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Supramolecular organic frameworks derived from bromoaryl-substituted dichlorodiazabutadienes *via* Cl···Br halogen bonding

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1. General remarks

Unless stated otherwise, all the reagents used in this study were obtained from the commercial sources (Aldrich, TCI-Europe, Strem, ABCR). NMR spectra were recorded on a Bruker Avance 300 (^{1}H: 300 MHz); chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references ($CDCl_3$: δ_C = 77.16 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm; CD_2Cl_2: δ_C = 53.84 ppm; residual $CHDCl_2$ in CD_2Cl_2: δ_H = 5.32 ppm); ^{1}H and ^{13}C assignments were established using NOESY, HSQC and HMBC experiments; numbering schemes as shown in the Inserts. IR: Perkin-Elmer Spectrum One spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. C, H, and N elemental analyses were carried out on a Euro EA 3028HT CHNS/O analyzer. Mass-spectra were obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source; MeOH, CH_2Cl_2 or MeOH/CH_2Cl_2 mixture was used as a solvent. Thermogravimetric analysis (TGA) and differential thermal analysis were determined using a Netzsch TG 209F1 Libra apparatus. Solvents were purified by distillation over the indicated drying agents and were transferred under Ar: Et_2O (Mg/anthracene), CH_2Cl_2 (CaH_2), hexane (Na/K). Flash chromatography: Merck Geduran® Si 60 (40–63 μm).

The single point calculations based on the experimental X-ray geometries of **2a** and **2c** have been carried out at the DFT level of theory using the dispersion-corrected hybrid functional ωB97XD[28] with the help of Gaussian-09 program package (M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, M. J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, C. J.;, D. J. Fox, Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, 2010] program package). The 6-311++G** basis sets were used for all atoms. The topological analysis of the electron density distribution with the help of the atoms in molecules (QTAIM) method developed by Bader[18] has been performed by using the Multiwfn program (version 3.7).[29] The Chemcraft program [http://www.chemcraftprog.com] was used for the visualization of electrostatic surface potential distribution. The Cartesian atomic coordinates for model supramolecular associates are presented in Table S1. The Hirshfeld surfaces analysis has been performed by using the CrystalExplorer program (version 17.5)[30] The normalized contact distances (d_{norm})[31] based on Bondi's van der Waals radii[20] were mapped into the Hirshfeld surfaces.

2. X-Ray Data

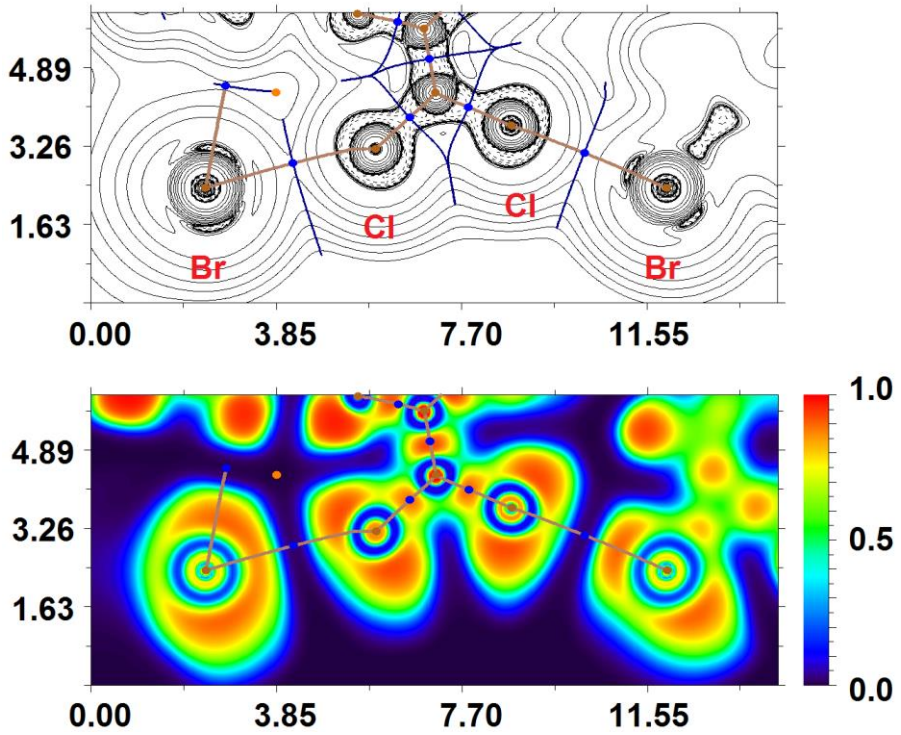


Figure S1 Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (top) and visualization of electron localization function (ELF) analysis (bottom) for halogen bonds Cl···Br in **2a**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, ring critical points (3, +1) – in orange, length units – Å, bond paths are shown as pale brown lines, and the color scale for the ELF map is presented in a.u.

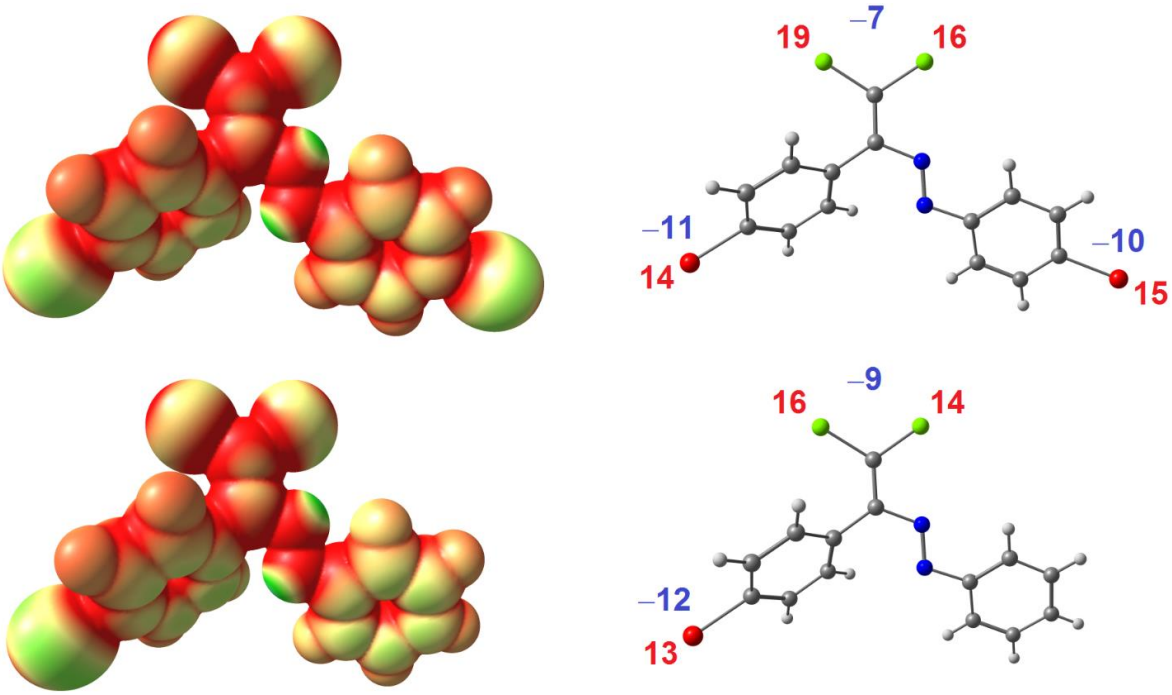


Figure S2 Visualization of electrostatic surface potential distribution in isolated molecules **2a** (top) and **2c** (bottom) with selected $V_{s,max}$ and $V_{s,min}$ values on halogen atoms corresponding to σ-holes and electron density "belts" (in kcal mol^{-1}, red and blue fonts, respectively).

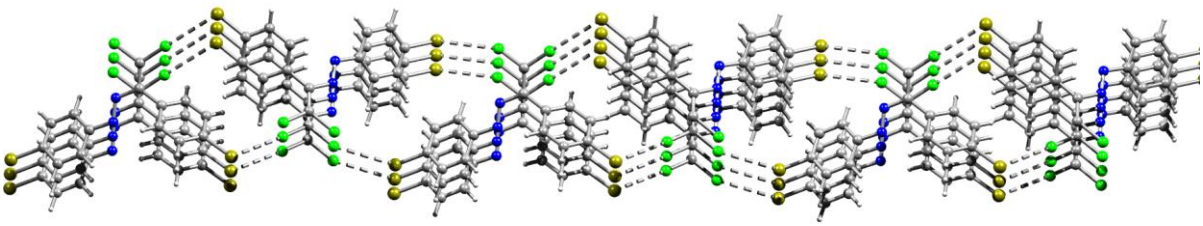


Figure S3 Ball-and-stick representation of the structure of **2a** in the crystal. Blue, green, yellow-green, grey and light grey spheres represent nitrogen, chlorine, bromine, carbon, hydrogen atoms, respectively.

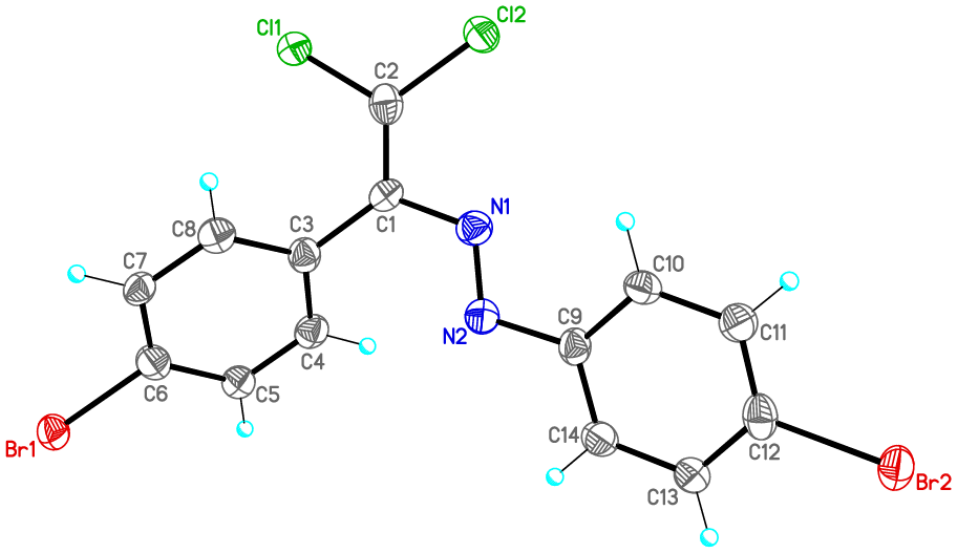


Figure S4 Molecular structure of complex **2a** in the solid state.

