Supporting information for

Palladium-Catalyzed Desulfinative C-H Arylation of Azoles with Sodium Sulfinates

Ru Chen, Saiwen Liu, Xinhua Liu, Luo Yang and Guo-Jun Deng*

Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China
E-mail: gjdeng@xtu.edu.cn

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General information:

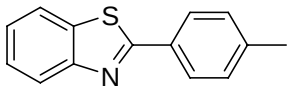
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to $SiMe_4$ or chloroform signals. MS analyses were performed on an Agilent 5975 GC-MS instrument (EI). All products are known compounds and were characterized by ^{1}H NMR, ^{13}C NMR and MS.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Aromatic sulfinic acid sodium salts **2a**, **2b**, **2f** and **2g** were purchased from Alfa Aesar, others were prepared according to the literature procedures. Solvents were used as received without further purification. Unless otherwise indicated, all reagents were added to the reaction vessel under air and sealed for heating for 24 h.

General procedure: 2-p-tolylbenzothiazole (3a):

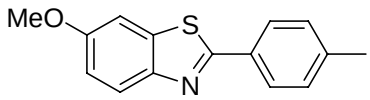
A 10 mL oven-dried reaction vessel was charged with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol), sodium 4-methylbenzenesulfinate (**2a**, 52.5 mg, 0.3 mmol). benzothiazole (**1a**, 21.8 μL, 0.2 mmol), the mixture of 1,4-dioxane (0.2 mL) and diglyme (0.6 mL) were added to the sealed reaction vessel by syringe. The resulting solution was stirred at 120 ^{o}C for 24 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 50:1) to give **3a** as white solid; yield: 37.4 mg (83%).

2-p-Tolylbenzothiazole (3a) (CAS: 16112-21-3) [1]



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.08 (d, J = 8.1 Hz, 1H), 8.01 (d, J = 7.9 Hz, 2H), 7.91 (d, J = 7.9, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 7.8 Hz, 2H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.2, 154.3, 141.4, 135.0, 131.1, 129.7, 127.5, 126.2, 125.0, 123.1, 121.5, 21.5; MS (EI) *m/z* (%) 225 (100), 108, 91, 69.

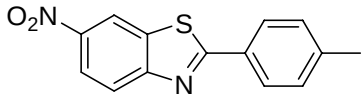
6-Methoxy-2-p-tolylbenzothiazole (CAS: 101078-51-7) (3b) [2]



The reaction was conducted with 6-methoxybenzothiazole (**1b**, 33.0 mg, 0.2 mmol) and 4-methylbenzenesulfinate (**2a**, 52.5 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol), 1,4-dioxane (0.2 mL) and diglyme (0.6 mL) at 120 °C for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 38.9 mg, 76% yield of **3b** as white solid.

1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.94 (d, J = 8.3 Hz, 3H), 7.37 (s, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.09 (m, 1H), 3.91 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 165.8, 157.7, 148.8, 140.9, 136.4, 131.2, 129.7, 127.2, 123.6, 115.5, 104.4, 55.8, 21.4; MS (EI) m/z (%) 255 (100), 240, 212, 128, 95.

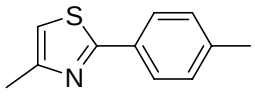
6-Nitro-2-p-tolylbenzothiazole (CAS: 53544-69-7) (3c) [3]



The reaction was conducted with 6-nitrobenzothiazole (**1c**, 36 mg, 0.2 mmol) and 4-methylbenzenesulfinate (**2a**, 52.5 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol), *N*-methyl-2-pyrrolidone (0.2 mL) and diglyme (0.6 mL) at 120 °C for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 21.6 mg, 40% yield of **3c** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.88 (s, 1H), 8.41 (m, 1H), 8.16 (d, J = 8.9 Hz, 1H), 8.07 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 7.9 Hz, 2H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 173.9, 144.9, 143.0, 130.8, 130.2, 130.0, 128.8, 127.9, 123.1, 121.8, 118.1, 21.6; MS (EI) *m/z* (%) 270, 240 (100), 224, 209, 63.

4-Methyl-2-p-tolylthiazole (CAS: 58765-88-1) (3d) [4]

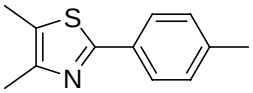


The reaction was conducted with 4-methylthiazole (**1d**, 18.2 μL, 0.2 mmol) and sodium 4-methylbenzenesulfinate (**2a**, 52.5 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol), *N*-methyl-2-pyrrolidone (0.2 mL) and diglyme (0.6 mL) at 120 °C for 24 h. The crude mixture was purified by flash column chromatography on silica

(petroleum ether/ethyl acetate = 50:1) to provide 44.9 mg, 56% yield of **3d** as light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.94 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 7.0 (s, 1H), 2.62 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 153.7, 139.9, 131.3, 129.5, 126.4, 112.9, 21.3, 17.2; MS (EI) *m/z* (%) 189 (100), 118, 72.

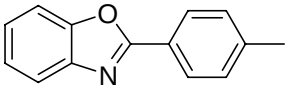
4,5-Dimethyl-2-p-tolylthiazole (3e): [5]



The reaction was conducted with 4,5-dimethylthiazole (**1e**, 21.1 μL, 0.2 mmol) and 4-methylbenzenesulfinate (**2a**, 52.5 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol), *N*-methyl-2-pyrrolidone (0.2 mL) and diglyme (0.6 mL) at 120 ^{o}C for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 18.3 mg, 45% yield of **3e** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.87 (d, J = 7.9 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 2.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.6, 149.1, 139.4, 131.5, 129.5, 126.1, 125.9, 21.3, 14.8, 11.4; MS (EI) *m/z* (%) 203 (100), 118, 86, 71.

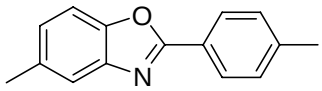
2-p-Tolylbenzoxazole (CAS: 835-71-2) (3f) [6]



The reaction was conducted with benzoxazole (**1f**, 37.9 μL, 0.2 mmol) and 4-methylbenzenesulfinate (**2a**, 52.5 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol), 1,4-dioxane (0.2 mL) and diglyme (0.6 mL) at 120 ^{o}C for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 33.9 mg, 81% yield of **3f** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.20 (d, J = 8.0 Hz, 2H), 7.80-7.82 (m, 1H), 7.61-7.64 (m, 1H), 7.38-7.40 (m 4H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.3, 150.8, 142.3, 142.1, 129.7, 127.6, 124.9, 124.5, 124.4, 119.9, 110.5, 21.6; MS (EI) *m/z* (%) 209 (100), 180, 91, 63.

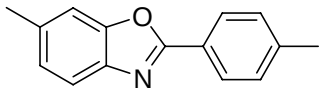
5-Methyl-2-p-tolylbenzoxazole (CAS: 16155-94-5) (3g) [7]



The reaction was conducted with 5-methylbenzoxazole (**1g**, 26.6 mg, 0.2 mmol) and 4-methylbenzenesulfinate (**2a**, 52.5 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol), 1,4-dioxane (0.2 mL) and diglyme (0.6 mL) at 120 ^oC for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 39.2 mg, 88% yield of **3g** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.14 (d, J = 8.0 Hz, 2H), 7.55 (s, 1H), 7.45 (d, J = 8.2 Hz, 1H), 7.34 (d, J = 7.9 Hz, 2H), 7.15 (d, J = 8.1 Hz, 1H), 2.50 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.4, 149.0, 142.5, 134.3, 129.6, 127.6, 126.0, 124.7, 119.9, 109.8, 21.6, 21.5; MS (EI) *m/z* (%) 223 (100), 91, 78, 51.

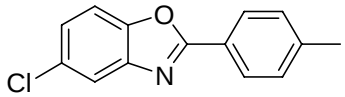
6-Methyl-2-p-tolylbenzoxazole (CAS: 16155-95-6) (3h) [8]



The reaction was conducted with 6-methylbenzoxazole (**1h**, 26.6 mg, 0.2 mmol) and 4-methylbenzenesulfinate (**2a**, 52.5 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol), 1,4-dioxane (0.2 mL) and diglyme (0.6 mL) at 120 ^oC for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 34.8 mg, 78% yield of **3h** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.14 (d, J = 7.9 Hz, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.39 (s, 1H), 7.33 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 8.0 Hz, 1H), 2.52 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 162.9, 151.1, 141.7, 140.1, 135.3, 129.6, 127.5, 125.7, 124.7, 119.2, 110.7, 21.7, 21.6; MS (EI) m/z (%) 223 (100), 208, 194, 119.

5-Chloro-2-p-tolylbenzoxazole (CAS: 16715-75-6) (3i) [7]

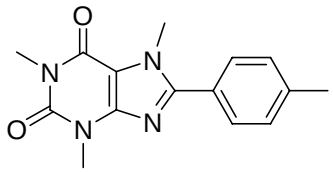


The reaction was conducted with 5-chlorobenzoxazole (**1i**, 30.6 mg, 0.2 mmol) and

4-methylbenzenesulfinate (**2a**, 52.5 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2$ •H_2O (80 mg, 0.4 mmol), 1,4-dioxane (0.2 mL) and diglyme (0.6 mL) at 120 ^oC for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 39.4 mg, 81% yield of **3i** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.12 (d, J = 8.0 Hz, 2H), 7.72 (s, 1H), 7.48 (d, J = 8.6 Hz, 1H), 7.33 (m, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 164.6, 149.3, 143.4, 142.5, 130.0, 129.7, 127.7, 125.1, 124.0, 119.8, 111.1, 21.6; MS (EI) *m/z* (%) 243 (100), 121, 91, 63.

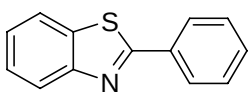
1,3,7-Trimethyl-8-p-tolyl-1H-purine-2,6 (3H,7H)-dione (3j) [5]



The reaction was conducted with 1,3,7-trimethyl-1H-purine-2,6(3H,7H)-dione (**1j**, 38.8 mg, 0.2 mmol) and 4-methylbenzenesulfinate (**2a**, 52.5 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2$ •H_2O (80 mg, 0.4 mmol), 1,4-dioxane (0.2 mL) and diglyme (0.6 mL) at 120 ^oC for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 23.9 mg, 42% yield of **3j** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.70 (d, J = 7.9 Hz, 2H), 7.45 (d, J = 7.8 Hz, 2H), 4.17 (s, 3H), 3.75 (s, 3H), 3.56 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.6, 152.4, 151.8, 148.4, 140.7, 129.6, 129.1, 125.6, 108.5, 33.8, 29.8, 27.9, 21.4; MS (EI) *m/z* (%) 284 (100), 82, 67.

