[3+2] Cycloaddition of nonstabilized azomethine ylides and 2–benzothioazolimines to access imidazolidine derivatives

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Supporting Information

Table of Contents

1. General methods

2. Some substrates of 2-benzothiazolimines and 2-benzoxazolimine 1

3. General procedure for synthesis of imidazolidine derivatives 3

4. Procedure for preparation of compound 4

5. Crystal data and structural refinement for 3h

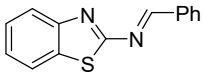
6. NMR spectra

1. General methods

NMR data were obtained for ^{1}H at 400 MHz MHz, and for ^{13}C at 100 MHz, and ^{19}F at 376 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. ESI HRMS was recorded on a Waters SYNAPT G2. Column chromatography was performed on silica gel (200-300 mesh) eluting with ethyl acetate/petroleum ether. TLC was performed on glass-backed silica plates. UV light, I_2, and solution of potassium permanganate were used to visualize products. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether and ethyl acetate were distilled. THF was freshly distilled from sodium/benzophenone. Unless otherwise noted, experiments involving moisture and/or air sensitive components were performed under a positive pressure of argon in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes. The 2-benzothiazolimines and 2-benzoxazolimines **1** [1]were prepared according to the literature procedures.

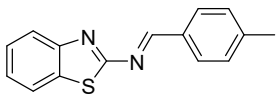
(1) (a) Liu, Si-Jia; Chen, Zhi-Han; Chen, Jia-Yi; Ni, Shao-Fei; Zhang, Yu-Chen; Shi, Feng. Rational Design of Axially Chiral Styrene-Based Organocatalysts and Their Application in Catalytic Asymmetric (2+4) Cyclizations. *Angew. Chem., Int. Ed.* **2022**, *61*, e202112226. (b) Jarrige, Lucie; Glavač, Danijel; Levitre, Guillaume; Retailleau, Pascal; Bernadat, Guillaume; Neuville, Luc; Masson, Géraldine. Chiral phosphoric acid-catalyzed enantioselective construction of structurally diverse benzothiazolopyrimidines. *Chem. Sci.* **2019**, *10*, 3765-3769. (c) Ni, Qijian; Wang, Xuyang; Xu, Fangfang; Chen, Xiaoyun; Song, Xiaoxiao. Organocatalytic asymmetric [4+2] cyclization of 2-benzothiazolimines with azlactones: access to chiral benzothiazolopyrimidine derivatives. *Chem. Commun.* **2020**, *56*, 3155-3158. (d) Ke, Chaoqi; Liu, Zhenzhong; Ruan, Sai; Feng, Xiaoming; Liu, Xiaohua. Organocatalytic asymmetric synthesis of benzothiazolopyrimidines via a [4 + 2] cycloaddition of azlactones with 2-benzothiazolimines. *Org. Chem. Front.* **2021**, *8*, 5705-5709. (e) Frías, María; Carrasco, Ana Cristina; Fraile, Alberto; Alemán, José. A General Asymmetric Formal Synthesis of Aza-Baylis–Hillman Type Products under Bifunctional Catalysis. *Chem. Eur. J.* **2018**, *24*, 3117-3121.

2. Some substrates of 2-benzothiazolimines and 2-benzoxazolimine 1



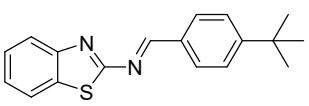
1a

***(E)-N*-(benzo[*d*]thiazol-2-yl)-1-phenylmethanimine (1a)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.03 (d, *J* = 7.6 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.53 – 7.46 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 1H) ppm.



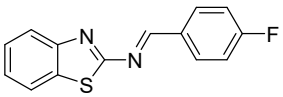
1b

1b, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.31 (m, 3H), 2.45 (s, 3H) ppm.



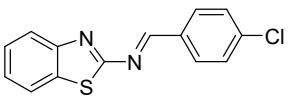
1c

1c, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.98 – 7.95 (m, 3H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 1.37 (s, 9H) ppm.



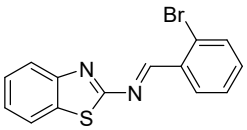
1d

1d, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.05 (dd, *J* = 8.0, 6.0 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 8.8 Hz, 2H) ppm.



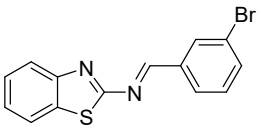
1e

1e, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 3H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.47 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 1H) ppm.



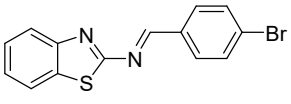
1f

1f, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.37 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.36 (m, 4H) ppm.



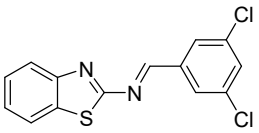
1g

1g, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.22 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.40 – 7.37 (m, 2H) ppm.



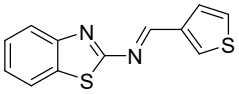
1h

1h, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H) ppm.



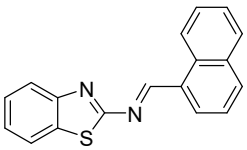
1j

1j, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.88 (s, 2H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H) ppm.



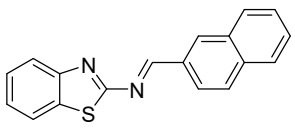
1l

1l, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.06 – 8.05 (m, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 4.8 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.43 – 7.41 (m, 1H), 7.36 (t, *J* = 7.6 Hz, 1H) ppm.



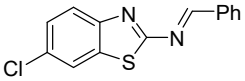
1m

1m, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 9.21 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 6.8 Hz, 1H), 8.04 (dd, *J* = 14.4, 8.4 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H) ppm.



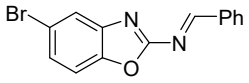
1n

1n, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.37 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.01 – 7.84 (m, 5H), 7.63 – 7.55 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H) ppm.



1p

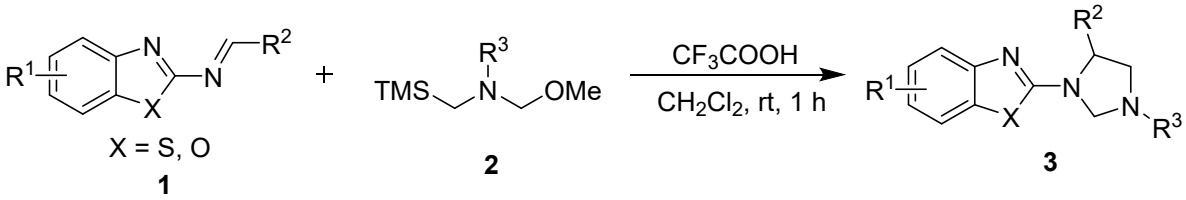
1p, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.80 (s, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 1H) ppm.



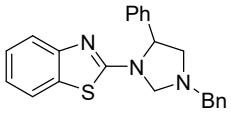
1q

1q, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.85 (s, 1H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.43 (dd, *J* = 19.6, 8.4 Hz, 2H) ppm.

3. General procedure for synthesis of imidazolidine derivatives 3

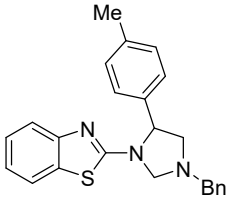


To a solution of 2-benzothiazolimines or 2-benzoxazolimines **1** (0.1 mmol), *N*-alkyl-*N*-(methoxymethyl)-*N*-trimethylsilylmethylamine **2** (0.12 mmol) in CH_2Cl_2 (1 mL) was added TFA (0.01 mmol). The solution was stirred at rt for 1 h. After completion, saturated sodium bicarbonate solution (1 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 1 mL). The combined organic layers were dried and concentrated under reduced pressure followed by silica gel column chromatography purification (petroleum ether/ethyl acetate = 6:1 to 5:1) to give the products **3**.



3a

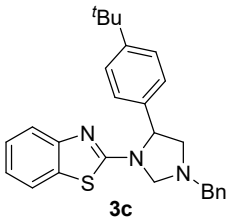
3a, white solid (36.4 mg, 98% yield); m.p. 92-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.30 (m, 7H), 7.29 – 7.24 (m, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 4.83 (t, *J* = 6.4 Hz, 1H), 4.78 (d, *J* = 6.8 Hz, 1H), 4.65 (d, *J* = 6.8 Hz, 1H), 3.80 – 3.73 (m, 2H), 3.44 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.96 (dd, *J* = 10.0, 6.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 152.3, 139.7, 137.6, 131.0, 128.8, 128.7, 128.5, 128.1, 127.5, 126.9, 125.8, 121.2, 120.7, 119.0, 72.6, 63.7, 62.4, 58.0. ESI-HRMS: $C_{23}H_{21}N_3S+H^+$ 372.1529, found 372.1519.



3b

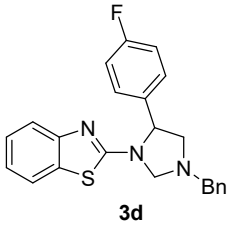
3b, white solid (36.6 mg, 95% yield); m.p. 131-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.23 (m, 8H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 4.78 (t, *J* = 6.8 Hz, 2H), 4.63 (d, *J* = 6.8 Hz, 1H), 3.79 – 3.72 (m, 2H), 3.42 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.93 (dd, *J* = 10.0, 6.4 Hz, 1H), 2.34 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 152.3, 137.9, 137.7, 136.6,

131.0, 129.5, 128.7, 128.5, 127.5, 126.9, 125.8, 121.2, 120.7, 119.0, 72.6, 63.5, 62.5, 58.0, 21.2 ppm. ESI-HRMS: $C_{24}H_{23}N_3S+H^+$ 386.1685, found 386.1675.



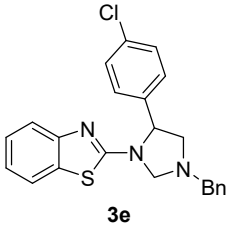
3c

3c, white solid (41.0 mg, 96% yield); m.p. 100-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.31 (m, 8H), 7.28 (d, *J* = 6.9 Hz, 1H), 7.23 (s, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 4.82 – 4.77 (m, 2H), 4.63 (d, *J* = 6.8 Hz, 1H), 3.79 (d, *J* = 13.2 Hz, 1H), 3.73 (d, *J* = 12.8 Hz, 1H), 3.43 (dd, *J* = 10.0, 7.2 Hz, 1H), 2.96 (dd, *J* = 10.0, 6.4 Hz, 1H), 1.31 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 152.3, 151.0, 137.7, 136.5, 131.0, 128.7, 128.5, 127.5, 126.6, 125.8, 125.7, 121.2, 120.7, 119.0, 72.6, 63.4, 62.4, 58.0, 34.6, 31.3 ppm. ESI-HRMS: $C_{27}H_{29}N_3S+H^+$ 428.2155, found 428.2144.



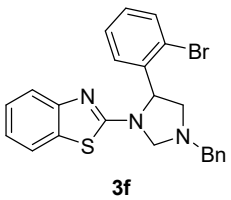
3d

3d, white solid (37.7 mg, 97% yield); m.p. 94-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.39 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.34 – 7.25 (m, 6H), 7.06 – 7.01 (m, 3H), 4.82 (t, *J* = 6.0 Hz, 1H), 4.67 (q, *J* = 6.8 Hz, 2H), 3.80 – 3.73 (m, 2H), 3.39 (dd, *J* = 10.0, 7.2 Hz, 1H), 2.94 (dd, *J* = 10.0, 6.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 162.5 (d, *J* = 245.1 Hz), 152.3, 137.5, 135.6 (d, *J* = 3.1 Hz), 130.9, 128.7, 128.6, 127.6, 125.9, 121.4, 120.7, 119.2, 115.7 (d, *J* = 21.5 Hz), 72.5, 63.1, 62.2, 57.9 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.1 ppm. ESI-HRMS: $C_{23}H_{20}FN_3S+H^+$ 390.1435, found 390.1424.



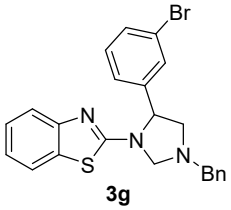
3e

3e, white solid (38.9 mg, 96% yield); m.p. 93-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.25 (m, 10H), 7.03 (t, *J* = 7.6 Hz, 1H), 4.82 (t, *J* = 6.0 Hz, 1H), 4.68 – 4.64 (m, 2H), 3.80 – 3.73 (m, 2H), 3.39 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.93 (dd, *J* = 9.6, 5.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 152.3, 138.5, 137.5, 133.8, 130.9, 129.0, 128.65, 128.57, 128.3, 127.6, 126.0, 121.4, 120.7, 119.2, 72.5, 63.1, 62.0, 57.9 ppm. ESI-HRMS: $C_{23}H_{20}ClN_3S+H^+$ 406.1139, found 406.1129.



3f

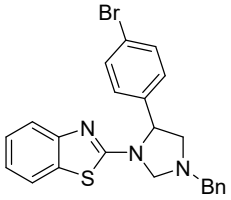
3f, white solid (42.7 mg, 95% yield); m.p. 106-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 6.8 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.41 (m, 1H), 7.32 – 7.25 (m, 7H), 7.18 – 7.14 (m, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 5.25 (t, *J* = 6.4 Hz, 1H), 4.71 (q, *J* = 6.4 Hz, 2H), 3.81 – 3.73 (m, 2H), 3.55 (dd, *J* = 10.0, 7.2 Hz, 1H), 2.97 (dd, *J* = 10.4, 5.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 152.5, 138.7, 137.5, 133.0, 131.0, 129.4, 128.7, 128.5, 128.0, 127.7, 127.6, 125.9, 122.8, 121.4, 120.8, 119.2, 72.5, 63.4, 60.4, 57.9 ppm. ESI-HRMS: $C_{23}H_{20}BrN_3S+H^+$ 450.0634 (^{79}Br) and 452.0614 (^{81}Br), found 450.0625, 452.0602.



3g

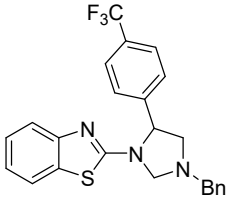
3g, white solid (43.1 mg, 96% yield); m.p. 119-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.25 (m, 7H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 4.81 (t, *J* = 6.0 Hz, 1H), 4.66 (q, *J* = 6.4 Hz, 2H), 3.80 – 3.73 (m, 2H), 3.40 (dd, *J* = 10.0, 7.2 Hz, 1H), 2.95 (dd, *J* =

10.0, 5.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 152.3, 142.5, 137.5, 131.2, 131.0, 130.3, 129.9, 128.7, 128.6, 127.6, 126.0, 125.5, 122.9, 121.5, 120.8, 119.3, 72.5, 63.2, 61.9, 57.8 ppm. ESI-HRMS: $C_{23}H_{20}BrN_3S+H^+$ 450.0634 (^{79}Br) and 452.0614 (^{81}Br), found 450.0624, 452.0602.



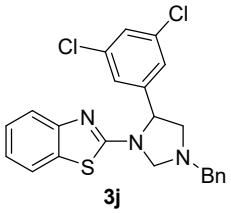
3h

3h, white solid (44.0 mg, 98% yield); m.p. 114-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.45 (m, 3H), 7.32 – 7.23 (m, 8H), 7.02 (t, *J* = 7.6 Hz, 1H), 4.79 (t, *J* = 6.0 Hz, 1H), 4.64 (s, 2H), 3.77 – 3.70 (m, 2H), 3.38 – 3.33 (m, 1H), 2.91 (dd, *J* = 9.6, 5.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 152.4, 139.2, 137.5, 131.9, 131.0, 128.7, 128.63, 128.61, 127.6, 126.0, 121.9, 121.5, 120.8, 119.3, 72.5, 63.2, 61.9, 57.9 ppm. ESI-HRMS: $C_{23}H_{20}BrN_3S+H^+$ 450.0634 (^{79}Br) and 452.0614 (^{81}Br), found 450.0625, 452.0603.



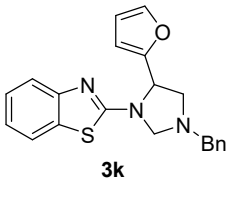
3i

3i, white solid (41.7 mg, 95% yield); m.p. 98-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.49 (m, 6H), 7.33 – 7.24 (m, 6H), 7.04 (t, *J* = 7.6 Hz, 1H), 4.93 (t, *J* = 6.0 Hz, 1H), 4.65 (dd, *J* = 18.8, 6.4 Hz, 2H), 3.80 – 3.72 (m, 2H), 3.40 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.96 (dd, *J* = 10.0, 5.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 152.4, 144.3, 137.4, 130.9, 130.2 (q, *J* = 32.0 Hz), 128.64, 128.60, 127.6, 127.1, 126.0, 125.8 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 270.3 Hz), 121.6, 120.8, 119.3, 72.5, 63.3, 61.7, 57.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.5 ppm. ESI-HRMS: $C_{24}H_{20}F_3N_3S+H^+$ 440.1403, found 440.1393.



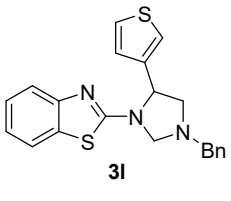
3j

3j, white solid (42.6 mg, 97% yield); m.p. 148-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.34 – 7.25 (m, 9H), 7.07 (t, *J* = 7.6 Hz, 1H), 4.83 (t, *J* = 5.6 Hz, 1H), 4.65 (d, *J* = 6.4 Hz, 1H), 4.58 (d, *J* = 6.4 Hz, 1H), 3.80 – 3.73 (m, 2H), 3.39 – 3.34 (m, 1H), 2.95 (dd, *J* = 9.6, 5.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 152.3, 144.0, 137.3, 135.3, 130.9, 128.6, 128.1, 127.6, 126.0, 125.3, 121.6, 120.8, 119.4, 72.3, 62.8, 61.3, 57.6 ppm. ESI-HRMS: $C_{23}H_{19}Cl_2N_3S+H^+$ 440.0750, found 440.0741.



3k

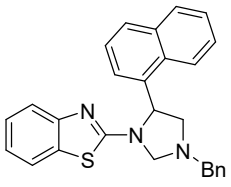
3k, white solid (33.2 mg, 92% yield); m.p. 53-54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.40 (s, 1H), 7.36 – 7.25 (m, 6H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 3.2 Hz, 1H), 6.36 (d, *J* = 1.2 Hz, 1H), 4.94 (t, *J* = 6.4 Hz, 1H), 4.69 (d, *J* = 6.8 Hz, 1H), 4.55 (d, *J* = 6.8 Hz, 1H), 3.78 (s, 2H), 3.37 (dd, *J* = 10.4, 7.2 Hz, 1H), 3.22 (dd, *J* = 10.4, 6.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 152.2, 151.7, 142.6, 137.6, 130.9, 128.7, 128.5, 127.5, 125.9, 121.4, 120.7, 119.2, 110.5, 108.9, 72.0, 58.6, 58.1, 56.9 ppm. ESI-HRMS: $C_{21}H_{19}N_3OS+H^+$ 362.1322, found 362.1312.



3l

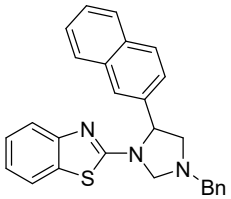
3l, white solid (35.4 mg, 94% yield); m.p. 104-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.28 (m, 8H), 7.14 (d, *J* = 4.8 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 4.95 (t, *J* = 6.0 Hz, 1H), 4.65 – 4.61 (m, 2H), 3.81 – 3.74 (m, 2H), 3.35 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.03 (dd, *J* = 9.6, 5.2 Hz, 1H) ppm. ^{13}C

NMR (100 MHz, $CDCl_3$) δ 164.5, 152.2, 140.9, 137.6, 130.9, 128.7, 128.5, 127.5, 126.6, 126.3, 125.9, 123.0, 121.3, 120.7, 119.0, 72.0, 61.1, 59.4, 58.0 ppm. ESI-HRMS: $C_{21}H_{19}N_3S_2$+H^+ 378.1093, found 378.1084.



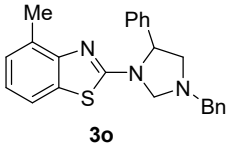
3m

3m, white solid (44.4 mg, 96% yield); m.p. 116-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.50 (m, 4H), 7.45 – 7.39 (m, 2H), 7.31 – 7.23 (m, 6H), 6.99 (t, *J* = 7.2 Hz, 1H), 5.65 (t, *J* = 6.0 Hz, 1H), 4.87 (d, *J* = 6.8 Hz, 1H), 4.75 (d, *J* = 6.8 Hz, 1H), 3.82 (d, *J* = 13.2 Hz, 1H), 3.76 (d, *J* = 13.2 Hz, 1H), 3.68 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.04 (dd, *J* = 10.0, 5.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 152.5, 137.6, 134.7, 134.0, 131.1, 130.8, 129.3, 128.7, 128.5, 128.4, 127.5, 126.4, 125.9, 125.8, 125.7, 123.4, 122.4, 121.3, 120.7, 119.1, 72.4, 61.3, 61.1, 58.1 ppm. ESI-HRMS: $C_{27}H_{23}N_3S$+H^+ 422.1685, found 422.1675.



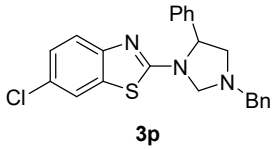
3n

3n, white solid (40.0 mg, 95% yield); m.p. 107-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 4H), 7.57 – 7.46 (m, 5H), 7.39 – 7.30 (m, 4H), 7.28 – 7.22 (m, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 5.00 (t, *J* = 6.4 Hz, 1H), 4.83 (d, *J* = 6.8 Hz, 1H), 4.72 (d, *J* = 6.4 Hz, 1H), 3.83 – 3.76 (m, 2H), 3.50 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.03 (dd, *J* = 10.0, 6.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 152.3, 137.6, 137.1, 133.3, 133.2, 131.0, 128.9, 128.7, 128,5, 127.9, 127.8, 127.5, 126.3, 126.2, 126.1, 125.8, 124.3, 121.3, 120.7, 119.1, 72.7, 63.9, 62.2, 58.0 ppm. ESI-HRMS: $C_{27}H_{23}N_3S$+H^+ 422.1685, found 422.1676.



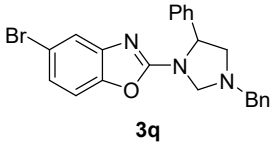
3o

3o, white solid (36.6 mg, 95% yield); m.p. 43-44 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.28 (m, 9H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 4.84 (t, *J* = 6.4 Hz, 2H), 4.62 (d, *J* = 6.8 Hz, 1H), 3.79 (d, *J* = 12.8 Hz, 1H), 3.73 (d, *J* = 12.8 Hz, 1H), 3.45 (dd, *J* = 10.0, 7.2 Hz, 1H), 2.95 (dd, *J* = 10.0, 6.8 Hz, 1H), 2.54 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 151.5, 140.0, 137.8, 130.8, 129.0, 128.8, 128.7, 128.5, 127.9, 127.5, 126.9, 126.5, 121.1, 118.1, 72.6, 63.7, 62.4, 58.0, 18.3 ppm. ESI-HRMS: $C_{24}H_{23}N_3S$+H^+ 386.1685, found 386.1678.



