Supporting Information

Nitrogen-inversion-based racemate aggregation and interenantiomer π-stacking-caused solid-state fluorescence enhancement

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Contents

General

All the starting materials were purchased from commercial suppliers and used without further purification. All melting points were measured using a X-5 micro melting point apparatus and were uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded on a Brucker Avance 400 MHz NMR spectrometer in Chloroform-*d* with tetramethylsilane (TMS) as the internal standard. ^{1}H NMR chemical shifts were referenced to TMS at 0.00 ppm. ^{13}C NMR chemical shifts were referenced to DMSO-d_6 at 39.50 ppm. IR spectra were obtained as potassium bromide pellets or as liquid films on potassium bromide pellets with a Bruker Vector 22 spectrometer. High resolution mass spectra (HRMS) were recorded on an Agilent 6210 ESI/TOF mass spectrometer. Single-crystal X-ray diffraction data were measured by Bruker D8 Venture or bruker smart apexii. The energy levels of HOMOs and LUMOs of TTHPs were calculated by DFT/B3LYP/6-31G (d, p), Gaussian 09 program. The reactions were monitored by thin-layer chromatography (TLC) using 100–400 mesh silica gel plates (GF254) and were visualized using UV lamp (254 and 365 nm). The absolute fluorescence quantum yield was measured on FLS980 fluorescence spectrometer by using calibrated integrating sphere. The fluorescence lifetimes were measured on FLS980 using a laser with 320 nm or 405 nm as excitation light source via FLS980. Absorption and fluorescence emission properties were analyzed by METASH 6000 and FluoroMax-4 spectrofluorophotometer, respectively. The photos were taken by iphone 12. The solvents tetrahydrofuran (THF) and cyclohexane (CH) for optical experiments were purchased from Shanghai Macklin Biochemical Co., Ltd or Shanghai Boer Chemistry Reagent Co., Ltd.

Preparation of TTHPs

TTHPs were prepared by the four-component reaction that we previous reported.[1] The product mixture was purified by preparative TLC with n-hexane/ethyl acetate (10:1-1:1) as eluent to afford the desired products in 60–89% yields.

Preparation of the single crystals of TTHPs

The single crystals of TTHPs were prepared by recrystallization from dichloromethane-*n*-hexane at room temperature for different time in the following procedures: dissolving TTHPs

using dichloromethane as little as possible, then adding *n*-hexane in the TTHPs solution until they were almost saturated and finally keeping them at room temperature for different time.

Characterization data of products

Dimethyl 1,2,3,6-tetrahydro-1,3-diphenylpyrimidine-4,5-dicarboxylate (5a) 80% yield, light yellow crystal, Mp: 82.4 – 84.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.22 (m,5H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 3H), 4.92 (s, 2H), 4.27 (s, 2H), 3.74 (s, 3H), 3.58 (s, 3H). The data are consistent with those reported[2].

Dimethyl 1,3-bis(4-pheylphenyl)-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylate (5b) 78% yield, yellow crystal, Mp: 150.2 – 150.6 °C; IR (KBr) ν_{max} = 3031, 1742, 1698, 1636, 1607, 1521, 1258, 763 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.61 – 7.42 (m, 11H), 7.42 – 7.27 (m, 3H), 7.17 – 7.07 (m, 2H), 7.06 – 6.94 (m, 2H), 5.03 (s, 2H), 4.36 (s, 2H), 3.80 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 166.0, 164.6, 147.4, 146.3, 142.7, 140.5, 139.9, 139.1, 133.8, 128.8, 128.7, 128.7, 127.9, 127.7, 127.5, 127.3, 127.0, 126.9, 126.8, 126.7, 126.5, 124.9, 122.9, 119.4, 117.8, 101.0, 68.5, 52.6, 51.6, 48.2, 47.6; HRMS (ESI) calculated for $C_{32}H_{28}N_2O_4$ $[M+Na]^+$ 527.1947 m/z, found 527.1946 m/z.

Dimethyl 1,3-bis(4-ethoxyphenyl)-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylate (5c) 60% yield, white solid, Mp: 133.4 – 134.0 ℃; IR (KBr) ν_{max} = 2980, 1744, 1696, 1577, 1508, 1477, 1435, 765 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.05 – 6.65 (m, 8H), 4.79 (s, 2H), 4.19 (s, 2H), 4.06 – 3.90 (m, 4H), 3.74 (s, 3H), 3.58 (s, 3H), 1.47 – 1.25 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 166.2, 164.5, 157.6, 154.0, 142.1, 135.8, 127.3, 120.3, 115.1, 114.7, 97.2, 70.6, 63.7, 63.6, 52.4, 51.3, 47.6, 14.8, 14.7; HRMS (ESI) calculated for $C_{24}H_{28}N_2O_6$ $[M+Na]^+$: 463.1845 m/z, found: 463.1844 m/z .

Dimethyl 1,3-bis(4-(trifluoromethyl)phenyl)-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylate (5d) 74% yield, white crystal, Mp: 162.5 – 163.5 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.68 – 7.52 (m, 2H), 7.50 – 7.38 (m, 2H), 7.13 (m, 2H), 6.94 – 6.77 (m, 2H), 5.02 (s, 2H), 4.35 (d, *J* = 2.5 Hz, 2H), 3.80 (s, 3H), 3.68 (s, 3H). The data are consistent with those reported[2].

Dimethyl 1,3-bis(4-fluorophenyl)-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylate (5e) 65% yield, white crystal, Mp: 93.1 – 94.3 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.95 (t, *J* =

6.7 Hz, 8H), 4.83 (s, 2H), 4.23 (s, 2H), 3.77 (s, 3H), 3.60 (s, 3H). The data are consistent with those reported[2].

Dimethyl 1,3-bis(4-chlorophenyl)-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylate (5f) 80% yield, white crystal, Mp: 127.2 – 128.2 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.26 (dd, *J* = 9.2, 2.7 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.97 – 6.90 (m, 2H), 6.85 (dd, *J* = 8.6, 2.2 Hz, 2H), 4.87 (s, 2H), 4.25 (s, 2H), 3.77 (s, 3H), 3.63 (s, 3H). The data are consistent with those reported[2].

Dimethyl 1,3-bis(3-(trifluoromethyl)phenyl)-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylate (5g) 78% yield, yellow crystal, Mp: 90.1 – 90.6 ℃; IR (KBr) ν_{max} = 2954, 1742, 1701, 1589, 1456, 1436, 1262, 700 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.48 – 7.39 (m, 2H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 2.6 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.07 – 6.97 (m, 2H), 4.97 (s, 2H), 4.31 (s, 2H), 3.78 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 165.5, 164.1, 148.1, 145.2, 144.1, 130.1, 129.9, 127.1, 122.8, 120.8, 120.5, 117.7, 113.9, 104.0, 68.1, 52.6, 51.7, 47.7; HRMS (ESI) calculated for $C_{22}H_{18}F_6N_2O_4$ $[M+Na]^+$: 511.1068 m/z, found: 511.1072 m/z.

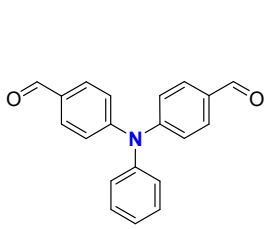
Dimethyl 1,3-bis(3-fluorophenyl)-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylate (5h) 69% yield, white crystal, Mp: 104.0 –104.3 ℃; IR (KBr) ν_{max} = cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (dd, *J* = 8.2, 6.3 Hz, 1H), 7.16 (m, 1H), 6.91 (m, 1H), 6.83 – 6.73 (m, 2H), 6.66 – 6.61 (m, 1H), 6.61 – 6.54 (m, 2H), 4.91 (s, 2H), 4.26 (s, 2H), 3.78 (s, 3H), 3.66 (s, 3H), 3.49 (s, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 164.8, 164.3, 164.1, 145.4, 130.6, 130.5, 130.4, 119.8, 113.4, 113.2, 112.7, 111.5, 111.3, 107.7, 107.5, 104.6, 104.3, 103.1, 77.2, 68.1, 52.7, 51.7, 50.8, 47.4. HRMS (ESI) calculated for $C_{20}H_{18}F_2N_2O_4$ $[M+Na]^+$ 411.1132 m/z, found: 411.1135 m/z.

Dimethyl 1,3-bis(2-fluorophenyl)-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylate (5i) 74% yield, yellow crystal, Mp: 111.7 – 112.1 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 (m, 2H), 7.08 (m, 2H), 7.04 – 6.90 (m, 3H), 6.77 (m, 1H), 4.84 (s, 2H), 4.26 (s, 2H), 3.77 (s, 3H), 3.58 (s, 3H). The data are consistent with those reported[3].

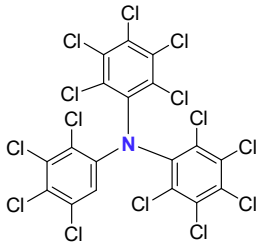
Diethyl 1,2,3,6-tetrahydro-1,3-diphenylpyrimidine-4,5-dicarboxylate (5j) 89% yield, white solid, Mp: 85.5 – 86.4 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.38 – 7.13 (m, 5H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.93 (t, *J* = 7.1 Hz, 3H), 4.94 (s, 2H), 4.30 (s, 2H), 4.22 (m, 2H), 4.05 (m, 2H), 1.30 (m, 3H), 1.01 (m, 3H). The data are consistent with those reported[4].

Diethyl 1,3-bis(4-(trifluoromethyl)phenyl)-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylate (5k) 80% yield, yellow crystal, Mp: 89.6 – 90.3 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.57 (s, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.01 (s, 2H), 4.34 (s, 2H), 4.26 (m, 2H), 4.11 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). The data are consistent with those reported[5].

Table S1. Bond angles of N atom in several reported trivalent amines, THP-1b and 1g, and TTHPs



TPA-1



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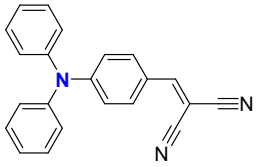

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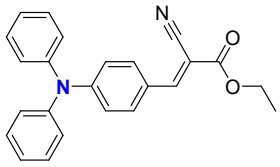
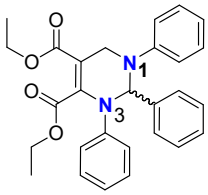
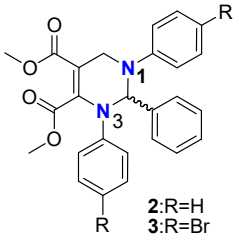


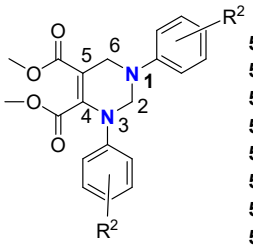
TPA-4



THP-1

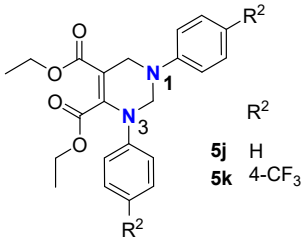


THP-2 and 3



TTHP 5a-5i

5a	H
5b	4-Ph
5c	4-EtO
5d	4-CF_3
5e	4-F
5f	4-Cl
5g	3-CF_3
5h	3-F
5i	2-F



TTHP 5j and 5k

5j	H
5k	4-CF_3

entry	TPA	R^2	θ_{SN3}/°	θ_{AN3}/°	θ_{SN1}/°	θ_{AN1}/°	Ref/CCDC
1	**TPA-1**		360	120			747280
2	**TPA-2**		360	120			1127309
3	**TPA-3**		360	120			Ref[6]
4	**TPA-4**		360	120			Ref[6]
5	**TTHP-5a**	H	358	119	338	113	
6	**TTHP-5b**	4-Ph	358	119	342	114	
7	**TTHP-5c**	4-EtO	357	119	337	112	
8	**TTHP-5d**	4-CF_3	357	119	349	116	
9	**TTHP-5e**	4-F	358	119	339	113	
10	**TTHP-5f**	4-Cl	359	120	342	114	
11	**TTHP-5g**	3-CF_3	358	119	347	116	
12	**TTHP-5h**	3-F	356	119	339	113	
13	**TTHP-5i**	2-F	358	119	347	116	
14	**TTHP-5j**	H (Et)	359	120	347	116	
15	**TTHP-5k**	4-CF_3 (Et)	347	116	352	117	
16	**THP-1b**		360	120	346	115	Ref[7]
17	**THP-1c**		358	119	344	115	Ref[7]
18	**THP-2c**		359	120	341	114	Ref[7]
19	**THP-2c′**		358	119	347	116	Ref[7]
20	**THP-3p**		359	120	344	115	Ref[7]
21	**THP-3b**		359	120	344	115	Ref[7]
22	**THP-3c**		358	119	342	114	Ref[7]

Table S2. Crystallographic data of seven TTHPs

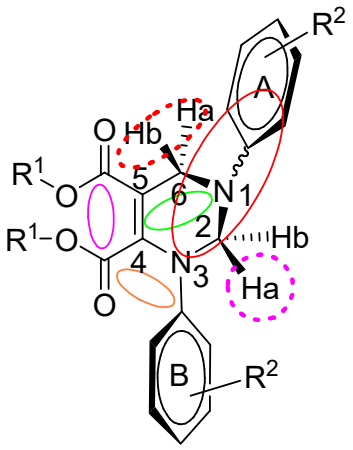
TTHPs 5a–f

TTHP	**5a**	**5b**	**5c**	**5d**	**5e**	**5f**
Ar	Ph(Me)	4-Ph-Ph	4-OEtPh	4-CF_3Ph	4-FPh	4-ClPh
T^a [K]	296.00	149.99	150.01	150.00	296.00	298.00
crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	monoclinic
space group	*P***Error!**	*P***Error!**	*P***Error!**	*P***Error!**	*P***Error!**	$P2_1/n$
a[Å]	9.2322(3)	9.5517(6)	9.8663(3)	10.0378(4)	8.5390(19)	14.5906(2)
b[Å]	10.6070(2)	11.8115(7)	11.2440(3)	10.2421(4)	10.598(2)	11.6185(2)
c[Å]	11.0640(3)	23.1264(12)	12.1222(4)	12.1929(5)	10.874(2)	24.5111(4)
α[Å]	75.441(2)	83.899(5)	64.929(3)	106.213(2)	104.078(4)	90
β[deg]	82.029(1)	85.964(5)	89.007(2)	98.313(2)	102.440(4)	107.3010(10)
γ[deg]	75.037(1)	89.561(5)	67.849(3)	112.792(1)	90.465(4)	90
V [Å^3]	1009.95(5)	2587.9(3)	1111.81(7)	1063.50(8)	930.2(3)	3967.15(11)
Z	2	2	2	2	2	8
D_{calcu} [g/m^3]	1.340	1.295	1.316	1.525	1.387	1.411
R	0.0418(3653)	0.0920(7487)	0.0336(3947)	0.0667(4011)	0.0528(1557)	0.0399(6565)
wR_2	0.1323(4570)	0.2797(9712)	0.0905(4189)	0.1821(4306)	0.1256(3247)	0.1112(7457)

TTHPs 5g–k

TTHP	**5g**	**5h**	**5i**	**5j**	**5k**
Ar	3-CF_3Ph	3-FPh	2-FPh	Ph(Et)	4-CF_3Ph(Et)
T^a [K]	296.00	298.00	298.00	100.00(10)	298.00
crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	monoclinic
space group	$P2_1/n$	*P***Error!**	*P***Error!**	*P***Error!**	$P2_1$
a[Å]	16.285(2)	8.7578(2)	9.5188(4)	8.4654(6)	10.7459(6)
b[Å]	11.5946(14)	9.7459(3)	9.7000(4)	8.6484(6)	8.0948(5)
c[Å]	24.451(3)	12.3859(4)	11.0300(4)	12.7988(8)	14.1993(7)
α[Å]	75.441(2)	96.6910(10)	80.686(2)	106.213(2)	90
β[deg]	82.029(1)	108.3500(10)	85.148(2)	98.313(2)	101.606(2)
γ[deg]	75.037(1)	106.1870(10)	68.439(2)	112.792(1)	90
V [Å^3]	1009.95(5)	939.12(5)	934.33(7)	1063.50(8)	1209.89(12)
Z	2	2	2	2	2
D_{calcu} [g/m^3]	1.340	1.373	1.380	1.525	1.418
R	0.0418(3653)	0.0763(3314)	0.0449(3442)	0.0667(4011)	0.0753(3194)
wR_2	0.1323(4570)	0.2544(4626)	0.1340(4636)	0.1821(4306)	0.2510(5745)

Table S3. Delocalization of the HOMOs and LUMOs of seven TTHPs in crystals



entry	TTHP	R^2	Through-space conjugation				Hyperconjugation	
			N_1@C_4=C_5 (green)	N_3@ringA (red)	ringB@C_4COO (orange)	C_4COO@C_5COO (pink)	C_2-Ha	C_6-H
1	**5a**	H	+	+	+	+	+[a]	++[b]
2	**5b**	4-Ph			+		+	++
3	**5c**	4-EtO		+	+		+	++
4	**5d**	4-CF_3	+		+	+	+	++
5	**5e**	4-F	+		+	+	+	++
6	**5f**	4-Cl	+	+	+		+	++
7	**5g**	3-CF_3	+		+	+	+	++
8	**5h**	3-F	+		+		+	++
9	**5i**	2-F	+		+	+	+	++
10	**5j**	H (Et)	+		+	+	+	++
11	**5k**	4-CF3 (Et)			+	+	+	++

[a] One plus sign "+" represents that only $\sigma_{C6\text{-}Ha}$ participates in conjugation. [b] Two plus signs "++" represent that both $\sigma_{C6\text{-}Ha}$ and $\sigma_{C6\text{-}Hb}$ participate in conjugation.

Table S4. Energy gaps between the HOMOs and LUMOs of these TTHPs in crystals

entry	TTHP	R^2	λ_{ab} [a]/nm	λ_{bg}[b]/nm	E_{bg}[b]/ev
1	**5a**	H	300	289	4.296
2	**5b**	4-Ph	324	322	3.845
3	**5c**	4-EtO	299	305	4.067
4	**5d**	4-CF_3	314	285	4.353
5	**5e**	4-F	299	290	4.275
6	**5f**	4-Cl	306	283	4.384
7	**5g**	3-CF_3	311	269	4.61
8	**5h**	3-F	307	267	4.648
9	**5i**	2-F	304	264	4.704
10	**5j**	H (Et)	309	263	4.726
11	**5k**	4-CF3 (Et)	318	279	4.448

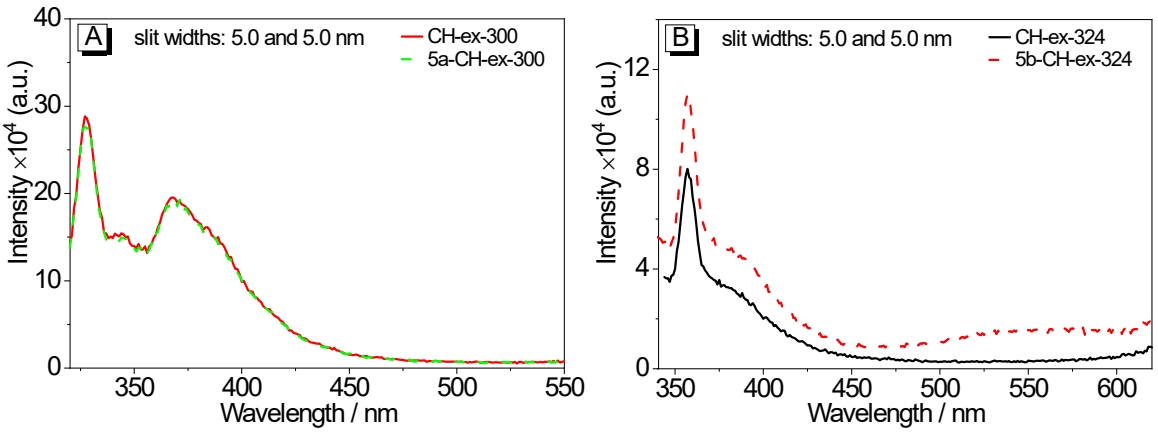
[a] Data in cyclohexane solutions (10 μM). [b] Energy gap between the calculated HOMO and LUMO of the conformation of TTHPs in crystals.

