

## An expedient synthesis of 5-alkynyl-6-aryl-2,2'-bipyridines

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**General.** All common reagents and solvents were used as purchased. Melting points were measured on the instrument Boetius. NMR spectra were acquired on a Bruker Avance-400 spectrometer, 298 K, digital resolution  $\pm 0.01$  ppm, using TMS as internal standard. Mass-spectra were recorded on MicrOTOF-Q II (Bruker Daltonics), electrospray as a method of ionization. Microanalyzes (C, H, N) were performed using a Perkin–Elmer 2400 elemental analyzer.

The starting 1,2,4-triazines **1** were synthesized as described [D. S. Kopchuk, I. L. Nikonov, A. F. Khasanov, K. Giri, S. Santra, I. S. Kovalev, E. V. Nosova, S. Gundala, P. Venkatapuram, G. V. Zyryanov, A. Majee and O. N. Chupakhin, *Org. Biomol. Chem.*, 2018, **16**, 5119].

*General procedure for the synthesis of triazines 4.* A solution of Bu<sup>n</sup>Li in hexane (2.5 M, 0.8 ml) was added to a solution of the corresponding acetylene (2 mmol) in dry THF (5 ml) in a Schlenk flask at  $-78^{\circ}\text{C}$  in argon atmosphere. The resulting mixture was stirred for 5 min under the same conditions. Then a solution of the corresponding 1,2,4-triazine **1** (1.6 mmol) in dry toluene (35 ml) was added, and the mixture was stirred under the same conditions for 10 min. Then a solution of DDQ (305 mg, 1.34 mmol) in dry toluene (10 ml) was added. The resulting mixture was stirred overnight at room temperature. Methanol (10 ml) was added, the resulting mixture was stirred at room temperature for 5 min. The solvents were removed under reduced pressure. The residue was separated by column chromatography (neutral Al<sub>2</sub>O<sub>3</sub>, EtOAc–CH<sub>2</sub>Cl<sub>2</sub> (4:1) as the eluent, R<sub>f</sub> 0.7).

**5-(4-Methoxyphenyl)-6-phenylethynyl-3-(pyridin-2-yl)-1,2,4-triazine (4a).** Yield 466 mg (1.28 mmol, 80%). M.p. 190–192 °C. NMR <sup>1</sup>H (CDCl<sub>3</sub>,  $\delta$ , ppm): 3.92 (s, 3H, OCH<sub>3</sub>), 7.08 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 7.37–7.49 (m, 4H, H-5 (py), Ph), 7.59–7.65 (m, 2H, Ph), 7.93 (ddd, 1H, <sup>3</sup>J 7.6, 7.6 Hz, <sup>4</sup>J 1.6 Hz, H-4 (py)), 8.47 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 8.68 (d, 1H, <sup>3</sup>J 8.0 Hz, H-3 (py)), 8.93 (d, 1H, <sup>3</sup>J 4.8 Hz, H-6 (py)). NMR <sup>13</sup>C (CDCl<sub>3</sub>,  $\delta$ , ppm): 55.5, 85.7, 99.6, 114.0, 121.5, 124.4, 125.5, 126.7, 128.6, 130.0, 131.8, 132.1, 137.0, 143.3, 150.5, 152.9, 157.0, 159.3, 162.9. ESI-MS, m/z: 365.14 (M+H)<sup>+</sup>. Calcd for C<sub>23</sub>H<sub>16</sub>N<sub>4</sub>O: C 75.81, H 4.43, N 15.37. Found: C 75.76, H 4.38, N 15.31.

**5-(4-Methoxyphenyl)-6-(4-methoxyphenylethynyl)-3-(pyridin-2-yl)-1,2,4-triazine (4b).** M.p. 182–184 °C. Yield 466 mg (1.18 mmol, 74%). NMR <sup>1</sup>H (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 3.87 (s, 3H, OCH<sub>3</sub>), 3.95 (s, 3H, OCH<sub>3</sub>), 7.04–7.06 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 7.19–7.21 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 7.59–

7.62 (m, 3H, 4-MeOC<sub>6</sub>H<sub>4</sub>, H-5 (py)), 8.05-8.06 (ddd, 1H, <sup>3</sup>J 7.6, 7.6 Hz, <sup>4</sup>J 1.6 Hz, H-4 (py)), 8.44-8.47 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 8.58 (d, 1H, <sup>3</sup>J 8.0 Hz, H-3 (py)), 8.56 (d, 1H, <sup>3</sup>J 4.8 Hz, H-6 (py)). ESI-MS, m/z: 395.15 (M+H)<sup>+</sup>. Calcd for C<sub>24</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>: C 73.08, H 4.60, N 14.20. Found: C 73.01, H 4.50, N 14.15.

**5-(4-Methoxyphenyl)-3-(pyridin-2-yl)-6-(trimethylsilylethynyl)-1,2,4-triazine (4c).** M.p. 177-179 °C. Yield 375 mg (1.04 mmol, 65%). NMR <sup>1</sup>H (DMSO-*d*<sub>6</sub>, δ, ppm): 0.35 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 3.92 (s, 3H, OCH<sub>3</sub>), 7.08-7.11 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 7.58-7.59 (m, 1H, H-5 (py)), 8.03 (ddd, 1H, <sup>3</sup>J 7.6, 7.6 Hz, <sup>4</sup>J 1.6 Hz, H-4 (py)), 8.42-8.44 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 8.57 (d, 1H, <sup>3</sup>J 8.0 Hz, H-3 (py)), 8.84 (d, 1H, <sup>3</sup>J 4.8 Hz, H-6 (py)). ESI-MS, m/z: 361.15 (M+H)<sup>+</sup>. Calcd for C<sub>20</sub>H<sub>20</sub>N<sub>4</sub>OSi: C 66.64, H 5.59, N 15.54. Found: C 66.59, H 5.51, N 15.48.

**6-Phenylethynyl-3-(pyridin-2-yl)-5-*p*-tolyl-1,2,4-triazine (4d).** Yield 418 mg (1.20 mmol, 75%). M.p. 193-195 °C. NMR <sup>1</sup>H (DMSO-*d*<sub>6</sub>, δ, ppm): 2.51 (s, 3H, CH<sub>3</sub>), 7.46-7.52 (m, 5H, Tol, Ph), 7.59-7.65 (m, 3H, Ph, H-5 (py)), 8.03-8.06 (ddd, 1H, <sup>3</sup>J 7.6, 7.6 Hz, <sup>4</sup>J 1.6 Hz, H-4 (py)), 8.31-8.33 (m, 2H, Tol), 8.60 (d, 1H, <sup>3</sup>J 8.0 Hz, H-3 (py)), 8.88 (d, 1H, <sup>3</sup>J 4.8 Hz, H-6 (py)). ESI-MS, m/z: 349.14 (M+H)<sup>+</sup>. Calcd for C<sub>23</sub>H<sub>16</sub>N<sub>4</sub>: C 79.29, H 4.63, N 16.08. Found: C 79.21, H 4.58, N 16.01.

**6-(4-Methoxyphenylethynyl)-3-(pyridin-2-yl)-5-*p*-tolyl-1,2,4-triazine (4e).** Yield 435 mg (1.15 mmol, 72%). M.p. 186-188 °C. NMR <sup>1</sup>H (DMSO-*d*<sub>6</sub>, δ, ppm): 2.51 (s, 3H, CH<sub>3</sub>), 3.87 (s, 3H, CH<sub>3</sub>), 7.00-7.03 (m, 2H, Tol), 7.45-7.47 (m, 2H, Tol), 7.56-7.62 (m, 3H, 4-MeOC<sub>6</sub>H<sub>4</sub>, H-5 (py)), 8.03-8.06 (ddd, 1H, <sup>3</sup>J 7.6, 7.6 Hz, <sup>4</sup>J 1.6 Hz, H-4 (py)), 8.32-8.34 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 8.60 (d, 1H, <sup>3</sup>J 8.0 Hz, H-3 (py)), 8.85 (d, 1H, <sup>3</sup>J 4.8 Hz, H-6 (py)). ESI-MS, m/z: 379.15 (M+H)<sup>+</sup>. Calcd for C<sub>24</sub>H<sub>18</sub>N<sub>4</sub>O: C 76.17, H 4.79, N 14.80. Found: C 76.15, H 4.70, N 14.72.

*The general procedure for the synthesis of bipyridines 5.* The corresponding triazine **4** (0.5 mmol) was suspended in 1,2-dichlorobenzene (25 ml), 2,5-norbornadiene (0.15 ml, 1.5 mmol) was added, and the resulting mixture was stirred at 150 °C in argon atmosphere for 20 h in an autoclave. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (chloroform as eluent). The analytical samples were obtained by recrystallization from MeCN.

