Electronic Supplementary Material (ESI) for Chemical Communications.

Ligand –Promoted Intramolecular Dehydrogenative Cross-Coupling with Cu Catalyst: A Direct Access to Polycyclic Heteroarenes

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Supporting Information

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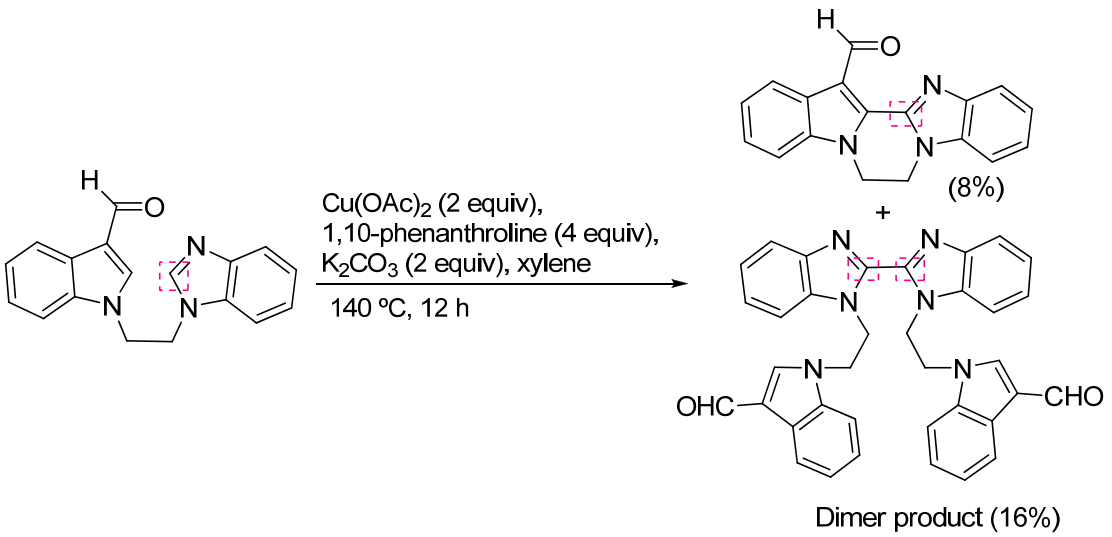
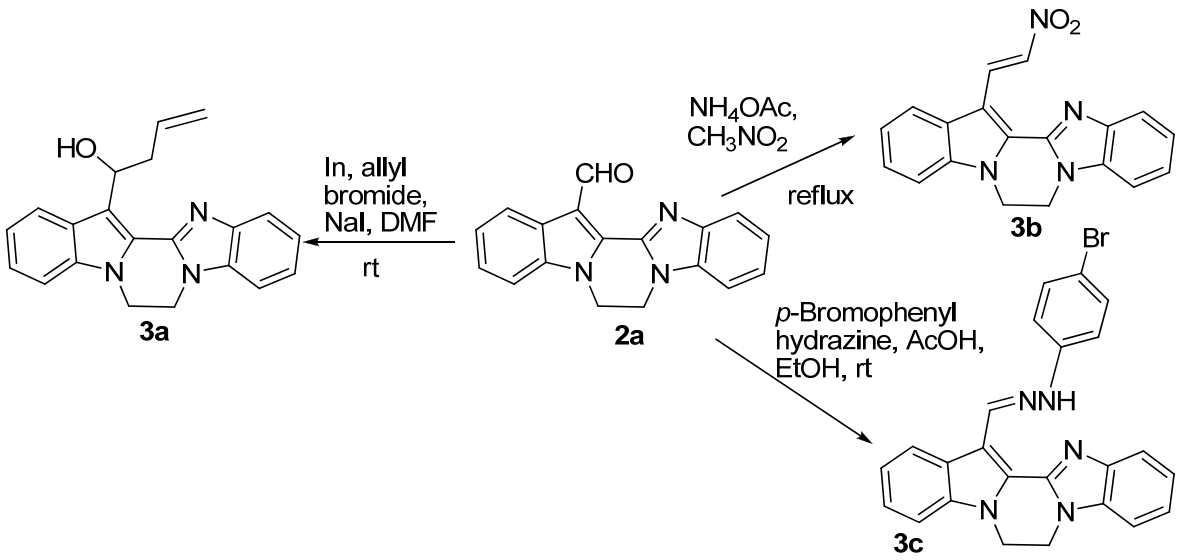
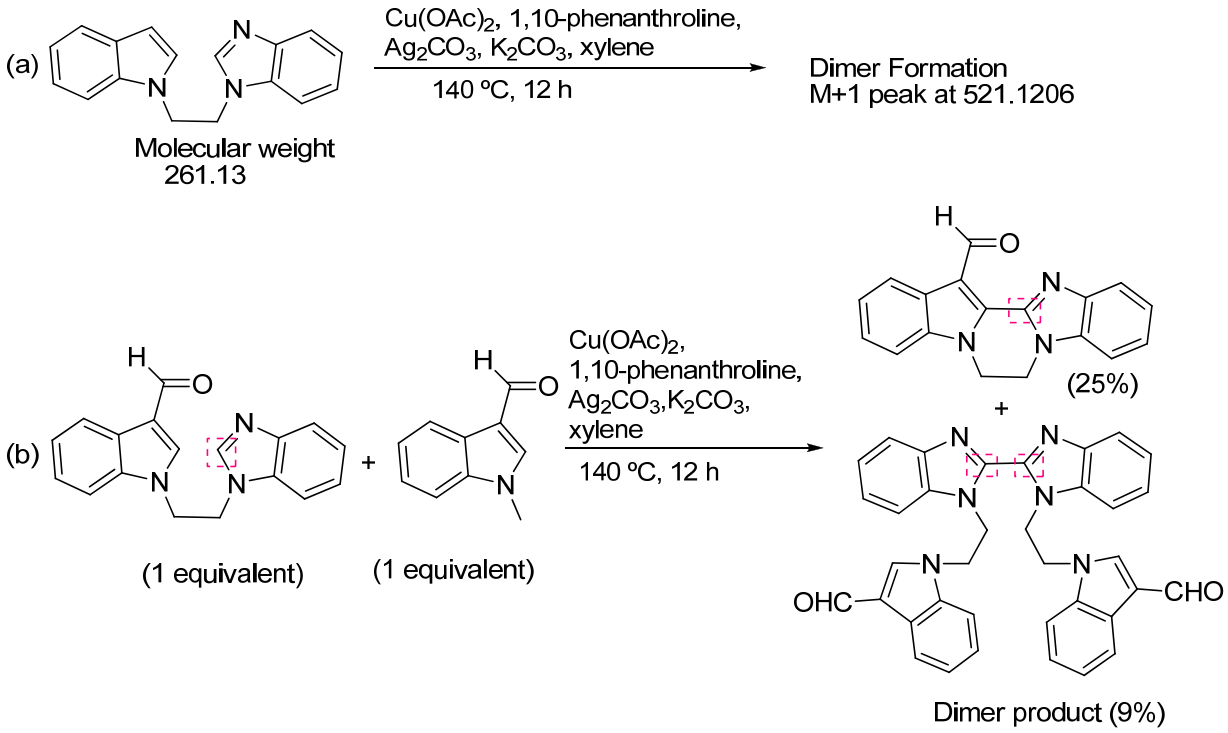


Scheme S1: Cross dehydrogenative coupling of **1a** in presence of higher equivalent of $Cu(OAc)_2$



Scheme S2: Transformation of cyclized product **2a** to different derivatives



No 1-methyl-1*H*-indole-3-carbaldehyde incorporated product.

Scheme S3: Coupling reactions for mechanistic studies

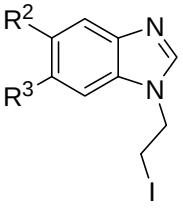
Experimental Procedure:

General method

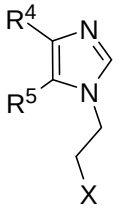
Nuclear magnetic resonance (NMR) spectra were recorded in deuterated solvents with residual protonated solvent signal as internal reference on a BrückerAva-300 or JNM-ECA 400. Chemical shifts are reported in parts per million using the solvent resonance internal standard (chloroform, 7.26 and 77.0 ppm or DMSO, 2.50 and 40.0 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs =broad singlet), coupling constant, and integration. FT-IR, infrared spectra were recorded on a Nicolet protégé 460 FTIR spectrometer and are reported in frequency of absorption. Electrospray and electron impact high resolution mass spectrometry was performed by Brücker mass spectrometer. The data is recorded as the ionization method followed by the calculated and measured masses. Solvents for starting material preparation and coupling reactions were dried before use.

Preparation of starting materials:

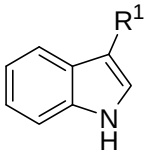
Materials:



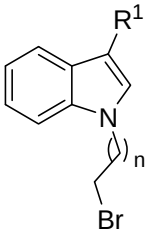
$R^2 = R^3 = H$ **(Ia)**
$R^2 = CH_3$, $R^3 = H$ **(Ib)**
$R^2 = H$, $R^3 = CH_3$ **(Ib')**
$R^2 = R^3 = Cl$ **(Ic)**



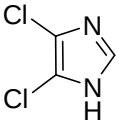
$R^4 = R^5 = Ph$, X= I **(Id)**
$R^4 = R^5 = p$-tolyl, X= Cl **(Ie)**



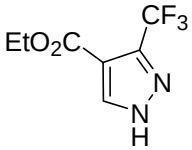
R^1 = CHO **(IIa)**, NO_2 **(IIb)**



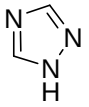
n= 1, R^1 = CHO **(IIIa)**, NO_2 **(IIIb)**
n= 2, R^1 = CHO **(IIIc)**



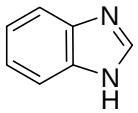
(IVa)



(IVb)



(IVc)



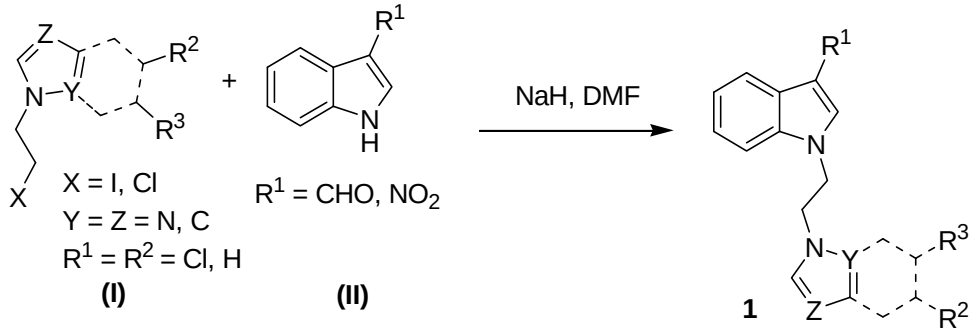
(IVd)

The following starting materials were either purchased and used as it is or they were synthesized using known literature procedure. Compounds (**IVa**), (**IVb**) and (**IVc**) are purchased from Sigma-Aldrich and Alfa aesar, used without further purification. Compounds (**IIa**) and (**IIb**) were prepared from indole following literature procedure.[1] Compounds (**IIIa-c**) were prepared from corresponding 3-carboxy or 3-nitro indole following literature procedure.[2] Compounds (**Ia-e**) were

prepared from the corresponding substituted benzimidazole and imidazole derivatives following literarure procedure.[3]

General procedure A for N-alkylation of 3-substituted indoles:

To a suspension of NaH (1.1 equivalent) in dry DMF at 0 ºC was dropwise added a solution of indole-3-carboxyaldehyde or 3-nitroindole (**IIa** or **IIb**) (1.0 equivalent) in dry DMF and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-haloethyl)-1H-azole derivative (**Ia-e**) (1.0 equivalent) in DMF was added to it and the resulting solution was heated at 80 °C for 16 hr. The completion of reaction was monitored by TLC. Once the reaction completed, saturated brine solution was added to the reaction mixture and it was extracted with EtOAc (three times).



Scheme S4: Coupling of 1-(2-haloethyl)-1H-azole derivatives with 3-substituted indoles

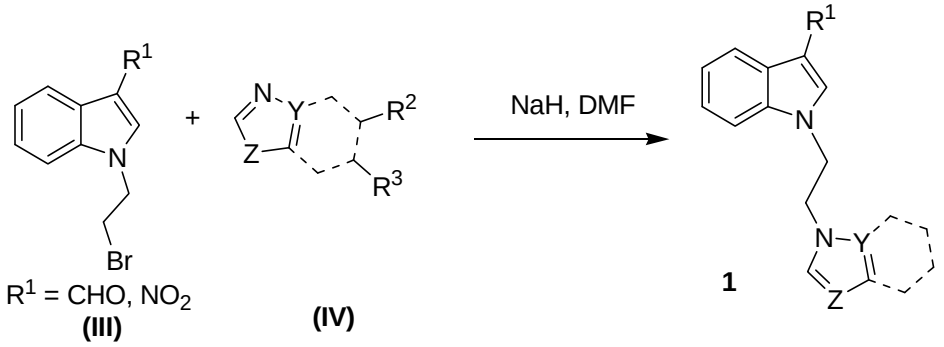
The combined organic layers were washed with brine and dried over Na_2SO_4. Further, it was filtered and concentrated under reduced pressure to provide an organic residue. The residue was purified by silica gel column chromatography to provide the desired product.

General procedure B for N-alkylation of substituted imidazoles:

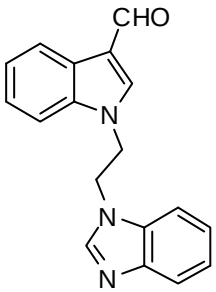
To a suspension of NaH (1.1 equivalent) in dry DMF at 0 ºC was dropwise added a solution of azole derivatives (**IVa-d**) (1.0 equivalent) in dry DMF and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-bromoethyl)-1H-indole-3-carbaldehyde or 1-(2-bromoethyl)-3-nitro-1H-indole (**IIIa-c**) (1.0 equivalent) in DMF was added to it and the resulting solution was heated at 80 °C for 16 hr. The completion of reaction was monitored by TLC. Once the reaction completed, saturated brine solution was added to the reaction mixture and it was extracted with EtOAc (three times).

1. (a) P. N. Naik, A. Khan, R. S. Kusurkar, *Tetrahedron* 2013, **69**, 10733. (b) N. Nowrouzi, A. M. Mehranpour, E. Bashiri, Z. Shayan, *Tetrahedron Lett.* 2012, **53**, 4841.
2. W. Breitenstein, T. Ehara, C. Ehrhardt, P. Grosche, Y. Hitomi, Y. Iwaki, T. Kanazawa, K. Konishi, J. K. Maibaum, K. Masuya, A. Nihonyanagi, N. Ostermann, M. Suzuki, A. Toyao, F. Yokokawa, *PCT Int. Appl.* 2006, 633pp.
3. R. C. F. Jones, L. J. Crumpling, J. N. Iley, *ARKIVOC* 2011, 82.

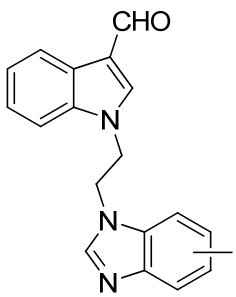
The combined organic layers were washed with brine and dried over Na_2SO_4. The resulting solution was filtered and concentrated under reduced pressure to provide an organic residue. The residue was purified by silica gel column chromatography to provide the desired product.



Scheme S5: Coupling of 1-(2-bromoethyl)-1H-indole derivatives with substituted azoles

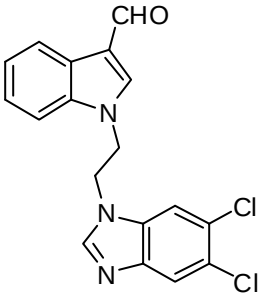


Compound 1a: Following the general procedure A, to the NaH (158 mg, 60 wt% in mineral oil, 3.96 mmol) suspension in dry DMF (4 mL) at 0 ºC was dropwise added a indole-3-carboxyaldehyde (**IIa**) (522 mg, 3.6 mmol) in dry DMF (6 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-iodoethyl)-1H-benzimidazole (**Ia**) (1.0 g, 3.6 mmol) in DMF (6 mL) was added to it and the resulting solution was heated at 80 °C for 16 hr. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 94:6) to give the product **1a** as brown solid (416 mg, yield = 40%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.76 (1H, s), 8.34-8.31 (1H, m), 7.81 (1H, d, *J*= 7.5 Hz), 7.41-7.07 (8H, m), 4.61 (4H, bs); **^{13}C NMR** (75 MHz, $CDCl_3$): 184.54, 138.05, 136.38, 125.50, 124.58, 123.59, 123.42, 122.77, 122.70, 120.84, 118.93, 109.11, 108.71, 46.76, 44.32; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{18}H_{16}N_3O$: 290.1249; found 290.1288; **IR** (thin film): ν_{max}1613, 1533, 1389, 744 cm^{-1}

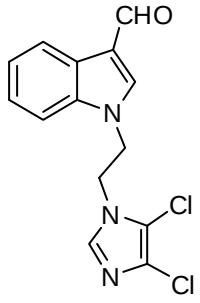


Compound 1b: 1b' (1:1): to the NaH (88 mg, 60 wt% in mineral oil, 2.2 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added a indole-3-carboxyaldehyde (**IIa**) (290 mg, 2.0 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1:1 inseparable mixture of 1-(2-Iodo-ethyl)-5-methyl-1H-benzimidazole and 1-(2-Iodo-ethyl)-5-methyl-1H-benzimidazole (**Ib** and **Ib'**) (572 g, 2.0 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 hr. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl

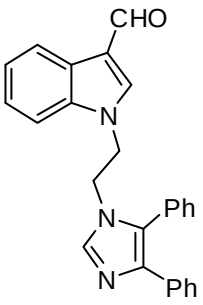
acetate: MeOH 98: 2) to give the product **1b: 1b' (1:1)** as white solid (236 mg, yield = 38%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.64 (1H, s), 9.61 (1H, s), 8.21 (2H, d, *J* = 4.2 Hz), 7.51-7.19 (10H, m), 6.99-6.92 (6H, m), 4.48 (8H, s), 2.38 (3H, s), 2.28 (3H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 184.43, 184.36, 138.13, 138.07, 136.25, 133.60, 125.36, 125.30, 125.01, 124.38, 124.20, 123.22, 122.48, 118.69, 109.01, 46.75, 46.51, 21.52, 21.34; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{19}H_{18}N_3O$: 340.1444; found 340.1460; **IR** (thin film): ν_{max} 1656, 1533, 1388, 748 cm^{-1}



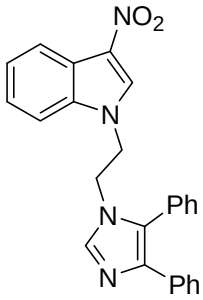
Compound 1c: Following the general procedure A, to the NaH (46 mg, 60 wt% in mineral oil, 1.15 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added a indole-3-carboxyaldehyde (**IIa**) (153 mg, 1.05 mmol) in dry DMF (3 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 5,6-Dichloro-1-(2-iodo-ethyl)-1H-benzoimidazole (**Ic**) (360 mg, 1.05 mmol) in DMF (3 mL) was added to it and the resulting solution was heated at 80 °C for 16 hr. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 94:6) to give the product **1c** as brown solid (132 mg, yield = 35%). **^{1}H NMR** (300 MHz, DMSO-d_6): 9.80 (1H, s), 8.07-8.02 (3H, m), 7.85 (1H, s), 7.67 (1H, s), 7.45-7.42 (1H, m), 7.22-7.19 (2H, m), 4.75 (4H, s); **^{13}C NMR** (75 MHz, DMSO-d_6): 185.86, 136.51, 135.51, 133.53, 126.92, 125.17, 125.05, 124.07, 122.13, 115.16, 113.45, 111.39, 42.22; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{18}H_{14}Cl_2N_3O$: 358.0508; found 358.0507; **IR** (thin film): ν_{max} 2922, 1632, 739 cm^{-1}



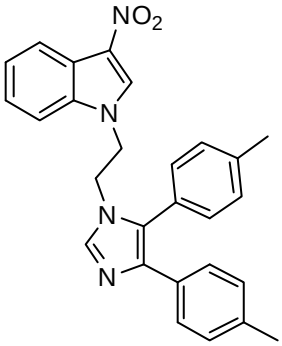
Compound 1d: Following the general procedure B, to the NaH (88 mg, 60 wt% in mineral oil, 2.2 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added a 4,5-Dichloroimidazole (**IVa**) (274 mg, 2.0 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-Bromoethyl)-1H-indole-3-carbaldehyde (**IIIa**) (500 mg, 2.0 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 hr. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (DCM: MeOH 96:4) to give the product **1d** as brown solid (272 mg, yield = 45%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.89 (1H, s), 8.28-8.25 (1H, m), 7.34-7.26 (3H, m), 7.21-7.18 (2H, m), 6.83 (1H, s), 4.46 (2H, t, *J* = 5.4 Hz), 4.31 (2H, t, *J* = 5.7 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): 184.75, 137.94, 136.50, 134.60, 126.89, 125.36, 124.73, 123.52, 122.54, 119.05, 112.88, 109.04, 46.68, 45.45; **HRMS** (ES+) cald. for $(M+Na)^+$: $C_{14}H_{11}Cl_2N_3NaO$: 330.0171; found 330.0184; **IR** (thin film): ν_{max} 2362, 1656, 1576, 1395, 750 cm^{-1}



Compound 1e: Following the general procedure A, to the NaH (47 mg, 60 wt% in mineral oil, 1.18 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added a indole-3-carboxyaldehyde (**IIa**) (156 mg, 1.07 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-iodoethyl)-4,5-diphenyl-*1H*-imidazole (**Id**) (400 mg, 1.07 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 hr. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate) to give the product **1e** as brown solid (168 mg, yield = 40%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.82 (1H, s), 8.20 (1H, d, *J* = 7.5 Hz), 7.41-7.30 (6H, m), 7.24-7.16 (2H, m), 7.13-7.05 (6H, m), 6.71 (1H, d, *J* = 8.1 Hz), 4.22-4.15 (4H, m);**^{13}C NMR** (100 MHz, $CDCl_3$): 184.71, 138.98, 138.06, 136.82, 136.68, 134.04, 130.71, 129.84, 129.58, 129.22, 128.76, 128.37, 128.27, 128.00, 126.87, 126.74, 125.50, 124.53, 123.38, 122.57, 119.07, 109.17, 47.74, 44.30; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{26}H_{22}N_3O$: 392.1757; found 392.1758; **IR** (thin film): ν_{max} 1653, 1533, 1396, 753 cm^{-1}

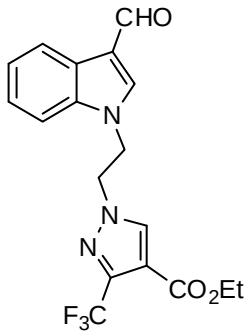


Compound 1f: Following the general procedure A, to the NaH (53 mg, 60 wt% in mineral oil, 1.32 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added a 3-Nitroindole (**IIb**) (200 mg, 1.2 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-iodoethyl)-4,5-diphenyl-*1H*-imidazole (**Id**) (449 mg, 1.2 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 hr. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 96:4) to give the product **1f** as white solid (282 mg, yield = 56%). ^{1}H NMR (300 MHz, DMSO-d_6): 8.37 (1H, s), 8.05 (1H, d, *J* = 7.8 Hz), 7.86 (1H, bs), 7.37-7.09 (11H, m), 6.92 (2H, d, *J* = 7.8 Hz), 4.51 (2H, bs), 4.32 (2H, bs);^{13}C NMR (75 MHz, DMSO-d_6): 137.90, 135.40, 133.03, 130.77, 129.70, 129.26, 129.08, 128.68, 128.51, 126.71, 126.48, 124.66, 124.58, 120.67, 120.02, 111.49, 47.86, 44.43; HRMS (ES+) cald. for $(M+H)^+$: $C_{25}H_{21}N_4O_2$: 409.1659; found 409.1666; IR (thin film): ν_{max} 1525, 1443, 1372, 757 cm^{-1}

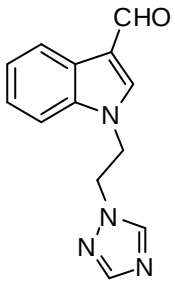


Compound 1g: Following the general procedure A, to the NaH (68 mg, 60 wt% in mineral oil, 1.69 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added a 3-Nitroindole (**IIb**) (250 mg, 1.54 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-chloroethyl)-4,5-ditolyl-*1H*-imidazole (**Ie**) (480 mg, 1.54 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 hr. The reaction mixture was quenched according to general procedure and the

resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 94:6) to give the product **1g** as brown solid (202 mg, yield = 30%). **^{1}H NMR** (300 MHz, DMSO-d_6): 8.26 (1H, d, *J* = 8.1 Hz), 7.69 (1H, s), 7.45-7.22 (7H, m), 7.09-7.03 (4H, m), 6.76 (1H, d, *J* = 8.4 Hz), 4.33 (2H, t, *J* = 6.0 Hz), 4.23 (2H, t, *J* = 5.7 Hz); **^{13}C NMR** (75 MHz, DMSO-d_6): 137.76, 137.32, 135.53, 135.35, 133.01, 132.41, 130.54, 130.10, 129.79, 129.03, 128.34, 128.08, 127.01, 126.38, 124.53, 124.49, 120.73, 119.99, 111.51, 47.97, 44.17, 21.29, 21.09; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{27}H_{25}N_4O_2$: 437.1972; found 437.1968; **IR** (thin film): ν_{max} 2362, 1524, 1447, 1307, 756 cm^{-1}

