Supplementary Information

Light-induced one-pot synthesis of pyrimidine derivatives from vinyl azides

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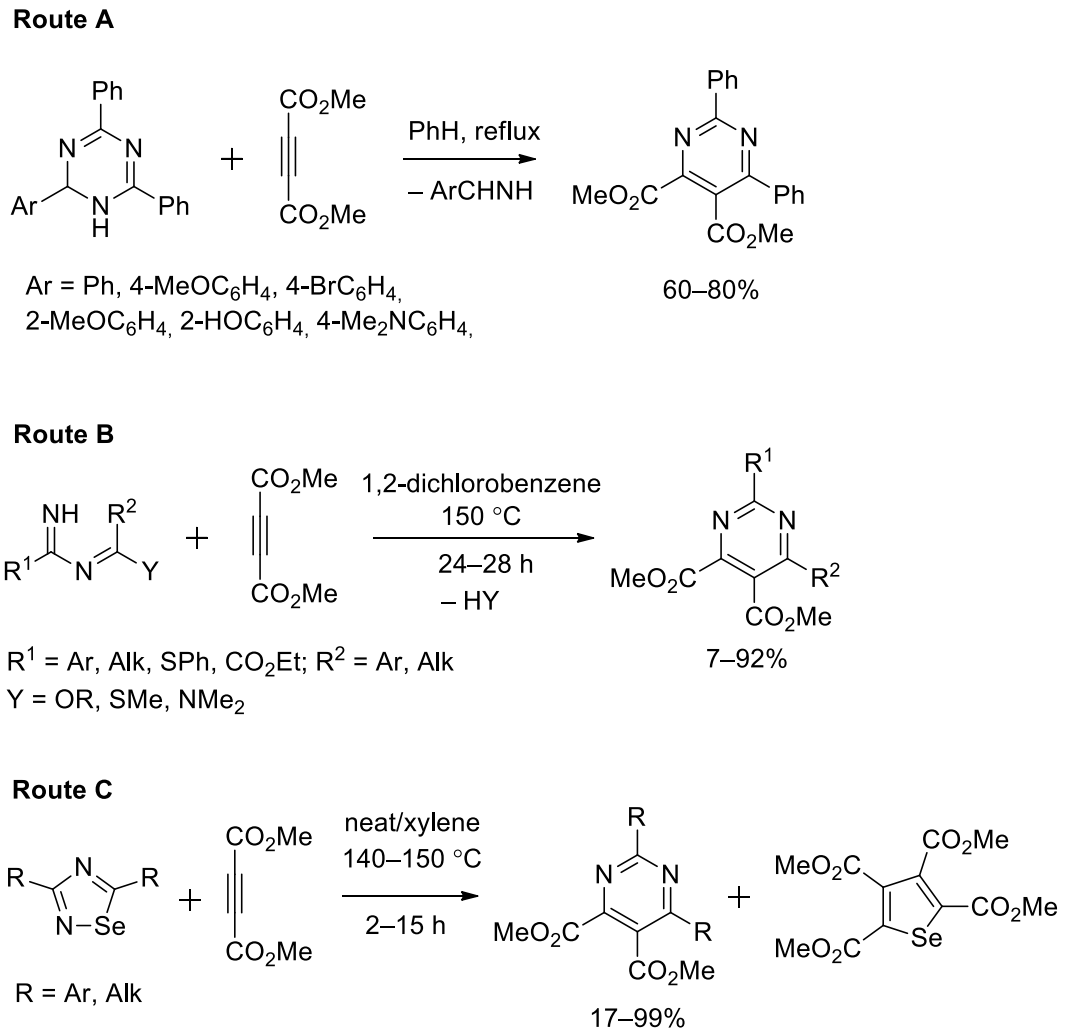
S1. Known approaches to the tetrasubstituted pyrimidine derivatives bearing aryl substituents at C2 and C4 and carbonyl substituents at C5 and C6



Scheme S1. Known approaches to the tetrasubstituted pyrimidine derivatives bearing aryl substituents at the C2 and C4 positions and carbonyl substituents at the C5 and C6 positions (Route A – ref. [1], Route B – ref. [2], Route C – ref. [3]).

S2. Irradiation of azidocinnamates

General information: for all photoreactions, a solution was purged with argon for 5–10 min, and then irradiated at RT. The LED was placed opposite to the solution at a distance of 2 cm from the tube. An evolution of nitrogen occurs in the reaction, and therefore **a reaction tube must not be closed tightly**.

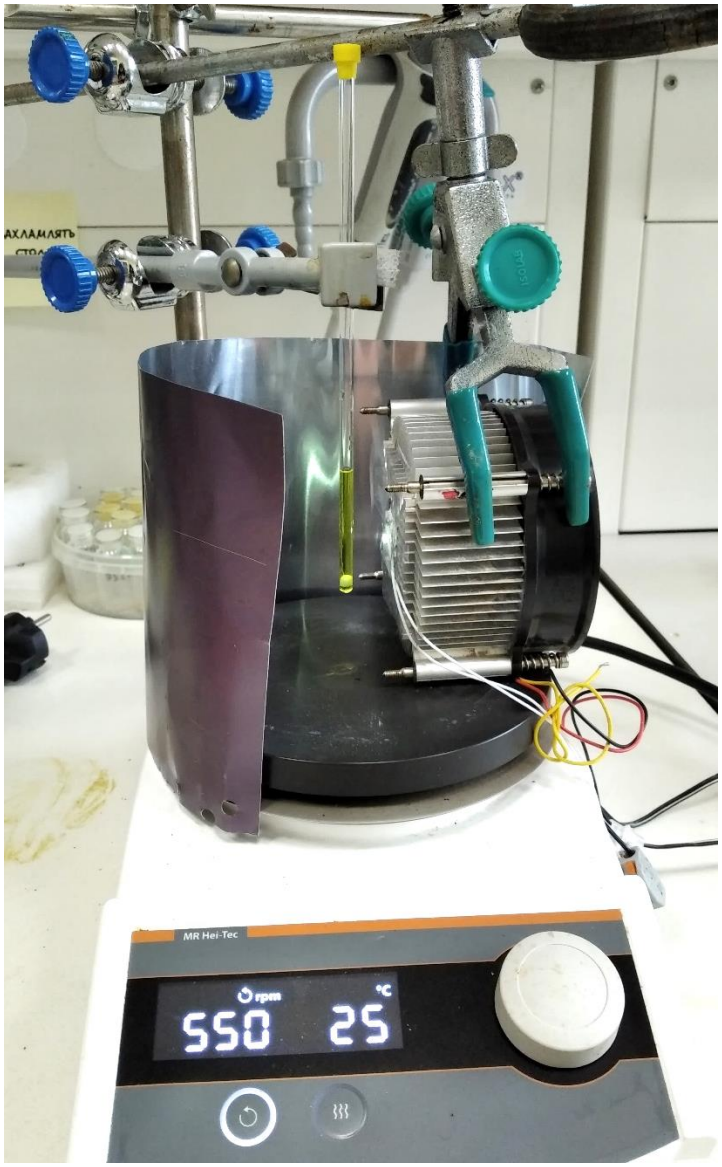


Figure S1. A typical setup for irradiation of azidocinnamates.

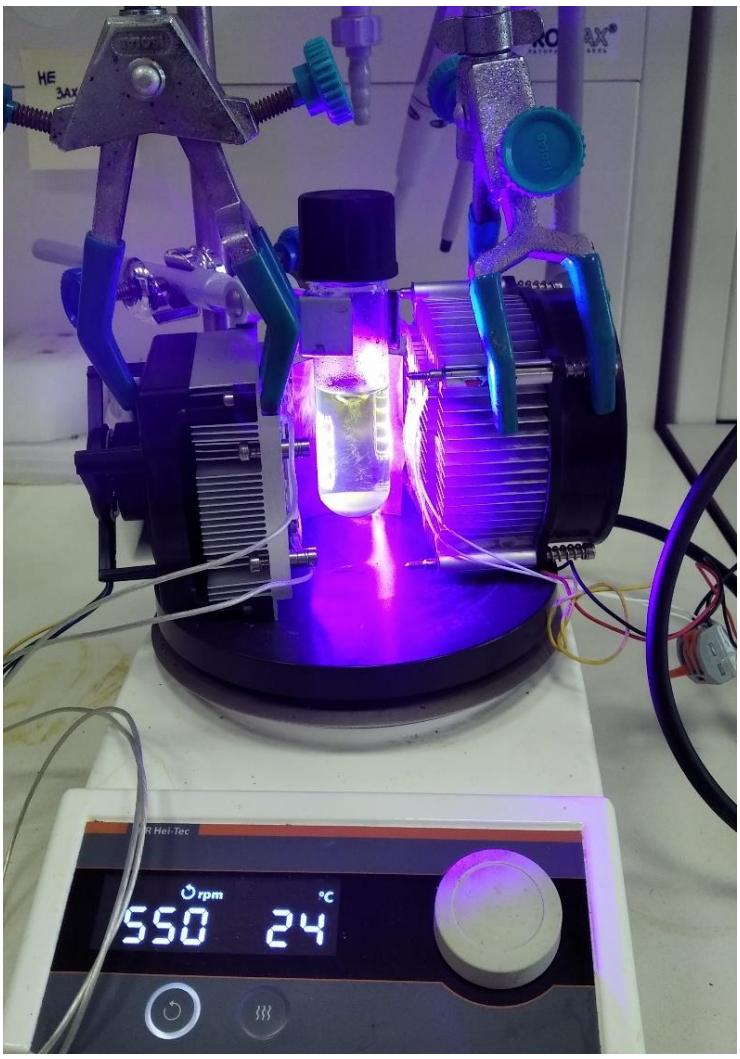
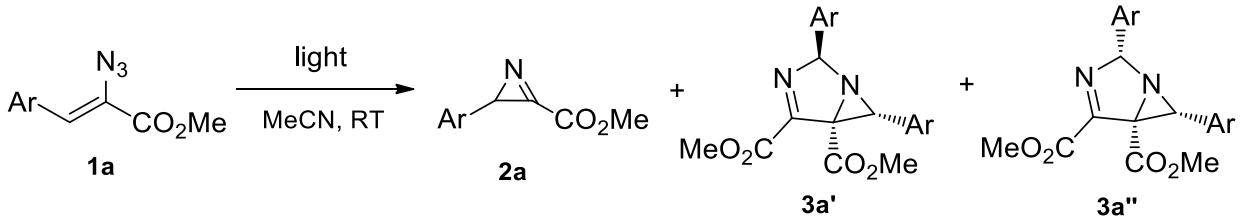


Figure S2. A setup for "gram scale" irradiation of azidocinnamates.

S2.1. Irradiation by different light sources

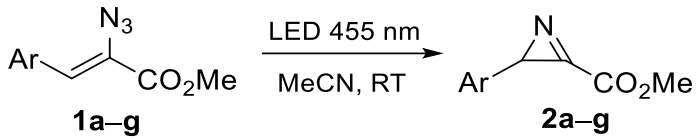


Scheme S2. Irradiation of azidocinnamate **1a** by different light sources.

Table S1. Irradiation of azidocinnamate **1a** by different light sources.

Light source	**^{1}H NMR conversion of 1a, %**	**^{1}H NMR yield of 2a, %**	**Overall ^{1}H NMR yield of 3a' and 3a'', %**
LED 465 nm, 3 W	0	0	0
LED 455 nm, 10 W	87	87	0
LED 425 nm, 3 W	98	49	49
LED 410 nm, 3 W	100	51	49
LED 395 nm, 3 W	100	0	*ca*. 100
LED 365 nm, 3 W	100	0	*ca*. 100
Natural sunlight	100	0	85
CFL, 30 W	78	55	23
254 nm, 30 W	80	75	5
Reaction conditions: azidocinnamate **1a** (15 mg, 0.063 mmol), MeCN (0.7 mL), in an NMR tube, 2.5 h.			

S2.2. Irradiation by blue light (LED 455 nm)



1a–g **2a–g**

Scheme S3. Irradiation of azidocinnamates **1a**–**g** by blue light (LED 455 nm).

Table S2. Irradiation of azidocinnamate **1a** by blue light (LED 455 nm) with photoredox catalysts.

Catalyst	**^{1}H NMR conversion of 1a, %**	**^{1}H NMR yield of 2a, %**
none	88	88
$[Ru(bpy)_3](BF_4)_2$	87	87
$[Ir(ppy)_2(CNC_6H_4\text{-}4\text{-}Cl)_2](OTf)$	85	85
Reaction conditions: azidocinnamate **1a** (15 mg, 0.063 mmol), catalyst (1 mg, *ca*. 3 mol %), MeCN (0.7 mL), in an NMR tube, LED 455 nm (3W), 2.5 h.		

Table S3. Irradiation of azidocinnamates **1a**–**g** by blue light (LED 455 nm).

Substrate	**Ar**	**Time, h**	**^{1}H NMR conversion of 1b–g, %**	**^{1}H NMR yield of azirines 2b–g, %**
1a	$4\text{-}ClC_6H_4$	2.5	88	88
1b	$4\text{-}BrC_6H_4$	4	100	85
1c	$4\text{-}IC_6H_4$	3	100	87
1d	$2\text{-}MeOC_6H_4$	4	100	76
1e	$4\text{-}MeOC_6H_4$	2.5	90	65[a]
1f	$2,4\text{-}Cl_2C_6H_3$	2.5	93	72
1g	$4\text{-}MeC_6H_4$	4	95	84
Reaction conditions: azidocinnamate **1a**–**g** (15 mg, 0.046–0.069 mmol), mixture of MeCN and CD_3CN (0.6 and 0.1 mL, respectively), in an NMR tube, LED 455 nm (10W). CH_2Br_2 (5 mkL) was added as a standard after the end of the irradiation. [a] Dimers **3e** (5%) were formed along with **2e**.				

General procedure for the synthesis of 2*H*-azirines 2a–g

Azidocinnamate **1a–g** (0.1 mmol) was dissolved in MeCN (0.7 mL) in an NMR tube or a Pyrex screw cap tube. The solution was purged by argon for 5 min and then irradiated with 455 nm LED (10W) at RT for 2.5 h. After irradiation, the solvent was removed on a rotary evaporator to give crude azirine **2a–g**. Compounds **2a–g** decomposed during standard column chromatography on silica gel.

Methyl 2-(4-chlorophenyl)-2*H*-azirine-3-carboxylate (2a)

^{1}H NMR (400 MHz, $CDCl_3$, δ) 3.46 (s, 1H, CH), 4.05 (s, 3H, CH_3), 7.08 (d, *J* = 8.5 Hz, 2H, H_{Ar}), 7.32 (d, *J* = 8.5 Hz, 2H, H_{Ar}).

Methyl 2-(4-bromophenyl)-2*H*-azirine-3-carboxylate (2b)

^{1}H NMR (400 MHz, $CDCl_3$, δ) 3.44 (s, 1H, CH), 4.04 (s, 3H, CH_3), 7.01 (d, *J* = 8.5 Hz, 2H, H_{Ar}), 7.46 (d, *J* = 8.5 Hz, 2H, H_{Ar}).

Methyl 2-(4-iodophenyl)-2*H*-azirine-3-carboxylate (2c)

^{1}H NMR (400 MHz, $CDCl_3$, δ) 3.42 (s, 1H, CH), 4.03 (s, 3H, CH_3), 6.88 (d, *J* = 8.4 Hz, 2H, H_{Ar}), 7.66 (d, *J* = 8.4 Hz, 2H, H_{Ar}).

Methyl 2-(2-methoxyphenyl)-2*H*-azirine-3-carboxylate (2d)

^{1}H NMR (400 MHz, $CDCl_3$, δ) 3.70 (s, 1H, CH), 3.82 (s, 3H, CH_3), 4.03 (s, 3H, CH_3), 6.86–6.93 (m, 2H, H_{Ar}), 6.97–6.99 (m, 1H, H_{Ar}), 7.23–7.28 (m, 1H, H_{Ar}).

Methyl 2-(4-methoxyphenyl)-2*H*-azirine-3-carboxylate (2e)

^{1}H NMR (400 MHz, $CDCl_3$, δ) 3.46 (s, 1H, CH), 3.80 (s, 3H, CH_3), 4.02 (s, 3H, CH_3), 6.87 (d, *J* = 8.7 Hz, 2H, H_{Ar}), 7.07 (d, *J* = 8.7 Hz, 2H, H_{Ar}).

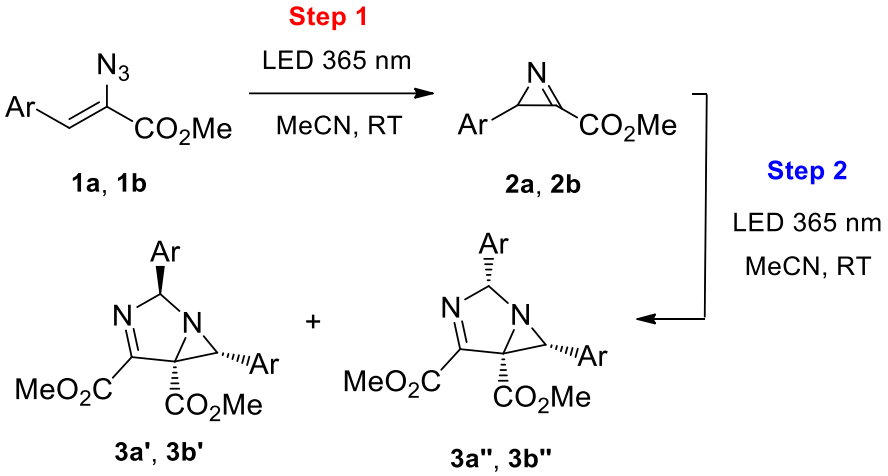
Methyl 2-(2,4-dichlorophenyl)-2*H*-azirine-3-carboxylate (2f)

^{1}H NMR (400 MHz, $CDCl_3$, δ) 3.80 (s, 1H, CH), 4.04 (s, 3H, CH_3), 6.75 (d, *J* = 8.4 Hz, 1H, H_{Ar}), 7.18–7.20 (m, 1H, H_{Ar}), 7.40–7.42 (m, 1H, H_{Ar}).

Methyl 2-(*p*-tolyl)-2*H*-azirine-3-carboxylate (2g)

^{1}H NMR (400 MHz, $CDCl_3$, δ) 2.35 (s, 3H, CH_3), 3.46 (s, 1H, CH), 4.02 (s, 3H, CH_3), 7.03 (d, *J* = 7.8 Hz, 2H, H_{Ar}), 7.15 (d, *J* = 7.8 Hz, 2H, H_{Ar}).

S2.3. Irradiation by UV-A light (LED 365 nm)



Scheme S4. Irradiation of azidocinnamats **1a** and **1b** by UV-A light (LED 365 nm).

Table S4. Irradiation of azidocinnamate **1a** by UV-A light (LED 365 nm).

Time	**^{1}H NMR conversion of 1a, %**	**^{1}H NMR yield of azirine 2a, %**	**Overall ^{1}H NMR yield of 3a' and 3a'', %**
15 min	25	25	0
30 min	47	42	5
1.5 h	100	56	44
2.5 h	100	0	*ca*. 100
Reaction conditions: azidocinnamate **1a** (15 mg, 0.063 mmol), mixture of MeCN and CD_3CN (0.6 and 0.1 mL, respectively), in an NMR tube, LED 365 nm (3W). CH_2Br_2 (5 mkL) was added as a standard after the end of the irradiation.			

Table S5. Irradiation of azidocinnamates **1a,b** by UV-A light (LED 365 nm).

Substrate	**^{1}H NMR conversion of 1, %**	**^{1}H NMR yield of 3a,b, % (preparative yield)**
1a	100	100 (80)
1b	100	100 (70)
Reaction conditions: azidocinnamate **1a**,**b** (15 mg, 0.046–0.069 mmol), mixture of MeCN and CD_3CN (0.6 and 0.1 mL, respectively), in an NMR tube, LED 365 nm (3W), 2.5 h.		

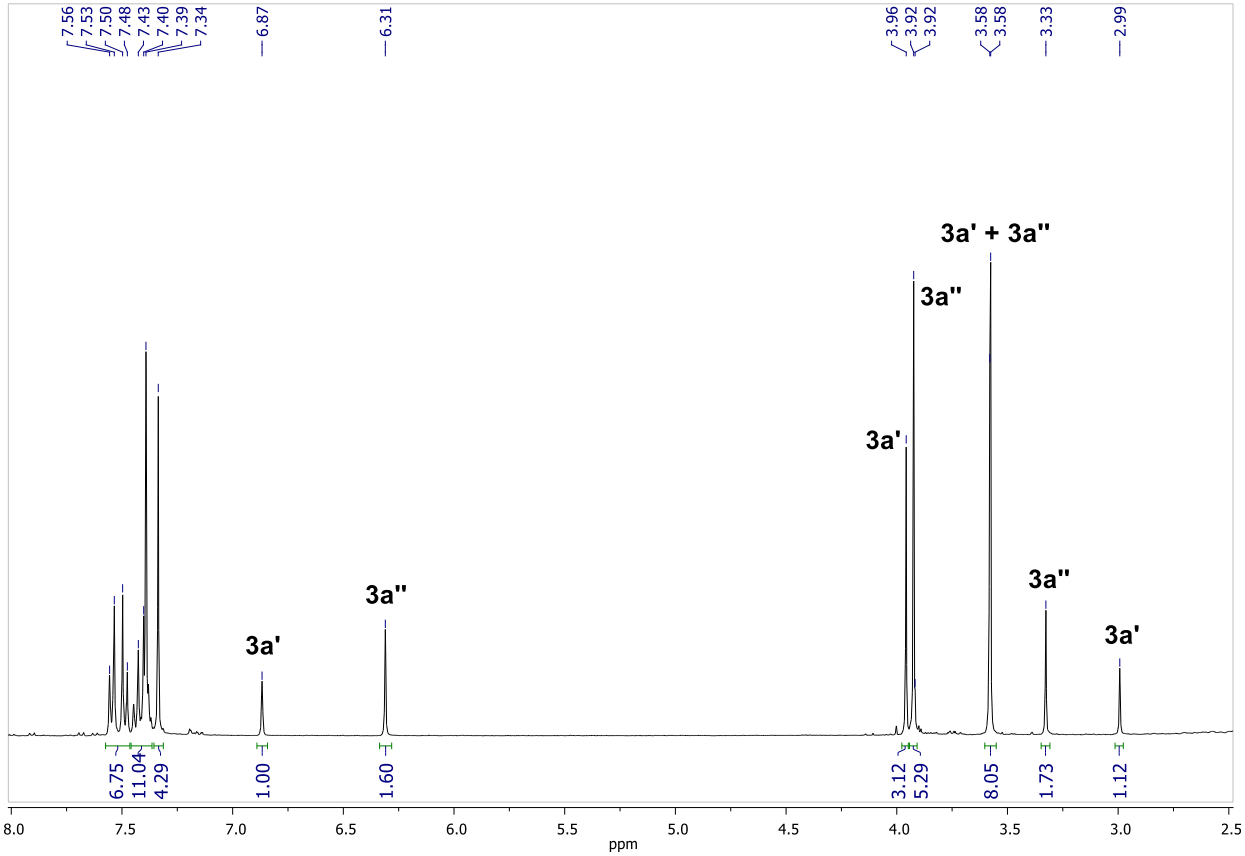
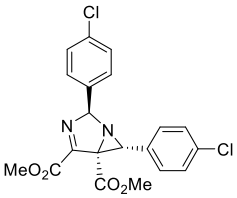


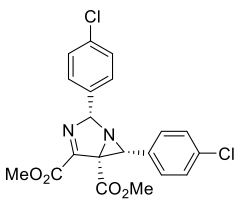
Figure S3. ^{1}H NMR spectrum (CD_3CN) of the reaction mixture after irradiation of azidocinnamate **1a** with 365 nm LED (3W) at RT for 2.5 h.

General procedure for the synthesis of diazabicyclo[3.1.0]hex-3-enes 3a,b

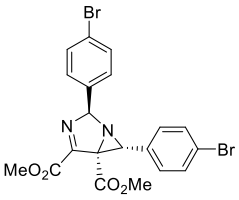
Azidocinnamate **1a,b** (0.1 mmol) was dissolved in MeCN (0.7 mL) in an NMR tube. The solution was purged by argon for 5 min and then irradiated with 365 nm LED (3W) at RT for 2.5 h. The solvent was removed on a rotary evaporator, and the products were purified by column chromatography on silica gel (PE – EtOAc, 3 : 1) to give separated diastereomers **3a'** and **3a"** or **3b'** and **3b"**.



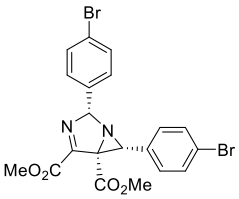
Compound **3a'**. Yellowish oil (6 mg, yield 30%). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 2.87 (s, 1H, CH), 3.61 (s, 3H, CH_3), 4.01 (s, 3H, CH_3) 6.85 (s, 1H, CH), 7.29–7.34 (m, 6H, H_{Ar}), 7.42 (d, J = 8.4 Hz, 2H, H_{Ar}). HR ESI^{+}-MS, *m/z*: $[M + H]^{+}$ calcd for $C_{20}H_{17}Cl_2N_2O_4^{+}$, 419.0560; found, 419.0588.



Compound **3a"**. Yellowish oil (10 mg, yield 50%). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 3.11 (s, 1H, CH), 3.60 (s, 3H, CH_3), 3.97 (s, 3H, CH_3) 6.17 (s, 1H, CH), 7.32 (d, J = 8.5 Hz, 2H, H_{Ar}), 7.38–7.42 (m, 4H, H_{Ar}), 7.52 (d, J = 8.5 Hz, 2H, H_{Ar}). HR ESI^{+}-MS, *m/z*: $[M + H]^{+}$ calcd for $C_{20}H_{17}Cl_2N_2O_4^{+}$, 419.0560; found 419.0588.



Compound **3b'**. Yellowish oil (6 mg, yield 25%). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 2.87 (s, 1H, CH), 3.61 (s, 3H, CH_3), 4.01 (s, 3H, CH_3) 6.85 (s, 1H, CH), 7.27–7.35 (m, 6H, H_{Ar}), 7.42 (d, *J* = 8.2 Hz, 2H, H_{Ar}).



Compound **3b"**. Yellowish oil (12 mg, yield 45%). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 3.11 (s, 1H, CH), 3.6 (s, 3H, CH_3), 3.97 (s, 3H, CH_3) 6.17 (s, 1H, CH), 7.32 (d, *J* = 8.5 Hz, 2H, H_{Ar}), 7.38–7.42 (m, 4H, H_{Ar}), 7.52 (d, J = 8.5 Hz, 2H, H_{Ar}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ) 52.7, 53.3, 53.7, 64.9, 97.3, 128.2 (2C), 128.3 (2C), 128.9 (2C), 129.1 (2C), 131.8, 134.3, 136.8, 161.3, 162.2, 164.8.

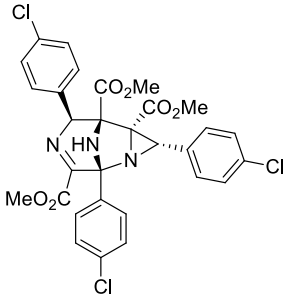
S2.4. Irradiation by UV-A light (LED 365 nm) with photocatalyst

Table S6. Irradiation of azidocinnamate **1a** by UV-A light (LED 365 nm) with photocatalyst.

Catalyst	**Time, h**	**Solvent**	**^{1}H NMR conversion of 1a, %**	**^{1}H NMR yield of 2a, %**	**^{1}H NMR overall yield of 3a' and 3a", %**	**^{1}H NMR yield of 4, %**
none	1	MeCN	100	48	52	0
$[Ir(ppy)_2(CNC_6H_4\text{-}4\text{-}Cl)_2](OTf)$, 1 mol %	1	MeCN	100	17	83	0
none	2.5	MeCN	100	0	*ca*. 100	0
$[Ir(ppy)_2(CNC_6H_4\text{-}4\text{-}Cl)_2](OTf)$, 1 mol %	2.5	MeCN	100	0	*ca*. 100	0
$[Ir(ppy)_2(CNC_6H_4\text{-}4\text{-}Cl)_2](OTf)$, 3 mol %	2.5	$CDCl_3$	100	0	85 (75% isolated yield)	7 (5% isolated yield)
Reaction conditions: azidocinnamate **1a** (15 mg, 0.063 mmol), photocatalyst, MeCN or $CDCl_3$ (0.7 mL), in an NMR tube, LED 365 nm (3W).						

Synthesis of (1*RS*,3*SR*,4*RS*,5*RS*,6*SR*)-trimethyl 1,3,6-tri(4-chlorophenyl)-2,7,9-triazatricyclo[3.3.1.0^{2,4}]non-7-ene-4,5,8-tricarboxylate (6)

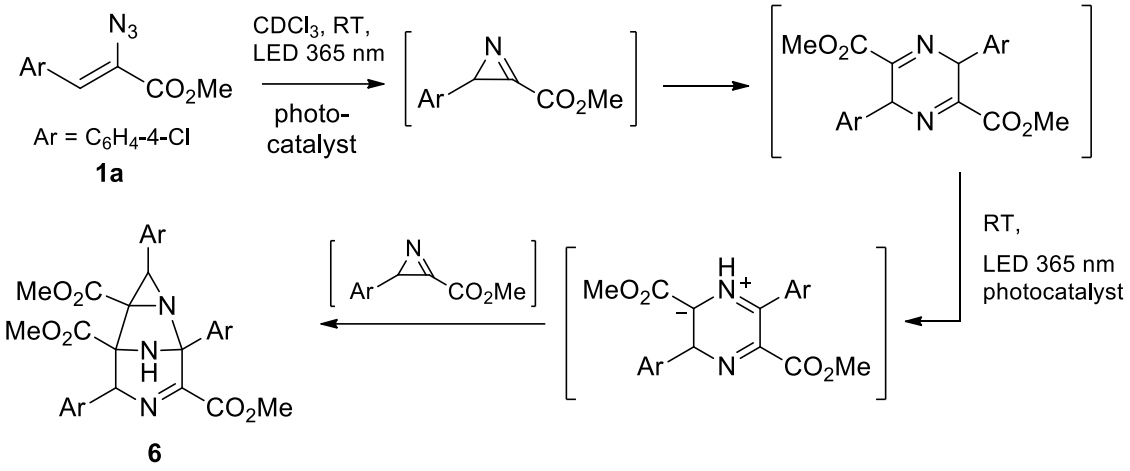
Azidocinnamate **1a** (24 mg, 0.1 mmol) and $[Ir(ppy)_2(CNC_6H_4\text{-}4\text{-}Cl)_2](OTf)$ (3 mg, 3 mol %) were dissolved in $CDCl_3$ (0.7 mL) in an NMR tube. The solution was purged by argon for 5 min and then irradiated with 365 nm LED (3W) at RT for 2.5 h. Three identical reactions were carried out. After that, the reaction mixtures were combined, the solvent was removed on a rotary evaporator, and the products were purified by column chromatography on silica gel (PE – EtOAc, 3 : 1) to give a mixture of **3a'**, **3a"** (47 mg, yield 75%) and **6** (3 mg, yield 5%).



Compound **6**. White solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 3.09 (s, 1H, CH), 3.48 (s, 1H, CH), 3.61 (s, 3H, CH_3), 3.65 (s, 3H, CH_3), 3.66 (s, 3H, CH_3), 5.32 (s, 1H, CH), 7.31–7.38 (m, 9H, NH, H_{Ar}), 7.48 (d, J = 8.6 Hz, 2H, H_{Ar}), 7.56 (d, J = 8.6 Hz, 2H, H_{Ar}). HR ESI$^+$-MS, *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{24}Cl_3N_3NaO_6^+$, 652.0593; found, 652.0628.

Single crystal X-ray data for compound **6** are given in section S4.

The tricyclic compound **6** has a structure different from previously described "trimer of azirine", generated by the photolysis of the azidocinnamates by middle ultraviolet [4]. We suggest that in the presence of the photocatalyst $[Ir(ppy)_2(CNC_6H_4\text{-}4\text{-}Cl)_2](OTf)$ [5, 6] the photochemical formation of dihydropyrazine occurs; subsequent cycloaddition of another one molecule of photogenerated azirine to this dihydropyrazine resulted in the tricyclic compound **6** (**Scheme S5**).



Scheme S5. Proposed mechanism for the formation of the tricyclic compound **6**.

S3. Isomerization to dihydropyrimidine

Table S7. Isomerization of **3a** into dihydropyrimidine **4a** by different bases.

Base	**Equiv.**	**Time, min**	**^{1}H NMR yield of 4a, %**
Pyridine	0.6	150	0
Trimethylamine	0.6	150	100
1,4-diazabicyclo[2.2.2]octane (DABCO)	0.6	100	100
N-methylmorpholine	0.5	15	100
1,8-diazabicyclo [5.4.0]undec-7-ene (DBU)	0.3	15	100
1,8-diazabicyclo [5.4.0]undec-7-ene (DBU)	0.2	15	100
1,8-diazabicyclo [5.4.0]undec-7-ene (DBU)	0.1	40	100
1,8-diazabicyclo [5.4.0]undec-7-ene (DBU)	0.05	60	100
Cs_2CO_3	0.5	45	100
Reaction conditions: base was added to a solution of dimers **3a** obtained by irradiation of azidocinnamate **1a** in MeCN. The reaction mixture was stirred till full conversion of **3a**.			

S4. Oxidation of dihydropyrimidine

Table S8. Oxidation of dihydropyrimidine **4a** to pyrimidine **5a** by different oxidants.

Entry	**Oxidation system**	**Time**	**^{1}H NMR yield of 5a, %**
1	air, reflux	1 day	0
2	air, LED 365 nm	10 h	0
3	air, LED 455 nm	10 h	0
4[a]	$[Ru(bpy)_3](BF_4)_2$, air , LED 455 nm	10 h	85
5[a]	$[Ru(bpy)_3](BF_4)_2$, O_2 (30%), LED 455 nm	4 h	85
6[a]	$[Ru(bpy)_3](BF_4)_2$, air, in dark	10 h	0
7	argon, LED 455 nm	10 h	0
8[b]	2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)	< 1 min	100

Reaction conditions: **4a** (20 mg, 0.047 mmol), MeCN (1 mL).

[a] $[Ru(bpy)_3](BF_4)_2$ (1 mg, 0.001 mmol) was added to the reaction mixture.

[b] 1 equiv of DDQ was added to the solution of **4a** in EtOAc (1 mL).

S5. X-ray structure determination

Single crystal X-ray data were collected by means of Agilent Technologies SuperNova (Single source at offset/far, HyPix3000), Agilent Technologies SuperNova (Dual, Cu at zero, Atlas) and Agilent Technologies Xcalibur (Mo, Eos) diffractometers. Structures have been solved by the Superflip [7, 8] structure solution program using Charge Flipping and refined by means of the ShelXL[9] program incorporated in the OLEX2 program package [10]. Empirical absorption correction was applied in CrysAlisPro (Agilent Technologies, 2012) program complex using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm. Crystallographic details are summarized in **Table S9**.

