Pd(II) pincer type complex catalyzed tandem C-H and N-H activation of acetanilide in aqueous media: A concise access to functionalized carbazoles in a single step

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Electronic Supplementary Information

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Experimental procedure

Synthesis of ligands

Pincer type ligands HL1 and HL2 were synthesized by refluxing equimolar quantity of 2-benzoylpyridine and isonicotinic acid hydrazide (HL1) or furoic acid hydrazide (HL2) in methanol for 5 h according to literature method (Scheme 1).[1] The corresponding solid pincer type hydrazone ligand obtained was filtered, washed several times with distilled water and recrystallized from ethanol in 85-90 % yield. Purity of the ligands was checked by various analytical techniques and compared with literature reports.[1]

General method for the synthesis of the palladium complexes 1 and 2:

To a warm methanolic solution (20–30 mL) of appropriate ligands (HL1 or HL2) (1 equiv.) was added a chloroform solution of $[PdCl_2(PPh_3)_2]$ (1 equiv.) followed by two drops of triethylamine. The resulting reaction mixture was refluxed for 5–9 h and kept at room-temperature for crystallization. Needle like reddish brown crystals of complexes **1** and **2** suitable for X-ray studies were obtained on slow evaporation over 45–60 days.

[Pd(L1)(PPh$_3$)] (complex **1)** Yield: 88%. M.p. 230–234 °C. Elemental analysis (%) calculated for C_{18} H_{13} Cl N_4 O Pd; C, 48.78; H, 2.96; N, 12.64. Found C, 48.79; H, 2.97; N, 12.65. UV-visible (solvent: DMSO, nm): 254, 265, 291, 304. Selected IR bands (KBr, ν in cm^{-1}): 1587 (C=N), 1478 (C−N=N−C), 1180 (imidolate −N=C–O). ^{1}H NMR ($CDCl_3$, δ ppm) : ^{1}H NMR: 7.81 (d, J = 7.6 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.64 (s, 1H), 7.55(t, J = 7.4 Hz, 2H), 7.39 (t, J = 5.8 Hz , 3H), 7.36 (d, J = 7.2 Hz, 2H), 7.24 (t, J = 8.6 Hz, 1H) ^{13}C NMR ($CDCl_3$, δ ppm) 161.6, 159.2, 137.7, 136.4, 136.2, 133.6, 132.9, 132.6, 131.5, 129.1, 128.8, 128.6, 127.9, 127.3, 127.1.

[Pd(L2)(PPh$_3$)] (complex **2)** Yield: 82%. M.p. 210–213 °C. Elemental analysis (%) calculated for C_{17} H_{12} Cl N_3 O_2 Pd; C, 47.25; H, 2.80; N, 9.72. Found C, 47. 26; H, 2.81; N, 9.73. UV-visible (solvent: DMSO, nm): 333, 346, 376, 404. Selected IR bands (KBr, ν in cm^{-1}): 1585 (C=N), 1474 (C−N=N−C), 1183 (imidolate −N= C–O). ^{1}H NMR ($CDCl_3$, δ ppm) : ^{1}H NMR: 7.76 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 2.4 Hz, 2H), 7.63 (s, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 7.2 Hz, 2H), 7.29 (t, J = 7.0 Hz, 2H), 7.23 (t, J = 3.0 Hz, 1H), 7.00-7.02 (m, 2H). ^{13}C NMR ($CDCl_3$, δ ppm) 165.6, 165.3, 145.3, 135.9, 135.5, 135.3, 135.1, 132.4, 131.2, 128.8, 128.5, 128.1, 127.8, 125.4, 125.1, 124.7.

Table S1: Selected bond lengths (Å) and angles (°) for the complex **1**

Complex	**1**
N(2) – Pd(1)	1.922(5)
N(3) – Pd(1)	2.010(5)
O(1) – Pd(1)	2.042(4)
Cl(1) – Pd(1)	2.3086(17)
C(6) – N(2)	1.307(7)
C(7) – N(1)	1.314(8)
C(7) – O(1)	1.294(7)
C(5) – N(3)	1.346(8)
N(1) – N(2)	1.365(7)
C(5) – C(6)	1.464(8)
N(2) – Pd(1)– O(1)	79.8(2)
N(2) – Pd(1)– N(3)	81.0(2)
N(2) – Pd(1)– Cl(1)	177.50(16)
N(3) – Pd(1)– O(1)	160.7(2)
O(1) – Pd(1)– Cl(1)	99.81(13)
N(3) – Pd(1)– Cl(1)	99.48(17)
C(6) – N(2) – Pd(1)	118.4(4)
N(1) – N(2)– Pd(1)	117.6(4)
C(5) – N(3)– Pd(1)	112.2(5)

Table S2: Selected bond lengths (Å) and angles (°) for the complex **2**

Complex	**2**
N(2) – Pd(1)	1.926(2)
N(3) – Pd(1)	2.005(3)
O(1) – Pd(1)	2.029(2)
Cl(1) – Pd(1)	2.3023(8)
C(11) – N(2)	1.304(4)
C(5) – N(1)	1.338(4)
C(5) – O(1)	1.303(4)
C(10) – N(3)	1.366(4)
N(1) – N(2)	1.373(4)
C(10) – C(11)	1.482(4)
N(2) – Pd(1)– O(1)	80.78(10)
N(2) – Pd(1)– N(3)	81.44(11)
N(2) – Pd(1)– Cl(1)	177.39(8)
N(3) – Pd(1)– O(1)	162.19(10)
O(1) – Pd(1)– Cl(1)	99.87(6)
N(3) – Pd(1)– Cl(1)	97.94(8)
C(11) – N(2) – Pd(1)	118.4(2)
N(1) – N(2)– Pd(1)	117.07(19)
C(10) – N(3)– Pd(1)	112.0(2)

Table S3: Crystal data and structure refinement for complexes **1**and **2**

Complex	**1**	**2**
CCDC number	1415316	1415317
Empirical formula	C_{18} H_{13} Cl N_4 O Pd	C_{17} H_{12} Cl N_3 O_2 Pd
Formula weight	443.17	432.15
Temperature (K)	130(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	P 2_1/c	P n a 21
Unit cell dimensions		
a (Å)	13.0361(7)	18.2644(11)
b (Å)	12.7404(8)	9.0854(6)
c (Å)	20.0773(16)	19.0450(11)
α (°)	90	90
β (°)	94.398(2)°.	90
γ (°)	90	90
Volume ($Å^3$)	3324.7(4)	3160.3(3)
Z	8	8
Density (calculated) (Mg m^{-3})	1.771	1.817
Absorption coefficient (mm^{-1})	1.291	1.358
F(000)	1760	1712
Crystal size (mm^3)	0.48 x 0.05 x 0.05	0.50 x 0.05 x 0.03
Reflections collected	14812	122932
Independent reflections	7972 [R(int) = 0.1507]	7874 [R(int) = 0.0638]
Max. and min. transmission	0.9383 and 0.5762	0.9604 and 0.5500
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7972 / 126 / 457	7874 / 4 / 435
Goodness-of-fit on F^2	0.846	1.024
Final R indices [I > 2σ(I)]	R1 = 0.0553, wR2 = 0.0944	R1 = 0.0271, wR2 = 0.0575
R indices (all data)	R1 = 0.1934, wR2 = 0.1258	R1 = 0.0322, wR2 = 0.0595
Largest diff. peak and hole (e.$Å^{-3}$)	1.253 and -1.543	0.591 and -0.916

Catalysis

General procedure for catalytic reaction and reusability:

A mixture of acetanilide (2.0 mmol) and phenylboronic acid (2 mmol) and K_2CO_3 (4 mmol) in double distilled water (10 mL) was filled into a 20 mL round bottom flask. To this reaction mixture, catalyst **2** (0.01 mol %) was added and stirred at 60 °C for 8-12 h and the progress of the reaction was monitored by thin layer chromatography (R_f value: 0.47) with 5% ethyl acetate in petroleum ether as solvent. After the completion, the reaction mixture was cooled to ambient temperature and the solid product thus formed was filtered. The colorless solid product *N*-acetylcarbazole was washed with distilled water to remove catalyst and inorganic bases and dried. Then, the filtrate was diluted with ethyl acetate to separate the catalyst and inorganic salt as a by-product. The identity of the obtained carbazoles was confirmed by ^1H, ^{13}C NMR, and mass spectral techniques and the data were compared with literature report.

The recovered catalyst (complex **2**) was dried and utilized in successive cycles under the same reaction conditions and the trend of the yield is summarized in Fig. 4 in the manuscript

Spectral data of the diverse functionalized carbazoles listed in table 2 and 3:

^1H and ^{13}C NMR spectra were recorded in deuterated $CHCl_3$ as solvent on BRUKER 400 and 100 MHZ instruments, respectively. Mass spectra of the carbazoles were recorded in LCQ Fleet mass spectrometer, Thermo Fisher Instruments Limited, US. Electrospray ionisation mass spectrometry (ESI-MS) analysis was performed in the positive ion and negative ion mode on a liquid chromatography ion trap.

Entry 1a: 1-carbazol-9-yl-ethanone[2a]: ^1H NMR: 7.49-7.53 (m, 2H), 7.39-7.42 (m, 2H), 7.23-7.28 (m, 2H), 7.11-7.20 (m, 2H), 2.83 (s, 3H). ^{13}C NMR: 195.4, 144.2, 132.4, 130.3, 129.8, 128.6, 128.1, 126.8, 124.9, 124.6, 123.3, 113.2, 29.2. ESI MS: m/z calculated: 209.08; found: 210.0 (M^+).

Entry 1b: 1-(4-methyl-carbazol-9-yl)-ethanone[2b]: ^1H NMR: 9.48 (s, 1H), 8.48 (d, J = 6.0 Hz, 1H), 8.26 (d, J = 6.0 Hz, 1H), 7.95 (d, J = 6.0 Hz, 2H), 7.50 (t, J = 5.8 Hz, 1H), 7.39(t, J = 5.8 Hz, 1H), 3.36 (s, 3H), 2.49 (s, 3H). ^{13}C NMR: 205.7, 144.5, 131.3, 128.1, 126.4, 124.5, 124.2, 132.7, 30.8, 28.2. ESI MS: m/z calculated: 223.10; found: 224.91 (M^+).

Entry 1c: 1-(2-methyl-carbazol-9-yl)ethanone[2b]: ^{1}H NMR: 9.40 (s, 1H), 8.18 (d, J = 6.8 Hz, 2H), 8.14 (d, J = 6.8 Hz, 1H), 7.98 (d, J = 6.0 Hz, 1H), 7.51(t, J = 6.0 Hz, 1H), 7.40 (t, J = 5.8 Hz, 1H), 3.38 (s, 3H), 2.50(s, 3H). ^{13}C NMR: 206.5, 158.3, 133.2, 131.6, 128.9, 128.5, 128.2, 123.8, 114.3, 32.3, 30.1. ESI MS: m/z calculated: 223.10; found: 224.62 (M^+).

Entry 1d: 1-(3, 4-dimethyl-carbazol-9-yl)ethanone[2b]: ^{1}H NMR: 8.24 (d, J = 6.0 Hz, 1H), 8.05 (d, J = 6.4 Hz, 1H), 7.96 (d, J = 5.6 Hz, 2H), 7.52 (t, J = 5.4 Hz, 1H), 7.41 (d, J = 5.6 Hz, 1H), 3.33(s, 3H), 2.50 (s, 3H), 2.20 (s, 3H). ^{13}C NMR: 202.5, 137.5, 136.4, 133.6, 133.4, 132.5, 131.8, 131.5, 131.4, 129.4, 128.9, 128.6, 128.4, 128.2, 128.1, 128.0, 127.4, 123.8, 123.4, 25.2, 16.4, 16.0. ESI MS: m/z calculated: 237.12; found: 238.19 (M^+).

Entry 1e: 1-(4-methoxy-carbazole-9-yl)ethanone[2b]: ^{1}H NMR: 7.89 (dd, J = 2.0, 4.2 Hz, 2H), 7.94 (d, J = 10.0 Hz, 2H), 7.45 (t, J = 6.8 Hz, 1H), 7.40 (t, J = 6.2 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 4.18 (s, 3H), 2.50 (s, 3H). ^{13}C NMR: 190.3, 144.1, 134.4, 133.2, 132.6, 131.8, 128.6, 127.1, 123.5, 114.8, 48.8, 24.2. ESI MS: m/z calculated: 239.09; found: 240.10 (M^+).

Entry 1f: 1-(2-methoxy-carbazol-9-yl)ethanone[2b]: ^{1}H NMR: 7.93 (d, J = 7.2 Hz, 1H), 7.63 (d, J = 4.8 Hz, 1H), 7.45 (t, J = 7.4, 2H), 7.35 (t, J = 6.2 Hz, 1H), 7.32 (s, 2H), 4.44 (s, 3H), 2.43 (s, 3H).^{13}C NMR: 209.2, 144.7, 131.1, 128.8, 128.4, 126.4, 125.6, 124.7, 123.0, 42.7, 25.0. ESI MS: m/z calculated: 239.09; found: 240.11 (M^+).

Entry 1g: 1-(2-*t*-butyl-carbazol-9-yl)ethanone [2c]: ^{1}H NMR: 8.01 (d, J = 5.6 Hz, 1H), 7.99 (d, J = 5.6 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.64 (t, J = 7.8 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.33-7.49 (m, 1H), 3.36 (s, 3H), 2.50 (s, 3H). ^{13}C NMR: 206.4, 158.5, 138.3, 133.8, 131.1, 129.2, 128.4, 120.8, 114.9, 32.2, 30.6, 21.8. ESI MS: m/z calculated: 265.15; found: 266.14 (M^+).

Entry 1h: 1-(3-hydroxy-carbazol-9-yl)ethanone: ^{1}H NMR: 9.31 (s, 1H), 7.95 (t, J = 7.4 Hz, 2H), 7.63 (t, J = 5.8 Hz, 2H), 7.59 (d, J = 4.4 Hz, 2H), 7.43 (t, J = 9.2 Hz, 1H), 3.44 (s, 3H). ^{13}C NMR: 197.7, 158.3, 137.5, 137.2, 133.9, 133.4, 131.8, 129.7, 128.6, 128.4, 128.2, 120.9, 114.5, 21.3. ESI MS: m/z calculated: 225.08; found: 226.10 (M^+).

Entry 1i: 1-benzo[b]carbazol-5-yl-ethanone[2d]: ^{1}H NMR: 8.52 (s, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.04 (d, J =8.8 Hz, 1H), 7.99 (d, J = 7.2 Hz, 2H), 7.95 (d, J = 7.2 Hz, 1H), 7.67 (d, J = 7.2 Hz, 2H), 7.50-7.63 (m,1H), 2.58 (s, 3H). ^{13}C NMR: 195.1, 147.6, 136.1, 133.4, 132.3, 129.2, 128.9, 128.5, 128.1, 127.8, 126.4, 126.2, 123.6, 123.2, 120.4, 21.9. ESI MS: m/z calculated: 259.10; found: 260.13 (M^+).

Entry 1j: 1-(2-phenyl-carbazol-9-yl)ethanone: ^{1}H NMR: 8.91 (s, 1H), 8.24 (s, 1H), 8.02 (t, J = 6.2 Hz, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.79 (d, J = 7.2 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H) 7.23-7.42(m, 2H), 2.55 (s, 3H). ^{13}C NMR: 197.2, 143.1, 137.4, 136.8, 129.3, 128.2, 125.7, 122.7, 122.62, 120.9, 120.7, 119.1, 116.2, 111.5, 106.3, 21.4. ESI MS: m/z calculated: 285.12; found: 286.11 (M^+).

Entry 1k: 1-(3-chloro-carbazol-9-yl)ethanone[2c]: ^{1}H NMR: 8.19 (s, 1H), 7.78 (t, *J* = 9.2 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR: 197.1, 148.6, 138.4, 137.1, 129.8, 129.2, 128.3, 127.8, 125.2, 120.4, 117.7, 21.8. ESI MS: m/z calculated: 243.05; found: 244.09 (M^+).

Entry 1l: 1-(2-bromo-carbazol-9-yl)ethanone[2b]: ^{1}H NMR: 8.28 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 6.0 Hz, 1H), 6.93 (d, *J* = 7.6Hz, 1H), 2.20 (s, 3H). ^{13}C NMR: 195.0, 148.5, 136.1, 131.3, 129.6, 129.4, 128.2, 120.9, 118.5, 117.8, 114.9, 1110.1, 21.3. ESI MS: m/z calculated: 286.99; found: 288.01 (M^+).

Entry 1m: 1-(2-dimethylamino-carbazol-9-yl)ethanone: ^{1}H NMR: 8.10 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.6Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.01(d, *J* = 8.4 Hz, 1H), 2.86 (s, 6H), 2.33 (s, 3H). ^{13}C NMR: 196.8, 155.3, 143.4, 137.9, 129.6, 129.2, 128.5, 127.3, 120.7, 120.6, 120.1, 118.2, 110.4, 55.6, 21.81. ESI MS: m/z calculated: 252.13; found: 253.19 (M^+).

Entry 1n: 1-(3-acetyl-carbazole-9-yl)ethanone: ^{1}H NMR: 8.26 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.73(d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.26-7.40 (m, 1H), 2.84 (s, 3H), 2.36 (s, 3H). ^{13}C NMR: 203.3, 202.7, 146.7, 136.2, 129.1, 128.4, 127.8, 127.1, 126.8, 126.1, 119.8, 119.4, 116.2, 115.5, 25.4, 24.3. ESI MS: m/z calculated: 251.09; found: 252.12 (M^+).

Entry 1o: 1-(2-acetyl carbazol-9-yl)ethanone: ^{1}H NMR: 8.16 (s, 1H), 7.75-7.79 (m, 2H), 7.50-7.55 (m, 1H), 7.41-7.45 (m, 1H), 7.35-7.37 (m, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 2.56 (s, 3H), 2.51 (s, 3H), 2.51 (s, 3H). ^{13}C NMR: 203.9, 202.6, 149.3, 149.3, 148.6, 136.3, 129.7, 128.4, 123.1, 118.2, 116.3, 111.6, 108.4, 23.6, 22.8. ESI MS: m/z calculated: 251.09; found: 252.10 (M^+).

Entry 1p: 9-acetyl-9-H-carbazol-2-carbaldehyde : ^{1}H NMR: 9.35 (s, 1H), 7.87-7.97 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 2H), 7.51(t, *J* = 7.0 Hz, 1H), 2.43 (s, 3H).^{13}C NMR: 206.8, 192.2, 147.5, 137.9, 135.8, 130.3, 129.8, 129.1, 128.8, 128.5, 128.2, 126.7, 120.8, 119.2, 21.3. ESI MS: m/z calculated: 237.08; found: 238.15 (M^+).

Entry 1q: 1-(2-trifluoromethyl-carbazol-9-yl)ethanone[2b]: ^{1}H NMR: 8.06 (s, 1H), 7.80 (dd, *J* = 7.2, 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 6.8 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR: 205.7, 149.5, 139.8, 138.6, 130.3, 130.2, 130.1, 128.4, 127.7, 126.6, 126.4, 124.6, 122.8, 120.1, 119.5, 22.2. ESI MS: m/z calculated: 237.08; found: 238.07 (M^+).

Entry 2a: 1-benzol[b]carbazol-5-yl ethanone [2d]: ^{1}H NMR: 7.86 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.31-7.39 (m, 2H), 7.23-7.28 (m, 2H), 2.56 (s, 3H). ^{13}C NMR: 196.7, 141.4, 138.1, 136.5, 131.3, 129.2, 128.8, 128.6, 128.2, 127.4, 127.3, 123.5, 101.3, 20.8. ESI MS: m/z calculated: 259.10; found: 260.07 (M^+).

Entry 2b: 1-(1-methyl-benzo[b]carbazol-5-yl)ethanone: ^{1}H NMR: 8.01 (d, J = 8.0 Hz, 2H), 7.52-7.58 (m, 1H), 7.41-7.48 (m, 2H), 7.34-7.36 (m, 2H), 7.24-7.26 (m, 1H), 6.87 (t, J = 6.0 Hz, 1H), 2.64 (s, 3H), 1.78 (s, 3H). ^{13}C NMR: 197.5, 158.3, 136.5, 133.7, 133.3, 131.6, 128.7, 128.5, 128.3, 127.7, 123.5, 114.5, 22.9, 20.2. ESI MS: m/z calculated: 273.12; found: 274.14 (M^+).

Entry 2c: 1-(3-methyl-benzo[b]carbazol-5-yl)ethanone: ^{1}H NMR: 7.83 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.35 (dd, J = 2.0, 7.6 Hz, 1H), 7.25 (t, J = 8.4 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 2.25 (s, 3H), 1.66 (s, 3H). ^{13}C NMR: 196.3, 158.2, 138.8, 136.6, 133.4, 131.5, 129.2, 128.7, 128.3, 128.0, 123.4, 114.2, 101.8, 25.4, 21.6. ESI MS: m/z calculated: 273.12; found: 274.16 (M^+).

Entry 2d: 1-(1,2-dimethyl-benzo[b]carbazol-5-yl)-ethanone: ^{1}H NMR: 7.94 (t, J = 4.4 Hz, 2H), 7.44 (d, J = 12.4 Hz, 2H), 7.32-7.36 (m, 1H), 7.22-7.28 (m, 1H), 6.85-6.98 (m, 2H), 2.77 (s, 3H), 1.62 (s, 3H). ^{13}C NMR: 195.1, 158.3, 133.6, 131.4, 130.9, 130.2, 128.9, 128.5, 127.6, 123.1, 114.3, 113.7, 26.8, 21.7, 21.3. ESI MS: m/z calculated: 287.13; found: 288.12 (M^+).

Entry 2e: 1-(1-methoxy-benzo[b]carbazol-5-yl)ethanone: ^{1}H NMR: 7.88 (d, J = 8.4 Hz, 2H), 7.41-7.46 (m, 2H), 7.32-7.36 (m, 2H), 7.21-7.27 (m, 1H), 6.88 (dd, J = 2.4, 8.4 Hz, 2H), 3.78 (s, 3H), 2.37 (s, 3H). ^{13}C NMR: 196.7, 144.6, 134.7, 133.3, 131.5, 129.7, 128.8, 128.6, 128.1, 127.2, 123.3, 114.9, 55.9, 21.2. ESI MS: m/z calculated: 289.11; found: 290.20 (M^+).

Entry 2f: 1-(3-methoxy-benzo[b]carbazo-5-yl)ethanone: ^{1}H NMR: 7.55 (dd, J = 2.0, 6.4 Hz, 1H), 7.41-7.46 (m, 1H), 7.33-7.37(m, 2H), 7.21-7.27(m, 3H), 6.87 (t, J = 3.4 Hz, 1H), 6.77-6.85 (m, 1H), 3.78 (s, 3H), 2.49 (s, 3H). ^{13}C NMR: 195.8, 148.6, 133.7, 131.8, 131.2, 128.7, 128.2, 127.5, 124.4, 123.8, 114.2, 108.5, 107.5, 101.8, 55.7, 23.5. ESI MS: m/z calculated: 289.11; found: 290.13 (M^+).

Entry 2g: 1-(3-*t*-butyl-benzo[b]carbazol-5-yl)-ethanone: ^{1}H NMR: 7.81 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.31-7.35 (m, 2H), 7.25 (t, J = 5.2 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H), 2.65 (s, 3H), 2.03 (s, 9H). ^{13}C NMR: 196.8, 135.1, 133.3, 132.5, 131.3, 129.7, 129.2, 128.9, 128.5, 128.3, 123.6, 114.4, 47.6, 33.4, 20.6. ESI MS: m/z calculated: 315.16; found: 316.17 (M^+).

Entry 2h: 1-(2-hydroxybenzo[b]carbazol-5-yl)-ethanone: ^{1}H NMR: 8.45 (d, J = 7.2 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 10.0 Hz, 2H), 7.51 (t, J = 8.2 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H), 6.12 (s, 1H), 2.53 (s, 3H). ^{13}C NMR: 201.5, 158.2, 141.8, 133.7, 132.5, 131.9, 131.5, 128.8, 128.7, 128.3, 127.8, 127.5, 123.7, 118.9, 114.5, 23.3. ESI MS: m/z calculated: 275.09; found: 276.08 (M^+).

Entry 2i:1-(dibenzo[b,h]carbazol-6-yl)ethanone[2e]: ^{1}H NMR: 7.67 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 4.4 Hz, 2H), 7.31-7.37(m, 2H), 7.25 (t, J = 6.8 Hz, 3H), 7.07 (t, J = 8.4 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR: 202.4 139.8, 133.4, 132.9, 132.3, 131.8, 131.5, 129.8, 128.7,

128.6, 128.5, 128.3, 128.1, 128.0, 127.8, 123.6, 123.3, 114.8, 113.4, 25.1. ESI MS: m/z calculated: 309.12; found: 310.13 (M^+).

Entry 2j: 1-(3-phenyl benzo[b] carbazol-5-yl)ethanone: ^{1}H NMR: 7.60 (t, *J* = 6.2 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 3H), 7.22-7.28 (m, 2H), 7.22 (d, *J*=6.4 Hz, 2H), 7.15-7.18 (m, 3H), 6.86 (dd, *J* = 1.6, 4.8Hz, 1H), 6.71 (s, 1H), 2.35 (s, 3H). ^{13}C NMR: 197.7, 148.6, 138.3, 130.7, 128.8, 128.5, 128.2, 127.4, 126.8, 126.4, 124.7, 123.3, 114.5, 106.1, 23.0. ESI MS: m/z calculated: 335.13; found: 336.15 (M^+).

Entry 2k: 1-(2-chlorobenzo[b] carbazol-5-yl)ethanone: ^{1}H NMR: 7.97 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.40-7.45(m, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR: 197.6, 137.6, 137.4, 133.8, 133.3, 131.4, 129.2, 128.8, 128.7, 128.4, 120.6, 114.2, 21.8. ESI MS: m/z calculated: 209.06; found: 210.09 (M^+).

Entry 2l: 1-(3-bromo benzo[b] carbazol-5-yl) ethanone: ^{1}H NMR: 7.96 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 8.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.4Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 2.41(s, 3H). ^{13}C NMR: 190.6, 145.8, 139.3, 133.5, 130.6, 129.7, 128.8, 128.1, 127.9, 125.4, 117.5, 113.9, 20.4. ESI MS: m/z calculated: 337.01; found: 337.05 (M^+).

Entry 2m: 1-(3-dimethyl amino benzo[b] carbazol-5-yl) ethanone: ^{1}H NMR: 7.53 (t, *J* = 8.0 Hz, 2H), 7.20-7.48 (m, 3H), 7.18 (t, *J* = 8.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.96 (dd, *J* = 7.6, 1.6 Hz, 1H), 2.95 (s, 6H), 2.39 (s, 3H). ^{13}C NMR: 195.7, 144.5, 131.7, 130.1, 129.2, 128.3, 128.0, 126.7, 126.0, 124.1, 123.1, 113.1, 47.8, 21.6. ESI MS: m/z calculated: 302.14; found: 303.12 (M^+).

Entry 2n: 1-(2-acetyl benzo[b] carbazol-5-yl) ethanone: ^{1}H NMR: 9.16 (s, 1H), 7.92-7.96(m, 2H), 7.60-7.64 (m, 2H), 7.58-7.59 (m, 1H), 7.50-7.55 (m, 1H), 7.49 (t, *J* = 1.0 Hz, 1H), 7.18 (dd, *J* = 2.6 Hz, 1H), 2.50 (s, 3H), 2.49 (s, 3H). ^{13}C NMR: 203.8, 201.0, 148.2, 138.8, 134.7, 130.3, 130.2, 128.8, 128.3, 125.8, 120.4, 117.6, 24.8, 21.4. ESI MS: m/z calculated: 301.11; found: 302.17 (M^+).

Entry 2o: 1-(3-acetyl benzo[b] carbazol-5-yl) ethanone: ^{1}H NMR: 7.93-7.96 (m, 2H), 7.36-7.39 (m, 2H), 7.24-7.26 (m, 1H), 7.15-7.17 (m, 1H), 7.08-7.09 (m, 2H), 6.88-6.94 (m, 1H), 2.76 (s, 3H), 2.31 (s, 3H). ^{13}C NMR: 203.2, 202.5, 143.4, 137.9, 136.4, 129.7, 128.5, 125.9, 122.4, 120.5, 120.4, 119.6, 116.5, 111.7, 106.4, 25.1, 24.2. ESI MS: m/z calculated: 301.11; found: 302.10 (M^+).

