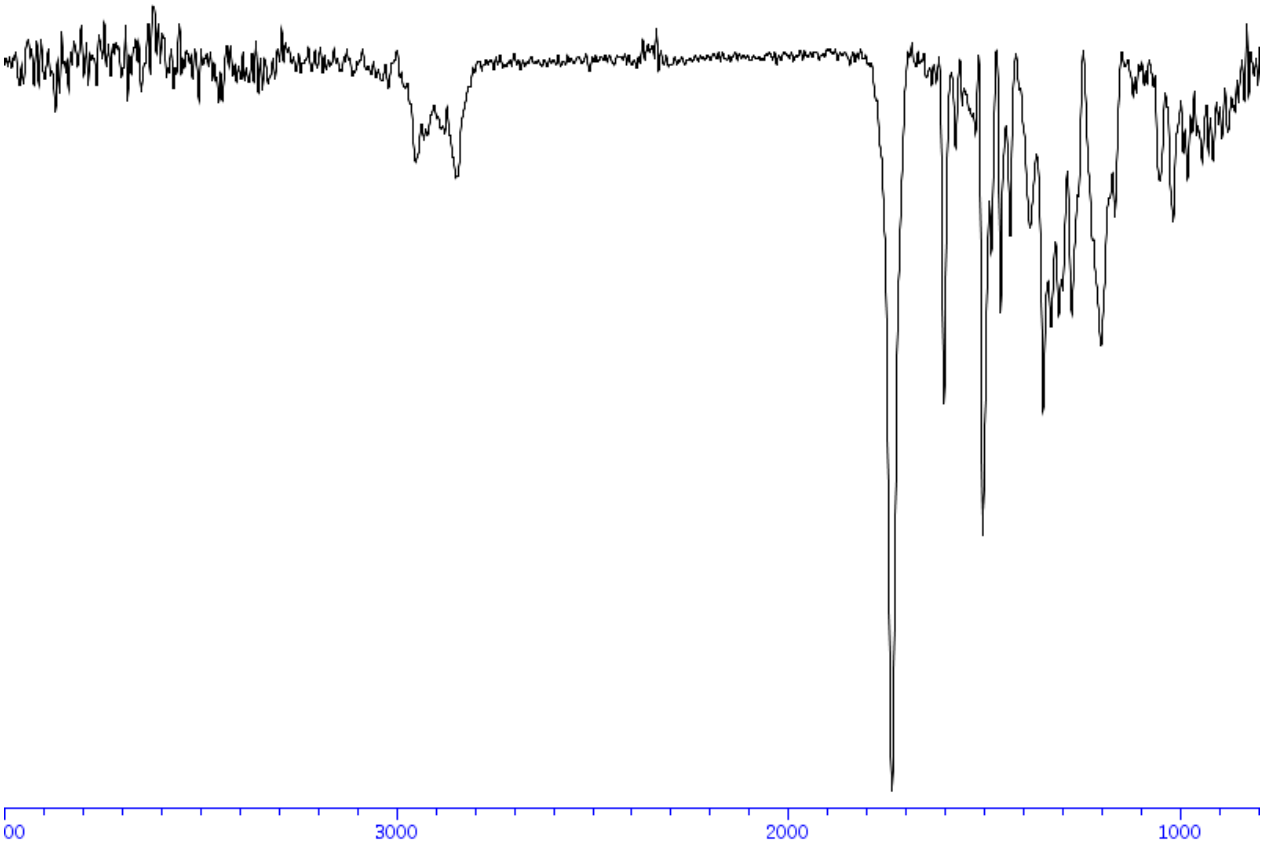




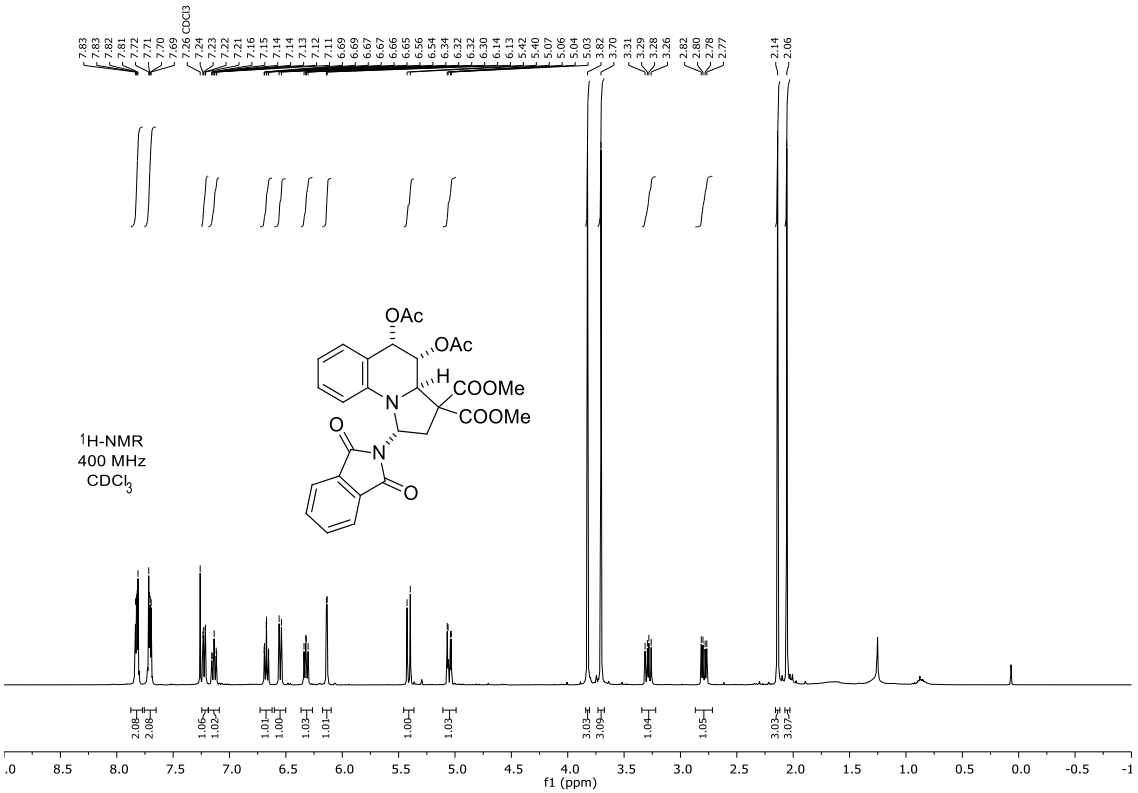
(3*S*,3a*R*)-methyl 1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinoline-3-carboxylate (62).