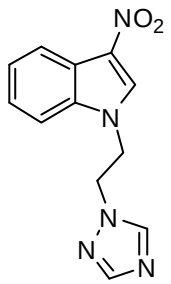


Compound 1h: Following the general procedure B, to the NaH (139 mg, 60 wt% in mineral oil, 3.48 mmol) suspension in dry DMF (4 mL) at 0 ºC was dropwise added 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate (**IVb**) (660 mg, 3.17 mmol) in dry DMF (6 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-Bromoethyl)-1H-indole-3-carbaldehyde (**IIIa**) (800 mg, 3.17 mmol) in DMF (6 mL) was added to it and the resulting solution was heated at 80 °C for 16 hr. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 98:2) to give the product **1h** as brown solid (782 mg, yield = 65%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.94 (1H, s),8.35-8.32 (1H, m), 7.47-7.26 (4H, m),7.25 (1H, s), 4.77 (2H, t, *J* = 5.4 Hz), 4.58 (2H, t, *J* = 5.4 Hz), 4.21 (2H, q, *J* = 7.2 Hz), 1.26 (3H, t, *J* = 7.2 Hz); **^{13}C NMR** (75 MHz, DMSO-d_6): 185.16, 160.49, 141.16, 138.45, 137.55, 125.05, 124.08, 123.11, 121.56, 118.28, 112.58, 111.10, 60.97, 52.42, 46.41, 14.48; **HRMS** (ES+) cald. for $(M+Na)^+$: $C_{18}H_{16}F_3N_3NaO_3$: 402.1036; found 402.1045; **IR** (thin film): ν_{max}1724, 1645, 1301, 1143, 1052 cm^{-1}

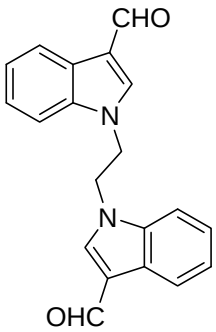


Compound 1i: Following the general procedure B, to the NaH (35 mg, 60 wt% in mineral oil, 0.88 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added 1,2,4-Triazole (**IVc**) (55 mg, 0.8 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-Bromoethyl)-1H-indole-3-carbaldehyde (**IIIa**) (200 mg, 0.8 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 hr. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (DCM: MeOH 95:5) to give the product **1i** as brown solid (82 mg, yield = 43%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.72 (1H, s), 8.17 (1H, d, *J* = 5.7 Hz), 8.08 (1H, s), 7.99-7.87 (1H, m), 7.52 (1H, s), 7.21-7.17 (3H, m), 4.60-4.49 (4H, m); **^{13}C NMR** (75 MHz, $CDCl_3$): 184.57, 152.85, 143.97, 138.17, 136.46, 125.24, 124.50, 123.33, 122.42, 118.75, 109.24, 48.77, 46.26; **HRMS** (ES+) cald. for

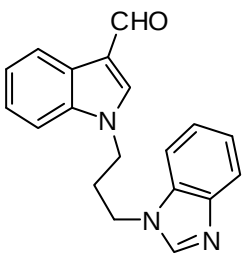
$(M+Na)^+$: $C_{13}H_{12}N_4NaO$: 263.0903; found 263.0903; **IR** (thin film): ν_{max} 2923, 1653, 1529 cm^{-1}



Compound 1j: Following the general procedure B, to the NaH (72 mg, 60 wt% in mineral oil, 1.8 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added 1,2,4-Triazole (**IVc**) (113 mg, 1.64 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-bromoethyl)-3-nitro-*1H*-indole (**IIIb**) (440 mg, 1.64 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 hr. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 98:2) to give the product **1j** as brown solid (130 mg, yield = 31%). **^{1}H NMR** (300 MHz, $CDCl_3$): 8.22-8.20 (1H, m), 7.96 (1H, bs), 7.74 (1H, s), 7.61 (1H, bs), 7.37-7.28 (2H, m),7.20 (1H, d, *J* = 5.7 Hz), 4.69-4.63 (2H, m), 4.55 (1H, t, *J* = 5.4 Hz); **^{13}C NMR** (75 MHz, DMSO-d_6): 152.20, 145.09, 135.56, 133.27, 128.26, 124.69, 124.52, 120.39, 120.00, 111.80, 48.71, 46.77; **HRMS** (ES+) cald. For $(M+H)^+$: $C_{12}H_{12}N_5O_2$: 258.0983; found 258.0985; **IR** (thin film): ν_{max} 2362, 1522, 1302, 739 cm^{-1}



Compound1k[4]**:** Following the general procedure A or B, , to the NaH (76 mg, 60 wt% in mineral oil, 1.9 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added indole-3-carboxyaldehyde (**IIa**) (250 mg, 1.72 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-Bromoethyl)-1H-indole-3-carbaldehyde (**IIIa**) (434 mg, 1.72 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 hr. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 98:2) to give the product **1j** as brown solid (130 mg, yield = 31%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.72 (1H, s), 8.27 (2H, bs), 7.28-7.14 (6H, m), 7.00 (2H, s), 4.55 (4H, s); **^{13}C NMR** (75 MHz, DMSO-d_6): 185.15, 141.20, 137.52, 125.11, 124.17, 123.15, 121.59, 118.20, 111.14, 46.52.



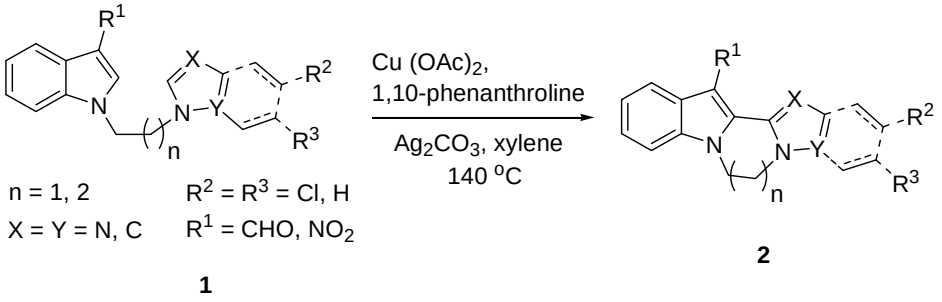
Compound1l[5]**:** Following the general procedure B, to the NaH (70 mg, 60 wt% in mineral oil, 1.76 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added benzimidazole (**IVd**) (189 mg, 1.6 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(3-bromopropyl)-1*H*-indole-3-carbaldehyde (**IIIc**) (424 mg, 1.6 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 hr. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 98:2) to give the product **1l** as white solid (485 mg, yield

= 80%).after purification with silica gel column chromatography (Ethyl acetate: MeOH 92:8) the product **1l** was obtained as brown solid. Yield: 80%. **^{1}H NMR** (300 MHz, $CDCl_3$): 9.95 (1H, s), 8.29-8.26 (1H, m), 8.11 (1H, s), 7.82 (1H, t, *J* = 2.1 Hz), 7.61 (1H, s), 7.33-7.18 (6H, m), 4.25-4.18 (4H, m), 2.59-2.50 (2H, m).

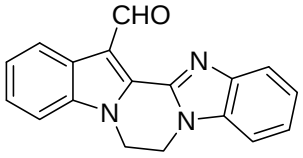
4. A. Agarwal, S. Porwal, P. M. S. Chauhan, *Lett. Org. Chem.* 2006, **3**, 712.
5. D. G. Di Pintori, M. F. Greaney, *J. Am. Chem. Soc.* 2011, **133**, 1209.

General procedure C for dehydrogenative cross coupling of N-alkylated 3-indolecarboxaldehydes:

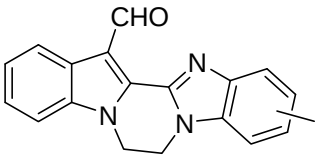
To a sealed tube with screw cap was loaded N-alkylated 3-indole carboxaldehyde or N-alkylated 3-nitroindole (1 equiv), copper acetate (1 equiv), 1,10-phenanthrolene (2 equiv), silver carbonate (2 equiv) and potassium carbonate (2 equiv) in xylene. The reaction mixture was stirred in a preheated silicon oil bath at 140 ^{o}C for 12h. The mixture was allowed to cool and transferred to a silica gel column. The product was eluted with a mixture of solvents to obtain pure product.



Scheme S6: Dehydrogenative cross coupling of heteroaromatics

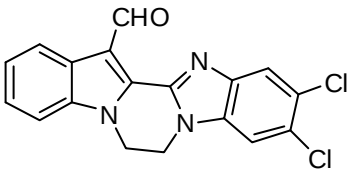


Compound 2a: Following the general procedure C, substrate **1a** (58 mg, 0.2 mmol), copper acetate (37 mg, 0.2 mmol), 1,10-phenanthrolene (73 mg, 0.4 mmol), silver carbonate (111 mg, 0.4 mmol) and potassium carbonate (56 mg, 0.4 mmol) in xylene (1mL) was heated at 140 ^{o}C for 12h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: hexane 3:2) to afford product **2a** as yellow solid (36 mg, yield: 63%). **^{1}H NMR** (300 MHz, $CDCl_3$): 11.11 (1H, s), 8.45 (1H, d, *J* = 7.5 Hz),7.85 (1H, d, *J* = 7.5 Hz), 7.48-7.30 (6H, m), 4.65 (4H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 187.65, 143.84, 141.66, 136.24, 133.43, 125.49, 125.22, 124.29, 123.88, 123.56, 123.28, 120.50, 116.35, 109.16, 109.12, 40.36, 40.21; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{18}H_{14}N_3O$: 288.1131; found 288.1118; **IR** (thin film): ν_{max} 1643, 1419, 1329, 733 cm^{-1}

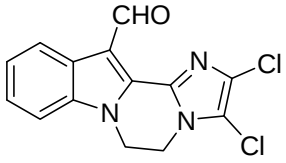


Compound 2b:2b' (1:1): Following the general procedure C, substrate **1b:1b' (1:1)** (63 mg, 0.2 mmol), copper acetate (37 mg, 0.2 mmol), 1,10-phenanthrolene (73 mg, 0.4 mmol), silver carbonate (111 mg, 0.4 mmol) and potassium carbonate (55 mg, 0.4 mmol) in xylene (1mL) was heated at 140 ^{o}C for 12h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: hexane 3:2) to afford product **2b:2b' (1:1)** as white solid (28 mg, yield: 45%). **^{1}H NMR** (300 MHz, $CDCl_3$): 10.97 (2H, s), 8.34 (2H, d, *J* = 7.8 Hz), 7.58 (1H, d, *J* = 8.1 Hz), 7.47 (1H, s), 7.30-7.19 (8H, m), 7.13-7.01 (2H, m),

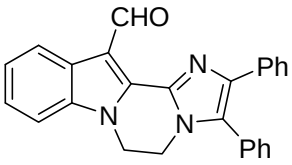
4.51 (4H, s), 2.43 (3H, s), 2.36 (3H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 188.01, 136.60, 135.12, 134.01, 131.90, 126.38, 125.87, 125.69, 125.52, 124.17, 123.48, 120.16,116.39, 109.55, 109.36, 109.07, 40.54, 22.19, 21.83; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{19}H_{16}N_3O$: 302.1288; found 302.1299; **IR** (thin film): ν_{max} 2360, 1642, 745 cm^{-1}



Compound 2c: Following the general procedure C, substrate **1c** (71 mg, 0.2 mmol), copper acetate (37 mg, 0.2 mmol), 1,10-phenanthrolene (73 mg, 0.4 mmol), silver carbonate (111 mg, 0.4 mmol) and potassium carbonate (56 mg, 0.4 mmol) in xylene (1mL) was heated at 140 ^oC for 12h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: hexane 1:1) to afford product **2c (1:1)** as white solid (28 mg, yield: 40%). **^{1}H NMR** (300 MHz, DMSO-d_6): 10.96 (1H, s), 8.27-8.18 (1H, m), 8.09 (1H, s), 7.77 (1H, d, *J* = 8.4 Hz),7.48-7.43 (1H, m), 7.39-7.30 (1H, m), 4.80 (4H, s); **^{13}C NMR** (100 MHz, DMSO-d_6): 186.84, 144.48, 143.32, 136.97, 133.91, 133.61, 126.68, 126.02, 125.67, 125.02, 124.32, 122.33, 121.18, 115.65, 113.21, 111.76, 40.46; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{18}H_{12}Cl_2N_3O_2$: 356.0352; found 356.0351; **IR** (thin film): ν_{max} 1642, 1341, 1034, 753 cm^{-1}

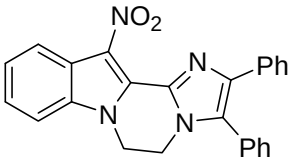


Compound 2d: Following the general procedure C, substrate **1d** (62 mg, 0.2 mmol), copper acetate (37 mg, 0.2 mmol), 1,10-phenanthrolene (73 mg, 0.4 mmol), silver carbonate (111 mg, 0.4 mmol) and potassium carbonate (56 mg, 0.4 mmol) in xylene (1mL) was heated at 140 ^oC for 12h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: hexane 2:3) to afford product **2d** as white solid (22 mg, yield: 35%). **^{1}H NMR** (300 MHz, DMSO-d_6): 10.66 (1H, s), 8.20 (1H, d, *J* = 7.5 Hz), 7.69 (1H, d, *J* = 8.1 Hz), 7.45-7.29 (2H, m), 4.68 (2H, t, *J* = 6 Hz), 4.52 (2H, t, *J* = 6.6 Hz); **^{13}C NMR** (75 MHz, DMSO-d_6): 185.86, 136.51, 135.51, 133.53, 126.92, 125.17, 125.05, 124.08, 122.13, 115.17, 113.45, 111.39, 42.22; **HRMS** (ES+) cald. for $(M+Na)^+$: $C_{14}H_9Cl_2N_3NaO$: 328.0015; found 328.0013; **IR** (thin film): ν_{max} 2922, 1642, 1340, 752 cm^{-1}

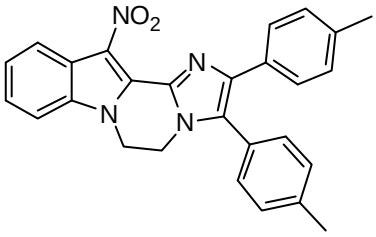


Compound 2e: : Following the general procedure C, substrate **1e** (70 mg, 0.18 mmol), copper acetate (33 mg, 0.18 mmol), 1,10-phenanthrolene (65 mg, 0.36 mmol), silver carbonate (99 mg, 0.36 mmol) and potassium carbonate (50 mg, 0.36 mmol) in xylene (1mL) was heated at 140 ^oC for 12h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: hexane 1:1) to

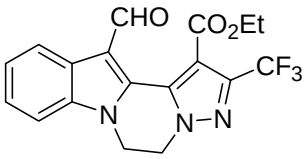
afford product **2e** as yellow solid (44 mg, yield: 63%). **^{1}H NMR** (300 MHz, $CDCl_3$): 11.15 (1H, s), 8.48 (1H, d, *J* = 5.1 Hz), 7.61 (3H, d, *J* = 6.9 Hz), 7.53 (3H, s), 7.46-7.44 (3H, m), 7.36 (4H, s), 4.47 (2H, t, *J* = 5.7 Hz), 4.31(2H, d, *J* = 5.7 Hz); **^{13}C NMR** (75 MHz, DMSO-d_6): 186.26, 139.27, 136.16, 135.19, 133.80, 130.41, 129.68, 129.25, 128.93, 128.37, 127.02, 126.58, 124.94, 124.27, 123.34, 121.56, 112.78, 110.76, 41.42; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{26}H_{20}N_3O$: 390.1600; found 390.1608; **IR** (thin film): ν_{max} 1637, 1469, 1346, 1123, 698 cm^{-1}



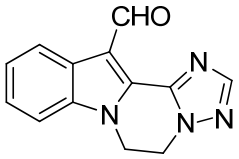
Compound 2f: : Following the general procedure C, substrate **1f** (73 mg, 0.18 mmol), copper acetate (33 mg, 0.18 mmol), 1,10-phenanthrolene (65 mg, 0.36 mmol), silver carbonate (99 mg, 0.36 mmol) and potassium carbonate (50 mg, 0.36 mmol) in xylene (1mL) was heated at 140 ^oC for 12h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: hexane 1:1) to afford product **2f** as yellow solid (60 mg, yield: 83%). **^{1}H NMR** (300 MHz, $CDCl_3$): 8.14 (1H, d, *J* = 2.4 Hz),7.47-7.44 (2H, m), 7.38-7.33 (3H, m), 7.27-7.19 (5H, m), 7.13-7.09 (3H, m), 4.30 (2H, t, *J* = 5.1 Hz), 4.10 (2H, t, *J* = 6 Hz); **^{13}C NMR** (100 MHz, DMSO-d_6): 139.55, 134.88, 134.49, 134.34, 130.97, 130.65, 129.86, 129.77, 129.34, 128.86, 128.57, 127.57, 127.29, 125.52, 124.93, 123.99, 121.75, 120.72, 111.89, 41.65, 40.66; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{25}H_{18}N_4O_2$: 407.1508; found 407.1501; **IR** (thin film): ν_{max}1637, 1260, 749 cm^{-1}



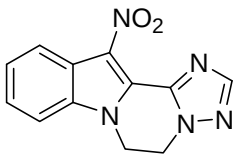
Compound 2g: : Following the general procedure C, substrate **1g** (87 mg, 0.2 mmol), copper acetate (37 mg, 0.2 mmol), 1,10-phenanthrolene (73 mg, 0.4 mmol), silver carbonate (111 mg, 0.4 mmol) and potassium carbonate (56 mg, 0.4 mmol) in xylene (1mL) was heated at 140 ^oC for 12h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: hexane 2:3) to afford product **2g** as yellow solid (73 mg, yield: 84%). **^{1}H NMR** (300 MHz, DMSO-d_6): 8.20 (1H, d, *J* = 6.6 Hz), 7.75 (1H, d, *J* = 7.2 Hz), 7.45-7.38 (8H, m), 7.11 (2H, d, *J* = 7.8 Hz), 4.62 (2H, bs), 4.34 (2H, bs), 2.42 (3H, s), 2.28 (3H,s); **^{13}C NMR** (100 MHz, DMSO-d_6): 139.59, 139.30, 136.73, 134.61, 134.32, 131.78, 130.80, 130.31, 129.41, 128.71, 127.23, 126.43, 125.46, 124.87, 123.90, 121.78, 120.70, 111.84, 41.56, 41.24, 21.51, 21.29; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{27}H_{23}N_4O_2$: 435.1787; found 435.1788; **IR** (thin film): ν_{max} 2922, 1560, 1344, 741 cm^{-1}



Compound 2h: Following the general procedure C, substrate **1h** (76 mg, 0.2 mmol), copper acetate (37 mg, 0.2 mmol), 1,10-phenanthrolene (73 mg, 0.4 mmol), silver carbonate (111 mg, 0.4 mmol) and potassium carbonate (55 mg, 0.4 mmol) in xylene (1mL) was heated at 140 ^{o}C for 12h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: hexane 1:1) to afford product **2h** as colorless solid (15 mg, yield: 20%). **^{1}H NMR** (300 MHz, $CDCl_3$): 10.18 (1H, s), 8.43 (1H, d, *J* = 7.8 Hz), 7.51-7.38 (3H, m), 4.72 (2H, t, *J* = 4.8 Hz), 4.61 (2H, t, *J* = 5.1 Hz), 4.42 (2H, q, *J* = 6.9 Hz), 1.37 (3H, t, *J* = 7.2 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): 184.47, 161.27, 136.00, 134.05, 129.62, 125.83, 125.70, 123.89, 122.54, 114.66, 111.86, 109.44, 62.02, 47.49, 40.53, 13.72; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{18}H_{14}F_3N_3NaO_3$: 400.0879; found 400.0876; **IR** (thin film): ν_{max}1725, 1658, 1338, 1302, 1137, 744 cm^{-1}

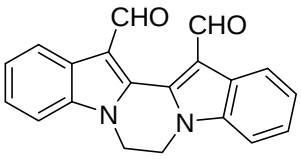


Compound 2i: Following the general procedure C, substrate **1i** (50 mg, 0.21 mmol), copper acetate (38 mg, 0.21 mmol), 1,10-phenanthrolene (76 mg, 0.42 mmol), silver carbonate (116 mg, 0.42 mmol) and potassium carbonate (58 mg, 0.42 mmol) in xylene (1mL) was heated at 140 ^{o}C for 12h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: hexane 3:2) to afford product **2i** as white solid (34 mg, yield: 68%). **^{1}H NMR** (300 MHz, $CDCl_3$): 10.88 (1H, s), 8.45 (1H, d, *J* = 7.5Hz), 8.11 (1H, s), 7.41-7.35 (3H, m), 4.76 (2H, d, *J* = 4.8 Hz), 4.63 (2H, bs); **^{13}C NMR** (75 MHz, DMSO-d_6): 186.15, 152.73, 144.97, 137.10, 133.18, 125.74,125.08, 124.27, 122.50, 114.49, 111.85, 45.38; **HRMS** (ES+) cald. for $(M+Na)^+$: $C_{13}H_{10}N_4NaO$: 261.0752; found 261.0781; **IR** (thin film): ν_{max} 2922, 1644, 1044, 734 cm^{-1}

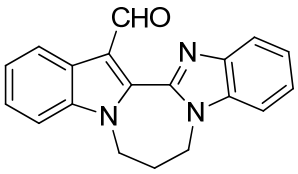


Compound 2j: Following the general procedure C, substrate **1j** (51 mg, 0.2 mmol), copper acetate (36 mg, 0.2 mmol), 1,10-phenanthrolene (72 mg, 0.4 mmol), silver carbonate (110 mg, 0.4 mmol) and potassium carbonate (55 mg, 0.4 mmol) in xylene (1mL) was heated at 140 ^{o}C for 12h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: hexane 3:2) to afford product **2j** as yellow solid (26 mg, yield: 50%); **^{1}H NMR** (300 MHz, DMSO-d_6): 8.39 (1H, s), 8.27 (1H, d, *J* = 7.8 Hz), 7.92 (1H, d, *J* =

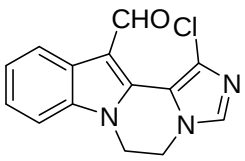
8.1 Hz), 7.68-7.53 (3H, m), 4.88 (4H, s); **^{13}C NMR** (75 MHz, DMSO-d_6): 152.22, 143.50, 134.69, 126.26, 125.82, 125.25, 125.16, 121.14, 120.89, 112.37, 45.14, 41.50; **HRMS** (ES+) cald. for $(M+Na)^+$: $C_{12}H_9N_5NaO_2$: 278.0654; found 278.0648; **IR** (thin film): ν_{max} 2362, 1483, 1305, 731 cm^{-1}



Compound 2k: Following the general procedure C, substrate **1k** (63 mg, 0.2 mmol), copper acetate (37 mg, 0.2 mmol), 1,10-phenanthrolene (73 mg, 0.4 mmol), silver carbonate (111 mg, 0.4 mmol) and potassium carbonate (56 mg, 0.4 mmol) in xylene (1mL) was heated at 140 ^oC for 12h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: hexane 2:3) to afford product **2k** as yellow solid (31 mg, yield: 50%). **^{1}H NMR** (300 MHz, $CDCl_3$): 10.14 (2H, s), 8.45 (2H, d, *J* = 7.8 Hz), 7.40-7.33 (6H, m), 4.54 (4H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 185.03, 136.23, 125.91, 124.16,123.19, 118.27, 116.52, 109.24, 41.08; **HRMS** (ES+) cald. for $(M+Na)^+$: $C_{20}H_{14}N_2NaO_2$: 337.09476; found 337.0939; **IR** (thin film): ν_{max} 2923, 1432, 1337, 1043, 745 cm^{-1}

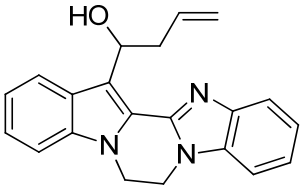


Compound 2l[2]: Following the general procedure C, substrate **1l** (123 mg, 0.37 mmol), copper acetate (67 mg, 0.37 mmol), 1,10-phenanthrolene (133 mg, 0.74 mmol), silver carbonate (204 mg, 0.74 mmol) and potassium carbonate (102 mg, 0.74 mmol) in xylene (1mL) was heated at 140 ^oC for 12h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: hexane 3:2) to afford product **2l** as yellow solid (15 mg, yield: 12%). **^{1}H NMR** (300 MHz, $CDCl_3$): 10.63 (1H, s), 8.52 (1H, d, *J* = 7.5 Hz), 7.93 (1H, d, *J* = 6.9 Hz), 7.47-7.40 (6H, m), 4.38 (2H, d, *J* = 3 Hz), 2.65 (1H, t, *J* = 6.3 Hz); **HRMS** (ES+) cald. for $(M+H)^+$: $C_{19}H_{16}N_3O$: 302.1288; found 302.1314.