2-Phenylbenzothiazole (3k) (CAS: 883-93-2) [1]

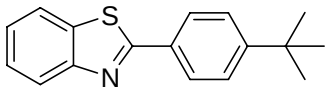


The reaction was conducted with benzothiazole (**1a**, 21.8 μL, 0.2 mmol) and dihydrate sodium benzenesulfinate (**2b**, 59.1 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2$ • H_2O (80 mg, 0.4 mmol), 1,4-dioxane (0.2 mL) and diglyme (0.6 mL) at 120 ^oC for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to

provide 30.0 mg, 71% yield of **3k** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.10 (d, J = 8.3 Hz, 3H), 7.93 (d, J = 7.9 Hz, 1H), 7.52 (s, 4H), 7.41 (t, J = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.0, 154.2, 135.1, 133.7, 130.9, 129.0, 127.6, 126.3, 125.2, 123.3, 121.6; MS (EI) *m/z* (%) 211 (100), 108, 82, 69.

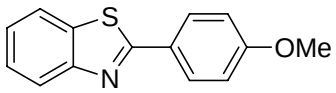
2-(4-*Tert*-butylphenyl)benzothiazole (3l) (CAS: 56048-52-3) [1]



The reaction was conducted with benzothiazole (**1a**, 21.8 μL, 0.2 mmol) and sodium 4-*tert*-butylbenzenesulfinate (**2c**, 65.1 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2$ •H_2O (80 mg, 0.4 mmol), 1,4-dioxane (0.2 mL) and diglyme (0.6 mL) at 120 ^{o}C for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 40.0 mg, 75% yield of **3l** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.15 (m, 3H), 8.0 (d, J = 8 Hz, 1H), 7.61 (m, 3H), 7.49 (m, 1H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.1, 154.4, 154.3, 135.1, 131.0, 127.4, 126.2, 126.0, 125.0, 123.1, 121.5, 35.0, 31.2; MS (EI) *m/z* (%) 267, 252 (100), 236, 224, 111.

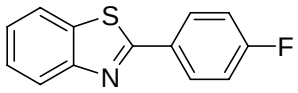
2-(4-Methoxyphenyl)benzothiazole (3m) (CAS: 6265-92-5) [1]



The reaction was conducted with benzothiazole (**1a**, 21.8 μL, 0.2 mmol) and sodium 4-methoxybenzenesulfinate (**2d**, 57.3 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2$ • H_2O (80 mg, 0.4 mmol), *N*-methyl-2-pyrrolidone (0.2 mL) and diglyme (0.6 mL) at 120 ^{o}C for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 33.7 mg, 70% yield of **3m** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.16 (d, J = 8.5 Hz, 3H), 8.00 (d, J = 7.9 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H) 7.47 (t, J = 7.5 Hz, 1H), 7.12 (d, J = 8.5 Hz, 2H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.9, 162.0, 154.4, 135.0, 129.1, 126.6, 126.1, 124.8, 122.9, 121.4, 114.4, 55.4; MS (EI) *m/z* (%) 241 (100), 226, 198, 69.

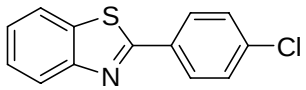
2-(4-Fluorophenyl)benzothiazole (CAS: 1629-26-1) (3n) [1]



The reaction was conducted with benzothiazole (**1a**, 21.8 μL, 0.2 mmol) and sodium 4-fluorobenzenesulfinate (**2e,** 53.7 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol), *N*-methyl-2-pyrrolidone (0.2 mL) and diglyme (0.6 mL) at 120 ^oC for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 26.6 mg, 58% yield of **3n** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.17-8.23 (m, 3H), 8.02 (d, J = 7.9 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.7, 164.5 (d, J = 250.3 Hz), 154.2, 135.1, 130.1 (d, J = 29.0 Hz), 129.6 (d, J = 8.7 Hz), 126.4, 125.2, 123.3, 121.6, 116.1 (d, J = 22.0 Hz); MS (EI) *m/z* (%) 229 (100), 108, 82, 69.

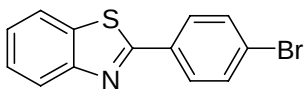
2-(4-Chlorophenyl)benzothiazole (CAS: 6265-91-4) (3o) [1]



The reaction was conducted with benzothiazole (**1a**, 21.8 μL, 0.2 mmol) and sodium 4-chlorobenzenesulfinate (**2f**, 55.8 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol), 1,4-dioxane (0.2 mL) and diglyme (0.6 mL) at 120 ^oC for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 33.5 mg, 68% yield of **3o** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.08-8.13 (m, 3H), 7.96 (d, J = 7.9 Hz, 1H), 7.52-7.58 (m, 3H), 7.45 (t, J = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.6, 154.2, 137.1, 135.2, 132.2, 129.3, 128.8, 126.5, 125.4, 123.4, 121.7; MS (EI) *m/z* (%) 245 (100), 210, 108, 82, 69.

2-(4-Bromophenyl)benzothiazole (CAS: 19654-19-4) (3p) [9]

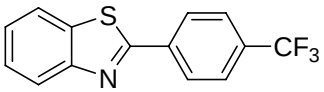


The reaction was conducted with benzothiazole (**1a**, 21.8 μL, 0.2 mmol) and sodium 4-bromobenzenesulfinate (**2g,** 72 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol),

$Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol), 1,4-dioxane (0.2 mL) and diglyme (0.6 mL) at 120 °C for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 29.0 mg, 50% yield of **3p** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.08 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 7.9, 1H), 7.65 (d, J = 8.3 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H),7.42 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.7, 154.2, 135.1, 132.7, 132.3, 128.9, 126.5, 125.4, 124.0, 123.4, 121.7; MS (EI) *m/z* (%) 291(100), 210, 108, 82, 69.

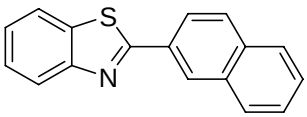
2-(4-(Trifluoromethyl)phenyl)benzothiazole (CAS: 134384-31-9) (3q) [10]



The reaction was conducted with benzo[d]thiazole (**1a**, 21.8 μL, 0.2 mmol) and sodium 4-(trifluoromethyl)benzenesulfinate (**2h**, 68.7 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol), *N*-methyl-2-pyrrolidone (0.2 mL) and diglyme (0.6 mL) at 120 °C for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 19.5 mg, 35% yield of **3q** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.27 (d, J = 8.0 Hz, 2H), 8.16 (d, J = 8.1 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.81 (d, J = 8.1 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.0, 154.2, 136.9, 135.3, 132.5 (q, J = 32.4 Hz), 127.8, 126.6, 126.0 (q, J = 3.8 Hz), 125.8, 125.2, 123.9 (q, J = 270.8 Hz), 123.7, 121.7; MS (EI) *m/z* (%) 279 (100), 139, 108, 82, 69.

2-(Naphthalen-2-yl)benzothiazole (CAS: 56048-51-2) (3r) [11]



The reaction was conducted with benzothiazole (**1a**, 21.8 μL, 0.2 mmol) and sodium naphthalene-2-sulfinate (**2i**, 63.3 mg, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol), *N*-methyl-2-pyrrolidone (0.2 mL) and diglyme (0.6 mL) at 120 °C for 24 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 50:1) to provide 44.9 mg, 86% yield of **3r** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.70 (s, 1H), 8.34 (d, J = 7.7 Hz, 1H), 8.24 (d, J = 8.1 Hz, 1H), 8.08 (m, 3H), 8.01 (t, J = 5.3 Hz, 1H), 7.67 (m, 3H), 7.53 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.1, 154.3, 135.2, 134.7, 133.3, 131.1, 128.8, 127.9, 127.6, 127.5, 126.9, 126.4, 125.2, 124.5, 123.3, 121.6; MS (EI) *m/z* (%) 261(100), 130, 108, 69.

