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Reaction of benzonitriles with acetylene in the KOBu^t/DMSO/THF system: self-organization of 2-aryl-3-ethynyl-4-aroyl-5-methylpyrroles and aminoacroleins

Elena Yu. Schmidt, Natal'ya A. Lobanova, Inna V. Tatarinova, Igor A. Ushakov and Boris A. Trofimov

Contents

1. General information

The NMR spectra were recorded on a Bruker DPX-400 and Bruker AV-400 spectrometers (400.1 MHz for ^{1}H, 100.6 MHz for ^{13}C, and 40.5 MHz for ^{15}N) in $CDCl_3$. The assignment of signals in the ^{1}H NMR spectra was made using COSY and NOESY experiments. Resonance signals of carbon atoms were assigned based on ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC experiments. The values of the δ ^{15}N were measured through the 2D ^{1}H-^{15}N HMBC experiment and were referenced to CH_3NO_2 (0.0 ppm). Multiplicities were abbreviated as following: s (singlet), br. s (broad singlet), m (multiplet). The IR spectra were recorded on a Varian 3100 FT-IR spectrometer. Mass spectra of positive electron ionization ions (70 eV) were registered on a Shimadzu GCMS-QP5050A with a DI-50 direct sample injection system (quadrupole mass analyzer, range of detected masses 34 - 650 Da). Melting points (uncorrected) were measured on a Kofler micro hot-stage apparatus. The microanalyses were performed on a Flash EA 1112 Series elemental analyzer. Thin layer chromatography was carried out on Merck silica gel 60 F_{254} pre-coated aluminium foil sheets (eluent: diethyl ether) and were visualized using UV light (254 nm). Column chromatography was carried out using slurry packed Sigma Aldrich silica gel, 70-230 mesh, pore size 60 Å (eluent: hexane/diethyl ether with gradient from 10:1 to 0:1).

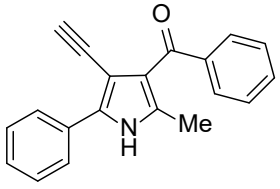
2. Starting materials

Nitrile **1b** was synthesized from 3-methoxybenzaldehyde and hydroxylamine hydrochloride by the published procedure.[S1] Physical–chemical characteristics of nitrile **1b** were identical to the literature data.[S2] DMSO was dried over molecular sieves (4 Å, 4–8 mesh). Acetylene and all other chemicals and solvents are commercially available and were used without further purification.

3. Reaction of nitriles 1 with acetylene gas (*general procedure*)

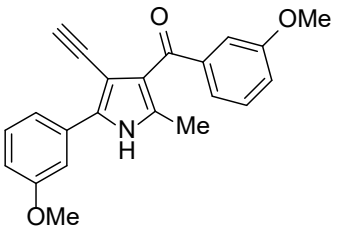
Acetylene gas was bubbled (~10–15 mL min^{-1}) at rt for 15 min through a mixture of $KOBu^t$ (1.5 mmol, 0.168 g) in DMSO (4 mL) and THF (0.6 mL), then, nitrile **1** (2 mmol) in DMSO (2 mL) was added to this mixture at 12-14 ºC for 10 min and the reaction mixture was stirred for another 5 min. The reaction mixture was diluted with solution of NH_4Cl (0.1 g) in H_2O (18 mL) and extracted with Et_2O (8 mL × 4). The organic extract was washed with H_2O (5 mL × 4) and dried over K_2CO_3. Et_2O was evaporated in a vacuum, and the residue was purified by column chromatography (SiO_2) to give pure pyrrole **2,** aminoacroleine **3,** and unreacted nitrile **1**.

(4-Ethynyl-2-methyl-5-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (2a). Following the general procedure, **2a** was prepared from **1a** (2 mmol, 0.206 g). Pure **2a** was isolated as a beige powder (0.040 g, 21% yield, based on nitrile **1a** consumed). Unreacted nitrile **1a** (0.065g, 68% conversion) was



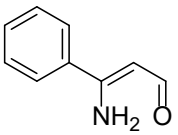
recovered. M. p. = 103-105 °C. Elemental analysis calcd (%) for $C_{20}H_{15}NO$ (285.34): C, 84.19; H, 5.30; N, 4.91; found: C, 84.28; H, 5.43; N, 4.89. ^{1}H NMR: δ 9.05 (br. s, 1H, NH), 7.86 – 7.79 (m, 5H, *Ph*), 7.59 – 7.49 (m, 2H, *Ph*), 7.42 – 7.29 (m, 3H, *Ph*), 2.89 (s, 1H, H-C≡), 2.32 (s, 3H, -CH_3) ppm. ^{13}C{^{1}H} NMR: δ 188.4, 139.8, 134.9, 134.6, 132.1, 131.2, 129.9, 129.2, 128.8, 128.0, 126.3, 125.9, 95.8, 81.7, 78.6, 13.3 ppm. ^{15}N NMR: δ -216.8 ppm. IR (film): ν_{max} 3300, 3264, 3060, 3011, 2956, 2924, 2854, 2172, 1959, 1891, 1813, 1631, 1611, 1603, 1575, 1532, 1486, 1449, 1431, 1368, 1345, 1302, 1267, 1242, 1217, 1173, 1152, 1123, 1074, 1057, 1028, 1002, 993, 968, 910, 889, 849, 828, 794, 765, 756, 732, 696, 667, 644, 619, 593, 575 cm^{-1}. MS (EI), m/z (%): 285.10 $[M]^{+\cdot}$. Calc. for $C_{20}H_{15}NO$, m/z: 285.12.

