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Supporting information for

Iron-Catalyzed Arylation of Benzoazoles with Aromatic Aldehydes Using Oxygen as Oxidant

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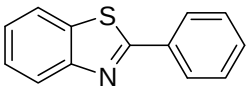
General information:

All experiments were carried out under an atmosphere of oxygen. Flash column chromatography was performed over silica gel 48-75 μm. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to $SiMe_4$ or chloroform signals. MS analyses were performed on Agilent 5975 GC-MS instrument (EI). The new compounds were characterized by ^{1}H NMR, ^{13}C NMR, MS and HRMS. The structure of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. All reagents were used as received from commercial sources without further purification. $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot xH_2O$ were purchased from Alfa Aesar (99.999% and Reagent Grade, respectively).

General procedure: 2-Phenylbenzothiazole (3aa):

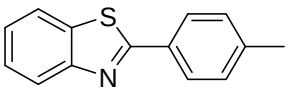
An oven-dried pressure tube (10 mL) was charged with $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), benzaldehyde (**2a**, 20.4 μL, 0.2 mmol), benzothiazole (**1a**, 32.7 μL, 0.3 mmol), H_2O (0.2 mL) and diglyme (0.2 mL). The reaction vessel was flushed with oxygen and sealed. The resulting solution was heated to 150 ^{o}C for 20 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 = 98:2) to give **3aa** as white solid; yield: 37.6 mg (89%).

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



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.11 (d, J = 7.9 Hz, 3H), 7.92 (d, J = 7.9 Hz, 1H), 7.51 (m, 4H), 7.40 (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-*p*-Tolylbenzothiazole (3ab, CAS: 16112-21-3) [1]



The reaction was conducted with 4-methylbenzaldehyde (**2b**, 23.6 μL, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and

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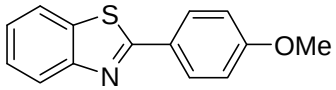
diglyme (0.2 mL) under oxygen at 150 °C for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 39.2 mg, 87% yield of **3ab** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.06 (d, J = 8.1 Hz, 1H), 7.99 (d, J = 7.9 Hz, 2H), 7.90 (d, J = 7.9 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.30 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.2, 153.3, 140.4, 134.1, 130.1, 128.7, 126.6, 125.2, 124.0, 122.1, 120.6, 20.5; MS (EI) *m/z* (%) 225 (100), 108, 91, 69.

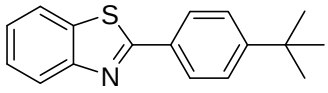
2-(4-Methoxyphenyl)benzothiazole (3ac, CAS: 6265-92-5) [1]



The reaction was conducted with 4-methoxybenzaldehyde (**2c**, 24.3 μL, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and diglyme (0.2 mL) under oxygen at 150 °C for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 41.0 mg, 85% yield of **3ac** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05 (d, J = 8.7 Hz, 3H), 7.88 (d, J = 7.9 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 8.7 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 162.0, 154.3, 135.0, 129.1, 126.6, 126.2, 124.8, 122.9, 121.5, 114.4, 55.5; MS (EI) *m/z* (%) 241 (100), 226, 198, 69.

2-(4-*tert*-Butylphenyl)benzothiazole (3ad, CAS: 56048-52-3) [1]

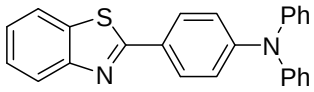


The reaction was conducted with 4-tert-butylbenzaldehyde (**2d**, 33.4 μL, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and diglyme (0.2 mL) under oxygen at 150 °C for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 45.9 mg, 86% yield of **3ad** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05 (m, 3H), 7.90 (d, J = 7.9 Hz, 1H), 7.50 (m, 3H), 7.37 (m,

1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.2, 153.6, 153.3, 134.1, 130.0, 126.4, 125.2, 125.0, 124.0, 122.2, 120.6, 34.0, 30.2; MS (EI) *m/z* (%) 267, 252 (100), 236, 224, 111.

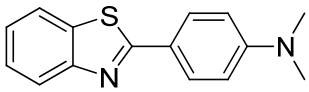
_N_-(4-(Benzothiazol-2-yl)phenyl)-_N_-phenylbenzenamine (3ae)



The reaction was conducted with 4-(diphenylamino)benzaldehyde (**2e**, 54.6 mg, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and dimethyl sulfoxide (0.2 mL) under oxygen at 150 ^{o}C for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 60.1 mg, 80% yield of **3ae** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.06 (d, J = 7.6 Hz, 1H), 7.95 (d, J = 8.3 Hz, 2H), 7.87 (d, J = 7.9 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.38-7.30 (m, 5H), 7.18-7.09 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 154.3, 150.5, 147.0, 134.9, 129.5, 128.6, 126.6, 126.2, 125.5, 124.7, 124.1, 122.8, 121.8, 121.5; MS (EI) *m/z* (%) 378 (100), 253, 207, 189, 77; HRMS calcd. for : $C_{25}H_{19}N_2S$ $[M+1]^+$ 379.1264, found 379.1259.

4-(Benzothiazol-2-yl)-_N_,_N_-dimethylaniline (3af, CAS: 10205-56-8) [2]



The reaction was conducted with 4-(dimethylamino)benzaldehyde (**2f**, 29.8 mg, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and dimethyl sulfoxide (0.2 mL) under oxygen at 150 ^{o}C for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 26.4 mg, 52% yield of **3af** as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.02-7.98 (m, 3H), 7.84 (d, J = 7.9 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 6.76 (d, J = 8.7 Hz, 2H), 3.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.8, 154.4, 152.3, 134.6, 128.9, 126.0, 124.2, 122.3, 121.5, 121.3, 111.8, 40.2; MS (EI) *m/z* (%) 254 (100), 238, 210, 145, 127.

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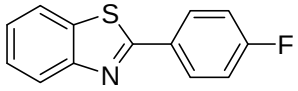
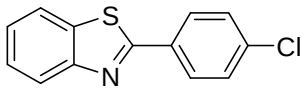
2-(4-Fluorophenyl)benzothiazole (3ag, CAS: 1629-26-1) [1]



The reaction was conducted with 4-fluorobenzaldehyde (**2g**, 21.4 μL, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and diglyme (0.2 mL) under oxygen at 150 ^oC for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 40.3 mg, 88% yield of **3ag** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.11-8.06 (m, 3H), 7.91 (d, J = 7.9 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.19 (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.

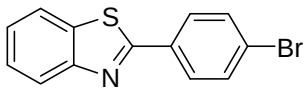
2-(4-Chlorophenyl)benzothiazole (3ah, CAS: 6265-91-4) [1]



The reaction was conducted with 4-chlorobenzaldehyde (**2h**, 28 mg, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and diglyme (0.2 mL) under oxygen at 150 ^oC for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 40.3 mg, 82% yield of **3ah** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.09-8.03 (m, 3H), 7.91 (d, J = 7.9 Hz, 1H), 7.53-7.49 (m, 3H), 7.41 (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 (3ai, CAS: 19654-19-4) [1]

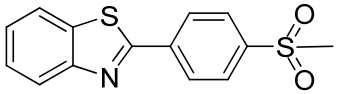


The reaction was conducted with 4-bromobenzaldehyde (**2i**, 37.0 mg, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and

dimethyl sulfoxide (0.2 mL) under oxygen at 150 °C for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 41.2 mg, 71% yield of **3ai** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.08 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 7.9 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 165.7, 153.2, 134.1, 131.7, 131.3, 128.0, 125.5, 124.5, 124.5, 122.4, 120.7; MS (EI) *m/z* (%) 291 (100), 210, 108, 82, 69.

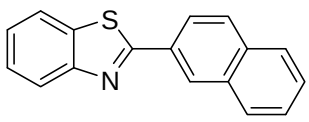
2-(4-(Methylsulfonyl)phenyl)benzothiazole (3aj, CAS: 67363-00-2)



The reaction was conducted with 4-(methylsulfonyl)benzaldehyde (**2j**, 36.8 mg, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and dimethyl sulfoxide (0.2 mL) under oxygen at 150 °C for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 43.4 mg, 75% yield of **3aj** as white solid.

1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.31 (d, J = 8.3 Hz, 2H), 8.14 (d, J = 8.1 Hz, 1H), 8.08 (d, J = 8.3 Hz, 2H), 7.96 (d, J = 7.9 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 164.3, 153.1, 141.4, 137.5, 134.4, 127.3, 127.2, 125.9, 125.1, 122.9, 120.8, 43.5; MS (EI) m/z (%) 289 (100), 226, 210, 198, 139.

2-(Naphthalen-2-yl)benzothiazole (3ak, CAS: 56048-51-2) [1]

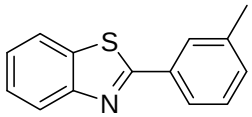


The reaction was conducted with 2-naphthaldehyde (**2k**, 31.2 mg, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and diglyme (0.2 mL) under oxygen at 150 °C for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 36.5 mg, 70% yield of **3ak** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.66 (s, 1H), 8.25 (d, J = 8.5 Hz, 1H), 8.20 (d, J = 8.2 Hz,

1H), 8.01-7.99 (m, 4H), 7.58-7.55 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.1, 154.3, 135.2, 134.7, 133.3, 131.1, 128.9, 128.8, 127.9, 127.6, 127.5, 126.9, 126.4, 125.3, 124.5, 123.3, 121.6; MS (EI) m/z (%) 261 (100), 130, 108, 69.

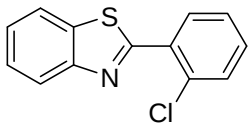
2-*m*-Tolylbenzothiazole (3al, CAS: 1211-32-1) [3]



The reaction was conducted with 3-methylbenzaldehyde (**2l**, 23.6 μL, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and diglyme (0.2 mL) under oxygen at 150 °C for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 32.0 mg, 71% yield of **3al** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) *δ* 8.01 (d, *J* = 8.1 Hz, 1H), 7.96 (s, 1H), 7.87-7.93 (m, 2H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.4 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) *δ* 168.3, 154.2, 138.9, 135.1, 133.6, 131.8, 128.9, 128.1, 126.3, 125.1, 124.9, 123.2, 121.6, 21.3; MS (EI) *m/z* (%) 225 (100), 210, 108, 82, 69.

2-(2-Chlorophenyl)benzothiazole (3am, CAS: 6269-46-1) [4]



The reaction was conducted with 2-chlorobenzaldehyde (**2m**, 23.6 μL, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and diglyme (0.2 mL) under oxygen at 150 °C for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 35.7 mg, 72% yield of **3am** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.23-8.21 (m, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.55-7.52 (m, 2H), 7.46-7.41 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) *δ* 164.2, 152.6, 136.2, 132.8, 132.4, 131.8, 131.1, 130.8, 127.1, 126.3, 125.5, 123.5, 121.4; MS (EI) *m/z* (%) 245 (100), 210, 108, 82, 69.

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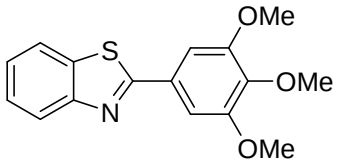
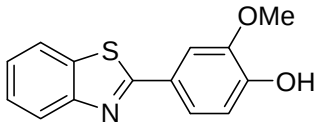
2-(3,4,5-Trimethoxyphenyl)benzothiazole (3an, CAS: 76088-45-4) [5]



The reaction was conducted with 3,4,5-trimethoxybenzaldehyde (**2n**, 39.2 mg, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and dimethyl sulfoxide (0.2 mL) under oxygen at 150 ^oC for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 44.0 mg, 83% yield of **3an** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.08 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.35 (s, 2H), 4.00 (s, 6H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.7, 154.1, 153.6, 140.9, 135.1, 129.0, 126.3, 125.1, 123.1, 121.5, 105.1, 60.9, 56.4; MS (EI) *m/z* (%) 301 (100), 281, 258, 228, 172.

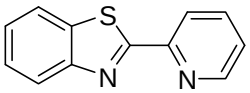
4-(Benzothiazol-2-yl)-2-methoxyphenol (3ao, CAS: 36341-25-0) [6]



The reaction was conducted with 4-hydroxy-3-methoxybenzaldehyde (**2o**, 30.4 mg, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and dimethyl sulfoxide (0.2 mL) under oxygen at 150 ^oC for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 31.9 mg, 62% yield of **3ao** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.75 (s, 1H), 7.55 (d, J = 8.2 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 7.01 (d, J = 8.3 Hz, 1H), 4.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.2, 154.0, 148.7, 147.0, 134.8, 126.3, 126.2, 124.9, 122.8, 122.0, 121.5, 114.8, 109.5, 56.3; MS (EI) *m/z* (%) 257 (100), 242, 214, 186, 129.

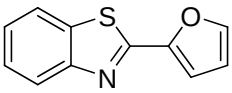
2-(Pyridin-2-yl)benzothiazole (3ap, CAS: 716-80-3) [5]



The reaction was conducted with picolinaldehyde (**2p**, 19.0 μL, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and dimethyl sulfoxide (0.2 mL) under oxygen at 150 ^oC for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 33.1 mg, 78% yield of **3ap** as yellow solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.70-8.69 (m, 1H), 8.39 (d, J = 7.9 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.86 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.46-7.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 169.4, 154.4, 151.5, 149.7, 136.9, 136.2, 126.2, 125.6, 125.2, 123.6, 122.0, 120.8; MS (EI) *m/z* (%) 212 (100), 186, 168, 108, 78.

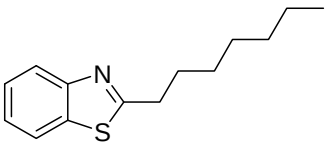
2-(Furan-2-yl)benzothiazole (3aq, CAS: 1569-98-8) [6]



The reaction was conducted with furan-2-carbaldehyde (**2q**, 16.6 μL, 0.2 mmol) and benzothiazole (**1a**, 32.7 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and dimethyl sulfoxide (0.2 mL) under oxygen at 150 ^oC for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 21.3 mg, 53% yield of **3aq** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.07 (d, J = 7.9 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.62 (s, 1H), 7.50 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.24 (d, J = 12.1 Hz, 1H), 6.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.6, 153.8, 148.9, 144.7, 134.4, 126.5, 125.2, 123.2, 121.6, 112.5, 111.4; MS (EI) *m/z* (%) 201 (100), 173, 146, 108, 69.

2-Heptylbenzothiazole (3ar, CAS: 69938-51-8)[7]

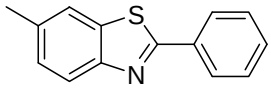


The reaction was conducted with octanal (**2r**, 62.4 μL, 0.4 mmol) and benzothiazole (**1a**, 21.8 μL,

0.2 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and diglyme (0.2 mL) under oxygen at 150 ^oC for 30 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 14.8 mg, 30% yield of **3ar** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.99 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 7.2 Hz, 1H), 7.47 (m, 1H), 7.37 (m, 1H), 3.14 (m, 2H), 1.90 (m, 2H), 1.31-1.45 (m, 8H), 0.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.5, 153.3, 135.2, 125.9, 124.6, 122.5, 121.5, 34.4, 31.7, 29.8, 29.2, 29.0, 22.6, 14.1; MS (EI) *m/z* (%) 233, 204, 162, 149 (100).

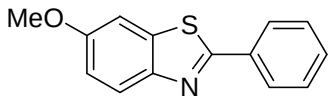
6-Methyl-2-phenylbenzothiazole (3ba, CAS: 10205-58-0) [8]



The reaction was conducted with benzaldehyde (**2a**, 20.4 μL, 0.2 mmol) and 6-methylbenzothiazole (**1b**, 34.4 μL, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and diglyme (0.2 mL) under oxygen at 150 ^oC for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 45.0 mg, 78% yield of **3ba** as white solid.

1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.09-8.08 (m, 2H), 7.97 (d, J = 8.3 Hz, 1H), 7.71 (s, 1H), 7.50 (m, 3H), 7.31 (d, J = 8.2 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.2, 152.3, 135.3, 135.3, 133.9, 130.7, 128.9, 127.9, 127.4, 122.7, 121.3, 21.5; MS (EI) m/z (%) 225 (100), 121, 112, 77, 69.

6-Methoxy-2-phenylbenzothiazole (3ca, CAS: 10205-69-3) [9]



The reaction was conducted with benzaldehyde (**2a**, 20.4 μL, 0.2 mmol) and 6-methoxybenzothiazole (**1c**, 49.5 mg, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and diglyme (0.2 mL) under oxygen at 150 ^oC for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 41.9 mg, 87% yield of **3ca** as white solid.

1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05 (m, 2H), 7.95 (d, J = 8.9 Hz, 1H), 7.49-7.47 (m, 3H),

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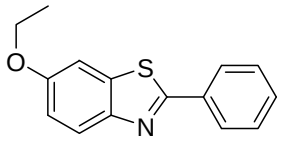
7.36 (s, 1H), 7.11-7.08 (m, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 165.5, 157.8, 148.7, 136.4, 133.8, 130.5, 129.0, 127.2, 123.7, 115.7, 104.2, 55.8; MS (EI) m/z (%) 241 (100), 226, 198, 95, 69.

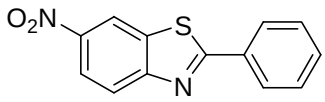
6-Ethoxy-2-phenylbenzothiazole (3da)



The reaction was conducted with benzaldehyde (**2a**, 20.4 μL, 0.2 mmol) and 6-ethoxybenzothiazole (**1d**, 53.7 mg, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and diglyme (0.2 mL) under oxygen at 150 ^{o}C for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 40.8 mg, 80% yield of **3da** as white solid.

1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.07-8.05 (m, 2H), 7.97 (d, J = 8.9 Hz, 1H), 7.49-7.48 (m, 3H), 7.36 (s, 1H), 7.08-7.11 (m, 1H), 4.11 (q, J = 6.9 Hz, 2H), 1.47 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 165.5, 157.2, 148.6, 136.4, 133.8, 130.5, 129.0, 127.2, 123.7, 116.1, 104.8, 64.1, 14.8; MS (EI) m/z (%) 255 (100), 227, 198, 95, 69; HRMS calcd. for: $C_{15}H_{14}NOS$ $[M+1]^+$ 256.0791, found 256.0791.

6-Nitro-2-phenylbenzothiazole (3ea, CAS: 38338-23-7) [9]



The reaction was conducted with benzaldehyde (**2a**, 20.4 μL, 0.2 mmol) and 6-nitrobenzothiazole (**1e**, 50.4 mg, 0.3 mmol), $FeSO_4 \cdot 7H_2O$ (11.1 mg, 0.04 mmol), H_2O (0.2 mL) and dimethyl sulfoxide (0.2 mL) under oxygen at 150 ^{o}C for 20 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 33.3 mg, 65% yield of **3ea** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.85 (s, 1H), 8.37 (d, J = 8.9 Hz, 1H), 8.16-8.13 (m, 3H), 7.58-7.54 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.8, 156.9, 144.1, 134.4, 131.9, 131.2, 128.3, 127.0, 122.4, 120.9, 117.2; MS (EI) *m/z* (%) 256 (100), 226, 210, 107, 63.

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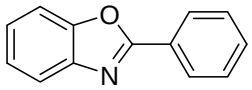
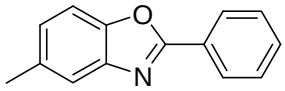
2-Phenylbenzoxazole (3fa, CAS: 833-50-1) [10]



The reaction was conducted with benzaldehyde (**2a**, 20.4 μL, 0.2 mmol) and benzooxazole (**1f**, 32.1 mg, 0.3 mmol), $Fe_2(SO_4)_3 \cdot xH_2O$ (16.0 mg, 0.04 mmol), tris(pentafluorophenyl)phosphine (10.6 mg, 0.02 mmol), diglyme (0.4mL) under air at 110 ^oC for 36 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 27.3 mg, 70% yield of **3fa** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.28-8.27 (m, 2H), 7.80-7.78 (m, 1H), 7.61-7.54 (m, 4H), 7.38-7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.0, 150.8, 142.1, 131.5, 128.9, 127.6, 127.2, 125.1, 124.6, 120.0, 110.6; MS (EI) *m/z* (%) 195 (100), 167, 139, 77, 63.

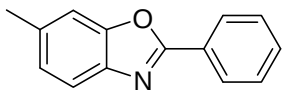
5-Methyl-2-phenylbenzoxazole (3ga, CAS: 7420-86-2) [11]



The reaction was conducted with benzaldehyde (**2a**, 20.4 μL, 0.2 mmol) and 5-methylbenzooxazole (**1g**, 39.9 mg, 0.3 mmol), $Fe_2(SO_4)_3 \cdot xH_2O$ (16.0 mg, 0.04 mmol), tris(pentafluorophenyl)phosphine (10.6 mg, 0.02 mmol), diglyme (0.4mL) under air at 110 ^oC for 36 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 31.8 mg, 76% yield of **3ga** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.27-8.25 (m, 2H), 7.57-7.53 (m, 4H), 7.46 (d, J = 8.3 Hz, 1H), 7.17 (d, J = 8.2 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.1, 149.0, 142.3, 134.4, 131.4, 128.9, 127.6, 127.3, 126.2, 119.9, 109.9, 21.5; MS (EI) *m/z* (%) 209 (100), 180, 105, 78, 51.

6-Methyl-2-phenylbenzoxazole (3ha, CAS: 14016-00-3) [12]



The reaction was conducted with benzaldehyde (**2a**, 20.4 μL, 0.2 mmol) and

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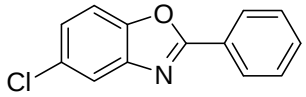
6-methylbenzooxazole (**1h**, 39.9 mg, 0.3 mmol), $Fe_2(SO_4)_3 \cdot xH_2O$ (16.0 mg, 0.04 mmol), tris(pentafluorophenyl)phosphine (10.6 mg, 0.02 mmol), diglyme (0.4mL) under air at 110 ^oC for 36 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 30.1 mg, 72% yield of **3ha** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.25-8.24 (m, 2H), 7.65 (d, J = 8.1 Hz, 1H), 7.53-7.52 (m, 3H), 7.40 (s, 1H), 7.18 (d, J = 8.0 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 162.6, 151.1, 140.0, 135.5, 131.2, 128.8, 127.5, 127.4, 125.8, 119.3, 110.7, 21.7; MS (EI) *m/z* (%) 209 (100), 180, 105, 78, 51.