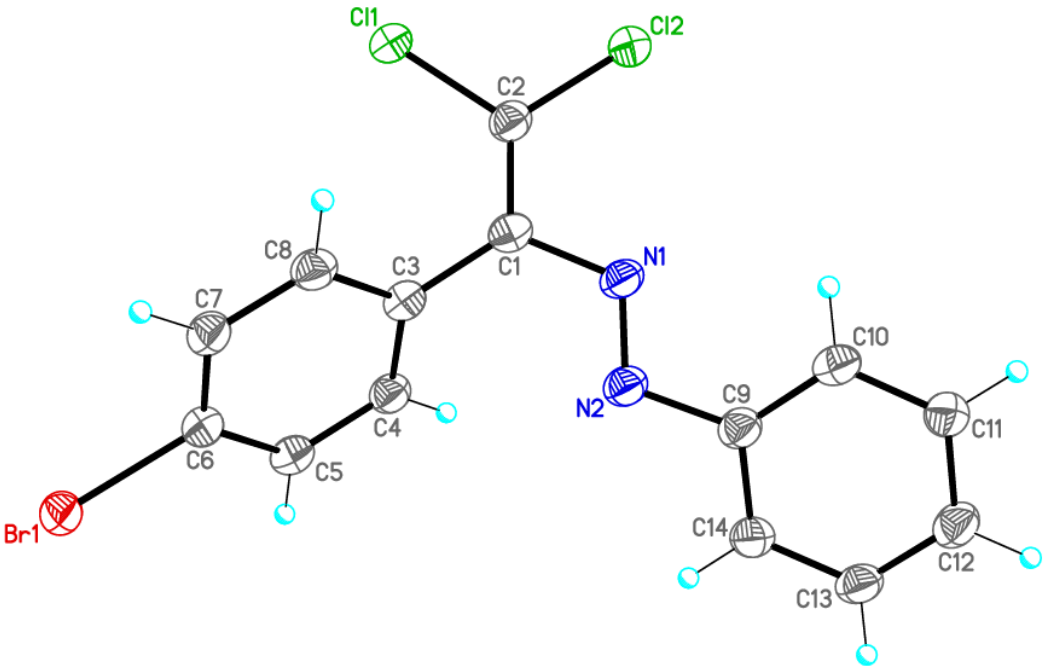


Figure S5 Molecular structure of complex **2c** in the solid state.

Table S1 Cartesian atomic coordinates for model supramolecular associates.

Atom	X	Y	Z
2a			
Br	2.246862	3.929990	7.369469
Br	6.481384	-0.228838	18.090754
Cl	-1.570232	4.243538	12.911746
Cl	-0.742514	3.279207	15.474304
N	1.696573	2.493129	14.265862
N	2.865877	2.236188	13.874084
C	0.838001	3.083290	13.303891
C	-0.340912	3.480745	13.820744
C	1.196486	3.243878	11.871051
C	2.374630	3.906303	11.490310
H	2.970367	4.219450	12.159827
C	2.683623	4.107038	10.165990
H	3.471487	4.578364	9.921359
C	1.827059	3.613230	9.192983
C	0.670242	2.922702	9.535099
H	0.091438	2.581051	8.863743
C	0.383418	2.738025	10.864937
H	-0.397033	2.253853	11.104050
C	3.661842	1.629968	14.883878
C	3.130498	0.975572	16.000353
H	2.188586	0.914549	16.108873
C	3.971697	0.413514	16.947609
H	3.616208	-0.029307	17.709092
C	5.317650	0.513882	16.767354
C	5.887379	1.128131	15.672952
H	6.830413	1.175906	15.573628
C	5.035199	1.674130	14.716499
H	5.400926	2.079213	13.940300
Br	4.208019	5.937340	29.417179
Br	-0.026502	1.778512	18.695894
Cl	8.025113	6.250888	23.874903
Cl	7.197395	5.286557	21.312345
N	4.758308	4.500479	22.520786
N	3.589004	4.243538	22.912564
C	5.616880	5.090640	23.482757
C	6.795793	5.488095	22.965905
C	5.258395	5.251228	24.915597
C	4.080252	5.913653	25.296339
H	3.484515	6.226800	24.626822
C	3.771259	6.114388	26.620658
H	2.983394	6.585714	26.865289
C	4.627823	5.620580	27.593665
C	5.784640	4.930052	27.251549
H	6.363443	4.588401	27.922905
C	6.071464	4.745375	25.921712
H	6.851914	4.261203	25.682599
C	2.793040	3.637318	21.902770
C	3.324383	2.982922	20.786296
H	4.266296	2.921899	20.677775
C	2.483184	2.420864	19.839039

H	2.838674	1.978043	19.077556
C	1.137232	2.521232	20.019294
C	0.567502	3.135481	21.113697
H	-0.375531	3.183256	21.213021
C	1.419682	3.681480	22.070150
H	1.053955	4.086563	22.846348
Br	-3.949922	5.937340	11.023855
Br	-8.184443	1.778512	0.302570
Cl	-0.132828	6.250888	5.481578
Cl	-0.960546	5.286557	2.919021
N	-3.399633	4.500479	4.127462
N	-4.568937	4.243538	4.519240
C	-2.541060	5.090640	5.089433
C	-1.362148	5.488095	4.572580
C	-2.899546	5.251228	6.522273
C	-4.077689	5.913653	6.903015
H	-4.673426	6.226800	6.233498
C	-4.386682	6.114388	8.227334
H	-5.174546	6.585714	8.471965
C	-3.530118	5.620580	9.200341
C	-2.373301	4.930052	8.858225
H	-1.794498	4.588401	9.529581
C	-2.086477	4.745375	7.528388
H	-1.306026	4.261203	7.289274
C	-5.364901	3.637318	3.509446
C	-4.833558	2.982922	2.392971
H	-3.891645	2.921899	2.284451
C	-5.674756	2.420864	1.445715
H	-5.319267	1.978043	0.684232
C	-7.020709	2.521232	1.625970
C	-7.590439	3.135481	2.720373
H	-8.533472	3.183256	2.819697
C	-6.738258	3.681480	3.676825
H	-7.103985	4.086563	4.453024
2c			
Br	3.796119	1.130517	27.172680
Cl	-0.018699	0.729818	21.619558
Cl	0.862178	1.560810	19.029722
N	3.282874	2.425394	20.252044
N	4.445061	2.682929	20.675129
C	2.411543	1.860335	21.222810
C	1.234810	1.453237	20.697415
C	2.759828	1.719170	22.661233
C	3.918877	1.058135	23.044812
H	4.504009	0.713022	22.379964
C	4.233277	0.895376	24.387340
H	5.024431	0.438290	24.649025
C	3.376458	1.409248	25.335821
C	2.224279	2.095476	24.995124
H	1.653666	2.454186	25.665375
C	1.927597	2.244639	23.654960
H	1.141705	2.714121	23.403067
C	5.266382	3.269183	19.667220
C	4.768722	3.956611	18.566793

H	3.831098	4.059385	18.449626
C	5.647362	4.488478	17.646676
H	5.314703	4.963559	16.893023
C	7.023368	4.332117	17.817193
H	7.623896	4.688428	17.173279
C	7.512278	3.662684	18.914919
H	8.449270	3.557910	19.027021
C	6.639097	3.141614	19.855971
H	6.976438	2.699725	20.627519
Br	-2.449277	3.130017	23.476001
Cl	1.365542	2.729318	29.029123
Cl	0.484665	3.560310	31.618959
N	-1.936031	4.424894	30.396637
N	-3.098218	4.682429	29.973552
C	-1.064700	3.859835	29.425871
C	0.112032	3.452737	29.951266
C	-1.412985	3.718670	27.987448
C	-2.572035	3.057635	27.603869
H	-3.157167	2.712522	28.268717
C	-2.886435	2.894876	26.261341
H	-3.677588	2.437790	25.999656
C	-2.029616	3.408748	25.312860
C	-0.877436	4.094976	25.653557
H	-0.306824	4.453686	24.983306
C	-0.580754	4.244139	26.993721
H	0.205138	4.713621	27.245614
C	-3.919539	5.268683	30.981460
C	-3.421880	5.956111	32.081887
H	-2.484255	6.058885	32.199055
C	-4.300520	6.487978	33.002005
H	-3.967861	6.963059	33.755658
C	-5.676526	6.331617	32.831488
H	-6.277054	6.687928	33.475402
C	-6.165435	5.662184	31.733762
H	-7.102428	5.557410	31.621660
C	-5.292254	5.141114	30.792710
H	-5.629596	4.699225	30.021161

Table S2 Values of the density of all electrons – $\rho(\mathbf{r})$, Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$ and appropriate λ_2 eigenvalues (with promolecular approximation), energy density – H_b, potential energy density – $V(\mathbf{r})$, and Lagrangian kinetic energy – $G(\mathbf{r})$ (a.u.) at the bond critical points (3, –1), corresponding to halogen bonds Cl···Br in **2a** and **2c**, and estimated energies for these interactions E_{int} (kcal mol^{-1}).

Short halogen···halogen contact*	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	λ_2	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	E_{int}[a]	E_{int}[b]
2a								
Cl···Br, 3.478 Å (97% from the sum of Bondi's vdW radii)	0.008	0.029	-0.011	0.002	-0.004	0.006	1.2	1.8
Cl···Br, 3.625 Å (101% from the sum of Bondi's vdW radii)	0.006	0.022	-0.008	0.001	-0.003	0.004	0.9	1.2
2c								
Cl···Br, 3.451 Å (96% from the sum of Bondi's vdW radii)	0.008	0.031	-0.011	0.002	-0.005	0.006	1.5	1.8

* Two types of short halogen···halogen contacts usually discussed in the literature.[19] Type I is believed to depend on the effects of crystal packing, while type II is due to a classic halogen bonding (a halogen atom with a 90° angle provides its lone pair (electron density "belt") for interaction and the other one provides its σ-hole). Short halogen···halogen contacts presented in **Table S2** could be classified as halogen bonds (type II contacts). The Bondi's (shortest) van der Waals (vdW) radii for chlorine and bromine atoms are 1.75 and 1.83 Å.[20]

[a] $E_{int} = 0.49(-V(\mathbf{r}))$ (this correlation between the interaction energy and the potential energy density of electrons at the bond critical points (3, –1) was specifically developed for noncovalent interactions involving chlorine atoms as halogen bond donors)[21]

[b] $E_{int} = 0.47G(\mathbf{r})$ (this correlation between the interaction energy and the kinetic energy density of electrons at the bond critical points (3, –1) was specifically developed for noncovalent interactions involving chlorine atoms as halogen bond donors) [21]

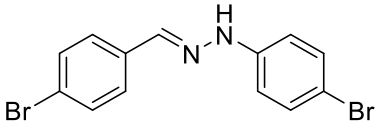
Table S3 Main partial contributions of different interatomic contacts to the Hirshfeld surfaces of X-ray structures **2a** and **2c**.