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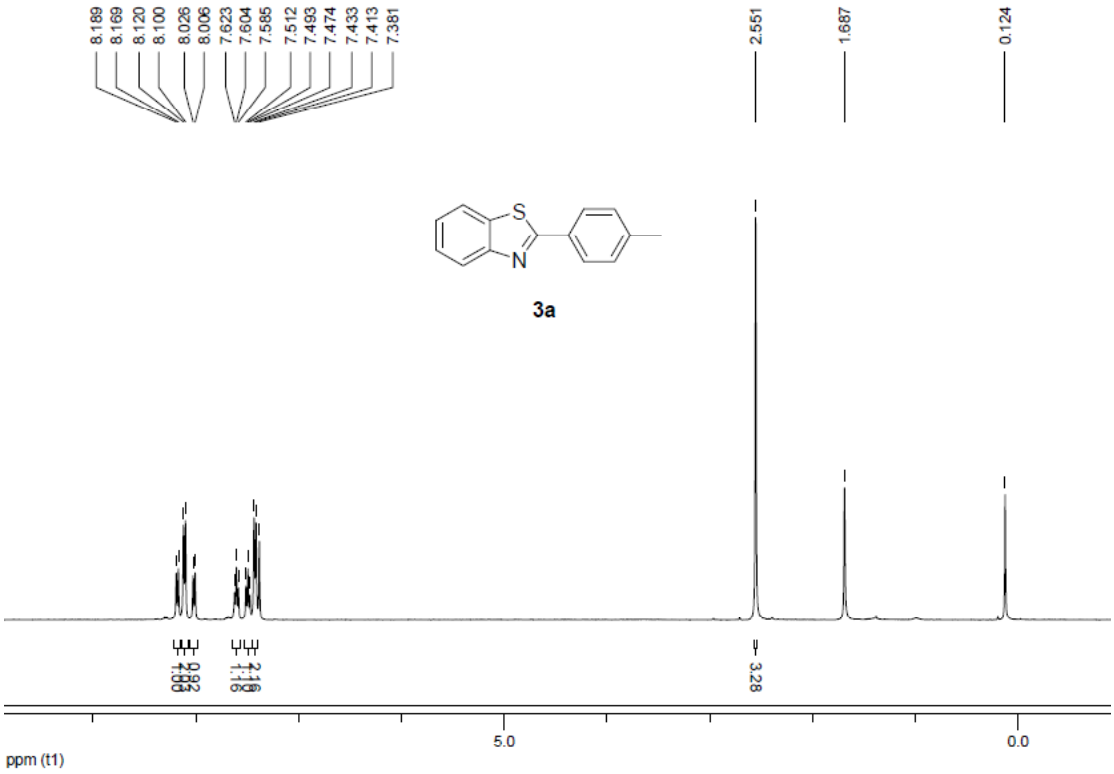
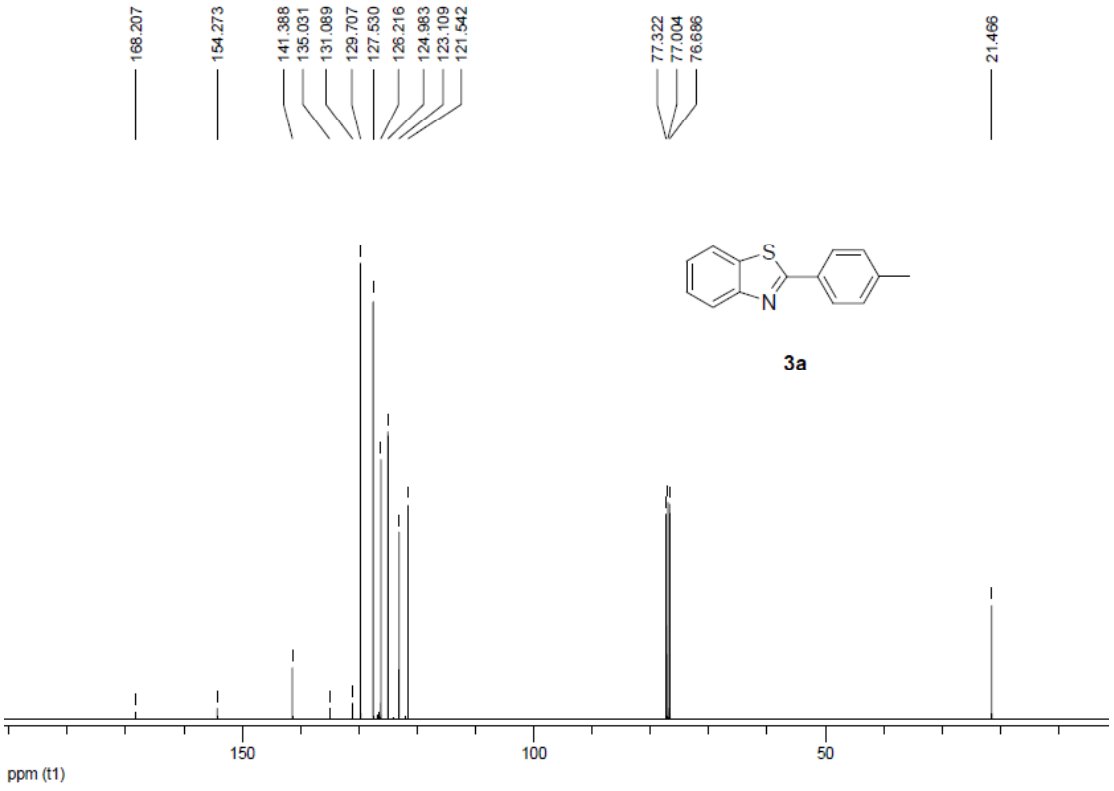
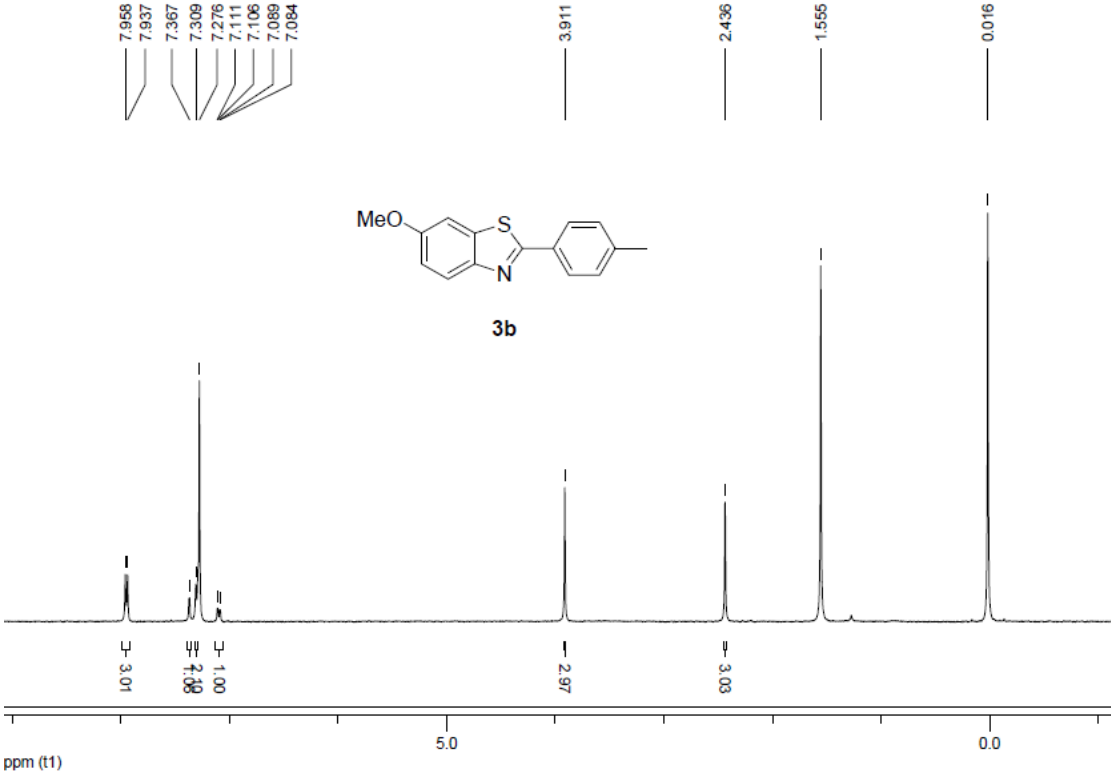
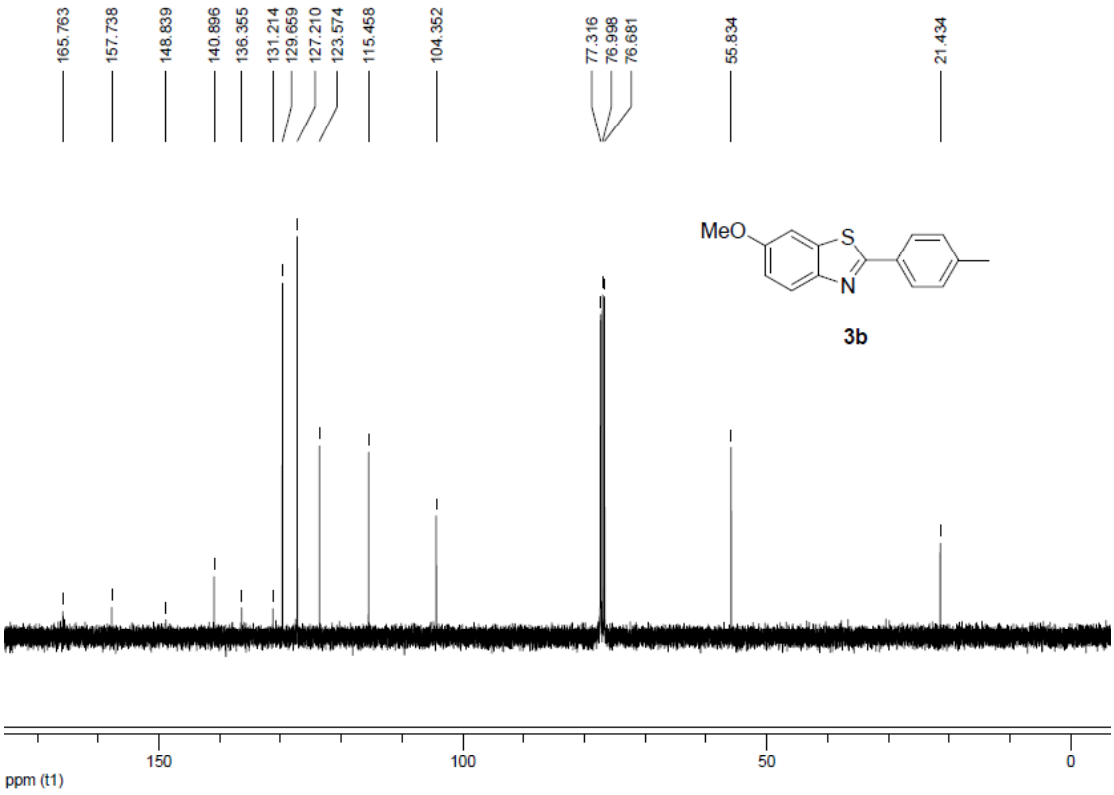
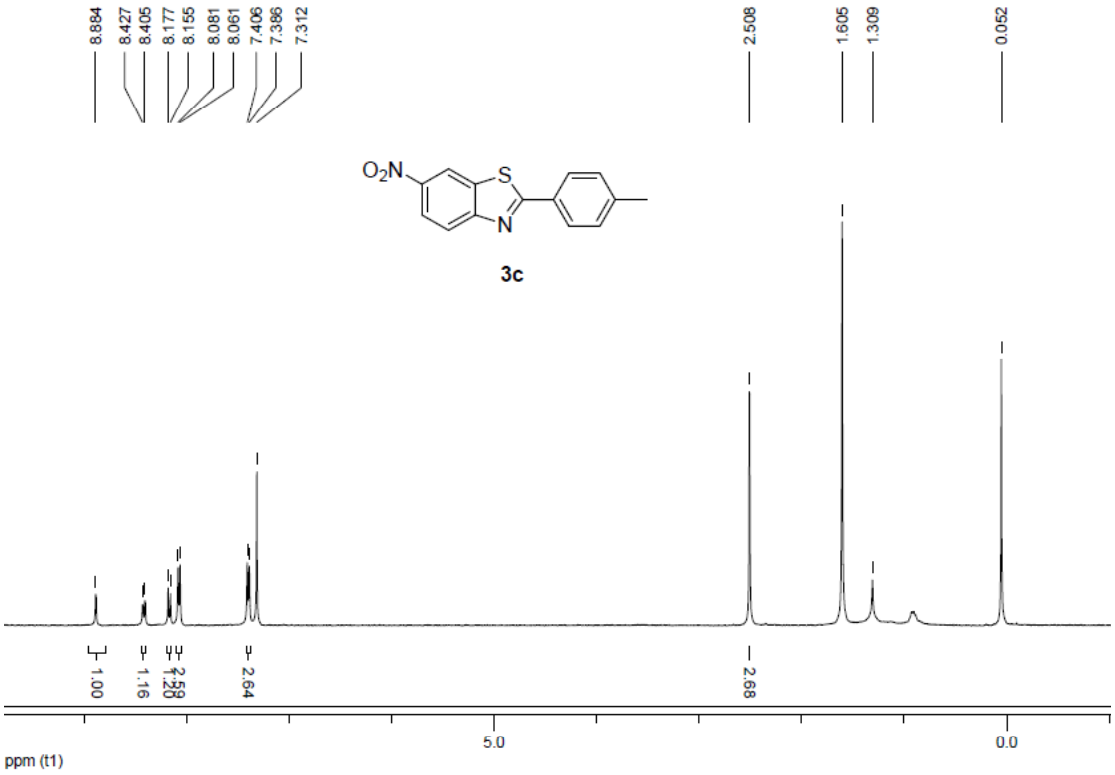
^{1}H and ^{13}C NMR spectra