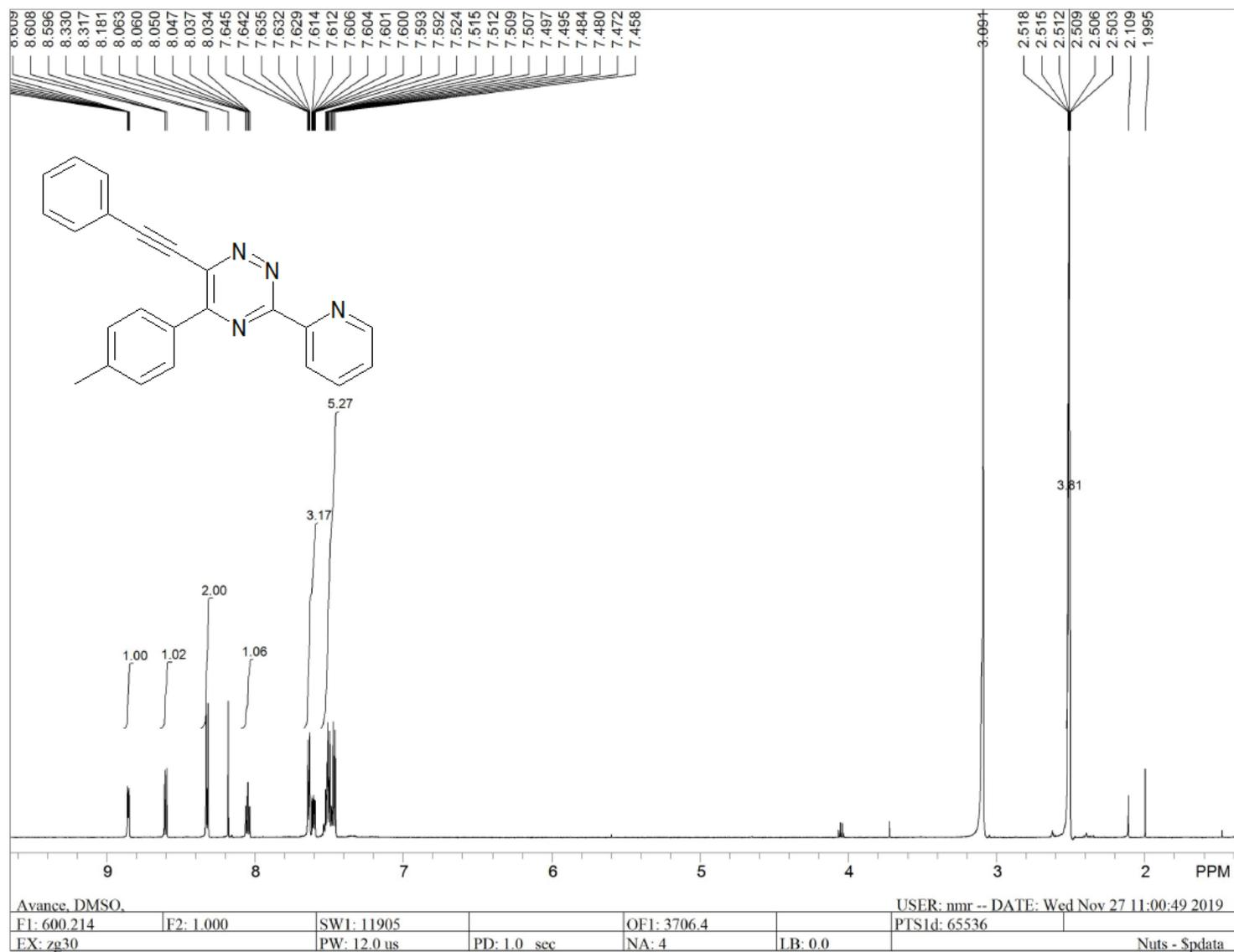
**6-(4-Methoxyphenyl)-5-phenylethynyl-2,2'-bipyridine (5a).** M.p. 156-158 °C. Yield 145 mg (0.40 mmol, 80%). NMR <sup>1</sup>H (DMSO-*d*<sub>6</sub>, δ, ppm): 3.82 (s, 3H, OCH<sub>3</sub>), 6.96-6.98 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 7.17-7.27 (m, 4H, Ph, H-5'), 7.38-7.39 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 7.72-7.76 (ddd, 1H, <sup>3</sup>J 7.6, 7.6 Hz, <sup>4</sup>J 1.6 Hz, H-4'), 7.94-7.97 (d, 1H, <sup>3</sup>J 7.9 Hz, H-3), 8.10-8.13 (m, 2H, Ph), 8.27 (d, 1H, <sup>3</sup>J 7.9 Hz, H-4), 8.50 (d, 1H, <sup>3</sup>J 8.0 Hz, H-3'), 8.61 (dd, 1H, <sup>3</sup>J 4.8 Hz, H-6'). NMR <sup>13</sup>C (CDCl<sub>3</sub>, δ, ppm): 55.4, 88.4, 95.2, 113.3, 117.1, 117.9, 121.6, 123.1, 123.9, 128.4, 128.6, 130.9, 131.5, 132.2, 136.9, 141.9, 149.1, 154.4, 155.7, 158.1, 160.4. ESI-MS, m/z: 363.15 (M+H)<sup>+</sup>. Calcd for C<sub>25</sub>H<sub>18</sub>N<sub>2</sub>O: C 82.85, H 5.01, N 7.73. Found: C 82.78, H 4.98, N 7.65.

**6-(4-Methoxyphenyl)-5-(4-methoxyphenylethynyl)-2,2'-bipyridine (5b).** M.p. 144-146 °C. Yield 153 mg (0.39 mmol, 78%). NMR <sup>1</sup>H (DMSO-*d*<sub>6</sub>, δ, ppm): 3.85 (s, 3H, OCH<sub>3</sub>), 3.93 (s, 3H, OCH<sub>3</sub>), 6.89-6.91 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 7.06-7.07 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 7.28-7.35 (m, 1H, H-5'), 7.42-7.44 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 7.82-7.84 (ddd, 1H, <sup>3</sup>*J* 7.6, 7.6 Hz, <sup>4</sup>*J* 1.6 Hz, H-4'), 8.03 (d, 1H, <sup>3</sup>*J* 7.9 Hz, H-3), 8.22-8.24 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 8.36 (d, 1H, <sup>3</sup>*J* 7.9 Hz, H-4), 8.60 (d, 1H, <sup>3</sup>*J* 8.0 Hz, H-3'), 8.71 (dd, 1H, <sup>3</sup>*J* 4.8 Hz, H-6'). NMR <sup>13</sup>C (CDCl<sub>3</sub>, δ, ppm): 55.3, 87.2, 95.4, 113.3, 114.1, 115.2, 117.5, 117.9, 121.5, 123.8, 129.6, 130.9, 132.4, 132.9, 136.8, 141.7, 149.1, 154.1, 155.8, 157.8, 159.9, 160.3. ESI-MS, *m/z*: 393.16 (M+H)<sup>+</sup>. Calcd for C<sub>26</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C 79.57, H 5.14, N 7.14. Found: C 79.51, H 5.05, N 7.09.

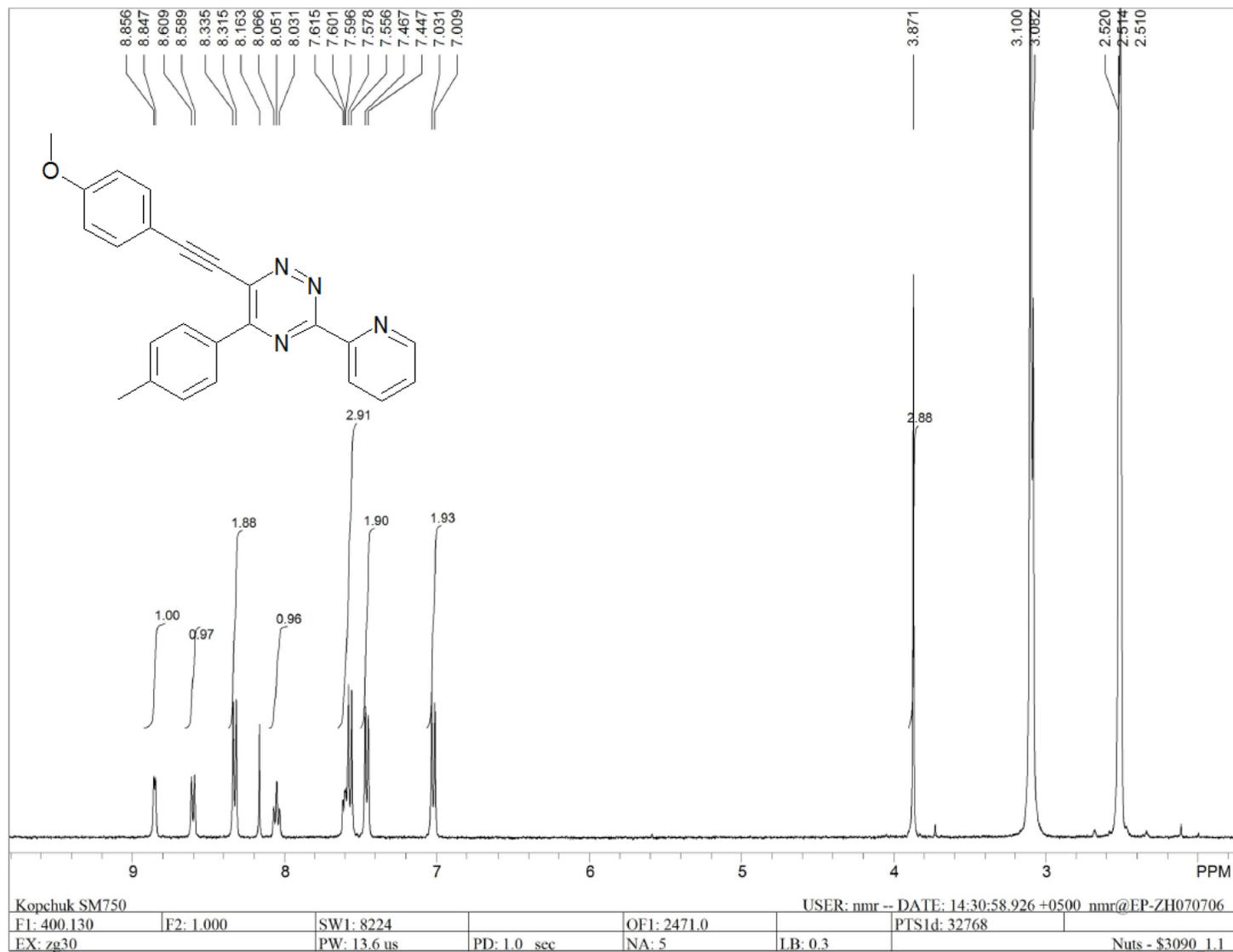
**6-(4-Methoxyphenyl)-5-(trimethylsilylethynyl)-2,2'-bipyridine (5c).** Yield 134 mg (0.37 mmol, 75%). M.p. 144-146 °C. NMR <sup>1</sup>H (DMSO-*d*<sub>6</sub>, δ, ppm): 0.25 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 3.82 (s, 3H, OCH<sub>3</sub>), 6.98-7.01 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 7.43 (m, 1H, H-5'), 7.92 (ddd, 1H, <sup>3</sup>*J* 7.6, 7.6 Hz, <sup>4</sup>*J* 1.6 Hz, H-4'), 8.00 (d, 1H, <sup>3</sup>*J* 7.9 Hz, H-3), 8.07-8.12 (m, 2H, 4-MeOC<sub>6</sub>H<sub>4</sub>), 8.31 (d, 1H, <sup>3</sup>*J* 7.9 Hz, H-4), 8.51 (d, 1H, <sup>3</sup>*J* 8.0 Hz, H-3'), 8.68 (dd, 1H, <sup>3</sup>*J* 4.8 Hz, H-6'). NMR <sup>13</sup>C (CDCl<sub>3</sub>, δ, ppm): 0.0 (3C), 55.7, 101.6, 104.0, 113.4, 118.1, 121.9, 124.2, 130.1, 131.3, 132.3, 137.2, 142.9, 149.4, 154.8, 156.0, 158.6, 160.7. ESI-MS, *m/z*: 359.16 (M+H)<sup>+</sup>. Calcd for C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>OSi: C 73.70, H 6.19, N 7.81. Found: C 73.62, H 6.10, N 7.75.