X-ray structure	Contributions of different interatomic contacts to the Hirshfeld surfaces
2a	Cl–H 19.1%, Br–H 17.2%, H–H 14.8%, C–H 13.6%, Br–Cl 9.1%, C–C 7.5%, N–H 5.3%, Br–Br 4.8%, N–C 3.0%, Br–C 2.4%, Cl–C 1.8%, Cl–Cl 1.1%, Br–N 0.1%
2c	Cl–H 24.5%, H–H 20.5%, C–H 16.1%, Br–H 13.1%, C–C 7.6%, N–H 5.9%, Br–Cl 3.6%, N–C 2.9%, Cl–C 2.5%, Br–Br 1.4%, Cl–Cl 1.0%, Br–C 0.6%, Br–N 0.1%, Cl–N 0.1%

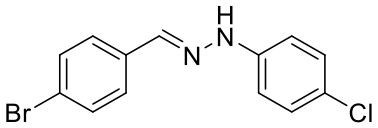
3. Synthetic part

Synthesis of hydrazones

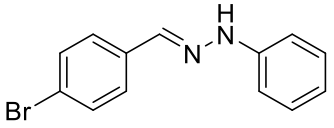
Hydrazones **1a–1g** were synthesized according to a following method (similar procedures for the synthesis of hydrazones were reported earlier).[7,32–34] A mixture of the corresponding hydrazine (10.2 mmol), AcONa (0.82 g) and *p*-bromobenzaldehyde (10 mmol) was refluxed with stirring in ethanol (50 ml) for 2 h. The reaction mixture was cooled to room temperature and water (50 ml) was added to cause precipitation of the crude product, which was filtered off, washed with diluted ethanol (1:1 with water) and dried *in vacuo*.



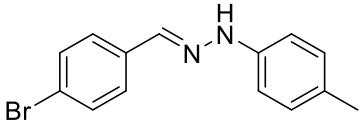
1a. (*E*)-1-(4-Bromobenzylidene)-2-(4-bromophenyl)hydrazine (described compound[S1,S2]). White solid (75%), m. p. 110 °C, ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.59 (s, 1H, NH), 7.83 (s, 1H, CH), 7.68 – 7.49 (m, 4H, arom), 7.37 (d, *J* = 8.7 Hz, 2H, arom), 7.03 (d, *J* = 8.8 Hz, 2H, arom). ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.7, 140.2, 131.9, 130.7, 123.4, 116.8, 109.8, 105.7.



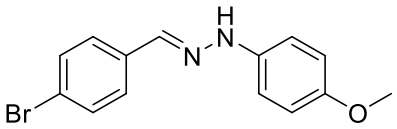
1b. (*E*)-1-(4-Bromobenzylidene)-2-(4-chlorophenyl)hydrazine. White solid (82%), m. p. 145 °C, ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.58 (s, 1H, NH), 7.84 (s, 1H, CH), 7.57 (t, *J* = 6.7 Hz, 4H, arom), 7.25 (d, *J* = 8.8 Hz, 2H, arom), 7.08 (d, *J* = 8.8 Hz, 2H, arom). ^{13}C NMR (75 MHz, DMSO-d_6) δ 139.8, 131.8, 130.7, 127.4, 124.8, 123.4, 118.1, 116.8, 109.3.



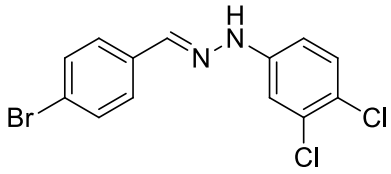
1c. (*E*)-1-(4-Bromobenzylidene)-2-phenylhydrazine (described compound[S3,S4,S5]). White solid (82%), m. p. 113 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.45 (s, 1H, NH), 7.83 (s, 1H, CH), 7.64 – 7.50 (m, 4H, arom), 7.22 (t, *J* = 7.8 Hz, 2H, arom), 7.08 (d, *J* = 7.8 Hz, 2H, arom), 6.76 (t, *J* = 7.2 Hz, 1H, arom). ^{13}C NMR (75 MHz, DMSO-d_6) δ 140.9, 131.0, 130.8, 127.4, 125.0, 123.3, 116.5, 114.8, 107.9.



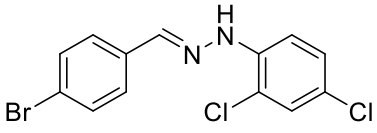
1d. (*E*)-1-(4-Bromobenzylidene)-2-(*p*-tolyl)hydrazine. white solid (97%), m. p. 152°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.34 (s, 1H, NH), 7.79 (s, 1H, CH), 7.63 – 7.46 (m, 4H, arom), 7.01 (q, *J* = 8.4 Hz, 4H, arom), 2.21 (s, 3H, CH_3).^{13}C NMR (75 MHz, DMSO-d_6) δ 138.6, 131.1, 130.1, 127.3, 125.4, 123.4, 123.1, 116.3, 107.9, 16.1.



1e. (*E*)-1-(4-Bromobenzylidene)-2-(4-methoxyphenyl)hydrazine. White solid (67%), m. p. 93°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.25 (s, 1H, NH), 7.76 (s, 1H, CH), 7.55 (s, 3H, arom), 7.01 (d, *J* = 8.9 Hz, 2H, arom), 6.84 (d, *J* = 8.9 Hz, 2H, arom), 2.09 (s, 3H, OCH_3).^{13}C NMR (75 MHz, DMSO-d_6) δ 131.2, 129.6, 127.3, 123.0, 118.4, 116.1, 110.5, 108.9, 105.6, 51.1, 35.6.



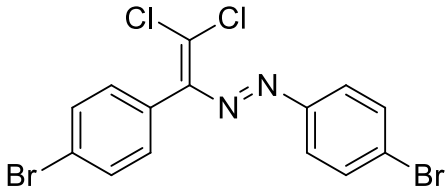
1f. (*E*)-1-(4-Bromobenzylidene)-2-(3,4-dichlorophenyl)hydrazine. Pale yellow solid (90%), m. p. 135 °C. IR (ν, cm^{-1}): 3318 (N-H), 1594 (C=N). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62 (s, 2H, arom), 7.31 (s, 1H, NH), 7.29 (s, 1H, CH), 7.27 (s, 1H, arom), 7.26 (d, *J* = 2.6 Hz, 2H, arom), 6.89 (d, *J* = 2.6 Hz, 1H, arom), 6.87 (d, *J* = 2.6 Hz, 1H, arom). ^{13}C NMR (101 MHz, DMSO- d_6) δ 145.0, 137.4, 134.5, 131.7, 131.0, 127.9, 121.5, 119.7, 112.9, 112.4. ESI-HRMS (m/z): calcd. for ($C_{13}H_{10}BrCl_2N_2$) [M+H$^+$] 342.9399, found 342.9394.



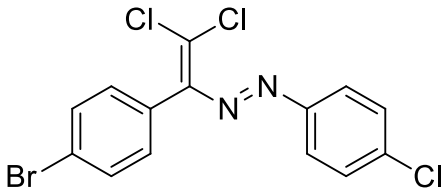
1g. (*E*)-1-(4-Bromobenzylidene)-2-(2,4-dichlorophenyl)hydrazine. White solid (89%), m. p. 170 °C. IR (ν, cm^{-1}): 3334 (N-H), 1581 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H, NH), 7.79 (s, 1H, CH), 7.52 (dd, *J* = 9.1, 3.7 Hz, 5H, arom), 7.18 (t, *J* = 8.1 Hz, 1H, arom), 6.98 (d, *J* = 9.3 Hz, 1H, arom). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 138.5, 133.2, 132.3, 131.5, 127.5, 122.6, 120.4, 114.8, 111.8, 109.6. ESI-HRMS (m/z): calcd. for ($C_{13}H_{10}BrCl_2N_2$) [M+H^+] 342.9399, found 342.9395.

Synthesis of dichloro diaza dienes

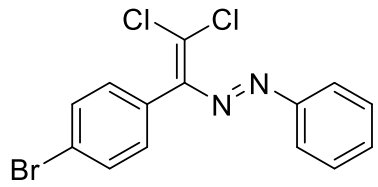
A 20 ml screw neck vial was charged with DMSO (10 ml), hydrazone **1a**–**g** (1 mmol), tetramethylethylenediamine (TMEDA, 295 mg, 2.5 mmol), CuCl (2 mg, 0.02 mmol) and CCl_4 (20 mmol, 10 equiv). After 1-3 hours (until TLC analysis showed complete consumption of the hydrazone), the mixture was poured into ~0.01 M solution of HCl (100 ml, ~pH = 2), and extracted with dichloromethane (3x20 ml). The combined organic phase was washed with water (3x50 ml), brine (30 ml), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using appropriate mixtures of hexane and dichloromethane (3:1–1:1).



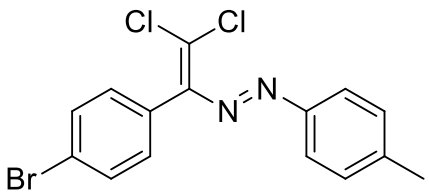
2a. (*E*)-1-(4-Bromophenyl)-2-(1-(4-bromophenyl)-2,2-dichlorovinyl)diazene. Pale orange solid (72%), m. p. 91 °C. IR (ν, cm^{-1}): 1589, 1569, 1551. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H, arom), 7.58 (ddd, *J* = 8.4, 4.0, 2.0 Hz, 4H, arom), 7.07 – 7.02 (m, 2H, arom). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 151.0, 136.1, 131.9, 131.2, 131.1, 130.7, 125.9, 124.3, 122.7. ESI-HRMS (m/z): calcd. for ($C_{14}H_9Br_2Cl_2N_2$) [M+H^+] 432.8504, found 432.8494.



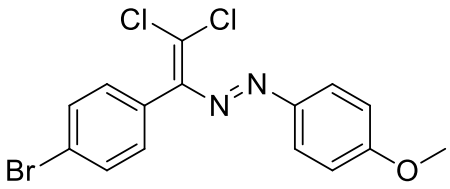
2b. (*E*)-1-(1-(4-Bromophenyl)-2,2-dichlorovinyl)-2-(4-chlorophenyl)diazene. Orange solid (79%), m. p. 114 °C. IR (ν, cm^{-1}): 1588, 1571, 1552. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.8 Hz, 2H, arom), 7.57 (d, *J* = 8.5 Hz, 2H, arom), 7.42 (d, *J* = 8.8 Hz, 2H, arom), 7.07 – 7.02 (m, 2H, arom). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 150.7, 137.4, 136.0, 131.2, 131.1, 130.8, 129.0, 124.1, 122.8. ESI-HRMS (m/z): calcd. for ($C_{14}H_9BrCl_3N_2$) [M+H^+] 388.9009, found 388.9006.



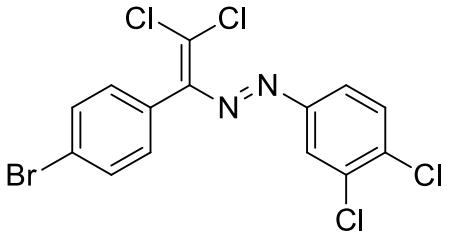
2c. (*E*)-1-(1-(4-Bromophenyl)-2,2-dichlorovinyl)-2-phenyldiazene (described compound[S7]). Red solid (75%), m. p. 100 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 2.6 Hz, 2H, arom), 7.61 (d, *J* = 8.1 Hz, 2H, arom), 7.56 – 7.43 (m, 3H, arom), 7.10 (d, *J* = 8.1 Hz, 2H, arom).^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 146.8, 131.2, 127.2, 126.9, 125.1, 124.5, 118.7.