Entry 2p: 5-acetyl-5H-benzo[b]carbazol-3-carbaldehyde: ^{1}H NMR: 9.43 (s, 1H), 7.40-7.47(m, 2H), 7.27-7.31 (m, 3H), 7.19 (dd, *J* = 1.2, 4.0Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.94 (dd, *J* = 11.6, 1.6Hz, 1H), 2.19 (s, 3H). ^{13}C NMR: 206.17, 197.4, 141.9, 135.7, 133.3, 132.8, 132.5, 129.3, 129.1, 128.8, 128.7, 127.5, 30.8. ESI MS: m/z calculated: 287.09; found: 288.10 (M^+).

Entry 2q: 1-(3-trifluoromethylbenzo[b]carbazol-5-yl)ethanone: ^{1}H-NMR: 7.77 (d, J = 9.6 Hz, 1H), 7.72 (d,7.6 Hz, 2H), 7.64 (s, 1H), 7.39 (t, J = 6.6 Hz, 1H), 7.37 (d, J = 8.0, 1H), 7.27 (d, J = 7.2 Hz, 1H), 7.21-7.25 (m, 2H), 2.39 (s, 3H). ^{13}C NMR: 200.1, 144.4, 135.8, 135.6, 135.1, 132.7, 131.6, 129.8, 129.3, 129.1, 127.8, 127.2, 125.7, 125.2, 124.4, 27.4, 22.8. ESI MS: m/z calculated: 327.09; found: 328.05 (M^{+}).

References:

1) R. Bikas, H. H. Monfared, G. Zoppellaro, R. Herchel, J. Tucek, A. M. Owczarzak, M. Kubicki and R. Zboril, *Dalton Trans*., 2013, **42,** 2803.
2) (a) R. K. Chinnagolla and M. Jeganmohan, *Chem. Commun.,* 2014, **50,** 2442; (b) W. C. P. Tsang, R. H. Munday, G. Brasche, N. Zheng and S. L. Buchwald*, J. Org. Chem,* 2008, **73,** 7603; (c) S. Choi, T. Chatterjee, W. J. Choi, Y. You and E. J. Cho, *ACS Catal.,* 2015, **5,** 4796; (d) P. Mabille and X. P. Buu-Hoi, *J. Org. Chem.,* 1960, **25,** 1937; (e) W. Xue, K. La Dow and D. Warshawsky, *Chem. Res. Toxicol,* 1997, **10,** 432.