Table S5. Fluorescence decay components of TTHP 5a – k in crystals

Entry	TTHP	Ar	τ_{ave}[a]/ns	τ_i[b] /ns (component ratio%)
1	**5a**	H	9.19	8.31 (83.32%), 13.62 (16.68%)
2	**5b**	4-Ph	7.15	0.34 (3.85%), 7.42 (96.14%)
3	**5c**	4-EtO	7.70	7.70 (100%)
4	**5d**[8]	4-CF_3	9.75	9.75 (100%)
5	**5e**	4-F	10.13	10.77 (93.89%), 0.32 (6.11%)
6	**5f**	4-Cl	6.46	0.80 (23.80%), 8.22 (76.20%)
7	**5g**	3-CF_3	7.13	1.55 (64.85%), 17.43 (35.15%)
8	**5h**	3-F	10.95	10.95 (100%)
9	**5i**	2-F	14.07	14.07 (100%)
10	**5j**	H (Et)	11.19	11.19 (100%)
11	**5k**	4-CF_3(Et)	8.45	0.88 (4.78%), 8.83 (95.22%)

[a] Average fluorescence decay time. [b] Fluorescence decay time for different components, excited at 320 nm for all TTHPs except **5b** excited at 405 nm. Emitted at their emission peaks, respectively.

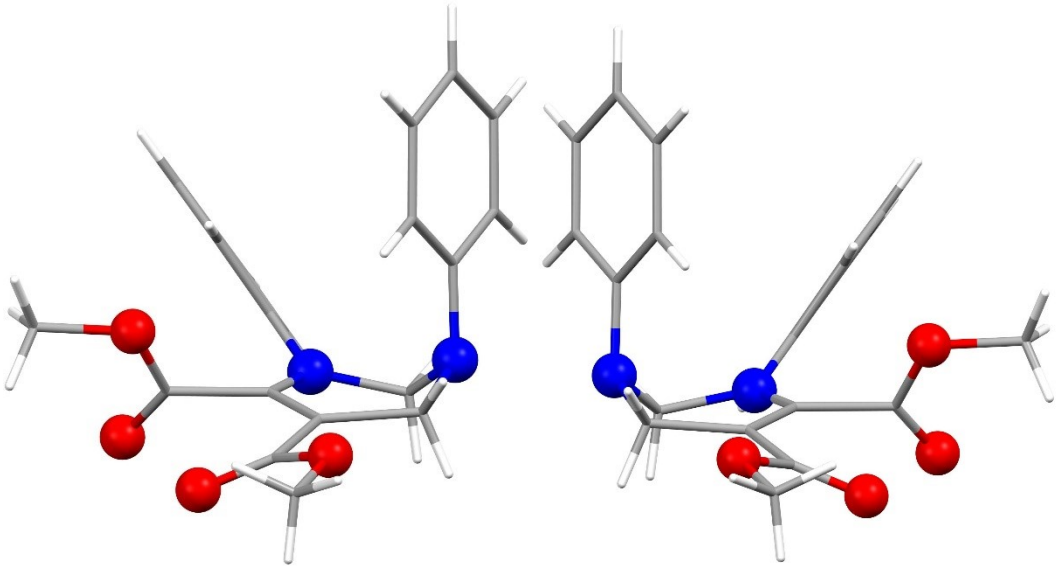
Figure S1. Emission spectra of 5a and 5b cyclohexane solution and pure cyclohexane



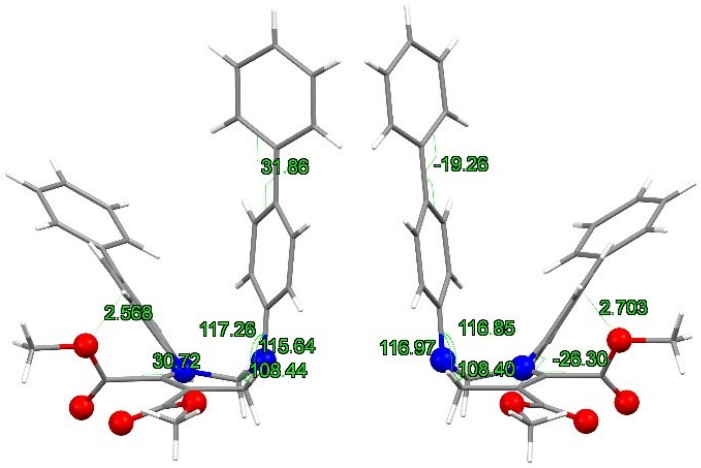
A. excitation and emission spectra of **5a** cyclohexane solution and cyclohexane solution.

B. excitation and emission spectra of **5b** cyclohexane solution and cyclohexane solution.

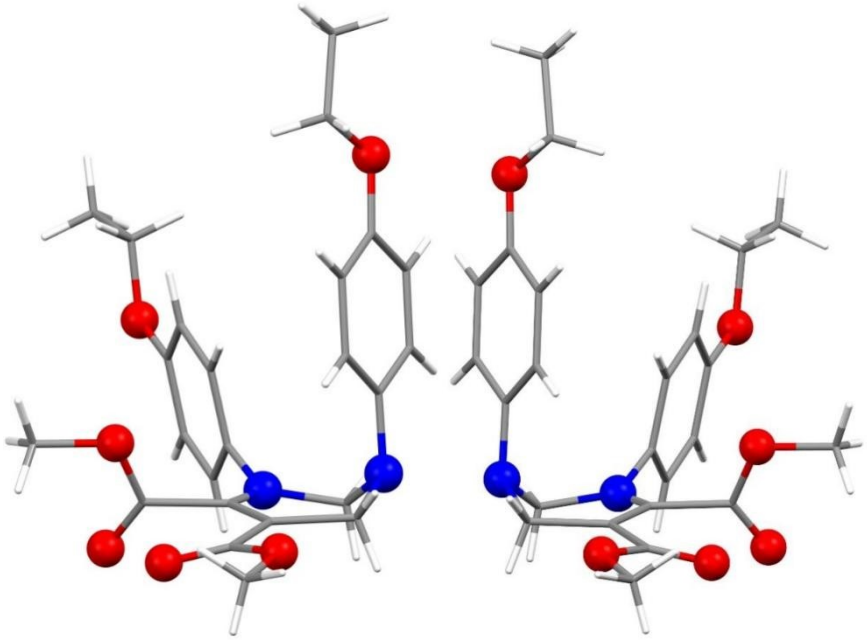
Figure S2. Racemic enantiomer conformations of TTHPs in crystals