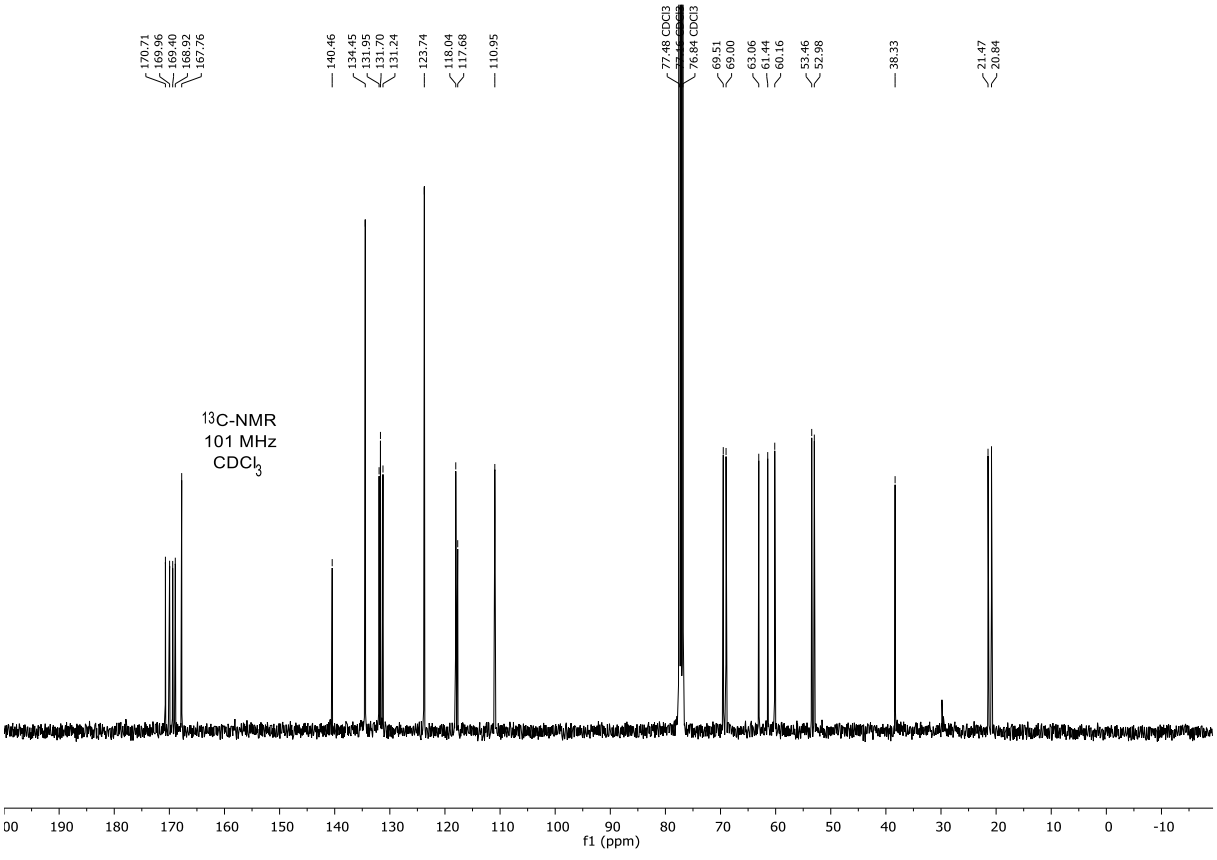


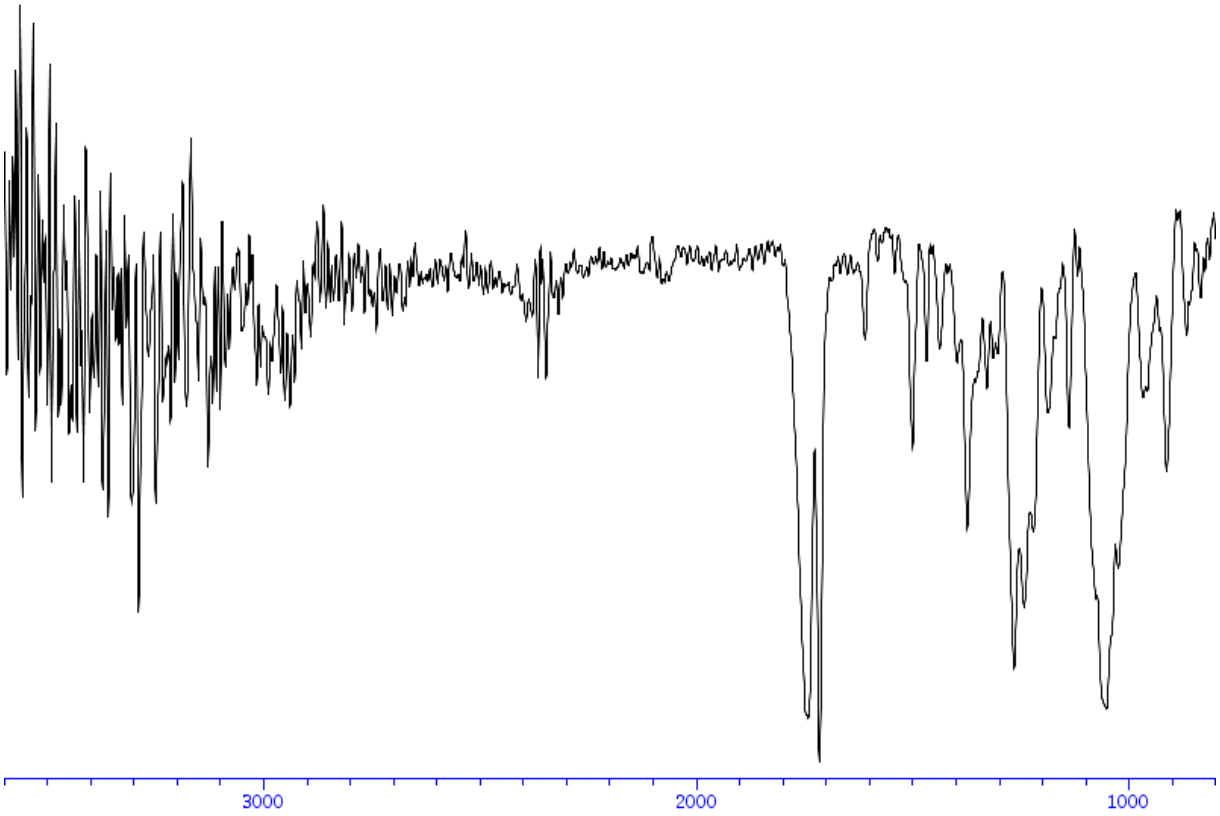

173.42
144.09
128.49
127.23
121.35
115.81
110.24
77.32 CDCl3
76.68 CDCl3
60.46
51.94
49.97
46.36
27.79
27.59
26.40
13C-NMR
101 MHz
CDCl3