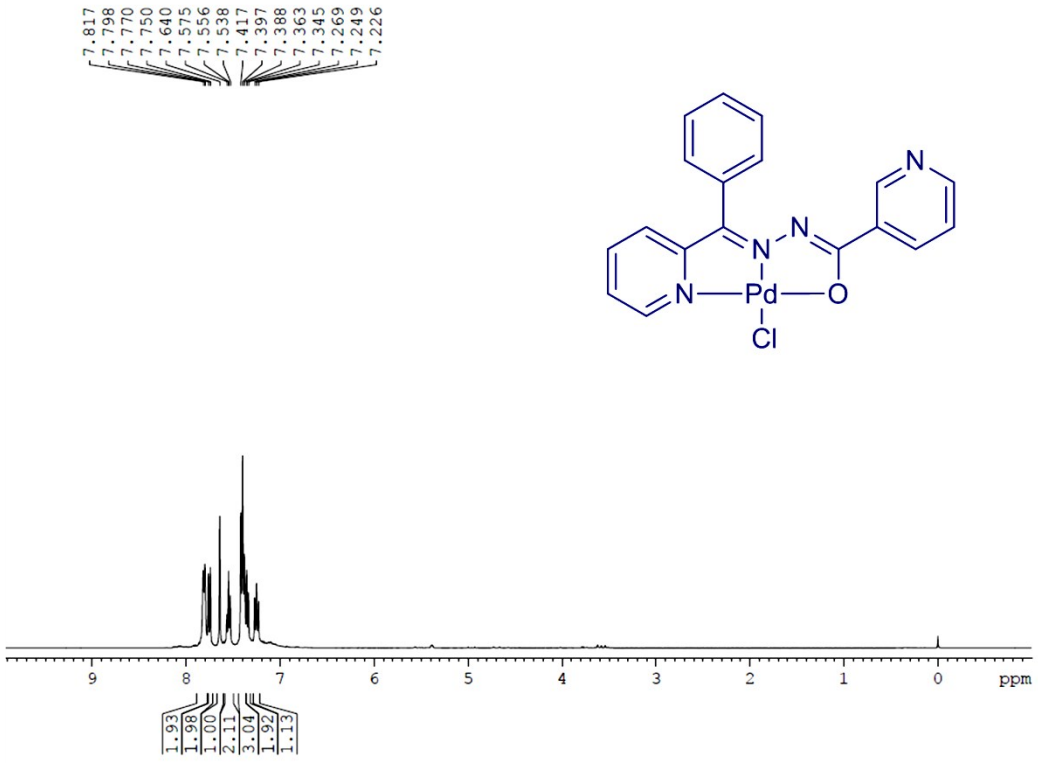

Fig. S1: ^{1}H NMR spectrum of complex **1**

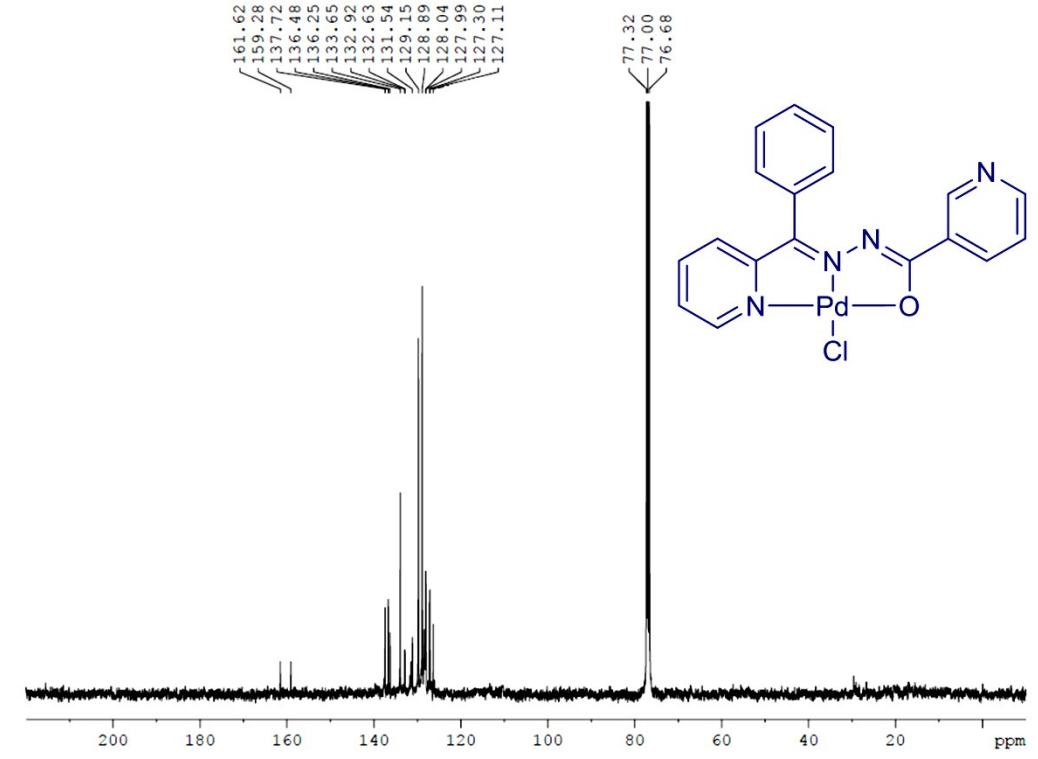

Fig. S2: ^{13}C NMR spectrum of complex **1**

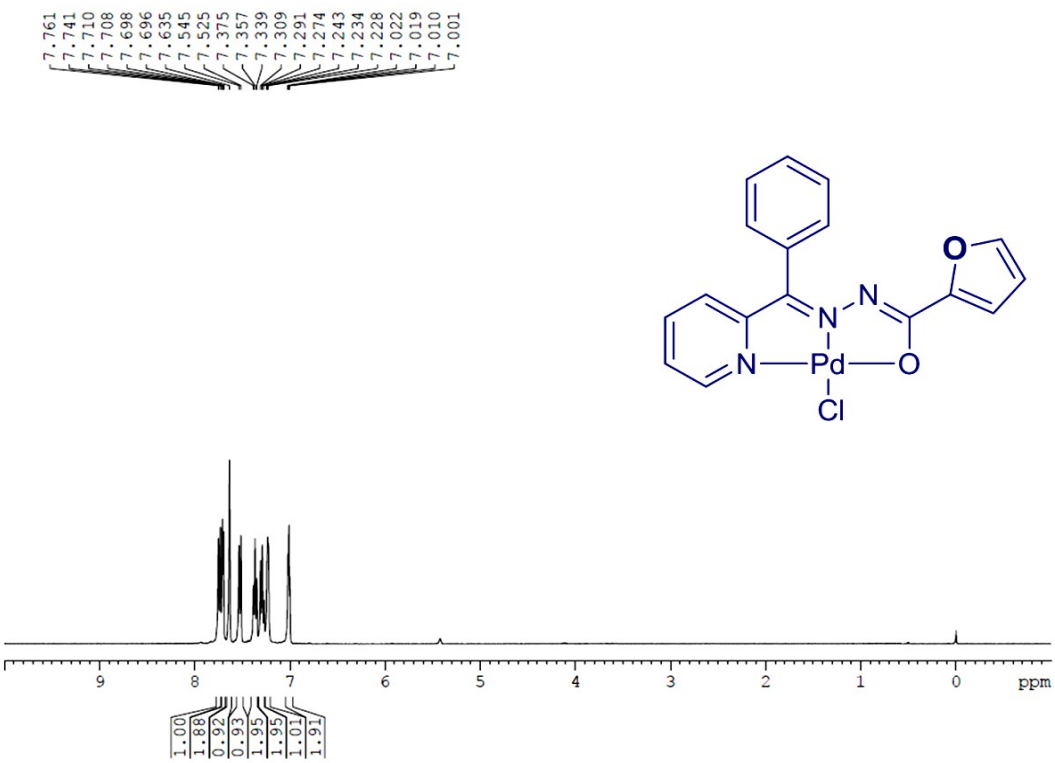

Fig. S3: ^{1}H NMR spectrum of complex **2**

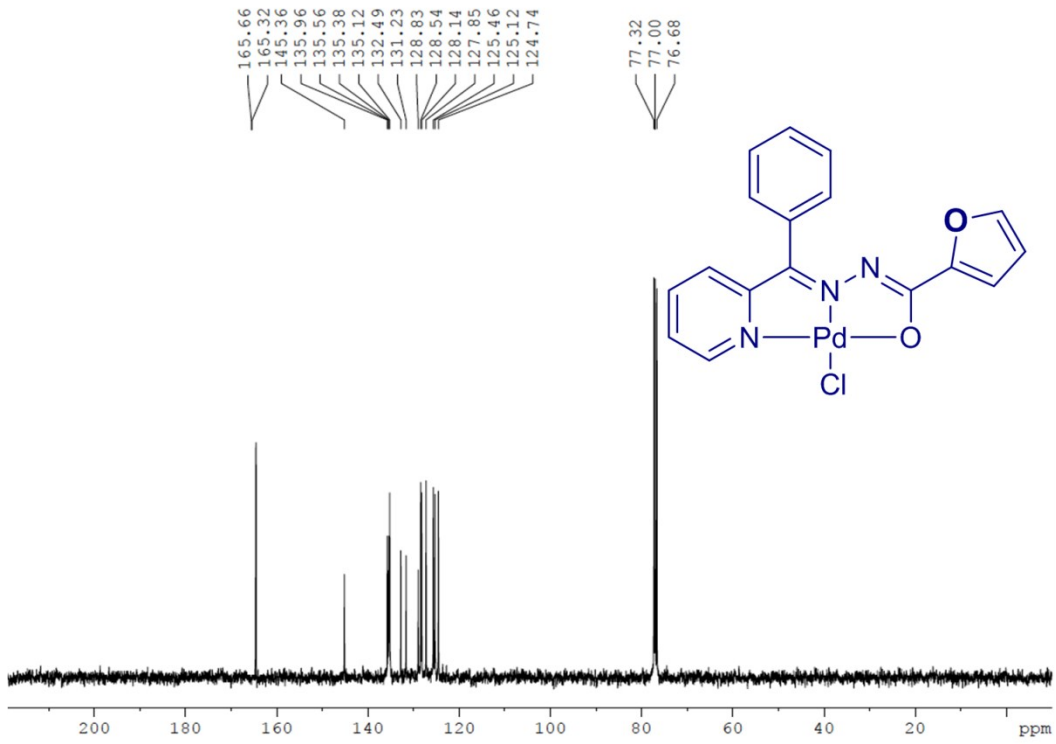

Fig. S4: ^{13}C NMR spectrum of complex **2**

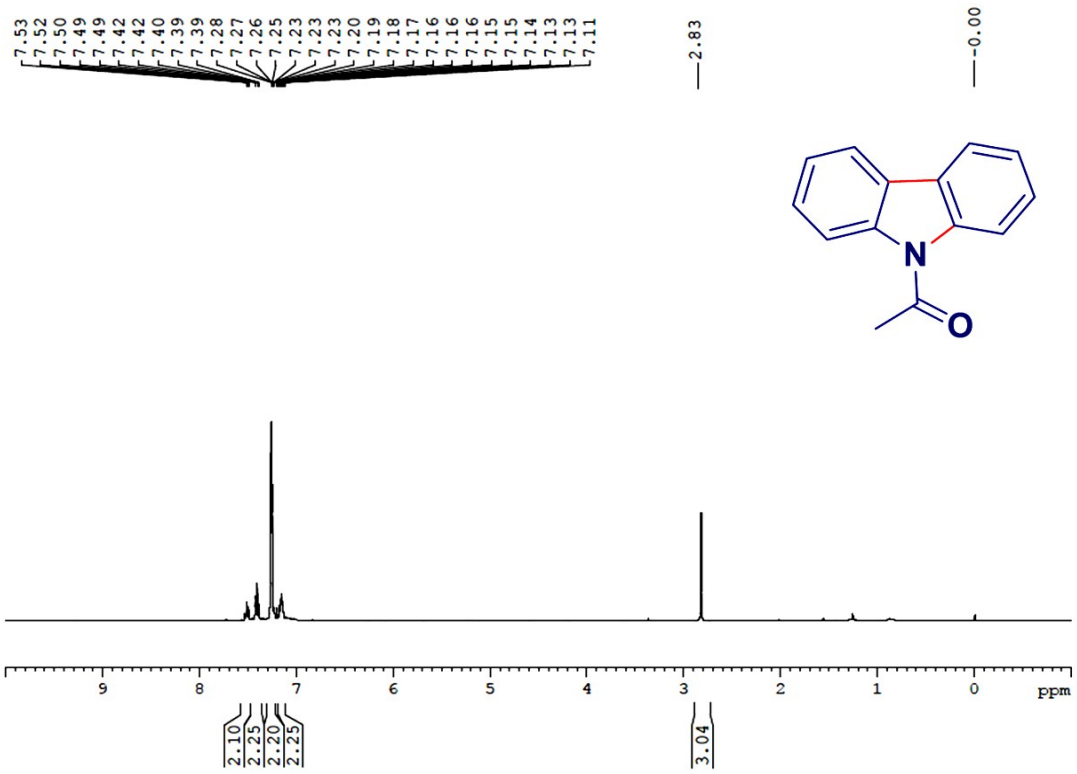

Fig. S5: [1]H NMR spectrum of 1-carbazol-9-yl-ethanone

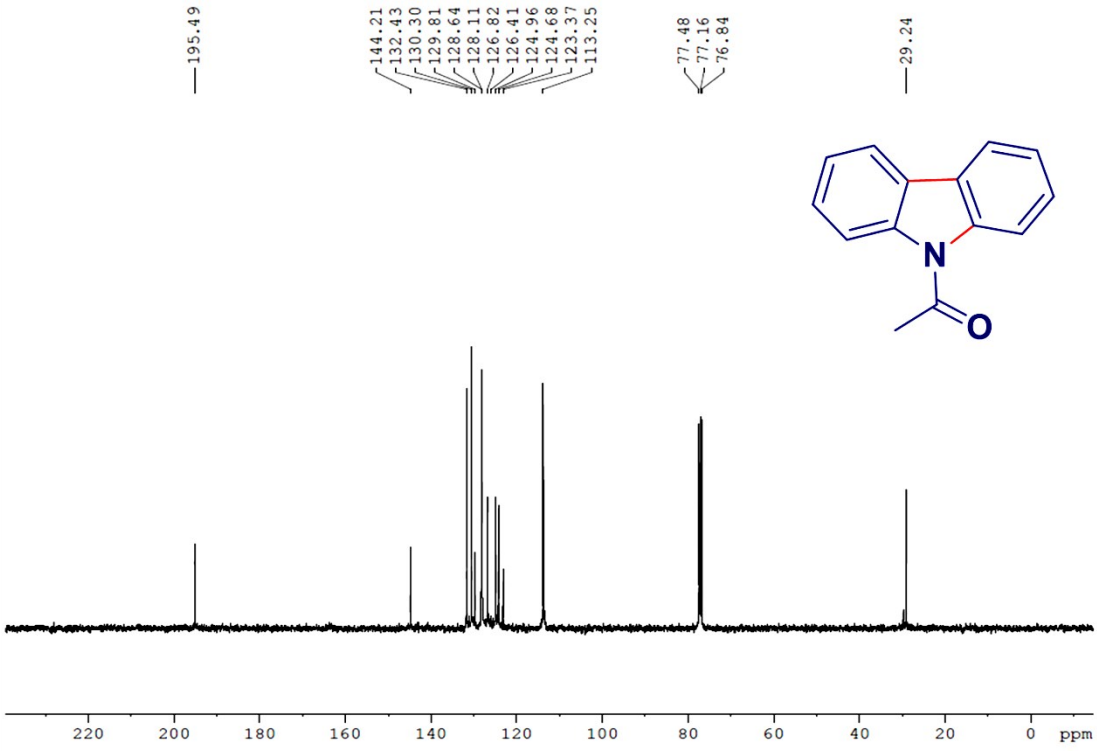

Fig. S6: [13]C NMR spectrum of 1-carbazol-9-yl-ethanone

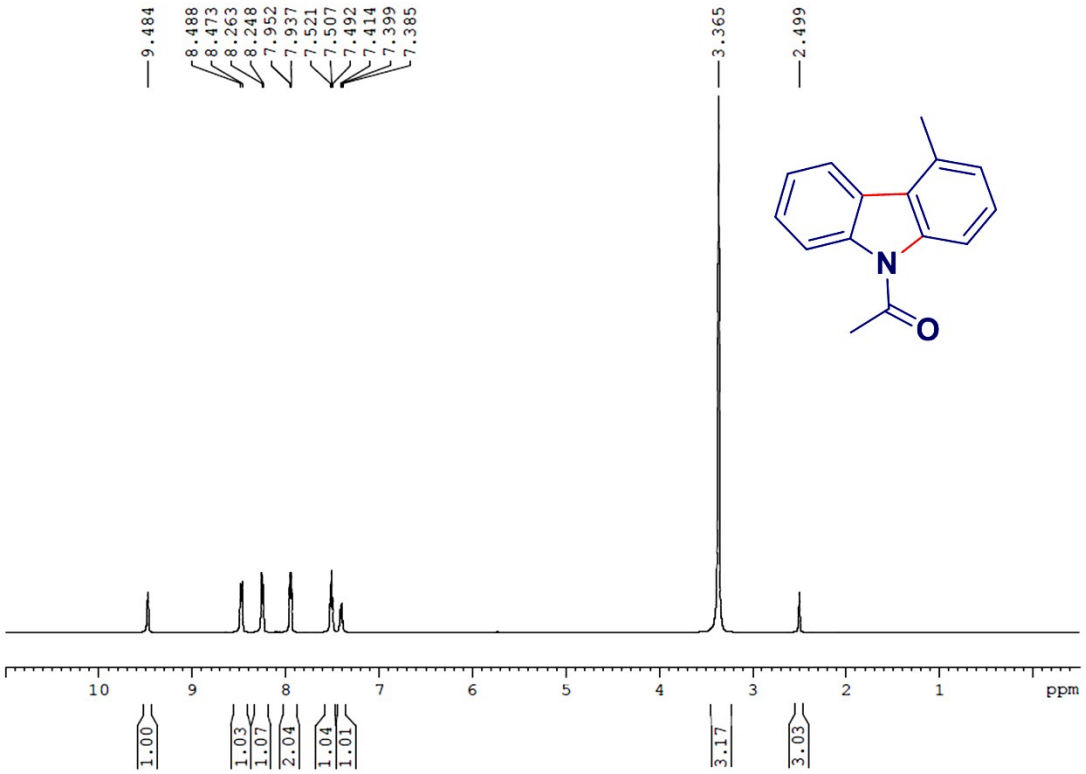

Fig. S7: ^{1}H NMR spectrum of 1-(4-methyl-carbazol-9-yl)-ethanone

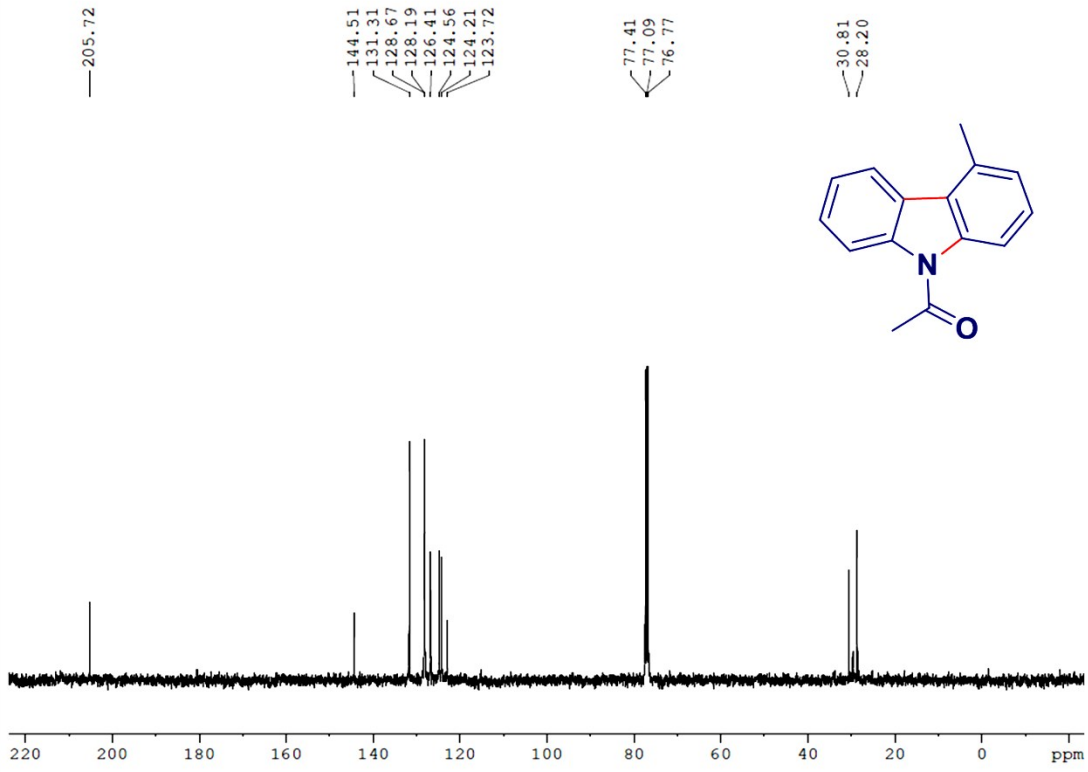

Fig. S8: ^{13}C NMR spectrum of 1-(4-methyl-carbazol-9-yl)-ethanone

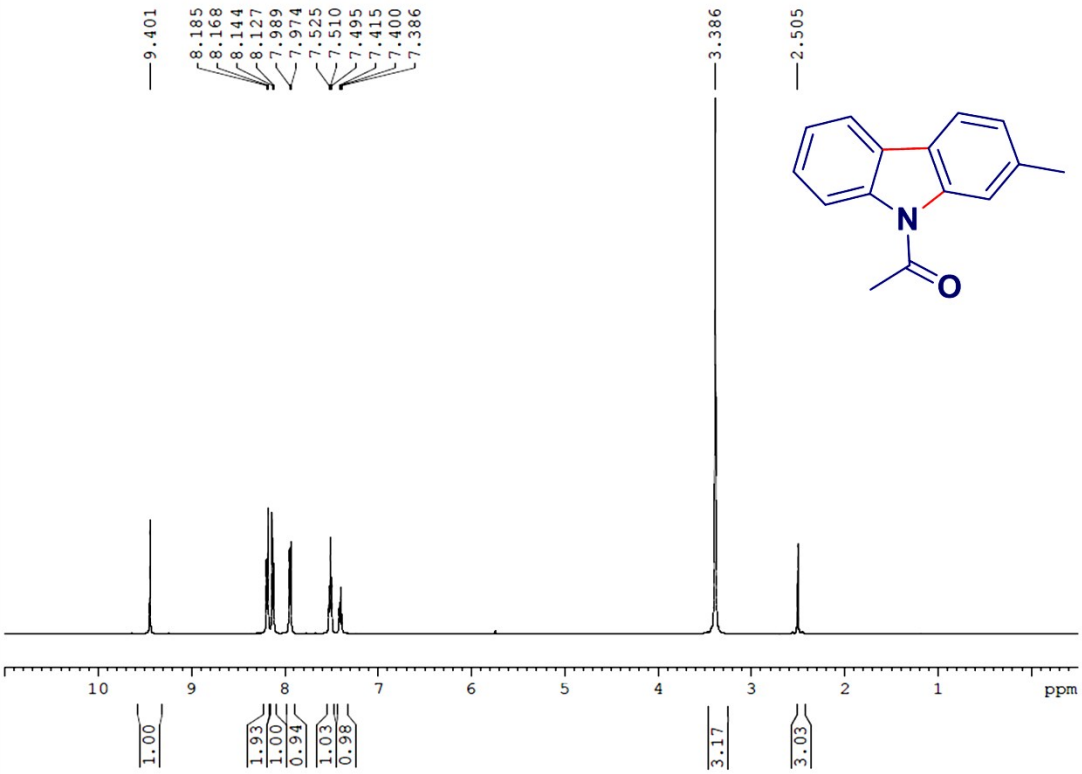

Fig. S9: ^{1}H NMR spectrum of 1-(2-methyl-carbazol-9-yl)-ethanone

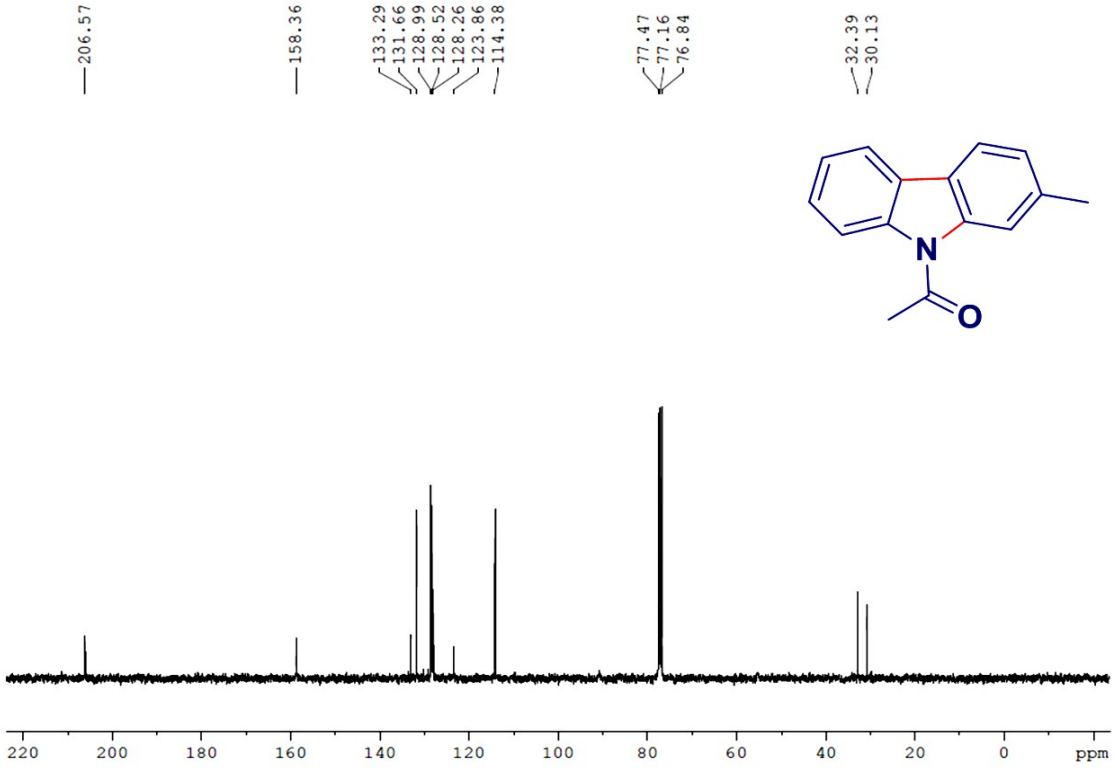

Fig. S10: ^{13}C NMR spectrum of 1-(2-methyl-carbazol-9-yl)-ethanone

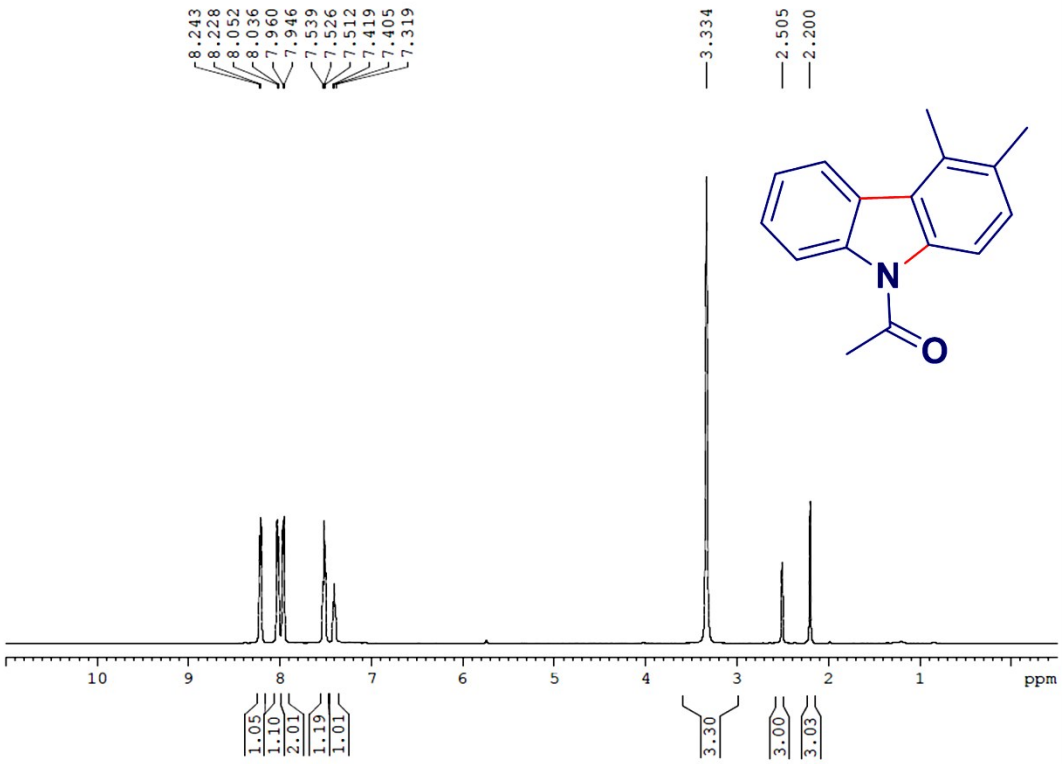

Fig. S11: ^{1}H NMR spectrum of 1-(3, 4-dimethyl-carbazol-9-yl)-ethanone

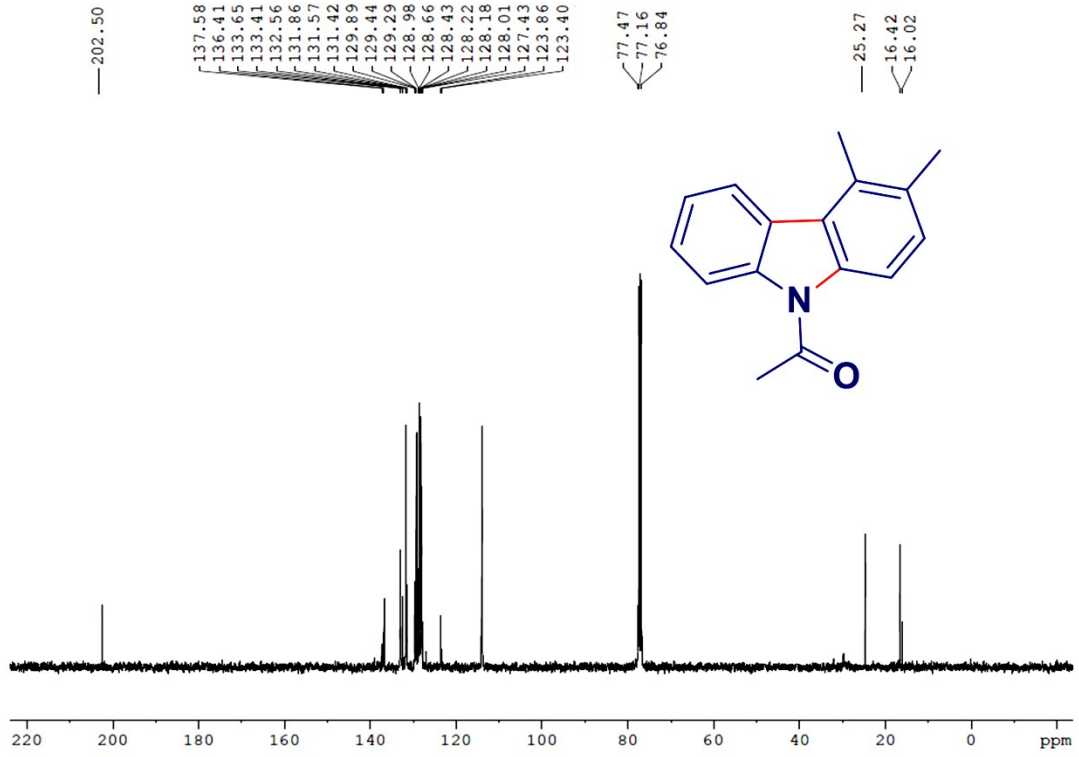

Fig. S12: ^{13}C NMR spectrum of 1-(3, 4-dimethyl-carbazol-9-yl)-ethanone

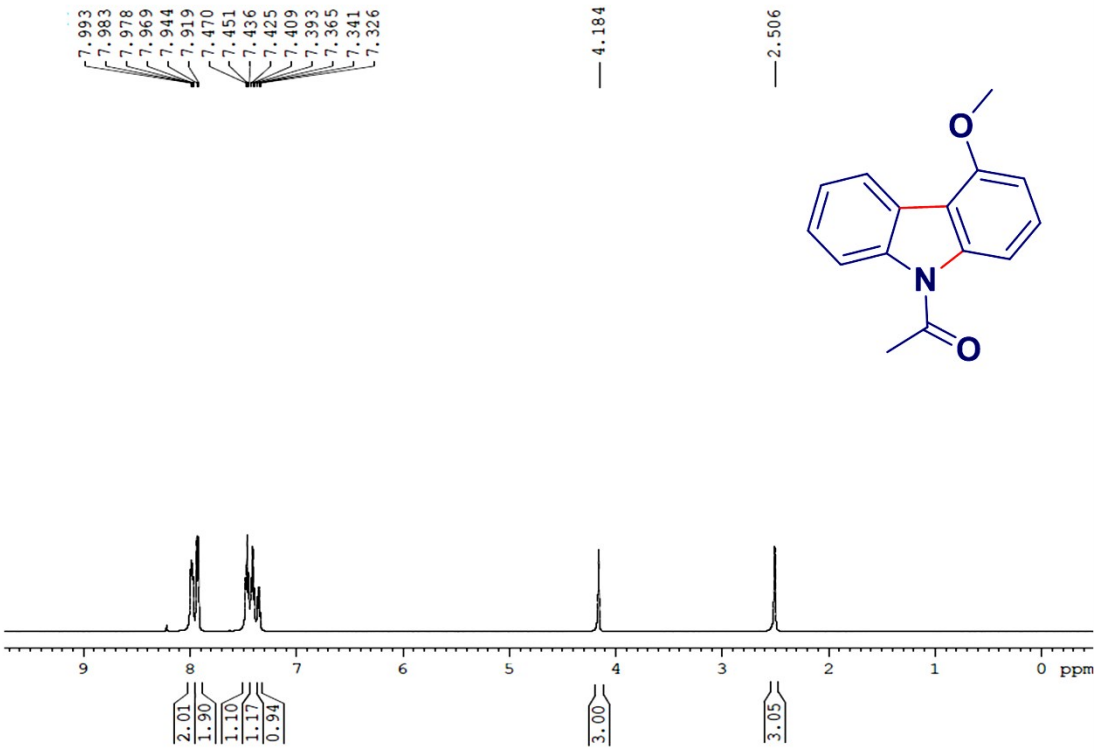

Fig. S13: ^{1}H NMR spectrum of 1-(4-methoxy-carbazol-9-yl)-ethanone

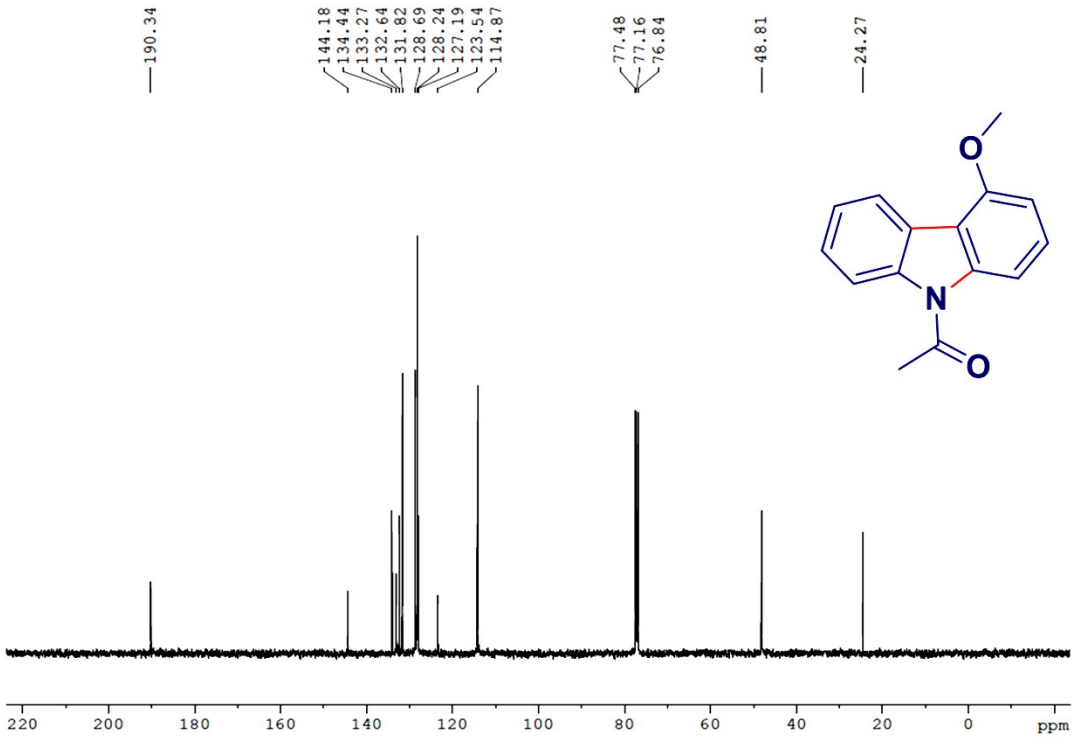

Fig. S14: ^{13}C NMR spectrum of 1-(4-methoxy-carbazol-9-yl)-ethanone

