Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

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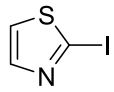
1. General methods

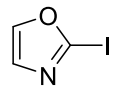
All commercial chemicals, reagents and solvents were purchased from Aldrich (Merck), Acros, TCI, and Penta and were used as received. Column chromatography was carried out with silicagel 60 (particle size 0.040–0.063 mm, 230–400 mesh; Merck) and commercially available solvents. Thin-layer chromatography (TLC) was conducted on aluminium sheets coated with silica gel 60 F254, obtained from Merck, with visualization by a UV lamp (254 or 360 nm). ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, with a Bruker AVANCE400 instrument or at 500 and 125 MHz, respectively, with a Bruker Ascend TM 500 at 25 °C. Chemical shifts are reported in ppm relative to the signal of Me_4Si. The residual solvent signal in the ^{1}H and ^{13}C NMR spectra was used as an internal reference ($CDCl_3$ δ = 7.25 and 77.23 ppm; d_6-acetone δ = 2.05 and 206.68 ppm). Apparent resonance multiplicities are described as s (singlet), d (doublet), dd (doublet of doublet) and m (multiplet), apparent coupling constants of multiplets are given in Hz. High-resolution MALDI MS spectra were measured with a MALDI mass spectrometer LTQ Orbitrap XL (Thermo Fisher Scientific, Bremen, Germany) equipped with nitrogen UV laser (337 nm, 60 Hz). The LTQ Orbitrap instrument was operated in positive-ion mode over a normal mass range (m/z 50–2000) with resolution 100 000 at m/z = 400. The survey crystal positioning system (survey CPS) was set for the random choice of shot position by automatic crystal recognition. trans-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) and 2,5-dihydroxybenzoic acid (DHB) were used as a matrix. Mass spectra were averaged over the whole MS record for all measured samples. Absorption and fluorescence spectra were measured on a Duetta™ HORIBA spectrophotometer in DMSO at room temperature. Voltammetric measurements were performed by using an integrated potentiostat system ER466 (eDAQ Europe, Warszawa, Poland) operated with EChem Electrochemistry software.

2. Synthesis and characterizations of intermediates



10

In a Schlenk flask under argon atmosphere, thiazole (0.2 ml, 2.82 mmol) was dissolved in dry THF (15 ml). The resulting reaction mixture was cooled at −78 °C and *n*BuLi (2.3 ml, 1.6 M sol. In hexane) was added dropwise. After one hour, solution of $ZnBr_2$ in THF (10 ml) was added and the mixture was heated to room temperature. Addition of I_2 (0.9 g, 7.1 mmol) was followed by stirring for additional 18 hours. Subsequently, $K_2S_2O_3$ (sat. aq. sol. 10 ml) was poured into the mixture and additional Et_2O (20 ml) and poured into citric acid (10% aq. Sol., 50 ml). Combined organic layers were washed with NaCl (sat. Aq. Sol. 20 ml), dried (Na_2SO_4) and the solvents were evaporated *in vacuo*. The crude product was purified by flash chromatography (SiO_2, DCM:Hex 1:1). 2-Iodohiazole **10** is orange-brown liquid (50 mg; 84 %); n_D^{25} = 1.6553 (lit.[1] 1.6662). R_f = 0.87 (SiO_2; DCM:Hex = 1:1).. ^{1}H-NMR (400 MHz, 25 °C, $CDCl_3$): δ = 7.59 (d, *J* = 2.4 Hz, 1H), 7.32 (d, *J* = 2.4 Hz, 1H) ppm. Spectral data according to the literature.[2]



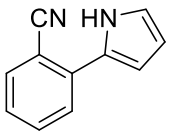
11

In a Schlenk flask under argon atmosphere, oxazole (0.19 ml, 2.82 mmol) was dissolved in dry THF (15 ml). The resulting reaction mixture was cooled at −78 °C and *n*BuLi (2.3 ml, 1.6 M sol. In hexane) was added dropwise. After one hour, solution of $ZnBr_2$ in THF (10 ml) was added and the mixture was heated to room temperature. Addition of I_2 (0.9 g, 7.1 mmol) was followed by stirring for additional 1 hour. Subsequently, Na_2SO_3 (sat. aq. sol. 10 ml) was poured into the mixture and extraxted with Et_2O (3 × 20 ml). Combined organic layers were washed with NaCl (sat. aq. sol. 20 ml), dried (Na_2SO_4) and the solvents were evaporated *in vacuo*. The crude product was purified by flash chromatography (SiO_2, DCM:Hex 1:1). 2-Iodooxazole **11** is yellow liquid (13 mg; 23 %); n_D^{25} = 1.561. R_f = 0.45 (SiO_2; DCM:Hex = 1:1). ^{1}H-NMR (500 MHz, 25 °C, $CDCl_3$): δ = 7.75 (d, *J* = 0.85 Hz, 1H), 7.09 (d, *J* = 0.6 Hz, 1H) ppm. Spectral data according to the literature.[3]

3. Catalysis

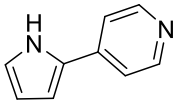
General procedure A: The substrate (1.95×10^{-4} mol, 1 eq) and photoredox catalyst DPZ (10 mol%) were dissolved in DMSO (2 ml). Subsequently, DIPEA (3.9×10^{-4} mol, 2 eq) and the trapping reagent (3.9×10^{-3} mol, 20 eq) were added. Resulting reaction mixture was irradiated by Royal Blue LED from 5 cm distance at room temperature for 24 hours. All reactions were performed in a Schlenk flask under argon atmosphere. Addition of water (10 ml) was followed by extraction with DCM (3 × 10 ml). The combined organic extracts were dried over Na_2SO_4 and the solvents were evaporated *in vacuo*. The crude product was purified by column chromatography.

General procedure B: The procedure was analogous to the *General procedure A* without the use of photoredox catalyst DPZ.



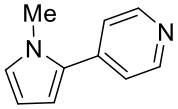
21

The title compound was prepared from **1** (27 mg) and **16** (270 µL) following the general methods A and B with the yields 16 mg (50 %) and 6 mg (18 %), respectively. The compound **21** was isolated as a violet-brown viscous liquid. R_f = 0.49 (SiO_2; PE:EtAc = 5:1). ^{1}H-NMR (500 MHz, 25 °C, $CDCl_3$): δ = 9.21 (s, 1H), 7.67–7.66 (m, 1H), 7.66–7.65 (m, 1H), 7.59–7.56 (t, *J* = 7.5 Hz, 1H), 7.28–7.26 (m, 1H), 6.99 (s, 1H), 6.84 (s, 1H), 6.37–6.36 (m, 1H) ppm. ^{13}C-NMR (100 MHz, 25 °C, $CDCl_3$): δ = 135.90; 134.28; 133.36; 128.42; 126.91; 126.11; 121.11; 120.41;110.60; 110.57; 106.17 ppm. HR-FT-MALDI-MS (DHB): *m/z* calcd. for $C_{11}H_8N_2$ ([M+H]$^+$): 169.07603; found: 169.07602. Spectral data according to the literature.[4]



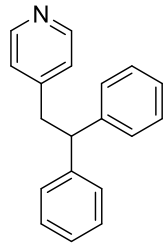
22

The title compound was prepared from **2** (40 mg) and **16** (270 µL) following the general methods A and B with the yields 20 mg (72 %) and 6 mg (23 %), respectively. The compound **22** was isolated as a brown viscous liquid. R_f = 0.2 (SiO_2; EtAc:Hex = 5:1). ^{1}H-NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.83 (s, 1H), 8.53 (d, *J* = 6 Hz, 2 H), 7.34–7.33 (m, 2H), 6.97– 6.95 (m, 1H), 6.75–6.74 (m, 1H), 6.35–6.33 (q, J = 2.5 Hz) ppm. ^{13}C-NMR (125 MHz, 25 °C, $CDCl_3$): δ = 150.15; 140.00; 129.28; 121.47; 118.01; 111.04; 109.31 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd for $C_9H_8N_2$ ([M+H]$^+$): 145.07602; found: 145.07600. Spectral data according to the literature.[5]



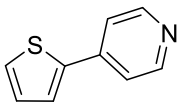
23

The title compound was prepared from **2** (40 mg) and **17** (346 µL) following the general methods A and B with the yields 22 mg (71 %) and 13 mg (43 %), respectively. The compound **23** was isolated as a brown viscous liquid. R_f = 0.39 (SiO_2; EtAc). ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 8.55–8.53 (m, 2H), 7.43–7.42 (m, 2H), 6.89–6.88 (t, *J* = 2 Hz, 1H), 6.44–6.43 (m, 1H), 6.14–6.13 (q, *J* = 2.7 Hz, 1 H); 3.81 (s, 3H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_6-acetone): δ = 151.70; 151.28; 141.64; 132.50; 127.91; 122.88; 122.18; 112.08; 109.46; 36.42 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd for $C_{10}H_{10}N_2$ ([M+H]$^+$): 159.09167; found: 159.09166. Spectral data according to the literature.[6]



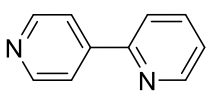
24

The title compound was prepared from **2** (40 mg) and **18** (689 µL) following the general methods A and B with the yields 41 mg (80 %) and 0 mg (0 %), respectively. The compound **24** was isolated as a yellow-orange viscous liquid. R_f = 0.45 (SiO_2; EtAc:DCM = 1:1). ^{1}H-NMR (500 MHz, 25 °C, $CDCl_3$): δ = 8.41 (d, *J* = 6 Hz, 2H), 7.30–7.27 (m, 4H), 7.22–7.19 (m, 6H), 6.96 (d, *J* = 6 Hz, 2H), 4.27–4.24 (t, *J* = 8 Hz, 1H), 3.38 (d, *J* = 8 Hz, 2H) ppm. ^{13}C-NMR (100 MHz, 25 °C, $CDCl_3$): δ = 149.62; 149.51; 143.75; 128.73; 128.07; 126.74; 124.66; 60.59; 52.29; 41.58 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd for $C_{19}H_{17}N$ ([M+H]$^+$): 260.14338; found: 260.14316. Spectral data according to the literature.[7]



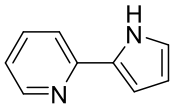
25

The title compound was prepared from **2** (40 mg) and **19** (313 µL) following the general methods A and B with the yields 5 mg (19 %) and 0 mg (0 %), respectively. The compound **25** was isolated as a brown viscous liquid. R_f = 0.46 (SiO_2; EtAc:Hex = 5:2). ^{1}H-NMR (500 MHz, 25 °C, $CDCl_3$): δ = 8.60 (s, 2H), 7.51–7.50 (dd, *J* = 1 and 3.7 Hz, 1H), 7.49–7.48 (m, 2H), 7.42–7.41 (dd, *J* = 1 and 5 Hz, 1H), 7.14–7.13 (dd, *J* = 3.7 and 5 Hz, 1H) ppm. ^{13}C-NMR spectrum was not measured due to the low amount of **25**. HR-FT-MALDI-MS (DCTB): *m/z* calcd for C_9H_7NS ([M+H]$^+$): 162.03720; found: 162.03708. Spectral data according to the literature.[8]



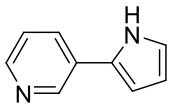
26

The title compound was prepared from **2** (40 mg) and **20** (315 µL) following the general methods A and B with the yields 14 mg (45 %) and 6 mg (20 %), respectively. The compound **26** was isolated as a yellow viscous liquid. R_f = 0,25 (SiO_2; EtAc:Hex = 10:1). ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 8.74 (d, J = 4 Hz, 1H), 8.74–8.69 (m, 2H), 8.07–8.04 (m, 3H), 7.96–7.93 (td, J = 2 and 8 Hz, 1H), 7.46–7.43 (m, 1H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_6-acetone): δ = 155.89; 151.99; 151.60; 147.61; 138.81; 125.55; 122.29; 122.24 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd for $C_{10}H_8N_2$ ([M+H]$^+$): 157.07602; found: 157. 07603. Spectral data according to the literature.[9]



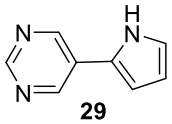
27

The title compound was prepared from **3** (40 mg) and **16** (270 µL) following the general methods A and B with the yields 6 mg (20 %) and 2 mg (6 %), respectively. The compound **27** was isolated as a brown viscous liquid. R_f = 0.33 (SiO_2; EtAc). ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 10.65 (s, 1H), 8.44 (d, J = 4.8 Hz, 1H), 7.71–7.67 (m, 1H), 7.65–7.63 (m, 1H), 7.08–7.06 (t, 1H), 6.94 (s, 1H), 6.75 (s, 1H), 6.19–6.18 (m, 1H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_6-acetone): δ = 152.53; 150.29; 137.76; 132.85; 121.56; 121.56; 121.56; 119.05; 110.85; 108.63 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd for $C_9H_8N_2$ ([M]$^+$): 144.06820; found: 144.06808. Spectral data according to the literature.[10]



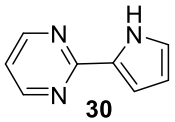
28

The title compound was prepared from **4** (40 mg) and **16** (270 µL) following the general methods A and B with the yields 17 mg (60%) and 6 mg (20 %), respectively. The compound **28** was isolated as a brown viscous liquid. R_f = 0.44 (SiO_2; EtAc). ^{1}H-NMR (500 MHz, 25 °C, $CDCl_3$): δ = 8.82 (s, 1H), 8.78 (d, J = 1.95 Hz, 1H), 8.43–8.42 (m, 1H), 7.76–7.74 (m, 1H), 7.29–7.26 (m, 1H), 6.93–6.92 (q, J = 2.55 Hz, 1H), 6.59–6.58 (q, J = 3.7, 1H), 6.33–6.32 (q, J = 2.65, 1H) ppm. ^{13}C-NMR (125 MHz, 25 °C, $CDCl_3$): δ = 147.27; 145.47; 131.26; 129.12; 128.97; 123.92; 120.26; 110.76; 107.56 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd for $C_9H_9N_2$ ([M+H]$^+$): 145.07603; found: 145.07595. Spectral data according to the literature.[11]



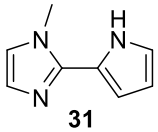
29

The title compound was prepared from **7** (31 mg) and **16** (270 µL) following the general methods A and B with the yields 16 mg (56 %) and 0 mg (0 %), respectively. The compound **29** was isolated as a yellow solid. R_f = 0.30 (SiO_2; EtAc:Hex = 1:1); mp > 150 °C (decomp). ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 10.85 (s, 1H), 9.01 (s, 2H), 8.92 (s, 1H), 7.02–7.02 (m, 1H), 6.78–6.76 (m, 1H), 6.27–6.25 (m, 1H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_6-acetone): δ = 156.38; 152.25; 128.18; 126.03; 122.15; 110.95; 108.79 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd. for $C_8H_7N_3^+$ ([M+H]$^+$), 146.07127; found 146.07115. Spectral data according to the literature.[12]



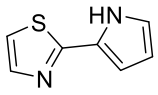
30

The title compound was prepared from **8** (31 mg) and **16** (270 µL) following the general methods A and B with the yields 18 mg (63 %) and 0 mg (0 %), respectively. The compound **30** was isolated as a yellow solid. R_f = 0.25 (SiO_2; EtAc:Hex = 1:1); mp > 195 °C (decomp). ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 10.81 (s, 1H), 8.94–8.94 (m, 1H), 8.42–8.42 (m, 1H), 8.28 (d, J = 2.5 Hz, 1H), 7.04–7.04 (m, 1H), 6.94 (s, 1H), 6.27–6.25 (m, 1H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_6-acetone): δ = 147.90; 144.48; 141.59; 141.37; 129.56; 122.80; 111.02; 109.82 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd. for $C_8H_7N_3^+$ ([M+H]$^+$), 146.07127; found: 146.07118.



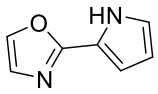
31

The title compound was prepared from **9** (41 mg) and **16** (270 µL) following the general methods A and B with the yields 20 mg (70 %) and 12 mg (43 %), respectively. The compound **31** was isolated as a brown viscous liquid. R_f = 0,28 (SiO_2; EtAc). ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 10.93 (s, 1H), 7.03 (s, 1H), 6.90 (s, 2H), 6.48 (s, 1H), 6.19 (d, J = 2 Hz, 1H), 3.83 (s, 3H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_8-acetone): δ = 143.32; 128.16; 124.14; 122.84; 120.50; 110.09; 108.03; 35.12 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd for $C_8H_9N_3$ ($[M+H]^+$): 148.08692; found: 148.08675.



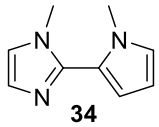
32

The title compound was prepared from **10** (41mg) and **16** (270 µL) following the general methods A and B with the yields 23 mg (80 %) and 15 mg (51 %), respectively. The compound **32** was isolated as a brown viscous liquid. R_f = 0.15 (SiO_2; DCM:Hex = 5:1). ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 10.86 (s, 1H), 7.69 (d, J = 3 Hz, 1H), 7.38 (d, J = 3 Hz, 1H), 6.97 (s, 1H), 6.68 (s, 1H), 6.20 (d, J = 2.5 Hz, 1H) ppm. ^{13}C-NMR (100 MHz, 25 °C, d_6-acetone): δ = 161.94; 143.89; 127.83; 122.11; 117.57; 110.88; 110.63 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd for $C_7H_6N_2S$ ($[M+H]^+$): 151.03245; found: 151.03239. Spectral data according to the literature.[13]



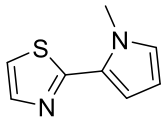
33

The title compound was prepared from **11** (38 mg) and **16** (270 µL) following the general methods A and B with the yields 20 mg (78 %) and 9 mg (36 %), respectively. The compound **33** was isolated as a yellowish solid. R_f = 0.65 (SiO_2; EtAc:Hex = 1:1); mp = 117–118 °C. ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 10.98 (s, 1H), 7.85 (s, 1H), 7.17 (s, 1H), 7.02–7.00 (m, 1H), 6.75–6.73 (m, 1H), 6.24–6.22 (m, 1H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_6-acetone): δ = 158.02, 138.37, 128.56, 122.38, 121.40, 110.65, 110.40 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd for $C_7H_6N_2O$ ($[M+H]^+$): 135.05529; found: 135.05519.



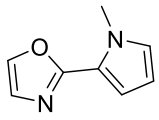
34

The title compound was prepared from **9** (41 mg) and **17** (346 µL) following the general methods A and B with the yields 26 mg (85 %) and 12 mg (39 %), respectively. The compound **34** was isolated as a brown viscous liquid. R_f = 0,34 (SiO_2; EtAc). ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 7.09 (s, 1H), 6.97 (s, 1H), 6.81–6.79 (t, J = 2 Hz, 1H), 6.32–6.31 (m, 1H), 6.11–6.09 (t, J = 3.5 Hz, 1H), 3.78 (s, 3H), 3.72 (s, 3H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_6-acetone): δ = 142.52; 128.86; 125.61; 124.11; 122.69; 111.54; 108.40; 36.25; 34.90 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd. for $C_9H_{11}N_3$ ($[M+H]^+$): 162.10257; found: 162.10254. Spectral data according to the literature.[14]



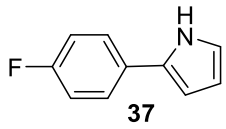
35

The title compound was prepared from **10** (41 mg) and **17** (346 µL) following the general methods A and B with the yields 30 mg (93 %) and 15 mg (46 %), respectively. The compound **35** was isolated as a brown viscous liquid. R_f = 0.13 (SiO_2; DCM:Hex = 5:1). ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 7.74 (d, J = 3 Hz, 1H), 7.40 (d, J = 3.5 Hz, 1H), 6.87 (s, 1H), 6.64–6.63 (m, 1H), 6.10–6.09 (m, 1H), 4.01 (s, 3H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_6-acetone): δ = 162.34; 144.19; 128.08; 127.84; 118.01; 113.51; 109.43; 37.37 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd. for $C_8H_8N_2S$ ($[M]^+$): 164.04027; found: 164.04014. Spectral data according to the literature.[15]



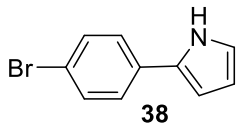
36

The title compound was prepared from **11** (38 mg) and **17** (346 µL) following the general methods A and B with the yields 30 mg (93 %) and 15 mg (46 %), respectively. The compound **36** was isolated as a yellow oil. R_f = 0.9 (SiO_2; EtAc:Hex = 1:2); n_D^{25} = 1.4052. ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 7.86 (s, 1H), 7.20 (s, 1H), 6.91–6.90 (m, 1H), 6.74–6.73 (m, 1H), 6.13–6.12 (m, 1H), 4.01 (s, 3H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_6-acetone): δ = 157.78, 138.10, 128.50, 127.89, 122.10, 112.77, 108.86, 36.80 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd. for $C_8H_8N_2O$ ($[M+H]^+$): 149.07094; found: 149.07087.



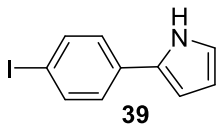
37

The title compound was prepared from **12** (43 mg) and **16** (270 µL) following the general methods A and B with the yields 31 mg (95 %) and 0 mg (0 %), respectively. The compound **37** was isolated as a white solid. R_f = 0.68 (SiO_2; DCM:Hex = 2:1); mp = 120–122 °C (lit.[16] 119–120 °C) . ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 10.48 (s, 1H), 7.66–7.62 (m, 2H), 7.14–7.09 (m, 2H), 6.86–6.84 (m, 1H), 6.49–6.47 (m, 1H), 6.16–6.14 (m, 1H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_6-acetone): δ = 162.42 (d, J = 241 Hz); 132.13; 126.64 (d, J = 7.5 Hz); 120.41; 120.24; 116.80 (d, J = 21 Hz); 110.69; 110.65; 106.91 ppm. ^{19}F-NMR (470 MHz, 25 °C, d_6-acetone): δ = –119.05 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd. for $C_{10}H_8NF^+$ ($[M]^+$), 161.06353; found 161.06357. Spectral data according to the literature. [17]



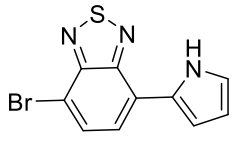
38

The title compound was prepared from **13** (55 mg) and **16** (270 µL) following the general methods A and B with the yields 27 mg (63 %) and 4 mg (10 %), respectively. The compound **38** was isolated as a beige solid. R_f = 0.84 (SiO_2; DCM:Hex = 2:1); mp = 137 °C, decomp. (lit.[18] 158 °C) . ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 10.60 (s, 1H), 7.59–7.56 (m, 2H), 7.51–7.49 (m, 2H), 6.89–6.88 (m, 1H), 6.57–6.56 (m, 1H), 6.18–6.16 (m, 1H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_6-acetone): δ = 133.57, 132.60, 131.37, 126.20, 119.25, 110.47, 107.26 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd. for $C_{10}H_8BrN$ ($[M]^+$), 220.98346; found: 220.98336. Spectral data according to the literature.[19]



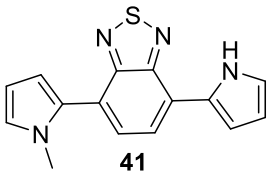
39

The title compound was prepared from **14** (64 mg) and **16** (270 µL) following the general methods A and B with the yields 45 mg (87 %) and 3 mg (5 %), respectively. The compound **39** was isolated as a white solid. R_f = 0.68 (SiO_2; DCM:Hex = 2:1); mp = 183–185 °C. ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 10.59 (s, 1 H), 7.69–7.68 (m, 2H); 7.46–7.43 (m, 2H); 6.89-6.88 (m, 1H), 6.58–6.57 (m, 1H), 6.18–6.16 (q, J = 2.5 Hz, 1H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_6-acetone): δ = 138.98; 134.36; 131.78; 126.75;121.01; 110.83;107.65; 90.54 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd. for $C_{10}H_8IN$ ($[M]^+$): 268.96959; found: 268.96951. Spectral data according to the literature. [20]



40

The title compound was prepared from **15** (57 mg) and **16** (270 µL) following the general methods A and B with the yields 37 mg (68 %) and 0 mg (0 %), respectively. The compound **40** was isolated as a red solid. R_f = 0.46 (SiO_2; EtAc:Hex = 1:7); mp = 122–124 °C. ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 11.16 (s, 1H), 7.95 (d, J = 10 Hz, 1H), 7.85 (d, J = 10 Hz, 1H), 7.16–7.15 (m, 1H), 7.14–7.12 (m, 1H), 6.31–6.30 (m, 1H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_6-acetone): δ = 154.68; 152.33; 133.91; 128.70; 126.12; 123.19; 122.48; 110.96; 110.75; 109.59 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd. for $C_{10}H_6BrN_3S^+$ ($[M]^+$), 278.946024; found 278.94588.