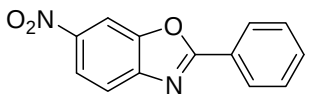
5-Chloro-2-phenylbenzoxazole (3ia, CAS: 1019-90-5) [13]



The reaction was conducted with benzaldehyde (**2a**, 20.4 μL, 0.2 mmol) and 5-chlorobenzooxazole (**1i**, 46.2 mg, 0.3 mmol), $Fe_2(SO_4)_3 \cdot xH_2O$ (16.0 mg, 0.04 mmol), tris(pentafluorophenyl)phosphine (10.6 mg, 0.02 mmol), diglyme (0.4mL) under air at 110 ^oC for 36 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 34.5 mg, 75% yield of **3ia** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.25 (d, J = 6.4 Hz, 2H), 7.76 (s, 1H), 7.55-7.50 (m, 4H), 7.33 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 164.4, 149.4, 143.3, 131.9, 130.1, 128.9, 127.8, 126.8, 125.3, 120.0, 111.2; MS (EI) *m/z* (%) 229 (100), 201, 166, 126, 98.

6-Nitro-2-phenylbenzoxazole (3ja, CAS: 3164-28-1) [14]



The reaction was conducted with benzaldehyde (**2a**, 20.4 μL, 0.2 mmol) and 6-nitrobenzooxazole (**1j**, 49.2 mg, 0.3 mmol), $Fe_2(SO_4)_3 \cdot xH_2O$ (16.0 mg, 0.04 mmol), tris(pentafluorophenyl)phosphine (10.6 mg, 0.02 mmol), diglyme (0.4mL) under air at 110 ^oC for 36 h. The crude mixture was purified by flash column chromatography on silica (petroleum ether/ethyl acetate = 98:2) to provide 28.8 mg, 60% yield of **3ja** as white solid.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.50 (s, 1H), 8.34-8.29 (m, 3H), 7.85 (d, J = 8.7 Hz, 1H),

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7.65-7.56 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.4, 149.9, 147.4, 145.1, 132.9, 129.2, 128.2, 125.9, 120.8, 119.8, 107.2; MS (EI) *m/z* (%) 240 (100), 210, 166, 139, 63.

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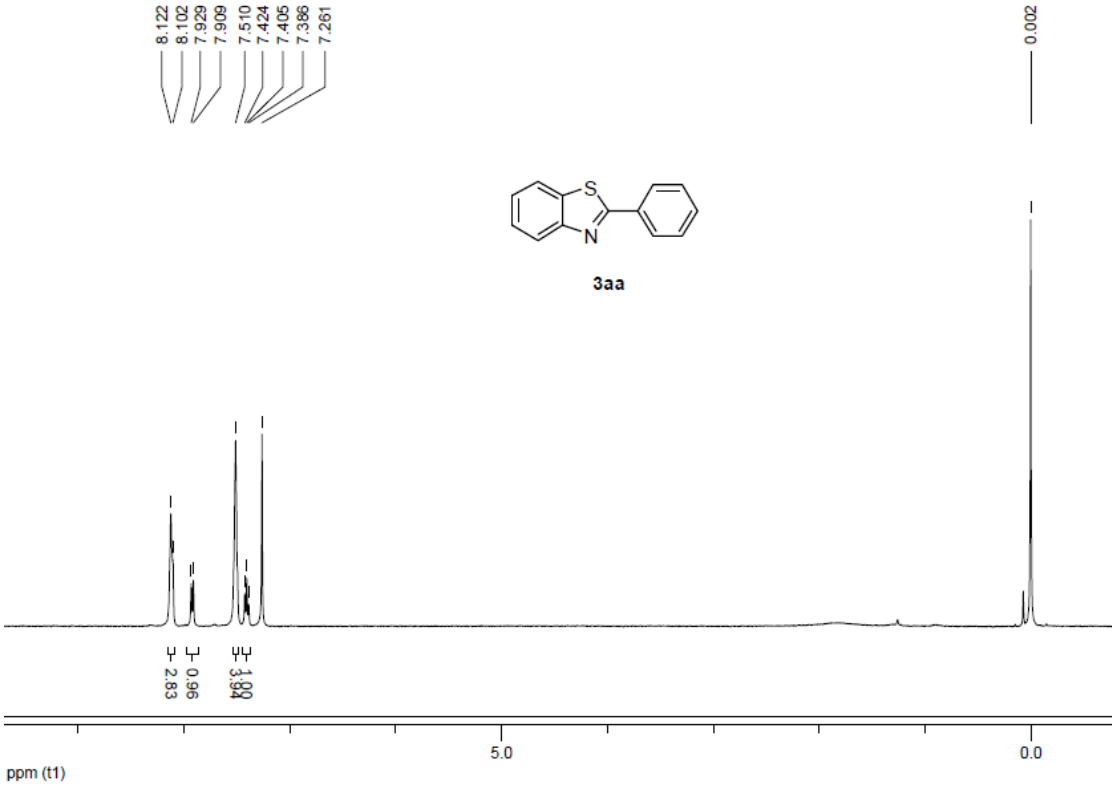
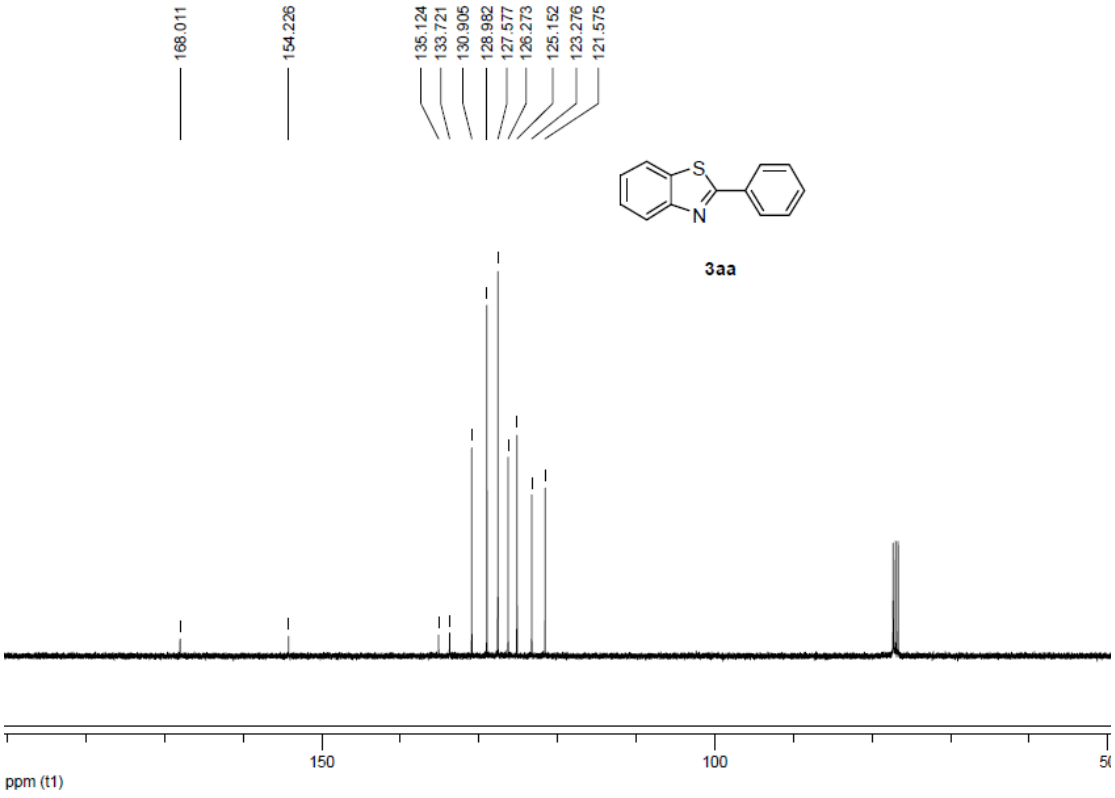
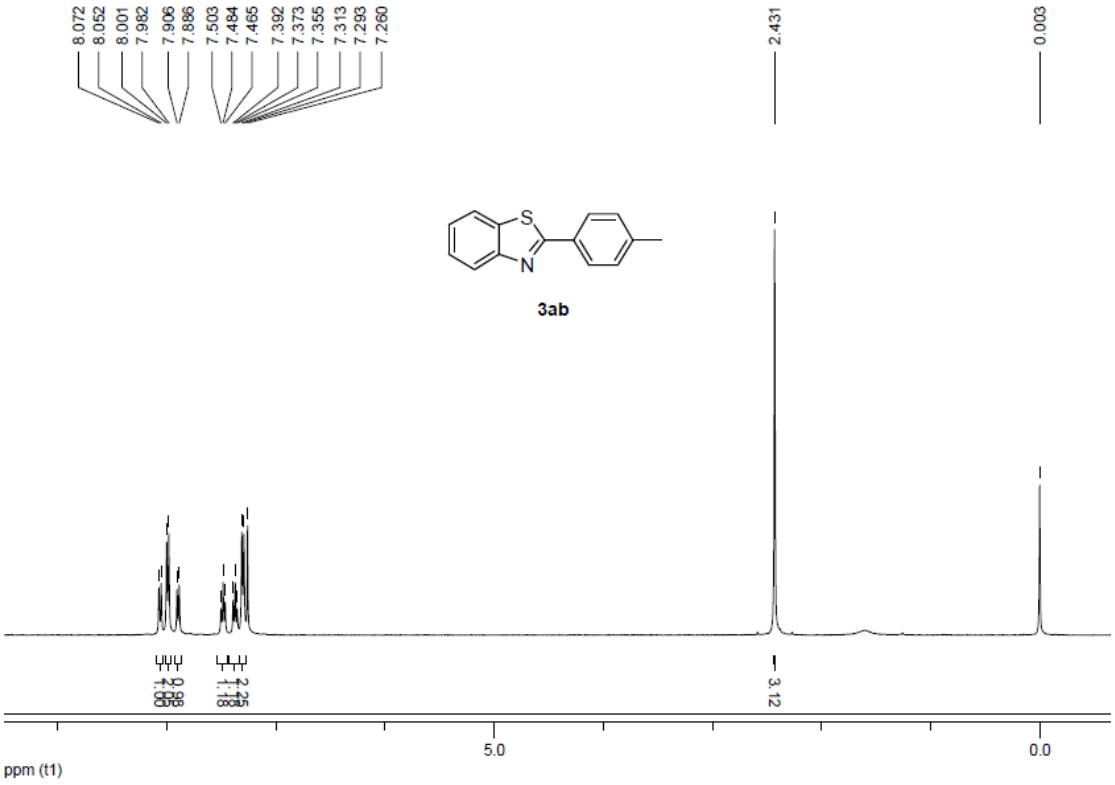
^{1}H and ^{13}C NMR spectra



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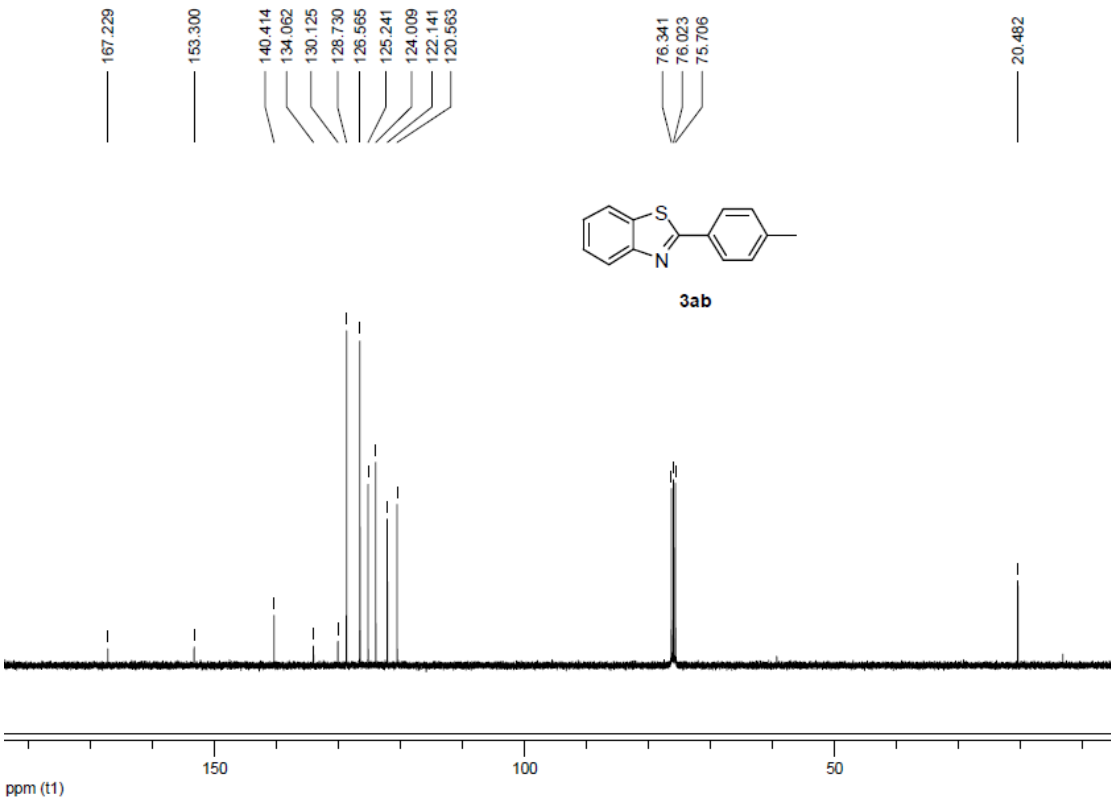
ppm (t1)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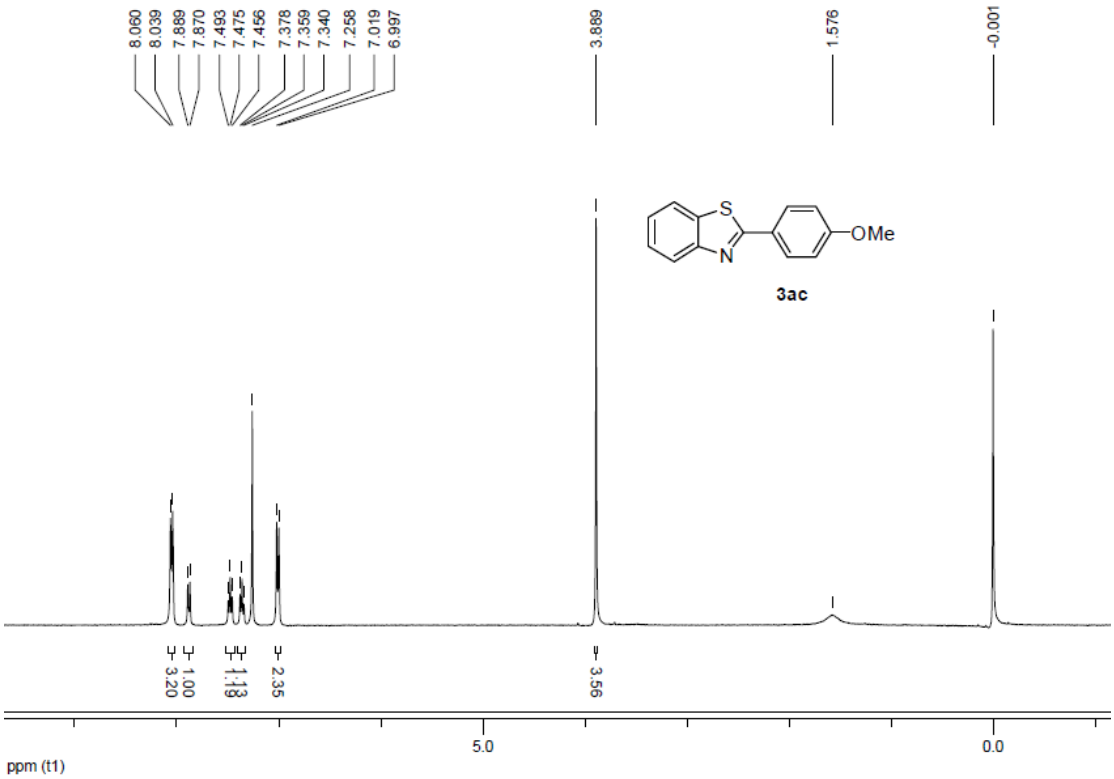
ppm (t1)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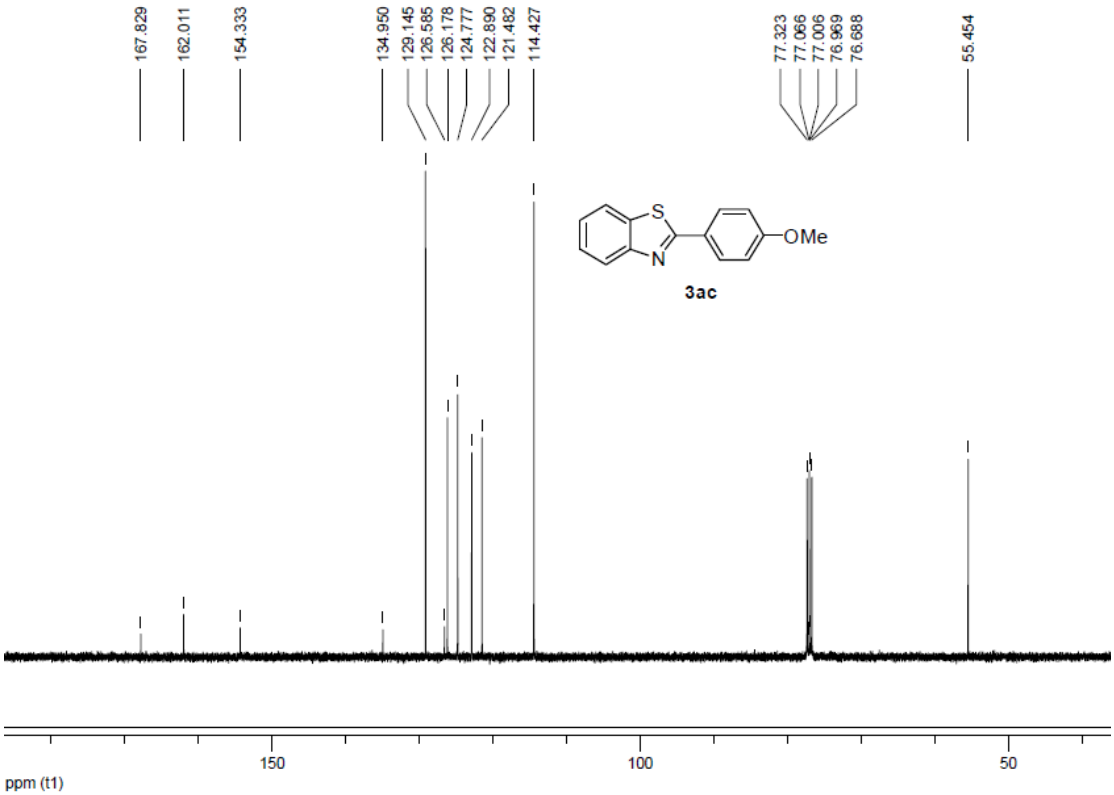
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ppm (t1)

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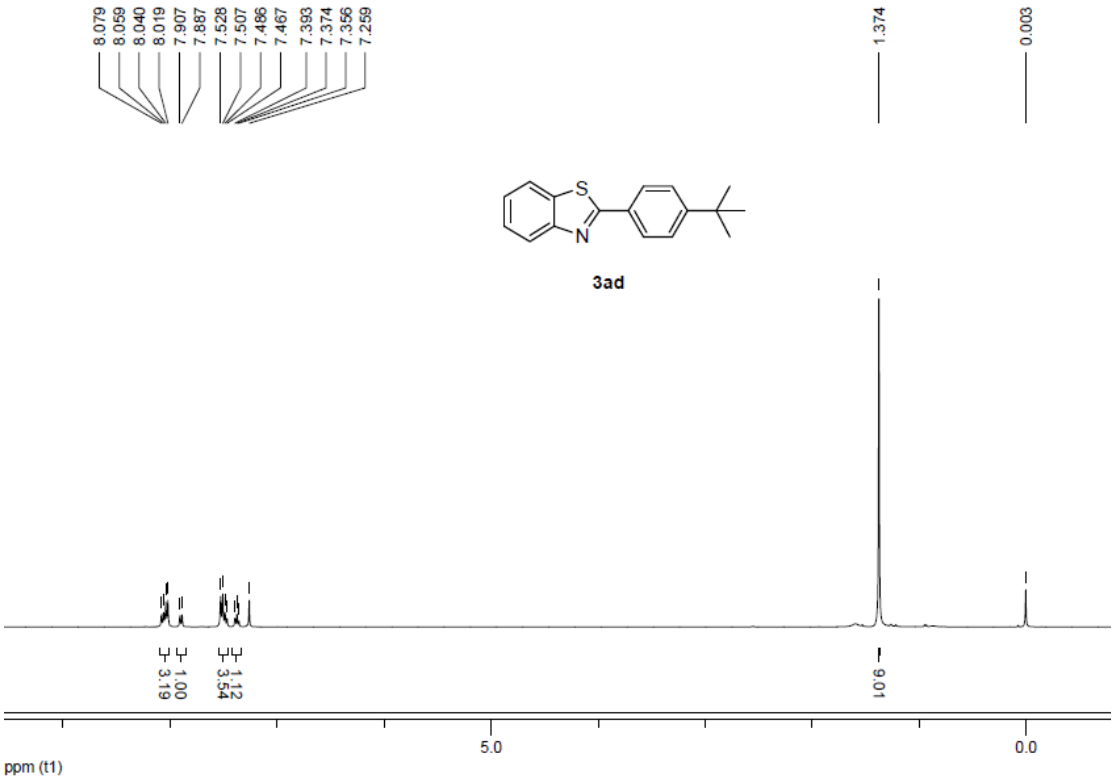