(4-Ethynyl-5-(3-methoxyphenyl)-2-methyl-1H-pyrrol-3-yl)(3-methoxyphenyl)methanone (2b).

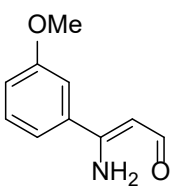


Following the general procedure, **2b** was prepared from **1b** (2 mmol, 0.264 g). Pure **2b** was isolated as a cream powder (0.024 g, 10% yield, based on nitrile **1b** consumed). Unreacted nitrile **1b** was recovered (0.076g, 71% conversion). M. p. = 98-101 °C. Elemental analysis calcd (%) for $C_{22}H_{19}NO_3$ (345.39): C, 76.50; H, 5.54; N, 4.06; found: C, 76.57; H, 5.59; N, 4.09. ^{1}H NMR: δ 8.91 (br. s, 1H, NH), 7.68 – 7.62 (m, 1H, *Ar*), 7.60 – 7.38 (m, 2H, *Ar*), 7.34 – 7.26 (m, 3H, *Ar*), 7.09 – 7.04 (m, 1H, *Ar*), 6.89 – 6.80 (m, 1H, *Ar*), 3.83 (s, 3H, OMe), 3.81 (s, 3H, OMe), 2.95 (s, 1H, H-C≡), 2.32 (s, 3H, -CH_3) ppm. ^{13}C{^{1}H} NMR: δ 192.8, 159.9, 159.4, 141.0, 134.7, 134.6, 132.2, 129.9, 129.1, 123.9, 122.8, 118.8, 117.9, 113.9, 113.7, 111.4, 101.7, 81.9, 78.6, 55.5, 55.4, 13.3 ppm. ^{15}N NMR: δ -225.5 ppm. IR (film): ν_{max} 3298, 3075, 3002, 2961, 2926, 2836, 2170, 1942, 1845, 1785, 1720 1621, 1601, 1580, 1519, 1485, 1454, 1434, 1338, 1286, 1262, 1233, 1181, 1162, 1090, 1041, 995, 962, 947, 911, 875, 837, 797, 737, 711, 694, 668, 648, 580 cm^{-1}. MS (EI), m/z (%): 345.15 $[M]^{+\cdot}$. Calc. for $C_{22}H_{19}NO_3$, m/z: 345.14.

(Z)-3-Amino-3-phenylacrylaldehyde (3a). Following the general procedure, **3a** was prepared from **1a** (2 mmol, 0.206 g). Pure **3a** was isolated as a white crystals (0.011 g, 6% yield, based on nitrile **1a** consumed). M. p. = 72-74 °C, lit.[S3] 73-74.5 °C. Spectral data of **3a** of were identical to the literature data.[S4]



(Z)-3-Amino-3-(3-methoxyphenyl)acrylaldehyde (3b). Following the general procedure, **3b** was prepared from **1b** (2 mmol, 0.264 g). Pure **3b** was isolated as a cream crystals (0.010 g, 3% yield, based on nitrile **1b** consumed). M. p. = 70-72 °C. Elemental analysis calcd (%) for $C_{10}H_{11}NO_2$ (177.20): C, 67.78; H, 6.26; N, 7.90; found: C, 67.81; H, 6.33; N, 7.88. ^{1}H NMR: δ 10.03 (br. s, 1H, NH_2), 9.33 (s, 1H, H-C=O), 7.40 – 7.36 (m, 1H, *Ar*), 7.19 – 7.17 (m, 1H, *Ar*), 7.12 – 7.05 (m, 2H, *Ar*), 5.54 (br. s, 1H, NH_2), 5.46 (s, 1H,



H-C=C), 3.89 (s, 3H, OMe) ppm. $^{13}C\{^{1}H\}$ NMR: δ 188.29, 162.01, 159.85, 130.05, 118.39, 118.02, 116.30, 111.84, 95.62, 55.30 ppm. IR (film): ν_{max} 3273, 3074, 3000, 2959, 2927, 2852, 2835, 1672, 1602, 1581, 1485, 1464, 1433, 1366, 1287, 1234, 1180, 1163, 1047, 994, 955, 907, 875, 824, 781, 736, 703, 693, 631, 527 cm^{-1}. MS (EI), m/z (%): 177.10 $[M]^{+\cdot}$. Calc. for $C_{10}H_{11}NO_2$, m/z: 177.08.

Oligomer **–C(Ph)=N–[CH=CH–]$_{(3\text{-}4)}$** was obtained as a brown powder (0.104 g, 59% yield on nitrile **1a** consumed) from the reaction of **1a** (2 mmol, 0.206 g) with acetylene gas (see procedure for the synthesis of pyrrole **2a**). M. p. = 222-228 °C. Elemental analysis (%) found: C, 80.47; H, 4.99; N, 7.84. IR (KBr): ν_{max} 3393, 3198, 3059, 3031, 2922, 2851, 1958, 1896, 1812, 1657, 1599, 1565, 1538, 1490, 1448, 1384, 1292, 1181, 1157, 1073, 1027, 970, 909, 845, 761, 731, 695, 617 cm^{-1}.