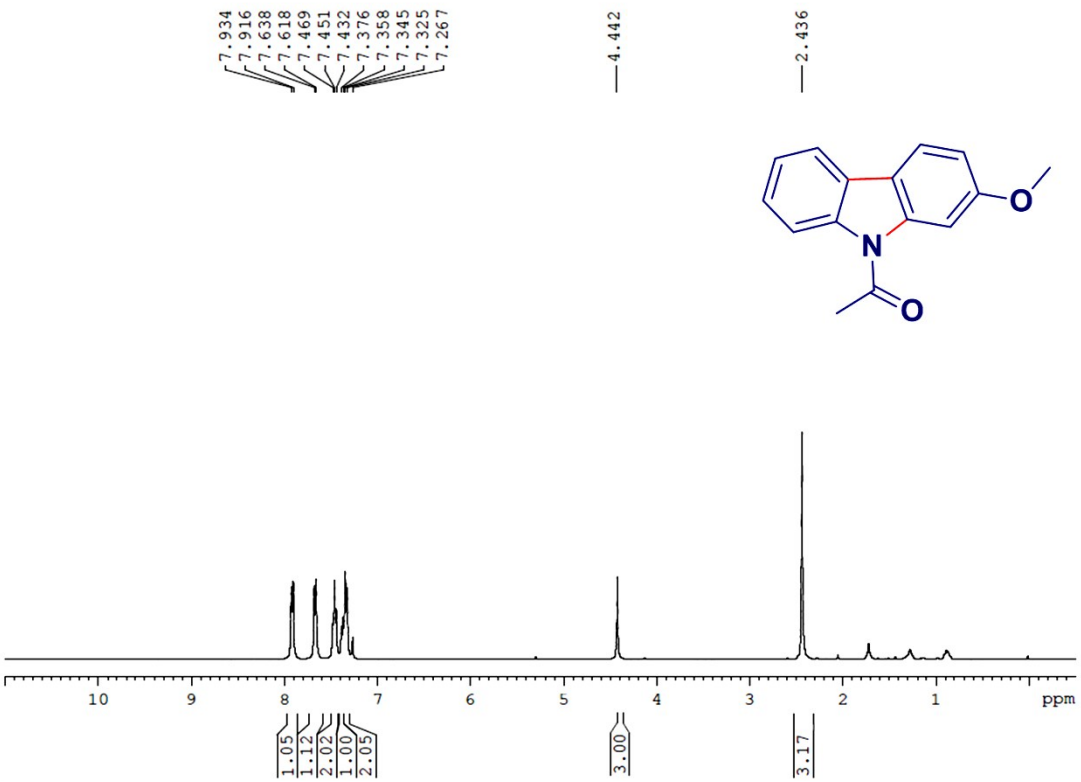

Fig. S15: ^{1}H NMR spectrum of 1-(2-methoxy-carbazol-9-yl)-ethanone

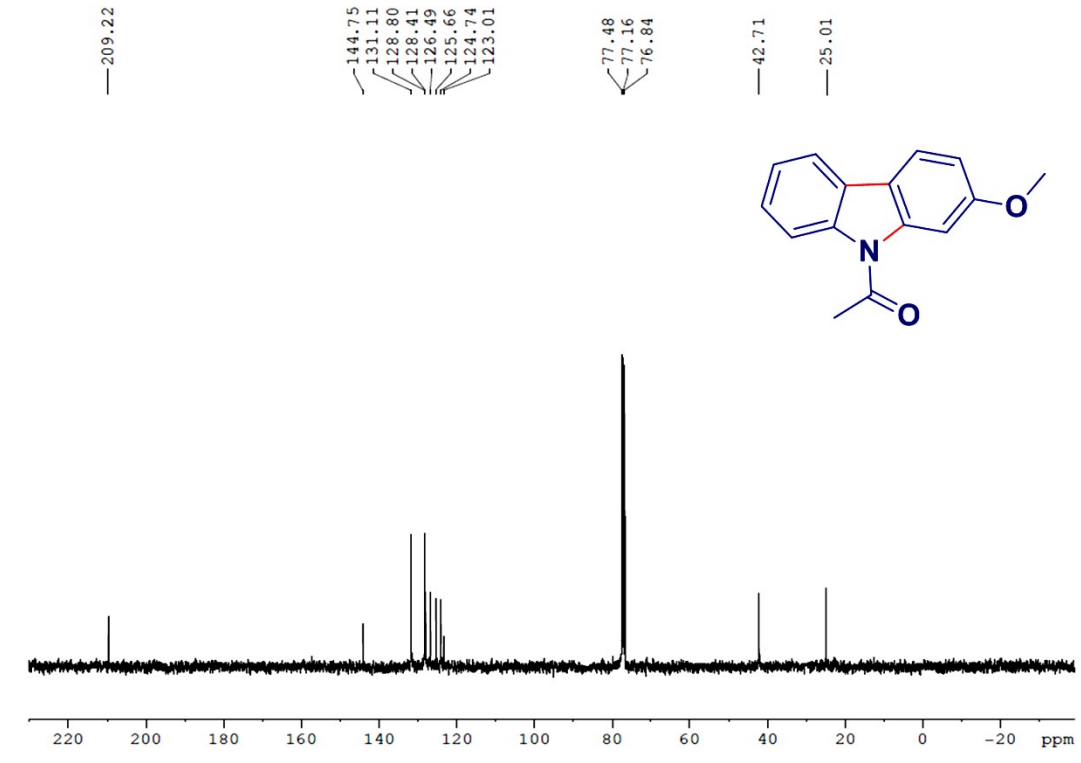

Fig. S16: ^{13}C NMR spectrum of 1-(2-methoxy-carbazol-9-yl)-ethanone

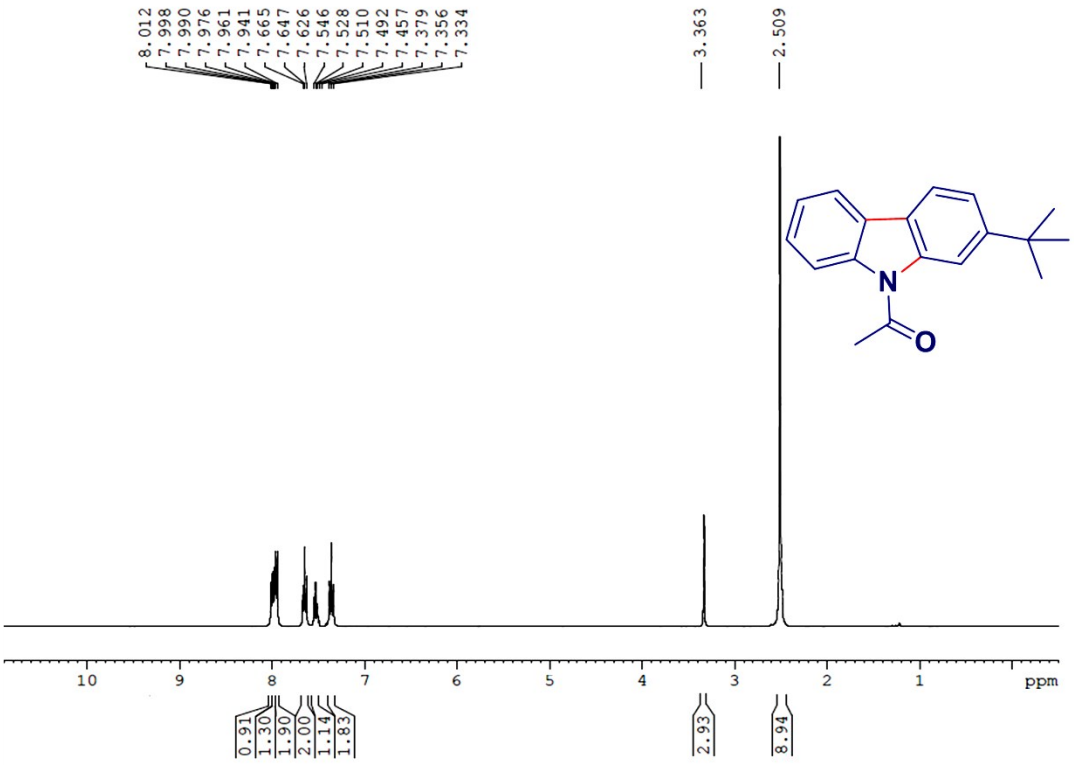

Fig. S17: ^{1}H NMR spectrum of 1-(2-*tert*-butyl-carbazol-9-yl)-ethanone

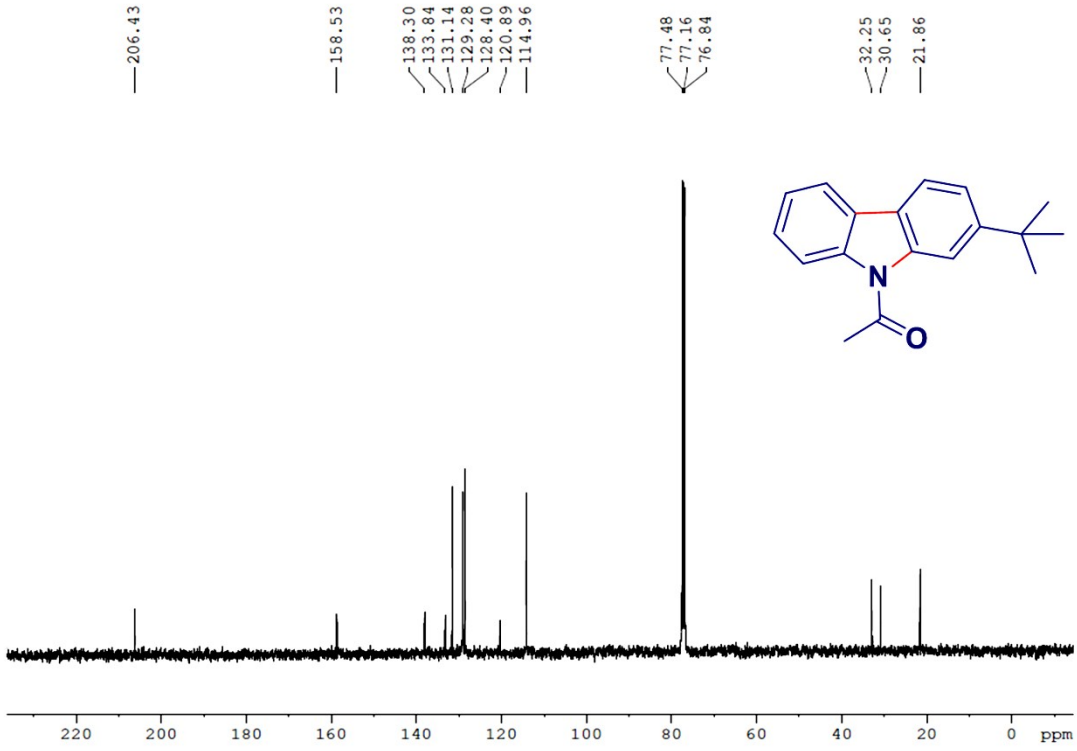

Fig. S18: ^{13}C NMR spectrum of 1-(2-*tert*-butyl-carbazol-9-yl)-ethanone

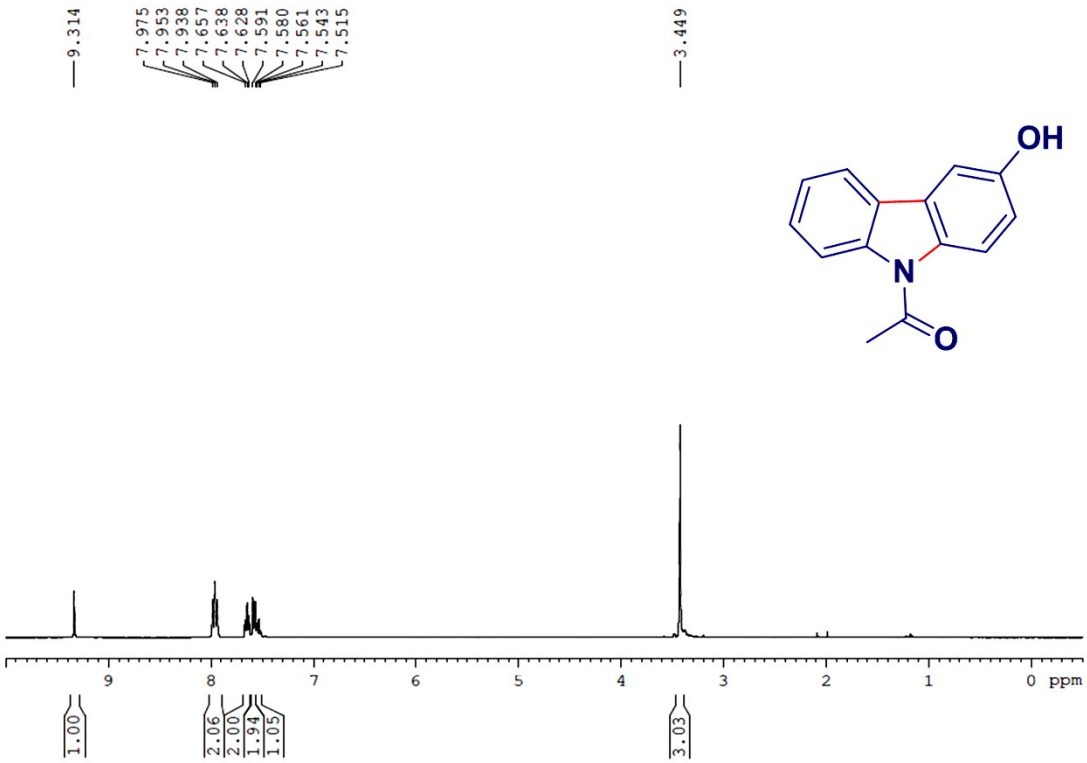

Fig. S19: ^{1}H NMR spectrum of 1-(3-hydroxy-carbazol-9-yl)-ethanone

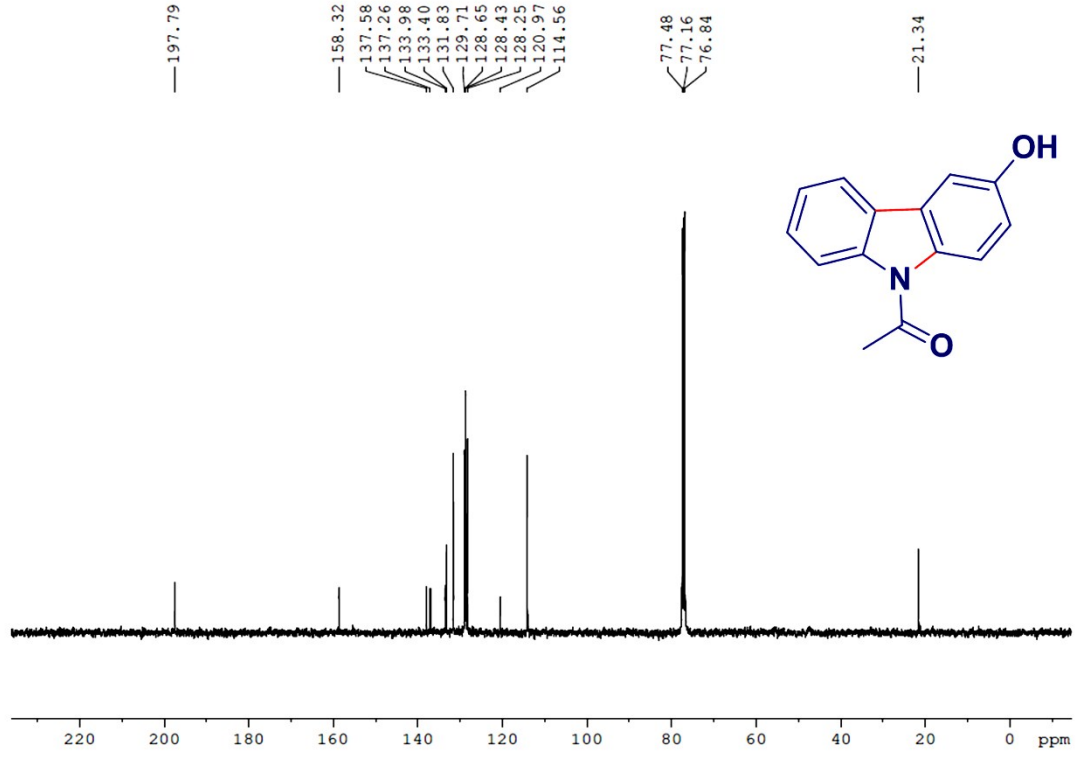

Fig. S20: ^{13}C NMR spectrum of 1-(3-hydroxy-carbazol-9-yl)-ethanone

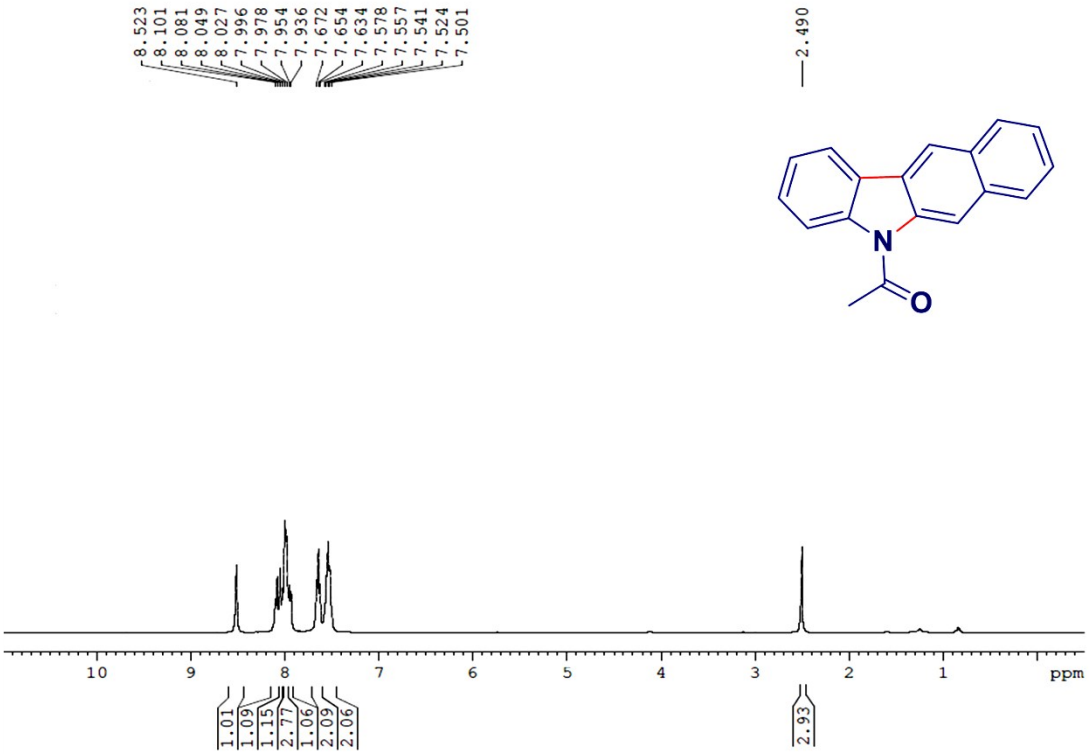

Fig. S21: ^{1}H NMR spectrum of 1-benzo[b]carbazol-5-yl-ethanone

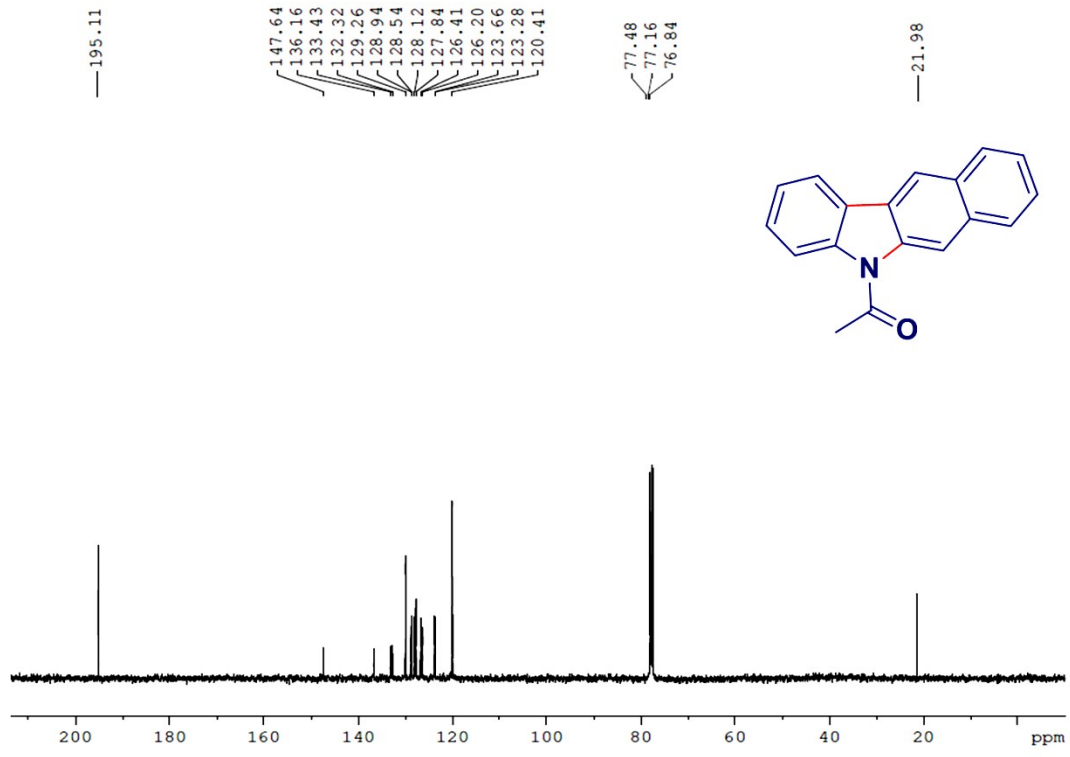

Fig. S22: ^{13}C NMR spectrum of 1-benzo[b]carbazol-5-yl-ethanone

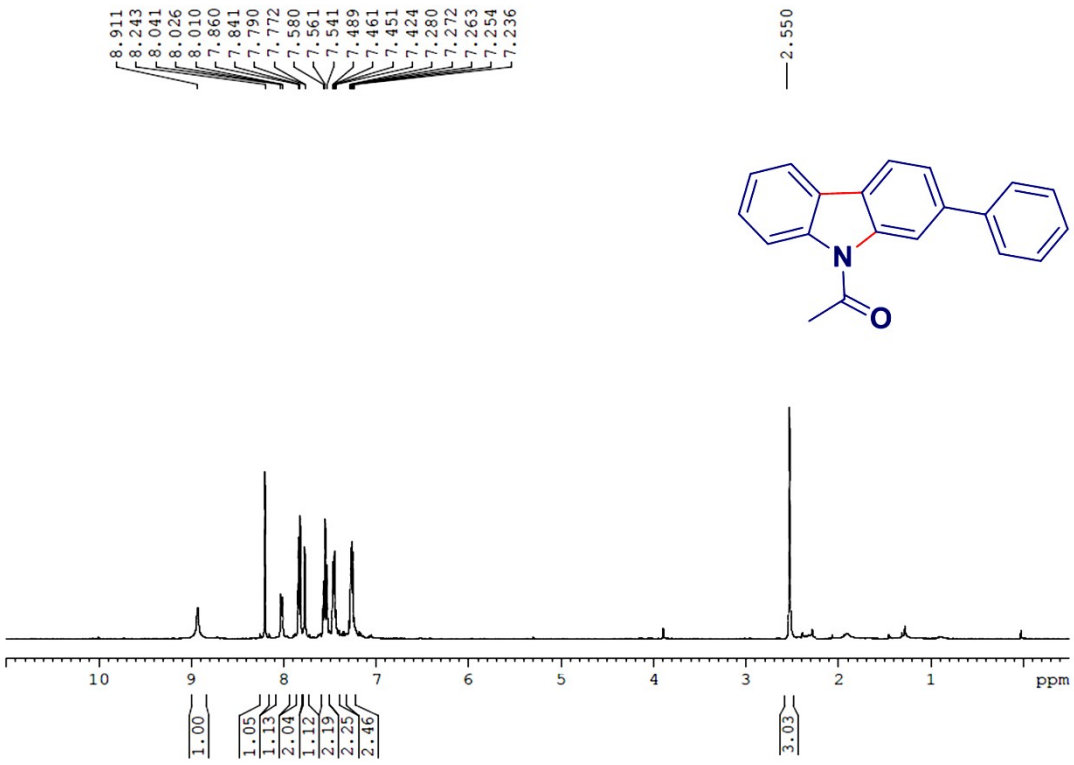

Fig. S23: ^{1}H NMR spectrum of 1-(2-phenyl-carbazol-9-yl)-ethanone

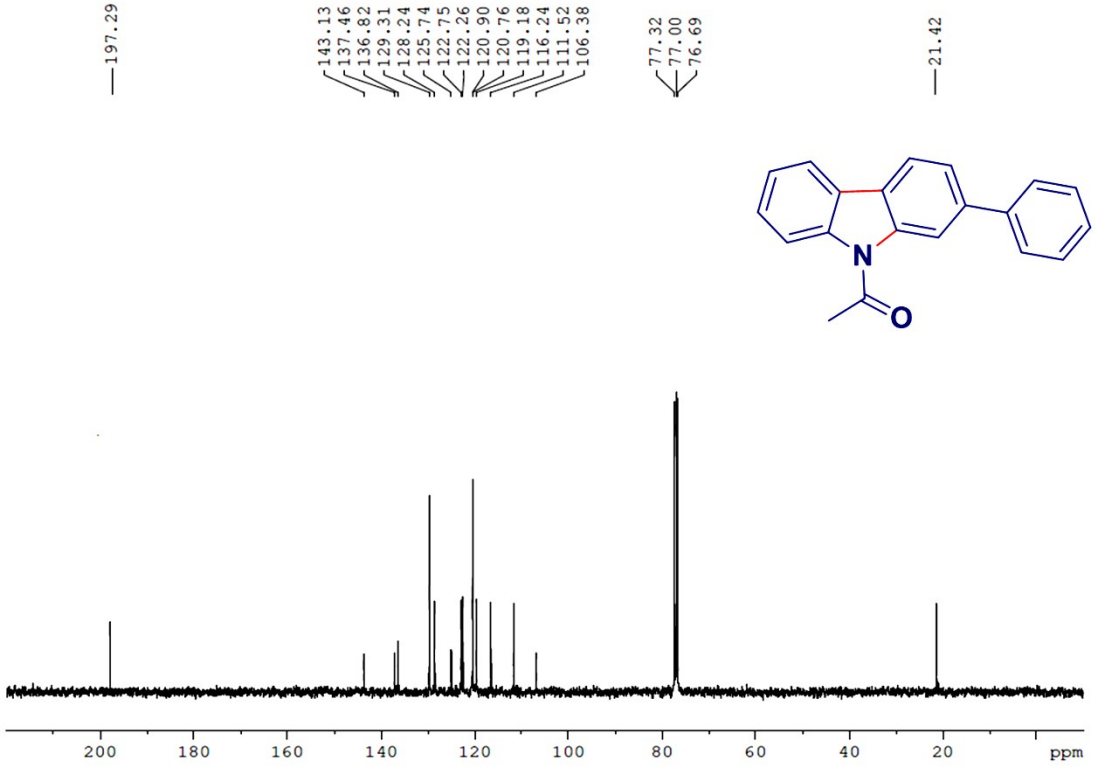

Fig. S24: ^{13}C NMR spectrum of 1-(2-phenyl-carbazol-9-yl)-ethanone

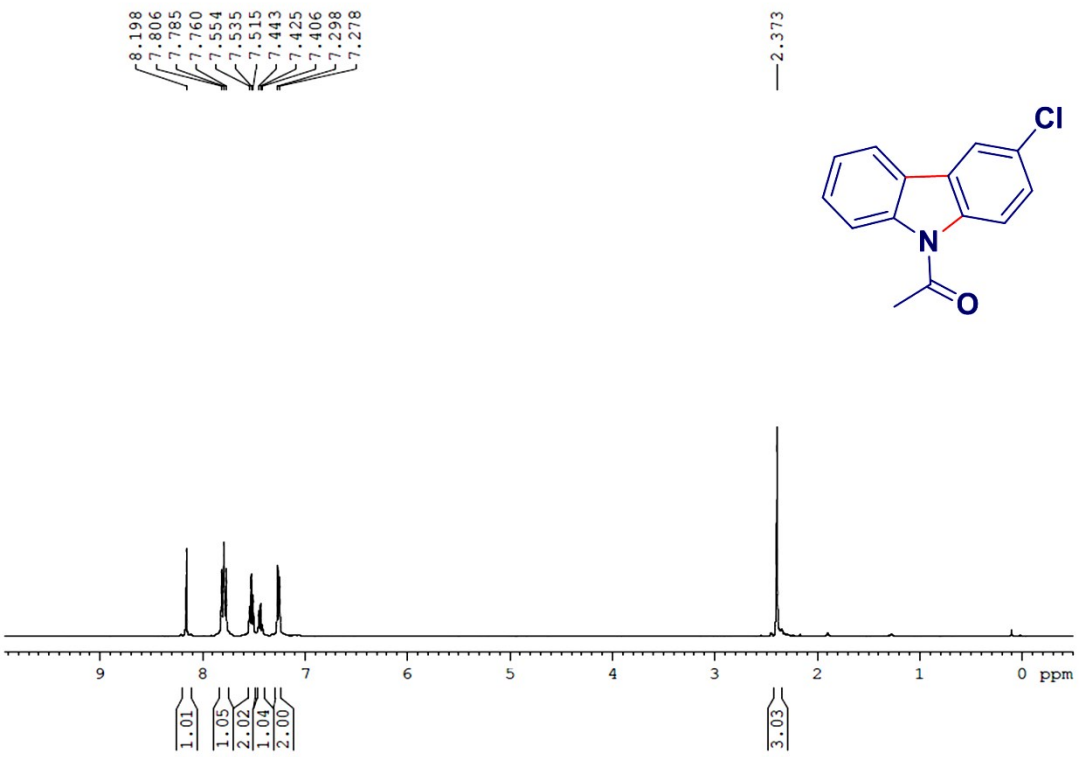

Fig. S25: ^{1}H NMR spectrum of 1-(3-chloro-carbazol-9-yl)-ethanone

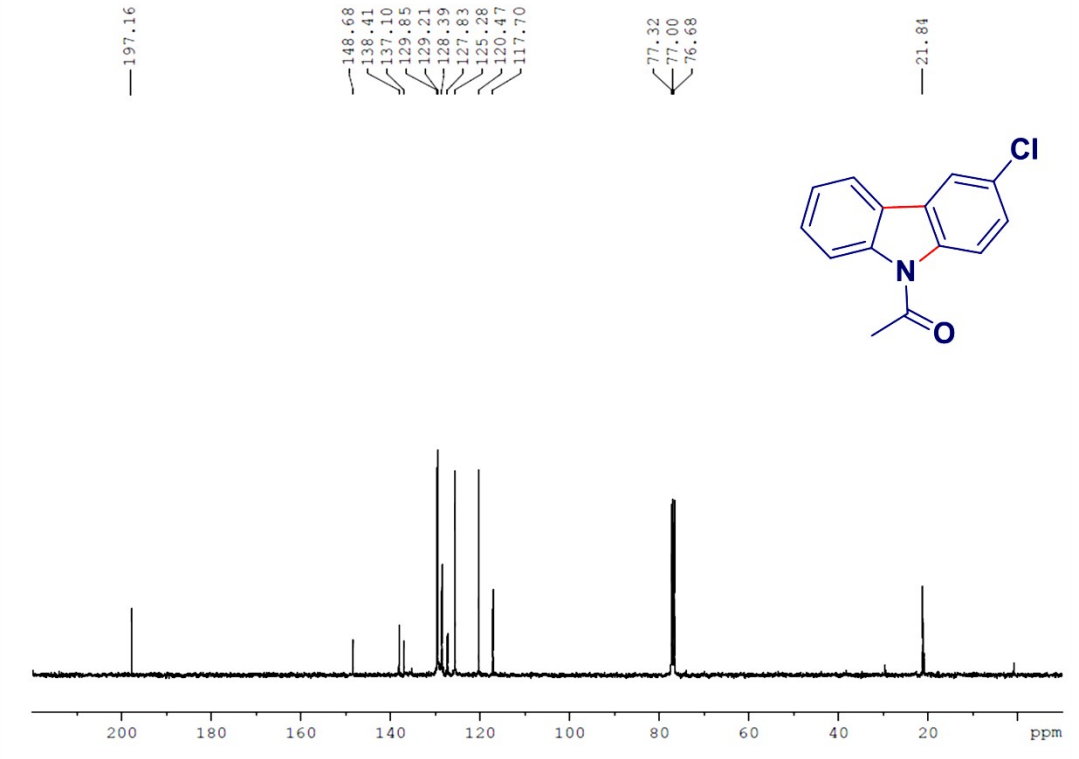

Fig. S26: ^{13}C NMR spectrum of 1-(3-chloro-carbazol-9-yl)-ethanone

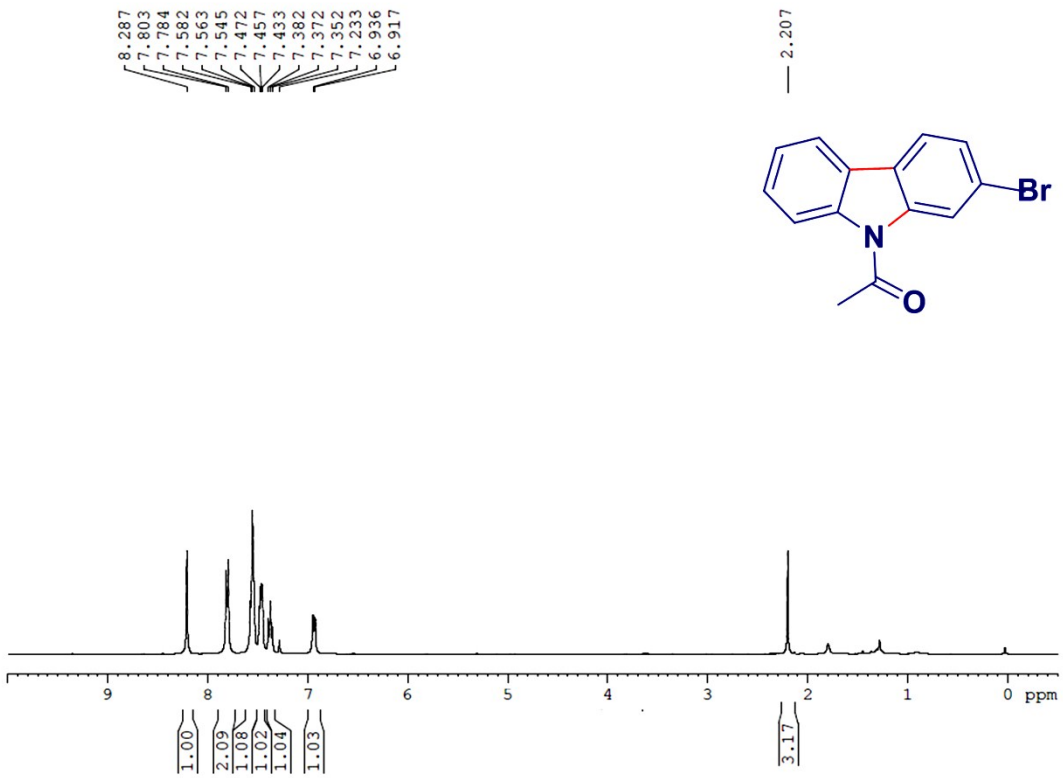

