Aromatic layered foldamer based on (cis, cis)-squaramide: Chiral induction and absolute structure

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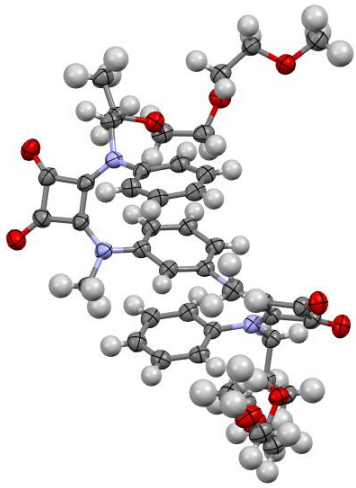
Contents

Table S1 Crystal data of compound **9**

Recrystallization solvent	benzene/EtOH
Formula	$C_{44}H_{54}N_4O_{10}$
Formula wt.	798.91
Crystal system	monoclinic
Space group	$P2_1$
a (Å)	16.050 (3)
b (Å)	8.8300 (18)
c (Å)	16.355 (3)
β (Å)	116.59 (3)
Z value	2
R	0.0585
Rw	0.1811
CCDC	2423502



ORTEP drawing of **9** (50% probability)

Table S2 Excited states and oscillator strengths for compound **9** without solvent effect

No.	Energy (eV)	Wavelength (nm)	*f*	$R/10^{-40}$	Major contribs
1	3.93	315.3	0.0051	37.67	H-3->L+2 (63%)
2	3.97	312.1	0.1755	126.37	H-2->L+1 (10%), H-2->L+3 (39%), H-1->LUMO (10%)
3	4.00	310.1	0.2618	-302.32	H-2->L+3 (19%), H-1->LUMO (33%), HOMO->LUMO (25%)
4	4.07	304.3	0.0562	42.21	H-2->L+1 (11%), H-1->L+1 (10%), HOMO->L+1 (39%)
5	4.11	301.8	0.0200	76.86	H-3->LUMO (51%)
6	4.24	292.5	0.0709	-13.13	H-2->L+1 (41%), H-2->L+6 (11%), HOMO->L+1 (24%)
7	4.51	274.8	0.3687	39.76	H-1->L+2 (58%), HOMO->L+2 (26%)
8	4.55	272.7	0.0468	-95.96	H-1->LUMO (20%), H-1->L+1 (13%), HOMO->LUMO (24%)
9	4.64	267.4	0.3070	60.44	H-1->L+3 (16%), HOMO->L+3 (68%)
10	4.91	252.5	0.0053	13.41	H-1->L+1 (30%), HOMO->LUMO (10%), HOMO->L+4 (13%)
11	4.99	248.3	0.0050	-41.33	H-1->L+4 (19%), H-1->L+5 (20%), HOMO->L+5 (31%)
12	5.00	247.8	0.0046	-9.31	H-1->L+5 (14%), HOMO->L+4 (43%)
13	5.32	233.1	0.0524	18.41	HOMO->L+6 (41%), HOMO->L+7 (17%)
14	5.46	227.0	0.0287	-46.44	H-1->L+2 (19%), HOMO->L+2 (30%), HOMO->L+8 (11%)
15	5.48	226.1	0.0400	73.05	H-4->LUMO (17%), HOMO->L+7 (15%), HOMO->L+9 (16%)
16	5.55	223.4	0.0369	70.32	H-1->L+6 (15%), H-1->L+7 (13%), HOMO->L+7 (14%)
17	5.61	221.2	0.0798	95.49	H-1->L+7 (14%), HOMO->L+8 (16%)
18	5.66	219.2	0.0217	-58.50	H-1->L+3 (25%)
19	5.69	217.8	0.0604	-20.22	H-4->LUMO (31%)
20	5.76	215.1	0.0480	-32.84	H-10->L+4 (3%), H-9->L+1 (8%), H-9->L+3 (3%), H-9->L+7 (2%), H-7->L+1 (2%), H-5->L+4 (7%), H-5->L+5 (2%), H-4->LUMO (6%), H-1->L+3 (6%), H-1->L+8 (4%), H-1->L+9 (2%), HOMO->L+4 (7%), HOMO->L+7 (6%), HOMO->L+9 (2%)

Figure S1 Orbital energy and some frontier MOs for compound **9** without solvent effect

