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Evaluating the isomeric effects of donors on the structures and photophysical properties of Donor-Acceptor-π Bridge-Donor (D1-A-π-D2) prototype fluorophores

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Table S1. Crystal data and structure refinements of four compounds.

Compd	**MNM**	***p*-BMNM**	***o*-BMNM**	***m*-BMNM**
Formula	$C_{16}H_{12}N_2O$	$C_{29}H_{20}N_2O$	$C_{29}H_{20}N_2O$	$C_{29}H_{20}N_2O$
Formula weight	248.28	412.47	412.47	412.47
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	11.021(6)	4.1510(3)	9.6109(5)	25.2179(13)
b/ Å	7.962(4)	32.660(2)	10.0070(4)	11.4889(6)
c/ Å	15.851(8)	15.7551(13)	23.2959(11)	7.5967(4)
α/ °	90	90	90	90
β/ °	103.442(17)	93.710(3)	91.533(2)	95.619(2)
γ/ °	90	90	90	90
V/Å^3	1352.8(11)	2131.5(3)	2239.71(18)	2190.4(2)
Z	4	4	4	4
Dcalc (Mg m^{-3})	1.219	1.285	1.223	1.251
T/K	296(2)	296(2)	296(2)	296(2)
μ (mm^{-1})	0.078	0.078	0.075	0.076
Cryst dimensions	0.210×0.170×0.150	0.280×0.220×0.120	0.230×0.230×0.170	0.250×0.190×0.160
No. of felns collected	13108	15413	17698	21542
No. of unique reflns	3095	4884	5072	4947
Goodness-of-fit on F^2	1.027	1.005	1.019	1.005
R_1,wR_2 (I>2σ(I))	R_1=0.0536, wR_2=0.1379	R_1=0.0574, wR_2=0.1219	R_1=0.0598, wR_2=0.1270	R_1=0.0612, wR_2=0.1099
R_1 , wR_2 (all data)	R_1=0.0950, wR_2=0.1586	R_1=0.1127, wR_2=0.1450	R_1=0.1455, wR_2=0.1531	R_1=0.1549, wR_2=0.1352
CCDC	2232678	2055960	2232682	2232679

Table S2 Summary of intermolecular interactions in crystal structures of four compounds

Compd	Interaction	d(Å)	A(°)
MNM	C5-H5...N1	2.675[a]	149.01
***o*-BMNM**	C7-H7...N1	2.666[a]	136.44
	C25-H25...π_1	2.766[b]	139.44
***m*-BMNM**	C5-H5...O1	2.694[c]	139.68
	C7-H7...O1	2.696[c]	155.45
***p*-BMNM**	C16-H16...N2	2.747 [a]	162.53
	C19-H19...N1	2.666[a]	149.30
	C25-H25...π_1	4.540[b]	165.25

[a]The distances were measured from the hydrogen atom to the nitrogen atom

π_1 corresponds to the 6-methoxynaphthalene moieties

[b]The distances were measured from the hydrogen atom to the center of 6-methoxynaphthalene moiety

[c]The distances were measured from the hydrogen atom to the oxygen atom

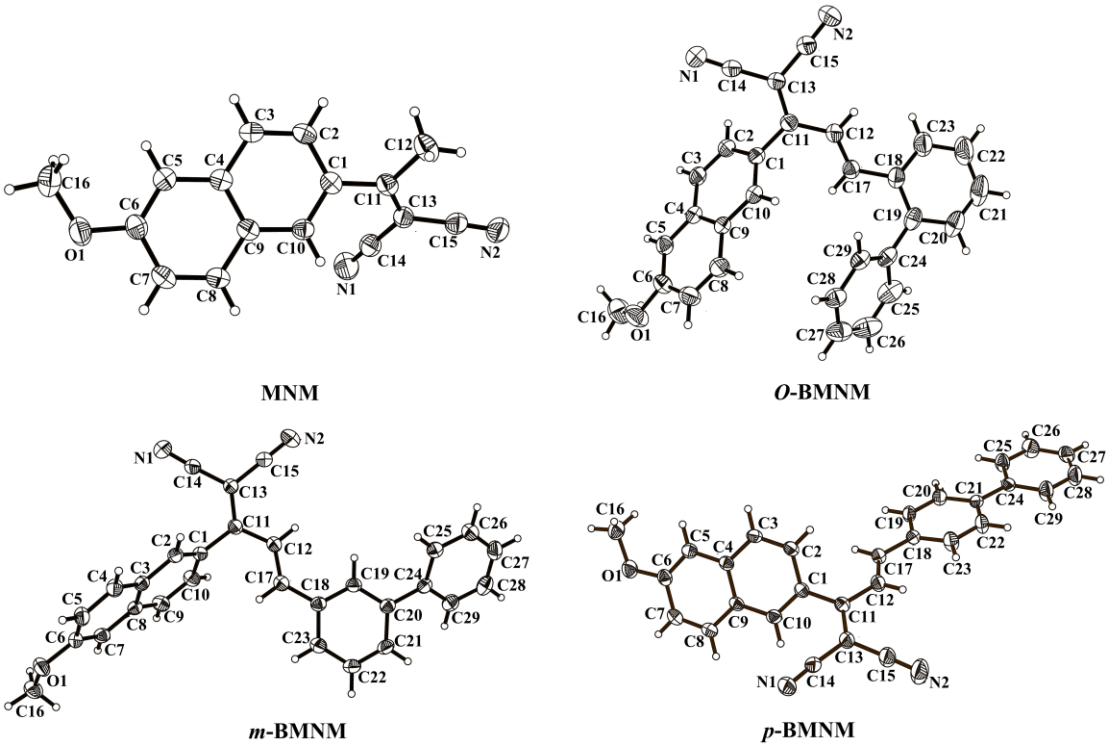

Fig.S1 Perspective views of four compounds. Thermal ellipsoids were at 30% probability.

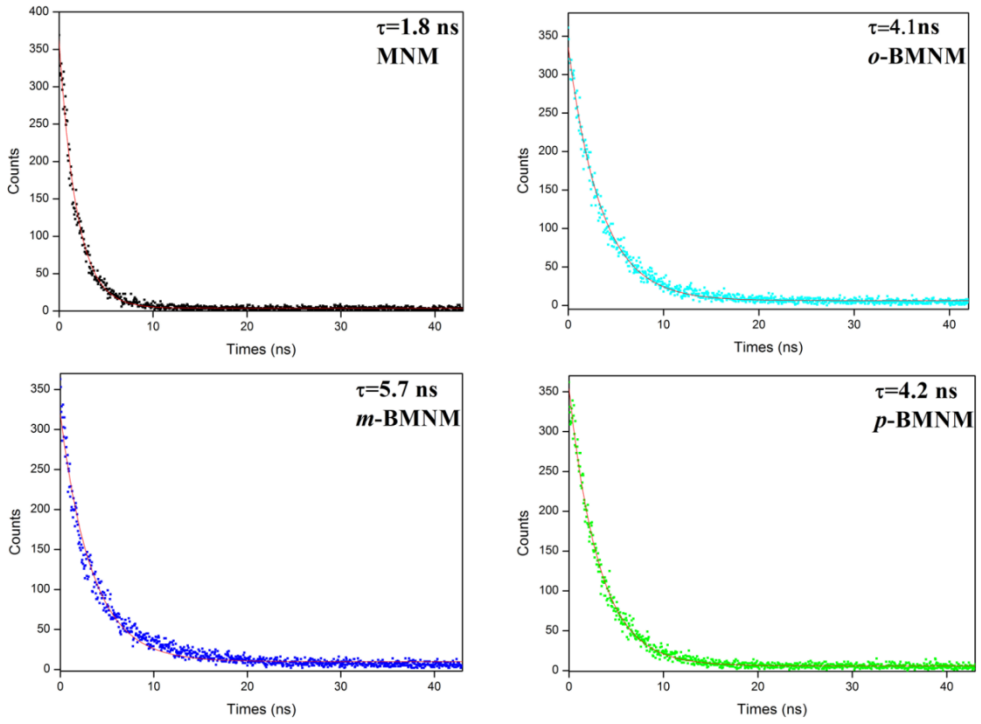

Fig.S2 Fluorescence decay curves of four compounds (Fluorescence lifetimes were measured at 467 nm)