Fig. S27: ^{1}H NMR spectrum of 1-(2-bromo-carbazol-9-yl)-ethanone

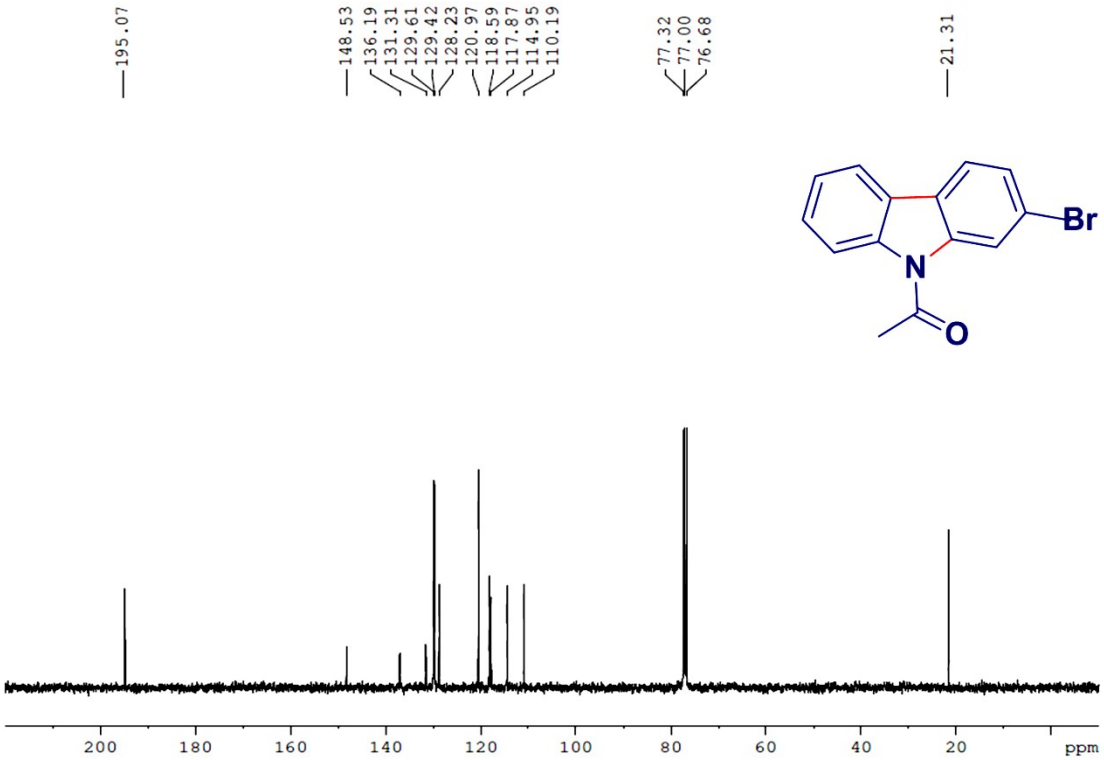

Fig. S28: ^{13}C NMR spectrum of 1-(2-bromo-carbazol-9-yl)-ethanone

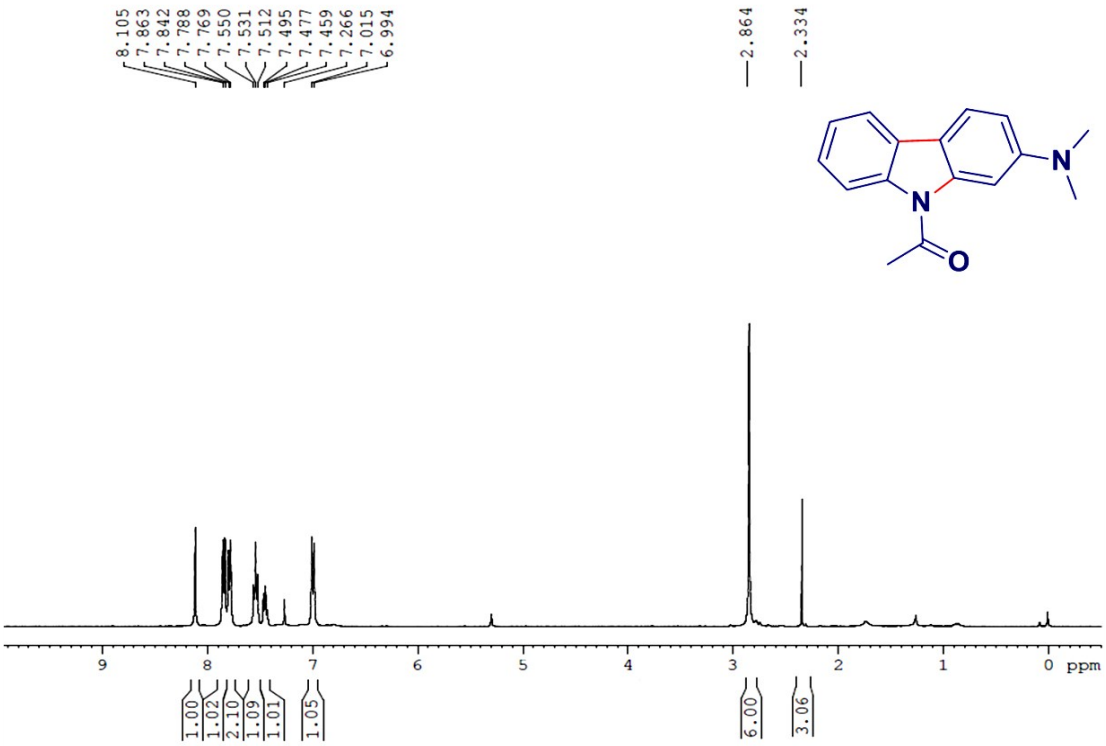

Fig. S29: ^{1}H NMR spectrum of 1-(2-dimethylamino-carbazol-9-yl)-ethanone

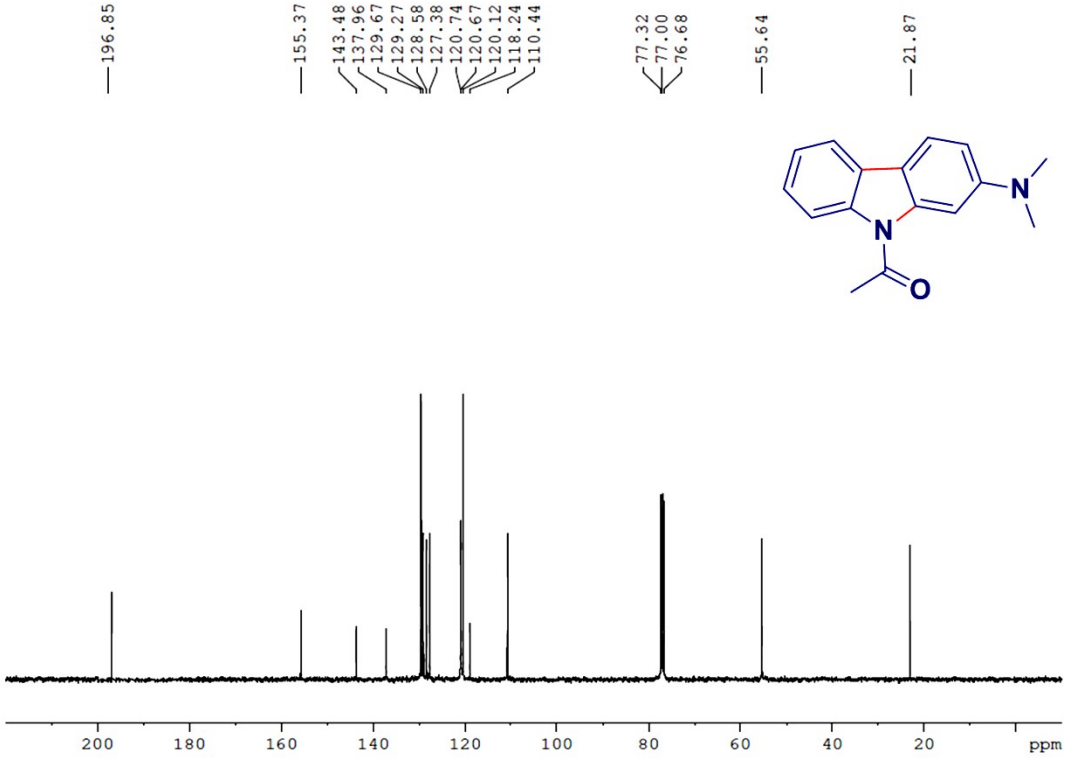

Fig. S30: ^{13}C NMR spectrum of 1-(2-dimethylamino-carbazol-9-yl)-ethanone

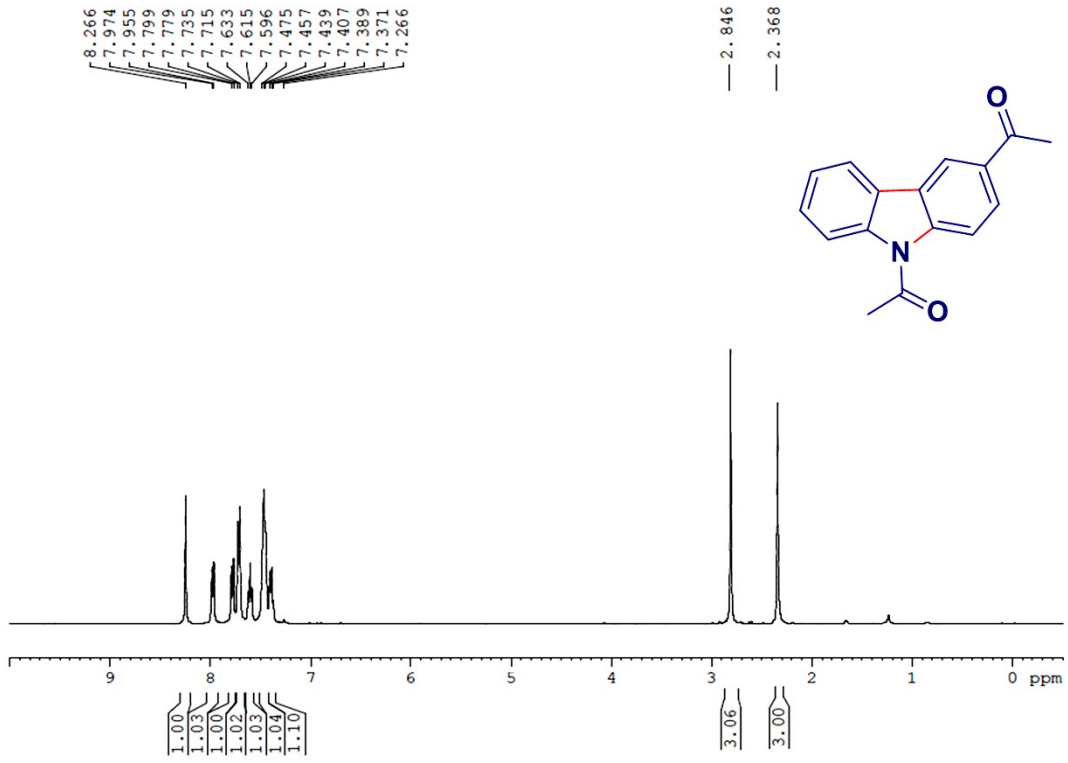

Fig. S31: ^{1}H NMR spectrum of 1-(3-acetyl-carbazol-9-yl)-ethanone

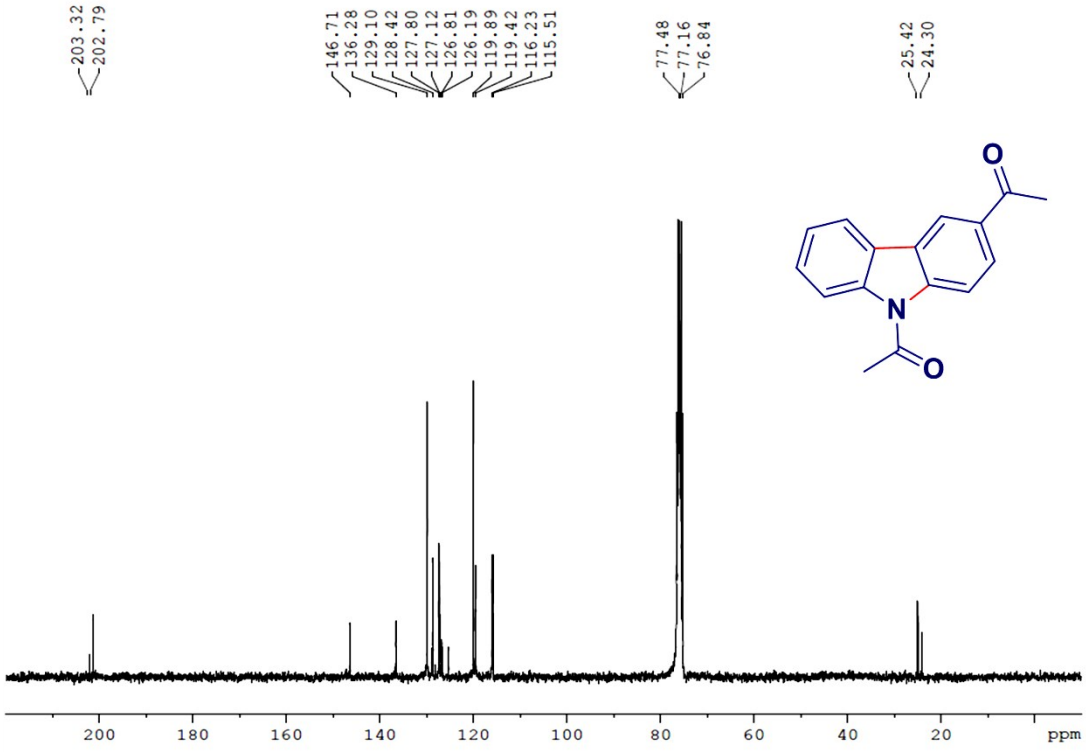

Fig. S32: ^{13}C NMR spectrum of 1-(3-acetyl-carbazol-9-yl)-ethanone

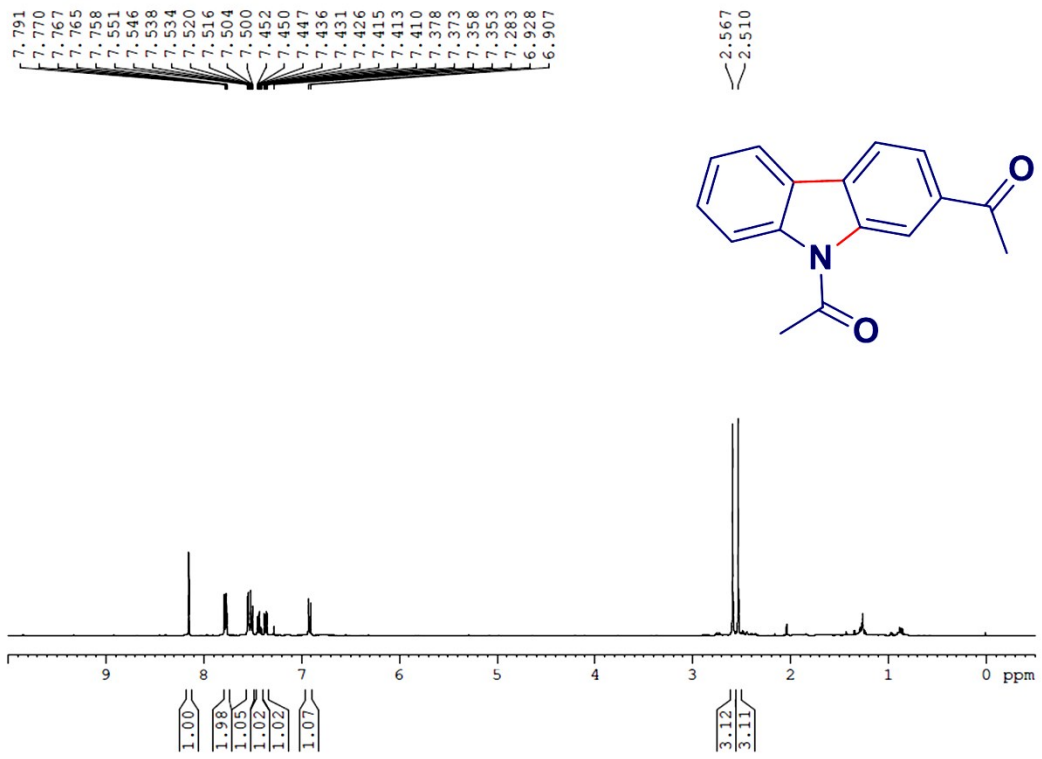

Fig. S33: ^{1}H NMR spectrum of 1-(2-acetyl-carbazol-9-yl)-ethanone

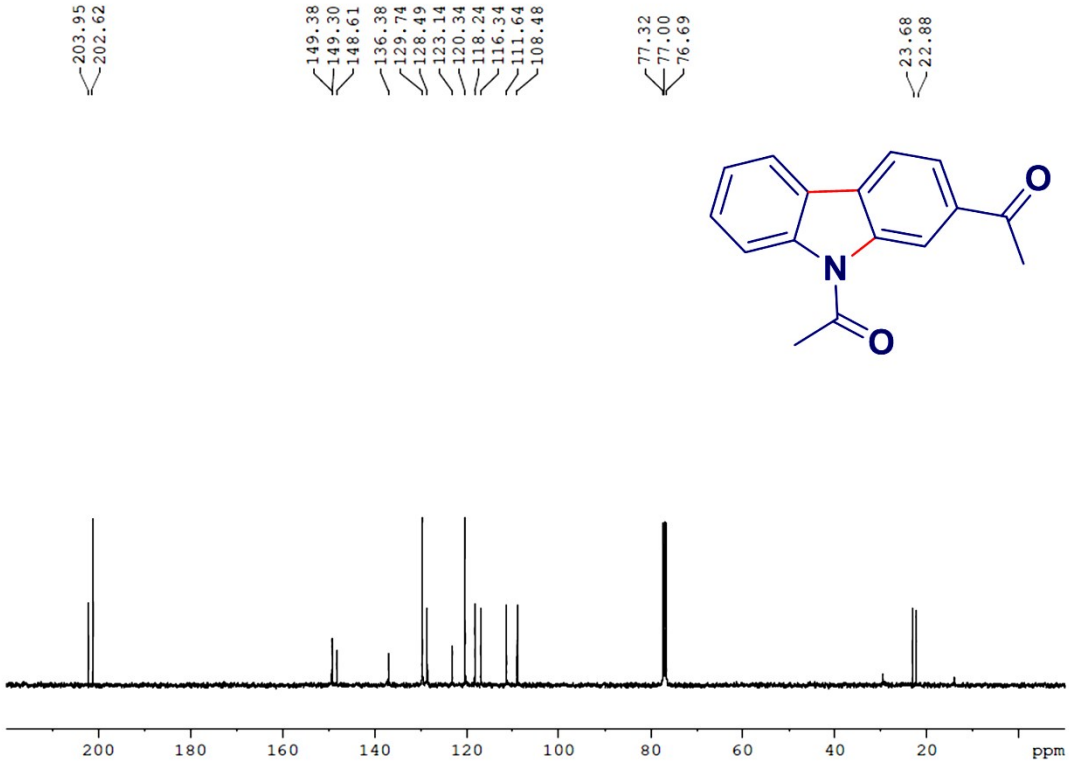

Fig. S34: ^{13}C NMR spectrum of 1-(2-acetyl-carbazol-9-yl)-ethanone

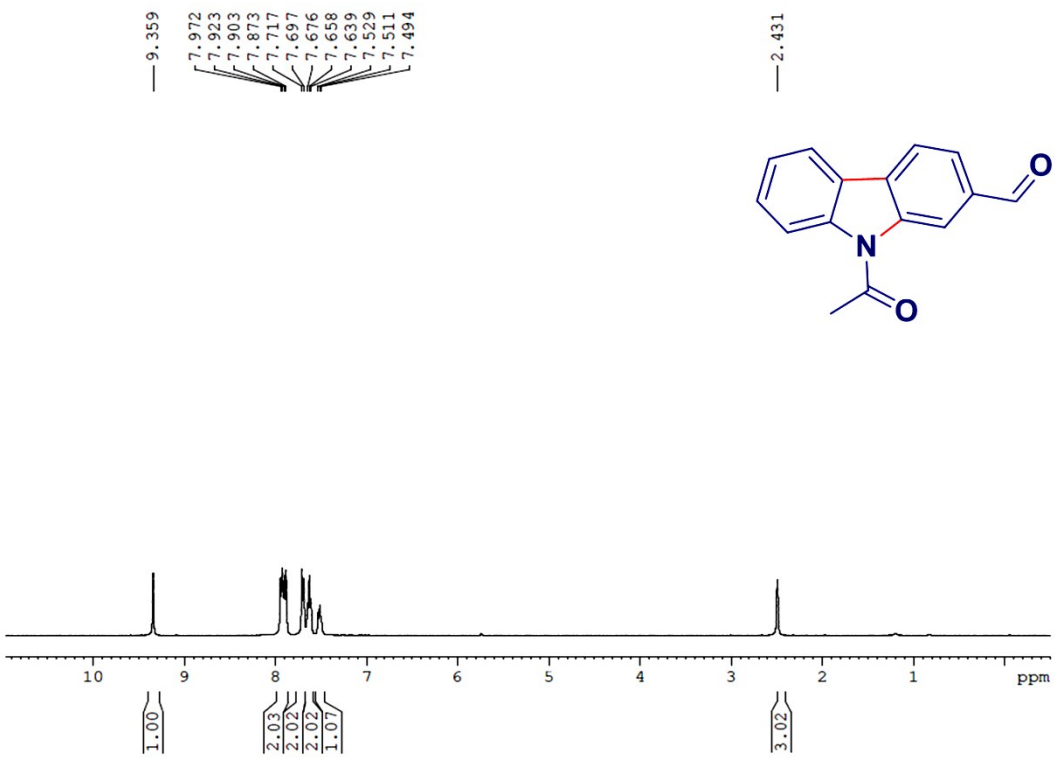

Fig. S35: ^{1}H NMR spectrum of 9-acetyl-9*H*-carbazole-2-carbaldehyde

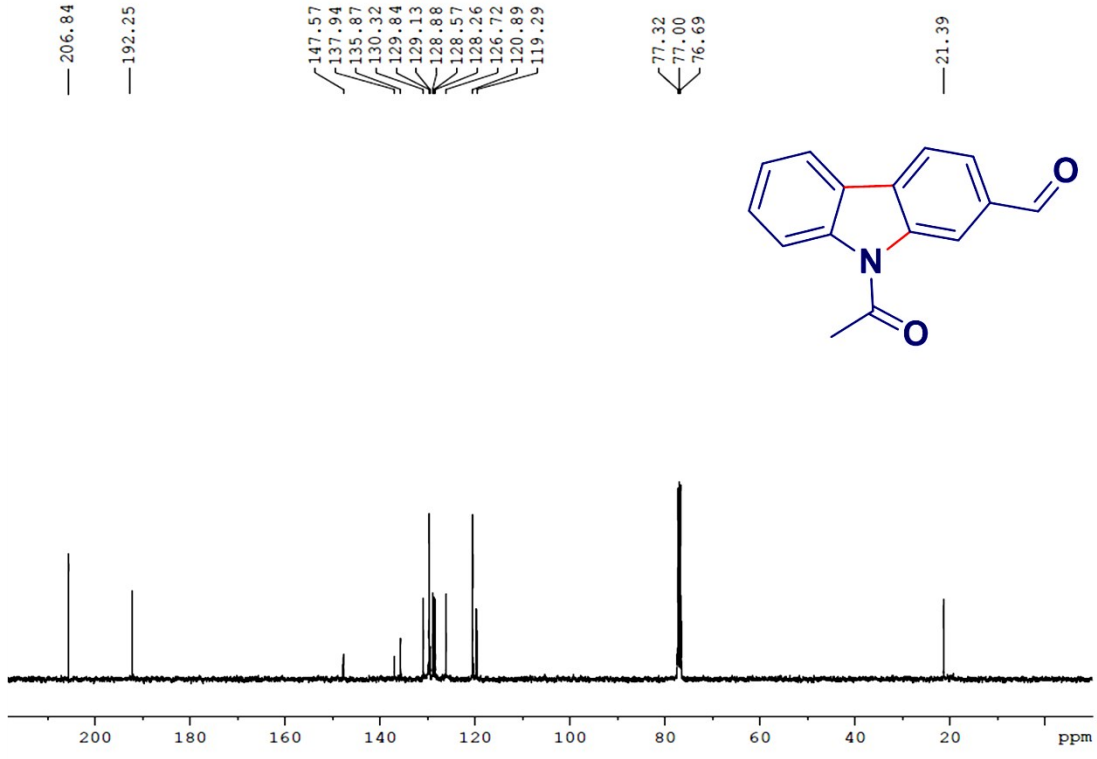

Fig. S36: ^{13}C NMR spectrum of 9-acetyl-9*H*-carbazole-2-carbaldehyde

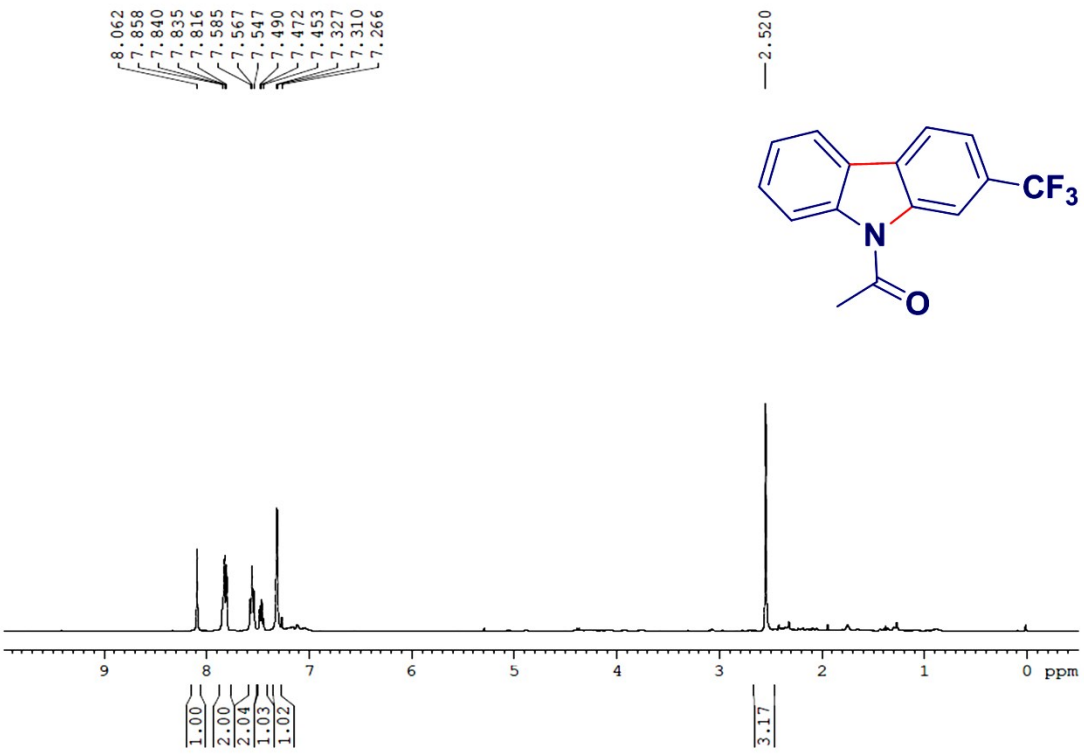

Fig. S37: ^{1}H NMR spectrum of 1-(2-trifluoromethyl-carbazol-9-yl)-ethanone

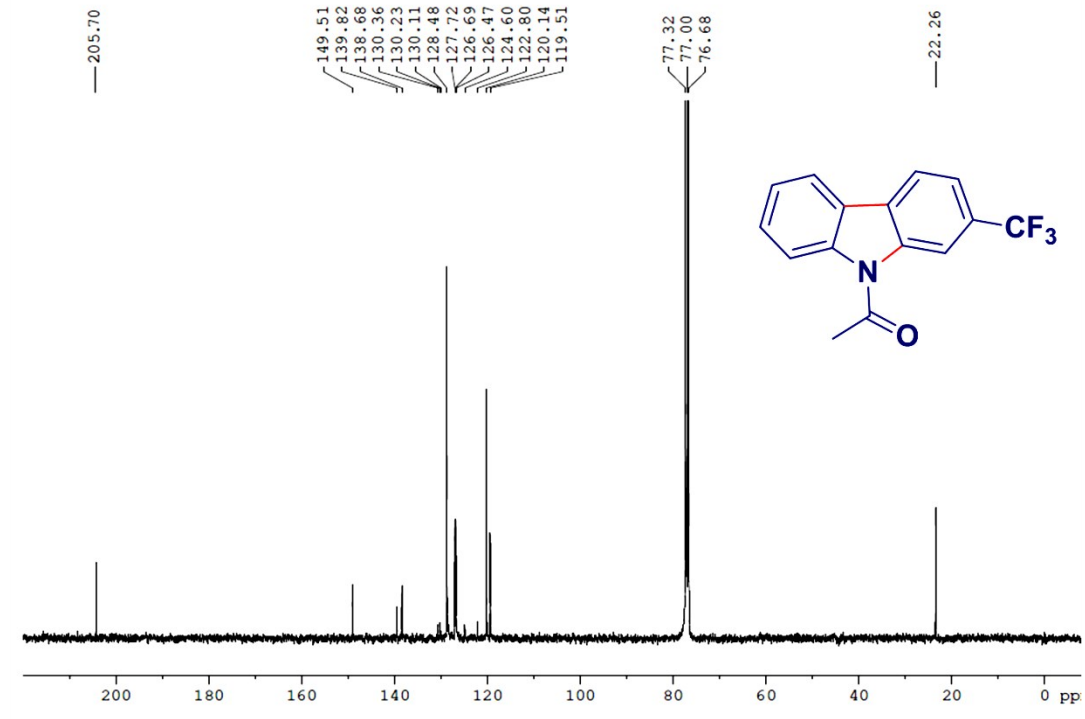

Fig. S38: ^{13}C NMR spectrum of 1-(2-trifluoromethyl-carbazol-9-yl)-ethanone

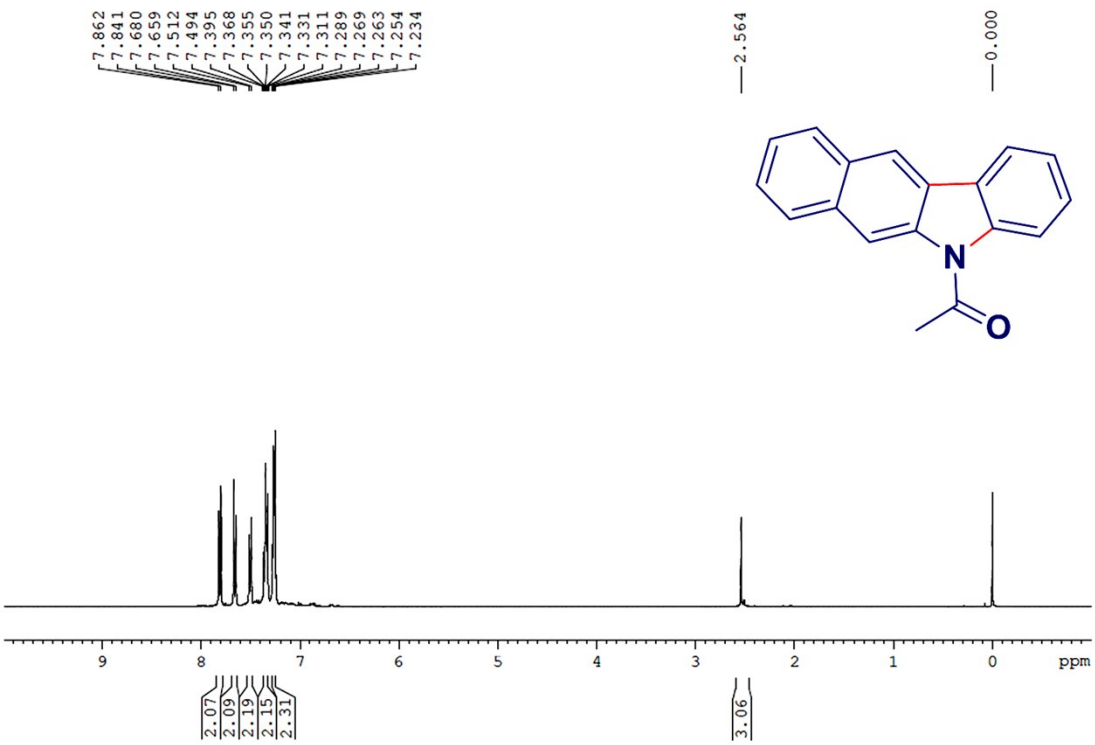

Fig. S39: ^{1}H NMR spectrum of 1-benzo[b]carbazol-5-yl-ethanone