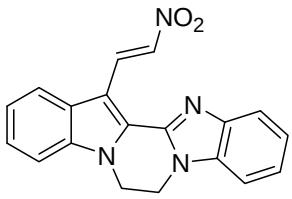


Compound 2m: Substrate **1d** (63 mg, 0.21 mmol), $Pd(OAc)_2$ (5 mg, 0.02 mmol), $Cu(OAc)_2$ (113 mg, 0.63 mmol) and K_2CO_3 (29 mg, 0.21 mmol) was placed in a sealed tube and anhydrous DMA (1 mL) was added to it. After degasification the resulting solution was heated to 120 ^oC for 8h. The resulting solution was quenched with water and extracted with ethyl acetate. The organic layer was washed with brine solution, dried and evaporated in vacuum. After column chromatography pure compound **2m** (3:2 ethyl acetate: hexane) along with **2d** (2:3 Ethyl acetate: hexane),

were both obtained as yellow solid in 1:1 ratio [combined yield for **2m** and **2d**= 17 mg (30%)]. **^{1}H NMR** (300 MHz, $CDCl_3$): 10.77 (1H, s), 8.34 (1H, d, *J* = 7.5 Hz), 7.29-7.19 (3H, m), 6.96 (1H, s), 4.40 (4H, s); **^{13}C NMR** (100 MHz, DMSO-d_6): 186.17, 136.65, 136.14, 134.45, 130.15, 125.00, 124.99, 123.96, 122.11, 118.29, 113.15, 111.33, 43.49; **HRMS** (ES+) cald. for $(M+Na)^+$: $C_{14}H_{10}ClN_3NaO$: 294.0405; found 294.0387

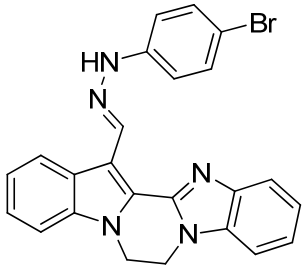


Compound 3a: Indium metal (20 mg, 0.17 mmol) was finely cut and placed in round bottomed flask. To it was added 4 mL of DMF, allyl bromide (51 mg, 0.42 mmol) and sodium iodide (84 mg, 0.56 mmol) and the solution was allowed to stir at rt for 30 mins until indium dissolves and form complex. A solution of compound **2a** (40 mg, 0.14 mmol) in 2 mL DMF was added to it and the resulting mixture was stirred overnight. The formation of product was monitored by TLC. The resulting reaction mixture was quenched in saturated ammonium chloride solution and extracted with ethyl acetate twice. The organic layer was washed with brine and the solvent was removed in vacuum which after column purification (Ethyl acetate: hexane 2:3) yielded product **3a** as yellow solid (34 mg, yield: 75%). **^{1}H NMR** (300 MHz, $CDCl_3$):7.78-7.75 (1H, m), 7.66 (1H, d, *J* = 7.8 Hz), 7.36-7.28 (5H, m), 7.20-7.16 (1H, m), 6.01-5.91 (1H, m), 5.33 (1H, t, *J* = 13.5 Hz), 5.12 (1H, d, *J* = 17.4 Hz), 5.04 (1H, d, *J* =9.9 Hz), 4.57-4.36 (4H, m), 2.88-2.81 (1H, m), 2.75-2.66 (1H, m); **^{13}C NMR** (75 MHz, $CDCl_3$): 144.36, 142.55, 136.43, 135.66, 133.55, 126.82, 124.32, 123.24, 123.12, 122.39, 120.79, 120.24, 119.52, 116.85, 109.35, 109.06, 67.58, 43.82, 40.78, 40.13; **HRMS** (ES+) cald. for $(M+K)^+$: $C_{21}H_{19}KN_3O$: 368.1159; found 368.1170; **IR** (thin film): ν_{max} 3254, 2921, 1422, 736 cm^1

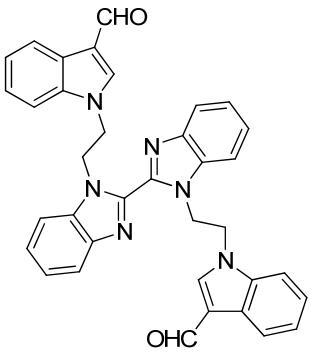


Compound 3b: A solution of compound **2a** (58 mg, 0.2 mmol) in nitromethane (1 mL) containing ammonium acetate (15.4 mg, 0.2 mmol) was refluxed for 1h. The solvent was evaporated under reduced pressure, and the residue was then dissolved in 30 mL of ethyl acetate. The organic phase was washed with water (10 mL), brine (10 mL) and dried over anhydrous sodium sulfate. Evaporation of solvent under reduced pressure, provided the product **3b** as bright red solid (63 mg, yield 95%); **^{1}H NMR** (300 MHz, DMSO-d_6): 9.55 (1H, d, *J* = 15.0 Hz), 8.37 (1H, d, *J* = 15.0 Hz), 8.16 (1H, d, *J* = 9.0 Hz), 7.88-7.78 (3H, m), 7.48-7.34 (4H, m), 4.79 (1H, s); **^{13}C NMR** (75 MHz, DMSO-d_6): 148.73, 147.36, 142.49, 139.24, 138.85, 137.90, 136.92, 130.17, 130.03, 129.03, 128.39, 128.29, 126.76, 124.89, 116.71, 115.92, 111.91, 45.56, 45.46; **HRMS** (ES+) cald. for

$(M+H)^+$: $C_{19}H_{15}N_4O_2$: 331.1189; found 331.1187; **IR** (thin film): ν_{max}1619, 1307, 1273, 729 cm^{-1}



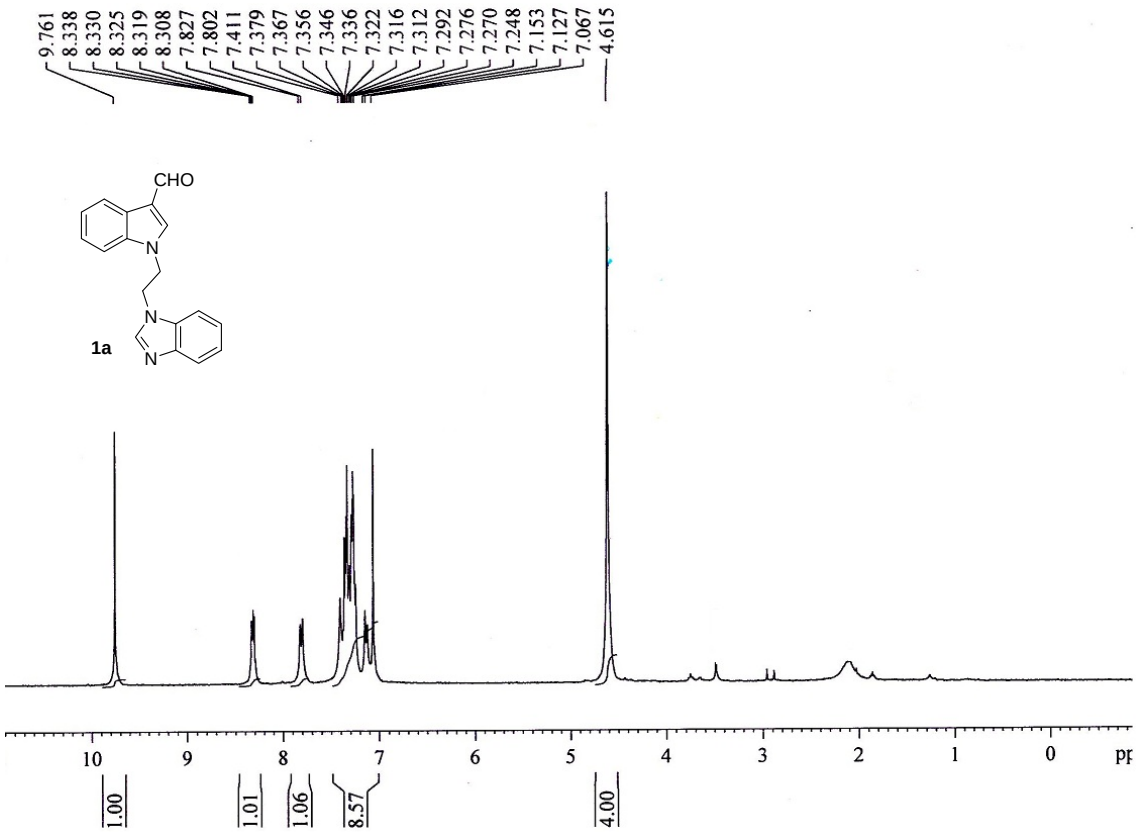
Compound 3c: To a solution of compound **2a** (50 mg, 0.17 mmol) in ethanol (1.5 mL) was added *p*-bromophenyl hydrazine hydrochloride (39 mg, 0.17 mmol) and AcOH (10 µL, 0.17 mmol) and stirred at rt for overnight. The resulting solution was filtered and the solid was dried in vucuum to afford hydrazone **3c** as red solid (71 mg, yield 90%); **^{1}H NMR** (300 MHz, DMSO-d_6): 9.17 (1H, s), 8.42 (1H, d, *J* = 7.8 Hz), 7.73-7.66 (3H, m), 7.40-7.25 (7H, m), 7.06 (1H, d, *J* = 8.7 Hz), 4.69 (4H, d, *J* = 3.6 Hz); **^{13}C NMR** (75 MHz, DMSO-d_6): 145.30, 142.75, 140.05, 137.94, 134.61, 133.49, 132.40, 125.84, 124.96, 124.53, 123.70, 122.50, 117.80, 114.37, 111.71, 111.34, 109.81, 41.53; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{24}H_{19}BrN_5$: 456.0818; found 456.0838; IR (thin film): ν_{max} 2362, 1622, 1483, 742 cm^{-1}



Dimeric compound:

Following the general procedure C, substrate **1a** (58 mg, 0.2 mmol), copper acetate (74 mg, 0.4 mmol), 1,10-phenanthrolene (146 mg, 0.8 mmol), potassium carbonate (56 mg, 0.4 mmol) in xylene (1mL) was heated at 140^{o}C for 12h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: MeOH 96:4) to afford dimeric product as yellow solid (yield: 16%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.48 (2H, s), 7.86 (2H, m),7.71 (2H, d, *J* = 7.2 Hz), 7.32-7.24 (6H, m), 7.06-7.02 (8H, s), 4.89 (4H, t, *J* = 6.3 Hz), 4.61 (4H, t, 6.0 Hz); **^{13}CNMR** (75 MHz, $CDCl_3$+4 drops of DMSO-d_6): 184.56, 138.55, 136.73, 133.78, 126.61, 125.71, 124.55, 124.39, 123.18, 121.86, 119.25, 118.61, 110.38, 109.07, 46.19, 45.31; **ESI-MS** for $(M+H)^+$: $C_{36}H_{29}N_6O_2$: 577.0999.

