Supporting Information

Shuli Gao, Xueyue Zhang, Pengze Yan, Jinling Miao, Guangning Liu, Xuchuan Jiang,* Yong Nie,* and Meng Li*

Synthesis, structures and optical properties of 3,3'-disubstituted biphenyl compounds

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***Corresponding authors: Xuchuan Jiang, Yong Nie,** Institute for Smart Materials and Engineering, University of Jinan, Jinan, 250022, P. R. China; E-mail: ism_jiangxc@ujn.edu.cn (XJ), chm_niey@ujn.edu.cn (YN), **Meng Li,** Beijing National Laboratory for Molecular Science, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China, E-mail: limeng@iccas.ac.cn

Shuli Gao, Xueyue Zhang, Pengze Yan: Institute for Smart Materials and Engineering, University of Jinan, Jinan, 250022, P. R. China

Jinling Miao, Guangning Liu: School of Chemistry and Chemical Engineering, Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials, University of Jinan, Jinan, 250022, P. R. China

1 NMR, IR and MS spectra of compounds 1–3 and 6

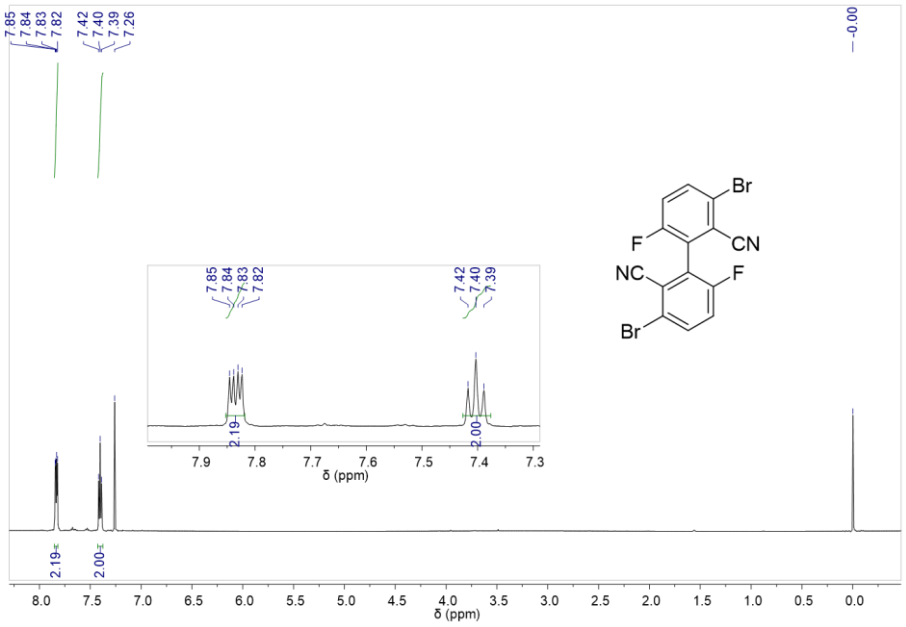

Figure S1: ^{1}H NMR spectrum of compound **1** (in $CDCl_3$).

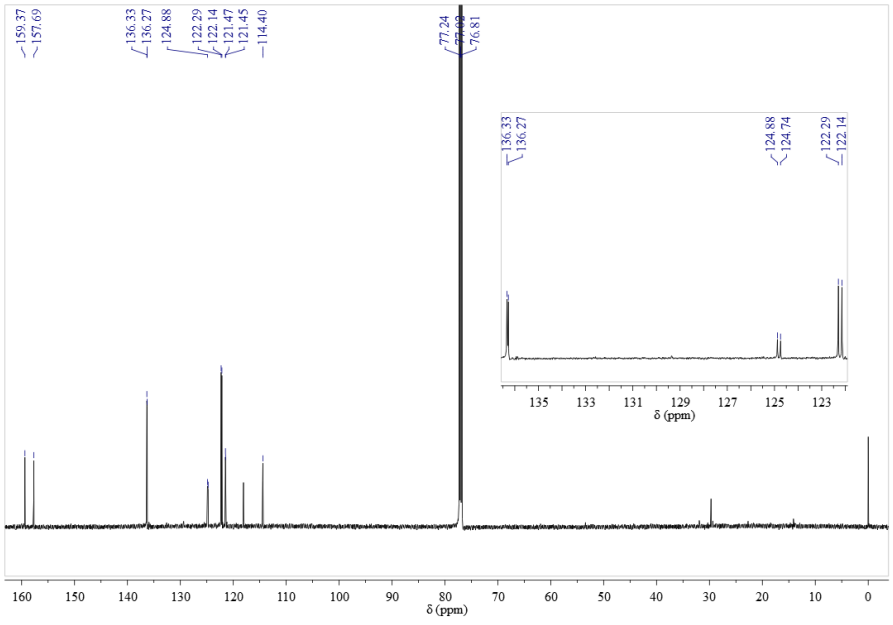

Figure S2: ^{13}C NMR spectrum of compound **1** (in $CDCl_3$).

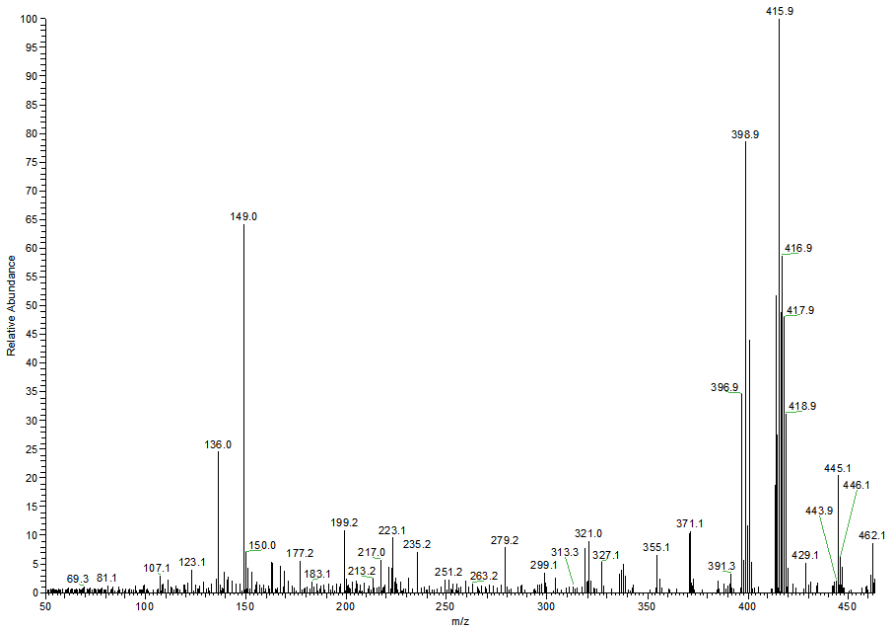

Figure S3: DART mass spectrum of compound **1**.

