Supporting Information

List of the contents

NMR and Crystalographic discussion :

Synthesized compounds were characterized by FTIR, ^{1}H NMR, ^{13}C NMR and HRMS analysis. Substitution at 2nd position, irrespective of its electron withdrawing and electron donating nature, shifts the stereogenic protons Ha towards deshielding region (**1b** > **1** > **2b** $\Rightarrow$ 5.04 > 4.60 > 4.53 δ ppm) and proton Hb towards shielding region (**1b** < **1** = **2b** $\Rightarrow$ 3.96 < 4.04 = 4.04 δ ppm) when compared to **1** and respective 4-sustituted compounds as shown in Figure S1 (SI). This was further confirmed by replacement of fluorine by bulkier trifluoromethyl group at 2nd position, which shifts proton Ha to more deshielding region (**1c** < **1e** = 5.01 < 5.12 δ ppm) and Hb towards shielding region (**1c** > **1e** = 3.86 > 3.72 δ ppm) (SI, Figure S2). The vinylic proton (Hc) shifts slightly towards deshielding region when electron withdrawing groups (-I effect) are present on benzylidine ring irrespective of their position whereas that of electron donating groups (+I effect) slightly shifts the proton towards shielding region (**1b** < **1** < **1c** = 6.78 < 6.82 < 6.84 δ ppm).

Single crystal structures of some of the representative compounds were determined to examine the conformations of these compounds. Earlier, we have reported structure of **1d**, (7E)-5-Benzyl-7-(2-chlorobenzylidene)-3-(2-chlorophenyl)-2-phenyl-3,3a,4,5,6,7-hexahydro-2H-pyrazolo[4,3-c]pyridine.[1] A search in Cambridge Structural Database (version 5.31) for 2H-pyrazolo[4,3-c]pyridines retrieved none except **1d**. The structures of **1b**, **1c**, **1f** with adopted atomic numbering scheme is shown in Figure 1 a-c. In **1b** and **1c**, asymmetric units comprise of two different molecules with minor conformational differences (RMSD of 0.794 Å and 0.972 Å between different molecules of asymmetric units, respectively for **1b** and **1c**). These compounds are racemic mixtures. Similar to **1d,** the stereogenic centers, C3 and C3A of the reported models of**1b** and **1f** possess (R, R)-configurations (SI, Table S2). Interestingly crystal structure of **1c** reveals coexistence of (S, R) and (R, S) configurations of the stereogenic centers, C3 and C3A. This observation suggests that both configurations are energetically accessible. The coexistence of two configurations within an asymmetric unit has been previously observed for Boc-Leu-Dpg-Val-OMe.[2] The five membered dihydropyrazole ring (N1/N2/C3/C3A/C7A) adopts an envelope conformation with atom C3 at the flap of the envelope and an adjacent 6-membered piperidine ring (C3A/C4/N5/C6/C7/C7A) assumes a chair conformation, but substantially distorted from ideal geometry. Short intra-molecular C—H•••halogen and C-H•••O contacts were observed in **1b**, **1c** and **1f** leading to modulation of their photophysical properties (vide infra). A dimer is formed in **1f** (similar to **1d**) by

C29—Cl3•••Cg5^{i} [symmetry code (i): 1 - x, 1 - y, 1 – z, Cg5 is the centroid of (C21–C26) ring]. The Cl3•••Cg5 distance and C29—Cl3•••Cg5 angle are 3.7407(15) Å and 137.9(1)°, respectively, whereas the minimum atomic distance in Cl3••• Cg5 is 3.366 (4) Å.. Cg5 is the centroid of (C21–C26) ring. The C—Halogen•••π dimeric interactions [also referred as PHD; π-halogen-dimer interactions] have been shown recently,[3] to play an important role in host–guest chemistry.[4] The notable interactions in the crystal packing are C-H…π interactions (SI, Table S3).

References

1. N. S. Karthikeyan, B. U. Mahesh, K. Sathiyanarayanan, P.Raghavaiah and R. S. Rathore,Acta Cryst., 2010, E66, o1734.
2. S. Prasad, S. Mitra, E. Subramanian, D. Velmurugan, R. B. Rao and P. Balaram, Biochem. Biophys. Res. Commun., 1994, 198, 424.
3. A. N. M. M. Rahman, R. Bishop, D. C. Craig and M. L. Scudder,Org. Biomol. Chem., 2004, 2, 175.
4. B. Nagaraj, T. Narasimhamurthy, H. S. Yathirajan, P. Nagaraja, R. S.Narasegowda and R. S. Rathore, Acta Cryst. C, 2005, 61, o177.

Scheme S1

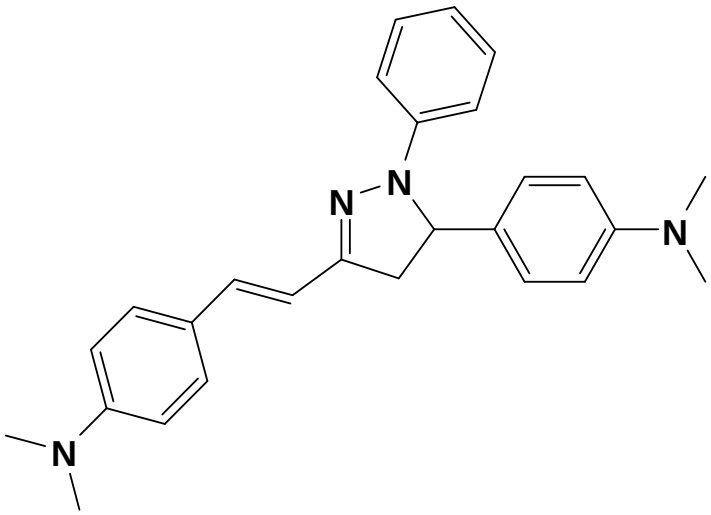
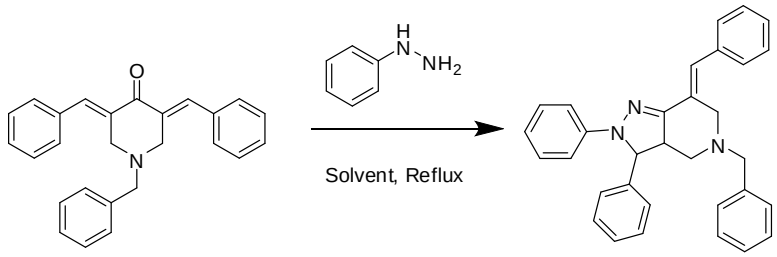


Table S1 Choice of solvents for the synthesis of **1** under reflux conditions[a]



Entry	Solvent	Time(h)	% Yield[b]
1	Methanol	48	**60**
2	Ethanol	48	**58**
3	Iso-Propanol	14	**86**
4	n-Butanol	18	**74**
5	Acetic acid	36	**68**
6	Acetonitrile	36	**30**
7	Toluene	48	**46**
8	Ethyl acetate	48	**10**
9	Chloroform	24	**0**
10	Tetrahydrofuran	24	**0**
11	Dichloromethane	24	**0**
12	Acetone	24	**0**
13	Diethyl ether	24	**0**
14	Dimethylformamide	36	**70**
15	Dimethysulfoxide	36	**74**

[a]All the reactions were carried out by employing 0.001mol of curcumin derivatives (3a-3p), 0.001 mol of phenyl hydrazine in 10 ml of given solvent [b]isolated yields

Table S2 Crystal data of selected compound

compounds	**1c**	**1f**	**1b**
Chemical formula	$C_{32}H_{27}F_2N_3$	$C_{32}H_{25}Cl_4N_3$	$C_{34}H_{33}N_3O_2$
Molecular Weight	491.57	593.35	515.63
Crystal size (mm)	0.6×0.4×0.2	0.4×0.4×0.4	0.4×0.4×0.3
Morphology	block, colorless	block, colorless	block, colorless
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P1bar	$P2_1/c$	P1bar
Unit cell parameters, a(Å), b(Å), c(c), α(°), β(°), γ(°)	12.8417(9), 14.1308(9), 16.3607(11), 81.235(5), 69.026(6), 69.420(6)	13.7524(4), 15.4132(5), 13.4826(4), 90.0, 101.715(3), 90.0	14.9779(8), 14.9860(8), 15.5420(9), 67.173(5), 88.293(4), 62.667(5)
Volume ($Å^3$)	2594.1(3)	2798.36(15)	2809.1(3)
Z/Z'	4/2	4/1	4/2
Cell measuring reflections	6319	12840	7106
θ-range (°)	2.7-29.4	2.6-29.2	2.6-29.2
μ(mm^{-1})absorption correction	0.084, multi-scan	0.451, multi-scan	0.076, multi-scan
F(000)	1032	1224	1096
D_x(calculated) (g cm^{-3})	0.071	0.224	2.318
Data Collection			
Radiation (Å)	0.71073 (MoKα)	0.71073 (MoKα)	0.71073 (MoKα)
Temperature (°K)	293	293	293
θ Range (°)	2.7-26.0	2.6-26.0	2.6-26.0
Indices	h = -15 → 15 k = -17 → 17 l = -19 → 20	h = -16 → 16 k = -19 → 18 l = -16 → 16	h = -18→ 18 k = -18 → 18 l = -19→19
Scan type	ω scans	ω scans	ω scans
Independent reflections	10192	5500	11037
Observed Reflections [I >2σ(I)]	4826	3932	7218
Refinement			
Final Indices	R = 0.0534, wR = 0.1529	R = 0.0482, wR = 0.1216	R = 0.0529, wR = 0.1232
Goodness of fit (S)	0.997	1.024	1.020
Extinction coefficient	nil	nil	nil
$(\Delta/\sigma)_{max}$	0.0	0.0	0.0
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e $Å^{-3}$)	0.177, -0.198	0.371, -0.406	0.158, -0.207
Data/restraints/ parameter	10192/0/668	5500/0/352	11037/0/707

$w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$, parameters a and b are: 0.0471, 0.0 (**1c**), 0.0473, 1.7119 (**1f**) and 0.0425, 0.4372 (**1b**), respectively.

Table S3 Interactions observed in **1b**, **1c**, and **1f**

	Interactions	D-H…A	D-H (Å)	H…A (Å)	D…A (Å)	D-H…A (º)
1c	Intra-molecular	C3A-H3A...F1A	0.98	2.39	2.781(4)	103
		C3B-H3B...F1B	0.98	2.44	2.781(4)	100
		C13A-H13A...N1A	0.93	2.40	2.730(3)	100
	Inter-molecular	C32A-H32A...Cg10^{i}	0.93	2.97	3.761(5)	144
1f	Intra-molecular	C3-H3…Cl1	0.98	2.62	3.135(3)	113
		C27-H27…Cl3	0.93	2.74	3.034(3)	100
1b	Intra-molecular	C4A-H4A2...O1A	0.97	2.41	3.079(2)	126
		C4B-H4B2...O1B	0.97	2.40	3.072(2)	126
		C19A-H19A...N2A	0.93	2.48	2.844(3)	103
		C19B-H19B...N2B	0.93	2.48	2.842(3)	103
		C20A-H20A...Cg11	0.97	2.96	3.923(3)	172
		C34B-H34F...Cg12	0.96	2.99	3.772(3)	140
	Inter-molecular	C12B-H12B...Cg13^{ii}	0.93	2.95	3.718(3)	141
		C16B-H16B...Cg13^{iii}	0.93	2.93	3.776(3)	152
		C25A-H25A...Cg10^{iv}	0.93	2.86	3.684(3)	149

Symmetry codes (i) 1-X,1-Y,1-Z, (ii), (iii).