NMR Spectra: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7.248
7.153
7.127
7.067
4.615
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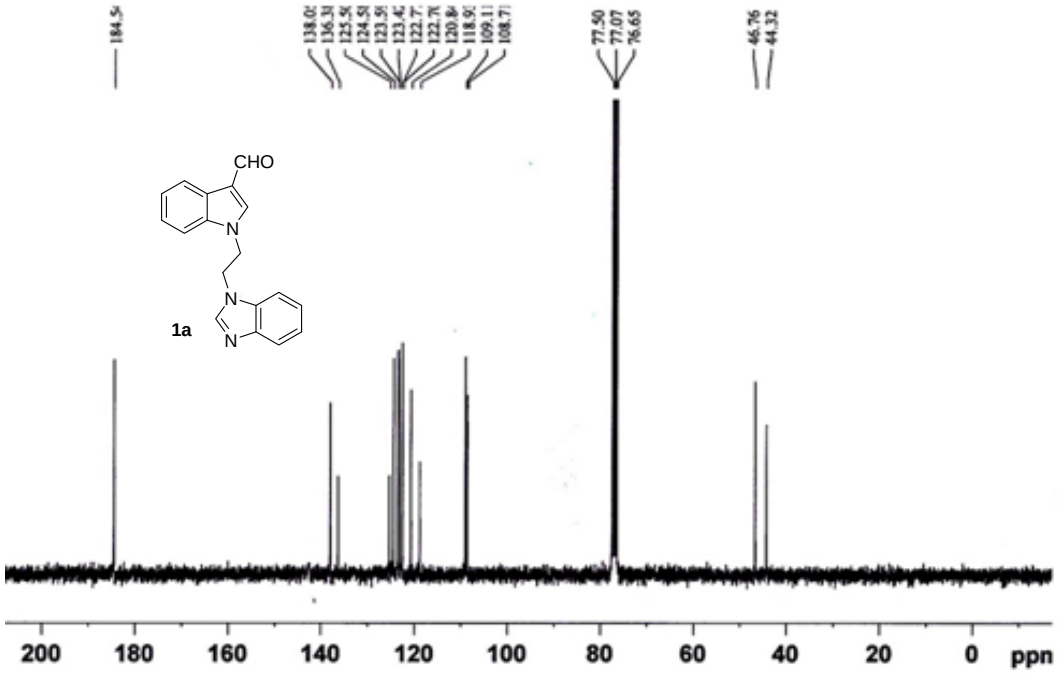
4.00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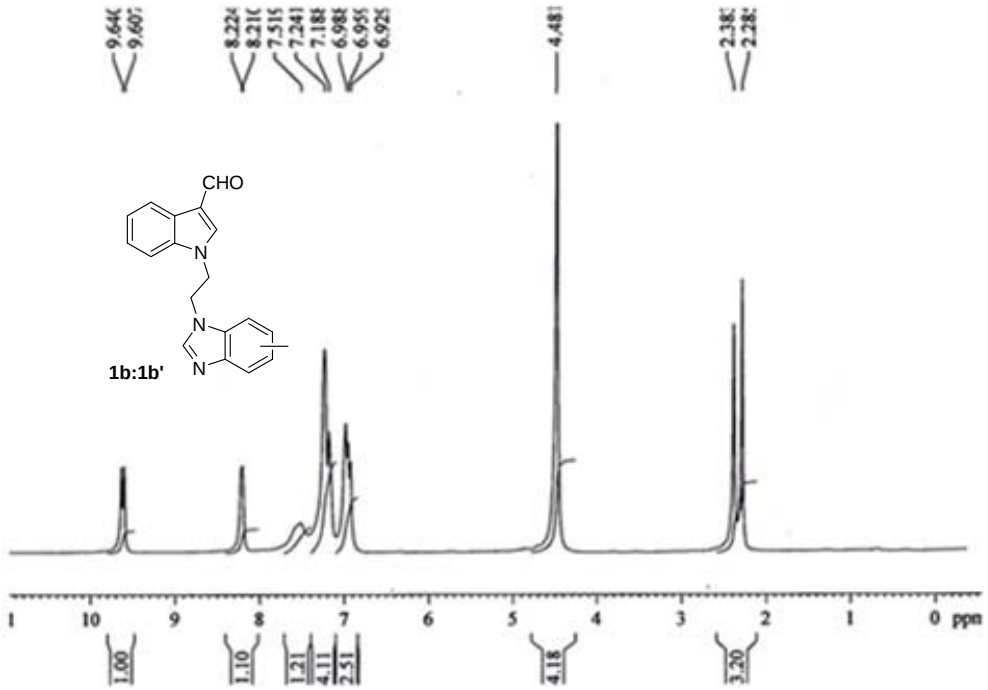
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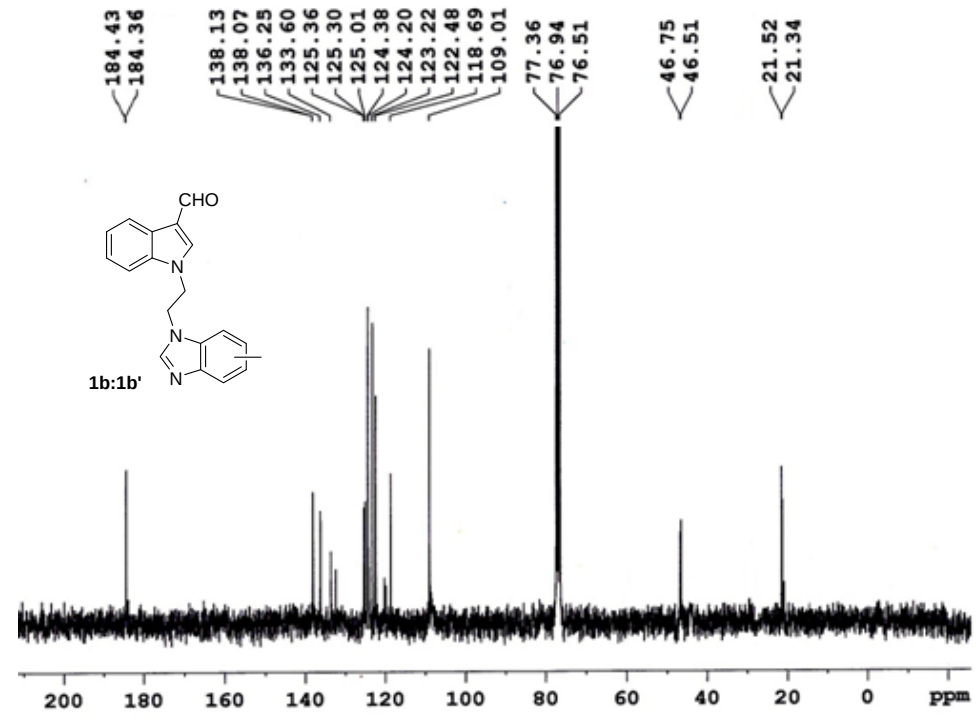
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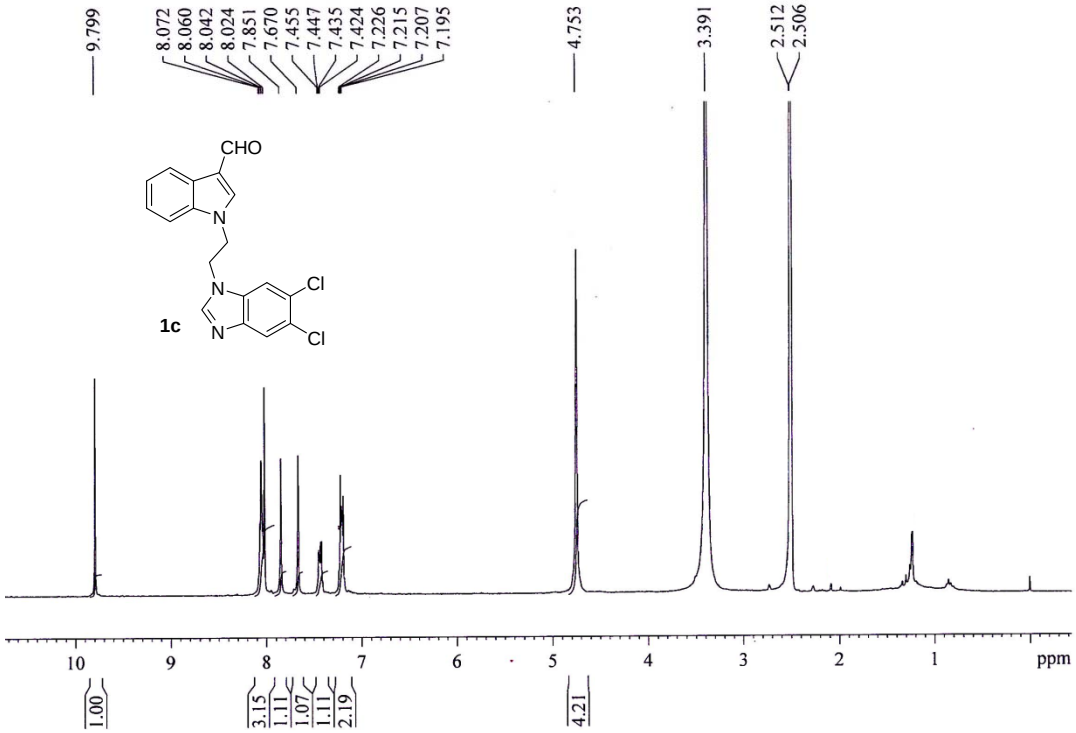
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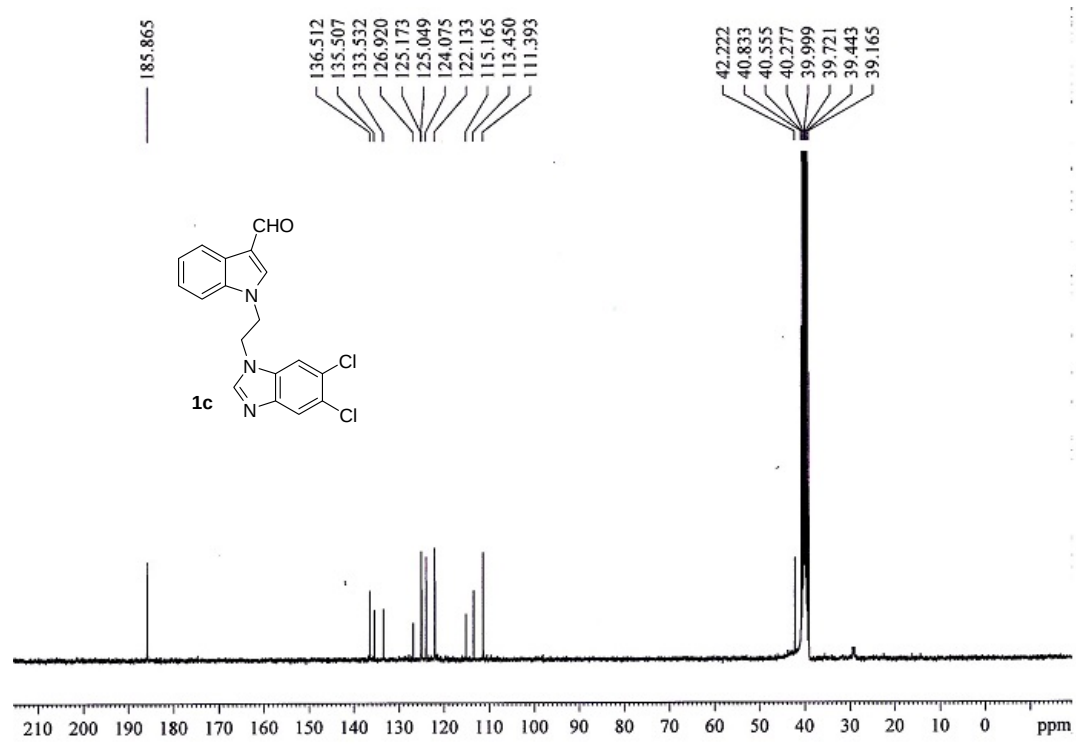
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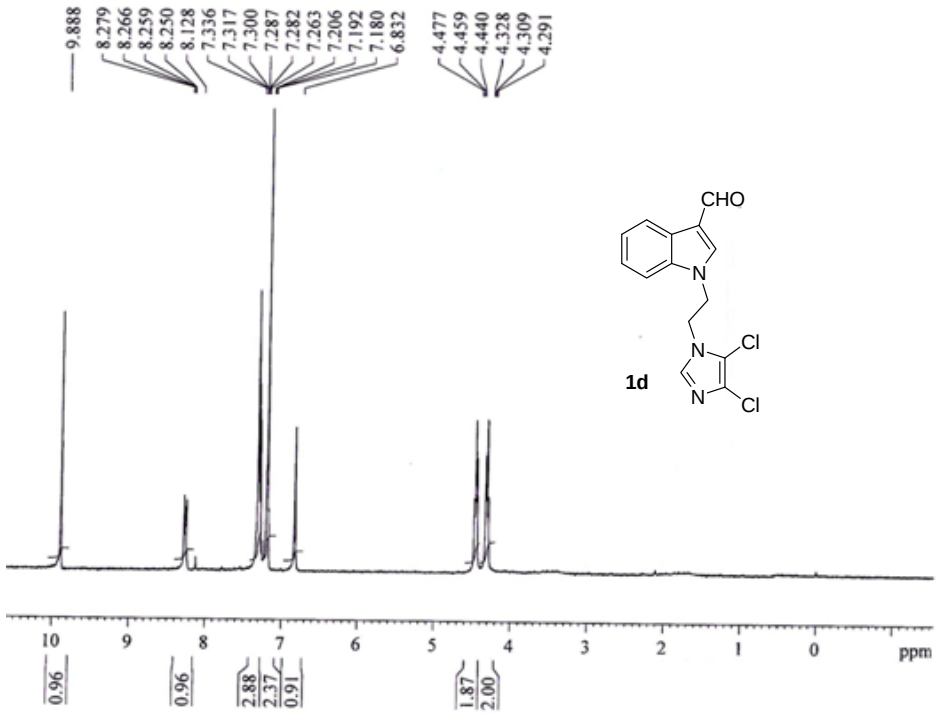
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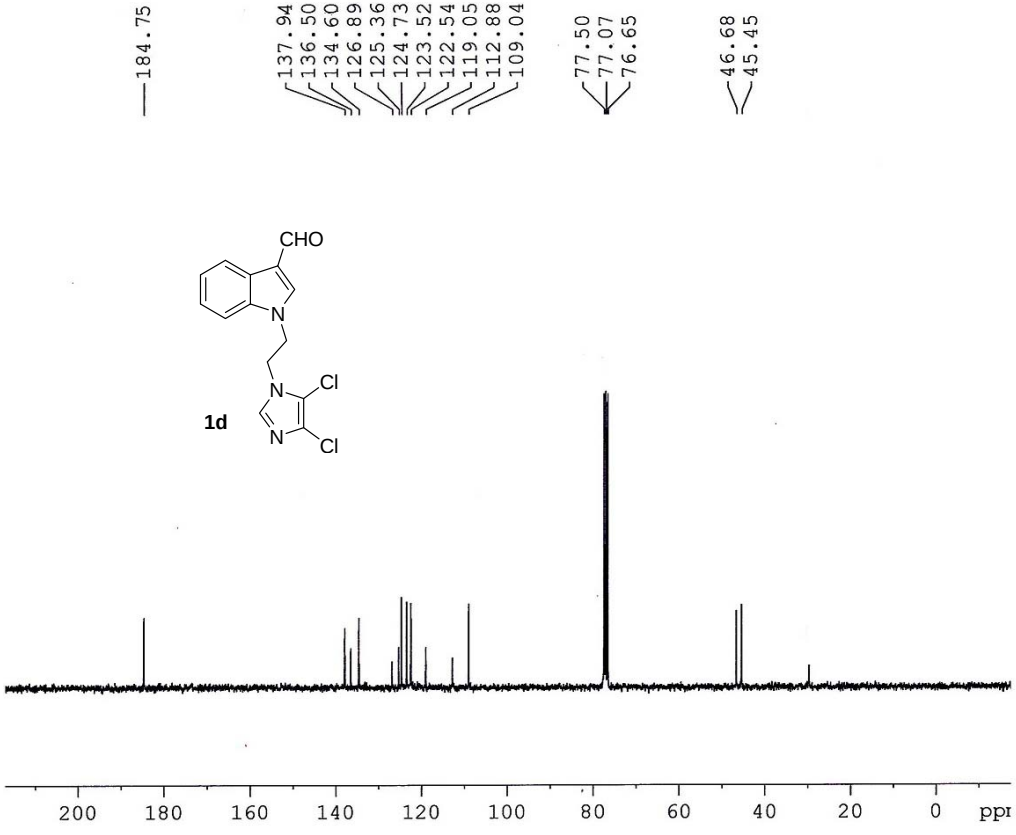
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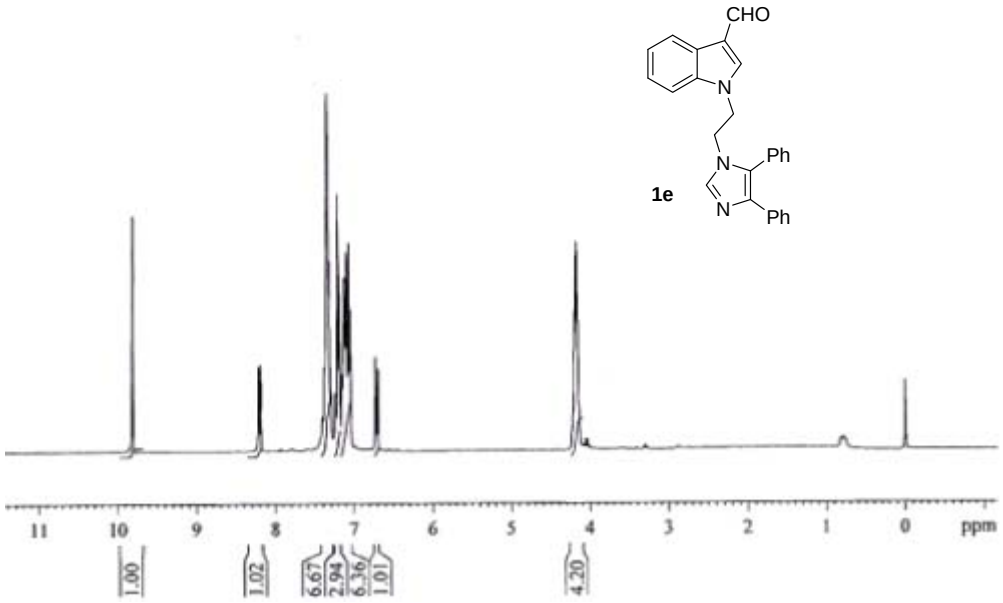
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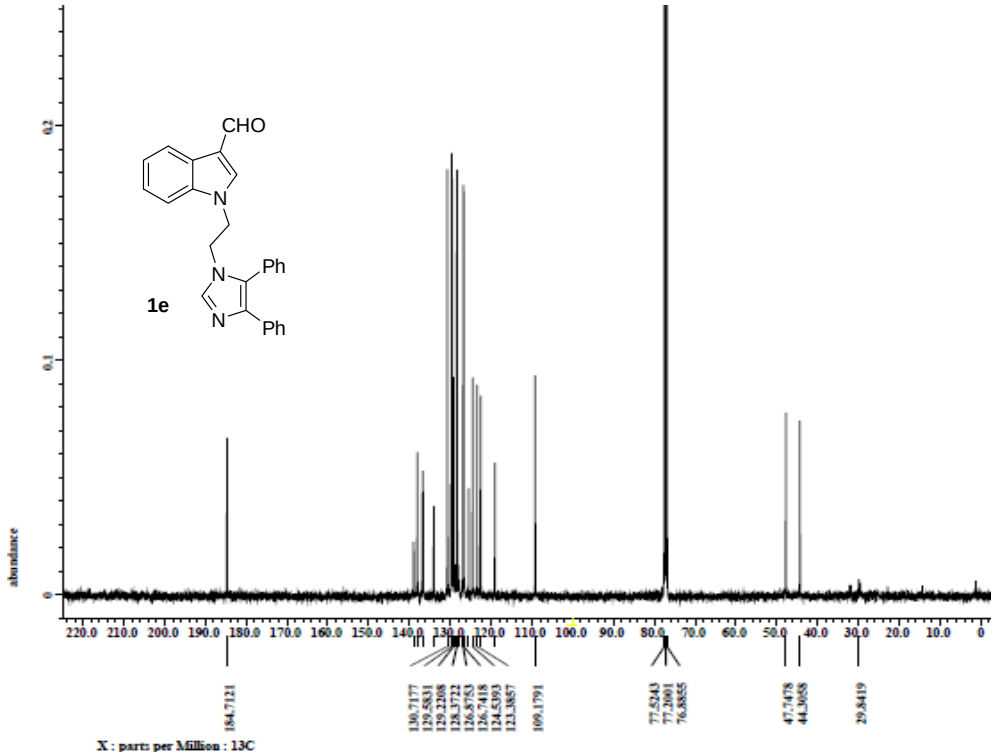
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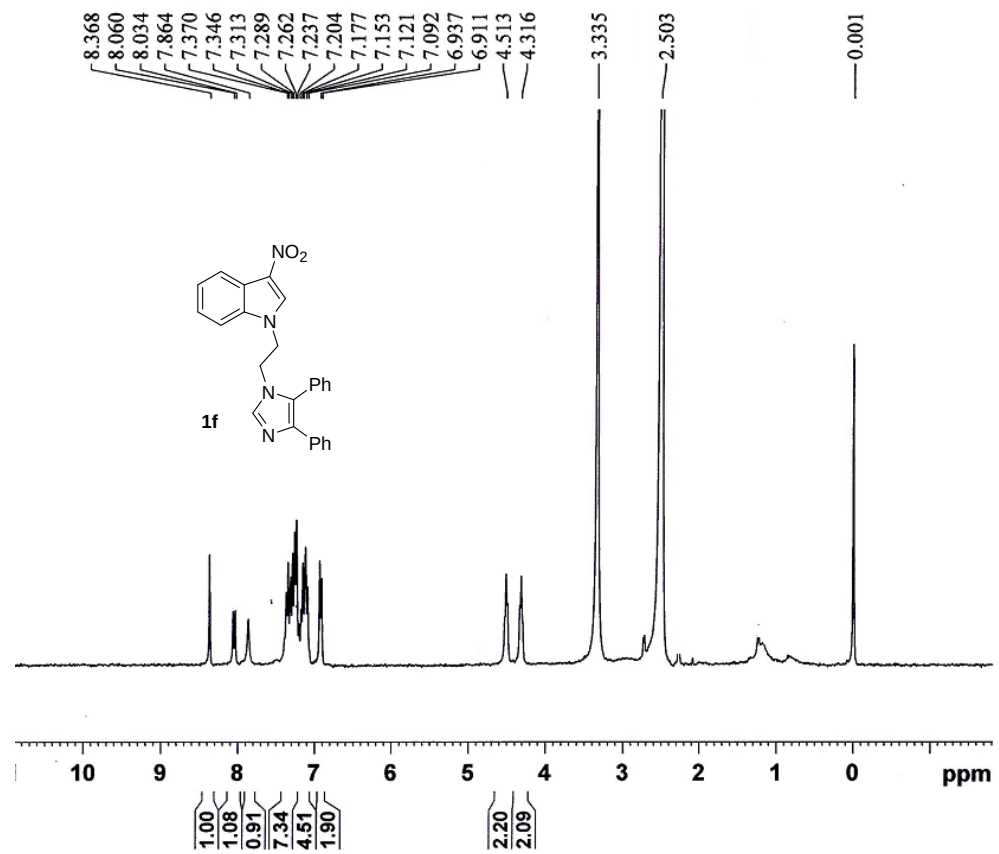
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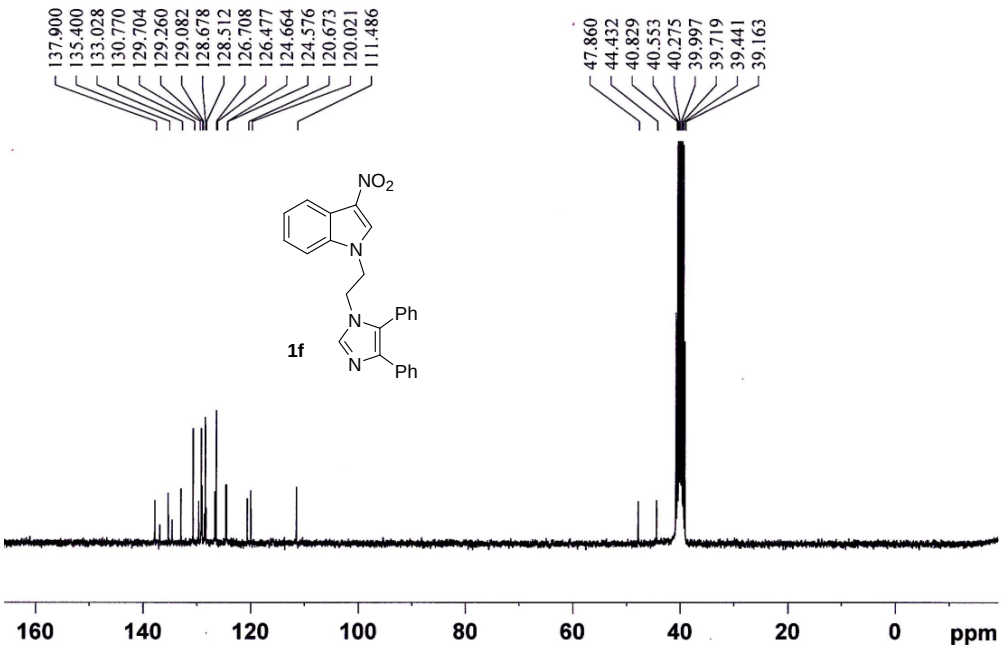
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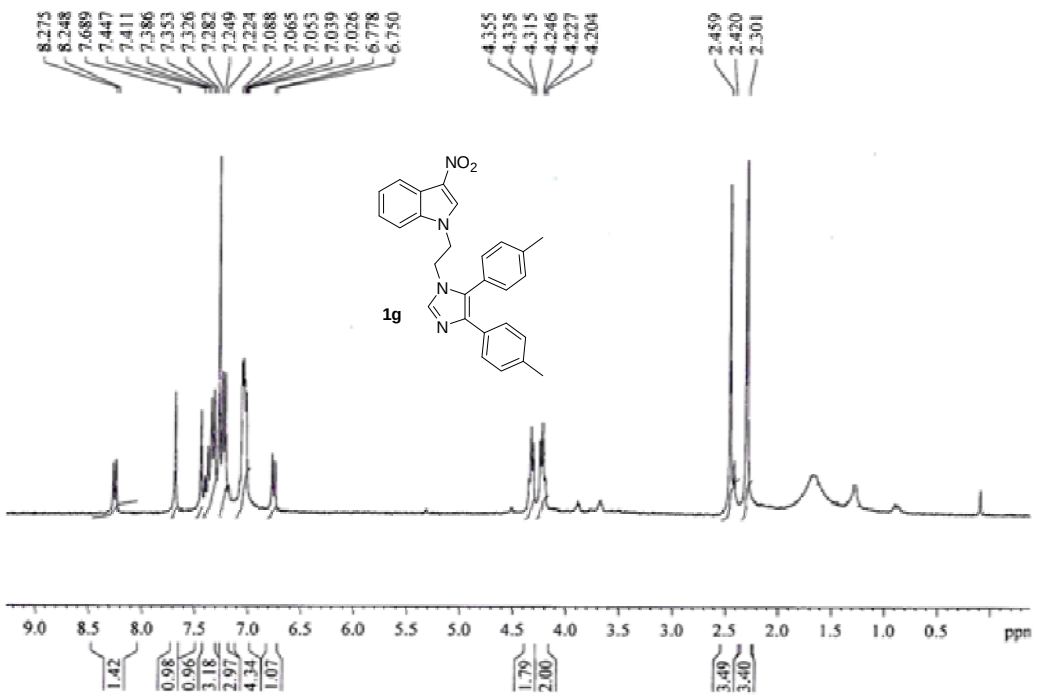
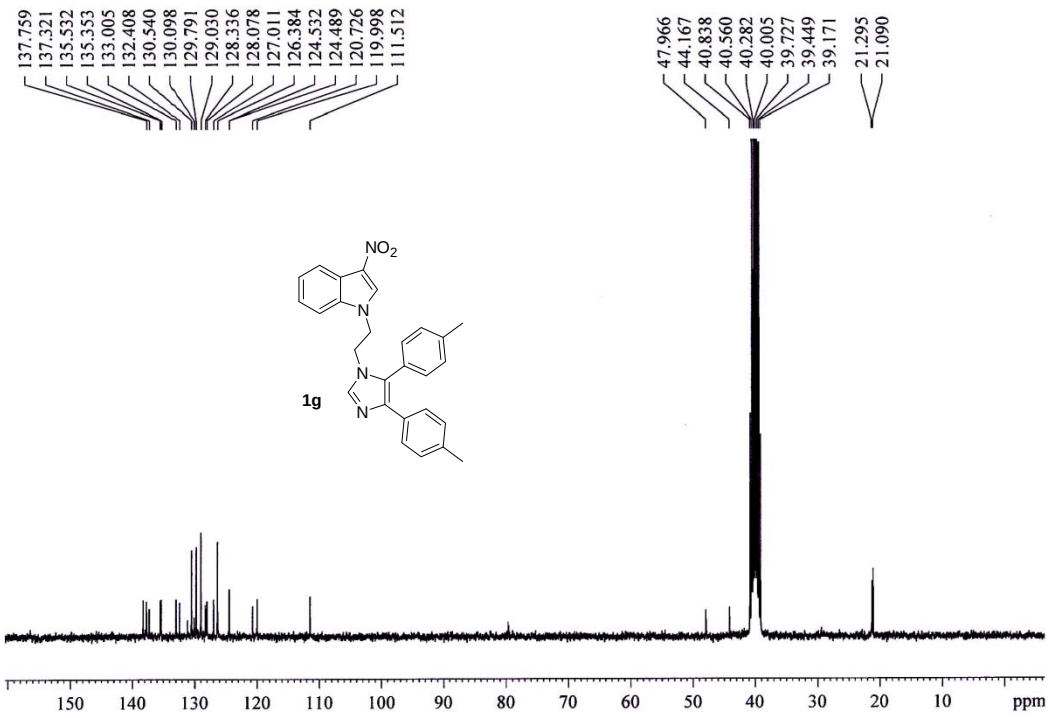
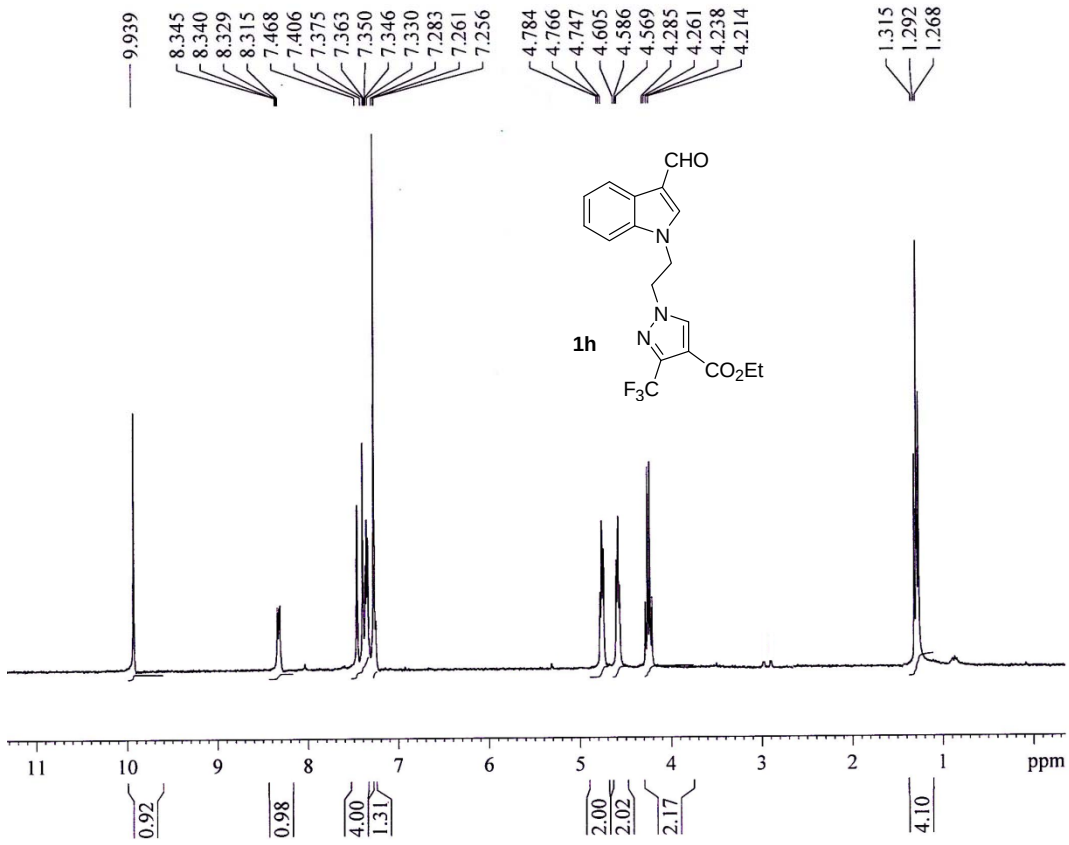
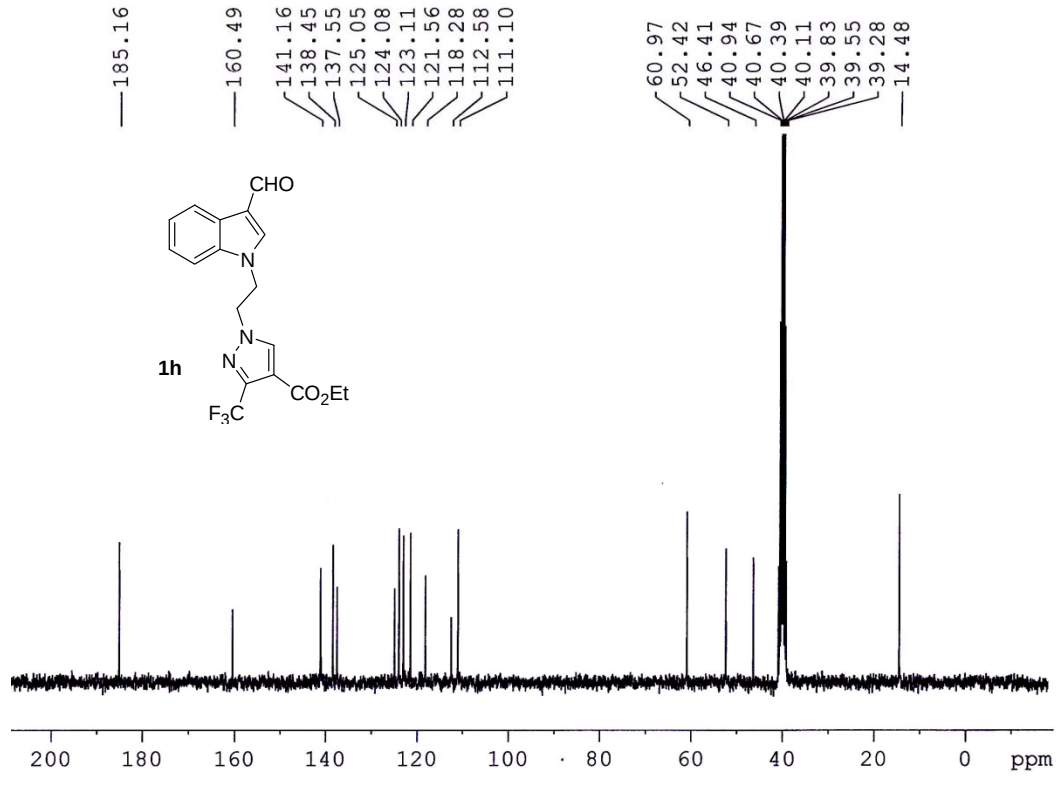
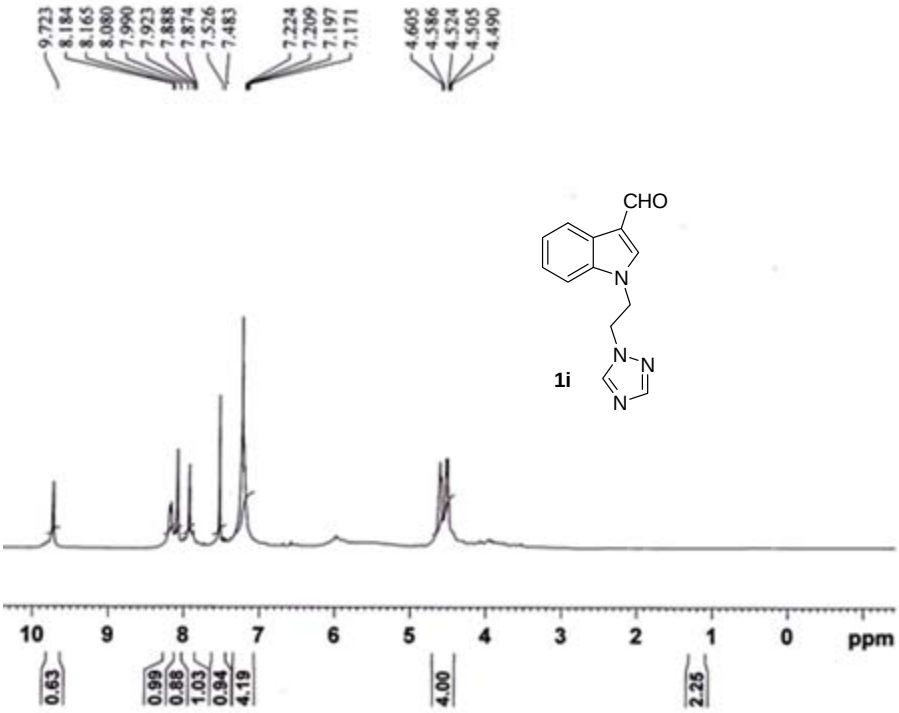
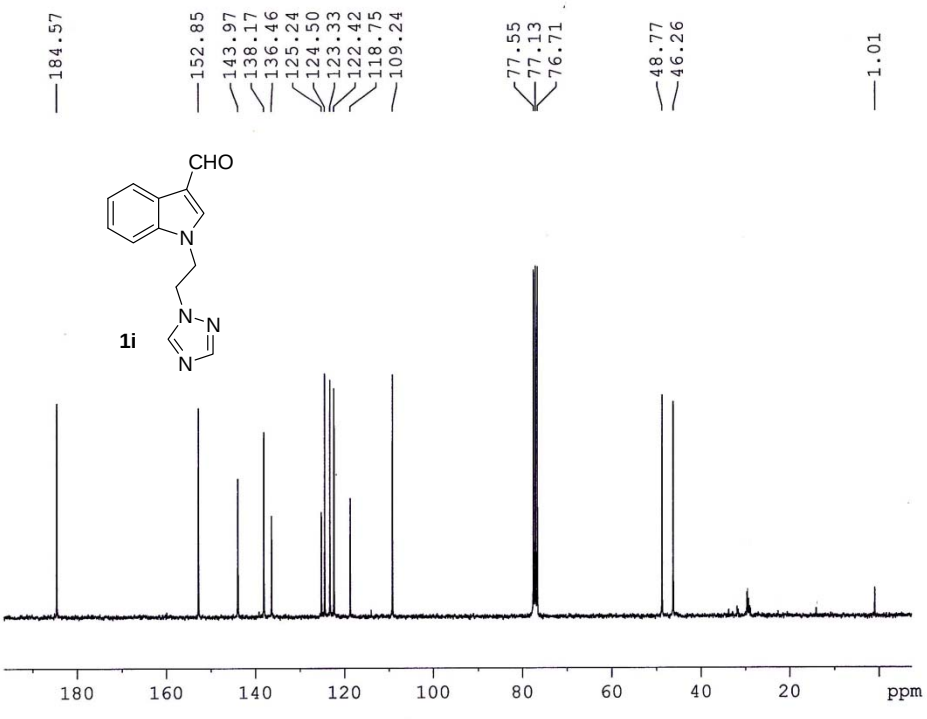