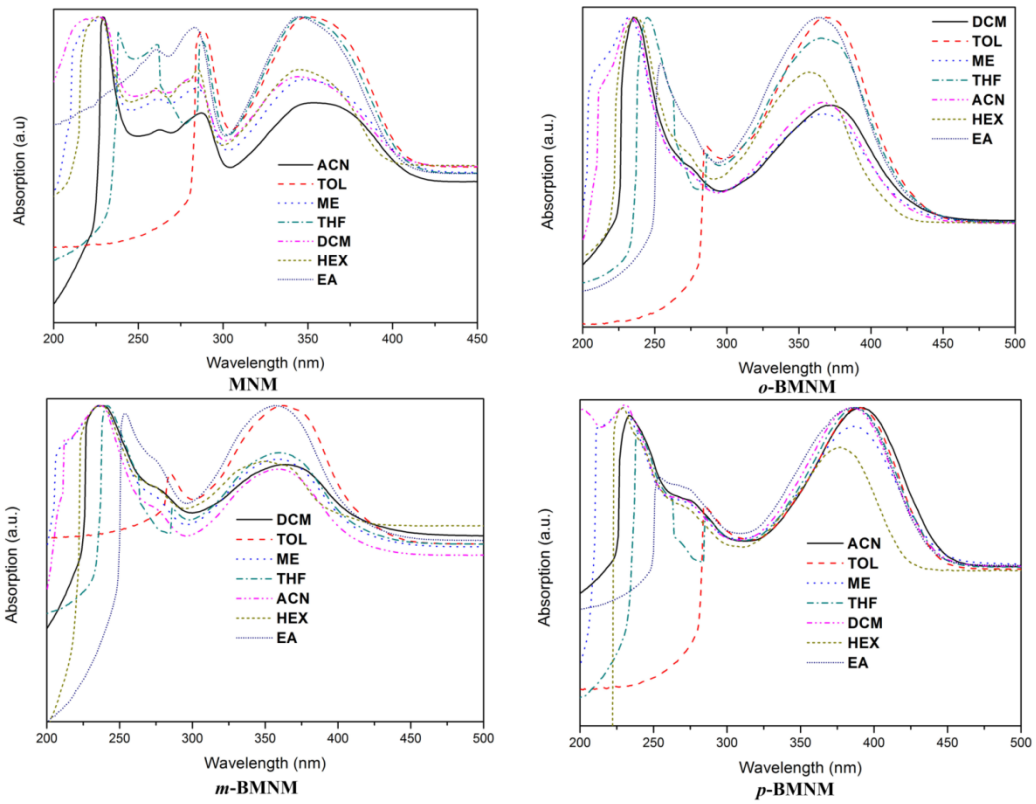

Fig.S3 The normalized absorption spectrum of four compounds in different solvents (10 μ M).

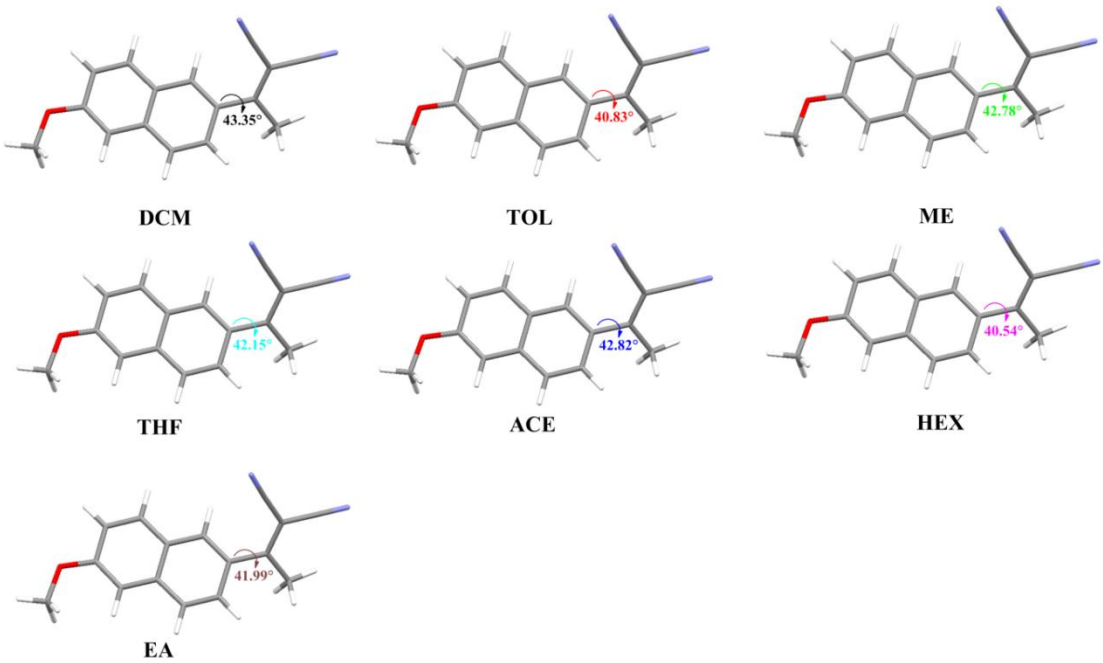

Fig.S4 The selected dihedral angles (θ/°) in optimized structures of ground state (S0) of **MNM.**

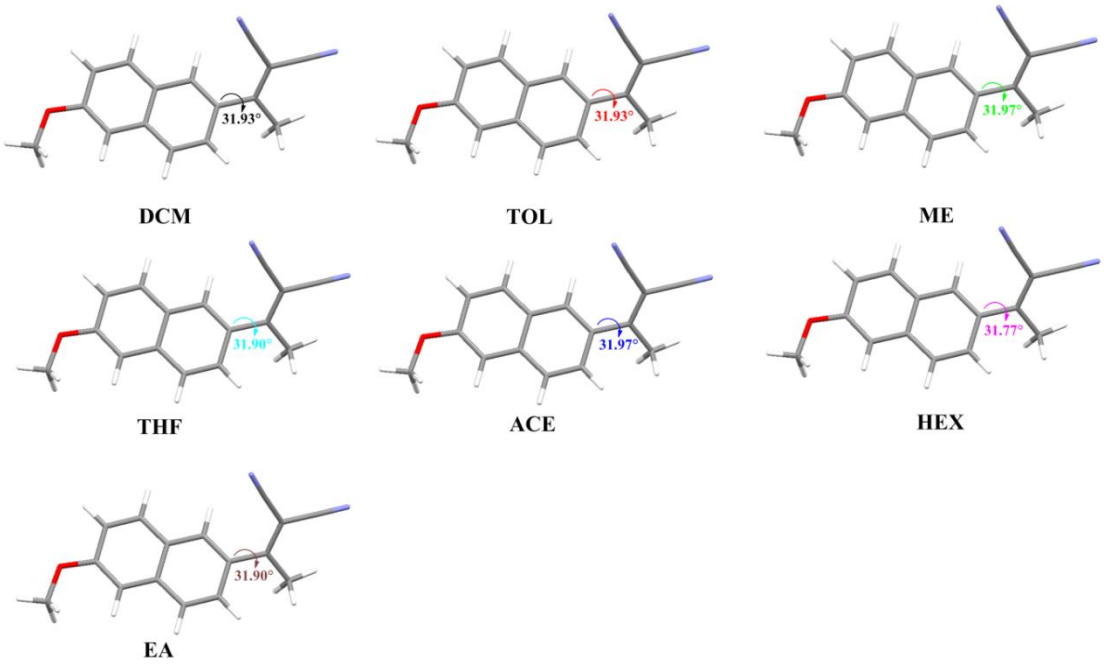

Fig.S5 The selected dihedral angles (θ/°) in optimized structures of excitation state (S1) of **MNM**

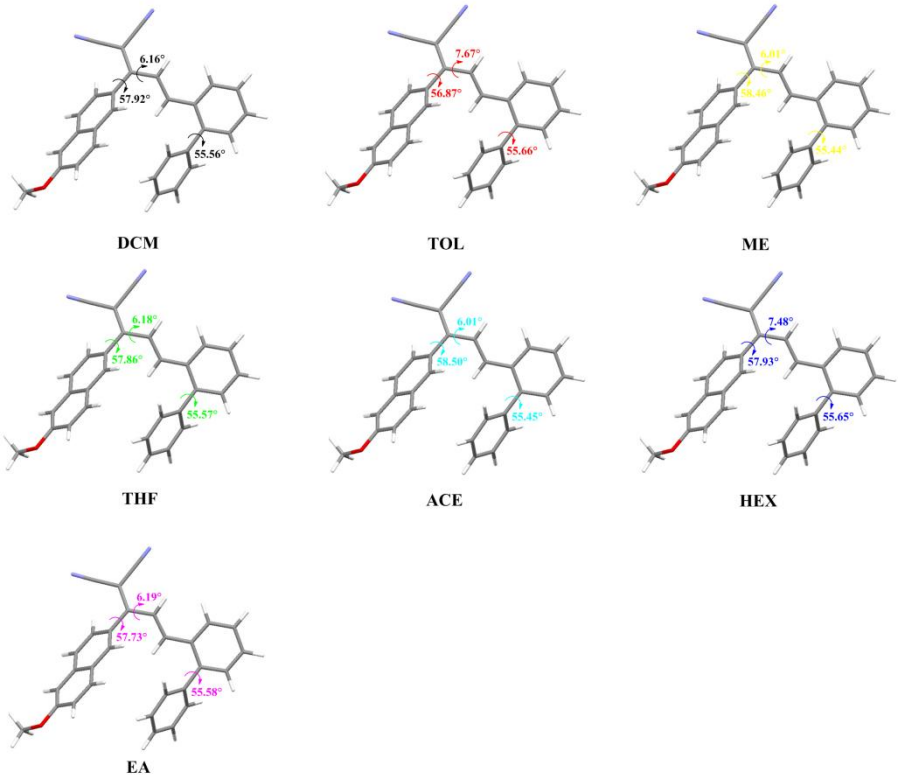

Fig.S6 The selected dihedral angles (θ/°) in optimized structures of ground state (S0) of ***o*-BMNM**