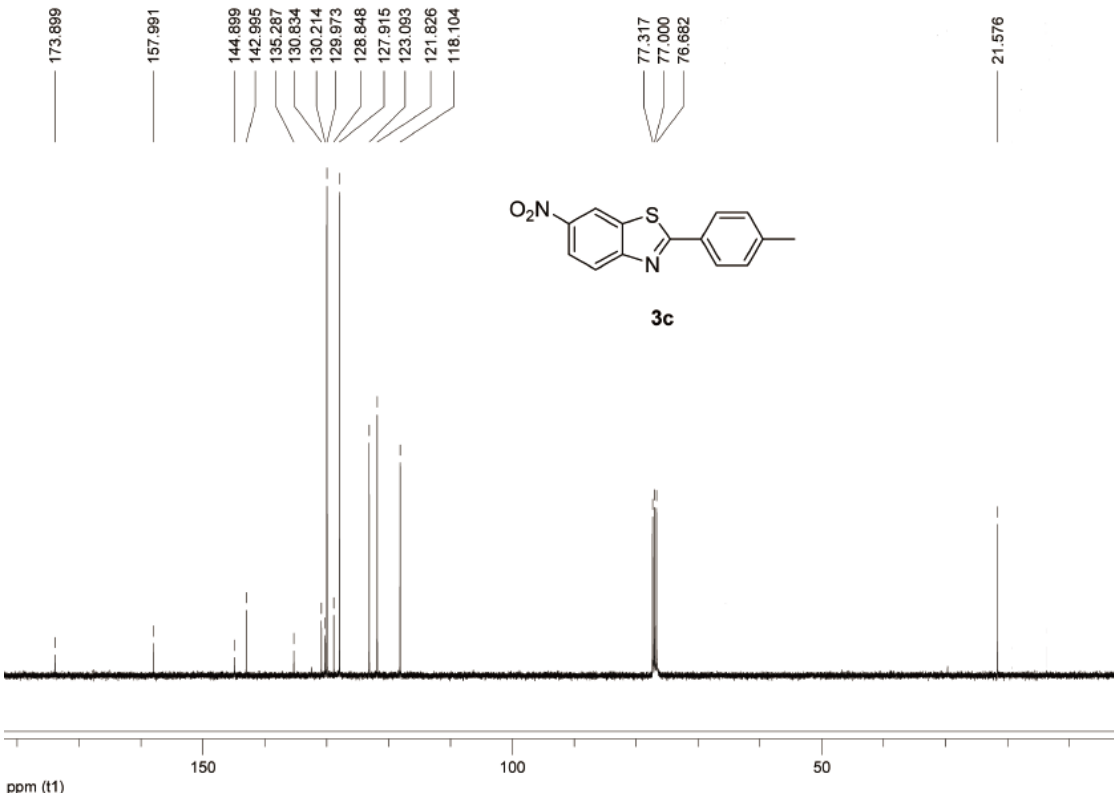


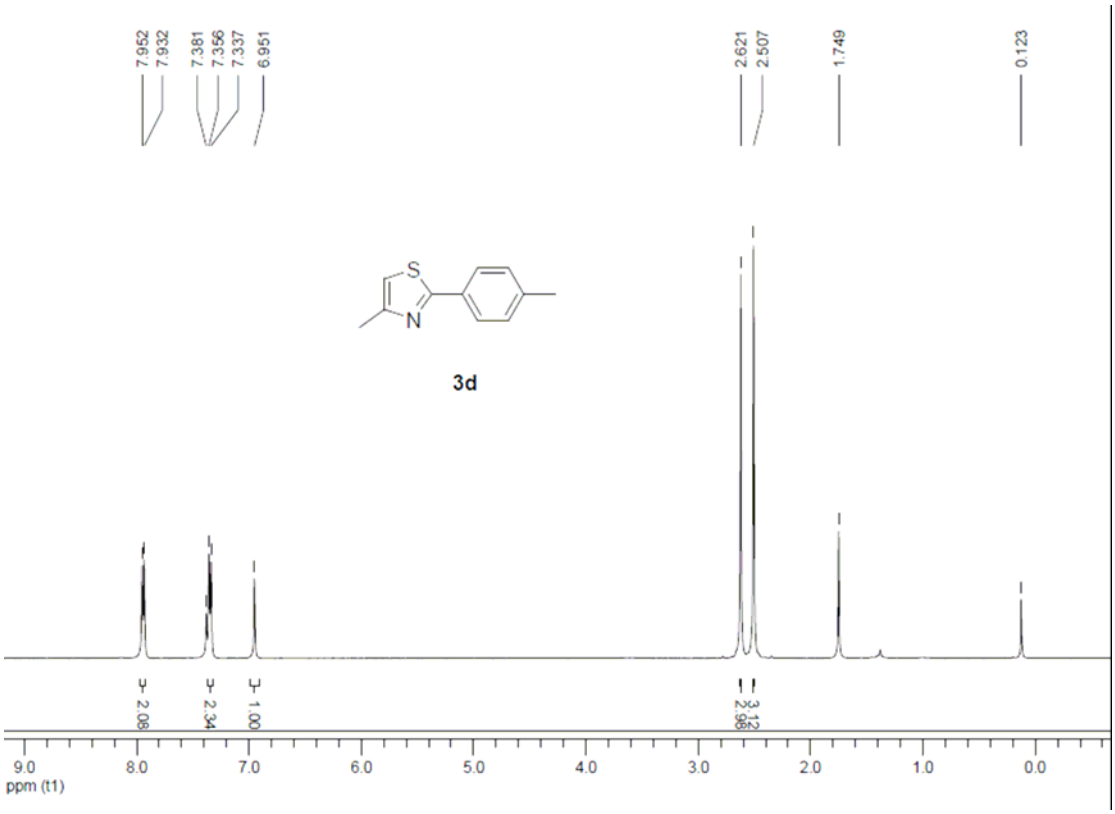


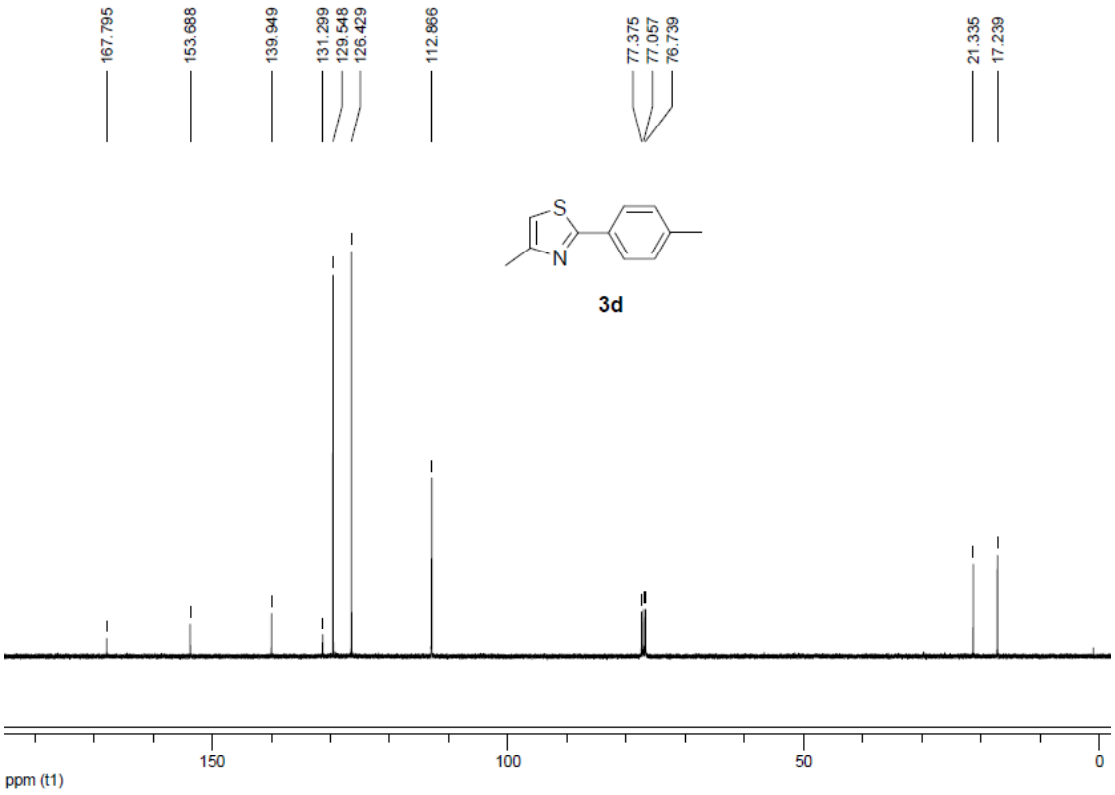


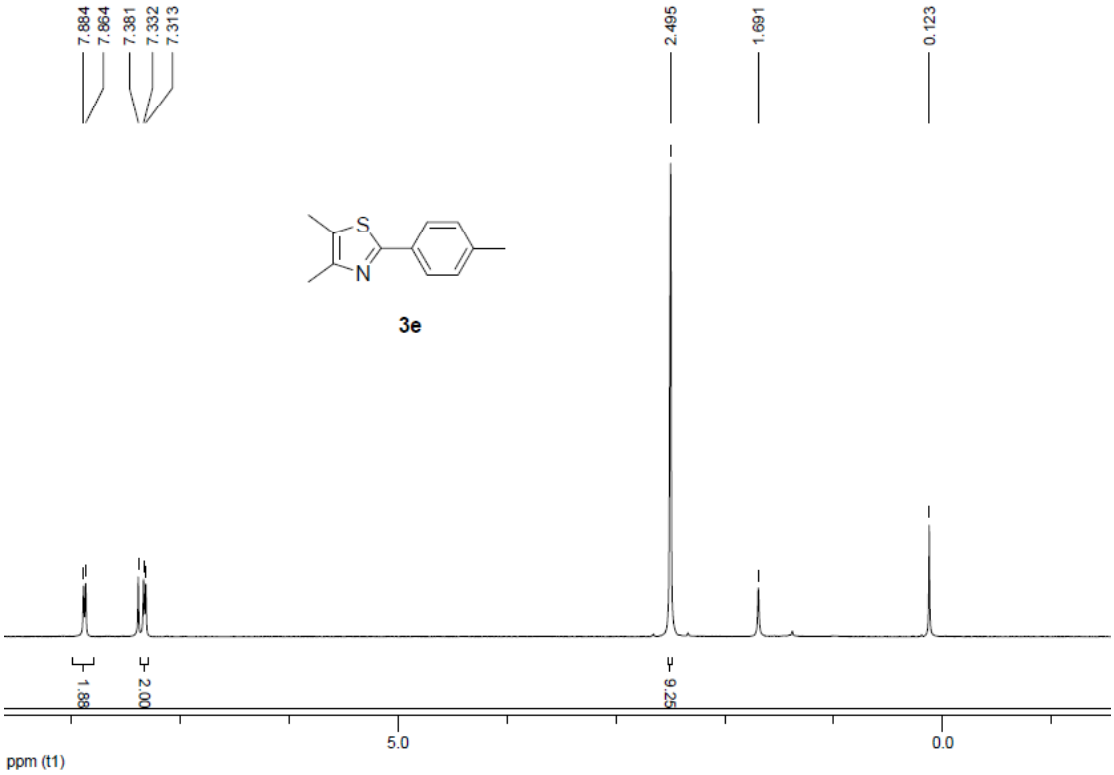