8.275
8.248
7.689
7.447
7.411
7.386
7.353
7.326
7.282
7.249
7.224
7.088
7.065
7.053
7.039
7.026
6.778
6.750
4.355
4.335
4.315
4.246
4.227
4.204
2.459
2.420
2.301
NO2
1g
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.42
0.98
0.96
3.18
2.97
4.34
1.07
1.79
2.00
3.49
3.40

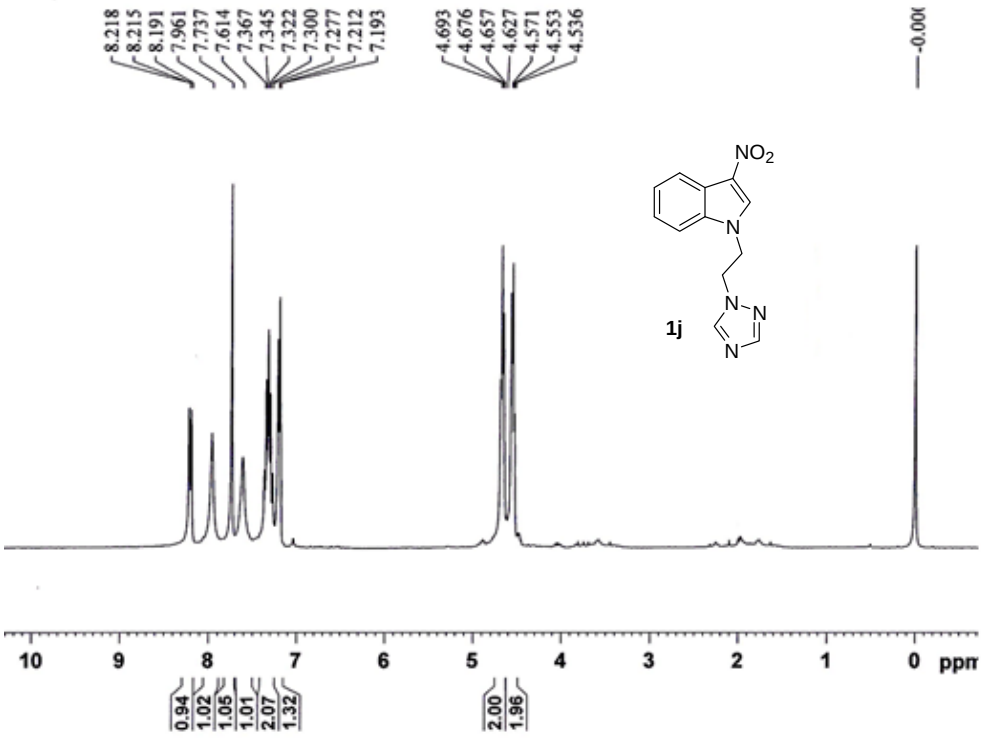

137.759
137.321
135.532
135.353
133.005
132.408
130.540
130.098
129.791
129.030
128.336
128.078
127.011
126.384
124.532
124.489
120.726
119.998
111.512
47.966
44.167
40.838
40.560
40.282
40.005
39.727
39.449
39.171
21.295
21.090
NO2
1g
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

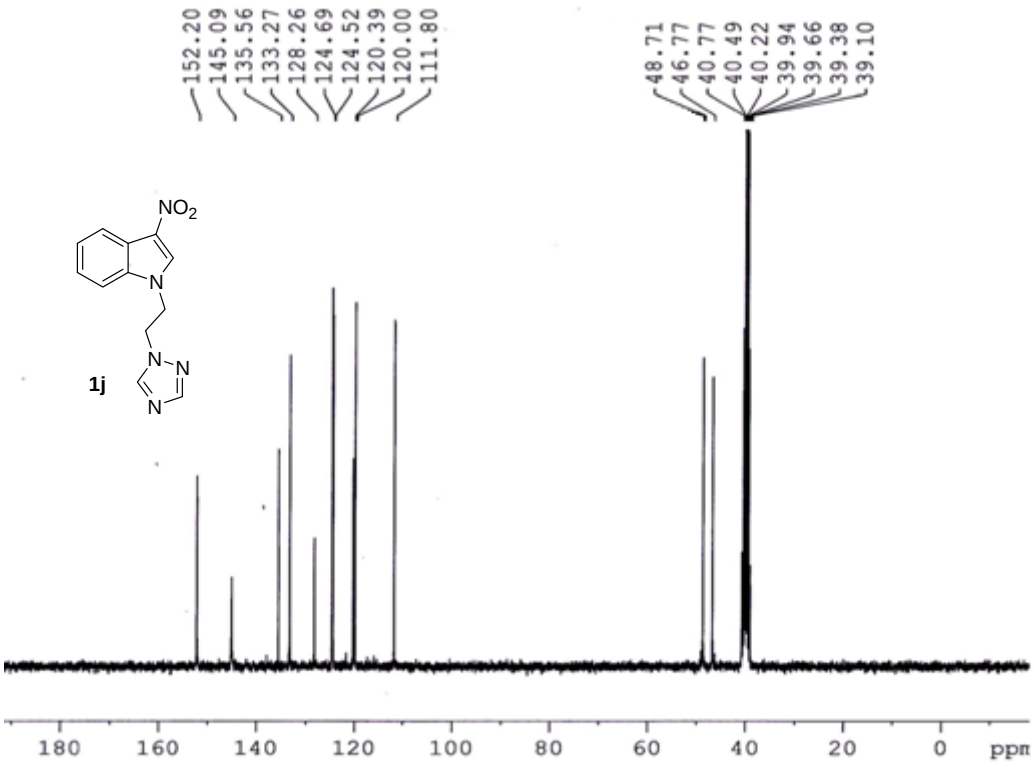

9.939
8.345
8.340
8.329
8.315
7.468
7.406
7.375
7.363
7.350
7.346
7.330
7.283
7.261
7.256
4.784
4.766
4.747
4.605
4.586
4.569
4.285
4.261
4.238
4.214
1.315
1.292
1.268
CHO
N
N
N
1h
CO2Et
F3C
11
10
9
8
7
6
5
4
3
2
1
ppm
0.92
0.98
4.00
1.31
2.00
2.02
2.17
4.10

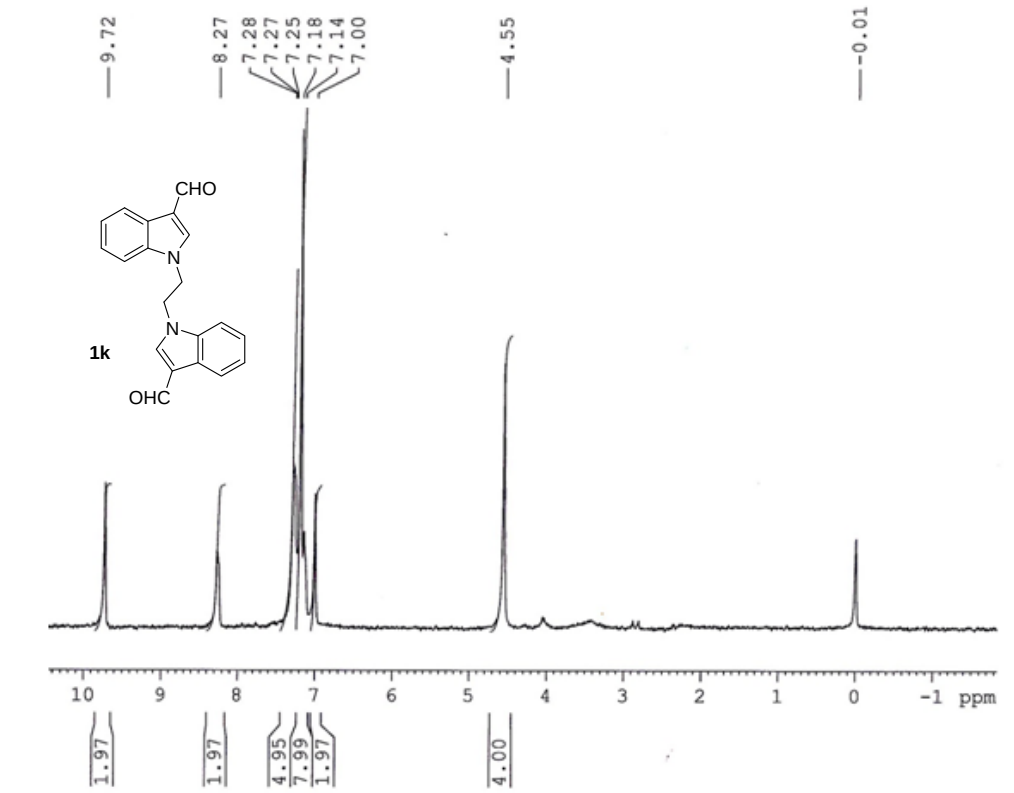

185.16
160.49
141.16
138.45
137.55
125.05
124.08
123.11
121.56
118.28
112.58
111.10
60.97
52.42
46.41
40.94
40.67
40.39
40.11
39.83
39.55
39.28
14.48
CHO
N
N
N
1h
CO2Et
F3C
200
180
160
140
120
100
80
60
40
20
0
ppm

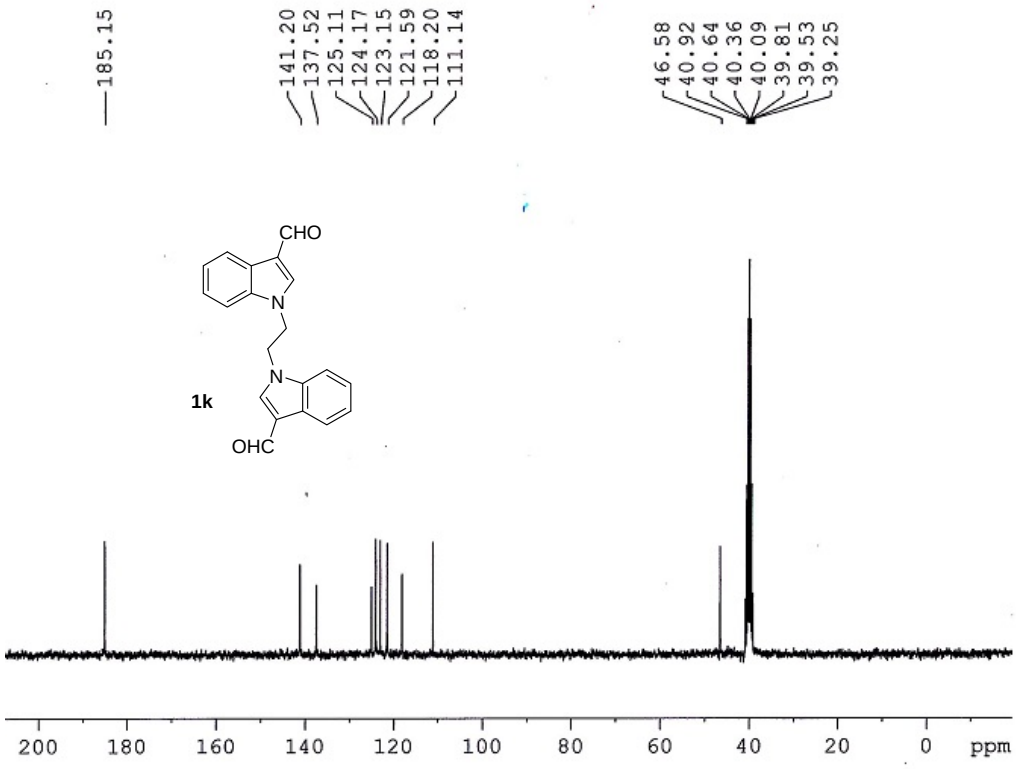

9.723
8.184
8.165
8.080
7.990
7.923
7.888
7.874
7.526
7.483
7.224
7.209
7.197
7.171
4.605
4.586
4.524
4.505
4.490
CHO
N
N
N
N
1i
10
9
8
7
6
5
4
3
2
1
0
ppm
0.63
0.99
0.88
1.03
0.94
4.19
4.00
2.25

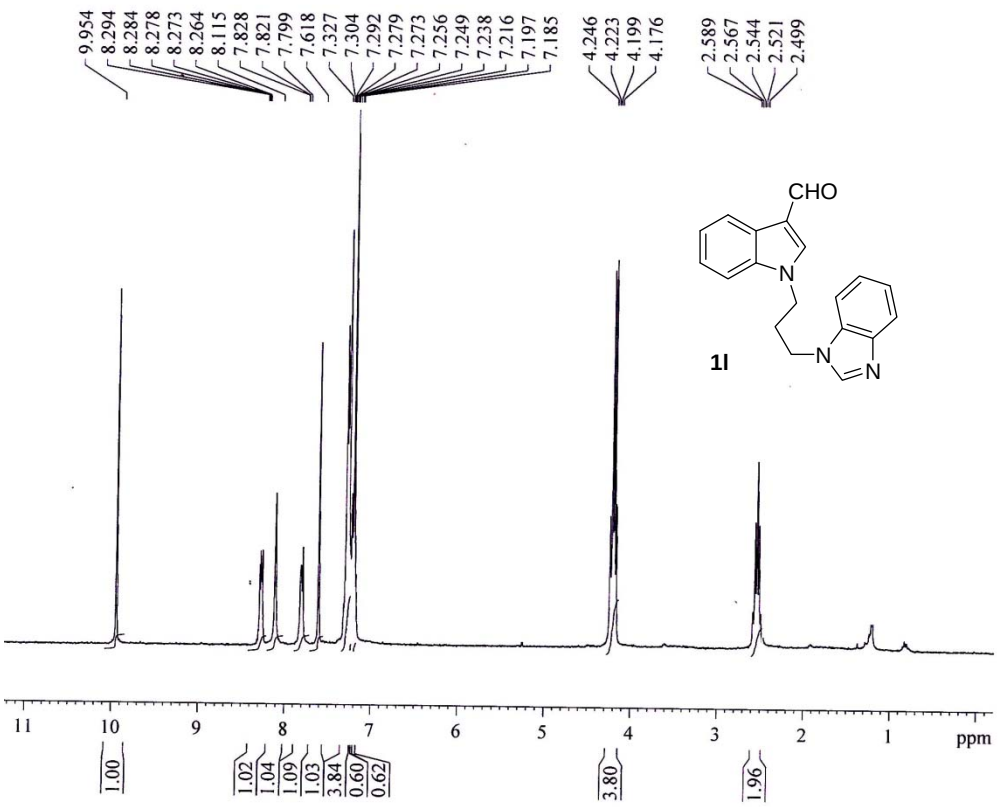

184.57
152.85
143.97
138.17
136.46
125.24
124.50
123.33
122.42
118.75
109.24
77.55
77.13
76.71
48.77
46.26
1.01
CHO
N
N
N
N
1i
180
160
140
120
100
80
60
40
20
ppm

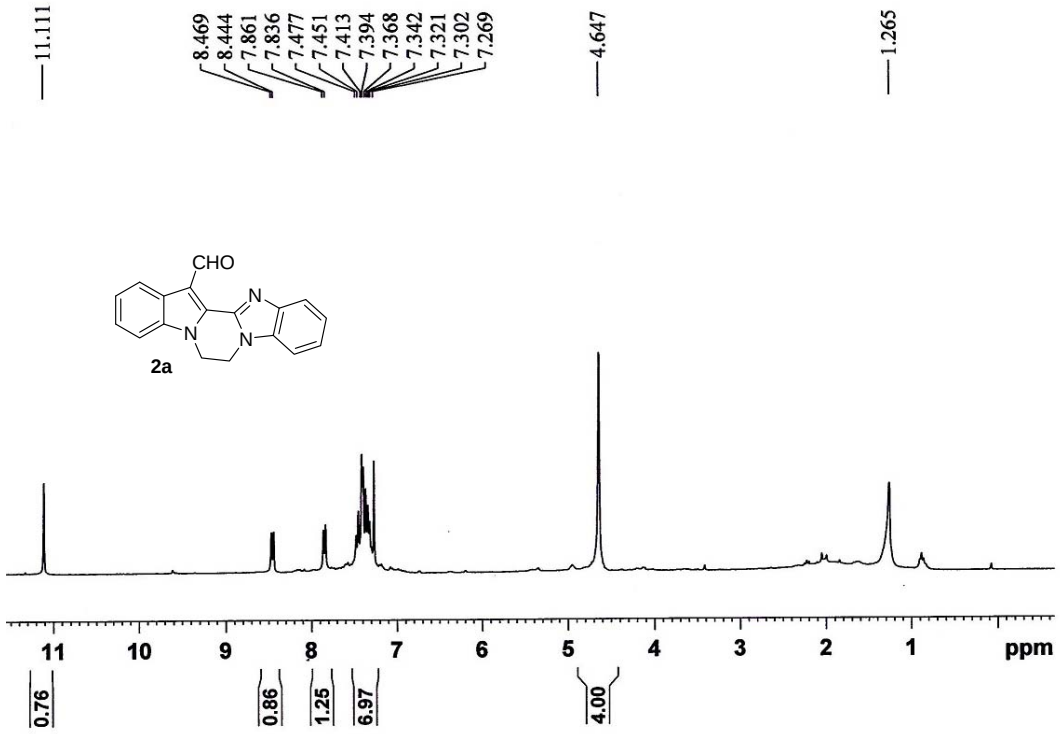

8.218
8.215
8.191
7.961
7.737
7.614
7.367
7.345
7.322
7.300
7.277
7.212
7.193
4.693
4.676
4.657
4.627
4.571
4.553
4.536
NO2
N
N
N
N
1j
10
9
8
7
6
5
4
3
2
1
0
ppm
0.94
1.02
1.05
1.01
2.07
1.32
2.00
1.96

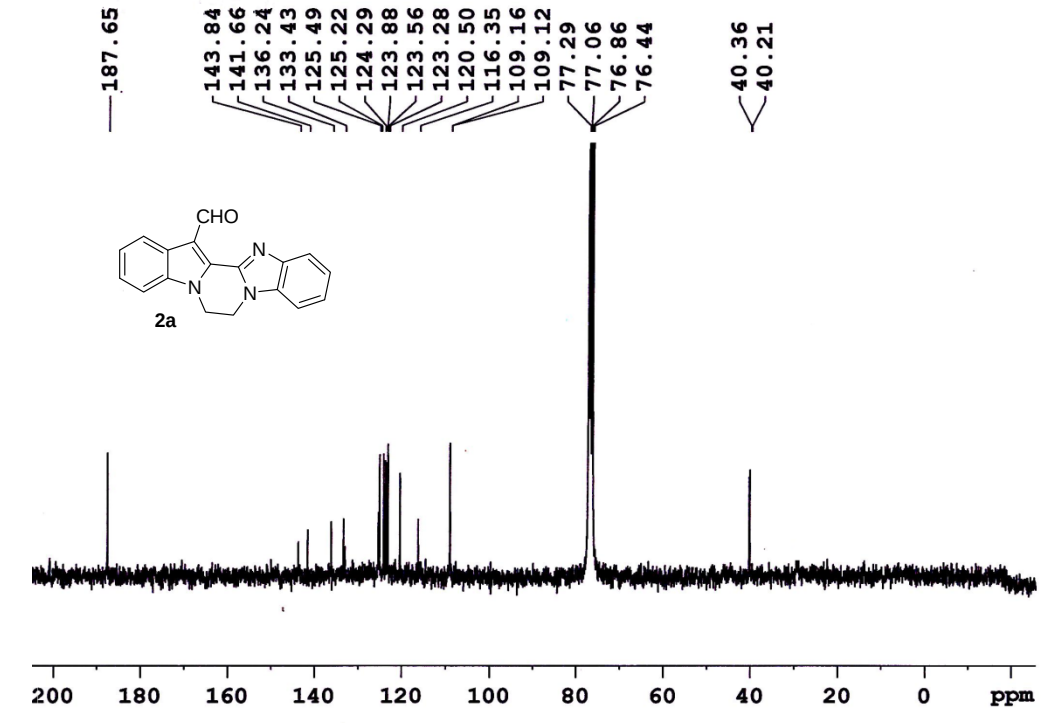

152.20
145.09
135.56
133.27
128.26
124.69
124.52
120.39
120.00
111.80
48.71
46.77
40.77
40.49
40.22
39.94
39.66
39.38
39.10
NO2
N
N
N
N
1j
180
160
140
120
100
80
60
40
20
0
ppm

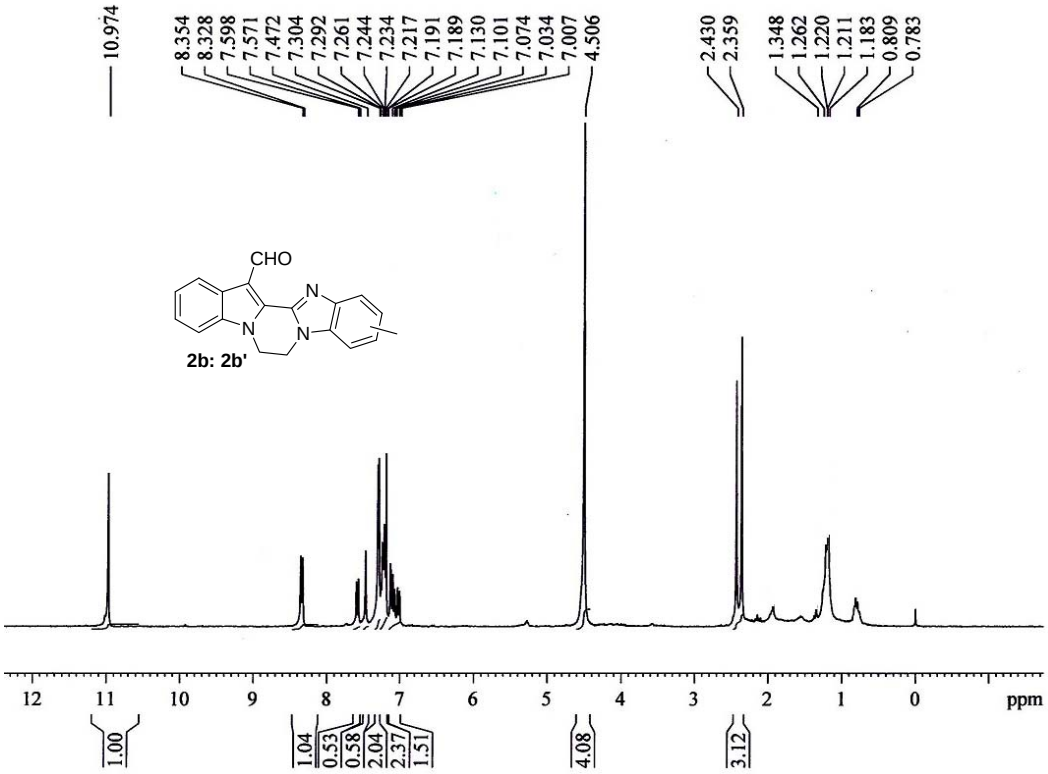

9.72
8.27
7.28
7.27
7.25
7.18
7.14
7.00
4.55
-0.01
CHO
N
N
OHC
1k
10
9
8
7
6
5
4
3
2
1
0
-1 ppm
1.97
1.97
4.95
7.99
1.97
4.00