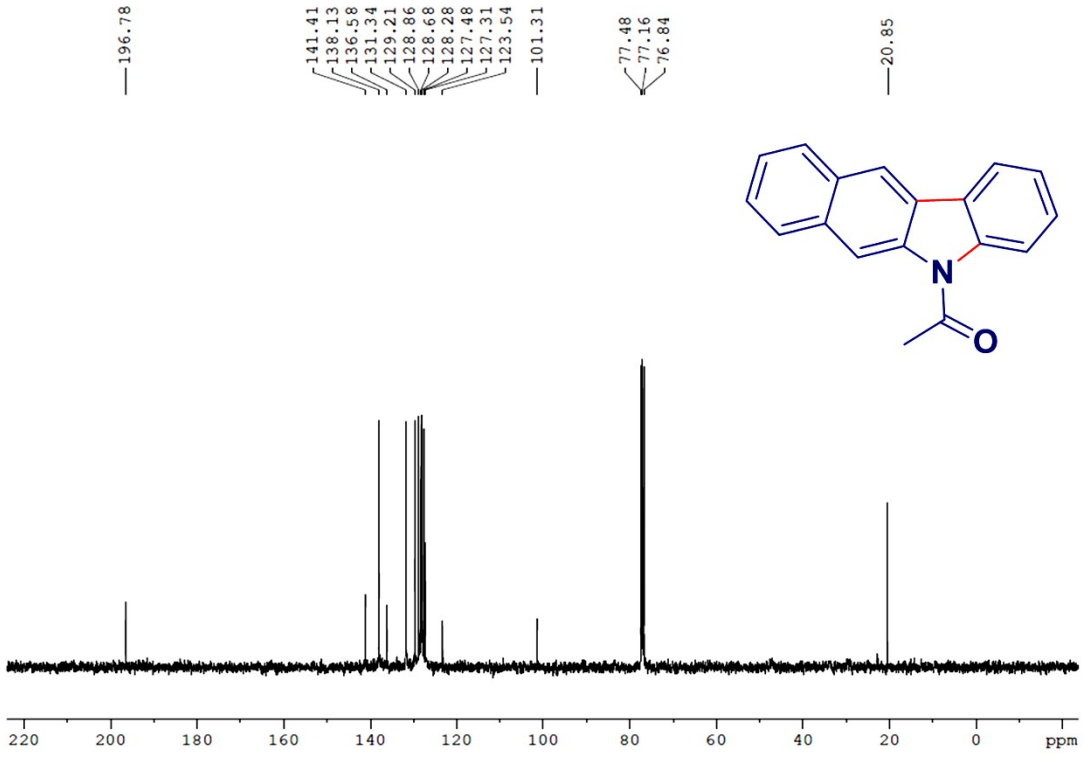

Fig. S40: ^{13}C NMR spectrum of 1-benzo[b]carbazol-5-yl-ethanone

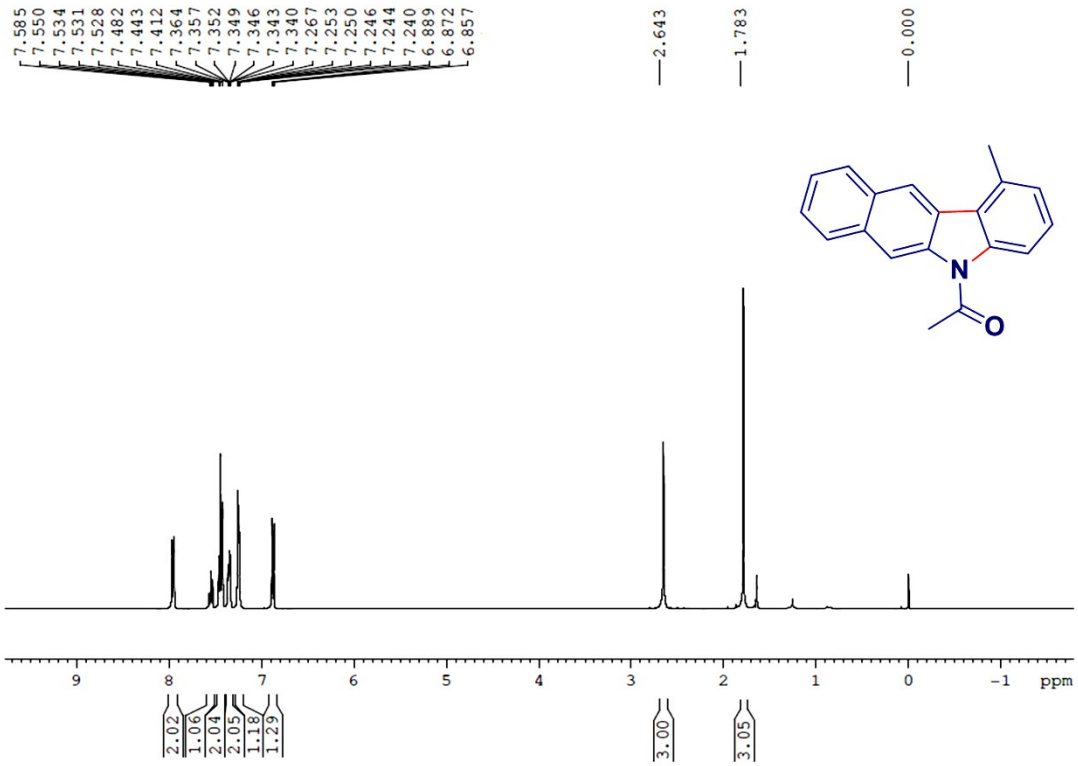

Fig. S41: ^{1}H NMR spectrum of 1-(1-methyl-benzo[b]carbazol-5-yl)-ethanone

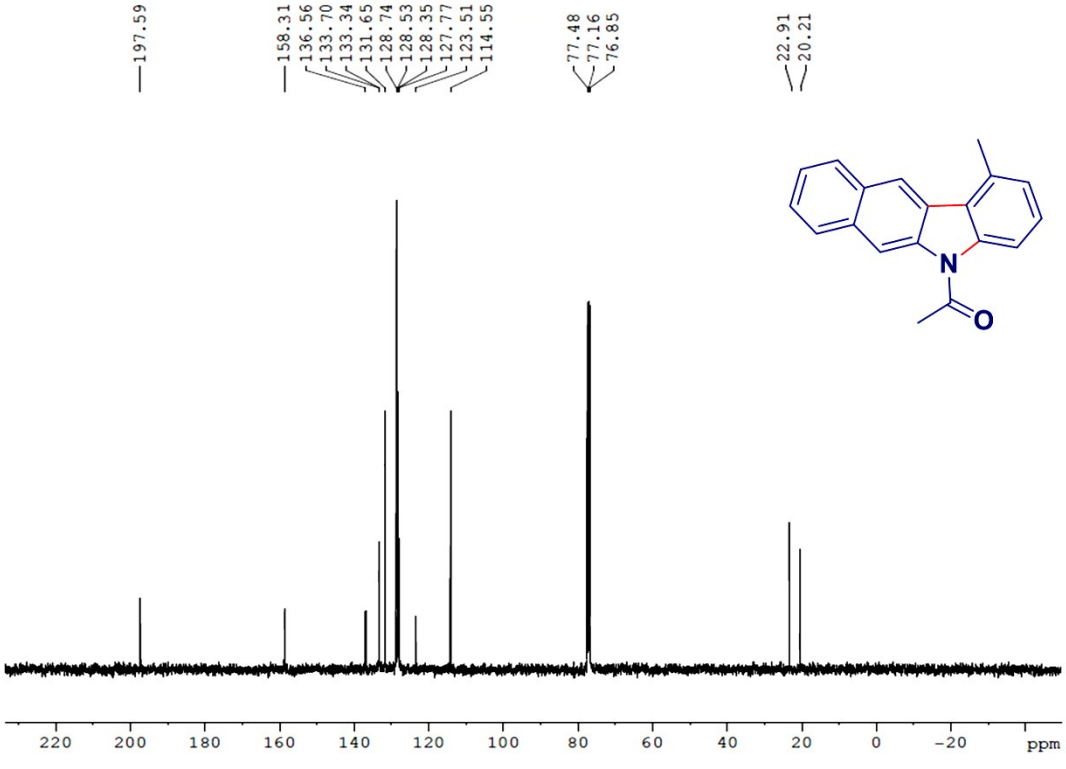

Fig. S42: ^{13}C NMR spectrum of 1-(1-methyl-benzo[b]carbazol-5-yl)-ethanone

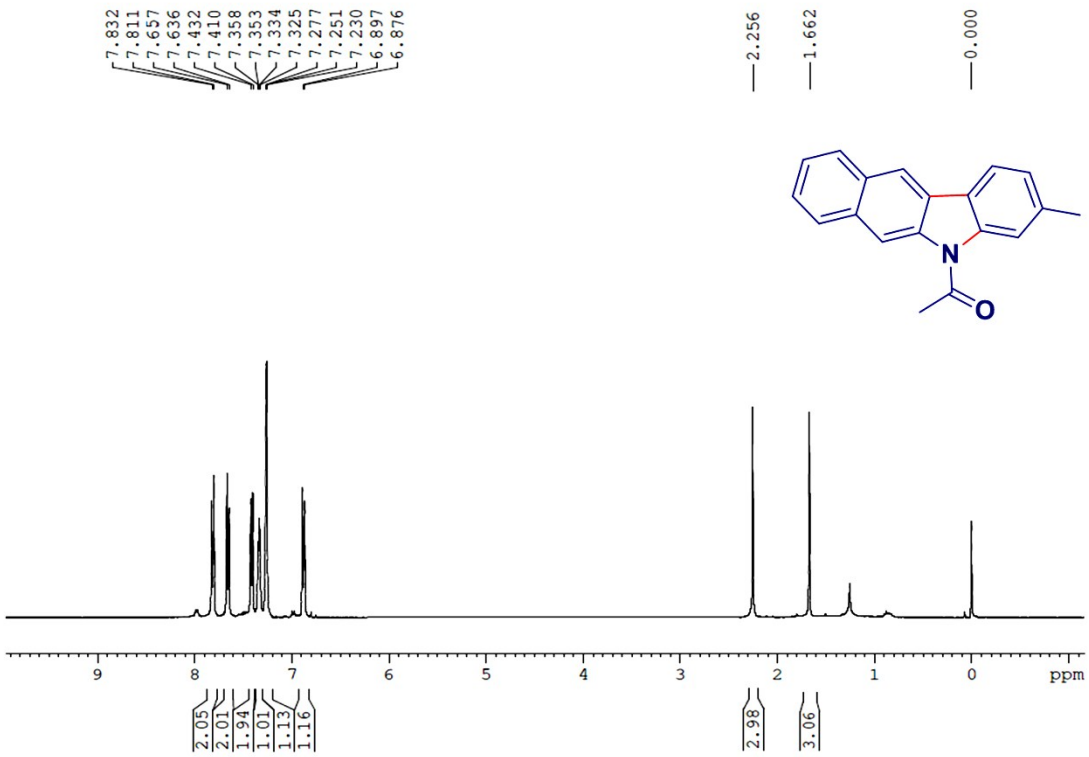

Fig. S43: ^{1}H NMR spectrum of 1-(3-methyl-benzo[b]carbazol-5-yl)-ethanone

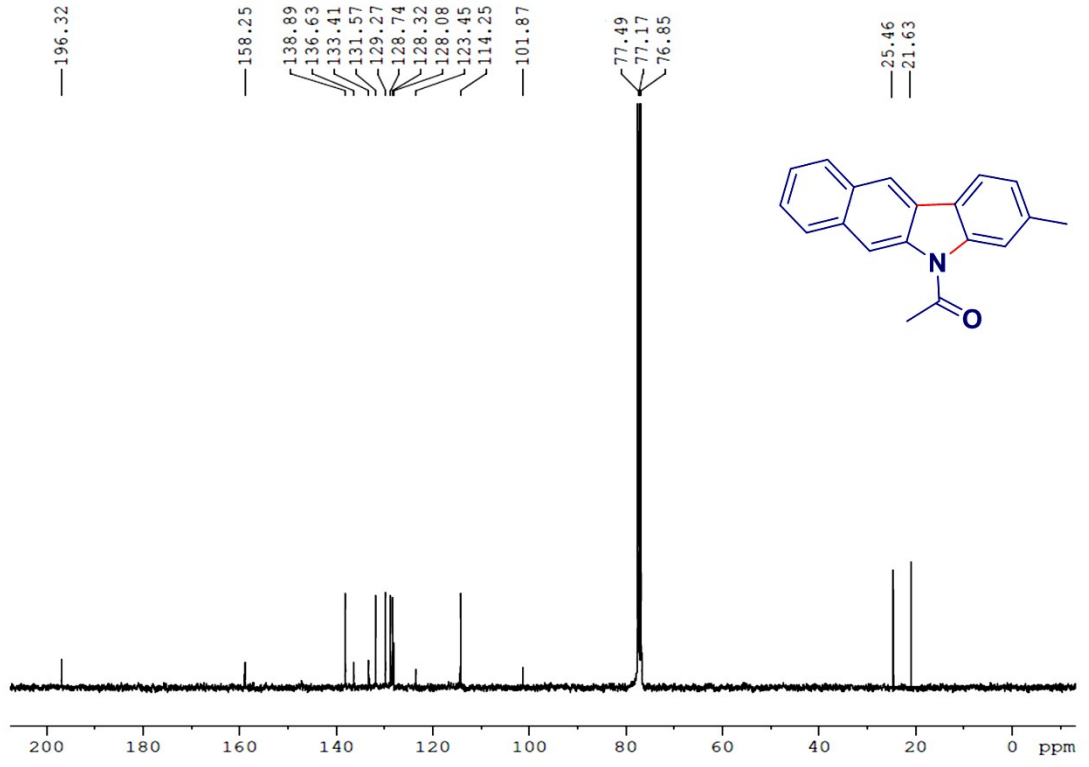

Fig. S44: ^{13}C NMR spectrum of 1-(3-methyl-benzo[b]carbazol-5-yl)-ethanone

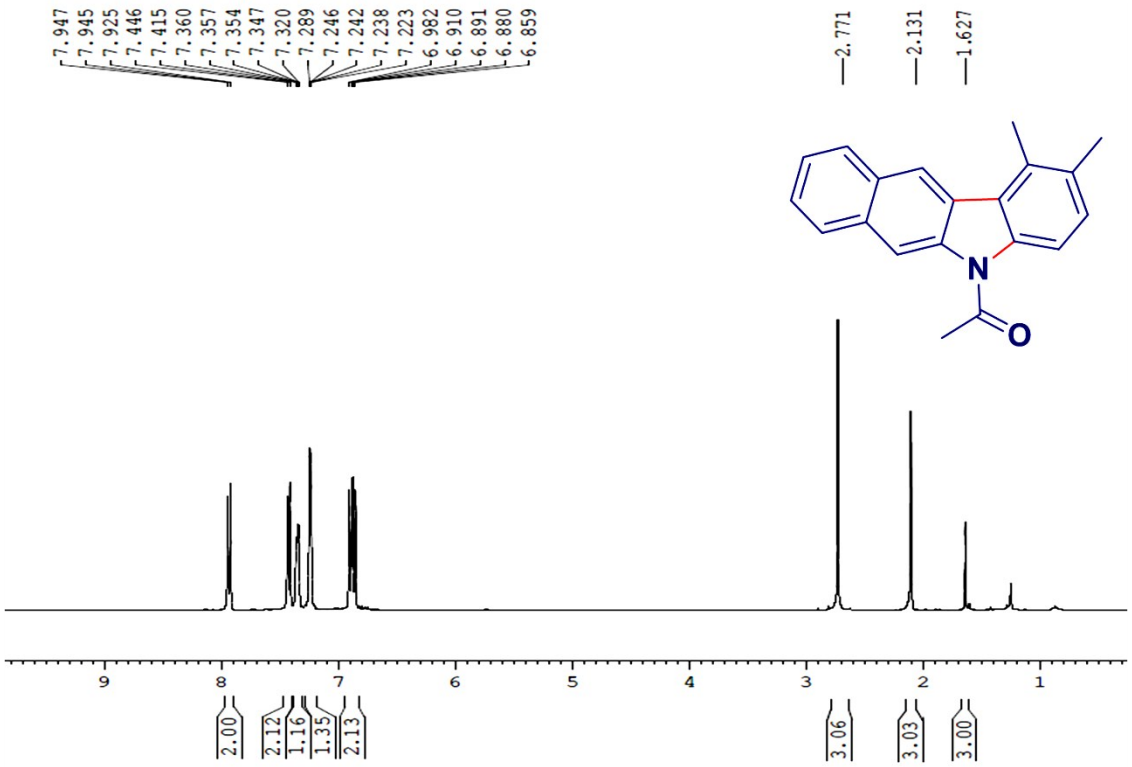

Fig. S45: ^{1}H NMR spectrum of 1-(1, 2-dimethyl-benzo[b]carbazol-5-yl)-ethanone

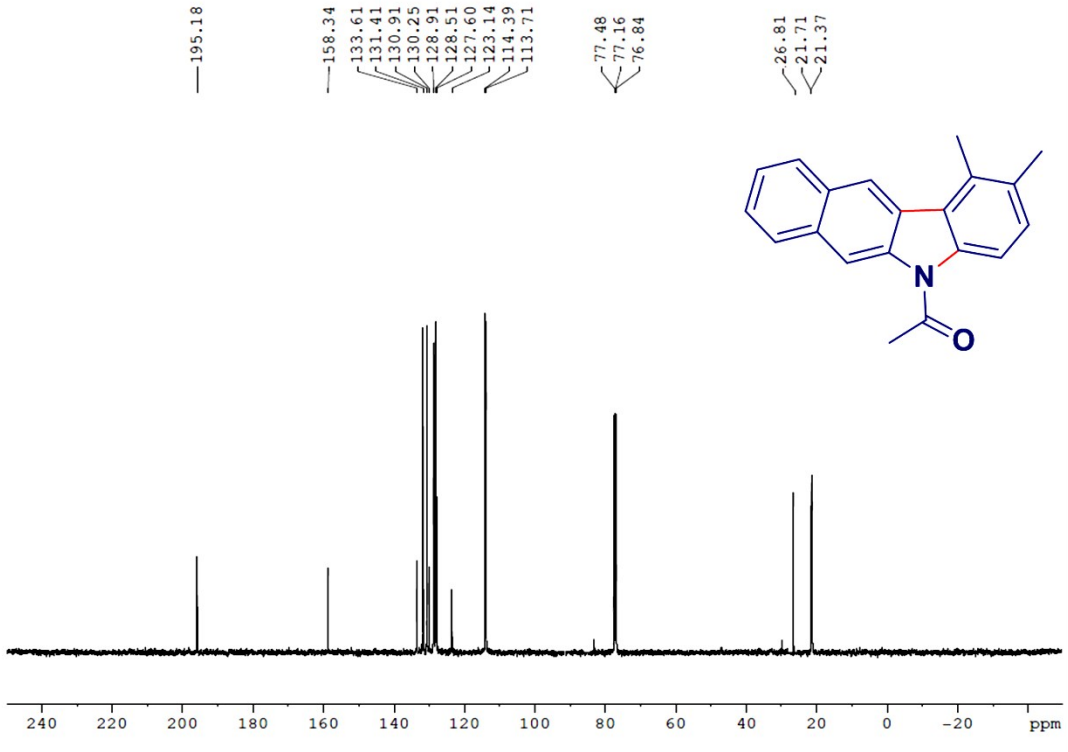

Fig. S46: ^{13}C NMR spectrum of 1-(1, 2-dimethyl-benzo[b]carbazol-5-yl)-ethanone

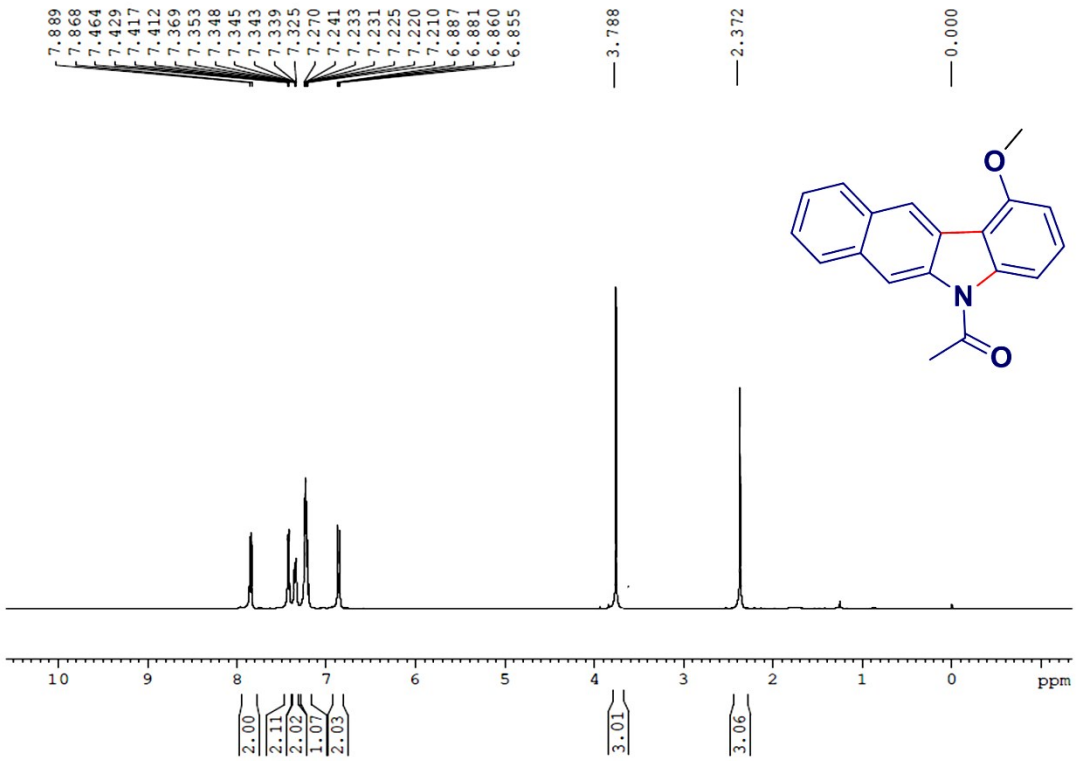

Fig. S47: ^{1}H NMR spectrum of 1-(1-methoxy-benzo[b]carbazol-5-yl)-ethanone

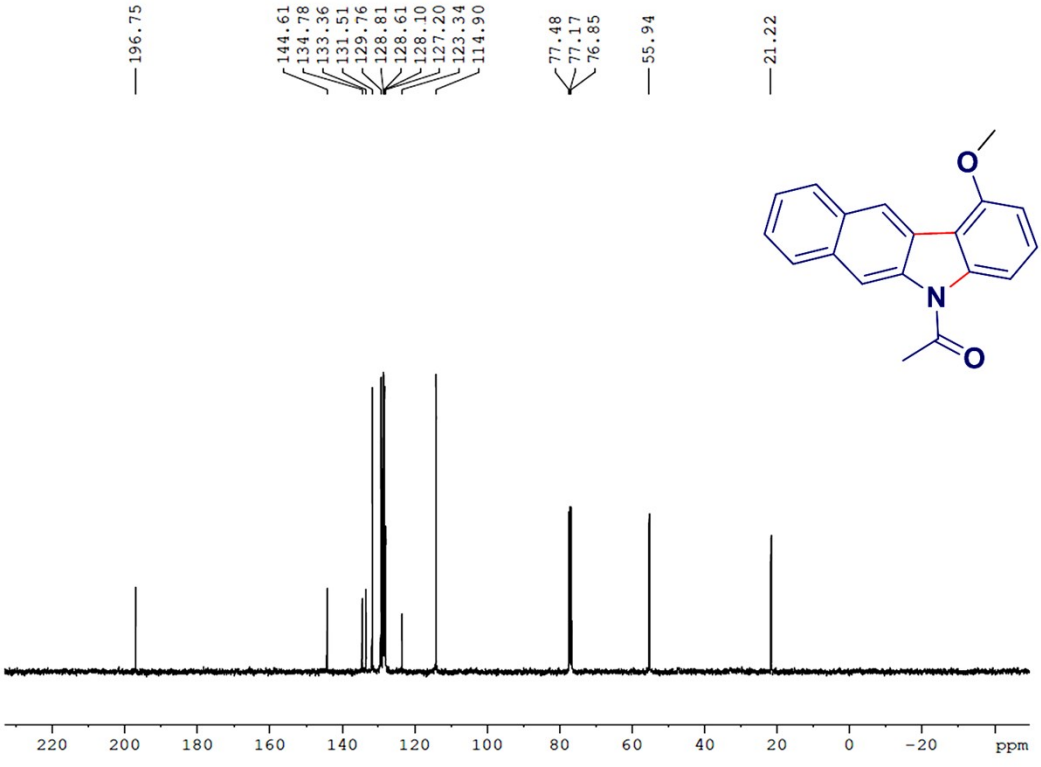

Fig. S48: ^{13}C NMR spectrum of 1-(1-methoxy-benzo[b]carbazol-5-yl)-ethanone

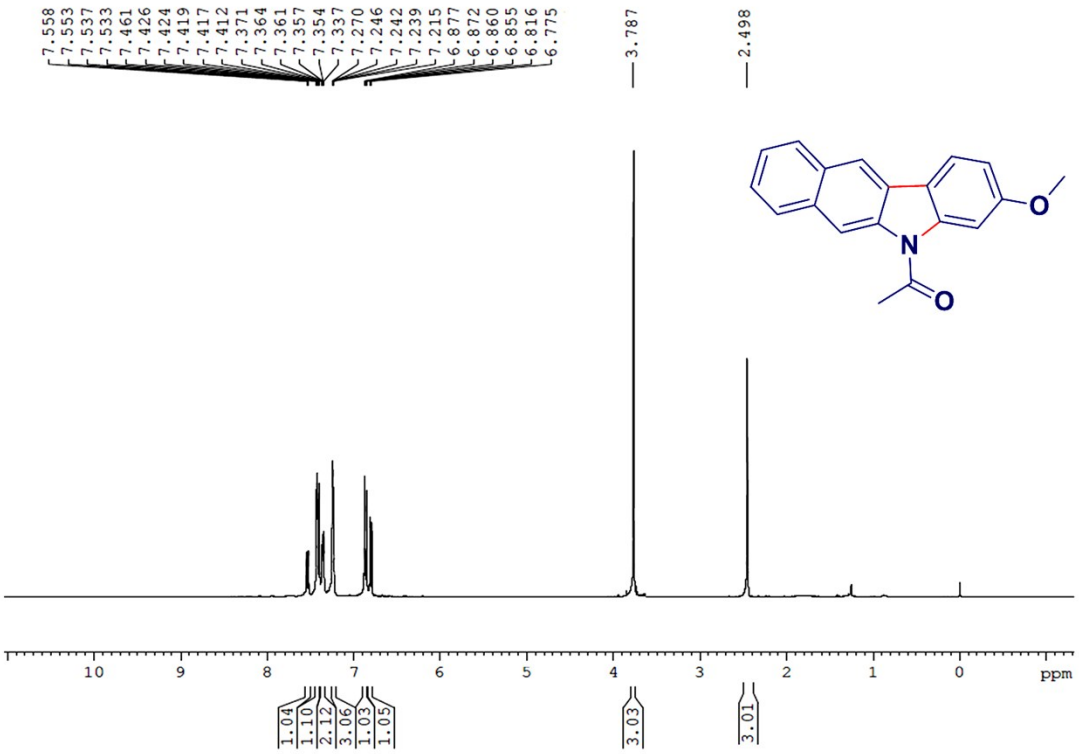

Fig. S49: ^{1}H NMR spectrum of 1-(3-methoxy-benzo[b]carbazol-5-yl)-ethanone

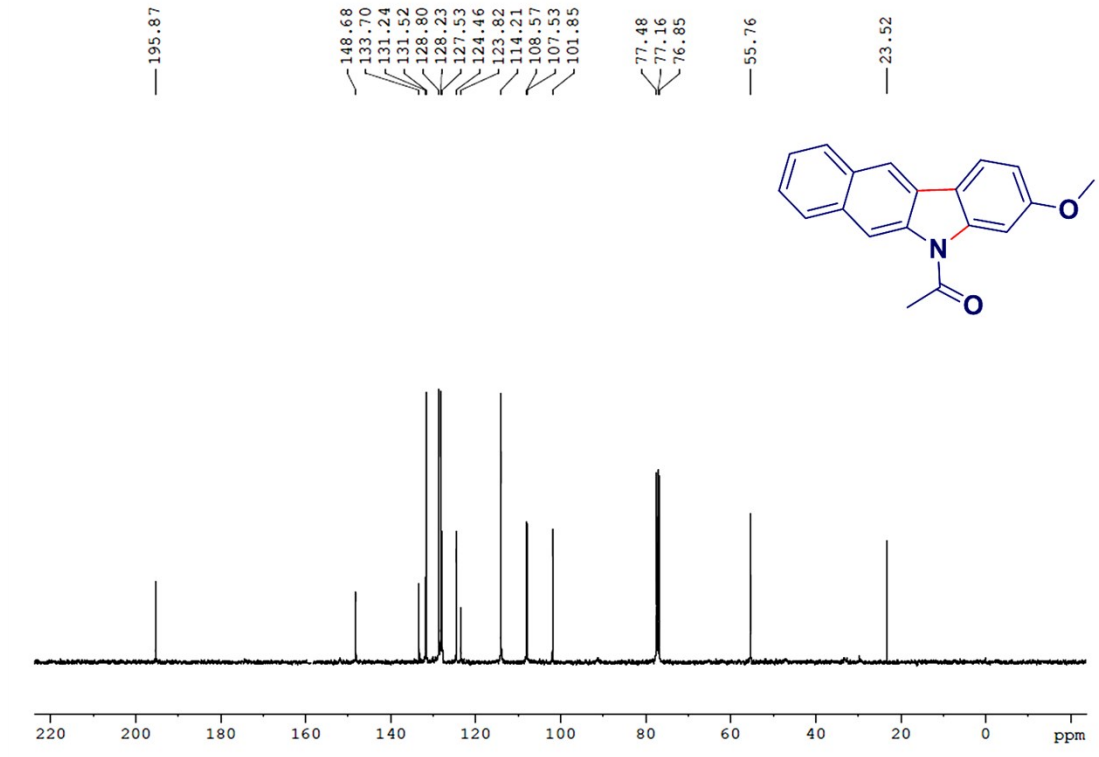

Fig. S50: ^{13}C NMR spectrum of 1-(3-methoxy-benzo[b]carbazol-5-yl)-ethanone

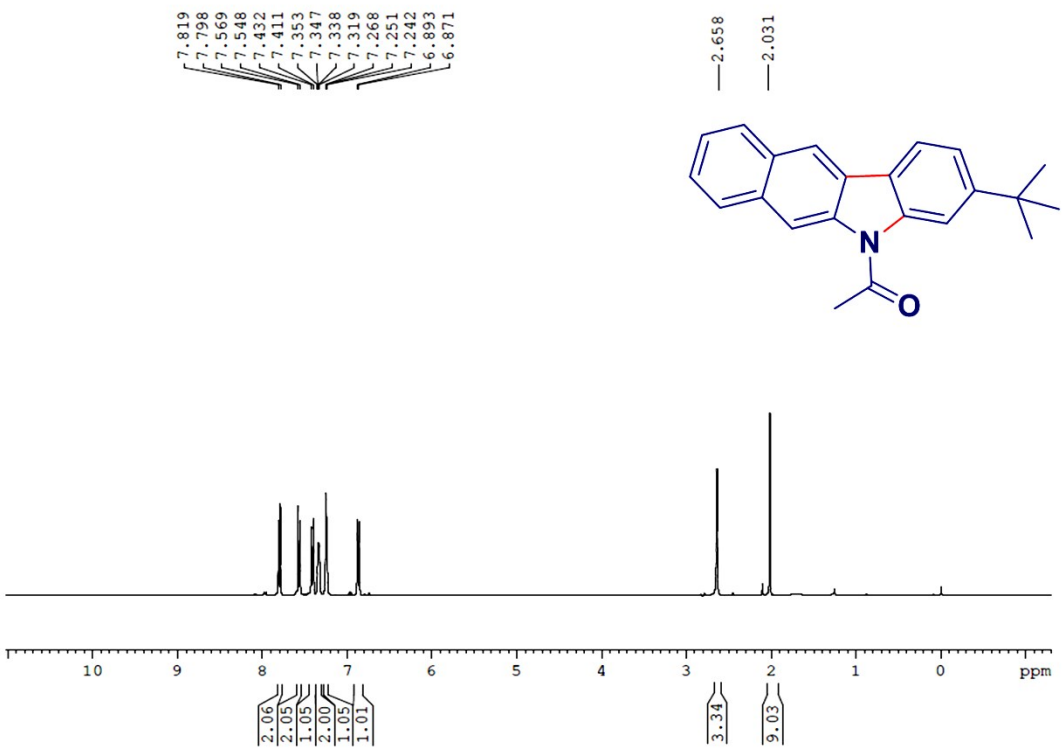

Fig. S51: ^{1}H NMR spectrum of 1-(3-*tert*-butyl-benzo[b]carbazol-5-yl)-ethanone

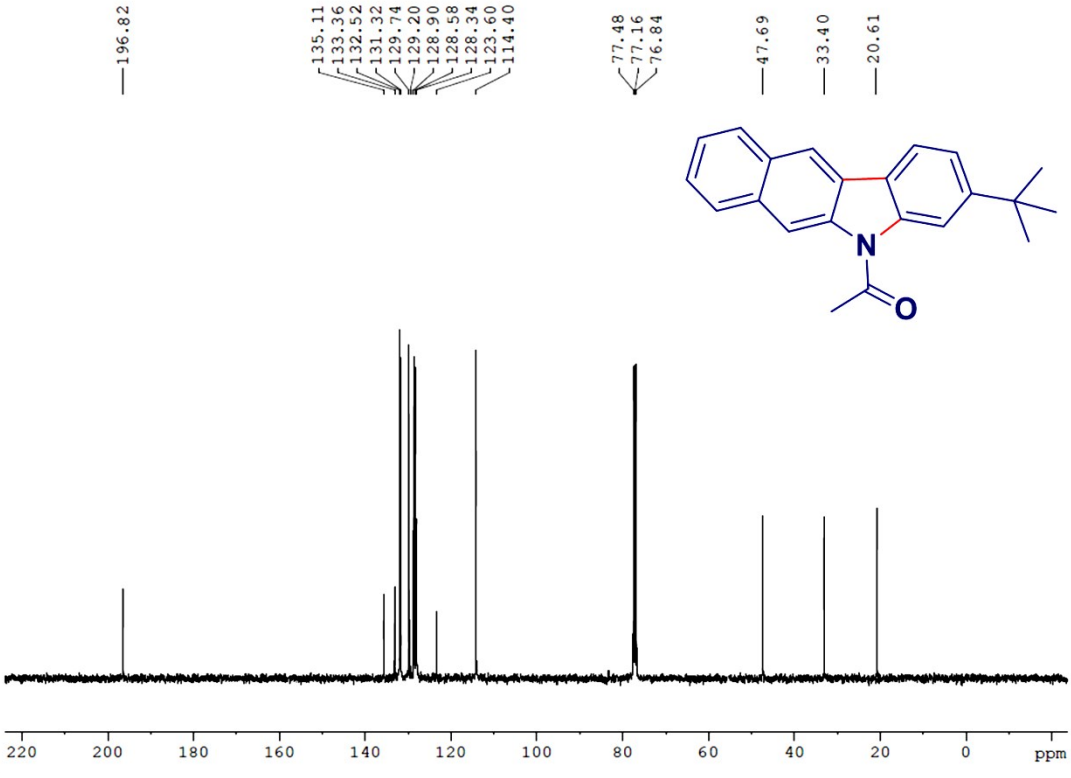

Fig. S52: ^{13}C NMR spectrum of 1-(3-*tert*-butyl-benzo[b]carbazol-5-yl)-ethanone

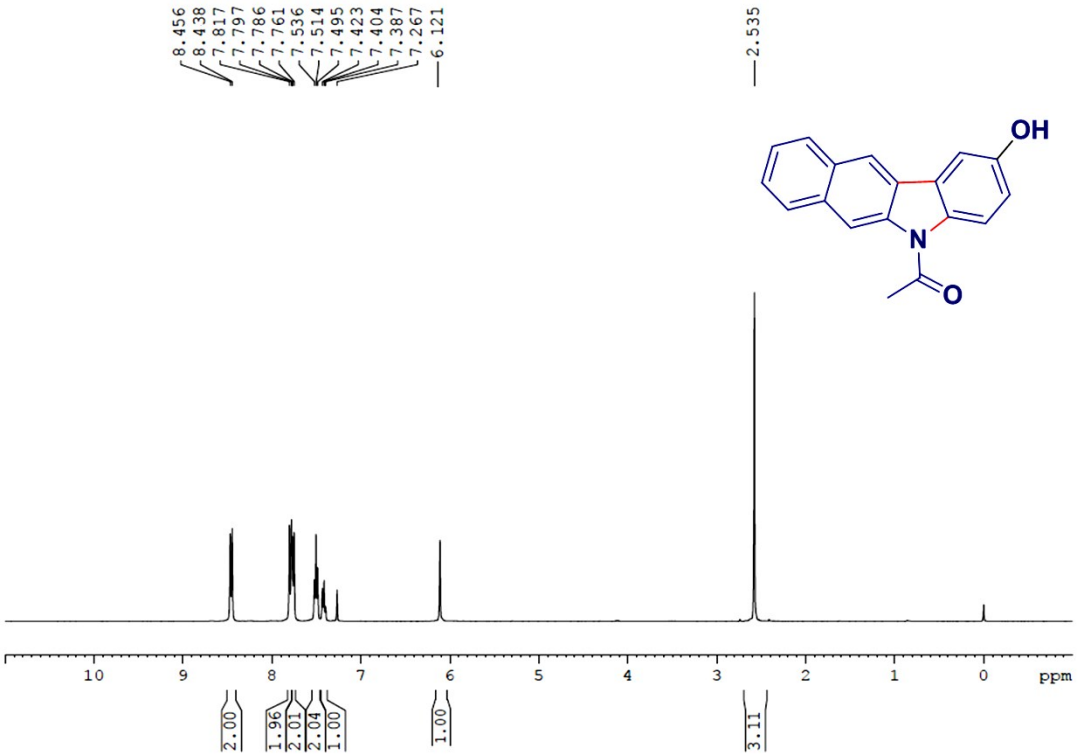

Fig. S53: ^{1}H NMR spectrum of 1-(2-hydroxy-benzo[b]carbazol-5-yl)-ethanone

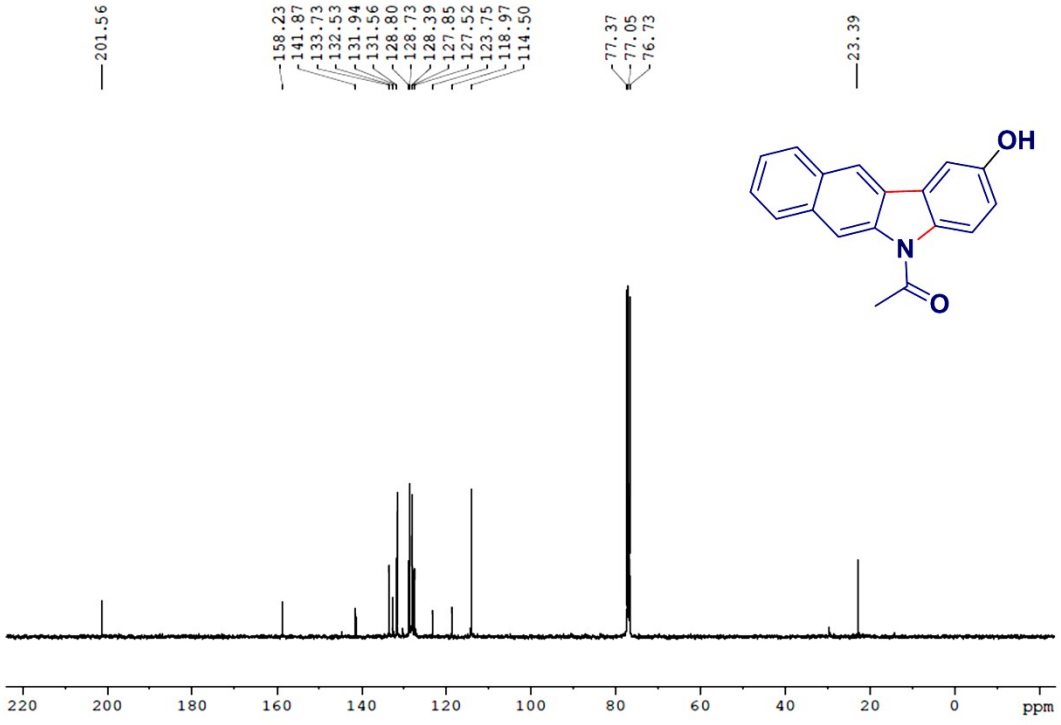

Fig. S54: ^{13}C NMR spectrum of 1-(2-hydroxy-benzo[b]carbazol-5-yl)-ethanone

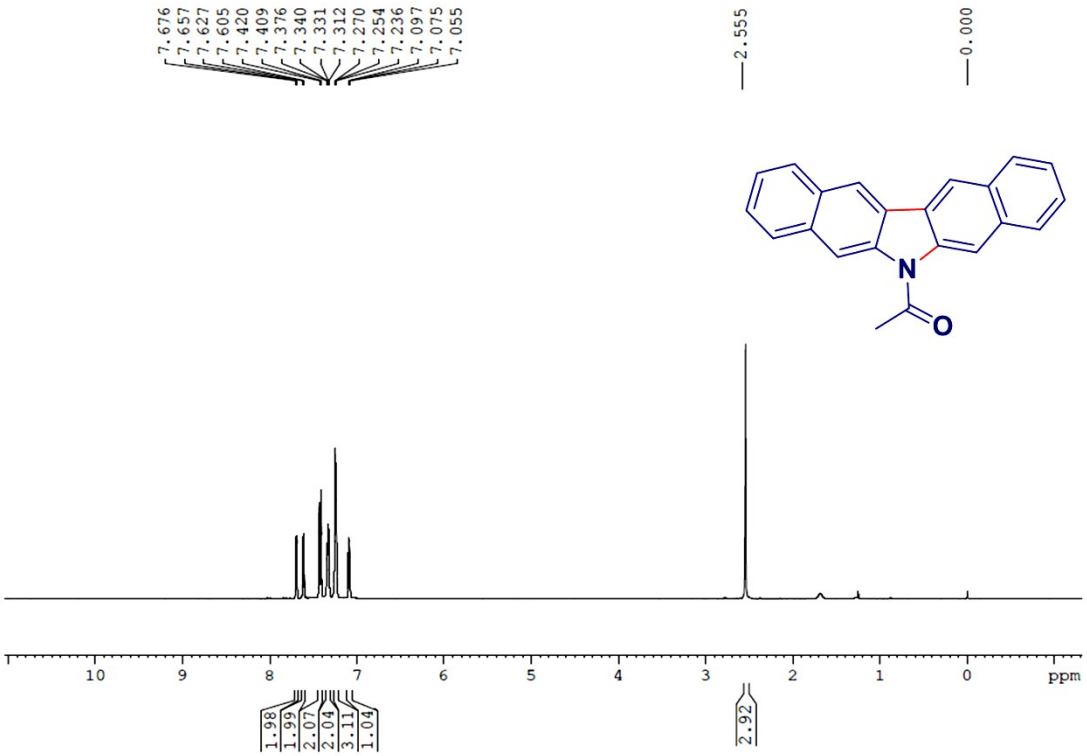

Fig. S55: ^{1}H NMR spectrum of 1-dibenzo[b,h]carbazol-6-yl-ethanone

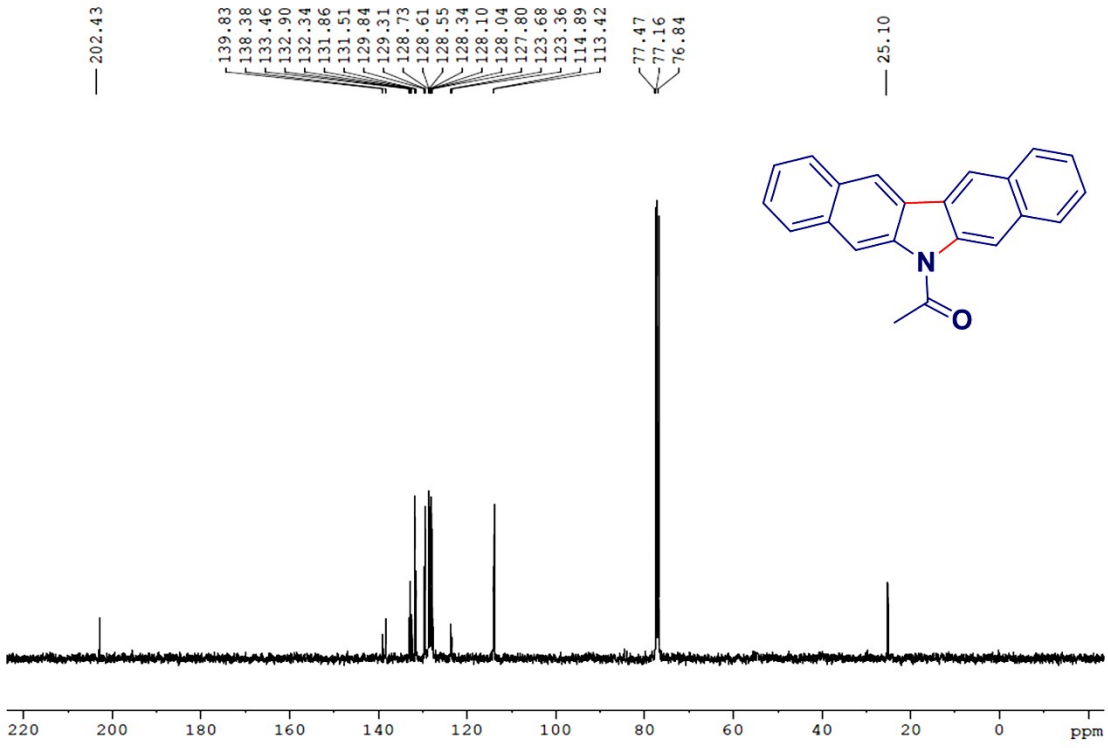

Fig. S56: ^{13}C NMR spectrum of 1-dibenzo[b,h]carbazol-6-yl-ethanone

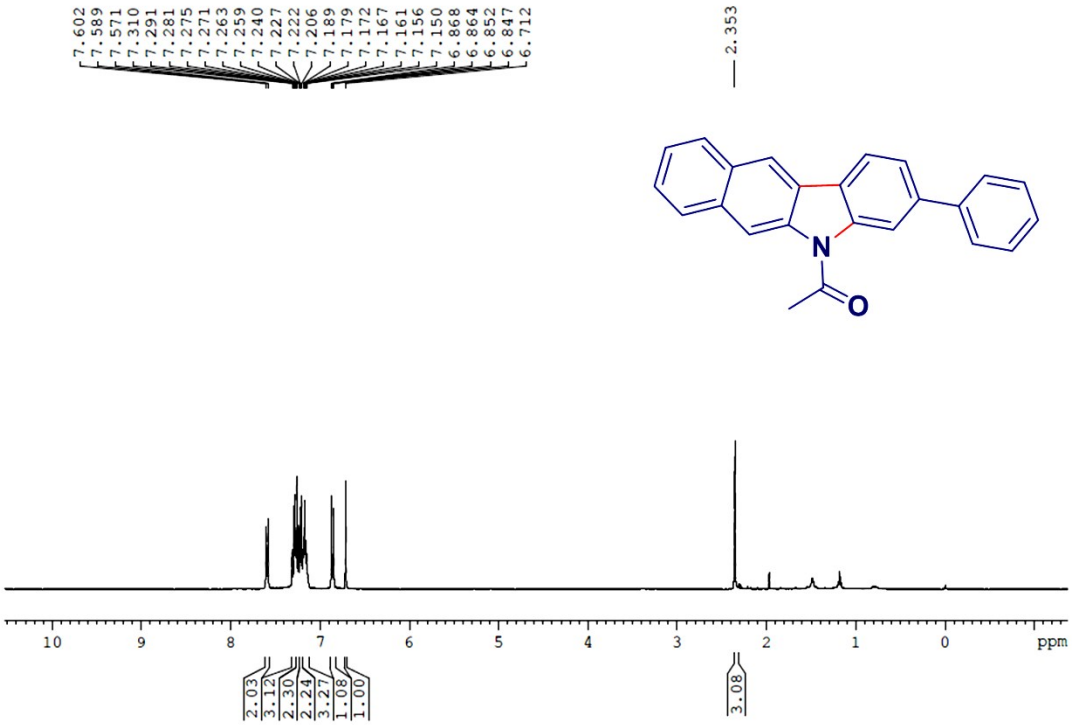

Fig. S57: ^{1}H NMR spectrum of 1-(3-phenyl-benzo[b]carbazol-5-yl)-ethanone

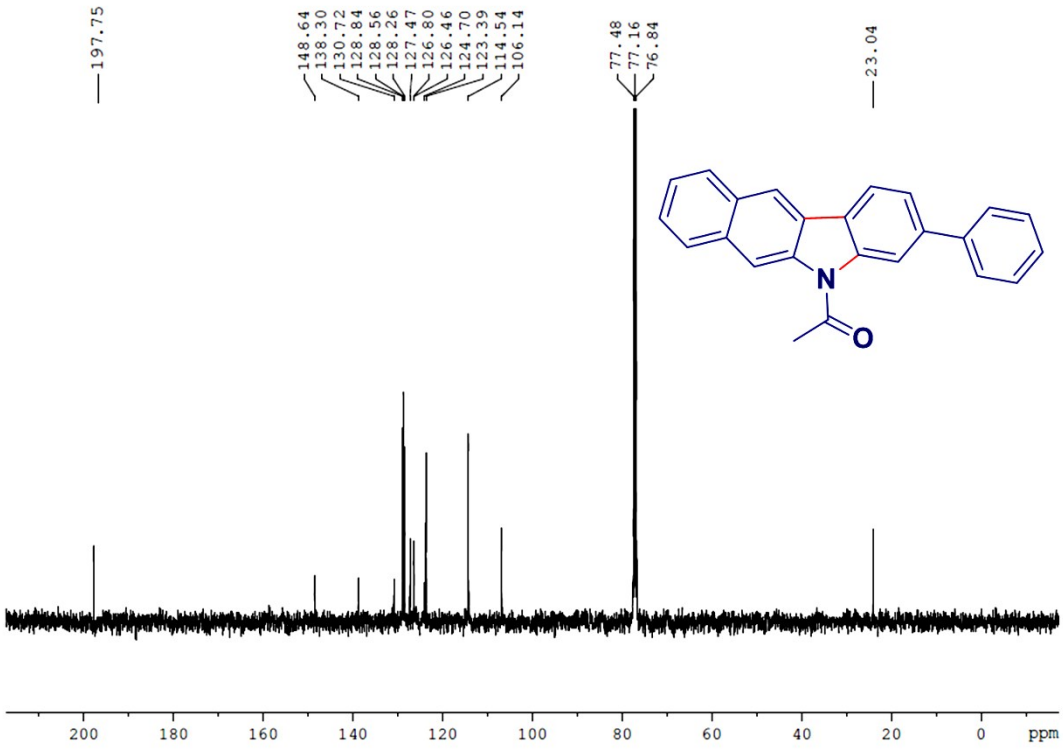

Fig. S58: ^{13}C NMR spectrum of 1-(3-phenyl-benzo[b]carbazol-5-yl)-ethanone

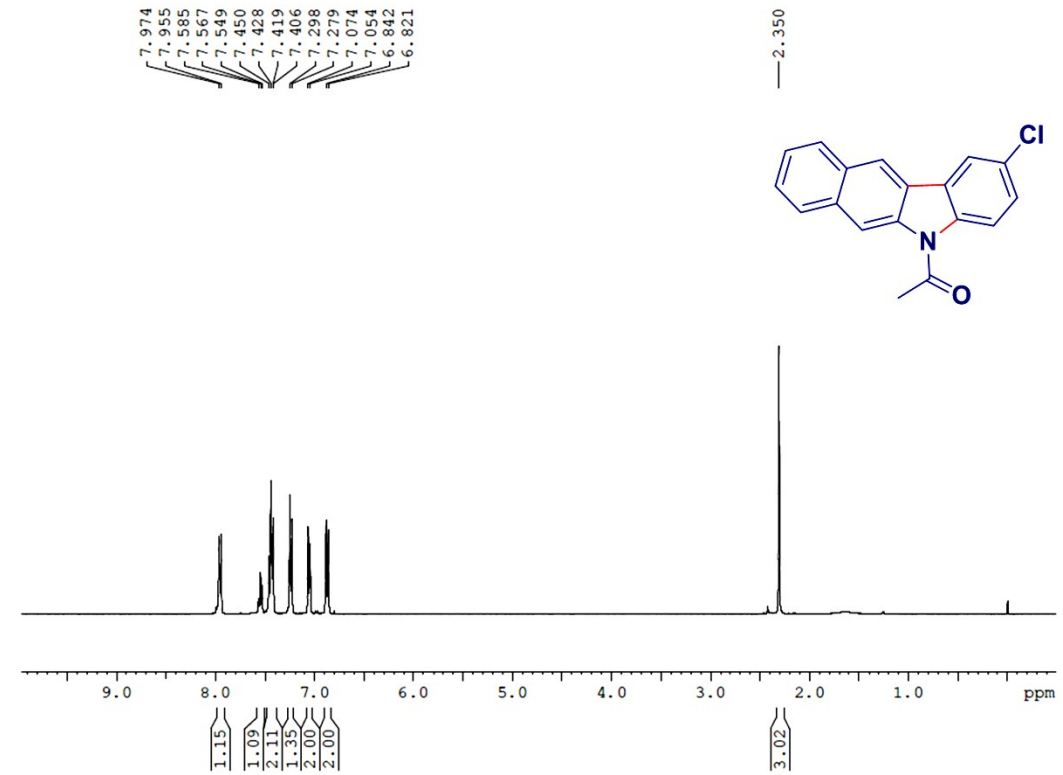

Fig. S59: ^{1}H NMR spectrum of 1-(2-chloro-benzo[b]carbazol-5-yl)-ethanone

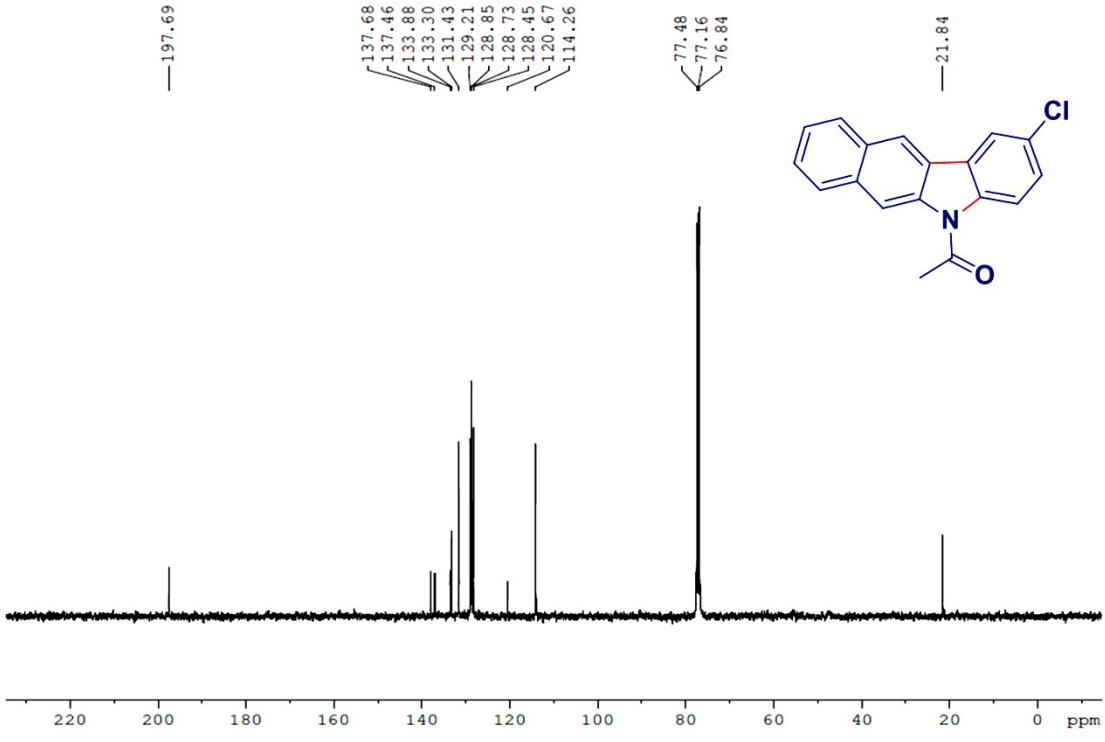

Fig. S60: ^{13}C NMR spectrum of 1-(2-chloro-benzo[b]carbazol-5-yl)-ethanone

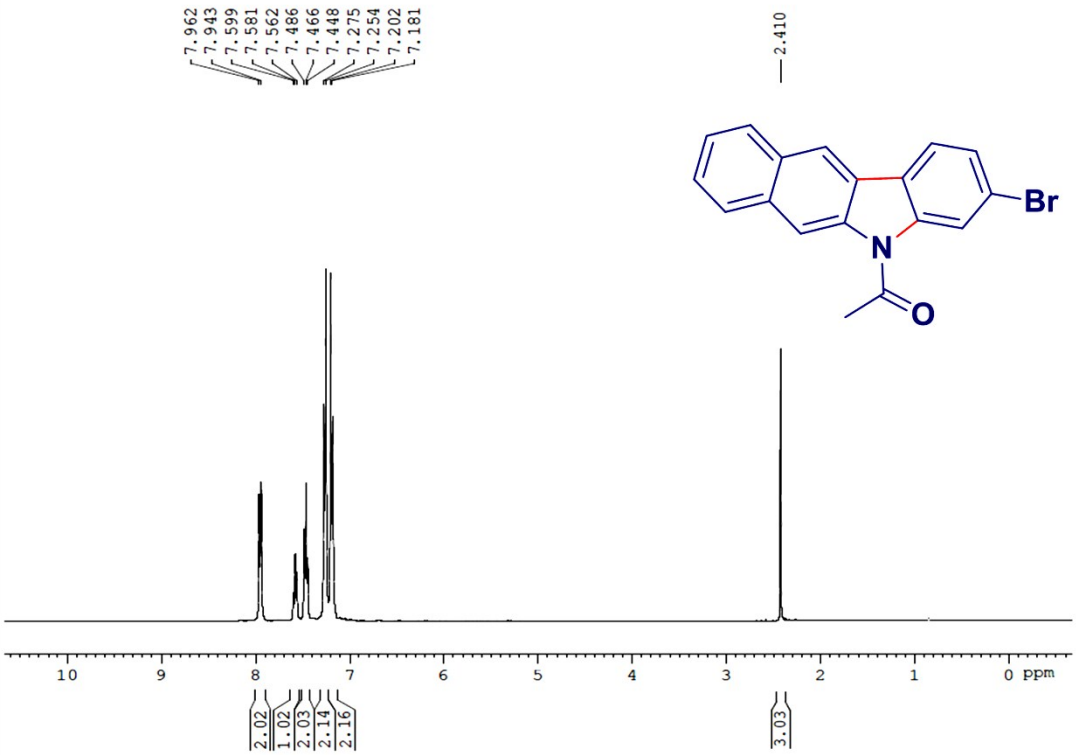

Fig. S61: ^{1}H NMR spectrum of 1-(3-bromo-benzo[b]carbazol-5-yl)-ethanone

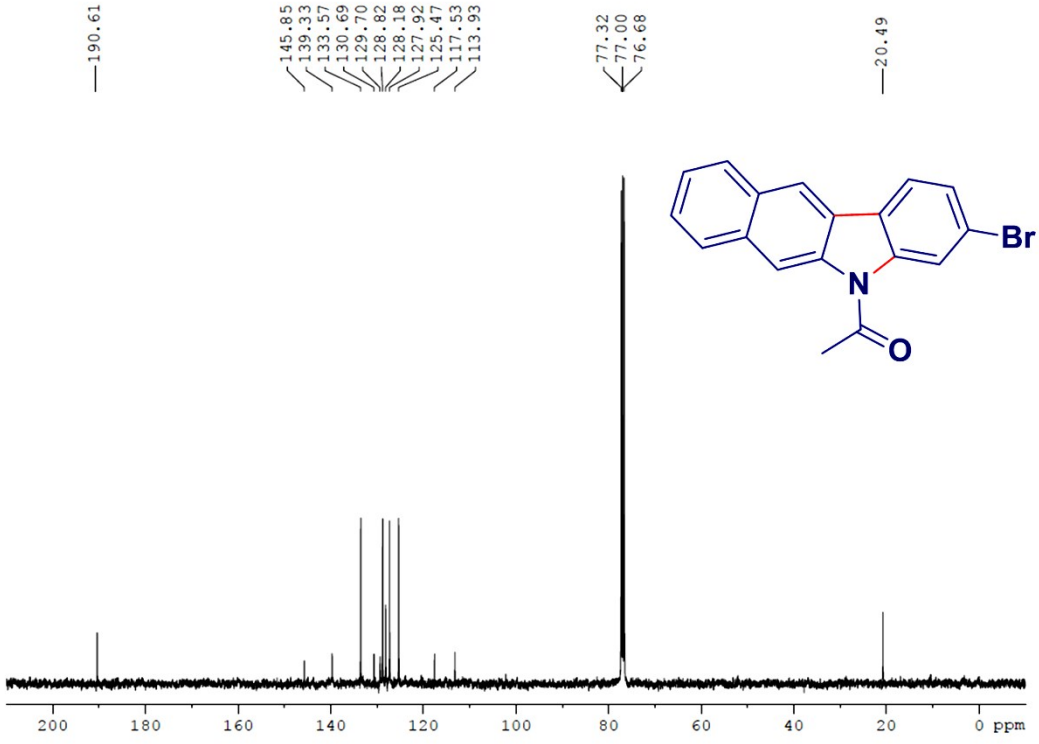

Fig. S62: ^{13}C NMR spectrum of 1-(3-bromo-benzo[b]carbazol-5-yl)-ethanone

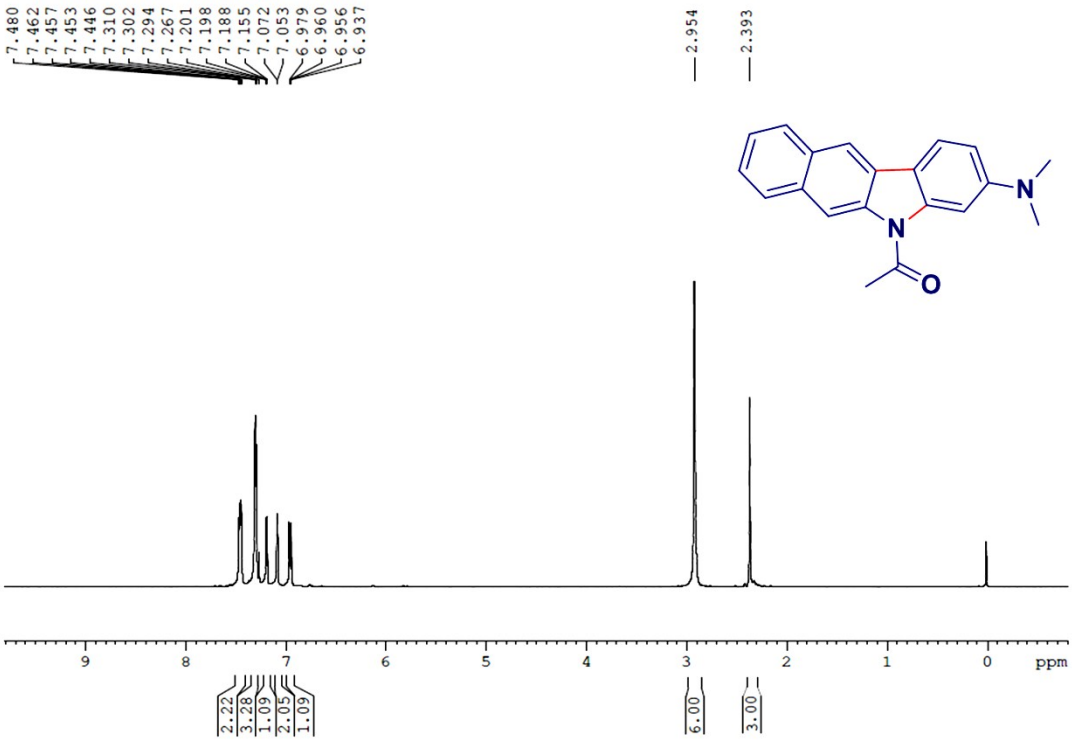

Fig. S63: ^{1}H NMR spectrum of 1-(3-dimethylamino-benzo[b]carbazol-5-yl)-ethanone