f1 (ppm)


3000
2000
1000

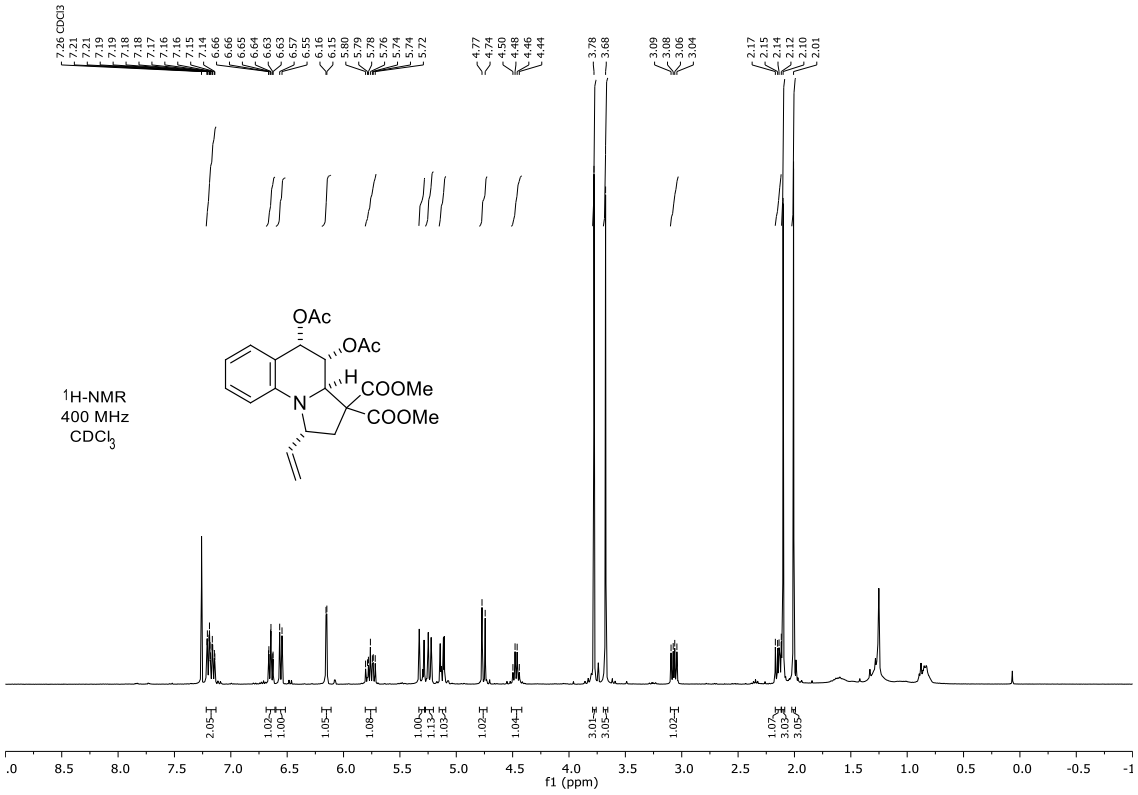
(1*R*,3a*S*,4*S*,5*R*)-Dimethyl 4,5-diacetoxy-1-(1,3-dioxoisoindolin-2-yl)-1,2,4,5-tetrahydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (**SI-76**).