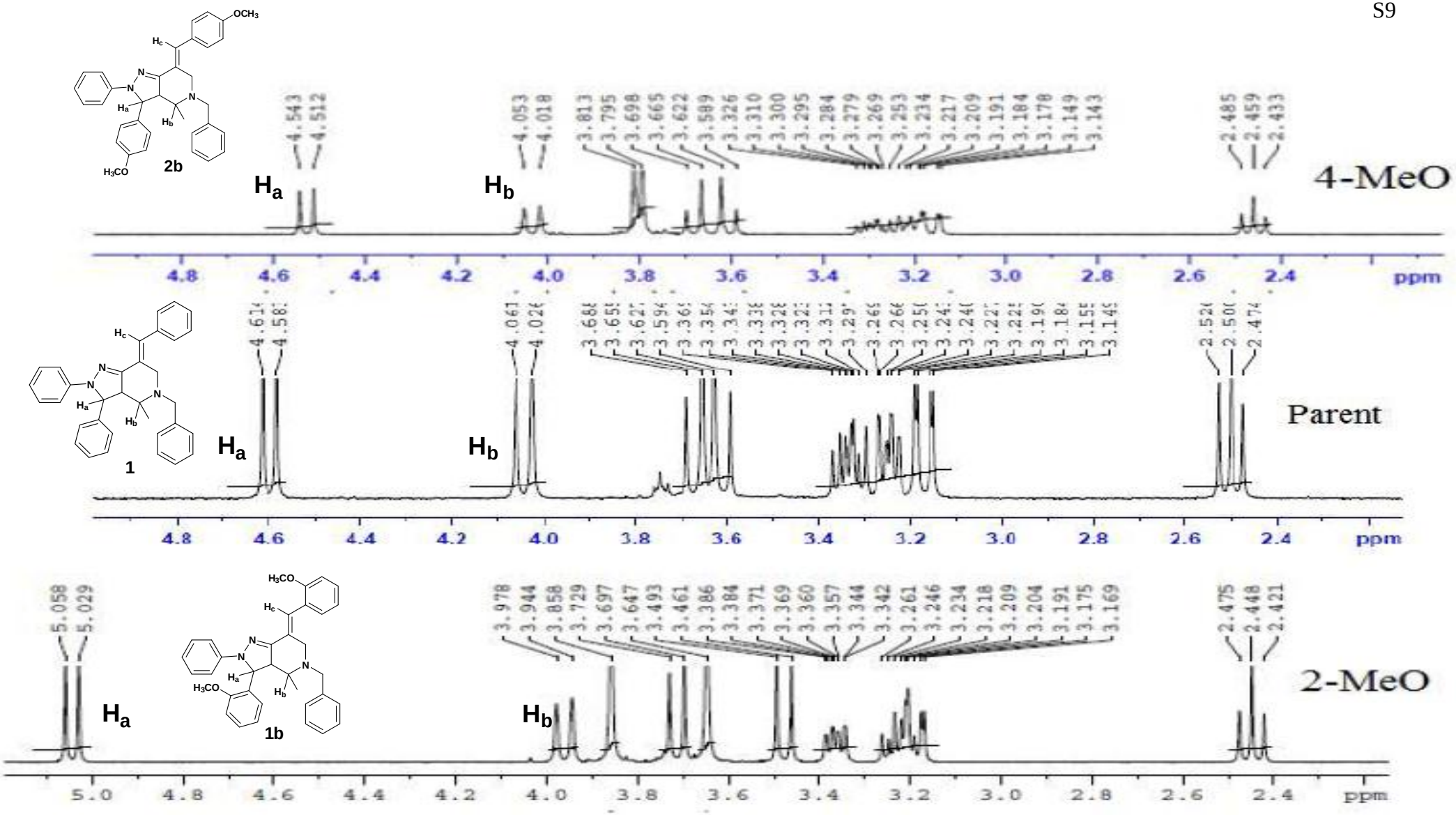
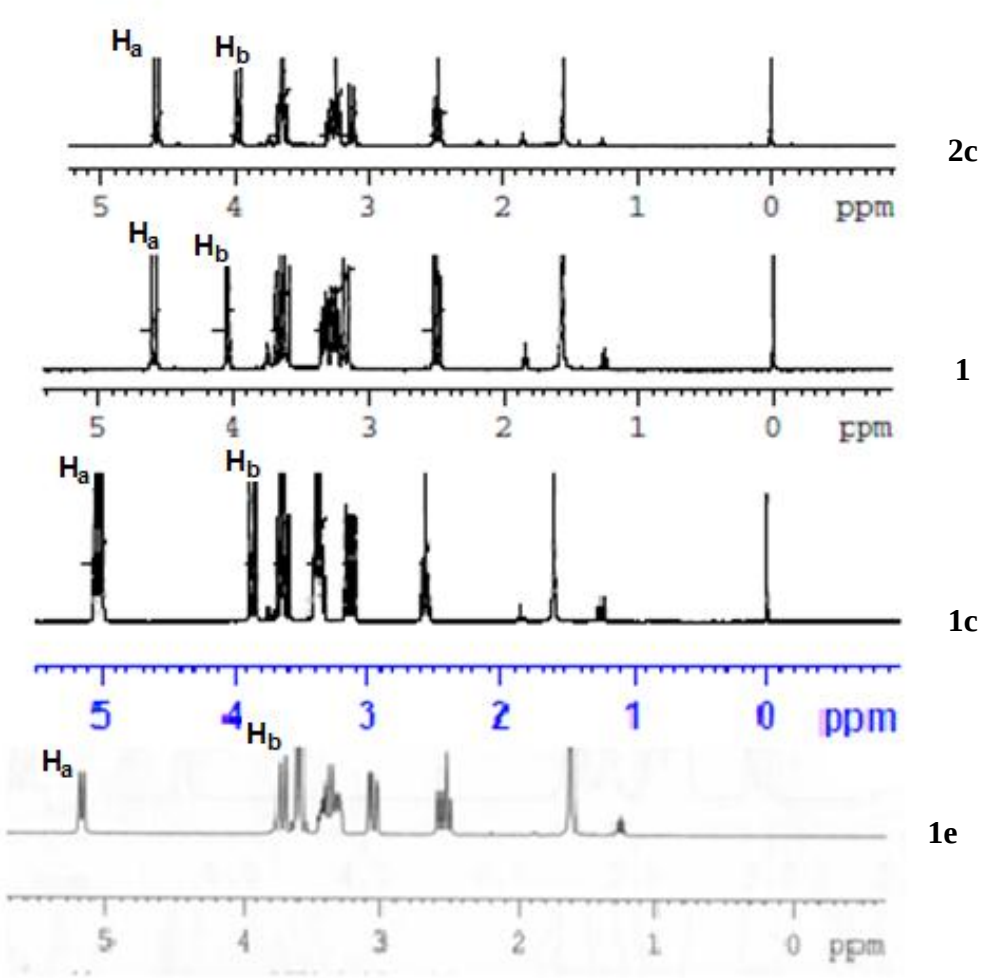


Figure S1 Deshielding of proton H_a and shielding of proton H_b with respect to position



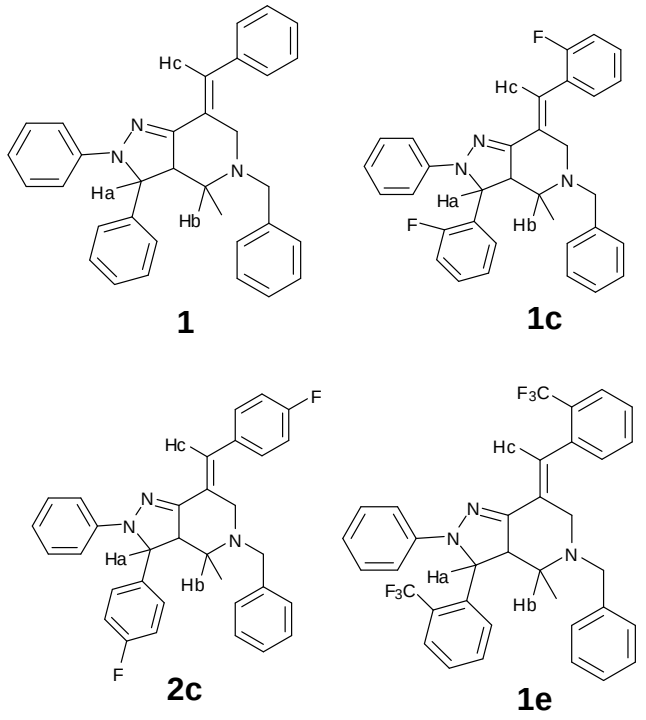


Figure S2 Deshielding of proton H_a and Shielding of proton H_b with respect to position and bulkiness