4. References

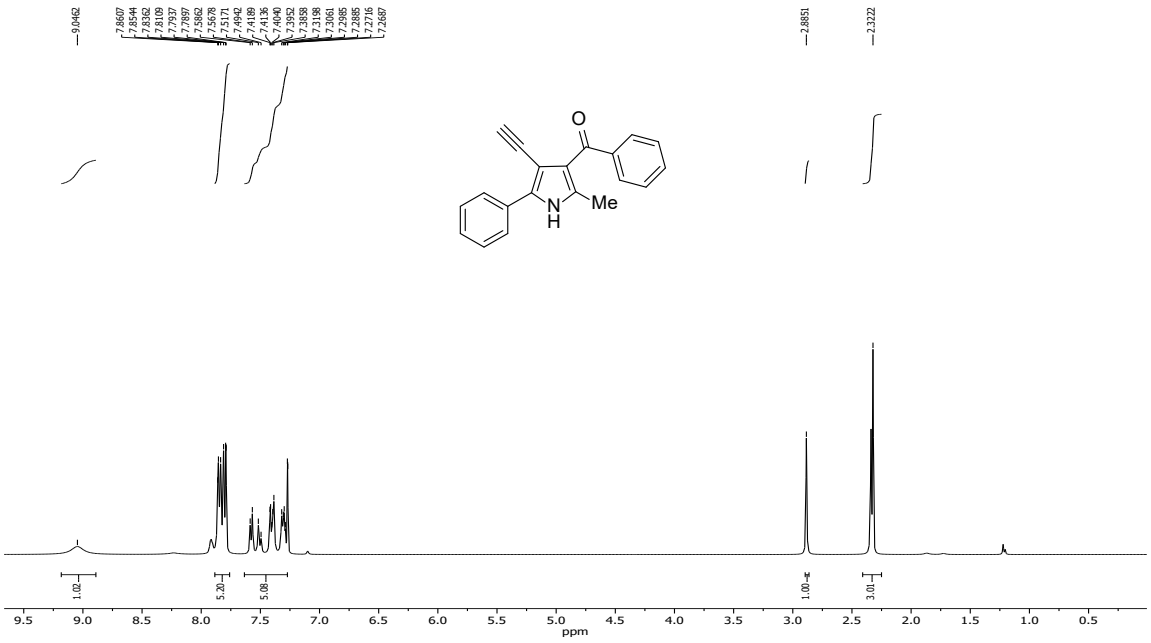
S1 H. M. S. Kumar, B. V. S. Reddy, P. T. Reddy and J. S. Yadav, *Synthesis*, 1999, 586; DOI: 10.1055/s-1999-3450

S2 C. Zhu, F. Chen, C. Liu, H. Zeng, Z. Yang, W. Wu and H. Jiang, *J. Org. Chem.*, 2018, **83**, 14713; https://doi.org/10.1021/acs.joc.8b02103.

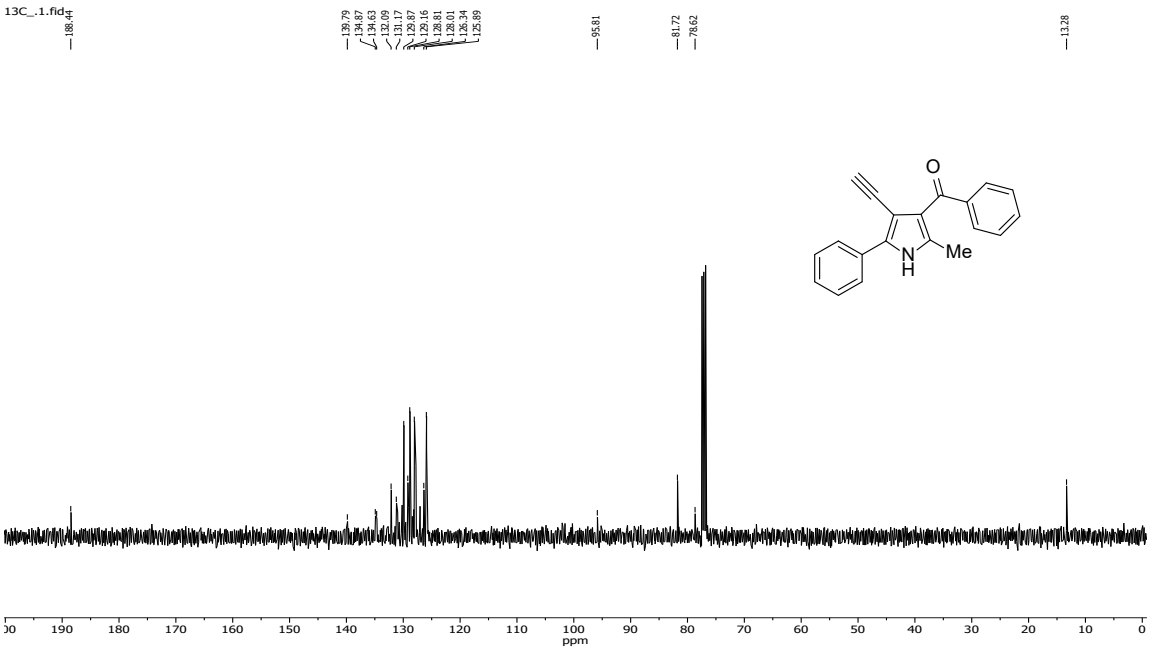
S3 T. Kumagai, K. Shimizu, Y. Kawamura and T. Mukai, *Tetrahedron*, 1981, **37**, 3365; https://doi.org/10.1016/S0040-4020(01)92385-3.

S4 E. Gayon, M. Szymczyk, H. Gérard, E. Vrancken and J.-M. Campagne, *J. Org. Chem.*, 2012, **77**, 9205; https://doi.org/10.1021/jo301675g.