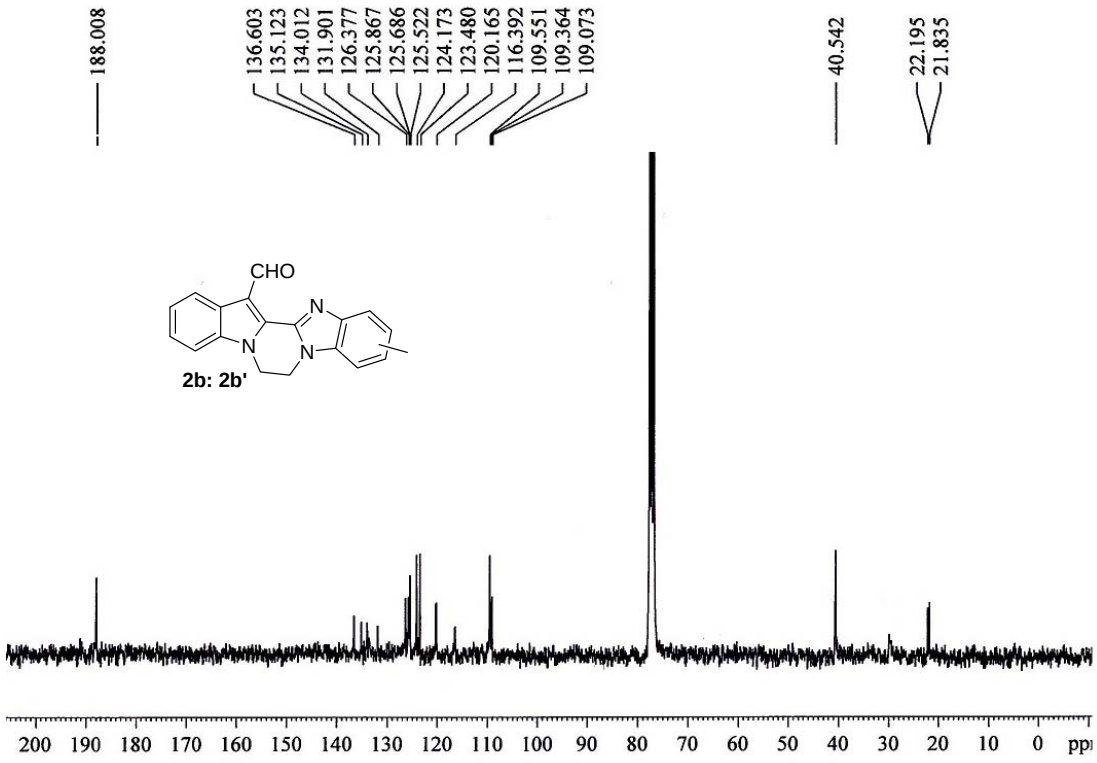

185.15
141.20
137.52
125.11
124.17
123.15
121.59
118.20
111.14
46.58
40.92
40.64
40.36
40.09
39.81
39.53
39.25
CHO
N
N
OHC
1k
200
180
160
140
120
100
80
60
40
20
0
ppm

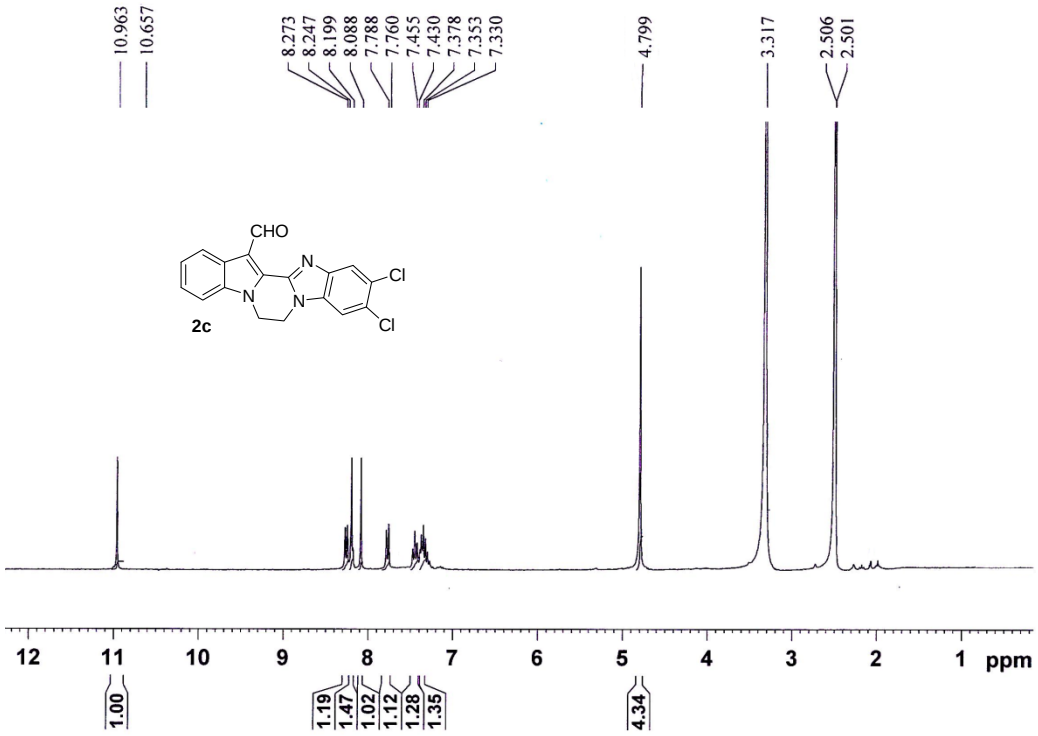

9.954
8.294
8.284
8.278
8.273
8.264
8.115
7.828
7.821
7.799
7.618
7.327
7.304
7.292
7.279
7.273
7.256
7.249
7.238
7.216
7.197
7.185
4.246
4.223
4.199
4.176
2.589
2.567
2.544
2.521
2.499
CHO
N
N
N
1l
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
1.04
1.09
1.03
3.84
0.60
0.62
3.80
1.96

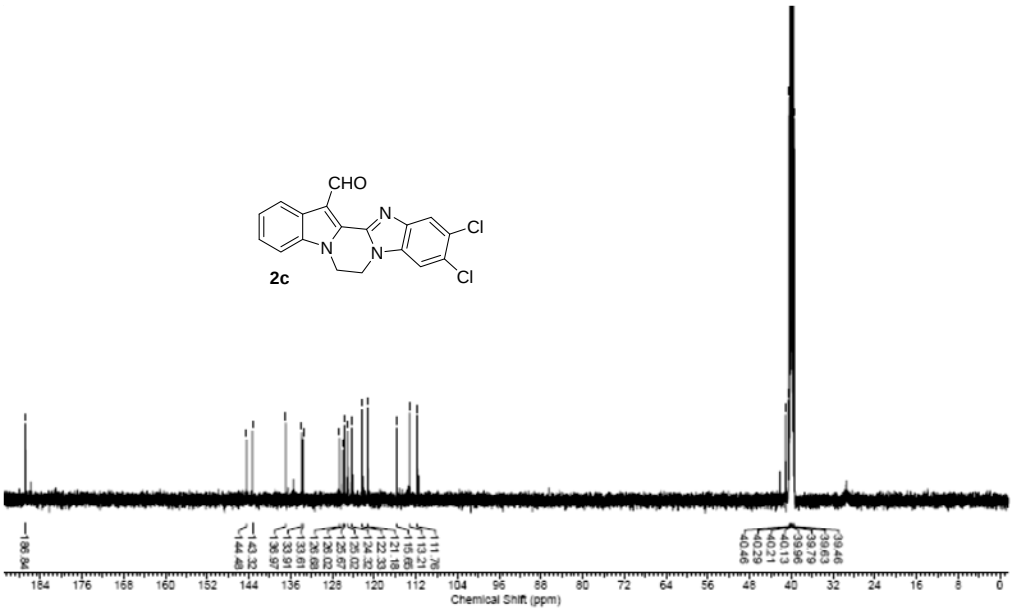

11.111
8.469
8.444
7.861
7.836
7.477
7.451
7.413
7.394
7.368
7.342
7.321
7.302
7.269
4.647
1.265
CHO
N
N
N
2a
11
10
9
8
7
6
5
4
3
2
1
ppm
0.76
0.86
1.25
6.97
4.00

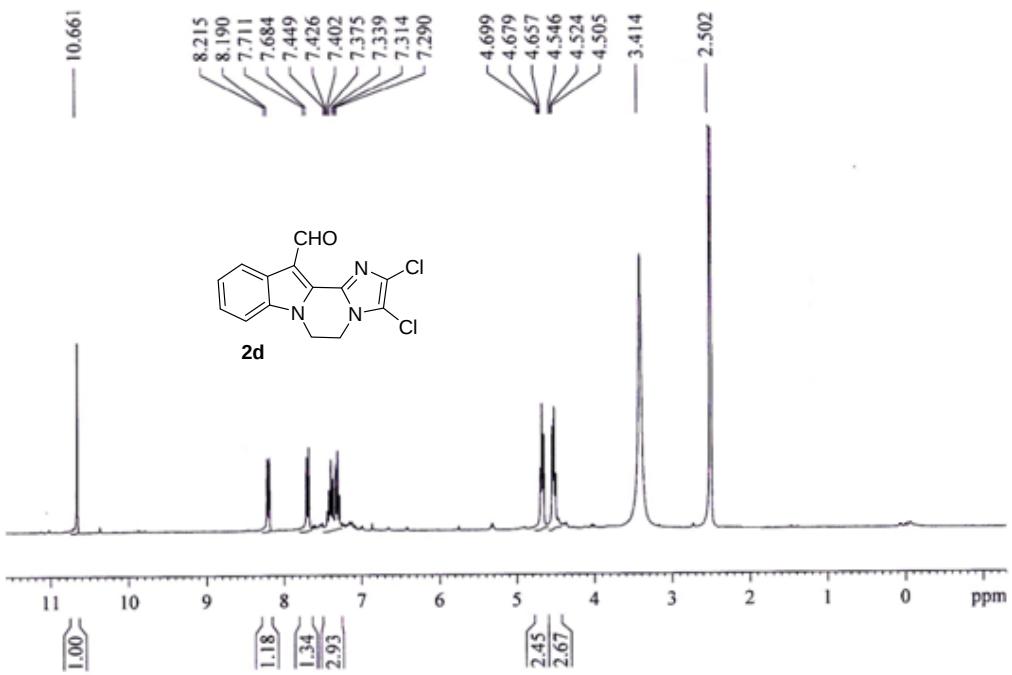

187.65
143.84
141.66
136.24
133.43
125.49
125.22
124.29
123.88
123.56
123.28
120.50
116.35
109.16
109.12
77.29
77.06
76.86
76.44
40.36
40.21
CHO
N
N
N
2a
200
180
160
140
120
100
80
60
40
20
0
ppm

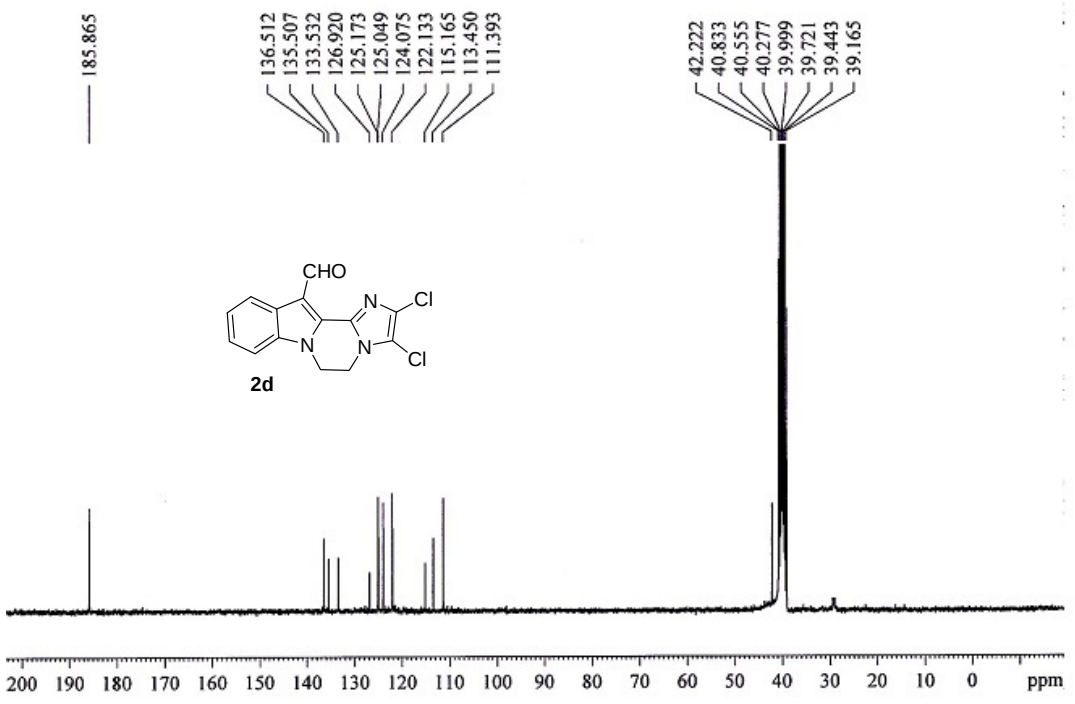

10.974
8.354
8.328
7.598
7.571
7.472
7.304
7.292
7.261
7.244
7.234
7.217
7.191
7.189
7.130
7.101
7.074
7.034
7.007
4.506
2.430
2.359
1.348
1.262
1.220
1.211
1.183
0.809
0.783
CHO
N
N
N
2b: 2b'
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
0.53
0.58
2.04
2.37
1.51
4.08
3.12

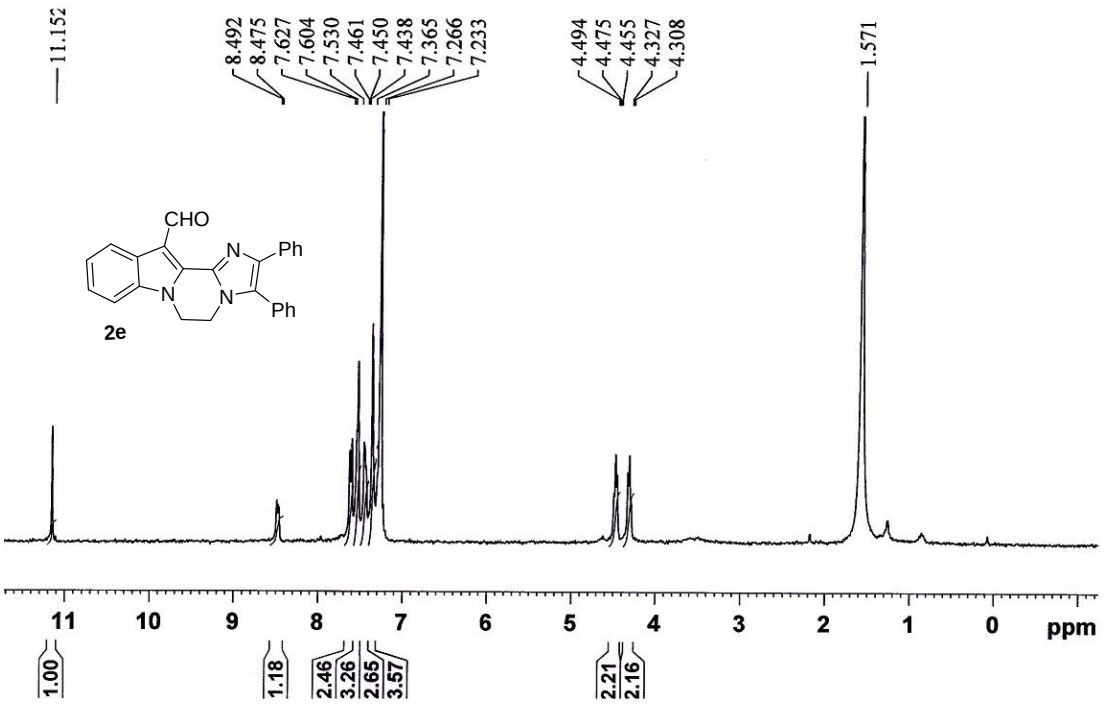

188.008
136.603
135.123
134.012
131.901
126.377
125.867
125.686
125.522
124.173
123.480
120.165
116.392
109.551
109.364
109.073
40.542
22.195
21.835
CHO
N
N
N
2b: 2b'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppı

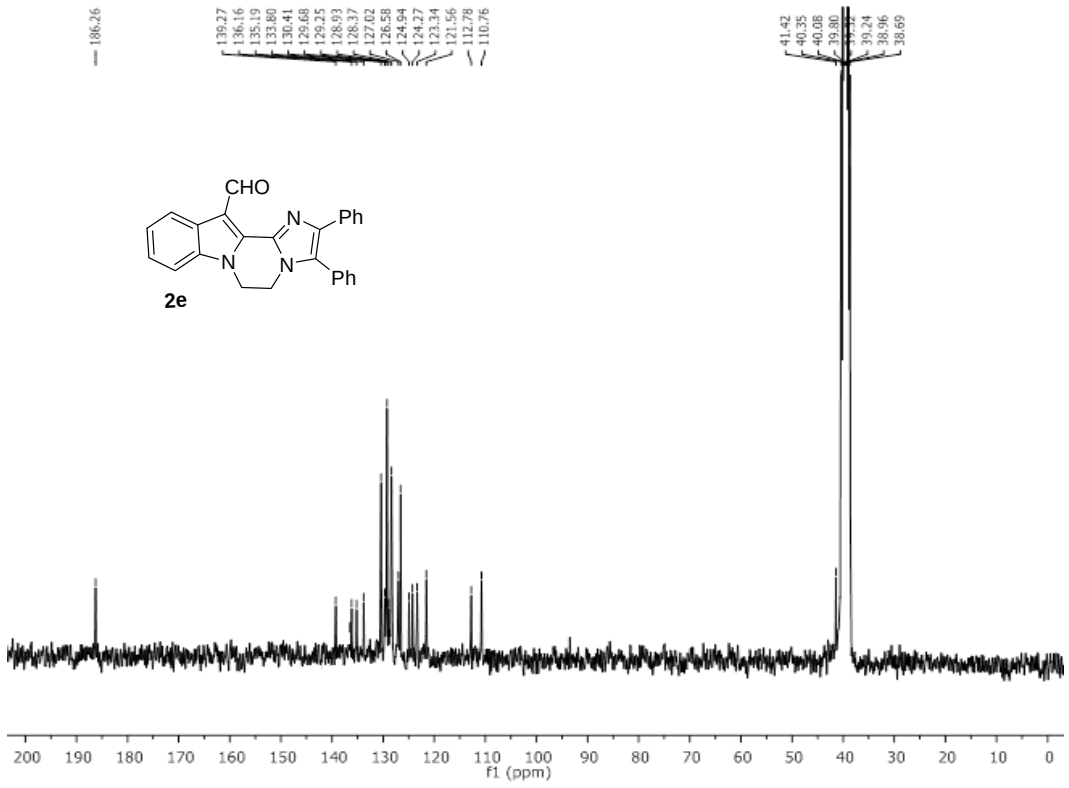

10.963
10.657
8.273
8.247
8.199
8.088
7.788
7.760
7.455
7.430
7.378
7.353
7.330
4.799
3.317
2.506
2.501
CHO
N
N
N
Cl
Cl
2c
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.19
1.47
1.02
1.12
1.28
1.35
4.34

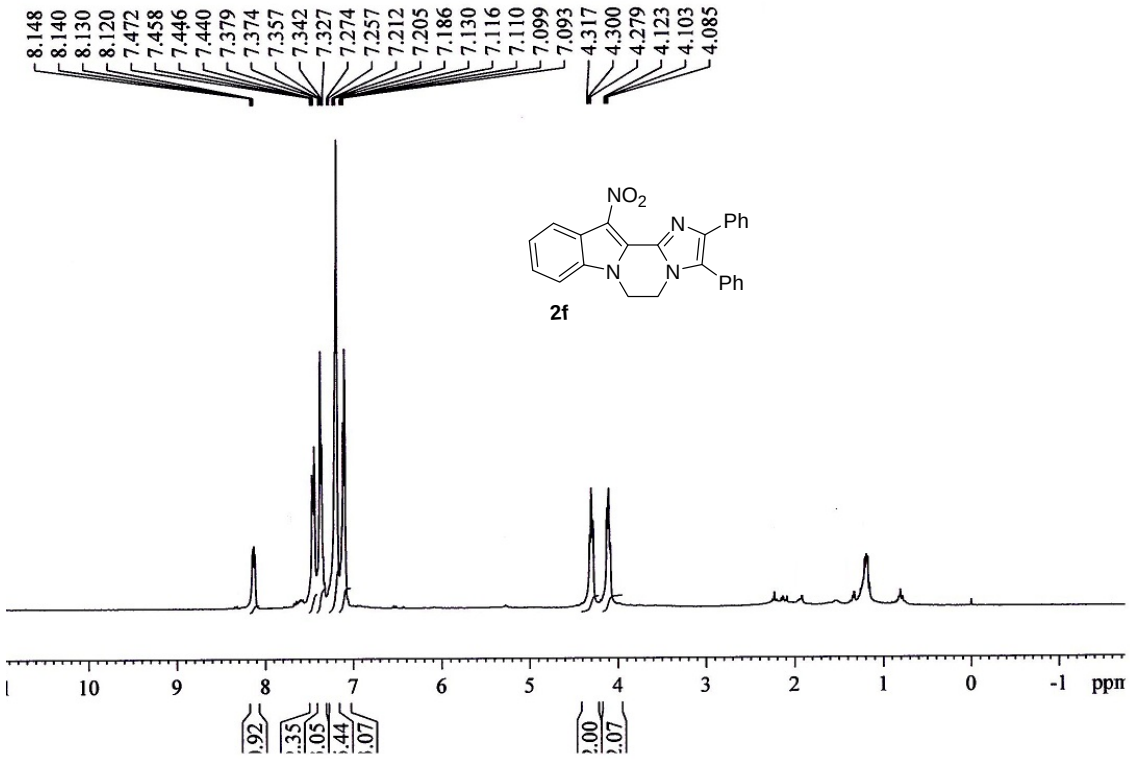

CHO
N
N
N
Cl
Cl
2c
Chemical Shift (ppm)

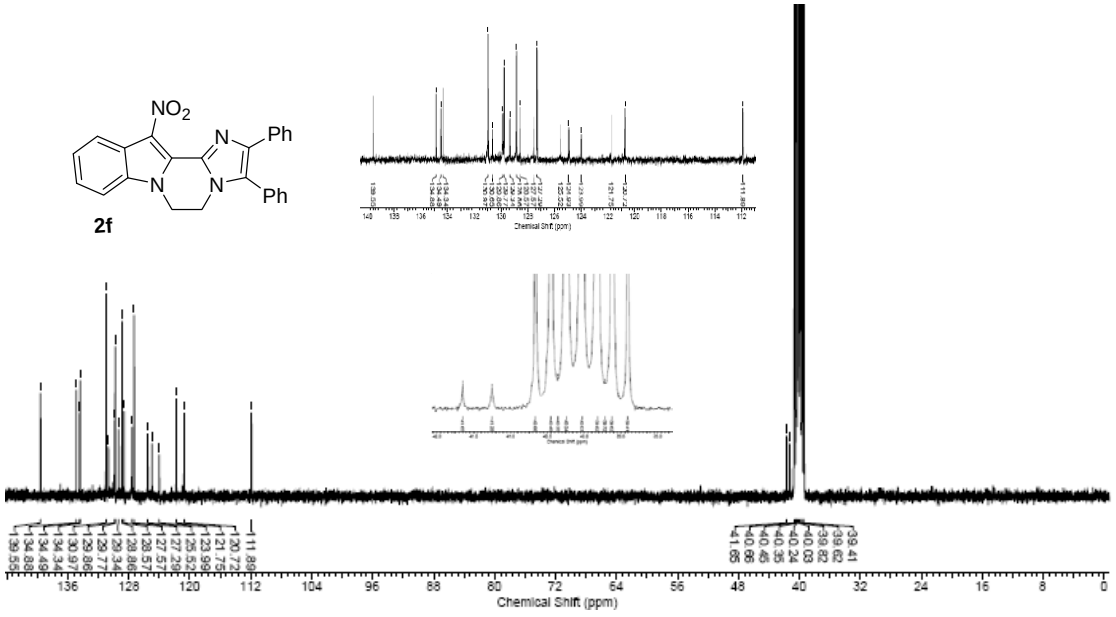

10.661
8.215
8.190
7.711
7.684
7.449
7.426
7.402
7.375
7.339
7.314
7.290
4.699
4.679
4.657
4.546
4.524
4.505
3.414
2.502
CHO
N
Cl
N
N
Cl
2d
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.18
1.34
2.93
2.45
2.67