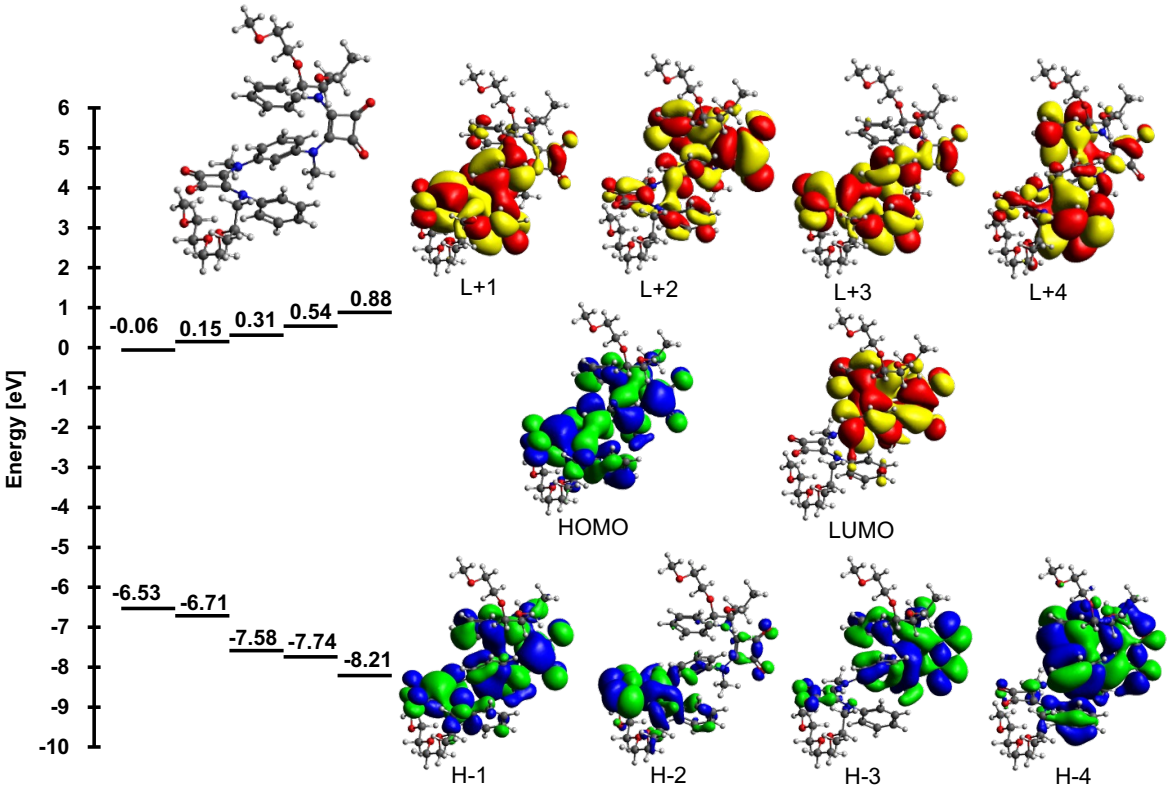


Table S3 Excited states and oscillator strengths for compound **9** with solvent (CH_3CN) effect

No.	Energy (eV)	Wave-length (nm)	*f*	$R/10^{-40}$	Major contribs
1	3.94	314.7	0.4686	404.67	H-1->LUMO (29%), HOMO->LUMO (10%), HOMO->L+1 (30%)
2	4.02	308.8	0.1219	-202.29	H-1->L+1 (15%), HOMO->LUMO (30%)
3	4.07	304.7	0.0988	-130.86	H-3->L+2 (10%), H-2->L+3 (22%)
4	4.07	304.4	0.0329	173.08	H-3->L+2 (19%), H-2->L+2 (14%), H-1->L+1 (10%), HOMO->LUMO (14%)
5	4.31	288.0	0.0431	62.84	H-3->LUMO (19%), H-3->L+1 (16%), H-2->L+1 (15%)
6	4.33	286.4	0.0549	-130.71	H-3->L+1 (15%), H-2->LUMO (15%), H-2->L+1 (10%)
7	4.48	276.9	0.4569	-384.05	H-1->L+2 (38%), HOMO->L+2 (33%), HOMO->L+3 (12%)
8	4.50	275.4	0.2844	354.86	H-1->L+3 (27%), HOMO->L+2 (13%), HOMO->L+3 (28%)
9	4.57	271.4	0.0186	15.40	H-1->LUMO (29%), HOMO->L+1 (21%)
10	4.94	250.8	0.0061	27.11	H-1->L+1 (55%), HOMO->LUMO (22%)
11	5.07	244.7	0.0029	22.69	H-1->L+4 (35%), HOMO->L+4 (29%)
12	5.12	242.1	0.0059	-26.52	H-1->L+5 (23%), HOMO->L+5 (37%)
13	5.31	233.7	0.0335	45.85	H-1->L+2 (16%), HOMO->L+1 (13%), HOMO->L+2 (11%), HOMO->L+4 (10%), HOMO->L+6 (21%)
14	5.45	227.5	0.0637	70.96	H-1->L+6 (14%), H-1->L+7 (13%), HOMO->L+7 (14%)
15	5.48	226.5	0.0279	-30.59	H-1->L+2 (14%), H-1->L+6 (11%), HOMO->L+2 (12%), HOMO->L+6 (14%), HOMO->L+8 (13%)
16	5.49	225.8	0.0133	-7.75	H-1->L+3 (18%), H-1->L+8 (10%), HOMO->L+7 (12%), HOMO->L+9 (10%)
17	5.54	223.7	0.0157	-57.41	H-1->L+3 (12%), H-1->L+7 (15%), HOMO->L+2 (10%), HOMO->L+7 (10%), HOMO->L+8 (19%)
18	5.58	222.4	0.0634	13.13	H-1->L+2 (12%), H-1->L+3 (10%), HOMO->L+3 (17%)
19	5.68	218.2	0.2088	-150.69	H-5->LUMO (26%), H-4->LUMO (10%), H-4->L+1 (12%)
20	5.73	216.4	0.0555	77.56	H-5->L+1 (21%), H-4->LUMO (19%)

Figure S2 Orbital energy and some frontier MOs for compound **9** with solvent (CH_3CN) effect