**5-Phenylethynyl-6-*p*-tolyl-2,2'-bipyridine (5d).** Yield 140 mg (0.40 mmol, 81%). M.p. 159-161 °C. NMR <sup>1</sup>H (DMSO-*d*<sub>6</sub>, δ, ppm): 2.51 (s, 3H, CH<sub>3</sub>), 7.35-7.37 (m, 2H, Tol), 7.41-7.48 (m, 6H, H-5', Ph), 7.95 (ddd, 1H, <sup>3</sup>*J* 7.6, 7.6 Hz, <sup>4</sup>*J* 1.6 Hz, H-4'), 8.05-8.07 (m, 2H, Tol), 8.14 (d, 1H, <sup>3</sup>*J* 7.9 Hz, H-3), 8.40 (d, 1H, <sup>3</sup>*J* 7.9 Hz, H-4), 8.52 (d, 1H, <sup>3</sup>*J* 8.0 Hz, H-3'), 8.70 (dd, 1H, <sup>3</sup>*J* 4.8 Hz, H-6'). NMR <sup>13</sup>C (CDCl<sub>3</sub>, δ, ppm): 20.4, 87.2, 94.2, 116.3, 117.2, 120.6, 122.1, 122.8, 127.4, 127.5, 127.6, 128.4, 130.4, 135.8, 135.8, 137.9, 140.8, 148.1, 153.5, 154.7, 157.5. ESI-MS, *m/z*: 347.15 (M+H)<sup>+</sup>. Calcd for C<sub>25</sub>H<sub>18</sub>N<sub>2</sub>: C 86.68, H 5.24, N 8.09. Found: C 86.60, H 5.18, N 8.01.

**5-(4-Methoxyphenylethynyl)-6-*p*-tolyl-2,2'-bipyridine (5e).** M.p. 146-148 °C. Yield 159 mg (0.42 mmol, 85%). NMR <sup>1</sup>H (DMSO-*d*<sub>6</sub>, δ, ppm): 2.51 (s, 3H, CH<sub>3</sub>), 3.83 (s, 3H, OCH<sub>3</sub>), 6.49-6.97 (m, 2H, Tol), 7.34-7.45 (m, 5H, H-5', 4-MeOC<sub>6</sub>H<sub>4</sub>), 7.92-7.96 (ddd, 1H, <sup>3</sup>*J* 7.6, 7.6 Hz, <sup>4</sup>*J* 1.6 Hz, H-4' (py)), 8.05-8.10 (m, 3H, Tol, H-3), 8.38 (d, 1H, <sup>3</sup>*J* 7.9 Hz, H-4), 8.51 (d, 1H, <sup>3</sup>*J* 8.0 Hz, H-3'), 8.70 (dd, 1H, <sup>3</sup>*J* 4.8 Hz, H-6'). NMR <sup>13</sup>C (CDCl<sub>3</sub>, δ, ppm): 21.4, 55.3, 87.1, 95.5, 114.1, 115.2, 117.8, 118.2, 121.6, 123.8, 128.6, 129.4, 132.9, 136.8, 136.9, 138.8, 141.6, 149.1, 154.1, 155.8, 158.2, 159.9. ESI-MS, *m/z*: 377.17 (M+H)<sup>+</sup>. Calcd for C<sub>26</sub>H<sub>20</sub>N<sub>2</sub>O: C 82.95, H 5.35, N 7.44. Found: C 82.88, H 5.26, N 7.36.