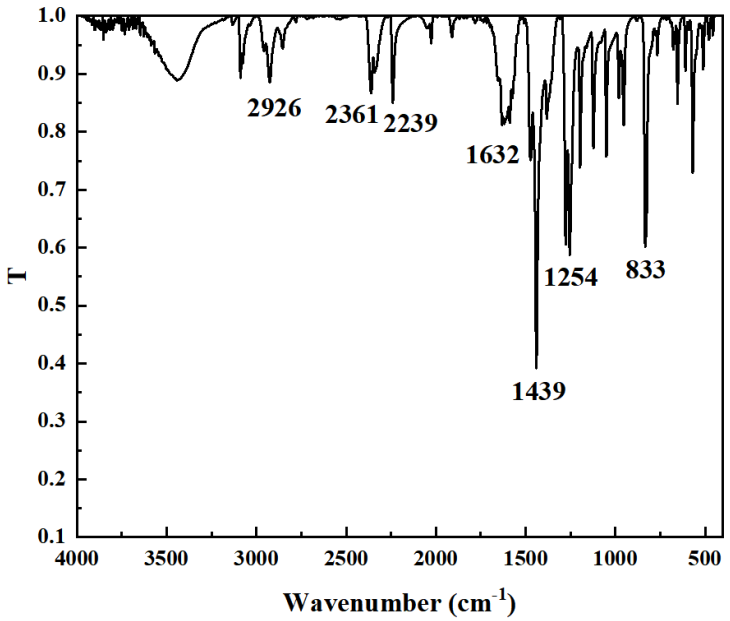

Figure S4: Infrared spectrum of compound **1** (KBr pellet).

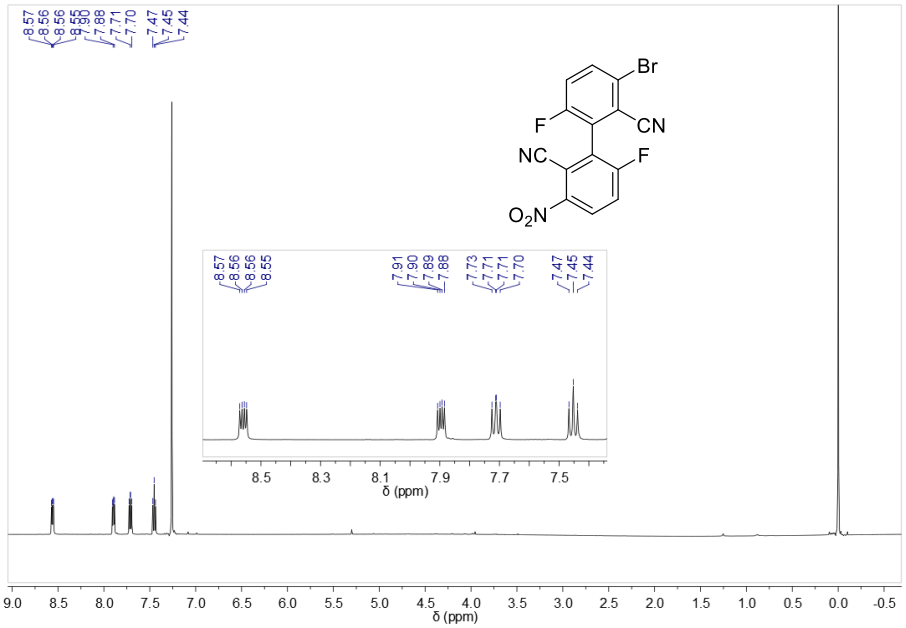

Figure S5: ^{1}H NMR spectrum of compound **2** (in $CDCl_3$).

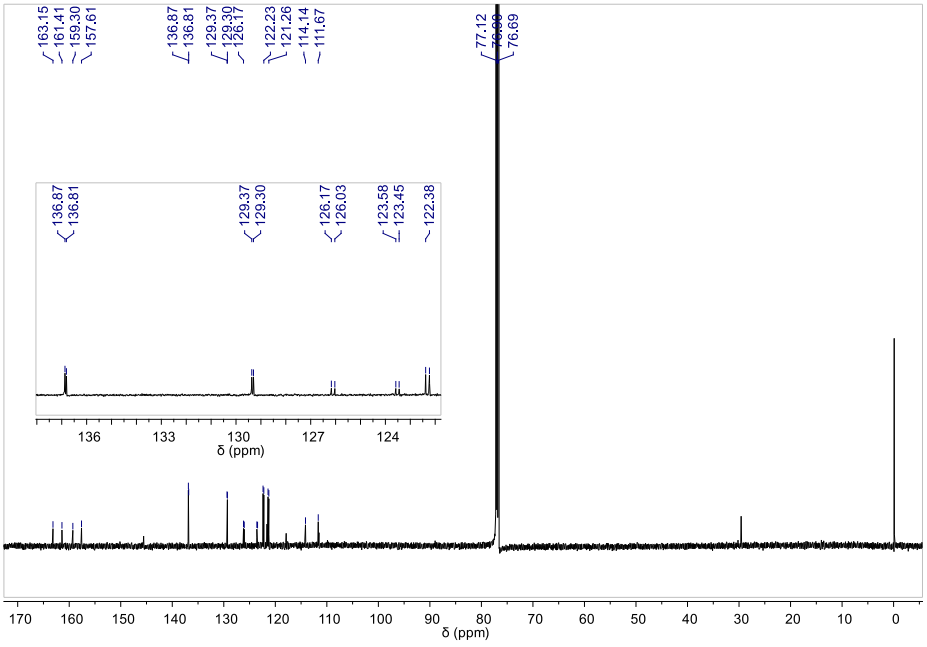

Figure S6: ^{13}C NMR spectrum of compound **2** (in $CDCl_3$).

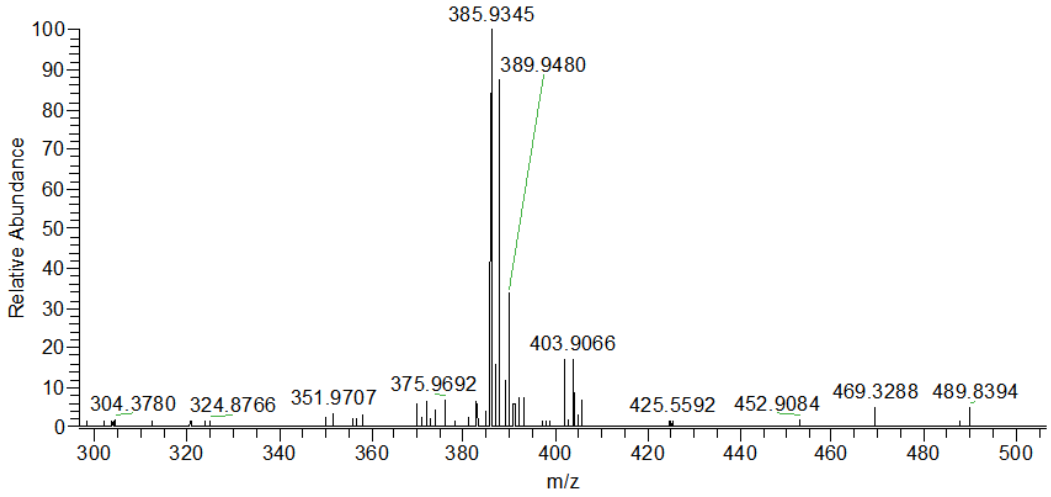

Figure S7: HR-ESI mass spectrum of compound **2**.