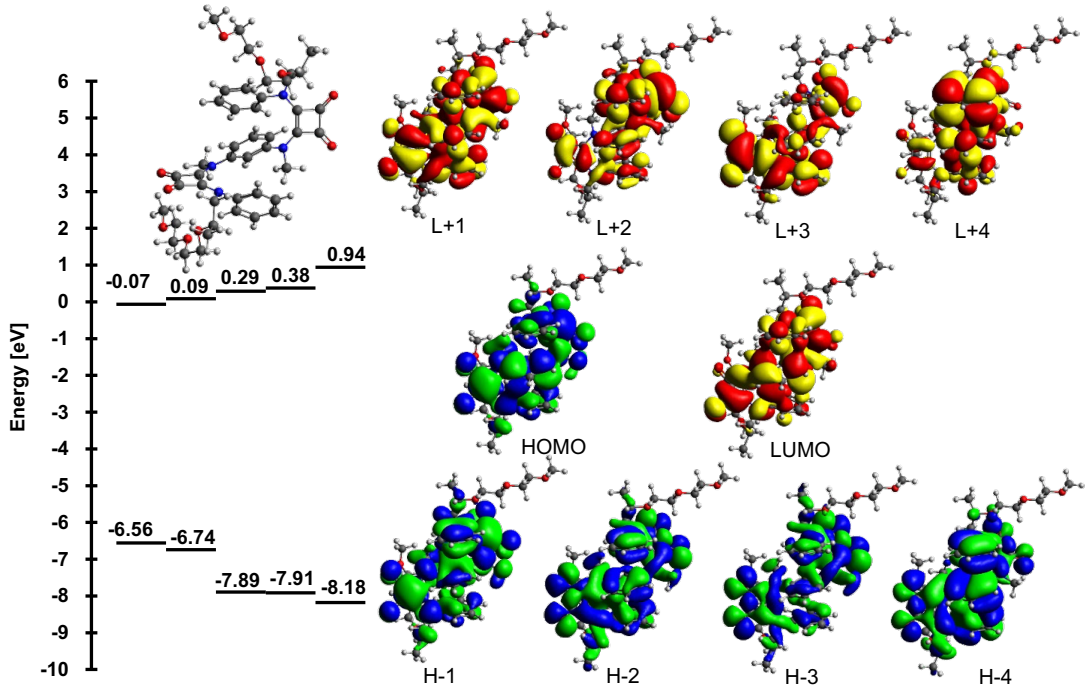
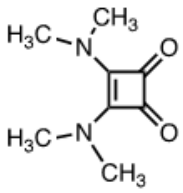
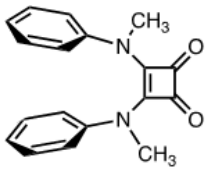


Table S4 Excited states and oscillator strengths for *N,N,N',N'*-tetramethylsquaramide



No.	Energy (eV)	Wavelength (nm)	*f*	$R/10^{-40}$	Major contribs
1	4.07	304.4	0.0003	-2.84	H-1->SOMO (95%)
2	4.39	282.4	0.0014	24.02	H-1->S+1 (92%)N2
3	4.73	262.0	0.2310	-59.62	HOMO->SOMO (97%)
4	4.85	255.4	0.4065	58.11	HOMO->SOMO+1 (98%)N1
5	6.12	202.5	0.0034	5.04	H-3->SOMO (88%)
6	6.64	186.9	0.0186	13.60	HOMO->L (88%)
7	6.68	185.8	0.0033	0.35	H-3->SOMO+1 (89%)
8	7.29	170.2	0.1547	31.05	H-2->SOMO (95%)
9	7.31	169.6	0.0858	47.06	H-2->SOMO+1 (55%), HOMO->L+1 (37%)
10	7.39	167.9	0.1246	-97.13	H-2->SOMO+1 (39%), HOMO->L+1 (56%)
11	7.76	159.8	0.0051	1.81	HOMO->L+2 (87%)
12	8.05	154.0	0.0000	0.16	H-1->L (15%), HOMO->L+3 (72%)
13	8.19	151.4	0.0182	-3.00	H-4->SOMO+1 (16%), HOMO->L+4 (61%)
14	8.21	151.0	0.0293	8.88	H-1->L (60%), HOMO->L+3 (16%)
15	8.35	148.4	0.0056	26.96	H-4->SOMO+1 (66%), HOMO->L+4 (19%)
16	8.44	146.9	0.0003	0.43	H-5->SOMO+1 (19%), H-4->SOMO (73%)
17	8.55	144.9	0.0145	-12.73	HOMO->L+5 (77%)
18	8.72	142.2	0.0046	0.76	HOMO->L+6 (69%)
19	8.88	139.7	0.0744	-9.82	H-5->SOMO (73%)
20	9.04	137.2	0.0027	-5.46	H-1->L (86%)

Table S5 Excited states and oscillator strengths for *N,N'*-dimethyl-*N,N'*-diphenylsquaramide (**6**)



No.	Energy (eV)	Wavelength (nm)	*f*	$R/10^{-40}$	Major contribs
1	3.93	315.6	0.0003	-12.24	H-2->S+1 (15%), H-1->S+1 (72%)
2	4.06	305.4	0.2784	-147.83	HOMO->SOMO (96%)
3	4.10	302.7	0.0070	56.73	H-2->SOMO (11%), H-1->SOMO (71%)
4	4.52	274.4	0.3790	76.24	HOMO->S+1 (95%)
5	4.95	250.5	0.0050	-33.59	HOMO->L (76%)
6	4.97	249.7	0.0056	-23.91	HOMO->L+1 (73%)
7	5.54	223.8	0.2332	151.64	H-2->SOMO (57%), H-1->SOMO (14%)
8	5.70	217.5	0.0033	-22.85	H-2->SOMO (11%), HOMO->L+2 (45%)
9	5.75	215.5	0.0217	-28.20	H-2->S+1 (18%), HOMO->L+1 (11%), HOMO->L+3 (40%)
10	5.96	207.9	0.0235	-36.67	H-4->SOMO (18%), H-3->S+1 (10%), H-2->S+1 (20%), H-2->L (11%), HOMO->L+1 (13%)
11	5.98	207.4	0.0167	-29.60	H-3->SOMO (33%), HOMO->L (11%), HOMO->L+2 (25%)
12	6.04	205.4	0.0641	6.45	H-2->S+1 (30%), H-1->S+1 (10%), HOMO->L+3 (48%)
13	6.06	204.7	0.0248	31.00	H-6->S+1 (62%), HOMO->L+2 (10%)
14	6.35	195.4	0.0352	3.98	H-5->SOMO (32%), H-4->SOMO (33%)
15	6.40	193.9	0.0346	124.63	H-3->SOMO (30%), H-2->L+1 (23%), H-1->L+1 (28%)
16	6.51	190.5	0.0055	-8.80	H-6->SOMO (74%)
17	6.63	187.1	0.0479	80.99	H-3->L (28%), H-1->L (29%)
18	6.64	186.7	0.1043	-134.83	H-5->SOMO (26%), H-4->SOMO (24%), H-1->L (24%)
19	6.67	186.0	0.2064	-107.02	H-5->S+1 (12%), H-4->S+1 (36%), H-3->L+1 (15%)
20	6.80	182.5	0.0257	26.30	H-4->S+1 (10%), H-3->SOMO (13%), H-1->L+1 (25%)