Table S9. Crystal data and structure refinements for **4d**, **4f** and **6**

Identification code	**4d**	**4f**	**6**
Empirical formula	$C_{22}H_{22}N_2O_6$	$C_{20}H_{14}Cl_4N_2O_4$	$C_{30}H_{24}Cl_3N_3O_6$
Formula weight	410.41	488.13	628.87
Temperature/K	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1$	P-1
a/Å	14.0485(3)	10.82480(10)	10.9534(8)
b/Å	13.9573(3)	16.44070(10)	12.5947(13)
c/Å	10.3547(3)	12.04070(10)	13.2276(10)
α/°	90	90	100.624(8)
β/°	99.580(2)	109.7710(10)	113.849(7)
γ/°	90	90	110.012(8)
Volume/Å^3	2002.03(8)	2016.53(3)	1453.4(2)
Z	4	4	2
ρ_{calc}g/cm^3	1.362	1.608	1.437
μ/mm^{-1}	0.100	5.619	3.272
F(000)	864.0	992.0	648.0
Crystal size/mm^3	0.41 × 0.32 × 0.3	0.1 × 0.08 × 0.04	0.34 × 0.28 × 0.18
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.402 to 54.998	7.802 to 140.896	7.884 to 152.83
Index ranges	-17 ≤ h ≤ 18, -18 ≤ k ≤ 16, -13 ≤ l ≤ 13	-13 ≤ h ≤ 13, -19 ≤ k ≤ 20, -14 ≤ l ≤ 14	-13 ≤ h ≤ 10, -15 ≤ k ≤ 15, -15 ≤ l ≤ 16
Reflections collected	13770	25202	10997
Independent reflections	4451 [R_{int} = 0.0318, R_{sigma} = 0.0368]	7584 [R_{int} = 0.0333, R_{sigma} = 0.0326]	5941 [R_{int} = 0.0482, R_{sigma} = 0.0549]
Data/restraints/parameters	4451/0/279	7584/1/553	5941/0/382
Goodness-of-fit on F^2	1.022	1.031	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0415, wR_2 = 0.0923	R_1 = 0.0233, wR_2 = 0.0580	R_1 = 0.0630, wR_2 = 0.1702

Final R indexes [all data]	R_1 = 0.0553, wR_2 = 0.0991	R_1 = 0.0241, wR_2 = 0.0585	R_1 = 0.0780, wR_2 = 0.1833
Largest diff. peak/hole / e Å^{-3}	0.29/-0.22	0.18/-0.20	1.25/-0.69
CCDC numbers	1994004	1994005	1994003

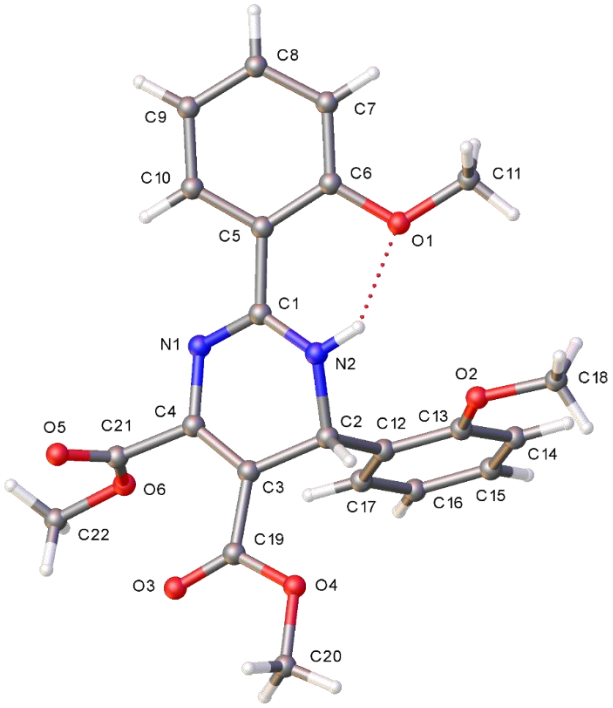


Figure S4. View of **4d** with the atomic numbering scheme. Thermal ellipsoids are drawn with the 50% probability. Hydrogen labels are omitted for simplicity.

Table S10. Bond Lengths for **4d**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C13	1.3707(17)	C4	C21	1.5085(19)
O2	C18	1.4273(17)	C3	C19	1.4672(19)
O1	C6	1.3729(16)	C3	C2	1.5031(18)
O1	C11	1.4318(17)	C6	C5	1.4114(19)
O6	C21	1.3358(17)	C6	C7	1.3925(19)
O6	C22	1.4495(17)	C5	C10	1.395(2)
O4	C19	1.3424(17)	C12	C2	1.5252(19)
O4	C20	1.4459(16)	C12	C17	1.3883(19)
O5	C21	1.1967(17)	C12	C13	1.4015(19)
N2	C1	1.3342(18)	C7	C8	1.386(2)
N2	C2	1.4769(16)	C10	C9	1.3875(19)
N1	C1	1.3243(17)	C17	C16	1.394(2)
N1	C4	1.3833(17)	C13	C14	1.389(2)
O3	C19	1.2114(18)	C14	C15	1.394(2)
C1	C5	1.4918(18)	C9	C8	1.382(2)
C4	C3	1.3524(19)	C16	C15	1.379(2)

Table S11. Bond Angles for **4d**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	O2	C18	117.39(11)	C10	C5	C1	117.72(12)
C6	O1	C11	117.82(11)	C10	C5	C6	117.95(12)
C21	O6	C22	115.81(11)	C17	C12	C2	123.07(12)
C19	O4	C20	116.37(11)	C17	C12	C13	118.81(13)
C1	N2	C2	122.15(11)	C13	C12	C2	118.10(12)
C1	N1	C4	115.26(12)	O4	C19	C3	111.32(12)
N2	C1	C5	118.94(12)	O3	C19	O4	123.37(13)
N1	C1	N2	123.61(12)	O3	C19	C3	125.30(14)
N1	C1	C5	117.37(12)	N2	C2	C3	106.97(11)
N1	C4	C21	112.42(12)	N2	C2	C12	109.93(11)
C3	C4	N1	125.20(12)	C3	C2	C12	113.55(11)
C3	C4	C21	122.38(12)	C8	C7	C6	119.76(13)
C4	C3	C19	121.42(12)	C9	C10	C5	122.06(14)
C4	C3	C2	118.22(12)	C12	C17	C16	120.95(14)
C19	C3	C2	120.28(12)	O2	C13	C12	114.44(12)
O6	C21	C4	109.85(11)	O2	C13	C14	124.75(13)
O5	C21	O6	124.45(13)	C14	C13	C12	120.79(13)
O5	C21	C4	125.58(13)	C13	C14	C15	119.04(14)
O1	C6	C5	117.18(11)	C8	C9	C10	118.71(14)
O1	C6	C7	122.54(12)	C15	C16	C17	119.29(14)
C7	C6	C5	120.27(13)	C9	C8	C7	121.24(13)
C6	C5	C1	124.31(12)	C16	C15	C14	121.12(14)

Table S12. Hydrogen bonds for **4d** [Å and °].

N−H•••O	d(H•••O)	d(N•••O)	∠(N−H−O)
N2−H•••O1	2.02	2.6825(15)	127

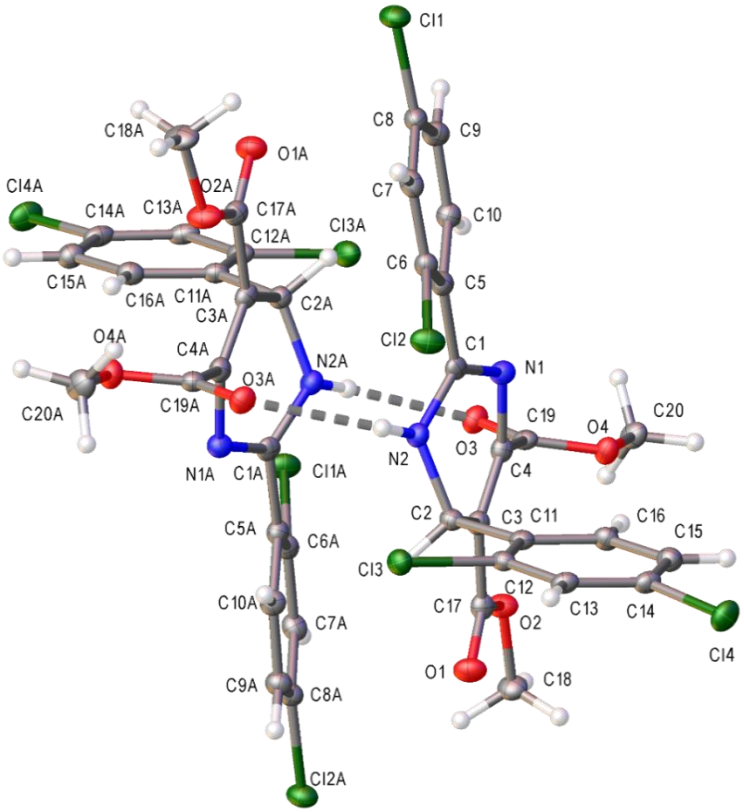


Figure S5. View of **4f** with the atomic numbering scheme. Thermal ellipsoids are drawn with the 50% probability. Hydrogen labels are omitted for simplicity.

Table S13. Bond Lengths for **4f**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl3	C12	1.741(3)	C19A	C4A	1.508(4)
Cl2A	C8A	1.739(3)	C19	C4	1.512(4)
Cl1	C8	1.738(3)	C4	C3	1.354(4)
Cl2	C6	1.744(3)	C2	C3	1.510(4)
Cl3A	C12A	1.742(3)	C2	C11	1.528(4)
Cl1A	C6A	1.741(3)	C5A	C1A	1.485(4)
Cl4	C14	1.738(3)	C5A	C10A	1.399(4)
Cl4A	C14A	1.736(3)	C5A	C6A	1.406(4)
O3A	C19A	1.215(3)	C7A	C6A	1.386(4)
O4	C19	1.326(3)	C7A	C8A	1.390(4)
O4	C20	1.451(3)	C16	C15	1.386(4)
O3	C19	1.209(3)	C16	C11	1.392(4)
O4A	C19A	1.323(3)	C15	C14	1.390(4)
O4A	C20A	1.448(3)	C15A	C16A	1.395(4)
O2	C17	1.347(3)	C15A	C14A	1.381(4)
O2	C18	1.444(3)	C10A	C9A	1.384(4)
O1A	C17A	1.213(4)	C13	C12	1.390(4)
O1	C17	1.208(4)	C13	C14	1.386(4)
O2A	C17A	1.340(3)	C7	C6	1.387(4)

O2A	C18A	1.441(3)	C7	C8	1.380(4)
N1A	C1A	1.317(4)	C10	C9	1.383(4)
N1A	C4A	1.384(4)	C3A	C4A	1.350(4)
N2	C1	1.341(4)	C3A	C2A	1.509(3)
N2	C2	1.473(3)	C12	C11	1.398(4)
N2A	C1A	1.342(4)	C3	C17	1.465(4)
N2A	C2A	1.471(3)	C11A	C12A	1.396(4)
N1	C1	1.318(4)	C11A	C2A	1.520(4)
N1	C4	1.385(4)	C11A	C16A	1.390(4)
C5	C1	1.485(4)	C9	C8	1.384(4)
C5	C10	1.405(4)	C13A	C12A	1.385(4)
C5	C6	1.407(4)	C13A	C14A	1.389(4)
C17A	C3A	1.475(4)	C9A	C8A	1.384(4)

Table S14. Bond Angles for **4f**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C19	O4	C20	114.6(2)	C13	C12	Cl3	117.1(2)
C19A	O4A	C20A	115.2(2)	C13	C12	C11	122.5(3)
C17	O2	C18	114.6(2)	C11	C12	Cl3	120.4(2)
C17A	O2A	C18A	116.3(2)	C4	C3	C2	116.8(2)
C1A	N1A	C4A	115.2(2)	C4	C3	C17	126.9(2)
C1	N2	C2	119.8(2)	C17	C3	C2	116.1(2)
C1A	N2A	C2A	119.7(2)	C12A	C11A	C2A	121.0(2)
C1	N1	C4	115.1(2)	C16A	C11A	C12A	117.3(2)
C10	C5	C1	116.5(2)	C16A	C11A	C2A	121.6(2)
C10	C5	C6	116.8(3)	C10	C9	C8	118.7(3)
C6	C5	C1	126.7(2)	C16	C11	C2	122.4(2)
O1A	C17A	O2A	123.9(2)	C16	C11	C12	117.1(2)
O1A	C17A	C3A	123.1(3)	C12	C11	C2	120.5(2)
O2A	C17A	C3A	113.0(2)	C12A	C13A	C14A	117.7(2)
O3A	C19A	O4A	125.4(3)	C5	C6	Cl2	122.2(2)
O3A	C19A	C4A	122.0(2)	C7	C6	Cl2	115.9(2)
O4A	C19A	C4A	112.5(2)	C7	C6	C5	121.9(3)
N2	C1	C5	120.1(2)	C10A	C9A	C8A	118.6(3)
N1	C1	N2	122.8(2)	C11A	C12A	Cl3A	119.8(2)
N1	C1	C5	117.0(2)	C13A	C12A	Cl3A	117.5(2)
O4	C19	C4	112.2(2)	C13A	C12A	C11A	122.7(3)
O3	C19	O4	124.9(2)	N1A	C4A	C19A	110.7(2)
O3	C19	C4	122.8(2)	C3A	C4A	N1A	124.9(2)
N1	C4	C19	110.5(2)	C3A	C4A	C19A	124.3(2)
C3	C4	N1	125.0(2)	N2A	C2A	C3A	107.2(2)
C3	C4	C19	124.3(2)	N2A	C2A	C11A	110.3(2)
N2	C2	C3	107.2(2)	C3A	C2A	C11A	113.8(2)
N2	C2	C11	110.9(2)	C7	C8	Cl1	120.0(2)
C3	C2	C11	113.8(2)	C7	C8	C9	121.7(3)
C10A	C5A	C1A	117.0(2)	C9	C8	Cl1	118.2(2)

C10A	C5A	C6A	117.1(2)	C15	C14	Cl4	119.3(2)
C6A	C5A	C1A	125.8(2)	C13	C14	Cl4	118.7(2)
C6A	C7A	C8A	118.2(2)	C13	C14	C15	121.9(3)
C15	C16	C11	122.2(2)	O2	C17	C3	113.7(2)
C16	C15	C14	118.4(3)	O1	C17	O2	123.3(3)
C14A	C15A	C16A	118.5(3)	O1	C17	C3	123.0(2)
N1A	C1A	N2A	122.8(2)	C11A	C16A	C15A	121.8(3)
N1A	C1A	C5A	116.5(2)	C5A	C6A	Cl1A	122.0(2)
N2A	C1A	C5A	120.6(2)	C7A	C6A	Cl1A	115.9(2)
C9A	C10A	C5A	122.1(3)	C7A	C6A	C5A	122.0(2)
C14	C13	C12	117.8(2)	C7A	C8A	Cl2A	119.4(2)
C8	C7	C6	118.7(3)	C9A	C8A	Cl2A	118.6(2)
C9	C10	C5	122.1(3)	C9A	C8A	C7A	122.0(3)
C17A	C3A	C2A	116.1(2)	C15A	C14A	Cl4A	119.2(2)
C4A	C3A	C17A	126.0(2)	C15A	C14A	C13A	122.0(3)
C4A	C3A	C2A	117.5(2)	C13A	C14A	Cl4A	118.7(2)

Table S15. Hydrogen bonds for **4f** [Å and °].

N−H•••O	d(H•••O)	d(N•••O)	∠(N−H−O)
N2−H•••O3A	2.36	3.098(3)	151
N2A−H•••O3	2.21	2.965(3)	153

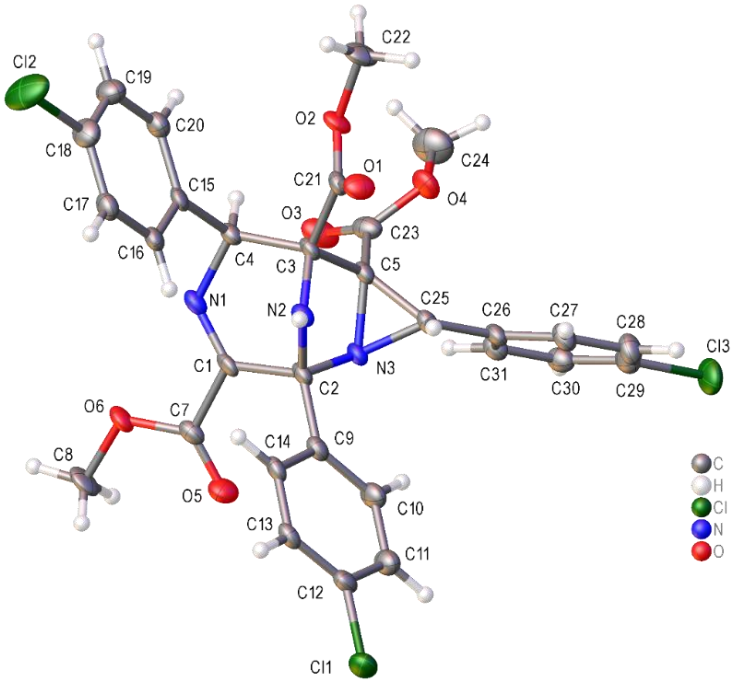


Figure S6. View of **6** with the atomic numbering scheme. Thermal ellipsoids are drawn with the 50% probability. Hydrogen labels are omitted for simplicity.

Table S16. Bond Lengths for **6**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C12	1.746(3)	C15	C4	1.524(4)
Cl3	C29	1.743(4)	C15	C16	1.391(5)
Cl2	C18	1.739(3)	C15	C20	1.393(5)
O6	C7	1.338(4)	C9	C14	1.387(4)
O6	C8	1.453(3)	C9	C2	1.510(4)
O2	C21	1.323(4)	C9	C10	1.391(5)
O2	C22	1.452(4)	C1	C7	1.518(4)
O1	C21	1.211(4)	C1	C2	1.535(4)
O5	C7	1.201(4)	C16	C17	1.389(4)
O4	C23	1.316(4)	C14	C13	1.387(5)
O4	C24	1.462(5)	C31	C26	1.393(5)
O3	C23	1.209(5)	C31	C30	1.384(4)
N2	C3	1.452(4)	C25	C26	1.484(4)
N2	C2	1.459(4)	C26	C27	1.394(5)
N3	C5	1.474(4)	C12	C13	1.379(5)
N3	C2	1.500(4)	C12	C11	1.385(5)
N3	C25	1.492(4)	C10	C11	1.383(5)
N1	C4	1.481(3)	C30	C29	1.388(5)
N1	C1	1.268(4)	C20	C19	1.392(5)
C5	C3	1.564(4)	C17	C18	1.387(5)
C5	C25	1.503(4)	C27	C28	1.386(5)
C5	C23	1.499(5)	C28	C29	1.380(5)
C3	C4	1.552(4)	C19	C18	1.376(5)
C3	C21	1.509(4)			

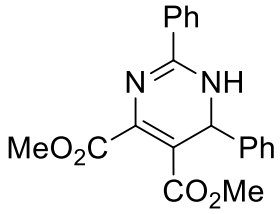
Table S17. Bond Angles for **6**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	O6	C8	115.1(3)	O5	C7	C1	123.4(3)
C21	O2	C22	116.1(3)	C17	C16	C15	121.0(3)
C23	O4	C24	112.9(3)	C13	C14	C9	121.1(3)
C3	N2	C2	101.9(2)	N2	C2	N3	108.5(2)
C5	N3	C2	103.4(2)	N2	C2	C9	110.5(3)
C5	N3	C25	60.88(19)	N2	C2	C1	104.7(2)
C25	N3	C2	112.4(2)	N3	C2	C9	112.9(2)
C1	N1	C4	119.6(3)	N3	C2	C1	102.6(2)
N3	C5	C3	106.3(2)	C9	C2	C1	117.0(2)
N3	C5	C25	60.15(19)	C30	C31	C26	120.8(3)
N3	C5	C23	117.5(3)	N3	C25	C5	58.97(18)
C25	C5	C3	115.3(3)	C26	C25	N3	116.4(3)
C23	C5	C3	119.0(3)	C26	C25	C5	124.4(3)
C23	C5	C25	122.6(3)	C31	C26	C25	122.6(3)
N2	C3	C5	103.7(2)	C31	C26	C27	118.9(3)
N2	C3	C4	105.7(2)	C27	C26	C25	118.4(3)
N2	C3	C21	112.4(3)	C13	C12	Cl1	118.9(3)
C4	C3	C5	110.7(2)	C13	C12	C11	121.9(3)
C21	C3	C5	112.5(2)	C11	C12	Cl1	119.2(3)
C21	C3	C4	111.4(2)	C11	C10	C9	120.3(3)
C16	C15	C4	121.4(3)	C31	C30	C29	119.0(3)
C16	C15	C20	119.1(3)	C19	C20	C15	120.6(3)
C20	C15	C4	119.5(3)	C18	C17	C16	118.4(3)
C14	C9	C2	118.5(3)	C28	C27	C26	120.7(3)
C14	C9	C10	119.4(3)	O4	C23	C5	112.3(3)
C10	C9	C2	122.1(3)	O3	C23	O4	125.3(3)
N1	C4	C3	112.1(2)	O3	C23	C5	122.4(3)
N1	C4	C15	108.6(2)	C12	C13	C14	118.3(3)
C15	C4	C3	111.8(3)	C29	C28	C27	119.2(3)
O2	C21	C3	110.6(3)	C10	C11	C12	119.1(3)
O1	C21	O2	125.1(3)	C30	C29	Cl3	119.2(3)
O1	C21	C3	124.3(3)	C28	C29	Cl3	119.4(3)
N1	C1	C7	117.5(3)	C28	C29	C30	121.4(3)
N1	C1	C2	123.6(2)	C18	C19	C20	118.9(3)
C7	C1	C2	118.8(3)	C17	C18	Cl2	118.8(3)
O6	C7	C1	112.1(3)	C19	C18	Cl2	119.2(3)
O5	C7	O6	124.5(3)	C19	C18	C17	122.0(3)

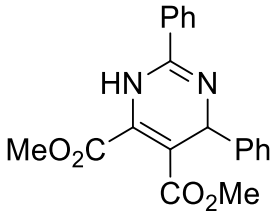
S6. Calculation details

All calculations were performed by using the Gaussian 09 suite of quantum chemical programs [11]. Geometry optimizations of stationary points were performed at the DFT B3LYP/6-31G(d) level using PCM model for acetonitrile (298.15K).

Table S18. Energies (au) and Cartesian coordinates of stationary points for conformers of 1,6-dihydropyrimidine **4l** and 1,4-dihydropyrimidine **4l'** (B3LYP/6-31G(d), PCM, acetonitrile).

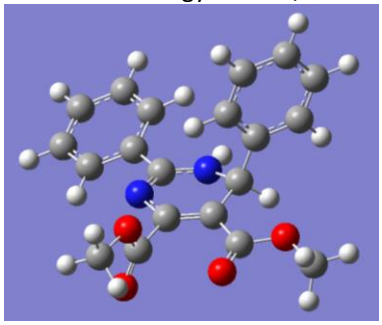


4l



4l'

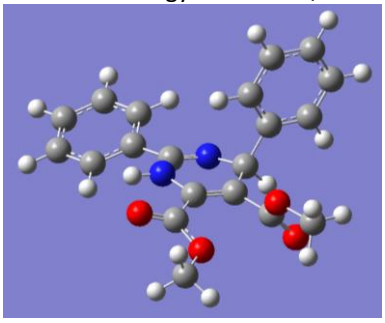
4l (conformation 1)
Relative energy = **0** kcal/mol



Sum of electronic and zero-point Energies = -1183.040169
Sum of electronic and thermal Energies = -1183.016701
Sum of electronic and thermal Enthalpies = -1183.015757
Sum of electronic and thermal Free Energies = -1183.096559
Imaginary frequency = 0.

N	-1.00902000	-1.27975800	0.13648200
C	0.34355900	-1.39808100	-0.08000700
C	1.14556700	-0.44109100	-0.62931200
C	0.55315100	0.91537400	-0.96797800
N	-0.91179800	0.73678400	-1.05648200
C	-1.59242400	-0.22141400	-0.39890600
C	0.91273000	2.03010200	0.01621700
C	-3.06738000	-0.10101200	-0.31254900
C	-3.70924600	1.14811800	-0.34609400
C	-5.09921900	1.22666600	-0.26521800
C	-5.86172300	0.06219200	-0.15008900
C	-5.22875500	-1.18399700	-0.10689300
C	-3.84095600	-1.26642700	-0.18378600
C	0.90537800	1.80920700	1.40018400
C	1.19409800	2.84982800	2.28407300

4l' (conformation 1)
Relative energy = **4.27** kcal/mol



Sum of electronic and zero-point Energies = -1183.033359
Sum of electronic and thermal Energies = -1183.009789
Sum of electronic and thermal Enthalpies = -1183.008845
Sum of electronic and thermal Free Energies = -1183.090685
Imaginary frequency = 0.

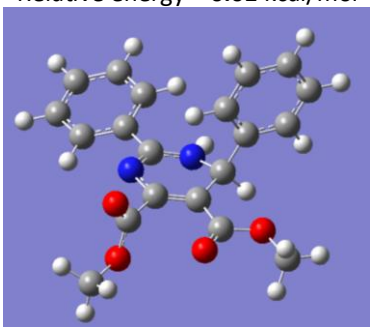
N	-0.95542200	-1.10011400	0.36536300
C	0.40066100	-1.28403700	0.11518800
C	1.08833600	-0.33365500	-0.55111500
C	0.35644400	0.93247300	-1.00518600
N	-1.10674000	0.80107300	-1.01410400
C	-1.66504000	-0.12341800	-0.31503900
C	0.77457100	2.15009300	-0.17586200
C	-3.14991500	-0.19429800	-0.22241800
C	-3.89463000	0.98929200	-0.34376700
C	-5.28509900	0.96015000	-0.26686900
C	-5.95260800	-0.25270300	-0.07076100
C	-5.22048300	-1.43582200	0.04378100
C	-3.82702200	-1.40867100	-0.03044300
C	0.59510000	2.17031400	1.21499800
C	0.96718200	3.28795600	1.96215400

C	1.49665600	4.12371000	1.79460400
C	1.50953800	4.35149600	0.41678600
C	1.21854700	3.30874900	-0.46531800
C	0.85554900	-2.76467300	0.32329900
O	0.72510100	-3.76067700	-0.35748800
O	1.35337100	-2.74591900	1.56663200
C	1.83666300	-4.01053000	2.06578900
C	2.56583000	-0.70615700	-0.88037100
O	3.15022500	-1.75189500	-0.62496900
O	3.18214400	0.35447200	-1.45058300
C	4.57870500	0.18328000	-1.75128300
H	-1.43085800	1.46357300	-1.53172800
H	-3.12957600	2.06536300	-0.39663700
H	-5.58435400	2.19810500	-0.28253300
H	-6.94446500	0.12532800	-0.08900100
H	-5.81839400	-2.09165000	-0.01612700
H	-3.33787100	-2.22639800	-0.15291700
H	0.68236500	0.81901700	1.78809000
H	1.18653400	2.66558400	3.35496700
H	1.72443400	4.93246600	2.48355500
H	1.74948200	5.33757600	0.02838400
H	1.23259300	3.48852700	-1.53816500
H	2.66382800	-4.36535600	1.44633800
H	2.17739300	-3.81117000	3.08113000
H	1.03490000	-4.75243300	2.06798600
H	4.72029000	-0.63796300	-2.45835000
H	4.89894800	1.12647400	-2.19319200
H	5.14387900	-0.02311500	-0.83909300
H	0.89228000	1.22700100	-1.96033600

C	1.52703000	4.40190600	1.32875900
C	1.71060700	4.39049800	-0.05501800
C	1.33473600	3.27013200	-0.80084900
C	0.87764500	-2.61734400	0.59860900
O	0.22602800	-3.27613000	1.39212900
O	2.02317000	-3.01310700	0.04657600
C	2.53065000	-4.29297900	0.48706400
C	2.52785500	-0.39860500	-0.92748300
O	2.92277400	-0.25547300	-2.07145000
O	3.33832200	-0.52130600	0.13524700
C	4.74934700	-0.58797900	-0.15639200
H	-3.36605500	1.92464000	-0.49247900
H	-5.84905900	1.88449600	-0.35496200
H	-7.03702400	-0.27496000	-0.00956100
H	-5.73184400	-2.38372900	0.18430600
H	-3.27980200	-2.34531600	0.02816200
H	0.16240300	1.30907600	1.71735800
H	0.82198100	3.28981400	3.03915700
H	1.81784700	5.27178200	1.91139200
H	2.14488500	5.25177100	-0.55562300
H	1.47660300	3.26643000	-1.87913000
H	1.81069000	-5.08085600	0.25650600
H	3.45531400	-4.44054300	-0.06827400
H	2.72381800	-4.27147800	1.56162800
H	5.07301200	0.31295700	-0.68245800
H	5.24184300	-0.66384500	0.81236500
H	4.96845500	-1.46703100	-0.76741000
H	0.67067400	1.13122600	-2.03766100
H	-1.42316400	-1.83281200	0.88175500

4l (conformation 2)

Relative energy = **0.01** kcal/mol



Sum of electronic and zero-point Energies = -1183.040153

Sum of electronic and thermal Energies = -1183.016787

Sum of electronic and thermal Enthalpies = -1183.015843

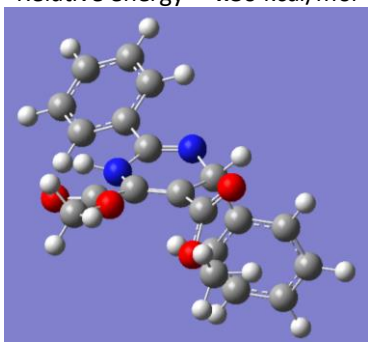
Sum of electronic and thermal Free Energies = -1183.095804

Imaginary frequency = 0.

N	1.00000200	1.19321000	0.34968000
C	-0.35803800	1.34109000	0.19031100
C	-1.18591100	0.44630400	-0.42069600
C	-0.61218900	-0.86606400	-0.92654400
N	0.84820600	-0.67884500	-1.05441400
C	1.55784900	0.19851300	-0.31803000
C	-0.94102900	-2.07777300	-0.05298300

4l' (conformation 2)

Relative energy = **4.30** kcal/mol



Sum of electronic and zero-point Energies = -1183.033313

Sum of electronic and thermal Energies = -1183.009831

Sum of electronic and thermal Enthalpies = -1183.008887

Sum of electronic and thermal Free Energies = -1183.090216

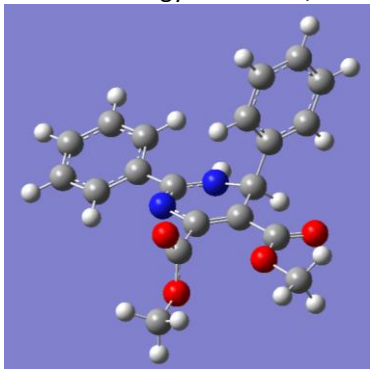
Imaginary frequency = 0.

N	-1.02287500	1.06308100	0.38066300
C	0.32496000	1.29588400	0.10783700
C	1.05139500	0.36003200	-0.53637100
C	0.37106500	-0.93877300	-0.97891500
N	-1.09253500	-0.87715000	-0.96152100
C	-1.68863700	0.04137400	-0.28972400
C	0.87079400	-2.12557900	-0.14937500

C	3.03380800	0.06348600	-0.29379400
C	3.66486600	-1.17562900	-0.49325200
C	5.05600600	-1.26890500	-0.46649500
C	5.83079500	-0.12920600	-0.23977100
C	5.20909100	1.10577900	-0.03075900
C	3.82026400	1.20251100	-0.05407100
C	-0.83749800	-2.01464800	1.34356000
C	-1.10518400	-3.13981800	2.12421300
C	-1.48300400	-4.34148600	1.51803600
C	-1.59180100	-4.41202000	0.12755200
C	-1.32110000	-3.28486800	-0.65151600
C	-0.85639900	2.62668700	0.81453000
O	-1.06471000	2.75186000	2.00369000
O	-0.91665900	3.61772800	-0.08322200
C	-1.35272500	4.89615100	0.42445900
C	-2.61924600	0.72275600	-0.56267600
O	-3.20654700	1.69014200	-0.09443500
O	-3.24596000	-0.23258400	-1.28681100
C	-4.66016700	-0.05074000	-1.47908200
H	1.34509400	-1.35172500	-1.62351400
H	3.07732900	-2.07857200	-0.63232500
H	5.53265900	-2.23363100	-0.61297300
H	6.91438100	-0.20349000	-0.22069500
H	5.80823700	1.99406800	0.14737500
H	3.32592700	2.15432700	0.10497800
H	-0.55430800	-1.08159200	1.82314800
H	-1.02258400	-3.07790500	3.20594200
H	-1.69438200	-5.21623900	2.12694600
H	-1.89024600	-5.34108800	-0.35049900
H	-1.41008800	-3.34165300	-1.73425600
H	-0.68764600	5.23844900	1.22050300
H	-1.31375100	5.57524700	-0.42646600
H	-2.37348000	4.81842800	0.80636900
H	-4.85764800	0.88183000	-2.01351300
H	-4.98548500	-0.90569100	-2.07125600
H	-5.17749800	-0.03321400	-0.51668600
H	-0.99328700	-1.06800200	-1.93167700

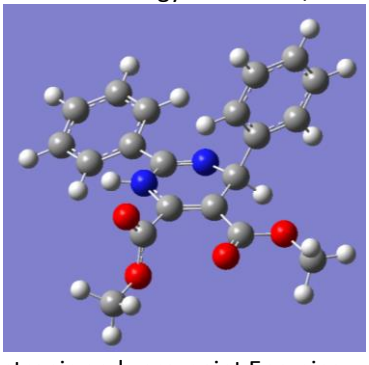
C	-3.17582800	0.06375300	-0.20563500
C	-3.84354600	0.68230900	0.86263800
C	-5.23833000	0.68216900	0.91821200
C	-5.98071800	0.06870400	-0.09202900
C	-5.32127000	-0.55475300	-1.15612300
C	-3.92968200	-0.56135800	-1.21102700
C	1.69201700	-3.09783800	-0.73176400
C	2.16757800	-4.17417700	0.02213800
C	1.82191700	-4.29018100	1.36952000
C	1.00020600	-3.32435400	1.95908600
C	0.52967600	-2.24942900	1.20493100
C	2.48952900	0.47165500	-0.90994300
O	2.88750800	0.36368900	-2.05659500
O	3.29526100	0.58821200	0.15629800
C	4.70524500	0.68959400	-0.13118800
C	0.74649100	2.66827700	0.52828300
O	0.03238500	3.36898400	1.22651800
O	1.92085000	3.04894400	0.02718700
C	2.37121400	4.37097400	0.39860700
H	-1.54179900	1.87638500	0.68842100
H	-3.28396000	1.13868900	1.67410900
H	-5.74168600	1.15750400	1.75515200
H	-7.06625800	0.07279500	-0.05004400
H	-5.89329200	-1.03401900	-1.94565800
H	-3.40877900	-1.04331500	-2.03109500
H	1.96035700	-3.01334800	-1.78225300
H	2.80301900	-4.92172000	-0.44513900
H	2.18785700	-5.12753900	1.95739700
H	0.72620900	-3.40897100	3.00731400
H	-0.10843000	-1.50411800	1.67221000
H	5.19436700	0.75727100	0.83986100
H	5.04830500	-0.19439200	-0.67348500
H	4.90685800	1.58439400	-0.72505800
H	1.65643000	5.12091700	0.05366700
H	2.48478000	4.43928200	1.48250900
H	3.33171900	4.49607200	-0.09840000
H	0.67968900	-1.12573200	-2.01572300

4l (conformation 3)
Relative energy = **0.62** kcal/mol



Sum of electronic and zero-point Energies = -1183.039179
Sum of electronic and thermal Energies = -1183.015708
Sum of electronic and thermal Enthalpies = -1183.014764
Sum of electronic and thermal Free Energies = -1183.095469

4l' (conformation 3)
Relative energy = **4.33** kcal/mol

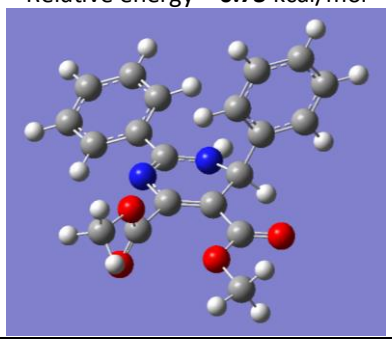


Sum of electronic and zero-point Energies = -1183.033267
Sum of electronic and thermal Energies = -1183.009610
Sum of electronic and thermal Enthalpies = -1183.008666
Sum of electronic and thermal Free Energies = -1183.090329

Imaginary frequency = 0.