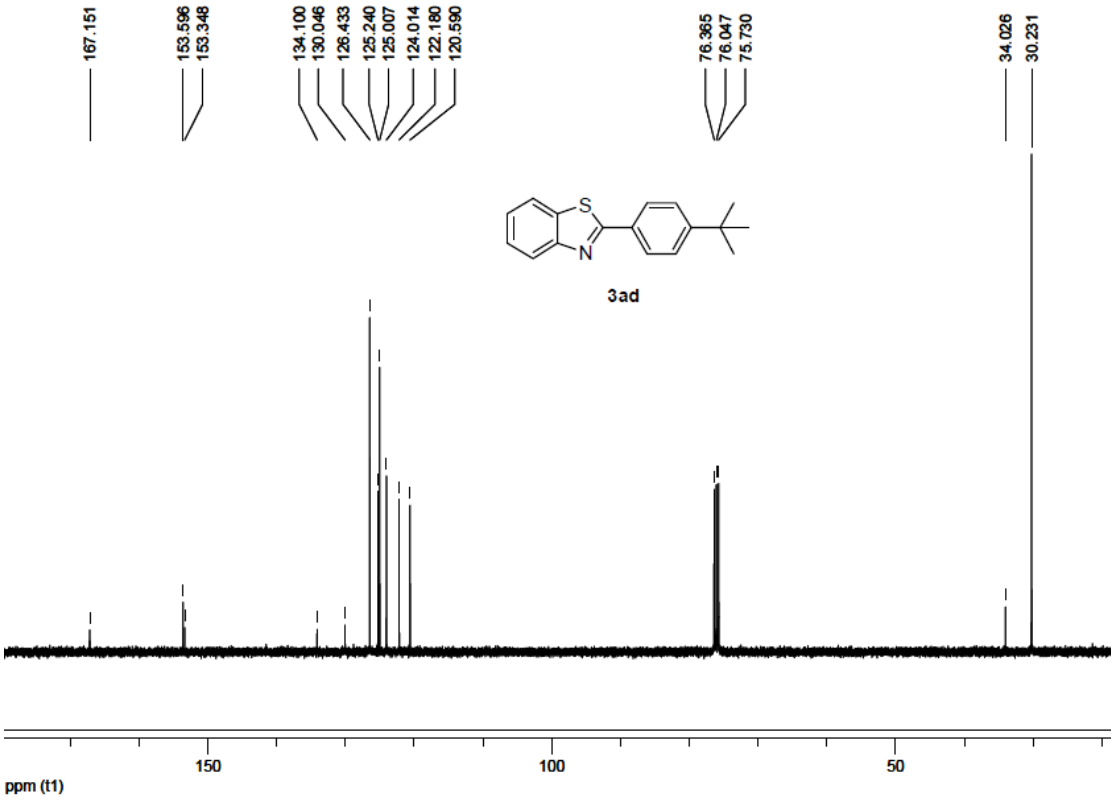

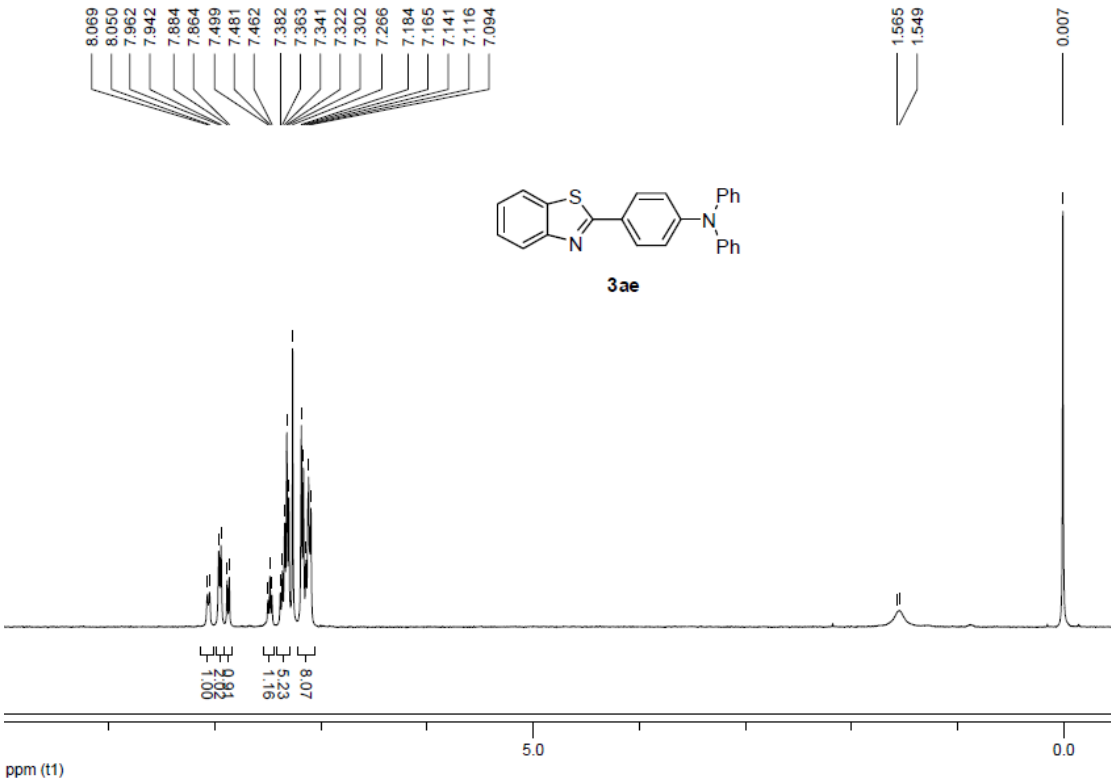
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7.141
7.116
7.094
1.565
1.549
0.007
S
N
Ph
N
Ph
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2.01
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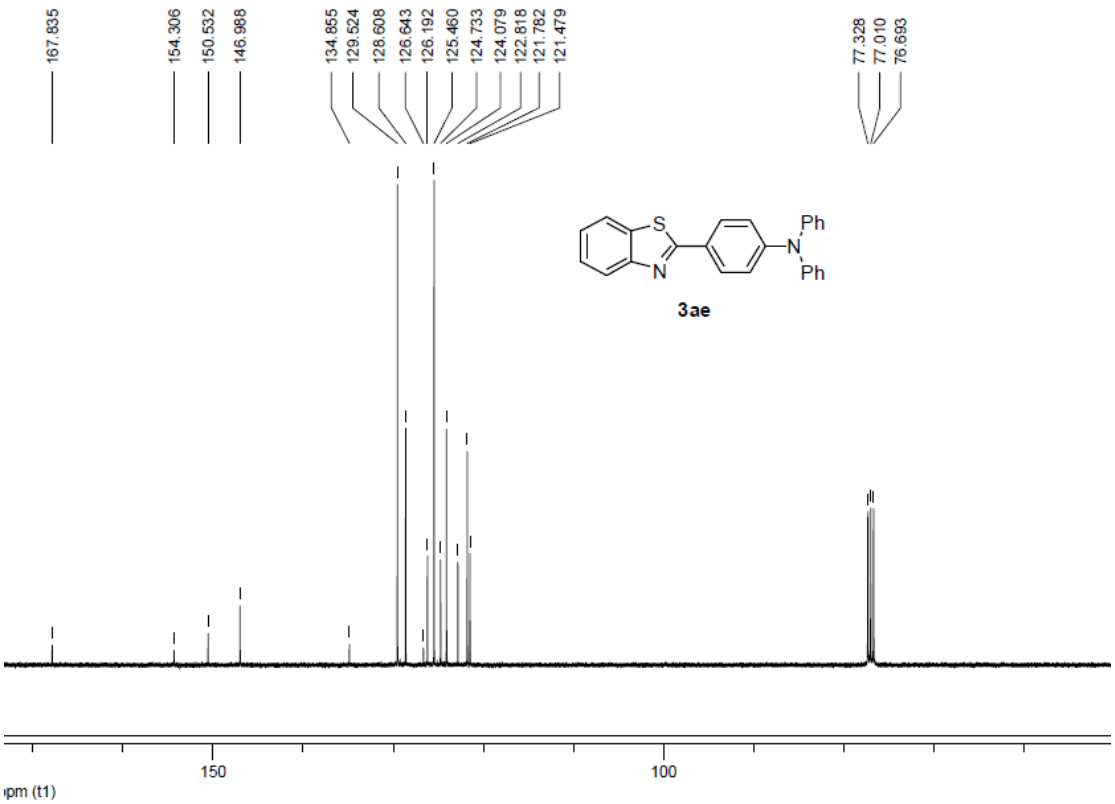
ppm (t1)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126.643
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Ph
N
Ph
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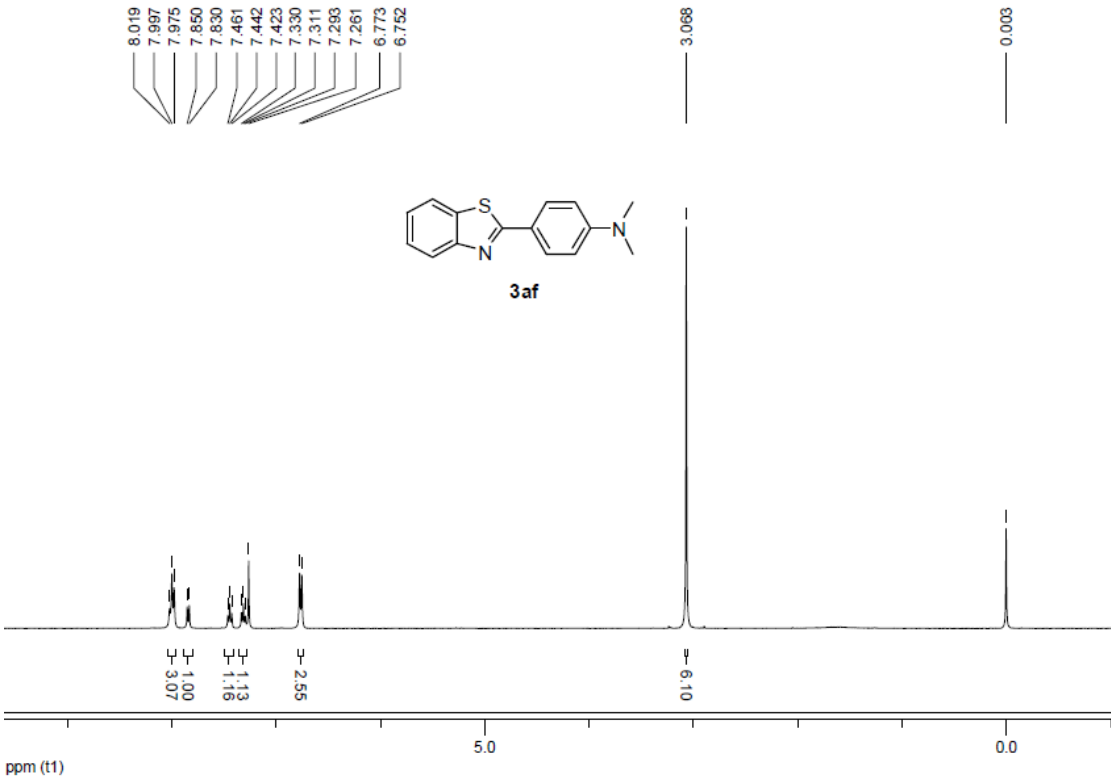
150
100
ppm (t1)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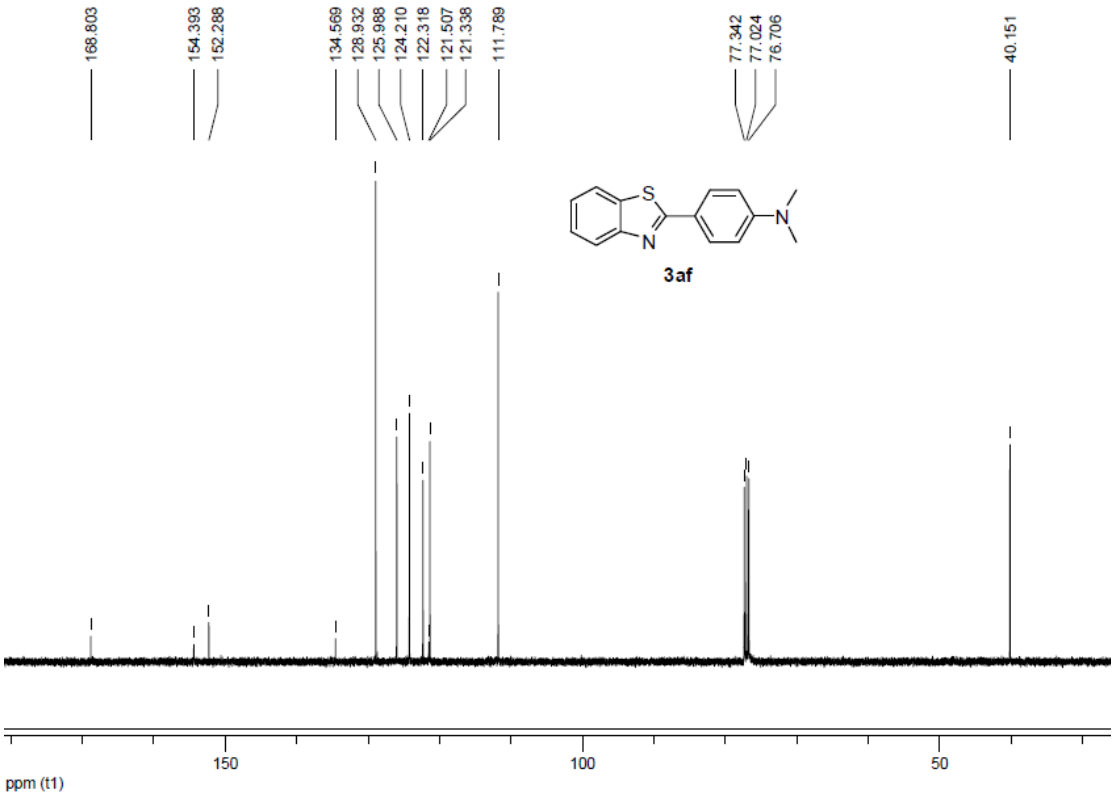
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40.151
S
N
N
3af
150
100
50
ppm (t1)

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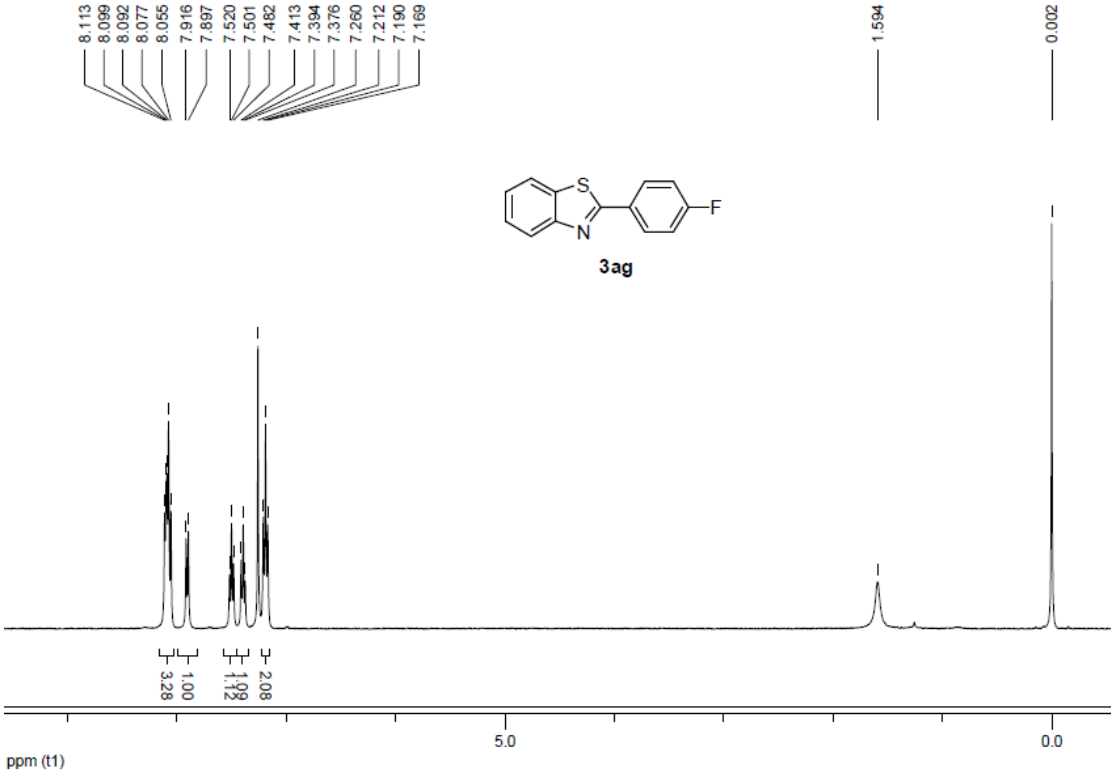