41

The title compound was prepared from **40** (55 mg) and **17** (346 µL) following the general methods A and B with the yields 25 mg (45 %) and 0 mg (0 %), respectively. The compound **41** was isolated as a dark red solid. R_f = 0.44 (SiO_2; EtAc:Hex = 1:7); mp = 48–50 °C. ^{1}H-NMR (500 MHz, 25 °C, d_6-acetone): δ = 11.21 (s, 1H), 7.99 (d, J = 7.5 Hz, 1H), 7.62 (d, J = 7,5 Hz, 1H), 7.14–7.11 (m, 2H), 6.91–6.90 (m, 1H), 6.47–6.45 (m, 1H), 6.32–6.29 (m, 1H), 6.19–6.18 (m, 1H), 3.69 (s, 3H) ppm. ^{13}C-NMR (125 MHz, 25 °C, d_6-acetone): δ = 155.79; 153.32; 131.54; 130.85; 129.86; 126.01; 125.28; 124.53; 123.37; 122.24; 122.06; 112.79; 110.94; 110.90; 110.39; 109.07; 36.37 ppm. HR-FT-MALDI-MS (DCTB): *m/z* calcd. for $C_{15}H_{12}N_4S^+$ ([M]$^+$), 280.07772; found 280.07757.

Table S1. Optimization of reaction conditions of non-catalysed C-C coupling between **2** and **16** in DMSO with DPZ.

Base	Atmosphere	LED	Isolated yield [%]
DIPEA	Ar	Royal-Blue	23
TEA	Ar	Royal-Blue	10
TMEDA	Ar	Royal-Blue	0
No	Ar	Royal-Blue	0
DIPEA	Ar	Blue	0
DIPEA	Ar	Red-Orange	0
DIPEA	Ar	No	0
DIPEA	Air	Royal-Blue	traces

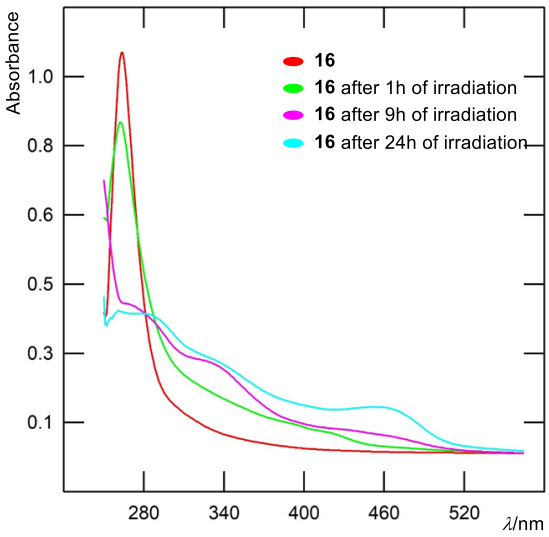


Figure S1. Absorption spectra of 1*H*-pyrrole **16** after 1, 6 and 24 hours of irradiation by Royal Blue LED.

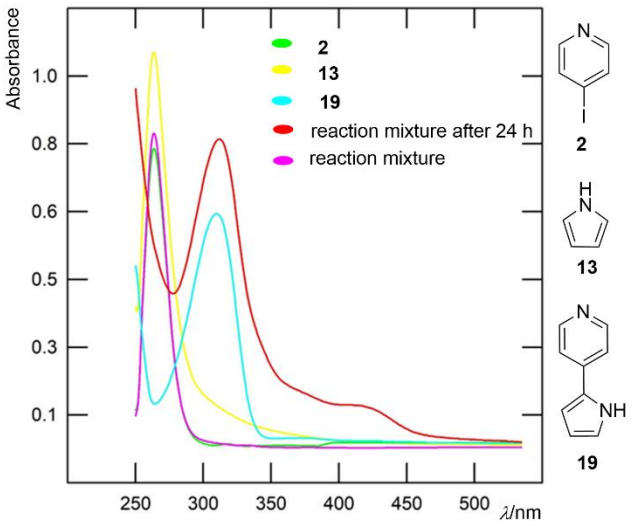


Figure S2. Absorption spectra of starting materials (**2** and **16**), product **22** and reaction mixture after irradiation by Royal Blue LED.

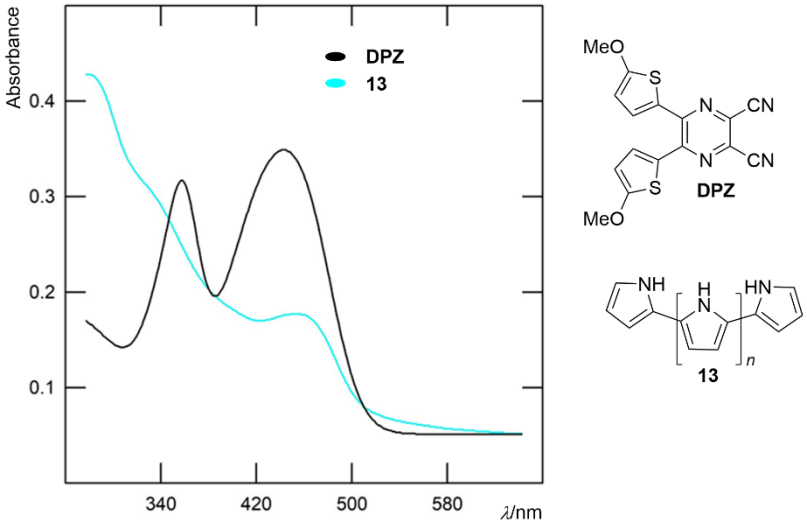


Figure S3. Absorption spectrum od (oligo)pyrrole **16** and DPZ.

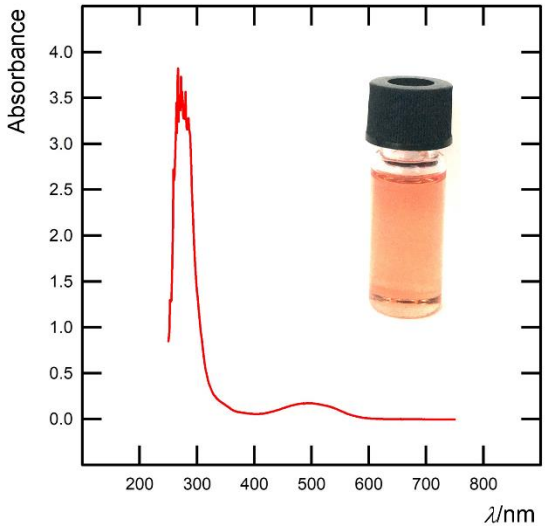


Figure S4. Absorption spectrum of **2** and DIPEA in DMSO. Picture of the solution as an inset.

4. Electrochemistry

The electrochemical behavior of selected (hetero)aromatics were investigated by cyclic voltammetry in DMSO containing 0.1 M Bu_4NPF_6 in a three electrode cell by cyclic voltammetry (CV). The working electrode was glassy carbon disk (1 mm in diameter). As the reference and auxiliary electrodes were used leakless Ag/AgCl electrode (SSCE) containing filling electrolyte (3.4 M KCl) and titanium rod with a thick coating of platinum, respectively. Voltammetric measurements were performed by using an integrated potentiostat system ER466 (eDAQ Europe) operated with EChem Electrochemistry software. Potential window of the aforementioned electrolyte ranges between -2.8 to +1.55 V vs. SSCE. Determined peak potentials of the first oxidations and reductions are given *vs*. silver chloride electrode (SSCE; +0.205 V vs. SHE) as well.

Table S2. *Electrochemical data of the investigated (hetero)aromatics.*

Compound	Oxidations	Reductions
	E_p^a (V)	E_p^c (V)
Pyrrole	+1.32	/
N-methylpyrrole	+1.35	/
2-iodo-*N*-methylimidazole	/	-1.93 -2.55
2-iodothiazole	/	-1.36 -2.67
Dibromobenzothiadiazole	/	-1.02[b] -1.92
2-chlorobenzonitrile	/	-1.76 -2.22
2-iodopyridine	/	-1.90 -2.59
3-iodopyridine	/	-1.92 -2.59
4-iodopyridine	/	-1.91 -2.59
4-bromopyridine	/	-2.12 -2.54
4-chloropyridine	/	-2.19 -2.55
1-fluoro-4-iodobenzene	/	-2.08 /
2-bromopyrazine	/	-1.56 -2.04
2-bromopyrimidine	/	-1.75 -2.24
5-bromopyrimidine	/	-1.79 -2.23

[a] E_p^a and E_p^c are anodic or cathodic peak potentials of the irreversible first oxidations and reductions, respectively, measured by CV at scan rate 100 mVs^{-1}; all potentials are given vs. SSCE.[b] Reversible first reduction.

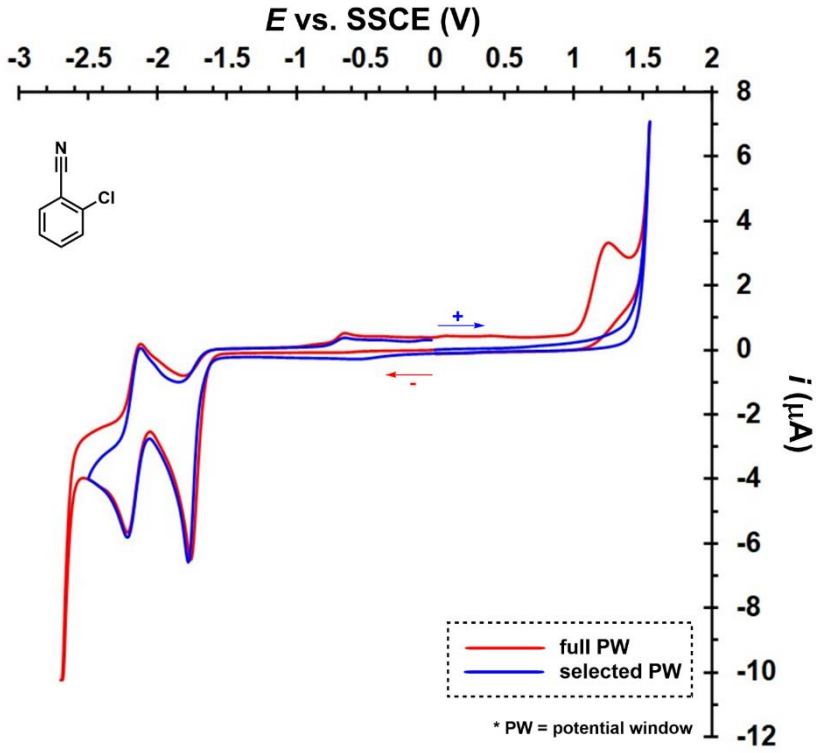


Figure S5. CV diagram of compound **1** at GC electrode in DMSO containing 0.1 M Bu_4NBF_4; v=100mV/s.

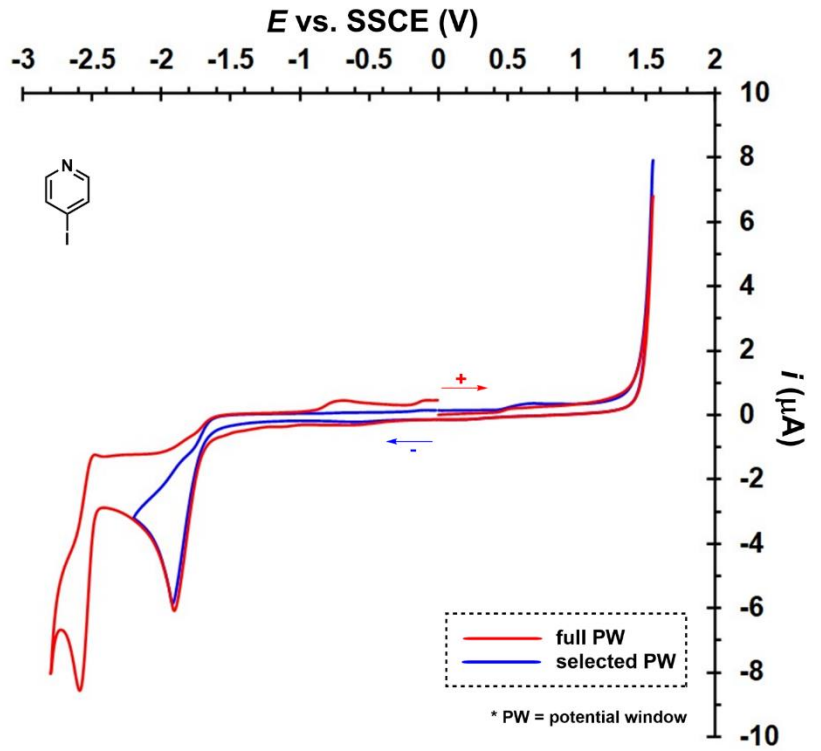


Figure S6. CV diagram of compound **2** at GC electrode in DMSO containing 0.1 M Bu_4NBF_4; v=100mV/s.

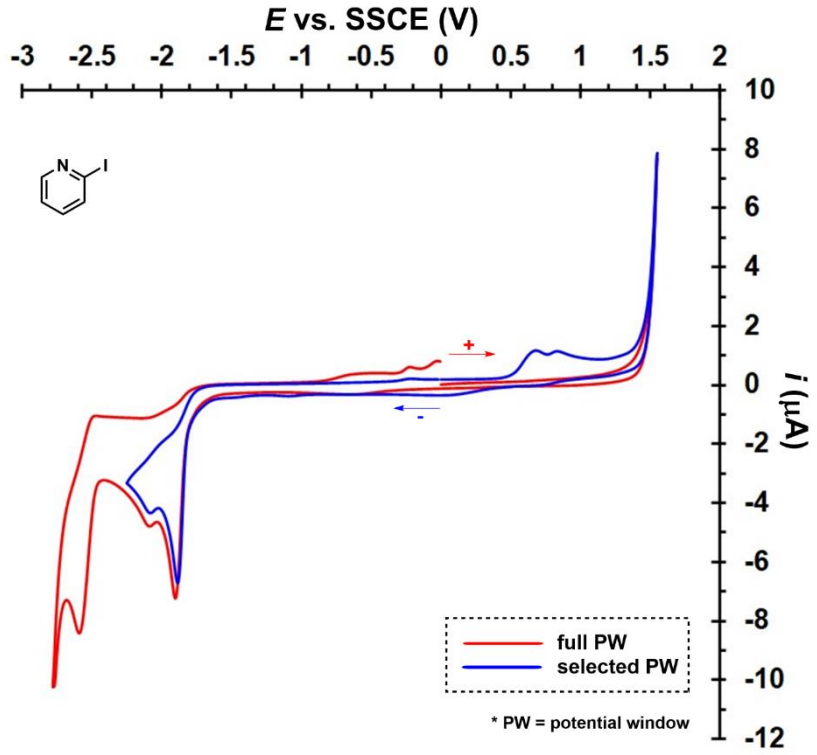


Figure S7. CV diagram of compound **3** at GC electrode in DMSO containing 0.1 M Bu_4NBF_4; v=100mV/s.

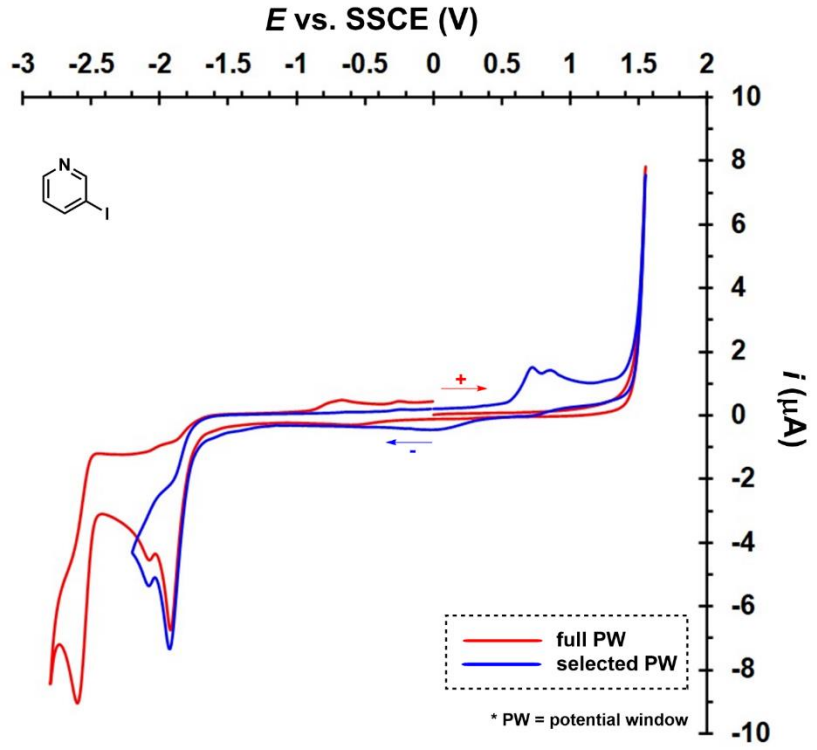


Figure S8. CV diagram of compound **4** at GC electrode in DMSO containing 0.1 M Bu_4NBF_4; v=100mV/s.

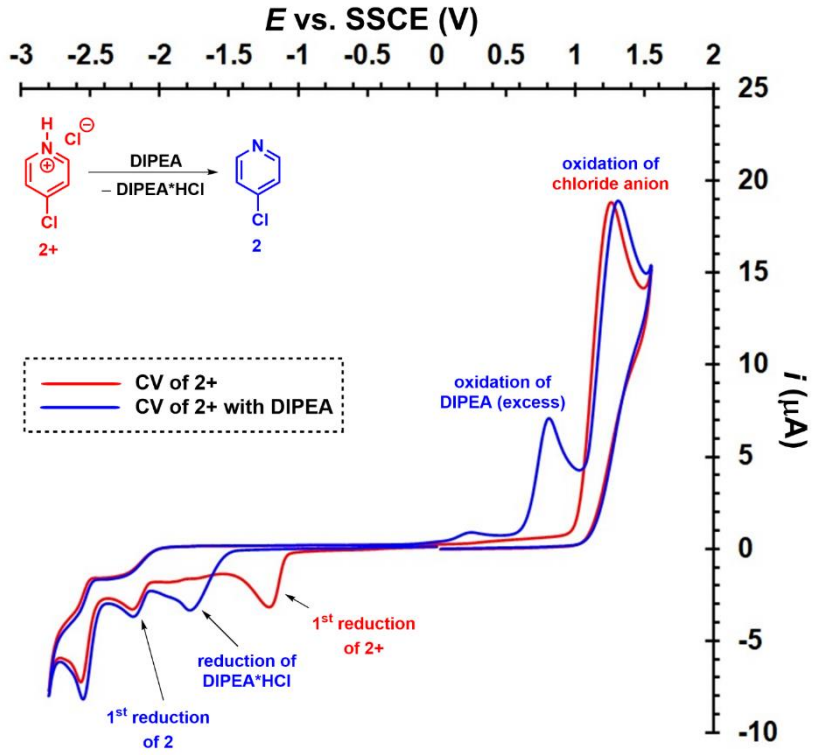


Figure S9. CV diagram of compound **5** at GC electrode in DMSO with DIPEA containing 0.1 M Bu_4NBF_4; v=100mV/s.

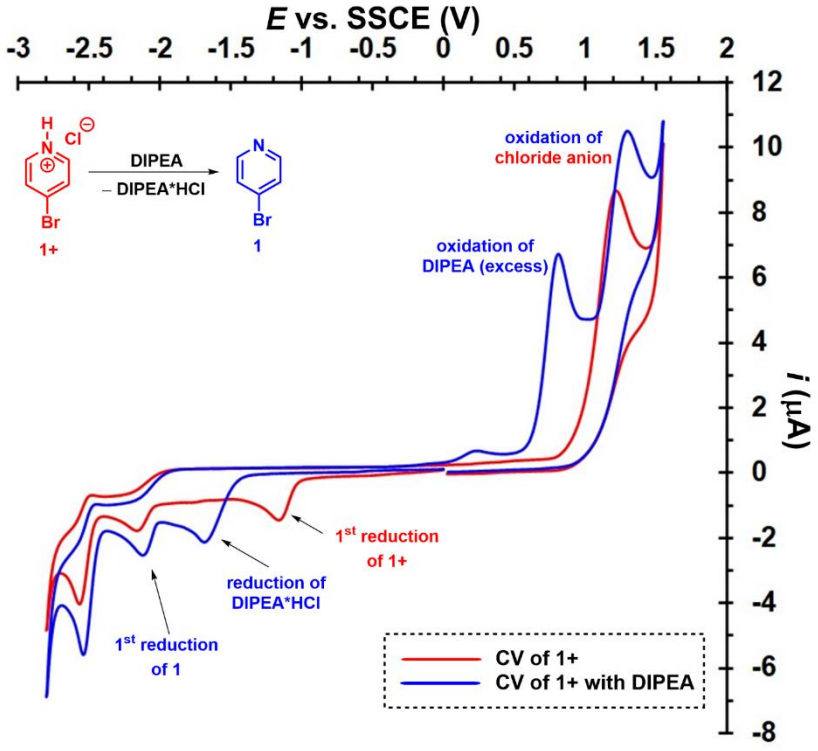


Figure S10. CV diagram of compound **6** at GC electrode in DMSO with DIPEA containing 0.1 M Bu_4NBF_4; v=100mV/s.

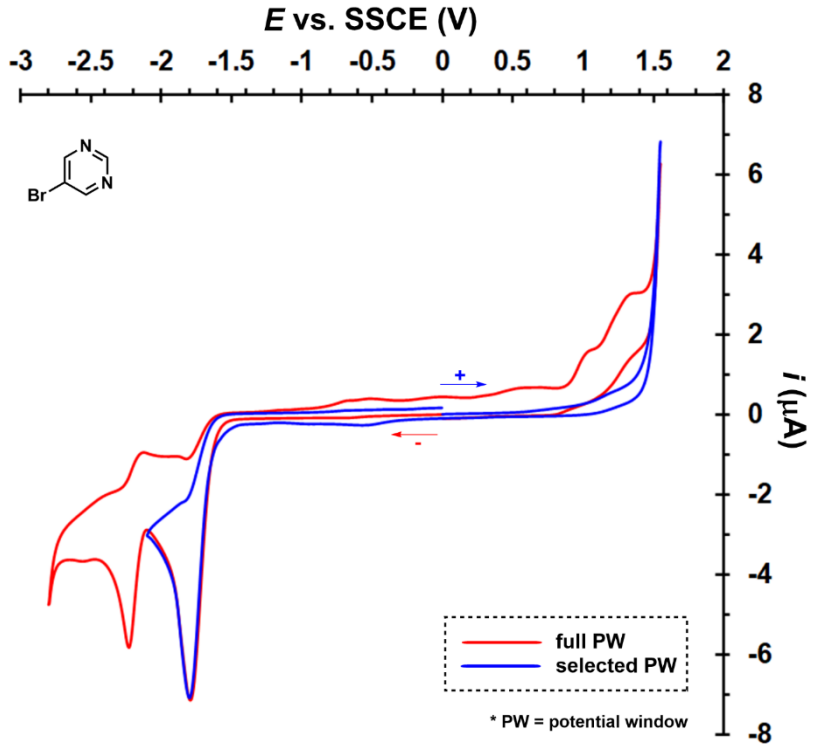


Figure S11. CV diagram of compound **7** at GC electrode in DMSO containing 0.1 M Bu_4NBF_4; v=100mV/s.