N	0.71761900	1.25704700	0.35548500
C	-0.63695400	1.12872300	0.13787800
C	-1.23147500	0.09267500	-0.52031900
C	-0.36909800	-1.05522500	-1.01665000
N	1.01789000	-0.55913000	-1.09433100
C	1.49878800	0.42601500	-0.31074700
C	-0.45985700	-2.32428100	-0.16819300
C	2.96812700	0.60692600	-0.23141800
C	3.85436500	-0.46536500	-0.42793600
C	5.23188900	-0.26349500	-0.34760900
C	5.73915300	1.00776100	-0.07006700
C	4.86285000	2.07794900	0.13520400
C	3.48673200	1.87992700	0.05835400
C	-0.41784000	-2.26726000	1.23184600
C	-0.46181000	-3.43845000	1.98923600
C	-0.55195600	-4.68146400	1.35606600
C	-0.59764900	-4.74710500	-0.03815100
C	-0.55084600	-3.57344900	-0.79368500
C	-1.39023000	2.28769200	0.75400700
O	-1.65037200	2.36000500	1.93696000
O	-1.63066000	3.25055900	-0.14384000
C	-2.30648400	4.42282100	0.35942200
C	-2.66405100	-0.03833600	-0.80986400
O	-3.12993800	-0.92203400	-1.51720500
O	-3.43049800	0.90294600	-0.21592700
C	-4.84235100	0.82940800	-0.48455600
H	1.66330300	-1.08998800	-1.66403200
H	3.47715000	-1.46822800	-0.60629800
H	5.90697000	-1.10178700	-0.49206500
H	6.81251000	1.16340500	-0.00904600
H	5.25352900	3.06793200	0.35220300
H	2.79745800	2.70241400	0.21320400
H	-0.35693600	-1.30458700	1.73229600
H	-0.42953000	-3.38089900	3.07389800
H	-0.58966000	-5.59263600	1.94682700
H	-0.67336600	-5.70925400	-0.53749600
H	-0.58898500	-3.62720000	-1.87952000
H	-1.72010000	4.88906300	1.15437400
H	-2.39764500	5.09358800	-0.49398200
H	-3.29354100	4.15253900	0.74211800
H	-5.24687400	-0.12646200	-0.14307300
H	-5.28694600	1.65285200	0.07359900
H	-5.03533500	0.94408800	-1.55401100
H	-0.67662900	-1.31487300	-2.03389100

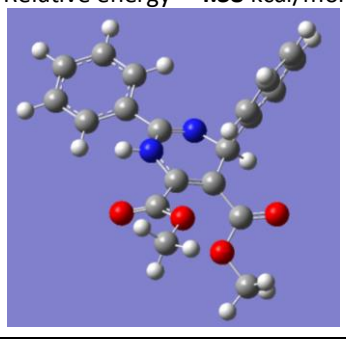
4l (conformation 4)
Relative energy = **0.73** kcal/mol



Imaginary frequency = 0.

N	-0.95915500	-1.06897500	0.40128600
C	0.38327200	-1.32213000	0.23084200
C	1.16448200	-0.43384400	-0.42853200
C	0.55598700	0.87987000	-0.90203200
N	-0.91966700	0.83982800	-0.98446600
C	-1.57334400	-0.03536600	-0.31420400
C	0.96113900	2.08140600	-0.04149900
C	-3.06087200	-0.01369200	-0.28924400
C	-3.72220500	1.21448200	-0.44827900
C	-5.11351000	1.27340600	-0.43546400
C	-5.86486300	0.10612600	-0.26681200
C	-5.21577000	-1.12049200	-0.11613000
C	-3.82146600	-1.18237700	-0.12663600
C	1.06584900	1.98534800	1.35216500
C	1.39177700	3.10585700	2.11937900
C	1.61528400	4.33912700	1.50242500
C	1.51123600	4.44514900	0.11310400
C	1.18627900	3.32263800	-0.65046300
C	0.85864300	-2.61888200	0.84582500
O	1.02807400	-2.75134900	2.04010800
O	0.94696000	-3.58871800	-0.06476800
C	1.39785100	-4.87150700	0.42625400
C	2.58818200	-0.73715000	-0.62941800
O	3.18427400	-1.69087900	-0.14446500
O	3.18988400	0.17995800	-1.41576100
C	4.59397000	-0.02273500	-1.65956000
H	-3.12915900	2.11374000	-0.57520400
H	-5.61319000	2.23096500	-0.55174500
H	-6.95011100	0.15310300	-0.25490500
H	-5.79232500	-2.03323400	0.00265700
H	-3.33783100	-2.15146800	-0.04150100
H	0.90161600	1.02963200	1.84244300
H	1.47302300	3.01417000	3.19929900
H	1.87144400	5.21021500	2.09942700
H	1.68764200	5.39946500	-0.37614900
H	1.10846300	3.40817100	-1.73206700
H	0.73023100	-5.23386800	1.21064300
H	1.37466900	-5.53445400	-0.43726300
H	2.41429500	-4.78120900	0.81577400
H	4.76027400	-0.97499600	-2.16914500
H	4.90131100	0.80812500	-2.29393200
H	5.14998400	-0.01253900	-0.71899400
H	0.91560800	1.08448900	-1.91626900
H	-1.51926600	-1.68976800	0.96795700

4l' (conformation 4)
Relative energy = **4.38** kcal/mol



Sum of electronic and zero-point Energies = -1183.039002
Sum of electronic and thermal Energies = -1183.015482
Sum of electronic and thermal Enthalpies = -1183.014538
Sum of electronic and thermal Free Energies = -1183.095729
Imaginary frequency = 0.

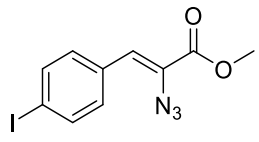
N	-0.77468400	-1.30946000	0.15882500
C	0.57504500	-1.20901900	-0.09699800
C	1.18411300	-0.14660500	-0.69800700
C	0.35298100	1.07359600	-1.05587600
N	-1.05805200	0.64376100	-1.10517600
C	-1.54642500	-0.39182200	-0.39568800
C	0.53799900	2.26028200	-0.10879800
C	-3.01760300	-0.52620000	-0.27024300
C	-3.86676700	0.59176900	-0.31929600
C	-5.24706200	0.43237000	-0.19986000
C	-5.79333500	-0.84170000	-0.03007300
C	-4.95325000	-1.95804300	0.02909000
C	-3.57434200	-1.80271900	-0.08647500
C	0.55891800	2.08289300	1.28155700
C	0.68765700	3.18090600	2.13305900
C	0.80059000	4.47005800	1.60447200
C	0.78396000	4.65539900	0.22036800
C	0.65262300	3.55480200	-0.62928300
C	1.29620900	-2.46784400	0.33634600
O	1.32487700	-3.48874100	-0.31850500
O	1.79737800	-2.33500500	1.57080100
C	2.45621200	-3.50099200	2.10971400
C	2.60462300	-0.05343700	-1.05196400
O	3.08976000	0.90351700	-1.64138700
O	3.33455800	-1.12759600	-0.67772900
C	4.73241800	-1.09049000	-1.01739000
H	-1.70444200	1.25112400	-1.59179400
H	-3.45588800	1.59303900	-0.41106300
H	-5.89321900	1.30468500	-0.22955900
H	-6.86883400	-0.96424100	0.06120800
H	-5.37456200	-2.95024100	0.16252300
H	-2.91240000	-2.66043100	-0.04353600
H	0.48196200	1.08292900	1.69966100
H	0.70354900	3.03026900	3.20911900
H	0.90415100	5.32416700	2.26813200
H	0.87667200	5.65391100	-0.19814400
H	0.64269000	3.70162900	-1.70708700
H	3.31767400	-3.76528700	1.49184600
H	2.77654400	-3.21620500	3.11112000
H	1.76324200	-4.34427700	2.15264900
H	5.22046600	-0.23913400	-0.53660200
H	5.14635700	-2.02730000	-0.64547700
H	4.86133700	-1.01891300	-2.10009000
H	0.62388600	1.40754400	-2.06180800

Sum of electronic and zero-point Energies = -1183.033190
Sum of electronic and thermal Energies = -1183.009759
Sum of electronic and thermal Enthalpies = -1183.008815
Sum of electronic and thermal Free Energies = -1183.089304
Imaginary frequency = 0.

N	-0.64347100	-1.03349200	0.49429100
C	0.70545500	-1.03042100	0.19935100
C	1.19547800	-0.07788000	-0.63455100
C	0.26667800	1.06214100	-1.02133000
N	-1.14516200	0.62202500	-1.09695300
C	-1.52961200	-0.31875100	-0.31237200
C	0.35313600	2.29149800	-0.10800200
C	-2.96197000	-0.71274000	-0.24223300
C	-3.35870700	-2.02298700	0.06880200
C	-4.71290800	-2.35671600	0.11670400
C	-5.68397600	-1.38811700	-0.14403400
C	-5.29569800	-0.08247900	-0.46000700
C	-3.94491600	0.25320300	-0.50997100
C	-0.15489300	3.50976100	-0.58395000
C	-0.14077300	4.65185200	0.21602700
C	0.38784800	4.59394600	1.50925400
C	0.89973400	3.38794800	1.98992900
C	0.88086900	2.24358900	1.18687200
C	2.54004300	-0.07697200	-1.24304700
O	3.09756800	0.94078400	-1.62463300
O	3.05702800	-1.31061000	-1.41398800
C	4.38718400	-1.36160300	-1.96327100
C	1.44392600	-2.13747400	0.89853800
O	0.92186800	-3.21187000	1.13545600
O	2.65585600	-1.76849800	1.30832400
C	3.42766800	-2.78217000	1.99095700
H	-0.98416000	-1.77322600	1.09408600
H	0.54012600	1.39881000	-2.02676700
H	-2.61906400	-2.80007400	0.24101500
H	-5.00636500	-3.37586500	0.35097400
H	-6.73780700	-1.64868300	-0.10290300
H	-6.04713800	0.67562900	-0.66180800
H	-3.63209700	1.26401500	-0.74886900
H	-0.56470000	3.55892600	-1.59010200
H	-0.53563100	5.58773500	-0.17066300
H	0.40441900	5.48323200	2.13352900
H	1.31803500	3.33408600	2.99166700
H	1.29503000	1.31557100	1.56922800
H	4.63166400	-2.42100000	-2.03468100
H	4.40901100	-0.89598900	-2.95133600
H	5.09325900	-0.84948200	-1.30463900
H	2.89337200	-3.12752200	2.87831600
H	3.61577100	-3.62407700	1.32109200
H	4.36077300	-2.29404600	2.26721500

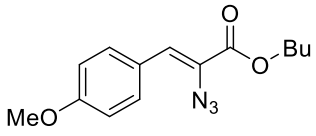
S7. Synthesis and characterization of azidocinnamates

(*Z*)-Methyl 2-azido-3-(4-iodophenyl)acrylate (1c)



This compound (1.10 g, yield 56%) was obtained according to the literature procedure [12]. Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 3.91 (s, 3H), 6.80 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ) 53.0, 95.6, 124.0, 126.1, 132.0, 132.5, 137.6, 163.7. HR ESI^{+}-MS, *m/z*: $[M + Na]^{+}$ calcd for $C_{10}H_8IN_3NaO_2^{+}$, 351.9553; found, 351.9561.

(*Z*)-Butyl 2-azido-3-(4-methoxyphenyl)acrylate (1k)



This compound (234 mg, yield 99%) was obtained according to the literature procedure [13]. Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 1.01 (t, *J* = 7.4 Hz, 3H), 1.44–1.54 (m, 2H), 1.73–1.80 (m, 2H), 3.86 (s, 3H), 4.32 (t, *J* = 6.7 Hz, 2H), 6.90 (s, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ) 13.6, 19.2, 30.6, 55.3, 65.9, 113.9, 123.4, 125.4, 126.0, 132.3, 160.4, 163.8. HR ESI^{+}-MS, *m/z*: $[M + Na]^{+}$ calcd for $C_{14}H_{17}N_3NaO_3^{+}$, 298.1162; found, 298.1161.

S8. NMR spectra

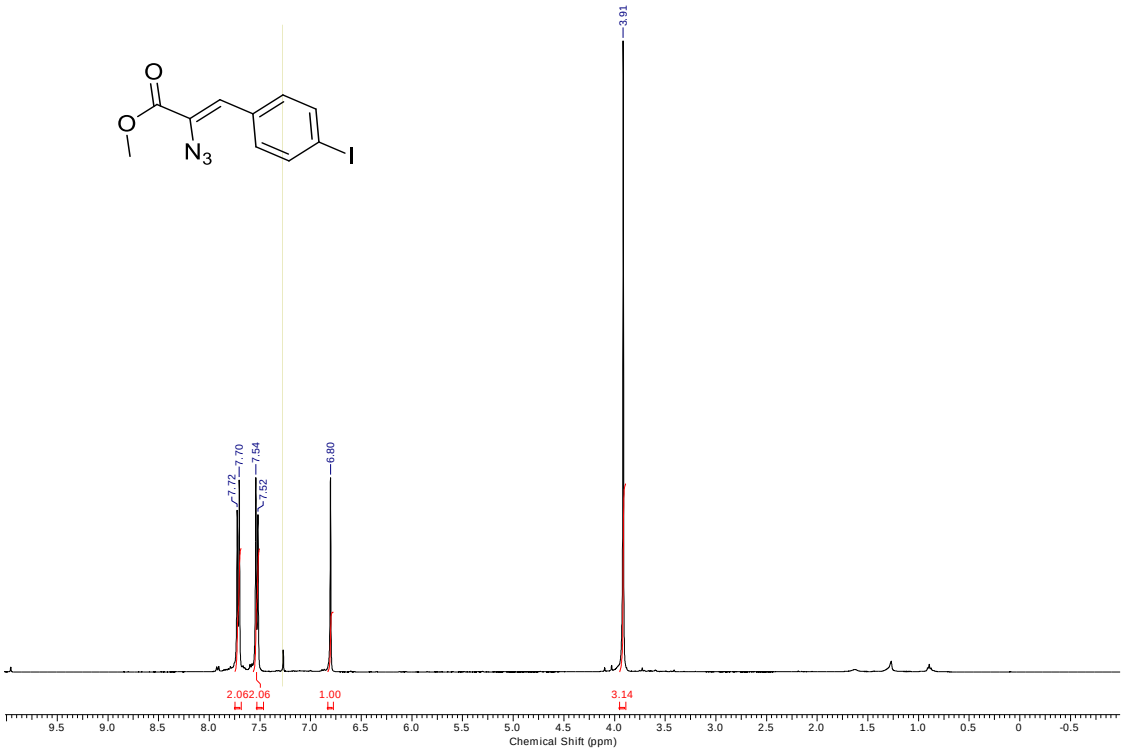


Figure S7. ^{1}H NMR spectrum of **1c** in $CDCl_3$.

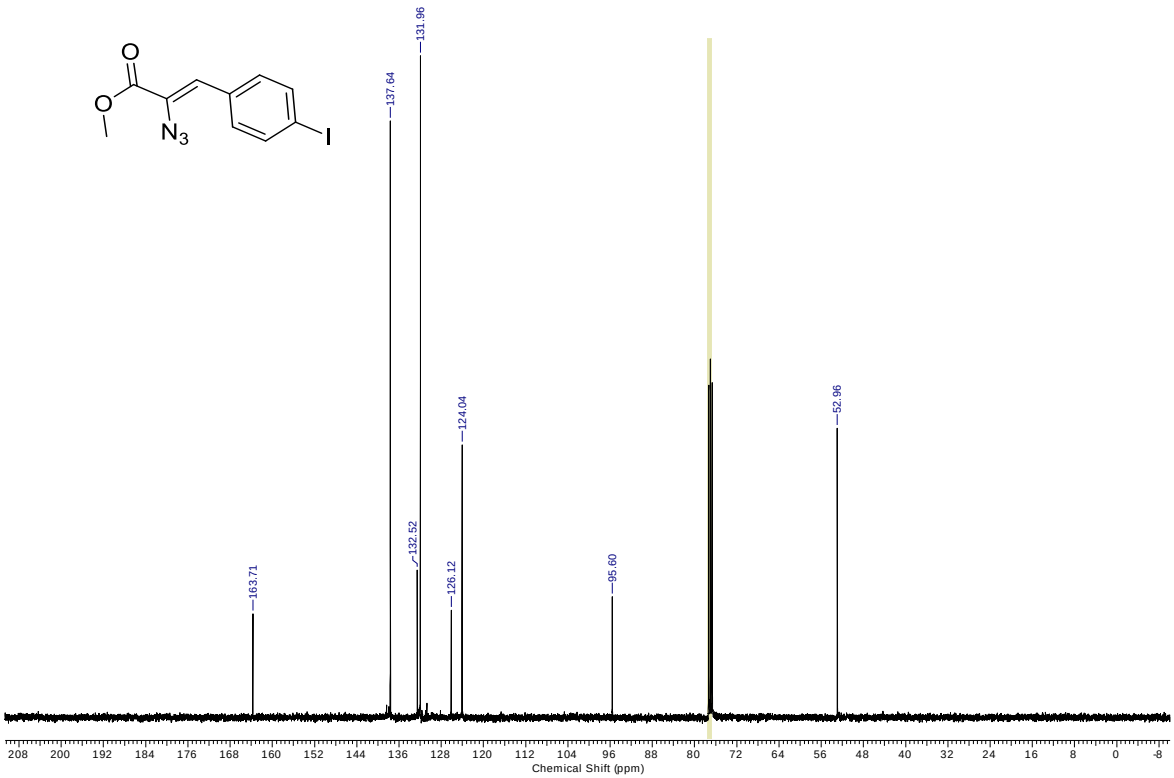


Figure S8. ^{13}C{^{1}H} NMR spectrum of **1c** in $CDCl_3$.

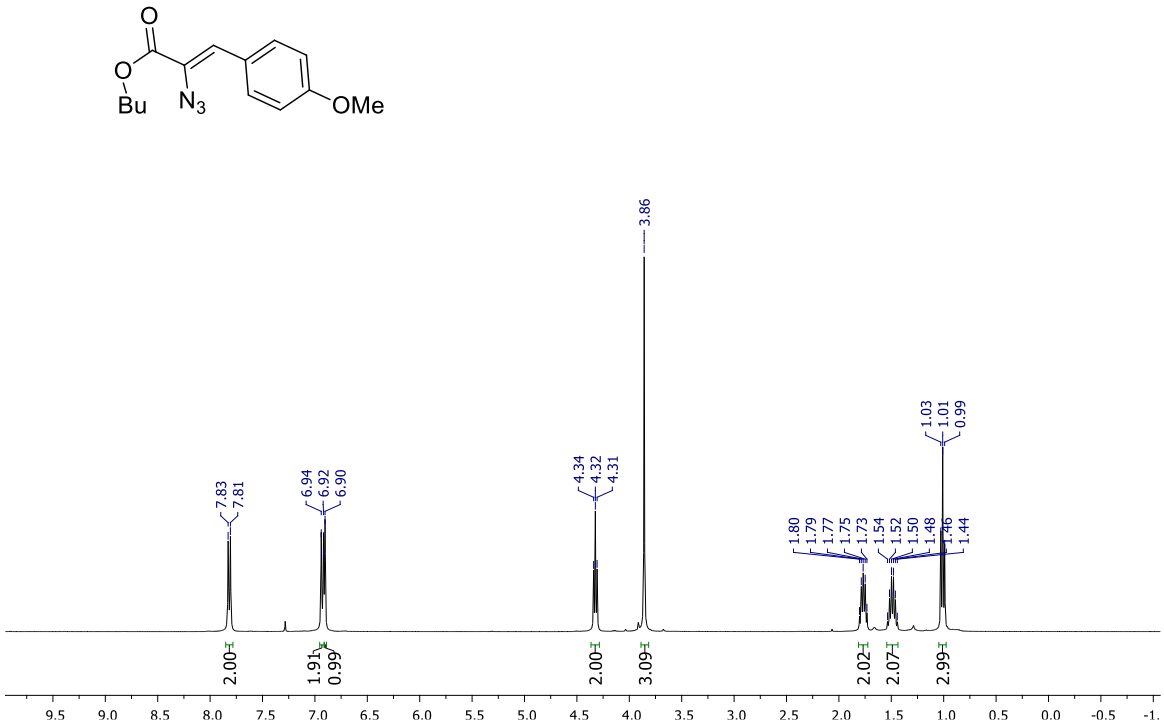


Figure S9. ^{1}H NMR spectrum of **1k** in $CDCl_3$.

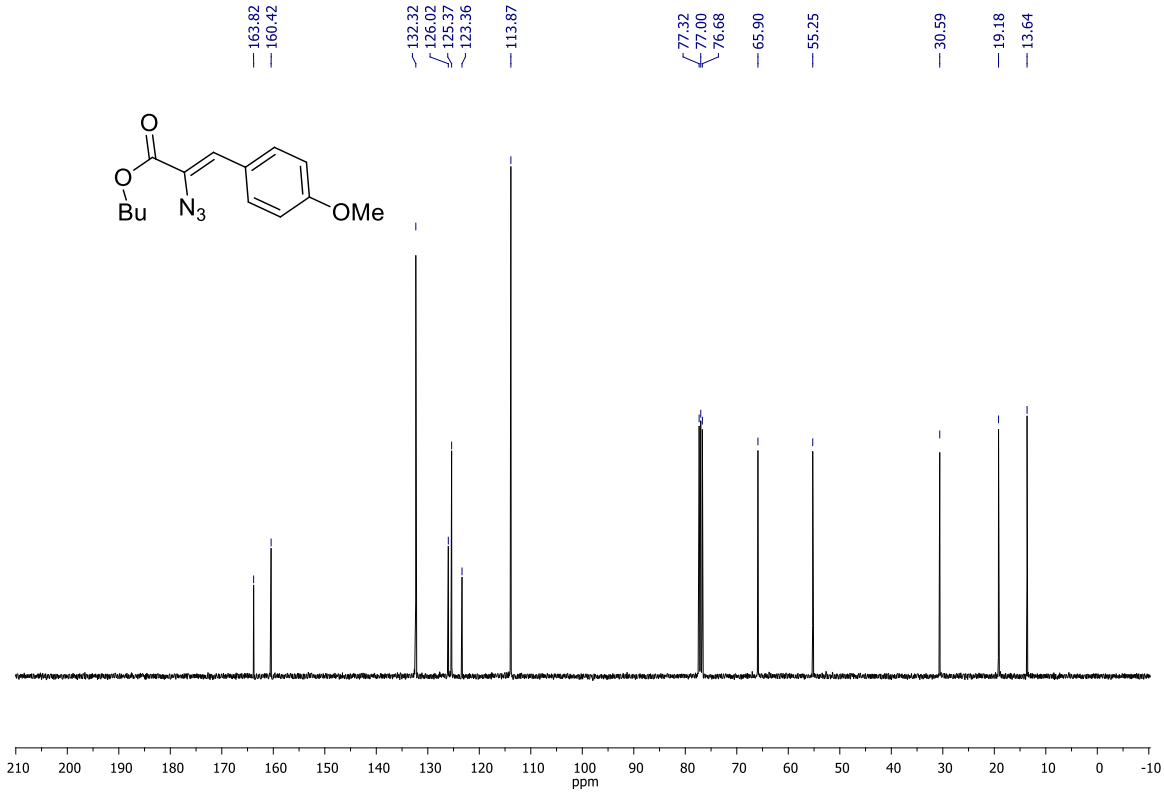


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **1k** in $CDCl_3$.

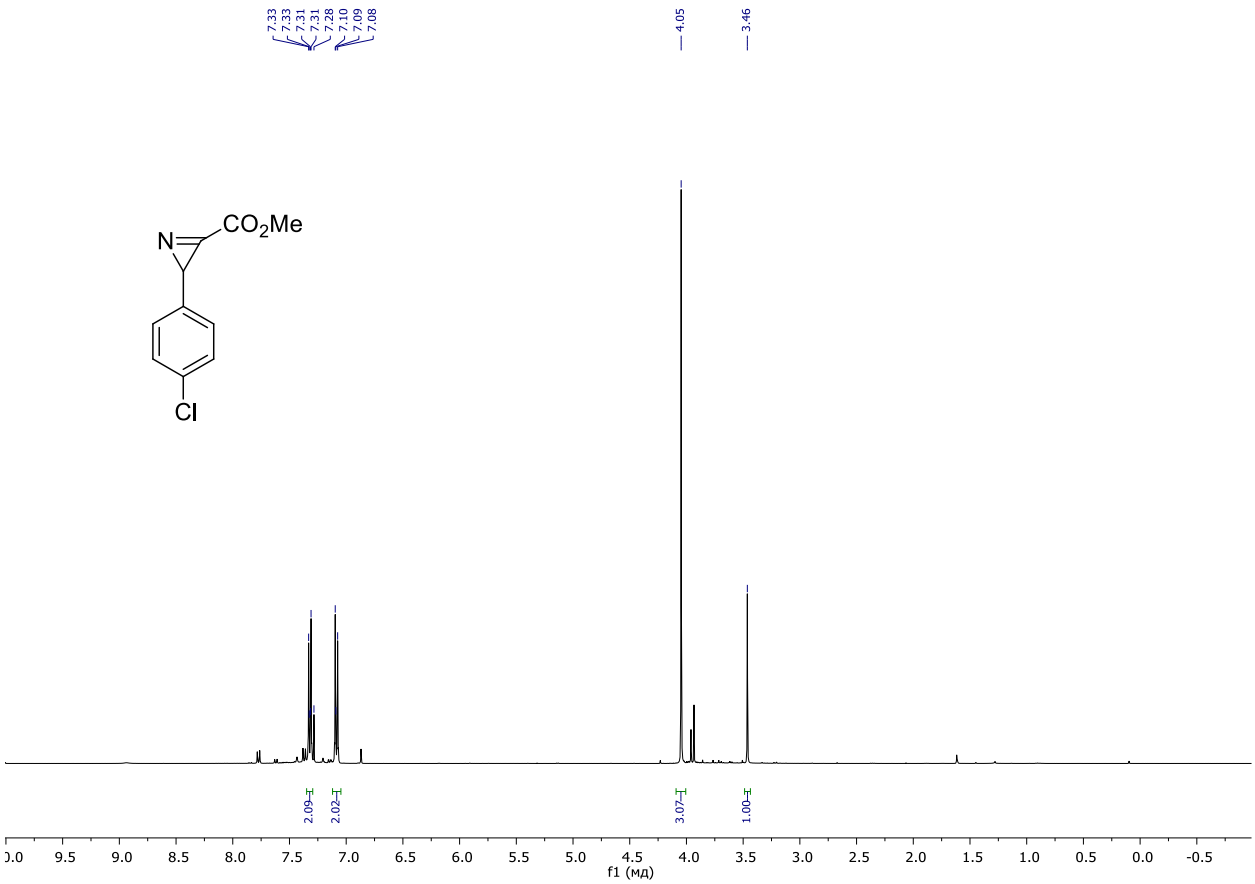


Figure S11. ^{1}H NMR spectrum of crude **2a** in $CDCl_3$.

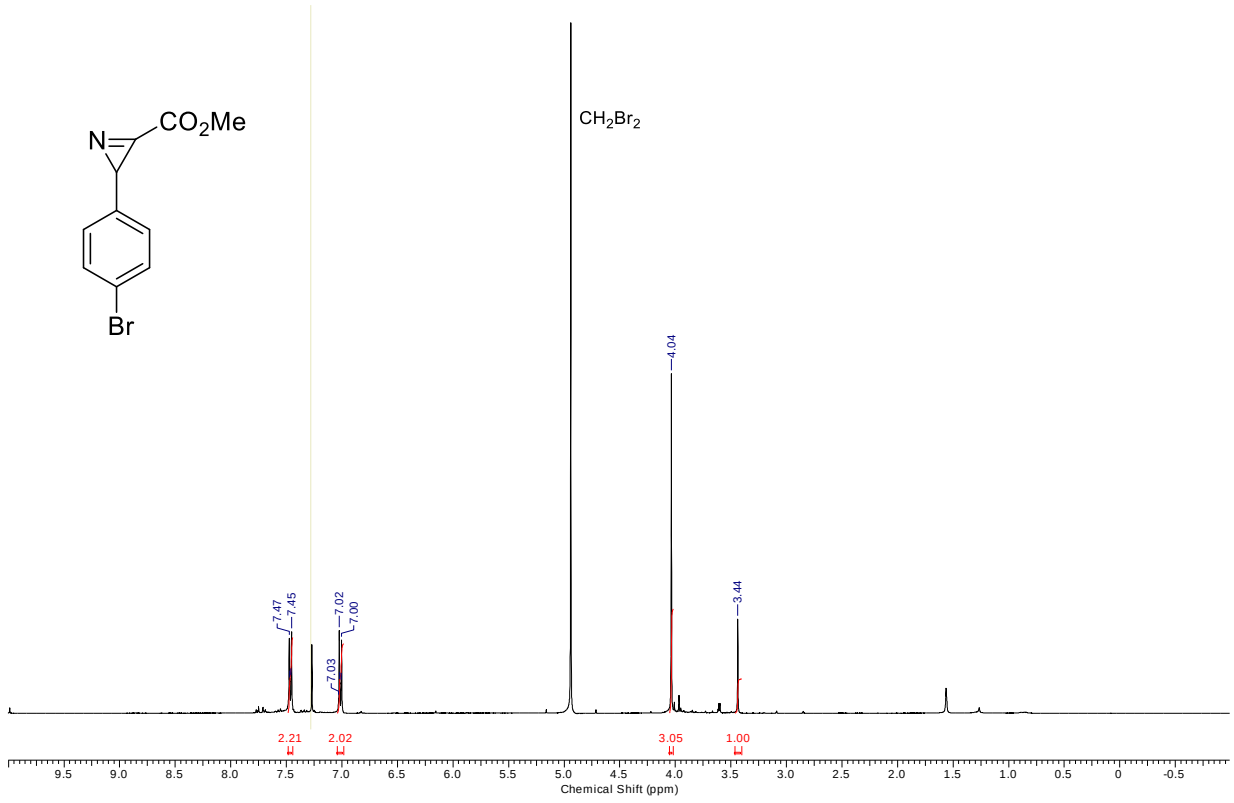


Figure S12. ^{1}H NMR spectrum of crude **2b** in $CDCl_3$.

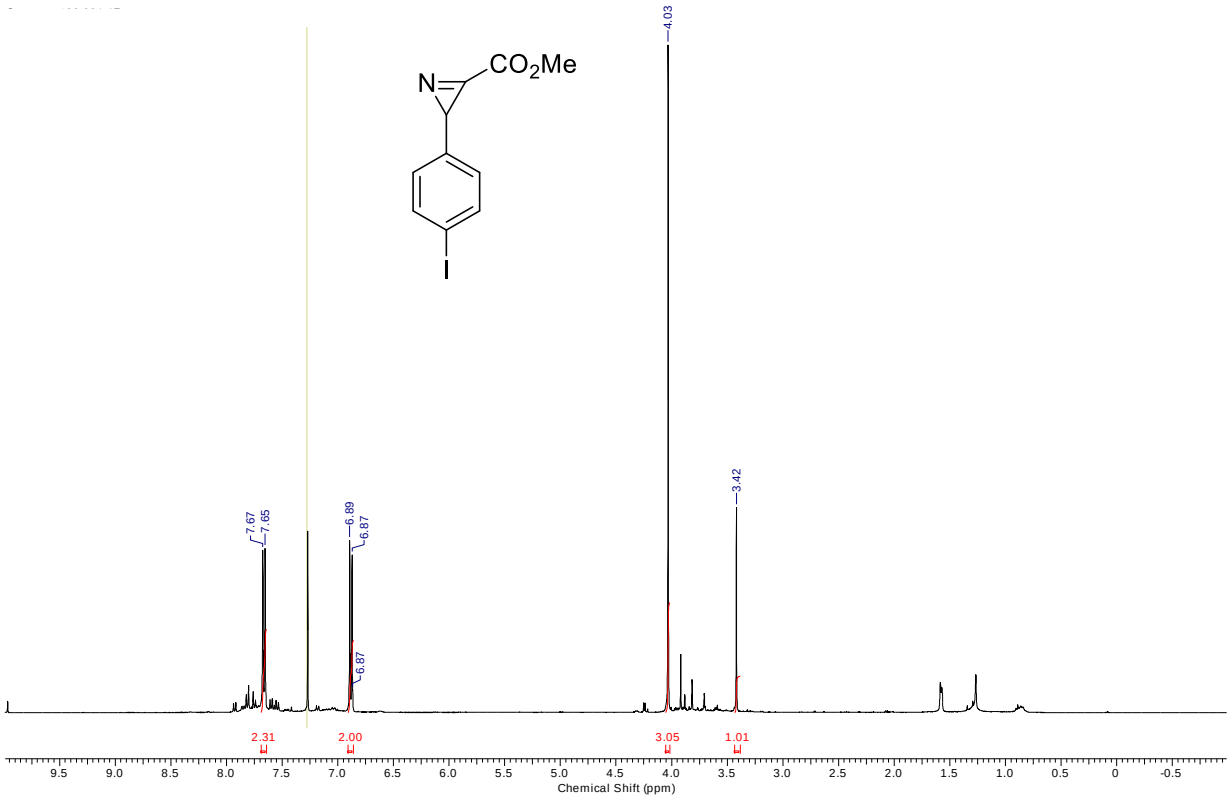


Figure S13. ^{1}H NMR spectrum of crude **2c** in $CDCl_3$.

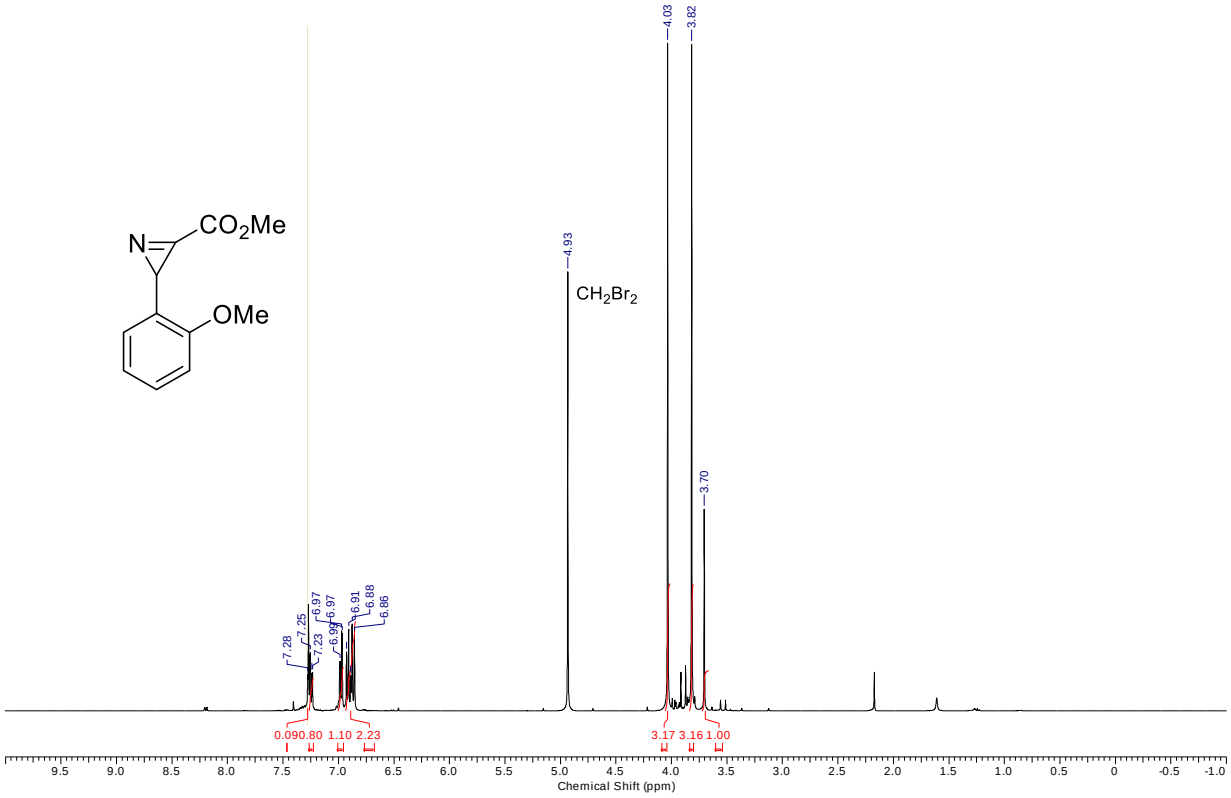


Figure S14. ^{1}H NMR spectrum of crude **2d** in $CDCl_3$.