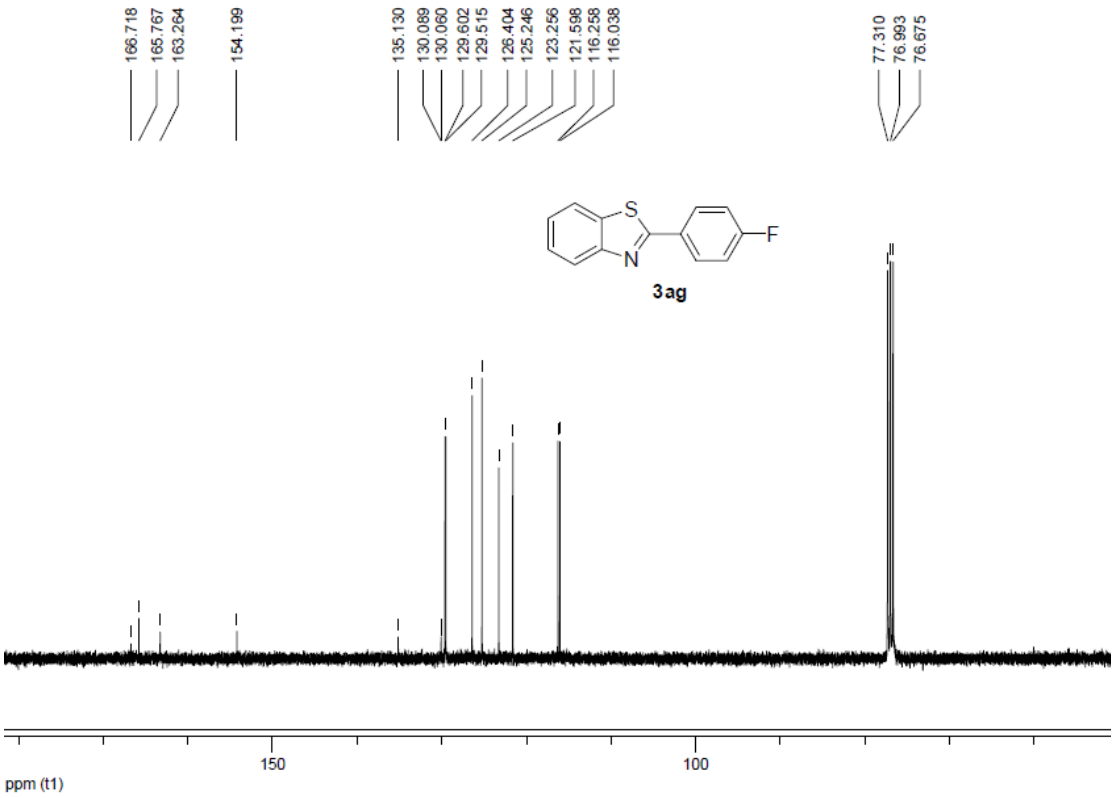

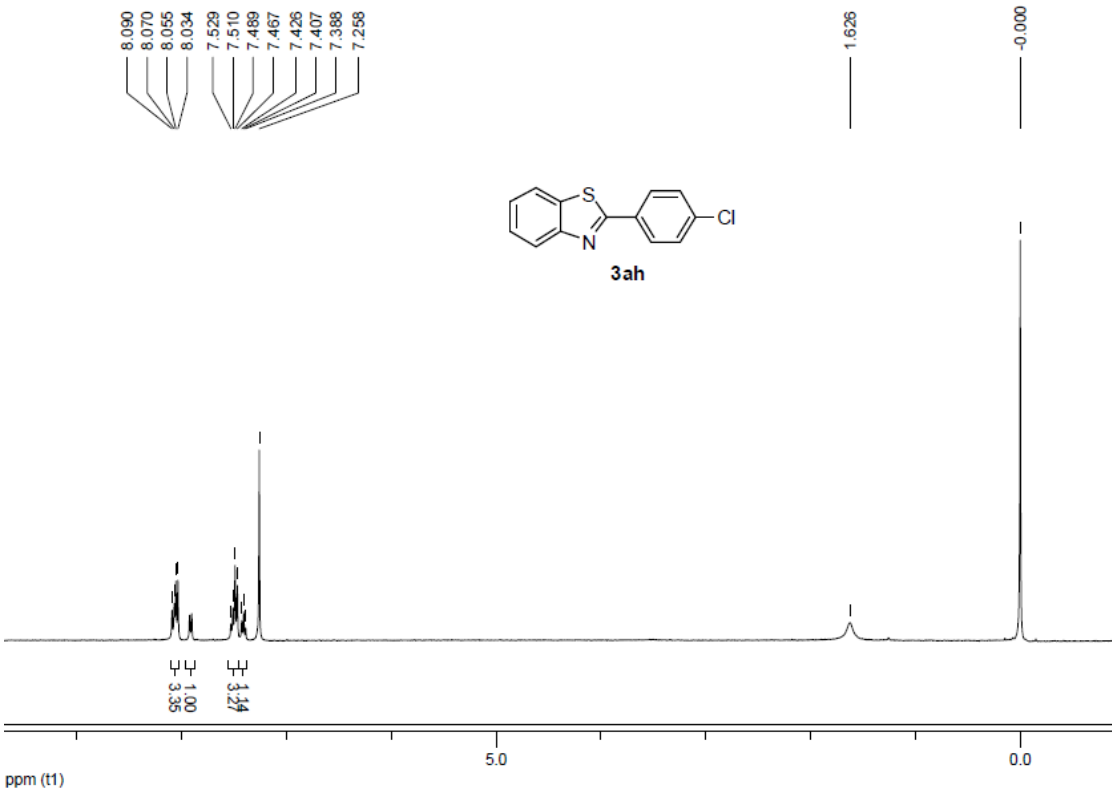
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7.407
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Cl
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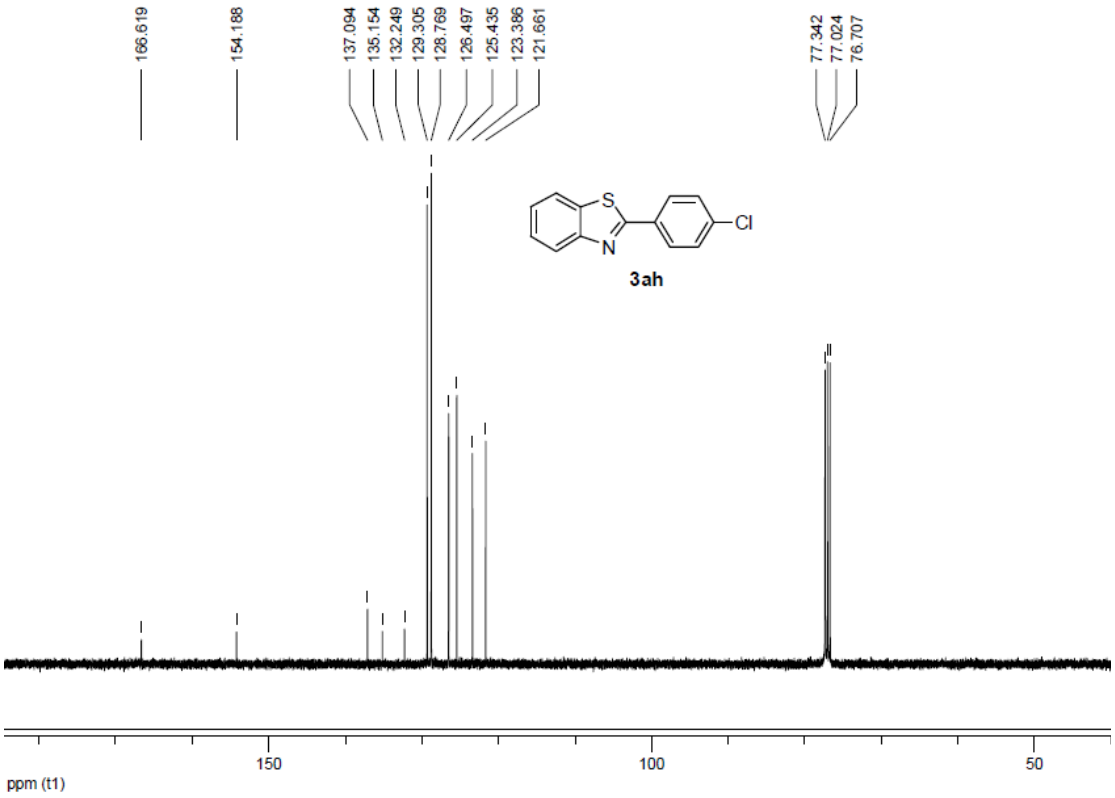
ppm (t1)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N
Cl
3ah
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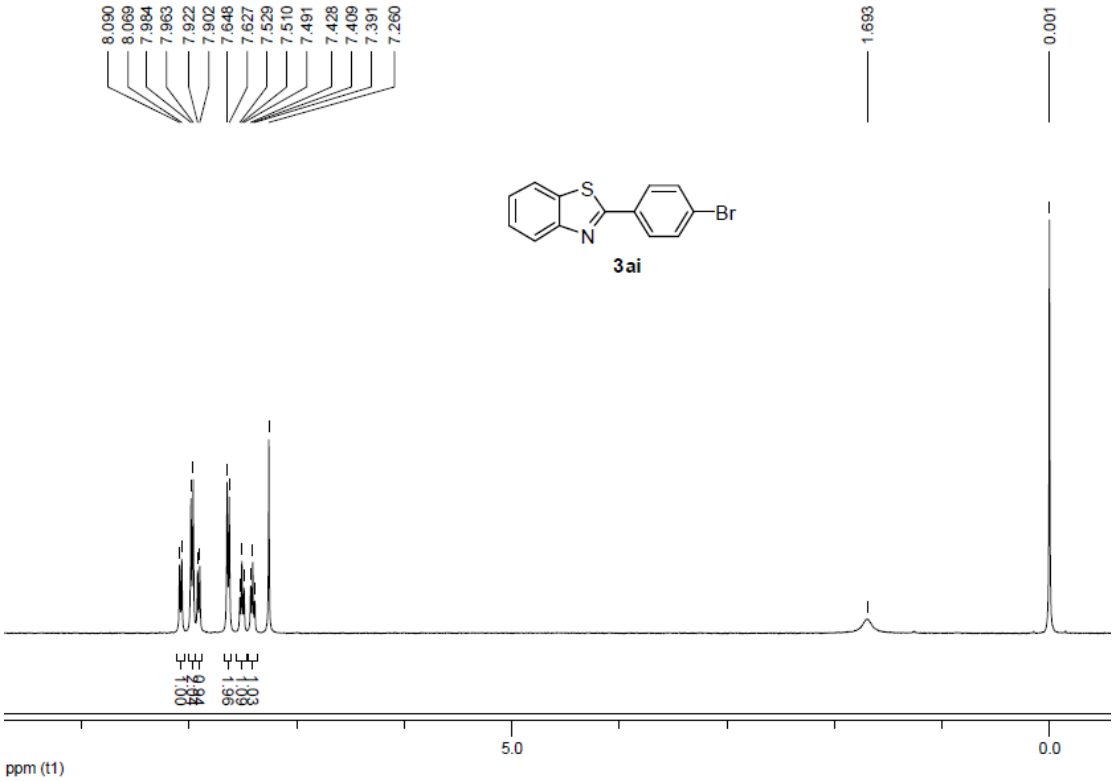
100
50
ppm (t1)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7.428
7.409
7.391
7.260
1.693
0.001
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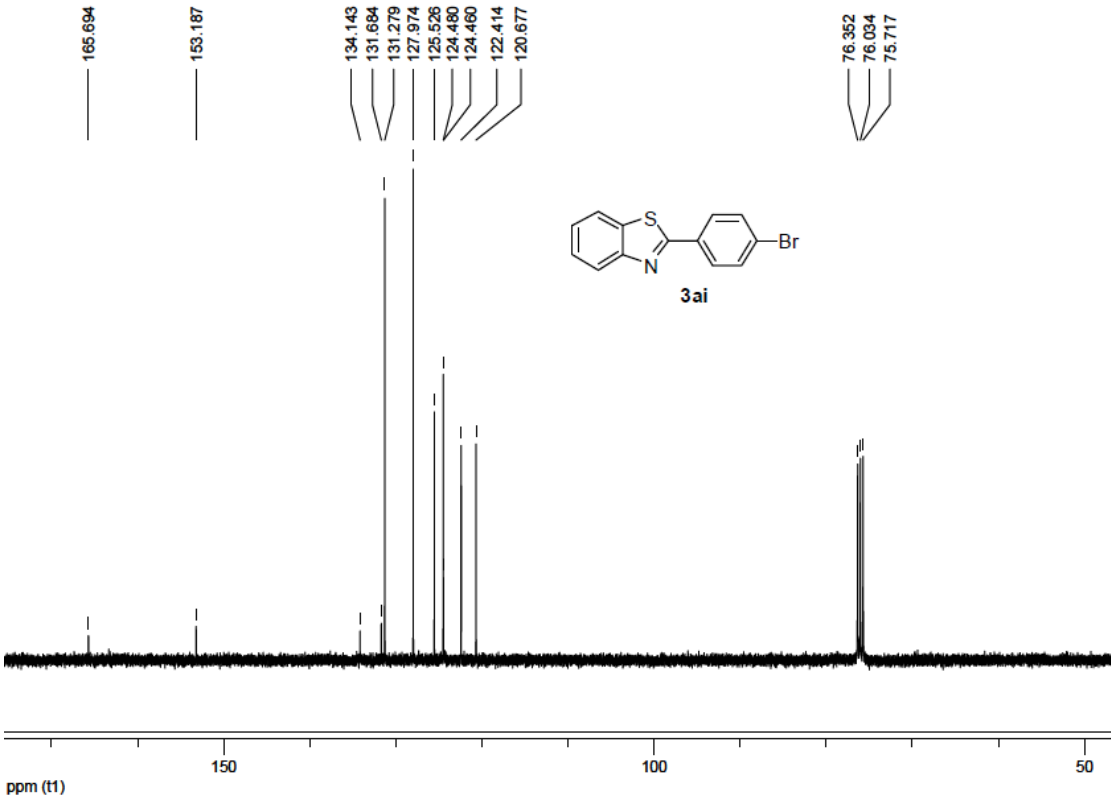
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Br
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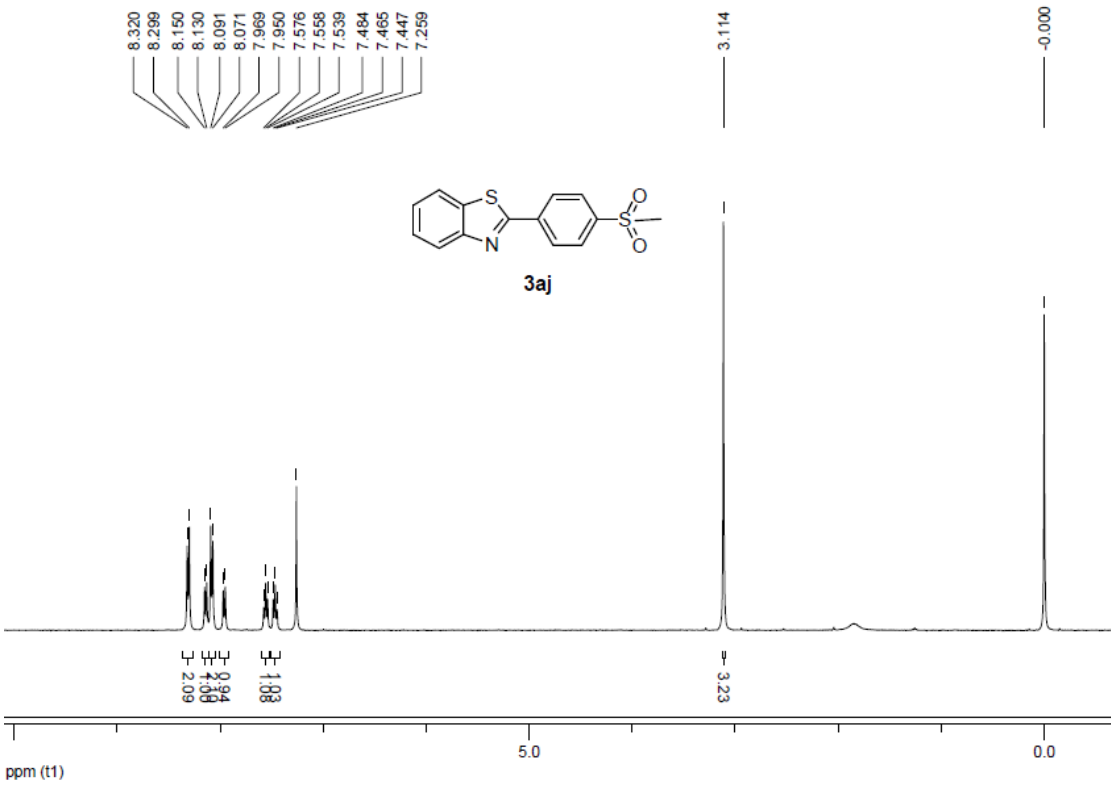
100
50
ppm (t1)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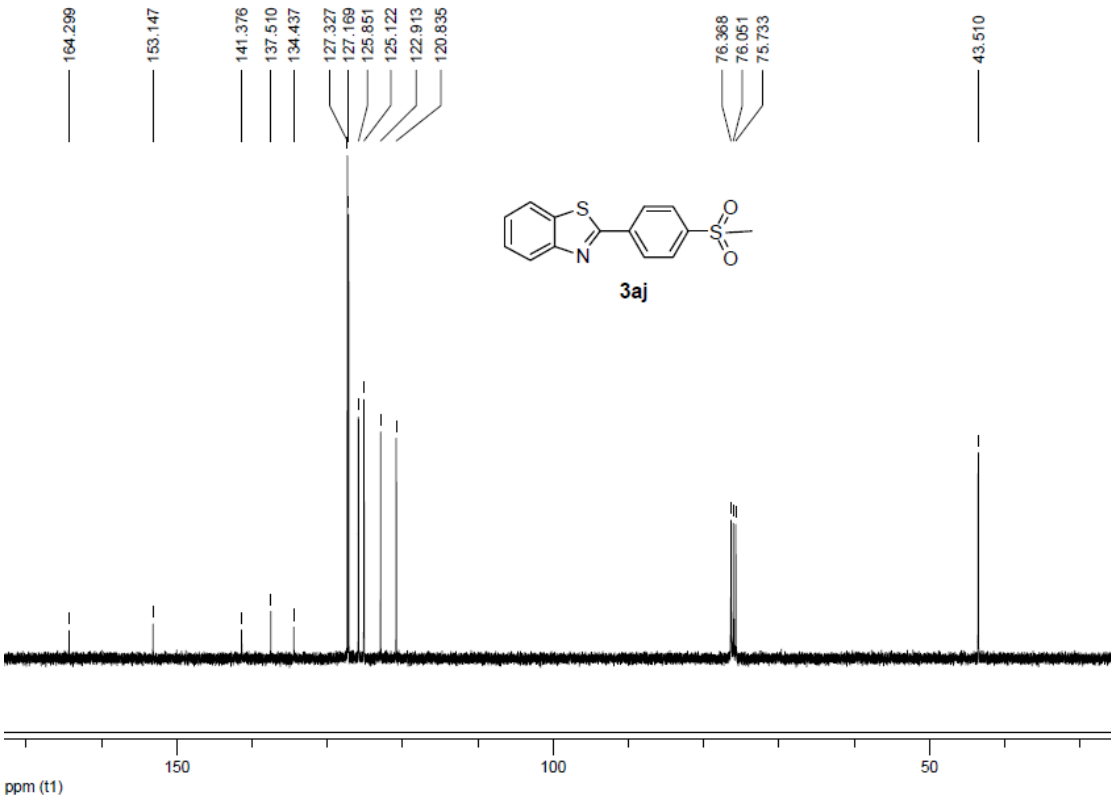
ppm (t1)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50
ppm (t1)

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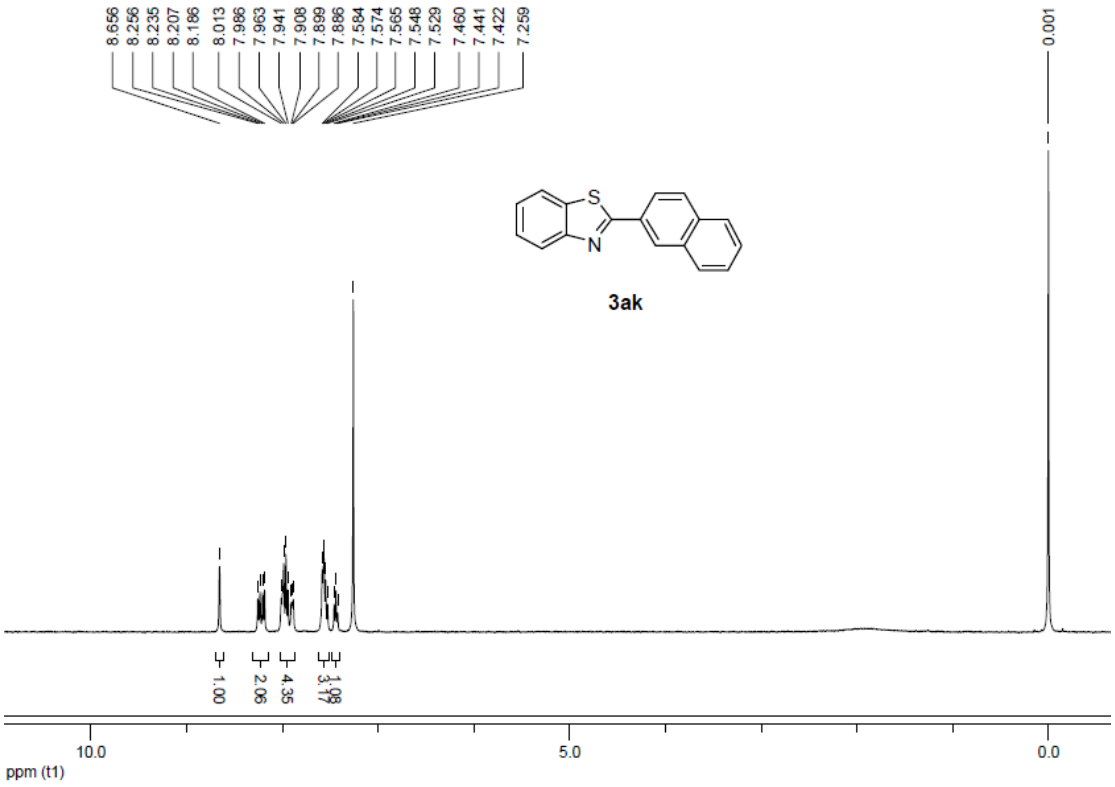

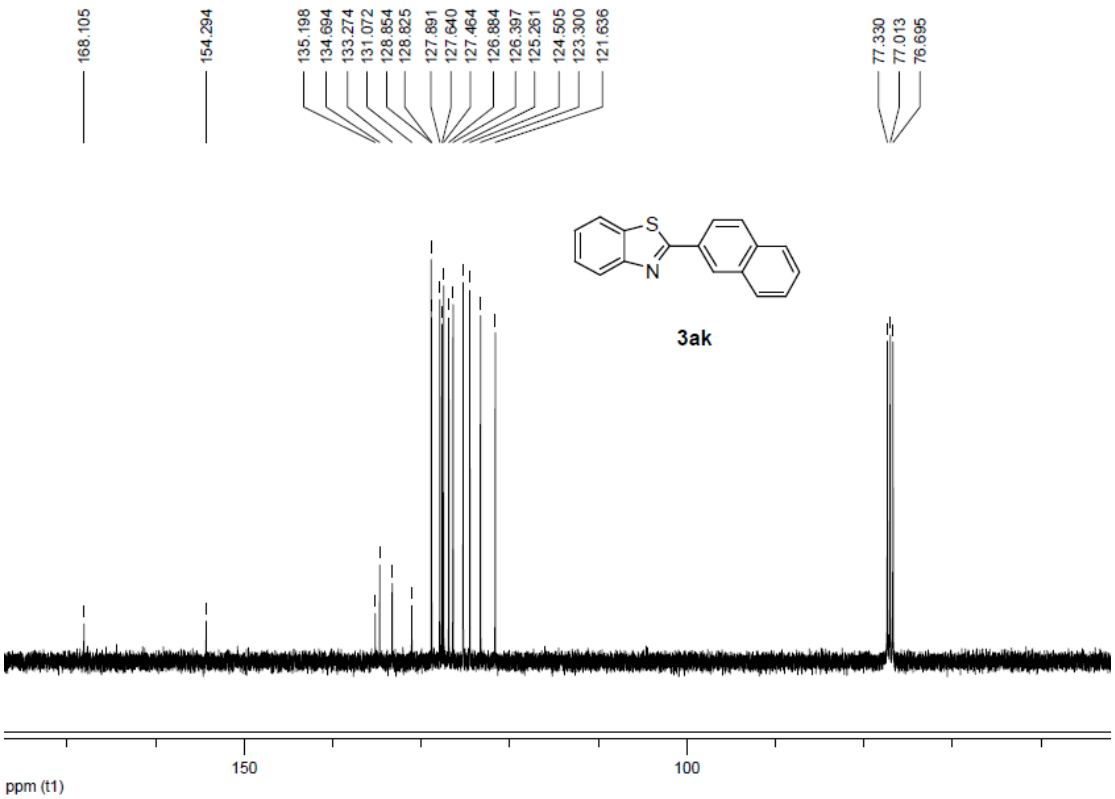

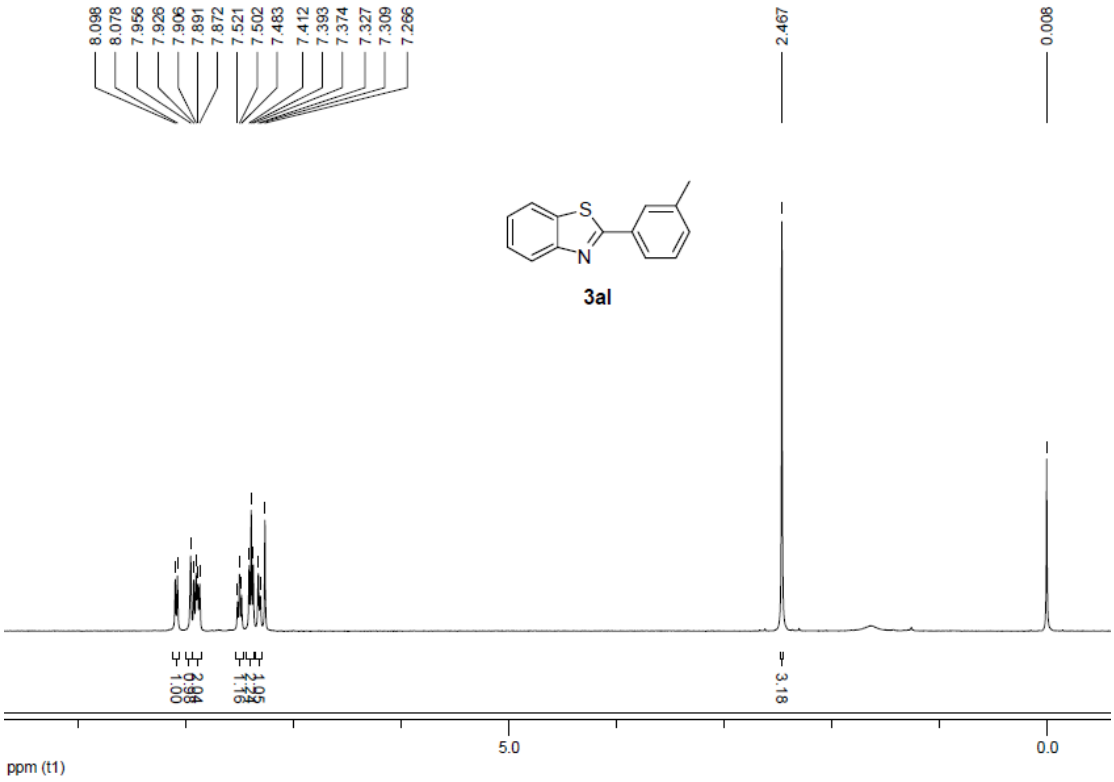
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7.309
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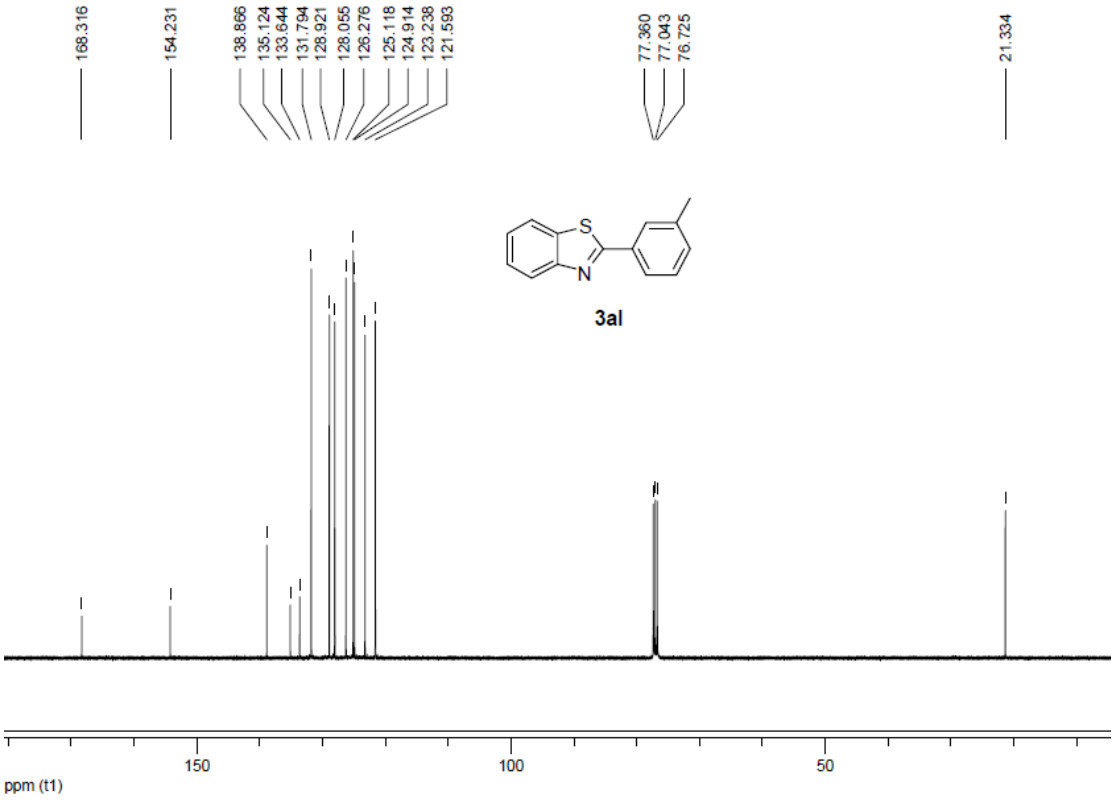
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50
ppm (t1)