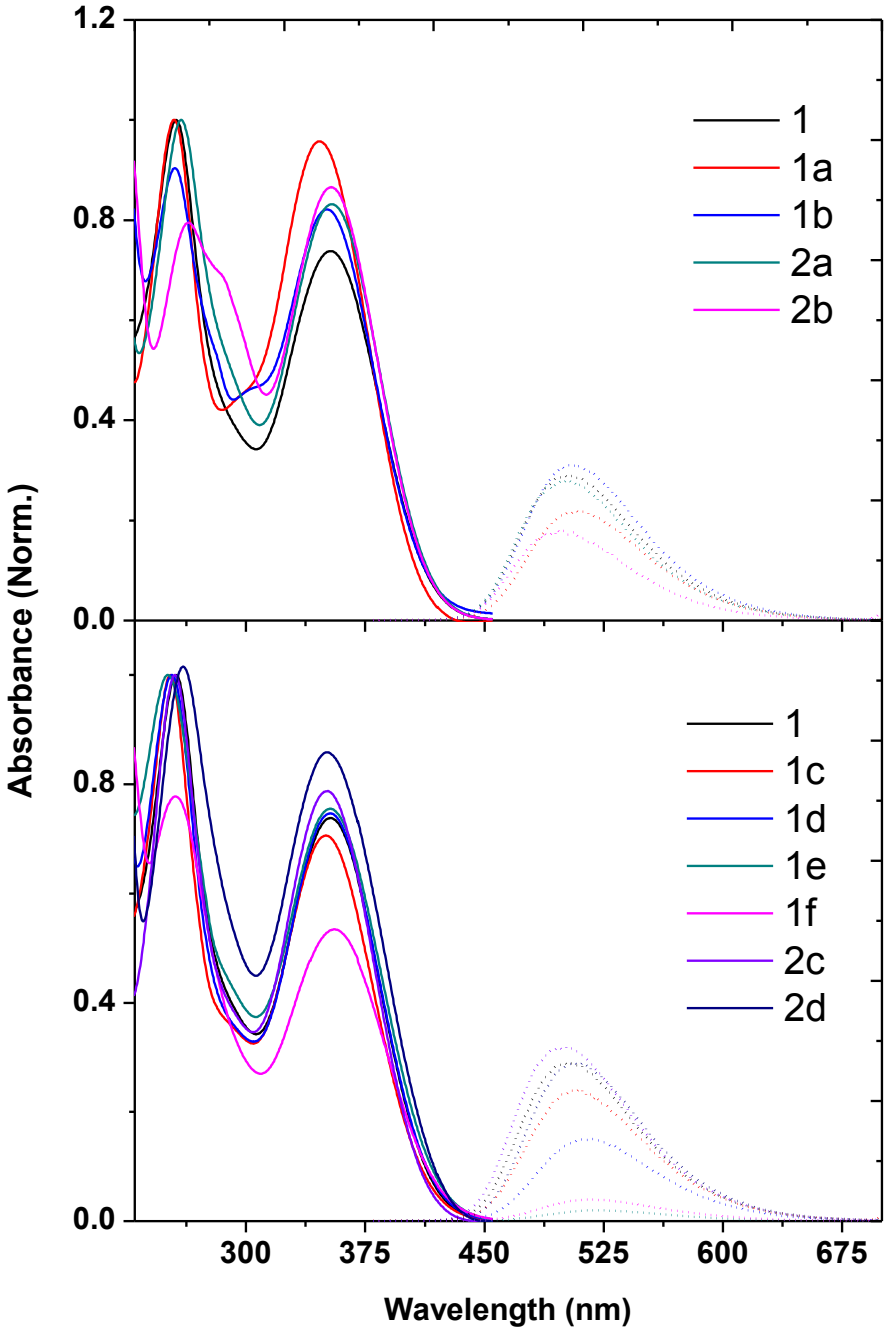


Figure S3 UV-visible and fluorescence spectra of pyrazolo pyridines dissolved in acetonitrile.

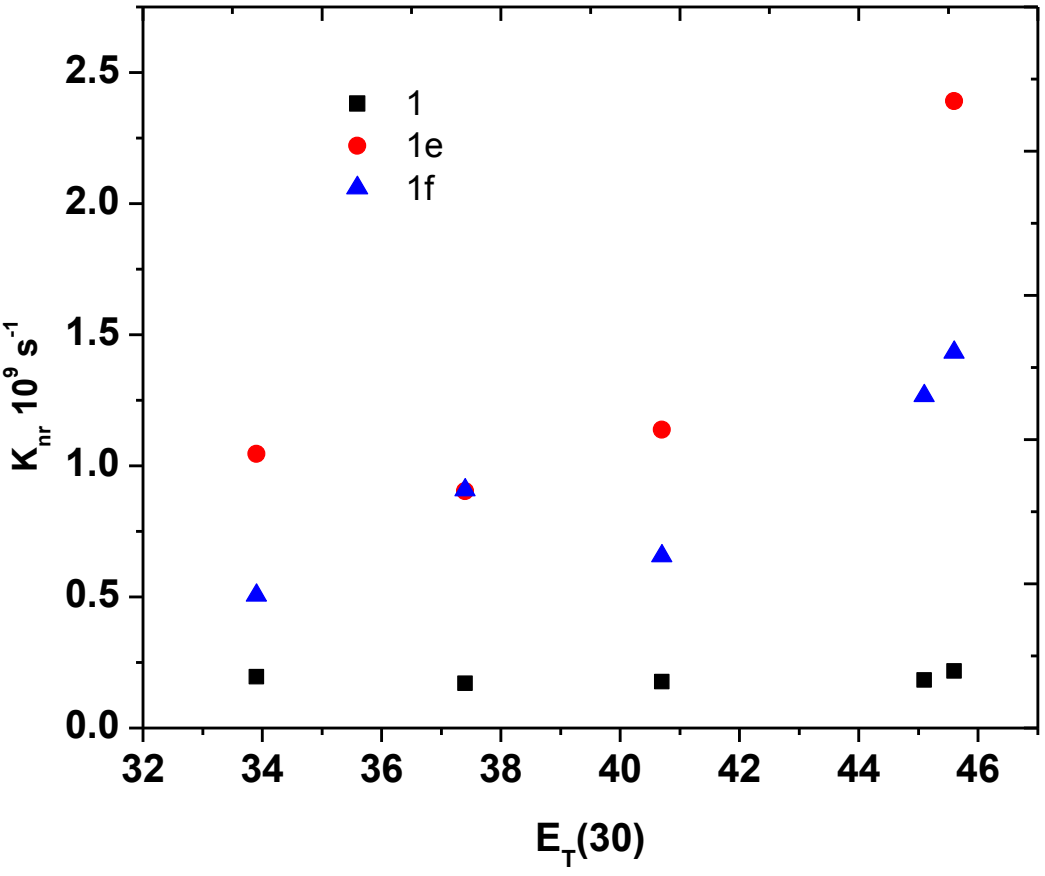


Figure S4 Plot of solvent polarity parameter $E_T(30)$ versus non-radiative rate constant (K_{nr}) of**1, 1e**, and **1f**

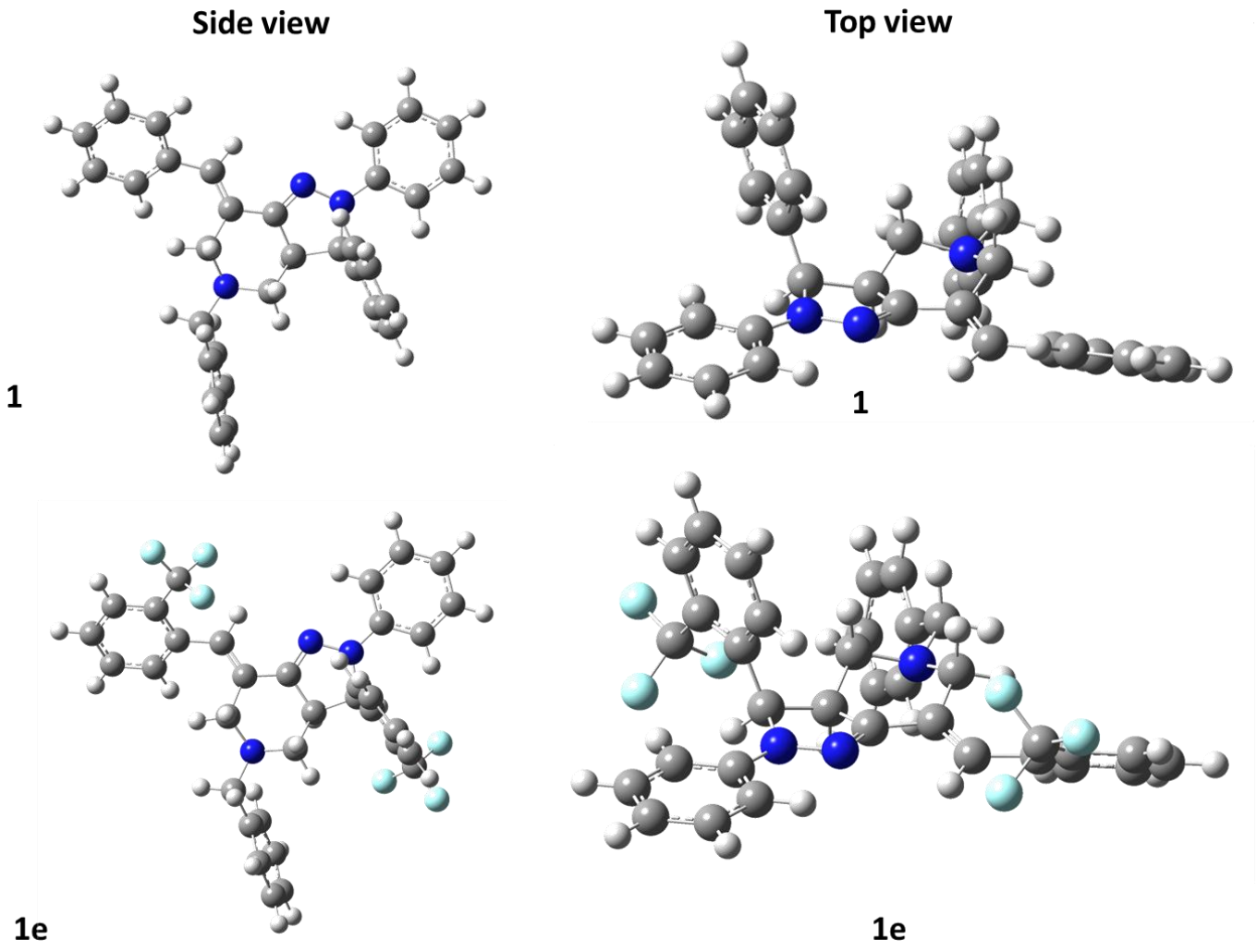


Figure S5 Optimized geometries of **1** and **1e** using Gaussian 03 at B3LYP/6-31G level