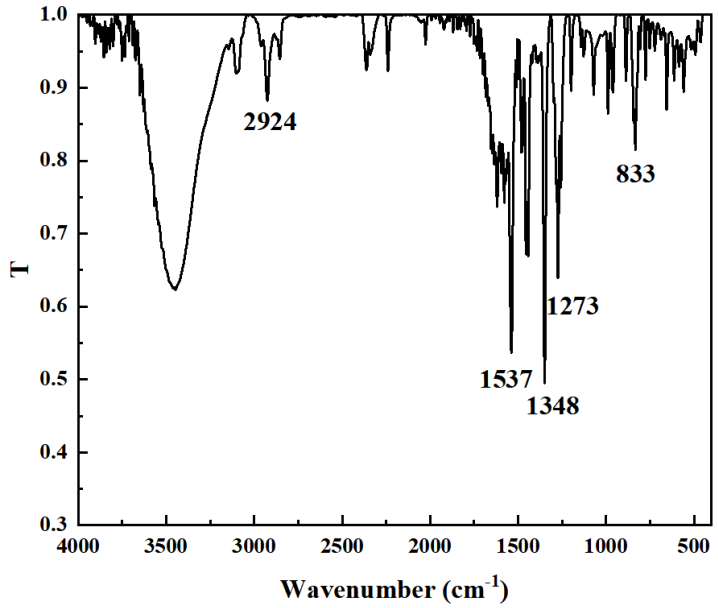

Figure S8: Infrared spectrum of compound **2** (KBr pellet).

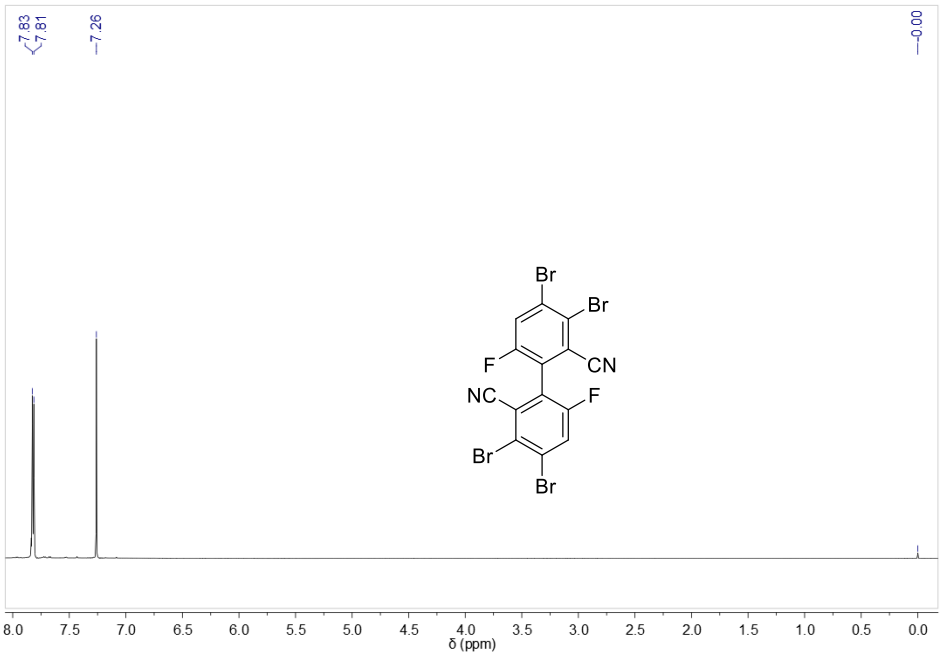

Figure S9: ^{1}H NMR spectrum of compound **3** (in $CDCl_3$).

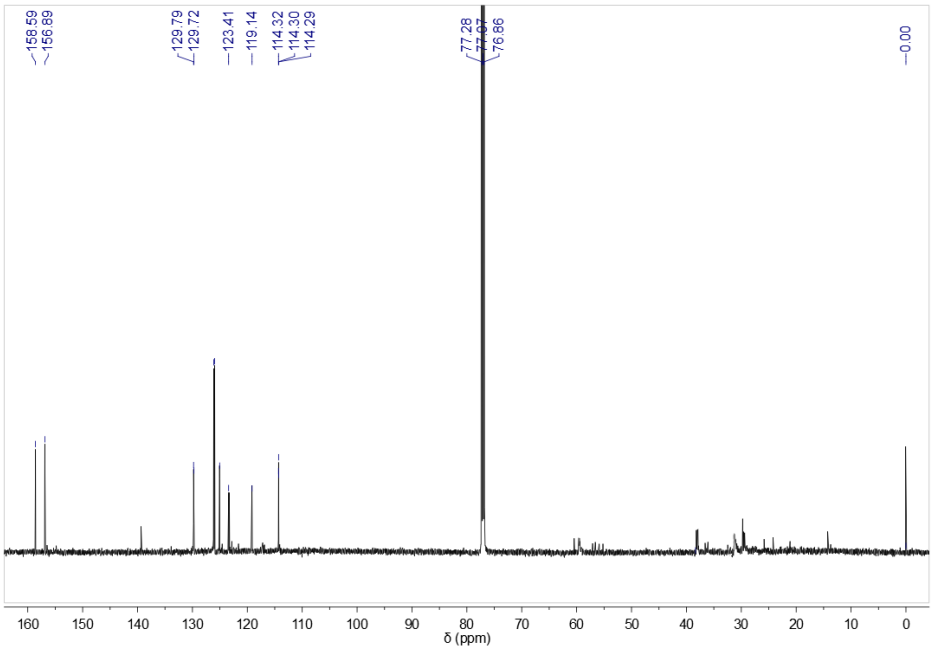

Figure S10: ^{13}C NMR spectrum of compound **3** (in $CDCl_3$).

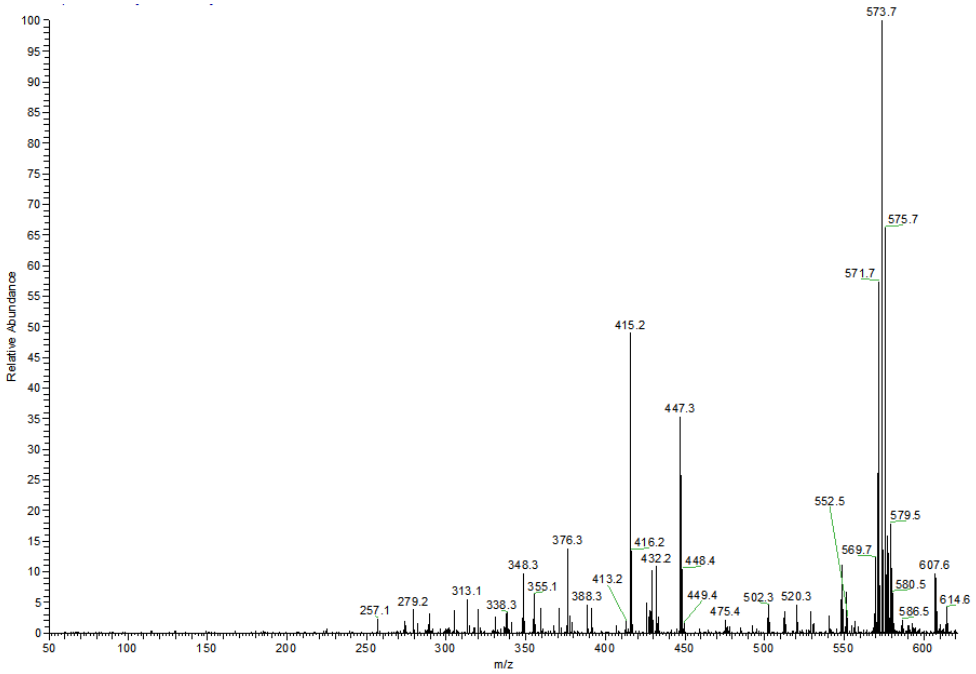

Figure S11: DART mass spectrum of compound **3**.