Figure S3 Orbital energy and some frontier MOs for *N,N'*-dimethyl-*N,N'*-diphenylsquaramide (**6**), optimized from the structure of compound **8**

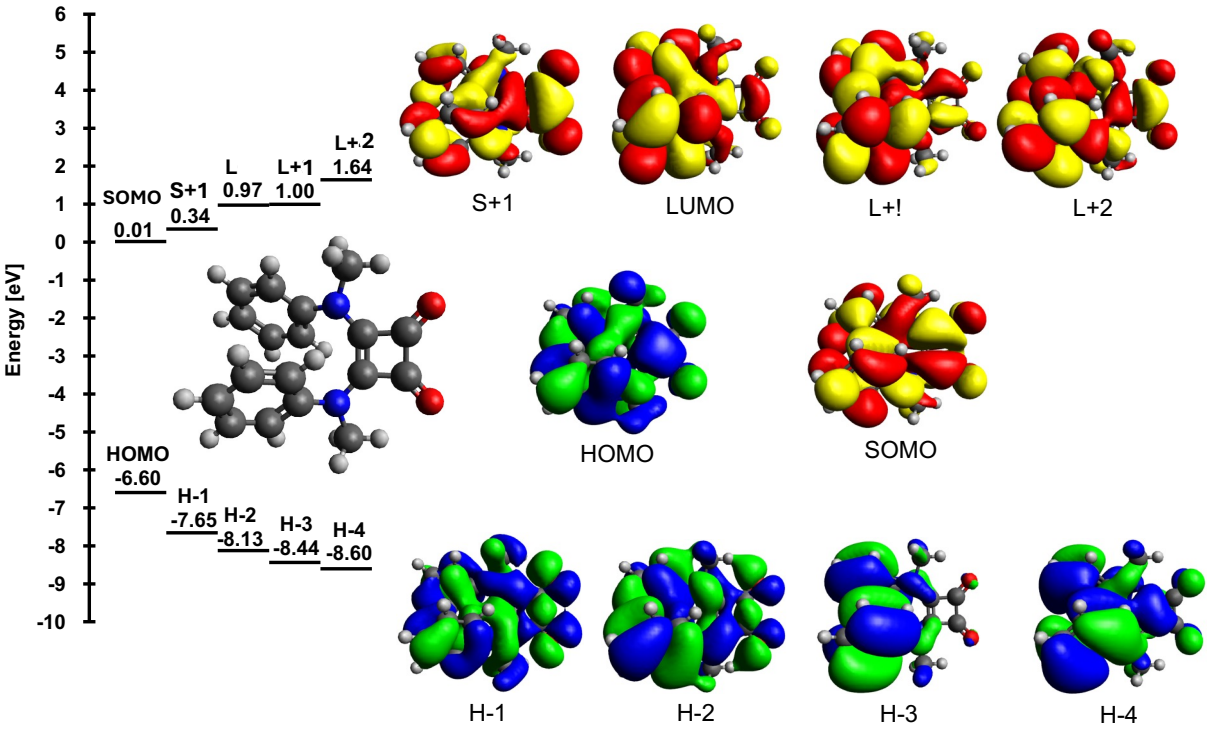
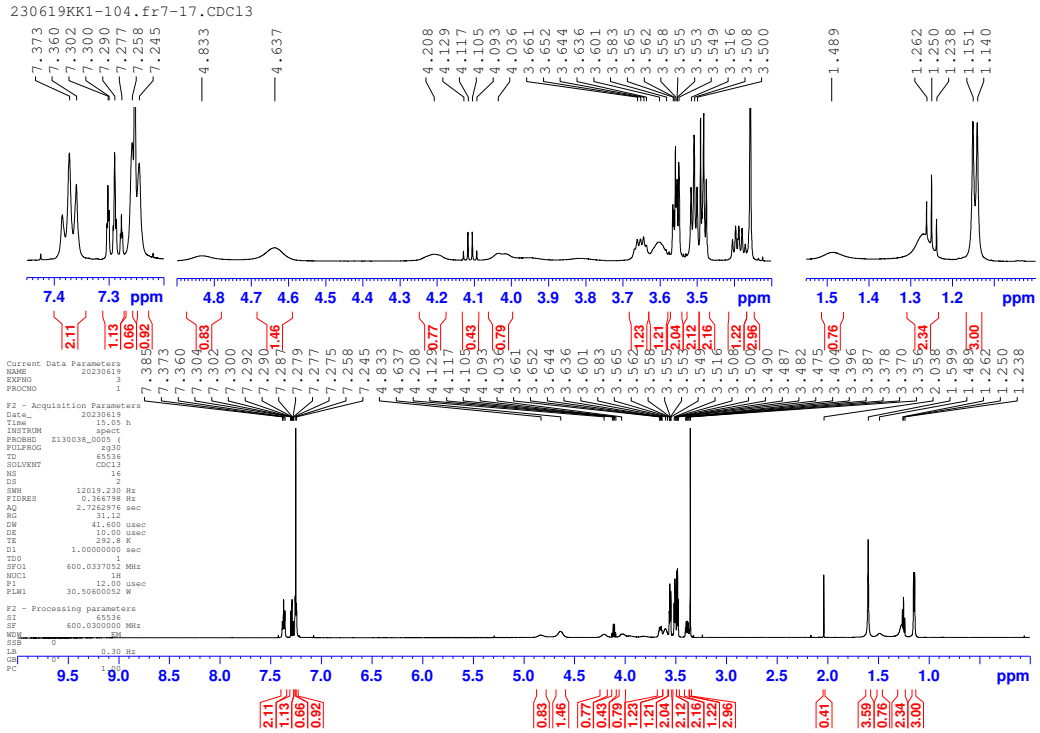
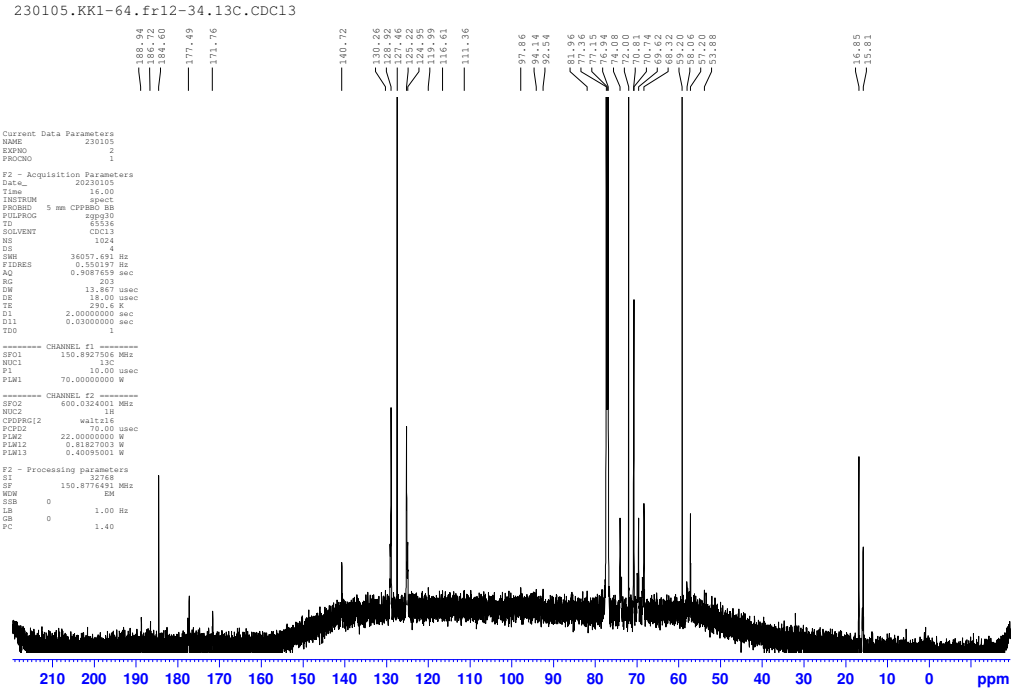