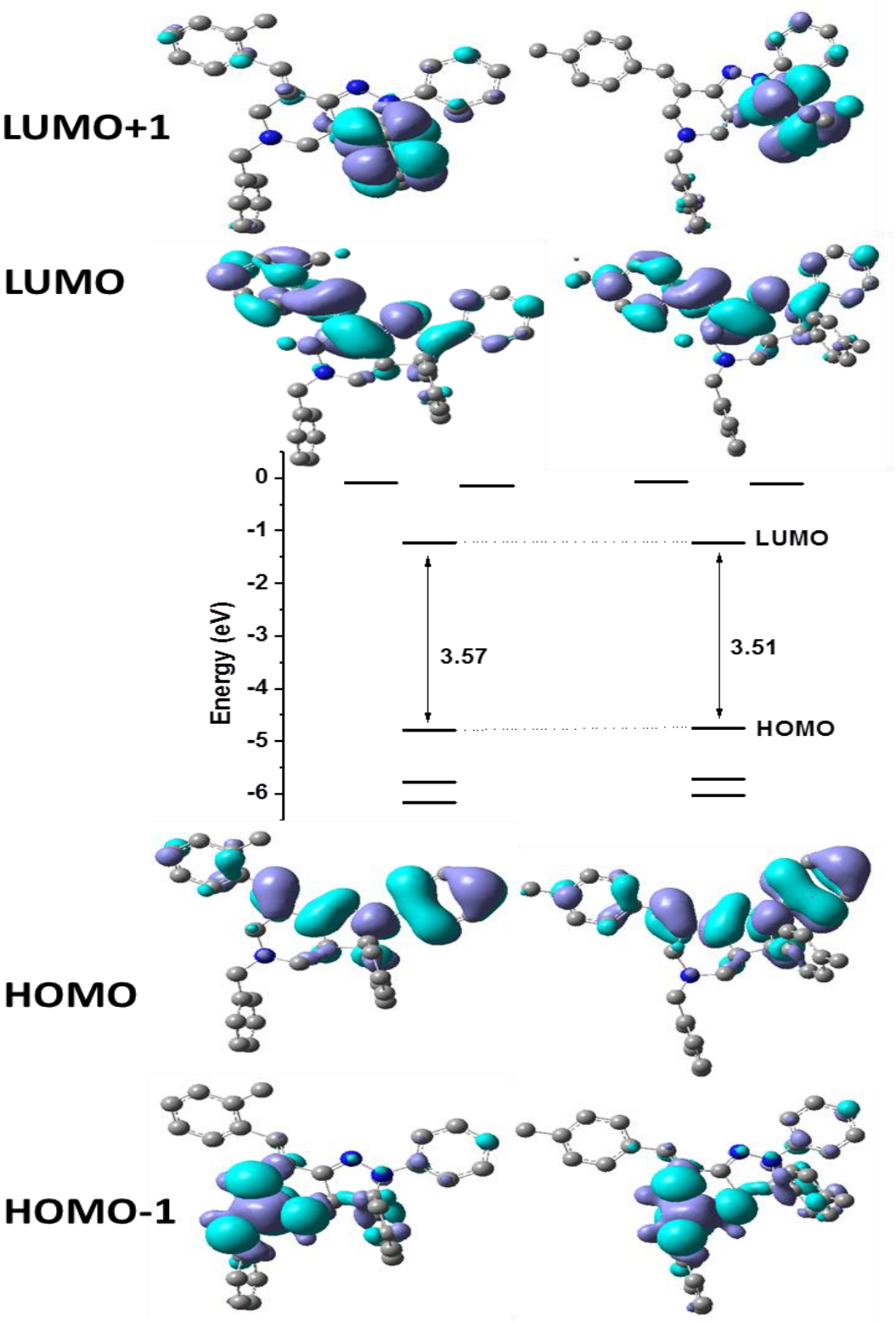


Figure S6 Molecular orbital diagrams of **1a** and **2a** calculated using Gaussian 03 at B3LYP/6-31G level of theory. Hydrogen atoms are omitted for clarity.

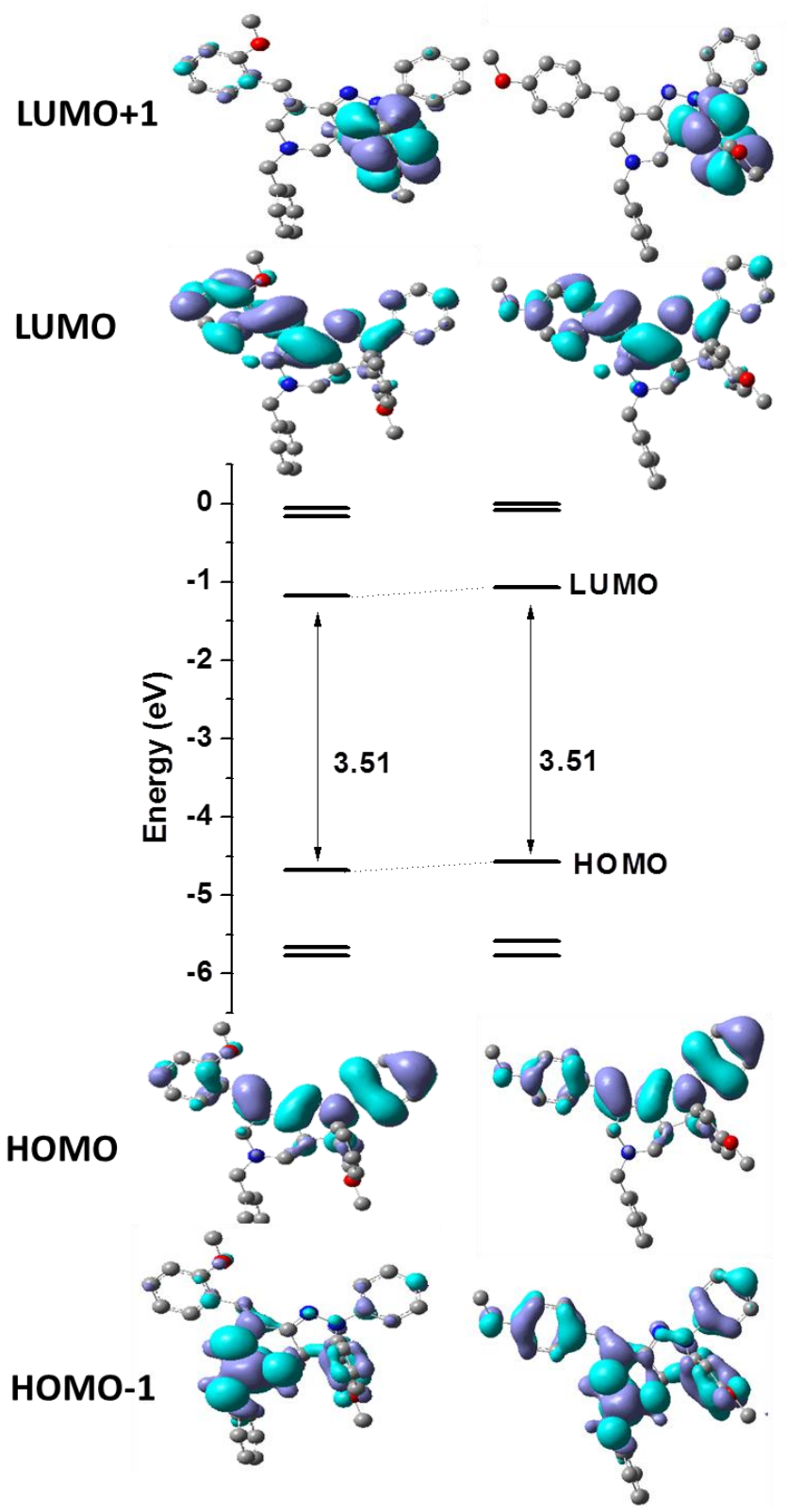


Figure S7 Molecular orbital diagrams of **1b** and **2b** calculated using Gaussian 03 at B3LYP/6-31G level of theory. Hydrogen atoms are omitted for clarity.

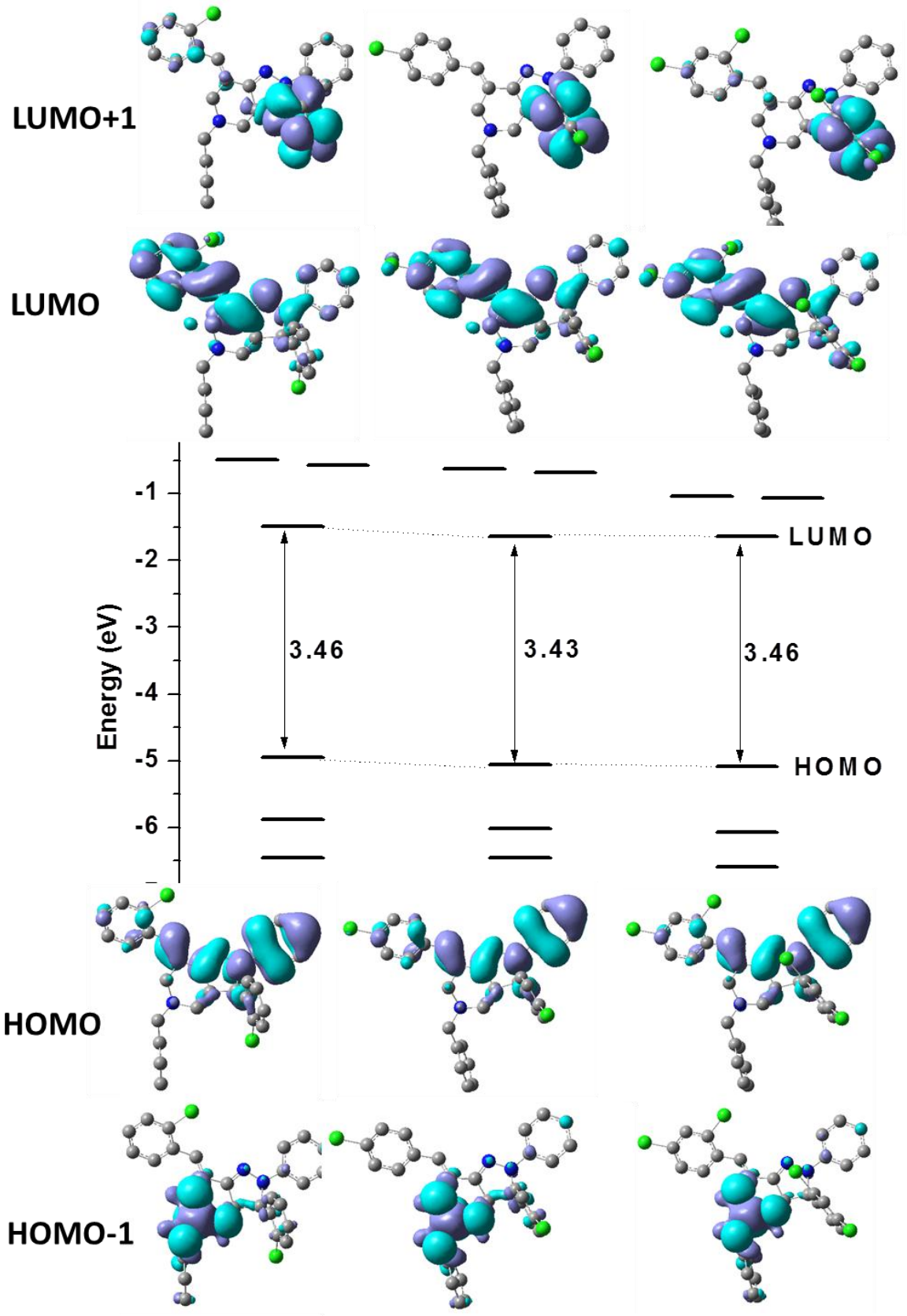


Figure S8 Molecular orbital diagrams of **1d**, **2d**, and **1f** calculated using Gaussian 03 at B3LYP/6-31G level of theory. Hydrogen atoms are omitted for clarity.