**Figure S1** <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>) for compound **4d**



**Figure S2** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) for compound **4e**

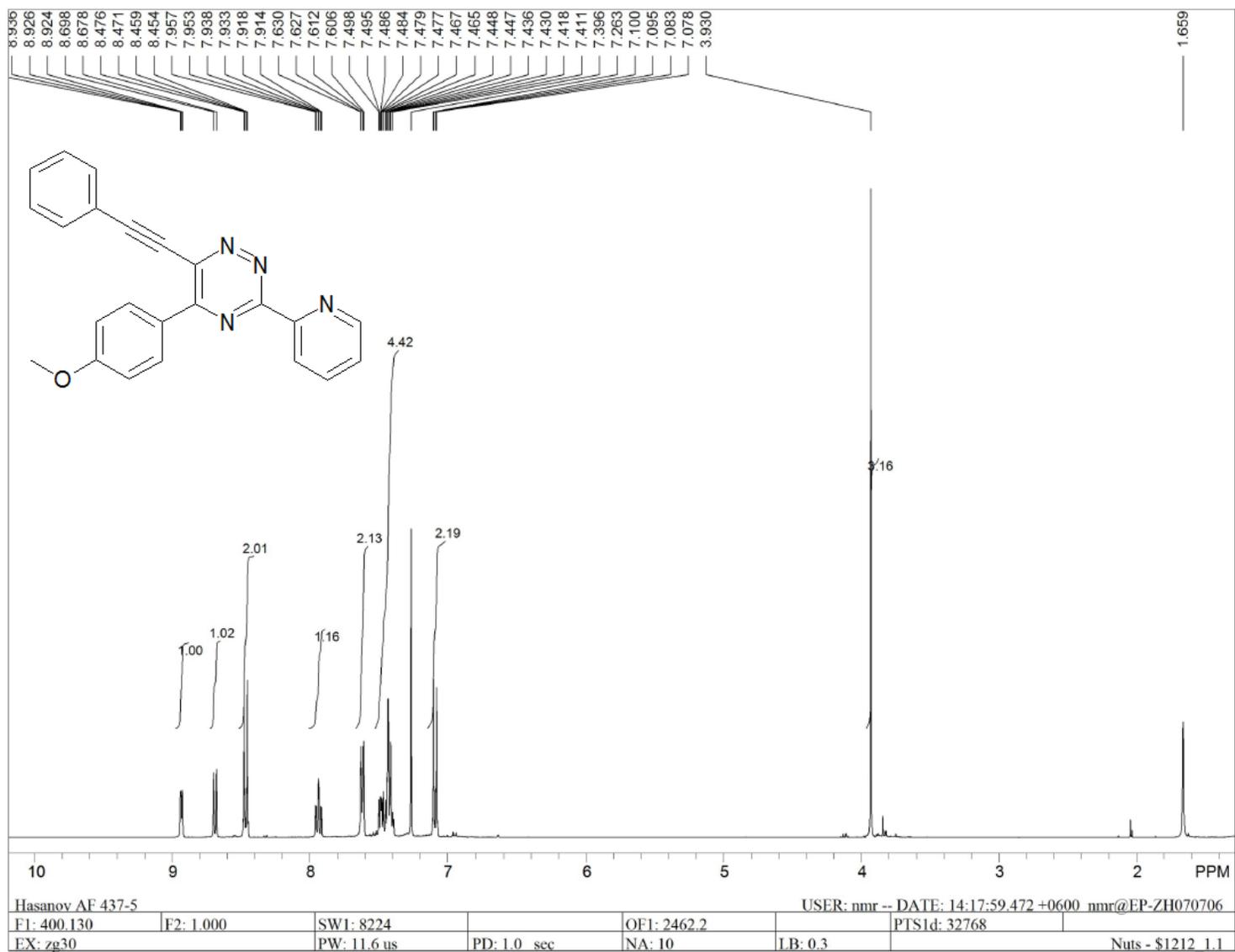
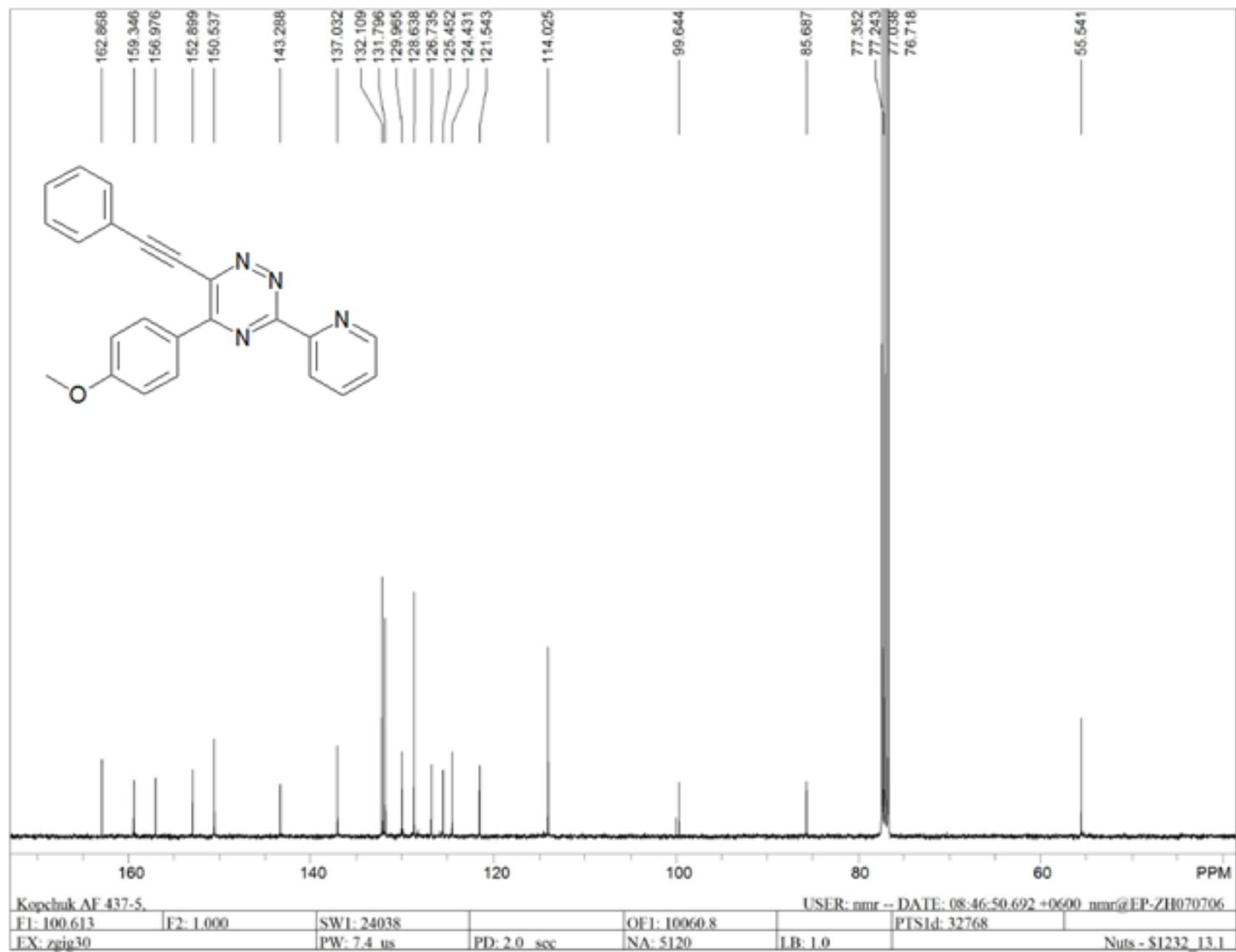
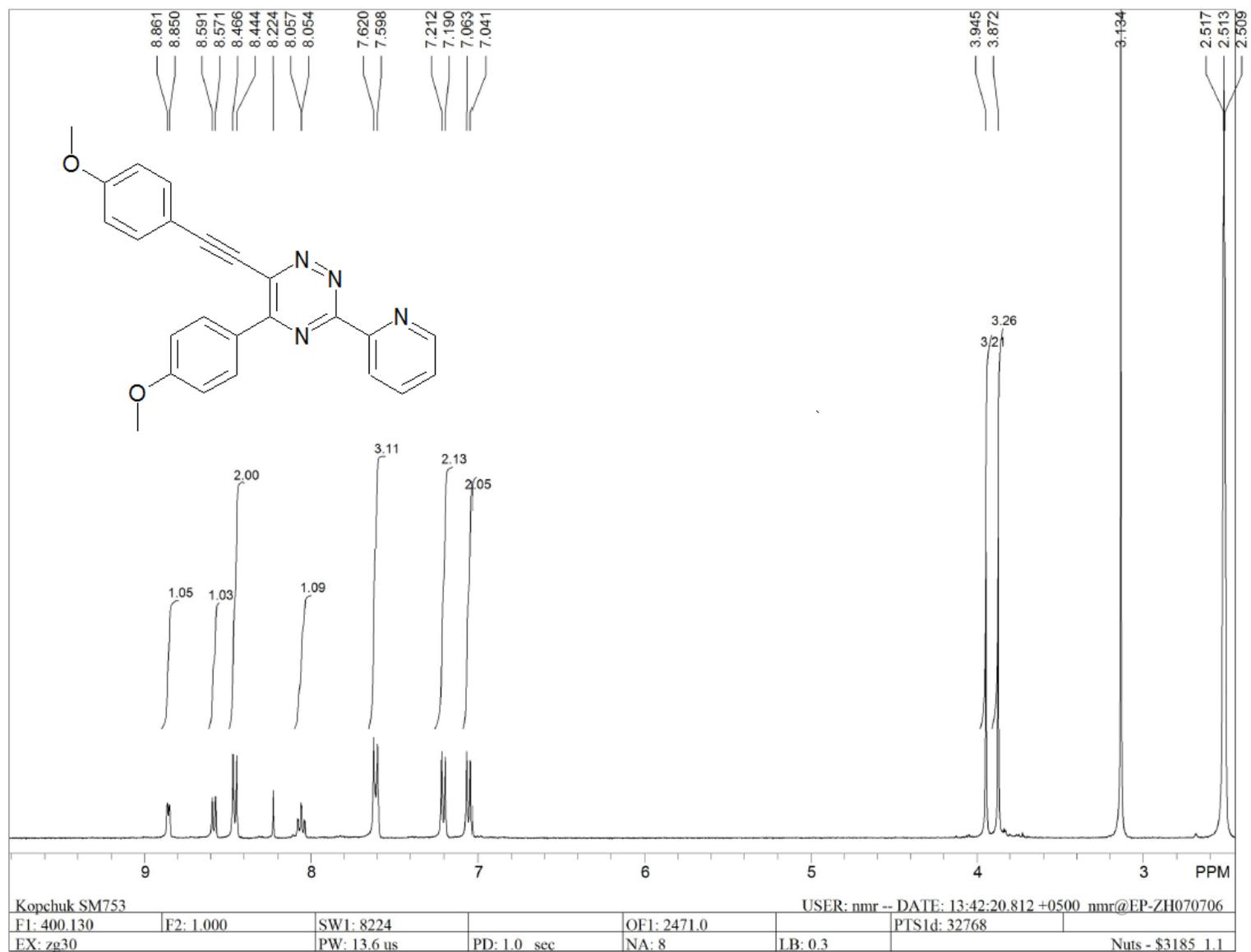