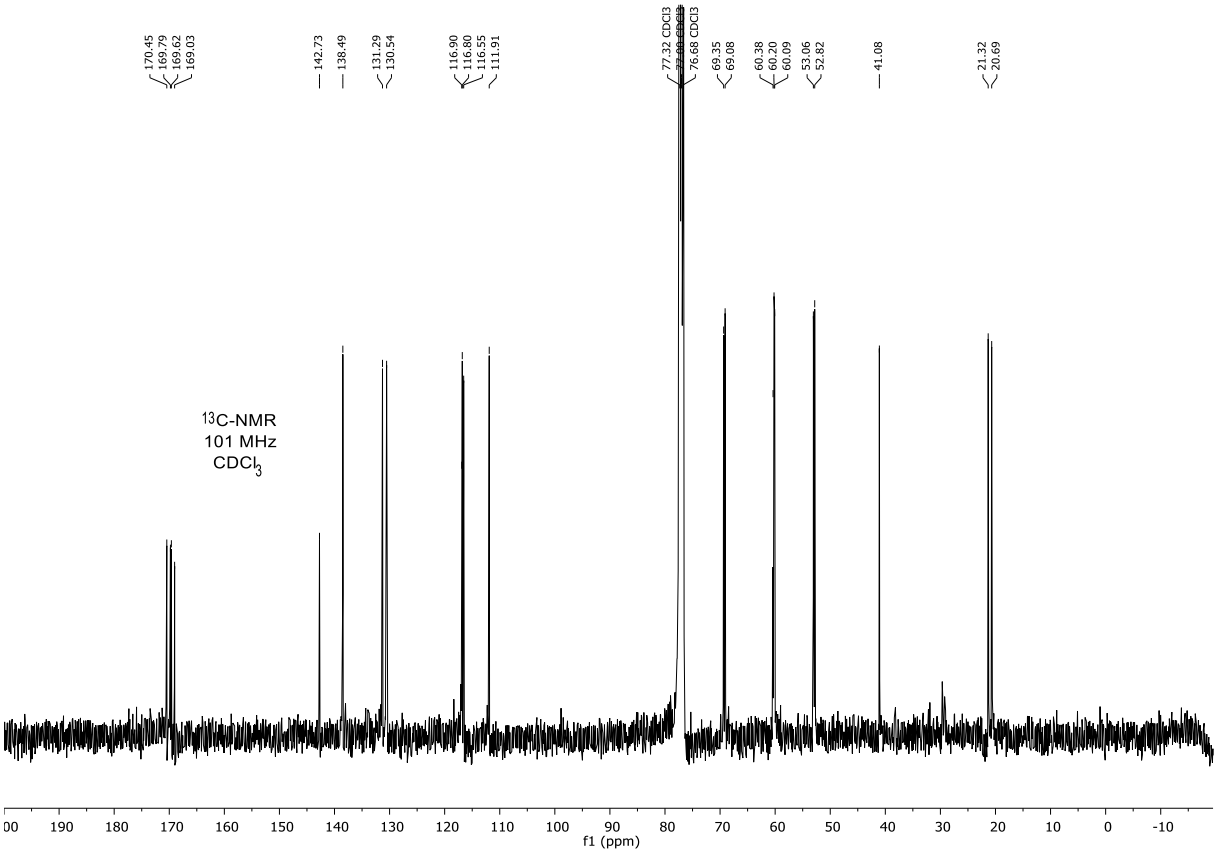


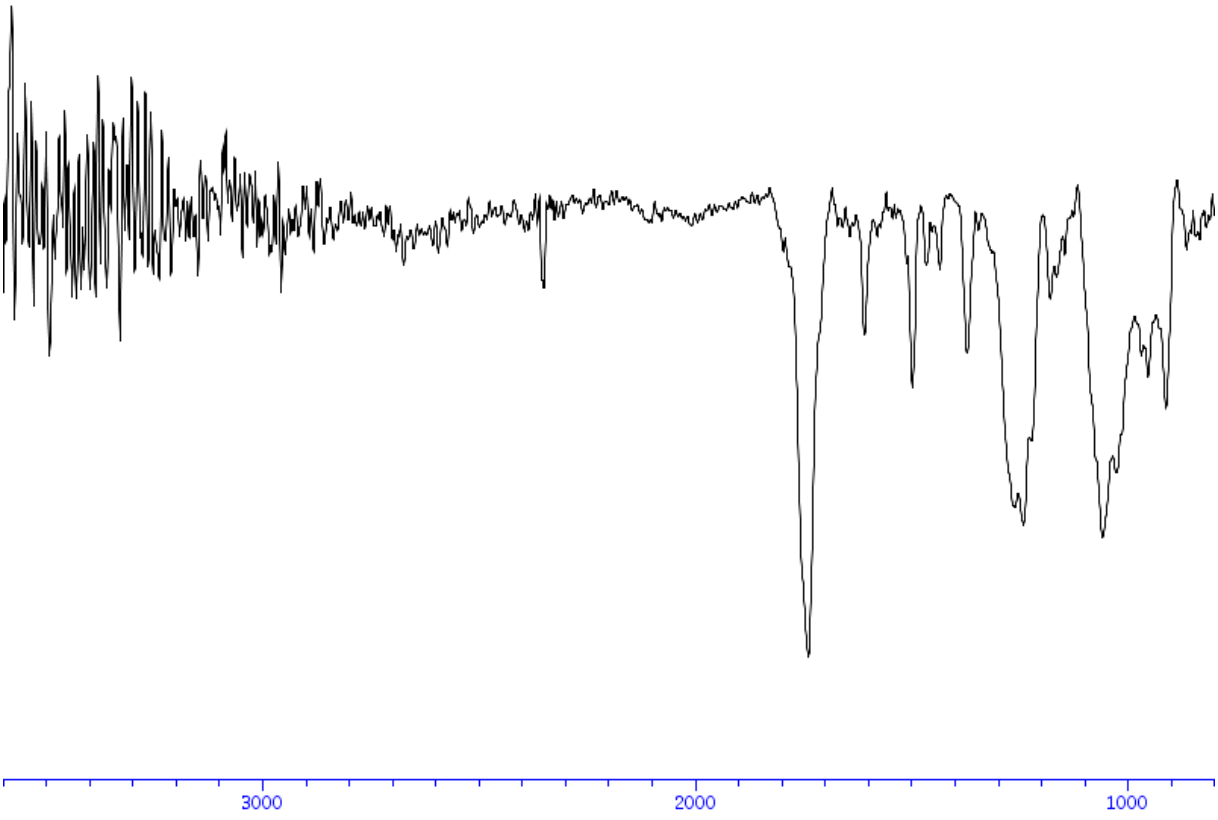




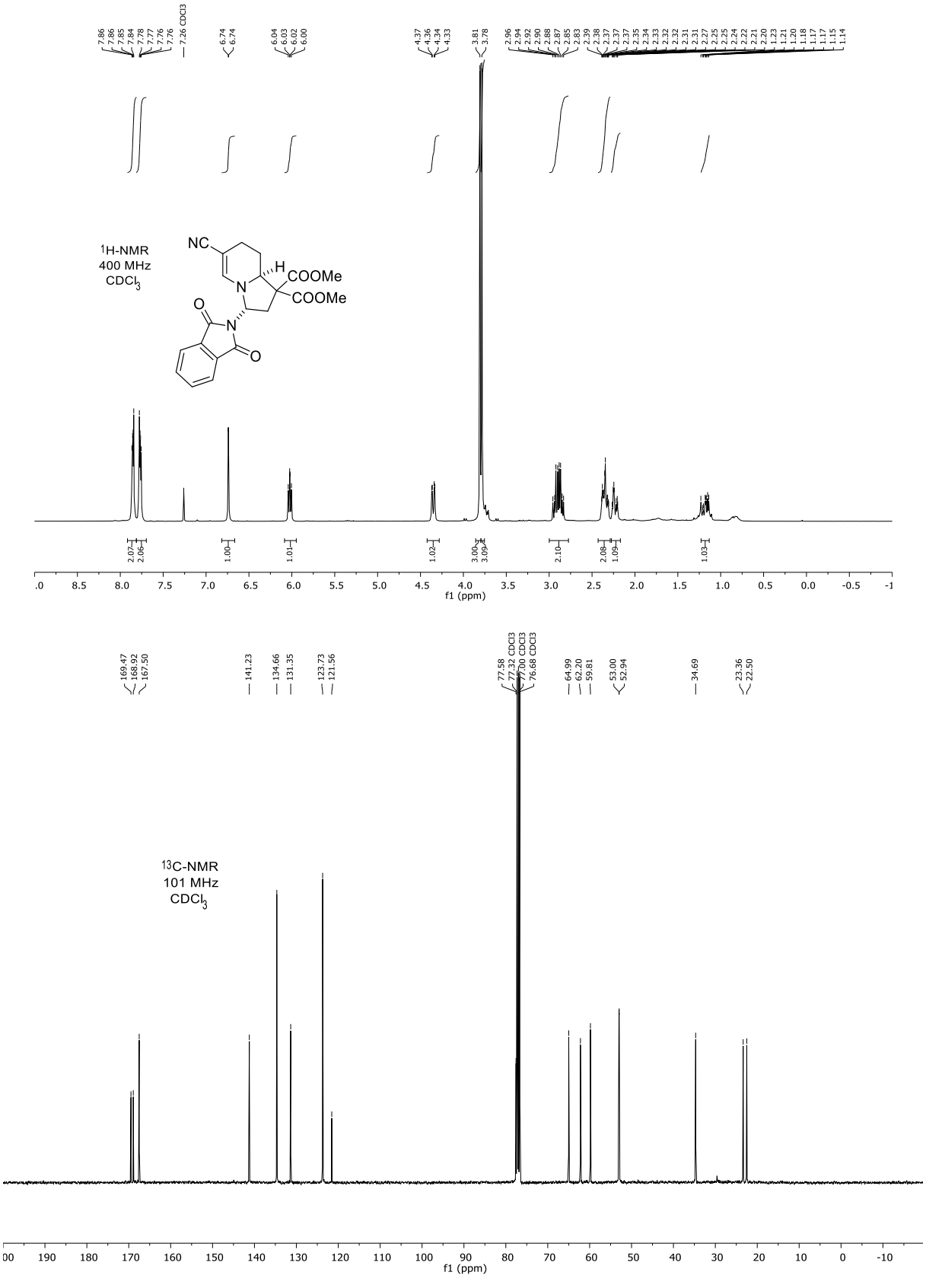
(1*S*,3a*S*,4*S*,5*R*)-Dimethyl 4,5-diacetoxy-1-vinyl-1,2,4,5-tetrahydropyrrolo[1,2-a]quinoline-3,3(3a*H*)-dicarboxylate (**63**).

