Supporting Information

Carbazole-benzimidazole based dyes for acid responsive ratiometric emissive switches

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Table S1: Absorbance, Emission peaks and fluorescence quantum yields in different solvents for **CBIM1**.

Solvents	n-hexane	toluene	THF	DCM	CH_3CN	DMSO	MeOH/H_2O (1/1)
Absorbance Peak (nm)	317	319	320	323	320	324	322
Emission Peak (nm)[a]	382	385	385	387	385	388	384
Fluorescence Quantum Yield (Φ)[b]	0.18	0.23	0.29	0.14	0.23	0.30	0.25
[a] excitation wavelength (nm) is 340 nm; [b] Φ was obtained by compared with anthracene (Φ = 0.27 in ethanol)							

Solvents	n-hexane	toluene	THF	DCM	CH_3CN	DMSO	MeOH/H_2O (1/1)
Absorbance Peak (nm)	353 nm	356 nm	350 nm	352 nm	343 nm	358 nm	353 nm
Emission Peak (nm)[a]	429 nm	445 nm	448 nm	456 nm	465 nm	473 nm	481 nm
Fluorescence Quantum Yield (Φ)[b]	0.49	0.50	0.44	0.57	0.47	0.58	0.62
[a] excitation wavelength (nm) is 370 nm; [b] Φ was obtained by compared with fluorescein (Φ = 0.97 in 1 N NaOH solution)							

Table S2: Absorbance, Emission peaks and fluorescence quantum yields in different solvents for **CBIM2**.

Table S3: Absorbance, Emission peaks and fluorescence quantum yields in different solvents for **CBIM3**.

Solvents	n-hexane	toluene	THF	DCM	CH_3CN	DMSO	MeOH/H_2O (1/1)
Absorbance Peak (nm)	317	319	320	323	320	324	323
Emission Peak (nm)[a]	382	385	385	387	385	388	384
Fluorescence Quantum Yield (Φ)[b]	0.18	0.23	0.29	0.14	0.23	0.30	0.25
[a] excitation wavelength (nm) is 340 nm; [b] Φ was obtained by compared with anthracene (Φ = 0.27 in ethanol)							

Computational Study:

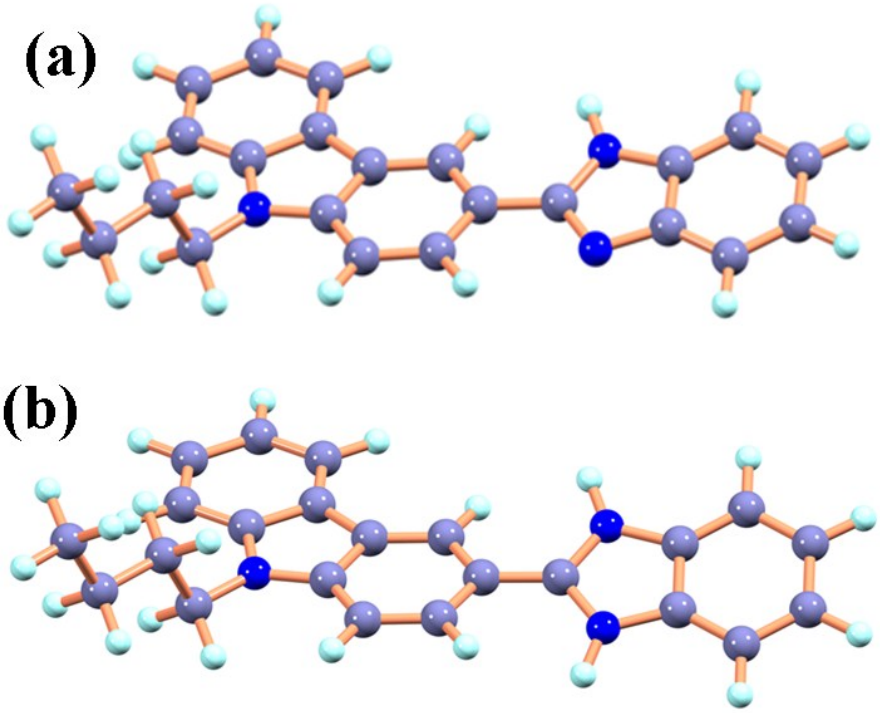


Figure S1: Optimized structure of (a) CBIM1 and (b) CBIM1-H^+ calculated by DFT/B3LYP/6-31+G(d) method.

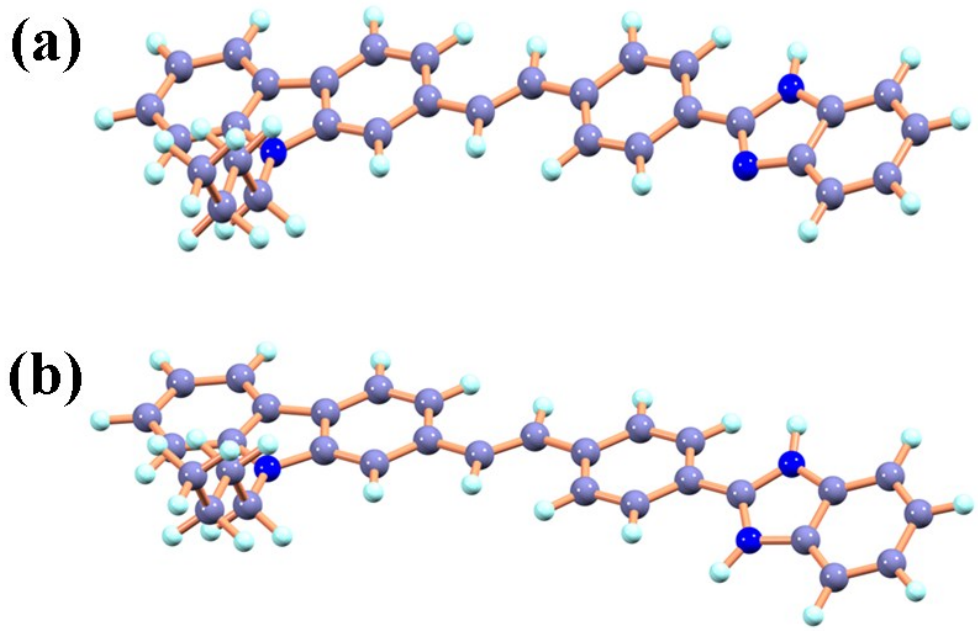


Figure S2: Optimized structure of (a) CBIM2 and (b) CBIM2-H^+ calculated by DFT/B3LYP/6-31+G(d) method .

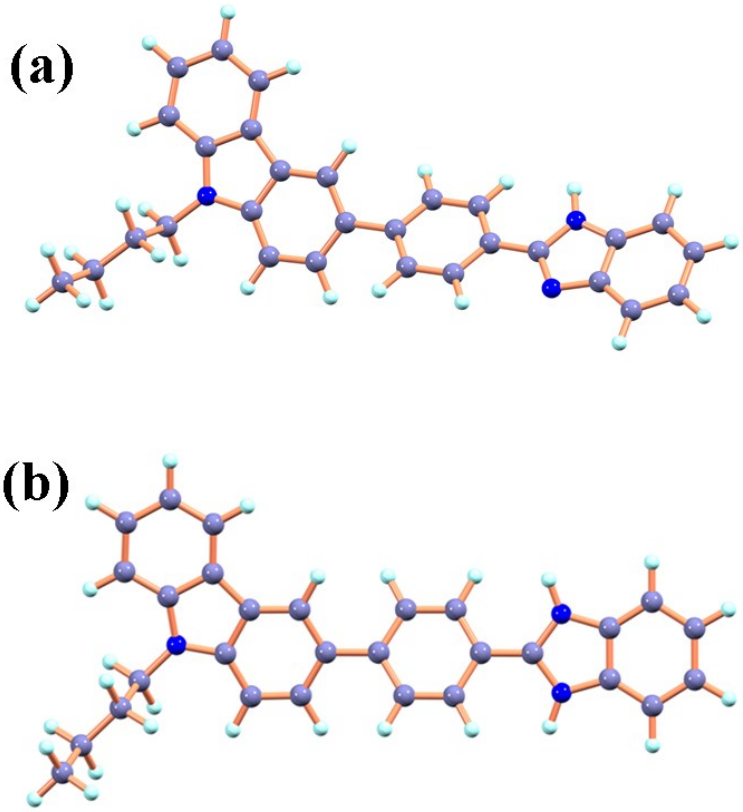


Figure S3: Optimized structure of (a) CBIM3 and (b) CBIM3-H^+ calculated by DFT/B3LYP/6-31+G(d) method.

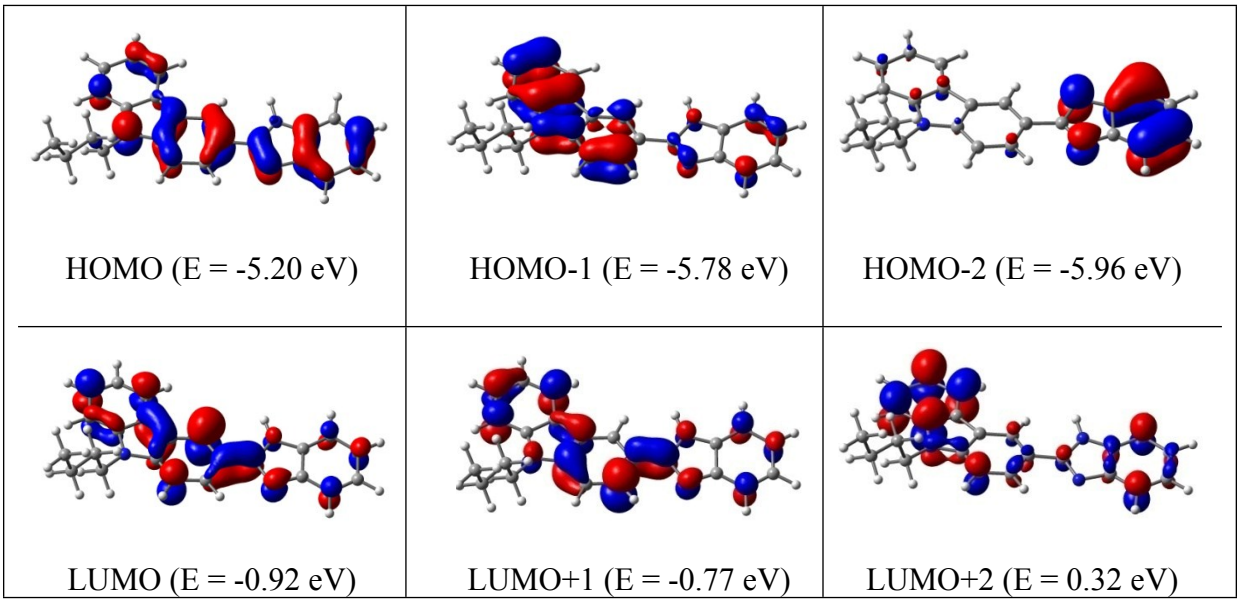


Figure S4: Contour plots of some selected molecular orbitals of CBIM1

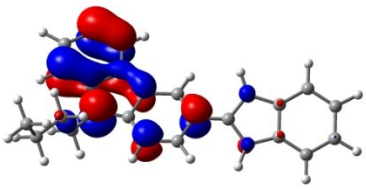
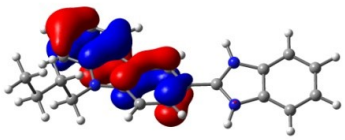
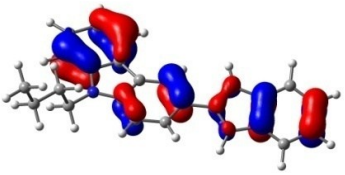
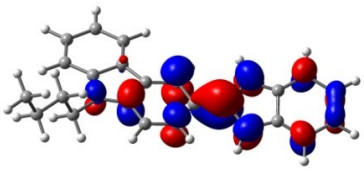
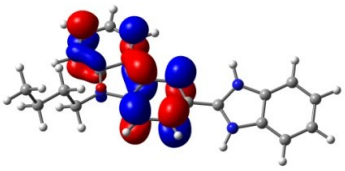
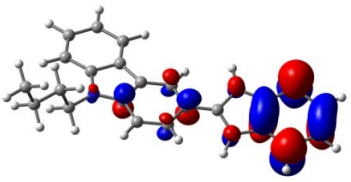
		
HOMO (E = -8.40 eV)	HOMO-1 (E = -8.80 eV)	HOMO-2 (E = -9.64 eV)
		
LUMO (E = -4.99 eV)	LUMO+1 (E = -3.86 eV)	LUMO+2 (E = -3.29 eV)

Figure S5: Contour plots of some selected molecular orbitals of CBIM1-H^+

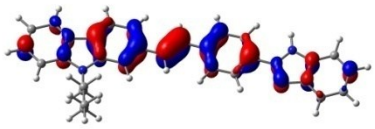
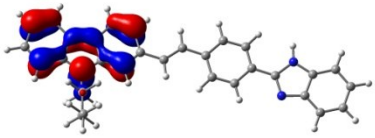
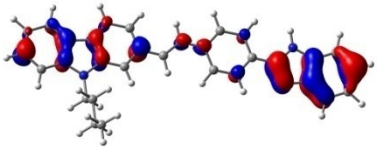
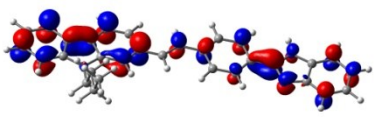
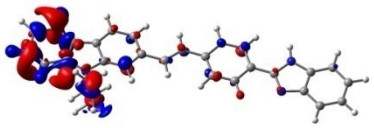
		