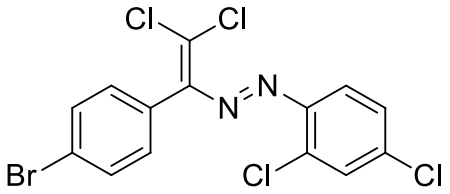
2d. (*E*)-1-(1-(4-Bromophenyl)-2,2-dichlorovinyl)-2-(*p*-tolyl)diazene. Orange solid (69%), m. p. 98 °C. IR (ν, cm^{-1}): 1600, 1571, 1558. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H, arom), 7.57 (d, *J* = 8.4 Hz, 2H, arom), 7.25 (d, *J* = 8.2 Hz, 2H, arom), 7.06 (d, *J* = 8.4 Hz, 2H, arom), 2.41 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 150.5, 142.2, 134.3, 131.3, 131.2, 131.0, 129.4, 122.9, 122.6, 21.20. ESI-HRMS (m/z): calcd. for ($C_{15}H_{12}BrCl_2N_2$) [M+H^+] 386.9555, found 386.9554.



2e. (*E*)-1-(1-(4-Bromophenyl)-2,2-dichlorovinyl)-2-(4-methoxyphenyl) diazene (described compound[S6]). Orange solid (72%), m. p. 101 ^{0}C. IR (ν, cm^{-1}): 1602, 1582, 1559. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 9.0 Hz, 1H, arom), 7.56 (d, *J* = 8.4 Hz, 1H, arom), 7.06 (d, *J* = 8.4 Hz, 1H, arom), 6.94 (d, *J* = 9.0 Hz, 1H, arom), 3.87 (s, 1H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 150.8, 146.8, 133.1, 131.3, 131.0, 124.9, 122.5, 113.8, 55.2. ESI-HRMS (m/z): calcd. for ($C_{15}H_{12}BrCl_2N_2O$) [M+H$^+$] 384.9505, found 384.9490.



2f. (*E*)-1-(1-(4-Bromophenyl)-2,2-dichlorovinyl)-2-(3,4-dichlorophenyl) diazene. Orange solid (67%), m. p. 117 °C. IR (ν, cm^{-1}): 1589, 1570, 1557. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.2 Hz, 1H, arom), 7.63 (dd, *J* = 8.6, 2.2 Hz, 1H, arom), 7.60 – 7.56 (m, 2H, arom), 7.53 (d, *J* = 8.6 Hz, 1H, arom), 7.07 – 7.01 (m, 2H, arom). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 151.0, 137.3, 135.3, 133.1, 131.2, 130.5, 124.1, 123.0, 122.4. ESI-HRMS (m/z): calcd. for ($C_{14}H_7BrCl_4N_2Ag$) [M+Ag] 532.7545, found 532.7534.



2g. (*E*)-1-(1-(4-Bromophenyl)-2,2-dichlorovinyl)-2-(2,4-dichlorophenyl) diazene. Pale orange solid (71%), m. p. 125 °C. IR (ν, cm^{-1}): 1589, 1570, 1555. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 2H, arom), 7.52 (ddd, *J* = 12.2, 8.0, 1.5 Hz, 2H, arom), 7.27 – 7.23 (m, 1H, arom), 7.13 – 7.08 (m, 2H, arom). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 150.1, 137.8, 133.9, 133.7, 132.1, 131.3, 131.0, 130.1, 126.9, 123.0, 115.3. ESI-HRMS (m/z): calcd. for ($C_{14}H_7BrCl_4N_2Ag$) [M+Ag] 532.7545, found 532.7553.

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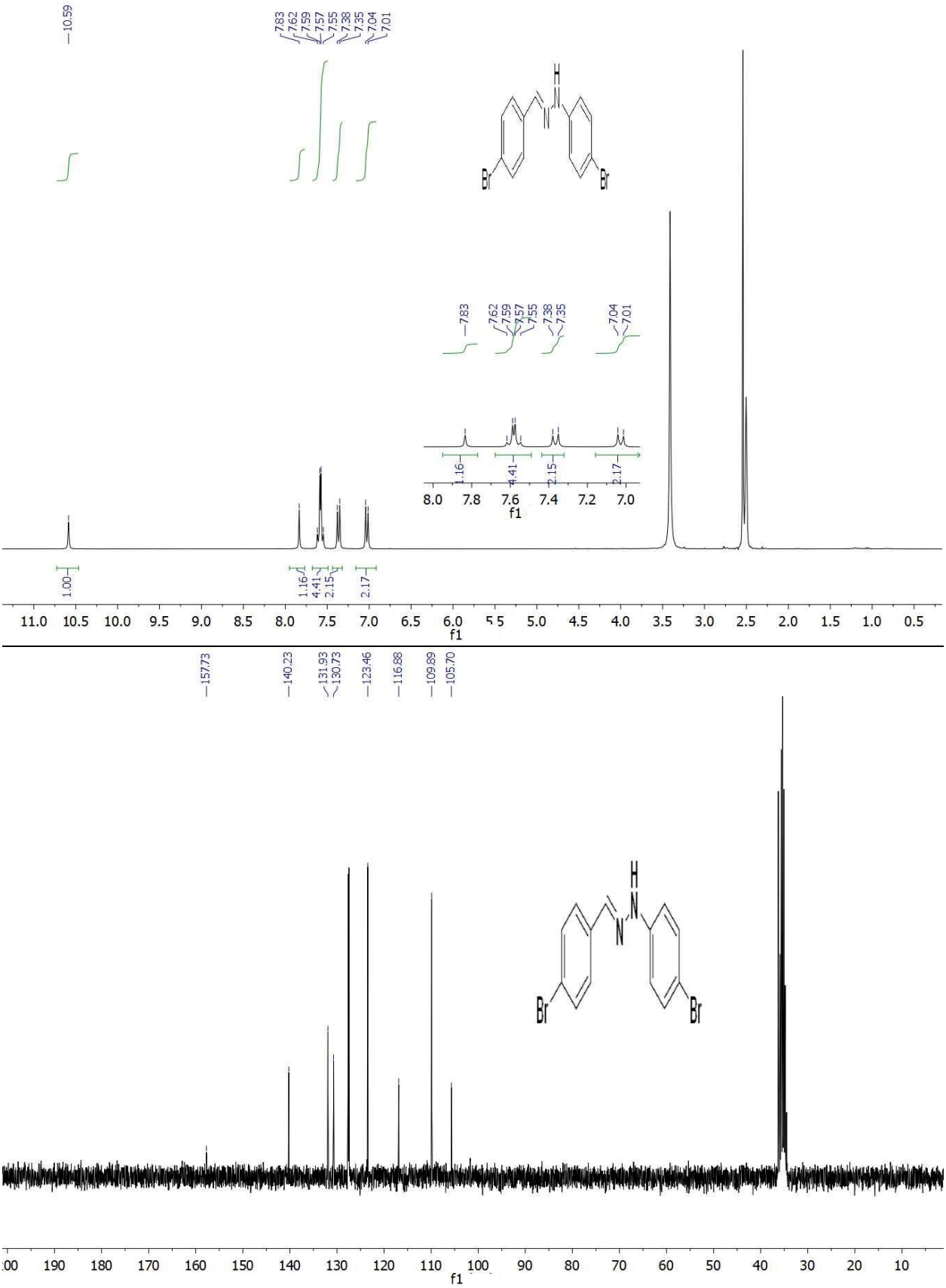
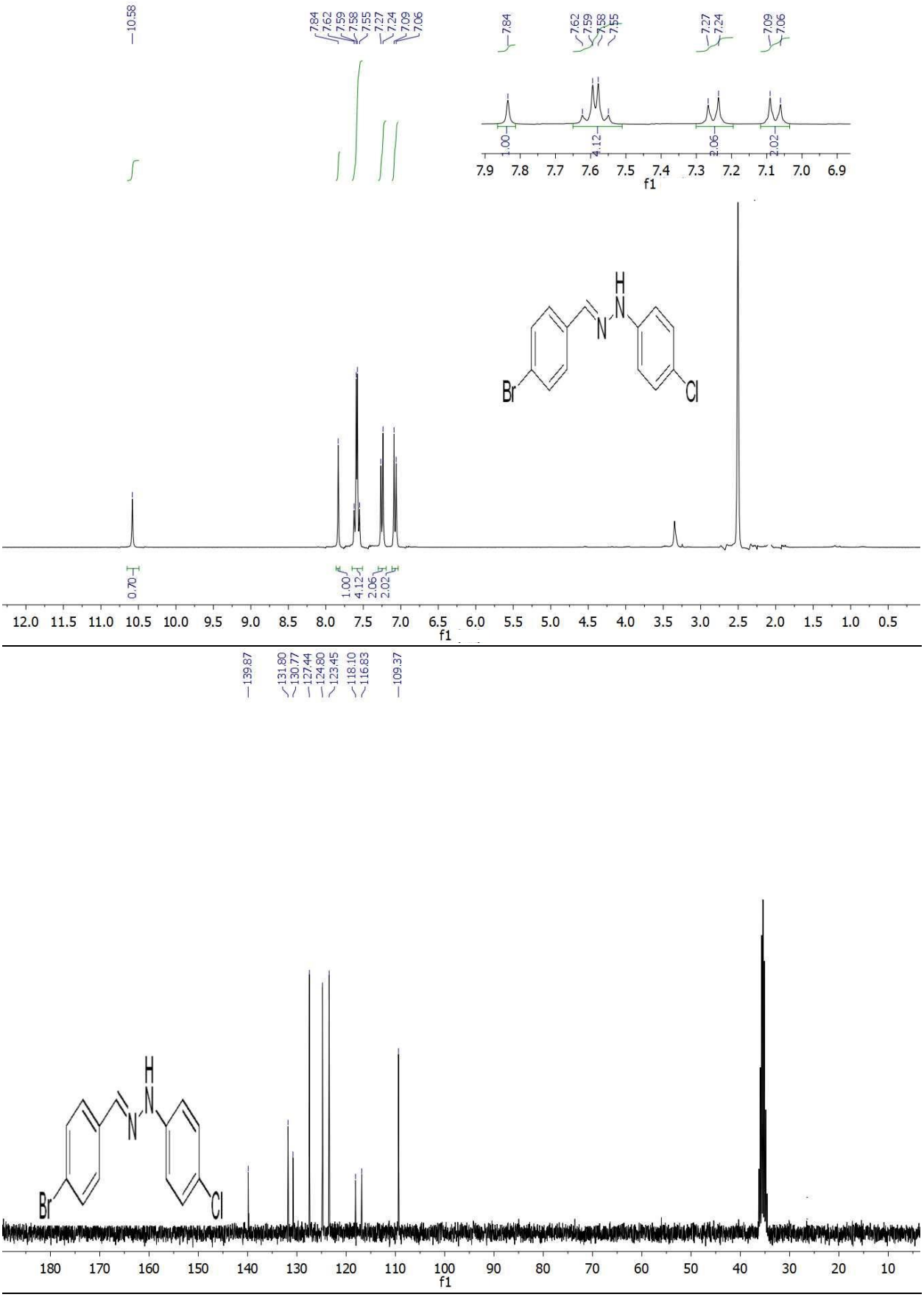
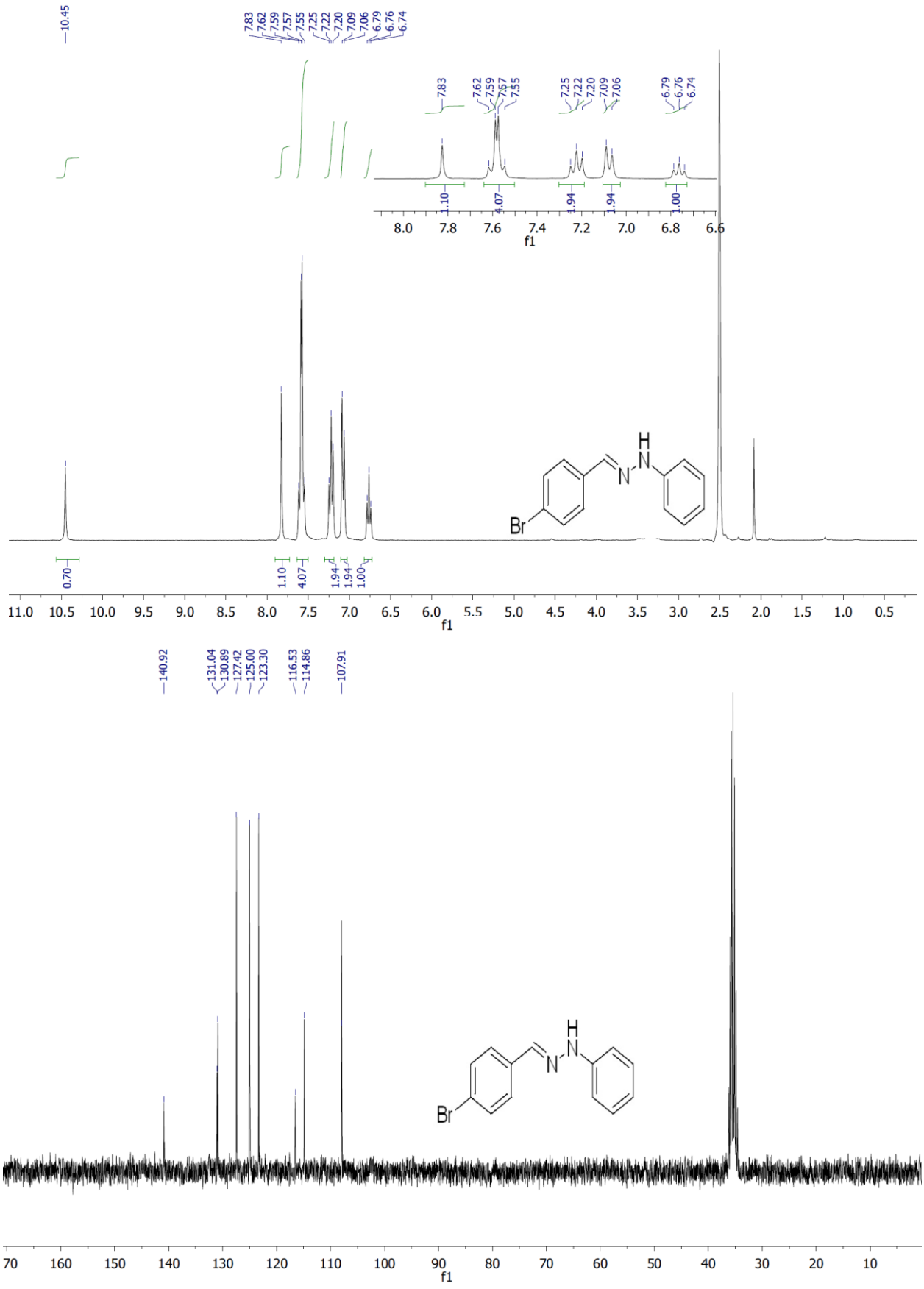
4. NMR Spectra data for obtained compounds