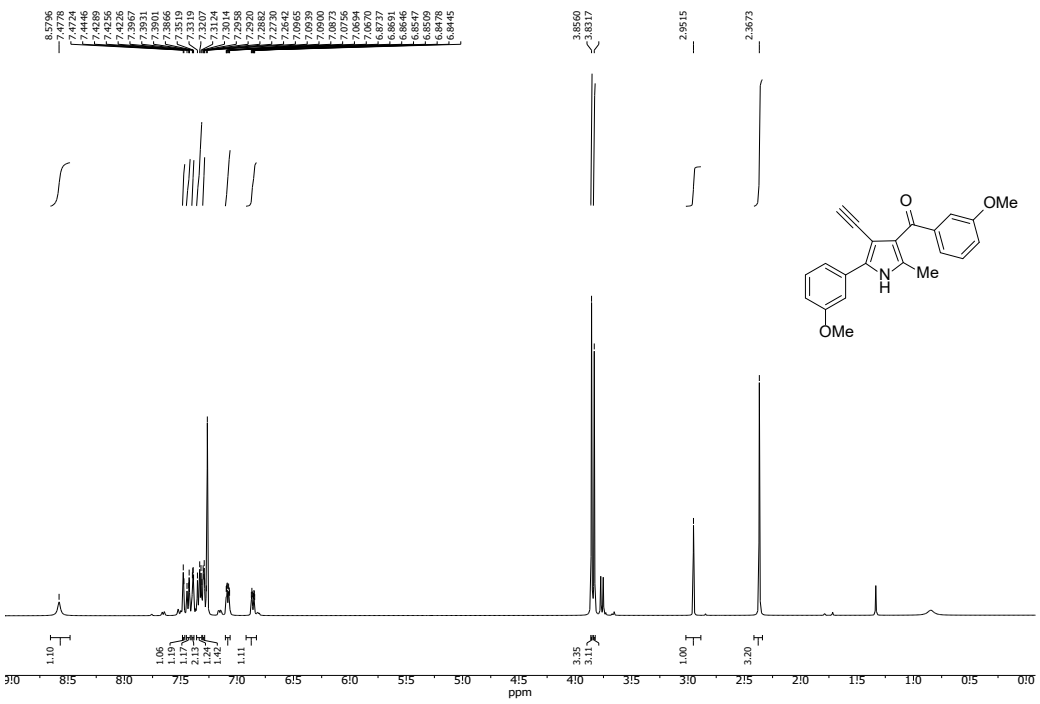
5. NMR Spectra



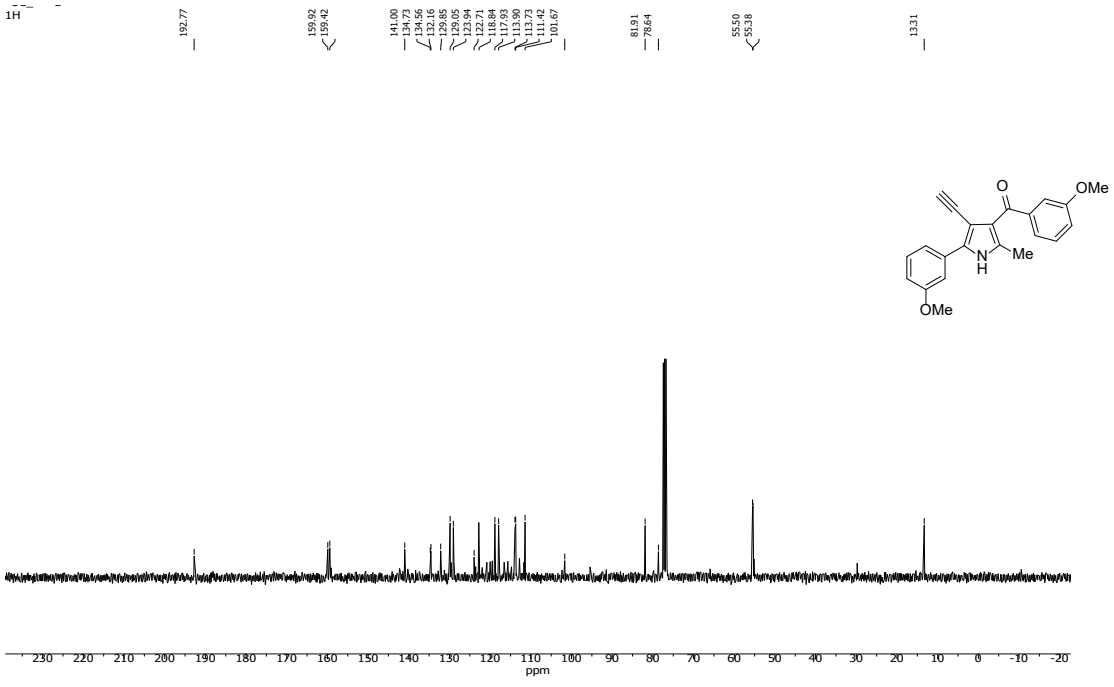
^{1}H NMR Spectrum of **2a** (400.1 MHz, $CDCl_3$)