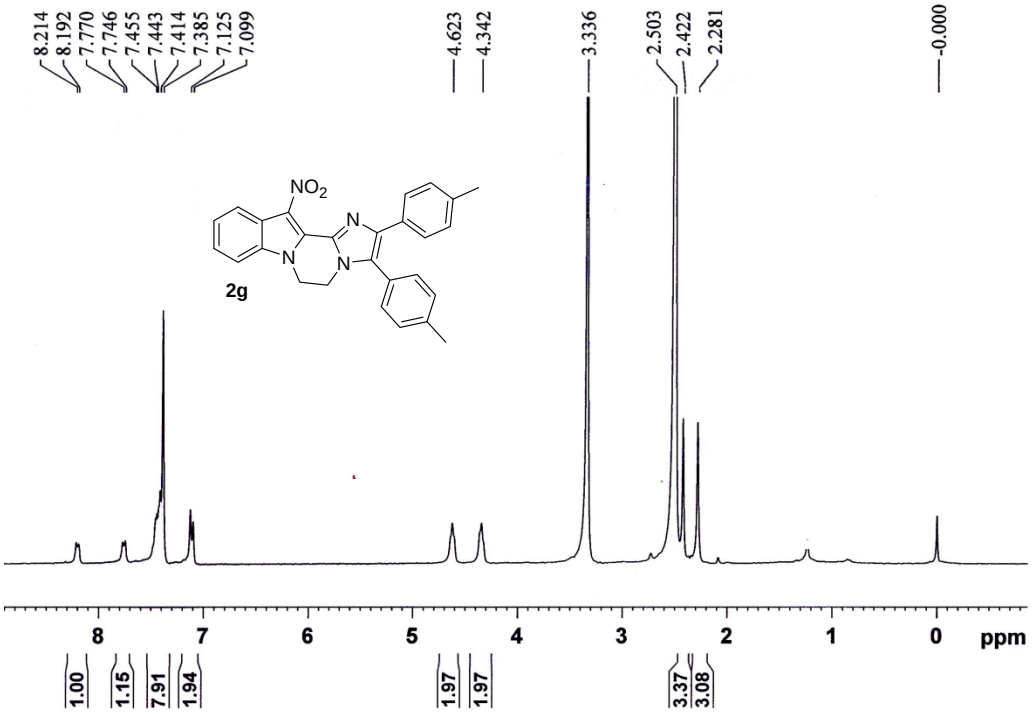

185.865
136.512
135.507
133.532
126.920
125.173
125.049
124.075
122.133
115.165
113.450
111.393
42.222
40.833
40.555
40.277
39.999
39.721
39.443
39.165
CHO
N
Cl
N
N
Cl
2d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

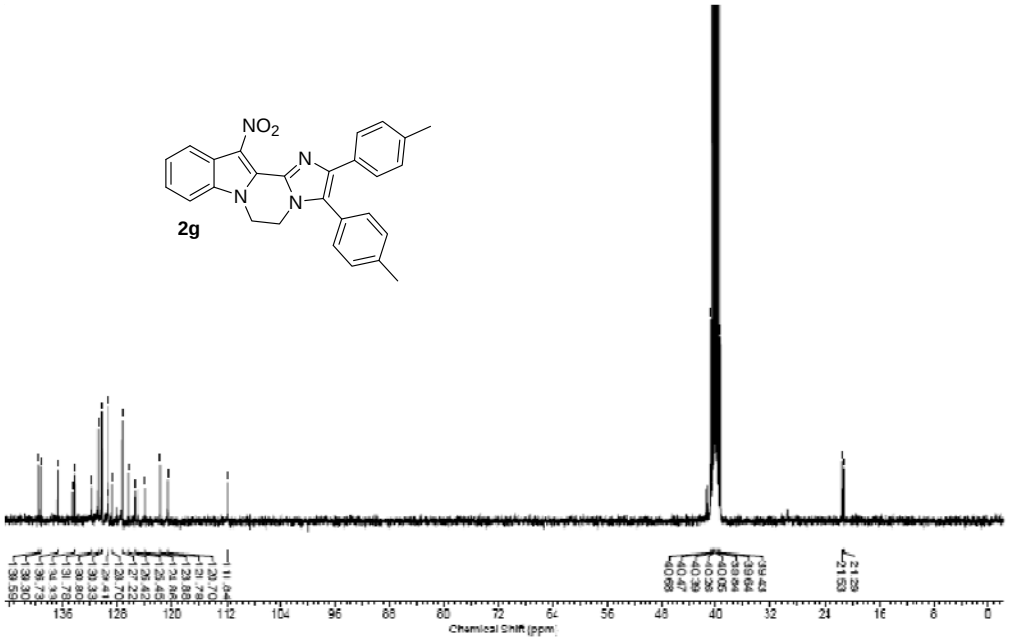

11.152
8.492
8.475
7.627
7.604
7.530
7.461
7.450
7.438
7.365
7.266
7.233
4.494
4.475
4.455
4.327
4.308
1.571
CHO
N
Ph
N
N
Ph
2e
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.18
2.46
3.26
2.65
3.57
2.21
2.16

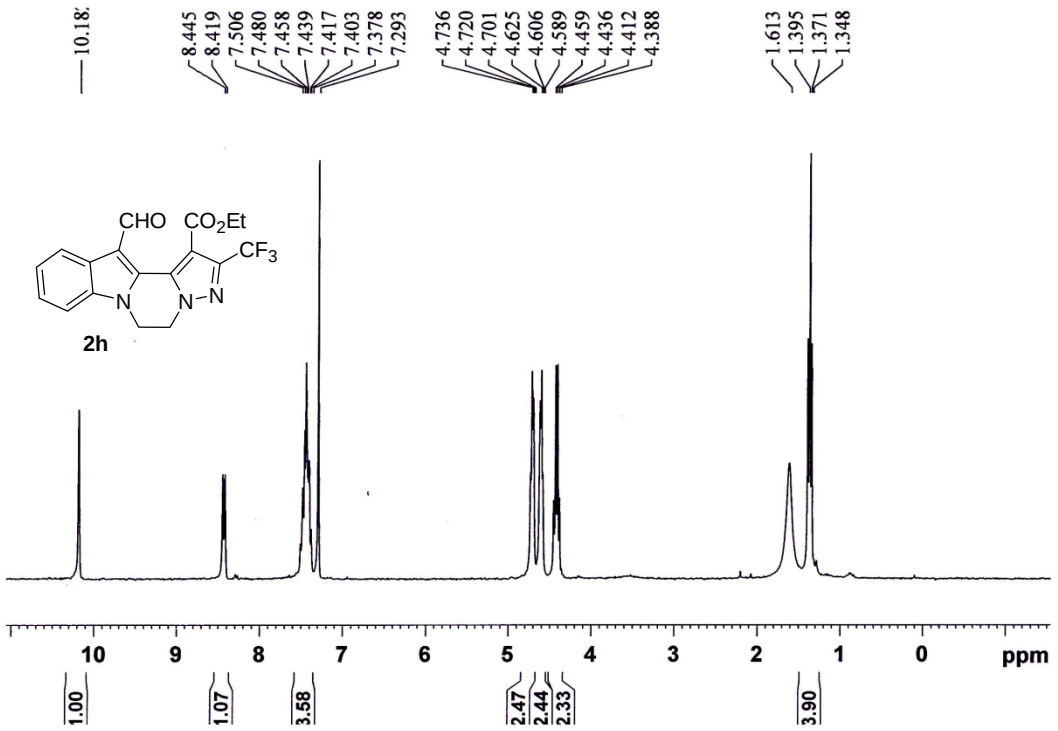

186.26
139.27
136.16
135.19
133.80
130.41
129.68
129.25
128.93
128.37
127.02
126.58
124.94
124.64
124.27
123.34
121.56
112.78
110.76
41.42
40.35
40.08
39.80
39.24
38.96
38.69
CHO
N
Ph
N
N
Ph
2e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

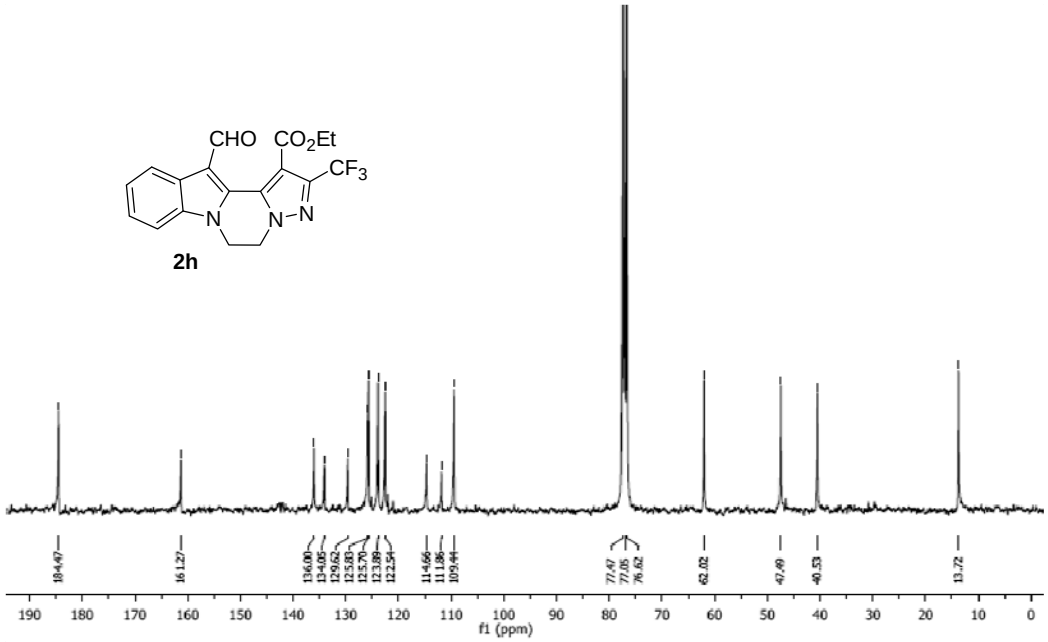

8.148
8.140
8.130
8.120
7.472
7.458
7.446
7.440
7.379
7.374
7.357
7.342
7.327
7.274
7.257
7.212
7.205
7.186
7.130
7.116
7.110
7.099
7.093
4.317
4.300
4.279
4.123
4.103
4.085
NO2
N
Ph
N
N
Ph
2f
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

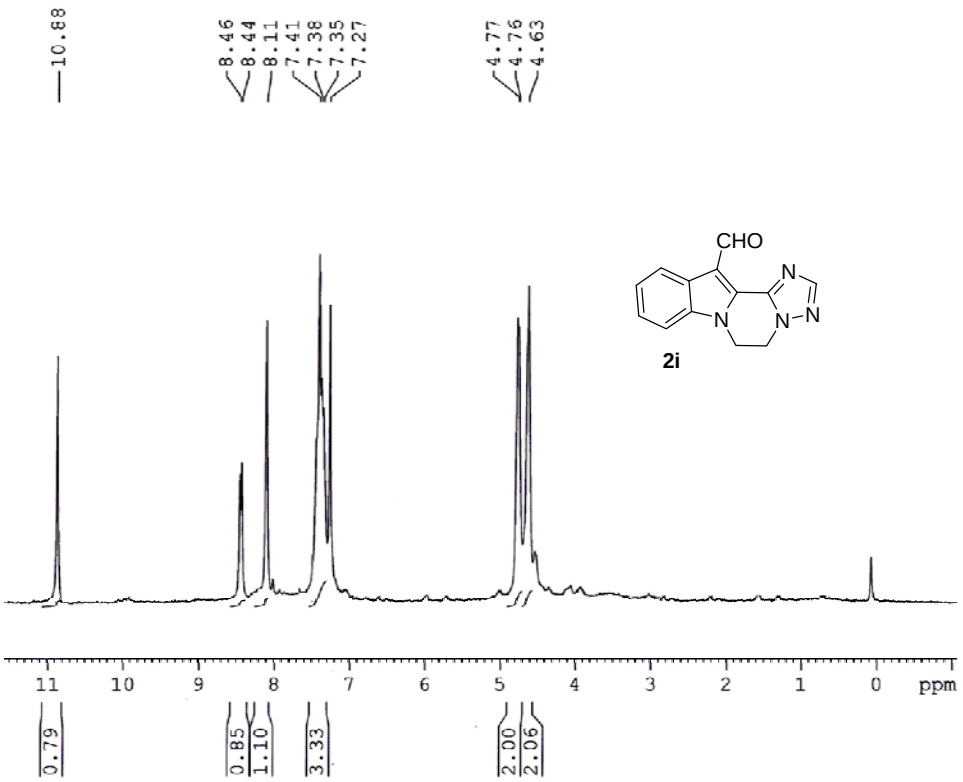

NO2
N
Ph
N
N
Ph
2f
Chemical Shift (ppm)

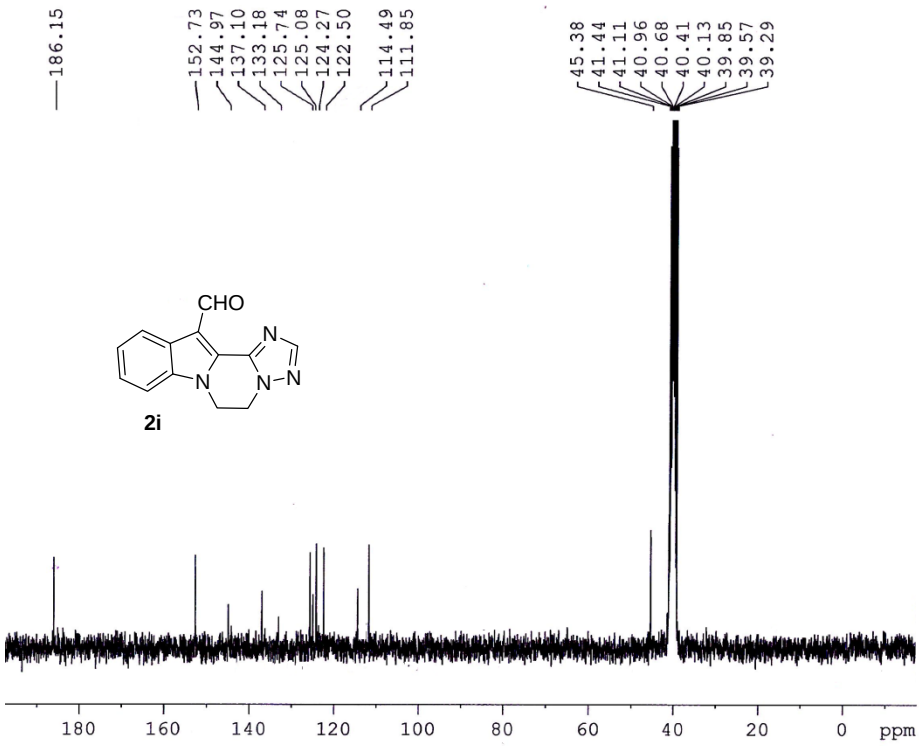

8.214
8.192
7.770
7.746
7.455
7.443
7.414
7.385
7.125
7.099
4.623
4.342
3.336
2.503
2.422
2.281
-0.000
NO2
N
N
N
2g
8
7
6
5
4
3
2
1
0
ppm
1.00
1.15
7.91
1.94
1.97
1.97
3.37
3.08

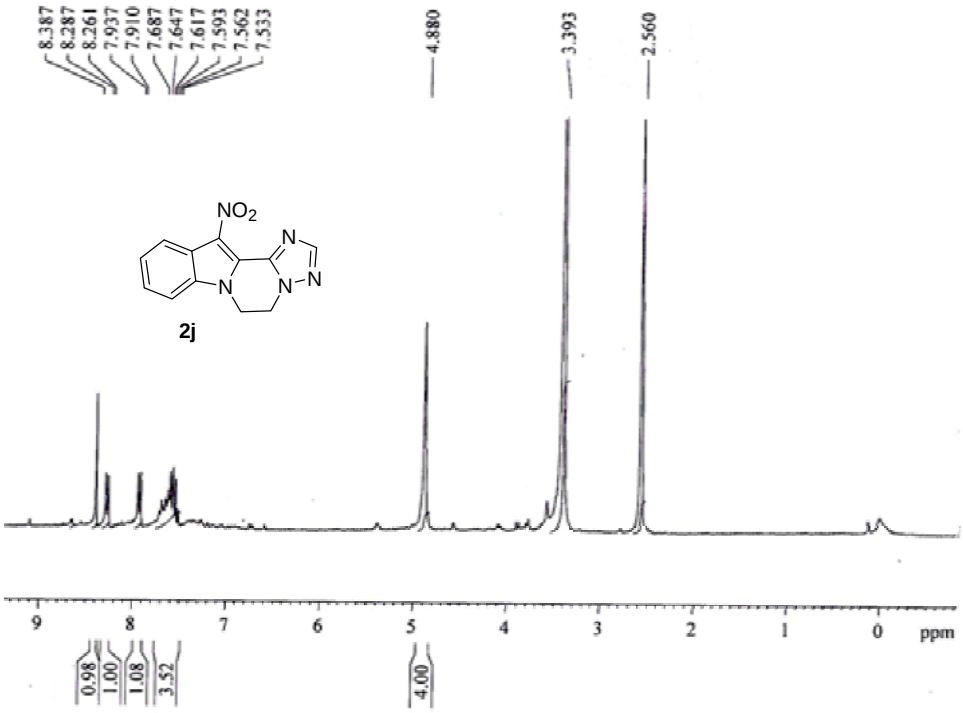

NO2
N
N
N
2g
Chemical Shift (ppm)

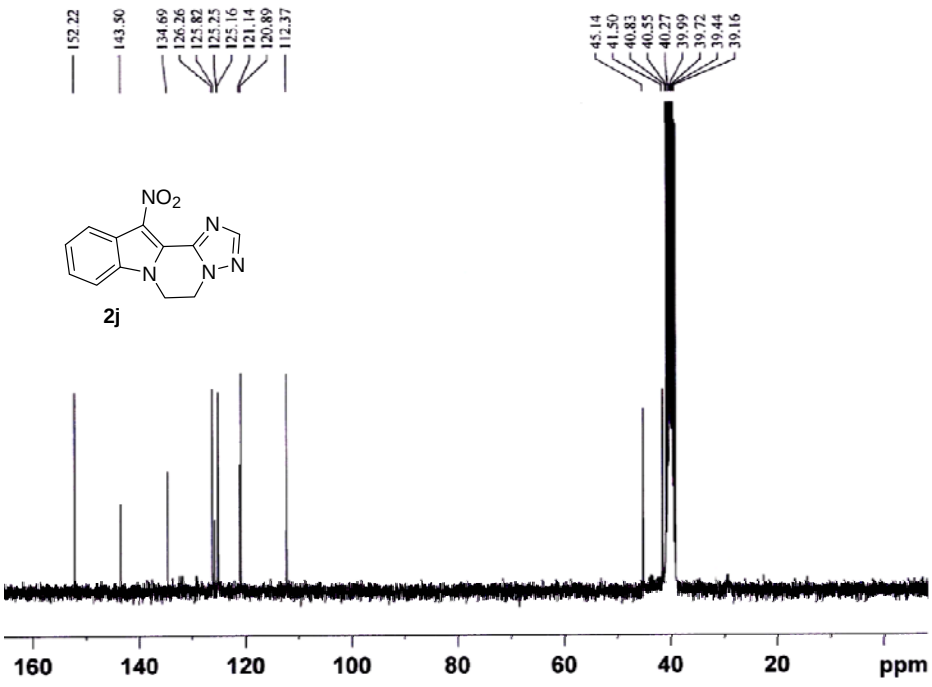

10.18
8.445
8.419
7.506
7.480
7.458
7.439
7.417
7.403
7.378
7.293
4.736
4.720
4.701
4.625
4.606
4.589
4.459
4.436
4.412
4.388
1.613
1.395
1.371
1.348
CHO
CO2Et
CF3
N
N-N
2h
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.07
3.58
2.47
2.44
2.33
3.90

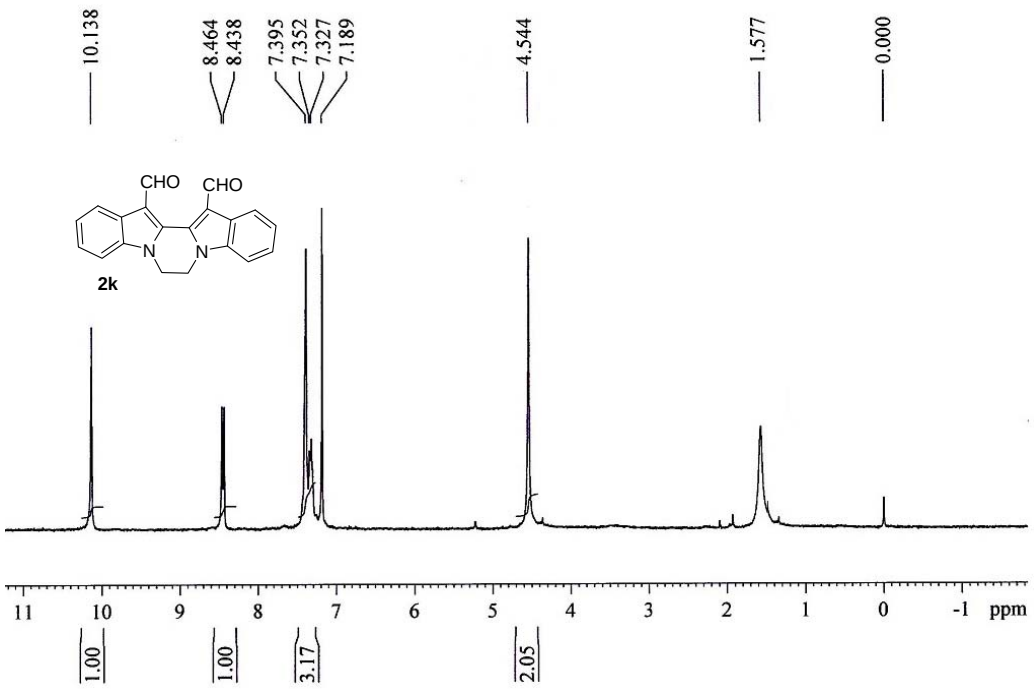

CHO
CO2Et
CF3
N
N-N
2h
184.47
161.27
136.00
134.05
129.62
125.83
125.70
123.89
122.54
114.66
111.38
109.44
77.47
77.05
76.62
62.02
47.49
40.53
13.72
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

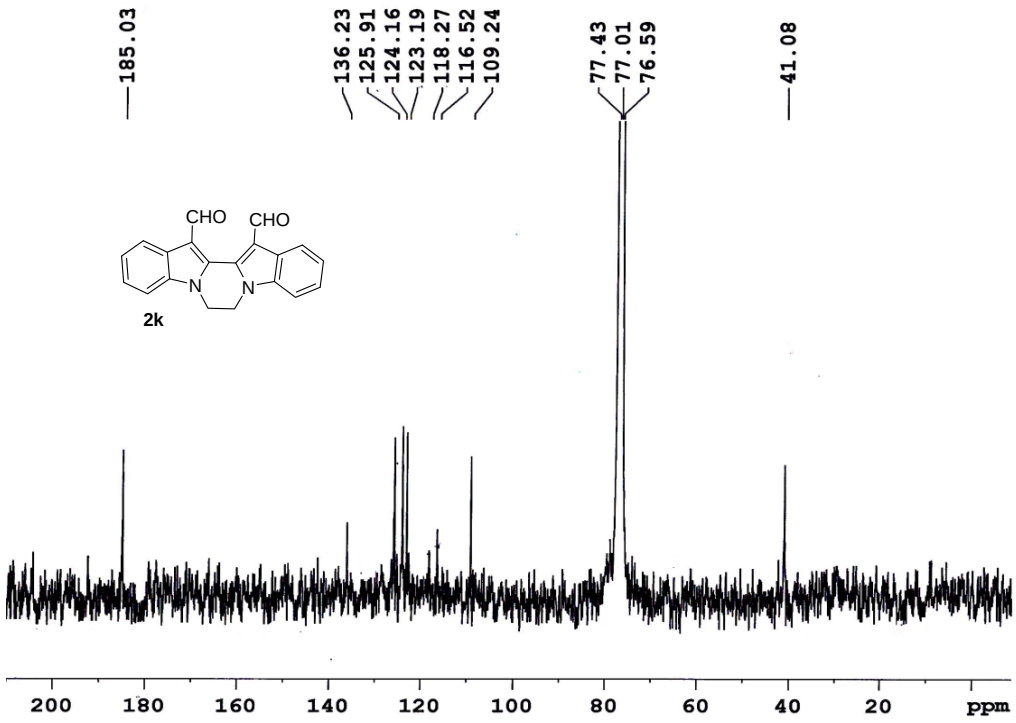

10.88
8.46
8.44
8.11
7.41
7.38
7.35
7.27
4.77
4.76
4.63
CHO
N
N
N
N
2i
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.79
0.85
1.10
3.33
2.00
2.06