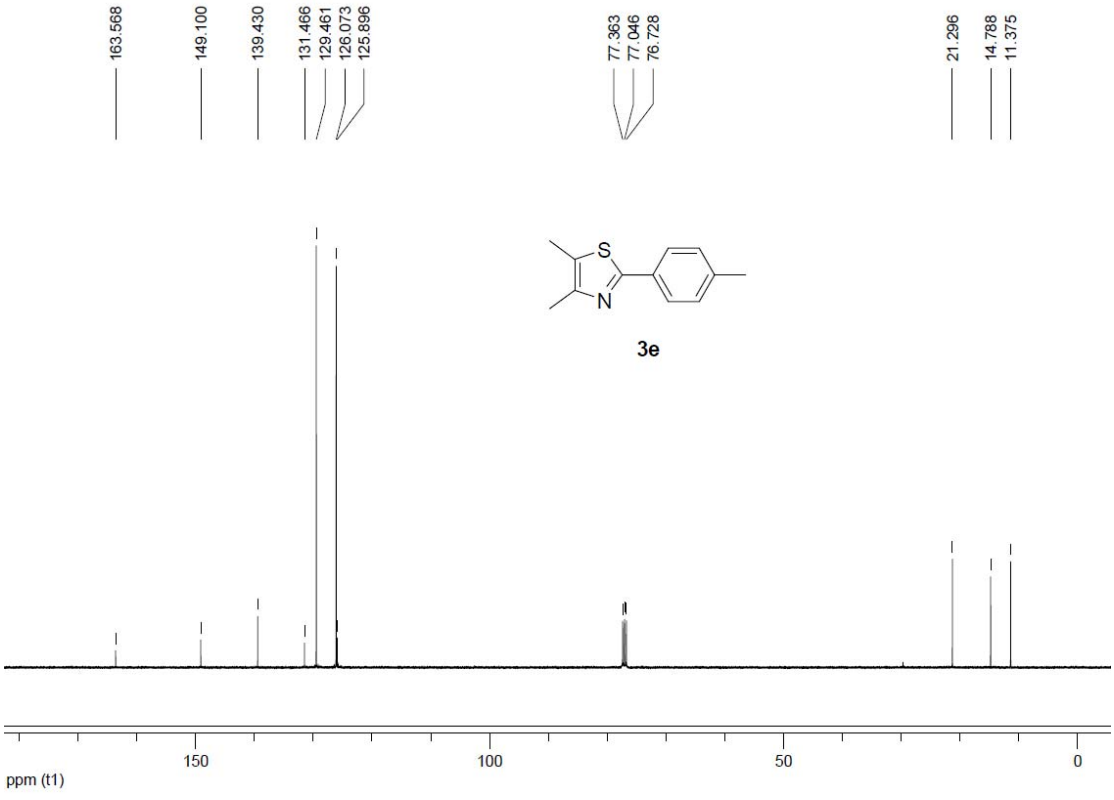


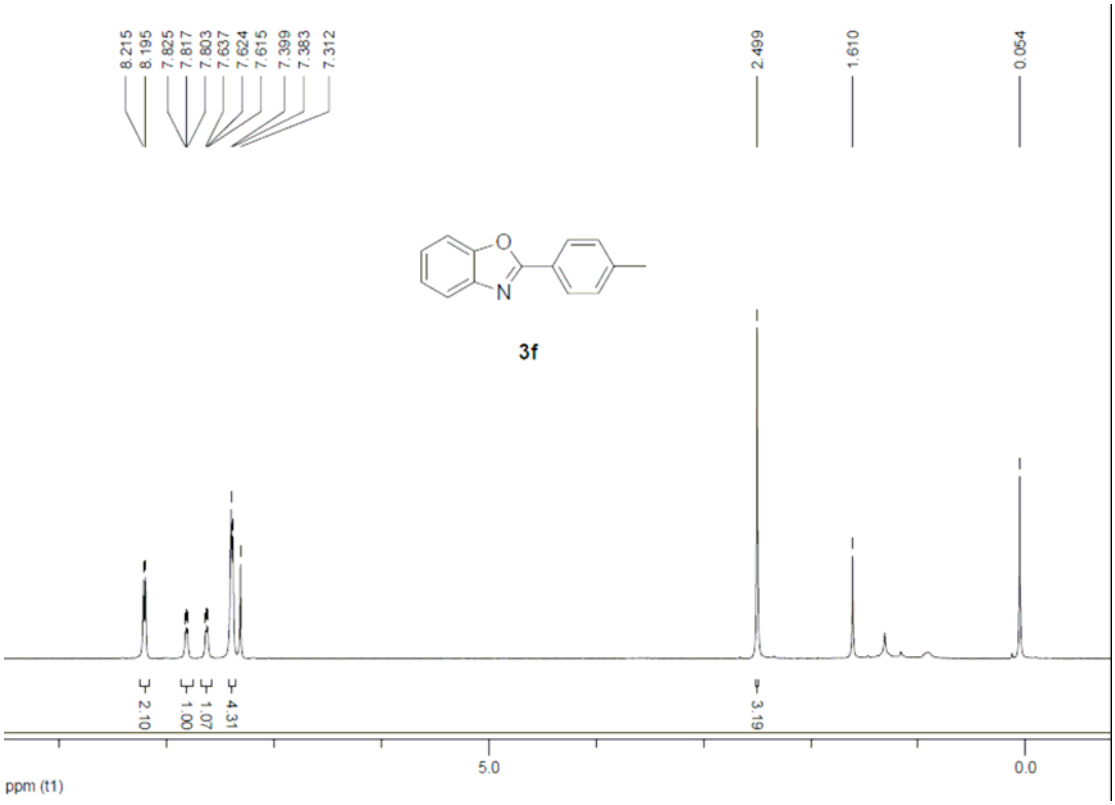


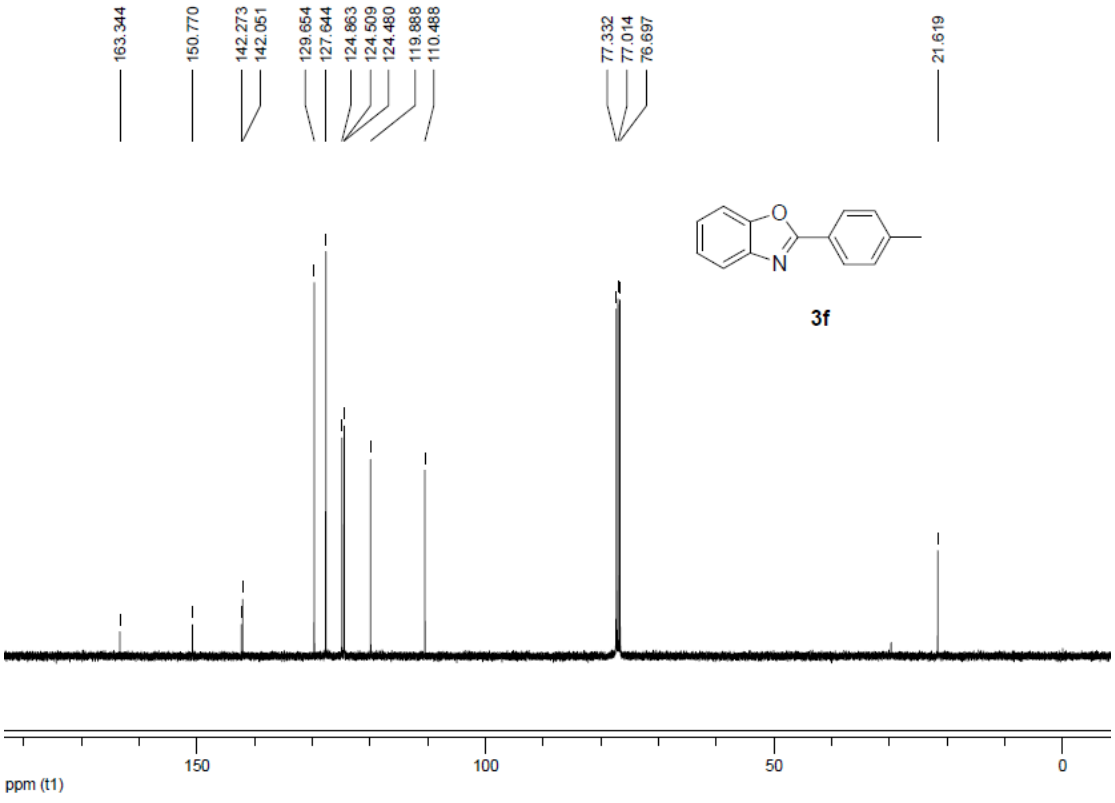


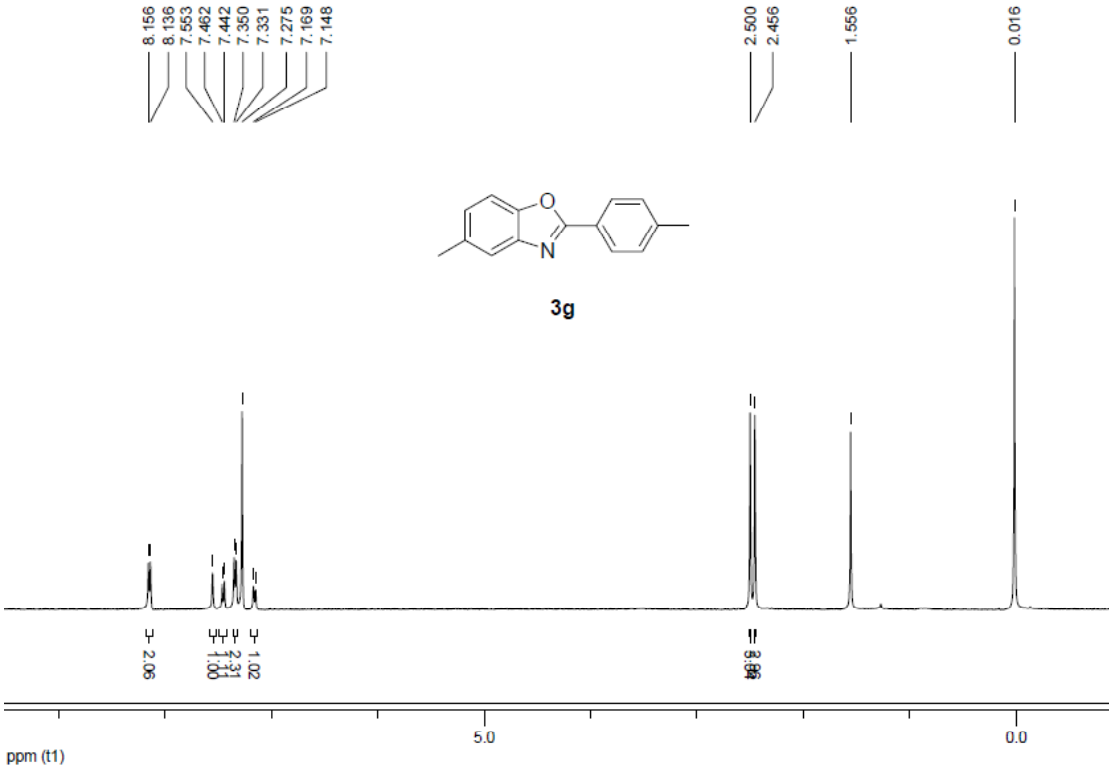


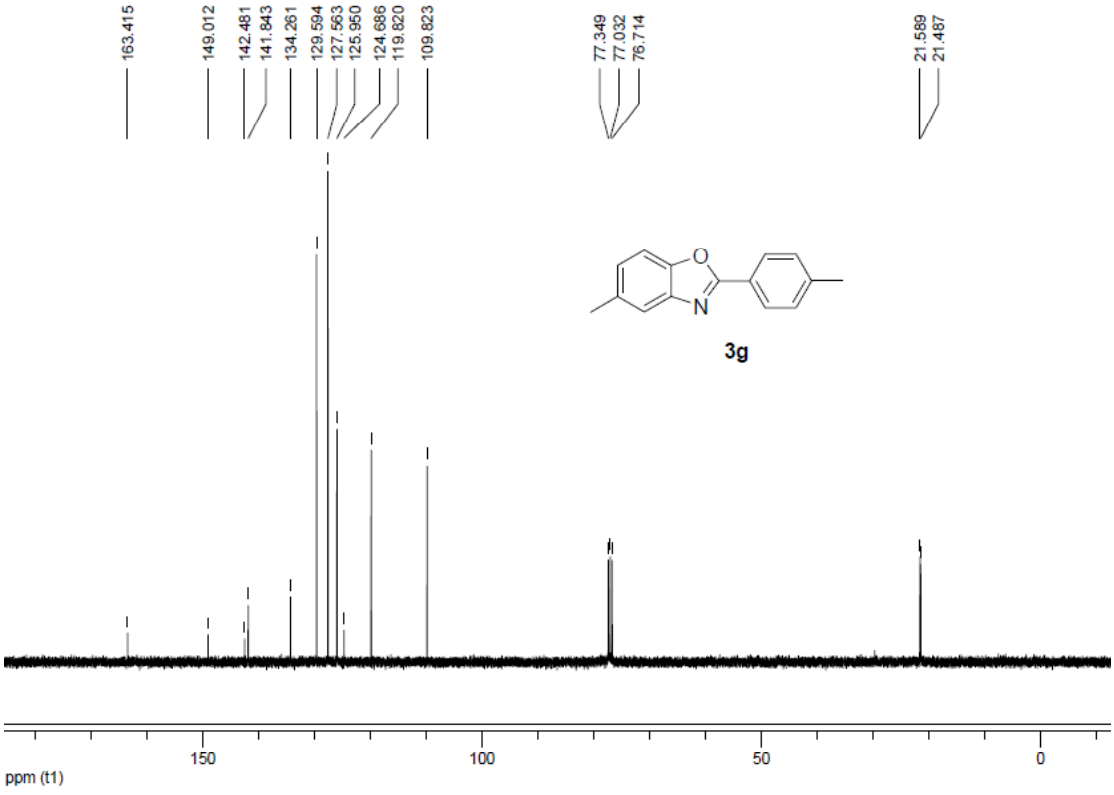