3p

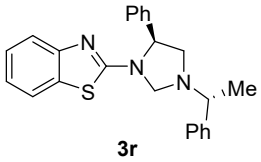
3p, white solid (38.9 mg, 96% yield); m.p. 87-88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.27 (m, 12H), 7.20 (d, *J* = 8.8 Hz, 1H), 4.81 (t, *J* = 6.4 Hz, 1H), 4.74 (d, *J* = 6.4 Hz, 1H), 4.62 (d, *J* = 6.8 Hz, 1H), 3.80 – 3.73 (m, 2H), 3.44 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.96 (dd, *J* = 10.0, 6.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 150.9, 139.3, 137.5, 132.2, 128.9, 1287, 128.6, 128.2, 127.6, 126.9, 126.4, 126.3, 120.3, 119.6, 72.6, 63.7, 62.3 57.9 ppm. ESI-HRMS: $C_{23}H_{20}ClN_3S$+H^+ 406.1139, found 406.1132.



3q

3q, white solid (40.7 mg, 94% yield); m.p. 99-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 11H), 7.07 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 5.15 (t, *J* = 6.4 Hz, 1H), 4.57 – 4.54 (m, 2H), 3.78 (d, *J* = 13.2 Hz, 1H), 3.72 (d, *J* =

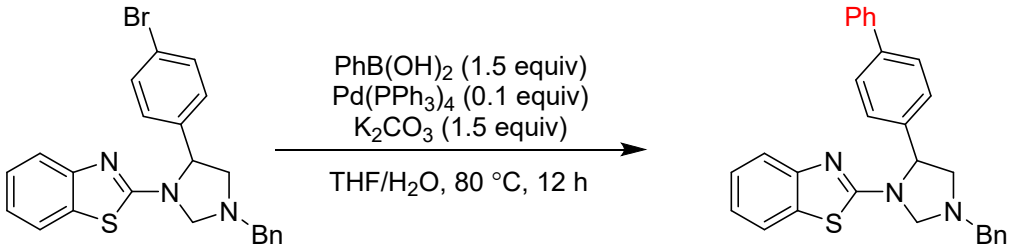
13.2 Hz, 1H), 3.40 (dd, *J* = 10.0, 7.2 Hz, 1H), 2.96 (dd, *J* = 10.0, 6.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 148.0, 144.8, 140.8, 137.4, 128.7, 128.6, 127.7, 127.6, 126.2, 123.3, 119.5, 116.6, 110.0, 70.9, 61.7, 61.4, 57.8 ppm. ESI-HRMS: $C_{23}H_{20}BrN_3O+H^+$ 434.0863 (^{79}Br) and 436.0842 (^{81}Br), found 434.0853, 436.0831.



3r

3r, white solid (36.6 mg, 95% yield); m.p. 61-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.36 – 7.29 (m, 7H), 7.27 – 7.23 (m, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 4.82 (d, *J* = 6.0 Hz, 1H), 4.77 (t, *J* = 6.0 Hz, 1H), 4.49 (d, *J* = 5.6 Hz, 1H), 3.45 (q, *J* = 6.4 Hz, 1H), 3.27 – 3.23 (m, 1H), 2.82 (dd, *J* = 9.2, 6.0 Hz, 1H), 1.42 (d, *J* = 6.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 152.3, 144.0, 139.7, 131.0, 128.7, 128.6, 128.1, 127.5, 127.03, 126.99, 125.8, 121.2, 120.7, 119.0, 71.7, 64.4, 63.3, 61.2, 23.0 ppm. ESI-HRMS: $C_{24}H_{23}N_3S+H^+$ 386.1685, found 386.1676.

4. Procedure for preparation of compound 4

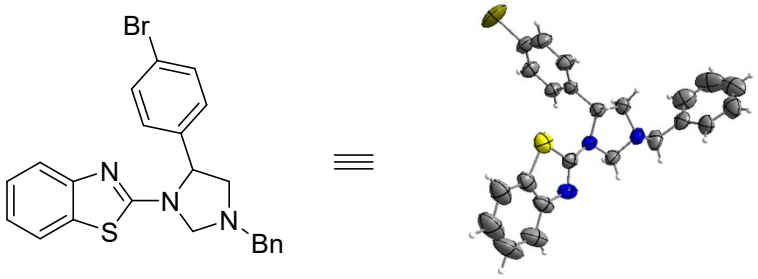


3h **4**

To a solution of **3h** (90 mg, 0.20 mmol) in THF/H_2O (2mL, 9:1) was added $Pd(PPh_3)_4$ (20 mg, 0.02 mmol), phenylboronic acid (37 mg, 0.30 mmol), and K_2CO_3 (41.4 mg, 0.3 mmol). The resulting mixture was stirred at 80 °C for 12 h under N_2. Upon completion of the reaction, water (5 mL) was added and the mixture was extracted with DCM (3 × 5 mL). The combined organic layers were dried and concentrated under reduced pressure followed by silica gel column chromatography purification (petroleum ether/ethyl acetate = 6:1) to give the product **4** (58.1 mg, 65% yield) as a white solid. m.p. 180-181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 5H), 7.47 (d, *J* = 7.2 Hz, 3H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.28 (m, 5H), 7.29 – 7.23 (m, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 4.88 (t, *J* = 6.0 Hz, 1H), 4.77 (d, *J* = 6.4 Hz, 1H), 4.67 (d, *J* = 6.4 Hz, 1H), 3.82 – 3.74 (m, 2H), 3.45 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.00 (dd, *J* = 10.0, 6.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7), 152.3, 141.0, 140.6, 138.8, 137.6, 131.0, 128.8, 128.7, 128.5, 127.53, 127.49, 127.4, 127.1, 125.9, 121.3, 120.7, 119.1, 72.6, 63.5, 62.3, 58.0 ppm. ESI-HRMS: calcd. for $C_{29}H_{25}N_3S+H^+$ 448.1842, found 448.1832.

5. Crystal data and structural refinement for 3h

Preparation of Single Crystal. Single crystal **3h** was obtained by the layer-to-layer diffusion method. Products **3h** were added to dichloromethane (1.0 mL) , and stratified with *n*-hexane after 3 days to obtain crystals suitable for single-crystal X-ray diffraction.



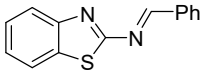
3h

CCDC 2182405

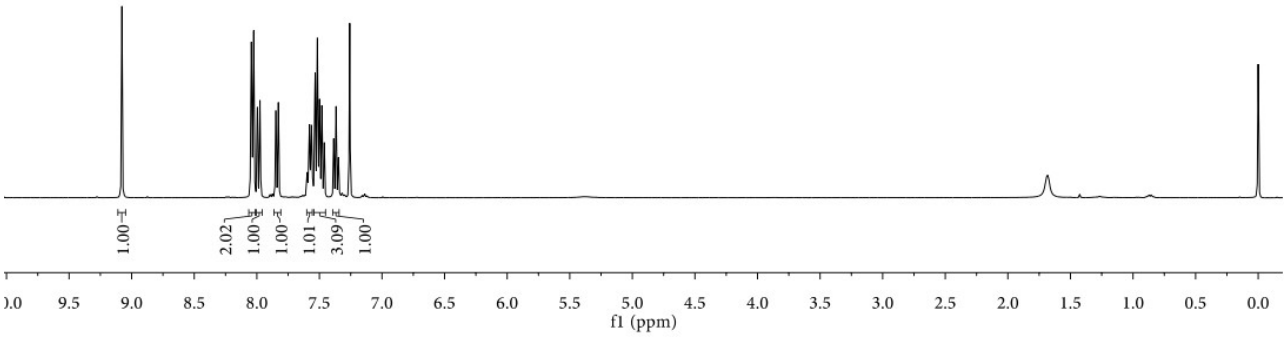
Identification code	**3h**
Empirical formula	$C_{23}H_{20}BrN_3S$
Formula weight	450.39
Temperature/K	296
Crystal system	triclinic
Space group	P -1
a/Å	9.0251(10)
b/Å	11.4612(13)
c/Å	11.5392(13)
α/°	64.078(2)
β/°	82.620(2)
γ/°	83.522(2)
Volume/Å^3	1062.5(2)
Z	2
ρ_{calc}g/cm^3	1.408
μ/mm^{-1}	2.046
F(000)	460
Crystal size/mm^3	0.26 × 0.25 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.88 to 24.00

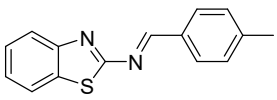
Index ranges	$-10 \leq h \leq 10, -8 \leq k \leq 13, -12 \leq l \leq 13$
Reflections collected	5465
Independent reflections	2504 [$R_{int} = 0.0412$]
Data/restraints/parameters	3717 / 0 / 253
Goodness-of-fit on F^2	0.993
Final R indexes [I>=2σ (I)]	$R_1 = 0.0412$, $wR_2 = 0.0896$
R indices (all data)	$R_1 = 0.0738$, $wR_2 = 0.0989$
Largest diff. peak and hole/ 1-sigma level	0.255 / − 0.481 / 0.044

6. NMR spectra

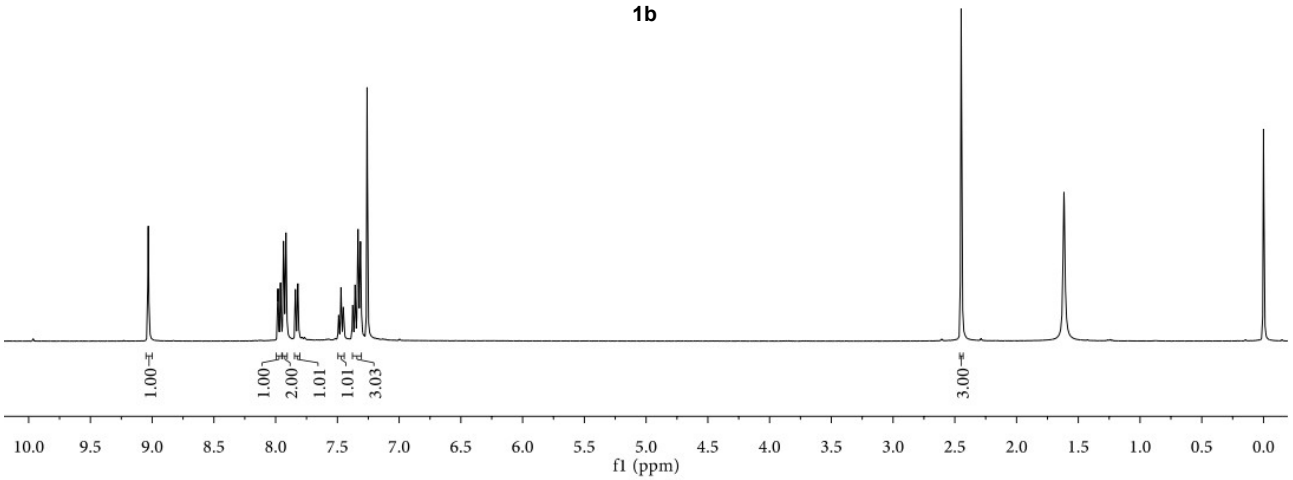


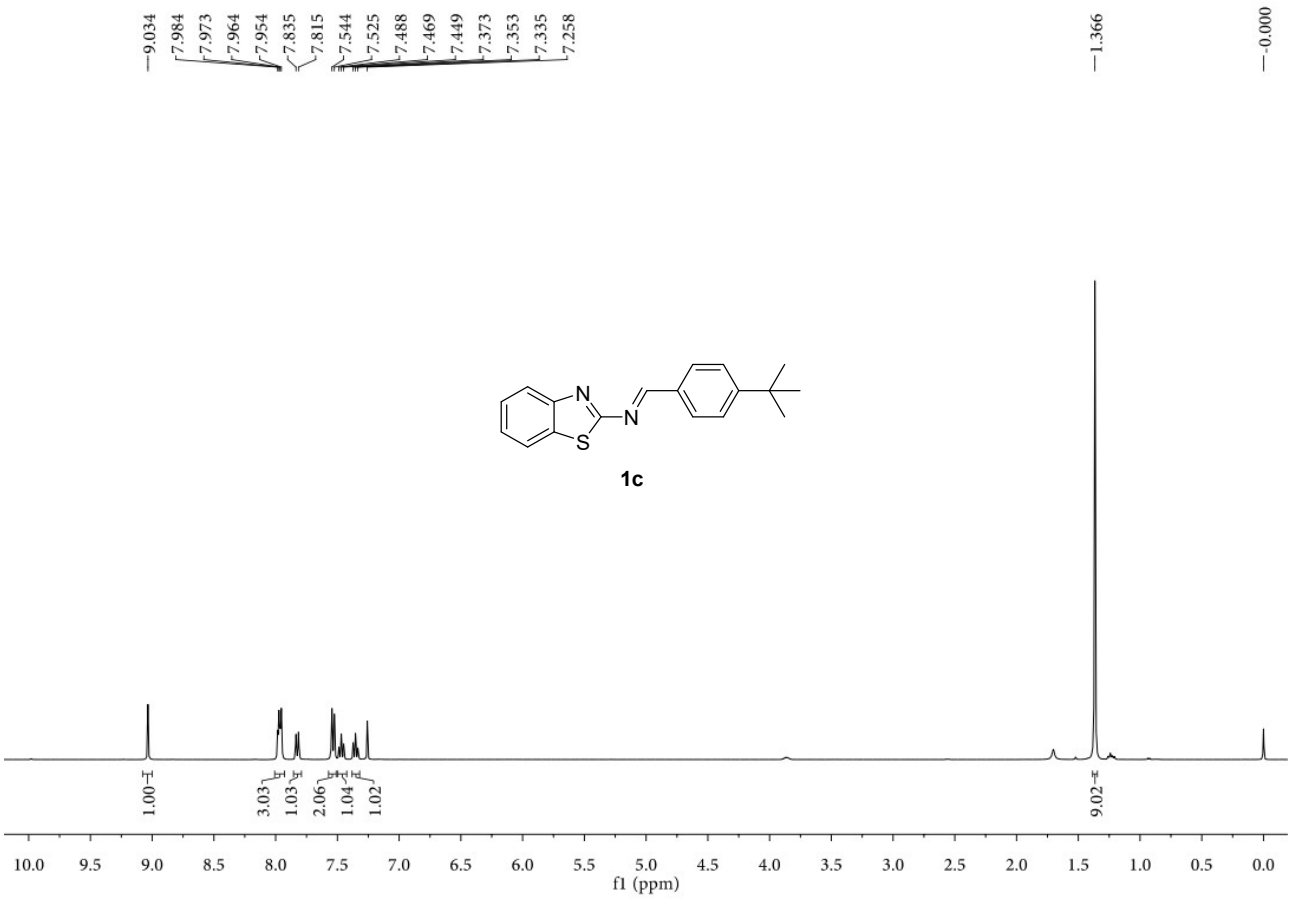
1a



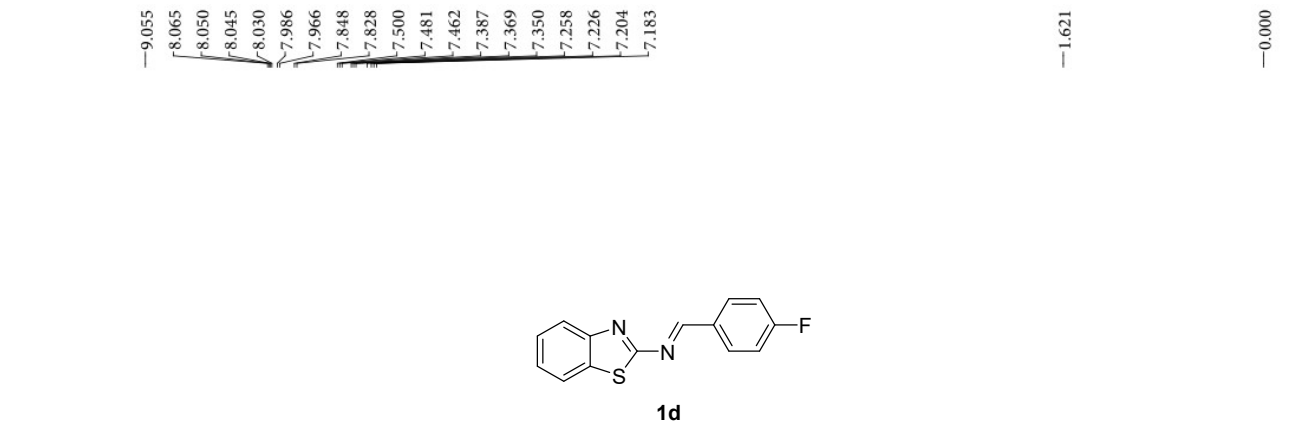


1b



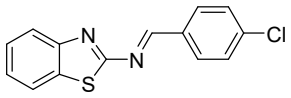

9.034
7.984
7.973
7.964
7.954
7.835
7.815
7.544
7.525
7.488
7.469
7.449
7.373
7.353
7.335
7.258
1.366
0.000
1.00
3.03
1.03
2.06
1.04
1.02
9.02
f1 (ppm)

1c

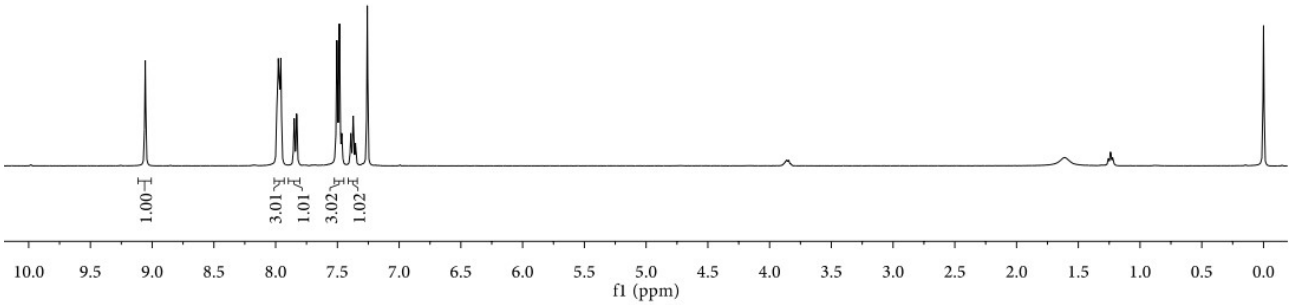

9.055
8.065
8.050
8.045
8.030
7.986
7.966
7.848
7.828
7.500
7.481
7.462
7.387
7.369
7.350
7.258
7.226
7.204
7.183
1.621
0.000
1.00
2.01
1.00
1.00
1.02
1.02
2.00
f1 (ppm)

1d

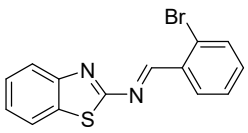

9.056
7.979
7.958
7.850
7.830
7.504
7.484
7.465
7.391
7.372
7.353
7.258
1.609
0.000


N
S
N
Cl

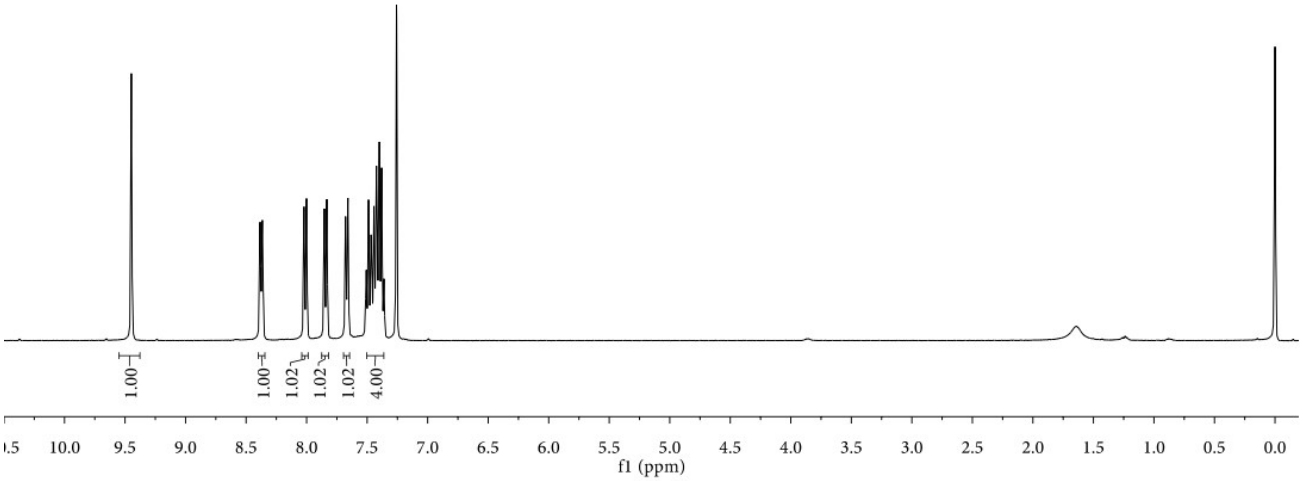
1e


1.00
3.01
1.01
3.02
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

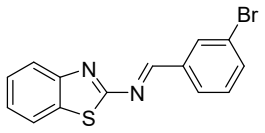

9.448
8.384
8.365
8.021
8.001
7.853
7.833
7.678
7.658
7.507
7.488
7.468
7.443
7.422
7.399
7.380
7.361
7.258
1.644
0.000


Br
N
S
N

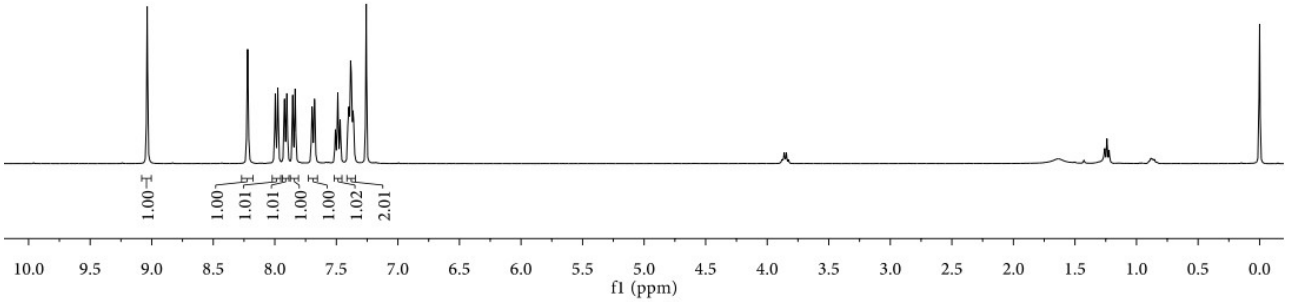
1f


1.00
1.00
1.02
1.02
1.02
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

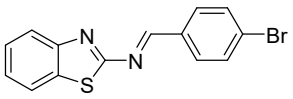

9.037
8.221
7.996
7.976
7.921
7.902
7.854
7.834
7.697
7.677
7.508
7.488
7.469
7.404
7.397
7.384
7.379
7.365
7.257
1.635
-0.000