Figure S3 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for compound 4a



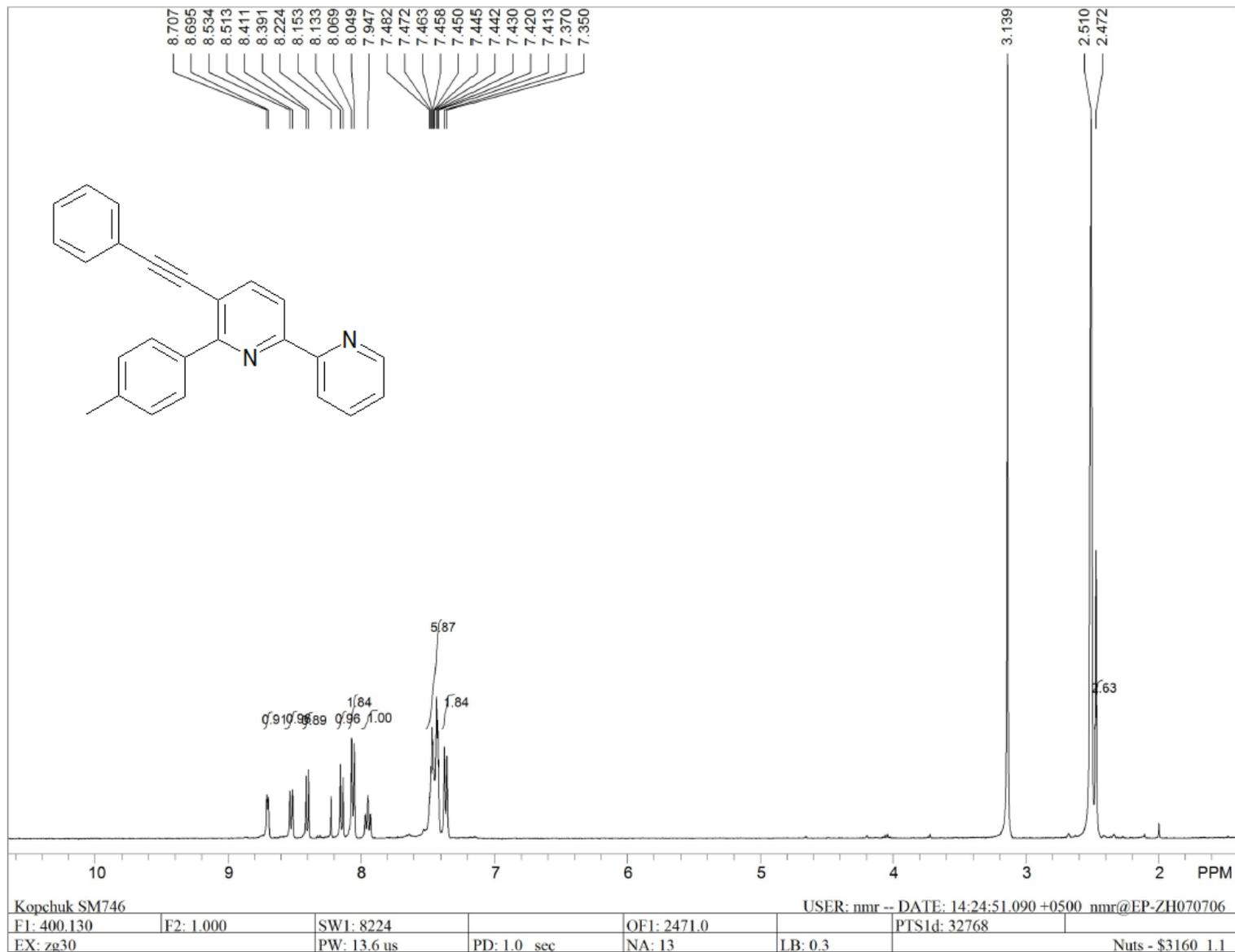
**Figure S4** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for compound **4a**



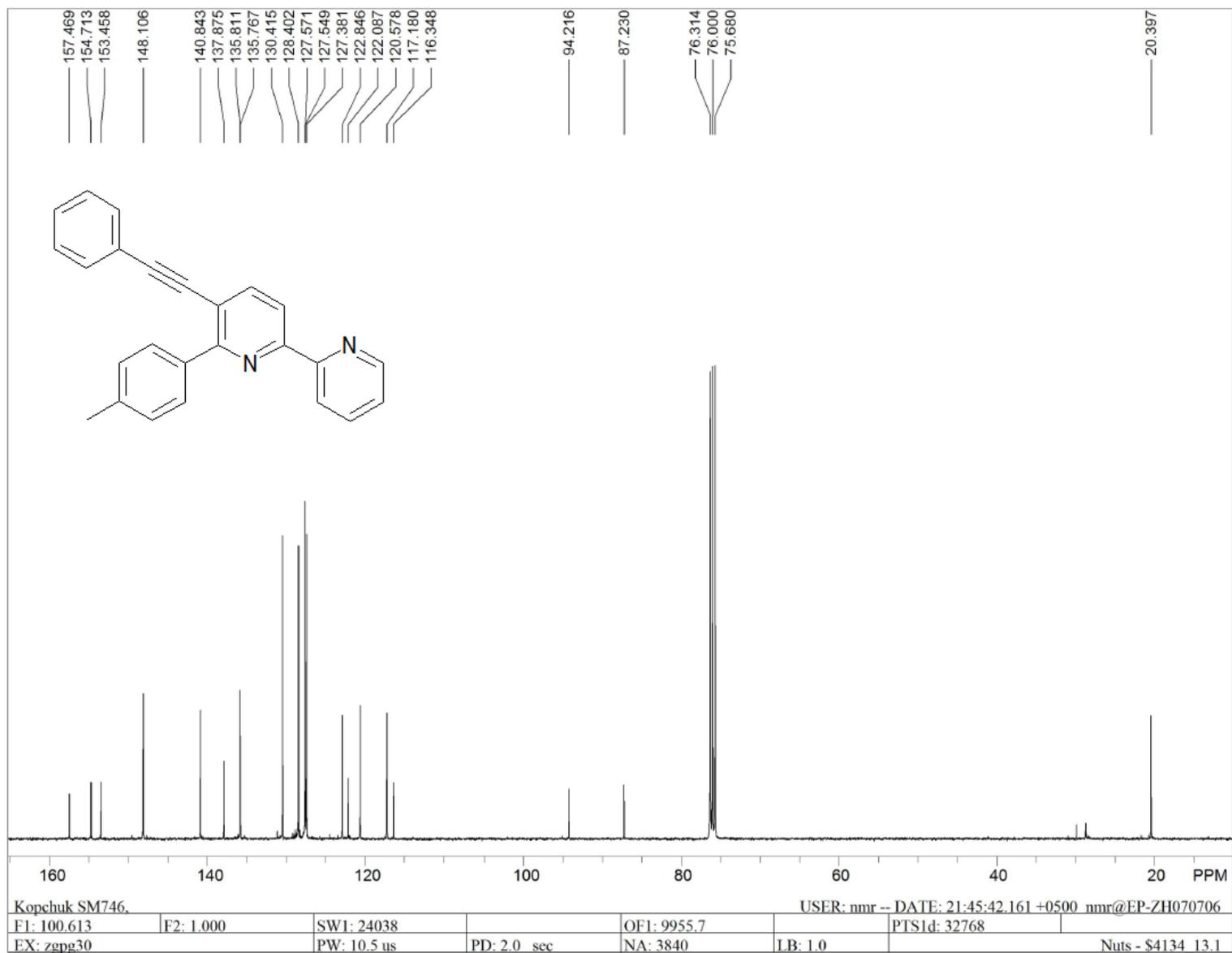
**Figure S5**  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ ) for compound **4b**



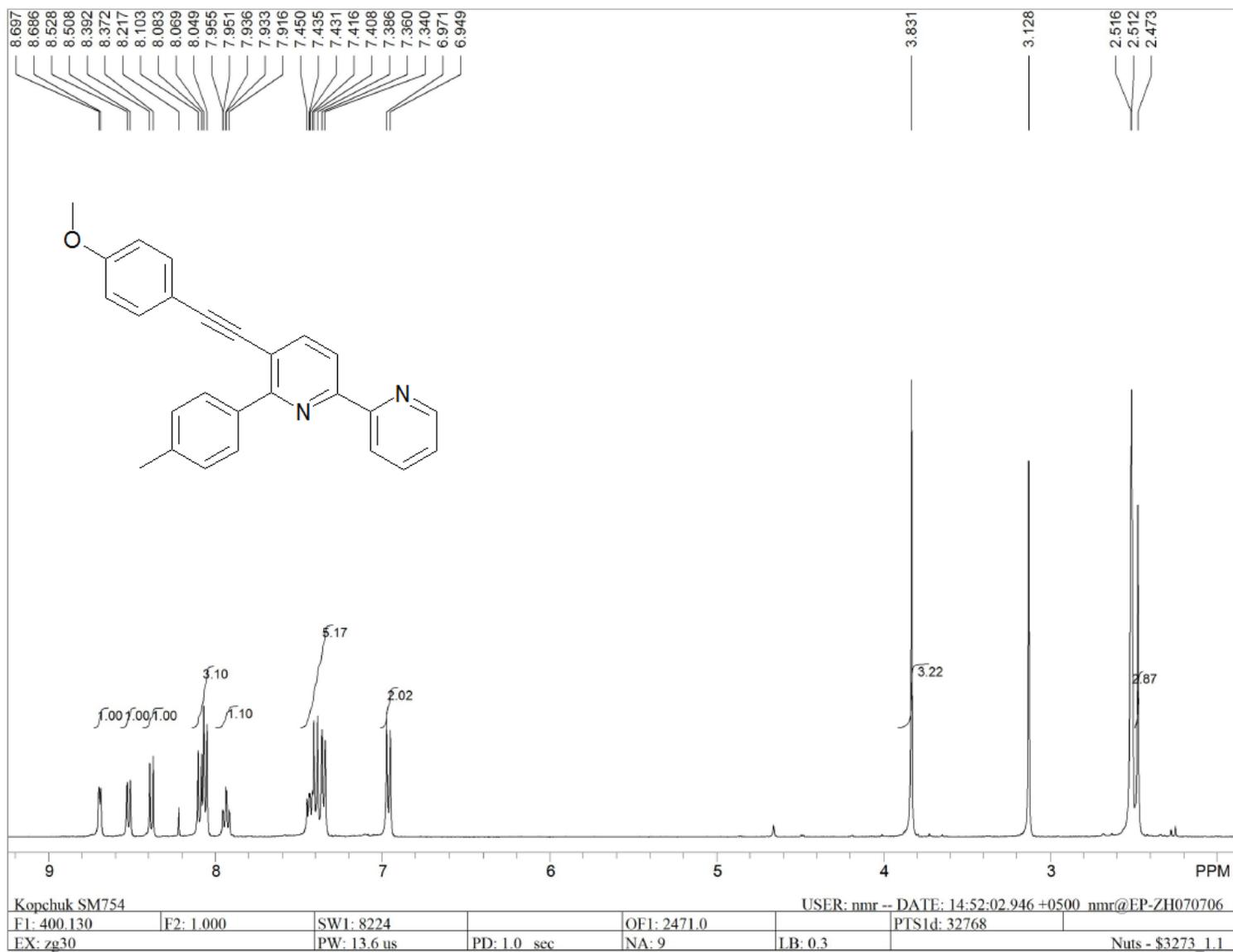
**Figure S6** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) for compound **4c**