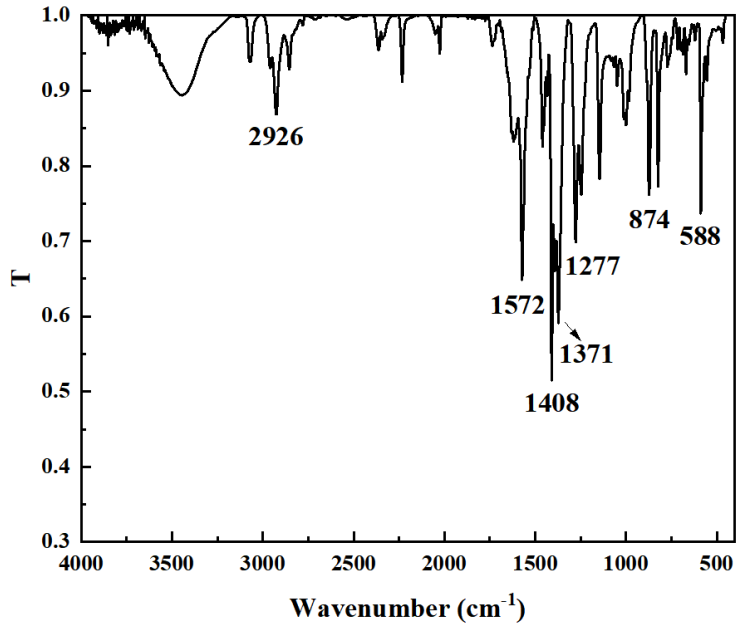

Figure S12: Infrared spectrum of compound **3** (KBr pellet).

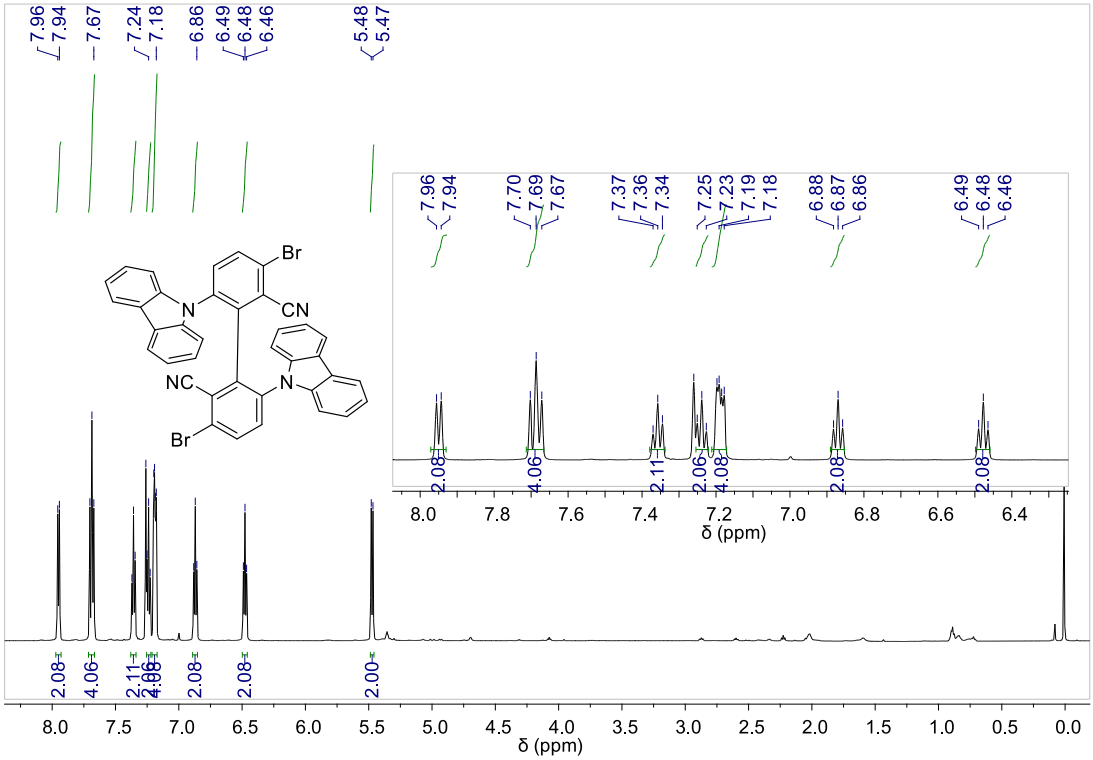

Figure S13: ^{1}H NMR spectrum of compound **6** (in $CDCl_3$).

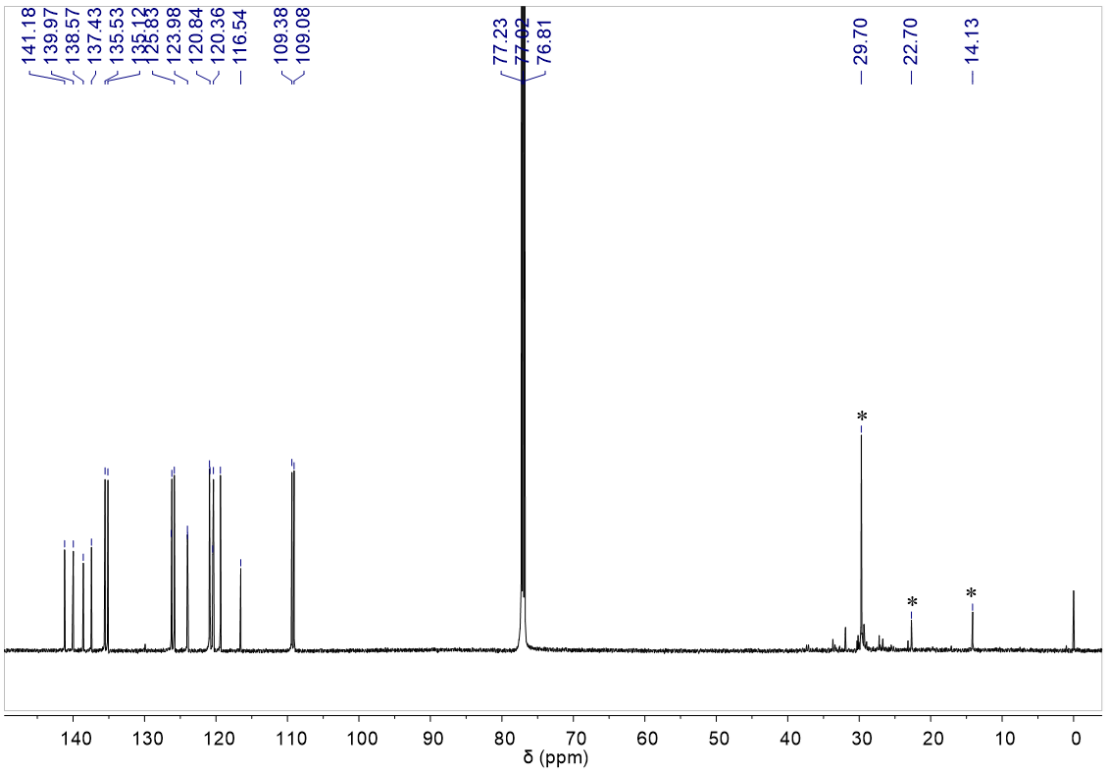

Figure S14: ^{13}C NMR spectrum of compound **6** (in $CDCl_3$, ∗Hexane).