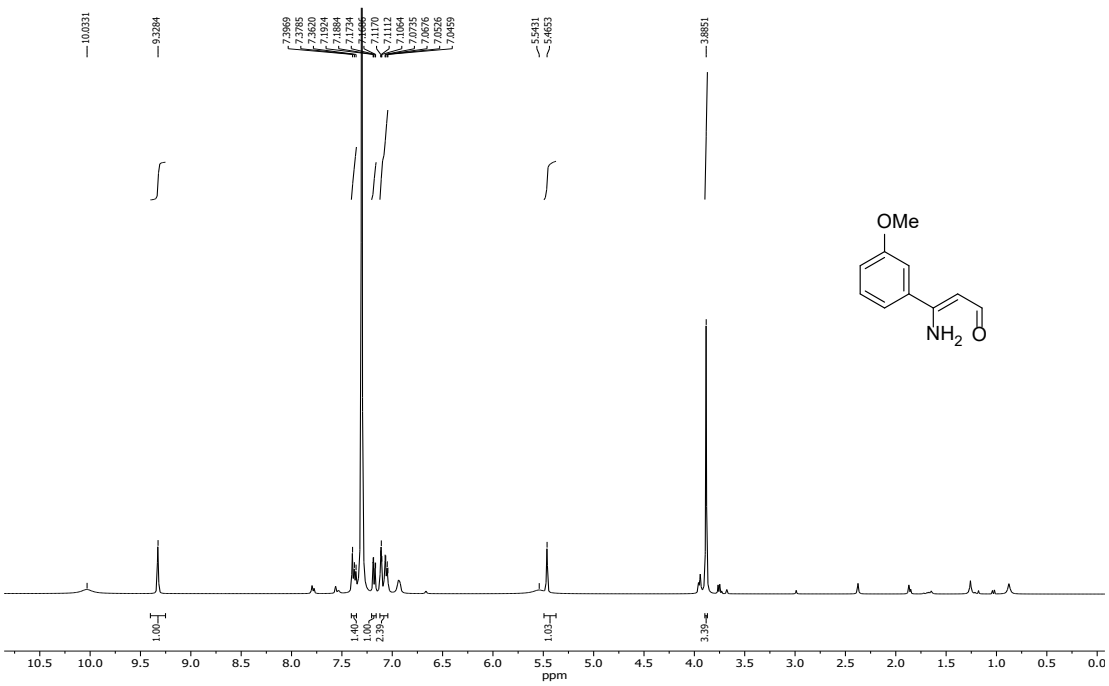
^{13}C{^{1}H} NMR Spectrum of **2a** (100.6 MHz, $CDCl_3$)



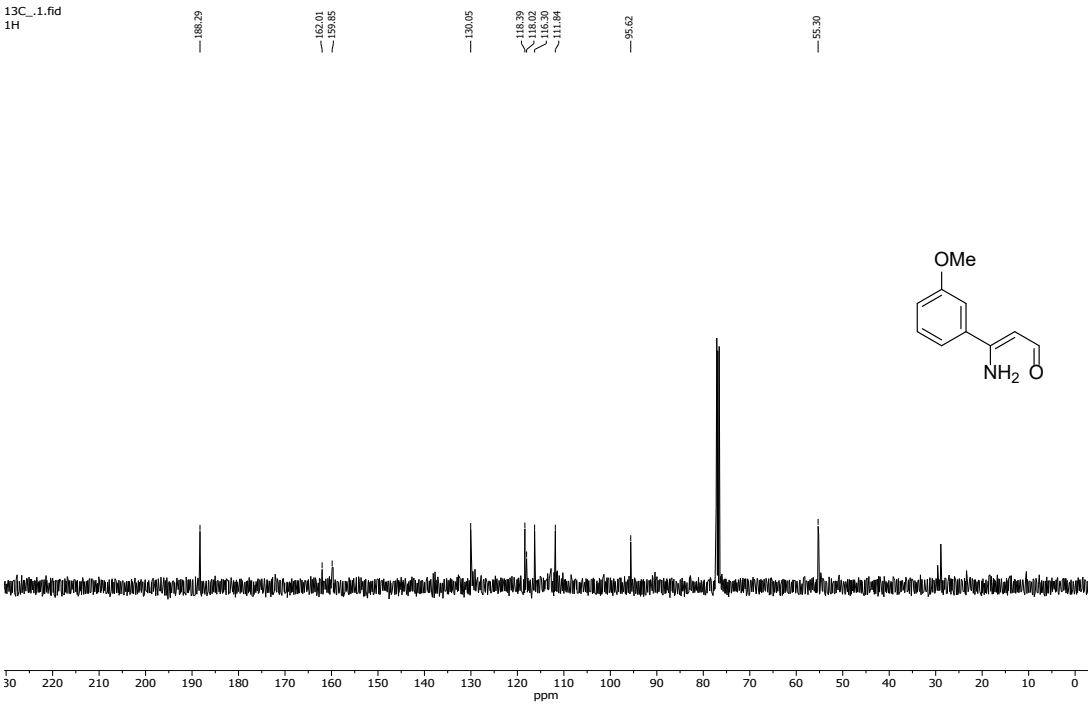
^{1}H NMR Spectrum of **2b** (400.1 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR Spectrum of **2b** (100.6 MHz, $CDCl_3$)