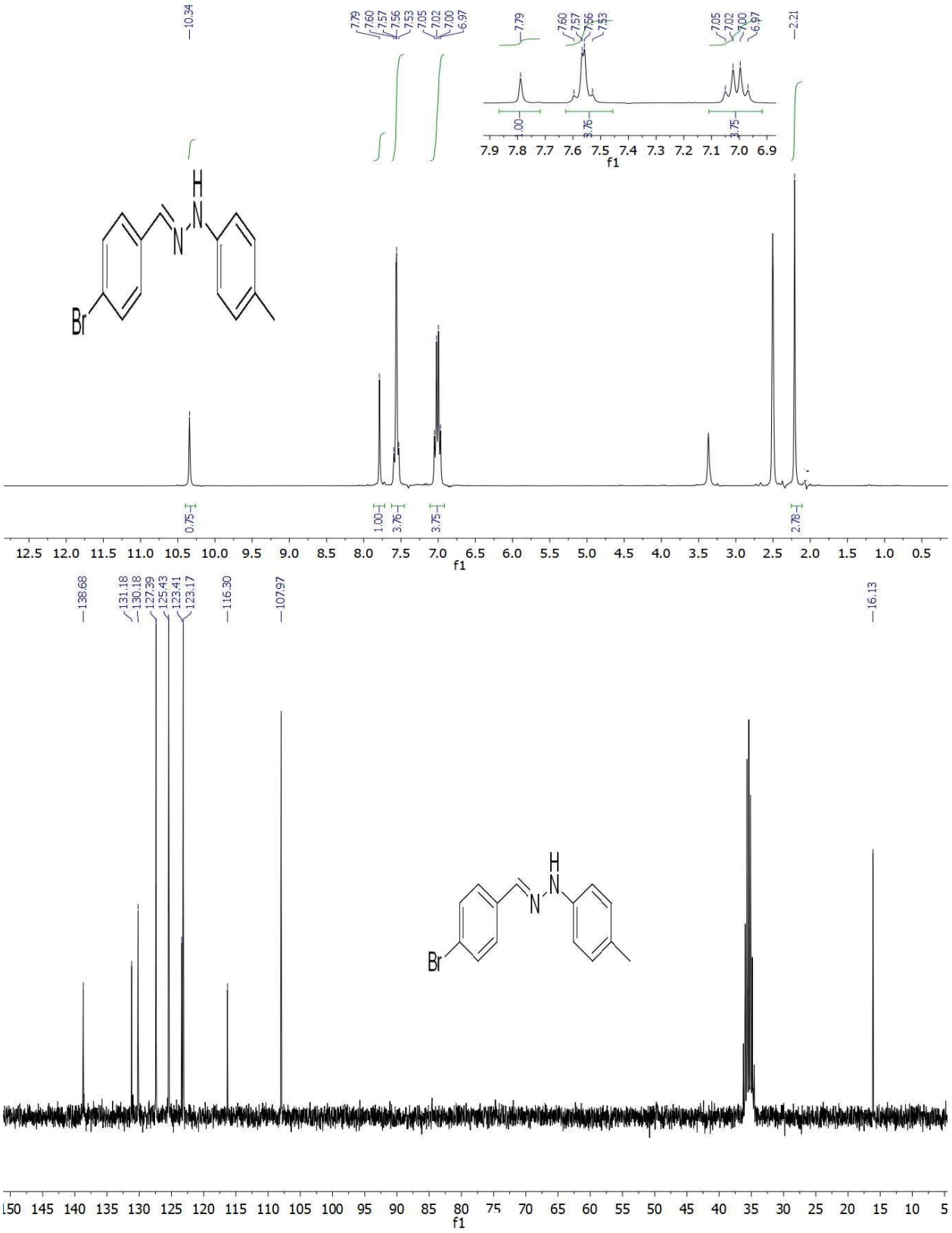
^{1}H and ^{13}C spectra for **1a**



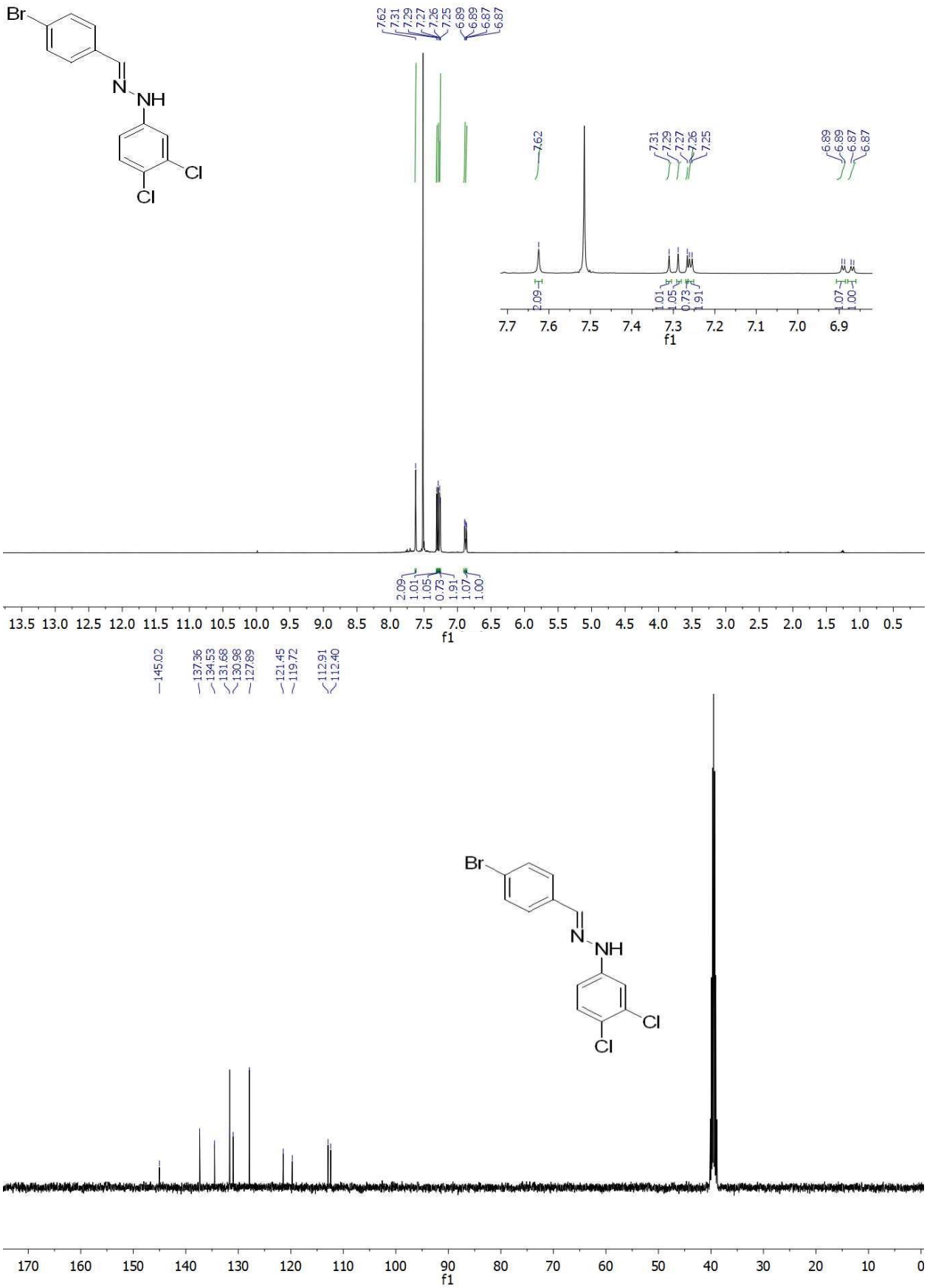
^{1}H and ^{13}C spectra for **1b**



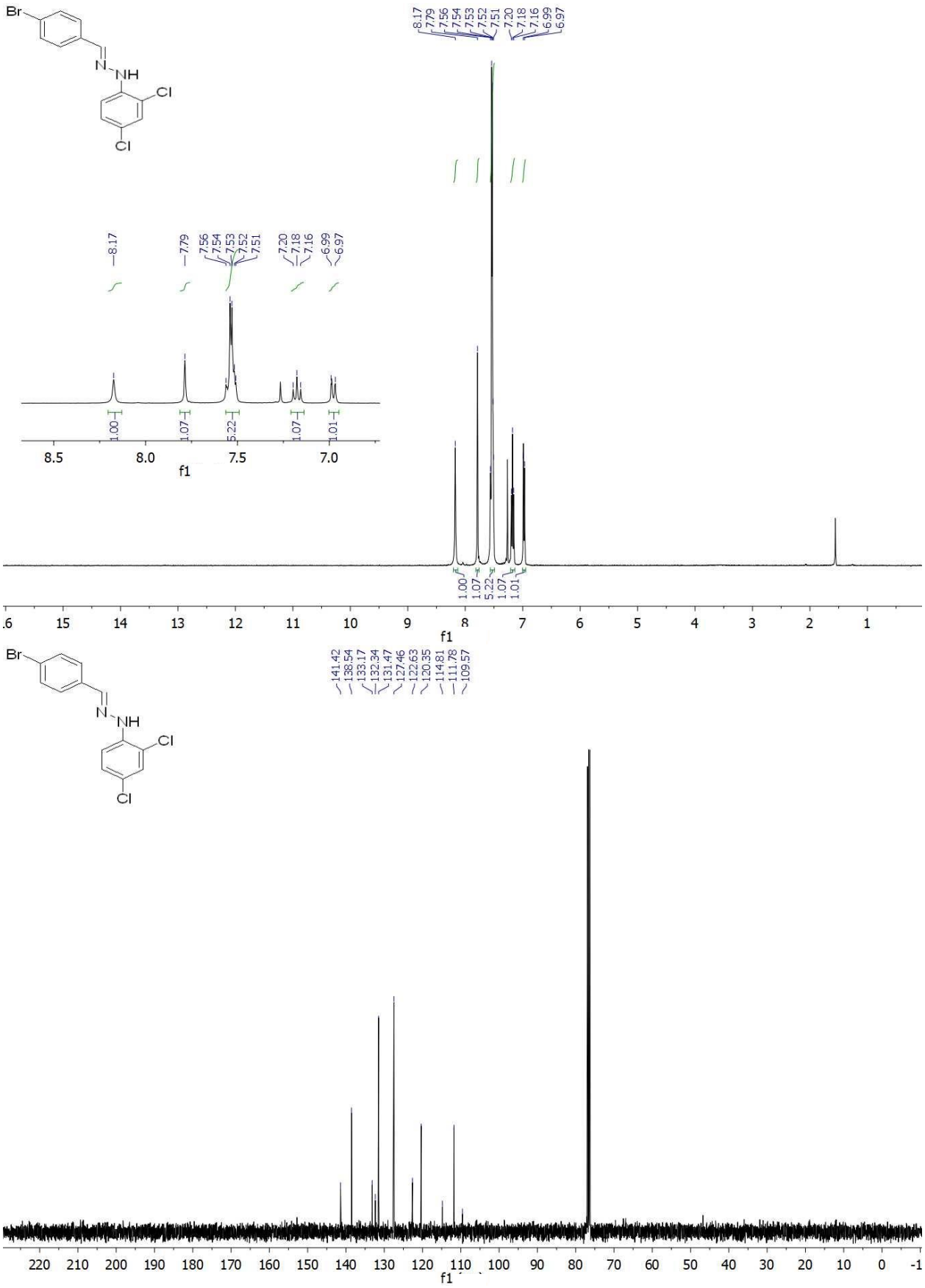
^{1}H and ^{13}C spectra for **1c**