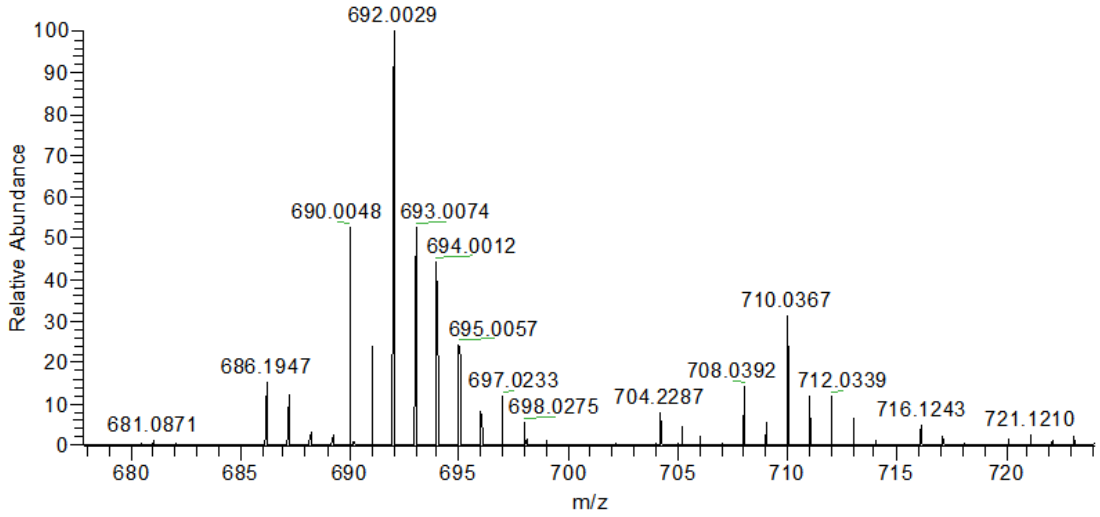

Figure S15: AP-MALDI mass spectrum of compound **6**.

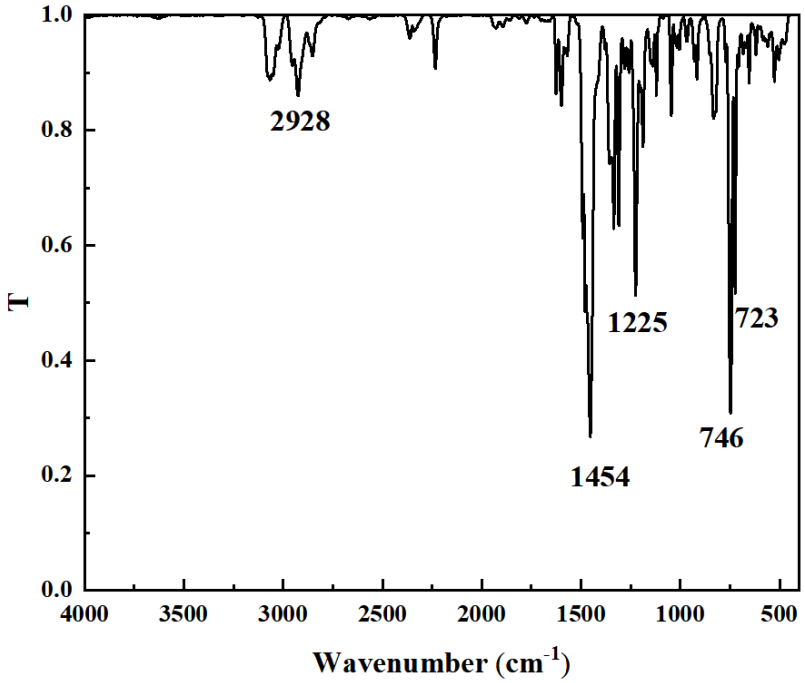

Figure S16: Infrared spectrum of compound **6** (KBr pellet).

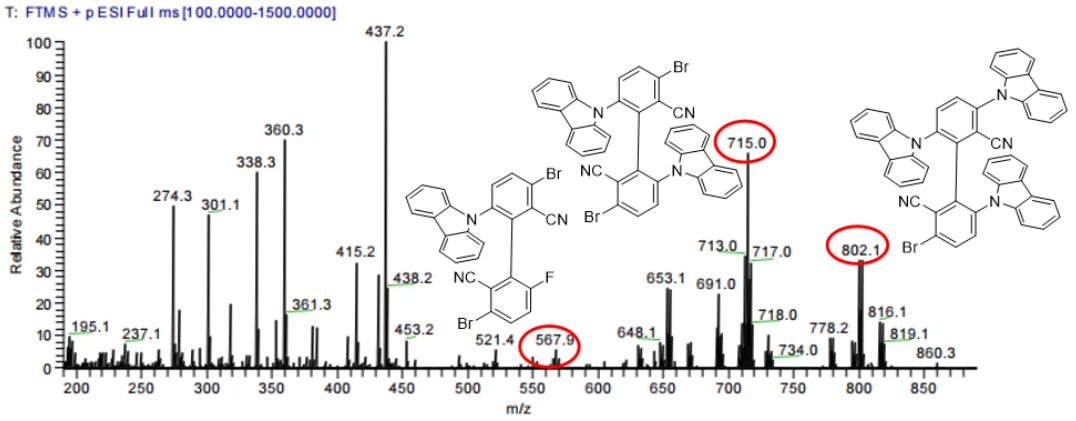

Figure S17: Low resolution mass spectrometry of mixtures **6**–**8** (ESI, all $[M+Na]^+$).