Br
N
N
S

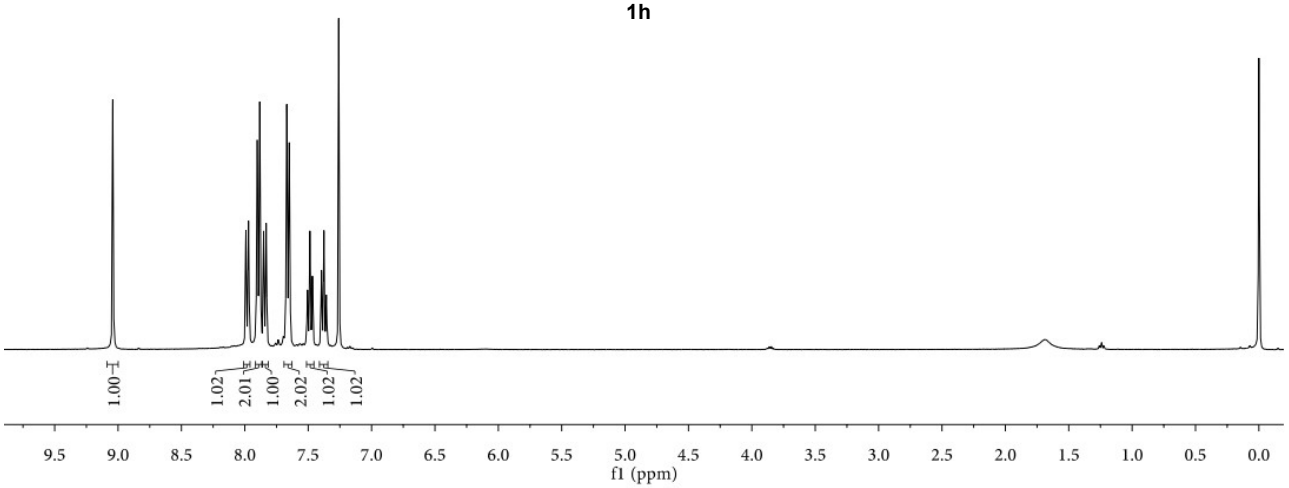
1g

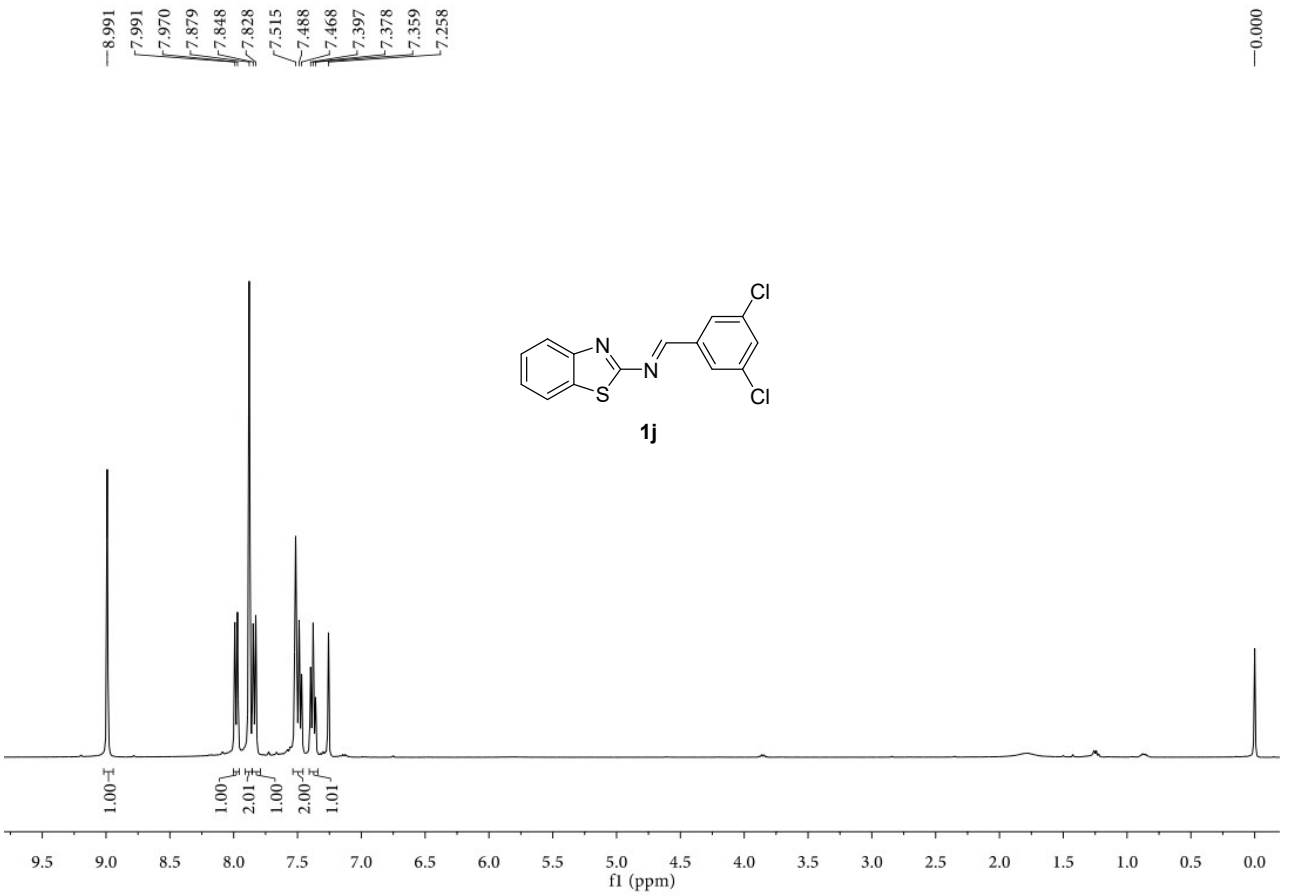

1.00
1.00
1.01
1.01
1.00
1.00
1.02
2.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

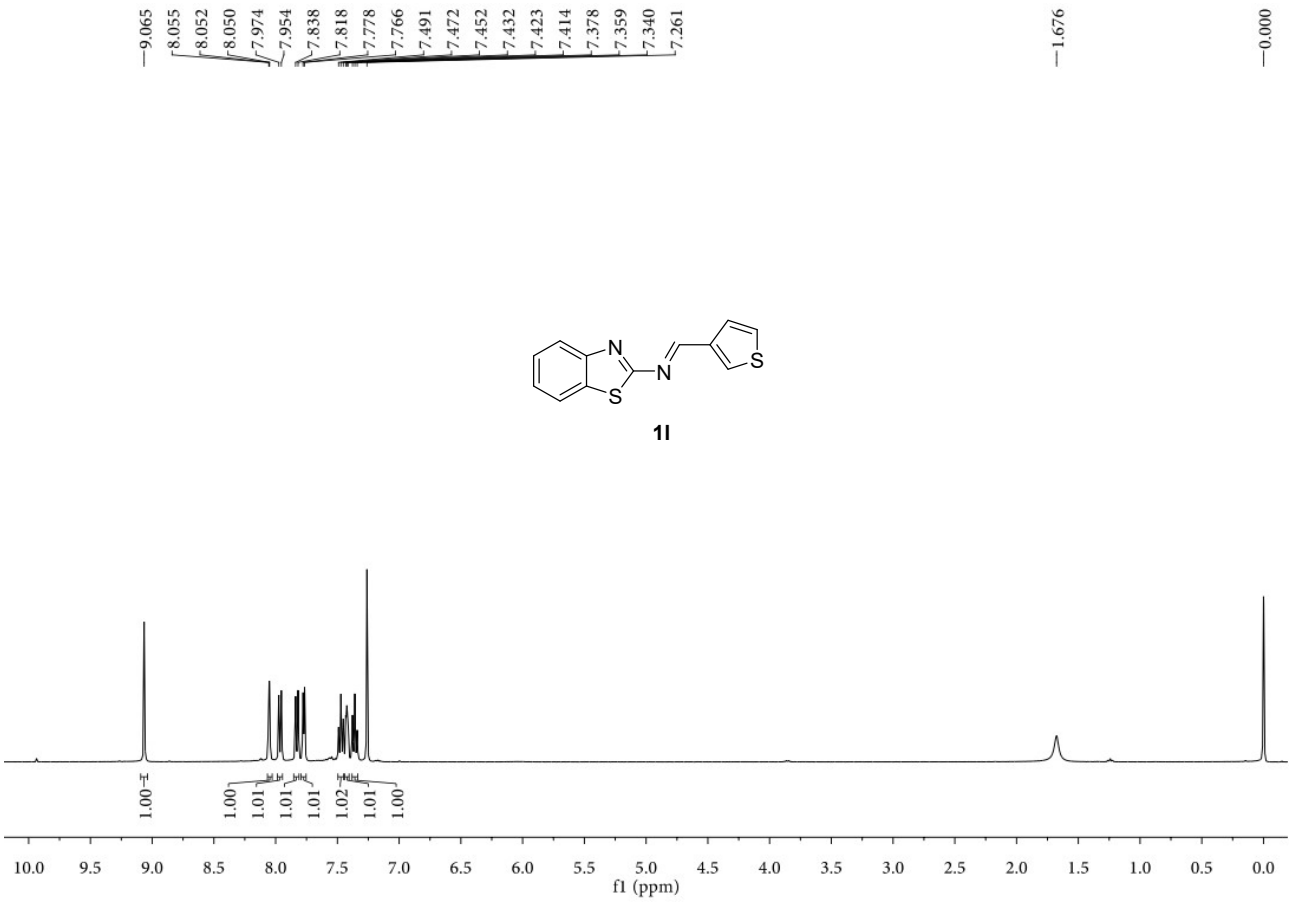

9.042
7.991
7.971
7.902
7.882
7.851
7.831
7.669
7.649
7.505
7.486
7.467
7.395
7.376
7.357
7.259
1.693
-0.000

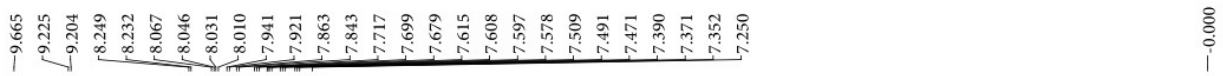

Br
N
N
S

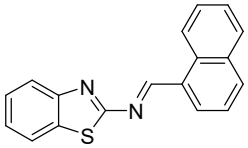
1h


1.00
1.02
2.01
1.00
2.02
1.02
1.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

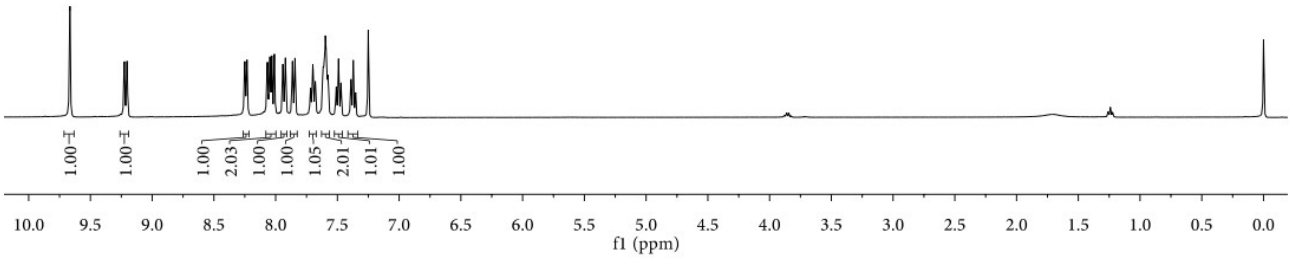

8.991
7.991
7.970
7.879
7.848
7.828
7.515
7.488
7.468
7.397
7.378
7.359
7.258
0.000
Cl
N
N
S
Cl
1j
1.00
1.00
2.01
1.00
2.00
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

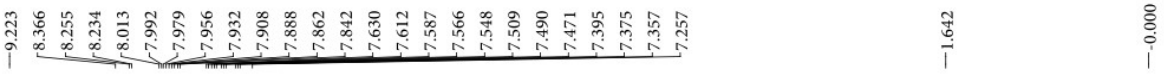

9.065
8.055
8.052
8.050
7.974
7.954
7.838
7.818
7.778
7.766
7.491
7.472
7.452
7.432
7.423
7.414
7.378
7.359
7.340
7.261
1.676
0.000
N
N
S
S
1l
1.00
1.00
1.01
1.01
1.01
1.02
1.01
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


9.665
9.225
9.204
8.249
8.232
8.067
8.046
8.031
8.010
7.941
7.921
7.863
7.843
7.717
7.699
7.679
7.615
7.608
7.597
7.578
7.509
7.491
7.471
7.390
7.371
7.352
7.250
0.000



1m


1.00
1.00
1.00
2.03
1.00
1.00
1.05
2.01
1.01
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


9.223
8.366
8.255
8.234
8.013
7.992
7.979
7.956
7.932
7.908
7.888
7.862
7.842
7.630
7.612
7.587
7.566
7.548
7.509
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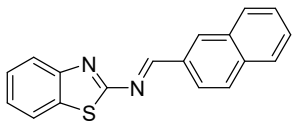
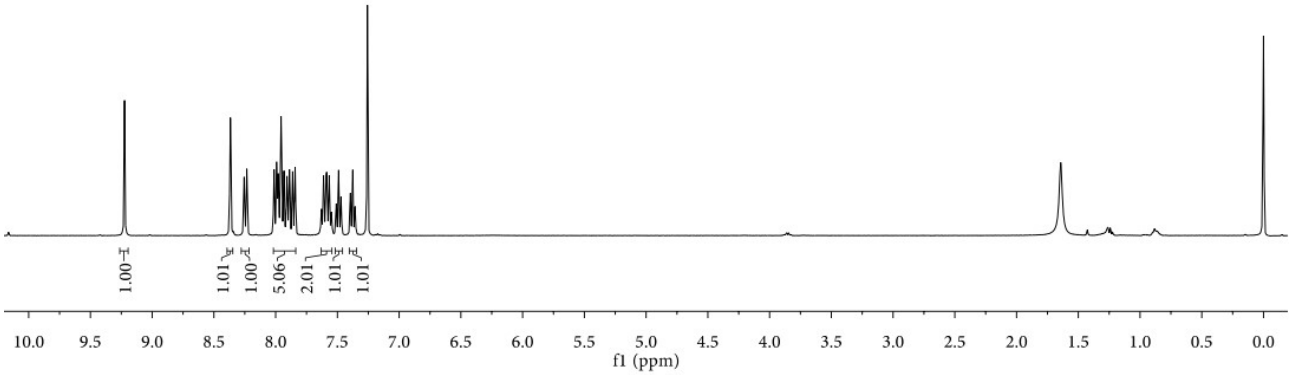
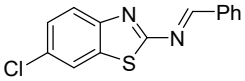
7.471
7.395
7.375
7.357
7.257
1.642
0.000



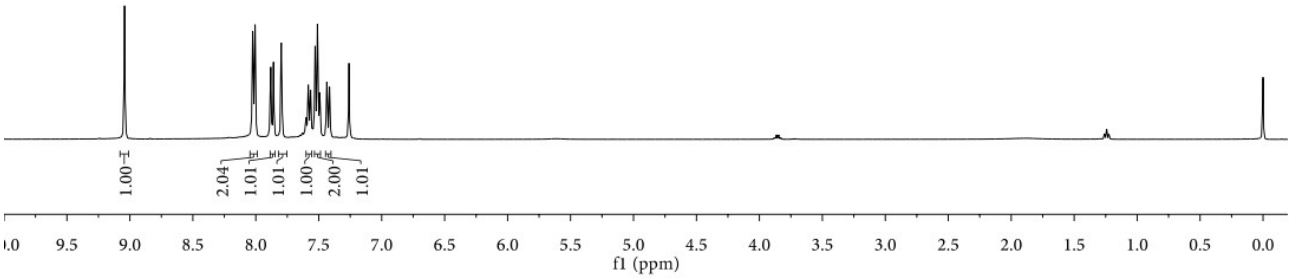
1n


1.00
1.01
1.00
5.06
2.01
1.01
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

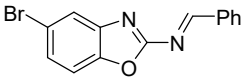

9.042
8.025
8.006
7.881
7.859
7.797
7.601
7.583
7.565
7.529
7.510
7.492
7.436
7.415
7.260
0.000


N
Ph
N
Cl
S

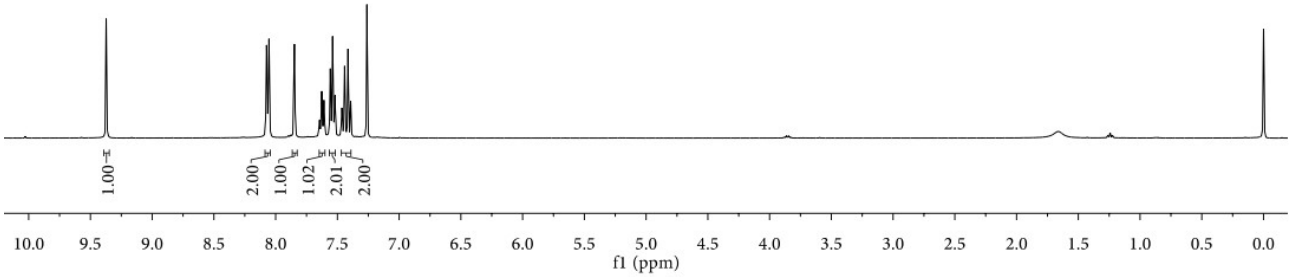
1p

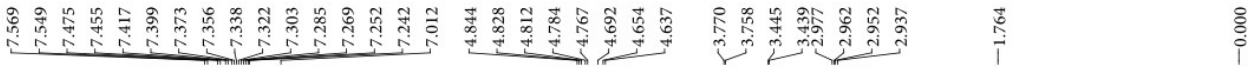

1.00
2.04
1.01
1.01
1.00
2.00
1.01
f1 (ppm)

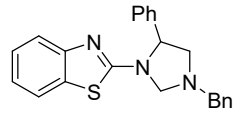

9.372
8.074
8.054
7.848
7.645
7.627
7.609
7.557
7.539
7.520
7.463
7.442
7.414
7.393
7.261
1.665
0.000


Br
N
Ph
N
O

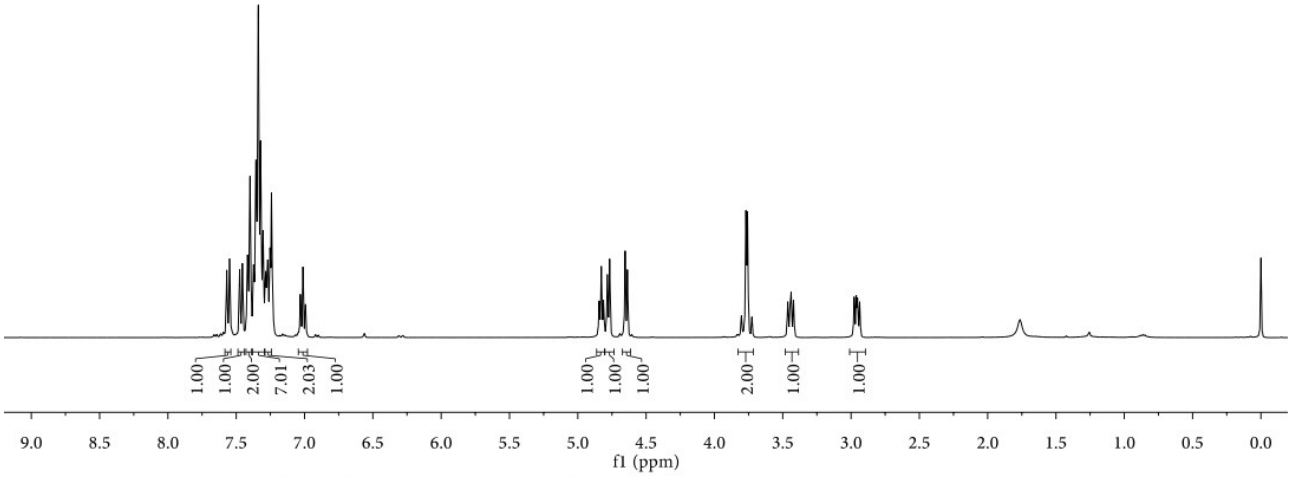
1q


1.00
2.00
1.00
1.02
2.01
2.00
f1 (ppm)

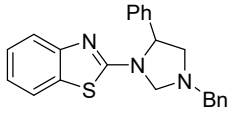

7.569
7.549
7.475
7.455
7.417
7.399
7.373
7.356
7.338
7.322
7.303
7.285
7.269
7.252
7.242
7.012
4.844
4.828
4.812
4.784
4.767
4.692
4.654
4.637
3.770
3.758
3.445
3.439
2.977
2.962
2.952
2.937
1.764
0.000


Ph
N
S
N
N
Bn

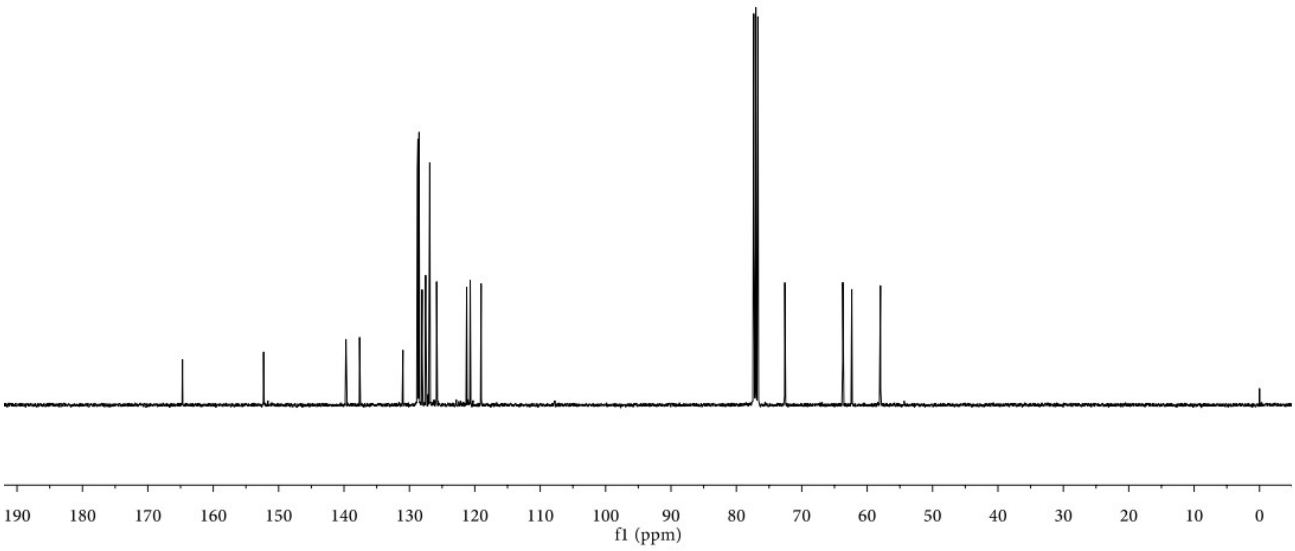
3a

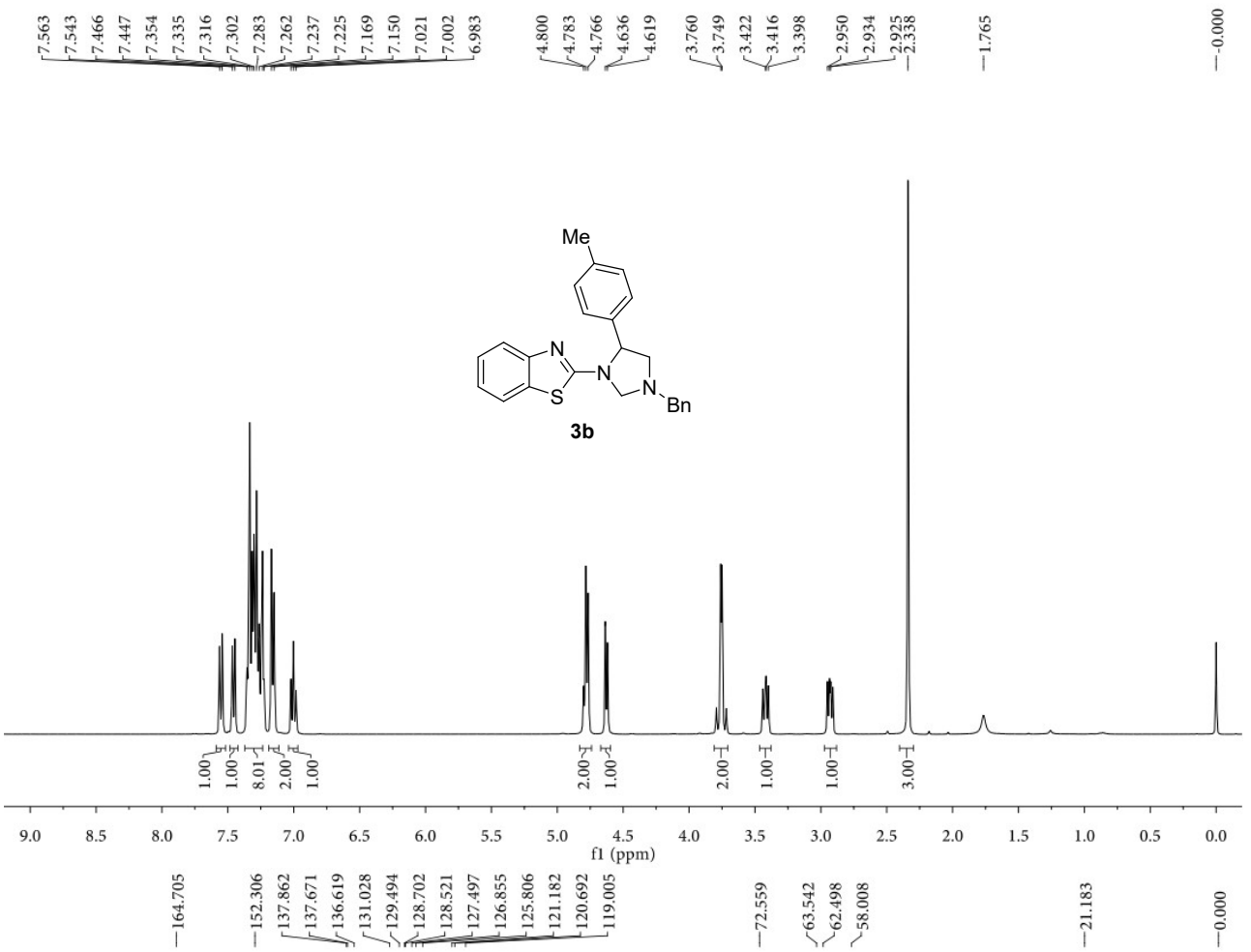

1.00
1.00
2.00
7.01
2.03
1.00
1.00
1.00
1.00
2.00
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