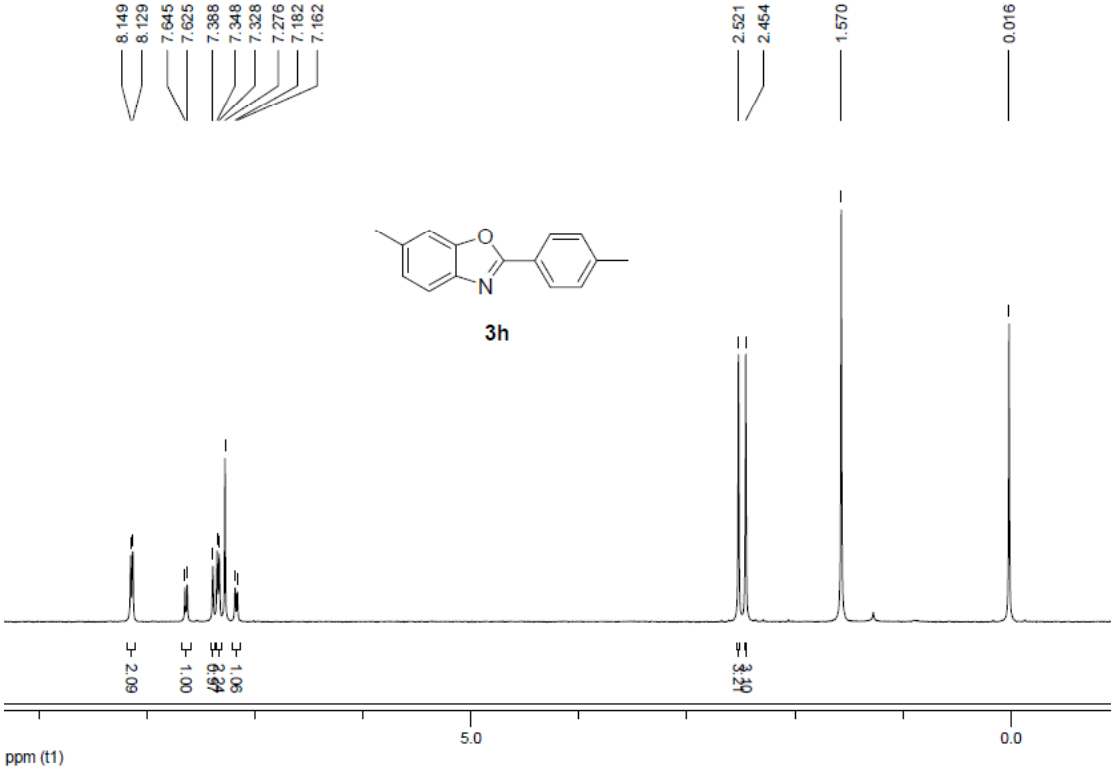


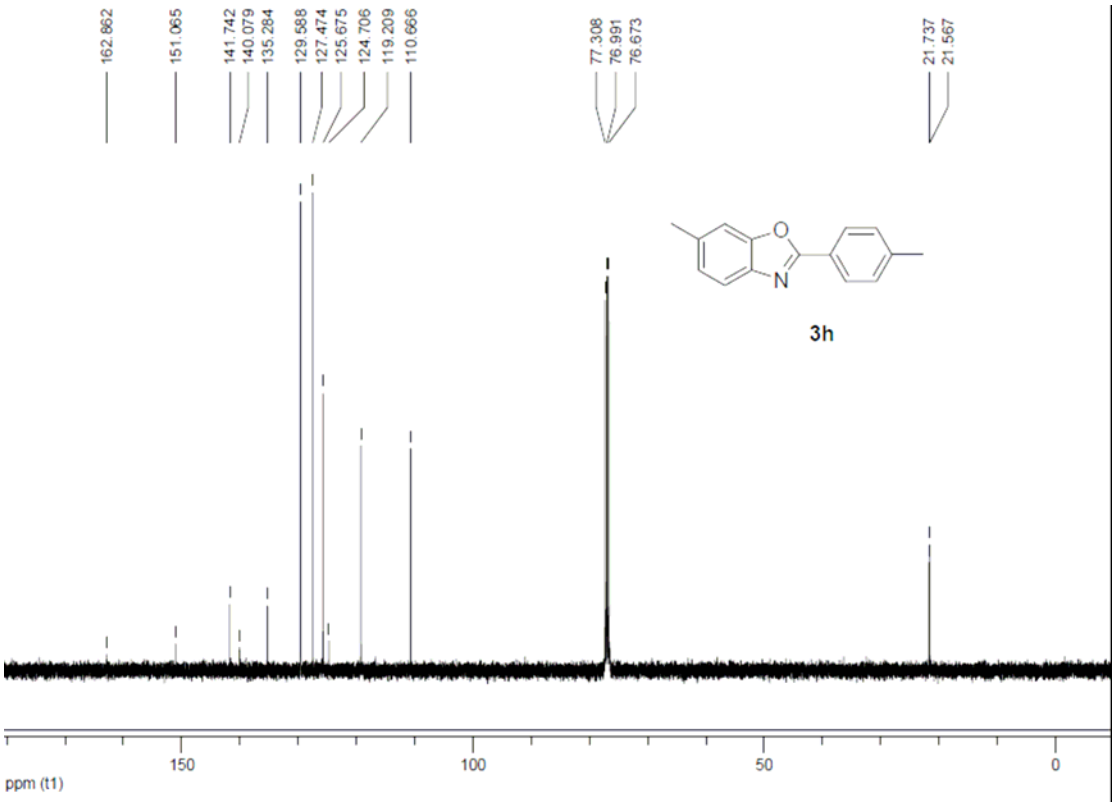


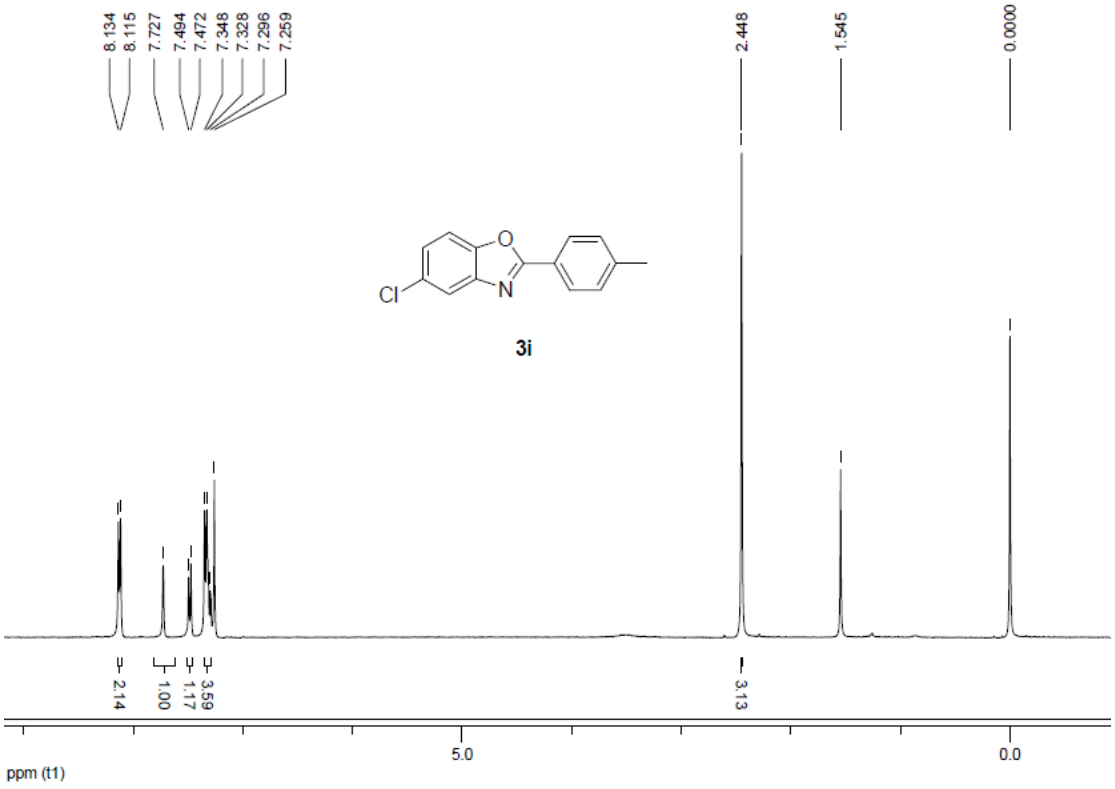


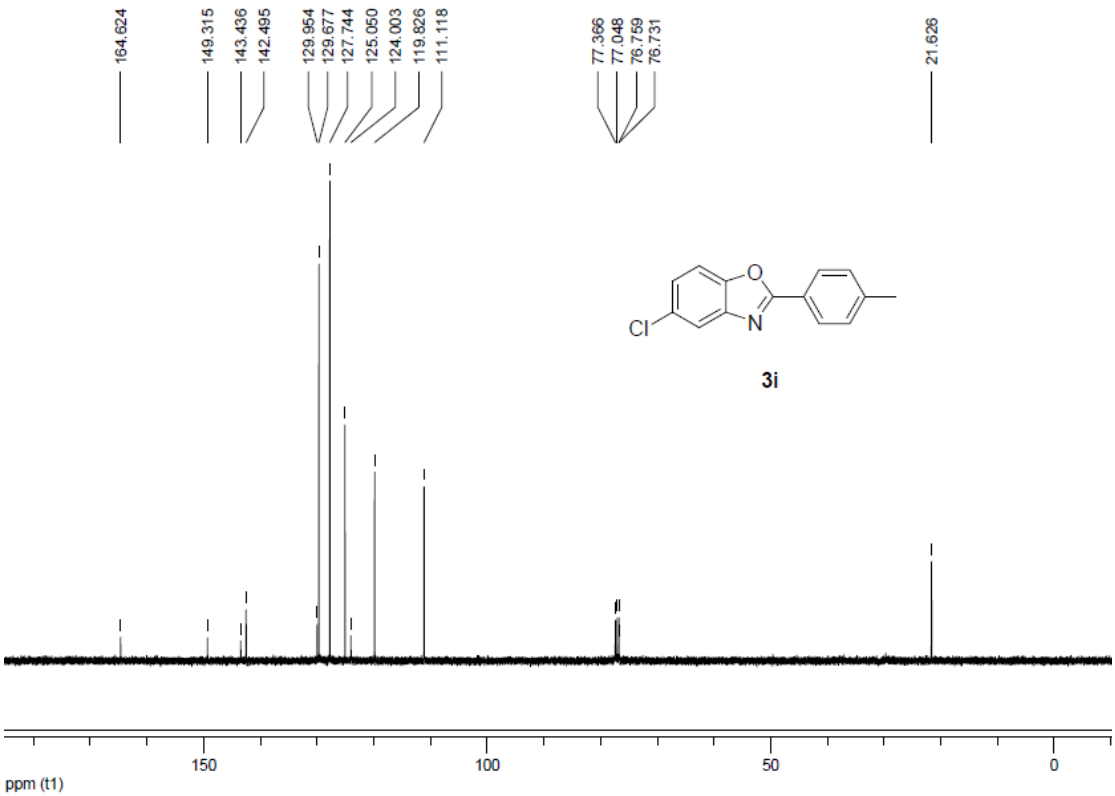