Figure S1 NMR and HRMS charts of compounds **11**, **12**, and **9**

(a) ^{1}H NMR of **11** (600 MHz, $CDCl_3$)



(b) ^{13}C NMR of **11** (150 MHz, $CDCl_3$)



(c) HRMS of **11**

Bruker ESI-QTOF: **20221223.KK1-64.fr12-34**

Analysis Info

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Sample Name	**20221223.KK1-64.fr12-34**	Instrument	compact 8255754.20279
Comment			

Acquisition Parameter

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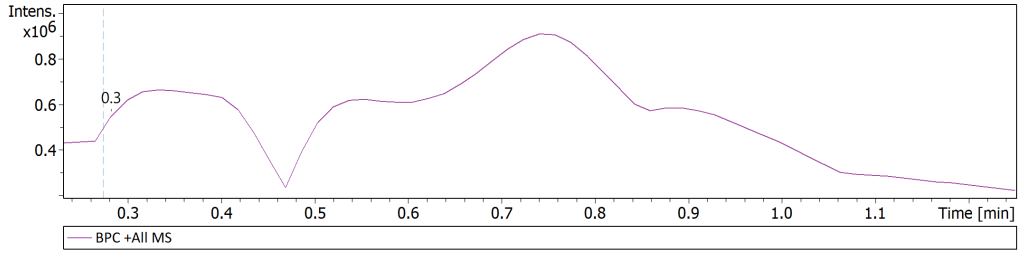
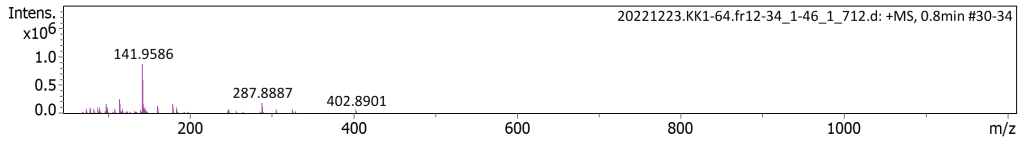
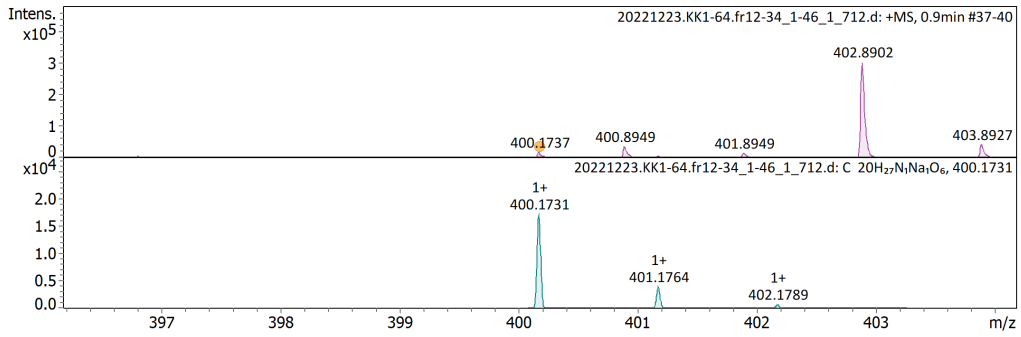
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1200 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C