HOMO (E = -5.14 eV)	HOMO-1 (E = -5.43 eV)	HOMO-2 (E = -5.84 eV)
		
LUMO (E = -1.75 eV)	LUMO+1 (E = -0.69 eV)	LUMO+2 (E = -0.11 eV)

Figure S6: Contour plots of some selected molecular orbitals of CBIM2

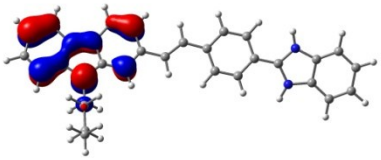
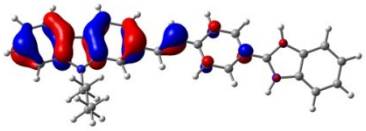
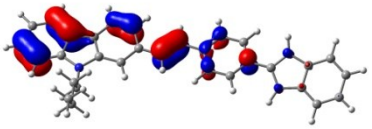
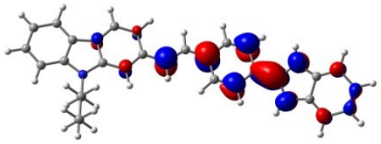
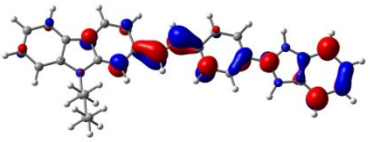
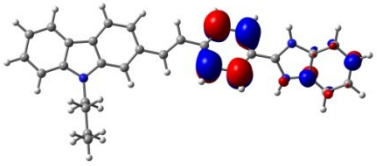
		
HOMO (E = -7.26 eV)	HOMO-1 (E = -7.43 eV)	HOMO-2 (E = -8.69 eV)
		
LUMO (E = -5.23 eV)	LUMO+1 (E = -3.68 eV)	LUMO+2 (E = -3.26 eV)

Figure S7: Contour plots of some selected molecular orbitals of CBIM2-H^+

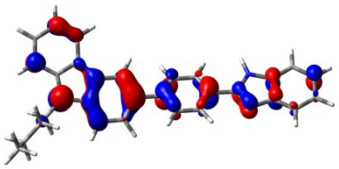
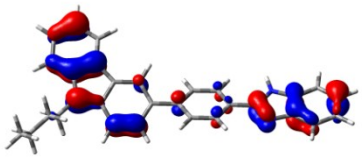
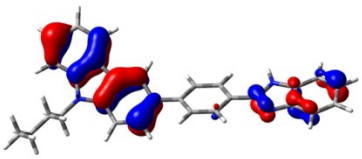
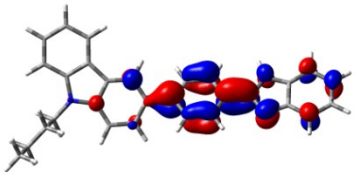
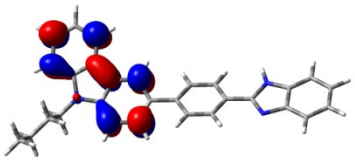
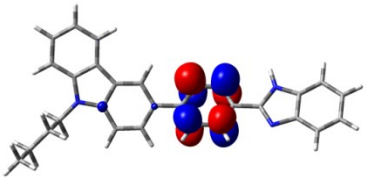
		
HOMO (E = -5.199 eV)	HOMO-1 (E = -5.681 eV)	HOMO-2 (E = -5.858 eV)
		
LUMO (E = -1.221eV)	LUMO+1 (E = -0.797 eV)	LUMO+2 (E = -0.082 eV)

Figure S8: Contour plots of some selected molecular orbitals of CBIM3

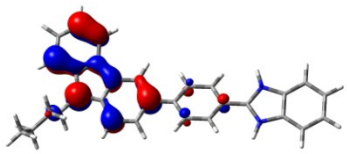
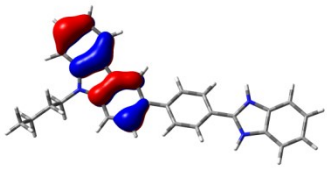
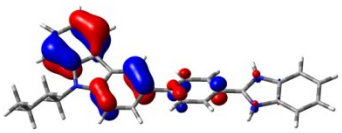
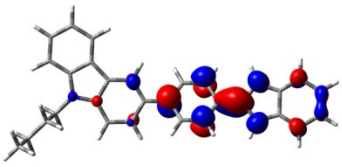
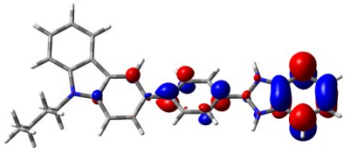
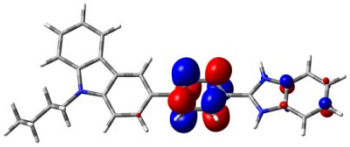
		
HOMO (E = -7.462 eV)	HOMO-1 (E = -7.880 eV)	HOMO-2 (E = -8.764 eV)
		
LUMO (E = -5.117 eV)	LUMO+1 (E = -3.418 eV)	LUMO+2 (E = -3.357 eV)

Figure S9: Contour plots of some selected molecular orbitals of CBIM3-H^+

Table S4: Vertical electronic excitations of CBIM1, CBIM2 and CBIM3 calculated by TDDFT/CPCM method

Compound	Excitation	Excitation wavelength (nm)	Oscillator strength (au)
CBIM1	HOMO→LUMO	330	0.3789
	HOMO→LUMO+1	321	0.5165
	HOMO-1→LUMO	290	0.6328
	HOMO-1→LUMO+1	273	0.1128
CBIM1-H^+	HOMO→LUMO	372	0.6822
	HOMO-1→LUMO	339	0.1043
	HOMO→LUMO+1	307	0.3789
	HOMO-2→LUMO	281	0.4678
CBIM2	HOMO→LUMO	407	0.1247
	HOMO-1→LUMO	389	0.9215
	HOMO-2→LUMO	327	0.2520
CBIM2-H^+	HOMO-1→LUMO	451	0.2835
	HOMO→LUMO	448	0.9928
	HOMO-2→LUMO	341	0.6066

CBIM3	HOMO→LUMO	358	0.9555
	HOMO→LUMO+1	310	0.5251
	HOMO-2→LUMO	294	0.1401
	HOMO→LUMO+3	254	0.4095
CBIM3-H^+	HOMO→LUMO	454	0.8711
	HOMO-1→LUMO	389	0.1133
	HOMO→LUMO+1	317	0.1703
	HOMO-3→LUMO	283	0.1169
	HOMO-1→LUMO+1	270	0.2781

Table S5: Fluorescence life time data of CBIM2

Entry	Φ	τ (ns)	k_r ($10^8 \times s^{-1}$)	k_{nr} ($10^8 \times s^{-1}$)
CBIM2	0.59	0.776	7.60	5.28
CBIM2-H^+	0.78	2.036	3.83	1.08

^{1}H NMR, ^{13}C NMR and HRMS spectra

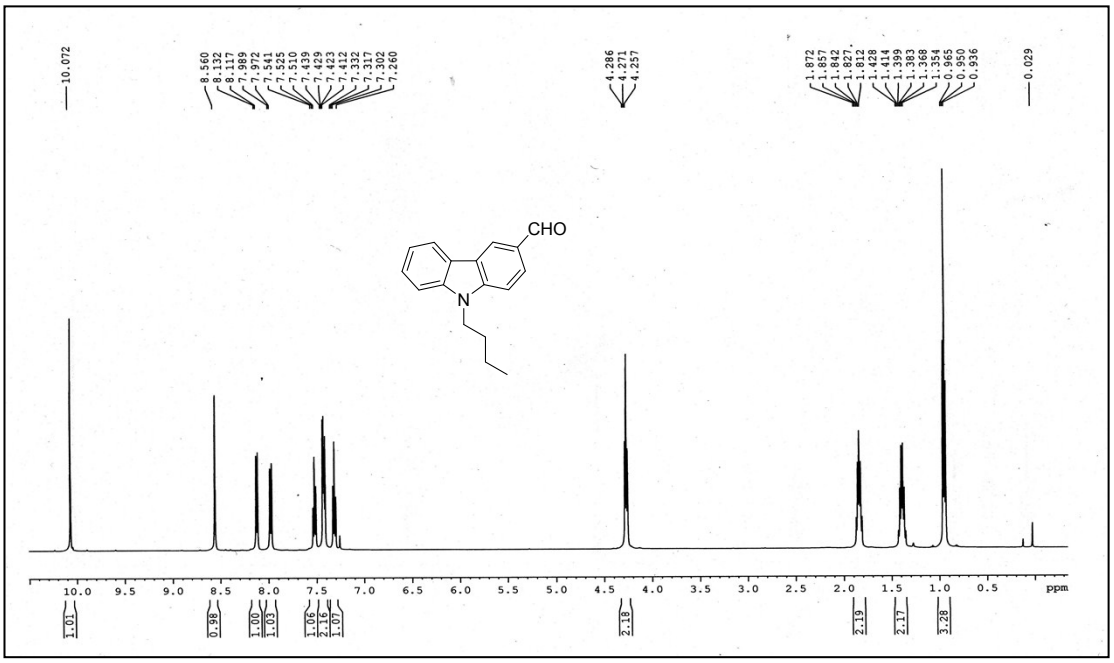


Figure S10: ^{1}H NMR (400 MHz) spectrum of compound 2 in $CDCl_3$

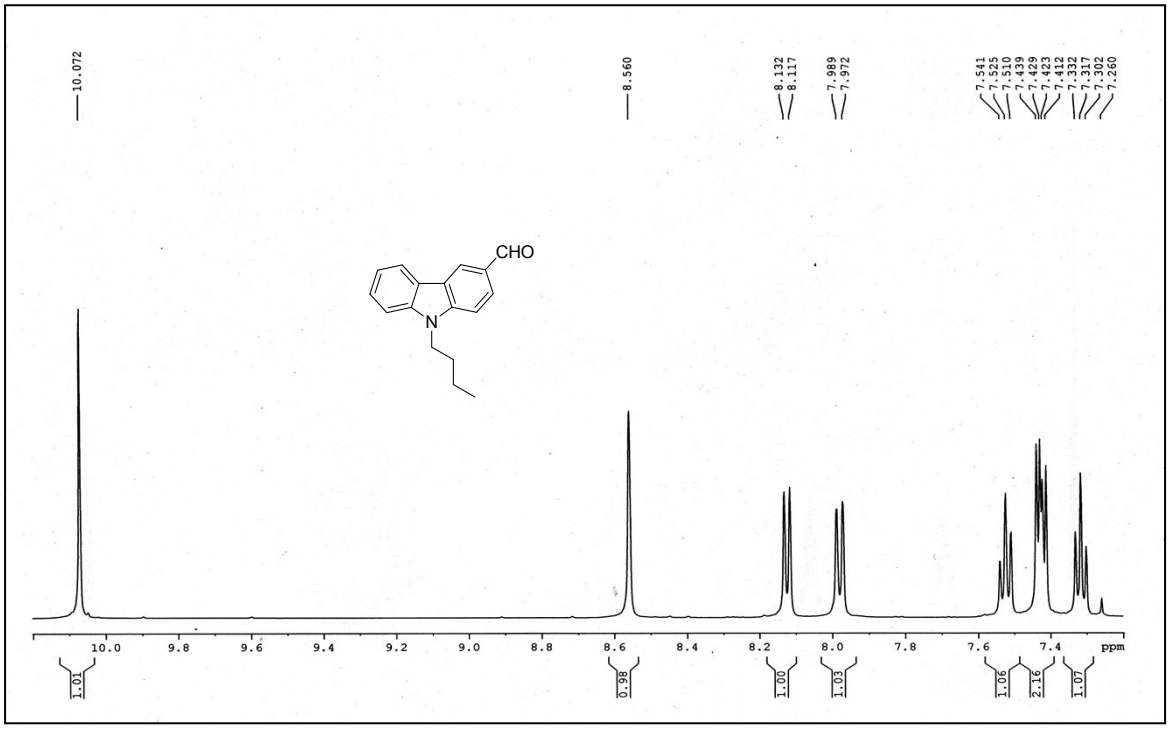


Figure S10a: Expansion mode of ^{1}H NMR (400 MHz) spectrum of compound 2 in $CDCl_3$

