

# Supporting Information

## Palladium(0)-Catalyzed Hydrogen-Transfer of Alcohols with 2-nitroanilines for the Synthesis of Benzimidazoles

Qianqian Guan, Qi Sun, Lixian Wen, Zhenggen Zha, Yu Yang\* and Zhiyong Wang\*

Hefei National Laboratory for Physical Sciences at Microscale, Center for Excellence in Molecular Synthesis of Chinese Academy of Sciences, Collaborative Innovation Center of Suzhou Nano Science and Technology & Department of Chemistry, University of Science and Technology of China, Hefei, Anhui

230026, P. R. China

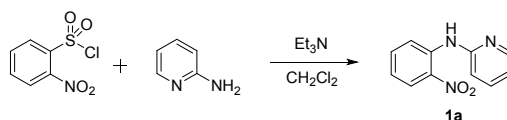
Fax: (+86)551-6360-3185; E-mail: zwang3@ustc.edu.cn

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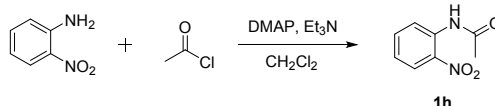
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## (A) General Procedures for the preparations of 1

To a solution of pyridin-2-amine (940 mg, 10 mmol, 1 equiv.) and triethylamine (1214 mg, 12 mmol, 1.2 equiv.) in dichloromethane (15 mL) in ice bath was added dropwise a solution of 2-nitrobenzenesulfonyl chloride (2651 mg, 12 mmol, 1.2 equiv.) in dichloromethane (10 mL). The mixture was allowed to warm to room temperature and stirred for 2 hours or until TLC showed no starting material left. Dichloromethane was removed in vacuum and the crude residue was redissolved in EtOAc, then washed with water (2 x 30 mL), saturated NaHCO<sub>3</sub> (2 x 15 mL), 1 M HCl (2 x 15 mL) and brine (2 x 30 mL). The crude was further purified by column chromatography (petroleum ether / ethyl acetate = 15:1) to give the product as a yellow solid (1538 mg, 72%). **1b**, **1d** were synthesized with the same procedures.



To a solution of 2-nitroaniline (553 mg, 4 mmol, 1 equiv.), DMAP (5 mg, 1 %) and triethylamine (81 mg, 0.8 mmol, 0.2 equiv.) in dichloromethane (10 mL) at room temperature was added dropwise a solution of acetyl chloride (628 mg, 8 mmol, 2 equiv.) in dichloromethane (5 mL). The mixture was stirred until TLC showed no starting material left. Then saturated NaHCO<sub>3</sub> 10 mL added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL x 2). The crude was further purified by column chromatography (petroleum ether / ethyl acetate = 5:1) to give the product **1h** as a yellow solid (715 mg, 99%).



Other 2-nitroanilines were synthesized according to previously reported procedures.<sup>1</sup>

### (2-nitro-phenyl)-pyridin-2-yl-amine (**1a**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 15:1) to give the product as a yellow solid: mp = 74 - 76 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 10.16 (s, 1H), 8.71 (dd, *J* = 8.7 Hz 0.9 Hz, 1H), 8.33 (dd, *J* = 5.6 Hz 1.7 Hz, 1H), 8.21 (dd, *J* = 8.5 Hz 1.5 Hz, 1H), 7.67 - 7.62 (m, 1H), 7.58 - 7.54 (m, 1H), 6.98 - 6.94 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 153.4, 147.5, 138.6, 138.2, 135.6, 135.0, 126.1, 119.9, 119.8, 117.7, 113.7. HRMS (ESI) *m/z* calcd for. C<sub>11</sub>H<sub>10</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 216.0773, found 216.0770.

### (2-nitro-4-trifluoromethyl-phenyl)-pyridin-2-yl-amine (**1b**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 15:1) to give the product as a yellow solid: mp = 116 - 118 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 10.41 (s, 1H), 9.01 (d, *J* = 9.1 Hz, 1H), 8.52 (d, *J* = 1.2 Hz, 1H), 8.39 (dd, *J* = 4.9 Hz 1.2 Hz, 1H), 7.76 - 7.69 (m, 2H), 7.05 (ddd, *J* = 7.3 Hz 5.0 Hz 0.8 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 152.8, 147.9, 141.3, 138.4, 133.4, 131.8 (q, *J* = 3.2 Hz), 124.0 (q, *J* = 4.3 Hz), 123.2 (q, *J* = 269.6), 121.4 (q, 34.2 Hz), 120.2, 118.9, 114.5. HRMS (ESI) *m/z* calcd for. C<sub>12</sub>H<sub>9</sub>F<sub>3</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 284.0647, found 284.0648.

### N-(4-methyl-2-nitrophenyl)pyridin-2-amine (**1c**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 15:1) to give the product as a yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 10.01 (s, 1H), 8.61 (d, *J* = 8.8 Hz, 1H), 8.33 - 8.32 (m, 1H), 8.03 - 8.02 (m, 1H), 7.64 - 7.60 (m, 1H), 7.40 - 7.37 (m, 1H), 6.94 - 6.91 (m, 2H), 2.35 (s, 3H).

### (3-methyl-pyridin-2-yl)-(2-nitro-phenyl)-amine (**1d**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 15:1) to give the product as a yellow solid; mp = 112 - 114 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 10.28 (s, 1H), 9.00 (dd, *J* = 8.8 Hz 1.2 Hz, 1H), 8.24 (dd, *J* = 8.6 Hz 1.6 Hz, 1H), 8.21 (dd, *J* = 4.9 Hz 1.4 Hz, 1H), 7.60 - 7.56 (m, 1H), 7.51 - 7.48 (m, 1H), 6.97 - 6.93 (m, 1H), 6.90 (dd, *J* = 7.3 Hz

5.0 Hz, 1H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 152.3, 145.0, 139.1, 138.6, 135.7, 134.5, 126.1, 121.5, 120.0, 119.5, 117.7, 17.4. HRMS (ESI)  $m/z$  calcd for.  $\text{C}_{12}\text{H}_{12}\text{N}_3\text{O}_2$   $[\text{M}+\text{H}]^+$  230.0930, found 230.0925.

***N*-methyl-2-nitroaniline (1f)**

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1) to give the product as a yellow solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 8.18 – 8.15 (m, 1H), 8.05 (s, 1H), 7.49 – 7.44 (m, 1H), 6.85 – 6.83 (m, 1H), 6.67 – 6.63 (m, 1H), 3.02 (s, 3H).

**2-nitro-*N*-phenylaniline (1g)**

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1) to give the product as a brown solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 9.50 (s, 1H), 8.20 (dd,  $J$  = 8.6 Hz 1.6 Hz, 1H), 7.44 – 7.34 (m, 3H), 7.29 – 7.21 (m, 4H), 6.79 – 6.75 (m, 1H).

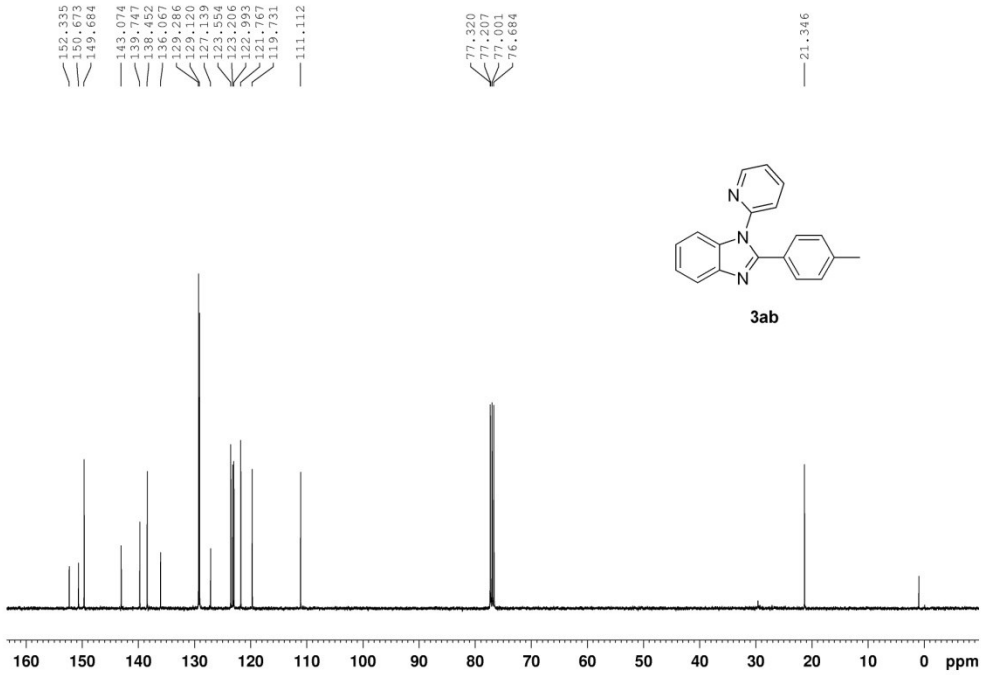
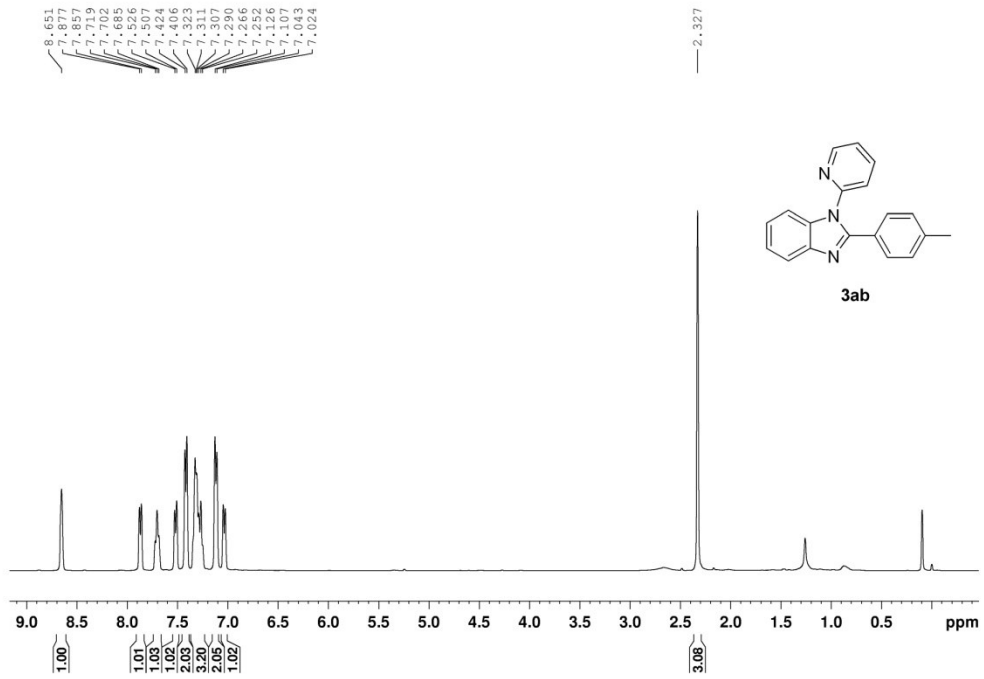
***N*-(2-nitrophenyl)acetamide (1h)**

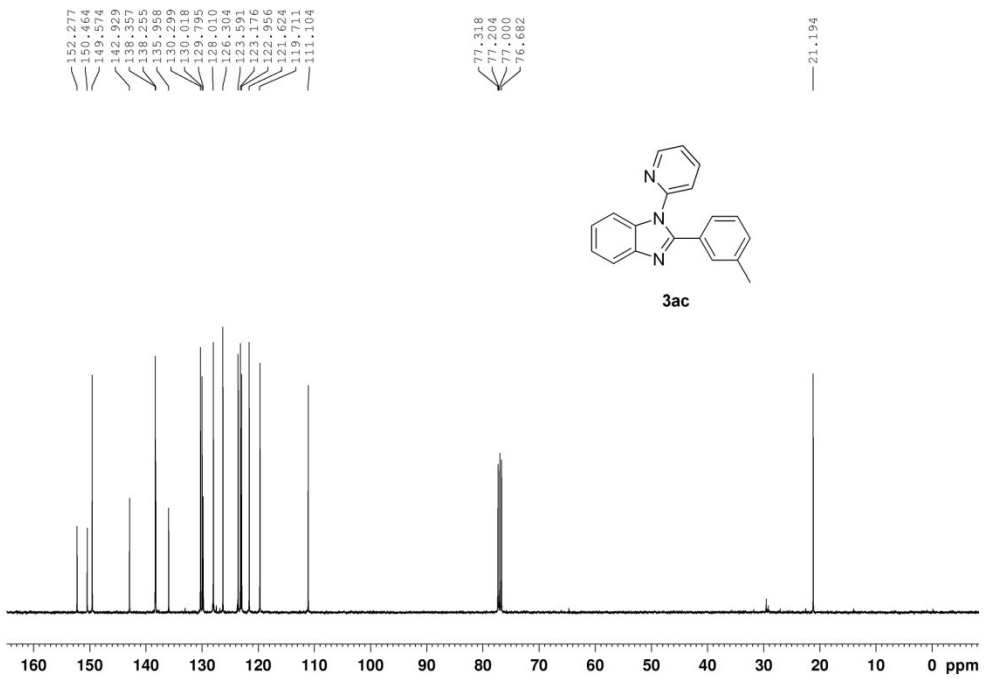
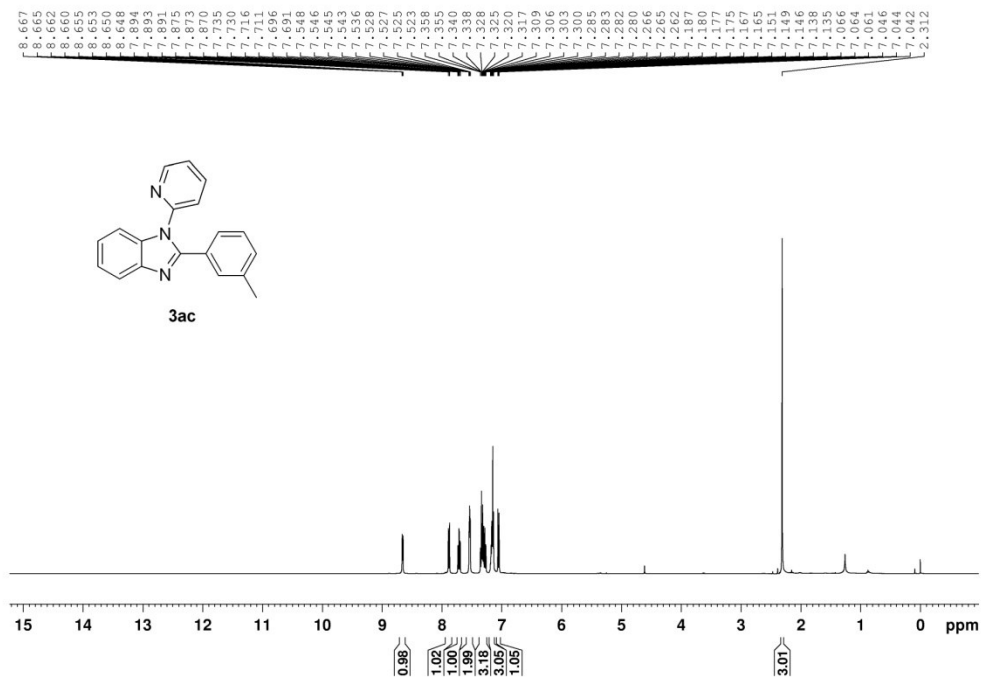
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1) to give the product as a yellow solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 10.34 (s, 1H), 8.78 – 8.76 (m, 1H), 8.22 – 8.20 (m, 1H), 7.68 – 7.63 (m, 1H), 7.21 – 7.16 (m, 1H), 2.30 (s, 3H).