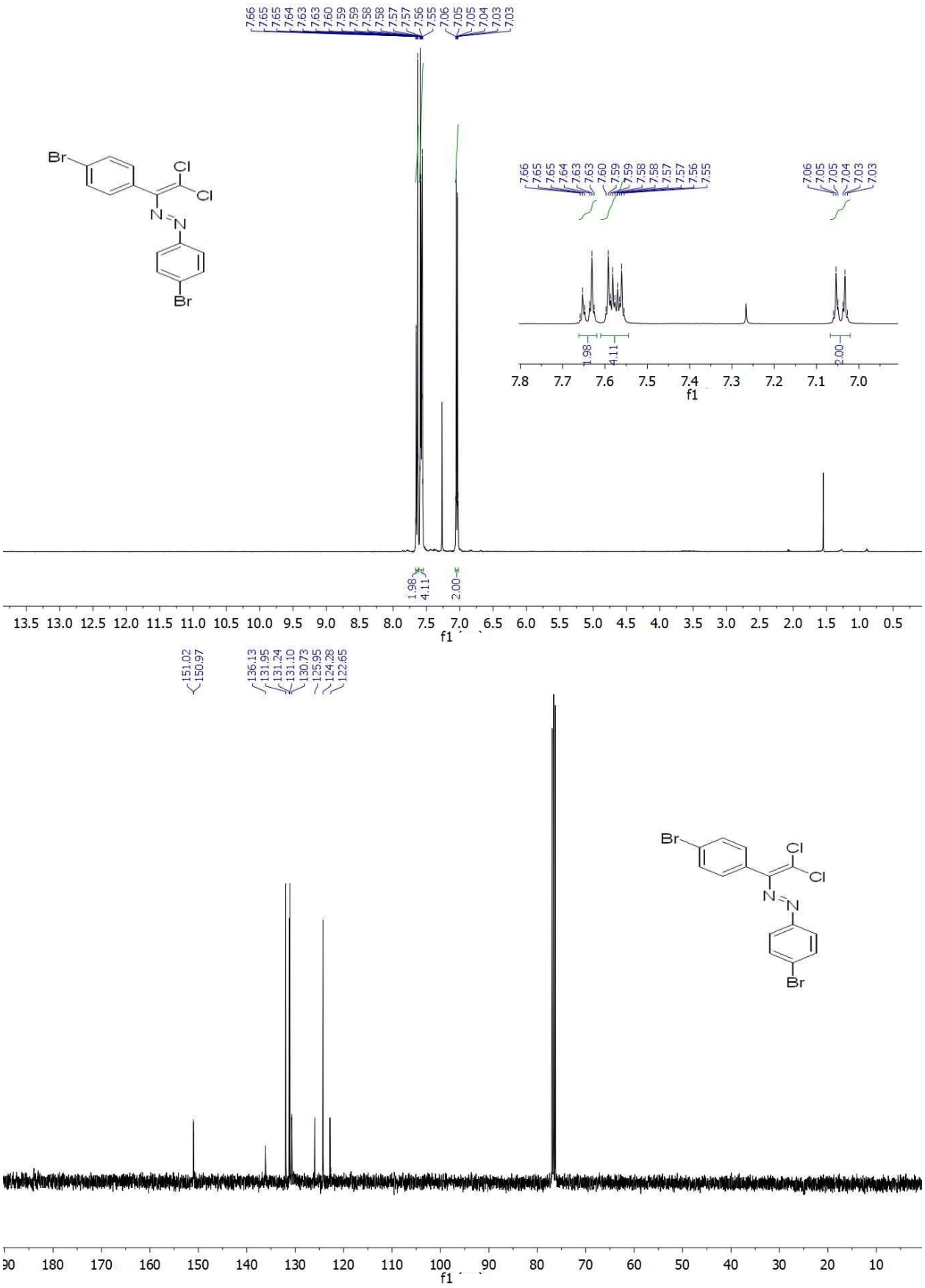
^{1}H and ^{13}C spectra for **1d**



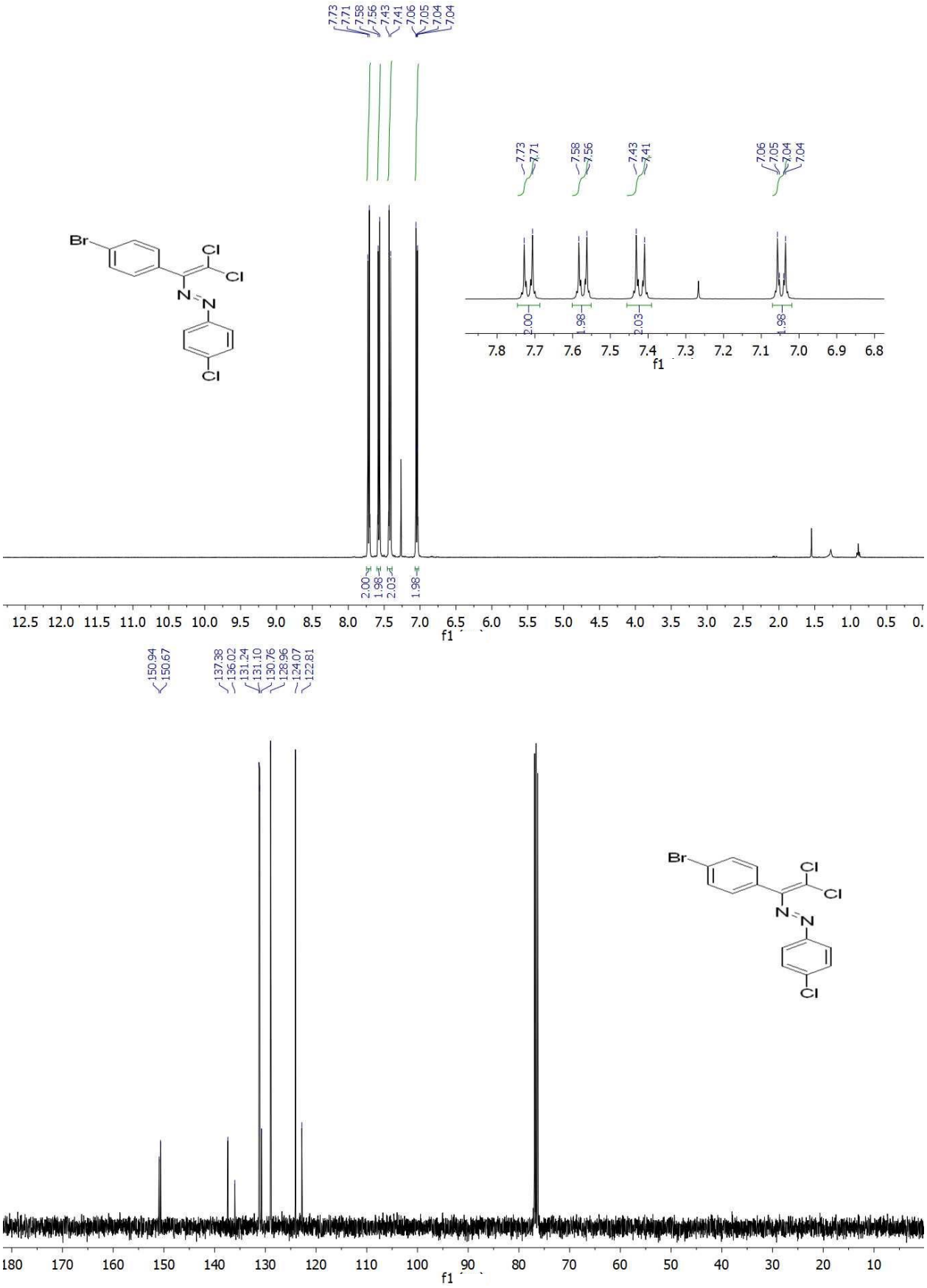
^{1}H and ^{13}C spectra for **1f**



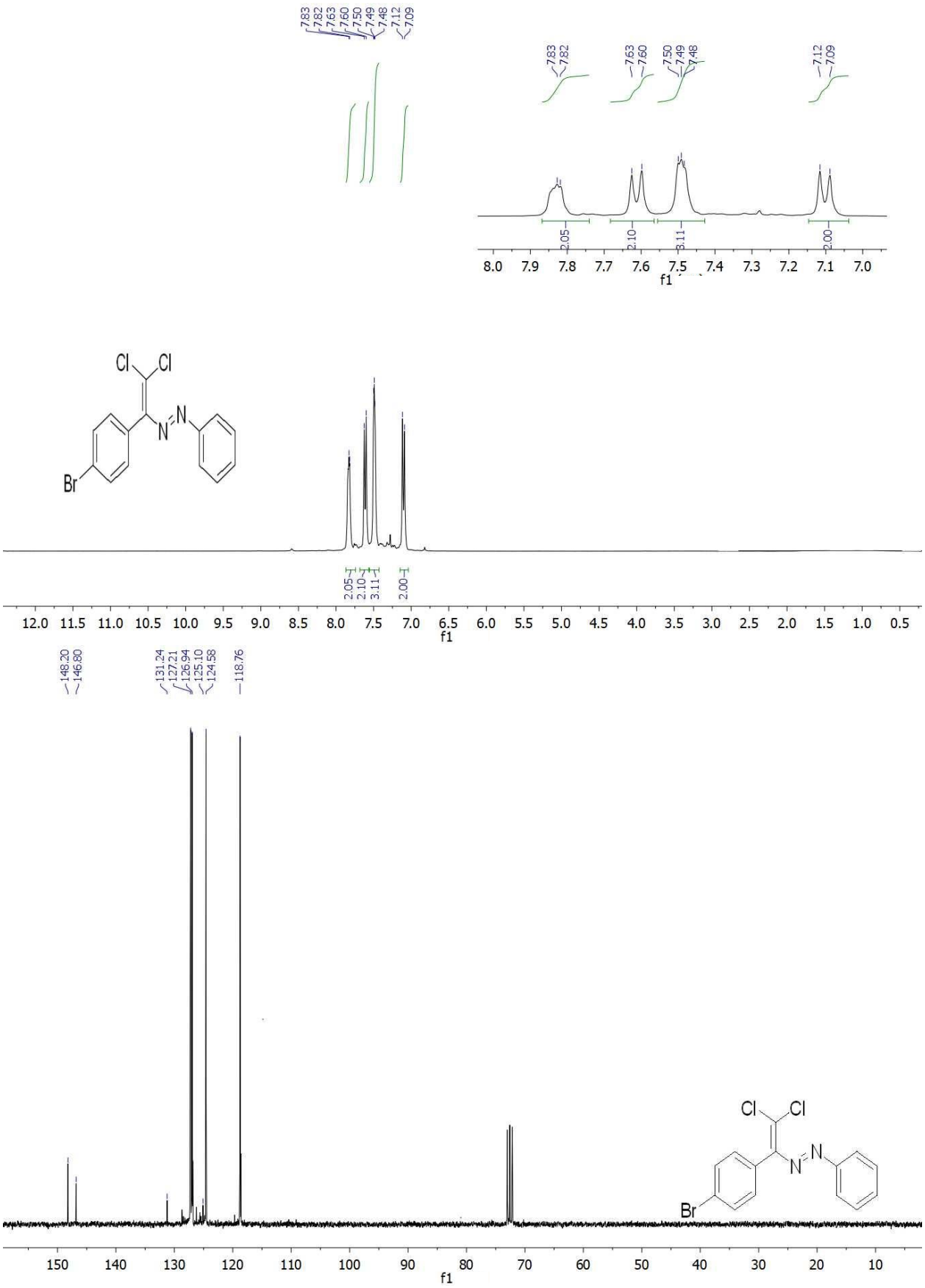
^{1}H and ^{13}C spectra for **1g**