+MS, 0.9min #37-40

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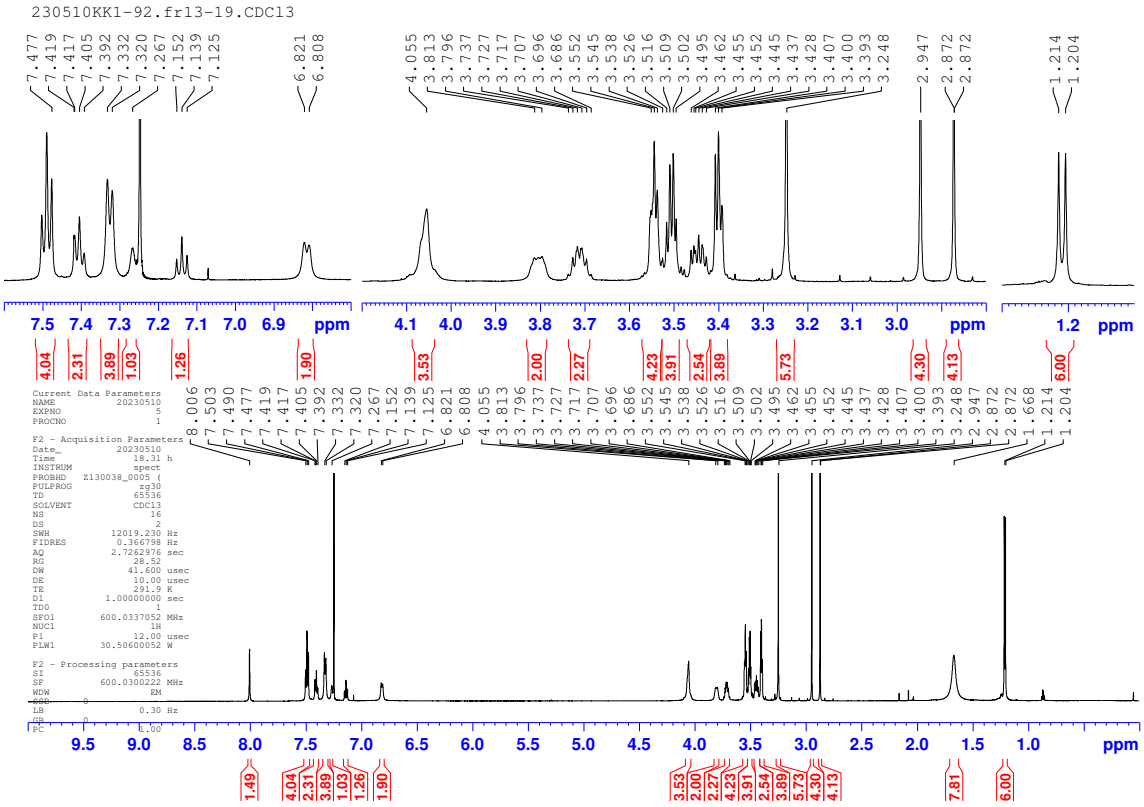
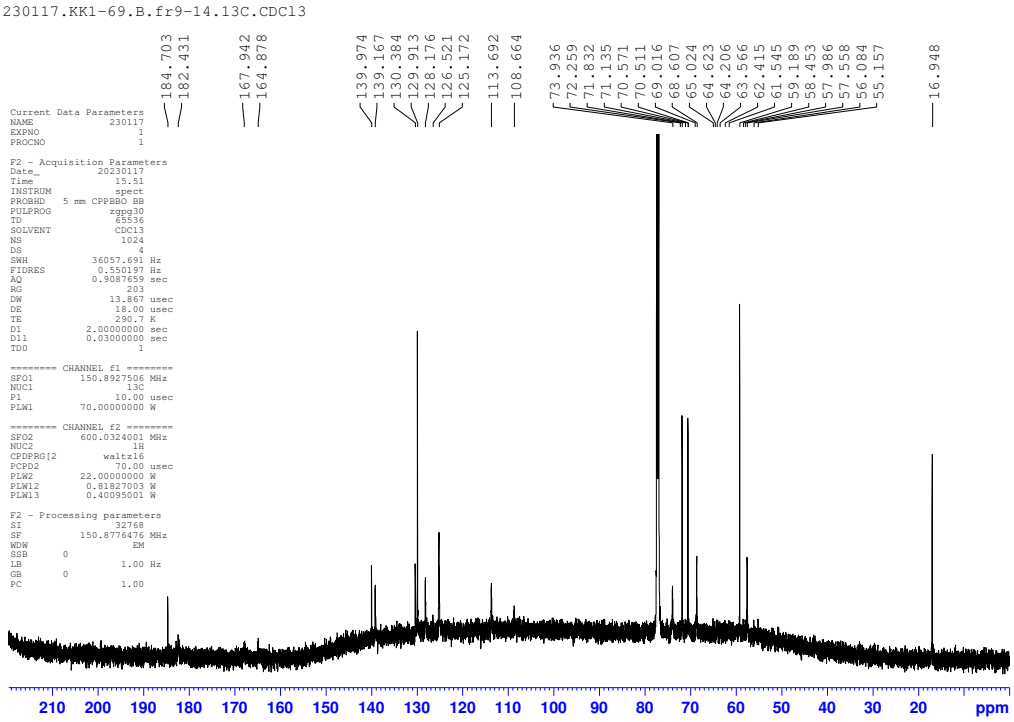
(d) ^{1}H NMR of **12** (600 MHz, $CDCl_3$)