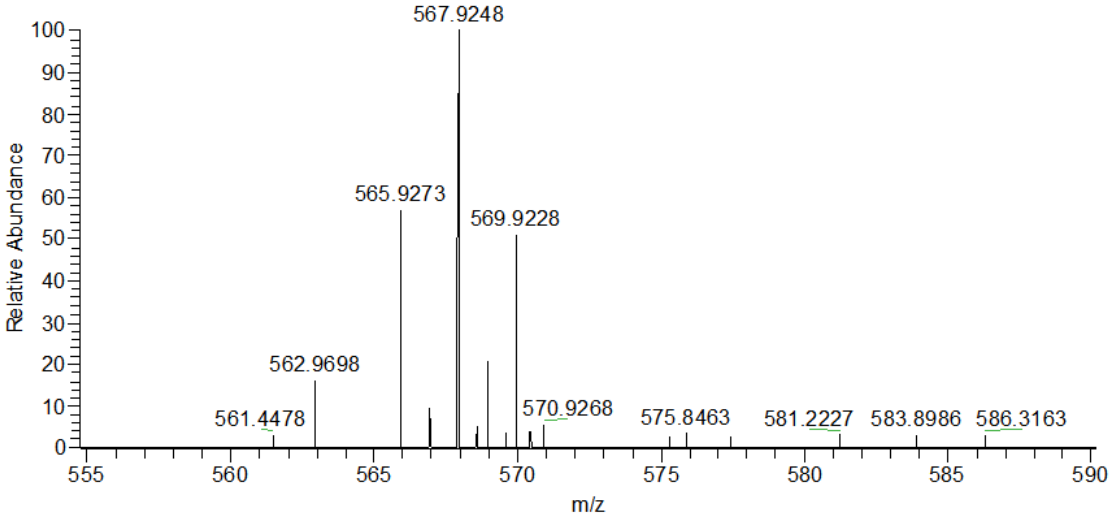

Figure S18: HR-ESI mass spectrum of compound **7**.

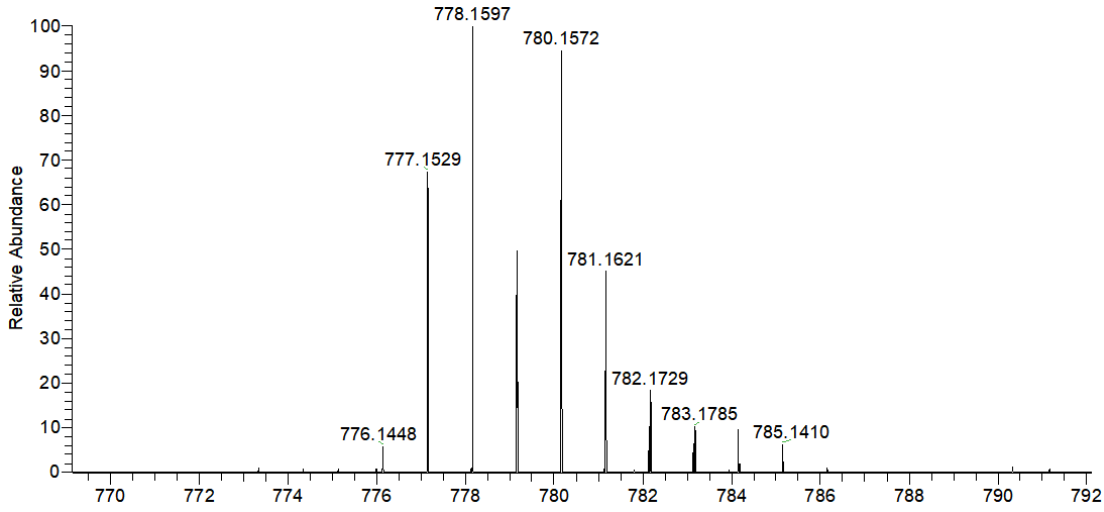

Figure S19: HR-AP-MALDI mass spectrum of compound **8**.

2 GC-MS results of compounds 4 and 5

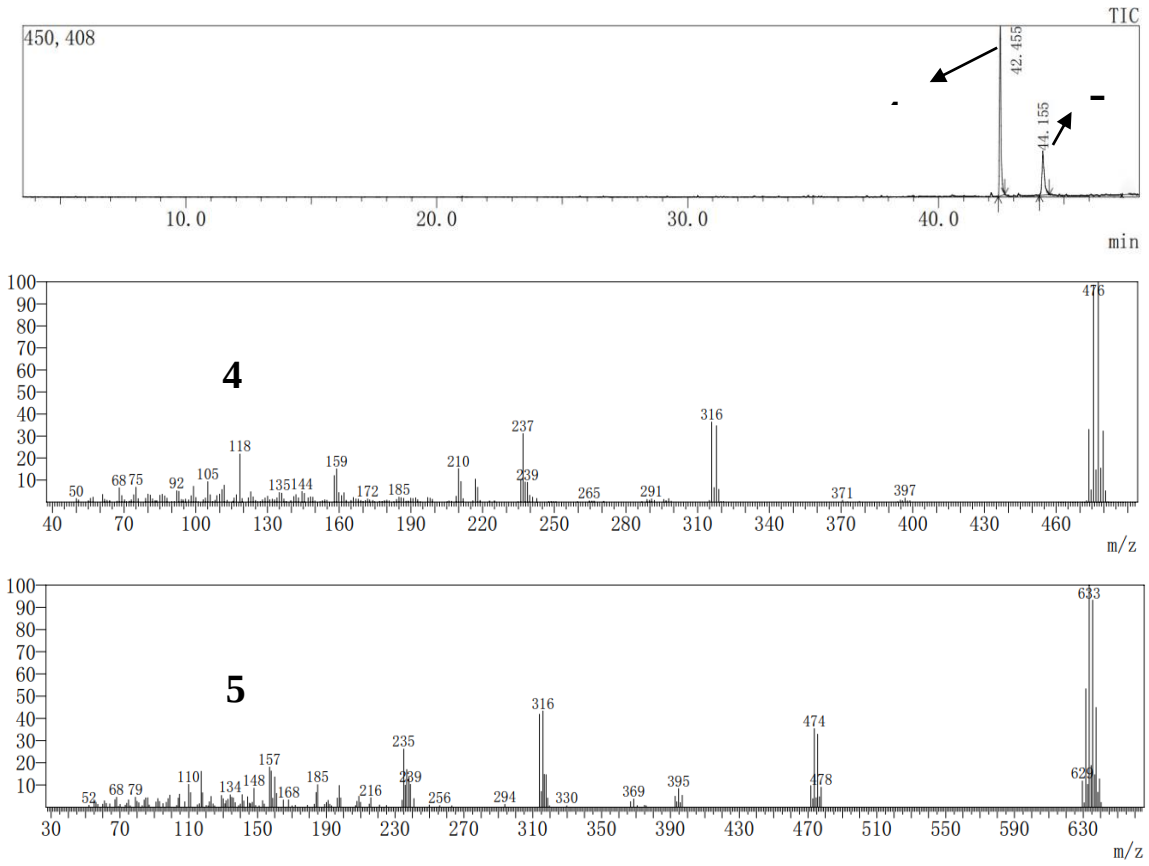

Figure 20: GC-MS results of compounds **4** and **5**.

3 Molecular packing diagrams and crystal data of compounds 1–3 and 6

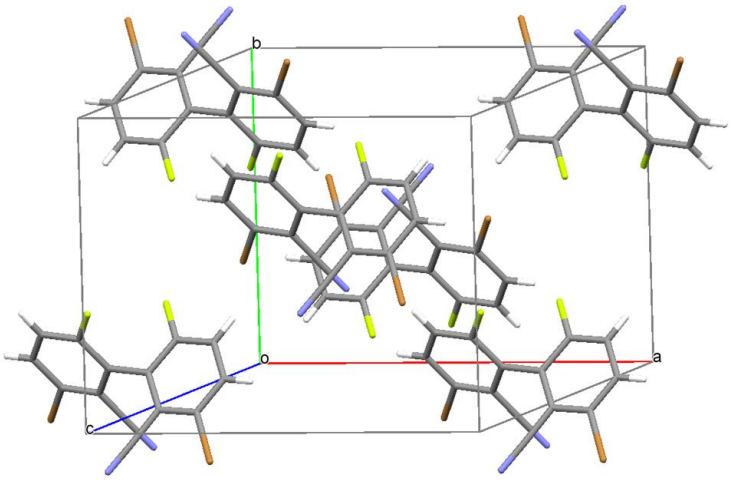

Figure 21: Unit cell of compound **1**.