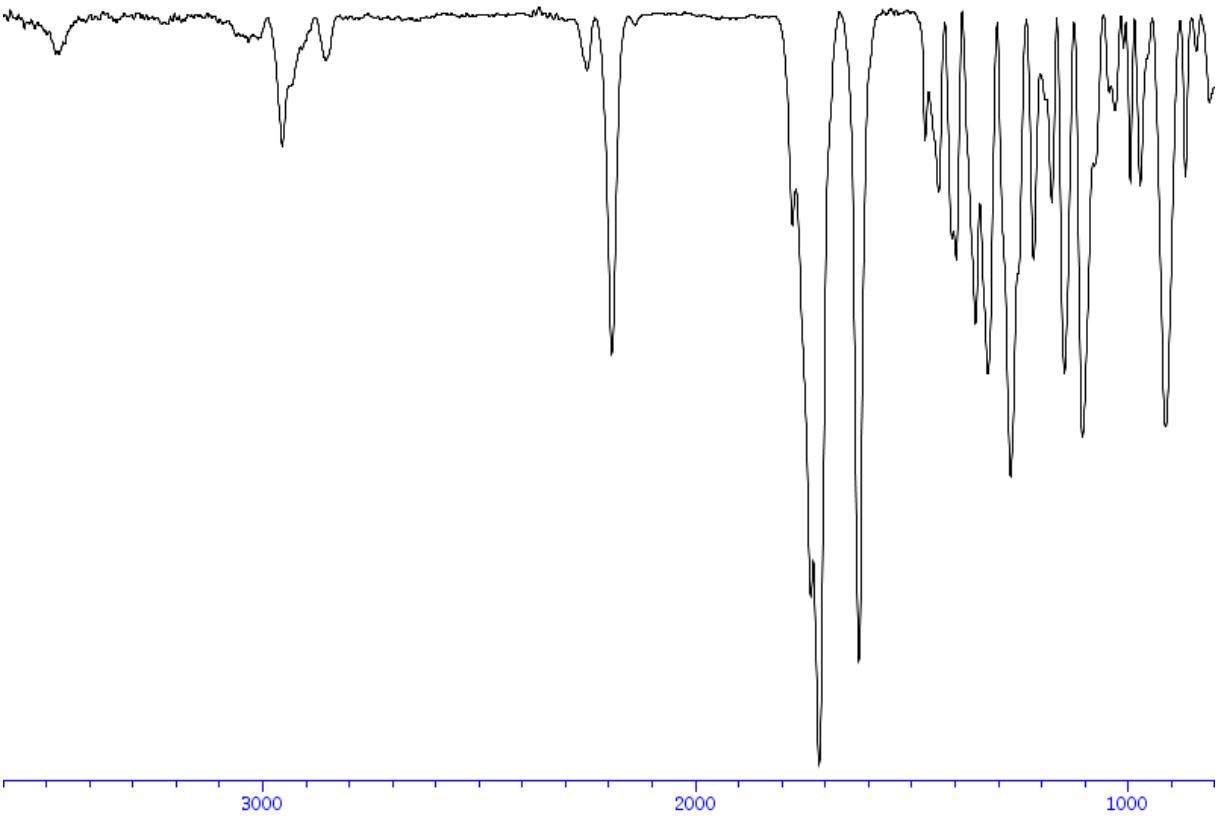



170.45
169.79
169.62
169.03
142.73
138.49
131.29
130.54
116.90
116.80
116.55
111.91
77.32 CDCl3
76.68 CDCl3
69.35
69.08
60.38
60.20
60.09
53.06
52.82
41.08
21.32
20.69
13C-NMR
101 MHz
CDCl3
f1 (ppm)