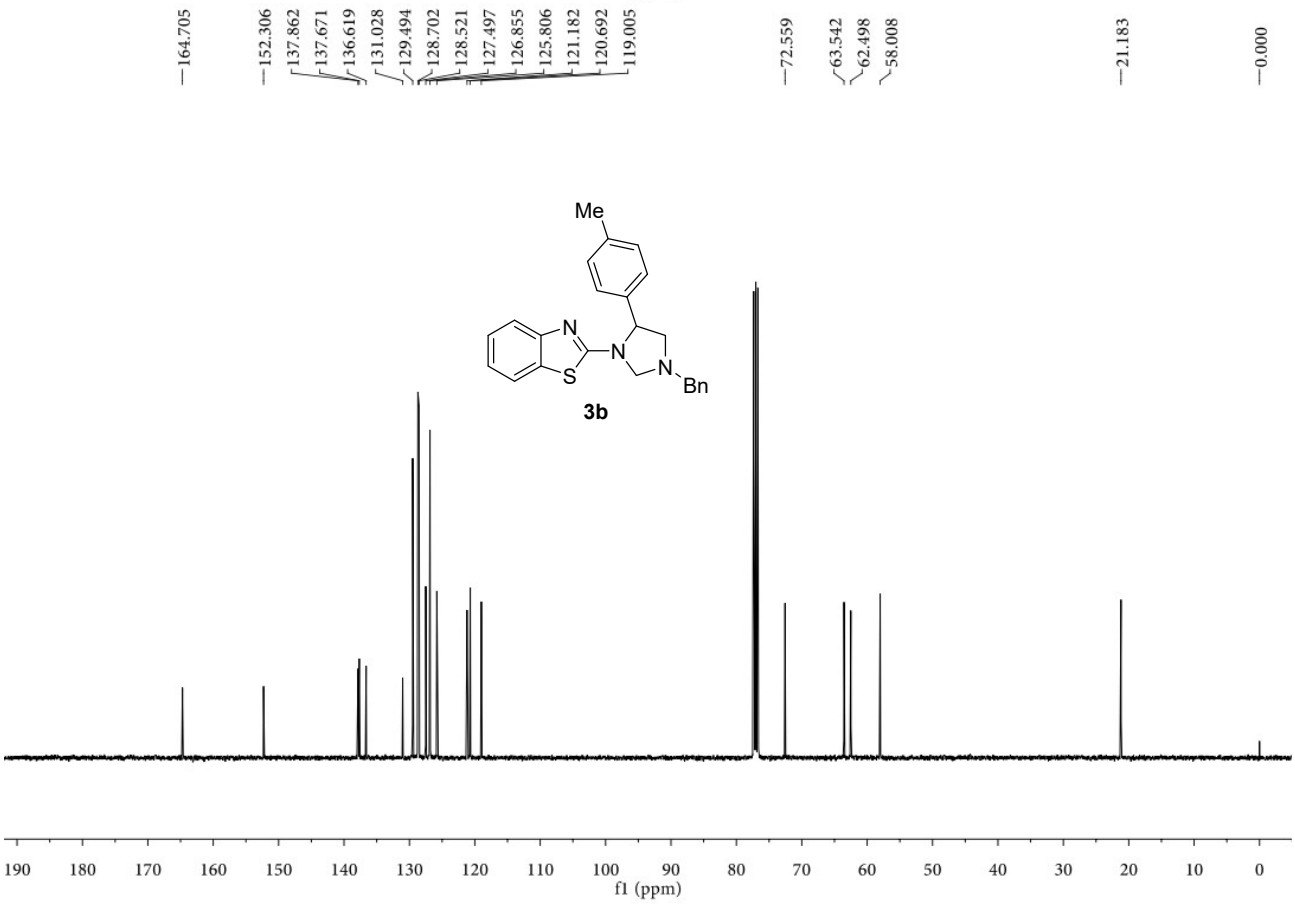

164.706
152.293
139.705
137.617
130.988
128.785
128.688
128.529
128.061
127.516
126.887
125.843
121.243
120.701
119.033
72.588
63.727
62.353
57.965
0.000

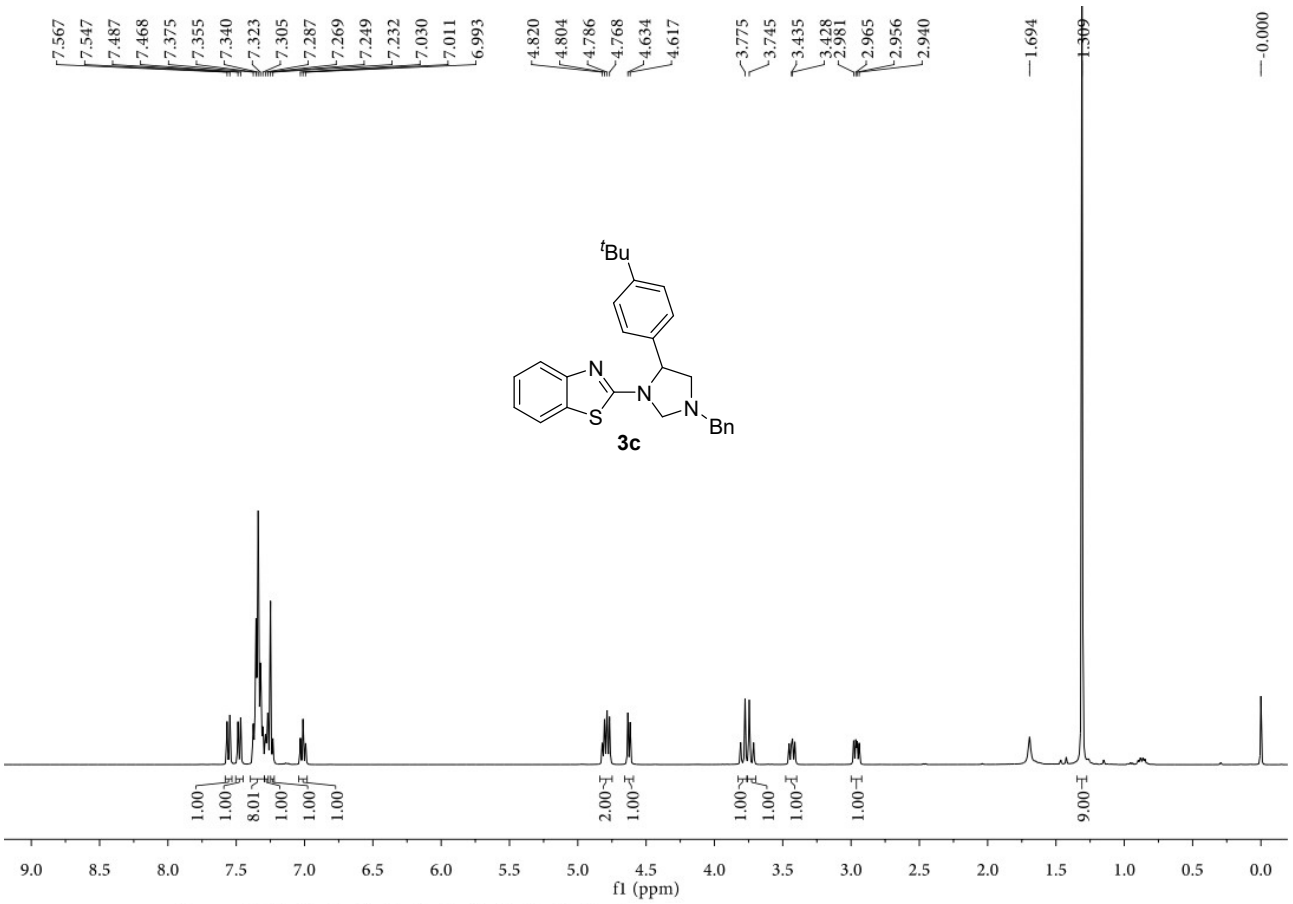

Ph
N
S
N
N
Bn

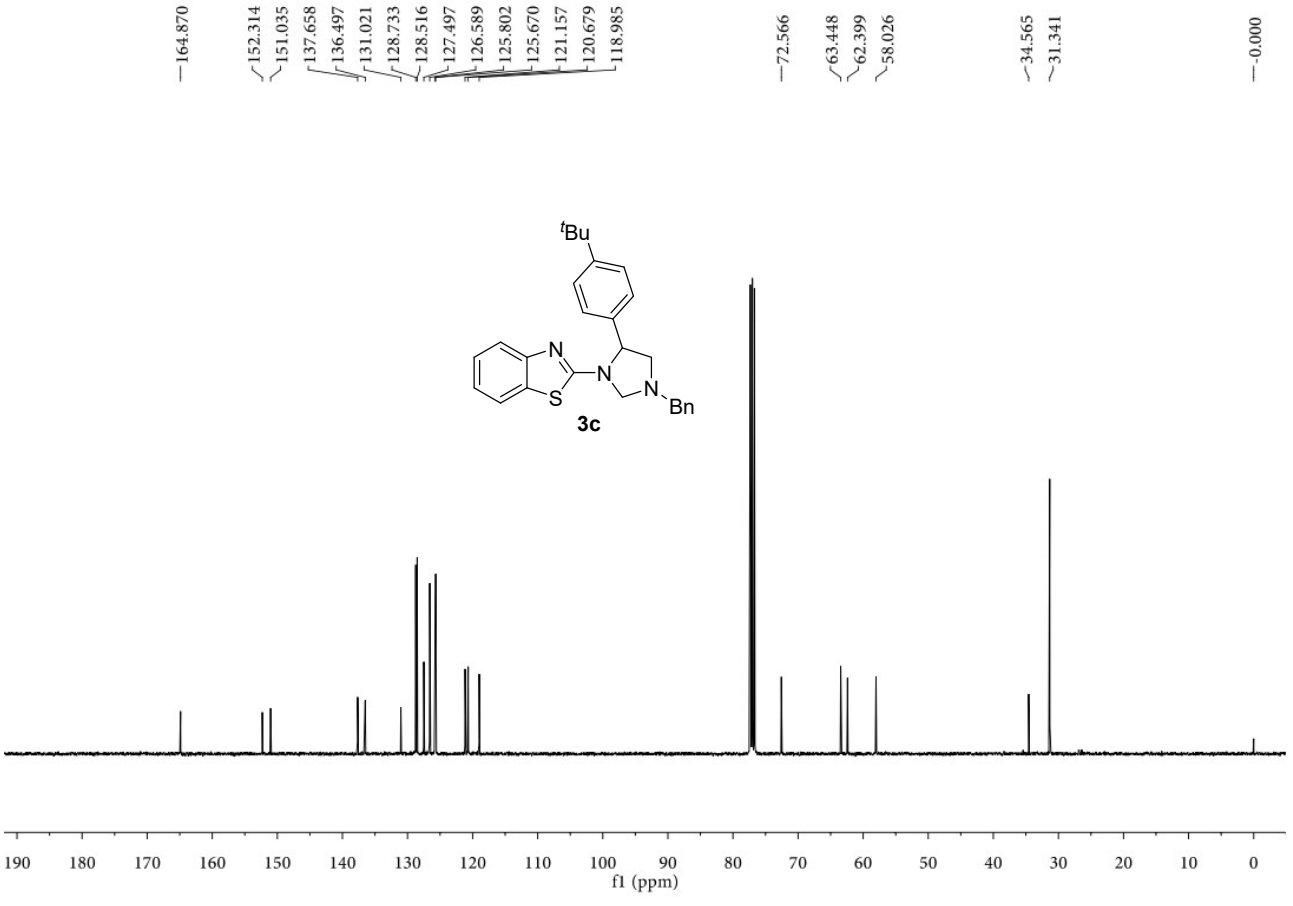
3a


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.563
7.543
7.466
7.447
7.354
7.335
7.316
7.302
7.283
7.262
7.237
7.225
7.169
7.150
7.021
7.002
6.983
4.800
4.783
4.766
4.636
4.619
3.760
3.749
3.422
3.416
3.398
2.950
2.934
2.925
2.338
1.765
-0.000
Me
N
S
N
N
Bn
3b
1.00
1.00
8.01
2.00
1.00
2.00
1.00
2.00
1.00
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.705
152.306
137.862
137.671
136.619
131.028
129.494
128.702
128.521
127.497
126.855
125.806
121.182
120.692
119.005
72.559
63.542
62.498
58.008
21.183
0.000
Me
N
S
N
N
Bn
3b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.567
7.547
7.487
7.468
7.375
7.355
7.340
7.323
7.305
7.287
7.269
7.249
7.232
7.030
7.011
6.993
4.820
4.804
4.786
4.768
4.634
4.617
3.775
3.745
3.435
3.428
2.981
2.965
2.956
2.940
1.694
1.309
-0.000
tBu
N
S
N
N
Bn
3c
1.00
1.00
8.01
1.00
1.00
1.00
2.00
1.00
1.00
1.00
1.00
1.00
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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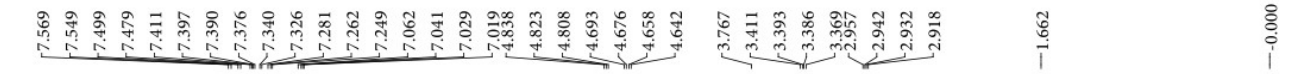
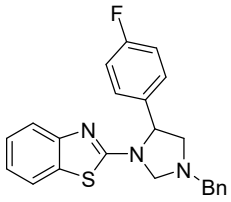
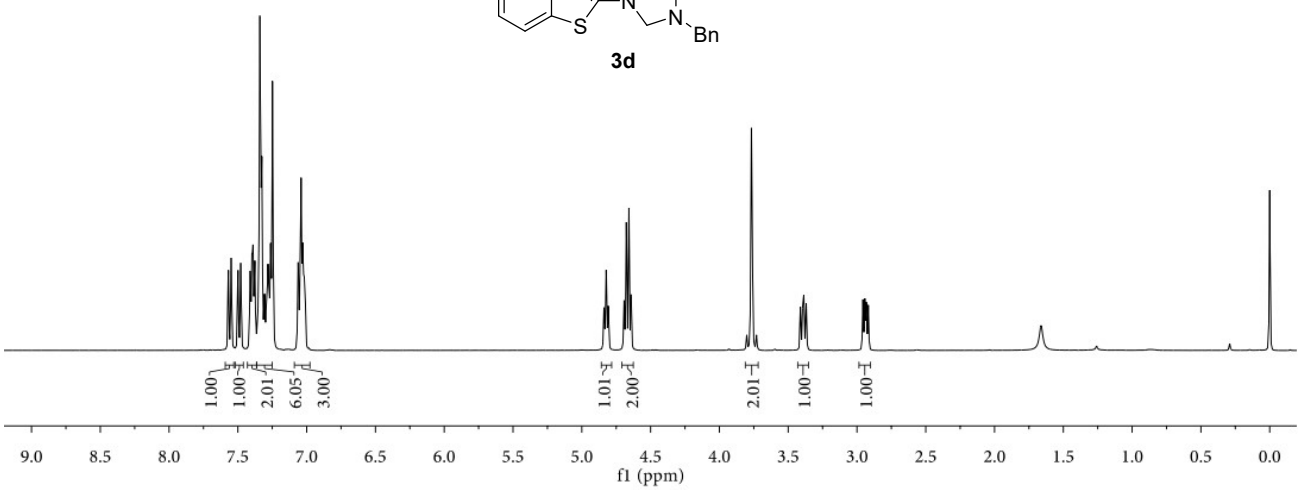
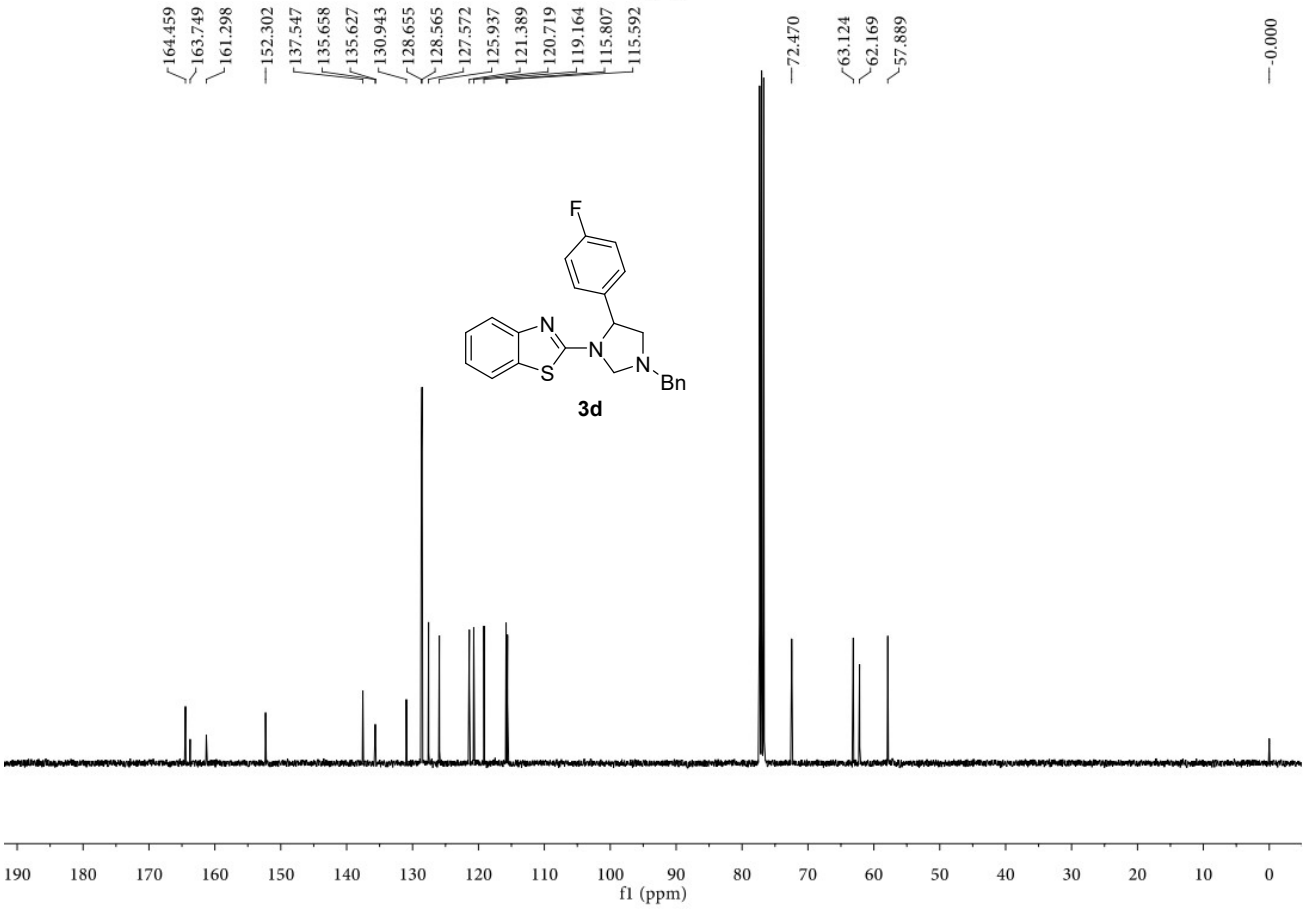
152.314
151.035
137.658
136.497
131.021
128.733
128.516
127.497
126.589
125.802
125.670
121.157
120.679
118.985
72.566
63.448
62.399
58.026
34.565
31.341
-0.000
tBu
N
S
N
N
Bn
3c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.569
7.549
7.499
7.479
7.411
7.397
7.390
7.376
7.340
7.326
7.281
7.262
7.249
7.062
7.041
7.029
7.019
4.838
4.823
4.808
4.693
4.676
4.658
4.642
3.767
3.411
3.393
3.386
3.369
2.957
2.942
2.932
2.918
1.662
0.000