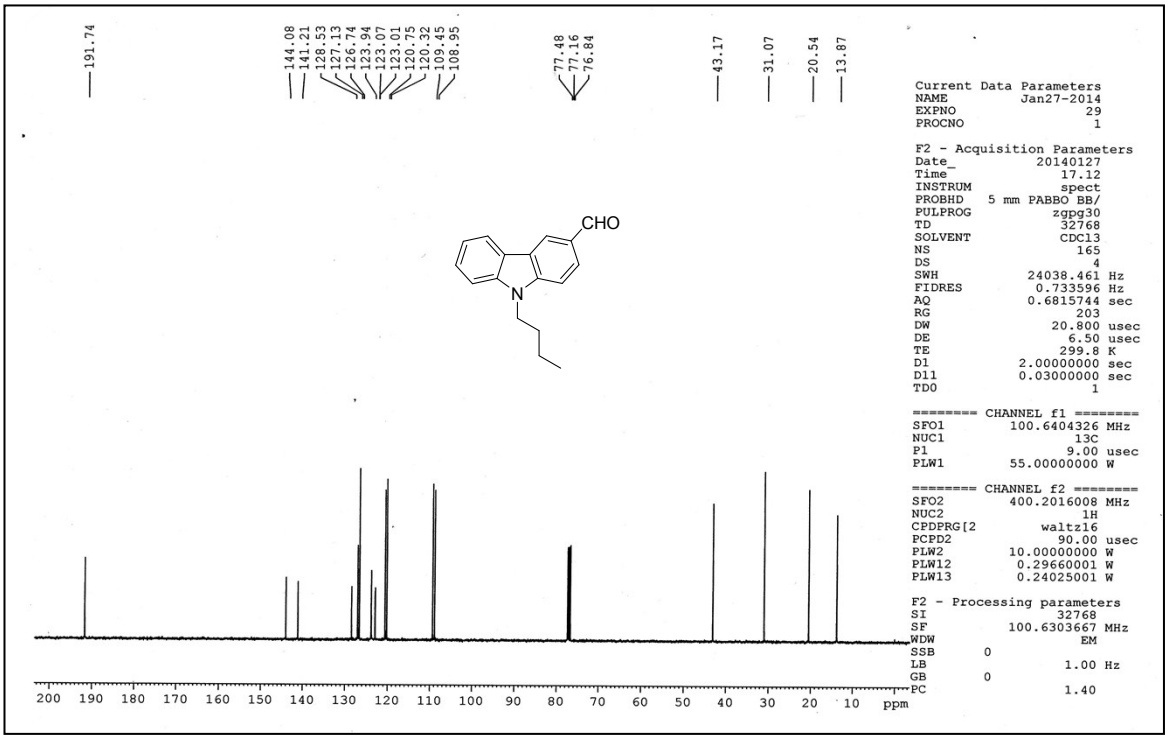


Figure S11: ^{13}C NMR (100 MHz) spectrum of compound 2 in $CDCl_3$

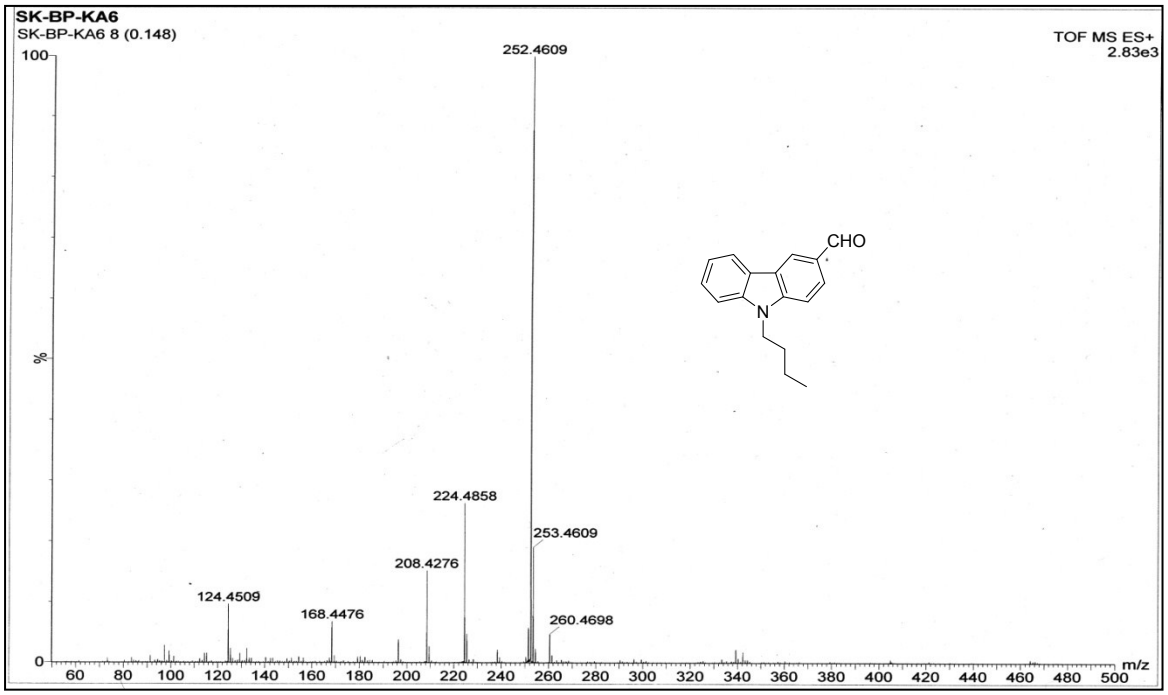


Figure S12: ESI MS spectrum of compound 2

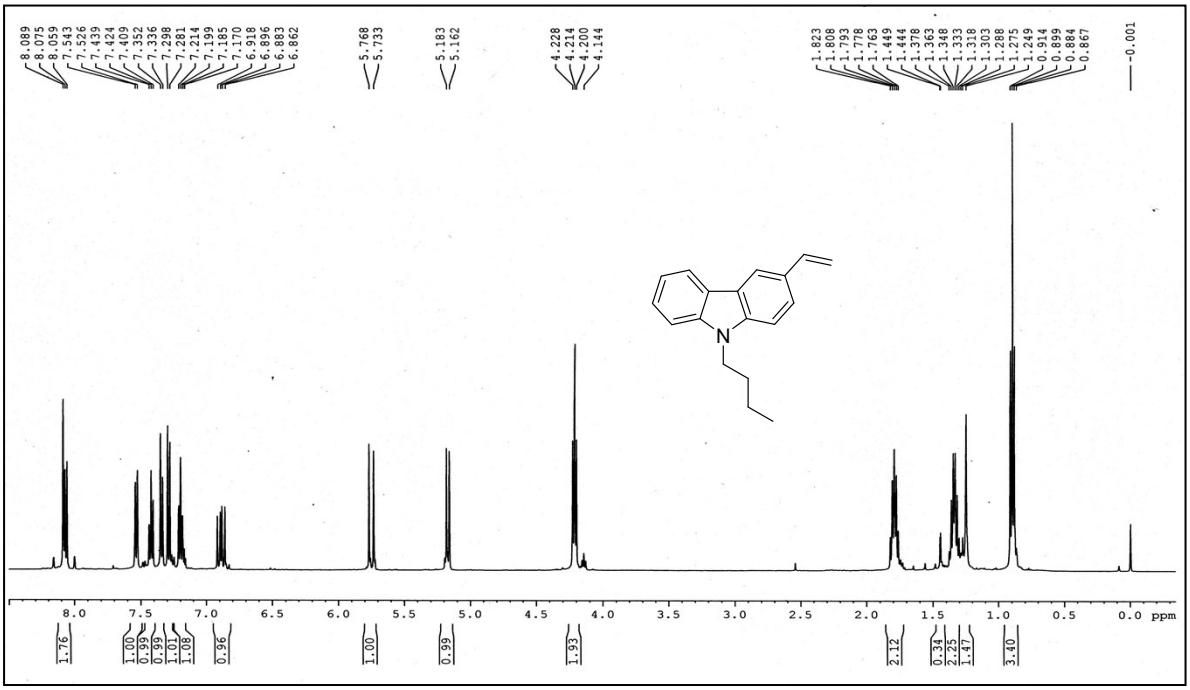


Figure S13: ^{1}H NMR (400 MHz) spectrum of 9-butyl-3-vinyl-9H-carbazole (3) in $CDCl_3$

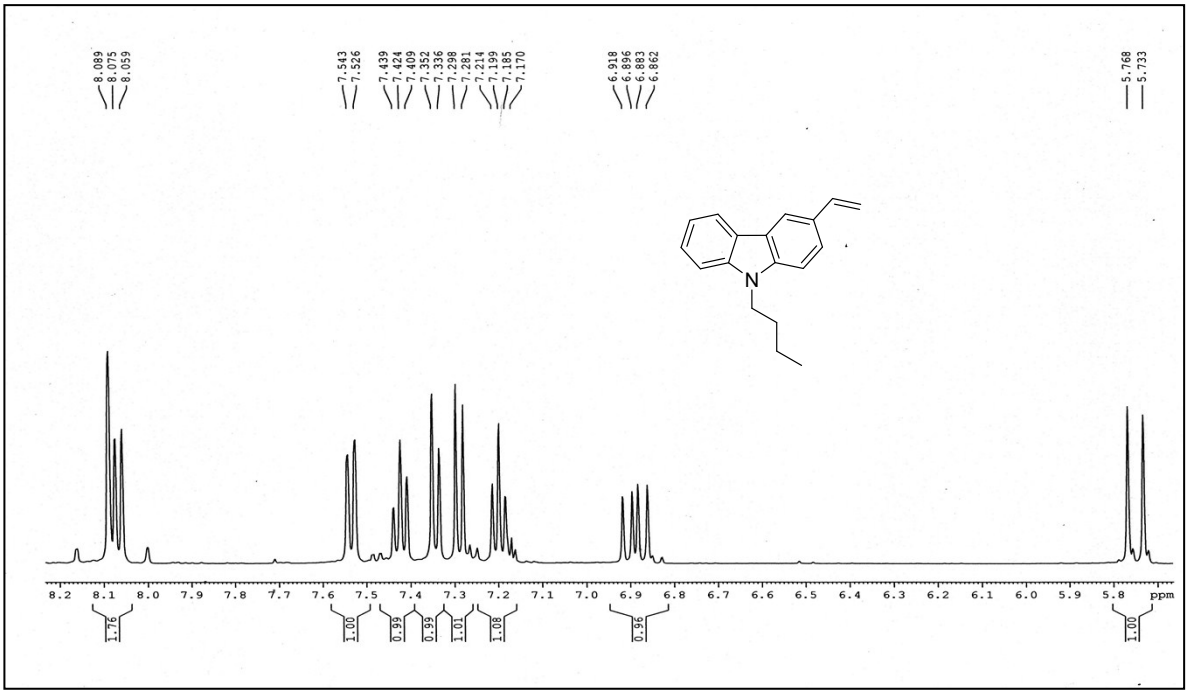


Figure S13a: Expansion mode of ^{1}H NMR (400 MHz) spectrum of 9-butyl-3-vinyl-9H-carbazole (3) in $CDCl_3$

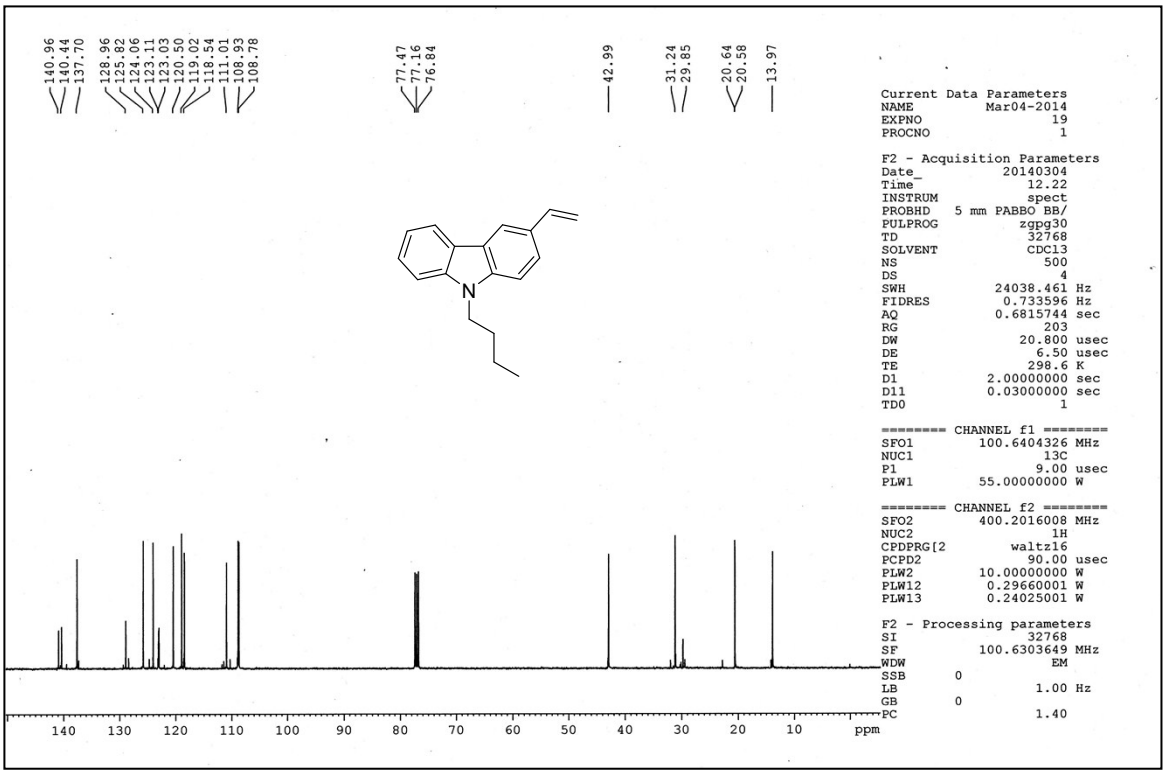


Figure S14: ^{13}C NMR (100 MHz) spectrum of 9-butyl-3-vinyl-9H-carbazole (3) in $CDCl_3$