***N*-Pyridin-2-yl-benzene-1,2-diamine (1a')**

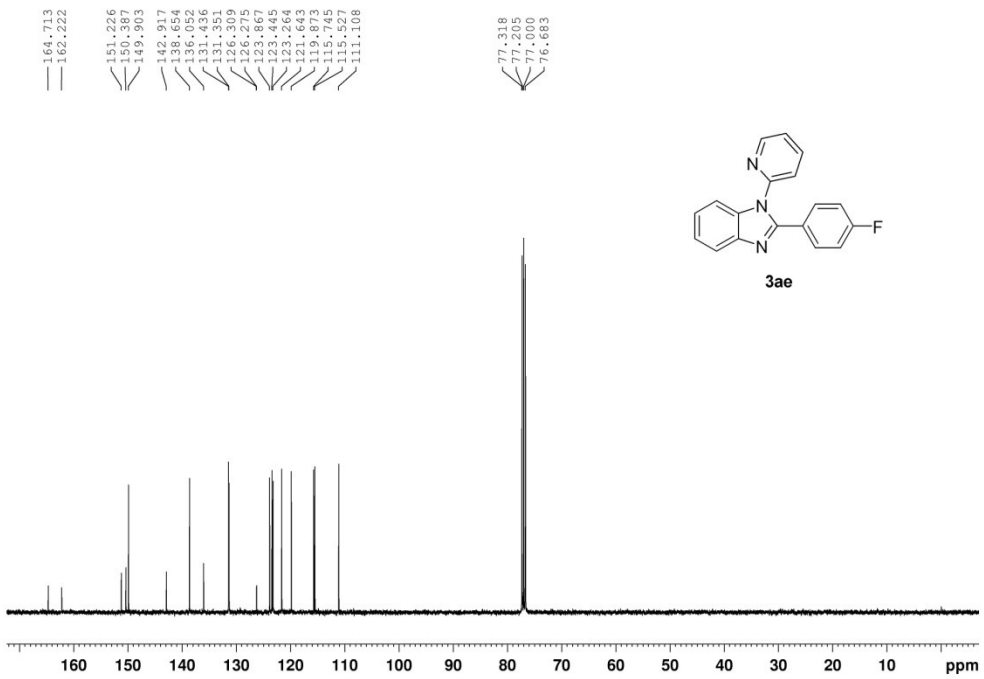
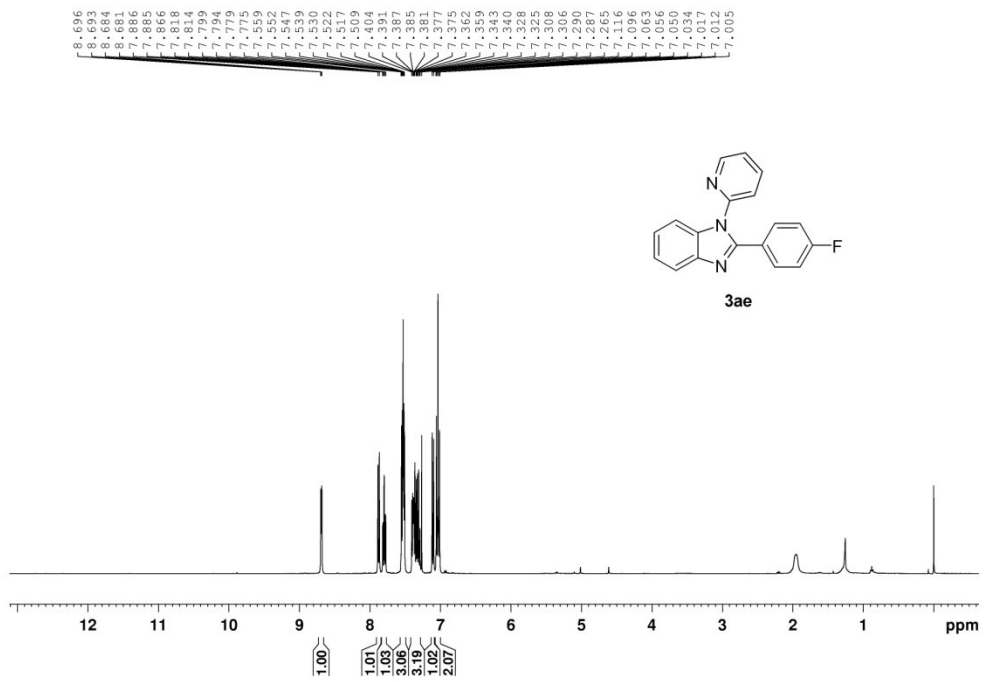
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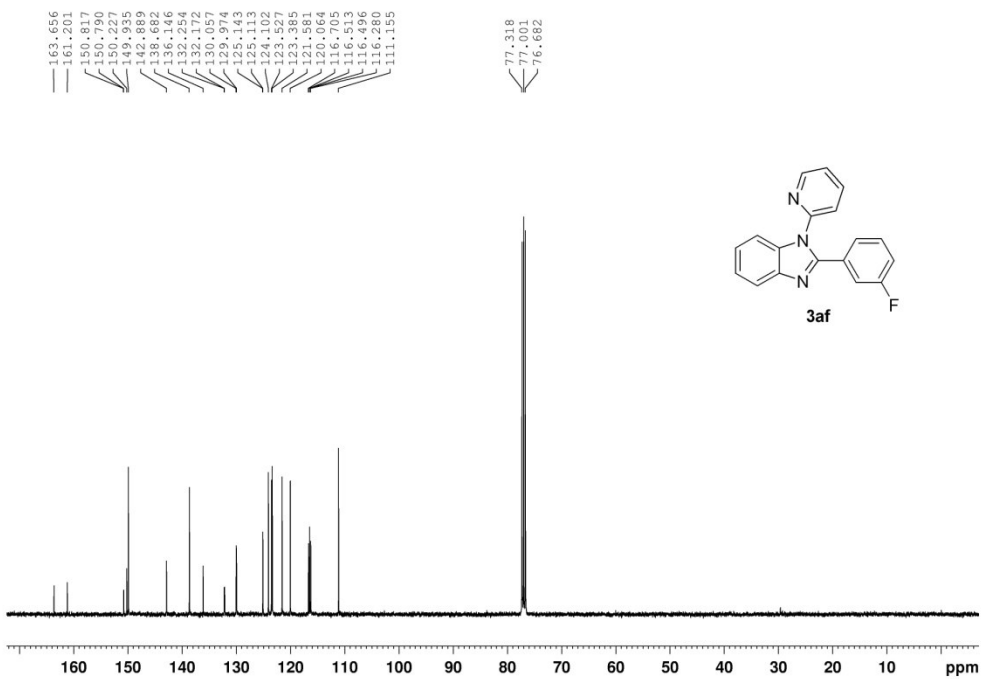
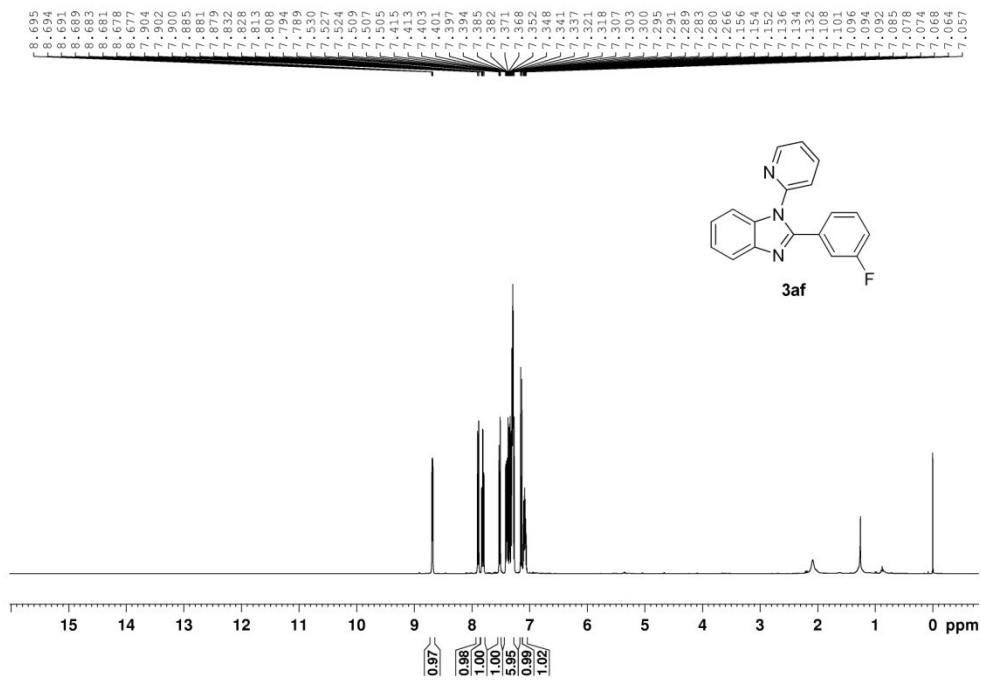


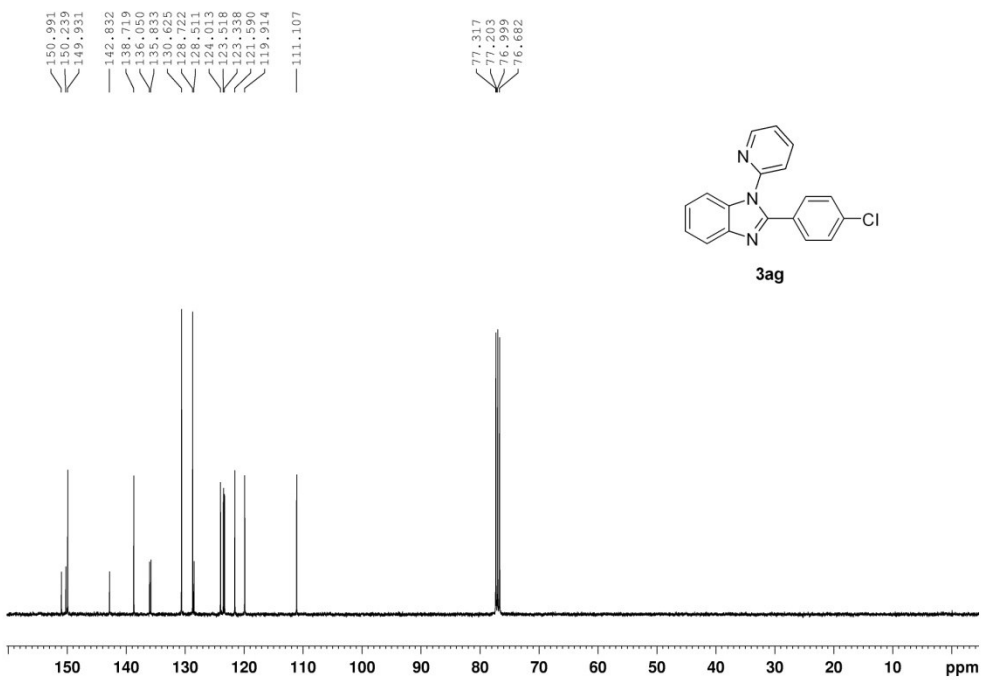
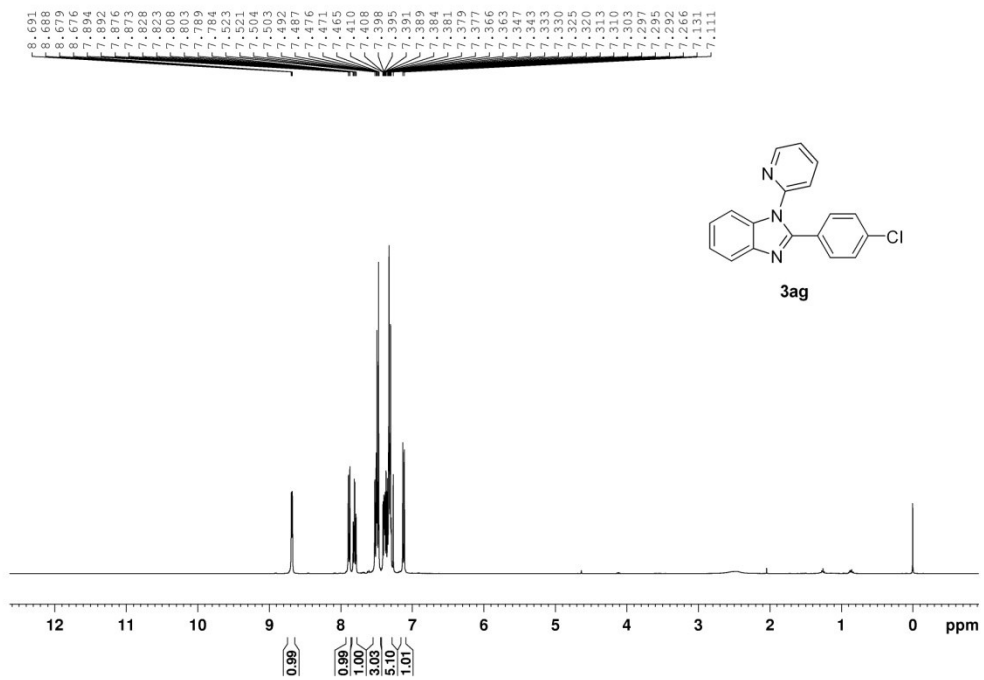


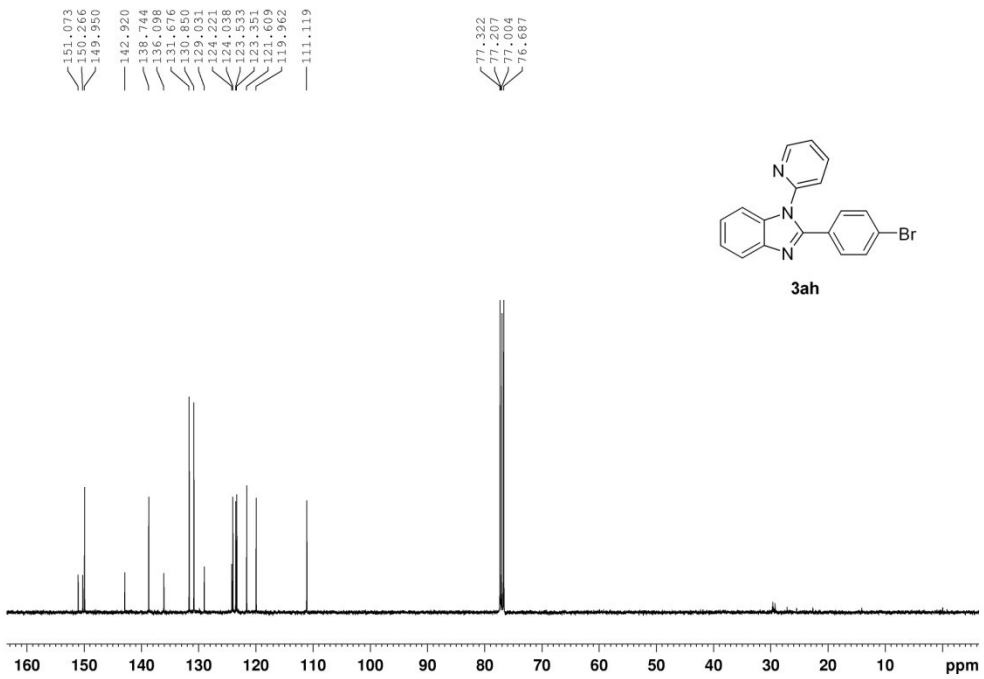
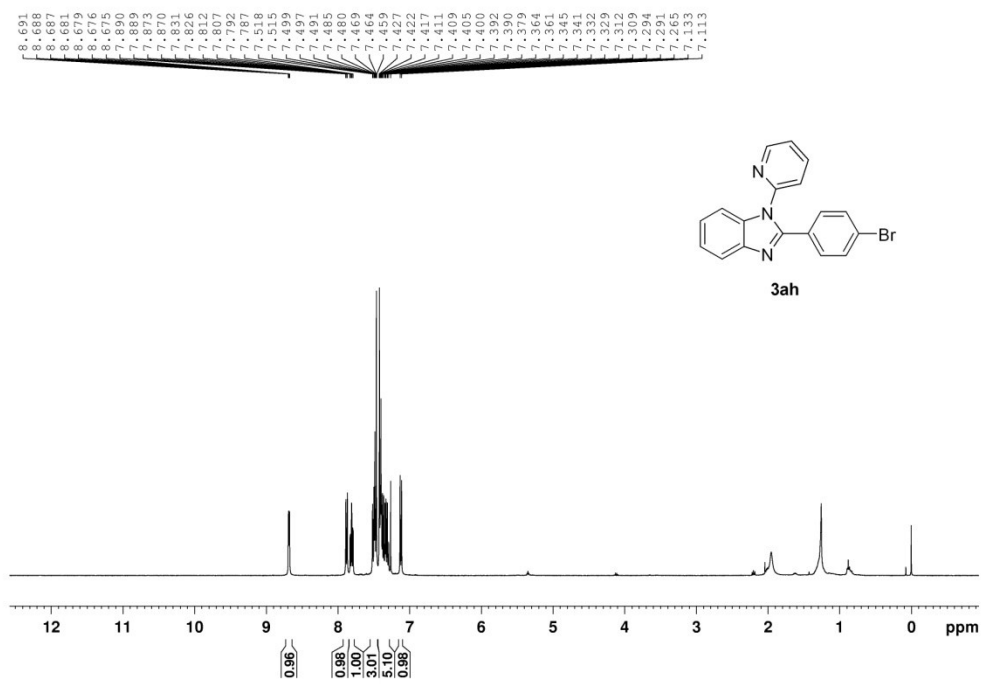