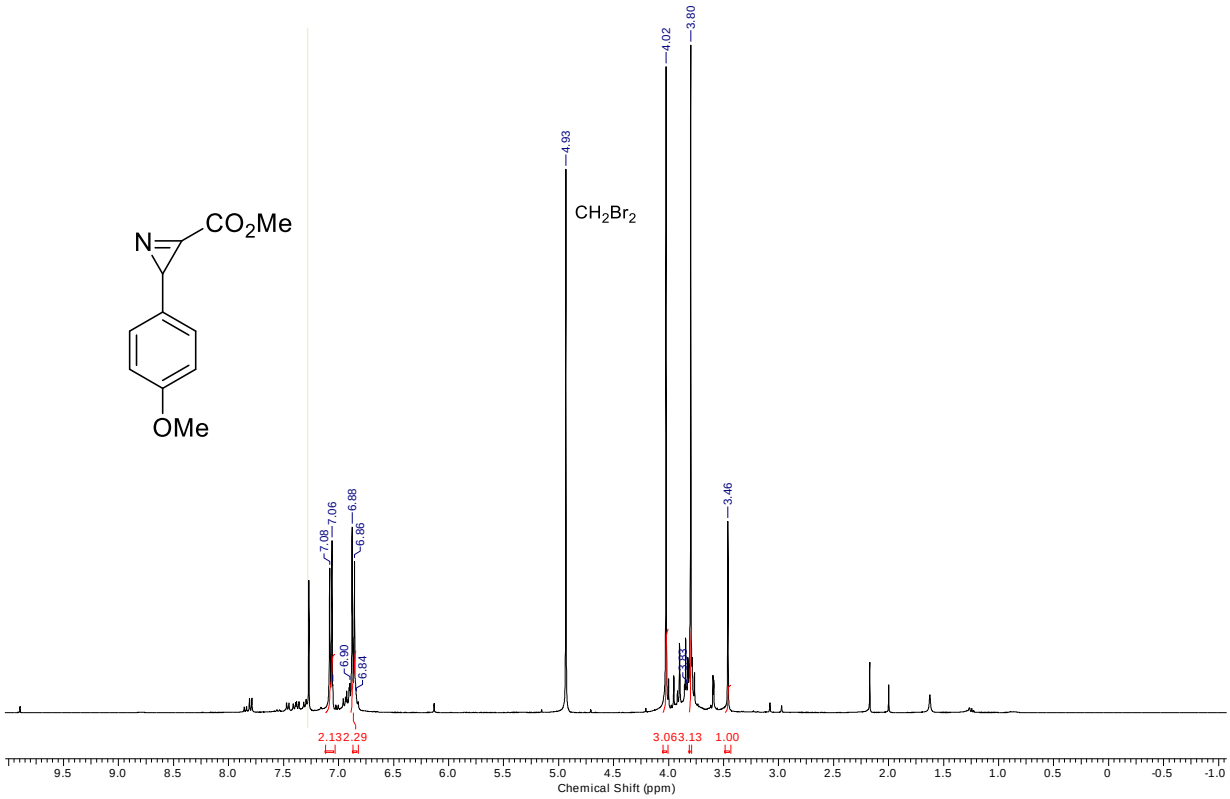


Figure S15. ^{1}H NMR spectrum of crude **2e** in $CDCl_3$.

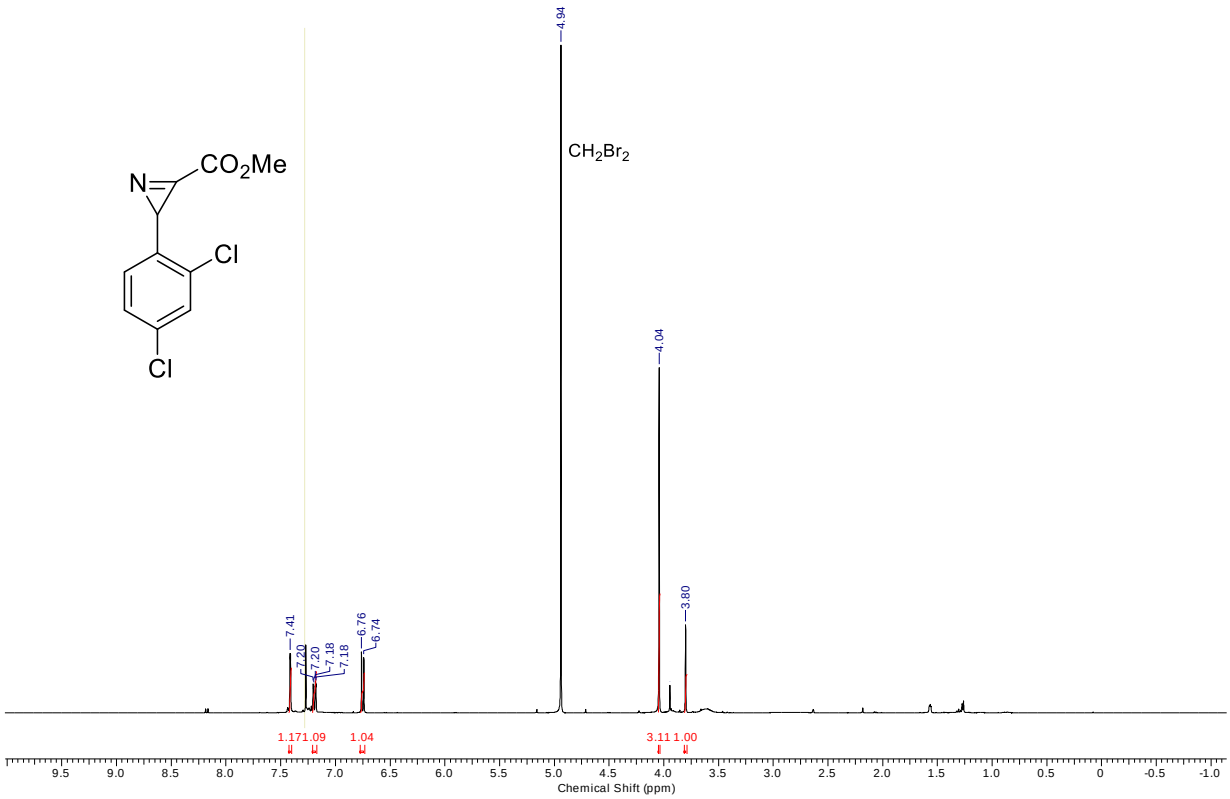


Figure S16. ^{1}H NMR spectrum of crude **2f** in $CDCl_3$.

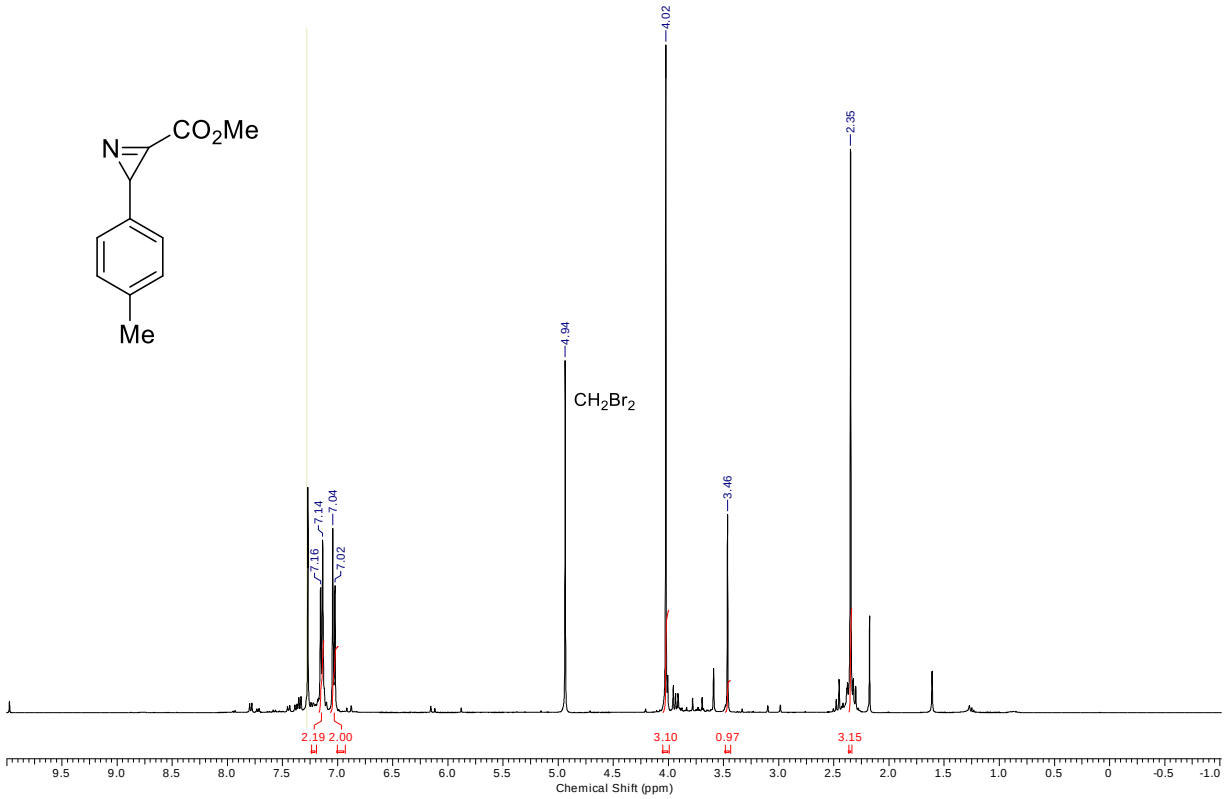


Figure S17. ^{1}H NMR spectrum of crude **2g** in $CDCl_3$.

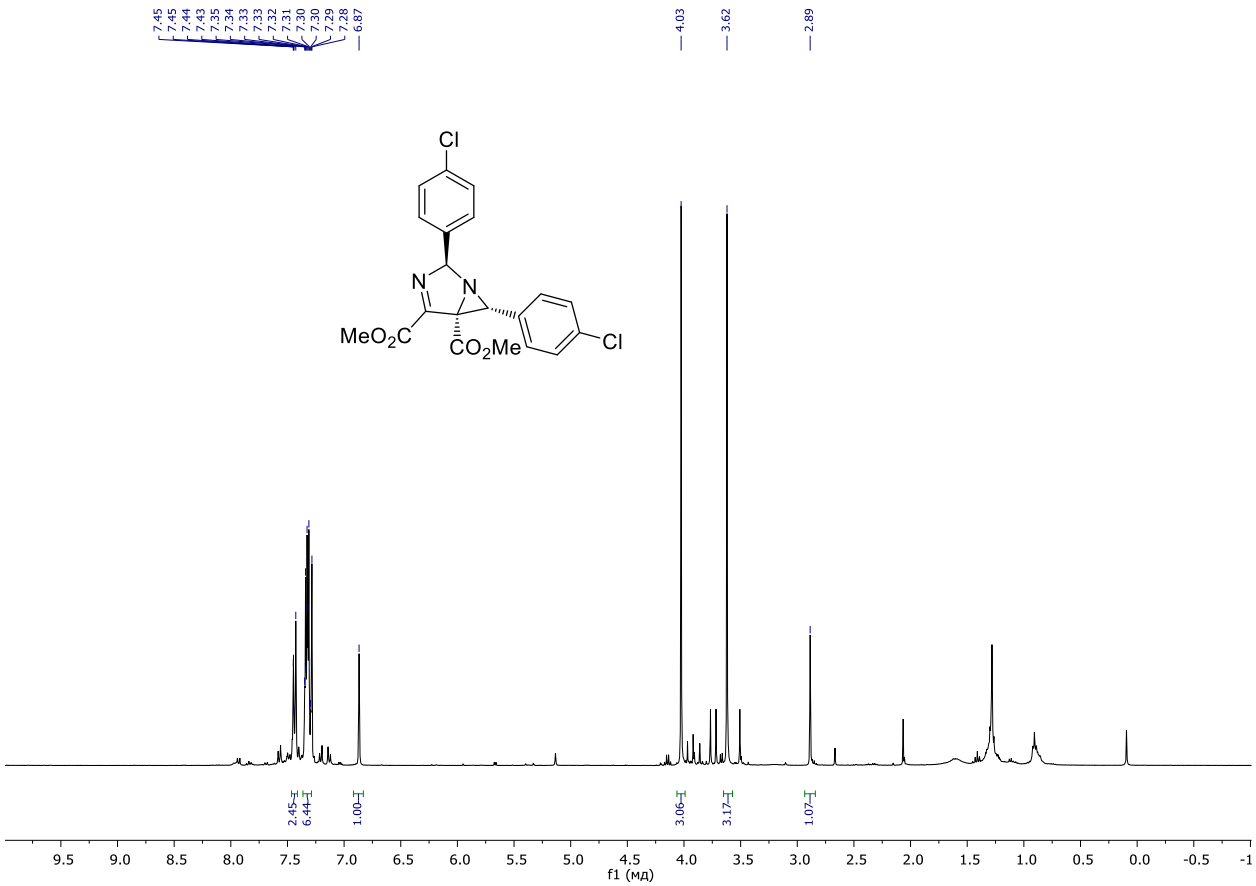


Figure S18. ^{1}H NMR spectrum of **3a'** in $CDCl_3$.

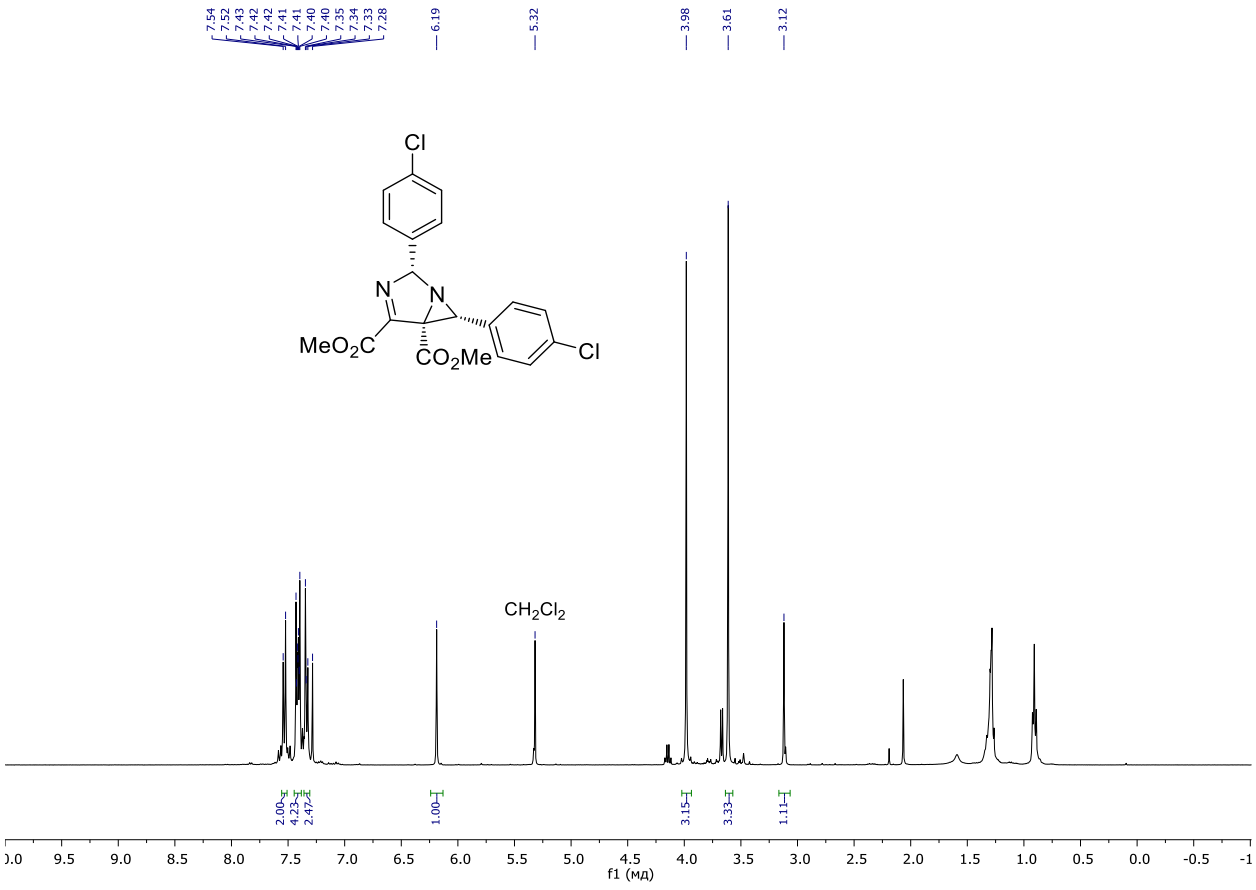


Figure S19. ^{1}H NMR spectrum of **3a"** in $CDCl_3$.

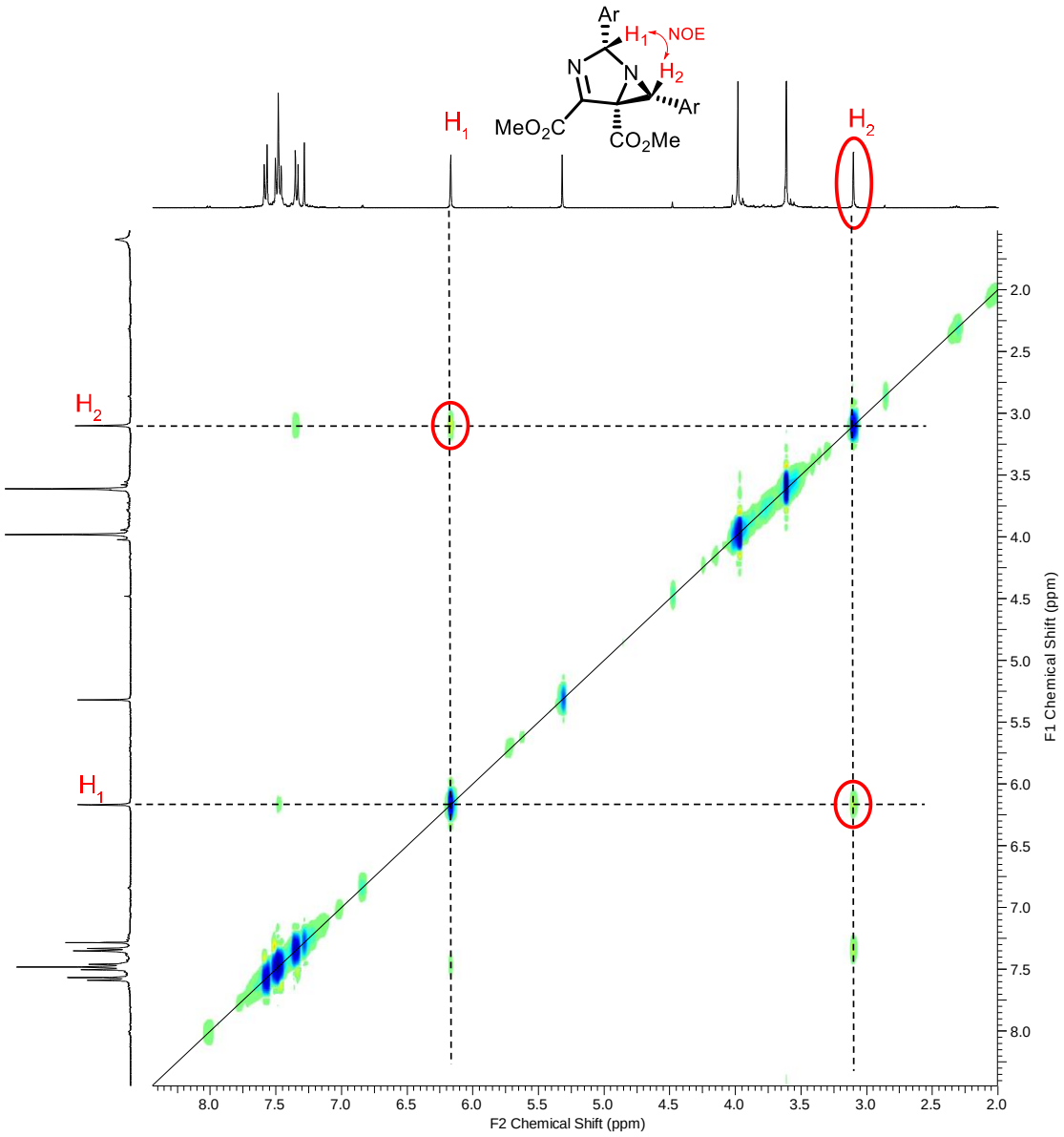


Figure S20. Fragment of the ^{1}H,^{1}H-NOESY NMR spectrum of **3a"** in $CDCl_3$**.**

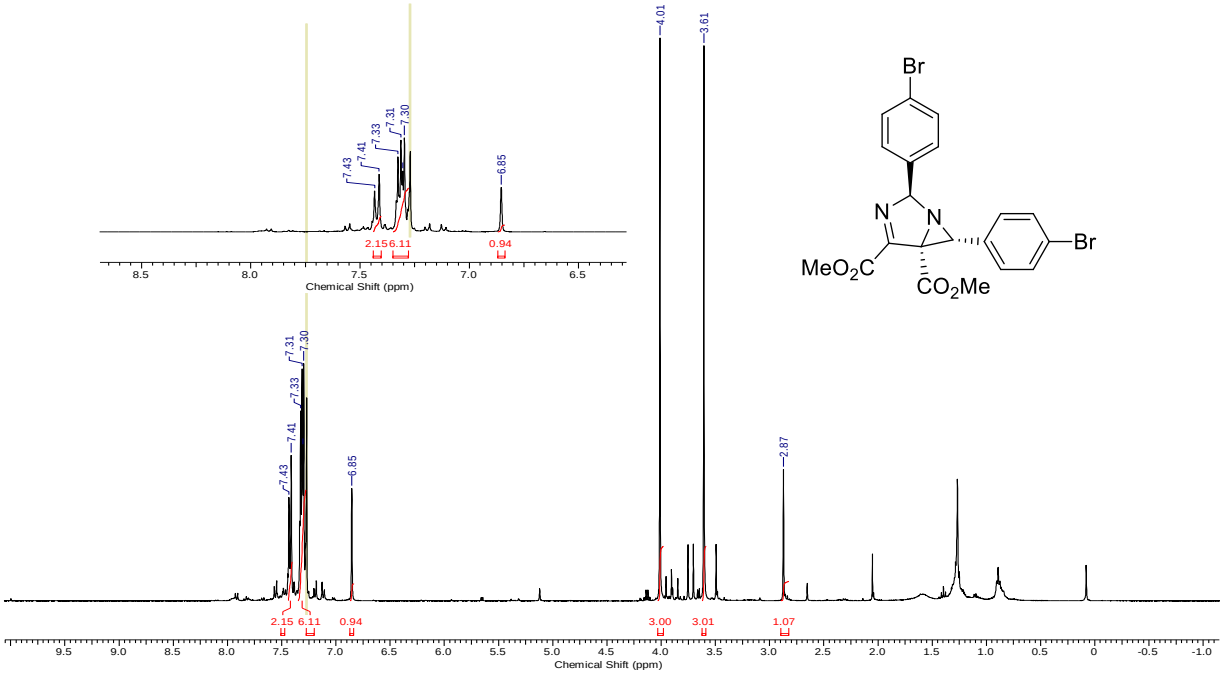


Figure S21. ^{1}H NMR spectrum of **3b'** in $CDCl_3$.

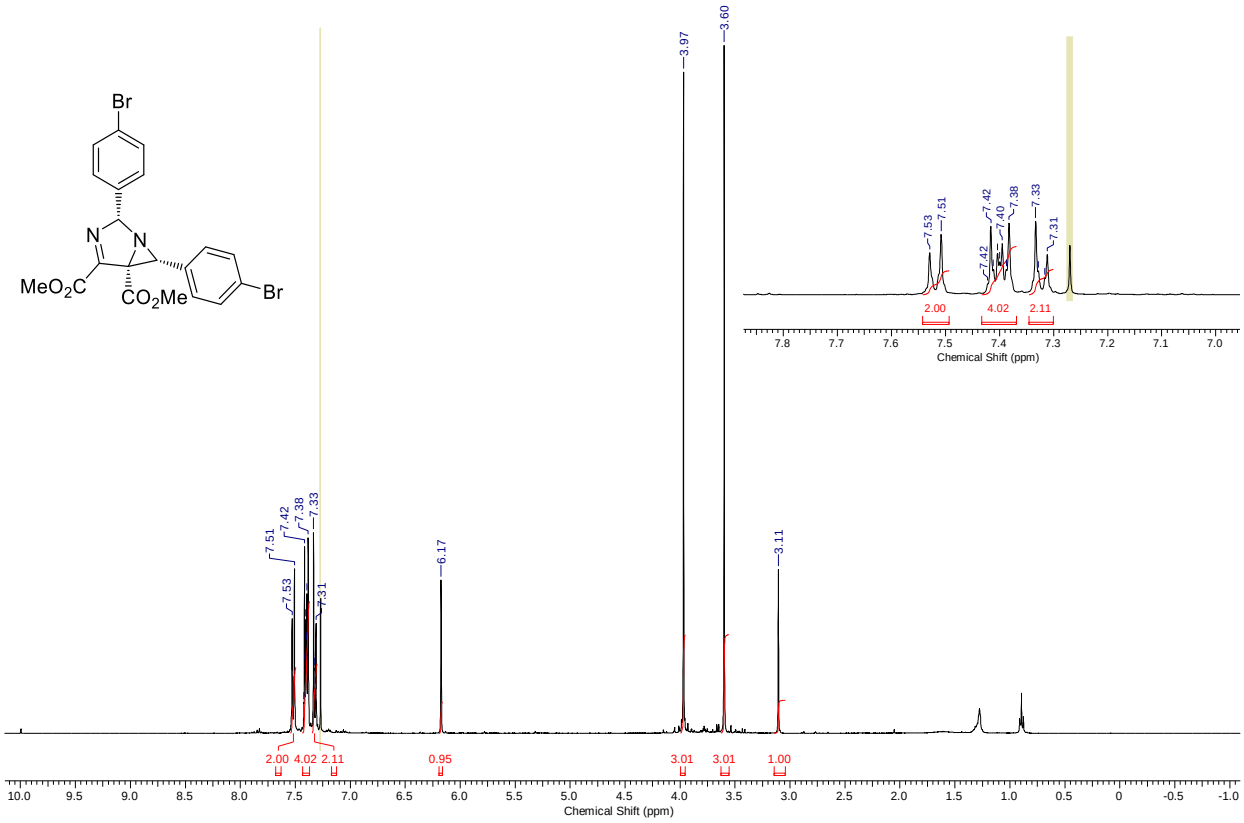


Figure S22. ^{1}H NMR spectrum of **3b"** in $CDCl_3$.

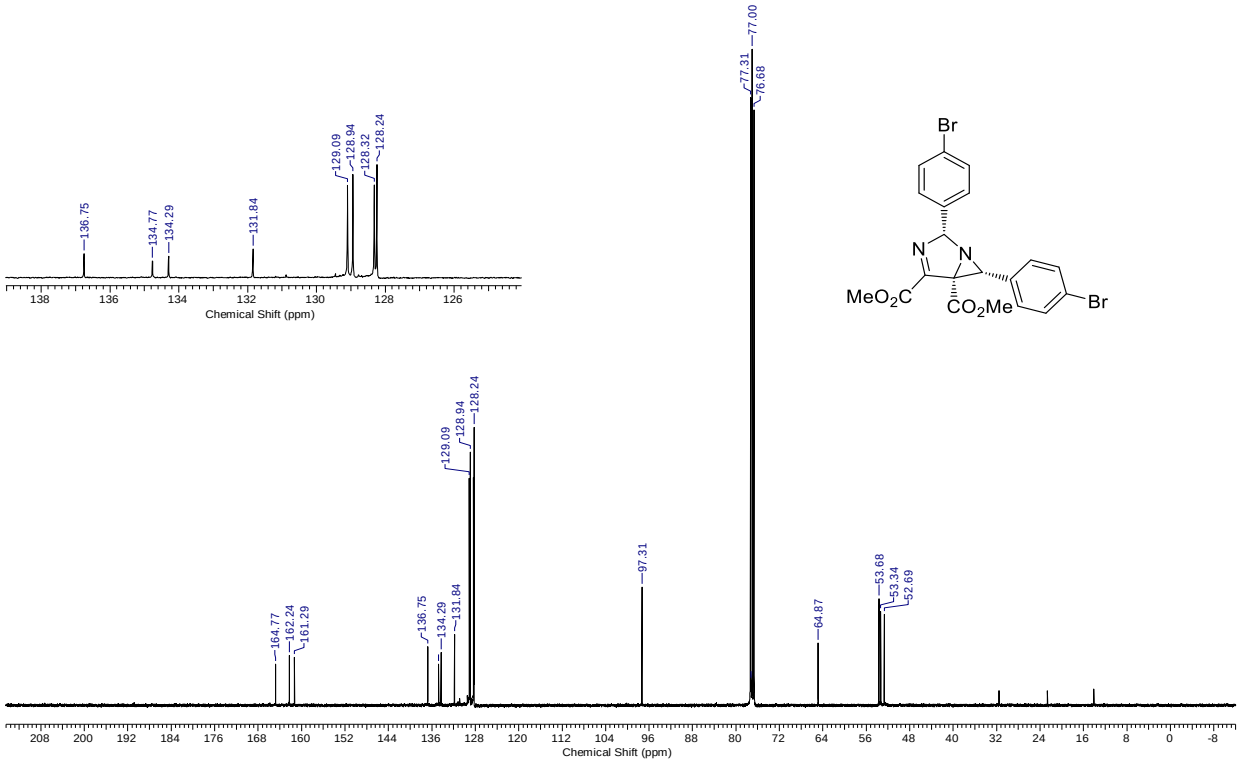


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **3b"** in $CDCl_3$.

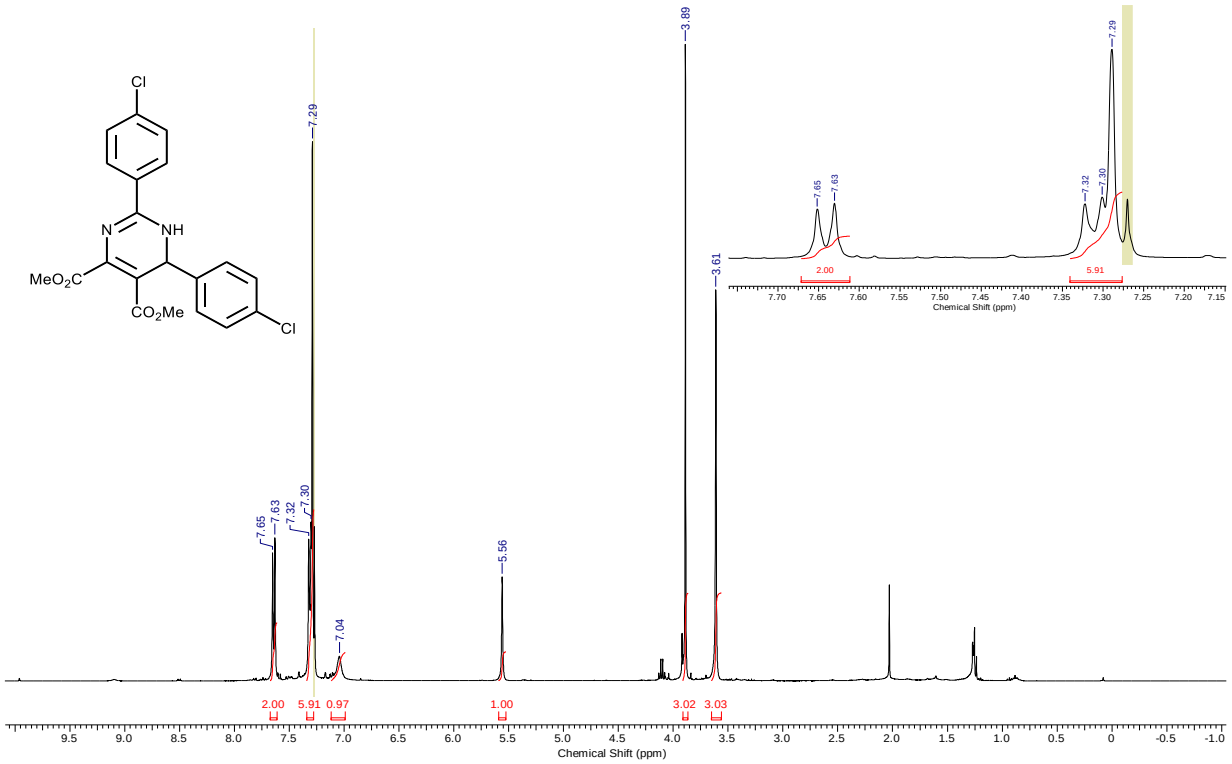


Figure S24. ^{1}H NMR spectrum of **4a** in $CDCl_3$.

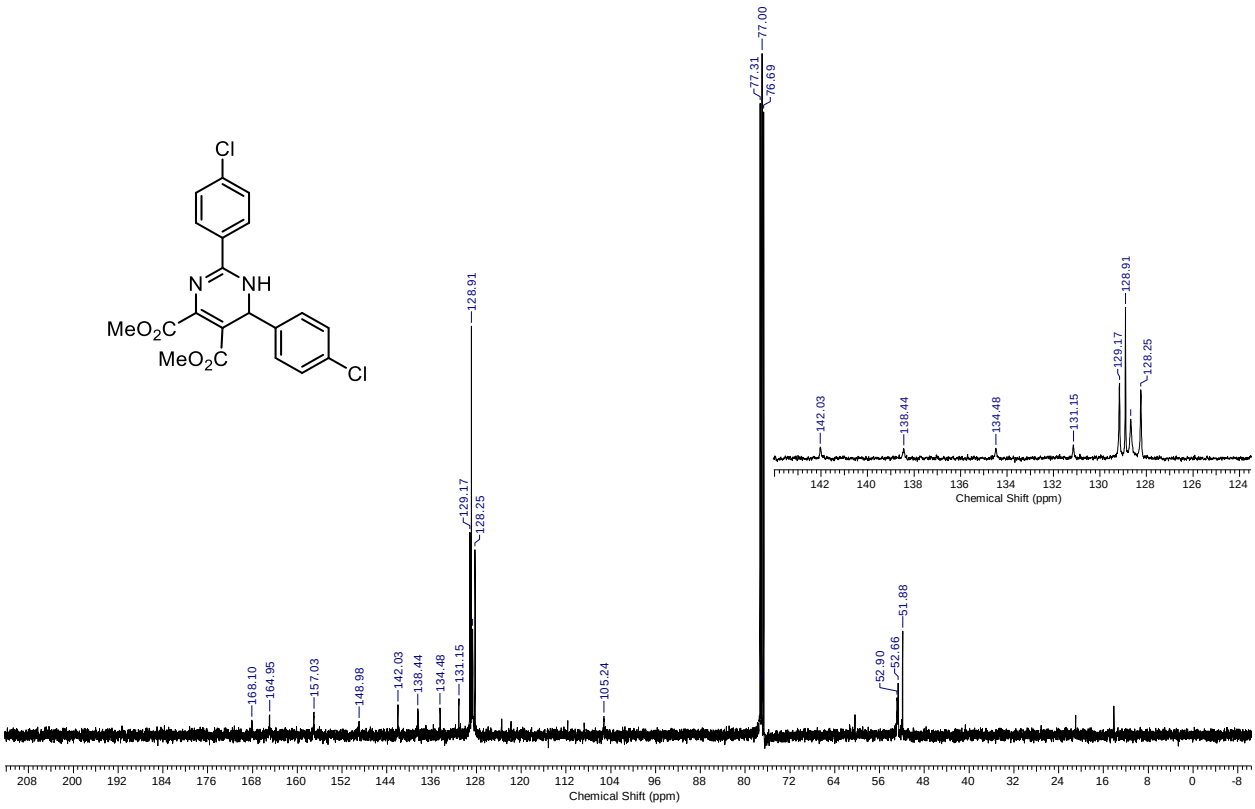


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **4a** in $CDCl_3$.

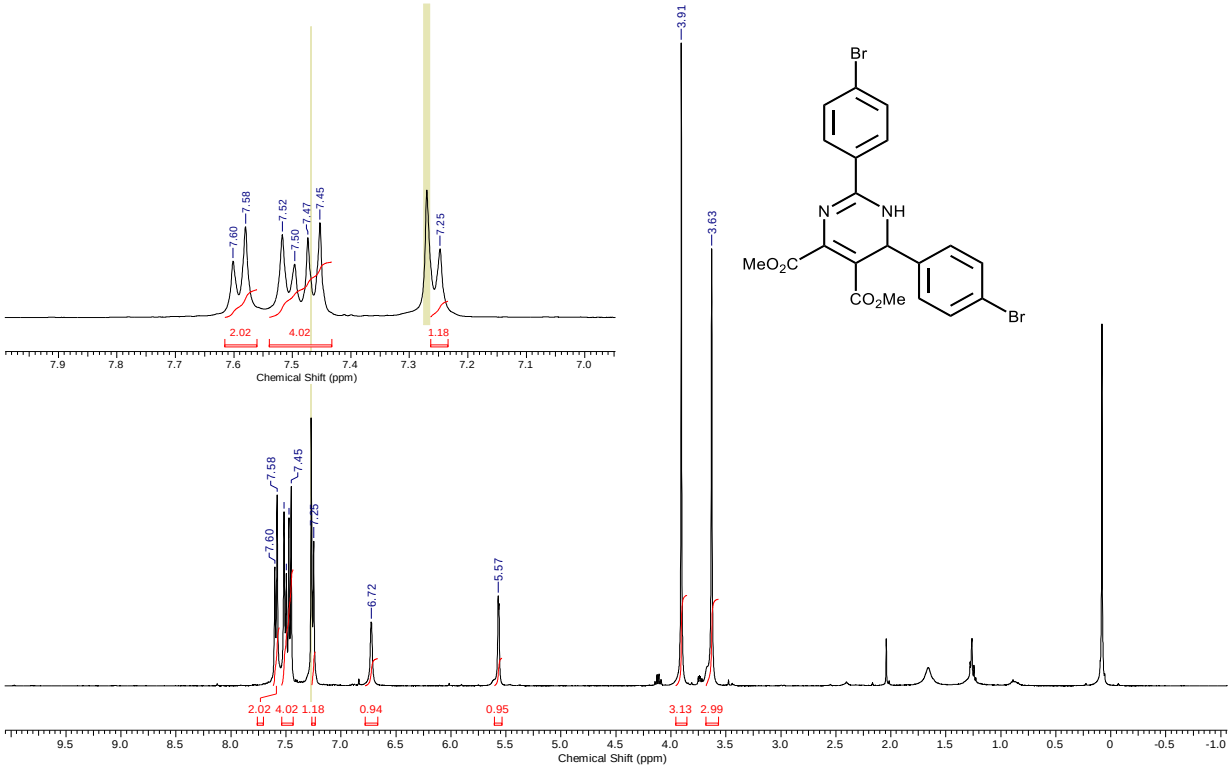


Figure S26. ^{1}H NMR spectrum of **4b** in $CDCl_3$.

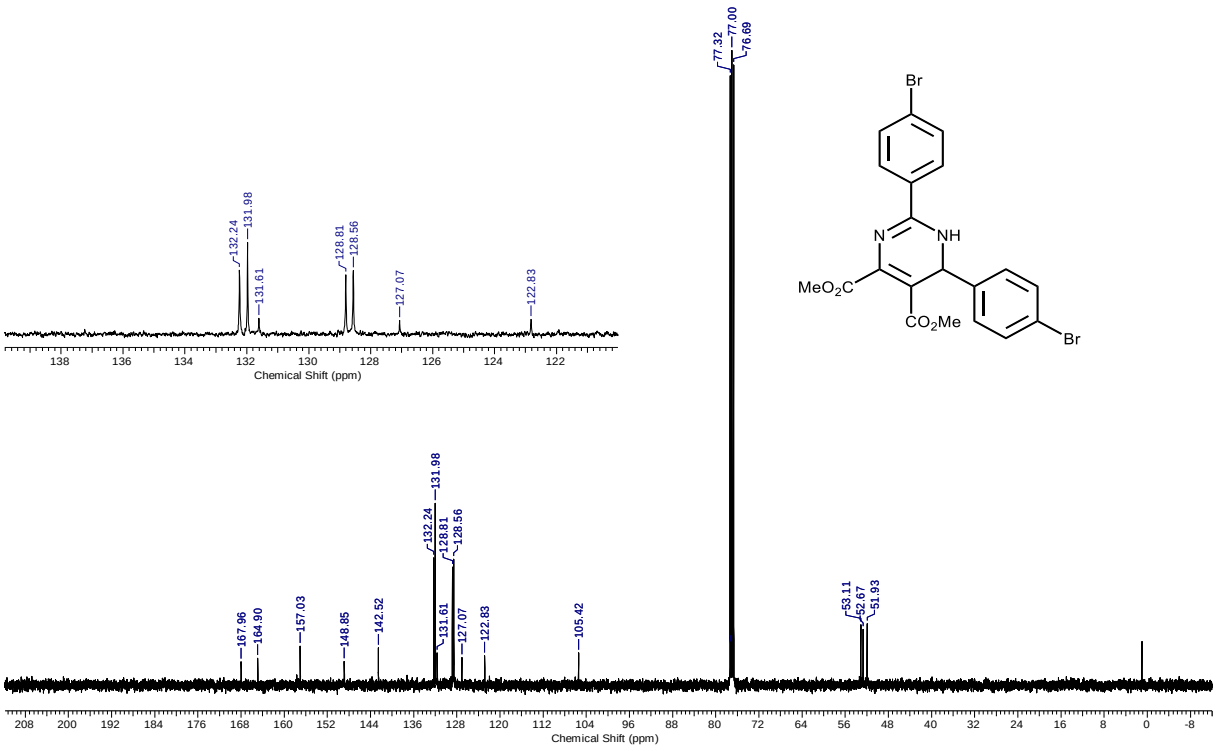


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **4b** in $CDCl_3$.

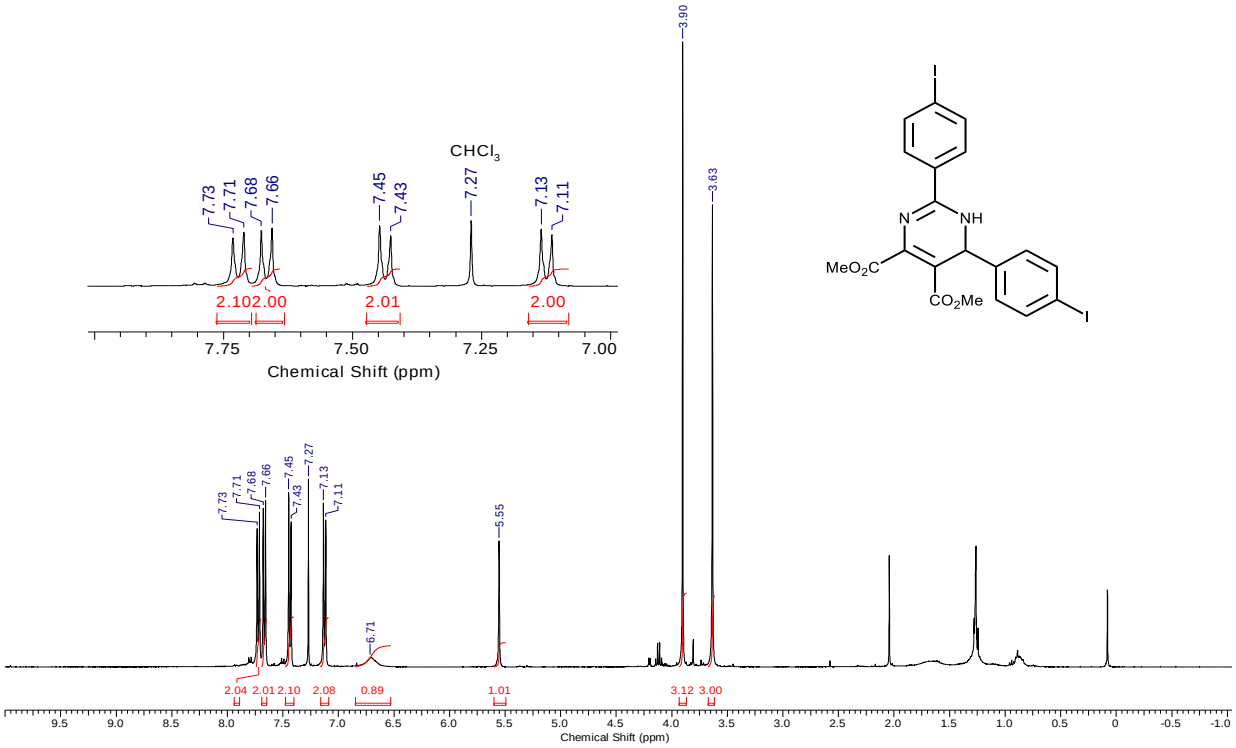


Figure S28. ^{1}H NMR spectrum of **4c** in $CDCl_3$

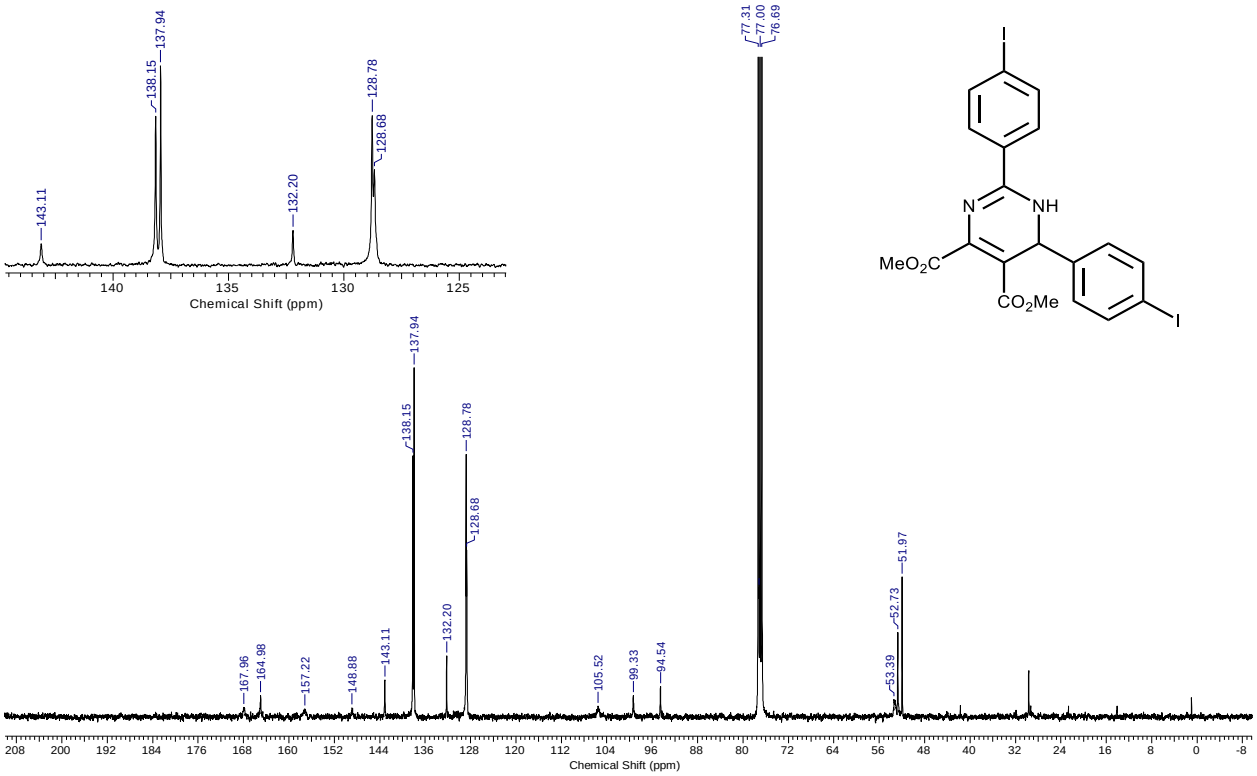


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **4c** in $CDCl_3$.

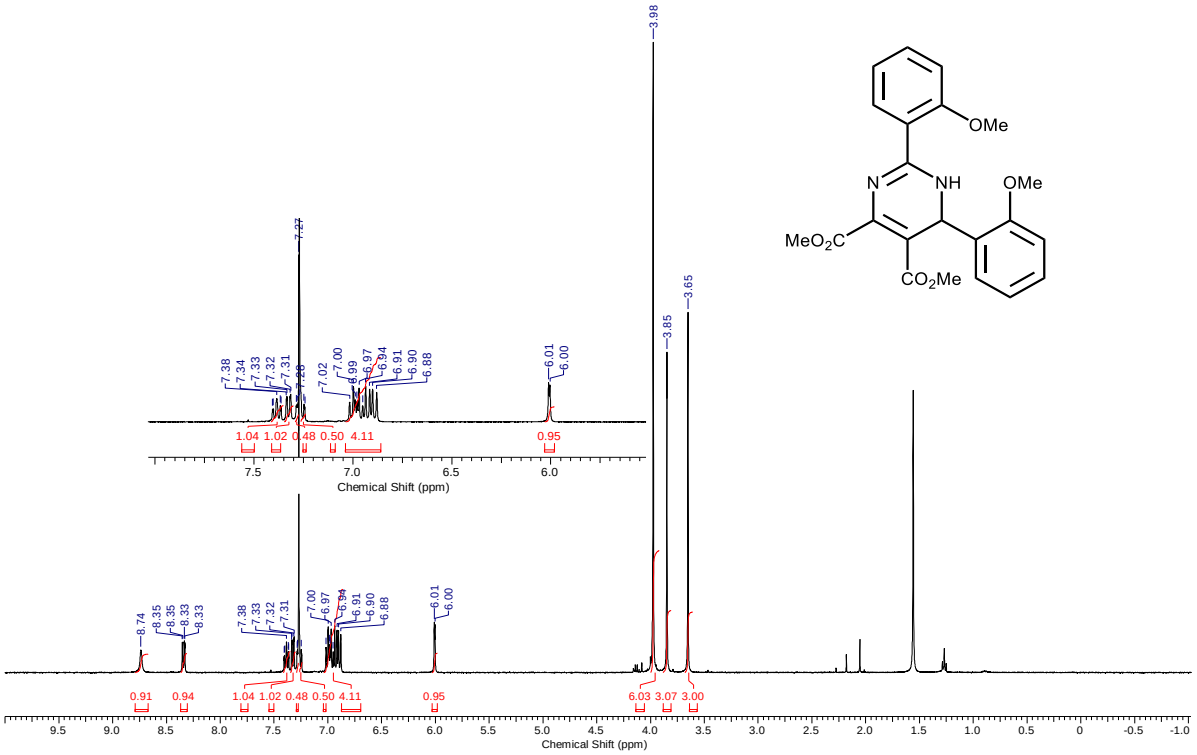


Figure S30. ^{1}H NMR spectrum of **4d** in $CDCl_3$.

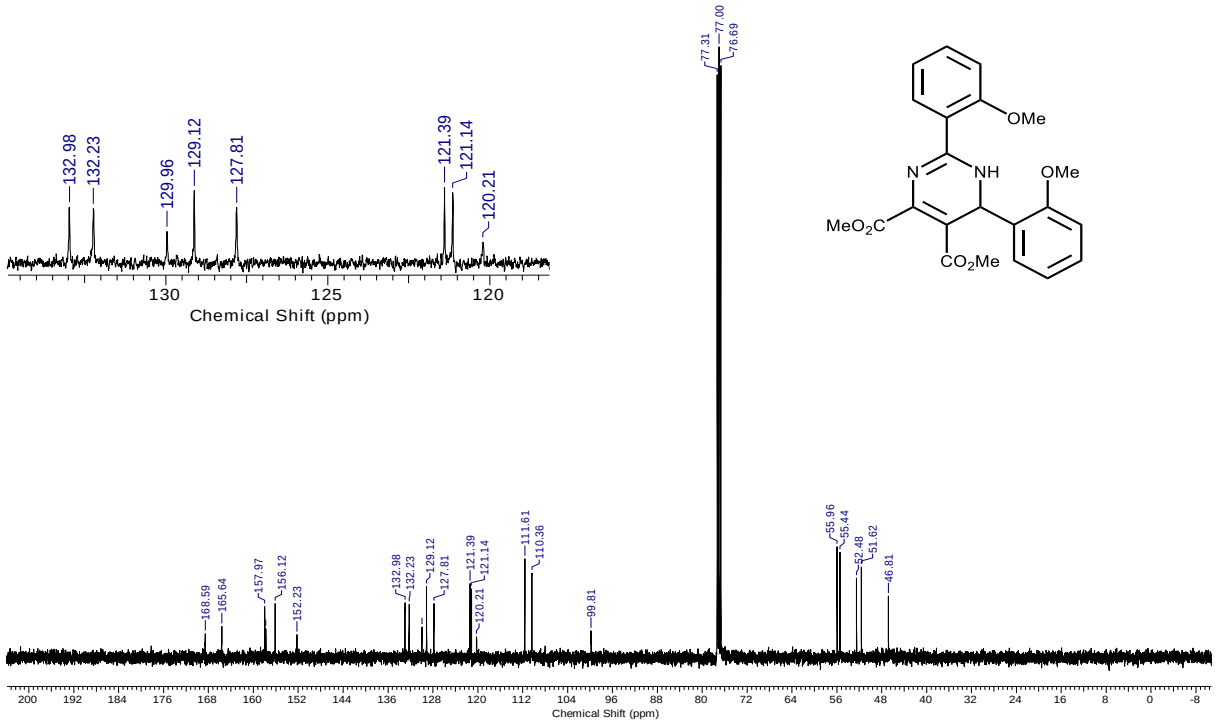


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **4d** in $CDCl_3$.

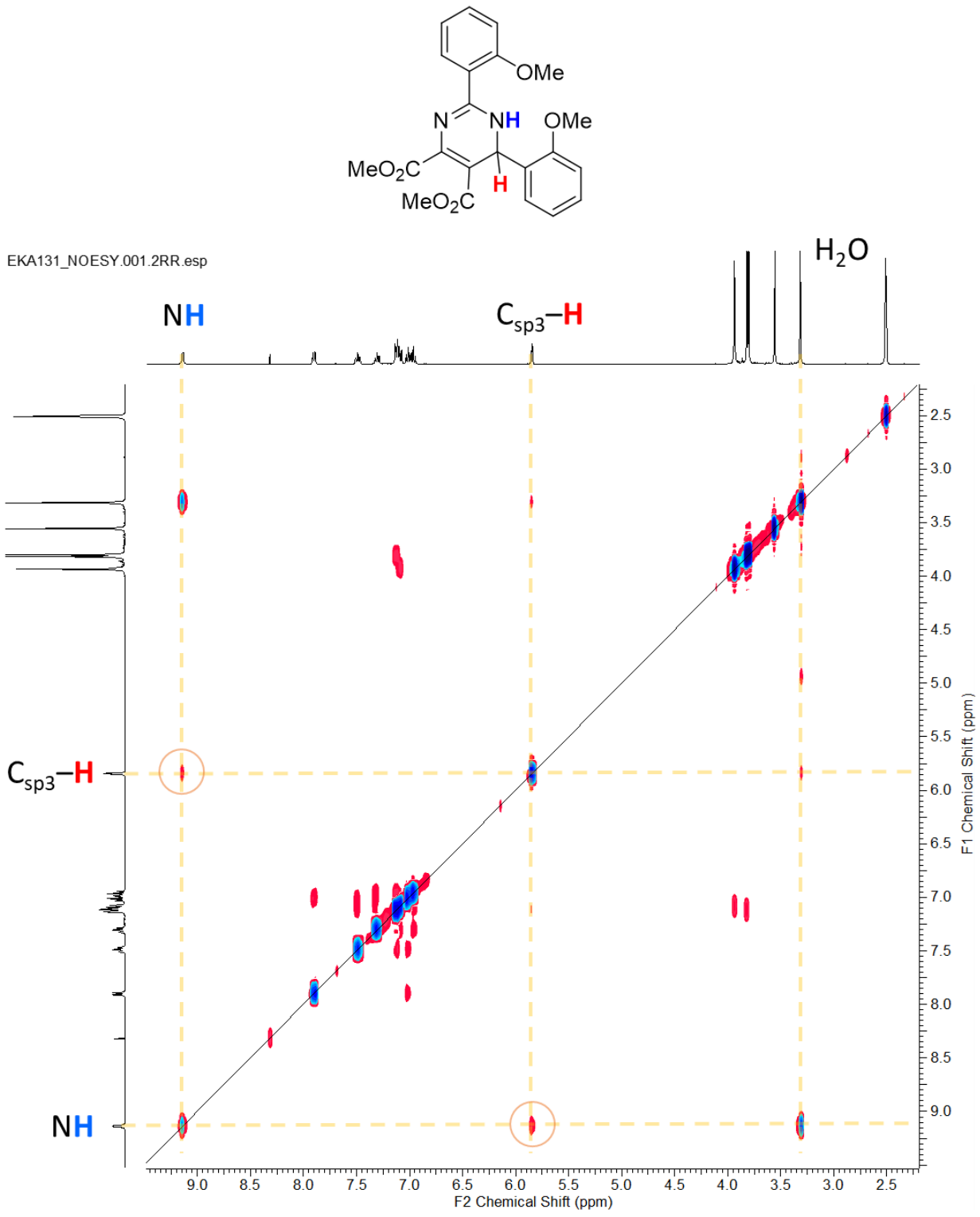


Figure S32. Fragment of the ^{1}H,^{1}H-NOESY NMR spectrum of **4d** in DMSO-d$_6$**.**

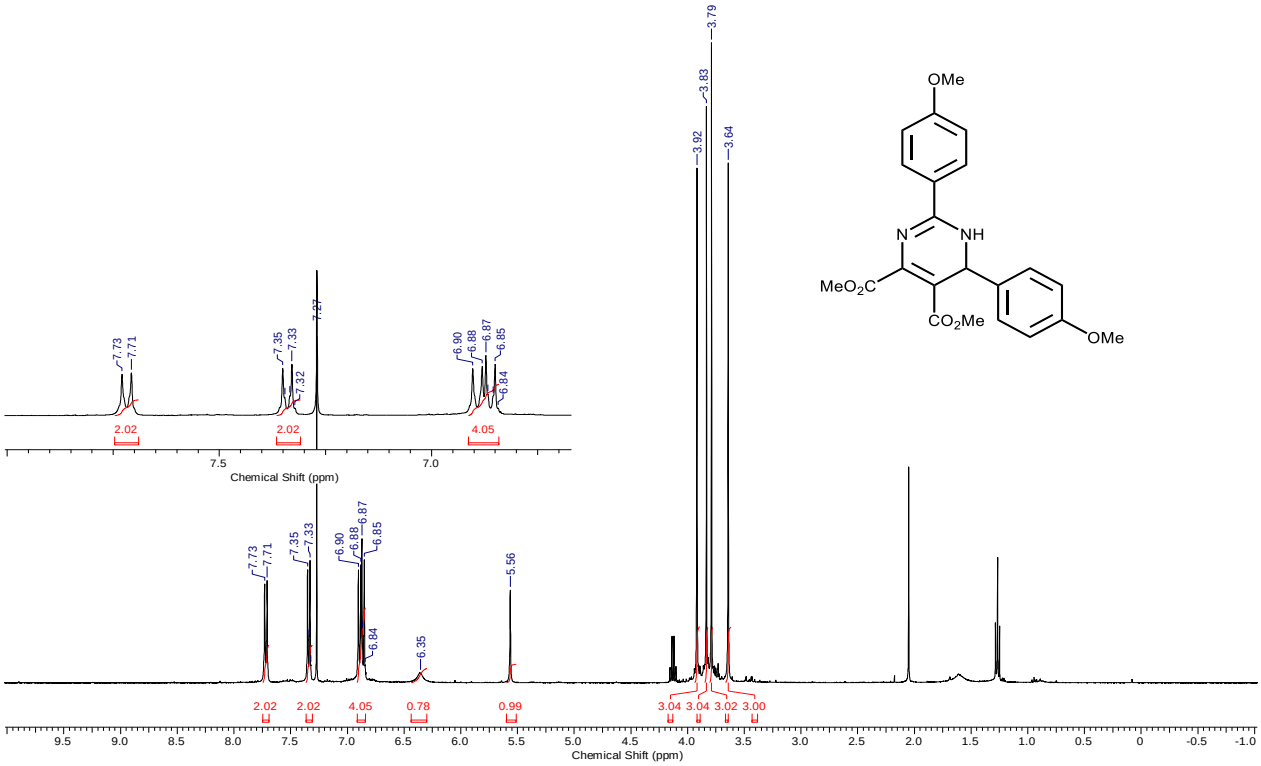


Figure S33. ^{1}H NMR spectrum of **4e** in $CDCl_3$.

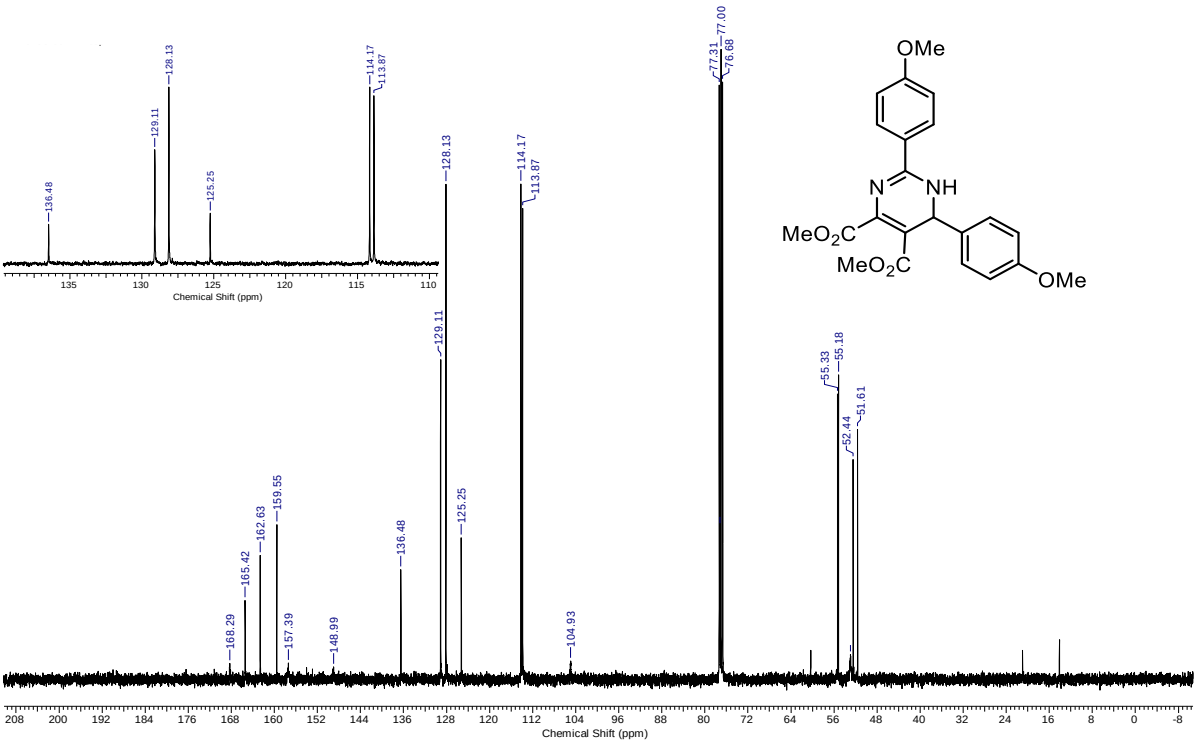


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of **4e** in $CDCl_3$.

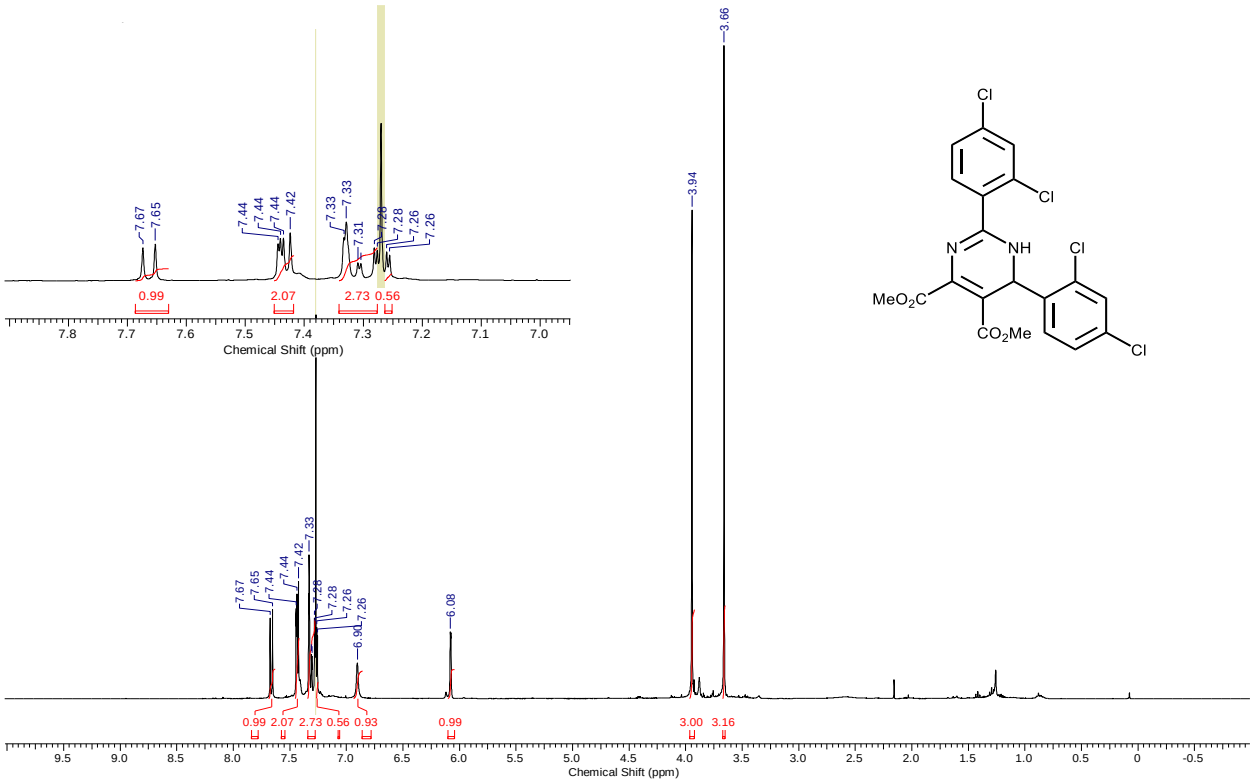


Figure S35. ^{1}H NMR spectrum of **4g** in $CDCl_3$.

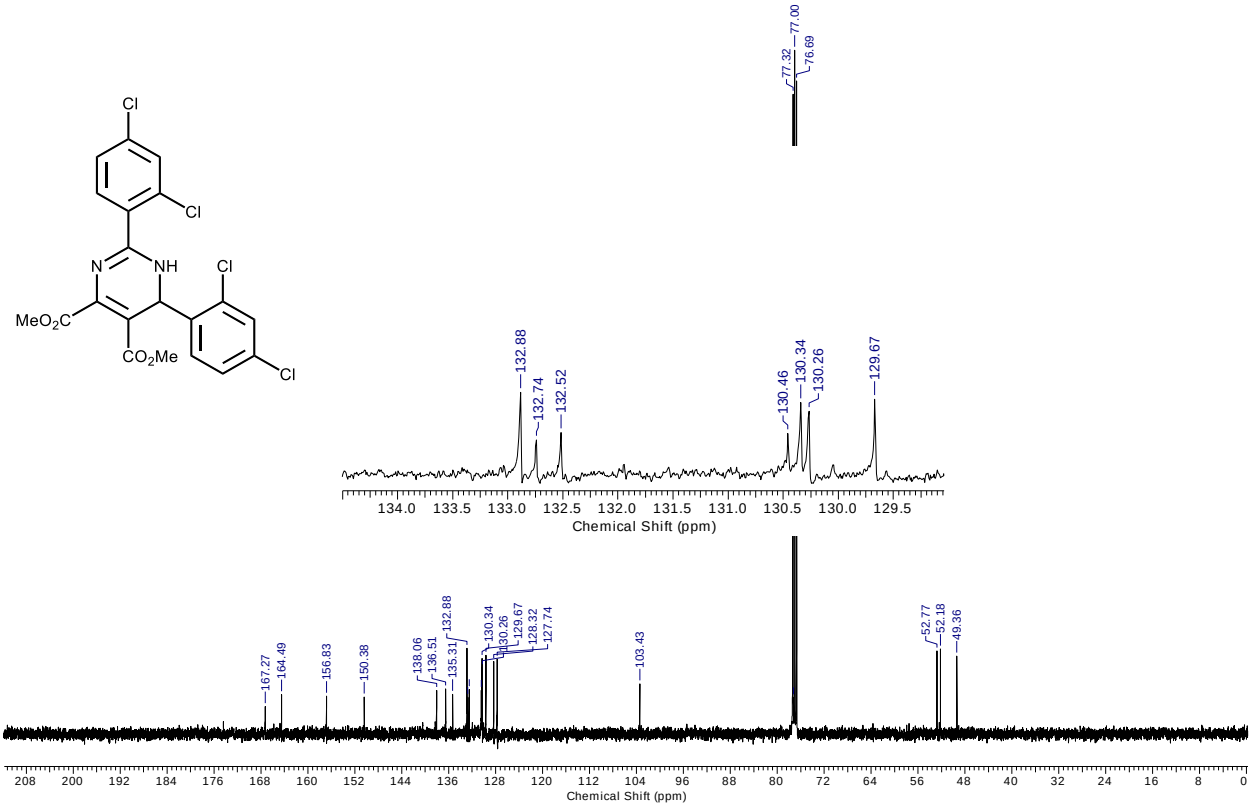


Figure S36. ^{13}C{^{1}H} NMR spectrum of **4f** in $CDCl_3$.

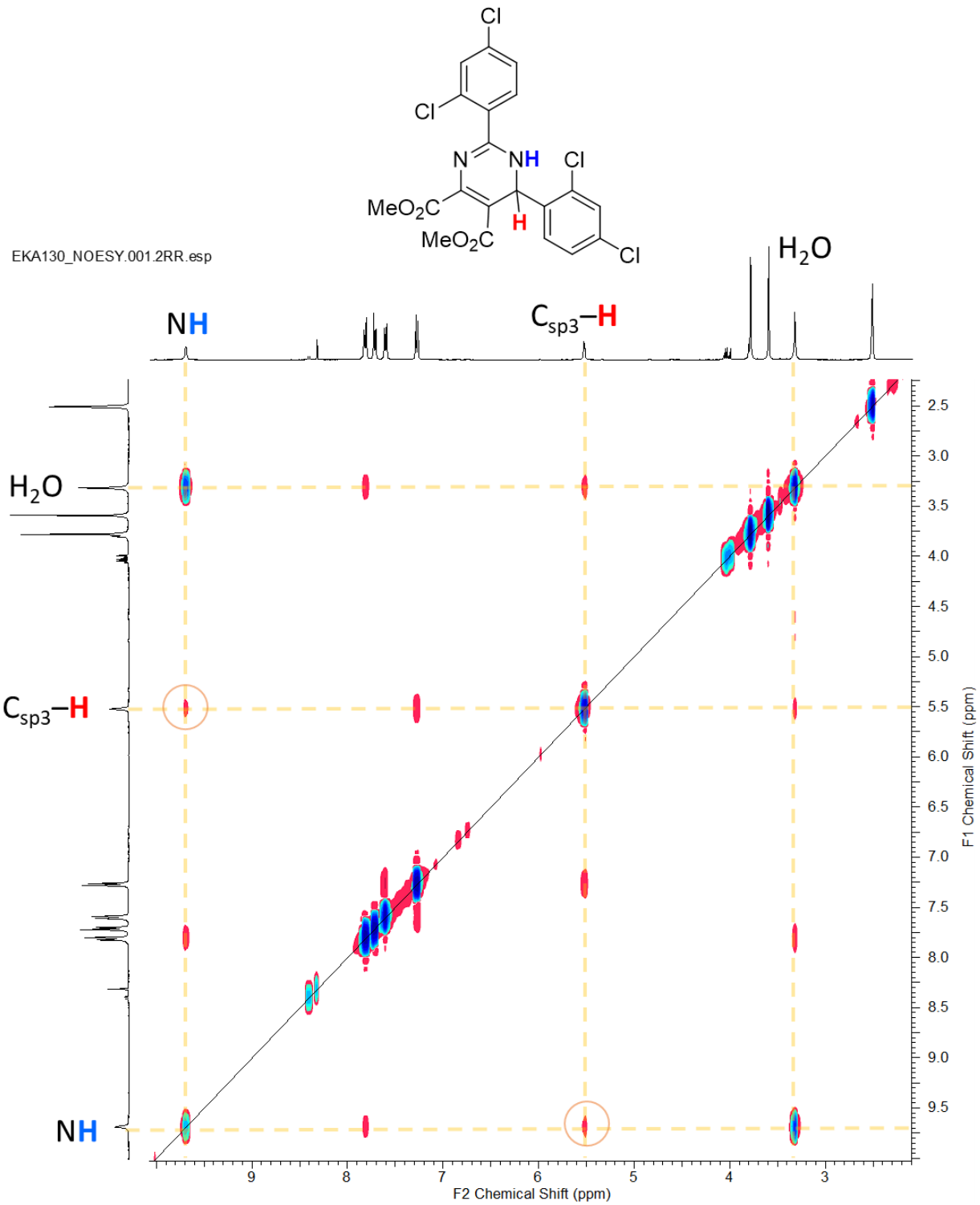


Figure S37. Fragment of the ^{1}H,^{1}H-NOESY NMR spectrum of **4f** in DMSO-d_6.

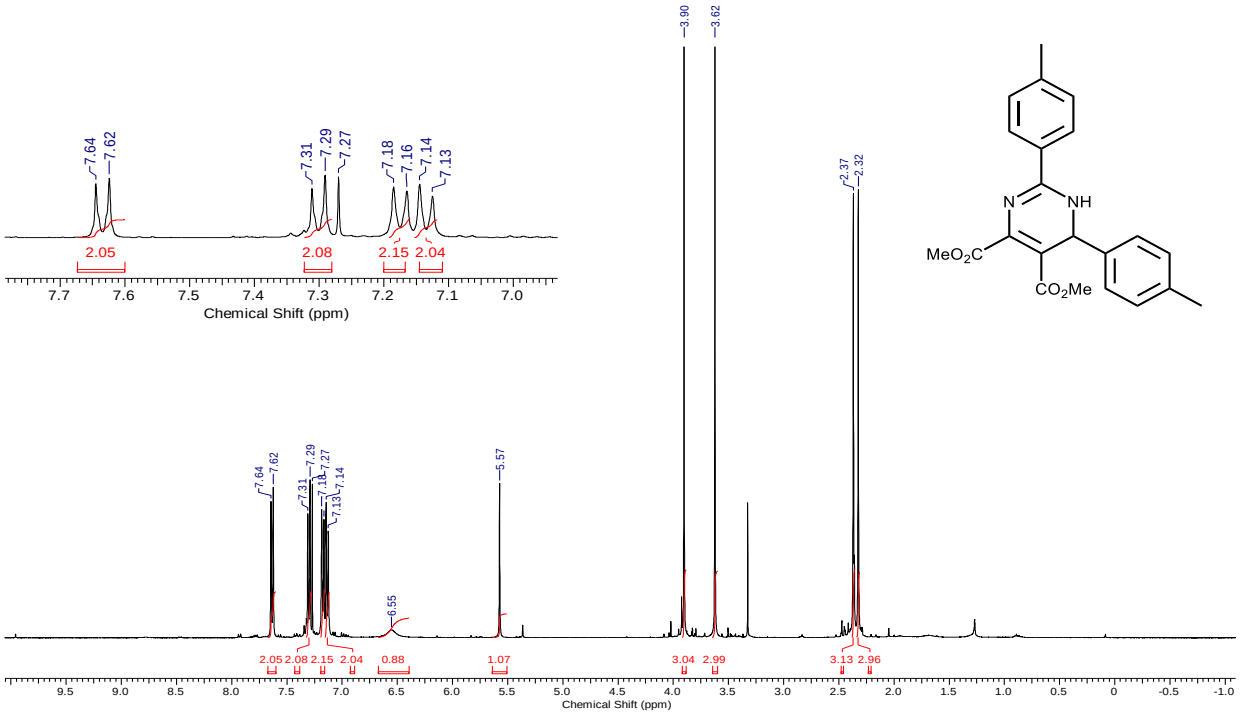


Figure S38. ^{1}H NMR spectrum of **4g** in $CDCl_3$.

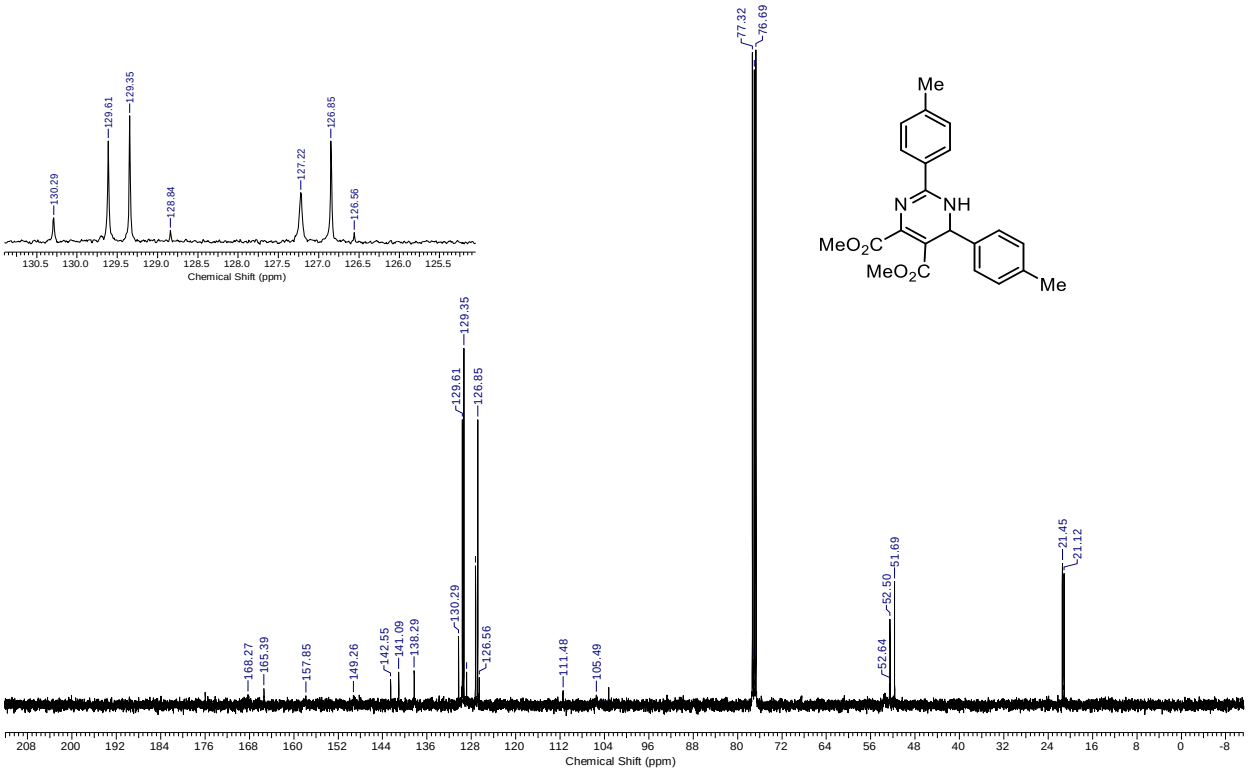


Figure S39. ^{13}C{^{1}H} NMR spectrum of **4g** in $CDCl_3$.

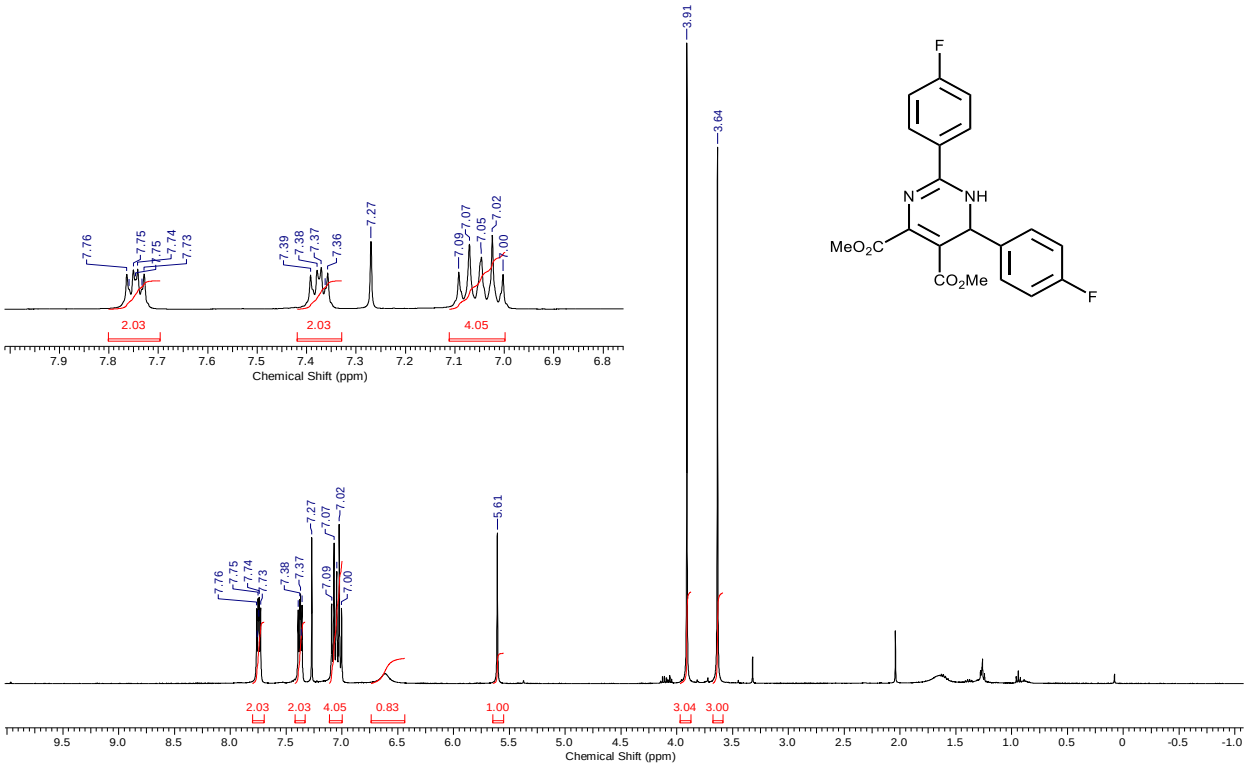


Figure S40. ^{1}H NMR spectrum of **4h** in $CDCl_3$.

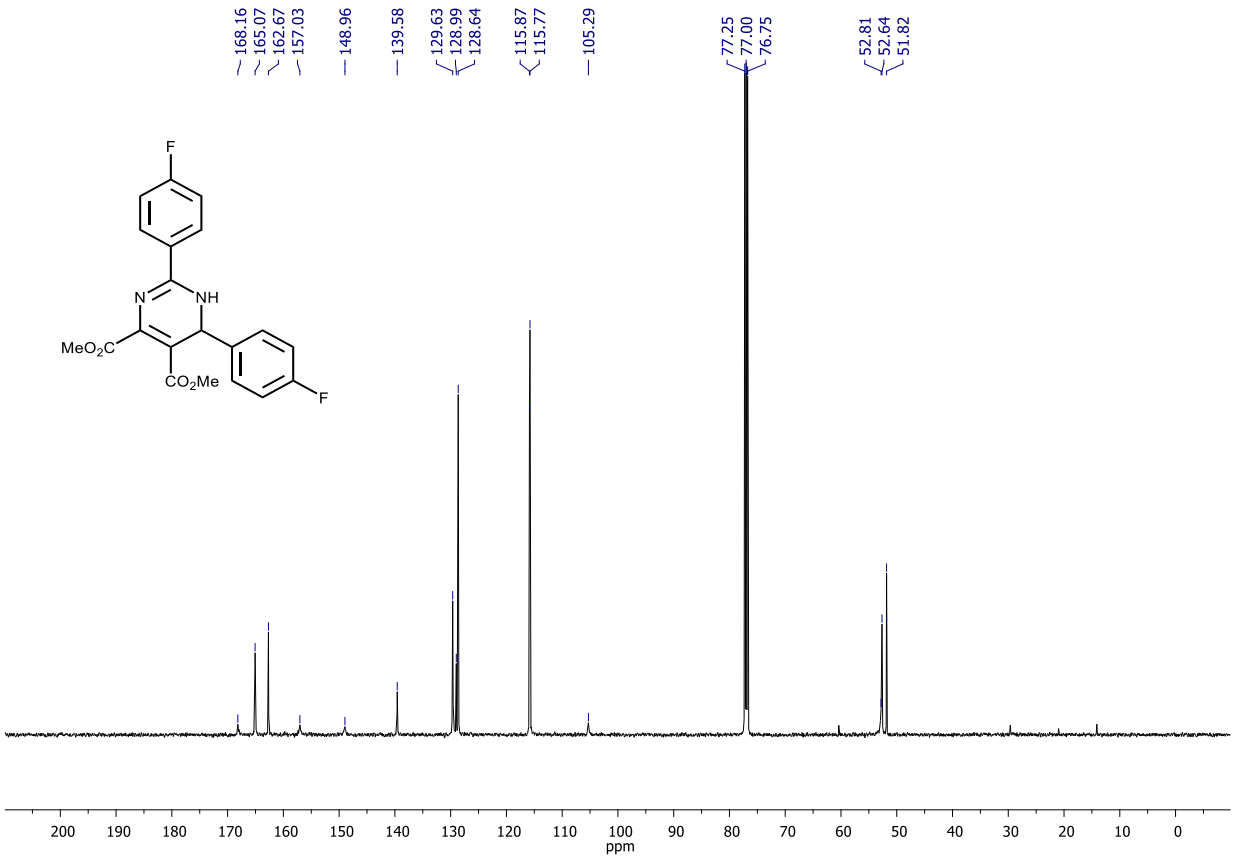


Figure S41. $^{13}C\{^{1}H,^{19}F\}$ NMR spectrum of **4h** in $CDCl_3$.

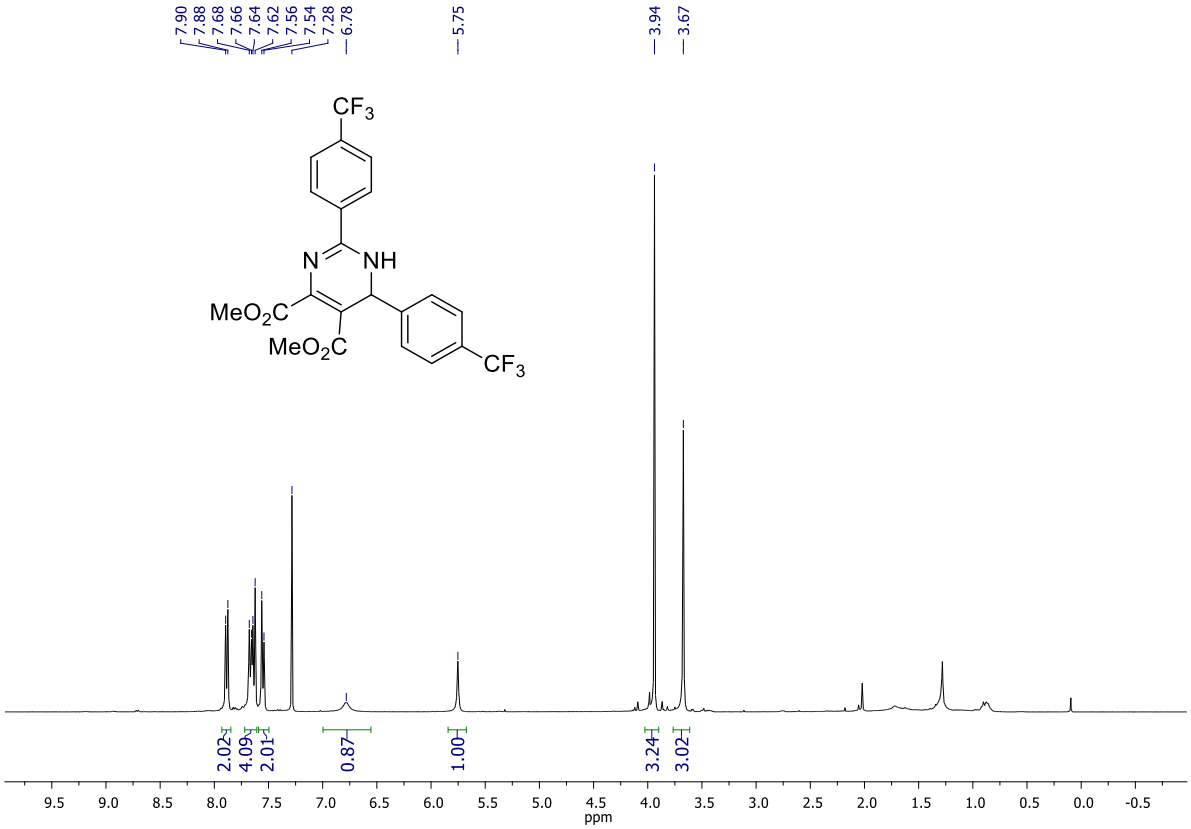


Figure S42. ^{1}H NMR spectrum of **4i** in $CDCl_3$.

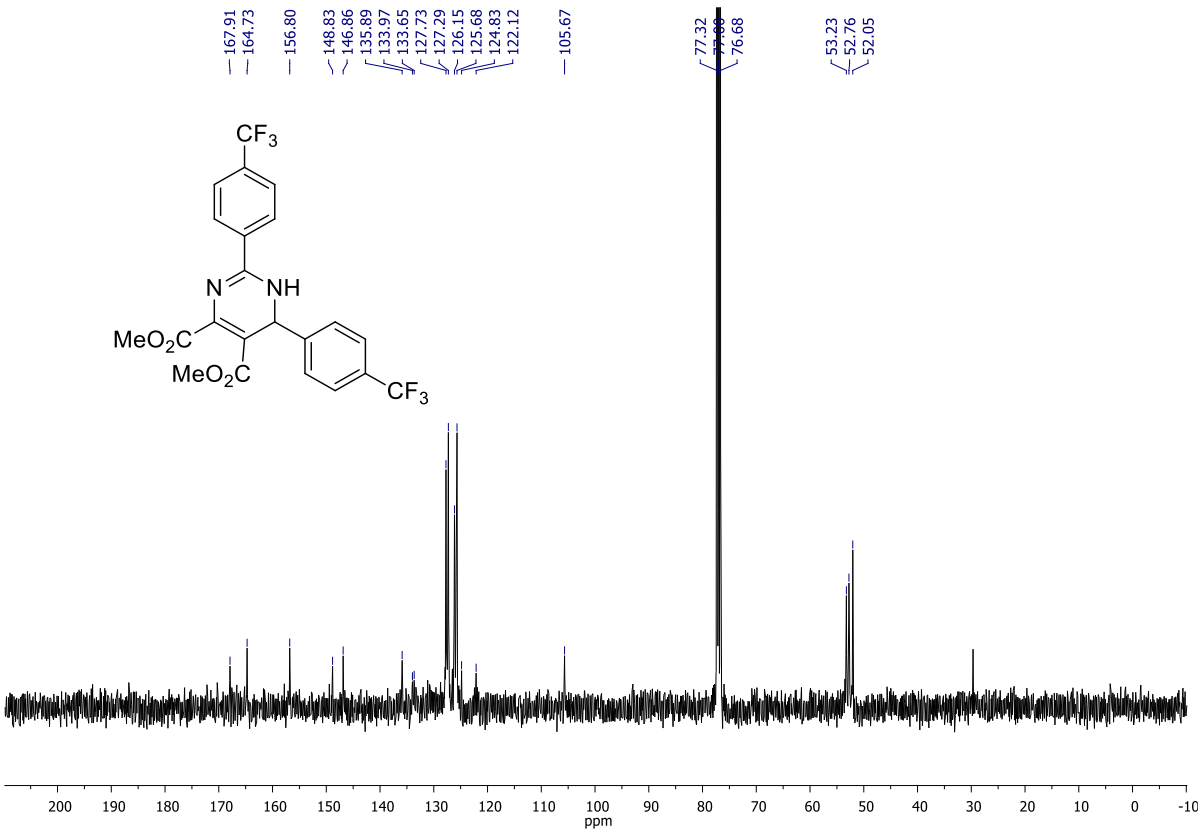


Figure S43. ^{13}C{^{1}H} NMR spectrum of **4i** in $CDCl_3$.

Figure S44. $^{19}F\{^{1}H\}$ NMR spectrum of **4i** in $CDCl_3$.

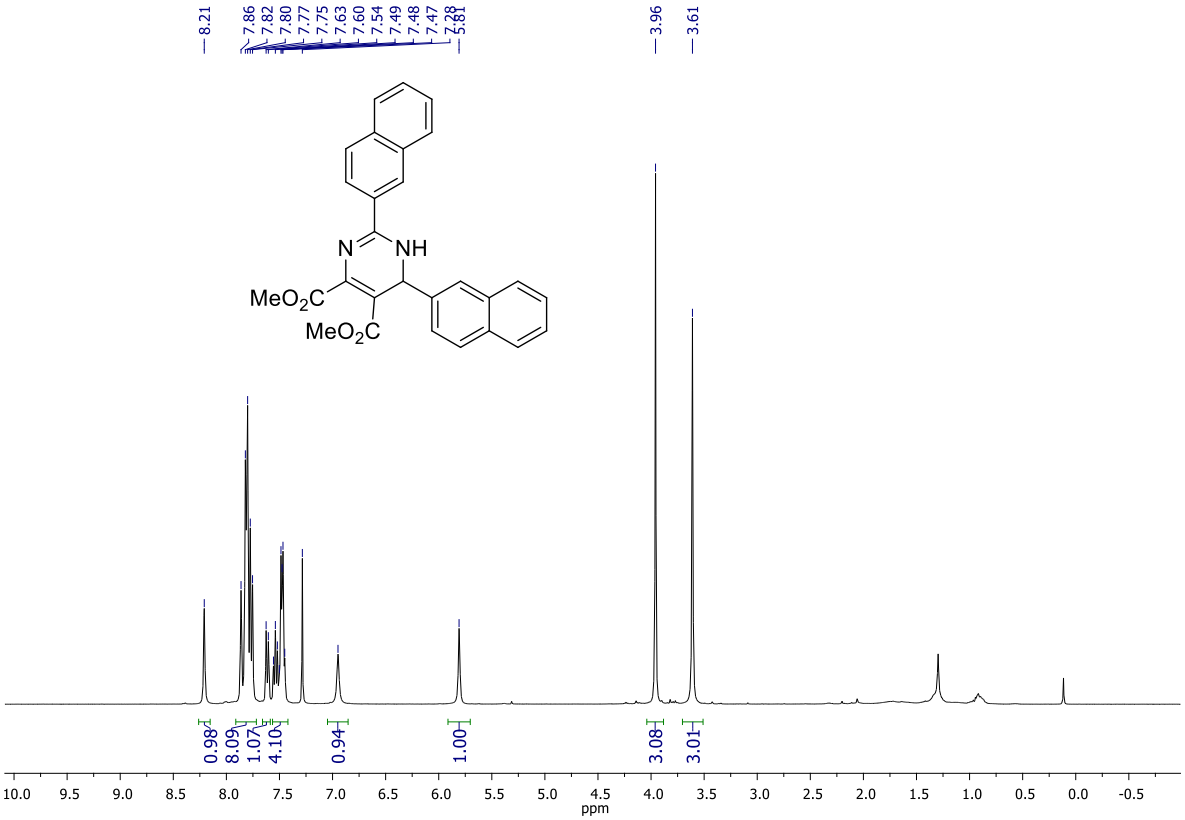


Figure S45. ^{1}H NMR spectrum of **4j** in $CDCl_3$.

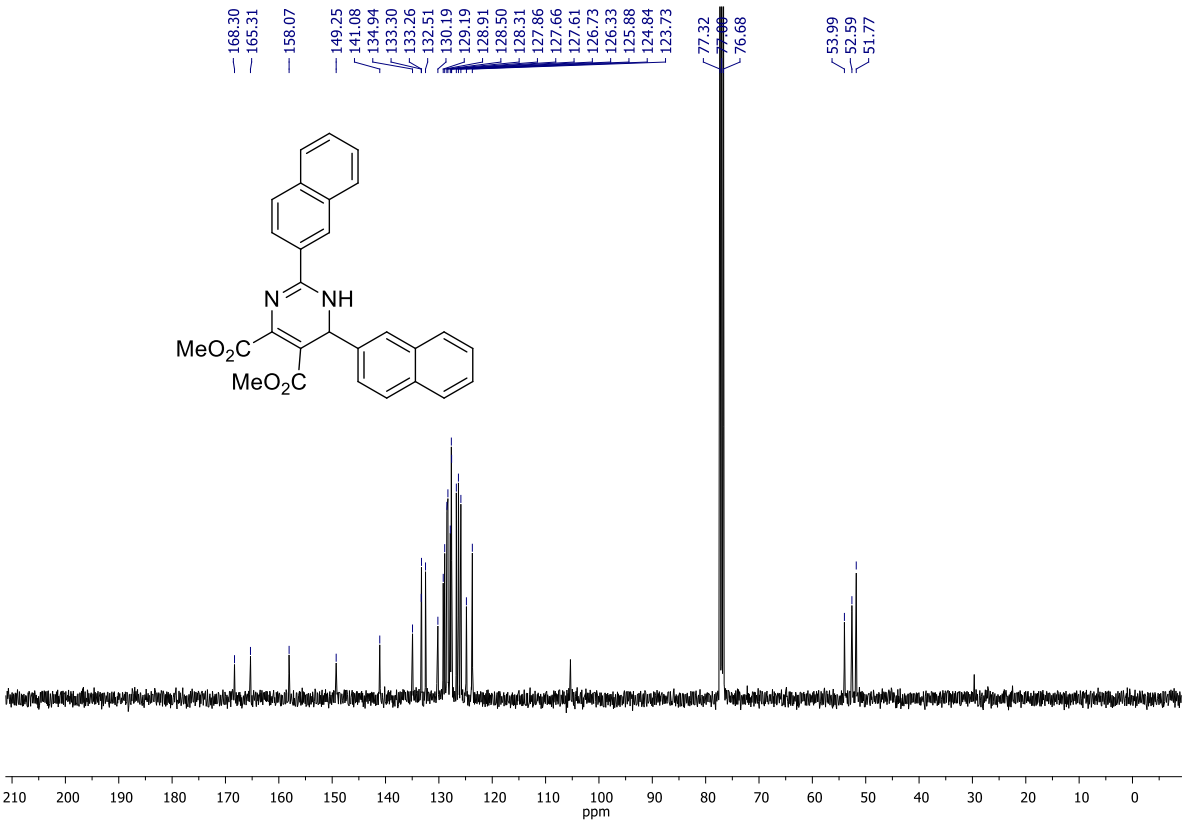


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of **4j** in $CDCl_3$.

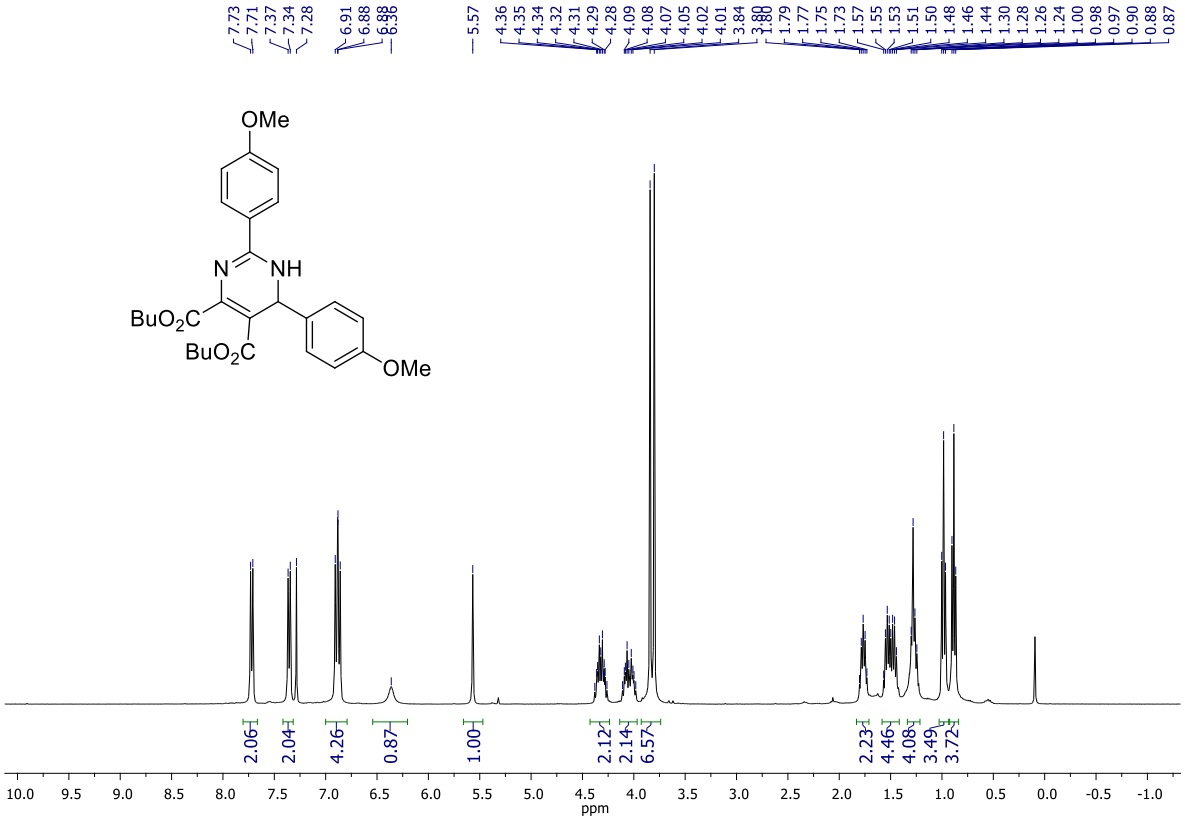


Figure S47. ^{1}H NMR spectrum of **4k** in $CDCl_3$.

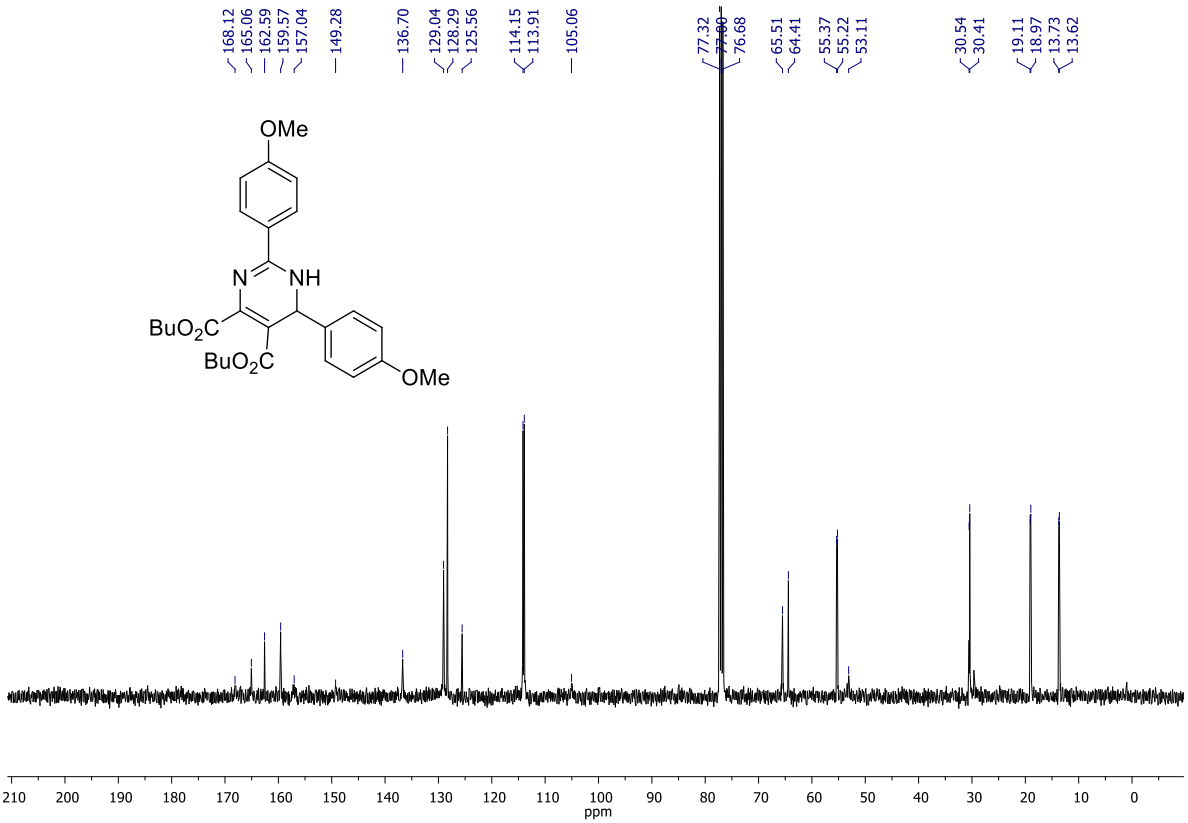


Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of **4k** in $CDCl_3$.

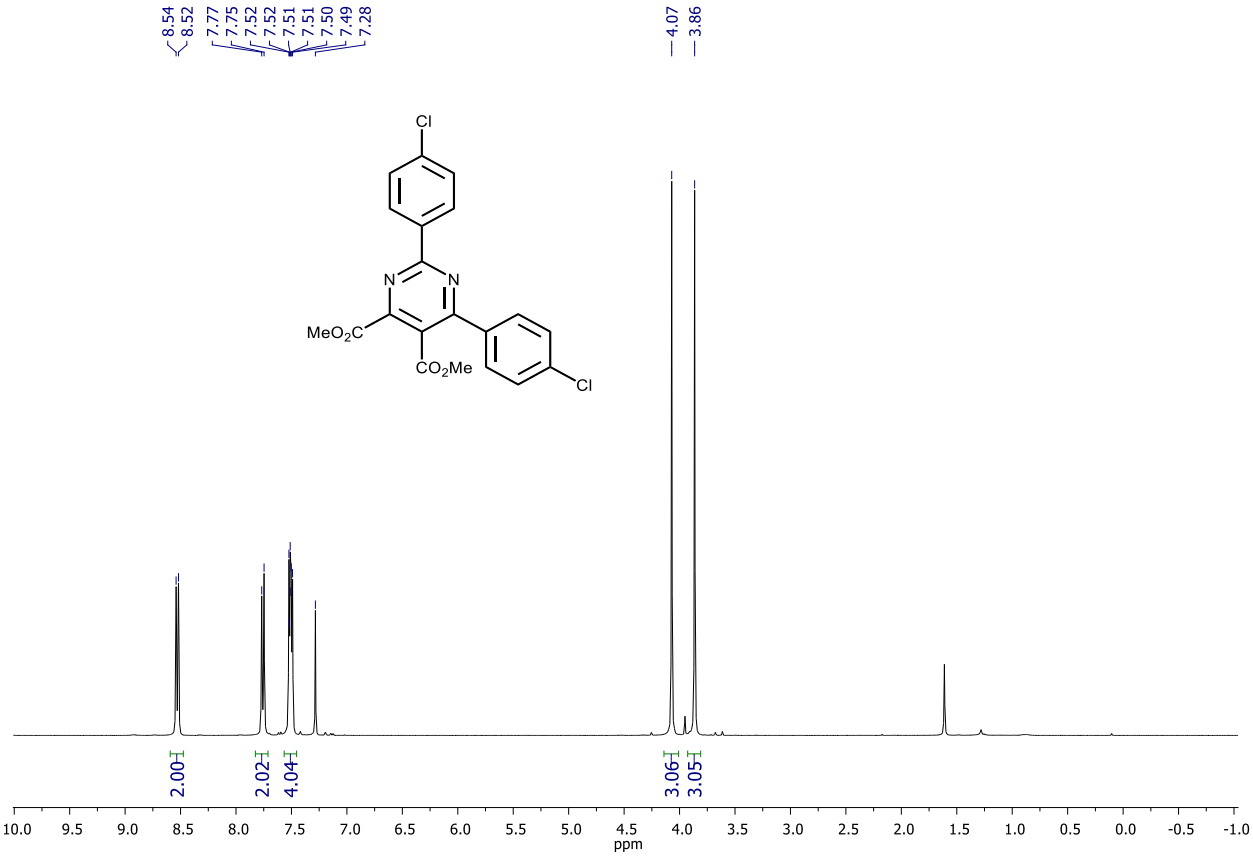


Figure S49. ^{1}H NMR spectrum of **5a** in $CDCl_3$.

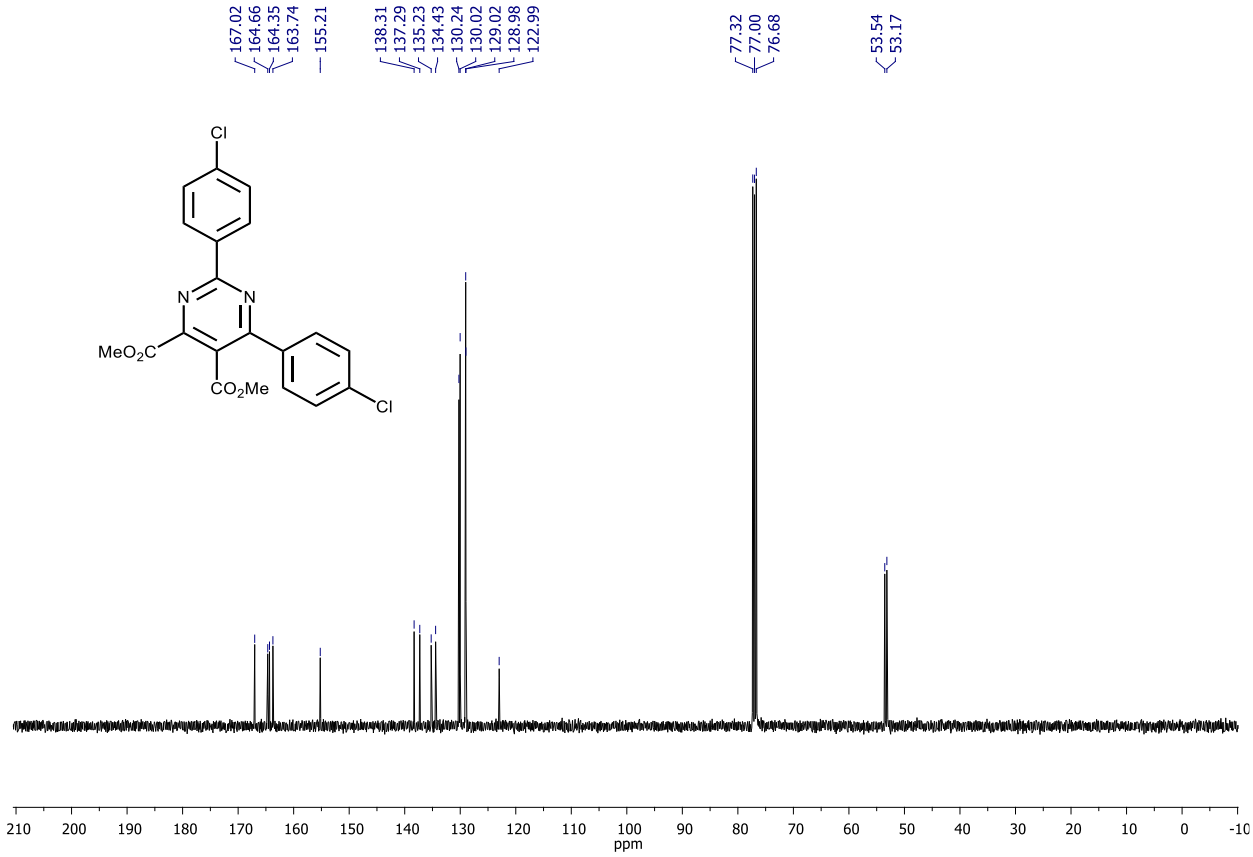


Figure S50. ^{13}C{^{1}H} NMR spectrum of **5a** in $CDCl_3$.

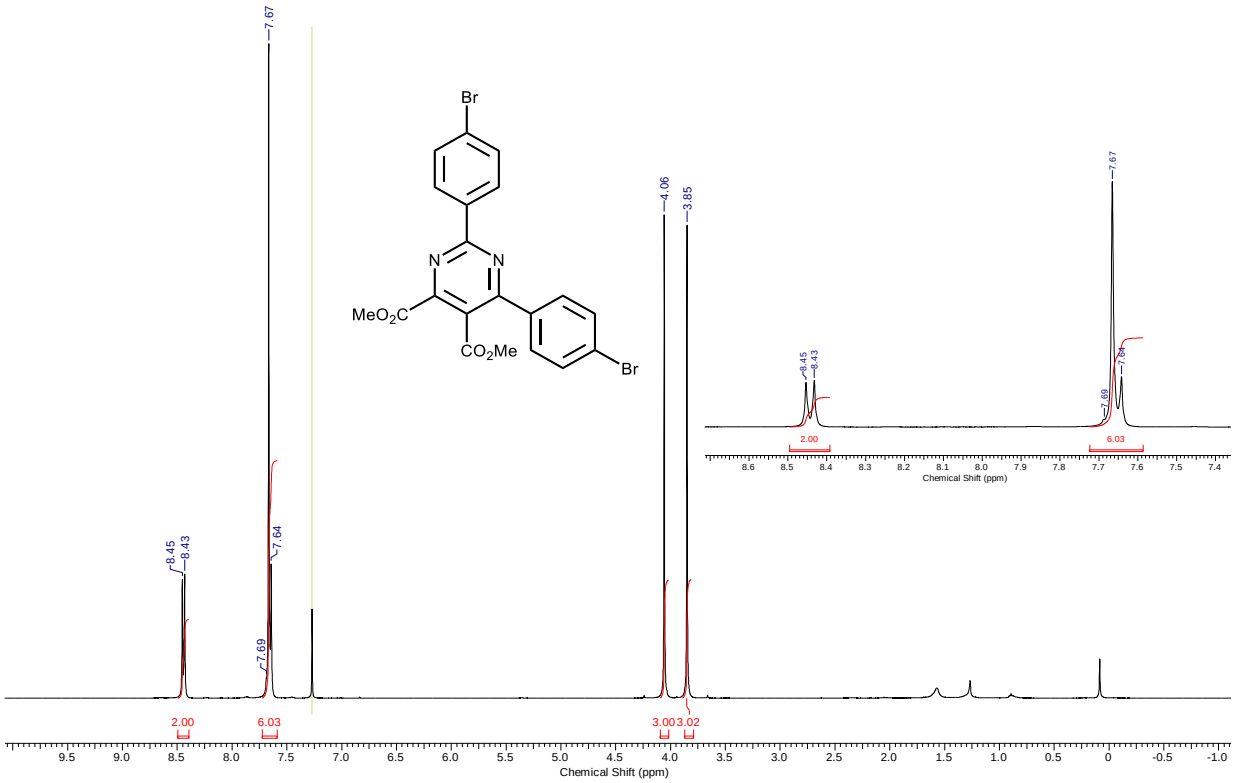


Figure S51. ^{1}H NMR spectrum of **5b** in $CDCl_3$.

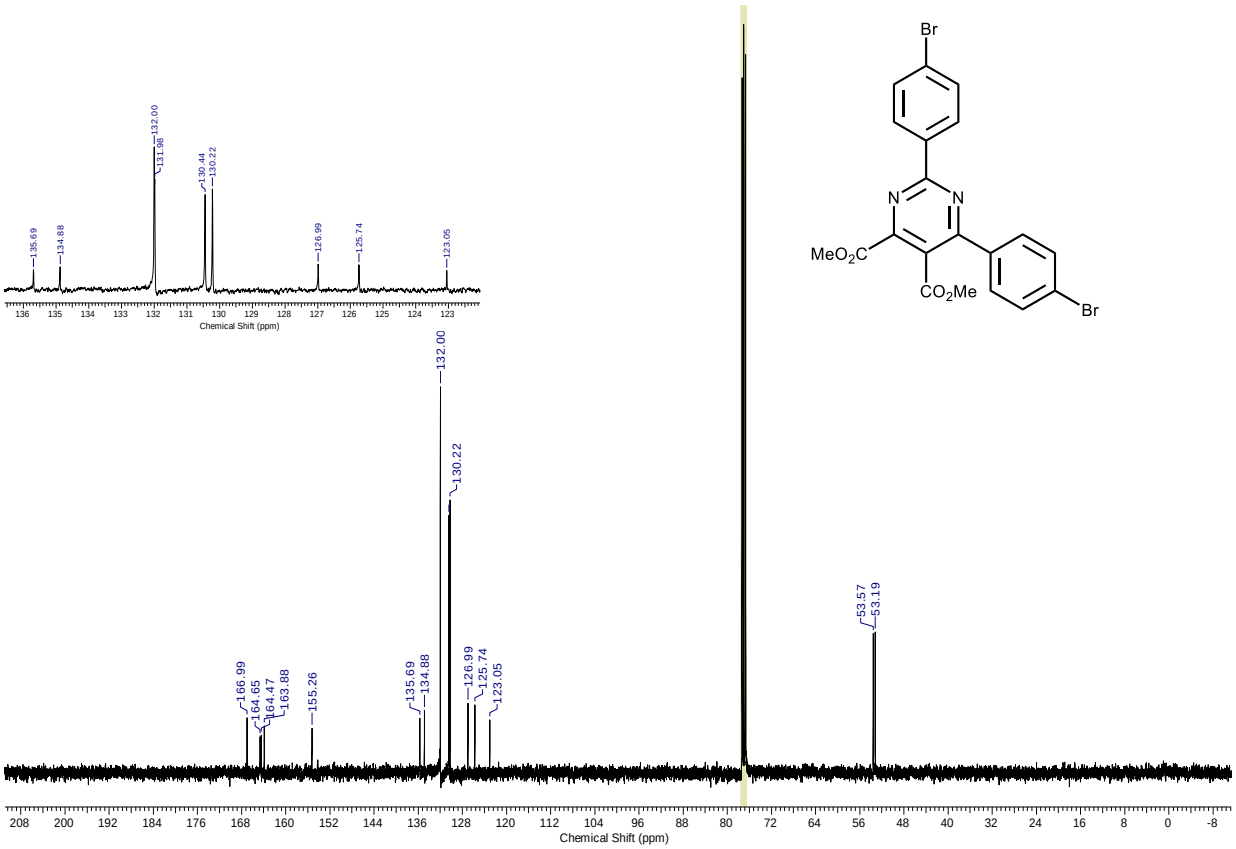


Figure S52. ^{13}C{^{1}H} NMR spectrum of **5b** in $CDCl_3$.

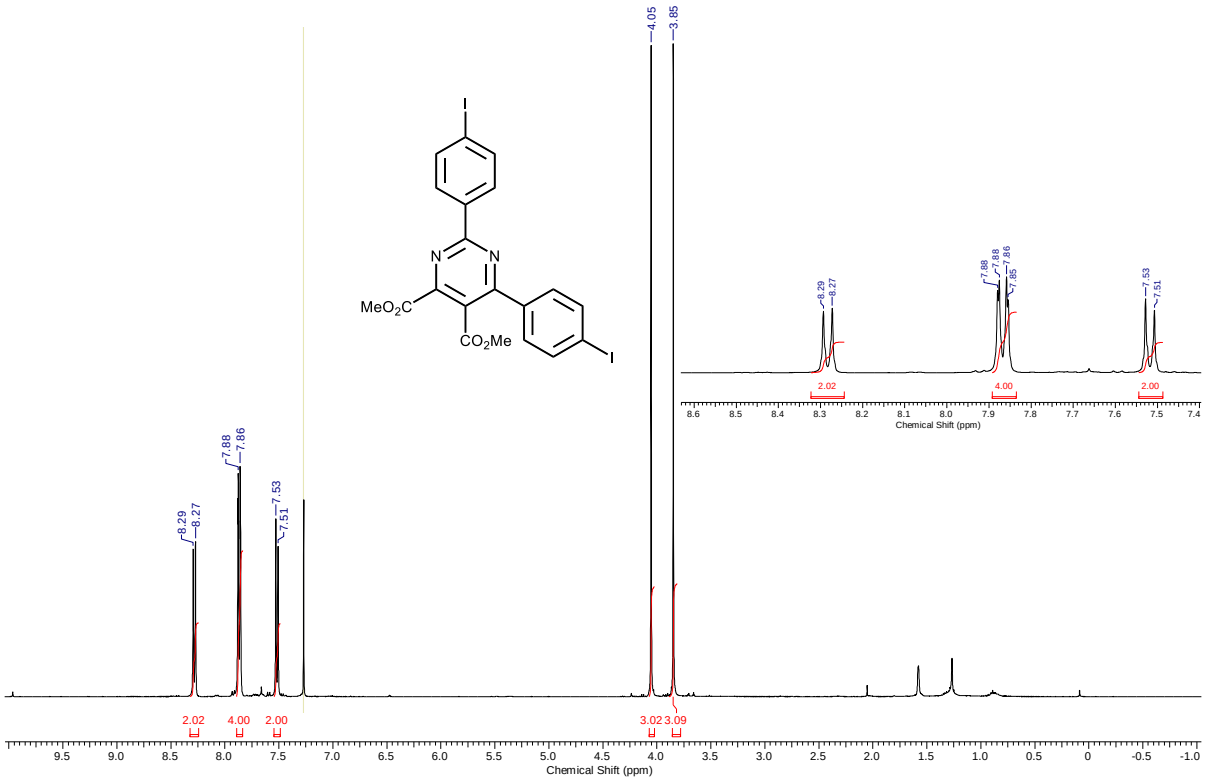


Figure S53. ^{1}H NMR spectrum of **5c** in $CDCl_3$.

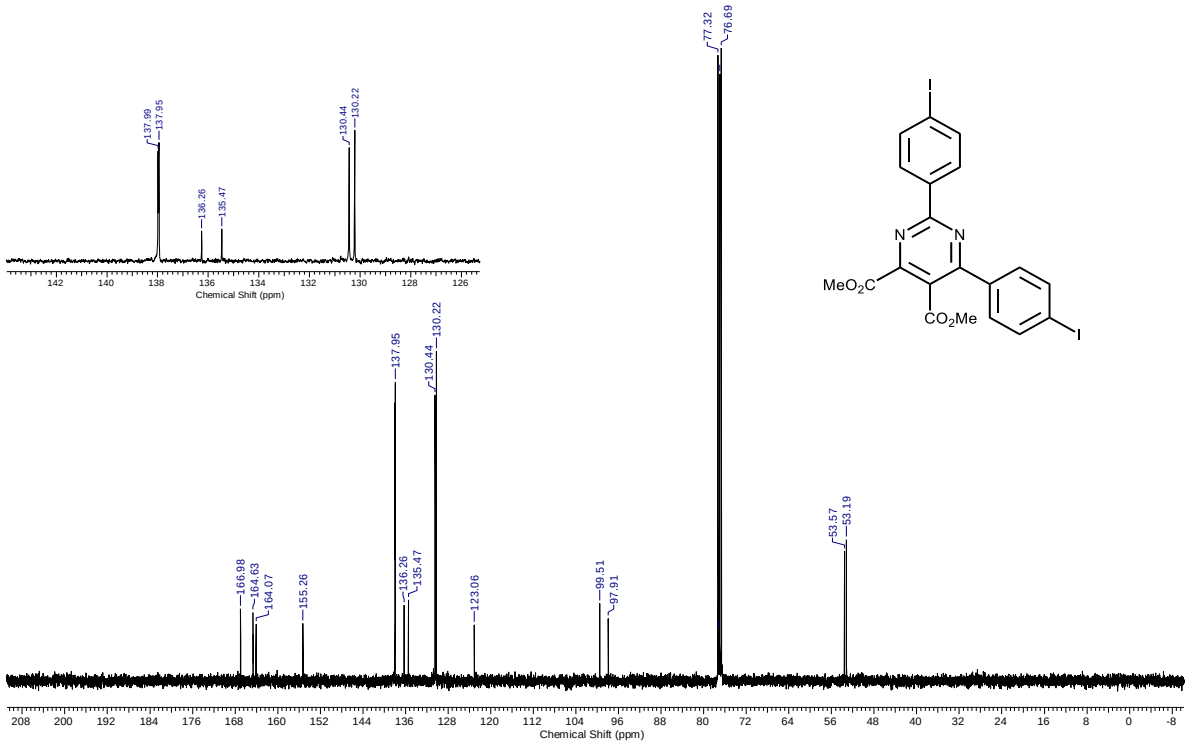


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum of **5c** in $CDCl_3$.

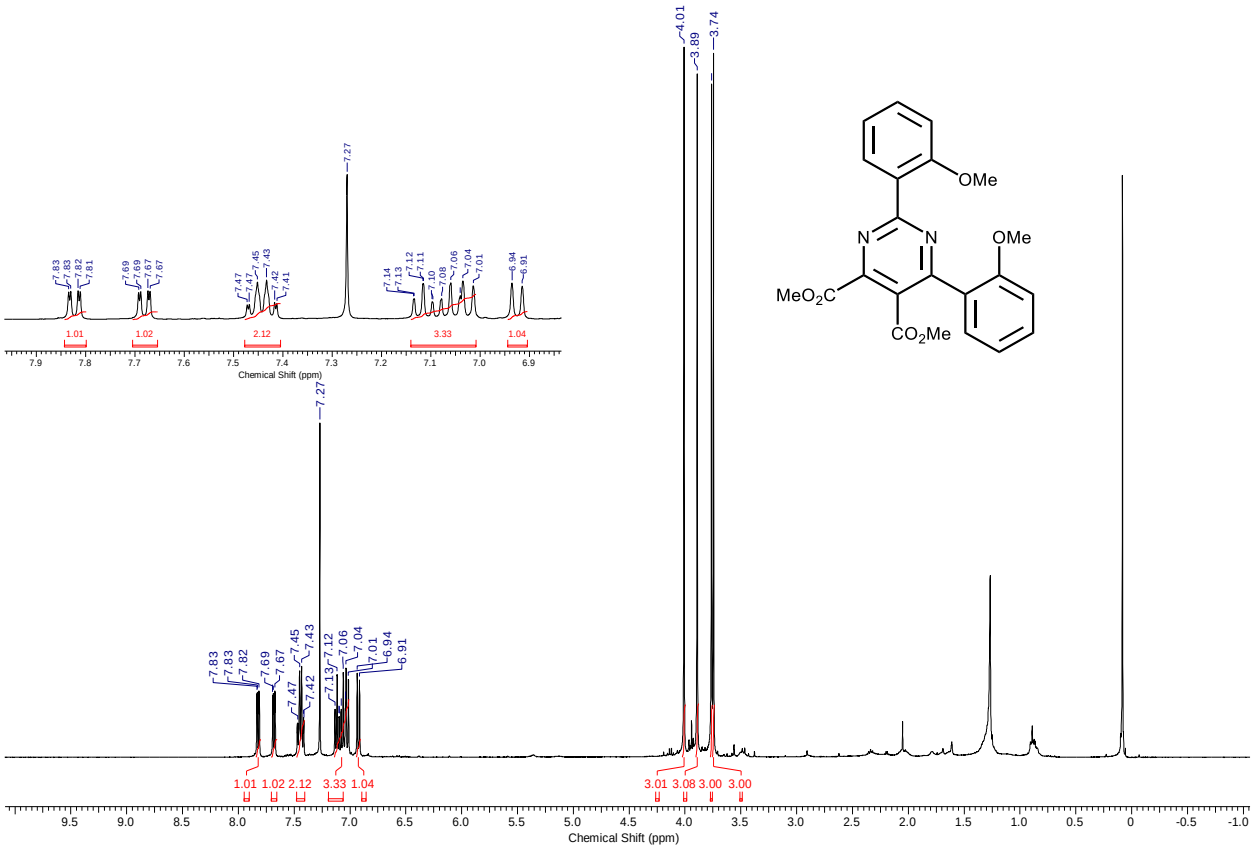


Figure S55. ^{1}H NMR spectrum of **5d** in $CDCl_3$.

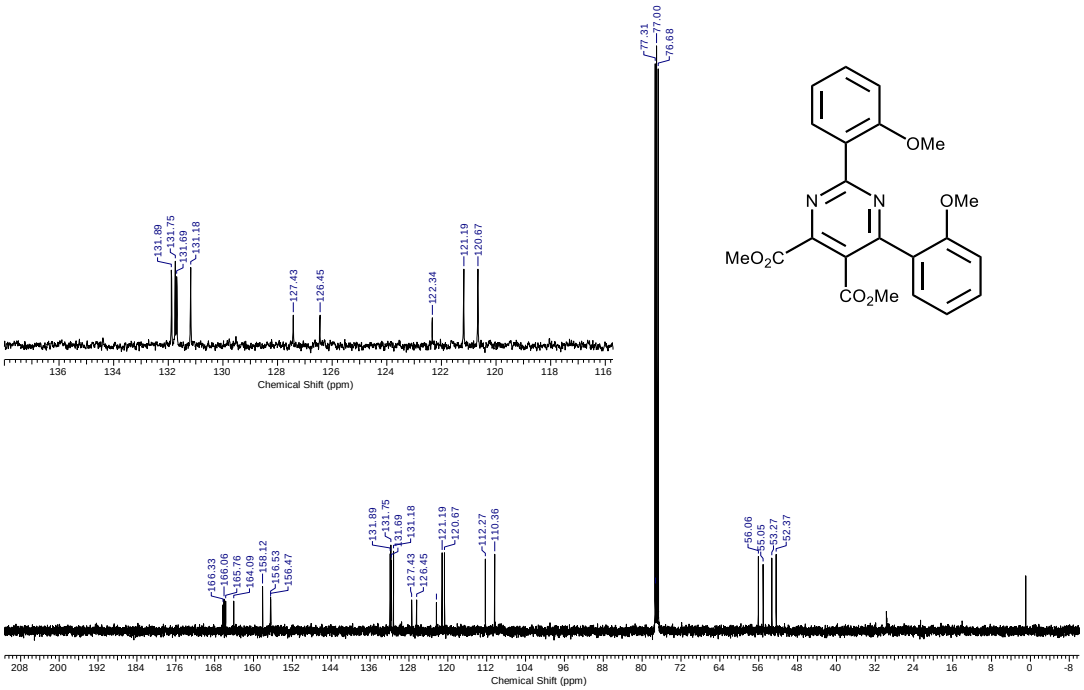


Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of **5d** in $CDCl_3$.

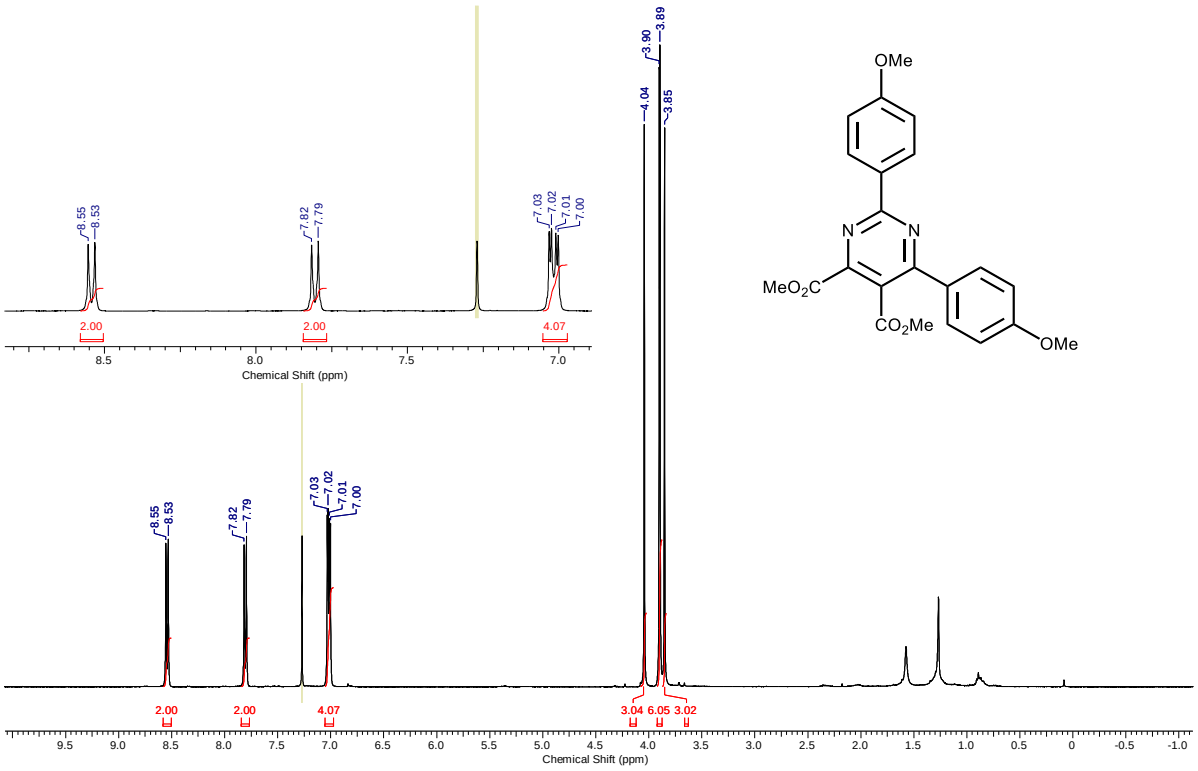


Figure S57. ^{1}H NMR spectrum of **5e** in $CDCl_3$.

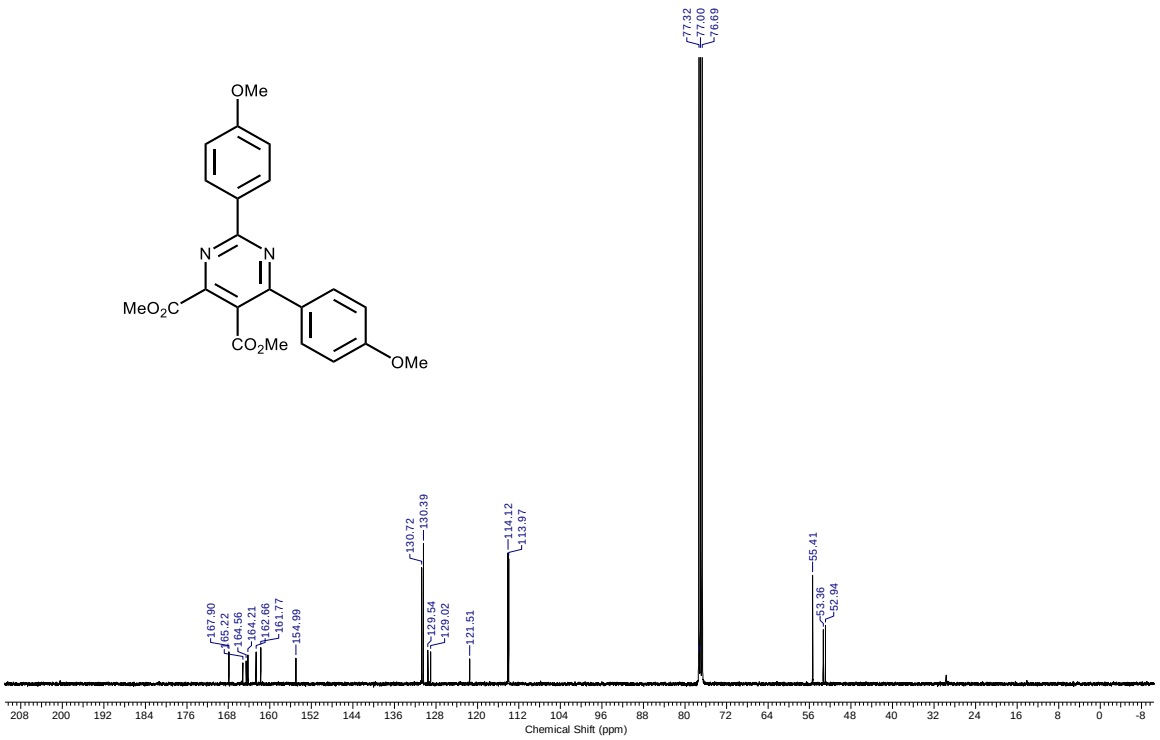


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of **5e** in $CDCl_3$.

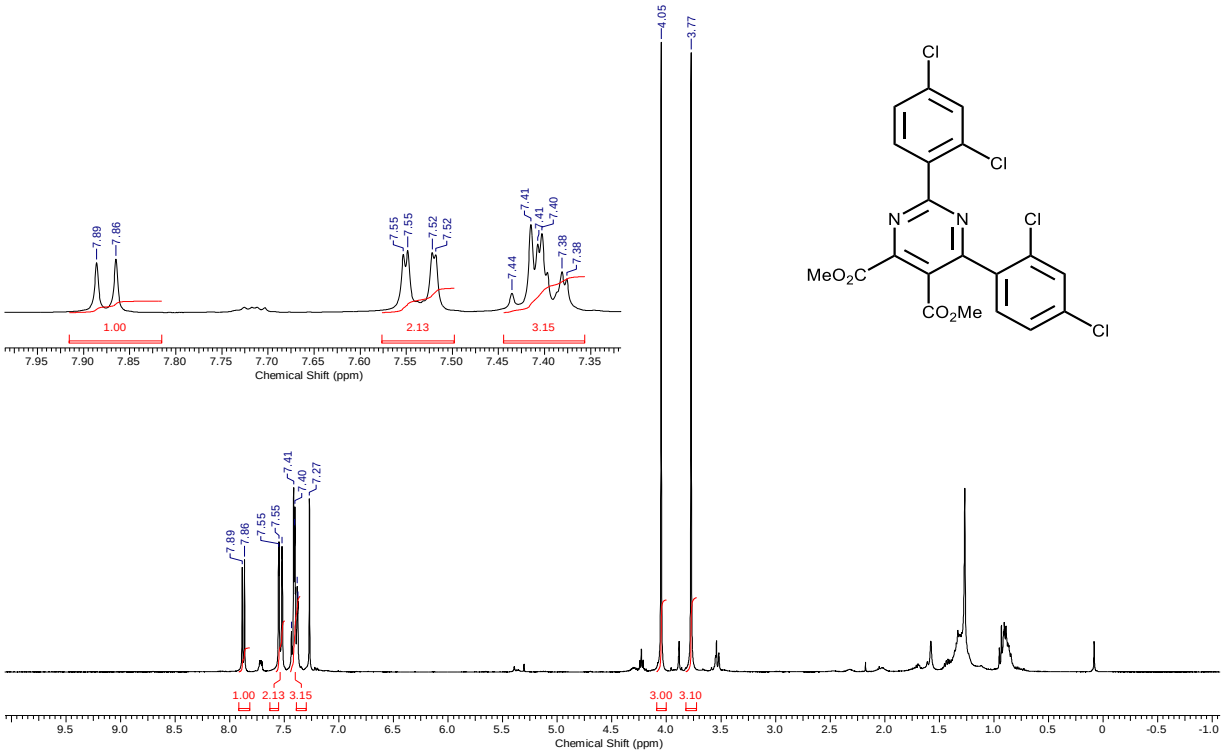


Figure S59. ^{1}H NMR spectrum of **5f** in $CDCl_3$.

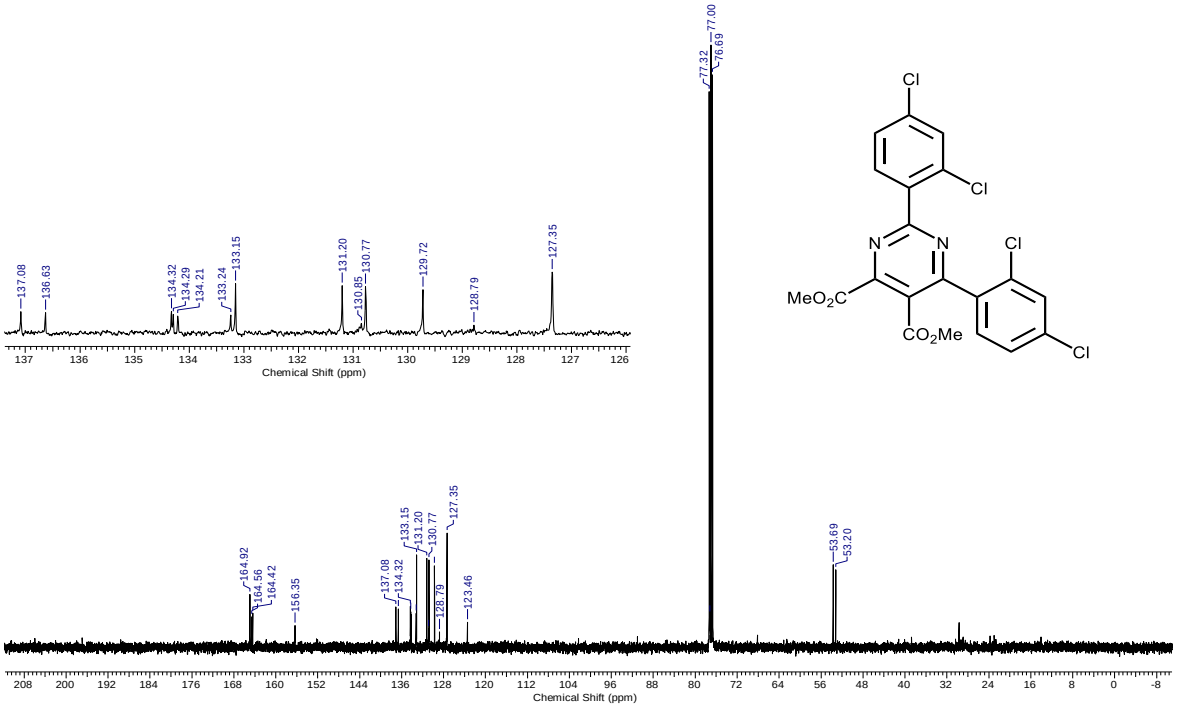


Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum of **5f** in $CDCl_3$.