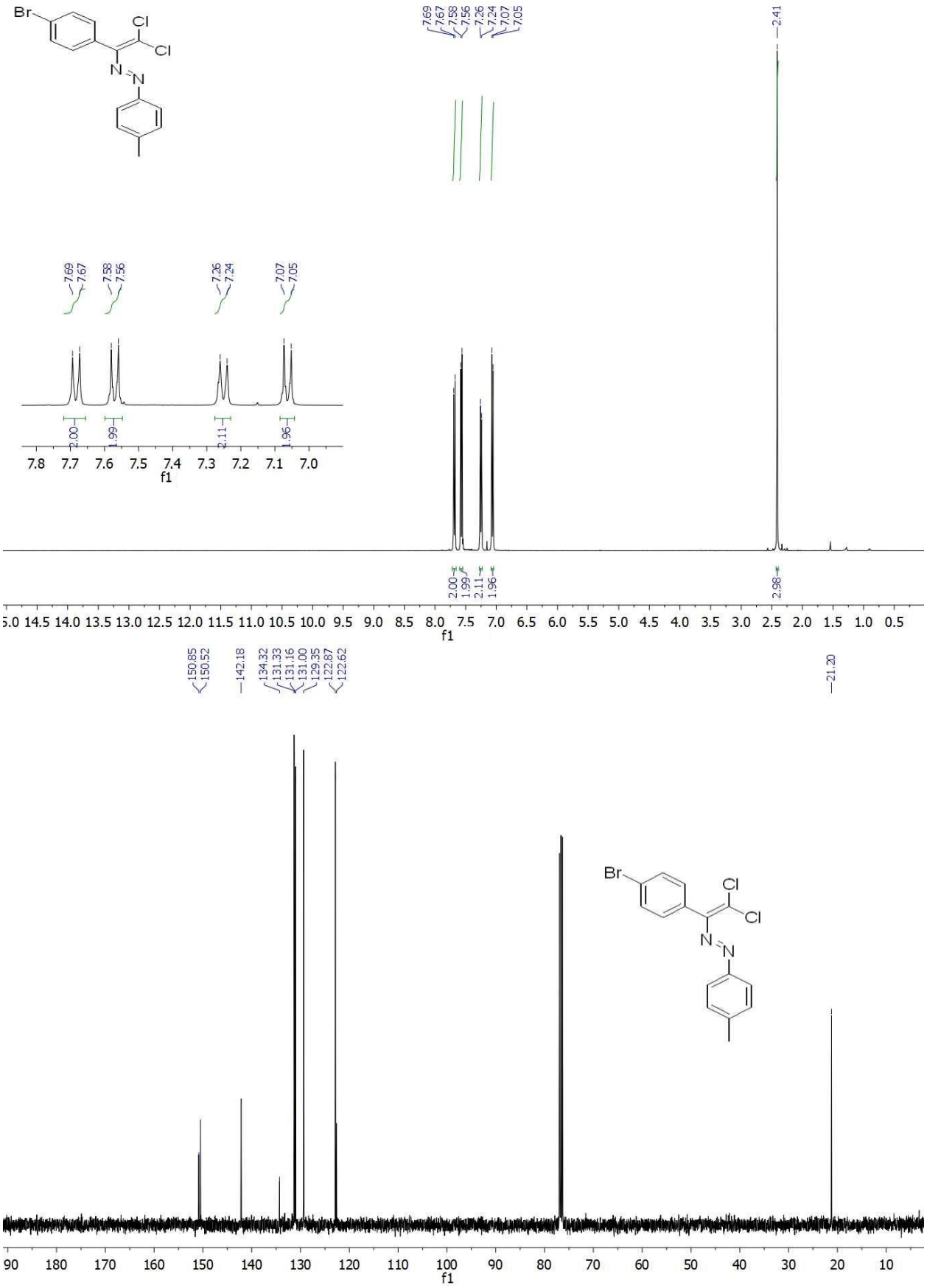
^{1}H and ^{13}C spectra for **2a**



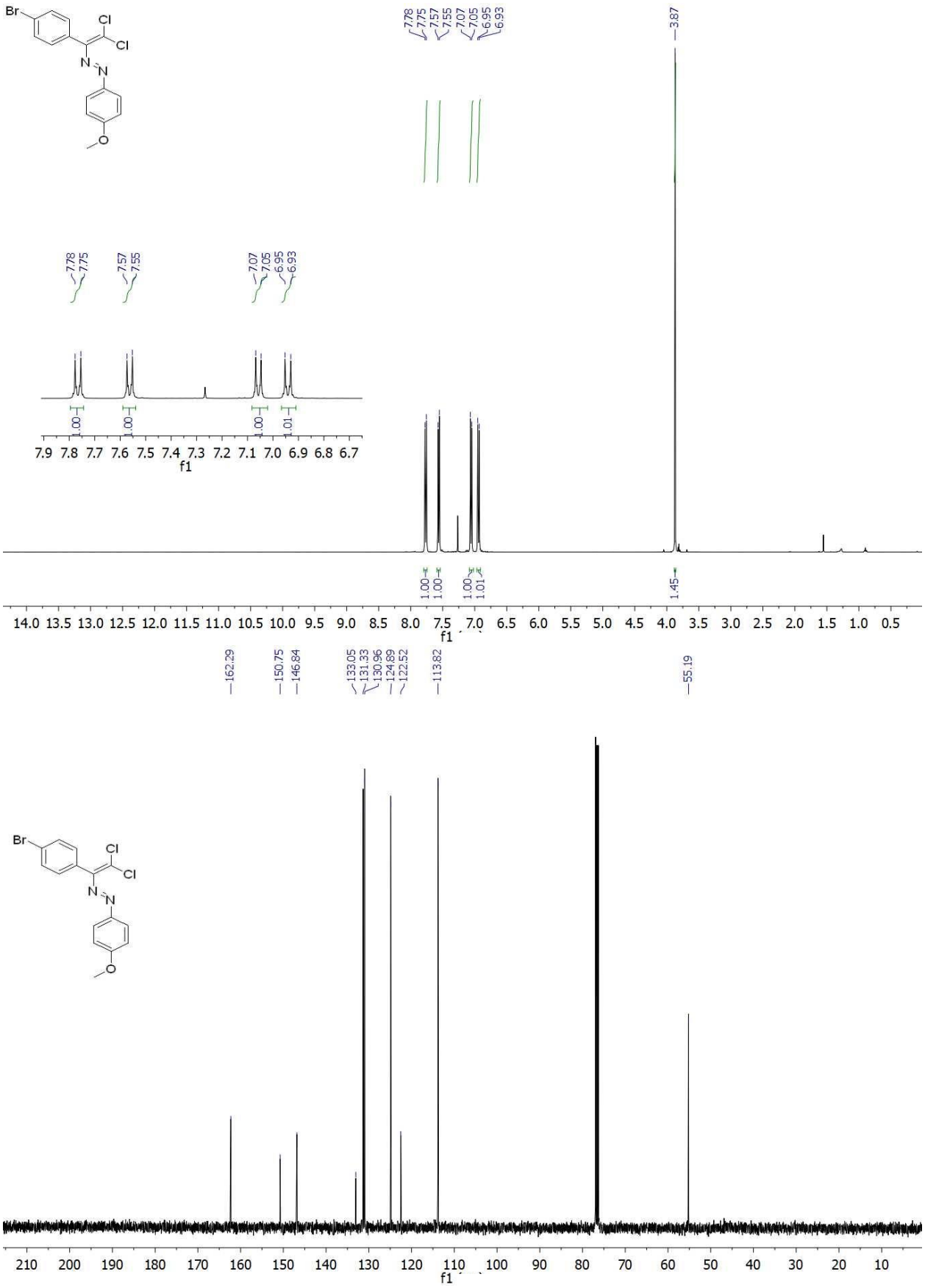
^{1}H and ^{13}C spectra for **2b**



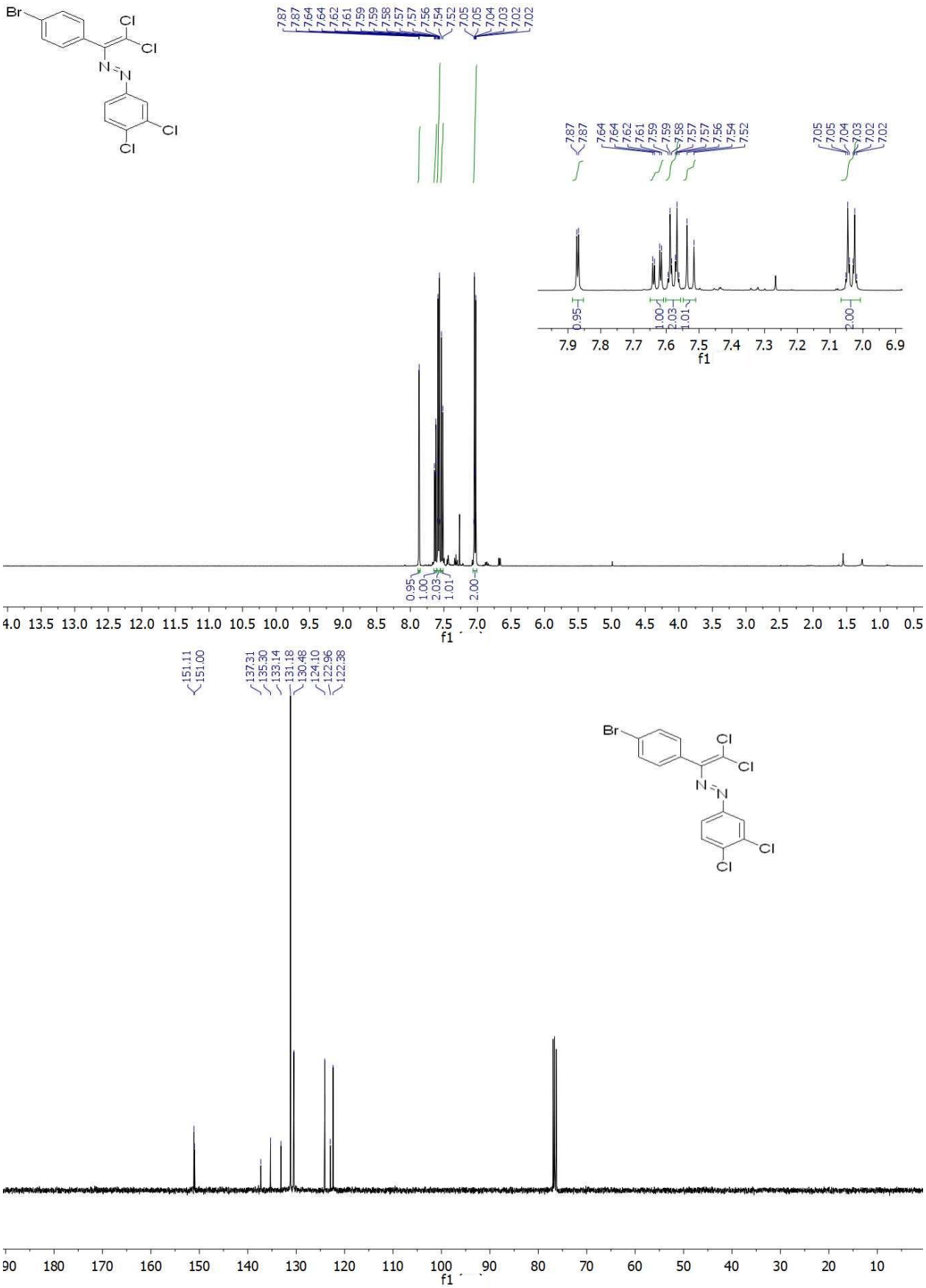