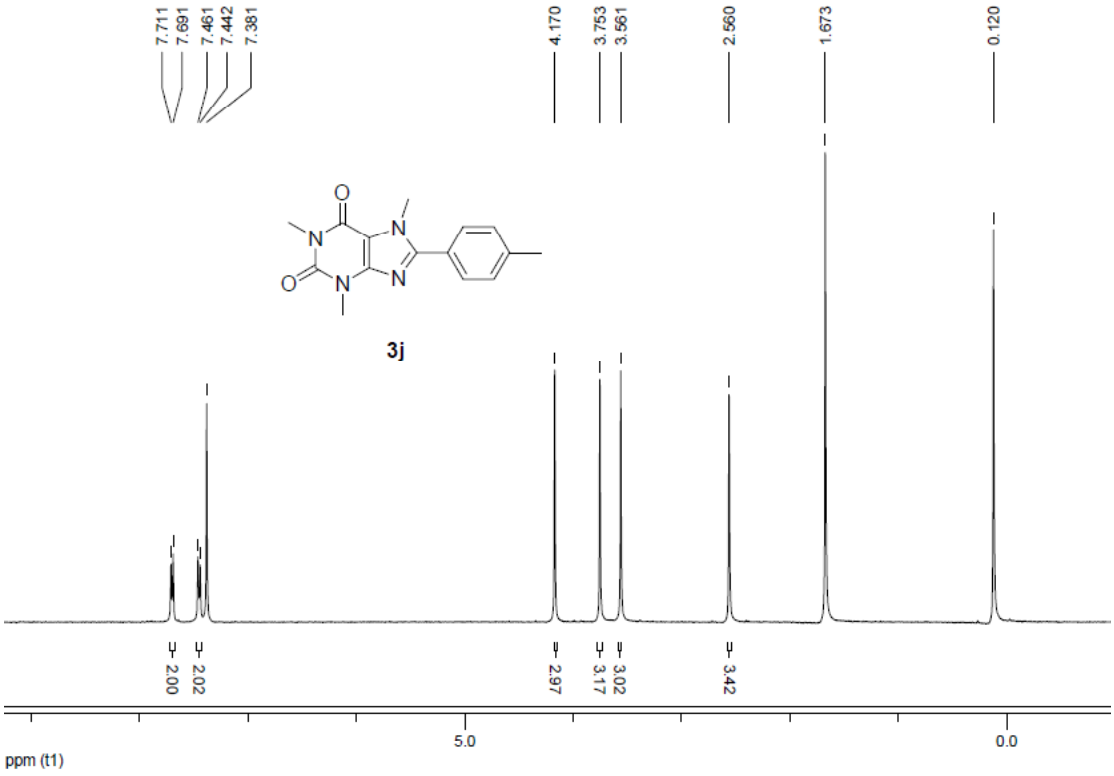


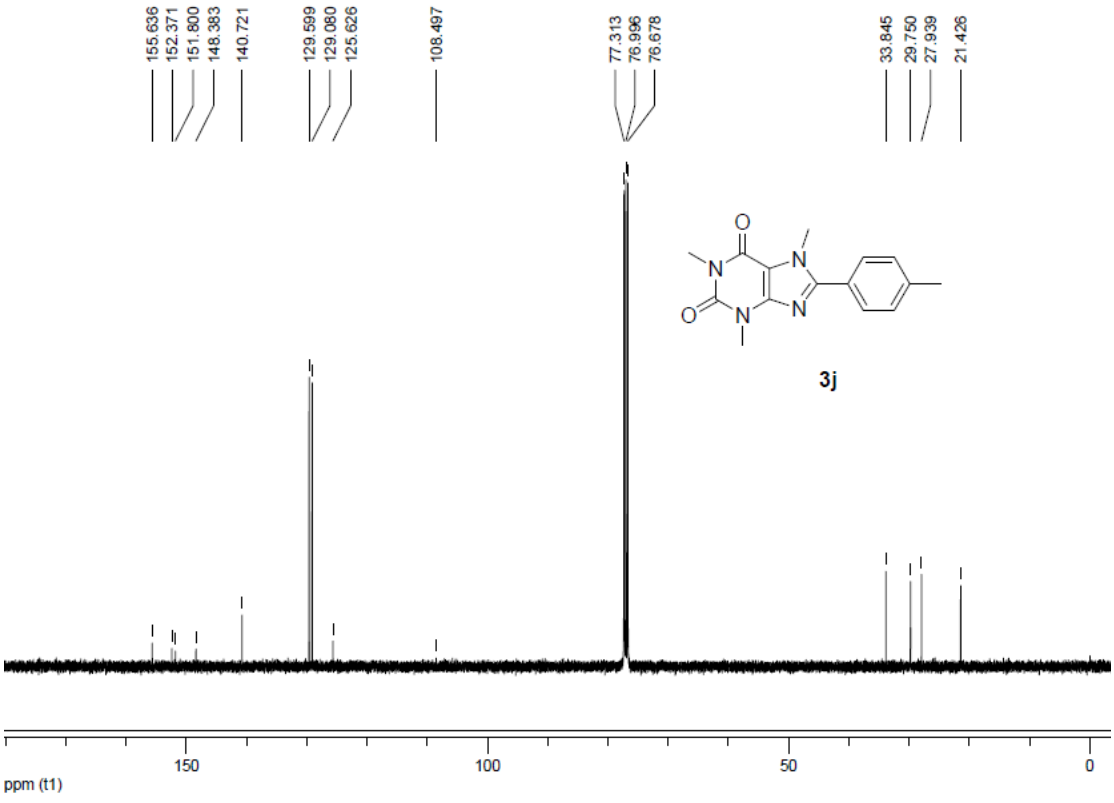


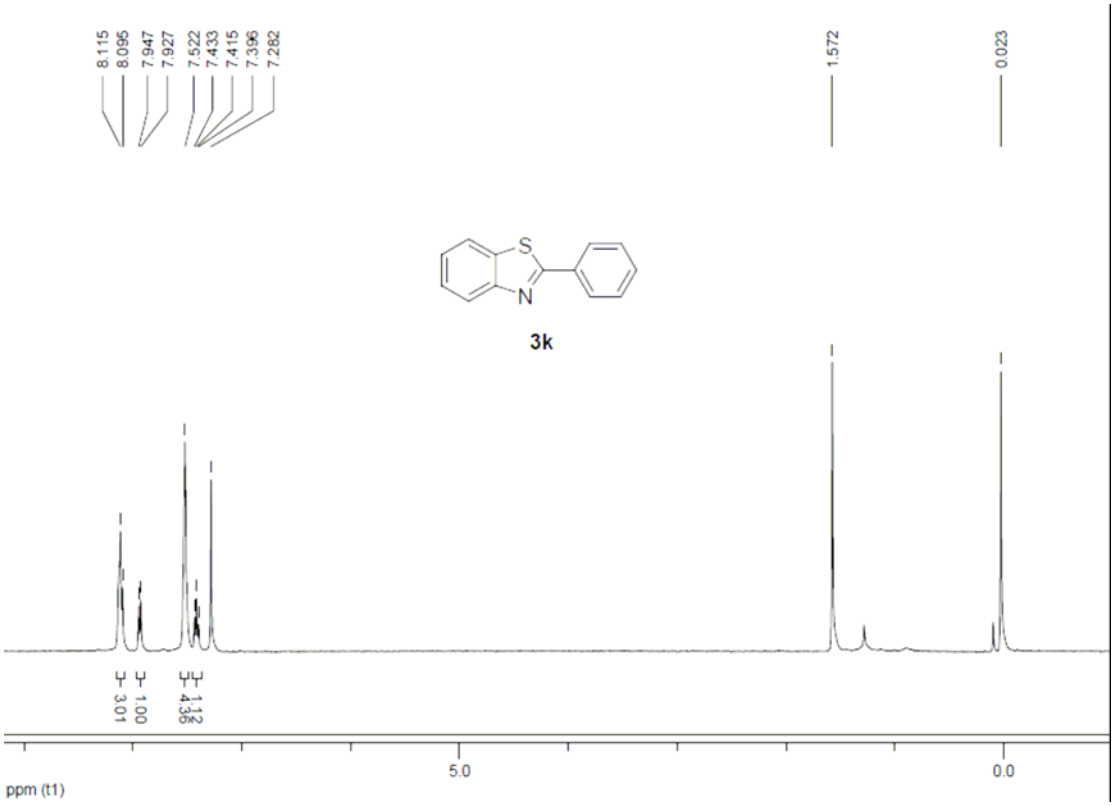


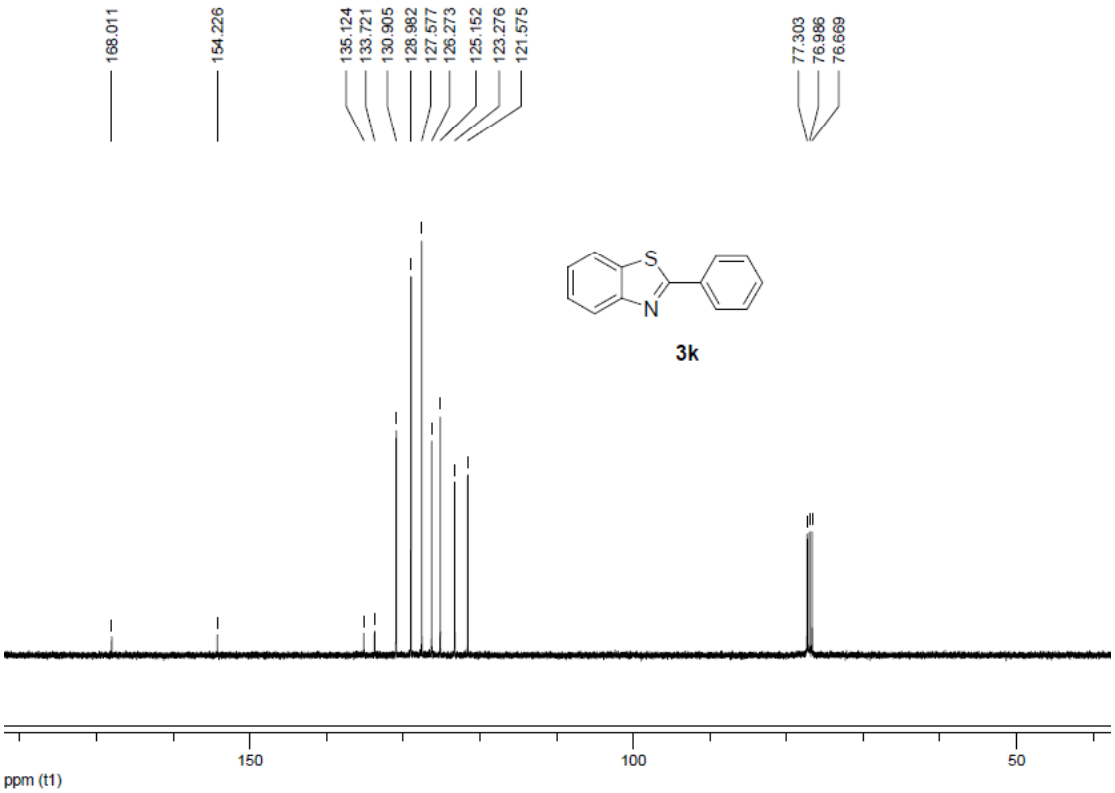