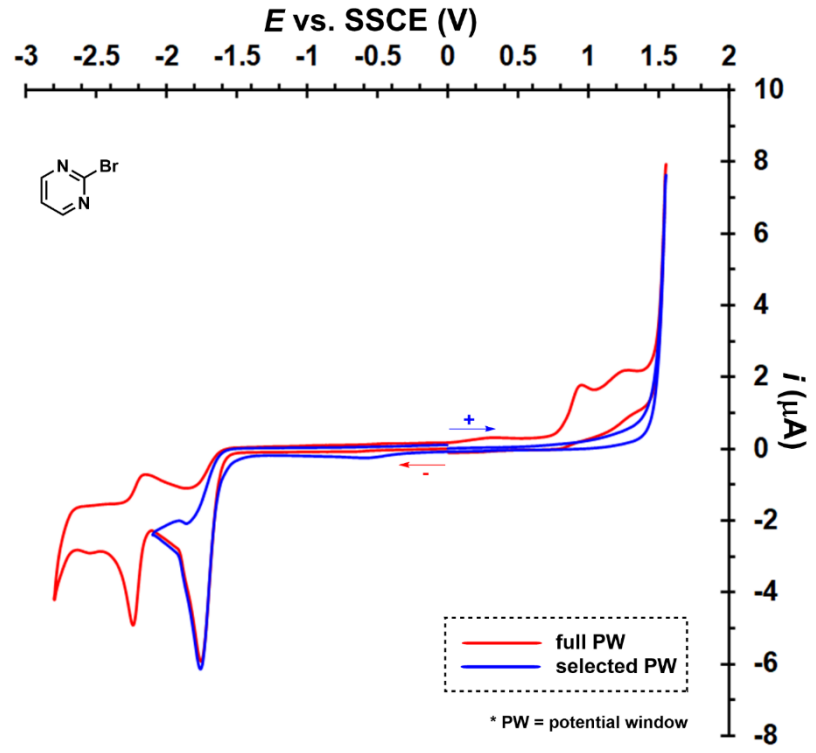


Figure S12. CV diagram of compound **8** at GC electrode in DMSO containing 0.1 M Bu_4NBF_4; v=100mV/s.

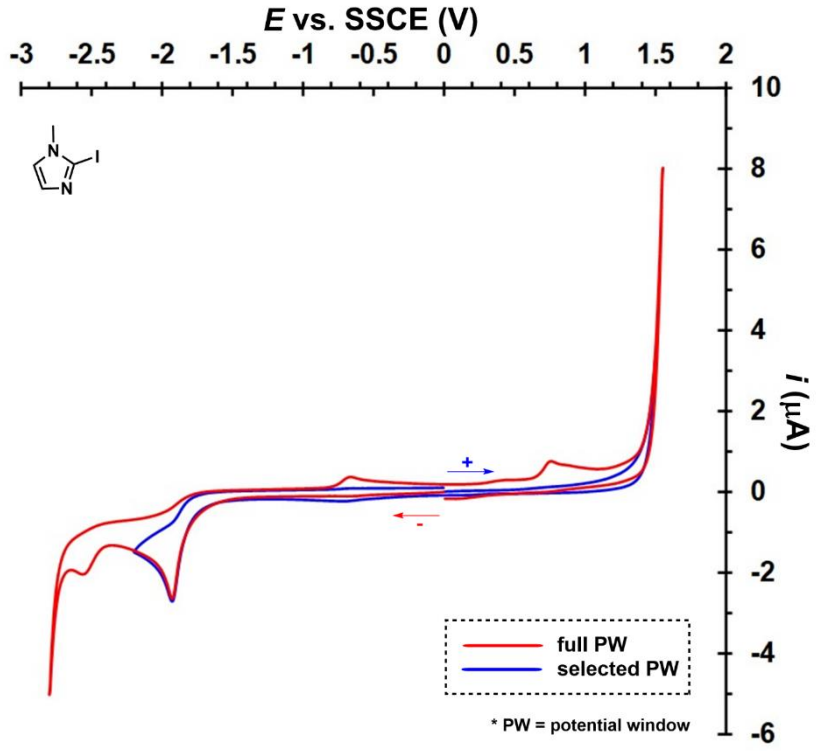


Figure S13. CV diagram of compound **9** at GC electrode in DMSO containing 0.1 M Bu_4NBF_4; v=100mV/s.

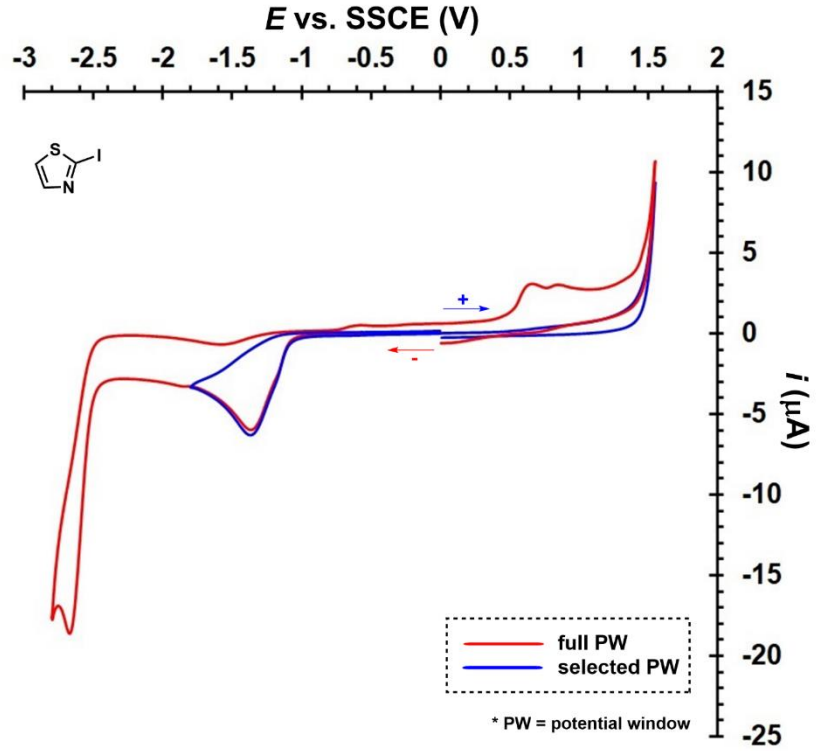


Figure S14. CV diagram of compound **10** at GC electrode in DMSO containing 0.1 M Bu_4NBF_4; v=100mV/s.

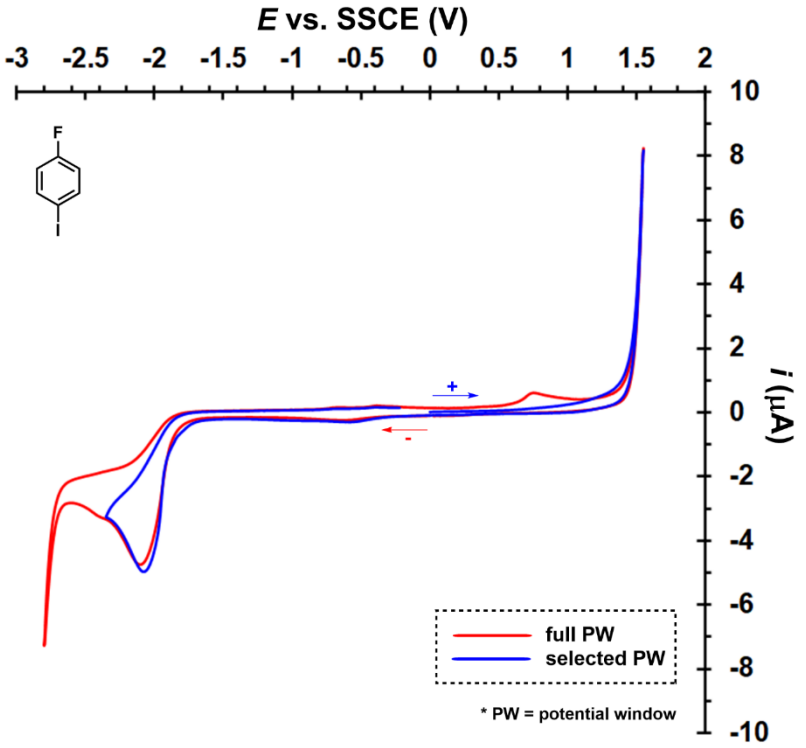


Figure S15. CV diagram of compound **12** at GC electrode in DMSO containing 0.1 M Bu_4NBF_4; v=100mV/s.

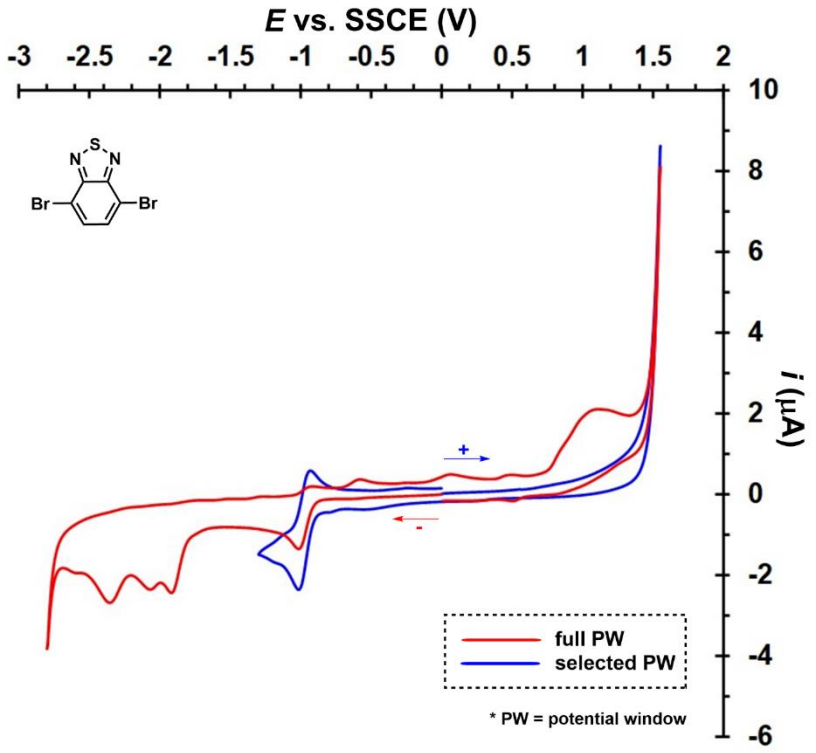


Figure S16. CV diagram of compound **15** at GC electrode in DMSO containing 0.1 M Bu_4NBF_4; v=100mV/s.

5. ^{1}H and ^{13}C NMR spectra

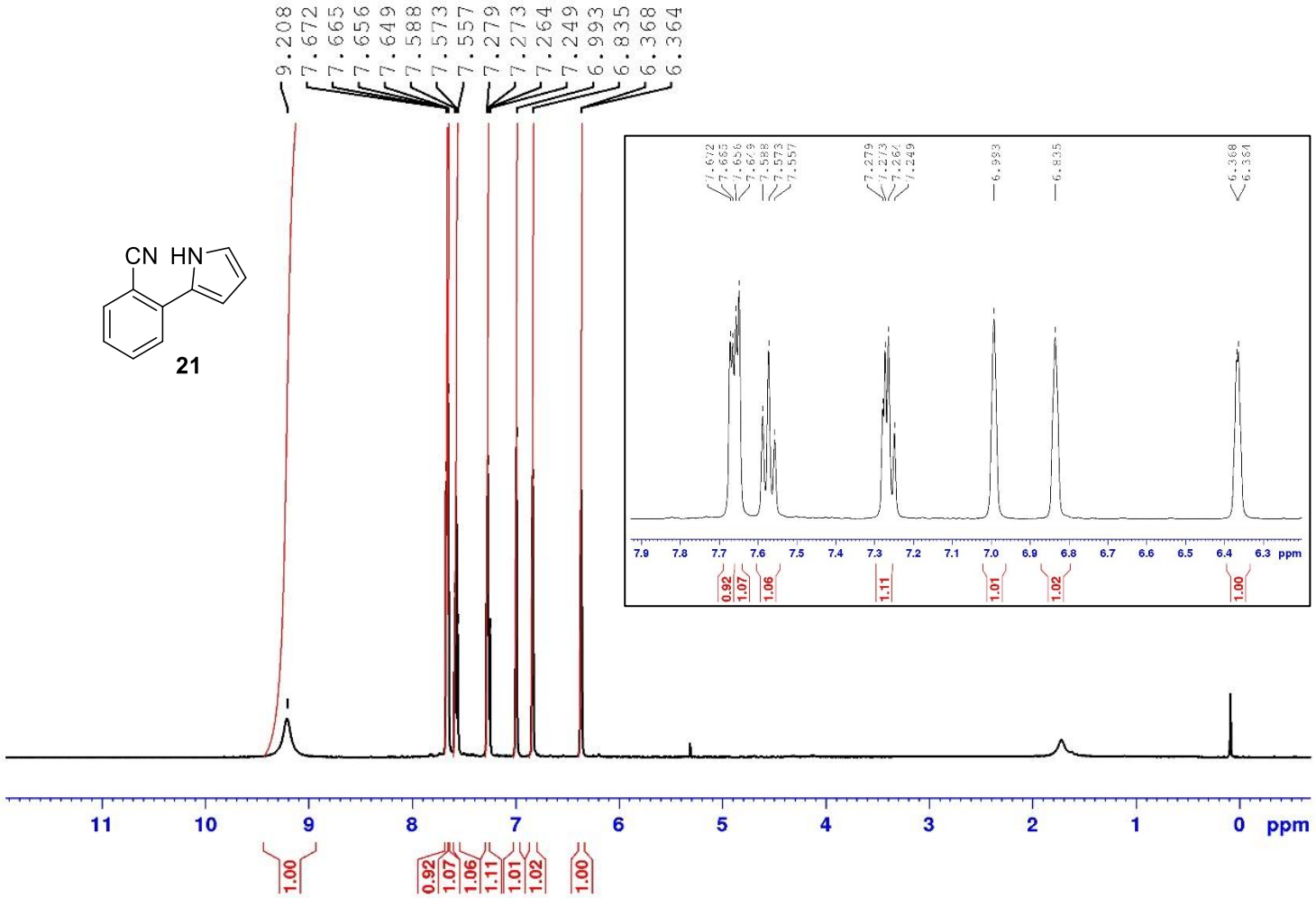


Figure S17. ^{1}H NMR spectrum of **21** (500 MHz, $CDCl_3$, 25 °C).

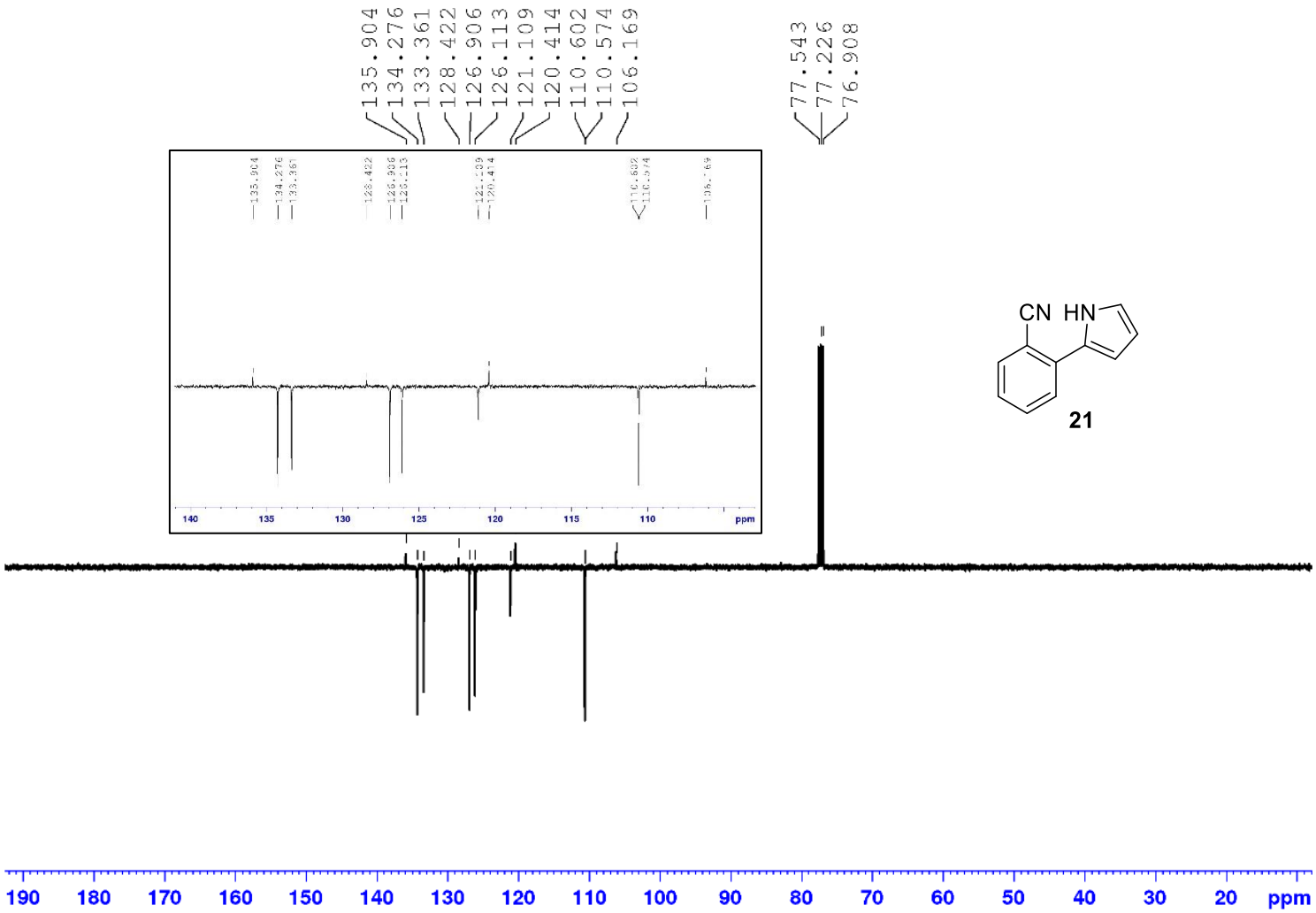


Figure S18. ^{13}C NMR APT spectrum of **21** (100 MHz, $CDCl_3$, 25 °C).

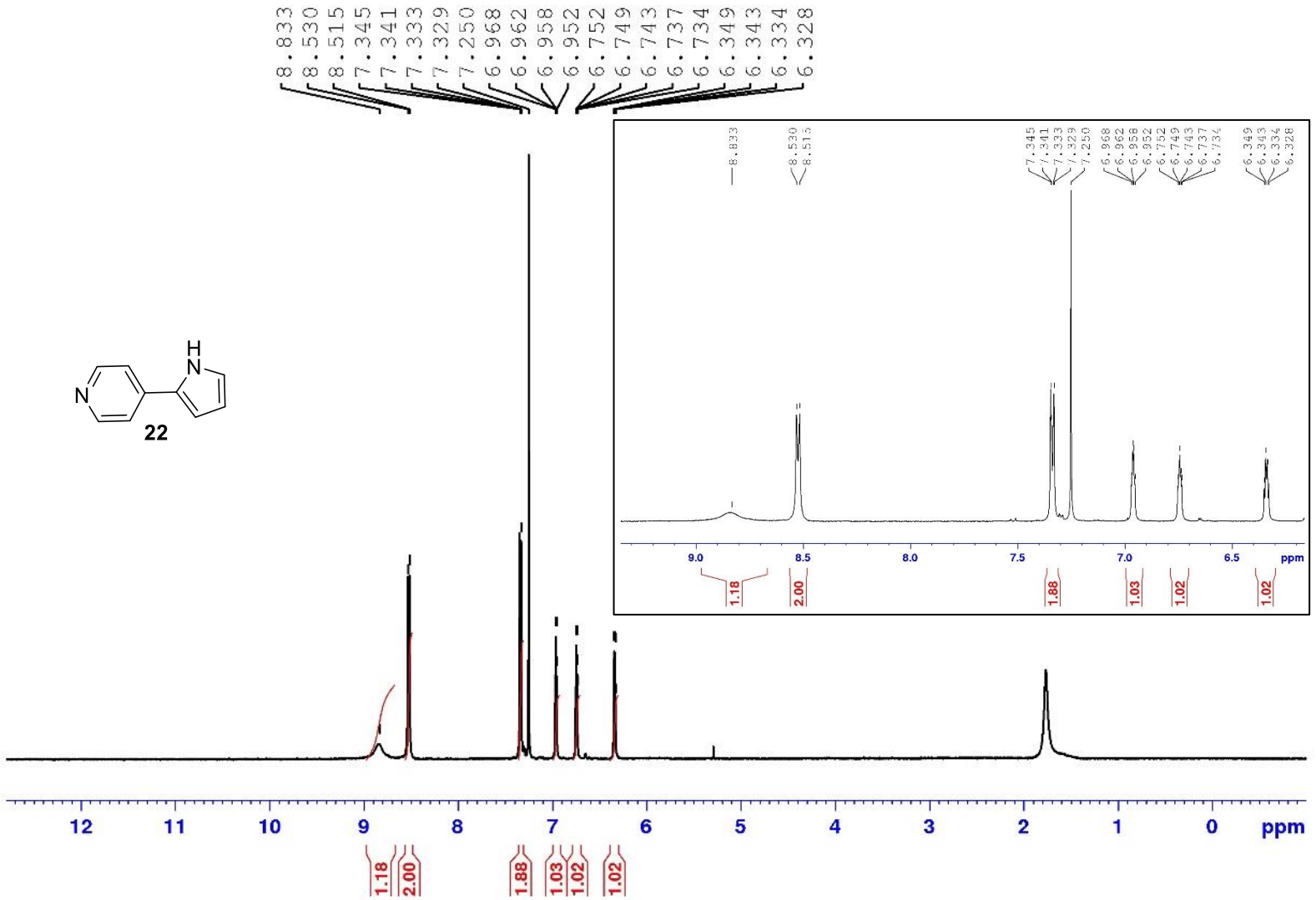


Figure S19. ^{1}H NMR spectrum of **22** (400 MHz, $CDCl_3$, 25 °C).

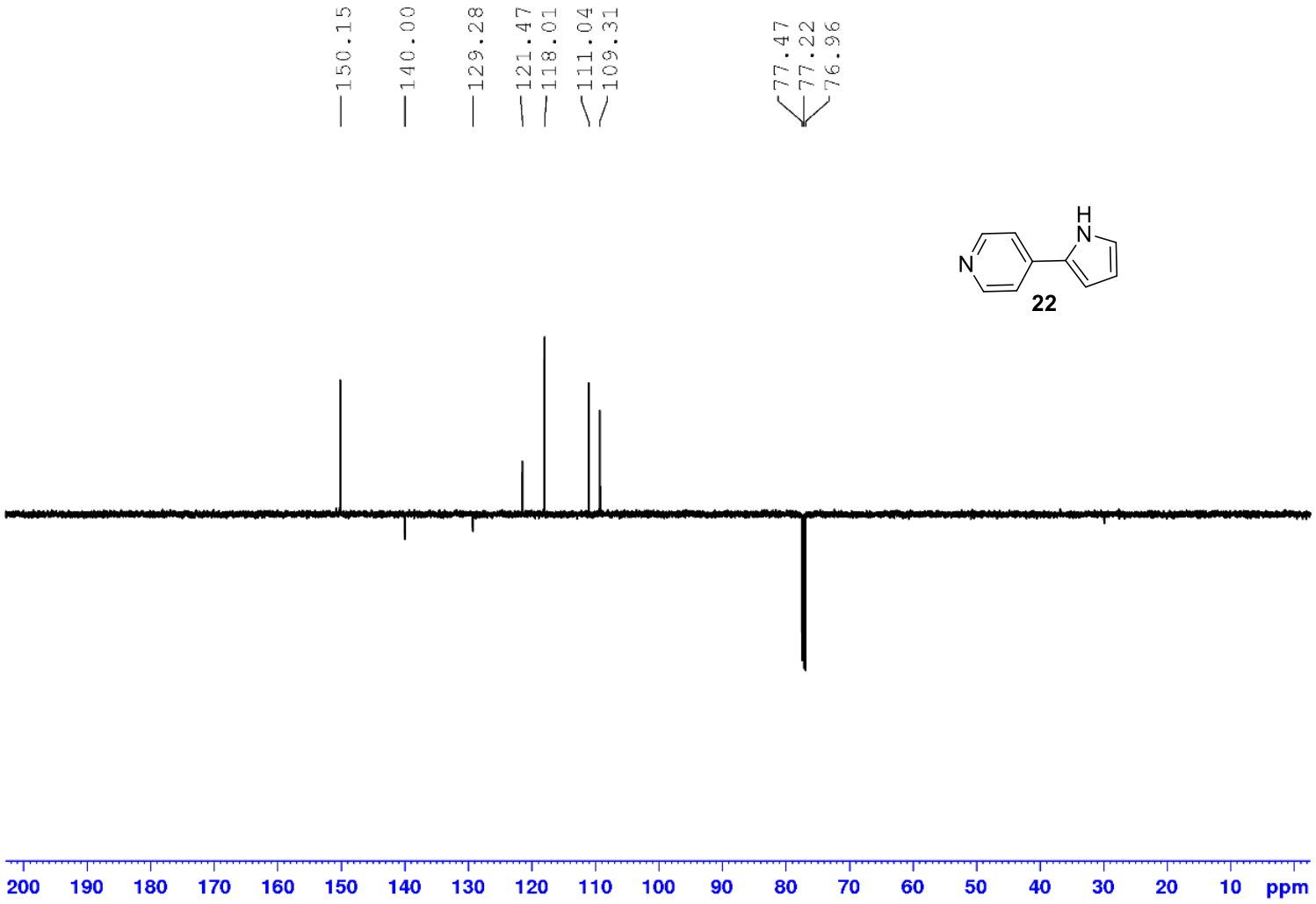


Figure S20. ^{13}C NMR APT spectrum of **22** (125 MHz, $CDCl_3$, 25 °C).