(e) ^{13}C NMR of **12** (150 MHz, $CDCl_3$)



(f) HRMS of **12**

Bruker ESI-QTOF: **20250207.KK1-92.pos2**

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Comment			

Acquisition Parameter

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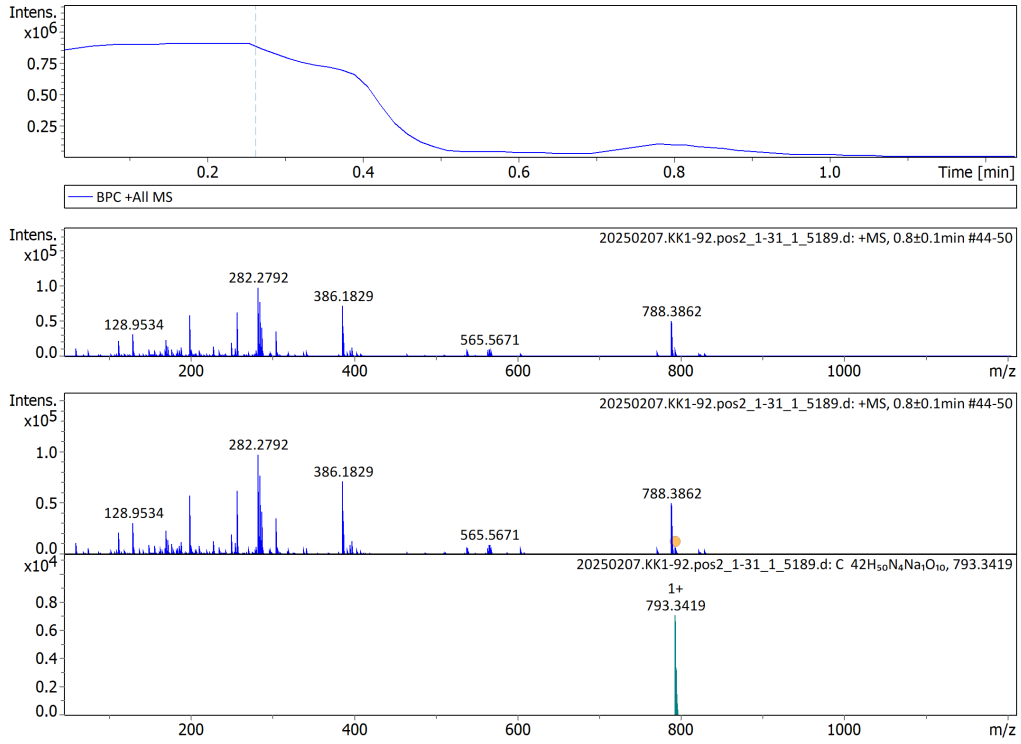
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1200 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



+MS, 0.8±0.1min #44-50

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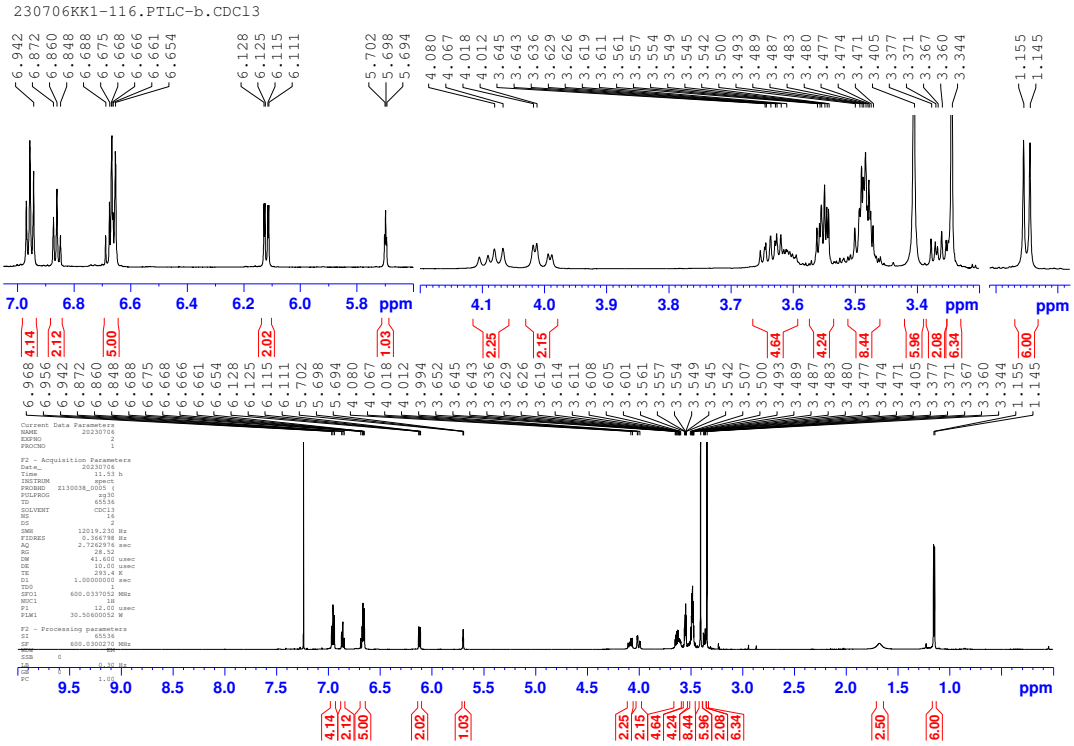
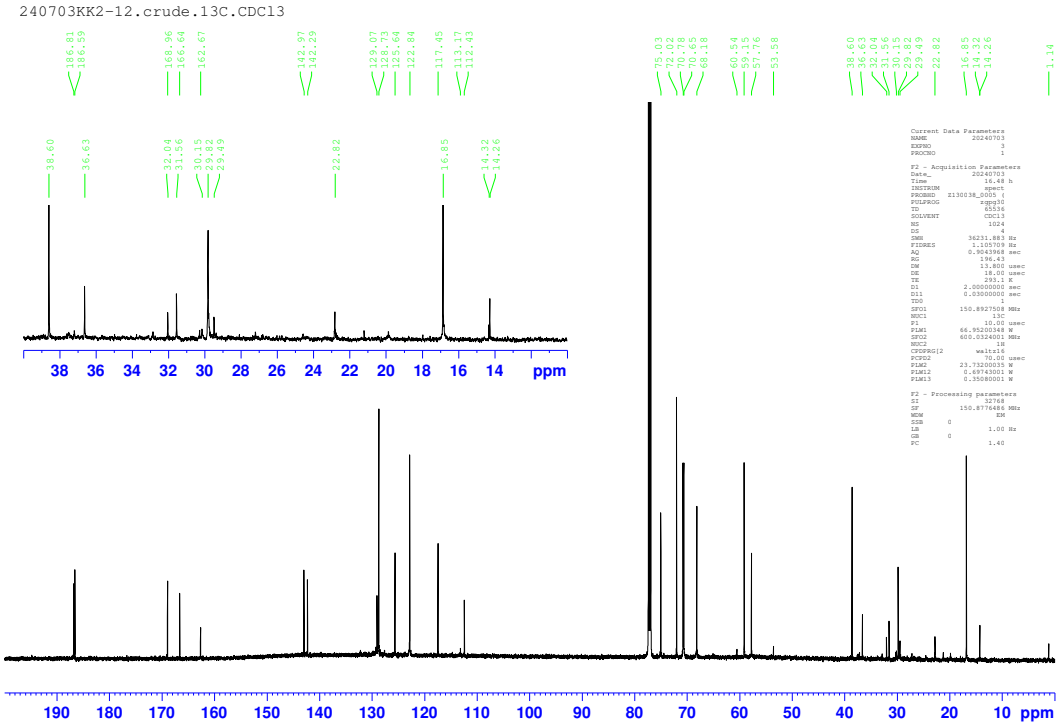
M+Na	793.342222	1	C42H50N4NaO10	793.341915	-0.4	-3.1	20.0	ok	even	15.7	18.1	n.a.	n.a.	n.a.	n.a.