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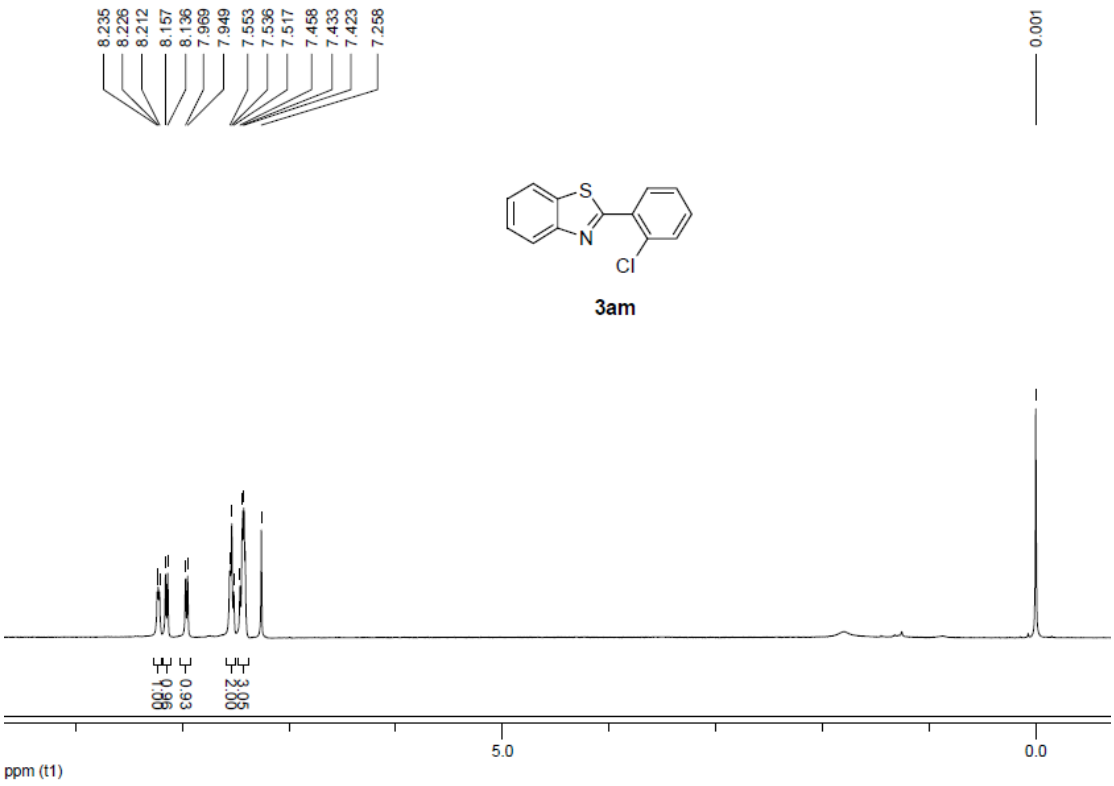

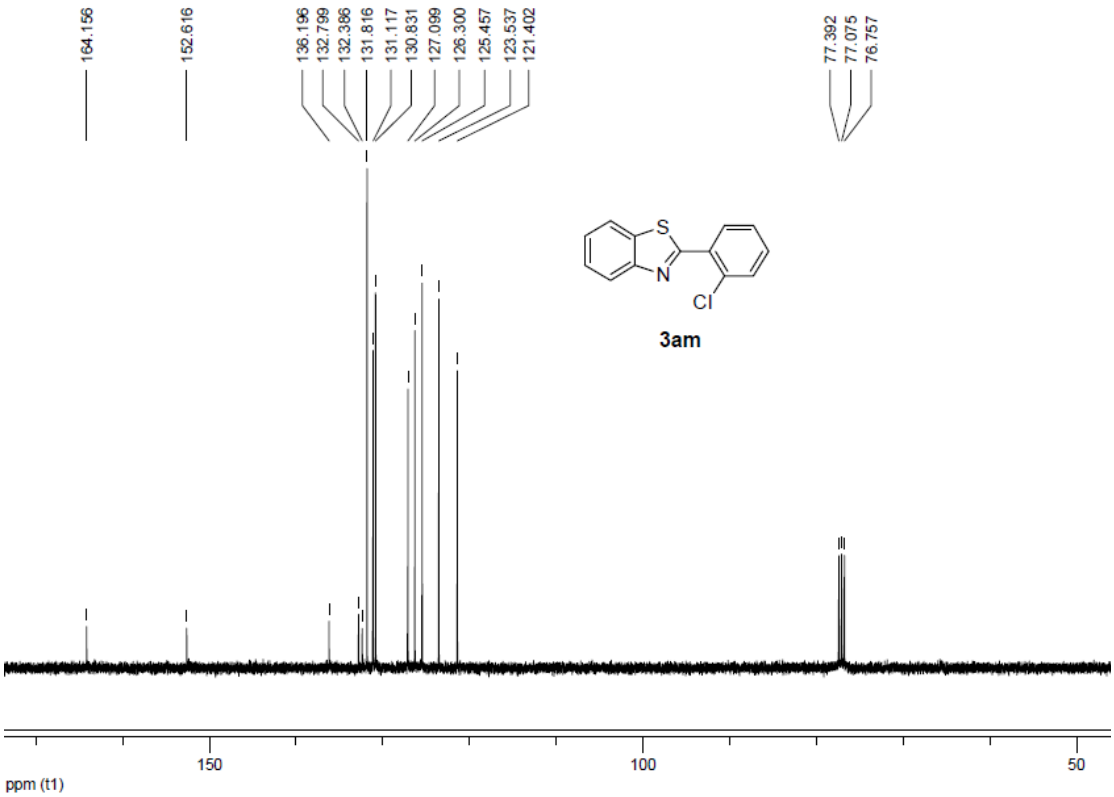

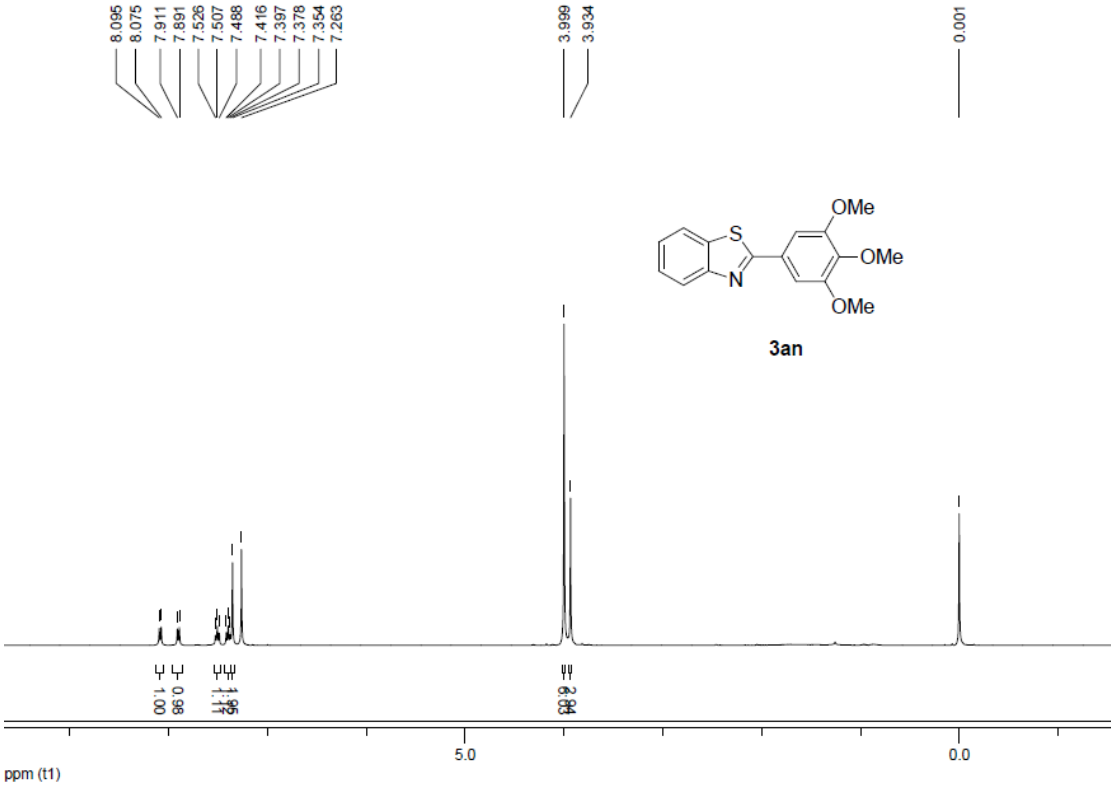
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3.934
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OMe
OMe
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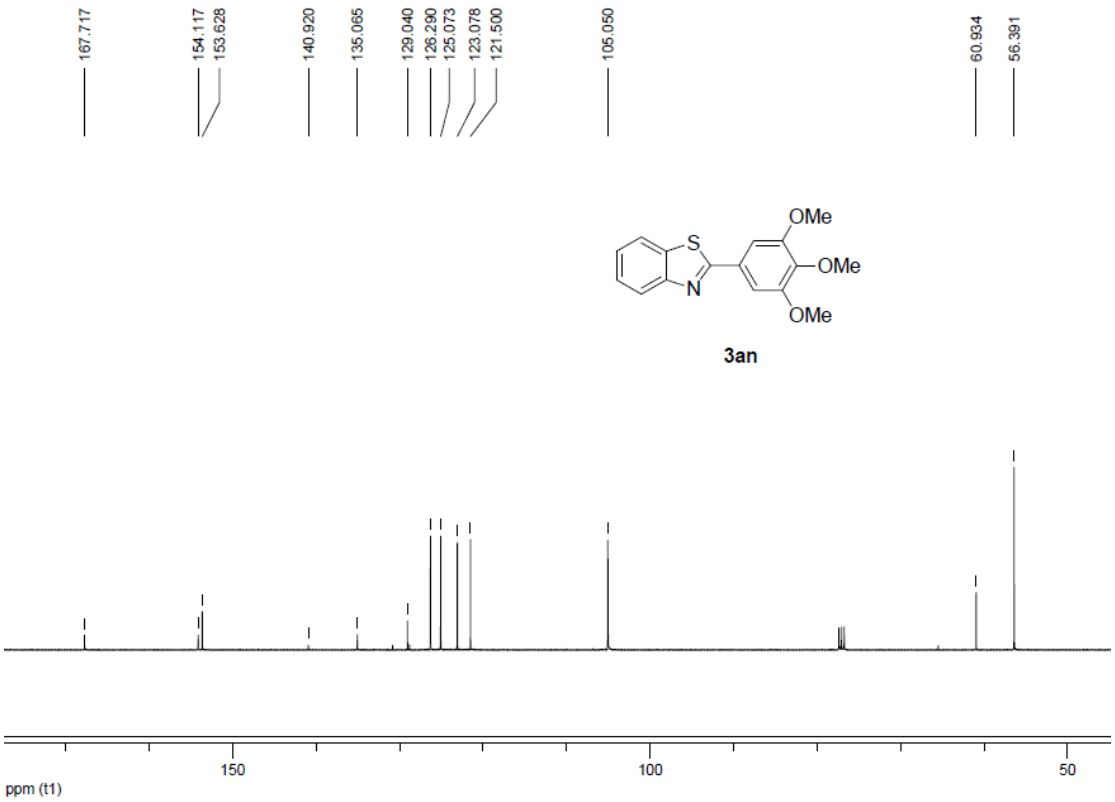
ppm (t1)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OMe
OMe
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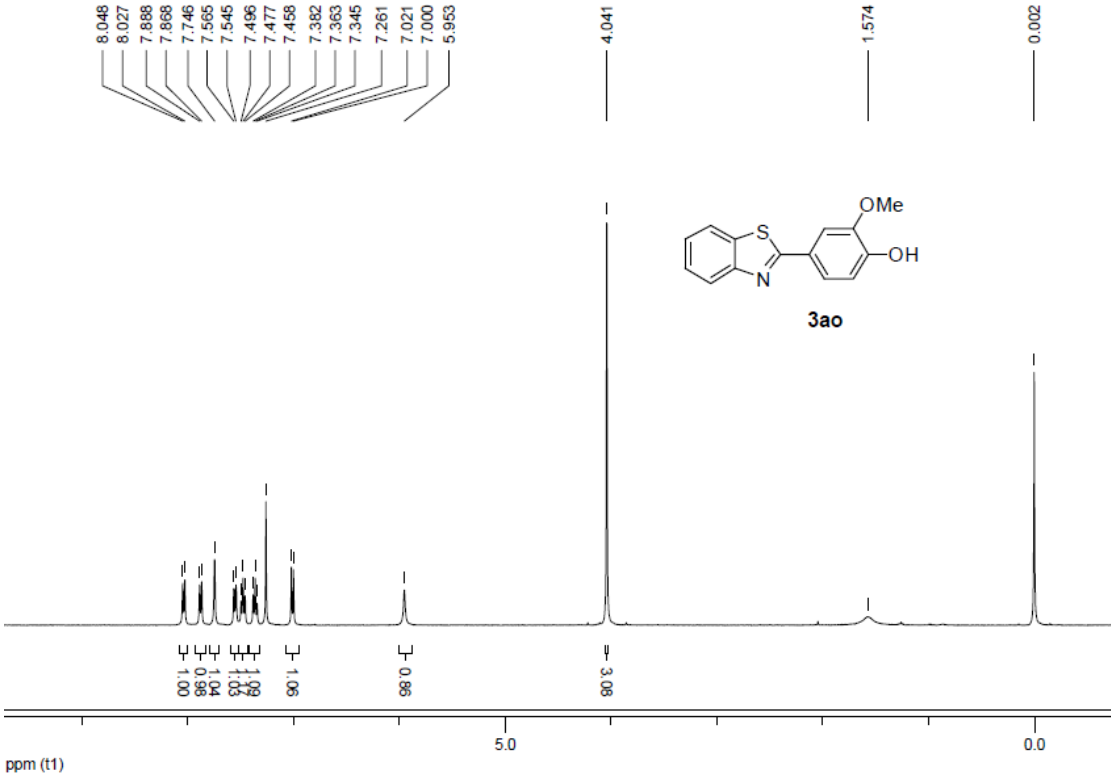
N
3an
150
100
50
ppm (t1)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7.345
7.261
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7.000
5.953
4.041
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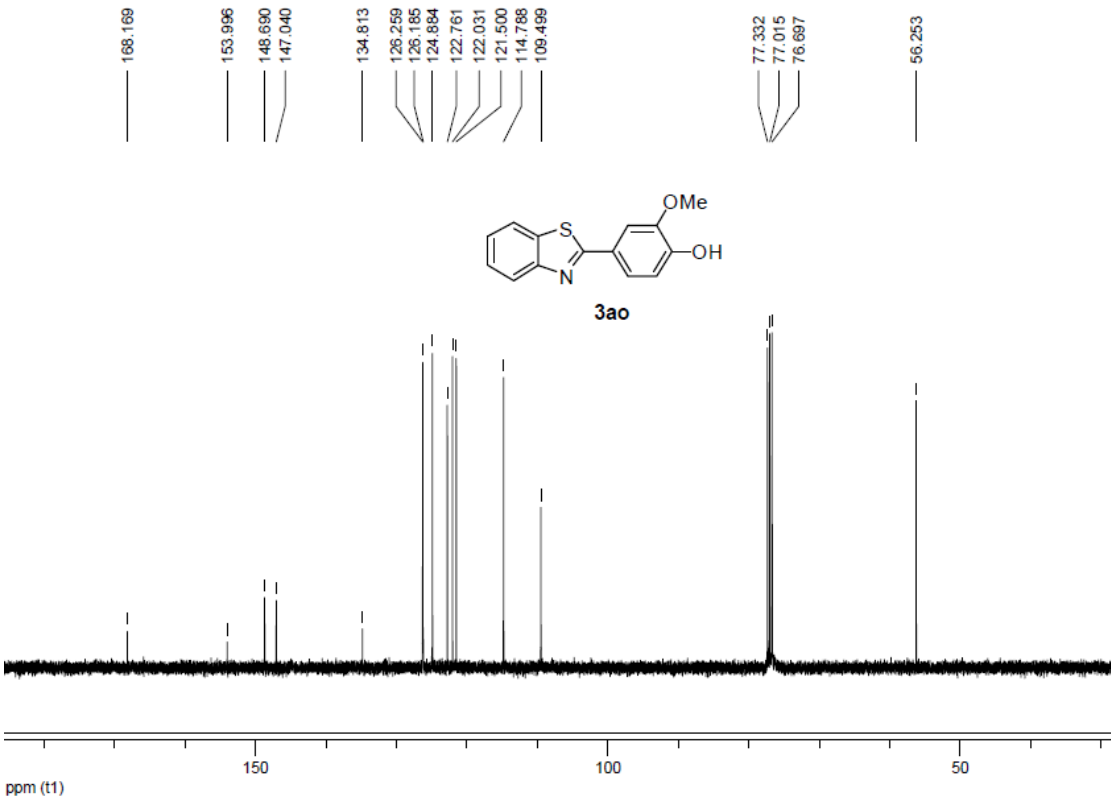
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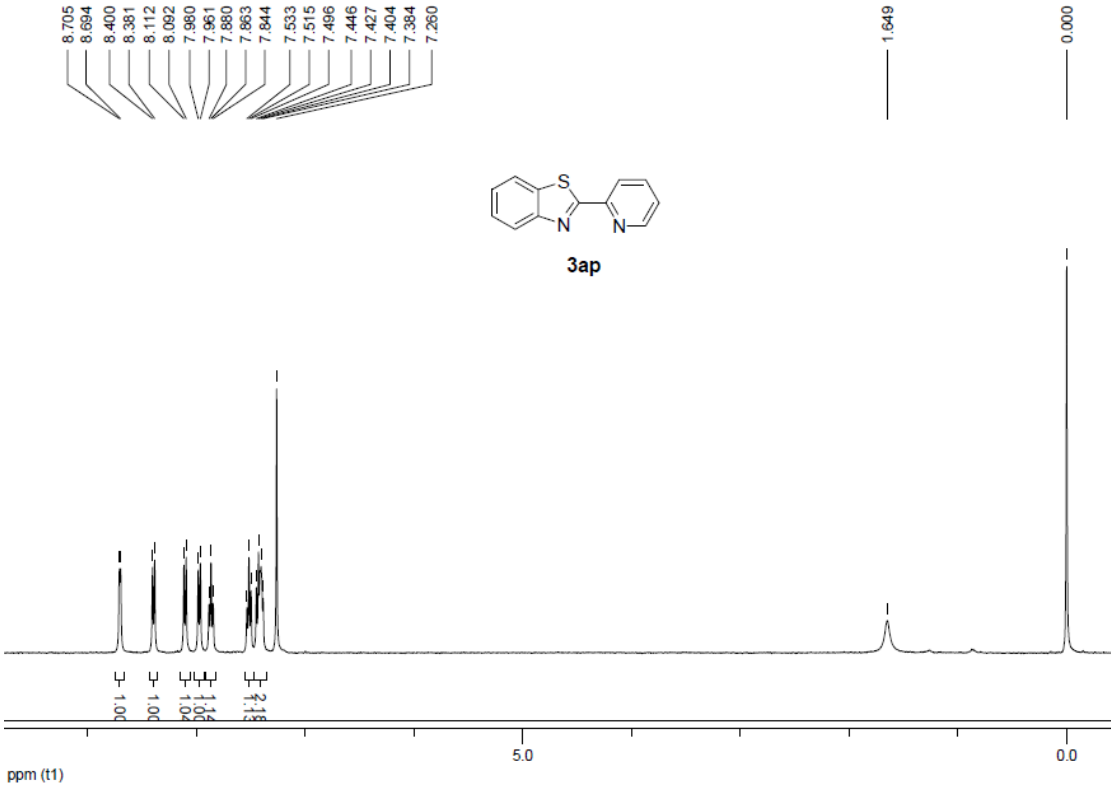
ppm (t1)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7.496
7.446
7.427
7.404
7.384
7.260
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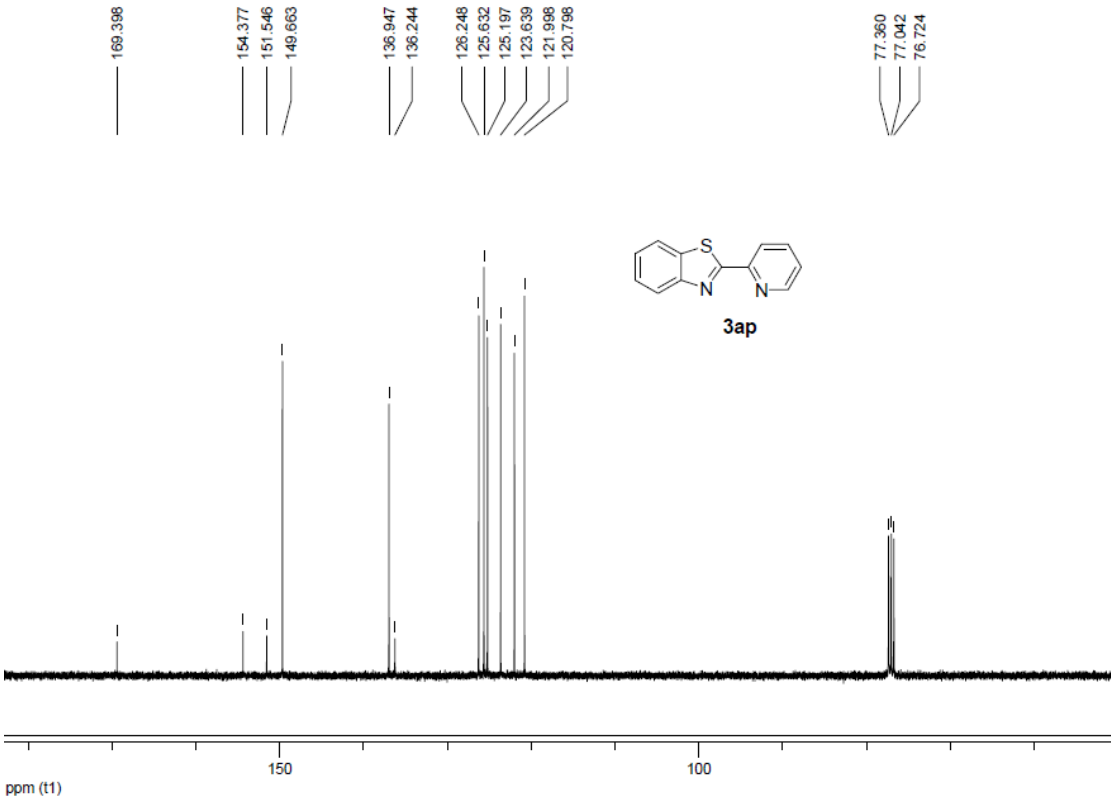
ppm (t1)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100
ppm (t1)