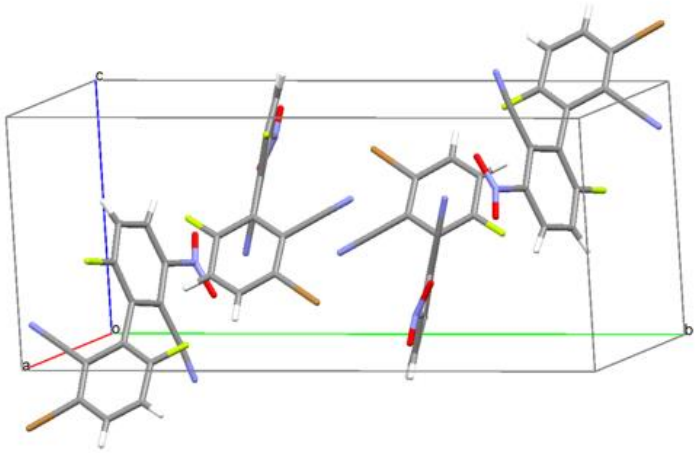

Figure 22: Unit cell of compound **2**.

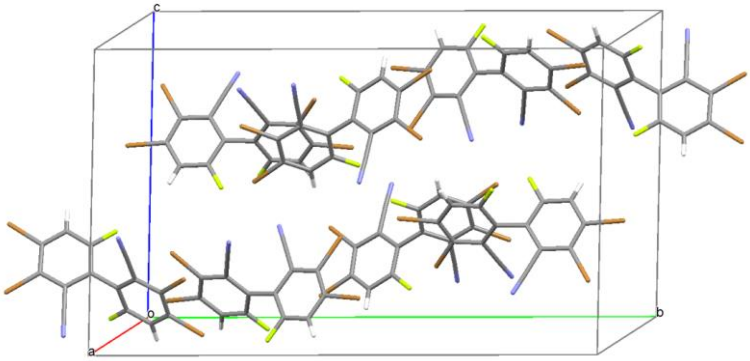

Figure 23: Unit cell of compound **3**.

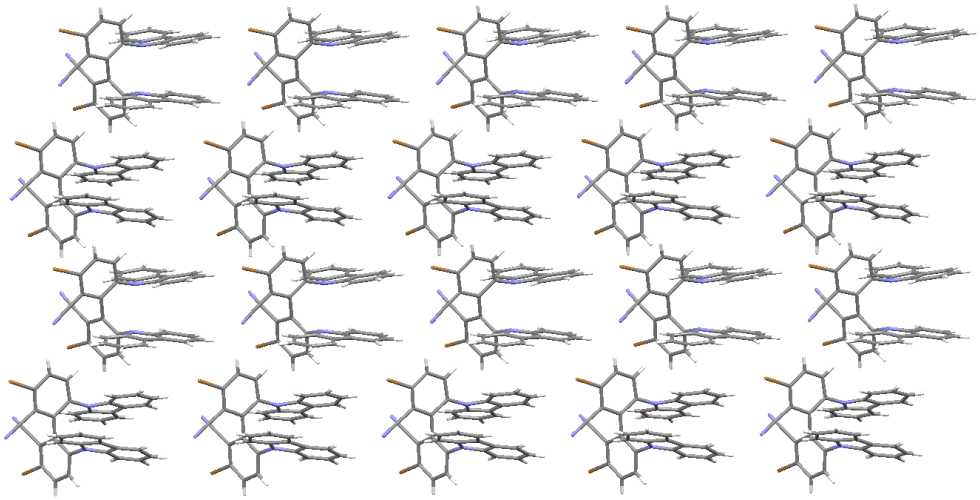

Figure 24: Stacking of compound **6** in the crystal.

Table S1: Crystal data and refinement parameters for compounds **1**–**3**.

	1	**2**	**3**
CCDC number	2369405	2370364	2369404
Empirical formula	$C_{14}H_4Br_2F_2N_2$	$C_{14}H_4BrF_2N_3O_2$	$C_{14}H_2Br_4F_2N_2$
Formula weight	398.01	364.11	555.82
Temperature/K	193(2)	293(2)	193(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/c	$P2_1/c$	$P2_1/c$
a/Å	12.6601(10)	7.6244(7)	8.3856(5)
b/Å	10.3583(10)	20.883(2)	25.9698(13)
c/Å	10.9581(8)	8.5815(8)	14.6463(8)
α/°	90	90	90
β/°	115.272(2)	90.675(8)	106.096(2)
γ/°	90	90	90
Volume/$Å^3$	1299.48(19)	1366.2(2)	3064.5(3)
Z	4	4	8
$\rho_{calc}g/cm^3$	2.034	1.770	2.409
μ/mm^{-1}	6.250	4.446	10.522
F(000)	760.0	712.0	2064
Crystal size/mm^3	0.4×0.2×0.3	0.4×0.35×0.28	0.3×0.3×0.25
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.11 to 50.984	8.468 to 177.686	4.168 to 50.99
Index ranges	$-16 \le h \le 16$, $-13 \le k \le 11$, $-14 \le l \le 14$	$-9 \le h \le 8$, $-25 \le k \le 23$, $-9 \le l \le 8$	$-10 \le h \le 10$, $-31 \le k \le 28$, $-17 \le l \le 17$
Reflections collected	5024	5882	65448
Independent reflections	2394 [R_{int} = 0.0414, R_{sigma} = 0.0533]	2455 [R_{int} = 0.0842, R_{sigma} = 0.0971]	5690 [R_{int} = 0.0950, R_{sigma} = 0.1410]
Data/restraints/parameters	2394/0/181	2455/66/188	5690/0/397
Goodness-of-fit on F^2	1.072	1.299	1.039
Final R indexes [I>=2σ (I)]	R1 = 0.0326, wR2 = 0.0751	R1 = 0.1489, wR2 = 0.3947	R1 = 0.0502, wR2 = 0.1333
Final R indexes [all data]	R1 = 0.0413, wR2 = 0.0801	R1 = 0.1772, wR2 = 0.4412	R1 = 0.0658, wR2 = 0.1410
Largest diff. peak/hole / e $Å^{-3}$	0.45/–0.53	1.41/–0.76	2.75/–0.81

Table S2: Selected bond lengths, bond angles and torsion angles of compounds **1–3**.