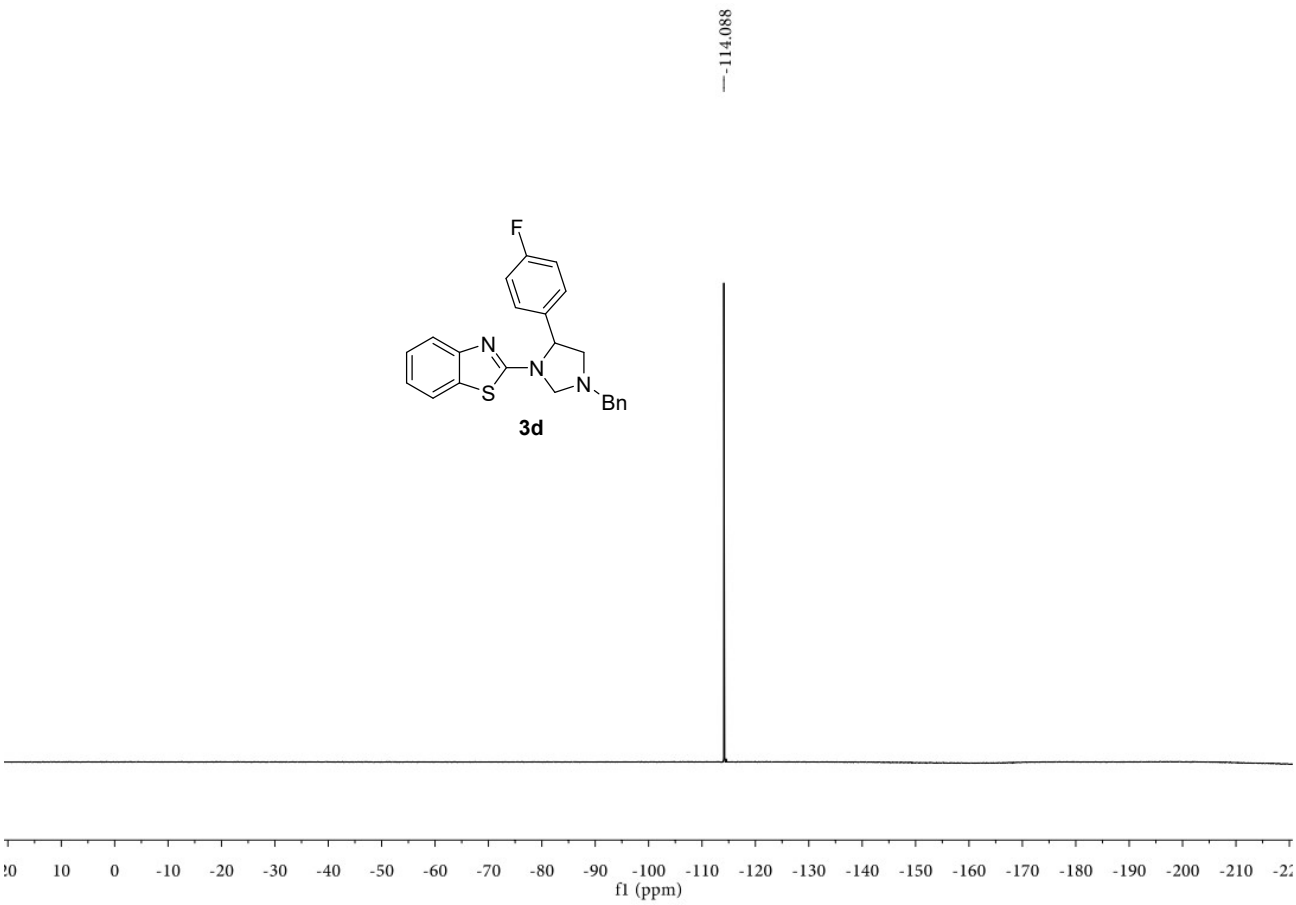

F
N
S
N
N
Bn

3d

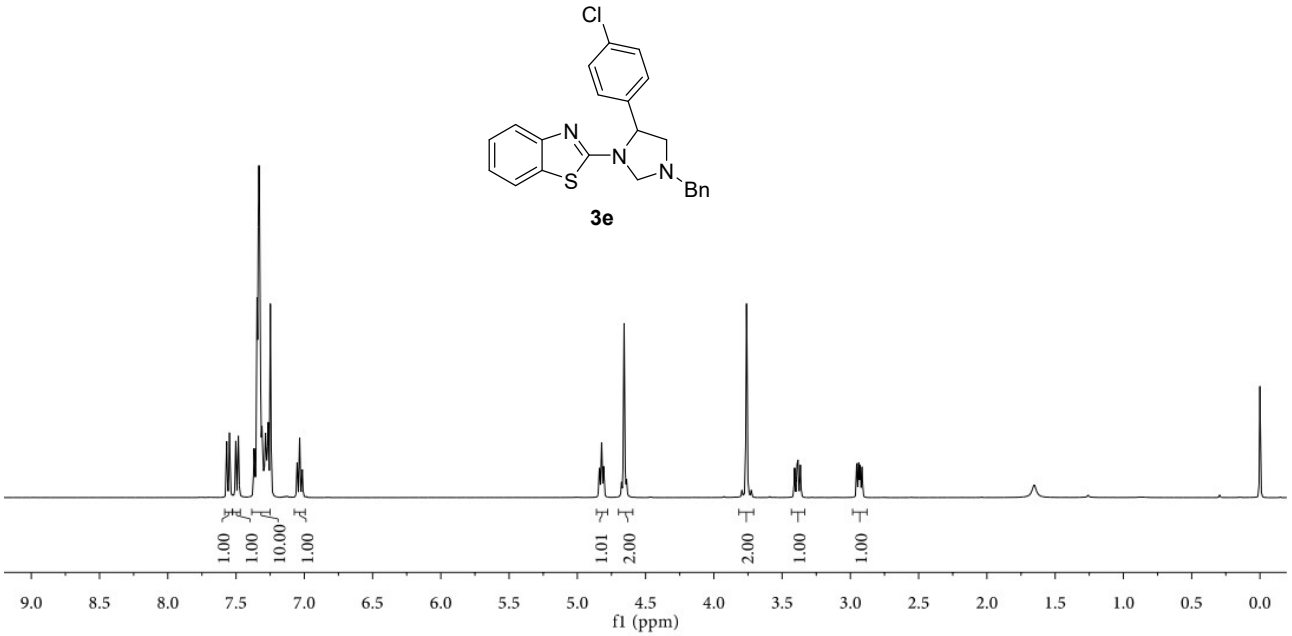

1.00
1.00
2.01
6.05
3.00
1.01
2.00
2.01
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.459
163.749
161.298
152.302
137.547
135.658
135.627
130.943
128.655
128.565
127.572
125.937
121.389
120.719
119.164
115.807
115.592
72.470
63.124
62.169
57.889
0.000
F
N
S
N
N
Bn
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

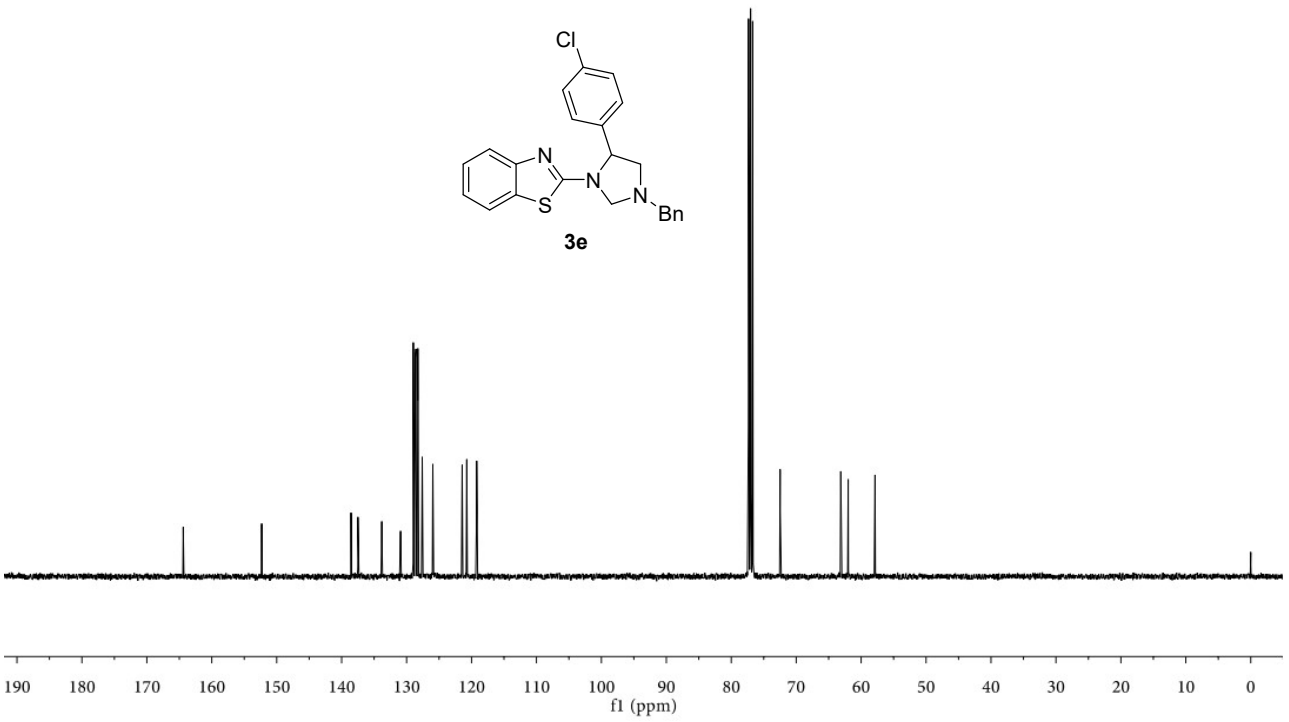
3d

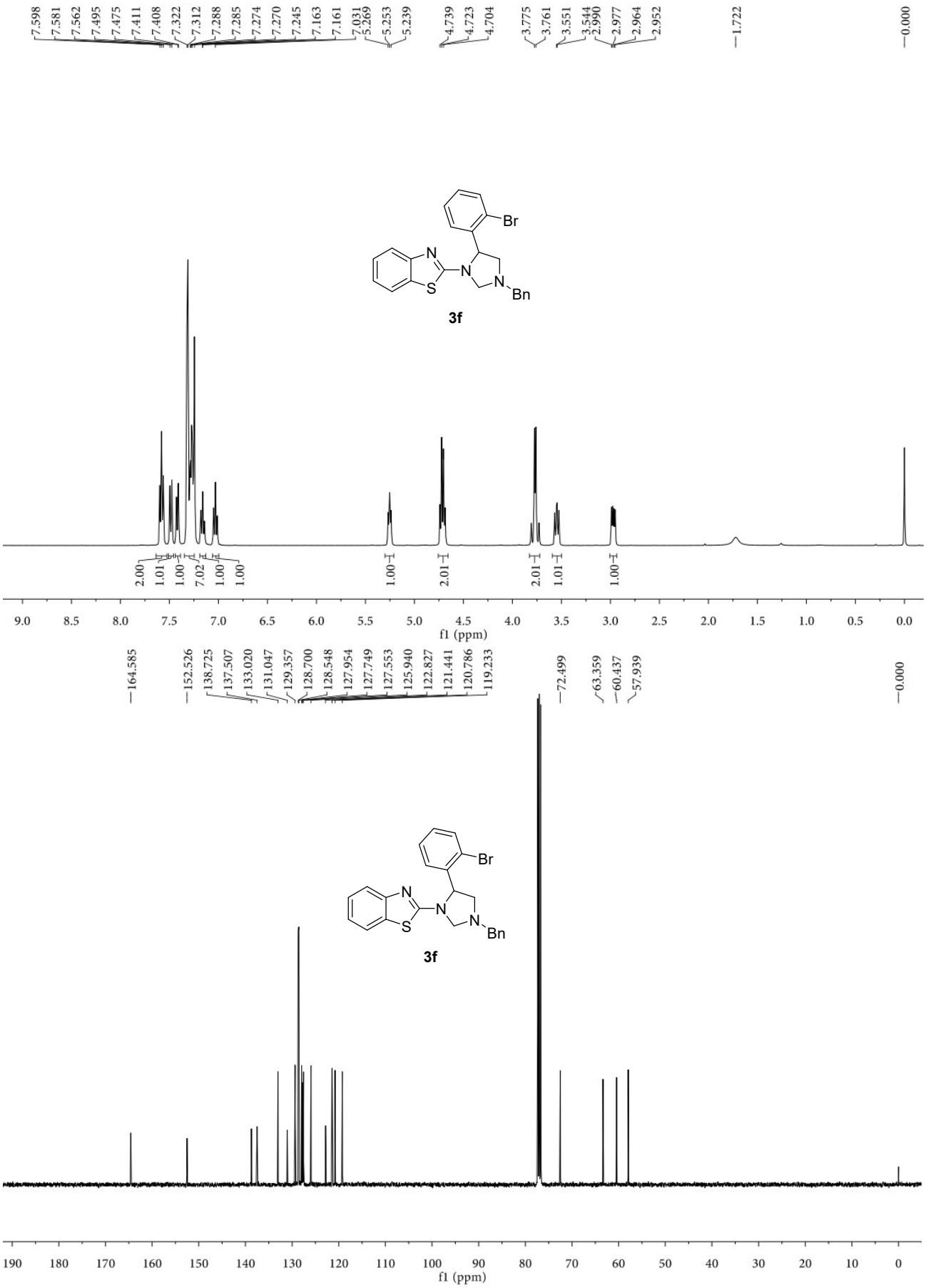

-114.088
F
N
S
N
N
Bn
3d
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

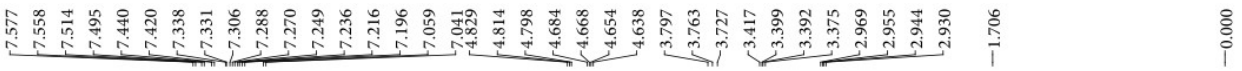

7.568
7.548
7.502
7.483
7.368
7.346
7.332
7.310
7.293
7.284
7.264
7.248
7.053
7.034
7.015
4.838
4.823
4.807
4.676
4.657
4.640
3.761
3.408
3.390
3.384
3.366
2.953
2.940
2.929
2.915
1.653
-0.000

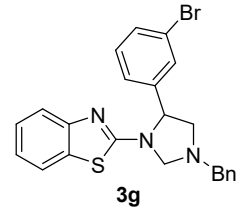

Cl
N
S
N
N
Bn
3e
1.00
1.00
10.00
1.00
1.01
2.00
2.00
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.398
152.315
138.549
137.491
133.819
130.921
128.966
128.645
128.572
128.261
127.588
125.962
121.442
120.734
119.203
72.471
63.143
61.994
57.863
-0.000

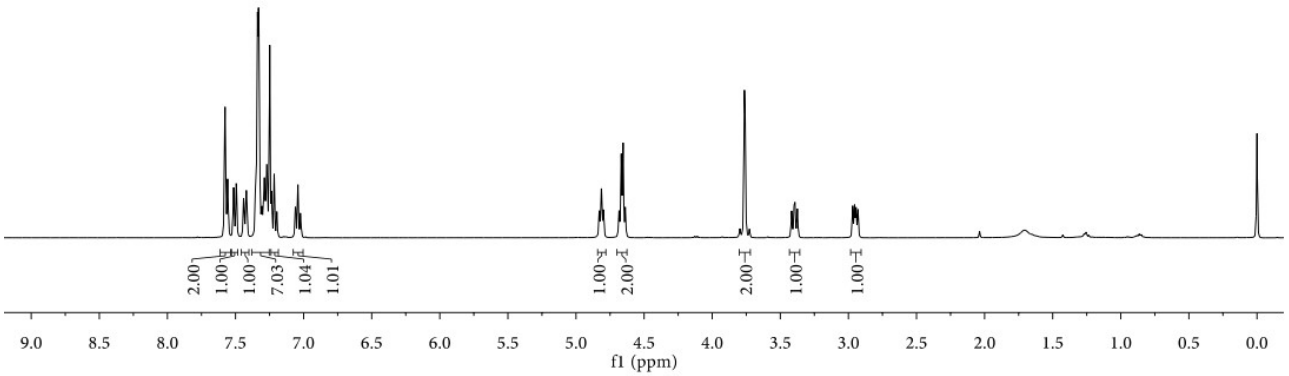

Cl
N
S
N
N
Bn
3e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

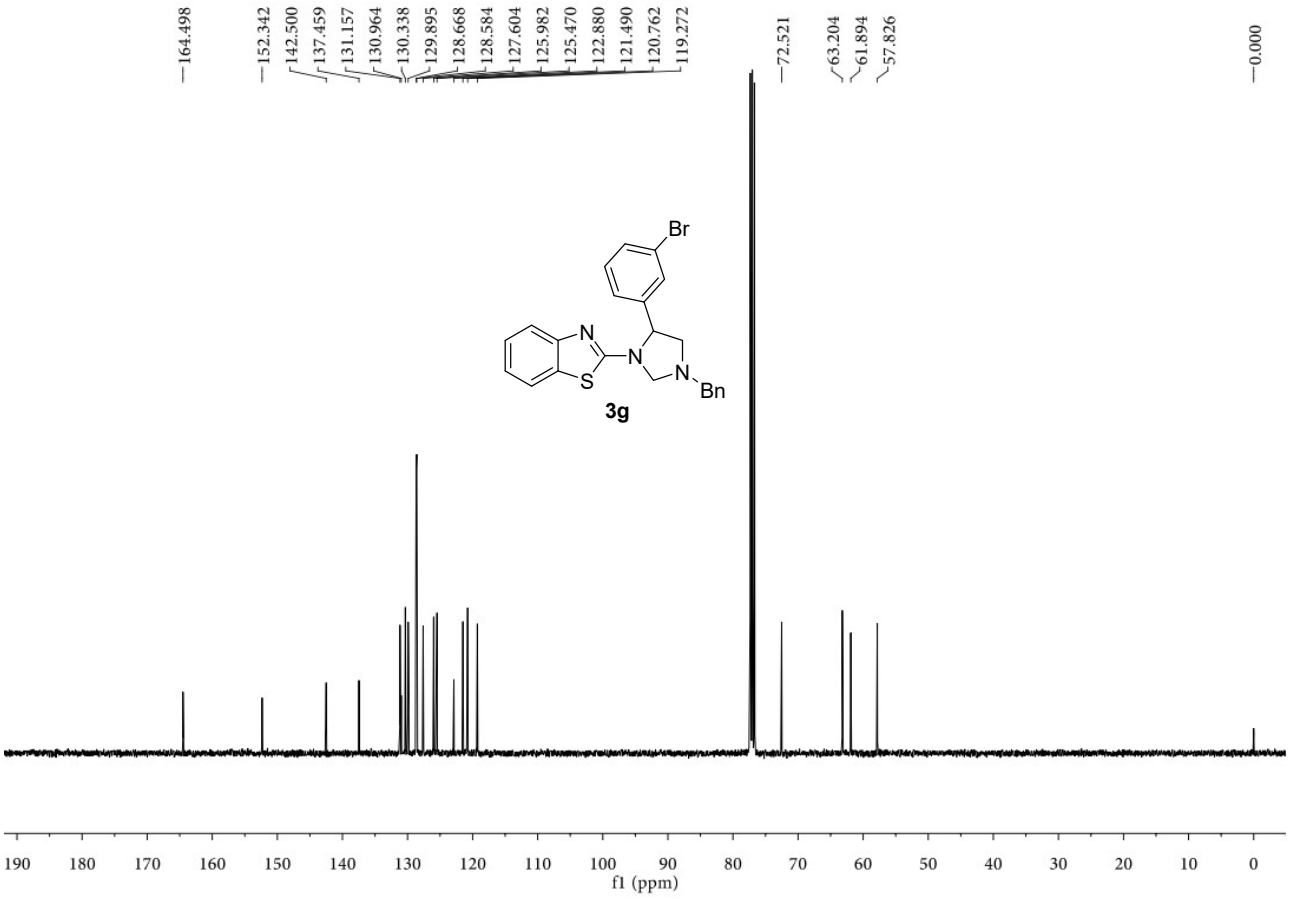

7.598
7.581
7.562
7.495
7.475
7.411
7.408
7.322
7.312
7.288
7.285
7.274
7.270
7.245
7.163
7.161
7.031
5.269
5.253
5.239
4.739
4.723
4.704
3.775
3.761
3.551
3.544
2.990
2.977
2.964
2.952
1.722
0.000
Br
N
S
N
N
Bn
3f
2.00
1.01
1.00
7.02
1.00
1.00
1.00
2.01
2.01
1.01
1.00
f1 (ppm)
164.585
152.526
138.725
137.507
133.020
131.047
129.357
128.700
128.548
127.954
127.749
127.553
125.940
122.827
121.441
120.786
119.233
72.499
63.359
60.437
57.939
0.000
Br
N
S
N
N
Bn
3f
f1 (ppm)


7.577
7.558
7.514
7.495
7.440
7.420
7.338
7.331
7.306
7.288
7.270
7.249
7.236
7.216
7.196
7.059
7.041
4.829
4.814
4.798
4.684
4.668
4.654
4.638
3.797
3.763
3.727
3.417
3.399
3.392
3.375
2.969
2.955
2.944
2.930
1.706
0.000

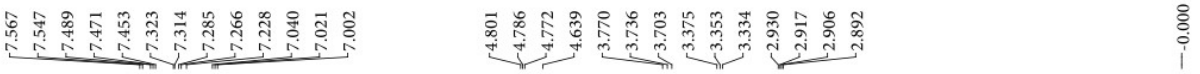

Br
N
N
S
N
Bn

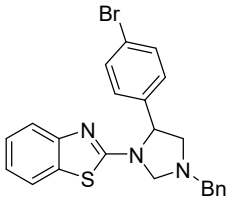
3g


2.00
1.00
1.00
7.03
1.04
1.01
1.00
2.00
2.00
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

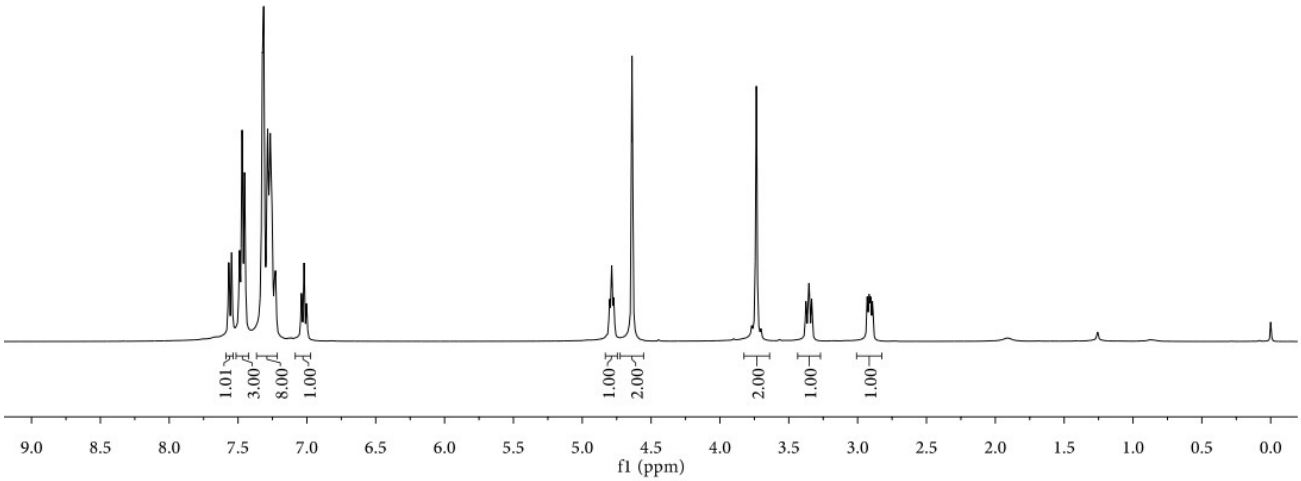

164.498
152.342
142.500
137.459
131.157
130.964
130.338
129.895
128.668
128.584
127.604
125.982
125.470
122.880
121.490
120.762
119.272
72.521
63.204
61.894
57.826
0.000
Br
N
N
S
N
Bn
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

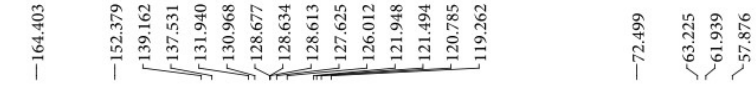
3g


7.567
7.547
7.489
7.471
7.453
7.323
7.314
7.285
7.266
7.228
7.040
7.021
7.002
4.801
4.786
4.772
4.639
3.770
3.736
3.703
3.375
3.353
3.334
2.930
2.917
2.906
2.892
0.000


Br
N
S
N
N
Bn

3h


1.01
3.00
8.00
1.00
1.00
2.00
2.00
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.403
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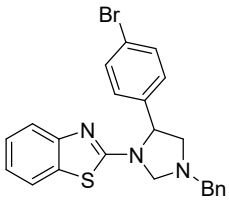
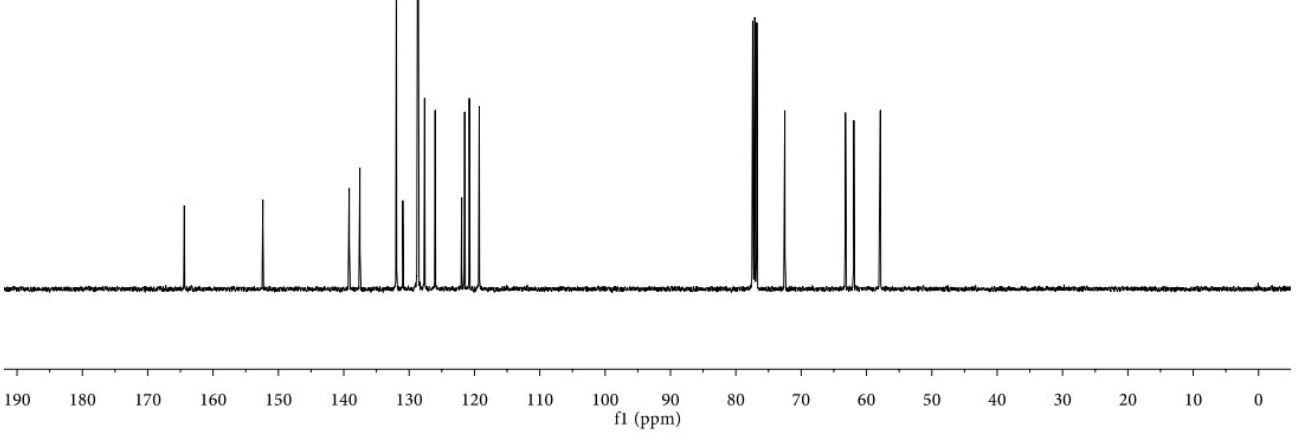
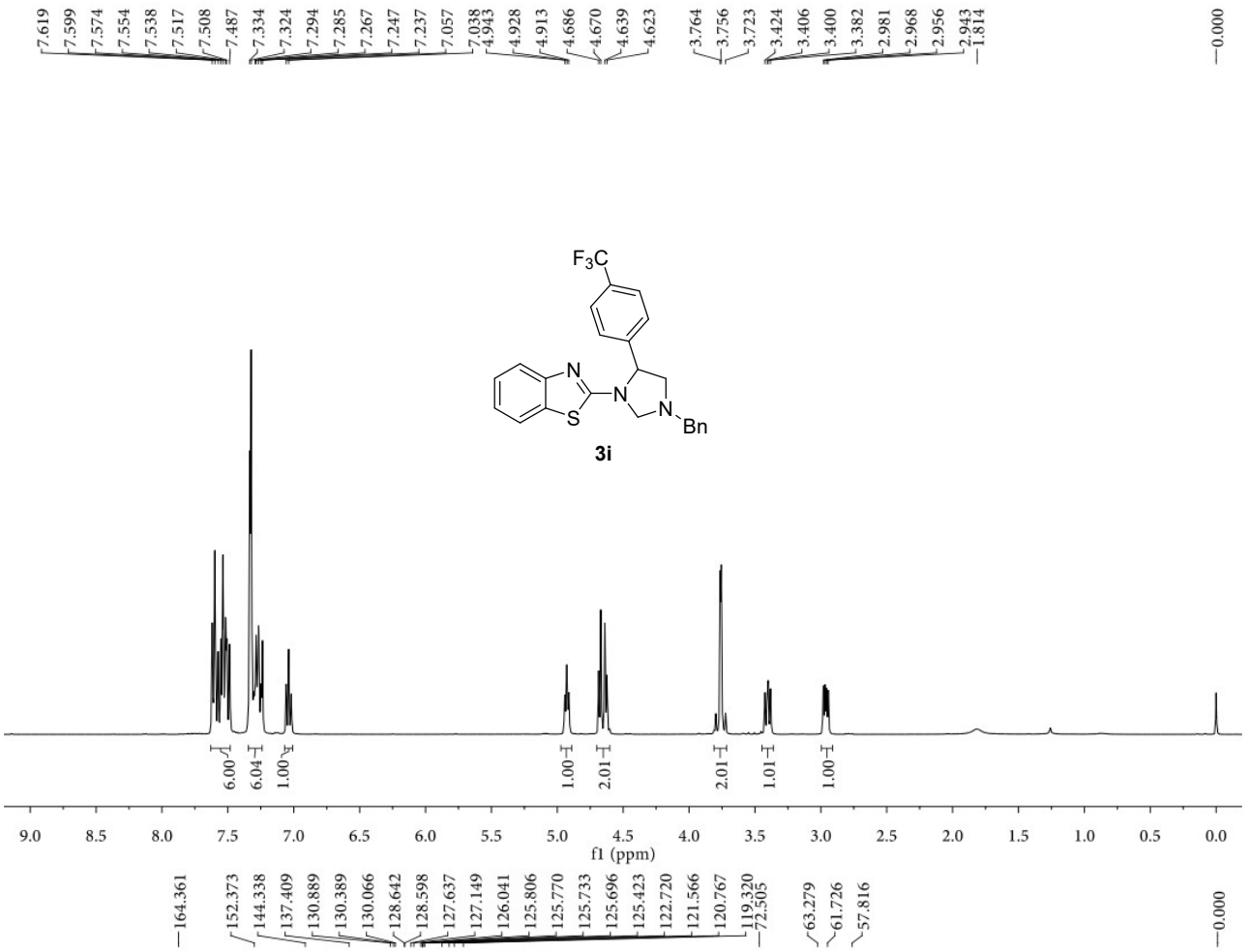
139.162
137.531
131.940
130.968
128.677
128.634
128.613
127.625
126.012
121.948
121.494
120.785
119.262
72.499
63.225
61.939
57.876


Br
N
S
N
N
Bn

3h


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.599
7.574
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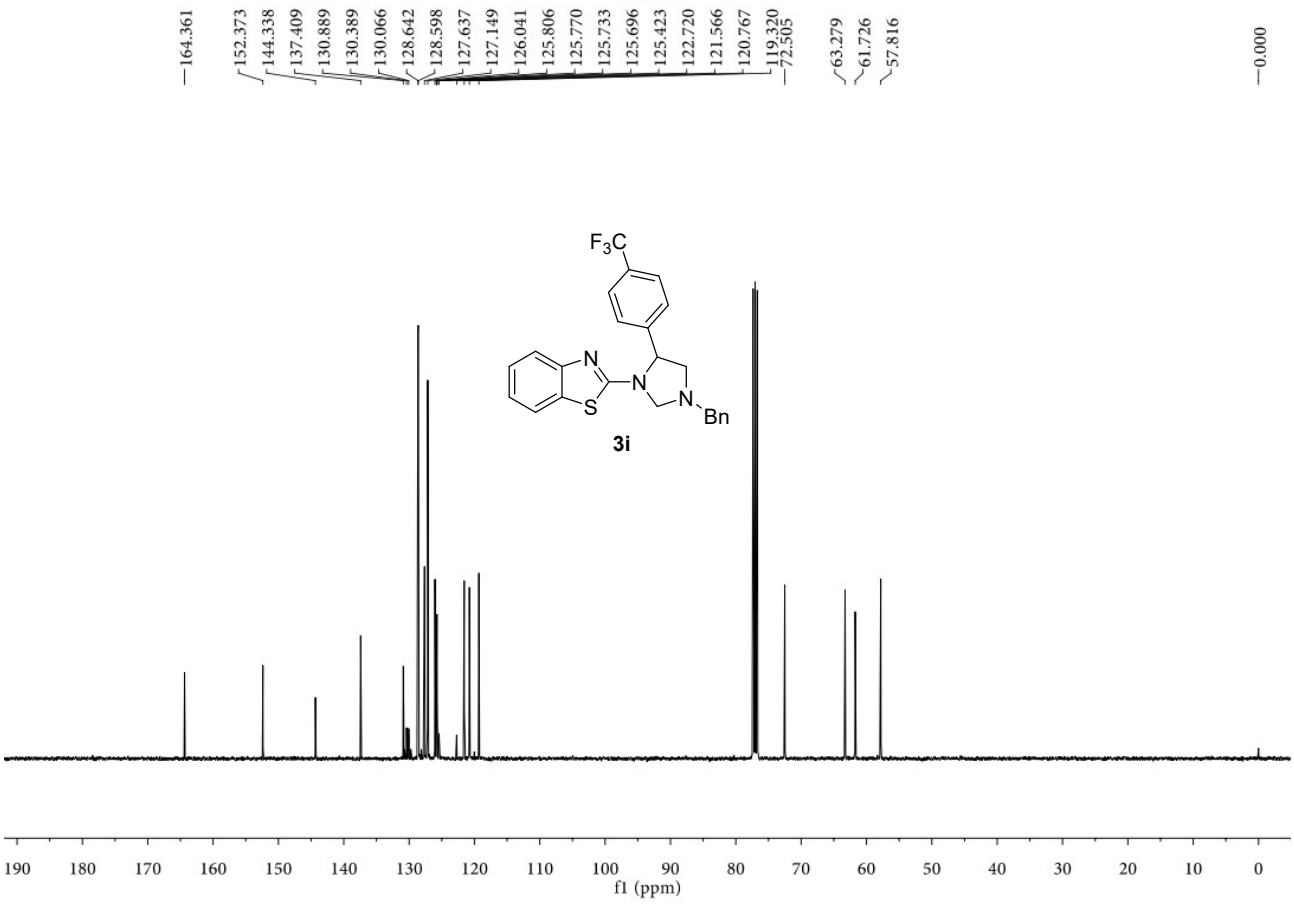
7.538
7.517
7.508
7.487
7.334
7.324
7.294
7.285
7.267
7.247
7.237
7.057
7.038
4.943
4.928
4.913
4.686
4.670
4.639
4.623
3.764
3.756
3.723
3.424
3.406
3.400
3.382
2.981
2.968
2.956
2.943
1.814
0.000
F3C
N
S
N
N
Bn
3i
6.00
6.04
1.00
1.00
2.01
2.01
1.01
1.00
f1 (ppm)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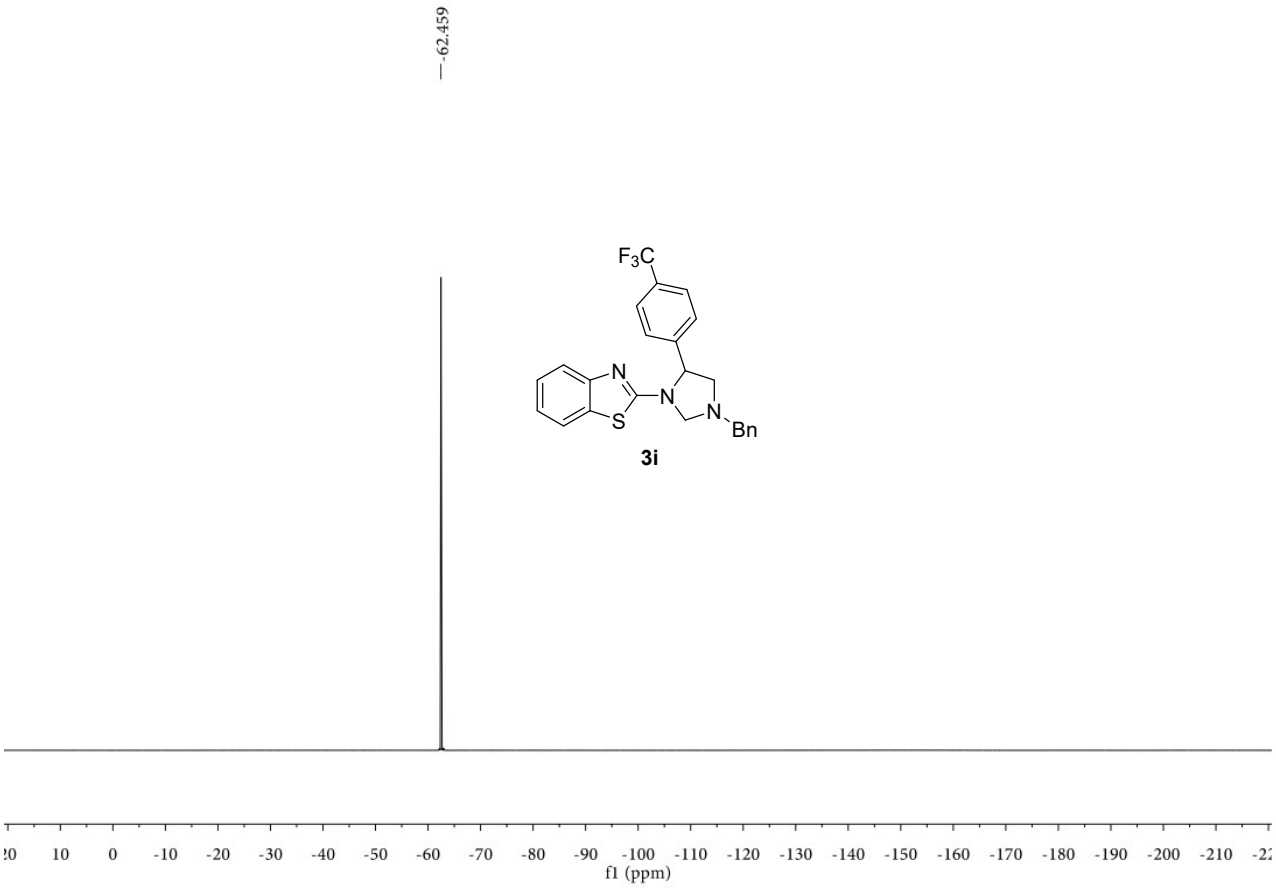
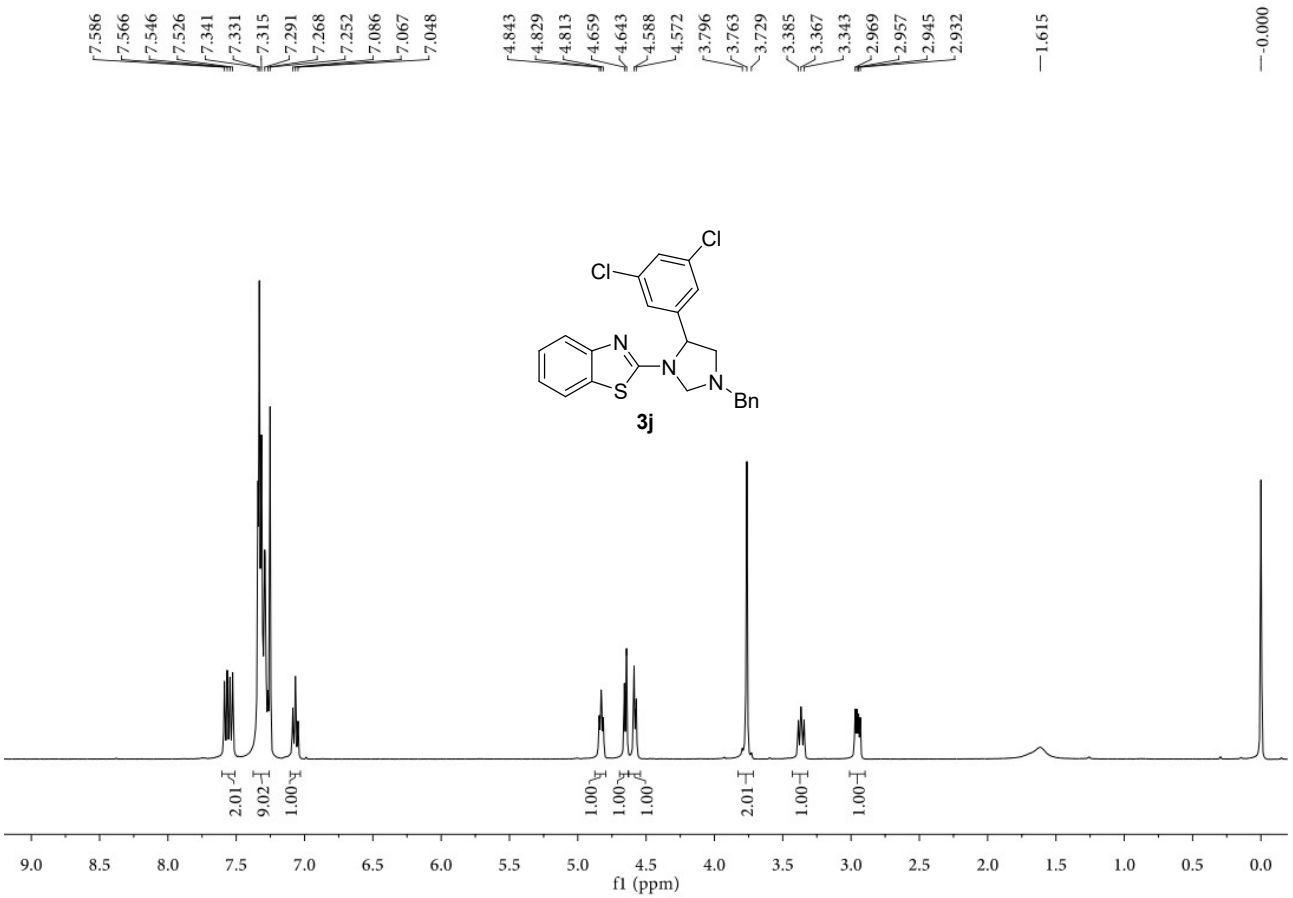
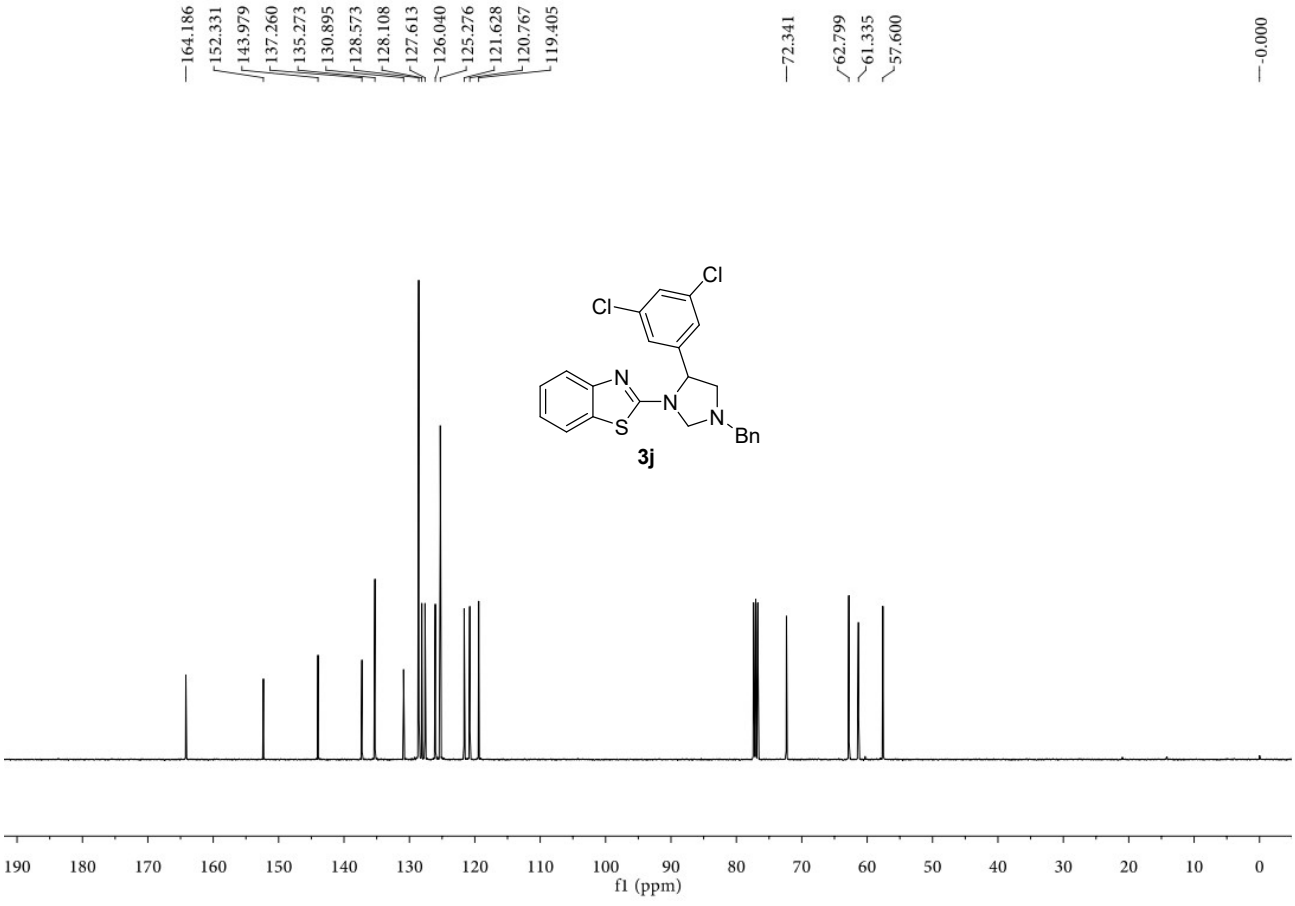
152.373
144.338
137.409
130.889
130.389
130.066
128.642
128.598
127.637
127.149
126.041
125.806
125.770
125.733
125.696
125.423
122.720
121.566
120.767
119.320
72.505
63.279
61.726
57.816
0.000
F3C
N
S
N
N
Bn
3i
f1 (ppm)


-62.459
F3C
N
S
N
N
Bn
3i
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.586
7.566
7.546
7.526
7.341
7.331
7.315
7.291
7.268
7.252
7.086
7.067
7.048
4.843
4.829
4.813
4.659
4.643
4.588
4.572
3.796
3.763
3.729
3.385
3.367
3.343
2.969
2.957
2.945
2.932
1.615
-0.000
Cl
Cl
N
S
N
N
Bn
3j
2.01
9.02
1.00
1.00
1.00
1.00
2.01
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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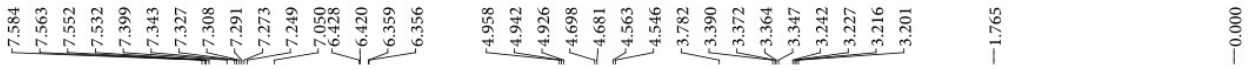
143.979
137.260
135.273
130.895
128.573
128.108
127.613
126.040
125.276
121.628
120.767
119.405
72.341
62.799
61.335
57.600
-0.000
Cl
Cl
N
S
N
N
Bn
3j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.584
7.563
7.552
7.532
7.399
7.343
7.327
7.308
7.291
7.273
7.249
7.050
6.428
6.420
6.359
6.356
4.958
4.942
4.926
4.698
4.681
4.563
4.546
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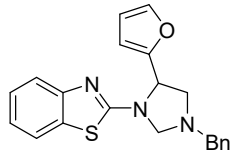
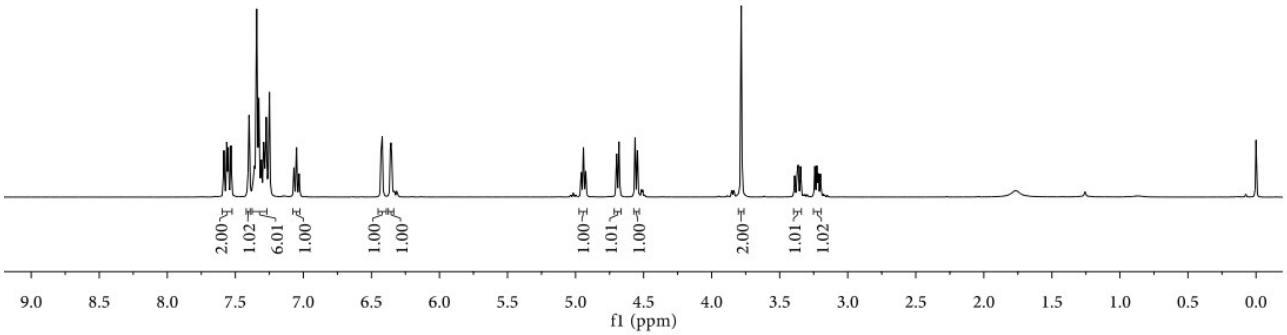
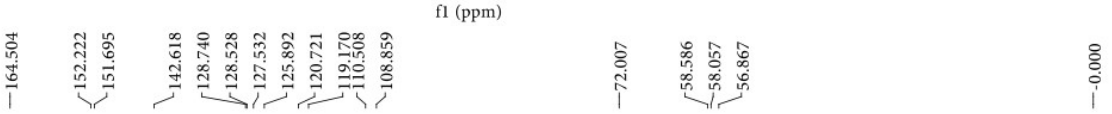
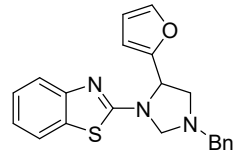
3.390
3.372
3.364
3.347
3.242
3.227
3.216
3.201
1.765
0.000


O
N
S
N
N
Bn

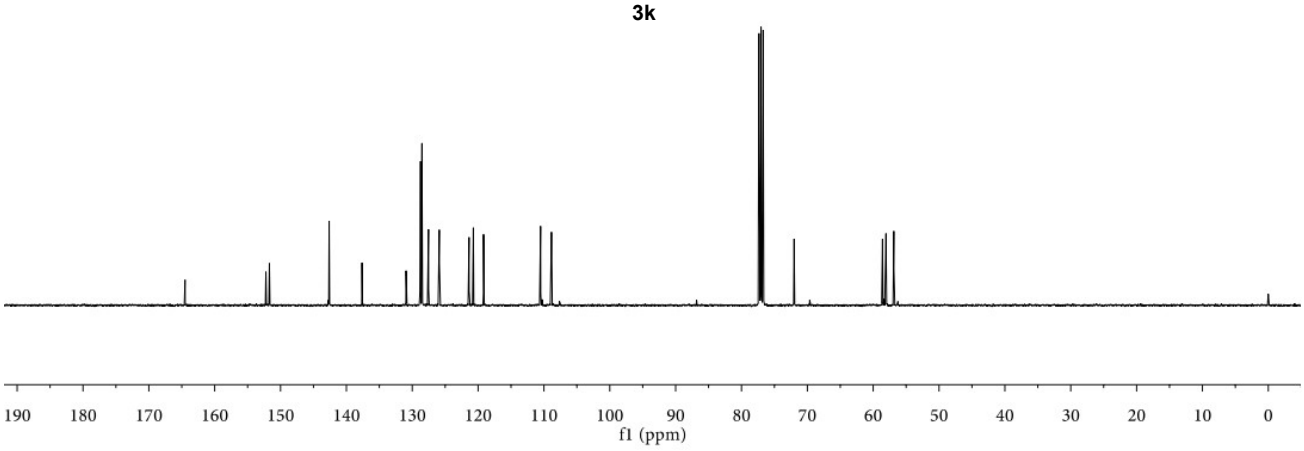
3k

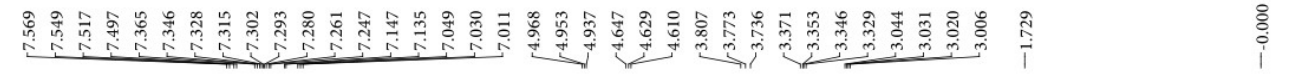

2.00
1.02
6.01
1.00
1.00
1.00
1.00
1.01
1.00
2.00
1.01
1.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

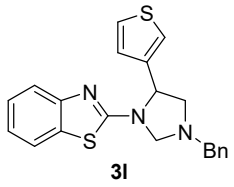

164.504
152.222
151.695
142.618
128.740
128.528
127.532
125.892
120.721
119.170
110.508
108.859
72.007
58.586
58.057
56.867
-0.000


O
N
S
N
N
Bn

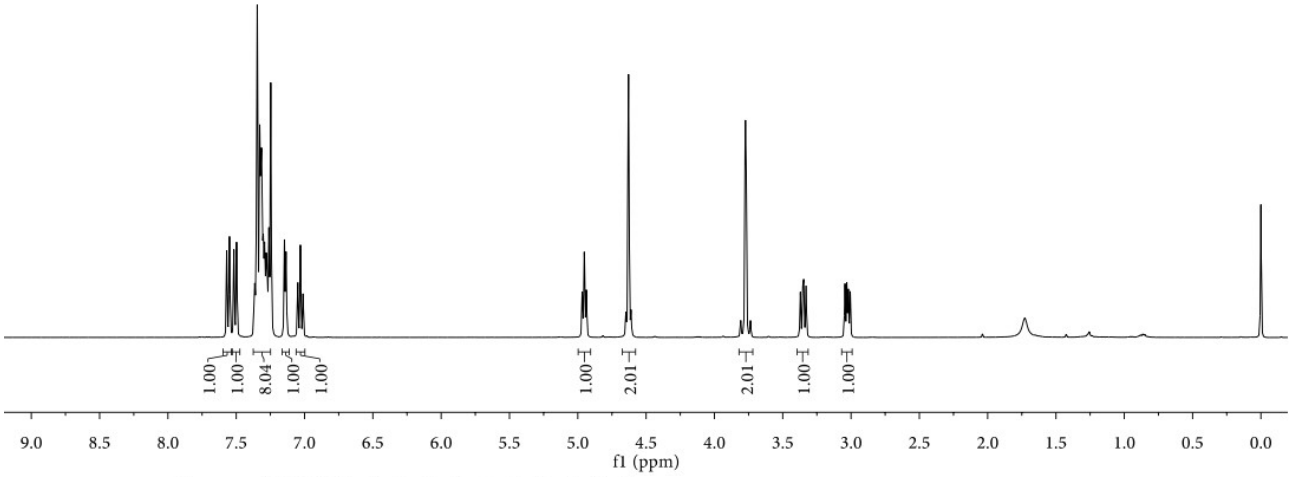
3k


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

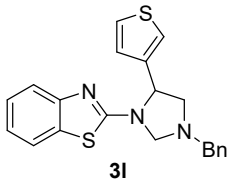

7.569
7.549
7.517
7.497
7.365
7.346
7.328
7.315
7.302
7.293
7.280
7.261
7.247
7.147
7.135
7.049
7.030
7.011
4.968
4.953
4.937
4.647
4.629
4.610
3.807
3.773
3.736
3.371
3.353
3.346
3.329
3.044
3.031
3.020
3.006
1.729
0.000


S
N
N
S
N
Bn

3l


1.00
1.00
8.04
1.00
1.00
1.00
2.01
2.01
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

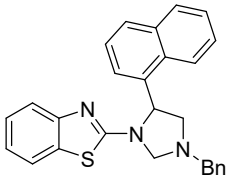

164.505
152.232
140.893
137.622
130.929
128.673
128.542
127.534
126.606
126.259
125.869
122.972
121.281
120.713
119.042
72.039
61.124
59.428
57.968
0.000


S
N
N
S
N
Bn

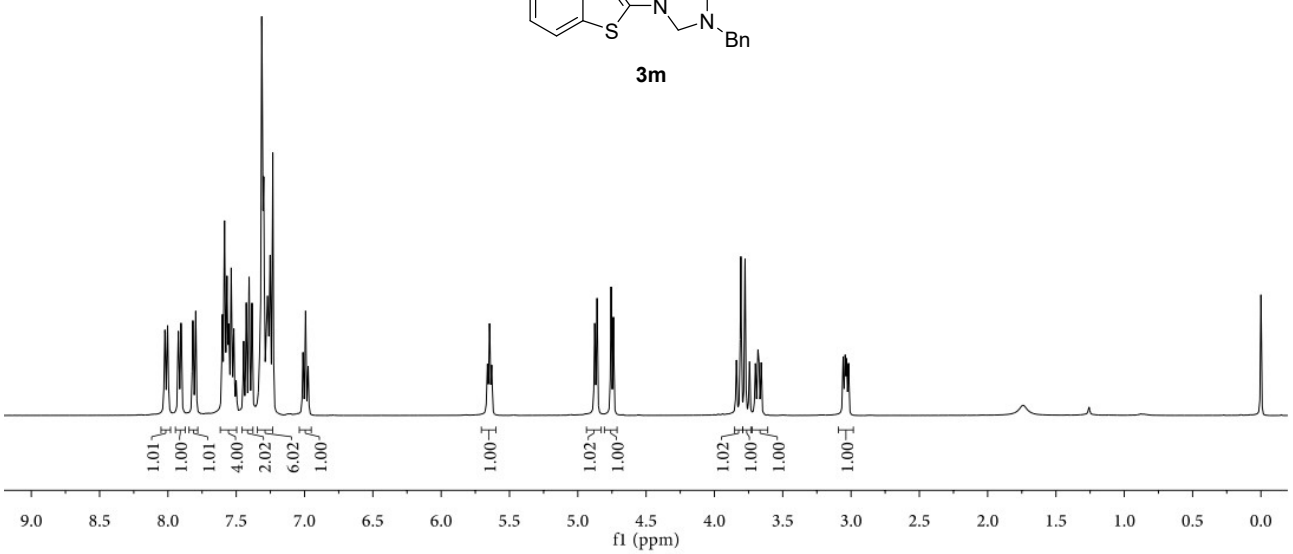
3l

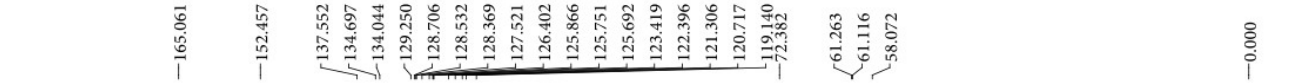
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

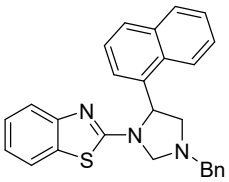

8.022
8.002
7.923
7.904
7.817
7.797
7.602
7.586
7.568
7.556
7.537
7.518
7.501
7.446
7.427
7.406
7.385
7.313
7.299
7.271
7.252
7.232
7.011
6.993
6.974
5.661
5.646
5.630
4.876
4.859
4.756
4.739
3.839
3.806
3.776
3.743
3.700
3.681
3.676
3.657
3.057
3.043
3.032
3.018
0.000


N
S
N
N
Bn

3m

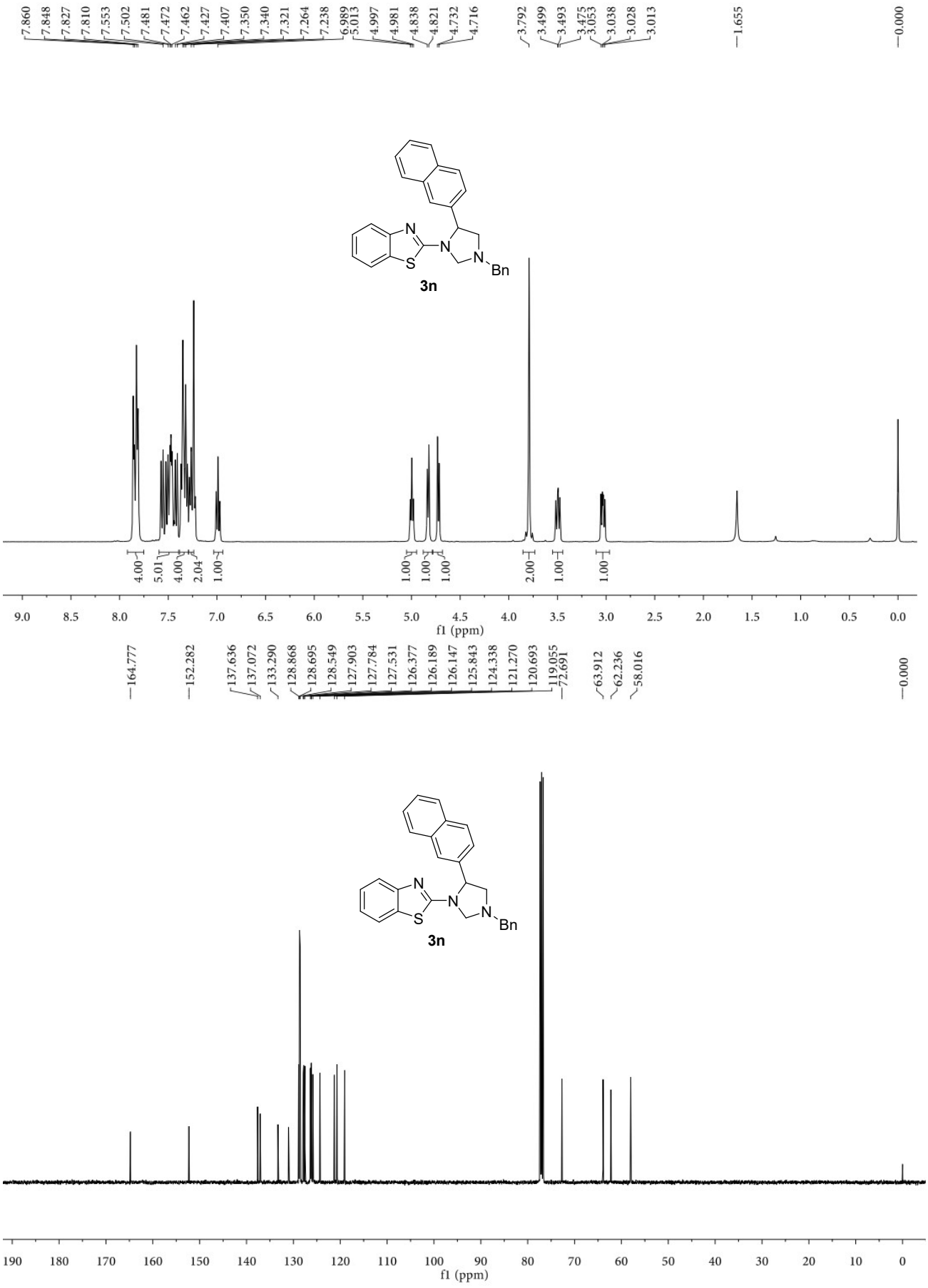

1.01
1.00
1.01
4.00
2.02
6.02
1.00
1.00
1.02
1.00
1.02
1.00
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

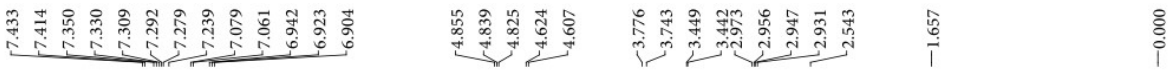

165.061
152.457
137.552
134.697
134.044
129.250
128.706
128.532
128.369
127.521
126.402
125.866
125.751
125.692
123.419
122.396
121.306
120.717
119.140
72.382
61.263
61.116
58.072
0.000

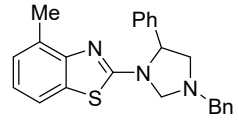

N
S
N
N
Bn

3m

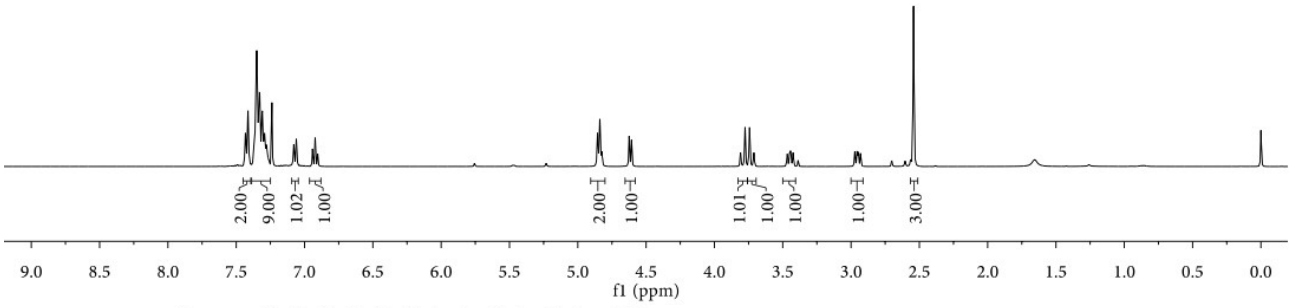
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.860
7.848
7.827
7.810
7.553
7.502
7.481
7.472
7.462
7.427
7.407
7.350
7.340
7.321
7.264
7.238
6.989
5.013
4.997
4.981
4.838
4.821
4.732
4.716
3.792
3.499
3.493
3.475
3.053
3.038
3.028
3.013
1.655
0.000
N
N
S
N
Bn
3n
4.00
5.01
4.00
2.04
1.00
1.00
1.00
1.00
2.00
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
164.777
152.282
137.636
137.072
133.290
128.868
128.695
128.549
127.903
127.784
127.531
126.377
126.189
126.147
125.843
124.338
121.270
120.693
119.055
72.691
63.912
62.236
58.016
0.000
N
N
S
N
Bn
3n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

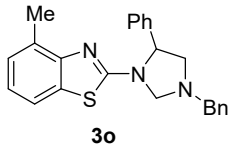

7.433
7.414
7.350
7.330
7.309
7.292
7.279
7.239
7.079
7.061
6.942
6.923
6.904
4.855
4.839
4.825
4.624
4.607
3.776
3.743
3.449
3.442
2.973
2.956
2.947
2.931
2.543
1.657
0.000


Me
Ph
N
N
S
N
Bn

3o

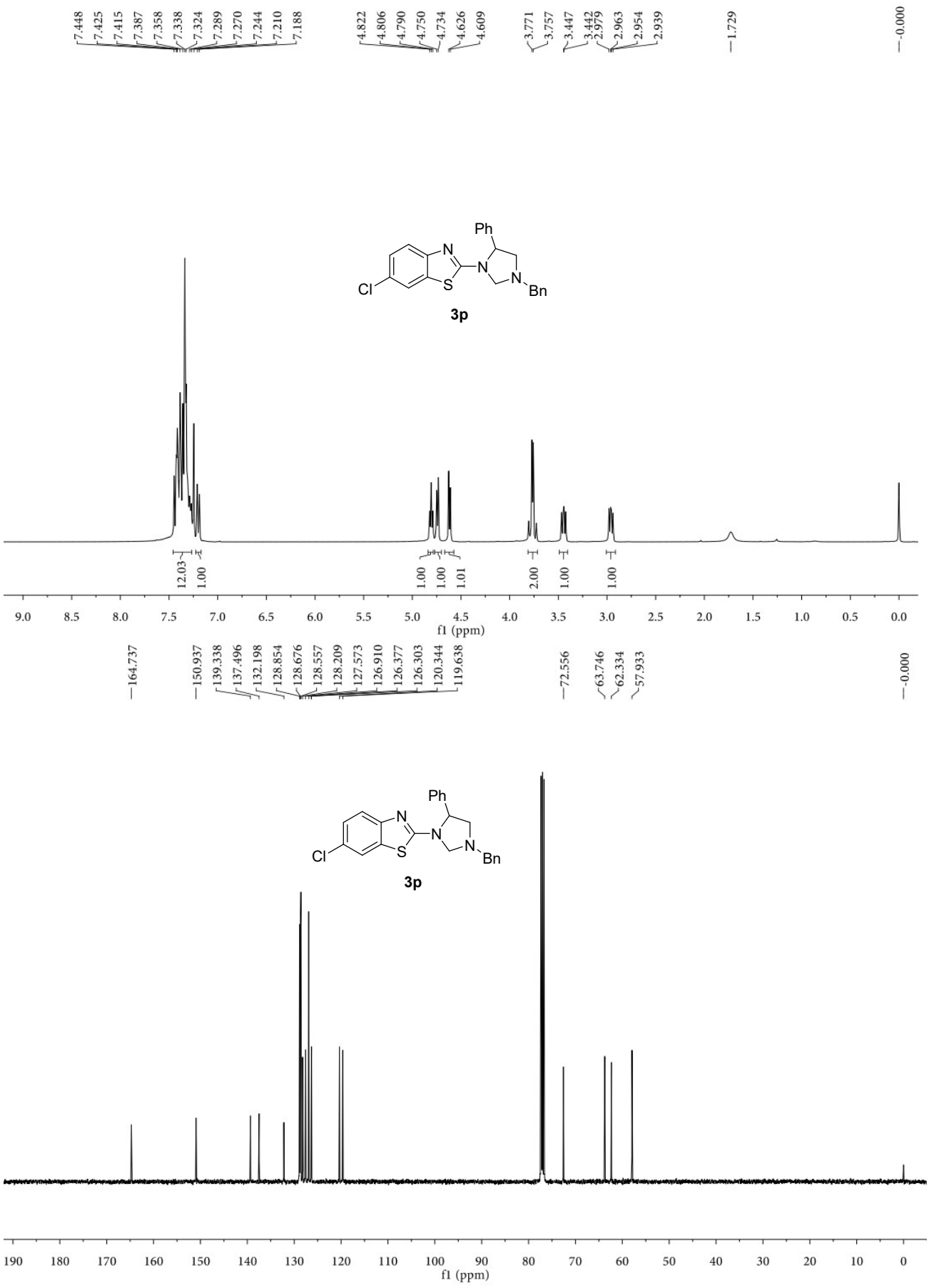

2.00
9.00
1.02
1.00
2.00
1.00
1.01
1.00
1.00
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

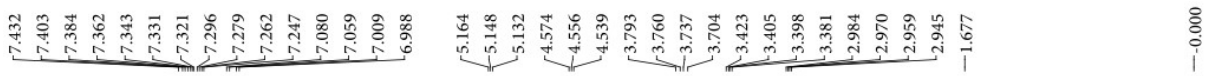

163.997
151.455
139.996
137.783
130.825
128.960
128.756
128.707
128.507
127.936
127.487
126.932
126.477
121.081
118.106
72.647
63.675
62.372
57.976
18.295
-0.000