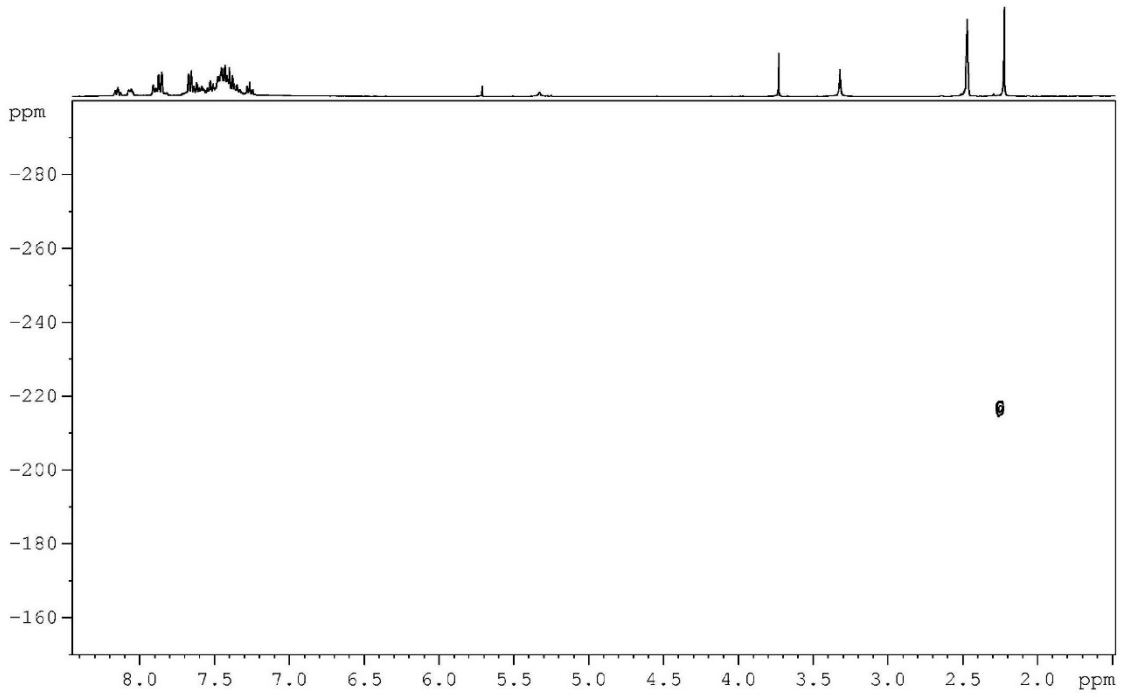


^{1}H NMR Spectrum of **3b** (400.1 MHz, $CDCl_3$)

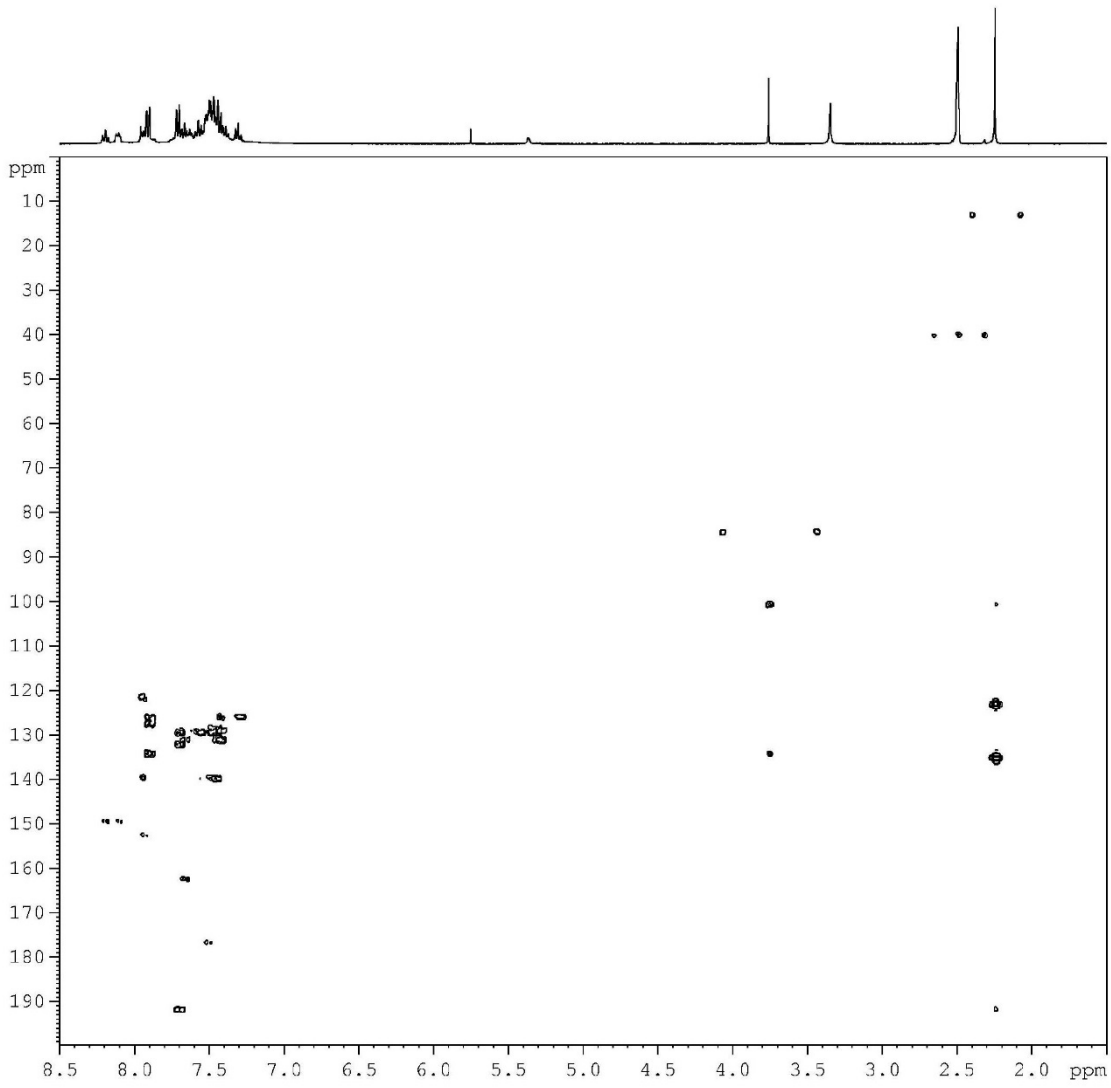


^{13}C{^{1}H} NMR Spectrum of **3b** (100.6 MHz, $CDCl_3$)