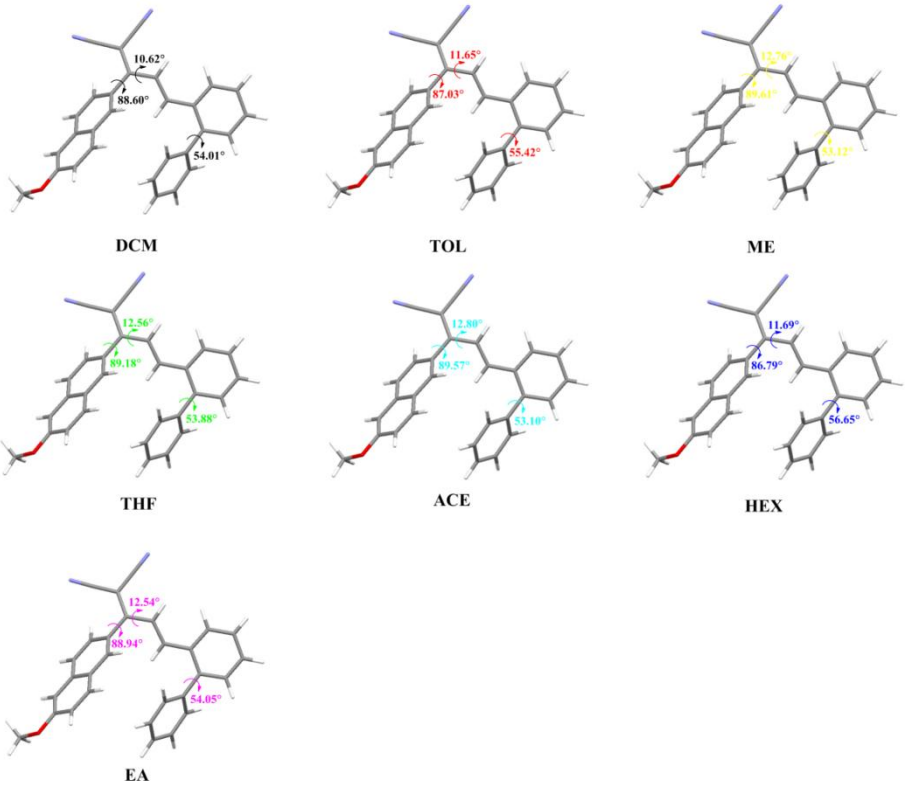

Fig.S7 The selected dihedral angles (θ/°) in optimized structures of excitation state (S1) of ***o*-BMNM**.

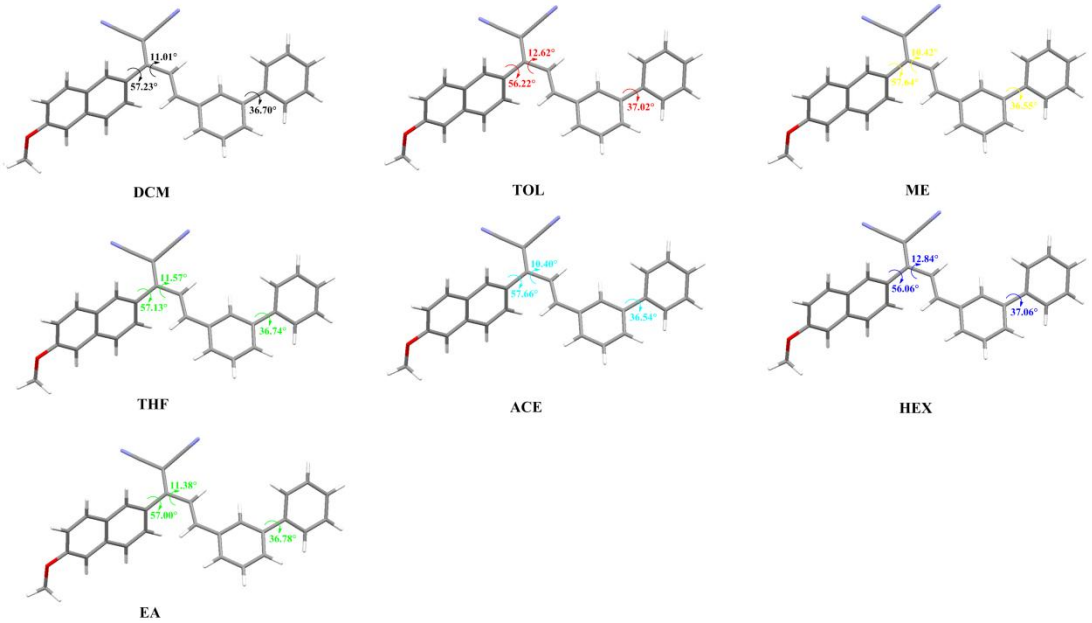

Fig.S8 The selected dihedral angles (θ/°) in optimized structures of ground state (S0) of ***m*-BMNM**.

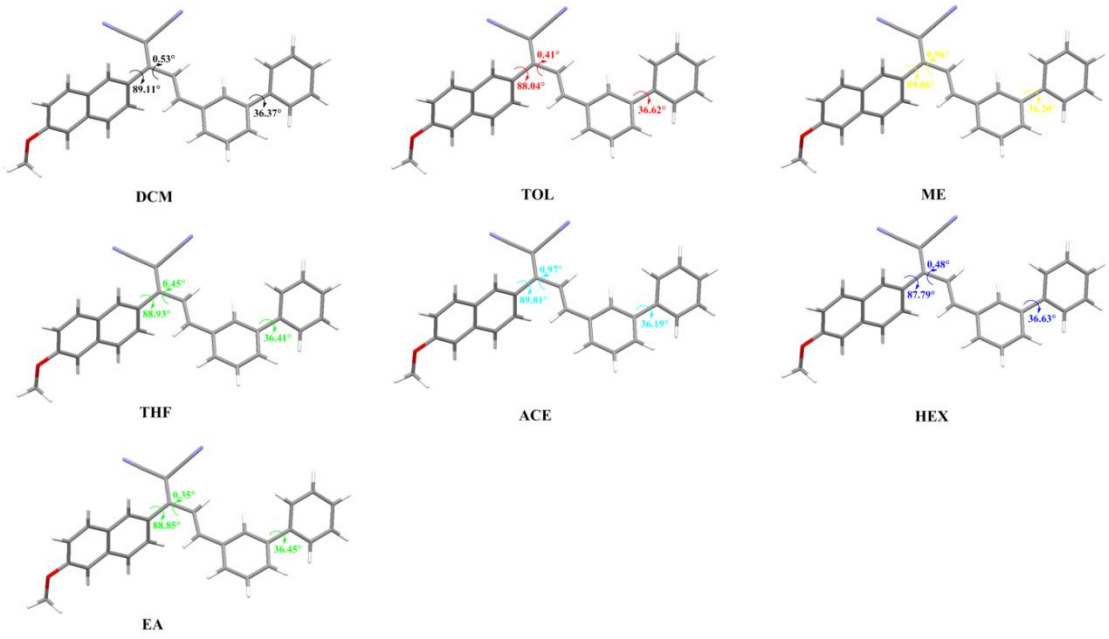

Fig.S9 The selected dihedral angles (θ/°) in optimized structures of excitation state (S1) of ***m*-BMNM**.

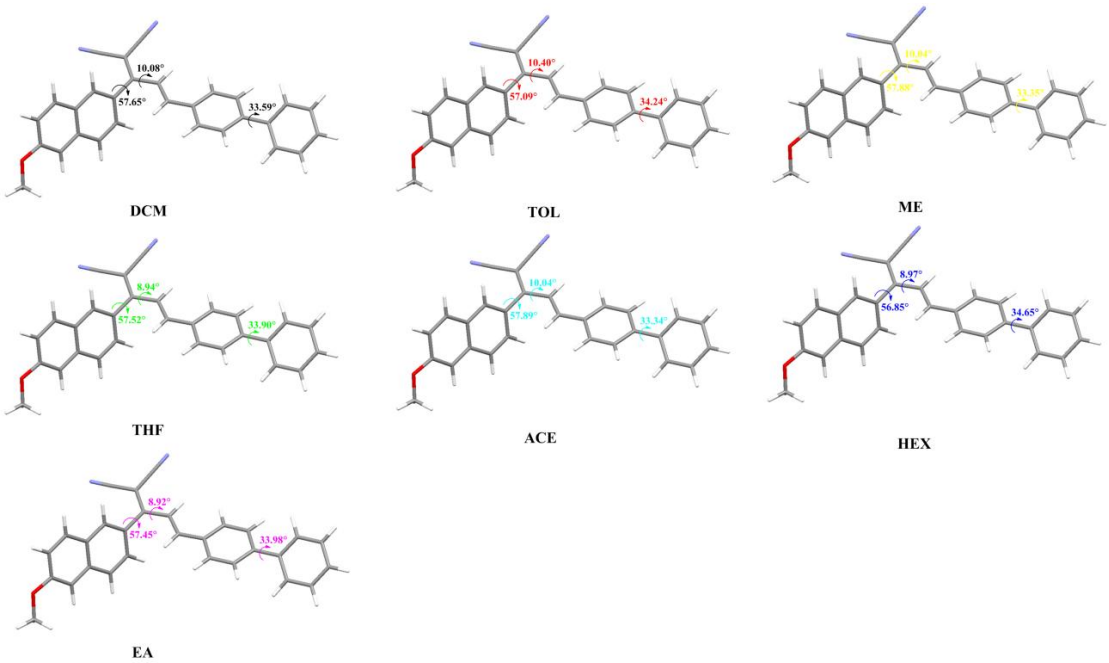

Fig.S10 The selected dihedral angles (θ/°) in optimized structures of ground state (S0) of ***p*-BMNM**.