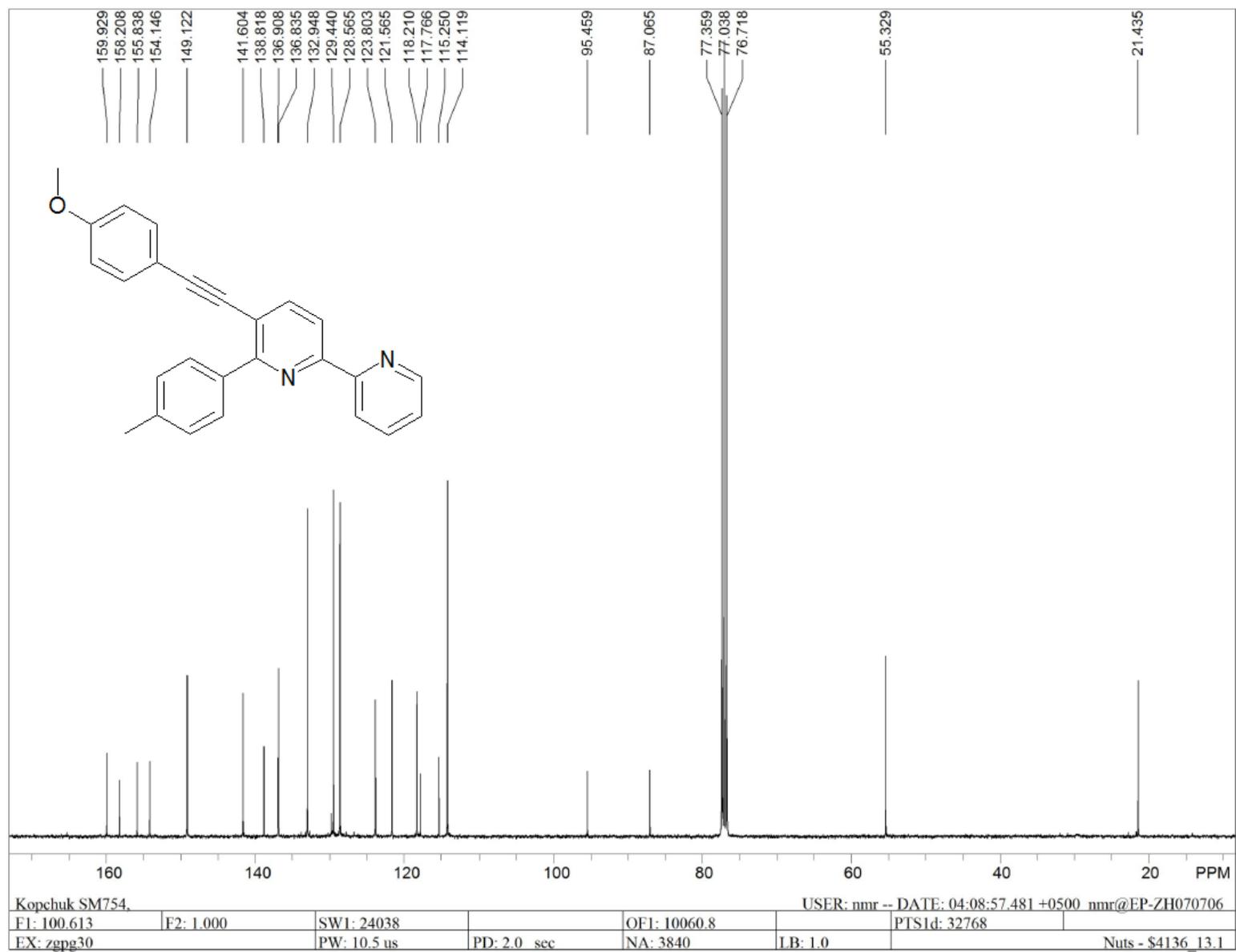
**Figure S7** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) for compound **5d**



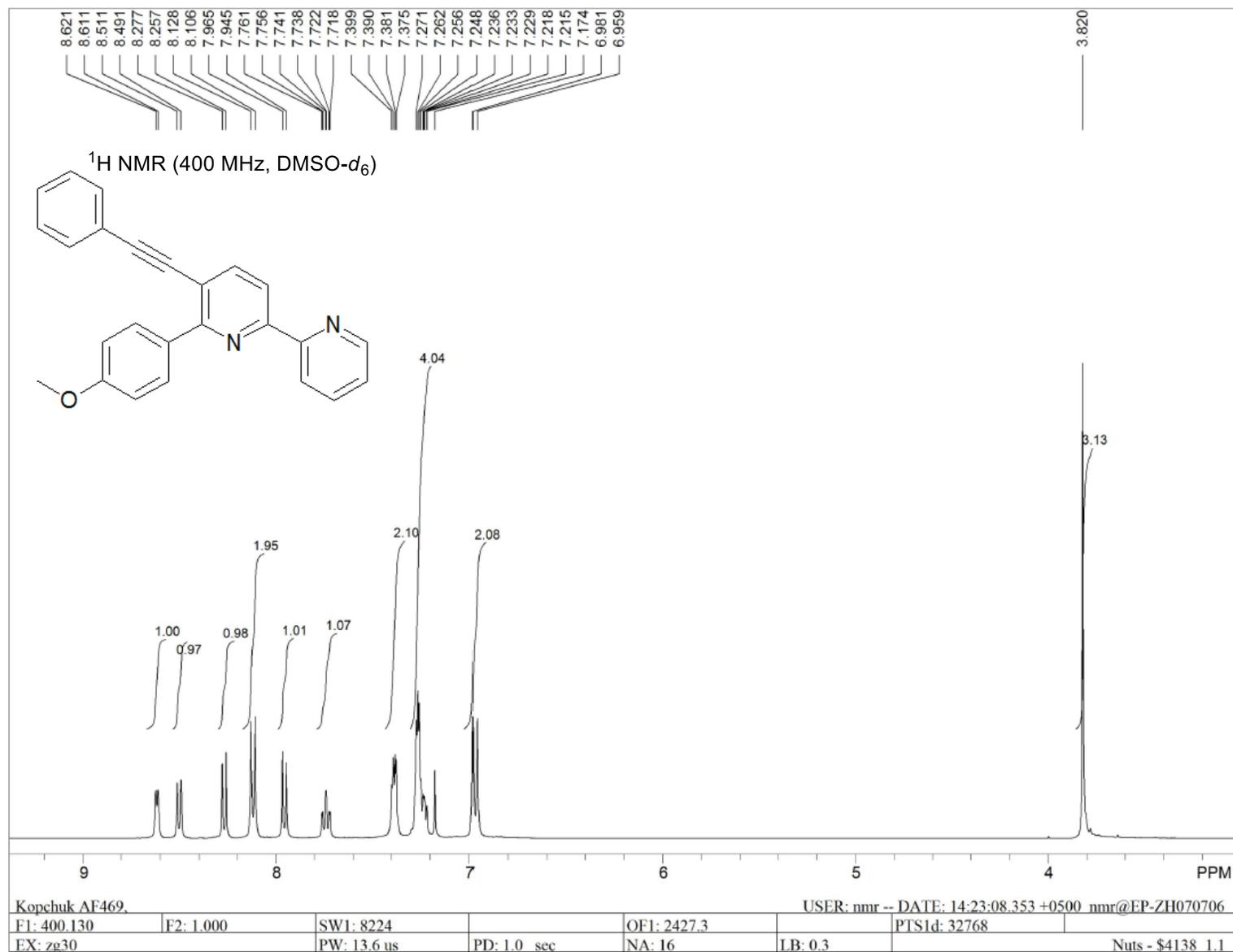
**Figure S8**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) for compound **5d**