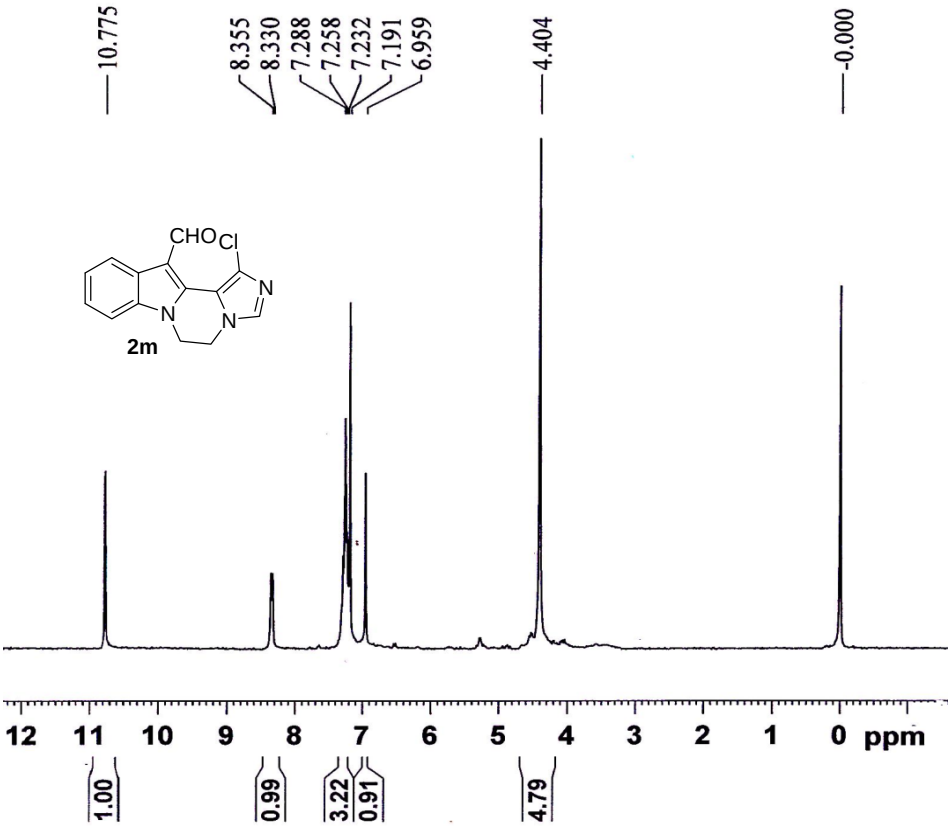

186.15
152.73
144.97
137.10
133.18
125.74
125.08
124.27
122.50
114.49
111.85
45.38
41.44
41.11
40.96
40.68
40.41
40.13
39.85
39.57
39.29
CHO
N
N
N
N
2i
180
160
140
120
100
80
60
40
20
0
ppm

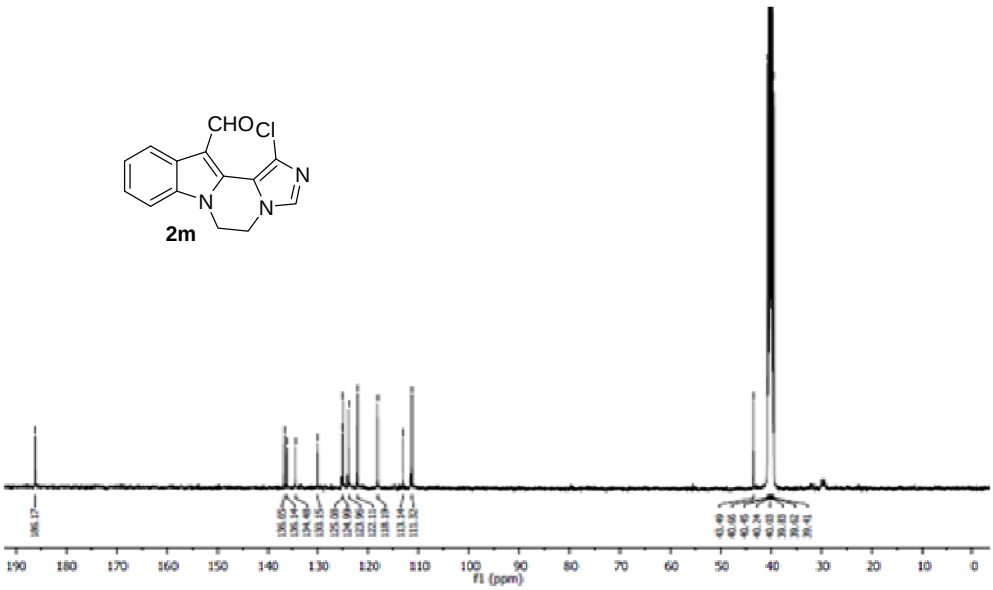

8.387
8.287
8.261
7.937
7.910
7.687
7.647
7.617
7.593
7.562
7.533
4.880
3.393
2.560
NO2
N
N
N
N
2j
9
8
7
6
5
4
3
2
1
0
ppm
0.98
1.00
1.08
3.52
4.00

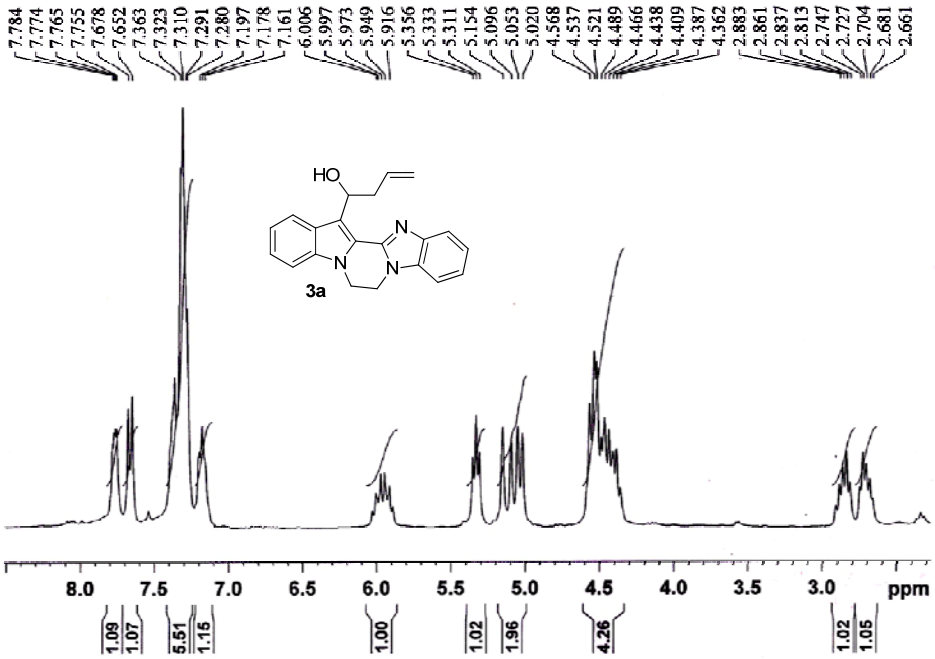

152.22
143.50
134.69
126.26
125.82
125.25
125.16
121.14
120.89
112.37
45.14
41.50
40.83
40.55
40.27
39.99
39.72
39.44
39.16
NO2
N
N
N
N
2j
160
140
120
100
80
60
40
20
ppm

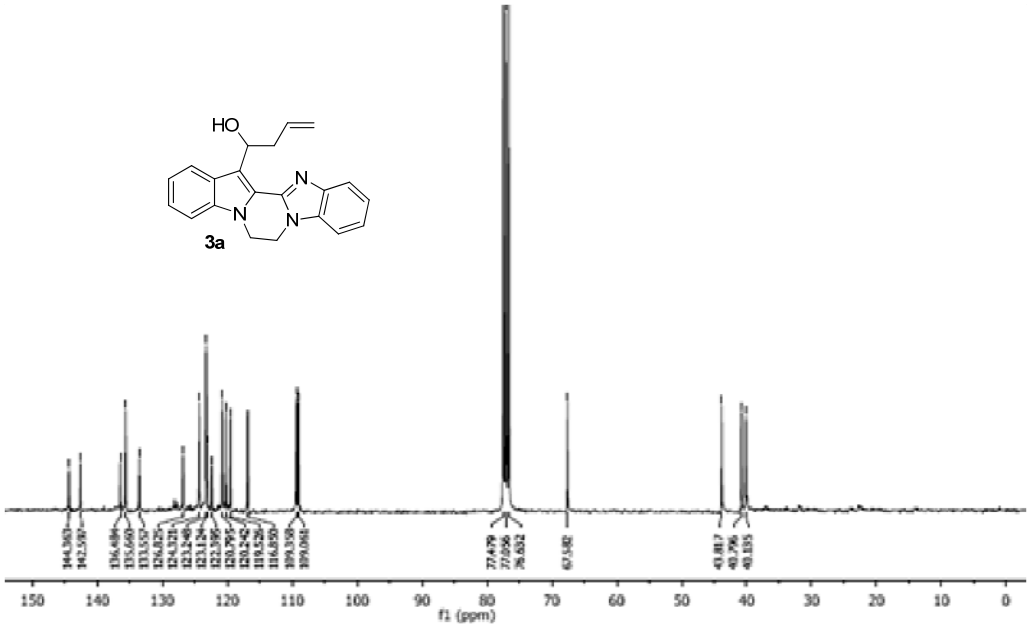

10.138
8.464
8.438
7.395
7.352
7.327
7.189
4.544
1.577
0.000
CHO
CHO
N
N
2k
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.00
3.17
2.05

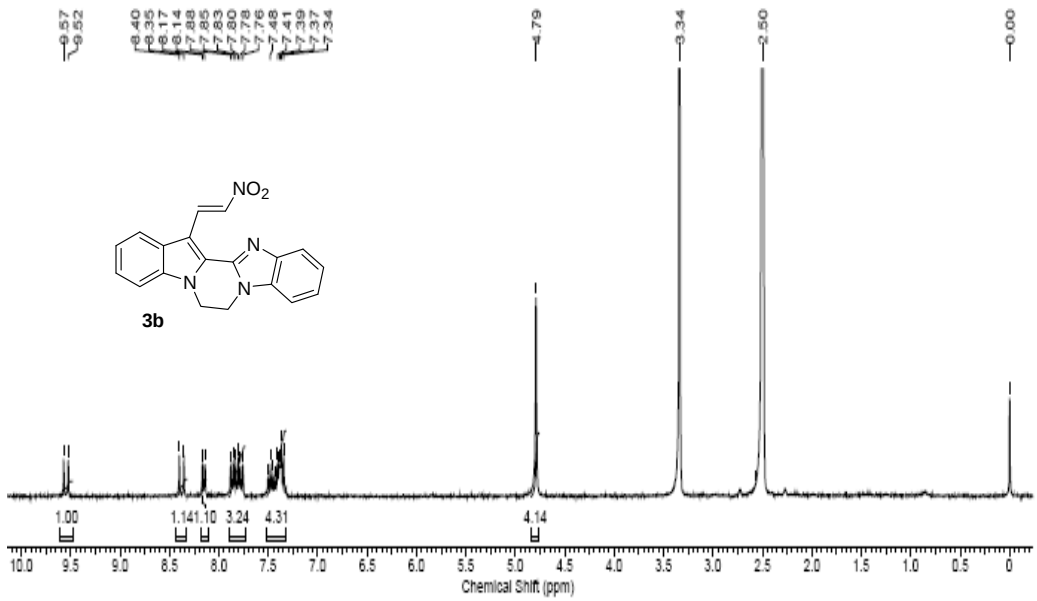

185.03
136.23
125.91
124.16
123.19
118.27
116.52
109.24
77.43
77.01
76.59
41.08
CHO
CHO
N
N
2k
200
180
160
140
120
100
80
60
40
20
ppm

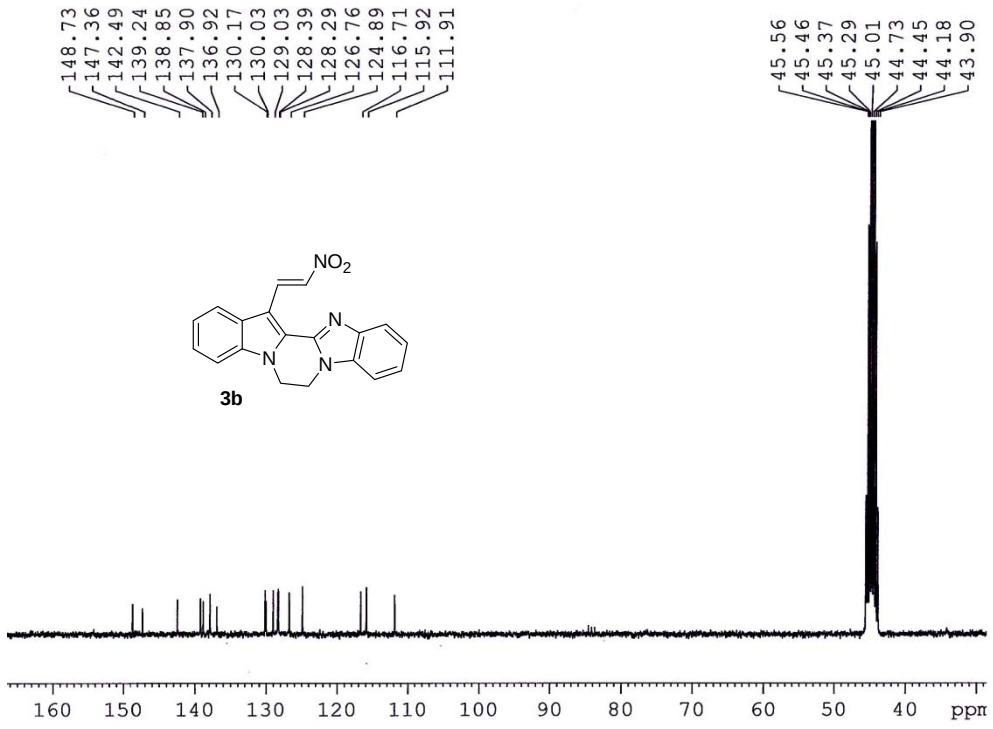

10.775
8.355
8.330
7.288
7.258
7.232
7.191
6.959
4.404
-0.000
CHO
Cl
N
N
N
2m
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
0.99
3.22
0.91
4.79

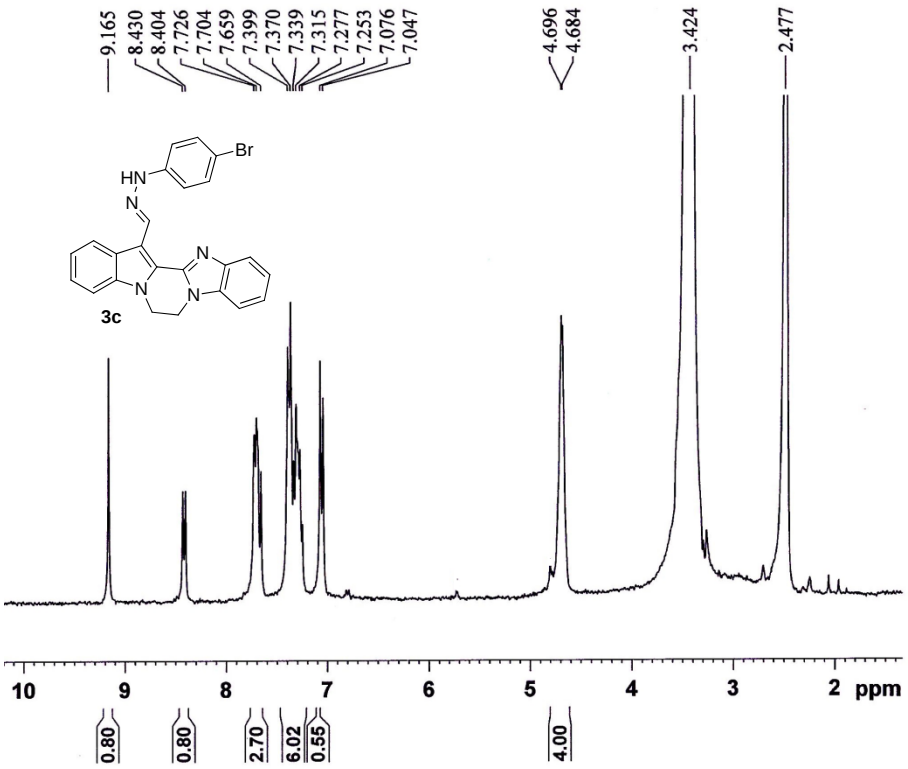

CHO
Cl
N
N
N
2m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

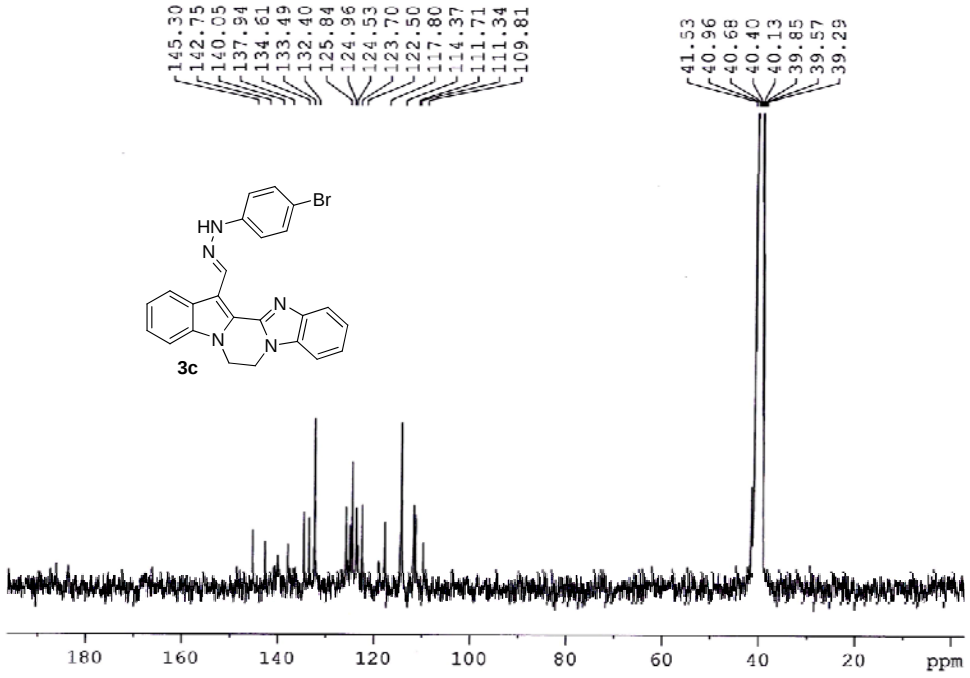

7.784
7.774
7.765
7.755
7.678
7.652
7.363
7.323
7.310
7.291
7.280
7.197
7.178
7.161
6.006
5.997
5.973
5.949
5.916
5.356
5.333
5.311
5.154
5.096
5.053
5.020
4.568
4.537
4.521
4.489
4.466
4.438
4.409
4.387
4.362
2.883
2.861
2.837
2.813
2.747
2.727
2.704
2.681
2.661
HO
N
N
N
3a
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
1.09
1.07
5.51
1.15
1.00
1.02
1.96
4.26
1.02
1.05

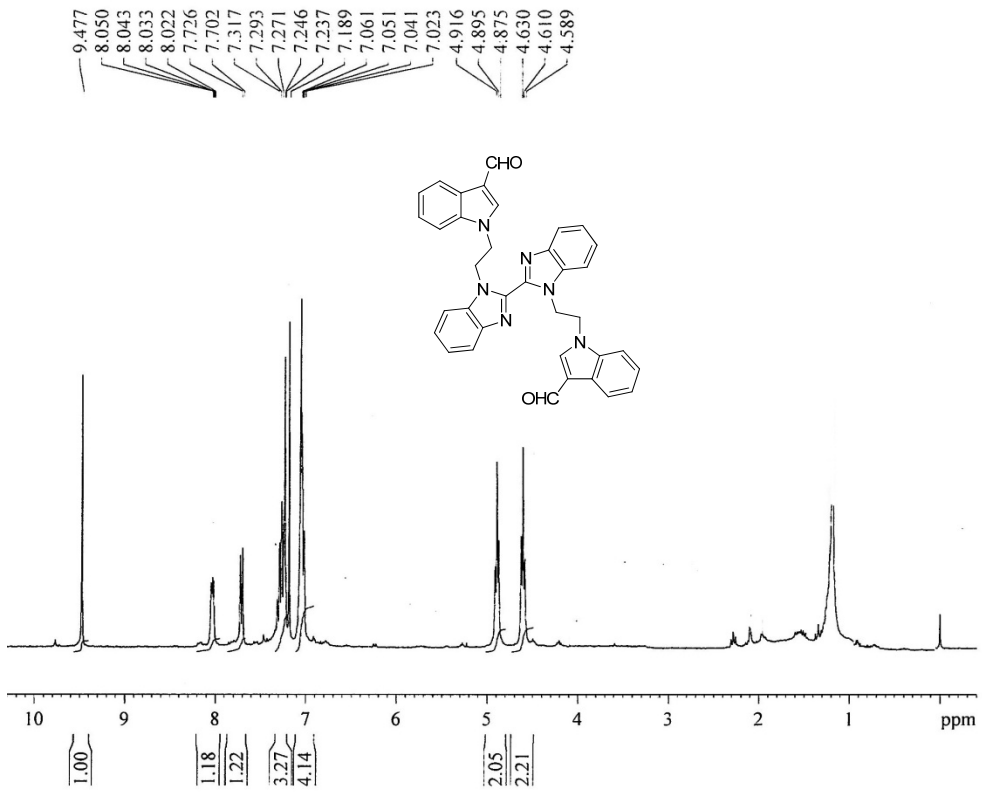

HO
N
N
N
3a
77.479
77.056
76.632
67.582
43.817
43.396
43.155
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

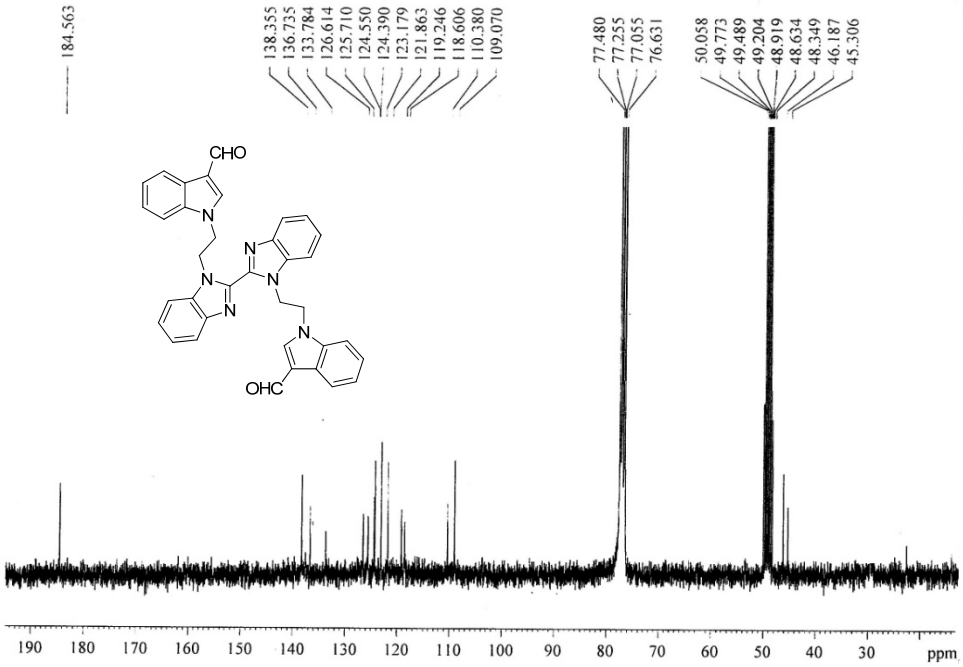

9.57
9.52
8.40
8.35
8.17
8.14
7.88
7.85
7.83
7.80
7.78
7.76
7.48
7.41
7.39
7.37
7.34
4.79
3.34
2.50
0.00
NO2
N
N
N
3b
1.00
1.14
1.10
3.24
4.31
4.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


148.73
147.36
142.49
139.24
138.85
137.90
136.92
130.17
130.03
129.03
128.39
128.29
126.76
124.89
116.71
115.92
111.91
45.56
45.46
45.37
45.29
45.01
44.73
44.45
44.18
43.90
NO2
N
N
N
3b
160 150 140 130 120 110 100 90 80 70 60 50 40 ppm


9.165
8.430
8.404
7.726
7.704
7.659
7.399
7.370
7.339
7.315
7.277
7.253
7.076
7.047
4.696
4.684
3.424
2.477
Br
HN
N
N
N
N
3c
10
9
8
7
6
5
4
3
2
ppm
0.80
0.80
2.70
6.02
0.55
4.00


145.30
142.75
140.05
137.94
134.61
133.49
132.40
125.84
124.96
124.53
123.70
122.50
117.80
114.37
111.71
111.34
109.81
41.53
40.96
40.68
40.40
40.13
39.85
39.57
39.29
Br
HN
N
N
N
N
3c
180
160
140
120
100
80
60
40
20
ppm


9.477
8.050
8.043
8.033
8.022
7.726
7.702
7.317
7.293
7.271
7.246
7.237
7.189
7.061
7.051
7.041
7.023
4.916
4.895
4.875
4.630
4.610
4.589
CHO
OHC
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.18
1.22
3.27
4.14
2.05
2.21


184.563
138.355
136.735
133.784
126.614
125.710
124.550
124.390
123.179
121.863
119.246
118.606
110.380
109.070
77.480
77.255
77.055
76.631
50.058
49.773
49.489
49.204
48.919
48.634
48.349
46.187
45.306
CHO
OHC
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

Crystal structure for compound 2h: