ELECTRONIC SUPPORTING INFORMATION

Efficient electron transfer through a triazole link in ruthenium(II) polypyridine type complexes

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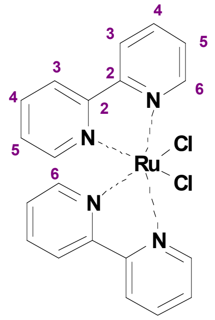
SYNTHESIS

Thin layer chromatography was performed over Merck 60 F254 or Macherey-Nagel ALUGRAM® Xtra SIL G/UV_{254} sheets with detection by UV. Silica gel 60 63-200 μm or SDS 60 ACC 5-35 μm were used for flash column chromatography. NMR spectra were taken on Bruker DPX 250, AM 300, AV 360 or AV 400 spectrometers, using the residual protonated solvent as internal standard. Chemical shifts δ are given in *parts per million* (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), doublet of doublet (dd), doublet of doublet of doublet (ddd). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Mass spectra were taken on a ThermoFinnigan Mat 95 or on a Thermo Scientific TSQ or on a Bruker micrOTOFq, with electrospray ionization in the positive (ESI^+) mode of detection. IR-FT spectra were recorded with KBr plates on a Bruker IFS 66 spectrometer.

***cis*-Dichloro-bis-(bipyridine) ruthenium:**[1]



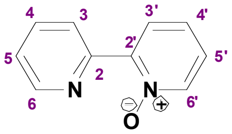
In a typical reaction $RuCl_3$ (2.00 g, 9.6 mmol, 1.0 eq.), lithium chloride (2.86 g, 67.5 mmol, 7.0 eq.) and 2,2'-bipyridine (3.31 g, 21.2 mmol, 2.2 eq.) were dissolved in dry DMF (20 mL). The mixture was heated at reflux overnight under an argon atmosphere. At this time the reaction mixture was allowed to reach room temperature and acetone (100 mL) was added. The solution was placed at -20°C overnight and the resulting black precipitate filtered. The black solid was washed with cold acetone. Typical yield: 70-75 %.

***cis*-Dichloro-bis-(bipyridine) ruthenium:** $C_{20}H_{16}Cl_2N_4Ru$

^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 9.97 (dd, 2H, ^3J 5.7, ^4J 1.0 Hz, 2 **H-6a**); 8.63 (dt, 2H, ^3J 8.1, ^4J 0.9 Hz, 2 **H-3a**); 8.48 (dt, 2H, ^3J 8.1, ^4J 1.0 Hz, 2 **H-3b**); 8.06 (ddd, 2H, ^3J 8.1, ^3J 7.5, ^4J 1.5 Hz, 2 **H-4a**); 7.77 (ddd, 2H, ^3J 7.5, ^3J 5.7, ^4J 1.4 Hz, 2 **H-5a**); 7.68 (ddd, 2H, ^3J 8.1, ^3J

7.5, ^4J 1.4 Hz, 2 **H-4b**); 7.51 (dd, 2H, ^3J 5.7, ^4J 0.7 Hz, 2 **H-6b**); 7.10 (ddd, 2H, ^3J 7.5, ^3J 5.7, ^4J 1.3 Hz, 2 **H-5b**). (in accordance with lit. values[2]) **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ: 160.2 (2 **C-2b**); 158.2 (2 **C-2a**); 153.1 (2 **C-6a**); 151.9 (2 **C-6b**); 134.5 (2 **C-4a**); 133.3 (2 **C-4b**); 125.3 (2 **C-5a**); 125.2 (2 **C-5b**); 122.8 (2 **C-3b**); 122.5 (2 **C-3a**).

2,2'-Bipyridine-1-oxide[3] (1):

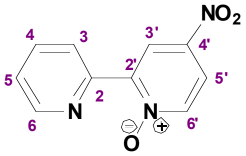


To a solution of 2,2'-bipyridine (7.8 g, 0.05 mol, 1.0 eq.) in trifluoroacetic acid (40.0 mL, 57.0 g, 0.50 mol, 10 eq.) was added 30% hydrogen peroxide (8.5 mL, 2.6 g, 0.075 mol, 1.5 eq.). After stirring at room temperature for 4 h, the reaction mixture was neutralised by addition of aqueous 6N NaOH and extracted with chloroform (4 x 50 mL). The combined organic layers were washed with aqueous saturated NaCl, dried over Na_2SO_4, filtered and concentrated to afford a colourless oil, which solidified under vacuum into a white solid (7.57 g, 0.044 mol, 88 %).

2,2'-Bipyridine-*N*'-oxide (1): $C_{10}H_7N_3O_3$

^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.83 (ddd, 1H, $J_{3,4}$ 8.1, $^4J_{3,5}$ 0.9, $^5J_{3,6}$ 0.8 Hz, **H-3**); 8.67 (ddd, 1H, $J_{6,5}$ 4.7, $^4J_{6,4}$ 1.7, $^5J_{6,3}$ 0.8 Hz, **H-6**); 8.26 (dd, 1H, $J_{6',5'}$ 6.4, $^4J_{6',4'}$ 1.1 Hz, **H-6'**); 8.11 (dd, 1H, $J_{3',4'}$ 8.0, $^4J_{3',5'}$ 2.2 Hz, **H-3'**); 7.77 (ddd, 1H, $J_{4,3}$ 8.1, $J_{4,5}$ 7.5, $^4J_{4,6}$ 1.7 Hz, **H-4**); 7.31 (ddd, 1H, $J_{4',3'}$ 8.0, $J_{4',5'}$ 7.4, $^4J_{4',6'}$ 1.1 Hz, **H-4'**); 7.29 (ddd, 1H, $J_{5,4}$ 7.5, $J_{5,6}$ 4.7, $^4J_{5,3}$ 0.9 Hz, **H-5**), 7.21 (ddd, 1H, $J_{4',5'}$ 7.4, $J_{5',6'}$ 6.4, $^4J_{5',3'}$ 2.2 Hz, **H-5'**). (in accordance with lit. values[3]) **^{13}C NMR (100 MHz, CDCl$_3$)** δ: 149.7 (**C-2**); 149.5 (**C-6**); 147.4 (**C-2'**); 140.7 (**C-6'**); 136.3 (**C-4**); 127.9 (**C-3'**); 127.7 (**C-4'**); 125.5 (**C-3**); 125.3 (**C-5'**); 124.3 (**C-5**).**MS (ESI$^+$)**: *m/z* 195.1 $[M+Na]^+$.**HRMS (ESI$^+$)**: calculated for $C_{10}H_8N_2ONa$ 195.0529, found 195.0526.

4'-Nitro-2,2'-bipyridine-*N*'-oxide[4] (2):

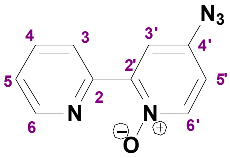


2,2’-Bipyridine-*N’*-oxide (**1**) (3.0 g, 17.0 mmol, 1 eq.) was dissolved in concentrated sulphuric acid (19 mL, 34.2 g, 0.349 mol, 20 eq.) under stirring. A mixture of fuming nitric acid (30 mL, 43.9 g, 0.697 mol, 40 eq.) in concentrated sulphuric acid (14 mL, 25.7 g, 0.262 mol, 15 eq.) was added dropwise over 15 min and the reaction mixture was heated at 100°C for 5 hours. Once cooled, the solution was poured into ice (150 g) and adjusted to pH 8 using 38% aqueous NaOH. The light yellow precipitate was filtered and washed with water. The solid was dissolved in methylene chloride, water was added and the mixture was extensively extracted with methylene chloride. The combined organic layers were dried over sodium sulfate, filtered and concentrated to yield 1.52 g (7.0 mmol, 40 %) of *4’-nitro-2,2’-bipyridine-N’-oxide* as a beige solid.

4’-Nitro-2,2’-bipyridine-*N*’-oxide (2): $C_{10}H_7N_3O_3$

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.14 (d, 1H, $^{4}J_{3',5'}$ 3.3 Hz, **H-3’**); 8.86 (ddd, 1H, $J_{3,4}$ 8.1, $^{4}J_{3,5}$ 1.0, $^{5}J_{3,6}$ 0.8 Hz, **H-3**); 8.77 (ddd, 1H, $J_{6,5}$ 4.7, $^{4}J_{6,4}$ 1.8, $^{5}J_{6,3}$ 0.8 Hz, **H-6**); 8.34 (d, 1H, $J_{6',5'}$ 7.2 Hz, **H-6’**); 8.04 (dd, 1H, $J_{5',6'}$ 7.2, $^{4}J_{5',3'}$ 3.3 Hz, **H-5’**); 7.86 (ddd, 1H, $J_{4,3}$ 8.1, $J_{4,5}$ 7.6, $^{4}J_{4,6}$ 1.8 Hz, **H-4**); 7.41 (ddd, 1H, $J_{5,4}$ 7.6, $J_{5,6}$ 4.7, $^{4}J_{5,3}$ 1.0 Hz, **H-5**). (in accordance with lit. values[5]) **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 150.0 (**C-6**); 148.4 (**C-2**); 147.8 (**C-2’**); 142.6 (**C-4’**); 142.1 (**C-6’**); 136.8 (**C-4**); 125.5 (**C-3**); 125.2 (**C-5**); 122.7 (**C-3’**); 119.0 (**C-5’**). **MS (ESI$^+$)**: *m/z* 218.1 $[M+H]^+$.

4’-Azido-2,2’-bipyridine-*N*’-oxide (3):



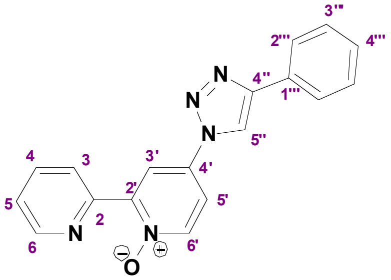
4’-Nitro-2,2’-bipyridine-*N’*-oxide (**2**) (1.09 g, 5.0 mmol, 1 eq.) and sodium azide (1.17 g, 18.0 mmol, 3.6 eq.) were suspended in anhydrous DMF (50 mL) and heated at 80°C for 48 hours under an argon atmosphere. After evaporation of the solvent, water was added and the mixture was extensively extracted with methylene chloride. The combined organic layers were dried over sodium sulfate, filtered and concentrated to yield 0.97 g (4.6 mmol, 91 %) of *4’-azido-2,2’-bipyridine-N’-oxide* as an orange solid.

4’-Azido-2,2’-bipyridine-*N*’-oxide (3): $C_{10}H_7N_5O$

^{1}H NMR (360 MHz, $CDCl_3$) δ: 8.99 (ddd, 1H, $J_{3,4}$ 8.1, $^{4}J_{3,5}$ 1.1, $^{5}J_{3,6}$ 0.9 Hz, **H-3**); 8.70 (ddd, 1H, $J_{6,5}$ 4.8, $^{4}J_{6,4}$ 1.8, $^{5}J_{6,3}$ 0.9 Hz, **H-6**); 8.22 (d, 1 H, $J_{6',5'}$ 7.0 Hz, **H-6’**); 7.94 (d, 1H, $^{4}J_{3',5'}$

3.3 Hz, **H-3'**); 7.82 (ddd, 1H, $J_{4,3}$ 8.1, $J_{4,5}$ 7.5, $^4J_{4,6}$ 1.8 Hz, **H-4**); 7.35 (ddd, 1H, $J_{5,4}$ 7.5, $J_{5,6}$ 4.8, $^4J_{5,3}$ 1.1 Hz, **H-5**); 6.87 (dd, 1H, $J_{5',6'}$ 7.0, $^4J_{5',3'}$ 3.3 Hz, **H-5'**). **^{13}C NMR (90 MHz, CDCl$_3$)** δ: 149.6 (**C-6**); 149.0 (**C-2**); 148.1 (**C-2'**); 142.0 (**C-6'**); 138.5 (**C-4'**); 136.6 (**C-4**); 125.8 (**C-3**); 124.9 (**C-5**); 117.7 (**C-3'**); 116.3 (**C-5'**). **MS (ESI$^+$)**: *m/z* 236.1 [M+Na]$^+$. **HRMS (ESI$^+$)**: calculated for $C_{10}H_7N_5ONa$ 236.05428, found 236.05452. **IR:** υ (cm^{-1}) = 3425, 3055, 2923, 2112 **(N$_3$)**, 1621, 1479, 1463, 1446, 1408, 1253, 1230, 1135, 1121.

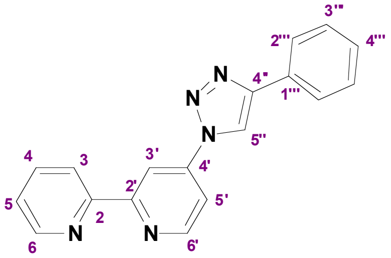
4'-(4''-Phenyl-1*H*-1'',2'',3''-triazol-1''-yl)-2,2'-bipyridine-*N*'-oxide (5a):



4'-Azido-2,2'-bipyridine-*N'*-oxide (**3**) (42.6 mg, 200 µmol, 1 eq.) was suspended in CH_2Cl_2 (1.67 mL)[6] under an argon atmosphere. Phenyl acetylene (**4a**) (22.0 µL, 20.4 mg, 200 µmol, 1 eq.) was added, followed by successive addition of water (1.51 mL), sodium ascorbate (80 µL, 0.250 M in water, 4.0 mg, 20 µmol, 0.10 eq.) and copper sulfate pentahydrate (80 µL, 0.125 M in water, 2.5 mg, 10 µmol, 0.05 eq.). After 20 hours of stirring at room temperature TLC in CH_2Cl_2/CH_3OH (9:1) showed quantitative conversion. The reaction mixture was diluted with 6 mL of CH_2Cl_2/H_2O (1:1) and extensively extracted with CH_2Cl_2. The organic layers were combined and washed with water, dried over sodium sulfate, filtered and concentrated to yield 61.5 mg (195 µmol, 98 %) of *4'-(4''-phenyl-1H-1'',2'',3''-triazol-1''-yl)-2,2'-bipyridine-N'-oxide* as a light yellow solid.

4'-(4''-Phenyl-1*H*-1'',2'',3''-triazol-1''-yl)-2,2'-bipyridine-*N*'-oxide (5a): $C_{18}H_{13}N_5O$
^{1}H NMR (360 MHz, CDCl$_3$) δ: 9.10 (d, 1H, $J_{3,4}$ 8.1 Hz, **H-3**); 8.76 (d, 1H, $J_{6,5}$ 4.2 Hz, **H-6**); 8.65 (d, 1H, $^4J_{3',5'}$ 3.3 Hz, **H-3'**); 8.42 (d, 1H, $J_{6',5'}$ 7.2 Hz, **H-6'**); 8.34 (s, 1H, **H-5''**); 7.94 (dd, 1H, $J_{5',6'}$ 7.2, $^4J_{5',3'}$ 3.3 Hz, **H-5'**); 7.93-7.88 (m, 2H, 2 **H-2'''**); 7.87 (ddd, 1H, $J_{4,3}$ 8.1, $J_{4,5}$ 7.5, $^4J_{4,6}$ 1.8 Hz, **H-4**); 7.50-7.35 (m, 4H, 2 **H-3'''**, **H-5**, **H-4'''**). **^{13}C NMR (90 MHz, CDCl$_3$)** δ: 149.7 (**C-6**); 149.5 (**C-4''**); 148.5 (**C-2**); 148.3 (**C-2'**); 142.5 (**C-6'**); 136.9 (**C-4**); 133.3 (**C-4'**); 129.7 (**C-1'''**); 129.3 (2 **C-3'''**); 129.1 (**C-4'''**); 126.2 (2 **C-2'''**, **C-6'''**); 125.8 (**C-3**); 125.3 (**C-5**); 117.5 (**C-3'**); 117.0 (**C-5''**); 116.4 (**C-5'**). **MS (ESI$^+$)**: *m/z* 338.1 [M+Na]$^+$. **HRMS (ESI$^+$)**: calculated for $C_{18}H_{13}N_5ONa$ 338.10123, found 338.10183.

4’-(4’’-Phenyl-1*H*-1’’,2’’,3’’-triazol-1’’-yl)-2,2'-bipyridine (6a):

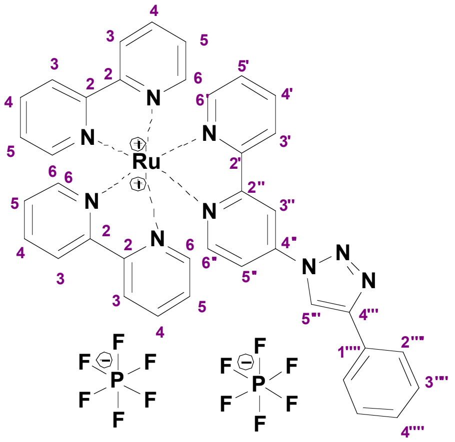


To a solution of 4’-(4’’-phenyl-1*H*-1’’,2’’,3’’-triazol-1’’-yl)-2,2'-bipyridine-*N’*-oxide (**5a**) (59.8 mg, 190 µmol, 1 eq.) in CH_2Cl_2 (3.8 mL) phosphorous trichloride (49.7 µL, 78.3 mg, 570 µmol, 3.0 eq.) was added at 0°C under an argon atmosphere.[7] The reaction mixture was heated at reflux for 3 hours, then poured into 4 mL of ice and neutralised with 38.5% sodium hydroxide. The aqueous layer was extensively extracted with CH_2Cl_2. The organic layers were combined and washed with water, then dried over sodium sulfate, filtered and concentrated. The residue was purified by flash chromatography using silica gel (CH_2Cl_2/CH_3OH 95:5), to yield 49.2 mg (164 µmol, 87 %) of *4’-(4’’-phenyl-1H-1’’,2’’,3’’-triazol-1’’-yl)-2,2'-bipyridine* as a light yellow solid.

4’-(4’’-Phenyl-1*H*-1’’,2’’,3’’-triazol-1’’-yl)-2,2'-bipyridine (6a): $C_{18}H_{13}N_5$

^{1}H NMR (360 MHz, CDCl$_3$) δ: 8.82 (d, 1H, $J_{6',5'}$ 5.4 Hz, **H-6’**); 8.73 (d, 1H, $^4J_{3',5'}$ 2.2 Hz, **H-3’**); 8.70 (ddd, 1H, $J_{6,5}$ 4.5, $^4J_{6,4}$ 1.8, $^5J_{6,3}$ 0.9 Hz, **H-6**); 8.48 (ddd, 1H, $J_{3,4}$ 7.9, $^4J_{3,5}$ 1.0, $^5J_{3,6}$ 0.9 Hz, **H-3**); 8.46 (s, 1H, **H-5’’**); 7.97 (dd, 1H, $J_{5',6'}$ 5.4, $^4J_{5',3'}$ 2.2 Hz, **H-5’**); 7.92 (dt, 2H, ^3J 7.1, ^4J 1.5 Hz, 2 **H-2’’’**); 7.85 (ddd, 1H, $J_{3,4}$ 8.1, $^3J_{4,5}$ 7.4, $^4J_{4,6}$ 1.8 Hz, **H-4**); 7.46 (dddd, 2H, ^3J 7.5, ^3J 7.1, ^4J 1.5, ^4J 1.3 Hz, 2 **H-3’’’**); 7.38 (tt, 1H, ^3J 7.5, ^{4}J 1.3 Hz, **H-4’’’**); 7.36 (ddd, 1H, $J_{5,4}$ 7.4, $J_{5,6}$ 4.5, $^4J_{5,3}$ 1.0 Hz, **H-5**). **^{13}C NMR (90 MHz, CDCl$_3$)** δ: 158.6 (**C-2’**); 154.9 (**C-2**); 151.3 (**C-6’**); 149.4 (**C-6**); 149.2 (**C-4’’**); 144.3 (**C-4’**); 137.4 (**C-4**); 129.9 (**C-1’’’**); 129.2 (2 **C-3’’’**); 129.0 (**C-4’’’**); 126.2 (2 **C-2’’’**); 124.8 (**C-5**); 121.6 (**C-3**); 117.1 (**C-5’’**); 114.1 (**C-5’**); 110.4 (**C-3’**). **MS (ESI$^+$)**: *m/z* 322.1 $[M+Na]^+$. **HRMS (ESI$^+$)**: calculated for $C_{18}H_{13}N_5Na$ 322.10632, found 322.10645.

(Bipyridine)$_2$-(bipyridine-triazol-phenyl) ruthenium hexafluorophosphate[8] (7a):

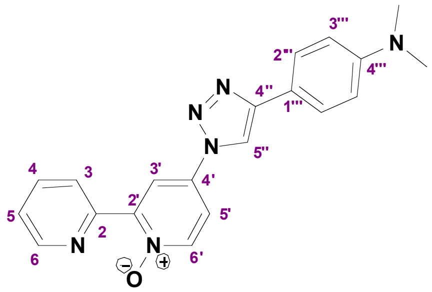


Ru-bipyridine dichloride (126 mg, 0.259 mmol, 1.0 eq.) was reacted with silver nitrate (88.1 mg, 0.518 mmol, 2.0 eq.) in methanol (17.0 mL) for 3 hours at room temperature under an argon atmosphere. The suspension was filtered in order to remove the silver salt, and the filtrate was added to 4'-(4''-phenyl-1*H*-1'',2'',3''-triazol-1''-yl)-2,2'-bipyridine (**6a**) (85.3 mg, 0.285 mmol, 1.1 eq.). The solution was heated at reflux in the dark overnight under an argon atmosphere. The reaction mixture was allowed to reach room temperature and the solvent was evaporated. The remaining solid was re-dissolved in a minimum amount of methanol, and the desired compound was precipitated by dropwise addition of a saturated aqueous solution of ammonium hexafluorophosphate. The precipitate was filtered and dried under vacuum to yield 120 mg (0.199 mmol, 77 %) of the desired hexafluorophosphate ruthenium complex (**7a**) as a red solid.

(Bipyridine)$_2$-(bipyridine-triazol-phenyl) ruthenium hexafluorophosphate (7a): $C_{38}H_{29}F_{12}N_9P_2Ru$.

^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 9.64 (s, 1H, **H-5'''**); 9.32 (d, 1H, ^4J 2.3 Hz, **H-3''**); 9.03 (ddd, 1H, ^3J 8.2, ^4J 1.0, ^5J 0.9 Hz, **H-3');** 8.89-8.82 (m, 4H, 4 **H-3**); 8.28 (ddd, 1H, ^3J 8.2, ^3J 7.7, ^4J 1.4 Hz, **H-4'**); 8.23-8.15 (m, 4H, 4 **H-4**); 8.15 (dd, 1H, ^3J 6.3, ^4J 2.3 Hz, **H-5''**); 7.97-7.93 (m, 2H, 2 **H-2''''**); 7.95 (br d, 1H, ^3J 5.7 Hz, **H-6a**); 7.93 (d, 1H, ^3J 6.3 Hz, **H-6''**); 7.81 (dd, 1H, ^3J 5.5, ^4J 1.4 Hz, **H-6'**); 7.80-7.73 (m, 3H, 3 **H-6**); 7.61 (ddd, 1H, ^3J 7.7, ^3J 5.5, ^4J 1.1 Hz, **H-5'**); 7.59-7.53 (m, 5H, 2 **H-3''''**, 3 **H-5**); 7.52 (ddd, 1H, ^3J 7.6, ^3J 5.7, ^4J 1.3 Hz, **H-5a**); 7.49-7.43 (m, 1H, **H-4''''**). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ: 158.5 (**C-2''**); 156.5 (4 **C-2**); 156.1 (**C-2'**); 152.9 (**C-6''**); 151.6-151.2 (4 **C-6**, **C-6'**); 148.1 (**C-4'''**); 143.2 (**C-4''**); 138.0 (4 **C-4**, **C-4'**); 129.5-127.5 (**C-1''''**, **C-4''''**, 2 **C-3''''**, 4 **C-5**, **C-5'**); 125.5 (2 **C-2''''**); 125.0 (**C-3'**); 124.5 (4 **C-3**); 119.6 (**C-5'''**); 117.1 (**C-5''**); 114.0 (**C-3''**). **MS (ESI$^+$)**: *m/z* 858.1 $[M+PF_6]^+$. **HRMS (ESI$^+$)**: calculated for $C_{38}H_{29}F_6N_9PRu$ 858.1236, found 858.1186.

4’-(4’’-(4’’’-(Dimethylamino)phenyl)-1*H*-1’’,2’’,3’’-triazol-1’’-yl)-2,2'-bipyridine-*N*’-oxide (5b):

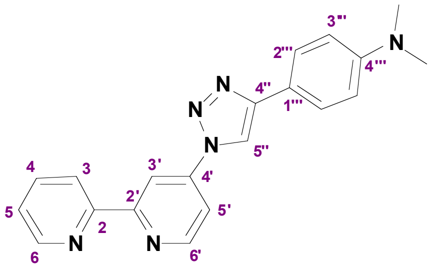


4’-Azido-2,2’-bipyridine-*N’*-oxide (**3**) (32.0 mg, 150 µmol, 1.00 eq.) and 4-ethynyl-*N*,*N*-dimethylaniline (**4b**) (22.5 mg, 97 %, 150 µmol, 1.00 eq.) were suspended in CH_2Cl_2 (1.20 mL) under an argon atmosphere. Water (1.08 mL) was added to the reaction mixture, followed by successive addition of sodium ascorbate (60 µL, 0.250 M in water, 3.0 mg, 15 µmol, 0.10 eq.) and copper sulfate pentahydrate (60 µL, 0.125 M in water, 1.9 mg, 7.5 µmol, 0.05 eq.). After 20 hours of stirring at room temperature TLC in CH_2Cl_2/CH_3OH (9:1) showed quantitative conversion. The reaction mixture was diluted with 5 mL of CH_2Cl_2/H_2O (1:1) and extensively extracted with CH_2Cl_2. The organic layers were combined and washed with water, dried over sodium sulfate, filtered and concentrated to yield 51.4 mg (144 µmol, 96 %) of *4’-(4’’-(4’’’-(dimethylamino)phenyl)-1H-1’’,2’’,3’’-triazol-1’’-yl)-2,2'-bipyridine-N’-oxide* as an orange solid.

4’-(4’’-(4’’’-(Dimethylamino)phenyl)-1*H*-1’’,2’’,3’’-triazol-1’’-yl)-2,2'-bipyridine-*N*’-oxide (5b): $C_{20}H_{18}N_6O$

^{1}H NMR (360 MHz, CDCl$_3$) δ: 9.07 (d, 1H, $J_{3,4}$ 8.3 Hz, **H-3**); 8.75 (d, 1H, $J_{6,5}$ 4.6 Hz, **H-6**); 8.58 (d, 1H, $^4J_{3’,5’}$ 3.0 Hz, **H-3’**); 8.39 (d, 1H, $J_{6’,5’}$ 7.1 Hz, **H-6’**); 8.18 (s, 1H, **H-5’’**); 7.91 (dd, 1H, $J_{5’,6’}$ 7.1, $^4J_{5’,3’}$ 3.0 Hz, **H-5’**); 7.86 (dd, 1H, $J_{4,3}$ 8.3, $J_{4,5}$ 7.5 Hz, **H-4**); 7.75 (d, 2H, ^3J 8.6 Hz, 2 **H-2’’’**); 7.39 (dd, 1H, $J_{5,4}$ 7.5, $J_{5,6}$ 4.6 Hz, **H-5**); 6.76 (d, 2H, ^3J 8.6 Hz, 2 **H-3’’’**); 2.99 (s, 6H, 2 CH_3). **^{13}C NMR (90 MHz, CDCl$_3$)** δ: 151.0 (**C-4’’’**); 150.0 (**C-4’’**); 149.7 (**C-6**); 148.6 (**C-2**); 148.1 (**C-2’**); 142.3 (**C-6’**); 136.8 (**C-4**); 133.6 (**C-4’**); 127.2 (2 **C-2’’’**); 125.7 (**C-3**); 125.2 (**C-5**); 117.5 (**C-1’’’**); 117.2 (**C-3’**); 116.3 (**C-5’**); 115.1 (**C-5’’**); 112.5 (2 **C-3’’’**); 40.6 (2 CH_3). **MS (ESI$^+$)**: *m/z* 381.1 $[M+Na]^+$. **HRMS (ESI$^+$)**: calculated for $C_{20}H_{18}N_6ONa$ 381.14343, found 381.14463.

4’’’-(1’’-([2,2’-Bipyridin]-4’-yl)-1*H*-1’’,2’’,3’’-triazol-4’’-yl)-*N*,*N*-dimethylaniline (6b):



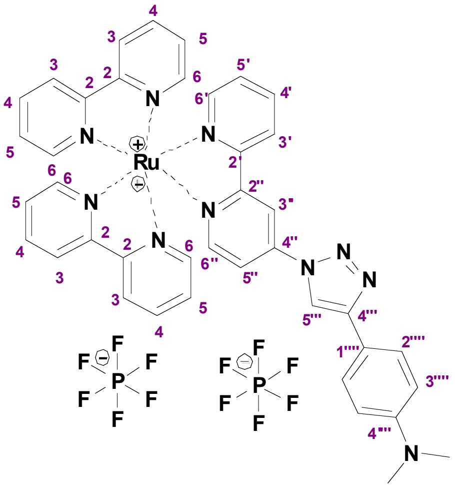
To a solution of 4’-(4’’-(4’’’-(dimethylamino)phenyl)-1*H*-1’’,2’’,3’’-triazol-1’’-yl)-2,2'-bipyridine-*N’*-oxide (**5b**) (53.4 mg, 149 µmol, 1 eq.) in CH_2Cl_2 (3.0 mL) phosphorous trichloride (39.0 µL, 61.4 mg, 447 µmol, 3.0 eq.) was added at 0°C under an argon atmosphere. The reaction mixture was heated at reflux for 3 hours, then poured into 3 mL of ice and neutralised with 38.5% sodium hydroxide. The aqueous phase was extensively extracted with CH_2Cl_2. The organic layers were combined and washed with water, then dried over sodium sulfate, filtered and concentrated. The residue was purified by flash chromatography using silica gel (CH_2Cl_2/CH_3OH 95:5), to yield 40.1 mg (117 µmol, 79 %) of *4’’’-(1’’-([2,2’-bipyridin]-4’-yl)-1H-1’’,2’’,3’’-triazol-4’’-yl)-N,N-dimethylaniline* as an yellow powder.

4’’’-(1’’-([2,2’-Bipyridin]-4’-yl)-1*H*-1’’,2’’,3’’-triazol-4’’-yl)-*N*,*N*-dimethylaniline (6b):

$C_{20}H_{18}N_6$

^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.79 (d, 1H, $J_{6',5'}$ 5.4 Hz, **H-6’**); 8.70 (ddd, 1H, $J_{6,5}$ 4.9, $^4J_{6,4}$ 1.8, $^5J_{6,3}$ 0.9 Hz, **H-6**); 8.70 (d, 1H, $^4J_{3',5'}$ 2.1 Hz, **H-3’**); 8.47 (ddd, 1H, $J_{3,4}$ 7.9, $^4J_{3,5}$ 1.2, $^5J_{3,6}$ 0.9 Hz, **H-3**); 8.31 (s, 1H, **H-5’’**); 7.97 (dd, 1H, $J_{5',6'}$ 5.4, $^4J_{5',3'}$ 2.1 Hz, **H-5’**); 7.85 (ddd, 1H, $J_{4,3}$ 8.0, $J_{4,5}$ 7.5, $^4J_{4,6}$ 1.8 Hz, **H-4**); 7.78 (d, 2H, ^3J 8.9 Hz, 2 **H-2’’’**); 7.36 (ddd, 1H, $J_{5,4}$ 7.5, $J_{5,6}$ 4.9, $^4J_{5,3}$ 1.2 Hz, **H-5**); 6.78 (d, 2H, ^3J 8.9 Hz, 2 **H-3’’’**); 2.99 (s, 6H, 2 **CH_3**). **^{13}C NMR (90 MHz, $CDCl_3$)** δ: 158.5 (**C-2’**); 155.1 (**C-2**); 151.2 (**C-6’**); 151.0 (**C-4’’’**); 149.7 (**C-4’’**); 149.4 (**C-6**); 144.5 (**C-4’**); 137.5 (**C-4**); 127.2 (2 **C-2’’’**); 124.7 (**C-5**); 121.6 (**C-3**); 117.9 (**C-1’’’**); 115.3 (**C-5’’**); 114.1 (**C-5’**); 112.6 (2 **C-3’’’**); 110.4 (**C-3’**); 40.6 (2 **C**H_3). **MS (ESI$^+$)**: *m/z* 365.1 $[M+Na]^+$. **HRMS (ESI$^+$)**: calculated for $C_{20}H_{18}N_6Na$ 365.14852, found 365.14836.

(Bipyridine)$_2$-(bipyridine-triazol-phenyl-N(Me)$_2$) ruthenium hexafluorophosphate (7b):



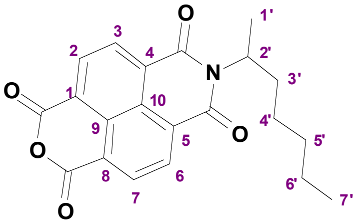
Ru-bipyridine dichloride (123 mg, 0.253 mmol, 1.0 eq.) was reacted with silver nitrate (86.1 mg, 0.507 mmol, 2.0 eq.) in methanol (17.0 mL) for 3 hours at room temperature under an argon atmosphere. The suspension was filtered in order to remove the silver salt, and the filtrate was added to 4’’’-(1’’-([2,2’-bipyridin]-4’-yl)-1*H*-1’’,2’’,3’’-triazol-4’’-yl)-*N*,*N*-dimethylaniline (**6b**) (95.4 mg, 0.279 mmol, 1.1 eq.). The solution was heated at reflux in the dark overnight under an argon atmosphere. The reaction mixture was allowed to reach room temperature and the solvent was evaporated. The remaining solid was re-dissolved in a minimum amount of methanol, and the desired compound was precipitated by drop wise addition of a saturated aqueous solution of ammonium hexafluorophosphate. The precipitate was filtered and dried under vacuum to yield 223 mg (0.213 mmol, 84 %) of the desired hexafluorophosphate ruthenium complex (**7b**) as a red solid.

(Bipyridine)$_2$-(bipyridine-triazol-phenyl-N(Me)$_2$) ruthenium hexafluorophosphate (7b): $C_{40}H_{34}F_{12}N_{10}P_2Ru$.

^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 9.41 (s, 1H, **H-5’’’**); 9.28 (d, 1H, ^4J 2.3 Hz, **H-3’’**); 9.03 (ddd, 1H, ^3J 8.2, ^4J 1.1, ^5J 0.9 Hz, **H-3’);** 8.89-8.82 (m, 4H, 4 **H-3**); 8.28 (ddd, 1H, ^3J 8.2, ^3J 7.6, ^4J 1.4 Hz, **H-4’**); 8.23-8.15 (m, 4H, 4 **H-4**); 8.13 (dd, 1H, ^3J 6.3, ^4J 2.3 Hz, **H-5’’**); 7.92 (d, 1H, ^3J 5.6 Hz, **H-6a**); 7.89 (d, 1H, ^3J 6.3 Hz, **H-6’’**); 7.80 (br dd, 1H, ^3J 5.6, ^4J 1.4 Hz, **H-6’**); 7.80-7.72 (m, 3H, 3 **H-6**); 7.75 (br d, 2H, ^3J 9.0 Hz, 2 **H-2’’’’**); 7.60 (ddd, 1H, ^3J 7.6, ^3J 5.5, ^4J 1.2 Hz, **H-5’**); 7.58-7.53 (m, 3H, 3 **H-5**); 7.52 (ddd, 1H, ^3J 7.7, ^3J 5.6, ^4J 1.2 Hz, **H-5a**); 6.87 (br d, 2H, ^3J 9.0 Hz, 2 **H-3’’’’**); 2.98 (s, 6H, 2 CH_3). **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ: 158.4 (**C-2’’**); 156.5 (4 **C-2**); 156.1 (**C-2’**); 152.8 (**C-6’’**); 151.6-151.1 (4 **C-6**, **C-6’**)); 150.6 (**C-4’’’’**); 148.9 (**C-4’’’**); 143.2 (**C-4’’**); 138.0 (4 **C-4**, **C-4’**); 128.4 (**C-5’**); 127.9 (4 **C-5**); 126.4 (2 **C-2’’’’**); 125.0 (**C-3’**); 124.5 (4 **C-3**); 117.2 (**C-5’’’**); 116.9 (**C-1’’’’**); 116.7 (**C-**

5''); 113.8 (**C-3''**); 112.4 (2 **C-3''''**); 39.5 (2 **C**H_3). **MS (ESI$^+$)**: *m/z* 901.17 [M+PF_6]$^+$. **HRMS (ESI$^+$)**: calculated for $C_{40}H_{34}F_6N_{10}PRu$ 901.1658, found 901.1624.

N-(Heptan-2'-yl)-naphthalene-1,8-dicarboxyanhydride-4,5-dicarboxyimide[9] (4'c):



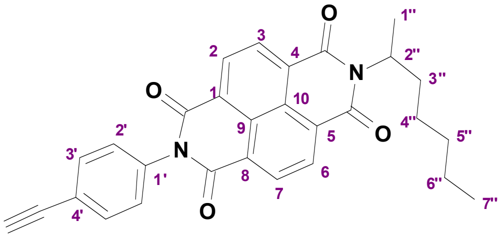
1,4,5,8-Naphthalenetetracarboxylic dianhydride (4.02 g, 15.0 mmol, 1 eq.) was dissolved in dry DMF (80 mL) under an argon atmosphere. The reaction mixture was heated to 130 °C and 2-aminoheptane (2.26 mL, 1.73 g, 15.0 mmol, 1 eq.) in dry DMF (30 mL), added dropwise over a period of two hours. The reaction mixture was heated at 130 °C for two days, and then concentrated under vacuum. The residue was solubilised in CH_2Cl_2 and filtered through a silica plug and washed with CH_2Cl_2. The filtrate was evaporated to dryness. The product was obtained as a 2:3 molar mixture of the bis- and monoimide and was used without further purification (the bisimide is an inert impurity which is easily removed in the next reaction step). Crude yield of 2.47 g was obtained, containing 1.34 g (3.67 mmol, 25 %) of monoimide (**4'c**).

N-(Heptan-2'-yl)-naphthalene-1,8-dicarboxyanhydride-4,5-dicarboxyimide (4'c):

$C_{21}H_{19}NO_5$

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (d, 2H, ^3J 7.6 Hz, **H-2**, **H-7**); 8.77 (d, 2H, ^3J 7.6 Hz, **H-3**, **H-6**); 5.24 (m, 1H, **H-2'**); 2.20-2.08 (m, 1H, **H-3a'**); 1.95-1.83 (m, 1H, **H-3b'**); 1.56 (d, 3H, ^3J 6.9 Hz, 3 **H-1'**); 1.37-1.13 (m, 6H, 2 **H-4'**, 2 **H-5'**, 2 **H-6'**); 0.81 (t, 3H, ^3J 7.0 Hz, 3 **H-7'**). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 162.7 (2 NC=O); 159.1 (2 OC=O); 133.4 (**C-3**, **C-6**); 131.4 (**C-2**, **C-7**); 129.0 (**C-10**); 128.5 (**C-1**, **C-8**); 127.1 (**C-9**); 122.8 (**C-4**, **C-5**); 51.0 (**C-2'**); 33.5 (**C-3'**); 31.8 (**C-5'**); 26.9 (**C-4'**); 22.7 (**C-6'**); 18.4 (**C-1'**); 14.2 (**C-7'**). **MS (EI$^-$)**: *m/z* 396.1 [$C_{22}H_{22}NO_6$]$^-$. **HRMS (ESI$^+$)**: calculated for $C_{22}H_{22}NO_6^-$ 396.1453, found 396.1440.

N-(4’-Ethynylphenyl)-*N*-(heptan-2’’-yl)-naphthalene-1,8:4,5-tetracarboxydiimide[10] (4c):



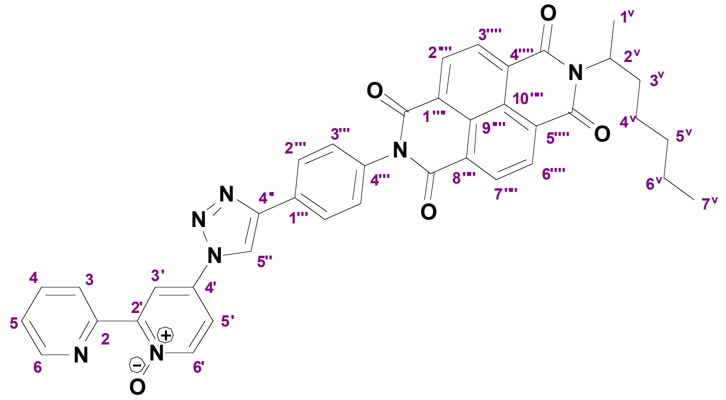
A mixture of 4-ethynylaniline (221 mg, 1.8 mmol, 1.2 eq.), 1.01 g of the previous mixture of monoimide and bisimide, containing *N*-(heptan-2’-yl)-naphthalene-1,8-dicarboxyanhydride-4,5-dicarboxyimide (**4’c**) (548 mg, 1.5 mmol, 1.0 eq.), and $Zn(OAc)_2$ (165 mg, 0.9 mmol, 0.6 eq.) in pyridine (10 mL) was heated at reflux for 4 hours under an argon atmosphere. After cooling to room temperature, hydrochloric acid (4% solution, 80 mL) was added and the solid was filtered off, washed with water and dried. The residue was solubilised in CH_2Cl_2 and washed with water and brine. The organic layers were concentrated to dryness to yield 1.00 g of crude product. The residue was purified by column chromatography using silica gel (CH_2Cl_2 100%) to yield 454 mg (0.97 mmol, 65 %) of *N-(4’-ethynylphenyl)-N-(heptan-2’’-yl)-naphthalene-1,8:4,5-tetracarboxydiimide* as an yellow solid.

N-(4’-Ethynylphenyl)-*N*-(heptan-2’’-yl)-naphthalene-1,8:4,5-tetracarboxydiimide (4c):

$C_{21}H_{19}NO_5$

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78 (d, 2H, ^3J 7.6 Hz, 2 **H-NDI**); 8.75 (d, 2H, ^3J 7.6 Hz, 2 **H-NDI**); 7.67 (d, 2H, $J_{3',2'}$ 8.5 Hz, 2 **H-3’**); 7.28 (d, 2H, $J_{2',3'}$ 8.5 Hz, 2 **H-2’**); 5.26 (m, 1H, **H-2’’**); 3.15 (s, 1H, PhCC**H**); 2.25-2.10 (m, 1H, **H-3a’’**); 2.00-1.85 (m, 1H, **H-3b’’**); 1.58 (d, 3H, ^3J 7.0 Hz, 3 **H-1’’**); 1.35-1.15 (m, 6H, 2 **H-4’’**, 2 **H-5’’**, 2 **H-6’’**); 0.82 (t, 3H, ^3J 7.0 Hz, 3 **H-7’’**). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 163.3 (2 N**C**=O); 163.1 (2 N**C**=O); 135.0 (**C-1’**); 133.5 (2 **C-3’**); 131.7, 131.2 (**C-2**, **C-3**, **C-6**, **C-7**); 128.9 (2 **C-2’**); 127.9, 127.2, 127.1, 126.4 (**C-1/C-8**, **C-4/C-5**, **C-9**, **C-10**); 123.5 (**C-4’**); 82.9 (Ph**C**CH); 78.1 (PhC**C**H); 50.8 (**C-2’’**); 33.6 (**C-3’’**); 31.8 (**C-5’’**); 26.9 (**C-4’’**); 22.7 (**C-6’’**); 18.5 (**C-1’’**); 14.2 (**C-7’’**). **MS (EI$^+$)**: *m/z* 487.2 $[M+H]^+$. **HRMS (ESI$^+$)**: calculated for $C_{29}H_{24}N_2O_4Na$ 487.1634, found 487.1616.

4’-(4’’-(4’’’-(*N*-(Heptan-2^{v}-yl)-naphthalene-1’’’’,8’’’’:4’’’’,5’’’’-tetracarboxydiimide-*N*-yl)phenyl)-1*H*-1’’,2’’,3’’-triazol-1’’-yl)-2,2’-bipyridine-*N’*-oxide (5c):



4’-Azido-2,2’-bipyridine-*N’*-oxide (**3**) (42.6 mg, 0.2 mmol, 1.00 eq.) was suspended in CH_2Cl_2 (5.0 mL) under an argon atmosphere. *N*-(4’-Ethynylphenyl)-*N*-(heptan-2’’-yl)-naphthalene-1,8:4,5-tetracarboxydiimide (**4c**) (93.1 mg, 0.2 mmol, 1.00 eq.) was added to the suspension, followed by successive addition of water (4.84 mL), sodium ascorbate (80 µL, 0.250 M in water, 4.0 mg, 20 µmol, 0.10 eq.) and copper sulfate pentahydrate (80 µL, 0.125 M in water, 2.5 mg, 10 µmol, 0.05 eq.). After 4 hours of stirring at room temperature TLC in CH_2Cl_2/CH_3OH (9:1) showed quantitative conversion. The reaction mixture was diluted with 20 mL of CH_2Cl_2/H_2O (1:1) and extensively extracted with CH_2Cl_2. The organic layers were combined and washed with water, saturated aqueous NaCl, dried over sodium sulfate, filtered and concentrated to yield 133 mg (196 µmol, 98 %) of *4’-(4’’-(4’’’-(N-(heptan-2^{v}-yl)-naphthalene-1’’’’,8’’’’:4’’’’,5’’’’-tetracarboxydiimide-N-yl)phenyl)-1H-1’’,2’’,3’’-triazol-1’’-yl)-2,2’-bipyridine-N’-oxide* as an yellow solid with very poor solubility.

4’-(4’’-(4’’’-(*N*-(Heptan-2^{v}-yl)-naphthalene-1’’’’,8’’’’:4’’’’,5’’’’-tetracarboxydiimide-*N*-yl)phenyl)-1*H*-1’’,2’’,3’’-triazol-1’’-yl)-2,2’-bipyridine-*N’*-oxide (5c): $C_{39}H_{31}N_7O_5$

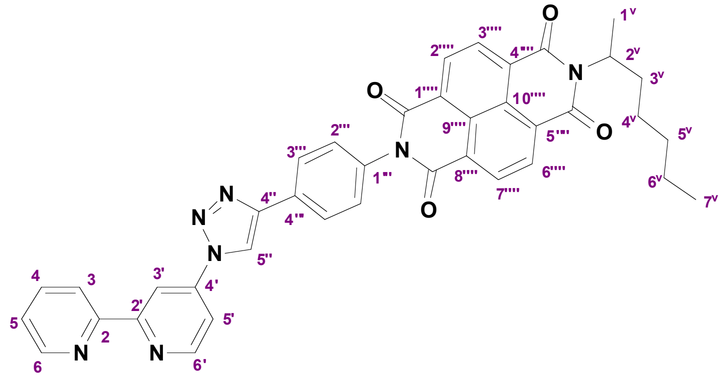
^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.11 (br d, 1H, $J_{3,4}$ 8.0 Hz, **H-3**); 8.81 (d, 2H, ^{3}J 7.6 Hz, 2 **H-NDI**); 8.77 (d, 2H, ^{3}J 7.6 Hz, 2 **H-NDI**); 8.77 (br d, 1H, $J_{6,5}$ 4.5 Hz, **H-6**); 8.68 (d, 1H, $^{4}J_{3',5'}$ 3.0 Hz, **H-3’**); 8.46 (d, 1H, $J_{6',5'}$ 7.0 Hz, **H-6’**); 8.43 (s, 1H, **H-5’’**); 8.13 (d, 2H, $J_{2''',3'''}$ 8.3 Hz, 2 **H-3’’’**); 7.99 (dd, 1H, $J_{5',6'}$ 7.0, $^{4}J_{5',3'}$ 3.0 Hz, **H-5’**); 7.89 (ddd, 1H, $J_{4,3}$ 8.0, $J_{4,5}$ 7.6, $^{4}J_{4,6}$ 1.1 Hz, **H-4**); 7.45 (dd, 2H, $J_{2''',3'''}$ 8.3 Hz, 2 **H-2’’’**); 7.43 (dd, 1H, $J_{5,4}$ 7.6, $J_{5,6}$ 4.5 Hz, **H-5**); 5.32-5.20 (m, 1H, **H-2^{v}**); 2.23-2.10 (m, 1H, **H-3a^{v}**); 1.97-1.86 (m, 1H, **H-3b^{v}**); 1.59 (d, 3H, ^{3}J 6.9 Hz, 3 **H-1^{v}**); 1.45-1.20 (m, 6H, 2 **H-4^{v}**, 2 **H-5^{v}**, 2 **H-6^{v}**); 0.83 (t, 3H, ^{3}J 6.9 Hz, 3 **H-7^{v}**).

^{13}C NMR (100 MHz, CDCl$_3$) δ: 163.4 (2 NC=O); 163.3 (2 NC=O); 149.9 (**C-6**); 142.3 (**C-6’**); 137.0 (**C-4**); 131.7 (4 CH, **C-2’’’’, C-3’’’’, C-6’’’’, C-7’’’’**); 129.5 (2 **C-2’’’**); 127.3 (2

C-3’’’); 126.1 (**C-3**); 125.6 (**C-5**); 117.8 (**C-3’**); 117.4 (**C-5’’**); 116.5 (**C-5’**); 50.8 (**C-2^{v}**); 33.6 (**C-3^{v}**); 31.8 (**C-5^{v}**); 26.9 (**C-4^{v}**); 22.7 (**C-6^{v}**); 18.5 (**C-1^{v}**); 14.2 (**C-7^{v}**).

MS (ESI^{+}): *m/z* 700.2 [M+Na]$^{+}$. **HRMS (ESI^{+})**: calculated for $C_{39}H_{31}N_{7}O_{5}Na$ 700.2279, found 700.2271.

N-(4’’’-(1’’-(2,2’-Bipyridin-4’-yl)-1*H*-1’’,2’’,3’’-triazole-4’’-yl)phenyl)-*N*-(heptan-2^{v}-yl)-naphthalene-1,8:4,5-tetracarboxydiimide (6c):



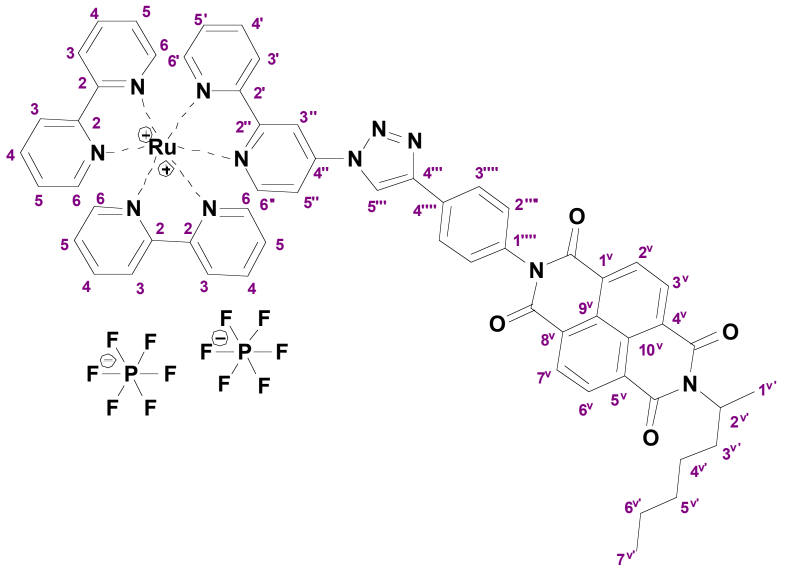
To a solution of 4’-(4’’-(4’’’-(*N*-(heptan-2^{v}-yl)-naphthalene-1’’’’,8’’’’:4’’’’,5’’’’-tetracarboxydiimide-*N*-yl)phenyl)-1*H*-1’’,2’’,3’’-triazol-1’’-yl)-2,2’-bipyridine-*N’*-oxide (**5c**) (126 mg, 186 µmol, 1 eq.) in dry CH_2Cl_2 (7.5 mL), phosphorous trichloride (49 µL, 76.6 mg, 558 µmol, 3 eq.) was added at 0°C under an argon atmosphere. The reaction mixture was heated at reflux for 24 hours, then poured into 5 mL of ice and neutralised with 38.5% sodium hydroxide. The aqueous phase was extensively extracted with CH_2Cl_2. The organic layers were combined, washed with water, dried over sodium sulfate, filtered and concentrated. The residue was purified by flash chromatography using silica gel (CH_2Cl_2/CH_3OH 95:5), to yield 78.9 mg (119 µmol, 64 %) of *N-(4’’’-(1’’-(2,2’-bipyridin-4’-yl)-1H-1’’,2’’,3’’-triazole-4’’-yl)phenyl)-N-(heptan-2^{v}-yl)-naphthalene-1,8:4,5-tetracarboxydiimide* as a yellow powder.

N-(4’’’-(1’’-(2,2’-Bipyridin-4’-yl)-1*H*-1’’,2’’,3’’-triazole-4’’-yl)phenyl)-*N*-(heptan-2^{v}-yl)-naphthalene-1,8:4,5-tetracarboxydiimide (6c): $C_{39}H_{31}N_{7}O_{4}$

^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.86 (d, 1H, $J_{6',5'}$ 5.4 Hz, **H-6’**); 8.81 (d, 2H, ^{3}J 7.5 Hz, 2 **H-NDI**); 8.77 (d, 2H, ^{3}J 7.5 Hz, 2 **H-NDI**); 8.76 (dd, 1H, $^{4}J_{3',5'}$ 2.2, $^{5}J_{3',6'}$ 0.5 Hz, **H-3’**); 8.72 (ddd, 1H, $J_{6,5}$ 4.8, $^{4}J_{6,4}$ 1.8, $^{5}J_{6,3}$ 0.8 Hz, **H-6**); 8.57 (s, 1H, **H-5’’**); 8.51 (ddd, 1H, $J_{3,4}$ 8.0, $^{4}J_{3,5}$ 1.1, $^{5}J_{3,6}$ 0.8 Hz, **H-3**); 8.15 (d, 2H, $J_{2''',3'''}$ 8.5 Hz, 2 **H-3’’’**); 8.02 (dd, 1H, $J_{5',6'}$ 5.4, $^{4}J_{5',3'}$ 2.2 Hz, **H-5’**); 7.88 (ddd, 1H, $J_{4,3}$ 8.0, $J_{4,5}$ 7.5, $^{4}J_{4,6}$ 1.8 Hz, **H-4**); 7.45 (dd, 2H, $J_{2''',3'''}$ 8.5 Hz, 2 **H-2’’’**); 7.39 (ddd, 1H, $J_{5,4}$ 7.5, $J_{5,6}$ 4.8, $^{4}J_{5,3}$ 1.1 Hz, **H-5**); 5.27 (m, 1H, **H-2^{v}**); 2.25-2.10 (m, 1H,

H-3a^{v}); 2.00-1.85 (m, 1H, **H-3b**^{v}); 1.59 (d, 3H, ^{3}J 6.9 Hz, 3 **H-1**^{v}); 1.45-1.20 (m, 6H, 2 **H-4**^{v}, 2 **H-5**^{v}, 2 **H-6**^{v}); 0.83 (t, 3H, ^{3}J 6.9 Hz, 3 **H-7**^{v}). **^{13}C NMR (100 MHz, CDCl$_3$)** δ: 163.4 (2 NC=O); 163.3 (2 NC=O); 158.7 (**C-2’**); 154.9 (**C-2**); 151.4 (**C-6’**); 149.5 (**C-6**); 148.3 (**C-4’’**); 144.3 (**C-4’**); 137.5 (**C-4**); 135.1 (**C-1’’’** ou **C-4’’’**); 131.7, 131.2 (**C-2’’’’, C-3’’’’, C-6’’’’, C-7’’’’**); 130.9 (**C-1’’’** ou **C-4’’’**); 129.5 (2 **C-2’’’**); 127.7 (1 ou 2 **Cq-NDI**); 127.3 (2 **C-3’’’**); 127.2, 127.1, 126.6 (**4 ou 5 Cq-NDI**); 124.9 (**C-5**); 121.9 (**C-3**); 117.6 (**C-5’’**); 114.3 (**C-5’**); 110.5 (**C-3’**); 50.8 (**C-2**^{v}); 33.6 (**C-3**^{v}); 31.8 (**C-5**^{v}); 27.0 (**C-4**^{v}); 22.7 (**C-6**^{v}); 18.5 (**C-1**^{v}); 14.2 (**C-7**^{v}). **MS (ESI^{+})**: *m/z* 684.2 [M+Na]$^{+}$. **HRMS (ESI^{+})**: calculated for $C_{39}H_{31}N_7O_4Na$ 684.2330, found 684.2102.

(Bipyridine)$_2$-(bipyridine-triazol-naphthalene diimide) ruthenium hexafluorophosphate (7c):



Ru-bipyridine dichloride (42.3 mg, 89 µmol, 1.0 eq.) was reacted with silver nitrate (30.3 mg, 179 µmol, 2.0 eq.) in methanol (25 mL) for 3 hours at room temperature under an argon atmosphere. The suspension was filtered in order to remove the silver salt, and the filtrate was added to *N*-(4’’’-(1’’-(2,2’-bipyridin-4’-yl)-1*H*-1’’,2’’,3’’-triazole-4’’-yl)phenyl)-*N*-(heptan-2^{v}-yl)-naphthalene-1,8:4,5-tetracarboxydiimide (**6c**) (65.0 mg, 98 µmol, 1.1 eq.). The solution was refluxed in the dark overnight under an argon atmosphere. The reaction mixture was allowed to reach room temperature and the solvent was evaporated. The remaining solid was re-dissolved in a minimum amount of methanol, and the desired compound was precipitated by dropwise addition of a saturated aqueous solution of ammonium hexafluorophosphate. The precipitate was filtered, washed with cold methanol and dried under vacuum to yield 47.7 mg

(35 μmol, 39 %) of the desired hexafluorophosphate ruthenium complex (**7c**) as a dark red solid.

(Bipyridine)$_2$-(bipyridine-triazol-naphthalene diimide) ruthenium hexafluorophosphate (15): $C_{59}H_{47}F_{12}N_{11}O_4P_2Ru$.

^{1}H NMR (400 MHz, CD$_3$CN) δ: 9.06 (s, 1H, **H-5’’’**); 9.00 (br s, 1H, **H-3’’**); 8.74 (ddd, 1H, $J_{3',4'}$ 8.2, $^{4}J_{3,'5'}$ 1.0, $^{5}J_{3',6'}$ 0.7 Hz, **H-3’);** 8.73 (d, 2H, ^{3}J 7.6 Hz, 2 **H-NDI**); 8.70 (d, 2H, ^{3}J 7.6 Hz, 2 **H-NDI**); 8.56-8.49 (m, 4H, 4 **H-3**); 8.17 (br d, 2H, ^{3}J 8.2 Hz, 2 **H-2’’’’**); 8.14 (ddd, 1H, ^{3}J 8.2, ^{3}J 7.7, ^{4}J 1.4 Hz, **H-4’**); 8.12-8.05 (m, 4H, 4 **H-4**); 7.95-7.89 (m, 2H, **H-5’’**, **H-6’’**); 7.86 (ddd, 1H, ^{3}J 5.6, ^{4}J 1.4, ^{5}J 0.7 Hz, **H-6a**); 7.78 (ddd, 1H, ^{3}J 5.6, ^{4}J 1.4, ^{5}J 0.7 Hz, **H-6’**); 7.81-7.72 (m, 3H, 3 **H-6**); 8.09 (br d, 2H, ^{3}J 8.5 Hz, 2 **H-3’’’’**); 7.47 (ddd, 1H, ^{3}J 7.7, ^{3}J 5.6, ^{4}J 1.0 Hz, **H-5’**); 7.46-7.38 (m, 4H, 4 **H-5**); 5.29-5.19 (m, 1H, **H-2^{v}’**); 2.20-2.10 (m, 1H, **H-3a^{v}’**); 2.00-1.80 (m, 1H, **H-3b^{v}’**); 1.57 (d, 3H, ^{3}J 6.9 Hz, 3 **H-1^{v}’**); 1.40-1.25 (m, 6H, 2 **H-4^{v}’**, 2 **H-5^{v}’**, 2 **H-6^{v}’**); 0.84 (t, 3H, ^{3}J 6.9 Hz, 3 **H-7^{v}’**). **^{13}C NMR (100 MHz, CD$_3$CN)** δ: 164.8 (2 NC=O); 164.7 (2 NC=O); 158.3 (4 **C-2**, **C-2**’, **C-2’’**); 154.8 (**C-6’’**); 153.3-153.0 (4 **C-6**, **C-6’**); 149.5 (**C-4’’’**); 145.1 (**C-4’’**); 139.6, 139.3 (4 **C-4**, **C-4’**); 137.6 (**C-1’’’’** ou **C-4’’’’**); 132.0, 131.8 (**C-2^{v}, C-3^{v}, C-6^{v}, C-7^{v});** 131.4 (**C-1’’’’** ou **C-4’’’’**); 131.1 (**2 C-3’’’’**); 129.6 (1 ou 2 **Cq-NDI**); 129.0 (4 **C-5**); 128.9 (**C-5’**); 128.3, 128.2, 128.1 (**4 ou 5 Cq-NDI**); 127.9 (2 **C-2’’’’**); 126.3 (**C-3’**); 125.7 (4 **C-3**); 120.9 (**C-5’’’**); 118.2 (**C-5’’**); 115.5 (**C-3’’**); 51.8 (**C-2^{v}’**); 34.4 (**C-3^{v}’**); 32.7 (**C-5^{v}’**); 27.7 (**C-4^{v}’**); 23.6 (**C-6^{v}’**); 18.7 (**C-1^{v}’**); 14.62 (**C-7^{v}’**). **MS (ESI^{+})**: *m/z* 1220.2 $[M+PF_6]^{+}$. **HRMS (ESI^{+})**: calculated for $C_{59}H_{47}F_6N_{11}O_4PRu$ 1220.2508, found 1220.2491.

COMPUTATIONAL DETAILS

Density Functional Theory calculations were carried out using Becke's three-parameter hybrid functional B3LYP.[11, 12] along with the valence double-ζ basis set LanL2DZ[13, 14] including the Los Alamos effective core potential for heavy atoms. All calculations were performed using the *Gaussian 03*[15] software package.

In a first step geometry optimisations were performed in gas phase for the singlet ground state of the exogenous ligands and complexes. However, in case of large dissymmetrical molecules, it is necessary to consider solvation effects to prevent the occurrence of computed excited states at too low energy.[16] Consequently, in a second step the solvent medium was taken into account in the framework of the polarized dielectric model (PCM)[17, 18] using the integral equation formalism (IEF).[17, 19] The selected solvent was water and all parameters were kept to their implemented *Gaussian 03* values.

Time dependent calculations on the singlet state were also performed in a modelled water medium. For each transition, the calculated wavelength λ and corresponding oscillator strength f allow to represent the stick-spectrum (f *vs* λ). Simulation of the absorption spectrum is obtained by convolution with gaussian functions of full-width at half-maximum (fwhm) 3200 cm^{-1} and a band area proportional to the calculated oscillator strength.

The interpretation of the photophysical experiments, in absence as well as in presence of an electron acceptor, may involve the lowest triplet state and the ground doublet state of the oxidised complex. Calculations on these non closed-shell states were unrestricted ones. As the systems are very large, no geometry optimisations were attempted for these states and only the Ru-N distances were optimised.

LIGAND CLICK-NME_2

Owing to the interesting properties of the **Ru-NMe_2** complex, the corresponding ligand click-NMe_2 was more extensively studied and its geometry optimised. The HOMO is localised in the dimethylamino and phenylene regions, while the LUMO is essentially developed on the triazole ring and the bipyridine.

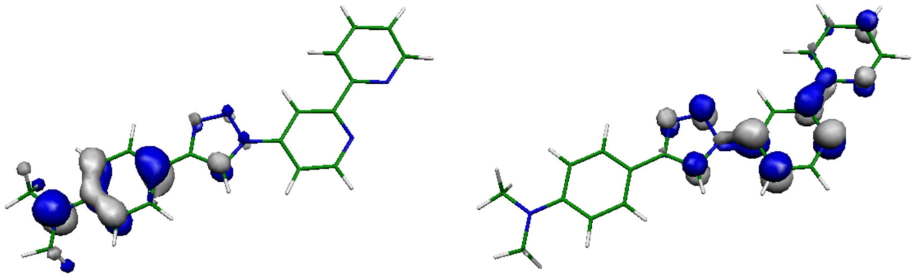


Figure 1: HOMO (left) and LUMO (right) of the ligand click-NMe_2.

The lowest triplet state of the ligand is calculated 4.96 eV higher in energy than the singlet state in the geometry of the singlet. However, after geometry optimisation of the triplet, this state lies 2.50 eV above the singlet, both states being considered in their own geometry. This important decrease in energy is explained by a striking difference between the two structures in the triazole region, as shown in the Figure 2. One N-N bond is considerably elongated and the connections of the triazole with both phenyl and pyridine rings are strengthened.

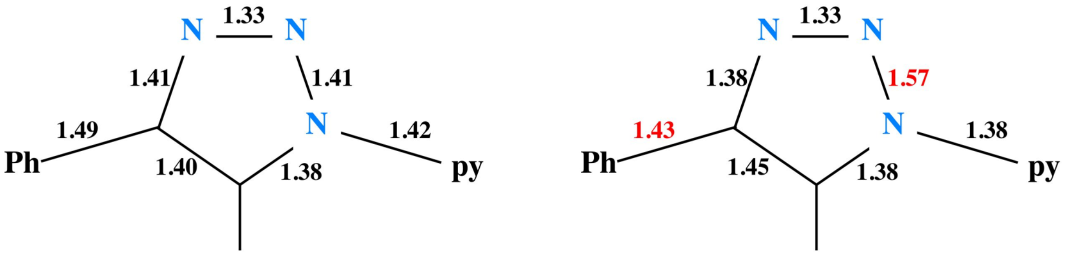


Figure 2: Comparison of optimised triazole bond distances for the ligand click-NMe2 in the singlet state (left) and in the triplet state (right).

The lowest triplet state is generated by an HOMO to LUMO charge transfer as shown on the spin density map.-

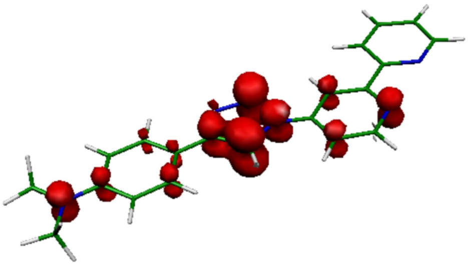


Figure 3: Map of the spin density distribution for the lowest triplet state of the ligand click-NMe_2.

DFT CALCULATIONS ON RU-NME$_2$.

In **Ru-NMe$_2$**, the dimethylamino substituent exerts an important electrodonor effect on the phenyl ring and destabilises all orbitals developed in this region. It results that the HOMO of the complex is no longer a d_π ruthenium orbital, but an orbital localised on the NMe_2-C_6H_4 fragment. The HOMO-LUMO energy gap is small: 2.39 eV as compared to 3.19 eV in **Ru-H**. This fact has important consequences on the lowest excited singlet and triplet states.

As shown on the Figure 4, the HOMO of complex **Ru-NMe$_2$** is localised on the dimethylaminophenyl fragment of the modified bipyridine ligand and the LUMO is developed on the bipyridine part of the same ligand. We stress out the outstanding fact that these orbitals are precisely the HOMO and LUMO of the corresponding ligand.

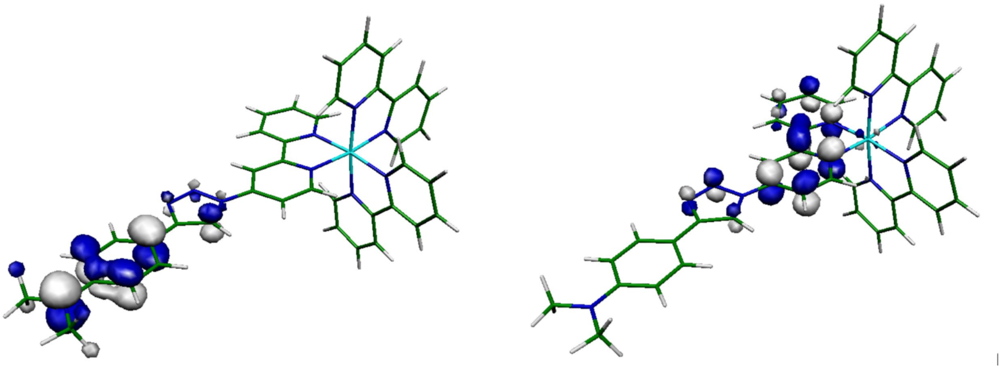


Figure 4: HOMO (left) and LUMO (right) of complex **Ru-NMe$_2$**.

The calculated lowest triplet state is located on the ligand and no longer involves the ruthenium as shown on the spin density map.

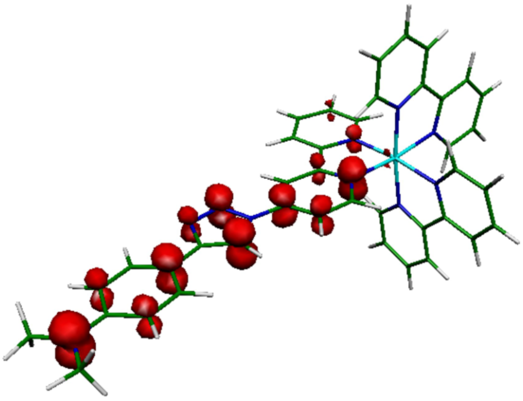


Figure 5: Spin density distribution for the lowest triplet state of **Ru-NMe$_2$**

It results from an HOMO to LUMO electron shift, which is from an intra ligand charge transfer generating a ^{3}ILCT state. The direction of the electron transfer is nicely evidenced by the difference between the total electron density of the triplet state and that of the singlet state.

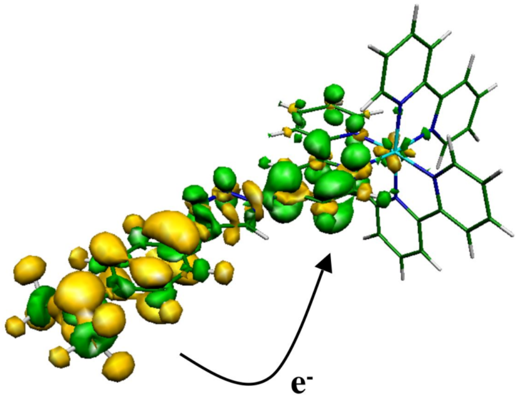


Figure 6: Differential electronic density between the triplet and singlet states of **Ru-NMe$_2$** (T-S). green = positive sign, that is increase of electron density in T as compared to S ; yellow = negative sign. The direction of the electron transfer that generates the ^{3}ILCT state is hence evidenced.

Metal to ligand charge transfer triplet states (^{3}MLCT) lie at slightly higher energy.

As can be seen, the lowest triplet of **Ru-NMe$_2$** is reminiscent of the triplet state of the corresponding ligand. Although no full geometry optimisation has been performed on the triplet state of **Ru-NMe$_2$**, it is likely that in this state important changes occur in the geometry of the exogenous ligand.

CALCULATED ELECTRONIC SPECTRUM OF RU-H.

Time-dependant DFT calculations in solvent were undertaken for **Ru-H**.

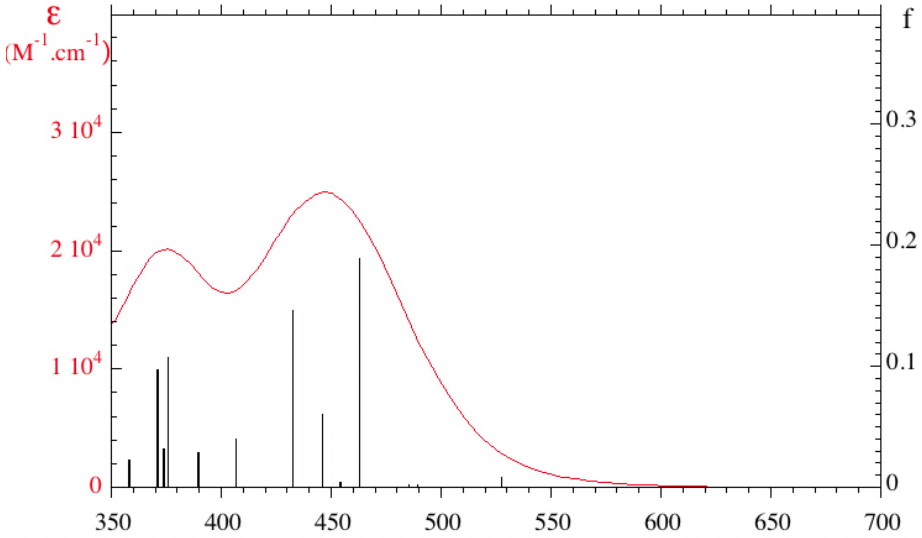


Figure 7: Calculated electronic spectrum of **Ru-H**. Calculated stick spectrum drawn according to TD-DFT wavelengths and oscillator strengths f and simulated spectrum obtained by convolution with gaussian functions of fwhm 3200 cm^{-1}.

For this complex, an absorption band culminating around 450 nm is simulated. It results from essentially three intense excitations from the d_π orbitals of the ruthenium to the π^* orbital of the bipyridine part of the exogenous ligand.

EXPERIMENTAL CHARACTERISATIONS

Ground state absorption spectra were measured in a Specord spectrophotometer with 1 cm quartz cells. Steady state emission spectra were recorded in a Varian Eclipse Spectrofluorimeter. Samples were excited at 450 nm with absorbances optically matched at 0.1. $[Ru(bpy)_3]^{2+}$ was used as reference for emission quantum yield (Φ_{em}) calculation in acetonitrile with a $\Phi_{em} = 0.059$.[20] A cut-off filter at 435 nm was put in front of the emission monochromator to avoid excitation light. Samples were purged for 20 min with Argon prior to each experiment. For transient absorption kinetic and spectral measurements in the time range 10 ns to 100 ms we used an Edinburgh Instruments LP920 Flash Photolysis Spectrometer system that incorporated a Continuum Surelite OPO for sample excitation (~7 ns pulse duration). The OPO was pumped by a Continuum Q-switched Nd:YAG laser operating at 355 nm. The LP920 system uses a 450 W Xenon arc lamp as the probe for the transient absorption kinetic measurements. Detection of the signal was performed either by a PMT or a water-cooled ICCD camera. The presented transient absorption spectra were typically the average of 20-50 measurements.

Cyclic voltammetry was performed with an EGG PAR (model 273 A) electrochemical workstation. Acetonitrile was distilled prior to each experiment and the solution (1 mM for the complexes, 0.1 M of tetrabutylammonium perchlorate) was introduced in an Argon purged electrochemical cell. The experiments were performed using a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, and an $Ag/AgClO_4$ (0.01 M) electrode in acetonitrile as the reference electrode (0.29V vs. SCE).

GROUND STATE ABSORPTION SPECTRA

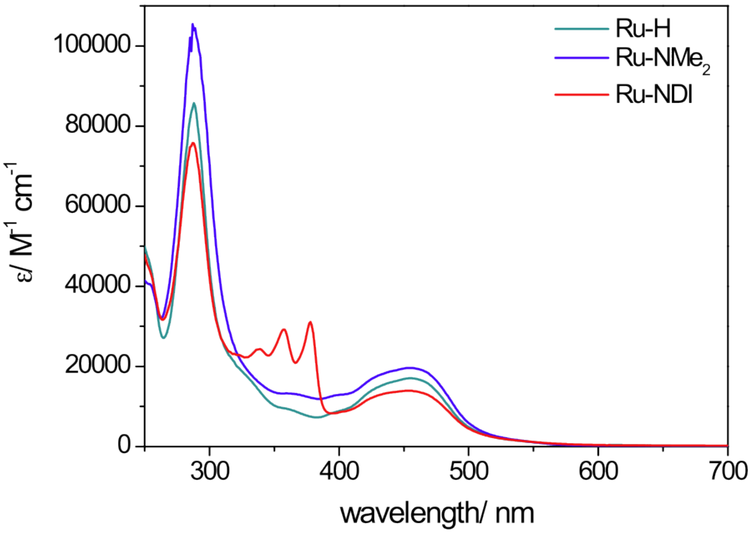


Figure 8: Extinction molar coefficient for the **Ru-H**, **Ru-NMe$_2$** and **Ru-NDI** in acetonitrile.

STEADY-STATE EMISSION SPECTRA

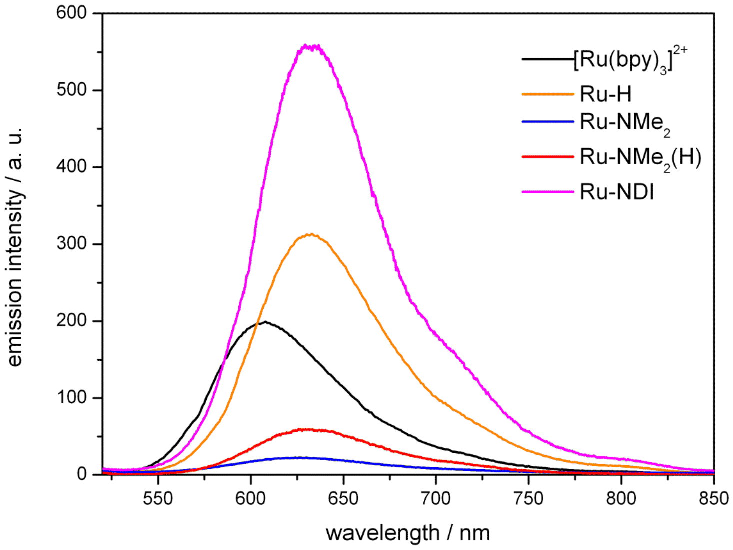


Figure 9: Steady-state emission spectra in MeCN for the complexes studied. Excitation wavelength: 450 nm. Absorbances at 450 nm 0.1.

TRANSIENT ABSORPTION SPECTRA

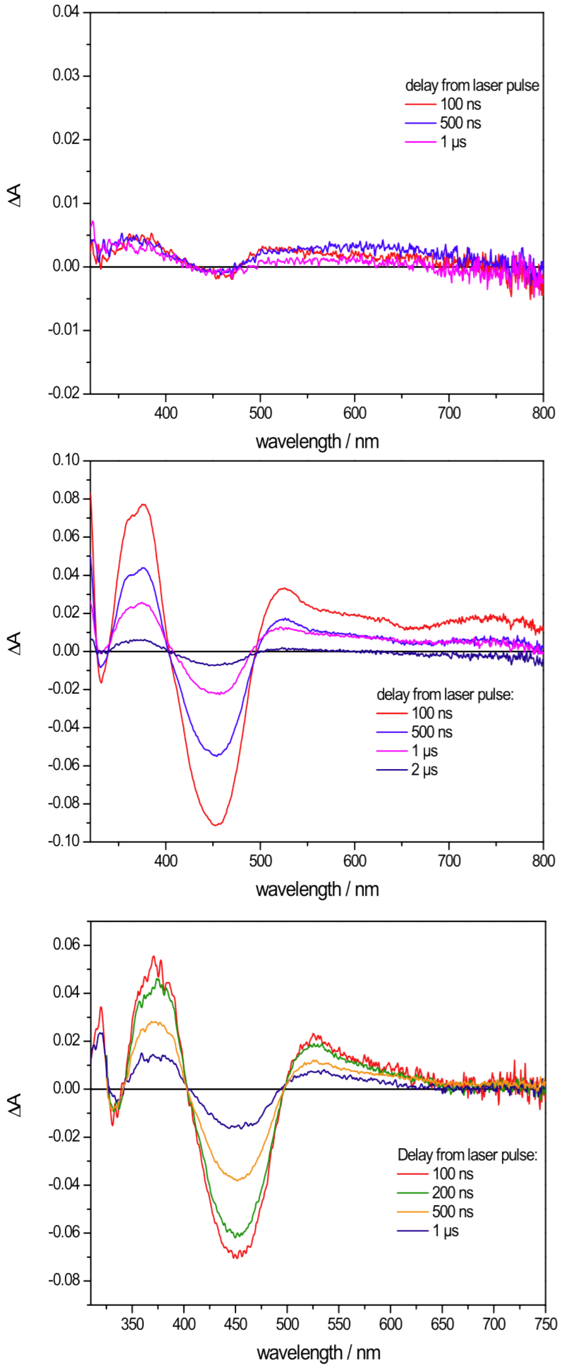


Figure 10: Transient absorption spectra obtained for **Ru-NMe$_2$**, **Ru-H** and **Ru-NDI** in MeCN. Excitation wavelength: 450 nm. Absorbance at 450 nm: 0.3-0.4. Laser energy ~10 mJ. Solutions were purged with Argon for 10 minutes prior to measurement.

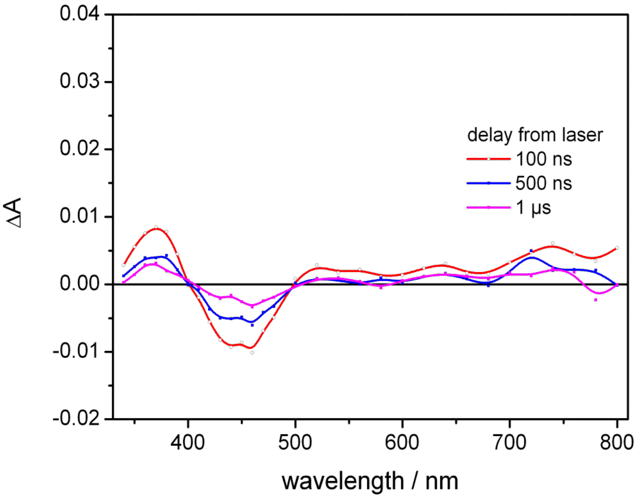


Figure 11. Transient absorption spectra obtained for **Ru-NMe$_2$** in presence of formic acid in MeCN. Excitation wavelength: 450 nm. Absorbance at 450 nm: 0.3. Laser energy ~10 mJ. Solution was purged with argon for 10 minutes prior to measurement.

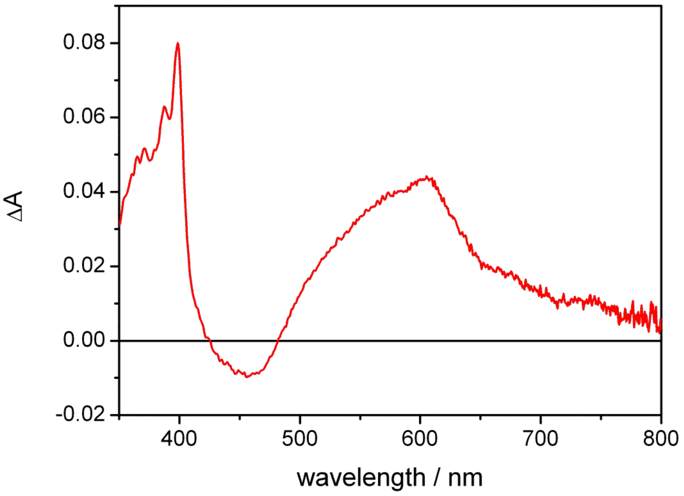


Figure 12. Transient absorption spectra obtained for Ru-NMe$_2$ in presence 10 mM MV^{2+} and formic acid in MeCN. Excitation wavelength: 450 nm. Absorbance at 450 nm: 0.3. Laser energy ~10 mJ. Solution was purged with argon for 10 minutes prior to measurement.

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$Ru(Bpy)_2Cl_2$

^{1}H all

^{1}H zoom

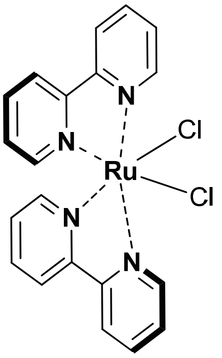
Cosy

^{13}C all

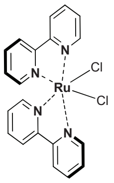
^{13}C zoom

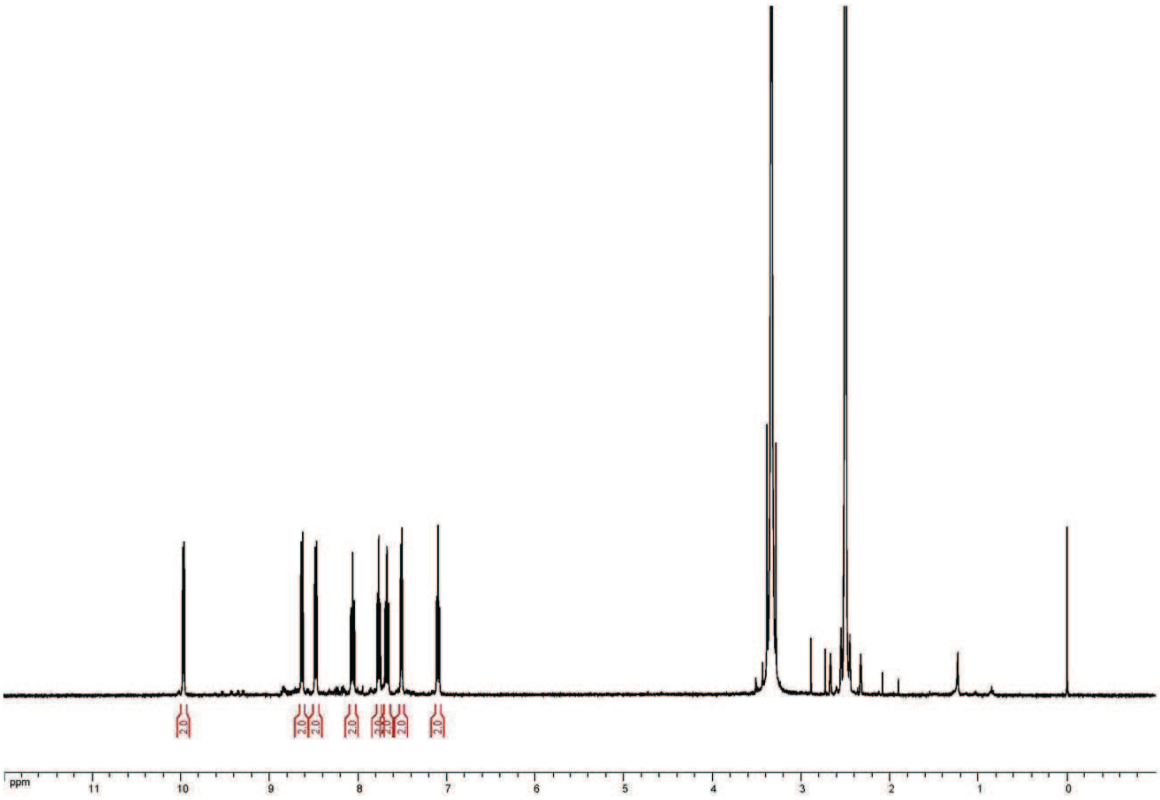
Hsqc

Hmbc

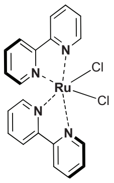


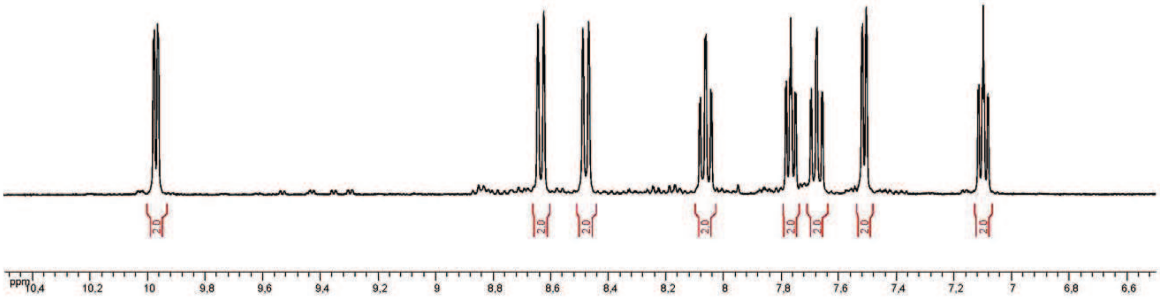
$Ru(Bpy)_2Cl_2$ ^{1}H



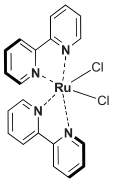


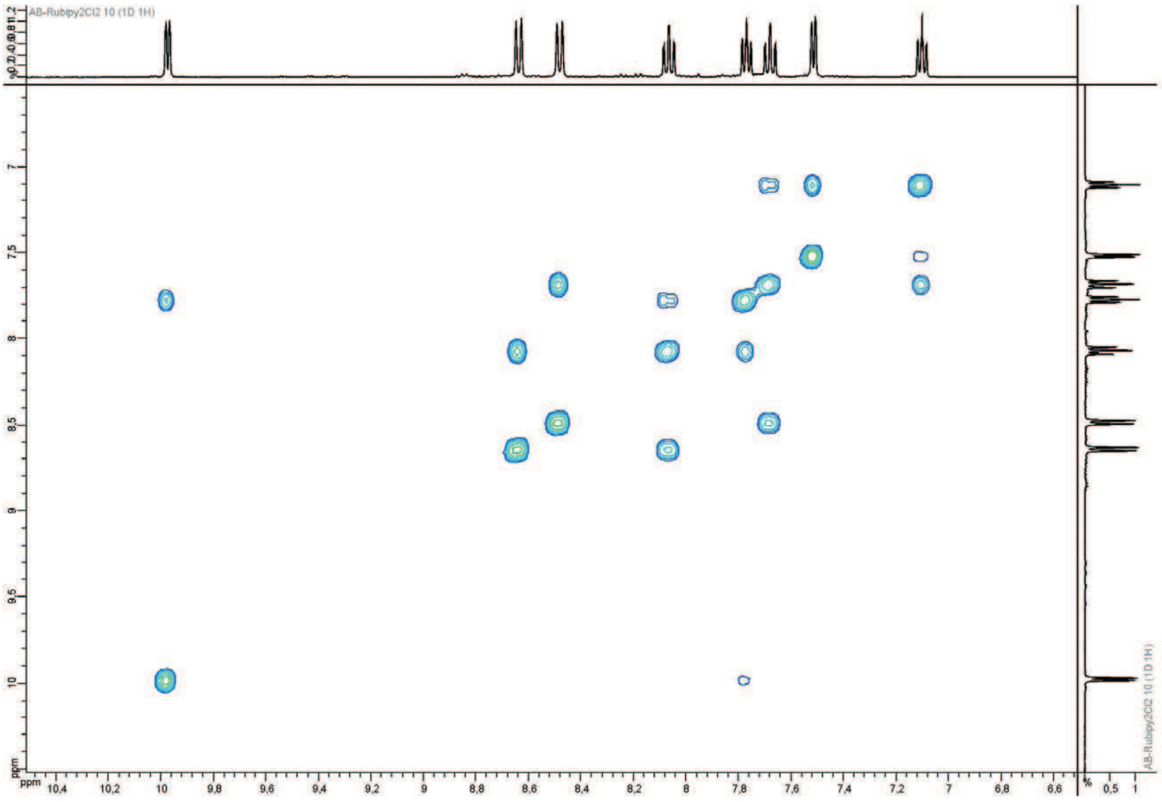
$Ru(Bpy)_2Cl_2$ ^1H



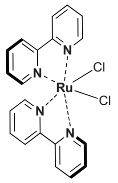


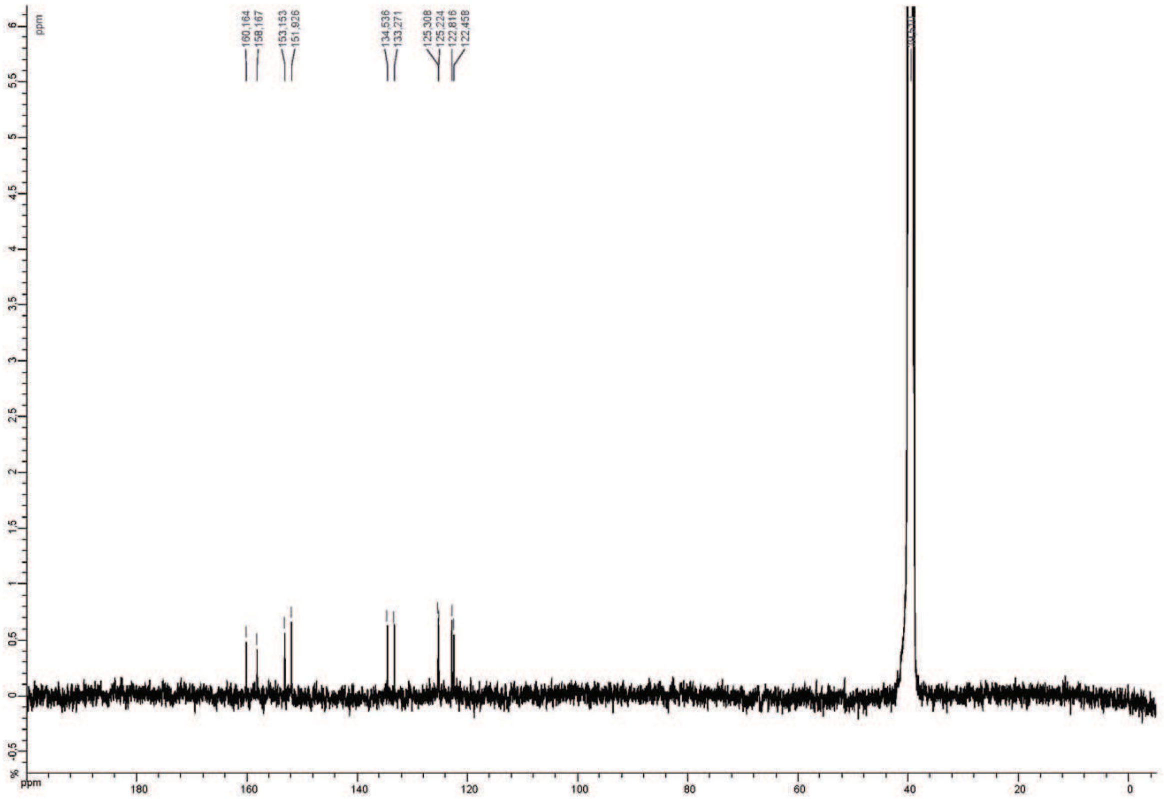
$Ru(Bpy)_2Cl_2$ Cosy



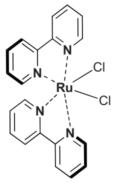


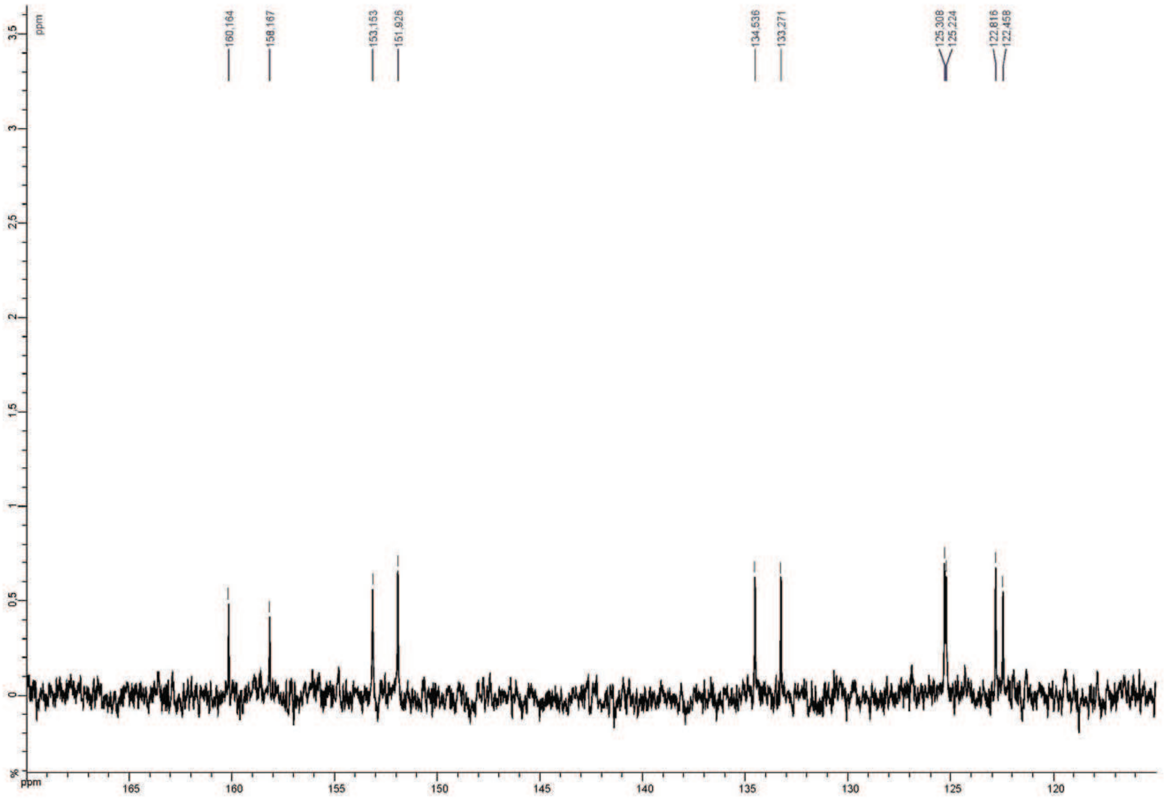
Ru(Bpy)$_2$Cl$_2$ ^{13}C



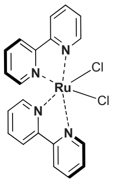


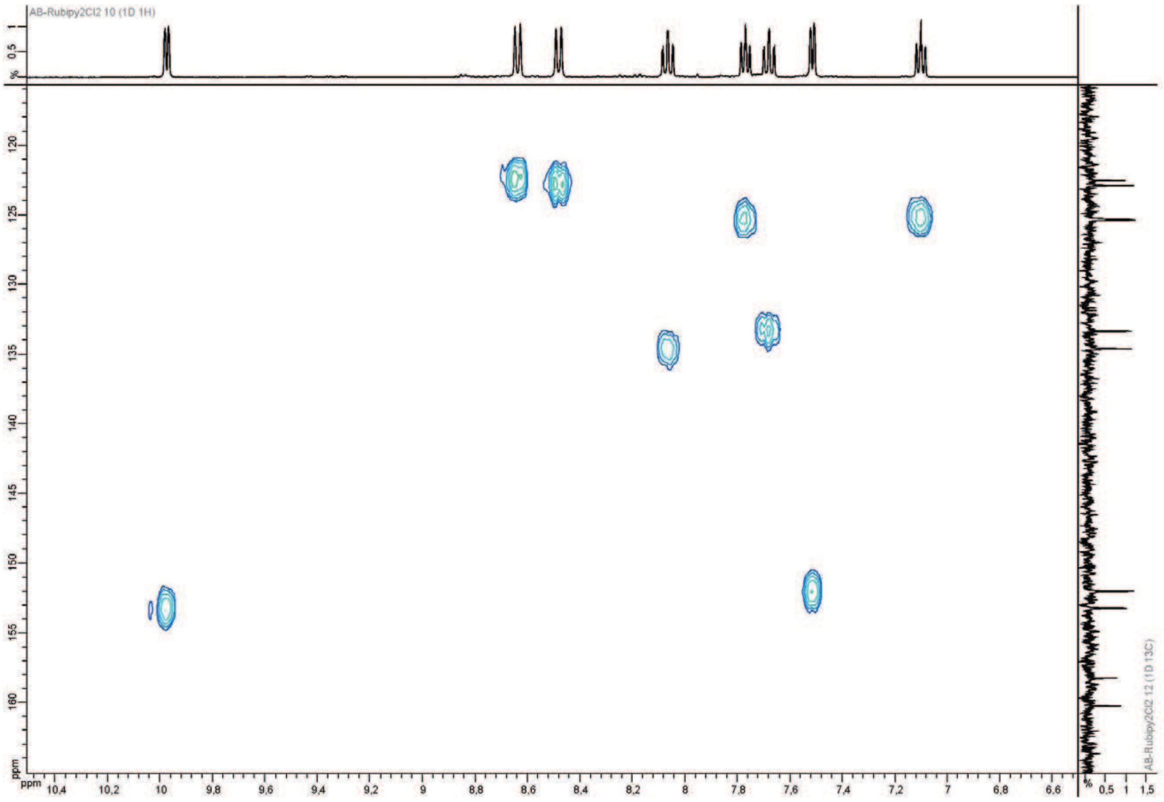
Ru(Bpy)$_2$Cl$_2$ ^{13}C



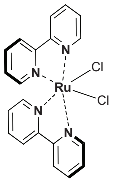


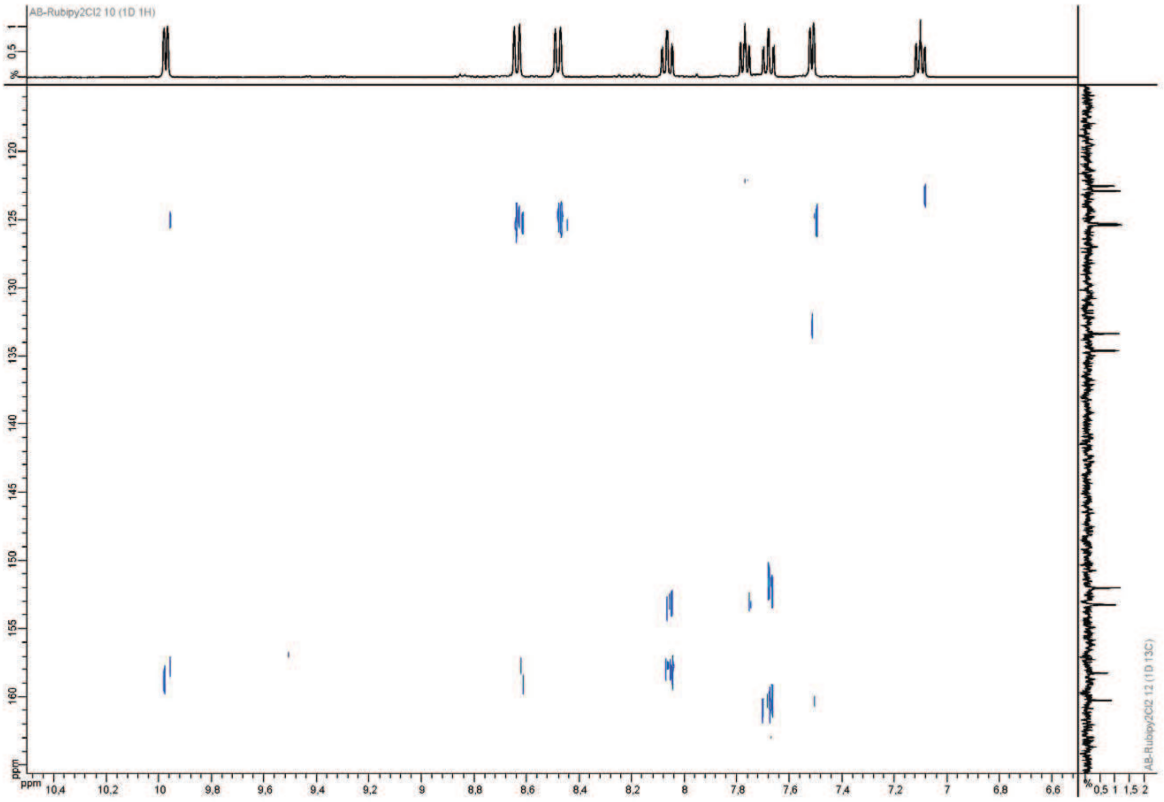
Ru(Bpy)$_2$Cl$_2$ Hsqc





Ru(Bpy)$_2$Cl$_2$ Hmbc





Bpy-*N*-oxide (**1**)

^{1}H all

^{1}H zoom

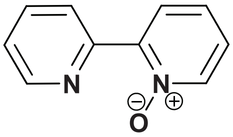
Cosy

^{13}C all

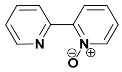
^{13}C zoom

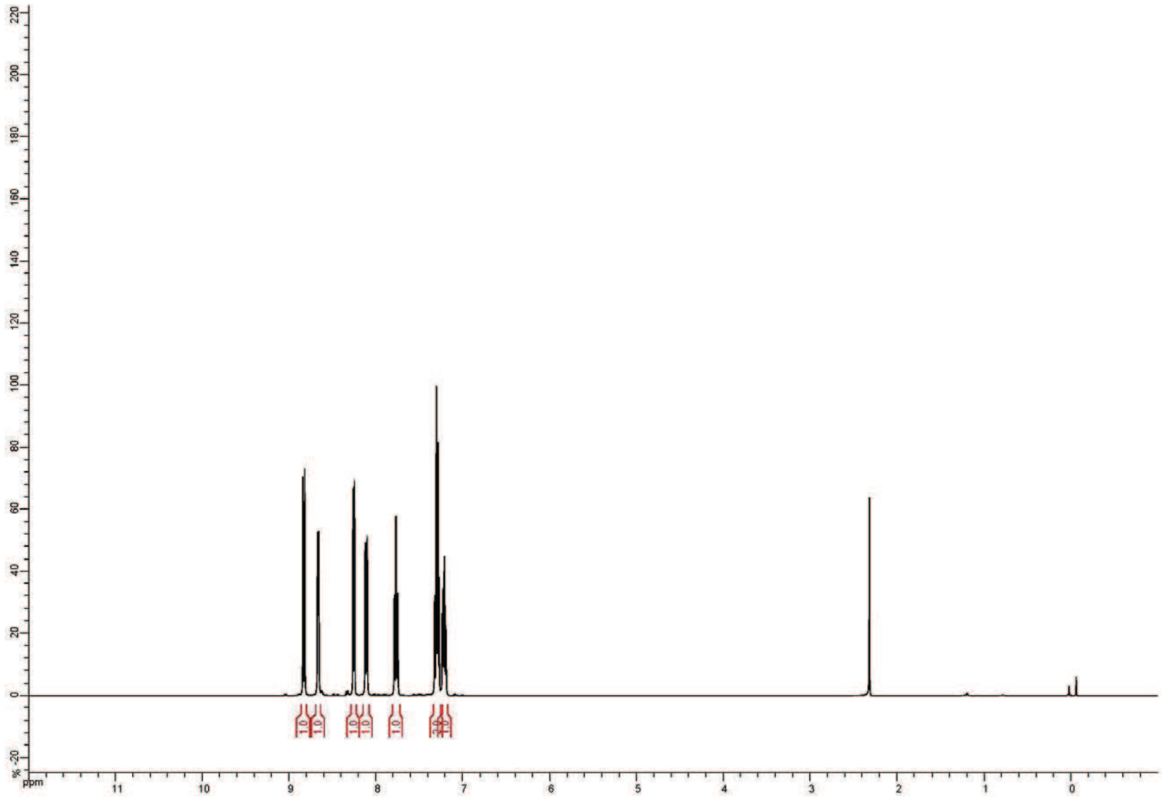
Hsqc

Hmbc

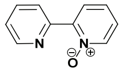


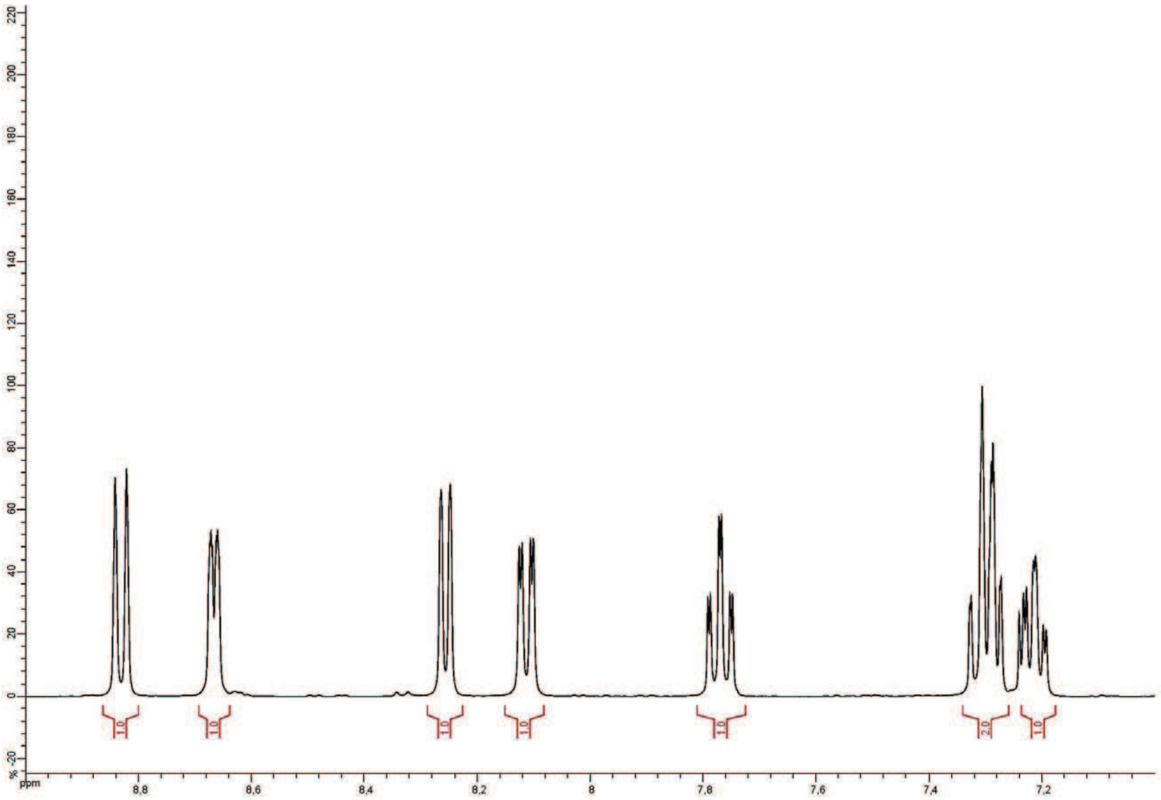
(**1**) ^{1}H



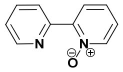


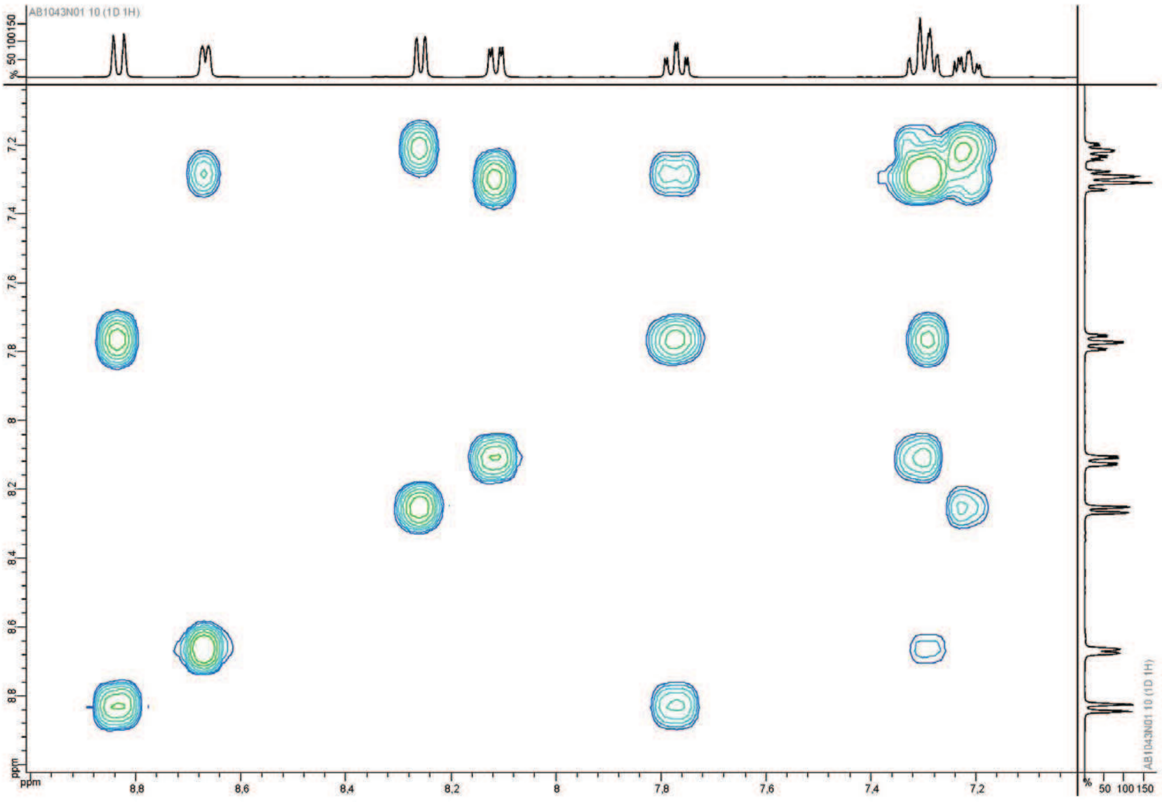
(**1**) ^{1}H


N
N
O

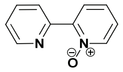

220
200
180
160
140
120
100
80
60
40
20
0
-20
%
ppm
1.0
1.0
1.0
1.0
1.0
2.0
1.0
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2

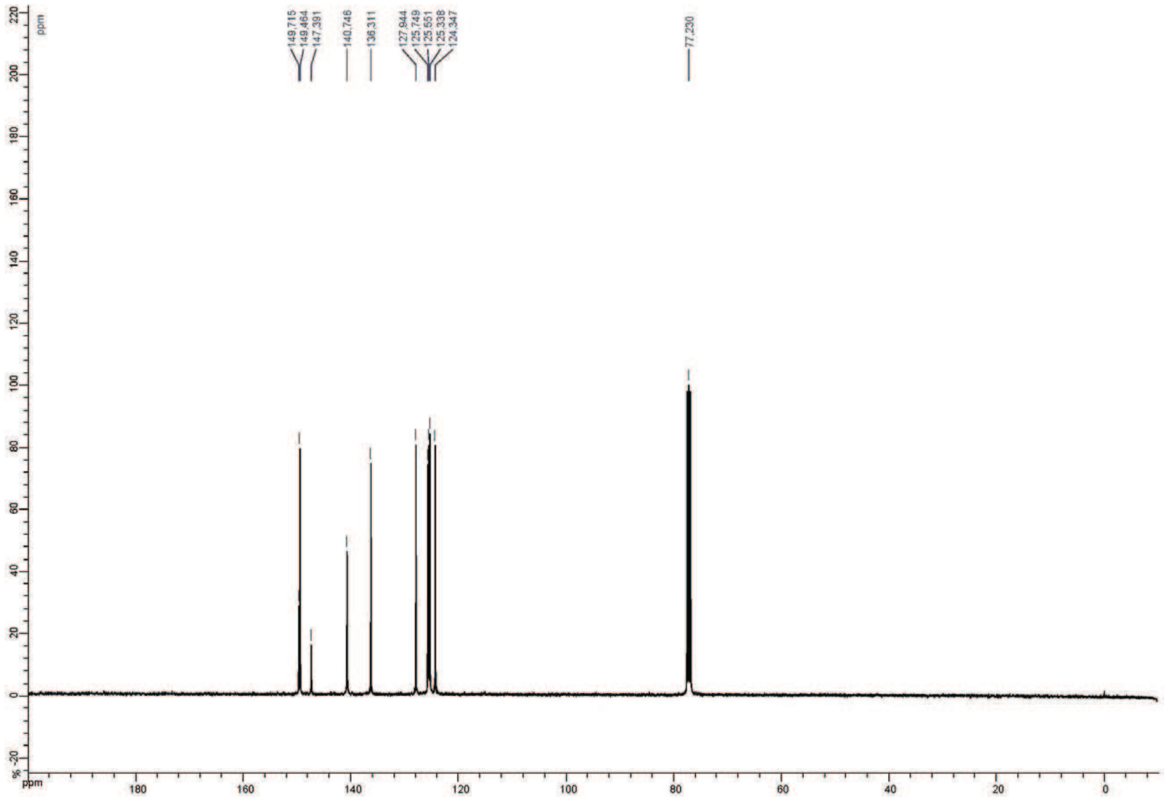
(**1**) Cosy


N
N
O

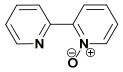

AB1043N01 10 (1D 1H)
150
100
50
%
7,2
7,4
7,6
7,8
8
8,2
8,4
8,6
8,8
ppm
ppm
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
AB1043N01 10 (1D 1H)
%
50
100
150

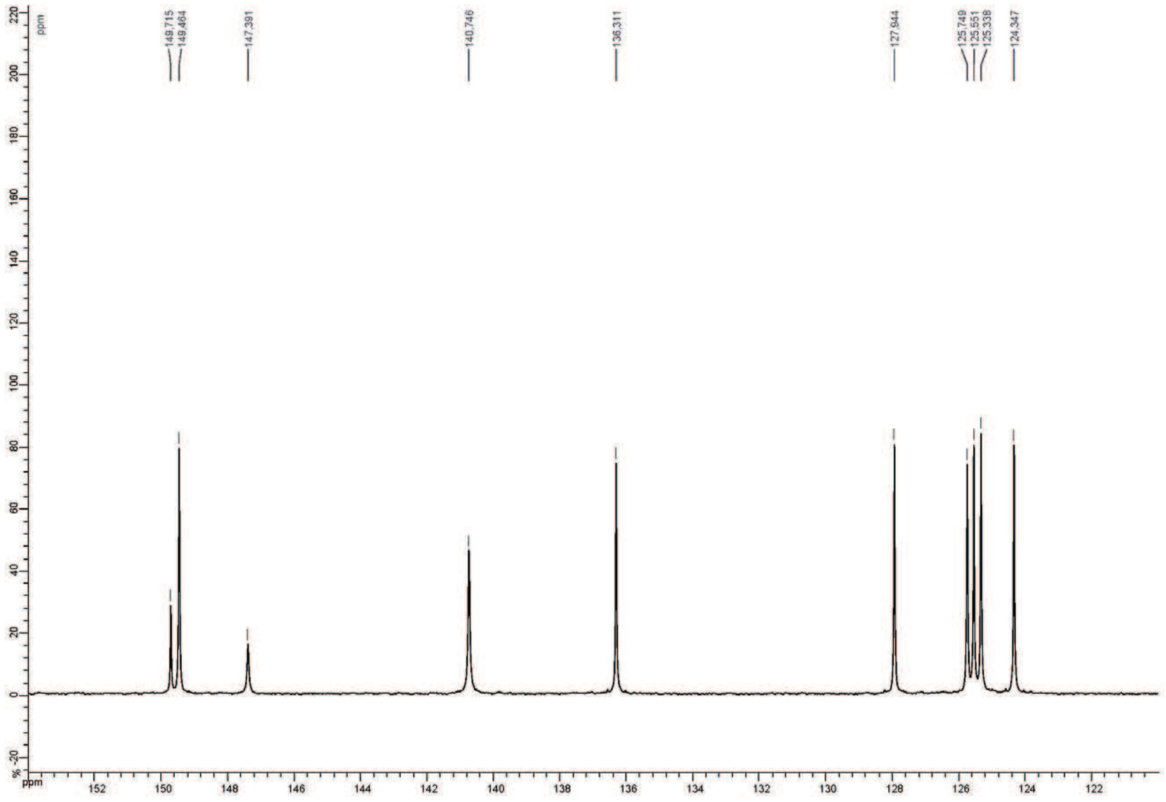
(**1**) ^{13}C


N
N
O

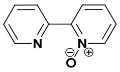

149.715
149.464
147.391
140.746
136.311
127.944
125.749
125.551
125.338
124.347
77.230
ppm
%
220
200
180
160
140
120
100
80
60
40
20
0
-20
180
160
140
120
100
80
60
40
20
0

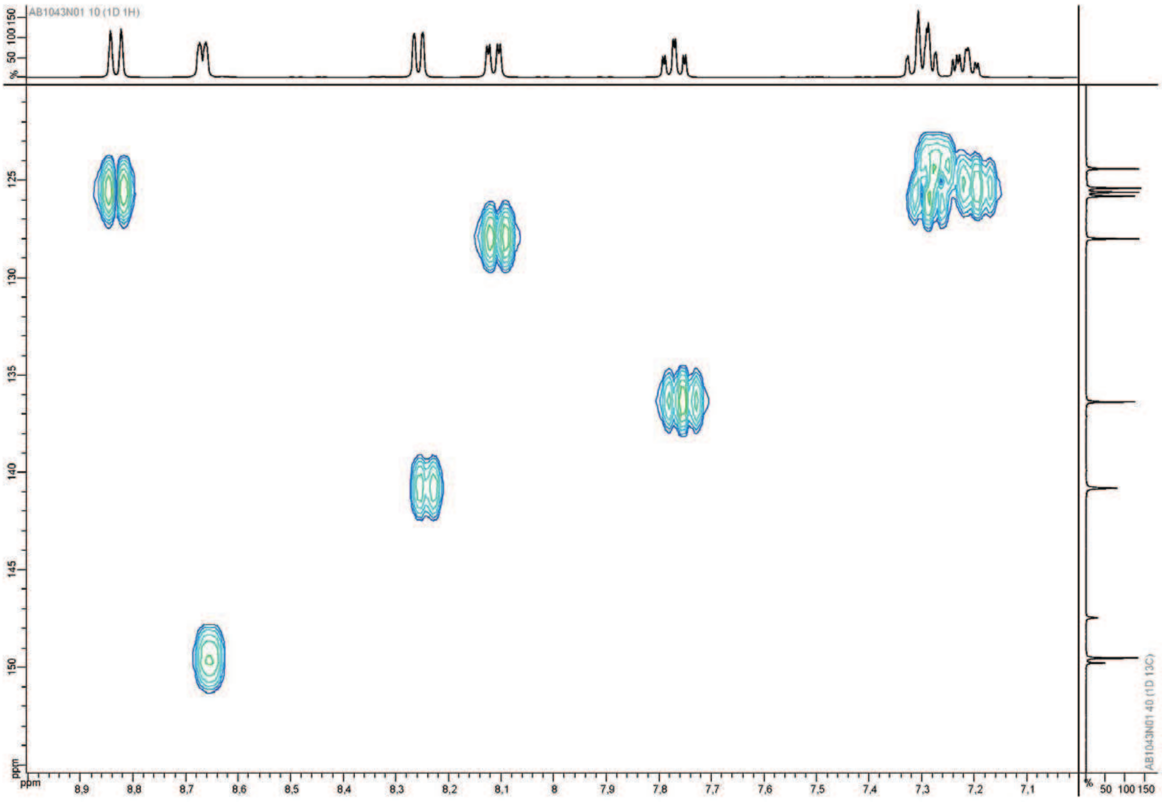
(**1**) ^{13}C


N
N
O

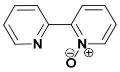

149.715
149.464
147.391
140.746
136.311
127.944
125.749
125.551
125.338
124.347
ppm
%
220
200
180
160
140
120
100
80
60
40
20
0
-20
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122

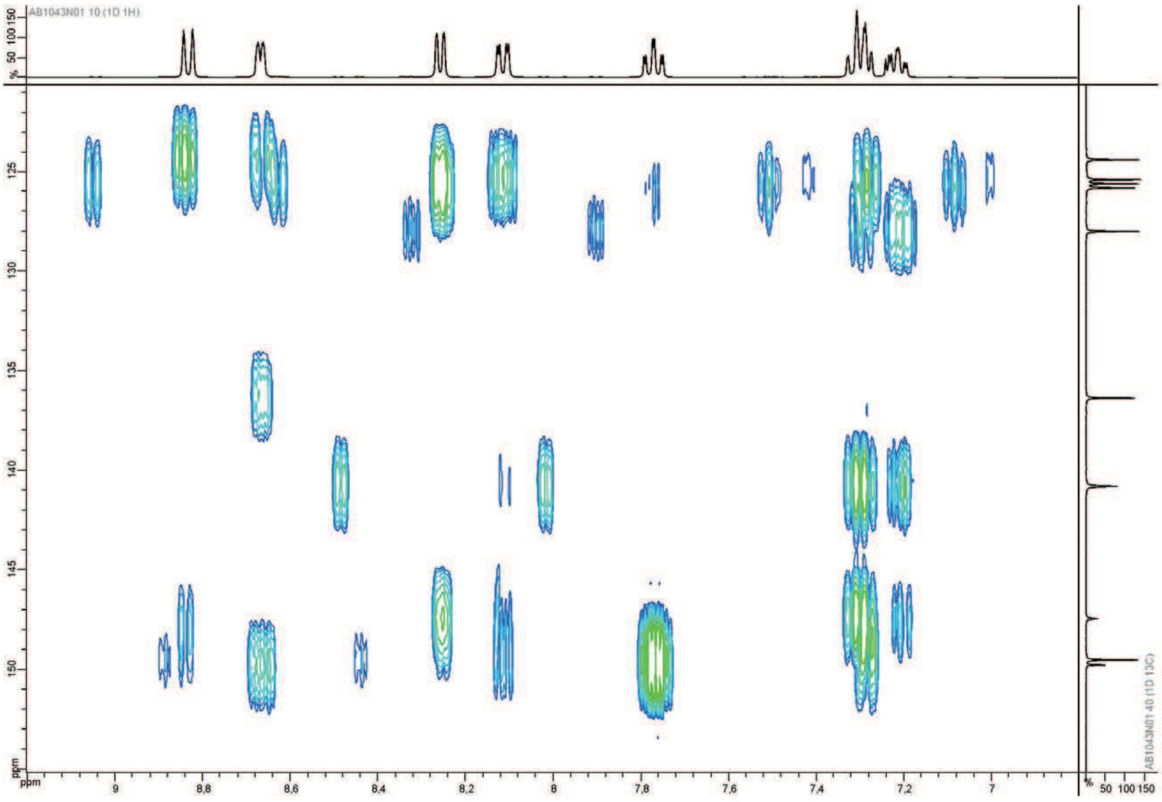
(**1**) Hsqc


N
N
⊕
⊖
O


AB1043N01 10 (1D 1H)
% 50 100 150
125
130
135
140
145
150
ppm
ppm
8,9
8,8
8,7
8,6
8,5
8,4
8,3
8,2
8,1
8
7,9
7,8
7,7
7,6
7,5
7,4
7,3
7,2
7,1
% 50 100 150
AB1043N01 40 (1D 13C)

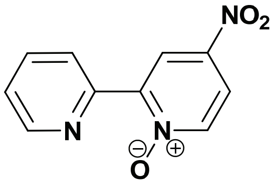
(**1**) Hmbc


N
N
⊕
⊖
O

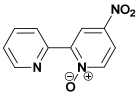

AB1043N01 10 (1D 1H)
% 50 100 150
125
130
135
140
145
150
ppm
ppm
9
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
7
% 50 100 150
AB1043N01 40 (1D 13C)

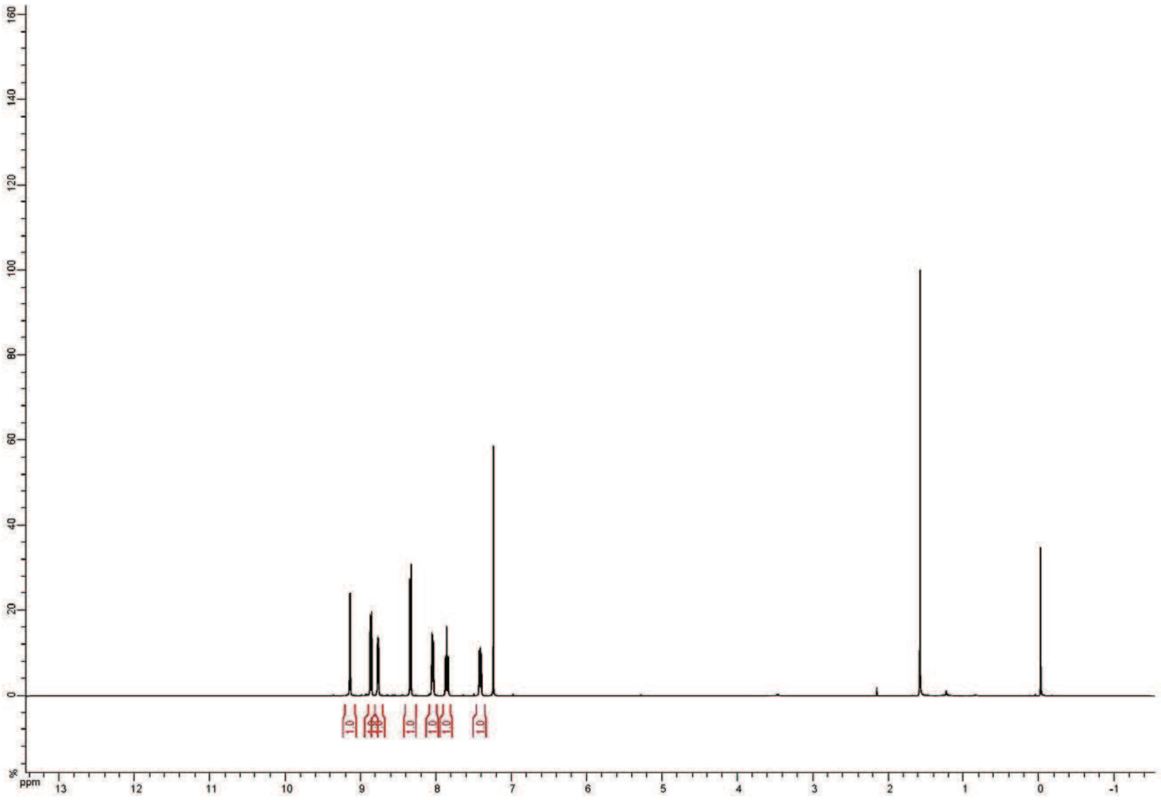
$BpyNO_2$-*N*-oxide (**2**)

^1H all
^1H zoom
Cosy
^{13}C all
^{13}C zoom

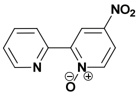


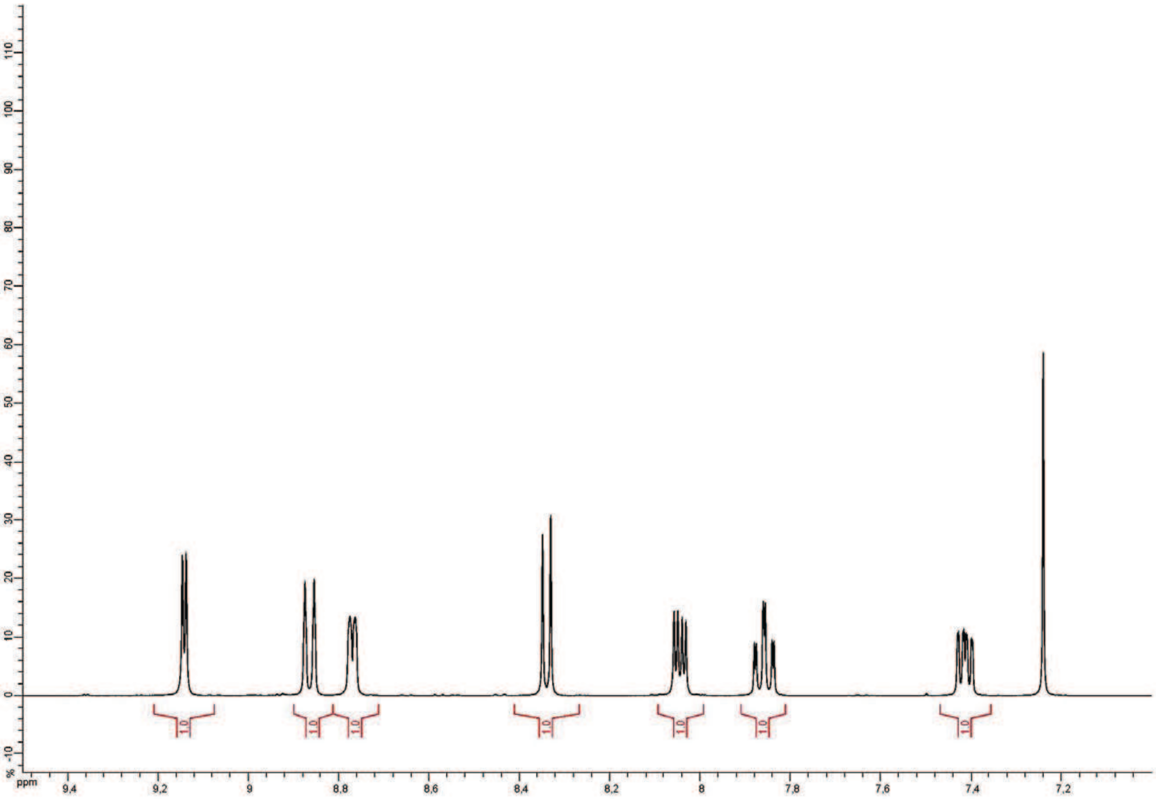
(**2**) ^1H



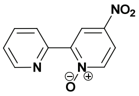


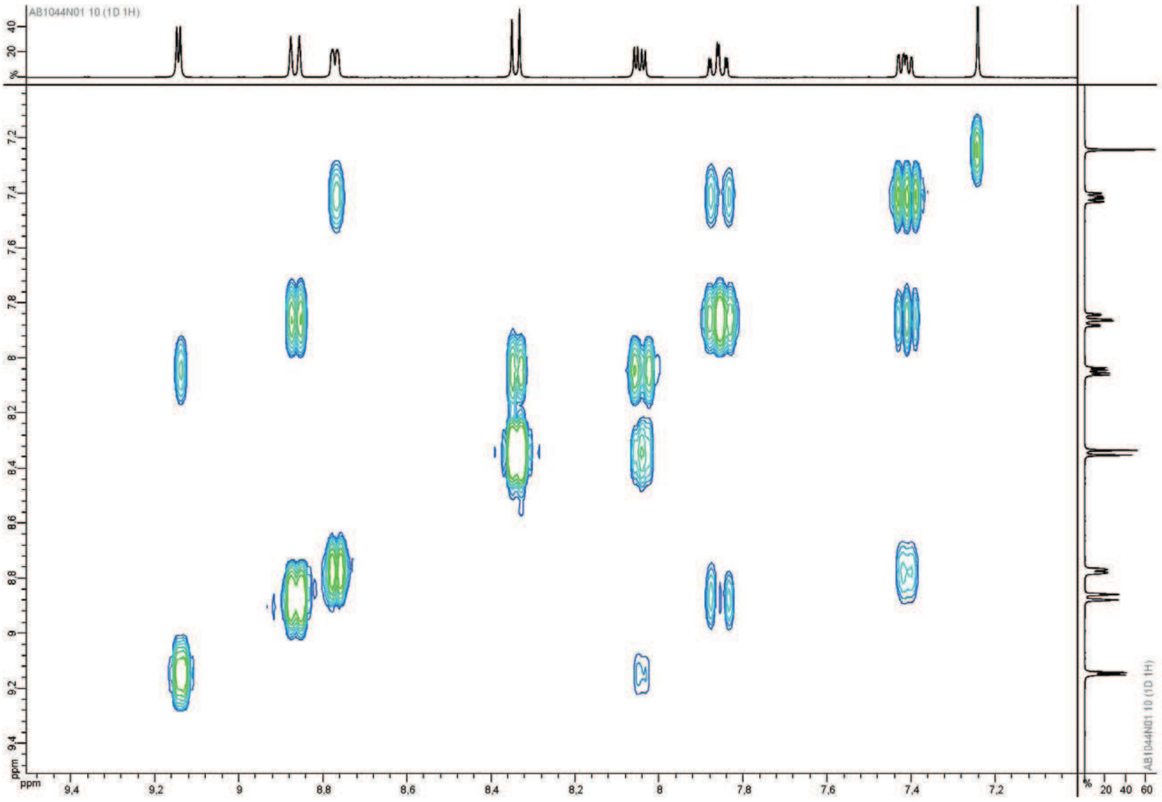
(**2**) ^{1}H


NO2
N
N
O

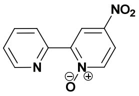

%
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm
9,4
9,2
9
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2

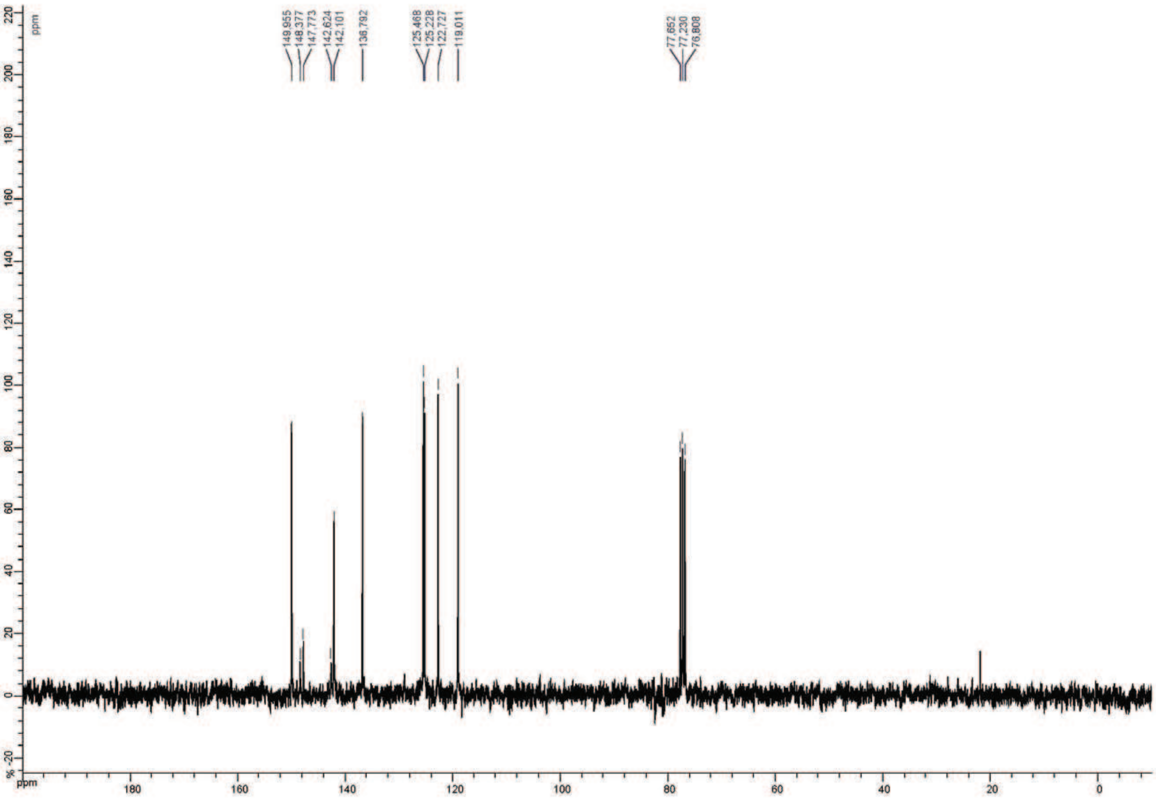
(**2**) Cosy


NO2
N
N
O

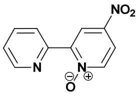

AB1044N01 10 (1D 1H)
40
20
%
7,2
7,4
7,6
7,8
8
8,2
8,4
8,6
8,8
9
9,2
9,4
ppm
ppm
9,4
9,2
9
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
%
20
40
60
AB1044N01 10 (1D 1H)

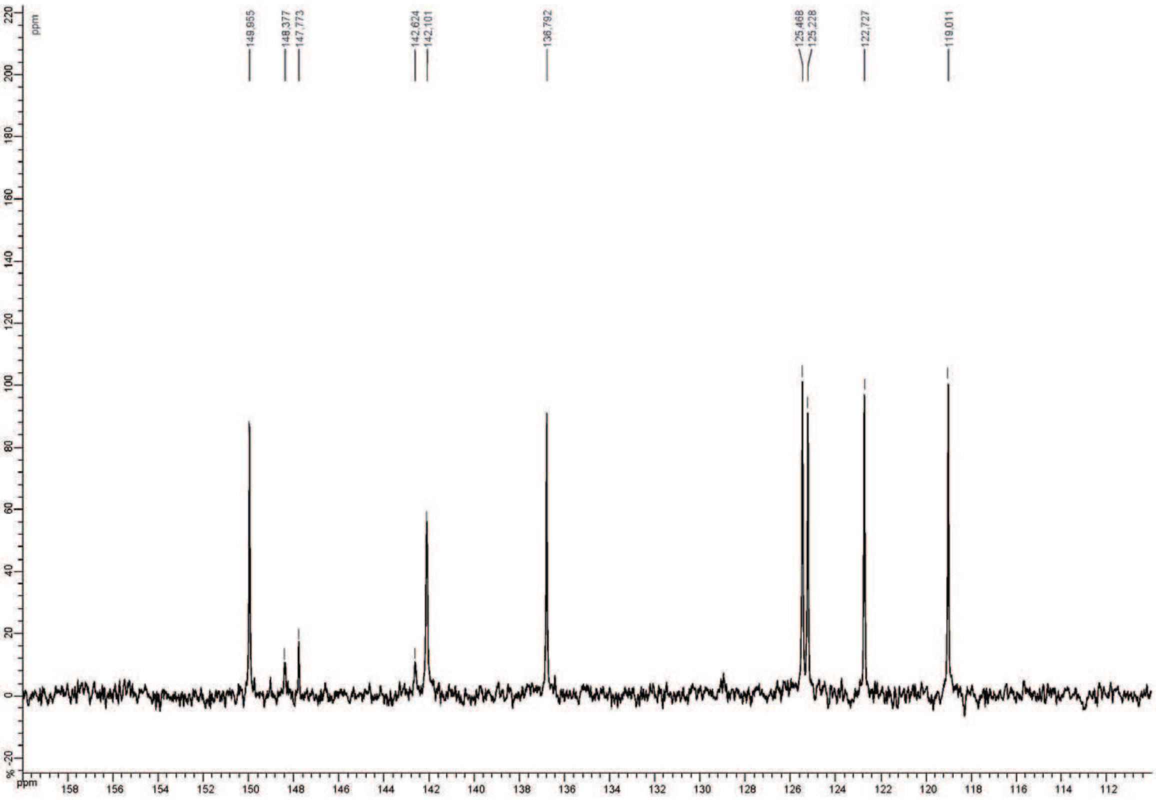
(**2**) ^{13}C


NO$_2$
N
N
O


149.955
148.377
147.773
142.624
142.101
136.792
125.468
125.228
122.727
119.011
77.652
77.230
76.808
ppm
%
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm
180
160
140
120
100
80
60
40
20
0

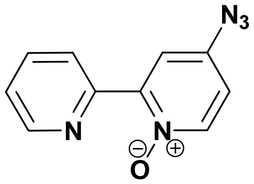
(**2**) ^{13}C


NO$_2$
N
N
O

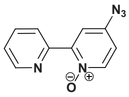

149.955
148.377
147.773
142.624
142.101
136.792
125.468
125.228
122.727
119.011
ppm
%
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm
158
156
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112

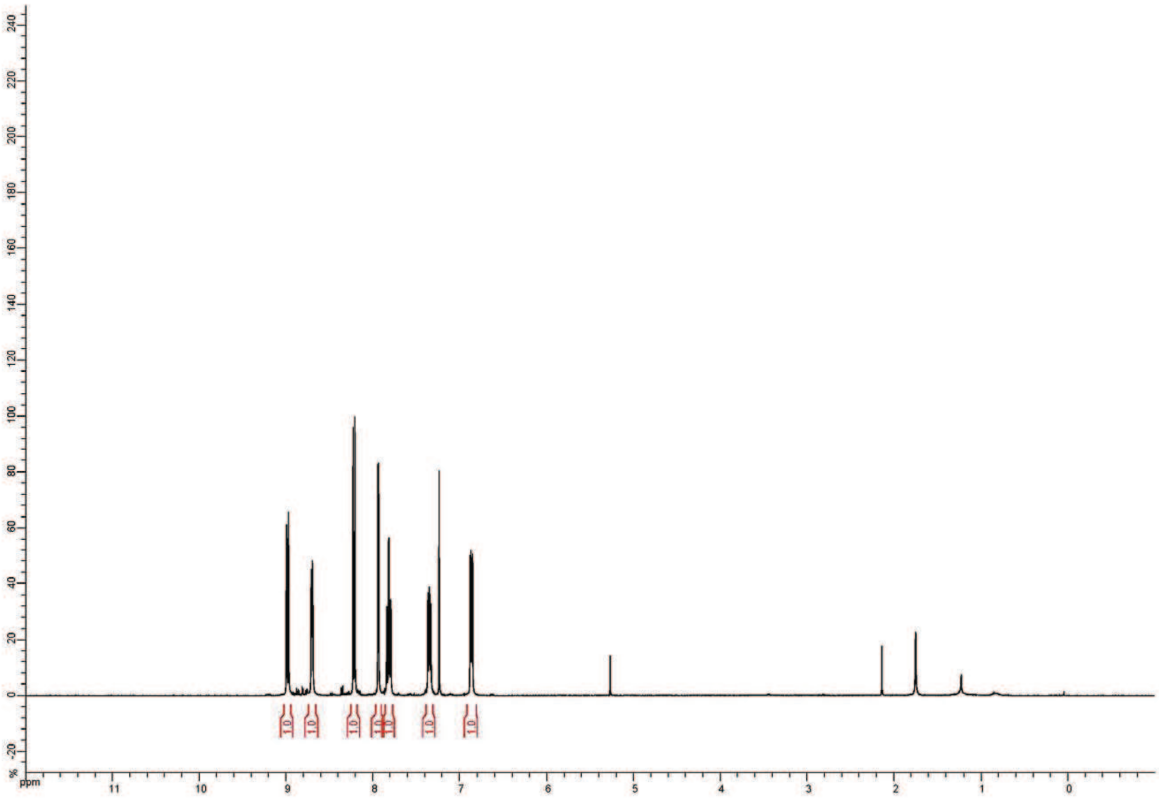
BpyN$_3$-*N*-oxide (**3**)

^{1}H all
^{1}H zoom
Cosy
^{13}C all
^{13}C zoom
Hsqc
Hmbc

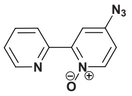


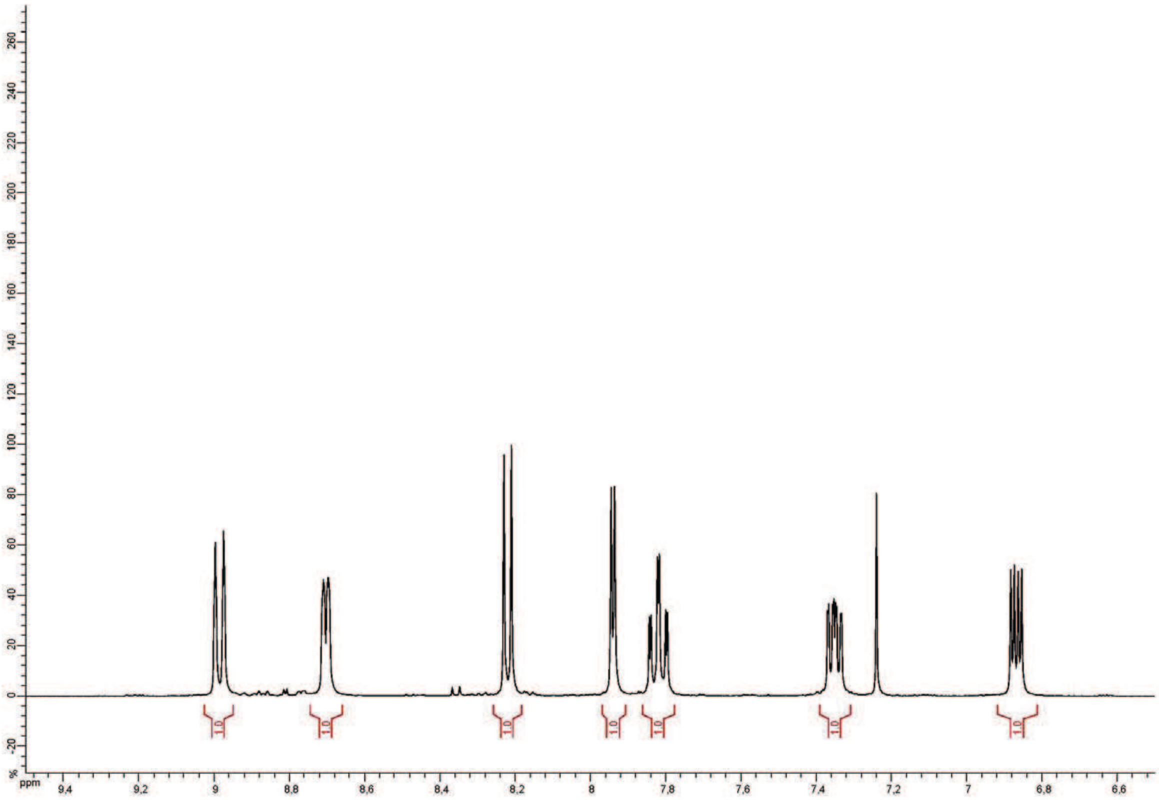
(**3**) ^{1}H



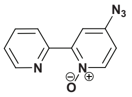


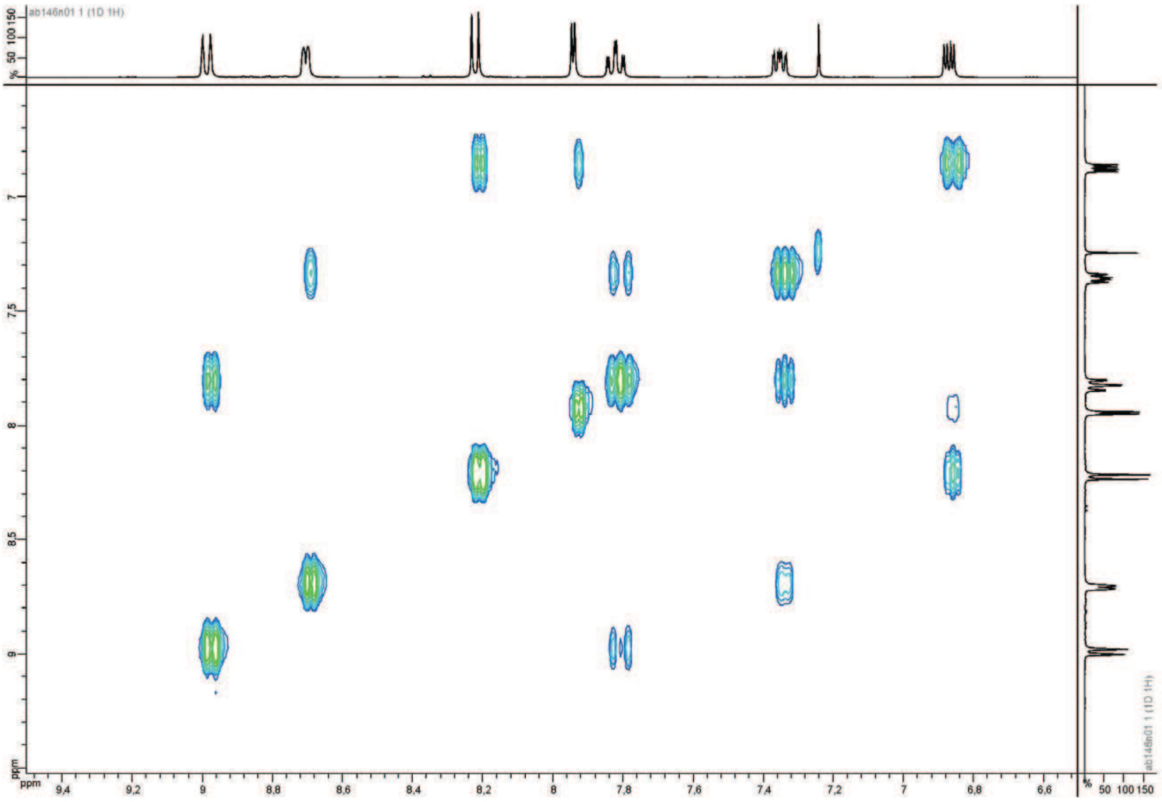
(**3**) ^{1}H


N3
N
N
O

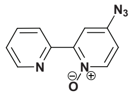

%
ppm
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
9,4
9,2
9
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
7
6,8
6,6

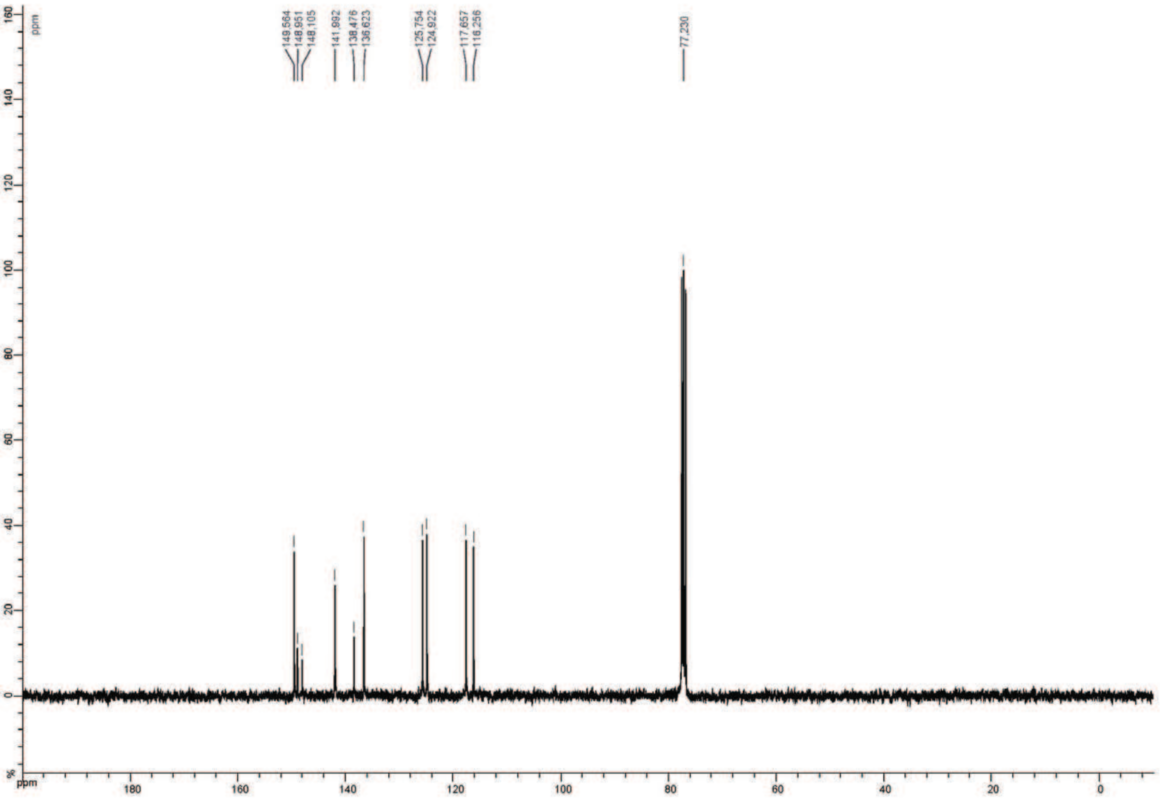
(**3**) Cosy


N3
N
N
O

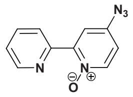

ab146n01 1 (1D 1H)
150
100
50
%
7
7,5
8
8,5
9
ppm
ppm
9,4
9,2
9
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
7
6,8
6,6
%
50
100
150
ab146n01 1 (1D 1H)

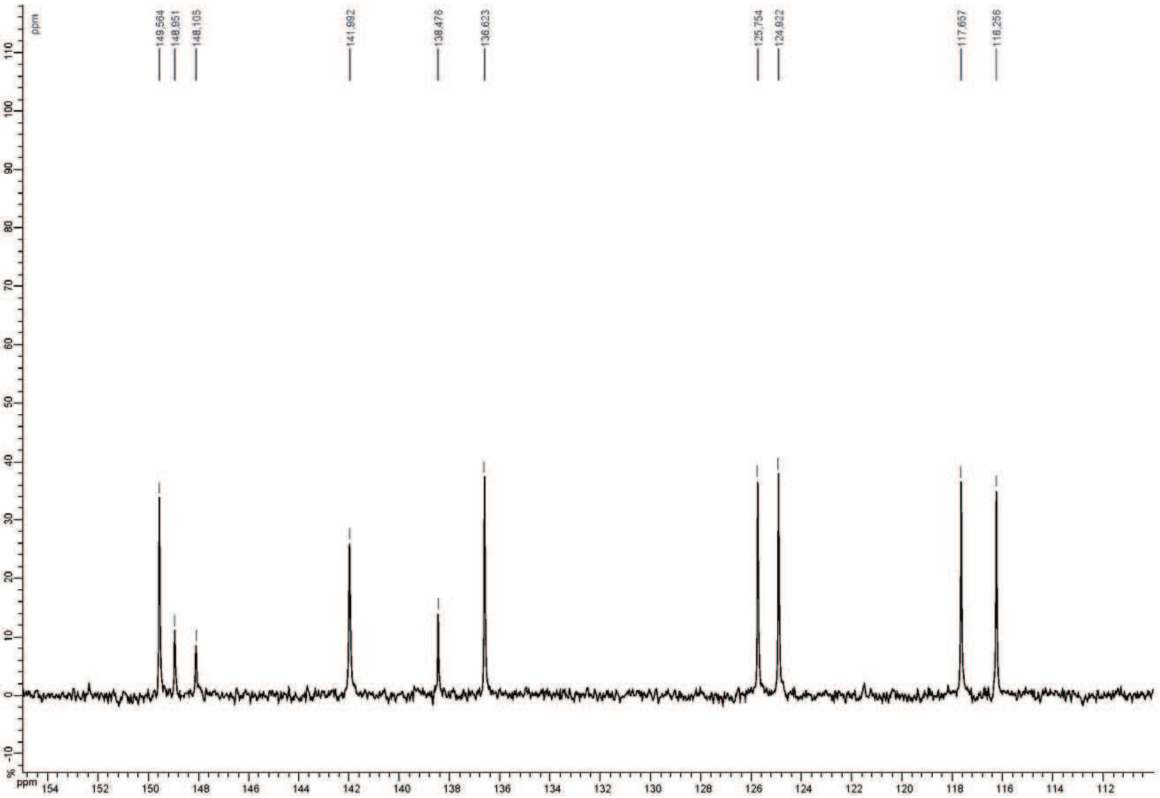
(**3**) ^{13}C


N$_3$
N
N
O
⊖
⊕

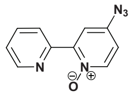

149.564
148.951
148.105
141.992
138.476
136.623
125.754
124.922
117.657
116.256
77.230
ppm
%
160
140
120
100
80
60
40
20
0
ppm
180
160
140
120
100
80
60
40
20
0

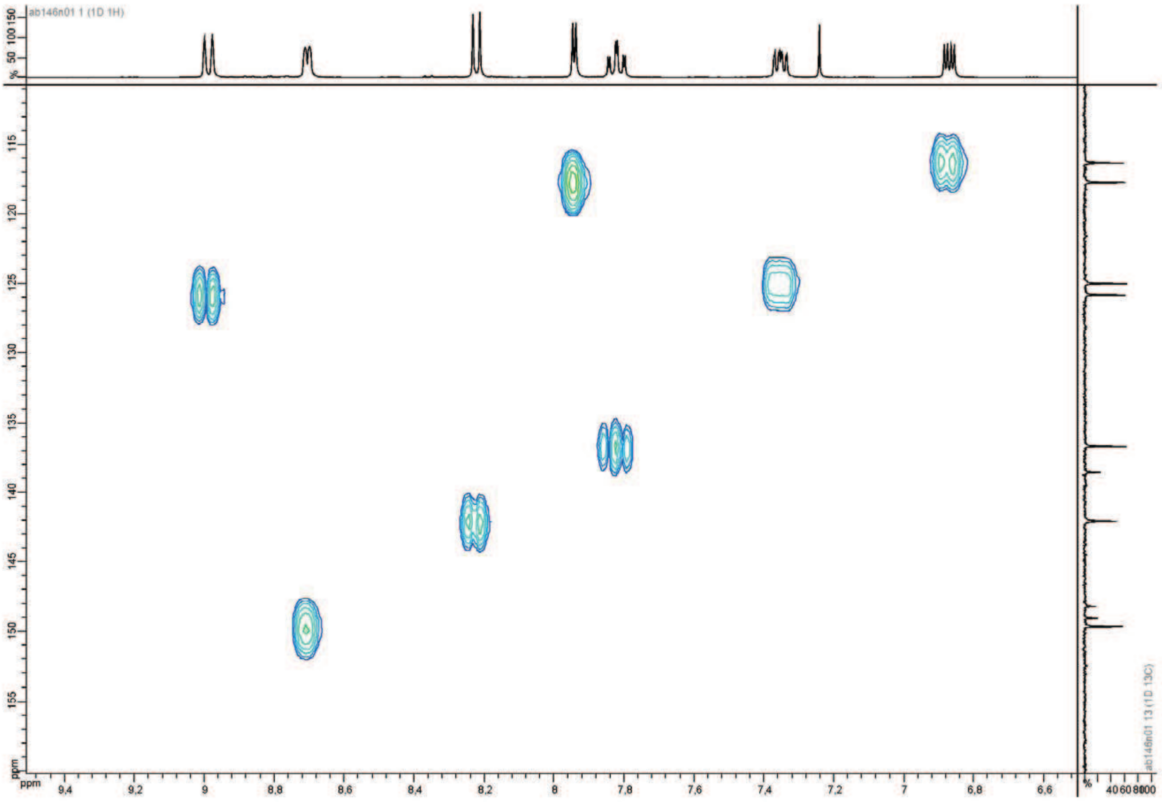
(**3**) ^{13}C


N$_3$
N
N
O
⊖
⊕

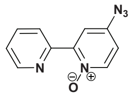

149.564
148.951
148.105
141.992
138.476
136.623
125.754
124.922
117.657
116.256
ppm
%
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112

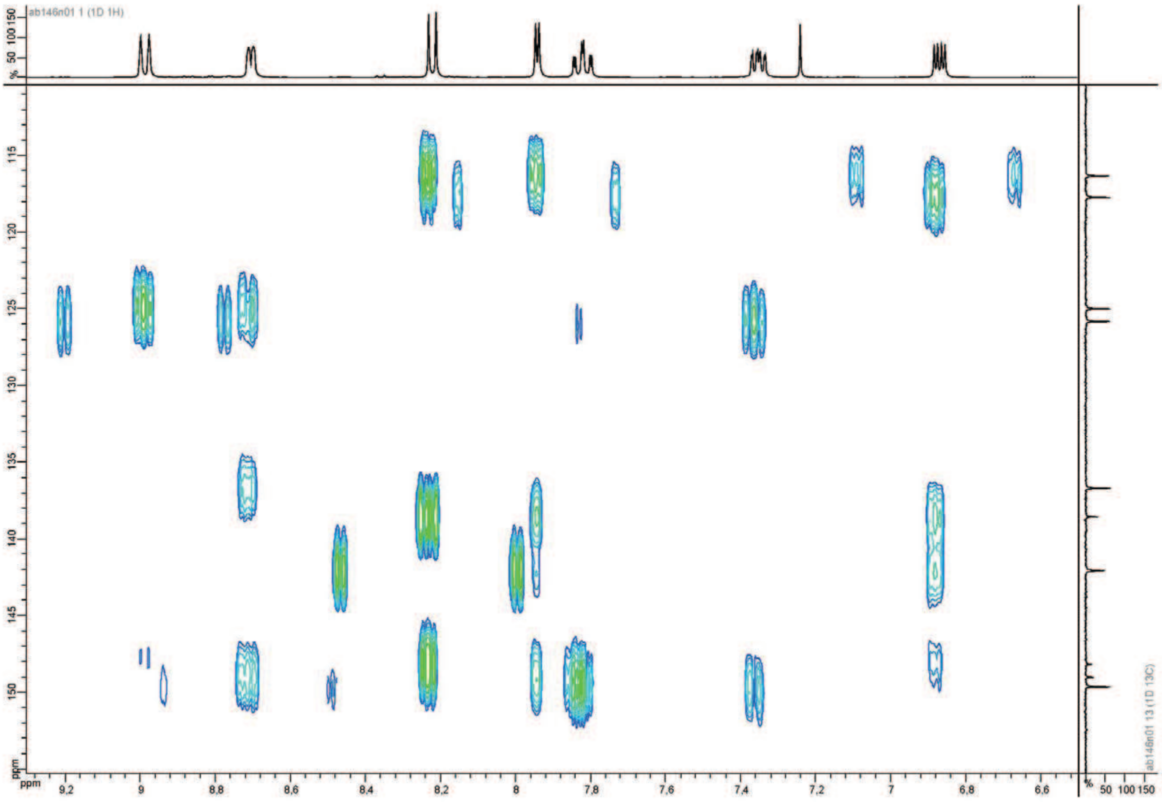
(**3**) Hsqc


N3
N
N
O


ab146n01 1 (1D 1H)
% 50 100 150
ab146n01 13 (1D 13C)
ppm
115
120
125
130
135
140
145
150
155
ppm 9,4 9,2 9 8,8 8,6 8,4 8,2 8 7,8 7,6 7,4 7,2 7 6,8 6,6
% 40 60 80 100

(**3**) Hmbc


N3
N
N
O


ab146n01 1 (1D 1H)
% 50 100 150
ab146n01 13 (1D 13C)
ppm
115
120
125
130
135
140
145
150
ppm 9,2 9 8,8 8,6 8,4 8,2 8 7,8 7,6 7,4 7,2 7 6,8 6,6
% 50 100 150

BpyTPh-*N*-oxide (**5a**)

^{1}H all

^{1}H zoom

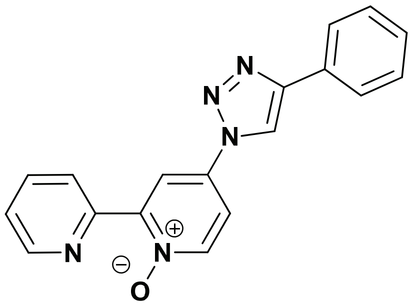
Cosy

^{13}C all

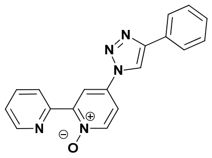
^{13}C zoom

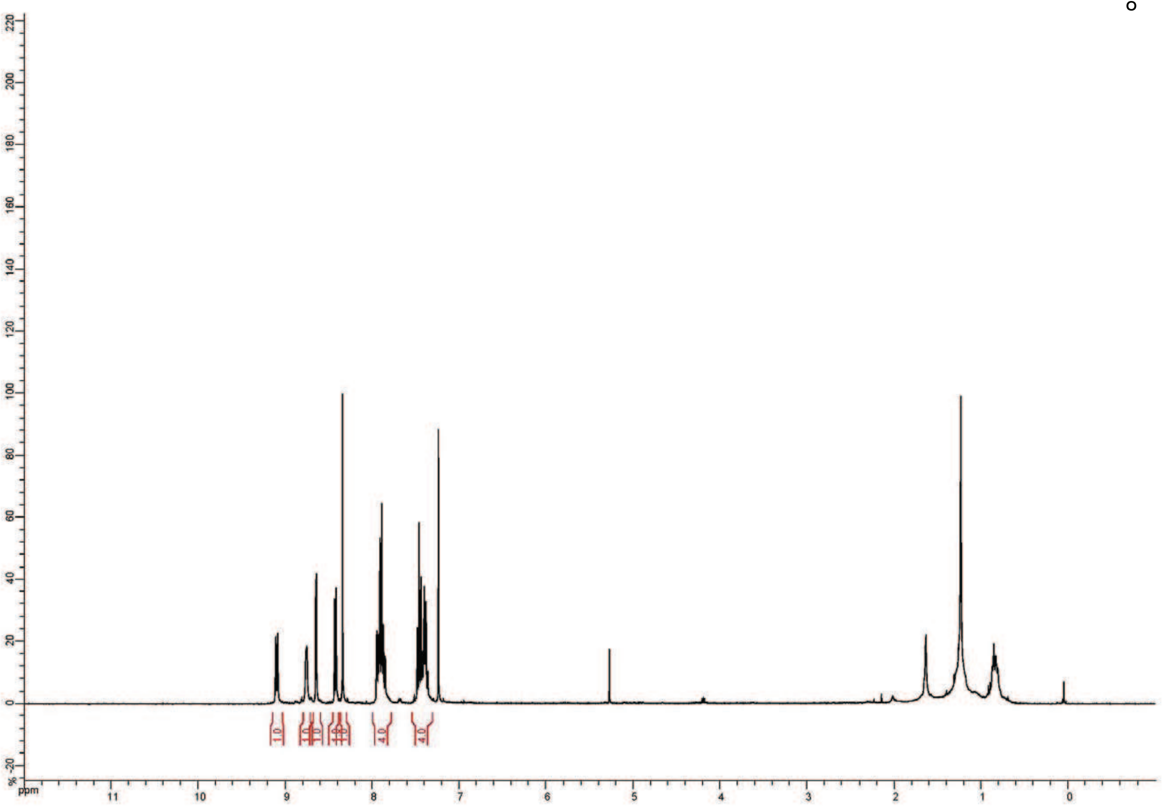
Hsqc

Hmbc

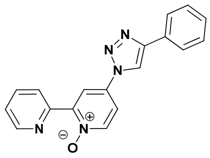


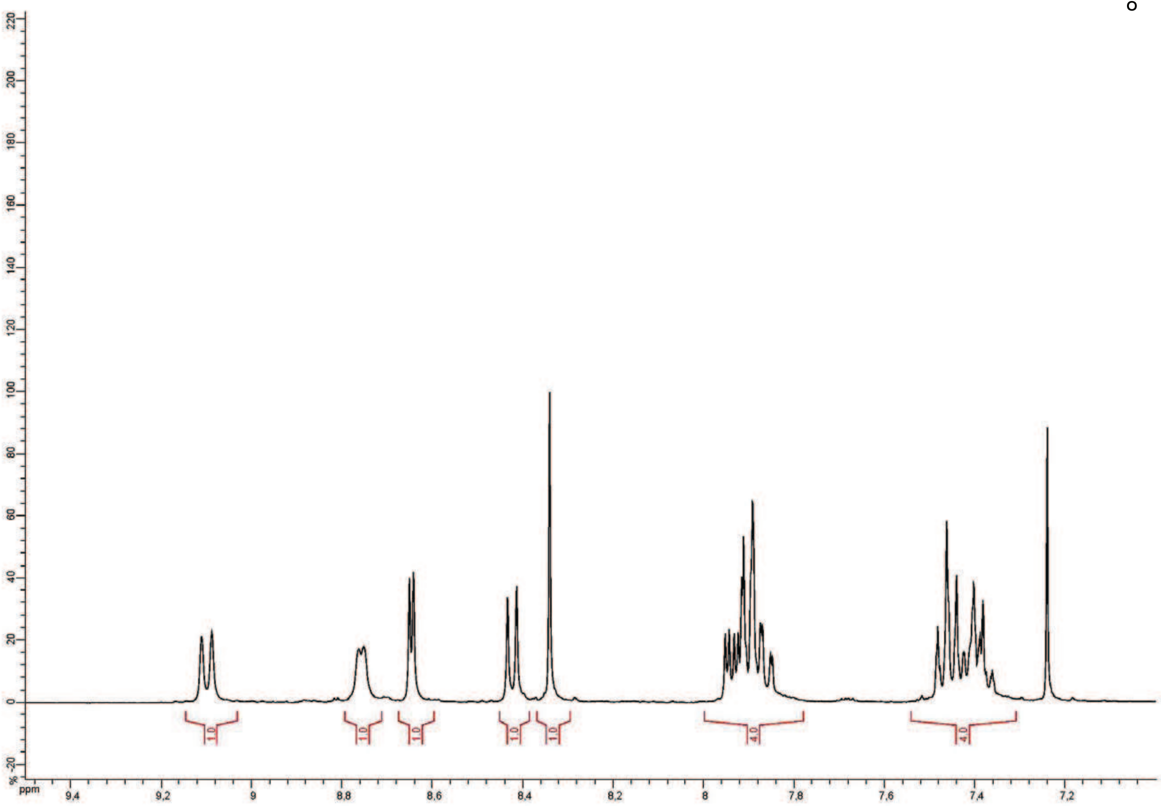
(**5a**) ^{1}H



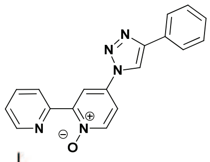


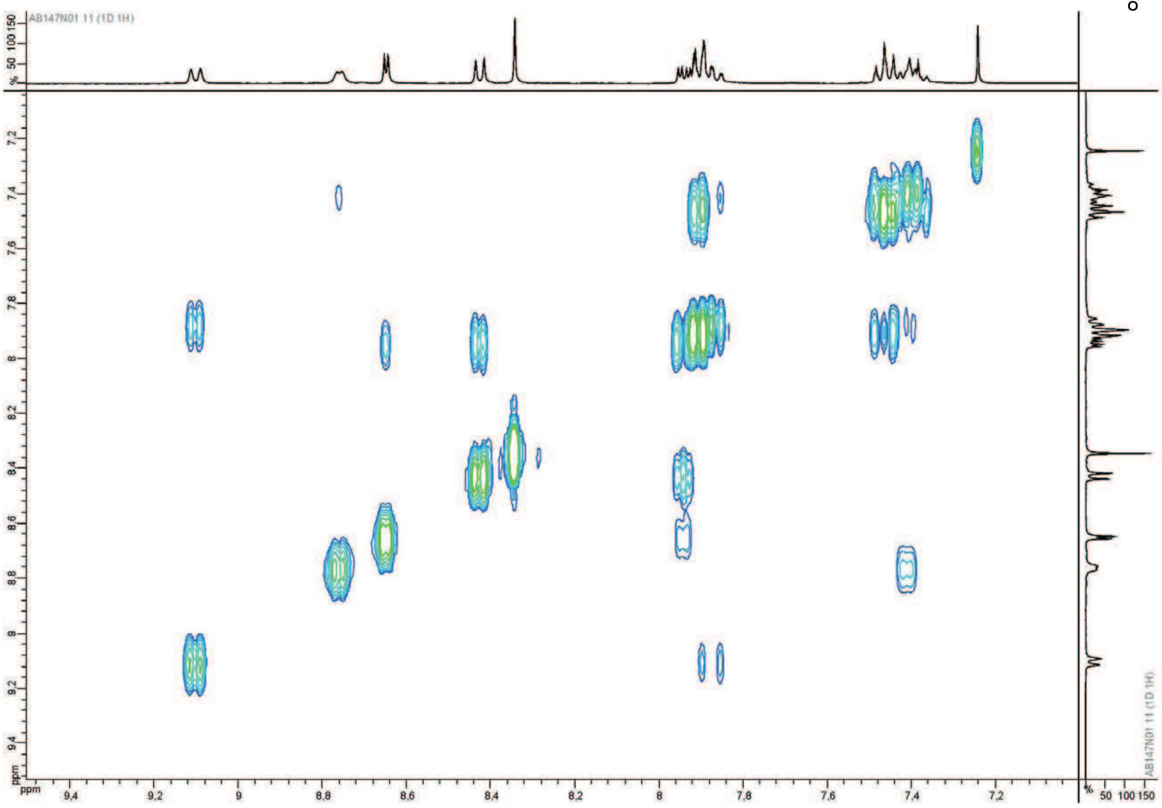
(**5a**) ^{1}H


N
N
N
N
N
O
⊕
⊖

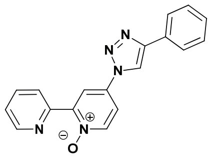

%
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm
9,4
9,2
9
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
1.0
1.0
1.0
1.0
1.0
4.0
4.0

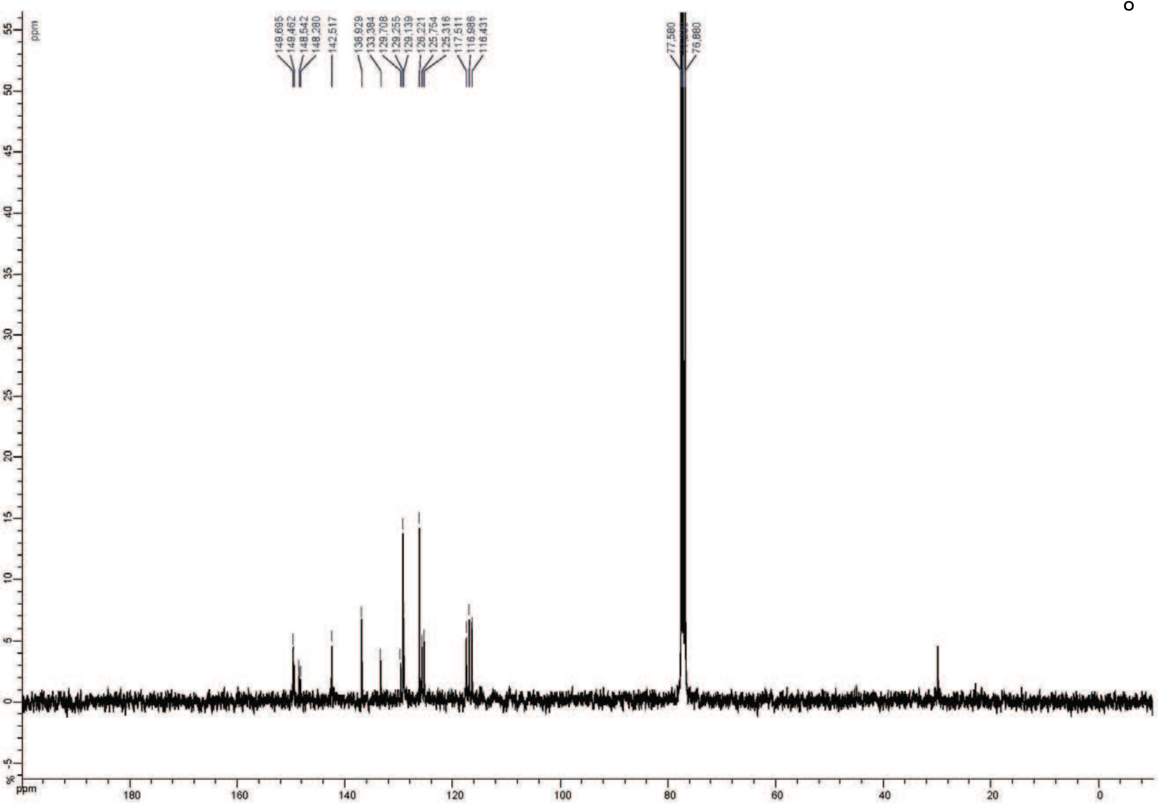
(**5a**) Cosy


N
N
N
N
N
O
⊕
⊖

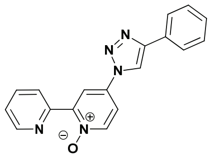

AB147N01 11 (1D 1H)
%
50
100
150
ppm
9,4
9,2
9
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
AB147N01 11 (1D 1H)

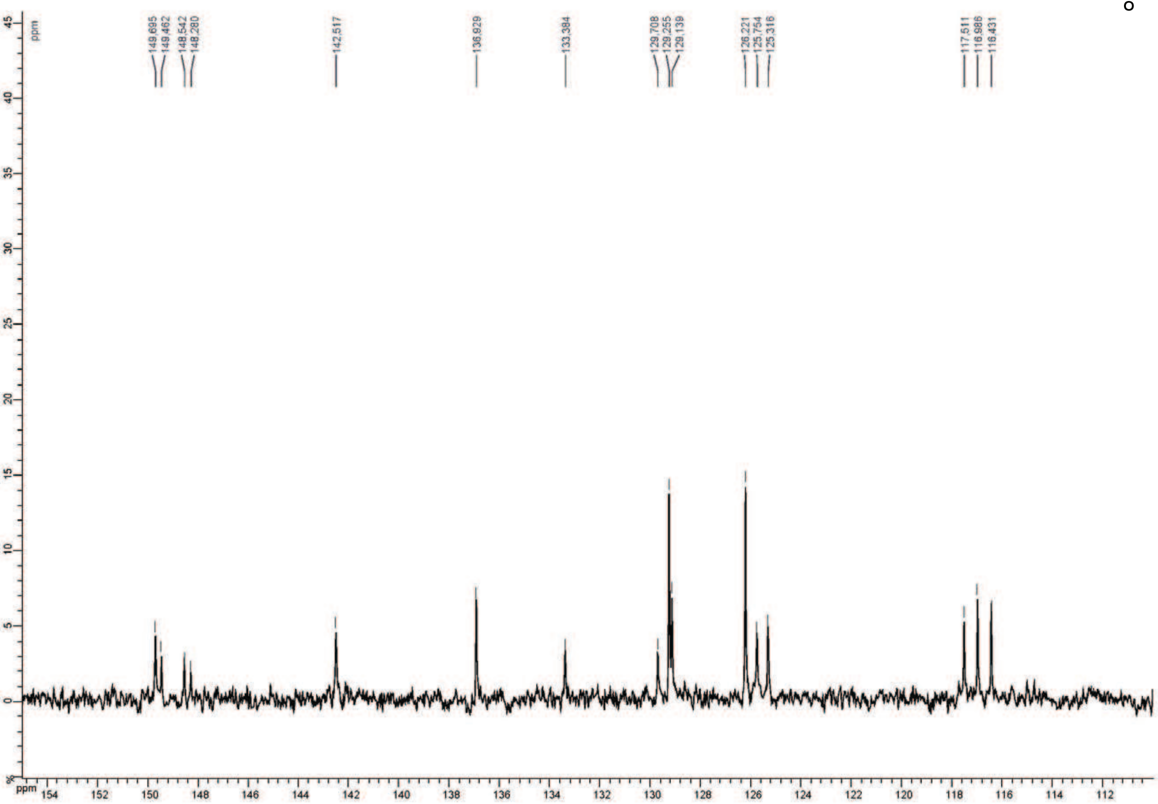
(**5a**) ^{13}C


N
N
N
N
N
O

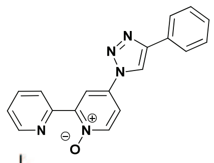

149.695
149.462
148.542
148.280
142.517
136.929
133.384
129.708
129.255
129.139
126.221
125.754
125.316
117.511
116.986
116.431
77.580
76.880
ppm
%
ppm
180
160
140
120
100
80
60
40
20
0

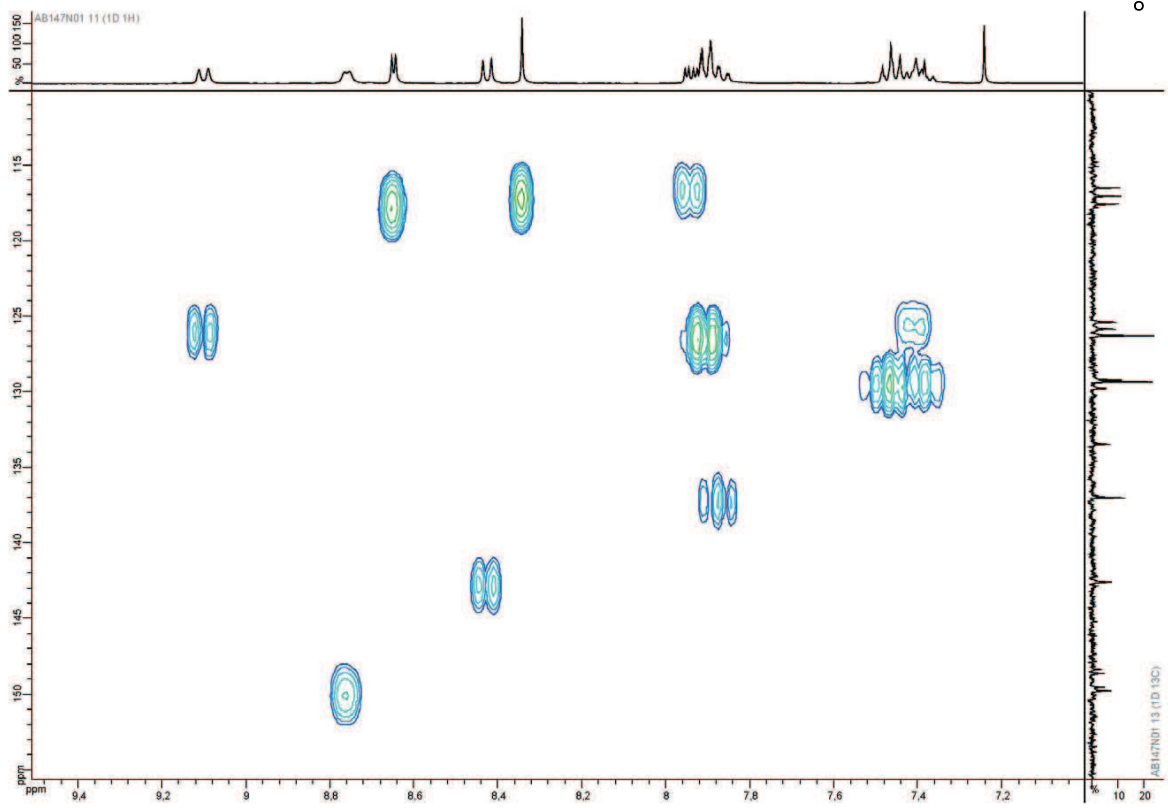
(**5a**) ^{13}C


N
N
N
N
N
O

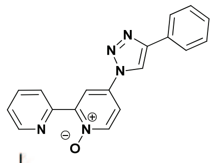

149.695
149.462
148.542
148.280
142.517
136.929
133.384
129.708
129.255
129.139
126.221
125.754
125.316
117.511
116.986
116.431
ppm
%
ppm
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112

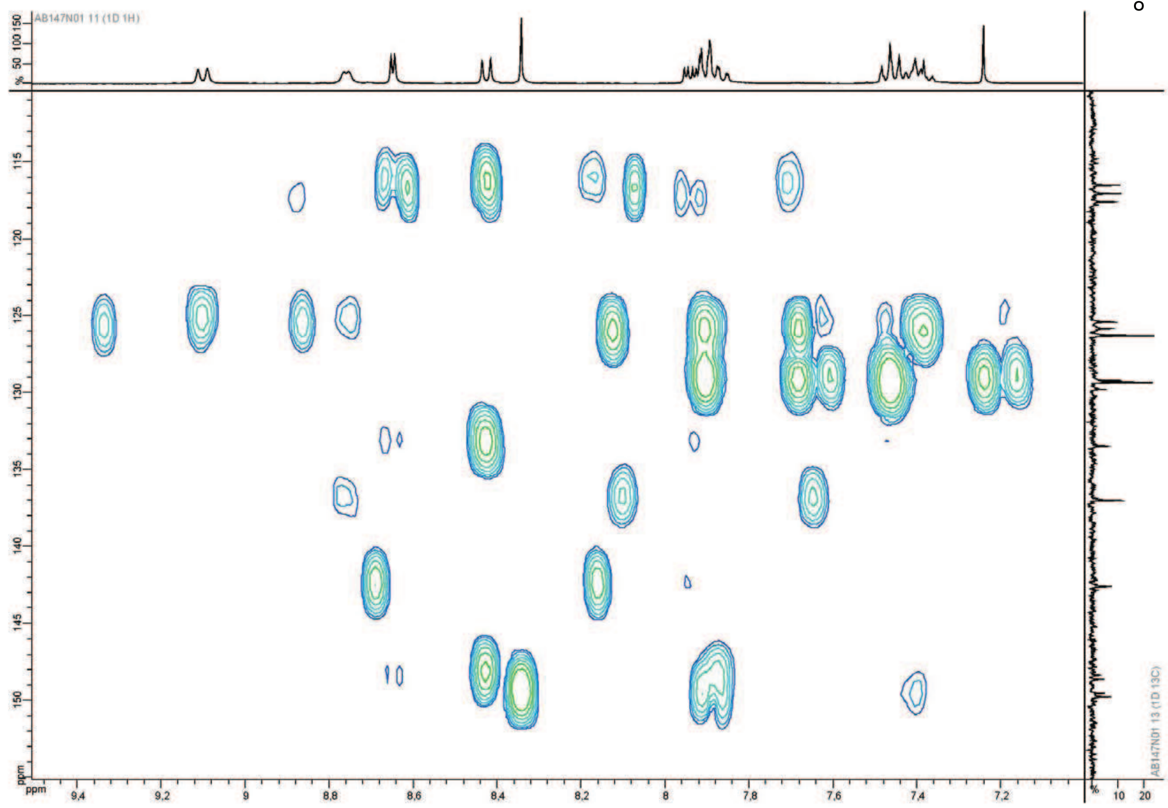
(**5a**) Hsqc





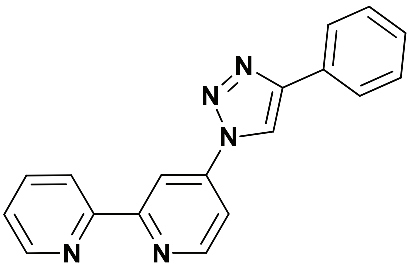
(**5a**) Hmbc



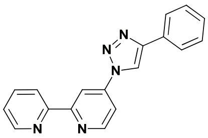


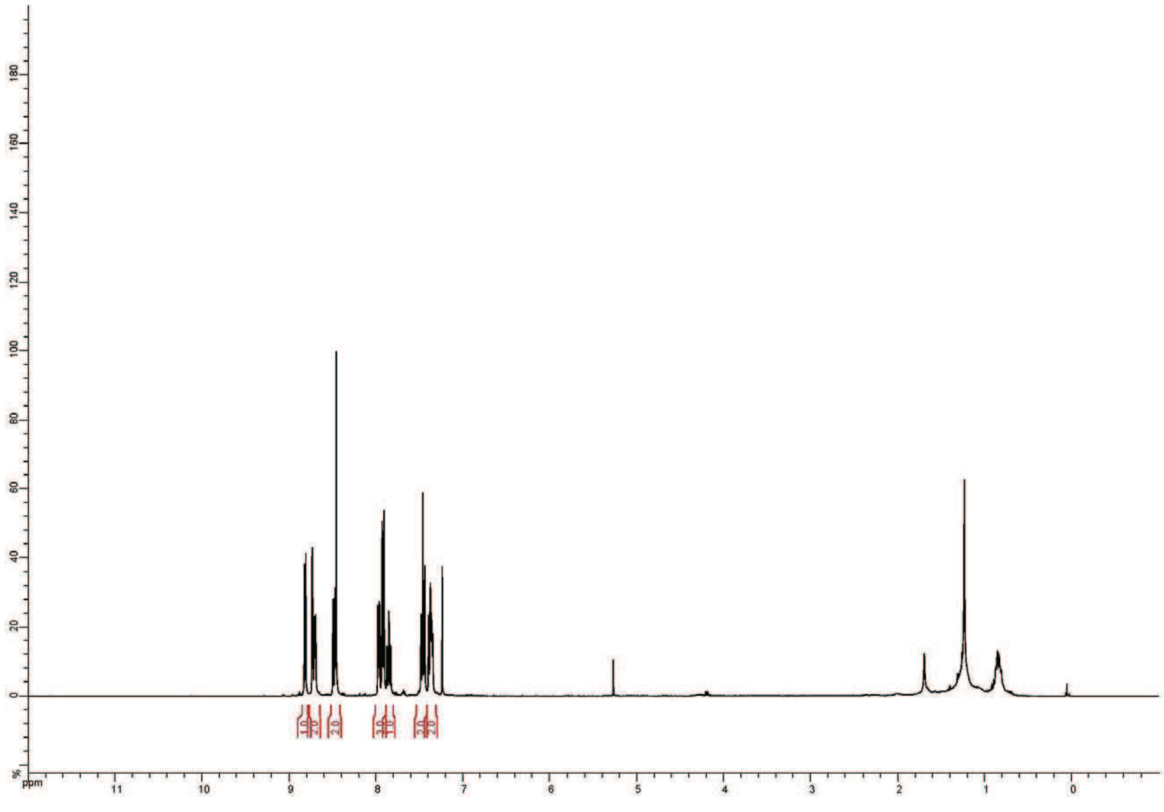
BpyTPh (**6a**)

^{1}H all
^{1}H zoom
Cosy
^{13}C all
^{13}C zoom
Hsqc

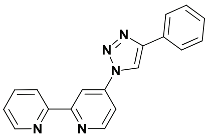


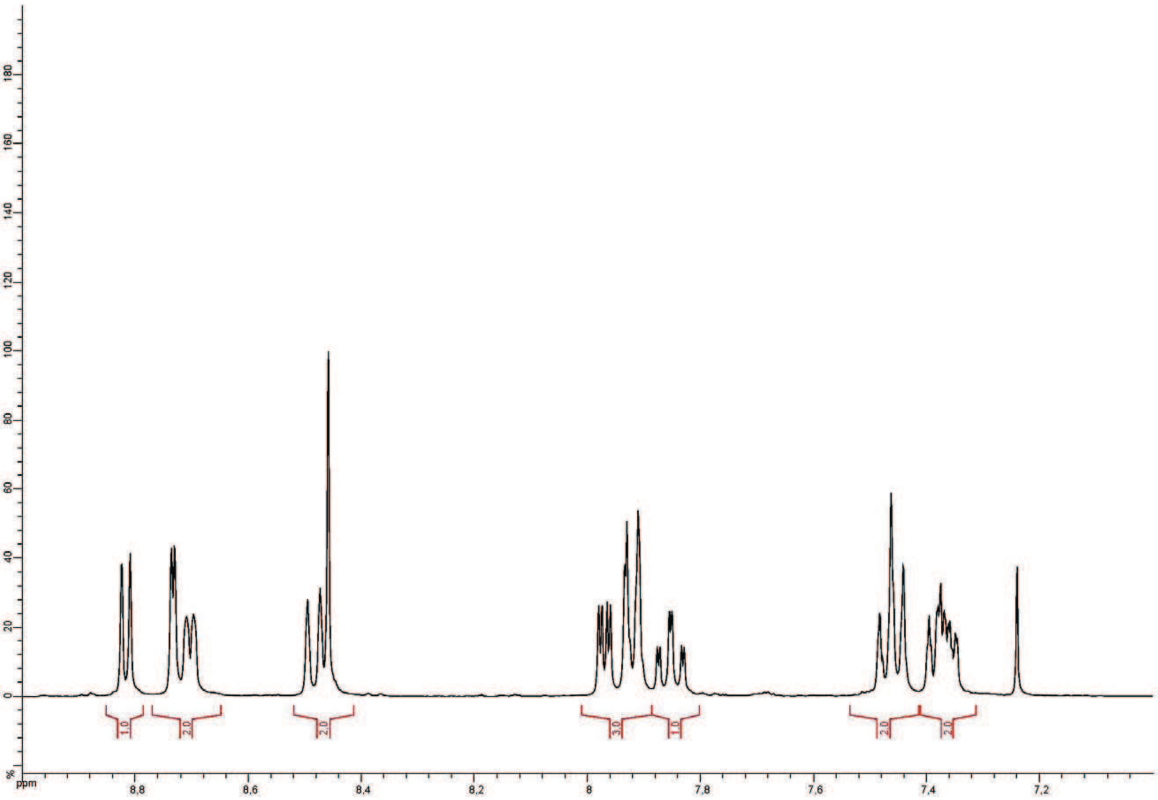
(**6a**) ^{1}H



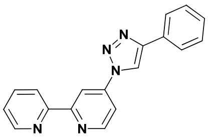


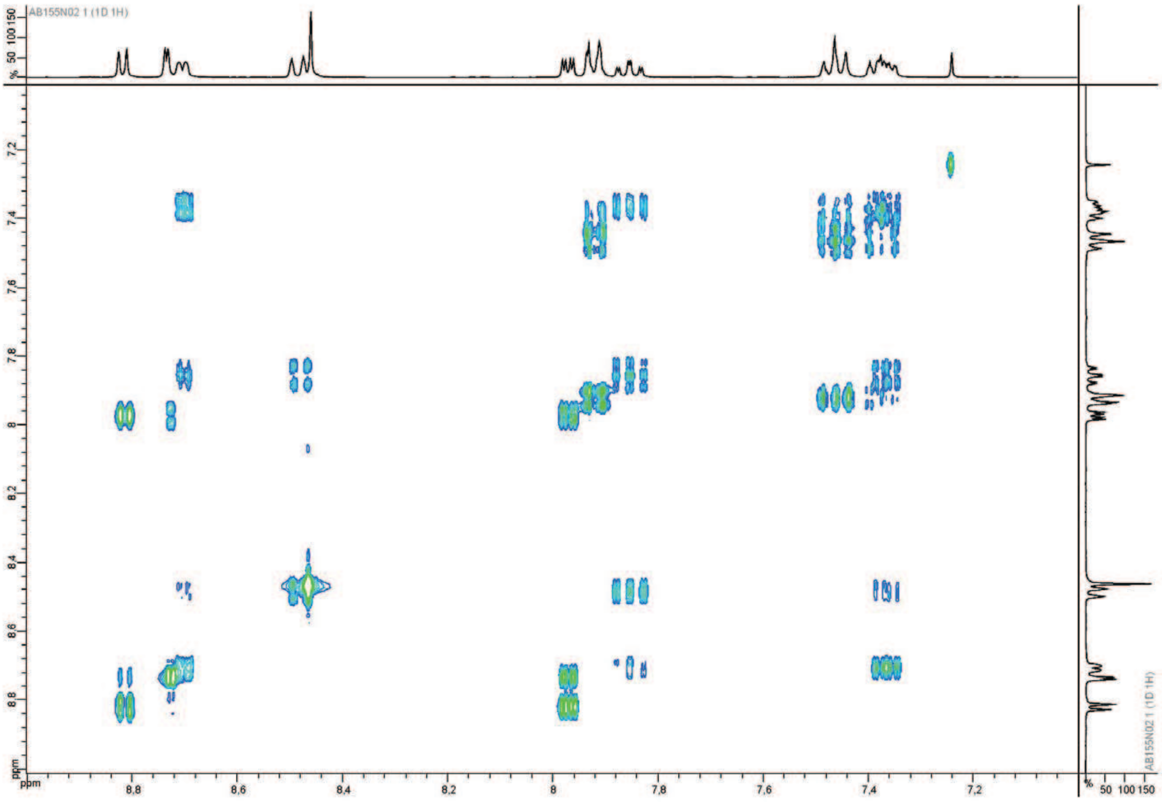
(**6a**) ^{1}H


N
N
N
N
N

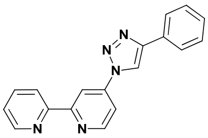

180
160
140
120
100
80
60
40
20
0
%
ppm
1.0
2.0
2.0
3.0
1.0
2.0
2.0
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2

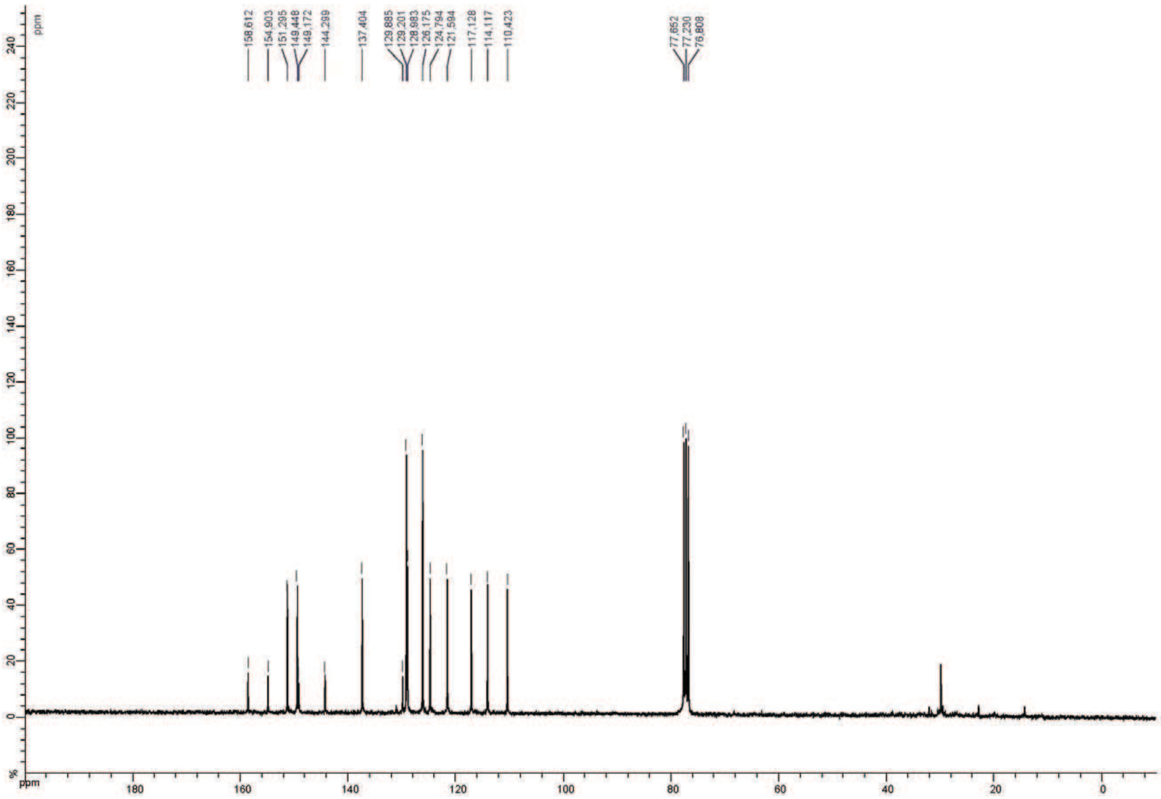
(**6a**) Cosy


N
N
N
N
N

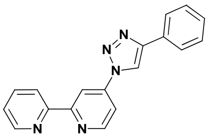

AB155N02 1 (1D 1H)
150
100
50
%
7,2
7,4
7,6
7,8
8
8,2
8,4
8,6
8,8
ppm
ppm
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
%
50
100
150
AB155N02 1 (1D 1H)

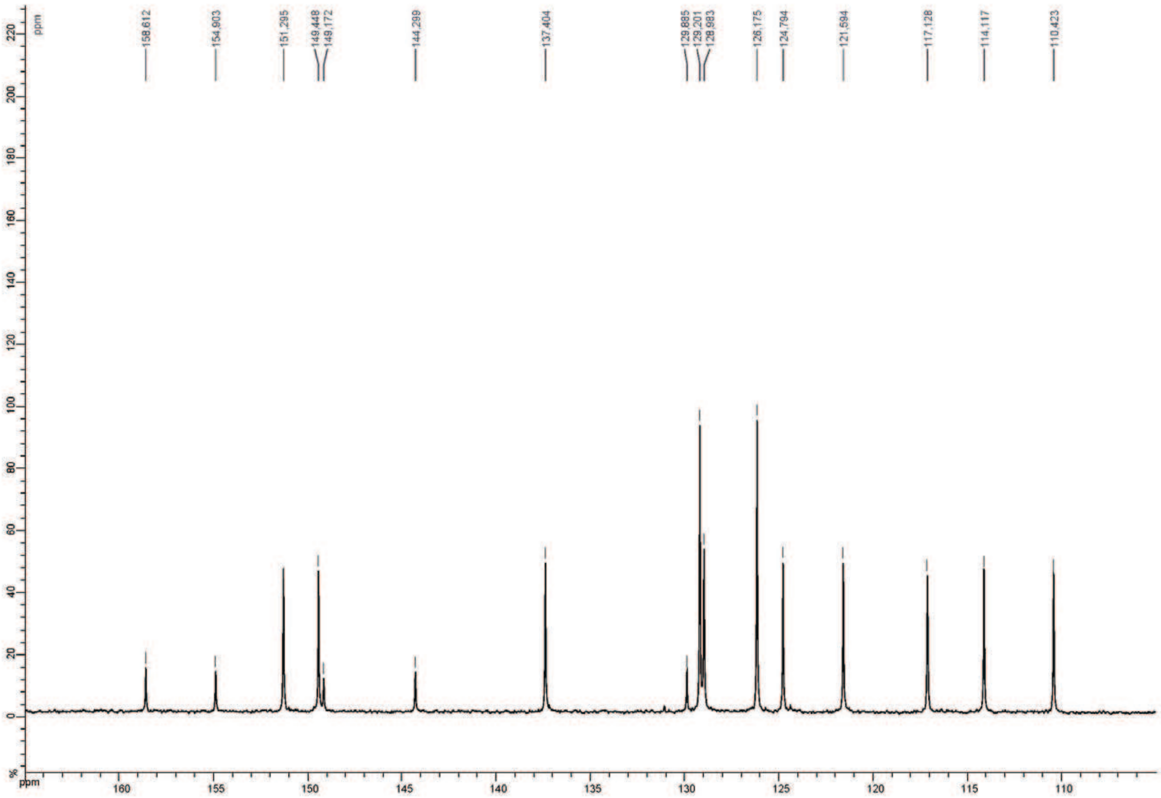
(**6a**) ^{13}C


N
N
N
N
N

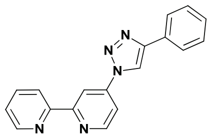

ppm
158.612
154.903
151.295
149.448
149.172
144.299
137.404
129.885
129.201
128.983
126.175
124.794
121.594
117.128
114.117
110.423
77.652
77.230
76.808
%
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
180
160
140
120
100
80
60
40
20
0

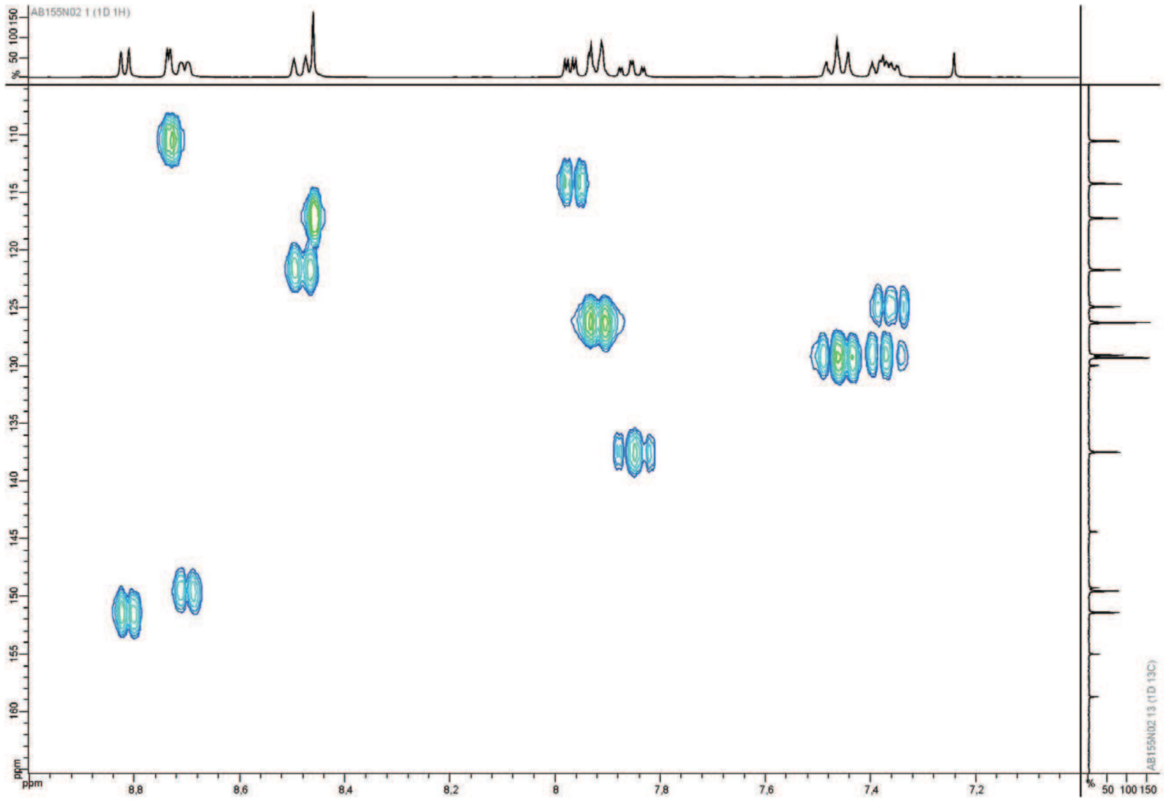
(**6a**) ^{13}C


N
N
N
N
N


ppm
158.612
154.903
151.295
149.448
149.172
144.299
137.404
129.885
129.201
128.983
126.175
124.794
121.594
117.128
114.117
110.423
%
220
200
180
160
140
120
100
80
60
40
20
0
ppm
160
155
150
145
140
135
130
125
120
115
110

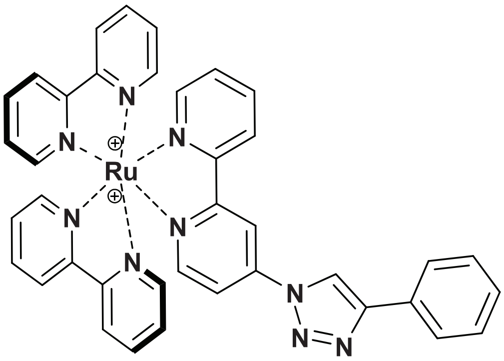
(**6a**) Hsqc


N
N
N
N
N

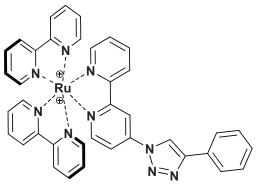

AB155N02 1 (1D 1H)
%
50
100
150
ppm
110
115
120
125
130
135
140
145
150
155
160
ppm
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
%
50
100
150
AB155N02 13 (1D 13C)

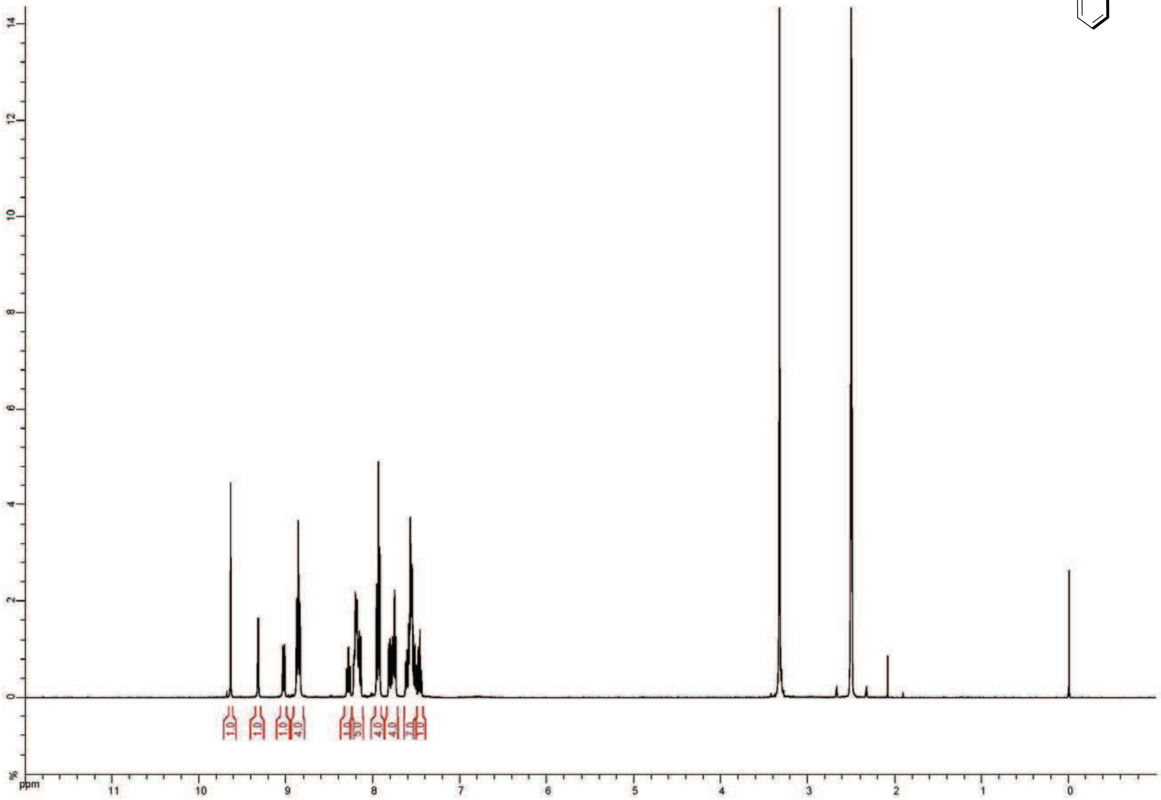
Ru-H (**7a**)

^{1}H all
^{1}H zoom
Cosy
^{13}C all
^{13}C zoom
Hsqc
Hmbc

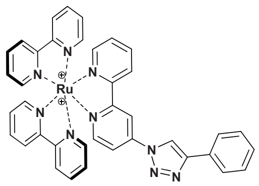


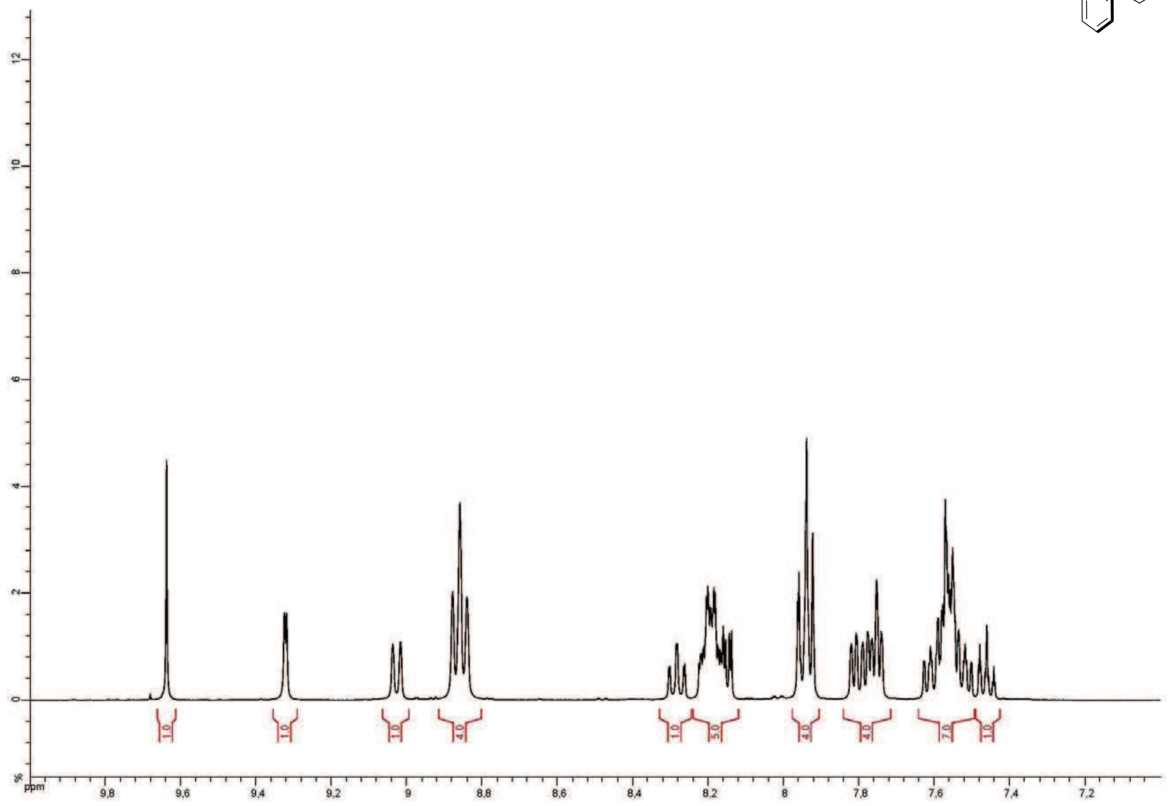
(**7a**) ^{1}H



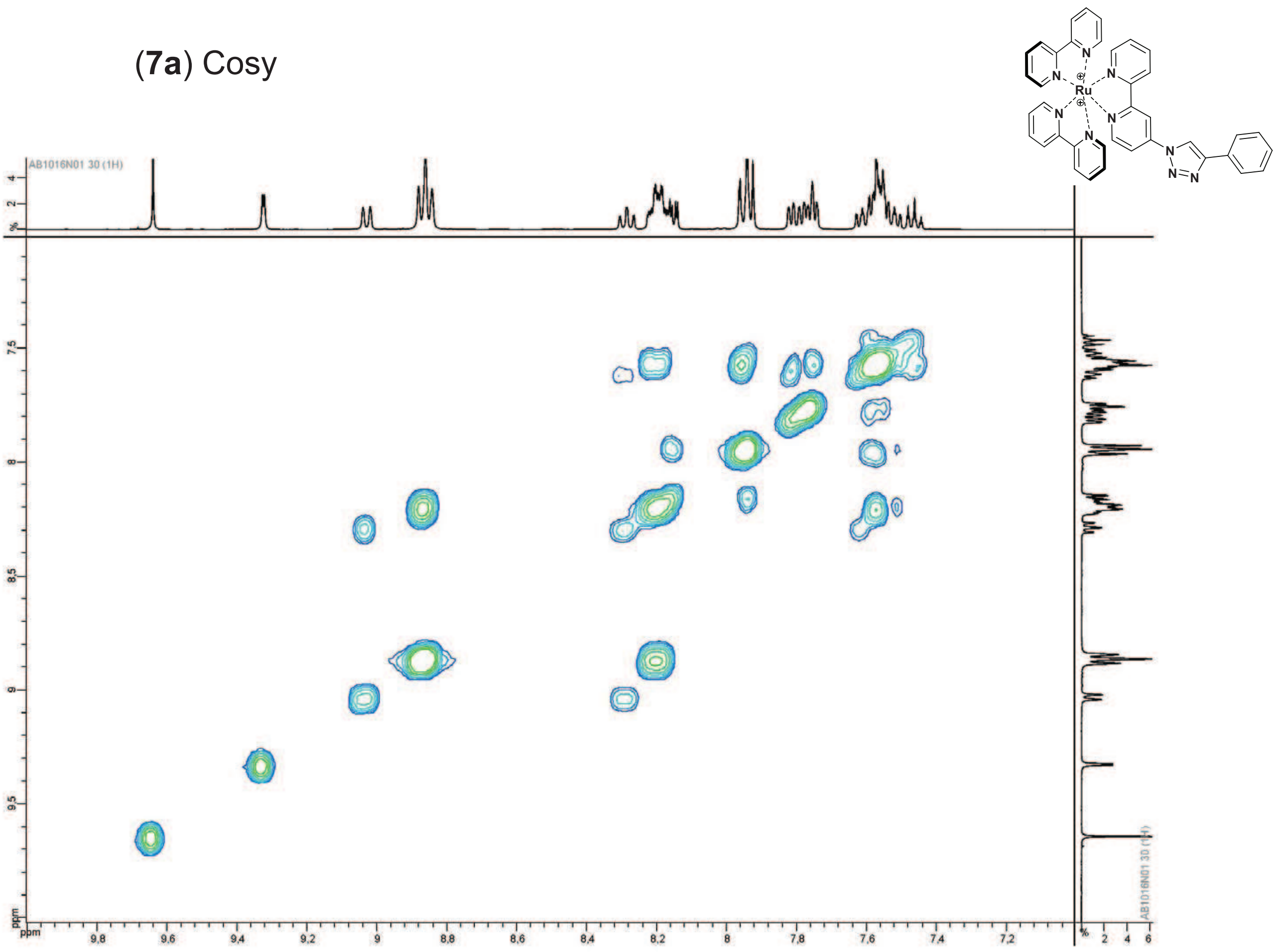


(**7a**) ^{1}H

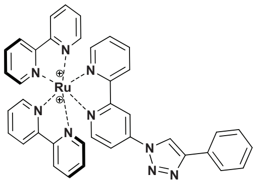

N
N
N
N
Ru
N
N
N
N
N
N

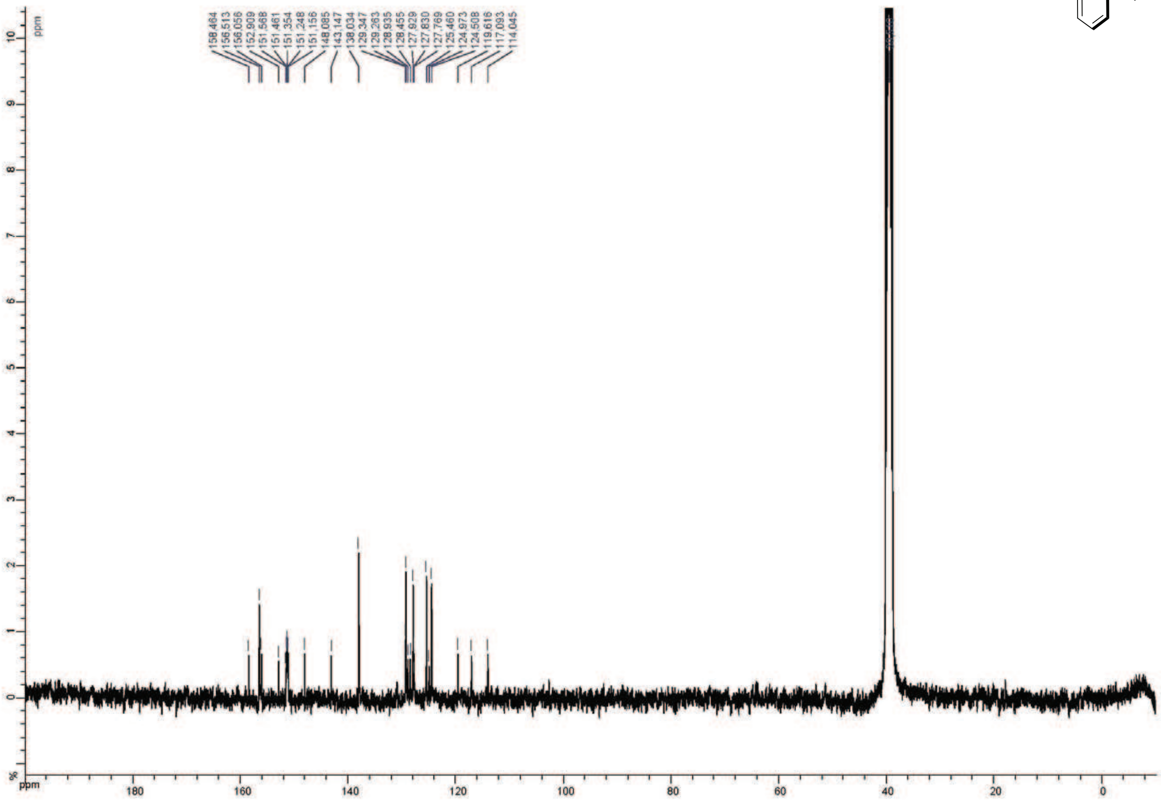

12
10
8
6
4
2
0
%
1,0
1,0
1,0
4,0
1,0
5,0
4,0
4,0
7,0
1,0
ppm
9,8
9,6
9,4
9,2
9
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2

(**7a**) Cosy

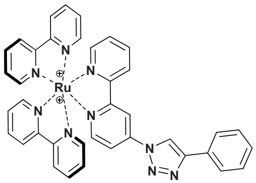

N
N
N
N
Ru
N
N
N
N
N
N
AB1016N01 30 (1H)
4
2
%
7,5
8
8,5
9
9,5
ppm
ppm
9,8
9,6
9,4
9,2
9
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
AB1016N01 30 (1H)
%
2
4
6

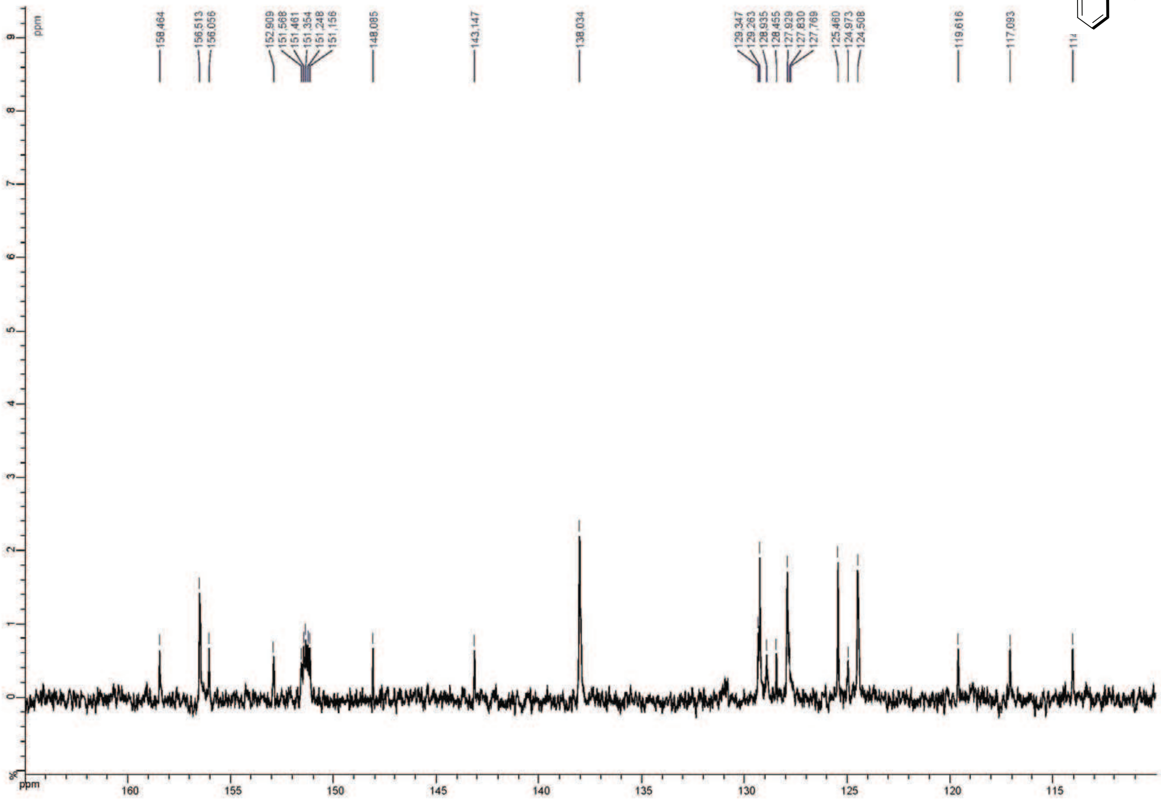
(**7a**) ^{13}C


N
N
Ru
⊕
⊕
N
N
N
N
N
N
N

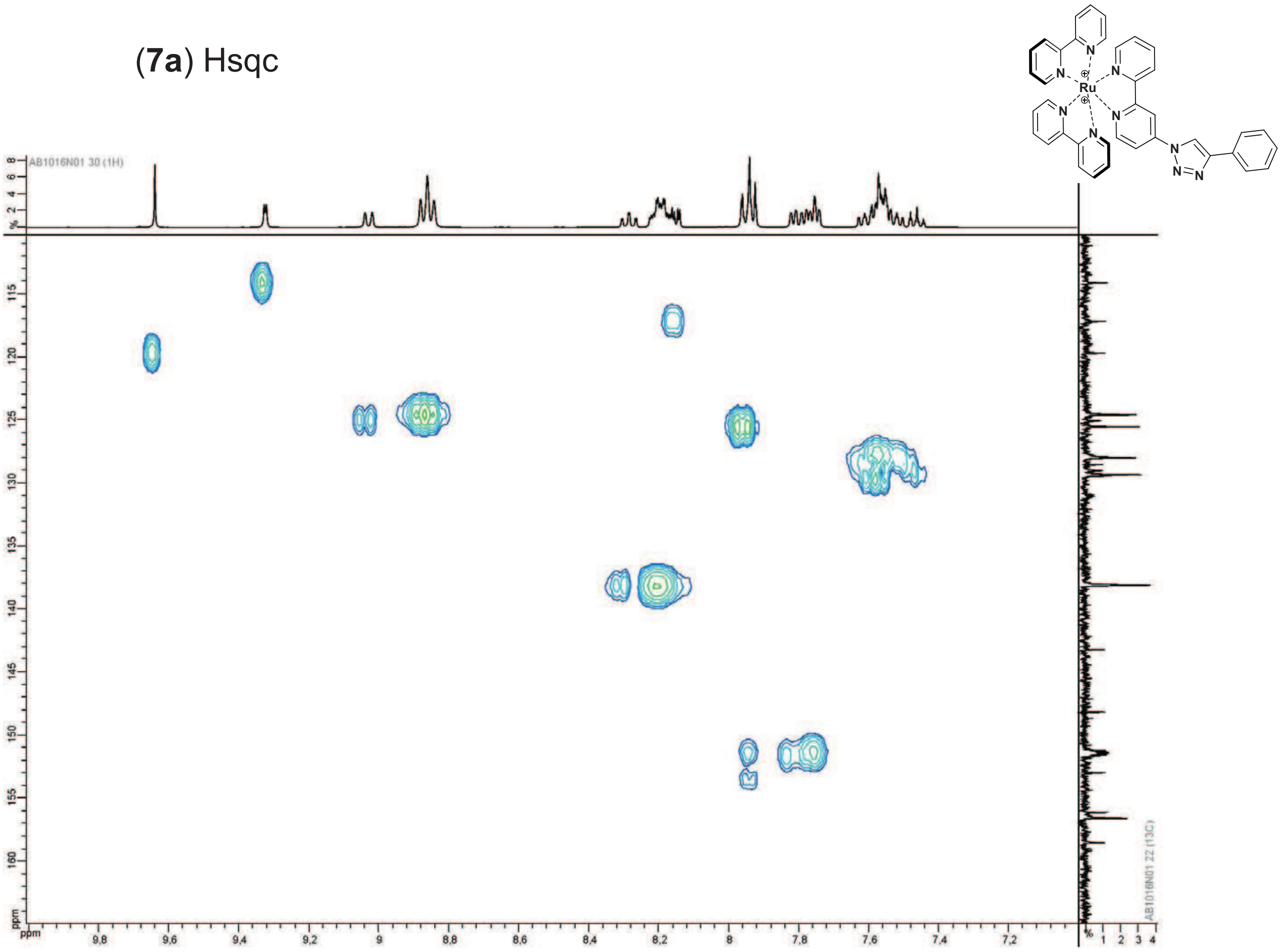

158.464
156.513
156.056
152.909
151.568
151.461
151.354
151.248
151.156
148.085
143.147
138.034
129.347
129.263
128.935
128.455
127.929
127.830
127.769
125.460
124.973
124.508
119.616
117.093
114.045
ppm
10
9
8
7
6
5
4
3
2
1
0
%
ppm
180
160
140
120
100
80
60
40
20
0

(**7a**) ^{13}C

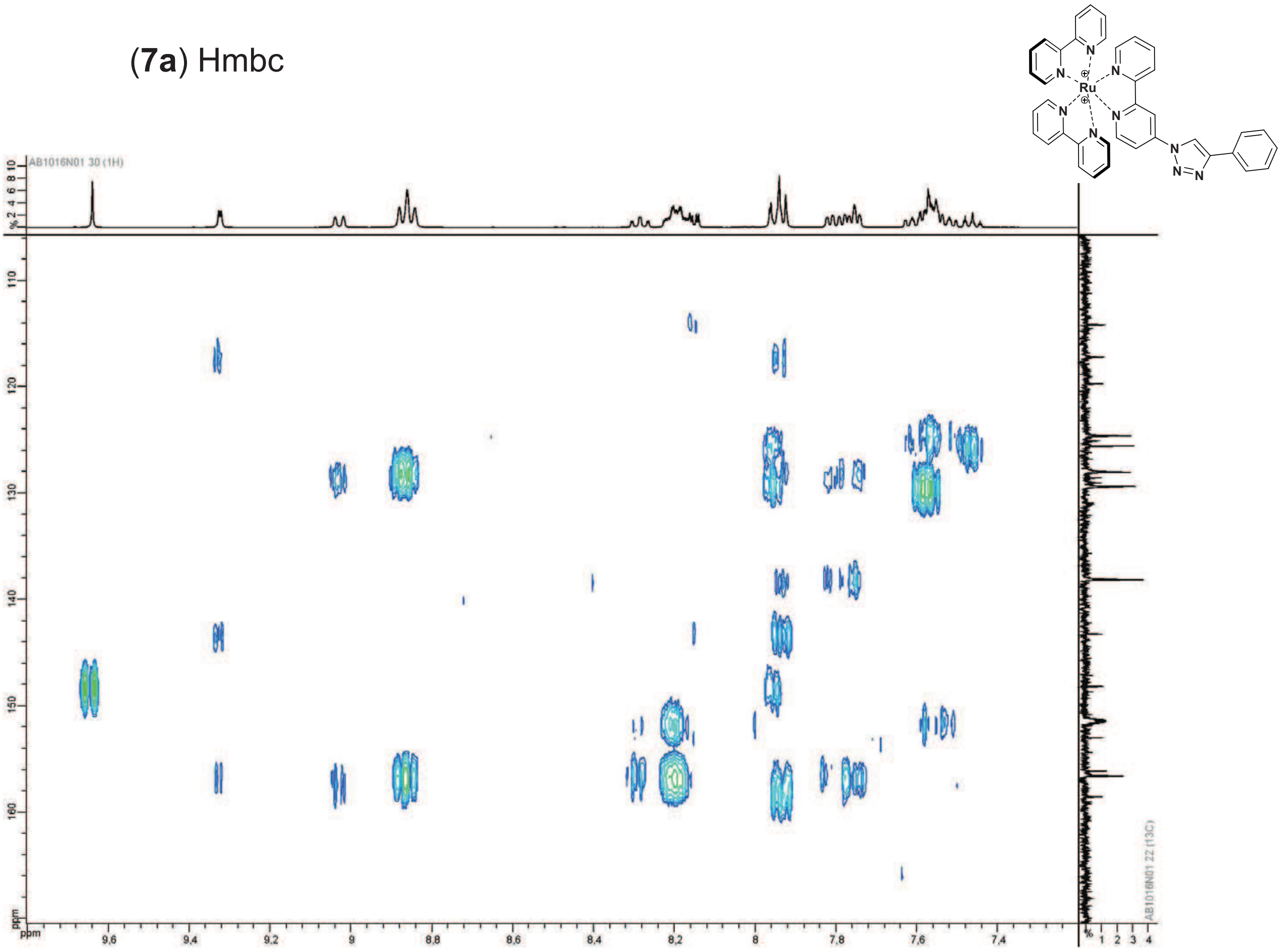

N
N
Ru
⊕
⊕
N
N
N
N
N
N
N


158.464
156.513
156.056
152.909
151.568
151.461
151.354
151.248
151.156
148.085
143.147
138.034
129.347
129.263
128.935
128.455
127.929
127.830
127.769
125.460
124.973
124.508
119.616
117.093
114
ppm
9
8
7
6
5
4
3
2
1
0
%
ppm
160
155
150
145
140
135
130
125
120
115

(**7a**) Hsqc

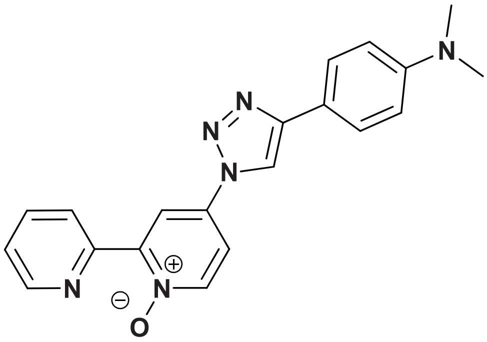


(**7a**) Hmbc

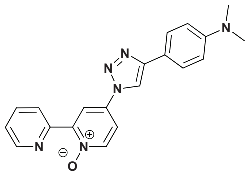


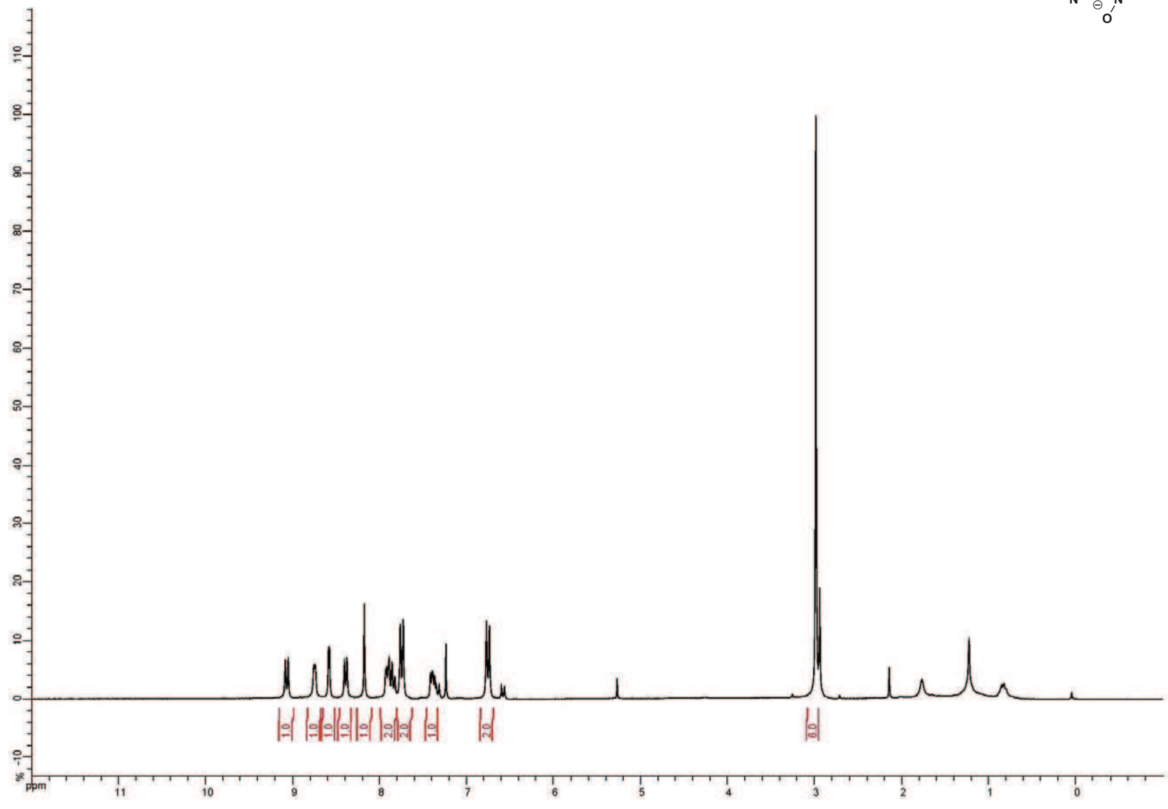
BpyTNMe$_2$-*N*-oxide (**5b**)

^{1}H all
^{1}H zoom
Cosy all
Cosy zoom
^{13}C all
^{13}C zoom
Hsqc all
Hsqc zoom

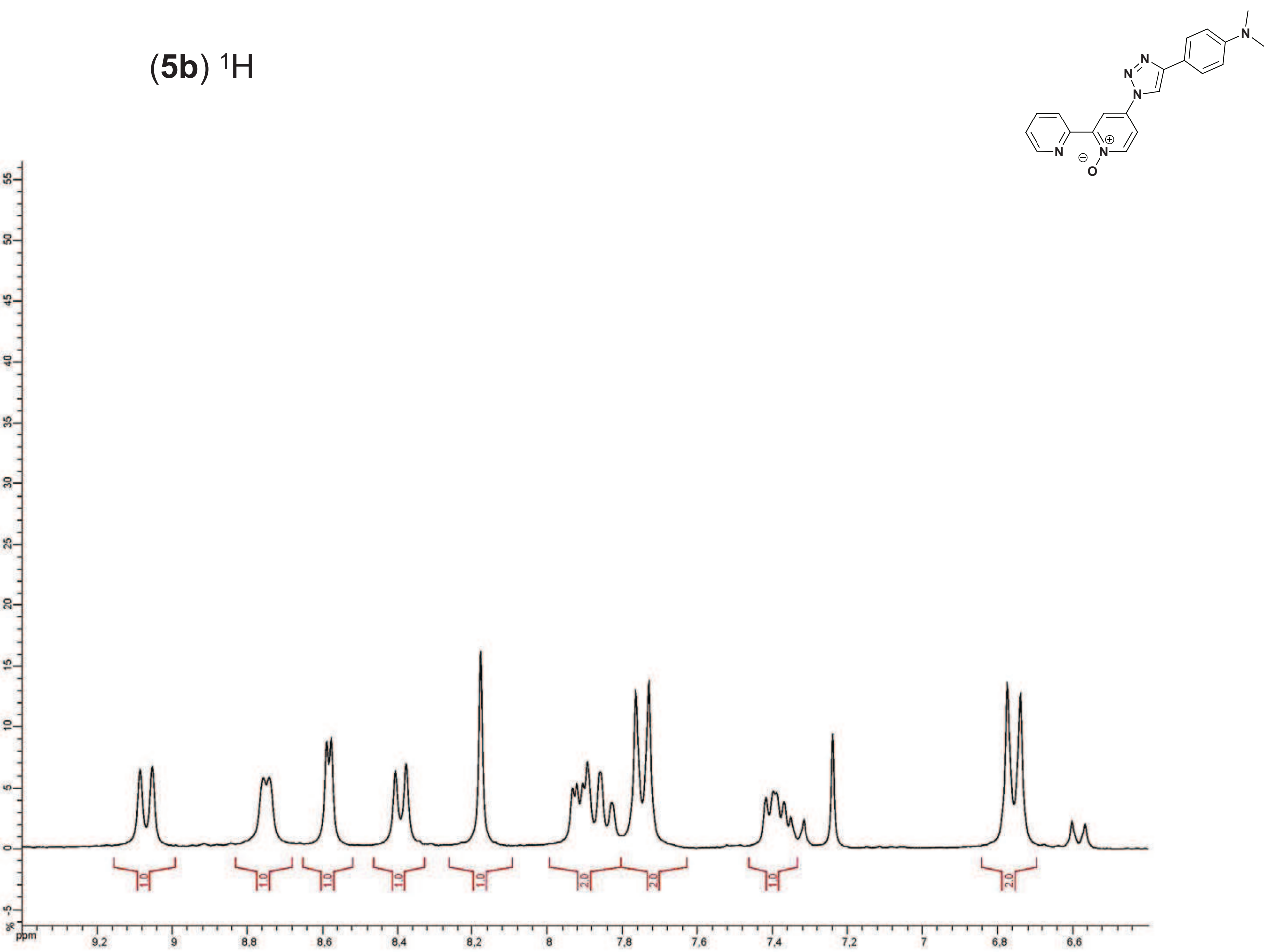


(**5b**) ^{1}H

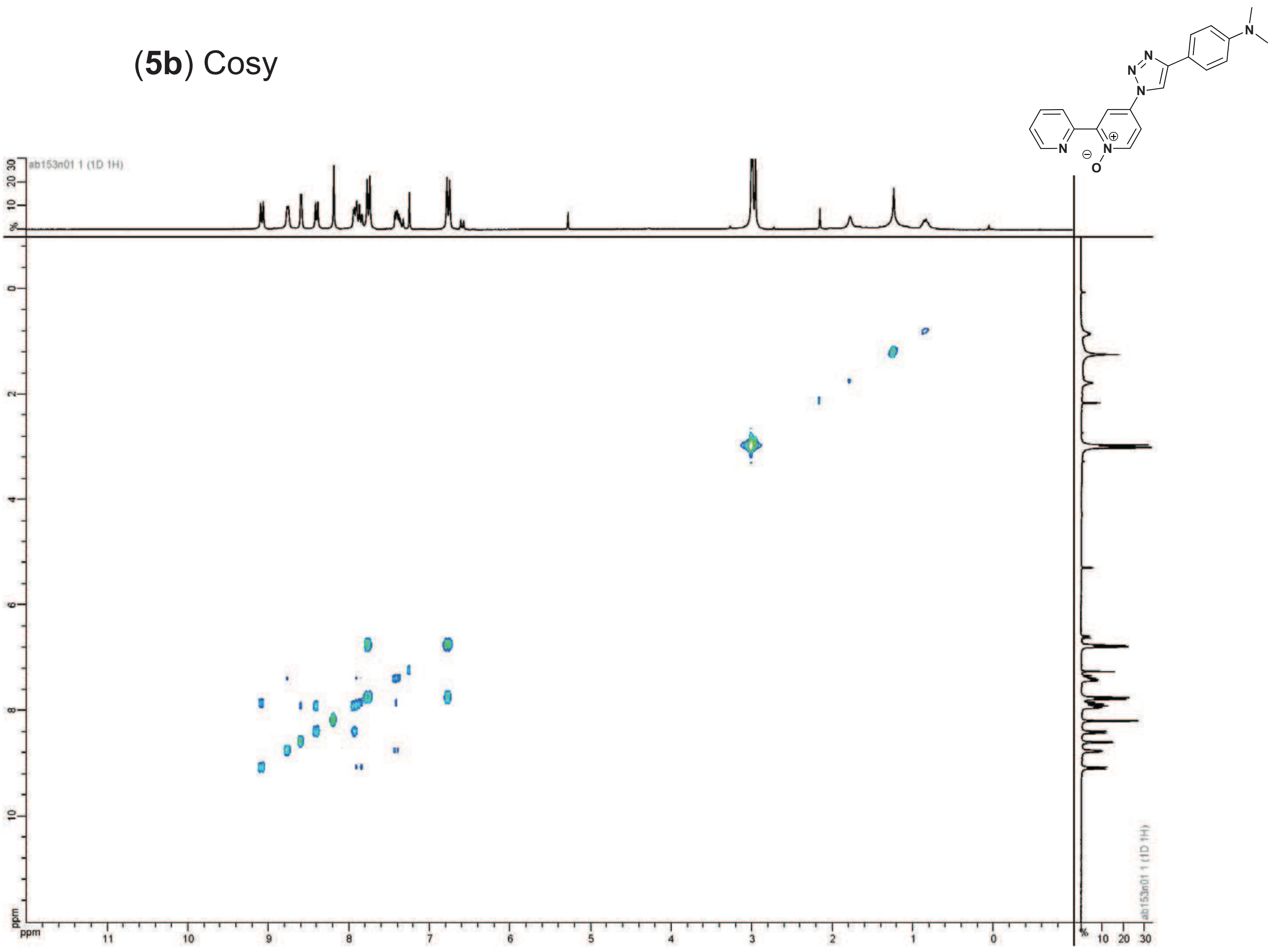




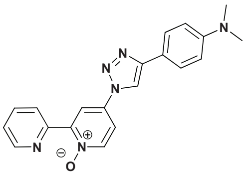
(**5b**) ^{1}H

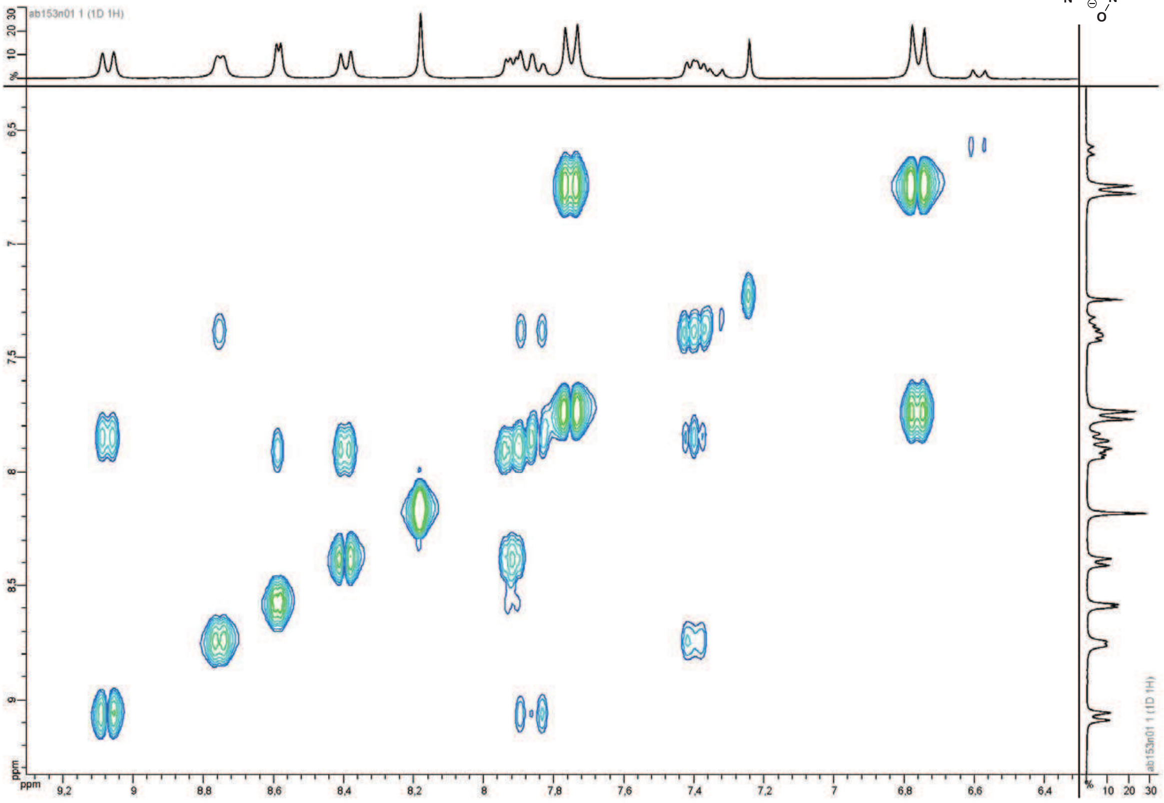

N
N
N
N
N
⊕
⊖
O
%
ppm
-5
0
5
10
15
20
25
30
35
40
45
50
55
1.0
1.0
1.0
1.0
1.0
2.0
2.0
1.0
2.0
9,2
9
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
7
6,8
6,6

(**5b**) Cosy

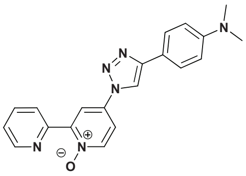

N
N
N
N
N
⊕
⊖
O
ab153n01 1 (1D 1H)
%
10
20
30
ppm
0
2
4
6
8
10
ppm
11
10
9
8
7
6
5
4
3
2
1
0
%
10
20
30
ab153n01 1 (1D 1H)

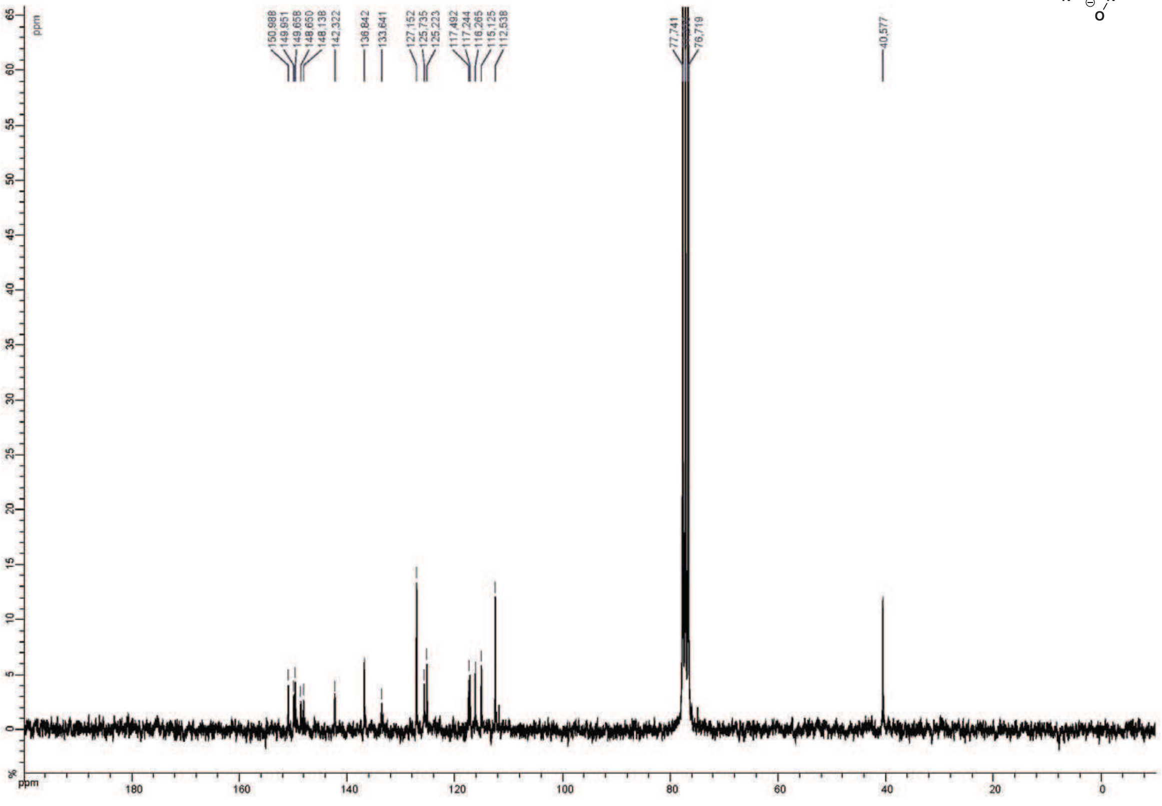
(**5b**) Cosy



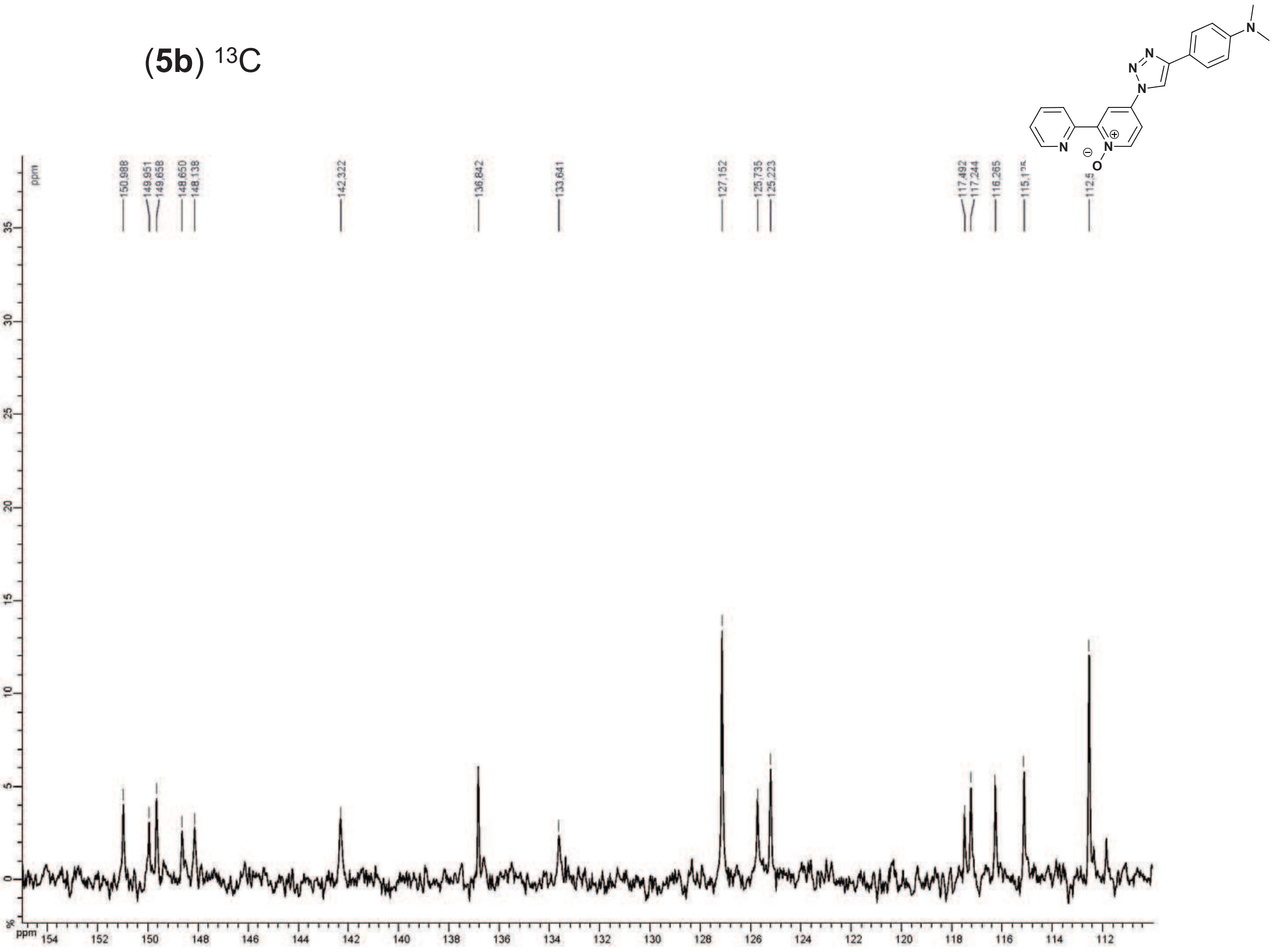


(**5b**) ^{13}C

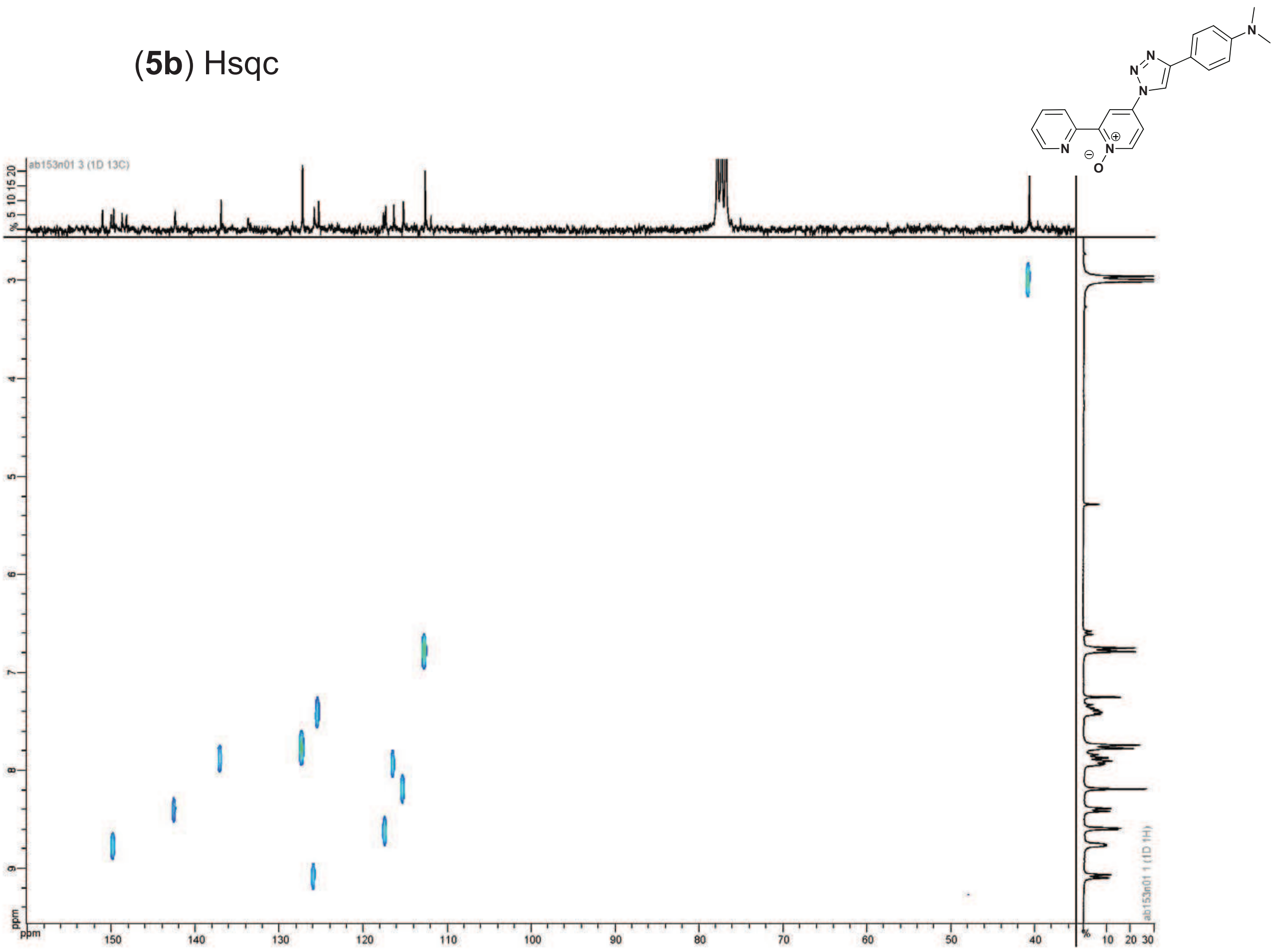




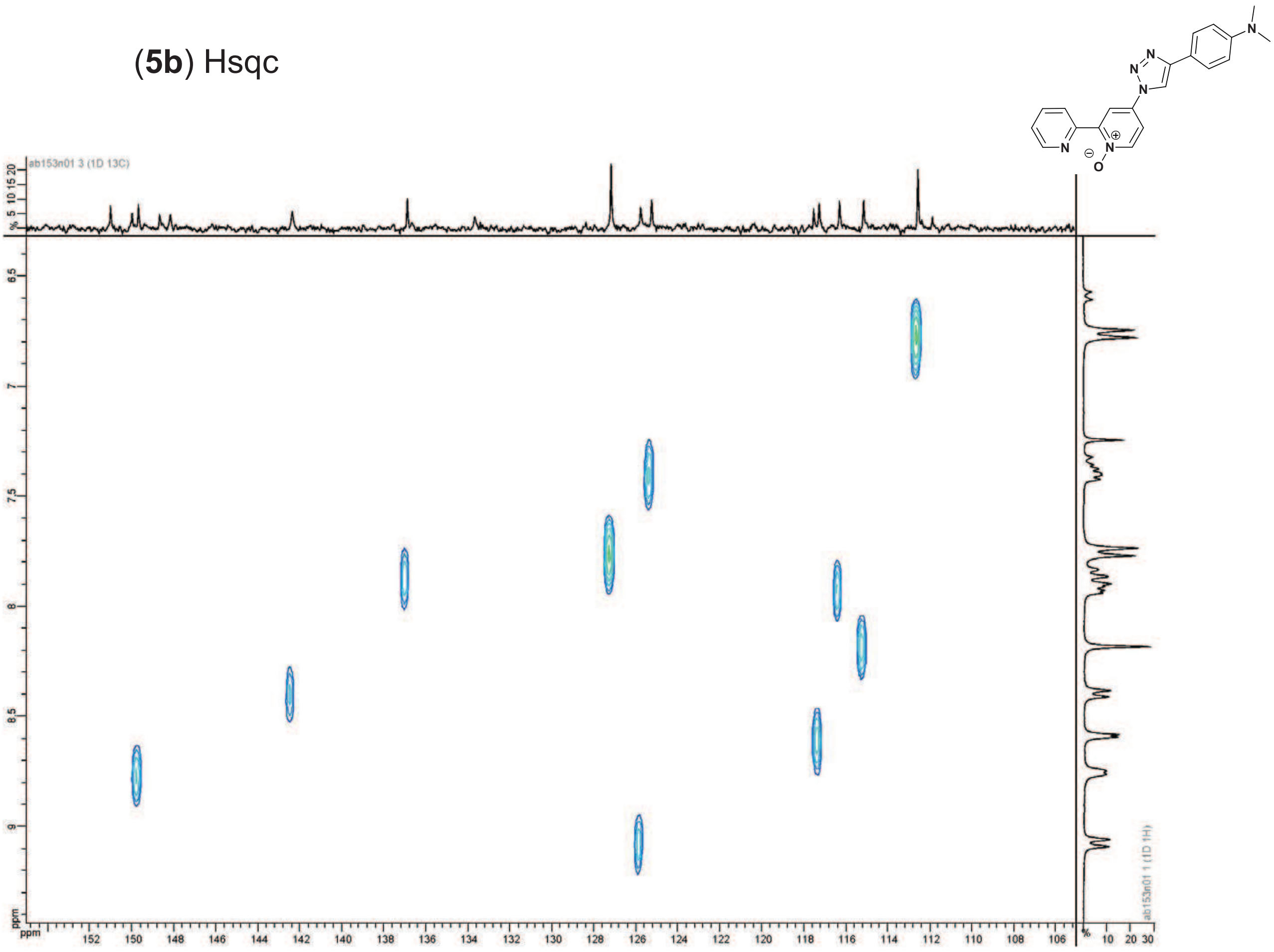
(**5b**) ^{13}C



(**5b**) Hsqc

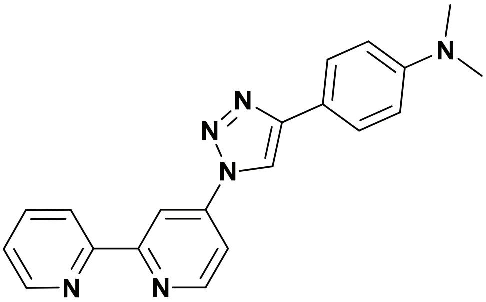


(**5b**) Hsqc

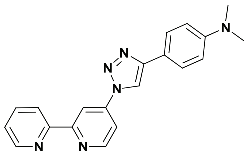

ab153n01 3 (1D 13C)
% 5 10 15 20
ab153n01 1 (1D 1H)
% 10 20 30
ppm
152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106
ppm
6.5 7 7.5 8 8.5 9
N
N
N
N
N
O

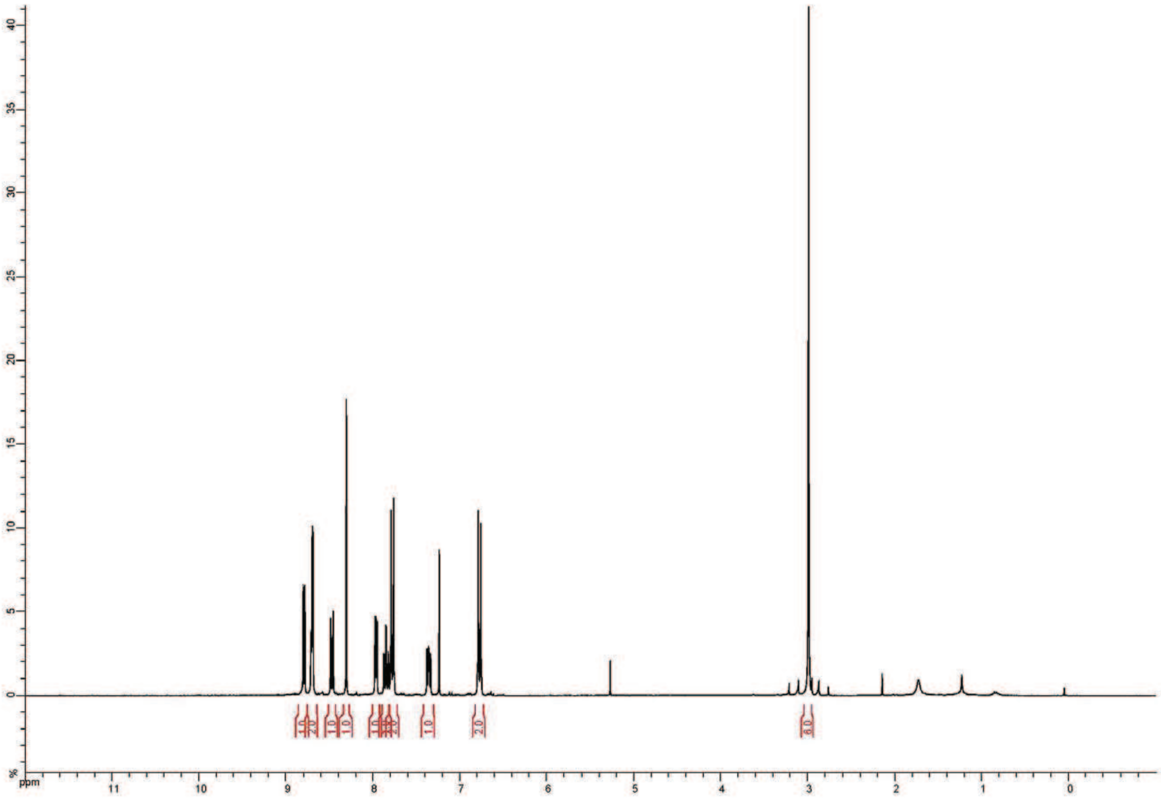
BpyTNMe$_2$ (**6b**)

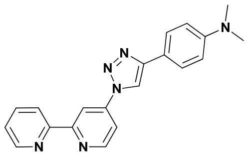
^{1}H all
^{1}H zoom
Cosy all
Cosy zoom
Jmod all
Jmod zoom
Hsqc all
Hsqc zoom



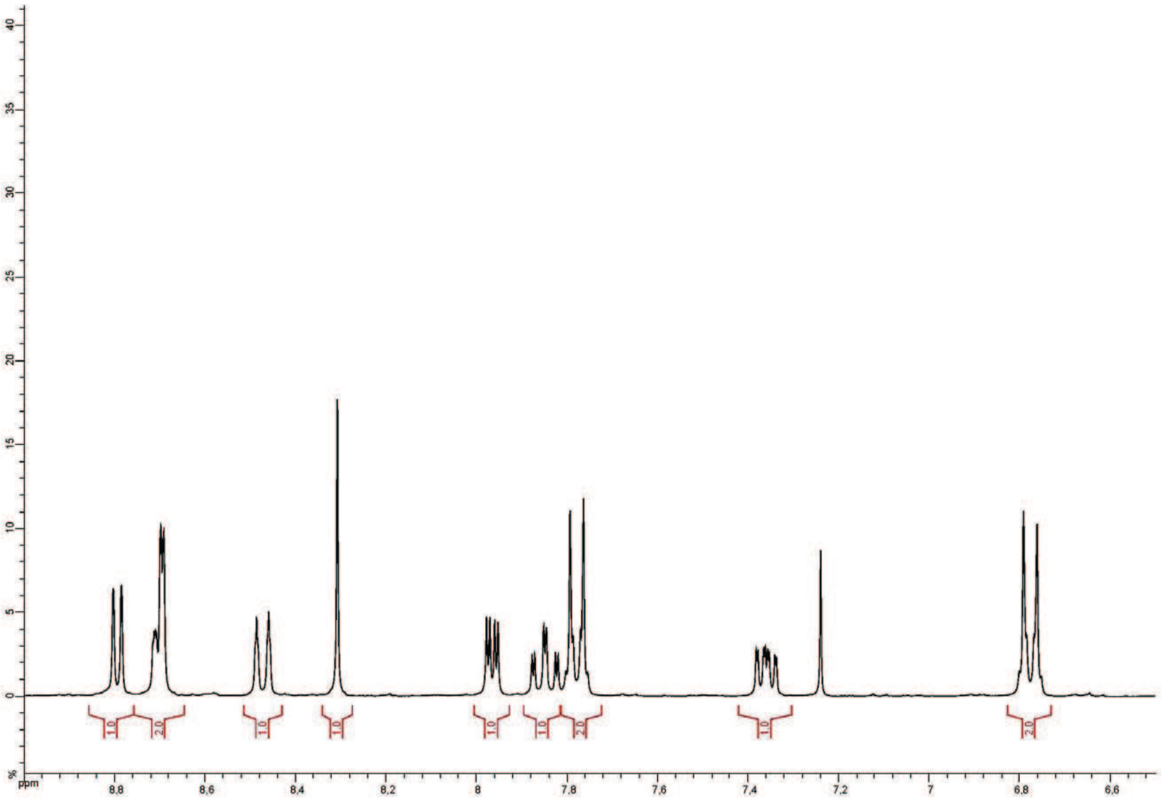
(**6b**) ^{1}H

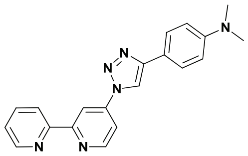




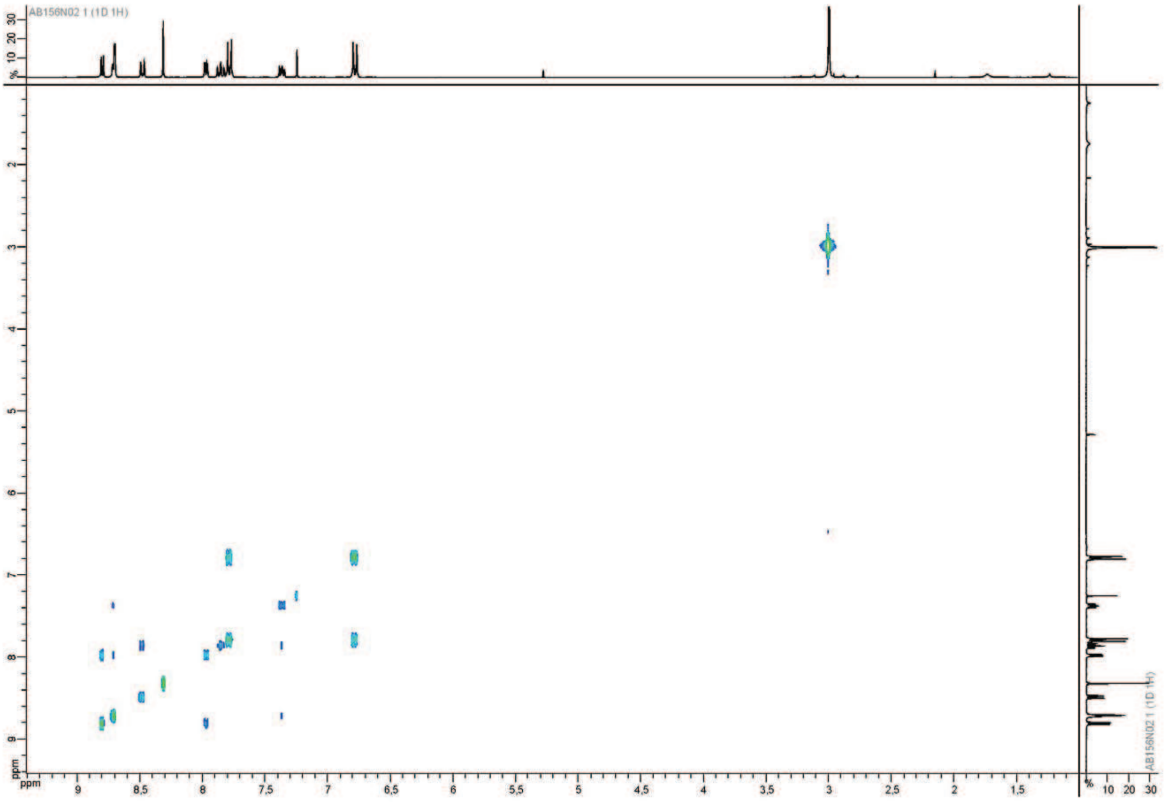

N
N
N
N
N
N

(**6b**) ^{1}H

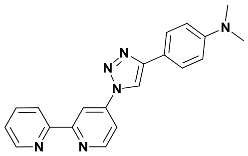

40
35
30
25
20
15
10
5
0
%
ppm
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
7
6,8
6,6
1.0
2.0
1.0
1.0
1.0
1.0
2.0
1.0
2.0

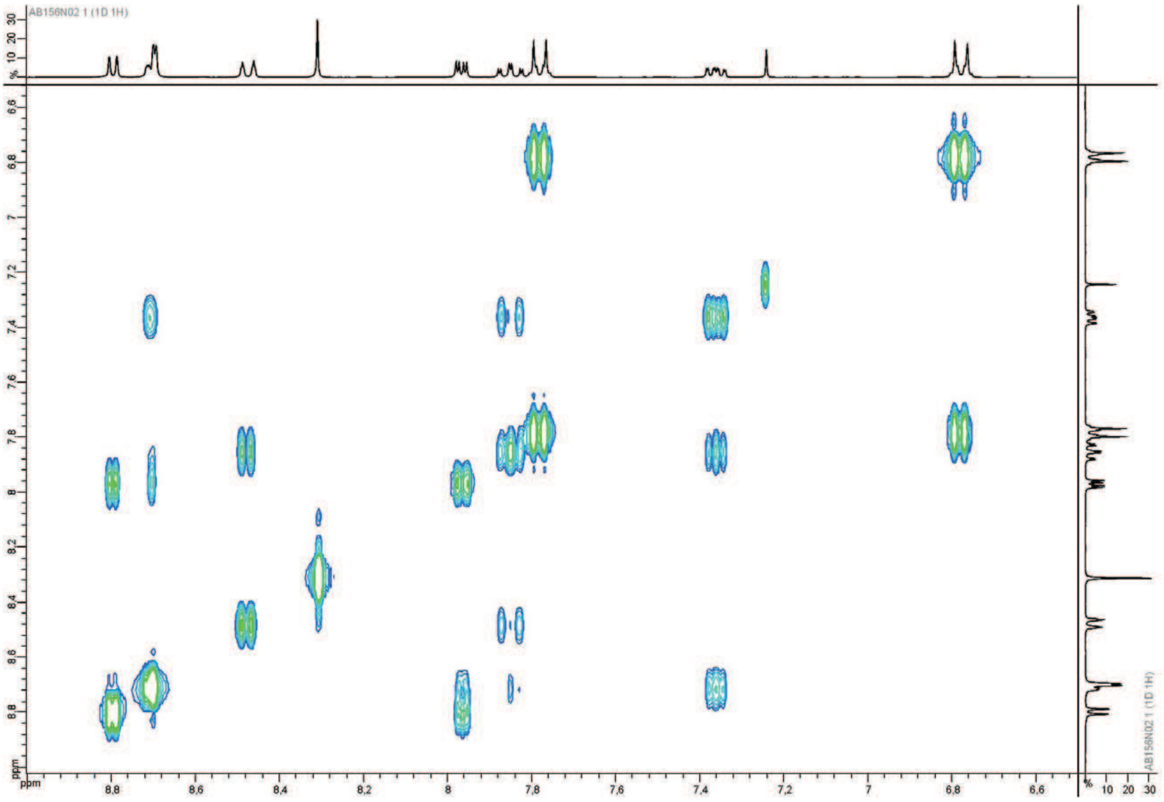

N
N
N
N
N
N

(**6b**) Cosy

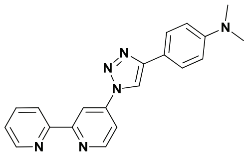

AB156N02 1 (1D 1H)
30
20
10
%
2
3
4
5
6
7
8
9
ppm
ppm
9
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
%
10
20
30
AB156N02 1 (1D 1H)

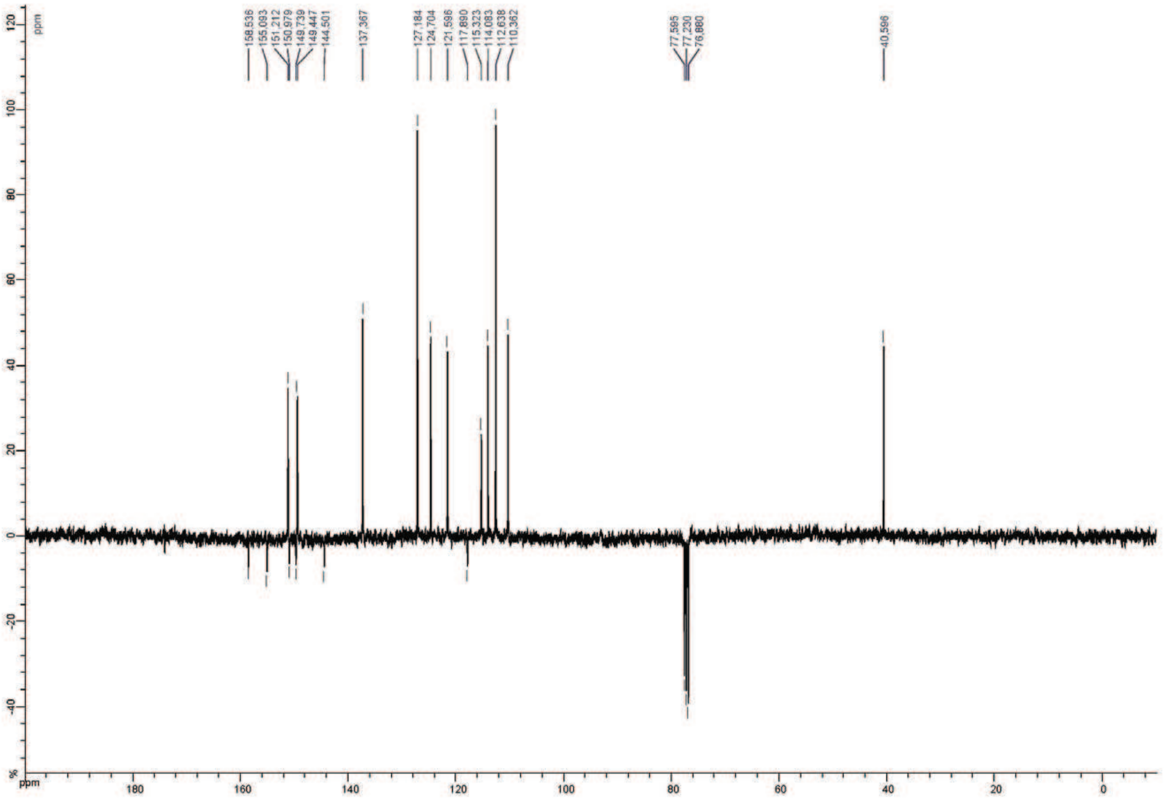
(**6b**) Cosy



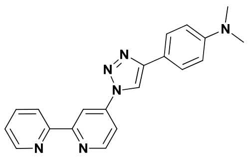


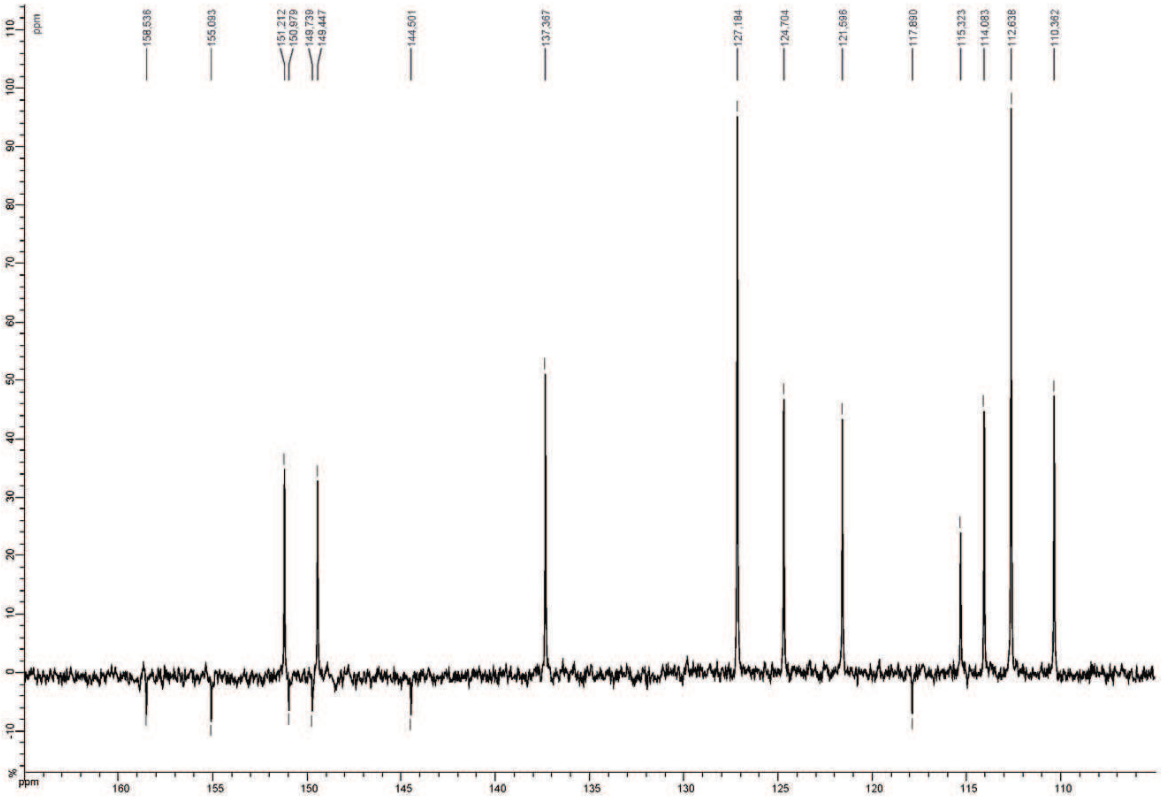
(**6b**) ^{13}C Jmod



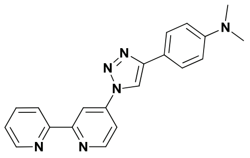


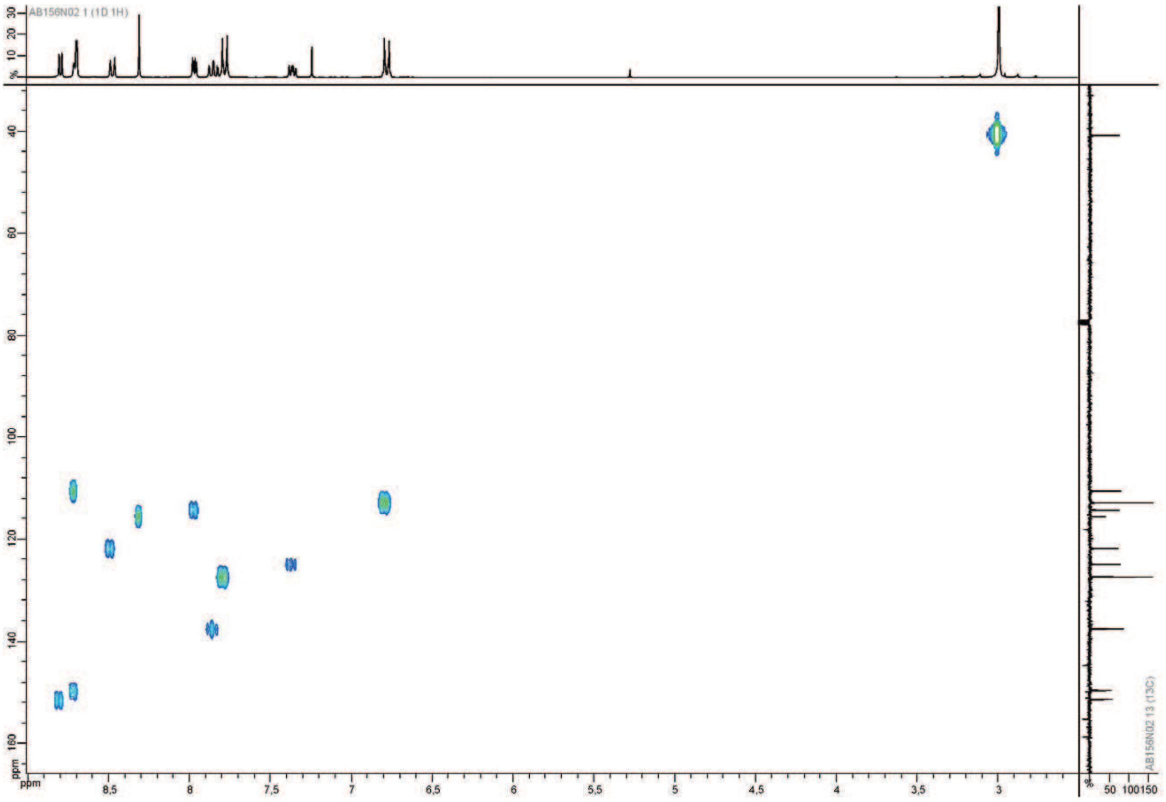
(**6b**) ^{13}C Jmod



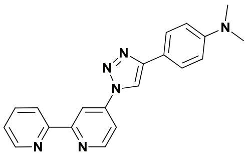


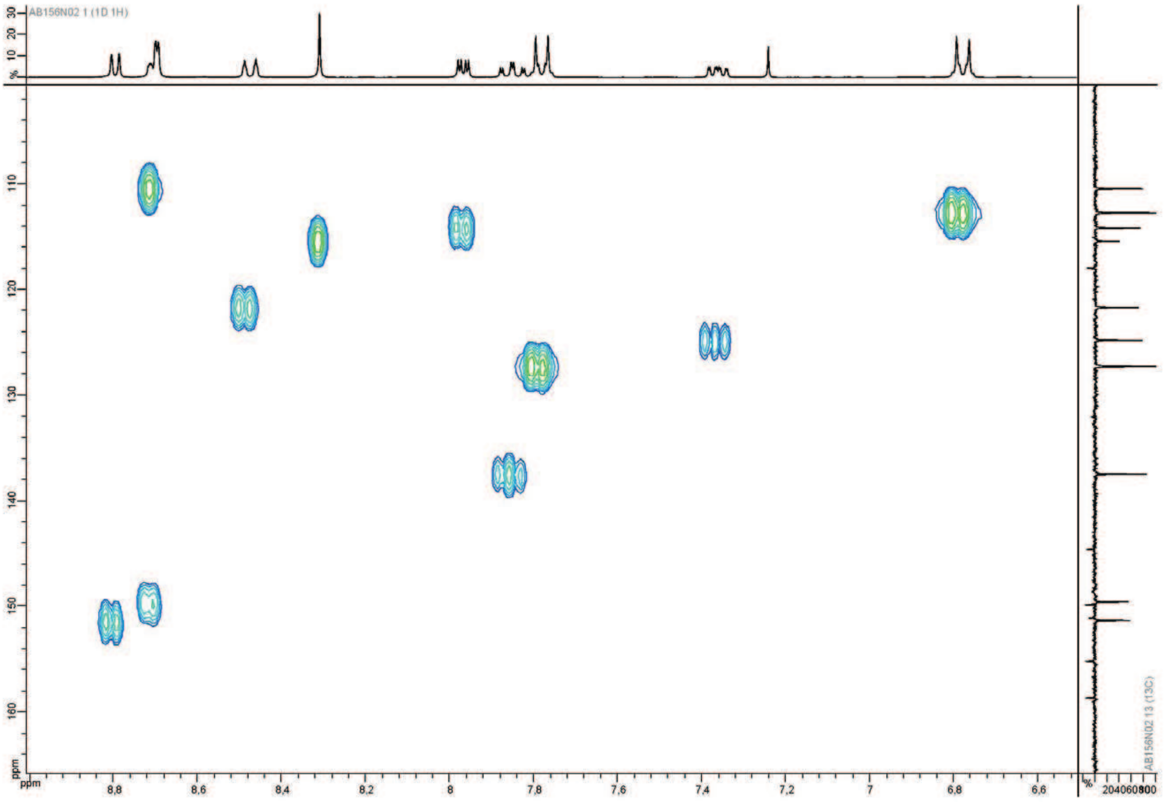
(**6b**) Hsqc





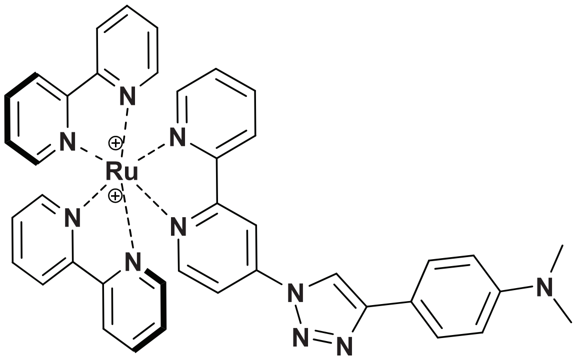
(**6b**) Hsqc


N
N
N
N
N
N

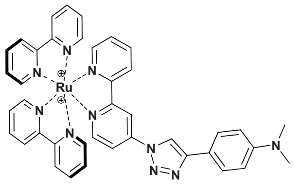

AB156N02 1 (1D 1H)
%
10
20
30
110
120
130
140
150
160
ppm
ppm
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
7
6,8
6,6
%
20406080100
AB156N02 13 (13C)

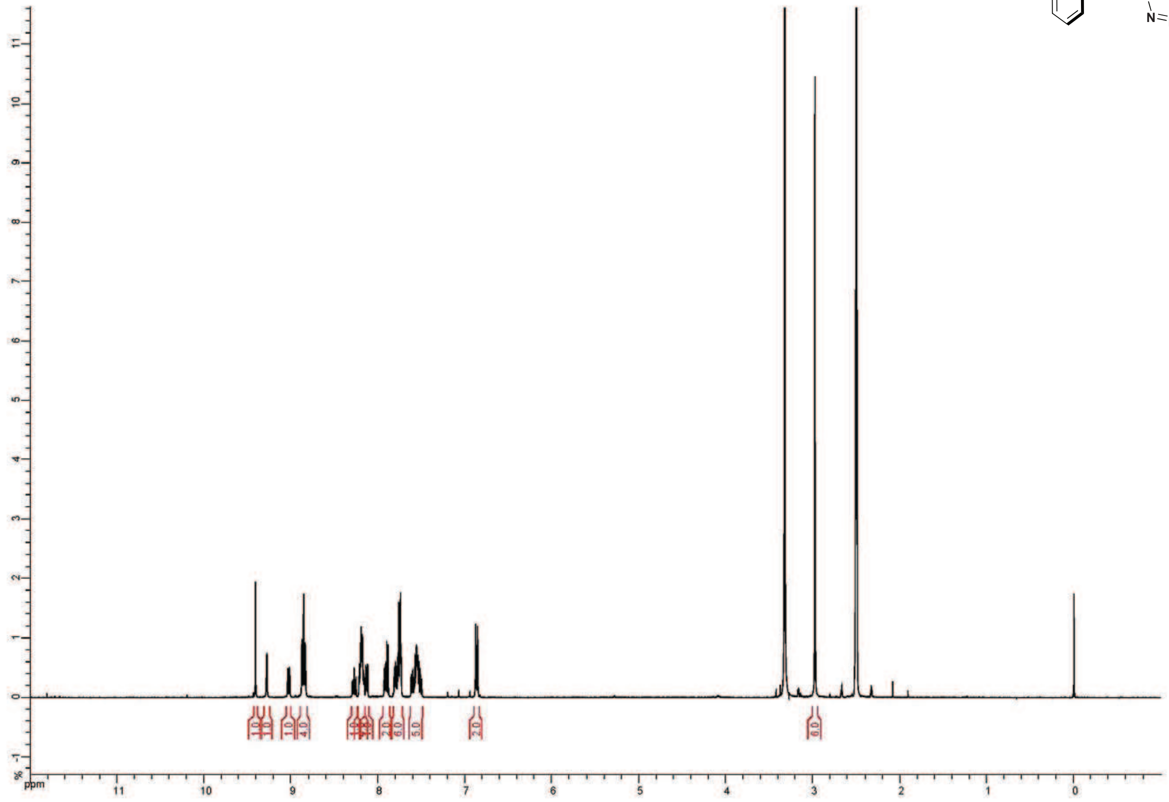
Ru-NMe$_2$ (**7b**)

^{1}H all
^{1}H zoom
Cosy all
Cosy zoom
^{13}C all
^{13}C zoom
Hsqc all
Hsqc zoom

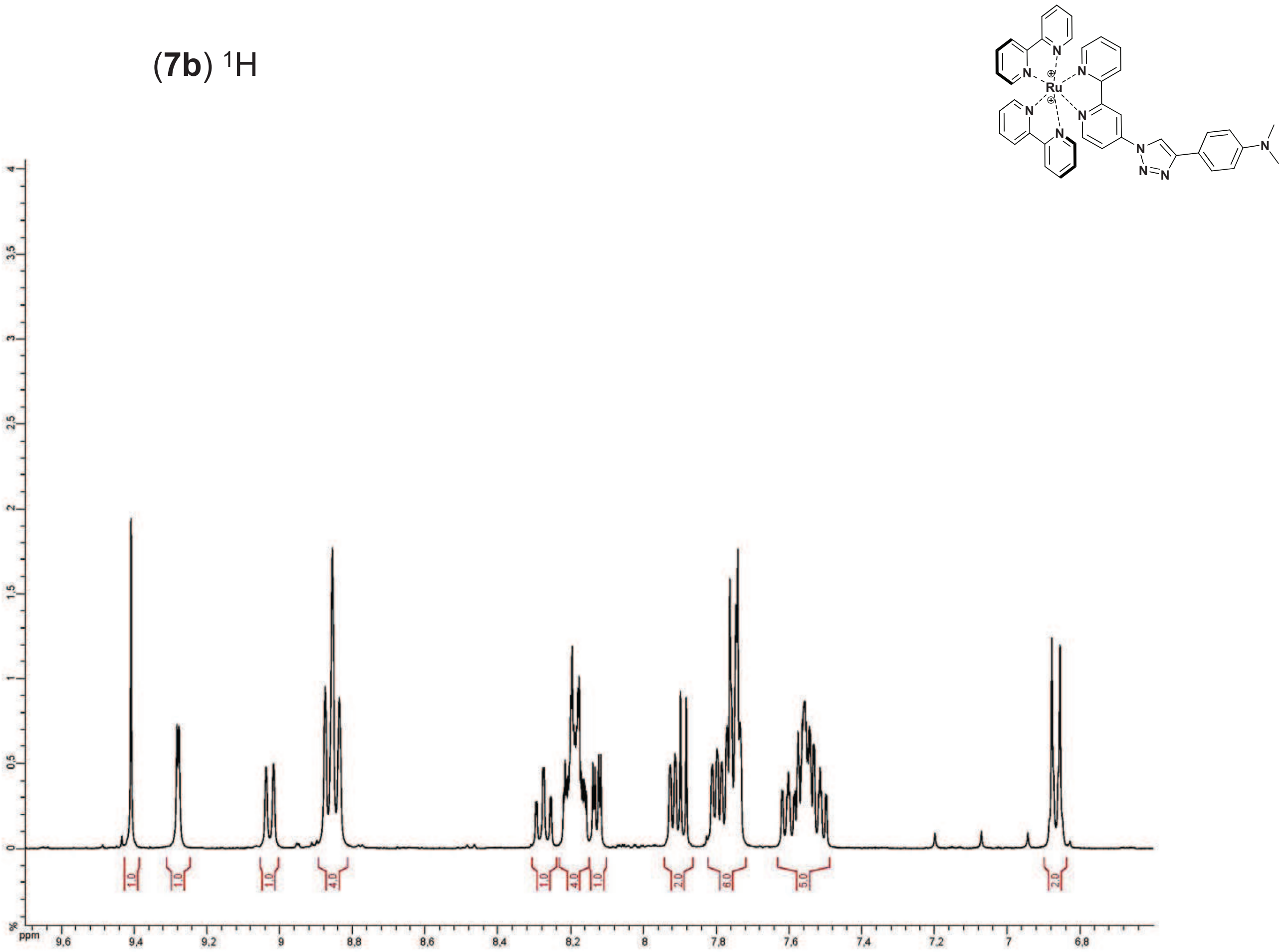


(**7b**) ^{1}H

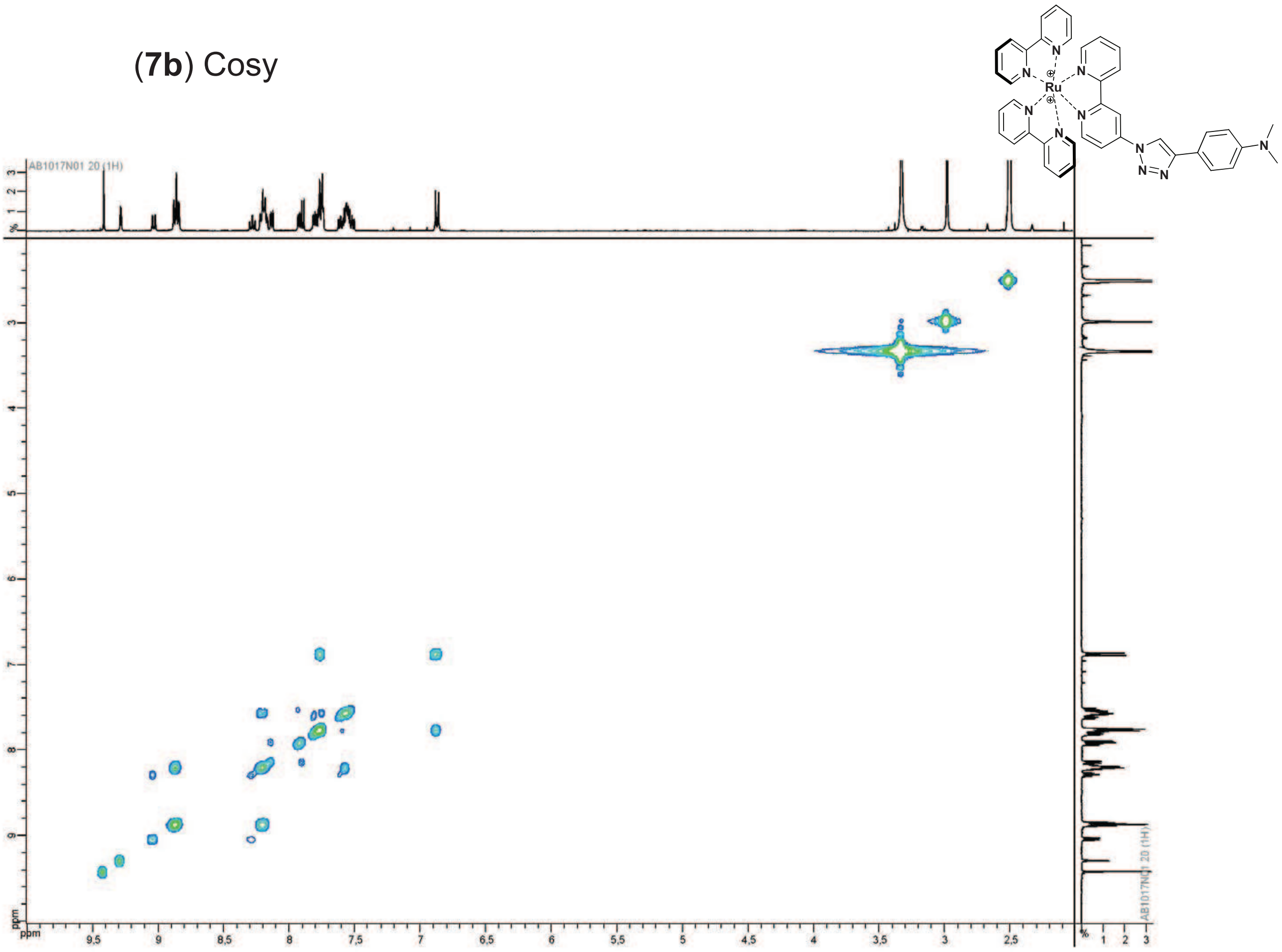




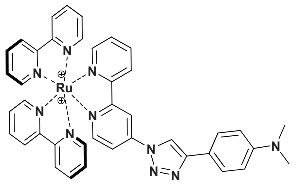
(**7b**) ^{1}H

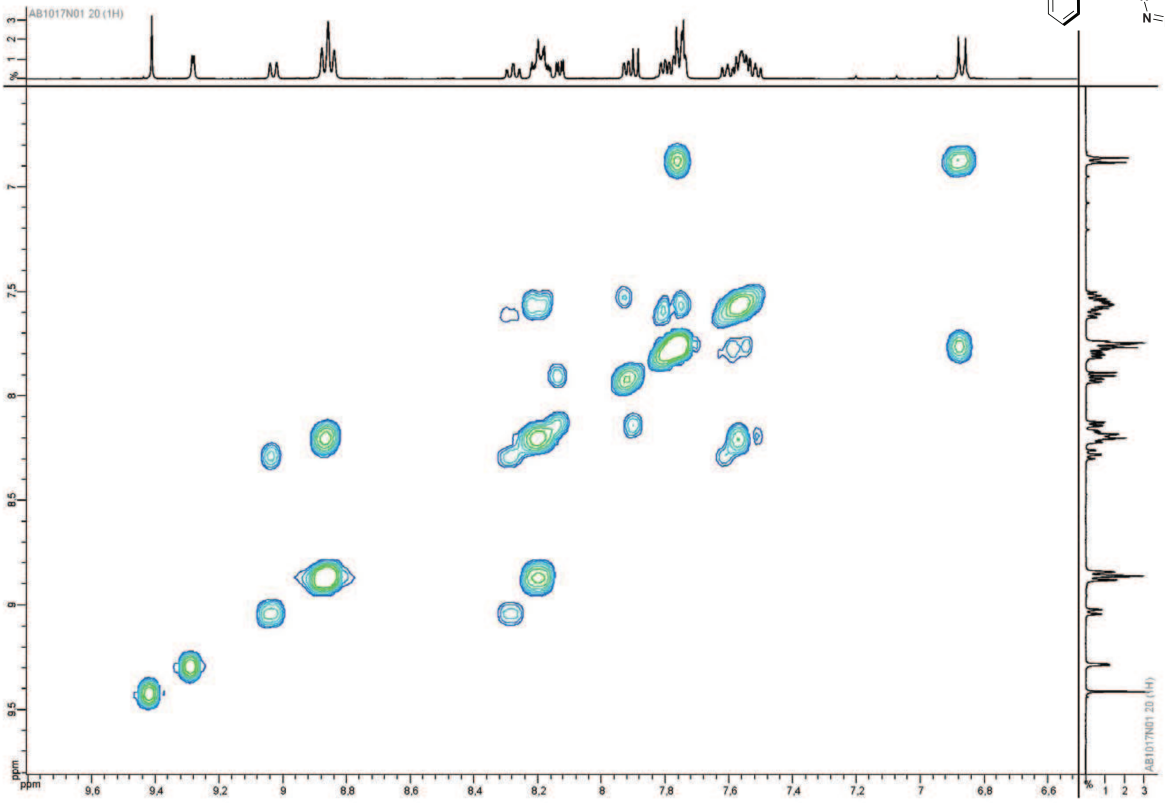

Ru
N
%
ppm
9,6
9,4
9,2
9
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
7
6,8
0
0,5
1
1,5
2
2,5
3
3,5
4
1.0
1.0
1.0
4.0
1.0
4.0
1.0
2.0
6.0
5.0
2.0

(**7b**) Cosy

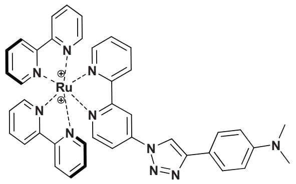

Ru
N
AB1017N01 20 (1H)
ppm
9,5
9
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
%
1
2
3

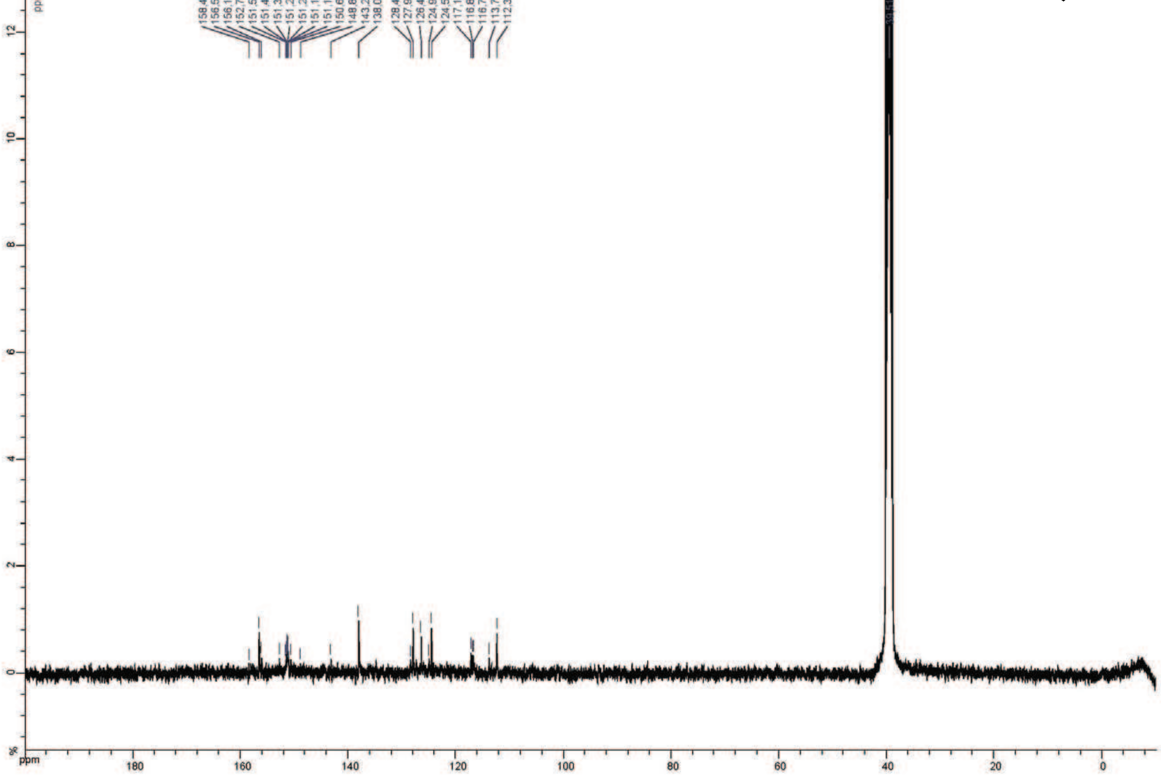
(**7b**) Cosy



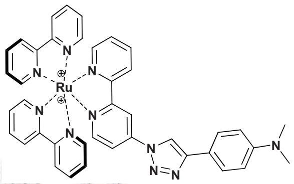


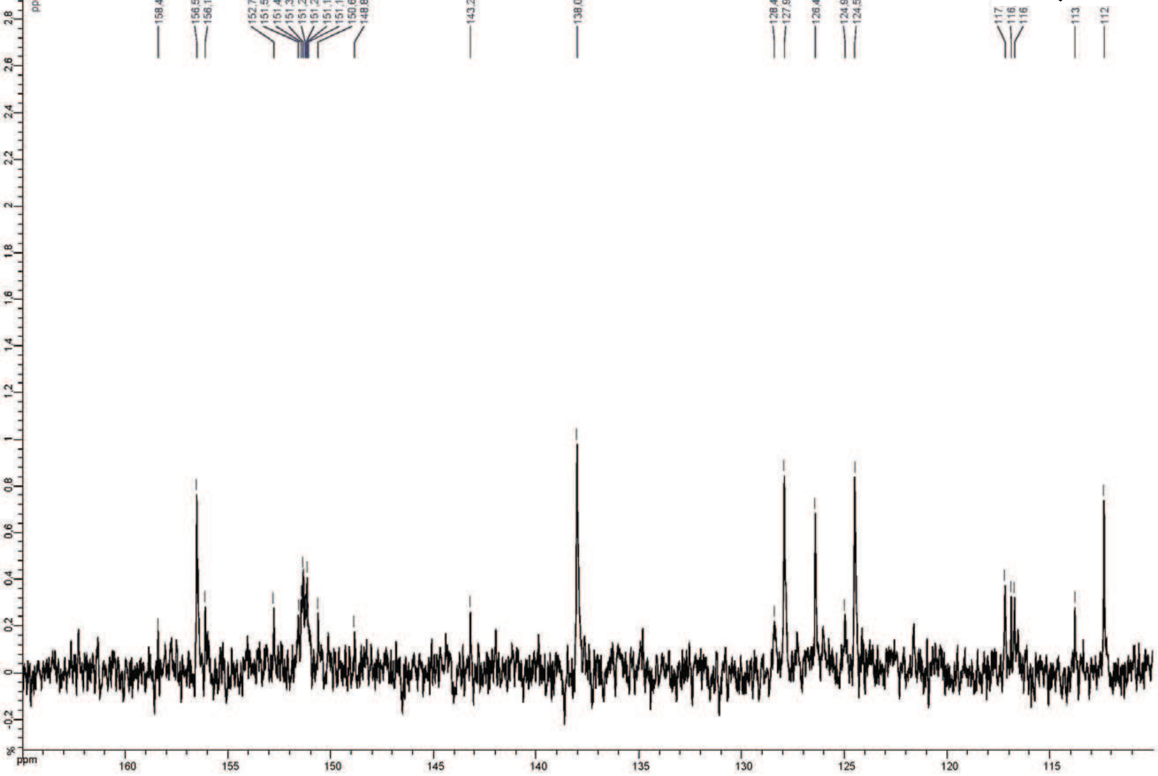
(**7b**) ^{13}C



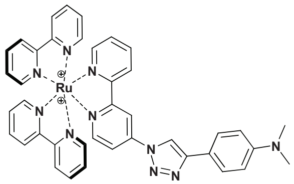


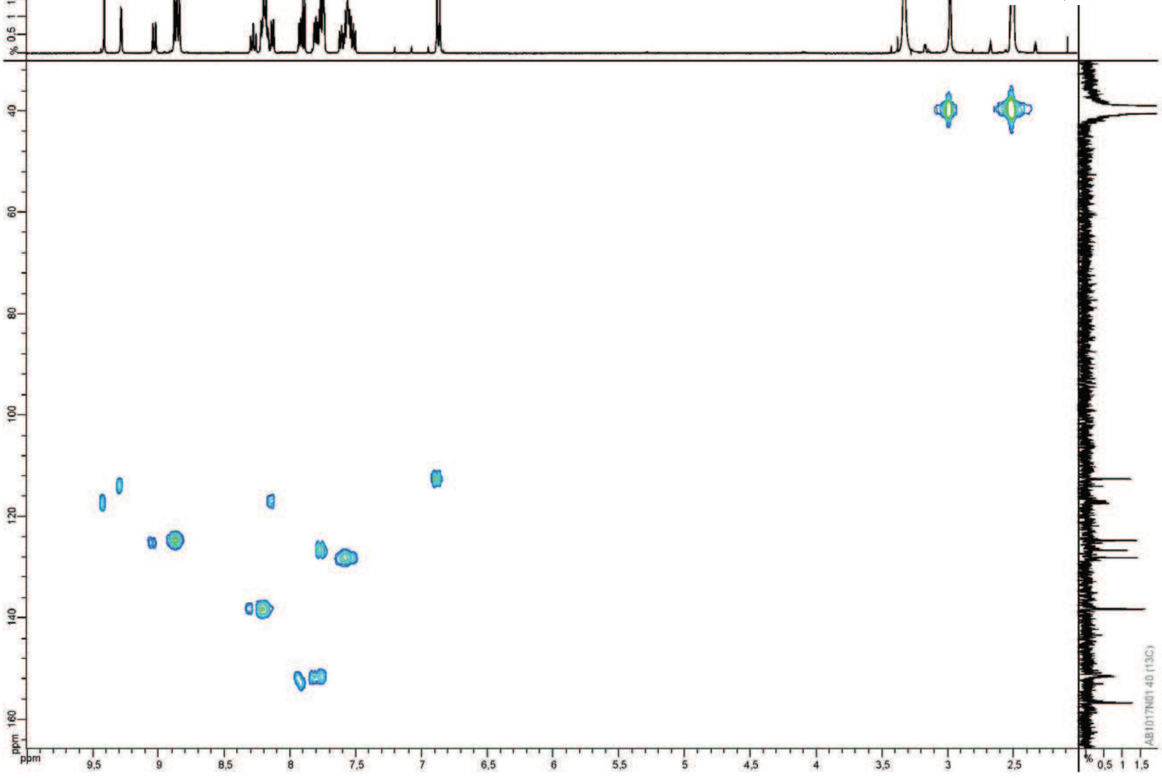
(**7b**) ^{13}C



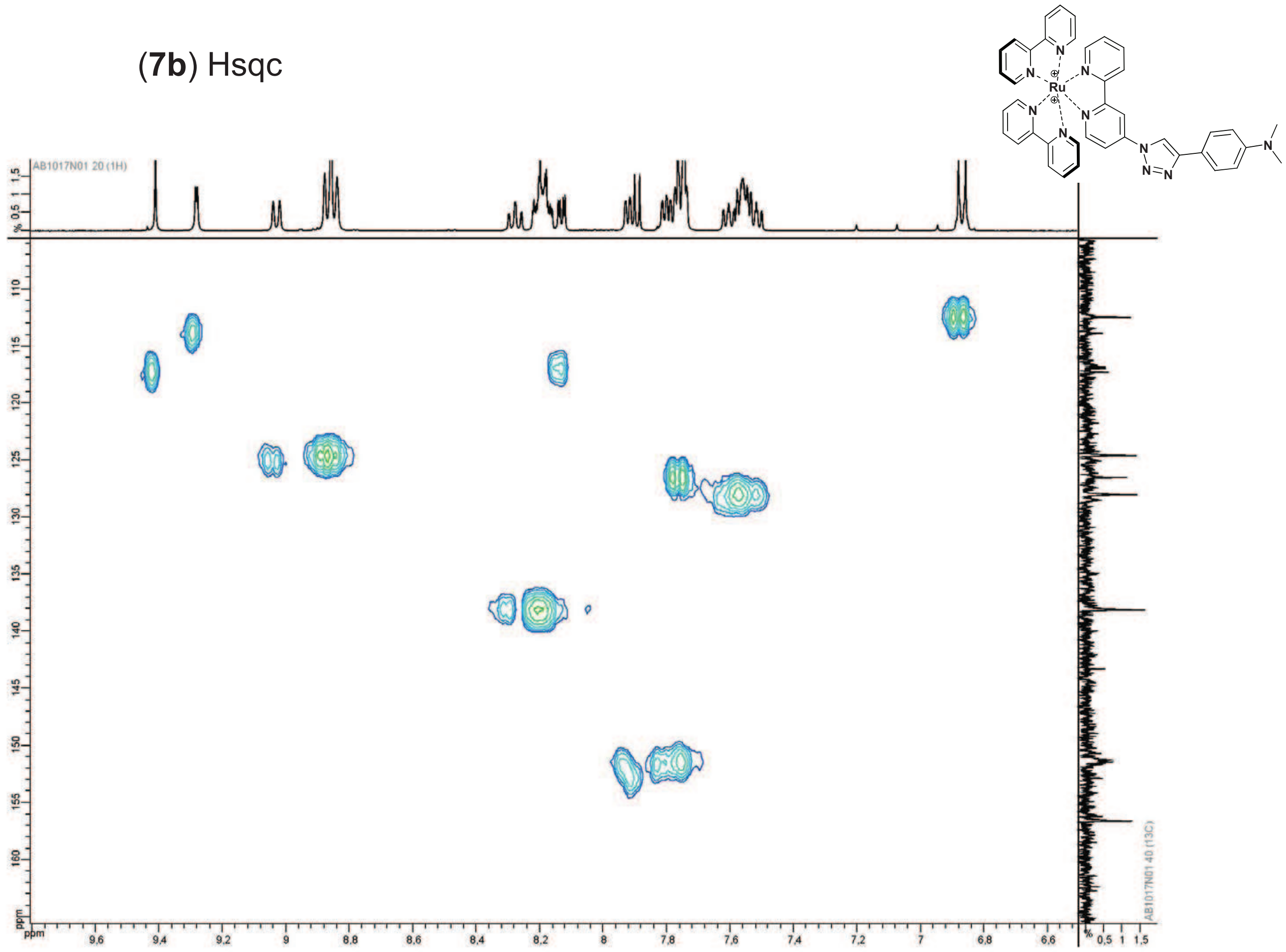


(**7b**) Hsqc





(**7b**) Hsqc


N
N
Ru
N
N
N
N
N
N
N
N
AB1017N01 20 (1H)
%
0,5
1
1,5
ppm
110
115
120
125
130
135
140
145
150
155
160
ppm
9,6
9,4
9,2
9
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
7
6,8
6,6
AB1017N01 40 (13C)
%
0,5
1
1,5

Monoimide (**4'c**)

^{1}H all

Cosy all

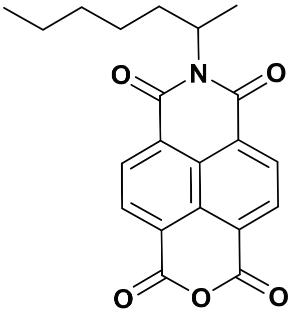
Cosy zoom

^{13}C all

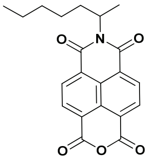
Hsqc all

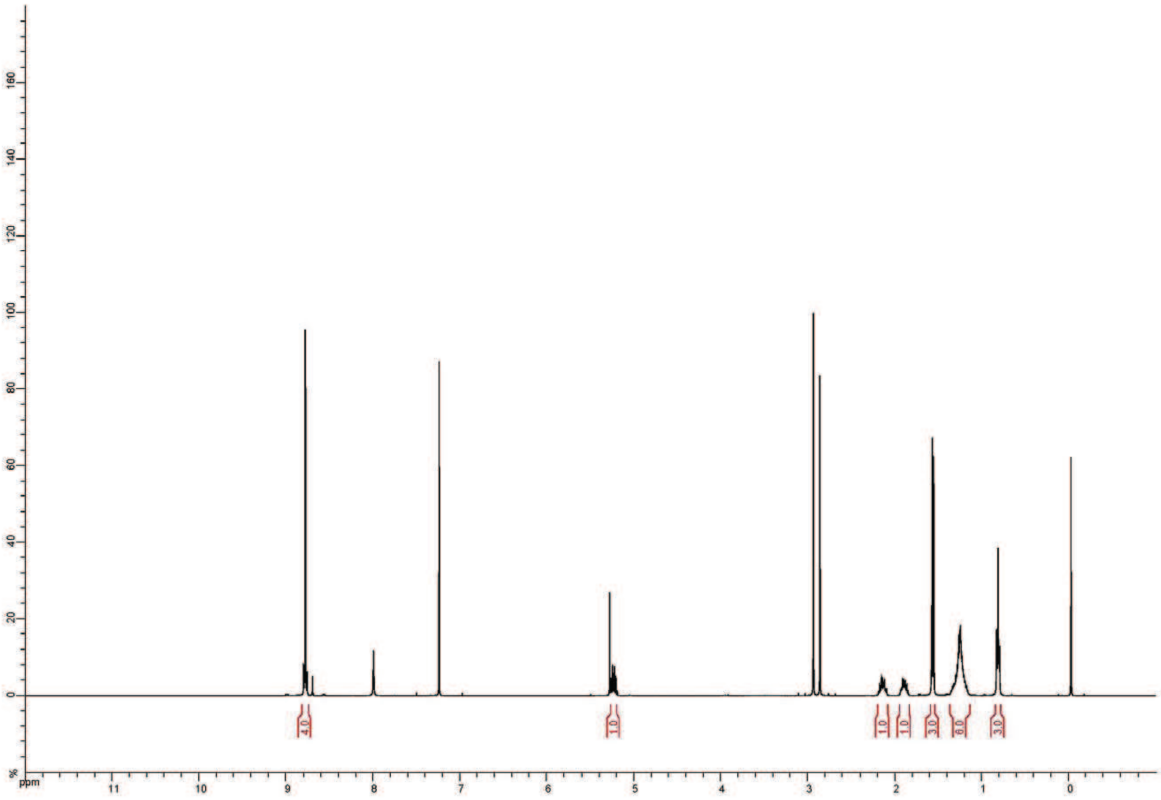
Hsqc zoom

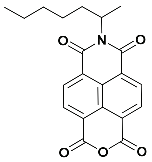
Hmbc



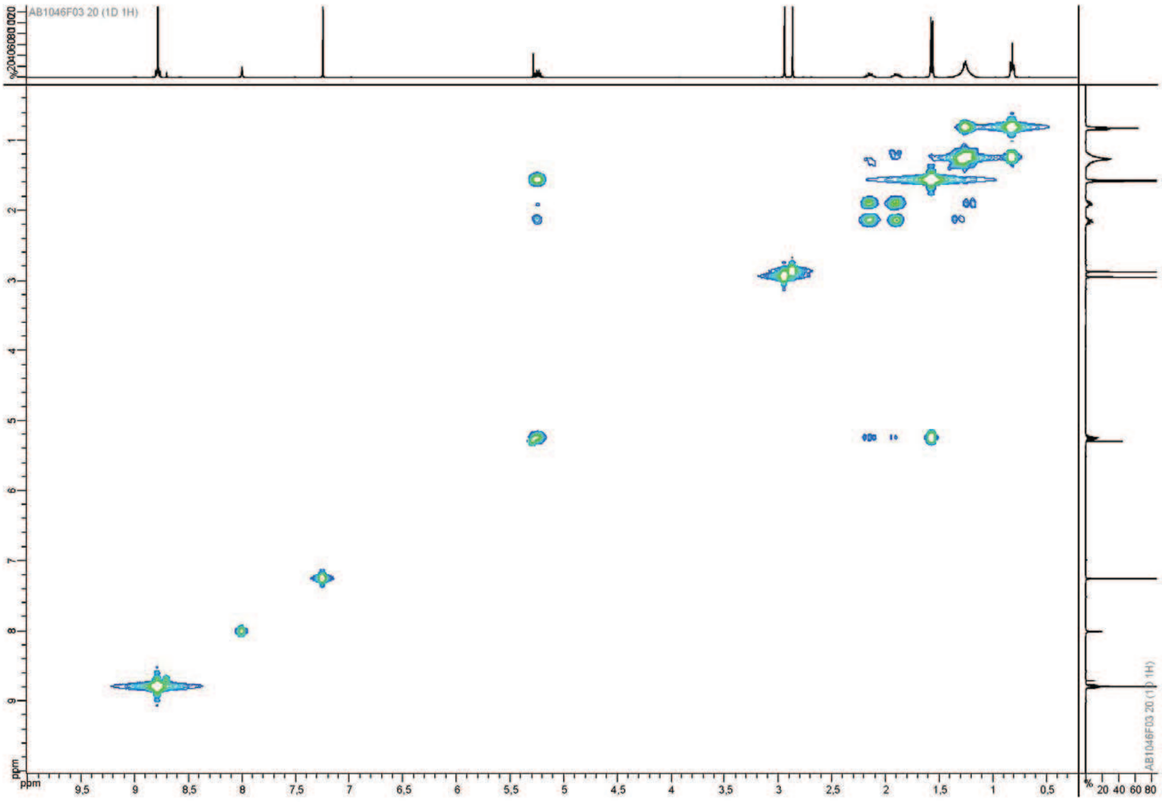
(**4'c**) ^{1}H

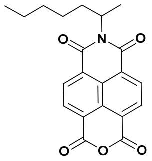




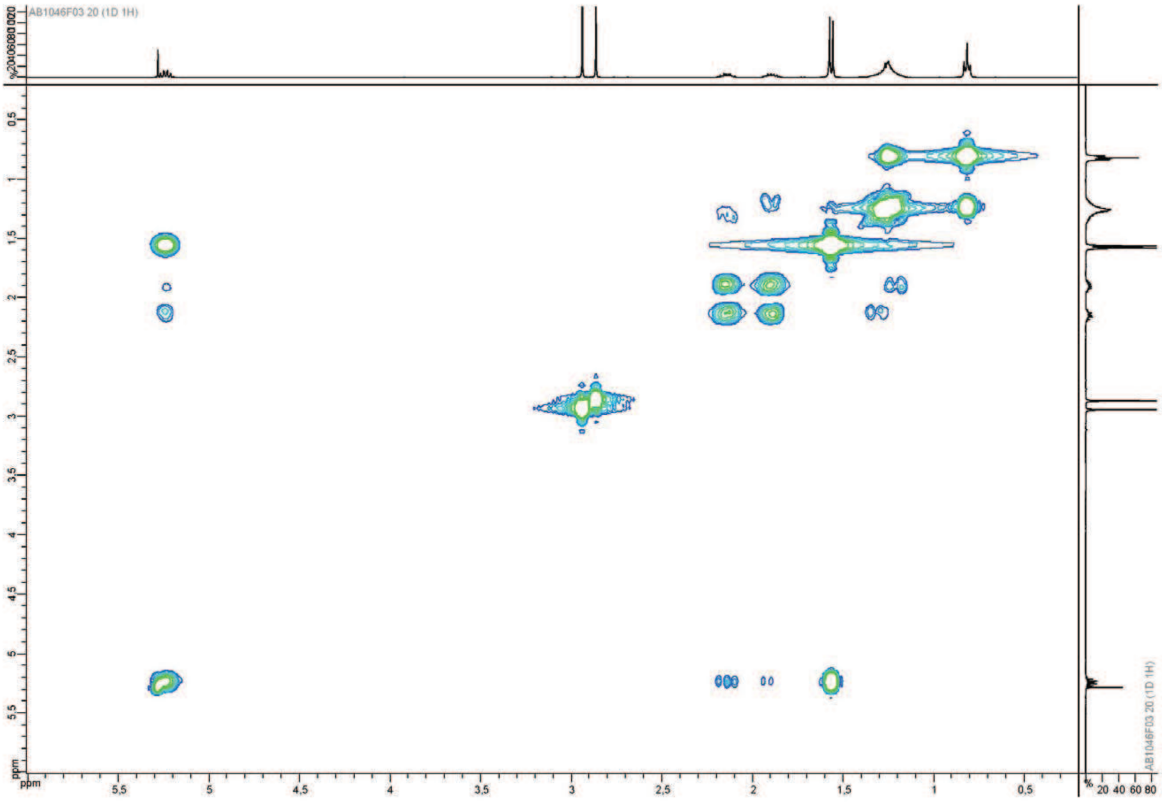


(**4’c**) Cosy

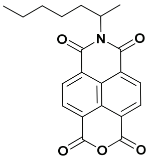


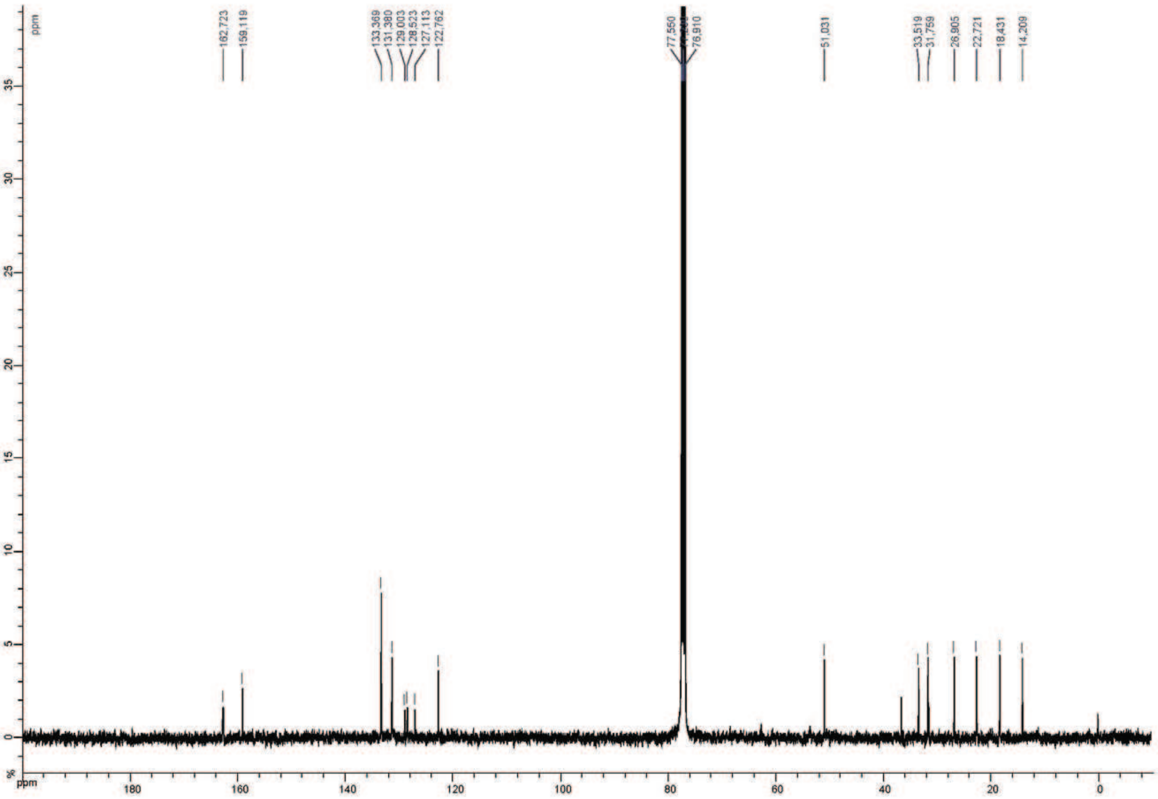


(**4’c**) Cosy

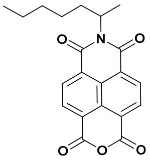


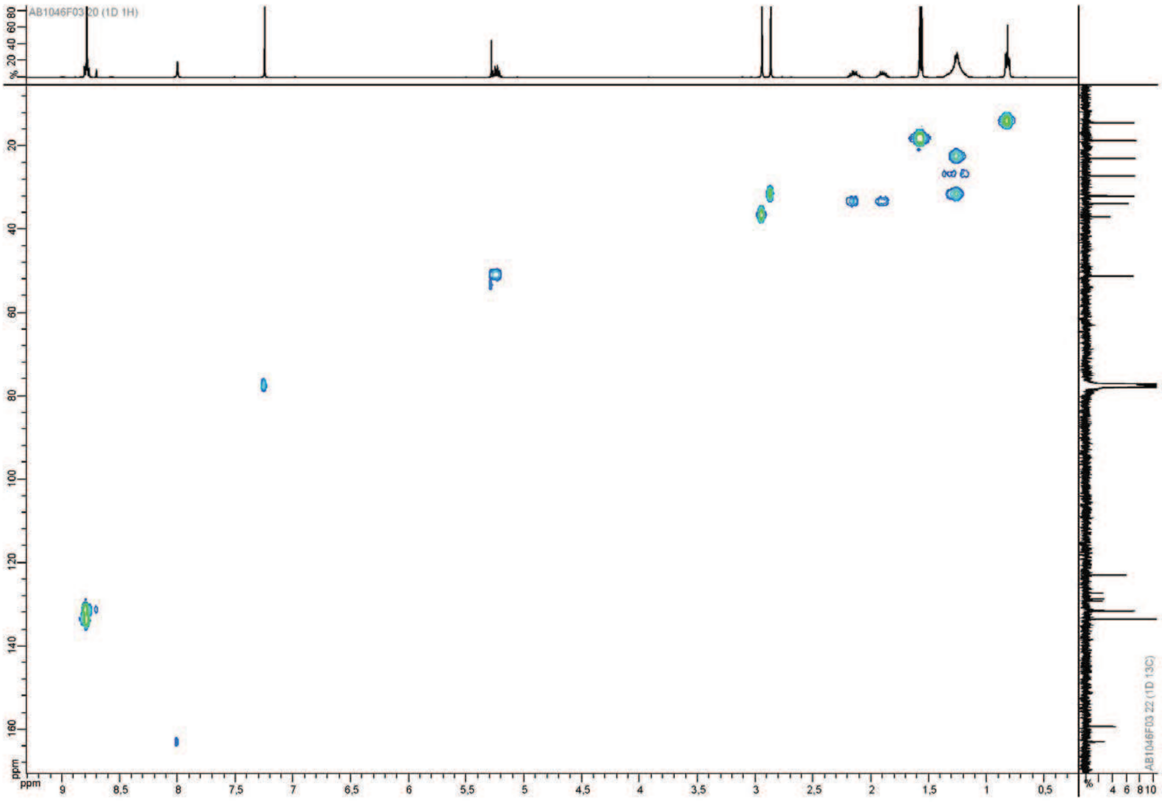
(**4'c**) ^{13}C



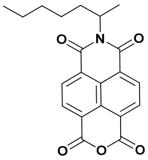


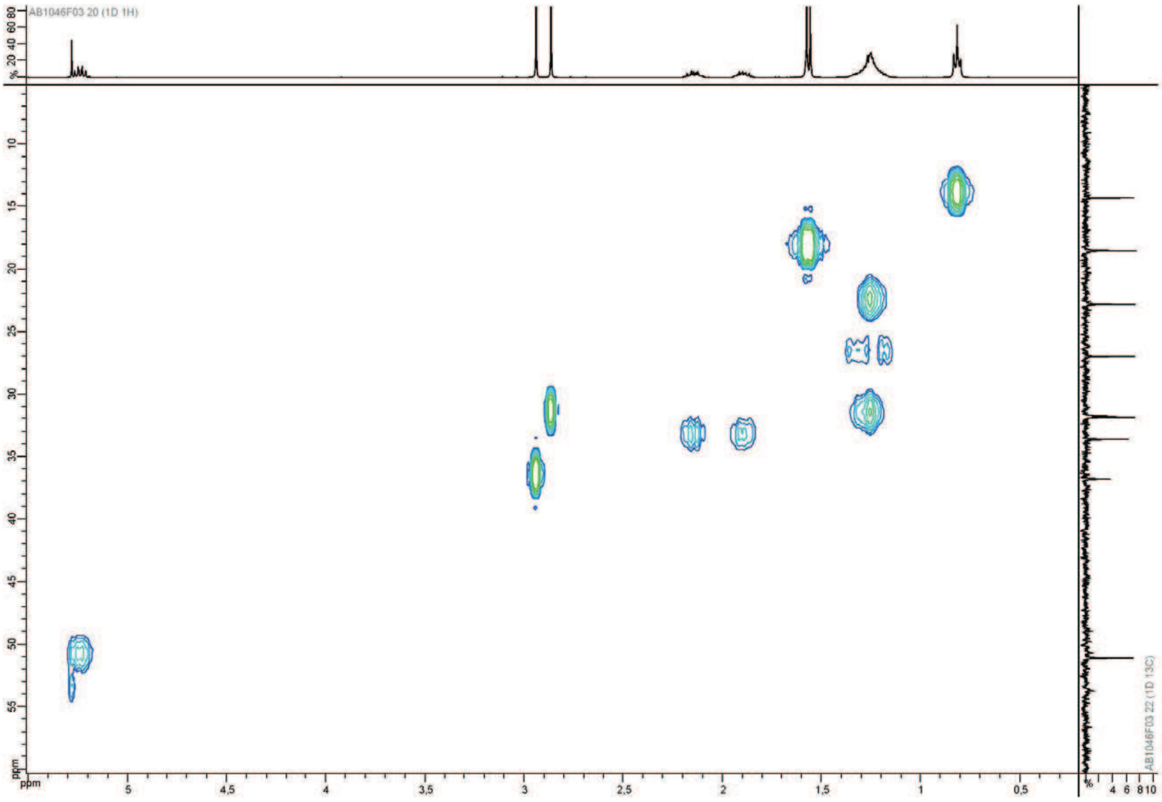
(**4'c**) Hsqc



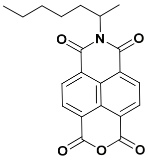


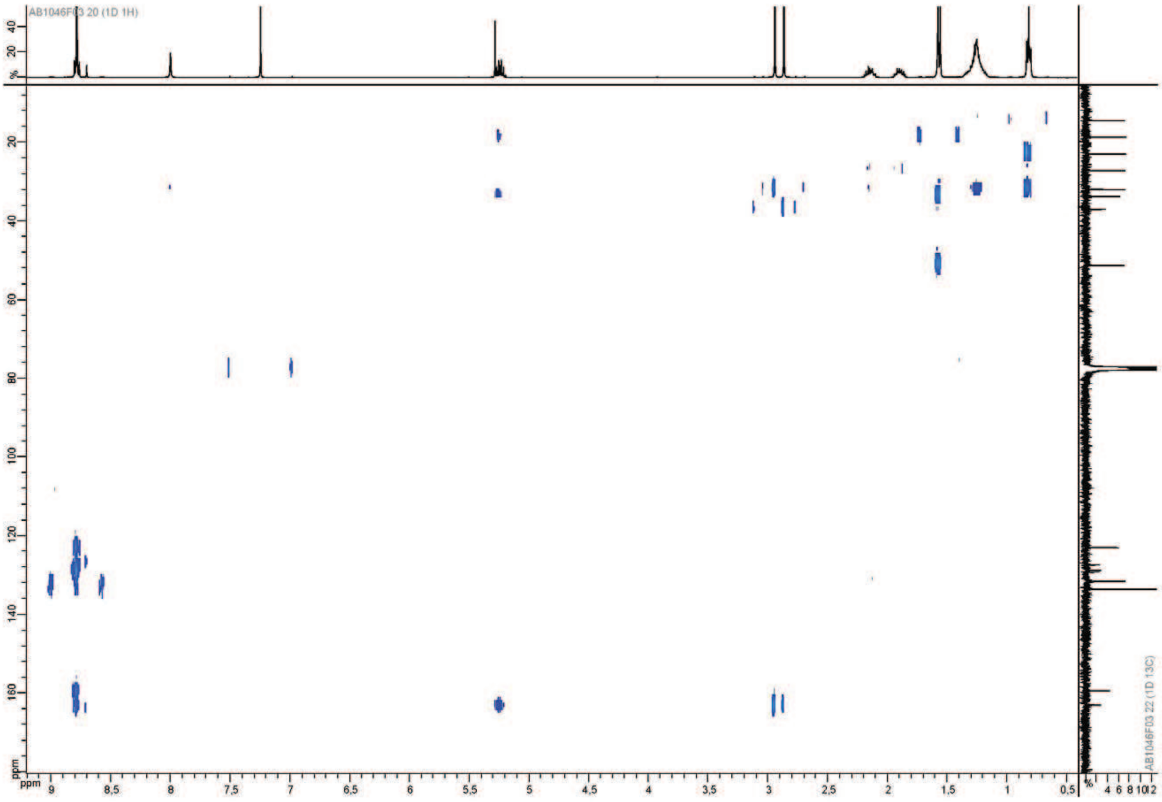
(**4’c**) Hsqc



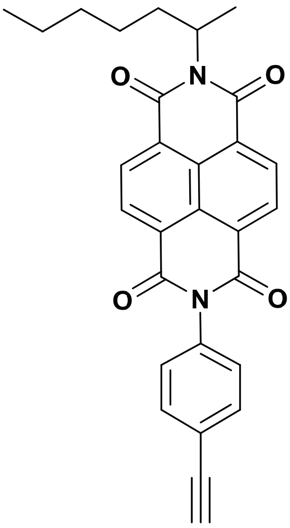


(**4’c**) Hmbc





Diimide NDI (**4c**)



^{1}H all

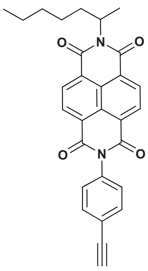
Cosy

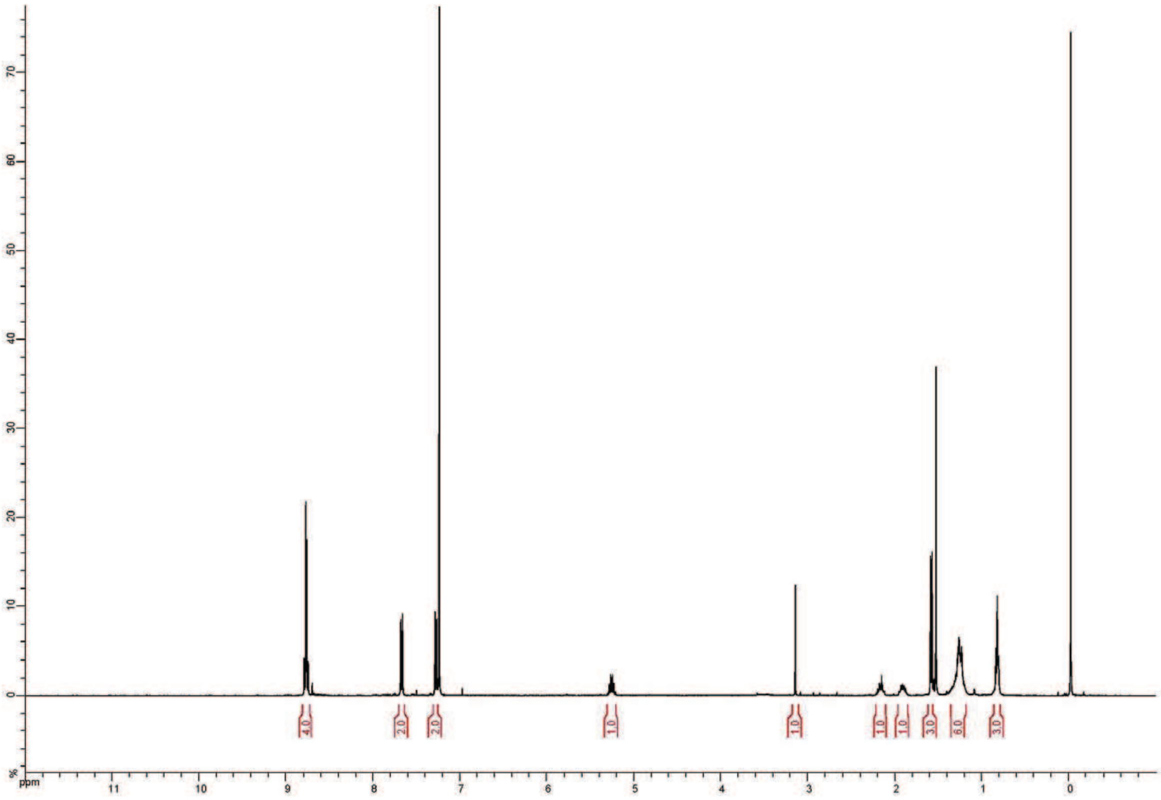
^{13}C all

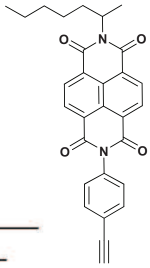
Hsqc

Hmbc

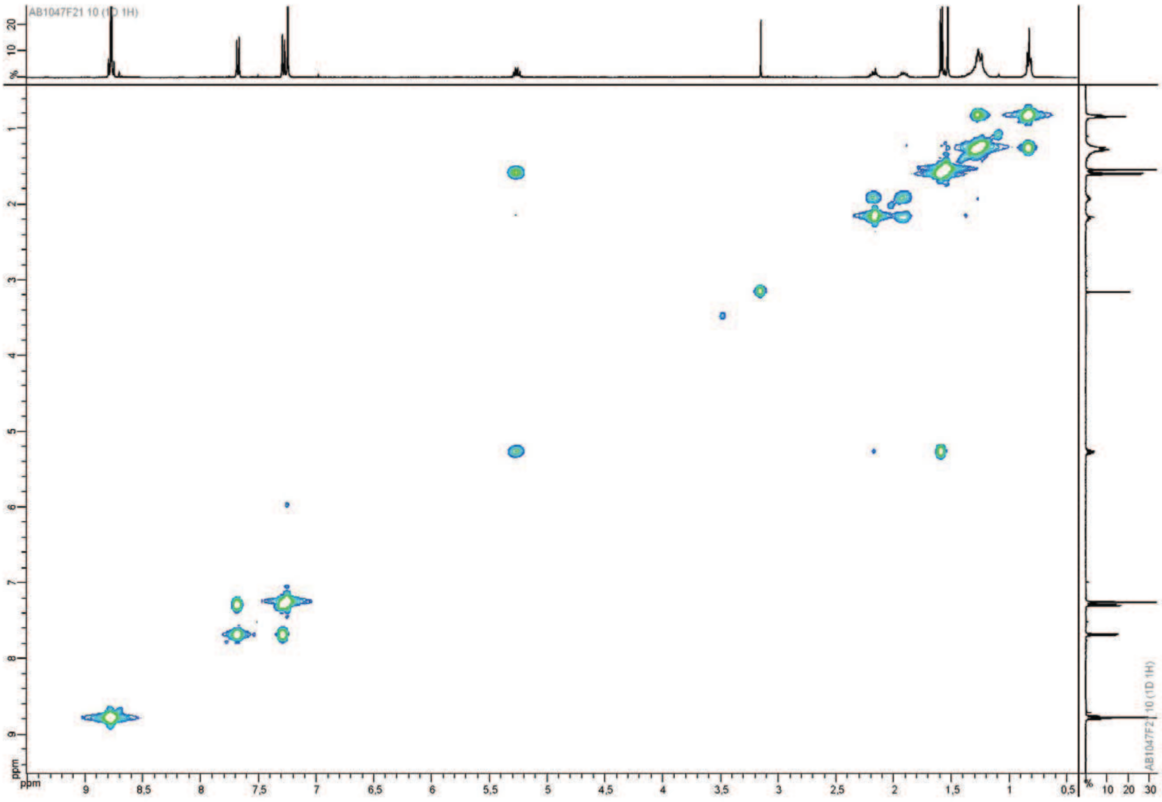
(**4c**) ^{1}H

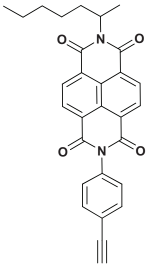




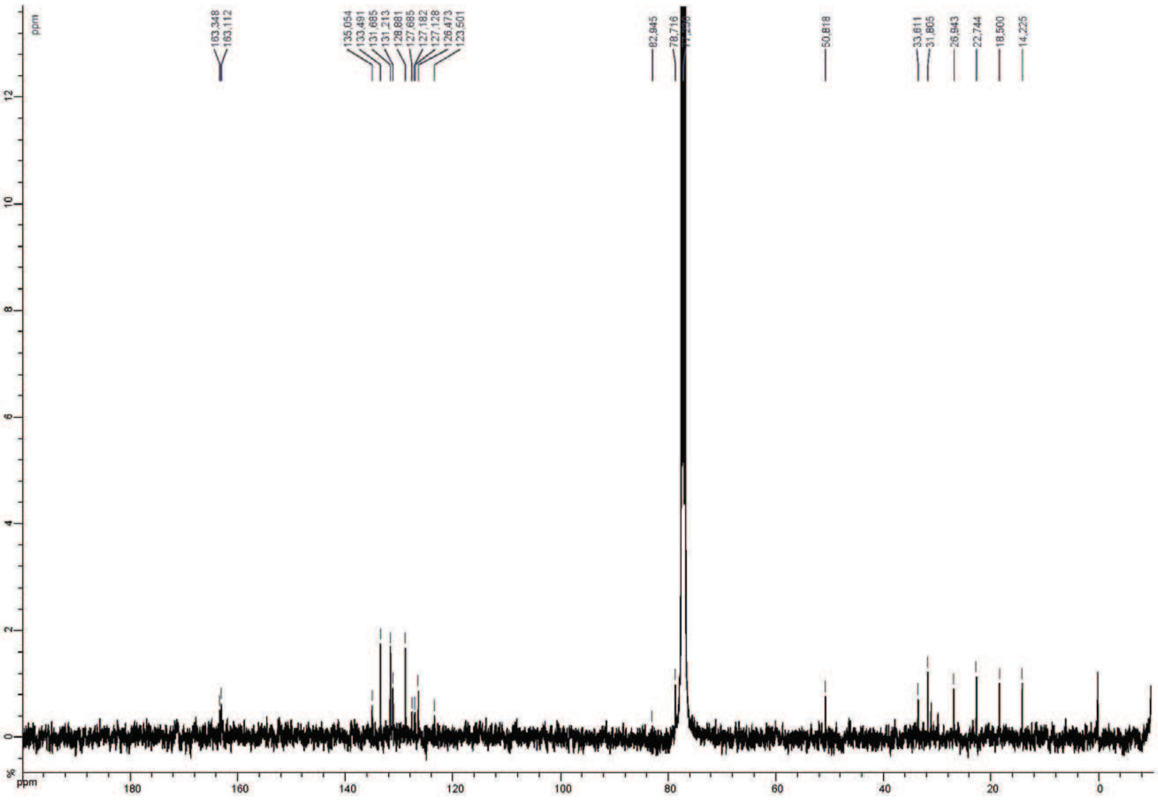


(**4c**) Cosy

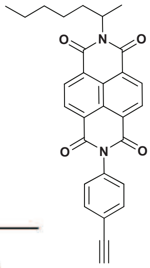


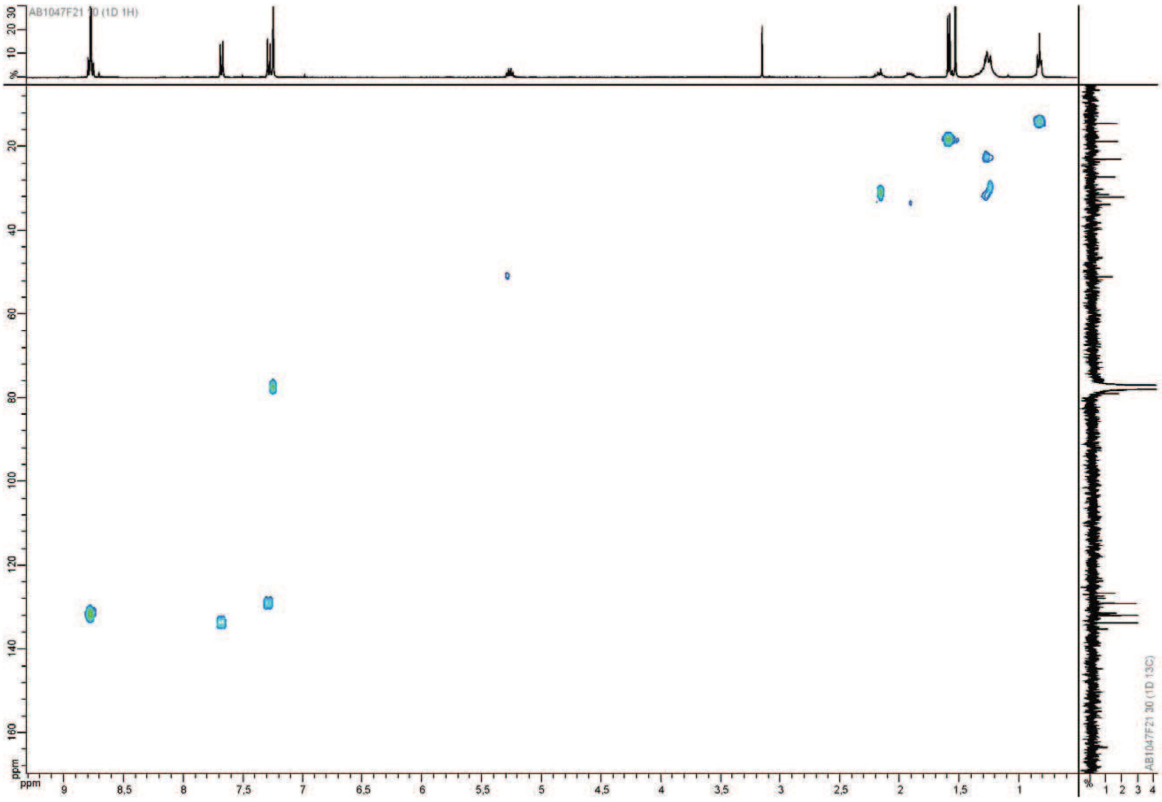


(**4c**) ^{13}C

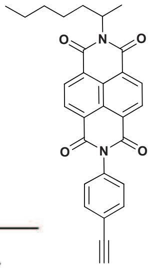


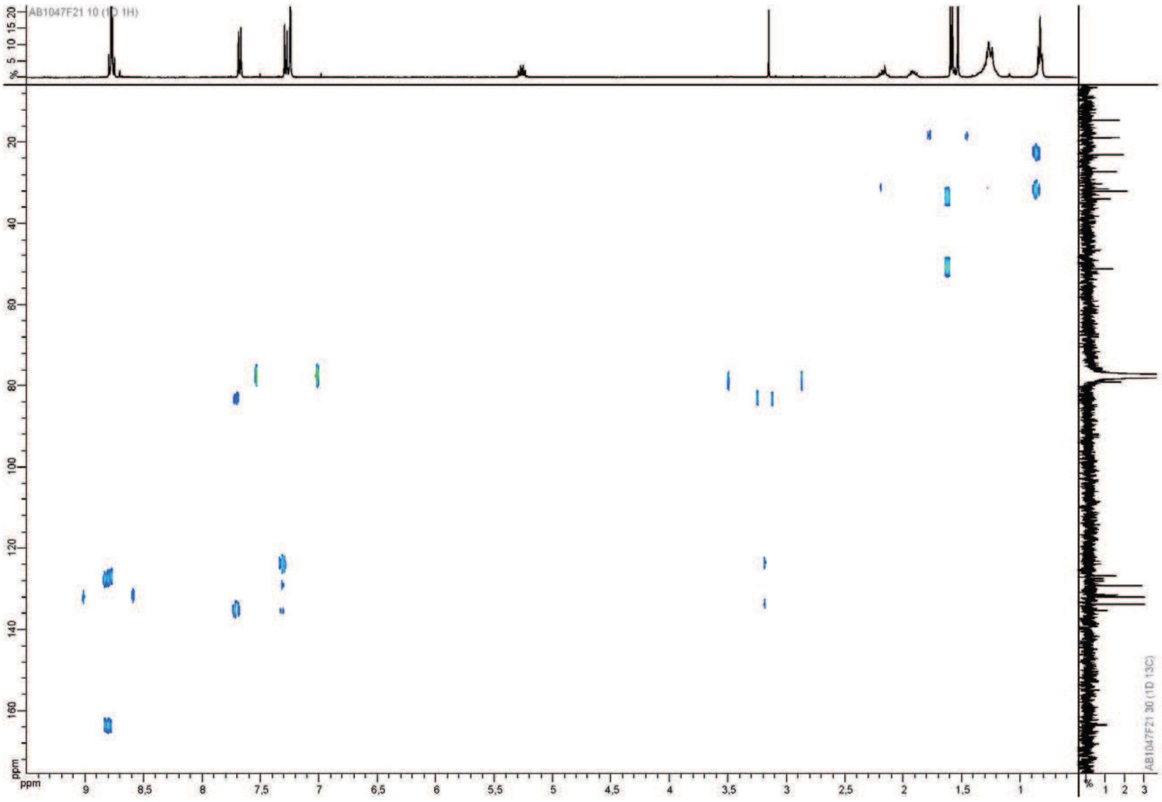
(**4c**) Hsqc



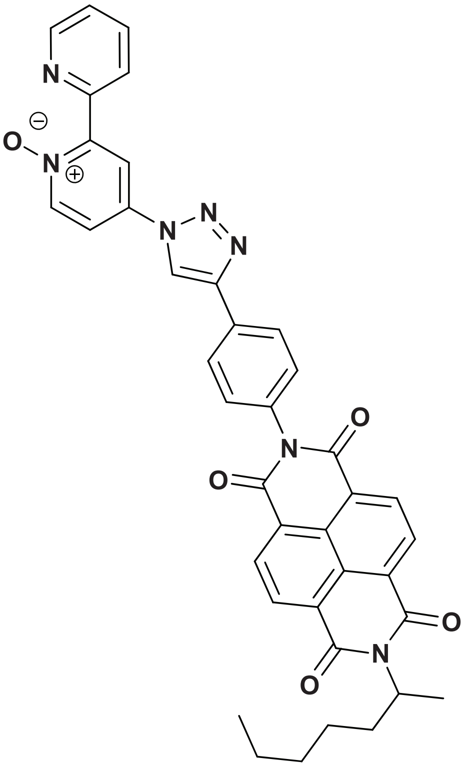


(**4c**) Hmbc





BpyTNDI-*N*-oxide (**5c**)



^{1}H all

^{1}H zoom

Cosy all

Cosy zoom

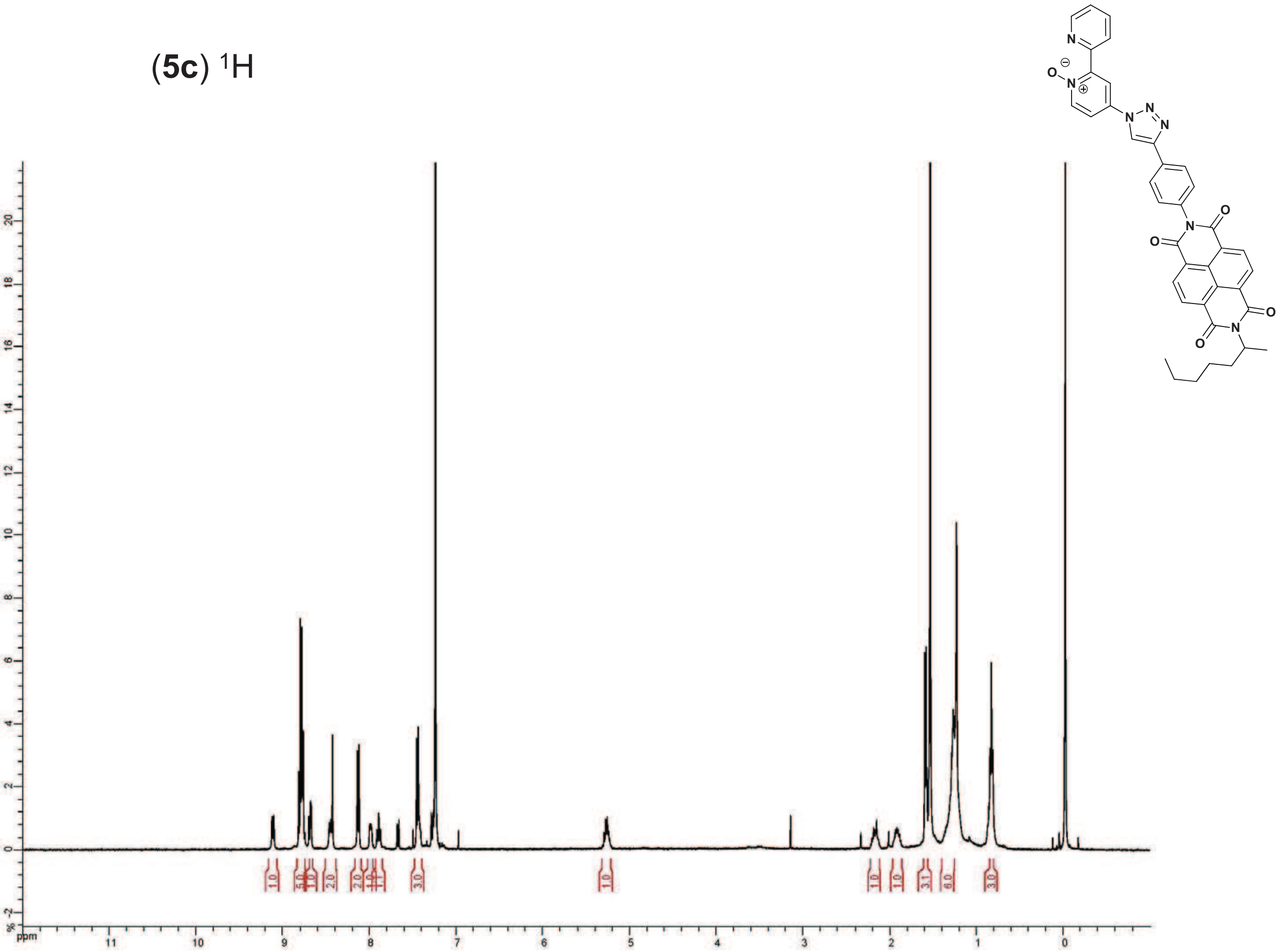
^{13}C all

Hsqc all

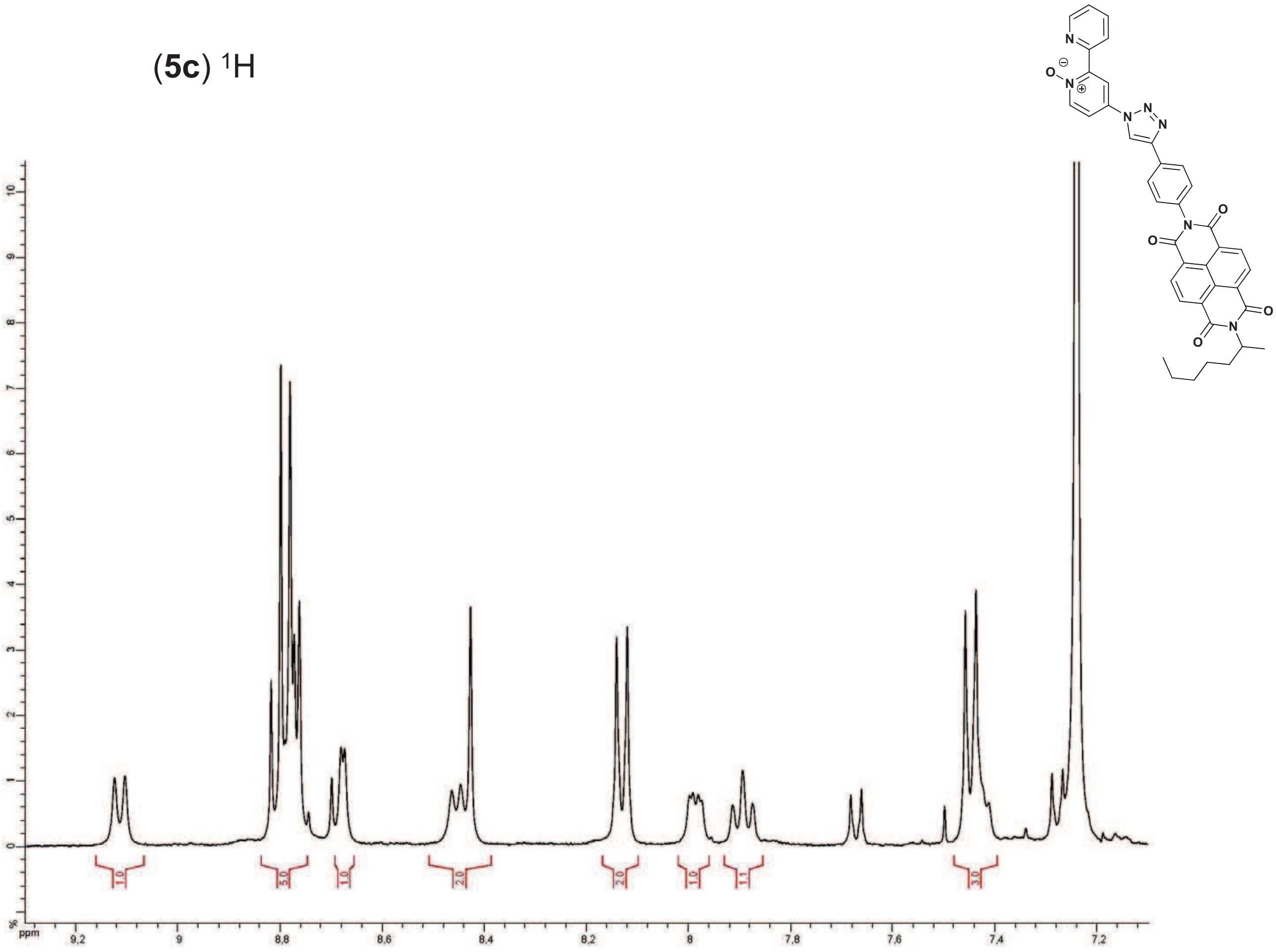
Hsqc zooms

Hmbc all

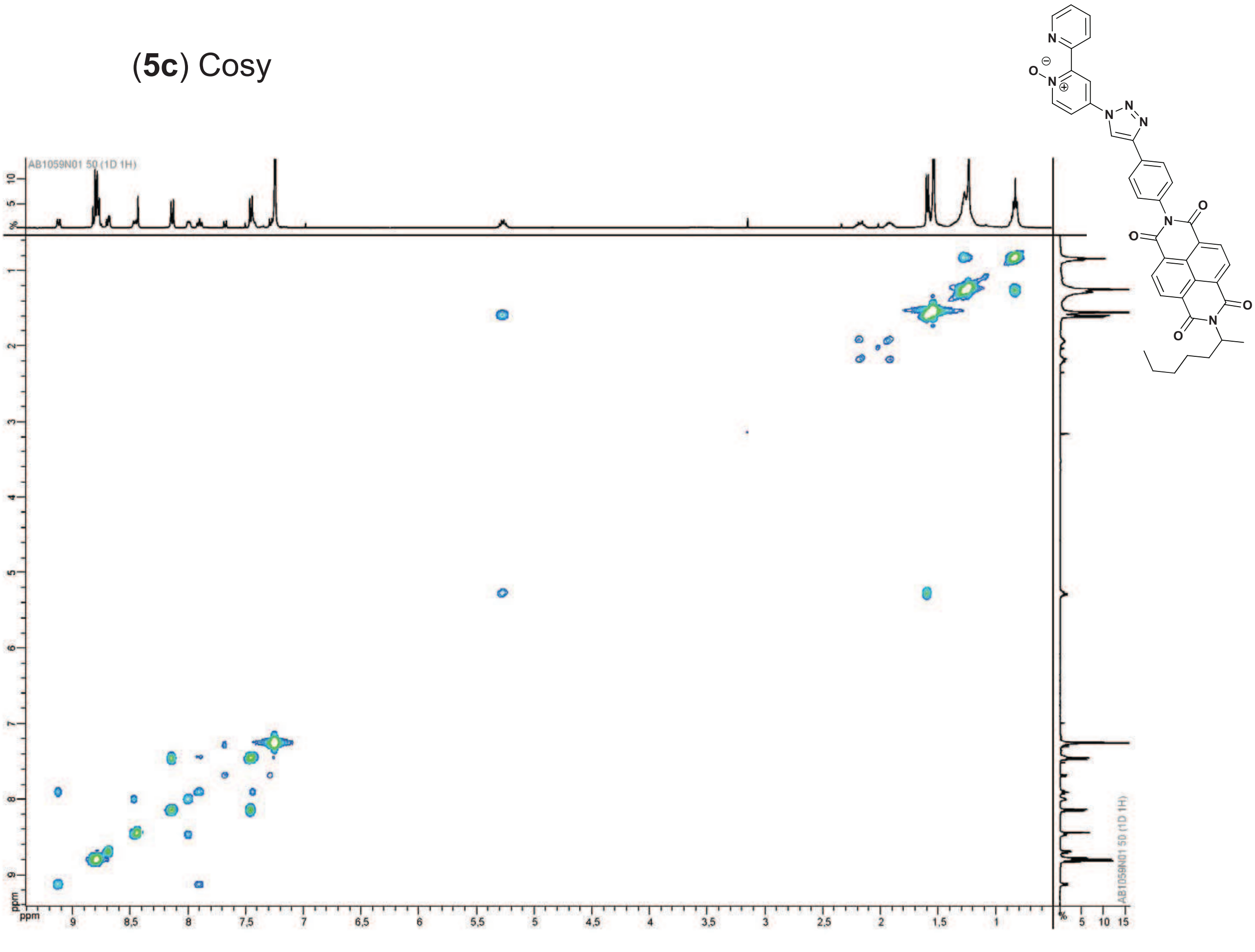
(**5c**) ^{1}H



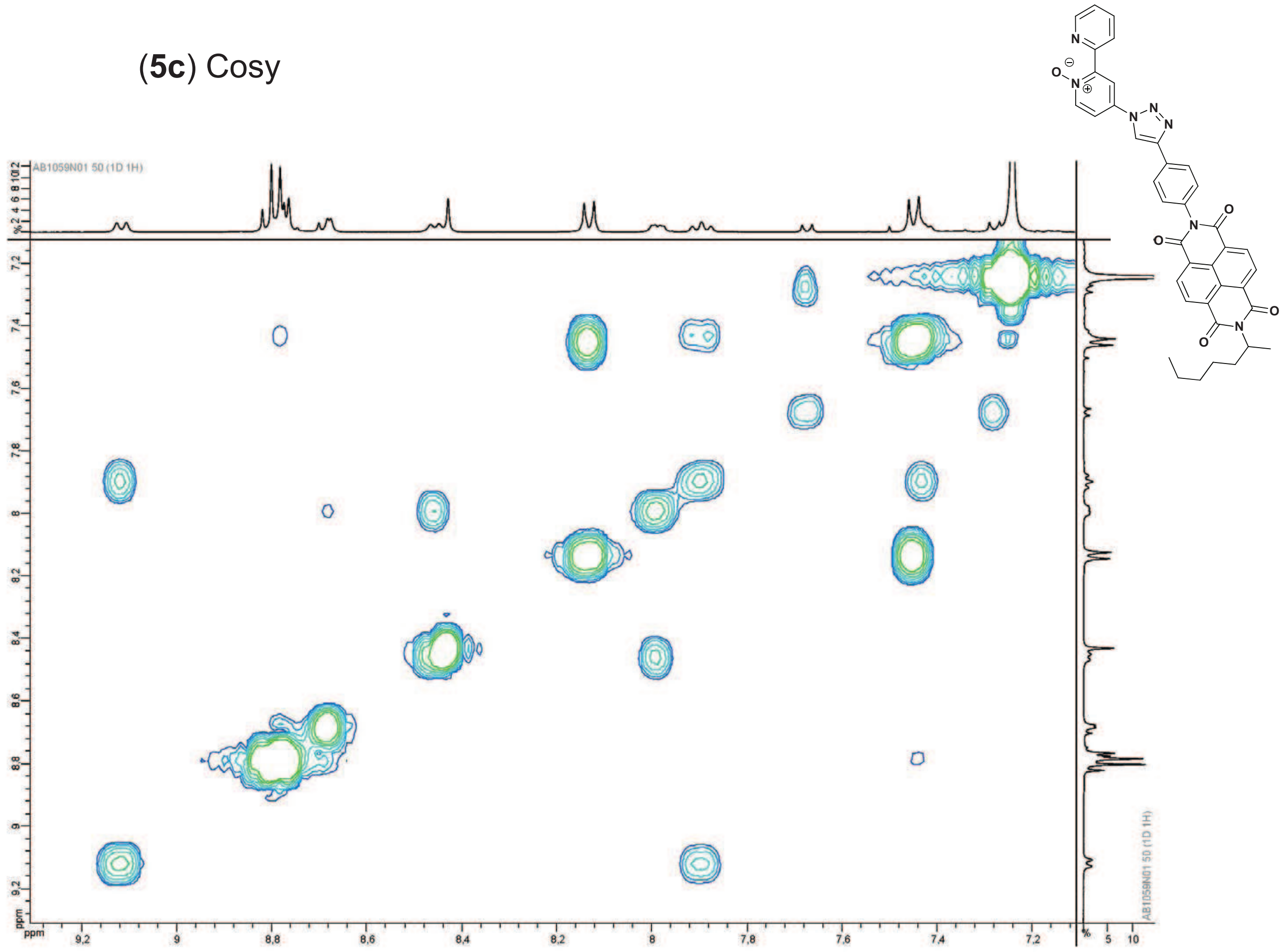
(**5c**) ^{1}H


1.0
5.0
1.0
2.0
2.0
1.0
1.1
3.0
ppm
9,2
9
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
%
N
O
N
N
N
N
O
N
O
O
N
O

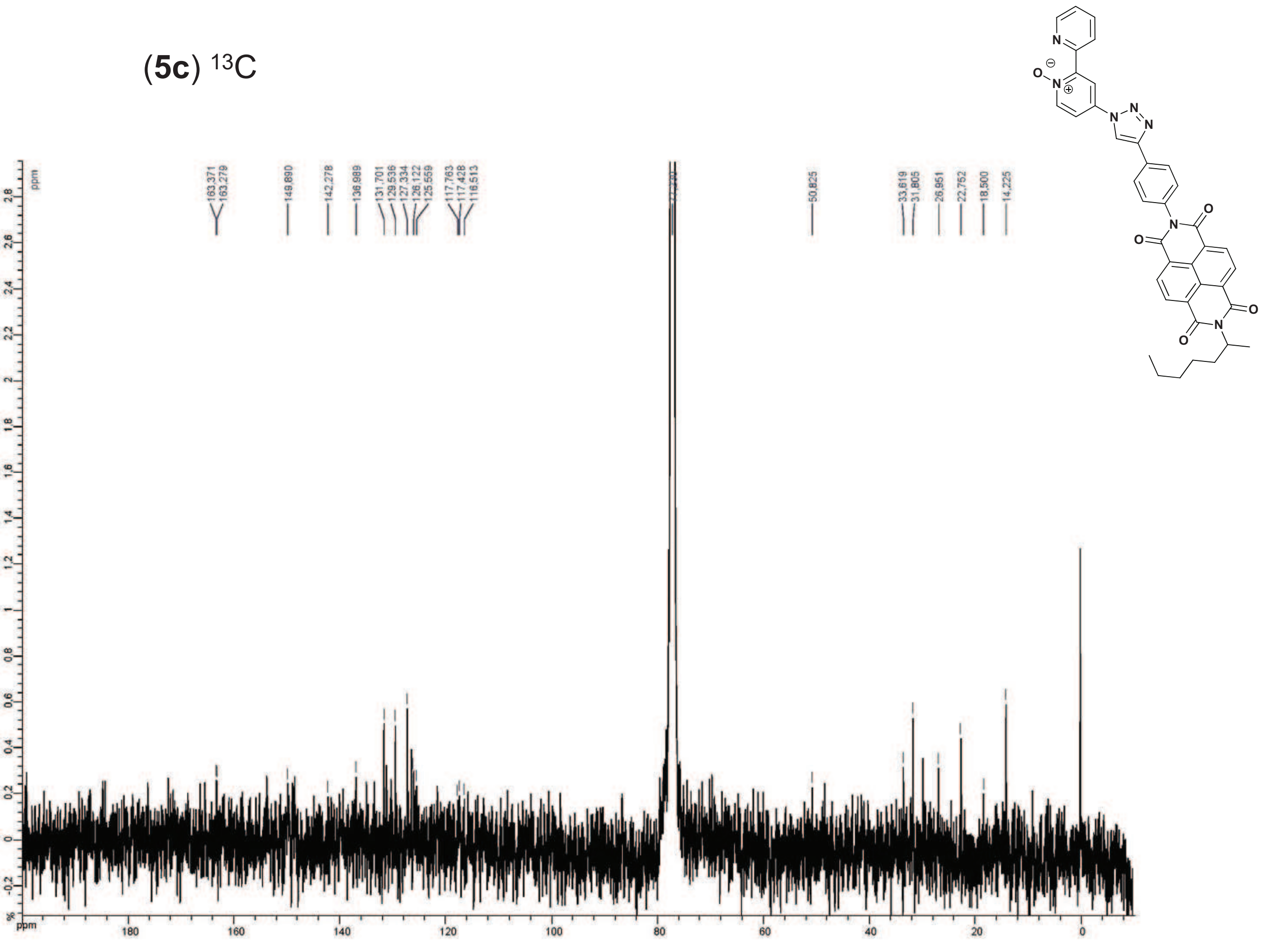
(**5c**) Cosy


AB1059N01 50 (1D 1H)
ppm
9
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
%
5
10
15
N
O
N
N
N
N
O
N
O
O
N
O

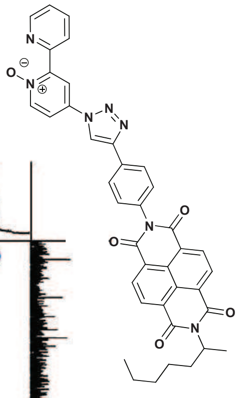
(**5c**) Cosy

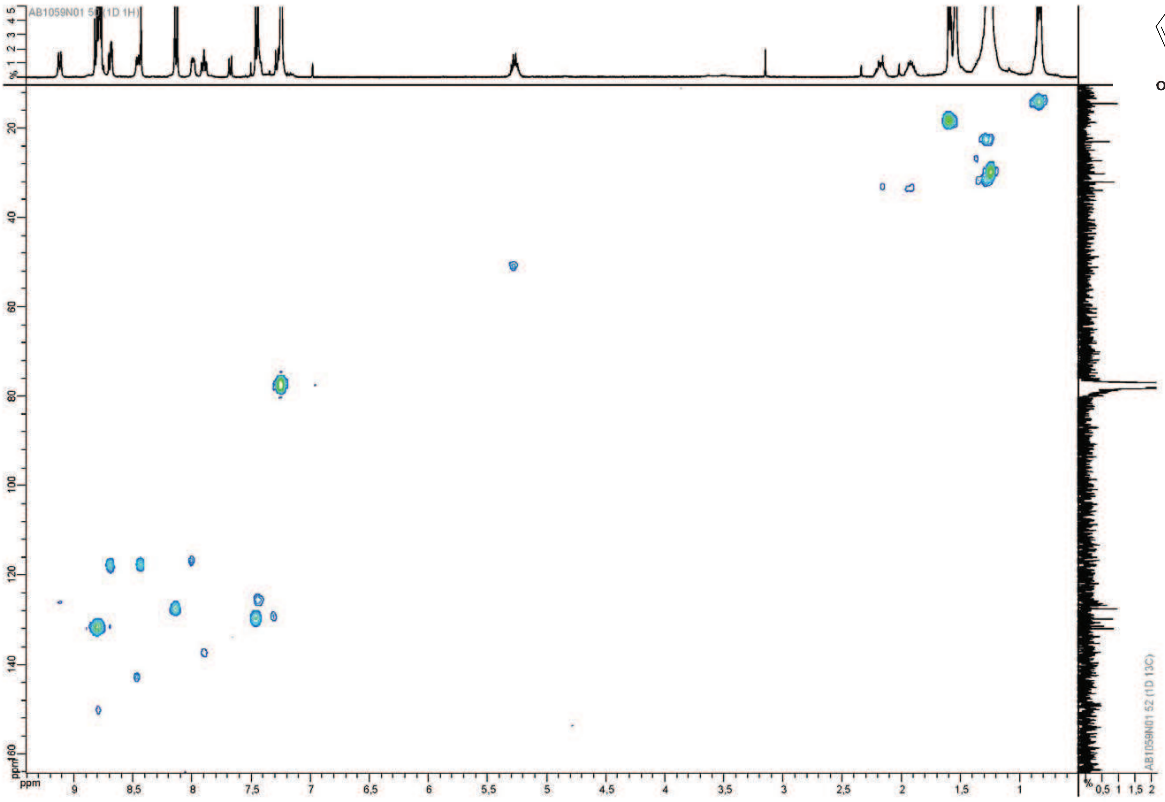


(**5c**) ^{13}C

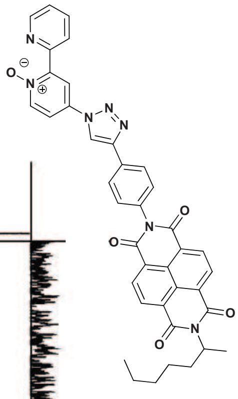


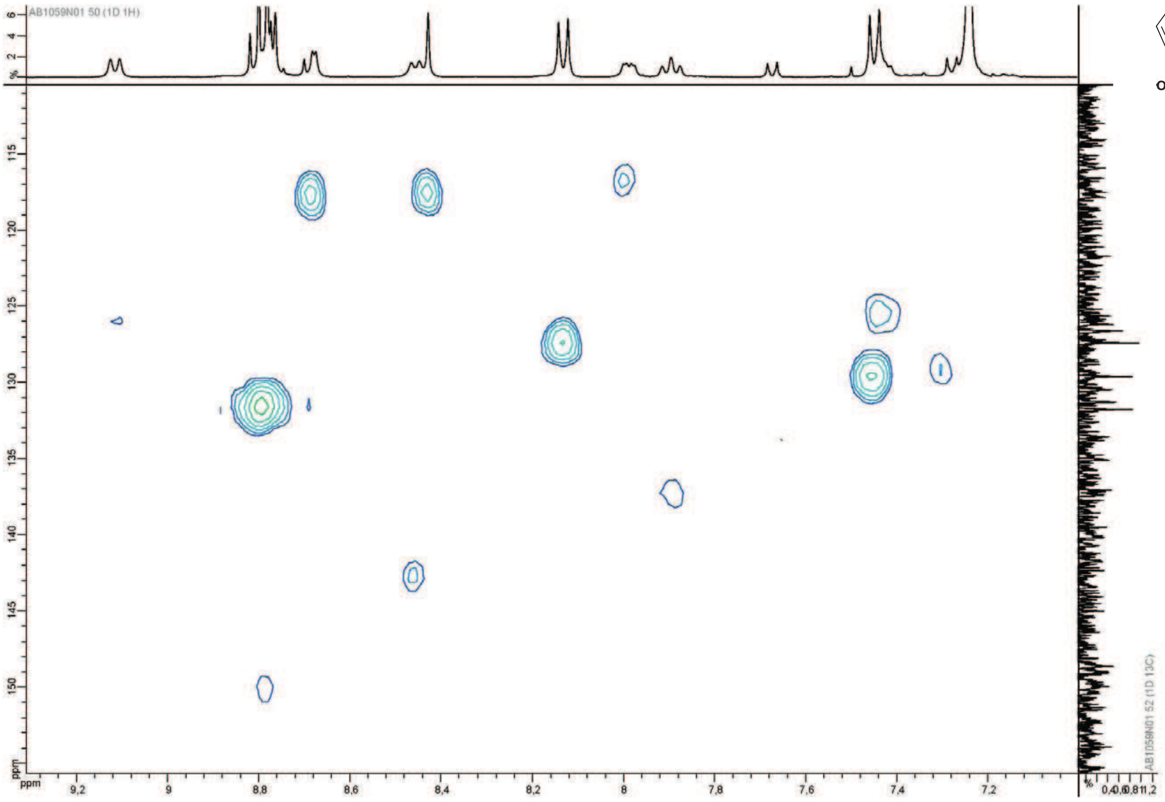
(**5c**) Hsqc



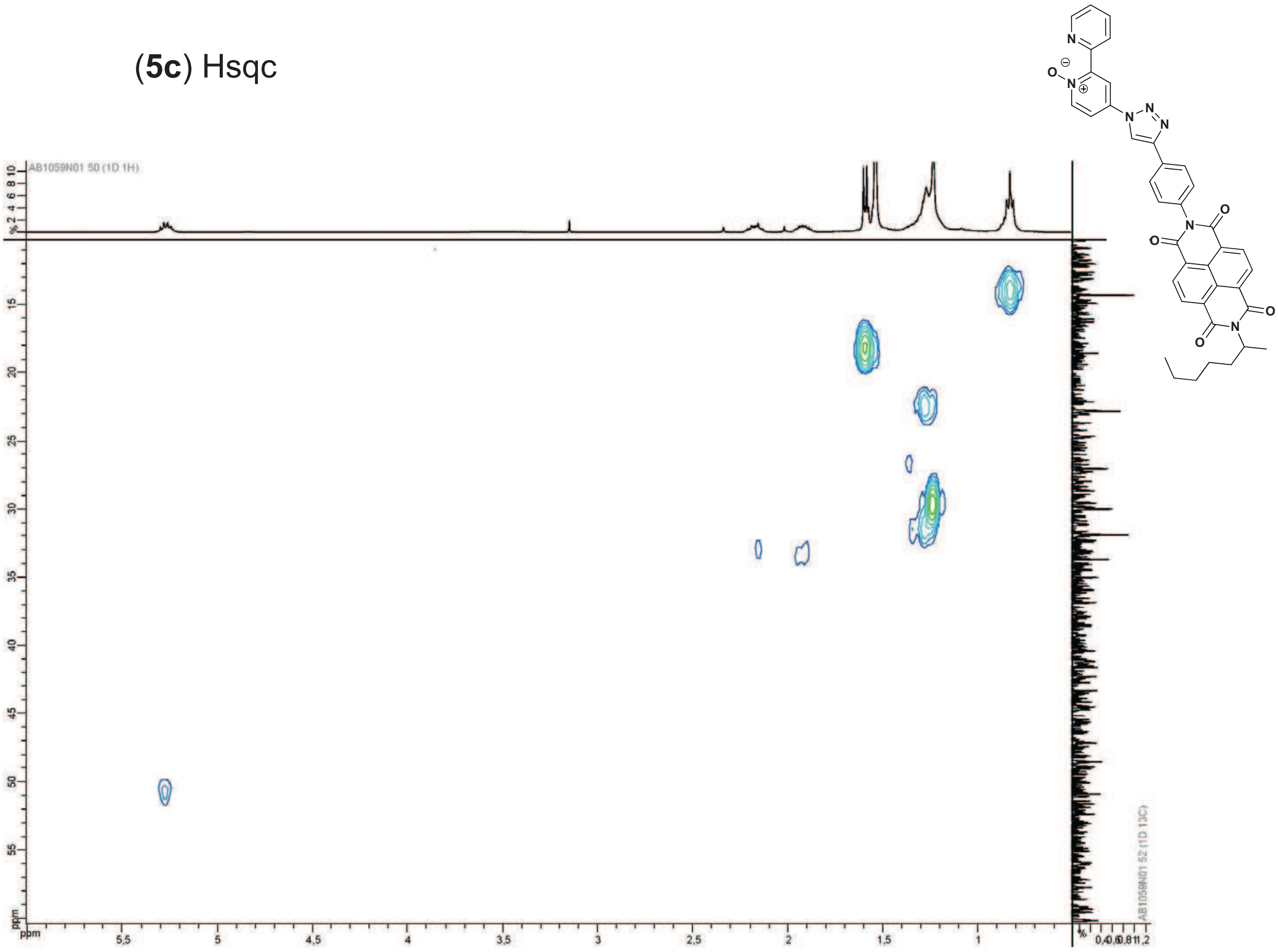


(**5c**) Hsqc

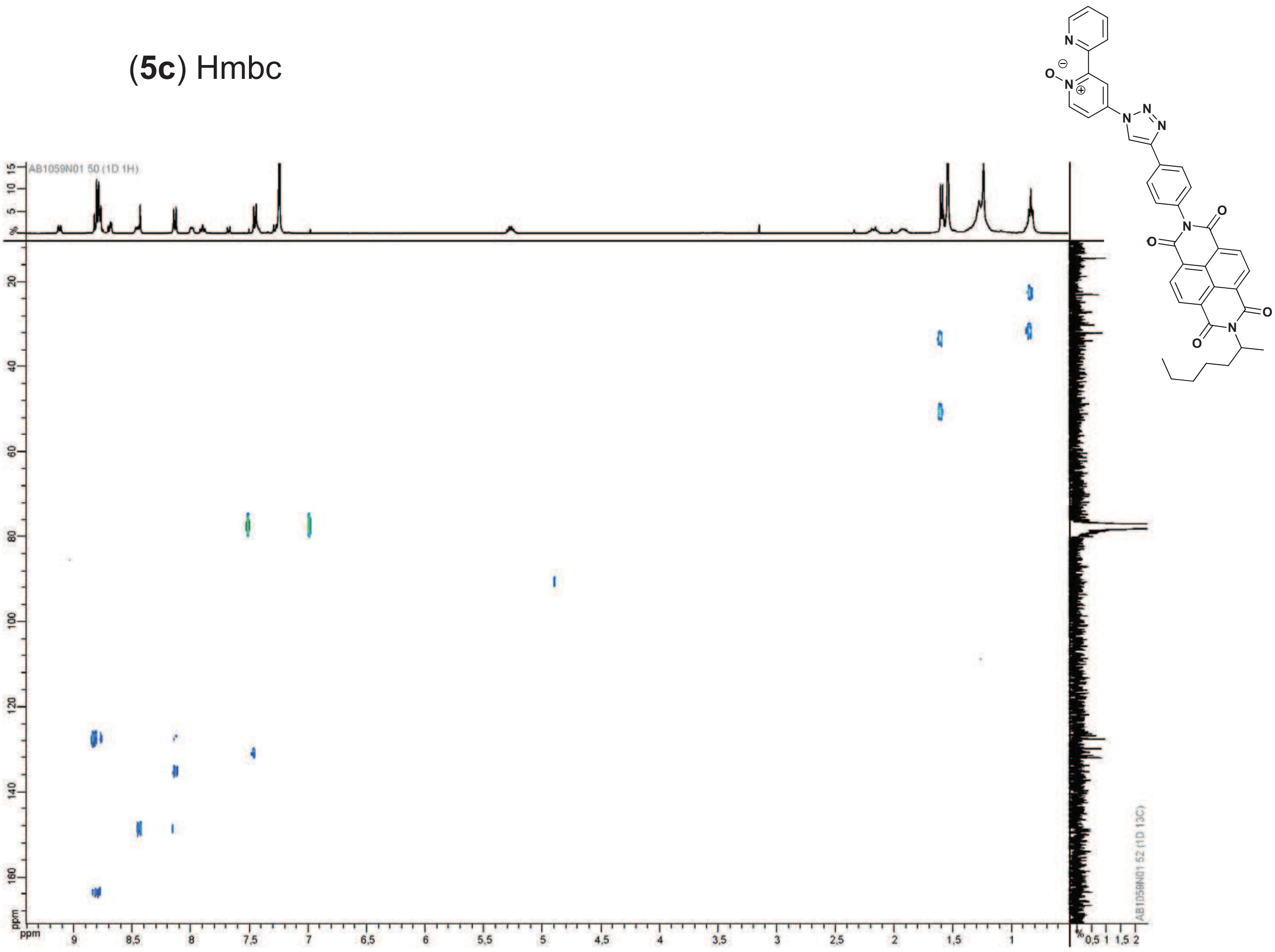




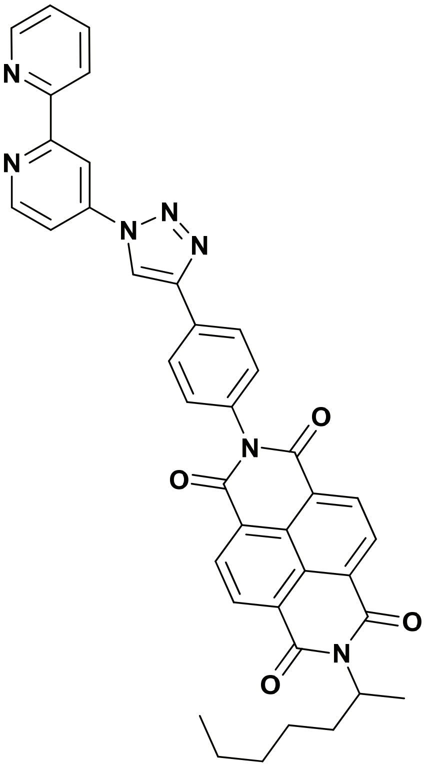
(**5c**) Hsqc



(**5c**) Hmbc



BpyTNDI (**6c**)



^{1}H all

^{1}H zoom

Cosy all

Cosy zoom

^{13}C all

^{13}C zoom

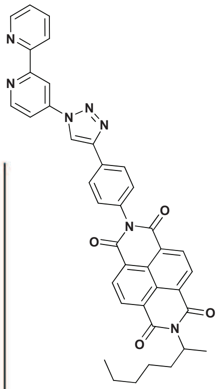
Hsqc all

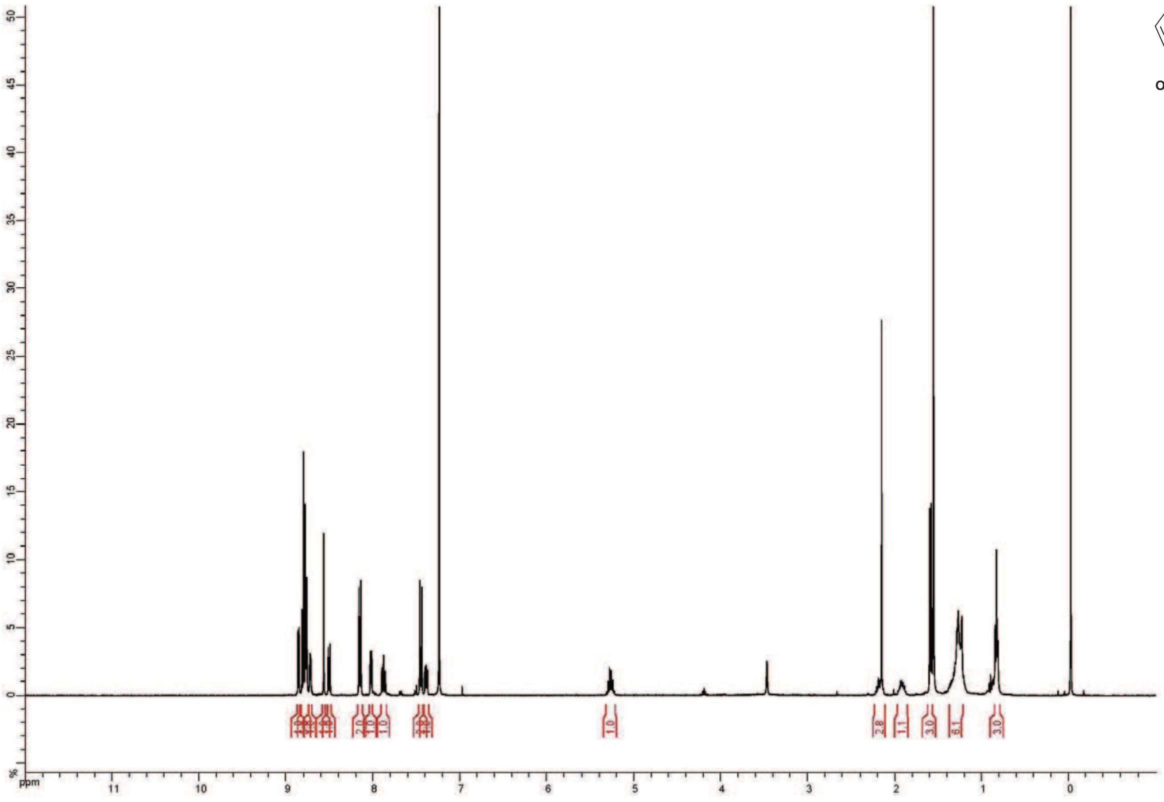
Hsqc zoom

Hmbc all

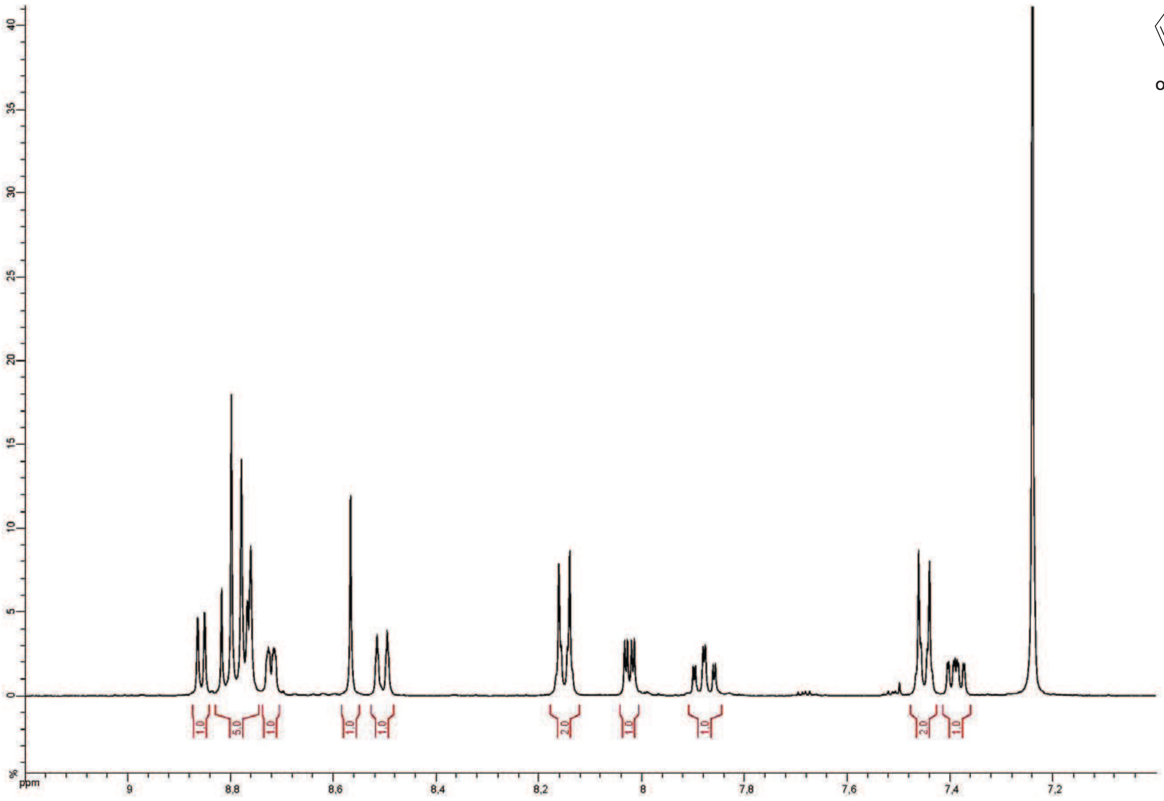
Hmbc zoom

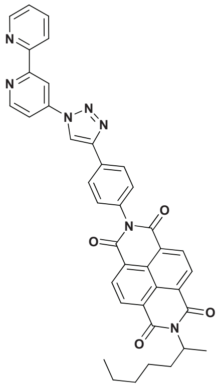
(**6c**) ^{1}H



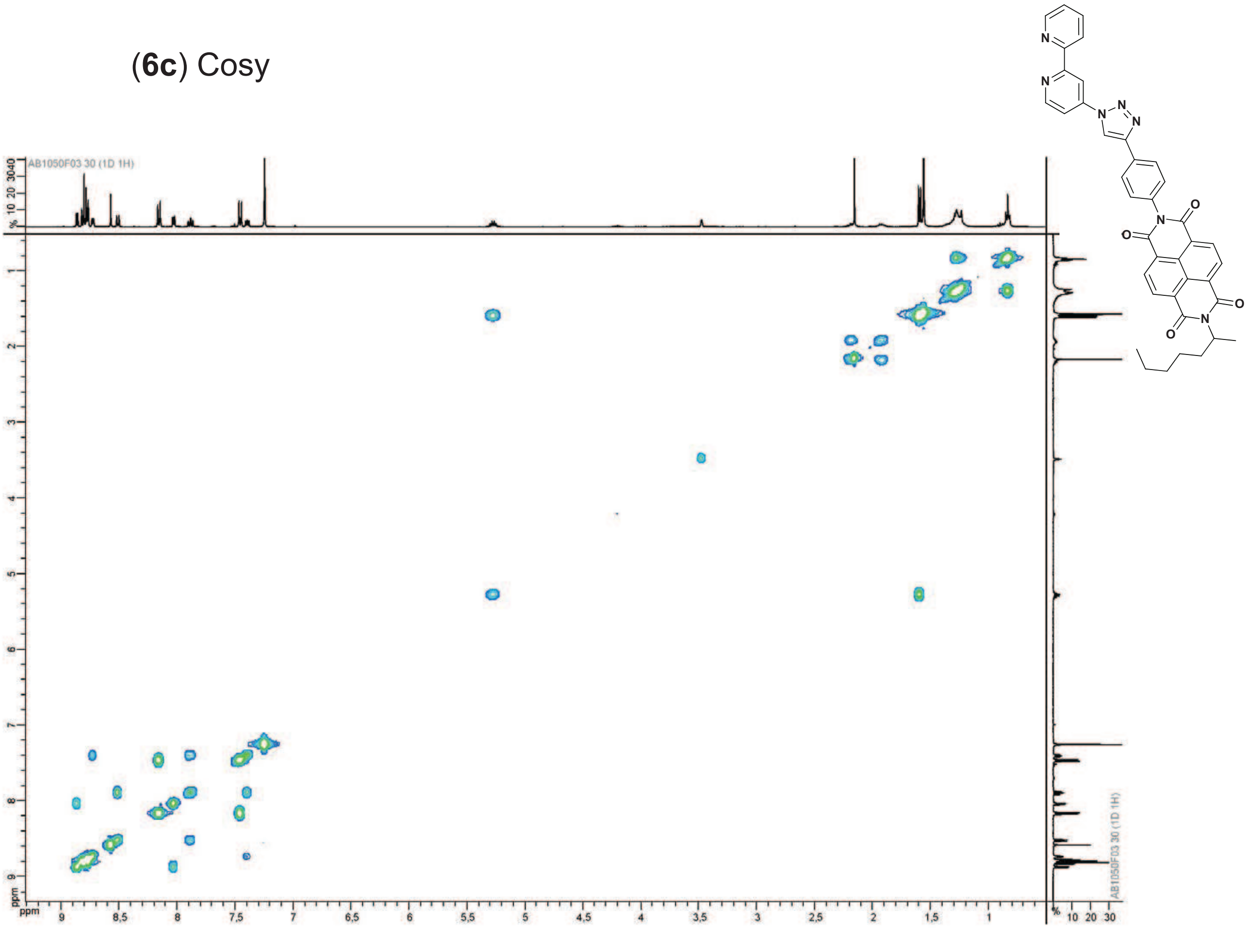


(**6c**) ^1H

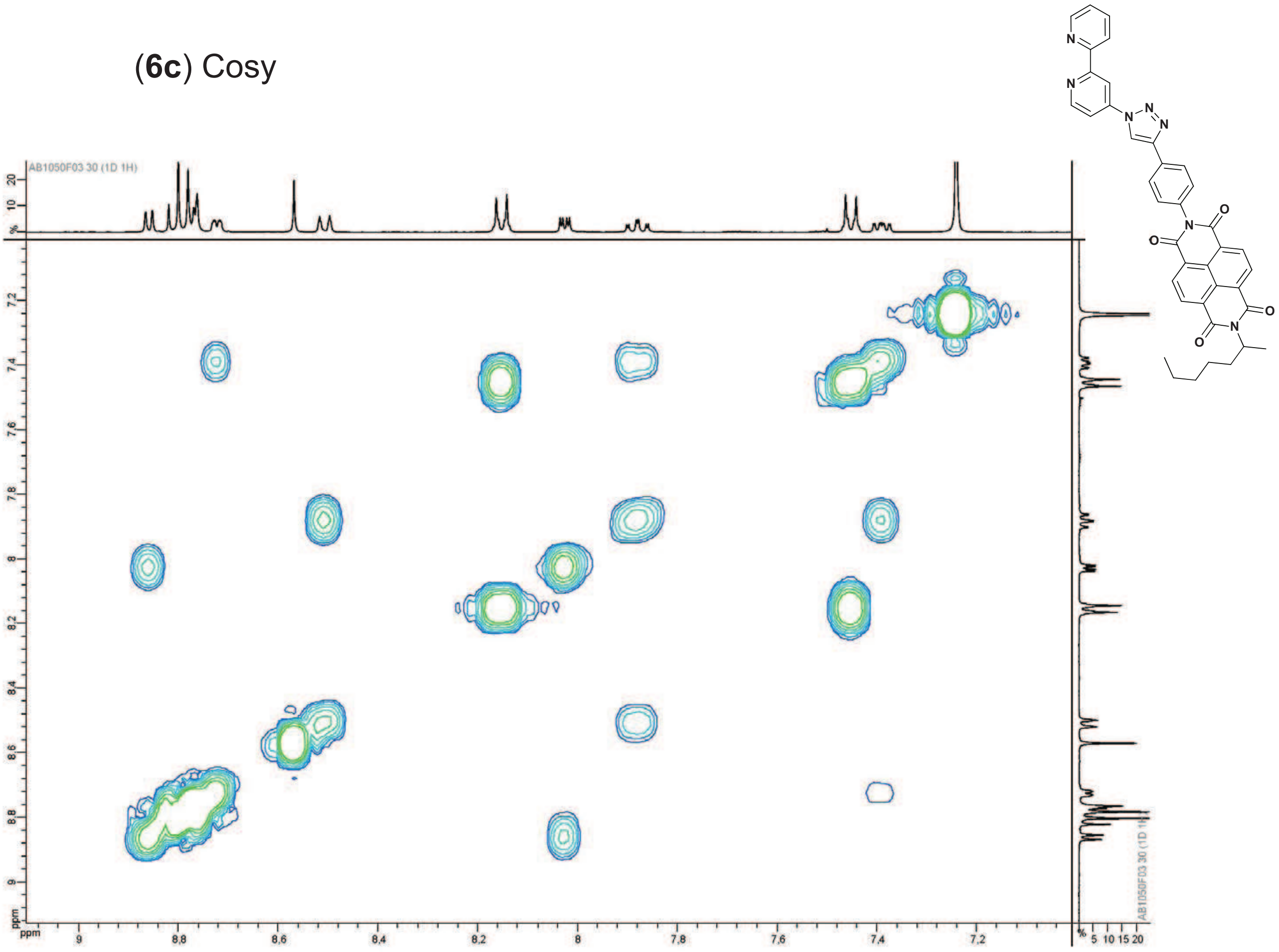

40
35
30
25
20
15
10
5
0
%
ppm
9
8,8
8,6
8,4
8,2
8
7,8
7,6
7,4
7,2
1.0
5.0
1.0
1.0
1.0
2.0
1.0
1.0
2.0
1.0


N
N
N
N
N
O
N
O
O
N
O

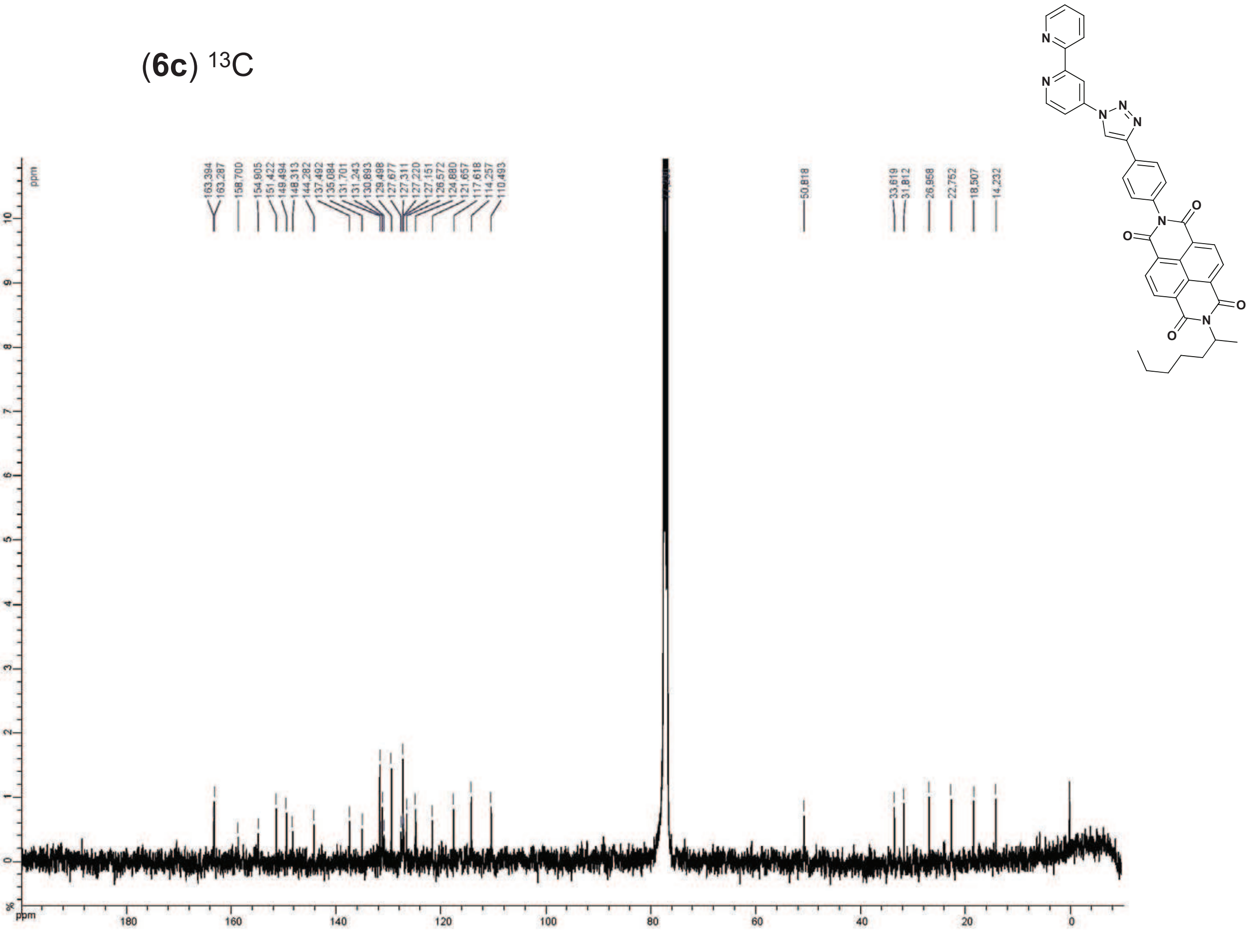
(**6c**) Cosy


AB1050F03 30 (1D 1H)
40
30
20
10
%
1
2
3
4
5
6
7
8
9
ppm
9
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
%
10
20
30
AB1050F03 30 (1D 1H)
N
N
N
N
N
O
N
O
O
N
O

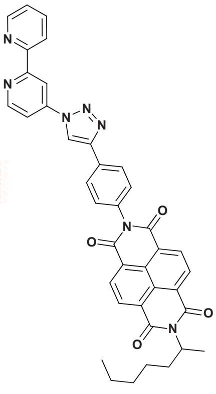
(**6c**) Cosy

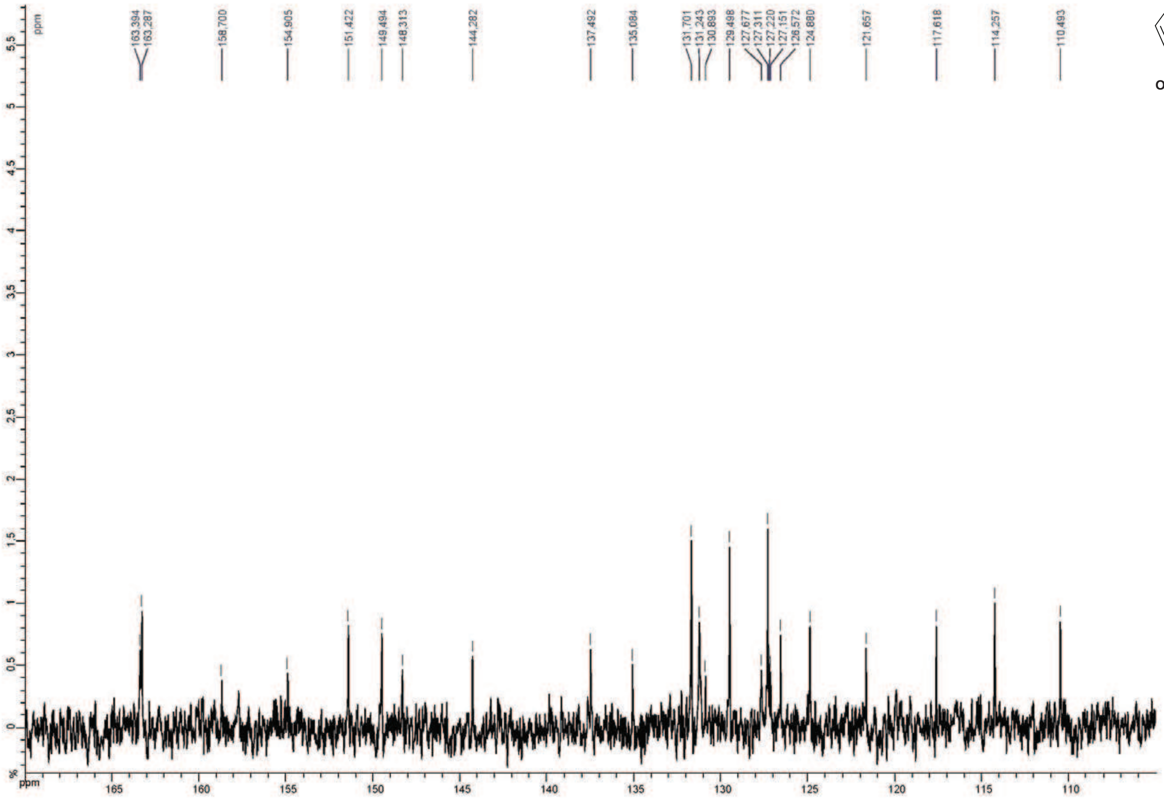


(**6c**) ^{13}C

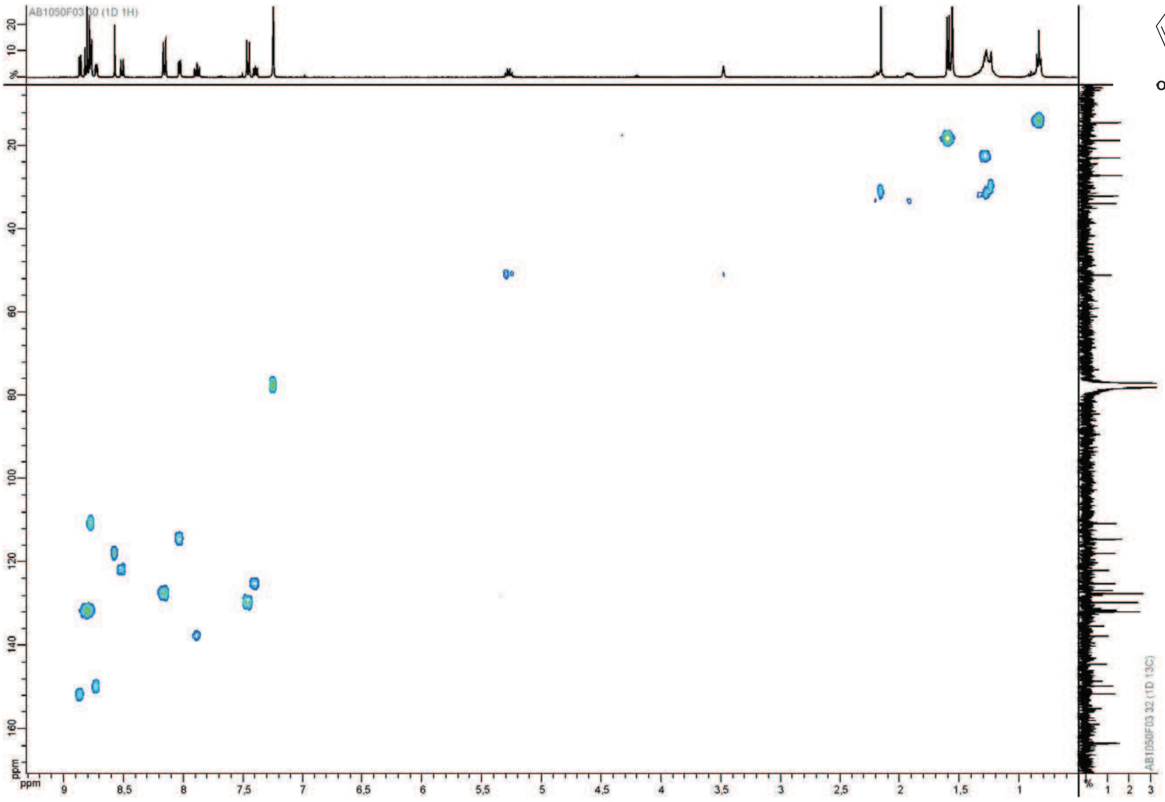


(**6c**) ^{13}C

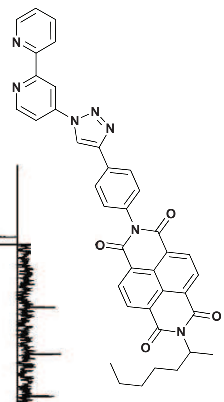


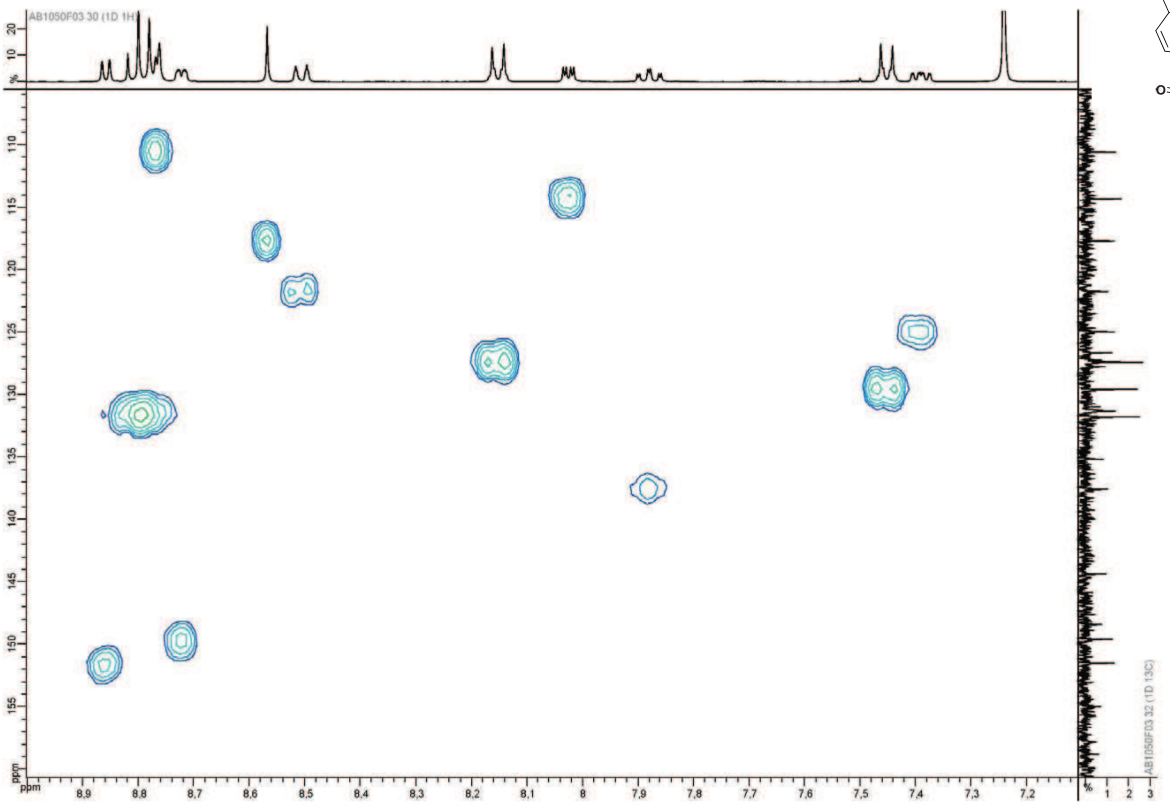


(**6c**) Hsqc

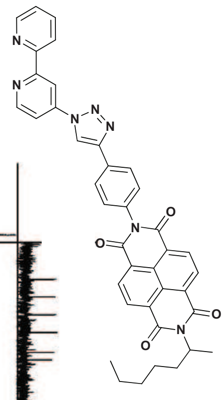


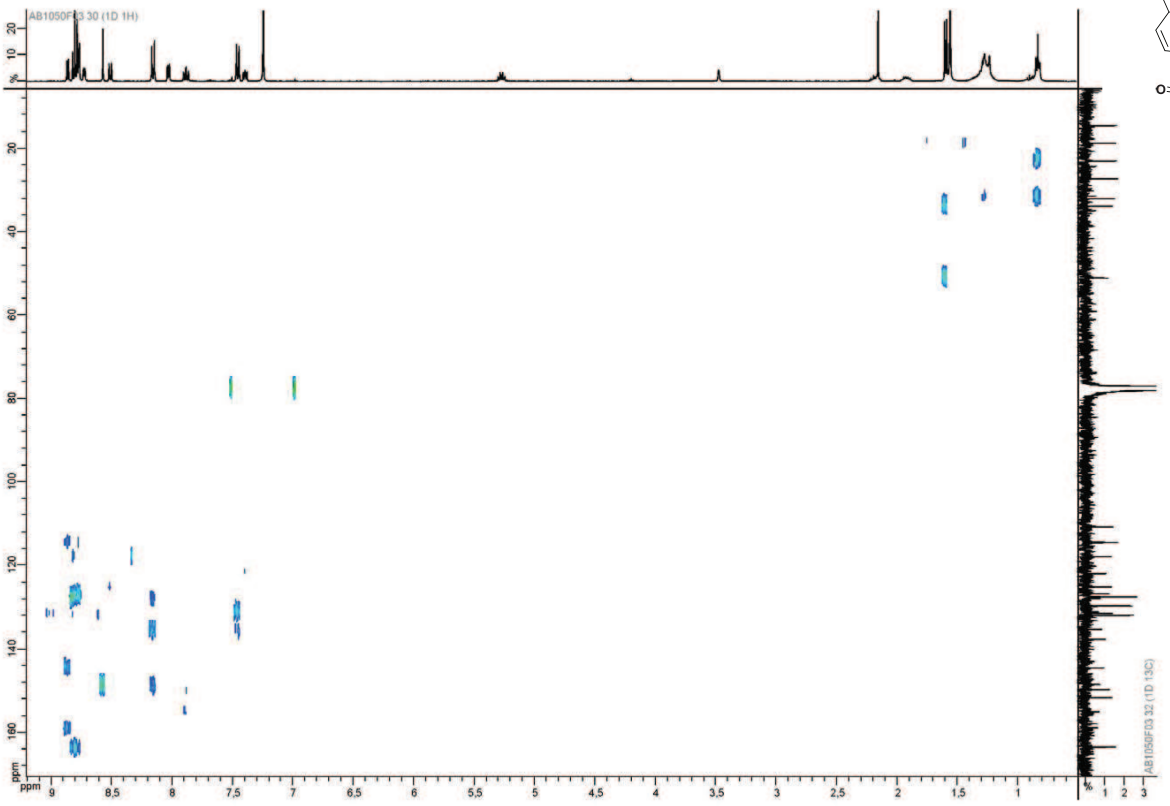
(**6c**) Hsqc



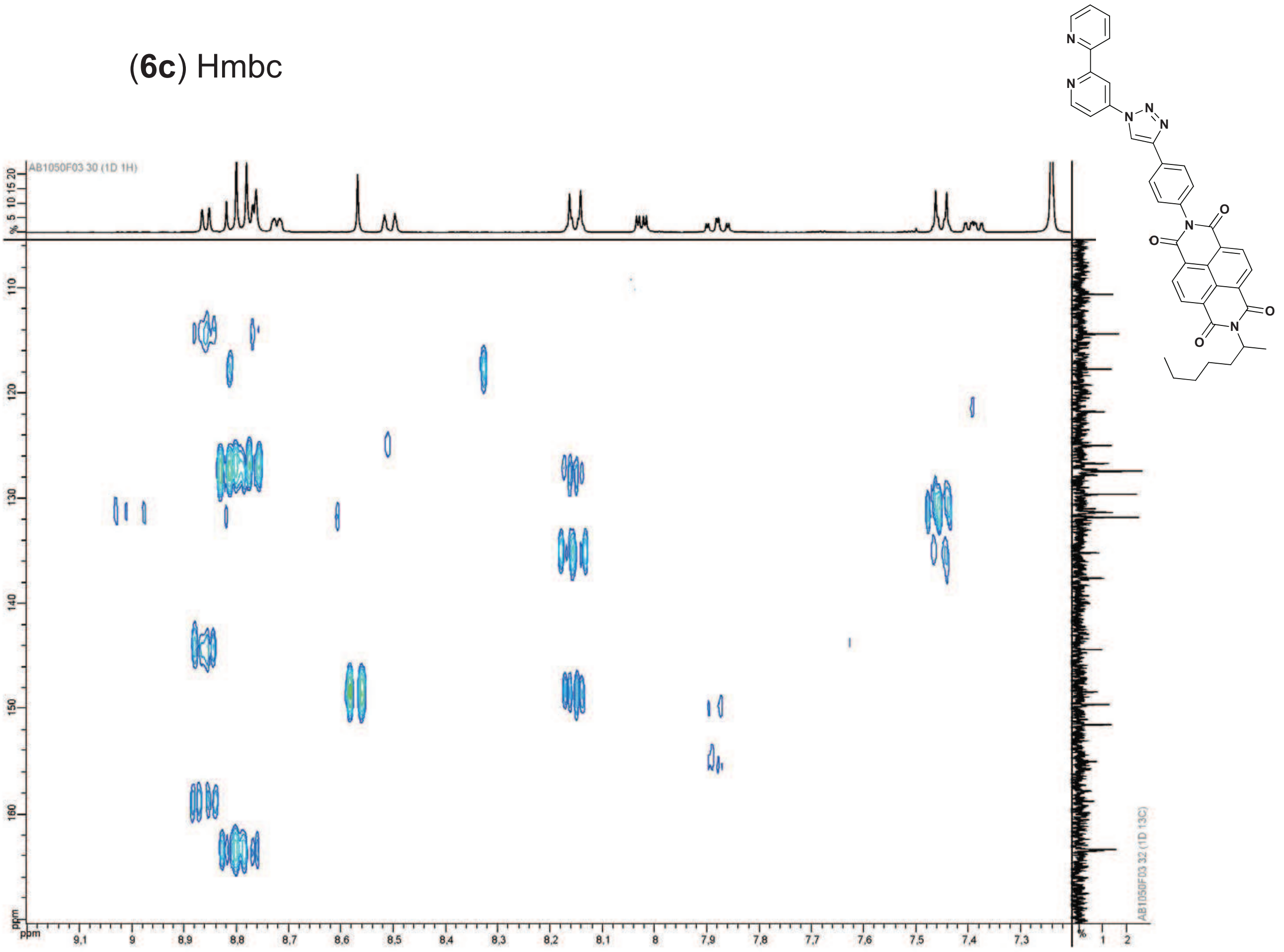


(**6c**) Hmbc

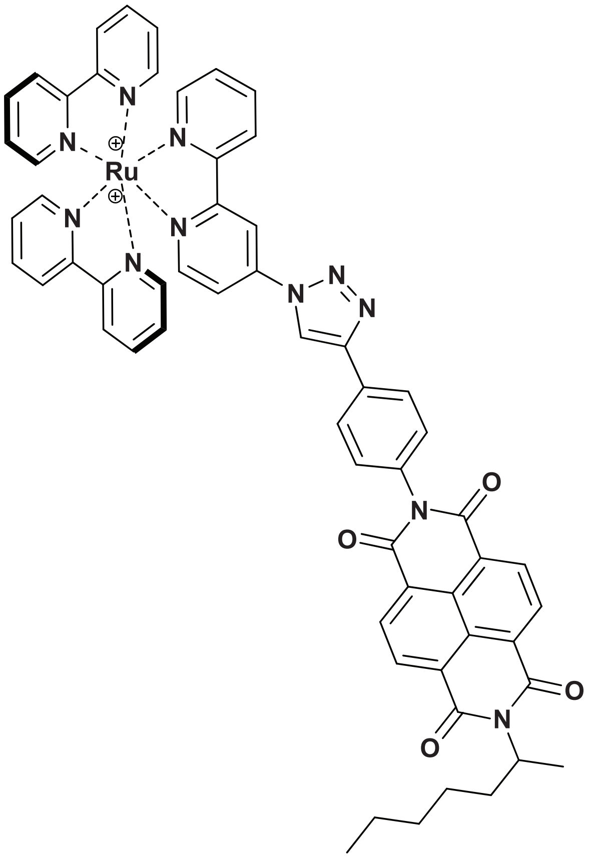




(**6c**) Hmbc


N
N
N
N
N
O
N
O
O
N
O
AB1050F03 30 (1D 1H)
% 5 10 15 20
AB1050F03 32 (1D 13C)
% 1 2
ppm
110
120
130
140
150
160
ppm
9,1
9
8,9
8,8
8,7
8,6
8,5
8,4
8,3
8,2
8,1
8
7,9
7,8
7,7
7,6
7,5
7,4
7,3

Ru-NDI (**7c**)



^{1}H all

^{1}H zoom

Cosy all

Cosy zoom

^{13}C all

^{13}C zoom

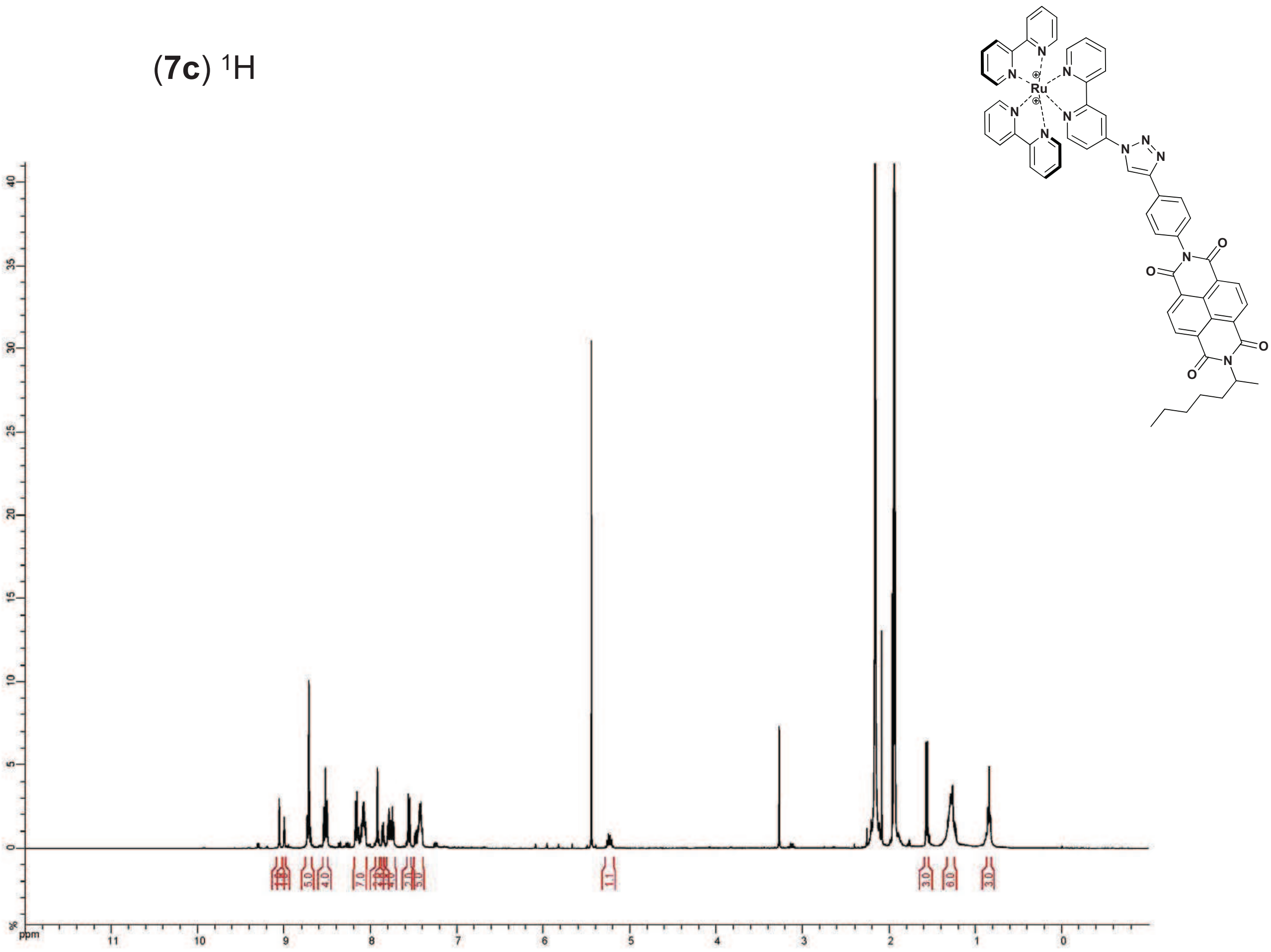
Hsqc all

Hsqc zoom

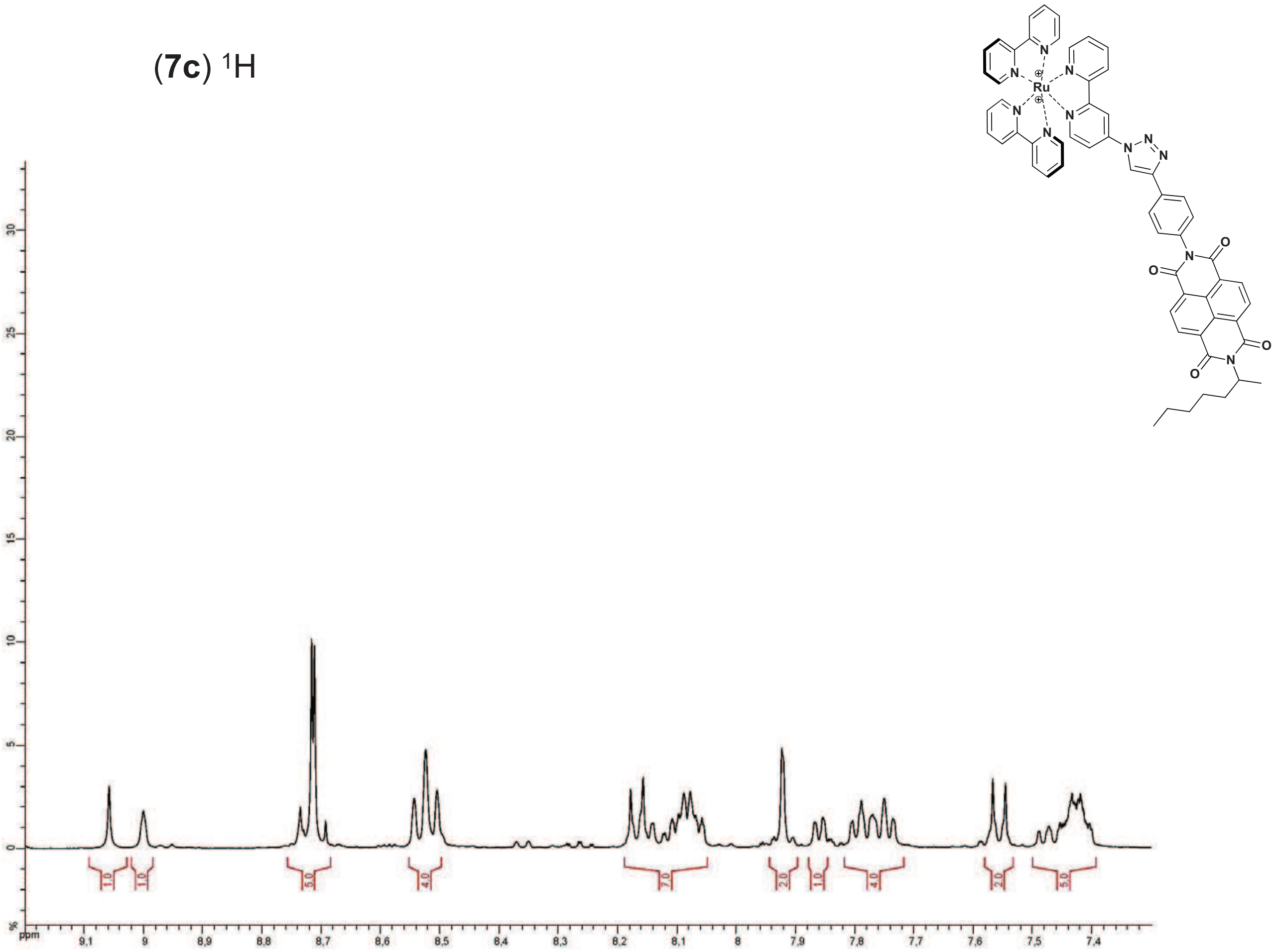
Hmbc all

Hmbc zoom

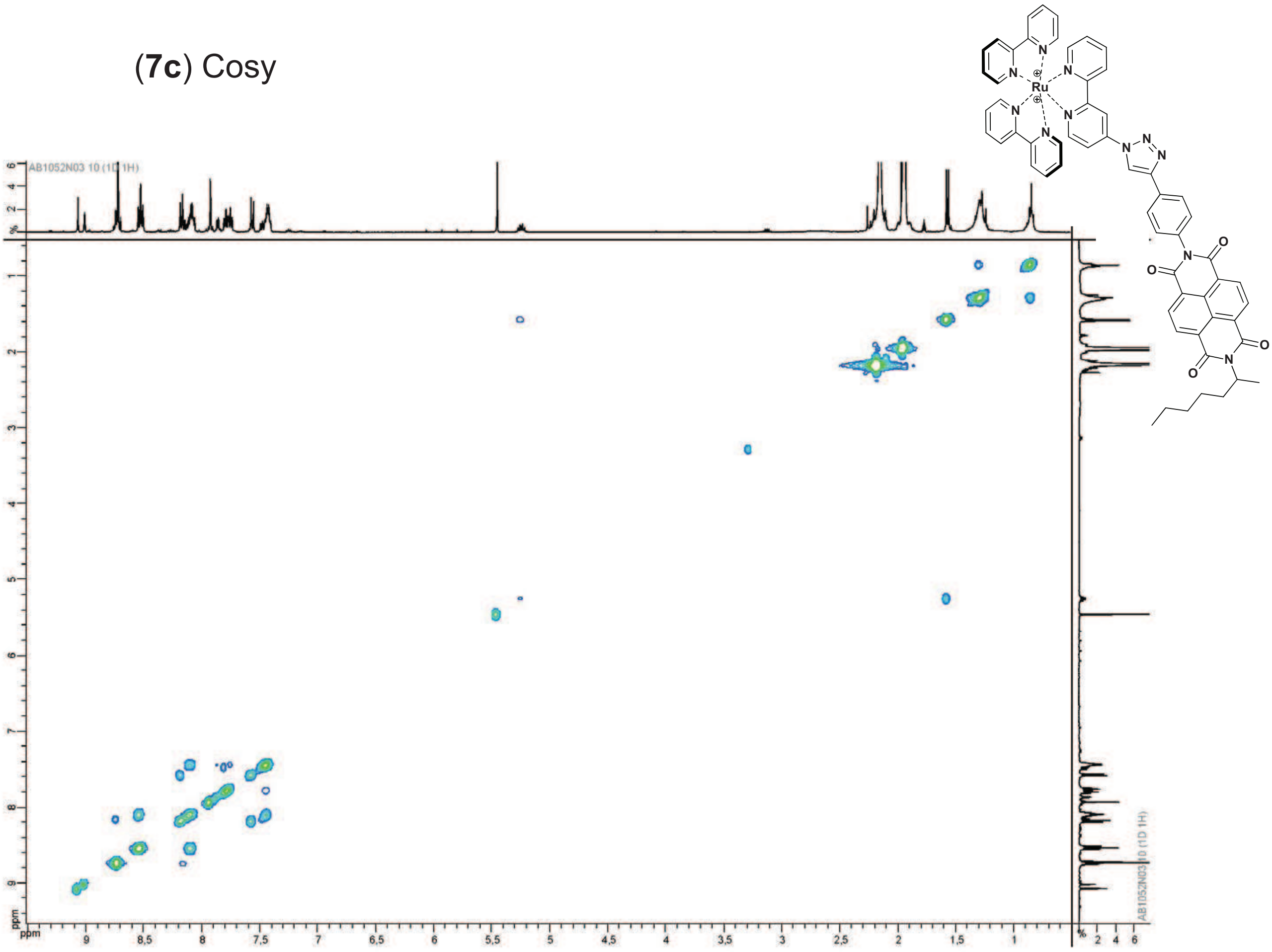
(**7c**) ^{1}H



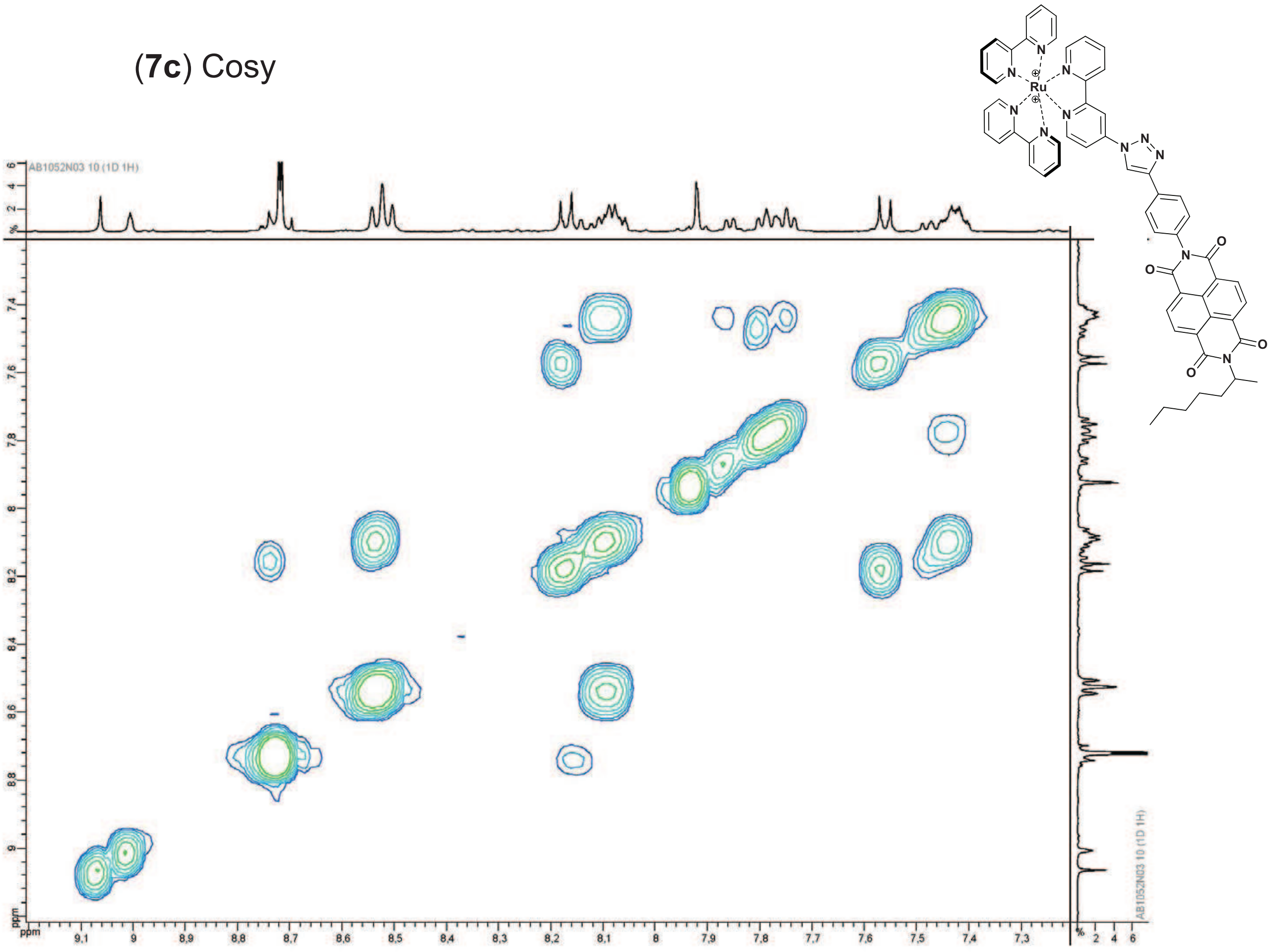
(**7c**) ^{1}H


Ru
N
O
%
ppm
0
5
10
15
20
25
30
1.0
1.0
5.0
4.0
7.0
2.0
1.0
4.0
2.0
5.0
9,1
9
8,9
8,8
8,7
8,6
8,5
8,4
8,3
8,2
8,1
8
7,9
7,8
7,7
7,6
7,5
7,4

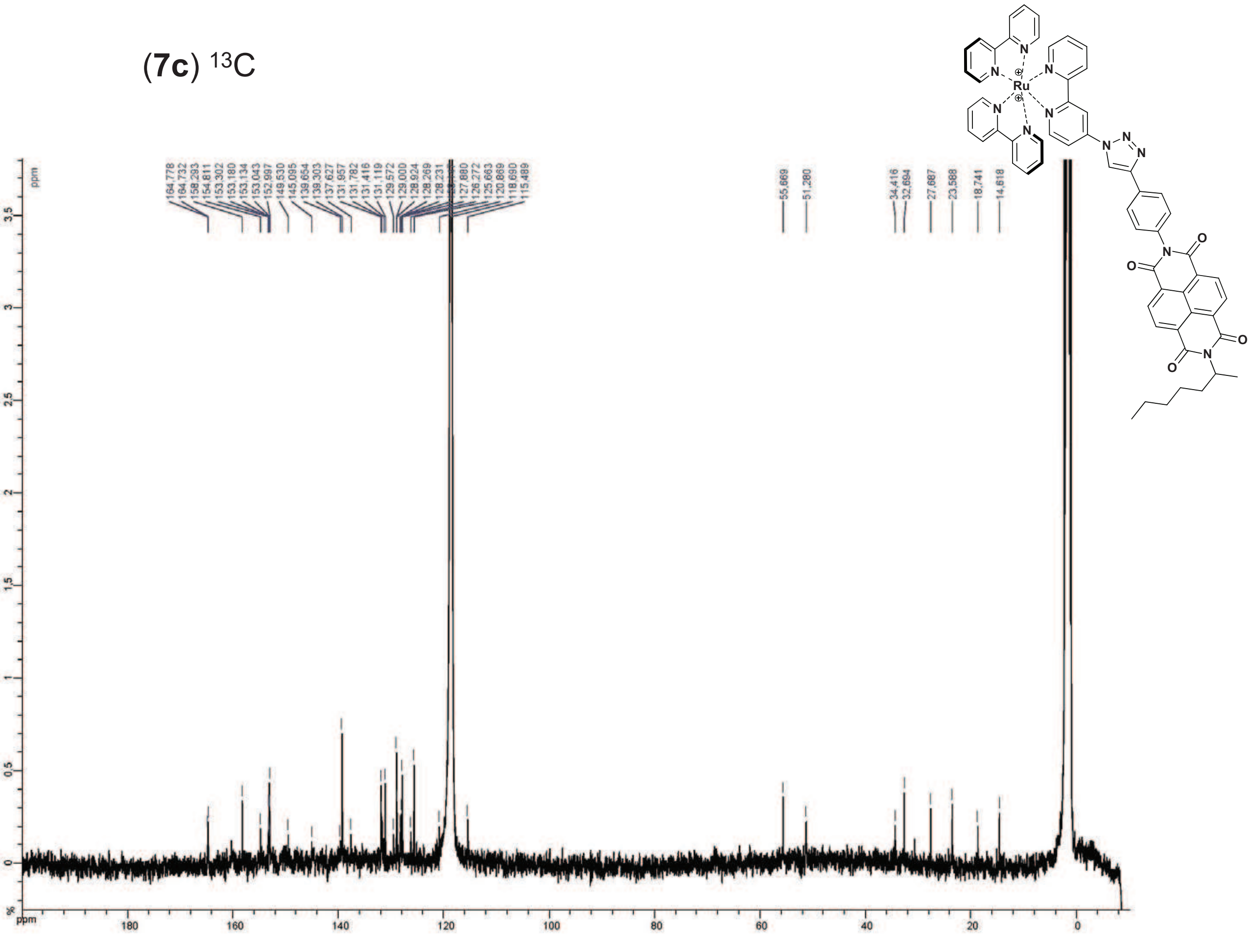
(**7c**) Cosy


AB1052N03 10 (1D 1H)
Ru
N
O
ppm
%
9
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
2
4
6

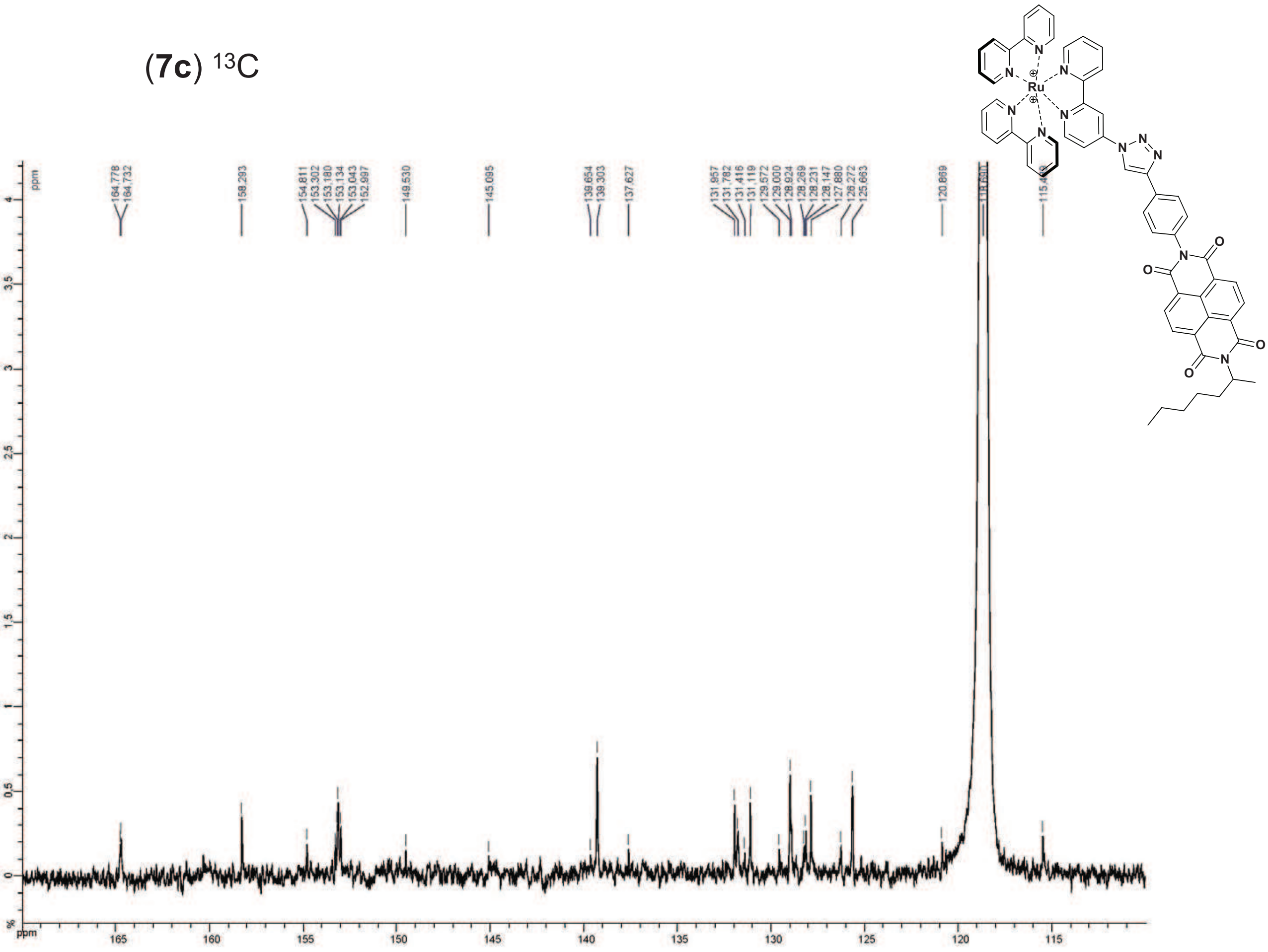
(**7c**) Cosy



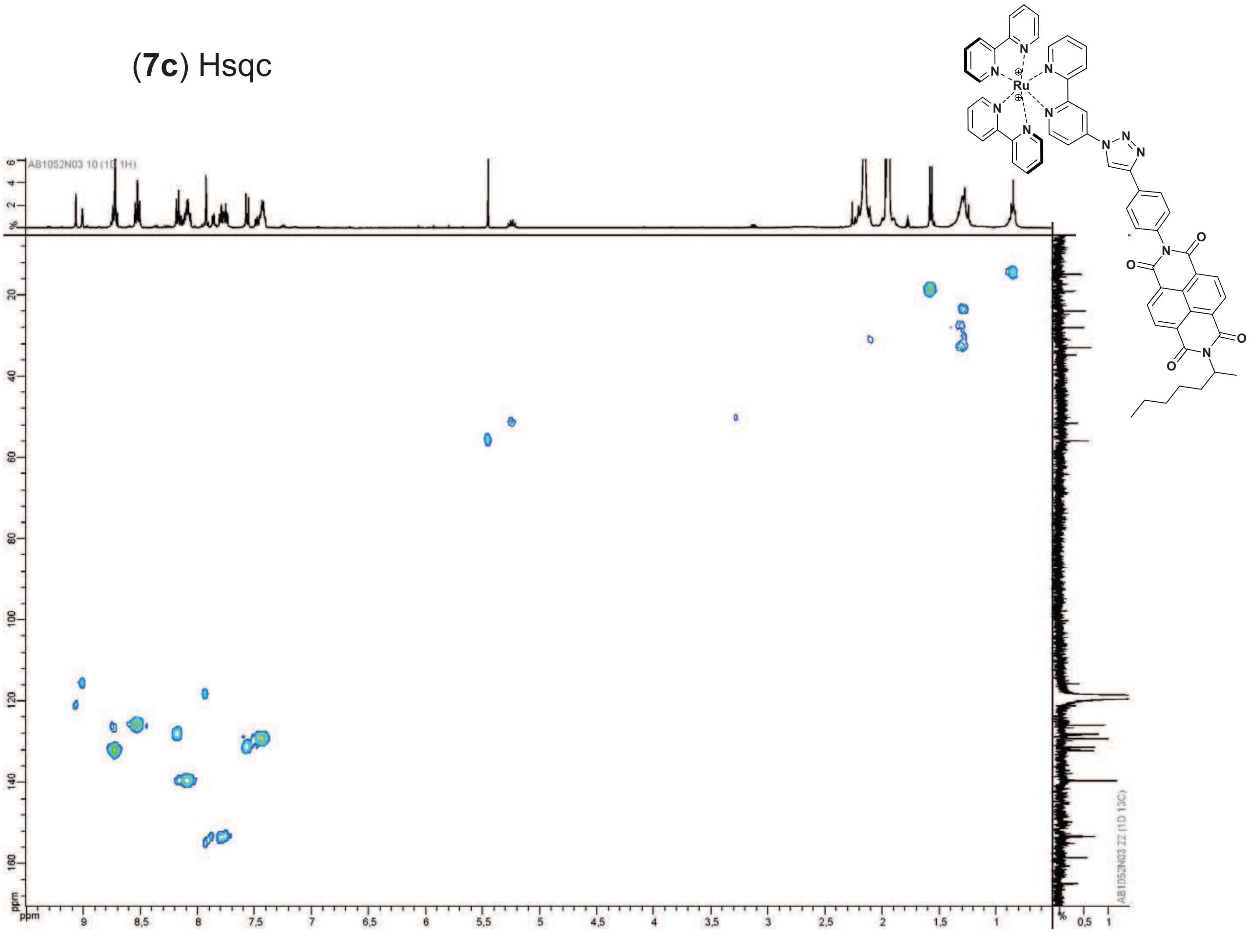
(**7c**) ^{13}C



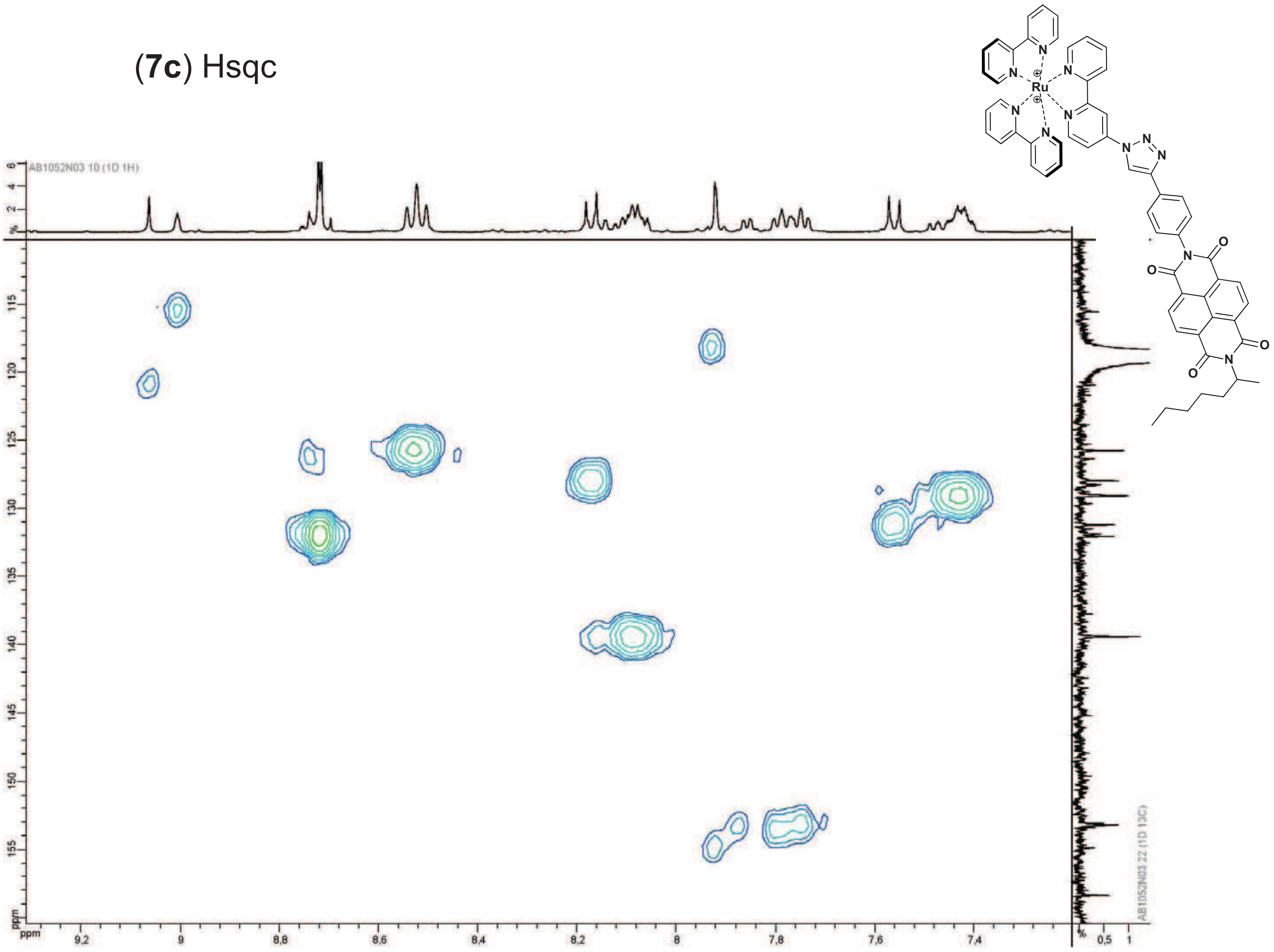
(**7c**) ^{13}C



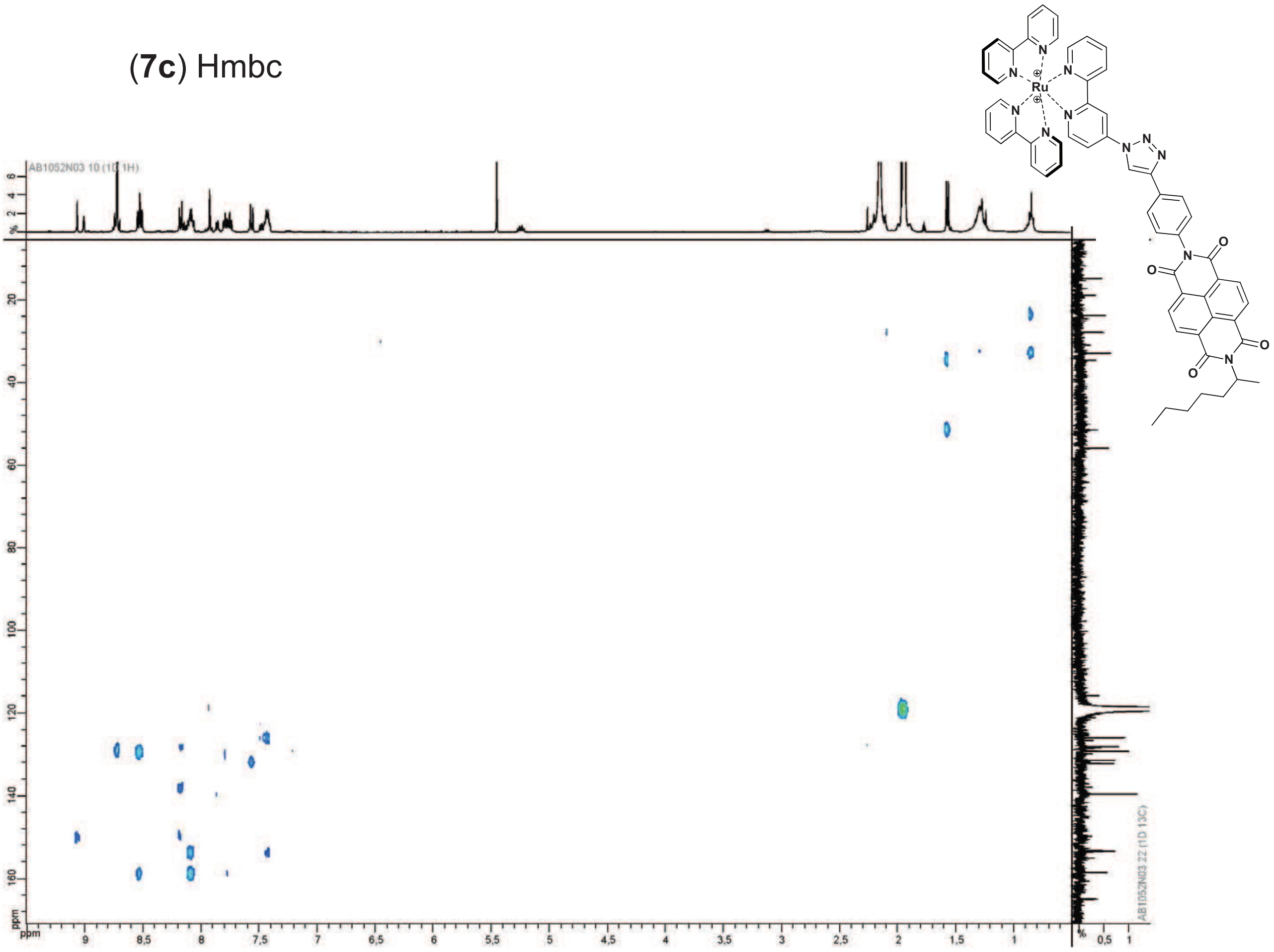
(**7c**) Hsqc



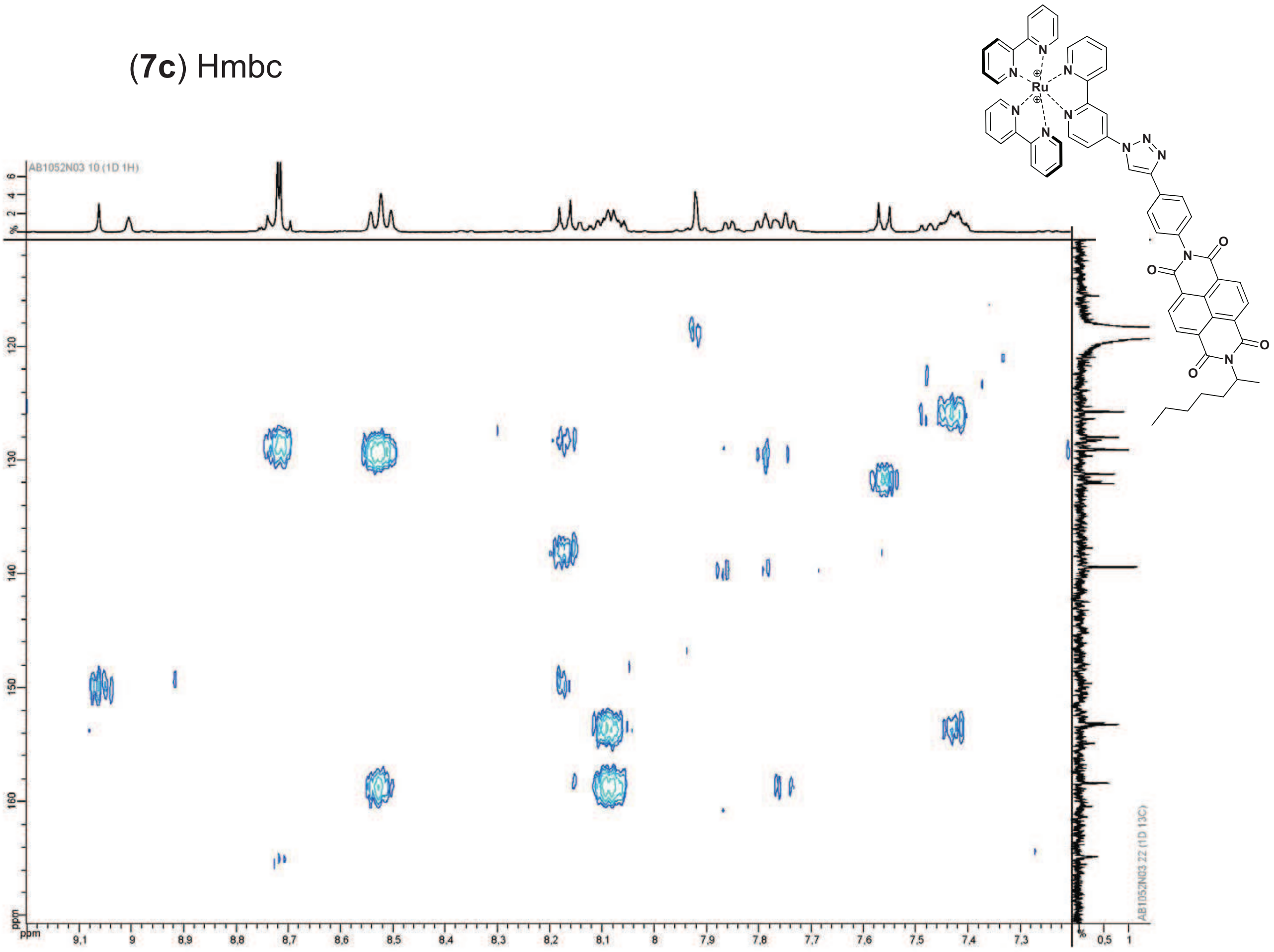
(**7c**) Hsqc



(**7c**) Hmbc



(**7c**) Hmbc


AB1052N03 10 (1D 1H)
AB1052N03 22 (1D 13C)
%
ppm
120
130
140
150
160
9,1
9
8,9
8,8
8,7
8,6
8,5
8,4
8,3
8,2
8,1
8
7,9
7,8
7,7
7,6
7,5
7,4
7,3
0,5
1
Ru
N
O