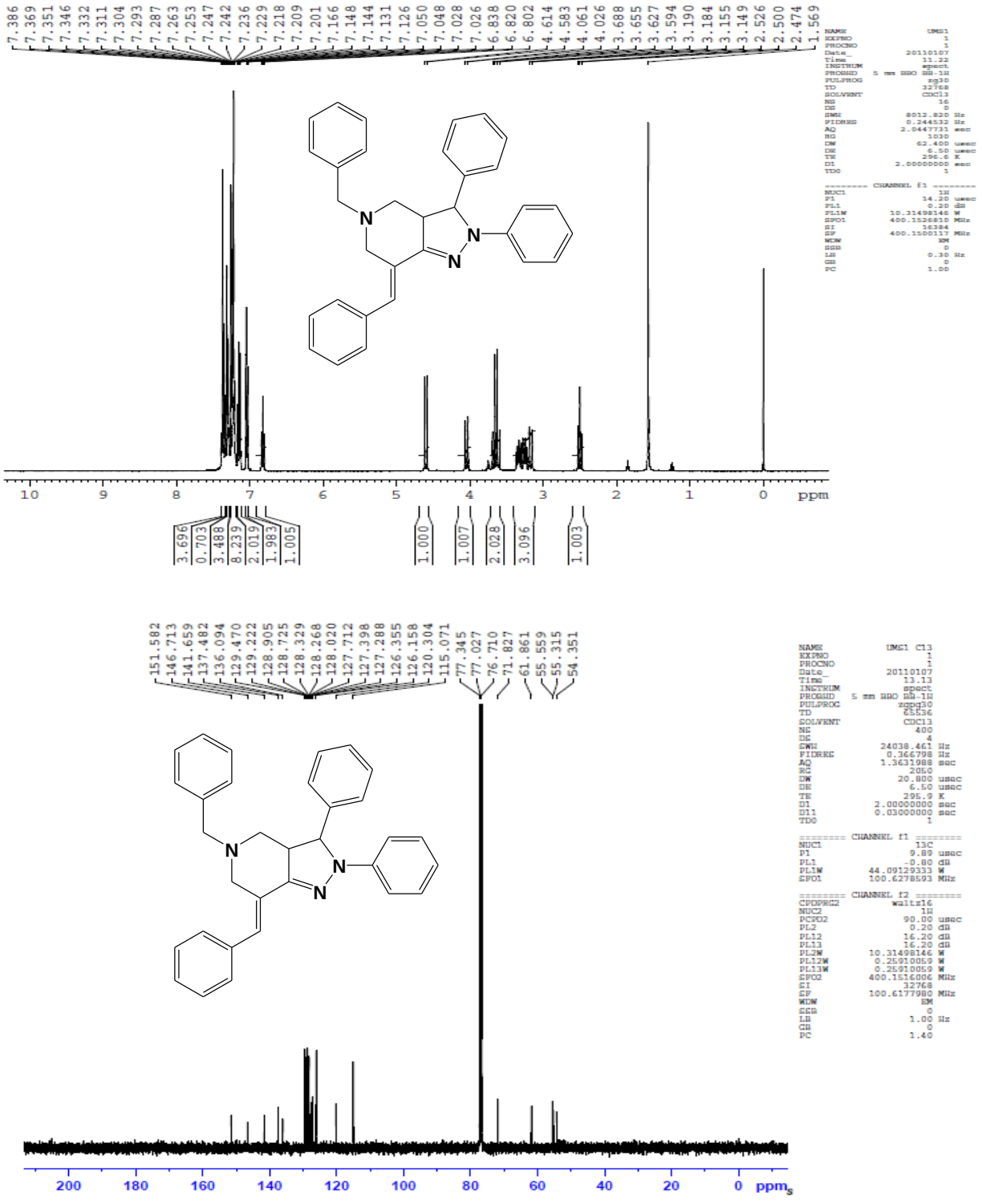


Figure S9 ^{1}H (top) and ^{13}C (bottom)-NMR spectra of compound **1**

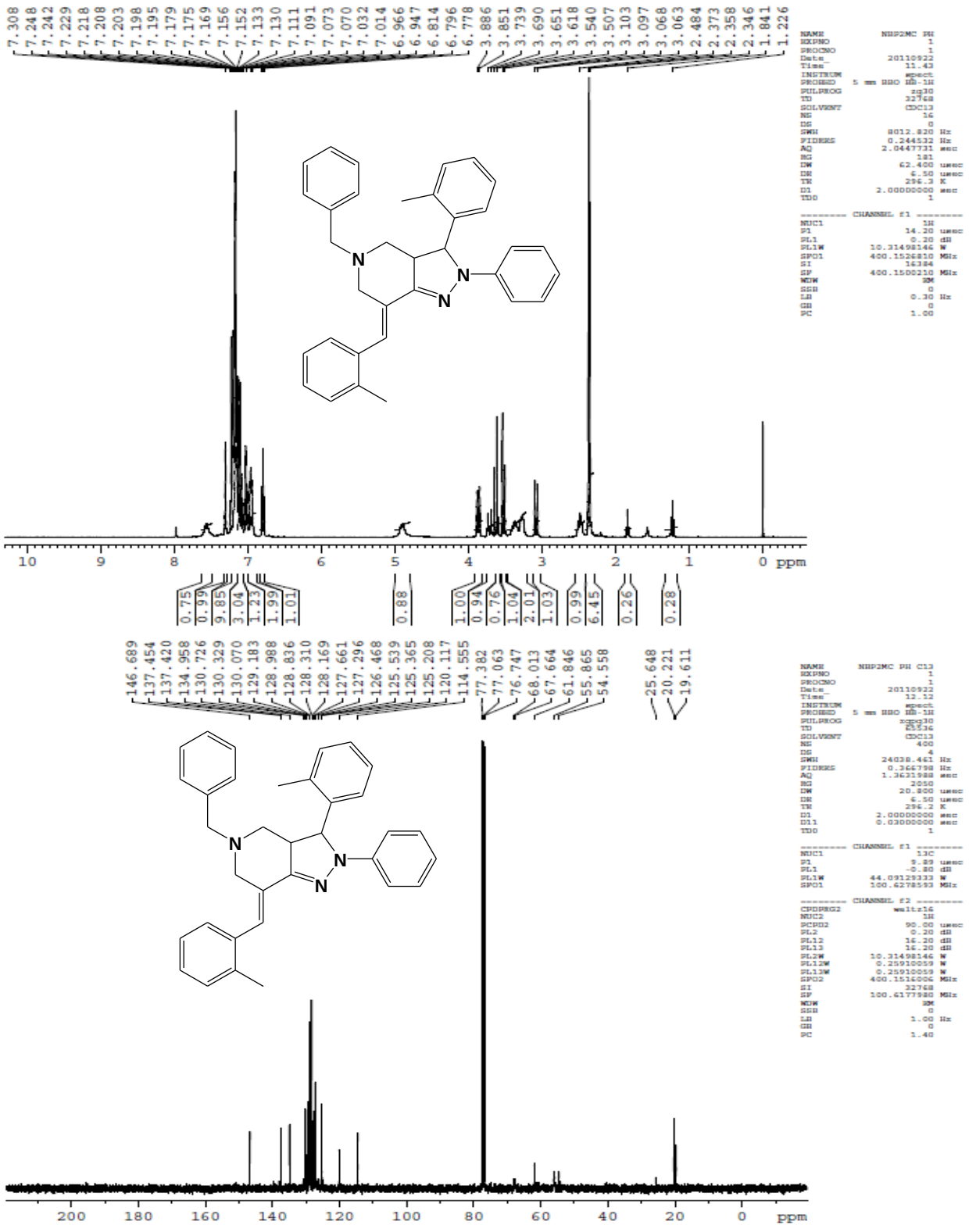


Figure S10 ^{1}H (top) and ^{13}C (bottom)-NMR spectra of compound **1a**

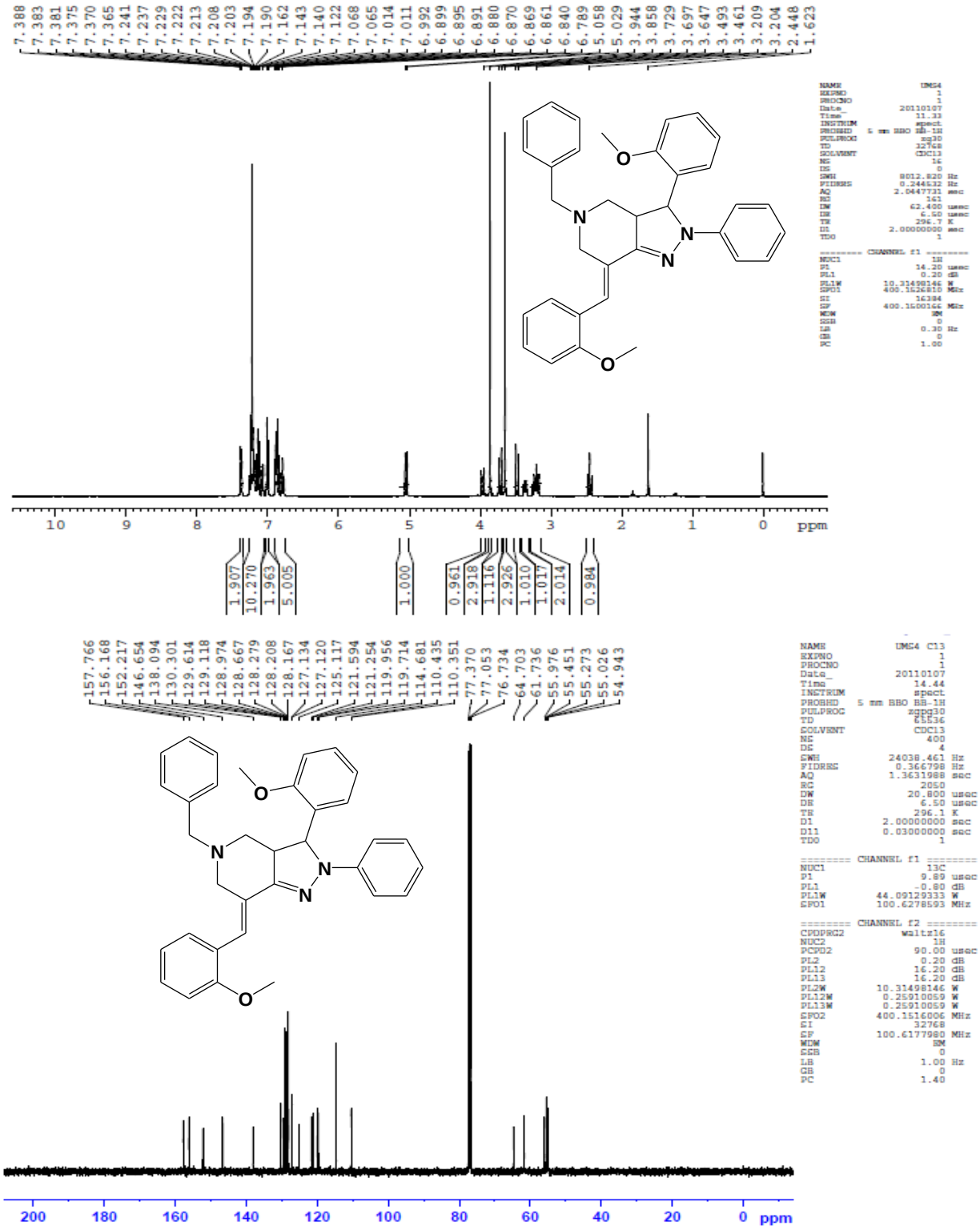


Figure S11 ^{1}H (top) and ^{13}C (bottom)-NMR spectra of compound **1b**

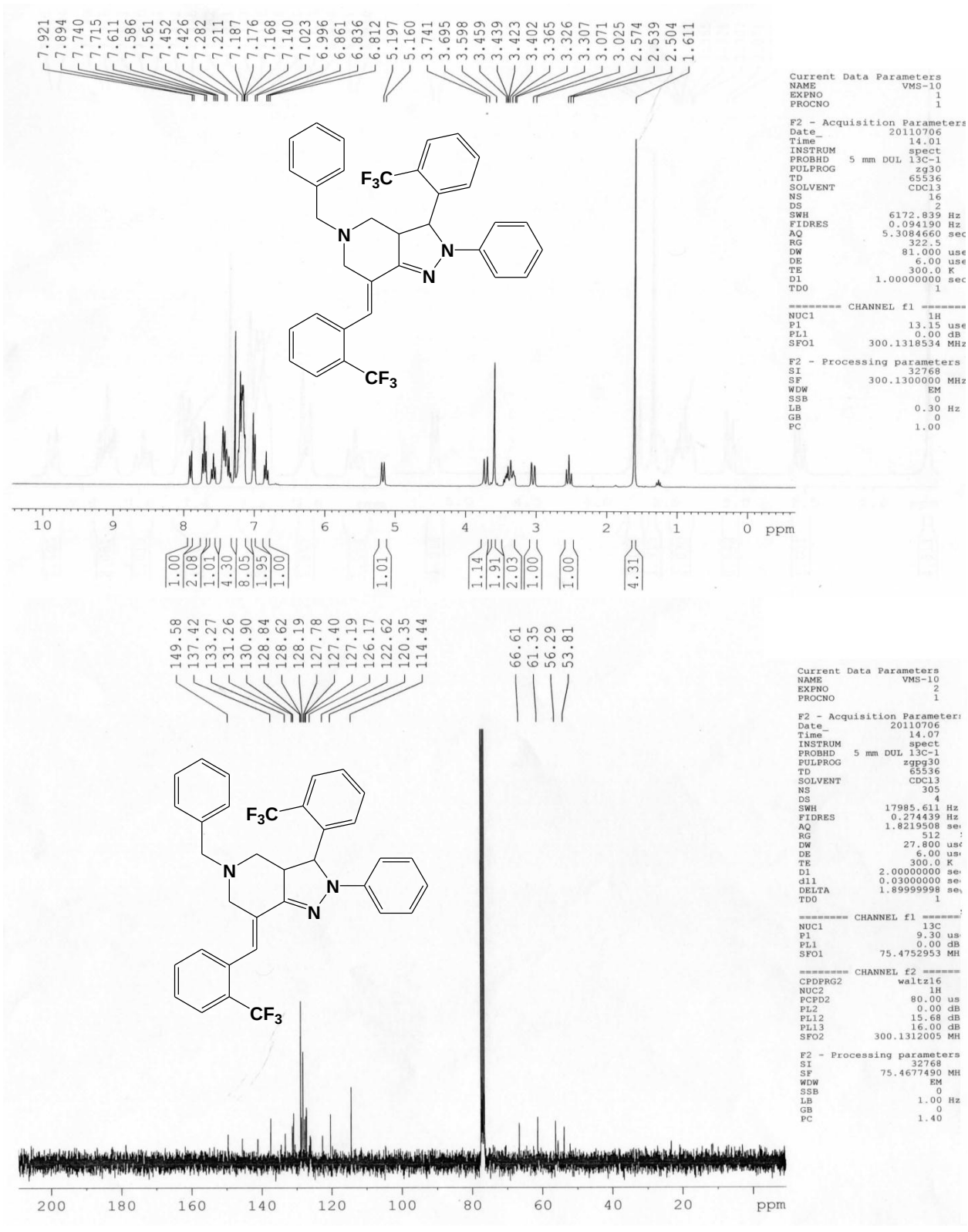


Figure S12 ^{1}H (top) and ^{13}C (bottom)-NMR spectra of compound **1e**

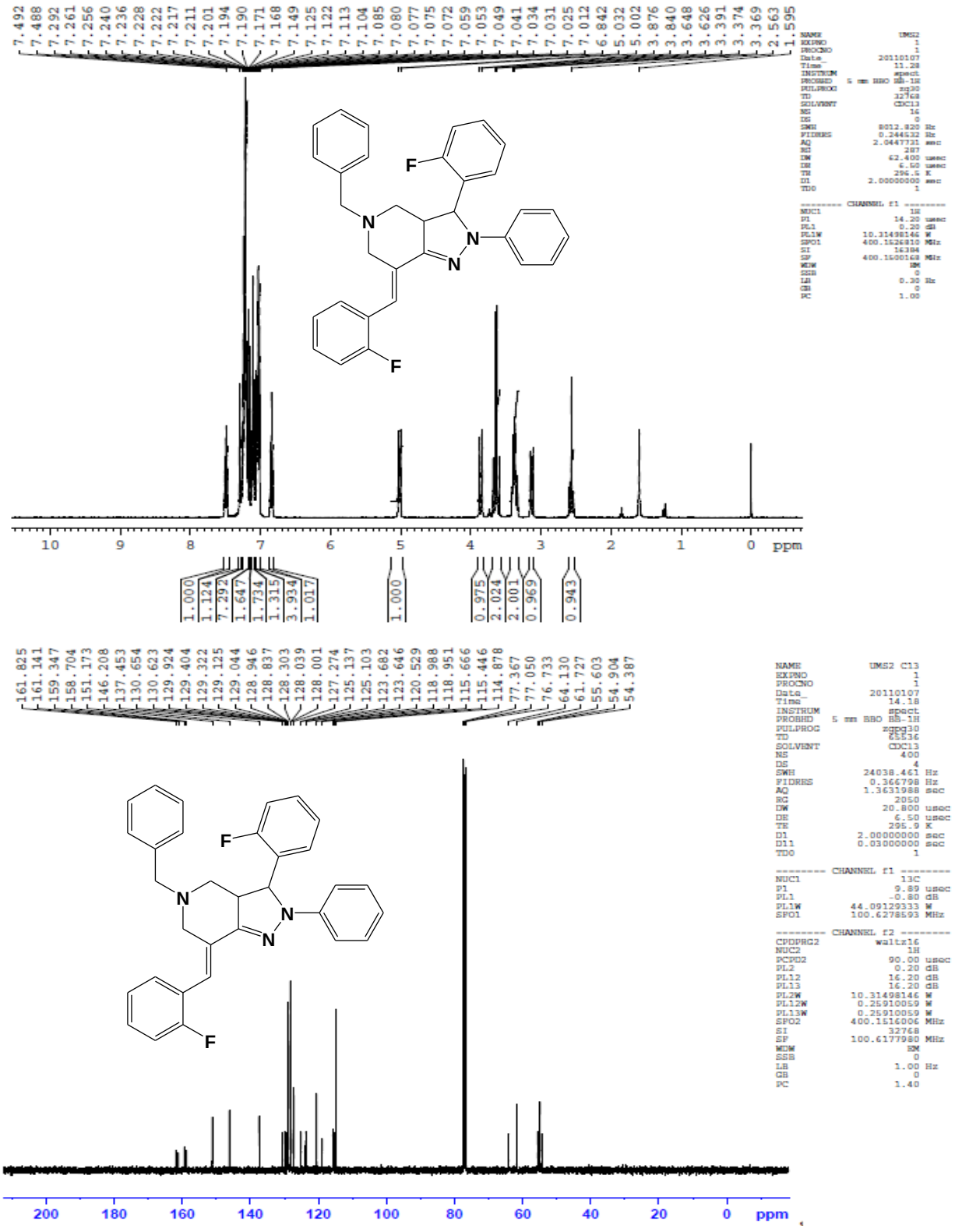


Figure S13 ^{1}H (top) and ^{13}C (bottom)-NMR spectra of compound **1c**

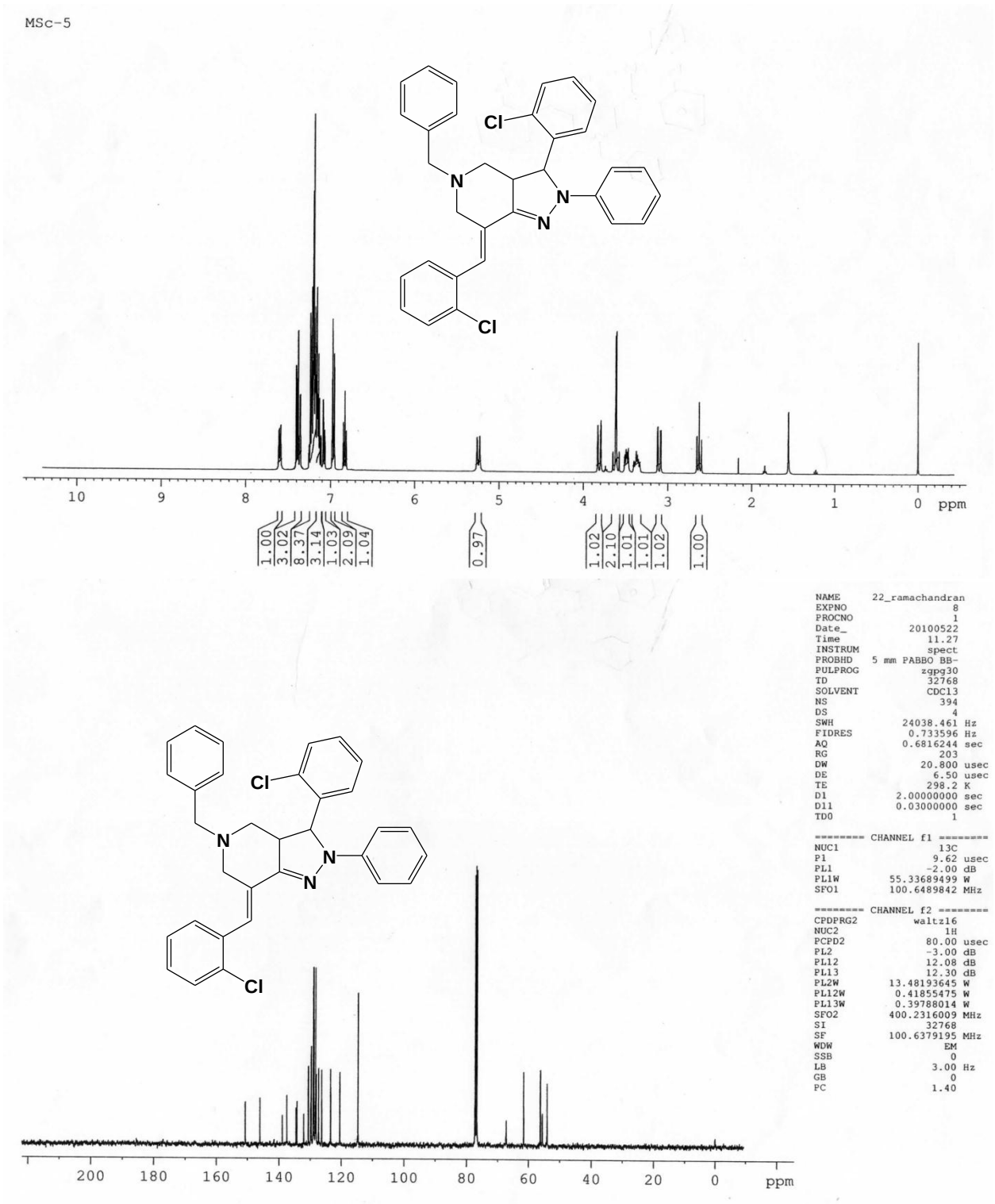


Figure S14 ^{1}H (top) and ^{13}C (bottom)-NMR spectra of compound **1d**

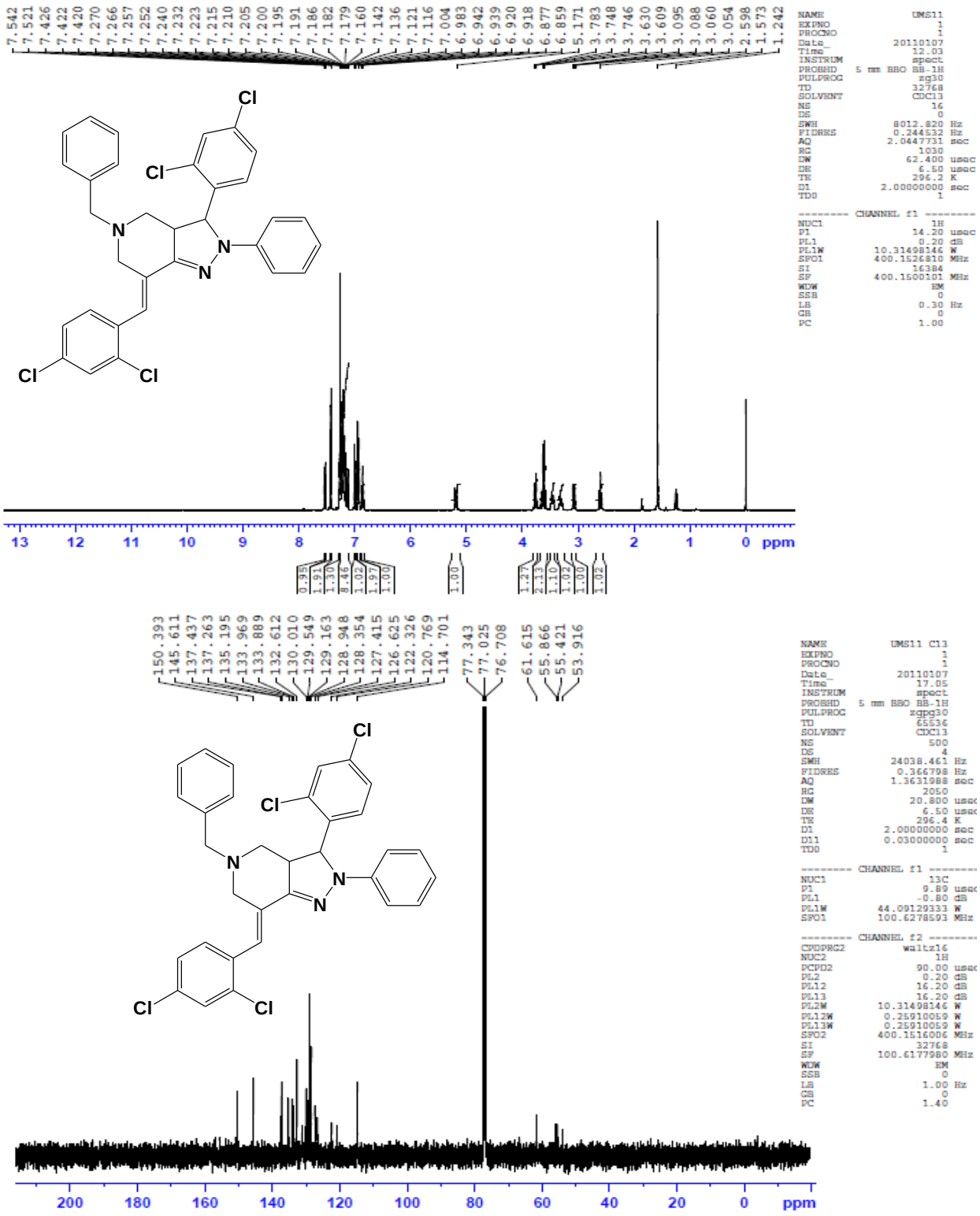


Figure S15 ^{1}H (top) and ^{13}C (bottom)-NMR spectra of compound **1f**

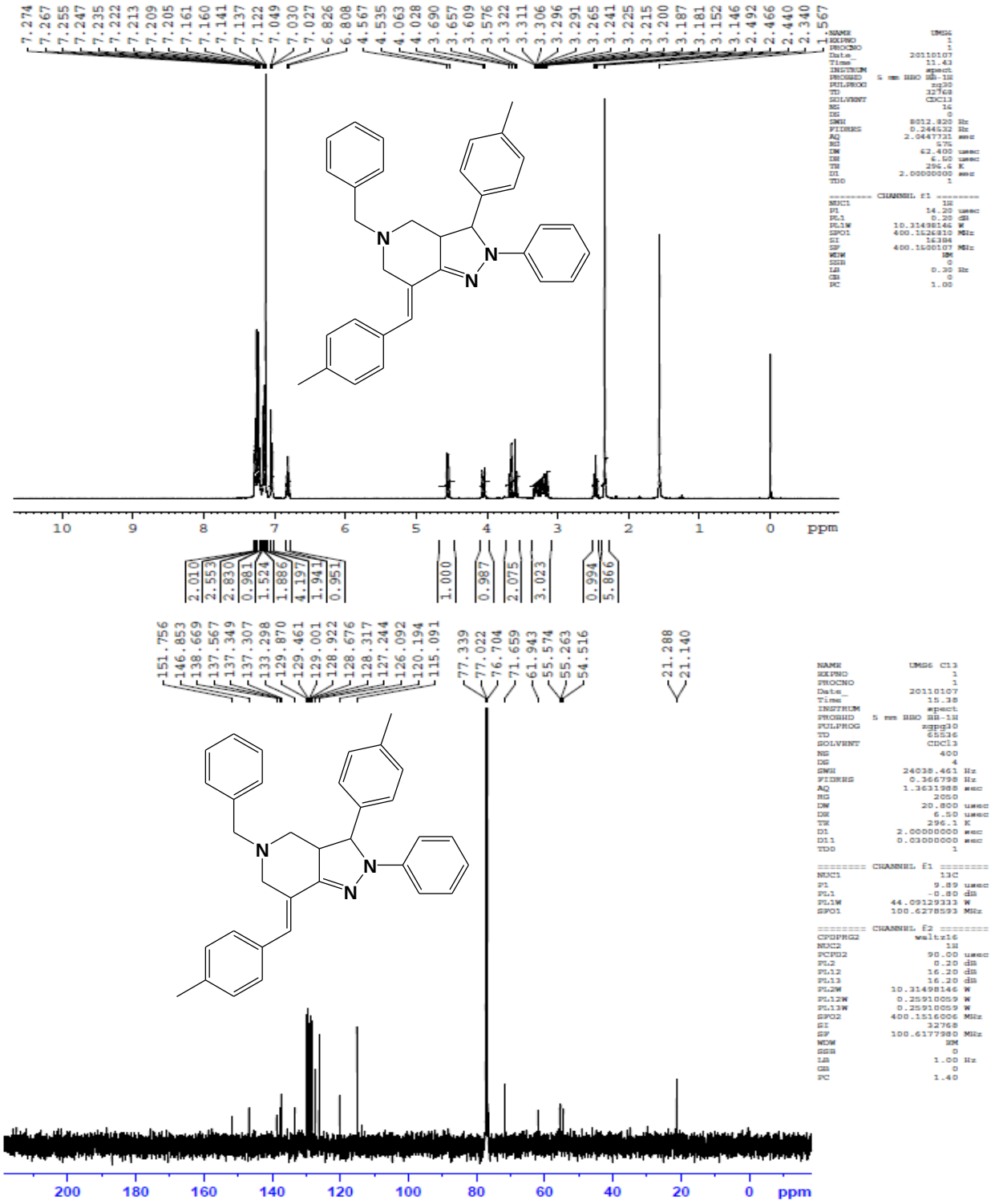


Figure S16 ^{1}H (top) and ^{13}C (bottom)-NMR spectra of compound**2a**

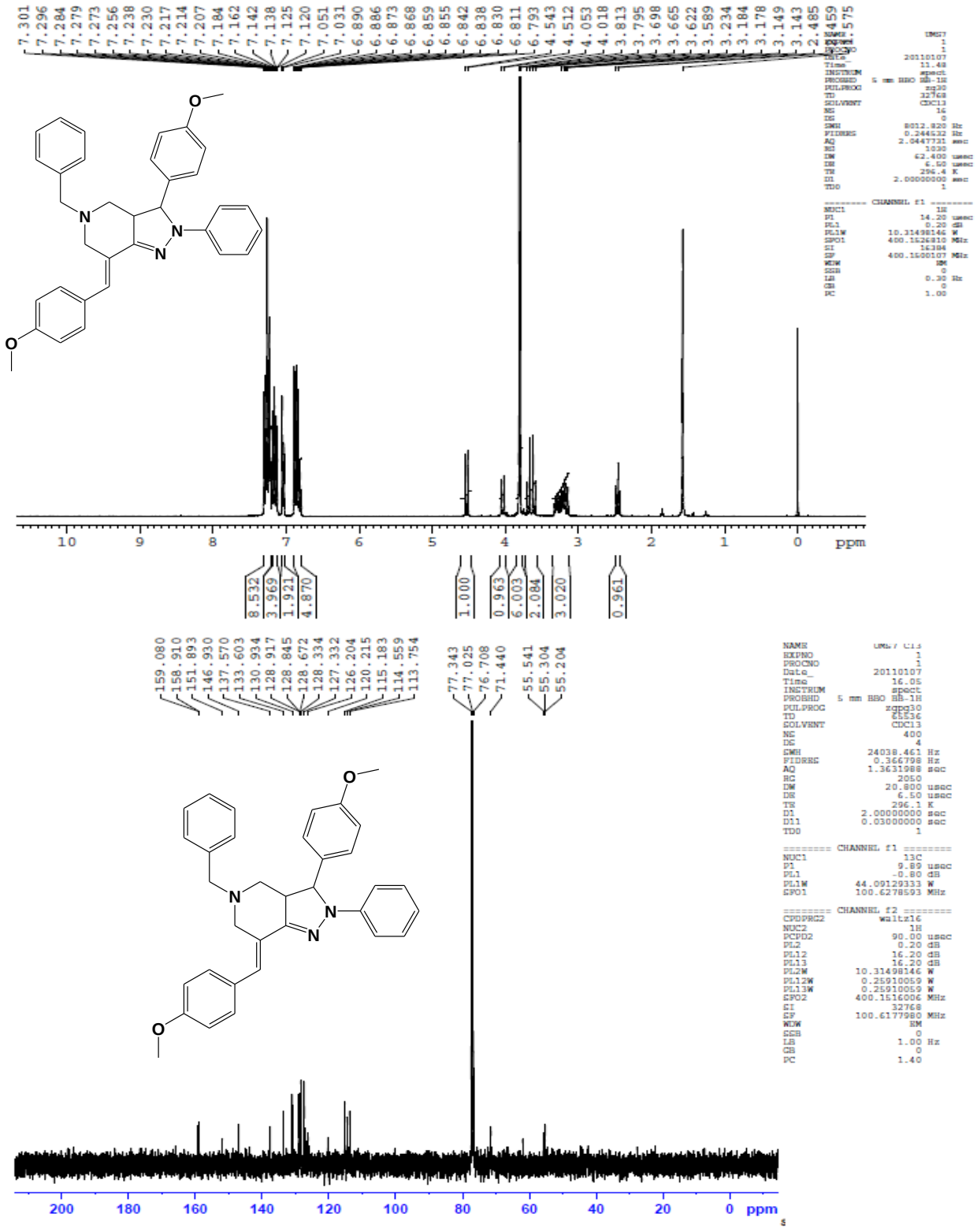


Figure S17 ^{1}H (top) and ^{13}C (bottom)-NMR spectra of compound**2b**

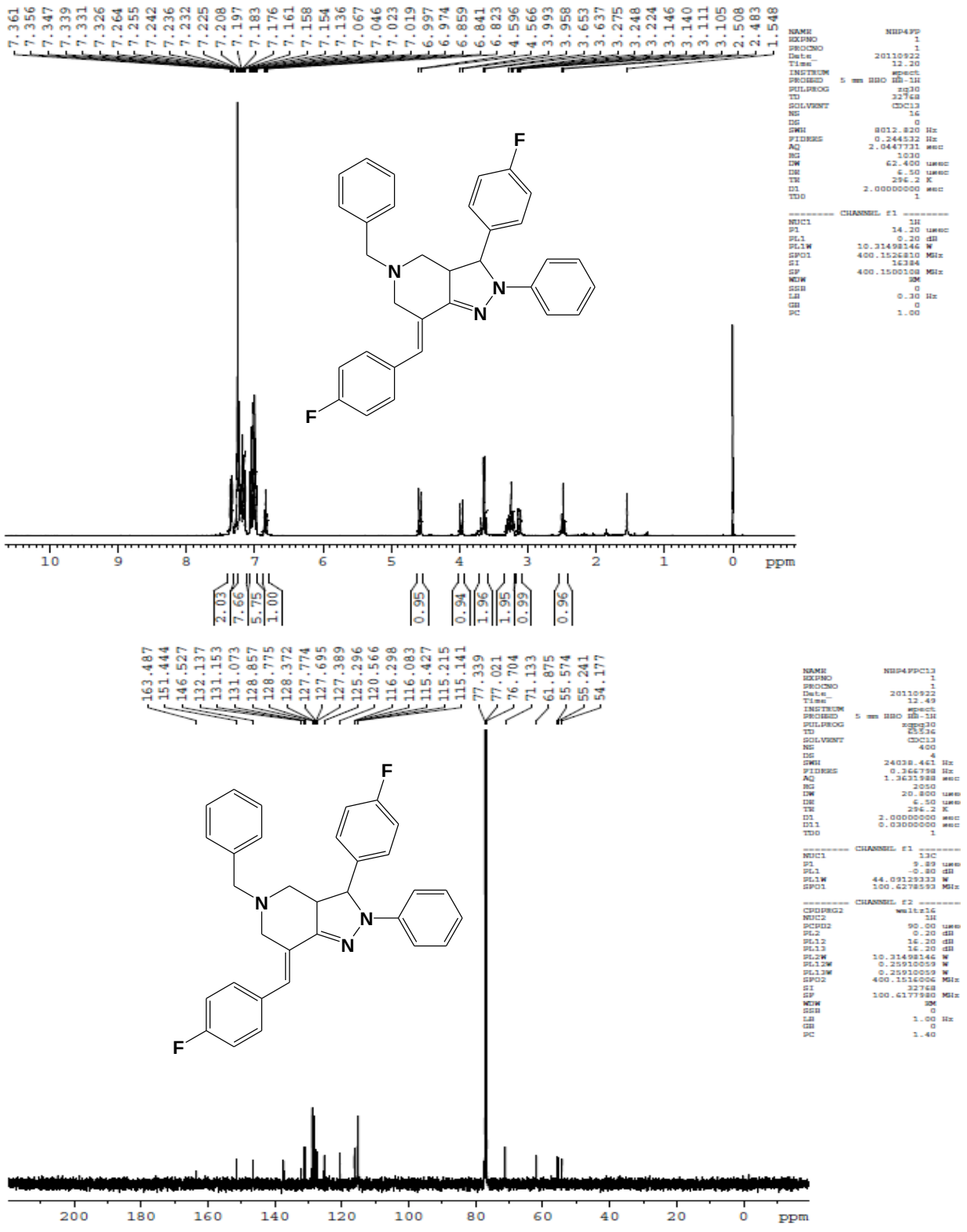


Figure S18 ^{1}H (top) and ^{13}C (bottom)-NMR spectra of compound**2c**

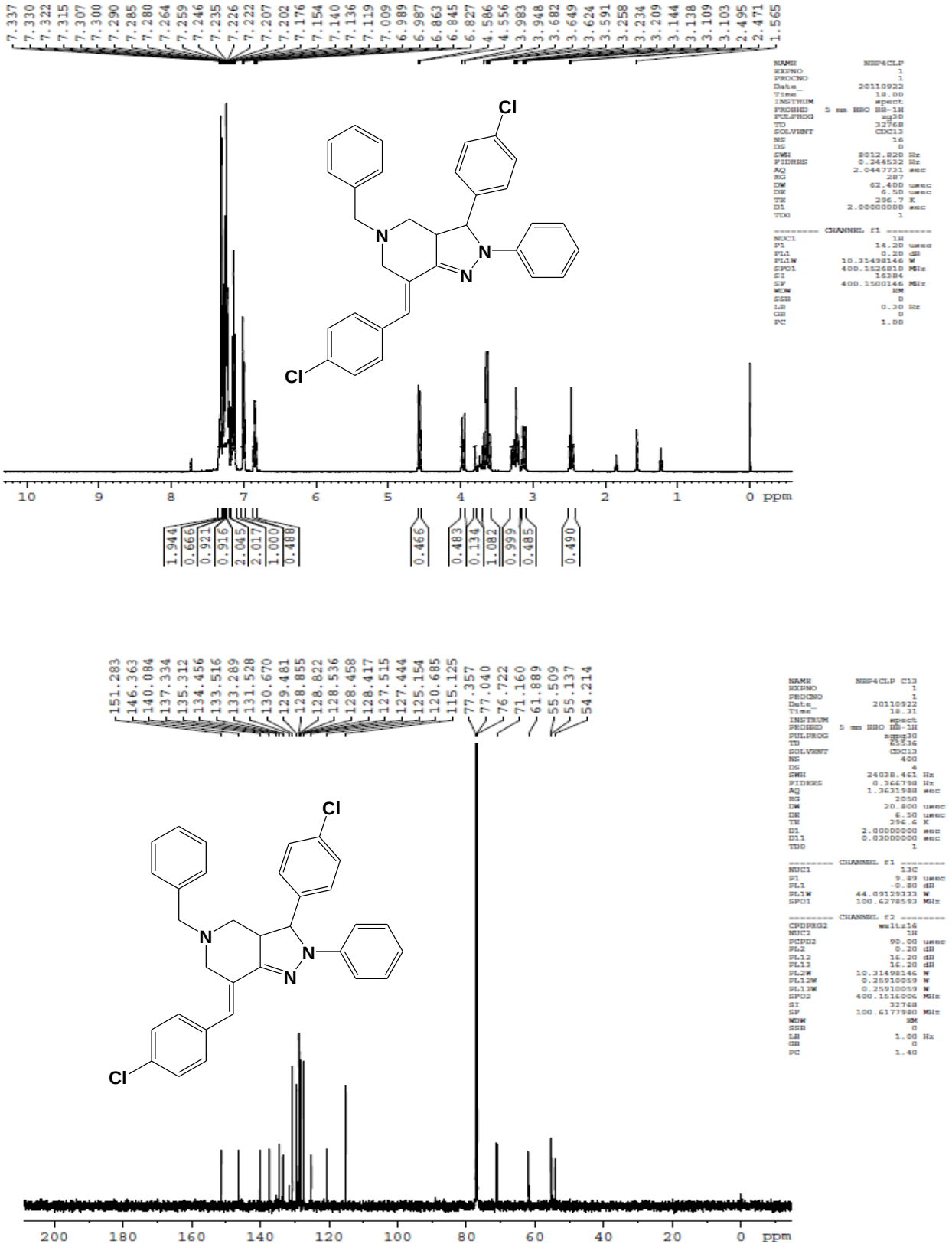


Figure S19 ^{1}H (top) and ^{13}C (bottom)-NMR spectra of compound**2d**

Cartesian coordinates of compound **1**

C	0.34732600	-0.54418000	-0.61765000
C	0.19108200	0.93678100	-0.30921800
C	-1.11129200	1.50370800	0.02384100
C	-2.05575500	0.51004600	0.69442200
C	-0.55746700	-1.39637400	0.27741400
C	1.90101300	-0.72583000	-0.56008800
H	-1.82877400	0.51996900	1.78367500
H	-0.20660400	-1.37125900	1.32519800