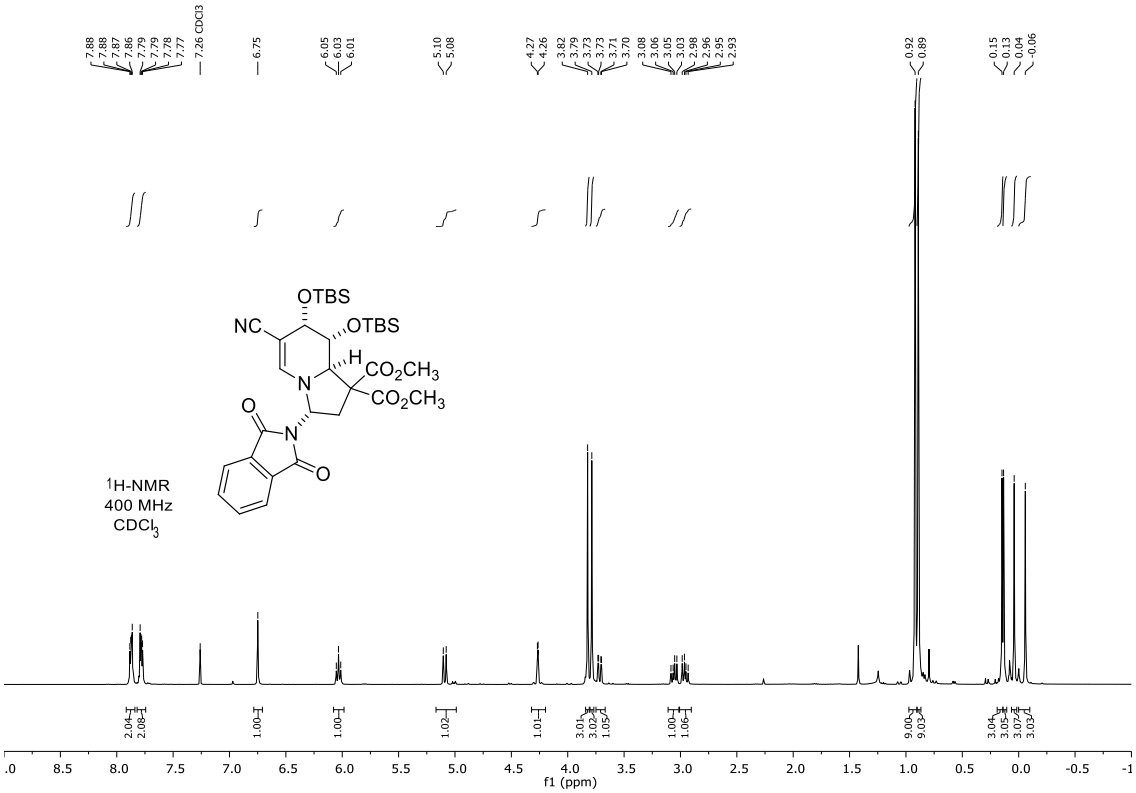

3000
2000
1000

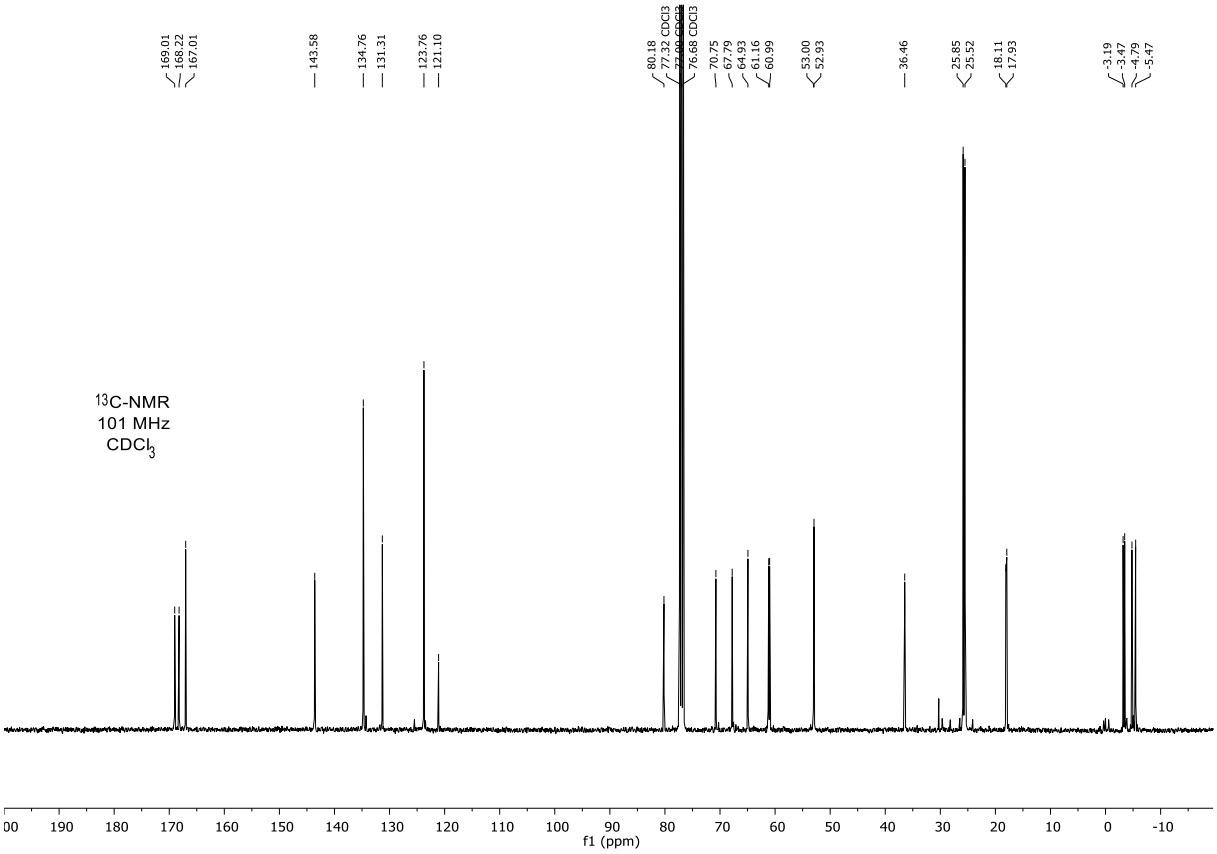
(3*R*,8a*R*)-Dimethyl 6-cyano-3-(1,3-dioxoisoindolin-2-yl)-2,3,8,8a-tetrahydroindolizine-1,1(7*H*)-dicarboxylate (**64**).