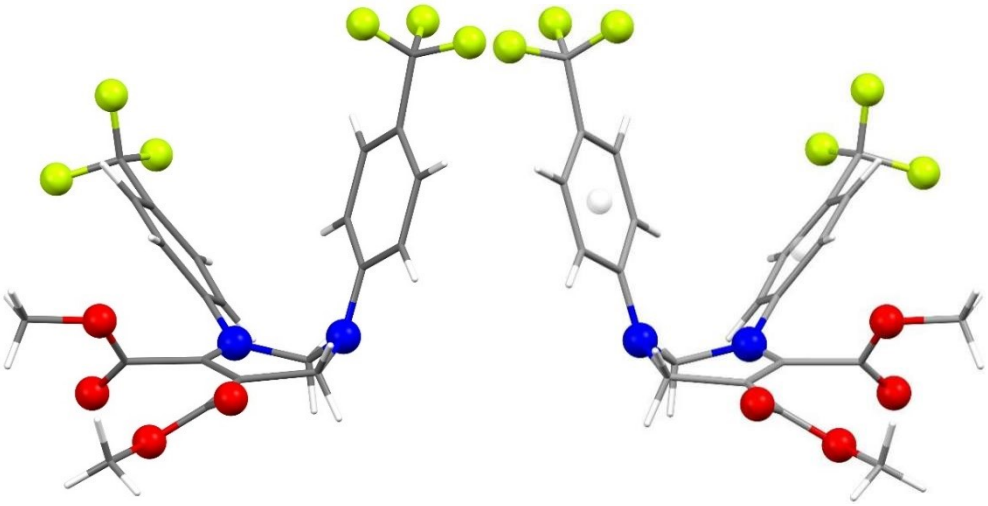
5a Ph



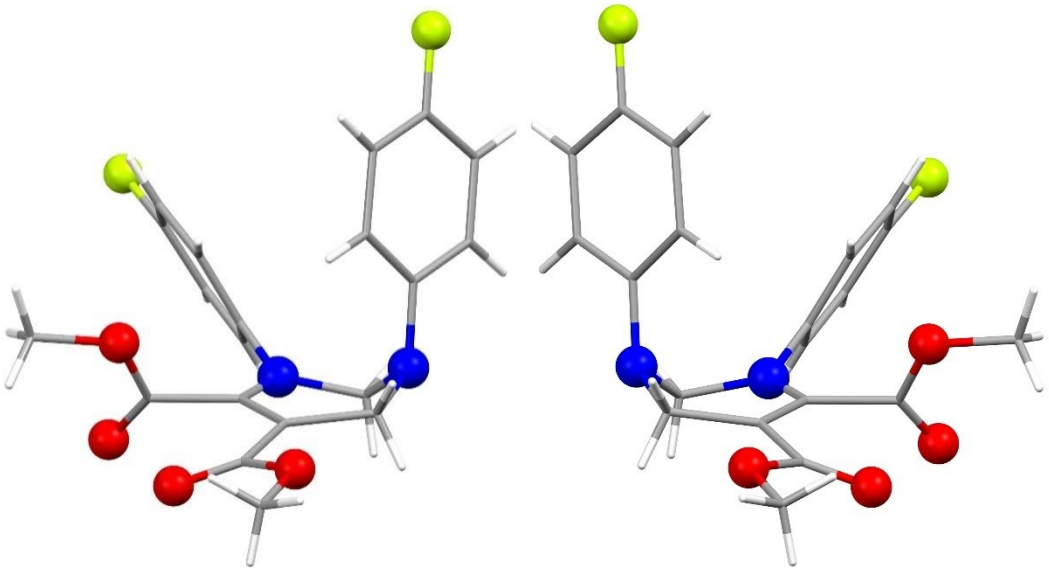
5b Ph-Ph



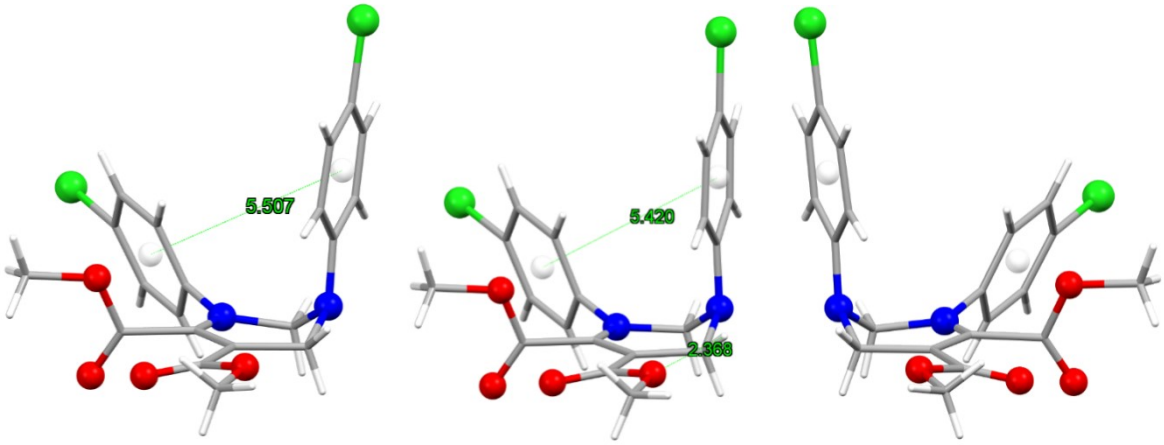
5c EtOPh



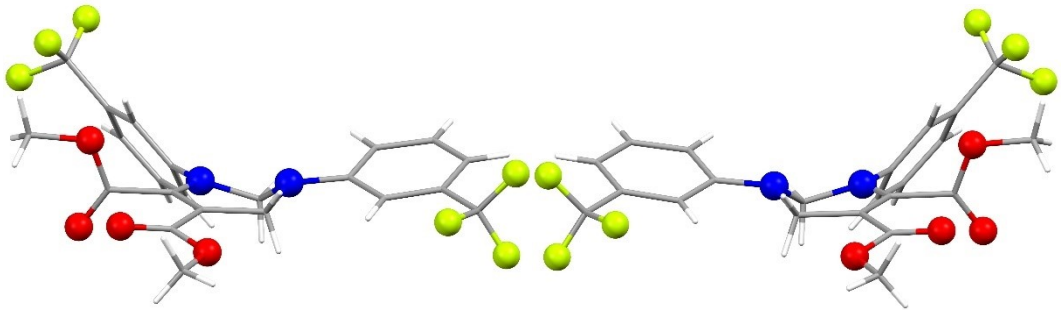
5d CF_3Ph



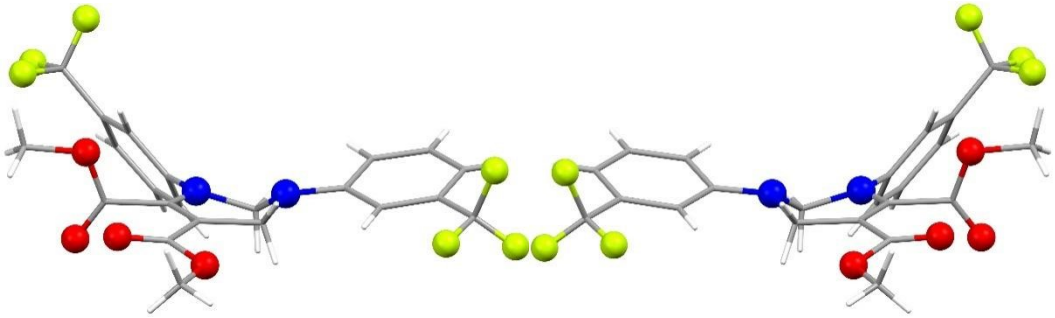
5e FPh



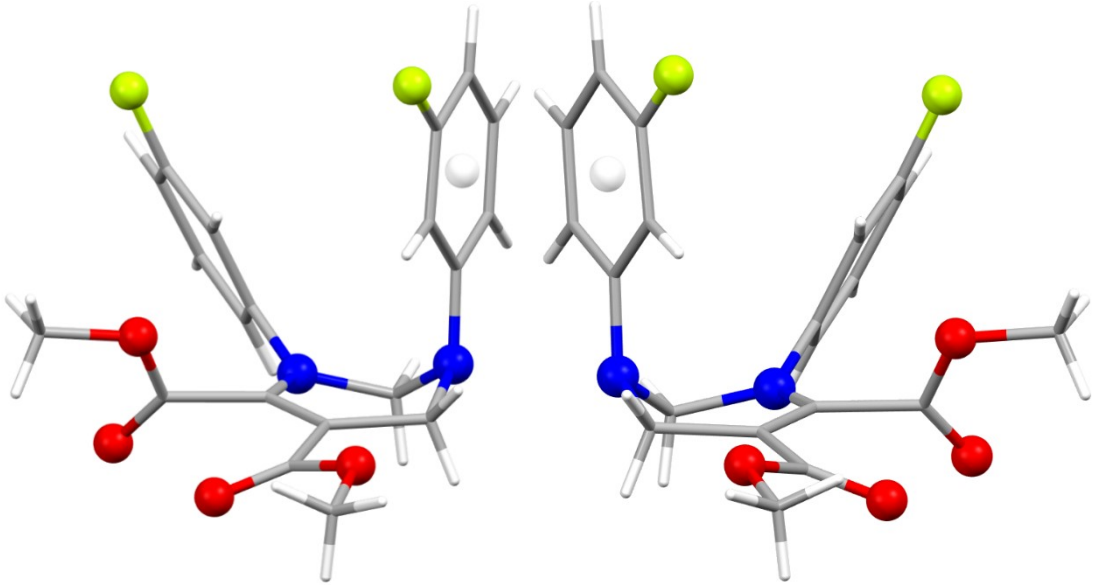
5f ClPh



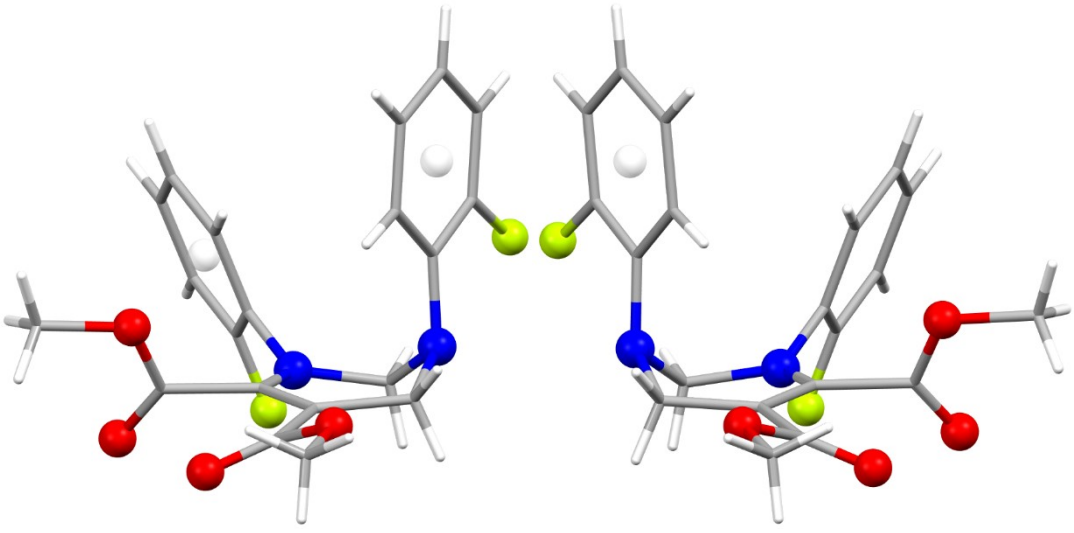
5g R1-S1 3-CF_3Ph



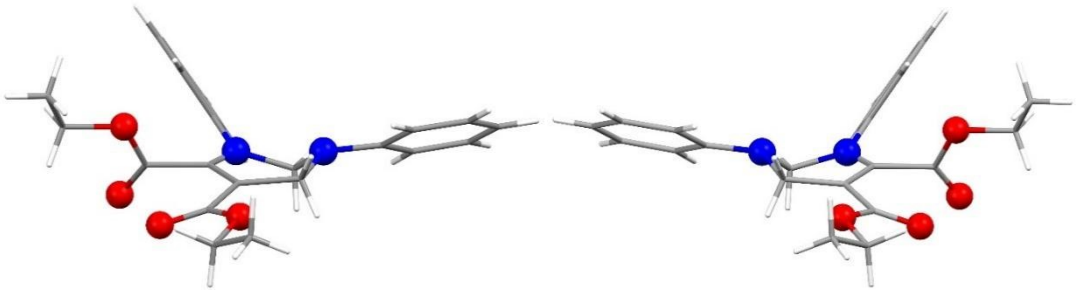
5g R2-S2 3-CF_3Ph



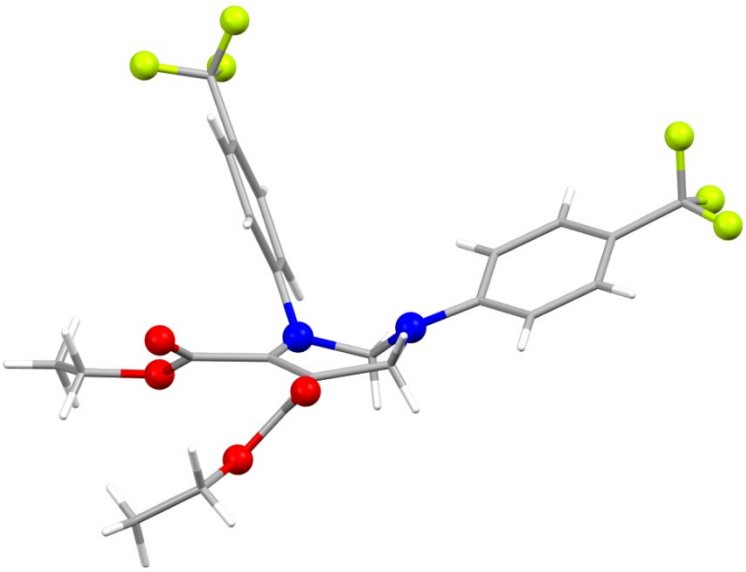
5h 3-FPh



5i 2-FPh

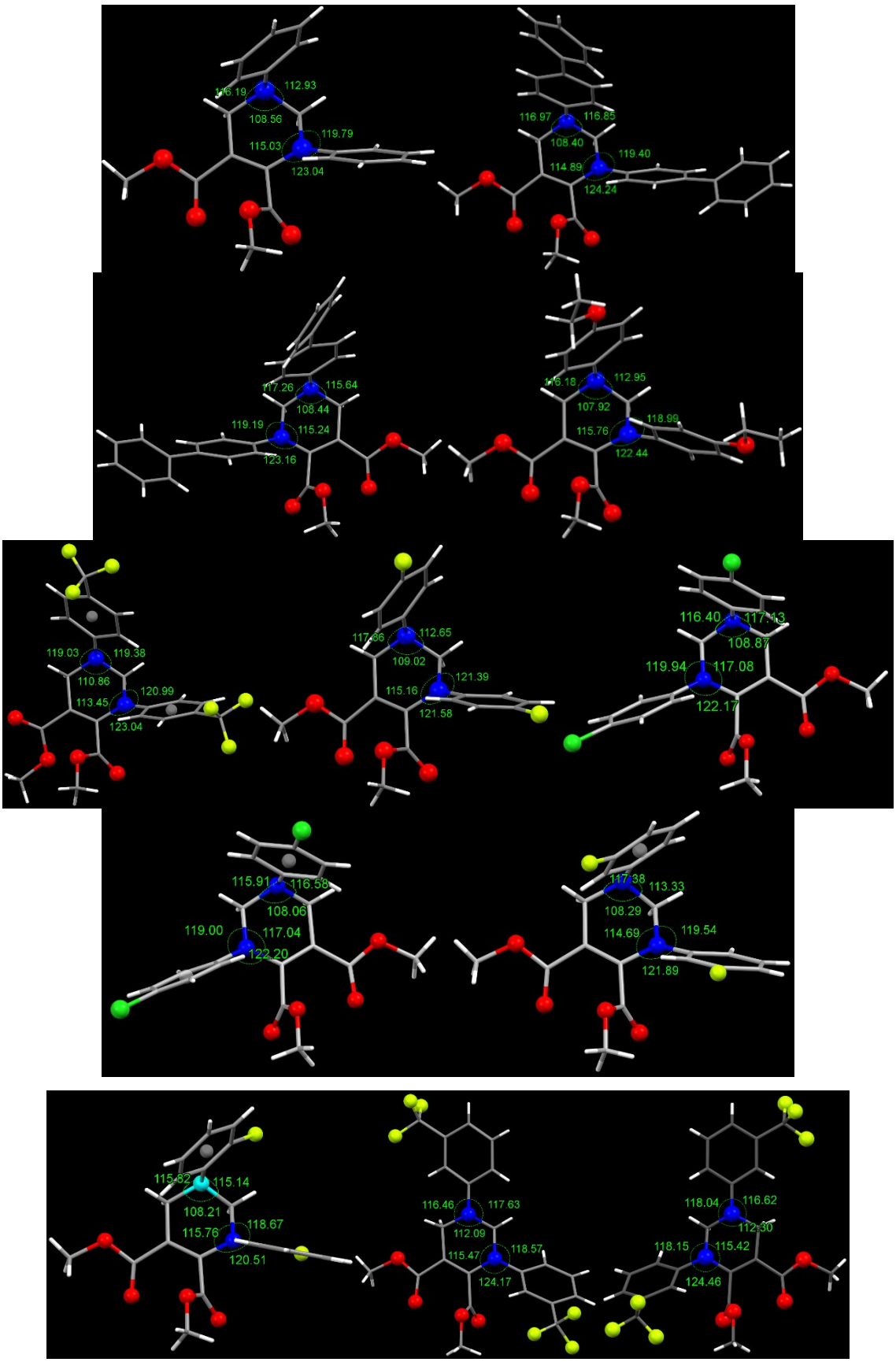


5j Et-Ph



5k Et-4-CF_3Ph

Figure S3. C-N1-C angles and C-N3-C angles of TTHPs in crystals



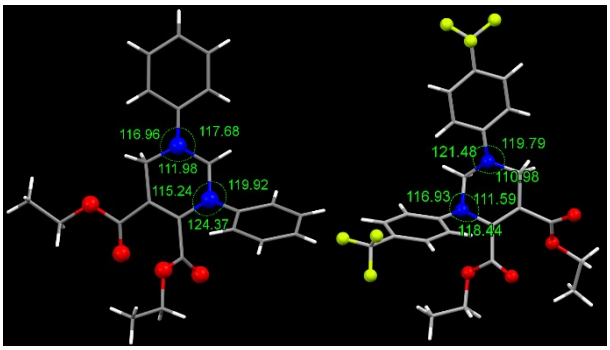

116.96
117.68
111.98
115.24
119.92
124.37
121.48
119.79
110.98
116.93
111.59
118.44

Figure S4. Conformations, HOMOs and LUMOs of TTHPs in single crystals

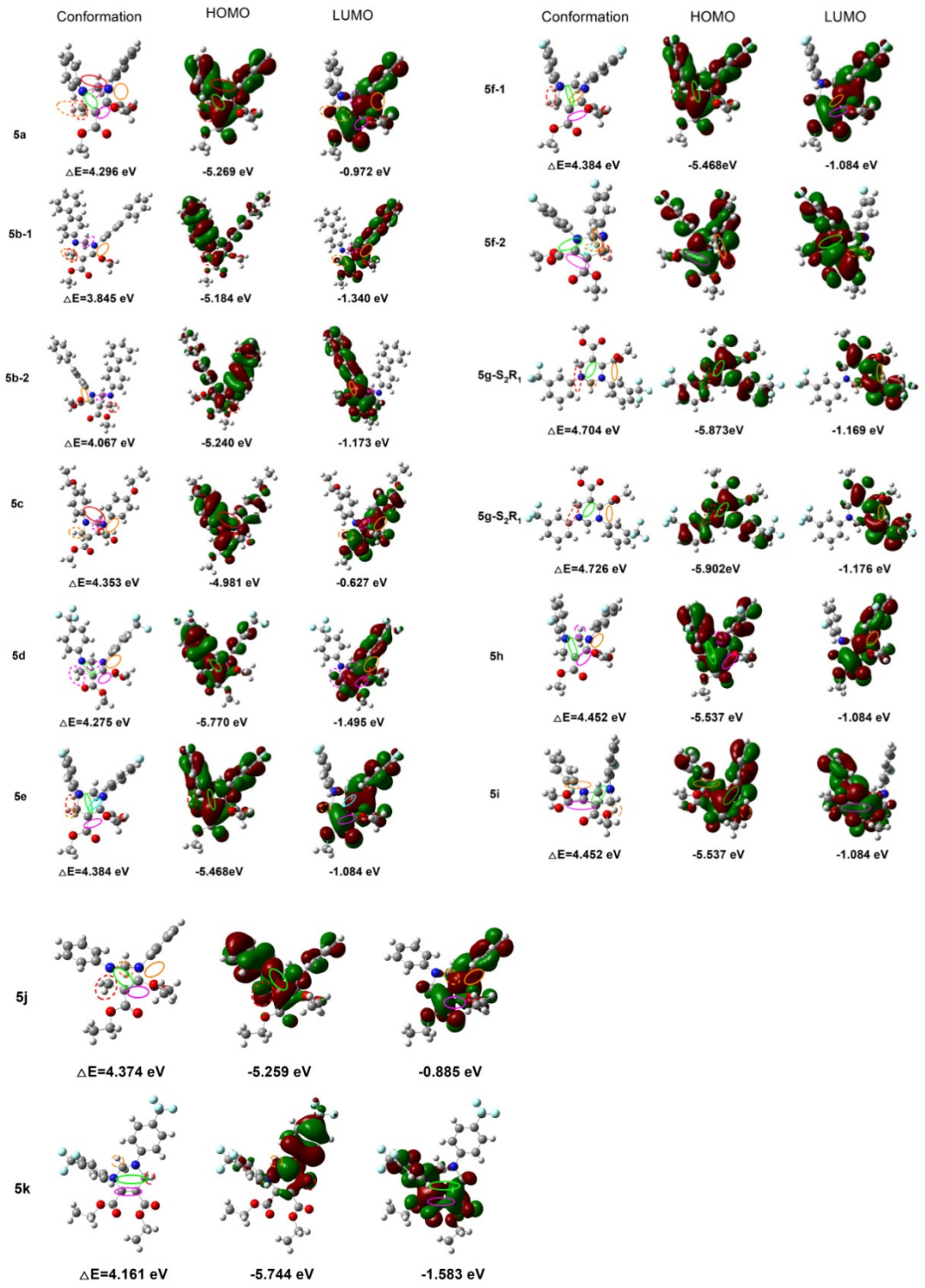
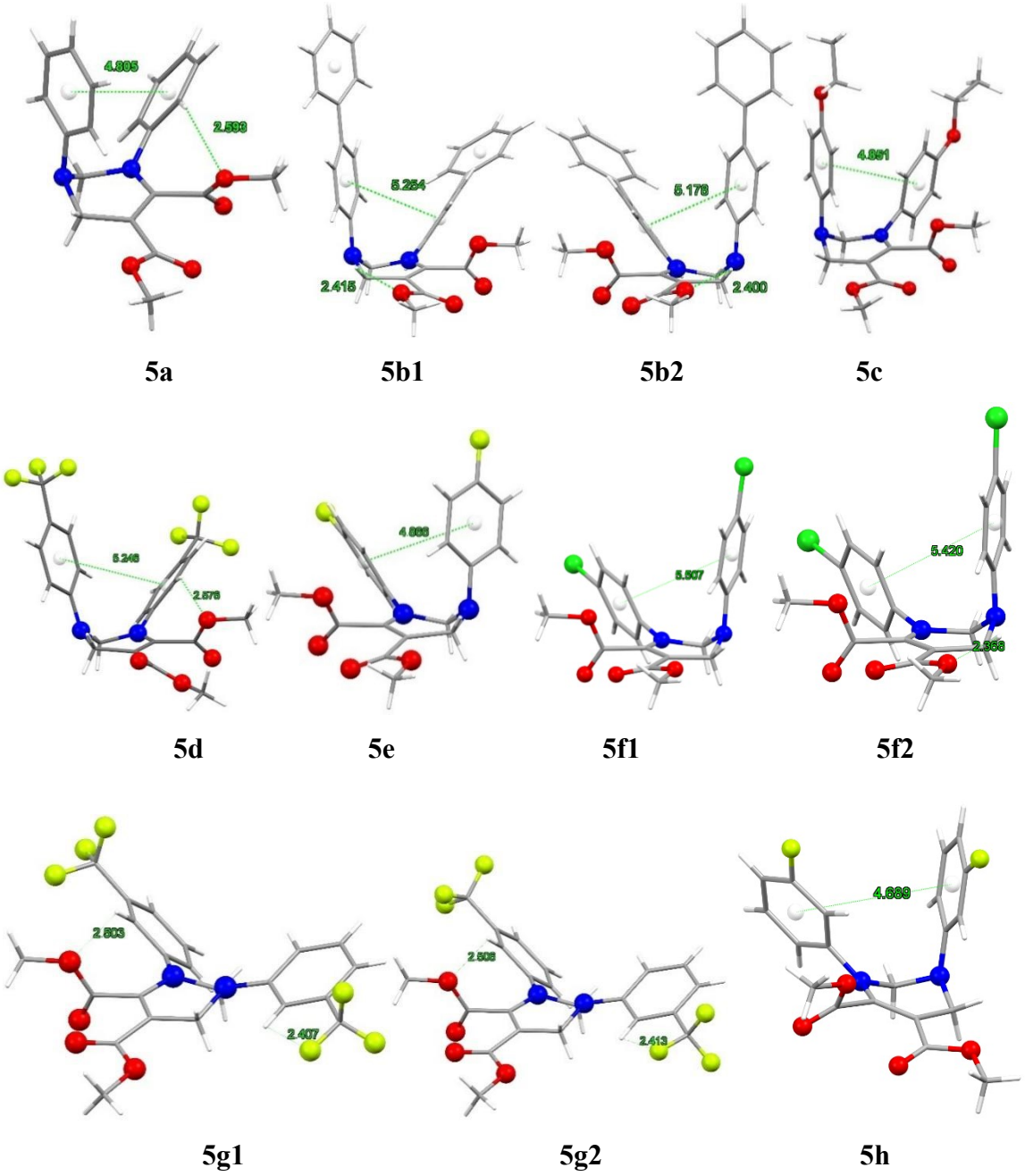


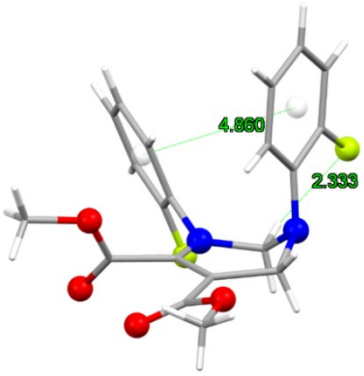
Figure S5. Intramolecular interaction of TTHPs in crystals



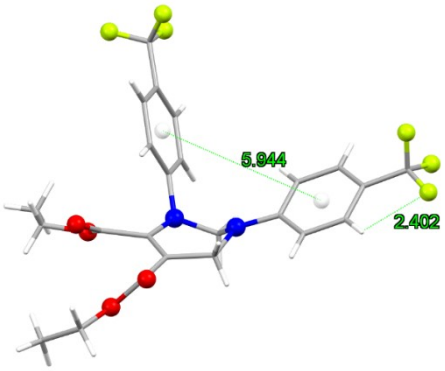
5a **5b1** **5b2** **5c**

5d **5e** **5f1** **5f2**

5g1 **5g2** **5h**



5i

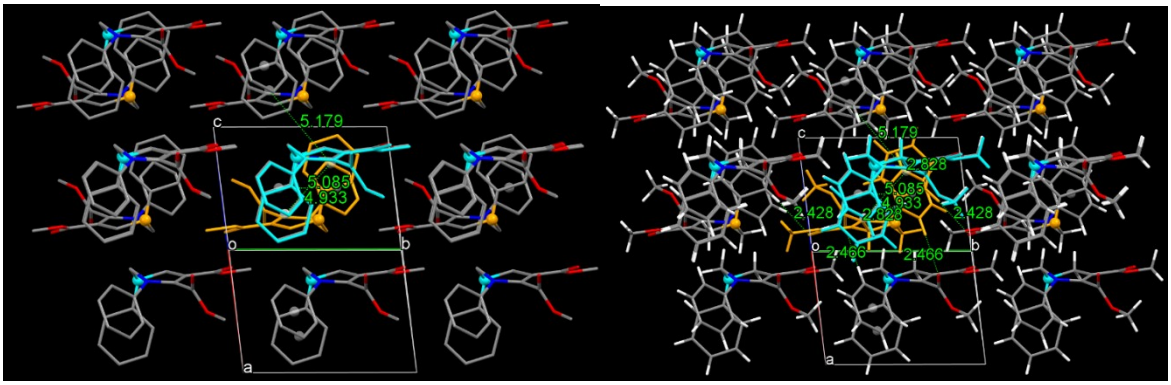


5k

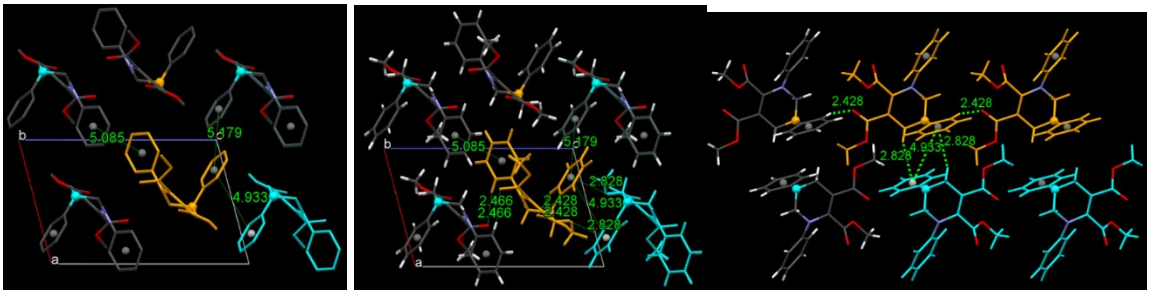
Figure S6. Overall arrangements of TTHPs in crystals and the intermolecular interactions around a molecule

Reversely packing

5a (Me-Ph)

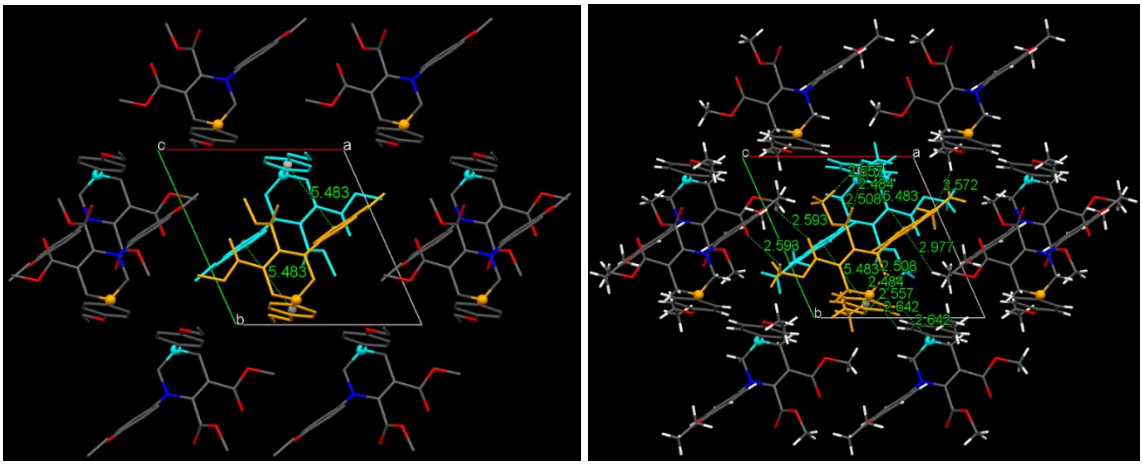


Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5a** (The stacking direction with the most intermolecular π-π interactions). The front and the side view of the colored *R*- and *S*-paired molecules see Figure 5 of the manuscript.

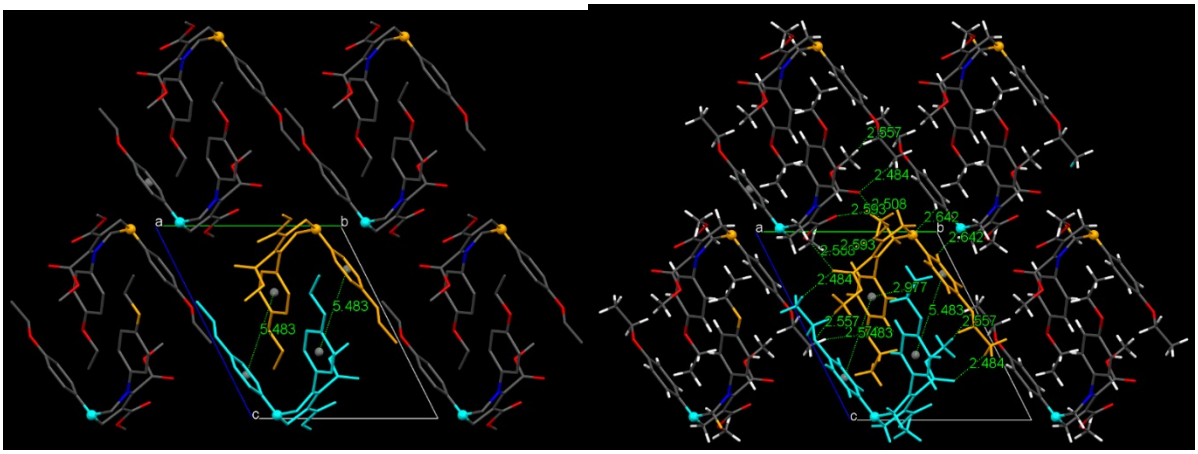


Overall molecular stacking arrangement without (left) and with (middle) hydrogen atoms of **5a** (Me-Ph) (The stacking direction with the most intermolecular weak hydrogen bonds), as well as the side view of the closely packed *RS*-paired molecules (right) (the side view of the colored *R*- and *S*-paired molecules in middle).

5c (Me-EtOPh)

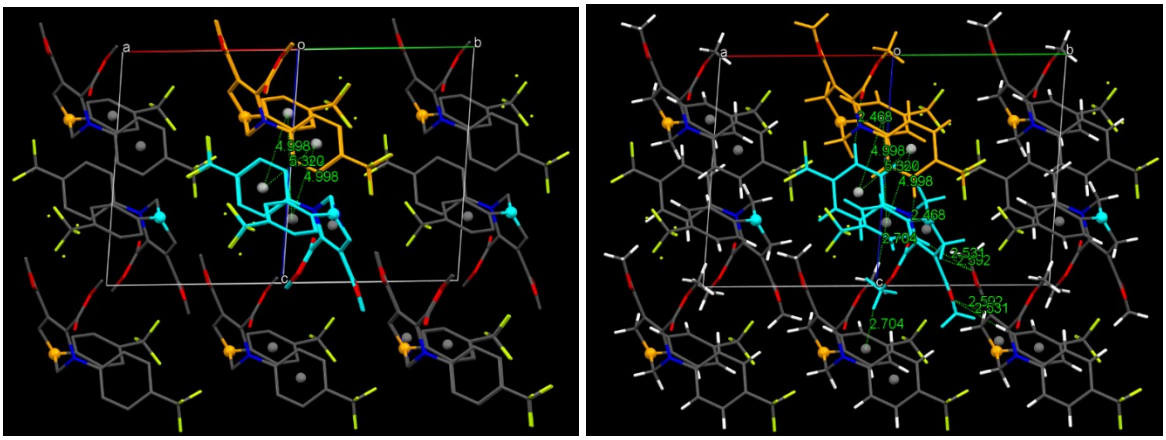


Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5c** (The stacking direction with the most intermolecular interactions). The front and the side view of the colored *R*- and *S*-paired molecules see Figure 5 of the manuscript.

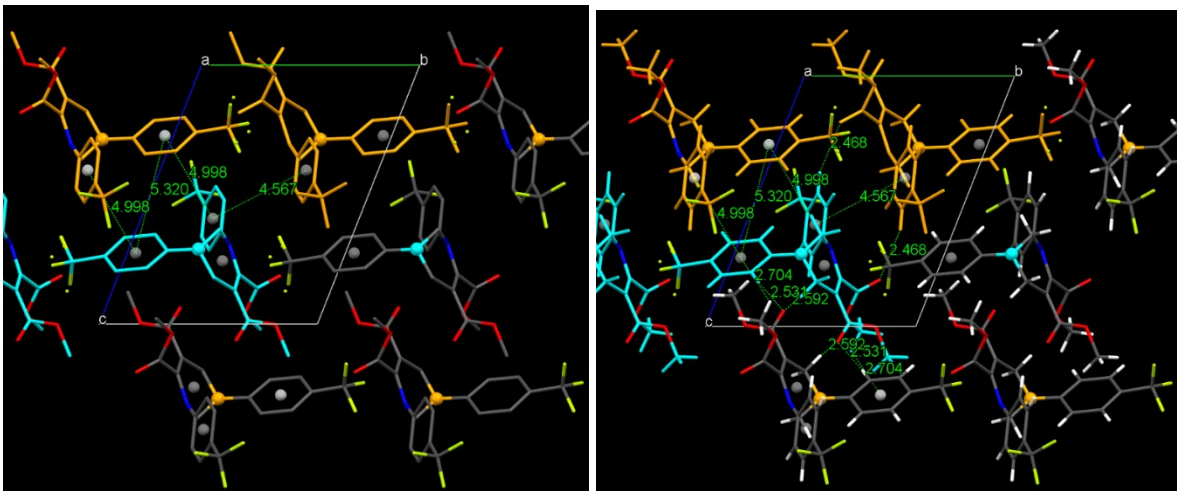


Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5c** on *bc* plane

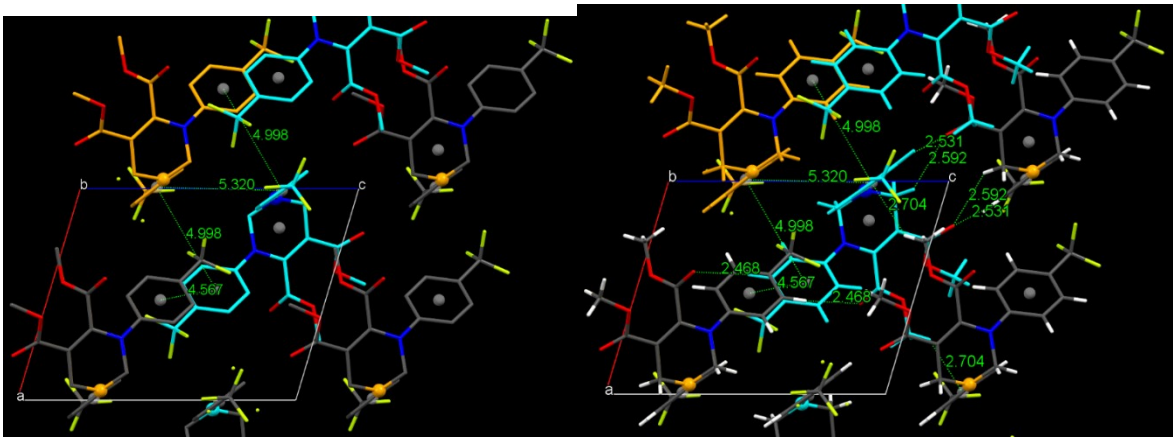
5d (Me-4-CF_3)



Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5d** (The stacking direction with the most intermolecular interactions). The front and the side view of the colored *R*- and *S*-paired molecules see Figure 5 of the manuscript.

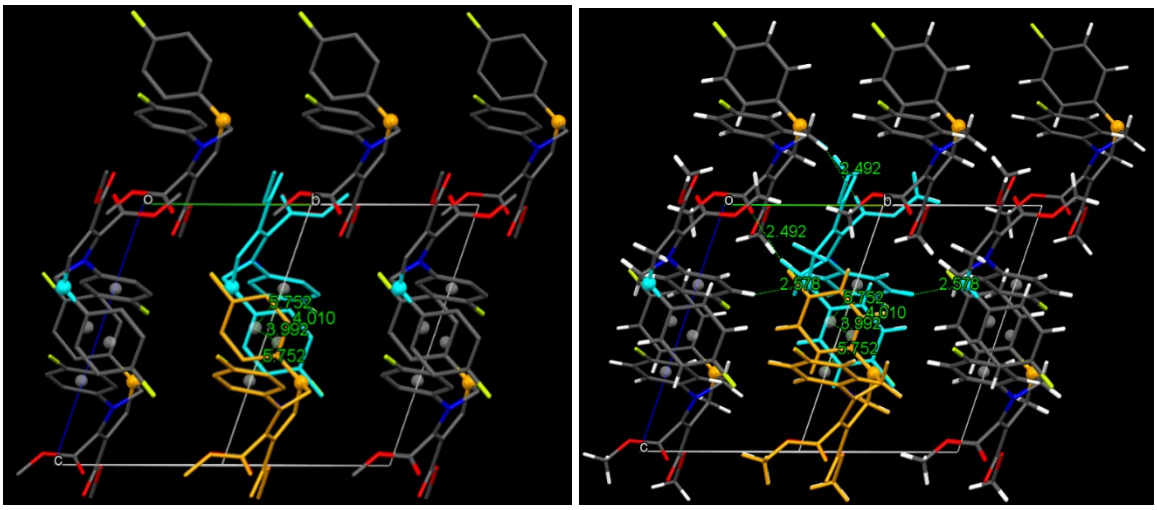


Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5d** on *bc* planes



Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5d** on *ac* planes

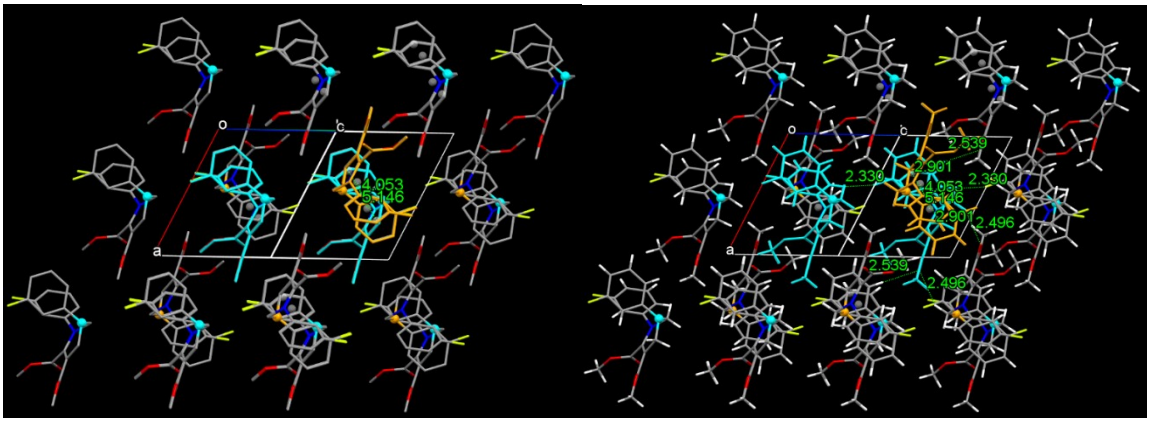
5e (4-FPh)



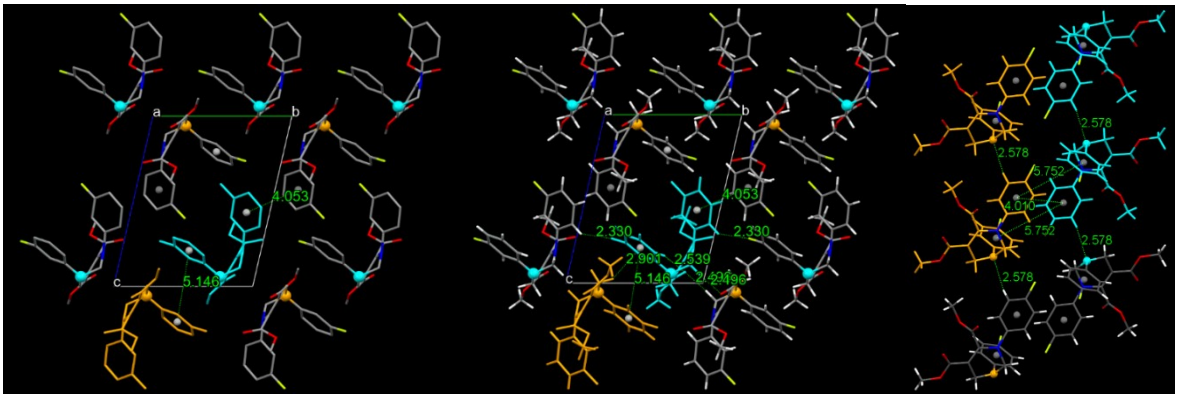
Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5e** (The stacking direction with the most intermolecular π–π interactions). The front and the side view of the colored *R*- and *S*-paired molecules see Figure 5 of the manuscript.

Overall molecular stacking arrangement without (left) and with (middle) hydrogen atoms of **5e** (The stacking direction with the most intermolecular weak hydrogen bonds), as well as the side view of the closely packed *RS*-paired molecules (right) (the side view of the colored *R*- and *S*-paired molecules in middle).

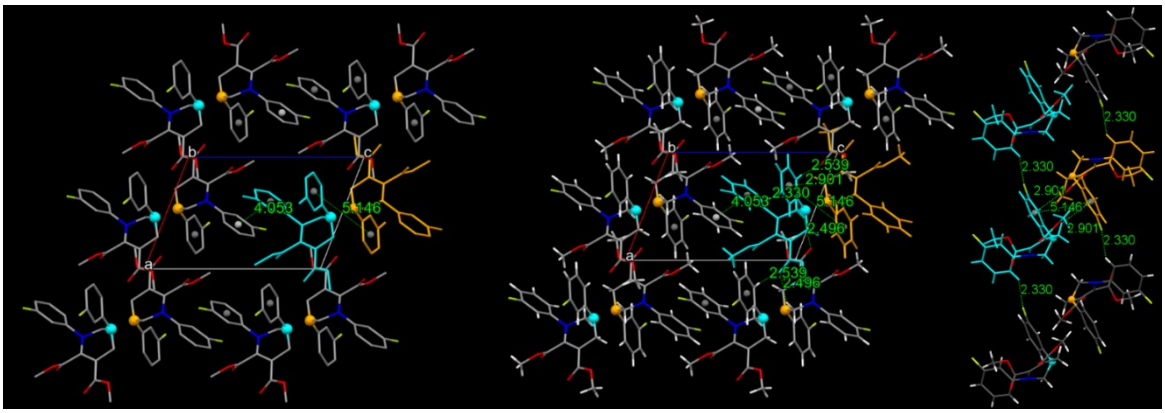
5h (Me-3-F)



Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5h** (The stacking direction with the most intermolecular π–π interactions). The front and the side view of the colored *R*- and *S*-paired molecules see Figure 5 of the manuscript.



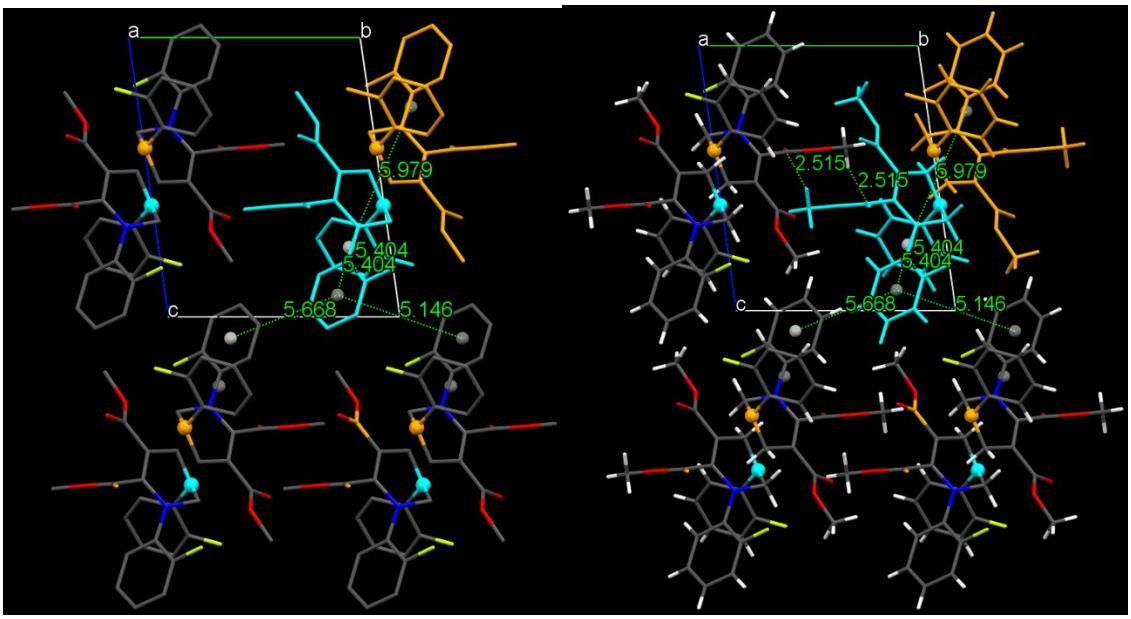
arrangement without (left) and with (middle) hydrogen atoms of **5h** on *bc* planes (The stacking direction with the intermolecular ArC-H…N bonds), as well as the side view of the closely packed *RS*-paired molecules (right) (the side view of the colored *R*- and *S*-paired molecules in middle).



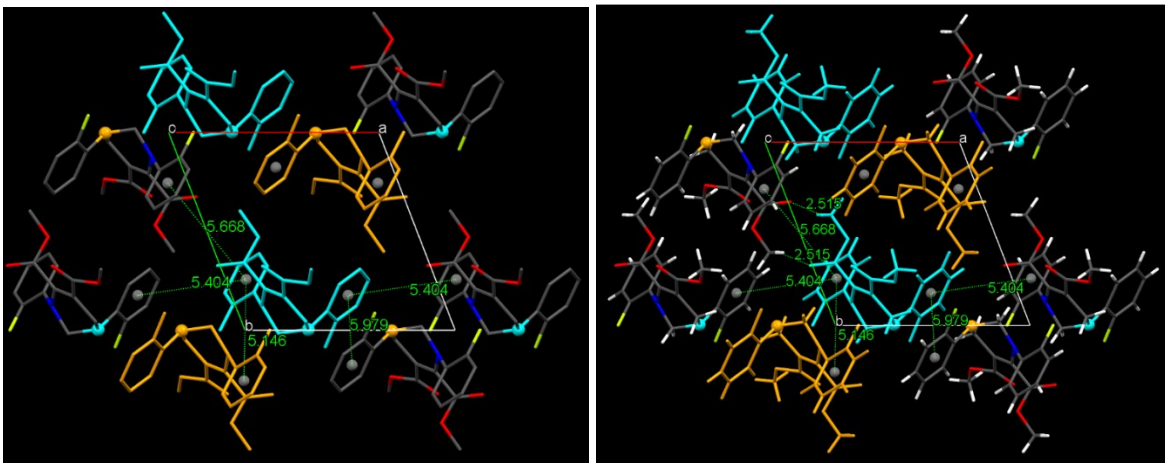
Overall molecular stacking arrangement without (left) and with (middle) hydrogen atoms of **5h** on *ac* plane (The stacking direction with weak ArC-H…F bonds), as well as the side view

of the closely packed *RS*-paired molecules (right) (the side view of the colored *R*- and *S*-paired molecules in middle).

5i (Me-2-F)

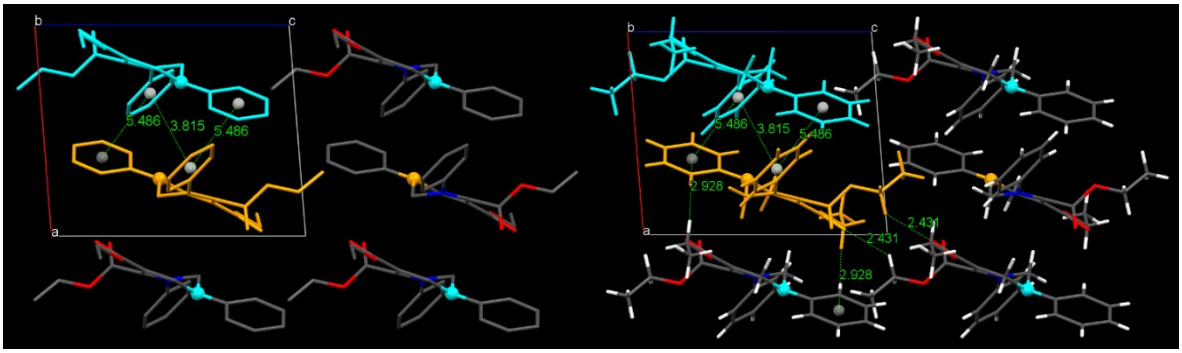


Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5i** (The stacking direction with the most intermolecular π–π interactions). The front and the side view of the colored *R*- and *S*-paired molecules see Figure 5 of the manuscript.

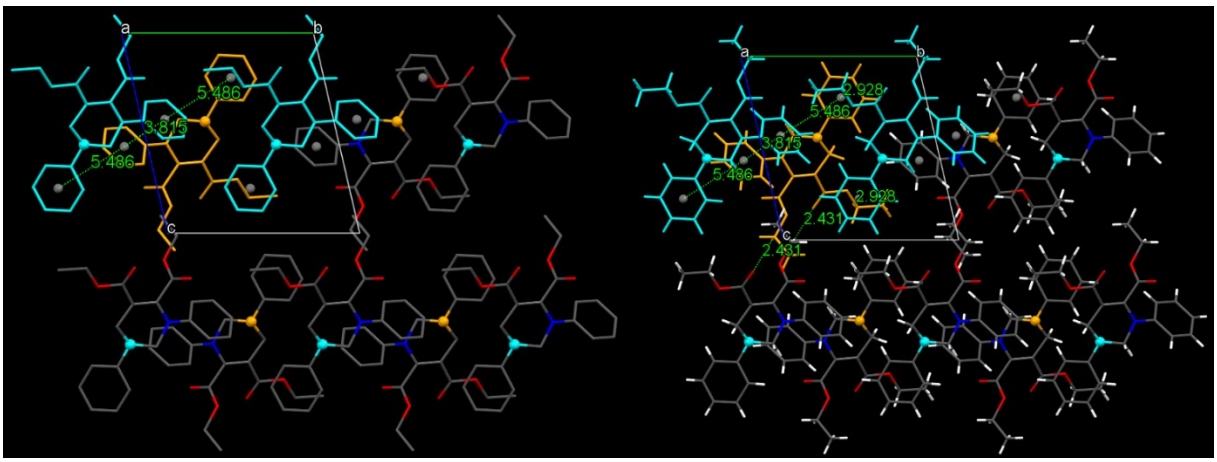


Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5i** on *ab* plane

5j (Et-Ph)

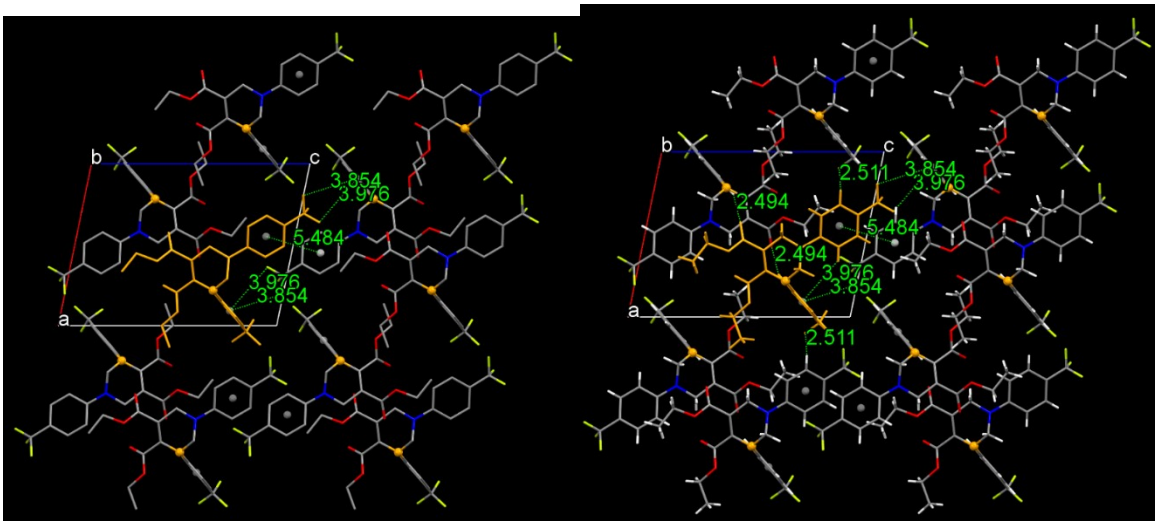


Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5j** (Et-Ph) on *ac* plane



Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5j** (Et-Ph) on *bc* plane.

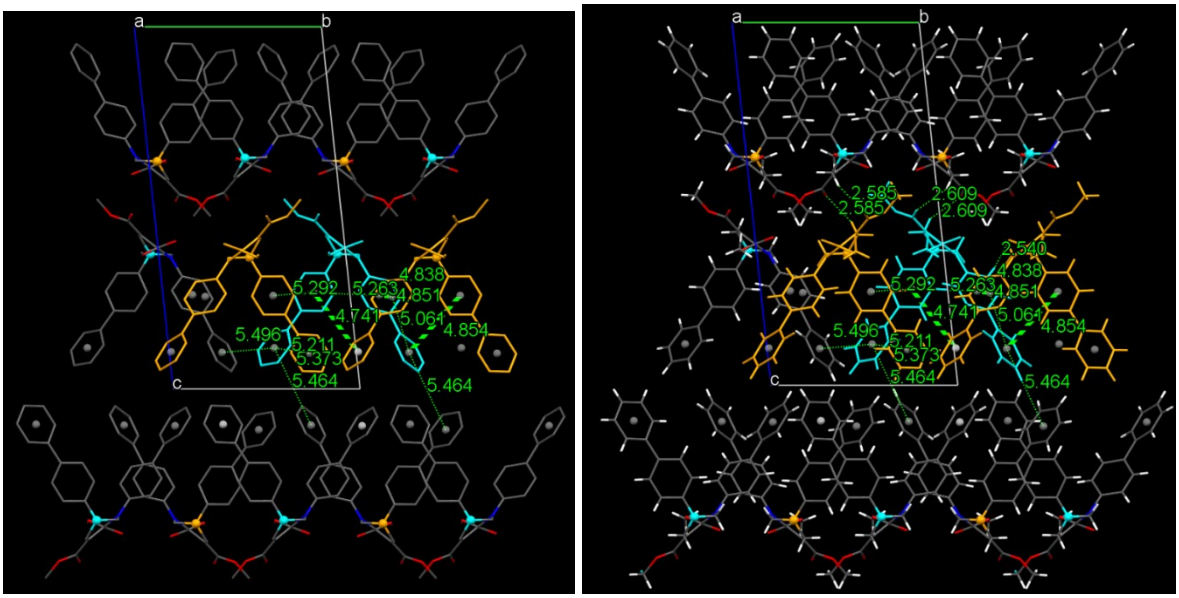
5k (Et-4-CF3Ph)



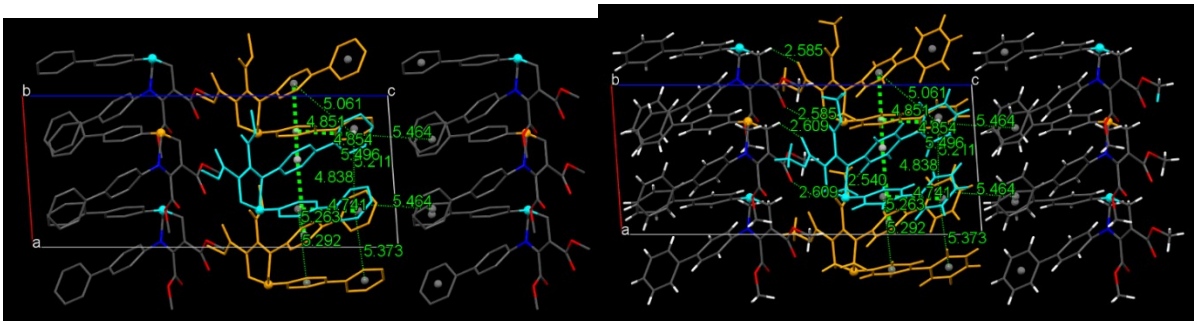
Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5k** (Et-4-CF3Ph).

Crossly-reversely packing

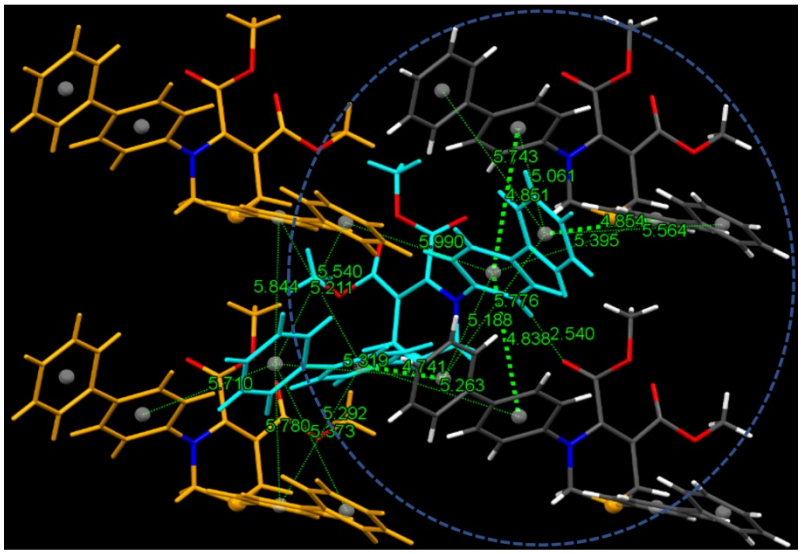
5b (PhPh)



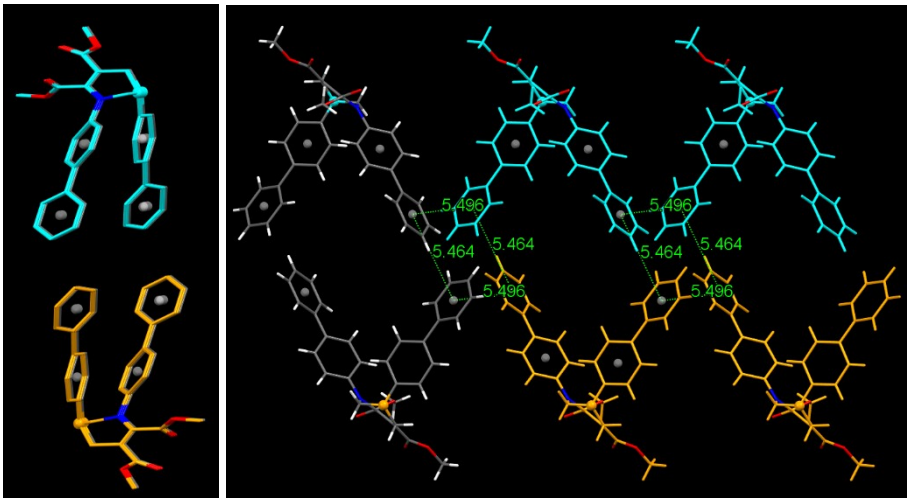
Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5b** (Me-PhPh) on *bc* plane.

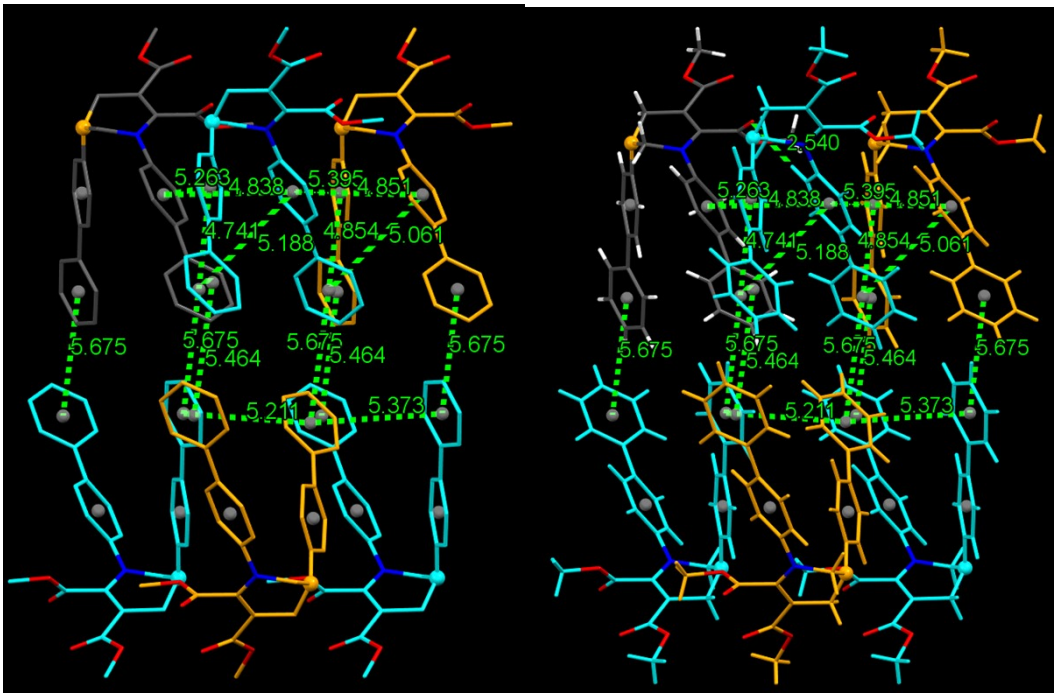


Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5b** (Me-PhPh) on *ac* plane

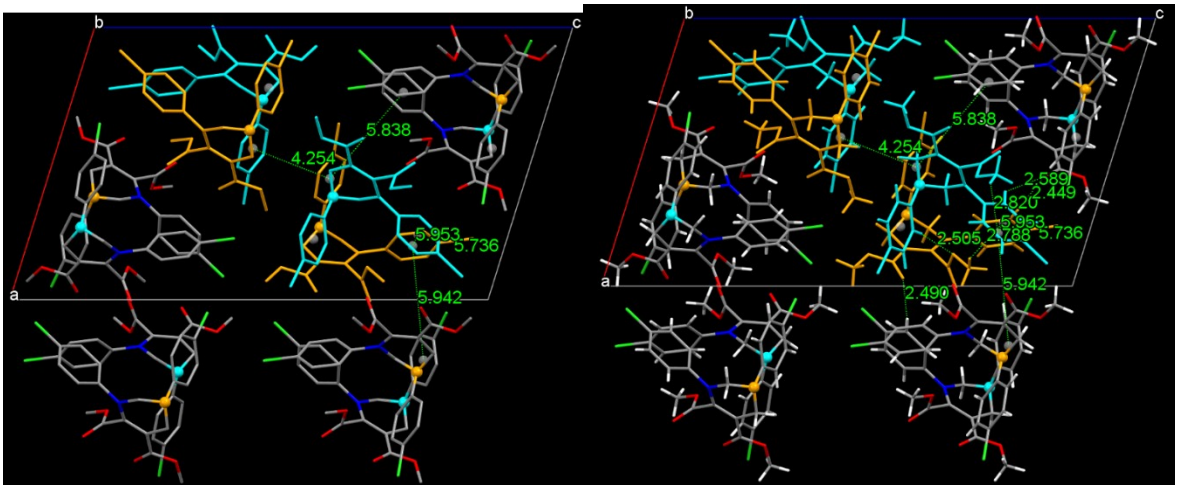


Side view of the packed molecules with multi-intermolecular short-range ring interactions of **5b**. The front and the side view of the stacking arrangement of the molecules in the blue circle see Figure 5 of the manuscript.

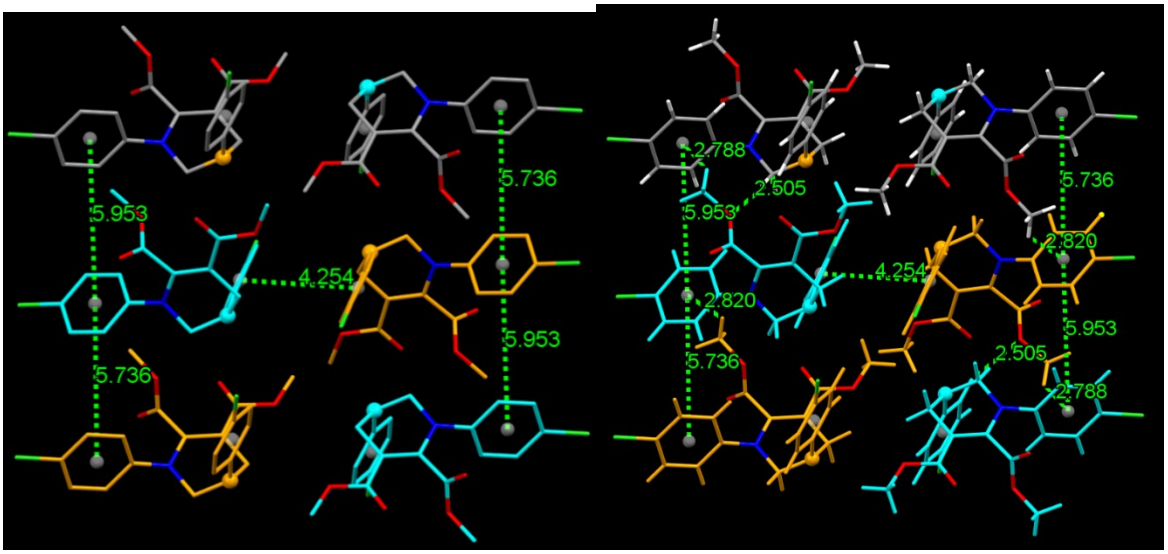




5f (4-ClPh)

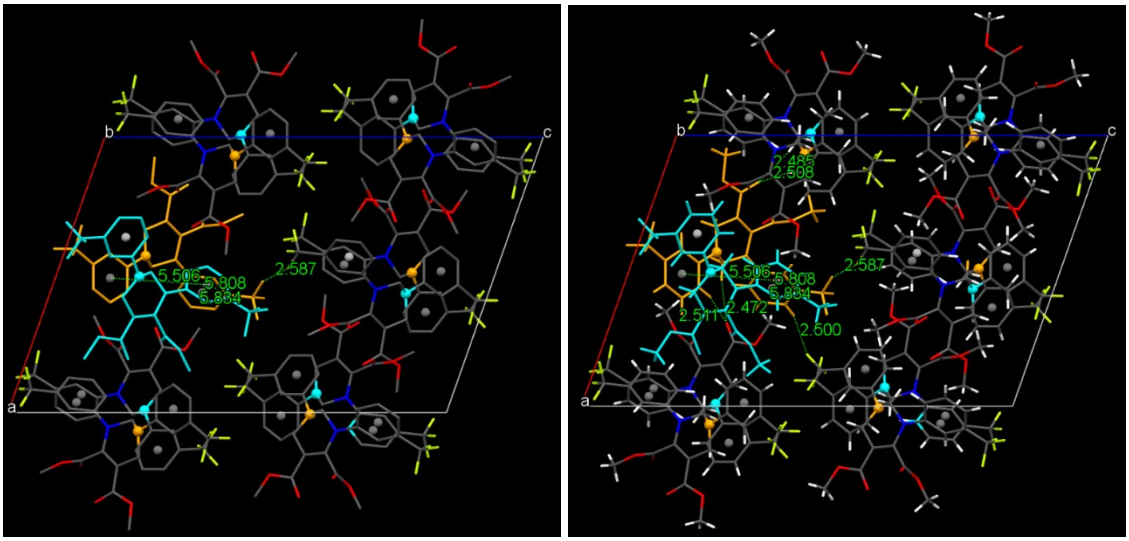


Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5f** (The stacking direction with the most intermolecular π–π interactions). The front and the side view of the colored *R*- and *S*-paired molecules see Figure 5 of the manuscript and the side view of the colored *R*- and *S*-paired molecules see the Figures below.



Crossly packing

5g(3-CF_3Ph)



Overall molecular stacking arrangement without (left) and with (right) hydrogen atoms of **5g**(3-CF_3Ph). The front and the side view of the colored *R*- and *S*-paired molecules see Figure 5 of the manuscript and the side view of the colored *R*- and *S*-paired molecules see the Figures below.

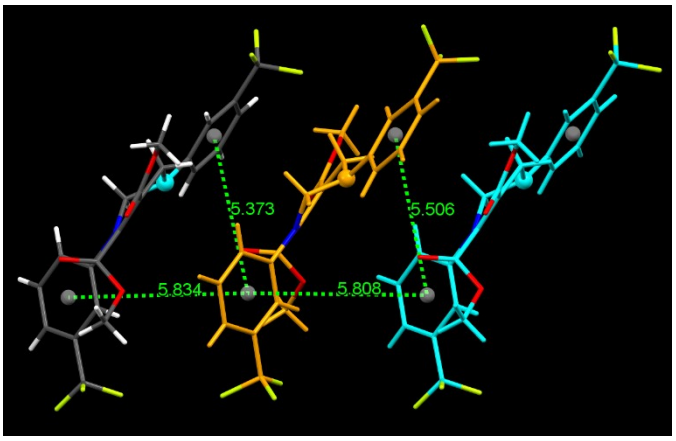
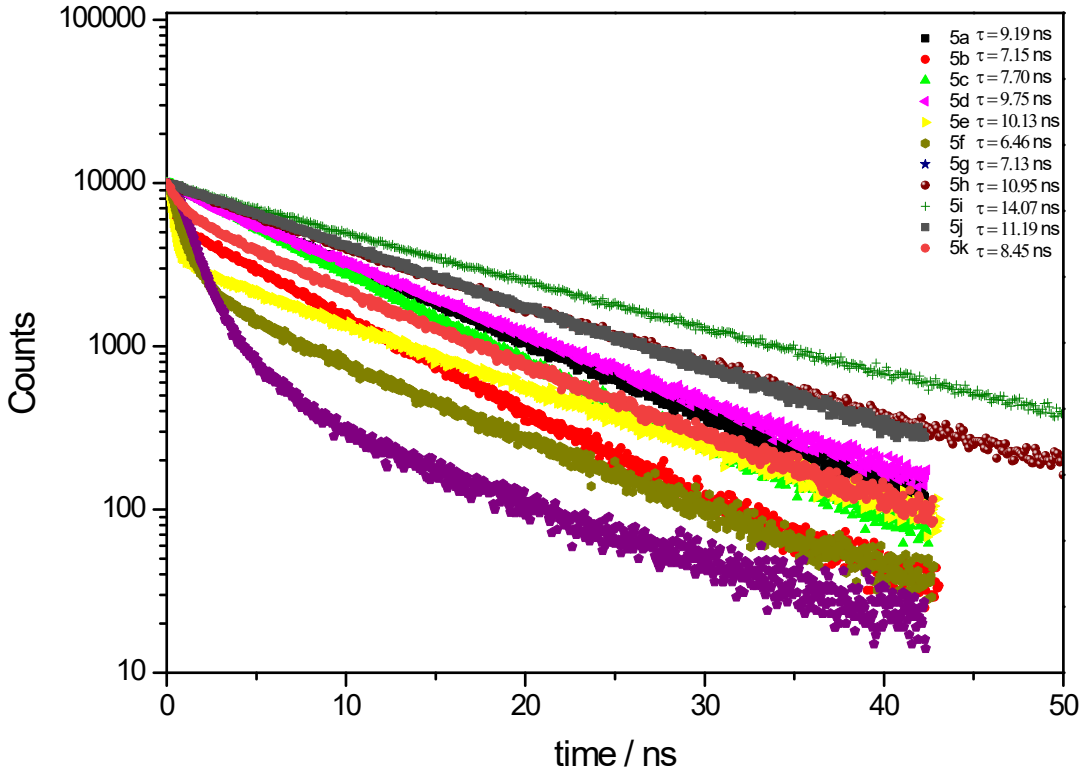
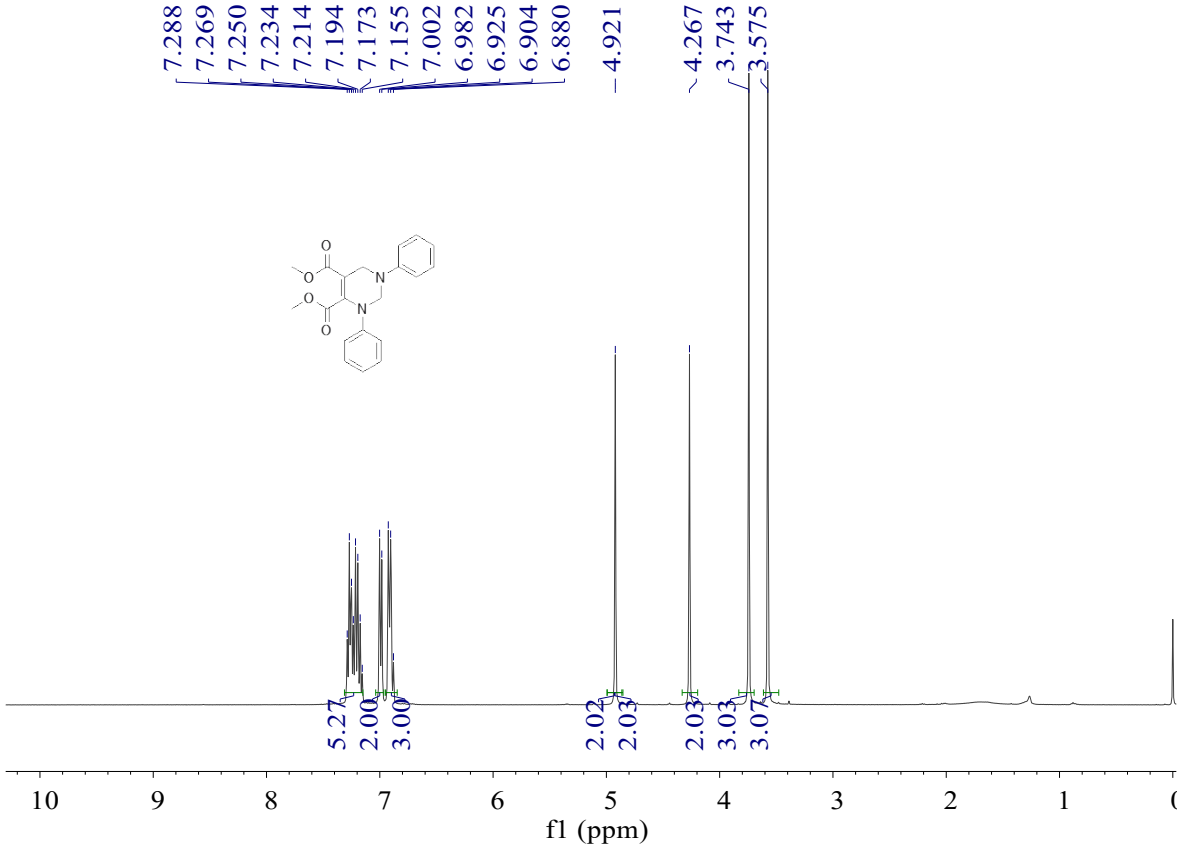


Figure S7. Fluorescence decay profiles of 5a-5k in solids.

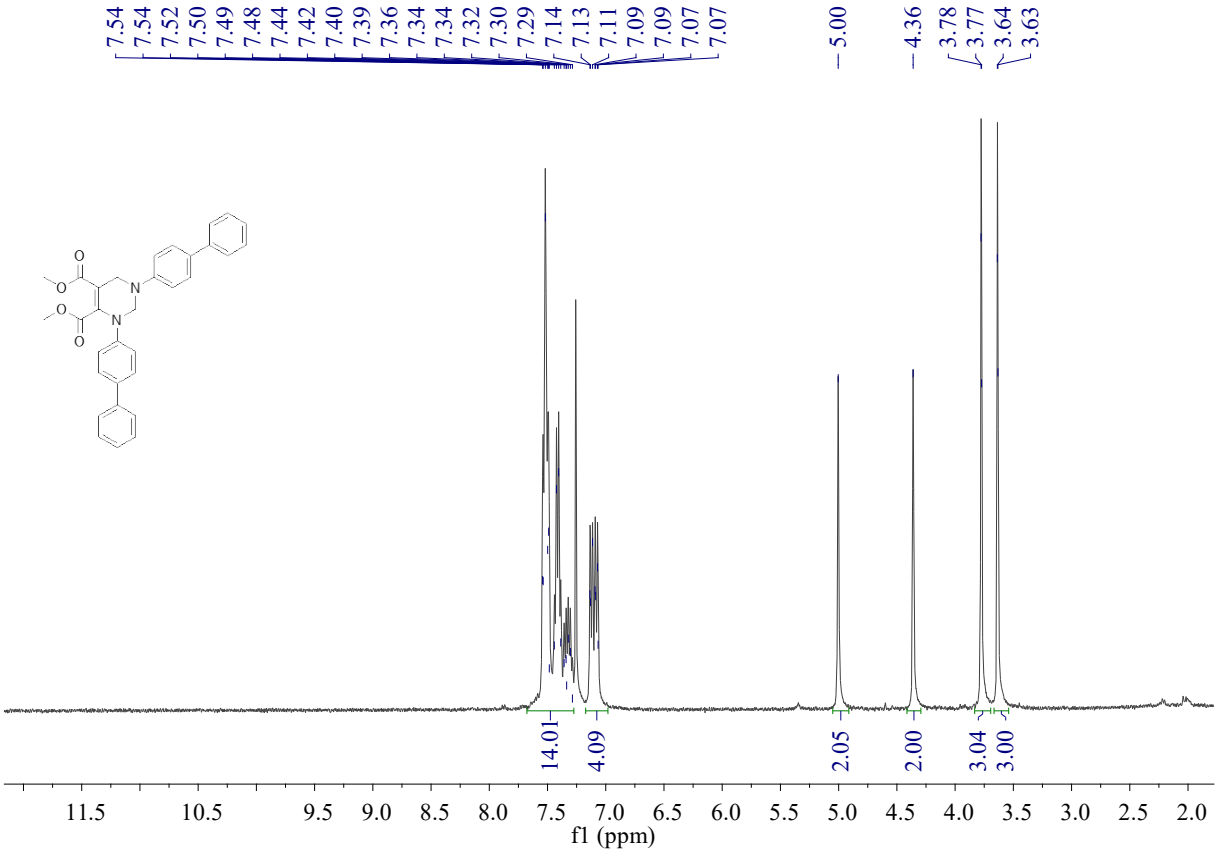


Excited at 320 nm for all TTHPs except **5b** excited at 405 nm, emitted at their emission peaks, respectively.

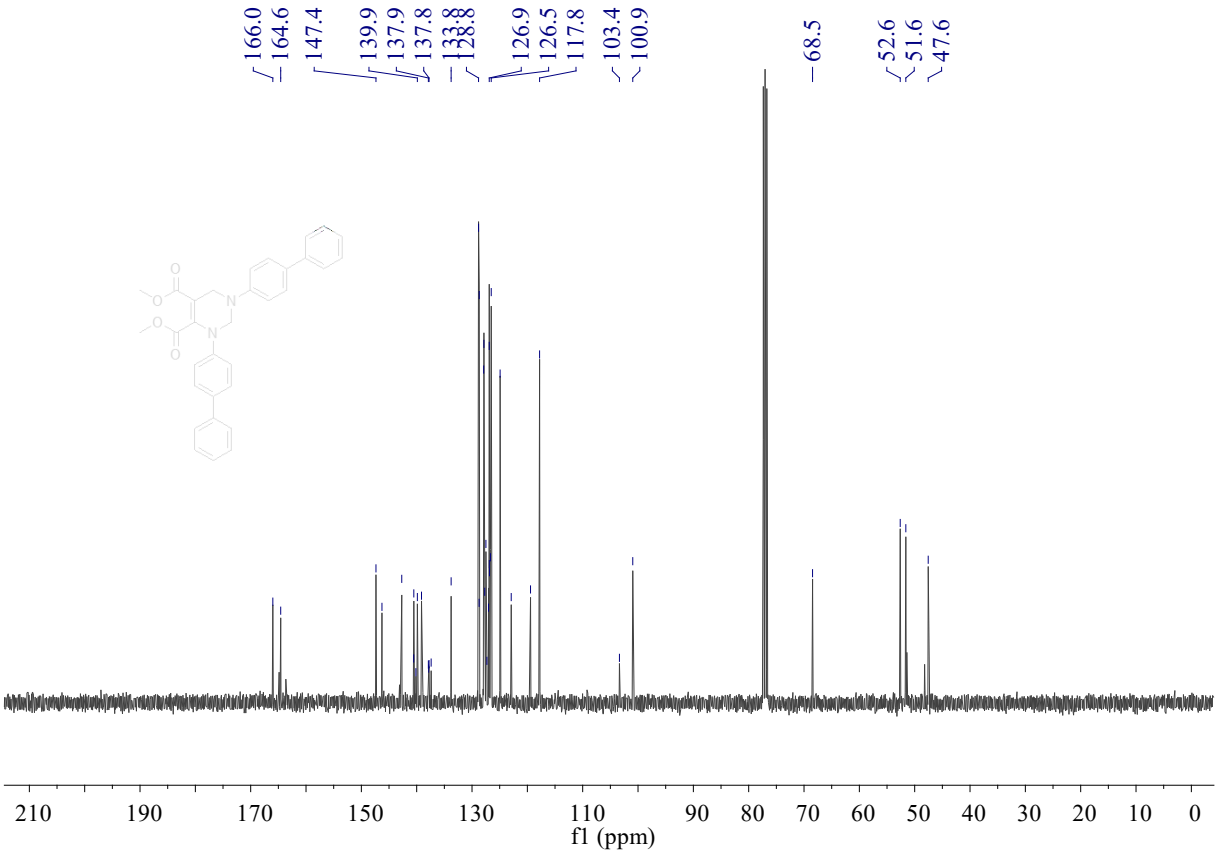
^{1}H and ^{13}C NMR spectra of products



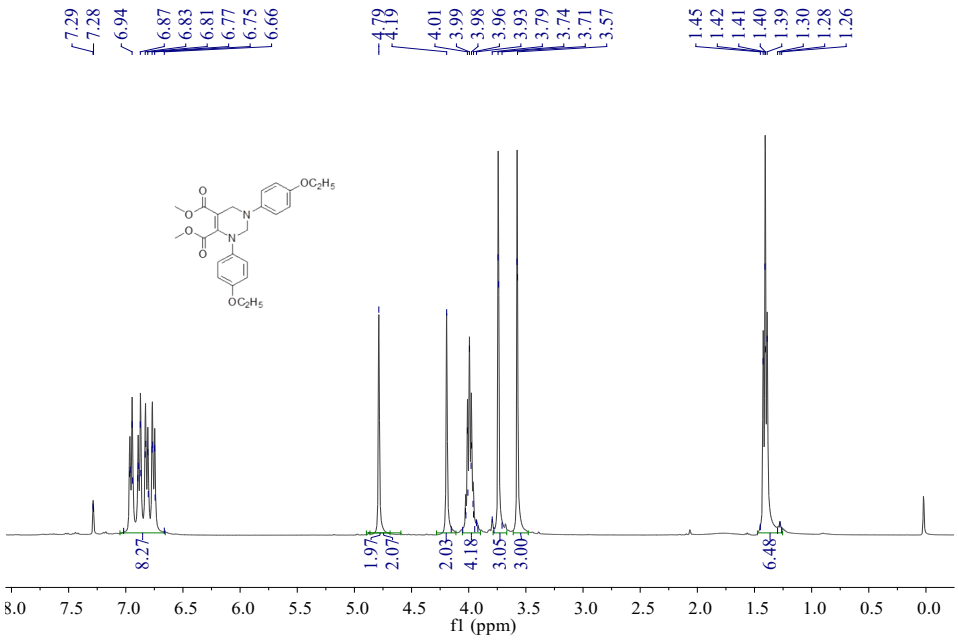
^{1}H NMR spectra of compound **5a**



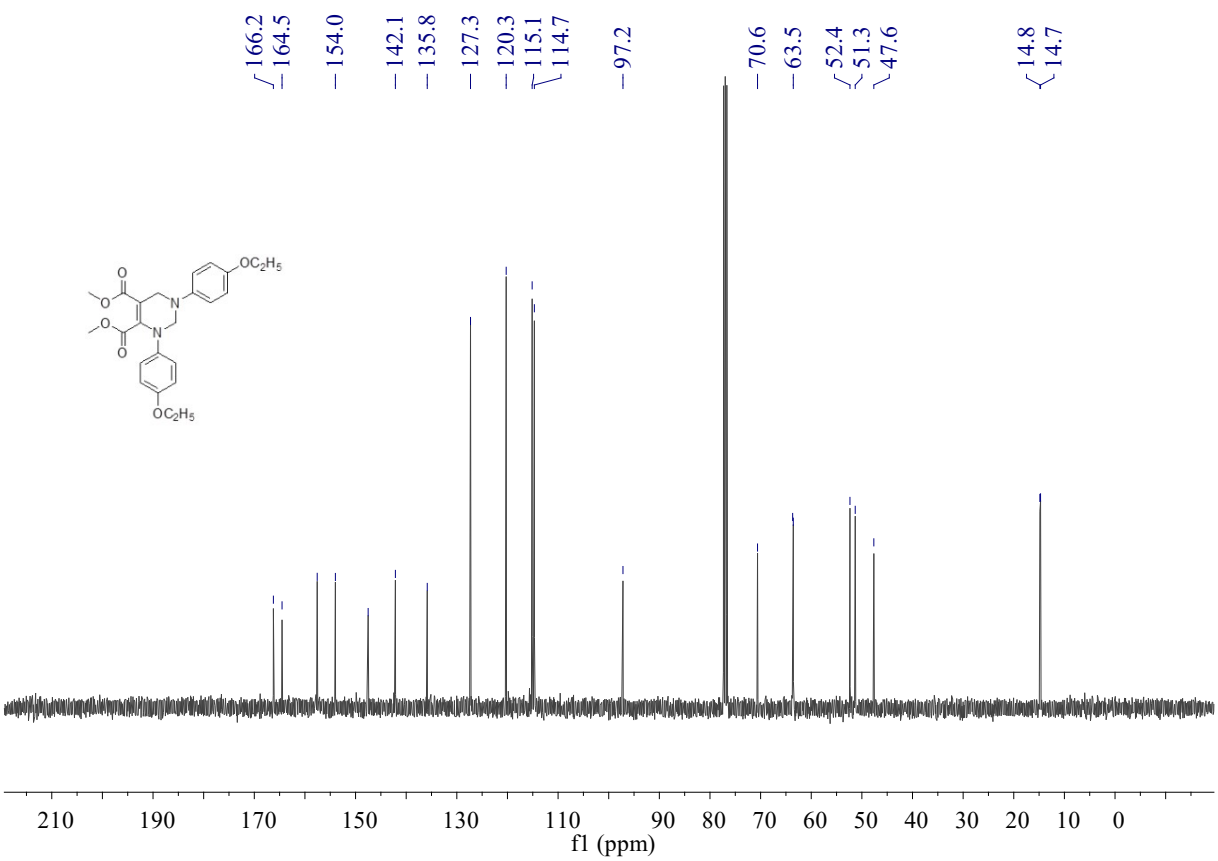
^{1}H NMR spectra of compound **5b**



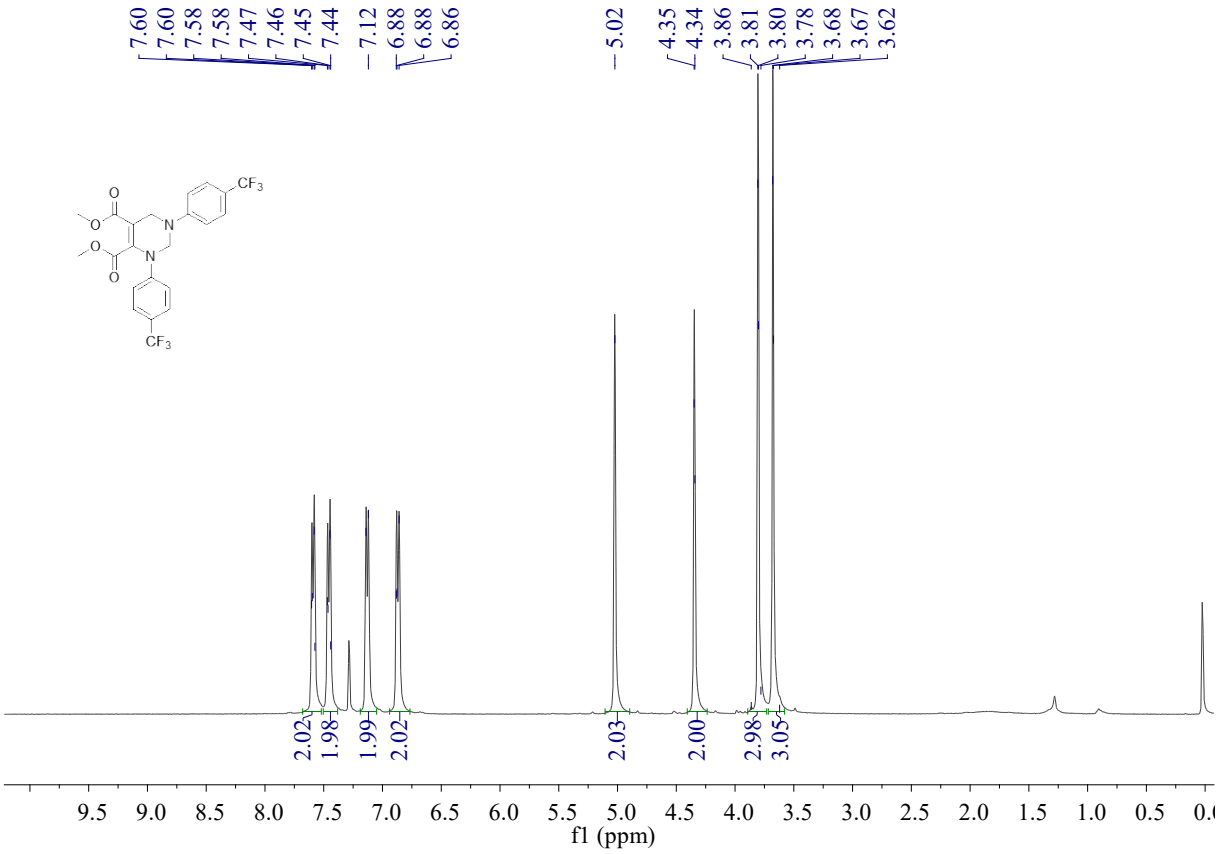
^{13}C NMR spectra of compound **5b**



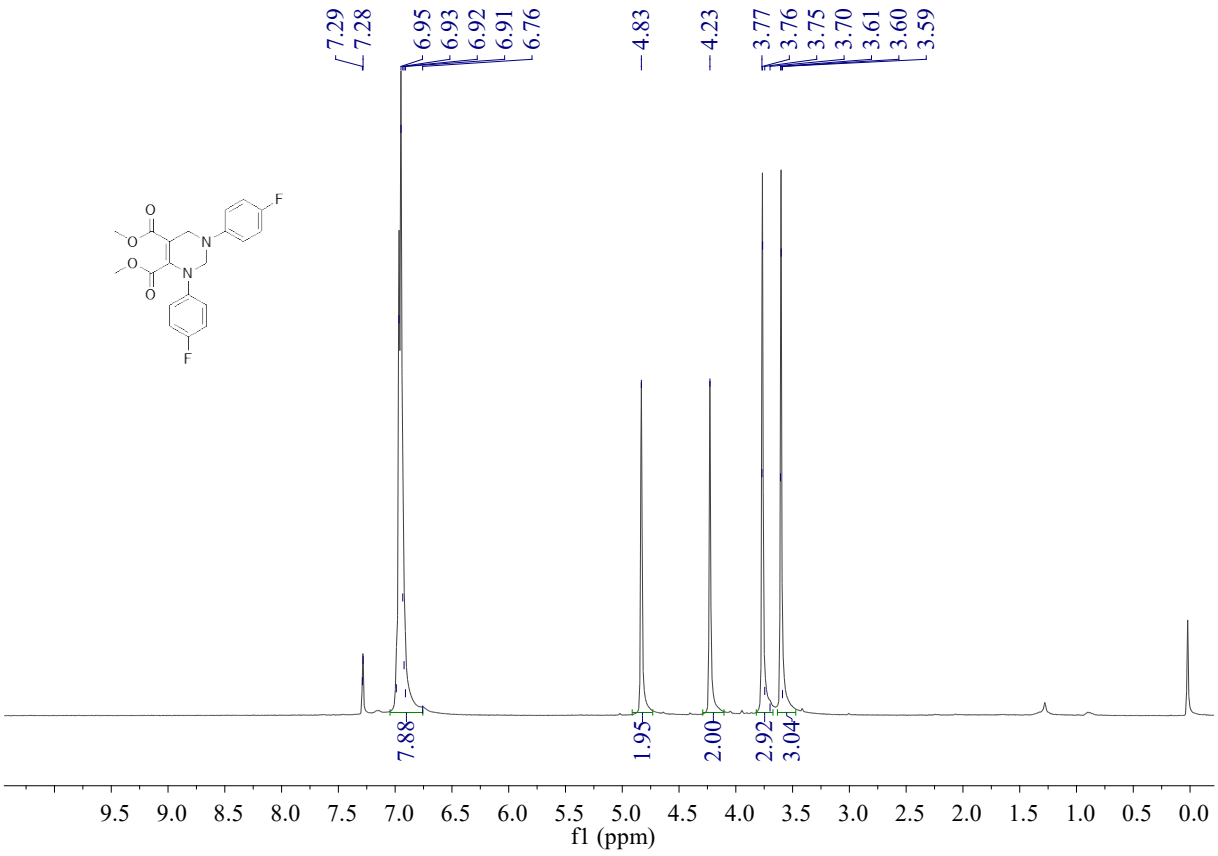
^{1}H NMR spectra of compound **5c**



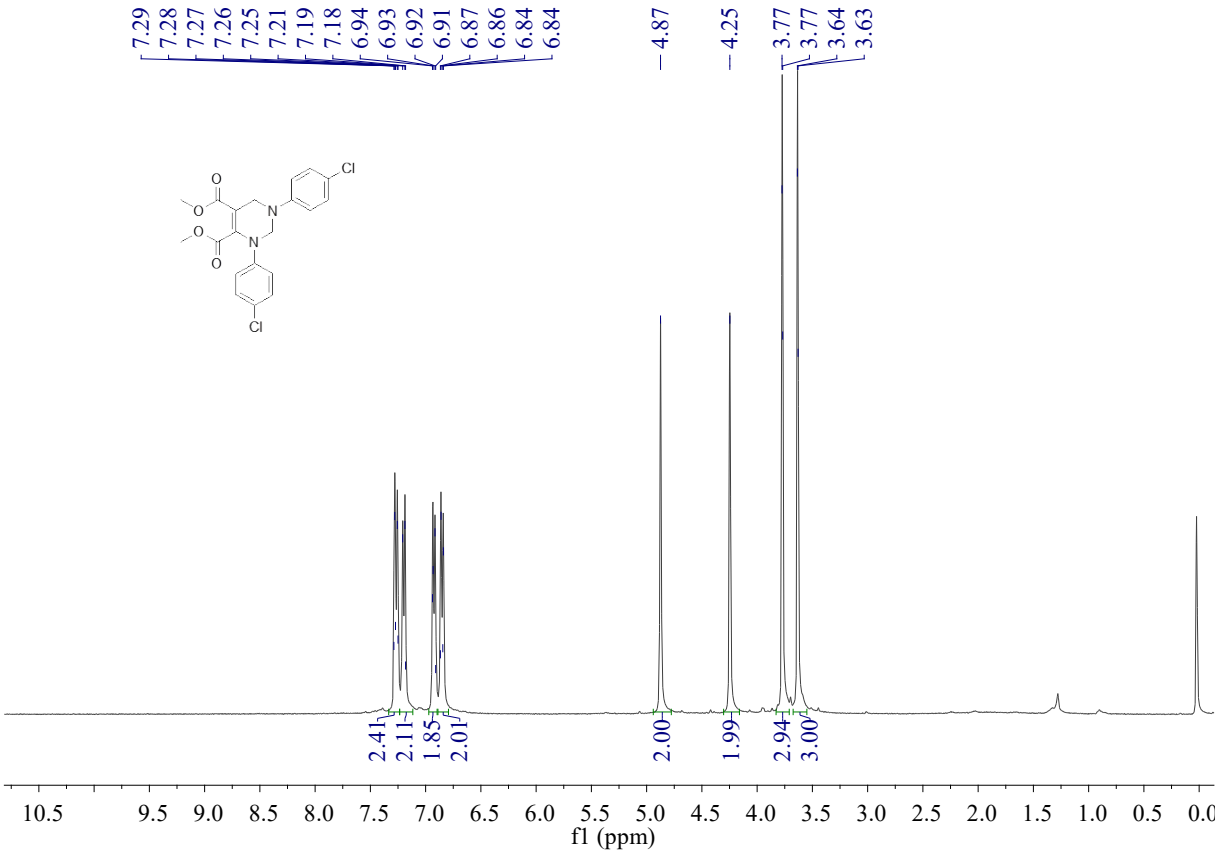
^{13}C NMR spectra of compound **5c**



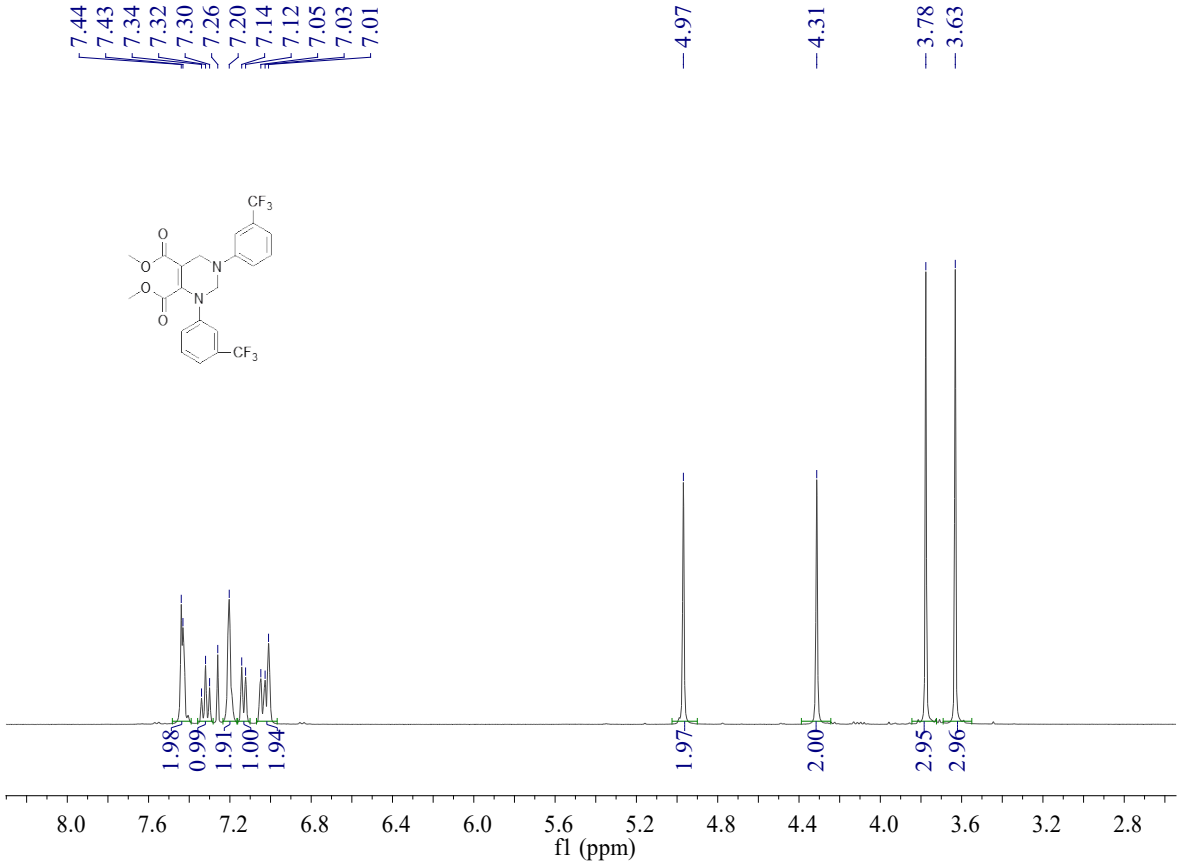
^{1}H NMR spectra of compound **5d**



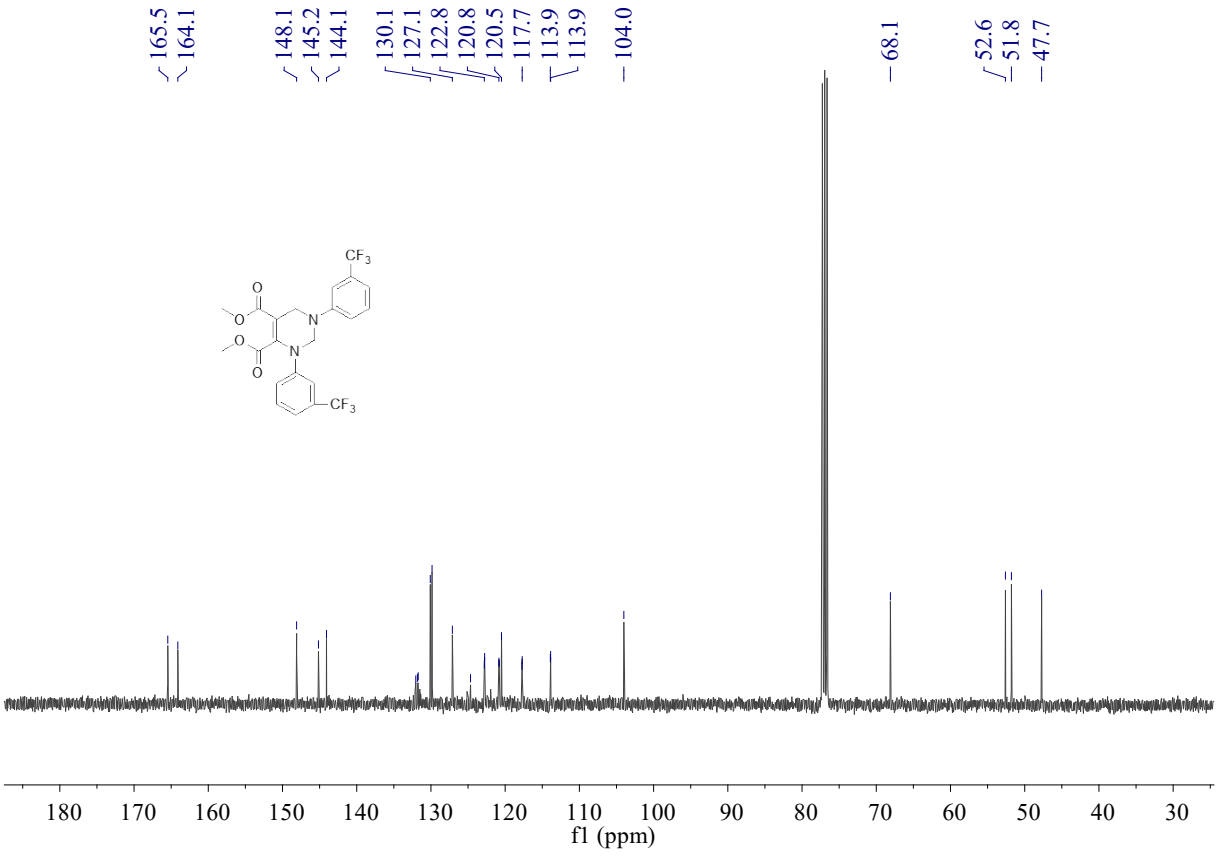
^{1}H NMR spectra of compound **5e**



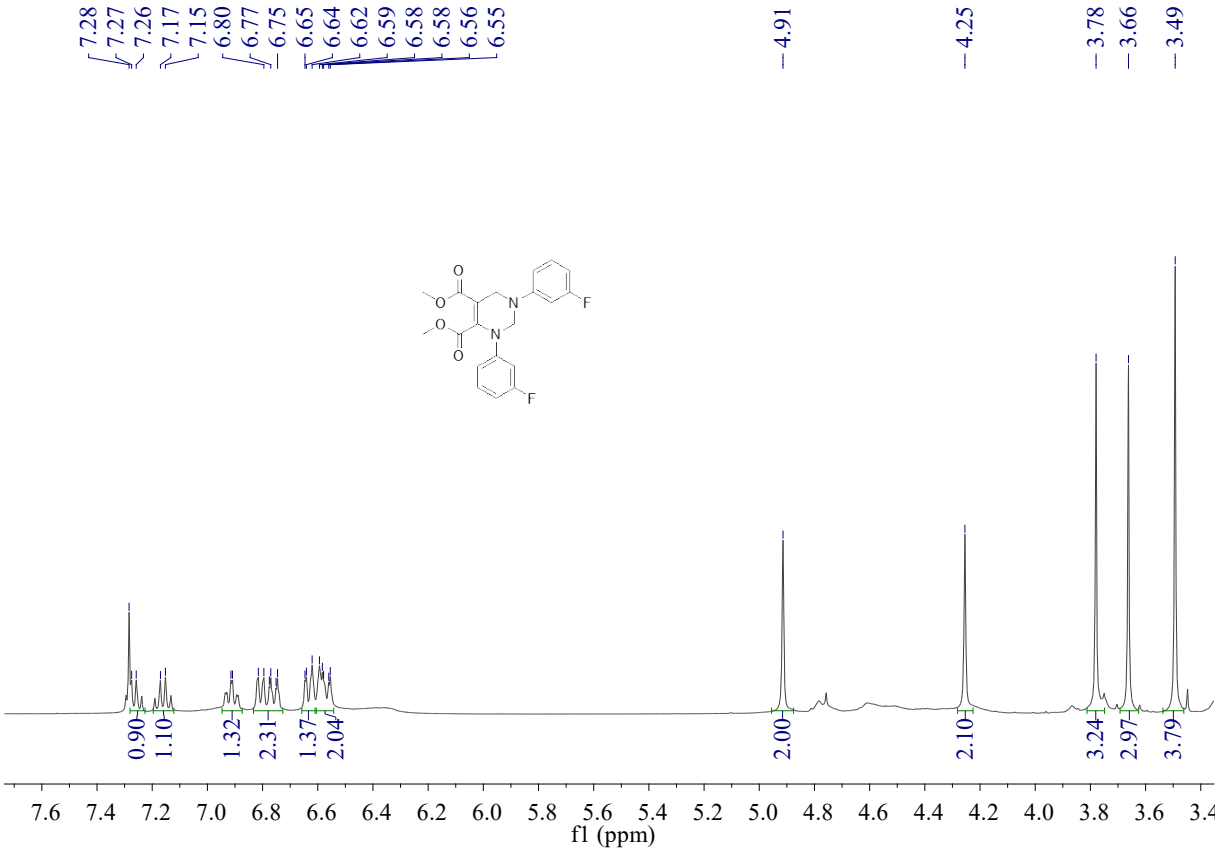
^{1}H NMR spectra of compound **5f**



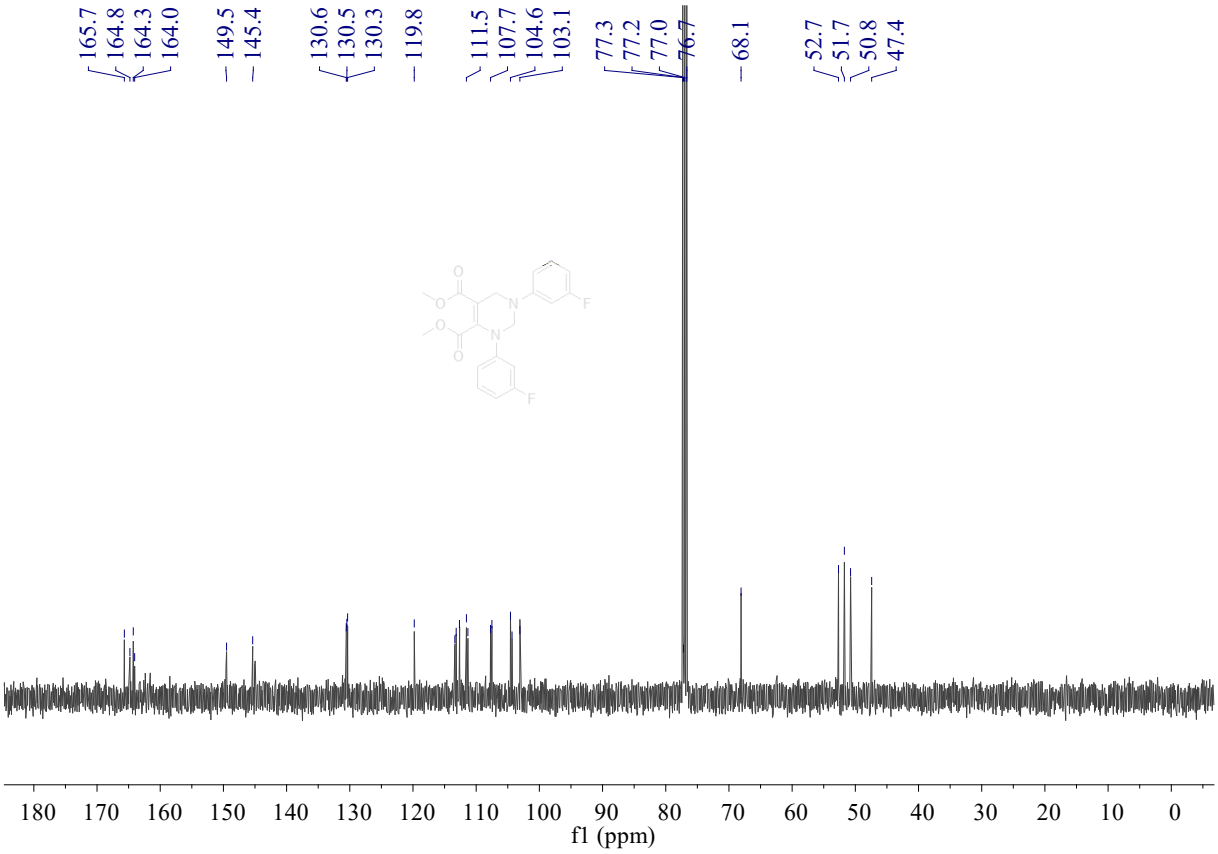
^{1}H NMR spectra of compound **5g**



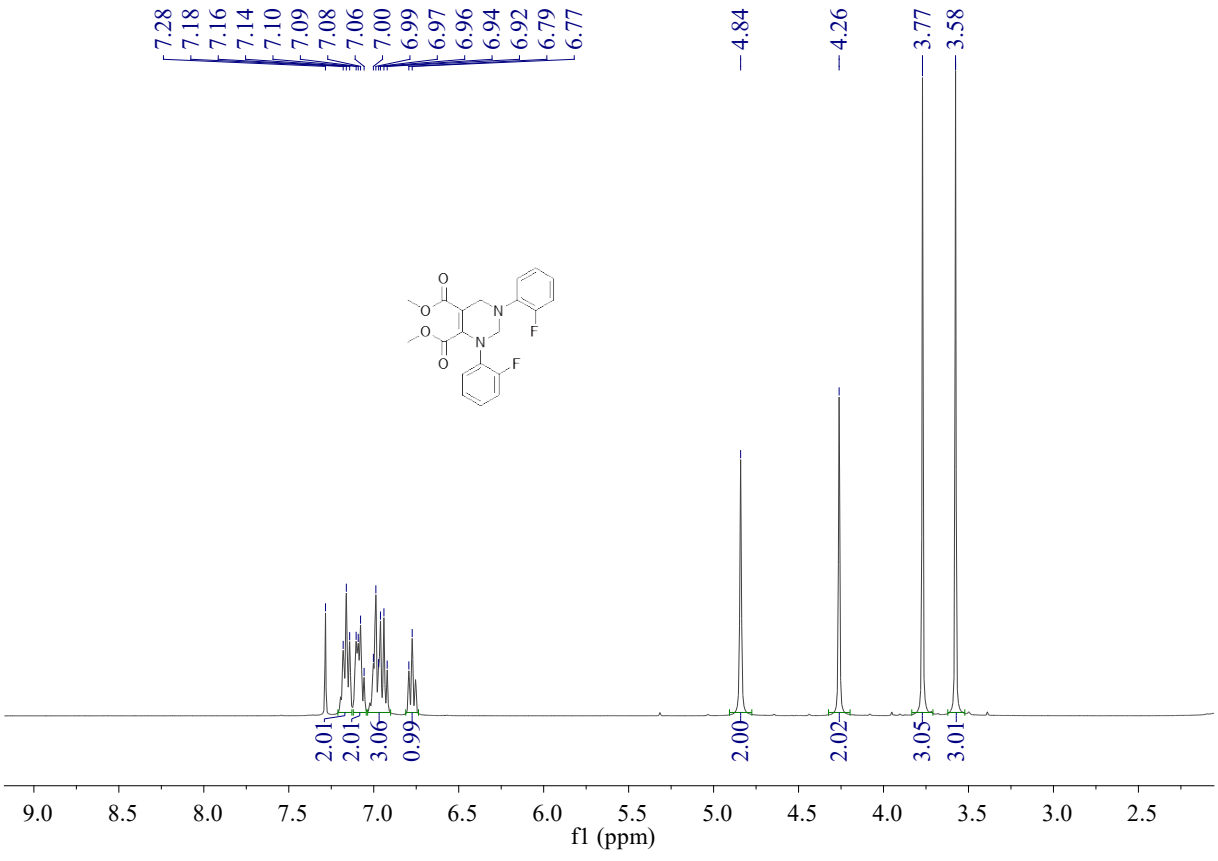
^{13}C NMR spectra of compound **5g**



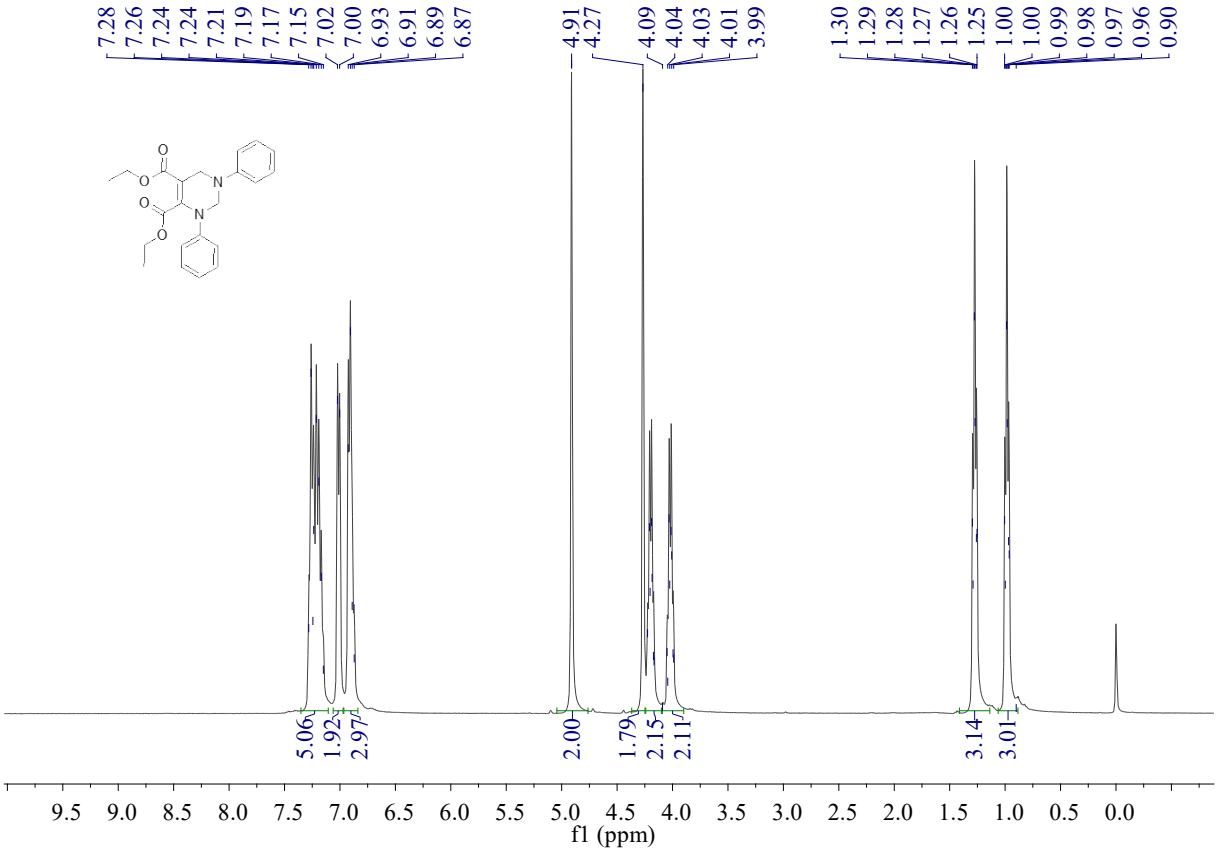
^{1}H NMR spectra of compound **5h**



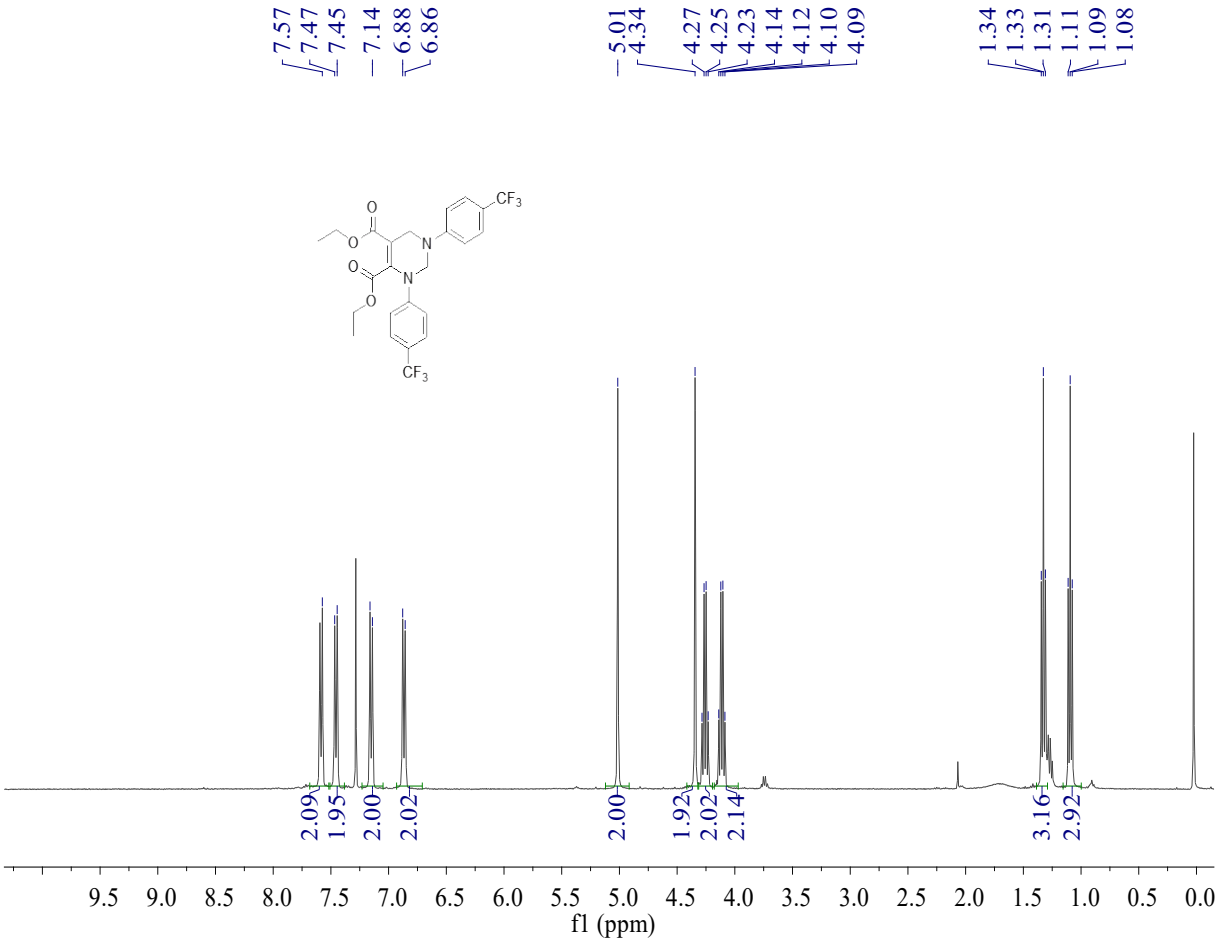
^{13}C NMR spectra of compound **5h**



^{1}H NMR spectra of compound **5i**

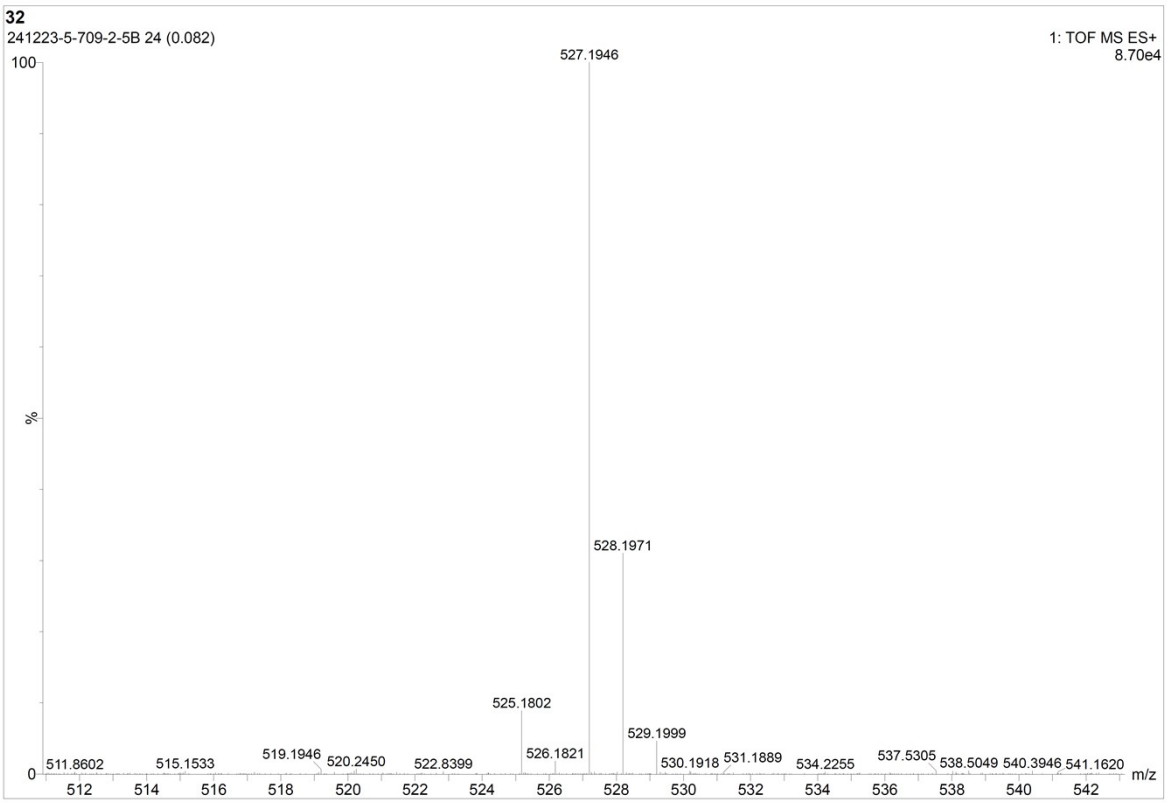


^{1}H NMR spectra of compound **5j**

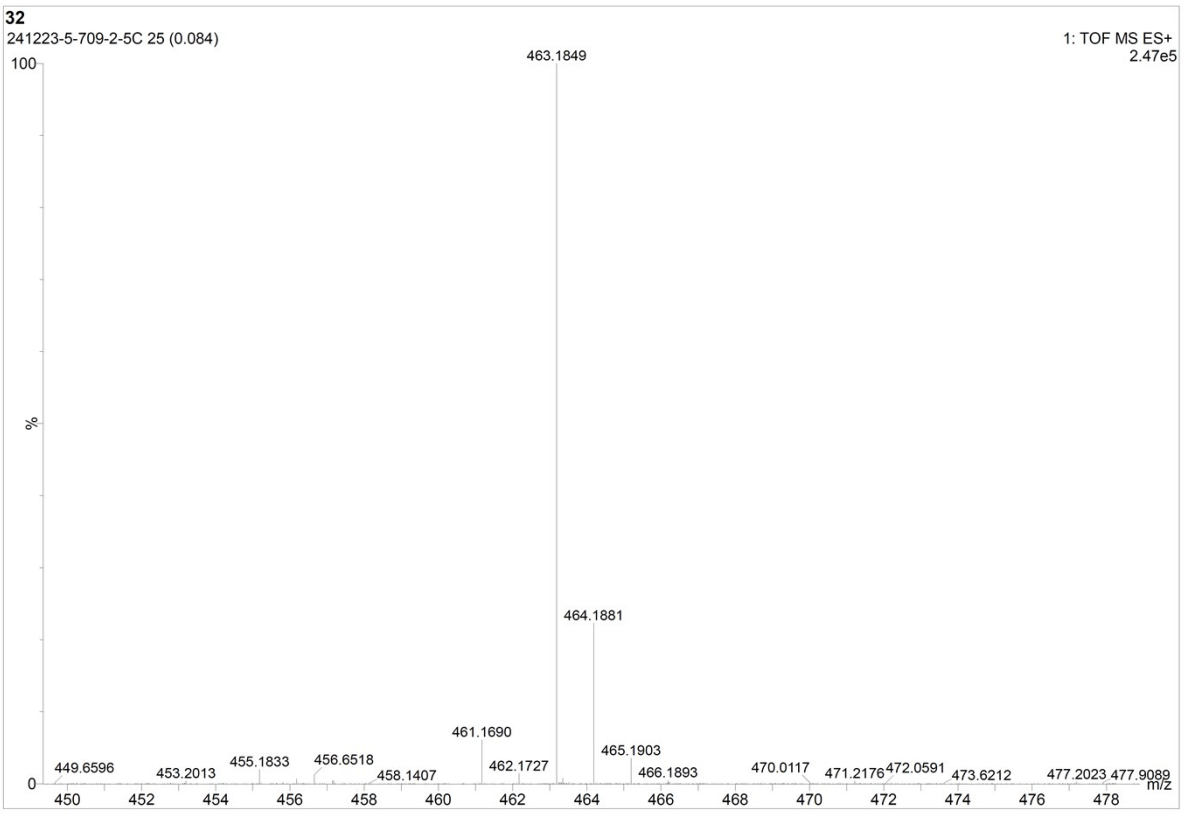


^{1}H NMR spectra of compound **5k**

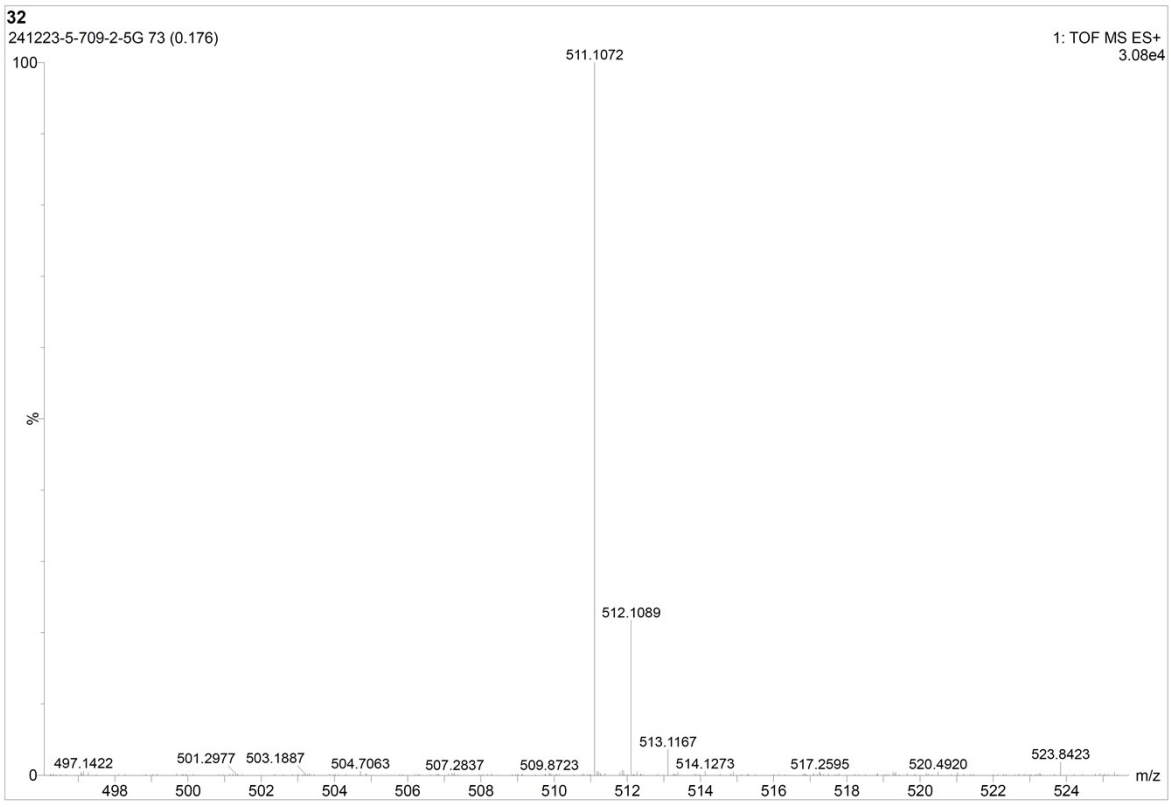
HRMS spectra



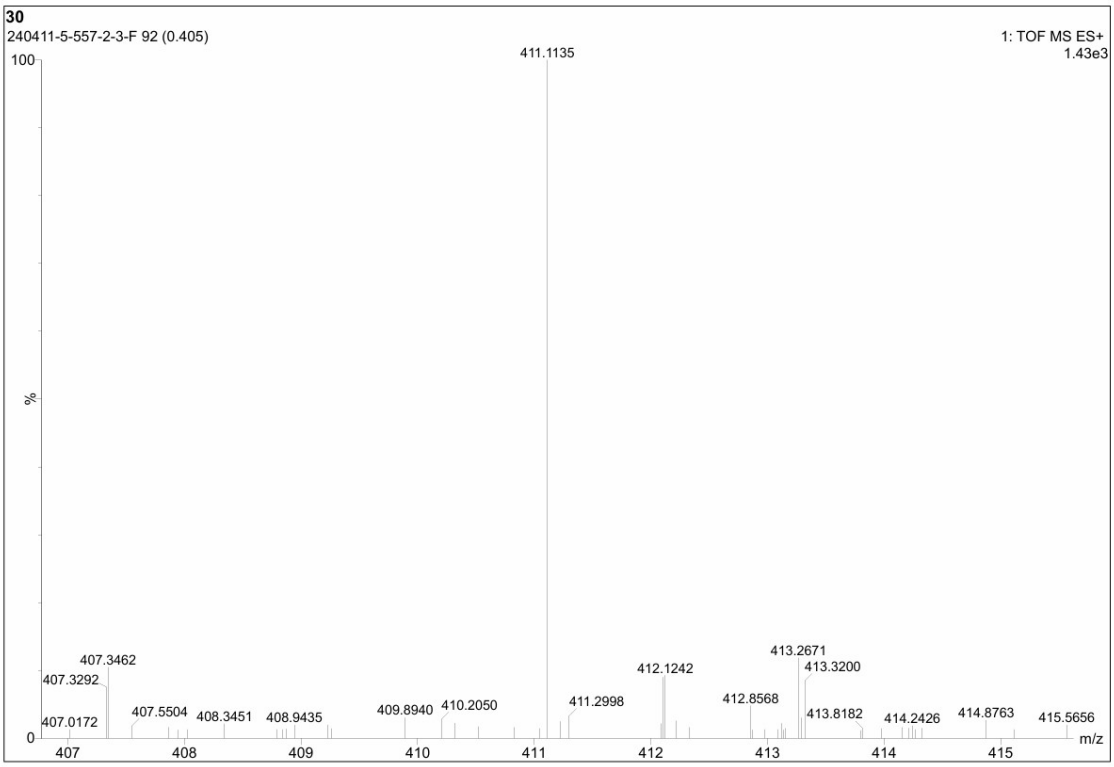
HRMS spectra of compound **5b**



HRMS spectra of compound **5c**



HRMS spectra of compound **5g**



HRMS spectra of compound **5h**

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