^{1}H and ^{13}C spectra for **2c**



^{1}H and ^{13}C spectra for **2d**



^{1}H and ^{13}C spectra for **2e**



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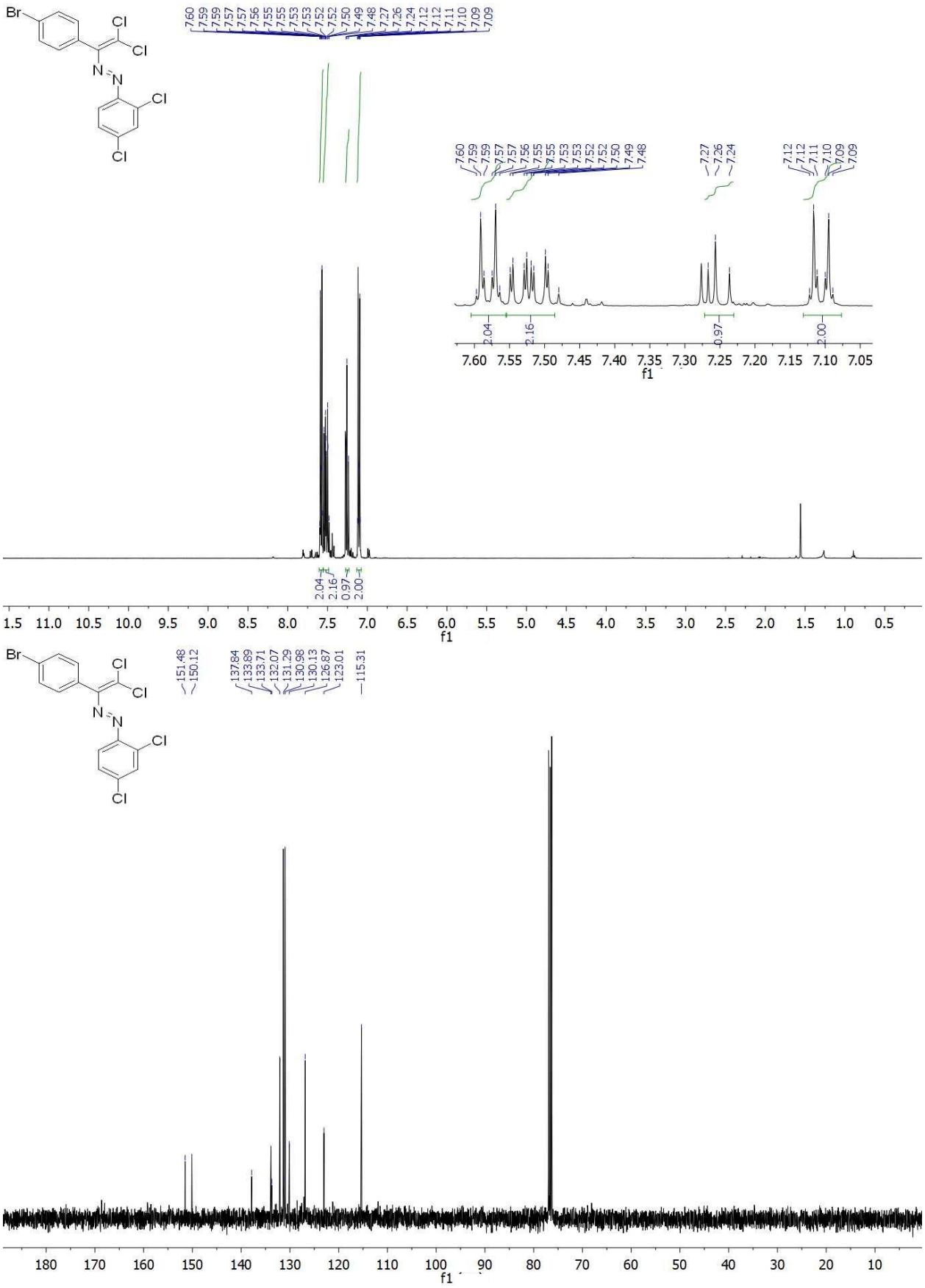

^{1}H and ^{13}C spectra for **2g**