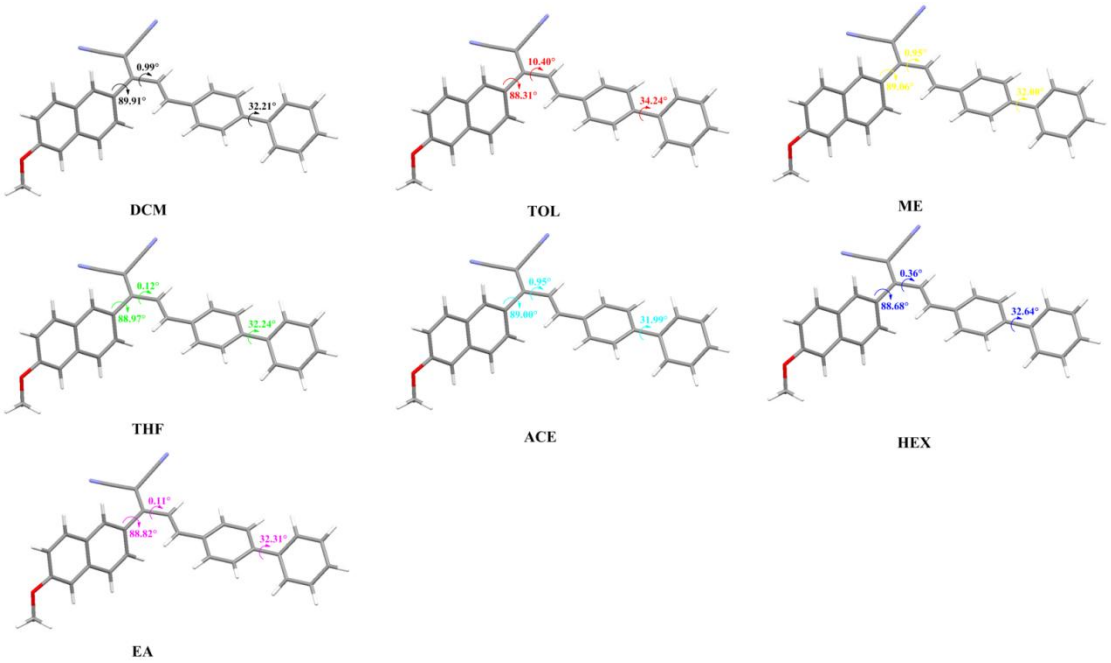

Fig.S11 The selected dihedral angles (θ/°) in optimized structures of excitation state (S1) of ***p*-BMNM**.

Experimental Section

All reagents were purchased from Aldrich and Acros without further purification. The three isomers in this study were synthesized by the condensation reaction and knoevenagel reaction in a respectable yield. The ^{1}H NMR and ^{13}C NMR spectra of four compounds were recorded at 303K on a Bruker Avance NMR spectrometer using $CDCl_3$ as solvent and TMS as an internal reference. The two fluorescent isomers were characterized by a Flash EA 1112, CHNS-O elemental analysis instrument.

Synthesis of 2-(1-(6-methoxynaphthalen-2-yl)-ethylidene)malononitrile (MNM)

Initially, 2-acetyl-6-methoxynaphthalene 1 (2.35 g, 11.75 mmol) and malononitrile (1.16 g, 17.625 mmol) were dissolved in mixture of dichloromethane (20 mL) and methanol (10 mL), and then ammonium acetate (1.36 g, 17.625 mmol) was added into the reaction mixture. The mixture was stirred at 40℃ for 6 hours. After cooling to room temperature, the solvent was removed under vacuum and subsequently separated with chromatography on silical gel (ethyl acetate/petroleum ether = 5/1) to give rise to **MNM** as a yellow solid (2.1g, 80%). Anal. Calcd. (%) : C, 77.40; H, 4.87; N, 11.28. Found: C, 77.38; H, 4.82; N, 11.33. ^{1}H NMR 8.07 (d, *J* = 1.7 Hz, 1H, Ar), 7.85 (d, *J* = 8.8 Hz, 2H, Ar), 7.63 (dd, *J* = 8.6, 2.0 Hz, 1H, Ar), 7.26 (dd, *J* = 9.0, 2.5 Hz, 1H, Ar), 7.19 (d, *J* = 2.4 Hz, 1H, Ar), 3.98 (s, 3H, OCH3), 2.75 (s, 3H, CH3). (Fig. S12). ^{13}C NMR (300 MHz, $CDCl_3$):174.942, 159.993, 136.583, 130.747, 128.495, 127.853, 127.700, 124.250, 120.465, 113.431, 105.745, 83.303, 77.352, 77.237, 77.036, 76.719, 55.522 ppm (Fig. S13). IR (KBr pellet, cm^{-1}): 3331, 3275, 2488, 1655, 1448, 1404, 1311, 1244, 1134, 1041, 972, 941, 885, 829, 771, 738, 690, 578, 532, 410, 399. (Fig. S14).

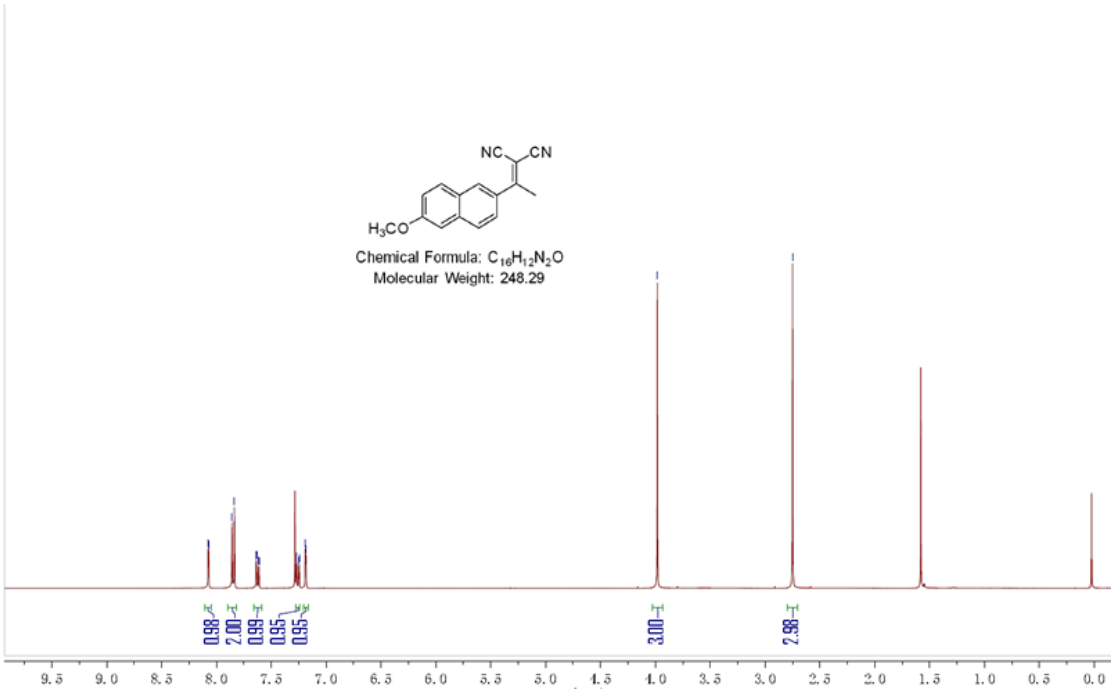

Fig. S12 The ^{1}H-NMR spectra of **MNM**

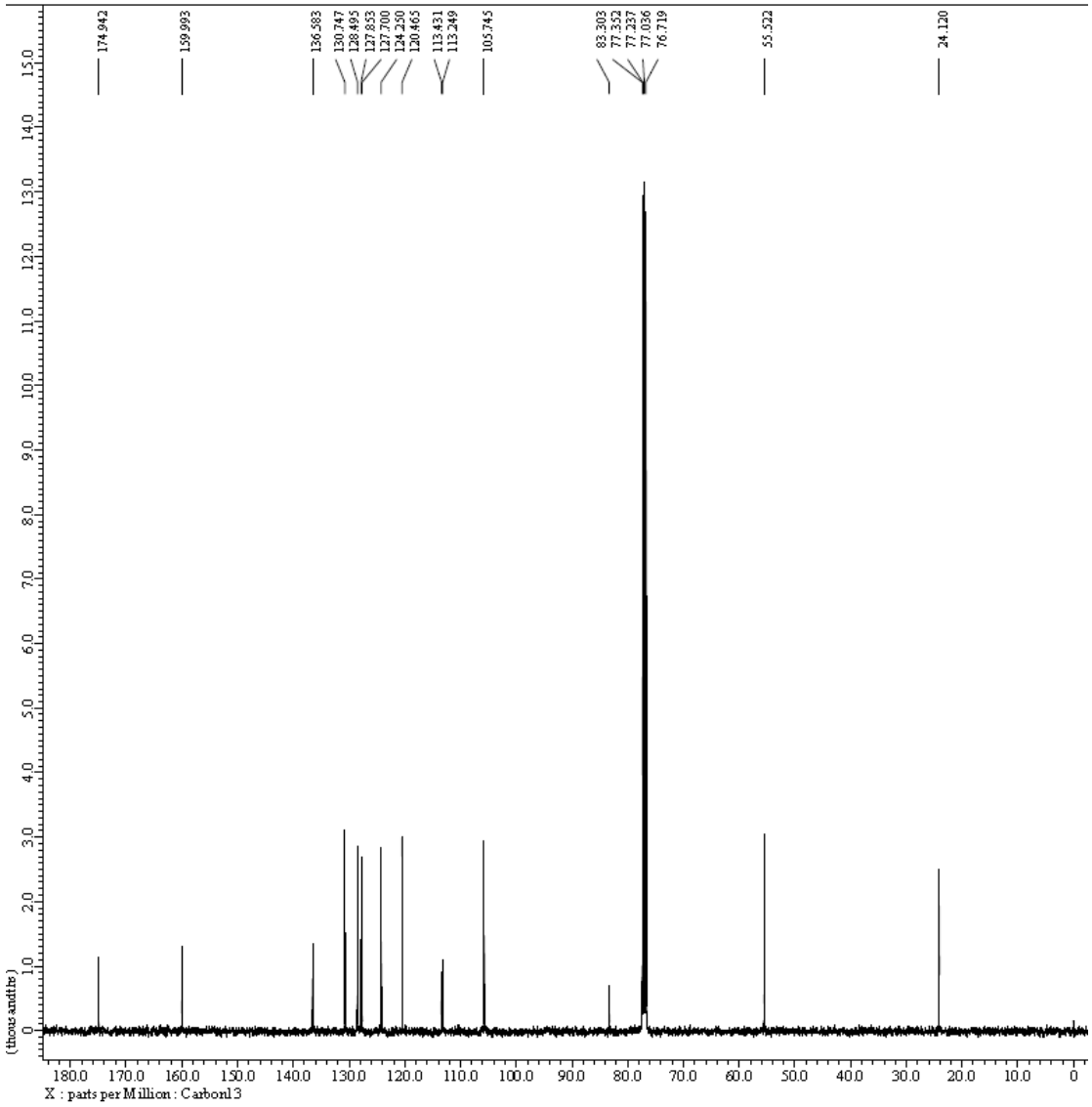

Fig. S13 The ^{13}C-NMR spectra of **MNM**

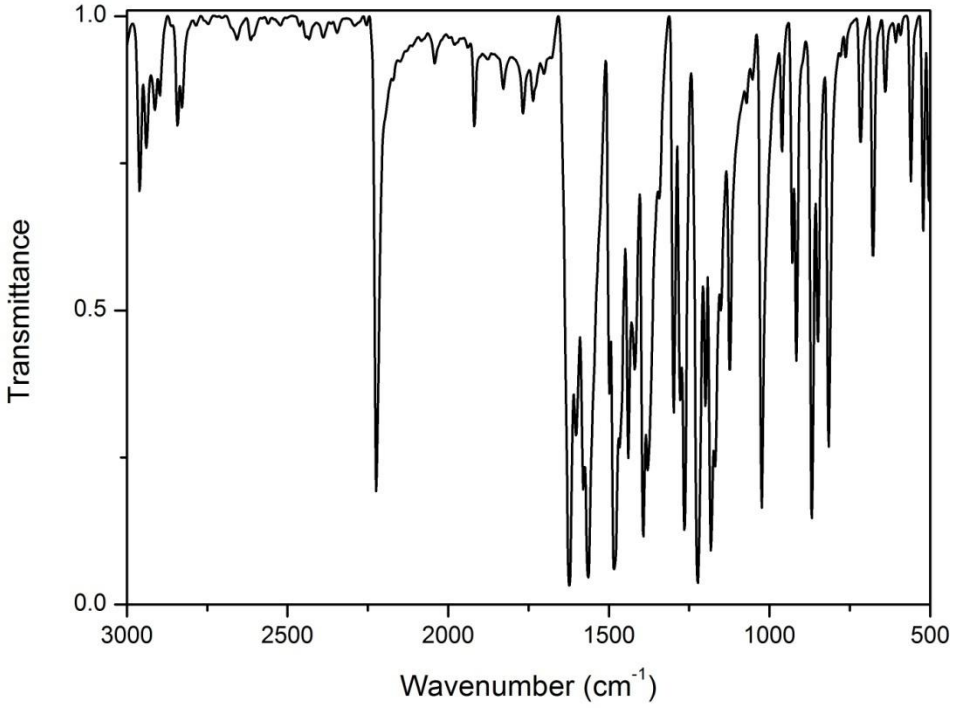

Fig. S14 The IR spectra of **MNM**

Synthesis of (E)-2-(3-([1,1'-biphenyl]-4-yl)-1-(6-methoxynaphthalen-2-yl)allylidene)malononitrile (*p*-BMNM)

Compound **MNM** (0.23 g, 0.92 mmol) and biphenyl-4-carboxaldehyde (0.17 g, 0.92 mmol) were stirred in 2-propanol (20 mL). Then, a catalytic amount of piperidine was added to the mixture. The mixture was stirred at 70℃ for 3 hours. The mixture was cooled to room temperature, and the solution was filtered to obtain a yellow solid. The solid was subsequently separated with chromatography on silical gel (dichloromethane/methanol = 4/1) to give pure ***p*-BMNM** as a yellow solid. Yield: 0.31g (81%). Anal. Calcd. (%) : C, 84.44; H, 4.89; N, 6.79. Found: C, 84.47; H, 4.82; N, 6.74. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96-7.82 (m, 3H, Ar), 7.72 (d, *J* = 15.5 Hz, 1H, Ar), 7.69-7.59 (m, 6H, Ar), 7.48 (qd, *J* = 8.5, 7.8, 1.8 Hz, 3H, Ar), 7.44-7.39 (m, 1H, Ar), 7.30 (d,

J = 2.5 Hz, 1H, CH=CH), 7.25 (d, *J* = 2.4 Hz, 1H, CH=CH), 7.01 (d, *J* = 15.6 Hz, 1H, Ar), 4.01 (s, 3H, O CH3) (Fig. S15). ^{13}C NMR (300 MHz, $CDCl_3$): δ 171.311, 159.457, 148.829, 144.354, 139.659, 133.325, 130.306, 129.376, 129.348, 128.993, 128.255, 128.140, 128.083, 127.767, 127.623, 127.067, 126.243, 124.623, 120.302, 113.824, 113.201, 105.774, 81.702, 77.630, 77.333, 77.218, 77.016, 76.700, 55.522 ppm (Fig. S16). IR (KBr pellet, cm^{-1}): 2214, 1593, 1487, 1388, 1344, 1307, 1263, 1218, 1193, 1176, 1026, 985, 912, 854, 759, 686 (Fig. S17).

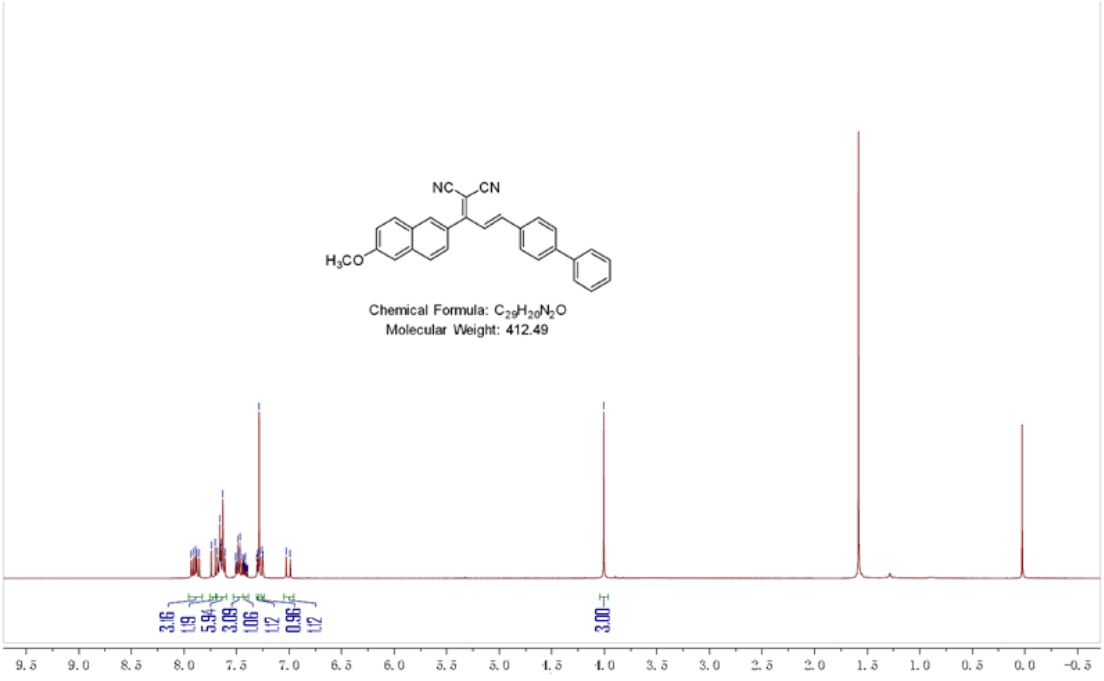

Fig. S15 The ^{1}H-NMR spectra of ***p*-BMNM**

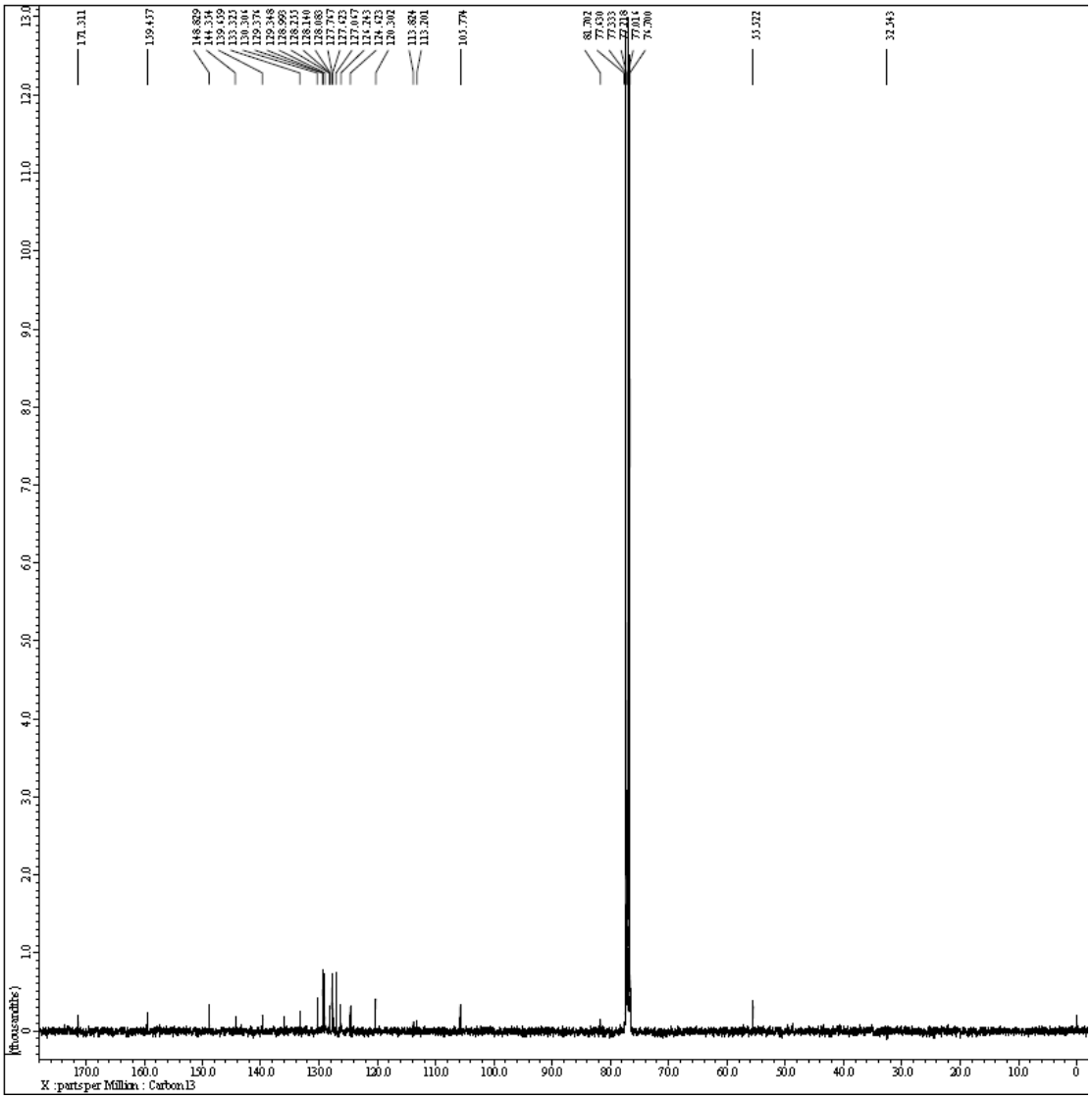

Fig. S16 The ^{13}C-NMR spectra of ***p*-BMNM**

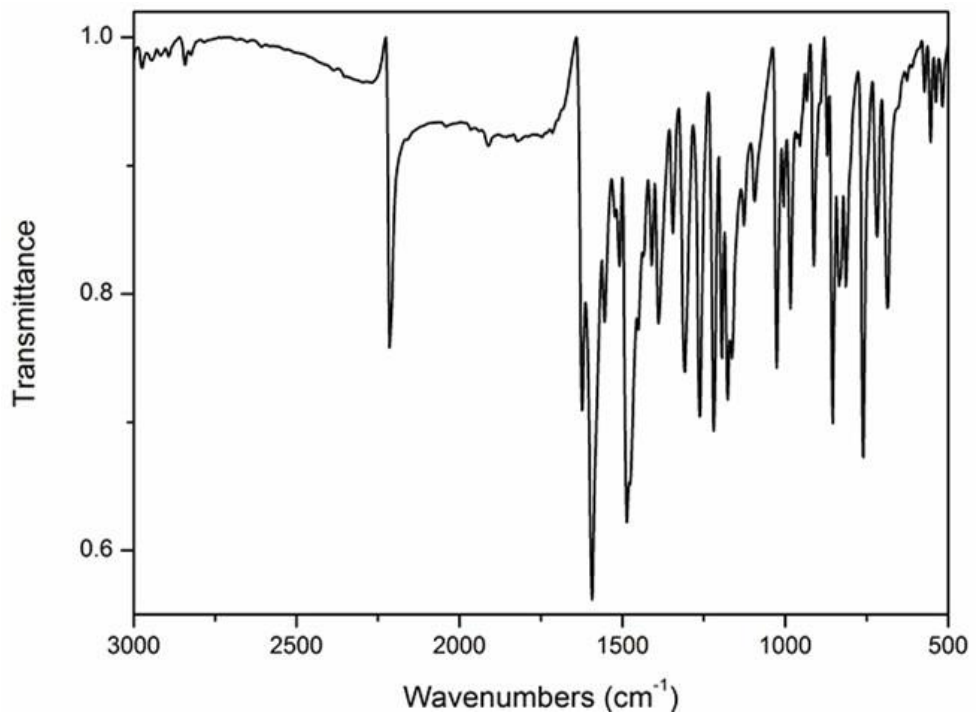

Fig. S17 The IR spectra of ***p*-BMNM**

Synthesis of (E)-2-(3-([1,1'-biphenyl]-2-yl)-1-(6-methoxynaphthalen-2-yl)allylidene)malononitrile (*o*-BMNM)

This compound was synthesized by the same procedure as described for ***p*-BMNM** except that biphenyl-2-carboxaldehyde was used instead of biphenyl-4-carboxaldehyde. Anal. Calcd. (%) : C, 84.44; H, 4.89; N, 6.79. Found: C, 84.43; H, 4.90; N, 6.78. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88-7.84 (m, 1H, Ar), 7.73-7.66 (m, 3H, Ar), 7.58 (d, *J* = 15.7 Hz, 1H, CH=CH), 7.51-7.43 (m, 2H, Ar), 7.37-7.33 (m, 1H, Ar), 7.29-7.26 (m, 1H, Ar), 7.24-7.15 (m, 4H, Ar), 7.15-7.10 (m, 3H, Ar), 7.03 (d, *J* = 15.7 Hz, 1H, CH=CH), 3.95 (s, 3H, OCH_3) (Fig. S18). ^{13}C NMR (300 MHz, $CDCl_3$): δ 171.608, 159.255, 148.906, 131.034, 130.565, 130.229, 129.549, 129.099, 128.083, 127.805, 127.556, 127.393, 127.010, 125.917, 125.266, 119.947, 113.805, 113.153, 105.630, 81.616, 77.342, 77.227, 77.026, 76.700, 55.455 ppm (Fig. S19). IR (KBr pellet, cm^{-1}): 2246, 1613,

1595, 1579, 1563, 1548, 1502, 1491, 1460, 1443, 1425, 1402, 1380, 1355, 1326, 1291, 1237, 1188, 1170, 1143, 1116, 1098, 1049, 932, 892, 832, 793, 727, 714, 684 (Fig. S20).

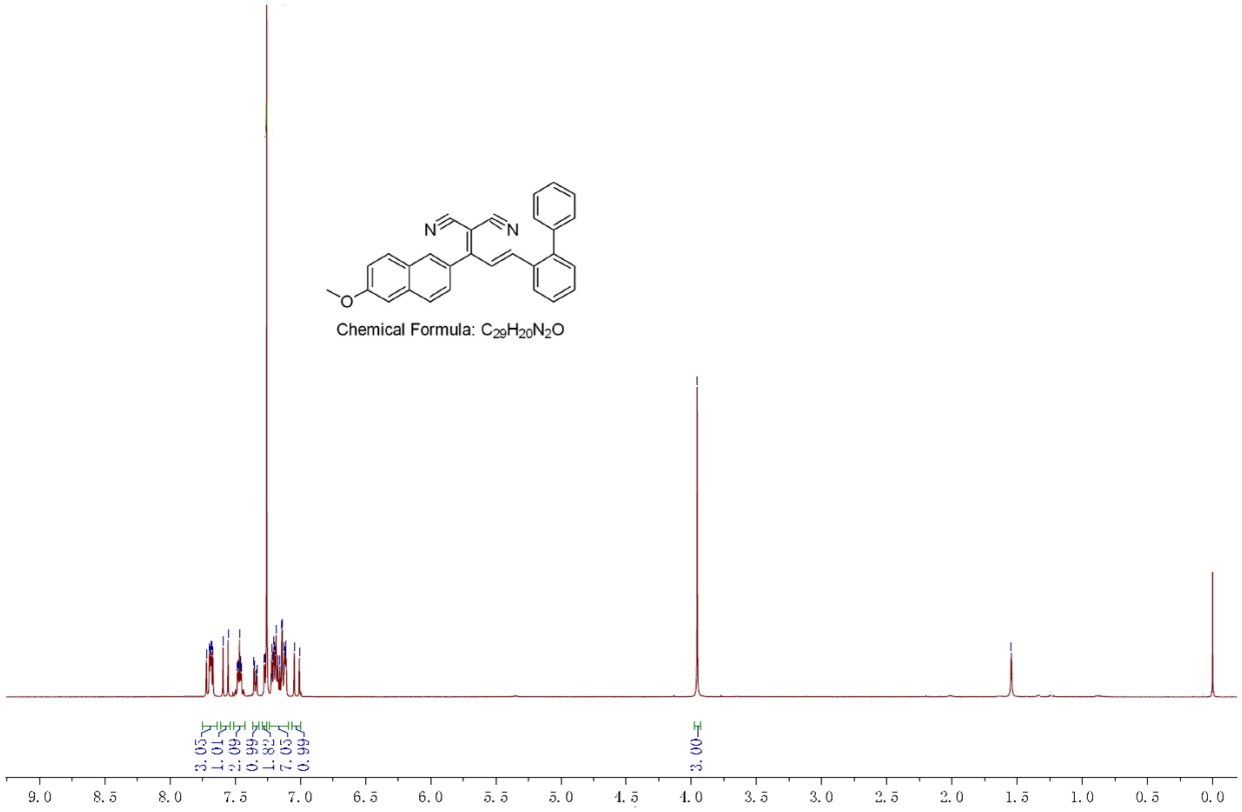

Fig. S18 The ^{1}H-NMR spectra of ***o*-BMNM**

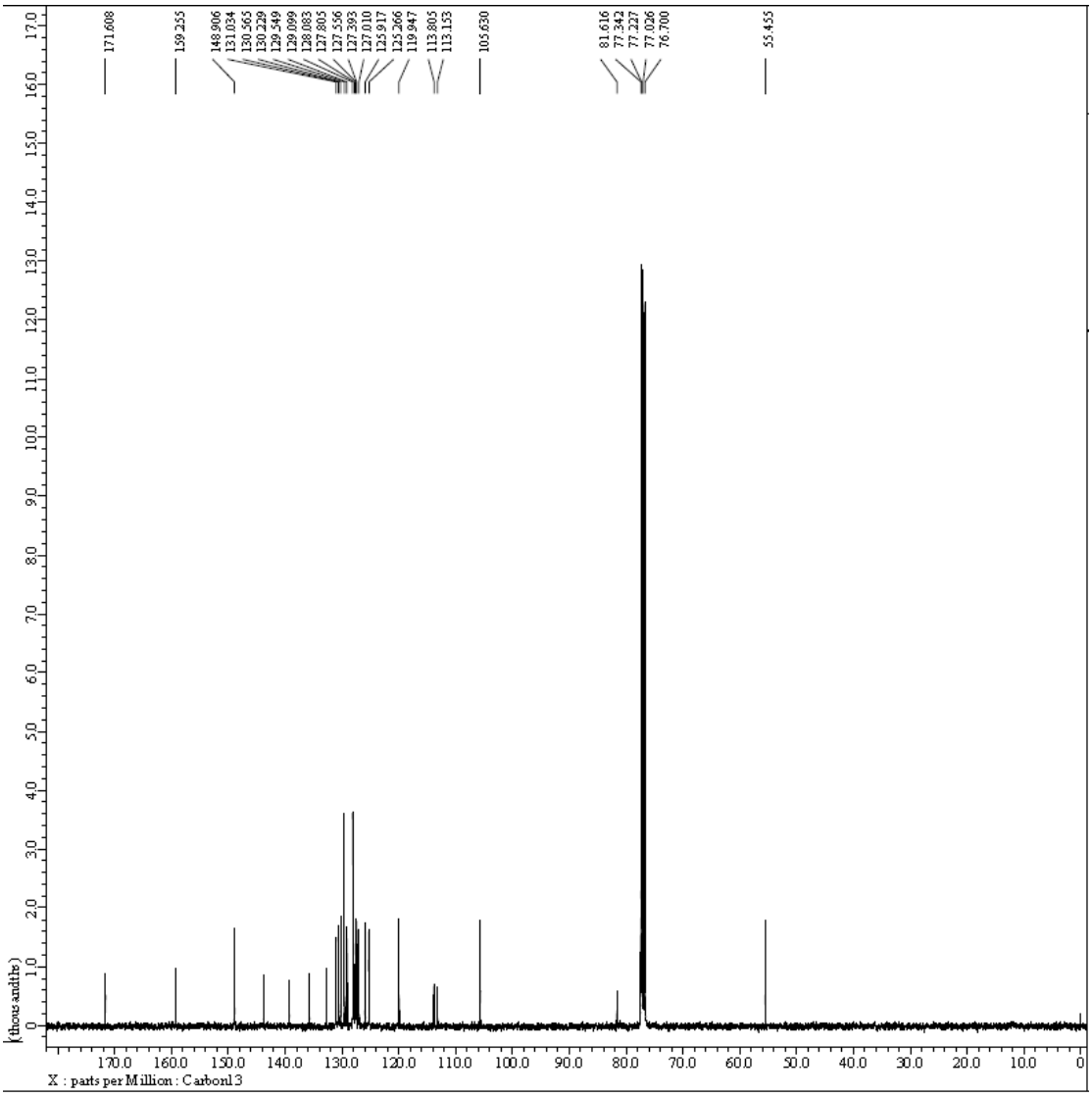

Fig. S19 The ^{13}C-NMR spectra of ***o*-BMNM**

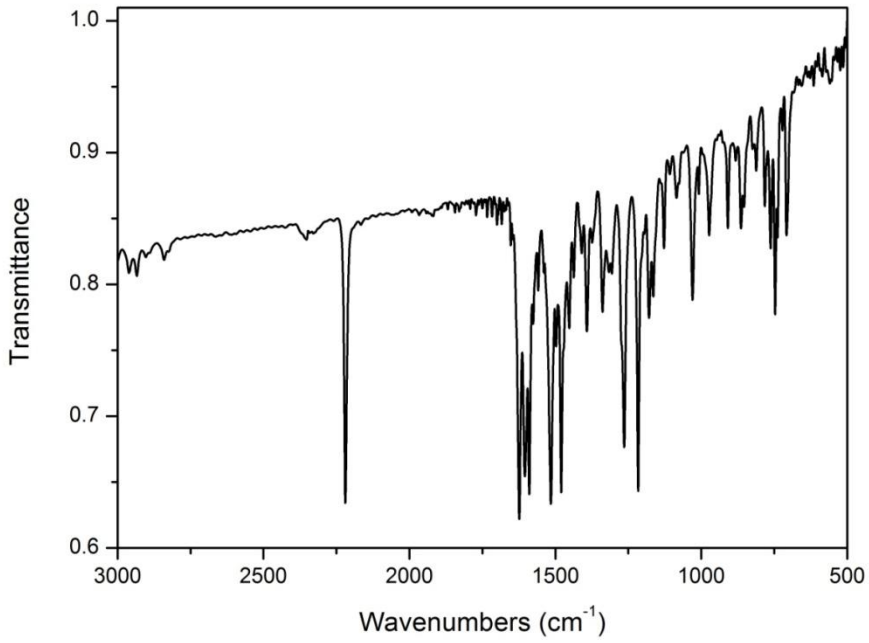

Fig. S20 The IR spectra of ***o*-BMNM**

Synthesis of (E)-2-(3-([1,1'-biphenyl]-3-yl)-1-(6-methoxynaphthalen-2-yl)allylidene)malononitrile (*m*-BMNM)

This compound was synthesized by the same procedure as described for ***p*-BMNM** except that biphenyl-3-carboxaldehyde was used instead of biphenyl-4-carboxaldehyde. Anal. Calcd. (%) : C, 84.44; H, 4.89; N, 6.79. Found: C, 84.46; H, 4.91; N, 6.76. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.7 Hz, 1H, Ar), 7.87 (d, *J* = 2.2 Hz, 1H, Ar), 7.84 (d, *J* = 9.3 Hz, 1H, Ar), 7.72 (d, *J* = 15.5 Hz, 1H, CH=CH), 7.68-7.63 (m, 2H, Ar), 7.58-7.52 (m, 3H, Ar), 7.50 (d, *J* = 8.0 Hz, 1H, Ar), 7.47-7.43 (m, 2H, Ar), 7.43-7.41 (m, 1H, Ar), 7.40-7.34 (m, 1H, Ar), 7.29 -7.25 (m, 1H, Ar), 7.22 (d, *J* = 2.6 Hz, 1H, Ar), 7.01 (d, *J* = 15.7 Hz, 1H, CH=CH), 3.98 (s, 3H, OCH_3) (Fig. S21). ^{13}C NMR (300 MHz, $CDCl_3$): δ 171.330, 159.485, 149.318, 130.316, 129.654, 129.405, 128.945, 127.910, 127.862, 127.652,

127.105, 126.214, 120.321, 113.728, 113.095, 105.774, 82.105, 77.342, 77.227, 77.016, 76.700, 55.522 ppm (Fig. S22). IR (KBr pellet, cm^{-1}): 2280, 1618, 1587, 1564, 1548, 1508, 1488, 1469, 1442, 1428, 1401, 1356, 1205, 1172, 1140, 1115, 1060, 1009, 990, 944, 912, 880, 835, 781, 732, 716, 665, 640 (Fig. S23).

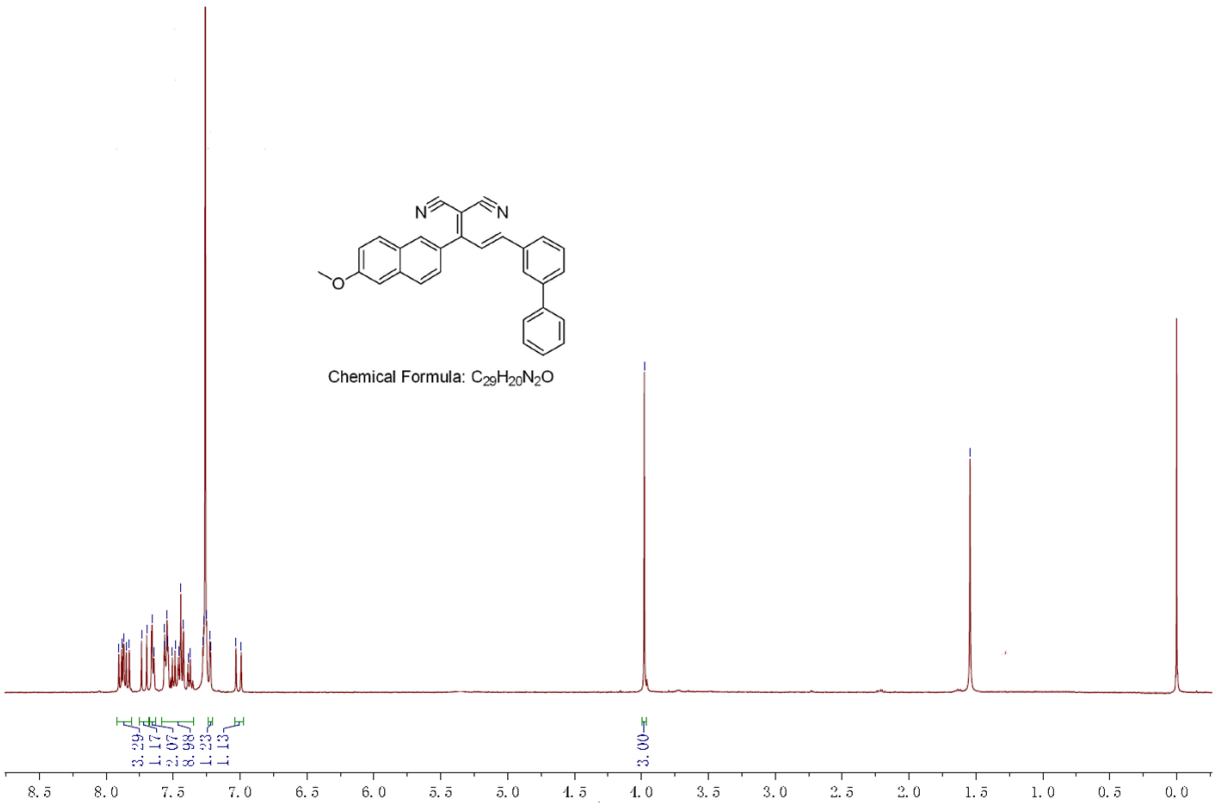

Fig. S21 The ^{1}H-NMR spectra of ***m*-BMNM**

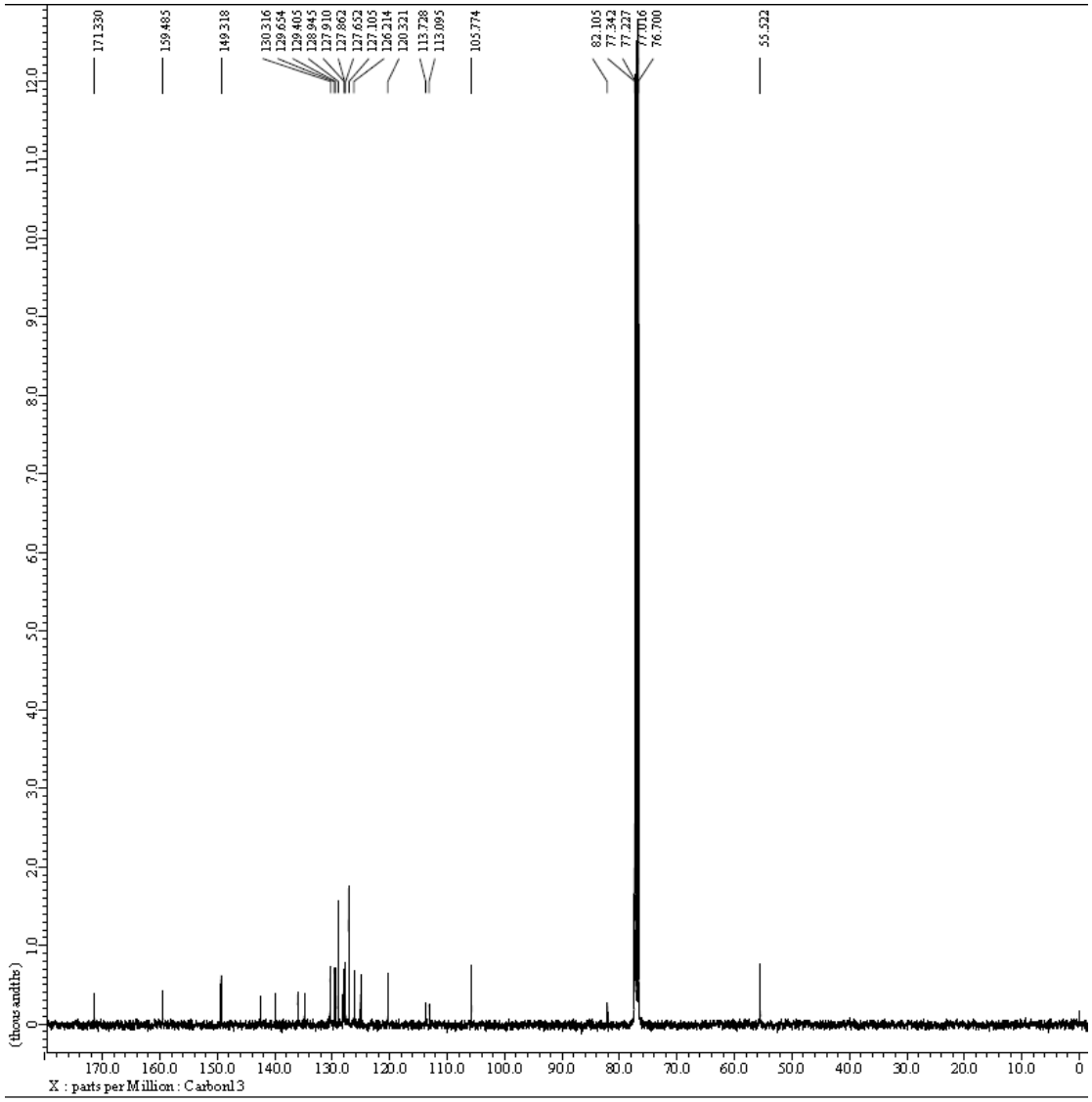

Fig. S22 The ^{13}C-NMR spectra of ***m*-BMNM**

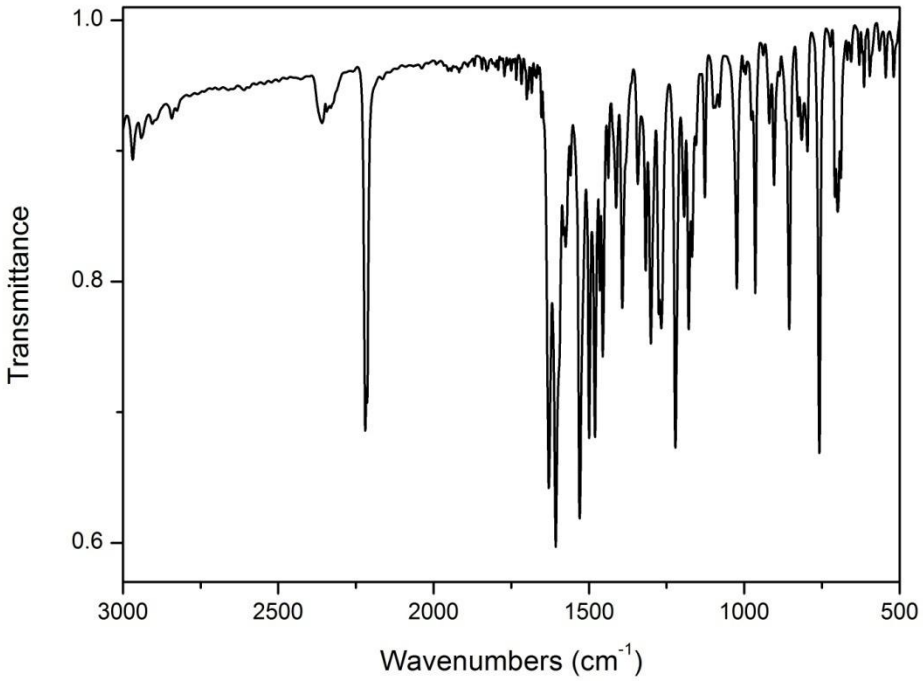

Fig. S23 The IR spectra of ***m*-BMNM**