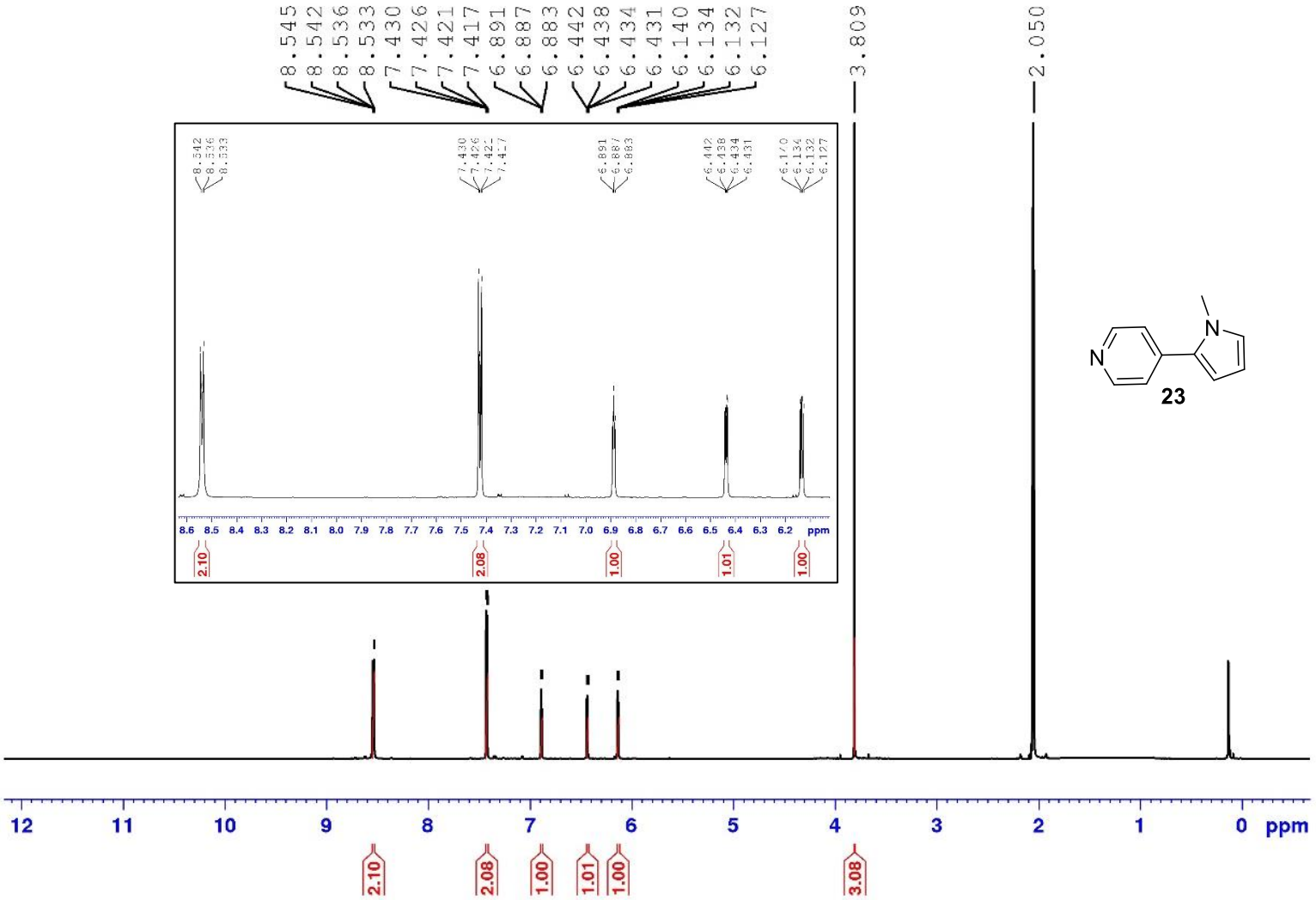


Figure S21. ^{1}H NMR spectrum of **23** (500 MHz, d_6-acetone, 25 °C).

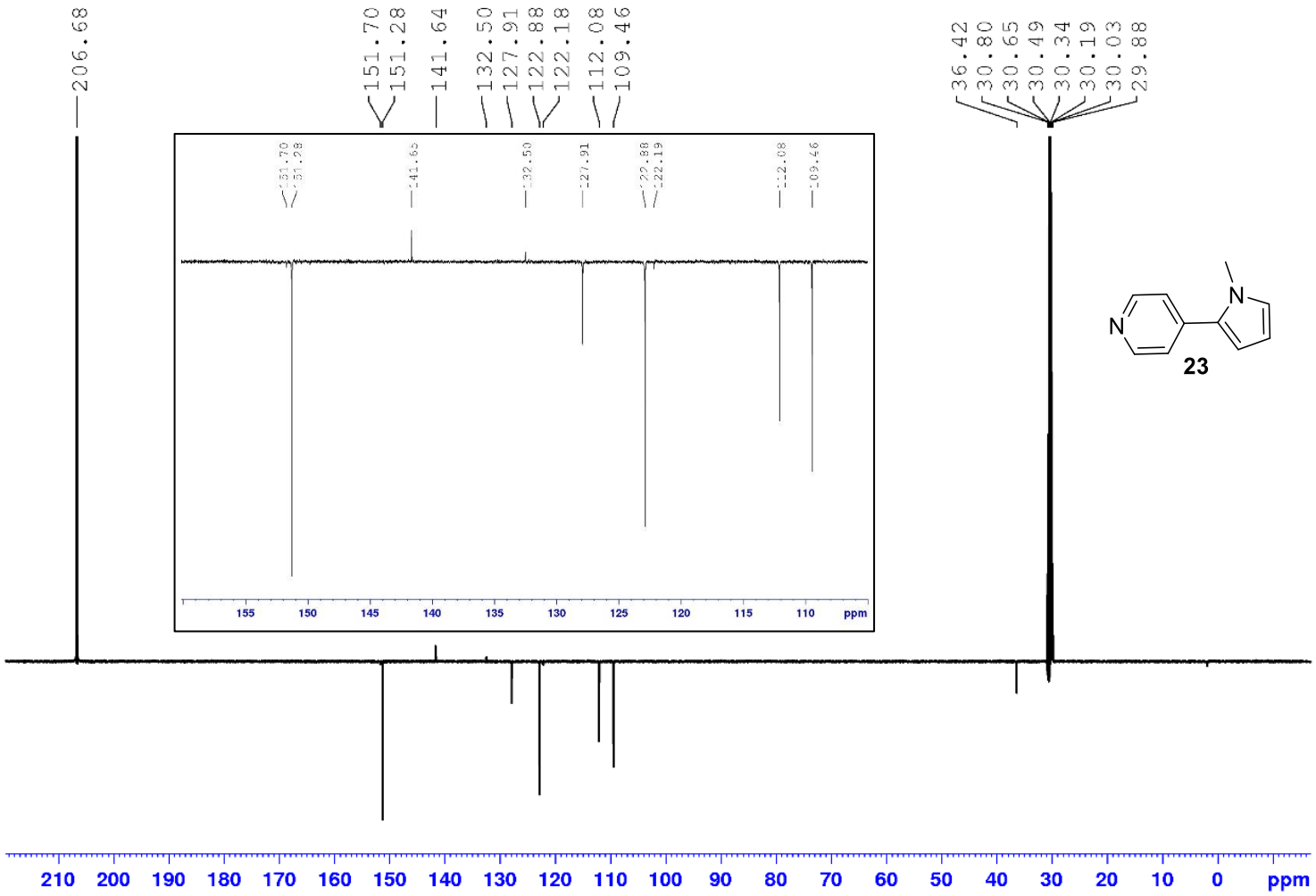


Figure S22. ^{13}C NMR APT spectrum of **23** (125 MHz, d_6-acetone, 25 °C).

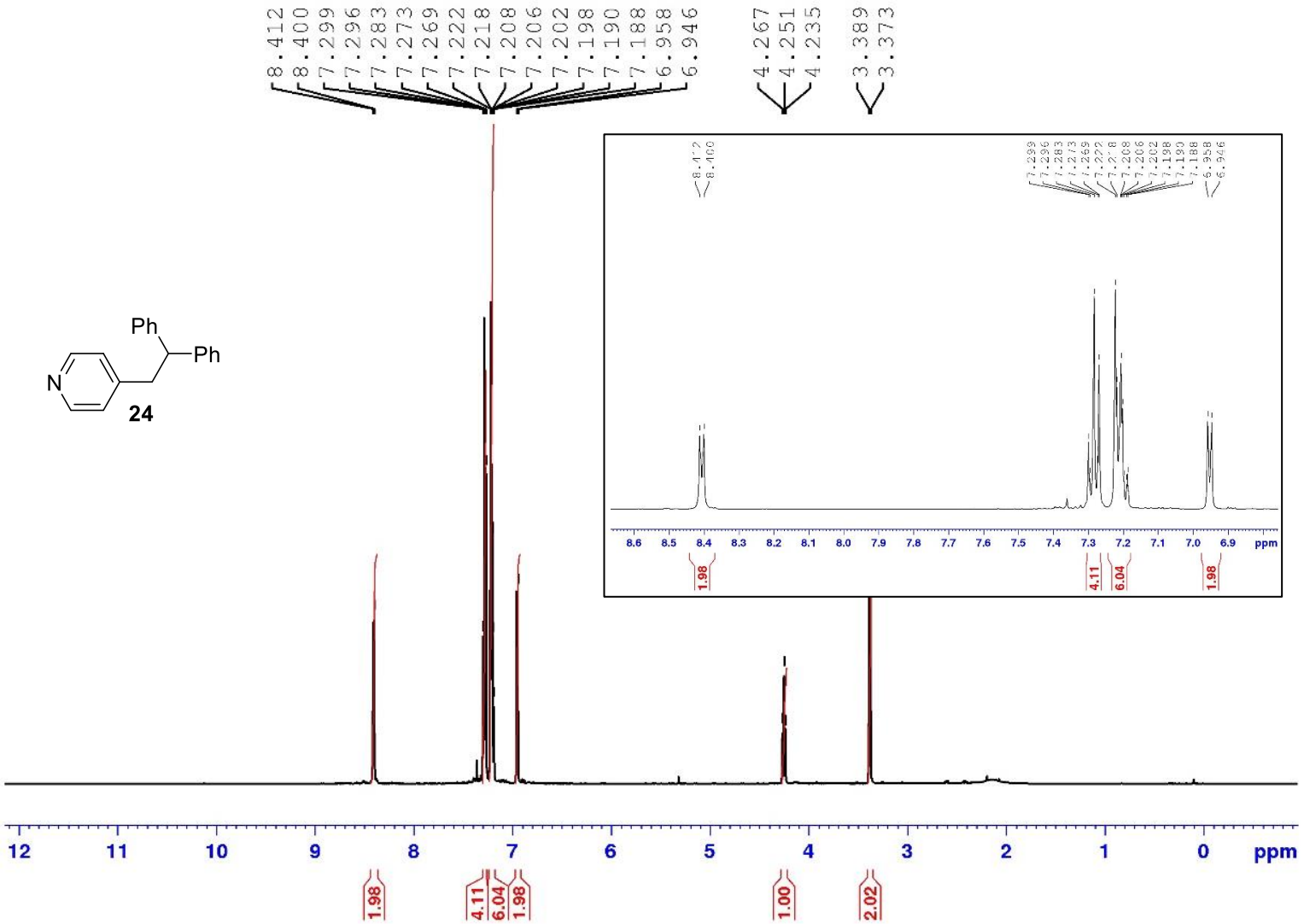


Figure S23. ^{1}H NMR spectrum of **24** (500 MHz, $CDCl_3$, 25 °C).

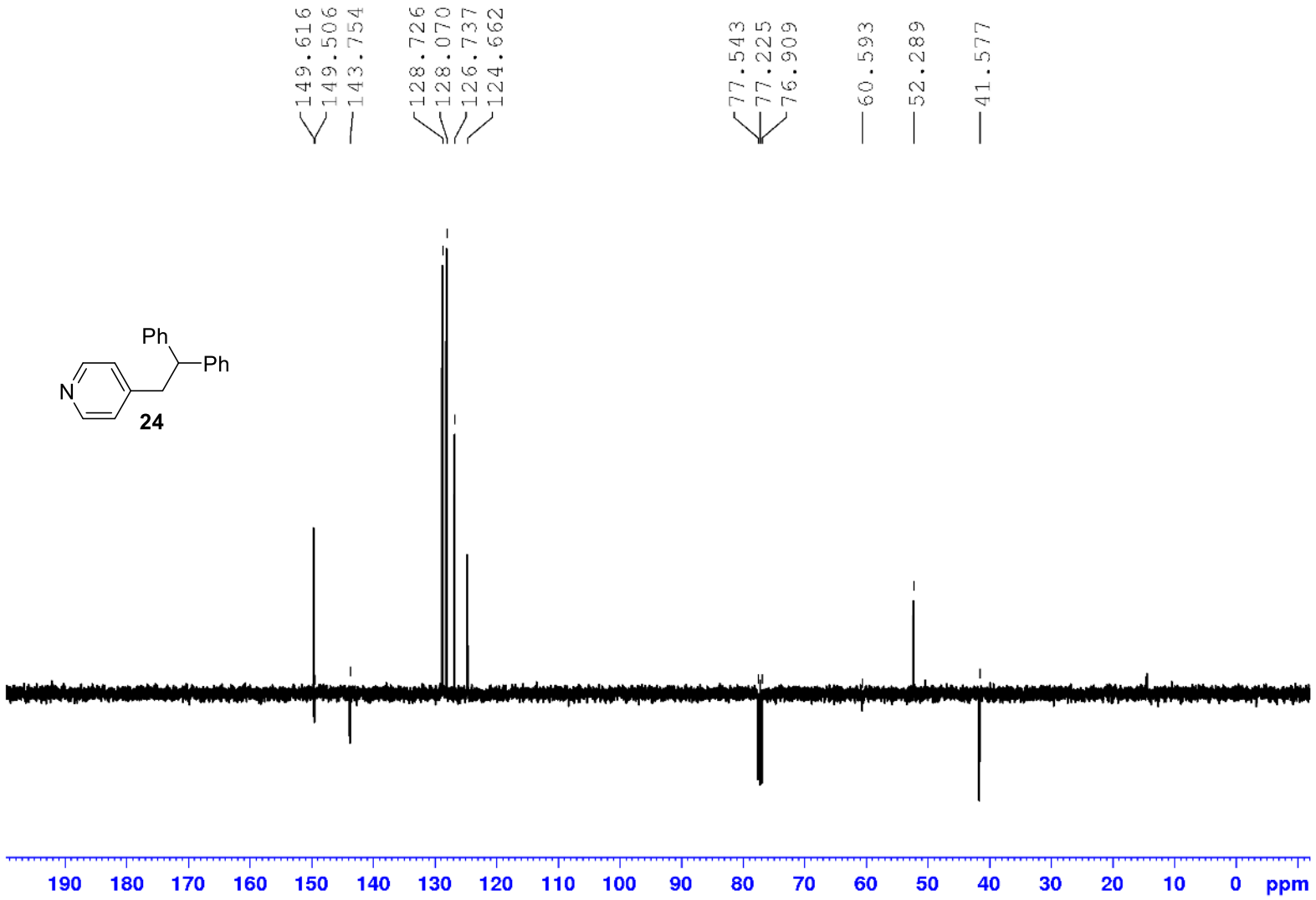


Figure S24. ^{13}C NMR APT spectrum of **24** (100 MHz, $CDCl_3$, 25 °C).

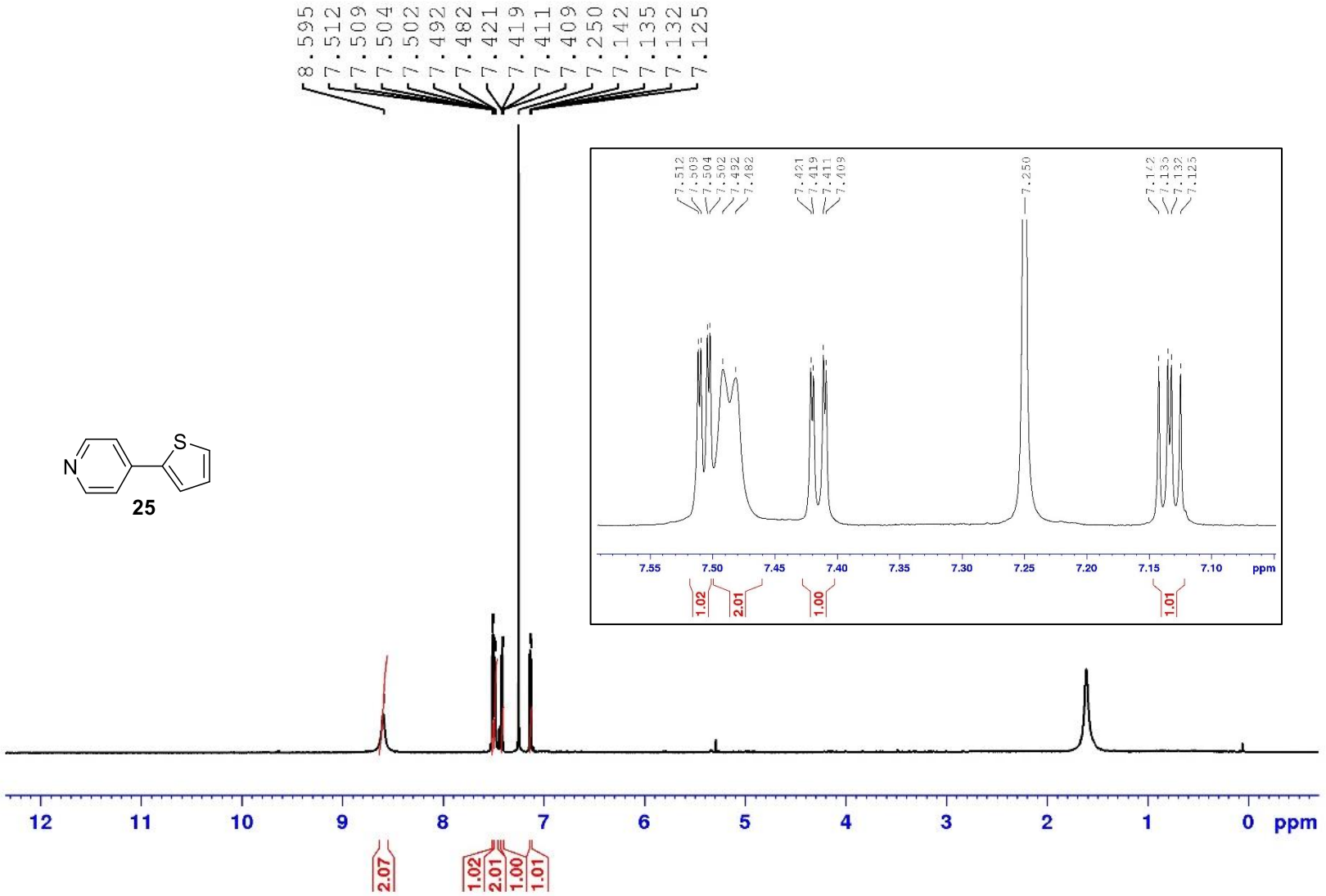


Figure S25. ^{1}H NMR spectrum of **25** (500 MHz, $CDCl_3$, 25 °C).

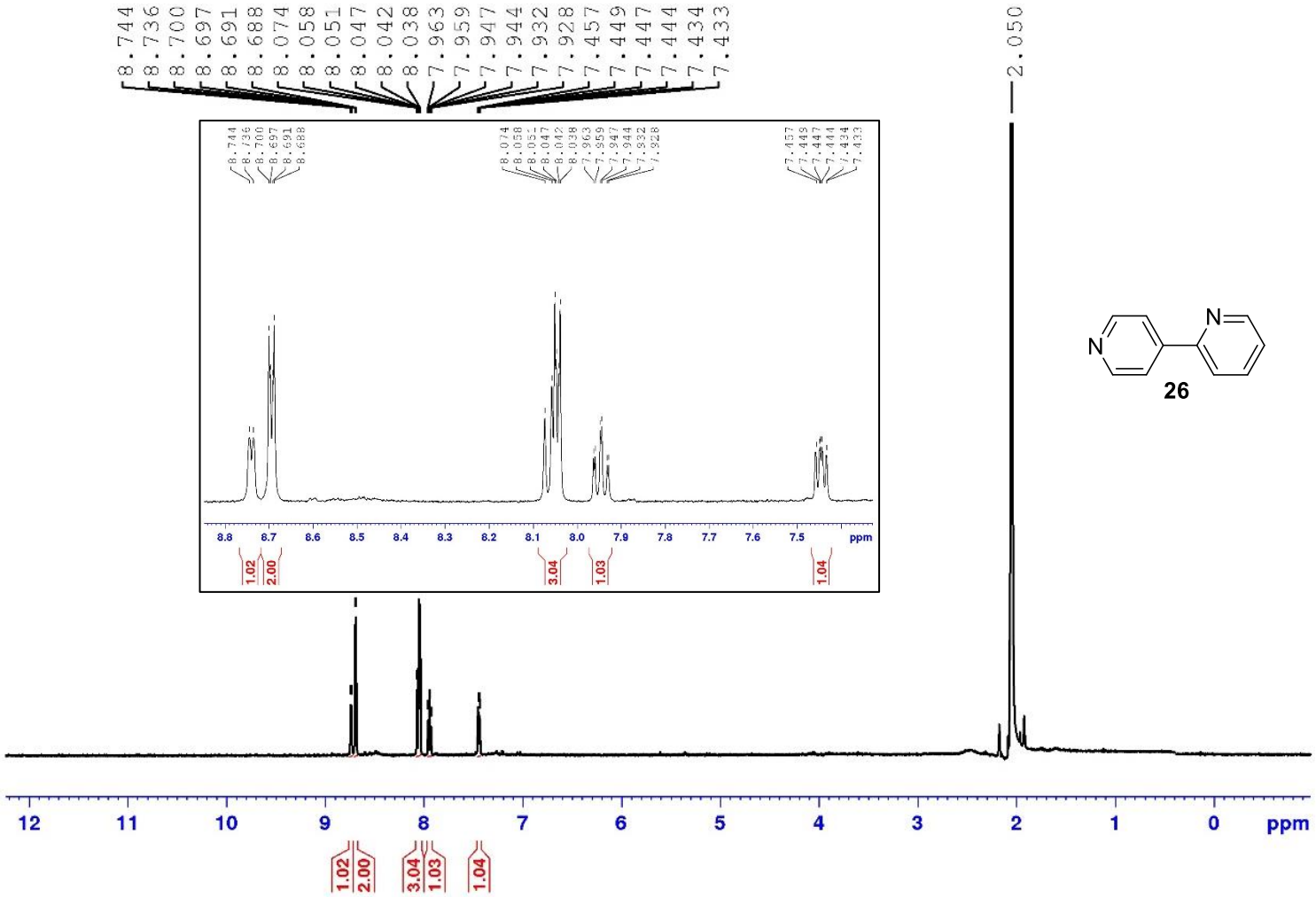


Figure S26. ^{1}H NMR spectrum of **26** (500 MHz, d_6-acetone, 25 °C).