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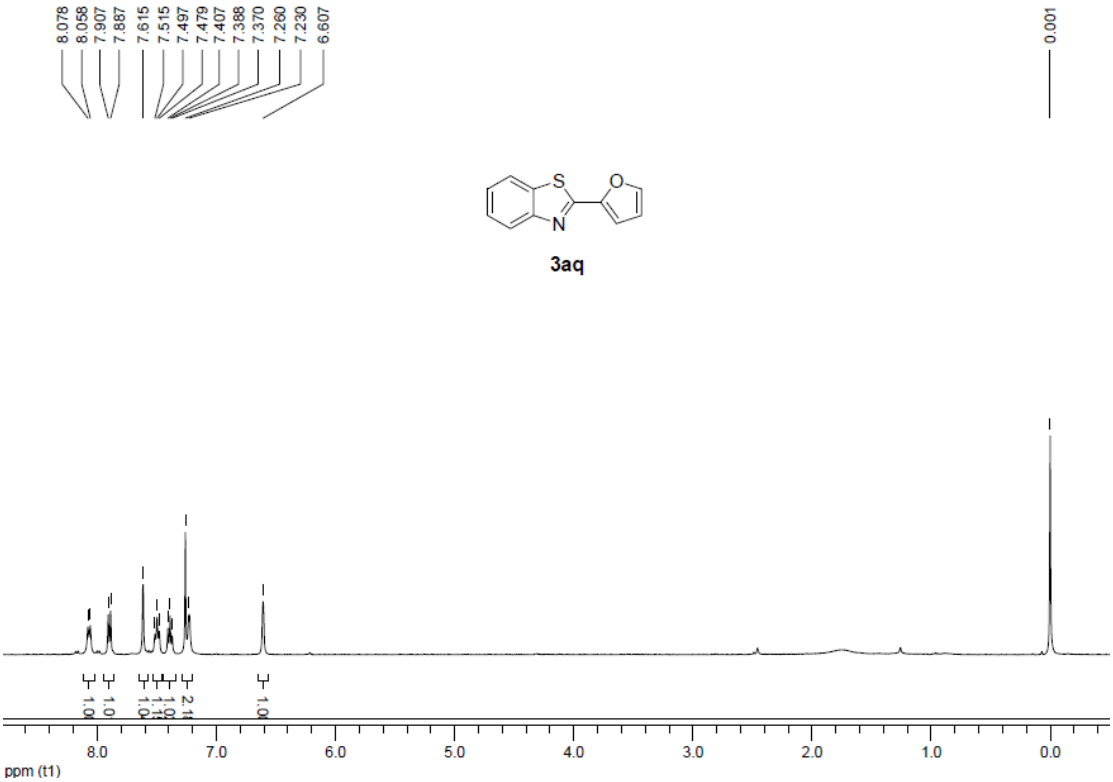

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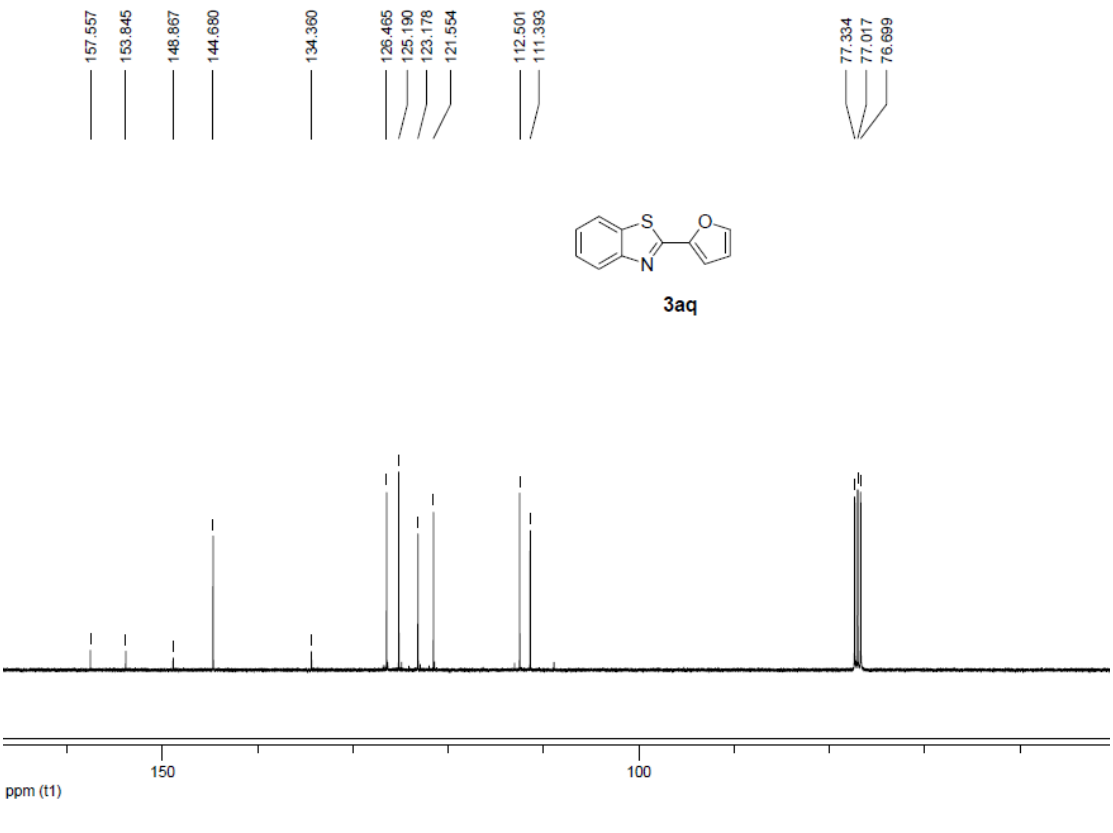