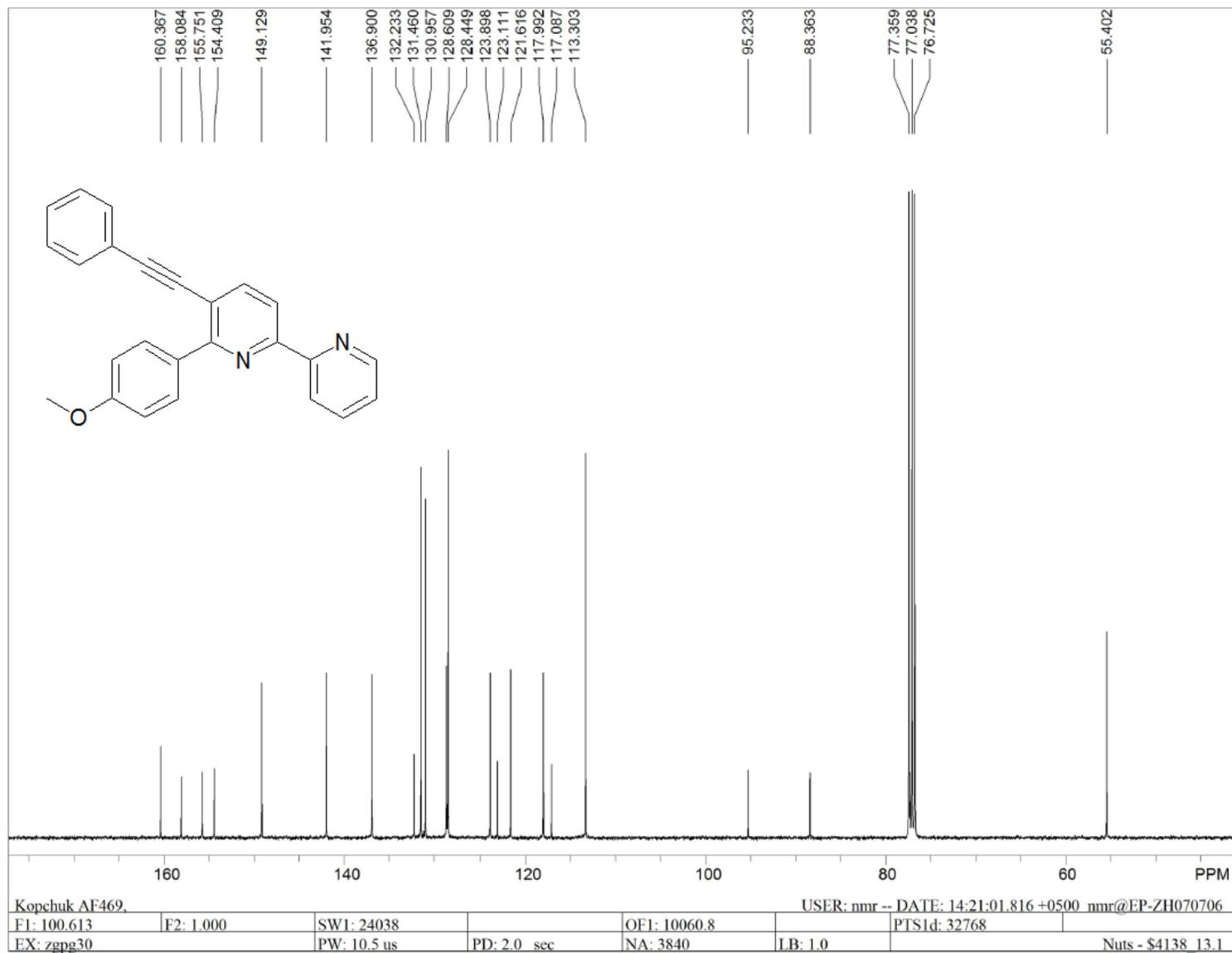
**Figure S9** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) for compound **5e**



**Figure S10**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) for compound **5e**



**Figure S11** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) for compound **5a**



**Figure S12** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for compound **5a**

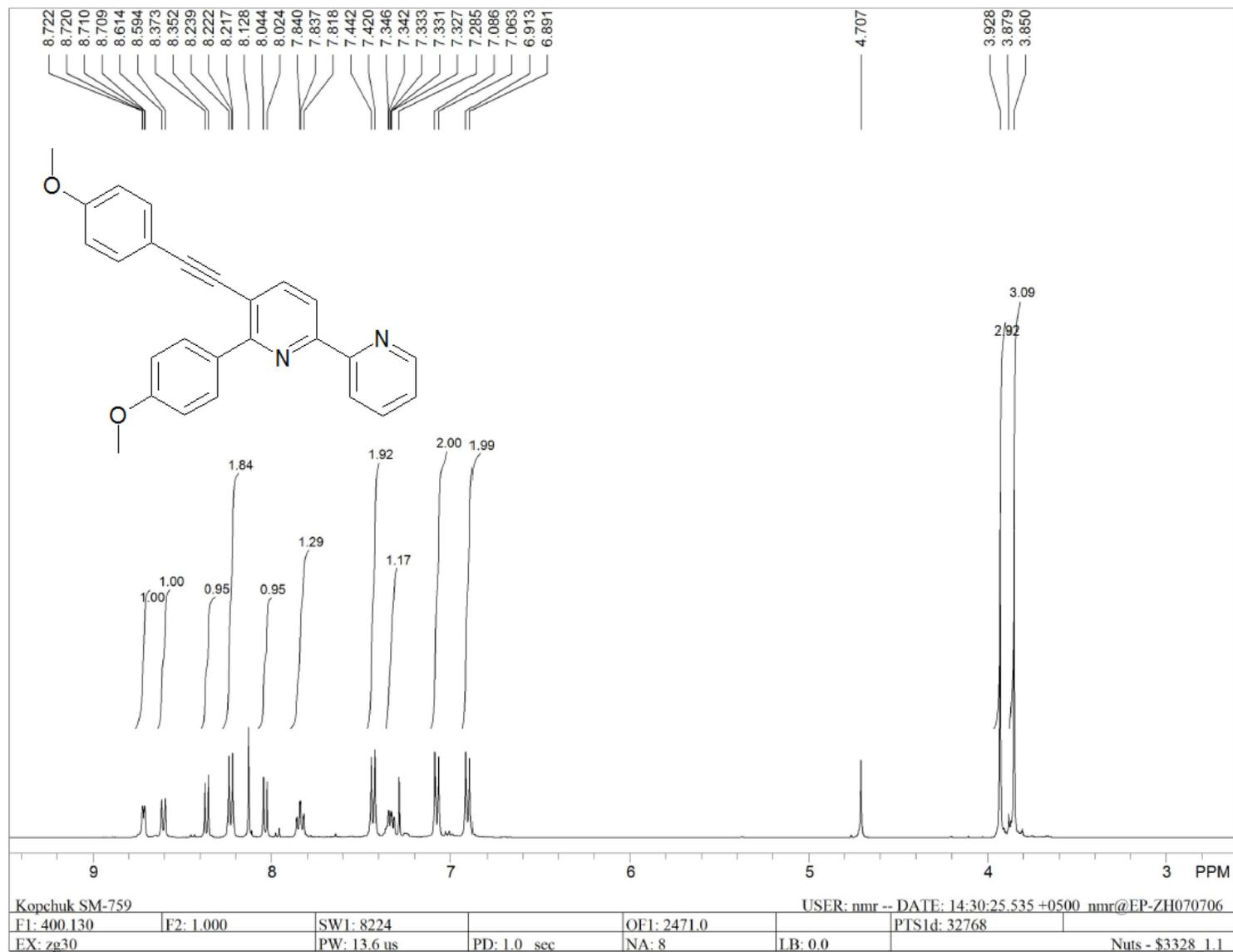
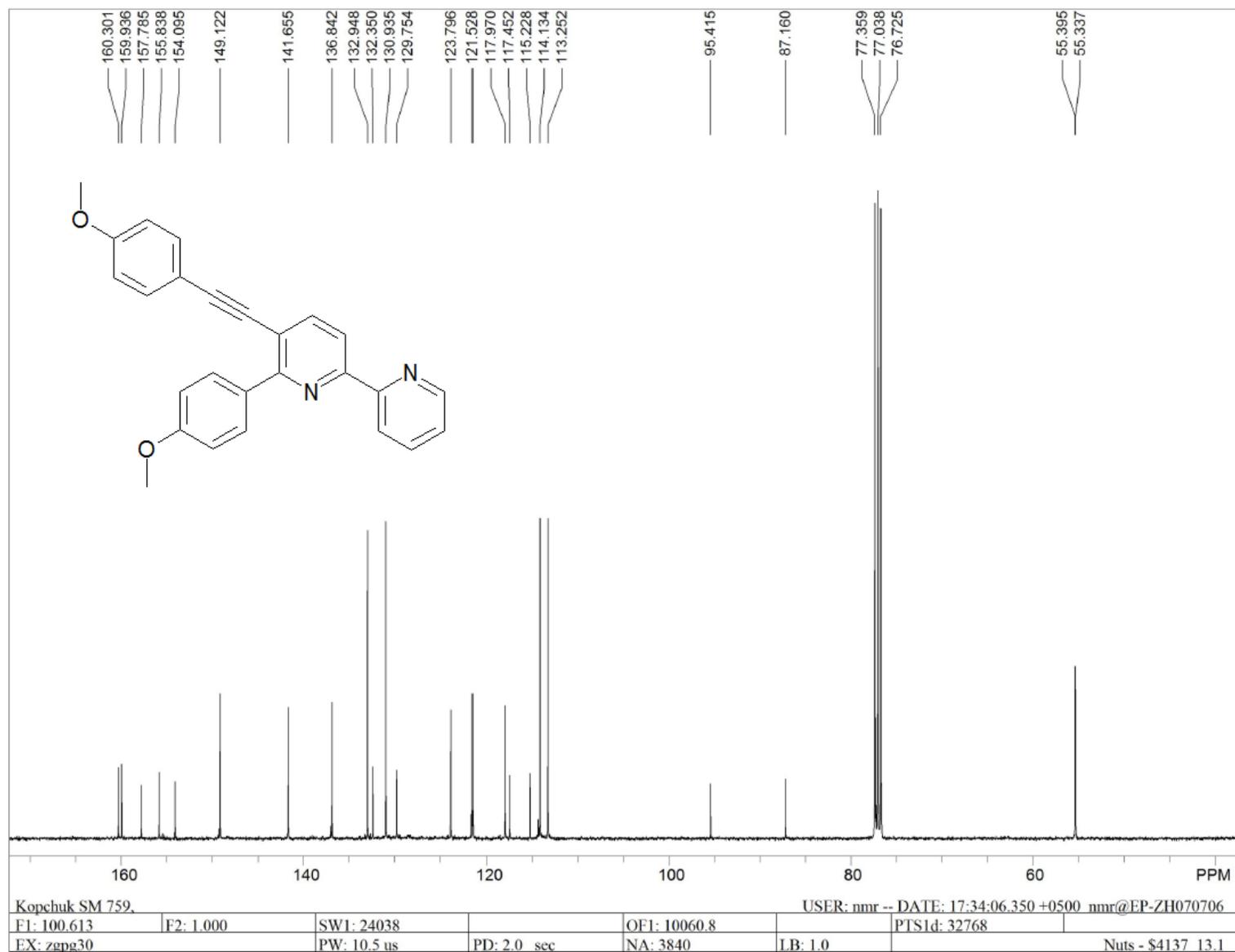
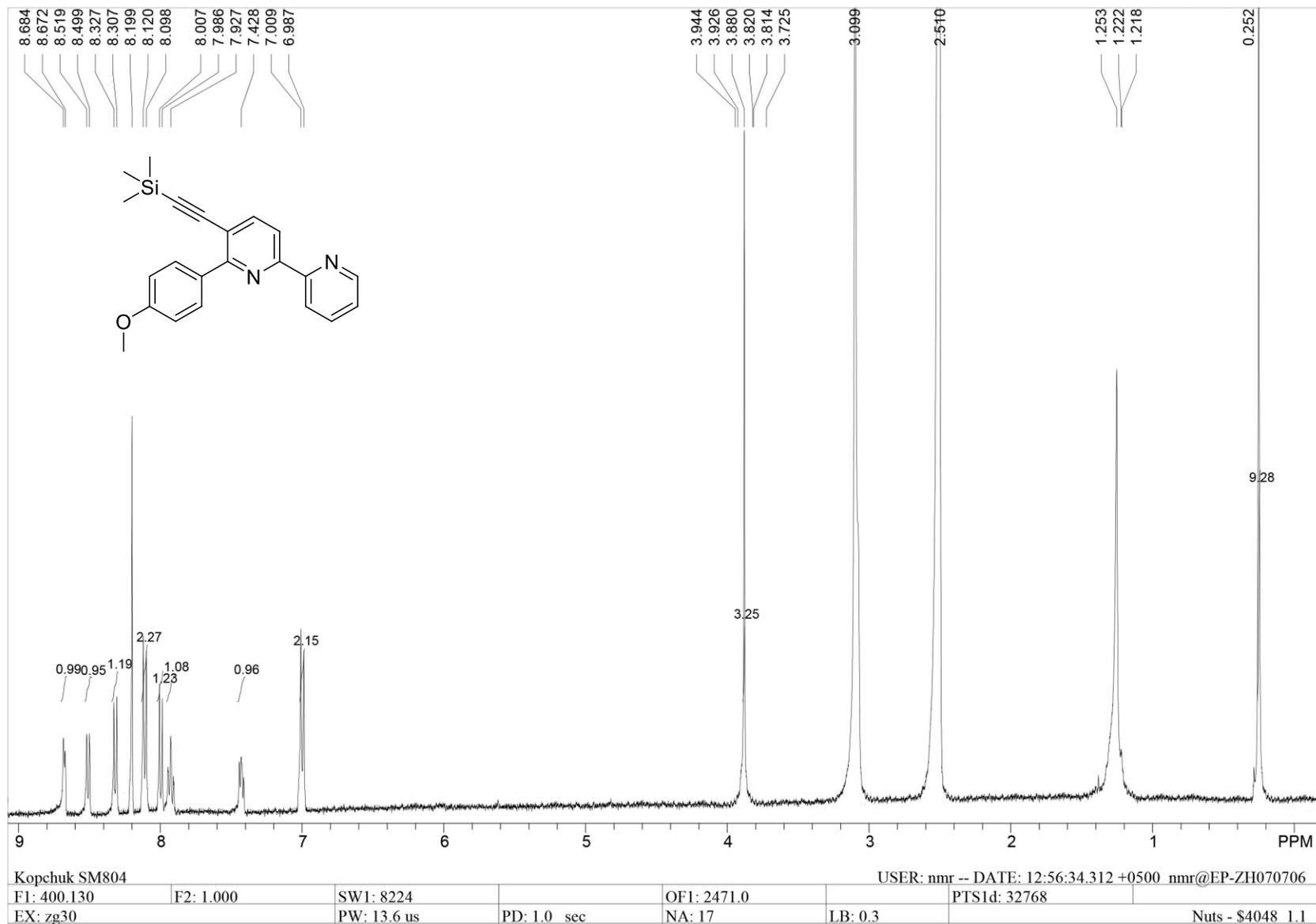