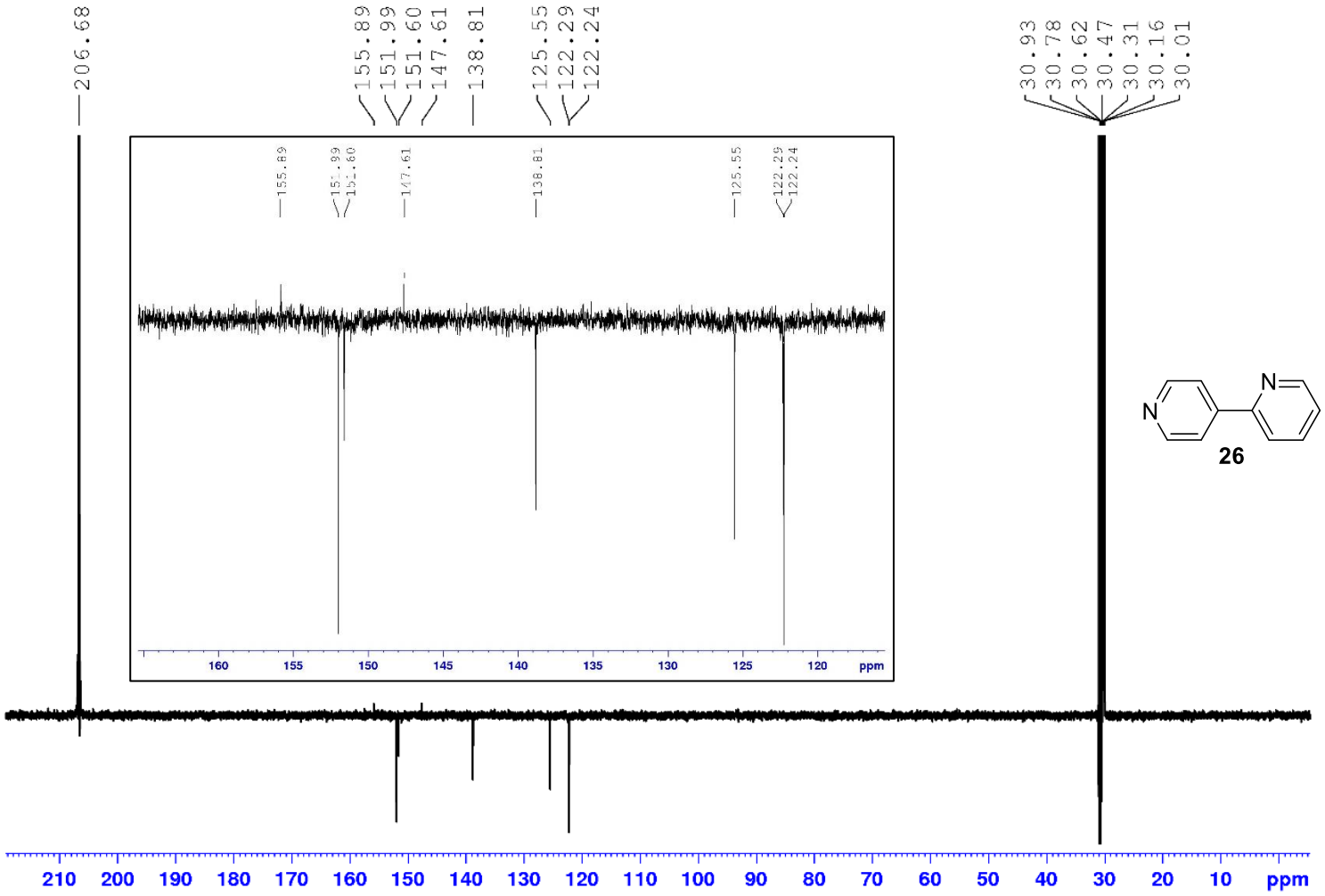


Figure S27. ^{13}C NMR APT spectrum of **26** (125 MHz, d_6-acetone, 25 °C).

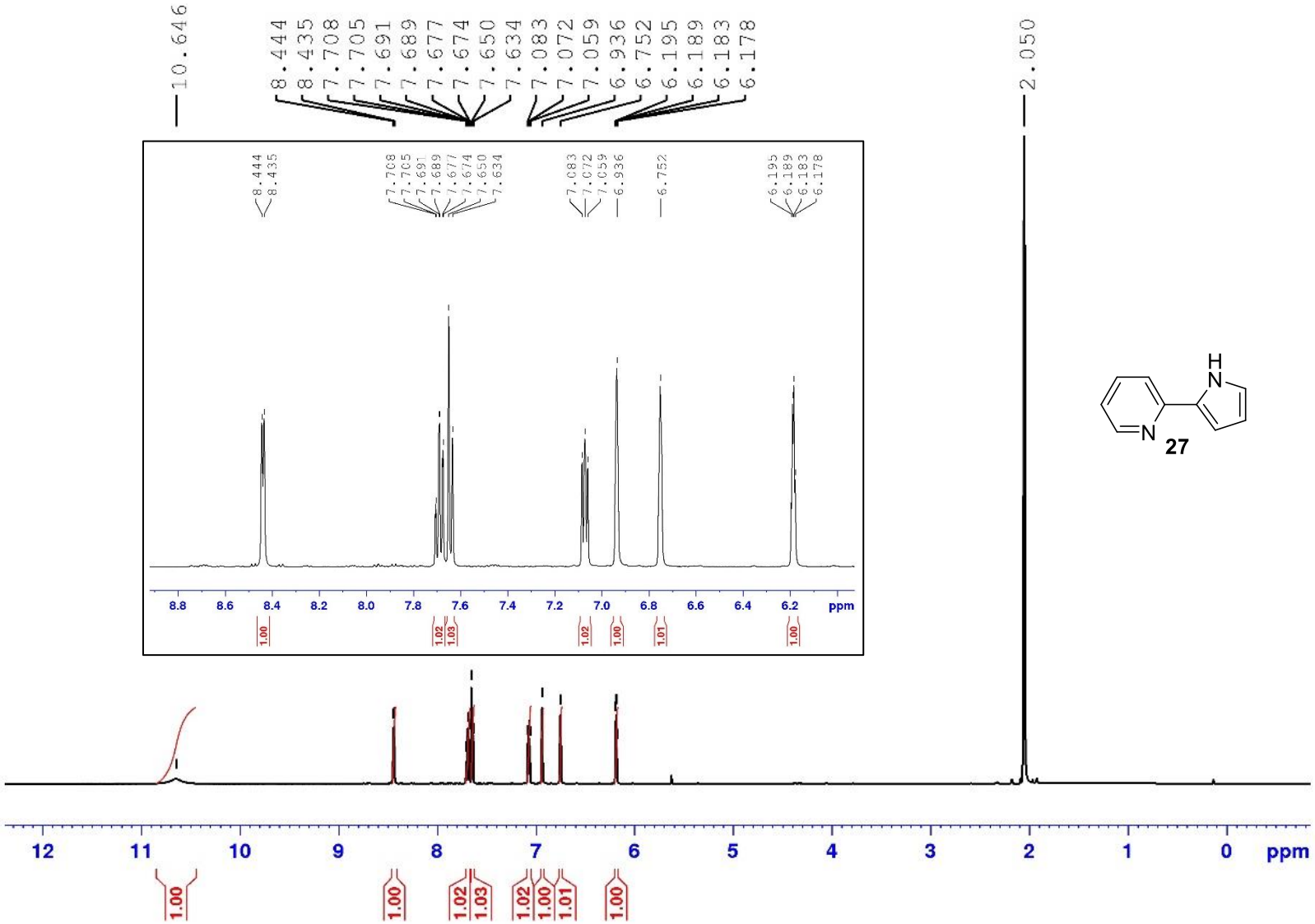


Figure S28. ^{1}H NMR spectrum of **27** (500 MHz, d_6-acetone, 25 °C).

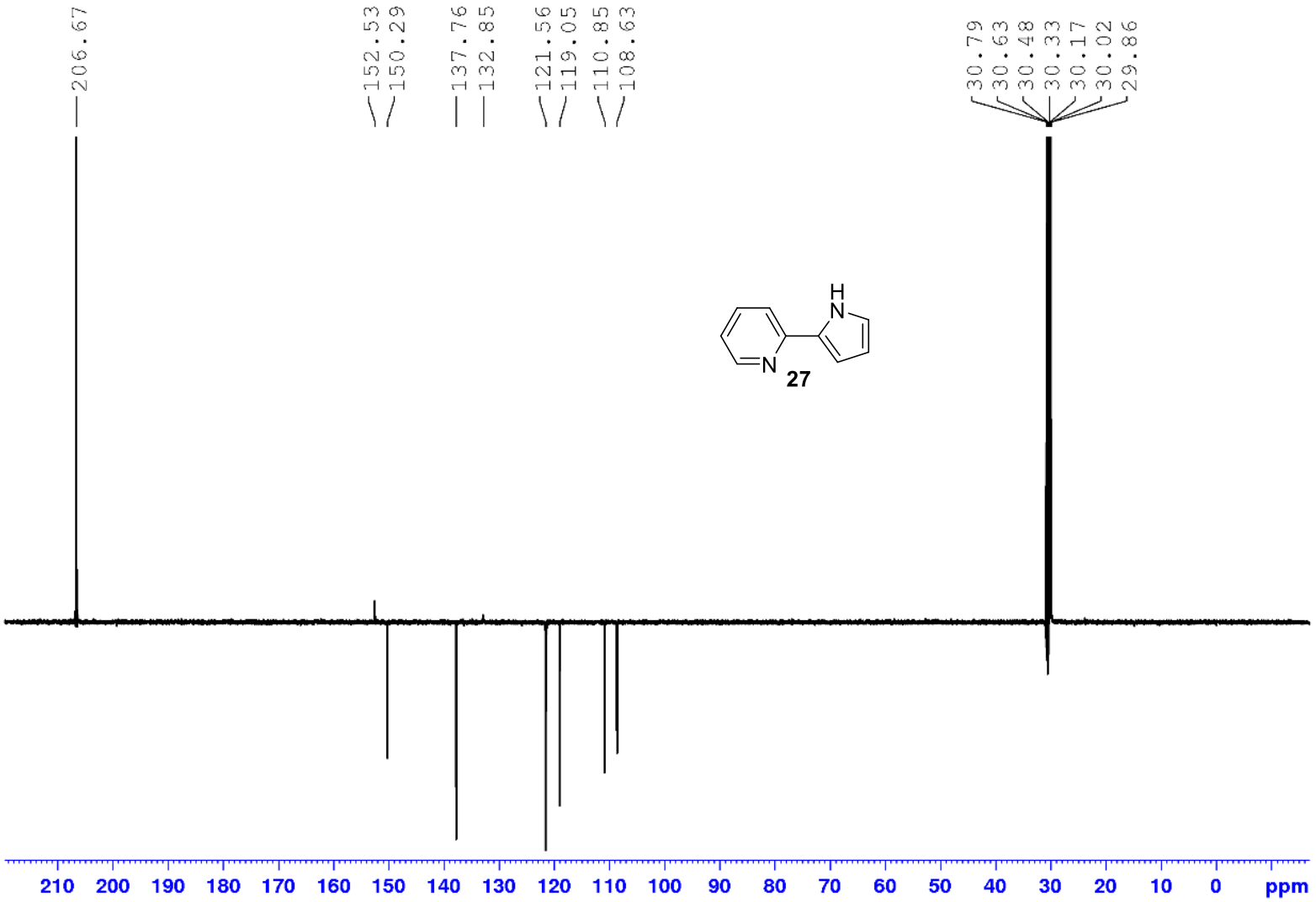


Figure S29. ^{13}C NMR APT spectrum of **27** (125 MHz, d_6-acetone, 25 °C).

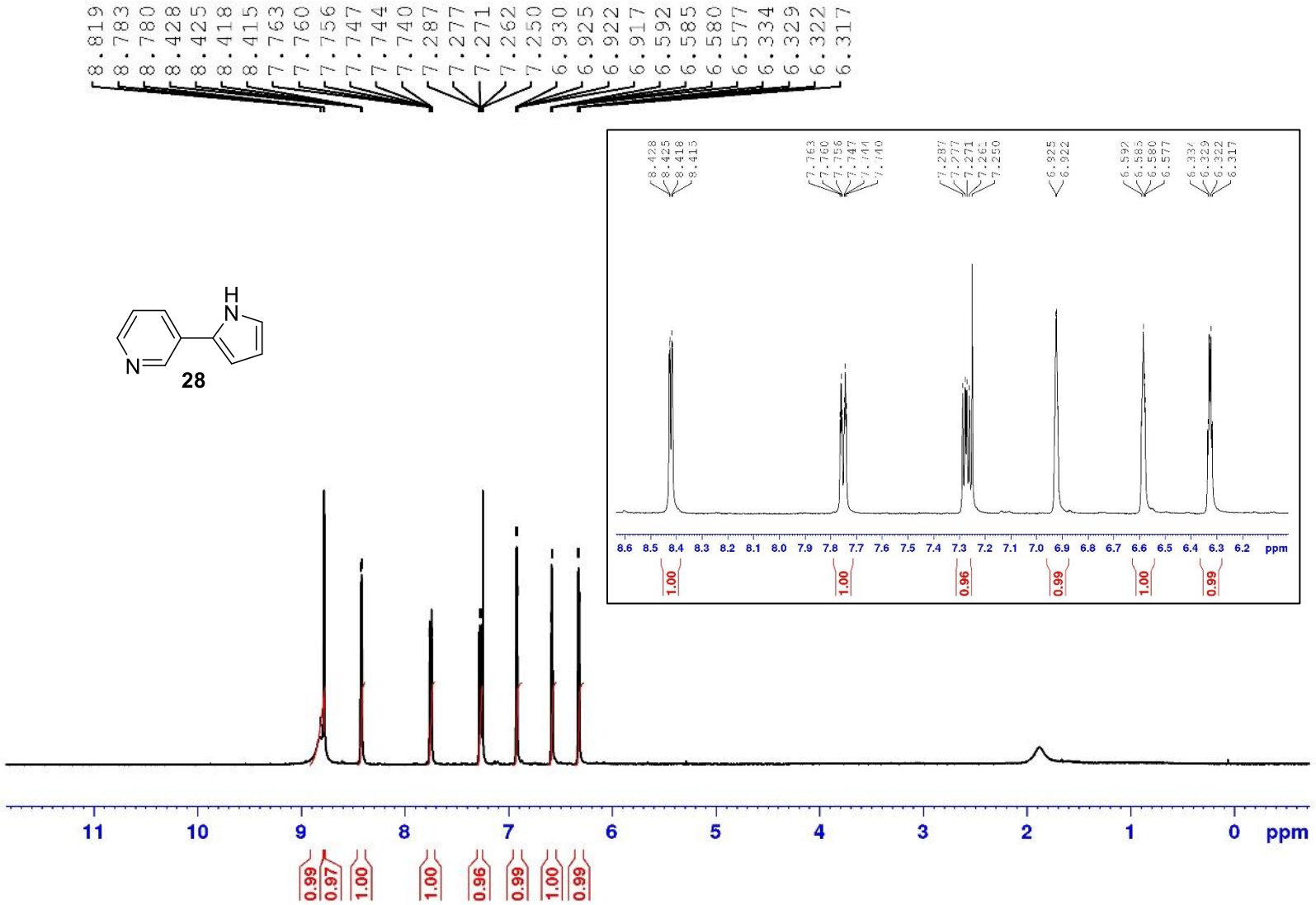


Figure S30. ^{1}H NMR spectrum of **28**(500 MHz, $CDCl_3$, 25 °C).

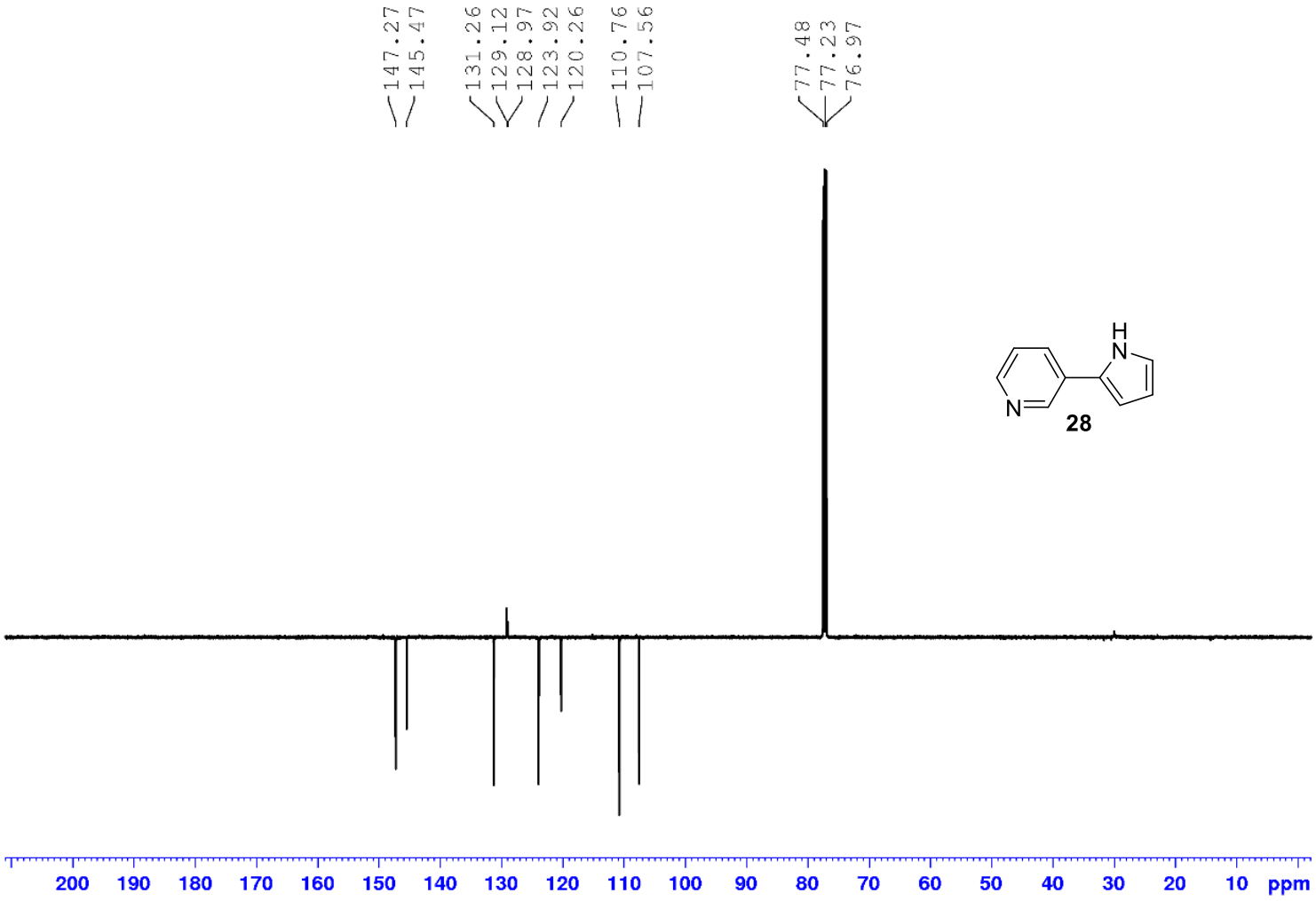


Figure S31. ^{13}C NMR APT spectrum of **28** (125 MHz, $CDCl_3$, 25 °C).

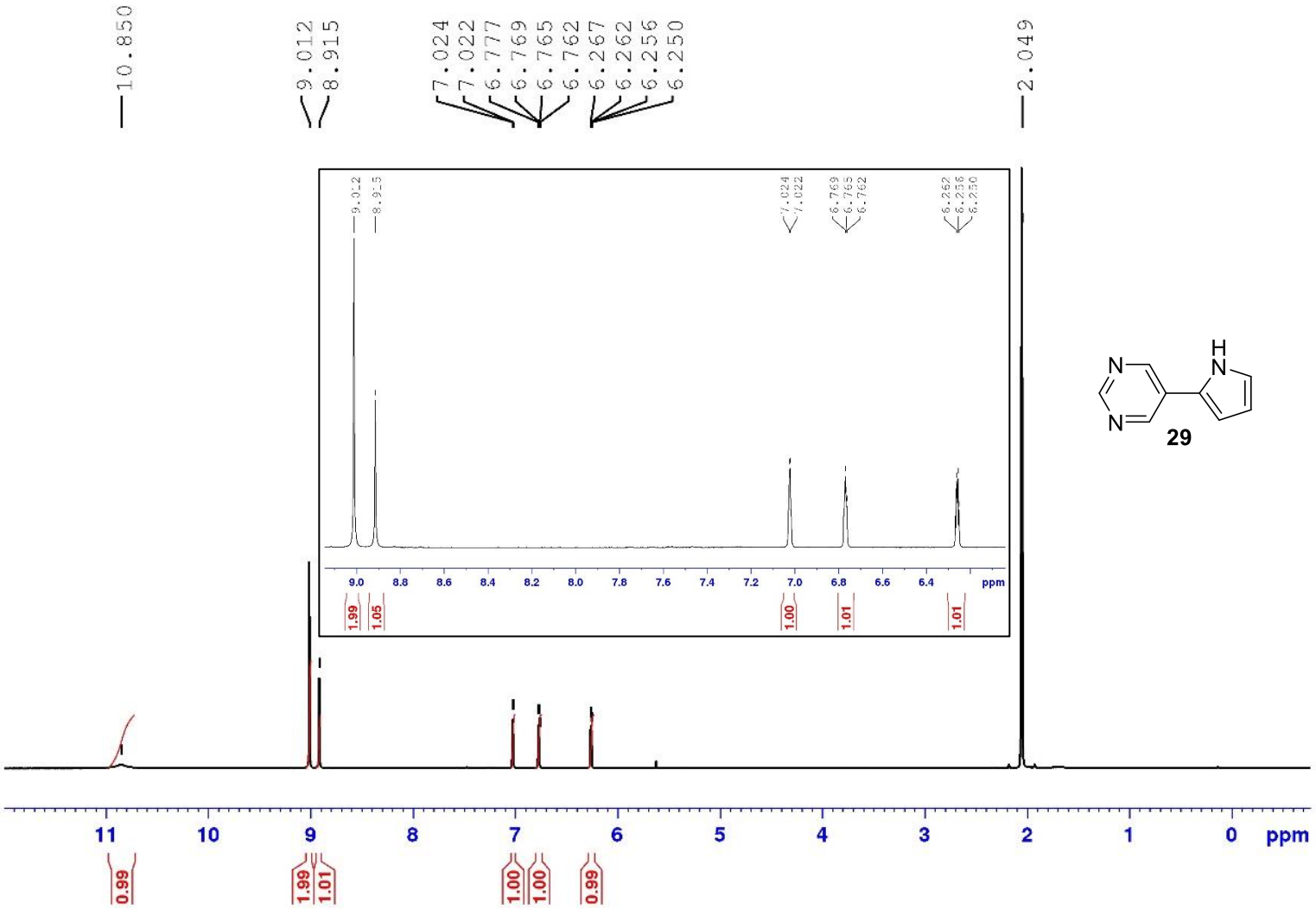


Figure S32. ^{1}H NMR spectrum of **29** (500 MHz, d_6-acetone, 25 °C).