C	-1.36811500	2.82394600	-0.14990500
C	-2.60864700	3.57451900	0.12699500
C	-2.51973200	4.83402500	0.75821500
C	-3.88505400	3.12271300	-0.27118600
C	-3.66357800	5.59202900	1.02006800
H	-1.54346100	5.20936900	1.05109300
C	-5.02866100	3.88406600	-0.01346600
H	-3.97459500	2.19184400	-0.82128100
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C	3.91772200	2.52721600	-0.98841800
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C	5.21364600	2.96762400	-1.25376800
H	3.11179600	3.22955900	-0.82325900
C	5.97839100	0.68650300	-1.42080800
H	4.50108400	-0.84098700	-1.10089800
C	6.25555900	2.05618800	-1.47401000
H	5.41005500	4.03504500	-1.29141700
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C	2.65742500	-2.79050600	0.69132000
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H	2.53072300	0.39418200	1.88296700
C	3.10685100	-3.44645500	1.84267300
H	2.48295400	-3.35852200	-0.21933500
C	3.34371000	-2.71940500	3.01471500
H	3.32216200	-0.76421500	3.92997900
H	3.27834600	-4.51818100	1.82168000
H	3.69777500	-3.22465100	3.90767400
N	2.33886700	0.69413300	-0.68875800
N	1.31356300	1.59630300	-0.40565300
N	-1.93111800	-0.86118100	0.15364500
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H	-3.91672300	-1.22112600	0.64733500
C	-3.11531000	-3.03698400	-0.17004200

C	-3.14443800	-2.96287500	-1.57343500
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H	-3.23753300	-4.35829400	1.52974400
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H	-3.34821800	-4.04572700	-3.42490500
H	-3.57247800	-6.40604100	0.16922700
H	-3.63058700	-6.25648500	-2.31532000
H	-2.79077500	-2.05457200	1.72233100