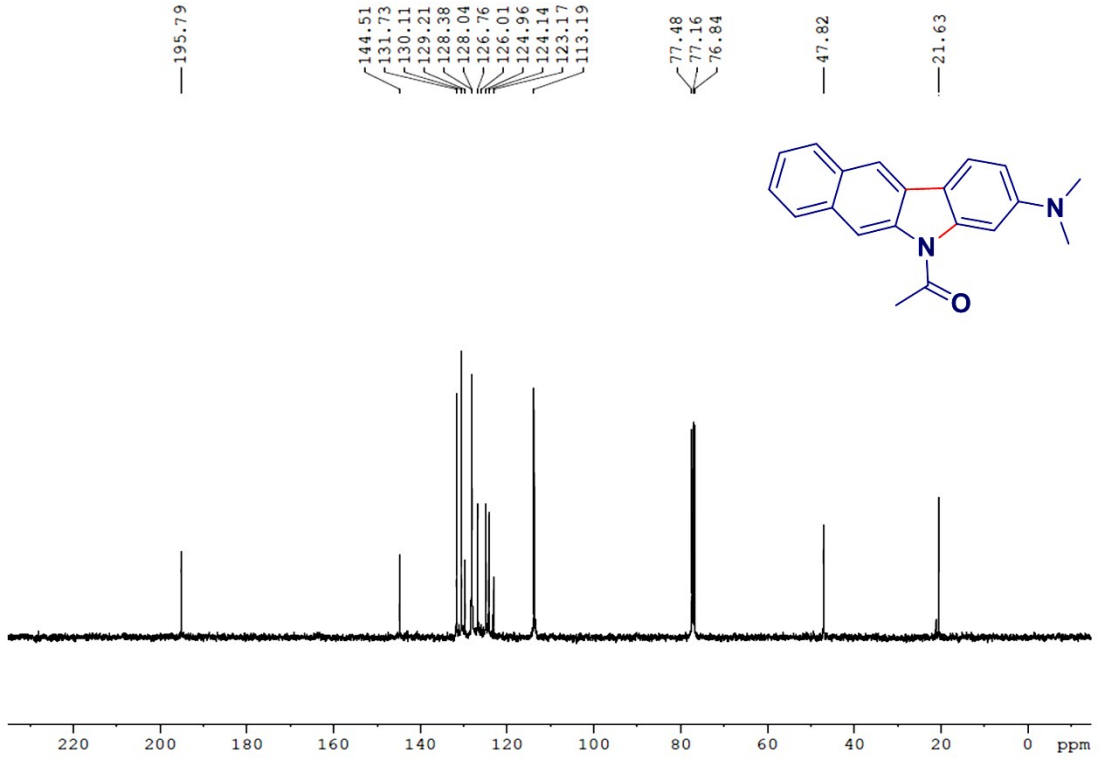

Fig. S64: ^{13}C NMR spectrum of 1-(3-dimethylamino-benzo[b]carbazol-5-yl)-ethanone

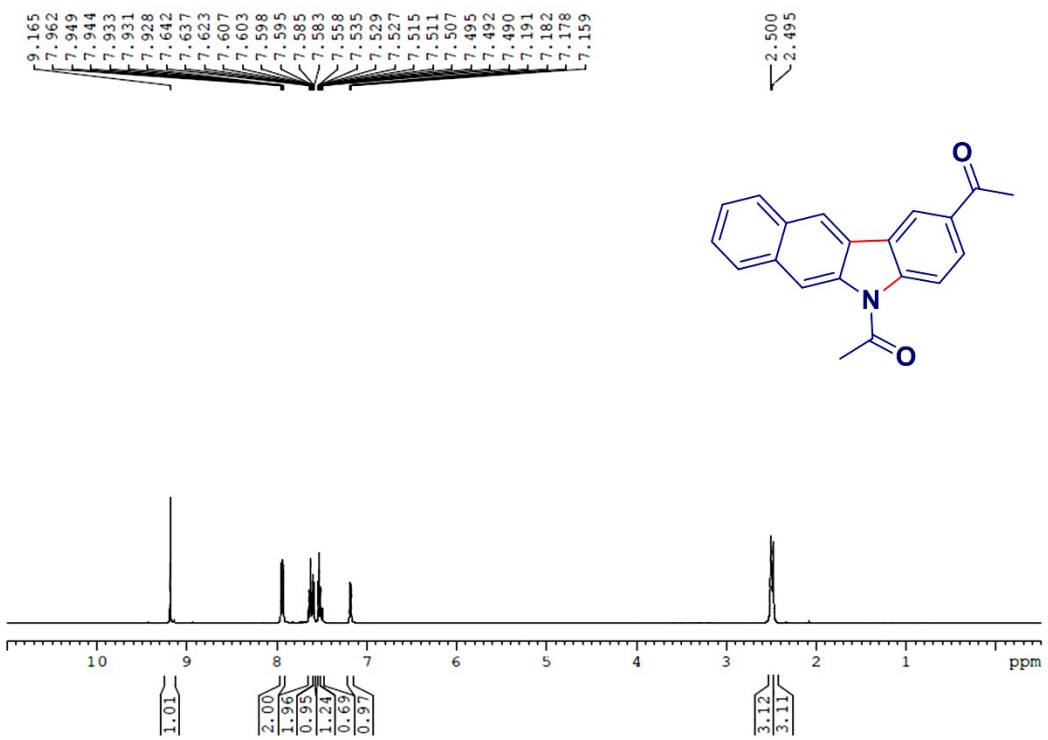

Fig. S65: [1]H NMR spectrum of 1-(2-acetyl-benzo[b]carbazol-5-yl)-ethanone

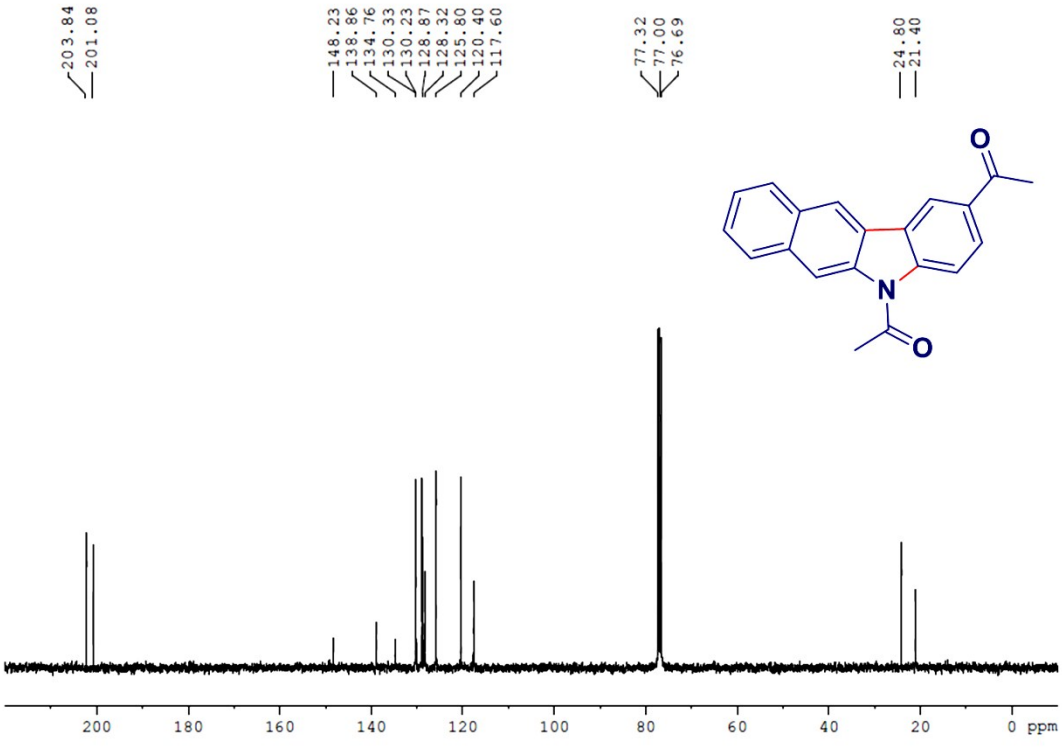

Fig. S66: [13]C NMR spectrum of 1-(2-acetyl-benzo[b]carbazol-5-yl)-ethanone

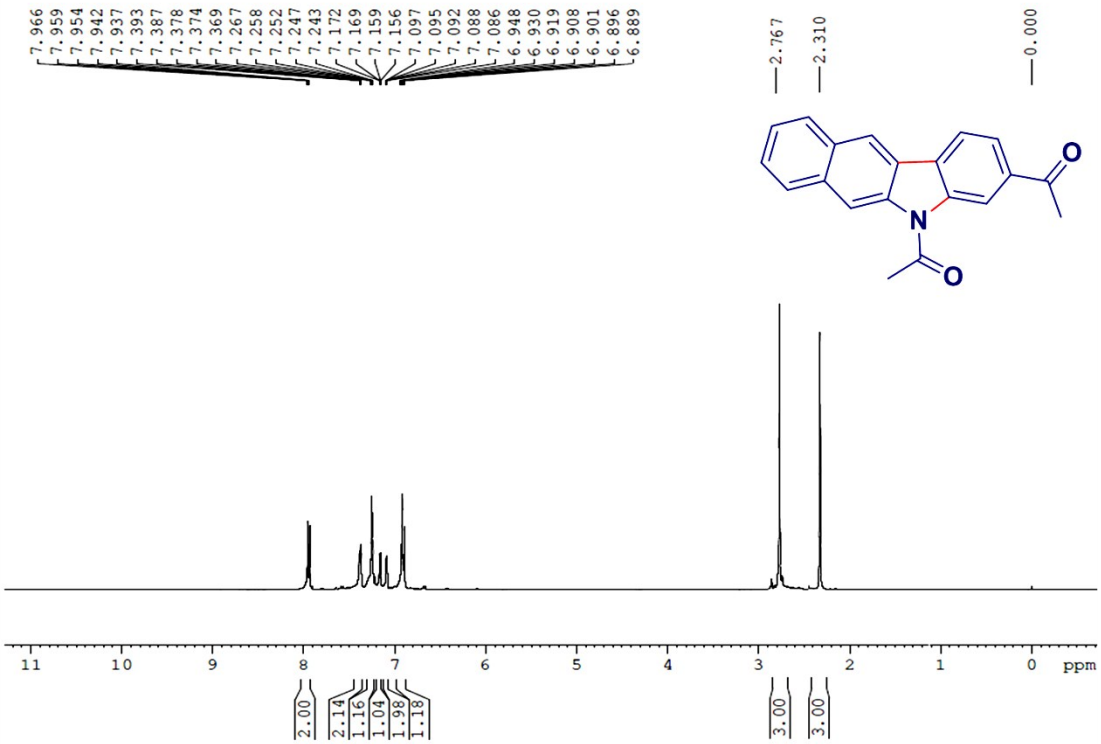

Fig. S67: ^{1}H NMR spectrum of 1-(3-acetyl-benzo[b]carbazol-5-yl)-ethanone

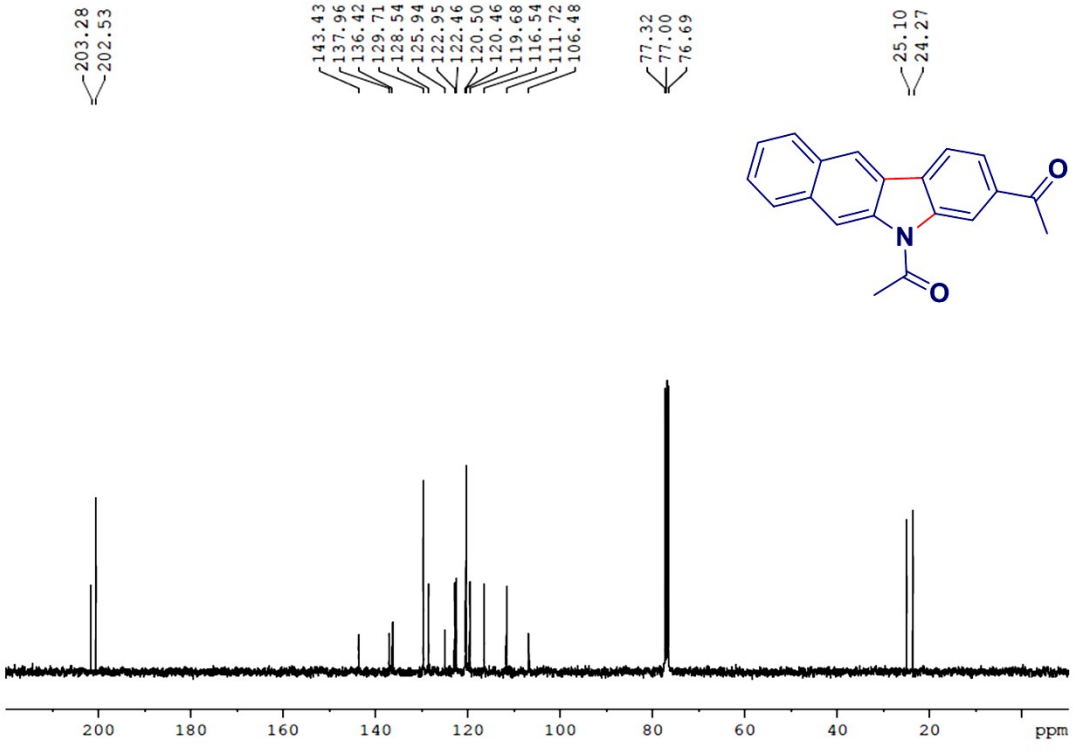

Fig. S68: ^{13}C NMR spectrum of 1-(3-acetyl-benzo[b]carbazol-5-yl)-ethanone

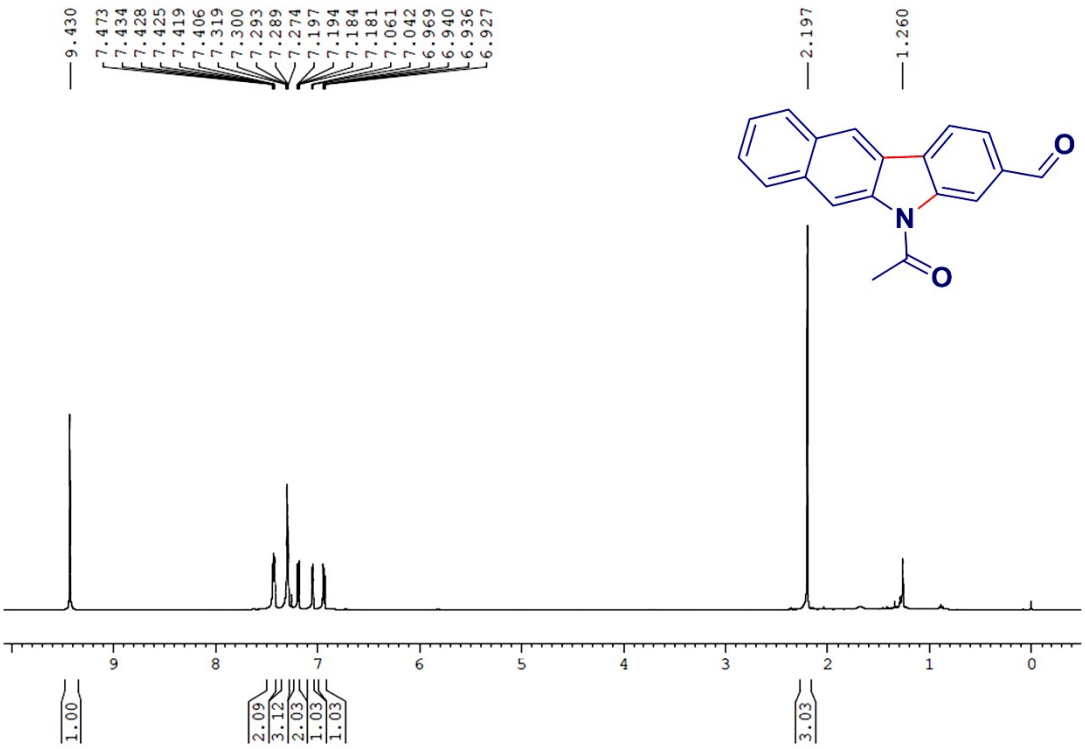

Fig. S69: ^{1}H NMR spectrum of 5-acetyl-5*H*-benzo[b]carbazole-3-carbaldehyde

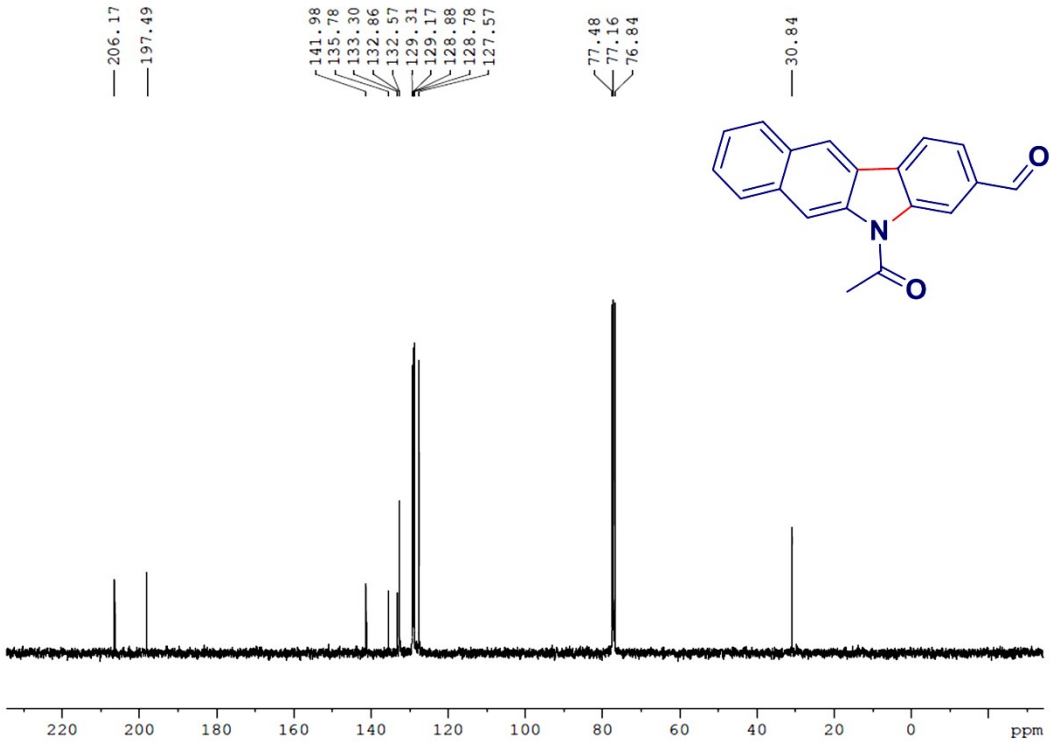

Fig. S70: ^{13}C NMR spectrum of 5-acetyl-5*H*-benzo[b]carbazole-3-carbaldehyde

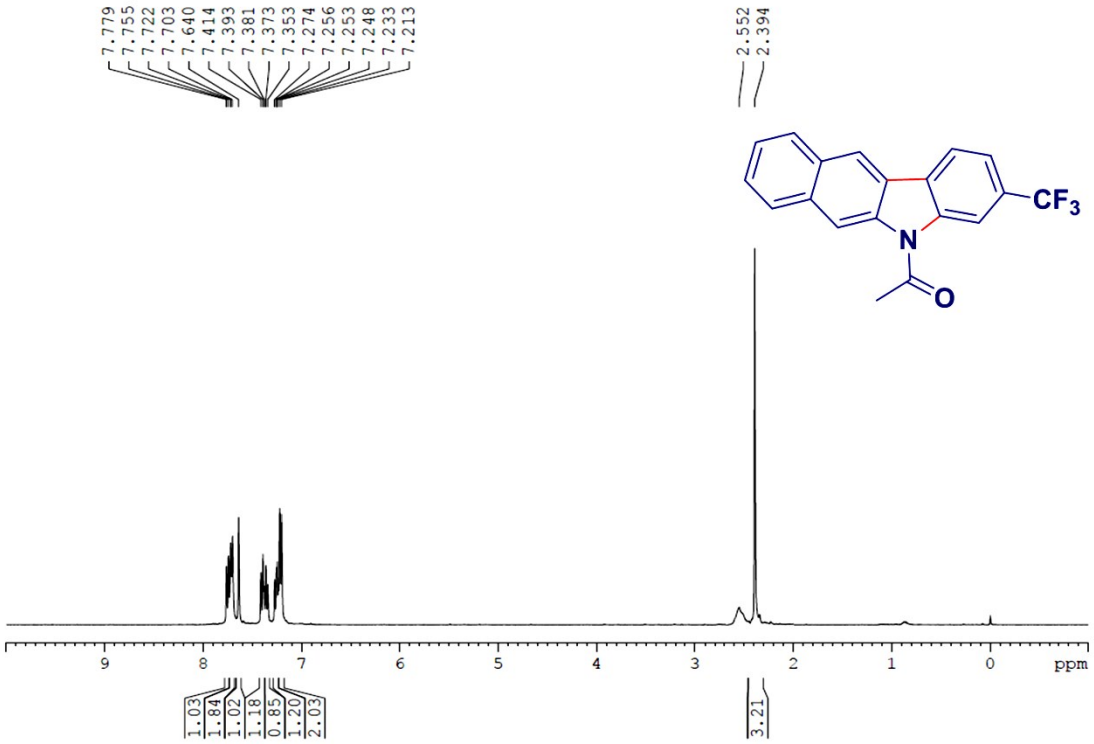

Fig. S71: ^{1}H NMR spectrum of 1-(3-trifluoromethyl-benzo[b]carbazol-5-yl)-ethanone

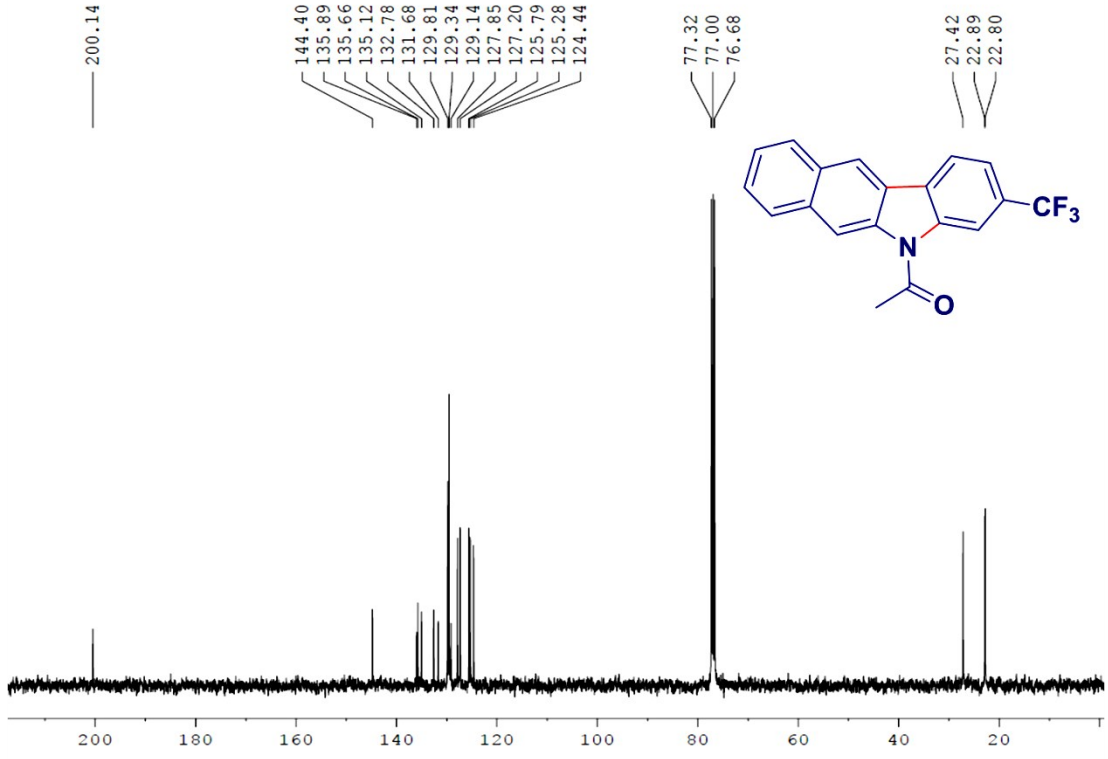

Fig. S72: ^{13}C NMR spectrum of 1-(3-trifluoromethyl-benzo[b]carbazol-5-yl)-ethanone