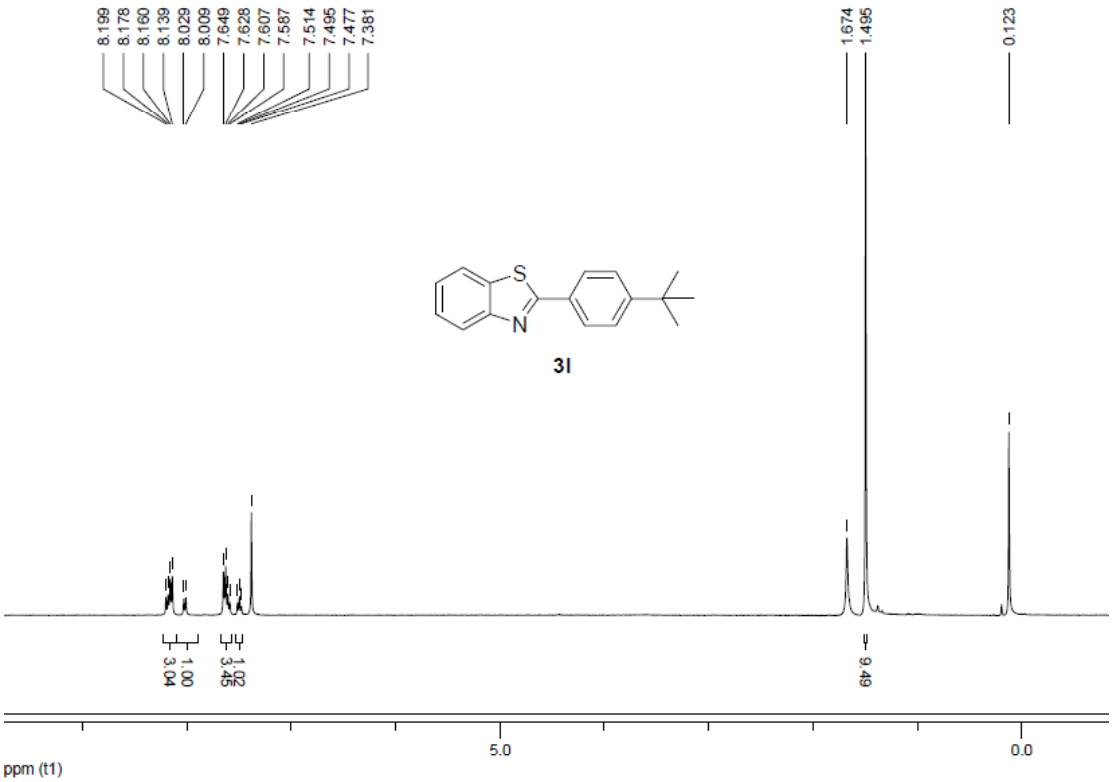












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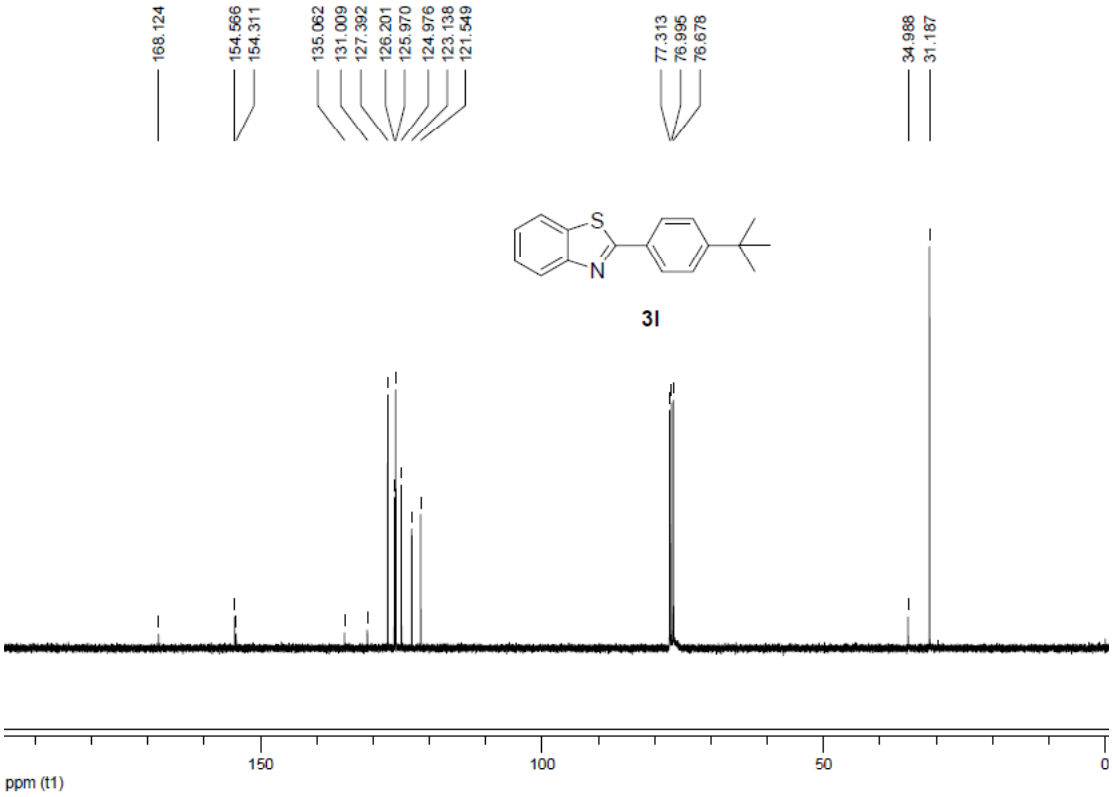

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