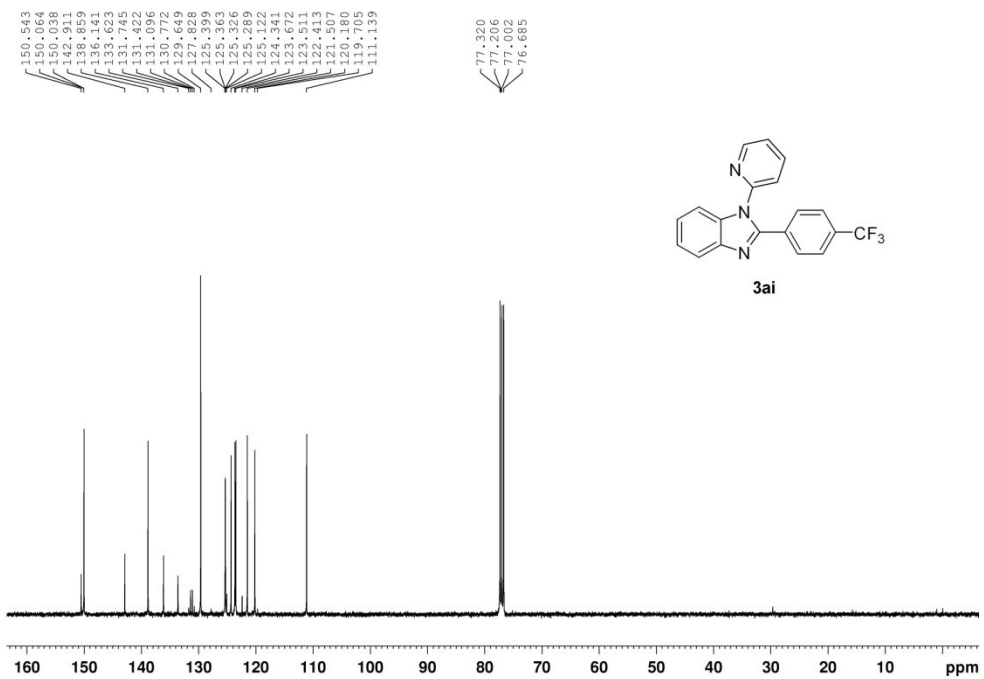
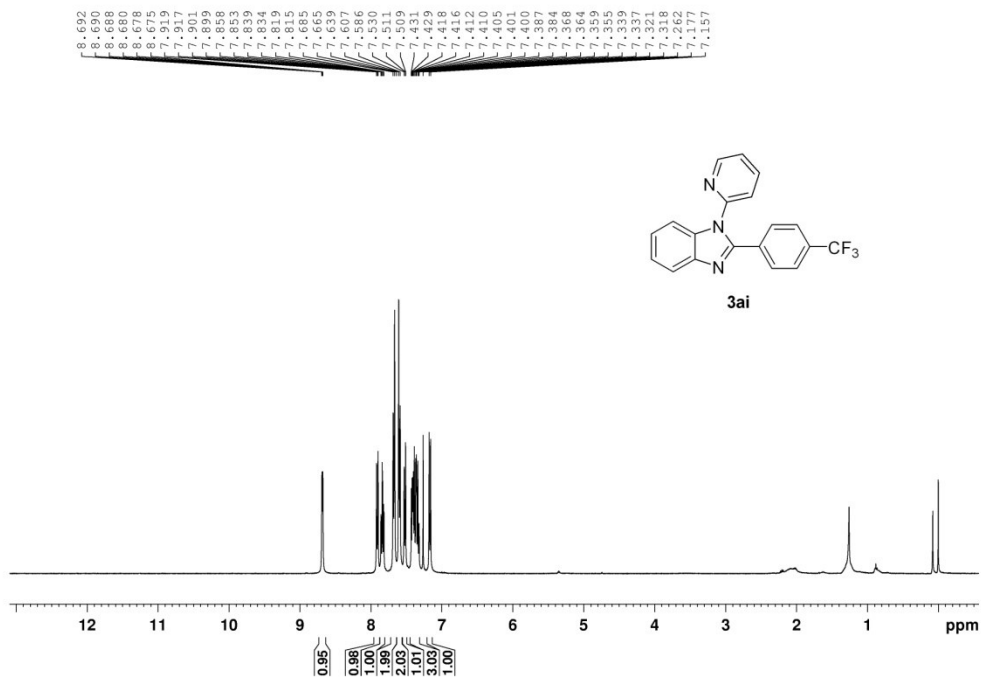


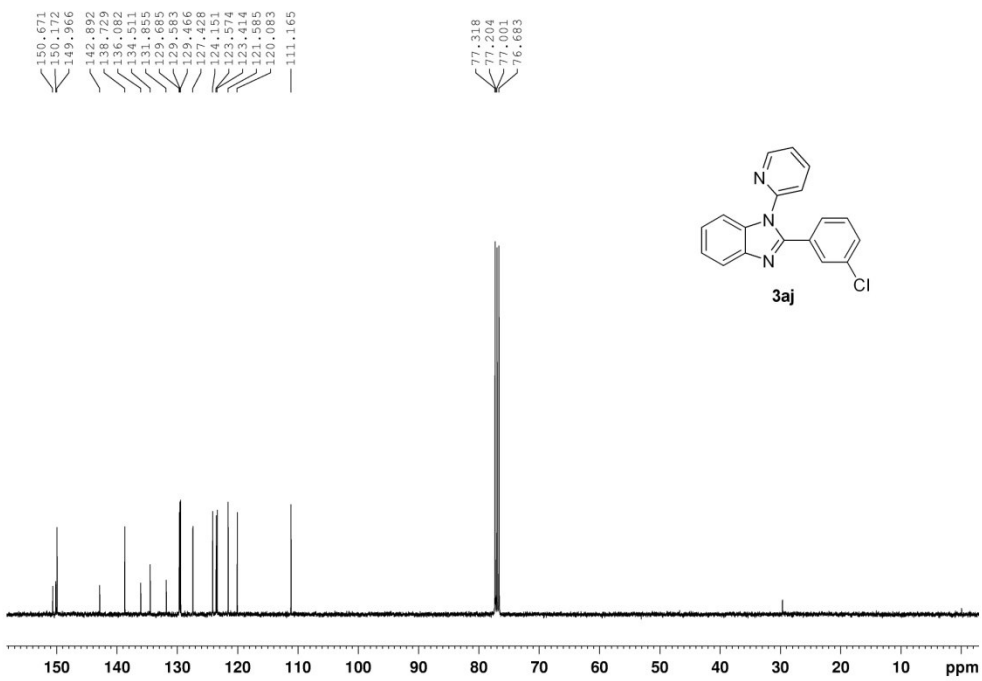
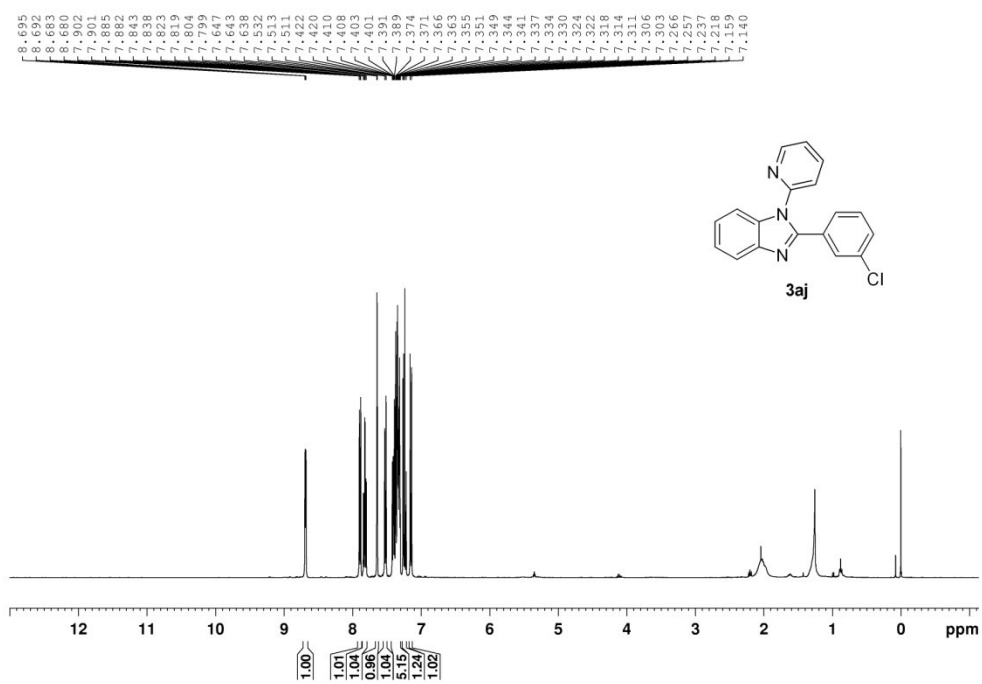


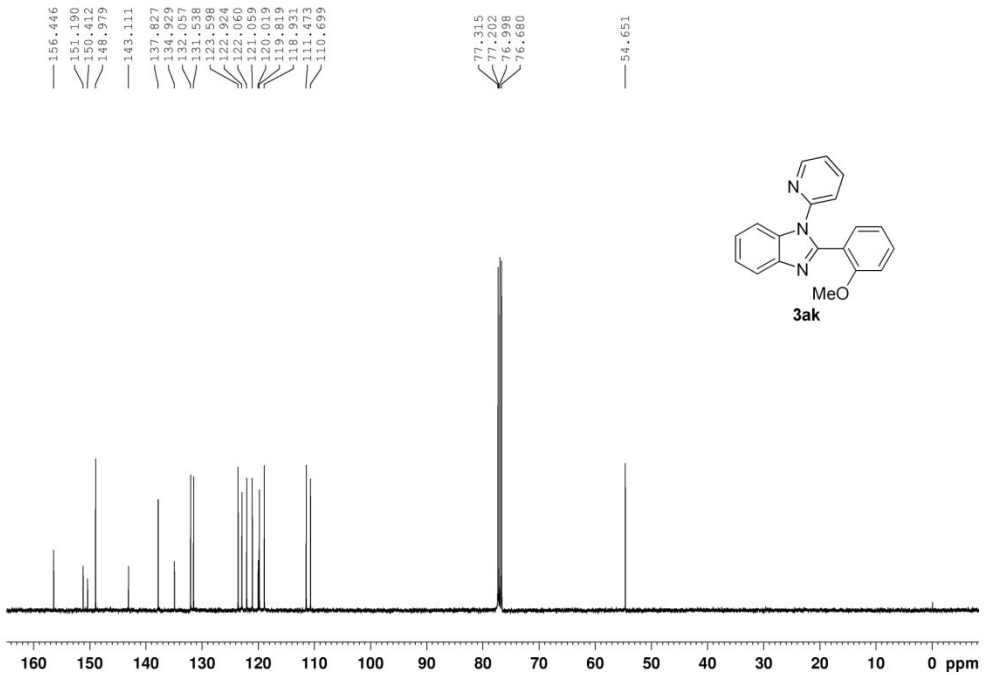
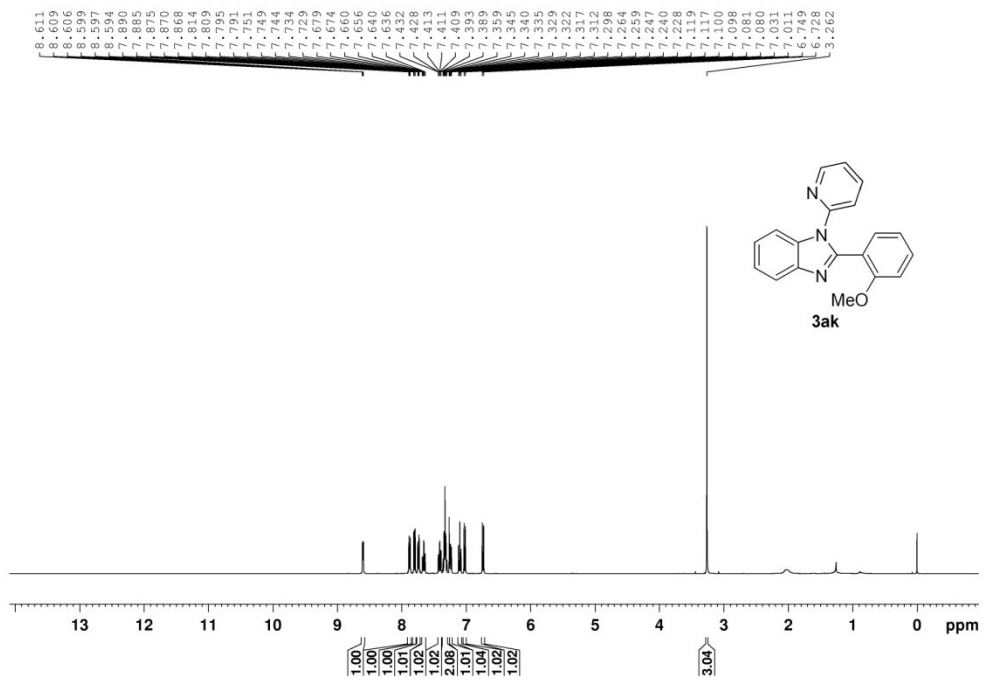


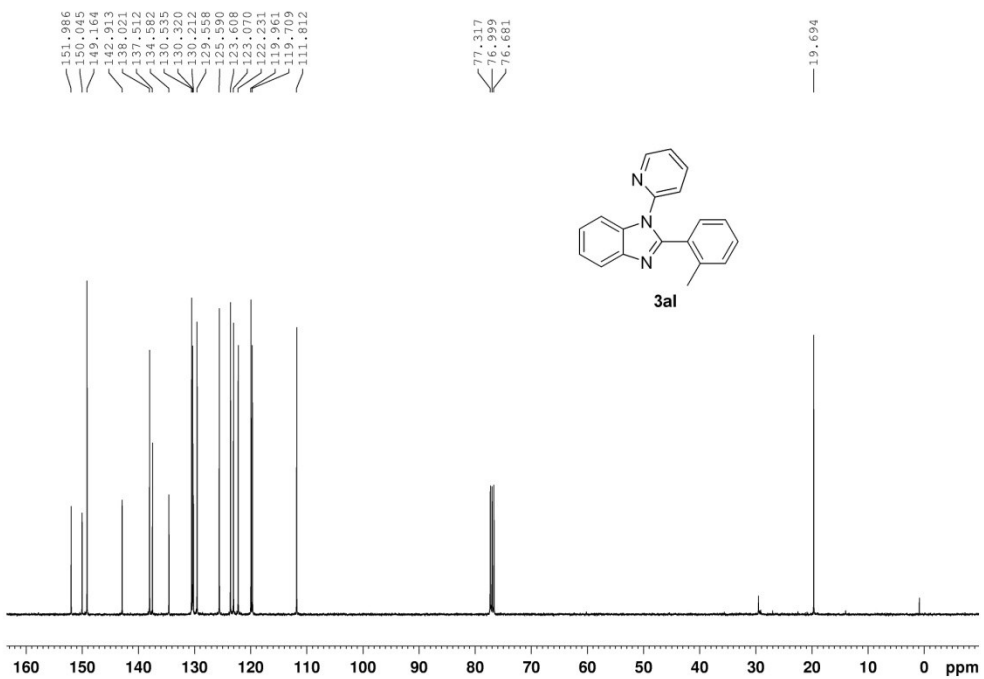
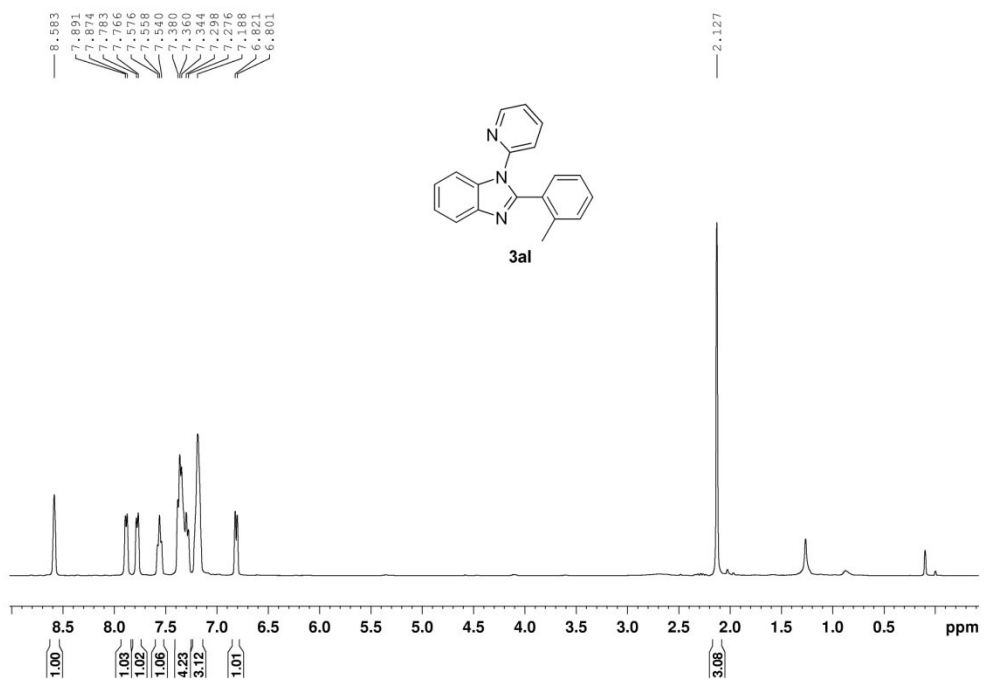