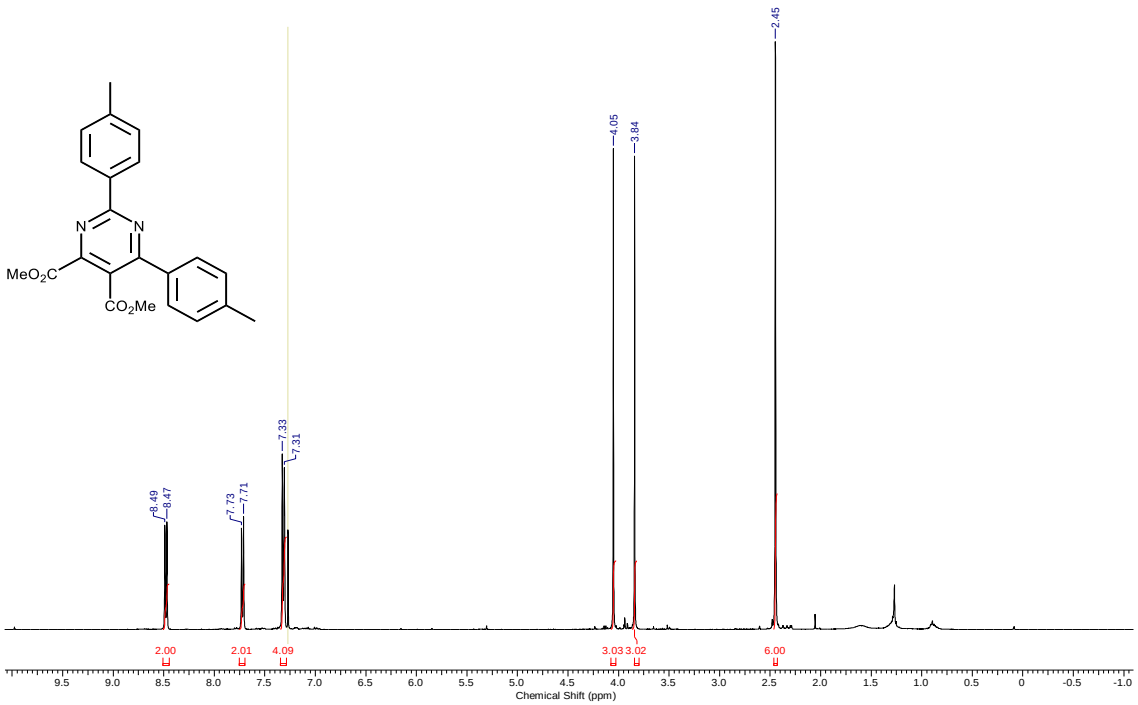


Figure S61. ^{1}H NMR spectrum of **5g** in $CDCl_3$

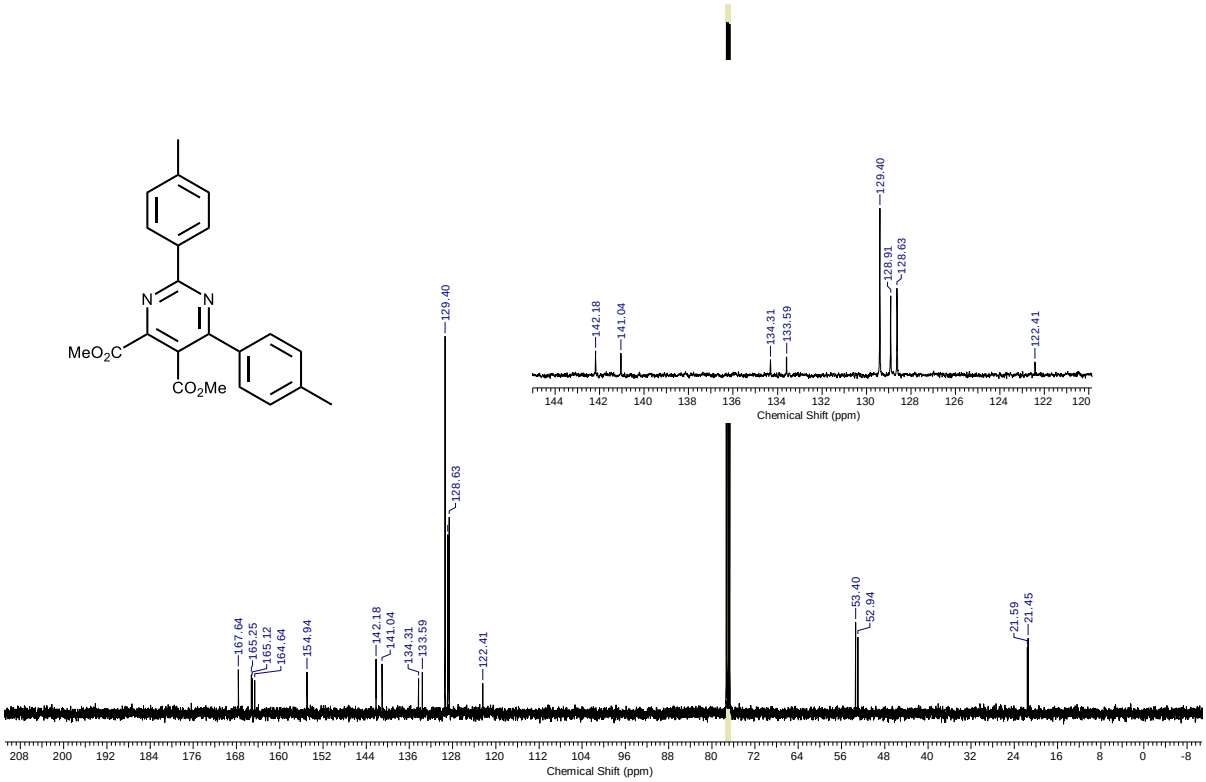


Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum of **5g** in $CDCl_3$.

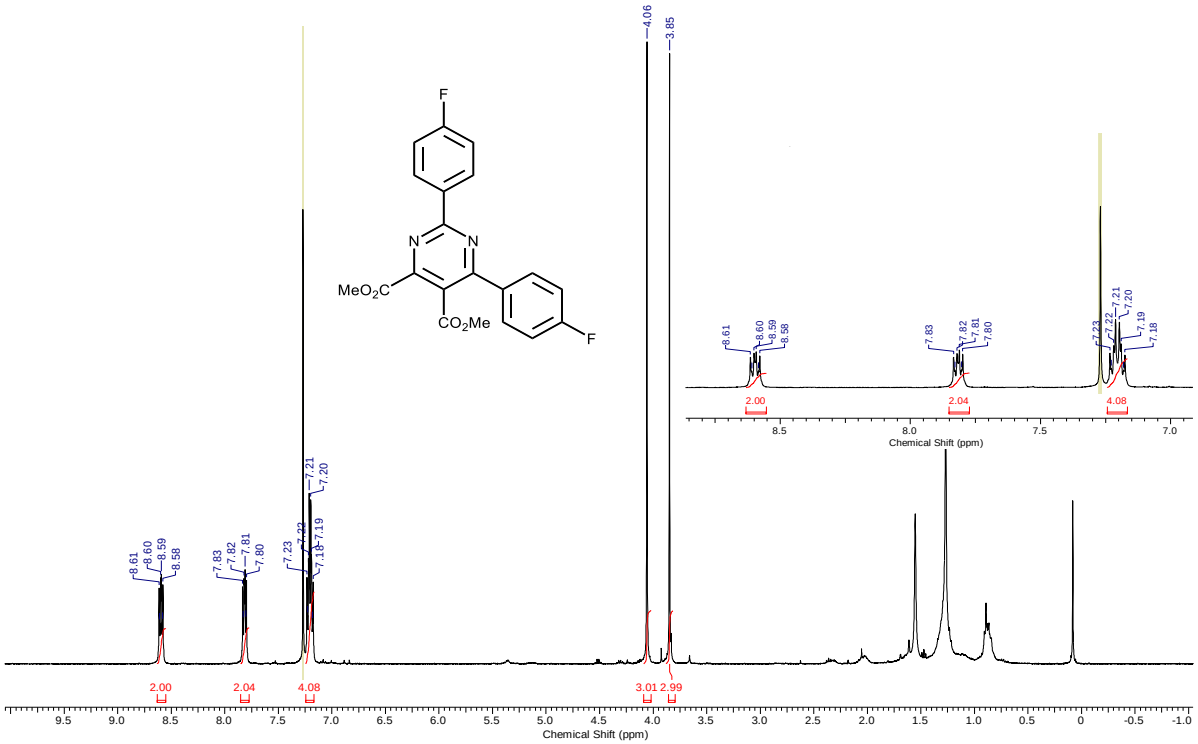


Figure S63. ^{1}H NMR spectrum of **5h** in $CDCl_3$

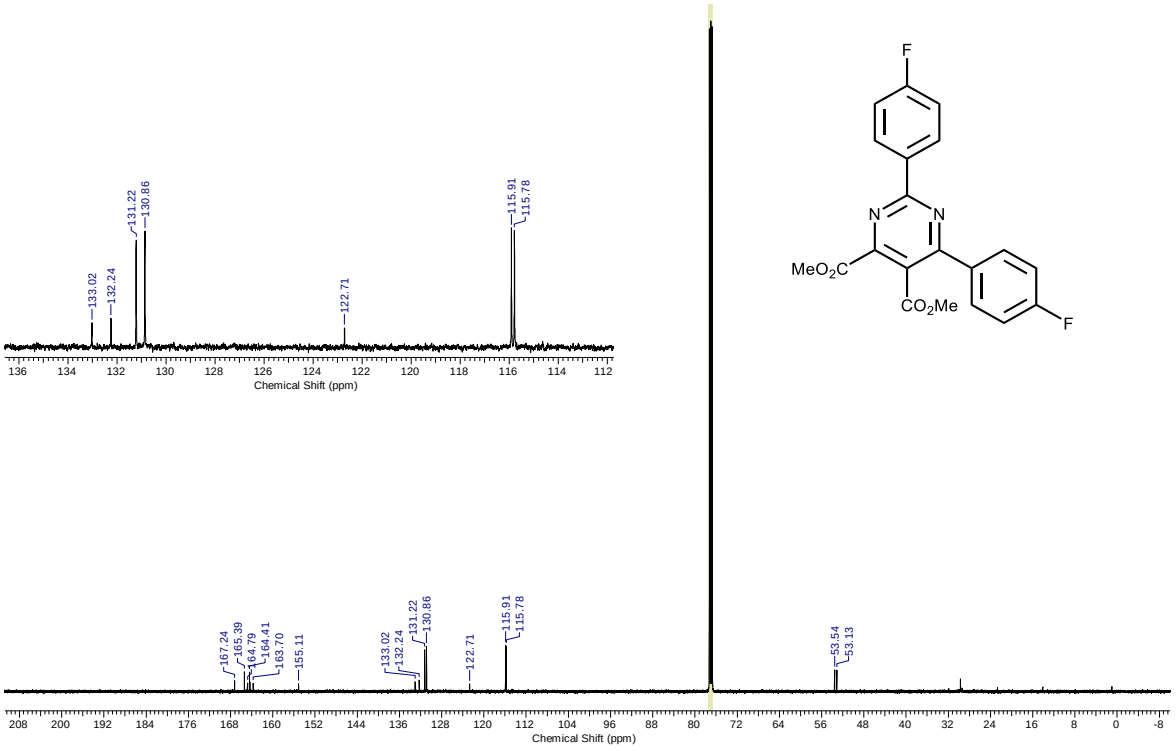


Figure S64. $^{13}C\{^{1}H,^{19}F\}$ NMR spectrum of **5h** in $CDCl_3$.

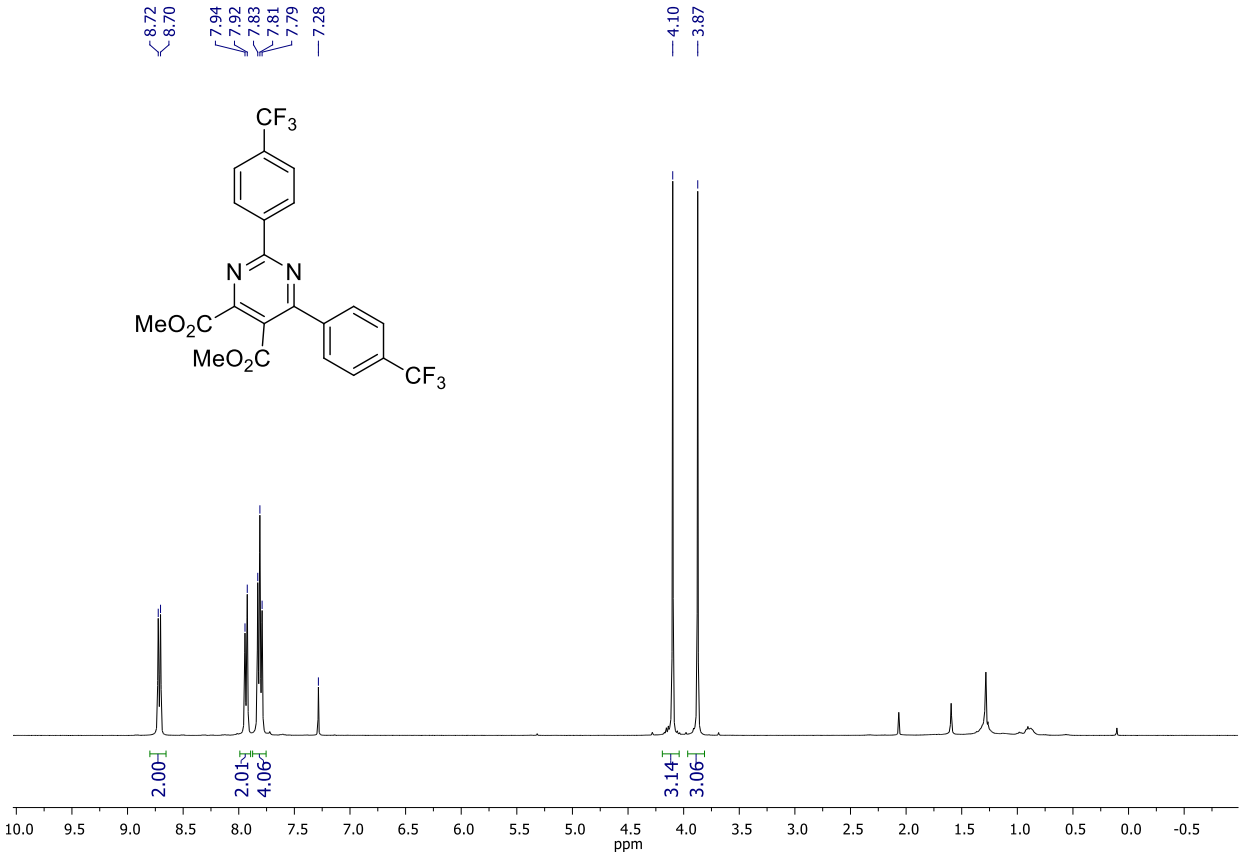


Figure S65. ^{1}H NMR spectrum of **5i** in $CDCl_3$.

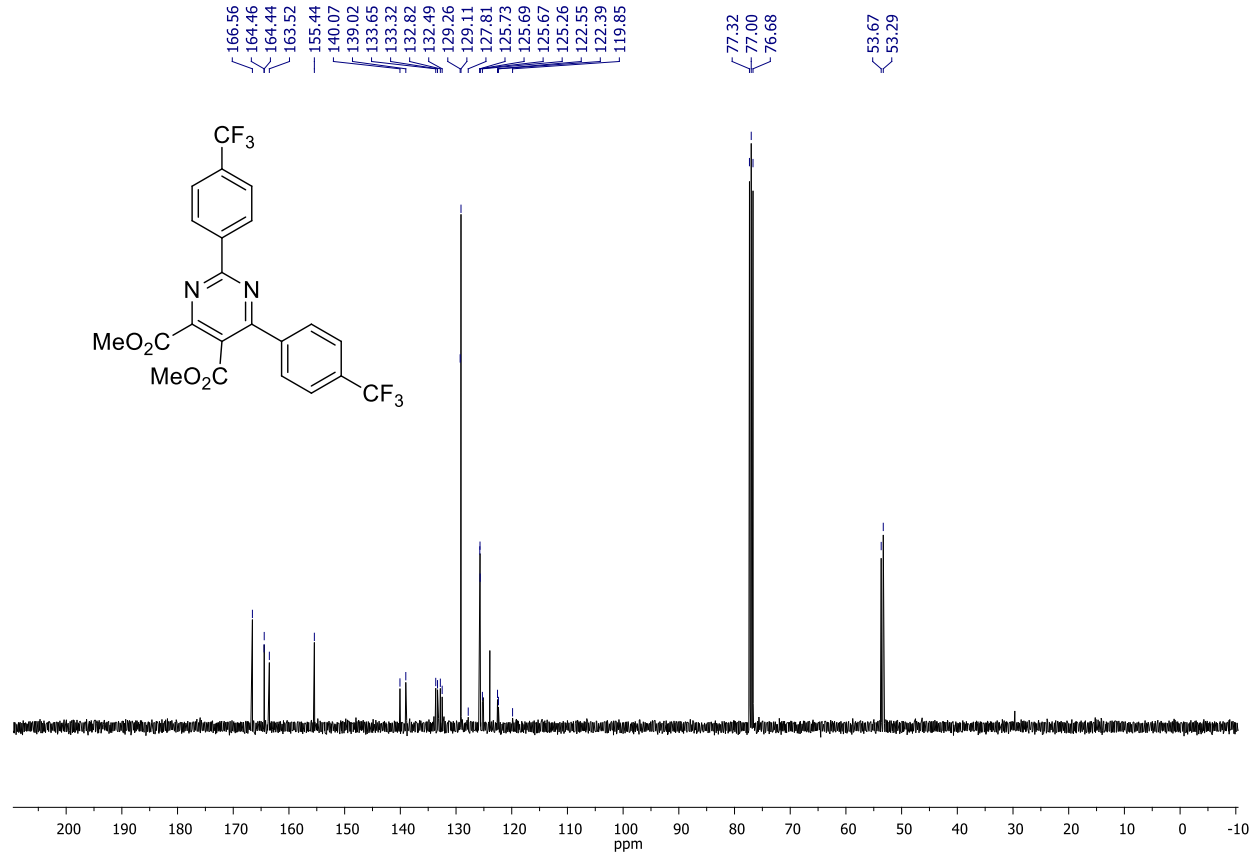


Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum of **5i** in $CDCl_3$.

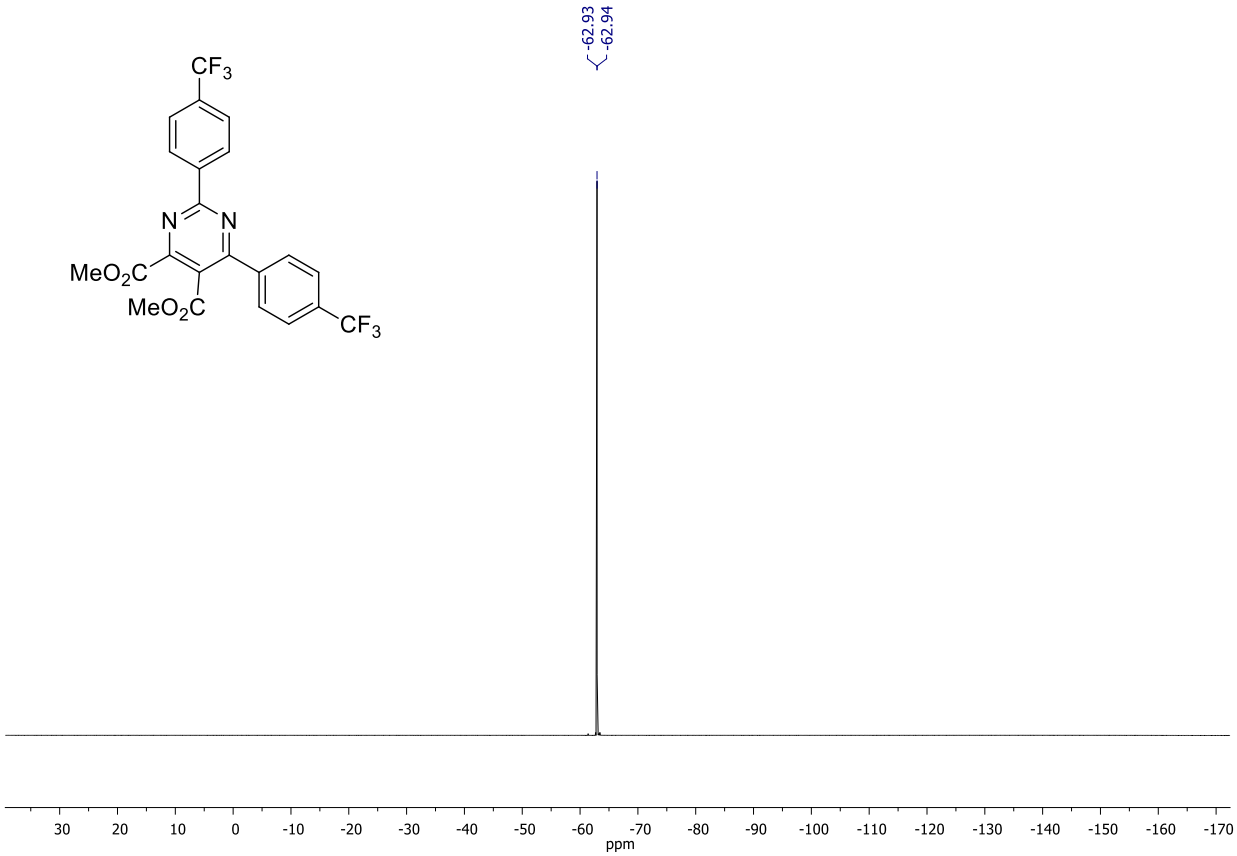


Figure S67. $^{19}F\{^{1}H\}$ NMR spectrum of **5i** in $CDCl_3$.

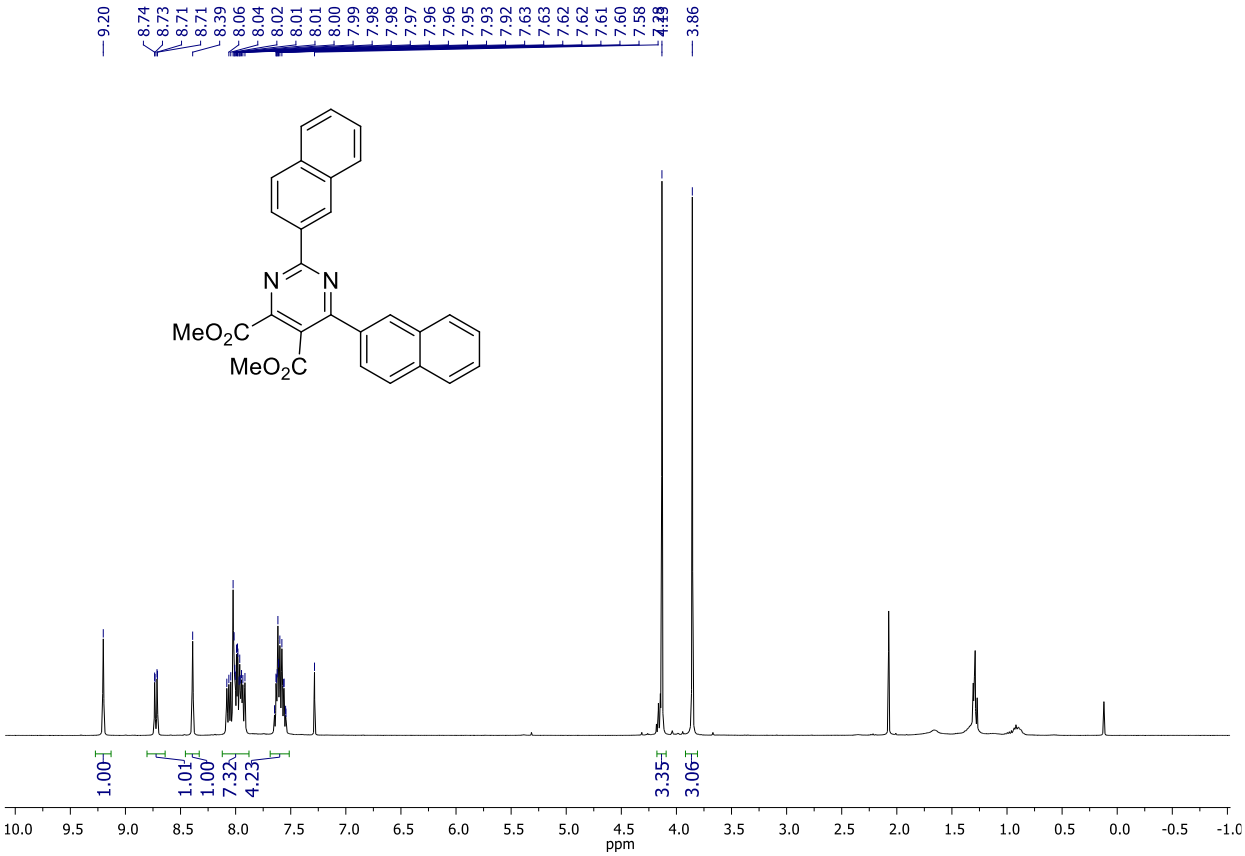


Figure S68. ^{1}H NMR spectrum of **5j** in $CDCl_3$.

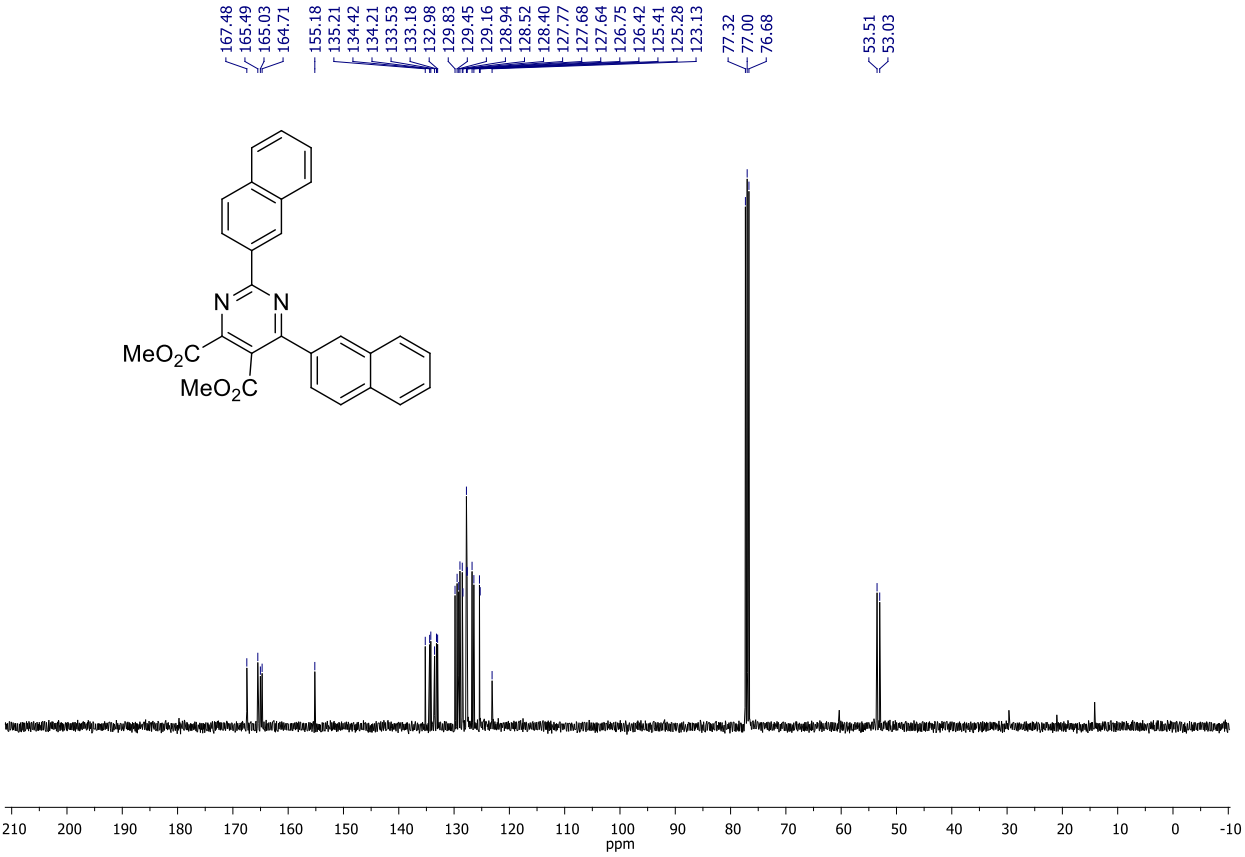


Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum of **5j** in $CDCl_3$.

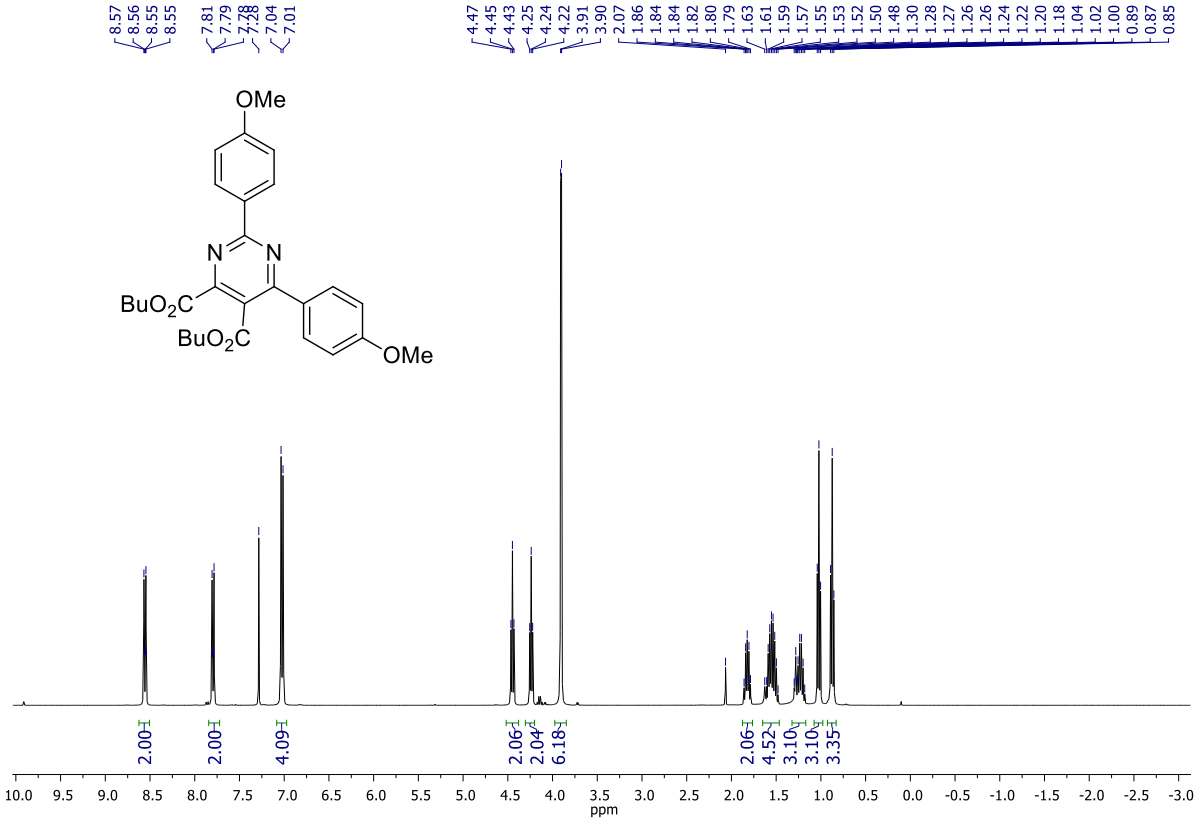


Figure S70. ^{1}H NMR spectrum of **5k** in $CDCl_3$.

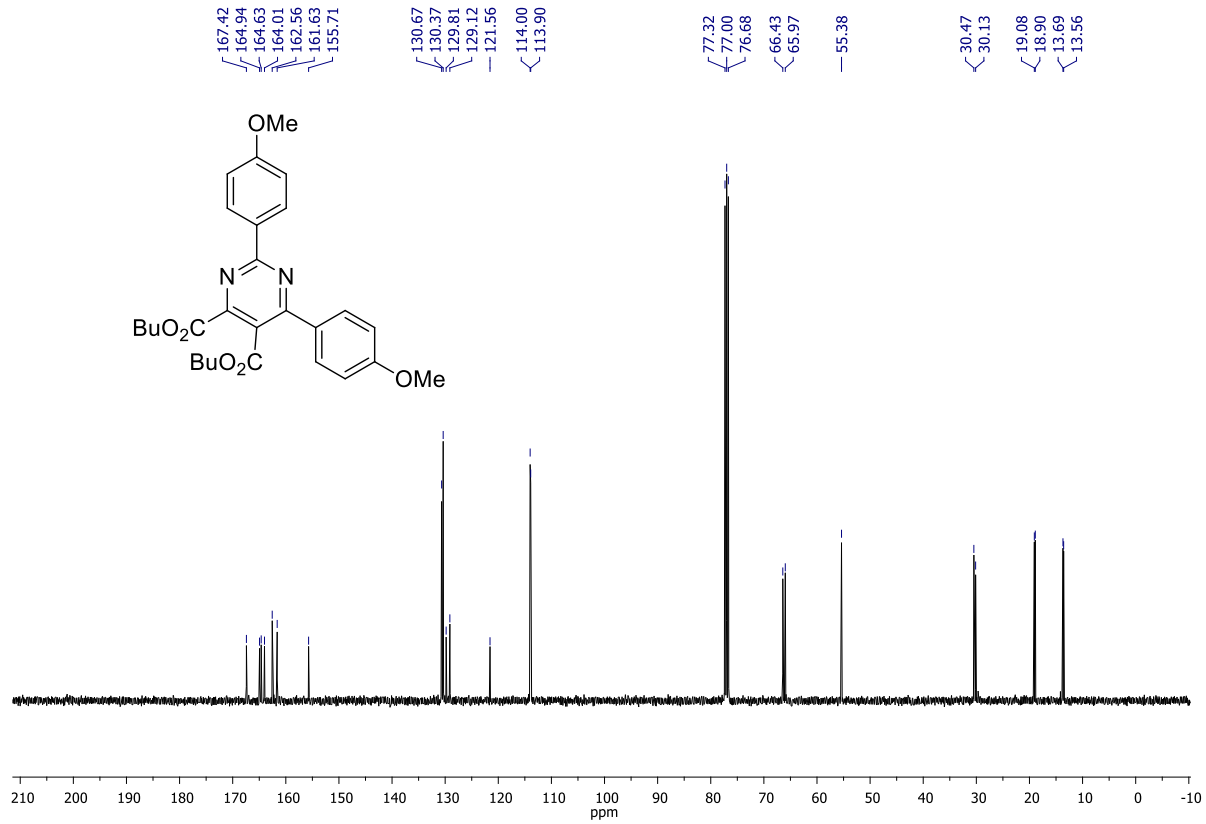


Figure S71. ^{13}C{^{1}H} NMR spectrum of **5k** in $CDCl_3$.

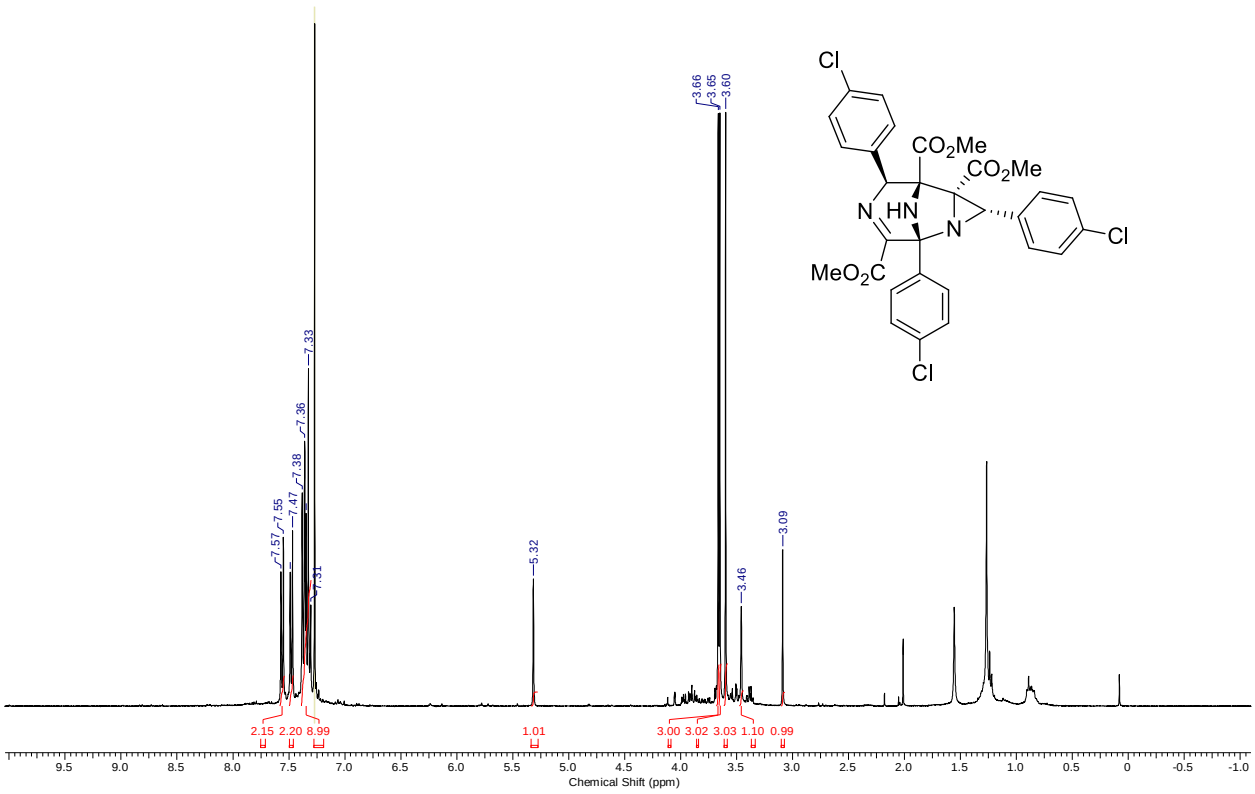


Figure S72. ^{1}H NMR spectrum of **6** in $CDCl_3$.

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