Compd	Bond length (Å)		Bond angle (deg)		Torsion angle (deg)	
1	C3–Br1	1.881(3)	C2–C3–Br1	119.7(2)	F1–C6–C7–C7	1.2(5)
	C6–F1	1.341(3)	C7–C6–F1	119.1(3)		
	C1–C2	1.441(4)	C1–C2–C3	120.0(3)		
	C1–N1	1.137(4)	N1–C1–C2	178.1(3)		
2	N1–C1	1.159(19)	N1–C1–C2	179.7(18)	C2–C7–C8–C13	115.9(10)
	C14–N2	1.253(2)	Br1–C3–C4	115.3(11)	N3–C12–C13–C14	–6.9(12)
	C1–C2	1.437(17)	C7–C6–F1	116.4(15)		
	C13–C14	1.719(16)	C2–C7–C8	120.1(10)		
	C3–Br1	1.974(15)	C8–C9–F2	128.2(9)		
	C6–F1	1.346(2)	C8–C13–C14	110.3(7)		
	C9–F2	1.083(10)	C13–C14–N2	177.5(13)		
	C7–C8	1.564(14)	C12–N3–O1	99.8(12)		
	C12–N3	1.361(14)	C12–N3–O2	108.7(12)		
	N3–O1	1.197(12)				
	N3–O2	1.238(14)				
3	C1–F1	1.340(9)	Br2–C4–C5	119.8(6)	C5–C7–C8–C13	118.3(8)
	C9–F2	1.338(8)	C5–C6–N1	176.6(9)	C16–C21–C22–C27	63.7(10)
	C3–Br1	1.891(8)	C7–C8–C13	121.7(6)		
	C4–Br2	1.859(8)	C13–C14–N2	177.7(8)		
	C5–C6	1.436(11)	C16–C15–N3	177.8(9)		
	C6–N1	1.123(10)	C21–C22–C27	122.6(6)		
	C7–C8	1.499(10)	C27–C28–N4	179.0(9)		
	C13–C14	1.449(11)				
	C14–N2	1.123(10)				
	C11–Br3	1.886(7)				
	C12–Br4	1.866(7)				
	C17–Br5	1.876(8)				
	C18–Br6	1.895(8)				
	C15–C16	1.432(11)				
	C15–N3	1.120(10)				
	C28–N4	1.122(10)				
	C20–F3	1.339(9)				
	C23–F4	1.318(9)				
	C21–C22	1.500(10)				
	C25–Br7	1.887(7)				
	C26–Br8	1.864(8)				
	C27–C28	1.453(11)				

Table S3: Interactions in crystals of compounds **1**–**3**.

Compd	D–X···A	*d*(X···A) (Å)	*d*(D···A) (Å)	∠(D–X···A) (deg)
1	C(4)–H(4)···F(1)	2.572	3.350	161.58
	C(5)–H(5)···N(1)	2.717	3.347	139.23
2	C(5)–H(5)···O(2)	2.684	3.563	157.85
	C(6)–F(1)···Cg1[b]	3.688	4.579	123.8
3	C(2)–H(2)···N(2)	2.535	3.463	165.40
	C(4)–Br(2)···Cg1[a]	3.522	4.070	93.08
	C(12)–Br(4)···Cg2[a]	3.585	4.197	95.50
	C(17)–Br(5)···Cg3[a]	3.501	3.963	89.67
	C(18)–Br(6)···Cg3[a]	3.800	4.221	89.13
	C(25)–Br(7)···Cg4[a]	3.843	4.333	91.77
	C(26)–Br(8)···Cg4[a]	3.507	3.998	90.92

[a]Compound **2**: Cg1: centroid of benzene ring (C8-C9-C10-C11-C12-C13). [b]Compound **3**: Cg1: centroid of benzene ring (C16-C17-C18-C19-C20-C21); Cg2: centroid of benzene ring (C22-C23-C24-C25-C26-C27); Cg3: centroid of benzene ring (C1-C2-C3-C4-C5-C7); Cg4: centroid of benzene ring (C8-C9-C10-C11-C12-C13).

Table S4: Crystal data and refinement parameters for compound **6**.

	6
CCDC number	2413554
Empirical formula	$2(C_{19}H_{10}BrN_2)$
Formula weight	692.40
Temperature/K	293(2)
Crystal system	monoclinic
Space group	I121
a/Å	15.2151(2)
b/Å	11.88210(10)
c/Å	18.0635(3)
α/°	90
β/°	105.6010(10)
γ/°	90
Volume/Å^3	3145.34(7)
Z	4
ρ_{calc}g/cm^3	1.462
μ/mm^{-1}	3.525
F(000)	1384.0
Crystal size/mm^3	0.3×0.12×0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.874 to 143.562
Index ranges	−18 ≤ h ≤ 18, −14≤ k ≤ 14, −22 ≤ l ≤ 18
Reflections collected	17599
Independent reflections	6069 [R_{int} = 0.0226, R_{sigma} = 0.0208]
Data/restraints/parameters	6069/49/397
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0580, wR_2 = 0.1643
Final R indexes [all data]	R_1 = 0.0600, wR_2 = 0.1686
Largest diff. peak/hole / e Å^{-3}	0.93/−0.38

Table S5: Selected bond lengths, bond angles and torsion angles of compound **6**.

Compd	Bond lengths (Å)		Bond angles (deg)		Torsion angles (deg)	
6	Br1–C16	1.906(5)	C17–C16–Br1	119.6(4)	C1–N1–C13–C19	–129.56
	C13–N1	1.423(7)	C13–N1–C12	122.0(5)	C6–C1–N1–C13	–158.65
	C17–C18	1.445(7)	C1–N2–C13	124.2(7)	C20–N3–C32–C38	–125.46
	C18–N2	1.132(8)	C17–C18–N2	176.9(6)	C26–C31–N3–C32	–172.15
	C32–N3	1.402(7)	C32–N3–C31	127.8(6)		
	C37–N4	1.117(11)	C36–C37–N4	178.6(9)		
	Br2–C35	1.916(7)	Br2–C35–C34	118.2(6)		
	C36–C37	1.451(9)	C36–C37–N4	178.6(9)		
	C37–N4	1.117(11)				

Table S6: Interactions in crystal of compound **6**.

D–H···A	*d*(H···A) (Å)	*d*(D···A) (Å)
C(14)–H(14)···Cg1	3.060	3.749
C(15)–H(15)···Cg2	2.879	3.663
C(4)–H(4)···N2	2.746	3.465
Cg1···Cg3		3.498
C(9)–H(9)···N2	2.611	3.403

Cg1:centroid of benzene ring (C25-C20-C21-C22-C23-C24); Cg2: centroid of benzene ring (C26-C27-C28-C29-C30-C31); Cg1: centroid of benzene ring (C21-C20-C25-C24-C23-C22).

X-ray structure determinations

Single crystals of compounds **1** and **3** were selected and mounted on Xcalibur, Eos, Gemini diffractometer. The crystals were kept at 193(2) K during the data collection. Using OLEX2,[1] the structures were solved with the OLEX2.SOLVE[2] structure solution program using Charge Flipping and refined with the SHELXL[3] refinement package using Least Squares minimization.

Singles crystals of compounds **2** and **6** were selected and mounted on a Xcalibur, Eos, Gemini diffractometer. The crystals were kept at 293(2) K during the data collection. Using OLEX2,[1] the structures were solved with the SHELXT[4] structure solution program using Intrinsic Phasing and refined with the SHELXL[3] refinement package using least-squares minimization.

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

2. Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *Acta Crystallogr.* **2015**, *A71*, 59–75.

3. Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8.

4. Sheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8.

CCDC 2369405, 2369404, 2370364 and 2413554 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.