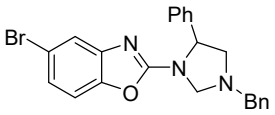

Me
Ph
N
N
S
N
Bn

3o

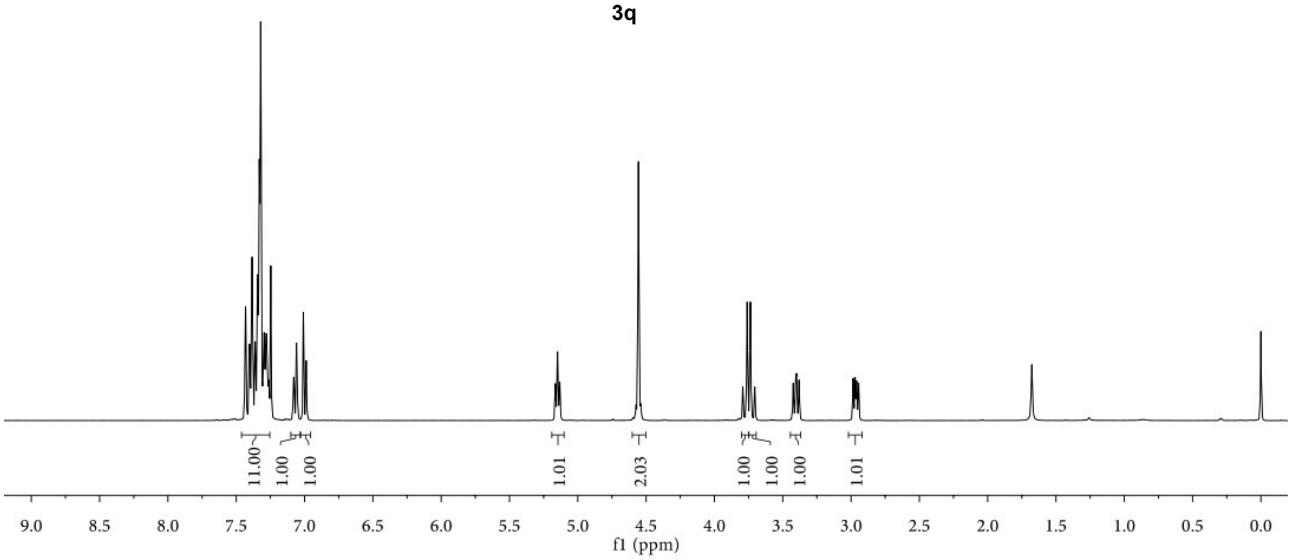
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.448
7.425
7.415
7.387
7.358
7.338
7.324
7.289
7.270
7.244
7.210
7.188
4.822
4.806
4.790
4.750
4.734
4.626
4.609
3.771
3.757
3.447
3.442
2.979
2.963
2.954
2.939
1.729
-0.000
Ph
N
N
N
Cl
S
Bn
3p
12.03
1.00
1.00
1.00
1.01
2.00
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
164.737
150.937
139.338
137.496
132.198
128.854
128.676
128.557
128.209
127.573
126.910
126.377
126.303
120.344
119.638
72.556
63.746
62.334
57.933
-0.000
Ph
N
N
N
Cl
S
Bn
3p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

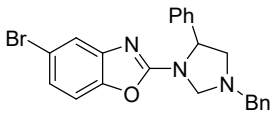

7.432
7.403
7.384
7.362
7.343
7.331
7.321
7.296
7.279
7.262
7.247
7.080
7.059
7.009
6.988
5.164
5.148
5.132
4.574
4.556
4.539
3.793
3.760
3.737
3.704
3.423
3.405
3.398
3.381
2.984
2.970
2.959
2.945
1.677
-0.000


Br
N
O
N
N
Ph
Bn

3q

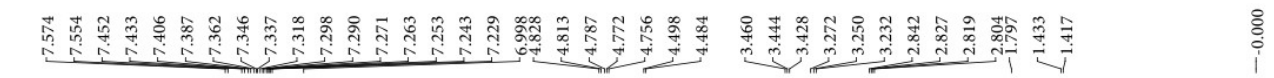

11.00
1.00
1.00
1.01
2.03
1.00
1.00
1.00
1.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

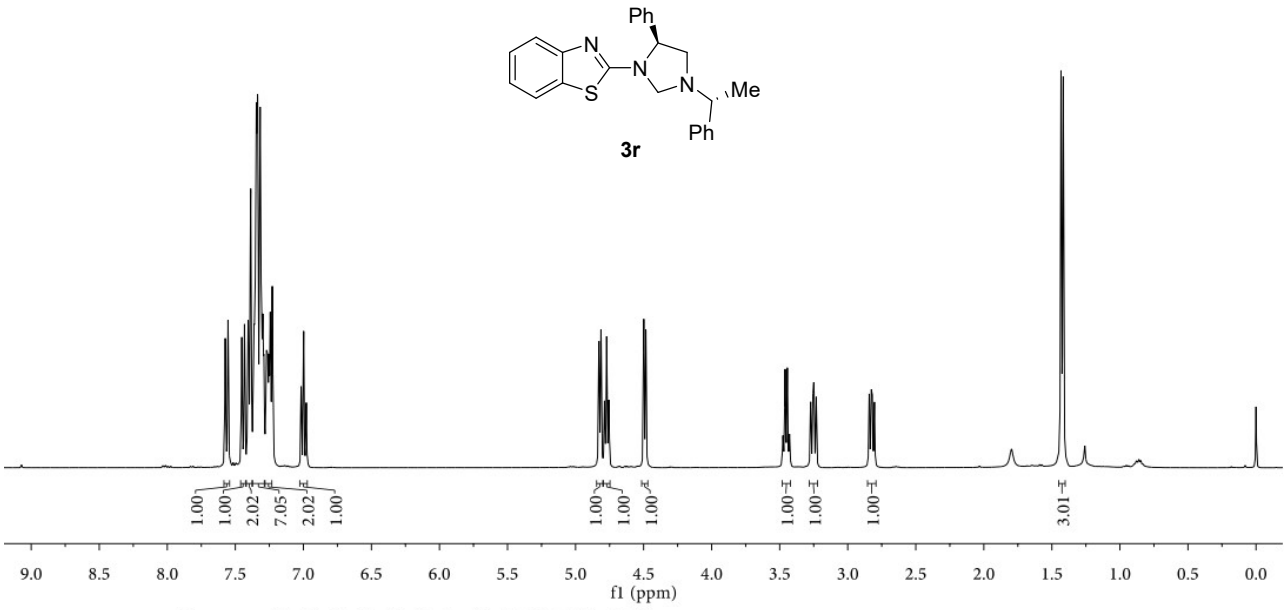

160.850
148.017
144.836
140.803
137.417
128.663
128.577
127.730
127.609
126.215
123.310
119.547
116.617
109.980
70.905
61.696
61.423
57.782
-0.000

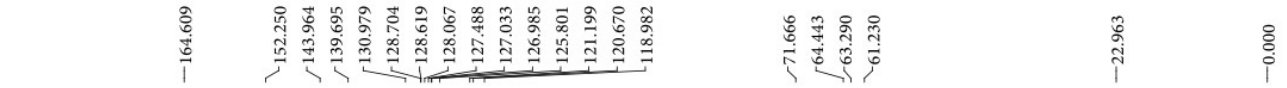

Br
N
O
N
N
Ph
Bn

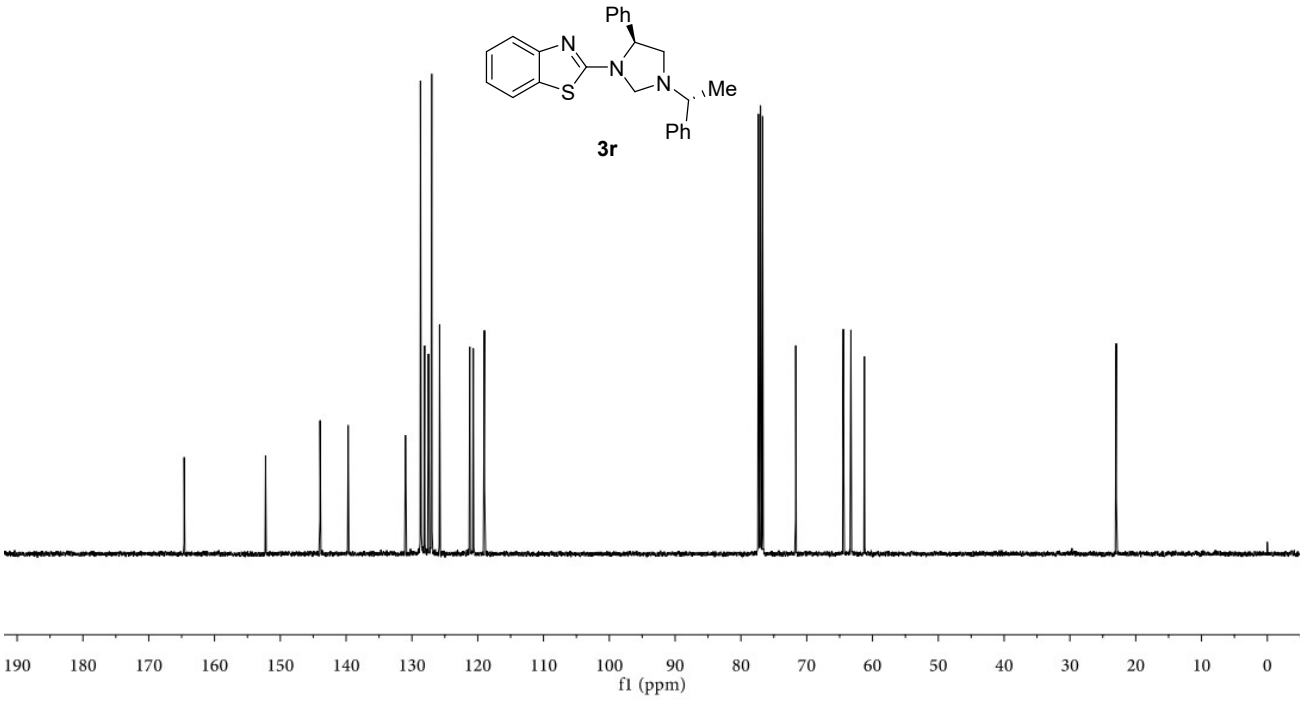
3q

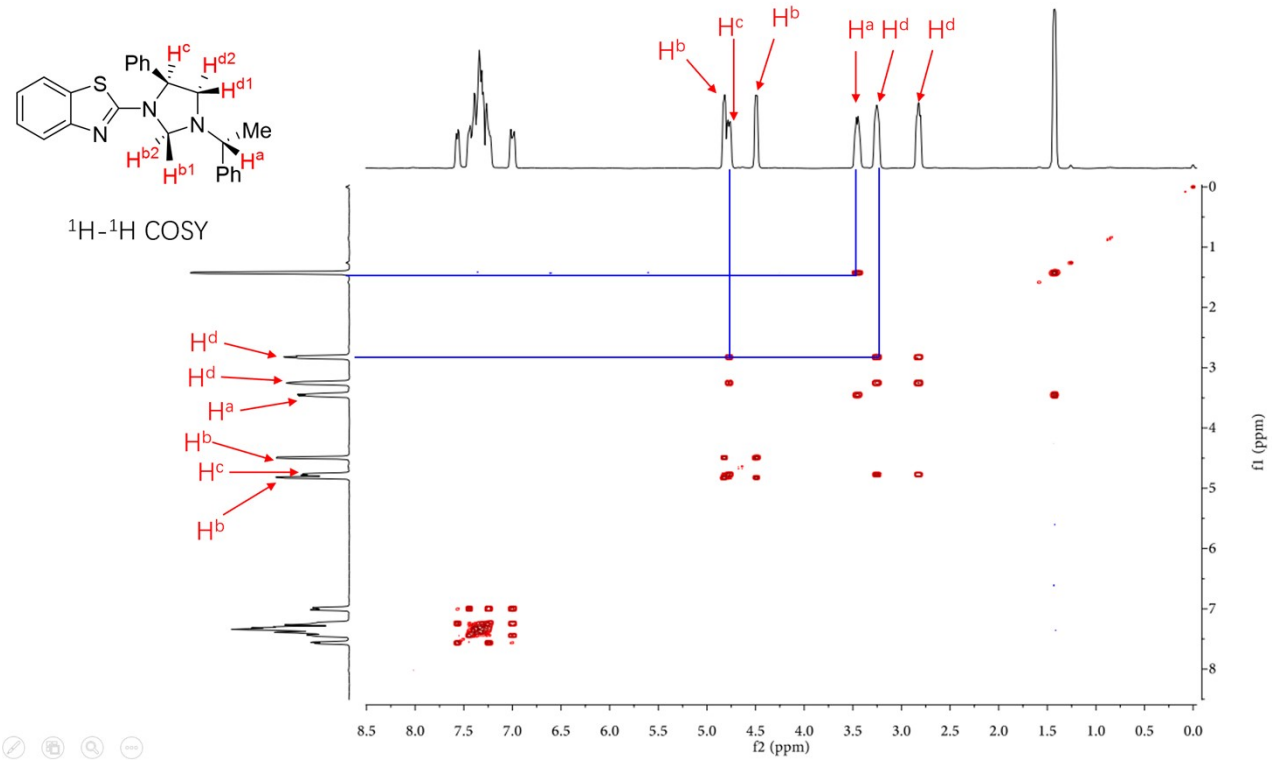
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

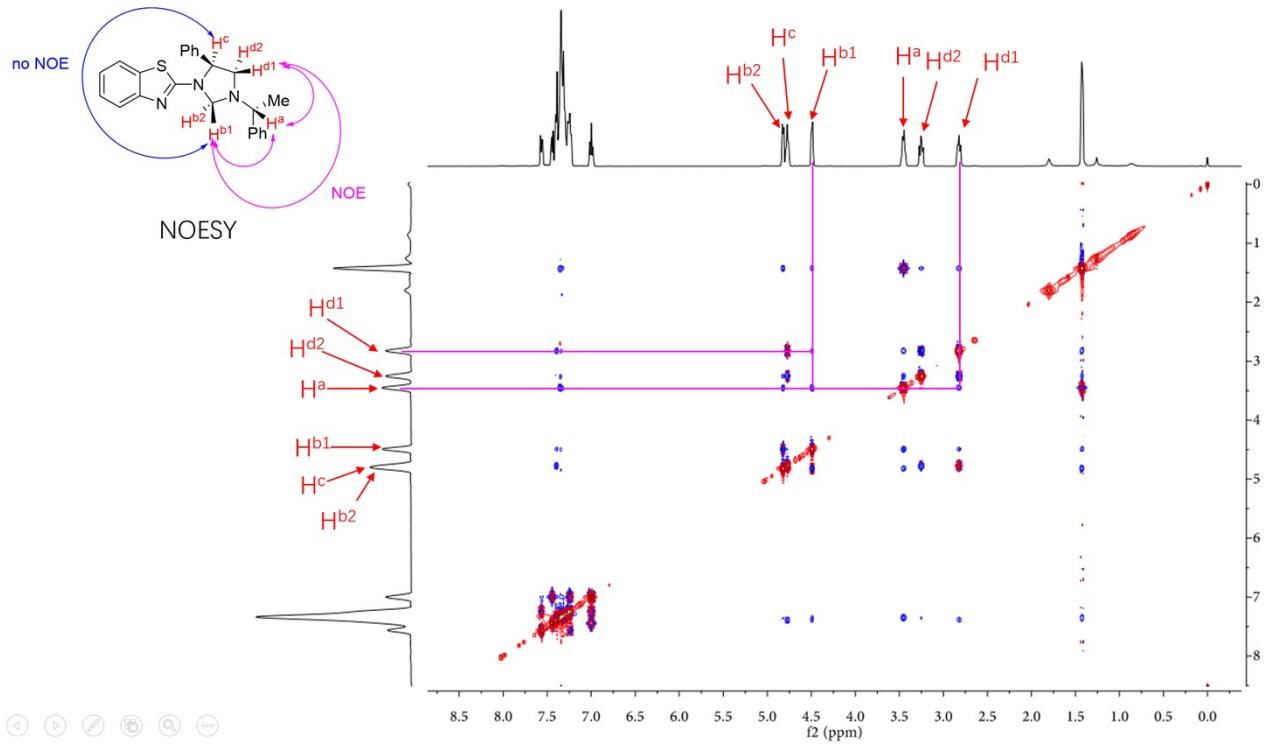

7.574
7.554
7.452
7.433
7.406
7.387
7.362
7.346
7.337
7.318
7.298
7.290
7.271
7.263
7.253
7.243
7.229
6.998
4.828
4.813
4.787
4.772
4.756
4.498
4.484
3.460
3.444
3.428
3.272
3.250
3.232
2.842
2.827
2.819
2.804
1.797
1.433
1.417
-0.000

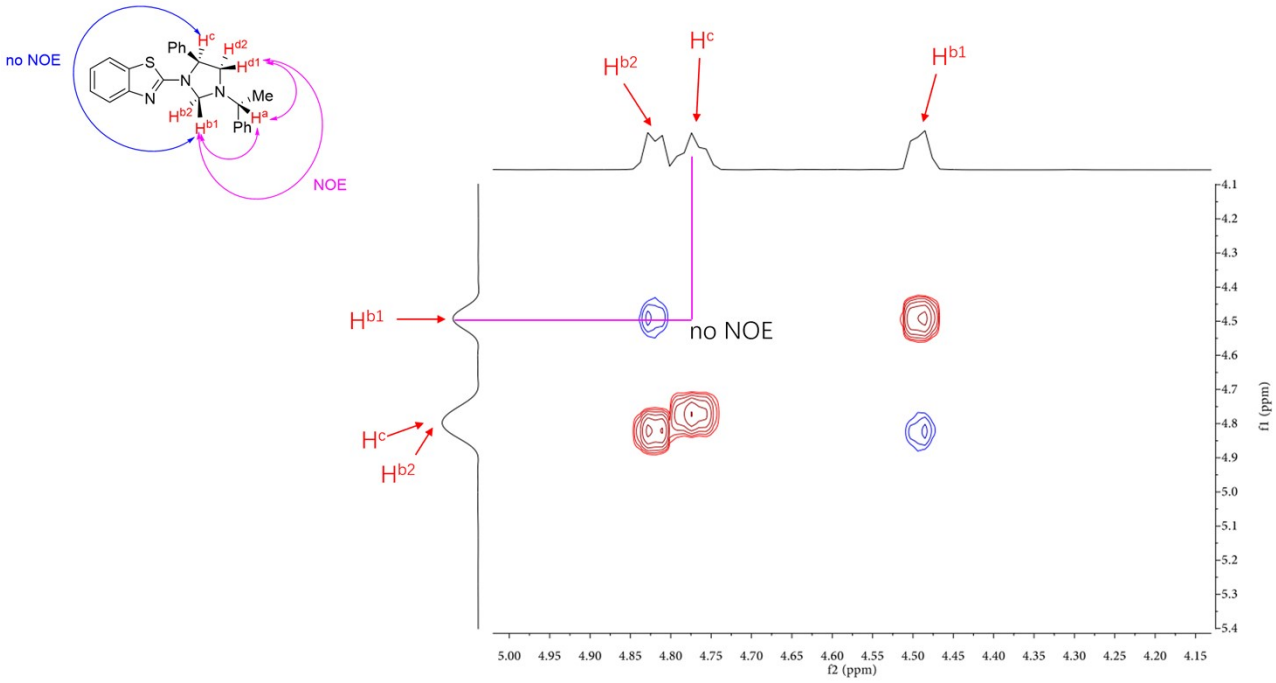

Ph
N
S
N
N
Me
Ph
3r
1.00
1.00
2.02
7.05
2.02
1.00
1.00
1.00
1.00
1.00
1.00
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

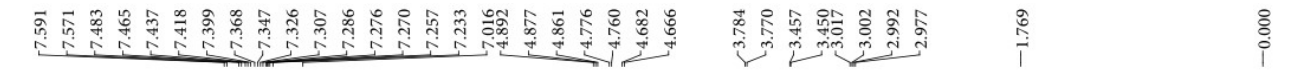

164.609
152.250
143.964
139.695
130.979
128.704
128.619
128.067
127.488
127.033
126.985
125.801
121.199
120.670
118.982
71.666
64.443
63.290
61.230
22.963
0.000

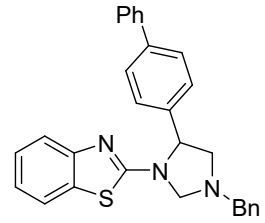

Ph
N
S
N
N
Me
Ph
3r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
Hc
Hd2
Hd1
S
N
N
Me
Hb2
Hb1
Ph
Ha
1H-1H COSY
Hb
Hc
Hb
Ha
Hd
Hd
Hd
Hd
Ha
Hb
Hc
Hb
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)

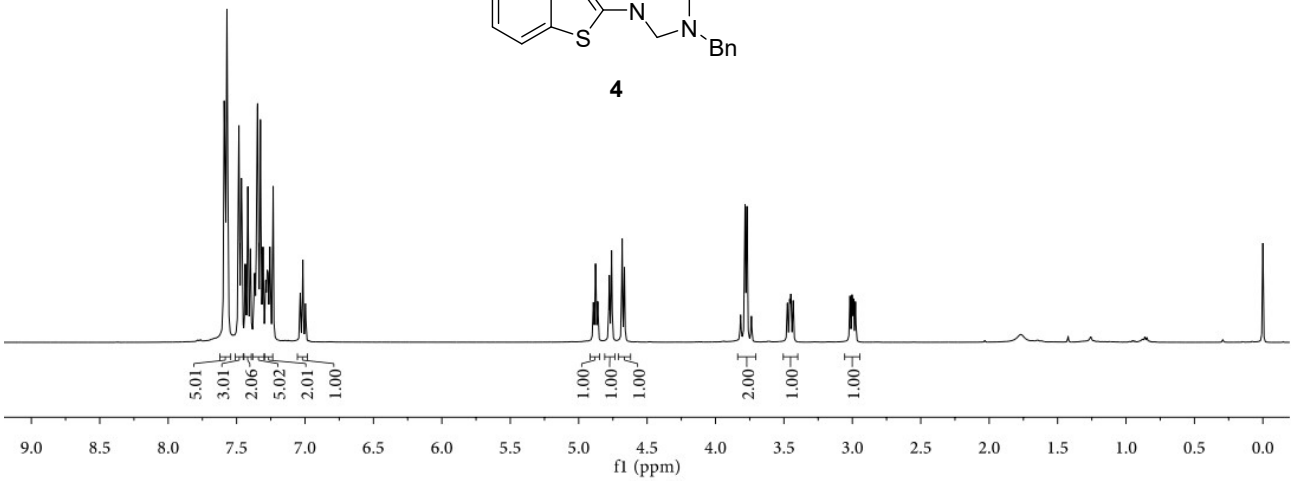

no NOE
Ph
Hc
Hd2
Hd1
S
N
N
Me
Hb2
Hb1
Ph
Ha
NOE
NOESY
Hc
Hb2
Hb1
Ha
Hd2
Hd1
Hd1
Hd2
Ha
Hb1
Hc
Hb2
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)

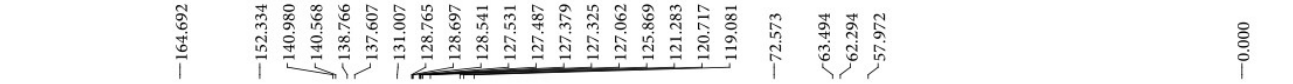

no NOE
NOE
Ph
S
N
N
Me
Ph
H^c
H^{d2}
H^{d1}
H^{b2}
H^{b1}
H^a
H^{b2}
H^c
H^{b1}
H^{b1}
no NOE
H^c
H^{b2}
5.00 4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15
f2 (ppm)
4.1 4.2 4.3 4.4 4.5 4.6 4.7 4.8 4.9 5.0 5.1 5.2 5.3 5.4
f1 (ppm)

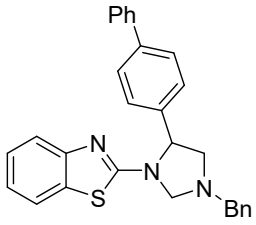

7.591
7.571
7.483
7.465
7.437
7.418
7.399
7.368
7.347
7.326
7.307
7.286
7.276
7.270
7.257
7.233
7.016
4.892
4.877
4.861
4.776
4.760
4.682
4.666
3.784
3.770
3.457
3.450
3.017
3.002
2.992
2.977
1.769
0.000


Ph
N
N
S
N
Bn

4


5.01
3.01
2.06
5.02
2.01
1.00
1.00
1.00
1.00
2.00
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.692
152.334
140.980
140.568
138.766
137.607
131.007
128.765
128.697
128.541
127.531
127.487
127.379
127.325
127.062
125.869
121.283
120.717
119.081
72.573
63.494
62.294
57.972
0.000


Ph
N
N
S
N
Bn

4

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)