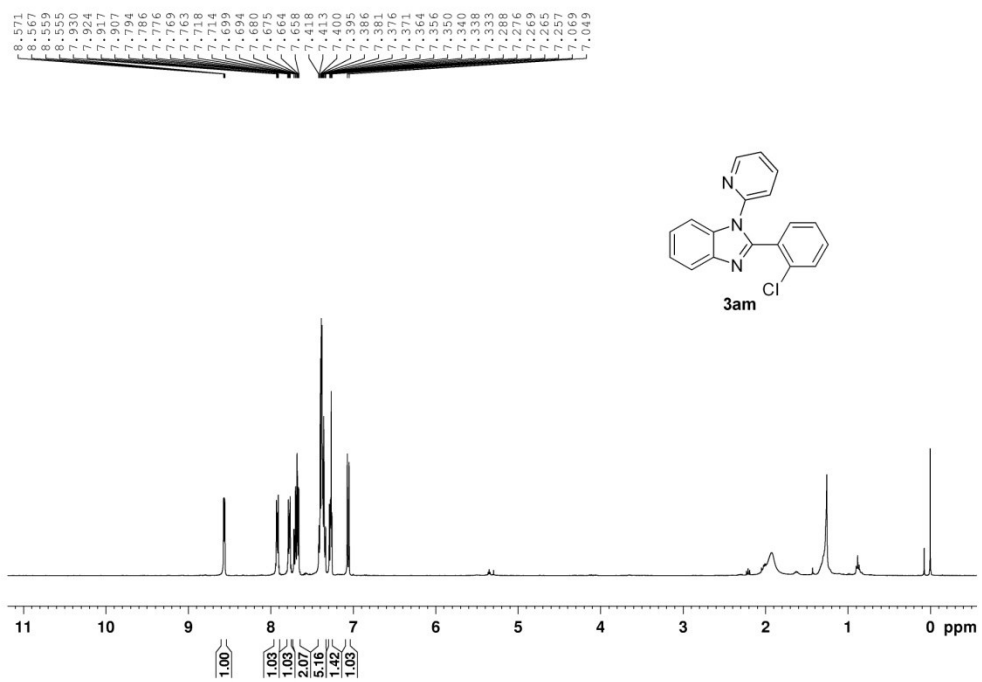




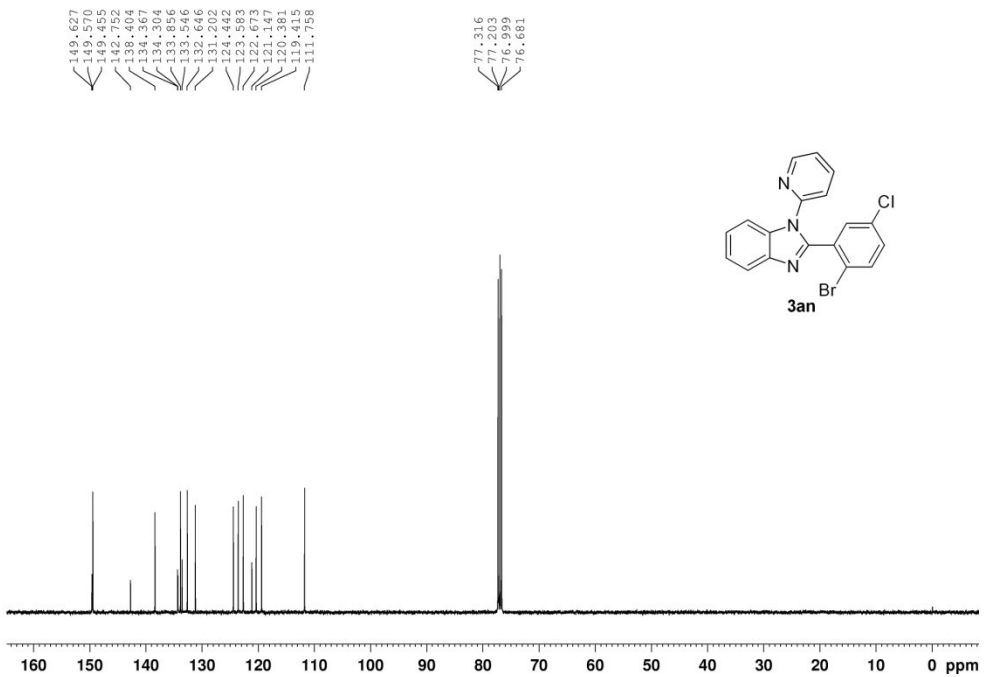
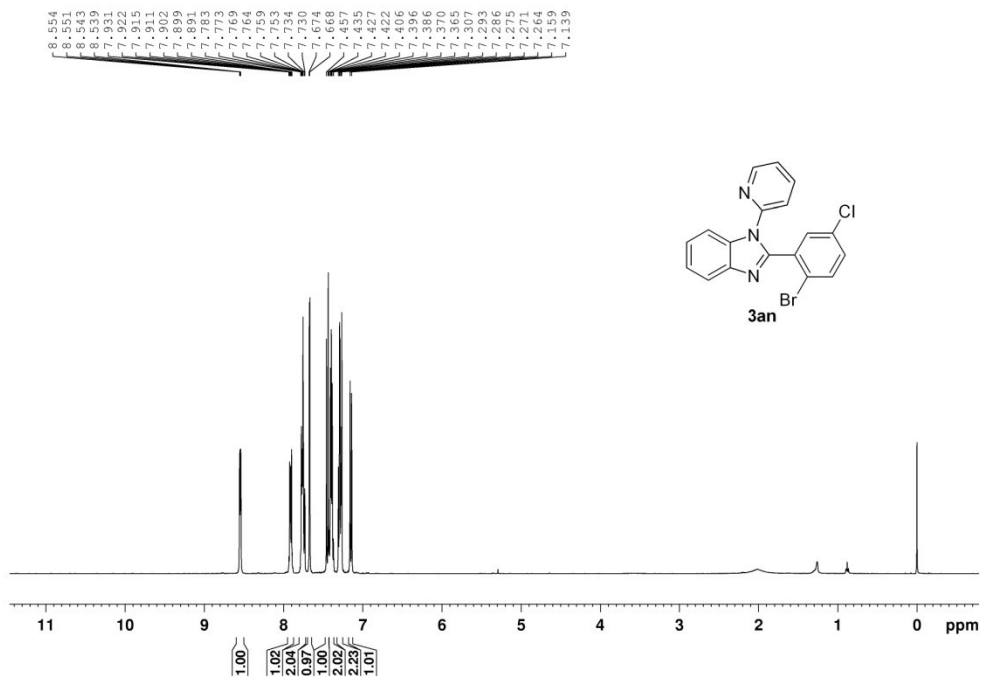


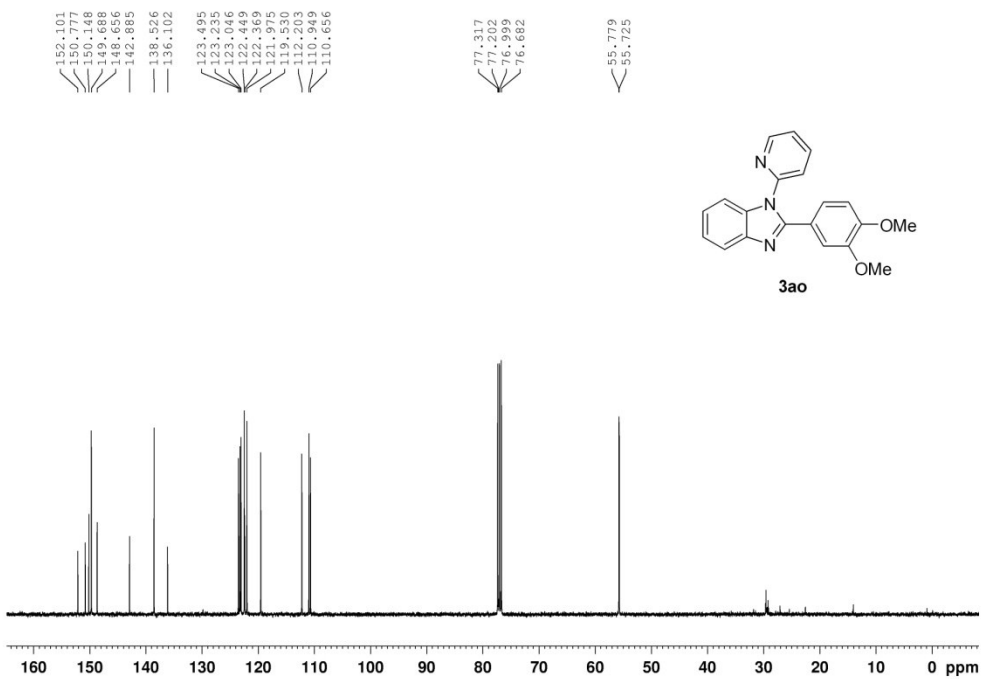
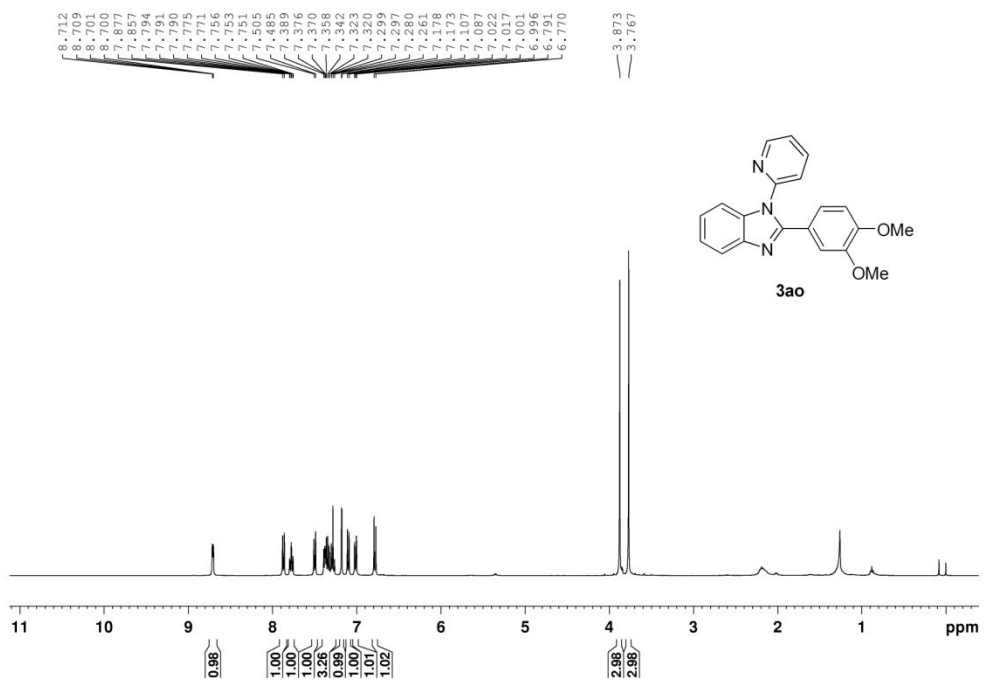


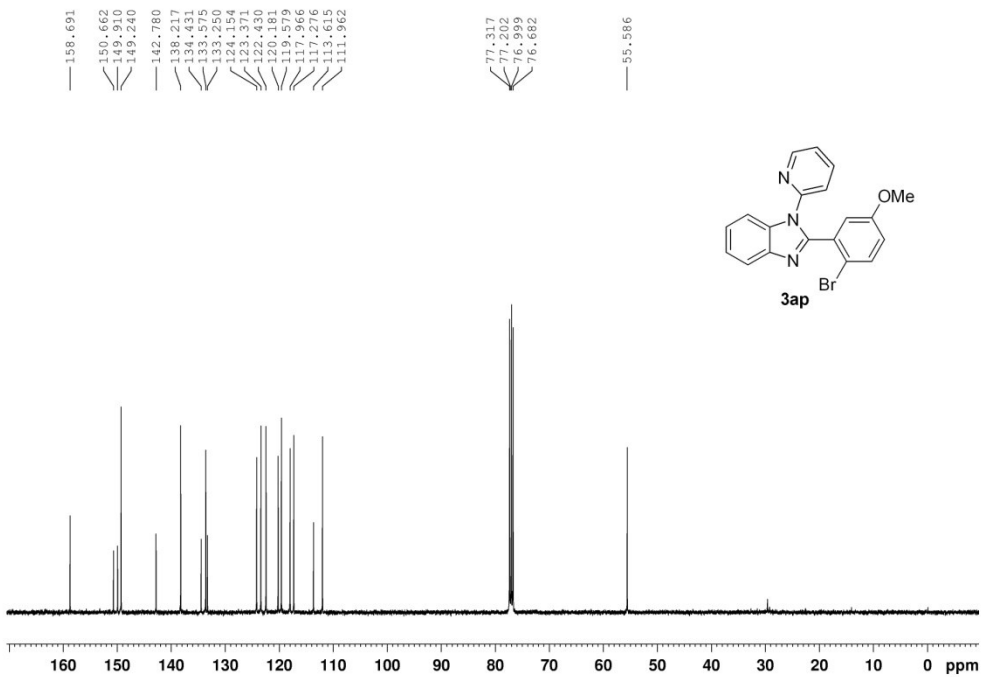
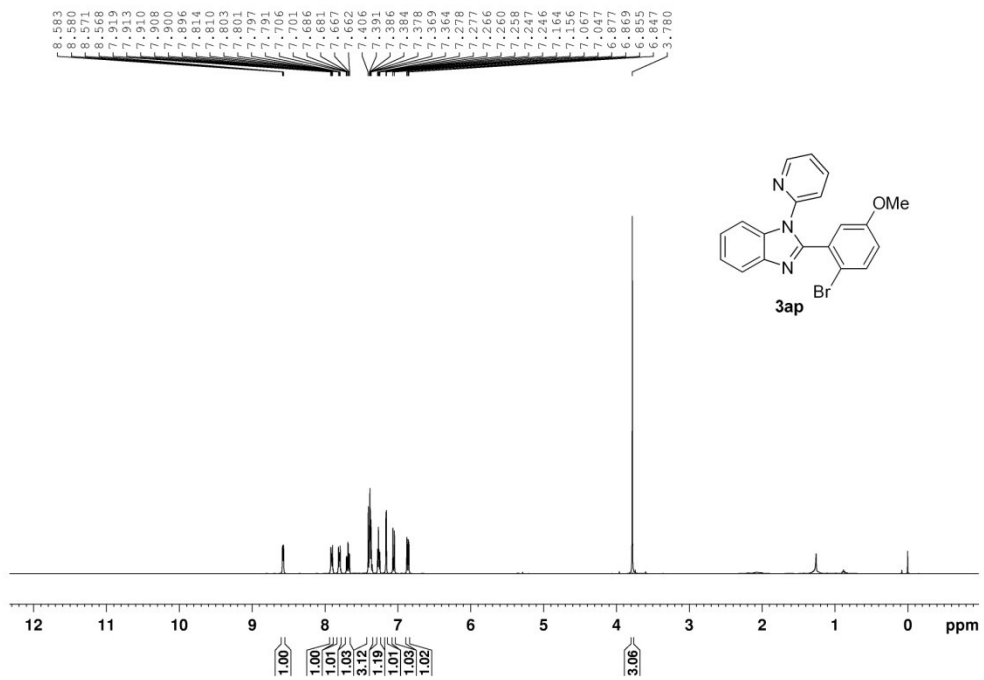


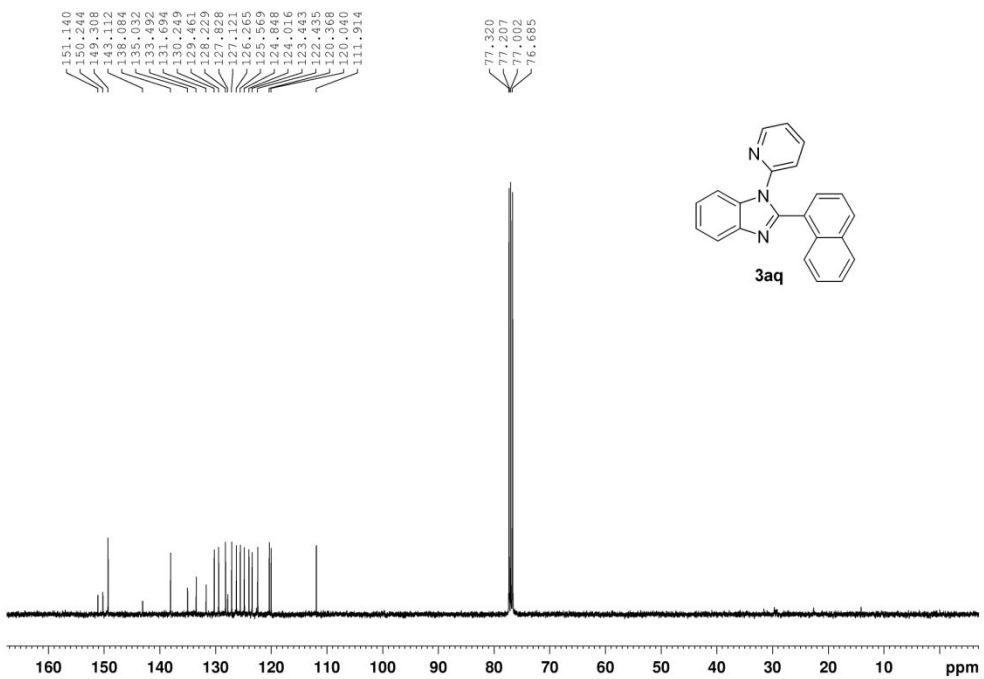
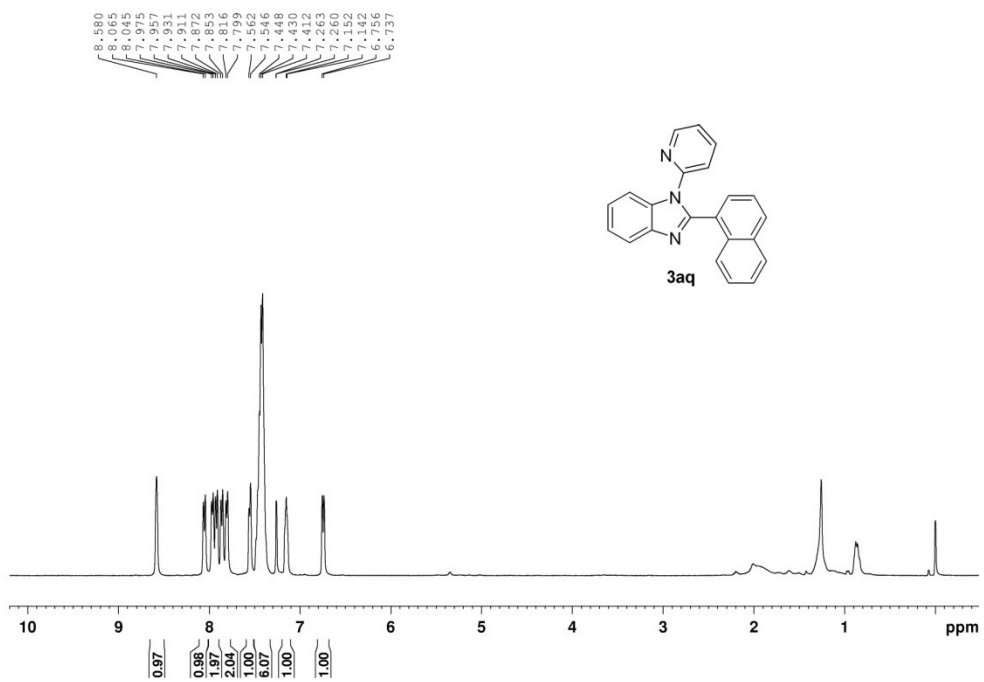


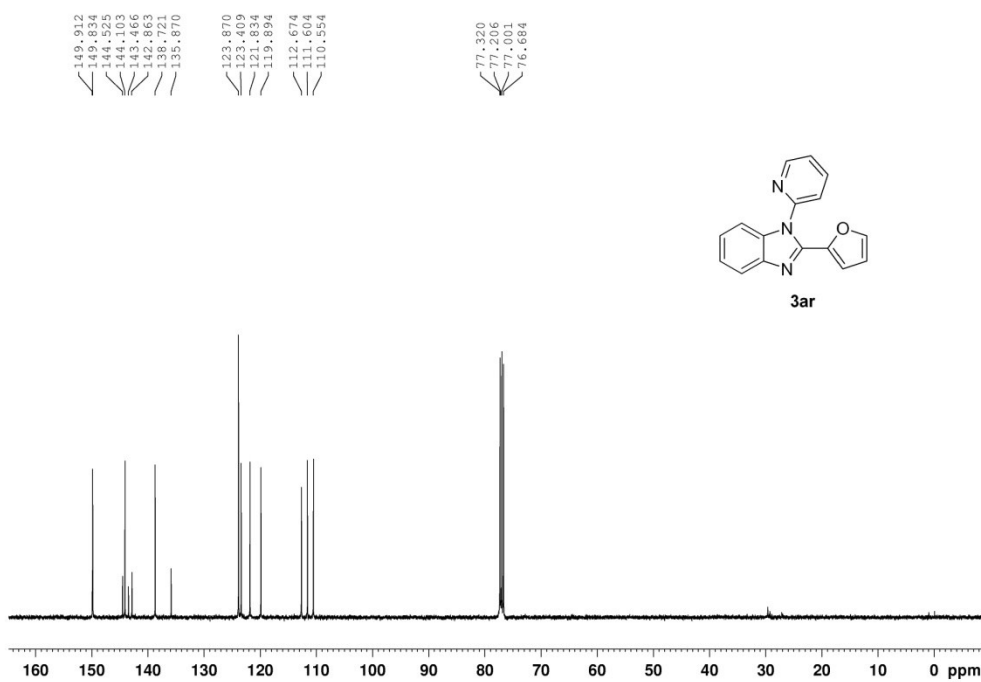
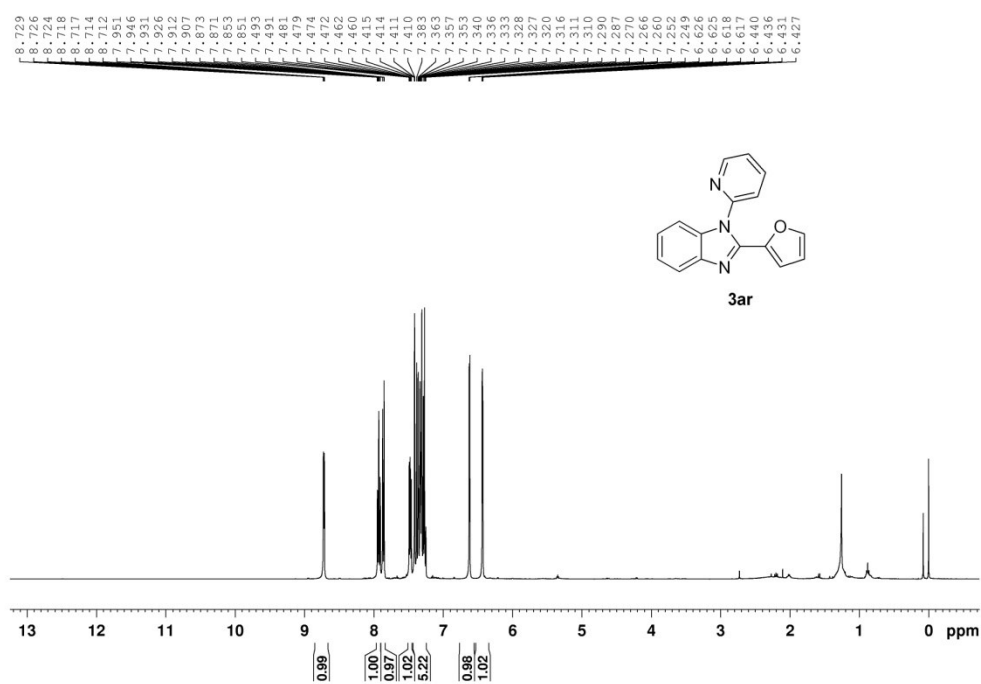




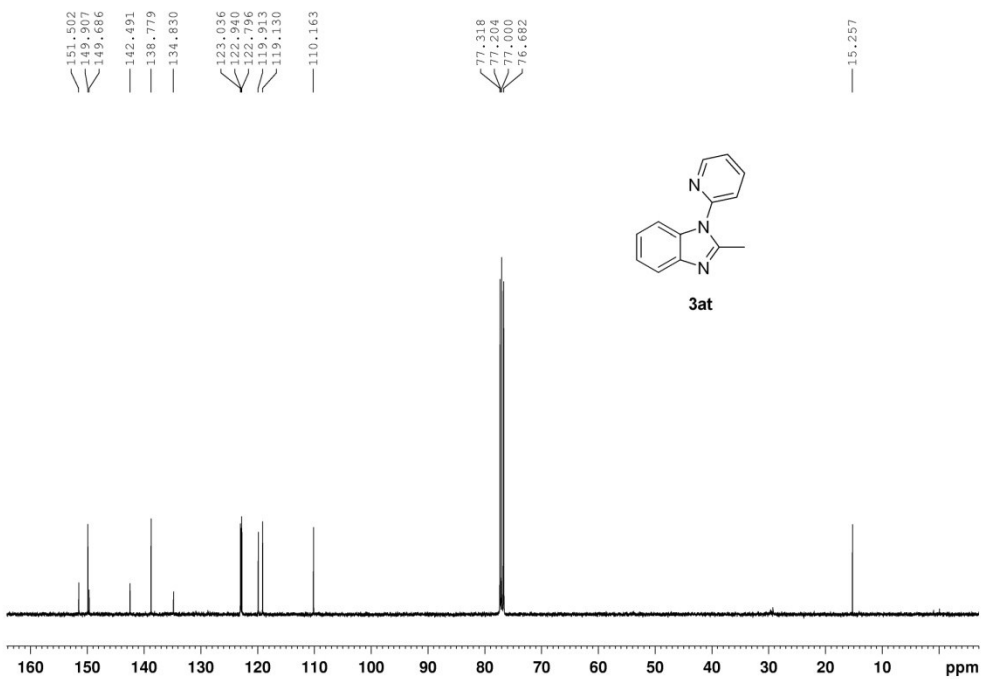
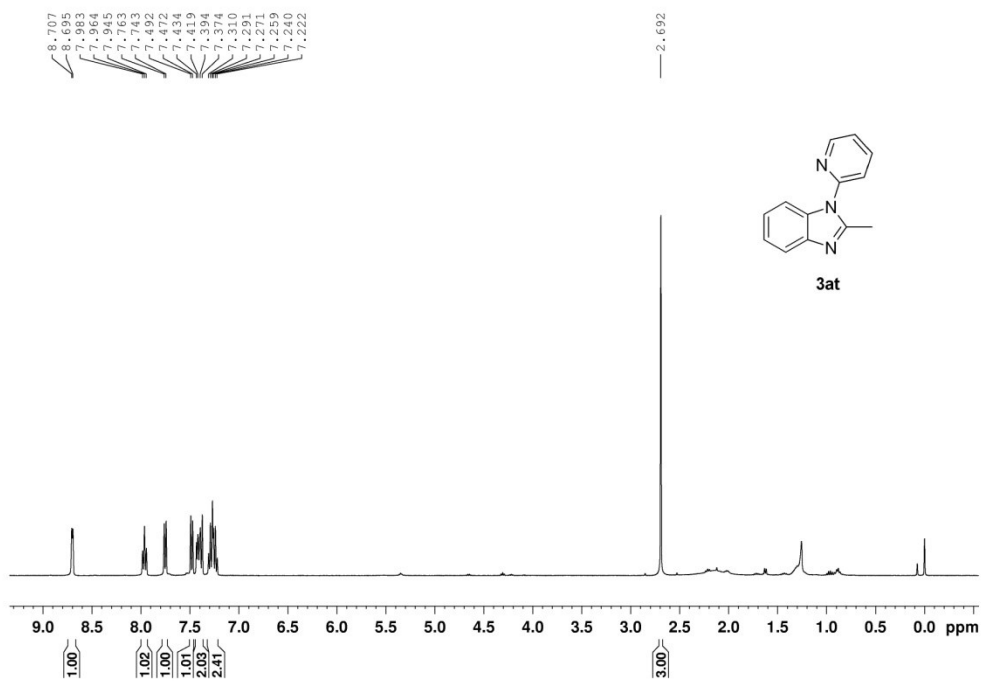


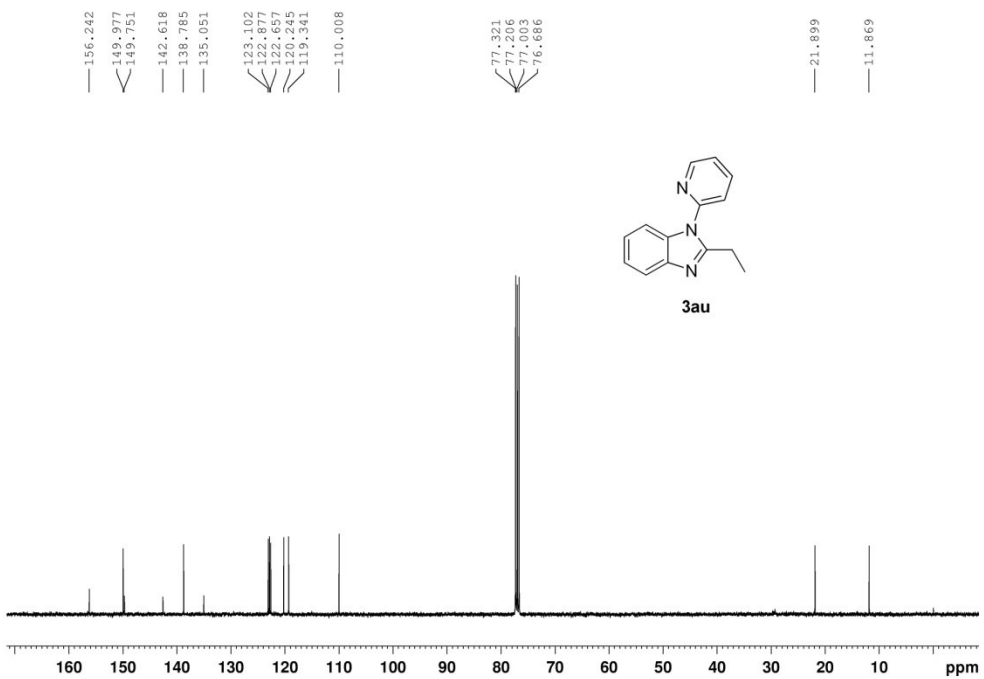
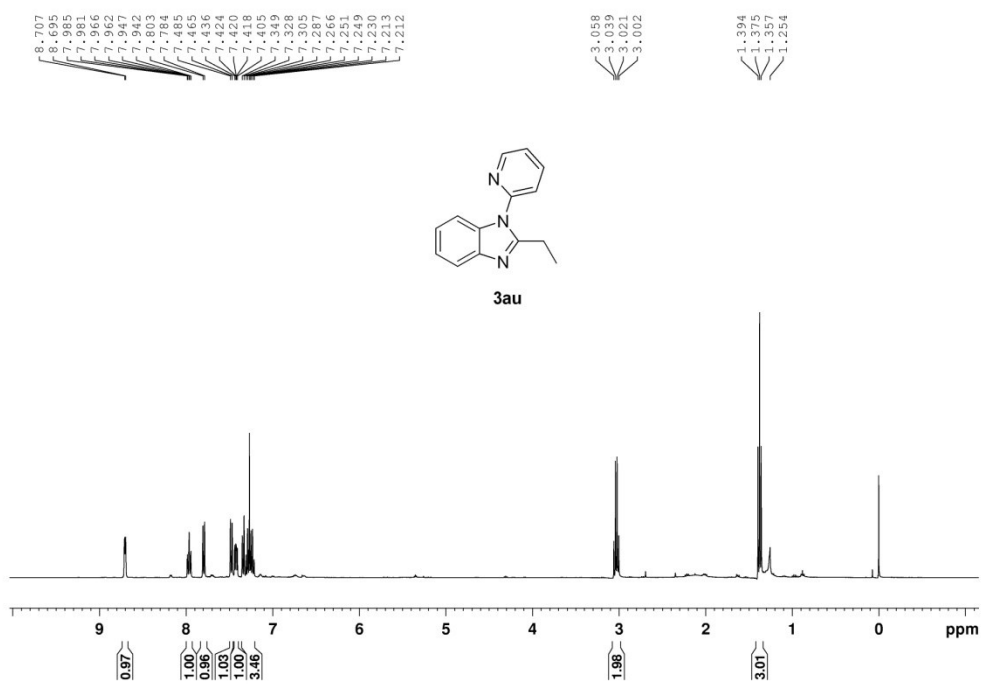




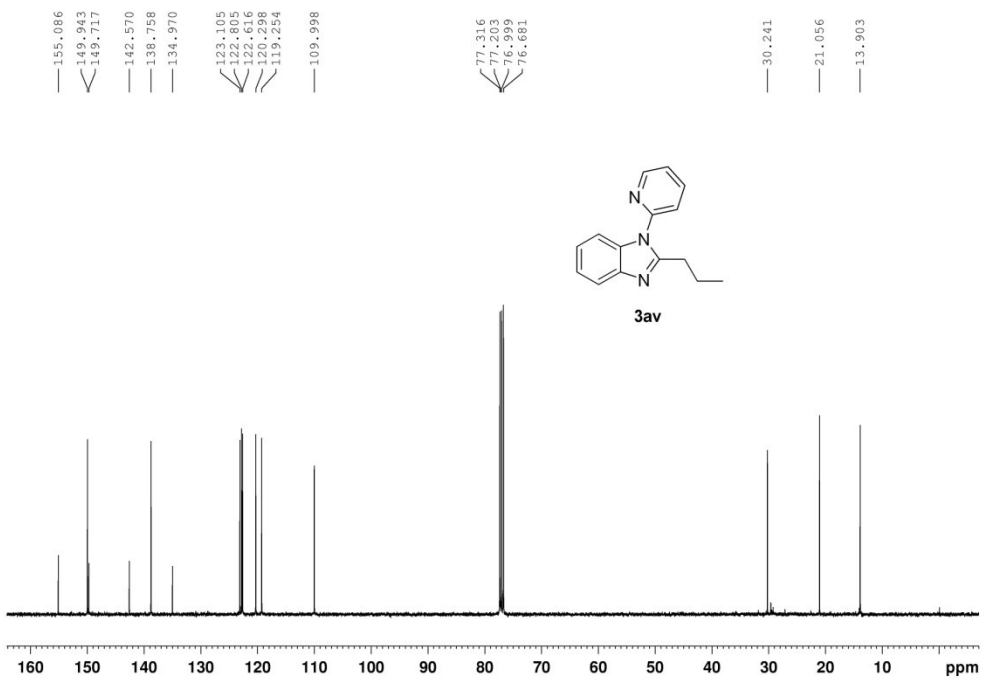
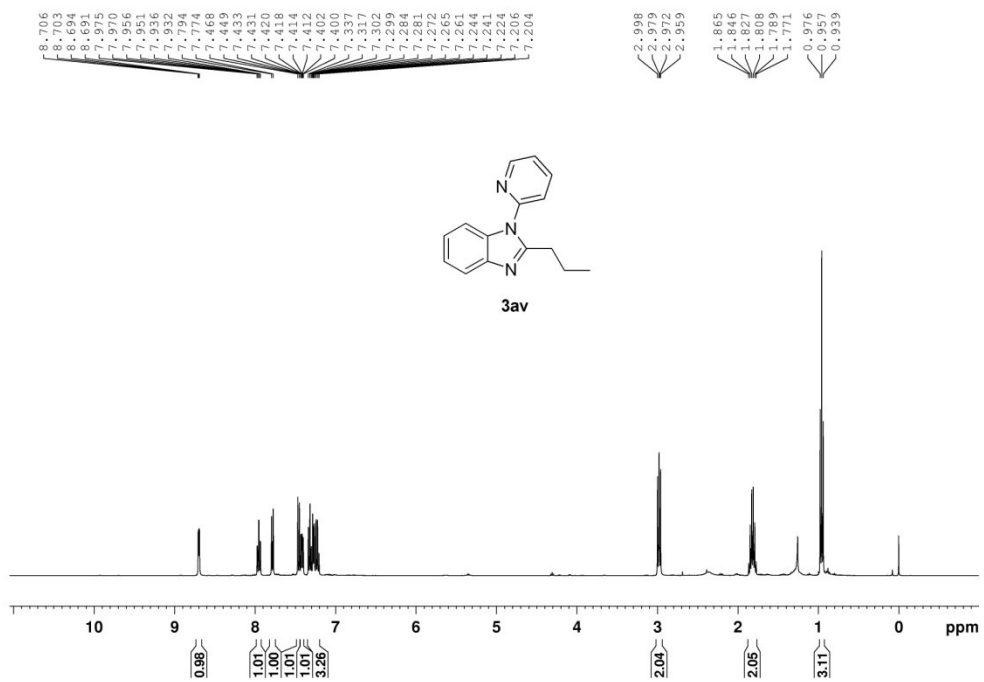


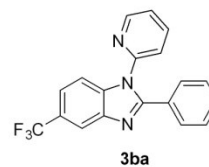
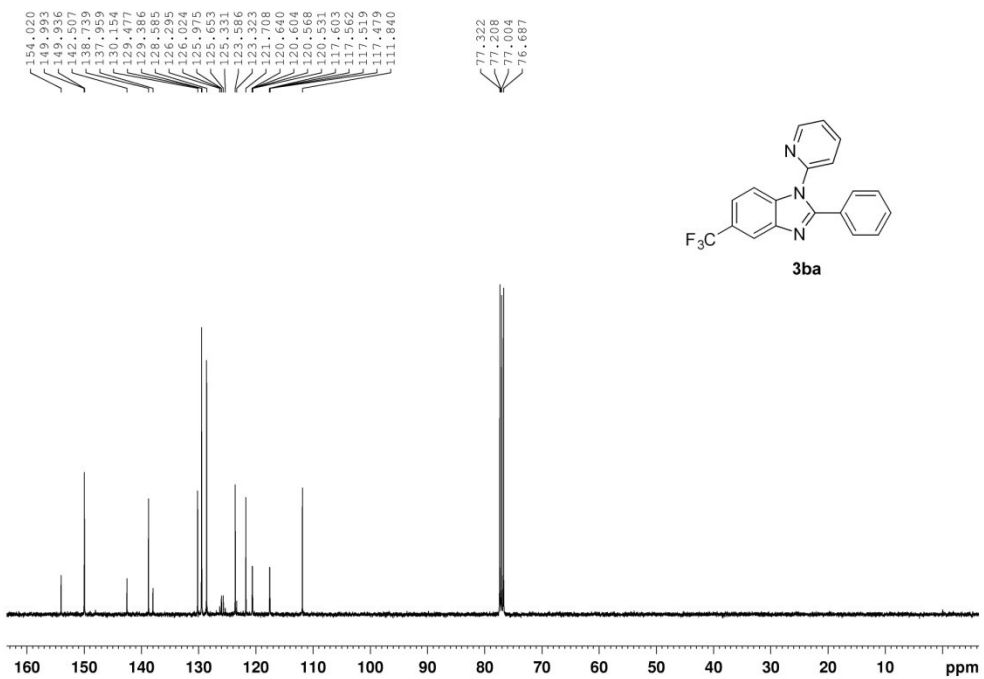
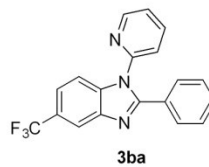
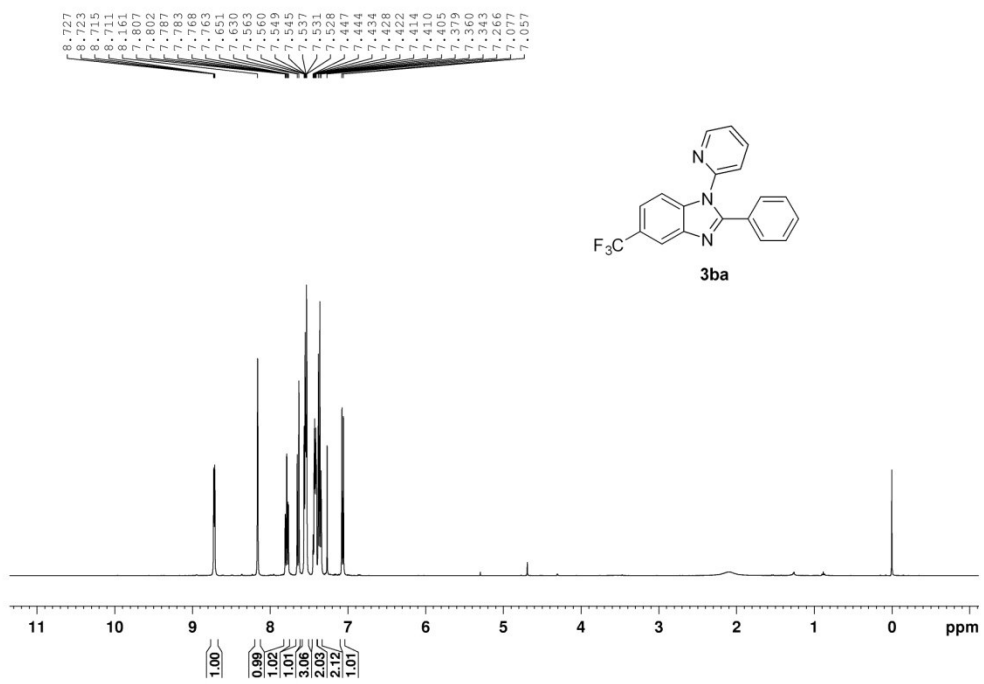


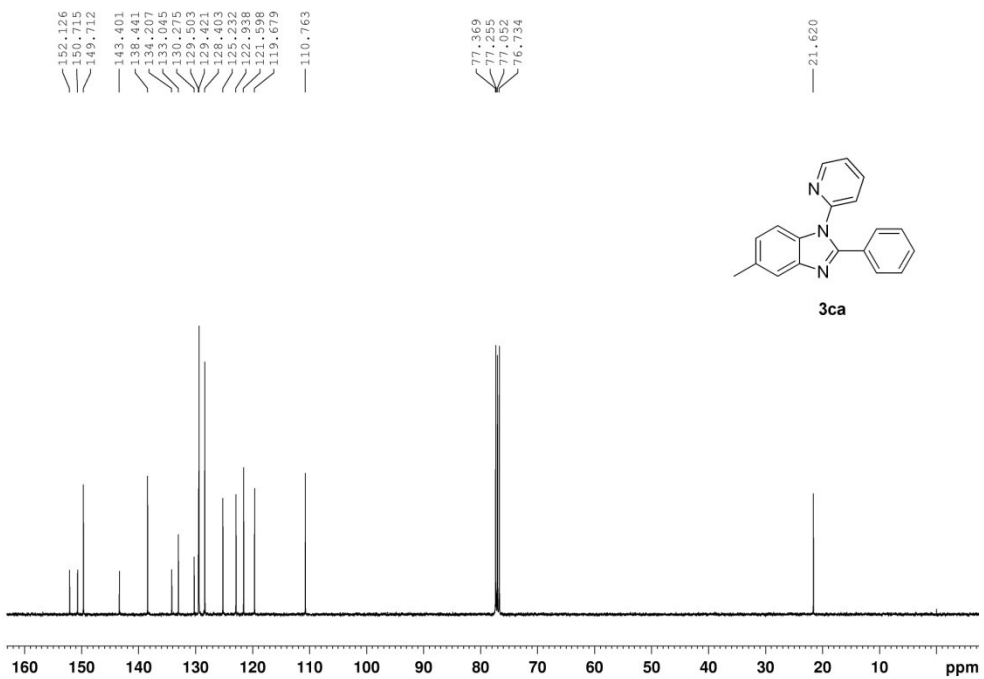
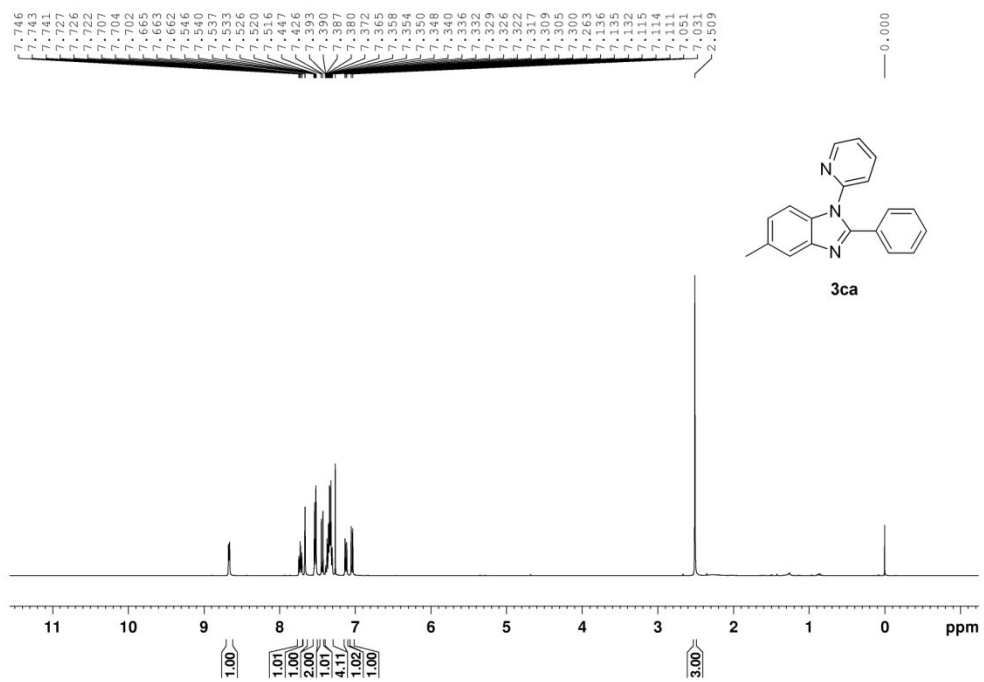


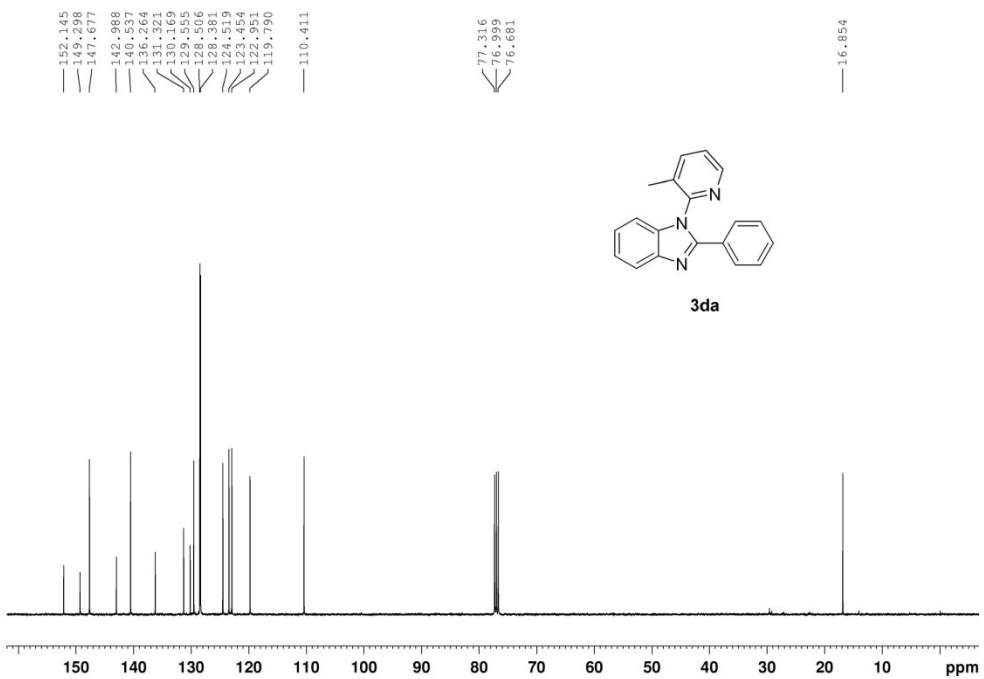
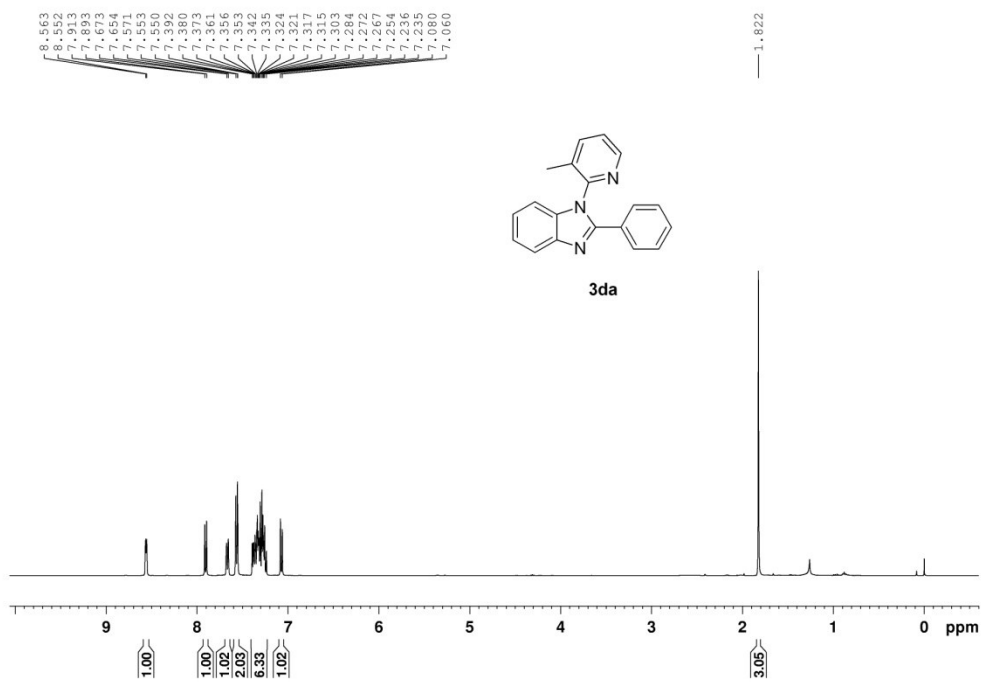


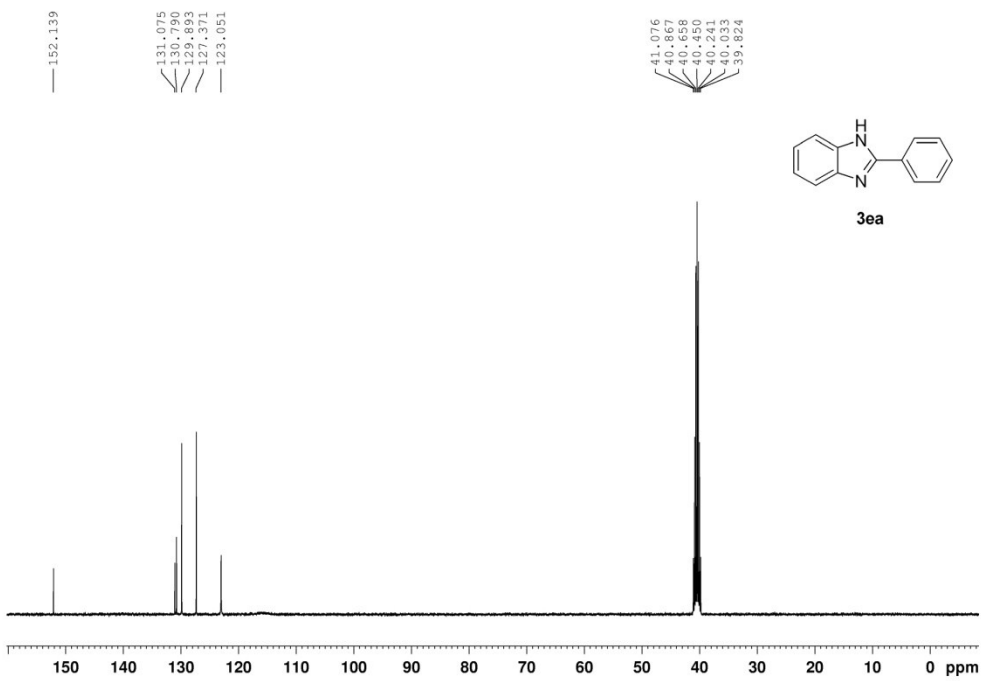
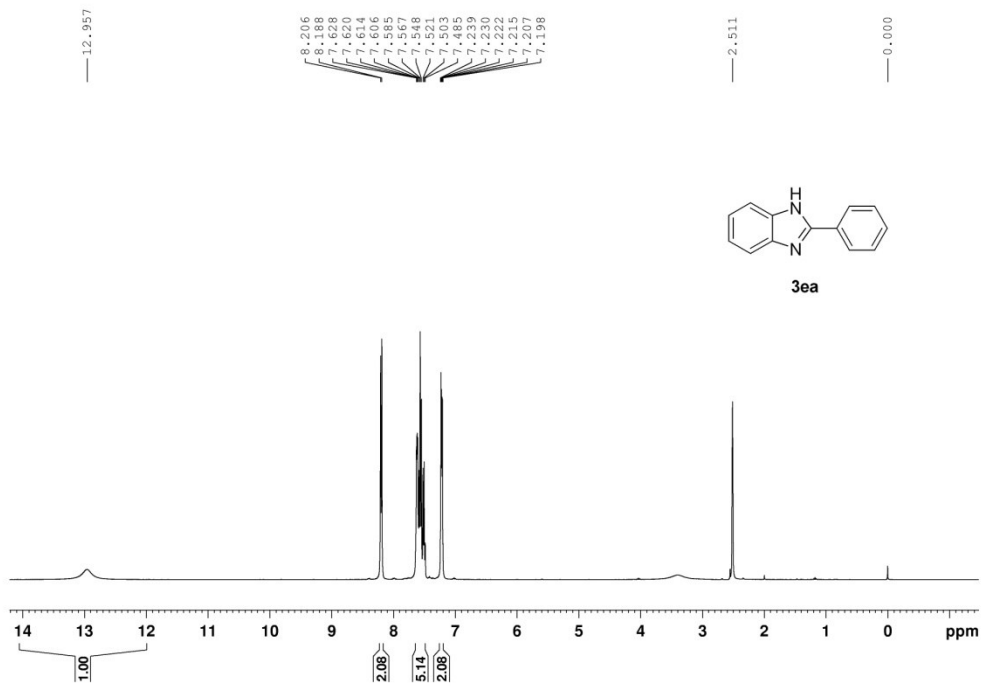




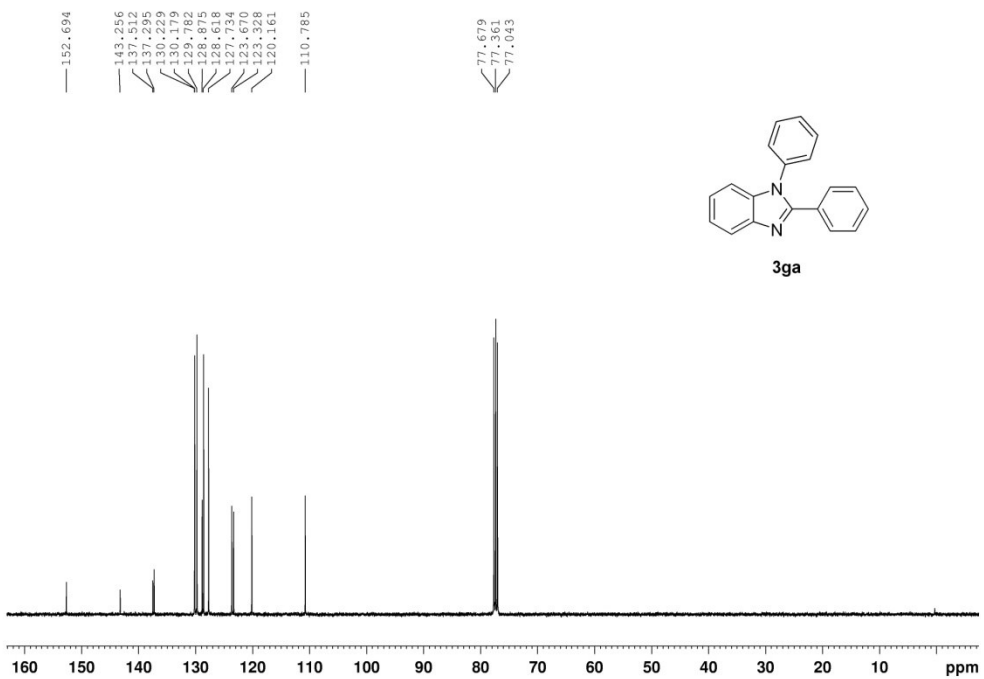
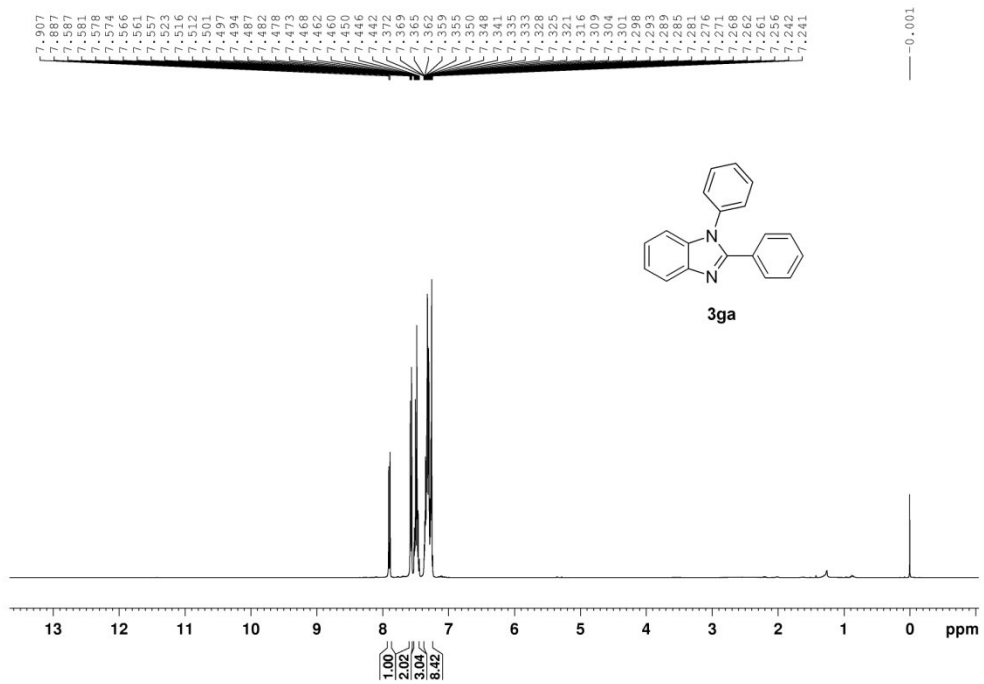


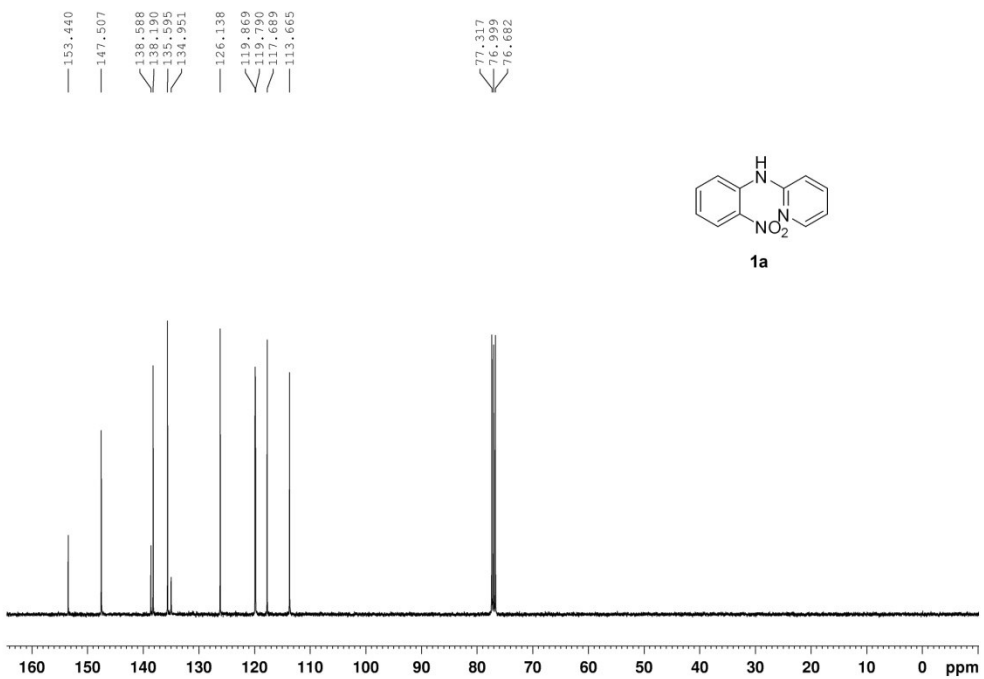
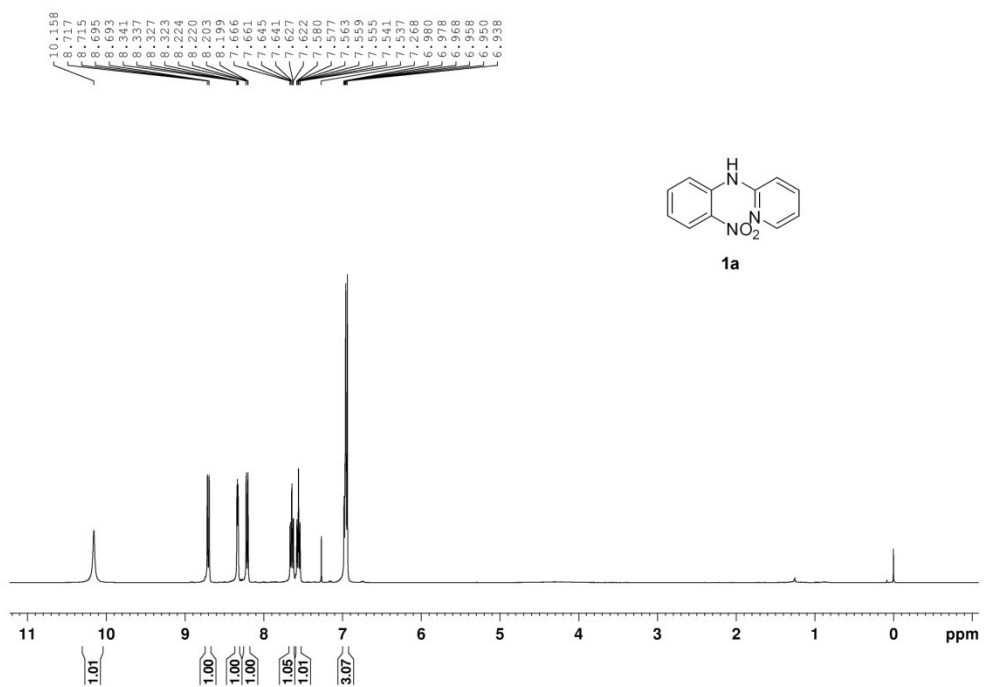




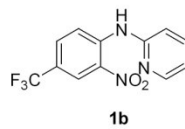
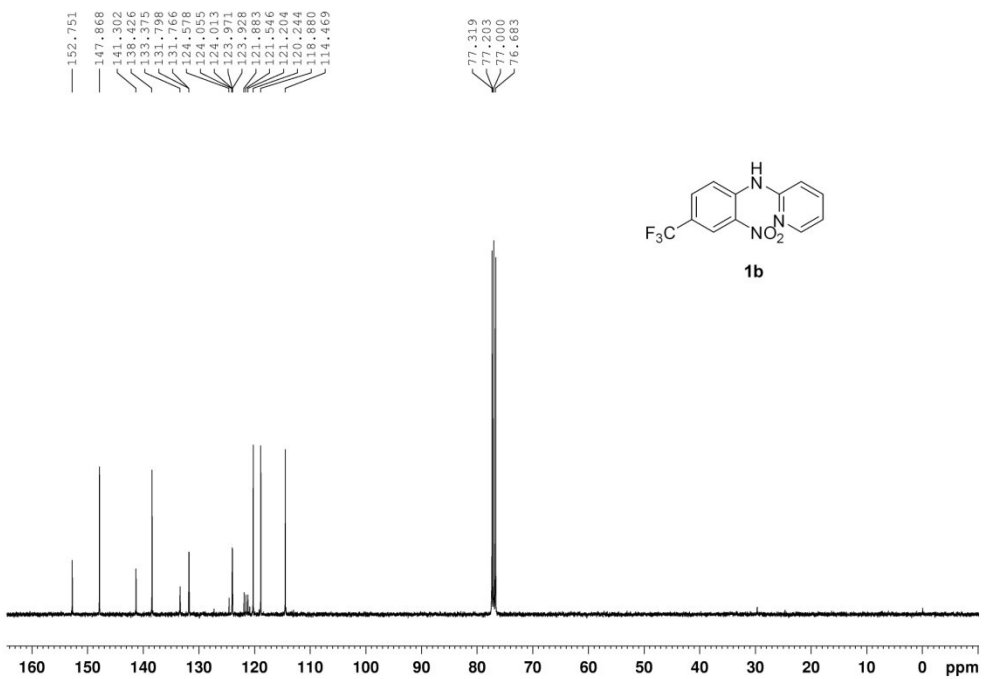
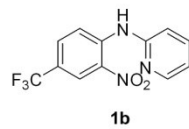
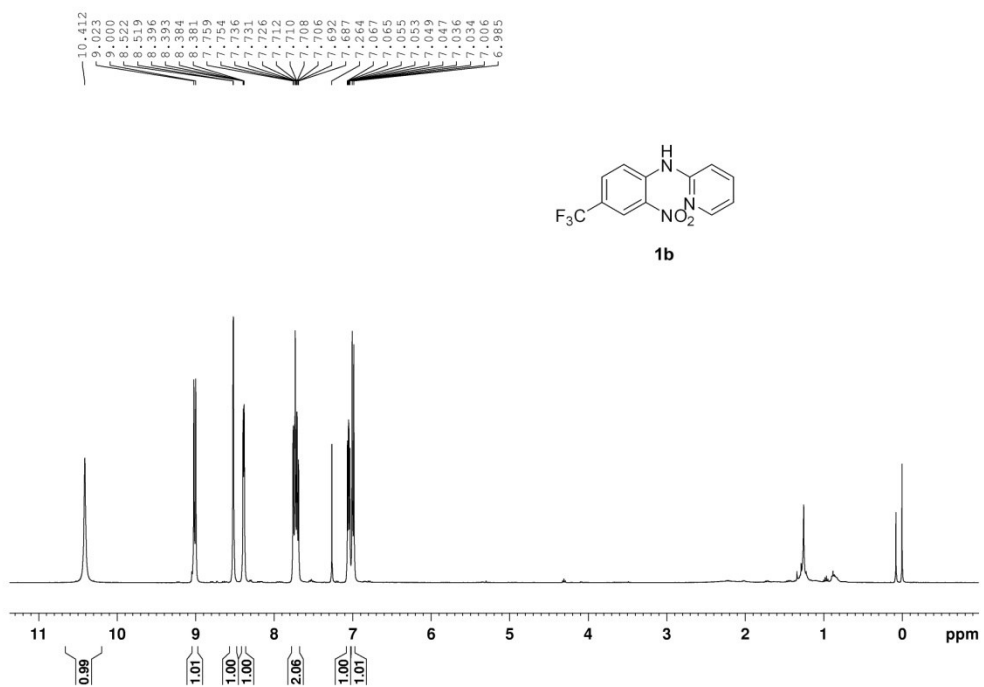


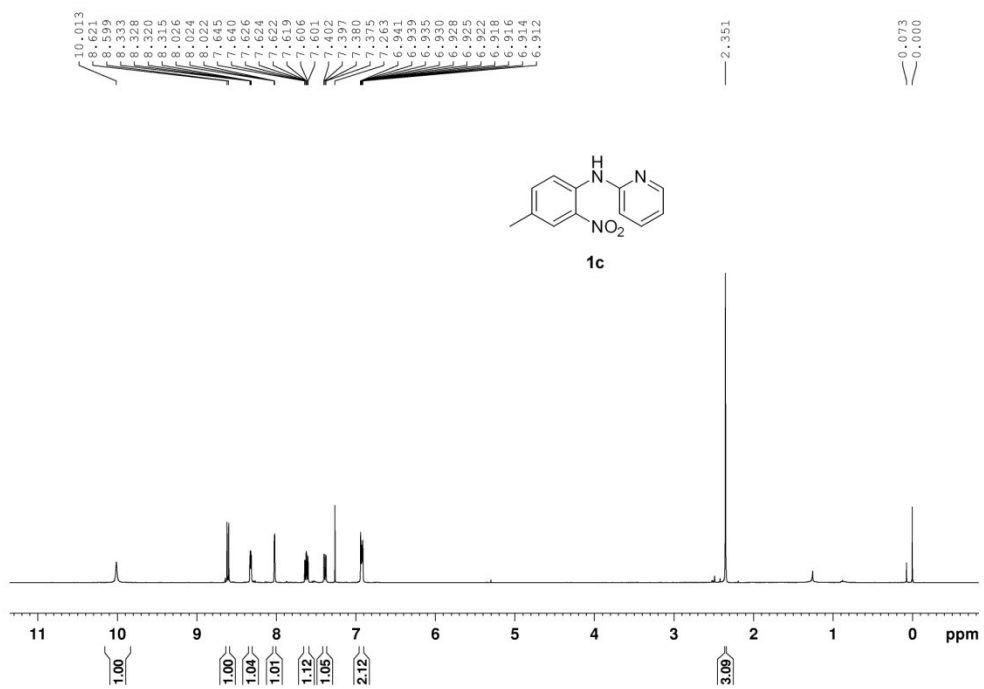


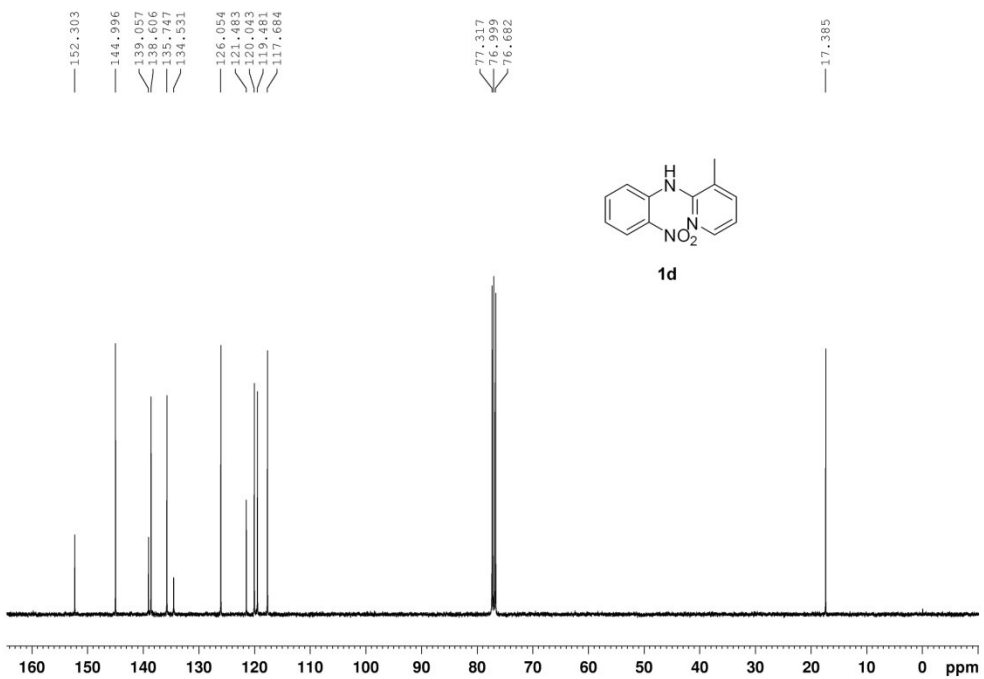
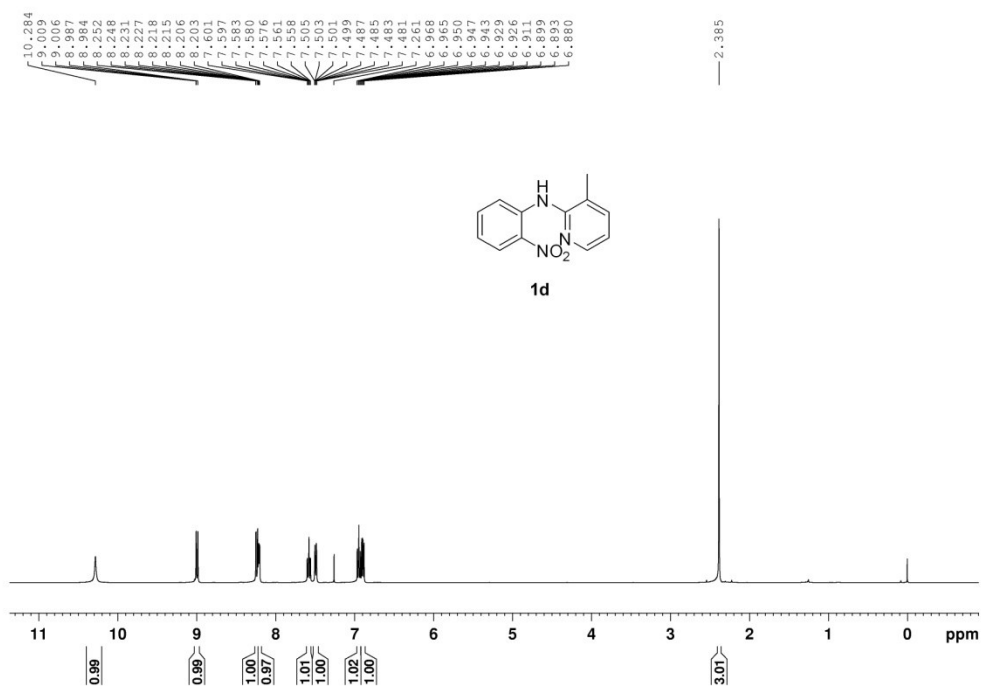


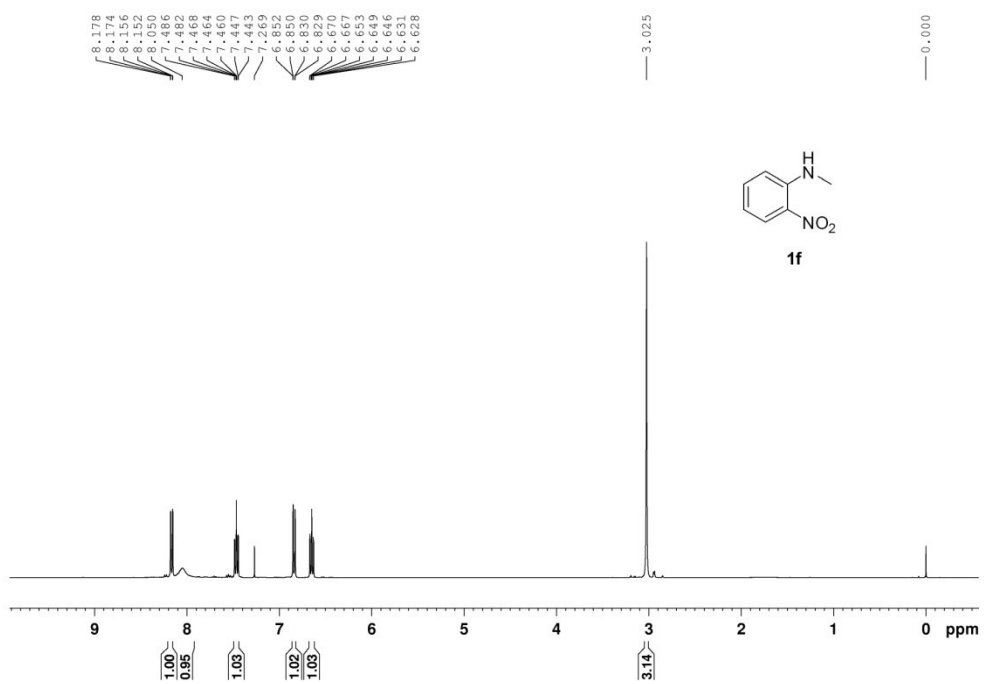


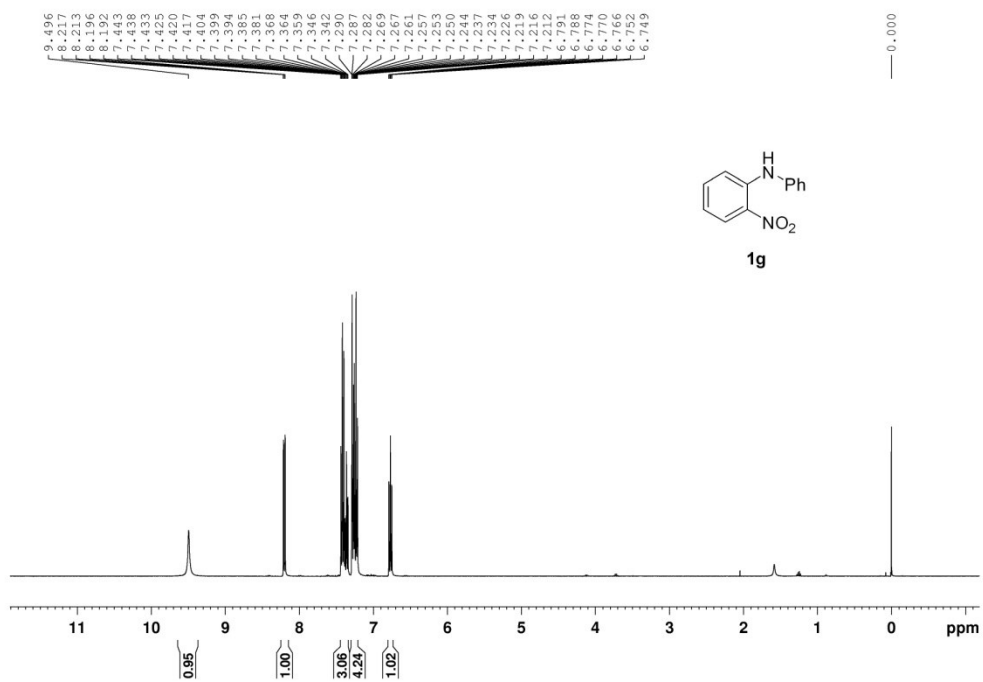


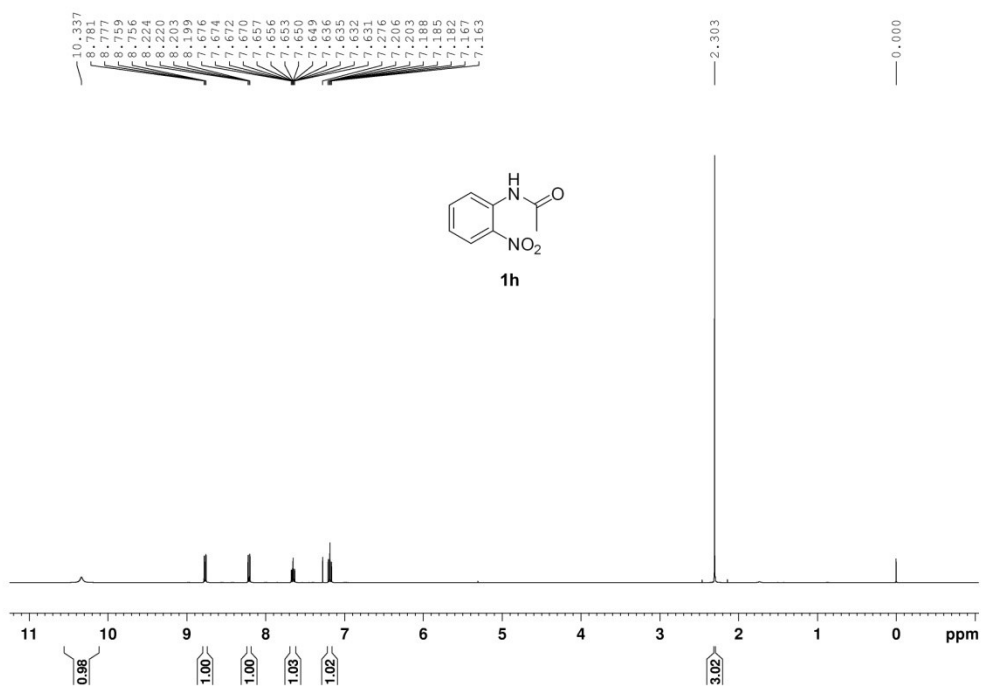


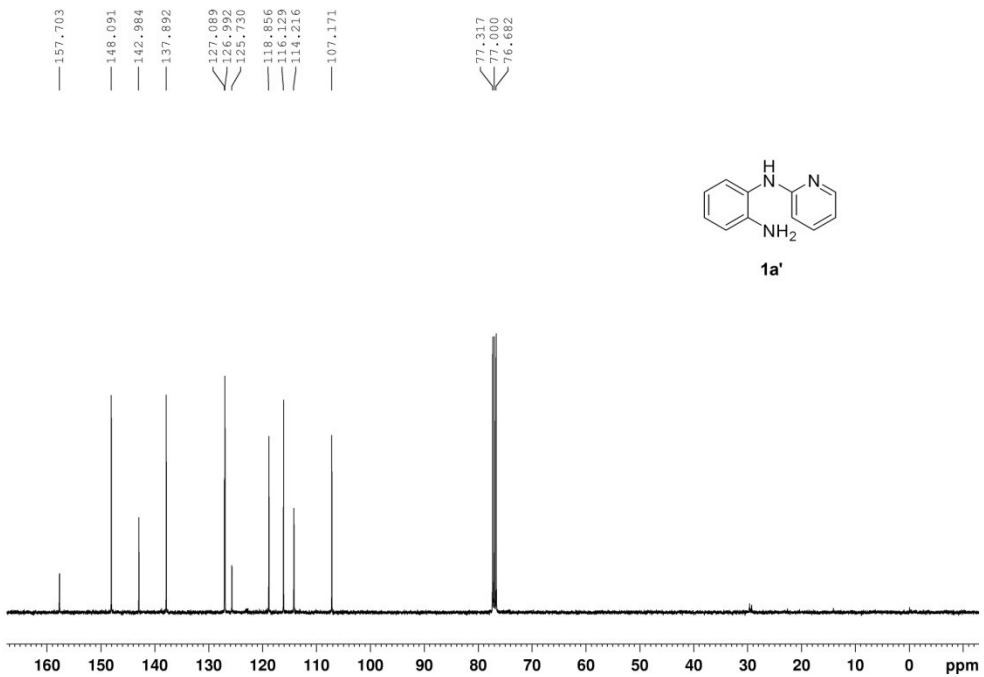
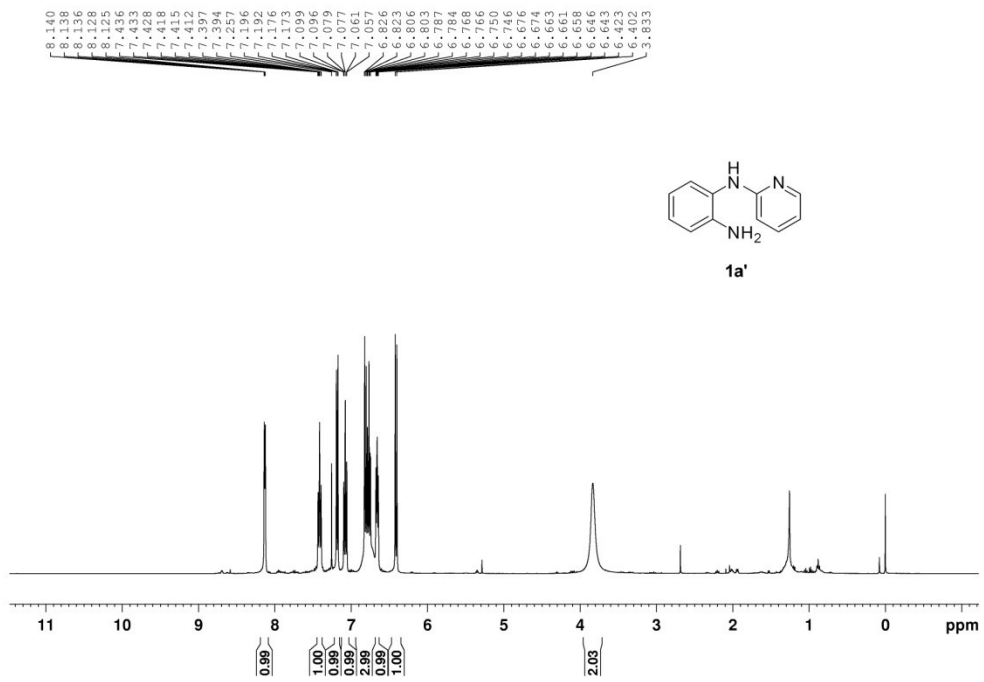






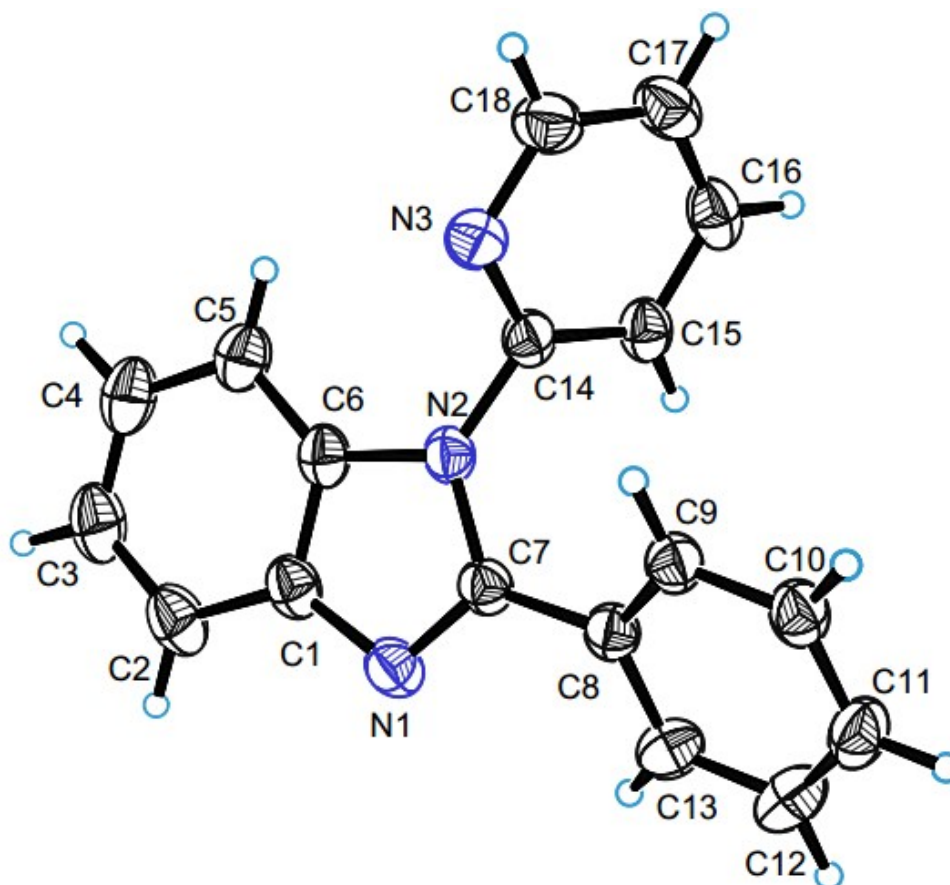






### (C) Crystal structure data

A single crystal for X-ray analysis of **3aa** was obtained by recrystallation from acetone/petroleum ether. CCDC-1551540 contains the supplementary crystallo-graphic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



### CCDC 1551540

Table 1 Crystal data and structure refinement for 3aa.

Identification code	GQQ-07
Empirical formula	C <sub>18</sub> H <sub>13</sub> N <sub>3</sub>
Formula weight	271.31
Temperature/K	292(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	8.9797(2)
b/Å	17.5384(3)
c/Å	9.3882(2)



$\alpha / ^\circ$	90
$\beta / ^\circ$	108.488(2)
$\gamma / ^\circ$	90
Volume/ $\text{\AA}^3$	1402.24(5)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.285
$\mu / \text{mm}^{-1}$	0.612
F(000)	568.0
Crystal size/ $\text{mm}^3$	$0.25 \times 0.21 \times 0.2$
Radiation	CuK $\alpha$ ( $\lambda = 1.54184$ )
$2\theta$ range for data collection/ $^\circ$	10.088 to 142.44
Index ranges	$-9 \leq h \leq 10, -21 \leq k \leq 19, -11 \leq l \leq 9$
Reflections collected	4882
Independent reflections	2630 [ $R_{\text{int}} = 0.0134, R_{\text{sigma}} = 0.0165$ ]
Data/restraints/parameters	2630/0/191
Goodness-of-fit on $F^2$	1.036
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0360, wR_2 = 0.0983$
Final R indexes [all data]	$R_1 = 0.0403, wR_2 = 0.1028$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.16/-0.14

1. J. Jiao, X. R. Zhang, N. H. Chang, J. Wang, J. F. Wei, X. Y. Shi and Z. G. Chen, *J. Org. Chem.*, 2011, **76**, 1180.