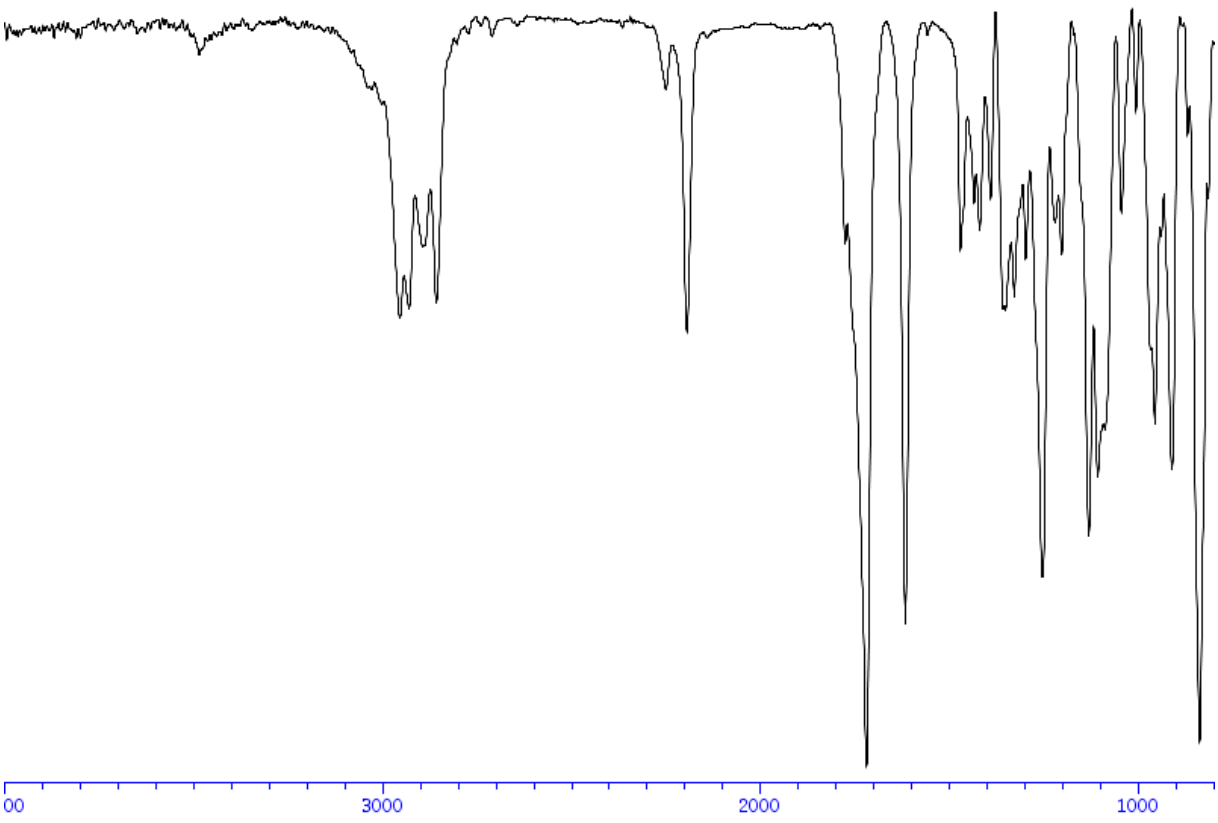




(3*R*,7*R*,8*S*,8a*S*)-Dimethyl 7,8-bis((*tert*-butyldimethylsilyl)oxy)-6-cyano-3-(1,3-dioxoisoindolin-2-yl)-2,3,8,8a-tetrahydroindolizine-1,1(7*H*)-dicarboxylate (**65**).




169.01
168.22
167.01
143.58
134.76
131.31
123.76
121.10
80.18
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
70.75
67.79
64.93
61.16
60.99
53.00
52.93
36.46
25.85
25.52
18.11
17.93
-3.19
-3.47
-4.79
-5.47
13C-NMR
101 MHz
CDCl3
f1 (ppm)


3000
2000
1000