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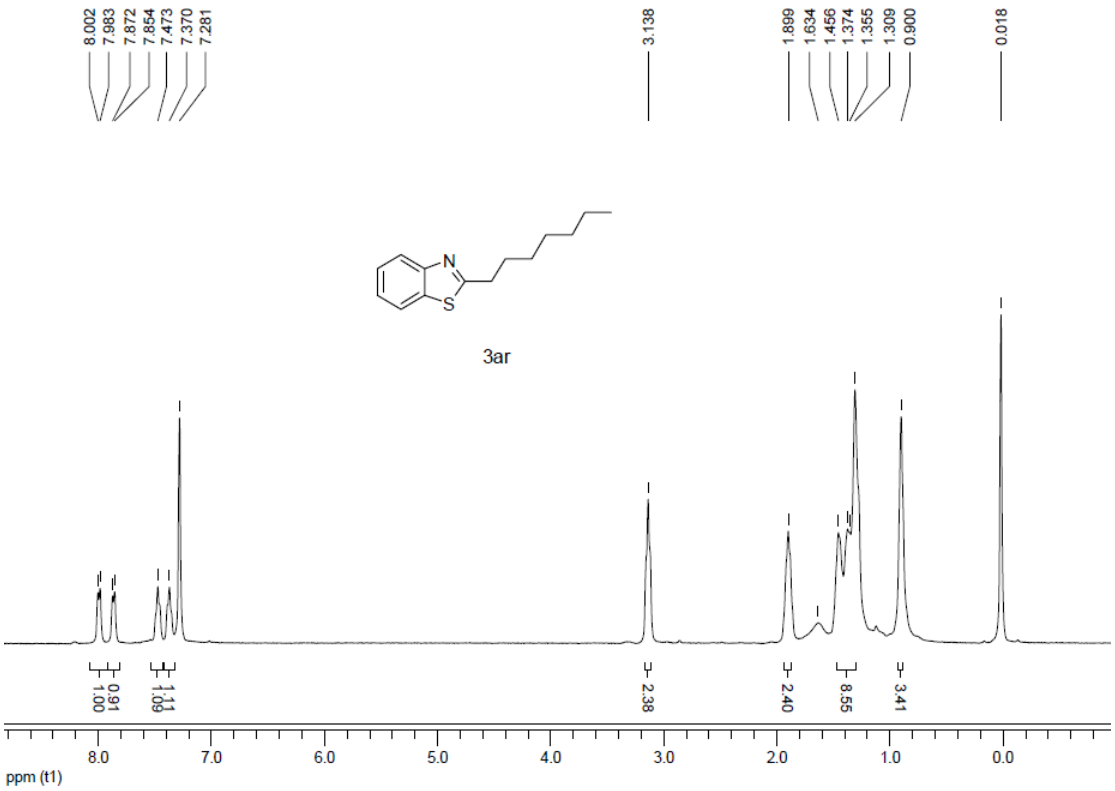
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S
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1.11
1.09
2.38
2.40
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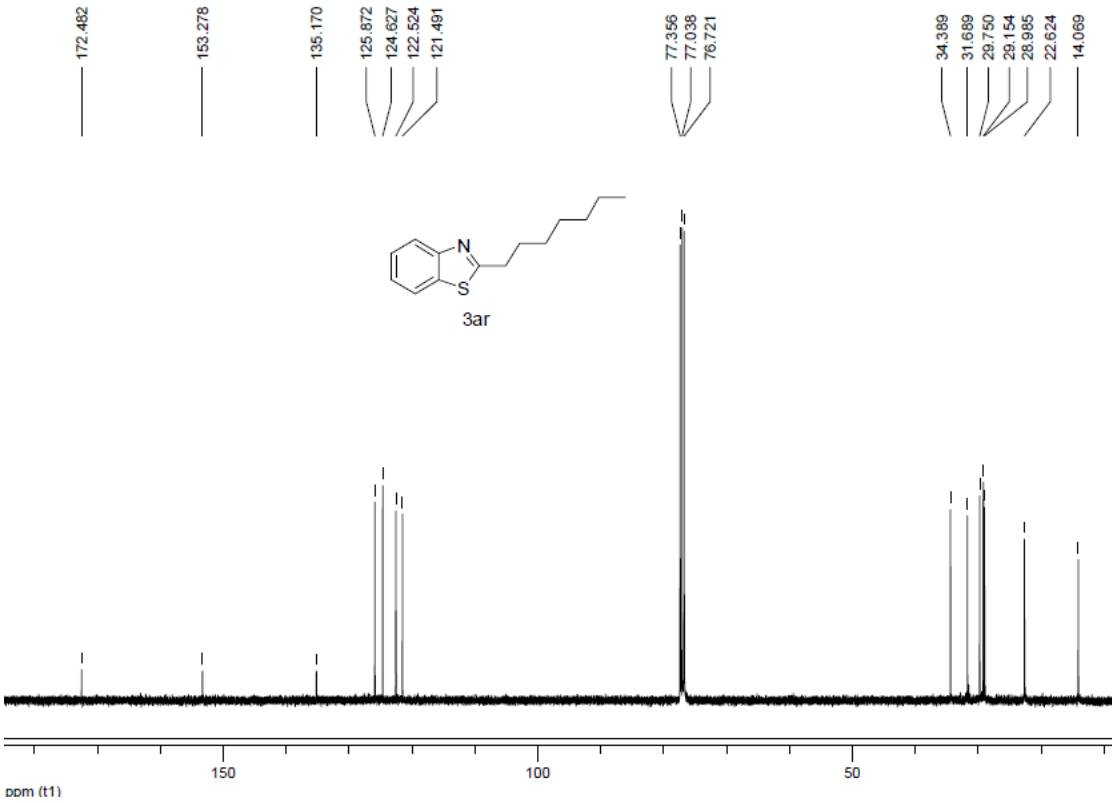
ppm (t1)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77.356
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76.721
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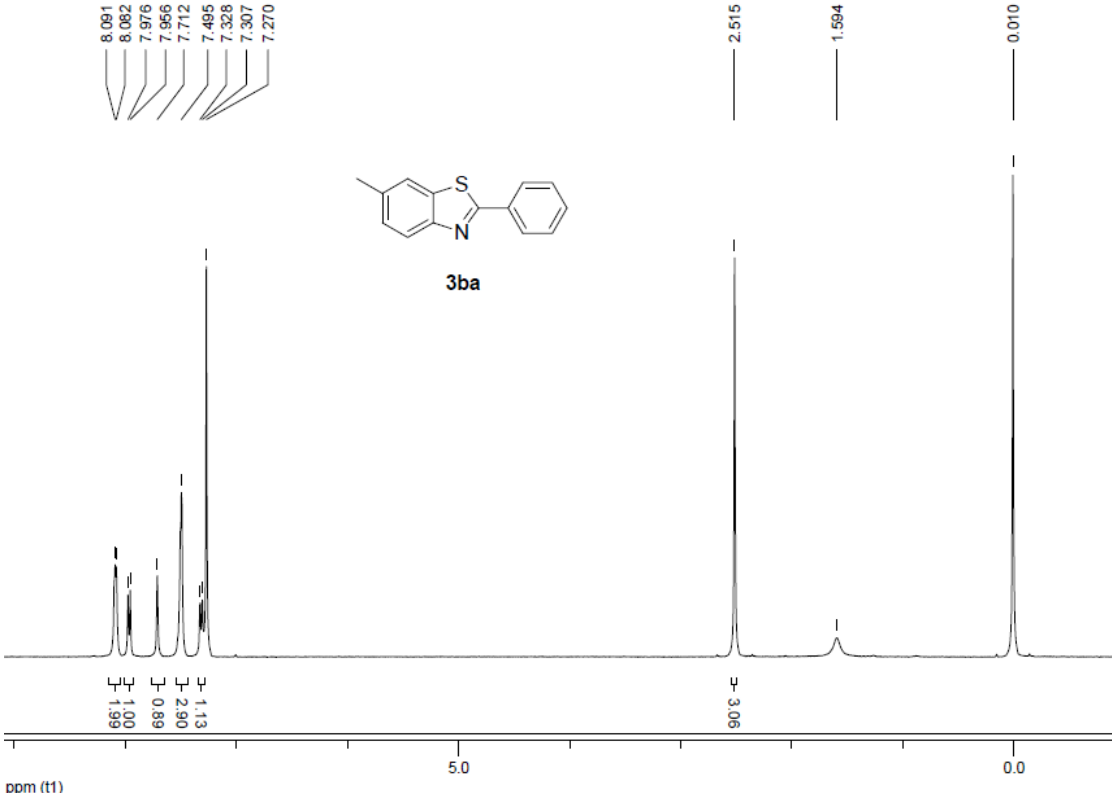
S
3ar
150
100
50
ppm (t1)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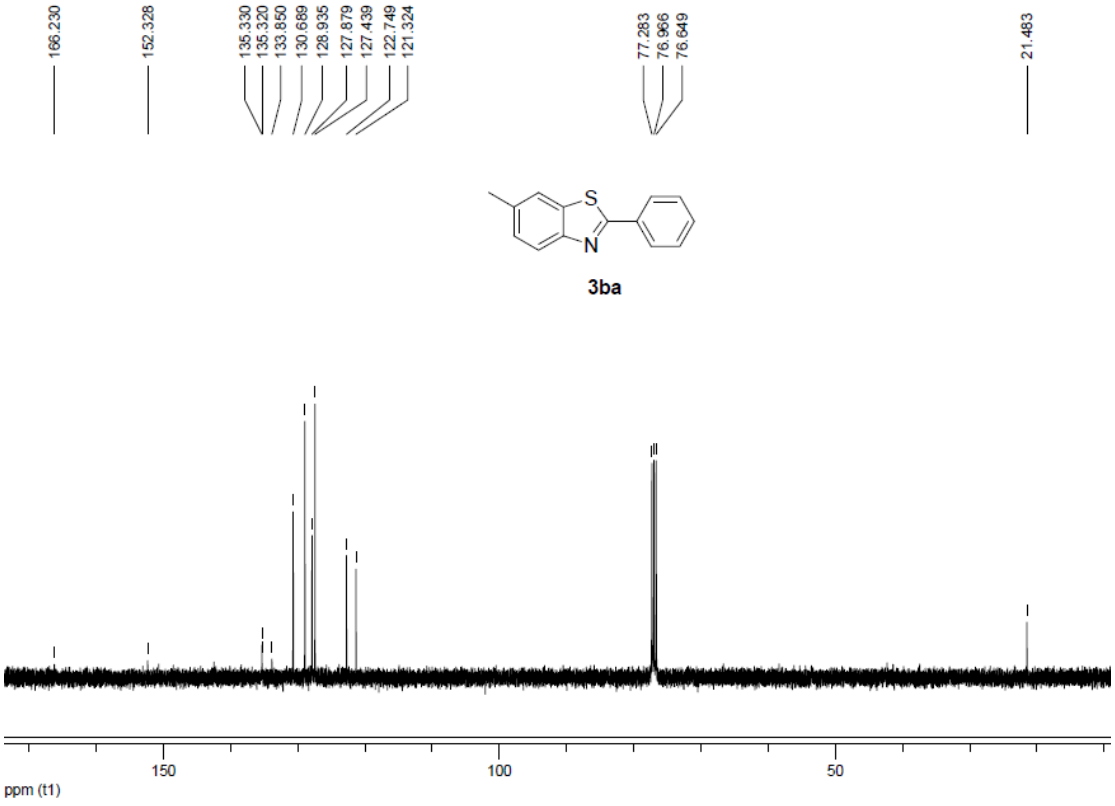
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N
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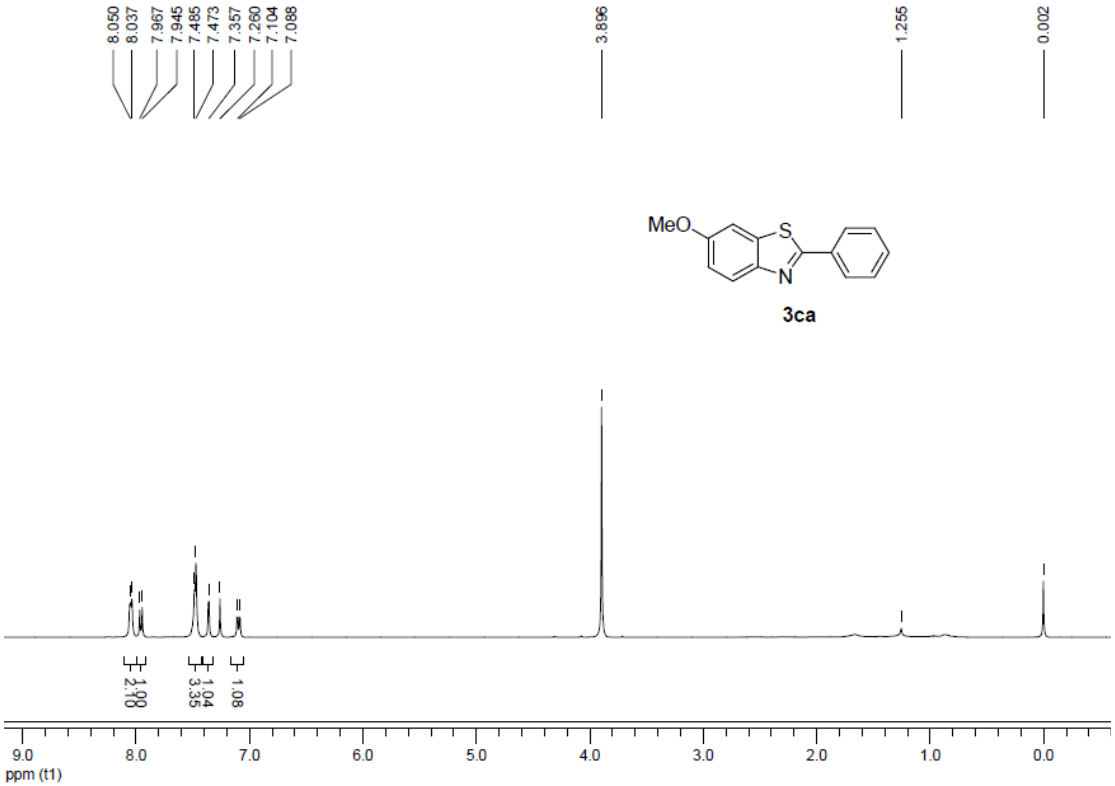
ppm (t1)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0.002
MeO
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N
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3.35
1.04
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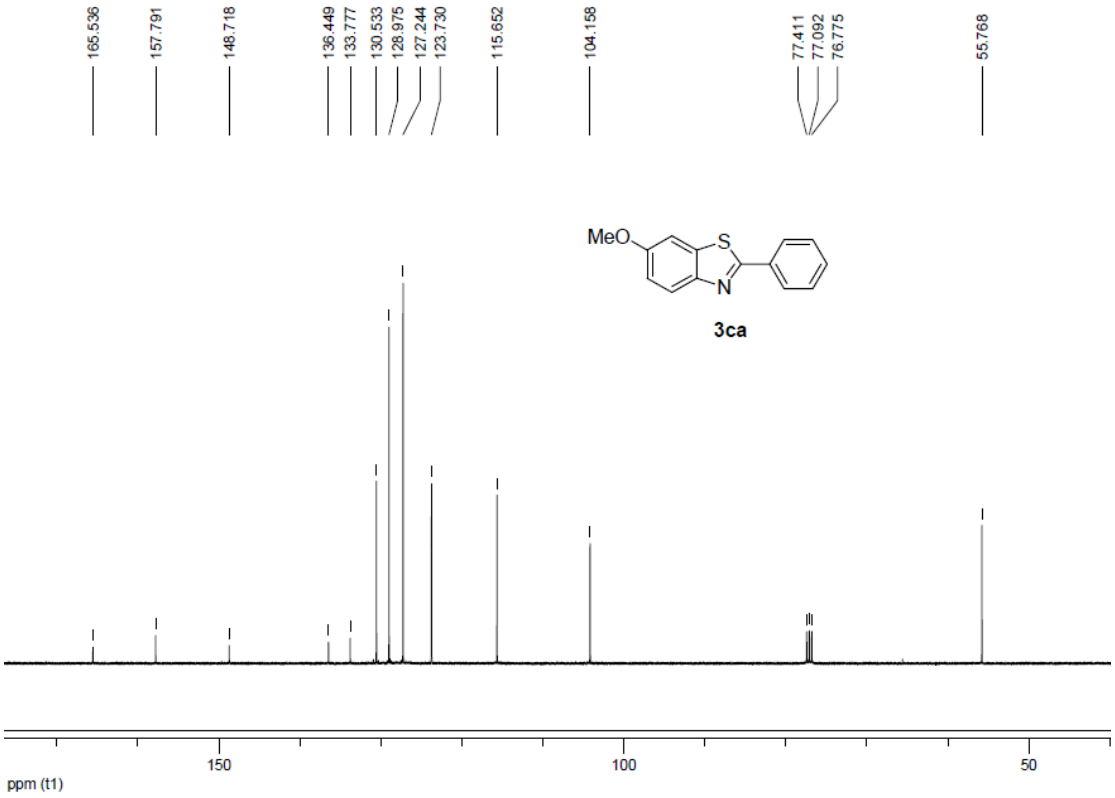
ppm (t1)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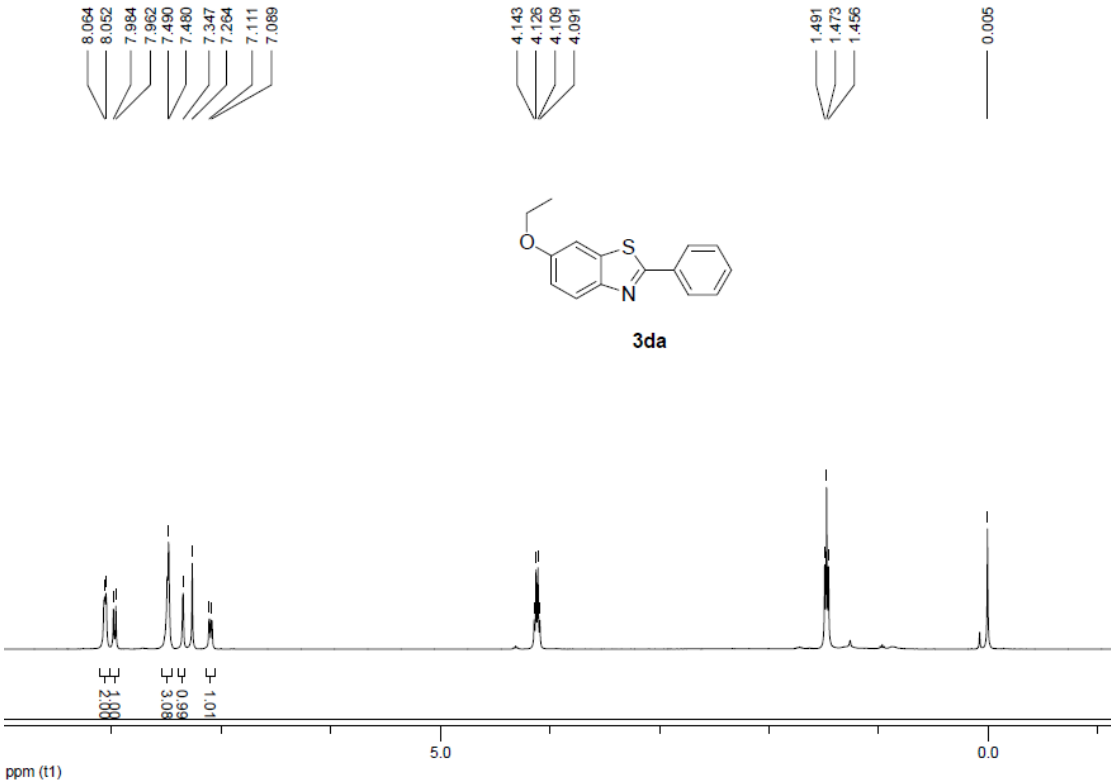
ppm (t1)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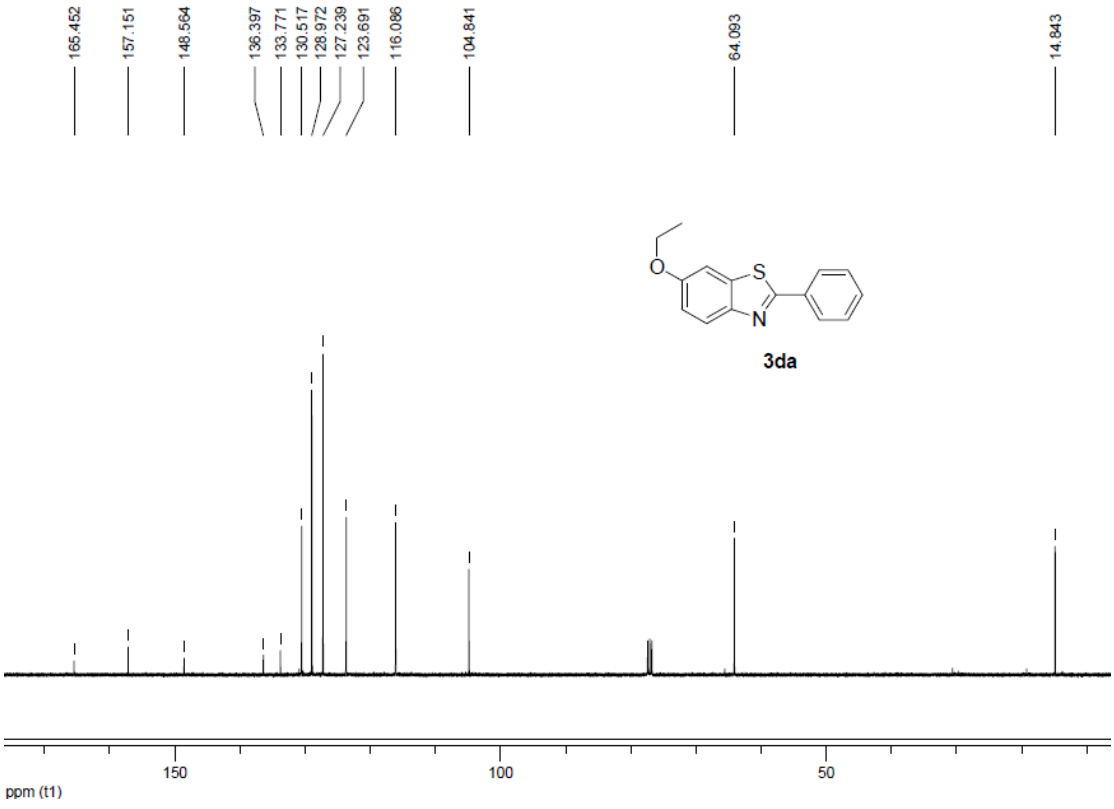
3da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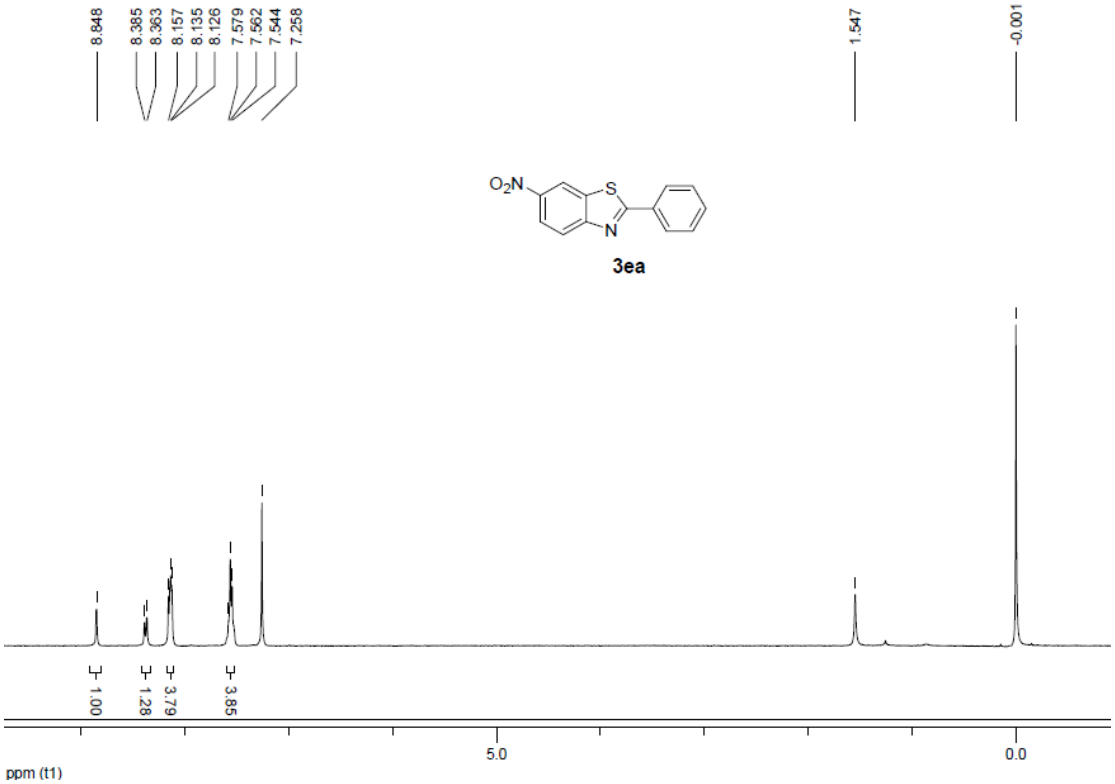
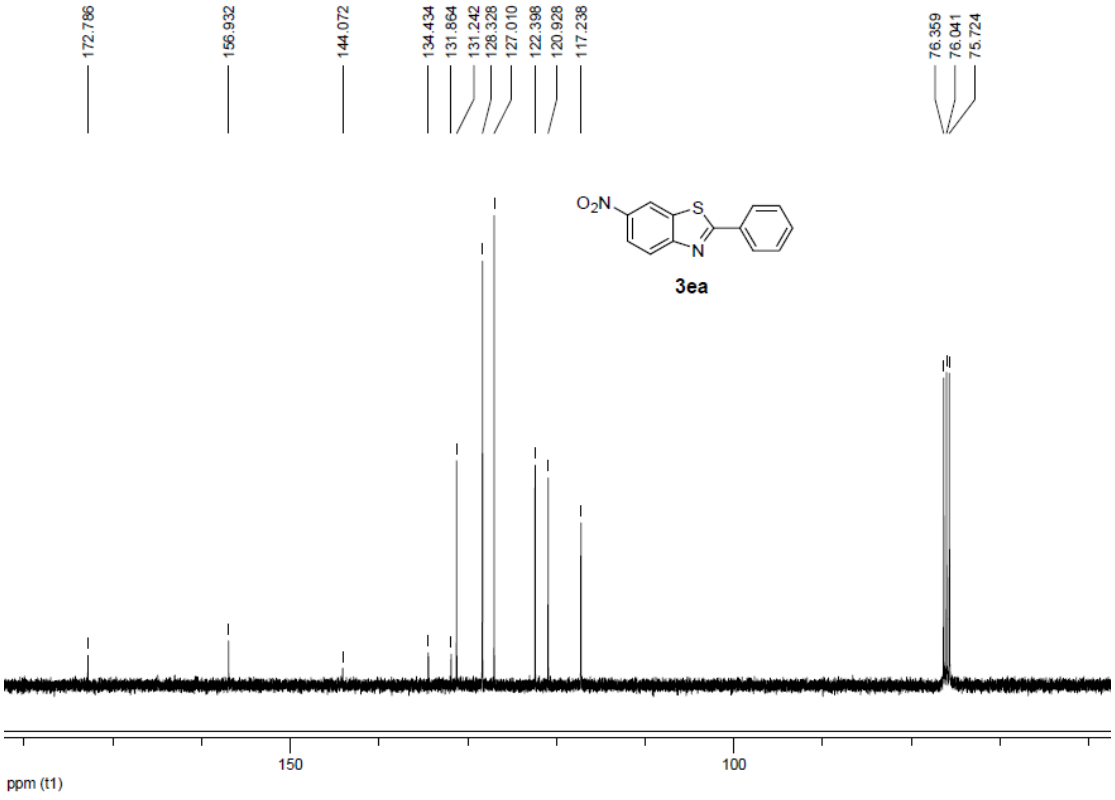
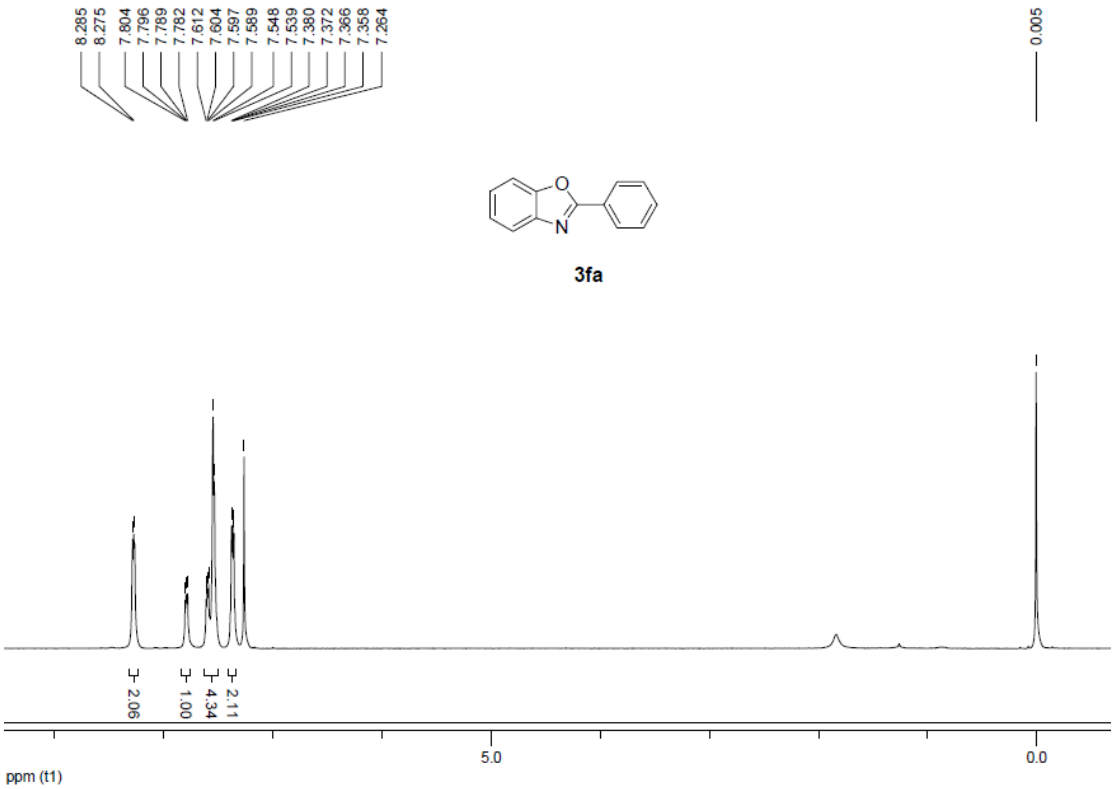
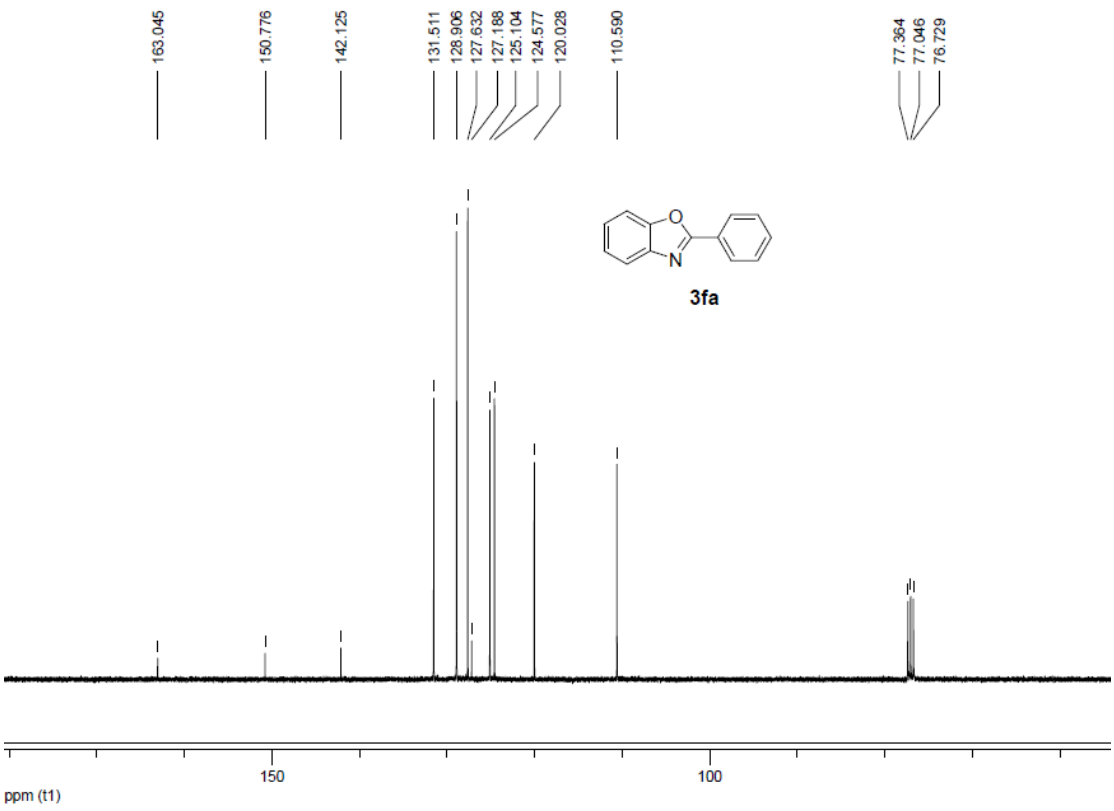
64.093
14.843
O
S
N
150
100
50
ppm (t1)

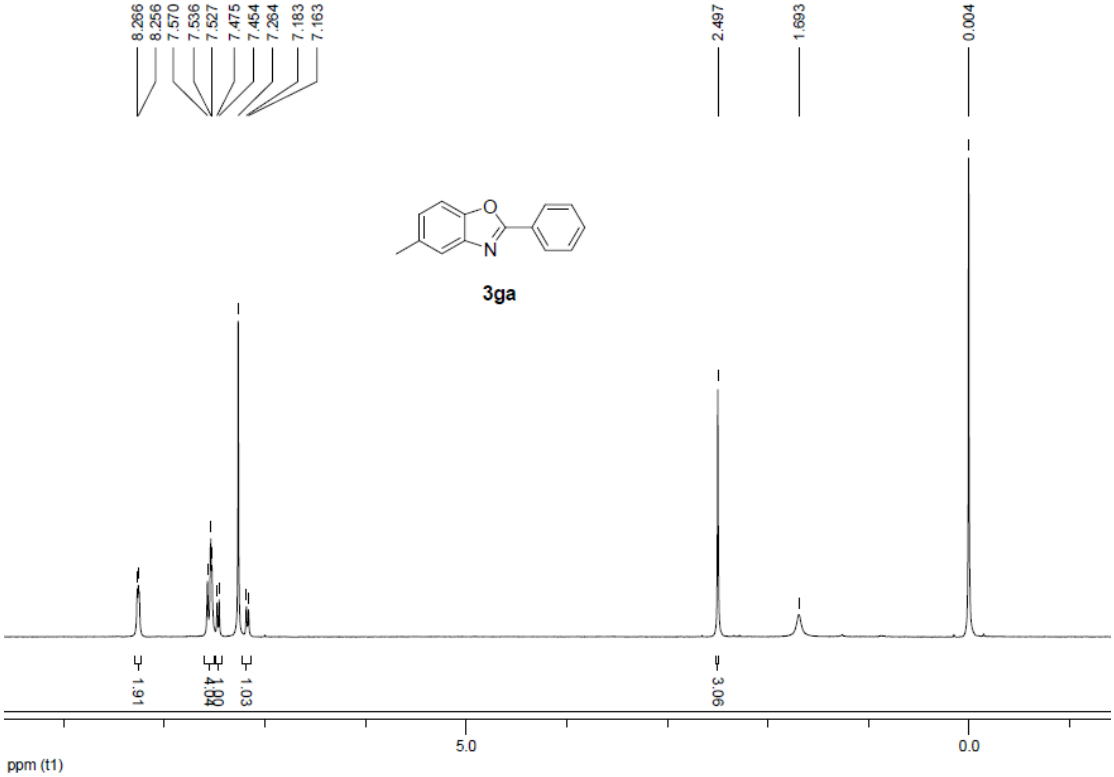
3da

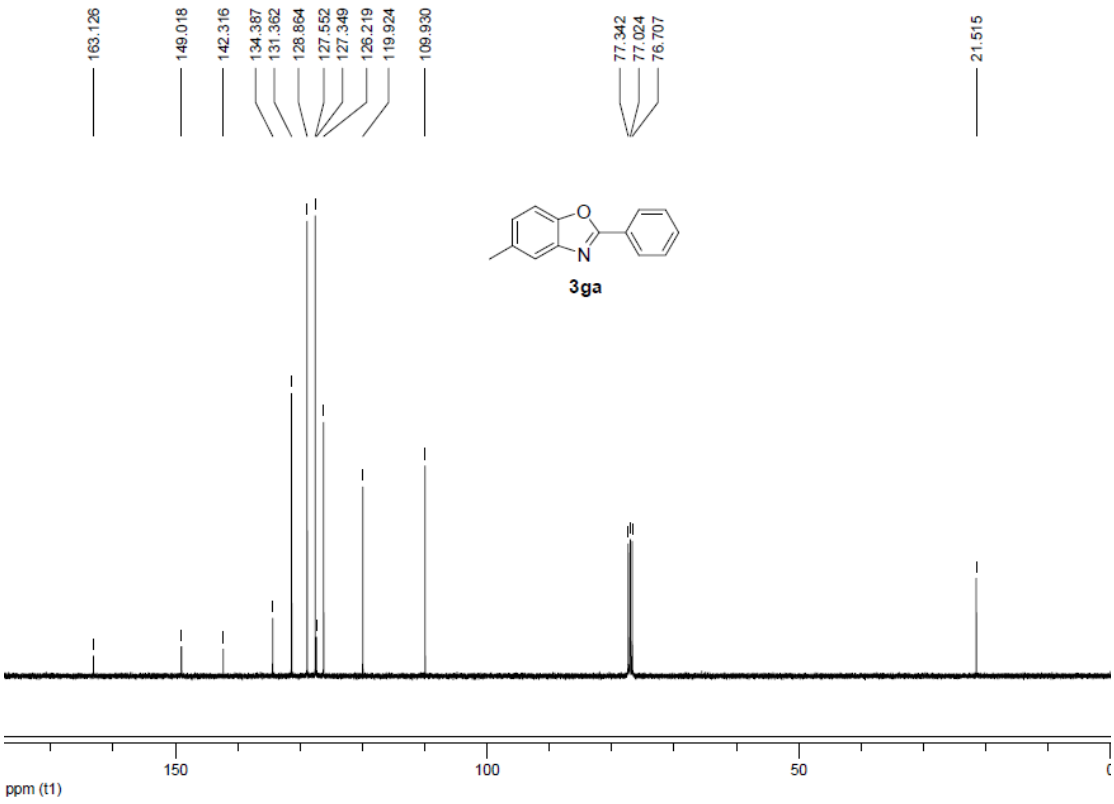

8.848
8.385
8.363
8.157
8.135
8.126
7.579
7.562
7.544
7.258
1.547
-0.001
O2N
S
N
3ea
1.00
1.28
3.79
3.85
5.0
0.0
ppm (t1)

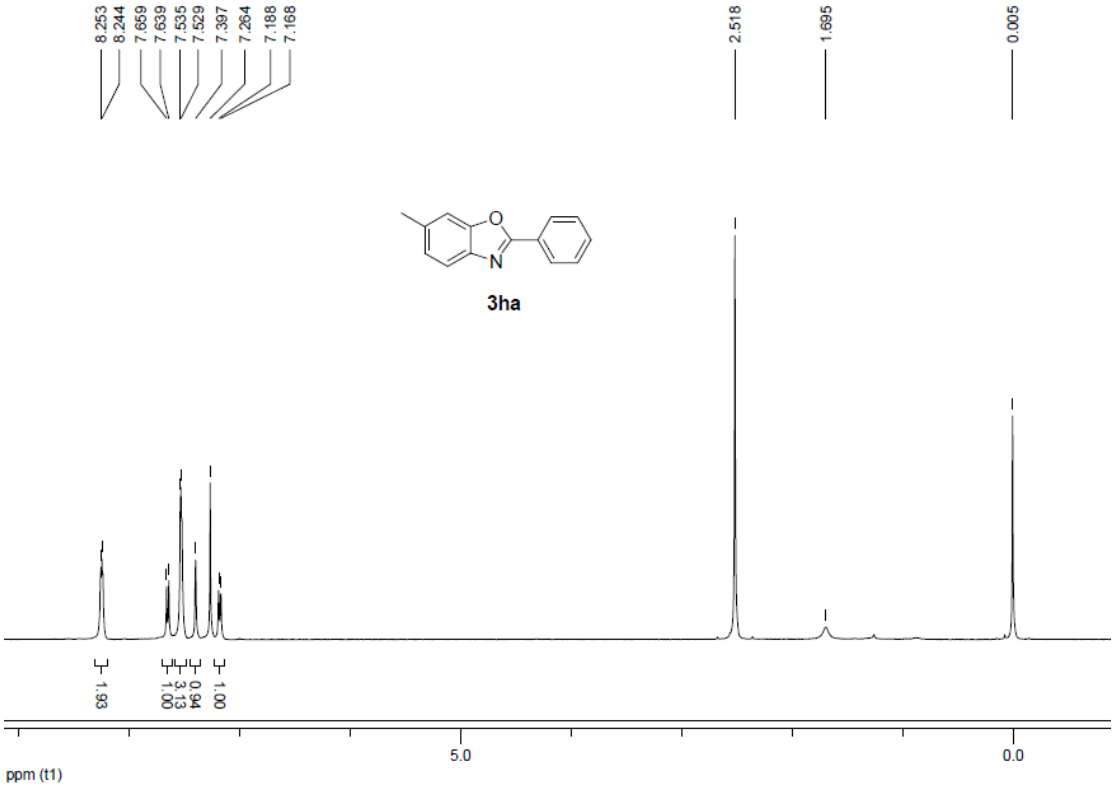

172.786
156.932
144.072
134.434
131.864
131.242
128.328
127.010
122.398
120.928
117.238
76.359
76.041
75.724
O2N
S
N
3ea
150
100
ppm (t1)

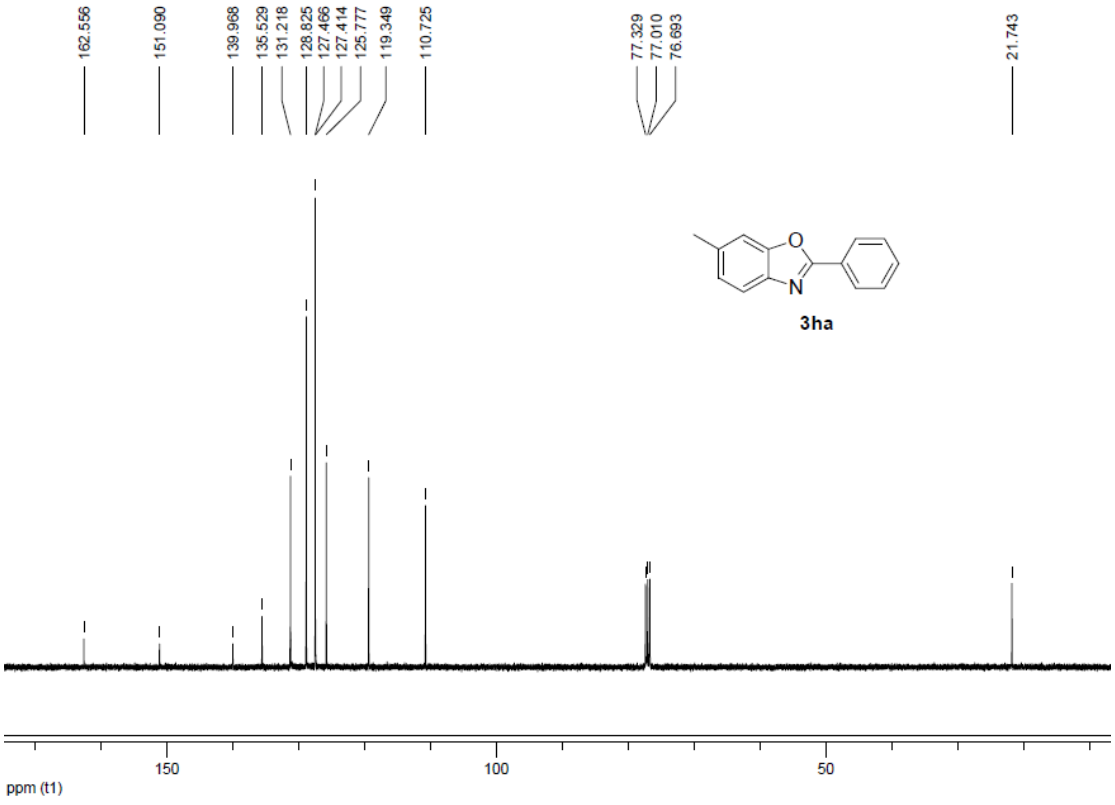

8.285
8.275
7.804
7.796
7.789
7.782
7.612
7.604
7.597
7.589
7.548
7.539
7.380
7.372
7.366
7.358
7.264
0.005
3fa
2.06
1.00
4.34
2.11
5.0
0.0
ppm (t1)

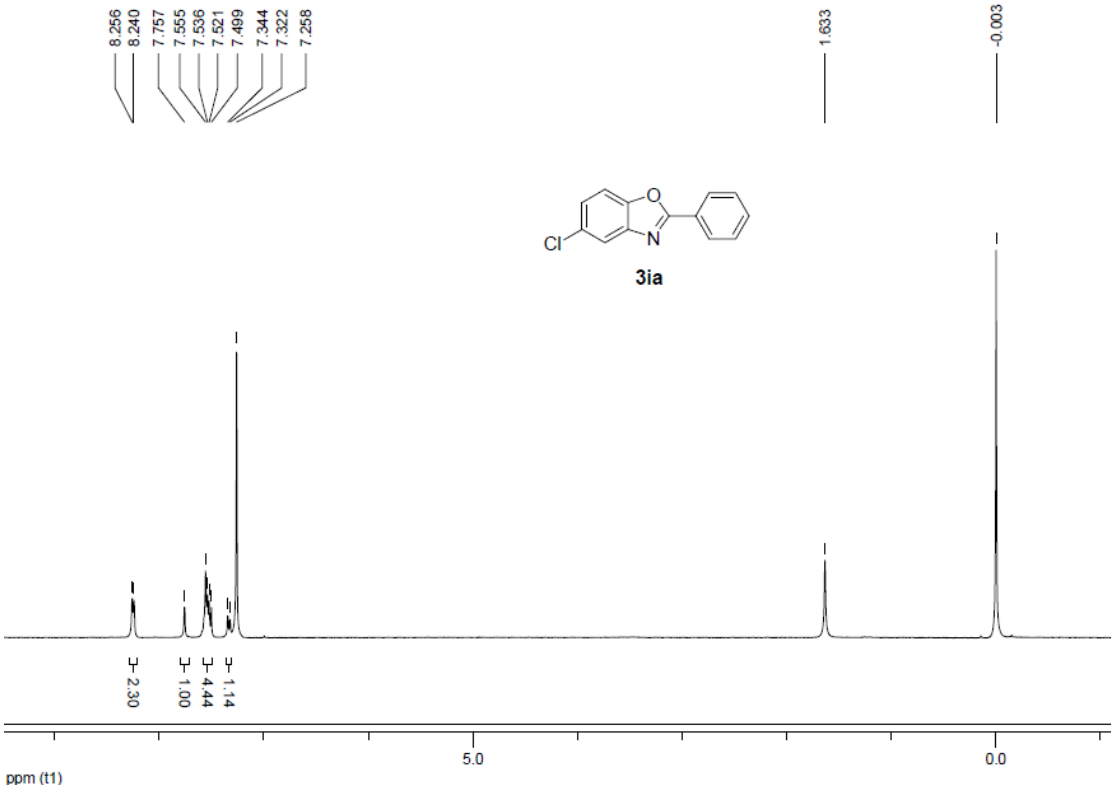

163.045
150.776
142.125
131.511
128.906
127.632
127.188
125.104
124.577
120.028
110.590
77.364
77.046
76.729
3fa
150
100
ppm (t1)

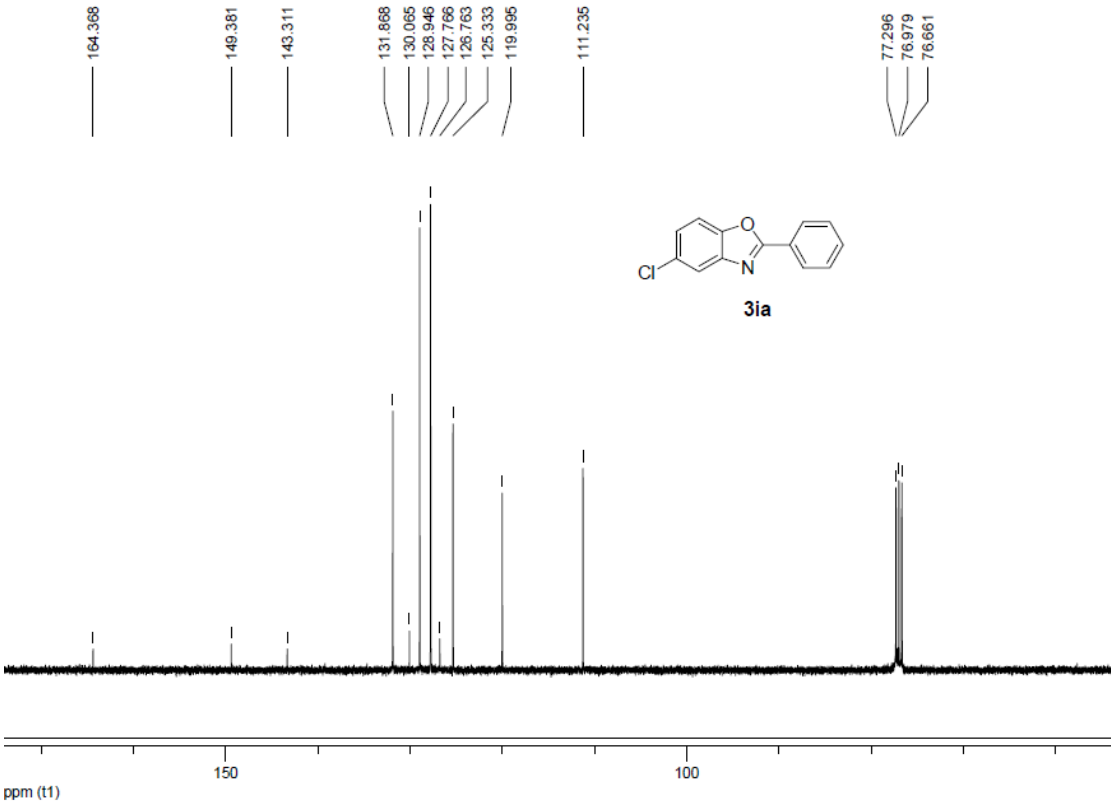

8.266
8.256
7.570
7.536
7.527
7.475
7.454
7.264
7.183
7.163
2.497
1.693
0.004
3ga
1.91
4.08
1.03
3.06
5.0
0.0
ppm (t1)

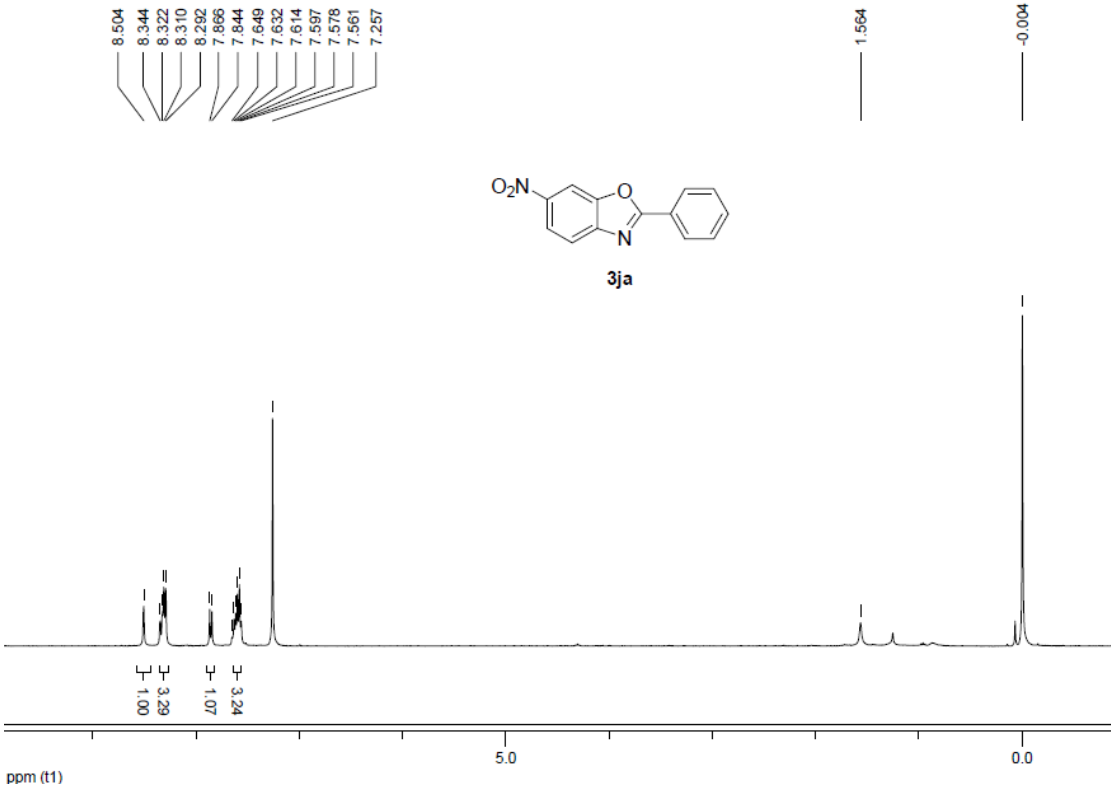

163.126
149.018
142.316
134.387
131.362
128.864
127.552
127.349
126.219
119.924
109.930
77.342
77.024
76.707
21.515
3ga
150
100
50
ppm (t1)

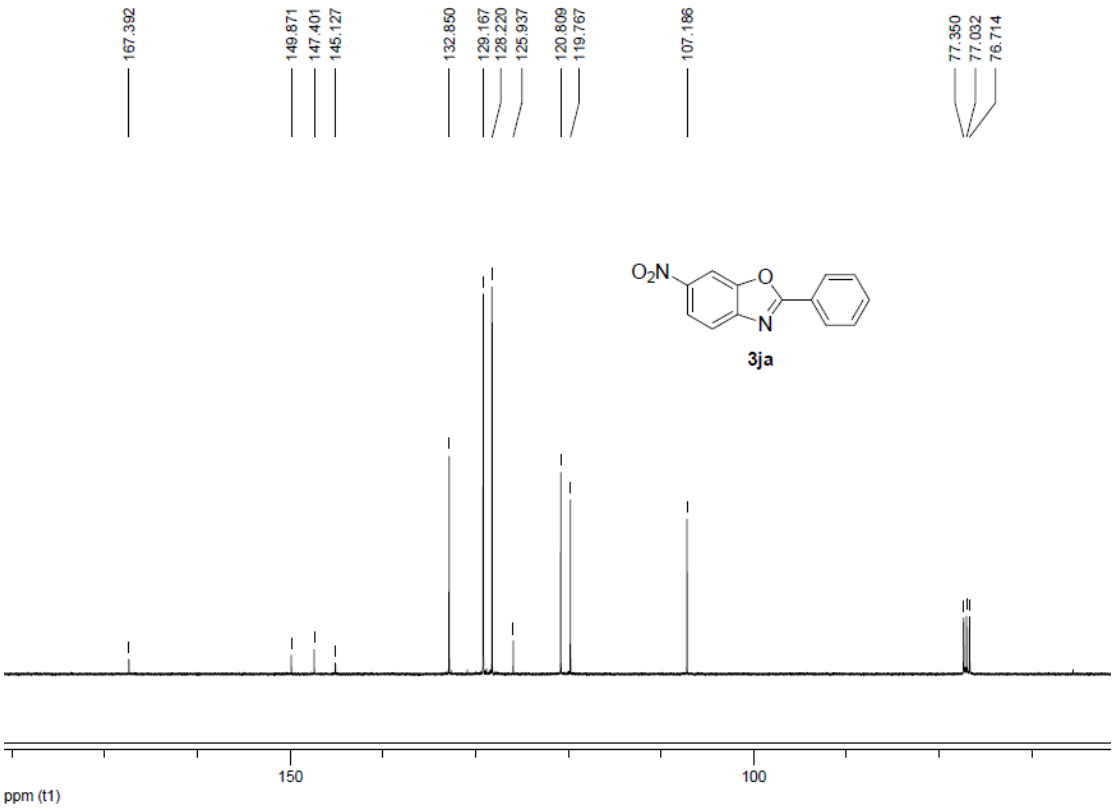

8.253
8.244
7.659
7.639
7.535
7.529
7.397
7.264
7.188
7.168
2.518
1.695
0.005
3ha
1.93
3.13
1.00
0.94
1.00
5.0
0.0
ppm (t1)


162.556
151.090
139.968
135.529
131.218
128.825
127.466
127.414
125.777
119.349
110.725
77.329
77.010
76.693
21.743
3ha
150
100
50
ppm (t1)


8.256
8.240
7.757
7.555
7.536
7.521
7.499
7.344
7.322
7.258
1.633
-0.003
Cl
O
N
3ia
2.30
1.00
4.44
1.14
5.0
0.0
ppm (t1)


164.368
149.381
143.311
131.868
130.065
128.946
127.766
126.763
125.333
119.995
111.235
77.296
76.979
76.661
Cl
O
N
3ia
150
100
ppm (t1)


8.504
8.344
8.322
8.310
8.292
7.866
7.844
7.649
7.632
7.614
7.597
7.578
7.561
7.257
1.564
-0.004
O2N
O
N
3ja
1.00
3.29
1.07
3.24
5.0
0.0
ppm (t1)


167.392
149.871
147.401
145.127
132.850
129.167
128.220
125.937
120.809
119.767
107.186
77.350
77.032
76.714
O2N
O
N
3ja
150
100
ppm (t1)