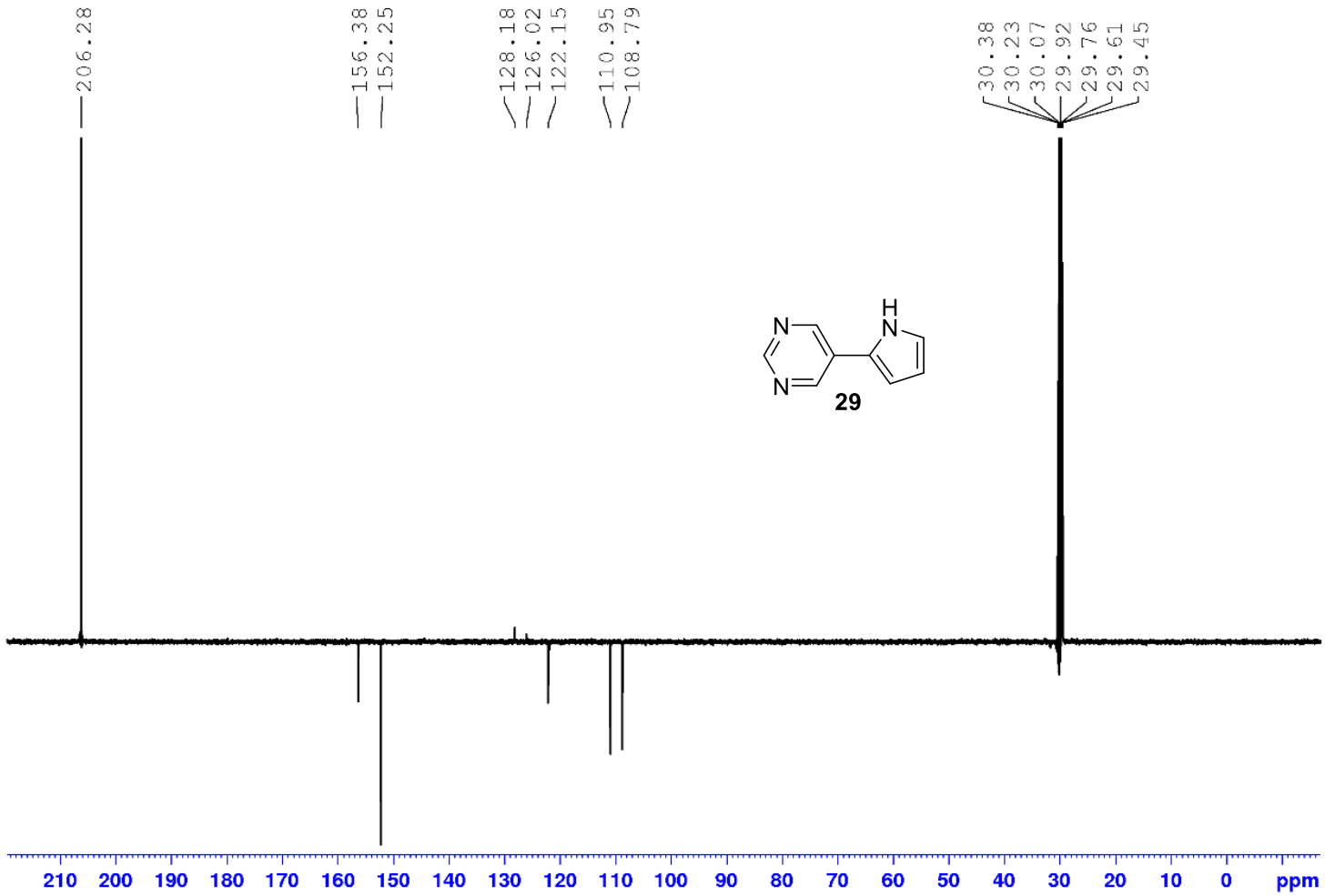


Figure S33. ^{13}C NMR APT spectrum of **29** (125 MHz, d_6-acetone, 25 °C).

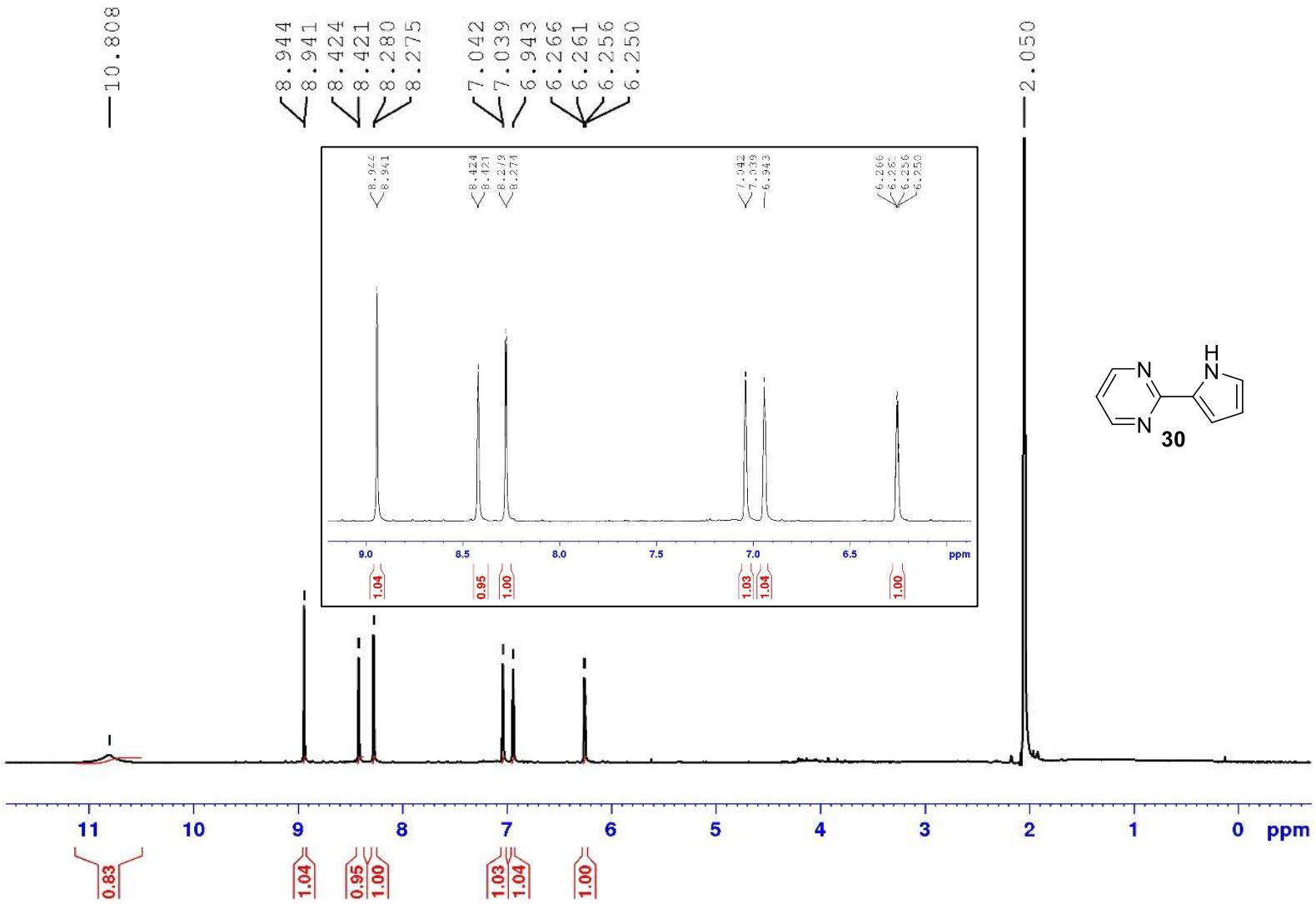


Figure S34. ^{1}H NMR spectrum of **30** (500 MHz, d_6-acetone, 25 °C).

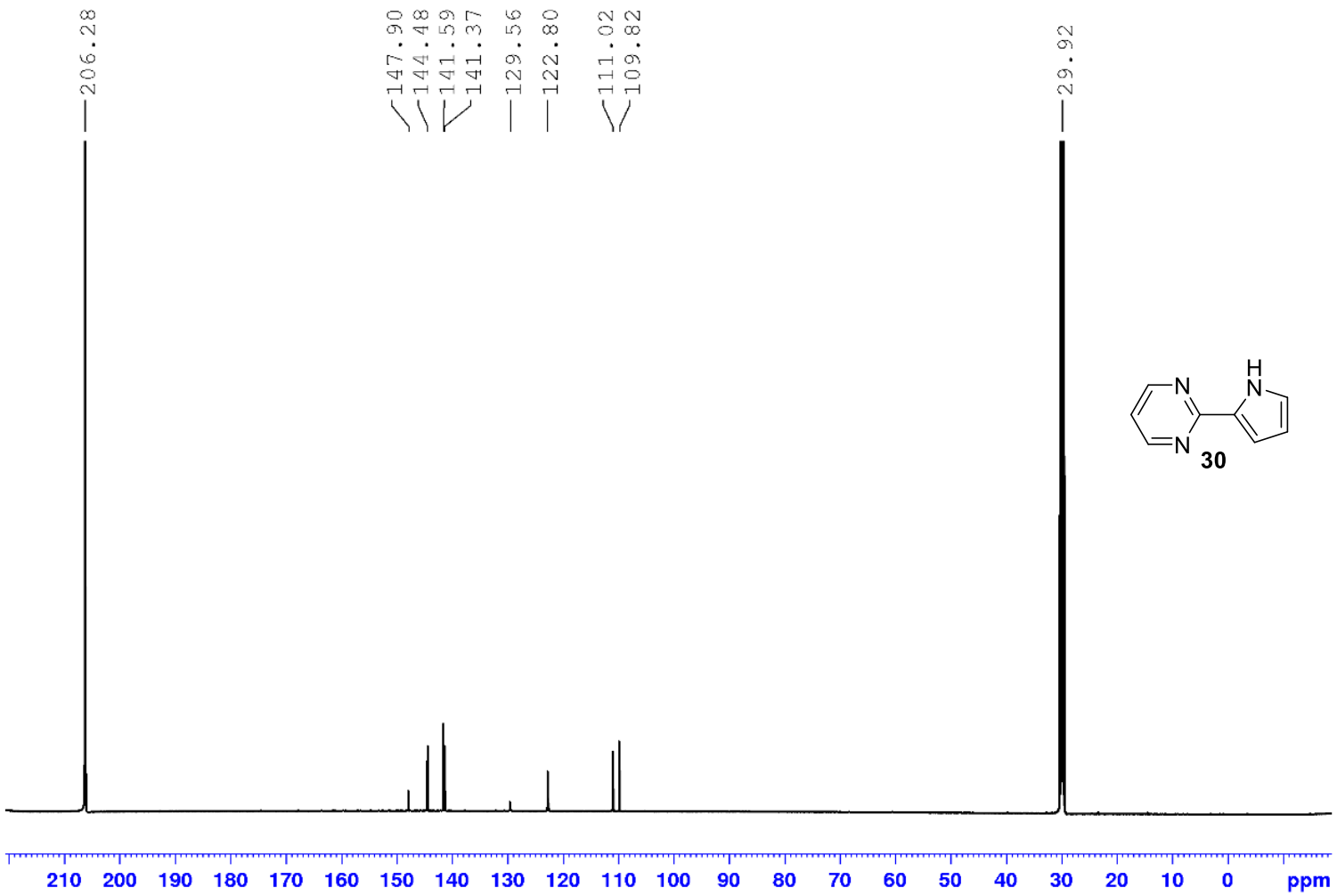


Figure S35. ^{13}C NMR spectrum of **30** (125 MHz, d_6-acetone, 25 °C).

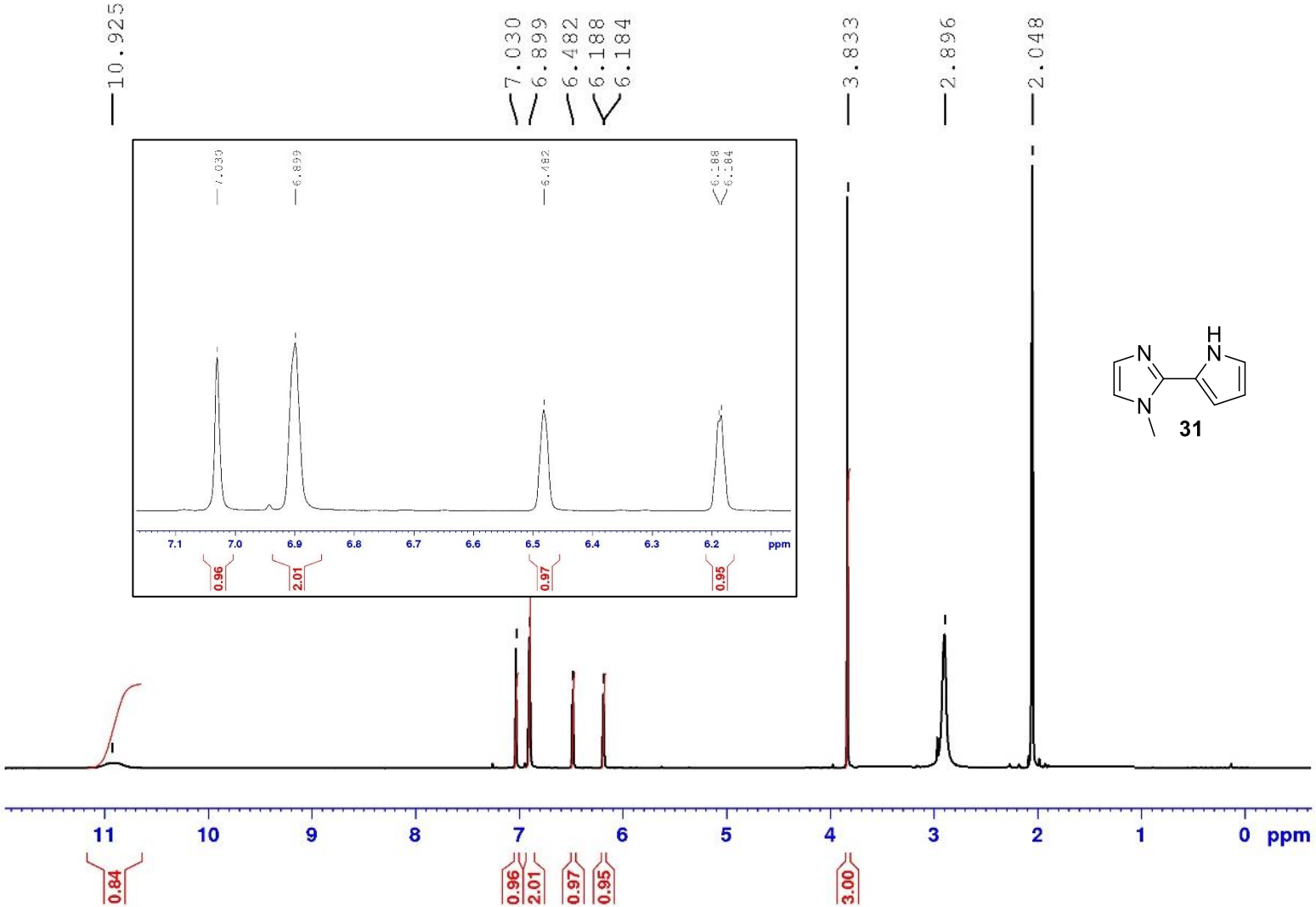


Figure S36. ^{1}H NMR spectrum of **31** (500 MHz, d_6-acetone, 25 °C).

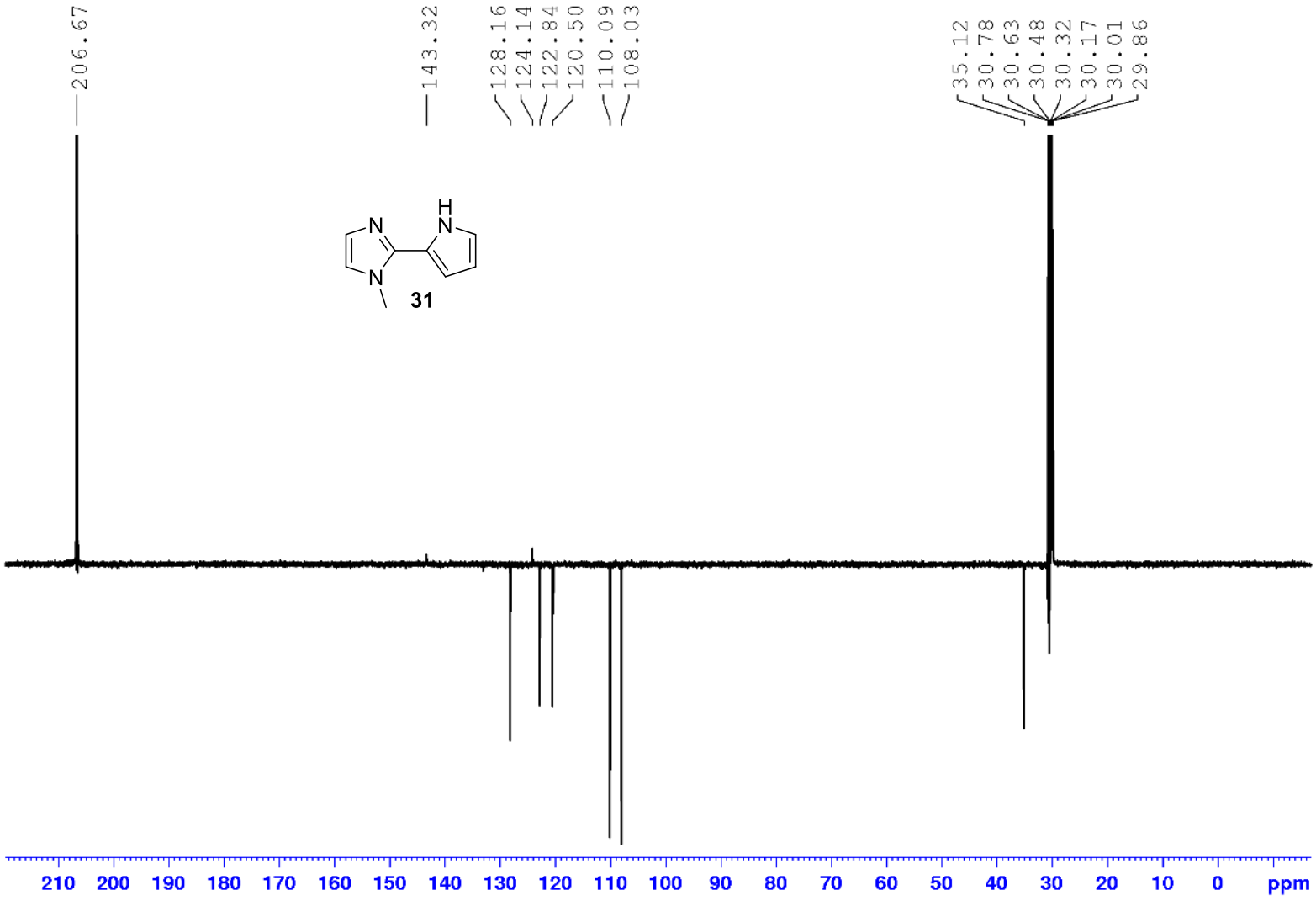


Figure S37. ^{13}C NMR APT spectrum of **31** (125 MHz, d_6-acetone, 25 °C).

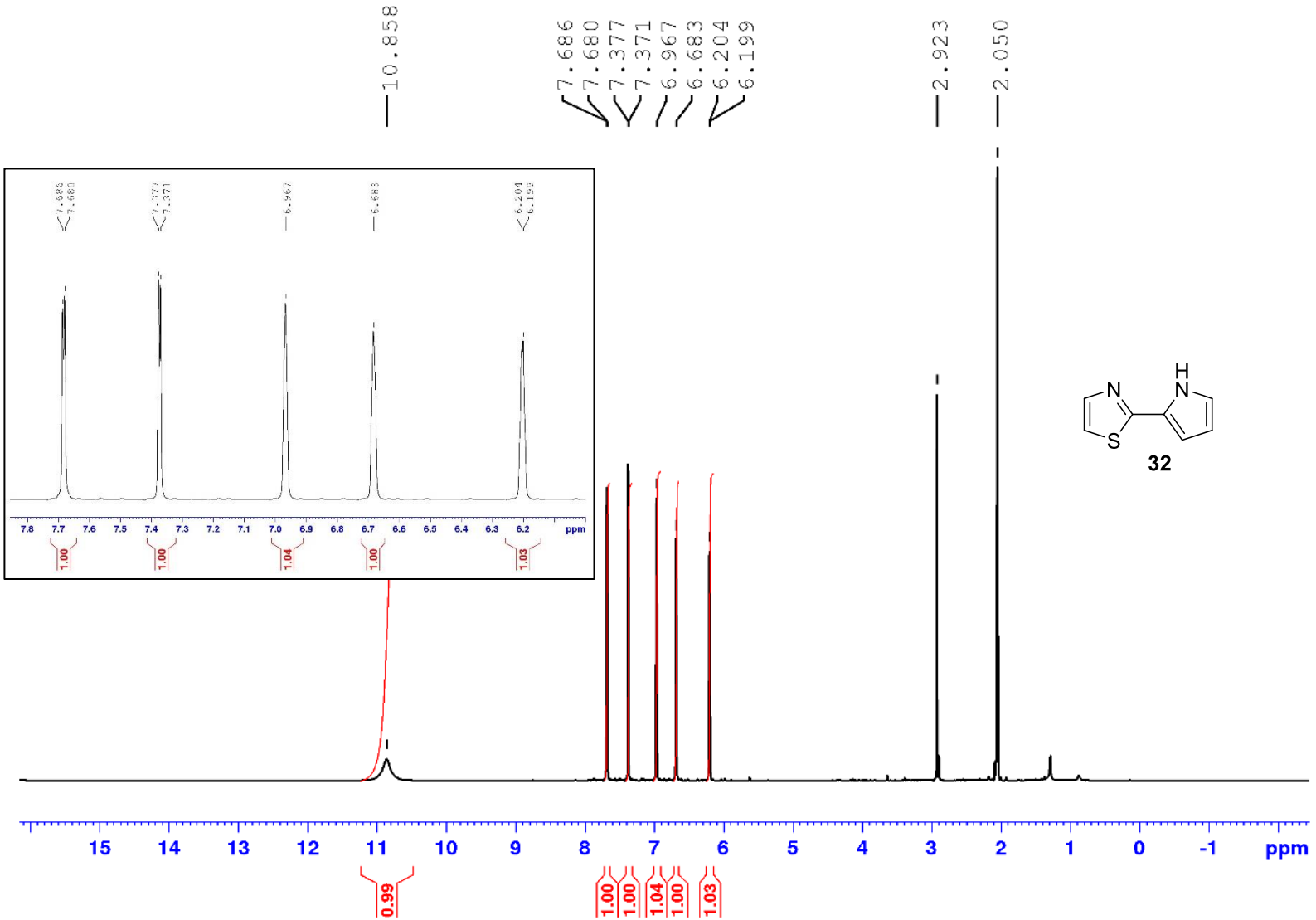


Figure S38. ^{1}H NMR spectrum of **32** (500 MHz, d_6-acetone, 25 °C).

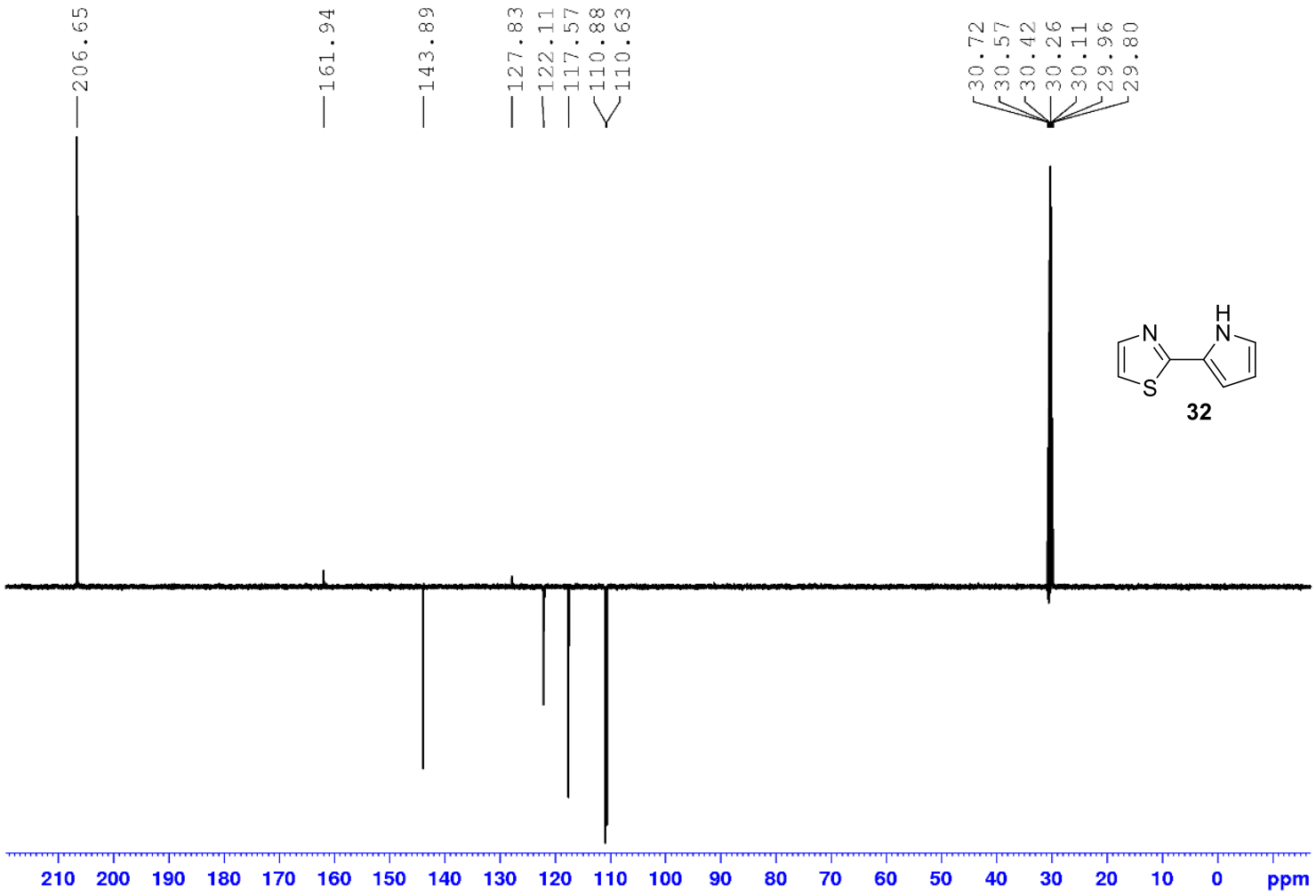


Figure S39. ^{13}C NMR APT spectrum of **32** (125 MHz, d_6-acetone, 25 °C).