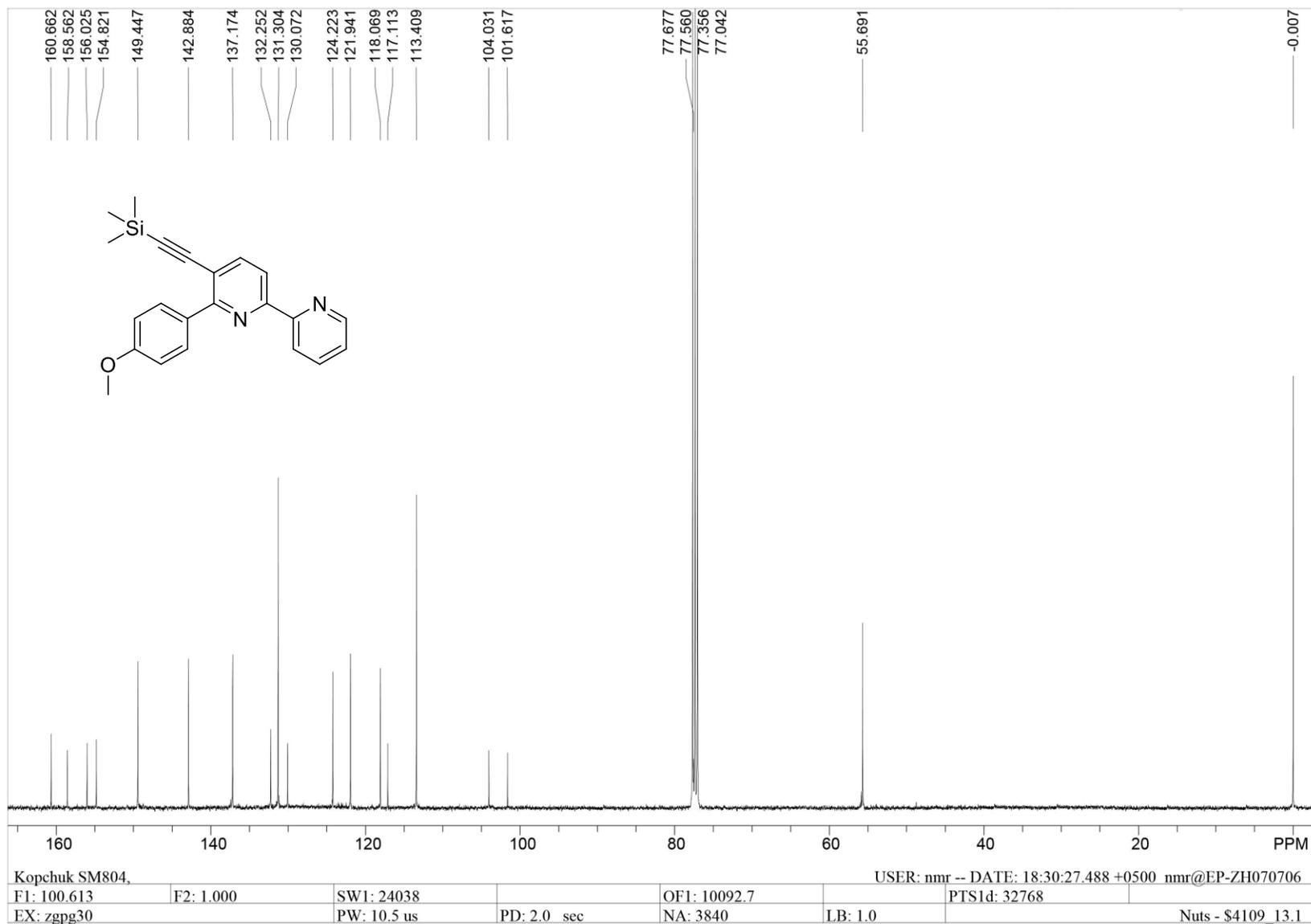
Figure S13 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for compound **5b**



**Figure S14** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for compound **5b**



**Figure S15** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) for compound **5c**



**Figure S16**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) for compound **5c**