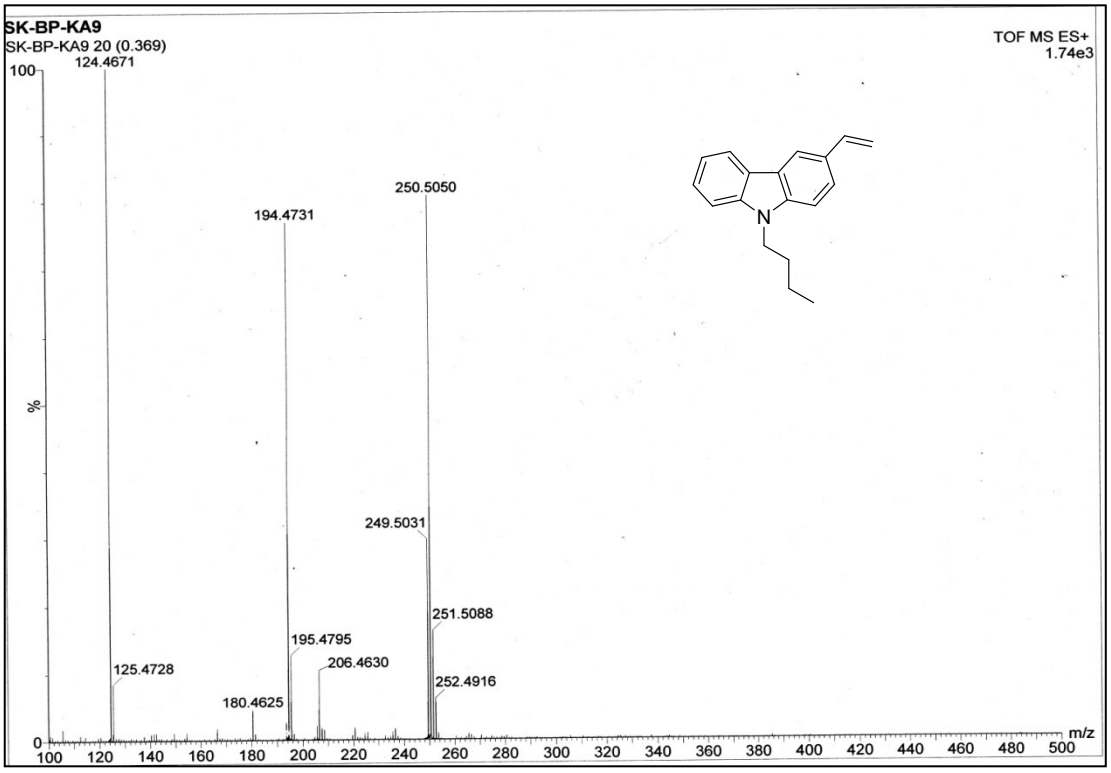


Figure S15: ESI MS spectrum of 9-butyl-3-vinyl-9H-carbazole (3)

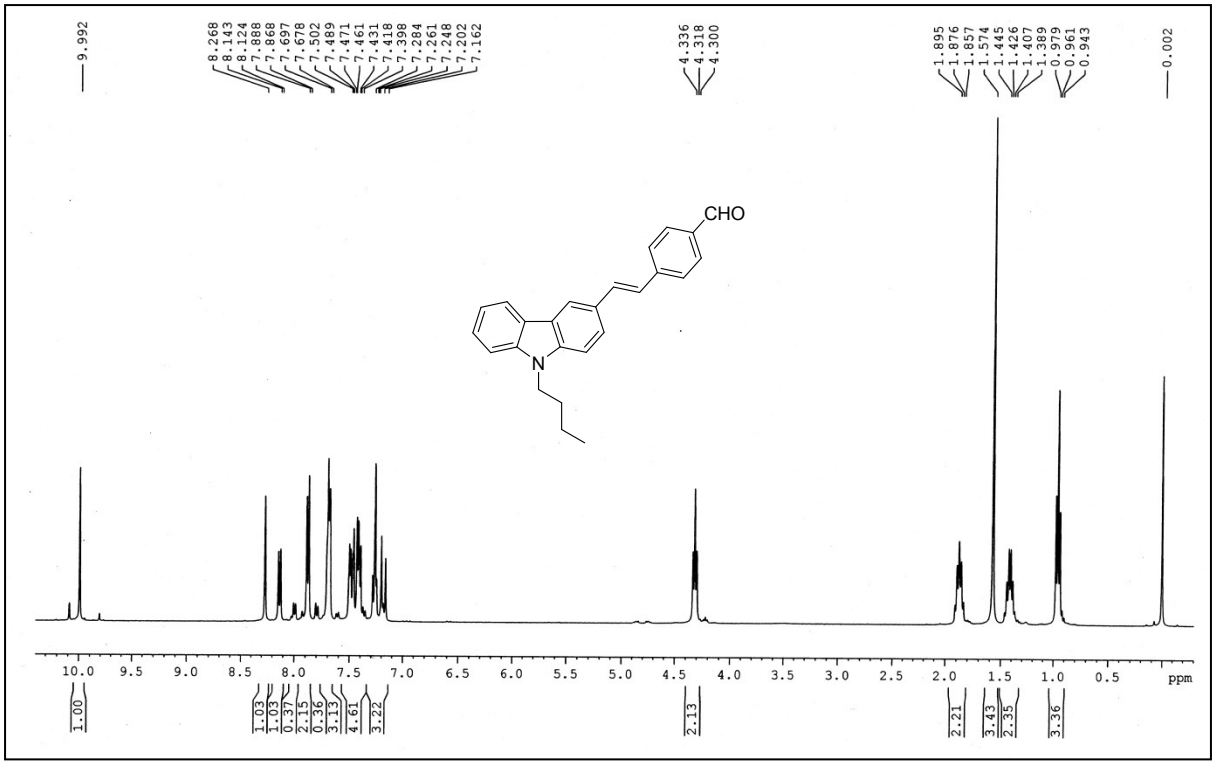


Figure S16: ^{1}H NMR (400 MHz) spectrum of compound 4 in $CDCl_3$

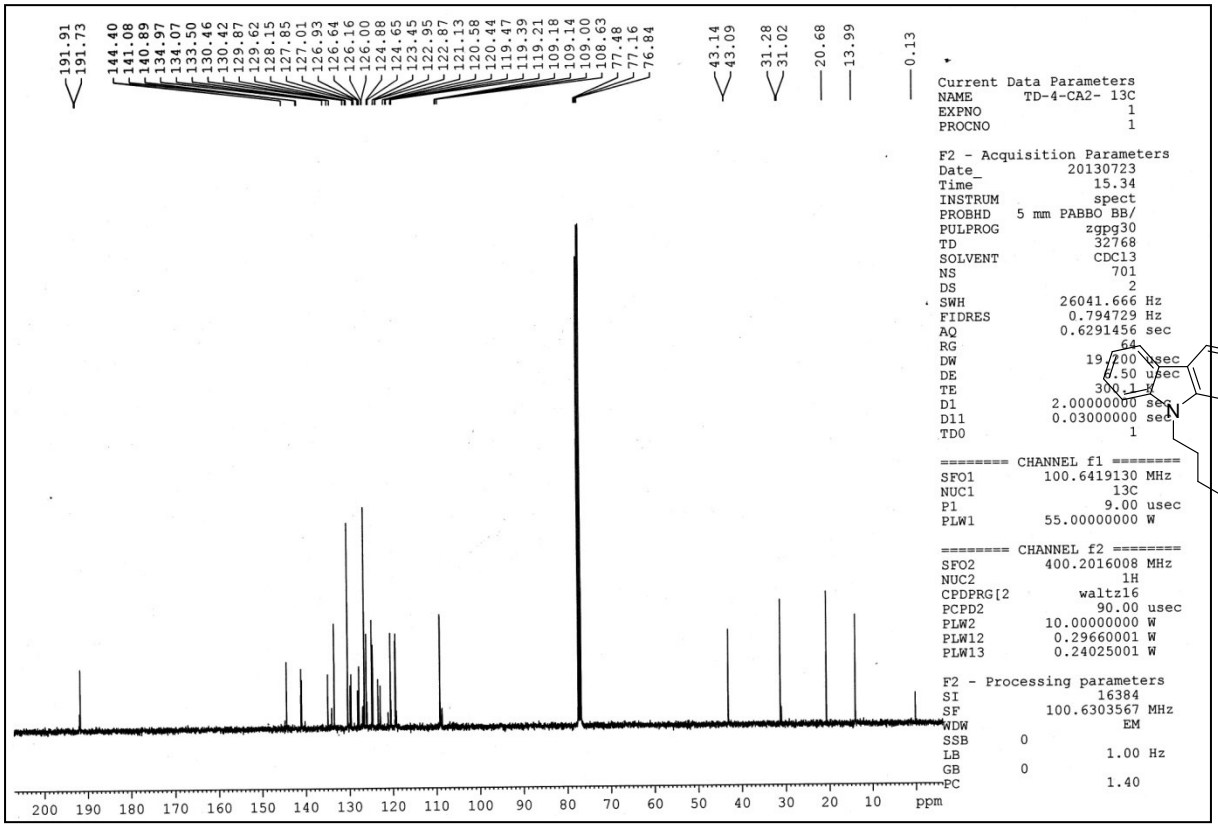


Figure S17: ^{13}C NMR (100 MHz) spectrum of compound 4 in $CDCl_3$

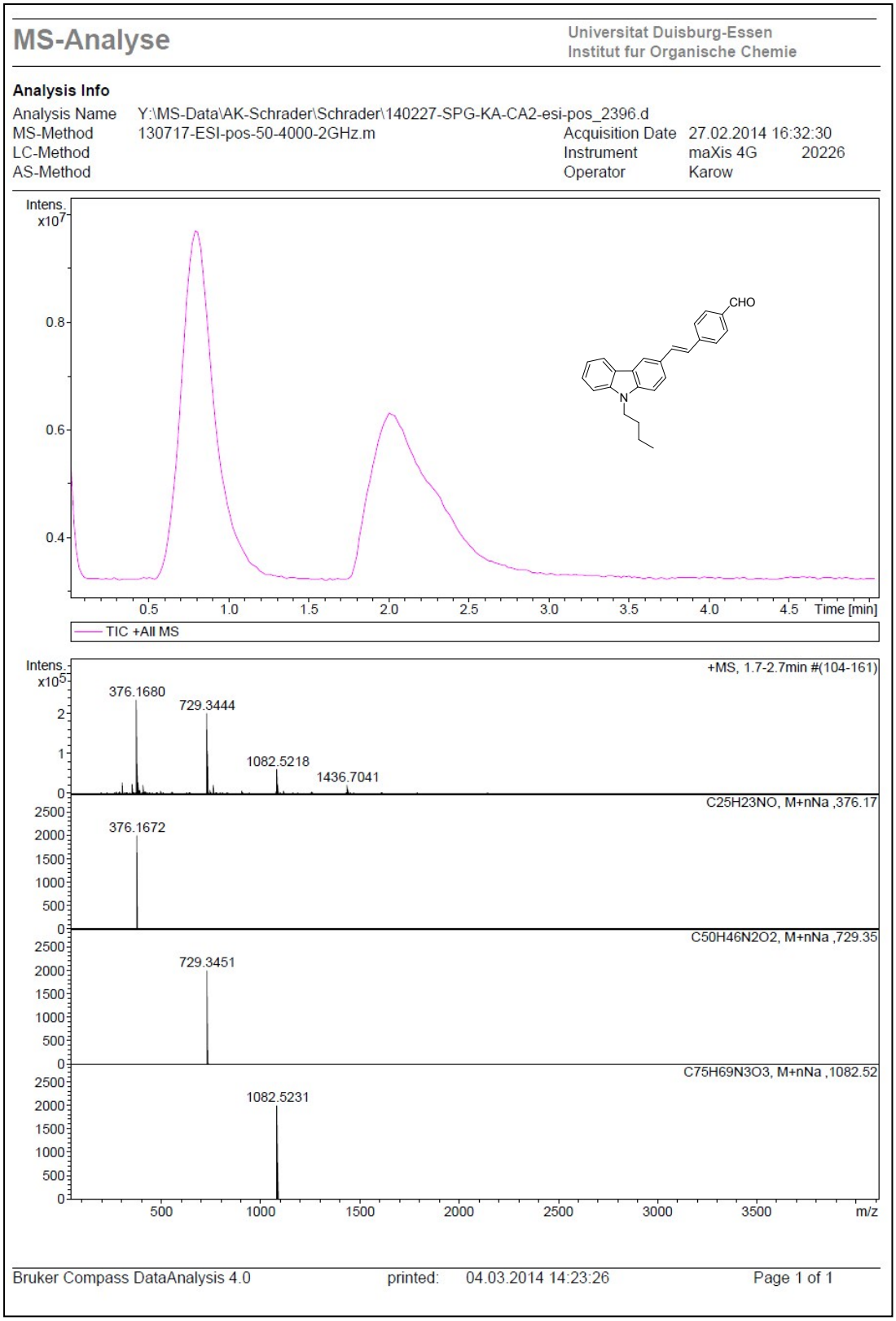


Figure S18: HRMS spectrum of compound 4

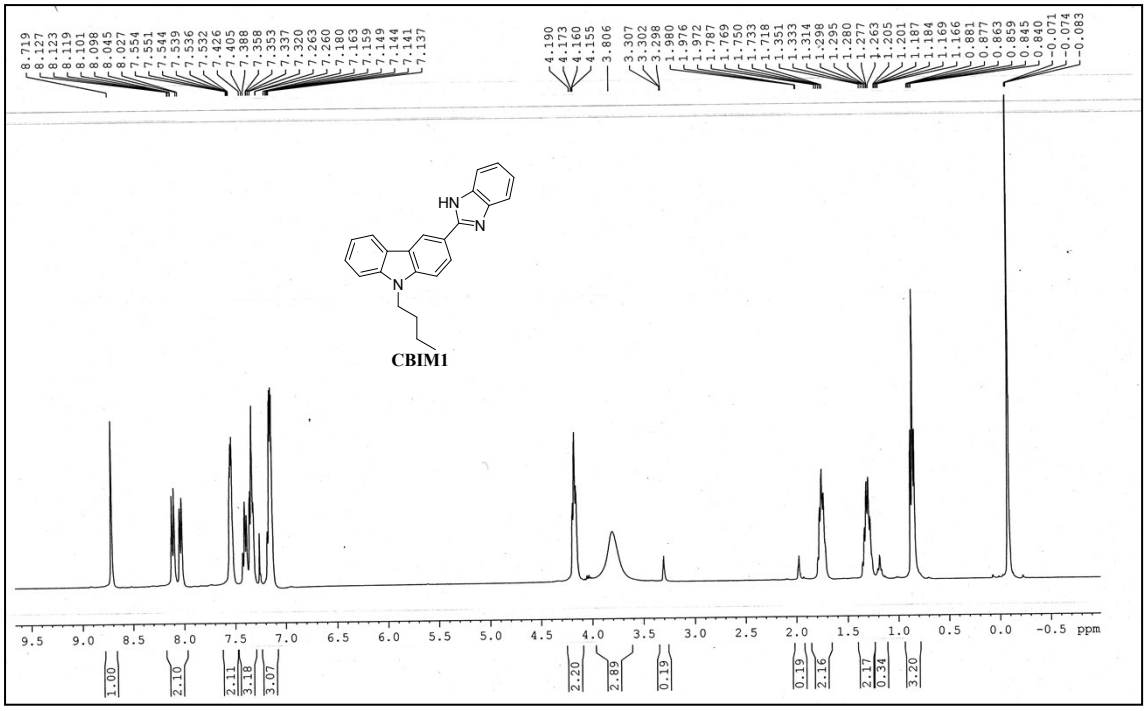


Figure S19: ^{1}H NMR (400 MHz) spectra of CBIM1 in $CDCl_3$

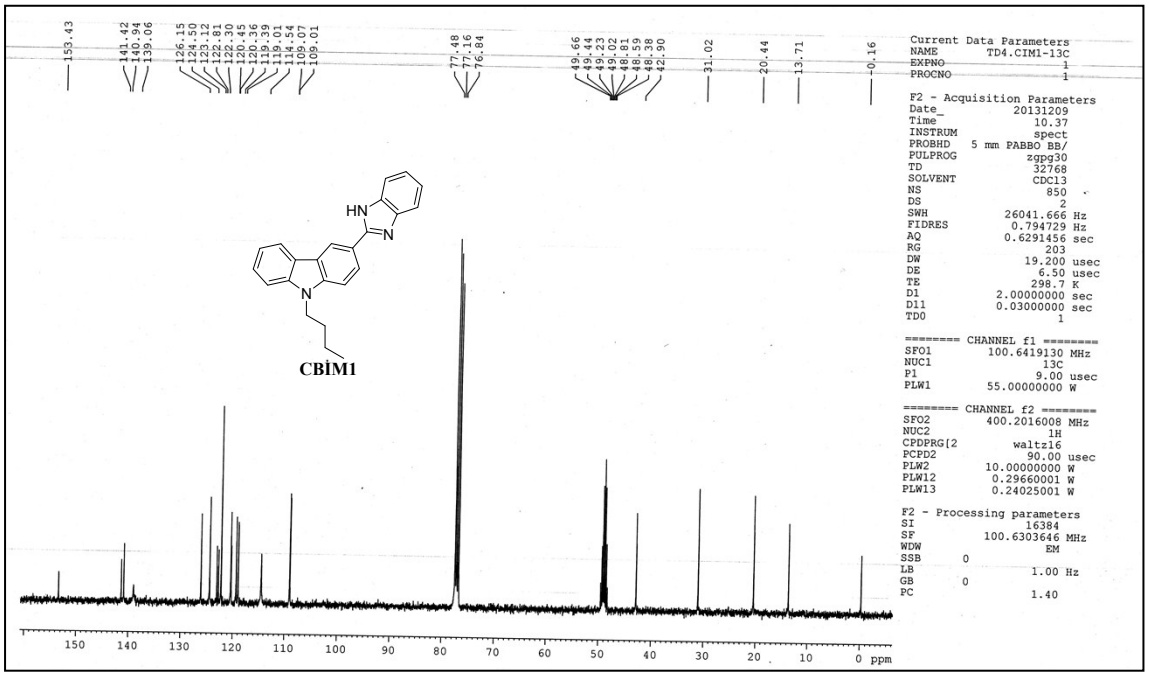


Figure S20: ^{13}C NMR (100 MHz) spectrum of CBIM1 in $CDCl_3$

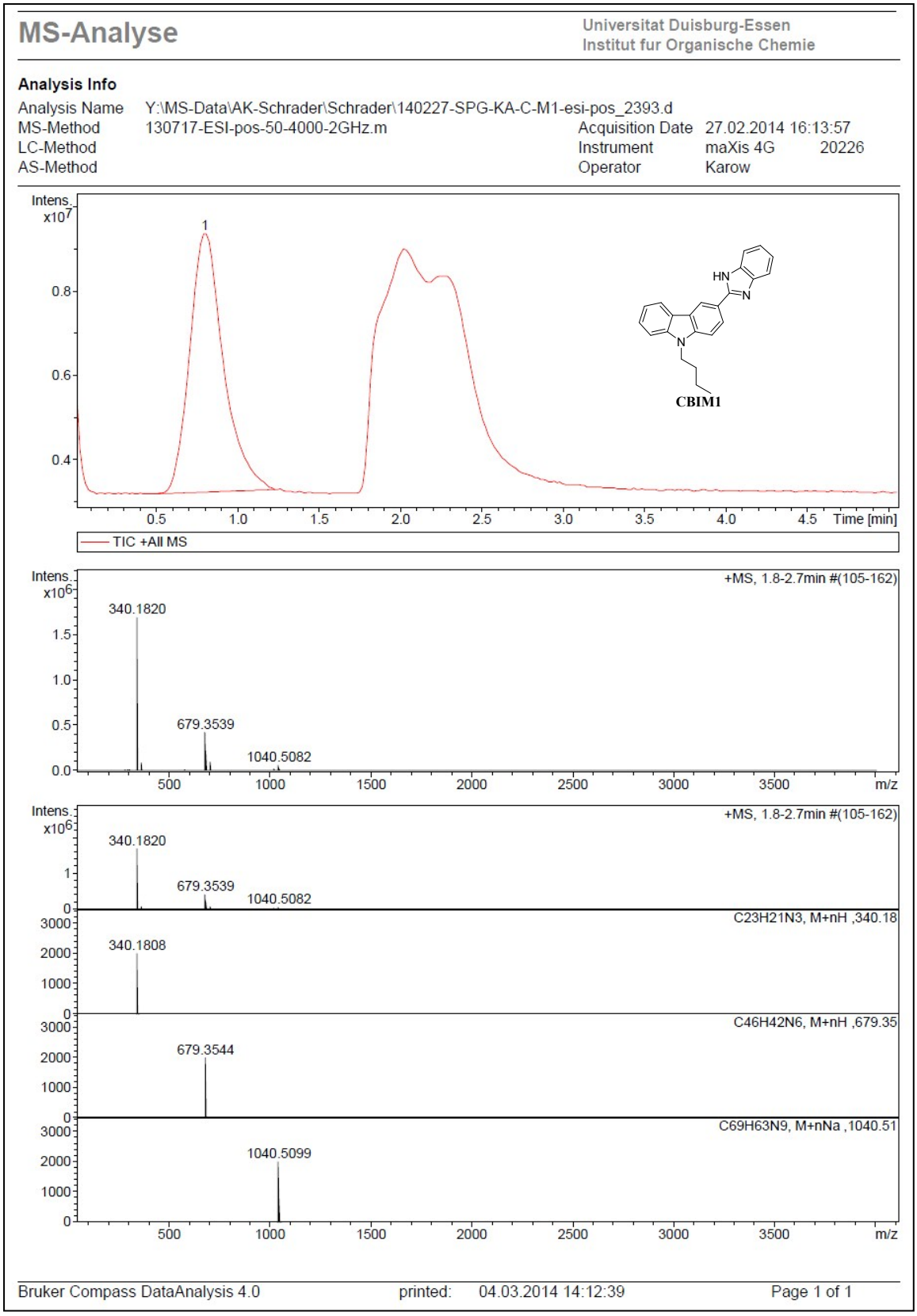


Figure S21: HRMS spectrum of CBIM1

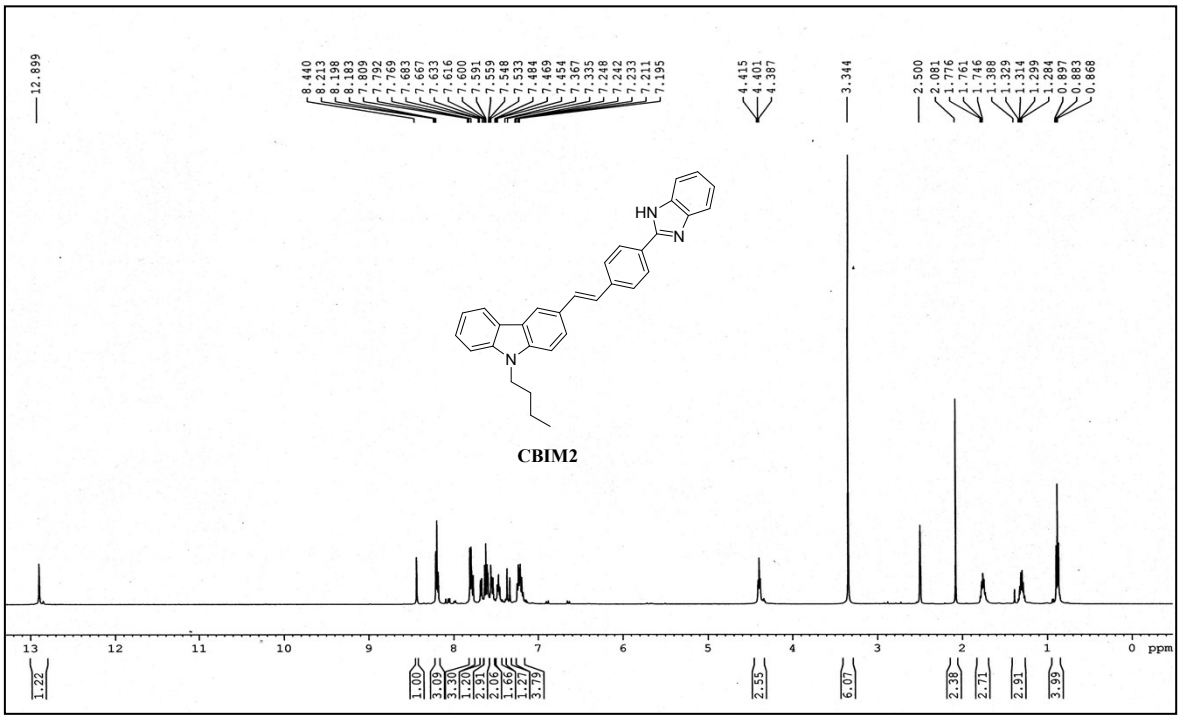


Figure S22: ^{1}H NMR (400 MHz) spectrum of CBIM2 in d_6-DMSO

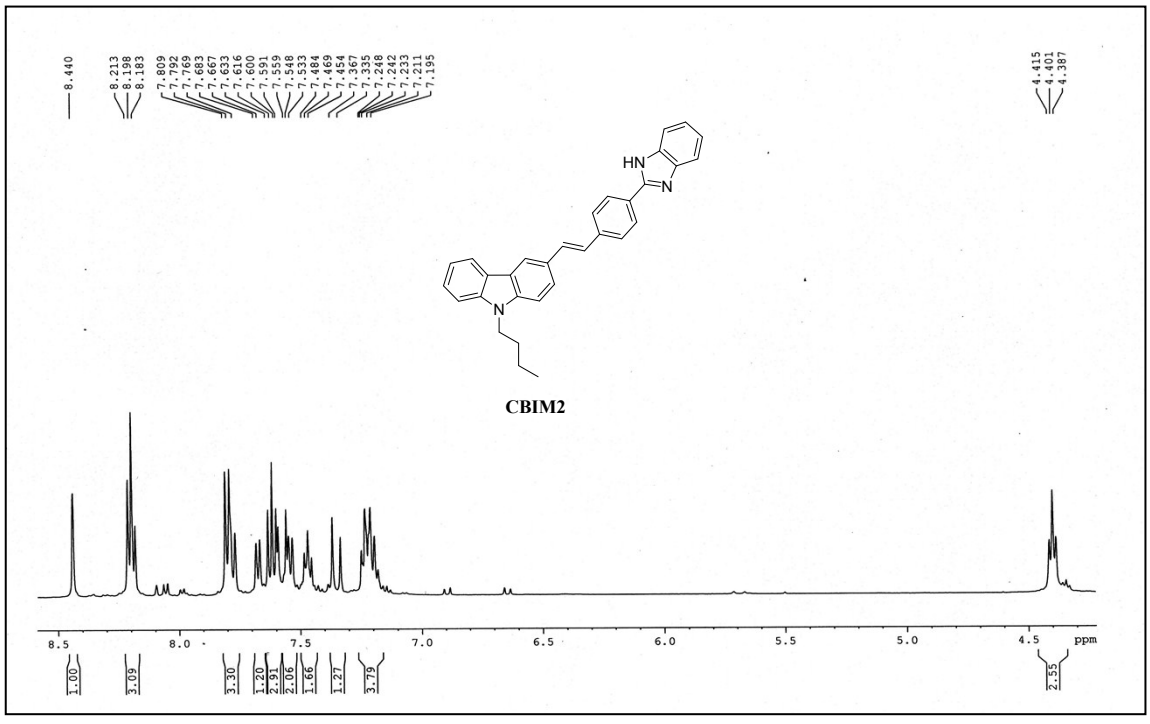


Figure S22a: Expansion mode of ^{1}H NMR (400 MHz) spectrum of CBIM2 in d_6-DMSO

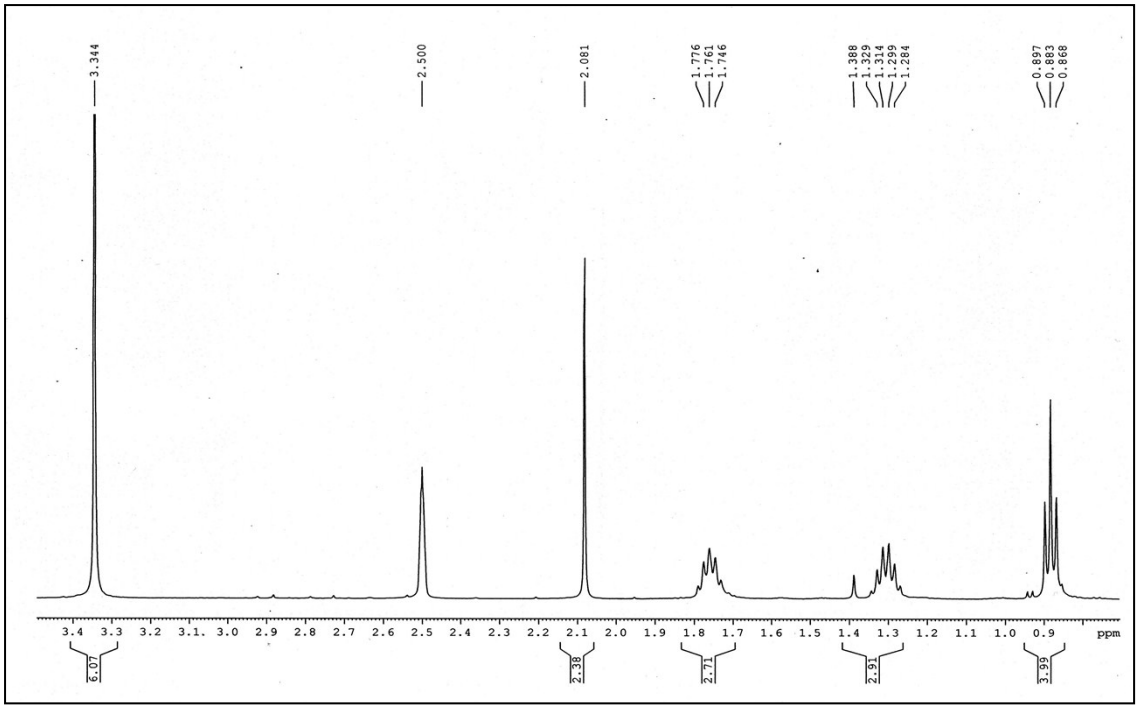


Figure S22b: Expansion mode of ^{1}H NMR (400 MHz) spectrum of CBIM2 in d_6-DMSO

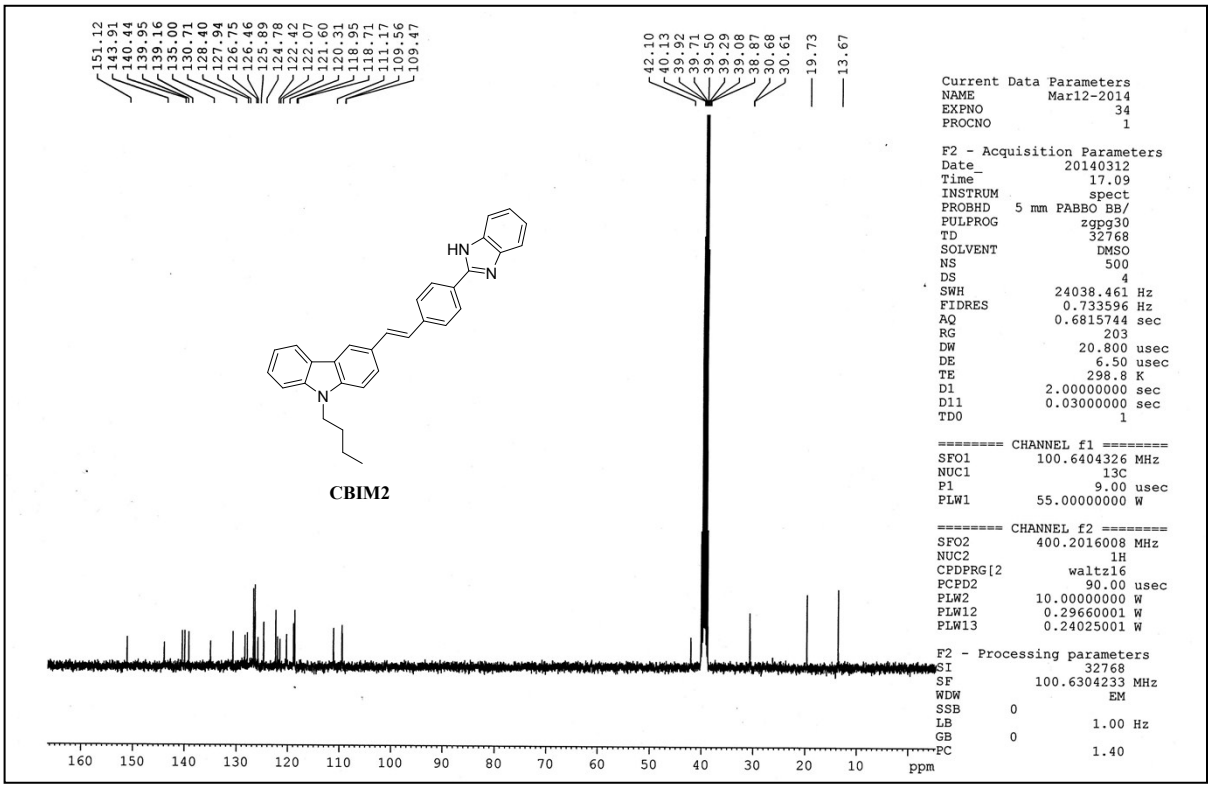


Figure S23: ^{13}C spectrum of CBIM2 in d_6-DMSO

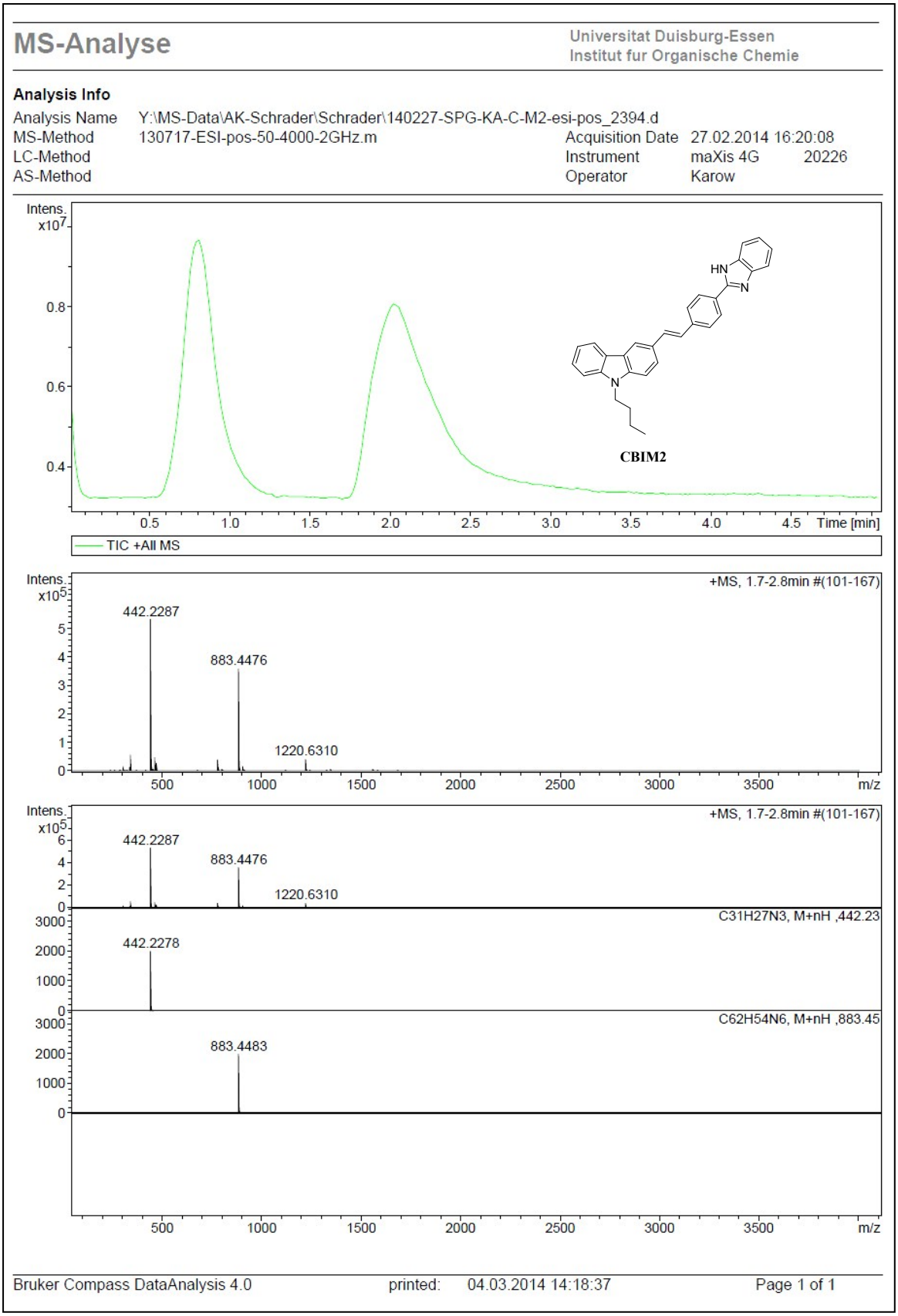


Figure S24: HRMS spectrum of CBIM2

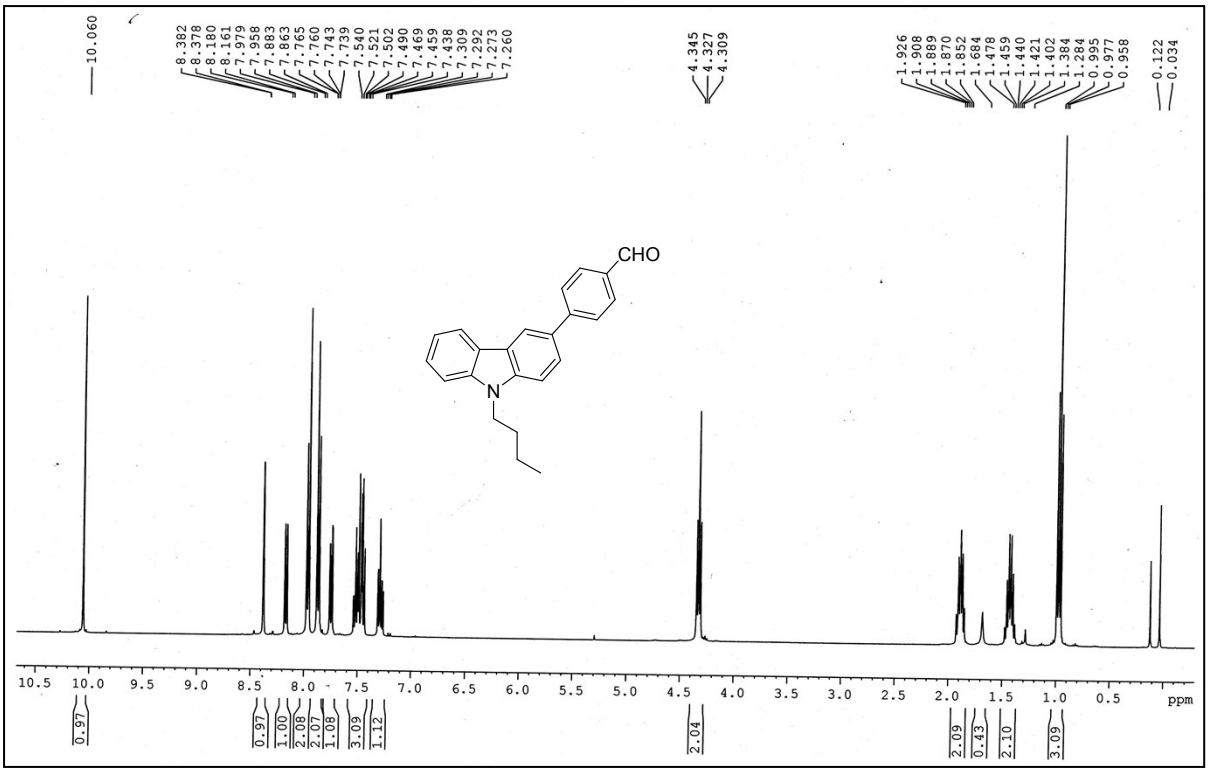


Figure S25: ^{1}H NMR (400 MHz) of compound 6 in $CDCl_3$.

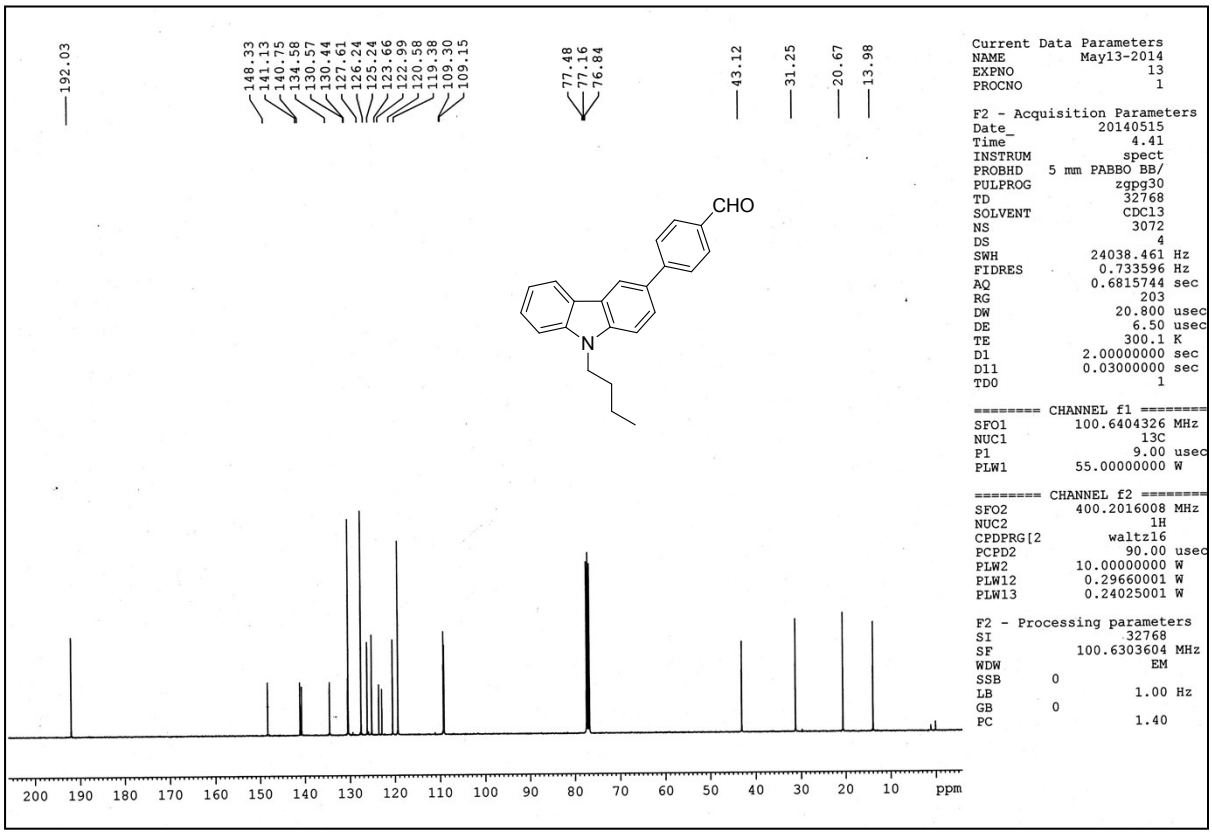


Figure S26: ^{13}C NMR (100 MHz) of compound 6 in $CDCl_3$.

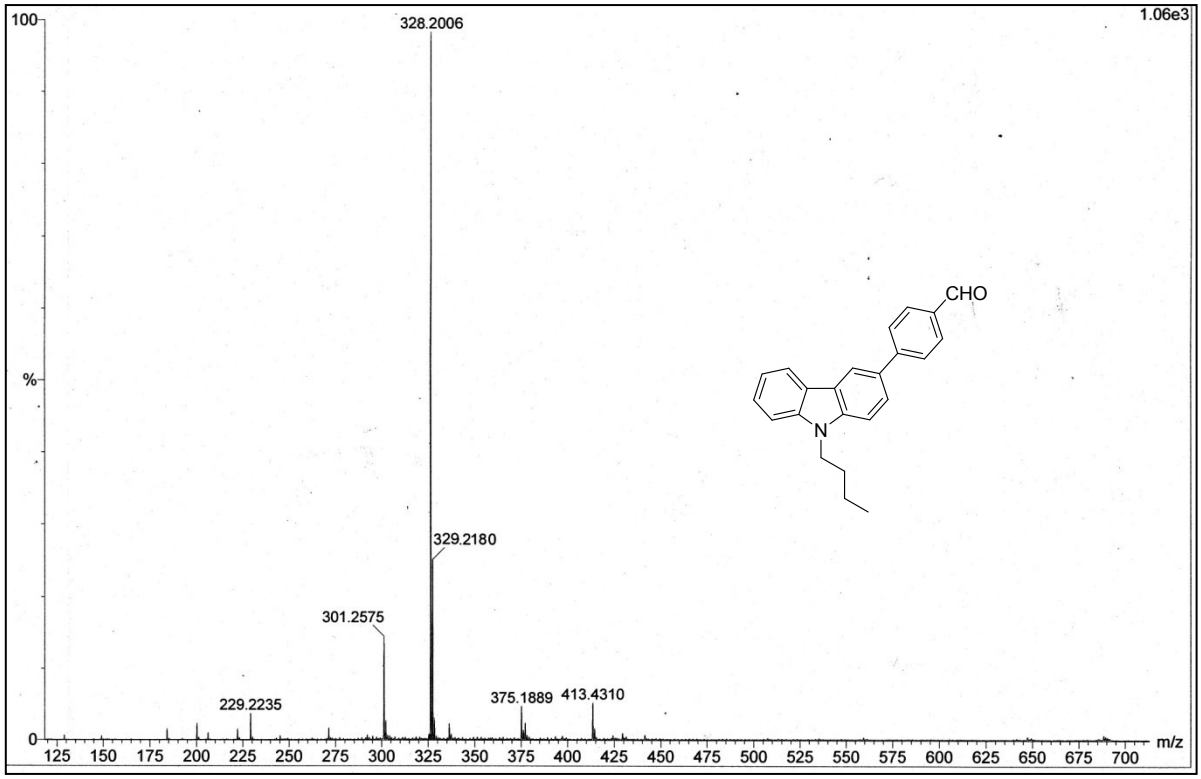


Figure S27: HRMS of compound 6

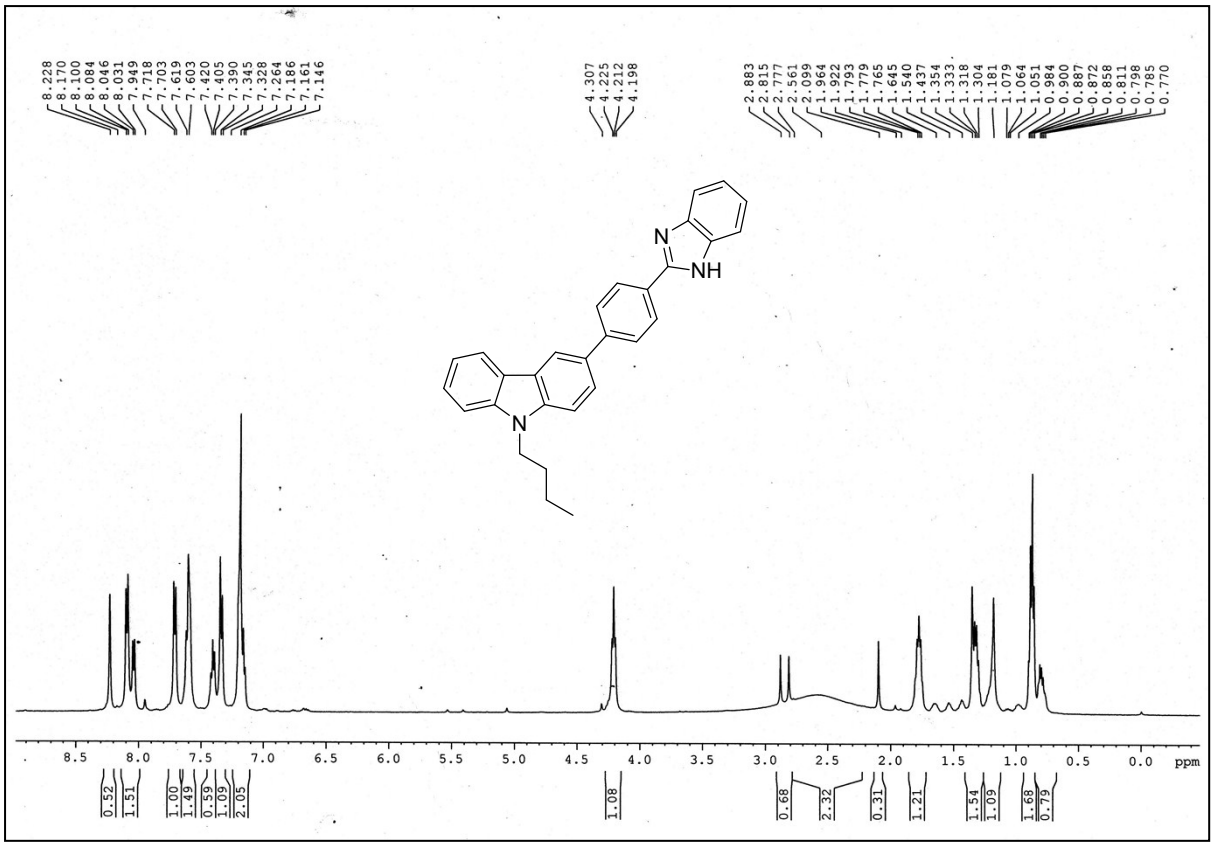


Figure S28: ^{1}H NMR (500 MHz) of CBIM3 in $CDCl_3$.

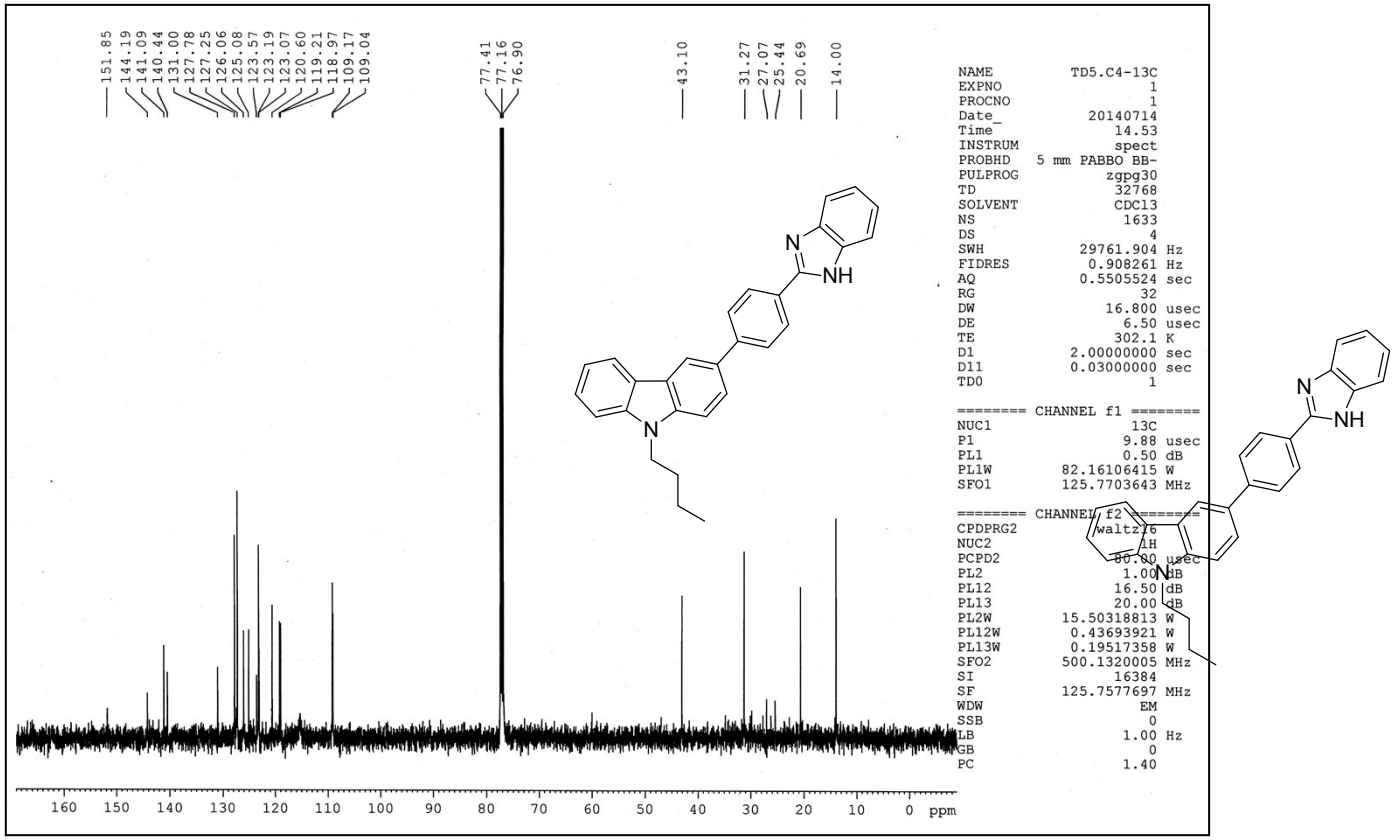
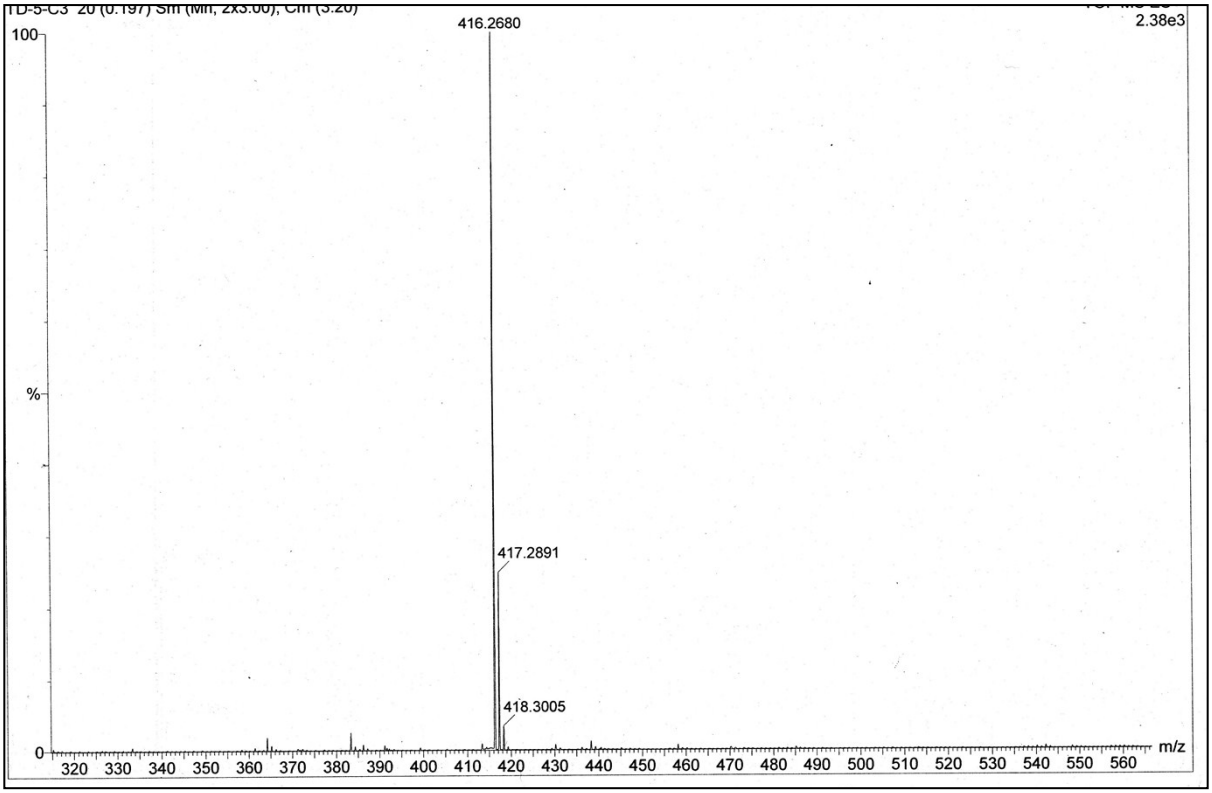


Figure S29: ^{13}C NMR (125 MHz) of CBIM3 in $CDCl_3$

Figure S30: HRMS of CBIM3



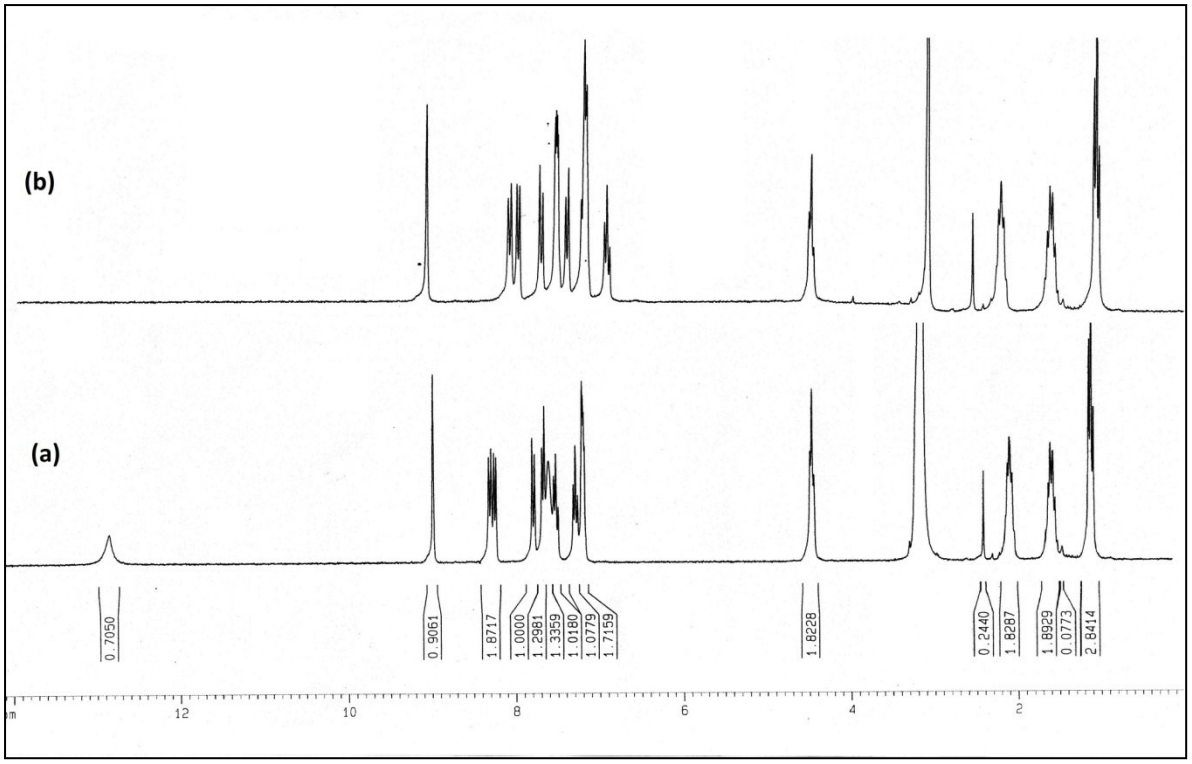


Figure S31: Partial ^{1}H NMR (400 MHz) spectra of (a) CBIM1 (2.5×10^{-3} M) and (b) [CBIM1+ TFA (2.4×10^{-3} M)] in d_6 DMSO.

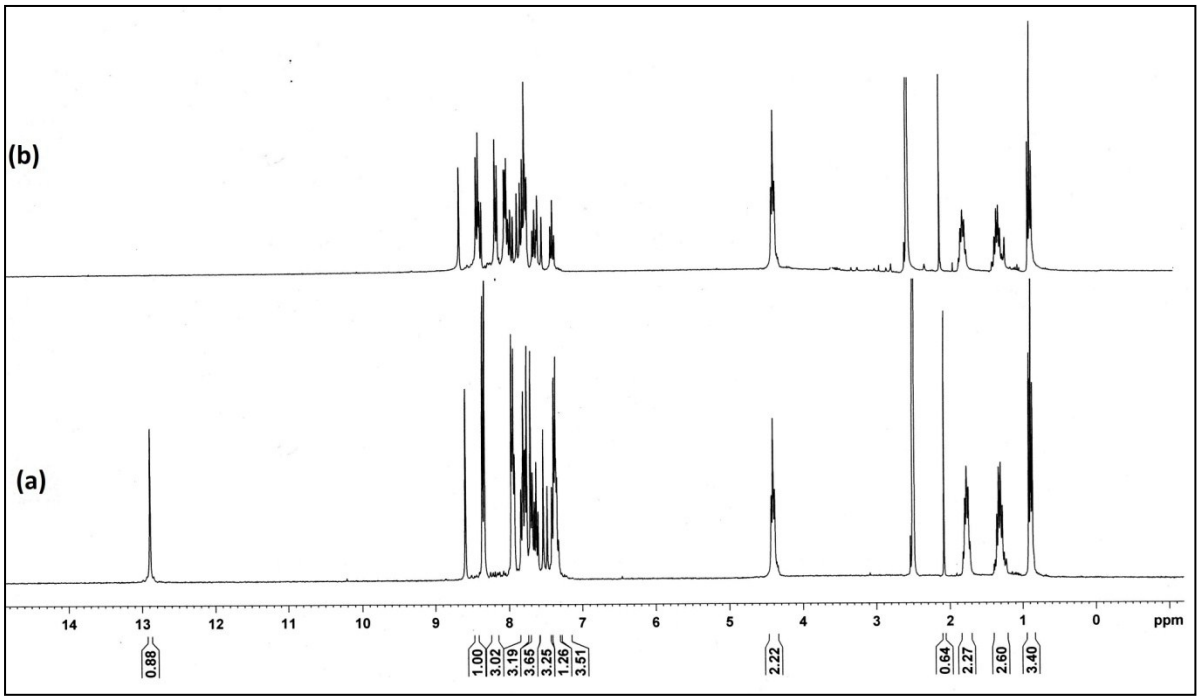


Figure S32: Partial ^{1}H NMR (400 MHz) spectra of (a) CBIM2 (2.0×10^{-3} M) and (b) [CBIM2 + TFA (2.2×10^{-3} M)] in d_6 DMSO.

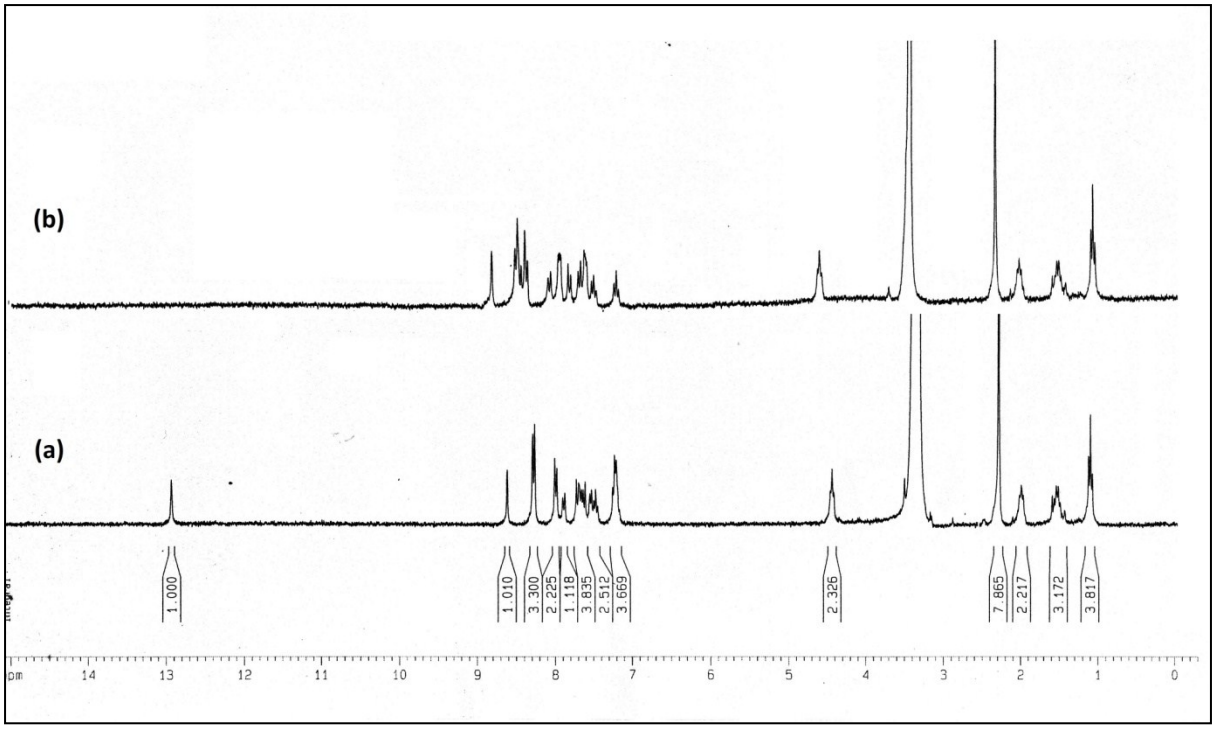


Figure S33: Partial ^{1}H NMR (400 MHz) spectra of (a) CBIM3 (1.2×10^{-3} M) and (b) [CBIM3 + TFA (1.4×10^{-3} M)] in d_6 DMSO.

Table S6: X-ray crystallographic data of compound 4.

Compound	Compound 4
Formula	$C_{25}H_{23}NO$
Formula Weight	353.44
Crystal System	Triclinic
Space Group	*P*-1
T, K	115
Z	4
a,Å	9.5496 (7)
b,Å	113126 (8)
c,Å	18.0480 (13)
α,deg	80.204 (5)
β,deg	86.141 (5)

γ,deg	89.079 (13)
V, Å^3	1916.9 (2)
d_{calcd} , g/cm^3	1.225
μ, mm^{-1}	0.07
Reflections with *I* > 2σ(*I*)	2873
Independent reflections	6765
θ range, deg	1.8–25.0
hkl range	*h* = −11→11 *k* = −13→13 *l* = −21→19
GOF (F^2)	1.05
R_1 (wR_2), %	0.098, 0.327
Completeness, %	99.9
T_{min}, T_{max}	0.945, 0.993

Table S7: Hydrogen-bond geometry (Å, ^{0}) of compound 4

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C24A—H24*A*···O1B^{i}	0.99	2.60	3.330 (8)	131
C22A—H22*B*···Cg1^{ii}	0.99	2.79	3.721 (6)	156
C22B—H22*D*···Cg2^{iii}	0.99	2.90	3.760 (6)	145

Symmetry code: (i) *-x+2, -y+1, -z* (ii) *-1+x,y,z* (iii) *x,y,z*.

* Cg1 and Cg2 are the centroids of the C1B—C3B/C10B—C12B and C1A—C3A/C10A—C12A rings.

Table S8: X-ray crystallographic details of compound 6

Crystal data	
Chemical formula	$C_{23}H_{21}NO$
M_r	327.41

Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	294
a, b, c (Å)	9.7031 (13), 11.7775 (14), 31.570 (4)
β (°)	95.921 (2)
V (Å^3)	3588.6 (8)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.07
Crystal size (mm)	0.77 × 0.56 × 0.27
Data collection	
Diffractometer	Bruker *SMART APEX* II DUO CCD area-detector diffractometer
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.946, 0.980
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26365, 7043, 4208
R_{int}	0.034
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.061, 0.202, 1.04
No. of reflections	7043
No. of parameters	481
No. of restraints	2
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.39, −0.17