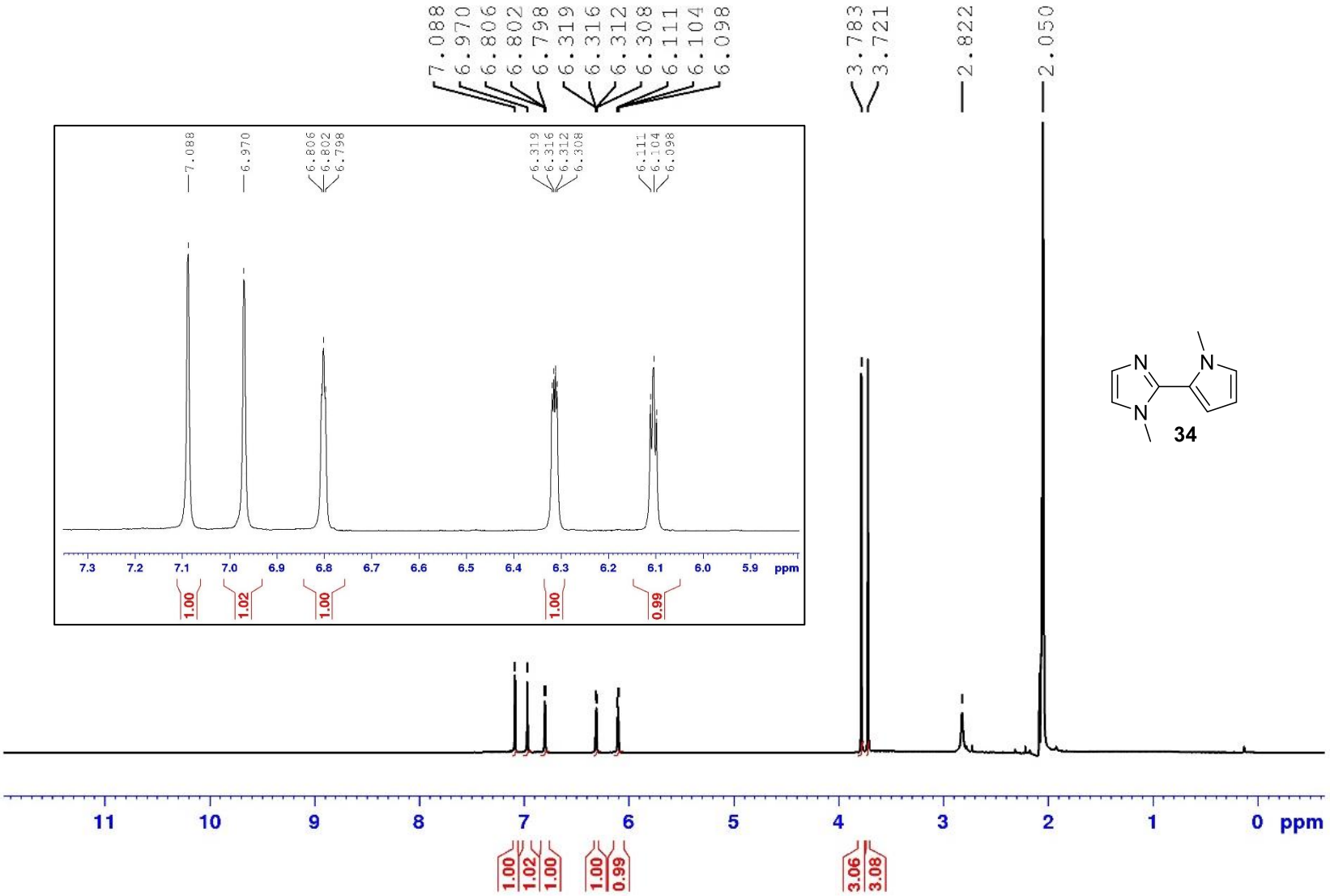


Figure S40. ^{1}H NMR spectrum of **34** (500 MHz, d_6-acetone, 25 °C).

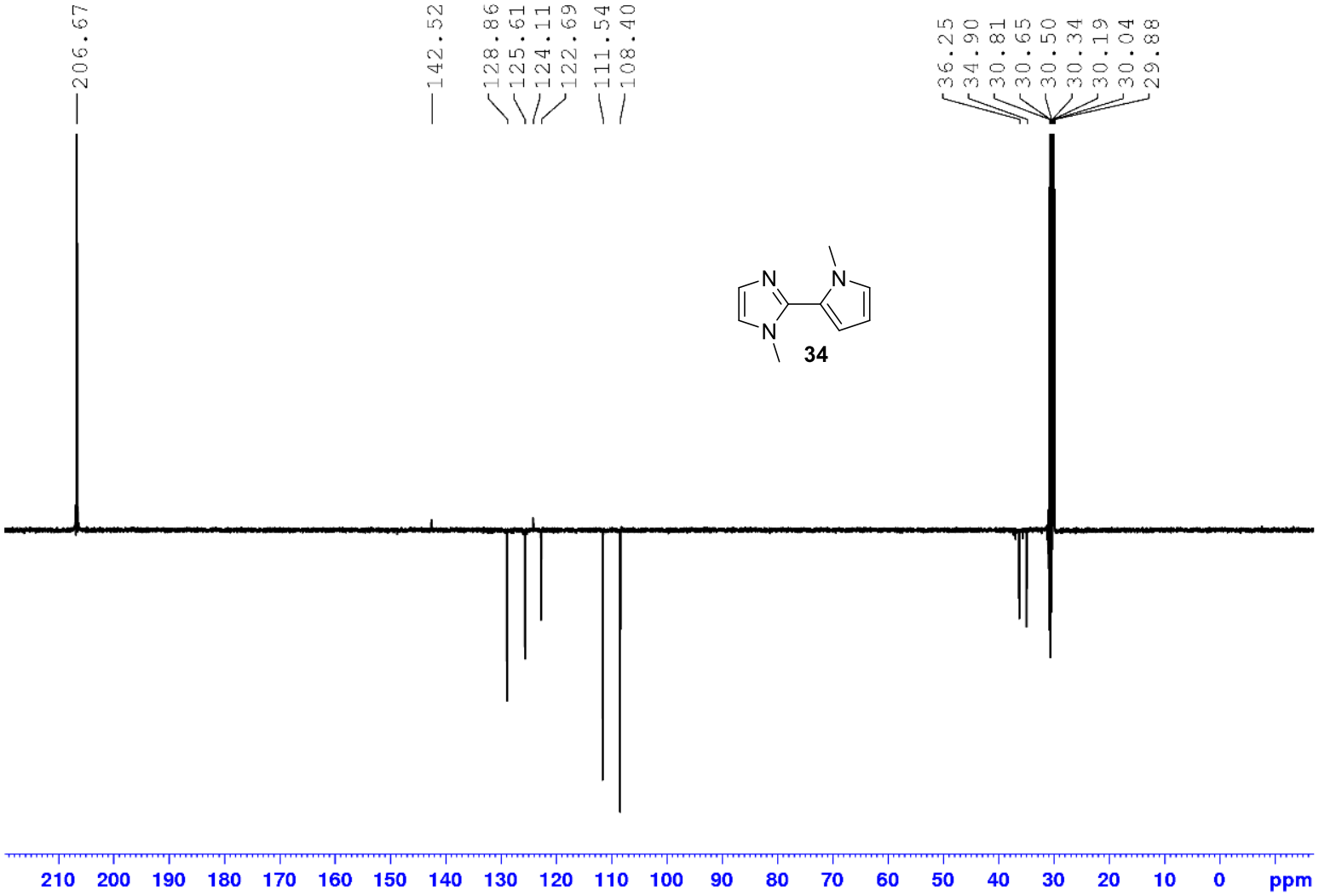


Figure S41. ^{13}C NMR APT spectrum of **34** (125 MHz, d_6-acetone, 25 °C).

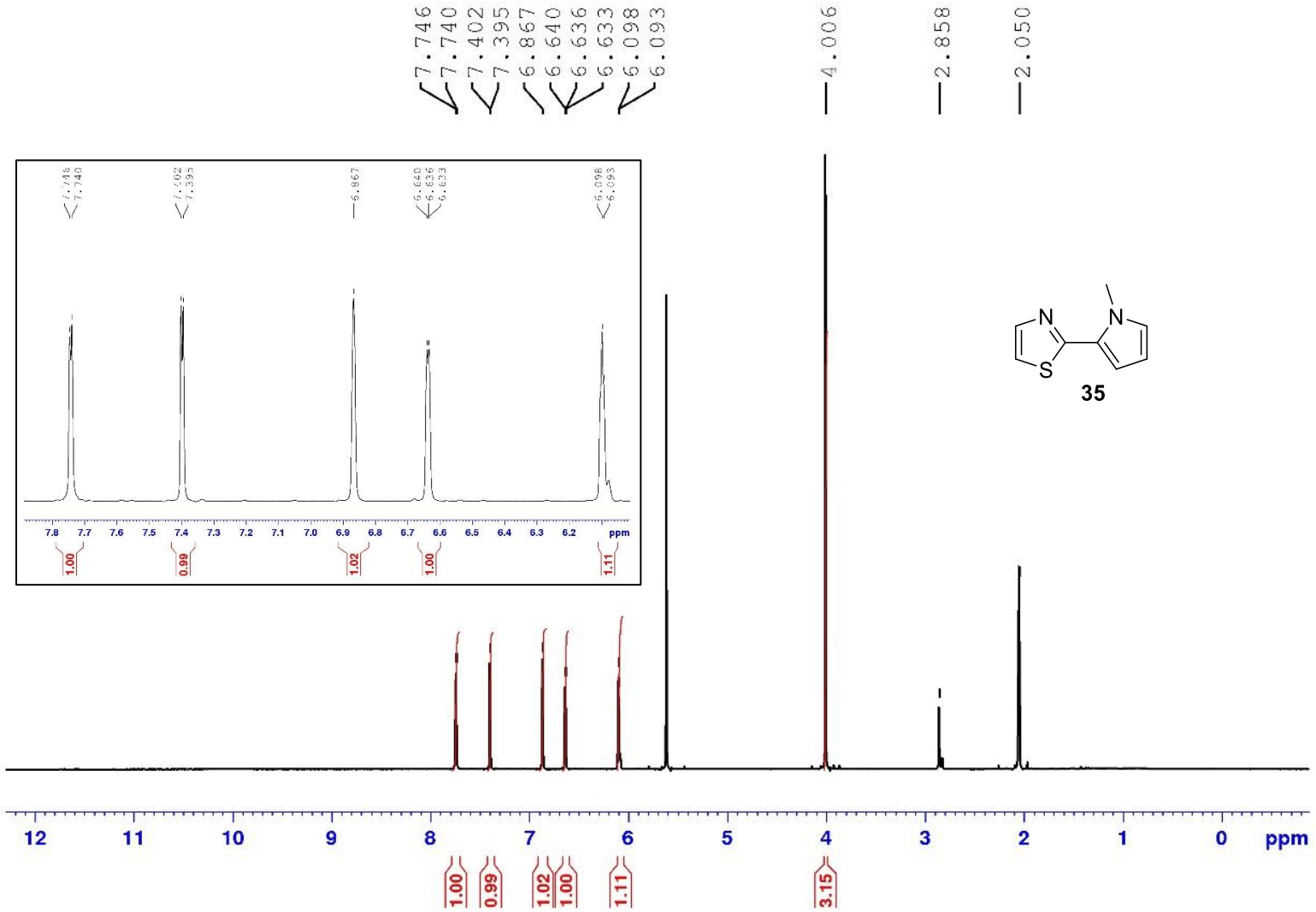


Figure S42. ^{1}H NMR spectrum of **35** (500 MHz, d_6-acetone, 25 °C).

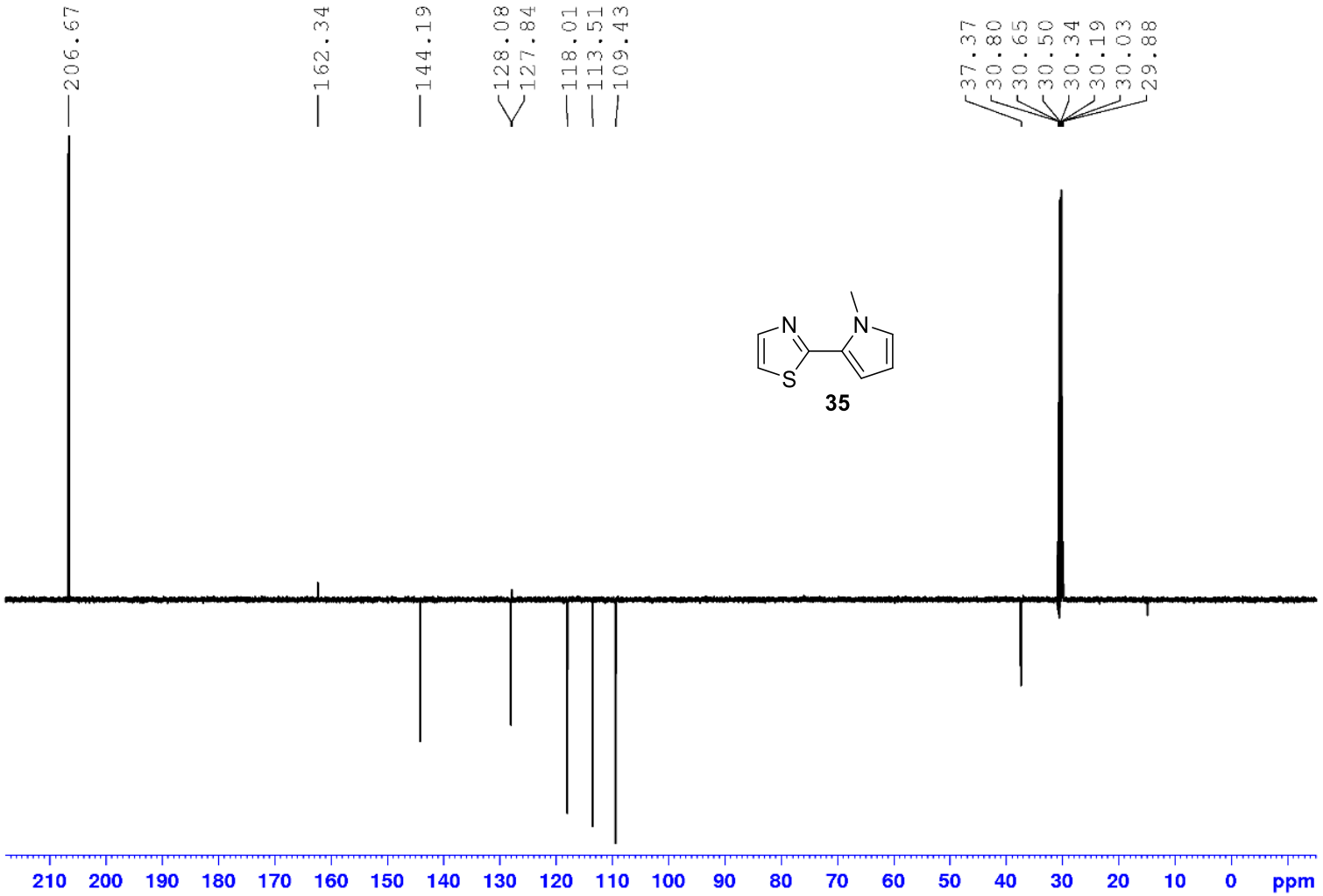


Figure S43. ^{13}C NMR APT spectrum of **35** (125 MHz, d_6-acetone, 25 °C).

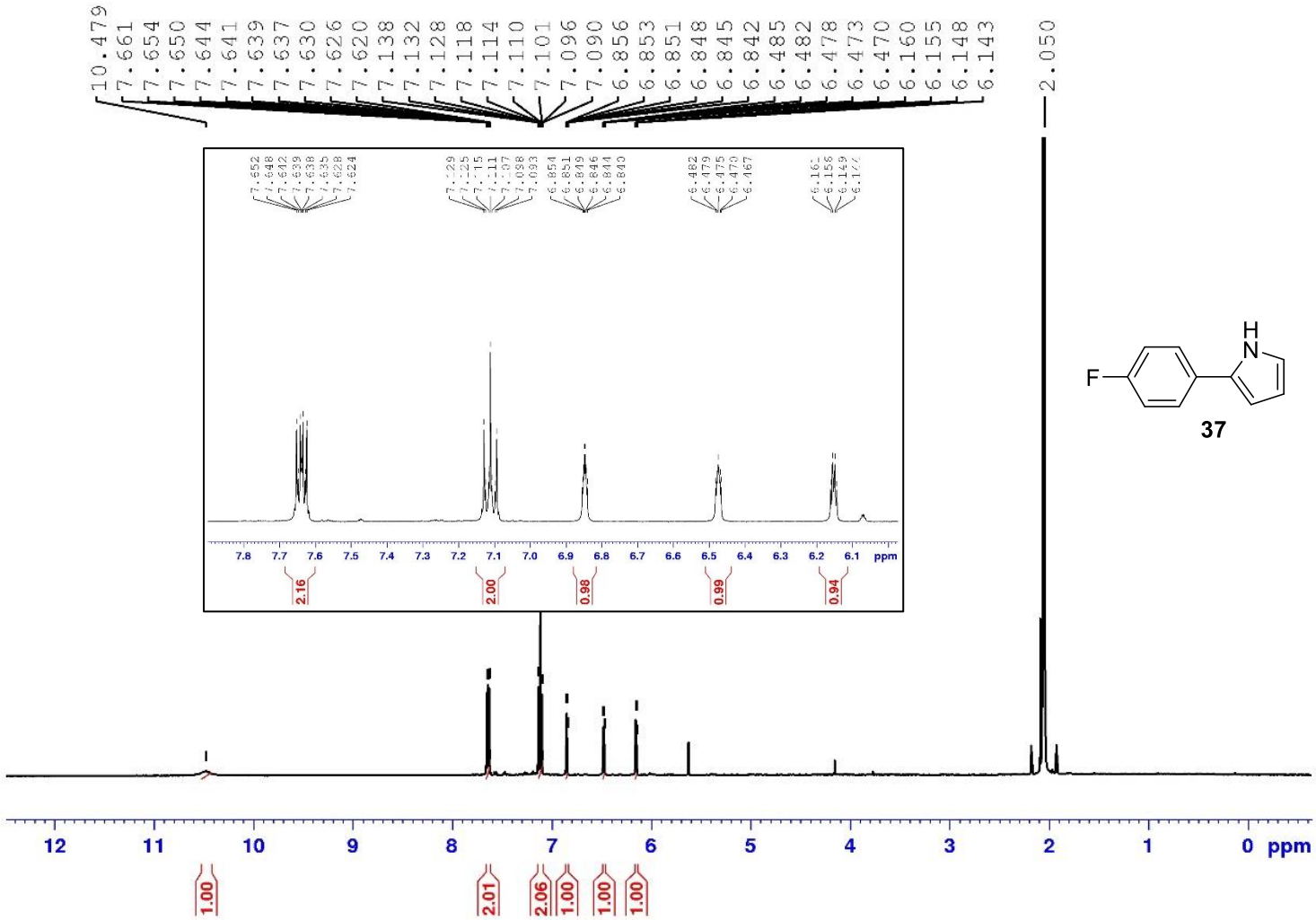


Figure S44. ^{1}H NMR spectrum of **37** (500 MHz, d_6-acetone, 25 °C).

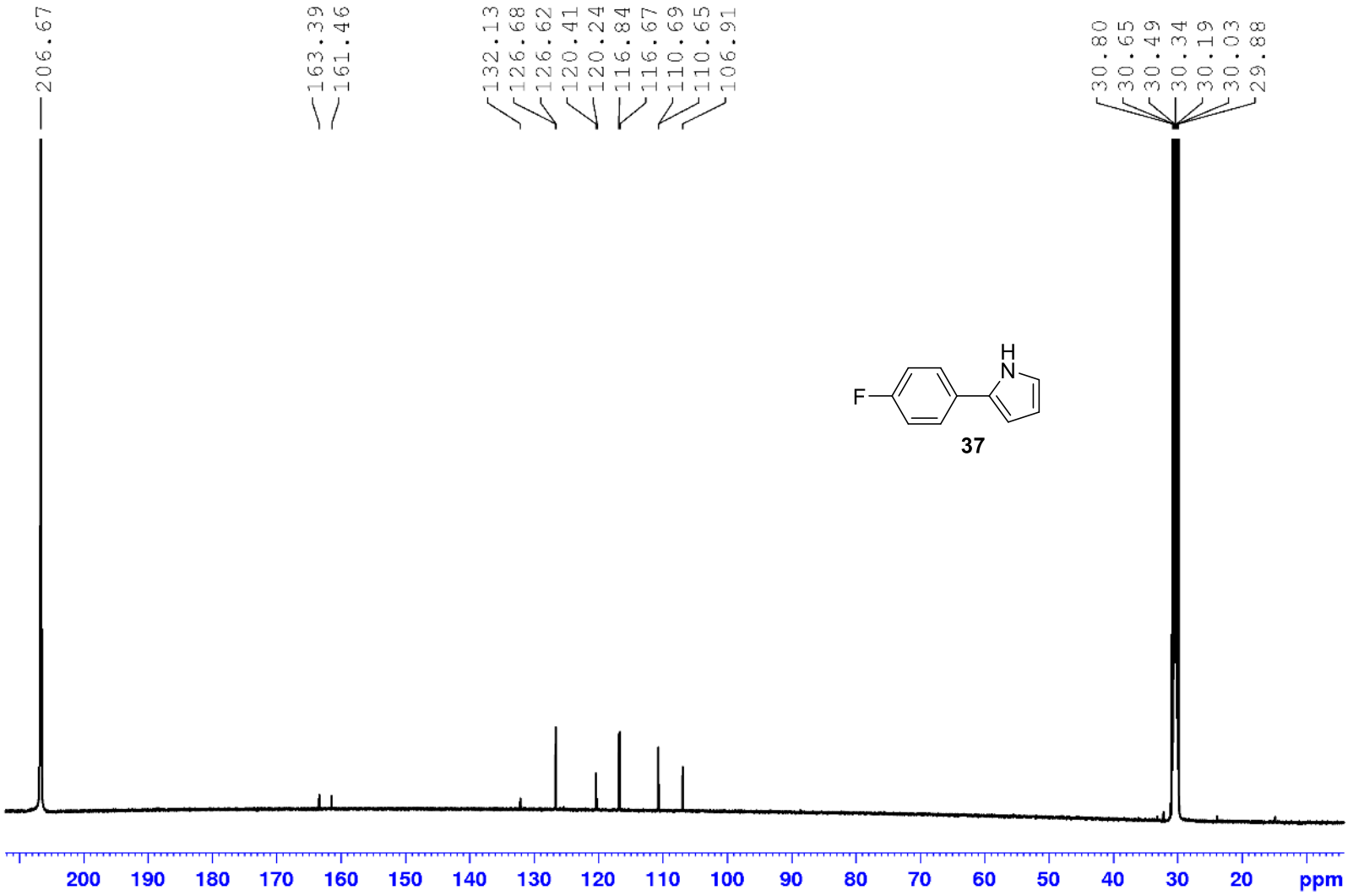


Figure S45. ^{13}C NMR spectrum of **37** (125 MHz, d_6-acetone, 25 °C).