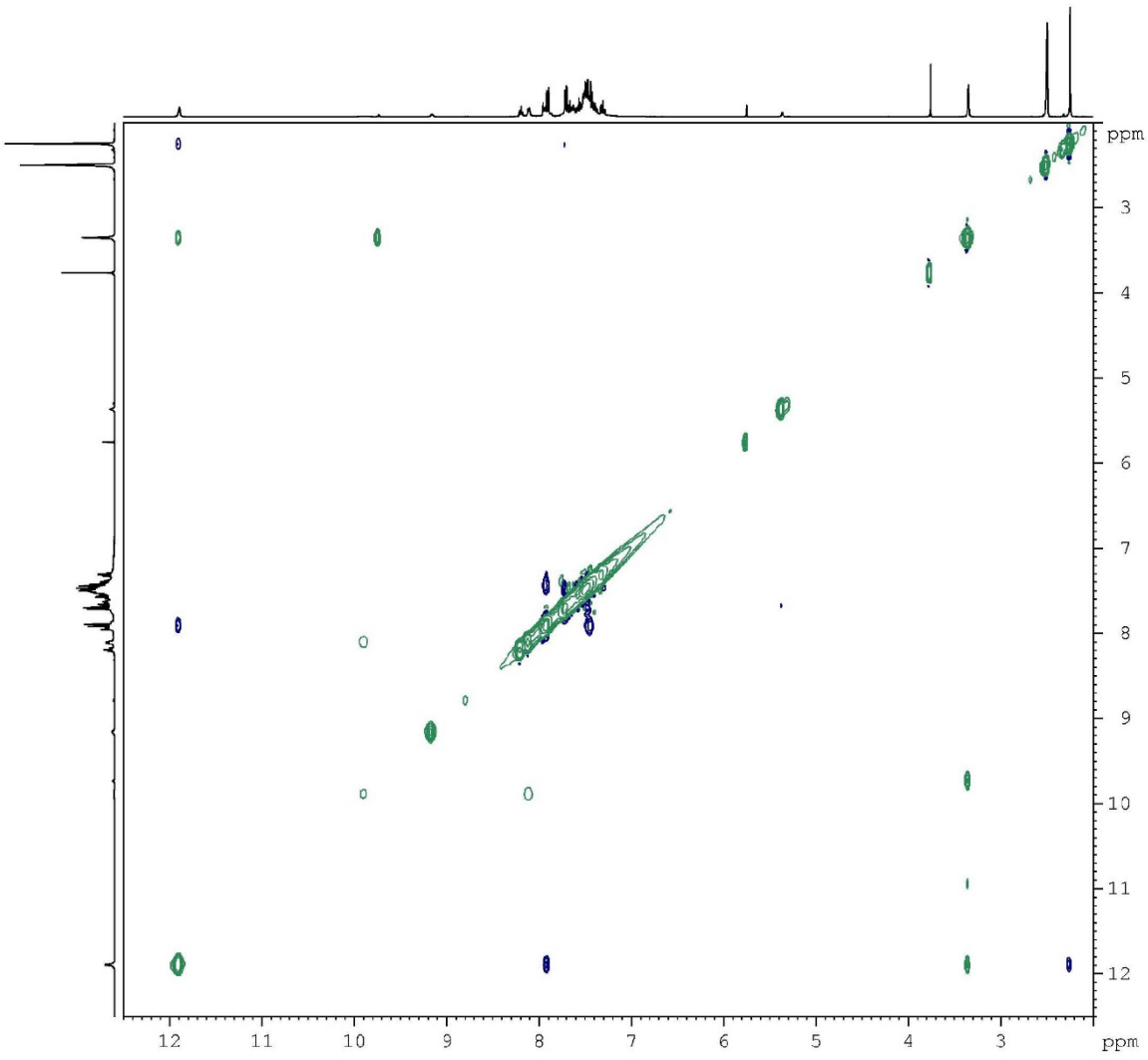
2D NMR Spectra



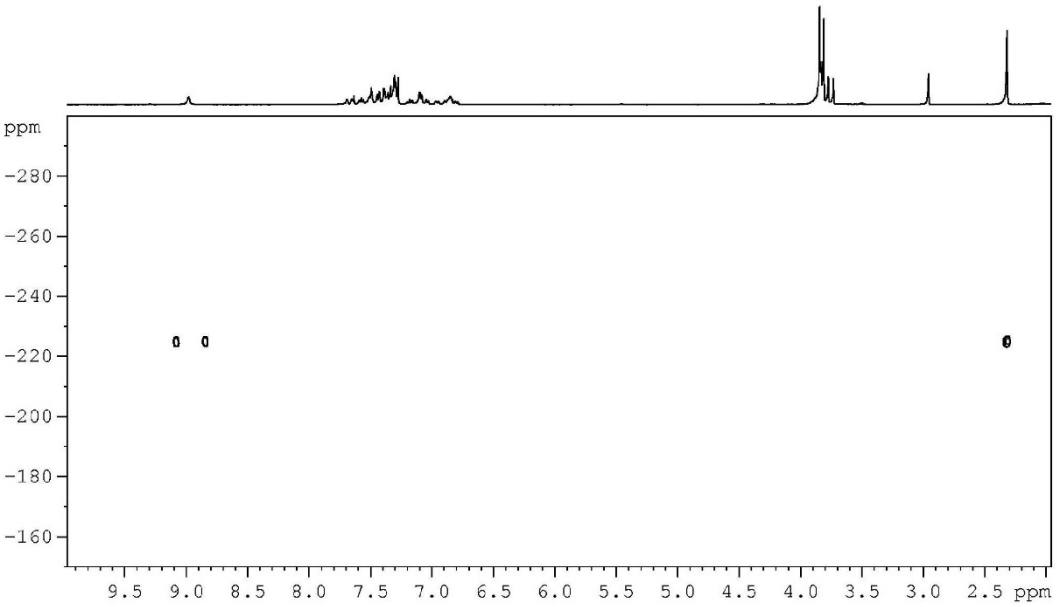
2D ^{1}H-^{15}N HMBC NMR spectrum of **2a**



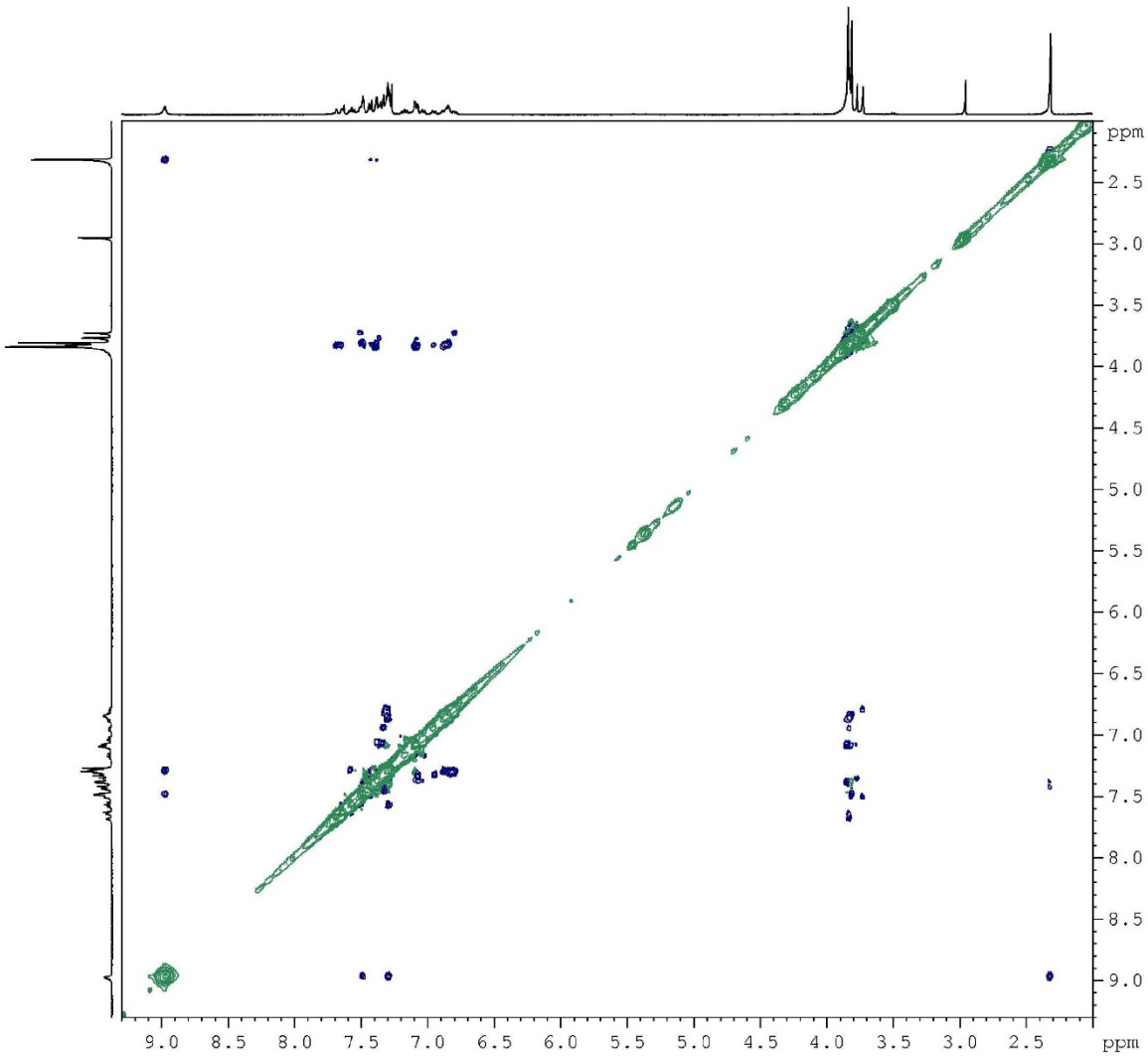
2D ^{1}H-^{13}C HMBC NMR spectrum of **2a**



2D NOESY spectrum of **2a**



2D ^{1}H-^{15}N HMBC NMR spectrum of **2b**



2D NOESY spectrum of **2b**