+MS, 0.8±0.1min #44-50

(g) ^{1}H NMR of **9** (600 MHz, $CDCl_3$)



(h) ^{13}C NMR of **9** (150 MHz, $CDCl_3$)



(i) HRMS of **9**

Bruker ESI-QTOF: **20250207.KK1-116.pos**

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Comment			

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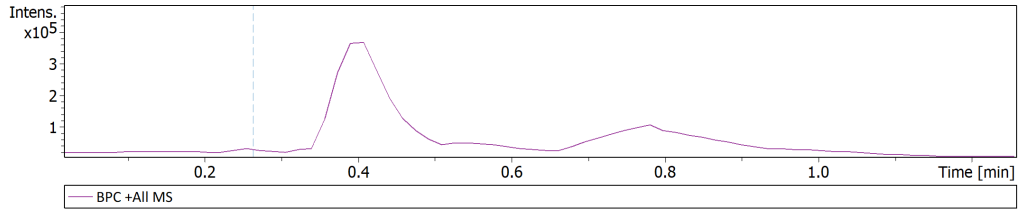
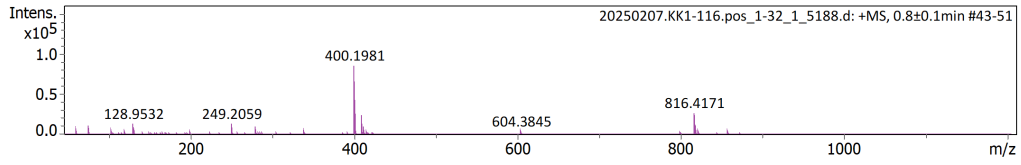
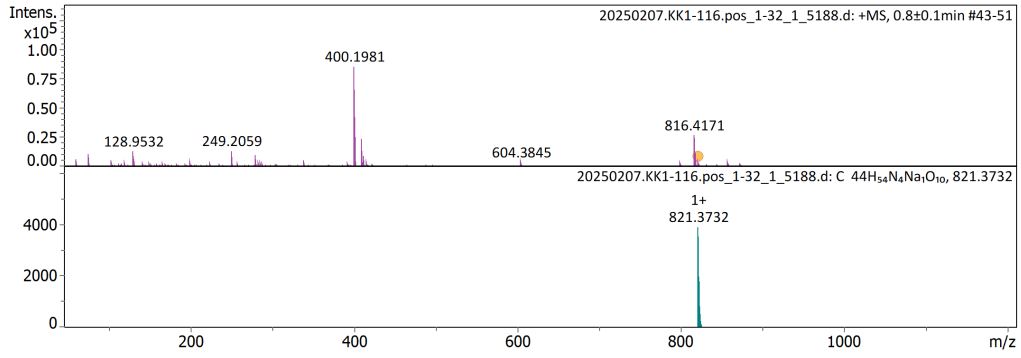
		Set Corona	0 nA	Set APCI Heater	0 °C







+MS, 0.8±0.1min #43-51

Adduct	Meas. m/z	#	Ion Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
M+Na	821.372880	1	C44H54N4NaO10	821.373215	0.4	-1.6	20.0	ok	even	7.0	8.4	n.a.	n.a.	n.a.	n.a.

+MS, 0.8±0.1min #43-51