Figure 46. ^{19}F NMR spectrum of **37** (470 MHz, d_6-acetone, 25 °C).

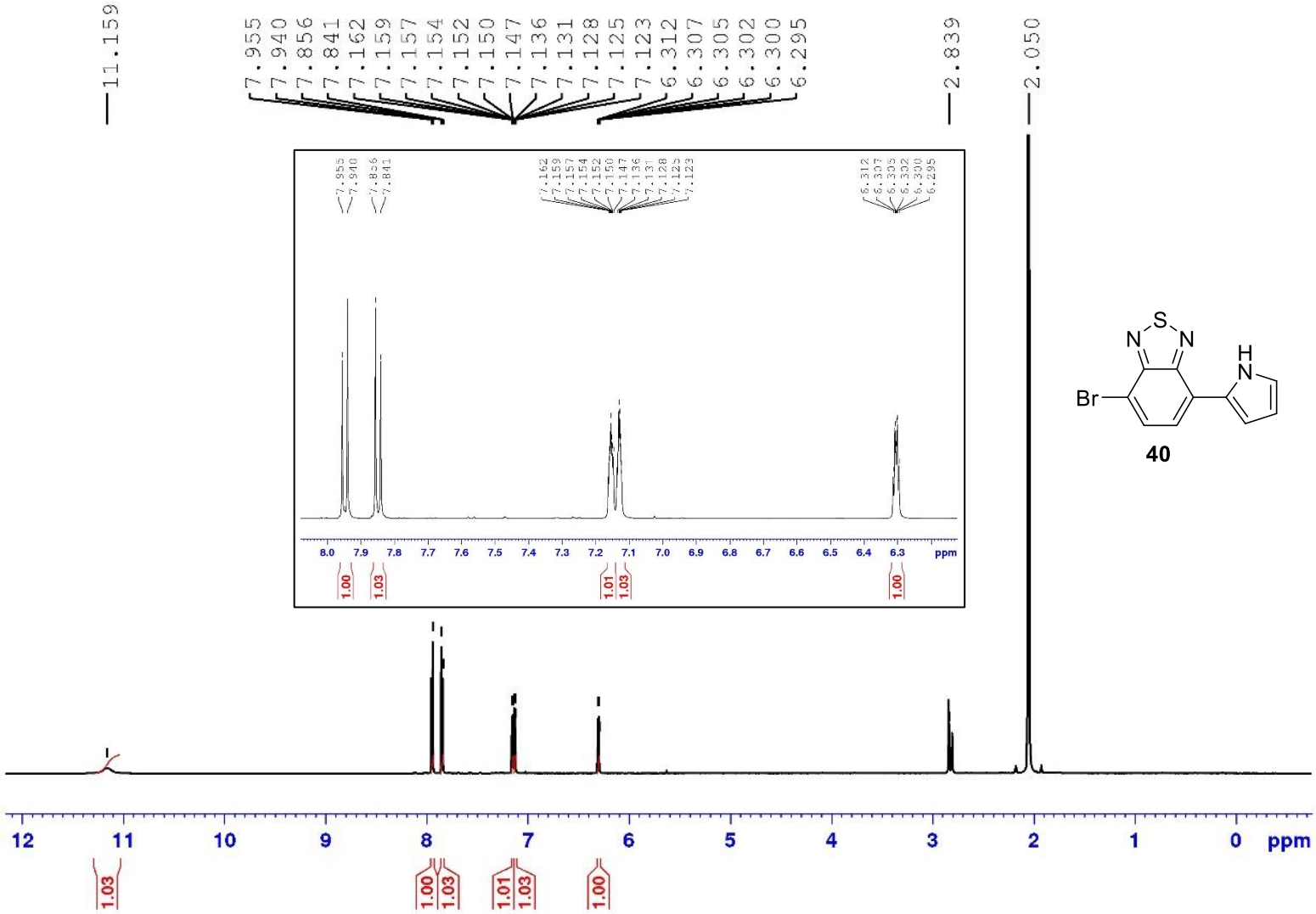


Figure S47. ^{1}H NMR spectrum of **40** (500 MHz, d_6-acetone, 25 °C).

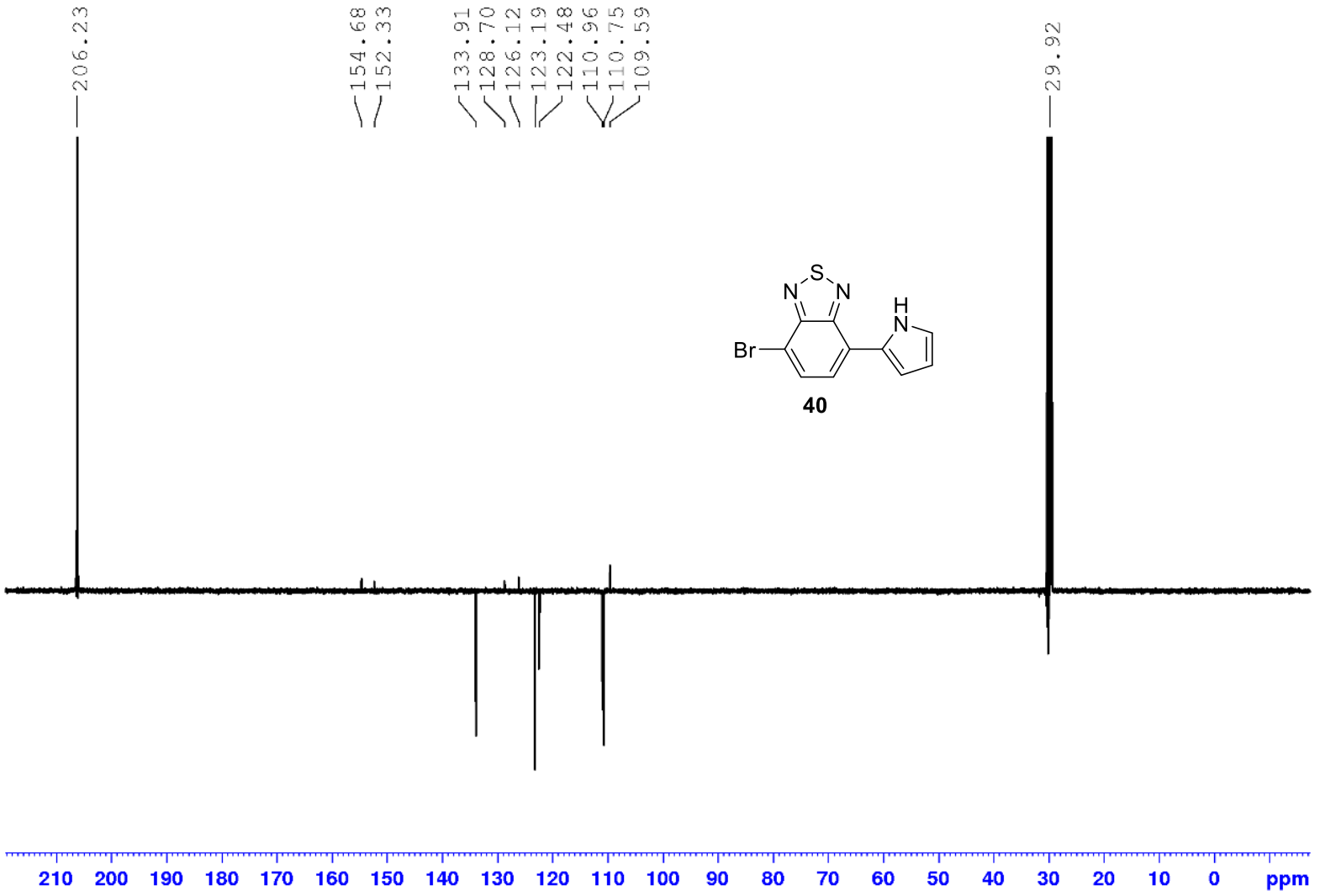


Figure S48. ^{13}C NMR APT spectrum of **40** (125 MHz, d_6-acetone, 25 °C).

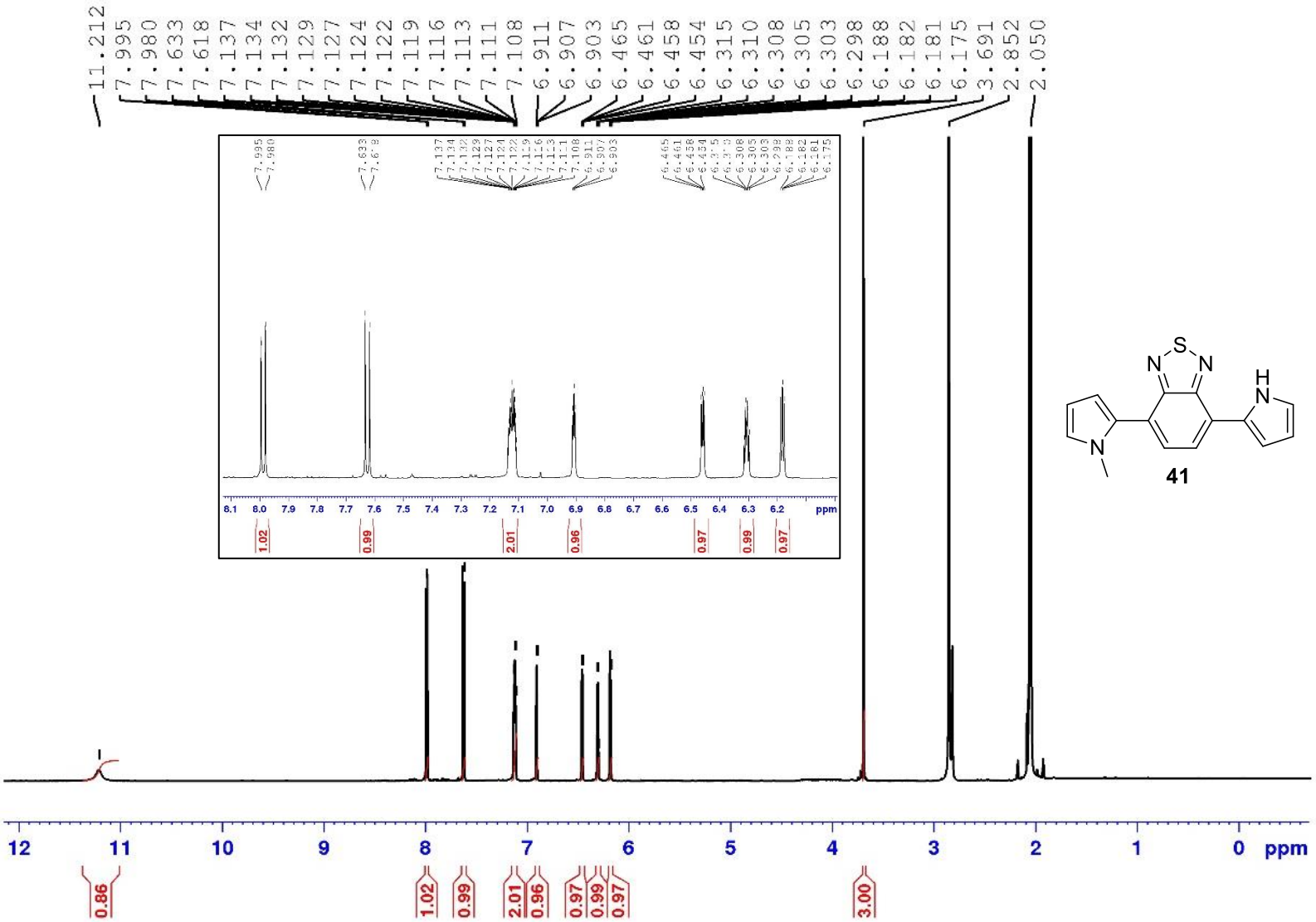


Figure S49. ^{1}H NMR spectrum of **41** (500 MHz, d_6-acetone, 25 °C).

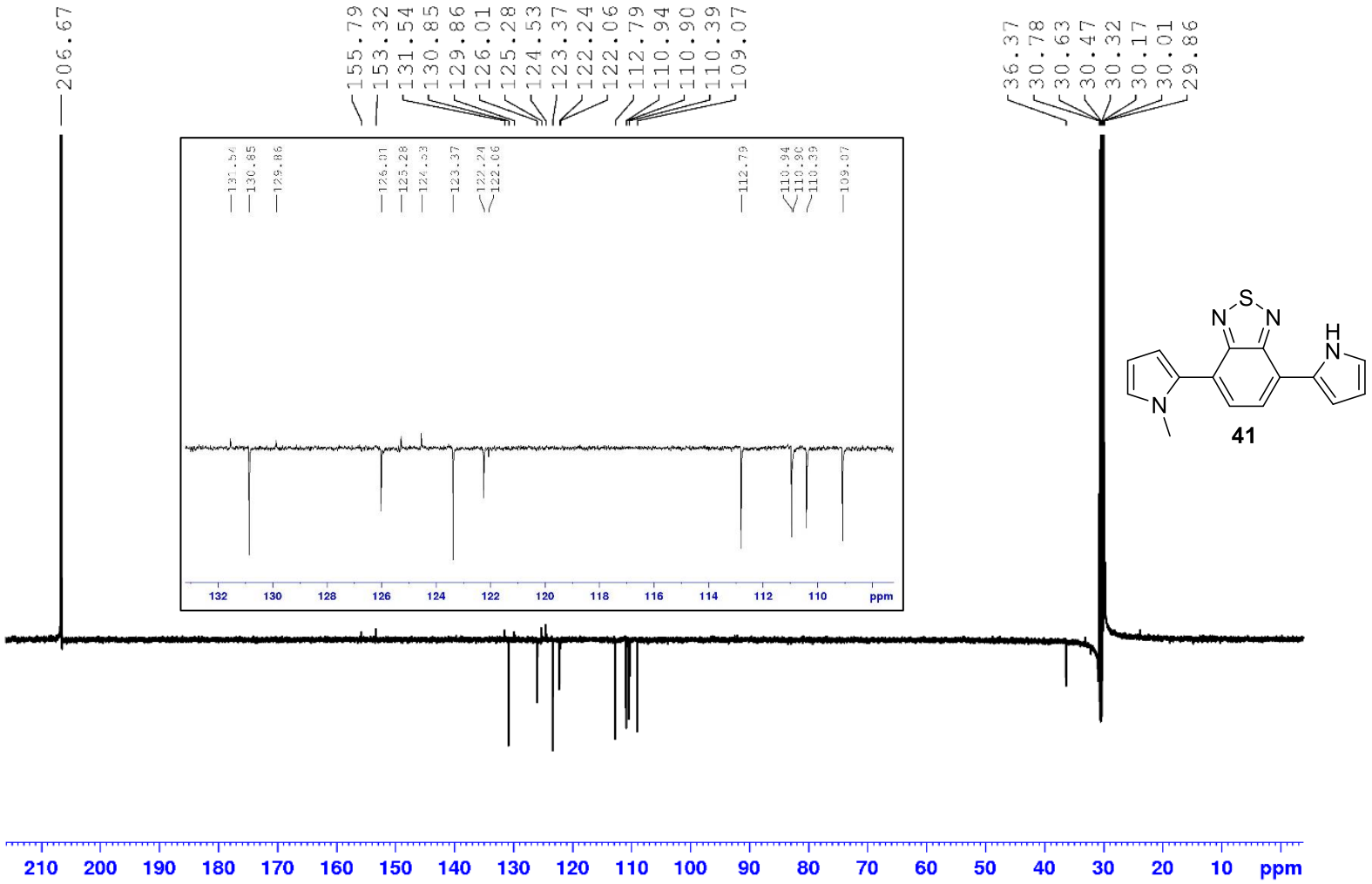


Figure S50. ^{13}C NMR APT spectrum of **41** (125 MHz, d_6-acetone, 25 °C).

6. GC/MS records

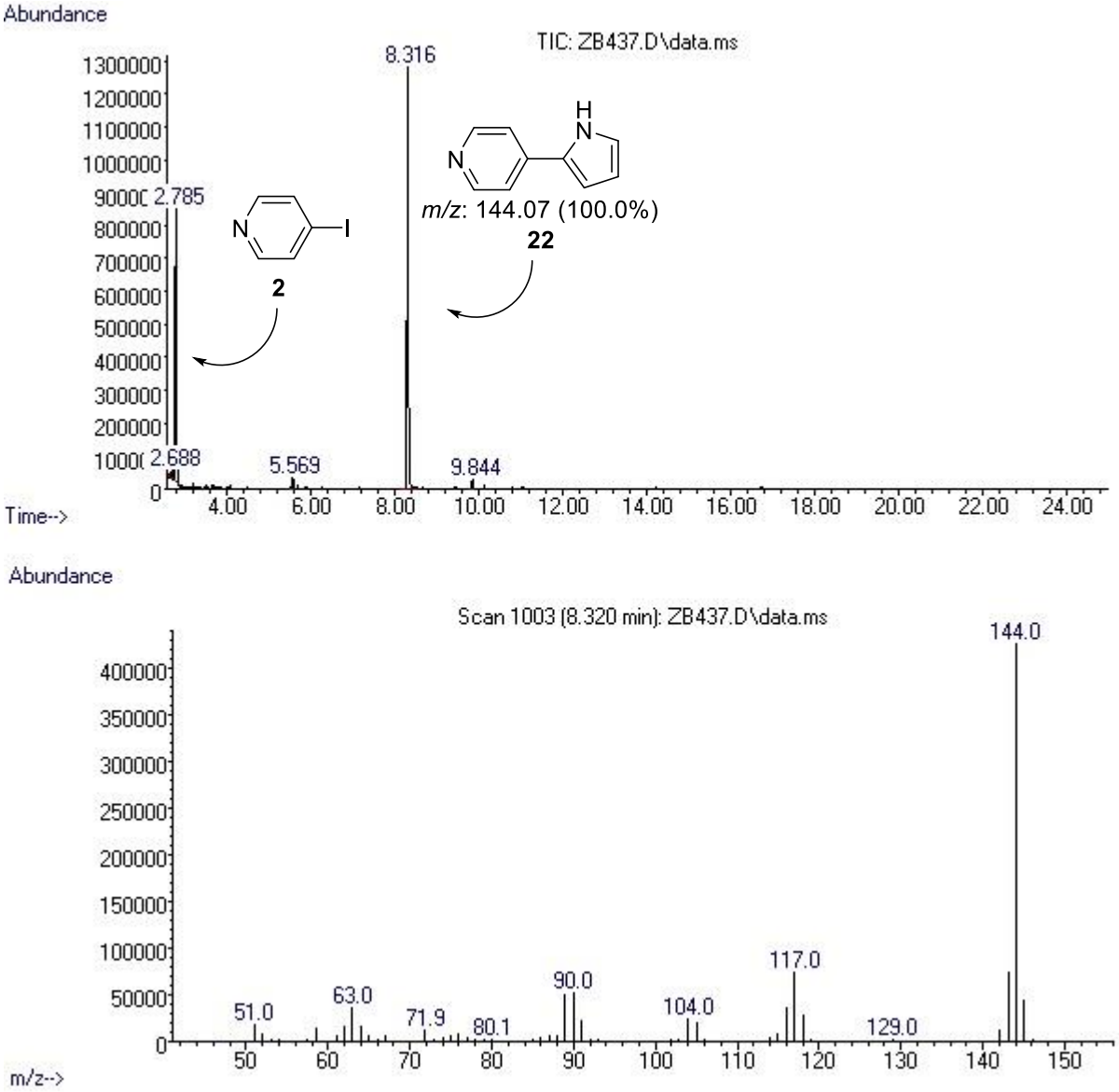


Figure S51. Representative GC/MS record of the reaction between 2-iodopyridine (**2**) and 1*H*-pyrrole (**16**) affording product **22**.

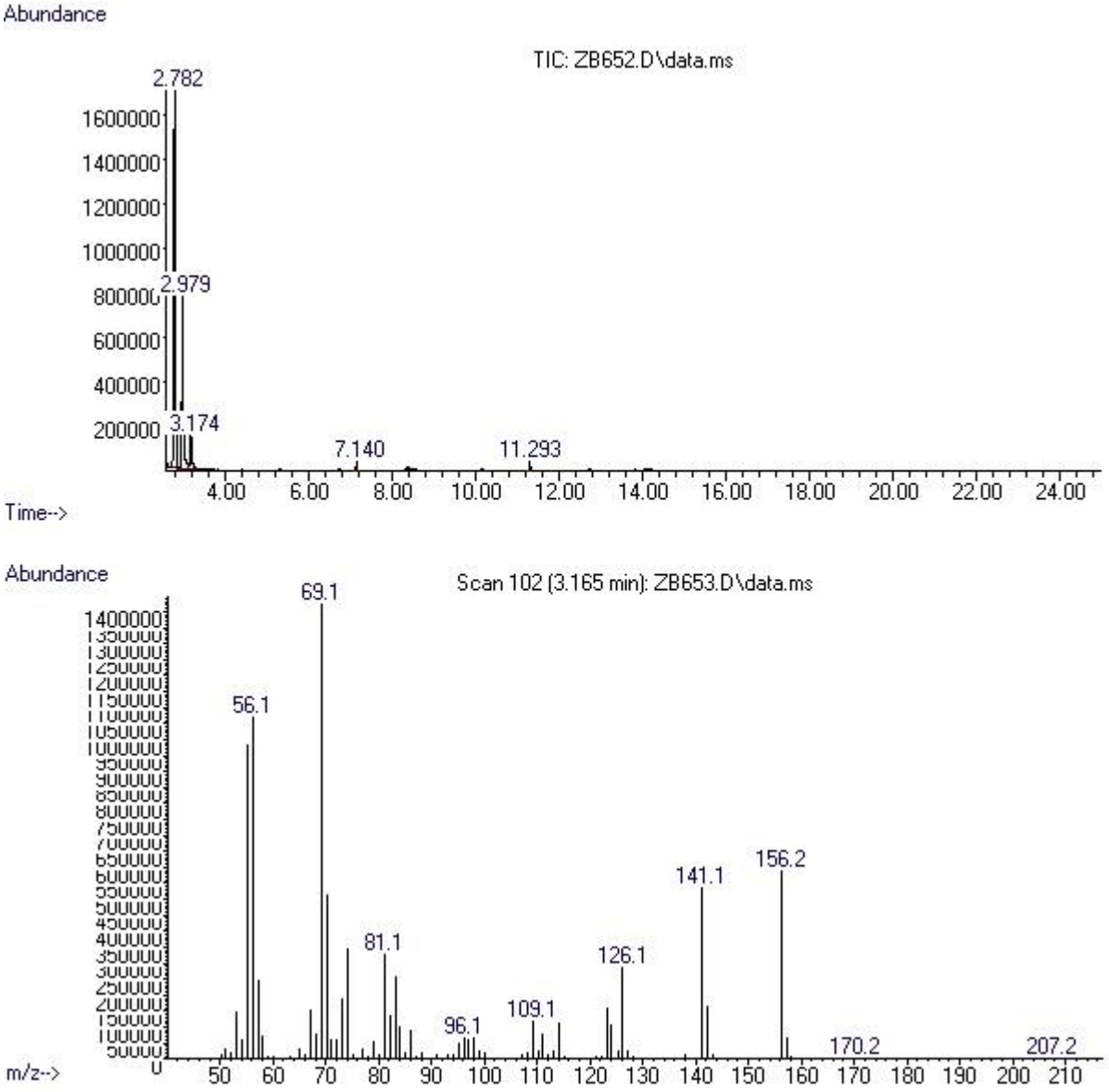


Figure S52. GC/MS record of the reaction between 2-iodopyridine (**2**) and 1*H*-pyrrole (**16**) in the presence of TEMPO (2 eq.).

7. References

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